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I. General Methods

All C—H oxidations were carried out under air with magnetic stirring, with no precautions to exclude oxygen or moisture. All other reactions were performed with oven dried or flame dried glassware under inert atmosphere of dry nitrogen or argon. Fe(PDP)$^1$, Fe(CF$_3$-PDP)$^2$, (Me$_3$tacn)RuCl$_3$ and cis-[Ru(dtbpy)$_2$Cl$_2$]$^4$ catalysts were synthesized according to literature procedures. Preparation of Mn(PDP)(MeCN)$_2$(SbF$_6$)$_2$ $^5$ and Mn(CF$_3$-PDP)(MeCN)$_2$(SbF$_6$)$_2$ $^1$ catalysts are described in section II. All catalysts were stored at 0 ºC. The catalysts were warmed to room temperature prior to use and weighted out in air. Chloroacetic acid was purchased from Sigma-Aldrich and broke into small pieces before use. H$_2$O$_2$ (50% wt. aqueous solution) was purchased from Sigma-Aldrich and used as received. AgSbF$_6$ used for catalyst metathesis was purchased from Strem Chemicals and stored in the glove box to avoid light prior to use. Solvents including THF, DCM, diethyl ether, DMF, toluene and benzene were dried by passing through a bed of activated alumina (Glass Contour, Laguna Beach, CA). Triethylamine and pyridine were distilled over calcium hydride prior to use. All other commercially available reagents were purchased from common sources (e.g. Sigma-Aldrich, Strem Chemicals, Oakwood, Alfa-Aesar, TCI America, etc.) and were used as received.

Thin-layer chromatography was conducted with E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized with UV and/or staining including potassium permanganate, ceric ammonium molybdate, or phosphomolybdic acid/cerium sulfate. Flash column chromatography was performed as described by Still et. al $^5$ using EM reagent silica gel 60 (230-400 mesh).

$^1$H NMR were recorded using a Varian Unity-500 (500 MHz), Varian Unity Inova-500 (500 MHz), Bruker Avance-500 (500 MHz) and Agilent VNMR S NMR (750 MHz) spectrometer, using solvent as internal standard (CDCl$_3$ at 7.26 ppm). Data are reported as: s=singlet, d=doublet, t=triplet, q=quartet, p=pentat, oct=octet, m=multiplet, br=broad, app=apparent; coupling constants in Hz; integration. Proton-decoupled $^{13}$C NMR were recorded using a Varian Unity-500 (500 MHz), Bruker Avance-500 (500 MHz) and Agilent VNMR S NMR (750 MHz) spectrometer, using solvent as internal standard (CDCl$_3$ at 77.16 ppm). $^{19}$F NMR were recorded using a Varian Unity-500 (470 MHz), Bruker Avance-500 (500 MHz) and Agilent VNMR S NMR (750 MHz) spectrometer, using external standard (CFCl$_3$ at 0 ppm). High resolution mass spectrometry (HRMS) was performed with a Waters Q-TOF Ultima spectrometer or Waters GCT Premier EI spectrometer. Optical rotations were obtained using a JASCO P2000 polarimeter (cell dimensions: 3.5 X 50 mm) and were reported as $[\alpha]_D^{T/\circ}$ concentration (c = g/100 mL, solvent).
II. Synthesis and Characterization of Catalysts

Synthesis and Characterization of Mn(PDP)(MeCN)$_2$(SbF$_6$)$_2$ (R,R)-Mn(PDP)Cl$_2$ [S1].

In a 50 mL recovery flask was charged (2R,2’R)-1,1’-bis(pyridin-2-ylmethyl)-2,2’-bipyrrrolidine ligand (1.0684 g, 3.31 mmol) synthesized according to literature procedure$^1$, a stir bar and MeCN (20 mL, 0.166 M). Freshly grinded MnCl$_2$$•$4H$_2$O (purchased from Strem, 655.7 mg, 3.313 mmol, 1.0 equiv.) was added and the reaction was allowed to stir vigorously for 24 hours under nitrogen atmosphere. Fine white solid was formed during the course of reaction and there should be no pink non-ligated manganese salt remained. Diethyl ether freshly taken from solvent delivery system was added to the reaction to precipitate out the complex. The solvent was removed via pipette and the remaining solids were washed thoroughly with diethyl ether five times and dried under a stream of dry nitrogen gas overnight to yield (R,R)-Mn(PDP)Cl$_2$ (1.3566 g, 3.03 mmol, 91% yield) as white solid. HRMS (TOF ESI+) m/z calculated for C$_{20}$H$_{26}$N$_4$ClMn [M-Cl]$^+$: 412.1226, found 412.1213.

(R,R)-Mn(PDP)(MeCN)$_2$(SbF$_6$)$_2$ [5].

In a flamed dried 100 mL recovery flask was charged (R,R)-Mn(PDP)Cl$_2$ S1 (1.2073 g, 2.69 mmol), a stir bar and 35 mL anhydrous MeCN. AgSbF$_6$ (purchased from Strem, 1.8508 g, 5.39 mmol, 2.0 equiv.) was weighed under argon atmosphere in glove box and then added to the reaction under a stream of nitrogen. The flask was wrapped with aluminum foil to protect from light and the reaction was vigorously stirred for 24 hours. AgCl precipitated out and the reaction was filtered through a pad of Celite® and concentrated under vacuum to a minimum amount of MeCN remaining. The residue was redissolved in a minimum amount of MeCN and filtered through a 0.22 µm Acrodisc® LC PVDF filter (HPLC certified) and concentrated. The filtration-concentration process was repeated two more times and the residue was concentrated to a minimum amount of MeCN remaining and then dried under a positive stream of nitrogen for 24 hours. (R,R)-Mn(PDP)(MeCN)$_2$(SbF$_6$)$_2$ 5 was obtained as a white solid (2.3795 g, 2.56 mmol, 95% yield). HRMS (TOF ESI+) m/z calculated for C$_{20}$H$_{26}$Na$_4$ClMnSb [M-SbF$_6$-2(MeCN)]$^+$: 612.0480, found 612.0469.

The (S,S)-Mn(PDP)(MeCN)$_2$(SbF$_6$)$_2$ can be synthesized with the same procedure from (2S,2’S)-1,1’-bis(pyridin-2-ylmethyl)-2,2’-bipyrrrolidine ligand.
A single crystal for X-ray crystallography was obtained by dissolving ~20 mg (S,S)-
Mn(PDP)(MeCN)₂(SbF₆)₂ (S,S)-5 in 0.2 mL MeCN and 0.1 mL benzene, followed by diethyl ether
diffuse into the catalyst solution at room temperature.

Supplementary X-Ray Table 1. Crystal data and structure refinement for (S,S)-5.

| Property                        | Value                                      |
|--------------------------------|--------------------------------------------|
| Empirical formula              | C24 H32 F12 Mn N6 Sb2                     |
| Formula weight                 | 930.99                                     |
| Temperature                    | 100(2) K                                  |
| Wavelength                     | 0.71073 Å                                 |
| Crystal system                 | Trigonal                                   |
| Space group                    | P3221                                      |
| Unit cell dimensions           | a = 10.5506(4) Å                          |
|                                | b = 10.5506(4) Å                          |
|                                | c = 25.2210(12) Å                         |
| Volume                         | 2431.3(2) Å³                              |
| Z                              | 3                                          |
| Density (calculated)           | 1.908 Mg/m³                                |
| Absorption coefficient         | 2.134 mm⁻¹                                 |
| F(000)                         | 1359                                       |
| Crystal size                   | 0.404 x 0.385 x 0.327 mm³                 |
| Theta range for data collection| 2.229 to 30.510°.                         |
| Index ranges                   | -15<=h<=15, -15<=k<=15, -36<=l<=36          |
Reflections collected 49619
Independent reflections 4947 [R(int) = 0.0425]
Completeness to theta = 25.242° 100.0 %
Absorption correction Integration
Max. and min. transmission 0.64747 and 0.51756
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 4947 / 0 / 206
Goodness-of-fit on F² 1.130
Final R indices [I>2sigma(I)] R1 = 0.0204, wR2 = 0.0420
R indices (all data) R1 = 0.0214, wR2 = 0.0423
Absolute structure parameter -0.029(7)
Extinction coefficient 0.0046(2)
Largest diff. peak and hole 0.434 and -0.592 e.Å⁻³

Crystallographic data for 5 can be obtained free of charge from www.ccdc.cam.ac.uk/structures/ with deposit number CCDC 1869257.

Synthesis and Characterization of Mn(CF₃-PDP)(MeCN)₂(SbF₆)₂

(R,R)-Mn(CF₃-PDP)Cl₂ [S2].

In a 50 mL recovery flask was charged (2R,2'R)-1,1'-bis((5-(2,6-bis(trifluoromethyl)phenyl)pyridin-2-yl)methyl)-2,2'-bipyrrolidineligand (1.5076 g, 2.02 mmol) synthesized according to literature procedure², a stir bar and MeCN (12 mL, 0.166 M). Freshly grinded MnCl₂•4H₂O (purchased from Strem, 399.6 mg, 2.02 mmol, 1.0 equiv.) was added and the reaction was allowed to stir vigorously for 24 hours under nitrogen atmosphere. Fine white solid was formed during the course of reaction and there should be no pink non-ligated manganese salt remained. Diethyl ether freshly taken from solvent delivery system was added to the reaction to precipitate out the complex. The solvent was removed via pipette and the remaining solids were washed thoroughly with diethyl ether five times and dried under a stream of dry nitrogen gas overnight to yield (R,R)-Mn(CF₃-PDP)Cl₂ (1.6075 g, 1.84 mmol, 91% yield) as white solid. HRMS (TOF ESI⁺) m/z calculated for C₃₆H₃₀N₄ClMnF₁₂ [M-Cl]⁺: 836.1348, found 836.1353.
A single crystal for X-ray crystallography was obtained by dissolving ~20 mg \((R,R)\)-Mn(CF₃-PDP)Cl₂ S2 in 0.2 mL MeCN and 0.1 mL benzene, followed by diethyl ether diffuse into the catalyst solution at room temperature.

---

**Supplementary X-Ray Table 2. Crystal data and structure refinement for S2.**

- **Empirical formula**: C₃₆ H₃₀ Cl₂ F₁₂ Mn N₄
- **Formula weight**: 872.48
- **Temperature**: 100(2) K
- **Wavelength**: 1.54178 Å
- **Crystal system**: Hexagonal
- **Space group**: P6₃
- **Unit cell dimensions**:
  - \(a = 9.2109(4)\) Å \(\text{a} = 90^\circ\).
  - \(b = 9.2109(4)\) Å \(\text{b} = 90^\circ\).
  - \(c = 76.327(3)\) Å \(\text{g} = 120^\circ\).
- **Volume**: 5608.1(5) Å³
- **Z**: 6
Density (calculated) 1.550 Mg/m³
Absorption coefficient 5.029 mm⁻¹
F(000) 2646
Crystal size 0.431 x 0.296 x 0.160 mm³
Theta range for data collection 3.474 to 68.327°.
Index ranges -11<=h<=11, -10<=k<=11, -91<=l<=91
Reflections collected 35026
Independent reflections 6638 [R(int) = 0.0531]
Completeness to theta = 67.679° 99.9 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.7531 and 0.5280
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 6638 / 1 / 497
Goodness-of-fit on F² 1.129
Final R indices [I>2sigma(I)] R1 = 0.0493, wR2 = 0.1197
R indices (all data) R1 = 0.0495, wR2 = 0.1199
Absolute structure parameter 0.198(9)
Extinction coefficient n/a
Largest diff. peak and hole 0.470 and -0.414 e.Å⁻³

Crystalllographic data for S2 can be obtained free of charge from www.ccdc.cam.ac.uk/structures/ with deposit number CCDC 1869260.

(R,R)-Mn(CF₃-PDP)(MeCN)₂(SbF₆)₂ [1].

In a flamed dried 100 mL recovery flask was charged (R,R)-Mn(CF₃-PDP)Cl₂ S2 (1.6075 g, 1.84 mmol), a stir bar and 24 mL dry MeCN. AgSbF₆ (purchased from Strem, 1.2662 g, 3.68 mmol, 2.0 equiv.) was weighed under argon atmosphere in glove box and then added to the reaction under nitrogen protection. The flask was wrapped with aluminum foil to protect from light and the reaction was vigorously stirred for 24 hours. AgCl was precipitated out and the reaction was filtered through a pad of Celite® and concentrated under vacuum to a minimum amount of MeCN remaining. The residue was redissolved in a minimum amount of MeCN and filtered through a 0.22 μm Acrodisc® LC PVDF filter
HPLC certified) and concentrated. The filtration-concentration process was repeated two more times and the residue was concentrated to a minimum amount of MeCN remaining and dried under a positive stream of nitrogen for 24 hours. \((R,R)\)-Mn(CF₃-PDP)(MeCN)₂(SbF₆)₂ was obtained as a white solid (2.3420 g, 1.73 mmol, 94% yield). HRMS (TOF ESI+) \(m/z\) calculated for C₃₆H₃₀N₄F₁₈MnSb [M-SbF₆-2(MeCN)]⁺: 1036.0602, found 1036.0624.

The \((S,S)\)-Mn(CF₃-PDP)(MeCN)₂(SbF₆)₂ can be synthesized with the same procedure.

A single crystal for X-ray crystallography was obtained by dissolving ~20 mg \((S,S)\)-Mn(CF₃-PDP)(MeCN)₂(SbF₆)₂ in 0.2 mL MeCN and 0.1 mL benzene, followed by diethyl ether diffuse into the catalyst solution at room temperature. However, a concise resolved structure from the single crystal cannot be obtained due to heavy modulation.

UV-Vis spectra for Mn(CF₃-PDP) 1: In a 10 mL volumetric flask, 19.8 mg (0.0146 mmol) of \((R,R)\)-Mn(CF₃-PDP) 1 was dissolved in MeCN to make a 10 mL solution (1.46 M). 250 \(\mu\)L of this solution was diluted to a 10 mL solution (0.0365 M) in a 10 mL volumetric flask. A UV-Vis spectra was taken from 800-220 nm in a quartz cuvette (path length = 1 cm).
III. Supplementary Table 1. Optimization of C—H oxidation protocol

Supplementary Table 1. Optimization of C—H oxidation protocol

| entry | catalyst | additive | oxidant | temperature | protocol | yield | selectivity |
|-------|----------|----------|---------|-------------|----------|-------|-------------|
| 1     | —        | —        | TFDO    | -20 ºC      | —        | trace | N. D.       |
| 2     | —        | —        | TFDO    | 0 ºC        | —        | trace | N. D.       |
| 3     | Ru(Me₃TACN) (2%) | —        | CAN     | RT          | —        | trace | N. D.       |
| 4     | cis-Ru(dbtpy)₂Cl₂ (5%) | —        | H₃IO₆   | RT          | —        | 0%    | N. D.       |
| 5     | Mn(OTf)₂, 0.1% bipy, 1% | —        | AcOOH   | RT          | —        | 26%   | 43%         |
| 6     | Mn(PDP)(OTf)₂ (0.1%) | CH₃COOH  | H₂O₂    | 0 ºC        | —        | 9%    | 69%         |
| 7     | Fe(PDP) (3X5%) | CH₃COOH  | H₂O₂    | RT          | iterative | 1%   | 2%          |
| 8     | Mn(PDP) (3X5%) | CH₃COOH  | H₂O₂    | RT          | iterative | 7%   | 59%         |
| 9     | Mn(PDP) (25%) | CH₃COOH  | H₂O₂    | RT          | double slow | 36% | 71%         |
| 10    | Fe(CF₃-PDP) (25%) | CH₃COOH  | H₂O₂    | RT          | double slow | 24% | 27%         |
| 11    | Mn(CF₃-PDP) (25%) | CH₃COOH  | H₂O₂    | RT          | double slow | 21% | 95%         |
| 12    | Mn(CF₃-PDP) (25%) | C₂H₂CO₂H | H₂O₂    | RT          | double slow | 73% | 90%         |
| 13    | Mn(CF₃-PDP) (25%) | C₂H₂CO₂H | H₂O₂    | RT          | double slow | 66% | 77%         |
| 14    | Mn(PDP) (25%) | C₂H₂CO₂H | H₂O₂    | RT          | double slow | 32% | 65%         |
| 15    | Mn(CF₃-PDP) (10%) | C₂H₂CO₂H | H₂O₂    | 0 ºC        | single catalyst | 86% | 94%         |
| 16    | Mn(PDP) (10%) | C₂H₂CO₂H | H₂O₂    | 0 ºC        | single catalyst | 38% | 85%         |
| 17    | Fe(CF₃-PDP) (10%) | C₂H₂CO₂H | H₂O₂    | 0 ºC        | single catalyst | 5%  | 7%          |
| 18    | Mn(CF₃-PDP) (10%) | CH₃COOH  | H₂O₂    | 0 ºC        | single catalyst | 20% | 75%         |

TFDO: methyl(trifluoromethyl)dioxirane. Abbreviation of catalysts: Ru(Me₃TACN) = Ru(Me₃TACN)(ClO₄)₃, Fe(PDP) = Fe(PDP)(MeCN)₂(SbF₆)₂, Fe(CF₃-PDP) = Fe(CF₃-PDP)(MeCN)₂(SbF₆)₂, Mn(PDP) = Mn(PDP)(MeCN)₂(SbF₆)₂. Mn(CF₃-PDP) = Mn(CF₃-PDP)(MeCN)₂(SbF₆)₂.
Chemoselectivity is defined as the yield of desired remote oxidation product over the conversion of starting material.

\[
\text{chemoselectivity} = \frac{\text{yield of remote oxidation product}}{\text{conversion of starting material}}
\]

**Synthesis of 1-(4-bromophenyl)cyclopentane-1-carbonitrile [2].**

In a flame dried 50 mL flask, 1.9604 g (10.0 mmol) of 2-(4-bromophenyl)acetonitrile was dissolved in 15 mL anhydrous DMF. 632.0 mg (95% purity, 25.0 mmol, 2.5 equiv.) of NaH was added in portions at 0 ºC and the reaction was allowed to stir for 1 hour at 0 ºC. 2.1593 g (1.18 mL, 10.0 mmol, 1.0 equiv.) of 1,4-dibromobutane was added dropwise at 0 ºC and the reaction was allowed to stir overnight at room temperature. The reaction was quenched carefully with ~10 mL water and extracted with 30 mL EtOAc three times. The combined organic layer was washed with 50 mL brine, dried with MgSO4, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO2) using 5% EtOAc/hexanes \(\rightarrow\) 10% EtOAc/hexanes as eluent gave 2.1143 g (8.45 mmol) of pure product as a white solid (85% yield).

\[
^1H-NMR\ (500\ MHz, CDCl_3)\ \delta\ 7.50\ (d, J = 8.6\ Hz, 2H),\ 7.33\ (d, J = 8.5\ Hz, 2H),\ 2.49\ \rightarrow\ 2.43\ (m, 2H),\ 2.08\ \rightarrow\ 1.89\ (m, 6H).\ \ ^{13}C-NMR\ (126\ MHz, CDCl_3)\ \delta\ 139.0,\ 132.0,\ 127.9,\ 124.0,\ 121.9,\ 47.5,\ 40.6,\ 24.3.\ \ HRMS\ (TOF\ ESI^+)\ m/z\ calculated\ for\ C_{11}H_{12}Br\ [M-CN]^+:\ 223.0122,\ found\ 223.0123.
\]

**Generation of TFDO:** Methyl(trifluoromethyl)dioxirane (TFDO) was synthesized according to the reported procedure in literature.\(^6\) Titration according to the reported method shows the concentration of the TFDO trifluoroacetone solution is about 0.4M. The TFDO solution was stored at -78 ºC and was used up within a week. The quality of TFDO was checked by oxidizing 2-methylpentyl 4-chlorobenzoate under the reported condition.\(^6\) **Reported:** 60% combined yield, 1.9:1 δ:β ratio. **Observed with home-made TFDO:** 60% combined yield, 2.1:1 δ:β ratio.

**General precautions of reactions using TFDO:** All solvents and TFDO transfer during the reaction setup was done with a plastic syringe equipped with plastic micropipette tips to avoid any metal contamination. Due to the sensitivity of TFDO to light, the reaction was wrapped with aluminum foil during the course of reaction.
Entry 1
The reaction was proceeded with the reported condition under low temperature that prevent free-radical formation. In a 1-dram vial charged with 1-(4-bromophenyl)cyclopentane-1-carbonitrile \( \text{2} \) (12.5 mg, 0.05 mmol, 1.0 equiv.) and a stir bar. 0.5 mL dichloromethane (DCM) freshly obtained from SDS was transferred into the vial via plastic syringe equipped with micropipette tip. The reaction was cooled to -20 ºC, and 0.38 mL 0.4M TFDO solution was added into the vial in 1-2 portions and the reaction was kept at -20 ºC for 48 h. The reaction was concentrated on rotvap to remove all volatiles and the crude mixture was analyzed by quantitative \(^1\)H NMR with nitrobenzene added as internal standard.

**Run 1:** <5% product, (10.0 mg, 0.040 mmol, 80.0% rsm). **Run 2:** <5% product, (10.3 mg, 0.041 mmol, 82.0% rsm). **Average:** <5% product, 81.0% rsm.

Entry 2
The reaction was proceeded at 0 ºC according to the reported condition. In a 1-dram vial charged with 1-(4-bromophenyl)cyclopentane-1-carbonitrile \( \text{2} \) (25.0 mg, 0.10 mmol, 1.0 equiv.) and a stir bar. 1.0 mL DCM freshly obtained from SDS was transferred into the vial via plastic syringe equipped with micropipette tip. The reaction was cooled to 0 ºC, and 0.75 mL 0.4M TFDO solution was added into the vial in 2-3 portions and the reaction was kept at 0 ºC for 6 h. The reaction was concentrated on rotvap to remove all volatiles and the crude mixture was analyzed by quantitative \(^1\)H NMR with nitrobenzene added as internal standard.

**Run 1:** <5% product, (18.6 mg, 0.075 mmol, 74.5% rsm). **Run 2:** <5% product, (18.8 mg, 0.075 mmol, 75.1% rsm). **Average:** <5% product, 74.8% rsm.

TFDO oxidation with 3+3 equiv. oxidant: The reaction was proceeded at 0 ºC with an extra addition of TFDO to push the conversion. In a 1-dram vial charged with 1-(4-bromophenyl)cyclopentane-1-carbonitrile \( \text{2} \) (12.5 mg, 0.05 mmol, 1.0 equiv.) and a stir bar. 0.5 mL DCM freshly obtained from SDS was transferred into the vial via plastic syringe equipped with micropipette tip. The reaction was cooled to -0 ºC, and 0.38 mL 0.4M TFDO solution was added into the vial in 1-2 portions and the reaction was kept at 0 ºC for 6 h. Another portion of 0.38 mL 0.4M TFDO solution was added into the vial in 1-2 portions and the reaction was allowed to react at 0 ºC for another 12 h. The reaction was concentrated on rotvap to remove all volatiles and the crude mixture was analyzed by quantitative \(^1\)H NMR with nitrobenzene added as internal standard.

**Run 1:** (1.6 mg, 0.006 mmol, 12.3% product), (5.0 mg, 0.020 mmol, 39.9% rsm). **Run 2:** (1.3 mg, 0.005 mmol, 10.1% product), (4.8 mg, 0.019 mmol, 38.3% rsm). **Average:** 11.2% product, 39.1% rsm.

Selectivity = 11.2/(100-39.1) = 18.4%. 
Entry 3
This reaction was conducted according to the reported general procedure. In a 16 x 125 mm disposable test tube fitted with a stir bar and a rubber septum. 2 mg (5 µmol, 0.02 equiv.) Ru(Me3TACN)Cl3, 2.0 mL H2O and 4 mg AgClO4 (0.02 mmol, 0.08 equiv.) was added sequentially and stirred at 80 ºC for 5 min. White AgCl participated was observed and the mixture was cooled to room temperature. 1-(4-bromophenyl)cyclopentane-1-carbonitrile 2 (62.5 mg, 0.25 mmol, 1.0 equiv.) was dissolved in 2.0 mL tert-butanol and added to the reaction followed by ceric ammonium nitrate (411 mg, 0.75 mmol, 3.0 equiv.). The dark red reaction was allowed to stir at room temperature for 30 min and another batch of ceric ammonium nitrate (411 mg, 0.75 mmol, 3.0 equiv.) was added. The reaction was further stirred for 14 hours and quenched with 1 mL of MeOH, diluted with water and extracted with 25 mL X3 ethyl acetate. The combined organic layer was dried with MgSO4, filtered and concentrated under reduced pressure. The crude mixture was analyzed by quantitative 1H NMR analysis with nitrobenzene added as internal standard.

Run 1: trace product, (58.2 mg, 0.233 mmol, 93.1% rsm). Run 2: trace product, (53.7 mg, 0.215 mmol, 85.9% rsm). Run 3: trace product, (54.9 mg, 0.220 mmol, 87.9% rsm). Average: trace product, 89.0% rsm ± 3.7%.

Entry 4
This reaction was conducted according to the reported general procedure. In a 20 mL vial charged with 1-(4-bromophenyl)cyclopentane-1-carbonitrile 2 (62.5 mg, 0.25 mmol, 1.0 equiv.), a magnetic stir bar and a solution of cis-Ru(dtbpy)2Cl2 (8.9 mg, 13 µmol, 0.05 equiv.) in 2.0 mL acetic acid. 2.0 mL water was added to the vial and the purple solution was stirred at room temperature for 2 min before a single portion of H5IO6 (114 mg, 0.50 mmol, 2.0 equiv.) was added. The reaction was wrapped with aluminum foil and stirred at room temperature for 4 hours. The reaction was transferred to a separatory funnel with 4 mL CH2Cl2 and 30 mL water. The aqueous layer was extracted with 3 x 15 mL CH2Cl2 and the combined organic layer was dried over Na2SO4. The crude reaction was concentrated and analyzed by quantitative 1H NMR analysis with nitrobenzene added as internal standard.

Run 1: 0% product, (57.9 mg, 0.231 mmol, 92.5% rsm). Run 2: 0% product, (52.4 mg, 0.209 mmol, 83.8% rsm). Run 3: 0% product, (54.2 mg, 0.217 mmol, 86.6% rsm). Average: 0% product, 87.6% rsm ± 4.4%.

Entry 5
This reaction was conducted according to the reported general procedure. To a 20 mL vial containing 1-(4-bromophenyl)cyclopentane-1-carbonitrile 2 (62.5 mg, 0.25 mmol, 1.0 equiv.), AcOH (1.25 mL),
Mn(OTf)₂ solution (20 µL, 12.5 mM solution in 9:1 AcOH/H₂O, 0.25 µmol, 0.001 equiv.) and bipyridine solution (100 µL, 0.025 M solution in AcOH, 2.5 µmmol, 0.01 equiv.). The mixture was stirred for 10 minutes and modified peracetic acid solution (220 µL, prepared by mixing 1.0 mL of commercial peracetic acid (35% Sigma-Aldrich) with 0.3 mL of 10% KOH solution, 0.75 mmol, 3.0 equiv.) was added dropwise in 30 seconds. The reaction was stirred for another 60 seconds and then diluted with 5 mL acetone. After 30 seconds stirring, the mixture was filtered through Celite® and the filtrate was concentrated under reduced temperature. The crude mixture was analyzed by quantitative ¹H NMR analysis with nitrobenzene added as internal standard.

Run 1: (18.7 mg, 0.071 mmol, 28.3% yield), (25.1 mg, 0.100 mmol, 40.1% rsm). Run 2: (16.2 mg, 0.061 mmol, 24.5% yield), (23.5 mg, 0.094 mmol, 37.6% rsm). Run 3: (17.1 mg, 0.065 mmol, 25.9% yield), (24.1 mg, 0.096 mmol, 38.5% rsm). Average: 26.2% yield ± 1.9%, 38.7% rsm ± 1.3%. Selectivity = 26.2/(100-38.7) = 42.7%.

Entry 6
This reaction was conducted according to the “cyclohexane oxidation under practical conditions” procedure.⁹ Mn(PDP)(OTf)₂ was prepared by metathesis between Mn(PDP)Cl₂ and AgOTf according to a similar procedure as Mn(PDP)(MeCN)₂(SbF₆)₂ reported in Section II of Supplementary Information. To a 20 mL vial containing 1-(4-bromophenyl)cyclopentane-1-carbonitrile 2 (75.0 mg, 0.30 mmol, 1.0 equiv.), AcOH (0.24 mL, 14 equiv.), Mn(PDP)(OTf)₂ solution (60 µL, 5 mM solution in MeCN, 0.30 µmol, 0.001 equiv.) and MeCN (1.14 mL). The mixture was thermostatted at 0 ºC and a solution of H₂O₂ (50%, 51.0 mg, 0.75 mmol, 2.5 equiv.) in 0.3 mL MeCN was added via syringe pump over 1h. The reaction was stirred for another 1h at 0 ºC before concentrated on rotvap. The crude mixture was analyzed by quantitative ¹H NMR analysis with nitrobenzene added as internal standard.

Run 1: (7.6 mg, 0.029 mmol, 9.6% yield), (66.3 mg, 0.265 mmol, 88.4% rsm). Run 2: (6.5 mg, 0.025 mmol, 8.2% yield), (65.5 mg, 0.262 mmol, 87.3% rsm). Run 3: (7.2 mg, 0.027 mmol, 9.0% yield), (64.2 mg, 0.256 mmol, 85.5% rsm). Average: 8.9% yield ± 0.7%, 87.1% rsm ± 1.5%. Selectivity = 8.9/(100-87.1) = 69.0%.

Entry 7
The reaction was conducted according to the iterative addition protocol.¹ In a 40 mL vial was charged with 1-(4-bromophenyl)cyclopentane-1-carbonitrile 2 (75.0 mg, 0.30 mmol, 1.0 equiv.), (R,R)-Fe(PDP) catalyst 4 (14.0 mg, 0.015 mmol, 0.05 equiv.), AcOH (9.0 mg, 0.15 mmol, 0.5 equiv.), MeCN (0.45 mL) and a stir bar. The vial was stirred vigorously and a solution of H₂O₂ (50 wt%, 24.5 mg, 1.2 equiv.) in MeCN (3.75 mL) in a 10 mL syringe equipped with 25G needle was added dropwise over 60-75 seconds.
The reaction was allowed to stir for 10 minutes at room temperature and a second batch of catalyst (14.0 mg, 0.015 mmol, 0.05 equiv.) and AcOH (9.0 mg, 0.15 mmol, 0.5 equiv.) dissolved in 0.3 mL MeCN was added via pipette. This was followed by a solution of H₂O₂ (50 wt%, 24.5 mg, 1.2 equiv.) in MeCN (3.75 mL) in a 10 mL syringe equipped with 25G needle dropwise over 60-75 seconds. After another 10 minutes a third batch of catalyst and H₂O₂ was added in the same manner. The third addition was allowed to stir for 10 minutes for a total reaction time of 30 minutes. **Significant decrease in yield was observed when the peroxide solution was added rapidly.**

Upon completion of the reaction, the mixture was concentrated *in vacuo* to a minimum amount of MeCN. 20 mL ether was added to crush the iron complex out and the mixture was filtered via a Celite® plug. The filtrate was dried over Na₂SO₄, concentrated and analyzed by quantitative ¹H NMR analysis with nitrobenzene added as internal standard.

**Run 1:** (1.2 mg, 0.005 mmol, 1.5% yield), (35.4 mg, 0.141 mmol, 47.1% rsm). **Run 2:** (1.3 mg, 0.005 mmol, 1.5% yield), (35.0 mg, 0.140 mmol, 46.5% rsm). **Run 3:** (0.6 mg, 0.002 mmol, 0.9% yield), (33.8 mg, 0.135 mmol, 45.1% rsm). **Average:** 1.3% yield ± 0.3%, 46.2% rsm ± 1.0%. Selectivity = 1.3/(100-46.2) = 2.4%.

**Entry 8**

The reaction was conducted according to the iterative addition protocol.¹ In a 40 mL vial was charged with 1-(4-bromophenyl)cyclopentane-1-carbonitrile 2 (75.0 mg, 0.30 mmol, 1.0 equiv.), (R,R)-Mn(PDP) catalyst 5 (14.0 mg, 0.015 mmol, 0.05 equiv.), AcOH (9.0 mg, 0.15 mmol, 0.5 equiv.), MeCN (0.45 mL) and a stir bar. The vial was stirred vigorously and a solution of H₂O₂ (50 wt%, 24.5 mg, 1.2 equiv.) in MeCN (3.75 mL) in a 10 mL syringe equipped with 25G needle was added dropwise over 60-75 seconds. The reaction was allowed to stir for 10 minutes at room temperature and a second batch of catalyst (14.0 mg, 0.015 mmol, 0.05 equiv.) and AcOH (9.0 mg, 0.15 mmol, 0.5 equiv.) dissolved in 0.3 mL MeCN was added via pipette. This was followed by a solution of H₂O₂ (50 wt%, 24.5 mg, 1.2 equiv.) in MeCN (3.75 mL) in a 10 mL syringe equipped with 25G needle dropwise over 60-75 seconds. After another 10 minutes a third batch of catalyst and H₂O₂ was added in the same manner. The third addition was allowed to stir for 10 minutes for a total reaction time of 30 minutes. **Significant decrease in yield was observed when the peroxide solution was added rapidly.**

Upon completion of the reaction, the mixture was concentrated *in vacuo* to a minimum amount of MeCN. 20 mL ether was added and the mixture was filtered via a Celite® plug. The filtrate was dried over Na₂SO₄, concentrated and analyzed by quantitative ¹H NMR analysis with nitrobenzene added as internal standard.

**Run 1:** (5.6 mg, 0.021 mmol, 7.1% yield), (66.3 mg, 0.265 mmol, 88.4% rsm). **Run 2:** (4.5 mg, 0.017 mmol, 5.7% yield), (65.5 mg, 0.262 mmol, 87.3% rsm). **Run 3:** (5.5 mg, 0.021 mmol, 6.9% yield), (68.0
Entry 9

The reaction was conducted in slow addition protocol. In a 40 mL vial was charged with 1-(4-bromophenyl)cyclopentane-1-carbonitrile (75.0 mg, 0.30 mmol, 1.0 equiv), AcOH (90.1 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.60 mL) and a stir bar. A 1mL syringe was charged with a solution of (R,R)-Mn(PDP) catalyst (69.9 mg, 0.075 mmol, 0.25 equiv.) in MeCN (0.375 mL). A 10 mL syringe was charged with a solution of H2O2 (183.6 mg, 2.7 mmol, 9.0 equiv.) in MeCN (3.75 mL). Both syringes were fitted with 25G needles and the solution was added dropwise via syringe pump over 1 hour. Upon completion of addition, the reaction was concentrated in vacuo to a minimum amount of MeCN and purified by column chromatography on silica (35 mm fritted glass column, 150 mL SiO2) using 20% acetone/hexanes to 30% acetone/hexanes as eluent to give both recovered starting material and product.

Run 1: (28.5 mg, 0.108 mmol, 36.0% yield), (38.0 mg, 0.152 mmol, 50.6% rsm). Run 2: (28.1 mg, 0.106 mmol, 35.5% yield), (38.7 mg, 0.155 mmol, 51.6% rsm). Run 3: (28.2 mg, 0.107 mmol, 35.6% yield), (35.6 mg, 0.142 mmol, 47.4% rsm). Average: 35.7% yield ± 0.3%, 49.9% rsm ± 2.2%. Selectivity = 35.7/(100-49.9) = 71.3%.

Entry 10

The reaction was conducted in slow addition protocol. In a 40 mL vial was charged with 1-(4-bromophenyl)cyclopentane-1-carbonitrile (75.0 mg, 0.30 mmol, 1.0 equiv), AcOH (90.1 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.60 mL) and a stir bar. A 1mL syringe was charged with a solution of (R,R)-Fe(CF3-PDP) catalyst (101.6 mg, 0.075 mmol, 0.25 equiv.) in MeCN (0.375 mL). A 10 mL syringe was charged with a solution of H2O2 (183.6 mg, 2.7 mmol, 9.0 equiv.) in MeCN (3.75 mL). Both syringes were fitted with 25G needles and the solution was added dropwise via syringe pump over 1 hour. Upon completion of addition, the reaction was concentrated in vacuo to a minimum amount of MeCN and purified by column chromatography on silica (35 mm fritted glass column, 150 mL SiO2) using 20% acetone/hexanes to 30% acetone/hexanes as eluent to give both recovered starting material and product.

Run 1: (18.5 mg, 0.070 mmol, 23.3% yield), (7.2 mg, 0.029 mmol, 9.6% rsm). Run 2: (21.2 mg, 0.080 mmol, 26.8% yield), (7.5 mg, 0.030 mmol, 10.0% rsm). Run 3: (17.0 mg, 0.064 mmol, 21.5% yield), (7.5 mg, 0.030 mmol, 10.0% rsm). Average: 23.9% yield ± 2.7%, 9.9% rsm ± 0.2%. Selectivity = 23.9/(100-9.9) = 26.5%.

Entry 11
The reaction was conducted in slow addition protocol. In a 40 mL vial was charged with 1-(4-bromophenyl)cyclopentane-1-carbonitrile \((\text{75.0 mg, 0.30 mmol, 1.0 equiv})\), AcOH \((\text{90.1 mg, 1.5 mmol, 5.0 equiv})\), MeCN \((\text{0.60 mL})\) and a stir bar. A 1mL syringe was charged with a solution of \((R,R)-\text{Mn(CF}_3\text{-PDP)}\) catalyst \((\text{101.6 mg, 0.075 mmol, 0.25 equiv})\) in MeCN \((\text{0.375 mL})\). A 10 mL syringe was charged with a solution of \(\text{H}_2\text{O}_2\) \((\text{183.6 mg, 2.7 mmol, 9.0 equiv})\) in MeCN \((\text{3.75 mL})\). Both syringes were fitted with 25G needles and the solution was added dropwise via syringe pump over 1 hour. Upon completion of addition, the reaction was concentrated \(\text{in vacuo}\) to a minimum amount of MeCN and purified by column chromatography on silica \((\text{35 mm fritted glass column, 150 mL SiO}_2)\) using 20% acetone/hexanes \(\rightarrow\) 30% acetone/hexanes as eluent to give both recovered starting material and product.

**Run 1:** \((\text{16.6 mg, 0.063 mmol, 20.9% yield), (58.6 mg, 0.234 mmol, 78.1% rsm})\). **Run 2:** \((\text{17.2 mg, 0.065 mmol, 21.7% yield), (57.3 mg, 0.229 mmol, 76.4% rsm})\). **Run 3:** \((\text{14.9 mg, 0.056 mmol, 18.8% yield), (60.4 mg, 0.241 mmol, 80.5% rsm})\). **Average:** \(20.5\%\ \text{yield} \pm 1.5\%, \ 78.3\%\ \text{rsm} \pm 2.1\%.\ \text{Selectivity} = \frac{20.5}{(100-78.3)} = 94.5\%\).

**Entry 12**

The reaction was conducted in slow addition protocol. In a 40 mL vial was charged with 1-(4-bromophenyl)cyclopentane-1-carbonitrile \((\text{75.0 mg, 0.30 mmol, 1.0 equiv})\), ClCH\(_2\)COOH \((\text{141.7 mg, 1.5 mmol, 5.0 equiv})\), MeCN \((\text{0.60 mL})\) and a stir bar. A 1mL syringe was charged with a solution of \((R,R)-\text{Mn(CF}_3\text{-PDP)}\) catalyst \((\text{101.6 mg, 0.075 mmol, 0.25 equiv})\) in MeCN \((\text{0.375 mL})\). A 10 mL syringe was charged with a solution of \(\text{H}_2\text{O}_2\) \((\text{183.6 mg, 2.7 mmol, 9.0 equiv})\) in MeCN \((\text{3.75 mL})\). Both syringes were fitted with 25G needles and the solution was added dropwise via syringe pump over 1 hour. Upon completion of addition, the reaction was concentrated \(\text{in vacuo}\) to a minimum amount of MeCN. The residue was dissolved in \(\sim\)20 mL DCM and washed with 9 mL sat. NaHCO\(_3\) solution (CAUTION: CO\(_2\) was released) to remove ClCH\(_2\)CO\(_2\)H. The aqueous layer was extracted with \(\sim\)15 mL DCM twice and the combined organic layer was dried with Na\(_2\)SO\(_4\). After filtration, the filtrate was concentrated and purified by column chromatography on silica \((\text{35 mm fritted glass column, 150 mL SiO}_2)\) using 20% acetone/hexanes \(\rightarrow\) 30% acetone/hexanes as eluent to give both recovered starting material and product.

**Run 1:** \((\text{55.6 mg, 0.210 mmol, 70.2% yield), (17.4 mg, 0.070 mmol, 23.2% rsm})\). **Run 2:** \((\text{58.7 mg, 0.222 mmol, 74.1% yield), (12.5 mg, 0.050 mmol, 16.7% rsm})\). **Run 3:** \((\text{58.1 mg, 0.220 mmol, 73.3% yield), (14.1 mg, 0.056 mmol, 18.8% rsm})\). **Average:** \(72.5\%\ \text{yield} \pm 2.1\%, \ 19.6\%\ \text{rsm} \pm 3.3\%.\ \text{Selectivity} = \frac{72.5}{(100-19.6)} = 90.2\%\).

**Entry 13**
The reaction was conducted in slow addition protocol. In a 40 mL vial was charged with 1-(4-bromophenyl)cyclopentane-1-carbonitrile 2 (75.0 mg, 0.30 mmol, 1.0 equiv), ClCHCOOH (193.4 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.60 mL) and a stir bar. A 1mL syringe was charged with a solution of (R,R)-Mn(CF3-PDP) catalyst 1 (101.6 mg, 0.075 mmol, 0.25 equiv.) in MeCN (0.375 mL). A 10 mL syringe was charged with a solution of H2O2 (183.6 mg, 2.7 mmol, 9.0 equiv.) in MeCN (3.75 mL). Both syringes were fitted with 25G needles and the solution was added dropwise via syringe pump over 1 hour. Upon completion of addition, the reaction was concentrated in vacuo to a minimum amount of MeCN. The residue was dissolved in ~20 mL DCM and washed with 9 mL sat. NaHCO3 solution (CAUTION: CO2 was released) to remove ClCH2CO2H. The aqueous layer was extracted with ~15 mL DCM twice and the combined organic layer was dried with Na2SO4. After filtration, the filtrate was concentrated and purified by column chromatography on silica (35 mm fritted glass column, 150 mL SiO2) using 20% acetone/hexanes → 30% acetone/hexanes as eluent to give both recovered starting material and product.

Run 1: (53.9 mg, 0.204 mmol, 68.0% yield), (10.3 mg, 0.041 mmol, 13.7% rsm). Run 2: (50.8 mg, 0.192 mmol, 64.1% yield), (10.3 mg, 0.041 mmol, 13.7% rsm). Run 3: (53.0 mg, 0.201 mmol, 66.9% yield), (9.3 mg, 0.037 mmol, 12.4% rsm). Average: 66.3% yield ± 2.0%, 13.3% rsm ± 0.8%. Selectivity = 66.3/(100-13.3) = 76.5%.

Entry 14

The reaction was conducted in slow addition protocol. In a 40 mL vial was charged with 1-(4-bromophenyl)cyclopentane-1-carbonitrile 2 (75.0 mg, 0.30 mmol, 1.0 equiv), ClCH2COOH (141.7 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.60 mL) and a stir bar. A 1mL syringe was charged with a solution of (R,R)-Mn(PDP) catalyst 5 (69.8 mg, 0.075 mmol, 0.25 equiv.) in MeCN (0.375 mL). A 10 mL syringe was charged with a solution of H2O2 (183.6 mg, 2.7 mmol, 9.0 equiv.) in MeCN (3.75 mL). Both syringes were fitted with 25G needles and the solution was added dropwise via syringe pump over 1 hour. Upon completion of addition, the reaction was concentrated in vacuo to a minimum amount of MeCN. The residue was dissolved in ~20 mL DCM and washed with 9 mL sat. NaHCO3 solution (CAUTION: CO2 was released) to remove ClCH2CO2H. The aqueous layer was extracted with ~15 mL DCM twice and the combined organic layer was dried with Na2SO4. After filtration, the filtrate was concentrated and purified by column chromatography on silica (35 mm fritted glass column, 150 mL SiO2) using 20% acetone/hexanes → 30% acetone/hexanes as eluent to give both recovered starting material and product.

Run 1: (26.4 mg, 0.110 mmol, 33.3% yield), (39.2 mg, 0.157 mmol, 52.2% rsm). Run 2: (24.1 mg, 0.091 mmol, 30.4% yield), (39.6 mg, 0.158 mmol, 52.8% rsm). Run 3: (25.9 mg, 0.098 mmol, 32.7% yield), (35.2 mg, 0.141 mmol, 46.9% rsm). Average: 32.1% yield ± 1.5%, 50.6% rsm ± 3.2%. Selectivity = 32.1/(100-50.6) = 65.0%.
Entry 15
The reaction was conducted with Method A: single catalyst addition protocol (*vide infra*, Section IV). In a 40 mL vial was charged with 1-(4-bromophenyl)cyclopentane-1-carbonitrile 2 (75.0 mg, 0.30 mmol, 1.0 equiv), ClCH$_2$COOH (425.3 mg, 4.5 mmol, 15.0 equiv.), (R,R)-Mn(CF$_3$-PDP) catalyst 1 (40.7 mg, 0.03 mmol, 0.10 equiv.) MeCN (0.60 mL) and a stir bar. A 10 mL syringe was charged with a solution of H$_2$O$_2$ (204 mg, 3.0 mmol, 10.0 equiv.) in MeCN (3.75 mL), fitted with 25G needles and the solution was added dropwise *via* syringe pump over 3 hours (1.25 mL/hour) while the reaction vial was maintained at 0 °C. Upon completion of addition, the reaction was concentrated *in vacuo* to a minimum amount of MeCN. The residue was dissolved in ~20 mL DCM and washed with 9 mL sat. NaHCO$_3$ solution (CAUTION: CO$_2$ was released) to remove ClCH$_2$CO$_2$H. The aqueous layer was extracted with ~15 mL DCM twice and the combined organic layer was dried with Na$_2$SO$_4$. After filtration, the filtrate was concentrated and purified by column chromatography on silica (35 mm fritted glass column, 150 mL SiO$_2$) using 20% acetone/hexanes $\rightarrow$ 30% acetone/hexanes as eluent to give both recovered starting material and product.

Run 1: (67.8 mg, 0.257 mmol, 85.6% yield), (8.7 mg, 0.035 mmol, 11.6% rsm). Run 2: (68.3 mg, 0.259 mmol, 86.2% yield), (5.5 mg, 0.022 mmol, 7.3% rsm). Run 3: (67.2 mg, 0.254 mmol, 84.8% yield), (5.9 mg, 0.024 mmol, 7.9% rsm). **Average: 85.5% yield ± 0.7%, 8.9% rsm ± 2.3%. Selectivity = 85.5/(100-8.9) = 93.9%.

Entry 16
The reaction was conducted with Method A: single catalyst addition protocol (*vide infra*, Section IV). In a 40 mL vial was charged with 1-(4-bromophenyl)cyclopentane-1-carbonitrile 2 (75.0 mg, 0.30 mmol, 1.0 equiv), ClCH$_2$COOH (425.3 mg, 4.5 mmol, 15.0 equiv.), (R,R)-Mn(PDP) catalyst 5 (27.9 mg, 0.03 mmol, 0.10 equiv.) MeCN (0.60 mL) and a stir bar. A 10 mL syringe was charged with a solution of H$_2$O$_2$ (204 mg, 3.0 mmol, 10.0 equiv.) in MeCN (3.75 mL), fitted with 25G needles and the solution was added dropwise *via* syringe pump over 3 hours (1.25 mL/hour) while the reaction vial was maintained at 0 °C. Upon completion of addition, the reaction was concentrated *in vacuo* to a minimum amount of MeCN. The residue was dissolved in ~20 mL DCM and washed with 9 mL sat. NaHCO$_3$ solution (CAUTION: CO$_2$ was released) to remove ClCH$_2$CO$_2$H. The aqueous layer was extracted with ~15 mL DCM twice and the combined organic layer was dried with Na$_2$SO$_4$. After filtration, the filtrate was concentrated and purified by column chromatography on silica (35 mm fritted glass column, 150 mL SiO$_2$) using 20% acetone/hexanes $\rightarrow$ 30% acetone/hexanes as eluent to give both recovered starting material and product.

Run 1: (31.0 mg, 0.117 mmol, 39.1% yield), (41.6 mg, 0.166 mmol, 55.4% rsm). Run 2: (30.3 mg, 0.115 mmol, 38.2% yield), (40.4 mg, 0.162 mmol, 53.8% rsm). Run 3: (28.0 mg, 0.106 mmol, 35.3% yield),
(43.5 mg, 0.174 mmol, 58.0% rsm). **Average: 37.5% yield ± 2.0%, 55.7% rsm ± 2.1%. Selectivity = \(37.5/(100-55.7) = 84.7\%\).**

**Entry 17**

The reaction was conducted with Method A: single catalyst addition protocol (*vide infra*, Section IV). In a 40 mL vial was charged with 1-(4-bromophenyl)cyclopentane-1-carbonitrile 2 (75.0 mg, 0.30 mmol, 1.0 equiv), ClCH2COOH (425.3 mg, 4.5 mmol, 15.0 equiv.), \((R,R)\)-Fe(CF3-PDP) catalyst 6 (40.7 mg, 0.03 mmol, 0.10 equiv.) MeCN (0.60 mL) and a stir bar. A 10 mL syringe was charged with a solution of H2O2 (204 mg, 3.0 mmol, 10.0 equiv.) in MeCN (3.75 mL), fitted with 25G needles and the solution was added dropwise *via* syringe pump over 3 hours (1.25 mL/hour) while the reaction vial was maintained at 0 ºC. Upon completion of addition, the reaction was concentrated *in vacuo* to a minimum amount of MeCN. The residue was dissolved in ~20 mL DCM and washed with 9 mL sat. NaHCO3 solution (CAUTION: CO2 was released) to remove ClCH2CO2H. The aqueous layer was extracted with ~15 mL DCM twice and the combined organic layer was dried with Na2SO4. After filtration, the filtrate was concentrated and purified by column chromatography on silica (35 mm fritted glass column, 150 mL SiO2) using 20% acetone/hexanes \(\rightarrow\) 30% acetone/hexanes as eluent to give both recovered starting material and product.

**Run 1:** (4.2 mg, 0.016 mmol, 5.3% yield), (18.7 mg, 0.075 mmol, 24.9% rsm). **Run 2:** (4.5 mg, 0.017 mmol, 5.7% yield), (18.8 mg, 0.075 mmol, 25.1% rsm). **Run 3:** (4.2 mg, 0.016 mmol, 5.3% yield), (17.8 mg, 0.071 mmol, 23.7% rsm). **Average: 5.4% yield ± 0.2%, 24.6% rsm ± 0.8%. Selectivity = 5.4/(100-24.6) = 7.2%.**

**Entry 18**

The reaction was conducted with Method A: single catalyst addition protocol (*vide infra*, Section IV). In a 40 mL vial was charged with 1-(4-bromophenyl)cyclopentane-1-carbonitrile 2 (75.0 mg, 0.30 mmol, 1.0 equiv), CH3COOH (270.2 mg, 4.5 mmol, 15.0 equiv.), \((R,R)\)-Mn(CF3-PDP) catalyst 1 (40.7 mg, 0.03 mmol, 0.10 equiv.) MeCN (0.60 mL) and a stir bar. A 10 mL syringe was charged with a solution of H2O2 (204 mg, 3.0 mmol, 10.0 equiv.) in MeCN (3.75 mL), fitted with 25G needles and the solution was added dropwise *via* syringe pump over 3 hours (1.25 mL/hour) while the reaction vial was maintained at 0 ºC. Upon completion of addition, the reaction was concentrated *in vacuo* to a minimum amount of MeCN. The residue was dissolved in ~20 mL DCM and washed with 9 mL sat. NaHCO3 solution (CAUTION: CO2 was released) to remove CH3CO2H. The aqueous layer was extracted with ~15 mL DCM twice and the combined organic layer was dried with Na2SO4. After filtration, the filtrate was concentrated and purified by column chromatography on silica (35 mm fritted glass column, 150 mL SiO2) using 20% acetone/hexanes \(\rightarrow\) 30% acetone/hexanes as eluent to give both recovered starting material and product.
Run 1: (16.0 mg, 0.061 mmol, 20.2% yield), (56.3 mg, 0.225 mmol, 75.0% rsm). Run 2: (13.1 mg, 0.050 mmol, 16.5% yield), (55.9 mg, 0.223 mmol, 74.5% rsm). Run 3: (17.8 mg, 0.067 mmol, 22.5% yield), (53.5 mg, 0.214 mmol, 71.3% rsm). Average: 19.7% yield ± 3.0%, 73.6% rsm ± 2.0%. Selectivity = 19.7/(100-73.6) = 74.6%.

Characterization of 1-(4-bromophenyl)-3-oxocyclopentane-1-carbonitrile [3].

\[
\begin{align*}
\text{1H-NMR (500 MHz, CDCl}_3\text{)} & \delta 7.59 – 7.57 (m, 2H), 7.35 – 7.32 (m, 2H), 3.05 (d, J = 18.1 Hz, 1H), 2.83 (ddd, J = 10.3, 8.5, 3.9 Hz, 1H), 2.75 (d, J = 18.2 Hz, 1H), 2.70 – 2.64 (m, 1H), 2.56 – 2.50 (m, 1H), 2.41 (ddd, J = 12.9, 9.9, 8.2 Hz, 1H). \\
\text{13C-NMR (126 MHz, CDCl}_3\text{)} & \delta 211.6, 136.6, 132.7, 127.6, 123.1, 122.1, 49.8, 43.9, 36.7, 36.3.
\end{align*}
\]

HRMS (TOF ESI+) \textit{m/z} calculated for C\textsubscript{11}H\textsubscript{10}OBr [M-CN]: 236.9915, found 236.9915. Enantiomeric excess (\textit{ee}) of cyclic ketone oxidation products were not evaluated due to the generally low \textit{ee} (11% for 17, \textit{vide infra}).
IV. Supplementary Figure 1. Chemoselective methylene oxidation in aromatic substrates.

Method A: single catalyst addition protocol is used unless otherwise noted. Isolated yields are average of three runs.

Iterative catalyst addition protocol (method B): substrate (0.3 mmol) with Mn(CF<sub>3</sub>-PDP) 1 (0.015 mmol) and ClCH<sub>2</sub>CO<sub>2</sub>H (4.5 mmol) dissolved in MeCN (0.6 mL) maintained 0 ºC, a solution of H<sub>2</sub>O<sub>2</sub> (50% wt., 3.0 mmol) in MeCN (3.75 mL, 0.8 M) was added via syringe pump over 3 hours; two additional portions of Mn(CF<sub>3</sub>-PDP) 1 (0.015 mmol each) in MeCN (0.2 mL each) were added to the reaction after one and two hours.

25 mol% Fe(CF<sub>3</sub>-PDP) 6, slow addition protocol (supplementary ref. 10). Starting material recycled 1X. Ratios are statistically corrected. 7% chloroacetic ester, 8% recovered starting material.

Supplementary Figure 1. Electrochemical: 56%<sup>a</sup> 2º:3º ratio. Cat.: 6b: 0%. Mn(OTf)<sub>2</sub>/bipy: 17%.

Mn(CF<sub>3</sub>-PDP) 1 (10-15 mol%) ClCH<sub>2</sub>CO<sub>2</sub>H (15 equiv.) H<sub>2</sub>O<sub>2</sub> (10 equiv.) in MeCN, 0 ºC, 3 hours.
Preparation of Substrates and Compounds Characterization for Supplementary Figure 1

General procedure for the synthesis of substrate S3-S6

1-phenylcyclopentane-1-carbonitrile [S3].

In a flamed dried 100 mL flask, 1.1715 g (10.0 mmol) of 2-phenylacetonitrile was dissolved in 15 mL anhydrous DMF. 632.0 mg (95% purity, 25.0 mmol, 2.5 equiv.) of NaH was added in portions at 0 ºC and the reaction was allowed to stir for 1 hour at 0 ºC. 2.1593 g (1.18 mL, 10.0 mmol, 1.0 equiv.) of 1,4-dibromobutane was added dropwise at 0 ºC and the reaction was stirred overnight at room temperature. The reaction was quenched carefully with ~10 mL water and extracted with 30 mL EtOAc three times. The combined organic layer was washed with 50 mL brine, dried with MgSO₄, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO₂) using 3% EtOAc/hexanes → 5% EtOAc/hexanes as eluent gave 1.2535 g (7.31 mmol) of pure product as a slightly yellowish oil (73% yield).

1H-NMR (500 MHz, CDCl₃) δ 7.48 – 7.45 (m, 2H), 7.40 – 7.37 (m, 2H), 7.33 – 7.29 (m, 1H), 2.51 – 2.47 (m, 2H), 2.12 – 1.91 (m, 6H). 13C-NMR (126 MHz, CDCl₃) δ 139.9, 129.0, 127.9, 126.1, 124.5, 47.9, 40.6, 24.4. HRMS (EI+) m/z calculated for C₁₂H₁₂N [M-H]⁺: 170.09697, found 170.09660.

1-(4-(tert-butyl)phenyl)cyclopentane-1-carbonitrile [S4].

In a flamed dried 100 mL flask, 1.7326 g (10.0 mmol) of 2-(4-tert-butylphenyl)acetonitrile was dissolved in 15 mL anhydrous DMF. 632.0 mg (95% purity, 25.0 mmol, 2.5 equiv.) of NaH was added in portions at 0 ºC and the reaction was allowed to stir for 1 hour at 0 ºC. 2.1593 g (1.18 mL, 10.0 mmol, 1.0 equiv.) of 1,4-dibromobutane was added dropwise at 0 ºC and the reaction was stirred overnight at room temperature. The reaction was quenched carefully with ~10 mL water and extracted with 30 mL EtOAc three times. The combined organic layer was washed with 50 mL brine, dried with MgSO₄, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO₂) using 2% EtOAc/hexanes → 5% EtOAc/hexanes as eluent gave 1.5612 g (6.87 mmol) of pure product as a slightly yellowish solid (69% yield).

1H-NMR (500 MHz, CDCl₃) δ 7.41 – 7.37 (m, 4H), 2.49 – 2.44 (m, 2H), 2.11 – 1.91 (m, 6H), 1.33 (s, 9H). 13C-NMR (126 MHz, CDCl₃) δ 150.8, 136.9, 125.9, 125.8, 124.7, 47.5, 40.5, 34.6, 31.4, 24.3. HRMS (EI+) m/z calculated for C₁₆H₂₁N [M⁺]: 227.1674, found 227.1678.
1-(4-chlorophenyl)cyclopentane-1-carbonitrile [S5].

In a flamed dried 50 mL flask, 1.5159 g (10.0 mmol) of 2-(4-chlorophenyl)acetonitrile was dissolved in 15 mL anhydrous DMF. 632.0 mg (95% purity, 25.0 mmol, 2.5 equiv.) of NaH was added in portions at 0 ºC and the reaction was allowed to stir for 1 hour at 0 ºC. 2.1593 g (1.18 mL, 10.0 mmol, 1.0 equiv.) of 1,4-dibromobutane was added dropwise at 0 ºC and the reaction was stirred overnight at room temperature. The reaction was quenched carefully with ~10 mL water and extracted with 30 mL EtOAc three times. The combined organic layer was washed with 50 mL brine, dried with MgSO₄, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO₂) using 5% EtOAc/hexanes → 10% EtOAc/hexanes as eluent gave 1.6928 g (8.23 mmol) of pure product as a clear oil (82% yield).

\[^{1}\text{H}-\text{NMR (500 MHz, CDCl}_3\) \delta 7.40 – 7.37 (m, 2H), 7.36 – 7.33 (m, 2H), 2.49 – 2.44 (m, 2H), 2.08 – 1.90 (m, 6H). \[^{13}\text{C}-\text{NMR (126 MHz, CDCl}_3\) \delta 138.5, 133.8, 129.1, 127.5, 124.1, 47.4, 40.6, 24.3. HRMS (TOF ESI+) \text{m/z} \text{calculated for } C_{11}H_{12}Cl [M-CN]^+: 179.0628, \text{found } 179.0635.\]

1-(4-fluorophenyl)cyclopentane-1-carbonitrile [S6].

In a flamed dried 100 mL flask, 2.7030 g (20.0 mmol) of 2-(4-fluorophenyl)acetonitrile was dissolved in 30 mL anhydrous DMF. 1.2630 g (95% purity, 50.0 mmol, 2.5 equiv.) of NaH was added in portions at 0 ºC and the reaction was allowed to stir for 1 hour at 0 ºC. 4.3186 g (2.37 mL, 20.0 mmol, 1.0 equiv.) of 1,4-dibromobutane was added dropwise at 0 ºC and the reaction was allowed to stir overnight at room temperature. The reaction was quenched carefully with ~10 mL water and extracted with 60 mL EtOAc three times. The combined organic layer was washed with 50 mL brine, dried with MgSO₄, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO₂) using 5% EtOAc/hexanes → 10% EtOAc/hexanes as eluent gave 2.9857 g (15.8 mmol) of pure product as a clear oil (79% yield).

\[^{1}\text{H}-\text{NMR (500 MHz, CDCl}_3\) \delta 7.42 (dd, \(J = 8.8, 5.1 \text{ Hz, 2H}), 7.06 (t, \(J = 8.6, 8.6 \text{ Hz, 2H}), 2.50 – 2.43 (m, 2H), 2.08 – 1.89 (m, 6H). \[^{13}\text{C}-\text{NMR (126 MHz, CDCl}_3\) \delta 162.2 (d, \(J = 247.1 \text{ Hz}), 135.7 (d, \(J = 3.2 \text{ Hz}), 127.8 (d, \(J = 8.2 \text{ Hz}), 124.3, 115.8 (d, \(J = 21.7 \text{ Hz}), 47.2, 40.6, 24.2. \[^{19}\text{F}-\text{NMR (470 MHz, CDCl}_3\) \delta -114.93. HRMS (EI+) \text{m/z} \text{calculated for } C_{12}H_{12}NF [M]^+: 189.0954, \text{found } 189.0958.\]

1-(4-(1,3-dioxoisindolin-2-yl)phenyl)cyclopentane-1-carbonitrile [S7].
In a flamed dried 100 mL flask, 4.0538 g (25.0 mmol) of 2-(4-nitrophenyl)acetonitrile was dissolved in 50 mL anhydrous DMF. 1.58 g (95% purity, 62.5 mmol, 2.5 equiv.) of NaH was added in portions at 0 ºC and the reaction was allowed to stir for 1 hour at 0 ºC. 5.40 g (3.0 mL, 25.0 mmol, 1.0 equiv.) of 1,4-dibromobutane was added dropwise at 0 ºC and the reaction was allowed to stir overnight at room temperature. The reaction was quenched carefully with ~20 mL water and extracted with 50 mL EtOAc three times. The combined organic layer was washed with 50 mL brine, dried with MgSO₄, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO₂) using 10% EtOAc/hexanes → 25% EtOAc/hexanes as eluent gave 2.2851 g (10.6 mmol) of 1-(4-nitrophenyl)cyclopentane-1-carbonitrile as a yellow solid (42% yield). ¹H-NMR (500 MHz, CDCl₃) δ 8.28 – 8.22 (m, 2H), 7.69 – 7.61 (m, 2H), 2.55 (dt, J = 7.1, 4.6 Hz, 2H), 2.17 – 1.92 (m, 6H). This solid was dissolved in 30 mL MeOH and charged with 228 mg Pd/C (5% wt.) and the reaction was stirred under a balloon of H₂ overnight to obtain 1-(4-aminophenyl)cyclopentane-1-carbonitrile in quantitative yield. ¹H-NMR (500 MHz, CDCl₃) δ 7.24 – 7.18 (m, 2H), 6.71 – 6.64 (m, 2H), 3.69 (br. s, 2H), 2.48 – 2.34 (m, 2H), 2.09 – 1.79 (m, 6H). In a 50 mL flask was charged with 558.9 mg (3.0 mmol, 1 equiv.) of 1-(4-aminophenyl)cyclopentane-1-carbonitrile, 12 mL acetic acid and 533.2 mg (3.6 mmol, 1.2 equiv.) of phthalic anhydride. The reaction was refluxed overnight before concentrated. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO₂) using 50% EtOAc/hexanes → 100% Acetone as eluent gave 464.5 mg (1.47 mmol) of 1-(4-(1,3-dioxoisindolin-2-yl)phenyl)cyclopentane-1-carbonitrile as a slightly brown solid (49% yield).

¹H-NMR (500 MHz, acetone-d₆) δ 7.97 – 7.92 (m, 4H), 7.71 – 7.69 (m, 2H), 7.60 – 7.57 (m, 2H), 2.53 – 2.48 (m, 2H), 2.25 – 2.18 (m, 2H), 2.03 – 2.00 (m, 4H). ¹³C-NMR (126 MHz, acetone-d₆) δ 167.7, 140.6, 135.4, 132.92, 132.86, 128.3, 127.5, 124.6, 124.2, 48.5, 40.9, 24.7. HRMS (TOF ESI+) m/z calculated for C₂₀H₁₇N₂O₂ [M+H]+: 317.1290, found 317.1284.

**methyl 3-(1-cyanocyclopentyl)benzoate [S8].**

In a flamed dried 50 mL flask, 753.4 mg (3.5 mmol) of 3-(1-cyanocyclopentyl)benzoic acid was dissolved in 20 mL anhydrous DCM. 533.1 mg (355 µL, 4.2 mmol, 1.2 equiv.) of (COCl)₂ was dropwise at 0 ºC, followed by a drop of anhydrous DMF and the reaction was allowed to stir for 2 hours at room temperature before 10 mL anhydrous MeOH was added. The reaction was stirred overnight and concentrated. Flash column chromatography on silica (50
mm fritted glass column, 300 mL SiO2) using 5% EtOAc/hexanes as eluent gave 721.3 mg (3.1 mmol) of pure product as a clear oil (90% yield).

$^1$H-NMR (500 MHz, CDCl3) δ 8.09 (app. t, $J = 2.3$ Hz, 1H), 7.98 (dt, $J = 7.7, 1.3$ Hz, 1H), 7.69 (ddd, $J = 7.9, 2.1, 1.0$ Hz, 1H), 7.46 (t, $J = 7.8, 1$H), 3.93 (s, 3H), 2.53 – 2.49 (m, 2H), 2.11 – 1.95 (m, 6H). $^{13}$C-NMR (126 MHz, CDCl3) δ 166.7, 140.4, 131.0, 130.9, 129.14, 129.12, 127.0, 124.1, 52.4, 47.8, 40.6, 24.3. HRMS (TOF ESI+) $m/z$ calculated for C$_{14}$H$_{16}$NO$_2$ [M+H]$^+$: 230.1181, found 230.1179.

**General procedure for the synthesis of substrate S9-S13**

**1-(3,5-difluorophenyl)cyclopentane-1-carbonitrile [S9].**

In a flamed dried 50 mL flask, 1.5313 g (10.0 mmol) of 2-(3,5-difluorophenyl)acetonitrile was dissolved in 15 mL anhydrous DMF. 632.2 mg (95% purity, 25.0 mmol, 2.5 equiv.) of NaH was added in portions at 0 ºC and the reaction was allowed to stir for 1 hour at 0 ºC. 2.1593 g (1.18 mL, 10.0 mmol, 1.0 equiv.) of 1,4-dibromobutane was added dropwise at 0 ºC and the reaction was allowed to stir overnight at room temperature. The reaction was quenched carefully with ~10 mL water and extracted with 30 mL EtOAc three times. The combined organic layer was washed with 50 mL brine, dried with MgSO$_4$, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO2) using 2% EtOAc/hexanes $\rightarrow$ 5% EtOAc/hexanes as eluent gave 1.8752 g (9.05 mmol) of pure product as a white solid (91% yield).

$^1$H-NMR (500 MHz, CDCl3) δ 7.02 - 6.97 (m, 2H), 6.78 – 6.74 (m, 1H), 2.51 – 2.43 (m, 2H), 2.07 – 1.93 (m, 6H). $^{13}$C-NMR (126 MHz, CDCl3) δ 163.2 (dd, $J = 249.6, 12.9$ Hz), 143.9 (t, $J = 8.9$ Hz), 123.4, 109.6 – 109.5 (m), 103.5 (t, $J = 25.2$ Hz), 47.7(t, $J = 2.2$ Hz), 40.6, 24.3. $^{19}$F-NMR (470 MHz, CDCl3) δ -108.62 – -108.66 (m). HRMS (TOF ESI+) $m/z$ calculated for C$_{11}$H$_{11}$F$_2$ [M-CN]$^+$: 181.0829, found 181.0831.

**Methyl 4-(1-cyanocyclopentyl)benzoate [S10].**

In a flamed dried 50 mL flask, 1.7519 g (10.0 mmol) of methyl 4-(cyanomethyl)benzoate was dissolved in 15 mL anhydrous DMF. 632.0 mg (95% purity, 25.0 mmol, 2.5 equiv.) of NaH was added in portions at 0 ºC and the reaction was allowed to stir for 1 hour at 0 ºC. 2.1593 g (1.18 mL, 10.0 mmol, 1.0 equiv.) of 1,4-dibromobutane was added dropwise at 0 ºC and the reaction was stirred overnight at room temperature. The reaction was quenched carefully with ~10 mL water and extracted with 30 mL EtOAc
three times. The combined organic layer was washed with 50 mL brine, dried with MgSO₄, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 200 mL SiO₂) using 15% EtOAc/hexanes \( \rightarrow \) 30% EtOAc/hexanes as eluent gave 794.0 mg (3.46 mmol) of pure product as a clear oil (34% yield).

\[^{1}\text{H}-\text{NMR} (500 \text{ MHz, } \text{CDCl}_3) \delta 8.04 \text{ (dd, } J = 8.3, 1.4 \text{ Hz, 2H}), 7.53 \text{ (dd, } J = 8.4, 1.4 \text{ Hz, 2H}), 3.92 \text{ (s, 3H),}
\]

\( 2.53 - 2.47 \text{ (m, 2H), 2.12 - 1.93 \text{ (m, 6H).} \)^{13}\text{C}-\text{NMR} (126 \text{ MHz, } \text{CDCl}_3) \delta 166.6, 144.9, 130.3, 129.8, 126.2, 123.9, 52.4, 48.0, 40.8, 24.5. \) HRMS (TOF ESI+) \( m/z \) calculated for C₁₄H₁₆NO₂ [M+H]^+ : 230.1181, found 230.1177.

4-(1-cyanocyclopentyl)benzonitrile \([S11]\).

\[\text{NC} \quad \text{CN} \]

In a flame dried 50 mL flask, 710.8 mg (5.0 mmol) of 2-(4-cyanophenyl)acetonitrile was dissolved in 7.5 mL anhydrous DMF. 316.0 mg (95% purity, 12.5 mmol, 2.5 equiv.) of NaH was added in portions at 0 ºC and the reaction was allowed to stir for 1 hour at 0 ºC. 1.0797 g (0.59 mL, 5.0 mmol, 1.0 equiv.) of 1,4-dibromobutane was added dropwise at 0 ºC and the reaction was allowed to stir overnight at room temperature. The reaction was quenched carefully with ~10 mL water and extracted with 30 mL EtOAc three times. The combined organic layer was washed with 50 mL brine, dried with MgSO₄, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO₂) using 5% EtOAc/hexanes \( \rightarrow \) 10% EtOAc/hexanes as eluent gave 880.1 mg (4.48 mmol) of pure product as a colorless oil (90% yield).

\[^{1}\text{H}-\text{NMR} (500 \text{ MHz, } \text{CDCl}_3) \delta 7.69 - 7.67 \text{ (m, 2H), 7.59 - 7.57 \text{ (m, 2H), 2.52 - 2.48 \text{ (m, 2H), 2.09 - 1.94 \text{ (m, 6H).} \)^{13}\text{C}-\text{NMR} (126 \text{ MHz, } \text{CDCl}_3) \delta 145.2, 132.8, 127.0, 123.3, 118.3, 112.0, 48.0, 40.7, 24.5. \) HRMS (EI+) \( m/z \) calculated for C₁₃H₁₂N₂ [M]^+ : 196.1000, found 196.1004.

methyl 1-(4-(trifluoromethoxy)phenyl)cyclopentane-1-carboxylate \([S12]\).

\[\text{F₃C} \quad \text{O} \quad \text{CO}_₂\text{Me} \]

In a flame dried 50 mL flask, 468.3 mg (2.0 mmol) of methyl 2-(4-(trifluoromethoxy)phenyl)acetate was dissolved in 4 mL anhydrous DMF. 125.0 mg (95% purity, 5.0 mmol, 2.5 equiv.) of NaH was added in portions at 0 ºC and the reaction was allowed to stir for 1 hour at 0 ºC. 431.8 mg (0.24 mL, 2.0 mmol, 1.0 equiv.) of 1,4-dibromobutane was added dropwise at 0 ºC and the reaction was allowed to stir overnight at room temperature. The reaction was quenched carefully with ~10 mL water and extracted with 30 mL EtOAc three times. The combined organic layer was washed with 50 mL brine, dried with MgSO₄, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO₂) using 2.5% EtOAc/hexanes \( \rightarrow \) 5% EtOAc/hexanes as eluent gave 260.8 mg (0.91 mmol) of pure product as a colorless oil (45% yield).
1H-NMR (500 MHz, CDCl3) δ 7.39 – 7.36 (m, 2H), 7.16 – 7.13 (m, 2H), 3.62 (s, 3H), 2.68 – 2.63 (m, 2H), 1.92 – 1.85 (m, 2H), 1.77 – 1.69 (m, 4H). 13C-NMR (126 MHz, CDCl3) δ 176.2, 148.1 (q, J = 1.9 Hz), 142.1, 128.4, 120.8, 120.6 (q, J = 257.0 Hz), 58.8, 52.6, 36.4, 23.7. 19F-NMR (471 MHz, CDCl3) δ -57.85. HRMS (TOF ESI+) m/z calculated for C14H16O3F3 [M+H]+: 289.1052, found 289.1047.

1-(4-(difluoromethoxy)phenyl)cyclopentane-1-carbonitrile [S13].

In a flamed dried 50 mL flask, 1.000 g (5.46 mmol) of 2-(4-(difluoromethoxy)phenyl)acetonitrile was dissolved in 12 mL anhydrous DMF. 344.8 mg (95% purity, 13.7 mmol, 2.5 equiv.) of NaH was added in portions at 0 ºC and the reaction was allowed to stir for 1 hour at 0 ºC. 1.179 g (0.65 mL, 5.46 mmol, 1.0 equiv.) of 1,4-dibromobutane was added dropwise at 0 ºC and the reaction was allowed to stir overnight at room temperature. The reaction was quenched carefully with ~10 mL water and extracted with 30 mL EtOAc three times. The combined organic layer was washed with 50 mL brine, dried with MgSO4, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 200 mL SiO2) using 2% EtOAc/hexanes → 5% EtOAc/hexanes as eluent gave 1.169 g (4.93 mmol) of pure product as a colorless oil (90% yield). Enantiomeric excess (ee) was determined by chiral HPLC (OJ-H, 90:10 hexanes:isopropanol, 1.0 mL/min, 30 ºC, 224nm): 11%.

1H-NMR (500 MHz, CDCl3) δ 7.45 (d, J = 8.7 Hz, 2H), 7.13 (d, J = 8.7 Hz, 2H), 6.51 (t, J = 73.6 Hz, 1H), 2.51 – 2.45 (m, 2H), 2.08 – 1.92 (m, 6H). 13C-NMR (126 MHz, CDCl3) δ 150.6 (t, J = 3.0 Hz), 137.1, 127.7, 124.2, 120.0, 115.8 (t, J = 260.5 Hz), 47.4, 40.6, 24.3. 19F-NMR (470 MHz, CDCl3) δ -81.4 (d, J = 73.2 Hz). HRMS (TOF ESI+) m/z calculated for C13H13NONaF2 [M+Na]+: 260.0863, found 260.0862.

2-((1-(4-bromophenyl)cyclopentyl)methyl)-5-nitroisoindoline-1,3-dione [S14].

In a flamed dried 50 mL flask, 227.7 mg (6.0 mmol, 1.5 equiv.) LiAlH4 was mixed with 12 mL anhydrous ether, a solution of 1.0006 g (4.0 mmol, 1.0 equiv.) of 1-(4-bromophenyl)cyclopentane-1-carbonitrile 2 in 6 mL anhydrous ether was added dropwise at 0 ºC. The reaction was allowed to reflux overnight before quenched with 250 µL water, 250 µL 15% NaOH and 750 µL water sequentially. After stirring for 1 h, MgSO4 was added and the mixture was filtered through Celite. The filtrate was concentrated and redissoved in 20 mL toluene, 772.0 mg (4.0 mmol, 1.0equiv.) of 4-nitrophthalic anhydride was added followed by 560 µL (4.0 mmol, 1.0 equiv.) NEt3. The
reaction was refluxed overnight and concentrated. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO$_2$) using 10% EtOAc/hexanes $\rightarrow$ 20% EtOAc/hexanes as eluent gave 790.2 mg (1.84 mmol) of pure product as a slightly yellow solid (46% yield over 2 steps).

$^1$H-NMR (500 MHz, CDCl$_3$) δ 8.57 – 8.55 (m, 2H), 7.95 (d, $J = 8.0$ Hz, 1H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.14 (d, $J = 8.4$ Hz, 2H), 3.85 (s, 2H), 2.08 – 1.87 (m, 6H), 1.74 – 1.66 (m, 2H). $^{13}$C-NMR (126 MHz, CDCl$_3$) δ 166.3, 166.1, 151.8, 144.3, 136.2, 133.2, 131.3, 129.3, 129.1, 124.6, 120.6, 118.8, 53.0, 47.5, 36.2, 22.9. HRMS (TOF ESI+) $m/z$ calculated for C$_{20}$H$_{18}$N$_2$O$_4$Br [M+H]$^+$: 429.0450, found 429.0446.

3'-H-spiro[cyclopentane-1,1'-isobenzofuran]-3'-one [S15].

In a flamed dried 300 mL flask, 2.0102 g (10.0 mmol) of 2-bromobenzoic acid was dissolved in 50 mL anhydrous THF. n-Butyl lithium (1.6 M, 13.1 mL, 21.0 mmol) was added dropwise at -78 °C and the reaction was allowed to stir for 1 hour at -78 °C. 841.2 mg (0.89 mL, 10.0 mmol, 1.0 equiv.) of cyclopentanone dissolved in 10 mL anhydrous THF was added dropwise at -78 °C and the reaction was allowed to warm to room temperature and stir overnight. The reaction was poured into 40 mL water and the aqueous layer was washed with 40 mL hexanes and 40 mL ether. The aqueous layer was adjusted to pH between 2-3 with 3M HCl. 50 mL DCM was added and the mixture was stirred for 1 hour before adjusted to neutral pH with 10% K$_2$CO$_3$ solution. Layers are separated and the aqueous layer was extracted with 30 mL DCM twice. The combined organic layer was washed with 50 mL brine, dried with Na$_2$SO$_4$, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO$_2$) using 10% EtOAc/hexanes $\rightarrow$ 20% EtOAc/hexanes as eluent gave 631.7 mg (3.36 mmol) of pure product as a white solid (34% yield).

$^1$H-NMR (500 MHz, CDCl$_3$) δ 7.84 (dt, $J = 8.0$, 2.2 Hz, 1H), 7.66 (td, $J = 7.5$, 1.4 Hz, 1H), 7.49 (td, $J = 7.5$, 2.4 Hz, 1H), 7.41 – 7.39 (m, 1H), 2.11 – 2.06 (m, 6H), 1.97 – 1.94 (m, 2H). $^{13}$C-NMR (126 MHz, CDCl$_3$) δ 170.0, 152.8, 134.2, 129.0, 126.3, 125.5, 121.0, 95.6, 39.8, 25.0. HRMS (TOF ESI+) $m/z$ calculated for C$_{12}$H$_{13}$O$_2$ [M+H]$^+$: 189.0916, found 189.0908.

5'-Bromo-1'-(phenylsulfonyl)spiro[cyclopentane-1,3'-indolin]-2'-one [S16].
A 100 mL round bottom flask was charged with a stir bar, 5-Bromooxindole (2.12 g, 10 mmol, 1.0 equiv.) and THF (12 mL) under an Ar atmosphere and cooled -15 °C. To the stirred mixture was added KO'Bu (3.36 g, 30 mmol, 3.0 equiv.) in THF (24 mL) dropwise over 30 min, while the temperature was maintained below -15 °C then the mixture was stirred. After 10 min, 1,4-dibromobutane (1.43 mL, 12 mmol, 1.2 equiv.) was added dropwise over 15 min with the temperature being maintained between -10 °C and -5 °C then the mixture was stirred at 0 °C. After 1 h, the reaction was quenched with 3.5% aqueous HCl solution (20 mL) and the mixture was stirred at room temperature for 1h. The mixture was separated and the yellow organic layer was washed with brine (30 mL), dried with Na2SO4, and filtered. The resulting solution diluted with MeCN (10 mL) and THF was removed under reduced pressure. MeCN (5 mL) was added and the mixture was cooled to 0 °C. The precipitate was collected by filtration and wased with cold MeCN (3 x 3 mL) to provide 1.87 g of 5'-bromospiro[cyclopentane-1,3'-indolin]-2'-one in 70% yield as a white solid. A 50 mL round bottom flask was charged with a stir bar, 5'-bromospiro[cyclopentane-1,3'-indolin]-2'-one (532 mg, 2.00 mmol, 1.0 equiv.), benzenesulfonyl chloride (307 µL, 2.40 mmol, 1.2 equiv.) and THF (8 mL) and cooled to 0 °C. To the stirred mixture was added LHMDS (402 mg, 2.40 mmol, 1.2 equiv.) in THF (2.4 mL) dropwise and the mixture was stirred at the same temperature. After 3 hours, the reaction was quenched with H2O (20 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine (20 mL), dried over Na2SO4, filtered and concentrated under reduced pressure. The residue was diluted with DCM and concentrated onto silica gel (5 mL) for dry loading onto the column (SiO2, 35 mL) and then eluted with 5% EtOAc/hexane to give 596 mg of the product in 73% yield as a white solid.

1H-NMR (500 MHz, CDCl3) δ 8.06 (dd, J = 8.4, 1.2 Hz, 2H), 7.80 (d, J = 8.7 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.55 – 7.52 (m, 2H), 7.43 (dd, J = 8.7, 2.1 Hz, 1H), 7.27 (d, J = 2.1 Hz, 1H), 2.09 – 1.86 (m, 6H), 1.79 – 1.74 (m, 2H). 13C-NMR (126 MHz, CDCl3) δ 179.8, 138.1, 137.5, 137.1, 134.6, 131.1, 129.3, 127.9, 126.0, 118.3, 115.2, 54.3, 39.8, 26.9. HRMS (TOF ESI+) m/z calculated for C18H17BrNO3S [M+H]+: 406.0113, found 406.0110.

1-((cyclopentylmethyl)sulfonyl)-4-fluorobenzene [S17].

533 µL (5.0 mmol) of 4-flourothiophenol was dissolved in 10 mL (0.5 M) acetone. 1.0695 g (6.0 mmol, 1.2 equiv.) of cyclopentylmethanesulfonate and 829.3 mg (6.0 mmol, 1.2 equiv.) of K2CO3 was added sequentially and the reaction was allowed
to stir overnight. The reaction was diluted with 20 mL water and extracted with 30 mL EtOAc three times. The combined organic layer was dried with Na₂SO₄, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 150 mL SiO₂) using 1% EtOAc/hexanes → 3% EtOAc/hexanes as eluent gave 746.6 mg (3.55 mmol) of (cyclopentylmethyl)(4-fluorophenyl)sulfane intermediate with minor impurity. The intermediate was dissolved in 32 mL 1:1 MeOH:H₂O and 3.274 g (10.65 mmol, 3.0 equiv.) Oxone® was added in portions at 0 °C. The reaction was allowed to warm up to room temperature and stirred overnight. The reaction was diluted with 30 mL water and extracted with 40 mL ether TWICE. The combined organic layer was washed with 40 mL brine, dried with MgSO₄, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 150 mL SiO₂) using 10% EtOAc/hexanes → 20% EtOAc/hexanes as eluent gave 788.2 mg (3.25 mmol) of pure product as a white solid in 65% yield over 2 steps.

¹H-NMR (500 MHz, CDCl₃) δ 7.96 – 7.92 (m, 2H), 7.27 – 7.22 (m, 2H), 3.14 (d, J = 6.9 Hz, 2H), 2.30 – 2.21 (m, 1H), 1.92 – 1.86 (m, 2H), 1.64 – 1.51 (m, 4H), 1.26 – 1.18 (m, 2H). ¹³C-NMR (126 MHz, CDCl₃) δ 165.9 (d, J = 255.9 Hz), 136.2, 131.0 (d, J = 9.5 Hz), 116.7 (d, J = 22.6 Hz), 62.3, 34.5, 32.8, 24.9. ¹⁹F-NMR (470 MHz, CDCl₃) δ -104.31. HRMS (TOF ESI+) m/z calculated for C₁₂H₁₆O₂SF [M+H]⁺: 243.0855, found 243.0860.

A 100 mL round bottom flask was charged with a stir bar and AlCl₃ (2.67 g, 20 mmol, 2.0 equiv.) under inert atmosphere and placed in an ice bath. THF (20 mL) was carefully added to dissolve AlCl₃ and the ice bath was replaced with a water bath. To the stirred solution was added n-BuLi (1.6 M in hexane, 37.5 mL, 60.0 mmol, 6.0 equiv.) dropwise over 30 minutes and the resulting suspension was stirred at room temperature. After 1 hour, THF was removed under the reduced pressure and the residue was dissolved with toluene (10 mL) under Ar atmosphere. A 20 mL syringe fitted with LC PVDF filter (HPLC certified) was used to remove white precipitate of LiCl, and the solid was rinsed with toluene (5 mL). A 300 mL round bottom flask was charged with a stir bar and 5-bromoisatin and toluene (50 mL) under Ar atmosphere. To the stirred suspension was added the prepared solution of Bu₃Al in toluene dropwise and the mixture was stirred at 70 °C. After 3 hours, the mixture was concentrated under reduced pressure and cooled to 0 °C, then quenched with saturated potassium sodium tartrate (100 mL), diluted with EtOAc (100 mL) and stirred at room temperature. After 1 hour, aqueous layer was separated and extracted with EtOAc (2 x 100 mL). The combined organic layers were washed with brine (50 mL), dried over Na₂SO₄ filtered and
concentrated under reduced pressure to give 1.76 g of a crude product. A 100 mL round bottom flask was charged with a stir bar, the crude mixture (1.76 g, less than 6.19 mmol) and DCM (20 mL). To the stirred mixture were added pyridine (1.50 mL, 18.6 mmol, 3.0 equiv.), 4-(dimethylamino)pyridine (DMAP, 151 mg, 1.24 mmol, 0.20 equiv.), and acetic anhydride (1.76 mL, 18.6 mmol, 3.0 equiv.) and the mixture was stirred at room temperature overnight. The reaction was quenched with H2O and extracted with DCM (3 x 20 mL). The combined organic layers were washed with H2O (20 mL) and brine (20 mL), dried over Na2SO4, filtered, and concentrated under reduced pressure. The residue was diluted with DCM and concentrated onto silica gel (15 mL) for dry loading onto the column (SiO2, 150 mL) and then eluted with 5% EtOAc/Hexane to afford 1-acetyl-5-bromo-3-butyl-2-oxoindolin-3-yl acetate and 5-bromo-3-butyl-2-oxoindolin-3-yl acetate. 1-acetyl-5-bromo-3-butyl-2-oxoindolin-3-yl acetate (260 mg, 0.706 mmol) could be converted to 5-bromo-3-butyl-2-oxoindolin-3-yl acetate by treatment with Na2CO3 (15.0 mg, 0.142 mmol) in MeOH (5 mL) at 0 °C for 30 min. A 100 mL round bottom flask was charged with a stir bar, 5-bromo-3-butyl-2-oxoindolin-3-yl acetate (638 mg, 1.96 mmol, 1.0 equiv.), benzenesulfonyl chloride (375 µL, 2.94 mmol, 1.5 equiv.), and DCM (10 mL). To the stirred mixture was added Et3N (546 µL, 3.92 mmol, 2.0 equiv.) and the mixture was stirred at 30 °C overnight. The reaction was quenched with H2O and extracted with DCM (3 x 20 mL). The combined organic layers were dried over Na2SO4, filtered, and concentrated under reduced pressure. The residue was diluted with DCM and concentrated onto silica gel (5 mL) for dry loading onto the column (SiO2, 100 mL) and then eluted with 5% EtOAc/Hexane to afford 544 mg (1.17 mmol) of the 5-bromo-1-((4-bromophenyl)sulfonyl)-3-butyl-2-oxoindolin-3-yl acetate in 60% yield as a white solid.

1H-NMR (500 MHz, CDCl3) δ 8.06 (d, J = 7.5 Hz, 2H), 7.83 (d, J = 8.7 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.54 – 7.49 (m, 3H), 7.28 (d, J = 2.1 Hz, 1H), 1.91 (s, 3H), 1.97 – 1.86 (m, 2H), 1.27 – 1.19 (m, 2H), 1.15 – 1.00 (m, 2H), 0.80 (t, J = 7.3 Hz, 3H). 13C-NMR (125 MHz, CDCl3) δ 172.4, 168.9, 138.4, 137.3, 134.8, 133.2, 129.7, 129.1, 128.2, 126.0, 118.3, 115.3, 79.0, 36.9, 23.8, 22.6, 20.3, 13.8. HRMS (TOF ESI+) m/z calculated for C20H20BrNNaO5S [M+Na]+: 488.0143, found 488.0130.

N-((4-bromophenyl)sulfonyl)-N-pentylacetamide [S19].

In a flamed dried 50 mL flask, 995 mg (3.25 mmol, 1.0 equiv.) of 4-bromo-N-pentylbenzenesulfonamide, 2.27 mL (16.25 mmol, 5.0 equiv.) of triethylamine and 39.7 mg (0.33 mmol, 10 mol%) of DMAP was dissolved in 14 mL DCM. 0.7 mL (9.75 mmol, 3.0 equiv.) acetic chloride was added dropwise at 0 °C and the reaction was allowed to warm to RT and stir overnight. 14 mL of water was added to quench the reaction.
and the aqueous layer was extracted with 14 mL DCM twice. The combined organic layer was washed with 30 mL brine and was dried with Na$_2$SO$_4$. Flash column chromatography on silica (150 mm fritted glass column, 200 mL SiO$_2$) using 5% EtOAc/hexanes $\rightarrow$ 15% EtOAc/hexanes as eluent gave 1.122 g (3.16 mmol) of pure product as a sticky colorless oil (97% yield).

$^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 7.78 – 7.75 (m, 2H), 7.70 – 7.67 (m, 2H), 3.77 – 3.74 (m, 2H), 2.29 (s, 3H), 1.74 – 1.68 (m, 2H), 1.40 – 1.28 (m, 4H), 0.91 (t, $J$ = 7.0 Hz, 3H). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 170.0, 138.9, 132.6, 129.3, 129.0, 47.6, 29.9, 29.0, 24.9, 22.4, 14.1. HRMS (TOF ESI$^+$) $m/z$ calculated for C$_{13}$H$_{19}$NO$_3$SBr [M+H]$^+$: 348.0269, found 348.0268.

1-(4-bromophenyl)cyclohexane-1-carbonitrile [S20].

In a flame-dried 50 mL flask, 1.9604 g (10.0 mmol) of 2-(4-bromophenyl)acetonitrile was dissolved in 15 mL anhydrous DMF. 632.0 mg (95% purity, 25.0 mmol, 2.5 equiv.) of NaH was added in portions at 0 ºC and the reaction was allowed to stir for 1 hour at 0 ºC. 2.2994 g (1.36 mL, 10.0 mmol, 1.0 equiv.) of 1,5-dibromopentane was added dropwise at 0 ºC and the reaction was allowed to stir overnight at room temperature. The reaction was quenched carefully with ~10 mL water and extracted with 30 mL EtOAc three times. The combined organic layer was washed with 50 mL brine, dried with MgSO$_4$, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO$_2$) using 5% EtOAc/hexanes $\rightarrow$ 10% EtOAc/hexanes as eluent gave 1.9307 g (7.3 mmol) of pure product as a white solid (73% yield).

$^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 7.53 – 7.50 (m, 2H), 7.38 – 7.35 (m, 2H), 2.15 – 2.11 (m, 2H), 1.90 – 1.78 (m, 5H), 1.72 (ddd, $J$ = 13.0, 12.8, 4.1 Hz, 2H), 1.32 – 1.22 (m, 1H). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 140.7, 132.1, 127.5, 122.4, 121.9, 44.2, 37.4, 25.0, 23.7. HRMS (EI$^+$) $m/z$ calculated for C$_{13}$H$_{14}$NBr [M]$^+$: 263.0310, found 263.0313.

2-((1-(4-bromophenyl)cyclobutyl)methyl)isoindoline-1,3-dione [S21].
In a flamed dried 50 mL flask, 232.0 mg (6.12 mmol, 1.5 equiv.) LiAlH₄ was mixed with 12 mL anhydrous ether, a solution of 963.0 mg (4.08 mmol, 1.0 equiv.) of 1-(4-bromophenyl)cyclobutane-1-carbonitrile in 6 mL anhydrous ether was added dropwise at 0 °C. The reaction was allowed to reflux overnight before quenched with 250 µL water, 250 µL 15% NaOH and 750 µL water sequentially. After stirring for 1 h, MgSO₄ was added and the mixture was filtered through Celite. The filtrate was concentrated and redissovled in 20 mL toluene, 604.2 mg (4.08 mmol, 1.0 equiv.) of phthalic anhydride was added followed by 570 µL (4.08 mmol, 1.0 equiv.) triethylamine. The reaction was refluxed overnight and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 200 mL SiO₂) using 5% EtOAc/hexanes → 15% EtOAc/hexanes as eluent gave 1.2621 g (3.41 mmol) of pure product as a white solid (84% yield over 2 steps).

H-NMR (500 MHz, CDCl₃) δ 7.77 (dd, J = 5.4, 3.1 Hz, 2H), 7.69 (dd, J = 5.5, 3.1 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.02 (d, J = 8.3 Hz, 2H), 3.95 (s, 2H), 2.51 (ddd, J = 12.7, 8.7, 4.7 Hz, 2H), 2.39 – 2.33 (m, 2H), 2.08 (dp, J = 11.4, 8.5 Hz, 1H), 1.87 – 1.79 (m, 1H). C-NMR (126 MHz, CDCl₃) δ 168.5, 146.3, 134.1, 131.8, 131.2, 128.1, 123.4, 120.0, 47.9, 47.8, 31.8, 16.1. HRMS (TOF ESI+) m/z calculated for C₁₉H₁₇NO₂Br [M+H]^+: 370.0443, found 370.0442.

bis(4-chlorophenyl)(cyclobutyl)methanol [S22].

In a flamed dried 100 mL flask, 572.8 mg (4.0 mmol, 1.0 equiv.) of N-methoxy-N-methylcyclobutanecarboxamide was dissolved in 20 mL THF, 11 mL THF solution containing 12 mmol (3.0 equiv.) freshly made 4-Chlorophenylmagnesium bromide was added dropwise at -78 °C. The reaction was allowed to stir at -78 °C for 1h then at RT for 1.5 h. The reaction was quenched with saturated NH₄Cl solution, extracted with 20 mL ether three times. The combined organic layer was concentrated, dissolved in 20 mL DCM and washed with 20 mL brine. Followed by drying with MgSO₄, the crude reaction was transferred into a 100 mL flamed dried flask and dissolved in 20 mL THF. Another portion of 11 mL THF solution containing 10 mmol (2.5 equiv.) 4-Chlorophenylmagnesium bromide was added dropwise at -78 °C. The reaction was allowed to warm up to RT and stirred overnight. The reaction was quenched with saturated NH₄Cl solution, extracted with 30 mL ether three times. The combined organic layer was washed with 30 mL brine and was dried with Na₂SO₄. Flash column chromatography on silica (150 mm fritted glass column, 200 mL
SiO₂) using 5% EtOAc/hexanes → 10% EtOAc/hexanes as eluent gave 905.8 mg (2.95 mmol) of pure product as a yellow solid (74% yield).

\(^{1}\)H-NMR (500 MHz, CDCl₃) δ 7.28 – 7.24 (m, 8H), 3.34 – 3.30 (m, 1H), 2.15 (br. s, 1H), 2.05 – 1.96 (m, 2H), 1.89 – 1.72 (m, 4H). \(^{13}\)C-NMR (126 MHz, CDCl₃) δ 144.3, 133.0, 128.4, 127.9, 78.0, 44.0, 22.9, 17.1. HRMS (EI⁺) m/z calculated for C\(_{17}\)H\(_{16}\)OCl₂ [M⁺]: 306.0578, found 306.0575.

**2-butyl-2-(4-chlorophenyl)-1\(^{H}\)-indene-1,3(2\(^{H}\))-dione [S23].**

In a 50 mL flask, 223.4 mg (0.87 mmol, 1.0 equiv.) of Clorindione was dissolved in 4.4 mL acetone followed by 360.7 mg (2.61 mmol, 3.0 equiv.) K₂CO₃ and 934 µL (8.70 mmol, 10 equiv.) 1-bromobutane. The flask was capped with polyethylene cap and sealed with electric tape and the reaction was allowed to stir under 60 °C for 24 hours. The reaction was concentrated, dissolved in 20 mL water and extracted with 20 mL EtOAc three times. The combined organic layer was dried with Na₂SO₄, filtered, and concentrated. Purification by CombiFlash on silica (40 g) using hexanes → 10% EtOAc/hexanes as eluent gave 145.4 mg (0.47 mmol) of pure product as a yellow solid (54% yield).

\(^{1}\)H-NMR (500 MHz, CDCl₃) δ 8.07 – 8.02 (m, 2H), 7.89 – 7.87 (m, 2H), 7.39 – 7.36 (m, 2H), 7.28 – 7.25 (m, 2H), 2.24 – 2.19 (m, 2H), 1.28 – 1.21 (m, 2H), 1.13 – 1.07 (m, 2H), 0.79 (t, J = 7.3 Hz, 3H). \(^{13}\)C-NMR (126 MHz, CDCl₃) δ 201.8, 142.0, 136.2, 135.7, 133.8, 129.0, 128.4, 123.7, 61.6, 36.6, 27.4, 23.2, 13.8. HRMS (TOF ESI⁺) m/z calculated for C\(_{19}\)H\(_{18}\)O₂Cl [M+H⁺]: 313.0995, found 313.0991.

**(±)-methyl 2-(3-benzoylphenyl)-2-cyclopentylpropanoate [S24].**

In a 50 mL recovery flask was charged 3.814 g (15 mmol) ketoprofen, 25 mL MeOH and 1 mL concentrated H₂SO₄. The reaction was refluxed overnight. After cooled to room temperature, the reaction was poured into 100 mL water and extract with 50 mL DCM 3 times. Combined organic layer was washed with sat. NaHCO₃, dried with MgSO₄ then purified by a plug of silica. In a 300 mL flamed dried flask, 1.3416 g (5 mmol) of ketoprofen methyl ester was dissolved in 50 mL anhydrous THF, cooled to -78 °C and 5.5 mmol (1.1 equiv.) freshly made LDA solution and 0.87 mL (5.0 mmol, 1.0 equiv.) HMPA was added sequentially. After stirring at
-78 °C for 10 minutes, 1.61 mL (2.2355 g, 15 mmol, 3.0 equiv.) of bromocyclopentane was added. The reaction was allowed to warm to room temperature and stirred overnight. The reaction was quenched with 10 mL saturated NH4Cl, extracted with 30 mL ether 3 times and dried over MgSO4. The crude mixture was purified by CombiFlash using a 40 g silica column and eluted with pure hexane → 10% ethyl acetate/hexane to give product in 631.9 mg (1.96 mmol, 39% yield).

1H-NMR (500 MHz, CDCl3) 7.80 – 7.78 (m, 3H), 7.65 (ddd, J = 7.6, 1.6, 1.1 Hz, 1H), 7.61 – 7.51 (m, 2H), 7.50 – 7.47 (m, 2H), 7.44 – 7.41 (m, 1H), 3.66 (s, 3H), 2.80 (tt, J = 9.3, 7.9 Hz, 1H), 1.75 – 1.72 (m, 1H), 1.55 (s, 3H), 1.59 – 1.37 (m, 6H), 1.14 (ddt, J = 12.5, 9.8, 7.8 Hz, 1H). 13C-NMR (126 MHz, CDCl3) δ 196.8, 176.3, 144.2, 137.7, 137.6, 132.6, 130.8, 130.2, 128.6, 128.4, 128.31, 128.27, 53.0, 52.2, 47.0, 28.6, 27.9, 26.0, 25.8, 18.7. HRMS (TOF ESI+) m/z calculated for C22H25O3 [M+H]+: 337.1804, found 337.1793.

1-cyclopentyl-3-(3,4-dichlorophenyl)propan-2-one [S25].

In a flamed dried 100 mL flask, 822.0 mg (4.8 mmol, 1.0 equiv.) of 2-cyclopentyl-N-methoxy-N-methylacetamide was dissolved in 24 mL anhydrous THF, 11 mL THF solution containing 5.3 mmol (1.1 equiv.) freshly made (3,4-dichlorobenzyl)magnesium bromide was added dropwise at -78 °C. The reaction was allowed to warm up to room temperature stir at -78 °C for 1h then at RT for 2 h. The reaction was quenched with saturated NH4Cl solution, extracted with 20 mL ether three times. The combined organic layer was washed with 20 mL brine, dried with MgSO4 and concentrated. Flash column chromatography on silica (150 mm fritted glass column, 150 mL SiO2) using 3% EtOAc/hexanes → 5% EtOAc/hexanes as eluent gave 672.8 mg (2.48 mmol) of pure product as a clear oil (52% yield).

1H-NMR (500 MHz, CDCl3) δ 7.39 (d, J = 8.2 Hz, 1H), 7.29 (d, J = 2.0 Hz, 1H), 7.02 (dd, J = 8.2, 1.9 Hz, 1H), 3.64 (s, 2H), 2.49 (d, J = 7.2 Hz, 2H), 2.23 (hept, J = 7.3 Hz, 1H), 1.84 – 1.78 (m, 2H), 1.62 – 1.51 (m, 4H), 1.09 – 1.00 (m, 2H). 13C-NMR (126 MHz, CDCl3) δ 207.0, 134.5, 132.7, 131.5, 131.3, 130.6, 129.0, 48.9, 48.9, 35.6, 32.7, 25.1. HRMS (TOF ESI+) m/z calculated for C14H17OCl2 [M+H]+: 271.0656, found 271.0666.
(±)-trans-4-methylcyclohexyl 4-chlorobenzoate [S26].

In an oven dried 50 mL recovery flask was charged with trans-4-methylcyclohexanol 628.0 mg (5.5 mmol, 1.1 equiv.) in 10 mL anhydrous DCM. 0.64 mL (5 mmol, 1.0 equiv.) 4-chlorobenzoyl chloride and 1.05 mL (7.5 mmol, 1.5 equiv.) of triethylamine was sequentially added at 0 °C. The reaction was warmed to room temperature and stirred overnight before quenched with 30 mL water. The aqueous layer was extracted with 30 mL DCM twice and the combined organic layer was washed with brine, dried with MgSO₄ and concentrated. Flash column chromatography on silica (150 mm fritted glass column, 250 mL SiO₂) using 1% EtOAc/hexanes → 2% EtOAc/hexanes → 5% EtOAc/hexanes as eluent gave 986.7 mg (3.90 mmol) of pure product as a white solid (78% yield).

1H-NMR (500 MHz, CDCl₃) δ 7.98 – 7.95 (m, 2H), 7.41 – 7.38 (m, 2H), 4.90 (tt, J = 11.1, 4.4 Hz, 1H), 2.09 – 2.05 (m, 2H), 1.80 – 1.76 (m, 2H), 1.50 – 1.44 (m, 3H), 1.12 – 1.09 (m, 2H), 0.92 (d, J = 6.6 Hz, 3H). 13C-NMR (126 MHz, CDCl₃) δ 165.4, 139.2, 131.1, 129.5, 128.7, 74.5, 33.2, 31.9, 31.8, 22.0. HRMS (TOF ESI+) m/z calculated for C₁₄H₁₇O₂NaCl [M+Na]⁺: 275.0815, found 275.0805.

(±)-2-methylbutyl 4-chlorobenzoate [S27].

In an oven dried 50 mL recovery flask was charged with 2-methylbutan-1-ol 1.08 mL (881.5 mg, 10.0 mmol, 1.0 equiv.) in 20 mL anhydrous DCM. 2.56 mL (20.0 mmol, 2.0 equiv.) 4-chlorobenzoyl chloride and 4.18 mL (30.0 mmol, 3.0 equiv.) of triethylamine was sequentially added at 0 °C. The reaction was warmed to room temperature and stirred overnight before quenched with 30 mL water. The aqueous layer was extracted with 30 mL DCM twice and the combined organic layer was washed with brine, dried with MgSO₄ and concentrated. Flash column chromatography on silica (150 mm fritted glass column, 250 mL SiO₂) using 1% EtOAc/hexanes → 2% EtOAc/hexanes → 5% EtOAc/hexanes as eluent gave 2.094 g (9.24 mmol) of pure product as a clear oil (92% yield).

1H-NMR (500 MHz, CDCl₃) δ 7.98 (d, J = 8.6 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 4.20 (dd, J = 10.7, 6.0 Hz, 1H), 4.12 (dd, J = 10.7, 6.7 Hz, 1H), 1.90 – 1.81 (m, 1H), 1.51 (dt, J = 13.3, 7.5, 5.7 Hz, 1H), 1.27 (dq, J = 13.6, 7.5 Hz, 1H), 1.01 (d, J = 6.8 Hz, 3H), 0.95 (t, J = 7.5 Hz, 3H). 13C-NMR (126 MHz, CDCl₃) δ 165.9, 139.4, 131.1, 129.1, 128.8, 69.9, 34.4, 26.3, 16.7, 11.4. HRMS (TOF ESI+) m/z calculated for C₁₂H₁₅O₂NaCl [M+Na]⁺: 249.0658, found 249.0670.
4-cyclopropylbutyl benzoate [S28].

In a flame dried 100 mL flask 14.2 mL of 1M diethyl zinc solution in toluene was added in 17 mL anhydrous 1,2-dichloroethane. 5.0 g (28.4 mmol) CH₂ClI was added dropwise over 5 minutes at 0 ºC. The reaction was kept at 0 ºC for 5 minutes before 801.3 mg (8.0 mmol) of 5-hexene-1-ol dissolved in 3 mL anhydrous 1,2-dichloroethane was added dropwise and the reaction was allowed to stir at RT overnight. 20 mL sat. NH₄Cl solution was used to quench the reaction and the aqueous layer was extracted with 20 mL DCM 3 times. The combined organic layer was washed with 40 mL 1:1 brine:water and dried with MgSO₄. The crude mixture was dissolved in 40 mL anhydrous DCM, treated with benzoyl chloride (3.374 g, 24.0 mmol, 2.8 mL) and triethylamine (4.048 g, 40 mmol, 5.65 mL) at 0 ºC, stirred overnight at room temperature before diluted with 50 mL DCM and worked up with 50 mL 1 M HCl. The organic layer was washed by 50 mL sat. NaHCO₃, 50 mL brine, dried with Na₂SO₄ and concentrated. The crude mixture was treated with 2.34 g (9.5 mmol) 70% wt. mCPBA to convert the unreacted olefin impurity to the corresponding epoxide, which can be removed via column chromatography on silica (50 mm fritted glass column, 200 mL SiO₂) using 5% EtOAc/hexanes → 10% EtOAc/hexanes as eluent to afford 389 mg (1.8 mmol) of pure product as a colorless oil (22% yield over 3 steps).

¹H-NMR (500 MHz, CDCl₃) δ 8.06 – 8.04 (m, 2H), 7.55 (td, J = 7.3, 1.5 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 4.32 (t, J = 6.7 Hz, 2H), 1.83 – 1.77 (m, 2H), 1.55 (tt, J = 7.6, 6.6 Hz, 2H), 1.27 (q, J = 7.2 Hz, 2H), 0.72 – 0.64 (m, 1H), 0.43 – 0.40 (m, 2H), 0.03 – 0.00 (m, 2H). ¹³C-NMR (126 MHz, CDCl₃) δ 166.8, 132.9, 130.6, 129.7, 128.4, 65.3, 34.5, 28.7, 26.2, 10.9, 4.6. HRMS (TOF ESI+) m/z calculated for C₁₄H₁₈O₂Na [M+Na]⁺: 241.1204, found 241.1212.
**General Oxidation Procedure for Supplementary Figure 1**

**Method A: Single Catalyst Addition Protocol**
A 40 mL vial was charged with substrate (0.3 mmol, 1.0 equiv.), catalyst (0.03 mmol, 10 mol%), ClCH$_2$CO$_2$H (425 mg, 4.5 mmol, 15.0 equiv.) and a stir bar. MeCN (0.6 mL, 0.50 M) was added along the wall to ensure all compounds were washed beneath the solvent level and the vial was sealed with a screw cap fitted with a PTFE/Silicone septum. The vial was cooled to 0 ºC with ice/water bath. A separate solution of H$_2$O$_2$ [(204 mg, 3.0 mmol, 10.0 equiv.), 50% wt. in H$_2$O, purchased from Sigma-Aldrich] in MeCN (3.75 mL) was loaded into a 10 mL syringe fitted with a 25G needle and was added dropwise to the stirring reaction over 3 hours via a syringe pump (1.25 mL/h addition rate) while maintain the reaction vial at 0 ºC. Upon completion, the reaction mixture was concentrated to a minimum amount of solvent. The residue was dissolved in ~20 mL DCM and washed with 9 mL sat. NaHCO$_3$ solution (CAUTION: CO$_2$ was released) to remove ClCH$_2$CO$_2$H. The aqueous layer was extracted with ~15 mL DCM two times and the combined organic layer was dried with Na$_2$SO$_4$. The filtrate was concentrated and purified by flash chromatography on silica gel.

**Method B: Iterative Catalyst Addition Protocol**
This protocol was used when Method A gave low conversions. A 40 mL vial was charged with substrate (0.3 mmol, 1.0 equiv.), catalyst (0.015 mmol, 5 mol%), ClCH$_2$CO$_2$H (425 mg, 4.5 mmol, 15.0 equiv.) and a stir bar. MeCN (0.6 mL, 0.50 M) was added along the wall to ensure all compounds were washed beneath the solvent level and the vial was sealed with a screw cap fitted with a PTFE/Silicone septum. The vial was cooled to -36 ºC with 1,2-dichloroethane/dry ice bath or to 0 ºC with ice/water bath. A separate solution of H$_2$O$_2$ [(204 mg, 3.0 mmol, 10.0 equiv.), 50% wt. in H$_2$O, purchased from Sigma-Aldrich] in MeCN (3.75 mL) was loaded into a 10 mL syringe fitted with a 25G needle and was added dropwise to the stirring reaction over 3 hours via a syringe pump (1.25 mL/h addition rate) while maintain at the corresponding temperature. The initial time is recorded as the time the first drop of H$_2$O$_2$ solution was added into the reaction. One hour after the initial time, another batch of catalyst (0.015 mmol, 5 mol%) was dissolved with 0.1 mL MeCN in a 0.5-dram vial and added dropwise into the reaction via syringe followed directly by another 0.1 mL MeCN that was used to rinse the vial. The addition of 5 mol% catalyst was repeated at two hours after the initial time using the same procedure. A total of 15 mol% of catalyst was used in this protocol. Upon completion, the reaction mixture was concentrated to a minimum amount of solvent. The residue was dissolved in ~20 mL DCM and washed with 9 mL sat. NaHCO$_3$ solution (CAUTION: CO$_2$ was released) to remove ClCH$_2$CO$_2$H. The aqueous layer was extracted with ~15 mL DCM two times and the combined organic layer was dried with Na$_2$SO$_4$. The filtrate was concentrated and purified by flash chromatography on silica gel.
Method C: Slow Catalyst Addition Protocol

This protocol was used when Method A and Method B gave low conversions. A 40 mL vial was charged with substrate (0.3 mmol, 1.0 equiv.), ClCH₂CO₂H (425 mg, 4.5 mmol, 15.0 equiv.) and a stir bar. MeCN (0.6 mL, 0.50 M) was added along the wall to ensure all compounds were washed beneath the solvent level and the vial was sealed with a screw cap fitted with a PTFE/Silicone septum. The vial was cooled to -36 ºC with 1,2-dichloroethane/dry ice bath or to 0 ºC with ice/water bath. A 1.0 mL syringe was filled with a solution of the catalyst (0.03 mmol, 10 mol%) in MeCN (0.375 mL, 0.083 M). A few drops of this solution were added to the reaction. A 10 mL syringe was filled with a solution of H₂O₂ (204 mg, 3.0 mmol, 10.0 equiv., 50% wt. in H₂O, purchased from Sigma-Aldrich) in MeCN (3.75 mL, 0.8 M). Both syringes were fitted with 25G needles and loaded to a syringe pump resulting a slow simultaneous addition of catalyst and oxidant solutions over 3 hours while maintain at the corresponding temperature (1.25 mL/h addition rate set for the H₂O₂ syringe; 0.125 mL/h for the catalyst syringe). Upon completion, the reaction mixture was concentrated to a minimum amount of solvent. The residue was dissolved in ~20 mL DCM and washed with 9 mL sat. NaHCO₃ solution (CAUTION: CO₂ was released) to remove ClCH₂CO₂H. The aqueous layer was extracted with ~15 mL DCM two times and the combined organic layer was dried with Na₂SO₄. The filtrate was concentrated and purified by flash chromatography on silica gel.

In all oxidations reported with Mn(CF₃-PDP)₁ with General Method A, B, C and D (vide infra), the yields of oxidation products are reported as isolated yields after column chromatography with >95% purity. Trace solvent residues are integrated out with quantitative ¹H NMR characterization of the oxidation product.
C—H Oxidation of Substrates and Products Characterization for Supplementary Figure 1

3-oxo-1-phenylcyclopentane-1-carbonitrile [7].

The reaction was run with **General Method A: Single Catalyst Addition Protocol:** 1-phenylcyclopentane-1-carbonitrile S3 (85.6 mg, 0.500 mmol, 1.0 equiv), (R,R)-Mn(CF3-PDP) (67.8 mg, 0.050 mmol, 10 mol%), ClCH2CO2H (709 mg, 7.5 mmol, 15.0 equiv.), 50% wt. H2O2 (340 mg, 5.0 mmol, 10.0 equiv.), MeCN (1.0 mL in 40 mL vial, 6.25 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with 15 mL saturated NaHCO3 and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO2) using 10% acetone/hexanes → 20% acetone/hexanes as eluent. Fractions contain products were collected and the yield was obtained by 1H NMR analysis by adding nitrobenzene as internal standard.

**Run 1:** (8.1 mg, 0.044 mmol, 8.7% yield), (17.7 mg, 0.103 mmol, 20.7% rsm). **Run 2:** (8.8 mg, 0.048 mmol, 9.5% yield), (20.4 mg, 0.120 mmol, 24.0% rsm). **Run 3:** (9.9 mg, 0.053 mmol, 10.7% yield), (19.8 mg, 0.116 mmol, 23.1% rsm). **Average:** 9.6% yield ± 1.0%, 22.6% rsm ± 1.7%.

1H-NMR (500 MHz, CDCl3) δ 7.46 – 7.37 (m, 5H), 3.06 (d, J = 18.2 Hz, 1H), 2.86 – 2.79 (m, 2H), 2.70 – 2.63 (m, 1H), 2.56 – 2.43 (m, 2H). 13C-NMR (126 MHz, CDCl3) δ 212.2, 137.6, 129.5, 128.9, 125.9, 122.6, 50.0, 44.2, 36.8, 36.5. HRMS (EI+) m/z calculated for C12H11ON [M]+: 185.08407, found 185.08379.

1-(4-(tert-butyl)phenyl)-3-oxocyclopentane-1-carbonitrile [8].

The reaction was run with **General Method A: Single Catalyst Addition Protocol:** 1-(4-(tert-butyl)phenyl)cyclopentane-1-carbonitrile S4 (113.7 mg, 0.500 mmol, 1.0 equiv), (R,R)-Mn(CF3-PDP) (67.8 mg, 0.050 mmol, 10 mol%), ClCH2CO2H (709 mg, 7.5 mmol, 15.0 equiv.), 50% wt. H2O2 (340 mg, 5.0 mmol, 10.0 equiv.), MeCN (1.0 mL in 40 mL vial, 6.25 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with 15 mL saturated NaHCO3 and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO2) using 10% acetone/hexanes → 20% acetone/hexanes as eluent afforded product as a white solid.

**Run 1:** (78.0 mg, 0.323 mmol, 64.6% yield), (11.8 mg, 0.052 mmol, 10.4% rsm). **Run 2:** (79.7 mg, 0.330 mmol, 66.0% yield), (10.8 mg, 0.048 mmol, 9.5% rsm). **Run 3:** (79.1 mg, 0.328 mmol, 65.6% yield), (13.1 mg, 0.058 mmol, 11.5% rsm). **Average:** 65.4% yield ± 0.7%, 10.5% rsm ± 1.0%.

1H-NMR (500 MHz, CDCl3) δ 7.46 – 7.44 (m, 2H), 7.39 – 7.36 (m, 2H), 3.03 (d, J = 18.2 Hz, 1H), 2.84 – 2.78 (m, 2H), 2.69 – 2.61 (m, 1H), 2.54 – 2.42 (m, 2H), 1.33 (s, 9H). 13C-NMR (126 MHz, CDCl3) δ 212.4, 152.0, 134.5, 126.4, 125.6, 122.8, 50.0, 43.8, 36.7, 36.4, 34.7, 31.3. HRMS (EI+) m/z calculated for C16H19ON [M]+: 241.1467, found 241.1468.
1-(4-chlorophenyl)-3-oxocyclopentane-1-carbonitrile [9].

The reaction was run with General Method A: Single Catalyst Addition Protocol:

\[
\text{1-(4-chlorophenyl)cyclopentane-1-carbonitrile S5 (102.8 mg, 0.500 mmol, 1.0 equiv), (R,R)-Mn(CF}_3\text{PDP) (67.8 mg, 0.050 mmol, 10 mol\%), ClCH}_2\text{CO}_2\text{H (709 mg, 7.5 mmol, 15.0 equiv.), 50\% wt. H}_2\text{O}_2 (340 mg, 5.0 mmol, 10.0 equiv.), MeCN (1.0 mL in 40 mL vial, 6.25 mL with oxidant). The reaction was run at 0 \degree\text{C with ice bath. The reaction was worked up with 15 mL saturated NaHCO}_3 \text{ and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO}_2 \text{) using 10\% acetone/hexanes} \rightarrow 20\% \text{ acetone/hexanes as eluent afforded product as a clear oil.}
\]

Run 1: (86.8 mg, 0.395 mmol, 79.0\% yield), (6.3 mg, 0.031 mmol, 6.2\% rsm). Run 2: (90.6 mg, 0.413 mmol, 82.5\% yield), (10.9 mg, 0.053 mmol, 10.6\% rsm). Run 3: (89.1 mg, 0.406 mmol, 81.1\% yield), (9.9 mg, 0.048 mmol, 9.6\% rsm). Average: 80.9\% yield \pm 1.8\%, 8.8\% rsm \pm 2.3\%.

Gram-scale reaction: The reaction was run with reduced catalyst and chloroacetic acid loading according to a modified General Method A: Single Catalyst Addition Protocol with a scale up of appropriate apparatus. 1-(4-chlorophenyl)cyclopentane-1-carbonitrile S5 (1028 mg, 5.0 mmol, 1.0 equiv), (R,R)-Mn(CF}_3\text{PDP) (339 mg, 0.25 mmol, 5 mol\%), ClCH}_2\text{CO}_2\text{H (3.545 g, 37.5 mmol, 7.5 equiv.), 50\% wt. H}_2\text{O}_2 (3400 mg, 50.0 mmol, 10.0 equiv.), MeCN (10 mL in 100 mL recovery flask with a stir bar, 60 mL with oxidant in a 60 mL syringe). The reaction was run at 0 \degree\text{C with ice bath. The reaction was worked up with 80 mL saturated NaHCO}_3 \text{ and DCM as described in General Method A. Flash column chromatography on silica (50 mm fritted glass column, 200 mL SiO}_2 \text{) using 10\% acetone/hexanes} \rightarrow 20\% \text{ acetone/hexanes as eluent afforded product as a clear oil.}

Run 1: (791.2 mg, 0.3.60 mmol, 72.0\% yield), (147.5 mg, 0.717 mmol, 14.3\% rsm).

\(^1\text{H-NMR (500 MHz, CDCl}_3 \text{) }\delta \text{ 7.43 – 7.38 (m, 4H), 3.05 (d, J = 18.1 Hz, 1H), 2.86 – 2.81 (m, 1H), 2.75 (d, J = 18.1 Hz, 1H), 2.67 (dt, J = 18.5, 9.2 Hz, 1H), 2.52 (ddd, J = 19.0, 8.3, 3.9 Hz, 1H), 2.42 (ddd, J = 13.0, 9.9, 8.1 Hz, 1H).}

\(^{13}\text{C-NMR (126 MHz, CDCl}_3 \text{) }\delta \text{ 211.6, 136.1, 134.9, 129.7, 127.3, 122.2, 49.8, 43.8, 36.7, 36.3. HRMS (TOF ESI+) m/z calculated for C}_11\text{H}_9\text{OCl [M-CN]}: 193.0420, found 193.0423.}

Site of oxidation was confirmed based on a combination of \(^1\text{H, gDQCOSY, gHSQC and gHMBC NMRs.}

1-(4-fluorophenyl)-3-oxocyclopentane-1-carbonitrile [10].

The reaction was run with General Method B: Iterative Catalyst Addition Protocol:

\[
\text{1-(4-fluorophenyl)cyclopentane-1-carbonitrile S6 (94.6 mg, 0.500 mmol, 1.0 equiv), (R,R)-Mn(CF}_3\text{PDP) (3 times addition of 33.9 mg, 0.025 mmol, 5 mol\% batch; 15 mol\% in total), ClCH}_2\text{CO}_2\text{H (709 mg, 7.5 mmol, 15.0 equiv.), 50\% wt. H}_2\text{O}_2 (340 mg, 5.0 mmol, 10.0 equiv.), MeCN (1.0 mL in 40 mL vial, 6.25 mL with oxidant). The reaction was run at 0 \degree\text{C}
\]
with ice bath. The reaction was worked up with 15 mL saturated NaHCO₃ and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO₂) using 20% acetone/hexanes \(\rightarrow\) 30% acetone/hexanes as eluent afforded product as a clear oil.

**Run 1:** (57.9 mg, 0.285 mmol, 57.0% yield), (9.3 mg, 0.049 mmol, 9.8% rsm). **Run 2:** (58.4 mg, 0.287 mmol, 57.4% yield), (9.3 mg, 0.049 mmol, 9.8% rsm). **Run 3:** (55.6 mg, 0.273 mmol, 54.6% yield), (9.9 mg, 0.052 mmol, 10.5% rsm). **Average:** 56.3% yield \(\pm\) 1.5%, 10.0% rsm \(\pm\) 0.4%.

\(^1\)H-NMR (500 MHz, CDCl₃) \(\delta\) 7.45 – 7.42 (m, 2H), 7.15 – 7.12 (m, 2H), 3.06 (d, \(J = 18.1\) Hz, 1H), 2.84 (ddddd, \(J = 12.7, 8.5, 3.9, 1.8\) Hz, 1H), 2.75 (d, \(J = 18.1\) Hz, 1H), 2.67 (ddd, \(J = 18.5, 9.7, 8.3\) Hz, 1H), 2.52 (dddt, \(J = 18.9, 8.2, 3.9, 1.1\) Hz, 1H), 2.42 (dd, \(J = 13.0, 9.9, 8.1\) Hz, 1H). \(^{13}\)C-NMR (126 MHz, CDCl₃) \(\delta\) 211.8, 162.7 (d, \(J = 240.0\) Hz), 133.4 (d, \(J = 3.3\) Hz), 127.7 (d, \(J = 8.4\) Hz), 122.4, 116.5 (d, \(J = 21.9\) Hz), 50.0, 43.6, 36.7, 36.4. \(^{19}\)F-NMR (470 MHz, CDCl₃) \(\delta\) -113.0. HRMS (TOF ESI+) \(m/z\) calculated for C₁₂H₁₁NOF \([M+H]^+\): 204.0825, found 204.0833.

1-(4-(1,3-dioxoisooindolin-2-yl)phenyl)-3-oxocyclopentane-1-carbonitrile \[11\].

The reaction was run with **General Method A: Single Catalyst Addition Protocol:** 1-(4-(1,3-dioxoisooindolin-2-yl)phenyl)cyclopentane-1-carbonitrile S7 (94.9 mg, 0.300 mmol, 1.0 equiv), \((R,R)\)-Mn(CF₃-PDP) (40.7 mg, 0.030 mmol, 10 mol%), ClCH₂CO₂H (425 mg, 4.5 mmol, 15.0 equiv.), 50% wt. H₂O₂ (204 mg, 3.0 mmol, 10.0 equiv.), 4:1 MeCN:DCM (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 °C with ice bath. The reaction was worked up with 9 mL saturated NaHCO₃ and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO₂) using 20% acetone/hexanes \(\rightarrow\) 30% acetone/hexanes as eluent afforded product as a white solid.

**Run 1:** (60.8 mg, 0.184 mmol, 61.3% yield), (17.4 mg, 0.055 mmol, 18.3% rsm). **Run 2:** (64.8 mg, 0.196 mmol, 65.3% yield), (20.1 mg, 0.064 mmol, 21.2% rsm). **Run 3:** (61.5 mg, 0.186 mmol, 62.1% yield), (18.8 mg, 0.060 mmol, 19.8% rsm). **Average:** 62.9% yield \(\pm\) 2.1%, 19.8% rsm \(\pm\) 1.5%.

\(^1\)H-NMR (500 MHz, acetone-\(d₆\)) \(\delta\) 7.98 – 7.93 (m, 4H), 7.78 (d, \(J = 8.6\) Hz, 2H), 7.65 (d, \(J = 8.6\) Hz, 2H), 3.14 (d, \(J = 17.9\) Hz, 1H), 3.05 (d, \(J = 17.8\) Hz, 1H), 2.94 (ddddd, \(J = 12.9, 5.8, 4.2, 1.9\) Hz, 1H), 2.72 – 2.55 (m, 3H). \(^{13}\)C-NMR (126 MHz, acetone-\(d₆\)) \(\delta\) 212.4, 167.7, 138.8, 135.5, 133.5, 132.9, 128.5, 127.5, 124.2, 123.4, 50.5, 45.2, 37.2, 36.4. HRMS (TOF ESI+) \(m/z\) calculated for C₂₀H₁₈N₂O₃ \([M+H]^+\): 331.1083, found 331.1074.

**methyl 3-(1-cyano-3-oxocyclopentyl)benzoate** \[12\].
The reaction was run with **General Method A: Single Catalyst Addition Protocol**: methyl 3-(1-cyanocyclopentyl)benzoate S8 (114.6 mg, 0.500 mmol, 1.0 equiv), (R,R)-Mn(CF3-PDP) (67.8 mg, 0.050 mmol, 10 mol%), ClCH2CO2H (709 mg, 7.5 mmol, 15.0 equiv.), 50% wt. H2O2 (340 mg, 5.0 mmol, 10.0 equiv.), MeCN (1.0 mL in 40 mL vial, 6.25 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with 15 mL saturated NaHCO3 and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO2) using 15% acetone/hexanes → 25% acetone/hexanes as eluent afforded product as a white solid.

**Run 1**: (89.9 mg, 0.370 mmol, 73.9% yield), (15.5 mg, 0.068 mmol, 13.5% rsm). **Run 2**: (88.8 mg, 0.365 mmol, 73.0% yield), (21.2 mg, 0.092 mmol, 18.5% rsm). **Run 3**: (85.8 mg, 0.353 mmol, 70.6% yield), (20.6 mg, 0.090 mmol, 17.9% rsm). **Average**: 72.5% yield ± 1.7%, 16.6% rsm ± 2.7%. **Selectivity** = 72.5/(100-16.6) = 87%.

1H-NMR (500 MHz, CDCl3) δ 8.11 (s, 1H), 8.06 (d, J = 7.7 Hz, 1H), 7.70 – 7.68 (m, 1H), 7.54 (t, J = 7.8 Hz, 1H), 3.95 (s, 3H), 3.10 (d, J = 18.2 Hz, 1H), 2.90 – 2.85 (m, 1H), 2.81 (d, J = 18.0 Hz, 1H), 2.74 – 2.67 (m, 1H), 2.59 – 2.53 (m, 1H), 2.48 (ddd, J = 12.9, 10.3, 8.1 Hz, 1H). 13C-NMR (126 MHz, CDCl3) δ 211.5, 166.2, 138.0, 131.5, 130.5, 130.0, 129.7, 126.8, 122.1, 52.5, 49.9, 44.2, 36.8, 36.2. HRMS (TOF ESI+) m/z calculated for C14H14NO3 [M+H]+: 244.0974, found 244.0969.

**Condition with Fe(CF3-PDP):** The reaction was conducted in slow addition protocol,10 same as Entry 10 of Supplementary Table 1. In a 40 mL vial was charged with methyl 3-(1-cyanocyclopentyl)benzoate S8 (68.8 mg, 0.30 mmol, 1.0 equiv), AcOH (90.1 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.60 mL) and a stir bar. A 1mL syringe was charged with a solution of (R,R)-Fe(CF3-PDP) catalyst (101.6 mg, 0.075 mmol, 0.25 equiv.) in MeCN (0.375 mL). A 10 mL syringe was charged with a solution of H2O2 (183.6 mg, 2.7 mmol, 9.0 equiv.) in MeCN (3.75 mL). Both syringes were fitted with 25G needles and the solution was added dropwise via syringe pump over 1 hour. Upon completion of addition, the reaction was concentrated in vacuo to a minimum amount of MeCN and purified by column chromatography on silica (35 mm fritted glass column, 150 mL SiO2) using 15% acetone/hexanes → 25% acetone/hexanes as eluent to give both recovered starting material and product. **Result**: (8.0 mg, 0.033 mmol, 10.9% yield), 0% rsm. **Selectivity** = 10.9/(100-0) = 11%.

1-(3,5-difluorophenyl)-3-oxocyclopentane-1-carbonitrile [13].

The reaction was run with **General Method A: Single Catalyst Addition Protocol**: 1-(3,5-difluorophenyl)cyclopentane-1-carbonitrile S9 (103.6 mg, 0.500 mmol, 1.0 equiv), (R,R)-Mn(CF3-PDP) (67.8 mg, 0.050 mmol, 10 mol%), ClCH2CO2H (709 mg, 7.5 mmol, 15.0 equiv.), 50% wt. H2O2 (340 mg, 5.0 mmol, 10.0 equiv.), MeCN (1.0 mL in 40 mL vial, 6.25 mL with oxidant). The reaction was run at 0 ºC with ice bath.
The reaction was worked up with 15 mL saturated NaHCO₃ and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO₂) using 10% acetone/hexanes → 20% acetone/hexanes as eluent afforded product as a white solid.

**Run 1:** (73.1 mg, 0.331 mmol, 66.1% yield), (16.3 mg, 0.079 mmol, 15.7% rsm). **Run 2:** (73.5 mg, 0.332 mmol, 66.4% yield), (24.2 mg, 0.117 mmol, 23.4% rsm). **Run 3:** (71.3 mg, 0.322 mmol, 64.4% yield), (23.0 mg, 0.111 mmol, 22.2% rsm). **Average:** 65.6% yield ± 1.1%, 20.4% rsm ± 4.1%. Selectivity = 65.6/(100-20.4) = 82%.

**1H-NMR** (500 MHz, CDCl₃) δ 7.03 – 6.98 (m, 2H), 6.87 – 6.83 (m, 1H), 3.05 (d, J = 18.8 Hz, 1H), 2.83 (dddd, J = 12.7, 8.4, 3.7, 1.9 Hz, 1H), 2.74 – 2.64 (m, 2H), 2.58 – 2.52 (m, 1H), 2.41 (ddd, J = 13.0, 10.3, 8.2 Hz, 1H). **13C-NMR** (126 MHz, CDCl₃) δ 210.8, 163.5 (dd, J = 251.3, 12.9 Hz), 141.3 (t, J = 9.0 Hz), 121.5, 109.6 – 109.4 (m), 104.6 (t, J = 25.1 Hz), 49.7, 44.1 (t, J = 2.2 Hz), 36.7, 36.2. **19F-NMR** (470 MHz, CDCl₃) δ -107.0 (t, J = 7.7 Hz). HRMS (TOF ESI+) m/z calculated for C₁₁H₉OF₂ [M-CN]⁺: 195.0621, found 195.0622.

**Condition with Fe(CF₃-PDP):** The reaction was conducted in slow addition protocol,¹⁰ same as Entry 10 of Supplementary Table 1. In a 40 mL vial was charged with 1-(3,5-difluorophenyl)cyclopentane-1-carbonitrile S₉ (62.2 mg, 0.30 mmol, 1.0 equiv), AcOH (90.1 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.60 mL) and a stir bar. A 1mL syringe was charged with a solution of (R,R)-Fe(CF₃-PDP) catalyst (101.6 mg, 0.075 mmol, 0.25 equiv.) in MeCN (0.375 mL). A 10 mL syringe was charged with a solution of H₂O₂ (183.6 mg, 2.7 mmol, 9.0 equiv.) in MeCN (3.75 mL). Both syringes were fitted with 25G needles and the solution was added dropwise via syringe pump over 1 hour. Upon completion of addition, the reaction was concentrated in vacuo to a minimum amount of MeCN and purified by column chromatography on silica (35 mm fritted glass column, 150 mL SiO₂) using 10% acetone/hexanes → 20% acetone/hexanes as eluent to give both recovered starting material and product. **Result:** (7.6 mg, 0.034 mmol, 11.4% yield), (23.0 mg, 0.111 mmol, 37.0% rsm). **Selectivity = 11.4/(100-37.0) = 18%.

**methyl 4-(1-cyano-3-oxocyclopentyl)benzoate [14].**

The reaction was run with **General Method A: Single Catalyst Addition Protocol:** methyl 4-(1-cyanocyclopentyl)benzoate S₁₀ (68.8 mg, 0.300 mmol, 1.0 equiv), (R,R)-Mn(CF₃-PDP) (40.7 mg, 0.030 mmol, 10 mol%), ClCH₂CO₂H (425 mg, 4.5 mmol, 15.0 equiv.), 50% wt. H₂O₂ (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 °C with ice bath. The reaction was worked up with 9 mL saturated NaHCO₃ and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO₂) using 20% acetone/hexanes → 30% acetone/hexanes as eluent afforded product as a white solid.
Run 1: (60.3 mg, 0.248 mmol, 82.6% yield), (9.1 mg, 0.040 mmol, 13.2% rsm). Run 2: (61.3 mg, 0.252 mmol, 83.9% yield), (9.1 mg, 0.040 mmol, 13.2% rsm). Run 3: (61.7 mg, 0.254 mmol, 84.6% yield), (6.9 mg, 0.030 mmol, 10.0% rsm). Average: 83.7% yield ± 1.0%, 11.9% rsm ± 1.7%. Selectivity = 83.7/(100-11.9) = 95%.

1H-NMR (500 MHz, CDCl₃) δ 8.11 – 8.09 (m, 2H), 7.55 – 7.52 (m, 2H), 3.93 (s, 3H), 3.08 (d, J = 18.2 Hz, 1H), 2.87 – 2.78 (m, 2H), 2.71 – 2.65 (m, 1H), 2.54 (dddt, J = 18.8, 8.0, 3.6, 1.0 Hz, 1H), 2.46 (ddd, J = 12.9, 10.0, 8.2 Hz, 1H). 13C-NMR (126 MHz, CDCl₃) δ 211.4, 166.2, 142.2, 130.8, 130.7, 126.0, 122.0, 52.5, 49.8, 44.4, 36.7, 36.4. HRMS (TOF ESI+) m/z calculated for C₁₄H₁₄NO₃ [M+H]⁺: 244.0974, found 244.0971.

Condition with Fe(CF₃-PDP): The reaction was conducted in slow addition protocol,¹⁰ same as Entry 10 of Supplementary Table 1. In a 40 mL vial was charged with methyl 4-(1-cyanocyclopentyl)benzoate S₁₀ (68.8 mg, 0.30 mmol, 1.0 equiv), AcOH (90.1 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.60 mL) and a stir bar. A 1mL syringe was charged with a solution of (R,R)-Fe(CF₃-PDP) catalyst (101.6 mg, 0.075 mmol, 0.25 equiv.) in MeCN (0.375 mL). A 10 mL syringe was charged with a solution of H₂O₂ (183.6 mg, 2.7 mmol, 9.0 equiv.) in MeCN (3.75 mL). Both syringes were fitted with 25G needles and the solution was added dropwise via syringe pump over 1 hour. Upon completion of addition, the reaction was concentrated in vacuo to a minimum amount of MeCN and purified by column chromatography on silica (35 mm fritted glass column, 150 mL SiO₂) using 20% acetone/hexanes → 30% acetone/hexanes as eluent to give both recovered starting material and product. Result: (20.2 mg, 0.083 mmol, 27.6% yield), (4.8 mg, 0.021 mmol, 7.0% rsm). Selectivity = 27.6/(100-7.0) = 30%.

4-(1-cyano-3-oxocyclopentyl)benzonitrile [15].

The reaction was run with General Method A: Single Catalyst Addition Protocol:

![Image of 4-(1-cyano-3-oxocyclopentyl)benzonitrile](image)

4-(1-cyanocyclopentyl)benzonitrile S₁₁ (58.9 mg, 0.300 mmol, 1.0 equiv), (R,R)-Mn(CF₃-PDP) (40.7 mg, 0.030 mmol, 10 mol%), ClCH₂CO₂H (425 mg, 4.5 mmol, 15.0 equiv.), 50% wt. H₂O₂ (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with 9 mL saturated NaHCO₃ and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO₂) using 10% acetone/hexanes → 20% acetone/hexanes as eluent afforded product as a white solid.

Run 1: (46.3 mg, 0.220 mmol, 73.4% yield), (12.2 mg, 0.062 mmol, 20.7% rsm). Run 2: (45.6 mg, 0.217 mmol, 72.3% yield), (11.7 mg, 0.060 mmol, 19.9% rsm). Run 3: (43.8 mg, 0.208 mmol, 69.4% yield), (12.7 mg, 0.065 mmol, 21.6% rsm). Average: 71.7% yield ± 2.1%, 20.7% rsm ± 0.8%. Selectivity = 71.7/(100-20.7)= 90%.
\(^{1}\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.73 (d, \(J = 8.8\) Hz, 2H), 7.60 – 7.58 (m, 2H), 3.05 (d, \(J = 18.1\) Hz, 1H), 2.87 – 2.81 (m, 1H), 2.76 (d, \(J = 18.2\) Hz, 1H), 2.71 – 2.63 (m, 1H), 2.57 – 2.50 (m, 1H), 2.43 (ddd, \(J = 12.9, 10.3, 8.1\) Hz, 1H). \(^{13}\)C-NMR (126 MHz, CDCl\(_3\)) \(\delta\) 210.8, 142.5, 133.2, 126.8, 121.4, 117.9, 112.9, 49.5, 44.4, 36.6, 36.1. HRMS (EI\(^+\)) \(m/z\) calculated for \(\text{C}_{13}\text{H}_{10}\text{ON}_2\) \([\text{M}]^+: 210.07932,\) found 210.07932.

**Condition with Fe(CF\(_3\)-PDP):** The reaction was conducted in slow addition protocol\(^{10}\) same as Entry 10 of Supplementary Table 1. In a 40 mL vial was charged with 4-(1-cyanocyclopentyl)benzonitrile \(\text{S11}\) (58.9 mg, 0.30 mmol, 1.0 equiv), AcOH (90.1 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.60 mL) and a stir bar. A 1mL syringe was charged with a solution of \((R,R)\)-Fe(CF\(_3\)-PDP) catalyst (101.6 mg, 0.075 mmol, 0.25 equiv.) in MeCN (0.375 mL). A 10 mL syringe was charged with a solution of \(\text{H}_2\text{O}_2\) (183.6 mg, 2.7 mmol, 9.0 equiv.) in MeCN (3.75 mL). Both syringes were fitted with 25G needles and the solution was added dropwise via syringe pump over 1 hour. Upon completion of addition, the reaction was concentrated in vacuo to a minimum amount of MeCN and purified by column chromatography on silica (35 mm fritted glass column, 150 mL SiO\(_2\)) using 10% acetone/hexanes \(\rightarrow\) 20% acetone/hexanes as eluent to give both recovered starting material and product. **Result:** (34.9 mg, 0.166 mmol, 55.3% yield), (4.5 mg, 0.023 mmol, 7.6% rsm). **Selectivity = 55.3/(100-7.6) = 60%.**

**methyl 3-oxo-1-(4-(trifluoromethoxy)phenyl)cyclopentane-1-carboxylate [16].**

The reaction was run with **General Method B: Iterative Catalyst Addition Protocol:** methyl 1-(4-(trifluoromethoxy)phenyl)cyclopentane-1-carboxylate \(\text{S12}\) (72.1 mg, 0.250 mmol, 1.0 equiv), (\(R,R\))-Mn(CF\(_3\)-PDP) (3 times addition of 16.9 mg, 0.013 mmol, 5 mol% batch; 15 mol% in total), ClCH\(_2\)CO\(_2\)H (354 mg, 3.75 mmol, 15.0 equiv.), 50% wt. \(\text{H}_2\text{O}_2\) (170 mg, 2.5 mmol, 10.0 equiv.), MeCN (0.5 mL in 40 mL vial, 3.13 mL with oxidant). The reaction was run at 0 °C with ice bath. The reaction was worked up with 9 mL saturated NaHCO\(_3\) and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO\(_2\)) using 20% acetone/hexanes \(\rightarrow\) 30% acetone/hexanes as eluent afforded product as a clear oil.

**Run 1:** (57.0 mg, 0.189 mmol, 75.4% yield), 0% rsm. **Run 2:** (58.4 mg, 0.193 mmol, 77.2% yield), 0% rsm. **Run 3:** (59.8 mg, 0.198 mmol, 79.1% yield), 0% rsm. **Average: 77.2% yield ± 1.8%, 0% rsm.**

\(^{1}\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.39 – 7.36 (m, 2H), 7.22 – 7.20 (m, 2H), 3.67 (s, 3H), 3.26 (d, \(J = 17.9\) Hz, 1H), 3.01 – 2.96 (m, 1H), 2.58 (d, \(J = 17.9\) Hz, 1H), 2.38 – 2.28 (m, 3H). \(^{13}\)C-NMR (126 MHz, CDCl\(_3\)) \(\delta\) 214.9, 174.5, 148.7, 139.8, 128.2, 121.2, 120.5 (q, \(J = 257.4\) Hz), 54.7, 53.2, 48.3, 37.1, 33.1. \(^{19}\)F-NMR (471 MHz, CDCl\(_3\)) \(\delta\) -57.9. HRMS (TOF ESI\(^+\)) \(m/z\) calculated for \(\text{C}_{14}\text{H}_{14}\text{O}_4\text{F}_3\) \([\text{M+H}]^+: 303.0844,\) found 303.0838.

**1-(4-(difluoromethoxy)phenyl)-3-oxocyclopentane-1-carbonitrile [17].**
The reaction was run with General Method B: Iterative Catalyst Addition Protocol:

1-(4-(difluoromethoxy)phenyl)cyclopentane-1-carbonitrile S13 (71.2 mg, 0.300 mmol, 1.0 equiv), (R,R)-Mn(CF3-PDP) (3 times addition of 20.4 mg, 0.015 mmol, 5 mol% batch; 15 mol% in total), ClCH2CO2H (425 mg, 4.50 mmol, 15.0 equiv.), 50% wt. H2O2 (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with 9 mL saturated NaHCO3 and DCM as described in General Method B. Flash column chromatography on silica (35 mm fritted glass column, 100 mL SiO2) using 10% acetone/hexanes \(\rightarrow\) 20% acetone/hexanes \(\rightarrow\) 30% acetone/hexanes as eluent afforded product as a clear oil.

**Run 1:** (40.7 mg, 0.162 mmol, 54.0% yield), 0% rsm. **Run 2:** (42.1 mg, 0.168 mmol, 55.9% yield), 0% rsm. **Run 3:** (40.4 mg, 0.161 mmol, 53.6% yield), 0% rsm. **Average:** 54.5% yield ± 1.2%, 0% rsm.

1H-NMR (500 MHz, CDCl3) \(\delta\) 7.47 – 7.44 (m, 2H), 7.22 – 7.18 (m, 2H), 6.54 (t, \(J = 73.2\) Hz, 1H), 3.06 (d, \(J = 18.1\) Hz, 1H), 2.84 (dddd, \(J = 12.7, 8.5, 3.9, 1.9\) Hz, 1H), 2.78 – 2.74 (m, 1H), 2.69 – 2.64 (m, 1H), 2.52 (dddt, \(J = 18.9, 8.2, 3.9, 1.0\) Hz, 1H), 2.43 (ddd, \(J = 12.9, 9.9, 8.1\) Hz, 1H). 13C-NMR (126 MHz, CDCl3) \(\delta\) 211.6, 151.2 (t, \(J = 2.9\) Hz), 134.7, 127.5, 122.3, 120.6, 115.6 (t, \(J = 261.6\) Hz), 50.0, 43.7, 36.7, 36.5. 19F-NMR (471 MHz, CDCl3) \(\delta\) -81.4. HRMS (TOF ESI+) \(m/z\) calculated for C13H11NO2F2Na [M+Na]+: 274.0656, found 274.0662.

Better selectivity can be obtained using General Method A: Single Catalyst Addition Protocol. 1-(4-(difluoromethoxy)phenyl)cyclopentane-1-carbonitrile S13 (71.2 mg, 0.300 mmol, 1.0 equiv), (R,R)-Mn(CF3-PDP) (40.7 mg, 0.030 mmol, 10 mol%), ClCH2CO2H (425 mg, 4.5 mmol, 15.0 equiv.), 50% wt. H2O2 (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was allowed to stir at 0 ºC for ~30 min to facilitate the solubility of starting material before adding H2O2 and run at 0 ºC with ice bath. The reaction was worked up with 9 mL saturated NaHCO3 and DCM as described in General Method A.

**Run 1:** (32.5 mg, 0.129 mmol, 43.1% yield), (24.8 mg, 0.105 mmol, 34.8% rsm). **Run 2:** (34.9 mg, 0.139 mmol, 46.3% yield), (20.1 mg, 0.085 mmol, 28.2% rsm). **Run 3:** (36.4 mg, 0.145 mmol, 48.3% yield), (21.6 mg, 0.091 mmol, 30.3% rsm). **Average:** 45.9% yield ± 2.6%, 31.1% rsm ± 3.4%.

2-((1-(4-bromophenyl)-3-oxocyclopentyl)methyl)-5-nitroisoindoline-1,3-dione [18].

The reaction was run with General Method A: Single Catalyst Addition Protocol: 2-((1-(4-bromophenyl)cyclopentyl)methyl)-5-nitroisoindoline-1,3-dione S14 (128.8 mg, 0.300 mmol, 1.0 equiv), (R,R)-Mn(CF3-PDP) (40.7 mg, 0.030 mmol, 10 mol%), ClCH2CO2H (425 mg, 4.5 mmol, 15.0 equiv.), 50% wt. H2O2 (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was allowed to stir at 0 ºC for ~30 min to facilitate the solubility of starting material before adding H2O2 and run at 0 ºC with ice bath. The reaction was worked up with 9 mL saturated NaHCO3 and DCM as described in General Method A.
was worked up with 9 mL saturated NaHCO₃ and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO₂) using 15% acetone/hexanes → 25% acetone/hexanes as eluent afforded product as a white solid.

**Run 1:** (76.1 mg, 0.172 mmol, 57.2% yield), <10% rsm. **Run 2:** (80.7 mg, 0.182 mmol, 60.7% yield), <10% rsm. **Run 3:** (83.8 mg, 0.189 mmol, 63.0% yield), <10% rsm. **Average:** 60.3% yield ± 2.9%, <10% rsm.

**1H-NMR (500 MHz, CDCl₃)** δ 8.60 – 8.58 (m, 2H), 8.01 – 7.99 (m, 1H), 7.44 (dd, J = 8.5, 1.9 Hz, 2H), 7.17 – 7.15 (m, 2H), 3.98 (d, J = 14.0 Hz, 1H), 3.91 (d, J = 14.1 Hz, 1H), 2.76 (d, J = 17.8 Hz, 1H), 2.71 (d, J = 18.2 Hz, 1H), 2.52 – 2.44 (m, 2H), 2.38 – 2.21 (m, 2H). **13C-NMR (126 MHz, CDCl₃)** δ 215.8, 166.3, 166.0, 152.0, 135.9, 133.0, 129.6, 128.5, 124.9, 121.7, 119.1, 49.2, 49.2, 47.7, 36.3, 32.5. HRMS (TOF ESI+) m/z calculated for C₂₀H₁₆N₂O₅Br [M+H]+: 443.0243, found 443.0237.

3′H-spiro[cyclopentane-1,1′-isobenzofuran]-3,3′-dione [19].

The reaction was run with a modified procedure according to General Method A:

**Single Catalyst Addition Protocol:** 3′H-spiro[cyclopentane-1,1′-isobenzofuran]-3′-one S15 (94.1 mg, 0.500 mmol, 1.0 equiv), (R,R)-Mn(CF₃-PDP) (67.8 mg, 0.050 mmol, 10 mol%), ClCH₂CO₂H (709 mg, 7.5 mmol, 15.0 equiv.), 50% wt. H₂O₂ (340 mg, 5.0 mmol, 10.0 equiv.), MeCN (1.0 mL in 40 mL vial, 6.25 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was concentrated to a minimal amount of solvent and directly load to column purification. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO₂) using 30% acetone/hexanes → 50% acetone/hexanes as eluent afforded product co-eluted with chloroacetic acid. The yield of product was determined by adding nitrobenzene as internal standard via quantitative 1H NMR. The chloroacetic acid can be later removed by NaHCO₃ wash with a slight loss of desired product.

**Run 1:** (59.8 mg, 0.296 mmol, 59.1% yield), <10% rsm. **Run 2:** (63.3 mg, 0.313 mmol, 62.7% yield), <10% rsm. **Run 3:** (64.7 mg, 0.320 mmol, 64.1% yield), <10% rsm. **Average:** 62.0% yield ± 2.6%, <10% rsm.

**1H-NMR (500 MHz, methylene chloride-d₂)** δ 7.89 (dt, J = 7.6, 1.0 Hz, 1H), 7.76 (td, J = 7.6, 1.1 Hz, 1H), 7.59 (td, J = 7.5, 0.9 Hz, 1H), 7.52 (dt, J = 7.7, 0.9 Hz, 1H), 2.80 (d, J = 18.4 Hz, 1H), 2.82 – 2.72 (m, 1H), 2.67 (ddt, J = 18.6, 2.9, 1.1 Hz, 1H), 2.63 – 2.50 (m, 2H), 2.39 (dddd, J = 13.7, 9.4, 2.9, 1.4 Hz, 1H). **13C-NMR (126 MHz, methylene chloride-d₂)** δ 213.4, 169.1, 150.8, 135.1, 130.3, 126.7, 126.2, 121.7, 90.8, 50.3, 38.0, 36.6. HRMS (TOF ESI+) m/z calculated for C₁₂H₁₀O₃ [M+H]+: 203.0708, found 203.0710.

5′-Bromo-1′-(phenylsulfonfonyl)sipro[cyclopentane-1,3′-indoline]-2′,3-dione [20a].
The reaction was run with **General Method A: Single Catalyst Addition Protocol**: 5'-Bromo-1'-(phenylsulfonyl)spiro[cyclopentane-1,3'-indolin]-2'-one S16 (81.3 mg, 0.200 mmol, 1.0 equiv), (R,R)-Mn(CF3-PDP) (27.1 mg, 0.020 mmol, 10 mol%), ClCH2CO2H (284 mg, 3.0 mmol, 15.0 equiv.), 50% wt. H2O2 (136 mg, 2.0 mmol, 10.0 equiv.), MeCN (0.4 mL in 40 mL vial, 2.50 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with 6 mL saturated NaHCO3 and DCM as described in General Method A. The crude mixture was dissolved with a small amount of DCM and concentrated onto silica (2 mL) for dry loading onto the column (35 mL silica) and then eluted with 10% EtOAc/hexane → 20% EtOAc/hexane → 40% EtOAc/hexane to afford 20a as a white solid and 20b alcohol diastereomers mixtures as a white solid. The recovered starting material was recycled 1X with same oxidation protocol.

**Run 1:** **cycle 1:** (20.1 mg, 0.0478 mmol, 23.9% yield of 20a), (10.4 mg, 0.0246 mmol, 12.3% yield of 20b), (38.7 mg, 0.0953 mmol, 47.6% rsm). **cycle 2:** (7.9 mg, 0.0188 mmol, 19.7% yield of 20a), (4.7 mg, 0.0111 mmol, 11.6% yield of 20b), (18.5 mg, 0.0455 mmol, 47.8% rsm). **Overall:** (28.0 mg, 0.066 mmol, 33.3% yield of 20a), (15.1 mg, 0.0358 mmol, 17.9% yield of 20b), (18.5 mg, 0.0455 mmol, 22.8% rsm).

**Run 2:** **cycle 1:** (20.7 mg, 0.0493 mmol, 24.6% yield of 20a), (10.3 mg, 0.244 mmol, 12.2% yield of 20b), (37.4 mg, 0.0921 mmol, 46.0% rsm). **cycle 2:** (8.2 mg, 0.195 mmol, 21.2% yield of 20a), (4.5 mg, 0.0107 mmol, 11.6% yield of 20b), (17.8 mg, 0.0438 mmol, 47.6% rsm). **Overall:** (28.9 mg, 0.0688 mmol, 34.4% yield of 20a), (14.8 mg, 0.0350 mmol, 17.5% yield of 20b), (17.8 mg, 0.0438 mmol, 21.9% rsm).

**Run 3:** **cycle 1:** (21.0 mg, 0.0500 mmol, 25.0% of 20a), (10.4 mg, 0.246 mmol, 12.3% yield of 20b), (39.6 mg, 0.0975 mmol, 48.7% rsm). **cycle 2:** (8.0 mg, 0.0190 mmol, 19.5% yield of 20a), (4.3 mg, 0.0102 mmol, 10.4% yield of 20b), (17.0 mg, 0.0418 mmol, 42.9% rsm). **Overall:** (29.0 mg, 0.0690 mmol, 34.5% yield of 20a), (14.7 mg, 0.0348 mmol, 17.4% yield of 20b), (17.0 mg, 0.0418 mmol, 20.9% rsm).

**Average:** (34.1% yield of 20a ± 0.7%), (17.6% yield of 20b ± 0.3%), (21.9% rsm ± 1.0%).

1H-NMR (500 MHz, CDCl3) δ 8.06 (d, J = 8.6 Hz, 2H), 7.85 (d, J = 8.7 Hz, 1H), 7.69 (td, J = 7.5, 1.2 Hz, 1H), 7.56 (t, J = 8.0 Hz, 2H), 7.51 (dd, J = 8.7, 2.1 Hz, 1H), 7.29 (d, J = 1.8 Hz, 1H), 2.75 (dd, J = 18.8, 9.1 Hz, 1H), 2.57 (d, J = 19.0 Hz, 1H), 2.55 – 2.48 (m, 1H), 2.38 (d, J = 18.5 Hz, 1H), 2.40 – 2.34 (m, 1H), 2.15 (dd, J = 13.5, 9.0 Hz, 1H). 13C-NMR (126 MHz, CDCl3) δ 213.5, 177.5, 137.5, 137.0, 134.0, 132.4, 129.5, 127.9, 126.0, 118.6, 115.7, 51.0, 47.2, 36.3, 34.5. HRMS (TOF ESI+) m/z calculated for C18H15BrNO4S [M+H]+: 419.9905, found 419.9897.

5'-Bromo-3-hydroxy-1'-(phenylsulfonyl)spiro[cyclopentane-1,3'-indolin]-2'-one [20b]. The ratio of diastereomers is approximately 1.5:1 and could be separated by using preparative TLC. The reduction of 20a using NaBH4 provided two diastereomers of alcohol and the spectroscopic data of them are consistent with those of both diastereomers of 20b.
Diastereomer 1: $^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J = 7.7$ Hz, 2H), 7.77 (d, $J = 8.7$ Hz, 1H), 7.66 (t, $J = 7.5$ Hz, 1H), 7.63 (d, $J = 2.1$ Hz, 1H), 7.54 (t, $J = 7.9$ Hz, 2H), 7.42 (dd, $J = 8.7$, 2.1 Hz, 1H), 4.66 – 4.62 (m, 1H), 2.32 (dd, $J = 14.3$, 4.9 Hz, 1H), 2.15 – 2.01 (m, 3H), 1.96 – 1.88 (m, 1H), 1.84 (dt, $J = 14.3$, 2.2 Hz, 1H), 1.58 (br. H, 1H).$^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 180.2, 138.0, 137.3, 137.2, 134.7, 131.3, 129.4, 127.9, 127.7, 118.7, 115.0, 74.3, 53.5, 47.3, 38.7, 36.6. HRMS (TOF ESI+) $m/z$ calculated for C$_{18}$H$_{17}$BrNO$_4$S [M+H]$^+$: 422.0062, found 422.0072.

Diastereomer 2: $^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 8.06 (d, $J = 8.1$ Hz, 2H), 7.81 (d, $J = 8.7$ Hz, 1H), 7.68 (t, $J = 7.5$ Hz, 1H), 7.56 (t, $J = 7.9$ Hz, 2H), 7.46 (dd, $J = 8.7$, 2.0 Hz, 1H), 7.24 (d, $J = 2.1$ Hz, 1H), 4.50 (dtt, $J = 10.2$, 5.1, 2.3 Hz, 1H), 3.25 (dd, $J = 10.1$, 3.0 Hz, 1H), 2.31 (dt, $J = 13.7$, 8.1 Hz, 1H), 2.23 – 2.16 (m, 1H), 2.11 – 2.01 (m, 3H), 1.88 (ddd, $J = 13.9$, 9.0, 5.3 Hz, 1H). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 181.6, 137.7, 137.5, 136.0, 135.0, 131.7, 129.5, 125.9, 118.7, 115.5, 74.6, 54.3, 47.3, 38.2, 36.8. HRMS (TOF ESI+) $m/z$ calculated for C$_{18}$H$_{17}$BrNO$_4$S [M+H]$^+$: 422.0062, found 422.0062.

3-(((4-fluorophenyl)sulfonyl)methyl)cyclopentan-1-one [21].

The reaction was run with General Method A: Single Catalyst Addition Protocol:

1-((cyclopentylmethyl)sulfonyl)-4-fluorobenzene S17 (121.2 mg, 0.500 mmol, 1.0 equiv), (R,R)-Mn(CF$_3$-PDP) (67.8 mg, 0.050 mmol, 10 mol%), ClCH$_2$CO$_2$H (709 mg, 7.5 mmol, 15.0 equiv.), 50% wt. H$_2$O$_2$ (340 mg, 5.0 mmol, 10.0 equiv.), MeCN (1.0 mL in 40 mL vial, 6.25 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with 15 mL saturated NaHCO$_3$ and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO$_2$) using 15% acetone/hexanes $\rightarrow$ 25% acetone/hexanes $\rightarrow$ 40% acetone/hexanes as eluent afforded product as a clear oil.

Run 1: (84.0 mg, 0.328 mmol, 65.6% yield), 0% rsm. Run 2: (84.6 mg, 0.330 mmol, 66.0% yield), 0% rsm. Run 3: (79.0 mg, 0.308 mmol, 61.6% yield), 0% rsm. Average: 64.4% yield $\pm$ 2.4%, 0% rsm.

$^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 7.97 – 7.93 (m, 2H), 7.29 – 7.25 (m, 2H), 3.27 (dd, $J = 14.0$, 6.0 Hz, 1H), 3.20 (dd, $J = 14.0$, 7.7 Hz, 1H), 2.76 – 2.66 (m, 1H), 2.55 (dd, $J = 18.6$, 7.7 Hz, 1H), 2.38 – 2.30 (m, 2H), 2.22 – 2.14 (m, 1H), 1.96 (dd, $J = 18.4$, 10.8 Hz, 1H), 1.69 (dt, $J = 12.5$, 10.8, 8.3 Hz, 1H). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 216.4, 166.0 (d, $J = 257.1$ Hz), 135.6 (d, $J = 3.3$ Hz), 130.9 (d, $J = 9.6$ Hz), 117.0 (d, $J = 22.6$ Hz), 61.4, 44.3, 37.9, 31.6, 29.5. $^{19}$F-NMR (470 MHz, CDCl$_3$) $\delta$ -103.2. HRMS (TOF ESI+) $m/z$ calculated for C$_{12}$H$_{14}$O$_3$SF [M+H]$^+$: 257.0648, found 257.0646.

Site of oxidation was assigned based on a combination of $^1$H, gCOSY, gHSQC and gHMBC NMRs.

5-Bromo-2-oxo-3-(3-oxobutyl)-1-(phenylsulfonyl)indolin-3-yl acetate [22].

The reaction was run with General Method B: Iterative Catalyst Addition Protocol: 5-bromo-1-((4-bromophenyl)sulfonyl)-3-butyl-2-oxoindolin-3-yl acetate S18 (93.3 mg, 0.200 mmol, 1.0 equiv), (R,R)-
Mn(CF3-PDP) (3 times addition of 20.4 mg, 0.015 mmol, 5 mol% batch; 15 mol% in total), ClCH2CO2H (284 mg, 3.0 mmol, 15.0 equiv.), 50% wt. H2O2 (136 mg, 2.0 mmol, 10.0 equiv.), MeCN (0.4 mL in 40 mL vial, 2.50 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with 6 mL saturated NaHCO3 and DCM as described in General Method B. The crude mixture was dissolved with a small amount of DCM and concentrated onto silica (2 mL) for dry loading onto the column (silica, 30 mL) and then eluted with 15% EtOAc/hexane → 30% EtOAc/hexane to afford 22 as a white solid.

**Run 1**: (59.2 mg, 0.123 mmol, 61.6% yield), (13.2 mg, 0.0283 mmol, 14.2% rsm). **Run 2**: (59.1 mg, 0.123 mmol, 61.5% yield), (13.4 mg, 0.0288 mmol, 14.4% rsm). **Run 3**: (58.0 mg, 0.121 mmol, 60.4% yield), (15.0 mg, 0.0322 mmol, 16.1% rsm). **Average**: 61.2% yield ± 0.7%, 14.9% rsm ± 1.0%.

1H-NMR (500 MHz, CDCl3) δ 8.05 (d, J = 7.7 Hz, 2H), 7.83 (d, J = 8.7 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.55 – 7.50 (m, 3H), 7.29 (d, J = 2.1 Hz, 1H), 2.55 (ddd, J = 18.0, 10.6, 5.1 Hz, 1H), 2.43 (ddd, J = 18.0, 10.3, 5.0 Hz, 1H), 2.31 – 2.25 (m, 1H), 2.10 (s, 3H), 2.14 – 2.08 (m, 1H), 1.91 (s, 3H). 13C-NMR (125 MHz, CDCl3) δ 206.0, 171.8, 168.7, 138.0, 137.1, 134.9, 133.5, 129.4, 129.2, 128.2, 126.0, 118.5, 115.4, 77.8, 35.7, 30.8, 30.1, 20.2. HRMS (TOF ESI+) m/z calculated for C20H18BrNNaO6S [M+Na]+: 501.9936, found 501.9922.

**N-((4-bromophenyl)sulfonyl)-N-(4-oxopentyl)acetamide [23a].**

The reaction was run with **General Method A: Single Catalyst Addition Protocol**: N-((4-bromophenyl)sulfonyl)-N-pentylacetamide S19 (104.5 mg, 0.300 mmol, 1.0 equiv), (R,R)-Mn(CF3-PDP) (40.7 mg, 0.030 mmol, 10 mol%), ClCH2CO2H (425 mg, 4.5 mmol, 15.0 equiv.), 50% wt. H2O2 (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with saturated 9 mL NaHCO3 and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO2) using 20% acetone/hexanes → 30% acetone/hexanes as eluent afforded N-((4-bromophenyl)sulfonyl)-N-(3-oxopentyl)acetamide (γ-ketone, 23b) product as a colorless oil and N-((4-bromophenyl)sulfonyl)-N-(4-oxopentyl)acetamide (δ-ketone, 23a) product as a colorless oil.

**Run 1**: (23.2 mg, 0.064 mmol, 21.3% yield of γ-ketone 22b), (64.7 mg, 0.179 mmol, 59.6% yield of δ-ketone 22a), (80.9% overall yield, 2.8:1 δ:γ ratio), <10% rsm. **Run 2**: (23.6 mg, 0.065 mmol, 21.7% yield of γ-ketone 22b), (67.1 mg, 0.185 mmol, 61.7% yield of δ-ketone 22a), (83.4% overall yield, 2.8:1 δ:γ ratio), <10% rsm. **Run 3**: (24.1 mg, 0.066 mmol, 22.1% yield of γ-ketone 22b), (63.2 mg, 0.175 mmol, 58.2% yield of δ-ketone 22a), (80.3% overall yield, 2.6:1 δ:γ ratio), <10% rsm. **Average**: 81.5% yield ± 1.6%, 2.8:1 δ:γ ratio, <10% rsm.
$^1$H-NMR (500 MHz, CDCl$_3$) δ 7.76 (d, $J = 8.2$ Hz, 2H), 7.68 (d, $J = 8.8$ Hz, 2H), 3.80 – 3.52 (m, 2H), 2.53 (m, 2H), 2.31 (s, 3H), 2.15 (s, 3H), 1.99 – 1.92 (m, 2H). $^{13}$C-NMR (126 MHz, CDCl$_3$) δ 207.6, 170.2, 138.5, 132.6, 129.3, 129.1, 46.5, 40.1, 30.0, 24.9, 23.7. HRMS (TOF ESI$^+$) m/z calculated for C$_{13}$H$_{17}$NO$_4$SBr [M+H]$^+$: 362.0062, found 362.0067.

*N*-(4-bromophenyl)sulfonyl)-*N*-(3-oxopentyl)acetamide [23b].

$^1$H-NMR (500 MHz, methylene Chloride-$d_2$) δ 7.78 – 7.75 (m, 2H), 7.73 – 7.71 (m, 2H), 3.98 – 3.95 (m, 2H), 2.88 – 2.85 (m, 2H), 2.43 (q, $J = 7.3$ Hz, 2H), 2.32 (s, 3H), 1.02 (t, $J = 7.3$ Hz, 3H). $^{13}$C-NMR (126 MHz, methylene Chloride-$d_2$) δ 209.2, 170.3, 138.8, 133.2, 129.6, 129.5, 42.9, 42.5, 36.5, 25.3, 7.9. HRMS (TOF ESI$^+$) m/z calculated for C$_{13}$H$_{17}$NO$_4$SBr [M+H]$^+$: 362.0062, found 362.0053.

1-(4-bromophenyl)-3-oxocyclohexane-1-carbonitrile [24a].

The reaction was run with **General Method A: Single Catalyst Addition Protocol**:

1-(4-bromophenyl)cyclohexane-1-carbonitrile S20 (79.3 mg, 0.300 mmol, 1.0 equiv), ($R,R$)-Mn(CF$_3$-PDP) (40.7 mg, 0.030 mmol, 10 mol%), ClCH$_2$CO$_2$H (425 mg, 4.5 mmol, 15.0 equiv.), 50% wt. H$_2$O$_2$ (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with 9 mL saturated NaHCO$_3$ and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO$_2$) using 20% acetone/hexanes → 30% acetone/hexanes as eluent afforded 1-(4-bromophenyl)-3-oxocyclohexane-1-carbonitrile (3-ketone, 24a) product as a white solid and 1-(4-bromophenyl)-4-oxocyclohexane-1-carbonitrile (4-ketone, 24b) as a white solid.

**Run 1:** (34.7 mg, 0.125 mmol, 41.5% yield of 3-ketone 24a), (18.7 mg, 0.067 mmol, 22.4% yield of 4-ketone 24b), (63.9% overall yield, 1.86:1 3-ketone:4-ketone ratio), (13.4 mg, 0.051 mmol, 16.9% rsm).

**Run 2:** (34.5 mg, 0.124 mmol, 41.3% yield of 3-ketone 24a), (18.5 mg, 0.067 mmol, 22.2% yield of 4-ketone 24b), (63.5% overall yield, 1.86:1 3-ketone:4-ketone ratio), (16.3 mg, 0.062 mmol, 20.6% rsm).

**Run 3:** (34.2 mg, 0.123 mmol, 41.0% yield of 3-ketone 24a), (19.2 mg, 0.069 mmol, 23.0% yield of 4-ketone 24b), (64.0% overall yield, 1.78:1 3-ketone:4-ketone ratio), (12.8 mg, 0.049 mmol, 16.2% rsm).

**Average:** 63.8% yield ± 0.3%, 1.83:1 3-ketone:4-ketone ratio, 17.9% rsm ± 2.4%.

$^1$H-NMR (500 MHz, CDCl$_3$) δ 7.58 – 7.55 (m, 2H), 7.36 – 7.33 (m, 2H), 2.88 (dt, $J = 14.6$, 1.8 Hz, 1H), 2.82 (d, $J = 14.7$, 1H), 2.57 (dddd, $J = 14.8$, 5.8, 3.7, 1.6 Hz, 1H), 2.43 – 2.34 (m, 2H), 2.26 – 2.06 (m, 3H). $^{13}$C-NMR (126 MHz, CDCl$_3$) δ 205.1, 137.6, 132.6, 127.4, 122.9, 120.9, 50.6, 45.4, 40.2, 36.3, 22.4. HRMS (EI$^+$) m/z calculated for C$_{13}$H$_{12}$ONBr [M$^+$]: 277.0102, found 277.0103.
Site of oxidation was assigned based on a combination of $^1$H, gDQOSY, gHSQC NMRs.

1-(4-bromophenyl)-4-oxocyclohexane-1-carbonitrile [24b].

$^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 7.59 – 7.55 (m, 2H), 7.41 – 7.38 (m, 2H), 2.91 (ddd, $J$ = 15.0, 13.8, 5.7 Hz, 2H), 2.58 (ddt, $J$ = 15.6, 4.4, 2.1 Hz, 2H), 2.47 (ddt, $J$ = 14.3, 5.9, 3.1 Hz, 2H), 2.25 (ddd, $J$ = 13.9, 13.9, 4.3 Hz, 2H). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 206.9, 137.8, 132.5, 127.3, 122.8, 120.9, 43.0, 38.6, 37.0. HRMS (EI+) m/z calculated for C$_{13}$H$_{12}$ONBr [M]+: 277.0102, found 277.0103.

2-((1-(4-bromophenyl)-3-oxocyclobutyl)methyl)isoindoline-1,3-dione [25].

The reaction was run with General Method B: Iterative Catalyst Addition Protocol using 4:1 MeCN: DCM as solvent to improve the solubility of the starting material: 2-((1-(4-bromophenyl)cyclobutyl)methyl)isoindoline-1,3-dione S21 (111.1 mg, 0.300 mmol, 1.0 equiv), $(R,R)$-Mn(CF$_3$-PDP) (3 times addition of 20.4 mg, 0.015 mmol, 5 mol% batch; 15 mol% in total), ClCH$_2$CO$_2$H (425 mg, 4.5 mmol, 15.0 equiv.), 50% wt. H$_2$O$_2$ (204 mg, 3.0 mmol, 10.0 equiv.), 4:1 MeCN: DCM mixture (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was allowed to stir at 0 ºC for ~5 min to facilitate the solubility of starting material before adding H$_2$O$_2$ and run at 0 ºC with ice bath. The reaction was worked up with 9 mL saturated NaHCO$_3$ and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO$_2$) using 20% acetone/hexanes $\rightarrow$ 30% acetone/hexanes as eluent afforded product as a white solid.

Run 1: (67.7 mg, 0.176 mmol, 58.7% yield), (14.9 mg, 0.040 mmol, 13.4% rsm). Run 2: (65.4 mg, 0.170 mmol, 56.7% yield), (23.2 mg, 0.063 mmol, 20.9% rsm). Run 3: (63.9 mg, 0.166 mmol, 55.4% yield), (20.9 mg, 0.056 mmol, 18.8% rsm). Average: 56.9% yield $\pm$ 1.7%, 17.7% rsm $\pm$ 3.9%.

$^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 7.80 (dd, $J$ = 5.4, 3.1 Hz, 2H), 7.72 (dd, $J$ = 5.5, 3.1 Hz, 2H), 7.45 (d, $J$ = 8.4 Hz, 2H), 7.17 (d, $J$ = 8.4 Hz, 2H), 4.04 (s, 2H), 3.68 – 3.63 (m, 2H), 3.45 – 3.39 (m, 2H). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 204.1, 168.5, 142.7, 134.5, 131.9, 131.6, 128.9, 123.7, 121.4, 56.6, 47.9, 39.2. HRMS (TOF ESI+) m/z calculated for C$_{19}$H$_{15}$NO$_3$Br [M+H]+: 384.0235, found 384.0225.

3-(bis(4-chlorophenyl)(hydroxy)methyl)cyclobutan-1-one [26a].

The reaction was run with General Method A: Single Catalyst Addition Protocol:

Bis(4-chlorophenyl)(cyclobutyl)methanol S22 (92.2 mg, 0.300 mmol, 1.0 equiv), $(R,R)$-Mn(CF$_3$-PDP) (40.7 mg, 0.030 mmol, 10 mol%), ClCH$_2$CO$_2$H (425 mg, 4.5 mmol, 15.0 equiv.), 50% wt. H$_2$O$_2$ (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with ice bath. The
reaction was worked up with saturated 9 mL NaHCO₃ and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO₂) using 10% acetone/hexanes → 20% acetone/hexanes as eluent afforded 2-(bis(4-chlorophenyl)(hydroxy)methyl)cyclobutan-1-one (γ-ketone, 26b) product as a white solid and 3-(bis(4-chlorophenyl)(hydroxy)methyl)cyclobutan-1-one (δ-ketone, 26a) product as a light yellow oil.

**Run 1:** (16.8 mg, 0.052 mmol, 17.4% yield of γ-ketone 26b), (32.2 mg, 0.100 mmol, 33.4% yield of δ-ketone 26a), (50.8% overall yield, 1.9:1 δ:γ ratio), 0% rsm. **Run 2:** (16.5 mg, 0.051 mmol, 17.1% yield of γ-ketone 26b), (33.0 mg, 0.103 mmol, 34.3% yield of δ-ketone 26a), (51.4% overall yield, 2.0:1 δ:γ ratio), 0% rsm. **Run 3:** (17.4 mg, 0.054 mmol, 18.1% yield of γ-ketone 26b), (34.8 mg, 0.108 mmol, 36.1% yield of δ-ketone 26a), (54.2% overall yield, 2.0:1 δ:γ ratio), 0% rsm. **Average:** 52.2% yield ± 1.8%, 2.0:1 δ:γ ratio, 0% rsm.

1H-NMR (500 MHz, methylene chloride-d₂) δ 7.35 – 7.30 (m, 8H), 3.39 (tt, J = 8.7, 6.6 Hz, 1H), 3.08 – 2.93 (m, 4H), 2.63 (br. s, 1H). 13C-NMR (126 MHz, methylene chloride-d₂) δ 206.3, 144.8, 133.8, 129.1, 128.1, 78.3, 48.5, 33.3. HRMS (EI+) m/z calculated for C₁₇H₁₄O₂Cl₂ [M]+: 320.0371, found 320.0372.

2-(bis(4-chlorophenyl)(hydroxy)methyl)cyclobutan-1-one [26b].

1H-NMR (500 MHz, methylene chloride-d₂) δ 7.33 – 7.27 (m, 8H), 4.43 – 4.38 (m, 1H), 3.02 – 2.94 (m, 1H), 2.80 – 2.72 (m, 2H), 2.02 (app. td, J = 9.1, 7.4 Hz, 2H). 13C-NMR (126 MHz, methylene chloride-d₂) δ 208.4, 144.2, 144.1, 133.9, 133.5, 128.9, 128.85, 128.83, 128.0, 77.9, 68.8, 45.2, 14.0. HRMS (EI+) m/z calculated for C₁₇H₁₄O₂Cl₂ [M]+: 320.0371, found 320.0374.

2-(4-chlorophenyl)-2-(3-oxobutyl)-1H-indene-1,3(2H)-dione [27].

The reaction was run with **General Method A: Single Catalyst Addition Protocol:** 2-butyl-2-(4-chlorophenyl)-1H-indene-1,3(2H)-dione S23 (93.8 mg, 0.300 mmol, 1.0 equiv), (R,R)-Mn(CF₃-PDP) (40.7 mg, 0.030 mmol, 10 mol%), ClCH₂CO₂H (425 mg, 4.5 mmol, 15.0 equiv.), 50% wt. H₂O₂ (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with saturated 9 mL NaHCO₃ and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO₂) using 20% acetone/hexanes → 30% acetone/hexanes as eluent afforded product as a white solid.
Run 1: (57.7 mg, 0.177 mmol, 58.9% yield), (13.0 mg, 0.042 mmol, 13.9% rsm). **Run 2:** (58.8 mg, 0.180 mmol, 60.0% yield), (13.0 mg, 0.042 mmol, 13.9% rsm). **Run 3:** (60.8 mg, 0.186 mmol, 62.0% yield), (13.4 mg, 0.043 mmol, 14.3% rsm). **Average:** 60.3% yield ± 1.6%, 14.0% rsm ± 0.2%.

$^{1}$H-NMR (500 MHz, CDCl$_3$) $\delta$ 8.04 – 8.00 (m, 2H), 7.91 – 7.87 (m, 2H), 7.38 (d, $J = 8.6$ Hz, 2H), 7.29 (d, $J = 8.6$ Hz, 2H), 2.44 (app. s, 4H), 2.05 (s, 3H). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 206.9, 200.9, 141.3, 136.4, 134.3, 134.1, 129.1, 128.6, 124.0, 59.8, 38.6, 30.0, 29.3. HRMS (TOF ESI+) m/z calculated for C$_{19}$H$_{16}$O$_3$Cl [M+H]$^+$: 327.0788, found 327.0795.

**methyl 2-(3-benzoylphenyl)-2-(3-oxocyclopentyl)propanoate [28a].**

The reaction was run with **General Method A: Single Catalyst Addition Protocol:** methyl 2-(3-benzoylphenyl)-2-cyclopentylpropanoate S24 (110.6 mg, 0.300 mmol, 1.0 equiv), (R,R)-Mn(CF$_3$-PDP) (40.7 mg, 0.030 mmol, 10 mol%), ClCH$_2$CO$_2$H (425 mg, 4.5 mmol, 15.0 equiv.), 50% wt. H$_2$O$_2$ (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with 9 mL saturated NaHCO$_3$ and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO$_2$) using 20% acetone/hexanes $\rightarrow$ 30% acetone/hexanes $\rightarrow$ 40% acetone/hexanes as eluent afforded methyl 2-(3-benzoylphenyl)-2-(3-oxocyclopentyl)propanoate ($\delta$-ketone, 28a) product as a yellow oil and methyl 2-(3-benzoylphenyl)-2-(2-oxocyclopentyl)propanoate ($\gamma$-ketone, 28b) as a yellow oil.

**Run 1:** (52.7 mg, 0.150 mmol, 50.1% yield of $\delta$-ketone 28a), (6.3 mg, 0.018 mmol, 6.0% yield of $\gamma$-ketone 28b), (56.1% overall yield, 8.3:1 $\delta$-ketone:$\gamma$-ketone ratio), 0% rsm. **Run 2:** (48.4 mg, 0.138 mmol, 46.1% yield of $\delta$-ketone 28a), (5.3 mg, 0.015 mmol, 5.1% yield of $\gamma$-ketone 28b), (51.2% overall yield, 9.0:1 $\delta$-ketone:$\gamma$-ketone ratio), 0% rsm. **Run 3:** (46.8 mg, 0.134 mmol, 44.6% yield of $\delta$-ketone 28a), (4.7 mg, 0.013 mmol, 4.5% yield of $\gamma$-ketone 28b), (49.1% overall yield, 9.9:1 $\delta$-ketone:$\gamma$-ketone ratio), 0% rsm. **Average:** 52.1% yield ± 3.6%, 9.1:1 $\delta$-ketone:$\gamma$-ketone ratio, 0% rsm.

The $\delta$-ketone product 28a is isolated as a mixture of ~1:1 ratio of diastereomers. Overlap of peaks are observed in both $^1$H and $^{13}$C NMR.

$^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 7.80 – 7.74(m, 3H), 7.70 – 7.67 (m, 1H), 7.62 – 7.59 (m, 1H), 7.54 – 7.44 (m, 4H), 3.71 & 3.70 (s, 3H), 3.09 – 2.99 (m, 1H), 2.43 – 2.04 (m, 4H), 1.89 – 1.68 (m, 1H), 1.65 & 1.63 (s, 3H), 1.57 – 1.47 (m, 1H). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 218.1, 217.8, 196.6, 196.5, 175.5, 175.4, 142.3, 142.1, 137.9, 137.5, 132.81, 132.79, 130.6, 130.5, 130.20, 130.19, 129.3, 129.2, 128.6, 128.54, 128.47, 127.9, 127.8, 52.57, 52.56, 52.3, 52.2, 44.9, 44.8, 41.4, 40.9, 38.8, 38.7, 25.1, 24.6, 18.94, 18.92. HRMS (TOF ESI+) m/z calculated for C$_{22}$H$_{23}$O$_4$ [M+H]$^+$: 351.1596, found 351.1599.
methyl 2-(3-benzoylphenyl)-2-(2-oxocyclopentyl)propanoate [28b].

The γ-ketone product 28b is isolated as a single diastereomer.

\[
\begin{align*}
\text{28b} & \quad \text{γ-ketone product}
\end{align*}
\]

\[\text{δ} 7.87 \text{ (t, } J = 1.9 \text{ Hz, 1H), 7.80 – 7.78 (m, 2H), 7.69 – 7.66 (m, 2H), 7.62 – 7.59 (m, 1H), 7.51 – 7.43 (m, 3H), 3.72 (s, 3H), 3.39 (dd, } J = 13.3, 7.8 \text{ Hz, 1H), 2.40 – 2.35 (m, 1H), 2.12 – 2.04 (m, 1H), 1.98 – 1.95 (m, 1H), 1.80 – 1.73 (m, 2H), 1.56 (s, 3H), 1.57 – 1.51 (m, 1H).}
\]

13C-NMR (126 MHz, CDCl3) δ 217.3, 196.7, 175.0, 142.1, 137.8, 137.5, 132.8, 130.6, 130.2, 129.2, 128.6, 128.4, 128.0, 56.9, 52.8, 50.1, 39.0, 25.9, 20.2, 17.1.HRMS (TOF ESI+) m/z calculated for C22H23O4 [M+H]+: 351.1596, found 351.1599.

3-(3-(3,4-dichlorophenyl)-2-oxopropyl)cyclopentan-1-one [29a].

The reaction was run with **General Method A: Single Catalyst Addition**

**Protocol**: 1-cyclopentyl-3-(3,4-dichlorophenyl)propan-2-one S25 (81.4 mg, 0.300 mmol, 1.0 equiv), (R,R)-Mn(CF3-PDP) (40.7 mg, 0.030 mmol, 10 mol%), ClCH2CO2H (425 mg, 4.5 mmol, 15.0 equiv.), 50% wt. H2O2 (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with saturated 9 mL NaHCO3 and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO2) using 10% acetone/hexanes → 20% acetone/hexanes as eluent afforded 2-(3-(3,4-dichlorophenyl)-2-oxopropyl)cyclopentan-1-one (γ-ketone, 29b) product as a white solid and 3-(3-(3,4-dichlorophenyl)-2-oxopropyl)cyclopentan-1-one (δ-ketone, 29a) product as a light yellow oil.

**Run 1**: (11.3 mg, 0.040 mmol, 13.2% yield of γ-ketone 29b), (35.0 mg, 0.123 mmol, 40.9% yield of δ-ketone 29a), (54.1% overall yield, 3.1:1 δ:γ ratio), 0% rsm. **Run 2**: (10.7 mg, 0.038 mmol, 12.5% yield of γ-ketone 29b), (32.3 mg, 0.113 mmol, 37.8% yield of δ-ketone 29a), (50.3% overall yield, 3.0:1 δ:γ ratio), 0% rsm. **Run 3**: (11.2 mg, 0.040 mmol, 13.1% yield of γ-ketone 29b), (35.2 mg, 0.124 mmol, 41.2% yield of δ-ketone 29a), (54.3% overall yield, 3.1:1 δ:γ ratio), 0% rsm. **Average**: 52.9% yield ± 2.3%, 3.1:1 δ:γ ratio, 0% rsm.

\[\text{δ} 7.42 \text{ (d, } J = 8.2 \text{ Hz, 1H), 7.31 (d, } J = 2.0 \text{ Hz, 1H), 7.05 (dd, } J = 8.3, 2.1 \text{ Hz, 1H), 3.67 (s, 2H), 2.69 – 2.55 (m, 3H), 2.44 – 2.38 (m, 1H), 2.27 – 2.09 (m, 3H), 1.71 (ddd, } J = 18.2, 9.9, 1.2 \text{ Hz, 1H), 1.51 – 1.41 (m, 1H).}
\]

13C-NMR (126 MHz, methylene chloride-d2) δ 218.4, 205.9, 135.0, 132.8, 132.0, 131.5, 131.0, 129.7, 49.2, 48.2, 45.0, 38.7, 32.7, 29.7. HRMS (TOF ESI+) m/z calculated for C14H15O2Cl2 [M+H]+: 285.0449, found 285.0453.

**Site of oxidation was assigned based on a combination of 1H, gDQCOSY, gHSQC, gHMBC NMRs.**
2-(3-(3,4-dichlorophenyl)-2-oxopropyl)cyclopentan-1-one [29b].

$$\delta_{1H-NMR} (500 \text{ MHz, methylene chloride-d}_2) \begin{array}{l} 7.41 (d, J = 8.2 \text{ Hz, 1H}), 7.31 \end{array}$$

$$\delta_{13C-NMR} (126 \text{ MHz, methylene chloride-d}_2) \begin{array}{l} 220.0, 205.6, 135.1, 132.8, 132.1, 131.5, 130.9, 129.8, 49.1, 45.5, 42.6, 37.8, 29.9, 21.3. \end{array}$$

HRMS (TOF ESI+) $m/z$ calculated for $C_{14}H_{15}O_2Cl_2 [M+H]^+$: 285.0449, found 285.0442.

Site of oxidation was assigned based on a combination of $^1H$, gCOSY, gHSQC, gHMBC NMRs.

$(\pm)$-trans-4-methyl-3-oxocyclohexyl 4-chlorobenzoate [30a].

The reaction was run with General Method A: Single Catalyst Addition Protocol. $(\pm)$-trans-4-methylcyclohexyl 4-chlorobenzoate S26 (75.8 mg, 0.300 mmol, 1.0 equiv), $(R,R)$-$\text{Mn(CF}_3\text{PDP)}$ (40.7 mg, 0.030 mmol, 10 mol%), ClCH$_2$CO$_2$H (425 mg, 4.5 mmol, 15.0 equiv.), 50% wt. H$_2$O$_2$ (204 mg, 3.0 mmol, 10.0 equiv.), 4:1 MeCN:DCM (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 °C with ice bath. The reaction was worked up with saturated 9 mL NaHCO$_3$ and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO$_2$) using 10% ethyl acetate/hexanes $\rightarrow$ 20% ethyl acetate/hexanes $\rightarrow$ 30% ethyl acetate/hexanes as eluent afforded $(\pm)$-trans-4-methyl-3-oxocyclohexyl 4-chlorobenzoate ($\gamma$-ketone, 30a) as a white solid and $(\pm)$-trans-4-hydroxy-4-methylcyclohexyl 4-chlorobenzoate ($\delta$-alcohol, 30b) as a white solid. A trace amount (<5% yield) of $(\pm)$-trans-4-methyl-2-oxocyclohexyl 4-chlorobenzoate ($\beta$-ketone) can be observed.

Run 1: (24.9 mg, 0.093 mmol, 31.1% yield of $\gamma$-ketone 30a), (20.6 mg, 0.077 mmol, 25.6% yield of $\delta$-alcohol 30b), (56.7% overall yield, 1.21:1 K:A ratio), (13.3 mg, 0.053 mmol, 17.5% rsm). Run 2: (26.8 mg, 0.101 mmol, 33.5% yield of $\gamma$-ketone 30a), (23.1 mg, 0.086 mmol, 28.7% yield of $\delta$-alcohol 30b), (62.2% overall yield, 1.17:1 K:A ratio), (12.5 mg, 0.049 mmol, 16.4% rsm). Run 3: This reaction was performed at 0.5 mmol scale with the same procedure. (40.0 mg, 0.150 mmol, 30.0% yield of $\gamma$-ketone 30a), (35.1 mg, 0.131 mmol, 26.1% yield of $\delta$-alcohol 30b), (56.1% overall yield, 1.15:1 K:A ratio), (21.8 mg, 0.086 mmol, 17.3% rsm). Average: 31.5% yield $\pm$ 1.8% of $\gamma$-ketone, 26.8% yield $\pm$ 1.7% of $\delta$-alcohol, 58.3% overall yield with 1.2:1 K:A ratio, 17.1% rsm $\pm$ 0.6%.

$^1H$-NMR (500 MHz, CDCl$_3$) $\delta_{1H-NMR} (500 \text{ MHz, methylene chloride-d}_2) \begin{array}{l} 7.96 (d, J = 8.5 \text{ Hz, 2H}), 7.42 (d, J = 8.5 \text{ Hz, 2H}), 5.21 (tt, J = 10.2, 4.7 \text{ Hz, 1H}), 2.92 (ddd, J = 13.6, 5.0, 2.0 \text{ Hz, 1H}), 2.57 (ddd, J = 13.6, 10.7, 1.3 \text{ Hz, 1H}), 2.42 – 2.33 (m, 2H), 2.15 – 2.11 (m, 1H), 1.91 (tdd, J = 12.7, 10.2, 4.0 \text{ Hz, 1H}), 1.42 (dtd, J = 13.8, 12.0, 3.6 \text{ Hz, 1H}), 1.10 (d,
$J = 6.6 \text{ Hz, 3H}$. $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 208.9, 164.7, 139.7, 131.2, 128.9, 128.6, 72.6, 47.0, 44.4, 30.4, 29.2, 14.5. HRMS (TOF ESI+) $m/z$ calculated for C$_{14}$H$_{15}$O$_3$ClNa $[\text{M+Na}]^+$: 289.0607, found 289.0601.

(±)-trans-4-hydroxy-4-methylcyclohexyl 4-chlorobenzoate [30b].

[Chemical structure image]

$^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 7.97 (d, $J = 8.6$ Hz, 2H), 7.40 (d, $J = 8.5$ Hz, 2H), 4.97 (tt, $J = 9.4$, 4.7 Hz, 1H), 1.95 – 1.85 (m, 4H), 1.79 – 1.74 (m, 2H), 1.57 (ddd, $J = 13.7$, 11.4, 4.7 Hz, 2H), 1.28 (s, 3H), 1.25 (br. s, 1H). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 165.3, 139.3, 131.1, 129.3, 128.8, 73.0, 68.8, 36.7, 30.1, 27.4. HRMS (TOF ESI+) $m/z$ calculated for C$_{14}$H$_{17}$O$_3$ClNa $[\text{M+Na}]^+$: 291.0764, found 291.0770.

(±)-2-methyl-3-oxobutyl 4-chlorobenzoate [31a].

The reaction was run with General Method C: Slow Catalyst Addition Protocol: 2-methylbutyl 4-chlorobenzoate S27 (113.4 mg, 0.500 mmol, 1.0 equiv), ClCH$_2$CO$_2$H (709 mg, 7.5 mmol, 15.0 equiv.) were dissolved in MeCN (1.0 mL). $(R,R)$-Mn(CF$_3$-PDP) (67.8 mg, 0.050 mmol, 10 mol%) and MeCN (0.625 mL) added in a 1 mL syringe, 50% wt. H$_2$O$_2$ (340 mg, 5.0 mmol, 10.0 equiv.) and MeCN (6.25 mL) added in a 10 mL syringe. The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 15 mL saturated NaHCO$_3$ and DCM as described in General Method C. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO$_2$) using 10% ethyl acetate/hexanes $\rightarrow$ 20% ethyl acetate/hexanes $\rightarrow$ 35% ethyl acetate/hexanes as eluent afforded 2-(±)-methyl-3-oxobutyl 4-chlorobenzoate (γ-ketone, 31a) product as a yellow oil and (±)-2-hydroxy-2-methylbutyl 4-chlorobenzoate (β-alcohol, 31b) as a yellow oil.

Run 1: (45.7 mg, 0.190 mmol, 38.0% yield of γ-ketone 31a), (21.6 mg, 0.089 mmol, 17.8% yield of β-alcohol 31b), (55.8% overall yield, 2.13:1 K:A ratio), <10% rsm. Run 2: (47.7 mg, 0.198 mmol, 39.6% yield of γ-ketone 31a), (23.6 mg, 0.097 mmol, 19.4% yield of β-alcohol 31b), (59.0% overall yield, 2.04:1 K:A ratio), <10% rsm. Run 3: (47.7 mg, 0.198 mmol, 39.6% yield of γ-ketone 31a), (22.4 mg, 0.092 mmol, 18.5% yield of β-alcohol 31b), (58.1% overall yield, 2.14:1 K:A ratio), <10% rsm. Average: 39.1% yield $\pm$ 0.9% of γ-ketone, 18.5% yield $\pm$ 0.8% of β-alcohol, 57.6% overall yield with 2.1:1 K:A, <10% rsm.

$^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 7.91 (d, $J = 8.8$ Hz, 2H), 7.39 (d, $J = 8.7$ Hz, 2H), 4.47 (ddd, $J = 11.1$, 7.3, 0.7 Hz, 1H), 4.39 (ddd, $J = 11.1$, 5.5, 0.7 Hz, 1H), 3.04 – 2.97 (m, 1H), 2.23 (s, 3H), 1.21 (d, $J = 7.2$ Hz, 3H). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 209.3, 165.5, 139.7, 131.1, 128.9, 128.4, 66.1, 46.2, 28.8, 13.5.
Oxidation with TFDO: The reaction was performed according to the reported condition in literature\(^7\) using TFDO generated according to method described in Supplementary Table 1. In a 1-dram vial charged with 2-methylbutyl 4-chlorobenzoate S27 (11.3 mg, 0.05 mmol, 1.0 equiv.) and a stir bar, 0.5 mL DCM freshly obtained from SDS was transferred into the vial via plastic syringe equipped with micropipette tip. The reaction was cooled to -20 °C, and 0.38 mL 0.4M TFDO solution was added into the vial in 1-2 portions and the reaction was kept at -20 °C for 48 h. The reaction was concentrated on rotvap to remove all volatiles and the crude mixture was analyzed by \(^1\)H NMR with nitrobenzene added as internal standard.

**Run 1:** (2.8 mg, 0.012 mmol, 23.3% yield of \(\gamma\)-ketone 31a), (5.6 mg, 0.023 mmol, 46.1% yield of \(\beta\)-alcohol 31b), (69.4% overall yield, 1:2.0 K:A ratio), (1.2 mg, 0.005 mmol, 10.6% rsm). **Run 2:** (2.5 mg, 0.010 mmol, 20.8% yield of \(\gamma\)-ketone 31a), (5.1 mg, 0.021 mmol, 42.0% yield of \(\beta\)-alcohol 31b), (62.8% overall yield, 1:2.0 K:A ratio), (1.9 mg, 0.008 mmol, 16.8% rsm). **Average:** 22.1% yield of \(\gamma\)-ketone, 44.1% yield of \(\beta\)-alcohol, 66.2% overall yield with 1:2.0 K:A, 13.7% rsm.

(±)-2-hydroxy-2-methylbutyl 4-chlorobenzoate [31b].

\[
\text{HO} \quad \text{O} \quad \text{Cl} \\
\text{HO} \quad \text{O} \quad \text{Cl}
\]

\(^1\)H-NMR (500 MHz, CDCl\(_3\)) 7.99 – 7.97 (m, 2H), 7.43 – 7.41 (m, 2H), 4.25 – 4.20 (m, 2H), 1.90 (br. s, 1H), 1.64 (q, \(J = 7.5\) Hz, 2H), 1.28 (s, 3H), 0.98 (t, \(J = 7.5\) Hz, 3H). \(^13\)C-NMR (126 MHz, CDCl\(_3\)) 165.9, 139.8, 131.1, 128.9, 128.5, 72.3, 71.5, 31.9, 23.6, 8.1. HRMS (TOF ESI+) \(m/z\) calculated for C\(_{12}\)H\(_{14}\)ClO\(_2\) [M-OH]\(^+\): 225.0677, found 225.0687. The NMR data matches with the literature.\(^7\)

**4-cyclopropyl-4-oxobutyl benzoate [32a].**

The reaction was run with **General Method A: Single Catalyst Addition Protocol.** 4-cyclopropylbutyl benzoate S28 (65.5 mg, 0.300 mmol, 1.0 equiv), (\(R,R\))-Mn(CF\(_3\)-PDP) (40.7 mg, 0.030 mmol, 10 mol%), ClCH\(_2\)CO\(_2\)H (425 mg, 4.5 mmol, 15.0 equiv.), 50% wt. H\(_2\)O\(_2\) (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 °C with ice bath. The reaction was worked up with saturated 9 mL NaHCO\(_3\) and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO\(_2\)) using 5% ethyl acetate/hexanes → 15% ethyl acetate/hexanes → 40% ethyl acetate/hexanes as eluent afforded 4-cyclopropyl-4-oxobutyl benzoate (ketone, 32a), 4-cyclopropyl-4-hydroxybutyl benzoate (alcohol, 32b) and 4-(2-chloroacetoxy)-4-cyclopropylbutyl benzoate (ester, 32c) products as colorless oils.

HRMS (TOF ESI+) \(m/z\) calculated for C\(_{12}\)H\(_{14}\)O\(_3\)Cl [M+H]\(^+\): 241.0631, found 241.0627. The NMR data matches with the literature.\(^7\)
Run 1: (31.2 mg, 0.134 mmol, 44.8% yield of ketone 32a), (6.4 mg, 0.027 mmol, 9.1% yield of alcohol 32b), (6.3 mg, 0.020 mmol, 6.8% yield of ester 32c), (5.6 mg, 0.026 mmol, 8.6% rsm), (60.7% combined oxidation yield, 69.3% mass balance). Run 2: (28.5 mg, 0.123 mmol, 40.9% yield of ketone 32a), (6.4 mg, 0.027 mmol, 9.1% yield of alcohol 32b), (6.5 mg, 0.021 mmol, 7.0% yield of ester 32c), (5.0 mg, 0.023 mmol, 7.6% rsm), (58.3% combined oxidation yield, 65.9% mass balance). Run 3: (32.3 mg, 0.139 mmol, 46.4% yield of ketone 32a), (6.9 mg, 0.029 mmol, 9.8% yield of alcohol 32b), (6.5 mg, 0.021 mmol, 7.0% yield of ester 32c), (5.2 mg, 0.024 mmol, 7.9% rsm), (62.6% combined oxidation yield, 70.5% mass balance). Average: 44.0% yield ± 2.8% of ketone, 9.8% yield ± 0.7% of alcohol, 6.7% yield ± 0.3% of ester, 8.0% rsm ± 0.5%, 60.5% overall oxidation yield with 68.5% mass balance.

1H-NMR (500 MHz, CDCl3) δ 8.04 (dt, J = 8.3, 1.2 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.44 (td, J = 7.7, 1.3 Hz, 2H), 4.34 (t, J = 6.4 Hz, 2H), 2.74 (t, J = 7.3 Hz, 2H), 2.09 (tt, J = 7.5, 6.9 Hz, 2H), 1.94 (tdd, J = 7.9, 5.1, 4.0 Hz, 1H), 1.05 – 1.02 (m, 2H), 0.87 (dtt, J = 7.3, 4.0, 3.1 Hz, 2H). 13C-NMR (126 MHz, CDCl3) δ 209.8, 166.6, 133.0, 130.3, 129.6, 128.4, 64.3, 39.8, 23.1, 20.6, 10.9. HRMS (TOF ESI+) m/z calculated for C14H16O3Na [M+Na]+: 255.0997, found 255.0991.

4-cyclopropyl-4-hydroxybutyl benzoate [32b].

1H-NMR (500 MHz, CDCl3) δ 8.05 – 8.03 (m, 2H), 7.55 (td, J = 7.2, 1.4 Hz, 1H), 7.43 (t, J = 7.8 Hz, 2H), 4.36 (t, J = 6.6 Hz, 2H), 2.94 – 2.90 (m, 1H), 2.00 – 1.86 (m, 2H), 1.81 – 1.72 (m, 2H), 1.70 (br. s, 1H), 0.93 (qt, J = 8.3, 4.9 Hz, 1H), 0.57 – 0.48 (m, 2H), 0.31 – 0.21 (m, 2H). 13C-NMR (126 MHz, CDCl3) δ 166.8, 133.0, 130.5, 129.7, 128.5, 76.6, 65.2, 33.6, 25.3, 18.1, 3.0, 2.7. HRMS (TOF ESI+) m/z calculated for C14H18O3Na [M+Na]+: 257.1154, found 257.1147.

4-(2-chloroacetoxy)-4-cyclopropylbutyl benzoate [32c].

1H-NMR (500 MHz, CDCl3) δ 8.05 – 8.03 (m, 2H), 7.58 – 7.55 (m, 1H), 7.45 (t, J = 7.8 Hz, 2H), 4.39 (dt, J = 8.9, 5.5 Hz, 1H), 4.33 (t, J = 5.8 Hz, 2H), 4.08 (s, 2H), 1.91 – 1.82 (m, 4H), 1.06 – 0.99 (m, 1H), 0.61 (tdd, J = 8.5, 5.9, 4.6 Hz, 1H), 0.53 (tdd, J = 8.9, 6.8, 5.2 Hz, 1H), 0.46 (dtt, J = 9.5, 5.9, 4.8 Hz, 1H), 0.33 – 0.29 (m, 1H). 13C-NMR (126 MHz, CDCl3) δ 167.3, 166.7, 133.1, 130.3, 129.7, 128.5, 80.9, 64.6, 41.3, 31.3, 24.9, 15.2, 3.6, 3.4. HRMS (TOF ESI+) m/z calculated for C16H19O4ClNa[M+Na]+: 333.0870, found 333.0864.
V. Supplementary Figure 2. Remote methylene oxidation of aromatic containing compounds with multiple substitutions of varied electronic and steric properties

Preparation of Substrates and Compounds Characterization for Supplementary Figure 2

1-(4-((tert-butoxy)phenyl)cyclopentane-1-carbonitrile [S29].

In a flamed dried 50 mL flask, 1.187 g (6.27 mmol) of 2-(4-((tert-butoxy)phenyl)acetonitrile was dissolved in 10 mL anhydrous DMF. 396 mg (95% purity, 15.68 mmol, 2.5 equiv.) of NaH was added in portions at 0 ºC and the reaction was allowed to stir for 1 hour at 0 ºC. 1.354 g (0.75 mL, 6.27 mmol, 1.0 equiv.) of 1,4-dibromobutane was added dropwise at 0 ºC and the reaction was allowed to stir overnight at room temperature. The reaction was quenched carefully with ~10 mL water and extracted with 30 mL EtOAc three times. The combined organic layer was washed with 50 mL brine, dried with MgSO4, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO2) using 10% EtOAc/hexanes → 20% EtOAc/hexanes as eluent gave 1.057 g (4.34 mmol) of pure product as a white solid (69% yield).

1H-NMR (500 MHz, CDCl3) δ 7.34 – 7.31 (m, 2H), 6.99 – 6.96 (m, 2H), 2.48 – 2.44 (m, 2H), 2.08 – 1.99 (m, 4H), 1.99 – 1.89 (m, 2H), 1.35 (s, 9H). 13C-NMR (126 MHz, CDCl3) δ 155.1, 134.5, 126.7, 124.8,
methyl 1-(4-(tert-butoxy)-3-chlorophenyl)cyclopentane-1-carboxylate [S30].

In a 100 mL recovery flask was added 3-chloro-4-hydroxylphenylacetic acid 3.30 g (17.7 mmol), 35 mL methanol and 0.4 mL concentrated sulfuric acid. The reaction was allowed to reflux overnight. The reaction was concentrated, diluted with 50 mL ethyl acetate and neutralized with concentrated NaHCO₃. The organic layer was dried with MgSO₄ and plugged with 20% ethyl acetate/hexanes as eluent to get methyl 2-(3-chloro-4-hydroxyphenyl)acetate in quantitative yield. The resulted compound was dissolved in 27 mL anhydrous DCM, treated with Mg(ClO₄)₂ 396 mg (1.77 mmol, 10 mol%) and 8.9 g Boc₂O (40.8 mmol, 2.3 equiv.) sequentially. The reaction was heated to 40 ºC for 24 hours and filtered through celite. The reaction was purified by CombiFlash (40g column, hexanes → 20% ethyl acetate/hexanes as eluent) to get methyl 2-(4-(tert-butoxy)-3-chlorophenyl)acetate 2.2624 g (8.81 mmol) in 50% yield. The product was dissolved in 18 mL anhydrous DMF in a flame dried 50 mL flask, 556 mg (95% purity, 22.0 mmol, 2.5 equiv.) of NaH was added in portions at 0 ºC and the reaction was allowed to stir for 1 hour at 0 ºC. 1.05 mL (8.81 mmol, 1.0 equiv.) of 1,4-dibromobutane was added dropwise at 0 ºC and the reaction was allowed to stir overnight at room temperature. The reaction was quenched carefully with ~15 mL water and extracted with 30 mL EtOAc three times, washed with 50 mL brine, dried with MgSO₄, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 200 mL SiO₂) using 2% EtOAc/hexanes → 5% EtOAc/hexanes as eluent gave 1.3232 g (4.26 mmol) of S30 in 48% yield.

¹H-NMR (500 MHz, CDCl₃) δ 7.36 (d, J = 2.3 Hz, 1H), 7.13 (dd, J = 8.5, 2.4 Hz, 1H), 7.02 (d, J = 8.5 Hz, 1H), 3.62 (s, 3H), 2.63 – 2.58 (m, 2H), 1.89 – 1.83 (m, 2H), 1.75– 1.67 (m, 4H), 1.40 (s, 9H). ¹³C-NMR (126 MHz, CDCl₃) δ 176.2, 150.8, 139.2, 128.8, 128.8, 125.7, 124.2, 81.3, 58.5, 52.6, 36.4, 29.0, 23.7. HRMS (TOF ESI+) m/z calculated for C₁₇H₂₃ClO₃Na [M+Na]⁺: 337.1233, found 337.1227.
(±)-methyl 2-(4-(tert-butoxy)-3-chlorophenyl)-3-cyclopentylpropanoate [S31].

2-(3-chloro-4-hydroxyphenyl)acetic acid (3.3g, 17.7 mmol) was dissolved in 35 mL MeOH and added concentrated H2SO4 (0.4 mL). The reaction was refluxed overnight and concentrated. The residue oil was diluted with ether, washed with sat. NaHCO3 twice, water 3 times and brine. The organic layer was dried over MgSO4 and concentrated. The crude methyl ester was dissolved in DCM (27 mL), added Mg(ClO4)2 (396 mg, 1.77 mmol) and Boc2O (8.9g, 40.8 mmol, 2.3 equiv.). The reaction was heated at 40 ºC for 24 hours. The reaction was concentrated and purified by CombiFlash (40 g column) eluting with pure hexanes → 80% ethyl acetate/hexanes. Methyl 2-(4-(tert-butoxy)-3-chlorophenyl)acetate was isolated as clear oil (1.4917 g, 5.81 mmol) in 33% yield. 1H-NMR (500 MHz, CDCl3) δ 7.30 (d, J = 1.9 Hz, 1H), 7.09 – 7.04 (m, 2H), 3.71 (s, 3H), 3.55 (s, 2H), 1.41 (s, 9H). In a flame dried 100 mL flask charged with HN(TMS)2 (2.11 g, 13.07 mmol, 2.25 equiv.), 13 mL anhydrous THF and a stir bar. The flask was cooled to -78 ºC and n-BuLi solution (1.6 M in hexanes, 7.6 mL, 12.2 mmol, 2.1 equiv.) was added dropwise and the reaction was stirred at -78 ºC for 15 min. A solution of ethyl 2-(4-(tert-butoxy)-3-chlorophenyl)acetate (1.4917 g, 5.81 mmol) in 12 mL THF was added and the reaction was stirred at -78 ºC for 30 minutes then at room temperature for 20 min. The reaction was cooled back to -78 ºC and charged with (iodomethyl)cyclopentane (1.83 g, 8.72 mmol, 1.5 equiv.) and DMPU (1.5 mL, 12.2 mmol, 2.1 equiv.). The reaction was allowed to gradually warmed up to room temperature and stirred overnight. The reaction was quenched with sat. NH4Cl and extracted with ethyl acetate 3 times. The combined organic layer was combined, washed with brine, dried with MgSO4 and concentrated. The crude material was plugged through silica using 5% ethyl acetate/hexanes to obtain a mixture of desired (±)-methyl 2-(4-(tert-butoxy)-3-chlorophenyl)-3-cyclopentylpropanoate and dialkylated methyl 2-(4-(tert-butoxy)-3-chlorophenyl)-3-cyclopentyl-2-(cyclopentylmethyl)propanoate. The mixture was purified by hydrolyzing in a mixture of MeOH (6 mL) and 3M NaOH (6 mL) at 60 ºC for 16h, cooled to room temperature and extracted with DCM 3 times to remove the unhydrolyzed methyl 2-(4-(tert-butoxy)-3-chlorophenyl)-3-cyclopentyl-2-(cyclopentylmethyl)propanoate. The aqueous layer was acidified with 3M HCl and the aqueous layer was extracted with DCM 3 times. The combined organic layer was plugged through silica using 5% ethyl acetate/hexanes → 20% aceton/hexanes doped with 1% acetic acid to obtain the pure 2-(4-(tert-butoxy)-3-chlorophenyl)-3-cyclopentylpropanoic acid. The resulted compound was dissolved in 9 mL benzene and 2 mL MeOH, and treated with trimethylsilyldiazomethane (2M solution, 3.5 mL, 7.0 mmol, 2.0 equiv.) for 1 hour. The reaction was concentrated and purified by flash column chromatography on silica (50 mm fritted glass column, 150 mL SiO2) using 2% EtOAc/hexanes → 5% EtOAc/hexanes as eluent gave 546.2 mg (1.61 mmol) of (±)-methyl 2-(4-(tert-butoxy)-3-chlorophenyl)-3-cyclopentylpropanoic acid in 28% yield. 1H-NMR (500 MHz, CDCl3) δ 7.33 (d, J = 2.2 Hz, 1H), 7.10 (dd, J = 8.4, 2.2 Hz, 1H), 7.04 (d, J = 8.4 Hz, 1H), 3.67 (s, 3H), 3.52 (t, J = 7.8 Hz, 1H), 2.05 (dt, J = 13.4, 7.7 Hz, 1H), 1.78 – 1.69 (m, 3H), 1.64
– 1.57 (m, 3H), 1.50 – 1.46 (m, 2H), 1.40 (s, 9H), 1.14 – 1.04 (m, 2H). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 174.6, 151.2, 135.2, 129.8, 129.2, 126.7, 124.6, 81.4, 52.2, 50.1, 38.0, 32.8, 32.5, 29.0, 25.2 (2 carbons). HRMS (TOF ESI+) $m/z$ calculated for C$_{19}$H$_{27}$O$_3$NaCl [M+Na$^+$]: 361.1546, found 361.1540.

General procedure for the synthesis of substrate S32-S33

methyl 1-(3-chloro-4-methoxyphenyl)cyclopentane-1-carboxylate [S32].

In a 50 mL flask charged methyl 2-(3-chloro-4-hydroxyphenyl)acetate (2.00 g, 10 mmol, 1.0 equiv.), K$_2$CO$_3$ (1.38 g, 1.0 equiv.) and anhydrous DMF (20 mL). MeI (0.65 mL, 1.1 equiv.) was added dropwise and the reaction was stirred overnight. The reaction was quenched with water and extracted with DCM and the crude compound was plugged through silica with 5% ethyl acetate/hexanes to get methyl 2-(3-chloro-4-methoxyphenyl)acetate (2.305 g, 9.48 mmol) in 95% yield. The resulted compound was dissolved in 15 mL anhydrous DMF, treated with NaH (95%, 599 mg, 23.7 mmol, 2.5 equiv.) at 0 ºC . After stirring at 0 ºC for 1 h, 1,4-dibromobutane (1.13 mL, 9.48 mmol, 1.0 equiv,) was added and the reaction was allowed to warm up to room temperature overnight. The reaction was quenched with water and extracted with ether (30 mL) 3 times. The combined organic layer was washed with brine and dried over Na$_2$SO$_4$. Flash column chromatography on silica (50 mm fritted glass column, 200 mL SiO$_2$) using 2% EtOAc/hexanes $\rightarrow$ 5% EtOAc/hexanes $\rightarrow$ 10% EtOAc/hexanes as eluent gave 967 mg (3.60 mmol) of pure product as a white solid (38% yield).

$^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 7.37 (d, $J = 2.4$ Hz, 1H), 7.21 (dd, $J = 8.6$, 2.4 Hz, 1H), 6.86 (d, $J = 8.6$ Hz, 1H), 3.88 (s, 3H), 3.61 (s, 3H), 2.63 – 2.58 (m, 2H), 1.89 – 1.83 (m, 2H), 1.74 – 1.69 (m, 4H). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 176.3, 153.9, 136.6, 129.0, 126.3, 122.2, 111.9, 58.3, 56.3, 52.6, 36.4, 23.6. HRMS (TOF ESI+) $m/z$ calculated for C$_{14}$H$_{18}$O$_3$Cl [M+H$^+$]: 269.0944, found 269.0945.

methyl 1-(3-chloro-4-(methoxy-d$_3$)phenyl)cyclopentane-1-carboxylate [S33].

The compound was prepared in the same procedure as S32 using CD$_3$I from methyl 2-(3-chloro-4-hydroxyphenyl)acetate (1.00 g, 5 mmol.). Product was isolated as a white solid (515 mg, 1.90 mmol) in 38% yield over 2 steps.

$^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 7.37 (d, $J = 2.4$ Hz, 1H), 7.21 (dd, $J = 8.6$, 2.4 Hz, 1H), 6.85 (d, $J = 8.6$ Hz, 1H), 3.61 (s, 3H), 2.62 – 2.57 (m, 2H), 1.89 – 1.83 (m, 2H), 1.74 – 1.68 (m, 4H). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 176.3, 153.8, 136.6, 129.0, 126.3, 122.2, 111.8, 58.3, 56.0 – 54.9 (m, 1C), 52.5, 36.3, 23.6. HRMS (TOF ESI+) $m/z$ calculated for C$_{14}$H$_{15}$D$_3$O$_3$Cl [M+H$^+$]: 272.1133, found 272.1142.
methyl 1-(3-methoxy-4-(((trifluoromethyl)sulfonyl)oxy)phenyl)cyclopentane-1-carboxylate [S34].

To a 300 mL flask added 2-(4-hydroxy-3-methoxyphenyl)acetic acid 1.8218 g (10mmol, 1.0 equiv.), 2.54 mL TMSCl (20mmol, 2.0 equiv.) and 100 mL MeOH. The reaction was stirred under room temperature for 24 hours before diluted with 100 mL DCM and extracted with 100 mL brine. The organic layer was dried with Na$_2$SO$_4$ and concentrated. The crude compound was redissolved in 50 mL anhydrous DCM, and treated with 1.809 g (12 mmol, 1.2 equiv.) TBSCl, 1.020 g (15 mmol, 1.5 equiv.) imidazole and 122 mg (1 mmol, 0.1 equiv.) DMAP. The reaction was stirred overnight, worked up with water and extracted with DCM. The combined organic layer was washed with brine and dried with Na$_2$SO$_4$. The crude product was dissolved in 15 mL anhydrous DMF and transferred to a 50 mL flamed dried flask. 632 mg (95% purity, 25 mmol, 2.5 equiv.) of NaH was added in portions at 0 ºC and the reaction was allowed to stir for 1 hour at 0 ºC. 1.18 mL (10.0 mmol, 1.0 equiv.) of 1,4-dibromobutane was added dropwise at 0 ºC and the reaction was allowed to stir overnight at room temperature. The reaction was quenched carefully with ~10 mL water and extracted with 30 mL EtOAc three times, washed with 50 mL brine, dried with MgSO$_4$, filtered, and concentrated. The product was dissolved in 2 mL THF and added 1.5 mL 1M TBAF solution and stirred overnight then concentrated. The previous aqueous layer was acidified with 3M HCl then extract with 30 mL EtOAc three times. The combined organic layer was washed with 50 mL brine, dried with MgSO$_4$, filtered, and concentrated to get 378 mg of crude phenol compound. The crude was dissolved in 5 mL anhydrous DCM, cooled to 0 ºC and treated with 0.31 mL (1.8 mmol, 1.2 equiv.) of triflate anhydride and 0.18 mL (2.27 mmol, 1.5 equiv.) of pyridine. The reaction was then stirred for 5 hours at room temperature before quenched with ~10 mL water. 15 mL DCM was used to extract the reaction 3 times and the combined organic layer was dried with Na$_2$SO$_4$ and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 200 mL SiO$_2$) using 5% EtOAc/hexanes → 10% EtOAc/hexanes as eluent gave 542.2 mg (1.42 mmol) of pure product as a colorless oil (14% yield over 5 steps).

**1H-NMR** (500 MHz, CDCl$_3$) δ 7.13 (d, $J$ = 8.4 Hz, 1H), 7.01 (d, $J$ = 2.1 Hz, 1H), 6.96 (dd, $J$ = 8.5, 2.2 Hz, 1H), 3.91 (s, 3H), 3.64 (s, 3H), 2.68 – 2.63 (m, 2H), 1.90 – 1.85 (m, 2H), 1.77 – 1.71 (m, 4H).

**13C-NMR** (126 MHz, CDCl$_3$) δ 175.8, 151.1, 145.0, 137.6, 122.1, 119.5, 118.87 (d, $J$ = 321.2 Hz), 112.2, 59.3, 56.3, 52.7, 36.4, 23.7. **19F-NMR** (470 MHz, CDCl$_3$) δ -73.9. **HRMS** (TOF ESI+) $m/z$ calculated for C$_{15}$H$_{18}$F$_3$O$_6$S [M]$^+$: 383.0771, found 383.0773.
4-(1-cyanocyclopentyl)-2-methylphenyl trifluoromethanesulfonate [S35].

To a 50 mL flask added 2-(4-methoxy-3-methylphenyl)acetonitrile 1.0 g (6.2 mmol, 1.0 equiv.), dissolved in 10 mL anhydrous DMF. 392 mg (95% purity, 15.5 mmol, 2.5 equiv.) of NaH was added in portions at 0 ºC and the reaction was allowed to stir for 1 hour at 0 ºC. 0.74 mL (6.2 mmol, 1.0 equiv.) of 1,4-dibromobutane was added dropwise at 0 ºC and the reaction was allowed to stir overnight at room temperature. The reaction was quenched carefully with ~10 mL water and extracted with 30 mL EtOAc three times, washed with 50 mL brine, dried with MgSO₄, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 200 mL SiO₂) using 5% EtOAc/hexanes → 10% EtOAc/hexanes as eluent gave 1.2217 g (5.67 mmol) of 1-(4-methoxy-3-methylphenyl)cyclopentane-1-carbonitrile in 91% yield. ¹H-NMR (500 MHz, CDCl₃) δ 7.23 (dd, J = 8.4, 2.6 Hz, 1H), 7.20 – 7.19 (m, 1H), 6.80 (d, J = 8.4 Hz, 1H), 3.83 (s, 3H), 2.46 – 2.41 (m, 2H), 2.23 (s, 3H), 2.07 – 1.90 (m, 6H). The product was dissolved in 20 mL dry DCM, followed by 28.4 mL BBr₃ solution (1M in DCM, 5 equiv.) at -78 ºC. The reaction was stirred at -78 ºC for 30 minutes then allowed to stir at room temperature for overnight. The reaction was quenched with NaHCO₃, separated, the organic layer washed with brine and dried with Na₂SO₄. Flash column chromatography on silica (50 mm fritted glass column, 200 mL SiO₂) using 10% EtOAc/hexanes → 20% EtOAc/hexanes as eluent gave 890.7 mg (4.43 mmol) of the free phenol in 78% yield. ¹H-NMR (500 MHz, CDCl₃) δ 7.20 (d, J = 2.5 Hz, 1H), 7.14 (dd, J = 8.3, 2.5 Hz, 1H), 6.76 (d, J = 8.3 Hz, 1H), 4.68 (br. s, 1H), 2.44 (dq, J = 10.0, 5.8, 5.0 Hz, 2H), 2.26 (s, 3H), 2.08 – 1.87 (m, 6H). The free phenol was dissolved in 25 mL anhydrous DCM, treated with 0.89 mL (5.32 mmol, 1.2 equiv.) Tf₂O and 0.54 mL (6.65 mmol, 1.5 equiv.) pyridine at 0 ºC then stirred at room temperature overnight. The reaction was quenched with ~10 mL water. 15 mL DCM was used to extract the reaction 3 times and the combined organic layer was dried with Na₂SO₄ and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 200 mL SiO₂) using 5% EtOAc/hexanes → 10% EtOAc/hexanes as eluent gave 1.294 g (3.88 mmol) of pure product as a colorless oil (88% yield).

¹H-NMR (500 MHz, CDCl₃) δ 7.41 (d, J = 2.5 Hz, 1H), 7.33 (dd, J = 8.7, 2.5 Hz, 1H), 7.24 (d, J = 8.6 Hz, 1H), 2.51 – 2.46 (m, 2H), 2.40 (s, 3H), 2.09 – 1.92 (m, 6H). ¹³C-NMR (126 MHz, CDCl₃) δ 147.8, 140.2, 131.6, 130.2, 125.4, 123.9, 121.8, 118.7 (q, J = 320.1 Hz), 47.5, 40.7, 24.4, 16.7. ¹⁹F-NMR (470 MHz, CDCl₃) δ -74.1. HRMS (TOF ESI+) m/z calculated for C₁₄H₁₁NF₃O₃S [M+H]⁺: 334.0725, found 334.0721.
1-(2,2-difluorobenzo[d][1,3]dioxol-5-yl)cyclopentane-1-carbonitrile [S36].

In a flame-dried 50 mL flask, 591.4 mg (3.0 mmol) of 2-(2,2-difluorobenzo[d][1,3]dioxol-5-yl)acetonitrile was dissolved in 6 mL anhydrous DMF. 344.8 mg (95% purity, 13.7 mmol, 2.5 equiv.) of NaH was added in portions at 0 ºC and the reaction was allowed to stir for 1 hour at 0 ºC. 647.7 mg (0.36 mL, 3.0 mmol, 1.0 equiv.) of 1,4-dibromobutane was added dropwise at 0 ºC and the reaction was allowed to stir overnight at room temperature. The reaction was quenched carefully with ~10 mL water and extracted with 30 mL EtOAc three times. The combined organic layer was washed with 50 mL brine, dried with MgSO₄, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 200 mL SiO₂) using 5% EtOAc/hexanes → 10% EtOAc/hexanes as eluent gave 396.9 mg (1.58 mmol) of pure product as a colorless oil (53% yield).

¹H-NMR (500 MHz, CDCl₃) δ 7.20 (dd, J = 8.4, 2.0 Hz, 1H), 7.16 (d, J = 1.9 Hz, 1H), 7.05 (d, J = 8.4 Hz, 1H), 2.54 – 2.48 (m, 2H), 2.09 – 1.91 (m, 6H). ¹³C-NMR (126 MHz, CDCl₃) δ 144.3, 143.3, 136.2, 131.8 (t, J = 256.1 Hz), 123.9, 121.6, 109.6, 107.8, 47.7, 40.7, 24.2. ¹⁹F-NMR (470 MHz, CDCl₃) δ -49.9. HRMS (TOF ESI+) m/z calculated for C₁₃H₁₁NO₂F₂ [M]⁺: 251.0758, found 251.0758.
C—H Oxidation of Substrates and Products Characterization for Supplementary Figure 2

1-(4-((tert-butoxy)phenyl)-3-oxocyclopentane-1-carbonitrile [33].

The reaction was run with General Method A: Single Catalyst Addition Protocol: 1-(4-((tert-butoxy)phenyl)cyclopentane-1-carbonitrile S29 (73.0 mg, 0.300 mmol, 1.0 equiv), (R,R)-Mn(CF3-PDP) (40.7 mg, 0.030 mmol, 10 mol%), ClCH2CO2H (425 mg, 4.5 mmol, 15.0 equiv.), 50% wt. H2O2 (204 mg, 3.0 mmol, 10.0 equiv.), 4:1 MeCN:DCM (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with 9 mL saturated NaHCO3 and DCM as described in General method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO2) using 20% acetone/hexanes → 30% acetone/hexanes as eluent. All fractions are collected and analyzed by 1H NMR with nitrobenzene as internal standard.

Result: 0% yield, (10.6 mg, 0.043 mmol, 14.5% rsm).

methyl 1-(4-((tert-butoxy)-3-chlorophenyl)-3-oxocyclopentane-1-carboxylate [34].

The reaction was run with General Method A: Single Catalyst Addition Protocol. Methyl 1-(4-((tert-butoxy)-3-chlorophenyl)cyclopentane-1-carboxylate S30 (93.2 mg, 0.300 mmol, 1.0 equiv), (R,R)-Mn(CF3-PDP) (40.7 mg, 0.030 mmol, 10 mol%), ClCH2CO2H (425 mg, 4.5 mmol, 15.0 equiv.), 50% wt. H2O2 (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with 9 mL saturated NaHCO3 and DCM as described in the general method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO2) using 10% acetone/hexanes → 20% acetone /hexanes → 30% acetone /hexanes as eluent afforded product as a clear oil.

Run 1: (71.9 mg, 0.221 mmol, 73.8% yield), 0% rsm. Run 2: (69.0 mg, 0.212 mmol, 70.8% yield), 0% rsm. Run 3: (71.7 mg, 0.221 mmol, 73.6% yield), 0% rsm. Average: 72.7% yield ± 1.7%, 0% rsm.

1H-NMR (500 MHz, CDCl3) δ 7.34 (d, J = 2.3 Hz, 1H), 7.11 (dd, J = 8.5, 2.4 Hz, 1H), 7.07 (d, J = 8.5 Hz, 1H), 3.66 (s, 3H), 3.21 (d, J = 17.9 Hz, 1H), 2.93 (dddd, J = 11.4, 7.7, 4.1, 1.9 Hz, 1H), 2.56 (d, J = 18.0 Hz, 1H), 2.36 – 2.27 (m, 3H), 1.40 (s, 9H). 13C-NMR (126 MHz, CDCl3) 215.1, 174.5, 151.7, 136.7, 129.4, 128.6, 125.4, 124.3, 81.6, 54.4, 53.1, 48.3, 37.1, 33.0, 29.0. HRMS (TOF ESI+) m/z calculated for C17H22ClO4 [M+H]+: 325.1207, found 325.1204.

methyl 2-(4-((tert-butoxy)-3-chlorophenyl)-3-(3-oxocyclopentyl)propanoate [35a].
The reaction was run with **General Method A: Single Catalyst Addition Protocol**. Methyl 2-(4-(tert-butoxy)-3-chlorophenyl)-3-cyclopentylpropanoate S31 (101.6 mg, 0.300 mmol, 1.0 equiv), (R,R)-Mn(CF3-PDP) (40.7 mg, 0.030 mmol, 10 mol%), ClCH2CO2H (425 mg, 4.5 mmol, 15.0 equiv.), 50% wt. H2O2 (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with 9 mL saturated NaHCO3 and DCM as described in the general method A. Flash column chromatography on silica (35 mm fritted glass column, 100 mL SiO2) using 5% ethyl acetate/hexanes → 15% ethyl acetate/hexanes → 25% ethyl acetate/hexanes as eluent afforded clean ε-ketone (35a) and δ-ketone (35b) with small impurity as clear oil.

The position of oxidation was assigned by analogy with all other compounds examined where oxidation is preferred at the sites most remote from electron-withdrawing groups (ester in this case). The assignment can be further supported by the relative 1H chemical shift of the benzylic proton where the proton in δ-ketone (35b) is more downfield than the proton in ε-ketone (35a).

**Run 1:** (44.1 mg, 0.125 mmol, 41.7% yield of ε-ketone 35a), (13.1 mg, 0.037 mmol, 12.4% yield of δ-ketone 35b), (54.1% overall yield, 3.36:1 ε:δ ratio), <10% rsm. **Run 2:** (43.7 mg, 0.124 mmol, 41.3% yield of ε-ketone 35a), (12.1 mg, 0.034 mmol, 11.4% yield of δ-ketone 35b), (52.7% overall yield, 3.62:1 ε:δ ratio), <10% rsm. **Run 3:** (45.2 mg, 0.128 mmol, 42.7% yield of ε-ketone 35a), (13.1 mg, 0.037 mmol, 12.4% yield of δ-ketone 35b), (55.1% overall yield, 3.44:1 ε:δ ratio), <10% rsm  **Average:** 41.9% yield ± 0.7% of ε-ketone, 12.1% yield ± 0.6% of δ-ketone, 54.0% overall yield with 3.5:1 ε:δ ratio, <10% rsm.

ε-ketone (35a) was isolated as a mixture of diastereomers with ~1:1 ratio. 1H-NMR (500 MHz, CDCl3) δ 7.33 (t, J = 2.3 Hz, 1H), 7.09 (app. ddd, J = 8.1, 4.4, 2.1 Hz, 1H), 7.05 (d, J = 8.3 Hz, 1H), 3.68 (s, 3H), 3.54 (app. td, J = 7.7, 4.2 Hz, 1H), 2.39 – 1.99 (m, 6H), 1.96 – 1.75 (m, 2H), 1.57 – 1.48 (m, 1H), 1.41 (s, 9H). 13C-NMR (126 MHz, CDCl3) 218.6 & 218.5, 174.0 & 173.9, 151.6, 134.33 & 134.25, 129.7 & 129.6, 129.5 & 129.4, 126.63 & 126.57, 124.7 & 124.6, 81.5, 52.42 & 52.40, 49.3 & 49.2, 45.1 & 44.8, 39.5 & 39.4, 38.6 & 38.5, 35.3 & 35.2, 29.7 & 29.5, 29.1. HRMS (TOF ESI+) m/z calculated for C19H25ClO4Na [M+Na]+: 375.1339, found 375.1330.

methyl 2-(4-(tert-butoxy)-3-chlorophenyl)-3-(2-oxocyclopentyl)propanoate [35b].

δ-ketone (35b) was isolated as a mixture of diastereomers with ~1:1 ratio and contain a minor impurity. 1H-NMR (500 MHz, CDCl3) δ 7.33 (app. dd, J = 9.8, 2.2 Hz, 1H), 7.12 – 7.09 (m, 1H), 7.05 – 7.03 (m, 1H), 3.66 (s, 3H), 3.71 – 3.65 (m, 1H), 2.32 – 1.85 (m, 6H), 1.76 – 1.66 (m, 2H), 1.54 – 1.44 (m, 1H), 1.40 (s, 9H). 13C-NMR (126 MHz, CDCl3) 220.3 & 220.2, 173.8 & 173.7, 151.44 & 151.36,
methyl 1-(3-chloro-4-methoxyphenyl)-3-oxocyclopentane-1-carboxylate [36].

The reaction was run with General Method A: Single Catalyst Addition Protocol: methyl 1-(3-chloro-4-methoxyphenyl)cyclopentane-1-carboxylate \( \text{S32} \) (80.6 mg, 0.300 mmol, 1.0 equiv), \((R,R)\)-Mn(CF\(_3\)-PDP) (40.7 mg, 0.030 mmol, 10 mol\%), ClCH\(_2\)CO\(_2\)H (425 mg, 4.5 mmol, 15.0 equiv.), 50% wt. \( \text{H}_2\text{O}_2 \) (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 °C with ice bath. The reaction was worked up with 9 mL saturated \( \text{NaHCO}_3 \) and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO\(_2\)) using 20% acetone/hexanes \( \rightarrow \) 40% acetone/hexanes as eluent to obtain pure product as a white solid.

**Run 1:** (32.8 mg, 0.116 mmol, 38.7% yield), (11.5 mg, 0.043 mmol, 14.3% rsm). **Run 2:** (27.0 mg, 0.096 mmol, 31.8% yield), (14.6 mg, 0.054 mmol, 18.1% rsm). **Run 3:** (29.4 mg, 0.104 mmol, 34.7% yield), (13.8 mg, 0.051 mmol, 17.1% rsm). **Average:** 35.1% yield ± 3.5%, 16.5% rsm ± 2.0%.

\(^1\)H-NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.36 (d, \( J = 2.4 \) Hz, 1H), 7.19 (dd, \( J = 8.6 \) Hz, 1H), 6.90 (d, \( J = 8.6 \) Hz, 1H), 3.89 (s, 3H), 3.66 (s, 3H), 3.21 (dd, \( J = 17.9 \) Hz, 2.4 Hz, 1H), 2.96 – 2.91 (m, 1H), 2.57 (d, \( J = 17.9 \) Hz, 1H), 2.36 – 2.26 (m, 3H). \(^{13}\)C-NMR (126 MHz, CDCl\(_3\)) \( \delta \) 215.1, 174.6, 154.6, 134.2, 128.7, 126.0, 122.9, 112.1, 56.3, 54.2, 53.1, 48.3, 37.1, 33.0. HRMS (TOF ESI+) \( m/z \) calculated for \( \text{C}_{14}\text{H}_{16}\text{O}_4\text{Cl} \) [M+H]+: 283.0737, found 283.0733.

methyl 1-(3-chloro-4-(methoxy-d\(_3\))phenyl)-3-oxocyclopentane-1-carboxylate [37].

The reaction was run with General Method A: Single Catalyst Addition Protocol: methyl 1-(3-chloro-4-(methoxy-d\(_3\))phenyl)cyclopentane-1-carboxylate \( \text{S33} \) (81.5 mg, 0.300 mmol, 1.0 equiv), \((R,R)\)-Mn(CF\(_3\)-PDP) (40.7 mg, 0.030 mmol, 10 mol\%), ClCH\(_2\)CO\(_2\)H (425 mg, 4.5 mmol, 15.0 equiv.), 50% wt. \( \text{H}_2\text{O}_2 \) (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 °C with ice bath. The reaction was worked up with 9 mL saturated \( \text{NaHCO}_3 \) and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO\(_2\)) using 20% acetone/hexanes \( \rightarrow \) 40% acetone/hexanes as eluent to obtain pure product as a white solid.

**Run 1:** (33.4 mg, 0.117 mmol, 39.0% yield), (10.1 mg, 0.037 mmol, 12.4% rsm). **Run 2:** (34.6 mg, 0.121 mmol, 40.4% yield), (9.5 mg, 0.035 mmol, 11.7% rsm). **Run 3:** (36.3 mg, 0.127 mmol, 42.3% yield), (9.9 mg, 0.036 mmol, 12.1% rsm). **Average:** 40.6% yield ± 1.7%, 12.1% rsm ± 0.4%.
$^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 7.35 (d, $J = 2.4$ Hz, 1H), 7.18 (dd, $J = 8.6, 2.4$ Hz, 1H), 6.89 (d, $J = 8.6$ Hz, 1H), 3.65 (s, 3H), 3.20 (dd, $J = 17.9, 2.0$ Hz, 1H), 2.95 – 2.90 (m, 1H), 2.56 (d, $J = 17.9$ Hz, 1H), 2.35 – 2.27 (m, 3H). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 215.0, 174.61, 154.5, 134.2, 128.6, 126.0, 122.8, 112.1, 55.84 – 55.18 (m, 1 carbon), 54.18, 53.11, 48.28, 37.04, 32.99. HRMS (TOF ESI+) m/z calculated for C$_{14}$H$_{13}$D$_3$O$_4$Cl [M+H]$^+$: 286.0925, found 286.0924.

**methyl 1-(3-methoxy-4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-3-oxocyclopentane-1-carboxylate** [38].

![Methyl 1-(3-methoxy-4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-3-oxocyclopentane-1-carboxylate](image)

The reaction was run with **General Method A: Single Catalyst Addition Protocol**. Methyl 1-(3-methoxy-4-(((trifluoromethyl)sulfonyl)oxy)phenyl)cyclopentane-1-carboxylate **S34** (114.7 mg, 0.300 mmol, 1.0 equiv), ($R,R$)-Mn(CF$_3$-PDP) (40.7 mg, 0.030 mmol, 10 mol%), ClCH$_2$CO$_2$H (425 mg, 4.5 mmol, 15.0 equiv.), 50% wt. H$_2$O$_2$ (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 °C with ice bath. The reaction was worked up with 9 mL saturated NaHCO$_3$ and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO$_2$) using 15% ethyl acetate/hexanes $\rightarrow$ 35% ethyl acetate/hexanes $\rightarrow$ 60% ethyl acetate/hexanes as eluent afforded product as a white solid.

**Run 1:** (64.6 mg, 0.163 mmol, 54.3% yield), (9.3 mg, 0.024 mmol, 8.1% rsm). **Run 2:** (59.6 mg, 0.150 mmol, 50.1% yield), (13.3 mg, 0.035 mmol, 11.6% rsm). **Run 3:** (61.8 mg, 0.156 mmol, 52.0% yield), (8.6 mg, 0.022 mmol, 7.5% rsm). **Average: 52.1% yield ± 2.1%, 9.1% rsm ± 2.1%.

$^1$H-NMR (500 MHz, methylene chloride-$d_2$) $\delta$ 7.22 (d, $J = 8.5$ Hz, 1H), 7.02 (d, $J = 2.2$ Hz, 1H), 6.98 (dd, $J = 8.5, 2.2$ Hz, 1H), 3.93 (s, 3H), 3.66 (s, 3H), 3.23 (dd, $J = 17.7, 2.1$ Hz, 1H), 3.02 – 2.93 (m, 1H), 2.57 (d, $J = 17.8$ Hz, 1H), 2.39 – 2.30 (m, 3H). $^{13}$C-NMR (126 MHz, methylene chloride-$d_2$) 214.6, 174.6, 151.9, 143.7, 138.5, 122.9, 119.7, 119.3 (q, $J = 320.4$ Hz), 112.4, 56.9, 55.5, 53.6, 48.7, 37.4, 33.5. $^{19}$F-NMR (471 MHz, methylene chloride-$d_2$) $\delta$ -74.3. HRMS (TOF ESI+) m/z calculated for C$_{15}$H$_{15}$O$_7$F$_3$SNa [M+Na]$^+$: 419.0388, found 419.0386.

**4-(1-cyano-3-oxocyclopentyl)-2-methylphenyl trifluoromethanesulfonate** [39].

![4-(1-cyano-3-oxocyclopentyl)-2-methylphenyl trifluoromethanesulfonate](image)

The reaction was run with **General Method A: Single Catalyst Addition Protocol**. 4-(1-cyano cyclopentyl)-2-methylphenyl trifluoromethanesulfonate **S35** (100.0 mg, 0.300 mmol, 1.0 equiv), ($R,R$)-Mn(CF$_3$-PDP) (40.7 mg, 0.030 mmol, 10 mol%), ClCH$_2$CO$_2$H (425 mg, 4.5 mmol, 15.0 equiv.), 50% wt. H$_2$O$_2$ (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 °C with ice bath. The reaction was worked up with 9 mL saturated NaHCO$_3$ and DCM as described in General Method
A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO₂) using 10% acetone/hexanes → 20% acetone/hexanes → 40% acetone/hexanes as eluent afforded product as a clear oil.

**Run 1:** (61.3 mg, 0.176 mmol, 58.8% yield), (21.9 mg, 0.066 mmol, 21.9% rsm). **Run 2:** (61.4 mg, 0.177 mmol, 59.0% yield), (23.1 mg, 0.069 mmol, 23.1% rsm). **Run 3:** (60.2 mg, 0.173 mmol, 57.8% yield), (21.9 mg, 0.066 mmol, 21.9% rsm). **Average: 58.5% yield ± 0.6%, 22.3% rsm ± 0.7%.

1H-NMR (500 MHz, CDCl₃) δ 7.42 (d, J = 2.3 Hz, 1H), 7.34 (dd, J = 8.7, 2.4 Hz, 1H), 7.32 (d, J = 8.7 Hz, 1H), 3.07 (d, J = 18.1 Hz, 1H), 2.85 (dddd, J = 12.9, 8.5, 3.8, 1.9 Hz, 1H), 2.76 (d, J = 18.2 Hz, 1H), 2.73 – 2.66 (m, 1H), 2.55 (dddt, J = 18.9, 8.2, 3.8, 1.1 Hz, 1H), 2.43 (s, 3H), 2.46 – 2.40 (m, 1H). 13C-NMR (126 MHz, CDCl₃) 211.3, 148.4, 137.7, 132.5, 130.0, 125.2, 122.4, 122.0, 118.66 (q, J = 320.1 Hz), 49.9, 43.9, 36.8, 36.4, 16.8. 19F-NMR (471 MHz, CDCl₃) δ -73.66. HRMS (TOF ESI+) m/z calculated for C₁₄H₁₂NO₄F₃SNa [M+Na]+: 370.0337, found 370.0350.

1-(2,2-difluorobenzo[d][1,3]dioxol-5-yl)-3-oxocyclopentane-1-carbonitrile [40].

The reaction was run with **General Method A: Single Catalyst Addition Protocol.** 1-(2,2-difluorobenzo[d][1,3]dioxol-5-yl)cyclopentane-1-carbonitrile S₃₆ (75.4 mg, 0.300 mmol, 1.0 equiv), (R,R)-Mn(CF₃-PDP) (40.7 mg, 0.030 mmol, 10 mol%), ClCH₂CO₂H (425 mg, 4.5 mmol, 15.0 equiv.), 50% wt. H₂O₂ (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with 9 mL saturated NaHCO₃ and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO₂) using 10% ethyl acetate/hexanes → 25% ethyl acetate/hexanes → 50% ethyl acetate/hexanes as eluent afforded product as a clear oil.

**Run 1:** (43.6 mg, 0.164 mmol, 54.8% yield), (19.1 mg, 0.076 mmol, 25.3% rsm). **Run 2:** (45.8 mg, 0.173 mmol, 57.6% yield), (19.0 mg, 0.076 mmol, 25.2% rsm). **Run 3:** (42.2 mg, 0.159 mmol, 53.0% yield), (23.5 mg, 0.094 mmol, 31.2% rsm). **Average: 55.1% yield ± 2.3%, 27.2% rsm ± 3.4%.

1H-NMR (500 MHz, CDCl₃) δ 7.19 – 7.17 (m, 2H), 7.13 – 7.12 (m, 1H), 3.07 (d, J = 18.0 Hz, 1H), 2.85 (dddd, J = 12.5, 8.5, 3.9, 1.9 Hz, 1H), 2.73 (d, J = 18.1 Hz, 1H), 2.73 – 2.65 (m, 1H), 2.54 (dd, J = 19.0, 8.2, 3.9 Hz, 1H), 2.41 (ddd, J = 13.0, 10.1, 8.2 Hz, 1H). 13C-NMR (126 MHz, CDCl₃) 211.1, 144.7, 144.0, 133.8, 131.8 (t, J = 257.4 Hz), 122.1, 121.5, 110.2, 107.7, 50.1, 44.1, 36.7, 36.5. 19F-NMR (471 MHz, CDCl₃) δ -49.8. HRMS (TOF ESI+) m/z calculated for C₁₃H₉NO₃F₂ [M]+: 265.0550, found 265.0553.
Supplementary Figure 3. Remote methylene oxidation of aromatic substrates with heteroaromatic or 3° amine substituents

Preparation of Substrates and Compounds Characterization for Supplementary Figure 3

General Procedure for Reductive Amination: To a round bottom flask equipped with a magnetic stir bar was added the corresponding amine (1.0 equiv.), 1,2-dichloroethane (0.1 M), the corresponding aldehyde (1.5 equiv.), and AcOH (1% v/v). After 30 minutes, NaBH(OAc)₃ (1.5 equiv.) was added in one portion and reaction solution was stirred overnight at room temperature. The reaction was quenched with saturated aqueous NaHCO₃ solution and extracted with CH₂Cl₂ 3 times. Combined organic layer was washed with saturated aqueous NaHCO₃ solution once and brine once, dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography.
4-(4-chlorophenyl)-1-pentylpiperidine-4-carbonitrile [S37].

According to general procedure for reductive amination, 4-(4-chlorophenyl)piperidine-4-carbonitrile (2.21 g, 10.0 mmol, 1.0 equiv.), valeraldehyde (1.6 mL, 15.0 mmol, 1.5 equiv.), acetic acid (1.0 mL, 1% v/v), and NaBH(OAc)₃ (3.18 g, 15.0 mmol, 1.5 equiv.) in DCE (100 mL, 0.1 M) were reacted. Flash column chromatography on silica eluting with 2% MeOH in CHCl₃ yielded S37 (1.57 g, 5.40 mmol, 54%) as a pale yellow oil.

1H-NMR (500 MHz, CDCl₃) δ 7.44 – 7.41 (m, 2H), 7.37 – 7.34 (m, 2H), 3.04 – 3.00 (m, 2H), 2.47 – 2.40 (m, 4H), 2.11 – 2.02 (m, 4H), 1.54 – 1.48 (m, 2H), 1.37 – 1.25 (m, 4H), 0.90 (t, J = 7.1 Hz, 3H). 13C-NMR (126 MHz, CDCl₃) δ 139.0, 134.1, 129.3, 127.2, 121.8, 58.7, 50.8, 42.6, 36.7, 29.9, 26.8, 22.7, 14.2. HRMS (TOF ESI+) m/z calculated for C₁₇H₂₄N₂Cl [M+H]⁺: 291.1628, found 291.1624.

4-(4-Chlorophenyl)-1-(cyclopentylmethyl)piperidine-4-carbonitrile [S38].

According to general procedure for reductive amination, 4-(4-chlorophenyl)piperidine-4-carbonitrile (1.10 g, 5.00 mmol, 1.0 equiv.), cyclopentanecarbaldehyde (540 mg, 5.50 mmol, 1.1 equiv.), acetic acid (0.5 mL, 1% v/v), and NaBH(OAc)₃ (1.17 g, 5.50 mmol, 1.1 equiv.) in DCE (100 mL, 0.1 M) were reacted. Flash column chromatography on silica eluting with 3% MeOH in CHCl₃ yielded compound S38 (615 mg, 2.03 mmol, 41%) as a pale yellow solid.

1H-NMR (500 MHz, CDCl₃) δ 7.47 – 7.41 (m, 2H), 7.40 – 7.33 (m, 2H), 3.08 – 2.95 (m, 2H), 2.53 – 2.39 (m, 2H), 2.36 (d, J = 7.3 Hz, 2H), 2.14 – 2.00 (m, 5H), 1.82 – 1.70 (m, 2H), 1.67 – 1.47 (m, 4H), 1.25 – 1.15 (m, 2H). 13C-NMR (126 MHz, CDCl₃) δ 139.2, 134.1, 129.2, 127.2, 121.8, 58.7, 50.8, 42.6, 36.7, 29.9, 26.8, 22.7, 14.2. HRMS (TOF ESI+) m/z calculated for C₁₈H₂₄N₂Cl [M+H]⁺: 303.1628, found 303.1624.
1-(4-Chlorobenzyl)-4-ethylpiperidine [S39].

A mixture of 4-ethylpyridine (1.14 mL, 10.0 mmol, 1.0 equiv.), platinum(IV) oxide (114 mg, 0.50 mmol, 0.05 equiv.) and HCl solution (2.75 ml, 11.0 mmol, 4 M in dioxane, 1.1 equiv.) in methanol (50 ml, 0.2 M) was hydrogenated at 100 psi overnight. The catalyst was removed by filtration through celite and the filtrate evaporated under reduced pressure. The residue was treated with saturated aqueous NaHCO₃ solution, and extracted with CH₂Cl₂ twice. The combined organic extracts were washed with water and brine. Dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The crude mixture was used in the next step without further purification. According to general procedure for reductive amination, the corresponding piperidine (10.0 mmol, 1.0 equiv.), p-chlorobenzaldehyde (2.11 g, 15.0 mmol, 1.5 equiv.), acetic acid (1.0 mL, 1% v/v), and NaBH(OAc)₃ (3.18 g, 15.0 mmol, 1.5 equiv.) were reacted. Flash column chromatography on silica eluting with 10% EtOAc/CHCl₃ yielded compound S39 (876 mg, 3.68 mmol, 37% over 2 steps) as a pale yellow oil.

1H-NMR (500 MHz, CDCl₃) δ 7.31 – 7.22 (m, 4H), 3.45 (s, 2H), 2.84 (dt, J = 12.1, 3.2 Hz, 2H), 1.95 – 1.90 (m, 2H), 1.67 – 1.63 (m, 2H), 1.29 – 1.09 (m, 5H), 0.87 (t, J = 7.4 Hz, 3H). 13C-NMR (126 MHz, CDCl₃) δ 137.5, 132.6, 130.6, 128.4, 62.9, 54.2, 37.6, 32.2, 29.4, 11.5. HRMS (TOF ESI+) m/z calcd for C₁₄H₂₁NCl [M+H]+: 238.1363, found 238.1358.

1-(4-Fluorophenyl)-4-(8-azaspiro[4.5]decan-8-yl)butan-1-one [S40].

A stirring mixture of the 4-chloro-1-(4-fluorophenyl)butan-1-one (1.25 mL, 7.67 mmol, 1.0 equiv.), KI (128 mg, 0.77 mmol, 0.1 equiv.), NaHCO₃ (1.93 g, 23.0 mmol, 3.0 equiv.), and 8-azaspiro[4.5]decane hydrochloride (1.35 g, 7.67 mmol, 1.0 equiv.) in toluene (15 mL, 0.5 M) was heated to reflux for 30 h under N₂. After this period, the reaction mixture was cooled down, filtered through a celite plug, and the solvent was removed under reduced pressure. Flash column chromatography on silica eluting with 5% MeOH/CHCl₃ yielded compound S40 (1.44 g, 4.75 mmol, 62%) as a pale yellow solid.

1H-NMR (500 MHz, CDCl₃) δ 8.01 – 7.98 (m, 2H), 7.11 (t, J = 8.6 Hz, 2H), 2.95 (t, J = 7.2 Hz, 2H), 2.38 – 2.35 (m, 6H), 1.92 (p, J = 7.2 Hz, 2H), 1.57 – 1.55 (m, 4H), 1.43 – 1.41 (m, 4H), 1.37 – 1.34 (m, 4H). 13C-NMR (126 MHz, CDCl₃) δ 198.7, 165.7 (d, J = 254.2 Hz), 133.7 (d, J = 2.9 Hz), 130.8 (d, J = 9.4 Hz), 115.7 (d, J = 21.9 Hz), 58.3, 51.5, 40.9, 37.7 (overlapped, 4 carbons), 36.5, 24.4, 22.0. 19F-NMR
(470 MHz, CDCl₃) δ −106.2. HRMS (TOF ESI+) m/z calcd for C₁₀H₂₇NOF [M+H]⁺: 304.2077, found 304.2082.

3-(1-(3,4-Difluorophenyl)pentyl)pyridine [S41].

A suspension of (E/Z)-3-(1-(3,4-difluorophenyl)pent-1-en-1-yl)pyridine (857 mg, 3.31 mmol, 1.0 equiv.), 10% Pd/C (359 mg, 0.337 mmol, 0.1 equiv.) in EtOH (50 mL, 0.07 M) was stirred under a balloon pressure of hydrogen for 14 hours. The reaction mixture was filtered through Celite with ethyl acetate. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica eluting 20% ethyl acetate/hexanes as eluent to yield the desired product (560 mg, 2.14 mmol, 65%) as a colorless oil.

¹H-NMR (500 MHz, CDCl₃) δ 8.48 (d, J = 2.3 Hz, 1H), 8.44 (dd, J = 4.8, 1.6 Hz, 1H), 7.47 (dt, J = 7.9, 2.0 Hz, 1H), 7.21 (dd, J = 7.9, 4.8 Hz, 1H), 7.06 (dt, J = 10.1, 8.3 Hz, 1H), 7.01 (ddd, J = 11.5, 7.6, 2.3 Hz, 1H), 6.93 (ddt, J = 8.1, 3.8, 1.7 Hz, 1H), 3.85 (t, J = 7.8 Hz, 1H), 2.02 – 1.97 (m, 2H), 1.36 – 1.29 (m, 2H), 1.24 – 1.17 (m, 2H), 0.85 (t, J = 7.3 Hz, 3H). ¹³C-NMR (126 MHz, CDCl₃) δ 150.7 (dd, J = 170.5, 12.7 Hz), 149.6, 149.2 (dd, J = 169.0, 13.4 Hz), 148.0, 141.2 (t, J = 4.4 Hz), 139.8, 135.0, 123.8 (dd, J = 6.1, 3.5 Hz), 123.7, 117.4 (d, J = 17.0 Hz), 116.6 (d, J = 17.2 Hz), 48.2, 35.2, 30.0, 22.6, 14.0. ¹⁹F-NMR (470 MHz, CDCl₃) δ −137.8 (m), −141.4 (m). HRMS (TOF ESI+) m/z calcd for C₁₆H₁₈NF₂ [M+H]⁺: 262.1407, found 262.1409.

4-(4-Chlorophenyl)-2-pentylpyridine [S42].

To a solution of diisopropylamine (298 mg, 2.95 mmol, 1.2 equiv.) in THF (1.5 mL, 2.0 M) at −78 °C was added n-butyllithium (1.8 mL, 2.88 mmol, 1.6 M in hexanes, 1.15 equiv.) dropwise. The reaction was stirred at −78 °C for 15 minutes, then warmed to room temperature for 5 minutes, then cooled back down to −78 °C. To the LDA solution was added 4-(4-chlorophenyl)-2-methylpyridine (509 mg, 2.5
mmol, 1 equiv.) in THF (5 mL, 0.5 M) dropwise, and this mixture was allowed to react for 1 hour at −78 °C. After this period, 1-bromobutane (383 mg, 2.8 mmol, 1.1 equiv.) was added dropwise at −78 °C and the reaction was allowed to warm to room temperature and stirred overnight. The reaction was quenched with water, and the aqueous layer was extracted with CH₂Cl₂ (3 times). The combined organics were dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica eluting 5% → 7.5% → 15% → 25% EtOAc:hexanes to yield the desired product (409 mg, 1.57 mmol, 63% yield) as a yellow oil.

1H-NMR (500 MHz, CDCl₃) δ 8.57 (dd, J = 5.2, 0.8 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.50 – 7.40 (m, 2H), 7.33 – 7.30 (m, 1H), 7.27 (dd, J = 5.2, 1.8 Hz, 1H), 2.84 (dd, J = 9.7, 6.2 Hz, 2H), 1.82 – 1.76 (m, 2H), 1.40 – 1.37 (m, 4H), 0.91 (t, J = 7.5 Hz, 3H). 13C-NMR (126 MHz, CDCl₃) δ 163.4, 149.8, 147.6, 137.1, 135.2, 129.4, 128.4, 120.6, 118.9, 38.7, 31.8, 29.8, 22.7, 14.2. HRMS (TOF ESI+) m/z calculated for C₁₆H₁₉NCl [M+H]⁺: 260.1206, found 260.1206.

5-(4-bromophenyl)-1-hexyl-1H-imidazole [S43].

In a flame dried 50 mL recovery flask was charged 5-(4-bromophenyl)-1H-imidazole (1.115g, 5.0 mmol, 1.0 equiv.) and anhydrous DMF (10 mL, 0.5 M). NaH (95%, 158 mg, 6.25 mmol, 1.25 equiv.) was added portionwise at 0 °C followed by 1-bromohexane (772 µL, 5.5 mmol, 1.1 equiv.). The reaction was allowed to warm up to room temperature and stirred overnight. The reaction was quenched with sat. NH₄Cl, extracted with ethyl acetate 3 times. The combined organic layer was washed with water 3 times, brine and dried with Na₂SO₄. Flash column chromatography on silica (50 mm fritted glass column, 200 mL SiO₂) using 30% ethyl acetate/hexanes → 50% ethyl acetate/hexanes → 80% ethyl acetate/hexanes as eluent twice to get product co-eluded with a yellow impurity. The resulted compound was dissolved in a minimum amount of DCM, crashed out with pentane, and the solid was washed with pentane until no yellow color was observed in the eluent. The product was obtained as white fluffy solid (939 mg, 3.06 mmol, 61% yield). The purity of the compound is crucial to the oxidation.

1H-NMR (500 MHz, CDCl₃) δ 7.65 – 7.62 (m, 2H), 7.50 – 7.47 (m, 3H), 7.19 (d, J = 1.3 Hz, 1H), 3.94 (t, J = 7.1 Hz, 2H), 1.81 (p, J = 7.2 Hz, 2H), 1.35 – 1.28 (m, 6H), 0.89 (t, J = 6.9 Hz, 3H). 13C-NMR (126 MHz, CDCl₃) δ 141.3, 137.6, 133.4, 131.8, 126.4, 120.4, 115.0, 47.5, 31.4, 31.1, 26.4, 22.6, 14.1. HRMS (TOF ESI+) m/z calced for C₁₅H₂₀N₂Br [M+H]⁺: 307.0810, found 307.0804.
1-(Cyclopentylmethyl)-1H-benzo[d]imidazole [S44].

To a stirring solution of benzimidazole (1.0 g, 8.46 mmol, 1.0 equiv.) in THF (6 mL, 1.4 M) at 0 °C was added NaH 95% (214 mg, 8.46 mmol, 1.0 equiv.). After 30 min, the cyclopentylmethyl 4-methylbenzenesulfonate (2.59 g, 10.2 mmol, 1.2 equiv.) in THF (2 mL, 5.1 M) was added dropwise and the reaction mixture was warmed and stirred under reflux overnight. The reaction was quenched with the addition of H2O. The layers were separated, and the aqueous layer was extracted with EtOAc (3 times). The combined organic layers were washed with brine (once), dried over MgSO4, filtered, and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography on silica eluting 30% EtOAc:CHCl3 as eluent to yield the desired product (1.51 g, 7.54 mmol, 89%) as a white solid.

\[ \text{H-NMR (500 MHz, CDCl}_3\text{)} \delta 7.86 (s, 1H), 7.83 – 7.74 (m, 1H), 7.43 – 7.35 (m, 1H), 7.33 – 7.20 (m, 2H), 4.04 (d, } J = 7.5 \text{ Hz, 2H}), 2.43 (hept, } J = 7.5 \text{ Hz, 1H}), 1.74 – 1.60 (m, 4H), 1.60 – 1.49 (m, 2H), 1.30 – 1.19 (m, 2H). 13C-NMR (126 MHz, CDCl3) \delta 143.9, 143.1, 134.0, 122.8, 122.0, 120.4, 109.8, 49.9, 40.3, 30.6, 25.0. HRMS (TOF ESI+) \text{m/z calcd for C}_{13}\text{H}_{17}\text{N}_2 [M + H]^+: 201.1392, found 201.1397.}

4-pentylquinoline [S45].

In a 50 mL flame dried flask was added DIPEA (1.84 mL, 13.1 mmol) and 12 mL anhydrous THF. n-BuLi (1.6M, 7.8 mL, 12.5 mmol) was added dropwise at -78 °C and kept at -78 °C for 10 min. After stirred for another 30 min at room temperature, the LDA solution was cooled back to -78 °C and added dropwise into a solution of 4-methylquinoline (1.45 mL, 11 mmol) in 40 mL anhydrous THF at -78 °C. After 2.5 h, 1-bromobutane (1.55 mL, 14.3 mmol, 1.3 equiv.) was added at -78 °C. The reaction was allowed to stir at -78 °C for another 3 h before warmed up to room temperature and stirred overnight. The reaction was worked up with NH4Cl and extracted with ether 3 time. The combined organic layer was washed with brine and dried with Na2SO4. Flash column chromatography on silica (50 mm fritted glass column, 200 mL SiO2) using 20% ethyl acetate/hexanes → 30% ethyl acetate/hexanes as eluent twice to get product as yellowish oil (1.823 g, 9.15 mmol, 83% yield).
\(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.80 (d, \(J = 4.4\) Hz, 1H), 8.11 (d, \(J = 8.4\) Hz, 1H), 8.03 (d, \(J = 8.5\) Hz, 1H), 7.68 (dd, \(J = 8.3, 6.8\) Hz, 1H), 7.54 (dd, \(J = 7.5, 6.9\) Hz, 1H), 7.22 (d, \(J = 4.4\) Hz, 1H), 3.07 – 3.03 (m, 2H), 1.76 (p, \(J = 7.5\) Hz, 2H), 1.45 – 1.34 (m, 4H), 0.91 (t, \(J = 7.0\) Hz, 3H). \(^{13}\)C-NMR (126 MHz, CDCl\(_3\)) \(\delta\) 150.3, 148.8, 148.5, 130.4, 129.0, 127.7, 126.3, 123.7, 120.9, 32.2, 32.0, 29.9, 22.6, 14.1. HRMS (TOF ESI\(^+\)) \(m/z\) calcd for C\(_{14}\)H\(_{18}\)N [M+H]\(^+\): 200.1439, found 200.1447.

**General procedure for the HBF\(_4\)•OEt\(_2\) protection in Supplementary Figure 3**

In a flamed dried 40 mL vial were charged with substrate (0.3 mmol, 1.0 equiv.) and a stir bar. 1.2 mL anhydrous DCM was added to dissolve the substrate and the vial was flushed with an argon stream and then cooled to 0 °C. HBF\(_4\)•OEt\(_2\) (45.5 µL, 1.1 equiv.) was added via syringe and the reaction was allowed to stir at 0 °C for 30 minutes then 1 h at room temperature. The reaction was concentrated \textit{in vacuo} and left on high vacuum overnight (12-24 h). Resultant HBF\(_4\) salt were used as substrates following the corresponding oxidation protocol described in Section IV.

**C—H Oxidation of Substrates and Products Characterization for Supplementary Figure 3**

4-(4-chlorophenyl)-1-(4-oxopentyl)piperidine-4-carbonitrile [41a].

Substrate 4-(4-chlorophenyl)-1-pentylpiperidine-4-carbonitrile S37 (87.2 mg, 0.300 mmol, 1.0 equiv), was protected with HBF\(_4\)•OEt\(_2\) (45.5 µL, 0.330 mmol, 54 wt.%, 1.1 equiv.) in CH\(_2\)Cl\(_2\) (1.2 mL, 0.25 M) according to the \textit{general procedure for the HBF\(_4\)•OEt\(_2\) protection in Supplementary Figure 3}. The reaction was run with \textit{General Method C: Slow Catalyst Addition Protocol} at 0 °C: the resultant S37•HBF\(_4\) (0.300 mmol, 1.0 equiv.), ClCH\(_2\)CO\(_2\)H (425 mg, 4.5 mmol, 15.0 equiv.), \((R,R)\)-Mn(CF\(_3\)-PDP) (40.7 mg, 0.030 mmol, 10 mol%), 50% wt. H\(_2\)O\(_2\) (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 0.38 mL with catalyst, 3.75 mL with oxidant). The reaction was run at 0 °C with ice/water bath. The reaction was worked up with 9 mL saturated NaHCO\(_3\) and DCM as described in General Method C. Flash column chromatography on silica using 2% MeOH/CHCl\(_3\) as eluent afforded 4-(4-chlorophenyl)-1-(4-oxopentyl)piperidine-4-carbonitrile (\(\delta\)-ketone, 41a) product as a yellow oil. 4-(4-chlorophenyl)-1-(3-oxopentyl)piperidine-4-carbonitrile (\(\gamma\)-ketone, 41b) was produced in very low amount and was not characterized.

**Run 1:** (56.1 mg, 0.184 mmol, 61.3% yield of \(\delta\)-ketone 41a), (4.3 mg, 0.014 mmol, 4.7% yield of \(\gamma\)-ketone 41b), (66.0% overall yield, 13.0:1 \(\delta\)-ketone:\(\gamma\)-ketone ratio), (2.4 mg. 0.008 mmol, 2.8% rsm). **Run 2:** (58.2 mg, 0.191 mmol, 63.6% yield of \(\delta\)-ketone 41a), (4.0 mg, 0.013 mmol, 4.4% yield of \(\gamma\)-ketone 41b), (68.0% overall yield, 14.4:1 \(\delta\)-ketone:\(\gamma\)-ketone ratio), (2.3 mg. 0.008 mmol, 2.6% rsm). **Run 3:** (56.0 mg, 0.184 mmol, 61.3% yield of \(\delta\)-ketone 41a), (5.2 mg, 0.017 mmol, 5.7% yield of \(\gamma\)-ketone 41b),
(67.0% overall yield, 10.8:1 δ-ketone:γ-ketone ratio), (3.7 mg. 0.013 mmol, 4.3% rsm). **Average: 67.0% yield ± 1.0%, 12.6:1 δ-ketone:γ-ketone ratio, 3.2% rsm ± 0.9%.**

$^1$H-NMR (400 MHz, CDCl$_3$) δ 7.44 – 7.41 (m, 2H), 7.38 – 7.35 (m, 2H), 3.01 – 2.97 (m, 2H), 2.48 – 2.41 (m, 6H), 2.16 (s, 3H), 2.10 – 1.99 (m, 4H), 1.80 (p, $J = 7.2$ Hz, 2H). $^{13}$C-NMR (126 MHz, CDCl$_3$) δ 208.5, 138.8, 134.1, 129.2, 127.1, 121.7, 57.5, 50.6, 42.5, 41.4, 36.6, 30.3, 21.2. HRMS (TOF ESI+) $m/z$ calculated for C$_{17}$H$_{22}$N$_2$OCl [M+H]$^+$: 305.1421, found 305.1427.

Other oxidation conditions for substrate S37:

Oxidizing the S37•HBF$_4$ using **General Method A: Single Catalyst Addition Protocol**: the resultant S37•HBF$_4$ (0.300 mmol, 1.0 equiv.), ClCH$_2$CO$_2$H (425 mg, 4.5 mmol, 15.0 equiv.), (R,R)-Mn(CF$_3$-PDP) (40.7 mg, 0.030 mmol, 10 mol%), 50% wt. H$_2$O$_2$ (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with 9 mL saturated NaHCO$_3$ and DCM as described in the general method A and columned with same column conditions. **Drop in conversion and maintained selectivity was observed under this condition.**

**Run 1:** (23.5 mg, 0.077 mmol, 25.7% yield of δ-ketone 41a), (1.8 mg, 0.006 mmol, 2.0% yield of γ-ketone 41b), (27.7% overall yield, 12.9:1 δ-ketone:γ-ketone ratio), (52.9 mg. 0.182 mmol, 60.7% rsm).

**Run 2:** (21.3 mg, 0.070 mmol, 23.3% yield of δ-ketone 41a), (1.6 mg, 0.005 mmol, 1.7% yield of γ-ketone 41b), (25.0% overall yield, 13.7:1 δ-ketone:γ-ketone ratio), (53.8 mg. 0.185 mmol, 61.7% rsm).

**Average: 26.4% yield, 13.3:1 δ-ketone:γ-ketone ratio, 61.2% rsm.**

Oxidizing the S37•HBF$_4$ using modified procedure of **General Method C: Slow Catalyst Addition Protocol at -36 ºC**: the resultant S37•HBF$_4$ (0.300 mmol, 1.0 equiv.), ClCH$_2$CO$_2$H (425 mg, 4.5 mmol, 15.0 equiv.), (R,R)-Mn(CF$_3$-PDP) (40.7 mg, 0.030 mmol, 10 mol%), 50% wt. H$_2$O$_2$ (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at -36 ºC with dry ice/1,2-dichloroethane bath. The reaction was worked up with 9 mL saturated NaHCO$_3$ and DCM as described in the general method C and columned with same column conditions. **A decrease in conversion and yield of ketone products was observed at this low temperature.**

**Run 1:** (44.5 mg, 0.146 mmol, 48.7% yield of δ-ketone 41a), (3.0 mg, 0.010 mmol, 3.3% yield of γ-ketone 41b), (52.0% overall yield, 14.8:1 δ-ketone:γ-ketone ratio), (29.0 mg. 0.100 mmol, 33.2% rsm).

Oxidizing the S37 using **General Method C: Slow Catalyst Addition Protocol without protection with HBF$_4$•OEt$_2$**: Substrate 4-(4-chlorophenyl)-1-pentylpiperidine-4-carbonitrile S37 (87.2 mg, 0.300 mmol, 1.0 equiv), ClCH$_2$CO$_2$H (425 mg, 4.5 mmol, 15.0 equiv.), (R,R)-Mn(CF$_3$-PDP) (40.7 mg, 0.030 mmol, 10 mol%), 50% wt. H$_2$O$_2$ (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 0.38 mL with catalyst, 3.75 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 9 mL saturated NaHCO$_3$ and DCM as described in the general method C.
No product formed without the HBF₄•OEt₂ protection indicating it is still necessary even with ClCH₂COOH used in reaction media.

**Run 1:** (79.6 mg, 0.274 mmol, 91.2% rsm). **Run 2:** (79.2 mg, 0.272 mmol, 90.8% rsm). **Run 3:** (79.7 mg, 0.274 mmol, 91.3% rsm). **Average:** 91.1% rsm ± 0.2%.

4-(4-chlorophenyl)-1-((3-oxocyclopentyl)methyl)piperidine-4-carbonitrile [42].

Substrate 4-(4-chlorophenyl)-1-(cyclopentylmethyl)piperidine-4-carbonitrile **S38** (90.9 mg, 0.300 mmol, 1.0 equiv), was protected with HBF₄•OEt₂ (45.5 µL, 0.330 mmol, 54 wt.%, 1.1 equiv.) in CH₂Cl₂ (1.2 mL, 0.25M) according to the **general procedure for the HBF₄•OEt₂ protection in Supplementary Figure 3**. The reaction was run with **General Method C: Slow Catalyst Addition Protocol**: the resultant **S38•HBF₄** (0.300 mmol, 1.0 equiv.), ClCH₂CO₂H (425 mg, 4.5 mmol, 15.0 equiv.), (R,R)-Mn(CF₃-PDP) (40.7 mg, 0.030 mmol, 10 mol%), 50% wt. H₂O₂ (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 0.38 mL with catalyst, 3.75 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 9 mL saturated NaHCO₃ and DCM as described in General Method C. Flash column chromatography on silica using 3% MeOH/CHCl₃ as eluent afforded product as a pale yellow solid. **Site of oxidation was confirmed based on a combination of ¹H, gHSQC and gHMBC NMRs.**

**Run 1:** (76.1 mg, 0.240 mmol, 80.1% yield), 0% rsm. **Run 2:** (76.2 mg, 0.240 mmol, 80.2% yield), 0% rsm. **Run 3:** (74.9 mg, 0.236 mmol, 78.8% yield), 0% rsm. **Average:** 79.7% yield ± 0.8%, 0% rsm.

¹H-NMR (500 MHz, CDCl₃) δ 7.44 – 7.42 (m, 2H), 7.39 – 7.36 (m, 2H), 3.01 – 2.96 (m, 2H), 2.55 – 2.27 (m, 7H), 2.22 – 2.12 (m, 2H), 2.11 – 2.01 (m, 4H), 2.00 – 1.91 (m, 1H), 1.74 – 1.56 (m, 1H). ¹³C-NMR (126 MHz, CDCl₃) δ 219.3, 138.8, 134.2, 129.3, 127.2, 121.7, 63.2, 51.4, 50.9, 43.9, 42.5, 37.9, 36.7, 34.7, 27.7. HRMS (TOF ESI+) m/z calculated for C₁₈H₂₂N₂OCl [M+H]⁺: 317.1421, found 317.1424.

1-(1-(4-chlorobenzyl)piperidin-4-yl)ethan-1-one [43].

Substrate 1-(4-chlorobenzyl)-4-ethylpiperidine **S39** (71.3 mg, 0.300 mmol, 1.0 equiv), was protected with HBF₄•OEt₂ (45.5 µL, 0.330 mmol, 54 wt.%, 1.1 equiv.) in CH₂Cl₂ (1.2 mL, 0.25M) according to the **general procedure for the HBF₄•OEt₂ protection in Supplementary Figure 3**. The reaction was run with **General Method C: Slow Catalyst Addition Protocol at 0 ºC**: the resultant **S39•HBF₄** (0.300 mmol, 1.0 equiv.), ClCH₂CO₂H (425 mg, 4.5 mmol, 15.0 equiv.), (R,R)-Mn(CF₃-PDP) (40.7 mg, 0.030 mmol, 10 mol%), 50% wt. H₂O₂ (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 0.38 mL with catalyst, 3.75 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with 9
mL saturated NaHCO₃ and DCM as described in General Method C. Flash column chromatography on silica using 2% MeOH/CHCl₃ as eluent afforded product as a pale yellow solid.

**Run 1:** (38.5 mg, 0.153 mmol, 51.0% yield), (11.6 mg, 0.049 mmol, 16.3% rsm). **Run 2:** (37.5 mg, 0.149 mmol, 49.7% yield), (13.8 mg, 0.058 mmol, 19.3% rsm). **Run 3:** (38.2 mg, 0.152 mmol, 50.6% yield), (14.1 mg, 0.059 mmol, 19.8% rsm). **Average:** 50.4% yield ± 0.7%, 18.5% rsm ± 1.9%.

**1H-NMR** (500 MHz, CDCl₃) δ 7.28 – 7.23 (m, 4H), 3.45 (s, 2H), 2.86 (dt, J = 11.9, 3.6 Hz, 2H), 2.28 (tt, J = 11.5, 3.8 Hz, 1H), 2.13 (s, 3H), 2.00 (td, J = 11.6, 2.5 Hz, 2H), 1.82 (dt, J = 13.3, 2.9 Hz, 2H), 1.65 (dtd, J = 13.2, 11.6, 3.8 Hz, 2H). **13C-NMR** (126 MHz, CDCl₃) δ 211.1, 137.0, 132.8, 130.4, 128.5, 62.5, 53.1, 49.4, 27.9, 27.8. **HRMS** (TOF ESI+) m/z calculated for C₁₄H₁₉NOCl [M+H]⁺: 252.1155, found 252.1161.

**8-(4-(4-fluorophenyl)-4-oxobutyl)-8-azaspiro[4.5]decan-2-one [44].**

![Substrate](image)

Substrate 1-(4-fluorophenyl)-4-(8-azaspiro[4.5]decan-8-yl)butan-1-one **S40** (91.0 mg, 0.300 mmol, 1.0 equiv), was protected with HBF₄•OEt₂ (45.5 µL, 0.330 mmol, 54 wt.%, 1.1 equiv.) in CH₂Cl₂ (1.2 mL, 0.25M) according to the general procedure for the HBF₄•OEt₂ protection in Supplementary Figure 3. The reaction was run with General Method C: Slow Catalyst Addition Protocol: the resultant **S40•HBF₄** (0.300 mmol, 1.0 equiv.), ClCH₂CO₂H (425 mg, 4.5 mmol, 15.0 equiv.), (R,R)-Mn(CF₃-PDP) (40.7 mg, 0.030 mmol, 10 mol%), 50% wt. H₂O₂ (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 0.38 mL with catalyst, 3.75 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 9 mL saturated NaHCO₃ and DCM as described in General Method C. Flash column chromatography on silica using 5% MeOH/CHCl₃ as eluent afforded product as a pale yellow solid.

**Run 1:** (82.8 mg, 0.261 mmol, 87.0% yield), 0% rsm. **Run 2:** (79.7 mg, 0.251 mmol, 83.7% yield), 0% rsm. **Run 3:** (78.1 mg, 0.246 mmol, 82.0% yield), 0% rsm. **Average:** 84.2% yield ± 2.5%, 0% rsm.

**1H-NMR** (500 MHz, CDCl₃) δ 8.01 – 7.98 (m, 2H), 7.13 – 7.10 (m, 2H), 2.96 (t, J = 7.1 Hz, 2H), 2.58 – 2.54 (m, 2H), 2.40 (t, J = 7.2 Hz, 2H), 2.26 – 2.20 (m, 4H), 2.10 (s, 2H), 1.94 (p, J = 7.1 Hz, 2H), 1.80 (t, J = 7.9 Hz, 2H), 1.58 – 1.49 (m, 4H). **13C-NMR** (126 MHz, CDCl₃) δ 219.3, 198.5, 165.7 (d, J = 254.4 Hz), 133.7 (d, J = 3.0 Hz), 130.8 (d, J = 9.2 Hz), 115.7 (d, J = 22.1 Hz), 58.0, 50.6 (2 carbons), 50.1 (broad), 38.5, 36.6 (2 carbons), 36.4, 36.3, 34.5 (broad), 21.9. **19F-NMR** (470 MHz, CDCl₃) δ -106.1. **HRMS** (TOF ESI+) m/z calculated for C₁₉H₂₅NO₂F [M+H]⁺: 318.1869, found 318.1858.

**5-(3,4-difluorophenyl)-5-(pyridin-3-yl)pentan-2-one [45].**
Substrate 3-(1-(3,4-difluorophenyl)pentyl)pyridine S41 (78.4 mg, 0.300 mmol, 1.0 equiv), was protected with HBF₄•OEt₂ (45.5 µL, 0.330 mmol, 54 wt.%, 1.1 equiv.) in CH₂Cl₂ (1.2 mL, 0.25M) according to the general procedure for the HBF₄•OEt₂ protection in Supplementary Figure 3. The reaction was run with General Method C: Slow Catalyst Addition Protocol: the resultant S41•HBF₄ (0.300 mmol, 1.0 equiv.), ClCH₂CO₂H (425 mg, 4.5 mmol, 15.0 equiv.), (R,R)-Mn(CF₃-PDP) (40.7 mg, 0.030 mmol, 10 mol%), 50% wt. H₂O₂ (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 0.38 mL with catalyst, 3.75 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 9 mL saturated NaHCO₃ and DCM as described in General Method C. Flash column chromatography on silica using 2% MeOH/CHCl₃ as eluent afforded product as a pale yellow oil.

**Run 1:** (44.9 mg, 0.163 mmol, 54.4% yield), (10.2 mg, 0.039 mmol, 13.0% rsm). **Run 2:** (44.5 mg, 0.162 mmol, 53.9% yield), (9.7 mg, 0.037 mmol, 12.4% rsm). **Run 3:** (44.2 mg, 0.161 mmol, 53.5% yield), (8.4 mg, 0.032 mmol, 10.7% rsm). **Average:** 53.9% yield ± 0.5%, 12.0% rsm ± 1.2%.

**1H-NMR (500 MHz, CDCl₃)**: 8.47 – 8.45 (m, 2H), 7.48 (dt, J = 8.0, 1.9 Hz, 1H), 7.22 (dd, J = 7.9, 4.7 Hz, 1H), 7.08 (dt, J = 10.1, 8.3 Hz, 1H), 7.00 (dd, J = 11.4, 7.5, 2.2 Hz, 1H), 6.94 – 6.91 (m, 1H), 3.91 (t, J = 7.9 Hz, 1H), 2.38 (t, J = 6.7 Hz, 2H), 2.30 – 2.25 (m, 2H), 2.07 (s, 3H). **13C-NMR (126 MHz, CDCl₃)**: δ 207.8, 151.0 (dd, J = 155.9, 12.6 Hz), 149.7, 149.1 (dd, J = 155.0, 12.7 Hz), 148.6, 140.4 (t, J = 4.4 Hz), 139.1, 135.1, 123.9, 123.9 (q, J = 3.4 Hz), 117.7 (d, J = 17.1 Hz), 116.8 (d, J = 17.4 Hz), 47.1, 41.5, 30.3, 29.0. **19F NMR (470 MHz, CDCl₃)**: δ -137.30 (dt, J = 20.8, 10.1 Hz), -140.79 (dt, J = 20.3, 9.9 Hz). HRMS (TOF ESI+) m/z calculated for C₁₆H₁₆NOF₂ [M+H]^+: 276.1200, found 276.1196.

Substrate 4-(4-chlorophenyl)-2-pentylpyridine S42 (77.9 mg, 0.300 mmol, 1.0 equiv), was protected with HBF₄•OEt₂ (45.5 µL, 0.330 mmol, 54 wt.%, 1.1 equiv.) in CH₂Cl₂ (1.2 mL, 0.25M) according to the general procedure for the HBF₄•OEt₂ protection in Supplementary Figure 3. The reaction was run with General Method C: Slow Catalyst Addition Protocol: the resultant S42•HBF₄ (0.300 mmol, 1.0 equiv.), ClCH₂CO₂H (425 mg, 4.5 mmol, 15.0 equiv.), (R,R)-Mn(CF₃-PDP) (40.7 mg, 0.030 mmol, 10 mol%), 50% wt. H₂O₂ (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 0.38 mL with catalyst, 3.75 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 9 mL saturated NaHCO₃ and DCM as described in General Method C. Flash column chromatography on silica using 20% ethyl acetate/hexanes as eluent afforded 5-(4-(4-chlorophenyl)pyridin-2-yl)pentan-2-one (δ-ketone, 46a) product as a yellow oil and 1-(4-(4-chlorophenyl)pyridin-2-yl)pentan-3-one (γ-ketone, 46b) as a yellow oil.
**Run 1:** (56.0 mg, 0.205 mmol, 68.2% yield of δ-ketone 46a), (11.8 mg, 0.043 mmol, 14.4% yield of γ-ketone 46b), (82.6% overall yield, 4.7:1 δ-ketone:γ-ketone ratio), (7.0 mg, 0.027 mmol, 9.0% rsm). **Run 2:** (52.1 mg, 0.190 mmol, 63.4% yield of δ-ketone 46a), (11.4 mg, 0.042 mmol, 13.9% yield of γ-ketone 46b), (77.3% overall yield, 4.6:1 δ-ketone:γ-ketone ratio), (12.1 mg, 0.047 mmol, 15.5% rsm). **Run 3:** (51.2 mg, 0.187 mmol, 62.4% yield of δ-ketone 46a), (10.3 mg, 0.038 mmol, 12.5% yield of γ-ketone 46b), (74.9% overall yield, 5.0:1 δ-ketone:γ-ketone ratio), (12.1 mg, 0.049 mmol, 16.3% rsm). **Average:** 78.3% yield ± 3.9%, 4.8:1 δ-ketone:γ-ketone ratio, 13.6% rsm ± 4.0%.

1H-NMR (500 MHz, CDCl3) δ 8.56 (d, J = 5.2 Hz, 1H), 7.57 – 7.55 (m, 2H), 7.46 – 7.44 (m, 2H), 7.33 (d, J = 1.5 Hz, 1H), 7.29 (dd, J = 5.2, 1.8 Hz, 1H), 2.85 (dd, J = 8.4, 6.9 Hz, 2H), 2.52 (t, J = 7.3 Hz, 2H), 2.14 (s, 3H), 2.06 (app. p, J = 7.5 Hz, 2H). 13C-NMR (126 MHz, CDCl3) δ 208.8, 162.2, 149.9, 147.8, 136.9, 135.4, 129.4, 128.4, 120.7, 119.2, 43.1, 37.6, 30.1, 23.9. HRMS (TOF ESI+) m/z calculated for C16H17NOCl [M+H]+: 274.0999, found 274.0990. 1-(4-(4-chlorophenyl)pyridin-2-yl)pentan-3-one [46b]. 1H-NMR (500 MHz, CDCl3) δ 8.54 (d, J = 5.2 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.46 – 7.43 (m, 2H), 7.37 (d, J = 1.7 Hz, 1H), 7.28 (dd, J = 5.2, 1.8 Hz, 1H), 3.13 (t, J = 7.2 Hz, 2H), 2.97 (t, J = 7.3 Hz, 2H), 2.48 (q, J = 7.3 Hz, 2H), 1.06 (t, J = 7.3 Hz, 3H). 13C-NMR (126 MHz, CDCl3) δ 210.8, 161.5, 149.9, 147.7, 136.9, 135.4, 129.4, 128.4, 120.7, 119.2, 41.3, 36.2, 32.0, 8.0. HRMS (TOF ESI+) m/z calculated for C16H17NOCl [M+H]+: 274.0999, found 274.0992.

6-(5-(4-bromophenyl)-1H-imidazol-1-yl)hexan-2-one [47]. Substrate 5-(4-bromophenyl)-1-hexyl-1H-imidazole S43 (92.2 mg, 0.300 mmol, 1.0 equiv), was protected with HBF 4•OEt2 (45.5 µL, 0.330 mmol, 54 wt.%, 1.1 equiv.) in CH2Cl2 (1.2 mL, 0.25M) according to the general procedure for the HBF4•OEt2 protection in Supplementary Figure 3. The reaction was run with General Method C: Slow Catalyst Addition Protocol: the resultant S43•HBF4 (0.300 mmol, 1.0 equiv.), CI(CH2CO2H (425 mg, 4.5 mmol, 15.0 equiv.), (R,R)-Mn(CF3-PDP) (40.7 mg, 0.030 mmol, 10 mol%), 50% wt. H2O2 (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 0.38 mL with catalyst, 3.75 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was concentrated to a minimum amount of solvent and dissolved in ~15 mL DCM. 15 mL 1M NaOH solution was added and the mixture was stirred vigorously at RT for 30 minutes before layers was separated. The aqueous layer was extracted with 30 mL DCM twice and the combined organic layer was dried with Na2SO4. Flash column chromatography on silica (35 mm fritted glass column, 100
mL SiO2) using 2% MeOH/CH2Cl2 → 5% MeOH/CH2Cl2 → 10% MeOH/CH2Cl2 as eluent afforded 6-(5-(4-bromophenyl)-1H-imidazol-1-yl)hexan-2-one (ε-ketone 47) and a mixture of ketones in other positions as a pale yellow oil.

**Run 1:** (30.1 mg, 0.094 mmol, 31.2% yield of ε-ketone 47), (17.4 mg, 0.054 mmol, 18.1% yield of ketone mixtures in other positions), (49.3% overall yield, 1.7:1 ε-ketone:other ketones ratio), <10% rsm. **Run 2:** (32.3 mg, 0.101 mmol, 33.5% yield of ε-ketone 47), (17.4 mg, 0.054 mmol, 18.1% yield of ketone mixtures in other positions), (51.6% overall yield, 1.9:1 ε-ketone:other ketones ratio), <10% rsm. **Run 3:** (29.8 mg, 0.093 mmol, 30.9% yield of ε-ketone 47), (16.1 mg, 0.050 mmol, 16.7% yield of ketone mixtures in other positions), (47.6% overall yield, 1.9:1 ε-ketone:other ketones ratio), <10% rsm. **Average:** 49.5% yield ± 2.0%, 1.8:1 ε-ketone:other ketones ratio, <10% rsm.

1H-NMR (500 MHz, CDCl3) δ 7.63 (d, J = 8.2 Hz, 2H), 7.49 – 7.47 (m, 3H), 7.19 (s, 1H), 3.95 (t, J = 7.1 Hz, 2H), 2.47 (t, J = 7.0 Hz, 2H), 2.13 (s, 3H), 1.84 – 1.78 (m, 2H), 1.64 – 1.58 (m, 2H). 13C-NMR (126 MHz, CDCl3) δ 207.9, 141.5, 137.5, 133.3, 131.8, 126.4, 120.5, 114.9, 47.3, 42.8, 30.6, 30.1, 20.7. HRMS (TOF ESI+) m/z calculated for C15H18N2OBr [M+H]+: 321.0602, found 321.0616.

Other oxidation conditions for substrate S43:

Oxidizing S43 using General Method C: Slow Catalyst Addition Protocol without protection with HBF4•OEt2: Substrate 5-(4-bromophenyl)-1-hexyl-1H-imidazole S43 (92.2 mg, 0.300 mmol, 1.0 equiv), ClCH2CO2H (425 mg, 4.5 mmol, 15.0 equiv.), (R,R)-Mn(CF3-PDP) (40.7 mg, 0.030 mmol, 10 mol%), 50% wt. H2O2 (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 0.38 mL with catalyst, 3.75 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was concentrated to a minimum amount of solvent and dissolved in ~15 mL DCM. 15 mL 1M NaOH solution was added and the mixture was stirred vigorously at RT for 30 minutes before layers was separated. The aqueous layer was extracted with 30 mL DCM twice and the combined organic layer was dried with Na2SO4. Flash column chromatography with the same condition and eluents was generously collected and concentrated via rotvap. The residue was analyzed by quantitative 1H-NMR using nitrobenzene as internal standard. **No product formed without the HBF4•OEt2 protection indicating it is still necessary even with ClCH2COOH was used for the less basic imidazole substrate.**

**Run 1:** 0% product, 0% rsm.

Oxidizing S43•HBF4 using Fe(CF3-PDP): Substrate 5-(4-bromophenyl)-1-hexyl-1H-imidazole S43 (92.2 mg, 0.300 mmol, 1.0 equiv), was protected with HBF4•OEt2 (45.5 µL, 0.330 mmol, 54 wt.%, 1.1 equiv.) in CH2Cl2 (1.2 mL, 0.25M) according to the general procedure for the HBF4•OEt2 protection in Supplementary Figure 3. The reaction was conducted in slow addition protocol, same as Entry 10 of Supplementary Table 1. In a 40 mL vial was charged with S43•HBF4 (0.30 mmol, 1.0 equiv), AcOH
(90.1 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.60 mL) and a stir bar. A 1mL syringe was charged with a solution of (S,S)-Fe(CF₃-PDP) catalyst (101.6 mg, 0.075 mmol, 0.25 equiv.) in MeCN (0.38 mL). A 10 mL syringe was charged with a solution of H₂O₂ (183.6 mg, 2.7 mmol, 9.0 equiv.) in MeCN (3.75 mL). Both syringes were fitted with 25G needles and the solution was added dropwise via syringe pump over 1 hour. Upon completion of addition, the reaction was concentrated in vacuo to a minimum amount of MeCN and dissolved in ~15 mL DCM. 15 mL 1M NaOH solution was added and the mixture was stirred vigorously at RT for 30 minutes before layers was separated. The aqueous layer was extracted with 30 mL DCM twice and the combined organic layer was dried with Na₂SO₄. Flash column chromatography with the same condition and eluents was generously collected and concentrated via rotvap. The residue was analyzed by quantitative ¹H-NMR using nitrobenzene as internal standard. No product formed with the Fe(CF₃-PDP) catalyst indicating the protonated imidazole substituted with an aromatic ring is still prone to aromatic oxidation with Fe catalyst.

Run 1: <10% rsm + ketone products combined.

3-((1H-benzo[d]imidazol-1-yl)methyl)cyclopentan-1-one [48a].

Substrate 1-(cyclopentylmethyl)-1H-benzo[d]imidazole S44 (60.1 mg, 0.300 mmol, 1.0 equiv), was protected with HBF₄•OEt₂ (45.5 µL, 0.330 mmol, 54 wt.%, 1.1 equiv.) in CH₂Cl₂ (1.2 mL, 0.25M) according to the general procedure for the HBF₄•OEt₂ protection in Supplementary Figure 3. The reaction was run with General Method B: Iterative Catalyst Addition Protocol: the resultant S44•HBF₄ (0.300 mmol, 1.0 equiv.), ClCH₂CO₂H (425 mg, 4.5 mmol, 15.0 equiv.), (R,R)-Mn(CF₃-PDP) (3 time addition of 20.4 mg, 0.015 mmol, 5 mol%; 15 mol% used in total), 50% wt. H₂O₂ (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 0.38 mL with catalyst, 3.75 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 9 mL saturated NaHCO₃ and DCM as described in General Method B. Flash column chromatography on silica using 5% MeOH/CHCl₃ as eluent afforded 3-((1H-benzo[d]imidazol-1-yl)methyl)cyclopentan-1-one (δ-ketone, 48a) and 2-((1H-benzo[d]imidazol-1-yl)methyl)cyclopentan-1-one (γ-ketone, 48b) as brown solid.

Run 1: (31.9 mg, 0.149 mmol, 49.6% yield of δ-ketone 48a), (3.1 mg, 0.014 mmol, 4.8% yield of γ-ketone 48b), (54.4% overall yield, 10.3:1 δ-ketone:γ-ketone ratio), 0% rsm. Run 2: (33.4 mg, 0.156 mmol, 52.0% yield of δ-ketone 48a), (3.5 mg, 0.016 mmol, 5.4% yield of γ-ketone 48b), (57.4% overall yield, 9.6:1 δ-ketone:γ-ketone ratio), 0% rsm. Run 3: (32.1 mg, 0.150 mmol, 49.9% yield of δ-ketone 48a), (2.9 mg, 0.014 mmol, 4.5% yield of γ-ketone 48b), (54.4% overall yield, 11.1:1 δ-ketone:γ-ketone ratio), 0% rsm. Average: 55.4% yield ± 1.7%, 10.3:1 δ-ketone:γ-ketone ratio, 0% rsm.
1H-NMR (500 MHz, CDCl3) δ 7.88 (s, 1H), 7.82 – 7.80 (m, 1H), 7.40 – 7.38 (m, 1H), 7.33 – 7.27 (m, 2H), 4.27 (dd, J = 14.4, 6.8 Hz, 1H), 4.20 (dd, J = 14.4, 7.5 Hz, 1H), 2.85 – 2.75 (m, 1H), 2.41 – 2.31 (m, 2H), 2.22 – 2.14 (m, 1H), 2.14 – 2.06 (m, 1H), 1.97 (ddd, J = 18.3, 10.2, 1.4 Hz, 1H), 1.71 – 1.63 (m, 1H).

13C-NMR (126 MHz, CDCl3) δ 216.3, 143.9, 142.9, 133.9, 123.3, 122.5, 120.7, 109.5, 49.1, 42.8, 38.0, 37.7, 27.4. HRMS (TOF ESI+) m/z calculated for C13H15N2O [M+H]+: 215.1184, found 215.1181.

Oxidizing S44 using General Method B: Iterative Catalyst Addition Protocol without protection with HBF4•OEt2: Substrate 1-(cyclopentylmethyl)-1H-benzo[d]imidazole S44 (60.1mg, 0.300 mmol, 1.0 equiv), CICH2CO2H (425 mg, 4.5 mmol, 15.0 equiv.), (R,R)-Mn(CF3-PDP) (3 time addition of 20.4 mg, 0.015 mmol, 5 mol%; 15 mol% used in total), 50% wt. H2O2 (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 0.38 mL with catalyst, 3.75 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 9 mL saturated NaHCO3 and DCM as described in General Method B. Flash column chromatography with the same condition and eluents was generously collected and concentrated via rotvap. The residue was analyzed by quantitative 1H-NMR using nitrobenzene as internal standard. No product formed without the HBF4•OEt2 protection indicating it is still necessary even with CICH2COOH was used for the less basic benzimidazole substrate.

Run 1: <5% product, <5% rsm.

Oxidizing S44•HBF4 using Fe(CF3-PDP): Substrate 1-(cyclopentylmethyl)-1H-benzo[d]imidazole S44 (60.1mg, 0.300 mmol, 1.0 equiv), was protected with HBF4•OEt2 (45.5 µL, 0.330 mmol, 54 wt.%, 1.1 equiv.) in CH2Cl2 (1.2 mL, 0.25M) according to the general procedure for the HBF4•OEt2 protection in Supplementary Figure 3. The reaction was conducted in slow addition protocol, same as Entry 10 of Supplementary Table 1. In a 40 mL vial was charged with S44•HBF4 (0.30 mmol, 1.0 equiv), AcOH (90.1 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.60 mL) and a stir bar. A 1mL syringe was charged with a solution of (S,S)-Fe(CF3-PDP) catalyst (101.6 mg, 0.075 mmol, 0.25 equiv.) in MeCN (0.38 mL). A 10 mL syringe was charged with a solution of H2O2 (183.6 mg, 2.7 mmol, 9.0 equiv.) in MeCN (3.75 mL). Both syringes were fitted with 25G needles and the solution was added dropwise via syringe pump over 1 hour. Upon completion of addition, the reaction was concentrated in vacuo to a minimum amount of MeCN and dissolved in ~15 mL DCM. 15 mL 1M NaOH solution was added and the mixture was stirred vigorously at RT for 30 minutes before layers was separated. The aqueous layer was extracted with 30 mL DCM twice and the combined organic layer was dried with Na2SO4. Flash column chromatography with the same condition and eluents was generously collected and concentrated via rotvap. The residue was analyzed by quantitative 1H-NMR using nitrobenzene as internal standard. No product formed with the Fe(CF3-PDP) catalyst indicating the protonated benzimidazole is still prone to aromatic oxidation with Fe catalyst.
Run 1: <5% product, <5% rsm.

2-((1H-benzo[d]imidazol-1-yl)methyl)cyclopentan-1-one [48b].

\[ \text{1H-NMR (500 MHz, CDCl}_3 \text{)} \delta \]

\[ 7.88 \text{ (s, 1H)}, \]

\[ 7.82 – 7.80 \text{ (m, 1H)}, \]

\[ 7.41 – 7.39 \text{ (m, 1H)}, \]

\[ 7.33 – 7.27 \text{ (m, 2H)}, \]

\[ 4.52 \text{ (dd, } J = 14.8, 4.6 \text{ Hz, 1H)}, \]

\[ 4.34 \text{ (dd, } J = 14.8, 6.8 \text{ Hz, 1H)}, \]

\[ 2.64 – 2.58 \text{ (m, 1H)}, \]

\[ 2.39 \text{ (ddq, } J = 18.7, 8.1, 1.7 \text{ Hz, 1H)}, \]

\[ 2.17 \text{ (dddt, } J = 12.2, 8.2, 6.2, 1.9 \text{ Hz, 1H)}, \]

\[ 2.07 \text{ (dd, } J = 19.2, 10.9, 8.9 \text{ Hz, 1H)}, \]

\[ 1.97 \text{ (dddt, } J = 13.1, 8.9, 6.7, 2.0 \text{ Hz, 1H)}, \]

\[ 1.81 – 1.72 \text{ (m, 1H)}, \]

\[ 1.53 \text{ (qd, } J = 11.9, 6.6 \text{ Hz, 1H)).} \]

\[ \text{13C-NMR (126 MHz, CDCl}_3 \text{)} \delta \]

\[ 217.8, \]

\[ 143.9, 143.5, 134.1, 123.3, 122.4, 120.7, 109.7, 50.3, 43.9, 38.0, 28.1, 20.4. \]

HRMS (TOF ESI+) \text{m/z calculated for } \text{C}_{13}\text{H}_{15}\text{N}_2\text{O} [\text{M+H}]^+: 215.1184, \text{found 215.1188.}

5-(quinolin-4-yl)pentan-2-one [49a].

Substrate 4-pentylquinoline S45 (59.8 mg, 0.300 mmol, 1.0 equiv), was protected with HBF₄•OEt₂ (45.5 µL, 0.330 mmol, 54 wt.%, 1.1 equiv.) in CH₂Cl₂ (1.2 mL, 0.25M) according to the general procedure for the HBF₄•OEt₂ protection in Supplementary Figure 3. The reaction was run with General Method C: Slow Catalyst Addition Protocol: the resultant S45•HBF₄ (0.300 mmol, 1.0 equiv.), ClCH₂CO₂H (425 mg, 4.5 mmol, 15.0 equiv.), (R,R)-Mn(CF₃-PDP) (40.7 mg, 0.030 mmol, 10 mol%), 50% wt. H₂O₂ (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 0.38 mL with catalyst, 3.75 mL with oxidant). The reaction was run at -36 °C with 1,2-dichloroethane/dry ice bath. The reaction was concentrated to a minimum amount of solvent and dissolved in ~15 mL DCM. 15 mL 1M NaOH solution was added and the mixture was stirred vigorously at RT for 30 minutes before layers was separated. The aqueous layer was extracted with 30 mL DCM twice and the combined organic layer was dried with Na₂SO₄. Flash column chromatography on silica (35 mm fritted glass column, 100 mL SiO₂) using 15% acetone/hexanes → 30% acetone/hexanes → 50% acetone/hexanes as eluent afforded 5-(quinolin-4-yl)pentan-2-one (δ-ketone, 49a) and 1-(quinolin-4-yl)pentan-3-one (γ-ketone, 49b) as pale yellow oil.

Run 1: (42.6 mg, 0.200 mmol, 66.6% yield of δ-ketone 49a), (11.3 mg, 0.053 mmol, 17.7% yield of γ-ketone 49b), (84.3% overall yield, 3.8:1 δ-ketone:γ-ketone ratio), <5% rsm. Run 2: (42.7 mg, 0.200 mmol, 66.7% yield of δ-ketone 49a), (11.7 mg, 0.055 mmol, 18.3% yield of γ-ketone 49b), (85.0% overall yield, 3.6:1 δ-ketone:γ-ketone ratio), <5% rsm. Run 3: (41.3 mg, 0.194 mmol, 64.5% yield of δ-ketone 49a), (11.5 mg, 0.054 mmol, 18.0% yield of γ-ketone 49b), (82.5% overall yield, 3.6:1 δ-ketone:γ-ketone ratio), <5% rsm. Average: 83.9% yield ± 1.3%, 3.7:1 δ-ketone:γ-ketone ratio, <5% rsm.

\[ \text{1H-NMR (500 MHz, CDCl}_3 \text{)} \delta \]

\[ 8.79 \text{ (d, } J = 4.3 \text{ Hz, 1H)}, \]

\[ 8.11 – 8.07 \text{ (m, 2H)}, \]

\[ 7.69 \text{ (dd, } J = 8.4, 6.8 \text{ Hz, 1H)}, \]

\[ 7.56 \text{ (dd, } J = 8.3, 6.8 \text{ Hz, 1H)}, \]

\[ 7.22 – 7.19 \text{ (m, 1H)}, \]

\[ 3.07 \text{ (dd, } J = 9.6, 6.8 \text{ Hz, 2H)}, \]

\[ 2.54 – 2.51 \text{ (m,} \]

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2H), 2.13 (s, 3H), 2.03 (p, J = 7.1 Hz, 2H). $^{13}$C-NMR (126 MHz, CDCl$_3$) δ 208.2, 150.3, 148.5, 147.8, 130.4, 129.2, 127.6, 126.6, 123.7, 121.0, 42.9, 31.4, 30.2, 23.9. HRMS (TOF ESI+) $m/z$ calculated for C$_{14}$H$_{16}$NO [M+H]$^+$: 214.1232, found 214.1232.

Oxidizing S45 using **General Method C: Slow Catalyst Addition Protocol without protection with HBF$_4$•OEt$_2$**: Substrate 4-pentylquinoline S45 (59.8 mg, 0.300 mmol, 1.0 equiv), CICH$_2$CO$_2$H (425 mg, 4.5 mmol, 15.0 equiv.), (R,R)-Mn(CF$_3$-PDP) (40.7 mg, 0.030 mmol, 10 mol%), 50% wt. H$_2$O$_2$ (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 0.38 mL with catalyst, 3.75 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was concentrated to a minimum amount of solvent and dissolved in ~15 mL DCM. 15 mL 1M NaOH solution was added and the mixture was stirred vigorously at RT for 30 minutes before layers was separated. The aqueous layer was extracted with 30 mL DCM twice and the combined organic layer was dried with Na$_2$SO$_4$. Flash column chromatography with the same condition and eluents was generously collected and concentrated via rotvap. The residue was analyzed by quantitative $^1$H-NMR using nitrobenzene as internal standard.

No product formed without the HBF$_4$•OEt$_2$ protection indicating quinoline substrate deactivate the catalyst in reaction conditions.

**Run 1:** <5% product, (45.7 mg, 0.229 mmol, 76.5% rsm).

**Oxidizing S45•HBF$_4$ using Fe(CF$_3$-PDP):** Substrate 4-pentylquinoline S45 (59.8 mg, 0.300 mmol, 1.0 equiv), was protected with HBF$_4$•OEt$_2$ (45.5 µL, 0.330 mmol, 54 wt.%, 1.1 equiv.) in CH$_2$Cl$_2$ (1.2 mL, 0.25M) according to the general procedure for the HBF$_4$•OEt$_2$ protection in Supplementary Figure 3. The reaction was conducted in slow addition protocol, same as Entry 10 of Supplementary Table 1. In a 40 mL vial was charged with S45•HBF$_4$ (0.30 mmol, 1.0 equiv), AcOH (90.1 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.60 mL) and a stir bar. A 1mL syringe was charged with a solution of (S,S)-Fe(CF$_3$-PDP) catalyst (101.6 mg, 0.075 mmol, 0.25 equiv.) in MeCN (0.38 mL). A 10 mL syringe was charged with a solution of H$_2$O$_2$ (183.6 mg, 2.7 mmol, 9.0 equiv.) in MeCN (3.75 mL). Both syringes were fitted with 25G needles and the solution was added dropwise via syringe pump over 1 hour. Upon completion of addition, the reaction was concentrated in vacuo to a minimum amount of MeCN and dissolved in ~15 mL DCM. 15 mL 1M NaOH solution was added and the mixture was stirred vigorously at RT for 30 minutes before layers was separated. The aqueous layer was extracted with 30 mL DCM twice and the combined organic layer was dried with Na$_2$SO$_4$. Flash column chromatography with the same condition and eluents was generously collected and concentrated via rotvap. The residue was analyzed by quantitative $^1$H-NMR using nitrobenzene as internal standard. No product formed with the Fe(CF$_3$-PDP) catalyst indicating the protonated quinoline is still prone to aromatic oxidation with Fe catalyst.

**Run 1:** <5% product, <5% rsm.
1-(quinolin-4-yl)pentan-3-one [49b].

\[ \begin{align*}
\text{1H-NMR (500 MHz, CDCl}_3) & \delta 8.80 - 8.79 (m, 1H), 8.12 (d, J = 8.3 \text{ Hz}, 1H), 8.01 (d, J = 8.5 \text{ Hz}, 1H), 7.71 (t, J = 6.9 \text{ Hz}, 1H), 7.57 (t, J = 6.9 \text{ Hz}, 1H), 7.24 - 7.21 (m, 1H), 3.37 (t, J = 7.7 \text{ Hz}, 2H), 2.88 (t, J = 7.7 \text{ Hz}, 2H), 2.44 (q, J = 7.3 \text{ Hz}, 2H), 1.07 (t, J = 7.3 \text{ Hz}, 3H). \\
\text{13C-NMR (126 MHz, CDCl}_3) & \delta 209.7, 150.4, 148.5, 147.2, 130.5, 129.3, 127.4, 126.7, 123.4, 120.9, 42.2, 36.3, 25.9, 7.9. \\
\text{HRMS (TOF ESI+)} & m/z \text{ calculated for C}_{14}H_{16}NO [M+H]^+: 214.1232, \text{ found 214.1222.}
\end{align*} \]
VII. Supplementary Figure 4. Oxidation of aromatic dipeptides

Preparation of Substrates and Compounds Characterization for Supplementary Figure 4

General procedure for the synthesis of substrate S46-S48

(+)-methyl (S)-2-(4-chlorophenyl)-2-((S)-2-((4-nitrophenyl)sulfonamido)hexanamido)acetate [(+)-S46].

A 50 mL round bottom flask was charged with a stir bar, (S)-4-chlorophenyl glycine (H-ClPhg-OH, 371 mg, 2.0 mmol, 1.0 equiv.), and MeOH and cooled to 0 ºC. To the stirred mixture was added TMSCl (1.04 mL, 8.2 mmol, 4.1 equiv.) dropwise at 0 ºC and the reaction was stirred at room temperature. After stirring for 24 h, the reaction was concentrated under reduced pressure to afford (S)-4-chlorophenylglycine methyl ester hydrochloride (H-ClPhg-OMe•HCl) as a white solid in quantitative yield. **Longer reaction time causes racemization of the amino acid and smaller amount of TMSCl gives lower conversion of the reaction.**

A 50 mL round bottom flask was charged with a stir bar, H-ClPhg-OMe•HCl, N-nitrobenzenesulfonyl norleucine (Ns-Nle-OH, 633 mg, 2.0 mmol, 1.0 equiv.), O-(7-azabenzotriazol-1-yl)-N,N,N',N'-tetramethyluronium hexafluorophosphate (HATU, 761 mg, 2.0 mmol, 1.0 equiv.) and DCM.
(10 mL) and cooled to 0 °C. To this suspension was added iPr2NEt (1 mL) dropwise and the reaction was stirred at 0 °C. After stirring for 6 h, saturated aqueous NaHCO3 (20 mL) was added then the mixture was separated and the aqueous layer was extracted with DCM (2 x 10 mL). The combined organic layers were washed with 10 wt% of aqueous citric acid (20 mL) and the aqueous layer was extracted with DCM (2 x 10 mL). The combined organic layers were washed with brine (20 mL), dried over Na2SO4, filtered, and concentrated under reduced pressure. The crude mixture was dissolved with a small amount of DCM and concentrated onto silica gel (10 mL) for dry loading onto the column (SiO2, 75 mL) and then eluted with 10% → 30% ethyl acetate/hexanes to give a coupling product with a small impurity. The additional column chromatography (SiO2, 75 mL) eluted by CHCl3 → 5% ethyl acetate/CHCl3 gave 801 mg (1.61 mmol) of Ns-Nle-ClPhg-OMe (+)-S46 as a white solid in 80% yield.

1H-NMR (500 MHz, CDCl3) 8.13 (d, J = 8.8 Hz, 2H), 7.91 (d, J = 8.8 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 7.1 Hz, 1H), 5.84 (br. s, 1H), 5.33 (d, J = 7.0 Hz, 1H), 3.88 (t, J = 6.7 Hz, 1H), 3.69 (s, 3H), 1.76 – 1.69 (m, 1H), 1.61 – 1.55 (m, 1H), 1.31 – 1.20 (m, 4H), 0.82 (t, J = 6.8 Hz, 3H). 13C-NMR (126 MHz, CDCl3) δ 170.6, 170.1, 150.1, 145.8, 135.1, 134.3, 129.3, 128.5, 128.4, 124.3, 57.0, 55.8, 53.4, 33.5, 27.3, 22.2, 13.9. [α]D24 = +124 (c = 1.02, CHCl3). HRMS (TOF ESI+) m/z calculated for C21H25N3O7SCl [M+H]+: 498.1102, found 498.1109.

(+)-methyl (S)-2-(4-chlorophenyl)-2-(1-(1,3-dioxoisindolin-2-yl)cyclopentane-1-carboxamido)-acetate [(+)-S47].

The preparation was performed according to the procedure for (+)-S46. Fleshy prepared H-ClPhg-OMe•HCl (3.0 mmol, 1.0 equiv.) reacted with N-phthaloyl cycloleucine (Phth-CyLeu-OH, 778 mg, 3.0 mmol, 1.0 equiv.), HATU (1.14 g, 3.0 mmol, 1.0 equiv.), and iPr2NEt (1.5 mL) in DCM (15 mL). The crude mixture was dissolved with a small amount of DCM and concentrated onto SiO2 (10 mL) for dry loading onto the column (SiO2, 150 mL) and then eluted with 20% ethyl acetate/hexane to afford 978 mg (2.22 mmol) of Phth-CyLeu-ClPhg-OMe (+)-S47 as a white solid in 74% yield.

1H-NMR (500 MHz, CDCl3) 7.83 – 7.79 (m, 2H), 7.73 – 7.69 (m, 2H), 7.30 – 7.24 (m, 4H), 6.97 (d, J = 6.6 Hz, 1H), 5.48 (d, J = 6.5 Hz, 1H), 3.67 (s, 3H), 2.69 – 2.64 (m, 1H), 2.59 – 2.56 (m, 2H), 2.50 – 2.46 (m, 1H), 1.84 – 1.75 (m, 4H). 13C-NMR (126 MHz, CDCl3) δ 171.6, 171.0, 169.0, 135.0, 134.5, 134.3, 131.8, 129.2, 128.6, 123.4, 70.9, 56.3, 53.1, 35.8, 35.7, 23.7, 23.7. [α]D24 = +98.0 (c = 1.01, CHCl3). HRMS (TOF ESI+) m/z calculated for C23H22N2O5Cl [M+H]+: 411.1217, found 411.1230.

(+)-methyl methyl (S)-2-(4-chlorophenyl)-2-((2S,3S)-3-methyl-2-((4-nitrophenyl)sulfonamido)pentanamido)acetate [(+)-S48].
The preparation was performed according to the procedure for (+)-S46. Fleshly prepared H-ClPhg-OMe•HCl (3.0 mmol, 1.0 equiv.) reacted with N-nitrobenzenesulfonyl norleucine (Ns-Ile-OH, 949 mg, 3.0 mmol, 1.0 equiv.), HATU (1.14 g, 3.0 mmol, 1.0 equiv.), and iPr2NEt (1.5 mL) in DCM (15 mL). The crude mixture was dissolved with a small amount of DCM and concentrated onto silica gel (10 mL) for dry loading onto the column (SiO2, 75 mL) and then eluted with 10% → 30% ethyl acetate/hexanes to give a coupling product with a small impurity. The additional column chromatography (SiO2, 75 mL) eluted by CHCl3 → 5% ethyl acetate/CHCl3 gave 1.03 g (2.07 mmol) of Ns-Ile-ClPhg-OMe (+)-S48 as a white solid in 69% yield.

\[^1\text{H}-\text{NMR}\ (500\ \text{MHz},\ \text{CDCl}_3)\ 8.13 - 8.10 (m, 2H), 7.91 - 7.88 (m, 2H), 7.28 (d, J = 8.4\ \text{Hz}, 2H), 7.08 (d, J = 8.5\ \text{Hz}, 2H), 6.66 (br. s, 1H), 5.53 (br. s, 1H), 5.29 (d, J = 6.9\ \text{Hz}, 1H), 3.72 - 3.69 (m, 1H), 3.69 (s, 3H), 1.79 (dtd, J = 9.8, 6.4, 3.6\ \text{Hz}, 1H), 1.44 (ddp, J = 14.9, 7.4, 3.8\ \text{Hz}, 1H), 1.12 (ddt, J = 14.1, 9.4, 7.2\ \text{Hz}, 1H), 0.94 (d, J = 6.8\ \text{Hz}, 3H), 0.87 (t, J = 7.4\ \text{Hz}, 3H).\ ^{13}\text{C}-\text{NMR}\ (126\ \text{MHz},\ \text{CDCl}_3)\ \delta\ 170.6, 169.5, 150.0, 145.7, 135.1, 134.2, 129.3, 128.5, 128.4, 124.2, 61.6, 55.8, 53.3, 38.6, 24.5, 15.5, 11.3.\ [\alpha]_D^{24} = +136\ (c = 1.04,\ \text{CHCl}_3).\ \text{HRMS}\ (\text{TOF ESI}+)\ m/z\ \text{calculated for C}_{21}\text{H}_{25}\text{N}_3\text{O}_7\text{SCl} [\text{M+H}]^+:\ 498.1102,\ \text{found} 498.1095.\]

**General procedure for the synthesis of substrate S49-S52**

\[
\text{(-)-methyl (S)-3-(4-bromophenyl)-2-((S)-1-((4-nitrophenyl)sulfonyl)pyrrolidine-2-carboxamido)propanoate [(-)-S49].}
\]

A round bottom flask was charged with a stir bar, (S)-4-bromophenylglycine methyl ester hydrochloride (H-BrPhe-OMe•HCl, 1.24 g, 4.1 mmol, 1.0 equiv.) and DCM (25 mL). To this suspension was added iPr2NEt (2 mL) to basify the mixture. Next were added N-nitrobenzenesulfonyl proline (Ns-Pro-OH, 1.24 g, 4.1 mmol, 1.0 equiv.), N-hydroxybenzotriazole hydrate (HOBt•xH2O, 20% by weight H2O, 944 mg) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC•HCl, 788 mg, 5.0 mmol, 1.0 equiv.) and the reaction was stirred overnight at room temperature. Saturated aqueous NaHCO3 (20 mL) was added then the mixture was separated and the aqueous layer was extracted with DCM (2 x 10 mL). The combined organic layers were washed with 10 wt% of aqueous citric acid (20 mL) and the aqueous layer was extracted with DCM (2 x 10 mL). The combined organic layers were washed with brine (20 mL), dried over Na2SO4, filtered, and concentrated under reduced pressure. The residue was diluted with DCM and...
concentrated under reduced pressure onto silica gel (~8 mL) for dry loading onto the column (SiO$_2$, 125 mL) and then eluted with 5% ethyl acetate/CHCl$_3$ to afford 1.74 g (3.22 mmol) of \textbf{Ns-Pro-BrPhe-OMe} (-)\textbf{S49} as a white solid in 79% yield.

$^1$H-NMR (500 MHz, CDCl$_3$) 8.38 (d, $J = 8.8$ Hz, 2H), 8.03 (d, $J = 8.8$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H), 7.05 – 7.01 (m, 3H), 4.88 – 4.80 (m, 1H), 4.15 – 4.13 (m, 1H), 3.78 (s, 3H), 3.40 (dd, $J = 10.0$, 6.9, 3.3 Hz, 1H), 3.24 – 3.14 (m, 2H), 3.02 (dd, $J = 14.0$, 7.1 Hz, 1H), 2.09 (dt, $J = 8.3$, 3.2 Hz, 1H), 1.70 – 1.59 (m, 3H). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 171.3, 170.2, 150.6, 142.3, 135.0, 131.8, 131.2, 129.2, 124.7, 121.3, 62.4, 53.2, 52.8, 49.7, 37.5, 30.2, 24.5. $[\alpha]_b^{24} = -48.6$ (c = 1.03, CHCl$_3$). HRMS (TOF ESI+) $m/z$ calculated for C$_{21}$H$_{23}$N$_3$O$_7$SBr [M+H]$^+$: 540.0440, found 540.0445.

(-)-methyl \textit{(S)-3-(4-fluorophenyl)-2-((S)-1-((4-nitrophenyl)sulfonyl)pyrrolidine-2-carboxamido)propanoate} [(-)-\textbf{S50}].

A round bottom flask was charged with a stir bar, (S)-4-fluorophenylglycine methyl ester hydrochloride (H-FPhe-OMe•HCl, 1.29 g, 5.5 mmol, 1.0 equiv.) and DCM (25 mL). To this suspension was added \textit{iPr}_{2}NEt (2 mL) to basify the mixture. Next were added \textit{N}-nitrobenzenesulfonyl proline (Ns-Pro-OH, 1.65 g, 5.5 mmol, 1.0 equiv.), \textit{N}-hydroxybenzotriazole hydrate (HOBt•xH$_2$O, 20% by weight H$_2$O, 1.29 g) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC•HCl, 1.06 g, 5.5 mmol, 1.0 equiv.) and the reaction was stirred overnight at room temperature. Saturated aqueous NaHCO$_3$ (20 mL) was added then the mixture was separated and the aqueous layer was extracted with DCM (2 x 10 mL). The combined organic layers were washed with 10 wt% of aqueous citric acid (20 mL) and the aqueous layer was extracted with DCM (2 x 10 mL). The combined organic layers were washed with brine (20 mL), dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The residue was diluted with DCM and concentrated under reduced pressure onto silica gel (~8 mL) for dry loading onto the column (SiO$_2$, 125 mL) and then eluted with 5% ethyl acetate/CHCl$_3$ to afford 1.87 g (3.90 mmol) of \textbf{Ns-Pro-FPhe-OMe} (-)\textbf{S50} as a white solid in 71% yield.

$^1$H-NMR (500 MHz, CDCl$_3$) 8.38 – 8.36 (m, 2H), 8.04 – 8.02 (m, 2H), 7.12 – 7.09 (m, 2H), 7.04 (d, $J = 7.9$ Hz, 1H), 6.98 – 6.95 (m, 2H), 4.84 – 4.80 (m, 1H), 4.15 – 4.13 (m, 1H), 3.77 (s, 3H), 3.40 (ddt, $J = 9.9$, 6.8, 3.1 Hz, 1H), 3.24 – 3.15 (m, 2H), 3.04 (dd, $J = 14.1$, 7.1 Hz, 1H), 2.10 – 2.08 (m, 1H), 1.70 – 1.59 (m, 3H). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 171.4, 170.2, 162.1 (d, $J = 245.6$ Hz), 150.6, 142.3, 131.7 (d, $J = 3.3$ Hz), 130.9 (d, $J = 7.9$ Hz), 129.1, 124.7, 115.5 (d, $J = 21.2$ Hz), 62.4, 53.4, 52.7, 49.7, 37.2, 30.2, 24.5. $^{19}$F-NMR (470 MHz, CDCl$_3$) $\delta$ -115.8. $[\alpha]_b^{25} = -69.1$ (c = 1.02, CHCl$_3$). HRMS (TOF ESI+) $m/z$ calculated for C$_{21}$H$_{23}$N$_3$O$_7$FCl [M+H]$^+$: 480.1241, found 480.1234.
A round bottom flask was charged with a stir bar, (S)-4-chlorophenylglycine methyl ester hydrochloride (H-ClPhe-OMe•HCl, 1.25 g, 5.0 mmol, 1.0 equiv.) and DCM (25 mL). To this suspension was added iPr2NEt (2 mL) to basify the mixture. Next were added N-nitrobenzenesulfonyl proline (Ns-Pro-OH, 1.50 g, 5.0 mmol, 1.0 equiv.), N-hydroxybenzotriazole hydrate (HOBT•xH2O, 20% by weight H2O, 1.15 g) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC•HCl, 959 mg, 5.0 mmol, 1.0 equiv.) and the reaction was stirred overnight at room temperature. Saturated aqueous NaHCO3 (20 mL) was added then the mixture was separated and the aqueous layer was extracted with DCM (2 x 10 mL). The combined organic layers were washed with 10 wt% of aqueous citric acid (20 mL) and then the aqueous layer was extracted with DCM (2 x 10 mL). The combined organic layers were washed with brine (20 mL), dried over Na2SO4, filtered, and concentrated under reduced pressure. The residue was diluted with DCM and concentrated under reduced pressure onto silica gel (~8 mL) for dry loading onto the column (SiO2, 125 mL) and then eluted with 5% ethyl acetate/CHCl3 to afford 2.04 g (4.11 mmol) of **Ns-Pro-ClPhe-OMe** (-)-S51 as a white solid in 82% yield.

**(-)-4-(**S**)-3-methoxy-2-(**S**)-1-((4-nitrophenyl)sulfonyl)pyrrolidine-2-carboxamido)-3-oxopropyl)phenyl pivalate [(-)-S52].**

A round bottom flask was charged with a stir bar, (S)-4-(2-amino-3-methoxy-3-oxopropyl)phenyl pivalate trifluoroacetic acid complex (H-OPivPhe-OMe•TFA, 1.18 g, 3.0 mmol, 1.0 equiv.) and DCM (15 mL). To this suspension was added iPr2NEt (0.6 mL) to basify the mixture. Next were added N-nitrobenzenesulfonyl proline (Ns-Pro-OH, 901 mg, 3.0 mmol, 1.0 equiv.), N-hydroxybenzotriazole hydrate (HOBT•xH2O, 20% by weight H2O, 557 mg) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC•HCl, 581 mg, 3.0 mmol, 1.0 equiv.) and the reaction was stirred overnight at room temperature. Saturated aqueous NaHCO3 (20 mL) was added then the mixture was separated and the aqueous layer was extracted with DCM (2 x 10 mL). The combined organic layers were washed with 10 wt% of aqueous citric acid (20 mL) and then the aqueous layer was extracted with DCM (2 x 10 mL). The combined organic layers were washed with...
brane (20 mL), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂, 200 mL) and then eluted with 40% ethyl acetate/hexanes → 80% ethyl acetate/hexanes, and the collected product was rotvaped with pentane 3 times to remove trace solvent residue to afford 1.01 g (1.80 mmol) of Ns-Pro-OPivPhe-OMe (-)-S52 as a white solid in 60% yield.

1H-NMR (500 MHz, CDCl₃) 8.37 (d, J = 8.8 Hz, 2H), 8.03 (d, J = 8.8 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 6.99 – 6.96 (m, 3H), 4.85 (td, J = 7.5, 5.6 Hz, 1H), 4.16 – 4.14 (m, 1H), 3.78 (s, 3H), 3.38 (ddd, J = 10.3, 7.2, 3.3 Hz, 1H), 3.26 (dd, J = 14.1, 5.6 Hz, 1H), 3.21 – 3.18 (m, 1H), 3.06 (dd, J = 14.1, 7.2 Hz, 1H), 2.09 – 2.06 (m, 1H), 1.68 – 1.56 (m, 3H), 1.33 (s, 9H). 13C-NMR (126 MHz, CDCl₃) δ 177.1, 171.5, 170.2, 150.6, 150.4, 142.6, 133.3, 130.3, 129.2, 124.7, 121.8, 62.4, 53.3, 52.7, 49.8, 39.2, 37.4, 30.3, 27.3, 24.5. [α]D²⁵ = -51.0 (c = 0.96, CHCl₃). HRMS (TOF ESI+) m/z calculated for C₂₆H₃₂N₃O₉S [M+H]+: 562.1859, found 562.1861.

(--)-methyl (2-(4-bromophenyl)acetyl)-L-prolanate [(-)-57].

The preparation was performed according to the procedure for (+)-S46. 4-Bromophenylacetic acid (1.08 g, 5.0 mmol, 1.0 equiv.) reacted with H-Pro-OMe•HCl (828 mg, 5.0 mmol, 1.0 equiv.), EDC•HCl (959 g, 5.0 mmol, 1.0 equiv.), HOBt•xH₂O (1.15 g), and iPr₂NEt (2 mL) in DCM (25 mL). The crude mixture was purified by flash column chromatography by using 5% ethyl acetate/CHCl₃ as eluent to afford 1.65 g (5.06 mmol) product as a colorless oil in quantitative yield.

A pair of rotamers are observed by NMR. 1H-NMR (500 MHz, CDCl₃) 7.45 – 7.42 (m, 2H), 7.17 – 7.11 (m, 2H), 4.50 (dd, J = 8.5, 3.9 Hz) & 4.42 (dd, J = 8.5, 2.6 Hz, 1H combined), 3.72 (s) & 3.69 (s, 3H combined), 3.72 – 3.45 (m, 4H), 2.23 – 1.89 (m, 4H). 13C-NMR (126 MHz, CDCl₃) δ 172.8, 169.3, 133.5, 131.8 & 131.7, 131.0 & 130.9, 120.9, 59.7 & 59.0, 52.7 & 52.4, 47.4 & 46.8, 41.3 & 41.1, 31.6 & 29.3, 25.0 & 22.6. [α]D²⁵ = -53.8 (c = 1.02, CHCl₃). HRMS (TOF ESI+) m/z calculated for C₁₄H₁₇NO₃Br [M+H]+: 326.0392, found 326.0392.

**General Oxidation Procedure for proline-containing peptides in Supplementary Figure 4**

**General Method D: Oxidation of Proline-Containing Peptides**

A 40 mL vial was charged with substrate (0.2 mmol, 1.0 equiv.), catalyst (0.02 mmol, 10 mol%), AcOH (172 µL, 3.0 mmol, 15.0 equiv.), MeCN (0.4 mL, 0.50 M), a stir bar and sealed with a screw cap incorporated with PTFE/Silicone septa. The vial was cooled to –36 °C with 1,2-dichloroethane/dry ice
bath. A separate solution of H$_2$O$_2$ [(56.7 µL, 1.0 mmol, 5.0 equiv.), 50 wt% in H$_2$O, purchased from Sigma-Aldrich] in MeCN (2.5 mL) was loaded into a 3 mL syringe fitted with a 25G needle and was added dropwise to the stirring reaction over 1 hour via a syringe pump (2.5 mL/h addition rate). Upon completion, the reaction mixture was allowed to warm to room temperature and concentrated in vacuo. The residue was dissolved with DCM (20 mL) and saturated aqueous NaHCO$_3$ (20 mL). The mixture was separated, and the aqueous layer was extracted with DCM (2 x 10 mL). The combined organic layers were washed with 0.1 M ethylenediaminetetraacetic acid (EDTA) disodium salt solution (30 mL) and the aqueous layer was extracted with DCM (2 x 10 mL). The combined organic layers were dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude mixture was dissolved with small amount of DCM and concentrated onto silica gel (~2 mL) for dry loading onto the column (SiO$_2$, 25 mL) and then eluted with ethyl acetate/CHCl$_3$ to give a desired hemiaminal. Recovered starting material was determined as $^1$H NMR yield with nitrobenzene as an internal standard after the column chromatography.

C—H Oxidation of Substrates and Products Characterization for Supplementary Figure 4

(+)-methyl (S)-2-(4-chlorophenyl)-2-((S)-2-((4-nitrophenyl)sulfonamido)-5-oxohexanamido)acetate [(+)-50].

The reaction was run with General Method B: Iterative Catalyst Addition Protocol: 

Ns-Nle-ClPhg-OMe (+)-S46 (99.6 mg, 0.200 mmol, 1.0 equiv), (R,R)-Mn(CF$_3$-PDP) (3 times addition of 13.6 mg, 0.010 mmol, 5 mol% batch; 15 mol% in total), ClCH$_2$CO$_2$H (284 mg, 3.00 mmol, 15.0 equiv.), 50% wt. H$_2$O$_2$ (136 mg, 2.0 mmol, 10.0 equiv.), MeCN (0.4 mL in 40 mL vial, 2.5 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with 9 mL saturated NaHCO$_3$ and DCM as described in General Method B. The combined organic layer was additionally washed with 30 mL 0.1M Na$_2$EDTA solution and dried with Na$_2$SO$_4$. The crude mixture was concentrated and redissolved with small amount of DCM and concentrated onto silica gel (2 mL) for dry loading onto the column (SiO$_2$, 30 mL) and then eluted with 10% $\rightarrow$ 20% ethyl acetate/CHCl$_3$ to afford a product as a white solid.

Run 1: (56.2 mg, 0.110 mmol, 54.9% yield), (13.6 mg, 0.027 mmol, 13.7% rsm). Run 2: (56.4 mg, 0.110 mmol, 55.1% yield), (14.7 mg, 0.030 mmol, 14.8% rsm). Run 3: (57.1 mg, 0.112 mmol, 55.8% yield), (15.4 mg, 0.031 mmol, 15.5% rsm). **Average: 55.3% yield ± 0.5%, 14.7% rsm ± 0.9%**.

$^1$H-NMR (500 MHz, CDCl$_3$) δ 8.13 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H), 7.38 (s, 1H), 7.27 (d, J = 7.7 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 6.11 (d, J = 8.4 Hz, 1H), 5.27 (d, J = 7.1 Hz, 1H), 3.88 (td, J = 8.8, 3.8 Hz, 1H), 3.68 (s, 3H), 2.84 (ddd, J = 19.0, 9.6, 4.0 Hz, 1H), 2.60 (ddd, J = 18.9, 6.3, 4.1 Hz, 1H), 2.19 (s, 3H), 2.06 (ddt, J = 13.9, 9.4, 4.0 Hz, 1H), 1.75 (ddddd, J = 13.9, 9.8, 6.2, 4.1 Hz, 1H), 1.32 (s, 3H).

$^{13}$C-NMR (126 MHz, CDCl$_3$) δ 210.0, 170.4, 169.7, 150.1, 145.2, 135.1, 134.2, 129.3, 128.5, 128.5, 128.5, 124.3,
56.0, 55.6, 53.3, 38.9, 30.3, 28.2. \[\alpha\]D\textsuperscript{24} = +146 (c = 1.07, CHCl\textsubscript{3}). HRMS (TOF ESI+) m/z calculated for C\textsubscript{21}H\textsubscript{22}N\textsubscript{3}O\textsubscript{8}S\textsubscript{2}ClNa [M+Na]\textsuperscript{+}: 534.0714, found 534.0729.

**Condition with Fe(CF\textsubscript{3}-PDP):** The reaction was conducted in slow addition protocol\textsuperscript{10}, same as Entry 10 of Supplementary Table 1. In a 40 mL vial was charged with Ns-Nle-ClPhg-OMe (+)-S\textsubscript{46} (99.6 mg, 0.200 mmol, 1.0 equiv), AcOH (60.1 mg, 1.0 mmol, 5.0 equiv.), MeCN (0.40 mL) and a stir bar. A 1mL syringe was charged with a solution of \((R,R)\)-Fe(CF\textsubscript{3}-PDP) catalyst (67.8 mg, 0.050 mmol, 0.25 equiv.) in MeCN (0.25 mL). A 10 mL syringe was charged with a solution of \(\text{H}_2\text{O}_2\) (122.4 mg, 1.8 mmol, 9.0 equiv.) in MeCN (2.5 mL). Both syringes were fitted with 25G needles and the solution was added dropwise via syringe pump over 1 hour. Upon completion of addition, the reaction was concentrated *in vacuo* to a minimum amount of MeCN. The crude mixture was concentrated and redissolved with small amount of DCM and concentrated onto silica gel (2 mL) for dry loading onto the column (SiO\textsubscript{2}, 30 mL) and then eluted with 10\% \(\rightarrow\) 20\% ethyl acetate/CHCl\textsubscript{3} and the result was analyzed by quantitative \(^1\)H NMR with nitrobenzene as internal standard.

**Result:** <5\% yield, <5\% rsm.

**methyl** (2\text{S})-2-(4-chlorophenyl)-2-(1-(1,3-dioxoisindolin-2-yl)-3-oxocyclopentane-1-carboxamido)acetate [51].

The reaction was run with **General Method A: Single Catalyst Addition Protocol:** Phth-CyLeu-ClPhg-OMe (+)-S\textsubscript{47} (88.2 mg, 0.200 mmol, 1.0 equiv), \((R,R)\)-Mn(CF\textsubscript{3}-PDP) (27.1 mg, 0.020 mmol, 10 mol\%), ClCH\textsubscript{2}CO\textsubscript{2}H (284 mg, 3.00 mmol, 15.0 equiv.), 50\% wt. \(\text{H}_2\text{O}_2\) (136 mg, 2.0 mmol, 10.0 equiv.), MeCN (0.4 mL in 40 mL vial, 2.5 mL with oxidant). The reaction was run at 0 \(^\circ\)C with ice bath. The reaction was worked up with 9 mL saturated NaHCO\textsubscript{3} and DCM as described in General Method A. The combined organic layer was additionally washed with 30 mL 0.1M Na\textsubscript{2}EDTA solution and dried with Na\textsubscript{2}SO\textsubscript{4}. The crude mixture was concentrated and redissolved with small amount of DCM and concentrated onto silica gel (2 mL) for dry loading onto the column (SiO\textsubscript{2}, 30 mL) and then eluted with 10\% \(\rightarrow\) 20\% ethyl acetate/CHCl\textsubscript{3} to afford a product as a white solid.

**Run 1:** (52.8 mg, 0.116 mmol, 58.0\% yield), <10\% rsm. **Run 2:** (54.3 mg, 0.119 mmol, 59.7\% yield), <10\% rsm. **Run 3:** (54.1 mg, 0.119 mmol, 59.5\% yield), <10\% rsm. **Average:** 59.1\% yield \(\pm\) 0.9\%, <10\% rsm.

The product is a mixture of diastereomers with ~1:1 diastereomeric ratio. \(^1\)H-NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.88 – 7.85 (m, 2H), 7.80 – 7.77 (m, 2H), 7.32 – 7.23 (m, 3H), 7.20 (d, \(J = 8.5\) Hz, 1H), 7.10 (d, \(J = 6.6\) Hz) & 7.05 (d, \(J = 6.5\) Hz, 1H combined), 5.47 – 5.44 (m, 1H), 3.68 (s) & 3.65 (s, 3H combined), 3.48 – 3.36 (m, 1H), 3.14 – 3.09 (m) & 2.96 – 2.87 (m, 3H combined), 2.47 – 2.33 (m, 2H). \(^{13}\)C-NMR (126 MHz,
CDCl3) δ 212.9 & 212.9, 170.7 & 170.7, 170.3 & 170.1, 168.6, 135.0, 134.8 & 134.8, 134.7 & 134.3, 131.4, 129.4 & 129.3, 128.6 & 128.6, 123.9, 66.6, 56.5 & 56.3, 53.3 & 53.3, 47.8 & 47.7, 36.0 & 36.0, 32.1 & 32.1. HRMS (TOF ESI+) m/z calculated for C23H20N2O6Cl [M+H]+: 455.1010, found 455.1028.

(+)-methyl (S)-2-(4-chlorophenyl)-2-((2S,3R)-3-methyl-2-((4-nitrophenyl)sulfonamido)-4-oxopentanamido)acetate [(+)-52].

The reaction was run with General Method B: Iterative Catalyst Addition Protocol with recycle the recovered starting material once: Ns-Ile-ClPhg-OMe (+)-S48 (99.6 mg, 0.200 mmol, 1.0 equiv), (R,R)-Mn(CF3-PDP) (3 times addition of 13.6 mg, 0.010 mmol, 5 mol% batch; 15 mol% in total), CICH2CO2H (284 mg, 3.00 mmol, 15.0 equiv.), 50% wt. H2O2 (136 mg, 2.0 mmol, 10.0 equiv.), MeCN (0.4 mL in 40 mL vial, 2.5 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with 9 mL saturated NaHCO3 and DCM as described in General Method B. The combined organic layer was additionally washed with 30 mL 0.1M Na2EDTA solution and dried with Na2SO4. The crude mixture was concentrated and redissolved with small amount of DCM and concentrated onto silica gel (2 mL) for dry loading onto the column (SiO2, 30 mL) and then eluted with 10% ethyl acetate/CHCl3 to afford a product as a white solid and recovered starting material. The recovered starting material was recycled to the oxidation with the same protocol and the products from both cycles are combined.

Run 1: cycle 1: (35.0 mg, 0.068 mmol, 34.2% yield), (<5% yield of 3º alcohol was also observed), (34.2 mg, 0.069 mmol, 34.3% rsm); cycle 2: (9.5 mg, 0.019 mmol, 27.0% yield), (13.0 mg, 0.026 mmol, 38.0% rsm); overall: (44.5 mg, 0.087 mmol, 43.5% yield), (<5% yield of 3º alcohol), (13.0 mg, 0.026 mmol, 13.1% rsm). Run 2: (35.5 mg, 0.069 mmol, 34.7% yield), (<5% yield of 3º alcohol was also observed), (34.8 mg, 0.070 mmol, 34.9% rsm); cycle 2: (9.6 mg, 0.019 mmol, 26.8% yield), (14.1 mg, 0.028 mmol, 40.5% rsm); overall: (45.1 mg, 0.088 mmol, 44.0% yield), (<5% yield of 3º alcohol), (14.1 mg, 0.028 mmol, 14.2% rsm). Run 3: (35.4 mg, 0.069 mmol, 34.6% yield), (<5% yield of 3º alcohol was also observed), (34.9 mg, 0.070 mmol, 35.0% rsm); cycle 2: (10.4 mg, 0.020 mmol, 29.1% yield), (13.6 mg, 0.027 mmol, 39.2% rsm); overall: (45.8 mg, 0.089 mmol, 44.7% yield), (<5% yield of 3º alcohol), (13.6 mg, 0.027 mmol, 13.7% rsm). Average: 44.1% yield ± 0.6%, <5% 3º alcohol, 9:1 K:A ratio, 13.7% rsm ± 0.6%.

1H-NMR (500 MHz, DMSO-d6) δ 9.06 (d, J = 7.1 Hz, 1H), 8.69 (d, J = 9.5 Hz, 1H), 8.13 (d, J = 8.9 Hz, 2H), 7.83 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 5.00 (d, J = 7.0 Hz, 1H), 4.19 (t, J = 10.0 Hz, 1H), 3.54 (s, 3H), 2.80 – 2.74 (m, 1H), 2.14 (s, 3H), 1.01 (d, J = 7.1 Hz, 3H). 13C-NMR (126 MHz, DMSO-d6) δ 208.8, 170.2, 168.5, 149.2, 146.2, 134.1, 133.2, 129.5, 128.6, 128.0, 123.9, 57.4, 55.3, 52.4, 48.6, 28.8, 13.1. [α]D24 = +164 (c = 0.97, CHCl3). HRMS (TOF ESI+) m/z calculated for C21H23N3O8SCl [M+H]+: 512.0894, found 512.0912.
methyl (2S)-3-(4-bromophenyl)-2-((2S)-5-hydroxy-1-((4-nitrophenyl)sulfonyl)pyrrolidine-2-carboxamido)propanoate [53].

The reaction was run with General Method D: Oxidation of Proline-Containing Peptides: Ns-Pro-BrPhe-OMe (-)-S49 (108 mg, 0.200 mmol, 1.0 equiv), (S,S)-Mn(CF₃-PDP) (27.1 mg, 0.020 mmol, 10 mol%), AcOH (172 µL, 3.00 mmol, 15.0 equiv.), 50% wt. H₂O₂ (68 mg, 1.0 mmol, 5.0 equiv.), MeCN (0.4 mL in 40 mL vial, 2.5 mL with oxidant). The reaction was run at -36 ºC with dry ice/1,2-dichloroethane bath. The reaction was worked up with 9 mL saturated NaHCO₃ and DCM. The combined organic layer was additionally washed with 30 mL 0.1M Na₂EDTA solution and dried with Na₂SO₄. The crude mixture was concentrated and redissolved with small amount of DCM and concentrated onto silica gel (2 mL) for dry loading onto the column (SiO₂, 30 mL) and then eluted with 10% ethyl acetate/CHCl₃ to afford a product as a colorless oil and recovered starting material.

Run 1: (78.7 mg, 0.141 mmol, 70.7% yield), (9.2 mg, 0.017 mmol, 8.5% rsm). Run 2: (76.2 mg, 0.137 mmol, 68.5% yield), (9.5 mg, 0.018 mmol, 8.8% rsm). Run 3: (75.4 mg, 0.136 mmol, 67.8% yield), (8.2 mg, 0.015 mmol, 7.6% rsm). Average: 69.0% yield ± 1.5%, 8.3% rsm ± 0.6%.

The product is isolated as a mixture of diastereomers approximately 5:1 ratio.¹H-NMR (500 MHz, CDCl₃) δ 8.32 – 8.28 (m, 2H), 8.06 – 8.00 (m, 2H), 7.45 – 7.38 (m, 2H), 7.19 – 7.10 (m, 1H), 7.08 – 7.02 (m, 2H), 5.63 (dt, J = 8.8, 4.2 Hz) & 5.54 (d, J = 3.8 Hz, 1H combined), 4.91 – 4.72 (m, 1H), 4.26 – 4.19 (m, 2H), 3.76 – 3.71 (m, 3H), 3.14 – 3.10 (m, 1H), 3.01 – 2.96 (m, 1H), 2.07 – 1.76 (m, 4H). ¹³C-NMR (126 MHz, CDCl₃) δ 171.4, 171.3, 171.1, 170.4, 150.5, 150.3, 144.9, 144.0, 134.9, 134.9, 131.9, 131.8, 131.2, 131.2, 129.3, 128.8, 124.6, 124.2, 123.8, 121.3, 86.2, 85.1, 62.5, 61.6, 53.4, 53.3, 52.8, 52.7, 37.4, 37.3, 33.3, 32.9, 29.2, 28.7. HRMS (TOF ESI-) m/z calculated for C₂₁H₂₁N₃O₈SBr [M-H]-: 554.0233, found 554.0225.

methyl (2S)-3-(4-fluorophenyl)-2-((2S)-5-hydroxy-1-((4-nitrophenyl)sulfonyl)pyrrolidine-2-carboxamido)propanoate [54].

The reaction was run with General Method D: Oxidation of Proline-Containing Peptides: Ns-Pro-FPhe-OMe (-)-S50 (95.9 mg, 0.200 mmol, 1.0 equiv), (S,S)-Mn(CF₃-PDP) (27.1 mg, 0.020 mmol, 10 mol%), AcOH (172 µL, 3.00 mmol, 15.0 equiv.), 50% wt. H₂O₂ (68 mg, 1.0 mmol, 5.0 equiv.), MeCN (0.4 mL in 40 mL vial, 2.5 mL with oxidant). The reaction was run at -36 ºC with dry ice/1,2-dichloroethane bath. The reaction was worked up with 9 mL saturated NaHCO₃ and DCM. The combined organic layer was additionally washed with 30 mL 0.1M Na₂EDTA solution and dried with Na₂SO₄. The crude mixture was concentrated and redissolved with small amount of DCM and concentrated onto silica gel (2 mL) for dry loading onto the
column (SiO2, 30 mL) and then eluted with 10% ethyl acetate/CHCl3 to afford a product as a colorless oil and recovered starting material.

**Run 1:** (61.5 mg, 0.124 mmol, 62.1% yield), (5.8 mg, 0.012 mmol, 6.0% rsm). **Run 2:** (59.9 mg, 0.121 mmol, 60.4% yield), (3.7 mg, 0.007 mmol, 3.9% rsm). **Run 3:** (60.7 mg, 0.123 mmol, 61.3% yield), (6.2 mg, 0.013 mmol, 6.5% rsm). **Average:** 61.3% yield ± 0.9%, 5.5% rsm ± 1.4%.

The product is isolated as a mixture of diastereomers approximately 5:1 ratio. \( ^1 \text{H-NMR (500 MHz, CDCl3)} \delta 8.32 – 8.28 (m, 2H), 8.08 – 8.00 (m, 2H), 7.22 – 7.07 (m, 3H), 6.99 – 6.96 (m, 2H), 5.62 (m) & 5.54 (m, 1H combined), 4.74 (q, \( J = 6.9 \) Hz, 1H), 4.27 – 4.18 (m, 1H), 3.94 (br. s) & 3.77 (br. s, 1H combined), 3.74 (s) & 3.72 (s, 3H combined), 3.14 (dd, \( J = 14.2, 5.4 \) Hz, 1H), 3.01 (dd, \( J = 14.1, 6.9 \) Hz, 1H), 2.09 – 1.74 (m, 4H). \( ^{13} \text{C-NMR (126 MHz, CDCl3)} \delta 171.4, 170.9, 162.3 (d, \( J = 245.8 \) Hz), 150.7, 144.4, 131.64 – 131.62 (m, 1C), 131.1 (d, \( J = 8.0 \) Hz), 129.3 & 128.9, 124.7 & 124.3, 115.71 (d, \( J = 21.0 \) Hz), 86.4 & 85.2, 62.7 & 61.9, 53.7, 52.7, 37.4, 33.4 & 32.9, 29.3 & 28.8. \( ^{19} \text{F-NMR (470 MHz, CDCl3)} \delta -115.6. \)

HRMS (TOF ESI+) \( m/z \) calculated for C\(_{21}\)H\(_{22}\)N\(_3\)O\(_8\)SNaF [M+H]\(^+\): 518.1009, found 518.0995.

methyl (2S)-3-(4-chlorophenyl)-2-((2S)-5-hydroxy-1-((4-nitrophenyl)sulfonyl)pyrrolidine-2-carboxamido)propanoate [55].

The reaction was run with General Method D: Oxidation of Proline-Containing Peptides: Ns-Pro-ClPhe-OMe (-)-S\(_{51}\) (99.2 mg, 0.200 mmol, 1.0 equiv), (S,S)-Mn(CF\(_3\)-PDP) (27.1 mg, 0.020 mmol, 10 mol%), AcOH (172 \( \mu \)L, 3.00 mmol, 15.0 equiv.), 50% wt. H\(_2\)O\(_2\) (68 mg, 1.0 mmol, 5.0 equiv.), MeCN (0.4 mL in 40 mL vial, 2.5 mL with oxidant). The reaction was run at -36 ºC with dry ice/1,2-dichloroethane bath. The reaction was worked up with 9 mL saturated NaHCO\(_3\) and DCM. The combined organic layer was additionally washed with 30 mL 0.1M Na\(_2\)EDTA solution and dried with Na\(_2\)SO\(_4\). The crude mixture was concentrated and redissolved with small amount of DCM and concentrated onto silica gel (2 mL) for dry loading onto the column (SiO2, 30 mL) and then eluted with 10% ethyl acetate/CHCl3 to afford a product as a colorless oil and recovered starting material.

**Run 1:** (69.3 mg, 0.135 mmol, 67.7% yield), (11.0 mg, 0.022 mmol, 11.1% rsm). **Run 2:** (73.9 mg, 0.144 mmol, 72.2% yield), (9.8 mg, 0.020 mmol, 9.9% rsm). **Run 3:** (71.5 mg, 0.140 mmol, 69.8% yield), (9.7 mg, 0.020 mmol, 9.8% rsm). **Average:** 69.9% yield ± 2.3%, 10.3% rsm ± 0.7%.

The product is isolated as a mixture of diastereomers approximately 5:1 ratio. \( ^1 \text{H-NMR (500 MHz, CDCl3)} \delta 8.33 – 8.29 (m, 2H), 8.06 – 7.99 (m, 2H), 7.27 – 7.25 (m, 2H), 7.18 – 7.06 (m, 3H), 5.64 – 5.61 (m) & 5.54 – 5.52 (m, 1H combined), 4.78 – 4.73 (m, 1H), 4.27 – 4.18 (m, 1H), 4.01 (d, \( J = 5.4 \) Hz, 1H), 3.77 – 3.72 (m, 3H), 3.15 (ddd, \( J = 14.0, 11.6, 5.4 \) Hz, 1H), 3.01 (dd, \( J = 14.1, 7.0 \) Hz, 1H), 2.08 – 1.76 (m, 4H). \( ^{13} \text{C-NMR (126 MHz, CDCl3)} \delta 171.4, 171.3, 171.0, 170.3, 150.5, 150.4, 144.9, 144.1, 134.4, 134.3, 133.3, 133.3, 130.9, 130.8, 129.3, 129.1, 128.9, 128.8, 124.6, 124.3, 86.3, 85.1, 62.6, 61.7, 53.5, 53.4, 52.8, 52.7, 51.0.
37.4, 37.3, 33.3, 32.8, 29.2, 28.7. HRMS (TOF ESI-) m/z calculated for C_{21}H_{21}N_{3}O_{8}SCl [M-H]: 510.0738, found 510.0729.

Other oxidation conditions for substrate S51:

**Condition with Fe(CF$_3$-PDP):** The reaction was proceeded with the same procedure by replacing (S,S)-Mn(CF$_3$-PDP) (27.1 mg, 0.020 mmol, 10 mol%) with (S,S)-Fe(CF$_3$-PDP) (27.1 mg, 0.020 mmol, 10 mol%). **Run 1:** 0% yield, (20.0 mg, 0.040 mmol, 20.2% rsm).

**Condition with Fe(PDP):** The reaction was proceeded with the standard iterative addition protocol reported with (S,S)-Fe(PDP).** Run 1:** trace yield, (18.5 mg, 0.037 mmol, 18.7% rsm).

4-((2S)-2-((2S)-5-hydroxy-1-((4-nitrophenyl)sulfonyl)pyrrolidine-2-carboxamido)-3-methoxy-3-oxopropyl)phenyl pivalate [56].

The reaction was run with **General Method D: Oxidation of Proline-Containing Peptides with slightly modifications:** Ns-Pro-OPivPhe-OMe (S)-SS52 (112.3 mg, 0.200 mmol, 1.0 equiv), (S,S)-Mn(CF$_3$-PDP) (27.1 mg, 0.020 mmol, 10 mol%), AcOH (172 µL, 3.00 mmol, 15.0 equiv.), 50% wt. H$_2$O$_2$ (102 mg, 1.5 mmol, 7.5 equiv.), MeCN (0.4 mL in 40 mL vial, 2.5 mL with oxidant). The hydrogen peroxide solution was added over 3 hours at -36 ºC with dry ice/1,2-dichloroethane bath. The reaction was worked up with 9 mL saturated NaHCO$_3$ and DCM. The combined organic layer was additionally washed with 30 mL 0.1M Na$_2$EDTA solution and dried with Na$_2$SO$_4$. The crude mixture was concentrated and purified with column chromatography (SiO$_2$, 100 mL) and then eluted with 20% ethyl acetate/CHCl$_3$ → 40% ethyl acetate/CHCl$_3$ to afford a product as a white solid and recovered starting material. **Run 1:** (82.6 mg, 0.143 mmol, 71.5% yield), (31.6 mg, 0.056 mmol, 28.1% rsm). **Run 2:** (78.5 mg, 0.136 mmol, 68.0% yield), (32.8 mg, 0.058 mmol, 29.2% rsm). **Run 3:** (79.1 mg, 0.137 mmol, 68.5% yield), (31.2 mg, 0.056 mmol, 27.8% rsm). **Average:** **69.3% yield ± 1.9%, 28.4% rsm ± 0.7%.

The product is isolated as a mixture of diastereomers approximately 5:1 ratio. **$^1$H-NMR** (500 MHz, CDCl$_3$) δ 8.32 – 8.28 (m, 2H), 8.07 – 7.98 (m, 2H), 7.18 – 7.12 (m, 2H), 7.04 – 6.92 (m, 3H), 5.61 – 5.53 (m, 1H), 4.92 – 4.71 (m, 1H), 4.22 (br. s, 1H), 3.90 – 3.72 (m, 4H), 3.22 – 3.15 (m, 1H), 3.08 – 3.00 (m, 1H), 2.08 – 1.66 (m, 4H), 1.34 (s, 9H). **$^{13}$C-NMR** (126 MHz, CDCl$_3$) δ 177.7, 171.4, 171.1, 150.3, 150.2, 144.4, 133.2, 130.4 & 130.2, 129.3 & 128.8, 124.5 & 124.2, 121.9 & 121.8, 86.1, 62.4, 53.2, 52.6, 39.1, 37.1, 33.5, 29.2, 27.1. HRMS (TOF ESI-) m/z calculated for C$_{26}$H$_{30}$N$_3$O$_{10}$S [M-H]: 576.1657, found 576.1652.

**Condition with Fe(CF$_3$-PDP):** The reaction was proceeded with the same procedure by replacing (S,S)-Mn(CF$_3$-PDP) (27.1 mg, 0.020 mmol, 10 mol%) with (S,S)-Fe(CF$_3$-PDP) (27.1 mg, 0.020 mmol, 10 mol%). **Run 1:** <5% yield, (30.2 mg, 0.054 mmol, 26.9% rsm).
methyl (3S)-9-bromo-5-oxo-1,2,3,5,6,10b-hexahydropyrrolo[2,1-a]isoquinoline-3-carboxylate [58].

The reaction was run with **General Method D: Oxidation of Proline-Containing Peptides**: methyl (2-(4-bromophenyl)acetyl)-L-prolinate (-)-57 (65.2 mg, 0.200 mmol, 1.0 equiv), (S,S)-Mn(CF3-PDP) (27.1 mg, 0.020 mmol, 10 mol%), AcOH (172 µL, 3.00 mmol, 15.0 equiv.), 50% wt. H2O2 (68 mg, 1.0 mmol, 5.0 equiv.), MeCN (0.4 mL in 40 mL vial, 2.5 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. After the completion of oxidation, the mixture was filter through a silica plug (SiO2,15 mL) with ethyl acetate (150 mL) and the resulting solution was concentrated *in vacuo*. The crude compound was transferred into a new 40 mL vial with DCM and dried on high vacuum for 2 hours. In a sealed tube charged with a stir bar and 1 mL anhydrous 1,2-dichloroethane and TfOH (177 µL, 2.0 equiv.) was added under Ar. The crude hemiaminal was dissolved in 2 mL anhydrous 1,2-dichloroethane under Ar and transferred into the sealed tube dropwise. The hemiaminal vial was rinsed with another 2 mL anhydrous 1,2-dichloroethane and transferred into the sealed tube. The reaction was heated at 90 ºC for 2 hours. After the reaction completed the mixture was diluted with water and basified with sat. NaHCO3. The aqueous layer was extracted with DCM x3. The combined organic layer dried with Na2SO4, filtered and concentrated. The crude mixture was purified by column chromatography (SiO2, 25 mL) and eluted with pure CHCl3 → 20% ethyl acetate/CHCl3 to give product as a colorless oil.

**Run 1**: 30.1 mg, 0.093 mmol, 46.4% yield. **Run 2**: 28.7 mg, 0.089 mmol, 44.3% yield. **Run 3**: 30.8 mg, 0.095 mmol, 47.5% yield. **Average**: 46.1% yield ± 1.6%.

The product is isolated as a mixture of diastereomers approximately 1.5:1 ratio. 1H-NMR (500 MHz, CDCl3) δ 7.37 (dd, J = 8.1, 1.6 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.06 – 7.03 (m, 1H), 4.88 – 4.84 (m) & 4.70 (dd, J = 11.0, 5.9 Hz, 1H combined), 4.57 (d, J = 9.3 Hz) & 4.51 (t, J = 8.4 Hz, 1H combined), 3.76 (s) & 3.64 (s, 3H combined), 3.66 – 3.48 (m, 2H), 2.65 – 2.31 (m, 2H), 2.22 – 1.88 (mm, 2H). 13C-NMR (126 MHz, CDCl3) δ 172.6 & 171.8, 167.5 & 166.9, 138.3 & 137.5, 132.0 & 131.4, 130.9 & 130.8, 129.14 & 129.06, 127.5 & 127.1, 120.9, 60.1, 59.9, 58.2, 57.8, 52.7, 52.6, 38.7, 38.0, 31.5, 29.5, 28.9, 28.3. HRMS (TOF ESI+) m/z calculated for C14H15NO3Br [M+H]+: 324.0235, found 324.0231.
VIII. Late-stage oxidation of aromatic drug derivatives.

**Oxidation of HIV-1 drug Efavirenz derivative**

(±)-6-chloro-4-(cyclopropylethynyl)-1-hexanoyl-4-(trifluoromethyl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one [59]

In a flame dried 50 mL recovery flask charged with (±)-efavirenz (1.263 g, 4.0 mmol, 1.0 equiv.) in anhydrous THF (8 mL, 0.5 M), NaH (95%, 121 mg, 4.8 mmol, 1.2 equiv.) was added at 0 ºC and the reaction was kept at 0 ºC for 10 min. Hexanoyl chloride (531 µL, 3.8 mmol, 0.95 equiv.) was added and the reaction was stirred at room temperature overnight. The reaction was diluted with water and extracted with ethyl acetate. The organic layer was washed with 30 mL 1 M acetic acid solution, 30 mL sat. NaHCO₃ then brine. The combined organic layer was dried over Na₂SO₄ and concentrated. Purified by CombiFlash (40 g column) flushing with hexanes → 100% ethyl acetate/hexanes yield product as a white solid (567 mg, 1.37 mmol) in 34% yield.

$^{1}$H-NMR (500 MHz, methylene chloride-$d_2$) 7.65 (d, $J$ = 8.9 Hz, 1H), 7.61 (d, $J$ = 2.4 Hz, 1H), 7.48 (dd, $J$ = 8.9, 2.4 Hz, 1H), 3.04 – 2.98 (m, 1H), 2.90 (dt, $J$ = 17.4, 7.4 Hz, 1H), 1.72 – 1.69 (m, 2H), 1.42 – 1.30 (m, 5H), 0.94 – 0.89 (m, 5H), 0.86 – 0.79 (m, 2H). $^{13}$C-NMR (126 MHz, methylene chloride-$d_2$) δ 173.8, 148.4, 133.0, 132.3, 131.2, 126.9, 125.1, 123.4, 122.5 (q, $J$ = 286.5 Hz), 97.4, 78.3 (q, $J$ = 35.1 Hz), 65.6, 38.6, 31.7, 25.0, 23.0, 14.2, 9.3, 9.2, -0.3. $^{19}$F-NMR (471 MHz, methylene chloride-$d_2$) δ -78.5. HRMS (TOF ESI+) m/z calculated for C$_{20}$H$_{19}$NO$_3$F$_3$NaCl [M+Na]$^+$: 436.0903, found 436.0893.
(±)-1-(6-chloro-4-(cyclopropylethynyl)-2-oxo-4-(trifluoromethyl)-2H-benzo[d][1,3]oxazin-1(4H)-yl)hexane-1,5-dione [60a].

The reaction was run with General Method A: Single Catalyst Addition Protocol. 6-chloro-4-(cyclopropylethynyl)-1-hexanoyl-4-(trifluoromethyl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one 59 (82.8 mg, 0.200 mmol, 1.0 equiv), (R,R)-Mn(CF3-PDP)6 (27.1 mg, 0.020 mmol, 10 mol%), ClCH2CO2H (284 mg, 3.0 mmol, 15.0 equiv.), 50% wt. H2O2 (136 mg, 2.0 mmol, 10.0 equiv.), MeCN (0.4 mL in 40 mL vial, 2.5 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with 9 mL saturated NaHCO3 and DCM as described in the General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO2) using 10% ethyl acetate/hexanes → 25% ethyl acetate/hexanes → 50% ethyl acetate/hexanes as eluent afforded δ-ketone (60a) and γ-ketone (60b) products as white solid.

Run 1: (11.3 mg, 0.026 mmol, 13.2% yield of γ-ketone 60b), (36.5 mg, 0.085 mmol, 42.7% yield of δ-ketone 60a), (55.9% overall yield, 3.2:1 δ:γ ratio), (18.3 mg, 0.044 mmol, 22.1% rsm). Run 2: (13.0 mg, 0.030 mmol, 15.2% yield of γ-ketone 60b), (36.9 mg, 0.086 mmol, 43.1% yield of δ-ketone 60a), (58.3% overall yield, 2.8:1 δ:γ ratio), (17.9 mg, 0.043 mmol, 21.6% rsm). Run 3: (12.0 mg, 0.028 mmol, 14.0% yield of γ-ketone 60b), (37.9 mg, 0.089 mmol, 44.3% yield of δ-ketone 60a), (58.3% overall yield, 3.2:1 δ:γ ratio), (21.1 mg, 0.051 mmol, 25.5% rsm). Average: 57.5% yield ± 1.4%, 3.1:1 δ:γ ratio, 23.1% rsm ± 2.1%.

1H-NMR (500 MHz, methylene chloride-d2) 7.66 (d, J = 8.9 Hz, 1H), 7.62 (d, J = 2.4 Hz, 1H), 7.48 (dd, J = 8.9, 2.4 Hz, 1H), 3.05 (ddd, J = 17.8, 7.7, 6.7 Hz, 1H), 2.91 (dt, J = 17.7, 7.3 Hz, 1H), 2.53 (t, J = 7.2 Hz, 2H), 2.11 (s, 3H), 1.95 (p, J = 7.2 Hz, 2H), 1.41 (tt, J = 8.3, 5.0 Hz, 1H), 0.95 – 0.92 (m, 2H), 0.83 (tdd, J = 6.2, 5.5, 3.2 Hz, 2H). 13C-NMR (126 MHz, methylene chloride-d2) δ 208.0, 173.2, 148.4, 132.8, 132.5, 131.2, 127.0, 125.2, 123.5, 122.5 (q, J = 286.7 Hz), 97.6, 78.4 (q, J = 35.1 Hz), 65.5, 42.6, 37.6, 30.2, 19.3, 9.3, 9.2, -0.3. 19F-NMR (471 MHz, methylene chloride-d2) δ -78.5. HRMS (TOF ESI+) m/z calculated for C20H17NO4F3NaCl [M+Na]+: 450.0696, found 450.0706.
(±)-1-(6-chloro-4-(cyclopropylethynyl)-2-oxo-4-(trifluoromethyl)-2H-benzo[d][1,3]oxazin-1(4H)-yl)hexane-1,4-dione [60b].

$^{1}$H-NMR (500 MHz, methylene chloride-$d_2$) 7.61 (d, $J = 2.5$ Hz, 1H), 7.59 (d, $J = 8.9$ Hz, 1H), 7.46 (dd, $J = 8.9, 2.4$ Hz, 1H), 3.28 (ddd, $J = 18.4, 7.5, 5.0$ Hz, 1H), 3.14 (ddd, $J = 18.4, 7.0, 4.7$ Hz, 1H), 2.90 – 2.78 (m, 2H), 2.49 (q, $J = 7.4$ Hz, 2H), 1.43 (tt, $J = 8.3, 5.0$ Hz, 1H), 1.04 (t, $J = 7.3$ Hz, 3H), 0.95 – 0.92 (m, 2H), 0.86 – 0.83 (m, 2H). $^{13}$C-NMR (126 MHz, methylene chloride-$d_2$) $\delta$ 209.5, 173.6, 148.1, 133.0, 132.3, 131.3, 127.1, 125.0, 123.1, 122.50 (q, $J = 286.8$ Hz), 97.6, 78.5 (q, $J = 35.2$ Hz), 65.5, 37.2, 36.2, 33.2, 9.24, 9.22, 8.1, -0.2. $^{19}$F-NMR (471 MHz, methylene chloride-$d_2$) $\delta$ -78.7. HRMS (TOF ESI+) $m/z$ calculated for C$_{20}$H$_{17}$NO$_4$F$_3$NaCl [M+Na]$^+$: 450.0696, found 450.0689.

**Oxidation of a γ-secretase modulator analogue**

(±)-Methyl 2-((2SR,4RS)-1-((RS)-1-(4-chlorophenyl)pentyl)-2-(4-(trifluoromethyl)phenyl)piperidin-4-yl)acetate [61].

A mixture of methyl (±)-2-((2SR,4RS)-2-(4-(trifluoromethyl)phenyl)piperidin-4-yl)acetate (557 mg, 1.85 mmol, 1.0 equiv.), 4-chlorobenzaldehyde (268 mg, 1.91 mmol, 1.03 equiv.), and benzotriazole (228 mg, 1.91 mmol, 1.03 equiv.) in toluene (10 ml, 0.18 M) was refluxed with a Dean-Stark apparatus for 18 hours. After cooling to room temperature, the solvent was evaporated, and the residual gum was dissolved in CH$_2$Cl$_2$ (17 ml, 0.11 M). In another flask, a solution of ZnCl$_2$$\cdot$OEt$_2$ (5.8 mL, 5.4 mmol, 1M in Et$_2$O, 3.1 equiv.) was added dropwise to a solution of butylmagnesium chloride (2.8 mL, 5.55 mmol, 2M in Et$_2$O, 3.1 equiv.) in Et$_2$O (3 mL, final concentration = 0.48 M) at 0 °C. The cooling bath was removed, and the mixture was stirred at room temperature for 1 hour, then recooled in an ice bath. The portion of the solution of the benzotriazole adduct in CH$_2$Cl$_2$ was added over 5 minutes, the cooling bath was removed, and the reaction was stirred at room temperature for 20 hours. After this period, the reaction was quenched with saturated aqueous solution of NH$_4$Cl. The mixture was partitioned with CH$_2$Cl$_2$ and
H₂O. The aqueous layer was extracted with CH₂Cl₂ (twice) and the combined extracts were washed with water (once), dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography on silica eluting 5% EtOAc/hexanes as eluent to yield the desired product (691 mg, 1.43 mmol, 77%) as a colorless oil.

¹H-NMR (500 MHz, CDCl₃) δ 7.63 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 7.8 Hz, 2H), 7.29 – 7.21 (m, 2H), 7.21 – 7.15 (m, 2H), 3.70 (dd, J = 11.0, 2.8 Hz, 1H), 3.62 (s, 3H), 3.41 (dd, J = 7.8, 6.2 Hz, 1H), 2.67 (dt, J = 11.6, 3.5 Hz, 1H), 2.32 (td, J = 11.8, 2.5 Hz, 1H), 2.23 (dd, J = 15.3, 6.7 Hz, 1H), 2.16 (dd, J = 15.3, 7.5 Hz, 1H), 1.99 – 1.86 (m, 1H), 1.80 (dq, J = 13.0, 3.0 Hz, 1H), 1.77 – 1.69 (m, 2H), 1.63 (dt, J = 13.0, 3.1 Hz, 1H), 1.36 – 1.27 (m, 1H), 1.21 – 1.15 (m, 2H), 1.12 (dd, J = 12.4, 4.1 Hz, 1H), 1.07 – 0.98 (m, 1H), 0.80 (t, J = 7.3 Hz, 3H), 0.85 – 0.71 (m, 1H). ¹³C-NMR (126 MHz, CDCl₃) δ 173.1, 148.8 (q, J = 1.0 Hz), 140.5, 132.3, 130.1, 129.7 (q, J = 32.3 Hz), 128.2 (2 carbons), 125.8 (q, J = 3.4 Hz), 124.3 (q, J = 271.8 Hz), 64.6, 60.9, 51.6, 44.6, 42.9, 41.0, 33.9, 32.5, 29.6, 23.0, 22.3, 14.1. ¹⁹F-NMR (470 MHz, CDCl₃) δ −62.7. HRMS (TOF ESI+) m/z calcd for C₂₆H₃₂NO₂F₃Cl [M+H]+: 482.2074, found: 482.2068.

(±)-methyl 2-((2SR,4RS)-1-(4-chlorophenyl)-4-oxopentyl)-2-(4-(trifluoromethyl)phenyl)piperidin-4-yl)acetate [62].

Substrate (±)-Methyl 2-((2SR,4RS)-1-(4-chlorophenyl)pentyl)-2-(4-(trifluoromethyl)phenyl)piperidin -4-yl)acetate 61 (154.0 mg, 0.300 mmol, 1.0 equiv), was protected with HBF₄•OEt₂ (45.5 µL, 0.330 mmol, 54 wt.%, 1.1 equiv.) in CH₂Cl₂ (1.2 mL, 0.25M) according to the general procedure for the HBF₄•OEt₂ protection in Supplementary Figure 3. The reaction was run with General Method C: Slow Catalyst Addition Protocol at 0 ºC: the resultant 61•HBF₄ (0.300 mmol, 1.0 equiv.), ClCH₂CO₂H (425 mg, 4.5 mmol, 15.0 equiv.), (R,R)-Mn(CF₃-PDP) (40.7 mg, 0.030 mmol, 10 mol%), 50% wt. H₂O₂ (204 mg, 3.0 mmol, 10.0 equiv.), MeCN (0.6 mL in 40 mL vial, 0.38 mL with catalyst, 3.75 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with 9 mL saturated NaHCO₃ and DCM as described in General Method C. Flash column chromatography on silica using 15% MeOH/CHCl₃ as eluent afforded product as a pale yellow oil.
Run 1: (76.6 mg, 0.154 mmol, 51.5% yield), (23.0 mg, 0.048 mmol, 15.9% rsm). Run 2: (85.3 mg, 0.172 mmol, 57.3% yield), (13.2 mg, 0.027 mmol, 9.1% rsm). Run 3: (84.4 mg, 0.170 mmol, 56.7% yield), (13.8 mg, 0.029 mmol, 9.5% rsm). Average: 55.2% yield ± 3.2%, 11.5% rsm ± 3.8%.

1H-NMR (500 MHz, CDCl3) δ 7.63 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 7.9 Hz, 2H), 7.29 – 7.23 (m, 2H), 7.16 – 7.09 (m, 2H), 3.72 (dd, J = 11.0, 2.8 Hz, 1H), 3.61 (s, 3H), 3.39 (dd, J = 10.6, 3.7 Hz, 1H), 2.69 (dt, J = 11.4, 3.4 Hz, 1H), 2.38 (td, J = 11.8, 2.5 Hz, 1H), 2.27 – 2.01 (m, 5H), 1.98 (s, 3H), 1.96 – 1.85 (m, 2H), 1.81 (dq, J = 12.9, 2.9 Hz, 1H), 1.64 (dt, J = 13.5, 2.5 Hz, 1H), 1.35 – 1.27 (m, 1H), 1.11 (qd, J = 12.2, 3.8 Hz, 1H). 13C-NMR (126 MHz, CDCl3) δ 207.8, 172.9, 148.5, 139.3, 132.8, 130.0, 129.7 (q, J = 32.0 Hz), 128.4, 128.2, 125.8 (q, J = 3.8 Hz), 124.2 (q, J = 272.1 Hz), 64.4, 60.6, 51.6, 44.4, 42.8, 41.3, 41.0, 33.7, 32.3, 30.1, 16.1. 19F-NMR (470 MHz, CDCl3) δ –62.7. HRMS (TOF ESI+) m/z calculated for C26H30NO3F3Cl [M+H]+: 496.1866, found 496.1858.

**Oxidative derivatization of antidepressant citalopram**

1-(3-(dimethylamino)propyl)-1-(4-fluorophenyl)-3-(2-hydroxynaphthalen-1-yl)-1,3-dihydroisobenzofuran-5-carbonitrile [64].

In a 20 mL vial charge with (±)-citalopram•HBr (commercially available from Sigma-Aldrich, 121.6 mg, 0.30 mmol, 1.0 equiv.) in 3 mL DCM. 3mL 3M NaOH solution was added and the reaction was stirred for 30 min. The reaction was extracted with 20 mL DCM 3 times and the combined organic layer was dried over Na2SO4 and concentrated. The residue was transferred into a 40 mL vial and the free amine citalopram was protected with HBF4•OEt2 (45.5 µL, 0.330 mmol, 54 wt.%, 1.1 equiv.) in CH2Cl2 (1.2 mL, 0.25M) according to the general procedure for the HBF4•OEt2 protection in Supplementary Figure 3. The reaction was run with **General Method A: Single Catalyst Addition Protocol with slightly modification**: the resultant citalopram•HBF4 (0.300 mmol, 1.0 equiv.), CICH2CO2H (425 mg, 4.5 mmol, 15.0 equiv.), (R,R)-Mn(CF3-PDP) (40.7 mg, 0.030 mmol, 10 mol%), 50% wt. H2O2 (40.8 mg, 0.6 mmol, 2.0 equiv.), MeCN (0.6 mL in 40 mL vial, 0.38 mL with catalyst, 3.75 mL with oxidant). The reaction was run at -36 ºC with dry ice/1,2-dichloroethane bath. The reaction was concentrated, redissolved in 15 mL DCM and quenched with 10 mL 1M NaOH solution for 30 min. The aqueous layer was extracted with 20 mL DCM 3 times and the combined organic layer was dried over Na2SO4 and
concentrated. Flash column chromatography on silica (35 mm fritted glass column, 50 mL SiO2) using 5% methanol/DCM → 10% methanol/DCM → 20% methanol/DCM as eluent afforded crude hemiacetal in about 50% yield. The crude hemiacetal was transferred into an oven-dried 40 mL vial and dried on high vacuum overnight. The crude hemiacetal was charged with 2-naphthol (43.3 mg, 0.3 mmol, 1.0 equiv.) and anhydrous DCM (1.6 mL), cooled to -78 ºC and BF₃•OEt₂ (73.8 µL, 0.6 mmol, 2.0 equiv.) was added dropwise. The reaction was allowed to react at -78 ºC for 1 h and 0 ºC for 2 h before diluted with DCM (10 mL) and quenched with 1M NaOH (15 mL) for 20 min. The aqueous layer was extracted with 20 mL DCM 3 times and the combined organic layer was dried over Na₂SO₄ and concentrated. Flash column chromatography on silica (35 mm fritted glass column, 50 mL SiO₂) using 2% methanol/DCM → 5% methanol/DCM → 10% methanol/DCM → 20% methanol/DCM as eluent afforded arylated product as a mixture of diastereomers.

**Run 1:** 62.9 mg, 0.135 mmol, 3.0:1 d.r., 44.9% yield over 2 steps. **Run 2:** 59.0 mg, 0.126 mmol, 3.4:1 d.r., 42.2% yield over 2 steps. **Run 3:** 56.3 mg, 0.121 mmol, 3.2:1 d.r., 40.2% yield over 2 steps. **Average:** 42.4% yield ± 2.4%, 3.2:1 d.r.

The site of arylation was assigned based on a combination of ¹H, gHSQC and gHMBC NMRs. The assigned site of reaction matches the reported arylation of proline-hemiaminal with 2-naphthol.¹¹

**Major diastereomer:** ¹H-NMR (500 MHz, CDCl₃) δ 7.85 – 7.79 (m, 3H), 7.67 – 7.63 (m, 2H), 7.55 – 7.48 (m, 3H), 7.38 (dd, J = 7.8, 6.8 Hz, 1H), 7.26 – 7.25 (m, 1H), 7.12 (s, 1H), 7.07 (t, J = 8.6 Hz, 2H), 6.94 (s, 1H), 2.86 (dt, J = 12.9, 7.3 Hz, 1H), 2.54 (ddd, J = 11.9, 8.3, 6.1 Hz, 1H), 2.41 (s, 6H), 2.46 – 2.38 (m, 2H), 1.81 – 1.70 (m, 2H). ¹³C-NMR (126 MHz, CDCl₃) δ 162.4 (d, J = 247.2 Hz), 154.9, 148.3, 143.4, 137.3 (d, J = 3.0 Hz), 132.9, 132.3, 131.4, 129.3, 129.0, 127.6, 127.2 (d, J = 8.1 Hz), 126.2, 123.4, 122.6, 121.0, 120.0, 118.6, 115.9 (d, J = 21.4 Hz), 113.0, 112.5, 90.7, 78.7, 58.9, 44.4, 38.7, 21.1. ¹⁹F-NMR (470 MHz, CDCl₃) δ −114.4. HRMS (TOF ESI+) m/z calcd for C₃₀H₂₈N₂O₂F [M+H]+: 467.2135, found: 467.2135.

Minor diastereomer is mixed with the major diastereomer and cannot be cleanly characterized.

**Rapid access of drug lead metabolite lead to piragliatin**

![Rapid access of drug lead metabolite lead to piragliatin](image)

(-)-methyl (R)-2-(3-chloro-4-(methylsulfonyl)phenyl)-3-cyclopentylpropanoate [(-)-66].
In a flame dried 50 mL recovery flask, (R)-2-(3-chloro-4-(methylsulfonyl)phenyl)-3-cyclopentylpropanoic acid synthesized according to literature procedure$^{12}$ (814 mg, 2.46 mmol, 1.0 equiv.) was dissolved in MeOH (24.6 mL) and cooled to -30 °C. SOCl$_2$ (1.25 mL, 17.2 mmol, 7.0 equiv.) was added dropwise and the reaction was warmed up to room temperature then refluxed at 70 °C for 8 h. The reaction was concentrated and plugged through a silica plug eluting with 40% ethyl acetate/hexanes to afford product as a colorless oil (777.0 mg, 2.25 mmol) in 92% yield. The enantiomeric excess (ee) was determined by chiral HPLC (AD-RH, 55:45 MeCN:H$_2$O, 0.5 mL/min flow rate, 254 nm): 93%.

$^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 8.09 (d, $J$ = 8.2 Hz, 1H), 7.53 (d, $J$ = 1.6 Hz, 1H), 7.41 (dd, $J$ = 8.2, 1.7 Hz, 1H), 3.69 (s, 3H), 3.69 – 3.65 (m, 1H), 3.26 (s, 3H), 2.09 (dd, $J$ = 13.4, 8.3, 7.2 Hz, 1H), 1.84 – 1.79 (m, 1H), 1.77 – 1.71 (m, 2H), 1.63 – 1.58 (m, 3H), 1.53 – 1.43 (m, 2H), 1.16 – 1.05 (m, 2H). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 173.3, 147.2, 136.9, 132.8, 131.5, 131.1, 127.4, 52.6, 50.6, 42.9, 39.9, 37.9, 32.9, 32.3, 25.2 (2 carbons). [$\alpha$]$^D_{25}$ = -44.8° (c = 0.87, CHCl$_3$). HRMS (TOF ESI+) $m$/z calcd for C$_{16}$H$_{22}$O$_4$SCl [M+H]$^+$: 345.0927, found: 345.0928.

HPLC trace for racemic compound:

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### Area Percent Report

| Signal | Multiplier | Dilution |
|--------|------------|----------|
| 1      | 1.0000     | 1.0000   |

Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref-off

| Peak RetTime | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|--------------|-------------|--------------|--------------|--------|
| 1            | 13.864      | 0.5301       | 3006.94995   | 88.84326 | 48.9790 |
| 2            | 15.593      | 0.6406       | 3132.31120   | 76.17677 | 51.0210 |

Totals: 6139.26123 165.02003

Results obtained with standard integrator!
HPLC trace for (-)-66 synthesized according to the described procedure:

The reaction was run with General Method A: Single Catalyst Addition Protocol. methyl (2R)-2-(3-chloro-4-(methylsulfonyl)phenyl)-3-(3-oxocyclopentyl)propanoate [67].

The reaction was run at 0 °C with ice bath. The reaction was worked up with 9 mL saturated NaHCO₃ and DCM as described in General Method A. Flash
column chromatography on silica (35 mm fritted glass column, 100 mL SiO$_2$) using 30% ethyl acetate/hexanes $\rightarrow$ 50% ethyl acetate/ as eluent afforded clean ε-ketone (67) as a colorless oil and a fraction of δ-ketone with small impurities.

**Run 1:** (57.6 mg, 0.161 mmol, 53.5% yield of ε-ketone, 1:1 d.r.), (~14% yield of δ-ketone), <5% rsm.

**Run 2:** (59.2 mg, 0.165 mmol, 55.0% yield of ε-ketone, 1:1 d.r.), (~12% yield of δ-ketone), <5% rsm.

**Run 3:** (58.5 mg, 0.163 mmol, 54.3% yield of ε-ketone, 1:1 d.r.), (~14% yield of δ-ketone), <5% rsm.

**Average:** 54.3% yield $\pm$ 0.8% of ε-ketone, 1:1 d.r., <5% rsm.

ε-ketone 67 was isolated as a mixture of diastereomers with ~1:1 ratio. $^1$H-NMR (500 MHz, methylene chloride-d$_2$) δ 8.08 (dd, $J = 8.3, 0.9$ Hz, 1H), 7.57 – 7.55 (m, 1H), 7.45 – 7.42 (m, 1H), 3.74 – 3.71 (m, 1H), 3.67 (s, 3H), 3.24 (s, 3H), 2.34 – 1.91 (m, 7H), 1.84 – 1.75 (m, 1H), 1.58 – 1.50 (m, 1H). $^{13}$C-NMR (126 MHz, methylene chloride-d$_2$) 217.42 & 217.41, 172.54 & 172.49, 146.42 & 146.37, 137.1, 132.7, 131.35 & 131.32, 131.0, 127.25 & 127.22, 52.4, 49.6 & 49.5, 44.7 & 44.3, 42.7, 38.97 & 38.94, 38.30 & 38.25, 34.98 & 34.92, 29.5 & 29.1. HRMS (TOF ESI+) $m/z$ calculated for C$_{16}$H$_{20}$O$_5$SCl [M+H]$^+$: 359.0720, found 359.0720.

(2R)-2-(3-chloro-4-(methylsulfonyl)phenyl)-3-(3-oxocyclopentyl)-N-(pyrazin-2-yl)propanamide [S53].

In a 20 mL vial charged with methyl (2R)-2-(3-chloro-4-(methylsulfonyl)phenyl)-3-(3-oxocyclopentyl)propanoate 67 (95.9 mg, 0.267 mmol) and 3:1 THF/H$_2$O solution (0.8 mL). LiOH•H$_2$O (56.0 mg, 1.335 mmol, 5 equiv,) was added in 1 portion at 0 ºC and the reaction was stirred at room temp for 24 hours. The reaction was cooled back to 0 ºC and quenched with 1M KHSO$_4$ solution until pH=2. The resulting mixture was extracted with 15 mL ethyl acetate, and the aqueous layer was extracted with 15 mL ethyl acetate twice. Combined organic layer was washed with brine and dried over MgSO$_4$ to obtain the crude acid. After drying under high vacuum overnight, the acid was dissolved in anhydrous DCM (2.7 mL) in an oven dried 20 mL vial, added oxalyl chloride (35 µL, 0.294 mmol, 1.1 equiv.) and 1 drop of DMF at 0 ºC. The reaction was kept at 0 ºC for 10 min then room temp for 25 min to get a soluble solution of acid chloride. A solution of 2-aminopyrazine (55.9 mg, 0.59 mmol, 2.2 equiv.), pyridine (47 µL, 0.59 mmol, 2.2 equiv.) in anhydrous THF (2.2 mL) was added to the reaction and solid was crushed out
immediately. The reaction was left at room temp for 24 h, concentrated and purified by flash column chromatography on silica (35 mm fritted glass column, 50 mL SiO2) using 70% ethyl acetate/hexanes → 90% ethyl acetate/ as eluent afforded product as a white solid.

**Result:** 60.9 mg, 0.144 mmol, 54% yield over 2 steps.

Product is a diastereomeric mixture with ~1:1 d.r. ¹H-NMR (500 MHz, methanol-ᵈ₂) δ 9.40 (s, 1H), 8.38 – 8.32 (m, 2H), 8.12 (d, J = 8.3 Hz, 1H), 7.82 – 7.80 (m, 1H), 7.70 – 7.68 (m, 1H), 4.10 – 4.04 (m, 1H), 3.34 (s, 3H), 2.44 – 1.90 (m, 8H), 1.69 – 1.60 (m, 1H). This NMR matches the reported spectra.¹² The reported δ-ketone isomer has a benzylic peak at 4.21 – 4.41 ppm. Better NMR can be obtained by using the more soluble chloroform solvent: ¹H-NMR (500 MHz, CDCl₃) δ 9.51 (s, 1H), 8.43 (t, J = 17.1 Hz, 1H), 8.35 (d, J = 2.5 Hz, 1H), 8.19 (s, 1H), 8.11 (ddd, J = 7.3, 4.6, 2.5 Hz, 1H), 7.63 – 7.61 (m, 1H), 7.51 (ddd, J = 8.4, 3.9, 1.7 Hz, 1H), 3.78 – 3.77 (m, 1H), 3.28 (s, 3H), 2.47 – 2.29 (m, 3H), 2.25 – 1.82 (m, 5H), 1.63 – 1.55 (m, 1H).¹³C-NMR (126 MHz, CDCl₃) 217.9, 169.9, 147.8, 146.6, 146.4, 142.2, 141.0, 137.2, 133.4, 131.7, 131.4 & 131.3, 127.1 & 127.1, 45.0 & 44.7, 43.0, 39.6, 39.68 & 39.53, 39.64 & 39.49, 35.3 & 35.1, 29.8 & 29.6. HRMS (TOF ESI+) m/z calculated for C₁₀H₂₁N₃O₄SCl [M+H]⁺: 422.0941, found 422.0929.
IX. Sequential 2º benzylic/2º aliphatic oxidation of ethinylestradiol

derivative

Synthesis of ethinylestradiol derivative (−)-69

(−)-methyl 3-((8R,9S,13S,14S,17S)-17-hydroxy-13-methyl-3-(pivaloyloxy)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)propiolate [(−)-69].
In a flame dried 100 mL flask, 2.4 mL (27.0 mmol, 1.5 equiv.) methyl propionate was dissolved in 36 mL anhydrous THF. 16.9 mL 1.6 M n-BuLi (27.0 mmol, 1.5 equiv.) solution was added slowly at -78 ºC and the mixture was stirred at -78 ºC for 10 min after which the organolithium reagent solution was cannulated into a 100 mL flame dried flask containing 6.38 g (18.0 mmol, 1.0 equiv.) pivalated estrone in 36 mL anhydrous THF at -78 ºC. The reaction was stirred at -78 ºC for 30 min then at room temperature for 10 min. Saturated NH₄Cl was added to quench the reaction and the aqueous layer was extracted with 3 x 30 mL ether. The combined organic layer was washed with 20 mL brine, dried with MgSO₄ and concentrated. The crude mixture was purified by CombiFlash (40g silica column) using hexanes 30% EtOAc/hexanes gradient eluent to provide 4.60 g (10.48 mmol) of pure product as a slightly yellow solid (58% yield).

1H-NMR (500 MHz, CDCl₃) δ 7.27 (d, J = 7.3 Hz, 1H), 6.81 (dd, J = 8.4, 2.6 Hz, 1H), 6.76 (d, J = 2.4 Hz, 1H), 3.79 (s, 3H), 2.87 – 2.85 (m, 2H), 2.42 – 2.36 (m, 2H), 2.28 (td, J = 11.1, 4.3 Hz, 1H), 2.09 – 2.02 (m, 2H), 1.90 – 1.77 (m, 4H), 1.67 (ddd, J = 12.0, 10.6, 7.4 Hz, 1H), 1.58 – 1.37 (m, 4H), 1.34 (s, 9H), 0.90 (s, 3H). 13C-NMR (126 MHz, CDCl₃) δ 177.5, 154.1, 149.0, 138.2, 137.5, 126.4, 121.5, 118.7, 90.9, 80.1, 78.0, 52.9, 50.0, 48.0, 43.7, 39.2, 39.2, 38.8, 33.1, 29.6, 27.3, 27.1, 26.3, 23.1, 12.8. [α]D₂³ = -14.6 (c = 0.96, CHCl₃). HRMS (TOF ESI+) m/z calculated for C₂₇H₃₅O₅ [M+H]+: 439.2484, found 439.2476.

**Benzylic oxidation of ethinylestradiol derivative (-)-69**

**Condition I:**

The reaction was run with **General Method A: Single Catalyst Addition Protocol:** methyl 3-((8R,9S,13S,14S,17S)-17-hydroxy-13-methyl-3-(pivaloyloxy)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)propiolate (-)-69 (131.6 mg, 0.300 mmol, 1.0 equiv), (R,R)-Mn(CF₃-PDP) (20.3 mg, 0.015 mmol, 5 mol%), ClCH₂CO₂H (213 mg, 2.25 mmol, 7.5 equiv.), 50% wt. H₂O₂ (204 mg, 3.0 mmol, 10.0 equiv.), 4:1 MeCN:DCM mixture (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath and worked up with 9 mL saturated NaHCO₃ and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO₂) using 20% EtOAc/hexanes 25% EtOAc/hexanes 50% EtOAc/hexanes as eluent afforded benzylic ketone oxidation product (-)-70 as a white solid.

**Run 1:** (100.6 mg, 0.222 mmol, 74.1% yield of benzylic ketone (-)-70), 0% rsm.  **Run 2:** (95.9 mg, 0.212 mmol, 70.6% yield of benzylic ketone (-)-70), 0% rsm.  **Average:** 72.4% yield of benzylic ketone (-)-70, 0% rsm.
This oxidation can be scaled up with further reduction of catalyst loading to 2 mol% without loss of reactivity. The reaction was run with General Method A: Single Catalyst Addition Protocol: methyl 3-(((8R,9S,13S,14S,17S)-17-hydroxy-13-methyl-3-(pivaloyloxy)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)propiolate (-)-69 (1316 mg, 3.0 mmol, 1.0 equiv), (R,R)-Mn(CF3-PDP) (81.3 mg, 0.060 mmol, 2 mol%), ClCH2CO2H (2.126 g, 22.5 mmol, 7.5 equiv.), 50% wt. H2O2 (2040 mg, 30.0 mmol, 10.0 equiv.), 4:1 MeCN:DCM mixture (6 mL in 100 mL recovery flask with a stir bar, 37.5 mL with oxidant in a 60 mL syringe). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath and worked up with 40 mL saturated NaHCO3 and DCM as described in General Method A. 

Run 1: (998.9 mg, 2.207 mmol, 73.6% yield of benzylic ketone (-)-70), 0% rsm.

Condition II:
The reaction was run with General Method A: Single Catalyst Addition Protocol: methyl 3-(((8R,9S,13S,14S,17S)-17-hydroxy-13-methyl-3-(pivaloyloxy)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)propiolate (-)-69 (877.1 mg, 2.000 mmol, 1.0 equiv), (R,R)-Mn(CF3-PDP) (135.5 mg, 0.100 mmol, 5 mol%), ClCH2CO2H (1.418 g, 15.0 mmol, 7.5 equiv.), 50% wt. H2O2 (272 mg, 4.0 mmol, 2.0 equiv.), 4:1 MeCN:DCM mixture (4.0 mL in 50 mL recovery flask, 25.0 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath and worked up with 30 mL saturated NaHCO3 and DCM as described in General Method A. Flash column chromatography on silica (50 mm fritted glass column, 200 mm SiO2) using 20% EtOAc/hexanes → 30% EtOAc/hexanes → 40% EtOAc/hexanes → 60% EtOAc/hexanes as eluent afforded benzylic ketone oxidation product (-)-70 and benzylic alcohol oxidation product (-)-71 separately as white solids.

Run 1: (359.2 mg, 0.790 mmol, 39.5% yield of benzylic alcohol (-)-71), (262.5 mg, 0.580 mmol, 29.0% yield of benzylic ketone (-)-70), (159.3 mg, 0.363 mmol, 18.2% rsm). Run 2: (386.0 mg, 0.849 mmol, 42.5% yield of benzylic alcohol (-)-71), (248.6 mg, 0.549 mmol, 27.5% yield of benzylic ketone (-)-70), (153.4 mg, 0.350 mmol, 17.5% rsm). Average: 41.0% yield of benzylic alcohol (-)-71, 28.3% yield of benzylic ketone (-)-70, 17.9% rsm.

(-)-methyl 3-((8R,9S,13S,14S,17S)-17-hydroxy-13-methyl-6-oxo-3-(pivaloyloxy)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)propiolate [(--)-70].

- 1H-NMR (749 MHz, methylene chloride- d2) δ 7.67 (d, J = 2.7 Hz, 1H), 7.48 (d, J = 8.6 Hz, 1H), 7.24 (dd, J = 8.5, 2.7 Hz, 1H), 3.77 (s, 3H), 2.73 (dd, J = 16.8, 3.4 Hz, 1H), 2.61 (td, J = 10.9, 4.7 Hz, 1H), 2.49 (dd, J = 13.3, 4.4, 2.8 Hz, 1H), 2.39 (ddd, J = 14.0, 9.3, 5.8 Hz, 1H), 2.35 (br. s, 1H), 2.31 (dd, J = 16.8, 13.4 Hz, 1H), 2.06 (ddd, J = 13.9, 12.0, 3.6 Hz, 1H), 2.03 – 1.99 (m, 1H), 1.92 – 1.80 (m, 4H), 1.66 (qd, J = 12.5, 4.5 Hz, 1H), 1.48 – 1.41 (m, 1H), 1.35 (s, 9H), 0.91 (s, 3H). 13C-NMR
(126 MHz, methylene chloride-$d_2$) $\delta$ 197.2, 177.6, 154.3, 150.3, 144.6, 134.1, 127.4, 127.3, 120.2, 90.7, 80.1, 78.5, 53.3, 50.2, 48.1, 43.1, 40.7, 39.5, 39.1, 33.1, 27.4, 26.0, 23.2, 12.8. $[\alpha]_D^{24} = -40.8$ (c = 1.00, CHCl$_3$). HRMS (TOF ESI+) $m/z$ calculated for C$_{27}$H$_{33}$O$_6$ [M+H]$^+$: 453.2277, found 453.2274.

$(-)$-methyl 3-((6R,8R,9S,13S,14S,17S)-6,17-dihydroxy-13-methyl-3-(pivaloyloxy)-7,8,9,11,12,13,14,15,16,17-decahydro-$6H$-cyclopenta[a]phenanthren-17-yl)propiolate $[(--)-71]$.

$^1$H-NMR (749 MHz, methylene chloride-$d_2$) $\delta$ 7.35 (d, $J = 8.6$ Hz, 1H), 7.05 (d, $J = 2.6$ Hz, 1H), 6.94 (dd, $J = 8.5$, 2.6 Hz, 1H), 4.76 (br. s, 1H), 3.76 (s, 3H), 2.43 – 2.40 (m, 1H), 2.37 (ddd, $J = 13.9$, 9.7, 5.7 Hz, 1H), 2.31 (s, 1H), 2.21 (td, $J = 11.4$, 4.4 Hz, 1H), 2.05 (ddd, $J = 13.9$, 11.9, 3.9 Hz, 1H), 2.01 – 1.98 (m, 2H), 1.85 – 1.78 (m, 4H), 1.71 (td, $J = 11.6$, 7.5 Hz, 1H), 1.65 – 1.54 (m, 2H), 1.51 – 1.45 (m, 1H), 1.34 (s, 9H), 0.92 (s, 3H). $^{13}$C-NMR (126 MHz, methylene chloride-$d_2$) $\delta$ 177.8, 154.4, 150.0, 140.0, 138.1, 126.9, 123.0, 121.6, 91.1, 80.3, 78.3, 67.6, 53.2, 50.0, 48.5, 44.1, 39.5, 39.2, 36.6, 33.9, 33.5, 27.4, 26.3, 23.3, 13.0. $[\alpha]_D^{24} = -34.4$ (c = 0.98, CHCl$_3$). HRMS (TOF ESI+) $m/z$ calculated for C$_{27}$H$_{34}$O$_6$Na [M+Na]$^+$: 477.2253, found 477.2252.

The stereochemistry of the benzylic alcohol was assigned based on the NMR of the following acetate protected compound.

$(-)$-methyl 3-((6R,8R,9S,13S,14S,17S)-6-acetoxy-17-hydroxy-13-methyl-3-(pivaloyloxy)-7,8,9,11,12,13,14,15,16,17-decahydro-$6H$-cyclopenta[a]phenanthren-17-yl)propiolate [+]72].

In a 20 mL vial, 444.9 mg (0.98 mmol, 1.0 equiv.) methyl 3-((6R,8R,9S,13S,14S,17S)-6,17-dihydroxy-13-methyl-3-(pivaloyloxy)-7,8,9,11,12,13,14,15,16,17-decahydro-$6H$-cyclopenta[a]phenanthren-17-yl)propiolate $[-]$71 was dissolved in 3 mL anhydrous DCM. 111 $\mu$L (1.18 mmol, 1.2 equiv.) acetic anhydride and 164 $\mu$L (1.18 mmol, 1.2 equiv.) triethylamine were added sequentially at 0 °C and the reaction was warmed to room temperature. Another batch of both 0.6 equiv. acetic anhydride and 0.6 equiv. triethylamine were added after 24 and 48 hours at room temperature. The crude mixture was loaded directly on silica (50 mm fritted glass column, 200 mm SiO$_2$) using 20% EtOAc/hexanes $\rightarrow$ 50% EtOAc/hexanes gradient eluent gave 419.0 mg (0.84 mmol) of pure product as a white solid (86% yield).
$^1$H-NMR (749 MHz, methylene chloride-$d_2$) $\delta$ 7.38 (d, $J = 8.6$ Hz, 1H), 6.98 (dd, $J = 8.5$, 2.6 Hz, 1H), 6.95 (d, $J = 2.5$ Hz, 1H), 5.97 (dd, $J = 4.4$, 2.1 Hz, 1H), 3.76 (s, 3H), 2.44 (dt, $J = 13.3$, 3.8 Hz, 1H), 2.40 (br. s, 1H), 2.37 (ddd, $J = 13.9$, 9.6, 5.6 Hz, 1H), 2.24 (td, $J = 11.4$, 4.4 Hz, 1H), 2.05 (s, 3H), 2.07 – 2.00 (m, 2H), 1.87 – 1.77 (m, 4H), 1.71 – 1.63 (m, 2H), 1.58 (qd, $J = 12.4$, 4.9 Hz, 1H), 1.43 (qd, $J = 12.1$, 5.9 Hz, 1H), 1.33 (s, 9H), 0.93 (s, 3H). 13C-NMR (126 MHz, methylene chloride-$d_2$) $\delta$ 177.7, 170.8, 154.4, 149.9, 138.9, 136.0, 126.9, 123.3, 122.3, 90.9, 80.3, 78.3, 69.4, 53.2, 49.8, 48.4, 44.0, 39.5, 39.2, 34.7, 34.1, 33.4, 27.4, 26.3, 23.3, 21.9, 13.0. $[\alpha]_D^{24} = +25.1$ (c = 0.94, CHCl$_3$). HRMS (TOF ESI+) $m/z$ calculated for C$_{29}$H$_{36}$O$_7$Na [M+Na]$^+$: 519.2359, found 519.2355.

Assignment of stereochemistry: 5.97 (dd, $J = 4.4$, 2.1 Hz, 1H) is assigned as the benzylic proton bearing OAc substitution based on HMBC and HSQC $^1$H-$^1$C 2D NMRs. The small coupling constants (4.4Hz and 2.1Hz) suggests the benzylic proton is in pseudo-equatorial conformation. This assignment can be further confirmed by the single crystal structure of the remote oxidation product.

Remote C12 methylene oxidation of (-)-70

(-)-methyl 3-((8R,9S,12R,13S,14S,17S)-12,17-dihydroxy-13-methyl-6-oxo-3-(pivaloyloxy)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)propiolate [(-)-73].

The reaction was run with General Method A: Single Catalyst Addition Protocol with 1X recycle of the recovered starting material: methyl 3-((8R,9S,13S,14S,17S)-17-hydroxy-13-methyl-6-oxo-3-(pivaloyloxy)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)propiolate (-)-70 (135.8 mg, 0.300 mmol, 1.0 equiv), (R,R)-Mn(CF$_3$-PDP) (40.7 mg, 0.030 mmol, 10 mol%), ClCH$_2$CO$_2$H (425 mg, 4.50 mmol, 15.0 equiv.), 50% wt. H$_2$O$_2$ (204 mg, 3.0 mmol, 10.0 equiv.), 4:1 MeCN:DCM mixture (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 °C with ice bath and worked up with 9 mL saturated NaHCO$_3$ and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO$_2$) using 20% acetone/hexanes $\rightarrow$ 25% acetone/hexanes $\rightarrow$ 40% acetone/hexanes as eluent afforded remote oxidation product (-)-73 and recovered starting material as white solids. The recovered starting material was transferred into a 2-dram vial and re-subjected to single catalyst addition C—H oxidation conditions: (R,R)-Mn(CF$_3$-PDP) (10 mol%), ClCH$_2$CO$_2$H (15.0 equiv.), 50% wt. H$_2$O$_2$ (10.0 equiv.), 4:1 MeCN:DCM mixture (0.25 M with starting material in 2-dram vial to enable full dissolution of starting material, 1.25 mL per 0.1 mmol starting material with oxidant).
Run 1: cycle 1: (55.6 mg, 0.119 mmol, 39.6% yield), (30.5 mg, 0.067 mmol, 22.5% rsm); cycle 2: (11.5 mg, 0.025 mmol, 36.4% yield), (<5 mg, rsm); overall: (67.1 mg, 0.143 mmol, 47.7% yield), <5% rsm.

Run 2: cycle 1: (55.3 mg, 0.118 mmol, 39.3% yield), (31.1 mg, 0.069 mmol, 22.9% rsm); cycle 2: (10.1 mg, 0.022 mmol, 31.3% yield), (<5 mg, rsm); overall: (65.4 mg, 0.140 mmol, 46.5% yield), <5% rsm.

Average: 47.1% yield, <5% rsm.

1H-NMR (749 MHz, methylene chloride-d2) δ 7.67 (d, J = 2.6 Hz, 1H), 7.45 (d, J = 8.6 Hz, 1H), 7.25 (dd, J = 8.5, 2.7 Hz, 1H), 4.30 (dd, J = 11.2, 4.7 Hz, 1H), 3.77 (s, 3H), 2.80 (br. s, 1H), 2.76 – 2.71 (m, 2H), 2.56 (dt, J = 12.5, 4.7 Hz, 1H), 2.38 (dd, J = 13.9, 9.5, 5.6 Hz, 1H), 2.26 (dd, J = 16.9, 13.4 Hz, 1H), 2.16 (br. s, 1H), 2.08 (ddd, J = 13.9, 11.9, 4.0 Hz, 1H), 2.00 (dt, J = 13.3, 11.0, 3.5 Hz, 1H), 1.85 (dddd, J = 12.1, 9.4, 7.7, 4.0 Hz, 1H), 1.77 (td, J = 11.4, 7.7 Hz, 1H), 1.70 (td, J = 12.4, 11.2 Hz, 1H), 1.55 (qd, J = 12.1, 5.6 Hz, 1H), 1.35 (s, 9H), 0.95 (s, 3H). 13C-NMR (126 MHz, methylene chloride-d2) δ 196.7, 177.6, 154.3, 150.6, 143.6, 134.0, 127.6, 127.1, 120.4, 90.2, 80.3, 78.5, 74.9, 55.3, 52.0, 49.1, 43.9, 42.1, 39.9, 39.5, 38.4, 34.8, 27.4, 23.0, 7.7. [α]D<sup>24</sup> = -63.3 (c = 1.00, CHCl3). HRMS (TOF ESI+) m/z calculated for C<sub>27</sub>H<sub>33</sub>O<sub>7</sub> [M+H]<sup>+</sup>: 469.2226, found 469.2221.

The site of remote oxidation was assigned based on 2D NMR analysis including DQCOSY, HSQC, HMBC and NOESY. The assignment was further confirmed by the crystal structure of the remote oxidation product (-)-73.

Crystal Structure for (-)-73

Ethanol was added dropwisely to a half dram vial containing 5 mg of (-)-73 with ~0.2 mL hexanes until the material fully dissolved. The vial was loosely capped allowing n-pentane to diffuse into the mixture. Single crystal for X-ray crystallography analysis was obtained in ~2 days.

Supplementary X-Ray Table 3. Crystal data and structure refinement for (-)-73.

| Property           | Value   |
|--------------------|---------|
| Empirical formula  | C27 H32 O7 |
| Formula weight     | 468.52  |
| Property                          | Value                                      |
|----------------------------------|--------------------------------------------|
| Temperature                      | 100(2) K                                  |
| Wavelength                       | 1.54178 Å                                 |
| Crystal system                   | Monoclinic                                 |
| Space group                      | I2                                         |
| Unit cell dimensions             | a = 10.7987(4) Å a= 90°.                  |
|                                  | b = 9.1936(3) Å b= 97.5430(10)°.          |
|                                  | c = 27.3628(11) Å g = 90°.                |
| Volume                           | 2693.04(17) Å³                            |
| Z                                | 4                                          |
| Density (calculated)             | 1.156 Mg/m³                                |
| Absorption coefficient           | 0.680 mm⁻¹                                 |
| F(000)                           | 1000                                       |
| Crystal size                     | 0.360 x 0.296 x 0.285 mm³                  |
| Theta range for data collection  | 3.258 to 68.446°.                         |
| Index ranges                     | -13<=h<=12, -11<=k<=10, -32<=l<=32         |
| Reflections collected            | 34276                                      |
| Independent reflections          | 4888 [R(int) = 0.0451]                     |
| Completeness to theta = 67.679°  | 100.0 %                                    |
| Absorption correction            | Semi-empirical from equivalents            |
| Max. and min. transmission       | 0.7488 and 0.6815                          |
| Refinement method                | Full-matrix least-squares on F²            |
| Data / restraints / parameters   | 4888 / 234 / 369                           |
| Goodness-of-fit on F²            | 1.074                                      |
| Final R indices [I>2sigma(I)]    | R1 = 0.0413, wR2 = 0.1168                  |
| R indices (all data)             | R1 = 0.0420, wR2 = 0.1175                  |
| Absolute structure parameter     | 0.14(9)                                    |
| Extinction coefficient           | 0.0040(4)                                  |
| Largest diff. peak and hole      | 0.231 and -0.170 e.Å⁻³                     |

Crystallographic data for 73 can be obtained free of charge from [www.ccdc.cam.ac.uk/structures/](http://www.ccdc.cam.ac.uk/structures/) with deposit number CCDC 1869258.

**Author’s Response to the Level B alert in the checkcif report:** The hydroxyl group protons were located in the difference map and assigned to the most reasonable H-bonding geometries. H1D points toward a void space that is likely at least partially occupied by ethanol, which can act as the acceptor for H1D. See
Remote C12 methylene oxidation of (+)-72

(+)-methyl 3-((6R,8R,9S,12R,13R,14S,17R)-6-acetoxy-12,17-dihydroxy-13-methyl-3-(pivaloyloxy)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)propiolate [(+)-74].

The reaction was run with General Method A: Single Catalyst Addition Protocol: methyl 3-((6R,8R,9S,13S,14S,17S)-6-acetoxy-17-hydroxy-13-methyl-3-(pivaloyloxy)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)propiolate (+)-72 (99.3 mg, 0.200 mmol, 1.0 equiv), (R,R)-Mn(CF3-PDP) (27.1 mg, 0.020 mmol, 10 mol%), ClCH2CO2H (284 mg, 3.00 mmol, 15.0 equiv.), 50% wt. H2O2 (136 mg, 2.0 mmol, 10.0 equiv.), 4:1 MeCN:DCM mixture (0.4 mL in 40 mL vial, 2.50 mL with oxidant). The reaction was run at 0 ºC with ice bath. The reaction was worked up with 9 mL saturated NaHCO3 and DCM as described in General Method A. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO2) using 20% acetone/hexanes → 30% acetone/hexanes → 50% acetone/hexanes as eluent afforded remote oxidation product (+)-74 and recovered starting material as white solids.

**Run 1:** (31.3 mg, 0.061 mmol, 30.5% remote alcohol (+)-74 yield), (16.7 mg, 0.034 mmol, 16.8% rsm);
**Run 2:** (35.1 mg, 0.068 mmol, 34.2% remote alcohol (+)-74 yield), (15.6 mg, 0.031 mmol, 15.7% rsm);
**Run 3:** (31.3 mg, 0.061 mmol, 30.5% remote alcohol (+)-74 yield), (17.7 mg, 0.036 mmol, 17.8% rsm).

**Average:** 31.7% ± 2.1% remote alcohol (+)-74 yield, 16.8% ± 1.1% rsm.

$^1$H-NMR (749 MHz, methylene chloride-$d_2$) δ 7.35 (dd, $J = 8.5, 1.2$ Hz, 1H), 6.99 (dd, $J = 8.5, 2.6$ Hz, 1H), 6.97 (d, $J = 2.5$ Hz, 1H), 5.99 (dd, $J = 4.6, 2.0$ Hz, 1H), 4.23 (dd, $J = 11.1, 4.7$ Hz, 1H), 3.76 (s, 3H), 2.92 (br. s, 1H), 2.52 (dt, $J = 12.5, 4.6$ Hz, 1H), 2.38 – 2.32 (m, 2H), 2.26 (br. s, 1H), 2.09 – 2.05 (m, 1H), 2.06 (s, 3H), 2.02 (dt, $J = 14.2, 2.4$ Hz, 1H), 1.83 (dtddd, $J = 13.0, 9.4, 6.4, 3.3$ Hz, 1H), 1.77 (ddd, $J = 13.5, 11.0, 2.6$ Hz, 1H), 1.65 – 1.60 (m, 3H), 1.54 (qd, $J = 12.0, 5.5$ Hz, 1H), 1.33 (s, 9H), 0.98 (s, 3H). $^{13}$C-NMR (126 MHz, methylene chloride-$d_2$) δ 177.7, 170.8, 154.4, 150.1, 138.0, 136.0, 126.7, 123.4, 122.4, 90.6, 80.4, 78.3, 75.3, 69.3, 53.3, 52.4, 48.7, 42.8, 39.5, 38.5, 35.2, 33.9, 33.9, 27.4, 27.4, 27.4.
23.1, 21.9, 7.8. \([\alpha]_D^{25} = +2.7\ (c = 0.78, \text{CHCl}_3)\). HRMS (TOF ESI+) \(m/z\) calculated for C_{29}H_{36}O_{8}Na [M+Na]^+: 535.2308, found 535.2304.

*The site of remote oxidation was assigned based on 2D NMR analysis including DQ COSY, HSQC, HMBC and NOESY. The assignment was further confirmed by the crystal structure of the remote oxidation product (+)-74.*

**Crystal structure for (+)-74**

Ethyl acetate was added dropwisely to a half dram vial containing 5 mg of (+)-74 with ~0.2 mL n-pentane until the material fully dissolved. The vial was loosely capped allowing n-pentane to diffuse into the mixture. Single crystal for X-ray crystallography analysis was obtained in ~ 2 days.

```

Supplementary X-Ray Table 4. Crystal data and structure refinement for (+)-74.

| Property                              | Value                      |
|---------------------------------------|----------------------------|
| Empirical formula                     | C_{58}H_{74}O_{17} [2(C_{29}H_{36}O_{8})·H_{2}O] |
| Formula weight                        | 1043.17                    |
| Temperature                           | 100(2) K                   |
| Wavelength                            | 1.54178 Å                  |
| Crystal system                        | Monoclinic                 |
| Space group                           | P2_1                       |
| Unit cell dimensions                  | a = 10.7688(3) Å, a = 90°  |
|                                       | b = 16.7429(4) Å, b = 101.6660(7)° |
|                                       | c = 15.5965(4) Å, g = 90° |
| Volume                                | 2753.97(12) Å³            |
| Z                                      | 2                          |
| Density (calculated)                  | 1.258 Mg/m³                |
| Absorption coefficient                | 0.757 mm⁻¹                 |
| F(000)                                | 1116                       |
| Crystal size                          | 0.292 x 0.222 x 0.155 mm³ |
```

122
Theta range for data collection 2.893 to 68.442°.
Index ranges -12<=h<=12, -20<=k<=20, -18<=l<=18
Reflections collected 28965
Independent reflections 10030 [R(int) = 0.0386]
Completeness to theta = 67.679° 99.9 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.7531 and 0.6795
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 10030 / 12 / 717
Goodness-of-fit on F² 1.096
Final R indices [I>2sigma(I)] R1 = 0.0438, wR2 = 0.1094
R indices (all data) R1 = 0.0467, wR2 = 0.1122
Absolute structure parameter -0.08(7)
Extinction coefficient 0.0109(5)
Largest diff. peak and hole 0.487 and -0.285 e.Å⁻³

Crystallographic data for 74 can be obtained free of charge from www.ccdc.cam.ac.uk/structures/ with deposit number CCDC 1869259.

**Oxidation of (+)-72 with TFDO**

![Chemical structure of (+)-72](image1)

![Chemical structure of (+)-75](image2)

(+)-methyl 3-((6R,8S,9R,13S,14S,17S)-6-acetoxy-9,17-dihydroxy-13-methyl-3-(pivaloyloxy)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)propiolate [(+)-75].

To a 1 dram vial charged with methyl 3-((6R,8R,9S,13S,14S,17S)-6-acetoxy-17-hydroxy-13-methyl-3-(pivaloyloxy)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)propiolate (+)-72 (24.8 mg, 0.05 mmol, 1.0 equiv) in 0.5 mL anhydrous DCM (0.1 M). 0.25 mL freshly made TFDO (0.4 M in trifluoroacetone, 0.1 mmol, 2.0 equiv.) was added in 1-2 portions at -20 ºC. The reaction was wrapped with aluminum foil and allowed to stir at -20 ºC. The reaction as monitored by TLC and full
conversion of starting material was reached after 40 min. The reaction was concentrated and purified by CombiFlash (12g column) to yield tertiary benzylic alcohol product (+)-75 as white solid.

**Run 1:** 21.7 mg, 0.042 mmol, 84.6% yield. **Run 2:** 21.2 mg, 0.041 mmol, 82.7% yield. **Average:** 83.7% yield.

\[
\begin{align*}
1H-NMR \ (500 \ MHz, \ methylene \ chloride-d_2) \ & \delta \ 7.59 \ (d, \ J = 8.6 \ Hz, \ 1H), \ 7.05 \ (dd, \ J = 8.6, 2.5 \ Hz, \ 1H), \ 7.00 \ (d, \ J = 2.5 \ Hz, \ 1H), \ 5.98 \\
& \ (dd, \ J = 4.6, 1.9 \ Hz, \ 1H), \ 3.76 \ (s, \ 3H), \ 2.51 - 2.33 \ (m, \ 3H), \ 2.06 \\
& \ (s, \ 3H), \ 2.22 - 2.02 \ (m, \ 5H), \ 1.86 \ (td, \ J = 13.7, 4.3 \ Hz, \ 1H), \ 1.78 \\
& \ - 1.69 \ (m, \ 2H), \ 1.64 \ (ddd, \ J = 12.7, 4.3, 2.6 \ Hz, \ 1H), \ 1.58 \ (br. \ s, \\
& \ 1H), \ 1.42 \ (tt, \ J = 12.1, 6.1 \ Hz, \ 1H), \ 1.34 \ (s, \ 9H), \ 0.94 \ (s, \ 3H). \ 13C-NMR \ (126 \ MHz, \ methylene \ chloride-d_2) \ & \delta \ 177.5, \ 170.9, \ 154.4, \ 151.3, \ 140.6, \ 136.0, \ 126.6, \ 123.9, \ 123.0, \ 91.1, \ 80.2, \ 78.2, \ 69.9, \ 69.2, \ 53.3, \ 48.3, \\
& \ 43.1, \ 39.5, \ 39.3, \ 37.6, \ 32.9, \ 29.5, \ 27.9, \ 27.4, \ 23.2, \ 21.8, \ 12.3. \ [\alpha]_D^{25} = +17.9 \ (c = 0.61, \ CHCl_3). \ HRMS \ (TOF \ ESI+) \ m/z \ calculated \ for \ C_{20}H_{36}O_8Na \ [M+Na]^+: \ 535.2308, \ found \ 535.2305.
\end{align*}
\]
X. References

1. Chen, M. S. & White, M. C. A predictably selective aliphatic C-H oxidation reaction for complex molecule synthesis. *Science* **318**, 783-787 (2007).

2. Gormisky, P. E. & White, M. C. Catalyst-controlled aliphatic C-H oxidations with a predictive model for site-selectivity. *J. Am. Chem. Soc.* **135**, 14052-14055 (2013).

3. McNeill, E. & Du Bois, J. Catalytic C–H oxidation by a triazamacrocyclic ruthenium complex. *Chem. Sci.* **3**, 1810-1813 (2012).

4. Mack, J. B. C., Gipson, J. D., Du Bois, J. & Sigman, M. S. Ruthenium-Catalyzed C-H Hydroxylation in Aqueous Acid Enables Selective Functionalization of Amine Derivatives. *J. Am. Chem. Soc.* **139**, 9503-9506 (2017).

5. Still, W. C., Kahn, M. & Mitra, A. Rapid chromatographic technique for preparative separations with moderate resolution. *J. Org. Chem.* **43**, 2923-2925 (1978).

6. Kawamata, Y. *et al.* Scalable, Electrochemical Oxidation of Unactivated C-H Bonds. *J. Am. Chem. Soc.* **139**, 7448-7451 (2017).

7. Asensio, G., Castellano, G., Mello, R. & González Núñez, M. E. Oxyfunctionalization of Aliphatic Esters by Methyl(trifluoromethyl)dioxirane. *J. Org. Chem.* **61**, 5564-5566 (1996).

8. Adams, A. M., Du Bois, J. & Malik, H. A. Comparative Study of the Limitations and Challenges in Atom-Transfer C-H Oxidations. *Org. Lett.* **17**, 6066-6069 (2015).

9. Ottenbacher, R. V., Samsonenko, D. G., Talsi, E. P. & Bryliakov, K. P. Highly efficient, regioselective, and stereospecific oxidation of aliphatic C-H groups with H2O2, catalyzed by aminopyridine manganese complexes. *Org. Lett.* **14**, 4310-4313 (2012).

10. Howell, J. M., Feng, K., Clark, J. R., Trzepkowski, L. J. & White, M. C. Remote Oxidation of Aliphatic C-H Bonds in Nitrogen-Containing Molecules. *J. Am. Chem. Soc.* **137**, 14590-14593 (2015).

11. Osberger, T. J., Rogness, D. C., Kohrt, J. T., Stepan, A. F. & White, M. C. Oxidative diversification of amino acids and peptides by small-molecule iron catalysis. *Nature* **537**, 214-219 (2016).

12. Sarabu, R. *et al.* Discovery of piragliatin--first glucokinase activator studied in type 2 diabetic patients. *J. Med. Chem.* **55**, 7021-7036 (2012).
| Parameter          | Value       |
|--------------------|-------------|
| Origin             | Varian      |
| Owner              |             |
| Instrument         | Inova       |
| Solvent            | CDCl3       |
| Temperature        | 20.0        |
| Pulse Sequence     | s2pul       |
| Experiment         | 1D          |
| Probe              | QUAD        |
| Number of Scans    | 4           |
| Receiver Gain      | 41          |
| Relaxation Delay   | 15.0000     |
| Pulse Width        | 6.5000      |
| Presaturation Frequency |       |
| Spectrometer Frequency | 499.69   |
| Spectral Width     | 7024.9      |
| Lowest Frequency   | 1021.9      |
| Nucleus            | 1H          |
| Acquired Size      | 32768       |
| Spectral Size      | 65536       |
| Parameter               | Value            |
|-------------------------|------------------|
| 1 Origin                | Varian           |
| 2 Owner                 |                  |
| 3 Instrument            | inova            |
| 4 Solvent               | CDCl3            |
| 5 Temperature           | 20.0             |
| 6 Pulse Sequence        | s2pul            |
| 7 Experiment            | 1D               |
| 8 Probe                 | QUAD             |
| 9 Number of Scans       | 512              |
| 10 Receiver Gain        | 60               |
| 11 Relaxation Delay     | 2.0000           |
| 12 Pulse Width          | 6.0000           |
| 13 Presaturation Frequency |              |
| 14 Spectrometer Frequency | 125.66         |
| 15 Spectral Width       | 30165.9          |
| 16 Lowest Frequency     | 1280.0           |
| 17 Nucleus              | 13C              |
| 18 Acquired Size        | 32768            |
| 19 Spectral Size        | 65536            |

![Chemical Structure Image]
Parameter | Value
--- | ---
1 Origin | Varian
2 Owner | Variance
3 Instrument | inova
4 Solvent | CDC13
5 Temperature | 20.0
6 Pulse Sequence | s2pul
7 Experiment | 1D
8 Probe | hcn
9 Number of Scans | 16
10 Receiver Gain | 54
11 Relaxation Delay | 15.0000
12 Pulse Width | 7.0000
13 Presaturation Frequency | 
14 Spectrometer Frequency | 500.07
15 Spectral Width | 8000.0
16 Lowest Frequency | -1520.1
17 Nucleus | 1H
18 Acquired Size | 32768
19 Spectral Size | 65536
Parameter | Value
---|---
1. Origin | Varian
2. Owner | 
3. Instrument | inova
4. Solvent | CDCl3
5. Temperature | 20.0
6. Pulse Sequence | s2pul
7. Experiment | 1D
8. Probe | QUAD
9. Number of Scans | 512
10. Receiver Gain | 60
11. Relaxation Delay | 2.0000
12. Pulse Width | 6.0000
13. Presaturation Frequency | 
14. Spectrometer Frequency | 125.66
15. Spectral Width | 30165.9
16. Lowest Frequency | 1277.0
17. Nucleus | 13C
18. Acquired Size | 32768
19. Spectral Size | 65536
The NMR spectrum shows a peak at approximately 2.5 ppm, which is labeled as H₂O. The spectrum also includes additional peaks, indicating the presence of other chemical environments. The parameters for the NMR experiment are listed as follows:

- Origin: Varian
- Owner: inf
- Spectrometer: inova
- Solvent: CDCl₃
- Temperature: 20.0
- Pulse Sequence: s2pul
- Experiment: 1D
- Probe: QUAD
- Number of Scans: 4
- Receiver Gain: 41
- Relaxation Delay: 15.0000
- Pulse Width: 6.5000
- Presaturation Frequency
- Spectrometer Frequency: 499.69
- Spectral Width: 7024.9
- Lowest Frequency: -1021.9
- Nucleus: 1H
- Acquired Size: 32768
- Spectral Size: 65536
| Parameter          | Value                      |
|-------------------|----------------------------|
| 1 Origin          | Varian                     |
| 2 Owner           |                            |
| 3 Spectrometer    | inova                      |
| 4 Solvent         | CDCl3                      |
| 5 Temperature     | 20.0                       |
| 6 Pulse Sequence  | s2pul                      |
| 7 Experiment      | 1D                         |
| 8 Probe           | QUAD                       |
| 9 Number of Scans | 970                        |
| 10 Receiver Gain  | 60                         |
| 11 Relaxation Delay | 1.0000                  |
| 12 Pulse Width    | 6.0000                     |
| 13 Presaturation Frequency |                |
| 14 Spectrometer Frequency | 125.66                   |
| 15 Spectral Width | 30165.9                    |
| 16 Lowest Frequency | -1279.0                   |
| 17 Nucleus        | 13C                        |
| 18 Acquired Size  | 32768                      |
| 19 Spectral Size  | 65536                      |
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| Origin             | Bruker BioSpin GmbH                                                  |
| Owner              | user1d                                                               |
| Spectrometer       | spect                                                                |
| Solvent            | CDCl₃                                                                |
| Temperature        | 298.0                                                                |
| Pulse Sequence     | zg30                                                                 |
| Experiment         | 1D                                                                   |
| Probe              | Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)                             |
| Number of Scans    | 16                                                                   |
| Receiver Gain      | 29.7                                                                 |
| Relaxation Delay   | 15.0000                                                              |
| Pulse Width        | 12.0000                                                              |
| Spectrometer Frequency | 500.35                |
| Spectral Width     | 10000.0                                                              |
| Lowest Frequency   | -1922.3                                                              |
| Nucleus            | 1H                                                                   |
| Acquired Size      | 32768                                                                |
| Spectral Size      | 65536                                                                |
| Parameter                        | Value                      |
|---------------------------------|----------------------------|
| 1 Origin                         | Varian                     |
| 2 Owner                          |                            |
| 3 Spectrometer                   | inova                      |
| 4 Solvent                        | CDCl3                      |
| 5 Temperature                    | 20.0                       |
| 6 Pulse Sequence                 | s2pul                      |
| 7 Experiment                     | 1D                         |
| 8 Probe                          | QUAD                       |
| 9 Number of Scans                | 154                        |
| 10 Receiver Gain                 | 60                         |
| 11 Relaxation Delay              | 1.0000                     |
| 12 Pulse Width                   | 6.0000                     |
| 13 Presaturation Frequency       |                            |
| 14 Spectrometer Frequency        | 125.66                     |
| 15 Spectral Width                | 30165.9                    |
| 16 Lowest Frequency             | -1277.5                    |
| 17 Nucleus                       | 13C                        |
| 18 Acquired Size                 | 32768                      |
| 19 Spectral Size                 | 65536                      |

![Chemical structure image]
| Parameter                  | Value                  |
|---------------------------|------------------------|
| 1 Origin                  | Varian                 |
| 2 Owner                   |                        |
| 3 Spectrometer            | inova                  |
| 4 Solvent                 | CDCl3                  |
| 5 Temperature             | 30.0                   |
| 6 Pulse Sequence          | s2pul                  |
| 7 Experiment              | 1D                     |
| 8 Probe                   | QUAD                   |
| 9 Number of Scans         | 8                      |
| 10 Receiver Gain          | 41                     |
| 11 Relaxation Delay       | 15.0000                |
| 12 Pulse Width            | 6.5000                 |
| 13 Presaturation Frequency|                        |
| 14 Spectrometer Frequency | 499.69                 |
| 15 Spectral Width         | 7024.9                 |
| 16 Lowest Frequency       | -1021.4                |
| 17 Nucleus                | 1H                     |
| 18 Acquired Size          | 32768                  |
| 19 Spectral Size          | 65536                  |
| Parameter                  | Value     |
|---------------------------|-----------|
| 1 Origin                  | Varian    |
| 2 Owner                   |           |
| 3 Spectrometer            | inova     |
| 4 Solvent                 | CDCl3     |
| 5 Temperature             | 30.0      |
| 6 Pulse Sequence          | s2pul     |
| 7 Experiment              | 1D        |
| 8 Probe                   | QUAD      |
| 9 Number of Scans         | 961       |
| 10 Receiver Gain          | 60        |
| 11 Relaxation Delay       | 2.0000    |
| 12 Pulse Width            | 6.0000    |
| 13 Presaturation Frequency|           |
| 14 Spectrometer Frequency | 125.66    |
| 15 Spectral Width         | 30165.9   |
| 16 Lowest Frequency       | -1277.8   |
| 17 Nucleus                | 13C       |
| 18 Acquired Size          | 32768     |
| 19 Spectral Size          | 65536     |
| Parameter                  | Value       |
|----------------------------|-------------|
| 1 Origin                   | Varian      |
| 2 Owner                    |             |
| 3 Spectrometer             | inova       |
| 4 Solvent                  | CDC13       |
| 5 Temperature              | 20.0        |
| 6 Pulse Sequence           | s2pul       |
| 7 Experiment               | 1D          |
| 8 Probe                    | QUAD        |
| 9 Number of Scans          | 4           |
| 10 Receiver Gain           | 41          |
| 11 Relaxation Delay        | 15.0000     |
| 12 Pulse Width             | 6.5000      |
| 13 Presaturation Frequency |             |
| 14 Spectrometer Frequency  | 499.69      |
| 15 Spectral Width          | 7024.9      |
| 16 Lowest Frequency        | -1021.4     |
| 17 Nucleus                 | 1H          |
| 18 Acquired Size           | 32768       |
| 19 Spectral Size           | 65536       |

![Chemical Structure](image)
| Parameter                | Value                        |
|--------------------------|------------------------------|
| Origin                   | Varian                       |
| Owner                    |                              |
| Spectrometer             | inova                        |
| Solvent                  | CDCl₃                         |
| Temperature              | 20.0                         |
| Pulse Sequence           | s2pul                        |
| Experiment               | 1D                            |
| Probe                    | QUAD                         |
| Number of Scans          | 512                          |
| Receiver Gain            | 60                           |
| Relaxation Delay         | 2.0000                       |
| Pulse Width              | 6.0000                       |
| Spectrometer Frequency   | 125.66                       |
| Spectral Width           | 30165.9                      |
| Lowest Frequency         | -1281.3                      |
| Nucleus                  | 13C                          |
| Acquired Size            | 32768                        |
| Spectral Size            | 65536                        |
| Parameter                  | Value          |
|----------------------------|----------------|
| 1  Origin                  | Varian         |
| 2  Owner                   |                |
| 3  Spectrometer            | inova          |
| 4  Solvent                 | CDCl3          |
| 5  Temperature             | 20.0           |
| 6  Pulse Sequence          | s2pul          |
| 7  Experiment              | 1D             |
| 8  Probe                   | QUAD           |
| 9  Number of Scans         | 64             |
| 10 Receiver Gain           | 52             |
| 11 Relaxation Delay        | 0.0000         |
| 12 Pulse Width             | 6.2500         |
| 13 Presaturation Frequency |                |
| 14 Spectrometer Frequency  | 470.15         |
| 15 Spectral Width          | 100000.0       |
| 16 Lowest Frequency        | -79501.3       |
| 17 Nucleus                 | 19F            |
| 18 Acquired Size           | 32768          |
| 19 Spectral Size           | 65536          |

![Chemical Structure](image-url)
| Parameter       | Value                                                                 |
|-----------------|----------------------------------------------------------------------|
| Origin          | Bruker BioSpin GmbH                                                  |
| Owner           | user1d                                                              |
| Instrument      | spect                                                               |
| Solvent         | Acetone                                                             |
| Temperature     | 298.0                                                               |
| Pulse Sequence  | zgpg30                                                              |
| Experiment      | 1D                                                                  |
| Probe           | Z127784_0002,CP BBO 50051 BBF_H_D_05 Z,                             |
| Number of Scans | 512                                                                |
| Receiver Gain   | 190.5                                                               |
| Relaxation Delay| 2.0000                                                              |
| Pulse Width     | 10.0000                                                             |
| Presaturation Frequency |                                                               |
| Spectrometer Frequency | 125.83                                                             |
| Spectral Width  | 31512.6                                                             |
| Lowest Frequency| 1805.5                                                              |
| Nucleus         | 13C                                                                 |
| Acquired Size   | 32768                                                               |
| Spectral Size   | 65536                                                               |

The spectrum displays peaks corresponding to the chemical shifts of the molecules with the given parameters.
| Parameter              | Value            |
|-----------------------|------------------|
| 1 Origin              | Varian           |
| 2 Owner               |                  |
| 3 Spectrometer        | inova            |
| 4 Solvent             | CDCl3            |
| 5 Temperature         | 20.0             |
| 6 Pulse Sequence      | s2pul            |
| 7 Experiment          | 1D               |
| 8 Probe               | QUAD             |
| 9 Number of Scans     | 5                |
| 10 Receiver Gain      | 41               |
| 11 Relaxation Delay   | 15.0000          |
| 12 Pulse Width        | 6.5000           |
| 13 Presaturation Frequency |        |
| 14 Spectrometer Frequency | 499.69          |
| 15 Spectral Width     | 7024.9           |
| 16 Lowest Frequency   | -1021.4          |
| 17 Nucleus            | 1H               |
| 18 Acquired Size      | 32768            |
| 19 Spectral Size      | 65536            |
| Parameter                  | Value                  |
|---------------------------|------------------------|
| 1 Origin                  | Varian                 |
| 2 Owner                   |                        |
| 3 Spectrometer            | inova                  |
| 4 Solvent                 | CDCl3                  |
| 5 Temperature             | 20.0                   |
| 6 Pulse Sequence          | s2pul                  |
| 7 Experiment              | 1D                     |
| 8 Probe                   | QUAD                   |
| 9 Number of Scans         | 1024                   |
| 10 Receiver Gain          | 60                     |
| 11 Relaxation Delay       | 1.0000                 |
| 12 Pulse Width            | 6.0000                 |
| 13 Presaturation Frequency|                        |
| 14 Spectrometer Frequency | 125.66                 |
| 15 Spectral Width         | 30165.9                |
| 16 Lowest Frequency       | -1276.4                |
| 17 Nucleus                | 13C                    |
| 18 Acquired Size          | 32768                  |
| 19 Spectral Size          | 65536                  |
| Parameter                  | Value          |
|----------------------------|----------------|
| 1  Origin                  | Varian         |
| 2  Owner                   |                |
| 3  Spectrometer            | inova          |
| 4  Solvent                 | CDCl3          |
| 5  Temperature             | 29.0           |
| 6  Pulse Sequence          | s2pul          |
| 7  Experiment              | 1D             |
| 8  Probe                   | QUAD           |
| 9  Number of Scans         | 8              |
| 10 Receiver Gain           | 41             |
| 11 Relaxation Delay        | 15.0000        |
| 12 Pulse Width             | 6.5000         |
| 13 Presaturation Frequency |                |
| 14 Spectrometer Frequency  | 499.69         |
| 15 Spectral Width          | 7024.9         |
| 16 Lowest Frequency        | -1021.4        |
| 17 Nucleus                 | 1H             |
| 18 Acquired Size           | 32768          |
| 19 Spectral Size           | 65536          |
| Parameter                  | Value                |
|----------------------------|----------------------|
| 1  Origin                  | Varian               |
| 2  Owner                   |                      |
| 3  Spectrometer            | inova                |
| 4  Solvent                 | CDCl3                |
| 5  Temperature             | 22.0                 |
| 6  Pulse Sequence          | s2pul                |
| 7  Experiment              | 1D                   |
| 8  Probe                   | QUAD                 |
| 9  Number of Scans         | 2048                 |
| 10 Receiver Gain           | 60                   |
| 11 Relaxation Delay        | 2.0000               |
| 12 Pulse Width             | 6.0000               |
| 13 Presaturation Frequency |                      |
| 14 Spectrometer Frequency  | 125.66               |
| 15 Spectral Width          | 30165.9              |
| 16 Lowest Frequency        | -1276.5              |
| 17 Nucleus                 | 13C                  |
| 18 Acquired Size           | 32768                |
| 19 Spectral Size           | 65536                |
| Parameter         | Value           |
|-------------------|-----------------|
| 1 Origin          | Varian          |
| 2 Owner           |                 |
| 3 Spectrometer    | inova           |
| 4 Solvent         | CDCl3           |
| 5 Temperature     | 22.0            |
| 6 Pulse Sequence  | s2pul           |
| 7 Experiment      | 1D              |
| 8 Probe           | QUAD            |
| 9 Number of Scans | 16              |
| 10 Receiver Gain  | 46              |
| 11 Relaxation Delay | 0.0000       |
| 12 Pulse Width    | 6.2500          |
| 13 Presaturation Frequency |          |
| 14 Spectrometer Frequency | 470.15   |
| 15 Spectral Width | 100000.0        |
| 16 Lowest Frequency | -79501.3    |
| 17 Nucleus        | 19F             |
| 18 Acquired Size  | 32768           |
| 19 Spectral Size  | 65536           |
| Parameter      | Value               |
|----------------|---------------------|
| 1 Origin       | Varian              |
| 2 Owner        |                     |
| 3 Spectrometer | inova               |
| 4 Solvent      | CDCl3               |
| 5 Temperature  | 20.0                |
| 6 Pulse Sequence| s2pul              |
| 7 Experiment   | 1D                  |
| 8 Probe        | QUAD                |
| 9 Number of Scans| 4                  |
| 10 Receiver Gain| 52                 |
| 11 Relaxation Delay | 10.0000  |
| 12 Pulse Width | 6.5000              |
| 13 Presaturation Frequency |       |
| 14 Spectrometer Frequency | 499.69 |
| 15 Spectral Width | 7024.9    |
| 16 Lowest Frequency | -1021.4  |
| 17 Nucleus     | 1H                  |
| 18 Acquired Size | 32768             |
| 19 Spectral Size | 65536             |
| Parameter                  | Value                  |
|---------------------------|------------------------|
| 1 Origin                  | Varian                 |
| 2 Owner                   |                        |
| 3 Spectrometer            | inova                  |
| 4 Solvent                 | CDCl3                  |
| 5 Temperature             | 20.0                   |
| 6 Pulse Sequence          | s2pul                  |
| 7 Experiment              | 1D                     |
| 8 Probe                   | QUAD                   |
| 9 Number of Scans         | 533                    |
| 10 Receiver Gain          | 60                     |
| 11 Relaxation Delay       | 2.0000                 |
| 12 Pulse Width            | 6.0000                 |
| 13 Presaturation Frequency|                        |
| 14 Spectrometer Frequency | 125.66                 |
| 15 Spectral Width         | 30165.9                |
| 16 Lowest Frequency       | -1275.5                |
| 17 Nucleus                | 13C                    |
| 18 Acquired Size          | 32768                  |
| 19 Spectral Size          | 65536                  |
| Parameter                  | Value                                                                 |
|----------------------------|-----------------------------------------------------------------------|
| 1  Origin                  | Bruker BioSpin GmbH                                                  |
| 2  Owner                   | user1d                                                               |
| 3  Spectrometer            | spect                                                                |
| 4  Solvent                 | CDCl3                                                                |
| 5  Temperature             | 298.0                                                                |
| 6  Pulse Sequence          | zg30                                                                 |
| 7  Experiment              | 1D                                                                   |
| 8  Probe                   | Z127784_0002 (CP BBO S00S1 BBF-H-D-05 Z)                              |
| 9  Number of Scans         | 16                                                                   |
| 10 Receiver Gain           | 29.7                                                                 |
| 11 Relaxation Delay        | 15.0000                                                              |
| 12 Pulse Width             | 12.0000                                                              |
| 13 Presaturation Frequency |                                                                       |
| 14 Spectrometer Frequency  | 500.35                                                               |
| 15 Spectral Width          | 10000.0                                                              |
| 16 Lowest Frequency        | -1922.3                                                              |
| 17 Nucleus                 | 1H                                                                   |
| 18 Acquired Size           | 32768                                                                |
| 19 Spectral Size           | 65536                                                                |

![NMR spectrum](image)
| Parameter                  | Value                                                                 |
|----------------------------|----------------------------------------------------------------------|
| 1 Origin                   | Bruker BioSpin GmbH                                                   |
| 2 Owner                    | user1d                                                               |
| 3 Spectrometer             | spect                                                                |
| 4 Solvent                  | CDCl3                                                                |
| 5 Temperature              | 298.0                                                                |
| 6 Pulse Sequence           | zgpg30                                                               |
| 7 Experiment               | 1D                                                                   |
| 8 Probe                    | Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)                              |
| 9 Number of Scans          | 128                                                                  |
| 10 Receiver Gain           | 190.5                                                                |
| 11 Relaxation Delay        | 2.0000                                                               |
| 12 Pulse Width             | 10.0000                                                              |
| 13 Presaturation Frequency |                                                                      |
| 14 Spectrometer Frequency  | 125.83                                                               |
| 15 Spectral Width          | 29761.9                                                              |
| 16 Lowest Frequency        | -2289.3                                                              |
| 17 Nucleus                 | 13C                                                                  |
| 18 Acquired Size           | 32768                                                                |
| 19 Spectral Size           | 65536                                                                |
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| Origin             | Bruker BioSpin GmbH                                                  |
| Owner              | user1d                                                              |
| Spectrometer       | spect                                                               |
| Solvent            | CDCl3                                                               |
| Temperature        | 298.0                                                               |
| Pulse Sequence     | zg30                                                                |
| Experiment         | 1D                                                                  |
| Probe              | Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)                             |
| Number of Scans    | 16                                                                  |
| Receiver Gain      | 61.8                                                                |
| Relaxation Delay   | 15.0000                                                             |
| Pulse Width        | 12.0000                                                             |
| Spectrometer Frequency | 500.35                                           |
| Spectral Width     | 10000.0                                                             |
| Lowest Frequency   | -1922.3                                                             |
| Nucleus            | 1H                                                                  |
| Acquired Size      | 32768                                                               |
| Spectral Size      | 65536                                                               |

![NMR Spectrum Image](image-url)
| Parameter                  | Value                                                                 |
|----------------------------|-----------------------------------------------------------------------|
| Origin                     | Bruker BioSpin GmbH                                                  |
| Owner                      | user1d                                                                |
| Spectrometer               | spect                                                                 |
| Solvent                    | CDCl₃                                                                 |
| Temperature                | 298.0                                                                |
| Pulse Sequence             | zgpg30                                                                |
| Experiment                 | 1D                                                                   |
| Probe                      | Z127784_0002 (CP BBO 500S1 BBF–H–D–05 Z)                             |
| Number of Scans            | 4096                                                                 |
| Receiver Gain              | 190.5                                                                |
| Relaxation Delay           | 2.0000                                                               |
| Pulse Width                | 10.0000                                                              |
| Spectrometer Frequency     | 125.83                                                               |
| Spectral Width             | 29761.9                                                              |
| Lowest Frequency           | -2281.6                                                              |
| Nucleus                    | 13C                                                                  |
| Acquired Size              | 32768                                                                |
| Spectral Size              | 65536                                                                |
| Parameter            | Value                                                                 |
|----------------------|----------------------------------------------------------------------|
| 1 Origin             | Bruker BioSpin GmbH                                                 |
| 2 Owner              | user1d                                                              |
| 3 Spectrometer       | spect                                                               |
| 4 Solvent            | CDCl3                                                               |
| 5 Temperature        | 298.0                                                              |
| 6 Pulse Sequence     | zgflqn                                                              |
| 7 Experiment         | 1D                                                                  |
| 8 Probe              | Z127784_0002 (CP BBO 500S1 BBF–H–D–05 Z)                           |
| 9 Number of Scans    | 32                                                                  |
| 10 Receiver Gain     | 190.5                                                              |
| 11 Relaxation Delay  | 1.0000                                                             |
| 12 Pulse Width       | 15.0000                                                             |
| 13 Presaturation Frequency |                                                              |
| 14 Spectrometer Frequency | 470.75                                                    |
| 15 Spectral Width    | 113636.4                                                            |
| 16 Lowest Frequency  | -103898.1                                                           |
| 17 Nucleus           | 19F                                                                 |
| 18 Acquired Size     | 65536                                                               |
| 19 Spectral Size     | 131072                                                              |
Parameter | Value
---|---
1 | Origin Varian
2 | Owner
3 | Instrument inova
4 | Solvent CDCl₃
5 | Temperature 20.0
6 | Pulse Sequence s2pul
7 | Experiment 1D
8 | Probe QUAD
9 | Number of Scans 4
10 | Receiver Gain 46
11 | Relaxation Delay 10.0000
12 | Pulse Width 6.5000
13 | Presaturation Frequency
14 | Spectrometer Frequency 499.69
15 | Spectral Width 7024.9
16 | Lowest Frequency 1021.9
17 | Nucleus 1H
18 | Acquired Size 32768
19 | Spectral Size 65536

![Chemical Structure](image)

**DCM**

**H₂O**
| Parameter          | Value       |
|--------------------|-------------|
| Origin             | Varian      |
| Owner              |             |
| Instrument         | inova       |
| Solvent            | CDCl3       |
| Temperature        | 20.0        |
| Pulse Sequence     | s2pul       |
| Experiment         | 1D          |
| Probe              | QUAD        |
| Number of Scans    | 512         |
| Receiver Gain      | 60          |
| Relaxation Delay   | 2.00000     |
| Pulse Width        | 6.00000     |
| Presaturation Frequency |         |
| Spectrometer Frequency | 125.66    |
| Spectral Width     | 30165.9     |
| Lowest Frequency   | 1260.2      |
| Nucleus            | 13C         |
| Acquired Size      | 32768       |
| Spectral Size      | 65536       |

![NMR Spectrum](image)

The spectrum shows the chemical shift of the compound with the chemical structure of 1,1-difluoro-2-buten-3-one.
| Parameter          | Value                  |
|--------------------|------------------------|
| 1 Origin           | Varian                 |
| 2 Owner            |                        |
| 3 Instrument       | inova                  |
| 4 Solvent          | CDCl3                  |
| 5 Temperature      | 20.0                   |
| 6 Pulse Sequence   | s2pul                  |
| 7 Experiment       | 1D                     |
| 8 Probe            | QUAD                   |
| 9 Number of Scans  | 64                     |
| 10 Receiver Gain   | 60                     |
| 11 Relaxation Delay| 0.0000                 |
| 12 Pulse Width     | 6.2500                 |
| 13 Presaturation Frequency |            |
| 14 Spectrometer Frequency | 470.15               |
| 15 Spectral Width  | 100000.0               |
| 16 Lowest Frequency| 7.95013                |
| 17 Nucleus         | 19F                    |
| 18 Acquired Size   | 32768                  |
| 19 Spectral Size   | 65536                  |
| Parameter       | Value          |
|-----------------|----------------|
| Origin          | Varian         |
| Owner           |                |
| Instrument      | inova          |
| Solvent         | CDCl3          |
| Temperature     | 20.0           |
| Pulse Sequence  | s2pul          |
| Experiment      | 1D             |
| Probe           | hcn            |
| Number of Scans | 8              |
| Receiver Gain   | 32             |
| Relaxation Delay| 15.0000        |
| Pulse Width     | 7.0000         |
| Spectrometer Frequency | 500.07       |
| Spectral Width  | 8000.0         |
| Lowest Frequency| 1520.1         |
| Nucleus         | 1H             |
| Acquired Size   | 32768          |
| Spectral Size   | 65536          |

![Chemical structure](image)

H$_2$O

![NMR spectrum](image)
| Parameter          | Value          |
|--------------------|----------------|
| 1 Origin           | Varian         |
| 2 Owner            |                |
| 3 Instrument       | inova          |
| 4 Solvent          | CDCl3          |
| 5 Temperature      | 22.0           |
| 6 Pulse Sequence   | s2pul          |
| 7 Experiment       | 1D             |
| 8 Probe            | QUAD           |
| 9 Number of Scans  | 512            |
| 10 Receiver Gain   | 60             |
| 11 Relaxation Delay| 2.00000        |
| 12 Pulse Width     | 6.00000        |
| 13 Presaturation Frequency |       |
| 14 Spectrometer Frequency | 125.66    |
| 15 Spectral Width  | 30165.9        |
| 16 Lowest Frequency| 126.2          |
| 17 Nucleus         | 13C            |
| 18 Acquired Size   | 32768          |
| 19 Spectral Size   | 65536          |

![Chemical Structure](image)
| Parameter                  | Value                                                                 |
|----------------------------|------------------------------------------------------------------------|
| Origin                     | Bruker BioSpin GmbH                                                    |
| Owner                      | user1d                                                                |
| Spectrometer               | spect                                                                 |
| Solvent                    | CDCl3                                                                 |
| Temperature                | 298.0                                                                 |
| Pulse Sequence             | zg30                                                                   |
| Experiment                 | 1D                                                                    |
| Probe                      | Z127784_0002 (CP BBO 500S1 BBF–H–D–05 Z)                              |
| Number of Scans            | 16                                                                    |
| Receiver Gain              | 29.7                                                                  |
| Relaxation Delay           | 15.0000                                                               |
| Pulse Width                | 12.0000                                                               |
| Spectrometer Frequency     | 500.35                                                                |
| Spectral Width             | 10000.0                                                               |
| Lowest Frequency           | -1921.8                                                               |
| Nucleus                    | 1H                                                                    |
| Acquired Size              | 32768                                                                 |
| Spectral Size              | 65536                                                                 |
| Parameter             | Value                                                                 |
|-----------------------|-----------------------------------------------------------------------|
| Origin                | Bruker BioSpin GmbH                                                   |
| Owner                 | user1d                                                                |
| Spectrometer          | spect                                                                 |
| Solvent               | CDCl3                                                                 |
| Temperature           | 298.0                                                                 |
| Pulse Sequence        | zgpg30                                                                |
| Experiment            | 1D                                                                    |
| Probe                 | Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)                              |
| Number of Scans       | 256                                                                  |
| Receiver Gain         | 190.5                                                                |
| Relaxation Delay      | 2.0000                                                               |
| Pulse Width           | 10.0000                                                              |
| Spectrometer Frequency| 125.83                                                                |
| Spectral Width        | 29761.9                                                              |
| Lowest Frequency      | -2285.8                                                              |
| Nucleus               | 13C                                                                  |
| Acquired Size         | 32768                                                                |
| Spectral Size         | 65536                                                                |

![Chemical Structure](image)
| Parameter       | Value            |
|-----------------|------------------|
| Origin          | Varian           |
| Owner           |                  |
| Instrument      | inova            |
| Solvent         | CDCl3            |
| Temperature     | 20.0             |
| Pulse Sequence  | s2pul            |
| Experiment      | 1D               |
| Probe           | hcn              |
| Number of Scans | 8                |
| Receiver Gain   | 42               |
| Relaxation Delay| 10.3000          |
| Pulse Width     | 7.0000           |
| Presaturation Frequency |          |
| Spectrometer Frequency | 500.07  |
| Spectral Width  | 8000.0           |
| Lowest Frequency| 1520.6           |
| Nucleus         | 1H               |
| Acquired Size   | 32768            |
| Spectral Size   | 65536            |

![NMR spectrum with water peak highlighted]
| Parameter       | Value          |
|-----------------|----------------|
| 1 Origin        | Varian         |
| 2 Owner         |                |
| 3 Instrument    | inova          |
| 4 Solvent       | CDCl3          |
| 5 Temperature   | 20.0           |
| 6 Pulse Sequence| s2pul          |
| 7 Experiment    | 1D             |
| 8 Probe         | QUAD           |
| 9 Number of Scans| 512           |
| 10 Receiver Gain| 60             |
| 11 Relaxation Delay| 1.0000    |
| 12 Pulse Width  | 6.0000         |
| 13 Presaturation Frequency|          |
| 14 Spectrometer Frequency| 125.66        |
| 15 Spectral Width| 30165.9       |
| 16 Lowest Frequency| 1275.5        |
| 17 Nucleus      | 13C            |
| 18 Acquired Size| 32768          |
| 19 Spectral Size| 65536          |

![NMR spectrum image](image_url)
Parameter | Value
--- | ---
1 Origin | Varian
2 Owner
3 Spectrometer | inova
4 Solvent | CDCl3
5 Temperature | 20.0
6 Pulse Sequence | s2pul
7 Experiment | 1D
8 Probe | QUAD
9 Number of Scans | 32
10 Receiver Gain | 60
11 Relaxation Delay | 10.0000
12 Pulse Width | 6.5000
13 Presaturation Frequency
14 Spectrometer Frequency | 499.69
15 Spectral Width | 7024.9
16 Lowest Frequency | -1021.9
17 Nucleus | 1H
18 Acquired Size | 32768
19 Spectral Size | 65536
| Parameter                | Value                  |
|--------------------------|------------------------|
| Origin                   | Varian                 |
| Owner                    |                        |
| Spectrometer             | inova                  |
| Solvent                  | CDCl3                  |
| Temperature              | 20.0                   |
| Pulse Sequence           | s2pul                  |
| Experiment               | 1D                     |
| Probe                    | QUAD                   |
| Number of Scans          | 512                    |
| Receiver Gain            | 60                     |
| Relaxation Delay         | 2.0000                 |
| Pulse Width              | 6.0000                 |
| Presaturation Frequency  |                        |
| Spectrometer Frequency   | 125.66                 |
| Spectral Width           | 30165.9                |
| Lowest Frequency         | -1273.3                |
| Nucleus                  | 13C                    |
| Acquired Size            | 32768                  |
| Spectral Size            | 65536                  |
| Parameter                  | Value         |
|----------------------------|---------------|
| 1 Origin                   | Varian        |
| 2 Owner                    |               |
| 3 Spectrometer             | inova         |
| 4 Solvent                  | CDCl3         |
| 5 Temperature              | 20.0          |
| 6 Pulse Sequence           | s2pul         |
| 7 Experiment               | 1D            |
| 8 Probe                    | QUAD          |
| 9 Number of Scans          | 16            |
| 10 Receiver Gain           | 46            |
| 11 Relaxation Delay        | 0.0000        |
| 12 Pulse Width             | 6.2500        |
| 13 Presaturation Frequency |               |
| 14 Spectrometer Frequency  | 470.15        |
| 15 Spectral Width          | 1000000.0     |
| 16 Lowest Frequency        | -79541.0      |
| 17 Nucleus                 | 19F           |
| 18 Acquired Size           | 32768         |
| 19 Spectral Size           | 65536         |
| Parameter          | Value       |
|--------------------|-------------|
| 1 Origin           | Varian      |
| 2 Owner            |             |
| 3 Instrument       | inova       |
| 4 Solvent          | CDCl3       |
| 5 Temperature      | 20.0        |
| 6 Pulse Sequence   | s2pul       |
| 7 Experiment       | 1D          |
| 8 Probe            | hcn         |
| 9 Number of Scans  | 8           |
| 10 Receiver Gain   | 42          |
| 11 Relaxation Delay| 103000      |
| 12 Pulse Width     | 7.00000     |
| 13 Presaturation Frequency |           |
| 14 Spectrometer Frequency | 500.07     |
| 15 Spectral Width  | 8000.0      |
| 16 Lowest Frequency| 1.5211      |
| 17 Nucleus         | 1H          |
| 18 Acquired Size   | 32768       |
| 19 Spectral Size   | 65536       |
Parameter | Value
--- | ---
1 | Origin Varian
2 | Owner
3 | Instrument inova
4 | Solvent CDC13
5 | Temperature 20.0
6 | Pulse Sequence s2pul
7 | Experiment 1D
8 | Probe QUAD
9 | Number of Scans 800
10 | Receiver Gain 60
11 | Relaxation Delay 1.0000
12 | Pulse Width 6.0000
13 | Presaturation Frequency
14 | Spectrometer Frequency 125.66
15 | Spectral Width 30165.9
16 | Lowest Frequency 1260.2
17 | Nucleus 13C
18 | Acquired Size 32768
19 | Spectral Size 65536
| Parameter      | Value |
|---------------|-------|
| Origin        | Bruker BioSpin GmbH |
| Owner         | user1d |
| Instrument    | spect |
| Solvent       | CDCl3 |
| Temperature   | 298.0 |
| Pulse Sequence| zg30 |
| Experiment    | 1D |
| Probe         | Z127784_0002, CPBB0 S05S1 BBF_H_D_05 Z |
| Number of Scans| 16 |
| Receiver Gain | 61.8 |
| Relaxation Delay| 15.0000 |
| Pulse Width   | 12.0000 |
| Presaturation Frequency | |
| Spectrometer Frequency | 500.35 |
| Spectral Width | 10000.0 |
| Lowest Frequency | 1.9223 |
| Nucleus       | 1H |
| Acquired Size | 32768 |
| Spectral Size | 65536 |

f1 (ppm)
| Parameter                  | Value |
|----------------------------|-------|
| Origin                     | Bruker BioSpin GmbH |
| Owner                      | user1d |
| Instrument                 | spect |
| Solvent                    | CDCl3 |
| Temperature                | 298.0 |
| Pulse Sequence             | zgpg30 |
| Experiment                 | 1D |
| Probe                      | Z127784_0002, CP BBO 00501 BBB-1.05 Z |
| Number of Scans            | 256 |
| Receiver Gain              | 190.5 |
| Relaxation Delay           | 2.0000 |
| Pulse Width                | 10.0000 |
| Presaturation Frequency    |       |
| Spectrometer Frequency     | 125.83 |
| Spectral Width             | 29761.9 |
| Lowest Frequency           | 2282.9 |
| Nucleus                    | 13C |
| Acquired Size              | 32768 |
| Spectral Size              | 65536 |

![Chemical Structure Image]
| Parameter          | Value      |
|--------------------|------------|
| Origin             | Varian     |
| Owner              |            |
| Instrument         | inova      |
| Solvent            | CDCl3      |
| Temperature        | 20.0       |
| Pulse Sequence     | s2pul      |
| Experiment         | 1D         |
| Probe              | QUAD       |
| Number of Scans    | 8          |
| Receiver Gain      | 50         |
| Relaxation Delay   | 15.0000    |
| Pulse Width        | 6.5000     |
| Presaturation Frequency |        |
| Spectrometer Frequency | 499.69 |
| Spectral Width     | 7024.9     |
| Lowest Frequency   | 1021.4     |
| Nucleus            | 1H         |
| Acquired Size      | 32768      |
| Spectral Size      | 65536      |
| Parameter             | Value            |
|-----------------------|------------------|
| 1. Origin             | Varian           |
| 2. Owner              |                  |
| 3. Instrument         | inova            |
| 4. Solvent            | CDCl3            |
| 5. Temperature        | 20.0             |
| 6. Pulse Sequence     | s2pul            |
| 7. Experiment         | 1D               |
| 8. Probe              | QUAD             |
| 9. Number of Scans    | 862              |
| 10. Receiver Gain     | 60               |
| 11. Relaxation Delay  | 1.0000           |
| 12. Pulse Width       | 6.0000           |
| 13. Presaturation     | Frequency        |
| 14. Spectrometer      | Frequency 125.66 |
| 15. Spectral Width    | 30165.9          |
| 16. Lowest Frequency  | 1273.8           |
| 17. Nucleus           | 13C              |
| 18. Acquired Size     | 32768            |
| 19. Spectral Size     | 65536            |

![NMR Spectrum](image)
| Parameter          | Value          |
|--------------------|----------------|
| 1 Origin           | Varian         |
| 2 Owner            |                |
| 3 Instrument       | inova          |
| 4 Solvent          | CDCl3          |
| 5 Temperature      | 20.0           |
| 6 Pulse Sequence   | s2pul          |
| 7 Experiment       | 1D             |
| 8 Probe            | hcn            |
| 9 Number of Scans  | 16             |
| 10 Receiver Gain   | 38             |
| 11 Relaxation Delay| 15.0000        |
| 12 Pulse Width     | 7.0000         |
| 13 Presaturation Frequency |          |
| 14 Spectrometer Frequency | 500.07       |
| 15 Spectral Width  | 8000.0         |
| 16 Lowest Frequency| 1520.1         |
| 17 Nucleus         | 1H             |
| 18 Acquired Size   | 32768          |
| 19 Spectral Size   | 65536          |
| Parameter     | Value          |
|---------------|----------------|
| 1 Origin      | Varian         |
| 2 Owner       |                |
| 3 Instrument  | inova          |
| 4 Solvent     | CDCl3          |
| 5 Temperature | 20.0           |
| 6 Pulse Sequence | s2pul    |
| 7 Experiment  | 1D             |
| 8 Probe       | QUAD           |
| 9 Number of Scans | 8           |
| 10 Receiver Gain | 41           |
| 11 Relaxation Delay | 15.0000 |
| 12 Pulse Width | 6.5000        |
| 13 Presaturation Frequency |            |
| 14 Spectrometer Frequency | 499.69    |
| 15 Spectral Width | 7024.9    |
| 16 Lowest Frequency | 1.0214    |
| 17 Nucleus    | 1H             |
| 18 Acquired Size | 32768     |
| 19 Spectral Size | 65536     |
| Parameter          | Value       |
|--------------------|-------------|
| Origin             | Varian      |
| Owner              |             |
| Instrument         | inova       |
| Solvent            | CDCl3       |
| Temperature        | 20.0        |
| Pulse Sequence     | s2pul       |
| Experiment         | 1D          |
| Probe              | QUAD        |
| Number of Scans    | 2048        |
| Receiver Gain      | 60          |
| Relaxation Delay   | 2.0000      |
| Pulse Width        | 6.0000      |
| Presaturation Frequency |      |
| Spectrometer Frequency | 125.66     |
| Spectral Width     | 30165.9     |
| Lowest Frequency   | 1274.0      |
| Nucleus            | 13C         |
| Acquired Size      | 32768       |
| Spectral Size      | 65536       |

![NMR spectrum image](image-url)
| Parameter      | Value                  |
|---------------|------------------------|
| 1 Origin      | Varian                 |
| 2 Owner       |                        |
| 3 Instrument  | inova                  |
| 4 Solvent     | CDCl3                  |
| 5 Temperature | 20.0                   |
| 6 Pulse Sequence | s2pul                |
| 7 Experiment  | 1D                     |
| 8 Probe       | QUAD                   |
| 9 Number of Scans | 8                    |
| 10 Receiver Gain | 41                    |
| 11 Relaxation Delay | 15.0000             |
| 12 Pulse Width | 6.5000                 |
| 13 Presaturation Frequency |          |
| 14 Spectrometer Frequency | 499.69               |
| 15 Spectral Width | 7024.9                |
| 16 Lowest Frequency | 1.0214               |
| 17 Nucleus    | 1H                     |
| 18 Acquired Size | 32768                |
| 19 Spectral Size | 65536                |
| Parameter       | Value            |
|-----------------|------------------|
| Origin          | Varian           |
| Owner           |                  |
| Instrument      | inova            |
| Solvent         | CDCl₃            |
| Temperature     | 20.0             |
| Pulse Sequence  | s2pul            |
| Experiment      | 1D               |
| Probe           | QUAD             |
| Number of Scans | 985              |
| Receiver Gain   | 60               |
| Relaxation Delay| 1.0000           |
| Pulse Width     | 6.0000           |
| Presaturation Frequency |             |
| Spectrometer Frequency | 125.66          |
| Spectral Width  | 30165.9          |
| Lowest Frequency| 1260.2           |
| Nucleus         | 13C              |
| Acquired Size   | 32768            |
| Spectral Size   | 65536            |
| Parameter         | Value |
|-------------------|-------|
| Origin            | Bruker BioSpin GmbH |
| Owner             | user1d |
| Instrument        | spect |
| Solvent           | CDCl3 |
| Temperature       | 298.0 |
| Pulse Sequence    | zg30  |
| Experiment        | 1D    |
| Probe             | Z127784_0002, CP880 500S1 BBF_H_D_05 Z |
| Number of Scans   | 16    |
| Receiver Gain     | 61.8  |
| Relaxation Delay  | 15.000 |
| Pulse Width       | 12.000 |
| Presaturation Frequency |     |
| Spectrometer Frequency | 500.35  |
| Spectral Width    | 10000.0 |
| Lowest Frequency  | 1922.3 |
| Nucleus           | 1H    |
| Acquired Size     | 32768 |
| Spectral Size     | 65536 |
| Parameter            | Value |
|----------------------|-------|
| 1 Origin             | Bruker BioSpin GmbH |
| 2 Owner              | user1d |
| 3 Instrument         | spect |
| 4 Solvent            | CDCl3 |
| 5 Temperature        | 298.0 |
| 6 Pulse Sequence     | zgpg30 |
| 7 Experiment         | 1D |
| 8 Probe              | Z127784_0002, CP880 500S1 BBF. H.D. 05 Z, |
| 9 Number of Scans    | 256 |
| 10 Receiver Gain     | 190.5 |
| 11 Relaxation Delay  | 2.0000 |
| 12 Pulse Width       | 10.0000 |
| 13 Presaturation Frequency | |
| 14 Spectrometer Frequency | 125.83 |
| 15 Spectral Width    | 29761.9 |
| 16 Lowest Frequency  | 2282.2 |
| 17 Nucleus           | 13C |
| 18 Acquired Size     | 32768 |
| 19 Spectral Size     | 65536 |
Parameter | Value
--- | ---
1 Origin | Varian
2 Owner | 
3 Instrument | inova
4 Solvent | CDCl3
5 Temperature | 20.0
6 Pulse Sequence | s2pul
7 Experiment | 1D
8 Probe | hcn
9 Number of Scans | 8
10 Receiver Gain | 38
11 Relaxation Delay | 15.0000
12 Pulse Width | 7.0000
13 Presaturation Frequency | 
14 Spectrometer Frequency | 500.07
15 Spectral Width | 8000.0
16 Lowest Frequency | 1.5206
17 Nucleus | 1H
18 Acquired Size | 32768
19 Spectral Size | 65536
| Parameter       | Value                          |
|-----------------|--------------------------------|
| 1 Origin        | Varian                         |
| 2 Owner         |                                |
| 3 Instrument    | inova                          |
| 4 Solvent       | CDCl3                          |
| 5 Temperature   | 20.0                           |
| 6 Pulse Sequence| s2pul                          |
| 7 Experiment    | 1D                             |
| 8 Probe         | QUAD                           |
| 9 Number of Scans | 1024                         |
| 10 Receiver Gain | 60                            |
| 11 Relaxation Delay | 2.0000                      |
| 12 Pulse Width  | 6.0000                         |
| 13 Presaturation Frequency |                |
| 14 Spectrometer Frequency | 125.66                    |
| 15 Spectral Width | 30165.9                      |
| 16 Lowest Frequency | 127.4                      |
| 17 Nucleus      | 13C                            |
| 18 Acquired Size | 32768                         |
| 19 Spectral Size | 65536                         |

![Chemical Structure](image)

![NMR Spectrum]
1 Origin: Bruker BioSpin GmbH
2 Owner: user1d
3 Instrument: spect
4 Solvent: CDCl3
5 Temperature: 298.0
6 Pulse Sequence: zgpg30
7 Experiment: 1D
8 Probe: Z127784_0002, CP880 500S1 BBF, H, D, 05 Z
9 Number of Scans: 256
10 Receiver Gain: 190.5
11 Relaxation Delay: 2.0000
12 Pulse Width: 10.0000
13 Presaturation Frequency
14 Spectrometer Frequency: 125.83
15 Spectral Width: 31512.6
16 Lowest Frequency: 1899.2
17 Nucleus: 13C
18 Acquired Size: 32768
19 Spectral Size: 65536
| Parameter     | Value          |
|---------------|----------------|
| Origin        | Varian         |
| Owner         |                |
| Instrument    | inova          |
| Solvent       | CDCl3          |
| Temperature   | 20.0           |
| Pulse Sequence| s2pul          |
| Experiment    | 1D             |
| Probe         | QUAD           |
| Number of Scans| 8              |
| Receiver Gain | 46             |
| Relaxation Delay| 10.0000       |
| Pulse Width   | 6.5000         |
| Presaturation Frequency|       |
| Spectrometer Frequency | 499.69       |
| Spectral Width | 7024.9        |
| Lowest Frequency | .1022 4       |
| Nucleus       | 1H             |
| Acquired Size | 32768          |
| Spectral Size | 65536          |
| Parameter          | Value                  |
|--------------------|------------------------|
| Origin             | Varian                 |
| Owner              |                        |
| Instrument         | inova                  |
| Solvent            | CDCl3                  |
| Temperature        | 20.0                   |
| Pulse Sequence     | s2pul                  |
| Experiment         | 1D                     |
| Probe              | QUAD                   |
| Number of Scans    | 512                    |
| Receiver Gain      | 60                     |
| Relaxation Delay   | 2.0000                 |
| Pulse Width        | 6.0000                 |
| Presaturation Frequency |                |
| Spectrometer Frequency | 125.66                |
| Spectral Width     | 30165.9                |
| Lowest Frequency   | 1273.6                 |
| Nucleus            | 13C                    |
| Acquired Size      | 32768                  |
| Spectral Size      | 65536                  |
| Parameter               | Value                                                                 |
|-------------------------|-----------------------------------------------------------------------|
| Origin                  | Bruker BioSpin GmbH                                                   |
| Owner                   | user1d                                                                |
| Instrument              | spect                                                                 |
| Solvent                 | CDCl3                                                                 |
| Temperature             | 298.1                                                                |
| Pulse Sequence          | zg30                                                                  |
| Experiment              | 1D                                                                    |
| Probe                   | Z127784_0002_CPBBDO500S1BBF_H.D.05_Z                                   |
| Number of Scans         | 16                                                                    |
| Receiver Gain           | 122.8                                                                 |
| Relaxation Delay        | 15.0000                                                              |
| Pulse Width             | 12.0000                                                              |
| Presaturation Frequency |                                                                       |
| Spectrometer Frequency  | 500.35                                                                |
| Spectral Width          | 10000.0                                                               |
| Lowest Frequency        | 1921.2                                                                |
| Nucleus                 | 1H                                                                    |
| Acquired Size           | 32768                                                                 |
| Spectral Size           | 65536                                                                 |

![NMR spectrum diagram](image)

- **grease**
- **H2O**
| Parameter                  | Value                                                                 |
|---------------------------|----------------------------------------------------------------------|
| 1  Origin                  | Bruker BioSpin GmbH                                                  |
| 2  Owner                   | user1d                                                              |
| 3  Instrument              | spect                                                               |
| 4  Solvent                 | CDCl3                                                               |
| 5  Temperature             | 298.2                                                               |
| 6  Pulse Sequence          | zgpg30                                                              |
| 7  Experiment              | 1D                                                                  |
| 8  Probe                   | Z127784_0002_CPBBO500S1BHF_D_05Z                                    |
| 9  Number of Scans         | 512                                                                 |
| 10 Receiver Gain           | 190.5                                                               |
| 11 Relaxation Delay        | 2.0000                                                              |
| 12 Pulse Width             | 10.0000                                                             |
| 13 Presaturation Frequency |                                                                      |
| 14 Spectrometer Frequency  | 125.83                                                               |
| 15 Spectral Width          | 31512.6                                                              |
| 16 Lowest Frequency        | .1900.5                                                              |
| 17 Nucleus                 | 13C                                                                 |
| 18 Acquired Size           | 32768                                                                |
| 19 Spectral Size           | 65536                                                                |

![NMR Spectrum](image)
| Parameter       | Value                                                                 |
|-----------------|-----------------------------------------------------------------------|
| Origin          | Bruker BioSpin GmbH                                                  |
| Owner           | user1d                                                                |
| Instrument      | spect                                                                |
| Solvent         | CDCl3                                                                 |
| Temperature     | 298.0                                                                |
| Pulse Sequence  | zg30                                                                  |
| Experiment      | 1D                                                                    |
| Probe           | Z127784_0002_CPBBO500S1BBF_H.D.05Z                                |
| Number of Scans | 8                                                                     |
| Receiver Gain   | 29.7                                                                 |
| Relaxation Delay| 15.0000                                                              |
| Pulse Width     | 12.0000                                                              |
| Presat Frequency|                                                                        |
| Spectrometer Frequency | 500.35                                         |
| Spectral Width  | 10000.0                                                              |
| Lowest Frequency| 1922.3                                                               |
| Nucleus         | 1H                                                                   |
| Acquired Size   | 32768                                                                |
| Spectral Size   | 65536                                                                |
| Parameter                  | Value |
|----------------------------|-------|
| Origin                     | Bruker BioSpin GmbH |
| Owner                      | user1d |
| Instrument                 | spect |
| Solvent                    | CDCl3 |
| Temperature                | 298.0 |
| Pulse Sequence             | zgpg30 |
| Experiment                 | 1D |
| Probe                      | Z127784_0002, CPBBO 500S1 BBF_H.D.05 Z |
| Number of Scans            | 256 |
| Receiver Gain              | 190 5 |
| Relaxation Delay           | 2.0000 |
| Pulse Width                | 10.0000 |
| Presaturation Frequency    |       |
| Spectrometer Frequency     | 125.83 |
| Spectral Width             | 29761.9 |
| Lowest Frequency           | 2288.3 |
| Nucleus                    | 13C |
| Acquired Size              | 32768 |
| Spectral Size              | 65536 |

![Chemical Structure Diagram](image)
| Parameter         | Value        |
|-------------------|--------------|
| 1 Origin          | Varian       |
| 2 Owner           |              |
| 3 Instrument      | inova        |
| 4 Solvent         | CDCl3        |
| 5 Temperature     | 30.0         |
| 6 Pulse Sequence  | s2pul        |
| 7 Experiment      | 1D           |
| 8 Probe           | QUAD         |
| 9 Number of Scans | 8            |
| 10 Receiver Gain  | 41           |
| 11 Relaxation Delay | 15.0000    |
| 12 Pulse Width    | 6.5000       |
| 13 Presaturation Frequency |          |
| 14 Spectrometer Frequency | 499.69    |
| 15 Spectral Width | 7024.9       |
| 16 Lowest Frequency | 1021.4     |
| 17 Nucleus        | 1H           |
| 18 Acquired Size  | 32768        |
| 19 Spectral Size  | 65536        |
| Parameter          | Value                  |
|--------------------|------------------------|
| Origin             | Varian                 |
| Owner              |                        |
| Instrument         | inova                  |
| Solvent            | CDCl3                  |
| Temperature        | 30.0                   |
| Pulse Sequence     | s2pul                  |
| Experiment         | 1D                     |
| Probe              | QUAD                   |
| Number of Scans    | 983                    |
| Receiver Gain      | 60                     |
| Relaxation Delay   | 2.0000                 |
| Pulse Width        | 6.0000                 |
| Presaturation Frequency |              |
| Spectrometer Frequency | 125.66               |
| Spectral Width     | 30165.9                |
| Lowest Frequency   | 1279.8                 |
| Nucleus            | 13C                    |
| Acquired Size      | 32768                  |
| Spectral Size      | 65536                  |

![NMR Spectrum](image)

**Parameter Value**

**f1 (ppm)**
H-H geminal coupling on * carbon
| Parameter          | Value          |
|--------------------|----------------|
| 1 Origin           | Varian         |
| 2 Owner            |                |
| 3 Instrument       | inova          |
| 4 Solvent          | CDCl3          |
| 5 Temperature      | 20.0           |
| 6 Pulse Sequence   | s2pul          |
| 7 Experiment       | 1D             |
| 8 Probe            | hcn            |
| 9 Number of Scans  | 8              |
| 10 Receiver Gain   | 32             |
| 11 Relaxation Delay| 15.0000        |
| 12 Pulse Width     | 7.0000         |
| 14 Spectrometer Frequency | 500.07    |
| 15 Spectral Width  | 8000.0         |
| 16 Lowest Frequency| 1518.6         |
| 17 Nucleus         | 1H             |
| 18 Acquired Size   | 32768          |
| 19 Spectral Size   | 65536          |

![Chemical Structure Image](image-url)
| Parameter       | Value                |
|-----------------|----------------------|
| Origin          | Varian               |
| Owner           |                      |
| Instrument      | inova                |
| Solvent         | CDCl₃                |
| Temperature     | 20.0                 |
| Pulse Sequence  | s2pul                |
| Experiment      | 1D                   |
| Probe           | QUAD                 |
| Number of Scans | 1024                 |
| Receiver Gain   | 60                   |
| Relaxation Delay| 2.0000               |
| Pulse Width     | 6.0000               |
| Presaturation Frequency |          |
| Spectrometer Frequency | 125.66          |
| Spectral Width  | 30165.9              |
| Lowest Frequency| 1282.3               |
| Nucleus         | 13C                  |
| Acquired Size   | 32768                |
| Spectral Size   | 65536                |
| Parameter          | Value                  |
|--------------------|------------------------|
| Origin             | Varian                 |
| Owner              |                        |
| Instrument         | inova                  |
| Solvent            | CDCl3                  |
| Temperature        | 20.0                   |
| Pulse Sequence     | s2pul                  |
| Experiment         | 1D                     |
| Probe              | QUAD                   |
| Number of Scans    | 64                     |
| Receiver Gain      | 50                     |
| Relaxation Delay   | 0.0000                 |
| Pulse Width        | 6.2500                 |
| Presaturation Frequency |                |
| Spectrometer Frequency | 470.15            |
| Spectral Width     | 1000000.0              |
| Lowest Frequency   | 79501.3                |
| Nucleus            | 19F                    |
| Acquired Size      | 32768                  |
| Spectral Size      | 65536                  |

![Chemical structure](image.png)
| Parameter          | Value                          |
|--------------------|-------------------------------|
| 1 Origin           | Varian                        |
| 2 Owner            |                               |
| 3 Instrument       | inova                         |
| 4 Solvent          | Acetone                       |
| 5 Temperature      | 20.0                          |
| 6 Pulse Sequence   | s2pul                         |
| 7 Experiment       | 1D                            |
| 8 Probe            | QUAD                          |
| 9 Number of Scans  | 8                             |
| 10 Receiver Gain   | 52                            |
| 11 Relaxation Delay| 15.0000                      |
| 12 Pulse Width     | 6.5000                        |
| 13 Presaturation Frequency |                   |
| 14 Spectrometer Frequency | 499.70                      |
| 15 Spectral Width  | 7024.9                        |
| 16 Lowest Frequency| 1.013.9                      |
| 17 Nucleus         | 1H                            |
| 18 Acquired Size   | 32768                         |
| 19 Spectral Size   | 65536                         |

![NMR Spectra](chart)
Parameter | Value
---|---
1 Origin | Bruker BioSpin GmbH
2 Owner | user1d
3 Instrument | spect
4 Solvent | Acetone
5 Temperature | 298.0
6 Pulse Sequence | zgpg30
7 Experiment | 1D
8 Probe | Z127784_0002_CP BBO 500S1 BBF_H.D.05 Z
9 Number of Scans | 256
10 Receiver Gain | 190.5
11 Relaxation Delay | 2.0000
12 Pulse Width | 10.0000
13 Presaturation Frequency
14 Spectrometer Frequency | 125.83
15 Spectral Width | 315126
16 Lowest Frequency | 1805.5
17 Nucleus | 13C
18 Acquired Size | 32768
19 Spectral Size | 65536
| Parameter          | Value                          |
|--------------------|--------------------------------|
| 1 Origin           | Varian                         |
| 2 Owner            |                                |
| 3 Instrument       | inova                          |
| 4 Solvent          | CDCl3                          |
| 5 Temperature      | 20.0                           |
| 6 Pulse Sequence   | s2pul                          |
| 7 Experiment       | 1D                             |
| 8 Probe            | hcn                            |
| 9 Number of Scans  | 0                              |
| 10 Receiver Gain   | 32                             |
| 11 Relaxation Delay| 15.0000                        |
| 12 Pulse Width     | 7.0000                         |
| 13 Presaturation Frequency |                  |
| 14 Spectrometer Frequency | 500.07                        |
| 15 Spectral Width  | 8000.0                         |
| 16 Lowest Frequency| 1520.6                         |
| 17 Nucleus         | 1H                             |
| 18 Acquired Size   | 32768                          |
| 19 Spectral Size   | 65536                          |

![NMR Spectrum](image.png)
| Parameter          | Value            |
|--------------------|------------------|
| Origin             | Varian           |
| Owner              |                  |
| Instrument         | inova            |
| Solvent            | CDCl3            |
| Temperature        | 30.0             |
| Pulse Sequence     | s2pul            |
| Experiment         | 1D               |
| Probe              | QUAD             |
| Number of Scans    | 258              |
| Receiver Gain      | 60               |
| Relaxation Delay   | 1.0000           |
| Pulse Width        | 6.0000           |
| Presaturation Frequency |            |
| Spectrometer Frequency | 125.66          |
| Spectral Width     | 30165.9          |
| Lowest Frequency   | 1281.4           |
| Nucleus            | 13C              |
| Acquired Size      | 32768            |
| Spectral Size      | 65536            |
| Parameter      | Value                      |
|----------------|----------------------------|
| 1 Origin       | Varian                     |
| 2 Owner        |                            |
| 3 Instrument   | inova                      |
| 4 Solvent      | CDCl3                      |
| 5 Temperature  | 29.0                       |
| 6 Pulse Sequence | s2pul                  |
| 7 Experiment   | 1D                         |
| 8 Probe        | QUAD                       |
| 9 Number of Scans | 32                      |
| 10 Receiver Gain | 40                      |
| 11 Relaxation Delay | 15.0000          |
| 12 Pulse Width | 6.5000                     |
| 13 Presaturation Frequency |                |
| 14 Spectrometer Frequency | 499.69                |
| 15 Spectral Width | 7024.9                   |
| 16 Lowest Frequency | .1021.4                  |
| 17 Nucleus     | 1H                         |
| 18 Acquired Size | 32768                   |
| 19 Spectral Size | 65536                   |
| Parameter          | Value               |
|--------------------|---------------------|
| 1 Origin           | Varian              |
| 2 Owner            |                     |
| 3 Instrument       | inova               |
| 4 Solvent          | CDCl3               |
| 5 Temperature      | 22.0                |
| 6 Pulse Sequence   | s2pul               |
| 7 Experiment       | 1D                  |
| 8 Probe            | QUAD                |
| 9 Number of Scans  | 512                 |
| 10 Receiver Gain   | 60                  |
| 11 Relaxation Delay| 5.0000              |
| 12 Pulse Width     | 6.0000              |
| 13 Presaturation Frequency |            |
| 14 Spectrometer Frequency | 125.66          |
| 15 Spectral Width  | 30165.9             |
| 16 Lowest Frequency| 1277.3              |
| 17 Nucleus         | 13C                 |
| 18 Acquired Size   | 32768               |
| 19 Spectral Size   | 65536               |
| Parameter       | Value       |
|-----------------|-------------|
| Origin          | Varian      |
| Owner           |             |
| Instrument      | inova       |
| Solvent         | CDC13       |
| Temperature     | 22.0        |
| Pulse Sequence  | s2pul       |
| Experiment      | 1D          |
| Probe           | QUAD        |
| Number of Scans | 32          |
| Receiver Gain   | 46.0000     |
| Relaxation Delay| 2.0000      |
| Pulse Width     | 6.2500      |
| Presaturation Frequency |             |
| Spectrometer Frequency | 470.15 |
| Spectral Width  | 100000.0    |
| Lowest Frequency| 795013.3    |
| Nucleus         | 19F         |
| Acquired Size   | 32768       |
| Spectral Size   | 65536       |
| Parameter          | Value                  |
|--------------------|------------------------|
| Origin             | Varian                 |
| Owner              |                        |
| Instrument         | inova                  |
| Solvent            | CDCl3                  |
| Temperature        | 20.0                   |
| Pulse Sequence     | s2pul                  |
| Experiment         | 1D                     |
| Probe              | QUAD                   |
| Number of Scans    | 1024                   |
| Receiver Gain      | 60                     |
| Relaxation Delay   | 2.0000                 |
| Pulse Width        | 6.0000                 |
| Presaturation Frequency |                |
| Spectrometer Frequency | 125.66               |
| Spectral Width     | 30165.9                |
| Lowest Frequency   | 1276.6                 |
| Nucleus            | 13C                    |
| Acquired Size      | 32768                  |
| Spectral Size      | 65536                  |

![Spectral graph](image-url)
| Parameter       | Value                                      |
|-----------------|--------------------------------------------|
| 1 Origin        | Bruker BioSpin GmbH                        |
| 2 Owner         | userid                                     |
| 3 Instrument    | spect                                      |
| 4 Solvent       | CDCl3                                      |
| 5 Temperature   | 298.0                                      |
| 6 Pulse Sequence| zg30                                       |
| 7 Experiment    | 1D                                         |
| 8 Probe         | Z127784_0002,CPBB0500S1,BBF,H.D.05,Z     |
| 9 Number of Scans| 16                                         |
| 10 Receiver Gain| 19.2                                       |
| 11 Relaxation Delay| 15.0000                                  |
| 12 Pulse Width  | 12.0000                                    |
| 13 Presaturation Frequency|                      |
| 14 Spectrometer Frequency| 500.35                                   |
| 15 Spectral Width| 10000.0                                   |
| 16 Lowest Frequency| .19223                                    |
| 17 Nucleus      | 1H                                         |
| 18 Acquired Size| 32768                                      |
| 19 Spectral Size| 65536                                      |

The graph shows a spectral analysis with resonances indicating DCM (dichloromethane) at specific ppm values.
| Parameter             | Value |
|-----------------------|-------|
| Origin                | Bruker BioSpin GmbH |
| Owner                 | user1d |
| Instrument            | spect |
| Solvent               | CDCl3 |
| Temperature           | 298.0 |
| Pulse Sequence        | zgpg30 |
| Experiment            | 1D |
| Probe                 | Z127784_0002 (CP880 500S1 BBF-H.D.05 Z) |
| Number of Scans       | 256 |
| Receiver Gain         | 190.5 |
| Relaxation Delay      | 2.0000 |
| Pulse Width           | 10.0000 |
| Presaturation Frequency|       |
| Spectrometer Frequency| 125.83 |
| Spectral Width        | 29761.9 |
| Lowest Frequency      | 2304.0 |
| Nucleus               | 13C |
| Acquired Size         | 32768 |
| Spectral Size         | 65536 |
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| Origin             | Bruker BioSpin GmbH                                                  |
| Owner              | user1d                                                                |
| Instrument         | spect                                                                |
| Solvent            | CDCl₃                                                                |
| Temperature        | 298.0                                                                |
| Pulse Sequence     | zg30                                                                 |
| Experiment         | 1D                                                                   |
| Probe              | Z127784_0002, CP880 500S1 BBF-H.D.05 Z₁                               |
| Number of Scans    | 16                                                                   |
| Receiver Gain      | 61.8                                                                 |
| Relaxation Delay   | 15.0000                                                              |
| Pulse Width        | 12.0000                                                              |
| Presaturation Frequency |                                                              |
| Spectrometer Frequency | 500.35                                                            |
| Spectral Width     | 10000.0                                                              |
| Lowest Frequency   | .19223                                                              |
| Nucleus            | 1H                                                                   |
| Acquired Size      | 32768                                                                |
| Spectral Size      | 65536                                                                |

![NMR Spectrum](image)
Parameter | Value
--- | ---
1 Origin | Bruker BioSpin GmbH
2 Owner | user1d
3 Instrument | spect
4 Solvent | CDCl3
5 Temperature | 298.0
6 Pulse Sequence | zgpg30
7 Experiment | 1D
8 Probe | Z127784_0002, CPBB050051 BBF-H-D-05 Z1
9 Number of Scans | 256
10 Receiver Gain | 190.5
11 Relaxation Delay | 2.0000
12 Pulse Width | 10.0000
13 Presaturation Frequency
14 Spectrometer Frequency | 125.83
15 Spectral Width | 29761.9
16 Lowest Frequency | 2282.7
17 Nucleus | 13C
18 Acquired Size | 32768
19 Spectral Size | 65536

![NMR Spectrum](image.png)
Parameter | Value
--- | ---
1 Origin | Bruker BioSpin GmbH
2 Owner | user1d
3 Instrument | spect
4 Solvent | CDCl3
5 Temperature | 298.0
6 Pulse Sequence | zgfhigqn 2
7 Experiment | 1D
8 Probe | Z127784_0002, CP/BBO 500S1 BBF, H.D. 05 Z
9 Number of Scans | 32
10 Receiver Gain | 190.5
11 Relaxation Delay | 1.0000
12 Pulse Width | 15.0000
13 Presaturation Frequency
14 Spectrometer Frequency | 470.75
15 Spectral Width | 113636.4
16 Lowest Frequency | 0.103898.1
17 Nucleus | 19F
18 Acquired Size | 65536
19 Spectral Size | 131072
Parameter | Value
--- | ---
1. Origin | Bruker BioSpin GmbH
2. Owner | user1d
3. Instrument | spect
4. Solvent | CDC13
5. Temperature | 298 1
6. Pulse Sequence | zg30
7. Experiment | 1D
8. Probe | Z127784_0002, CPBBO 500S1 BBF, H.D. 05 Z1
9. Number of Scans | 16
10. Receiver Gain | 69.2
11. Relaxation Delay | 15.0000
12. Pulse Width | 12.0000
13. Presaturation Frequency
14. Spectrometer Frequency | 500.35
15. Spectral Width | 10000.0
16. Lowest Frequency | 1922.3
17. Nucleus | 1H
18. Acquired Size | 32768
19. Spectral Size | 65536

\[ \text{H}_2\text{O} \]

\[ \text{grease} \]
| Parameter         | Value                                                                 |
|------------------|----------------------------------------------------------------------|
| Origin           | Bruker BioSpin GmbH                                                  |
| Owner            | user1d                                                              |
| Instrument       | spect                                                               |
| Solvent          | CDCl3                                                                |
| Temperature      | 298.1                                                               |
| Pulse Sequence   | zgpg30                                                              |
| Experiment       | 1D                                                                  |
| Probe            | Z127784_0002, CP880 500S1 BBF. H. D. 05 Z1                           |
| Number of Scans  | 512                                                                 |
| Receiver Gain    | 190.5                                                               |
| Relaxation Delay | 2.0000                                                              |
| Pulse Width      | 10.0000                                                             |
| Presaturation Frequency |                                                                  |
| Spectrometer Frequency | 125.83                                                               |
| Spectral Width   | 31512.6                                                             |
| Lowest Frequency | 1900.5                                                              |
| Nucleus          | 13C                                                                 |
| Acquired Size    | 32768                                                               |
| Spectral Size    | 65536                                                               |
| Parameter          | Value                                                                 |
|--------------------|------------------------------------------------------------------------|
| Origin             | Bruker BioSpin GmbH                                                    |
| Owner              | user1d                                                                 |
| Instrument         | spect                                                                   |
| Solvent            | CDCl3                                                                  |
| Temperature        | 298.1                                                                  |
| Pulse Sequence     | zgfhigqn 2                                                             |
| Experiment         | 1D                                                                     |
| Probe              | Z127784_0002, CPBB0 500S1 BBF. H. D. 05 Z | | |
| Number of Scans    | 16                                                                     |
| Receiver Gain      | 190.5                                                                  |
| Relaxation Delay   | 15.0000                                                                |
| Pulse Width        | 15.0000                                                                |
| Presaturation Frequency |                                                              |
| Spectrometer Frequency | 470.75                                                                 |
| Spectral Width     | 113636.4                                                               |
| Lowest Frequency   | 103898.1                                                               |
| Nucleus            | 19F                                                                    |
| Acquired Size      | 65536                                                                  |
| Spectral Size      | 131072                                                                 |
| Parameter      | Value            |
|----------------|------------------|
| 1 Origin       | Varian           |
| 2 Owner        |                  |
| 3 Instrument   | inova            |
| 4 Solvent      | CDCl3            |
| 5 Temperature  | 20.0             |
| 6 Pulse Sequence| s2pul           |
| 7 Experiment   | 1D               |
| 8 Probe        | QUAD             |
| 9 Number of Scans | 4              |
| 10 Receiver Gain| 50              |
| 11 Relaxation Delay | 0000          |
| 12 Pulse Width  | 6.5000           |
| 13 Presaturation Frequency |        |
| 14 Spectrometer Frequency | 499.69 |
| 15 Spectral Width      | 7024.9           |
| 16 Lowest Frequency    | 1021.4           |
| 17 Nucleus       | 1H               |
| 18 Acquired Size  | 32768            |
| 19 Spectral Size  | 65536            |
| Parameter            | Value           |
|----------------------|-----------------|
| Origin               | Varian          |
| Owner                |                 |
| Instrument           | inova           |
| Solvent              | CDCl3           |
| Temperature          | 20.0            |
| Pulse Sequence       | s2pul           |
| Experiment           | 1D              |
| Probe                | QUAD            |
| Number of Scans      | 120             |
| Receiver Gain        | 60              |
| Relaxation Delay     | 2.0000          |
| Pulse Width          | 6.0000          |
| Presaturation Frequency |            |
| Spectrometer Frequency | 125.66          |
| Spectral Width       | 30165.9         |
| Lowest Frequency     | 1276.1          |
| Nucleus              | 13C             |
| Acquired Size        | 32768           |
| Spectral Size        | 65536           |
| Parameter          | Value |
|--------------------|-------|
| Origin             | Bruker BioSpin GmbH |
| Owner              | user1d |
| Instrument         | spect |
| Solvent            | CD2Cl2 |
| Temperature        | 298.0 |
| Pulse Sequence     | zg30 |
| Experiment         | 1D |
| Probe              | Z127784_0002, CP3805 S0051 BBF/H.D.05 ZD |
| Number of Scans    | 16 |
| Receiver Gain      | 29.7 |
| Relaxation Delay   | 15.0000 |
| Pulse Width        | 12.0000 |
| Presaturation Frequency |       |
| Spectrometer Frequency | 500.35 |
| Spectral Width     | 10000.0 |
| Lowest Frequency   | 1.9298 |
| Nucleus            | 1H |
| Acquired Size      | 32768 |
| Spectral Size      | 65536 |

![NMR spectrum graph](image-url)
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| Origin             | Bruker BioSpin GmbH                                                  |
| Owner              | user1d                                                               |
| Instrument         | spect                                                                |
| Solvent            | CD2Cl2                                                               |
| Temperature        | 298.0                                                               |
| Pulse Sequence     | zgpg30                                                               |
| Experiment         | 1D                                                                   |
| Probe              | Z127784_0002, CPBBB50051 BBF_H.D.05 Z, Z127784_0002                 |
| Number of Scans    | 256                                                                  |
| Receiver Gain      | 190.5                                                                |
| Relaxation Delay   | 2.0000                                                              |
| Pulse Width        | 10.0000                                                              |
| Presaturation      |                                                                      |
| Spectrometer       | 125.83                                                               |
| Spectral Width     | 29761.9                                                              |
| Lowest Frequency   | 2227.7                                                               |
| Nucleus            | 13C                                                                  |
| Acquired Size      | 32768                                                                |
| Spectral Size      | 65536                                                                |
| Parameter       | Value            |
|-----------------|------------------|
| 1 Origin        | Varian           |
| 2 Owner         |                  |
| 3 Instrument    | inova            |
| 4 Solvent       | CDCl3            |
| 5 Temperature   | 20.0             |
| 6 Pulse Sequence| s2pul            |
| 7 Experiment    | 1D               |
| 8 Probe         | hcn              |
| 9 Number of Scans| 8               |
| 10 Receiver Gain| 42               |
| 11 Relaxation Delay| 10 3000       |
| 12 Pulse Width  | 7.0000           |
| 13 Presaturation Frequency |          |
| 14 Spectrometer Frequency| 500.07       |
| 15 Spectral Width | 8000.0         |
| 16 Lowest Frequency | 1521.1         |
| 17 Nucleus      | 1H               |
| 18 Acquired Size| 32768            |
| 19 Spectral Size| 65536            |
| Parameter          | Value       |
|--------------------|-------------|
| Origin             | Varian      |
| Owner              |             |
| Instrument         | inova       |
| Solvent            | CDCl3       |
| Temperature        | 20.0        |
| Pulse Sequence     | s2pul       |
| Experiment         | 1D          |
| Probe              | QUAD        |
| Number of Scans    | 512         |
| Receiver Gain      | 60          |
| Relaxation Delay   | 1.0000      |
| Pulse Width        | 6.0000      |
| Presaturation Frequency |       |
| Spectrometer Frequency | 125.66    |
| Spectral Width     | 30165.9     |
| Lowest Frequency   | 1275.9      |
| Nucleus            | 13C         |
| Acquired Size      | 32768       |
| Spectral Size      | 65536       |
| Parameter          | Value                        |
|--------------------|------------------------------|
| 1. Origin          | Varian                       |
| 2. Owner           |                              |
| 3. Instrument      | inova                        |
| 4. Solvent         | CDCl3                        |
| 5. Temperature     | 20.0                         |
| 6. Pulse Sequence  | s2pul                        |
| 7. Experiment      | 1D                           |
| 8. Probe           | hcn                          |
| 9. Number of Scans | 16                           |
| 10. Receiver Gain  | 50                           |
| 11. Relaxation Delay | 15.0000                     |
| 12. Pulse Width    | 6.8750                       |
| 13. Presaturation Frequency |                      |
| 14. Spectrometer Frequency | 500.07                      |
| 15. Spectral Width | 8000.0                       |
| 16. Lowest Frequency | 1521.1                      |
| 17. Nucleus        | 1H                           |
| 18. Acquired Size  | 32768                        |
| 19. Spectral Size  | 65536                        |

![NMR Spectrum](image)

**Diastereomer 1**

**H$_2$O**
| Parameter          | Value               |
|--------------------|---------------------|
| 1 Origin           | Varian              |
| 2 Owner            |                     |
| 3 Instrument       | inova               |
| 4 Solvent          | CDCl3               |
| 5 Temperature      | 20.0                |
| 6 Pulse Sequence   | s2pul               |
| 7 Experiment       | 1D                  |
| 8 Probe            | QUAD                |
| 9 Number of Scans  | 1600                |
| 10 Receiver Gain   | 60                  |
| 11 Relaxation Delay| 1.0000              |
| 12 Pulse Width     | 6.0000              |
| 13 Presaturation Frequency |             |
| 14 Spectrometer Frequency | 125.66            |
| 15 Spectral Width  | 30165.9             |
| 16 Lowest Frequency| 1273.9              |
| 17 Nucleus         | 13C                 |
| 18 Acquired Size   | 32768               |
| 19 Spectral Size   | 65536               |

![Diastereomer 1](image)
| Parameter       | Value            |
|-----------------|------------------|
| 1 Origin        | Varian           |
| 2 Owner         |                  |
| 3 Instrument    | inova            |
| 4 Solvent       | CDCl₃            |
| 5 Temperature   | 20.0             |
| 6 Pulse Sequence| s2pul            |
| 7 Experiment    | 1D               |
| 8 Probe         | hcn              |
| 9 Number of Scans| 16              |
| 10 Receiver Gain| 48               |
| 11 Relaxation Delay| 15.0000        |
| 12 Pulse Width  | 6.8750           |
| 13 Presaturation Frequency|          |
| 14 Spectrometer Frequency| 500.07        |
| 15 Spectral Width| 8000.0          |
| 16 Lowest Frequency| .15211         |
| 17 Nucleus      | 1H               |
| 18 Acquired Size| 32768            |
| 19 Spectral Size| 65536            |

Diastereomer 2
| Parameter          | Value                      |
|--------------------|----------------------------|
| 1 Origin           | Varian                     |
| 2 Owner            |                             |
| 3 Instrument       | inova                      |
| 4 Solvent          | CDCl3                      |
| 5 Temperature      | 20.0                       |
| 6 Pulse Sequence   | s2pul                      |
| 7 Experiment       | 1D                         |
| 8 Probe            | QUAD                       |
| 9 Number of Scans  | 1600                       |
| 10 Receiver Gain   | 60                         |
| 11 Relaxation Delay| 1.0000                     |
| 12 Pulse Width     | 6.0000                     |
| 13 Presaturation   | Frequency                  |
| 14 Spectrometer    | Frequency 125.66           |
| 15 Spectral Width  | 30165.9                    |
| 16 Lowest Frequency| 1274.3                     |
| 17 Nucleus         | 13C                        |
| 18 Acquired Size   | 32768                      |
| 19 Spectral Size   | 65536                      |

Diastereomer 2
| Parameter          | Value        |
|--------------------|--------------|
| Origin             | Varian       |
| Owner              |              |
| Instrument         | inova        |
| Solvent            | CDCl3        |
| Temperature        | 20.0         |
| Pulse Sequence     | s2pul        |
| Experiment         | 1D           |
| Probe              | hcn          |
| Number of Scans    | 8            |
| Receiver Gain      | 38           |
| Relaxation Delay   | 15.0000      |
| Pulse Width        | 7.0000       |
| Presaturation Frequency |          |
| Spectrometer Frequency | 500.07      |
| Spectral Width     | 8000.0       |
| Lowest Frequency   | 1.5191       |
| Nucleus            | 1H           |
| Acquired Size      | 32768        |
| Spectral Size      | 65536        |

![NMR Spectrogram](image-url)
| Parameter       | Value                          |
|-----------------|--------------------------------|
| 1 Origin        | Varian                         |
| 2 Owner         |                                |
| 3 Instrument    | inova                          |
| 4 Solvent       | CDCl3                          |
| 5 Temperature   | 20.0                           |
| 6 Pulse Sequence| s2pul                          |
| 7 Experiment    | 1D                             |
| 8 Probe         | QUAD                           |
| 9 Number of Scans| 955                           |
| 10 Receiver Gain| 60                             |
| 11 Relaxation Delay | 1.0000                      |
| 12 Pulse Width  | 6.0000                         |
| 14 Spectrometer Frequency | 125.66                      |
| 15 Spectral Width | 30165.9                      |
| 16 Lowest Frequency | 1278.3                       |
| 17 Nucleus      | 13C                            |
| 18 Acquired Size | 32768                          |
| 19 Spectral Size | 65536                          |
| Parameter       | Value               |
|-----------------|---------------------|
| Origin          | Varian              |
| Owner           |                     |
| Instrument      | inova               |
| Solvent         | CDCl3               |
| Temperature     | 20.0                |
| Pulse Sequence  | s2pul               |
| Experiment      | 1D                  |
| Probe           | QUAD                |
| Number of Scans | 4                   |
| Receiver Gain   | 50                  |
| Relaxation Delay| 0.00000             |
| Pulse Width     | 6.2500              |
| Presaturation Frequency |             |
| Spectrometer Frequency | 470.15      |
| Spectral Width  | 100000.0            |
| Lowest Frequency| 79501.3             |
| Nucleus         | 19F                 |
| Acquired Size   | 32768               |
| Spectral Size   | 65536               |

- Parameter 1 - Origin: Varian
- Parameter 2 - Owner: 
- Parameter 3 - Instrument: inova
- Parameter 4 - Solvent: CDCl3
- Parameter 5 - Temperature: 20.0
- Parameter 6 - Pulse Sequence: s2pul
- Parameter 7 - Experiment: 1D
- Parameter 8 - Probe: QUAD
- Parameter 9 - Number of Scans: 4
- Parameter 10 - Receiver Gain: 50
- Parameter 11 - Relaxation Delay: 0.00000
- Parameter 12 - Pulse Width: 6.2500
- Parameter 13 - Presaturation Frequency: 
- Parameter 14 - Spectrometer Frequency: 470.15
- Parameter 15 - Spectral Width: 100000.0
- Parameter 16 - Lowest Frequency: 79501.3
- Parameter 17 - Nucleus: 19F
- Parameter 18 - Acquired Size: 32768
- Parameter 19 - Spectral Size: 65536

The diagram shows a spectral plot with a peak at approximately -90 ppm, indicating the chemical shift of the compound.
gCOSY

tertiary H-methylene cross peaks
Parameter | Value
--- | ---
1 | Origin
2 | Varian
3 | Owner
4 | Instrument
5 | inova
6 | Solvent
7 | CDCl3
8 | Temperature
9 | 20.0
10 | Pulse Sequence
11 | s2pul
12 | Experiment
13 | 1D
14 | Probe
15 | hcn
16 | Number of Scans
17 | 8
18 | Receiver Gain
19 | 42
20 | Relaxation Delay
21 | 10.3000
22 | Pulse Width
23 | 7.0000
24 | Presaturation Frequency
25 | Spectrometer Frequency
26 | 500.07
27 | Spectral Width
28 | 8000.0
29 | Lowest Frequency
30 | 1.5211
31 | Nucleus
32 | 1H
33 | Acquired Size
34 | 32768
35 | Spectral Size
36 | 65536
Parameter | Value
---|---
1 Origin | Varian
2 Owner | 
3 Instrument | inova
4 Solvent | CDCl3
5 Temperature | 20.0
6 Pulse Sequence | s2pul
7 Experiment | 1D
8 Probe | QUAD
9 Number of Scans | 512
10 Receiver Gain | 60
11 Relaxation Delay | 1.0000
12 Pulse Width | 6.0000
13 Presaturation Frequency | 
14 Spectrometer Frequency | 125.66
15 Spectral Width | 30165.9
16 Lowest Frequency | 1274.3
17 Nucleus | 13C
18 Acquired Size | 32768
19 Spectral Size | 65536
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| 1 Origin           | Bruker BioSpin GmbH                                                  |
| 2 Owner            | user1d                                                               |
| 3 Instrument       | spect                                                                |
| 4 Solvent          | CDCl3                                                                |
| 5 Temperature      | 298.0                                                                |
| 6 Pulse Sequence   | zg30                                                                |
| 7 Experiment       | 1D                                                                  |
| 8 Probe            | Z127784_002, CPBBDO 500S1 BBF, H.D. 05Z1                             |
| 9 Number of Scans  | 16                                                                  |
| 10 Receiver Gain   | 29.7                                                                |
| 11 Relaxation Delay| 15.0000                                                             |
| 12 Pulse Width     | 12.0000                                                             |
| 13 Presaturation Frequency |                                                                   |
| 14 Spectrometer Frequency | 500.35                |
| 15 Spectral Width  | 10000.0                                                             |
| 16 Lowest Frequency| 1.9223                                                              |
| 17 Nucleus         | 1H                                                                  |
| 18 Acquired Size   | 32768                                                               |
| 19 Spectral Size   | 65536                                                              |

![Chemical structure](image)
| Parameter       | Value                                                                 |
|-----------------|----------------------------------------------------------------------|
| Origin          | Bruker BioSpin GmbH                                                  |
| Owner           | user1d                                                              |
| Instrument      | spect                                                               |
| Solvent         | CDCl3                                                               |
| Temperature     | 298.0                                                               |
| Pulse Sequence  | zgpg30                                                              |
| Experiment      | 1D                                                                  |
| Probe           | Z127784_0002, CP585 S500S1 BBF, H.D. 05 Z,                          |
| Number of Scans | 256                                                                 |
| Receiver Gain   | 190.5                                                               |
| Relaxation Delay| 2.0000                                                              |
| Pulse Width     | 10.0000                                                             |
| Presaturation Frequency |                                                                |
| Spectrometer Frequency | 125.83                                                             |
| Spectral Width  | 29761.9                                                             |
| Lowest Frequency| 2286.2                                                              |
| Nucleus         | 13C                                                                 |
| Acquired Size   | 32768                                                               |
| Spectral Size   | 65536                                                               |
| Parameter     | Value                   |
|---------------|-------------------------|
| Origin        | Varian                  |
| Owner         |                         |
| Instrument    | inova                   |
| Solvent       | CD2Cl2                  |
| Temperature   | 20.0                    |
| Pulse Sequence| s2pul                   |
| Experiment    | 1D                      |
| Probe         | QUAD                    |
| Number of Scans| 8                     |
| Receiver Gain | 48                      |
| Relaxation Delay | 15.0000       |
| Pulse Width   | 6.5000                  |
| Presaturation Frequency |            |
| Spectrometer Frequency | 499.69         |
| Spectral Width | 7024.9                 |
| Lowest Frequency | 1019.4                 |
| Nucleus       | 1H                      |
| Acquired Size | 32768                   |
| Spectral Size | 65536                   |
| Parameter    | Value                              |
|--------------|------------------------------------|
| 1 Origin     | Varian                             |
| 2 Owner      |                                    |
| 3 Instrument | inova                              |
| 4 Solvent    | CDCl3                              |
| 5 Temperature| 20.0                               |
| 6 Pulse Sequence | s2pul                          |
| 7 Experiment | 1D                                 |
| 8 Probe      | QUAD                               |
| 9 Number of Scans | 525                           |
| 10 Receiver Gain | 60                             |
| 11 Relaxation Delay | 2.0000                          |
| 12 Pulse Width | 6.0000                             |
| 13 Presaturation Frequency |                    |
| 14 Spectrometer Frequency | 125.66                           |
| 15 Spectral Width | 30165.9                           |
| 16 Lowest Frequency | 1463.5                           |
| 17 Nucleus   | 13C                                |
| 18 Acquired Size | 32768                             |
| 19 Spectral Size | 65536                            |

![NMR Spectrum of Compound](image)
| Parameter | Value          |
|-----------|----------------|
| 1 Origin  | Varian         |
| 2 Owner   |                |
| 3 Instrument | inova       |
| 4 Solvent | CDCl3          |
| 5 Temperature | 20.0        |
| 6 Pulse Sequence | s2pul      |
| 7 Experiment  | 1D            |
| 8 Probe   | QUAD           |
| 9 Number of Scans | 8            |
| 10 Receiver Gain | 46           |
| 11 Relaxation Delay | 15.0000    |
| 12 Pulse Width | 6.5000      |
| 13 Presaturation Frequency |         |
| 14 Spectrometer Frequency | 499.69   |
| 15 Spectral Width | 7024.9     |
| 16 Lowest Frequency | 1021.4     |
| 17 Nucleus | 1H             |
| 18 Acquired Size | 32768       |
| 19 Spectral Size     | 65536        |
| Parameter          | Value                      |
|--------------------|----------------------------|
| 1 Origin           | Varian                     |
| 2 Owner            |                             |
| 3 Instrument       | inova                      |
| 4 Solvent          | CDCl3                      |
| 5 Temperature      | 20.0                       |
| 6 Pulse Sequence   | s2pul                      |
| 7 Experiment       | 1D                         |
| 8 Probe            | QUAD                       |
| 9 Number of Scans  | 479                        |
| 10 Receiver Gain   | 60                         |
| 11 Relaxation Delay| 3.00000                    |
| 12 Pulse Width     | 6.00000                    |
| 13 Presaturation Frequency |                 |
| 14 Spectrometer Frequency | 125.66                |
| 15 Spectral Width  | 30165.9                    |
| 16 Lowest Frequency| 1275.5                     |
| 17 Nucleus         | 13C                        |
| 18 Acquired Size   | 32768                      |
| 19 Spectral Size   | 65536                      |

![Spectrum Image](image-url)
| Parameter          | Value               |
|--------------------|---------------------|
| 1. Origin          | Varian              |
| 2. Owner           |                     |
| 3. Instrument      | inova               |
| 4. Solvent         | CDCl₃               |
| 5. Temperature     | 20.0                |
| 6. Pulse Sequence  | s2pul               |
| 7. Experiment      | 1D                  |
| 8. Probe           | hcn                 |
| 9. Number of Scans | 8                   |
| 10. Receiver Gain  | 42                  |
| 11. Relaxation Delay| 15.0000             |
| 12. Pulse Width    | 7.0000              |
| 13. Presaturation Frequency |          |
| 14. Spectrometer Frequency | 500.07          |
| 15. Spectral Width | 8000.0              |
| 16. Lowest Frequency| 1.5206              |
| 17. Nucleus        | 1H                  |
| 18. Acquired Size  | 32768               |
| 19. Spectral Size  | 65536               |
| Parameter       | Value |
|-----------------|-------|
| 1 Origin        | Varian|
| 2 Owner         |       |
| 3 Instrument    | inova |
| 4 Solvent       | CDCl3 |
| 5 Temperature   | 20.0  |
| 6 Pulse Sequence| s2pul |
| 7 Experiment    | 1D    |
| 8 Probe         | QUAD  |
| 9 Number of Scans| 1024 |
| 10 Receiver Gain| 60    |
| 11 Relaxation Delay | 2.0000 |
| 12 Pulse Width  | 6.0000|
| 13 Presaturation Frequency |     |
| 14 Spectrometer Frequency | 125.66 |
| 15 Spectral Width | 30165.9 |
| 16 Lowest Frequency | 1274.8 |
| 17 Nucleus      | 13C   |
| 18 Acquired Size | 32768 |
| 19 Spectral Size | 65536 |
| Parameter             | Value     |
|-----------------------|-----------|
| 1 Origin              | Varian    |
| 2 Owner               |           |
| 3 Instrument          | inova     |
| 4 Solvent             | CDCl3     |
| 5 Temperature         | 20.0      |
| 6 Pulse Sequence      | s2pul     |
| 7 Experiment          | 1D        |
| 8 Probe               | QUAD      |
| 9 Number of Scans     | 5         |
| 10 Receiver Gain      | 50        |
| 11 Relaxation Delay   | 15.0000   |
| 12 Pulse Width        | 6.5000    |
| 13 Presaturation Frequency |        |
| 14 Spectrometer Frequency | 499.69   |
| 15 Spectral Width     | 7024.9    |
| 16 Lowest Frequency   | 1021.9    |
| 17 Nucleus            | 1H        |
| 18 Acquired Size      | 32768     |
| 19 Spectral Size      | 65536     |

The diagram shows a 1D NMR spectrum with peaks labeled from 0.0 to 20.0 ppm on the x-axis and chemical shifts from -2.0 to -380 on the y-axis.
| Parameter          | Value       |
|--------------------|-------------|
| 1 Origin           | Varian      |
| 2 Owner            |             |
| 3 Instrument       | inova       |
| 4 Solvent          | CDCl3       |
| 5 Temperature      | 20.0        |
| 6 Pulse Sequence   | s2pul       |
| 7 Experiment       | 1D          |
| 8 Probe            | QUAD        |
| 9 Number of Scans  | 512         |
| 10 Receiver Gain   | 60          |
| 11 Relaxation Delay| 2.0000      |
| 12 Pulse Width     | 6.0000      |
| 13 Presaturation Frequency |         |
| 14 Spectrometer Frequency | 125.66   |
| 15 Spectral Width  | 30165.9     |
| 16 Lowest Frequency| 1275.9      |
| 17 Nucleus         | 13C         |
| 18 Acquired Size   | 32768       |
| 19 Spectral Size   | 65536       |
| Parameter       | Value     |
|-----------------|-----------|
| 1 Origin        | Varian    |
| 2 Owner         |           |
| 3 Instrument    | inova     |
| 4 Solvent       | CD2Cl2    |
| 5 Temperature   | 20.0      |
| 6 Pulse Sequence| s2pul     |
| 7 Experiment    | 1D        |
| 8 Probe         | QUAD      |
| 9 Number of Scans| 8        |
| 10 Receiver Gain| 41        |
| 11 Relaxation Delay| 15.0000 |
| 12 Pulse Width  | 6.5000    |
| 13 Presaturation Frequency|   |
| 14 Spectrometer Frequency| 499.69   |
| 15 Spectral Width| 7024.9   |
| 16 Lowest Frequency| 1018.9   |
| 17 Nucleus      | 1H        |
| 18 Acquired Size| 32768     |
| 19 Spectral Size| 65536     |
| Parameter     | Value                  |
|---------------|------------------------|
| Origin        | Varian                 |
| Owner         |                        |
| Instrument    | inova                  |
| Solvent       | CD2Cl2                 |
| Temperature   | 20.0                   |
| Pulse Sequence| s2pul                  |
| Experiment    | 1D                     |
| Probe         | QUAD                   |
| Number of Scans| 868                  |
| Receiver Gain | 60                     |
| Relaxation Delay| 2.0000               |
| Pulse Width   | 6.0000                 |
| Presaturation Frequency |        |
| Spectrometer Frequency | 125.66               |
| Spectral Width | 30165.9               |
| Lowest Frequency | 121.86                |
| Nucleus       | 13C                    |
| Acquired Size | 32768                  |
| Spectral Size | 65536                  |
Parameter | Value
--- | ---
1 Origin | Varian
2 Owner | 
3 Instrument | inova
4 Solvent | CD2Cl2
5 Temperature | 20.0
6 Pulse Sequence | s2pul
7 Experiment | 1D
8 Probe | QUAD
9 Number of Scans | 8
10 Receiver Gain | 41
11 Relaxation Delay | 15.0000
12 Pulse Width | 6.5000
13 Presaturation Frequency | 
14 Spectrometer Frequency | 499.69
15 Spectral Width | 7024.9
16 Lowest Frequency | 1.0189
17 Nucleus | 1H
18 Acquired Size | 32768
19 Spectral Size | 65536
| Parameter     | Value            |
|---------------|------------------|
| 1 Origin      | Varian           |
| 2 Owner       |                  |
| 3 Instrument  | inova            |
| 4 Solvent     | CD2Cl2           |
| 5 Temperature | 20.0             |
| 6 Pulse Sequence | s2pul         |
| 7 Experiment  | 1D               |
| 8 Probe       | QUAD             |
| 9 Number of Scans | 8             |
| 10 Receiver Gain | 41              |
| 11 Relaxation Delay | 15 0000    |
| 12 Pulse Width | 6.5000           |
| 13 Presaturation Frequency |        |
| 14 Spectrometer Frequency | 499.69   |
| 15 Spectral Width | 7024.9        |
| 16 Lowest Frequency | 1018.9        |
| 17 Nucleus    | 1H               |
| 18 Acquired Size | 32768          |
| 19 Spectral Size | 65536          |
| Parameter          | Value                      |
|--------------------|----------------------------|
| 1 Origin           | Varian                     |
| 2 Owner            |                            |
| 3 Instrument       | inova                      |
| 4 Solvent          | CD2Cl2                     |
| 5 Temperature      | 20.0                       |
| 6 Pulse Sequence   | s2pul                      |
| 7 Experiment       | 1D                         |
| 8 Probe            | QUAD                       |
| 9 Number of Scans  | 836                        |
| 10 Receiver Gain   | 60                         |
| 11 Relaxation Delay| 2.0000                    |
| 12 Pulse Width     | 6.0000                     |
| 13 Presaturation Frequency |                  |
| 14 Spectrometer Frequency   | 125.66                    |
| 15 Spectral Width  | 30165.9                    |
| 16 Lowest Frequency| 1219.6                     |
| 17 Nucleus         | 13C                        |
| 18 Acquired Size   | 32768                      |
| 19 Spectral Size   | 65536                      |
Parameter | Value
--- | ---
1. Origin | Varian
2. Owner | 
3. Instrument | inova
4. Solvent | CDCl3
5. Temperature | 20.0
6. Pulse Sequence | s2pul
7. Experiment | 1D
8. Probe | hcn
9. Number of Scans | 8
10. Receiver Gain | 42
11. Relaxation Delay | 15.0000
12. Pulse Width | 7.0000
13. Presaturation Frequency | 
14. Spectrometer Frequency | 500.07
15. Spectral Width | 8000.0
16. Lowest Frequency | 1520.1
17. Nucleus | 1H
18. Acquired Size | 32768
19. Spectral Size | 65536

![NMR Spectrum](image)
corresponding to 2 methylene carbons
| Parameter      | Value                                                                                                                                 |
|----------------|-------------------------------------------------------------------------------------------------------------------------------------|
| 1 Origin       | Bruker BioSpin GmbH                                                                                                               |
| 2 Owner        | user1d                                                                                                                             |
| 3 Instrument   | spect                                                                                                                              |
| 4 Solvent      | CDCl3                                                                                                                               |
| 5 Temperature  | 288.6                                                                                                                              |
| 6 Pulse Sequence | zg30                                                                                                                                  |
| 7 Experiment   | 1D                                                                                                                                  |
| 8 Probe        | Z127784_0002, CP880 500S1 BBF. H.D. 05 Z1                                                                                          |
| 9 Number of Scans | 16                                                                                                                                     |
| 10 Receiver Gain | 94.3                                                                                                                                   |
| 11 Relaxation Delay | 15.0000                                                                                                                            |
| 12 Pulse Width  | 12.0000                                                                                                                             |
| 13 Presaturation Frequency |                                                                                                                                       |
| 14 Spectrometer Frequency | 500.35                                                                                                                               |
| 15 Spectral Width  | 10000.0                                                                                                                              |
| 16 Lowest Frequency | 1.9213                                                                                                                               |
| 17 Nucleus     | 1H                                                                                                                                  |
| 18 Acquired Size | 32768                                                                                                                                  |
| 19 Spectral Size | 65536                                                                                                                                   |
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| Origin             | Bruker BioSpin GmbH                                                  |
| Owner              | user1d                                                              |
| Instrument         | spect                                                               |
| Solvent            | CDCl3                                                               |
| Temperature        | 288.7                                                               |
| Pulse Sequence     | zgpg30                                                              |
| Experiment         | 1D                                                                  |
| Probe              | Z127784_0002_CPBBO500S1BBF_H.D.05Z                                  |
| Number of Scans    | 512                                                                 |
| Receiver Gain      | 190.5                                                               |
| Relaxation Delay   | 2.00000                                                             |
| Pulse Width        | 10.00000                                                            |
| Presaturation Frequency |                                                                |
| Spectrometer Frequency | 125.83                                                             |
| Spectral Width     | 31512.6                                                             |
| Lowest Frequency   | 190.33                                                              |
| Nucleus            | 13C                                                                 |
| Acquired Size      | 32768                                                               |
| Spectral Size      | 65536                                                               |
| Parameter            | Value                                                                 |
|----------------------|----------------------------------------------------------------------|
| 1 Origin             | Bruker BioSpin GmbH                                                  |
| 2 Owner              | user1d                                                               |
| 3 Instrument         | spect                                                                |
| 4 Solvent            | CDCl₃                                                                |
| 5 Temperature        | 288.8                                                                |
| 6 Pulse Sequence     | zg30                                                                 |
| 7 Experiment         | 1D                                                                   |
| 8 Probe              | Z127784_0002, CP8BO 500S1 BBF. H. D. 05 Z₁                           |
| 9 Number of Scans    | 16                                                                   |
| 10 Receiver Gain     | 76.2                                                                 |
| 11 Relaxation Delay  | 15.0000                                                             |
| 12 Pulse Width       | 12.0000                                                              |
| 13 Presaturation Frequency |                                                                  |
| 14 Spectrometer Frequency | 500.35                                                               |
| 15 Spectral Width    | 10000.0                                                              |
| 16 Lowest Frequency  | 1920.9                                                               |
| 17 Nucleus           | 1H                                                                   |
| 18 Acquired Size     | 32768                                                                |
| 19 Spectral Size     | 65536                                                                |

![Chemical Structure](image)

**grease**

![NMR Spectrum](image)
| Parameter          | Value                                                                 |
|--------------------|------------------------------------------------------------------------|
| 1 Origin           | Bruker BioSpin GmbH                                                   |
| 2 Owner            | user1d                                                                 |
| 3 Instrument       | spect                                                                  |
| 4 Solvent          | CDCl3                                                                  |
| 5 Temperature      | 288.6                                                                 |
| 6 Pulse Sequence   | zgpg30                                                                 |
| 7 Experiment       | 1D                                                                     |
| 8 Probe            | Z127784_0002, CPBBO 500S1 BBF.H.D.05 Z1                                 |
| 9 Number of Scans  | 512                                                                   |
| 10 Receiver Gain   | 190.5                                                                 |
| 11 Relaxation Delay| 2.0000                                                                |
| 12 Pulse Width     | 10.0000                                                               |
| 13 Presaturation Frequency |                                                        |
| 14 Spectrometer Frequency | 125.83                                                                |
| 15 Spectral Width  | 31512.6                                                               |
| 16 Lowest Frequency| 1902.4                                                                |
| 17 Nucleus         | 13C                                                                   |
| 18 Acquired Size   | 32768                                                                 |
| 19 Spectral Size   | 65536                                                                 |
| Parameter       | Value            |
|-----------------|------------------|
| 1 Origin        | Varian           |
| 2 Owner         |                  |
| 3 Instrument    | inova            |
| 4 Solvent       | CD2Cl2           |
| 5 Temperature   | 20.0             |
| 6 Pulse Sequence| s2pul            |
| 7 Experiment    | 1D               |
| 8 Probe         | hcn              |
| 9 Number of Scans| 8               |
| 10 Receiver Gain| 32               |
| 11 Relaxation Delay| 15.0000       |
| 12 Pulse Width  | 7.0000           |
| 13 Presaturation Frequency | 500.07   |
| 14 Spectrometer Frequency | 500.07   |
| 15 Spectral Width | 8000.0        |
| 16 Lowest Frequency | 1.518.1     |
| 17 Nucleus      | 1H               |
| 18 Acquired Size | 32768          |
| 19 Spectral Size | 65536         |

![NMR spectrum image](image-url)
| Parameter       | Value  |
|-----------------|--------|
| Origin          | Varian |
| Owner           |        |
| Instrument      | inova  |
| Solvent         | CD2Cl2 |
| Temperature     | 20.0   |
| Pulse Sequence  | s2pul  |
| Experiment      | 1D     |
| Probe           | QUAD   |
| Number of Scans | 1024   |
| Receiver Gain   | 60     |
| Relaxation Delay| 1.0000 |
| Pulse Width     | 6.0000 |
| Presaturation Frequency |        |
| Spectrometer Frequency | 125.66 |
| Spectral Width  | 30165.9|
| Lowest Frequency| 1220.8 |
| Nucleus         | 13C    |
| Acquired Size   | 32768  |
| Spectral Size   | 65536  |
C(ketone)

f1 (ppm)

f2 (ppm)

H3 & H4 crosspeaks

gHMBC

326
The diagram shows a 2D NMR spectrum with the chemical shifts for both dimensions labeled. The chemical structure on the left is labeled with carbon and hydrogen atoms. The spectrum is annotated with gHMBC (general heteronuclear multiple bond correlation) connectivities, indicating cross-peak correlations between different nuclei. The labels for the dimensions (f1 and f2) are provided, along with specific values for chemical shifts (ppm). The contour lines represent the intensity of the correlations across the spectrum.
| Parameter          | Value         |
|-------------------|--------------|
| 1 Origin          | Varian       |
| 2 Owner           |              |
| 3 Instrument      | Inova        |
| 4 Solvent         | CD2Cl2       |
| 5 Temperature     | 20.0         |
| 6 Pulse Sequence  | s2pul        |
| 7 Experiment      | 1D           |
| 8 Probe           | hcn          |
| 9 Number of Scans | 4            |
| 10 Receiver Gain  | 32           |
| 11 Relaxation Delay| 15.0000     |
| 12 Pulse Width    | 7.0000       |
| 13 Presaturation Frequency |      |
| 14 Spectrometer Frequency | 500.07      |
| 15 Spectral Width | 8000.0       |
| 16 Lowest Frequency| 1518.1      |
| 17 Nucleus        | 1H           |
| 18 Acquired Size  | 32768        |
| 19 Spectral Size  | 65536        |
| Parameter          | Value            |
|--------------------|------------------|
| 1 Origin           | Varian           |
| 2 Owner            |                  |
| 3 Instrument       | inova            |
| 4 Solvent          | CD2Cl2           |
| 5 Temperature      | 20.0             |
| 6 Pulse Sequence   | s2pul            |
| 7 Experiment       | 1D               |
| 8 Probe            | QUAD             |
| 9 Number of Scans  | 3883             |
| 10 Receiver Gain   | 60               |
| 11 Relaxation Delay| 1.0000           |
| 12 Pulse Width     | 6.0000           |
| 13 Presaturation Frequency |          |
| 14 Spectrometer Frequency | 125.66       |
| 15 Spectral Width  | 30165.9          |
| 16 Lowest Frequency| 1216.6           |
| 17 Nucleus         | 13C              |
| 18 Acquired Size   | 32768            |
| 19 Spectral Size   | 65536            |

![Chemical Structure](image)
| Parameter          | Value               |
|--------------------|---------------------|
| 1   Origin         | Varian              |
| 2   Owner           |                     |
| 3   Instrument      | inova               |
| 4   Solvent         | CDCl3               |
| 5   Temperature     | 20.0                |
| 6   Pulse Sequence  | s2pul               |
| 7   Experiment      | 1D                  |
| 8   Probe           | hcn                 |
| 9   Number of Scans | 8                   |
| 10  Receiver Gain   | 44                  |
| 11  Relaxation Delay| 10.0000             |
| 12  Pulse Width     | 7.00000             |
| 13  Presaturation Frequency |           |
| 14  Spectrometer Frequency | 500.07         |
| 15  Spectral Width  | 8000.0              |
| 16  Lowest Frequency| 1521.1              |
| 17  Nucleus         | 1H                  |
| 18  Acquired Size   | 32768               |
| 19  Spectral Size   | 65536               |
| Parameter       | Value                                                                 |
|-----------------|----------------------------------------------------------------------|
| Origin          | Bruker BioSpin GmbH                                                  |
| Owner           | user1d                                                               |
| Instrument      | spect                                                                |
| Solvent         | CDCl3                                                                |
| Temperature     | 289.1                                                                |
| Pulse Sequence  | zgpg30                                                               |
| Experiment      | 1D                                                                   |
| Probe           | Z127784_0002_CP800_50S1_BBF_H_D_05_Z                                 |
| Number of Scans | 256                                                                  |
| Receiver Gain   | 190.5                                                                |
| Relaxation Delay| 2.0000                                                               |
| Pulse Width     | 10.0000                                                              |
| Presaturation Frequency |                                                              |
| Spectrometer Frequency | 125.83                                                            |
| Spectral Width  | 31512.6                                                              |
| Lowest Frequency| 1901.0                                                               |
| Nucleus         | 13C                                                                  |
| Acquired Size   | 32768                                                                |
| Spectral Size   | 65536                                                                |
| Parameter                      | Value                                                                 |
|--------------------------------|----------------------------------------------------------------------|
| Origin                         | Bruker BioSpin GmbH                                                  |
| Owner                          | user1d                                                               |
| Instrument                     | spect                                                                 |
| Solvent                        | CDCl3                                                                |
| Temperature                    | 289.0                                                                |
| Pulse Sequence                 | zg30                                                                 |
| Experiment                     | 1D                                                                   |
| Probe                          | Z127784_0002_CPBBB500S1BBFH.D.05Z                                    |
| Number of Scans                | 16                                                                   |
| Receiver Gain                  | 94.3                                                                |
| Relaxation Delay               | 15.0000                                                             |
| Pulse Width                    | 12.0000                                                             |
| Presaturation Frequency        |                                                                    |
| Spectrometer Frequency         | 500.35                                                              |
| Spectral Width                 | 10000.0                                                             |
| Lowest Frequency               | 1921.3                                                              |
| Nucleus                        | 1H                                                                  |
| Acquired Size                  | 32768                                                               |
| Spectral Size                  | 65536                                                               |

![NMR spectrum](image-url)
| Parameter         | Value                                                                 |
|-------------------|----------------------------------------------------------------------|
| Origin            | Bruker BioSpin GmbH                                                  |
| Owner             | user1d                                                              |
| Instrument        | spect                                                               |
| Solvent           | CDCl3                                                               |
| Temperature       | 289.0                                                               |
| Pulse Sequence    | zgpg30                                                              |
| Experiment        | 1D                                                                  |
| Probe             | Z127784_0002, CPBBO 500S1 BBF, H.D. 05 Z,                          |
| Number of Scans   | 256                                                                 |
| Receiver Gain     | 190.5                                                               |
| Relaxation Delay  | 2.0000                                                              |
| Pulse Width       | 10.0000                                                             |
| Presaturation Frequency |                                                             |
| Spectrometer Frequency | 125.83                                                             |
| Spectral Width    | 31512.6                                                             |
| Lowest Frequency  | 1902.4                                                              |
| Nucleus           | 13C                                                                 |
| Acquired Size     | 32768                                                               |
| Spectral Size     | 65536                                                               |
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| Origin             | Bruker BioSpin GmbH                                                 |
| Owner              | user1d                                                              |
| Instrument         | spect                                                                |
| Solvent            | CDCl3                                                                |
| Temperature        | 298.0                                                               |
| Pulse Sequence     | zg30                                                                 |
| Experiment         | 1D                                                                  |
| Probe              | Z127784_0002, CP88D S0051 BBF_H_D_05 Z                                 |
| Number of Scans    | 16                                                                  |
| Receiver Gain      | 29.7                                                                |
| Relaxation Delay   | 15.0000                                                             |
| Pulse Width        | 12.0000                                                             |
| Presaturation Frequency |                                                              |
| Spectrometer Frequency | 500.35                                                             |
| Spectral Width     | 10000.0                                                             |
| Lowest Frequency   | 1.922.3                                                             |
| Nucleus            | 1H                                                                  |
| Acquired Size      | 32768                                                               |
| Spectral Size      | 65536                                                               |

![Chemical Structure](image)
f1 (ppm)
| Parameter          | Value                                                                 |
|--------------------|------------------------------------------------------------------------|
| Origin             | Bruker BioSpin GmbH                                                    |
| Owner              | user1d                                                                 |
| Instrument         | spect                                                                  |
| Solvent            | CDCl3                                                                  |
| Temperature        | 298.0                                                                  |
| Pulse Sequence     | zgpg30                                                                 |
| Experiment         | 1D                                                                     |
| Probe              | Z127784_0002_CPBBO500S1_BBF_HD05Z1                                    |
| Number of Scans    | 1024                                                                   |
| Receiver Gain      | 190.5                                                                  |
| Relaxation Delay   | 2.0000                                                                 |
| Pulse Width        | 10.0000                                                                |
| Presaturation Frequency |                                               |
| Spectrometer Frequency | 125.83                                                                            |
| Spectral Width     | 31512.6                                                                |
| Lowest Frequency   | 91902.0                                                                |
| Nucleus            | 13C                                                                    |
| Acquired Size      | 32768                                                                   |
| Spectral Size      | 65536                                                                   |

![Chemical Structure](image)
| Parameter                  | Value                                                                 |
|---------------------------|-----------------------------------------------------------------------|
| Origin                    | Bruker BioSpin GmbH                                                   |
| Owner                     | user1d                                                                |
| Instrument                | spect                                                                 |
| Solvent                   | CDCl3                                                                 |
| Temperature               | 298.0                                                                |
| Pulse Sequence            | zg30                                                                  |
| Experiment                | 1D                                                                   |
| Probe                     | Z127784_0002_CPBBO500S1BBF_H.D.05 Z                                            |
| Number of Scans           | 16                                                                   |
| Receiver Gain             | 29.7                                                                 |
| Relaxation Delay          | 15.0000                                                              |
| Pulse Width               | 12.0000                                                              |
| Presaturation Frequency   |                                                                       |
| Spectrometer Frequency    | 500.35                                                               |
| Spectral Width            | 10000.0                                                              |
| Lowest Frequency          | 1922.3                                                               |
| Nucleus                   | 1H                                                                   |
| Acquired Size             | 32768                                                                |
| Spectral Size             | 65536                                                                |

**Chemical Structure Image:**

The structure image shows the molecular formula and chemical bonds. The peaks in the spectrum correspond to specific proton resonances. The spectrum is labeled with the chemical shifts in parts per million (ppm) along the x-axis, while the y-axis represents the intensity in arbitrary units.
Parameter | Value
---|---
1 | Origin Bruker BioSpin GmbH
2 | Owner user1d
3 | Instrument spect
4 | Solvent CDCl₃
5 | Temperature 298.0
6 | Pulse Sequence zgpg30
7 | Experiment 1D
8 | Probe Z127784_0002, CPBB0 500S1 BBF. H.D. 05 Z
9 | Number of Scans 1024
10 | Receiver Gain 190.5
11 | Relaxation Delay 2.0000
12 | Pulse Width 10.0000
13 | Presaturation Frequency
14 | Spectrometer Frequency 125.83
15 | Spectral Width 31512.6
16 | Lowest Frequency .19004
17 | Nucleus 13C
18 | Acquired Size 32768
19 | Spectral Size 65536
| Parameter       | Value       |
|-----------------|-------------|
| 1 Origin        | Varian      |
| 2 Owner         |             |
| 3 Instrument    | inova       |
| 4 Solvent       | CDCl3       |
| 5 Temperature   | 20.0        |
| 6 Pulse Sequence| s2pul       |
| 7 Experiment    | 1D          |
| 8 Probe         | hcn         |
| 9 Number of Scans| 8          |
| 10 Receiver Gain| 38          |
| 11 Relaxation Delay| 15.0000   |
| 12 Pulse Width  | 7.0000      |
| 13 Presaturation Frequency |         |
| 14 Spectrometer Frequency | 500.07   |
| 15 Spectral Width | 8000.0     |
| 16 Lowest Frequency | 1519.1     |
| 17 Nucleus      | 1H          |
| 18 Acquired Size | 32768      |
| 19 Spectral Size | 65536      |
| Parameter          | Value               |
|--------------------|---------------------|
| Origin             | Varian              |
| Owner              |                     |
| Instrument         | inova               |
| Solvent            | CDCl₃               |
| Temperature        | 20.0                |
| Pulse Sequence     | s2pul               |
| Experiment         | 1D                  |
| Probe              | QUAD                |
| Number of Scans    | 64                  |
| Receiver Gain      | 60                  |
| Relaxation Delay   | 2.0000              |
| Pulse Width        | 6.0000              |
| Presaturation Frequency |              |
| Spectrometer Frequency | 125.66             |
| Spectral Width     | 30165.9             |
| Lowest Frequency   | 128.1               |
| Nucleus            | 13C                 |
| Acquired Size      | 32768               |
| Spectral Size      | 65536               |
| Parameter         | Value                      |
|-------------------|----------------------------|
| 1 Origin          | Varian                     |
| 2 Owner           |                            |
| 3 Instrument      | inova                      |
| 4 Solvent         | CDCl3                      |
| 5 Temperature     | 20.0                       |
| 6 Pulse Sequence  | s2pul                      |
| 7 Experiment      | 1D                         |
| 8 Probe           | QUAD                       |
| 9 Number of Scans | 8                          |
| 10 Receiver Gain  | 50                         |
| 11 Relaxation Delay| 30.0000                   |
| 12 Pulse Width    | 6.5000                     |
| 13 Presaturation Frequency|                    |
| 14 Spectrometer Frequency | 499.69                   |
| 15 Spectral Width | 7024.9                     |
| 16 Lowest Frequency| 1.0219                     |
| 17 Nucleus        | 1H                         |
| 18 Acquired Size  | 32768                      |
| 19 Spectral Size  | 65536                      |

![NMR Spectrum](image)
| Parameter       | Value               |
|-----------------|---------------------|
| 1 Origin        | Varian              |
| 2 Owner         |                     |
| 3 Instrument    | inova               |
| 4 Solvent       | CDCl3               |
| 5 Temperature   | 20.0                |
| 6 Pulse Sequence| s2pul               |
| 7 Experiment    | 1D                  |
| 8 Probe         | QUAD                |
| 9 Number of Scans| 680                |
| 10 Receiver Gain| 60                  |
| 11 Relaxation Delay| 2.0000          |
| 12 Pulse Width  | 6.0000              |
| 13 Presaturation Frequency |        |
| 14 Spectrometer Frequency | 125.66         |
| 15 Spectral Width | 30165.9           |
| 16 Lowest Frequency | 1276.5            |
| 17 Nucleus      | 13C                 |
| 18 Acquired Size| 32768               |
| 19 Spectral Size| 65536               |

![Chemical Structure](image-url)
| Parameter          | Value                |
|--------------------|----------------------|
| 1. Origin          | Varian               |
| 2. Owner           |                      |
| 3. Instrument      | inova                |
| 4. Solvent         | CDCl3                |
| 5. Temperature     | 20.0                 |
| 6. Pulse Sequence  | s2pul                |
| 7. Experiment      | 1D                   |
| 8. Probe           | QUAD                 |
| 9. Number of Scans | 16                   |
| 10. Receiver Gain  | 48                   |
| 11. Relaxation Delay | 15.0000            |
| 12. Pulse Width    | 6.5000               |
| 13. Presaturation Frequency |          |
| 14. Spectrometer Frequency | 499.69          |
| 15. Spectral Width | 7024.9               |
| 16. Lowest Frequency | .10214             |
| 17. Nucleus        | 1H                   |
| 18. Acquired Size  | 32768                |
| 19. Spectral Size  | 65536                |

![NMR Spectrum](image-url)
| Parameter           | Value          |
|---------------------|----------------|
| Origin              | Varian         |
| Owner               |                |
| Instrument          | inova          |
| Solvent             | CDCl3          |
| Temperature         | 20.0           |
| Pulse Sequence      | s2pul          |
| Experiment          | 1D             |
| Probe               | QUAD           |
| Number of Scans     | 512            |
| Receiver Gain       | 60             |
| Relaxation Delay    | 1.00000        |
| Pulse Width         | 6.00000        |
| Presaturation Frequency |            |
| Spectrometer Frequency | 125.66       |
| Spectral Width      | 30165.9        |
| Lowest Frequency    | 1275.3         |
| Nucleus             | 13C            |
| Acquired Size       | 32768          |
| Spectral Size       | 65536          |
| Parameter                  | Value                                                                 |
|----------------------------|----------------------------------------------------------------------|
| Origin                     | Bruker BioSpin GmbH                                                   |
| Owner                      | user1d                                                                |
| Instrument                 | spect                                                                 |
| Solvent                    | CDCl3                                                                 |
| Temperature                | 298.2                                                                 |
| Pulse Sequence             | zg30                                                                  |
| Experiment                 | 1D                                                                   |
| Probe                      | Z127784_0002_CPBBDO_05S1_BBF_H_D_05_Z                                |
| Number of Scans            | 16                                                                   |
| Receiver Gain              | 61.8                                                                 |
| Relaxation Delay           | 15.0000                                                               |
| Pulse Width                | 12.0000                                                               |
| Presaturation Frequency    |                                                                       |
| Spectrometer Frequency     | 500.35                                                                |
| Spectral Width             | 10000.0                                                               |
| Lowest Frequency           | 1921.3                                                                |
| Nucleus                    | 1H                                                                   |
| Acquired Size              | 32768                                                                 |
| Spectral Size              | 65536                                                                 |
| Parameter     | Value                                                                 |
|---------------|----------------------------------------------------------------------|
| Origin        | Bruker BioSpin GmbH                                                  |
| Owner         | user1d                                                              |
| Instrument    | spect                                                                |
| Solvent       | CDCl3                                                                |
| Temperature   | 298.2                                                               |
| Pulse Sequence| zgpg30                                                               |
| Experiment    | 1D                                                                   |
| Probe         | Z127784_0002 {CP}BBO 500S1 BBF_H.D. 05 Z,                           |
| Number of Scans| 256                                                                 |
| Receiver Gain | 190.5                                                                |
| Relaxation Delay| 2.0000                                                              |
| Pulse Width   | 10.0000                                                              |
| Presaturation Frequency |                                                                |
| Spectrometer Frequency| 125.83                                                              |
| Spectral Width | 31512.6                                                             |
| Lowest Frequency | .1900 1                                                              |
| Nucleus       | 13C                                                                 |
| Acquired Size | 32768                                                                |
| Spectral Size | 65536                                                                |

![NMR spectrum](image)

The spectrum shows the chemical shifts for various nuclei, with peaks at different ppm values.
| Parameter           | Value                                                                 |
|---------------------|------------------------------------------------------------------------|
| Origin              | Bruker BioSpin GmbH                                                    |
| Owner               | user1d                                                                 |
| Instrument          | spect                                                                 |
| Solvent             | CDCl3                                                                  |
| Temperature         | 298.2                                                                  |
| Pulse Sequence      | zg30                                                                   |
| Experiment          | 1D                                                                     |
| Probe               | Z127784_0002_CPBBDO_500S1_BBF_H_D_05_Z                                  |
| Number of Scans     | 16                                                                     |
| Receiver Gain       | 29.7                                                                   |
| Relaxation Delay    | 15.0000                                                                |
| Pulse Width         | 12.0000                                                                |
| Presaturation       |                                                                         |
| Spectrometer        | 500.35                                                                 |
| Spectral Width      | 10000.0                                                                |
| Lowest Frequency    | 1.9213                                                                 |
| Nucleus             | 1H                                                                     |
| Acquired Size       | 32768                                                                  |
| Spectral Size       | 65536                                                                  |

![Chemical Structure Image](image_url)
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| Origin             | Bruker BioSpin GmbH                                                   |
| Owner              | user1d                                                              |
| Instrument         | spect                                                               |
| Solvent            | CDCl3                                                               |
| Temperature        | 298.2                                                               |
| Pulse Sequence     | zgpg30                                                              |
| Experiment         | 1D                                                                  |
| Probe              | Z127784_0002,CP880 S50S1 BBF-H.D. 05 Z, (CP880 500/1 BBF-H.D. 05 Z) |
| Number of Scans    | 256                                                                 |
| Receiver Gain      | 190.5                                                               |
| Relaxation Delay   | 2.0000                                                              |
| Pulse Width        | 10.0000                                                             |
| Presaturation      |                                                                     |
| Frequency          |                                                                     |
| Spectrometer       | 125.83                                                              |
| Spectral Width     | 31512.6                                                             |
| Lowest Frequency   | .1899 7                                                             |
| Nucleus            | 13C                                                                 |
| Acquired Size      | 32768                                                               |
| Spectral Size      | 65536                                                               |

![Chemical Structure](image)
| Parameter       | Value          |
|-----------------|----------------|
| Origin          | Varian         |
| Owner           |                |
| Instrument      | inova          |
| Solvent         | CDCl3          |
| Temperature     | 25.0           |
| Pulse Sequence  | s2pul          |
| Experiment      | 1D             |
| Probe           | hcn            |
| Number of Scans | 8              |
| Receiver Gain   | 42             |
| Relaxation Delay| 15.0000        |
| Pulse Width     | 7.0000         |
| Presaturation Frequency |        |
| Spectrometer Frequency | 500.07 |
| Spectral Width | 8000.0         |
| Lowest Frequency| 1521.1         |
| Nucleus         | 1H             |
| Acquired Size   | 32768          |
| Spectral Size   | 65536          |

![NMR Spectrum](image)
| Parameter          | Value                      |
|--------------------|----------------------------|
| 1 Origin           | Varian                     |
| 2 Owner            |                            |
| 3 Instrument       | inova                      |
| 4 Solvent          | CDCl3                      |
| 5 Temperature      | 20.0                       |
| 6 Pulse Sequence   | s2pul                      |
| 7 Experiment       | 1D                         |
| 8 Probe            | QUAD                       |
| 9 Number of Scans  | 922                        |
| 10 Receiver Gain   | 60                         |
| 11 Relaxation Delay| 2.0000                     |
| 12 Pulse Width     | 6.0000                     |
| 13 Presaturation Frequency |                   |
| 14 Spectrometer Frequency | 125.66                    |
| 15 Spectral Width  | 30165.9                    |
| 16 Lowest Frequency| 1272.4                     |
| 17 Nucleus         | 13C                        |
| 18 Acquired Size   | 32768                       |
| 19 Spectral Size   | 65536                      |
correspond to 2 methylenes
| Parameter              | Value |
|------------------------|-------|
| Origin                 | Bruker BioSpin GmbH |
| Owner                  | user1d |
| Instrument             | spect |
| Solvent                | CDCl3 |
| Temperature            | 298.2K |
| Pulse Sequence         | zg30  |
| Experiment             | 1D    |
| Probe                  | Z127784_0002, CP BBO 500S1 BBF_H.D.05 Z |
| Number of Scans        | 16    |
| Receiver Gain          | 122.8 |
| Relaxation Delay       | 150000 |
| Pulse Width            | 120000 |
| Presaturation Frequency|       |
| Spectrometer Frequency | 500.35 |
| Spectral Width         | 100000 |
| Lowest Frequency       | 1922.3 |
| Nucleus                | 1H    |
| Acquired Size          | 32768 |
| Spectral Size          | 65536 |

**Chemical Structure**

- 

**Spectrum**

- 

**F1 (ppm)**

- 

**H2O**
| Parameter        | Value                                                                 |
|------------------|----------------------------------------------------------------------|
| Origin           | Bruker BioSpin GmbH                                                  |
| Owner            | user1d                                                              |
| Instrument       | spec                                                                |
| Solvent          | CDCl3                                                               |
| Temperature      | 298.1                                                               |
| Pulse Sequence   | zgpg30                                                              |
| Experiment       | 1D                                                                  |
| Probe            | Z127784_0002, CP BBO 50051 BBF_H.D.05 Z                               |
| Number of Scans  | 256                                                                 |
| Receiver Gain    | 190.5                                                               |
| Relaxation Delay | 2.0000                                                              |
| Pulse Width      | 10.0000                                                             |
| Presaturation Frequency |                                                                    |
| Spectrometer Frequency | 125.83                                                        |
| Spectral Width   | 31512.6                                                             |
| Lowest Frequency | 1898.5                                                              |
| Nucleus          | 13C                                                                 |
| Acquired Size    | 32768                                                               |
| Spectral Size    | 65536                                                               |

![NMR spectrum](image-url)
| Parameter                  | Value                                                                 |
|----------------------------|-----------------------------------------------------------------------|
| Origin                     | Bruker BioSpin GmbH                                                   |
| Owner                      | user1d                                                                |
| Instrument                 | spect                                                                |
| Solvent                    | CDCl₃                                                                |
| Temperature                | 298.1                                                                |
| Pulse Sequence             | zg30                                                                 |
| Experiment                 | 1D                                                                   |
| Probe                      | Z127784_0002, CP BBO 500S1 BBF.H.D. 05 Z,                            |
| Number of Scans            | 16                                                                   |
| Receiver Gain              | 29.7                                                                 |
| Relaxation Delay           | 150000                                                               |
| Pulse Width                | 120000                                                               |
| Presaturation Frequency    |                                                                       |
| Spectrometer Frequency     | 500.35                                                               |
| Spectral Width             | 100000.0                                                             |
| Lowest Frequency           | 1.9223                                                               |
| Nucleus                    | 1H                                                                   |
| Acquired Size              | 32768                                                                |
| Spectral Size              | 65536                                                                |

![NMR Spectrum](image.png)
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| 1 Origin           | Bruker BioSpin GmbH                                                  |
| 2 Owner            | user1d                                                              |
| 3 Instrument       | spect                                                               |
| 4 Solvent          | CDCl3                                                               |
| 5 Temperature      | 298.1                                                               |
| 6 Pulse Sequence   | zgpg30                                                              |
| 7 Experiment       | 1D                                                                  |
| 8 Probe            | Z127784_0002, CP BBO 50051 BBF. H. D. 05 Z,                         |
| 9 Number of Scans  | 256                                                                |
| 10 Receiver Gain   | 190.5                                                               |
| 11 Relaxation      | 2.0000                                                              |
| 12 Pulse Width     | 10.0000                                                             |
| 13 Presaturation   |                                                                     |
| 14 Spectrometer    | 125.83                                                              |
| 15 Spectral Width  | 31512.6                                                             |
| 16 Lowest Frequency| 1901.5                                                              |
| 17 Nucleus         | 13C                                                                 |
| 18 Acquired Size   | 32768                                                               |
| 19 Spectral Size   | 65536                                                               |
| Parameter          | Value |
|--------------------|-------|
| Origin             | Bruker BioSpin GmbH |
| Owner              | user1d |
| Instrument         | spect |
| Solvent            | CDCl₃ |
| Temperature        | 298.1 |
| Pulse Sequence     | zg30 |
| Experiment         | 1D |
| Probe              | Z127784_0002, CP860 S001 BBF H D 05 Z |
| Number of Scans    | 16 |
| Receiver Gain      | 94.3 |
| Relaxation Delay   | 15.0000 |
| Pulse Width        | 12.0000 |
| Presaturation Frequency |     |
| Spectrometer Frequency | 500.35 |
| Spectral Width     | 10000.0 |
| Lowest Frequency   | 1921.3 |
| Nucleus            | 1H |
| Acquired Size      | 32768 |
| Spectral Size      | 65536 |

![Chemical Structure](image)
| Parameter       | Value                                                                 |
|-----------------|----------------------------------------------------------------------|
| Origin          | Bruker BioSpin GmbH                                                  |
| Owner           | user1d                                                               |
| Instrument      | spect                                                                |
| Solvent         | CDCl3                                                                |
| Temperature     | 298.1                                                                |
| Pulse Sequence  | zgpg30                                                               |
| Experiment      | 1D                                                                   |
| Probe           | Z127784_0002_CPBB050051BBF_H_D_05Z_                                 |
| Number of Scans | 256                                                                  |
| Receiver Gain   | 190.5                                                                |
| Relaxation Delay| 2.0000                                                               |
| Pulse Width     | 10.0000                                                              |
| Presaturation Frequency |                                                              |
| Spectrometer Frequency | 125.83                                                                |
| Spectral Width  | 31512.6                                                              |
| Lowest Frequency| 1898.1                                                               |
| Nucleus         | 13C                                                                  |
| Acquired Size   | 32768                                                                |
| Spectral Size   | 65536                                                                |

The diagram shows a 1D NMR spectrum with peaks at various chemical shifts.

The chemical structure depicted includes a MeO group, a TfO group, and a CO₂Me group.
| Parameter          | Value          |
|--------------------|----------------|
| Origin             | Varian         |
| Owner              |                |
| Instrument         | inova          |
| Solvent            | CDCl3          |
| Temperature        | 20.0           |
| Pulse Sequence     | s2pul          |
| Experiment         | 1D             |
| Probe              | QUAD           |
| Number of Scans    | 8              |
| Receiver Gain      | 50             |
| Relaxation Delay   | 10.0000        |
| Pulse Width        | 6.5000         |
| Presaturation Frequency |            |
| Spectrometer Frequency | 499.69        |
| Spectral Width     | 7024.9         |
| Lowest Frequency   | 1022.9         |
| Nucleus            | 1H             |
| Acquired Size      | 32768          |
| Spectral Size      | 65536          |
| Parameter      | Value     |
|----------------|-----------|
| 1 Origin       | Varian    |
| 2 Owner        |           |
| 3 Instrument   | Inova     |
| 4 Solvent      | CDCl3     |
| 5 Temperature  | 20.0      |
| 6 Pulse Sequence| s2pul    |
| 7 Experiment   | 1D        |
| 8 Probe        | QUAD      |
| 9 Number of Scans| 582     |
| 10 Receiver Gain| 60      |
| 11 Relaxation Delay| 2.0000 |
| 12 Pulse Width | 6.0000   |
| 13 Presaturation Frequency|           |
| 14 Spectrometer Frequency| 125.66  |
| 15 Spectral Width| 30165.9 |
| 16 Lowest Frequency| 1260.2  |
| 17 Nucleus     | 13C       |
| 18 Acquired Size| 32768   |
| 19 Spectral Size| 65536   |
| Parameter          | Value          |
|-------------------|----------------|
| Origin            | Varian         |
| Owner             |                |
| Instrument        | inova          |
| Solvent           | CDCl3          |
| Temperature       | 20.0           |
| Pulse Sequence    | s2pul          |
| Experiment        | 1D             |
| Probe             | QUAD           |
| Number of Scans   | 64             |
| Receiver Gain     | 56             |
| Relaxation Delay  | 0.00000        |
| Pulse Width       | 6.2500         |
| Presaturation Frequency |        |
| Spectrometer Frequency | 470.15 |
| Spectral Width    | 100000.0       |
| Lowest Frequency  | 79501.3        |
| Nucleus           | 19F            |
| Acquired Size     | 32768          |
| Spectral Size     | 65536          |
| Parameter          | Value                  |
|--------------------|------------------------|
| Origin             | Varian                 |
| Owner              |                        |
| Instrument         | inova                  |
| Solvent            | CDCl₃                  |
| Temperature        | 20.0                   |
| Pulse Sequence     | s2pul                  |
| Experiment         | 1D                     |
| Probe              | QUAD                   |
| Number of Scans    | 8                      |
| Receiver Gain      | 52                     |
| Relaxation Delay   | 15.0000                |
| Pulse Width        | 6.5000                 |
| Presaturation Frequency |                |
| Spectrometer Frequency | 499.69                |
| Spectral Width     | 7024.9                 |
| Lowest Frequency   | 1011.9                 |
| Nucleus            | 1H                     |
| Acquired Size      | 32768                  |
| Spectral Size      | 65536                  |

![NMR Spectrum](image_url)
| Parameter             | Value                                                                 |
|-----------------------|-----------------------------------------------------------------------|
| 1 Origin              | Bruker BioSpin GmbH                                                   |
| 2 Owner               | user1d                                                               |
| 3 Instrument          | spect                                                                |
| 4 Solvent             | CDCl3                                                                |
| 5 Temperature         | 298.0                                                                |
| 6 Pulse Sequence      | zgpg30                                                               |
| 7 Experiment          | 1D                                                                   |
| 8 Probe               | Z127784_0002, CPBBDO5051 BBF-H.D.05 Z                                 |
| 9 Number of Scans     | 512                                                                  |
| 10 Receiver Gain      | 190.5                                                                |
| 11 Relaxation Delay   | 2.0000                                                               |
| 12 Pulse Width        | 10.0000                                                              |
| 13 Presaturation Frequency |                                                                     |
| 14 Spectrometer Frequency | 125.83                                                              |
| 15 Spectral Width     | 31512.6                                                              |
| 16 Lowest Frequency   | 1.18997                                                              |
| 17 Nucleus            | 13C                                                                  |
| 18 Acquired Size      | 32768                                                                |
| 19 Spectral Size      | 65536                                                                |

![Chemical structure](attachment:image.png)

![NMR spectrum](attachment:nmr_spectrum.png)
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| 1 Origin           | Bruker BioSpin GmbH                                                  |
| 2 Owner            | user1d                                                               |
| 3 Instrument       | spect                                                                |
| 4 Solvent          | CDCl₃                                                                |
| 5 Temperature      | 298.0                                                                |
| 6 Pulse Sequence   | zgfhigqn 2                                                           |
| 7 Experiment       | 1D                                                                   |
| 8 Probe            | Z127784_0002, CP-BBO 50051 805 D. 05 Z                               |
| 9 Number of Scans  | 64                                                                   |
| 10 Receiver Gain   | 190.5                                                                |
| 11 Relaxation Delay| 1.0000                                                               |
| 12 Pulse Width     | 15.0000                                                              |
| 13 Presaturation Frequency |                                                               |
| 14 Spectrometer Frequency | 470.75                                                               |
| 15 Spectral Width  | 113636.4                                                             |
| 16 Lowest Frequency| 103908.0                                                             |
| 17 Nucleus         | 19F                                                                  |
| 18 Acquired Size   | 65536                                                                |
| 19 Spectral Size   | 131072                                                               |
| Parameter          | Value                                                                 |
|--------------------|------------------------------------------------------------------------|
| Origin             | Bruker BioSpin GmbH                                                    |
| Owner              | user1d                                                                |
| Instrument         | spect                                                                  |
| Solvent            | CDCl3                                                                  |
| Temperature        | 298.2                                                                 |
| Pulse Sequence     | zg30                                                                   |
| Experiment         | 1D                                                                    |
| Probe              | Z127784_0002_CPBBO50051BBF_H.D.05Z,                                    |
| Number of Scans    | 16                                                                    |
| Receiver Gain      | 29.7                                                                  |
| Relaxation Delay   | 15.0000                                                              |
| Pulse Width        | 12.0000                                                              |
| Presaturation Frequency |                                                                   |
| Spectrometer Frequency | 500.35                                                        |
| Spectral Width     | 10000.0                                                               |
| Lowest Frequency   | .19213                                                                |
| Nucleus            | 1H                                                                    |
| Acquired Size      | 32768                                                                |
| Spectral Size      | 65536                                                                |
| Parameter       | Value |
|-----------------|-------|
| Origin          | Bruker BioSpin GmbH |
| Owner           | user1d |
| Instrument      | spect |
| Solvent         | CDCl3 |
| Temperature     | 298.1K |
| Pulse Sequence  | zgpg30 |
| Experiment      | 1D |
| Probe           | Z127784_0002,CP:BB0 500S1 BBF: H.D. 05 Z |
| Number of Scans | 256 |
| Receiver Gain   | 190.5 |
| Relaxation Delay| 2.0000 |
| Pulse Width     | 10.0000 |
| Presaturation Frequency | |
| Spectrometer Frequency | 125.83 |
| Spectral Width  | 31512.6 |
| Lowest Frequency| 1901.6 |
| Nucleus         | 13C |
| Acquired Size   | 32768 |
| Spectral Size   | 65536 |

![NMR Spectrum](image-url)
| Parameter          | Value                                                                 |
|-------------------|----------------------------------------------------------------------|
| 1 Origin          | Bruker BioSpin GmbH                                                 |
| 2 Owner           | user1d                                                              |
| 3 Instrument      | spect                                                               |
| 4 Solvent         | CDCl₃                                                               |
| 5 Temperature     | 298.2                                                               |
| 6 Pulse Sequence  | zg30                                                                |
| 7 Experiment      | 1D                                                                  |
| 8 Probe           | Z127784_0002, CP BBO 500S1 BBF. H. D. 05 Z,                         |
| 9 Number of Scans | 16                                                                  |
| 10 Receiver Gain  | 76.2                                                                |
| 11 Relaxation Delay| 15 0000                                                             |
| 12 Pulse Width    | 12 0000                                                             |
| 13 Presaturation Frequency |                                                                  |
| 14 Spectrometer Frequency | 500.35                                                             |
| 15 Spectral Width | 10000.0                                                             |
| 16 Lowest Frequency | -1922.3                                                            |
| 17 Nucleus        | 1H                                                                  |
| 18 Acquired Size  | 32768                                                               |
| 19 Spectral Size  | 65536                                                               |

![Chemical Structure](image)
| Parameter               | Value                                           |
|------------------------|-------------------------------------------------|
| Origin                 | Bruker BioSpin GmbH                             |
| Owner                  | user1d                                          |
| Instrument             | spect                                          |
| Solvent                | CDCl₃                                          |
| Temperature            | 298.1                                           |
| Pulse Sequence         | zgpg30                                         |
| Experiment             | 1D                                              |
| Probe                  | Z127784_0002, CP BBO 500S1 BBF, H, D, 05, Z    |
| Number of Scans        | 1024                                            |
| Receiver Gain          | 190.5                                           |
| Relaxation Delay       | 2.0000                                          |
| Pulse Width            | 10.0000                                         |
| Presaturation Frequency|                                                 |
| Spectrometer Frequency | 125.83                                          |
| Spectral Width         | 31512.6                                         |
| Lowest Frequency       | 1898.2                                          |
| Nucleus                | 13C                                             |
| Acquired Size          | 32768                                           |
| Spectral Size          | 65536                                           |

![Graph](image_url)
| Parameter          | Value |
|--------------------|-------|
| Origin             | Bruker BioSpin GmbH |
| Owner              | user1d |
| Instrument         | spect |
| Solvent            | CDCl3 |
| Temperature        | 298.2 |
| Pulse Sequence     | zg30  |
| Experiment         | 1D    |
| Probe              | Z127784_0002, CPBB 500S1 BBF, H. D. 05 Z |
| Number of Scans    | 16    |
| Receiver Gain      | 29.7  |
| Relaxation Delay   | 15.0000 |
| Pulse Width        | 12.0000 |
| Presaturation Frequency |      |
| Spectrometer Frequency | 500.35 |
| Spectral Width     | 10000.0 |
| Lowest Frequency   | 1921.8 |
| Nucleus            | 1H    |
| Acquired Size      | 32768 |
| Spectral Size      | 65536 |
| Parameter        | Value                                                                 |
|------------------|----------------------------------------------------------------------|
| Origin           | Bruker BioSpin GmbH                                                  |
| Owner            | user1d                                                              |
| Instrument       | spect                                                               |
| Solvent          | CDCl3                                                               |
| Temperature      | 298.2                                                               |
| Pulse Sequence   | zgpg30                                                              |
| Experiment       | 1D                                                                  |
| Probe            | Z127784_0002, CP88050051 BBO, H.D. 05 Z                              |
| Number of Scans  | 256                                                                 |
| Receiver Gain    | 190.5                                                               |
| Relaxation Delay | 2.0000                                                              |
| Pulse Width      | 10.0000                                                             |
| Presaturation Frequency |                                                                |
| Spectrometer Frequency | 125.83                                                     |
| Spectral Width   | 31512.6                                                             |
| Lowest Frequency | .18997                                                              |
| Nucleus          | 13C                                                                 |
| Acquired Size    | 32768                                                               |
| Spectral Size    | 65536                                                               |
| Parameter       | Value                                                                 |
|-----------------|----------------------------------------------------------------------|
| Origin          | Bruker BioSpin GmbH                                                  |
| Owner           | user1d                                                               |
| Instrument      | spect                                                                |
| Solvent         | CDCl3                                                                |
| Temperature     | 298.1                                                                |
| Pulse Sequence  | zg30                                                                 |
| Experiment      | 1D                                                                   |
| Probe           | Z127784_0002, CP BB0 500S1 BBF. H. D. 05 Z,                          |
| Number of Scans | 16                                                                   |
| Receiver Gain   | 76.2                                                                 |
| Relaxation Delay| 15.0000                                                             |
| Pulse Width     | 12.0000                                                             |
| Presaturation Frequency |                                                               |
| Spectrometer Frequency | 500.35                                                             |
| Spectral Width  | 10000.000                                                           |
| Lowest Frequency| 1.9223                                                               |
| Nucleus         | 1H                                                                   |
| Acquired Size   | 32768                                                                |
| Spectral Size   | 65536                                                                |

![Chemical Structure Image]
| Parameter             | Value                                                                 |
|----------------------|-----------------------------------------------------------------------|
| Origin               | Bruker BioSpin GmbH                                                   |
| Owner                | user1d                                                                |
| Instrument           | spect                                                                |
| Solvent              | CDCl3                                                                |
| Temperature          | 298.2                                                                |
| Pulse Sequence       | zgpg30                                                               |
| Experiment           | 1D                                                                   |
| Probe                | Z127784_0002, CP BBO 500S1 BBF. H. D. 05 Z                           |
| Number of Scans      | 256                                                                  |
| Receiver Gain        | 190.5                                                                |
| Relaxation Delay     | 2.0000                                                               |
| Pulse Width          | 10.0000                                                              |
| Presaturation Frequency |                                                                       |
| Spectrometer Frequency | 125.83                                                              |
| Spectral Width       | 31512.6                                                              |
| Lowest Frequency     | 1899.7                                                               |
| Nucleus              | 13C                                                                  |
| Acquired Size        | 32768                                                                |
| Spectral Size        | 65536                                                                |

![Chemical structure image](image)
| Parameter                  | Value                                                                 |
|----------------------------|-----------------------------------------------------------------------|
| 1 Origin                   | Bruker BioSpin GmbH                                                  |
| 2 Owner                    | user1d                                                                |
| 3 Instrument               | spect                                                                 |
| 4 Solvent                  | CDCl3                                                                 |
| 5 Temperature              | 298.1                                                                 |
| 6 Pulse Sequence           | zg30                                                                  |
| 7 Experiment               | 1D                                                                    |
| 8 Probe                    | Z127784_0002, CP BBO 50051 BBF H.D. 05 Z,                            |
| 9 Number of Scans          | 16                                                                   |
| 10 Receiver Gain           | 55.0                                                                  |
| 11 Relaxation Delay        | 15.0000                                                              |
| 12 Pulse Width             | 12.0000                                                              |
| 13 Presaturation Frequency |                                                                       |
| 14 Spectrometer Frequency  | 500.35                                                               |
| 15 Spectral Width          | 10000.0                                                              |
| 16 Lowest Frequency        | 1.9223                                                               |
| 17 Nucleus                 | 1H                                                                   |
| 18 Acquired Size           | 32768                                                                |
| 19 Spectral Size           | 65536                                                                |
Parameter | Value
--- | ---
Origin | Bruker BioSpin GmbH
Owner | user1d
Instrument | spect
Solvent | CDCl3
Temperature | 298.1
Pulse Sequence | zgpg30
Experiment | 1D
Probe | Z127784_0002, CP BBO 500S1 BBF. H.D. 05 Z,
Number of Scans | 2048
Receiver Gain | 190.5
Relaxation Delay | 2.0000
Pulse Width | 10.0000
Presaturation Frequency | 14 Spectrometer Frequency
 | 125.83
Spectral Width | 31512.6
Lowest Frequency | 1902.9
Nucleus | 13C
Acquired Size | 32768
Spectral Size | 65536

Nucleus: 13C
Acquired Size: 32768
Spectral Size: 65536

![NMR Spectrum](image)
| Parameter               | Value                                                                 |
|-------------------------|----------------------------------------------------------------------|
| Origin                  | Bruker BioSpin GmbH                                                  |
| Owner                   | user1d                                                              |
| Instrument              | spect                                                                |
| Solvent                 | CD2Cl2                                                              |
| Temperature             | 298.0                                                               |
| Pulse Sequence          | zg30                                                                |
| Experiment              | 1D                                                                  |
| Probe                   | Z127784_0002_CPBB0505S1BBF_H.D.05Z                                  |
| Number of Scans         | 16                                                                  |
| Receiver Gain           | 61.8                                                                |
| Relaxation Delay        | 15.0000                                                             |
| Pulse Width             | 12.0000                                                             |
| Presaturation Frequency |                                                                     |
| Spectrometer Frequency  | 500.35                                                              |
| Spectral Width          | 10000.0                                                             |
| Lowest Frequency        | 1929.9                                                              |
| Nucleus                 | 1H                                                                  |
| Acquired Size           | 32768                                                               |
| Spectral Size           | 65536                                                               |

![NMR Spectrum](image)
| Parameter           | Value                                                                 |
|---------------------|-----------------------------------------------------------------------|
| Origin              | Bruker BioSpin GmbH                                                  |
| Owner               | user1d                                                                |
| Instrument          | spect                                                                 |
| Solvent             | CD2Cl2                                                               |
| Temperature         | 298.0                                                                |
| Pulse Sequence      | zgpg30                                                               |
| Experiment          | 1D                                                                   |
| Probe               | Z127784_0002, CP880 500S1 BBF, H.D. 05 Z,                            |
| Number of Scans     | 512                                                                  |
| Receiver Gain       | 190.5                                                                |
| Relaxation Delay    | 2.0000                                                               |
| Pulse Width         | 10.0000                                                              |
| Presaturation Frequency |                                                               |
| Spectrometer Frequency | 125.83                                                              |
| Spectral Width      | 31512.6                                                              |
| Lowest Frequency    | 1843.8                                                              |
| Nucleus             | 13C                                                                  |
| Acquired Size       | 32768                                                                |
| Spectral Size       | 65536                                                                |

![Chemical Structure](image-url)
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| Origin             | Bruker BioSpin GmbH                                                 |
| Owner              | user1d                                                               |
| Instrument         | spect                                                                |
| Solvent            | CD2Cl2                                                               |
| Temperature        | 298.0                                                                |
| Pulse Sequence     | zgfhigq2                                                             |
| Experiment         | 1D                                                                   |
| Probe              | Z127784_0002, CP88D 50051 BBF-H-D-O5 Z                                |
| Number of Scans    | 64                                                                   |
| Receiver Gain      | 190.5                                                                |
| Relaxation Delay   | 1.0000                                                               |
| Pulse Width        | 15.0000                                                              |
| Presaturation Frequency |                                                               |
| Spectrometer Frequency | 470.75                                                           |
| Spectral Width     | 113636.4                                                             |
| Lowest Frequency   | 103898.1                                                             |
| Nucleus            | 19F                                                                  |
| Acquired Size      | 65536                                                                |
| Spectral Size      | 131072                                                               |
Parameter | Value
--- | ---
1 Origin | Bruker BioSpin GmbH
2 Owner | user1d
3 Instrument | spect
4 Solvent | CDCl3
5 Temperature | 288.9
6 Pulse Sequence | zg30
7 Experiment | 1D
8 Probe | Z127784_0002, CPBBO 500S1 BBF, H, D, 05 Z
9 Number of Scans | 16
10 Receiver Gain | 86.0
11 Relaxation Delay | 15.0000
12 Pulse Width | 12.0000
13 Presaturation Frequency
14 Spectrometer Frequency | 500.35
15 Spectral Width | 10000.0
16 Lowest Frequency | 1921.5
17 Nucleus | 1H
18 Acquired Size | 32768
19 Spectral Size | 65536

Spectrogram with chemical shifts and peaks.

Chemical structure with labels: Me, TfO, CN.
| Parameter          | Value |
|--------------------|-------|
| 1 Origin           | Bruker BioSpin GmbH |
| 2 Owner            | user1d |
| 3 Instrument       | spect |
| 4 Solvent          | CDCl3 |
| 5 Temperature      | 288.9 |
| 6 Pulse Sequence   | zgpg30 |
| 7 Experiment       | 1D |
| 8 Probe            | Z127784_0002, CP880 50051 BBF. H. D. 05 Z |
| 9 Number of Scans  | 512   |
| 10 Receiver Gain   | 190.5 |
| 11 Relaxation Delay| 2.0000 |
| 12 Pulse Width     | 10.0000 |
| 13 Presaturation Frequency |   |
| 14 Spectrometer Frequency | 125.83 |
| 15 Spectral Width  | 31512.6 |
| 16 Lowest Frequency| 1903.6 |
| 17 Nucleus         | 13C |
| 18 Acquired Size   | 32768 |
| 19 Spectral Size   | 65536 |
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| Origin             | Bruker BioSpin GmbH                                                 |
| Owner              | user1d                                                              |
| Instrument         | spect                                                               |
| Solvent            | CDCl3                                                               |
| Temperature        | 288.9                                                               |
| Pulse Sequence     | zgfhigqn 2                                                          |
| Experiment         | 1D                                                                  |
| Probe              | Z127784_0002, CPBB0 S00S1 BBF-H.D.05 Z,                             |
| Number of Scans    | 64                                                                  |
| Receiver Gain      | 190.5                                                               |
| Relaxation Delay   | 1.00000                                                             |
| Pulse Width        | 15.0000                                                             |
| Presaturation Frequency |                                                           |
| Spectrometer Frequency | 470.75                                                             |
| Spectral Width     | 113636.4                                                             |
| Lowest Frequency   | 103898.1                                                             |
| Nucleus            | 19F                                                                 |
| Acquired Size      | 65536                                                               |
| Spectral Size      | 131072                                                              |

![Chemical Structure Image]
| Parameter       | Value          |
|-----------------|----------------|
| Origin          | Varian         |
| Owner           |                |
| Instrument      | inova          |
| Solvent         | CDCl3          |
| Temperature     | 20.0           |
| Pulse Sequence  | s2pul          |
| Experiment      | 1D             |
| Probe           | QUAD           |
| Number of Scans | 8              |
| Receiver Gain   | 58             |
| Relaxation Delay| 10.0000        |
| Pulse Width     | 6.5000         |
| Presaturation Frequency |          |
| Spectrometer Frequency | 499.69 |
| Spectral Width  | 7024.9         |
| Lowest Frequency| -1022.4        |
| Nucleus         | 1H             |
| Acquired Size   | 32768          |
| Spectral Size   | 65536          |
| Parameter         | Value |
|-------------------|-------|
| Origin            | Bruker BioSpin GmbH |
| Owner             | user1d |
| Instrument        | spect |
| Solvent           | CDCl3 |
| Temperature       | 298.0 |
| Pulse Sequence    | zgpg30 |
| Experiment        | 1D |
| Probe             | Z127784_0002, CPBB500S1 BBF-H.D. 05 Z |
| Number of Scans   | 512 |
| Receiver Gain     | 190.5 |
| Relaxation Delay  | 2.0000 |
| Pulse Width       | 10.0000 |
| Presaturation Frequency |       |
| Spectrometer Frequency | 125.83 |
| Spectral Width    | 31512.6 |
| Lowest Frequency  | 1.8995 |
| Nucleus           | 13C |
| Acquired Size     | 32768 |
| Spectral Size     | 65536 |

![Chemical structure](image)
| Parameter       | Value                                                                 |
|-----------------|----------------------------------------------------------------------|
| Origin          | Bruker BioSpin GmbH                                                  |
| Owner           | user1d                                                               |
| Instrument      | spect                                                                |
| Solvent         | CDCl₃                                                                |
| Temperature     | 298.0                                                                |
| Pulse Sequence  | zgfhigqn 2                                                           |
| Experiment      | 1D                                                                   |
| Probe           | Z127784_0002_CPBB0 50051_BBF_H_D_05_Z                                |
| Number of Scans | 64                                                                   |
| Receiver Gain   | 190.5                                                                |
| Relaxation Delay| 1.0000                                                               |
| Pulse Width     | 15.0000                                                              |
| Presaturation Frequency |                                                             |
| Spectrometer Frequency | 470.75                                           |
| Spectral Width  | 113636.4                                                             |
| Lowest Frequency| 103898.1                                                             |
| Nucleus         | 19F                                                                  |
| Acquired Size   | 65536                                                                |
| Spectral Size   | 131072                                                               |
Parameter | Value
--- | ---
1 Origin | Bruker BioSpin GmbH
2 Owner | user1d
3 Instrument | spect
4 Solvent | CDCl3
5 Temperature | 298.0
6 Pulse Sequence | zg30
7 Experiment | 1D
8 Probe | Z127784_0002, CP880 500S1BFF-H.D.05Z
9 Number of Scans | 16
10 Receiver Gain | 21.9
11 Relaxation Delay | 1.0000
12 Pulse Width | 12.0000
13 Presaturation Frequency |
14 Spectrometer Frequency | 500.35
15 Spectral Width | 10000.0
16 Lowest Frequency | -1922.8
17 Nucleus | 1H
18 Acquired Size | 32768
19 Spectral Size | 65536
# Parameters and Values

| Parameter          | Value                                                                 |
|--------------------|-----------------------------------------------------------------------|
| Origin             | Bruker BioSpin GmbH                                                   |
| Owner              | user1d                                                               |
| Instrument         | spect                                                                |
| Solvent            | CDCl3                                                                |
| Temperature        | 298.0                                                                |
| Pulse Sequence     | zgpg30                                                               |
| Experiment         | 1D                                                                   |
| Probe              | Z127784_0002_CPBBO 500S1 BBF_H_D_05Z                                  |
| Number of Scans    | 128                                                                  |
| Receiver Gain      | 190.5                                                                |
| Relaxation Delay   | 2.0000                                                               |
| Pulse Width        | 10.0000                                                              |
| Presaturation Frequency |                                                                  |
| Spectrometer Frequency | 125.83                                                             |
| Spectral Width     | 31512.6                                                              |
| Lowest Frequency   | 1904.7                                                               |
| Nucleus            | 13C                                                                  |
| Acquired Size      | 32768                                                                |
| Spectral Size      | 65536                                                                |

![Chemical Structure](image)

![NMR Spectrum](chart)
| Parameter         | Value                                                                 |
|-------------------|------------------------------------------------------------------------|
| Origin            | Bruker BioSpin GmbH                                                    |
| Owner             | user1d                                                                 |
| Instrument        | spect                                                                  |
| Solvent           | CDC13                                                                  |
| Temperature       | 298.0                                                                 |
| Pulse Sequence    | zg30                                                                   |
| Experiment        | 1D                                                                     |
| Probe             | Z1227784_00002, CP880 500S1 BBF, H. D. 05 Z                                |
| Number of Scans   | 16                                                                     |
| Receiver Gain     | 107.0                                                                  |
| Relaxation Delay  | 100000.0                                                               |
| Pulse Width       | 12.000000                                                             |
| Presaturation Frequency |                                                             |
| Spectrometer Frequency | 500.35                                                                |
| Spectral Width    | 10000.0                                                                |
| Lowest Frequency  | 1922.8                                                                 |
| Nucleus           | 1H                                                                     |
| Acquired Size     | 32768                                                                  |
| Spectral Size     | 65536                                                                  |

![Chemical Structure Image]
| Parameter             | Value                                                                 |
|-----------------------|----------------------------------------------------------------------|
| 1 Origin              | Bruker BioSpin GmbH                                                  |
| 2 Owner               | user1d                                                               |
| 3 Instrument          | spect                                                                |
| 4 Solvent             | CDCl3                                                                |
| 5 Temperature         | 298.0                                                                |
| 6 Pulse Sequence      | zgpg30                                                               |
| 7 Experiment          | 1D                                                                   |
| 8 Probe               | Z127784_0002, CPBBO 500S1 BBF.H.D.05 Z1                               |
| 9 Number of Scans     | 128                                                                  |
| 10 Receiver Gain      | 190.5                                                                |
| 11 Relaxation Delay   | 2.0000                                                               |
| 12 Pulse Width        | 10.0000                                                              |
| 13 Presaturation       |                                                                       |
| 14 Spectrometer Frequency | 125.83                                                             |
| 15 Spectral Width     | 31512.6                                                              |
| 16 Lowest Frequency   | 1898.6                                                               |
| 17 Nucleus            | 13C                                                                  |
| 18 Acquired Size      | 32768                                                                |
| 19 Spectral Size      | 65536                                                                |

![Chemical Structure](image)

![NMR Spectrum](image)
| Parameter          | Value                                                                 |
|--------------------|-----------------------------------------------------------------------|
| Origin             | Bruker BioSpin GmbH                                                  |
| Owner              | user1d                                                               |
| Instrument         | spect                                                                |
| Solvent            | CDCl3                                                                |
| Temperature        | 298.0                                                               |
| Pulse Sequence     | zg30                                                                 |
| Experiment         | 1D                                                                   |
| Probe              | Z127784_0002_CP-BBO 500S1 BBF-H.D.05 Z                                |
| Number of Scans    | 16                                                                   |
| Receiver Gain      | 122.8                                                               |
| Relaxation Delay   | 1.0000                                                              |
| Pulse Width        | 12.0000                                                             |
| Presaturation Frequency |                                                              |
| Spectrometer Frequency | 500.35                                                             |
| Spectral Width     | 10000.0                                                             |
| Lowest Frequency   | 1.922.8                                                             |
| Nucleus            | 1H                                                                  |
| Acquired Size      | 32768                                                               |
| Spectral Size      | 65536                                                               |

![NMR spectrum](image)

**NMR Spectra**

- **Chemical Shifts**
  - f1 (ppm): 7.2, 6.5, 5.8, 4.3, 3.2, 2.1, 1.0, 0.0, -1.0, -2.0, -3.0
- **Lowest Frequency**: -1922.8
- **Nucleus**: 1H
- **Acquired Size**: 32768
- **Spectral Size**: 65536
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| Origin             | Bruker BioSpin GmbH                                                  |
| Owner              | user1d                                                               |
| Instrument         | spect                                                                |
| Solvent            | CDCl3                                                                |
| Temperature        | 298.0                                                                |
| Pulse Sequence     | zgpg30                                                               |
| Experiment         | 1D                                                                   |
| Probe              | Z127784_0002_CP85050001_BBF_H_D_05Z                                  |
| Number of Scans    | 128                                                                  |
| Receiver Gain      | 190.5                                                                |
| Relaxation Delay   | 2.0000                                                              |
| Pulse Width        | 10.0000                                                             |
| Presaturation Frequency |                                                              |
| Spectrometer Frequency | 125.83                                                            |
| Spectral Width     | 31512.6                                                             |
| Lowest Frequency   | 1898.6                                                              |
| Nucleus            | 13C                                                                 |
| Acquired Size      | 32768                                                               |
| Spectral Size      | 65536                                                               |
| Parameter       | Value       |
|-----------------|-------------|
| Origin          | Varian      |
| Owner           |             |
| Instrument      | inova       |
| Solvent         | CDCl3       |
| Temperature     | 20.0        |
| Pulse Sequence  | s2pul       |
| Experiment      | 1D          |
| Probe           | QUAD        |
| Number of Scans | 8           |
| Receiver Gain   | 41          |
| Relaxation Delay| 0.0000      |
| Pulse Width     | 6.5000      |
| Presaturation Frequency |             |
| Spectrometer Frequency | 499.69 |
| Spectral Width  | 7024.9      |
| Lowest Frequency| 1.0224      |
| Nucleus         | 1H          |
| Acquired Size   | 32768       |
| Spectral Size   | 65536       |
| Parameter        | Value        |
|------------------|--------------|
| Origin           | Varian       |
| Owner            |              |
| Instrument       | inova        |
| Solvent          | CDCl3        |
| Temperature      | 20.0         |
| Pulse Sequence   | s2pul        |
| Experiment       | 1D           |
| Probe            | QUAD         |
| Number of Scans  | 450          |
| Receiver Gain    | 60           |
| Relaxation Delay | 1.0000       |
| Pulse Width      | 6.0000       |
| Presaturation Frequency |          |
| Spectrometer Frequency | 125.66 |
| Spectral Width   | 30165.9      |
| Lowest Frequency | 1274.9       |
| Nucleus          | 13C          |
| Acquired Size    | 32768        |
| Spectral Size    | 65536        |

![Chemical Structure](image)
| Parameter     | Value |
|---------------|-------|
| Origin        | Varian|
| Owner         |       |
| Instrument    | inova |
| Solvent       | CDCl3 |
| Temperature   | 20.0  |
| Pulse Sequence| s2pul |
| Experiment    | 1D    |
| Probe         | QUAD  |
| Number of Scans| 32   |
| Receiver Gain | 52    |
| Relaxation Delay| 0.0000|
| Pulse Width   | 6.2500|
| Presaturation Frequency|       |
| Spectrometer Frequency| 470.15|
| Spectral Width | 100000.0 |
| Lowest Frequency | .795013 |
| Nucleus       | 19F   |
| Acquired Size | 32768 |
| Spectral Size | 65536 |
The HSQC spectrum indicates that the peaks correspond to 4 methylenes.
| Parameter          | Value                      |
|-------------------|----------------------------|
| Origin            | Varian                     |
| Owner             |                            |
| Instrument        | inova                      |
| Solvent           | CDCl3                      |
| Temperature       | 20.0                       |
| Pulse Sequence    | s2pul                      |
| Experiment        | 1D                         |
| Probe             | QUAD                       |
| Number of Scans   | 8                          |
| Receiver Gain     | 41                         |
| Relaxation Delay  | 15.0000                    |
| Pulse Width       | 6.5000                     |
| Presaturation Frequency |                |
| Spectrometer Frequency | 499.69                   |
| Spectral Width    | 7024.9                     |
| Lowest Frequency  | 1021.9                     |
| Nucleus           | 1H                         |
| Acquired Size     | 32768                      |
| Spectral Size     | 65536                      |
| Parameter         | Value          |
|-------------------|----------------|
| 1 Origin          | Varian         |
| 2 Owner           |                |
| 3 Instrument      | inova          |
| 4 Solvent         | CDCl3          |
| 5 Temperature     | 20.0           |
| 6 Pulse Sequence  | s2pul          |
| 7 Experiment      | 1D             |
| 8 Probe           | QUAD           |
| 9 Number of Scans | 2048           |
| 10 Receiver Gain  | 60             |
| 11 Relaxation Delay| 2.0000        |
| 12 Pulse Width    | 6.0000         |
| 13 Presaturation Frequency| | |
| 14 Spectrometer Frequency | 125.66       |
| 15 Spectral Width | 30165.9        |
| 16 Lowest Frequency| 1276.9         |
| 17 Nucleus        | 13C            |
| 18 Acquired Size  | 32768          |
| 19 Spectral Size  | 65536          |
| Parameter            | Value                      |
|----------------------|----------------------------|
| 1 Origin             | Varian                     |
| 2 Owner              |                            |
| 3 Instrument         | inova                      |
| 4 Solvent            | CDCl3                      |
| 5 Temperature        | 20.0                       |
| 6 Pulse Sequence     | s2pul                      |
| 7 Experiment         | 1D                         |
| 8 Probe              | QUAD                       |
| 9 Number of Scans    | 64                         |
| 10 Receiver Gain     | 56                         |
| 11 Relaxation Delay  | 0.0000                     |
| 12 Pulse Width       | 6.2500                     |
| 13 Presaturation Frequency |                    |
| 14 Spectrometer Frequency | 470.15                    |
| 15 Spectral Width    | 100000.0                   |
| 16 Lowest Frequency  | 79501.3                    |
| 17 Nucleus           | 19F                        |
| 18 Acquired Size     | 32768                      |
| 19 Spectral Size     | 65536                      |

![Diagram of molecular structure]
| Parameter                  | Value                                                                 |
|---------------------------|-----------------------------------------------------------------------|
| Origin                    | Bruker BioSpin GmbH                                                   |
| Owner                     | user1d                                                                |
| Instrument                | spect                                                                 |
| Solvent                   | CDCl3                                                                 |
| Temperature               | 298.2                                                                 |
| Pulse Sequence            | zg30                                                                  |
| Experiment                | 1D                                                                    |
| Probe                     | Z127784_0002, CP BBO 500S1 BBF.H.D. 05 Z                               |
| Number of Scans           | 16                                                                    |
| Receiver Gain             | 55.0                                                                  |
| Relaxation Delay          | 15.0000                                                              |
| Pulse Width               | 12.0000                                                              |
| Presaturation Frequency   |                                                                       |
| Spectrometer Frequency    | 500.35                                                                |
| Spectral Width            | 10000.0                                                               |
| Lowest Frequency          | 1916.3                                                                |
| Nucleus                   | 1H                                                                    |
| Acquired Size             | 32768                                                                 |
| Spectral Size             | 65536                                                                 |
| Parameter            | Value                                                                 |
|----------------------|----------------------------------------------------------------------|
| 1 Origin             | Bruker BioSpin GmbH                                                  |
| 2 Owner              | user1d                                                              |
| 3 Instrument         | spect                                                               |
| 4 Solvent            | CDCl3                                                               |
| 5 Temperature        | 298.1                                                               |
| 6 Pulse Sequence     | zgpg30                                                              |
| 7 Experiment         | 1D                                                                  |
| 8 Probe              | Z127784_0002, CP BBO 500S1 BBF. H.D. 05 Z,                           |
| 9 Number of Scans    | 512                                                                |
| 10 Receiver Gain     | 190.5                                                               |
| 11 Relaxation Delay  | 2.0000                                                              |
| 12 Pulse Width       | 10.0000                                                             |
| 13 Presaturation Frequency |                                                                |
| 14 Spectrometer Frequency | 125.83                                                              |
| 15 Spectral Width    | 31512.6                                                             |
| 16 Lowest Frequency  | 1899.9                                                              |
| 17 Nucleus           | 13C                                                                |
| 18 Acquired Size     | 32768                                                               |
| 19 Spectral Size     | 65536                                                               |
| Parameter       | Value                                                                 |
|-----------------|----------------------------------------------------------------------|
| Origin          | Bruker BioSpin GmbH                                                   |
| Owner           | user1d                                                                |
| Instrument      | spect                                                                |
| Solvent         | CDCl3                                                                |
| Temperature     | 289.2                                                                |
| Pulse Sequence  | zg30                                                                 |
| Experiment      | 1D                                                                   |
| Probe           | Z127784_0002_CPBBO500S1BBF-H.D.05.Z                                  |
| Number of Scans | 16                                                                   |
| Receiver Gain   | 122.8                                                                |
| Relaxation Delay| 15.0000                                                              |
| Pulse Width     | 12.0000                                                              |
| Presaturation Frequency |                                                                                 |
| Spectrometer Frequency | 500.35                                                             |
| Spectral Width  | 10000.0                                                              |
| Lowest Frequency| -1921.8                                                              |
| Nucleus         | 1H                                                                   |
| Acquired Size   | 32768                                                                |
| Spectral Size   | 65536                                                                |
| Parameter         | Value                                                                 |
|-------------------|----------------------------------------------------------------------|
| Origin            | Bruker BioSpin GmbH                                                  |
| Owner             | user1d                                                                |
| Instrument        | spect                                                                |
| Solvent           | CDCl3                                                                 |
| Temperature       | 289.2                                                                |
| Pulse Sequence    | zgpg30                                                               |
| Experiment        | 1D                                                                   |
| Probe             | Z127784_0002_CPBB50S1BBF_H_D_05Z_2                                    |
| Number of Scans   | 256                                                                  |
| Receiver Gain     | 190.5                                                                |
| Relaxation Delay  | 2.0000                                                               |
| Pulse Width       | 10.0000                                                              |
| Presaturation Frequency |                                                                  |
| Spectrometer Frequency | 125.83                                                               |
| Spectral Width    | 31512.6                                                              |
| Lowest Frequency  | 1901.8                                                               |
| Nucleus           | 13C                                                                  |
| Acquired Size     | 32768                                                                |
| Spectral Size     | 65536                                                                |

![Chemical Structure Image]
| Parameter      | Value                           |
|---------------|---------------------------------|
| Origin        | Varian                          |
| Owner         |                                 |
| Instrument    | inova                           |
| Solvent       | CDCl3                           |
| Temperature   | 20.0                            |
| Pulse Sequence| s2pul                           |
| Experiment    | 1D                              |
| Probe         | QUAD                            |
| Number of Scans| 9                              |
| Receiver Gain | 41                              |
| Relaxation Delay | 0.0000                       |
| Pulse Width   | 6.5000                          |
| Presaturation Frequency |                    |
| Spectrometer Frequency | 499.69                     |
| Spectral Width | 7024.9                         |
| Lowest Frequency | 10.264                        |
| Nucleus       | 1H                              |
| Acquired Size | 32768                           |
| Spectral Size | 65536                           |

**Diagram:**

- TMS
- Spectrum with peaks at various f1 (ppm) values.
Parameter       Value
1    Origin          Varian
2    Owner
3    Instrument     inova
4    Solvent        CDCl3
5    Temperature    20.0
6    Pulse Sequence s2pul
7    Experiment     1D
8    Probe          QUAD
9    Number of Scans 153
10   Receiver Gain   60
11   Relaxation Delay 1.0000
12   Pulse Width     6.0000
13   Presaturation Frequency
14   Spectrometer Frequency 125.66
15   Spectral Width  30165.9
16   Lowest Frequency 1284.3
17   Nucleus        13C
18   Acquired Size   32768
19   Spectral Size   65536

TMS
| Parameter               | Value                                                                 |
|------------------------|----------------------------------------------------------------------|
| Origin                 | Bruker BioSpin GmbH                                                  |
| Owner                  | user1d                                                              |
| Instrument             | spect                                                               |
| Solvent                | CDCl3                                                               |
| Temperature            | 298.1                                                               |
| Pulse Sequence         | zg30                                                                |
| Experiment             | 1D                                                                  |
| Probe                  | Z127784_0002, CBBBO S0051 BBF, D. 05 Z,                             |
| Number of Scans        | 16                                                                  |
| Receiver Gain          | 29.7                                                                |
| Relaxation Delay       | 15.0000                                                             |
| Pulse Width            | 12.0000                                                             |
| Presaturation Frequency|                                                                     |
| Spectrometer Frequency | 500.35                                                              |
| Spectral Width         | 10000.0                                                             |
| Lowest Frequency       | 1910.3                                                              |
| Nucleus                | 1H                                                                  |
| Acquired Size          | 32768                                                               |
| Spectral Size          | 65536                                                               |

![NMR spectrum graph](image)
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| 1 Origin           | Bruker BioSpin GmbH                                                  |
| 2 Owner            | user1d                                                               |
| 3 Instrument       | spect                                                                |
| 4 Solvent          | CDCl3                                                                |
| 5 Temperature      | 298.1                                                                |
| 6 Pulse Sequence   | zgpg30                                                               |
| 7 Experiment       | 1D                                                                   |
| 8 Probe            | Z127784_0002, CP880500S1 BBF_H.D.05Z                                 |
| 9 Number of Scans  | 256                                                                  |
| 10 Receiver Gain   | 190.5                                                                |
| 11 Relaxation Delay| 2.0000                                                              |
| 12 Pulse Width     | 10.0000                                                              |
| 13 Presaturation Frequency |                                                                |
| 14 Spectrometer Frequency | 125.83                                                              |
| 15 Spectral Width  | 31512.6                                                              |
| 16 Lowest Frequency| 1916.9                                                               |
| 17 Nucleus         | 13C                                                                  |
| 18 Acquired Size   | 32768                                                                |
| 19 Spectral Size   | 65536                                                                |

![Spectral Graph](image)
| Parameter          | Value        |
|--------------------|--------------|
| Origin             | Varian       |
| Owner              |              |
| Instrument         | inova        |
| Solvent            | CDCl3        |
| Temperature        | 20.0         |
| Pulse Sequence     | s2pul        |
| Experiment         | 1D           |
| Probe              | QUAD         |
| Number of Scans    | 8            |
| Receiver Gain      | 48           |
| Relaxation Delay   | 10.0000      |
| Pulse Width        | 6.5000       |
| Presaturation Frequency |          |
| Spectrometer Frequency | 499.69     |
| Spectral Width     | 7024.9       |
| Lowest Frequency   | 1021.9       |
| Nucleus            | 1H           |
| Acquired Size      | 32768        |
| Spectral Size      | 65536        |

![Chemical Structure](image)

![NMR Spectrum](image)
| Parameter         | Value |
|-------------------|-------|
| Origin            | Bruker BioSpin GmbH |
| Owner             | user1d |
| Instrument        | spect |
| Solvent           | CDCl3 |
| Temperature       | 298.0K |
| Pulse Sequence    | zg30 |
| Experiment        | 1D |
| Probe             | 2127784_0002, CP BBO 500S1 BBF. H.D. 052 |
| Number of Scans   | 16 |
| Receiver Gain     | 61.8 |
| Relaxation Delay  | 1.0000 |
| Pulse Width       | 12.0000 |
| Presaturation Frequency |       |
| Spectrometer Frequency | 500.35 |
| Spectral Width    | 10000.0 |
| Lowest Frequency  | -1922.3 |
| Nucleus           | 1H |
| Acquired Size     | 32768 |
| Spectral Size     | 65536 |
Parameter | Value
--- | ---
1 | Origin | Varian
2 | Owner | 
3 | Instrument | inova
4 | Solvent | CDCl3
5 | Temperature | 20.0
6 | Pulse Sequence | s2pul
7 | Experiment | 1D
8 | Probe | QUAD
9 | Number of Scans | 8
10 | Receiver Gain | 50
11 | Relaxation Delay | 0.0000
12 | Pulse Width | 6.5000
13 | Presaturation Frequency | 
14 | Spectrometer Frequency | 499.69
15 | Spectral Width | 7024.9
16 | Lowest Frequency | -1023.4
17 | Nucleus | 1H
18 | Acquired Size | 32768
19 | Spectral Size | 65536
Parameter | Value
--- | ---
1 | Origin
2 | Owner
3 | Instrument
4 | Solvent
5 | Temperature
6 | Pulse Sequence
7 | Experiment
8 | Probe
9 | Number of Scans
10 | Receiver Gain
11 | Relaxation Delay
12 | Pulse Width
13 | Presaturation Frequency
14 | Spectrometer Frequency
15 | Spectral Width
16 | Lowest Frequency
17 | Nucleus
18 | Acquired Size
19 | Spectral Size
| Parameter            | Value |
|----------------------|-------|
| Origin               | Bruker BioSpin GmbH |
| Owner                | user1d |
| Instrument           | spect |
| Solvent              | CDCl3 |
| Temperature          | 298.0 |
| Pulse Sequence       | zg30 |
| Experiment           | 1D |
| Probe                | 2127784_0002, CPBBO 500S1 BBF.H.D.05 Z, |
| Number of Scans      | 16 |
| Receiver Gain        | 48.8 |
| Relaxation Delay     | 1.0000 |
| Pulse Width          | 12.0000 |
| Presaturation Frequency |      |
| Spectrometer Frequency | 500.35 |
| Spectral Width       | 10000.0 |
| Lowest Frequency     | -1922.3 |
| Nucleus              | 1H |
| Acquired Size        | 32768 |
| Spectral Size        | 65536 |
Parameter | Value
--- | ---
1 Origin | Bruker BioSpin GmbH
2 Owner | user1d
3 Instrument | spect
4 Solvent | CDCl3
5 Temperature | 298.0
6 Pulse Sequence | zgpg30
7 Experiment | 1D
8 Probe | 2127784_0002, CP8BO 50051 BBF_H.D. 05 Z,
9 Number of Scans | 128
10 Receiver Gain | 190.5
11 Relaxation Delay | 2.0000
12 Pulse Width | 10.0000
13 Presaturation Frequency
14 Spectrometer Frequency | 125.83
15 Spectral Width | 31512.6
16 Lowest Frequency | 190.8
17 Nucleus | 13C
18 Acquired Size | 32768
19 Spectral Size | 65536
| Parameter       | Value            |
|-----------------|------------------|
| Origin          | Varian           |
| Owner           |                  |
| Instrument      | inova            |
| Solvent         | CDCl3            |
| Temperature     | 20.0             |
| Pulse Sequence  | s2pul            |
| Experiment      | 1D               |
| Probe           | QUAD             |
| Number of Scans | 32               |
| Receiver Gain   | 52               |
| Relaxation Delay| 0.0000           |
| Pulse Width     | 6.2500           |
| Presaturation Frequency |         |
| Spectrometer Frequency | 470.15      |
| Spectral Width  | 100000.0         |
| Lowest Frequency| -79501.3         |
| Nucleus         | 19F              |
| Acquired Size   | 32768            |
| Spectral Size   | 65536            |

![Chemical Structure](image-url)
| Parameter          | Value                |
|--------------------|----------------------|
| 1 Origin           | Varian               |
| 2 Owner            |                      |
| 3 Instrument       | inova                |
| 4 Solvent          | CDCl₃                |
| 5 Temperature      | 25.0                 |
| 6 Pulse Sequence   | s2pul                |
| 7 Experiment       | 1D                   |
| 8 Probe            | QUAD                 |
| 9 Number of Scans  | 16                   |
| 10 Receiver Gain   | 41                   |
| 11 Relaxation Delay| 0.0000               |
| 12 Pulse Width     | 6.5000               |
| 13 Presaturation Frequency |        |
| 14 Spectrometer Frequency | 499.69           |
| 15 Spectral Width  | 7024.9               |
| 16 Lowest Frequency| -1022.4              |
| 17 Nucleus         | 1H                   |
| 18 Acquired Size   | 32768                |
| 19 Spectral Size   | 65536                |
| Parameter      | Value       |
|---------------|-------------|
| 1 Origin      | Varian      |
| 2 Owner       |             |
| 3 Instrument  | inova       |
| 4 Solvent     | CDCl3       |
| 5 Temperature | 25.0        |
| 6 Pulse Sequence | s2pul   |
| 7 Experiment  | 1D          |
| 8 Probe       | QUAD        |
| 9 Number of Scans | 507     |
| 10 Receiver Gain | 60       |
| 11 Relaxation Delay | 1.0000 |
| 12 Pulse Width | 6.0000     |
| 13 Presaturation Frequency |         |
| 14 Spectrometer Frequency | 125.66  |
| 15 Spectral Width | 30165.9 |
| 16 Lowest Frequency | -1280.8  |
| 17 Nucleus    | 13C         |
| 18 Acquired Size | 32768    |
| 19 Spectral Size | 65536     |
| Parameter          | Value     |
|--------------------|-----------|
| 1 Origin           | Varian    |
| 2 Owner            |           |
| 3 Instrument       | inova     |
| 4 Solvent          | CDCl3     |
| 5 Temperature      | 25.0      |
| 6 Pulse Sequence   | s2pul     |
| 7 Experiment       | 1D        |
| 8 Probe            | QUAD      |
| 9 Number of Scans  | 32        |
| 10 Receiver Gain   | 52        |
| 11 Relaxation Delay| 0.0000    |
| 12 Pulse Width     | 6.250     |
| 13 Presaturation Frequency |       |
| 14 Spectrometer Frequency | 470.15   |
| 15 Spectral Width  | 100000.0  |
| 16 Lowest Frequency| -79501.3  |
| 17 Nucleus         | 19F       |
| 18 Acquired Size   | 32768     |
| 19 Spectral Size   | 65536     |
| Parameter           | Value                                                                 |
|---------------------|-----------------------------------------------------------------------|
| Origin              | Bruker BioSpin GmbH                                                   |
| Owner               | user1d                                                                |
| Instrument          | spect                                                                 |
| Solvent             | CDCl3                                                                 |
| Temperature         | 298.1                                                                 |
| Pulse Sequence      | zg30                                                                  |
| Experiment          | 1D                                                                    |
| Probe               | 2127784_0002_CP_BB05051_BBF_H_D_052                                  |
| Number of Scans     | 16                                                                    |
| Receiver Gain       | 76.2                                                                  |
| Relaxation Delay    | 15.0000                                                               |
| Pulse Width         | 12.0000                                                               |
| Presaturation       |                                                                        |
| Frequency           |                                                                        |
| Spectrometer Frequency | 500.35                                                                 |
| Spectral Width      | 10000.0                                                               |
| Lowest Frequency    | 1.921.8                                                               |
| Nucleus             | 1H                                                                    |
| Acquired Size       | 32768                                                                 |
| Spectral Size       | 65536                                                                 |

![Chemical Structure Image]
| Parameter     | Value                                      |
|---------------|--------------------------------------------|
| Origin        | Bruker BioSpin GmbH                         |
| Owner         | user1d                                      |
| Instrument    | spect                                      |
| Solvent       | CDCl3                                      |
| Temperature   | 298.2                                      |
| Pulse Sequence| zgpg30                                      |
| Experiment    | 1D                                          |
| Probe         | 2127784_0002, CP8BO 500S1 BBF H.D. 05 Z    |
| Number of Scans| 256                                         |
| Receiver Gain | 190.5                                      |
| Relaxation Delay | 2.0000                                   |
| Pulse Width   | 10.0000                                    |
| Presaturation Frequency |                       |
| Spectrometer Frequency | 125.83                                    |
| Spectral Width | 31512.6                                    |
| Lowest Frequency | .19169                                   |
| Nucleus       | 13C                                        |
| Acquired Size | 32768                                      |
| Spectral Size | 65536                                      |

![NMR spectrum](image)
Parameter | Value
--- | ---
1 Origin | Bruker BioSpin GmbH
2 Owner | user1d
3 Instrument | spect
4 Solvent | CDCl3
5 Temperature | 298.0
6 Pulse Sequence | zg30
7 Experiment | 1D
8 Probe | 2127784_0002, CPBBBO500S1BFB.D.05Z;
9 Number of Scans | 16
10 Receiver Gain | 94.3
11 Relaxation Delay | 1.0000
12 Pulse Width | 12.0000
13 Presaturation Frequency
14 Spectrometer Frequency | 500.35
15 Spectral Width | 10000.0
16 Lowest Frequency | -1922.3
17 Nucleus | 1H
18 Acquired Size | 32768
19 Spectral Size | 65536
| Parameter                  | Value                                                                 |
|----------------------------|-----------------------------------------------------------------------|
| Origin                     | Bruker BioSpin GmbH                                                   |
| Owner                      | user1d                                                                |
| Instrument                 | spect                                                                 |
| Solvent                    | CDCl3                                                                 |
| Temperature                | 298.0                                                                |
| Pulse Sequence             | zgpg30                                                                |
| Experiment                 | 1D                                                                   |
| Probe                      | 2127784_0002, CP 500S1 BDF, H. D. 05 Z,                              |
| Number of Scans            | 128                                                                  |
| Receiver Gain              | 190.5                                                                |
| Relaxation Delay           | 2.0000                                                               |
| Pulse Width                | 10.0000                                                              |
| Presaturation Frequency    |                                                                       |
| Spectrometer Frequency     | 125.83                                                               |
| Spectral Width             | 31512.6                                                              |
| Lowest Frequency           | 1.8990                                                               |
| Nucleus                    | 13C                                                                  |
| Acquired Size              | 32768                                                                |
| Spectral Size              | 65536                                                                |

![Chemical Structure Image]
| Parameter   | Value                                                                 |
|-------------|----------------------------------------------------------------------|
| Origin      | Bruker BioSpin GmbH                                                  |
| Owner       | user1d                                                              |
| Instrument  | spect                                                                |
| Solvent     | CDCl₃                                                               |
| Temperature | 298.2                                                               |
| Pulse Sequence | zg30                                                           |
| Experiment  | 1D                                                                  |
| Probe       | 2127784_0002_CP2BO 500S1 BBF_H.D.05 Z                               |
| Number of Scans | 16                                                      |
| Receiver Gain | 122.8                                                             |
| Relaxation Delay | 15.0000                                                             |
| Pulse Width | 12.0000                                                             |
| Presaturation Frequency |                                                               |
| Spectrometer Frequency | 500.35                                                              |
| Spectral Width | 10000.0                                                             |
| Lowest Frequency | -1.9223                                                            |
| Nucleus     | 1H                                                                  |
| Acquired Size | 32768                                                             |
| Spectral Size | 65536                                                             |
Parameter | Value
--- | ---
1 Origin | Bruker BioSpin GmbH
2 Owner | user1d
3 Instrument | spect
4 Solvent | CDCl₃
5 Temperature | 298.1
6 Pulse Sequence | zgpg30
7 Experiment | 1D
8 Probe | 2127784_0002, CP BBO 500S1 BBF.H.D.05 Z
9 Number of Scans | 256
10 Receiver Gain | 190.5
11 Relaxation Delay | 2.0000
12 Pulse Width | 10.0000
13 Presaturation Frequency | 
14 Spectrometer Frequency | 125.83
15 Spectral Width | 31512.6
16 Lowest Frequency | -199.4
17 Nucleus | 13C
18 Acquired Size | 32768
19 Spectral Size | 65536
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| 1 Origin           | Bruker BioSpin GmbH                                                  |
| 2 Owner            | user1d                                                               |
| 3 Instrument       | spect                                                                |
| 4 Solvent          | CDCl3                                                                |
| 5 Temperature      | 298.0                                                                |
| 6 Pulse Sequence   | zg30                                                                 |
| 7 Experiment       | 1D                                                                   |
| 8 Probe            | 2127784_0002, CPBBO 500S1 BBF .H.D. 05 Z,                           |
| 9 Number of Scans  | 16                                                                   |
| 10 Receiver Gain   | 29.7                                                                 |
| 11 Relaxation Delay| 1.0000                                                              |
| 12 Pulse Width     | 12.0000                                                              |
| 13 Presaturation Frequency |                                              |
| 14 Spectrometer Frequency | 500.35                                                           |
| 15 Spectral Width  | 10000.0                                                              |
| 16 Lowest Frequency| 1.19223                                                             |
| 17 Nucleus         | 1H                                                                   |
| 18 Acquired Size   | 32768                                                                |
| 19 Spectral Size   | 65536                                                                |

![Chemical Structure](image_url)
| Parameter      | Value                                                                 |
|---------------|----------------------------------------------------------------------|
| Origin        | Bruker BioSpin GmbH                                                  |
| Owner         | user1d                                                              |
| Instrument    | spect                                                               |
| Solvent       | CDCl3                                                              |
| Temperature   | 298.0                                                              |
| Pulse Sequence| zgpg30                                                              |
| Experiment    | 1D                                                                  |
| Probe         | 2127784_0002, CPBBBO 500S1 BBF.H.D.05 Z,                           |
| Number of Scans| 128                                                                |
| Receiver Gain | 190.5                                                              |
| Relaxation Delay| 2.0000                                                          |
| Pulse Width   | 10.0000                                                            |
| Presaturation Frequency |                                                              |
| Spectrometer Frequency| 125.83                                                              |
| Spectral Width | 31512.6                                                            |
| Lowest Frequency | -1905.7                                                            |
| Nucleus       | 13C                                                                |
| Acquired Size | 32768                                                              |
| Spectral Size | 65536                                                              |
HSQC
COSY

- Methylene B crosspeak
- Methylene A crosspeak
- Methylene B crosspeak
- Methylene A crosspeak

f1 (ppm)  f2 (ppm)
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| 1 Origin           | Bruker BioSpin GmbH                                                  |
| 2 Owner            | user1d                                                              |
| 3 Instrument       | spect                                                               |
| 4 Solvent          | CDCl3                                                               |
| 5 Temperature      | 298.0                                                               |
| 6 Pulse Sequence   | zgpg30                                                              |
| 7 Experiment       | 1D                                                                  |
| 8 Probe            | 2127784_0002,CPBBO 50051 BBF..H.D..05 Z,                           |
| 9 Number of Scans  | 256                                                                 |
| 10 Receiver Gain   | 190.5                                                               |
| 11 Relaxation Delay| 2.0000                                                             |
| 12 Pulse Width     | 10.0000                                                             |
| 13 Presaturation Frequency |                                                               |
| 14 Spectrometer Frequency | 125.83                                                              |
| 15 Spectral Width  | 31512.6                                                             |
| 16 Lowest Frequency| 1898.6                                                              |
| 17 Nucleus         | 13C                                                                 |
| 18 Acquired Size   | 32768                                                               |
| 19 Spectral Size   | 65536                                                               |
| Parameter       | Value                                                                 |
|-----------------|----------------------------------------------------------------------|
| 1 Origin        | Bruker BioSpin GmbH                                                  |
| 2 Owner         | user1d                                                              |
| 3 Instrument    | spect                                                               |
| 4 Solvent       | CDCl3                                                               |
| 5 Temperature   | 298.1                                                               |
| 6 Pulse Sequence| zg30                                                                |
| 7 Experiment    | 1D                                                                  |
| 8 Probe         | 2127784_0002, CPBBO 500S1 BBF.H.D.052,                               |
| 9 Number of Scans| 16                                                                 |
| 10 Receiver Gain| 55.0                                                                |
| 11 Relaxation Delay| 15.0000                                                            |
| 12 Pulse Width  | 12.0000                                                             |
| 13 Presaturation Frequency |                                                                  |
| 14 Spectrometer Frequency | 500.35                                                             |
| 15 Spectral Width| 10000.0                                                             |
| 16 Lowest Frequency | -1.9213                                                           |
| 17 Nucleus      | 1H                                                                  |
| 18 Acquired Size| 32768                                                               |
| 19 Spectral Size| 65536                                                               |
| Parameter       | Value                                      |
|-----------------|--------------------------------------------|
| Origin          | Bruker BioSpin GmbH                         |
| Owner           | user1d                                      |
| Instrument      | spect                                       |
| Solvent         | CDCl3                                       |
| Temperature     | 298.2                                       |
| Pulse Sequence  | zgpg30                                      |
| Experiment      | 1D                                          |
| Probe           | 2127784_0002,CP-BBO 500S1 BBF.H.D.052       |
| Number of Scans | 128                                         |
| Receiver Gain   | 190.5                                       |
| Relaxation Delay| 2.0000                                      |
| Pulse Width     | 10.0000                                     |
| Presaturation Frequency |                  |
| Spectrometer Frequency | 125.83                                    |
| Spectral Width  | 31512.6                                     |
| Lowest Frequency| -1902.4                                     |
| Nucleus         | 1H, 13C                                    |
| Acquired Size   | 32768                                       |
| Spectral Size   | 65536                                       |
| Parameter       | Value                                                                 |
|-----------------|----------------------------------------------------------------------|
| Origin          | Bruker BioSpin GmbH                                                   |
| Owner           | user1d                                                              |
| Instrument      | spect                                                               |
| Solvent         | CDCl3                                                               |
| Temperature     | 298.2                                                               |
| Pulse Sequence  | zg30                                                                |
| Experiment      | 1D                                                                  |
| Probe           | 2127784_0002_CPBB05051BBF_H.D.052                                    |
| Number of Scans | 16                                                                  |
| Receiver Gain   | 94.3                                                               |
| Relaxation Delay| 15.0000                                                            |
| Pulse Width     | 12.0000                                                             |
| Presaturation Frequency |                                                                |
| Spectrometer Frequency | 500.35                                                           |
| Spectral Width  | 10000.0                                                             |
| Lowest Frequency| 1.1920.3                                                            |
| Nucleus         | 1H                                                                  |
| Acquired Size   | 32768                                                              |
| Spectral Size   | 65536                                                              |

![NMR Spectrum](image)
| Parameter       | Value |
|-----------------|-------|
| Origin          | Bruker BioSpin GmbH |
| Owner           | user1d |
| Instrument      | spect |
| Solvent         | CDCl3 |
| Temperature     | 298.2 |
| Pulse Sequence  | zgpg30 |
| Experiment      | 1D |
| Probe           | 2127784_0002; CP-BBO 500S1 BBF_H.D.05 Z; |
| Number of Scans | 128   |
| Receiver Gain   | 190.5 |
| Relaxation Delay| 2.0000|
| Pulse Width     | 10.0000 |
| Presaturation Frequency | |
| Spectrometer Frequency | 125.83 |
| Spectral Width  | 31512.6 |
| Lowest Frequency| -1899.1 |
| Nucleus         | 13C |
| Acquired Size   | 32768 |
| Spectral Size   | 65536 |
| Parameter            | Value                        |
|----------------------|------------------------------|
| 1. Origin            | Varian                       |
| 2. Owner             |                              |
| 3. Instrument        | inova                        |
| 4. Solvent           | CDCl3                        |
| 5. Temperature       | 20.0                         |
| 6. Pulse Sequence    | s2pul                        |
| 7. Experiment        | 1D                           |
| 8. Probe             | hcn                          |
| 9. Number of Scans   | 16                           |
| 10. Receiver Gain    | 28                           |
| 11. Relaxation Delay | 10.3000                      |
| 12. Pulse Width      | 6.8750                       |
| 13. Presaturation Frequency |                    |
| 14. Spectrometer Frequency | 500.07                      |
| 15. Spectral Width   | 8000.0                       |
| 16. Lowest Frequency | -1521.1                      |
| 17. Nucleus          | 1H                           |
| 18. Acquired Size    | 32768                        |
| 19. Spectral Size    | 65536                        |
| Parameter        | Value                  |
|------------------|------------------------|
| Origin           | Varian                 |
| Owner            |                        |
| Instrument       | inova                  |
| Solvent          | CDCl3                  |
| Temperature      | 20.0                   |
| Pulse Sequence   | s2pul                  |
| Experiment       | 1D                     |
| Probe            | QUAD                   |
| Number of Scans  | 1200                   |
| Receiver Gain    | 60                     |
| Relaxation Delay | 1.0000                 |
| Pulse Width      | 6.0000                 |
| Presaturation Frequency |                |
| Spectrometer Frequency | 125.66               |
| Spectral Width   | 30165.9                |
| Lowest Frequency | 1274.5                 |
| Nucleus          | 13C                    |
| Acquired Size    | 32768                  |
| Spectral Size    | 65536                  |

![Chemical Structure](image)

The figure shows a 1D NMR spectrum with peaks at various ppm values. The chemical structure is also depicted, showing the molecular framework with functional groups.
| Parameter               | Value                  |
|-------------------------|------------------------|
| 1  Origin               | Varian                 |
| 2  Owner                |                        |
| 3  Instrument           | inova                  |
| 4  Solvent              | CDCl3                  |
| 5  Temperature          | 20.0                   |
| 6  Pulse Sequence       | s2pul                  |
| 7  Experiment           | 1D                     |
| 8  Probe                | hcn                    |
| 9  Number of Scans      | 16                     |
| 10 Receiver Gain        | 32                     |
| 11 Relaxation Delay     | 10.3000                |
| 12 Pulse Width          | 6.8750                 |
| 13 Presaturation Frequency |                      |
| 14 Spectrometer Frequency | 500.07                |
| 15 Spectral Width       | 8000.0                 |
| 16 Lowest Frequency     | -1.5216                |
| 17 Nucleus              | 1H                     |
| 18 Acquired Size        | 32768                  |
| 19 Spectral Size        | 65536                  |
| Parameter          | Value                        |
|--------------------|------------------------------|
| 1 Origin           | Varian                       |
| 2 Owner            |                               |
| 3 Instrument       | inova                        |
| 4 Solvent          | CDCl3                        |
| 5 Temperature      | 20.0                         |
| 6 Pulse Sequence   | s2pul                        |
| 7 Experiment       | 1D                           |
| 8 Probe            | QUAD                         |
| 9 Number of Scans  | 1600                         |
| 10 Receiver Gain   | 60                           |
| 11 Relaxation Delay| 1.0000                       |
| 12 Pulse Width     | 6.0000                       |
| 13 Presaturation Frequency |             |
| 14 Spectrometer Frequency | 125.66             |
| 15 Spectral Width  | 30165.9                      |
| 16 Lowest Frequency| -1275.4                      |
| 17 Nucleus         | 13C                          |
| 18 Acquired Size   | 32768                        |
| 19 Spectral Size   | 65536                        |

---

![Chemical Structure Image](image)

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Graph showing the NMR spectrum with chemical shifts ranging from 220 to 210 ppm.
| Parameter          | Value                      |
|--------------------|----------------------------|
| Origin             | Varian                     |
| Owner              |                            |
| Instrument         | inova                      |
| Solvent            | CDCl₃                      |
| Temperature        | 20.0ºC                     |
| Pulse Sequence     | s2pul                      |
| Experiment         | 1D                         |
| Probe              | hcn                        |
| Number of Scans    | 8                          |
| Receiver Gain      | 50                         |
| Relaxation Delay   | 15.0000                    |
| Pulse Width        | 6.8750                     |
| Presaturation Frequency |                  |
| Spectrometer Frequency | 500.07                   |
| Spectral Width     | 8000.0                     |
| Lowest Frequency   | 1.5211                     |
| Nucleus            | 1H                         |
| Acquired Size      | 32768                      |
| Spectral Size      | 65536                      |
| Parameter          | Value |
|--------------------|-------|
| 1 Origin           | Varian|
| 2 Owner            |       |
| 3 Instrument       | inova |
| 4 Solvent          | CDCl3 |
| 5 Temperature      | 20.0  |
| 6 Pulse Sequence   | s2pul |
| 7 Experiment       | 1D    |
| 8 Probe            | QUAD  |
| 9 Number of Scans  | 640   |
| 10 Receiver Gain   | 60    |
| 11 Relaxation Delay| 1.0000|
| 12 Pulse Width     | 6.0000|
| 13 Presaturation Frequency |   |
| 14 Spectrometer Frequency | 125.66 |
| 15 Spectral Width  | 30165.9|
| 16 Lowest Frequency| 1274.5|
| 17 Nucleus         | 13C   |
| 18 Acquired Size   | 32768 |
| 19 Spectral Size   | 65536 |

![Graph Image](image-url)
Parameter | Value
--- | ---
1 Origin | Varian
2 Owner | 
3 Instrument | inova
4 Solvent | CDCl3
5 Temperature | 21.0
6 Pulse Sequence | s2pul
7 Experiment | 1D
8 Probe | QUAD
9 Number of Scans | 32
10 Receiver Gain | 58
11 Relaxation Delay | 0.0000
12 Pulse Width | 6.5000
13 Presaturation Frequency | 
14 Spectrometer Frequency | 499.69
15 Spectral Width | 7024.9
16 Lowest Frequency | -1021.9
17 Nucleus | 1H
18 Acquired Size | 32768
19 Spectral Size | 65536
| Parameter          | Value                  |
|--------------------|------------------------|
| Origin             | Varian                 |
| Owner              |                        |
| Instrument         | inova                  |
| Solvent            | CDCl3                  |
| Temperature        | 21.0                   |
| Pulse Sequence     | s2pul                  |
| Experiment         | 1D                     |
| Probe              | QUAD                   |
| Number of Scans    | 600                    |
| Receiver Gain      | 60                     |
| Relaxation Delay   | 1.0000                 |
| Pulse Width        | 6.0000                 |
| Presaturation Frequency |                |
| Spectrometer Frequency | 125.66               |
| Spectral Width     | 30165.9                |
| Lowest Frequency   | 1273.1                 |
| Nucleus            | 13C                    |
| Acquired Size      | 32768                  |
| Spectral Size      | 65536                  |
| Parameter          | Value                        |
|--------------------|------------------------------|
| 1 Origin           | Varian                       |
| 2 Owner            |                              |
| 3 Instrument       | inova                        |
| 4 Solvent          | CDCl₃                        |
| 5 Temperature      | 20.0                         |
| 6 Pulse Sequence   | s2pul                        |
| 7 Experiment       | 1D                            |
| 8 Probe            | hcn                           |
| 9 Number of Scans  | 16                            |
| 10 Receiver Gain   | 28                            |
| 11 Relaxation Delay| 15.0000                      |
| 12 Pulse Width     | 9.0000                       |
| 13 Presaturation Frequency |                    |
| 14 Spectrometer Frequency | 500.07                     |
| 15 Spectral Width  | 8000.0                       |
| 16 Lowest Frequency| -1518.6                      |
| 17 Nucleus         | 1H                            |
| 18 Acquired Size   | 32768                         |
| 19 Spectral Size   | 65536                         |
| Parameter                  | Value                        |
|---------------------------|------------------------------|
| 1  Origin                  | Varian                       |
| 2  Owner                   |                              |
| 3  Instrument              | inova                        |
| 4  Solvent                 | CDCl3                        |
| 5  Temperature             | 20.0                         |
| 6  Pulse Sequence          | s2pul                        |
| 7  Experiment              | 1D                           |
| 8  Probe                   | QUAD                         |
| 9  Number of Scans         | 1200                         |
| 10 Receiver Gain           | 60                           |
| 11 Relaxation Delay        | 1.0000                       |
| 12 Pulse Width             | 6.0000                       |
| 13 Presaturation Frequency |                              |
| 14 Spectrometer Frequency  | 125.66                       |
| 15 Spectral Width          | 30165.9                      |
| 16 Lowest Frequency        | 1274.8                       |
| 17 Nucleus                 | 13C                          |
| 18 Acquired Size           | 32768                        |
| 19 Spectral Size           | 65536                        |

![Chemical Structure](image)
| Parameter       | Value       |
|-----------------|-------------|
| 1 Origin        | Varian      |
| 2 Owner         |             |
| 3 Instrument    | inova       |
| 4 Solvent       | CDCl3       |
| 5 Temperature   | 20.0        |
| 6 Pulse Sequence| s2pul       |
| 7 Experiment    | 1D          |
| 8 Probe         | QUAD        |
| 9 Number of Scans| 32         |
| 10 Receiver Gain| 52          |
| 11 Relaxation Delay| 0.00000  |
| 12 Pulse Width  | 6.2500      |
| 13 Presaturation Frequency|         |
| 14 Spectrometer Frequency| 470.15 |
| 15 Spectral Width| 1000000.0  |
| 16 Lowest Frequency| -79501.3 |
| 17 Nucleus      | 19F         |
| 18 Acquired Size| 32768       |
| 19 Spectral Size| 65536       |

![Chemical Structure](image)
| Parameter          | Value | Value          | Value          | Value          | Value          | Value          | Value          |
|--------------------|-------|----------------|----------------|----------------|----------------|----------------|----------------|
| Origin             | Varian |                |                |                |                |                |                |
| Owner              |        |                |                |                |                |                |                |
| Instrument         | inova  |                |                |                |                |                |                |
| Solvent            | CDCl3  |                |                |                |                |                |                |
| Temperature        | 20.0   |                |                |                |                |                |                |
| Pulse Sequence     | s2pul  |                |                |                |                |                |                |
| Experiment         | 1D     |                |                |                |                |                |                |
| Probe              | QUAD   |                |                |                |                |                |                |
| Number of Scans    | 600    |                |                |                |                |                |                |
| Receiver Gain      | 60     |                |                |                |                |                |                |
| Relaxation Delay   | 1.0000 |                |                |                |                |                |                |
| Pulse Width        | 6.0000 |                |                |                |                |                |                |
| Presaturation      |        |                |                |                |                |                |                |
| Spectrometer       | 125.66 |                |                |                |                |                |                |
| Spectral Width     | 30165.9|                |                |                |                |                |                |
| Lowest Frequency   | 1265.6 |                |                |                |                |                |                |
| Nucleus            | 13C    |                |                |                |                |                |                |
| Acquired Size      | 32768  |                |                |                |                |                |                |
| Spectral Size      | 65536  |                |                |                |                |                |                |
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| 1 Origin           | Bruker BioSpin GmbH                                                  |
| 2 Owner            | user1d                                                              |
| 3 Instrument       | spect                                                               |
| 4 Solvent          | CDCl3                                                               |
| 5 Temperature      | 298.1                                                               |
| 6 Pulse Sequence   | zg30                                                                |
| 7 Experiment       | 1D                                                                  |
| 8 Probe            | 2127784_0002, CP-2BO 500S1 BBF_H.D.05 Z,                            |
| 9 Number of Scans  | 16                                                                  |
| 10 Receiver Gain   | 76.2                                                                |
| 11 Relaxation Delay| 15.0000                                                             |
| 12 Pulse Width     | 12.0000                                                             |
| 13 Presaturation Frequency |                                                                |
| 14 Spectrometer Frequency | 500.35                                                            |
| 15 Spectral Width  | 10000.0                                                             |
| 16 Lowest Frequency| -1.1920.8                                                           |
| 17 Nucleus         | 1H                                                                  |
| 18 Acquired Size   | 32768                                                               |
| 19 Spectral Size   | 65536                                                               |
| Parameter       | Value                                                                 |
|-----------------|------------------------------------------------------------------------|
| Origin          | Bruker BioSpin GmbH                                                    |
| Owner           | user1d                                                                |
| Instrument      | spect                                                                  |
| Solvent         | CDCl3                                                                  |
| Temperature     | 298.2                                                                 |
| Pulse Sequence  | zgpg30                                                                 |
| Experiment      | 1D                                                                     |
| Probe           | 2127784_0002, CP8BO 50051 BBF.H.D.05 Z                                 |
| Number of Scans | 256                                                                   |
| Receiver Gain   | 190.55                                                                |
| Relaxation Delay| 2.0000                                                                |
| Pulse Width     | 10.0000                                                               |
| Presaturation Frequency |                                                                   |
| Spectrometer Frequency | 125.83                                                              |
| Spectral Width  | 31512.6                                                               |
| Lowest Frequency| -1898.1                                                               |
| Nucleus         | 13C                                                                   |
| Acquired Size   | 32768                                                                 |
| Spectral Size   | 65536                                                                 |
| Parameter      | Value |
|----------------|-------|
| 1 Origin       | Varian|
| 2 Owner        |       |
| 3 Instrument   | inova |
| 4 Solvent      | CDCl3 |
| 5 Temperature  | 20.0  |
| 6 Pulse Sequence| s2pul|
| 7 Experiment   | 1D    |
| 8 Probe        | QUAD  |
| 9 Number of Scans| 1600|
| 10 Receiver Gain| 60   |
| 11 Relaxation Delay| 1.0000|
| 12 Pulse Width | 6.0000|
| 13 Presaturation Frequency|       |
| 14 Spectrometer Frequency| 125.66|
| 15 Spectral Width| 30165.9|
| 16 Lowest Frequency| 1284.7|
| 17 Nucleus     | 13C   |
| 18 Acquired Size| 32768|
| 19 Spectral Size| 65536|
Parameter | Value
--- | ---
1 Origin | Varian
2 Owner | 
3 Instrument | inova
4 Solvent | CDCl₃
5 Temperature | 20.0
6 Pulse Sequence | s2pul
7 Experiment | 1D
8 Probe | hcn
9 Number of Scans | 16
10 Receiver Gain | 32
11 Relaxation Delay | 10.3000
12 Pulse Width | 6.8750
13 Presaturation Frequency | 
14 Spectrometer Frequency | 500.07
15 Spectral Width | 8000.0
16 Lowest Frequency | -1.5211
17 Nucleus | 1H
18 Acquired Size | 32768
19 Spectral Size | 65536
| Parameter          | Value |
|--------------------|-------|
| 1 Origin           | Varian |
| 2 Owner            |       |
| 3 Instrument       | inova |
| 4 Solvent          | CDCl3 |
| 5 Temperature      | 21.0  |
| 6 Pulse Sequence   | s2pul |
| 7 Experiment       | 1D    |
| 8 Probe            | QUAD  |
| 9 Number of Scans  | 1200  |
| 10 Receiver Gain   | 60    |
| 11 Relaxation Delay| 1.0000|
| 12 Pulse Width     | 6.0000|
| 13 Presaturation Frequency |     |
| 14 Spectrometer Frequency | 125.66 |
| 15 Spectral Width  | 30165.9|
| 16 Lowest Frequency| -1274.1|
| 17 Nucleus         | 13C   |
| 18 Acquired Size   | 32768 |
| 19 Spectral Size   | 65536 |
| Parameter             | Value                        |
|-----------------------|------------------------------|
| 1 Origin              | Varian                       |
| 2 Owner               |                              |
| 3 Instrument          | inova                        |
| 4 Solvent             | CDCl₃                        |
| 5 Temperature         | 20.0                         |
| 6 Pulse Sequence      | s2pul                        |
| 7 Experiment          | 1D                           |
| 8 Probe               | hcn                          |
| 9 Number of Scans     | 16                           |
| 10 Receiver Gain      | 32                           |
| 11 Relaxation Delay   | 10.300                      |
| 12 Pulse Width        | 6.8750                       |
| 13 Presaturation Frequency |                      |
| 14 Spectrometer Frequency | 500.07                    |
| 15 Spectral Width     | 8000.0                       |
| 16 Lowest Frequency   | -1.521.1                     |
| 17 Nucleus            | 1H                           |
| 18 Acquired Size      | 32768                        |
| 19 Spectral Size      | 65536                        |

The diagram shows a spectrum with peaks labeled as H₂O and grease.
| Parameter                  | Value     |
|---------------------------|-----------|
| 1 Origin                  | Varian    |
| 2 Owner                   |           |
| 3 Instrument              | inova     |
| 4 Solvent                 | CDCl3     |
| 5 Temperature             | 20.0      |
| 6 Pulse Sequence          | s2pul     |
| 7 Experiment              | 1D        |
| 8 Probe                   | QUAD      |
| 9 Number of Scans         | 1280      |
| 10 Receiver Gain          | 60        |
| 11 Relaxation Delay       | 1.0000    |
| 12 Pulse Width            | 6.0000    |
| 13 Presaturation Frequency|           |
| 14 Spectrometer Frequency | 125.66    |
| 15 Spectral Width         | 30165.9   |
| 16 Lowest Frequency       | -1274.4   |
| 17 Nucleus                | 13C       |
| 18 Acquired Size          | 32768     |
| 19 Spectral Size          | 65536     |
| Parameter          | Value  |
|--------------------|--------|
| 1 Origin           | Varian |
| 2 Owner            |        |
| 3 Instrument       | inova  |
| 4 Solvent          | DMSO   |
| 5 Temperature      | 20.0   |
| 6 Pulse Sequence   | s2pul  |
| 7 Experiment       | 1D     |
| 8 Probe            | hcn    |
| 9 Number of Scans  | 8      |
| 10 Receiver Gain   | 48     |
| 11 Relaxation Delay| 15.000 |
| 12 Pulse Width     | 6.8750 |
| 13 Presaturation Frequency |      |
| 14 Spectrometer Frequency | 500.07 |
| 15 Spectral Width  | 8000.0 |
| 16 Lowest Frequency| -1503.1|
| 17 Nucleus         | 1H     |
| 18 Acquired Size   | 32768  |
| 19 Spectral Size   | 65536  |

![Chemical Structure](image)
| Parameter       | Value                                      |
|-----------------|--------------------------------------------|
| 1 Origin        | Varian                                     |
| 2 Owner         |                                             |
| 3 Instrument    | inova                                      |
| 4 Solvent       | DMSO                                       |
| 5 Temperature   | 20.0                                       |
| 6 Pulse Sequence| s2pul                                      |
| 7 Experiment    | 1D                                         |
| 8 Probe         | QUAD                                       |
| 9 Number of Scans| 1600                                      |
| 10 Receiver Gain| 60                                          |
| 11 Relaxation Delay| 1.0000                                   |
| 12 Pulse Width  | 6.0000                                     |
| 13 Presaturation Frequency|                     |
| 14 Spectrometer Frequency| 125.66                                   |
| 15 Spectral Width| 30165.9                                    |
| 16 Lowest Frequency| -1343.3                                  |
| 17 Nucleus      | 13C                                        |
| 18 Acquired Size| 32768                                      |
| 19 Spectral Size| 65536                                      |
| Parameter               | Value                      |
|-------------------------|----------------------------|
| 1 Origin                | Varian                     |
| 2 Owner                 |                            |
| 3 Instrument            | inova                      |
| 4 Solvent               | CDCl3                      |
| 5 Temperature           | 20.0                       |
| 6 Pulse Sequence        | s2pul                      |
| 7 Experiment            | 1D                         |
| 8 Probe                 | hcn                        |
| 9 Number of Scans       | 16                         |
| 10 Receiver Gain        | 26                         |
| 11 Relaxation Delay     | 10.3000                    |
| 12 Pulse Width          | 6.8750                     |
| 13 Presaturation Frequency |                          |
| 14 Spectrometer Frequency | 500.07                     |
| 15 Spectral Width       | 8000.0                     |
| 16 Lowest Frequency     | -1520.6                    |
| 17 Nucleus              | 1H                         |
| 18 Acquired Size        | 32768                      |
| 19 Spectral Size        | 65536                      |
Parameter | Value
---|---
1 | Origin: Varian
2 | Owner
3 | Instrument: inova
4 | Solvent: CDCl3
5 | Temperature: 20.0
6 | Pulse Sequence: s2pul
7 | Experiment: 1D
8 | Probe: QUAD
9 | Number of Scans: 1600
10 | Receiver Gain: 60
11 | Relaxation Delay: 1.0000
12 | Pulse Width: 6.0000
13 | Presaturation Frequency
14 | Spectrometer Frequency: 125.66
15 | Spectral Width: 30165.9
16 | Lowest Frequency: -1279.5
17 | Nucleus: 13C
18 | Acquired Size: 32768
19 | Spectral Size: 65536
| Parameter          | Value  |
|--------------------|--------|
| 1 Origin           | Varian |
| 2 Owner            |        |
| 3 Instrument       | inova  |
| 4 Solvent          | CDCl3  |
| 5 Temperature      | 20.0   |
| 6 Pulse Sequence   | s2pul  |
| 7 Experiment       | 1D     |
| 8 Probe            | QUAD   |
| 9 Number of Scans  | 4      |
| 10 Receiver Gain   | 52     |
| 11 Relaxation Delay| 10.0000|
| 12 Pulse Width     | 6.5000 |
| 13 Presaturation Frequency |    |
| 14 Spectrometer Frequency | 499.69 |
| 15 Spectral Width  | 7024.9 |
| 16 Lowest Frequency| -1021.4|
| 17 Nucleus         | 1H     |
| 18 Acquired Size   | 32768  |
| 19 Spectral Size   | 65536  |
| Parameter          | Value               |
|--------------------|---------------------|
| 1 Origin           | Varian              |
| 2 Owner            |                     |
| 3 Instrument       | inova               |
| 4 Solvent          | CDCl3               |
| 5 Temperature      | 20.0                |
| 6 Pulse Sequence   | s2pul               |
| 7 Experiment       | 1D                  |
| 8 Probe            | QUAD                |
| 9 Number of Scans  | 512                 |
| 10 Receiver Gain   | 60                  |
| 11 Relaxation Delay| 2.0000              |
| 12 Pulse Width     | 6.0000              |
| 13 Presaturation Frequency |         |
| 14 Spectrometer Frequency | 125.66          |
| 15 Spectral Width  | 30165.9             |
| 16 Lowest Frequency| -1267.2             |
| 17 Nucleus         | 13C                 |
| 18 Acquired Size   | 32768               |
| 19 Spectral Size   | 65536               |

![Chemical Structure](image)
| Parameter        | Value          |
|------------------|----------------|
| Origin           | Varian         |
| Owner            |                |
| Instrument       | inova          |
| Solvent          | CDCl3          |
| Temperature      | 20.0           |
| Pulse Sequence   | s2pul          |
| Experiment       | 1D             |
| Probe            | QUAD           |
| Number of Scans  | 32             |
| Receiver Gain    | 56             |
| Relaxation Delay | 0.0000         |
| Pulse Width      | 6.2500         |
| Presaturation Frequency |       |
| Spectrometer Frequency | 470.15 |
| Spectral Width   | 1000000.0      |
| Lowest Frequency | -.795013       |
| Nucleus          | 19F            |
| Acquired Size    | 32768          |
| Spectral Size    | 65536          |
| Parameter               | Value       |
|------------------------|-------------|
| 1 Origin               | Varian      |
| 2 Owner                |             |
| 3 Instrument           | inova       |
| 4 Solvent              | CDCl3       |
| 5 Temperature          | 20.0        |
| 6 Pulse Sequence       | s2pul       |
| 7 Experiment           | 1D          |
| 8 Probe                | hcn         |
| 9 Number of Scans      | 16          |
| 10 Receiver Gain       | 32          |
| 11 Relaxation Delay    | 10.3000     |
| 12 Pulse Width         | 6.8750      |
| 13 Presaturation Frequency |         |
| 14 Spectrometer Frequency | 500.07     |
| 15 Spectral Width      | 8000.0      |
| 16 Lowest Frequency    | -1520.6     |
| 17 Nucleus             | 1H          |
| 18 Acquired Size       | 32768       |
| 19 Spectral Size       | 65536       |

![Chemical Structure](image-url)
| Parameter           | Value   |
|---------------------|---------|
| 1 Origin            | Varian  |
| 2 Owner             |         |
| 3 Instrument        | inova   |
| 4 Solvent           | CDCl3   |
| 5 Temperature       | 20.0    |
| 6 Pulse Sequence    | s2pul   |
| 7 Experiment        | 1D      |
| 8 Probe             | QUAD    |
| 9 Number of Scans   | 1200    |
| 10 Receiver Gain    | 60      |
| 11 Relaxation Delay | 1.0000  |
| 12 Pulse Width      | 6.0000  |
| 13 Presaturation Frequency |       |
| 14 Spectrometer Frequency | 125.66 |
| 15 Spectral Width   | 30165.9 |
| 16 Lowest Frequency | 1275.1  |
| 17 Nucleus          | 13C     |
| 18 Acquired Size    | 32768   |
| 19 Spectral Size    | 65536   |

![Chemical Structure](image)
| Parameter         | Value                        |
|-------------------|------------------------------|
| Origin            | Varian                       |
| Owner             |                              |
| Instrument        | inova                        |
| Solvent           | CDCl3                        |
| Temperature       | 20.0                         |
| Pulse Sequence    | s2pul                        |
| Experiment        | 1D                           |
| Probe             | hcn                          |
| Number of Scans   | 8                            |
| Receiver Gain     | 32                           |
| Relaxation Delay  | 15.0000                      |
| Pulse Width       | 7.0000                       |
| Presaturation Frequency |                  |
| Spectrometer Frequency | 500.06                   |
| Spectral Width    | 8000.0                       |
| Lowest Frequency  | -1513.1                      |
| Nucleus           | 1H                           |
| Acquired Size     | 32768                        |
| Spectral Size     | 65536                        |
| Parameter          | Value                                                                 |
|-------------------|----------------------------------------------------------------------|
| Origin            | Bruker BioSpin GmbH                                                  |
| Owner             | user1d                                                               |
| Instrument        | spect                                                                |
| Solvent           | CDCl3                                                                |
| Temperature       | 298.2                                                                |
| Pulse Sequence    | zgpg30                                                               |
| Experiment        | 1D                                                                   |
| Probe             | 2127784_0002_CPBBO 500S1 BBF_H.D.05 Z,                               |
| Number of Scans   | 256                                                                  |
| Receiver Gain     | 190.5                                                                |
| Relaxation Delay  | 2.0000                                                               |
| Pulse Width       | 10.0000                                                              |
| Presaturation Frequency |                                                                  |
| Spectrometer Frequency | 125.83                                                               |
| Spectral Width    | 31512.6                                                              |
| Lowest Frequency  | 1914.5                                                               |
| Nucleus           | 13C                                                                  |
| Acquired Size     | 32768                                                                |
| Spectral Size     | 65536                                                                |

![NMR Spectrogram](image)
| Parameter     | Value |
|---------------|-------|
| 1 Origin      | Varian|
| 2 Owner       |       |
| 3 Instrument  | inova |
| 4 Solvent     | CDCl3 |
| 5 Temperature | 20.0  |
| 6 Pulse Sequence | s2pul |
| 7 Experiment  | 1D    |
| 8 Probe       | QUAD  |
| 9 Number of Scans | 8     |
| 10 Receiver Gain | 41    |
| 11 Relaxation Delay | 15.0000 |
| 12 Pulse Width | 6.5000|
| 13 Presaturation Frequency |     |
| 14 Spectrometer Frequency | 499.69 |
| 15 Spectral Width | 7024.9 |
| 16 Lowest Frequency | 1011.9|
| 17 Nucleus    | 1H    |
| 18 Acquired Size | 32768 |
| 19 Spectral Size | 65536 |

![NMR Spectrum](image)
| Parameter               | Value                      |
|-------------------------|----------------------------|
| Origin                  | Varian                     |
| Owner                   |                            |
| Instrument              | inova                      |
| Solvent                 | CDCl3                      |
| Temperature             | 20.0                       |
| Pulse Sequence          | s2pul                      |
| Experiment              | 1D                         |
| Probe                   | QUAD                       |
| Number of Scans         | 1280                       |
| Receiver Gain           | 60                         |
| Relaxation Delay        | 1.0000                     |
| Pulse Width             | 6.0000                     |
| Presaturation Frequency |                            |
| Spectrometer Frequency  | 125.66                     |
| Spectral Width          | 30165.9                    |
| Lowest Frequency        | -1284.4                    |
| Nucleus                 | 13C                        |
| Acquired Size           | 32768                      |
| Spectral Size           | 65536                      |

![Spectral Graph](image)
| Parameter                  | Value                      |
|----------------------------|----------------------------|
| 1  Origin                  | Varian                     |
| 2  Owner                   |                            |
| 3  Instrument              | inova                      |
| 4  Solvent                 | CD2Cl2                     |
| 5  Temperature             | 20.0                       |
| 6  Pulse Sequence          | s2pul                      |
| 7  Experiment              | 1D                         |
| 8  Probe                   | QUAD                       |
| 9  Number of Scans         | 8                          |
| 10 Receiver Gain           | 52                         |
| 11 Relaxation Delay        | 15.0000                    |
| 12 Pulse Width             | 6.5000                     |
| 13 Presaturation Frequency |                            |
| 14 Spectrometer Frequency  | 499.69                     |
| 15 Spectral Width          | 7024.9                     |
| 16 Lowest Frequency        | -1019.4                    |
| 17 Nucleus                 | 1H                         |
| 18 Acquired Size           | 32768                      |
| 19 Spectral Size           | 65536                      |
| Parameter          | Value |
|--------------------|-------|
| 1 Origin           | Bruker BioSpin GmbH |
| 2 Owner            | user1d |
| 3 Instrument       | spect |
| 4 Solvent          | CD2Cl2 |
| 5 Temperature      | 298.0 |
| 6 Pulse Sequence   | zgpg30 |
| 7 Experiment       | 1D |
| 8 Probe            | 2127784_0002, CP BBO 500 S1 BBF H.D. 05 Z, |
| 9 Number of Scans  | 512 |
| 10 Receiver Gain   | 190.5 |
| 11 Relaxation Delay| 2.0000 |
| 12 Pulse Width     | 10.0000 |
| 13 Presaturation Frequency | |
| 14 Spectrometer Frequency | 125.83 |
| 15 Spectral Width  | 315.126 |
| 16 Lowest Frequency| 1842.9 |
| 17 Nucleus         | 13C |
| 18 Acquired Size   | 32768 |
| 19 Spectral Size   | 65536 |

![Chemical Structure](image-url)
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| 1 Origin           | Bruker BioSpin GmbH                                                  |
| 2 Owner            | user1d                                                              |
| 3 Instrument       | spect                                                               |
| 4 Solvent          | CD2Cl2                                                              |
| 5 Temperature      | 298.0                                                               |
| 6 Pulse Sequence   | zgfhigq2                                                            |
| 7 Experiment       | 1D                                                                  |
| 8 Probe            | 2127784_0002, CP-BBO 500S1 BBF.H.D.052,                               |
| 9 Number of Scans  | 64                                                                  |
| 10 Receiver Gain   | 190.5                                                               |
| 11 Relaxation Delay| 1.0000                                                             |
| 12 Pulse Width     | 15.0000                                                             |
| 13 Presaturation Frequency |                                                              |
| 14 Spectrometer Frequency | 470.75                                                           |
| 15 Spectral Width  | 113636.4                                                            |
| 16 Lowest Frequency| -103898.1                                                           |
| 17 Nucleus         | 19F                                                                 |
| 18 Acquired Size   | 65536                                                               |
| 19 Spectral Size   | 131072                                                              |
| Parameter       | Value                                                                 |
|-----------------|----------------------------------------------------------------------|
| Origin          | Bruker BioSpin GmbH                                                  |
| Owner           | user1d                                                               |
| Instrument      | spect                                                                |
| Solvent         | CD2Cl2                                                               |
| Temperature     | 298.0                                                                |
| Pulse Sequence  | zgpg30                                                               |
| Experiment      | 1D                                                                   |
| Probe           | 2127784_0002, CPBB0 50051 BBF_H.D.05 Z,                             |
| Number of Scans | 1024                                                                 |
| Receiver Gain   | 190.5                                                                |
| Relaxation Delay| 2.0000                                                               |
| Pulse Width     | 10.0000                                                              |
| Presaturation Frequency |                                                         |
| Spectrometer Frequency | 125.83                                                          |
| Spectral Width  | 3153.6                                                               |
| Lowest Frequency| 1843.7                                                               |
| Nucleus         | 13C                                                                  |
| Acquired Size   | 32768                                                                |
| Spectral Size   | 65536                                                                |
| Parameter   | Value |
|-------------|-------|
| Origin      | Bruker BioSpin GmbH |
| Owner       | user1d |
| Instrument  | spect |
| Solvent     | CD2Cl2 |
| Temperature | 298.0 |
| Pulse Sequence | zgfhigq2 |
| Experiment  | 1D |
| Probe       | 2127784_0002, CP BBO 500S1 BBF. H.D. 05 Z |
| Number of Scans | 64 |
| Receiver Gain | 190.5 |
| Relaxation Delay | 1.0000 |
| Pulse Width  | 15.0000 |
| Presaturation Frequency | |
| Spectrometer Frequency | 470.75 |
| Spectral Width | 113636.4 |
| Lowest Frequency | -103898.1 |
| Nucleus     | 19F |
| Acquired Size | 65536 |
| Spectral Size | 131072 |
| Parameter          | Value                                                                 |
|--------------------|-----------------------------------------------------------------------|
| 1 Origin           | Bruker BioSpin GmbH                                                  |
| 2 Owner            | user1d                                                               |
| 3 Instrument       | spect                                                                |
| 4 Solvent          | CD2Cl2                                                               |
| 5 Temperature      | 298.0                                                                |
| 6 Pulse Sequence   | zg30                                                                 |
| 7 Experiment       | 1D                                                                   |
| 8 Probe            | 2127784_0002, CP880 50051 BBF.H.D.05 Z,                              |
| 9 Number of Scans  | 16                                                                   |
| 10 Receiver Gain   | 69.2                                                                 |
| 11 Relaxation Delay| 15.0000                                                             |
| 12 Pulse Width     | 12.0000                                                              |
| 13 Presaturation Frequency |                                                                   |
| 14 Spectrometer Frequency | 500.35                                                           |
| 15 Spectral Width  | 10000.0                                                              |
| 16 Lowest Frequency| 1929.9                                                               |
| 17 Nucleus         | 1H                                                                   |
| 18 Acquired Size   | 32768                                                                |
| 19 Spectral Size   | 65536                                                                |
| Parameter         | Value |
|-------------------|-------|
| Origin            | Bruker BioSpin GmbH |
| Owner             | user1d |
| Instrument        | spect |
| Solvent           | CD2Cl2 |
| Temperature       | 298.0 |
| Pulse Sequence    | zgpg30 |
| Experiment        | 1D |
| Probe             | 2127784_0002, CP-BOBO 500S1 BBF.H.D.05 Z, |
| Number of Scans   | 2048 |
| Receiver Gain     | 190.5 |
| Relaxation Delay  | 2.0000 |
| Pulse Width       | 10.0000 |
| Presaturation Frequency | |
| Spectrometer Frequency | 125.83 |
| Spectral Width    | 31512.6 |
| Lowest Frequency  | 1843.4 |
| Nucleus           | 13C |
| Acquired Size     | 32768 |
| Spectral Size     | 65536 |
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| Origin             | Bruker BioSpin GmbH                                                  |
| Owner              | user1d                                                              |
| Instrument         | spect                                                               |
| Solvent            | CD2Cl2                                                              |
| Temperature        | 298.0                                                               |
| Pulse Sequence     | zgfhigq2                                                            |
| Experiment         | 1D                                                                  |
| Probe              | 2127784_0002, CP-BBO 500S1 BBF_H.D.052, Z_0001_(CP-BBO 500S1 BBF_H.D.052) |
| Number of Scans    | 64                                                                  |
| Receiver Gain      | 190.5                                                               |
| Relaxation Delay   | 1.0000                                                              |
| Pulse Width        | 15.0000                                                             |
| Presaturation Frequency |                                                                |
| Spectrometer Frequency | 470.75                                                             |
| Spectral Width     | 113636.4                                                            |
| Lowest Frequency   | 103898.1                                                            |
| Nucleus            | 19F                                                                 |
| Acquired Size      | 65536                                                               |
| Spectral Size      | 131072                                                              |
| Parameter      | Value        |
|----------------|--------------|
| 1 Origin       | Varian       |
| 2 Owner        |              |
| 3 Instrument   | inova        |
| 4 Solvent      | CDCl3        |
| 5 Temperature  | 20.0         |
| 6 Pulse Sequence| s2pul      |
| 7 Experiment   | 1D           |
| 8 Probe        | QUAD         |
| 9 Number of Scans | 8          |
| 10 Receiver Gain | 58         |
| 11 Relaxation Delay | 00000  |
| 12 Pulse Width  | 65000        |
| 13 Presaturation Frequency |            |
| 14 Spectrometer Frequency | 499.69    |
| 15 Spectral Width  | 7024.9        |
| 16 Lowest Frequency | -1022.4      |
| 17 Nucleus      | 1H           |
| 18 Acquired Size | 32768       |
| 19 Spectral Size  | 65536        |

![Chemical Structure](attachment:image.png)
| Parameter          | Value         |
|--------------------|---------------|
| Origin             | Varian        |
| Owner              |               |
| Instrument         | inova         |
| Solvent            | CDCl3         |
| Temperature        | 20.0          |
| Pulse Sequence     | s2pul         |
| Experiment         | 1D            |
| Probe              | QUAD          |
| Number of Scans    | 1933          |
| Receiver Gain      | 60            |
| Relaxation Delay   | 1.0000        |
| Pulse Width        | 6.0000        |
| Presaturation Frequency |          |
| Spectrometer Frequency | 125.66  |
| Spectral Width     | 30165.9       |
| Lowest Frequency   | 1272.7        |
| Nucleus            | 13C           |
| Acquired Size      | 32768         |
| Spectral Size      | 65536         |
| Parameter            | Value  |
|----------------------|--------|
| 1 Origin             | Varian |
| 2 Owner              |        |
| 3 Instrument         | inova  |
| 4 Solvent            | CDCl3  |
| 5 Temperature        | 20.0   |
| 6 Pulse Sequence     | s2pul  |
| 7 Experiment         | 1D     |
| 8 Probe              | QUAD   |
| 9 Number of Scans    | 8      |
| 10 Receiver Gain     | 40     |
| 11 Relaxation Delay  | 0.0000 |
| 12 Pulse Width       | 6.5000 |
| 13 Presaturation Frequency |   |
| 14 Spectrometer Frequency | 499.69 |
| 15 Spectral Width    | 7024.9 |
| 16 Lowest Frequency  | -1021.9|
| 17 Nucleus           | 1H     |
| 18 Acquired Size     | 32768  |
| 19 Spectral Size     | 65536  |
| Parameter            | Value     |
|----------------------|-----------|
| Origin               | Varian    |
| Owner                |           |
| Instrument           | inova     |
| Solvent              | CDCl3     |
| Temperature          | 20.0      |
| Pulse Sequence       | s2pul     |
| Experiment           | 1D        |
| Probe                | QUAD      |
| Number of Scans      | 261       |
| Receiver Gain        | 60        |
| Relaxation Delay     | 1.0000    |
| Pulse Width          | 6.0000    |
| Presaturation Frequency |       |
| Spectrometer Frequency | 125.66   |
| Spectral Width       | 30165.9   |
| Lowest Frequency     | 1278.0    |
| Nucleus              | 13C       |
| Acquired Size        | 32768     |
| Spectral Size        | 65536     |
| Parameter          | Value                  |
|--------------------|------------------------|
| 1. Origin          | Varian                 |
| 2. Owner           |                        |
| 3. Instrument      | inova                  |
| 4. Solvent         | CDCl3                  |
| 5. Temperature     | 20.0                   |
| 6. Pulse Sequence  | s2pul                  |
| 7. Experiment      | 1D                     |
| 8. Probe           | QUAD                   |
| 9. Number of Scans | 32                     |
| 10. Receiver Gain  | 58                     |
| 11. Relaxation Delay | 0.0000               |
| 12. Pulse Width    | 6.2500                 |
| 13. Presaturation Frequency |        |
| 14. Spectrometer Frequency | 470.15         |
| 15. Spectral Width | 1000000.0              |
| 16. Lowest Frequency | -.795013              |
| 17. Nucleus        | 19F                    |
| 18. Acquired Size  | 32768                  |
| 19. Spectral Size  | 65536                  |

![Chemical Structure Diagram]
| Parameter          | Value                                                                 |
|--------------------|-----------------------------------------------------------------------|
| 1 Origin           | Bruker BioSpin GmbH                                                   |
| 2 Owner            | user1d                                                                |
| 3 Instrument       | spect                                                                 |
| 4 Solvent          | CDCl3                                                                 |
| 5 Temperature      | 298.1 K                                                              |
| 6 Pulse Sequence   | zg30                                                                  |
| 7 Experiment       | 1D                                                                    |
| 8 Probe            | 2127784_0002, CP BBO 500S1 BBF H.D. 05 Z, (CP BBO 500S1 BBF-H.D. 05 Z) |
| 9 Number of Scans  | 16                                                                    |
| 10 Receiver Gain   | 76.2                                                                 |
| 11 Relaxation Delay| 30.0000                                                              |
| 12 Pulse Width     | 12.0000                                                              |
| 13 Presaturation Frequency |                                                                    |
| 14 Spectrometer Frequency | 500.35                                                              |
| 15 Spectral Width  | 10000.0                                                               |
| 16 Lowest Frequency| -1.922.3                                                             |
| 17 Nucleus         | 1H                                                                    |
| 18 Acquired Size   | 32768                                                                 |
| 19 Spectral Size   | 65536                                                                 |

**Diagram:**
- **Major Diastereomer**
- **DCM**
Parameter | Value
--- | ---
1 Origin | Bruker BioSpin GmbH
2 Owner | user1d
3 Instrument | spect
4 Solvent | CDCl3
5 Temperature | 298.1
6 Pulse Sequence | zgpg30
7 Experiment | 1D
8 Probe | 2127784_0002, CPBB0 500S1 BBF_H_D_052_
9 Number of Scans | 512
10 Receiver Gain | 190.5
11 Relaxation Delay | 2.0000
12 Pulse Width | 10.0000
13 Presaturation Frequency | 
14 Spectrometer Frequency | 125.83
15 Spectral Width | 31512.6
16 Lowest Frequency | -1901.5
17 Nucleus | 13C
18 Acquired Size | 32768
19 Spectral Size | 65536

![NMR Spectrum](image)

**major diastereomer**
| Parameter       | Value                                                                 |
|-----------------|-----------------------------------------------------------------------|
| Origin          | Bruker BioSpin GmbH                                                   |
| Owner           | user1d                                                                |
| Instrument      | spect                                                                 |
| Solvent         | CDCl3                                                                 |
| Temperature     | 298.1                                                                 |
| Pulse Sequence  | zgfhigqn 2                                                           |
| Experiment      | 1D                                                                    |
| Probe           | 2127784_0002, CP:BBO 500S1 BBF.H.D.05 Z                                    |
| Number of Scans | 64                                                                   |
| Receiver Gain   | 190.5                                                                |
| Relaxation Delay| 1.0000                                                               |
| Pulse Width     | 15.0000                                                              |
| Presaturation Frequency |                                                                |
| Spectrometer Frequency | 470.75                                                              |
| Spectral Width  | 113636.4                                                             |
| Lowest Frequency| -103898.1                                                            |
| Nucleus         | 19F                                                                  |
| Acquired Size   | 65536                                                                |
| Spectral Size   | 131072                                                               |

**major diastereomer**

![Chemical structure](attachment:image)
HMBC
crosspeak with H(doublet)  crosspeak with H(doublet)  crosspeak with H*

HMBC

C#

crosspeak with H(doublet)  crosspeak with H(doublet)  crosspeak with H*

f2 (ppm)

f1 (ppm)
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| Origin             | Bruker BioSpin GmbH                                                  |
| Owner              | user1d                                                               |
| Instrument         | spect                                                                |
| Solvent            | CDCl3                                                                |
| Temperature        | 298.1                                                                |
| Pulse Sequence     | zg30                                                                 |
| Experiment         | 1D                                                                   |
| Probe              | 2127784_0002_CP-BBO 500S1 BBF.H.D.05 Z,                              |
| Number of Scans    | 16                                                                   |
| Receiver Gain      | 107.0                                                                |
| Relaxation Delay   | 15.0000                                                             |
| Pulse Width        | 12.0000                                                             |
| Presaturation Frequency |                                                             |
| Spectrometer Frequency | 500.35                                                             |
| Spectral Width     | 10000.0                                                              |
| Lowest Frequency   | -1920.9                                                              |
| Nucleus            | 1H                                                                   |
| Acquired Size      | 32768                                                                |
| Spectral Size      | 65536                                                                |
| Parameter          | Value |
|--------------------|-------|
| 1 Origin           | Bruker BioSpin GmbH |
| 2 Owner            | user1d |
| 3 Instrument       | spect |
| 4 Solvent          | CDCl3 |
| 5 Temperature      | 298.1 |
| 6 Pulse Sequence   | zgpg30 |
| 7 Experiment       | 1D |
| 8 Probe            | 2127784-0002, CPBBO 500S1 BBF.H.D.05 Z1 |
| 9 Number of Scans  | 128 |
| 10 Receiver Gain   | 190.5 |
| 11 Relaxation Delay| 2.0000 |
| 12 Pulse Width     | 10.0000 |
| 13 Presaturation Frequency | |
| 14 Spectrometer Frequency | 125.83 |
| 15 Spectral Width  | 31512.6 |
| 16 Lowest Frequency| 1898.1 |
| 17 Nucleus         | 13C |
| 18 Acquired Size   | 32768 |
| 19 Spectral Size   | 65536 |
Parameter | Value
---|---
1 Origin | Bruker BioSpin GmbH
2 Owner | user1d
3 Instrument | spect
4 Solvent | CD2Cl2
5 Temperature | 298.2
6 Pulse Sequence | zg30
7 Experiment | 1D
8 Probe | 2127784_0002, CP:BBO 500S1 BBF_H.D.05 Z,
9 Number of Scans | 16
10 Receiver Gain | 137.4
11 Relaxation Delay | 15.0000
12 Pulse Width | 12.0000
13 Presaturation Frequency | 
14 Spectrometer Frequency | 500.35
15 Spectral Width | 10000.0
16 Lowest Frequency | 1929.4
17 Nucleus | 1H
18 Acquired Size | 32768
19 Spectral Size | 65536
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| Origin             | Bruker BioSpin GmbH                                                  |
| Owner              | user1d                                                               |
| Instrument         | spect                                                                |
| Solvent            | CD2Cl2                                                              |
| Temperature        | 298.2                                                                |
| Pulse Sequence     | zgpg30                                                               |
| Experiment         | 1D                                                                   |
| Probe              | 2127784_0002, CP-BBO 500S1 BBF-H.D. 05 Z,                            |
| Number of Scans    | 2048                                                                |
| Receiver Gain      | 190.5                                                                |
| Relaxation Delay   | 2.0000                                                              |
| Pulse Width        | 10.0000                                                              |
| Presaturation Frequency |                                                                    |
| Spectrometer Frequency | 125.83                                                             |
| Spectral Width     | 31512.6                                                              |
| Lowest Frequency   | 1842.1                                                               |
| Nucleus            | 13C                                                                  |
| Acquired Size      | 32768                                                                |
| Spectral Size      | 65536                                                                |

**Diagram:**

- Chemical structure and spectrum data.
| Parameter            | Value               |
|----------------------|---------------------|
| 1 Origin             | Varian              |
| 2 Owner              |                     |
| 3 Instrument         | inova               |
| 4 Solvent            | CDCl3               |
| 5 Temperature        | 20.0                |
| 6 Pulse Sequence     | s2pul               |
| 7 Experiment         | 1D                  |
| 8 Probe              | QUAD                |
| 9 Number of Scans    | 8                   |
| 10 Receiver Gain     | 52                  |
| 11 Relaxation Delay  | 15.0000             |
| 12 Pulse Width       | 6.5000              |
| 13 P Presaturation Frequency |        |
| 14 Spectrometer Frequency | 499.69             |
| 15 Spectral Width    | 7024.9              |
| 16 Lowest Frequency  | -1021.4             |
| 17 Nucleus           | 1H                  |
| 18 Acquired Size     | 32768               |
| 19 Spectral Size     | 65536               |

![Chemical Structure](image)
| Parameter         | Value          |
|-------------------|----------------|
| Origin            | Varian         |
| Owner             |                |
| Instrument        | inova          |
| Solvent           | CDCl3          |
| Temperature       | 20.0           |
| Pulse Sequence    | s2pul          |
| Experiment        | 1D             |
| Probe             | QUAD           |
| Number of Scans   | 512            |
| Receiver Gain     | 60             |
| Relaxation Delay  | 2.0000         |
| Pulse Width       | 6.0000         |
| Presaturation Frequency |       |
| Spectrometer Frequency | 125.66 |
| Spectral Width    | 30165.9        |
| Lowest Frequency  | -1267.7        |
| Nucleus           | 13C            |
| Acquired Size     | 32768          |
| Spectral Size     | 65536          |

Below is a diagram of the NMR spectrum with DCM indicated at the peak. The x-axis represents the frequency in ppm, ranging from 220 to 2200, and the y-axis represents the intensity from 0 to -200.
| Parameter               | Value                                                                 |
|-------------------------|-----------------------------------------------------------------------|
| 1 Origin                | Bruker BioSpin GmbH                                                   |
| 2 Owner                 | user1d                                                                |
| 3 Instrument            | spect                                                                 |
| 4 Solvent               | CDCl₃                                                                 |
| 5 Temperature           | 298.0                                                                 |
| 6 Pulse Sequence        | zg30                                                                  |
| 7 Experiment            | 1D                                                                    |
| 8 Probe                 | Z127784_0002, CPBD 500S1 BBF. H.D. 05 Z                                |
| 9 Number of Scans       | 16                                                                    |
| 10 Receiver Gain        | 86.0                                                                  |
| 11 Relaxation Delay     | 15.0000                                                              |
| 12 Pulse Width          | 12.0000                                                              |
| 13 Presaturation Frequency |                                                                      |
| 14 Spectrometer Frequency | 500.35                                                               |
| 15 Spectral Width       | 10000.0                                                               |
| 16 Lowest Frequency     | 1935.4                                                                |
| 17 Nucleus              | 1H                                                                   |
| 18 Acquired Size        | 32768                                                                 |
| 19 Spectral Size        | 65536                                                                 |

The diagram shows a ¹H NMR spectrum with peaks spaced across the spectrum, indicating the chemical shifts and intensities of various protons in the compound.
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| 1 Origin           | Bruker BioSpin GmbH                                                  |
| 2 Owner            | user1d                                                               |
| 3 Instrument       | spect                                                                |
| 4 Solvent          | CDCl₃                                                                |
| 5 Temperature      | 298.0                                                               |
| 6 Pulse Sequence   | zgpg30                                                               |
| 7 Experiment       | 1D                                                                   |
| 8 Probe            | Z127784_0002, CP/BBO 500S1 BBF. H.D. 05 Z₁                             |
| 9 Number of Scans  | 256                                                                  |
| 10 Receiver Gain   | 190.5                                                                |
| 11 Relaxation Delay| 2.0000                                                              |
| 12 Pulse Width     | 10.0000                                                              |
| 13 Presaturation Frequency |                                                                |
| 14 Spectrometer Frequency | 125.83                                                              |
| 15 Spectral Width  | 29761.9                                                              |
| 16 Lowest Frequency| 2266.9                                                               |
| 17 Nucleus         | 13C                                                                  |
| 18 Acquired Size   | 32768                                                                |
| 19 Spectral Size   | 65536                                                                |
Parameter | Value
---|---
1 Origin | Varian
2 Owner | 
3 Instrument | vnmrs
4 Solvent | cd2cl2
5 Temperature | 23.0
6 Pulse Sequence | s2pul
7 Experiment | 1D
8 Probe | triax
9 Number of Scans | 16
10 Receiver Gain | 32
11 Relaxation Delay | 10.0000
12 Pulse Width | 4.2500
13 Presaturation Frequency | 
14 Spectrometer Frequency | 749.38
15 Spectral Width | 12019.2
16 Lowest Frequency | 1517.8
17 Nucleus | 1H
18 Acquired Size | 32768
19 Spectral Size | 131072
| Parameter         | Value                     |
|-------------------|---------------------------|
| 1 Origin          | Varian                    |
| 2 Owner           |                           |
| 3 Instrument      | inova                     |
| 4 Solvent         | CD2Cl2                    |
| 5 Temperature     | 20.0                      |
| 6 Pulse Sequence  | s2pul                     |
| 7 Experiment      | 1D                        |
| 8 Probe           | QUAD                      |
| 9 Number of Scans | 2945                      |
| 10 Receiver Gain  | 60                        |
| 11 Relaxation Delay | 1.0000                   |
| 12 Pulse Width    | 6.0000                    |
| 13 Presaturation Frequency |           |
| 14 Spectrometer Frequency | 125.66                   |
| 15 Spectral Width | 30165.9                   |
| 16 Lowest Frequency | -1176.5                  |
| 17 Nucleus        | 13C                       |
| 18 Acquired Size  | 32768                     |
| 19 Spectral Size  | 65536                     |
| Parameter       | Value         |
|-----------------|---------------|
| Origin          | Varian        |
| Owner           |               |
| Instrument      | vnmrs         |
| Solvent         | cd2cl2        |
| Temperature     | 23.0          |
| Pulse Sequence  | s2pul         |
| Experiment      | 1D            |
| Probe           | triax         |
| Number of Scans | 16            |
| Receiver Gain   | 32            |
| Relaxation Delay| 10.0000       |
| Pulse Width     | 4.2500        |
| Presaturation Frequency |       |
| Spectrometer Frequency | 749.38      |
| Spectral Width  | 12019.2       |
| Lowest Frequency| -1517.1       |
| Nucleus         | 1H            |
| Acquired Size   | 32768         |
| Spectral Size   | 131072        |
| Parameter         | Value                        |
|-------------------|------------------------------|
| 1 Origin          | Varian                       |
| 2 Owner           |                              |
| 3 Instrument      | inova                        |
| 4 Solvent         | CD2Cl2                       |
| 5 Temperature     | 20.0                         |
| 6 Pulse Sequence  | s2pul                        |
| 7 Experiment      | 1D                           |
| 8 Probe           | QUAD                         |
| 9 Number of Scans | 2887                         |
| 10 Receiver Gain  | 60                           |
| 11 Relaxation Delay | 1.0000                      |
| 12 Pulse Width    | 6.0000                       |
| 13 Presaturation Frequency |                |
| 14 Spectrometer Frequency | 125.66                      |
| 15 Spectral Width | 30165.9                      |
| 16 Lowest Frequency | 1217.8                     |
| 17 Nucleus        | 13C                          |
| 18 Acquired Size  | 32768                        |
| 19 Spectral Size  | 65536                        |
| Parameter          | Value     |
|--------------------|-----------|
| 1 Origin           | Varian    |
| 2 Owner            |           |
| 3 Instrument       | inova     |
| 4 Solvent          | CD2Cl2    |
| 5 Temperature      | 20.0      |
| 6 Pulse Sequence   | s2pul     |
| 7 Experiment       | 1D        |
| 8 Probe            | QUAD      |
| 9 Number of Scans  | 4         |
| 10 Receiver Gain   | 48        |
| 11 Relaxation Delay| 10.0000   |
| 12 Pulse Width     | 6.5000    |
| 13 Presaturation Frequency |         |
| 14 Spectrometer Frequency | 499.69   |
| 15 Spectral Width  | 7024.9    |
| 16 Lowest Frequency| 1011.9    |
| 17 Nucleus         | 1H        |
| 18 Acquired Size   | 32768     |
| 19 Spectral Size   | 65536     |
Parameter | Value
--- | ---
1 | Origin: Varian
2 | Owner
3 | Instrument: vnmrs
4 | Solvent: cd2cl2
5 | Temperature: 23.0°C
6 | Pulse Sequence: s2pul
7 | Experiment: 1D
8 | Probe: triax
9 | Number of Scans: 16
10 | Receiver Gain: 28
11 | Relaxation Delay: 10.0000 s
12 | Pulse Width: 8.0000 s
13 | Presaturation Frequency
14 | Spectrometer Frequency: 749.38 MHz
15 | Spectral Width: 6377.6 Hz
16 | Lowest Frequency: -8.4 ppm
17 | Nucleus: 1H
18 | Acquired Size: 17387
19 | Spectral Size: 65536
| Parameter       | Value                       |
|-----------------|-----------------------------|
| 1 Origin        | Varian                      |
| 2 Owner         |                             |
| 3 Instrument    | inova                       |
| 4 Solvent       | CD2Cl2                      |
| 5 Temperature   | 20.0                        |
| 6 Pulse Sequence| s2pul                       |
| 7 Experiment    | 1D                          |
| 8 Probe         | QUAD                        |
| 9 Number of Scans| 4096                       |
| 10 Receiver Gain| 60                          |
| 11 Relaxation Delay| 1.0000                   |
| 12 Pulse Width  | 6.0000                      |
| 13 Presaturation Frequency|                |
| 14 Spectrometer Frequency| 125.66                |
| 15 Spectral Width| 30165.9                    |
| 16 Lowest Frequency| 1217.9                     |
| 17 Nucleus      | 13C                         |
| 18 Acquired Size| 32768                       |
| 19 Spectral Size| 65536                       |
| Parameter         | Value     |
|-------------------|-----------|
| Origin            | Varian    |
| Owner             |           |
| Instrument        | vnmrs     |
| Solvent           | cd2cl2    |
| Temperature       | 23.0      |
| Pulse Sequence    | s2pul     |
| Experiment        | 1D        |
| Probe             | triax     |
| Number of Scans   | 16        |
| Receiver Gain     | 36        |
| Relaxation Delay  | 25.0000   |
| Pulse Width       | 4.2500    |
| Spectrometer Frequency | 749.38  |
| Spectral Width    | 12019.2   |
| Lowest Frequency  | 1517.8    |
| Nucleus           | 1H        |
| Acquired Size     | 32768     |
| Spectral Size     | 131072    |
| Parameter         | Value         |
|-------------------|---------------|
| 1 Origin          | Varian        |
| 2 Owner           |               |
| 3 Instrument      | vnmrs         |
| 4 Solvent         | cd2cl2        |
| 5 Temperature     | 23.0          |
| 6 Pulse Sequence  | s2pul         |
| 7 Experiment      | 1D            |
| 8 Probe           | triax         |
| 9 Number of Scans | 1000          |
| 10 Receiver Gain  | 30            |
| 11 Relaxation Delay | 1.0000    |
| 12 Pulse Width    | 7.8000        |
| 13 Presaturation Frequency |         |
| 14 Spectrometer Frequency | 188.45   |
| 15 Spectral Width | 46296.3       |
| 16 Lowest Frequency | 2308.1      |
| 17 Nucleus        | 13C           |
| 18 Acquired Size  | 65536         |
| 19 Spectral Size  | 131072        |
1DNOESY
Parameter | Value
--- | ---
1 Origin | Varian
2 Owner |
3 Instrument | inova
4 Solvent | CDCl3
5 Temperature | 20.0
6 Pulse Sequence | s2pul
7 Experiment | 1D
8 Probe | QUAD
9 Number of Scans | 16
10 Receiver Gain | 54
11 Relaxation Delay | 15.0000
12 Pulse Width | 6.5000
13 Presaturation Frequency |
14 Spectrometer Frequency | 499.69
15 Spectral Width | 7024.9
16 Lowest Frequency | 1011.9
17 Nucleus | 1H
18 Acquired Size | 32768
19 Spectral Size | 65536

Heteroatoms identified as DCM and EtOAc. Spectral peaks are labelled with their relative positions in ppm.
| Parameter       | Value                          |
|-----------------|-------------------------------|
| Origin          | Varian                        |
| Owner           |                               |
| Instrument      | vnmrs                         |
| Solvent         | cd2cl2                         |
| Temperature     | 23.0                          |
| Pulse Sequence  | s2pul                         |
| Experiment      | 1D                            |
| Probe           | triax                         |
| Number of Scans | 16                            |
| Receiver Gain   | 26                            |
| Relaxation Delay| 10.0000                       |
| Pulse Width     | 8.0000                        |
| Presaturation Frequency |           |
| Spectrometer Frequency | 749.38    |
| Spectral Width  | 5980.9                        |
| Lowest Frequency| 3.3                           |
| Nucleus         | 1H                            |
| Acquired Size   | 16384                         |
| Spectral Size   | 65536                         |

The figure shows a spectral analysis with various peaks at different ppm values. The chemical structure at the top right of the page depicts the compound being analyzed.
| Parameter       | Value |
|-----------------|-------|
| Origin          | Varian|
| Owner           |       |
| Instrument      | vnmrs |
| Solvent         | cd2cl2|
| Temperature     | 23.0  |
| Pulse Sequence  | s2pul |
| Experiment      | 1D    |
| Probe           | triax |
| Number of Scans | 2048  |
| Receiver Gain   | 60    |
| Relaxation Delay| 1.0000|
| Pulse Width     | 7.8000|
| Presaturation Frequency |       |
| Spectrometer Frequency | 188.45|
| Spectral Width  | 40322.6|
| Lowest Frequency| 697.4 |
| Nucleus         | 13C   |
| Acquired Size   | 65536 |
| Spectral Size   | 131072|
gDQCOSY
1D NOESY
| Parameter          | Value          |
|-------------------|----------------|
| Origin            | Varian         |
| Owner             |                |
| Instrument        | inova          |
| Solvent           | CD2Cl2         |
| Temperature       | 20.0           |
| Pulse Sequence    | s2pul          |
| Experiment        | 1D             |
| Probe             | 5mmsw          |
| Number of Scans   | 8              |
| Receiver Gain     | 44             |
| Relaxation Delay  | 15.0000        |
| Pulse Width       | 5.5000         |
| Presaturation     |                |
| Spectrometer      | 499.43         |
| Spectral Width    | 80000.0        |
| Lowest Frequency  | 1502.7         |
| Nucleus           | 1H             |
| Acquired Size     | 32768          |
| Spectral Size     | 65536          |

The spectrum shows the chemical shifts in ppm with various peaks indicating the different chemical environments of the protons in the molecule.
| Parameter              | Value                  |
|------------------------|------------------------|
| 1 Origin               | Varian                 |
| 2 Owner                |                        |
| 3 Instrument           | inova                  |
| 4 Solvent              | CD2Cl2                 |
| 5 Temperature          | 20.0                   |
| 6 Pulse Sequence       | s2pul                  |
| 7 Experiment           | 1D                     |
| 8 Probe                | QUAD                   |
| 9 Number of Scans      | 1024                   |
| 10 Receiver Gain       | 60                     |
| 11 Relaxation Delay    | 1.0000                 |
| 12 Pulse Width         | 6.0000                 |
| 13 Presaturation       |                        |
| 14 Spectrometer Frequency| 125.66                |
| 15 Spectral Width      | 30165.9                |
| 16 Lowest Frequency    | 1216.9                 |
| 17 Nucleus             | 13C                    |
| 18 Acquired Size       | 32768                  |
| 19 Spectral Size       | 65536                  |
HMBC

3° benzylic alcohol carbon cross peak