Supplementary Information

Manganese-catalyzed benzylic C(sp³)—H amination for late-stage functionalization

Joseph R. Clark, Kaibo Feng,† Anasheh Sookezian† and M. Christina White*

Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois 61801, United States

†These authors contributed equally. *e-mail: mcwhite7@illinois.edu

I. General Information .................................................................2
II. Catalyst and iminoiodinane synthesis ........................................3
III. General amination procedures and optimization data for Table 1 ...7
IV. Experimental procedures and compound characterization for Figure 2 ...15
V. Experimental procedures and compound characterization for Figure 3 ...41
VI. Experimental procedures and compound characterization for Figure 4 ...56
VII. Preparation and characterization of newly reported starting materials ...66
VIII. HPLC methods for the determination of product selectivity .............94
IX. Experimental kinetic data and methods for Figure 5 .........................105
X. Site-selectivity probe for benzylic sites with different bond dissociation energies ...117
XI. X-ray crystal structure characterization data ..................................121
XII. References ..............................................................................129
XIII. Spectra .................................................................................130
I. General Information

The following commercially obtained reagents were used as received: Mn(II)Cl$_2$ (99.995%-Mn, Strem), tetrachlorophthalonitrile ($\geq$96%, TCI), PhI(OAc)$_2$ (Sigma-Aldrich or Oakwood Chemicals), Mn(OAc)$_2$ (Sigma-Aldrich) and powdered 3Å and 5Å molecular sieves (Sigma-Aldrich). 2,2,2-trichloroethyl sulfamate was synthesized according to a previously reported procedure and is also commercially available (Sigma-Aldrich). Anhydrous solvents were purified by passage through a bed of activated alumina immediately prior to use (Glass Countour, Laguna Beach, California). Chloroform-$d$ was stored over 3Å molecular sieves. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm) and visualized with UV and Cerium-ammonium-molybdate and potassium permanganate stains. Flash chromatography was performed using American International ZEOprep 60 ECO silica gel (230-400 mesh).

$^1$H-NMR spectra were recorded on a Varian Unity-400 (400 MHz), Varian VXR 500 (500 MHz), Varian Inova-500 (500 MHz), Varian Unity-500 (500 MHz) or Carver-Bruker 500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl$_3$ at 7.26 ppm). Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sxt = sextet, hept = septet, oct = octet, non = nonet, m = multiplet, br = broad, app = apparent; coupling constant(s) in Hz; integration. Proton-decoupled $^{13}$C-NMR spectra were recorded on a Varian Unity-400 (400 MHz), Varian Unity-500 (125 MHz) or Carver-Bruker 500 (125MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl$_3$ at 77.16 ppm). $^{19}$F spectra were recorded on a Varian VXR 500 (470 MHz), Varian Unity-500 (470 MHz) or Carver-Bruker 500 (470 MHz) and are reported in ppm using FCCl$_3$ (0 ppm) as an external standard. Labeled solvent impurities were calculated out when reporting isolated yields. High-resolution mass spectra were obtained at the University of Illinois Mass Spectrometry Laboratory. Electrospray ionization (ESI) spectra were performed on a Waters Q-Tof µLtima spectrometer, and electron ionization (EI) and field desorption (FD) spectra were performed on a Micromass 70-VSE spectrometer. X-ray crystallographic analysis was carried out by Dr. Toby Woods and Dr. Danielle Gray at the University of Illinois George L. Clark X-Ray Facility.
II. Catalyst and iminoiodinane synthesis

Manganese (III) Perchloro-Phthalocyanine Chloride [3]. In a 200 mL flame-dried round bottom flask under argon containing a Teflon stir bar and equipped with a water cooled condenser was added consecutively tetrachlorophthalonitrile (3.99 g, 15.00 mmol, 4 equiv), anhydrous Manganese (II) Chloride (472 mg, 3.75 mmol, 1 equiv), freshly distilled 1-Hexanol (45 mL, 0.33M) and 1,8-diazabicyclo[5.4.0]undec-7-ene (2.243 mL, 15.00 mmol, 4 equiv). The flask was placed in a 160 °C silicon oil bath and stirred for 8 h. Upon reaction completion, the flask was removed from the oil bath, allowed to cool to room temperature and cooled for 10 minutes in an ice bath. The contents were poured directly onto a glass fritted Buchner funnel and the solid washed consecutively and three times each with 5% HCl (aq) (3 x 20 mL), water (3 x 20 mL), and ethanol (3 x 40 mL). During the washes, the solid was broken up with a spatula to give a powdered turquoise solid after the last ethanol wash. The solid was collected and placed under vacuum at room temperature for 24 hours to remove any residual solvent to give a turquoise powdery solid (4.12 g, 95% yield) and transferred into the glove box for permanent storage. Manganese (II) perchlorophthalocyanine has been previously reported but there are no reports of the manganese (III) perchlorophthalocyanine chloride catalyst.

UV-Vis (1-Chloronaphthalene, $\lambda_{\text{max}}$ = nm, $\varepsilon$ = M$^{-1}$cm$^{-1}$)

770 ($\varepsilon$ = 84968), 691 ($\varepsilon$ = 20629), 525 ($\varepsilon$ = 10675), 400 ($\varepsilon$ = 23658), 356 ($\varepsilon$ = 25245)

IR (ATR, cm$^{-1}$)

3124, 2927, 2856, 1644, 1564, 1467, 1427, 1385, 1310, 1272, 1203, 1152, 1130, 1095, 1039, 954, 931, 763, 746, 734, 598, 572, 497

MS (MALDI) (DHB Matrix)

m/z calculated for C$_{32}$Cl$_7$MnN$_8$ [M-Cl]$^+$: 1110.464, found 1110.507.

**UV-Vis Studies:** In a 25 mL volumetric flask, 2.0 mg (0.0017 mmol) of manganese (III) perchlorophthalocyanine chloride was taken up in 1-chloronaphthalene to make a 25 mL solution (69
100 µL of this solution was diluted to 1 mL (6.9 µM) in a 1 mL volumetric flask. A UV-Vis was taken from 1100-350 nm in a quartz cuvette (path length = 1 cm).

**Figure 1.** UV-Vis spectrum for [Mn$^{III}$(ClPc)]Cl.

Synthesis of the perchlorophthalocyanine ligand then insertion of the metal:

The ligand was synthesized using a known literature procedure and characterized. The manganese metal was inserted into the ligand and tested in the intermolecular benzylic C—H amination protocol to validate the identity of the catalyst made from the phthalonitrile.
1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecachlorophthalocyanine [S1]. Synthesized using a previously reported procedure. Accordingly, in a 50 mL sealed tube vessel, tetrachlorophthalic anhydride (1.56 g, 5.44 mmol, 1 equiv), hexamethyldisilazane (5.74 mL, 27.2 mmol, 5 equiv), p-toluenesulfonic acid·H₂O (103.5 mg, 0.544 mmol, 0.1 equiv), and N,N-dimethylformamide (0.42 mL, 5.44 mmol, 1 equiv) were added and the vessel sealed, heated to 150 ºC and stirred overnight behind a blast shield. The reaction was brought to room temperature and then opened. The green solid was broken up and washed with MeOH (50 mL). The solid was then dissolved in concentrated H₂SO₄ (40 mL), stirred for 5 minutes then poured into a 250 mL Erlenmeyer flask containing ice water (about 120 mL ice water volume). The precipitate that crashes out of solution was collected and further washed with H₂O then MeOH. The green solid was transferred to a Soxhlet thimble and extracted using MeOH (150 mL) for 2 days. The solid remaining in the thimble (250 mg, 0.23 mmol, 17% yield) was collected and used in the next step.

^{13}C NMR (126 MHz, DMF)

δ 165.65, 139.56, 130.57, 129.50

IR (ATR, cm⁻¹)

3460, 3385, 3313, 2920, 1741, 1706, 1649, 1601, 1564, 1430, 1380, 1367, 1356, 1339, 1315, 1275, 1189, 1131, 1085, 1043, 921, 862, 747, 655.

MS (MALDI) (No Matrix)

m/z calculated for C₃₂H₃₁Cl₁₆N₈ [M+H]^+ : 1058.550, found 1058.304.

Manganese (III) Perchloro-Phthalocyanine Chloride [3]. Synthesized from S1 using a previously reported method. In a new, flame-dried 25 mL round bottom flask containing a new Teflon stir bar (free of trace metal impurities) under a N₂ atmosphere were added 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecachlorophthalocyanine S1 (110 mg, 0.103 mmol, 1 equiv), Mn(OAc)₂ (17.8 mg, 0.103 mmol, 1
equiv) and N,N-dimethylformamide (6 mL). The reaction was stirred for 12 h at 60 °C. Upon reaction completion, H₂O (10 mL) was added to crash out the catalyst and the catalyst was filtered then washed subsequently with 1M HCl, brine, H₂O then MeOH. The dark green solid was transferred to a Soxhlet thimble and extracted using Soxhlet extraction for 2 days using MeOH (40 mL). The remaining solid in the thimble was collected (50 mg, 0.43 mmol, 40% yield) and tested for intermolecular benzylic C—H amination reactivity using 3-phenylpropyl acetate using the exact conditions in Table 1 entry 9 to yield 3-phenyl-3-(((2,2,2-trichloroethoxy)sulfonyl)amino)propyl acetate 2 (52 mg, 0.129 mmol, 64% yield).

2,2,2-trichloroethyl (phenyl-λ³-iodanylidene)sulfamate [S2]. In a flame-dried 100 mL round bottom flask under nitrogen was added 2,2,2-trichloroethyl sulfamate (2.0 g, 8.75 mmol, 1 equiv), (diacetoxyiodo)benzene (2.82 g, 8.75 mmol, 1 equiv) and anhydrous methanol (35 mL, 0.25M). The contents were stirred to dissolve most of the (diacetoxyiodo)benzene and then cooled to 0 °C in an ice-water bath. Once cooled, potassium hydroxide (1.23 g, 21.88 mmol, 2.5 equiv) was added as pellets. The reaction was stirred for 30 minutes at 0 °C and then 7.5 hours at room temperature. Upon reaction completion, the contents were transferred to a separatory funnel containing 100 mL of water. Dichloromethane (100 mL) was added and the contents vigorously shaken to remove all excess potassium hydroxide (very important). The layers were separated and the aqueous layer was further extracted with dichloromethane (2 x 100 mL). The combined organic extracts were washed with water (1 x 100 mL), shaking vigorously to remove any trace potassium hydroxide, and transferred directly to a 500 mL round bottom flask and the solvent removed by rotary evaporation at room temperature (do not exceed 30 °C as the iminoiodinane will not perform optimally) to give a slightly yellow solid. The contents were transferred to a 100 mL round bottom flask using 20 mL of methanol and the solvent was removed by rotary evaporation leaving a slightly yellow solid. The contents were azeotroped once with 20 mL of benzene and placed under vacuum for an additional 20 minutes to give a slightly yellow solid. The solid was triturated with diethyl ether (5 x 10 mL) while breaking up any solid chunks into a powdery solid. After vacuum drying for one hour an off-white powdery solid was obtained (1.78 g, 47% yield) and used as is. The contents were capped with a polyethylene cap and stored in the freezer. The iminoiodinane is stable for at least 3 months in the freezer. This procedure was adapted from a previously reported procedure but deviates significantly in several steps and the above described procedure should be followed for best results.
**\(^1\)H NMR (499 MHz, Methanol-\(d_4\))**

\[ \delta 8.22 - 8.11 \text{ (d, } J = 7.4 \text{ Hz, } 0.6H) , 8.10 - 7.96 \text{ (m, } 1.4H) , 7.68 \text{ (t, } J = 7.5 \text{ Hz, } 0.3H) , 7.64 - 7.46 \text{ (m, } 2.7H) , 4.68 \text{ (s, } 1.4H) , 4.29 \text{ (s, } 0.6H) . \]

**\(^{13}\)C NMR (126 MHz, Methanol-\(d_4\))**

\[ \delta 136.3, 133.4, 133.3, 132.3, 132.2, 132.0, 122.6, 95.3, 79.0, 78.9. \]

**HRMS: (ESI-TOF MS ES-)**

\[ m/z \text{ calculated for C}_8\text{H}_7\text{Cl}_4\text{NI}_3\text{O}_3 \text{ [M+Cl]}^-: 463.7945 , \text{ found 463.7939}. \]

### III. General amination procedures and optimization data for Table 1

**Table 1.** Optimization of the base metal catalyzed C—H amination.

| Entry | Sulfamate Ester | Oxidant | Catalyst | Temp | % yield (% rsms) |
|-------|----------------|---------|----------|------|-----------------|
| 1     | NH\(_2\)Tces   | Phl(OPiv)\(_2\) | [Fe\(^{III}\)(Pc)]SbF\(_6\) | 23 °C | 0% (100%)       |
| 2     | NH\(_2\)Tces   | Phl(OPiv)\(_2\) | [Mn\(^{III}\)(Pc)]SbF\(_6\) | 23 °C | trace (96%)     |
| 3†    | NH\(_2\)Tces   | Phl(OPiv)\(_2\) | [Mn\(^{III}\)(Pc)]SbF\(_6\) | 23 °C | trace (95%)     |
| 4     | NH\(_2\)Tces   | Phl(OPiv)\(_2\) | [Mn\(^{III}\)(BuPc)]SbF\(_6\) | 23 °C | trace (94%)     |
| 5‡    | NH\(_2\)Tces   | Phl(OPiv)\(_2\) | Co\(^{II}\)(TPP) | 23 °C | 0% (99%)        |
| 6     | Phl=NTces     | Phl(OPiv)\(_2\) | [Fe\(^{III}\)(Pc)]SbF\(_6\) | 23 °C | 9% (85%)        |
| 7     | Phl=NTces     | Phl(OPiv)\(_2\) | [Mn\(^{III}\)(BuPc)]SbF\(_6\) | 23 °C | 12% (88%)       |
| 8     | Phl=NTces     | Phl(OPiv)\(_2\) | Co\(^{II}\)(TPP) | 23 °C | 17% (83%)       |
| 9     | Phl=NTces     | Phl(OPiv)\(_2\) | [Mn\(^{III}\)(ClPc)]SbF\(_6\) | 23 °C | 53% (41%)       |
| 10    | Phl=NTces     | Phl(OPiv)\(_2\) | [Mn\(^{III}\)(ClPc)]SbF\(_6\) | 40 °C | 68% (32%)       |
| 11‡   | Phl=NTces     | Phl(OPiv)\(_2\) | [Mn\(^{III}\)(ClPc)]SbF\(_6\) | 40 °C | 47% (49%)       |
| 12‡   | Phl=NTces     | Phl(OPiv)\(_2\) | [Mn\(^{III}\)(ClPc)]SbF\(_6\) | 40 °C | 42% (58%)       |
| 13‡   | Phl=NTces     | Phl(OPiv)\(_2\) | [Mn\(^{III}\)(ClPc)]SbF\(_6\) | 40 °C | 60% (24%)       |
| 14    | Phl=NTces     | Phl(OPiv)\(_2\) | [Mn\(^{III}\)(ClPc)]Cl | 40 °C | 50% (43%)       |
| 15    | Phl=NTces     | Phl(OPiv)\(_2\) | AgSbF\(_6\) | 40 °C | 0% (100%)       |
| 16    | Phl=NTces     | Phl(OPiv)\(_2\) | Co\(^{II}\)(TPP) | 40 °C | trace (95%)     |
| 17    | NH\(_2\)Tces   | Phl(OPiv)\(_2\) | [Mn\(^{III}\)(ClPc)]SbF\(_6\) | 40 °C | trace (87%)     |
**General procedure A for reaction optimization studies (in situ formation of iminoiodinane, entries 1-4, 15)**

In a 10 mL round bottom flask was added 5Å powdered molecular sieves (40 mg) and a Teflon stir bar. The flask was sealed with a Suba Seal rubber septum, placed under vacuum, flame-dried for 45 seconds to activate the molecular sieves, cooled under argon and wrapped in foil to exclude light. Once cooled, solvent (0.40 mL, 0.5 M to substrate), commercial 3-phenylpropyl acetate 1 (35.6 mg, 0.20 mmol, 1 equiv), and 2,2,2-trichloroethyl sulfamate (54.8 mg, 0.24 mmol, 1.2 equiv) were added and stirred for 10 minutes. Catalyst (0.020 mmol, 0.1 equiv) and silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) were weighed in a foil wrapped 1 dram vial in the glove box and sealed with a Teflon cap. The vial was removed from the glove box and the contents added directly to the round bottom flask while maintaining an argon atmosphere. The Suba Seal rubber septum was replaced by a polyethylene cap, sealed tightly and stirred for 8 hours at room temperature. Upon reaction completion, the reaction was filtered through a 1-inch silica gel plug using diethyl ether as the eluent. The solvent was evaporated and a crude $^1$H NMR was obtained using mesitylene (9.3 µL, 0.067 mmol, 0.33 equiv) as an internal standard to obtain the $^1$H NMR yield.

**General procedure B for reaction optimization studies (pre-formed iminoiodinane, entries 5-14)**

In a 10 mL round bottom flask was added 5Å powdered molecular sieves (40 mg) and a Teflon stir bar. The flask was sealed with a Suba Seal rubber septum, placed under vacuum, flame-dried for 45 seconds to activate the molecular sieves, cooled under a purged and completely air-free argon balloon and wrapped in foil to exclude light. Once cooled, solvent (0.40 mL, 0.5 M to substrate) and 3-phenylpropyl acetate 1 (35.6 mg, 0.20 mmol, 1 equiv) were added and stirred for 10 minutes. Catalyst (0.020 mmol, 0.1 equiv) and silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) were weighed in a foil wrapped 1 dram vial in the glove box and sealed with a Teflon cap. The vial was removed from the glove box and the contents added directly to the round bottom flask and stirred for 10 minutes while maintaining an argon atmosphere. In a 1 dram vial open to air, 2,2,2-trichloroethyl (phenyl-λ³-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) was weighed and added directly to the round bottom flask while maintaining an argon atmosphere. The Suba Seal rubber septum was replaced by a polyethylene cap, sealed tightly and stirred for 8 hours at the given temperature. Upon reaction completion, the reaction was filtered through a 1 inch silica gel plug using diethyl ether as the eluent. The solvent was evaporated and a crude $^1$H NMR in CDCl$_3$ was obtained using mesitylene (9.3 µL, 0.067 mmol, 0.33 equiv) as an internal standard to obtain the $^1$H NMR yield. The crude material was then concentrated and dry-loaded directly.
onto a silica gel column. Flash chromatography using gradient elution (500 mL of 100% dichloromethane (removes excess NH$_2$Tces) then 300 mL of 2% diethyl ether in 98% dichloromethane followed by 300 mL of 5% diethyl ether in 95% dichloromethane) gave the pure product as a white solid with slight discoloration.

**Entry 1.** According to the general procedure A for optimization studies, 5Å powdered molecular sieves (40 mg), 3-phenylpropyl acetate (35.6 mg, 0.20 mmol, 1 equiv), C$_6$H$_6$ (0.40 mL, 0.5M), [FePc]Cl (12.1 mg, 0.020 mmol, 0.1 equiv), AgSbF$_6$ (6.9 mg, 0.020 mmol, 0.1 equiv), NH$_2$Tces (54.8 mg, 0.24 mmol, 1.2 equiv) and PhI(OPiv)$_2$ (162.4 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8 h at room temperature.

**Run 1** (0% yield by $^1$H NMR yield, 100% rsm by $^1$H NMR)
**Run 2** (0% yield by $^1$H NMR yield, 100% rsm by $^1$H NMR)
**Run 3** (0% yield by $^1$H NMR yield, 100% rsm by $^1$H NMR)

**Entry 2.** According to the general procedure A for optimization studies, 5Å powdered molecular sieves (40 mg), 3-phenylpropyl acetate (35.6 mg, 0.20 mmol, 1 equiv), C$_6$H$_6$ (0.40 mL, 0.5M), [MnPc]Cl (12.1 mg, 0.020 mmol, 0.1 equiv), AgSbF$_6$ (6.9 mg, 0.020 mmol, 0.1 equiv), NH$_2$Tces (54.8 mg, 0.24 mmol, 1.2 equiv) and PhI(OPiv)$_2$ (162.4 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8 h at room temperature.

**Run 1** (trace yield by $^1$H NMR, 95% rsm by $^1$H NMR)
**Run 2** (trace yield by $^1$H NMR, 97% rsm by $^1$H NMR)
**Run 3** (trace yield by $^1$H NMR, 95% rsm by $^1$H NMR)

**Entry 3.** According to the general procedure A for optimization studies, 5Å powdered molecular sieves (40 mg) magnesium oxide (17.7 mg, 0.44 mmol, 2.2 equiv), 3-phenylpropyl acetate (35.6 mg, 0.20 mmol, 1 equiv), C$_6$H$_6$ (0.40 mL, 0.5M), [MnPc]Cl (12.1 mg, 0.020 mmol, 0.1 equiv), AgSbF$_6$ (6.9 mg, 0.020 mmol, 0.1 equiv), NH$_2$Tces (54.8 mg, 0.24 mmol, 1.2 equiv) and PhI(OPiv)$_2$ (162.4 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8 h at room temperature.

**Run 1** (trace yield by $^1$H NMR, 95% rsm by $^1$H NMR)
**Run 2** (trace yield by $^1$H NMR, 96% rsm by $^1$H NMR)
**Run 3** (trace yield by $^1$H NMR, 95% rsm by $^1$H NMR)

**Entry 4.** According to the general procedure A for optimization studies, 5Å powdered molecular sieves (40 mg), 3-phenylpropyl acetate (35.6 mg, 0.20 mmol, 1 equiv), C$_6$H$_6$ (0.40 mL, 0.5M), [Mn(BuPc)]Cl (16.5 mg, 0.020 mmol, 0.1 equiv), AgSbF$_6$ (6.9 mg, 0.020 mmol, 0.1 equiv), NH$_2$Tces (54.8 mg, 0.24
mmol, 1.2 equiv) and PhI(OPiv)$_2$ (162.4 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8 h at room temperature.

**Run 1** (trace yield by $^1$H NMR, 95% rsm by $^1$H NMR)

**Run 2** (trace yield by $^1$H NMR, 98% rsm by $^1$H NMR)

**Run 3** (trace yield by $^1$H NMR, 90% rsm by $^1$H NMR)

**Entry 5.** According to the general procedure A for optimization studies, 5Å powdered molecular sieves (40 mg), 3-phenylpropyl acetate (35.6 mg, 0.20 mmol, 1 equiv), C$_6$H$_6$ (0.40 mL, 0.5M), Co(TPP) (13.4 mg, 0.020 mmol, 0.1 equiv), NH$_2$Tces (54.8 mg, 0.24 mmol, 1.2 equiv) and PhI(OPiv)$_2$ (162.4 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8 h at room temperature.

**Run 1** (0% yield by $^1$H NMR, 100% rsm by $^1$H NMR)

**Run 2** (0% yield by $^1$H NMR, 97% rsm by $^1$H NMR)

**Run 3** (0% yield by $^1$H NMR, 99% rsm by $^1$H NMR)

**Entry 5.** According to the general procedure A for optimization studies, 5Å powdered molecular sieves (40 mg), 3-phenylpropyl acetate (35.6 mg, 0.20 mmol, 1 equiv), C$_6$H$_6$ (0.40 mL, 0.5M), Co(TPP) (13.4 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethoxycarbonyl azide (87.4 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8 h at room temperature.

**Run 1** (0% yield by $^1$H NMR, 86% rsm by $^1$H NMR)

**Run 2** (0% yield by $^1$H NMR, 97% rsm by $^1$H NMR)

**Run 3** (0% yield by $^1$H NMR, 99% rsm by $^1$H NMR)

**Entry 6.** According to the general procedure B for optimization studies, 5Å powdered molecular sieves (40 mg), 3-phenylpropyl acetate (35.6 mg, 0.20 mmol, 1 equiv), C$_6$H$_6$ (0.40 mL, 0.5M), [FePc]Cl (12.1 mg, 0.020 mmol, 0.1 equiv), AgSbF$_6$ (6.9 mg, 0.020 mmol, 0.1 equiv) and PhI=NTces (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8 h at room temperature.

**Run 1** (9% $^1$H NMR yield, 72% rsm by $^1$H NMR)

**Run 2** (8% $^1$H NMR yield, 92% rsm by $^1$H NMR)

**Run 3** (7 mg, 0.017 mmol, 9% isolated yield, 90% rsm by $^1$H NMR)

**Entry 7.** According to the general procedure B for optimization studies, 5Å powdered molecular sieves (40 mg), 3-phenylpropyl acetate (35.6 mg, 0.20 mmol, 1 equiv), C$_6$H$_6$ (0.40 mL, 0.5M), [Mn(BuPc)]Cl (16.5 mg, 0.020 mmol, 0.1 equiv), AgSbF$_6$ (6.9 mg, 0.020 mmol, 0.1 equiv) and PhI=NTces (172.2 mg,
0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8 h at room temperature.

Run 1 (10% $^1$H NMR yield, 86% rsm by $^1$H NMR)
Run 2 (9% $^1$H NMR yield, 91% rsm by $^1$H NMR)
Run 3 (10 mg, 0.025 mmol, 12% isolated yield, 88% rsm by $^1$H NMR)

Entry 8. According to the general procedure B for optimization studies, 5Å powdered molecular sieves (40 mg), 3-phenylpropyl acetate (35.6 mg, 0.20 mmol, 1 equiv), $C_6H_6$ (0.40 mL, 0.5M), [MnPc]Cl (12.1 mg, 0.020 mmol, 0.1 equiv), AgSbF$_6$ (6.9 mg, 0.020 mmol, 0.1 equiv) and PhI=NTces (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8 h at room temperature.

Run 1 (14% $^1$H NMR yield, 86% rsm by $^1$H NMR)
Run 2 (16% $^1$H NMR yield, 90% rsm by $^1$H NMR)
Run 3 (14 mg, 0.035 mmol, 17% isolated yield, 83% rsm by $^1$H NMR)

Entry 9. According to the general procedure B for optimization studies, 5Å powdered molecular sieves (40 mg), 3-phenylpropyl acetate (35.6 mg, 0.20 mmol, 1 equiv), $C_6H_6$ (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), AgSbF$_6$ (6.9 mg, 0.020 mmol, 0.1 equiv) and PhI=NTces (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8 h at room temperature.

Run 1 (60% $^1$H NMR yield, 40% rsm by $^1$H NMR)
Run 2 (60% $^1$H NMR yield, 37% rsm by $^1$H NMR)
Run 3 (43 mg, 0.106 mmol, 53% isolated yield, 45% rsm by $^1$H NMR)

Entry 10. According to the general procedure B for optimization studies, 5Å powdered molecular sieves (40 mg), 3-phenylpropyl acetate (35.6 mg, 0.20 mmol, 1 equiv), $C_6H_6$ (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), AgSbF$_6$ (6.9 mg, 0.020 mmol, 0.1 equiv) and PhI=NTces (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8 h at 40 °C.

Run 1 (53 mg, 0.131 mmol, 66% isolated yield, 33% rsm by $^1$H NMR)
Run 2 (54 mg, 0.133 mmol, 67% isolated yield, 33% rsm by $^1$H NMR)
Run 3 (57 mg, 0.141 mmol, 71% isolated yield, 29% rsm by $^1$H NMR)

Entry 11. According to the general procedure B for optimization studies, 5Å powdered molecular sieves (40 mg), 3-phenylpropyl acetate (35.6 mg, 0.20 mmol, 1 equiv), $C_6H_6$ (0.40 mL, 0.5M), manganese (III)
perchlorophthalocyanine chloride (11.5 mg, 0.010 mmol, 0.05 equiv), AgSbF$_6$ (3.4 mg, 0.010 mmol, 0.05 equiv) and PhI=NTces (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8 h at 40 °C.

**Run 1** (55% $^1$H NMR yield, 45% rsm by $^1$H NMR)

**Run 2** (50% $^1$H NMR yield, 50% rsm by $^1$H NMR)

**Run 3** (38 mg, 0.094 mmol, 47% isolated yield, 53% rsm by $^1$H NMR)

**Entry 12.** According to the general procedure B for optimization studies, 5Å powdered molecular sieves (40 mg), 3-phenylpropyl acetate (35.6 mg, 0.20 mmol, 1 equiv), C$_6$H$_6$ (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), AgSbF$_6$ (6.9 mg, 0.020 mmol, 0.1 equiv) and PhI=NTces (86.1 mg, 0.20 mmol, 1 equiv) were combined in a 10 mL round-bottom flask and stirred for 8 h at 40 °C.

**Run 1** (42% $^1$H NMR yield, 58% rsm by $^1$H NMR)

**Run 2** (40% $^1$H NMR yield, 60% rsm by $^1$H NMR)

**Run 3** (34 mg, 0.084 mmol, 42% isolated yield, 56% rsm by $^1$H NMR)

**Entry 13.** According to the general procedure B for optimization studies, 3Å powdered molecular sieves (40 mg), 3-phenylpropyl acetate (35.6 mg, 0.20 mmol, 1 equiv), 1,2-dichloroethane (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), AgSbF$_6$ (6.9 mg, 0.020 mmol, 0.1 equiv) and PhI=NTces (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8 h at 40 °C.

**Run 1** (61% $^1$H NMR yield, 26% rsm by $^1$H NMR)

**Run 2** (59% $^1$H NMR yield, 24% rsm by $^1$H NMR)

**Run 3** (49 mg, 0.121 mmol, 60% isolated yield, 22% rsm by $^1$H NMR)

**Entry 14.** According to the general procedure B for optimization studies, 5Å powdered molecular sieves (40 mg), 3-phenylpropyl acetate (35.6 mg, 0.20 mmol, 1 equiv), C$_6$H$_6$ (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv) PhI=NTces (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8 h at 40 °C.

**Run 1** (52% $^1$H NMR yield, 48% rsm by $^1$H NMR)

**Run 2** (55% $^1$H NMR yield, 36% rsm by $^1$H NMR)

**Run 3** (40 mg, 0.099 mmol, 50% isolated yield, 46% rsm by $^1$H NMR)
Entry 15. According to the general procedure B for optimization studies, 5Å powdered molecular sieves (40 mg), 3-phenylpropyl acetate (35.6 mg, 0.20 mmol, 1 equiv), \( C_6H_6 \) (0.40 mL, 0.5M), \( \text{AgSbF}_6 \) (6.9 mg, 0.020 mmol, 0.1 equiv) and PhI=NTces (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8 h at 40 °C.

Run 1 (0% yield by \(^1\)H NMR yield, 100% rsm by \(^1\)H NMR)
Run 2 (0% yield by \(^1\)H NMR yield, 100% rsm by \(^1\)H NMR)
Run 3 (0% yield by \(^1\)H NMR yield, 100% rsm by \(^1\)H NMR)

Entry 16. According to the general procedure B for optimization studies, 5Å powdered molecular sieves (40 mg), 3-phenylpropyl acetate (35.6 mg, 0.20 mmol, 1 equiv), \( C_6H_6 \) (0.40 mL, 0.5M), \( \text{Co(TPP)} \) (13.4 mg, 0.020 mmol, 0.1 equiv) and PhI=NTces (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8 h at 40 °C.

Run 1 (2% yield by \(^1\)H NMR yield, 98% rsm by \(^1\)H NMR)
Run 2 (0% yield by \(^1\)H NMR yield, 96% rsm by \(^1\)H NMR)
Run 3 (0% yield by \(^1\)H NMR yield, 90% rsm by \(^1\)H NMR)

Entry 17. According to the general procedure A for optimization studies, 5Å powdered molecular sieves (40 mg), 3-phenylpropyl acetate (35.6 mg, 0.20 mmol, 1 equiv), \( C_6H_6 \) (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), \( \text{AgSbF}_6 \) (6.9 mg, 0.020 mmol, 0.1 equiv), \( \text{NH}_2\text{Tces} \) (54.8 mg, 0.24 mmol, 1.2 equiv) and PhI(OPiv)_2 (162.4 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8 h at 40 °C.

Run 1 (trace yield by \(^1\)H NMR yield, 90% rsm by \(^1\)H NMR)
Run 2 (trace yield by \(^1\)H NMR yield, 86% rsm by \(^1\)H NMR)
Run 3 (trace yield by \(^1\)H NMR yield, 84% rsm by \(^1\)H NMR)

\[ \text{3-phenyl-3-((2,2,2-trichloroethoxy)sulfonyl)amino)propyl acetate [2].} \] According to the general amination procedure A, 5Å powdered molecular sieves (40 mg), commercial 3-phenylpropyl acetate \( \textbf{1} \) (35.6 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv)
and 2,2,2-trichloroethyl (phenyl-λ<sup>3</sup>-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using diethyl ether as the eluent (30 mL), the solvent was concentrated and the crude brown oil was loaded onto a silica gel column using dichloromethane to quantitatively transfer the product. Flash chromatography using gradient elution (500 mL of 100% dichloromethane then 300 mL of 2% diethyl ether in 98% dichloromethane followed by 300 mL of 5% diethyl ether in 95% dichloromethane) gave the pure product as a slightly yellow solid.

**Run 1** (53 mg, 0.131 mmol, 66% yield)

**Run 2** (54 mg, 0.133 mmol, 67% yield)

**Run 3** (57 mg, 0.141 mmol, 71% yield)

**Average overall yield: 68% yield ± 2.6**

<sup>1</sup>H NMR: (500 MHz, Chloroform-<i>d</i>)

δ 7.40 – 7.35 (m, 2H), 7.34 – 7.29 (m, 3H), 5.73 (d, <i>J</i> = 7.7 Hz, 1H), 4.68 (q, <i>J</i> = 7.4 Hz, 1H), 4.32 (d, <i>J</i> = 10.8 Hz, 1H), 4.27 (d, <i>J</i> = 10.8 Hz, 1H), 4.18-4.13 (m, 1H), 4.05-4.00 (m, 1H), 2.32-2.25 (m, 1H), 2.18-2.11 (m, 1H), 2.04 (s, 3H)

<sup>13</sup>C NMR: (126 MHz, CDCl<sub>3</sub>)

δ 171.2, 139.7, 129.2, 128.6, 126.7, 93.3, 78.1, 61.1, 56.9, 35.6, 21.0;

HRMS: (ESI-TOF MS ES+)

<sup>m/z</sup> calculated for C<sub>13</sub>H<sub>16</sub>NO<sub>5</sub>SCl<sub>3</sub>Na [M+Na]<sup>+</sup>: 425.9712, found 425.9706
IV. Experimental procedures and compound characterization for Figure 2

Figure 2. Intermolecular benzylic C—H amination substrate scope.

General amination procedure B for benzylic amination

In a 10 mL round bottom flask, 5Å powdered molecular sieves (40 mg) and a Teflon stir bar were added. The flask was sealed with a Suba Seal rubber septum, placed under vacuum, flame-dried for 45 seconds to activate the molecular sieves, cooled under a purged and completely air-free argon balloon and wrapped in foil to exclude light. Once cooled, solvent (0.40 mL, 0.5 M to substrate) and substrate (0.20 mmol, 1 equiv) were added and stirred for 10 minutes. [Mn^{III}(ClPc)]Cl (23.1 mg, 0.020 mmol, 0.1 equiv) and silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) were weighed in a foil wrapped 1 dram...
vial in the glove box and sealed with a Teflon cap. The vial was removed from the glove box and the contents added directly to the round bottom flask while maintaining an argon atmosphere then stirred for 10 minutes at room temperature. In a 1 dram vial open to air, 2,2,2-trichloroethyl (phenyl-\(\lambda^3\)-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) was weighed and added directly to the round bottom flask while maintaining an argon atmosphere. The Suba Seal rubber septum was replaced by a polyethylene cap, sealed tightly and placed in a 40 °C oil bath for 8 hours with stirring. Upon reaction completion, the reaction was filtered through a 1-inch silica gel plug using diethyl ether or ethyl acetate as the eluent. The crude material was concentrated and dry-loaded directly onto a silica gel column.

![Chemical structure](image)

**2,2,2-trichloroethyl (1-phenylethyl)sulfamate [5].** According to the general amination procedure B, 5Å powdered molecular sieves (40 mg), ethyl benzene S3 (21.2 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-\(\lambda^3\)-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using diethyl ether as the eluent (30 mL), the solvent was concentrated and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography using gradient elution (100 mL of 100% hexanes then 300 mL of 5% ethyl acetate in 95% hexanes followed by 600 mL of 7.5% ethyl acetate in 90% hexanes) gave the pure product as a yellow oil.

**Run 1** (48 mg, 0.144 mmol, 72% yield)

**Run 2** (48 mg, 0.144 mmol, 72% yield)

**Run 3** (48 mg, 0.144 mmol, 72% yield)

**Average overall yield:** 72% yield ± 0.0

**\(^1\)H NMR:** (500 MHz, Chloroform-\(d\))

\(\delta \) 7.41 – 7.34 (m, 4H), 7.34 – 7.30 (m, 1H), 5.15 (s, 1H), 4.73 (p, \(J = 6.5\) Hz, 1H), 4.41 (s, 2H), 1.63 (d, \(J = 6.6\) Hz, 3H)

**\(^13\)C NMR:** (126 MHz, CDCl\(_3\))

\(\delta \) 141.5, 129.1, 128.4, 126.4, 93.4, 78.2, 55.1, 23.0

**HRMS:** (ESI-TOF MS ES-)

16
According to the general amination procedure B, 5Å powdered molecular sieves (40 mg), 1-chloro-4-ethylbenzene S4 (28.1 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ3-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using diethyl ether as the eluent (80 mL), the solvent was concentrated and the crude brown oil was loaded onto a silica gel column. Flash chromatography using gradient elution (100 mL of 100% hexanes then 700 mL of 5% ethyl acetate in 95% hexanes) gave the pure product as a yellow oil.

**Run 1** (41.0 mg, 0.112 mmol, 56% yield)

**Run 2** (42.3 mg, 0.115 mmol, 58% yield)

**Run 3** (41.9 mg, 0.114 mmol, 57% yield)

**Average overall yield: 57% yield ± 1.0**

**1H NMR:** (500 MHz, CDCl₃)

\[ \delta 7.35 (d, J = 8.5 \text{ Hz}, 1\text{H}), 7.30 (d, J = 8.5 \text{ Hz}, 2\text{H}), 4.91 (br s, 1\text{H}), 4.73 (p, J = 6.7 \text{ Hz}, 1\text{H}), 4.51 (d, J = 10.8 \text{ Hz}, 1\text{H}), 4.48 (d, J = 10.8 \text{ Hz}, 1\text{H}), 1.61 (d, J = 6.9 \text{ Hz}, 3\text{H}) \]

**13C NMR:** (126 MHz, CDCl₃)

\[ \delta 139.97, 134.22, 129.26, 127.82, 93.39, 78.25, 54.41, 22.94 \]

**HRMS:** (ESI-TOF MS ES+)

\[ m/z \text{ calculated for } \text{C}_{10}\text{H}_{11}\text{NO}_{3}\text{NaSCl}_{3} \text{ [M+Na]}^{+}: 387.9111, \text{ found } 387.9117. \]

2,2,2-trichloroethyl (1-(4-chlorophenyl)ethyl)sulfamate [6] According to the general amination procedure B, 5Å powdered molecular sieves (40 mg), 1-chloro-4-ethylbenzene S4 (28.1 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ3-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using diethyl ether as the eluent (80 mL), the solvent was concentrated and the crude brown oil was loaded onto a silica gel column. Flash chromatography using gradient elution (100 mL of 100% hexanes then 700 mL of 5% ethyl acetate in 95% hexanes) gave the pure product as a yellow oil.

**Run 1** (41.0 mg, 0.112 mmol, 56% yield)

**Run 2** (42.3 mg, 0.115 mmol, 58% yield)

**Run 3** (41.9 mg, 0.114 mmol, 57% yield)

**Average overall yield: 57% yield ± 1.0**

**1H NMR:** (500 MHz, CDCl₃)

\[ \delta 7.35 (d, J = 8.5 \text{ Hz}, 1\text{H}), 7.30 (d, J = 8.5 \text{ Hz}, 2\text{H}), 4.91 (br s, 1\text{H}), 4.73 (p, J = 6.7 \text{ Hz}, 1\text{H}), 4.51 (d, J = 10.8 \text{ Hz}, 1\text{H}), 4.48 (d, J = 10.8 \text{ Hz}, 1\text{H}), 1.61 (d, J = 6.9 \text{ Hz}, 3\text{H}) \]

**13C NMR:** (126 MHz, CDCl₃)

\[ \delta 139.97, 134.22, 129.26, 127.82, 93.39, 78.25, 54.41, 22.94 \]

**HRMS:** (ESI-TOF MS ES+)

\[ m/z \text{ calculated for } \text{C}_{10}\text{H}_{11}\text{NO}_{3}\text{NaSCl}_{3} \text{ [M+Na]}^{+}: 387.9111, \text{ found } 387.9117. \]

2,2,2-trichloroethyl (1-(4-(trifluoromethyl)phenyl)ethyl)sulfamate [7] According to the general amination procedure B, 5Å powdered molecular sieves (40 mg), 1-ethyl-4-(trifluoromethyl)benzene S5
(34.8 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ3-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using diethyl ether as the eluent (80 mL), the solvent was concentrated and the crude brown oil was loaded onto a silica gel column. Flash chromatography using gradient elution (800 mL of 5% ethyl acetate in 95% hexanes) gave the pure product as a yellow oil.

**Run 1** (22.6 mg, 0.056 mmol, 28% yield)

**Run 2** (24.2 mg, 0.060 mmol, 30% yield)

**Run 3** (25.6 mg, 0.064 mmol, 32% yield)

**Average overall yield: 30% yield ± 2.0**

$^1$H NMR: (500 MHz, CDCl$_3$)

δ 7.65 (d, $J = 8.1$ Hz, 1H), 7.49 (d, $J = 8.1$ Hz, 2H), 4.93 (br d, $J = 6.4$ Hz, 1H), 4.81 (p, $J = 6.8$ Hz, 1H), 4.51 (d, $J = 10.9$ Hz, 1H), 4.49 (d, $J = 10.9$ Hz, 1H), 1.64 (d, $J = 6.9$ Hz, 3H)

$^{13}$C NMR: (126 MHz, CDCl$_3$)

δ 145.38, 130.69 (q, $J = 32.7$ Hz), 126.82, 126.13 (q, $J = 3.7$ Hz), 124.00 (q, $J = 272.2$ Hz), 93.34, 78.26, 54.60, 23.06

$^{19}$F NMR: (470 MHz, CDCl$_3$)

δ -63.15 (s, 3F)

HRMS: (CI+)

$m/z$ calculated for C$_{11}$H$_{12}$NO$_3$SCl$_3$F$_3$ [M+H]$^+:$ 399.95560, found 399.95510.

![3-(4-methoxyphenyl)-3-(((2,2,2-trichloroethoxy)sulfonyl)amino)propyl acetate](image)

3-(4-methoxyphenyl)-3-(((2,2,2-trichloroethoxy)sulfonyl)amino)propyl acetate [8]. According to the general procedure B, 5Å powdered molecular sieves (40 mg), 3-(4-methoxyphenyl)propyl acetate S6 (41.7 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ3-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were
combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using diethyl ether as the eluent (50 mL), the solvent was concentrated and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography on 75mL of silica using gradient elution (500 mL of 100% dichloromethane then 200 mL of 1% diethyl ether in 99% dichloromethane followed by 400 mL of 2% diethyl ether in 98% dichloromethane then 400 mL of 5% diethyl ether in 95% dichloromethane) gave the pure product as a white solid.

**Run 1** (60.9 mg, 0.140 mmol, 70% yield)

**Run 2** (56.5 mg, 0.130 mmol, 65% yield)

**Run 3** (57.0 mg, 0.131 mmol, 66% yield)

**Average overall yield: 67% yield ± 2.6**

**$^1$H NMR:** (500 MHz, CDCl$_3$)

$\delta$ 7.24 (d, $J = 8.5$ Hz, 2H), 6.89 (d, $J = 8.5$ Hz, 2H), 5.60 (br d, $J = 7.2$ Hz, 1H), 4.63 (q, $J = 7.2$ Hz, 1H), 4.35 (d, $J = 10.8$ Hz, 1H), 4.29 (d, $J = 10.8$ Hz, 1H), 4.13 (dt, $J = 11.6$, 5.9 Hz, 1H), 3.99 (dt, $J = 11.7$, 6.3 Hz, 1H), 3.79 (s, 3H), 2.28 (m, 1H), 2.15 – 2.08 (m, 1H), 2.04 (s, 3H).

**$^{13}$C NMR:** (126 MHz, CDCl$_3$)

$\delta$ 171.22, 159.75, 131.61, 127.99, 114.58, 93.38, 78.11, 61.17, 56.36, 55.49, 35.54, 21.02.

**HRMS:** (ESI-TOF MS ES-)

$m/z$ calculated for C$_{14}$H$_{17}$Cl$_3$NO$_6$S [M-H]: 431.9842, found 431.9839.

3-(4-bromophenyl)-3-(((2,2,2-trichloroethoxy)sulfonyl)amino)propyl acetate [9]. According to the general procedure B, 5Å powdered molecular sieves (40 mg), 3-(4-bromophenyl)propyl acetate S7 (51.4 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-$\lambda^3$-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using diethyl ether as the eluent (50 mL), the solvent was concentrated and the crude brown oil was loaded onto a silica gel column. Flash chromatography with 75mL of silica using gradient elution (500 mL of 100% dichloromethane then
250 mL of 1% diethyl ether in 99% dichloromethane followed by 250 mL of 2% diethyl ether in 98% dichloromethane) gave the pure product as a white solid.

**Run 1** (64.8 mg, 0.106 mmol, 53% yield)

**Run 2** (63.0 mg, 0.110 mmol, 55% yield)

**Run 3** (63.0 mg, 0.112 mmol, 56% yield)

**Average overall yield: 55% yield**

**1H NMR:** (500 MHz, CDCl₃)

δ 7.51 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 5.54 (d, J = 7.5 Hz, 1H), 4.67 (q, J = 7.3 Hz, 1H), 4.44 (d, J = 10.8 Hz, 1H), 4.40 (d, J = 10.8 Hz, 1H), 4.15 (ddd, J = 11.9, 6.8, 5.2 Hz, 1H), 4.04 (ddd, J = 11.8, 7.0, 5.2 Hz, 1H), 2.29 – 2.21 (m, 1H), 2.18 – 2.09 (m, 1H), 2.05 (s, 3H).

**13C NMR:** (126 MHz, CDCl₃)

δ 171.17, 138.77, 132.48, 128.53, 122.70, 93.40, 78.25, 61.04, 56.54, 35.61, 21.13.

**HRMS:** (ESI-TOF MS ES+)

m/z calculated for C₁₃H₁₅NO₅NaSCl₃Br [M+Na]⁺: 503.8818, found 503.8807.

---

**4-(3-acetoxy-1-(((2,2,2-trichloroethoxy)sulfonyl)amino)propyl)phenyl acetate [10].** According to the general procedure B, 5Å powdered molecular sieves (40 mg), 3-(4-acetoxyphenyl)propyl acetate **S8** (47.3 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ³-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using diethyl ether as the eluent (50 mL), the solvent was concentrated and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography on 75mL silica using gradient elution (500 mL of 100% dichloromethane then 200 mL of 2% diethyl ether in 98% dichloromethane followed by 400 mL of 4% diethyl ether in 96% dichloromethane then 400 mL of 8% diethyl ether in 92% dichloromethane) gave the product as a white solid with a minor impurity that was considered when calculating yield by the addition of mesitylene as an internal standard in the **1H NMR**.
Run 1 (53.7 mg, 0.116 mmol, 58% yield)
Run 2 (53.7 mg, 0.116 mmol, 58% yield)
Run 3 (51.8 mg, 0.112 mmol, 56% yield)
Average overall yield: 57% yield ± 1.1

$^1$H NMR: (500 MHz, CDCl$_3$)
\[\delta 7.34 \text{ (d, } J = 8.5 \text{ Hz, } 2\text{H}), 7.09 \text{ (d, } J = 8.5 \text{ Hz, } 2\text{H}), 5.75 \text{ (d, } J = 6.9 \text{ Hz, } 1\text{H}), 4.68 \text{ (q, } J = 7.1 \text{ Hz, } 1\text{H}), 4.40 \text{ (d, } J = 10.8 \text{ Hz, } 1\text{H}), 4.35 \text{ (d, } J = 10.8 \text{ Hz, } 1\text{H}), 4.16 \text{ (ddd, } J = 11.9, 7.1, 5.2 \text{ Hz, } 1\text{H}), 4.03 \text{ (ddd, } J = 11.8, 6.8, 5.1 \text{ Hz, } 1\text{H}), 2.30 \text{ (s, } 3\text{H}), 2.28 - 2.20 \text{ (m, } 1\text{H}), 2.13 \text{ (dt, } J = 14.0, 6.8, 5.0 \text{ Hz, } 1\text{H}), 2.03 \text{ (s, } 3\text{H}).

$^{13}$C NMR: (126 MHz, CDCl$_3$)
\[\delta 171.18, 169.53, 150.70, 137.29, 127.88, 122.38, 93.33, 78.13, 61.03, 56.34, 35.56, 21.26, 21.00.

HRMS: (ESI- TOF MS ES-)
m/z calculated for C$_{15}$H$_{18}$Cl$_{3}$NO$_7$SNa [M+Na]$^+$: 483.9767, found 483.9775.

Methyl 4-phenyl-4-(((2,2,2-trichloroethoxy)sulfonyl)amino)butanoate [11]. According to the general procedure B, 5Å powdered molecular sieves (40 mg), methyl 4-phenylbutanoate S9 (35.6 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ$^3$-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using diethyl ether as the eluent (30 mL), the solvent was concentrated and the crude brown oil was loaded onto a silica gel column using dichloromethane to quantitatively transfer the product. Flash chromatography using gradient elution (500 mL of 100% dichloromethane then 300 mL of 2% diethyl ether in 98% dichloromethane followed by 300 mL of 5% diethyl ether in 95% dichloromethane) gave the pure product as a clear and yellow oil.

Run 1 (57 mg, 0.141 mmol, 70% yield)
Run 2 (52 mg, 0.128 mmol, 64% yield)
Run 3 (53 mg, 0.131 mmol, 65% yield)
Average overall yield: 66% yield ± 3.2
$^1$H NMR: (500 MHz, Chloroform-d)

$\delta$ 7.40 – 7.35 (m, 2H), 7.35 – 7.28 (m, 3H), 5.94 (d, $J = 7.4$ Hz, 1H), 4.57 (q, $J = 7.3$ Hz, 1H), 4.33 (d, $J = 10.8$ Hz, 1H), 4.28 (d, $J = 10.8$ Hz, 1H), 3.68 (s, 3H), 2.51 – 2.37 (m, 2H), 2.25 (dq, $J = 14.7$, 7.4 Hz, 1H), 2.12 (dq, $J = 13.7$, 6.7 Hz, 1H)

$^{13}$C NMR: (126 MHz, CDCl$_3$)

$\delta$ 174.3, 140.1, 129.2, 128.5, 126.7, 93.4, 78.1, 59.2, 52.2, 31.8, 30.8

HRMS: (ESI-TOF MS ES+)

$m/\text{z}$ calculated for C$_{13}$H$_{16}$NO$_5$SCl$_3$Na [M+Na]$^+$: 425.9712, found 425.9710

2,2,2-trichloroethyl (1-phenyl-3-(2,2,2-trifluoroacetamido)propyl)sulfamate [12]. According to the general amination procedure B, 5Å powdered molecular sieves (40 mg), 2,2,2-trifluoro-N-(3-phenylpropyl)acetamide S10 (46.2 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-$\lambda^3$-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using diethyl ether as the eluent (30 mL), the solvent was concentrated and the crude brown oil was loaded onto a silica gel column using dichloromethane to quantitatively transfer the product. Flash chromatography using gradient elution (500 mL of 100% dichloromethane then 300 mL of 2% diethyl ether in 98% dichloromethane followed by 300 mL of 5% diethyl ether in 95% dichloromethane) gave the pure product as a light yellow solid.

Run 1 (61 mg, 0.133 mmol, 67% yield)

Run 2 (66 mg, 0.144 mmol, 72% yield)

Run 3 (61 mg, 0.133 mmol, 67% yield)

Average overall yield: 69% yield ± 2.9

$^1$H NMR: (500 MHz, Chloroform-d)

$\delta$ 7.42 – 7.36 (m, 2H), 7.36 – 7.31 (m, 3H), 6.75 (s, 1H), 5.41 (d, $J = 8.1$ Hz, 1H), 4.57 (q, $J = 7.7$ Hz, 1H), 4.45 (d, $J = 10.8$ Hz, 1H), 4.31 (d, $J = 10.8$ Hz, 1H), 3.74 – 3.66 (m, 1H), 3.42 – 3.34 (m, 1H), 2.22 – 2.15 (m, 2H)

$^{13}$C NMR: (126 MHz, CDCl$_3$)
δ 157.9 (q, \( J = 36.2 \) Hz), 139.6, 129.4, 128.9, 126.6, 115.8 (q, \( J = 287.4 \) Hz), 93.1, 78.1, 57.2, 37.1, 35.5

\(^{19}\text{F NMR:} (470 \text{ MHz, Chloroform-}d)\)

δ -76.44

\(\text{HRMS: (ESI-TOF MS ES+)}\)

\(m/z\) calculated for C\(_{13}\)H\(_{14}\)N\(_2\)O\(_4\)SCl\(_3\)F\(_3\)Na [M+Na]\(^+\): 478.9590, found 478.9555

2,2,2-trichloroethyl (1-phenyl-3-(2,2,2-trifluoroacetamido)butyl)sulfamate [13]. According to the general procedure B, 5Å powdered molecular sieves (40 mg), 2,2,2-trifluoro-N-(4-phenylbutan-2-yl)acetamide S11 (49.1 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ\(^3\)-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using ethyl acetate as the eluent (50 mL), the solvent was concentrated and the crude brown oil was loaded onto a silica gel column. Flash chromatography on 75mL silica using gradient elution (500 mL of 100% dichloromethane then 200 mL of 1% diethyl ether in 99% dichloromethane followed by 400 mL of 2% diethyl ether in 98% dichloromethane) gave the pure product as a white solid in a 1:1 diastereomeric mixture. This compound was characterized as a mixture of diastereomers.

Run 1 (61 mg, 0.130 mmol, 65% yield)
Run 2 (58.5 mg, 0.124 mmol, 62% yield)
Run 3 (64.2 mg, 0.136 mmol, 68% yield)
Average overall yield: 65% yield ± 3.0 (1:1 d.r.)

\(^1\text{H NMR:} (500 \text{ MHz, CDCl}_3\) (mixture of diastereomers)

δ 7.42 – 7.29 (m, 5H), 6.57 – 6.48 (m, 1H), 6.24 (d, \( J = 7.3 \) Hz, 0.5H), 5.91 (d, \( J = 7.9 \) Hz, 0.5H), 4.62 – 4.51 (m, 1H), 4.33 (d, \( J = 10.8 \) Hz, 0.5H), 4.32 (d, \( J = 10.8 \) Hz, 0.5H), 4.21 (d, \( J = 10.8 \) Hz, 0.5H), 4.18 (d, \( J = 10.8 \) Hz, 0.5H), 4.15 – 3.99 (m, 1H), 2.31 (dt, \( J = 14.6, 7.4 \) Hz, 0.5H), 2.21 (t, \( J = 7.0 \) Hz, 0.5H), 1.95 (dt, \( J = 13.9, 6.7 \) Hz, 1H), 1.33 (d, \( J = 6.7 \) Hz, 1.5H), 1.29 (d, \( J = 6.7 \) Hz, 1.5H).
**1^1^C NMR:** (126 MHz, CDCl₃) (mixture of diastereomers)

δ 157.08 (q, J_{CF} = 37.2 Hz), 156.96 (q, J_{CF} = 37.3 Hz), 139.85, 139.29, 129.46, 129.38, 128.95, 128.82, 126.75, 126.63, 115.77 (q, J_{CF} = 287.4 Hz), 115.75 (q, J_{CF} = 287.9 Hz), 93.20, 93.18, 78.12, 78.09, 56.80, 56.72, 44.43, 44.27, 43.07, 41.91, 20.03, 19.97.

**1^9^F NMR:** (471 MHz, CDCl₃)

δ -75.92, -75.98. (diastereomers).

**HRMS:** (ESI-TOF MS ES+)

m/z calculated for C_{14}H_{20}Cl_{3}F_{3}N_{3}O_{4}S [M+NH₄]^+: 488.0192, found 488.0197.

![Structure](image_url)

**2,2,2-trichloroethyl (3-methyl-1-phenylbutyl)sulfamate [14].** According to the general procedure B, 5Å powdered molecular sieves (40 mg), isopentylbenzene S12 (29.7 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5 M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ³-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using diethyl ether as the eluent (50 mL), the solvent was concentrated and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography using gradient elution (100 mL of 100% hexanes then 400 mL of 5% ethyl acetate in 95% hexanes followed by 200 mL of 10% ethyl acetate in 90% hexanes) gave the pure product as a colorless oil.

**Run 1** (37.2 mg, 0.099 mmol, 50% yield)

**Run 2** (41.2 mg, 0.110 mmol, 55% yield)

**Run 3** (41.2 mg, 0.110 mmol, 55% yield)

**Average overall yield: 53% yield ± 2.9**

**1^H NMR:** (500 MHz, CDCl₃)

δ 7.41 – 7.23 (m, 5H), 5.15 (br d, J = 7.2 Hz, 1H), 4.57 (q, J = 7.6 Hz, 1H), 4.26 (d, J = 10.8 Hz, 1H), 4.22 (d, J = 10.8 Hz, 1H), 1.80 (dt, J = 14.5, 7.5 Hz, 1H), 1.67 (dt, J = 13.9, 7.2 Hz, 1H), 1.62 – 1.51 (m, 1H), 0.94 (d, J = 6.6 Hz, 6H).

**1^3^C NMR:** (126 MHz, CDCl₃)
δ 140.96, 129.14, 128.37, 126.78, 93.36, 78.10, 57.97, 46.29, 24.88, 22.56, 22.32.

HRMS: (ESI- TOF MS ES-)

m/z calculated for C_{13}H_{17}Cl_{3}NO_{3}S [M-H]⁻: 371.9995, found 371.9991.

2,2,2-trichloroethyl (4-methyl-1-phenylpentyl)sulfamate [15]. According to the general procedure B, 5Å powdered molecular sieves (40 mg), (4-methylpentyl)benzene S13 (32.5 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ³-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using diethyl ether as the eluent (50 mL), the solvent was concentrated and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography on 75mL of silica using gradient elution (100 mL of 100% hexanes then 300 mL of 5% ethyl acetate in 95% hexanes followed by 600 mL of 10% ethyl acetate in 90% hexanes) gave the pure product as a colorless oil.

Run 1 (47 mg, 0.120 mmol, 60% yield)

Run 2 (45.1 mg, 0.116 mmol, 58% yield)

Run 3 (45.2 mg, 0.116 mmol, 58% yield)

Average overall yield: 59% yield ± 1.2

^1H NMR: (500 MHz, CDCl₃)

δ 7.41 – 7.27 (m, 5H), 4.97 (br d, J = 7.3 Hz, 1H), 4.46 (q, J = 7.5 Hz, 1H), 4.32 (d, J = 10.8 Hz, 1H), 4.28 (d, J = 10.8 Hz, 1H), 1.99 – 1.89 (m, 1H), 1.87 – 1.76 (m, 1H), 1.61 – 1.48 (m, 1H), 1.33 – 1.19 (m, 1H), 1.16 – 1.02 (m, 1H), 0.86 (d, J = 6.6 Hz, 6H).

^13C NMR: (126 MHz, CDCl₃)

δ 140.74, 129.13, 128.39, 126.78, 93.39, 78.13, 60.03, 35.14, 35.00, 27.88, 22.62, 22.52.

HRMS: (ESI- TOF MS ES+)

m/z calculated for C_{14}H_{19}Cl_{3}NO_{3}S [M-H]⁺: 386.0157, found 386.0145.
5-((2,2,2-trichloroethoxy)sulfonyl)amino)-5,6,7,8-tetrahydronaphthalen-1-yl acetate [16]. According to the general amination procedure B, 5Å powdered molecular sieves (40 mg), 5,6,7,8-tetrahydronaphthalen-1-yl acetate S14 (38.0 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ₃-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using diethyl ether as the eluent (30 mL), the solvent was concentrated and the crude brown oil was loaded onto a silica gel column using dichloromethane to quantitatively transfer the product. Flash chromatography using gradient elution (100 mL of 100% hexanes then 300 mL of 5% acetone in 95% hexanes followed by 600 mL of 7.5% acetone in 92.5% hexanes) gave the pure product as a clear and yellow oil.

Run 1 (56 mg, 0.134 mmol, 67% yield)
Run 2 (60 mg, 0.144 mmol, 72% yield)
Run 3 (58 mg, 0.139 mmol, 70% yield)

Average overall yield: 70% yield ± 2.5

¹H NMR: (500 MHz, CDCl₃)
\[\delta 7.42 \text{ (d, } J = 7.8 \text{ Hz, 1H), } 7.28 - 7.21 \text{ (m, 1H), } 7.00 - 6.93 \text{ (m, 1H), } 5.05 \text{ (d, } J = 7.8 \text{ Hz, 1H), } 4.82 - 4.76 \text{ (m, 1H), } 4.67 \text{ (s, 2H), } 2.62 \text{ (dt, } J = 17.4, 5.7 \text{ Hz, 1H), } 2.51 \text{ (dt, } J = 17.3, 7.1 \text{ Hz, 1H), } 2.30 \text{ (s, 3H), } 2.12 - 2.05 \text{ (m, 2H), } 1.89 - 1.80 \text{ (m, 2H)}\]

¹³C NMR: (126 MHz, CDCl₃)
\[\delta 169.4, 149.0, 136.5, 130.4, 127.2, 127.2, 121.8, 93.7, 78.2, 53.3, 29.8, 23.0, 20.9, 18.2\]

HRMS: (ESI-TOF MS ES+)
\[m/z \text{ calculated for } C_{14}H_{16}NO_5SCl_3Na [M+Na]^+: 437.9712, \text{ found } 437.9707\]
2.2,2-trichloroethyl isochroman-1-ylsulfamate [17]. According to the general amination procedure B, 5Å powdered molecular sieves (40 mg), isochroman S15 (46.2 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-\(\lambda^3\)-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using diethyl ether as the eluent (30 mL), the solvent was concentrated and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography using gradient elution (100 mL of 100% hexanes then 300 mL of 5% ethyl acetate in 95% hexanes followed by 600 mL of 10% ethyl acetate in 90% hexanes) gave the pure product as a yellow solid.

Run 1 (44 mg, 0.122 mmol, 61% yield)
Run 2 (41 mg, 0.114 mmol, 57% yield)
Run 3 (45 mg, 0.125 mmol, 62% yield)

Average overall yield: 60% yield ± 2.6

\(^1\)H NMR: (500 MHz, Chloroform-\(d\))
\[ \delta \ 7.33 - 7.22 (m, 3H), 7.15 (d, J = 7.3 Hz, 1H), 6.06 (d, J = 8.3 Hz, 1H), 5.77 (d, J = 8.3 Hz, 1H), 4.80 (d, J = 10.9 Hz, 1H), 4.73 (d, J = 10.8 Hz, 1H), 4.06 - 4.01 (m, 2H), 3.00 - 2.91 (m, 1H), 2.79 - 2.72 (m, 1H) \]

\(^13\)C NMR: (126 MHz, CDCl\(_3\))
\[ \delta \ 134.7, 131.7, 129.1, 129.0, 127.1, 127.0, 93.6, 80.6, 78.6, 59.8, 27.7 \]

HRMS: (ESI-TOF MS ES-)

\[ m/z \text{ calculated for } C_{11}H_{11}NO_4SCl}_3 [M-H]: 357.9474, \text{ found 357.9467} \]
4-(((2,2,2-trichloroethoxy)sulfonyl)amino)-1,2,3,4-tetrahydronaphthalen-1-yl acetate [18]. According to the general amination procedure B, 5Å powdered molecular sieves (40 mg), 1,2,3,4-tetrahydronaphthalen-1-yl acetate S16 (38.0 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ3-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using diethyl ether as the eluent (30 mL), the solvent was concentrated and the crude brown oil was loaded onto a silica gel column using dichloromethane to quantitatively transfer the product. Flash chromatography using gradient elution (500 mL of 100% dichloromethane then 300 mL of 2% diethyl ether in 98% dichloromethane followed by 300 mL of 5% diethyl ether in 95% dichloromethane) gave the pure product as a white solid in equal amounts of inseparable diastereomers.

Run 1 (50 mg, 0.120 mmol, 60% yield)
Run 2 (52 mg, 0.124 mmol, 62% yield)
Run 3 (48 mg, 0.115 mmol, 58% yield)
Average overall yield: 60% yield ± 2.0 (1:1 d.r.)

1H NMR: (500 MHz, Chloroform-d) (mixture of diastereomers)
δ 7.59 (d, J = 7.4 Hz, 0.5H), 7.53 (d, J = 7.4 Hz, 0.5H), 7.40 – 7.35 (m, 1H), 7.35 – 7.30 (m, 2H), 5.99 (t, J = 4.4 Hz, 0.5H), 5.92 (t, J = 5.2 Hz, 0.5H), 5.05 (d, J = 8.0 Hz, 0.5H), 4.94 – 4.88 (m, 0.5H), 4.88 – 4.83 (m, 0.5H), 4.76 (td, J = 7.9, 5.1 Hz, 0.5H), 4.70 (s, 1H), 4.69 (s, 1H) 2.40 – 2.31 (m, 0.5H), 2.31 – 2.22 (m, 0.5H), 2.22 – 2.10 (m, 2.5H), 2.09 (s, 1.5H), 2.07 (s, 1.5H), 2.02 – 1.95 (m, 0.5H)

13C NMR: (126 MHz, CDCl3) (mixture of diastereomers)
δ 170.8, 170.7, 135.7, 135.4, 135.2, 135.1, 129.9, 129.6, 129.5, 129.4, 129.3, 129.1, 128.9, 128.5, 93.7, 93.6, 78.3, 78.2, 69.4, 68.7, 53.5, 52.9, 26.9, 26.0, 25.8, 24.9, 21.5, 21.4.

HRMS: (ESI-TOF MS ES+)
m/z calculated for C14H16NO5SCl3Na [M+Na]+: 437.9712, found 437.9704
2,2,2-trichloroethyl (6-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)sulfamate [19]. According to the general procedure B, 5Å powdered molecular sieves (40 mg), 6-methoxy-1,2,3,4-tetrahydronaphthalene S17 (32.5 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-\(\lambda^3\)-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using ethyl acetate as the eluent (50 mL), the solvent was concentrated and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography using gradient elution (400 mL of 5% ethyl acetate in hexane followed by 400 mL of 10% ethyl acetate in hexanes) gave the pure product as well as the imine by-product as off-white solids.

**Run 1** (46.5 mg, 0.120 mmol, 60% yield + imine (10.2 mg, 0.026 mmol, 13% yield))

**Run 2** (47.3 mg, 0.122 mmol, 61% yield + imine (10.0 mg, 0.026 mmol, 13% yield))

**Run 3** (41 mg, 0.106 mmol, 53% yield + imine (7.0 mg, 0.014 mmol, 9% yield))

**Average overall yield: 58 % yield ± 4.4**

\(^1\)H NMR: (500 MHz, CDCl\(_3\))

\(\delta\) 7.39 (d, \(J = 8.6\) Hz, 1H), 6.76 (dd, \(J = 8.6, 2.7\) Hz, 1H), 6.61 (d, \(J = 2.7\) Hz, 1H), 4.83 (d, \(J = 7.7\) Hz, 1H), 4.76 – 4.72 (m, 1H), 4.67 (s, 2H), 3.78 (s, 3H), 2.79 (dt, \(J = 17.0, 5.4\) Hz, 1H), 2.76 – 2.66 (m, 1H), 2.16 – 2.09 (m, 1H), 2.08 – 2.01 (m, 1H), 1.89 – 1.79 (m, 2H).

\(^{13}\)C NMR: (126 MHz, CDCl\(_3\))

\(\delta\) 159.35, 139.22, 130.69, 126.75, 113.77, 113.12, 93.75, 78.18, 55.40, 53.19, 30.46, 29.31, 18.90.

**HRMS:** (ESI- TOF MS ES-)

\(m/z\) calculated for C\(_{13}\)H\(_{15}\)Cl\(_3\)NO\(_4\)S [M-H]\(^-\): 385.9787, found 385.9784.
2,2,2-trichloroethyl-(6-methoxy-3,4-dihydranaphthalen-1(2H)-ylidene)sulfamate [S18].
Isolated as part of the oxidation reaction of 6-methoxy-1,2,3,4-tetrahydronaphthalene.

$^1$H NMR: (500 MHz, CDCl$_3$)

δ 8.17 (d, $J = 8.9$ Hz, 1H), 6.84 (dd, $J = 9.0$, 2.6 Hz, 1H), 6.71 (d, $J = 2.4$ Hz, 1H), 4.84 (s, 2H), 3.88 (s, 3H), 3.26 – 3.20 (m, 2H), 2.89 (t, $J = 6.1$ Hz, 2H), 2.04 (dq, $J = 7.1$, 6.1 Hz, 2H).

$^{13}$C NMR: (126 MHz, CDCl$_3$)

δ 182.65, 165.06, 147.98, 130.66, 124.36, 114.17, 113.11, 93.61, 79.28, 55.77, 33.21, 29.96, 22.55.

HRMS: (ESI- TOF MS ES+)

$m/z$ calculated for C$_{13}$H$_{15}$Cl$_3$NO$_4$[M+H]$^+$: 385.9787, found 385.9778.

2,2,2-trichloroethyl (6-methoxy-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)sulfamate [20]. According to the general procedure B, 5Å powdered molecular sieves (40 mg), (4-methylpentyl)benzene S19 (35.2 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ$_3$-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using ethyl acetate as the eluent (50 mL), the solvent was concentrated and the crude brown oil was loaded onto a silica gel column. Flash chromatography on 75mL of silica using gradient elution (500 mL of 100% dichloromethane then 200 mL of 1% diethyl ether in 99% dichloromethane followed by 200 mL of 2% diethyl ether in dichloromethane and then 200 mL of 5% diethyl ether in 95% dichloromethane) gave the pure product as a colorless oil.

Run 1 (42.7 mg, 0.106 mmol, 53% yield)
Run 2 (41.0 mg, 0.102 mmol, 51% yield)
Run 3 (40.3 mg, 0.100 mmol, 50% yield)

Average overall yield: 51% yield ± 1.5

$^1$H NMR: (500 MHz, CDCl$_3$)

$\delta$ 7.53 (d, $J$ = 8.6 Hz, 1H), 7.41 (d, $J$ = 2.8 Hz, 1H), 7.14 (dd, $J$ = 8.5, 2.8 Hz, 1H), 5.43 (br d, $J$ = 7.8 Hz, 1H), 4.91 (td, $J$ = 7.1, 4.0 Hz, 1H), 4.71 (d, $J$ = 10.9 Hz, 1H), 4.69 (d, $J$ = 10.9 Hz, 1H), 3.82 (s, 3H), 2.86 (ddd, $J$ = 17.6, 9.3, 4.6 Hz, 1H), 2.65 (ddd, $J$ = 17.7, 7.6, 4.6 Hz, 1H), 2.48 (ddt, $J$ = 13.6, 9.0, 4.3 Hz, 1H), 2.41 – 2.32 (m, 1H).

$^{13}$C NMR: (126 MHz, CDCl$_3$)

$\delta$ 196.64, 160.15, 133.38, 133.11, 129.80, 122.43, 109.96, 93.59, 78.26, 55.77, 52.77, 34.73, 29.77.

HRMS: (ESI- TOF MS ES+) $m/z$ calculated for C$_{13}$H$_{15}$Cl$_3$NO$_5$S [M+H]$^+$: 401.9737, found 401.9727.

2,2,2-trichloroethyl (1-(2,2,2-trifluoroacetyl)-1,2,3,4-tetrahydroquinolin-4-yl)sulfamate [21]. According to the general amination procedure B, 5Å powdered molecular sieves (40 mg), 1-(3,4-dihydroquinolin-1(2H)-yl)-2,2,2-trifluoroethan-1-one S20 (46.0 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ$_3$-iodanylidenesulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using diethyl ether as the eluent (50 mL), the solvent was concentrated and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography on 75 mL silica using gradient elution (100 mL of 100% hexanes then 400 mL of 5% ethyl acetate in 95% hexanes followed by 200 mL of 10% ethyl acetate in 90% hexanes) gave the pure product as a white solid.

Run 1 (71.1 mg, 0.156 mmol, 78% yield)

Run 2 (68.3 mg, 0.150 mmol, 75% yield)

Run 3 (69.3 mg, 0.152 mmol, 76% yield)
Average overall yield: 76% yield ± 1.5

$^1$H NMR: (500 MHz, CDCl$_3$ at 50 °C)

$\delta$ 7.68 (d, $J = 7.5$ Hz, 1H), 7.55 (d, $J = 7.6$ Hz, 1H), 7.34 (t, $J = 7.55$ Hz, 1H), 7.28 (t, $J = 7.4$ Hz, 1H), 5.35 (d, $J = 7.5$ Hz, 1H), 4.85 (q, $J = 6.3$ Hz, 1H), 4.70 – 4.64 (m, 2H), 3.90 (t, $J = 5.9$ Hz, 2H), 2.44 (dq, $J = 12.3, 6.0$ Hz, 1H), 2.33 (dq, $J = 11.8, 5.9$ Hz, 1H).

$^{13}$C NMR: (126 MHz, CDCl$_3$ at 50 °C)

$\delta$ 156.16 (q, $J = 36.3$ Hz), 136.86, 129.25, 129.10, 128.75, 127.42, 124.71, 116.63 (q, $J_{CF} = 288.3$ Hz), 93.68, 78.45, 51.05, 42.80, 31.35.

$^{19}$F NMR: (471 MHz, DMSO at 23 °C)

$\delta$ -68.19, -75.08 (rotational isomers).

HRMS: (ESI-TOF MS ES$^+$)

$m/z$ calculated for C$_{13}$H$_{16}$Cl$_3$F$_3$O$_4$S [M+NH$_4$]$^+$: 471.9879, found 471.9880.

2,2,2-trichloroethyl (1-(9-(phenylsulfonyl)-9H-carbazol-3-yl)ethyl)sulfamate [22]. According to the general amination procedure B, 5Å powdered molecular sieves (40 mg), 3-ethyl-9-(phenylsulfonyl)-9H-carbazole S21 (67.1 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-$\lambda^3$-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using diethyl ether as the eluent (30 mL), the solvent was concentrated and the crude brown oil was loaded onto a silica gel column using dichloromethane to quantitatively transfer the product. Flash chromatography using gradient elution (500 mL of 100% dichloromethane then 300 mL of 2% diethyl ether in 98% dichloromethane followed by 300 mL of 5% diethyl ether in 95% dichloromethane) gave the pure product as an orange solid.

Run 1 (70 mg, 0.125 mmol, 62% yield)

Run 2 (74 mg, 0.132 mmol, 66% yield)

Run 3 (75 mg, 0.133 mmol, 67% yield)

Average overall yield: 65% yield ± 2.6

$^1$H NMR: (500 MHz, Chloroform-$_d$)
δ 8.30 (dd, J = 9.9, 8.5 Hz, 2H), 7.93 – 7.86 (m, 2H), 7.81 (dd, J = 8.5, 1.3 Hz, 2H), 7.54 – 7.44 (m, 3H), 7.41 – 7.31 (m, 3H), 5.12 (d, J = 7.1 Hz, 1H), 4.90 (p, J = 6.9 Hz, 1H), 4.48 (d, J = 10.8 Hz, 1H), 4.45 (d, J = 10.8 Hz, 1H), 1.70 (d, J = 6.8 Hz, 3H)

13C NMR: (126 MHz, CDCl3)
δ 138.8, 138.0, 137.9, 137.3, 134.1, 129.3, 128.0, 126.9, 126.6, 126.0, 125.7, 124.3, 120.3, 118.1, 115.5, 115.2, 93.4, 78.2, 55.0, 23.2.

HRMS: (ESI-TOF MS ES+)
m/z calculated for C22H19N2O5S2Cl3Na [M+Na]+: 582.9699, found 582.9702

2,2,2-trichloroethyl (1-(4-(2-methyl-5-oxopyrrolidin-1-yl)phenyl)ethyl)sulfamate [23]. According to the general amination procedure B, 5Å powdered molecular sieves (40 mg), 1-(4-ethylphenyl)-5-methylpyrrolidin-2-one S22 (40.7 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ3-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using ethyl acetate as the eluent (50 mL), the solvent was concentrated and the crude brown oil was loaded onto a silica gel column. Flash chromatography on 75 mL silica using gradient elution (500 mL of 100% dichloromethane then 200 mL of 5% diethyl ether in 95% dichloromethane followed by 400 mL of 10% diethyl ether in 90% dichloromethane and then 200 mL of 20% diethyl ether in 80% dichloromethane and finally 400 mL of 50% diethyl ether in 50% dichloromethane) gave the pure product as an off-white oil in a 1:1 diastereomeric mixture. This compound was characterized as a mixture of diastereomers.

Run 1 (56.0 mg, 0.130 mmol, 65% yield)
Run 2 (53.3 mg, 0.124 mmol, 62% yield)
Run 3 (52.0 mg, 0.121 mmol, 61% yield)
Average overall yield: 63% yield ± 2.1 (1:1 d.r.)

1H NMR: (500 MHz, CDCl3) (mixture of diastereomers)
δ 7.41 – 7.34 (m, 4H), 5.64 (d, J = 7.5 Hz, 0.5H), 5.61 (d, J = 7.4 Hz, 0.5H), 4.71 (dq, J = 6.9 Hz, 0.5H), 4.71 (dq, J = 6.9 Hz, 0.5H), 4.47 (d, J = 10.8 Hz, 0.5H), 4.47 (d, J = 10.8 Hz, 0.5H), 4.43 (d, J = 10.8 Hz, 1H), 4.36 – 4.25 (m, 1H), 2.71 – 2.62 (m, 1H), 2.60 – 2.51 (m, 1H), 2.43 – 2.34 (m, 1H), 1.82 – 1.71 (m, 1H), 1.60 (d, J = 6.5 Hz, 1.5H), 1.58 (d, J = 6.5 Hz, 1.5H), 1.26 (d, J = 6.2 Hz, 1.5H), 1.24 (d, J = 6.2 Hz, 1.5H).

^13^C NMR: (126 MHz, CDCl₃) (mixture of diastereomers)
δ 174.92, 139.59, 139.52, 137.03, 136.98, 127.15, 127.06, 124.28, 124.21, 93.59, 93.57, 78.05, 55.87, 55.85, 54.38, 54.34, 31.46, 26.71, 26.69, 23.24, 22.92, 20.21.

HRMS: (ESI- TOF MS ES⁺)
m/z calculated for C₁₅H₂₀N₂O₄SCl₃[M+H]^+: 429.0209, found 429.0209.

2,2,2-trichloroethyl (1-(4-(5-methyl-2-oxooxazolidin-3-yl)phenyl)ethyl)sulfamate [24]. According to the general amination procedure B, 5Å powdered molecular sieves (40 mg), 3-(4-ethylphenyl)-5-methylxazolidin-2-one S23 (41.1 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ³-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using ethyl acetate as the eluent (50 mL), the solvent was concentrated and the crude brown oil was loaded onto a silica gel column. Flash chromatography on 75mL silica using gradient elution (500 mL of 100% dichloromethane then 200 mL of 1% diethyl ether in 99% dichloromethane followed by 400 mL of 2% diethyl ether in 98% dichloromethane and then 200 mL of 5% diethyl ether in 95% dichloromethane) gave the pure product as an off-white solid in a 1:1 diastereomeric mixture. This compound was characterized as a mixture of diastereomers.

**Run 1** (45.0 mg, 0.104 mmol, 52% yield)
**Run 2** (44.9 mg, 0.104 mmol, 52% yield)
**Run 3** (41.4 mg, 0.096 mmol, 48% yield)

**Average overall yield: 51% yield ± 2.3 (1:1 d.r.)**

^1^H NMR: (500 MHz, CDCl₃) (mixture of diastereomers)
\[ \delta 7.50 \text{ (d, } J = 8.7 \text{ Hz, 2H)}, \; 7.37 \text{ (d, } J = 8.6 \text{ Hz, 2H)}, \; 5.47 \text{ (s, 1H)}, \; 4.79 \text{ (sxt, } J = 6.3 \text{ Hz, 1H)}, \; 4.75 \text{ – 4.66 (m, 1H)}, \; 4.50 \text{ (d, } J = 10.8 \text{ Hz, 1H)}, \; 4.45 \text{ (d, } J = 10.8 \text{ Hz, 1H)}, \; 4.10 \text{ (td, } J = 8.5, 3.5 \text{ Hz, 1H)}, \; 3.61 \text{ (ddd, } J = 8.6, 7.1, 2.6 \text{ Hz, 1H)}, \; 1.60 \text{ (d, } J = 6.9 \text{ Hz, 3H)}, \; 1.53 \text{ (d, } J = 6.2 \text{ Hz, 3H}). \]

\[ ^{13}C \text{ NMR: (126 MHz, CDCl}_3 \text{) (mixture of diastereomers)} \]

\[ \delta 155.15, \; 138.21, \; 137.33, \; 127.19, \; 118.71, \; 93.55, \; 78.21, \; 69.94, \; 69.93, \; 54.43, \; 52.01, \; 52.00, \; 22.91, \; 22.91, \; 20.82, \; 20.80. \]

**HRMS:** (ESI-TOF MS ES+)

\[ m/z \text{ calculated for } C_{14}H_{18}N_2O_5SCl}_3 [M+H]^+: 431.0002, \text{ found 431.0006.} \]

**General amination procedure C for benzylic C–H amination of 3° amines and pyridines.** To a 1 dram vial equipped with a stir bar were added the nitrogen-containing substrate (0.20 mmol, 1.0 equiv.) and methylene chloride (DCM) (0.8 mL). Tetrafluoroboric acid diethyl ether complex (HBF\(_4\).OEt\(_2\)) (30.2 \(\mu\)L, 35.6 mg, 0.22 mmol, 1.1 equiv.) was added dropwise while stirring. The reaction mixture was stirred for 1 h at room temperature. Upon reaction completion, the stir bar was removed, and the mixture was concentrated in vacuo and placed on vacuum overnight. In a 10 mL round-bottom flask equipped with a stir bar was added 40 mg of powdered 3Å molecular sieves. The flask was then flame-dried under vacuum for 45 seconds, and refilled with argon using an thrice purged argon-filled balloon. In the 1-dram vial carrying the protonated substrate was added 0.2 mL of anhydrous 1,2-dichloroethane (DCE). The resulting solution or suspension was added into the round-bottom flask containing the 3Å molecular sieves. This process is repeated 2x with 0.1 mL DCE each time to ensure complete transfer. The reaction flask was then wrapped in aluminum foil and stirred for 10 min, upon which time manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.02 mmol, 0.10 equiv.) and silver hexafluoroantimonate (AgSbF\(_6\)) (6.9 mg, 0.02 mmol, 0.10 equiv.) were added while maintaining an argon atmosphere. The mixture was stirred for 10 min, and 2,2,2-trichloroethyl (phenyl-\(\lambda^3\)-iodanylidene)sulfamate (PhI=NTces) (172.2 mg, 0.40 mmol, 2.0 equiv.) was added while maintaining an argon atmosphere. The septum was replaced by a polyethylene yellow cap, and the flask was placed into 40 °C oil bath and stirred for 15 h. Upon completion, the flask was removed from the oil bath. Sodium hydroxide solution (1M, 3 mL) and DCM (3 mL) were then added. The reaction mixture was vigorously stirred for 15 min, and the layers were separated. The aqueous layer was extracted with CH\(_2\)Cl\(_2\) (3x5 mL). The organic layers were combined, dried over anhydrous potassium carbonate, filtered and concentrated via rotary evaporation. The crude material was purified by flash chromatography to afford the aminated product. (Note: Significant ketone byproduct formation and yield decrease were observed when an aged bottle of HBF\(_4\).OEt\(_2\) was used, possibly due to water absorption and/or decomposition.)
2,2,2-trichloroethyl (1'-methyl-3,4-dihydro-2H-spiro[naphthalene-1,4'-piperidin]-4-yl)sulfamate [26]. According to the general amination procedure C, 1'-methyl-3,4-dihydro-2H-spiro[naphthalene-1,4'-piperidine] 25 (64.6 mg, 0.30 mmol, 1.0 equiv.) in CH₂Cl₂ (1.2 mL) was protonated with HBF₄·OEt₂ (45.3 µL, 53.4 mg, 0.33 mmol, 1.1 equiv.), reacted with manganese (III) perchlorophthalocyanine chloride (34.6 mg, 0.030 mmol, 0.10 equiv.), AgSbF₆ (10.3 mg, 0.030 mmol, 0.10 equiv.), PhI=NTces (258.3 mg, 0.60 mmol, 2.0 equiv.), and 5Å molecular sieves (60 mg) in DCE (0.6 mL) for 15 h. Following work-up, the crude material was purified by flash chromatography (50 mL basic Al₂O₃ Brockmann grade III, gradient elution 25% EtOAc/Hex (4 column volumes)→0%→1%→2%→3% MeOH/CH₂Cl₂ (2 column volumes each)), staining with KMnO₄ to afford the product as a green oil. To remove the minimal co-eluding manganese catalyst, the product was re-dissolved in CH₂Cl₂ (10 mL) and extracted with 3M HCl (2x10 mL) and water (2x10 mL). The aqueous layers were combined and basified with 50% NaOH, extracted with CH₂Cl₂ (3x10 mL). The organic layers were combined, dried over K₂CO₃, and concentrated via rotary evaporation to afford the pure product as a white solid. The remaining organic layer after the acid wash was also basified and extracted likewise to afford the product as a white solid with discoloration.

Run 1 (78.9 mg, 0.18 mmol, 60% yield; 3.1 mg, 0.014 mmol, 5% rsm)
Run 2 (68.4 mg, 0.15 mmol, 52% yield; 9.6 mg, 0.045 mmol, 15% rsm)
Run 3 (81.0 mg, 0.18 mmol, 61% yield; 6.5 mg, 0.030 mmol, 10% rsm)

Average overall yield: 58% (10% rsm) ± 4.9

¹H NMR: (500 MHz, CDCl₃)

δ 7.49 (d, J = 7.6 Hz, 1H), 7.43 (d, J = 7.8 Hz, 1H), 7.29 (t, J = 7.4 Hz, 1H), 7.21 (t, J = 7.4 Hz, 1H), 4.73 (t, J = 5.3 Hz, 1H), 4.69 (s, 2H), 2.69 (d, J = 11.4 Hz, 1H), 2.66 (d, J = 11.4 Hz, 1H), 2.31 (s, 3H), 2.27-2.17 (m, 2H), 2.17-1.94 (m, 4H), 1.90 (app t, J = 5.8 Hz, 2H), 1.51 (t, J = 12.9 Hz, 2H)

¹³C NMR: (126 MHz, CDCl₃)

δ 145.61, 134.79, 129.01, 128.81, 127.35, 126.66, 93.83, 78.10, 54.20, 51.57, 46.45, 38.26, 37.62, 34.82, 29.83, 26.24, 25.95

HRMS: (ESI-TOF MS ES+)
m/z calculated for C_{17}H_{24}Cl_{3}N_{2}O_{3}S [M+H]^+ : 441.0573, found 441.0565.

**Figure 2, Entry 1.**
Reaction without HBF₄ protection and base workup:

**Run 1** (0 mg, 0 mmol, 0% yield; 30.4 mg, 0.141 mmol, 47% rsm)

**Figure 2, Entry 3.**
Reaction with BF₃ protection (40.7 µL, 46.8 mg, 0.33 mmol, 1.1 equiv.) and base workup (1M NaOH, 5 mL, 4 h):

**Run 1** (64.8 mg, 0.147 mmol, 49% yield; 1.9 mg, 0.0090 mmol, 3% rsm)

**Run 2** (70.3 mg, 0.159 mmol, 53% yield; 1.3 mg, 0.0060 mmol, 2% rsm)

**Average overall yield:** 51% (2% rsm)

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

2,2,2-trichloroethyl (4-(dimethylamino)-1-phenylbutyl)sulfamate [27]. According to the general amination procedure C, N,N-dimethyl-4-phenylbutan-1-amine S24 (35.5 mg, 0.20 mmol, 1.0 equiv.) was protonated with HBF₄·OEt₂ (30.2 µL, 35.6 mg, 0.22 mmol, 1.1 equiv.), reacted with manganese (III) perchlorophthalocyanine chloride (34.6 mg, 0.030 mmol, 0.15 equiv.), AgSbF₆ (10.3 mg, 0.030 mmol, 0.15 equiv.), PhI=NTces (258.3 mg, 0.60 mmol, 3.0 equiv.), and 5Å molecular sieves (40 mg) in DCE (0.4 mL). PhI=NTces was added in one portion. Following work-up, the crude material was purified by flash chromatography (50 mL basic Al₂O₃ Brockmann grade III, gradient elution 30% EtOAc/Hex (4 column volumes) → 0% → 1% → 2% → 3% MeOH/CH₂Cl₂ (2 column volumes each)), staining with KMnO₄. The resulting solid was redissolved in acetonitrile, and the undissolved green solid was removed. The solution was concentrated via rotary evaporation to afford the product as a light yellow oil.

**Run 1** (40.5 mg, 0.10 mmol, 50% yield; 4.7 mg, 0.027 mmol, 13% rsm)

**Run 2** (39.2 mg, 0.097 mmol, 49% yield; 3.8 mg, 0.021 mmol, 11% rsm)

**Run 3** (41.0 mg, 0.10 mmol, 51% yield; 2.4 mg, 0.014 mmol, 7% rsm)

**Average overall yield:** 50% (10% rsm) ± 1.0

¹H NMR: (500 MHz, CDCl₃)
δ 7.39-7.30 (m, 4H), 7.24 (d, J = 6.9 Hz, 1H), 4.56 (t, J = 4.6 Hz, 1H), 4.38 (d, J = 11.2 Hz, 1H), 4.35 (d, J = 11.3 Hz, 1H), 2.46 (dt, J = 11.4, 4.9 Hz, 1H), 2.34 (t, 6H), 2.34-2.27 (m, 1H), 2.10-2.00 (m, 2H), 1.58 (p, J = 4.8 Hz, 2H)

13C NMR: (126 MHz, CDCl3)
δ 141.99, 128.54, 127.33, 126.64, 94.16, 77.70, 59.66, 57.57, 44.63, 37.76, 23.03

HRMS: (ESI-TOF MS ES+)
m/z calculated for C14H22Cl3N2O3S [M+H]+: 403.0417, found 403.0409.

2,2,2-trichloroethyl (3-(1-methylpiperidin-4-yl)-1-phenylpropyl)sulfamate [28]. According to the general amination procedure C, 1-methyl-4-(3-phenylpropyl)piperidine S25 (43.5 mg, 0.20 mmol, 1.0 equiv.) was protonated with HBF4·OEt2 (30.2 µL, 35.6 mg, 0.22 mmol, 1.1 equiv.), reacted with manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.10 equiv.), AgSbF6 (6.9 mg, 0.020 mmol, 0.10 equiv.), Phl=NTces (172.2 mg, 0.40 mmol, 2.0 equiv.), and 5Å molecular sieves (40 mg) in DCE (0.4 mL). After 2 h of reaction, another batch of Phl=NTces (86.1 mg, 0.20 mmol, 1.0 equiv.) was quickly added to the reaction mixture. The reaction was further stirred for 13 h. Following work-up, the crude material was purified by flash chromatography (50 mL basic Al2O3 Brockmann grade III, gradient elution 30% EtOAc/Hex (4 column volumes)→0%→1%→2%→3% MeOH/CH2Cl2 (2 column volumes each)), staining with KMnO4 to afford the product as a white solid with green discoloration.

Run 1 (53.9 mg, 0.12 mmol, 61% yield; 7.1 mg, 0.033 mmol, 16% rsm)
Run 2 (47.4 mg, 0.11 mmol, 53% yield; 7.6 mg, 0.035 mmol, 17% rsm)
Run 3 (51.0 mg, 0.11 mmol, 57% yield; 8.0 mg, 0.037 mmol, 18% rsm)
Average overall yield: 57% (17% rsm) ± 4.0

1H NMR: (500 MHz, CDCl3)
δ 7.36 (d, J = 7.2 Hz, 2H), 7.33-7.27 (m, 3H), 4.46 (t, J = 7.4 Hz, 1H), 4.33 (d, J = 10.8 Hz, 1H), 4.29 (d, J = 10.8 Hz, 1H), 2.81 (d, J = 11.4 Hz, 2H), 2.21 (s, 3H), 2.02-1.90 (m, 1H), 1.90-1.78 (m, 3H), 1.62 (d, J = 9.2 Hz, 2H), 1.40-1.28 (m, 1H), 1.28-1.14 (m, 4H)

13C NMR: (126 MHz, CDCl3)
δ 140.75, 129.12, 128.39, 126.78, 93.47, 78.07, 59.91, 56.00, 46.53, 35.00, 34.25, 32.96, 32.38, 32.31
HRMS: (ESI-TOF MS ES+)
m/z calculated for C_{17}H_{26}Cl_{3}N_{2}O_{3}S [M+H]^+: 443.0730, found 443.0727.

2,2,2-trichloroethyl (4-(pyridin-4-yl)-1,2,3,4-tetrahydronaphthalen-1-yl)sulfamate [29]. According to the general amination procedure C, 4-(1,2,3,4-tetrahydronaphthalen-1-yl)pyridine S26 (41.9 mg, 0.20 mmol, 1.0 equiv.) was protonated with HBF₄.OEt₂ (30.2 µL, 35.6 mg, 0.22 mmol, 1.1 equiv.), reacted with manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.10 equiv.), AgSbF₆ (6.9 mg, 0.020 mmol, 0.10 equiv.), PhI=NTces (172.2 mg, 0.40 mmol, 2.0 equiv.), and 3Å molecular sieves (40 mg) in DCE (0.4 mL). After 2 h of reaction, another batch of PhI=NTces (86.1 mg, 0.20 mmol, 1.0 equiv.) was quickly added to the reaction mixture. The reaction was further stirred for 13 h. Following work-up, the crude material was purified by flash chromatography (50 mL silica, gradient elution 20% → 40% → 60% → 80% EtOAc/hexanes (2 column volumes each)) to afford the product as a white solid with green discoloration as a mixture of diastereomers.

**Run 1** (38.4 mg, 0.088 mmol, 44% yield, 1:1 d.r.; 0.8 mg, 0.004 mmol, 2% rsm)

**Run 2** (35.6 mg, 0.082 mmol, 41% yield, 1:1 d.r.; 6.7 mg, 0.032 mmol, 16% rsm)

**Run 3** (35.6 mg, 0.082 mmol, 41% yield, 1:1 d.r.; 2.9 mg, 0.014 mmol, 7% rsm)

**Average overall yield: 42% (8% rsm) ± 1.7, 1:1 d.r.**

**¹H NMR:** (400 MHz, CDCl₃) (mixture of diastereomers)

δ 8.34 (m, 2H), 7.63 (dd, J = 7.7, 3.9 Hz, 1H), 7.30 (td, J = 7.6, 3.5 Hz, 1H), 7.24-7.18 (m, 1H), 6.94 (m, 2H), 6.82 (m, 1H), 6.65 (d, J = 7.7 Hz, 0.5H), 6.02 (d, J = 7.8 Hz, 0.5H), 4.93-4.83 (m, 1H), 4.71 (s, 1H), 4.69 (s, 1H), 4.16 (t, J = 6.1 Hz, 0.5H), 4.05 (d, J = 6.0 Hz, 0.5H), 2.39-2.28 (m, 0.5H), 2.24-2.07 (m, 2H), 2.07-1.94 (m, 1H), 1.88 (dt, J = 13.7, 7.0 Hz, 0.5H)

**¹³C NMR:** (101 MHz, CDCl₃) (mixture of diastereomers)

δ 156.21, 155.88, 149.07, 148.85, 137.81, 137.51, 135.73, 135.55, 130.39, 130.10, 129.85, 129.36, 128.63, 127.86, 127.78, 124.44, 124.25, 93.81, 93.77, 78.07, 78.02, 60.57, 53.15, 44.79, 44.12, 28.41, 28.31, 28.04, 27.47

HRMS: (ESI-TOF MS ES+)
m/z calculated for C_{17}H_{18}Cl_{3}N_{2}O_{3}S [M+H]^+: 435.0104, found 435.0104.
**2,2,2-trichloroethyl (4-amino-1-phenylbutyl)sulfamate boron trifluoride complex** [30]. Prepared according to the general amination procedure B. 4-phenylbutan-1-amine boron trifluoride complex S27 (43.4 mg, 0.20 mmol, 1.0 equiv.) was reacted with manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.10 equiv.), AgSbF$_6$ (6.9 mg, 0.020 mmol, 0.10 equiv.), PhI=NTces (172.2 mg, 0.40 mmol, 2.0 equiv.), and 5Å molecular sieves (40 mg) in DCE (0.4 mL) for 15 h. The crude material was purified by flash chromatography (50 mL silica, gradient elution CH$_2$Cl$_2$ (12 column volumes)→10%→20%→30%→40% EtOAc/Hex (4 column volumes each)), staining with ninhydrin to afford the product as a white solid with slight discoloration.

**Run 1** (48.7 mg, 0.11 mmol, 55% yield; 11.4 mg, 0.053 mmol, 26% rsm)

**Run 2** (54.4 mg, 0.12 mmol, 61% yield; 11.3 mg, 0.052 mmol, 26% rsm)

**Run 3** (46.9 mg, 0.11 mmol, 53% yield; 12.8 mg, 0.059 mmol, 30% rsm)

**Average overall yield:** 56% (27% rsm) ± 4.1

$^1$H NMR: (500 MHz, CD$_3$CN)

δ 7.43-7.35 (m, 4H), 7.35-7.29 (m, 1H), 6.64 (d, $J = 8.4$ Hz, 1H), 4.57 (br s, 2H), 4.44 (q, $J = 8.2$ Hz, 1H), 4.39 (d, $J = 11.0$ Hz, 1H), 4.20 (d, $J = 11.0$ Hz, 1H), 2.76 (p, $J = 7.1$ Hz, 2H), 1.93-1.86 (m, 1H), 1.83-1.75 (m, 1H), 1.75-1.65 (m, 1H), 1.58-1.47 (m, 1H)

$^{13}$C NMR: (101 MHz, CD$_3$CN)

δ 142.19, 129.69, 128.86, 127.65, 94.22, 78.48, 59.76, 41.21, 34.61, 25.88

$^{19}$F NMR: (470 MHz, CD$_3$CN)

δ -151.91 (dd, $J = 32.4$, 15.9 Hz, 3F)

HRMS: (ESI-TOF MS ES-)

$m/z$ calculated for C$_{12}$H$_{16}$BCl$_3$F$_3$N$_2$O$_3$S [M-H]$^-$: 440.9992, found 440.9984.
V. Experimental procedures and compound characterization for Figure 3

Figure 3. Late-stage benzylic C—H amination of bioactive molecules.

General procedures: In Figure 3 the general procedure B for benzylic amination was followed for non-basic nitrogen containing substrates and the general procedure C for benzylic amination was followed for substrates containing basic nitrogen functionality.

2,2,2-trichloroethyl (6,6,7,7,7-pentafluoro-5-oxo-1-phenylheptyl)sulfamate [31]. According to the general amination procedure B, 5Å powdered molecular sieves (40 mg), 1,1,1,2,2-pentafluoro-7-phenylheptan-3-one S28 (56.0 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ³-iodanylidene)sulfamate (172.2 mg, 0.40
mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using diethyl ether as the eluent (30 mL), the solvent was concentrated and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography using gradient elution (100 mL of 100% hexanes then 300 mL of 5% ethyl acetate in 95% hexanes followed by 600 mL of 10% ethyl acetate in 90% hexanes) gave the pure product as a yellow solid.

**Run 1** (53 mg, 0.105 mmol, 52% yield)
**Run 2** (53 mg, 0.105 mmol, 52% yield)
**Run 3** (50 mg, 0.099 mmol, 49% yield)

**Average overall yield: 51% yield ± 1.7**

**$^1$H NMR:** (500 MHz, Chloroform-$d$)
\[
\delta 7.39 \text{ (dd, } J = 8.1, 6.5 \text{ Hz, } 2H), 7.37 - 7.33 \text{ (m, } 1H), 7.32 - 7.28 \text{ (m, } 2H), 5.16 \text{ (d, } J = 7.7 \text{ Hz, } 1H), 4.51 \text{ (q, } J = 7.4 \text{ Hz, } 1H), 4.36 \text{ (d, } J = 10.8 \text{ Hz, } 1H), 4.30 \text{ (d, } J = 10.8 \text{ Hz, } 1H), 2.78 \text{ (t, } J = 6.9 \text{ Hz, } 2H), 2.05 - 1.94 \text{ (m, } 1H), 1.93 - 1.83 \text{ (m, } 1H), 1.83 - 1.72 \text{ (m, } 1H), 1.69 - 1.55 \text{ (m, } 1H)
\]

**$^{13}$C NMR:** (126 MHz, CDCl$_3$)
\[
\delta 194.0 \text{ (t, } J = 26.7 \text{ Hz), 139.9, 129.3, 128.7, 126.7, 117.9 (qt, } J = 286.6, 34.0 \text{ Hz), 106.9 (tq, } J = 266.8, 37.9 \text{ Hz), 93.3, 78.2, 59.3, 36.7, 35.6, 19.0}
\]

**$^{19}$F NMR:** (470 MHz, Chloroform-$d$)
\[
\delta -82.33, -123.79
\]

**HRMS:** (ESI-TOF MS ES-)
\[
m/z \text{ calculated for C}_{15}H_{14}NO_4S_iCl_3 [M-H]: 503.9629, found 503.9612}
\]

![Methyl 4'-(1-((2,2,2-trichloroethoxy)sulfonyl)amino)hexyl]-[1,1'-biphenyl]-4-carboxylate](image)

Methyl 4'-(1-((2,2,2-trichloroethoxy)sulfonyl)amino)hexyl]-[1,1'-biphenyl]-4-carboxylate [32]. According to the general amination procedure B, 5Å powdered molecular sieves (40 mg), methyl 4'-hexyl-[1,1'-biphenyl]-4-carboxylate S29 (59.3 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ$^3$-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask
and stirred for 8-12 h. After silica plug filtration using diethyl ether as the eluent (30 mL), the solvent was concentrated and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography using gradient elution (100 mL of 100% hexanes then 300 mL of 5% ethyl acetate in 95% hexanes followed by 600 mL of 10% ethyl acetate in 90% hexanes) gave the pure product as a white solid.

Run 1 (82 mg, 0.157 mmol, 78% yield)
Run 2 (83 mg, 0.159 mmol, 79% yield)
Run 3 (75 mg, 0.143 mmol, 72% yield)

**Average overall yield: 76% yield ± 3.8**

\(^1\)H NMR: (500 MHz, Chloroform-\(d\))

\(\delta\) 8.10 (d, \(J = 7.8\) Hz, 2H), 7.61 (dd, \(J = 8.1, 6.0\) Hz, 4H), 7.41 (d, \(J = 7.8\) Hz, 2H), 5.61 (d, \(J = 7.4\) Hz, 1H), 4.55 (q, \(J = 7.3\) Hz, 1H), 4.37 (d, \(J = 10.8\) Hz, 1H), 4.33 (d, \(J = 10.8\) Hz, 1H), 3.94 (s, 3H), 2.04 – 1.90 (m, 1H), 1.90 – 1.79 (m, 1H), 1.46 – 1.34 (m, 1H), 1.34 – 1.23 (m, 5H), 0.87 (d, \(J = 7.4\) Hz, 3H)

\(^13\)C NMR: (126 MHz, CDCl\(_3\))

\(\delta\) 167.2, 145.0, 140.9, 139.9, 130.3, 129.1, 127.9, 127.4, 127.1, 93.4, 78.1, 59.4, 52.4, 37.0, 31.4, 25.8, 22.5, 14.1

HRMS: (ESI-TOF MS ES+)

\(m/z\) calculated for C\(_{22}\)H\(_{27}\)NO\(_5\)S\(_3\)Cl\(_3\) [M+H]^+: 522.0676, found 522.0668

**Methyl 4’-(1-aminohexyl)-[1,1’-biphenyl]-4-carboxylate [33].** The reaction was performed according to a previously reported procedure.\(^1\) In a 50 mL round bottom flask under N\(_2\) containing a Teflon stir bar was added methyl 4’-(1-(((2,2,2-trichloroethoxy)sulfonyl)amino)hexyl)-[1,1’-biphenyl]-4-carboxylate 32 (205 mg, 0.39 mmol, 1 equiv), Zn/Cu couple (256 mg, 3.92 mmol, 10 equiv), and 1:1 MeOH:AcOH (12 mL). The reaction was vigorously stirred for 48 h then filtered through celite, using methanol to rinse the filter cake and concentrated. To the resulting solid was added methanolic HCl (prepared from mixing 1.22 mL acetyl chloride and 16 mL of MeOH) and the reaction heated to 40 °C for 12 h under N\(_2\). Upon reaction completion, 50 mL of EtOAc was added at room temperature and the solution was washed with K\(_2\)CO\(_3\) (1 x 15 mL). Additional EtOAc (2 x 50 mL) was used to extract the resulting aqueous layer.
organic layers were combined and dried over K$_2$CO$_3$, filtered, and concentrated. No further purification was necessary for the resulting white solid (108 mg, 88% yield).

$^1$H NMR: (400 MHz, Chloroform-$d$)

δ 8.09 (d, $J = 8.3$ Hz, 2H), 7.63 (d, $J = 8.6$ Hz, 2H), 7.58 (d, $J = 8.2$ Hz, 2H), 7.40 (d, $J = 8.2$ Hz, 2H), 3.97–3.91 (m, 4H), 2.74 (br s, 2H), 1.80–1.63 (m, 2H), 1.38–1.14 (m, 6H), 0.85 (t, $J = 6.7$ Hz, 3H);

$^{13}$C NMR: (101 MHz, CDCl$_3$)

δ 167.0, 145.7, 145.3, 138.7, 130.1, 128.8, 127.4, 127.1, 126.9, 56.0, 52.2, 39.1, 31.8, 26.2, 22.6, 14.1;

HRMS: (ESI-TOF MS ES$^+$)

$m/z$ calculated for C$_{20}$H$_{26}$NO$_2$ [M+H]$^+$: 312.1964, found 312.1964

rac-2,2,2-trichloroethyl (1-((9S,10R,11R,15S)-13-methyl-12,14-dioxo-9,10-dihydro-9,10-[3,4]epipyrroloanthracen-2-yl)ethyl)sulfamate [34]. Prepared according to the general amination procedure B. rac-(9S,10R,11R,15S)-2-ethyl-13-methyl-9,10-dihydro-9,10-[3,4]epipyrroloanthracene-12,14-dione S30 (63.5 mg, 0.20 mmol, 1.0 equiv.) was reacted with manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.10 equiv.), AgSbF$_6$ (6.9 mg, 0.020 mmol, 0.10 equiv.), PhI=NTces (172.2 mg, 0.40 mmol, 2.0 equiv.), and 5Å molecular sieves (40 mg) in benzene (0.4 mL) for 10 h. The crude reaction mixture was directly purified by flash chromatography (50 mL silica, 20%→30%→40%→50% EtOAc/Hex (2 column volumes each)) to afford the product as a white solid with slight discoloration as a mixture of diastereomers.

Run 1 (84.8 mg, 0.156 mmol, 78% yield, 1:1 d.r.)

Run 2 (95.8 mg, 0.176 mmol, 88% yield, 1:1 d.r.)

Run 3 (93.7 mg, 0.172 mmol, 86% yield, 1:1 d.r.)

Average overall yield: 84% yield ± 5.3, 1:1 d.r.

$^1$H NMR: (500 MHz, CDCl$_3$)
δ 7.39-7.33 (m, 2H), 7.30-7.23 (m, 2H), 7.18 (dd, J = 5.3, 3.2 Hz, 2H), 7.13 (d, J = 7.6 Hz, 1H), 5.15 (br s, 1H), 4.82-4.74 (m, 2H), 4.65 (app dq, J = 14.2, 7.0 Hz, 1H), 4.45-4.35 (m, 2H), 3.20 (app s, 2H), 2.50 (s, 3H), 1.54 (app t, J = 6.4 Hz, 3H)

13C NMR: (126 MHz, CDCl3)

δ 177.16, 177.08, 176.99, 176.98, 141.13, 141.10, 141.08, 141.06, 140.83, 140.75, 139.46, 138.76, 138.64, 127.03, 127.02, 126.99, 126.98, 125.41, 125.37, 125.33, 124.85, 124.47, 124.44, 124.42, 123.25, 122.30, 93.39, 93.36, 78.11, 54.72, 54.69, 46.99, 46.95, 45.73, 45.65, 45.29, 24.46, 24.43, 23.43, 22.98

HRMS: (ESI-TOF MS ES+)

m/z calculated for C23H21Cl3N2O5SNa [M+Na]+: 565.0134, found 565.0135.

For NOESY see Supporting Information: Spectral Data

Stereochemistry was assigned based on 1H NMR and NOESY 1D NMR methods.

2,2,2-trichloroethyl (1'-((2,2,2-trifluoroacetyl)-3,4-dihydro-2H-spiro[naphthalene-1,4'-piperidin]-4-yl)sulfamate [35]. According to the general amination procedure B, 5Å powdered molecular sieves (40 mg), 1-(3,4-dihydro-2H-spiro[naphthalene-1,4'-piperidin]-1'-yl)-2,2,2-trifluoroethan-1-one S31 (59.5 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-X3-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using diethyl ether as the eluent
(30 mL), the solvent was concentrated and the crude brown oil was loaded onto a silica gel column using dichloromethane to quantitatively transfer the product. Flash chromatography using gradient elution (500 mL of 100% dichloromethane then 300 mL of 2% diethyl ether in 98% dichloromethane followed by 300 mL of 5% diethyl ether in 95% dichloromethane) gave the pure product as a light yellow solid.

**Run 1** (87 mg, 0.166 mmol, 83% yield)

**Run 2** (89 mg, 0.170 mmol, 85% yield)

**Run 3** (92 mg, 0.176 mmol, 88% yield)

**Average overall yield: 85% yield ± 2.5**

**1H NMR:** (500 MHz, Chloroform-d)

\[ \delta \ 7.48 \ (dd, \ J = 7.7, 3.5 \ Hz, \ 1H), \ 7.37 - 7.29 \ (m, \ 2H), \ 7.27 - 7.23 \ (m, \ 1H), \ 5.26 \ (d, \ J = 7.4 \ Hz, \ 0.5H), \ 5.22 \ (d, \ J = 7.4 \ Hz, \ 0.5H), \ 4.78 - 4.73 \ (m, \ 1H), \ 4.67 \ (app \ s, \ 2H), \ 4.46 \ (app \ t, \ J = 14.8 \ Hz, \ 1H), \ 3.41 \ (app \ q, \ J = 11.9 \ Hz, \ 1H), \ 3.00 \ (q, \ J = 11.7 \ Hz, \ 1H), \ 2.18 - 1.98 \ (m, \ 5H), \ 1.99 - 1.87 \ (m, \ 1H), \ 1.70 \ (d, \ J = 13.8 \ Hz, \ 2H) \]

**13C NMR:** (101 MHz, CDCl3)

\[ \delta \ 155.7 \ (q, \ J = 35.7 \ Hz), \ 143.7, \ 134.4, \ 134.3, \ 129.4, \ 129.3, \ 129.2, \ 129.1, \ 127.3, \ 127.1, \ 116.7 \ (q, \ J = 287.9 \ Hz), \ 93.7, \ 78.1, \ 53.9, \ 53.8, \ 42.2, \ 39.9, \ 39.8, \ 38.7, \ 37.6, \ 37.6, \ 36.5, \ 35.6, \ 25.9, \ 25.8, \ 25.7 \]

**19F NMR:** (470 MHz, Chloroform-d)

\[ \delta \ -69.20 \ (d, \ J = 7.6 \ Hz) \]

**HRMS:** (ESI-TOF MS ES-)

\[ m/z \ \text{calculated for C}_{18}H_{19}N_{2}O_{4}SCl_{3}F_{3} [M-H]^{-}: 521.0083, \ \text{found} \ 521.0079 \]

**trans-2,2,2-trichloroethyl (6-cyano-3-(3-(dimethylamino)propyl)-3-(4-fluorophenyl)-1,3-dihydroisobenzofuran-1-yl)sulfamate [(±)36].** According to the general amination procedure C, 1-(3-(dimethylamino)propyl)-1-(4-fluorophenyl)-1,3-dihydroisobenzofuran-5-carbonitrile (±)S32 (64.9 mg, 0.20 mmol, 1.0 equiv.) in CH2Cl2 (1.2 mL) was protonated with HBF4OEt2 (30.2 µL, 35.6 mg, 0.22 mmol, 1.1 equiv.), reacted with manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.10 equiv.), AgSbF6 (6.9 mg, 0.020 mmol, 0.10 equiv.), PhI=NTces (172.2 mg, 0.40 mmol, 2.0 equiv.),
and 3Å molecular sieves (40 mg) in DCE (0.4 mL) for 15 h. Upon reaction completion, the reaction mixture was partitioned between 1M NaOH (3 mL) and CH₂Cl₂ (3 mL). The aqueous layer was extracted with CH₂Cl₂ (3x5 mL). The organic layers were combined, dried over anhydrous MgSO₄, condensed in vacuo, and purified by flash chromatography (50 mL basic Al₂O₃ Brockmann grade III, gradient elution 30% EtOAc/Hex (4 column volumes)→0%→1%→2%→3% MeOH/CH₂Cl₂ (2 column volumes each)). The resulting solid was re-dissolved in acetonitrile, and the undissolved green solid was removed. The solution was concentrated via rotary evaporation. The resulting oil was re-dissolved in CH₂Cl₂ and concentrated via rotary evaporation to afford the product as a white solid with slight discoloration. The relative configuration was determined by NOESY and crystallography data.

Run 1 (77.7 mg, 0.141 mmol, 71% yield, >20:1 d.r.)
Run 2 (78.2 mg, 0.142 mmol, 71% yield, >20:1 d.r.)
Run 3 (77.2 mg, 0.140 mmol, 70% yield, >20:1 d.r.)

Average overall yield: 71% (0% rsm) ±0.6, >20:1 d.r.

¹H NMR: (500 MHz, CDCl₃)
δ 11.89 (br s, 1H), 8.00 (s, 1H), 7.56-7.47 (m, 3H), 7.14 (d, J = 7.6 Hz, 1H), 7.07 (t, J = 8.6 Hz, 2H), 6.73 (s, 1H), 4.66 (d, J = 10.9 Hz, 1H), 4.53 (d, J = 10.9 Hz, 1H), 3.28 (dt, J = 11.4, 5.9 Hz, 1H), 2.71 (s, 6H), 2.65-2.59 (m, 1H), 2.48-2.39 (m, 1H), 2.38-2.29 (m, 1H), 1.85-1.66 (m, 2H)

¹³C NMR: (126 MHz, CDCl₃)
δ 162.40 (d, J = 247.4 Hz), 149.62, 142.09, 137.40, 132.65, 128.17, 126.99 (d, J = 8.1 Hz), 121.83, 118.56, 115.94 (d, J = 21.3 Hz), 112.48, 95.32, 90.96, 90.19, 77.78, 57.00, 42.88, 37.08, 20.67

¹⁹F NMR: (470 MHz, CDCl₃)
δ -114.82 (s, 1F)

HRMS: (ESI-TOF MS ES+)

m/z calculated for C₂₂H₂₅ClN₃O₄FS [M+H]⁺: 550.0537, found 550.0537.

For COSY and NOESY see Supporting Information: Spectral Data
Stereochemistry was assigned based on $^1$H NMR and NOESY 1D NMR methods.

2,2,2-trichloroethyl (trans-4-ethyl-1,2,3,4,4a,5,6,10b-octahydrobenzo[f]quinolin-6-yl)sulfamate [(±)37]. According to the general procedure C, trans-4-ethyl-1,2,3,4,4a,5,6,10b-octahydrobenzo[f]quinoline (±)S33 (43.1 mg, 0.20 mmol, 1.0 equiv.) was protonated with HBF$_4$OEt$_2$ (30.2 µL, 35.6 mg, 0.22 mmol, 1.1 equiv.), reacted with manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.10 equiv.), AgSbF$_6$ (6.9 mg, 0.020 mmol, 0.10 equiv.), PhI=NTces (172.2 mg, 0.40 mmol, 2.0 equiv.), and 3Å molecular sieves (40 mg) in DCE (0.4 mL). After 2 h of reacting, another batch of PhI=NTces (86.1 mg, 0.20 mmol, 1.0 equiv.) was quickly added to the reaction mixture. The reaction was further stirred for 13 h. Following work-up, the crude material was purified by flash chromatography (50 mL basic Al$_2$O$_3$ Brockmann grade III, gradient elution 30% EtOAc/Hex (4 column volumes)→0%→1%→2%→3% MeOH/CH$_2$Cl$_2$ (2 column volumes each)), staining with KMnO$_4$ to afford the product as a white solid with green discoloration as a mixture of diastereomers. The relative configuration was determined by NOESY and crystallography data.

**Run 1** (53.6 mg, 0.121 mmol, 61% yield, 5:1 d.r.)

**Run 2** (53.8 mg, 0.122 mmol, 61% yield, 6:1 d.r.)

**Run 3** (49.3 mg, 0.112 mmol, 56% yield, 5:1 d.r.; 4.3 mg, 0.020 mmol, 10% rsm)

**Average overall yield: 59% (3% rsm) ± 2.9, 5:1 dr**

Data for major diastereomer (±)37:

$^1$H NMR: (500 MHz, CDCl$_3$)

δ 7.48 (dd, $J = 7.6$, 1.2 Hz, 1H), 7.35 (d, $J = 7.7$ Hz, 1H), 7.31 (td, $J = 7.7$, 1.5 Hz, 1H), 7.26 (td, $J = 7.3$, 1.1 Hz, 1H), 4.98 (dd, $J = 4.2$, 2.7 Hz, 1H), 4.74 (d, $J = 10.9$ Hz, 1H), 4.72 (d, $J = 10.9$ Hz, 1H), 3.05 (dt, $J = 11.4$, 3.0 Hz, 1H), 2.95 (dq, $J = 14.4$, 7.2 Hz, 1H), 2.75 (dt, $J = 13.5$, 2.3 Hz, 1H), 2.70 (dq, $J = 14.0$, 6.7 Hz, 1H), 2.60-2.49 (m, 2H), 2.36-2.25 (m, 2H), 1.92-1.86 (m, 1H), 1.86-1.78 (m, 2H), 1.37 (qd, $J = 12.7$, 3.9 Hz, 1H), 1.08 (t, $J = 7.2$ Hz, 3H)

$^{13}$C NMR: (101 MHz, CDCl$_3$)

δ 139.92, 133.19, 129.69, 128.93, 127.08, 126.09, 93.72, 78.08, 57.90, 53.50, 52.36, 46.90, 42.47, 33.28, 29.18, 25.57, 9.64

HRMS: (ESI-TOF MS ES+)
m/z calculated for C₁₇H₂₄Cl₃N₂O₃S [M+H]⁺: 441.0573, found 441.0567.

For COSY and NOESY see Supporting Information: Spectral Data

Stereochemistry was assigned based on ¹H NMR, COSY, and NOESY ¹D NMR methods.

Data for minor diastereomer (+)S₃₄:

¹H NMR: (500 MHz, CDCl₃)

δ 7.61 (d, J = 6.9 Hz, 1H), 7.32 (t, J = 7.1 Hz, 1H), 7.28 (d, J = 6.7 Hz, 1H), 7.27-7.24 (m, 1H), 4.92 (dd, J = 11.2, 6.1 Hz, 1H), 4.74 (d, J = 10.8 Hz, 1H), 4.70 (d, J = 10.8 Hz, 1H), 3.01 (d, J = 11.5 Hz, 1H), 2.99-2.95 (m, 1H), 2.92 (dt, J = 14.3, 7.1 Hz, 1H), 2.68 (dq, J = 13.9, 7.3 Hz, 2H), 2.48 (dd, J = 12.6, 2.6 Hz, 1H), 2.30-2.19 (m, 2H), 1.89-1.76 (m, 2H), 1.63 (q, J = 11.7 Hz, 1H), 1.19 (qd, J = 12.7, 4.2 Hz, 1H), 1.03 (t, J = 7.1 Hz, 3H)

HRMS: (ESI-TOF MS ES⁺)

m/z calculated for C₁₇H₂₄Cl₃N₂O₃S [M+H]⁺: 441.0573, found 441.0566.

For COSY see Supporting Information: Spectral Data

(−)2,2,2-trichloroethyl ((4aS,9S,10aR)-4a-benzyl-2-oxo-1,2,3,4,4a,9,10,10a-octahydrophenanthren-9-yl)sulfamate [38]. According to the general amination procedure B, 5Å powdered molecular sieves (40 mg), (4aS,10aR)-4a-benzyl-3,4,4a,9,10,10a-hexahydrophenanthren-2(1H)-one (−)S₃₅ (58.1 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg,
0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ³-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using diethyl ether as the eluent (30 mL), the solvent was concentrated and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography using gradient elution (500 mL of 100% dichloromethane then 300 mL of 2% diethyl ether in 98% dichloromethane followed by 300 mL of 5% diethyl ether in 95% dichloromethane) gave the pure product as a white solid. The relative configuration was determined by crystallography data.

**Run 1** (55 mg, 0.106 mmol, 53% yield, 8:1 dr)

**Run 2** (60 mg, 0.116 mmol, 58% yield, 8:1 dr)

**Run 3** (60 mg, 0.116 mmol, 58% yield, 7:1 dr)

**Average overall yield:** 56% yield ± 2.9, 8:1 dr

Data for major diastereomer (–)38:

**¹H NMR:** (500 MHz, Chloroform-d)

δ 7.52 (d, J = 7.4 Hz, 1H), 7.27-7.24 (t, J = 7.3 Hz, 1H), 7.21 – 7.16 (m, 1H), 7.15 – 7.08 (m, 2H), 7.00 (t, J = 7.3 Hz, 1H), 6.55 (d, J = 7.2 Hz, 2H), 6.44 – 6.39 (m, 1H), 5.37 (d, J = 6.9 Hz, 1H), 4.87 (ddd, J = 6.0, 5.0, 1.2 Hz, 1H), 4.68 (s, 2H), 3.14 (d, J = 13.3 Hz, 1H), 2.89 – 2.79 (m, 1H), 2.74 (d, J = 13.4 Hz, 1H), 2.67 (t, J = 14.7 Hz, 1H), 2.60 – 2.50 (m, 2H), 2.46 – 2.34 (m, 2H), 2.29 (td, J = 13.7, 5.4 Hz, 1H), 2.06 (dt, J = 14.6, 2.0 Hz, 1H), 1.68 – 1.59 (m, 1H)

**¹³C NMR:** (101 MHz, CDCl₃)

δ 210.4, 142.4, 136.7, 133.3, 130.9, 130.5, 128.0, 127.9, 127.7, 127.6, 126.8, 93.7, 78.1, 53.1, 43.8, 40.1, 38.4 38.2, 37.0, 33.7, 32.2

**HRMS:** (ESI-TOF MS ES+)

m/z calculated for C₂₅H₂₃NO₄SCl₃Na [M+Na]⁺: 538.0389, found 538.0379

[α]D²⁴ = -92.7° (c = 1.0, CHCl₃)

2,2,2-trichloroethyl (4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)sulfamate [S36].

According to the general amination procedure B, 5Å powdered molecular sieves (40 mg), 1-(3,4-
dichlorophenyl)-1,2,3,4-tetrahydronaphthalene 39 (55.4 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ3-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using ethyl acetate as the eluent (50 mL), the solvent was removed by rotary evaporation and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography using gradient elution (400 mL of 5% ethyl acetate in hexane followed by 400 mL of 10% ethyl acetate in hexanes) gave the pure product as an off-white solid as a 1:1 mixture of separable diastereomers.

**Run 1** (72.7 mg, 0.144 mmol, 72% yield)

**Run 2** (74.7 mg, 0.148 mmol, 74% yield)

**Run 3** (73.5 mg, 0.146 mmol, 73% yield)

**Average overall yield: 73 % yield ± 1.0 (1:1 d.r.)**

**Characterized as two diastereomers:**

**D1 (syn):**

**1H NMR:** (500 MHz, CDCl3)

δ 7.44 (d, J = 7.7 Hz, 1H), 7.21 (d, J = 8.2 Hz, 1H), 7.11 (t, J = 7.5 Hz, 1H), 7.07 – 6.99 (m, 2H), 6.65 (d, J = 7.7 Hz, 1H), 6.59 (dd, J = 8.0, 2.1 Hz, 1H), 4.68 (q, J = 5.6 Hz, 1H), 4.55 – 4.47 (m, 3H), 3.58 (dd, J = 8.7, 5.6 Hz, 1H), 1.99 – 1.91 (m, 1H), 1.78 – 1.69 (m, 2H), 1.65 – 1.54 (m, 1H).

**13C NMR:** (126 MHz, CDCl3)

δ 146.31, 139.02, 134.95, 132.74, 130.75, 130.70, 130.66, 130.28, 129.69, 128.91, 128.25, 127.71, 93.68, 78.22, 53.48, 44.79, 28.66, 28.26.

**HRMS:** (ESI-TOF MS ES+)

m/z calculated for C18H16Cl3NO3SNa[M+Na]+: 523.9191, found 523.9200.

**D2 (anti):**

**1H NMR:** (500 MHz, CDCl3)

δ 7.61 (d, J = 7.0 Hz, 1H), 7.34 (d, J = 8.3 Hz, 1H), 7.30 (td, J = 7.9, 1.5 Hz, 1H), 7.21 (td, J = 7.4, 1.4 Hz, 1H), 7.10 (d, J = 1.1 Hz, 1H), 6.87 (d, J = 7.7 Hz, 1H), 6.83 (dd, J = 8.2, 2.1 Hz, 1H), 4.93 – 4.89 (m, 2H), 4.71 (s, 2H), 4.15 (t, J = 6.0 Hz, 1H), 2.35 – 2.20 (m, 2H), 2.05 – 1.95 (m, 1H), 1.87 (dddd, J = 12.9, 8.3, 6.5, 2.0 Hz, 1H).

**13C NMR:** (126 MHz, CDCl3)

δ 146.34, 138.60, 135.31, 132.63, 130.65, 130.59, 130.53, 128.99, 128.80, 128.47, 128.12, 127.82, 93.69, 78.26, 53.66, 44.04, 29.06, 27.78.

**HRMS:** (ESI-TOF MS ES+)
Figure 4. Synthesis of (±)-Sertraline 40.

Part 1:

The aminated product S36 was weighed out in a vial and added to a flame dried round bottom under argon (68.7 mg, 0.14 mmol) along with DMF (0.3 mL, 0.5M) and K₂CO₃ (37.6 mg, 0.27 mmol, 2 equiv.) and the reaction was stirred at room temperature for 5 minutes. The reaction was cooled to 0 °C and MeI (29.1 mg, 0.205 mmol, 1.5 equiv.) was added dropwise. The reaction was brought to room temperature and stirred for 2 h (monitored by TLC). Upon reaction completion, water (10 mL) and DCM (10 mL) was added to the round bottom. The phases were separated and the aqueous layer was extracted with DCM (2 x 20 mL). The combined organic layers were washed with water (2 x 20 mL), dried over Na₂SO₄, filtered and concentrated using rotary evaporation to give the crude product S37 in quantitative yield. This was carried directly to the next step without further purification.

Part 2:

The reaction was performed according to a previously reported procedure.¹ In a 25 mL round bottom flask under N₂ containing a Teflon stir bar was added rac-2,2,2-trichloroethyl ((1S,4S)-4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydranthalene-1-yl)sulfamate S37 (70.5 mg, 0.136 mmol, 1 equiv), Zn/Cu couple (96 mg, 1.36 mmol, 10 equiv), and 1:1 MeOH:AcOH (4.3 mL). The reaction was vigorously stirred for 48 h then filtered through celite, using methanol to rinse the filter cake and concentrated using rotary evaporation. To the resulting solid was added methanolic HCl (prepared from mixing 0.41 mL acetyl chloride and 5.4 mL of MeOH) and the reaction heated to 40 °C for 2 h under N₂. Upon reaction completion, 20 mL of EtOAc was added at room temperature and the solution was washed with K₂CO₃ (1 x 10 mL). Additional EtOAc (2 x 20 mL) was used to extract the resulting aqueous layer. The organic layers were combined and dried over K₂CO₃, filtered, and concentrated. Silica gel flash chromatography

m/z calculated for C₁₈H₁₆Cl₅NO₃S [M+NaCl]⁺: 558.3 found 557.9.
using gradient elution (0-10% methanol in dichloromethane) gave the pure product 40 as a white solid (39.5 mg, 0.129 mmol, 95% yield).

Characterization matched the reported characterization for the (±)-syn-diastereomer.⁶

¹H NMR: (500 MHz, CDCl₃)

δ 7.43 – 7.40 (m, 1H), 7.35 (d, J = 8.2 Hz, 1H), 7.28 (d, J = 2.1 Hz, 1H), 7.21 (t, J = 7.4 Hz, 1H), 7.13 (td, J = 7.5, 1.4 Hz, 1H), 7.00 (dd, J = 8.3, 2.1 Hz, 1H), 6.81 (d, J = 7.8 Hz, 1H), 3.99 (dd, J = 9.3, 5.5 Hz, 1H), 3.83 (t, J = 4.3 Hz, 1H), 3.35 (br s, 1H), 2.55 (s, 3H), 2.17 – 1.96 (m, 3H), 1.93 – 1.82 (m, 1H).

¹³C NMR: (126 MHz, CDCl₃)

δ 147.21, 139.01, 137.90, 132.43, 130.89, 130.48, 130.29, 130.06, 129.50, 128.45, 127.79, 126.88, 57.29, 45.43, 33.73, 28.43, 25.36.

HRMS: (ESI-TOF MS ES+)

m/z calculated for C₁₇H₁₈NCl₂ [M+H]⁺: 306.0816, found 306.0817.

4-(1-(((2,2,2-trichloroethoxy)sulfonyl)amino)ethyl)benzyl (2S,5R)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide [41]. According to the general amination procedure B, 5Å powdered molecular sieves (40 mg), 4-ethylbenzyl (2S,5R)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide S₃₈ (70.3 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ³-
iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using ethyl acetate as the eluent (50 mL), the solvent was removed by rotary evaporation and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography on 75 mL silica using gradient elution (400 mL of 20% ethyl acetate in hexane followed by 400 mL of 40% ethyl acetate in hexanes) gave the pure product as a yellow oil in an equal mixture of diastereomers.

**Run 1** (57.8 mg, 0.100 mmol, 50% yield)

**Run 2** (56.6 mg, 0.098 mmol, 49% yield)

**Run 3** (59.0 mg, 0.102 mmol, 51% yield)

**Average overall yield: 50% yield ± 1.0 (1:1 d.r.)**

**$^1$H NMR:** (500 MHz, CDCl$_3$)

$\delta$ 7.41 – 7.33 (m, 4H), 5.27 (br s, 1H), 5.22 (d, $J = 12.2$ Hz, 1H), 5.18 (d, $J = 12.1$ Hz, 1H), 4.74 (p, $J = 7.0$ Hz, 1H), 4.63 – 4.58 (m, 1H), 4.48 (d, $J = 10.9$ Hz, 1H), 4.45 (d, $J = 10.9$ Hz, 1H), 4.41 (s, 1H), 3.52 – 3.40 (m, 2H), 1.61 (d, $J = 6.8$ Hz, 3H), 1.56 (s, 3H), 1.32 (s, 3H).

**$^{13}$C NMR:** (126 MHz, CDCl$_3$)

$\delta$ 171.05, 166.98, 142.61, 134.34, 129.42, 126.87, 93.42, 78.17, 67.79, 63.29, 62.90, 61.21, 54.59, 38.42, 23.07, 20.31, 18.72.

**HRMS:** (ESI-TOF MS ES$^+$)  
$m/z$ calculated for C$_{19}$H$_{24}$Cl$_3$N$_2$O$_8$S$_2$ [M+H]$^+$: 577.0015, found 577.0040.

2,2,2-trichloroethyl (1-(4-((5,7-dibromo-2,3-dioxoindolin-1 yl)methyl)phenyl)ethyl) sulfamate [42]. According to the general procedure B, 5Å powdered molecular sieves (40 mg), 5,7-dibromo-1-(4-ethylbenzyl)indoline-2,3-dione S39 (84.6 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-$\lambda^3$-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using ethyl acetate as the eluent (50 mL), the solvent was removed by rotary evaporation and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography on 75 mL silica
using gradient elution (200 mL of 10% ethyl acetate in hexane followed by 400 mL of 20% ethyl acetate in hexanes, then 400 mL of 40% ethyl acetate in hexanes) gave the pure product as an orange solid.

**Run 1** (84.4 mg, 0.130 mmol, 65% yield)

**Run 2** (81.8 mg, 0.126 mmol, 63% yield)

**Run 3** (81.8 mg, 0.126 mmol, 63% yield)

**Average overall yield: 64% yield ± 1.2**

**1H NMR:** (500 MHz, CDCl₃)

δ 7.82 (d, J = 2.0 Hz, 1H), 7.72 (d, J = 2.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 5.40 (s, 2H), 5.19 (br d, J = 7.3 Hz, 1H), 4.71 (dq, J = 13.6, 7.1 Hz, 1H), 4.44 (d, J = 10.9 Hz, 1H), 4.40 (d, J = 11.0 Hz, 1H), 1.60 (d, J = 6.8 Hz, 3H).

**13C NMR:** (126 MHz, CDCl₃)

δ 181.28, 158.48, 146.62, 145.50, 141.25, 135.84, 127.80, 127.25, 126.95, 121.53, 117.50, 105.31, 93.42, 78.18, 54.57, 44.48, 23.00.

**HRMS:** (ESI-TOF MS ES+)

m/z calculated for C₁₉H₁₅N₂O₅SCl₃Br₂Na [M+Na]⁺: 668.8032, found 668.8028.

2,2,2-trichloroethyl (1-(4'-(1H-benzo[d]imidazol-1-yl)methyl)-[1,1'-biphenyl]-4-yl)butyl)sulfamate [43]. To a 1 dram vial equipped with a stir bar were added 1-((4'-butyl-[1,1'-biphenyl]-4-yl)methyl)-1H-benzo[d]imidazole S₄₀ (68.1 mg, 0.20 mmol, 1.0 equiv.) and methylene chloride (DCM) (0.8 mL). Boron trifluoride diethyl ether complex (BF₃·OEt₂) (27.2 µL, 31.2 mg, 0.22 mmol, 1.1 equiv.) was added dropwise while stirring. The reaction mixture was stirred for 1.5 h at room temperature. Upon reaction completion, the stir bar was removed, and the mixture was concentrated in vacuo and placed on vacuum overnight. The resulting white foamy solid was reacted with manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.10 equiv.), AgSbF₆ (6.9 mg, 0.020 mmol, 0.10 equiv.), PhI=NTces (172.2 mg, 0.40 mmol, 2.0 equiv.), and 3Å molecular sieves (40 mg) in DCE (0.4 mL), according to the general amination procedure A. The reaction was stirred for 15 h in 40 °C oil bath. Upon completion, the flask was taken out of oil bath. Tetramethylethlenediamine (TMEDA) (150 µL, 116 mg, 1.0 mmol, 5.0 equiv.) was added, and DCM (1 mL) was used to wash off the solid remaining on the wall. The reaction mixture was further stirred for 4 h for complete removal of the BF₃ protection. The resulting mixture was
directly loaded onto a flash column and purified (50 mL silica, gradient elution 20%→30%→40% (4 column volumes each)→50%→60%→70% (2 column volumes each)→80% EtOAc/hexanes (6 column volumes)) to afford the product as a white solid with slight green discoloration.

**Run 1** (57.9 mg, 0.102 mmol, 51% yield; 3.5 mg, 0.010 mmol, 5% rsm)

**Run 2** (66.2 mg, 0.117 mmol, 58% yield; 5.4 mg, 0.016 mmol, 8% rsm)

**Run 3** (57.2 mg, 0.101 mmol, 50% yield; 3.0 mg, 0.0088 mmol, 4% rsm)

Average overall yield: 53% (6% rsm) ± 4.4

**1**H NMR: (500 MHz, CDCl₃)

δ 8.00 (s, 1H), 7.85 (dd, J = 6.8, 1.6 Hz, 1H), 7.53 (d, J = 6.5 Hz, 2H), 7.51 (d, J = 6.5 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 7.35-7.31 (m, 1H), 7.31-7.27 (m, 2H), 7.25 (d, J = 8.8 Hz, 2H), 5.54 (d, J = 7.4 Hz, 1H), 5.41 (s, 2H), 4.57 (q, J = 7.4 Hz, 1H), 4.37 (d, J = 10.8 Hz, 1H), 4.34 (d, J = 10.8 Hz, 1H), 2.02-1.92 (m, 1H), 1.90-1.78 (m, 1H), 1.47-1.28 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H)

**13**C NMR: (126 MHz, CDCl₃)

δ 144.03, 143.38, 140.71, 140.35, 140.22, 134.84, 134.06, 127.82, 127.73, 127.70, 127.39, 123.35, 122.56, 120.60, 110.19, 93.45, 78.09, 59.18, 48.70, 39.13, 19.44, 13.76

HRMS: (ESI-TOF MS ES+)

m/z calculated for C₂₆H₂₇N₃O₃SCl₃ [M+H]+: 566.0839, found 566.0837.

VI. Experimental procedures and compound characterization for Figure 4

**Figure 5. Late-stage benzylic C—H amination of natural products.**
According to the general amination procedure B, 5Å powdered molecular sieves (40 mg), 2,2,2-trifluoro-N-((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)acetamide S41 (76.3 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ3-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using diethyl ether as the eluent (30 mL), the solvent was concentrated and a 1H NMR was taken of the crude brown oil to reveal 2 amination products determined to be a mixture of diastereomers at the 2° benzylc C–H bond. The sample was dry loaded onto a silica gel column. Flash chromatography using gradient elution (100 mL of 100% hexanes then 300 mL of 5% ethyl acetate in 95% hexanes followed by 600 mL of 10% ethyl acetate in 90% hexanes) gave the diastereomeric mixture as a slightly yellow solid. The same flash chromatography conditions were used to separate the major diastereomer from the minor diastereomer. The relative configuration was determined by crystallography data.

Run 1 (73 mg, 0.120 mmol, 60% yield, 5:1 d:r)
Run 2 (78 mg, 0.128 mmol, 64% yield, 6:1 d:r)
Run 3 (76 mg, 0.125 mmol, 63% yield, 6:1 d:r)
Average overall yield: 62% yield ± 2.1, 6:1 d:r

1H NMR: (500 MHz, CDCl3)
\[\delta \text{ 7.29} - \text{7.16 (m, 3H), 6.70 (t, } J = 6.6 \text{ Hz, 1H), 5.13 (d, } J = 4.7 \text{ Hz, 1H), 4.87 (t, } J = 4.4 \text{ Hz, 1H), 4.78 (s, 2H), 3.41 (dd, } J = 14.0, 8.5 \text{ Hz, 1H), 3.17 (dd, } J = 13.9, 5.1 \text{ Hz, 1H), 2.87 (septet, } J = 6.9 \text{ Hz, 1H), 2.37 - 2.20 (m, 2H), 2.07 - 1.95 (m, 1H), 1.90 - 1.67 (m, 2H), 1.64 (d, } J = 12.7 \text{ Hz, 1H), 1.52-1.42 (m, 1H), 1.38 - 1.27 (m, 2H), 1.24 (d, } J = 6.9 \text{ Hz, 6H), 1.19 (s, 3H), 0.98 (s, 3H)}\]

13C NMR: (101 MHz, CDCl3)
\[\delta \text{ 158.2 (q, } J = 36.8 \text{ Hz), 147.7, 147.6, 131.5, 127.8, 127.7, 125.3, 116.1 (q, } J = 288.0 \text{ Hz), 93.7, 78.1, 54.6, 49.5, 40.1, 38.1, 38.0, 37.9, 35.5, 33.6, 25.9, 24.9, 24.1, 23.9, 19.0, 18.5}\]

19F NMR: (470 MHz, CDCl3)
\[\delta \text{ -76.07}\]
(--)-\text{N}-(\text{((1R,4aS,9R,10aR)-9-amino-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-2,2,2-trifluoroacetamide} \ (\text{[(--)-45]}. The reaction was performed according to a previously reported procedure.\textsuperscript{1} In a 50 mL round bottom flask under N\textsubscript{2} containing a Teflon stir bar was added 2,2,2-trichloroethyl (\text{((1R,4aS,9R,10aR)-7-isopropyl-1,4a-dimethyl-1-((2,2,2-trifluoroacetamido)methyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthren-9-yl)sulfamate} \ (--)\textsuperscript{44} (42 mg, 0.069 mmol, 1 equiv), Zn/Cu couple (91 mg, 1.39 mmol, 20 equiv), and 1:1 MeOH:AcOH (4 mL). The reaction was vigorously stirred for 48 h then filtered through celite, using methanol to rinse the filter cake and concentrated using rotary evaporation. To the resulting solid was added methanolic HCl (prepared from mixing 0.44 mL acetyl chloride and 5.5 mL of MeOH) and the reaction heated to 40 °C for 12 h under N\textsubscript{2}. Upon reaction completion, 20 mL of EtOAc was added at room temperature and the solution was washed with K\textsubscript{2}CO\textsubscript{3} (1 x 10 mL). Additional EtOAc (2 x 20 mL) was used to extract the resulting aqueous layer. The organic layers were combined and dried over K\textsubscript{2}CO\textsubscript{3}, filtered, and concentrated. Silica gel flash chromatography using gradient elution (0-10% methanol in dichloromethane) gave the pure product as an oily slightly yellow solid (19 mg, 0.048 mmol, 70% yield).

\textsuperscript{1}H NMR: (500 MHz, Chloroform-\textit{d})
\begin{align*}
\delta &\quad \text{8.63} \text{ (s, 1H)}, \quad \text{7.19} \text{ (d, } J = 8.2 \text{ Hz, 1H}), \quad \text{7.11} \text{ (dd, } J = 8.2, 2.0 \text{ Hz, 1H}), \quad \text{7.05} \text{ (d, } J = 2.0 \text{ Hz, 1H}), \\
&\quad \text{4.31} - \text{4.19} \text{ (m, 1H)}, \quad \text{3.64} - \text{3.52} \text{ (m, 1H)}, \quad \text{3.00} \text{ (d, } J = 13.9 \text{ Hz, 1H}), \quad \text{2.87} \text{ (hept, } J = 6.8 \text{ Hz, 1H}), \\
&\quad \text{2.77} - \text{2.08} \text{ (m, 3H)}, \quad \text{2.01} \text{ (d, } J = 11.9 \text{ Hz, 1H}), \quad \text{1.89} - \text{1.71} \text{ (m, 2H)}, \quad \text{1.71} - \text{1.51} \text{ (m, 2H)}, \quad \text{1.45} - \text{1.35} \text{ (m, 1H)}, \quad \text{1.35} - \text{1.26} \text{ (m, 2H)}, \quad \text{1.25} \text{ (dd, } J = 6.9, 1.2 \text{ Hz, 6H}), \quad \text{1.22} \text{ (s, 3H)}, \quad \text{0.96} \text{ (s, 3H)}. \\
\end{align*}

\textsuperscript{13}C NMR: (126 MHz, CDCl\textsubscript{3})
\begin{align*}
\delta &\quad \text{158.1} \text{ (q, } J = 36.7 \text{ Hz), 147.8, 146.8, 137.2, 127.7, 126.3, 125.6, 116.4} \text{ (q, } J = 288.0 \text{ Hz), 49.9,} \\
&\quad \text{48.9, 39.6, 39.0, 38.2, 37.1, 35.3, 33.7, 28.1, 24.1, 24.0, 19.4, 18.8.} \\
\end{align*}

\textsuperscript{19}F NMR: (471 MHz, Chloroform-\textit{d})
\begin{align*}
\delta &\quad \text{-75.28} \\
HRMS: \ (\text{ESI-TOF MS ES+})
\end{align*}
m/z calculated for C_{22}H_{32}N_{2}O_{3}F_{3} [M+H]^{+}: 397.2467, found 397.2464

[\alpha]_{D}^{24} = -41.3^{\circ} (c = 0.50, CHCl_{3})

(\pm)-2,2,2-trichloroethyl  (1-(10-bromo-6-phenyl-cis-12H-6,12-methanodibenzo[d,g][1,3]dioxocin-2-yl)ethyl)sulfamate [46]. Prepared according to the general amination procedure B. 2-bromo-10-ethyl-6-phenyl-cis-12H-6,12-methanodibenzo[d,g][1,3]dioxocine (\pm)S42 (81.5 mg, 0.20 mmol, 1.0 equiv.) was reacted with manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.10 equiv.), AgSbF_{6} (6.9 mg, 0.020 mmol, 0.10 equiv.), PhI=NTces (172.2 mg, 0.40 mmol, 2.0 equiv.), and 5Å molecular sieves (40 mg) in benzene (0.4 mL) for 10 h. The crude reaction mixture was directly purified by flash chromatography (50 mL silica, 7.5% EtOAc/Hex (14 column volumes)) to afford the product as a white solid with slight discoloration as a mixture of diastereomers.

Run 1 (94.4 mg, 0.149 mmol, 75% yield, 1:1 d.r.)
Run 2 (96.9 mg, 0.153 mmol, 76% yield, 1:1 d.r.)
Run 3 (84.5 mg, 0.133 mmol, 67% yield, 1:1 d.r.)
Average overall yield: 73% yield ± 4.9, 1:1 d.r.

{\textsuperscript{1}}H NMR: (500 MHz, DMSO-\textit{d}_{6}) (mixture of diastereomers)
\[\delta\] 8.89 (d, J = 8.1 Hz, 0.5H), 8.87 (d, J = 8.4 Hz, 0.5H), 7.73-7.66 (m, 3H), 7.55-7.42 (m, 4H), 7.30 (dt, J = 8.6, 2.8 Hz, 1H), 7.27-7.19 (m, 1H), 6.99 (dd, J = 8.4, 2.8 Hz, 1H), 6.95 (d, J = 8.6 Hz, 1H), 4.51 (dq, J = 12.4, 4.9 Hz, 1H), 4.46 (dd, J = 11.1, 7.6 Hz, 1H), 4.38 (dd, J = 11.1, 3.3 Hz, 0.5H), 4.34 (t, J = 2.6 Hz, 0.5H), 4.31 (t, J = 2.4 Hz, 0.5H), 4.23 (d, J = 11.2 Hz, 0.5H), 2.44-2.38 (m, 1.5H), 2.36 (dd, J = 13.6, 2.8 Hz, 0.5H), 1.47 (app t, J = 7.5 Hz, 3H)

{\textsuperscript{13}}C NMR: (126 MHz, DMSO-\textit{d}_{6}) (mixture of diastereomers)
\[\delta\] 150.78, 150.76, 150.60, 150.53, 140.59, 136.33, 136.19, 130.56, 130.03, 129.99, 129.21, 128.92, 128.34, 128.33, 126.34, 125.96, 125.89, 125.85, 125.77, 125.54, 125.51, 118.38, 116.29, 116.20, 112.73, 112.70, 98.65, 93.74, 93.69, 77.07, 77.04, 53.29, 53.20, 32.10, 32.08, 31.47, 31.38, 23.54, 22.83

HRMS: (ESI-TOF MS ES+)
m/z calculated for C_{23}H_{32}Cl_{3}BrNO_{5}S [M+H]^{+}: 631.9468, found 631.9452.
For COSY see Supporting Information: Spectral Data

(±)-2,2,2-trichloroethyl (1-(-6-phenyl-10-(pyridin-3-yl)-cis-12H-6,12-methanodibenzo[d,g][1,3]dioxocin-2-yl)ethyl)sulfamate [47]. According to the general amination procedure C, 3-(10-ethyl-6-phenyl-cis-12H-6,12-methanodibenzo[d,g][1,3]dioxocin-2-yl)pyridine (±)S43 (81.0 mg, 0.20 mmol, 1.0 equiv.) in CH₂Cl₂ (1.2 mL) was protonated with HBF₄·OEt₂ (30.2 µL, 35.6 mg, 0.22 mmol, 1.1 equiv.), reacted with manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.10 equiv.), AgSbF₆ (6.9 mg, 0.020 mmol, 0.10 equiv.), PhI=NTces (172.2 mg, 0.40 mmol, 2.0 equiv.), and 3Å molecular sieves (40 mg) in DCE (0.4 mL) for 15 h. Following work-up, the crude material was purified by flash chromatography (50 mL silica, gradient elution 30%→40%→50% EtOAc/Hex (4 column volumes each)) to afford the product as a white solid with slight discoloration as a mixture of diastereomers.

Run 1 (66.0 mg, 0.104 mmol, 52% yield, 1:1 d.r.; 5.7 mg, 0.014 mmol, 7% rsm)
Run 2 (75.8 mg, 0.120 mmol, 60% yield, 1:1 d.r.; 4.1 mg, 0.010 mmol, 5% rsm)
Run 3 (76.1 mg, 0.120 mmol, 60% yield, 1:1 d.r.; 3.2 mg, 0.008 mmol, 4% rsm)

Average overall yield: 57% (5% rsm) ± 4.6, 1:1 d.r.

¹H NMR: (500 MHz, CDCl₃) (mixture of diastereomers)
δ 8.59 (d, J = 1.0 Hz, 0.5H), 8.51 (d, J = 1.1 Hz, 0.5H), 8.16 (d, J = 4.0 Hz, 0.5H), 8.04 (d, J = 4.2 Hz, 0.5H), 7.81-7.70 (m, 2H), 7.69-7.62 (m, 1H), 7.57 (d, J = 6.0 Hz, 0.5H), 7.52-7.41 (m, 3.5H), 7.38 (d, J = 2.0 Hz, 0.5H), 7.37 (br s, 0.5H), 7.31 (dd, J = 4.3, 2.2 Hz, 1H), 7.26-7.19 (m, 1.5H), 7.17 (dd, J = 8.4, 2.2 Hz, 0.5H), 7.12 (dd, J = 7.8, 4.9 Hz, 0.5H), 7.10-7.04 (m, 2.5H), 4.80-4.74 (m, 0.5H), 4.74-4.68 (m, 0.5H), 4.47 (d, J = 10.8 Hz, 0.5H), 4.44 (d, J = 10.8 Hz, 0.5H), 4.41 (d, J = 10.8 Hz, 0.5H), 4.41 (d, J = 10.8 Hz, 0.5H), 4.34 (d, J = 10.8 Hz, 0.5H), 4.17 (t, J = 3.1 Hz, 0.5H), 4.15 (t, J = 2.7 Hz, 0.5H), 2.47-2.36 (m, 2H), 1.67 (d, J = 6.9 Hz, 1.5H), 1.63 (d, J = 6.8 Hz, 1.5H)

¹³C NMR: (126 MHz, CDCl₃) (mixture of diastereomers)
δ 152.25, 152.20, 151.85, 151.77, 147.22, 140.92, 140.88, 135.99, 135.84, 135.11, 134.32, 134.16, 130.95, 130.85, 129.13, 128.56, 127.06, 126.90, 126.86, 126.83, 126.73, 126.69, 126.15, 126.01, 125.83, 125.79, 125.77, 125.67, 123.72, 123.66, 117.75, 117.73, 117.29, 117.18, 99.15, 99.13, 93.68, 93.66, 77.98, 77.94, 54.30, 53.99, 34.39, 33.22, 33.19, 22.75, 22.61
HRMS: (ESI-TOF MS ES+)

\[m/z \text{ calculated for } C_{30}H_{26}Cl_{3}N_{2}O_{5}S [M+H]^+: 631.0628, \text{ found 631.0612.}\]

For COSY see Supporting Information: Spectral Data

\[\text{(8R,9S,13S,14S,17S)-17-(formyloxy)-13-methyl-6-(((2,2,2-trichloroethoxy)sulfonyl)amino)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta}[a]\text{phenanthren-3-yl acetate [48].}\]

According to the general amination procedure B, 5Å powdered molecular sieves (40 mg), (13S,17S)-17-(formyloxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl acetate 48a (see page 88) (68.5 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-\(\lambda^3\)-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8-12 h. After silica plug filtration using ethyl acetate as the eluent (50 mL), the solvent was concentrated and the crude brown oil was loaded onto a silica gel column. Flash chromatography on 75 mL of silica gel using gradient elution (500 mL of 100% dichloromethane then 200 mL of 1% diethyl ether in 99% dichloromethane followed by 400 mL of 2% diethyl ether in dichloromethane) gave the pure products as colorless oils and separable diastereomers.

**Run 1** (70.5 mg, 0.124 mmol, 62% yield, 1.6:1 d.r.)

**Run 2** (74.0 mg, 0.130 mmol, 65% yield, 1.6:1 d.r.)

**Run 3** (77.4 mg, 0.136 mmol, 68% yield, 1.6:1 d.r.)

**Average overall yield: 65% yield ± 3.0**

\(^1\)H NMR: (500 MHz, CDCl\(_3\))

\(\delta\) 8.10 (s, 1H), 7.36 (d, \(J = 8.6\) Hz, 1H), 7.24 (d, \(J = 2.2\) Hz, 1H), 7.01 (dd, \(J = 8.5, 2.3\) Hz, 1H), 5.29 (br d, \(J = 7.5\) Hz, 1H), 4.82 (m, 2H), 4.71 (d, \(J = 10.9\) Hz, 1H), 4.69 (d, \(J = 10.9\) Hz, 1H), 2.39 – 2.22 (m, 2H), 2.30 (s, 3H), 2.23 – 2.15 (m, 1H), 1.95 (d, \(J = 12.3\) Hz, 1H), 1.78 (ddd, \(J = 11.8, 9.4, 4.9\) Hz, 1H), 1.72 – 1.32 (m, 8H), 0.89 (s, 3H).

\(^{13}\)C NMR: (126 MHz, CDCl\(_3\))
\[ \delta 169.87, 161.30, 149.22, 138.29, 135.24, 127.04, 123.16, 93.73, 82.30, 78.05, 52.81, 49.17, 43.85, 43.24, 36.68, 34.30, 33.18, 27.57, 25.76, 23.29, 21.15, 12.27. \]

HRMS: (ESI-TOF MS ES+)

\[ m/z \text{ calculated for } C_{23}H_{32}Cl_3N_2O_7S \text{ [M+NH}_4^+\text{]} : 585.0996, \text{ found 585.0995.} \]

Stereochemistry was assigned based on coupling constant and by analogy to compound 49.

Minor diastereomer S44:

\[ H_3C \]
\[ HN \]
\[ O \]
\[ O \]
\[ O \]
\[ O \]
\[ O \]
\[ O \]
\[ O \]
\[ O \]
\[ O \]
\[ O \]
\[ O \]
\[ O \]
\[ O \]
\[ O \]
\[ O \]
\[ O \]
\[ O \]
\[ O \]

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

\[ \delta 8.09 \text{ (s, 1H)}, 7.33 \text{ (d, } J = 2.4 \text{ Hz, 1H)}, 7.30 \text{ (d, } J = 8.6 \text{ Hz, 1H)}, 6.97 \text{ (dd, } J = 8.6, 2.5 \text{ Hz, 1H)}, 5.06 \text{ (d, } J = 8.6 \text{ Hz, 1H)}, 4.87 \text{ (td, } J = 10.0, 7.9 \text{ Hz, 1H)}, 4.79 \text{ (t, } J = 8.5 \text{ Hz, 1H)}, 4.74 \text{ (d, } J = 10.8 \text{ Hz, 1H)}, 4.68 \text{ (d, } J = 10.9 \text{ Hz, 1H)}, 2.55 \text{ (ddd, } J = 12.5, 6.5, 2.1 \text{ Hz, 1H)}, 2.36 – 2.20 \text{ (m, 2H)}, 2.30 \text{ (s, 3H)}, 1.96 – 1.88 \text{ (m, 1H)}, 1.77 – 1.69 \text{ (m, 1H)}, 1.67 – 1.58 \text{ (m, 3H)}, 1.51 – 1.30 \text{ (m, 5H)}, 0.84 \text{ (s, 3H).} \]

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

\[ \delta 169.89, 161.27, 149.36, 138.34, 136.48, 127.07, 121.60, 121.09, 93.75, 82.26, 78.20, 54.96, 49.24, 44.11, 43.01, 38.13, 36.71, 36.52, 27.60, 26.06, 23.34, 21.20, 12.11. \]

HRMS: (ESI-TOF MS ES+)

\[ m/z \text{ calculated for } C_{23}H_{28}NO_7SCl_3Na \text{ [M+Na]}^+ : 590.0550, \text{ found 590.0555.} \]

Stereochemistry was assigned based on coupling constant and by analogy to compound S45.
(8S,9S,13S,14S,17S)-13-methyl-17-(pyridin-3-yl)-6-(((2,2,2-trichloroethoxy)sulfonyl)amino)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl acetate [49]. In a 1 dram vial equipped with a stir bar were added (8S,9S,13S,17S)-13-methyl-17-(pyridin-3-yl)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl acetate 49a (see page 88) (75.1 mg, 0.20 mmol, 1.0 equiv.) and methylene chloride (DCM) (0.8 mL). Boron trifluoride diethyl ether complex (BF₃·OEt₂) (27.2 µL, 31.2 mg, 0.22 mmol, 1.1 equiv.) was added dropwise while stirring. The reaction mixture was stirred for 1.5 h at room temperature. Upon reaction completion the stir bar was taken out, and mixture was concentrated in vacuo and placed on vacuum overnight. The resulting white foamy solid was reacted with manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.10 equiv.), AgSbF₆ (6.9 mg, 0.020 mmol, 0.10 equiv.), PhI=NTces (172.2 mg, 0.40 mmol, 2.0 equiv.), and 3Å molecular sieves (40 mg) in DCE (0.4 mL), according to the general procedure A. After 2 h of reaction, another batch of PhI=NTces (86.1 mg, 0.20 mmol, 1.1 equiv.) was quickly added to the reaction mixture. The reaction was further stirred for 13 h. Upon completion, the flask was taken out of oil bath. Tetramethylethlenediamine (TMEDA) (150 µL, 116 mg, 1.0 mmol, 5.0 equiv.) was added, and DCM (1 mL) was used to wash off the solid remaining on the wall. The reaction mixture was further stirred for 4 h for complete removal of the BF₃ protection. The resulting mixture was directly loaded onto a flash column and purified (50 mL silica, gradient elution 20%→30%→40%→50%→60%→70% EtOAc/hexanes (2 column volumes each)), staining with CAM to afford the product as a white solid with slight green discoloration as a mixture of diastereomers.

Run 1 (61.0 mg, 0.101 mmol, 51% yield, 1.8:1 d.r.)
Run 2 (62.7 mg, 0.104 mmol, 52% yield, 1.5:1 d.r.)
Run 3 (60.2 mg, 0.100 mmol, 50% yield, 1.4:1 d.r.)

Average overall yield: 51% (0% rsm) ± 1.0 1.6:1 d.r.

Data for major diastereomer 49:

1H NMR: (500 MHz, CDCl₃)

δ 8.34 (br s, 1H), 8.16 (br s, 1H), 7.55 (d, J = 8.2 Hz, 1H), 7.33 (d, J = 8.7 Hz, 1H), 7.27 (d, J = 2.6 Hz, 1H), 7.23 (dd, J = 8.5, 5.0 Hz, 1H), 7.01 (dd, J = 8.6, 2.5 Hz, 1H), 6.94 (br s, 1H), 4.84
(t, J = 4.9 Hz, 1H), 4.71-4.66 (m, 2H), 2.72 (t, J = 9.8 Hz, 1H), 2.36-2.30 (m, 2H), 2.28 (s, 3H), 2.26-2.18 (m, 1H), 2.13-1.97 (m, 2H), 1.97-1.88 (m, 1H), 1.70 (td, J = 12.9, 4.7 Hz, 1H), 1.63-1.54 (m, 2H), 1.54-1.47 (m, 1H), 1.43 (td, J = 13.1, 4.0 Hz, 1H), 1.32 (qd, J = 14.0, 2.3 Hz, 1H), 0.37 (s, 3H)

$^{13}$C NMR: (126 MHz, CDCl₃)

δ 169.79, 149.60, 149.27, 146.93, 138.44, 136.53, 136.31, 135.76, 126.94, 123.30, 123.17, 121.99, 93.90, 78.00, 54.43, 54.38, 52.83, 44.86, 44.02, 37.44, 35.05, 33.83, 25.99, 25.86, 24.22, 21.17, 12.76

HRMS: (ESI-TOF MS ES+)

$m/z$ calculated for C$_{27}$H$_{32}$Cl$_3$N$_2$O$_5$S [M+H]$^+$: 601.1098, found 601.1110.

Stereochemistry was assigned based on coupling constant and by analogy. See below for an explanation of coupling constants and representative coupling constants for the NHTces in the axial and equatorial positions of the ring.

Data for minor diastereomer S45:

$^1$H NMR: (500 MHz, CDCl₃)

δ 8.45 (br s, 2H), 7.58 (d, J = 7.9 Hz, 1H), 7.35 (d, J = 1.8 Hz, 1H), 7.30 (d, J = 8.6 Hz, 1H), 7.28-7.24 (m, 1H), 6.97 (dd, J = 8.6, 2.5 Hz, 1H), 5.32 (d, J = 9.5 Hz, 1H), 4.90 (td, J = 10.2, 6.7 Hz, 1H), 4.76 (d, J = 10.7 Hz, 1H), 4.71 (d, J = 10.8 Hz, 1H), 2.78 (t, J = 9.8 Hz, 1H), 2.63 (ddd, J = 12.4, 6.5, 1.2 Hz, 1H), 2.40-2.33 (m, 1H), 2.33-2.30 (m, 1H), 2.28 (s, 3H), 2.29-2.26 (m, 1H), 2.20-1.99 (m, 2H), 1.95-1.86 (m, 1H), 1.73-1.67 (m, 1H), 1.66-1.57 (m, 1H), 1.57-1.38 (m, 4H), 0.51 (s, 3H)

$^{13}$C NMR: (126 MHz, CDCl₃)
δ 169.90, 149.83, 149.35, 147.21, 138.56, 136.58, 136.47, 136.37, 127.03, 123.24, 121.56, 121.14, 93.80, 78.21, 55.07, 54.58, 54.54, 44.72, 44.28, 38.80, 37.35, 37.14, 26.14, 26.01, 24.23, 21.21, 12.79

HRMS: (ESI-TOF MS ES+) m/z calculated for C_{27}H_{32}Cl_{3}N_{2}O_{5}S [M+H]^+: 601.1098, found 601.1086.

2,2,2-trichloroethyl(1-((4S,8aS,9S)-11-methyl-6,7,8,8a,9,10-hexahydro-5H-9,4b-(epiminoethano)phenanthren-3-yl)propyl)sulfamate [50]. According to the general amination procedure, C, (4bS,8aS,9S)-11-methyl-3-propyl-6,7,8,8a,9,10-hexahydro-5H-9,4b-(epiminoethano)phenanthrene S49 (56.7 mg, 0.20 mmol, 1.0 equiv.) in CH_{2}Cl_{2} (1.2 mL) was protonated with HBF_{4}OEt_{2} (30.2 µL, 35.6 mg, 0.22 mmol, 1.1 equiv.), reacted with manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.10 equiv.), AgSbF_{6} (6.9 mg, 0.020 mmol, 0.10 equiv.), PhI=NTces (172.2 mg, 0.40 mmol, 2.0 equiv.), and 3Å molecular sieves (40 mg) in DCE (0.4 mL). After 2 h of reaction, another batch of PhI=NTces (86.1 mg, 0.20 mmol, 1.0 equiv.) was quickly added to the reaction mixture. The reaction was further stirred for 13 h. Following work-up, the crude material was purified by flash chromatography (50 mL basic Al_{2}O_{3} Brockmann grade III, gradient elution 40%→50% EtOAc/Hex (4 column volumes each)→0%→1%→2%→3% MeOH/CH_{2}Cl_{2} (2 column volumes each)) to afford the product as a white solid with green discoloration as a mixture of diastereomers.

Run 1 (45.3 mg, 0.0888 mmol, 44% yield, 1:1 d.r.; 8.1 mg, 0.029 mmol, 14% rsm)
Run 2 (44.9 mg, 0.0880 mmol, 44% yield, 1.1 d.r.; 4.5 mg, 0.016 mmol, 8% rsm)
Run 3 (43.9 mg, 0.0861 mmol, 43% yield, 1:1 d.r.; 4.0 mg, 0.014 mmol, 7% rsm)

Average overall yield: 44% (10% rsm) ± 0.6, 1:1 d.r.

^{1}H NMR: (500 MHz, CDCl_{3}) (mixture of diastereomers)
δ 7.13 (s, 1H), 7.13-7.09 (m, 1H), 7.04 (app dt, J = 7.9, 1.7 Hz, 1H), 4.36 (q, J = 7.9 Hz, 1H), 4.27 (d, J = 10.9 Hz, 1H), 4.24 (app dd, J = 10.8, 1.4 Hz, 1H), 3.01 (d, J = 18.5 Hz, 1H), 2.82 (dd, J = 4.3, 3.1 Hz, 1H), 2.62 (dd, J = 18.5, 5.5 Hz, 1H), 2.46-2.37 (m, 2H), 2.39 (s, 3H), 2.05-1.92 (m, 2H), 1.88-1.72 (m, 3H), 1.62 (app d, J = 13.2 Hz, 1H), 1.53 (app d, J = 12.8 Hz, 1H), 1.45-1.25 (m, 5H), 1.24-1.14 (m, 1H), 1.12-1.00 (m, 2H), 0.90 (app td, J = 7.4, 2.4 Hz, 3H)

^{13}C NMR: (126 MHz, CDCl_{3}) (mixture of diastereomers)
δ 141.14, 138.48, 138.37, 137.89, 128.57, 128.49, 124.14, 124.12, 123.63, 123.54, 93.56, 93.54, 78.25, 78.23, 61.26, 61.18, 57.98, 47.32, 45.28, 42.86, 42.83, 42.08, 37.28, 37.26, 36.57, 36.55, 30.37, 30.27, 26.79, 26.78, 26.64, 26.62, 24.25, 24.18, 22.34, 22.26, 10.85, 10.77

HRMS: (ESI-TOF MS ES+)

\[ m/z \text{ calculated for } C_{22}H_{32}N_2O_3SCl_3 [M+H]^+ : 509.1199, \text{ found } 509.1195. \]

For COSY see Supporting Information: Spectral Data

**VII. Preparation and characterization of newly reported starting materials**

**General procedure for acetate protection of an alcohol.**

In a flame-dried 100 mL round-bottom flask at room temperature under nitrogen was added a Teflon stir bar, the alcohol substrate (36.7 mmol, 1 equiv), pyridine (37 mL 1.2M to substrate), 4-dimethylaminopyridine (1.84 mmol, 0.05 equiv) and acetic anhydride (73.4 mmol, 2 equiv). The reaction was stirred overnight at room temperature then slowly quenched with NaHCO₃ (sat) until bubbling ceased. The mixture was extracted with Et₂O (2 x 150 mL). The organic extracts were combined and washed with CuSO₄ (sat) (3 x 100 mL), H₂O (2 x 100 mL) then brine (1 x 100 mL). The organic layer was dried (anhydrous MgSO₄), filtered and the solvent removed using rotary evaporation. Purification of the desired compound was performed by either vacuum distillation or flash chromatography.

**General procedure for trifluoroacetate protection of an amine.**

In a flame-dried 200 mL round-bottom flask at 0 °C under nitrogen was added a Teflon stir bar, the amine substrate (18.79 mmol, 1 equiv), CH₂Cl₂ (47 mL, 0.4M to substrate), and pyridine (56.3 mmol, 3 equiv) followed by dropwise addition of trifluoroacetic anhydride (37.6 mmol, 2 equiv). The reaction was stirred overnight at room temperature then slowly quenched with H₂O, then extracted with CH₂Cl₂ (2 x 75 mL). The organic extracts were combined and washed with H₂O (2 x 100 mL) then brine (1 x 100 mL). The organic layer was dried (anhydrous Na₂SO₄), filtered and the solvent removed using rotary evaporation. Purification was of the desired compound was performed by flash chromatography.

Compounds **S₃, S₄, S₅** were obtained through commercial sources.

**S₆, S₇.** Prepared using the general procedure for acetate protection of commercial materials. The NMR data matched those reported in literature.⁷,⁸

![AcO](image)

3-(4-acetoxyphenyl)propyl acetate [S₈]. Prepared using the general procedure for acetate protection.
$^1$H NMR: (500 MHz, CDCl$_3$) 
$\delta$ 7.20 – 7.16 (m, 2H), 7.02 – 6.98 (m, 2H), 4.09 (t, $J = 6.5$ Hz, 2H), 2.70 – 2.66 (m, 2H), 2.28 (s, 3H), 2.05 (s, 3H), 1.98 – 1.91 (m, 2H).

$^{13}$C NMR: (126 MHz, CDCl$_3$) 
$\delta$ 171.24, 169.73, 149.01, 138.89, 129.41, 121.57, 63.85, 31.73, 30.27, 21.25, 21.08.

HRMS: (ESI-TOF MS ES$^+$) 
$m/z$ calculated for C$_{13}$H$_{17}$O$_4$[M+H]$^+$: 237.1116, found 237.1127.

S9. Prepared according to literatures, the NMR data matched those reported.$^9$

S10. Prepared according to the general procedure for trifluoroacetate protection of an amine and the NMR data matched those reported.$^{10}$

2,2,2-trifluoro-N-(4-phenylbutan-2-yl)acetamide [S11]. Synthesized via trifluoroacetylation of commercially available 4-phenylbutan-2-amine. In a flame-dried round bottom flask equipped with a septum and stir bar under nitrogen was added 4-phenylbutan-2-amine (2g, 13.4 mmol, 1 equiv.), pyridine (3.18g, 40.2 mmol, 3 equiv.), and DCM (33 mL, 0.4 M). The reaction was cooled to 0 °C and trifluoroacetic anhydride was added dropwise (5.63g, 26.8 mmol, 2 equiv.). The reaction was then warmed to room temperature and stirred to completion (monitored by TLC analysis). Upon completion, the reaction was quenched with H$_2$O and transferred to a separatory funnel. The mixture is extracted with DCM (2 x 40 mL). The organic layers were washed with H$_2$O, dried over Na$_2$SO$_4$, filtered and the solvent evaporated. The crude product is then purified using silica gel chromatography and eluted with 20% ethyl acetate in 80% hexane to give the product as a white solid (3.12 g, 12.7 mmol, 95% yield).

$^1$H NMR: (500 MHz, CDCl$_3$) 
$\delta$ 7.32 – 7.27 (m, 2H), 7.23 – 7.16 (m, 3H), 6.02 (s, 1H), 4.08 (hept, $J = 13.5$ Hz, 1H), 2.67 (t, $J = 7.8$ Hz, 2H), 1.90 – 1.84 (m, 2H), 1.27 (d, $J = 6.6$ Hz, 3H).

$^{13}$C NMR: (126 MHz, CDCl$_3$) 
$\delta$ 156.63 (q, $J = 36.6$ Hz), 140.92, 128.75, 128.39, 126.40, 115.96 (q, $J = 288.2$ Hz), 46.50, 37.99, 32.35, 20.56.

$^{19}$F NMR: (470.75 MHz, CDCl$_3$) 
$\delta$ -76.02
HRMS: (ESI- TOF MS ES+)  

\[ m/z \text{ calculated for } C_{12}H_{15}NO_3[M+H]^+ : 246.1106, \text{ found } 246.1111. \]

![Isopentylbenzene](image)

**Isopentylbenzene [S12].** Synthesized using a known procedure.\(^{11}\)

\(^1\)H NMR: (500 MHz, CDCl\(_3\))

\[ \delta 7.30 - 7.26 (m, 2H), 7.21 - 7.15 (m, 3H), 2.68 - 2.58 (m, 2H), 1.60 (\text{non, } J = 12.7 \text{ Hz, } 1H), 1.55 - 1.48 (m, 2H), 0.95 (d, J = 6.6 \text{ Hz, } 6H). \]

\(^{13}\)C NMR: (126 MHz, CDCl\(_3\)) \[ \delta 143.3, 128.5, 128.4, 125.7, 41.0, 34.0, 27.8, 22.7. \]

S13. Synthesized using a known procedure.\(^{11}\) The NMR data matched those reported.

S14, S16. Prepared using the general procedure for acetate protection of commercial materials. The NMR data matched those reported in literature.\(^{12,13}\)

Compounds S15, S17, and S19 were obtained through commercial sources.

S18 is an amination byproduct, see page 30.

S20. Prepared according to method reported in literature, the NMR data matched those reported.\(^{14}\)

![3-ethyl-9-(phenylsulfonyl)-9H-carbazole](image)

**3-ethyl-9-(phenylsulfonyl)-9H-carbazole [S21].** Prepared from commercial 3-ethylcarbazole according to method reported in literature.\(^{15}\)

\(^1\)H NMR: (500 MHz, CDCl\(_3\))

\[ \delta 8.32 (d, J = 8.4 \text{ Hz, } 1H), 8.23 (d, J = 8.5 \text{ Hz, } 1H), 7.88 (d, J = 7.7 \text{ Hz, } 1H), 7.84-7.78 (m, 2H), 7.71 (s, 1H), 7.47 (ddd, J = 8.6, 7.3, 1.3 \text{ Hz, } 1H), 7.43 (t, J = 7.5 \text{ Hz, } 1H). 7.38-7.27 (m, 4H), 2.79 (q, J = 7.6 \text{ Hz, } 2H), 1.31 (t, J = 7.6 \text{ Hz, } 3H). \]

\(^{13}\)C NMR: (126 MHz, CDCl\(_3\))

\[ \delta 140.33, 138.71, 138.02, 136.71, 133.81, 129.12, 127.74, 127.35, 126.66, 126.65, 126.58, 124.01, 120.05, 118.98, 115.27, 115.05, 28.84, 16.06. \]

HRMS: (ESI- TOF MS ES+)
1-(4-ethylphenyl)-5-methylpyrrolidin-2-one [S22]. 4-ethyl aniline (1.5g, 12.4 mmol, 1 equiv.), levulinic acid (2.88g, 24.76 mmol, 2 equiv.), Et$_3$N (1.25g, 12.4 mmol, 1 equiv.), and formic acid (0.570g, 12.4 mmol, 1 equiv.) were added to flame-dried round bottom flask equipped with water-cooled condenser. The reagents were dissolved in DMSO (25 mL, 0.5M) and refluxed at 100 °C for 12 h. The reaction was cooled and water (40 mL) and DCM (40 mL) were added. The organic layer was extracted with water (3 x 20 mL). The combined aqueous layers were then extracted with DCM (1 x 40 mL). The combined organic layers were dried over Na$_2$SO$_4$. Flash column chromatography on silica gel (1:1 hexanes:ethyl acetate) gives the product as a brown oil (504.2 mg, 2.48 mmol, 10% yield).

$^1$H NMR (500 MHz, CDCl$_3$)

$\delta$ 7.28 – 7.27 (m, 1H), 7.27 – 7.25 (m, 1H), 7.24 – 7.21 (m, 2H), 4.27 (d sxt, $J = 12.3, 1.3$ Hz, 1H), 2.69 – 2.60 (m, 3H), 2.55 (ddd, $J = 17.0, 9.5, 7.4$ Hz, 1H), 2.42-2.34 (m, 1H), 1.80-1.72 (m, 1H), 1.25 (t, $J = 7.6$ Hz, 3H), 1.21 (d, $J = 6.3$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$)

$\delta$ 174.34, 142.07, 135.22, 128.55, 124.39, 55.93, 31.43, 28.54, 26.96, 20.39, 15.63.

HRMS (ESI- TOF MS ES$^+$)

$m/z$ calculated for C$_{13}$H$_{18}$NO [M+H]$^+$: 204.1388, found 204.1395.

Figure 6. Synthesis of Oxazolidinone S23.

1-((4-ethylphenyl)amino)propan-2-ol [S23a]. 4-ethyl aniline (1.45g, 12 mmol, 1 equiv.), 1-bromo-2-
propanol (2 g, 14.4 mmol, 1.2 equiv.), diisopropyl ethyl amine (3.1 g, 24 mmol, 2 equiv.), NaI (1.8 g, 12 mmol, 1 equiv.) and acetonitrile (80 mL, 0.15M) were added to a round bottom flask equipped with a water-cooled condenser under a nitrogen atmosphere. The reaction was refluxed overnight and monitored by TLC. Upon completion, the reaction was poured into a separatory funnel and H₂O (20 mL) and DCM (40 mL) were added and shaken. The organic layer was separated and the aqueous layer extracted with DCM (2 x 20 mL). The combined organic layers were dried over Na₂SO₄, filtered and evaporated. Flash column chromatography on silica gel using 40% EtOAc in hexanes gives the amino alcohol as a colorless oil in (1.29 g, 7.2 mmol, 60% yield). This substrate contains rotational isomers in the ¹H NMR

¹H NMR: (400 MHz, Chloroform-d)

δ 7.03 (d, J = 8.2 Hz, 2H), 6.66 – 6.58 (m, 2H), 4.07-3.96 (m, 0.75H), 3.72 (dd, J = 10.6, 4.2 Hz, 0.25H), 3.67-3.55 (m, 0.25H), 3.48 (dd, J = 10.6, 6.3 Hz, 0.25H), 3.22 (dd, J = 12.9, 3.3 Hz, 0.75H), 3.14 (br s, 2H), 2.98 (dd, J = 12.9, 8.7 Hz, 0.75H), 2.55 (q, J = 7.6 Hz, 2H), 1.30 – 1.16 (m, 6H).

3-(4-ethylphenyl)-5-methyloxazolidin-2-one [S23]. In a flame-dried round bottom flask equipped with a water-cooled condenser was added NaOMe (227 mg, 4.2 mmol, 1.5 equiv.), 1-((4-ethylphenyl)amino)propan-2-ol S23a (500 mg, 2.8 mmol, 1 equiv.) and toluene (5.6 mL, 0.5M). The mixture was stirred for 5 minutes, then diethyl carbonate was added dropwise (500 mg, 4.2 mmol, 1.5 equiv.). The reaction was refluxed to completion (4 h) and monitored by TLC. Upon completion, the reaction was filtered through celite using DCM and concentrated. The crude product was then purified using silica gel flash chromatography with gradient elution (10% EtOAc in hexane to 50% EtOAc in hexane) to give a white solid (459.8 g, 2.24 mmol, 80% yield).

¹H NMR: (500 MHz, CDCl₃)

δ 7.43 (d, J = 8.6 Hz, 2H), 7.20 (d, J = 8.8 Hz, 2H), 4.78 (ddq, J = 8.2, 7.0, 6.2 Hz, 1H), 4.10 (t, J = 8.4 Hz, 1H), 3.61 (dd, J = 8.6, 7.0 Hz, 1H), 2.63 (q, J = 7.6 Hz, 2H), 1.53 (d, J = 6.2 Hz, 3H), 1.22 (t, J = 7.6 Hz, 3H).

¹³C NMR: (126 MHz, CDCl₃)

δ 155.12, 140.24, 136.21, 128.54, 118.54, 69.62, 52.22, 28.34, 20.89, 15.82.

HRMS: (ESI- TOF MS ES+)
$m/z$ calculated for C$_{12}$H$_{16}$NO$_2$ [M+H]$^+$: 206.1181, found 206.1172.

1'-methyl-3,4-dihydro-2H-spiro[naphthalene-1,4'-piperidine] [25]. Synthesized using a previously reported synthesis and the spectral data matches the previously reported data.$^{16}$

$^1$H NMR: (400 MHz, CDCl$_3$)

$\delta$ 7.49 (d, $J = 7.9$ Hz, 1H), 7.21-7.15 (m, 1H), 7.08 (td, $J = 7.3$, 1.2 Hz, 1H), 7.16-7.03 (m, 1H), 2.77 (t, $J = 6.2$ Hz, 2H), 2.76-2.70 (m, 2H), 2.35 (s, 3H), 2.26 (td, $J = 11.8$, 1.8 Hz, 2H), 2.16 (td, $J = 13.8$, 3.8 Hz, 2H), 1.87-1.80 (m, 2H), 1.78-1.70 (m, 2H), 1.65-1.57 (m, 2H)

$^{13}$C NMR: (101 MHz, CDCl$_3$)

$\delta$ 145.16, 137.41, 129.06, 126.92, 126.03, 125.42, 51.84, 46.69, 38.56, 34.86, 30.99, 30.83, 19.02

HRMS: (ESI-TOF MS ES$^+$)

$m/z$ calculated for C$_{15}$H$_{22}$N [M+H]$^+$: 216.1752, found 216.1748.

$N,N$-dimethyl-4-phenylbutan-1-amine [S24]. In a 100 mL round-bottom flask were added 4-phenylbutan-1-amine (1.58 mL, 1.49 g, 10.0 mmol, 1.0 equiv.) and formaldehyde (37 wt%, 7.5 mL, 3.02 g, 100 mmol, 10.0 equiv.). Formic acid (3.8 mL, 4.60 g, 100 mmol, 10.0 equiv.) was then added dropwise. The mixture was then refluxed in a 100 °C oil bath for 4 h, then partitioned between water (50 mL) and CH$_2$Cl$_2$ (50 mL), upon which time a saturated potassium carbonate solution (10 mL) was added. The organic layer was isolated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (3x50 mL). The organic layers were combined, dried over MgSO$_4$, and concentrated via rotary evaporation. The crude material was purified by flash chromatography (50 mL basic Al$_2$O$_3$ Brockmann grade III, 5% EtOAc/Hex (4 column volumes)) to afford the product as a light yellow oil (1.36 g, 7.65 mmol, 76% yield).

Data for S24: These spectral data matched those reported in literature.$^{17}$

$^1$H NMR: (400 MHz, CDCl$_3$)
δ 7.30-7.24 (m, 2H), 7.21-7.14 (m, 3H), 2.63 (t, J = 7.6 Hz, 2H), 2.27 (t, J = 7.5 Hz, 2H), 2.21 (s, 6H), 1.64 (app p, J = 7.2 Hz, 2H), 1.55-1.46 (m, 2H)

\[ ^{13}C \text{ NMR: (101 MHz, CDCl}_3 \]  
δ 142.60, 128.49, 128.34, 125.75, 59.82, 45.63, 35.97, 29.42, 27.52

**1-methyl-4-(3-phenylpropyl)piperidine [S25].** In a 100 mL round-bottom flask equipped with a magnetic stir bar were added 1-methyl-4-(3-phenylpropyl)-1,2,3,6-tetrahydropyridine (717 mg, 3.33 mmol), palladium hydroxide on carbon (20 wt%, 112 mg) and toluene (0.3 M, 11.2 mL). The flask was placed into a metal pressure reactor and filled with hydrogen gas (60 psi). The reaction mixture was stirred for a week. Upon completion, the mixture was filtered and condensed via rotary evaporation. The crude material was purified by flash chromatography (50 mL silica, 25% EtOAc/Hex (4 column volumes)) to afford the product as a colorless oil (392.2 mg, 1.80 mmol, 54% yield).

\[ ^{1}H \text{ NMR: (500 MHz, CDCl}_3 \]  
δ 7.30–7.25 (m, 2H), 7.20–7.15 (m, 3H), 2.82 (d, J = 11.5 Hz, 2H), 2.59 (t, J = 7.8 Hz, 2H), 2.24 (s, 3H), 1.86 (t, J = 11.1 Hz, 2H), 1.70-1.57 (m, 4H), 1.32-1.16 (m, 5H)

\[ ^{13}C \text{ NMR: (101 MHz, CDCl}_3 \]  
δ 142.83, 128.45, 128.33, 125.70, 56.18, 46.65, 36.36, 36.27, 35.20, 32.60, 28.89

HRMS: (ESI-TOF MS ES+)  
m/z calculated for C_{15}H_{24}N [M+H]^+: 218.1909, found 218.1910.

**Figure 7.** Synthesis of 4-(1,2,3,4-Tetrahydronaphthalen-1-yl)pyridine S26.
1-(pyridin-4-yl)-1,2,3,4-tetrahydronaphthalen-1-ol [S26a]. To a 500 mL separatory funnel was added 4-bromopyridine hydrochloride (3.12 g, 16.0 mmol) and diethyl ether (30 mL). Saturated sodium bicarbonate solution (30 mL) was then added. After the bubbles subsided, the substrate was partitioned between the two layers. The organic layer was isolated, and the aqueous layer was further extracted with Et₂O (2x30 mL). The organic layers were combined, dried over MgSO₄, and concentrated in vacuo in a 300 mL round-bottom flask. According to literature-reported method,¹⁸ anhydrous Et₂O (60 mL) and tetrahydrofuran (THF) (40 mL) were then added, and the resulting solution was placed in a -78 °C cold bath. n-Butyllithium (1.6 M, 9.9 mL, 15.8 mmol) was quickly added, and the reaction mixture was stirred for 5 s. α-Tetralone (2.10 g, 14.4 mmol) in THF (40 mL) was then quickly added. The reaction was then taken out of the cold bath and stirred overnight at room temperature. Saturated ammonium chloride (0.5 mL) was used to quench the reaction, and the resulting mixture was condensed in vacuo and directly loaded onto a flash column. Purification (150 mL silica, gradient elusion 2% (2 column columes)→5% MeOH/CH₂Cl₂ (4 column volumes)) afforded the product as an orange solid (1.53 g, 6.80 mmol, 47% yield).

¹H NMR: (500 MHz, CDCl₃)

δ 8.54 (d, J = 5.0 Hz, 2H), 7.30 (d, J = 5.3 Hz, 2H), 7.24 (dd, J = 7.4, 1.2 Hz, 1H), 7.19 (td, J = 7.6, 0.7 Hz, 1H), 7.13 (td, J = 7.5, 0.7 Hz, 1H), 6.93 (d, J = 7.5 Hz, 1H), 2.98-2.85 (m, 2H), 2.23 (s, 1H), 2.18-2.10 (m, 1H), 2.09-1.97 (m, 2H), 1.89-1.81 (m, 1H)

4-(3,4-dihydonaphthalen-1-yl)pyridine [S26b]. To a 100 mL recovery flask carrying 1-(pyridin-4-yl)-1,2,3,4-tetrahydronaphthalen-1-ol S26a (1.53 g, 6.80 mmol, 1.0 equiv.) were added isopropanol (30 mL) and concentrated hydrochloric acid (12M, 11.3 mL, 136 mmol, 20 equiv.). The resulting solution was refluxed for 4 h. Upon completion, the solvent was removed in vacuo and the residue was redissolved in DCM (30 mL) and basified with saturated K₂CO₃. The aqueous layer was extracted with DCM (3x30
mL). The organic layers were combined, dried over MgSO₄ and concentrated in vacuo. Purification by flash chromatography (50 mL silica, 40% EtOAc/Hex (8 column volumes)) afforded the product as an orange oil (1.27 g, 6.13 mmol, 90% yield).

**¹H NMR:** (500 MHz, CDCl₃)

| δ (ppm) | J (Hz) | Description |
|---------|--------|-------------|
| 8.61 | 4.4, 1.6 | 2H |
| 7.28 | 4.4, 1.6 | 2H |
| 7.22 | 7.4, 1.2 | 1H |
| 7.20 | 7.3, 1.3 | 1H |
| 7.14 | 7.4, 1.8 | 1H |
| 6.96 | 7.7 | 1H |
| 6.20 | 4.7 | 1H |
| 2.86 | 8.0 | 2H |
| 2.46-2.41 | | m (2H) |

**4-(1,2,3,4-tetrahydronaphthalen-1-yl)pyridine [S26].** To a 100 mL round-bottom flask carrying 4-(3,4-dihydronaphthalen-1-yl)pyridine S26b (1.27 g, 6.13 mmol) were added palladium hydroxide on carbon (20 wt%, 205 mg) and toluene (20.5 mL). The reaction was placed into a metal pressure reactor, sealed and purged with H₂ gas (3 x app. 100 psi). After purging the metal pressure reactor was pressurized with H₂ gas (app. 100 psi) and stirred for 2 days at room temperature. The resulting solution was filtered and concentrated in vacuo. Purification through flash chromatography (50 mL silica, gradient elution 20% (4 column volumes) → 40% (8 column volumes)) afforded the product as a colorless viscous oil (1.24 g, 5.90 mmol, 96% yield), which was azeotroped once with anhydrous benzene (5 mL).

**¹H NMR:** (400 MHz, CDCl₃)

| δ (ppm) | J (Hz) | Description |
|---------|--------|-------------|
| 8.49 | 4.5, 1.6 | 2H |
| 7.16 | 4.7, 0.8 | 2H |
| 7.09-7.04 | | (1H) |
| 7.02 | 4.7, 1.5 | 2H |
| 6.79 | 7.6 | 1H |
| 4.12 | 6.4 | 1H |
| 2.97-2.80 | | (2H) |
| 2.23-2.13 | | (m, 1H) |
| 1.90-1.70 | | (m, 3H) |

**¹³C NMR:** (101 MHz, CDCl₃)

| δ (ppm) | Description |
|---------|-------------|
| 157.06, 149.18, 137.76, 137.20, 130.11, 129.40, 126.65, 126.04, 124.43, 45.09, 32.68, 29.63, 20.61 |

**HRMS:** (ESI-TOF MS ES⁺)

m/z calculated for C₁₅H₁₆N [M+H⁺]: 210.1283, found 210.1286.
4-phenylbutan-1-amine boron trifluoride complex [S27]. In a flame-dried 100 mL round-bottom flask equipped with a stir bar were added 4-phenylbutan-1-amine (316 µL, 298.5 mg, 2.0 mmol, 1.0 equiv.) and CH₂Cl₂ (8 mL). The solution was placed in an ice bath, and boron trifluoride diethyl etherate (272 µL, 312.2 mg, 2.2 mmol, 1.1 equiv.) was added dropwise upon stirring. The reaction mixture was kept stirring in an ice bath for 30 min and then allowed to warm up to ambient temperature. The reaction mixture was then further stirred for 1 h, condensed through rotary evaporation and purified through flash chromatography (50 mL silica, 40% EtOAc/Hex (4 column volumes)) to afford the product as a white solid (296.0 mg, 1.36 mmol, 68% yield).

**¹H NMR:** (500 MHz, CD₃CN)
δ 7.33-7.26 (m, 2H), 7.24-7.16 (m, 3H), 4.56 (br s, 2H), 2.76 (p, J = 7.2 Hz, 2H), 2.63 (t, J = 7.3 Hz, 2H), 1.70-1.54 (m, 4H)

**¹³C NMR:** (126 MHz, CD₃CN)
δ 143.08, 129.27, 129.24, 126.71, 41.58, 35.73, 29.10, 28.56

**¹⁹F NMR:** (470 MHz, CD₃CN)
δ -151.98 (dd, J = 32.6, 15.9 Hz, 3F)

**HRMS:** (ESI-TOF MS ES-)
m/z calculated for C₁₀H₁₄BF₃N [M-H]⁺: 216.1171, found 216.1172.

S28. Prepared according to literature, the NMR data matched those reported.¹⁹

Methyl 4'-hexyl-[1,1'-biphenyl]-4-carboxylate [S29]. To a flame-dried 50 mL round-bottom flask under argon, equipped with a Teflon stir bar was added MeOH (20 mL) and placed in a 0 °C ice-water bath. Thionyl chloride (0.323 mL, 4.43 mmol, 2.5 equiv) was added and the reaction stirred for 15 minutes at which time 4'-hexyl-[1,1'-biphenyl]-4-carboxylic acid (0.50 g, 1.77 mmol, 1 equiv) was added in one portion. The reaction was stirred at room temperature overnight. The solvent was evaporated and the crude oil taken up in toluene and concentrated three consecutive times. The crude product was purified...
using gradient silica gel flash chromatography (5% ethyl acetate in 95% hexanes to 10% ethyl acetate in 90% hexanes) to give a white solid (0.48 g, 91% yield).

**$^1$H NMR:** (500 MHz, Chloroform-$d$)

$\delta$ 8.13 – 8.07 (m, 2H), 7.69 – 7.63 (m, 2H), 7.58 – 7.53 (m, 2H), 7.32 – 7.26 (m, 2H), 3.94 (s, 3H), 2.66 (app t, $J$ = 7.9 Hz, 2H), 1.71 – 1.61 (m, 2H), 1.43 – 1.28 (m, 6H), 0.95 – 0.87 (m, 3H)

**$^{13}$C NMR:** (126 MHz, CDCl$_3$)

$\delta$ 167.2, 145.7, 143.3, 137.4, 130.2, 129.1, 128.7, 127.2, 126.9, 52.2, 35.8, 31.9, 31.6, 29.2, 22.8, 14.3

**HRMS:** (ESI-TOF MS ES$^+$)

$m/z$ calculated for C$_{20}$H$_{25}$O$_2$ [M+H]$^+$: 297.1855, found 297.1851

**rac-(9S,10R,11R,15S)-2-ethyl-13-methyl-9,10-dihydro-9,10-[3,4]epipyrrroloanthracene-12,14-dione [(±)S30]** According to literature, a 50 mL round-bottom flask equipped with a magnetic stir bar was charged with 2-ethylanthracene (936 mg, 4.54 mmol, 1.08 equiv.), N-methylmaleimide (467 mg, 4.20 mmol, 1.0 equiv.) and m-xylene (10 mL). The reaction mixture was heated at reflux for 7 h. Upon completion, the solvent was removed under reduced pressure through rotary evaporation. Purification by flash chromatography on silica (150 mL) eluting with 10% (5 column volumes)$\rightarrow$20% EtOAc/hexanes (4 column volumes) yielded a light yellow solid as a mixture of diastereomers. The desired diastereomer was isolated through MPLC (40 g silica) four times eluting with 0%$\rightarrow$20% EtOAc/hexanes (40 column volumes) as a white solid (297 mg, 0.937 mmol, 22% yield).

**$^1$H NMR:** (500 MHz, CDCl$_3$)

$\delta$ 7.39-7.33 (m, 2H), 7.16 (m, 3H), 7.09 (s, 1H), 6.94 (d, $J$ = 7.5 Hz, 1H), 4.74 (m, 2H), 3.21-3.16 (m, 2H), 2.55 (q, $J$ = 7.5 Hz, 2H), 2.50 (s, 3H), 1.14 (t, $J$ = 7.6 Hz, 3H)

**$^{13}$C NMR:** (126 MHz, CDCl$_3$)

$\delta$ 177.17, 143.36, 141.82, 141.69, 138.53, 135.82, 126.76, 126.73, 126.42, 124.79, 124.55, 124.30, 124.27, 47.22, 47.17, 45.76, 45.32, 28.75, 24.36, 15.94

**HRMS:** (ESI-TOF MS ES$^+$)

$m/z$ calculated for C$_{21}$H$_{20}$N$_2$ [M+H]$^+$: 318.1494, found 318.1495.
1-(3,4-dihydro-2H-spiro[naphthalene-1,4'-piperidin]-1'-yl)-2,2,2-trifluoroethan-1-one [S31].

Synthesized using a previously reported synthesis and the spectral data matches the previously reported data.\textsuperscript{16}

\textsuperscript{1}H NMR: (400 MHz, Chloroform-\textit{d})

\[
\begin{align*}
\delta & 7.32 (dd, J = 7.9, 1.3 \text{ Hz}, 1H), 7.20 (td, J = 7.4, 1.8 \text{ Hz}, 1H), 7.15 - 7.06 (m, 2H), 4.56 - 4.45 (m, 1H), 3.99 - 3.88 (m, 1H), 3.42 (td, J = 13.90, 2.5 \text{ Hz}, 1H), 3.04 (app t, J = 13.4 \text{ Hz}, 1H), 2.81 (t, J = 6.3 \text{ Hz}, 2H), 2.12 - 1.99 (m, 2H), 1.99 - 1.89 (m, 2H), 1.85 - 1.77 (m, 2H), 1.77 - 1.69 (m, 2H).
\end{align*}
\]

1-(3-(dimethylamino)propyl)-1-(4-fluorophenyl)-1,3-dihydroisobenzofuran-5-carbonitrile [(\pm)S32].

To a 60 mL separatory funnel, commercial citalopram hydrobromide (203 mg, 0.5 mmol) was partitioned between CH\textsubscript{2}Cl\textsubscript{2} (5 mL) and water (5 mL). Sodium hydroxide (50\% wt, 5 mL) was then added, and the product was repartitioned between the layers. The aqueous layer was extracted with CH\textsubscript{2}Cl\textsubscript{2} (3x5 mL) and the organic layers were combined, dried over anhydrous MgSO\textsubscript{4}, filtered and condensed \textit{in vacuo}. The product was obtained as a colorless gel (163 mg, 0.5 mmol, quantitative yield).

Data for S32: These spectral data matched those reported in literature.\textsuperscript{21}

\textsuperscript{1}H NMR: (400 MHz, CDCl\textsubscript{3})

\[
\begin{align*}
\delta & 7.59 (dd, J = 7.9, 0.8 \text{ Hz}, 1H), 7.50 (s, 1H), 7.45-7.40 (m, 2H), 7.38 (d, J = 7.9 \text{ Hz}, 1H), 7.04-6.97 (m, 2H), 5.20 (d, J = 12.9 \text{ Hz}, 1H), 5.15 (d, J = 12.9 \text{ Hz}, 1H), 2.26-2.19 (m, 2H), 2.17 (dd, J = 9.3, 5.0 \text{ Hz}, 1H), 2.13 (s, 6H), 2.12-2.08 (m, 1H), 1.52-1.39 (m, 1H), 1.37-1.24 (m, 1H)
\end{align*}
\]
trans-4-ethyl-1,2,3,4a,5,6,10b-octahydrobenzo[f]quinoline [(±)S33]. To a 100 mL recovery flask equipped with a magnetic stir bar were added trans-1,2,3,4a,5,6,10b-octahydrobenzo[f]quinoline \(^{22}\) (209 mg, 1.10 mmol, 1.0 equiv.), acetic acid (0.22 mL, 1% v/v), and 1,2-dichloroethane (0.05 M, 22 mL). Acetaldehyde (0.31 mL, 242 mg, 5.50 mmol, 5.0 equiv.) was added dropwise as the solution turned orange. The mixture was stirred for 30 min, upon which sodium triacetoxyborohydride (350 mg, 1.65 mmol, 1.5 equiv.) was added in one portion and the reaction solution was stirred overnight at room temperature. The reaction was quenched with saturated NaHCO\(_3\) solution (50 mL) and extracted with CH\(_2\)Cl\(_2\) (3 x 25 mL). The combined organic layer was washed with saturated aqueous NaHCO\(_3\) solution (50 mL) and brine (50 mL). Dried over anhydrous MgSO\(_4\), filtered and concentrated. The crude material was thrice purified by column chromatography (20 mL silica, gradient elution 2% \(\rightarrow\) 5% \(\rightarrow\) 10% MeOH/CH\(_2\)Cl\(_2\) (5 column volumes each)) to afford the product as a white solid (109.7 mg, 0.509 mmol, 46% yield).

\(^1\)H NMR: (500 MHz, CDCl\(_3\))

\[\delta 7.29 (d, J = 7.6 Hz, 1H), 7.19-7.07 (m, 3H), 3.03 (app d, J = 11.3 Hz, 1H), 2.99-2.87 (m, 3H), 2.71 (dq, J = 13.9, 7.1 Hz, 1H), 2.67-2.60 (m, 1H), 2.53-2.46 (m, 1H), 2.34-2.25 (m, 2H), 2.16 (td, J = 10.5, 3.2 Hz, 1H), 1.89-1.77 (m, 2H), 1.69-1.58 (m, 1H), 1.32-1.22 (m, 1H), 1.05 (t, J = 7.2 Hz, 3H)\]

\(^{13}\)C NMR: (101 MHz, CDCl\(_3\))

\[\delta 138.83, 135.97, 128.51, 126.13, 126.08, 125.62, 63.31, 52.11, 46.62, 41.59, 29.26, 29.01, 26.11, 24.87, 9.28\]

HRMS: (ESI-TOF MS ES+)  
\[m/z\] calculated for C\(_{15}\)H\(_{22}\)N [M+H]\(^+\): 216.1752, found 216.1754.

(±)S34 is a minor diastereomer for (±)37, see page 49.

**Figure 8.** Synthesis of glucocorticoid receptor agonist analog.\(^{23}\)
(5R)-5-benzyl-8-hydroxy-8-methyl-5,6,7,8,9,10-hexahydro-5,9-methanobeno[8]annulen-11-one

[S35a]. To a flame-dried 300 mL round-bottom flask under argon, equipped with a Teflon stir bar was added 1-benzyl-3,4-dihydronaphthalen-2(1H)-one (5.97 g, 25.3 mmol, 1 equiv), (S)-(−)-methylbenzylamine (3.26 mL, 25.3 mmol, 1 equiv), and toluene (100 mL, 0.25M). The flask was fitted with a Dean-Stark apparatus and water-cooled condenser and refluxed overnight. The reaction was cooled to room temperature then placed in an ice-water bath and cooled to 0 °C. Freshly distilled methyl vinyl ketone (2.38 mL, 28.6 mmol, 1.13 equiv) was added dropwise to the reaction and stirred for 30 minutes at 0 °C then brought to 40 °C and stirred overnight. The solution was brought back to 0 °C and acetic acid (0.5 mL) and water (0.5 mL) were added and stirred at room temperature for 2 hours. The reaction was poured into water (100 mL), and extracted three times with ethyl acetate (3 x 100 mL). The organic extracts were combined and washed with 1M HCl (50 mL), water (50 mL), and saturated NaHCO₃ (aq) (50 mL). After removal of solvent the crude product was purified using gradient silica gel flash chromatography (15% ethyl acetate in 85% hexanes to 35% ethyl acetate in 65% hexanes) to give a light brown solid (2.18 g, 28% yield).

1H NMR: (500 MHz, Chloroform-d)

\[ \delta 7.21 - 7.16 (m, 1H), 7.16 - 7.07 (m, 7H), 7.07 - 7.02 (m, 1H), 3.69 (d, J = 15.6 Hz, 1H), 3.40 (dd, J = 17.9, 6.6 Hz, 1H), 3.24 (d, J = 15.6 Hz, 1H), 3.17 (d, J = 18.1 Hz, 1H), 2.65 (dt, J = 6.8, 1.5 Hz, 1H), 2.26 (td, J = 13.1, 4.3 Hz, 1H), 1.79 (s, 1H), 1.75 - 1.67 (m, 1H), 1.58 - 1.48 (m, 1H), 1.47 - 1.38 (m, 1H), 1.37 (s, 3H) \]

13C NMR: (126 MHz, CDCl₃)

\[ \delta 213.3, 140.4, 138.7, 134.3, 130.3, 127.8, 127.5, 127.1, 126.6, 126.5, 125.5, 79.2, 58.8, 54.2, 41.6, 38.4, 34.4, 33.0, 28.0 \]

HRMS: (ESI-TOF MS ES+)

\[ m/z \text{ calculated for } C_{21}H_{23}O_2 \text{ [M+H]}^+ : 307.1698, \text{ found } 307.1694 \]
(S)-4a-benzyl-4,4a,9,10-tetrahydrophenanthren-2(3H)-one [S35b]. To a 50 mL round bottom flask equipped with a Teflon stir bar, (5R)-5-benzyl-8-hydroxy-8-methyl-5,6,7,8,9,10-hexahydro-5,9-methanobenzo[8]annulen-11-one S35a (1.9 g, 6.20 mmol, 1 equiv), 1 M NaOMe (3.1 mL), and MeOH (10 mL) were combined and stirred at room temperature for 15 minutes. The reaction was heated to 75 °C for 3 hours and cooled to 0 °C then treated dropwise with AcOH (0.4 mL) and concentrated. The crude oil was dissolved in EtOAc, washed with saturated NaHCO₃ (aq) (50 mL) and brine (50 mL), dried over Na₂SO₄ (anhyd), filtered and concentrated to an oil. The crude product was purified using gradient silica gel flash chromatography (10% ethyl acetate in 90% hexanes to 20% ethyl acetate in 80% hexanes) to give an amber and clear oil (1.69 g, 95% yield).

1H NMR: (500 MHz, Chloroform-d)

δ 7.26 – 7.22 (m, 2H), 7.21 – 7.14 (m, 2H), 7.14 – 7.09 (m, 2H), 7.06 (d, J = 7.5 Hz, 1H), 6.77 – 6.70 (m, 2H), 6.01 (s, 1H), 3.29 (d, J = 13.2 Hz, 1H), 3.21 (d, J = 13.2 Hz, 1H), 2.88 – 2.69 (m, 3H), 2.59 – 2.45 (m, 2H), 2.33 (ddd, J = 13.8, 5.2, 3.4 Hz, 1H), 2.09 (td, J = 14.5, 14.1, 5.5 Hz, 1H), 1.98 – 1.87 (m, 1H)

13C NMR: (126 MHz, CDCl₃)

δ 198.6, 169.0, 140.9, 137.3, 136.0, 130.1, 128.6, 128.0, 127.0, 126.8, 126.6, 126.5, 125.7, 46.4, 44.2, 36.0, 34.7, 32.2, 30.6

HRMS: (ESI-TOF MS ES+)

m/z calculated for C₂₁H₂₁O [M+H]+: 289.1592, found 289.1589

(S)-4a-benzyl-4,4a,9,10-tetrahydro-3H-spiro[phenanthrene-2,2'-[1,3]dioxolane] [S35c]. In a flame-dried 200 mL round bottom flask under argon, equipped with a Teflon stir bar was added (S)-4a-benzyl-4,4a,9,10-tetrahydrophenanthren-2(3H)-one S35b (1.2 g, 4.16 mmol, 1 equiv), ethylene glycol (1.16 mL, 20.8 mmol, 5 equiv), p-toluenesulfonic acid (2 mg), and toluene (80 mL, 0.05M). The round bottom was fitted with a Dean-Stark apparatus and water-cooled reflux condenser and refluxed for 16 hours. The solvent was removed and the crude oil taken up in EtOAc (50 mL) and washed with water (20 mL) and brine (20 mL) then dried with K₂CO₃ (anhyd), filtered and concentrated. The crude product was purified using gradient silica gel flash chromatography (10% ethyl acetate in 90% hexanes to 20% ethyl acetate in 80% hexanes) to give an amber and clear oil (1.08 g, 78% yield).
**1H NMR:** (500 MHz, Chloroform-\(d\))
\[\delta 7.41 \text{ (d, } J = 7.9 \text{ Hz, 1H), } 7.23 \text{ (t, } J = 7.2 \text{ Hz, 1H), } 7.13 - 7.04 \text{ (m, 2H), } 6.98 \text{ (t, } J = 7.6 \text{ Hz, 2H), } 6.83 \text{ (d, } J = 7.5 \text{ Hz, 1H), } 6.57 - 6.50 \text{ (m, 2H), } 5.63 - 5.58 \text{ (m, 1H), } 4.05 - 3.98 \text{ (m, 3H), } 3.98 - 3.92 \text{ (m, 1H), } 3.38 \text{ (d, } J = 12.9 \text{ Hz, 1H), } 3.02 - 2.92 \text{ (m, 1H), } 2.92 - 2.84 \text{ (m, 1H), } 2.76 \text{ (d, } J = 12.9 \text{ Hz, 1H), } 2.50 - 2.38 \text{ (m, 2H), } 2.32 \text{ (dt, } J = 23.2, 4.1 \text{ Hz, 1H), } 2.19 - 1.12 \text{ (m, 1H), } 2.02 \text{ (td, } J = 13.6, 4.1 \text{ Hz, 1H), } 1.97 - 1.36 \text{ (m, 1H)}
\]

**13C NMR:** (126 MHz, CDCl3)
\[\delta 141.3, 138.1, 135.2, 134.3, 130.1, 127.7, 127.1, 126.1, 126.0, 125.9, 125.8, 123.8, 108.7, 64.5, 44.4, 43.2, 42.3, 36.4, 31.6, 29.9\]

**HRMS:** (ESI-TOF MS ES+)
\[m/z \text{ calculated for } C_{23}H_{25}O_2 [M+H]^+: 333.1855, \text{ found 333.1848}\]

\[(-)-(4aS,10aR)-4a-benzyl-3,4,4a,9,10,10a-hexahydrophenanthren-2(1H)-one [S35]. \text{To a flame-dried 50 mL round bottom flask under argon, equipped with a Teflon stir bar was added (S)-4a-benzyl-4,4a,9,10-tetrahydro-3H-spiro[phenanthrene-2,2'-[1,3]dioxolane] S35c (0.50 g, 1.49 mmol, 1 equiv), toluene (5 mL, 0.3M), and 20 wt% Pd(OH)$_2$/C (0.050 g). The solution was purged with a hydrogen atmosphere and placed in high-pressure reaction vessel, purged with hydrogen three times, and pressurized to 60 psi. The reaction was stirred at room temperature for 5 days, filtered through a celite plug using toluene to make the transfer quantitative, evaporated and purified using gradient silica gel flash chromatography (10% ethyl acetate in 90% hexanes to 20% ethyl acetate in 80% hexanes). After purification, the product was transferred to a 50 mL round-bottom flask and THF (5 mL) and 1M HCl (5 mL) were added and stirred at room temperature for 24 hours. Upon reaction complete by TLC analysis, the reaction was transferred to a separatory funnel and extracted with diethyl ether (2 x 20 mL), then washed with brine (1 x 30 mL), dried over Na$_2$SO$_4$ (anhyd), filtered, and evaporated. The crude product was purified using gradient silica gel flash chromatography (10% ethyl acetate in 90% hexanes to 20% ethyl acetate in 80% hexanes) to give a white solid (0.23 g, 54% over 2 steps).}\]

**1H NMR:** (500 MHz, Chloroform-\(d\))
\[\delta 7.23 - 7.10 \text{ (m, 5H), } 6.89 - 6.83 \text{ (m, 1H), } 6.62 \text{ (d, } J = 7.0 \text{ Hz, 2H), } 6.39 \text{ (d, } J = 7.9 \text{ Hz, 1H), } 3.17 \text{ (d, } J = 13.2 \text{ Hz, 1H), } 3.11 - 2.96 \text{ (m, 2H), } 2.86 \text{ (d, } J = 12.7 \text{ Hz, 1H), } 2.86 - 2.79 \text{ (m, 1H), } 2.63 \text{ (t, } J = 14.5 \text{ Hz, 1H), } 2.58 - 2.50 \text{ (m, 2H), } 2.46 - 2.37 \text{ (m, 1H), } 2.23 \text{ (tt, } J = 13.3, 3.9 \text{ Hz, 1H), } 2.09 - 1.94 \text{ (m, 1H), } 1.82 - 1.72 \text{ (m, 1H), } 1.70 - 1.60 \text{ (m, 1H)}
\]

**13C NMR:** (126 MHz, CDCl3)
δ 211.0, 142.0, 137.5, 135.6, 131.0, 129.3, 127.7, 127.4, 126.5, 126.4, 124.6, 44.8, 43.2, 40.1, 38.3, 36.5, 33.4, 28.2, 25.2

HRMS: (ESI-TOF MS ES+)

\[ m/z \text{ calculated for } C_{21}H_{23}O [M+H]^+ : 291.1749, \text{ found } 291.1744 \]

\[ [\alpha]_D^{24} = -123.2^\circ (c = 0.19, \text{ CHCl}_3) \]

\[
\begin{array}{c}
1-(3,4\text{-dichlorophenyl})-1,2,3,4\text{-tetrahydronaphthalene [39]. In a round-bottom flask were added 1-(3,4\text{-dichlorophenyl})-1,2\text{-dihydronaphthalene (500 mg, 1.82 mmol, 1 equiv.), EtOAc (3.64 mL, 0.5M) and, Pd/C (5 mol%). The flask was sealed with a rubber septum, purged with hydrogen (3 balloons of hydrogen), and kept on a hydrogen balloon atmosphere at room temperature until reaction completion by TLC (6 h). The reaction was filtered through celite using ethyl acetate as the eluent and concentrated using rotary evaporation. Flash column chromatography on silica gel using hexanes elutes the product as a colorless oil along with minor impurities (approximately 5%) that could not be fully separated and do not affect reactivity (454.6 mg, 1.64 mmol, 90% yield).

\[ ^1H \text{ NMR: (500 MHz, CDCl}_3 \]

\[ \delta 7.34 \text{ (d, } J = 8.2 \text{ Hz, 1H)}, 7.19 \text{ (d, } J = 2.1 \text{ Hz, 1H)}, 7.16 – 7.14 \text{ (m, 2H)}, 7.08 – 7.04 \text{ (m, 1H)}, 6.92 \text{ (dd, } J = 8.3, 2.1 \text{ Hz, 1H)}, 6.80 \text{ (dd, } J = 7.8, 1.1 \text{ Hz, 1H)}, 4.09 \text{ (t, } J = 6.5 \text{ Hz, 1H)}, 2.96 – 2.80 \text{ (m, 2H)}, 2.22 – 2.11 \text{ (m, 1H)}, 1.92 – 1.70 \text{ (m, 3H)}. \]

\[ ^{13}C \text{ NMR: (126 MHz, CDCl}_3 \]

\[ \delta 147.99, 138.12, 137.69, 132.33, 130.82, 130.30, 130.12, 130.03, 129.35, 128.39, 126.51, 126.03, 45.00, 33.23, 29.73, 20.86. \]

HRMS: (ESI-TOF MS ES+)

\[ m/z \text{ calculated for } C_{16}H_{14}Cl_2 [M]: 276.04726, \text{ found } 276.04669. \]

\textbf{S36} is the aminated product of \textit{39}, see page 50.

\textbf{S37} is the methylated product of \textbf{S36}, see page 52.
4-ethylbenzyl \((2S,5R)-3,3\text{-dimethyl}-7\text{-oxo}-4\text{-thia}-1\text{-azabicyclo}[3.2.0]\text{heptane}-2\text{-carboxylate 4,4\text{-dioxide}}\) [S38]. Sulbactam (250 mg, 1.07 mmol) was added to a flame-dried round bottom flask along with dichloromethane (3.15 mL, 0.3M). \(N\)-(3-Dimethylaminopropyl)-\(N'\)-ethylcarbodiimide hydrochloride (EDC-HCl) (307 mg, 1.6 mmol, 1.6 equiv.) and 4-dimethylaminopyridine (DMAP) (65.4 mg, 0.54 mmol, 0.5 equiv.) under a nitrogen atmosphere and the reaction was stirred at 0 °C for 5 minutes. 4-ethylbenzyl alcohol (218 mg, 1.6 mmol, 1.6 equiv.) was added and stirred at 0 °C for an additional 5 minutes, then warmed to room temperature and stirred for 48 h. After reaction completion, the reaction was diluted with DCM (5 mL) and transferred to separatory funnel. The organic layer was washed with sat. NaHCO\(_3\) (1 x 10 mL). The aqueous layer was then extracted with DCM (2 x 10 mL). The combined organic layers were washed with a 10% aqueous citric acid solution (1 x 10 mL). The aqueous layer was again extracted with DCM (2 x 10 mL). The combined organic layers were washed with brine (1 x 20 mL), dried over Na\(_2\)SO\(_4\), filtered and concentrated using rotary evaporation. Flash column chromatography on silica using gradient elution (20% EtOAc in hexane to 40% EtOAc in hexane) gave the product as a colorless oil (102 mg, 0.29 mmol, 27% yield).

\(^1\text{H NMR:}\) (500 MHz, CDCl\(_3\))
\[\delta 7.28 (d, J = 8.1 \text{ Hz}, 2\text{H}), 7.21 (d, J = 8.1 \text{ Hz}, 2\text{H}), 5.25 (d, J = 11.8 \text{ Hz}, 1\text{H}), 5.14 (d, J = 11.9 \text{ Hz}, 1\text{H}), 4.59 (dd, J = 4.2, 2.2 Hz, 1\text{H}), 4.40 (s, 1\text{H}), 3.47 (dd, J = 16.2, 4.2 Hz, 1\text{H}), 3.42 (dd, J = 16.2, 2.2 Hz, 1\text{H}), 2.66 (q, J = 7.6 Hz, 2\text{H}), 1.55 (s, 3\text{H}), 1.28 (s, 3\text{H}), 1.24 (t, J = 7.6 Hz, 3\text{H}).\]

\(^{13}\text{C NMR:}\) (126 MHz, CDCl\(_3\))
\[\delta 170.82, 166.96, 145.45, 131.71, 129.15, 128.43, 68.28, 63.29, 62.89, 61.19, 38.42, 28.74, 20.24, 18.72, 15.59.\]

\(\text{HRMS:}(\text{ESI-TOF MS ES}+)\)
\[m/z \text{ calculated for } C_{17}H_{22}NO_5S [M+H]^+: 352.1219, \text{ found 352.1214.}\]
5,7-dibromo-1-(4-ethylbenzyl)indoline-2,3-dione [S39]. Synthesis: In a flame-dried round bottom was added dibromoisatin (500mg, 1.64 mmol), K$_2$CO$_3$ (227 mg, 1.64 mmol), and DMF (1.6 mL). The reaction was cooled to 0 °C and stirred for 5 min. Then a solution of 1-(bromomethyl)-4-ethylbenzene (653 mg, 3.28 mmol) in DMF (1.6 mL) was added to the reaction dropwise. The reaction was warmed to room temperature and stirred to completion. After completion by TLC, the reaction was diluted with DCM (40 mL) and poured into a separatory funnel then washed with water (20 mL). The organic layer was separated and washed with water (2 x 20 mL). The combined aqueous layers were extracted with DCM (20 mL), and the organic layers combined and dried over Na$_2$SO$_4$. Column chromatography on silica using gradient elution, 10% EtOAc in hexane → 40% EtOAc in hexane gave the product as an orange/red solid (487 mg, 1.15 mmol, 70% yield).

$^1$H NMR: (500 MHz, CDCl$_3$)

δ 7.81 (d, $J = 2.0$ Hz, 1H), 7.71 (d, $J = 2.0$ Hz, 1H), 7.22 – 7.10 (m, 4H), 5.38 (s, 2H), 2.62 (q, $J = 7.6$ Hz, 2H), 1.21 (t, $J = 7.6$ Hz, 3H).

$^{13}$C NMR: (126 MHz, CDCl$_3$)

δ 181.52, 158.48, 146.99, 145.48, 144.05, 132.95, 128.47, 127.66, 126.69, 121.60, 117.26, 105.43, 44.64, 28.62, 15.60.

HRMS: (ESI-TOF MS ES+)

$m/z$ calculated for C$_{17}$H$_{14}$NO$_2$Br$_2$ [M+H]$^+$: 421.9391, found 421.9380.

1-((4'-butyl-[1,1'-biphenyl]-4-yl)methyl)-1H-benzo[d]imidazole [S40]. In a flame-dried 25 mL round-bottom flask under nitrogen with stirring was added K$_2$CO$_3$ (864 mg, 6.25 mmol, 5 equiv), benzimidazole (297 mg, 2.51 mmol, 2 equiv), 4-(bromomethyl)-4'-butyl-1,1'-biphenyl (380 mg, 1.25 mg, 1 equiv) and DMF (3 mL). The reaction was stirred for 2 h at 120 °C. The reaction was brought to room temperature and poured into a separatory funnel where water (20 mL) was added and the mixture extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with brine (20 mL), dried over Na$_2$SO$_4$, filtered and evaporated using rotary evaporation. The product was purified using gradient silica gel flash chromatography (100% DCM to 95/5 DCM/MeOH) to give the pure product as a white solid (217 mg, 51% yield).

$^1$H NMR: (500 MHz, CDCl$_3$)
δ 7.98 (s, 1H), 7.85 (d, J = 7.5 Hz, 1H), 7.55 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.36-7.32 (m, 1H), 7.32-7.27 (m, 2H), 7.25 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 5.39 (s, 2H), 2.65 (t, J = 7.7 Hz, 2H), 1.63 (p, J = 7.6 Hz, 2H), 1.38 (sxt, J = 7.4 Hz, 2H), 0.94 (t, J = 7.3 Hz, 3H)

13C NMR: (126 MHz, CDCl3)

δ 142.60, 141.37, 137.70, 134.18, 129.05, 127.67, 127.64, 127.00, 123.25, 122.44, 120.60, 110.20, 48.75, 35.42, 33.74, 22.52, 14.10

HRMS: (ESI-TOF MS ES+)
m/z calculated for C24H25N2 [M+H]+: 341.2018, found 341.2012.

2,2,2-trifluoro-N-(((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydropyrenanthrene-1-yl)methyl)acetamide [S41].

Spectral data matches the previously reported data.24

1H NMR: (400 MHz, Chloroform-d)

δ 7.18 (d, J = 8.2 Hz, 1H), 7.01 (dd, J = 8.1, 2.0 Hz, 1H), 6.90 (s, 1H), 6.24 (s, 1H), 3.36 – 3.22 (m, 2H), 3.00 – 2.90 (m, 1H), 2.89 – 2.75 (m, 2H), 2.32 (dt, J = 12.9, 2.8 Hz, 1H), 1.94 – 1.66 (m, 4H), 1.54 – 1.35 (m, 4H), 1.33 – 1.19 (m, 9H), 0.99 (s, 3H).

Figure 9. Synthesis of biflavanoid S42.
(E)-3-(5-bromo-2-hydroxyphenyl)-1-phenylprop-2-en-1-one [S42a]. Prepared according to literature-reported method. In a 100 mL round-bottom flask equipped with a magnetic stir bar in ice bath were added potassium hydroxide (7.5 g, 134 mmol, 13.4 equiv.), water (1.3 mL), and methanol (6.3 mL). Acetophenone (1.2 mL, 1.20 g, 10 mmol, 1.0 equiv.) was added, and the reaction was stirred for 10 min. 5-Bromosalicylaldehyde (2.01 g, 10 mmol, 1.0 equiv.) was then added. The reaction mixture was then removed from ice bath and stirred overnight. Upon completion, the dark red mixture was acidified with 3M HCl until pH ~ 2. The resulting yellow mixture was extracted with CH$_2$Cl$_2$ (3x20 mL). The combined organic layer was dried over MgSO$_4$ and concentrated in vacuo. Purification by flash chromatography on silica (150 mL) eluting with 20%→30%→40% (2 column volumes each)→100% EtOAc/hexanes (4 column volumes) yielded the product as a yellow powder (2.07 g, 6.83 mmol, 68% yield) with some minor impurities, which were removed in the subsequent step.

![Chemical structure](image)

2-bromo-10-ethyl-6-phenyl-cis-12H-6,12-methanodibenzo[d,g][1,3]dioxocine [(±)S42]. According to literature procedure, in a 250 mL round-bottom flask were added (E)-3-(5-bromo-2-hydroxyphenyl)-1-phenylprop-2-en-1-one S42a (1.5 g, 5.0 mmol, 1.0 equiv.), 4-ethylphenol (733 mg, 6.0 mmol, 1.2 equiv.), DL-10-camphorsulfonic acid (174 mg, 0.75 mmol, 0.15 equiv.) and toluene (63 mL). The reaction was placed in 120 °C oil bath and refluxed for 43 h. The resulting dark green mixture was condensed via rotary evaporation. Purification by MPLC (40 g silica) eluting with 0%→10% EtOAc/hexanes (40 column volumes) yielded the product as a light yellow powder (772 mg, 1.90 mmol, 38% yield).

$^1$H NMR: (500 MHz, CDCl$_3$)

δ 7.75-7.69 (m, 2H), 7.49-7.40 (m, 3H), 7.39 (d, $J$ = 2.4 Hz, 1H), 7.24 (dd, $J$ = 8.6, 2.4 Hz, 1H), 7.07 (d, $J$ = 2.0 Hz, 1H), 7.01 (dd, $J$ = 8.3, 2.1 Hz, 1H), 6.96 (d, $J$ = 8.3 Hz, 1H), 6.91 (d, $J$ = 8.6 Hz, 1H), 4.02 (t, $J$ = 2.9 Hz, 1H), 2.61 (qd, $J$ = 7.5, 2.1 Hz, 2H), 2.39 (dd, $J$ = 13.4, 3.0 Hz, 1H), 2.34 (dd, $J$ = 13.4, 3.0 Hz, 1H), 1.24 (t, $J$ = 7.6 Hz, 3H)

$^{13}$C NMR: (126 MHz, CDCl$_3$)

δ 151.41, 149.86, 141.20, 137.74, 130.95, 129.94, 129.02, 128.70, 128.50, 127.91, 126.61, 125.84, 125.37, 118.72, 116.79, 113.44, 98.89, 34.29, 33.18, 28.17, 15.92

HRMS: (ESI-TOF MS ES+)
m/z calculated for C_{23}H_{20}O_{2}Br [M+H]^+: 407.0647, found 407.0630.

3-(10-ethyl-6-phenyl-cis-12H-6,12-methanodibenzo[d,g][1,3]dioxocin-2-yl)pyridine [(±)S43]. In a flame-dried 100 mL round-bottom flask equipped with a magnetic stir bar were added 2-bromo-10-ethyl-6-phenyl-cis-12H-6,12-methanodibenzo[d,g][1,3]dioxocine (±)S42 (494 mg, 1.21 mmol, 1.0 equiv.), 3-pyridinylboronic acid (298 mg, 2.43 mmol, 2.0 equiv.), Pd(dppf)Cl₂·CH₂Cl₂ (99 mg, 0.121 mmol, 0.10 equiv.), and potassium carbonate (326 mg, 2.36 mmol, 2.0 equiv.) under N₂ atmosphere. Nitrogen-degassed water (0.5 mL) and 1,4-dioxane (2 mL) were added, and the septa was quickly replaced with a polyethylene yellow cap and secured with electric tape. The flask was then placed into 95 °C oil bath and stirred for 3 h. Upon completion, the reaction was quenched with water (10 mL), and extracted with EtOAc (3x10 mL). The organic layers were combined, dried over MgSO₄, and condensed through rotary evaporation. Purification by flash chromatography on silica (50 mL) eluting with 20% (6 column volumes) → 30% → 40% (4 column volumes each) EtOAc/hexanes yielded the product as a light yellow powder (291 mg, 0.718 mmol, 59% yield).

H NMR: (500 MHz, CDCl₃)
δ 8.82 (s, 1H), 8.57 (d, J = 4.2 Hz, 1H), 7.83 (dt, J = 7.9, 1.9 Hz, 1H), 7.79-7.74 (m, 2H), 7.51-7.45 (m, 3H), 7.45-7.40 (m, 1H), 7.39-7.32 (m, 2H), 7.14 (d, J = 8.4 Hz, 1H), 7.12 (d, J = 1.9 Hz, 1H), 7.01 (dd, J = 8.3, 1.9 Hz, 1H), 6.98 (d, J = 8.3 Hz, 1H), 4.15 (t, J = 2.8 Hz, 1H), 2.59 (q, J = 7.5 Hz, 2H), 2.44 (d, J = 2.9 Hz, 2H), 1.22 (t, J = 7.6 Hz, 3H)

C NMR: (126 MHz, CDCl₃)
δ 152.51, 149.91, 148.24, 148.19, 141.37, 137.69, 136.36, 134.14, 131.32, 128.99, 128.51, 127.81, 127.41, 127.04, 126.56, 126.08, 125.89, 125.82, 123.65, 117.65, 116.81, 99.01, 34.60, 33.48, 28.17, 15.94

HRMS: (ESI-TOF MS ES+)

m/z calculated for C_{28}H_{22}O_{2}N [M+H]^+: 406.1807, found 406.1804.

For COSY see Supporting Information: Spectral Data

S44 is the minor diastereomer of amination product 48, see page 62.
S45 is the minor diastereomer of amination product 49, see page 64.
(13S,17S)-17-(formyloxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl acetate [48a]. In a flame-dried round bottom flask equipped with a stir bar under nitrogen was added (8R, 9S, 13S, 14S, 17S)-17-hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl acetate (500 mg, 1.60 mmol, 1 equiv) and DMF (409 mg, 5.6 mmol, 3.5 equiv). The reaction was cooled to 0 °C and oxalyl chloride was added dropwise (630 mg, 4.96 mmol, 3.1 equiv). The reaction was warmed to room temperature and stirred overnight. Upon reaction completion, water (10 mL) was added and the contents were transferred to a separatory funnel. The contents were extracted with DCM (3 x 10 mL). The combined organic layers were washed with water (3 x 20 mL), dried over Na₂SO₄, filtered and concentrated using rotary evaporation. Silica gel flash column chromatography (20% EtOAc in 80% hexanes) gave the pure product as a white solid (411 mg, 1.2 mmol, 75% yield).

¹H NMR: (400 MHz, Chloroform-d)

δ 8.11 (s, 1H), 7.28 (d, J = 8.5 Hz, 1H), 6.84 (dd, J = 8.4, 2.4 Hz, 1H), 6.79 (d, J = 2.3 Hz, 1H), 4.79 (t, J = 8.4 Hz, 1H), 2.97 – 2.79 (m, 2H), 2.37 – 2.19 (m, 6H), 1.99 – 1.84 (m, 2H), 1.83 – 1.71 (m, 1H), 1.70 – 1.54 (m, 1H), 1.54 – 1.23 (m, 6H), 0.85 (s, 3H).

¹³C NMR: (126 MHz, CDCl₃)

δ 169.97, 161.32, 148.57, 138.25, 137.86, 126.54, 121.65, 118.75, 82.69, 49.91, 44.08, 43.08, 38.29, 36.90, 29.61, 27.71, 27.13, 26.10, 23.41, 21.27, 12.19

HRMS: (ESI-TOF MS ES+)

m/z calculated for C₁₉H₂₅O₃ [M-Ac+H⁺]: 301.1798, found 301.1797.

Figure 10. Synthesis of abiraterone analogue 49a.¹
(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl acetate [S46]. In a flame-dried 100 mL round bottom flask equipped with a stir bar was charged (+)-estrone (2.70 g, 10.0 mmol, 1.0 equiv.), pyridine (4.0 mL, 3.96 g, 50.0 mmol, 5.0 equiv.), 4-dimethylaminopyridine (DMAP) (122.2 mg, 1.0 mmol, 0.10 equiv.) and CH$_2$Cl$_2$ (20 mL). The reaction mixture was placed in ice bath with stirring, and acetic anhydride (2.8 mL, 3.06 g, 30.0 mmol, 3.0 equiv.) was added dropwise via syringe. The reaction mixture was stirred at 0 °C for 5 min and then allowed to warm to ambient temperature and stirred overnight. The reaction was washed with water (20 mL), 1 M HCl (4x20 mL) and brine (20 mL). The organic layer was separated, dried over MgSO$_4$ and concentrated in vacuo. Purification by flash chromatography on silica (75 mL) eluting with 10%→25%→40% EtOAc/hexanes (2.5 column volumes each) yielded the product as a white powder (3.03 g, 9.70 mmol, 97% yield).

$^1$H NMR: (500 MHz, CDCl$_3$) δ 7.29 (d, $J = 8.4$ Hz, 1H), 6.85 (dd, $J = 8.4$, 2.4 Hz, 1H), 6.81 (d, $J = 2.3$ Hz, 1H), 2.90 (dd, $J = 8.8$, 4.1 Hz, 2H), 2.51 (dd, $J = 19.0$, 8.6 Hz, 1H), 2.41 (dd, $J = 12.4$, 7.0, 3.7 Hz, 1H), 2.33-2.24 (m, 1H), 2.29 (s, 3H), 2.19-2.11 (m, 1H), 2.09-1.98 (m, 2H), 1.98-1.93 (m, 1H), 1.68-1.40 (m, 6H), 0.91 (s, 3H)

(8R,9S,13S,14S)-13-methyl-17-(((trifluoromethyl)sulfonyl)oxy)-7,8,9,11,12,13,14,15-octahydro-6H-cyclopenta[a]phenanthren-3-yl acetate [S47]. In a flame-dried 50 mL round bottom flask equipped with a stir bar was added S46 (661 mg, 2.11 mmol, 1.0 equiv.), 2,6-di-tert-butyl-4-methylpyridine (448 mg, 2.18 mmol, 1.03 equiv.) and CH$_2$Cl$_2$ (5.8 mL). Trifluoromethanesulfonyl anhydride (613 mg, 2.17 mmol, 1.03 equiv.) was added dropwise into the reaction mixture while stirring. The reaction was stirred for 6 h. Saturated NaHCO$_3$ (10 mL) was then added to quench the reaction and the aqueous layer was extracted with CH$_2$Cl$_2$ (3x10 mL). The combined organic layer was washed with saturated NaHCO$_3$ (5 mL) and brine (5 mL), dried over MgSO$_4$ and concentrated in vacuo. Purification by flash chromatography on silica (50 mL) eluting with 2% (4 column volumes)→5% EtOAc/hexanes (6 column volumes) yielded the product as a white solid (757 mg, 1.70 mmol, 81% yield).
\( ^1\text{H NMR:} \ (400 \text{ MHz, CDCl}_3) \)
\[ \delta \ 7.25 \ (d, \ J = 8.0 \text{ Hz, 1H}), \ 6.85 \ (dd, \ J = 8.5, 2.5 \text{ Hz, 1H}), \ 6.81 \ (d, \ J = 2.4 \text{ Hz, 1H}), \ 5.62 \ (dd, \ J = 3.3, 1.7 \text{ Hz, 1H}), \ 2.91 \ (dd, \ J = 9.8, 5.1 \text{ Hz, 2H}), \ 2.44-2.37 \ (m, \ 1H), \ 2.33 \ (ddd, \ J = 14.9, 6.3, 3.5 \text{ Hz, 2H}), \ 2.29 \ (s, \ 3H), \ 2.10 \ (ddd, \ J = 14.9, 11.2, 1.7 \text{ Hz, 1H}), \ 1.96-1.87 \ (m, \ 2H), \ 1.79 \ (td, \ J = 11.3, 6.3 \text{ Hz, 1H}), \ 1.71-1.57 \ (m, \ 3H), \ 1.51-1.37 \ (m, \ 1H), \ 1.00 \ (s, \ 3H) \]

\( ^1\text{H NMR:} \ (400 \text{ MHz, CDCl}_3) \)
\[ \delta \ 8.65 \ (d, \ J = 2.1 \text{ Hz, 1H}), \ 8.48 \ (dd, \ J = 4.8, 1.5 \text{ Hz, 1H}), \ 7.69 \ (app d, \ J = 8.1 \text{ Hz, 1H}), \ 7.29 \ (d, \ J = 8.2 \text{ Hz, 1H}), \ 7.27-7.23 \ (m, \ 1H), \ 6.85 \ (dd, \ J = 8.5, 2.3 \text{ Hz, 1H}), \ 6.81 \ (dd, \ J = 2.3 \text{ Hz, 1H}), \ 6.03 \ (dd, \ J = 3.0, 1.6 \text{ Hz, 1H}), \ 2.93 \ (dd, \ J = 11.3, 5.9 \text{ Hz, 2H}), \ 2.44-2.32 \ (m, \ 3H), \ 2.29 \ (s, \ 3H), \ 2.20-2.11 \ (m, \ 2H), \ 2.02-1.93 \ (m, \ 1H), \ 1.82 \ (td, \ J = 11.4, 6.5 \text{ Hz, 1H}), \ 1.75-1.64 \ (m, \ 3H), \ 1.56-1.44 \ (m, \ 1H), \ 1.04 \ (s, \ 3H) \]

(8S,9S,13S,14S)-13-methyl-17-(pyridin-3-yl)-7,8,9,11,12,13,14,15-octahydro-6H-cyclopenta[a]phenanthren-3-yl acetate [S48]. In a flame-dried 300 mL round-bottom flask containing LiCl (1.05 g, 24.7 mmol, 6.0 equiv.) and equipped with a magnetic stir bar were added S47 (1.83 g, 4.12 mmol, 1.0 equiv.), Pd(PPh\(_3\))\(_4\) (476 mg, 0.412 mmol, 0.10 equiv.), CuCl (2.04 g, 20.6 mmol, 5.0 equiv.), and DMSO (154 mL). 3-(tributylstannyl)pyridine (2.6 mL, 3.03 g, 8.24 mmol, 2.0 equiv.) was then added via syringe. The mixture was degassed through freeze-pump-thaw (-78 °C→0 °C) three times, and was stirred for 1 h at room temperature. The reaction flask was then placed into 60 °C oil bath and stirred vigorously for 13 h. Upon completion, the reaction was quenched with the mixed solution of concentrated NH\(_4\)OH (5.5 mL) and brine (200 mL), and extracted with diethyl ether (4x50 mL). The organic layers were then combined, dried over MgSO\(_4\) and concentrated in vacuo. Purification by flash chromatography on silica (150 mL) eluting with 40% EtOAc/hexanes (7.5 column volumes) yielded the product as a white powder (1.31 g, 3.52 mmol, 85% yield).

\( ^1\text{H NMR:} \ (400 \text{ MHz, CDCl}_3) \)
\[ \delta \ 8.65 (d, J = 2.1 \text{ Hz, 1H}), \ 8.48 (dd, J = 4.8, 1.5 \text{ Hz, 1H}), \ 7.69 (app d, J = 8.1 \text{ Hz, 1H}), \ 7.29 (d, J = 8.2 \text{ Hz, 1H}), \ 7.27-7.23 (m, 1H), \ 6.85 (dd, J = 8.5, 2.3 \text{ Hz, 1H}), \ 6.81 (dd, J = 2.3 \text{ Hz, 1H}), \ 6.03 (dd, J = 3.0, 1.6 \text{ Hz, 1H}), \ 2.93 (dd, J = 11.3, 5.9 \text{ Hz, 2H}), \ 2.44-2.32 (m, 3H), \ 2.29 (s, 3H), \ 2.20-2.11 (m, 2H), \ 2.02-1.93 (m, 1H), \ 1.82 (td, J = 11.4, 6.5 \text{ Hz, 1H}), \ 1.75-1.64 (m, 3H), \ 1.56-1.44 (m, 1H), \ 1.04 (s, 3H) \]
(85,95,135,145,175)-13-methyl-17-(pyridin-3-yl)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl acetate [49a]. In a flame-dried 200 mL round bottom flask equipped with a stir bar was added S48 (1.31 g, 3.52 mmol, 1.0 equiv.), THF (33 mL) and DMSO (33 mL). The mixture was cooled down to 0 °C upon stirring, and potassium azodicarboxylate (KOOC—N=N—COOK) (3x4.56 g, 70.5 mmol, 20 equiv.) was added in three equal portion over the course of 2 h, each followed by the addition of AcOH (3x2.7 mL, 3x2.82 g, 140.7 mmol, 40 equiv.). After adding the last portion of potassium azodicarboxylate, the reaction was allowed to warm to ambient temperature and stirred overnight. The reaction was quenched with brine (100 mL) and extracted with diethyl ether (3x50 mL). The organic layers were combined, dried over MgSO₄, condensed, transferred into a 100 mL round-bottom flask and concentrated in vacuo. Dichloromethane (7.0 mL), pyridine (1.4 mL, 1.39 g, 17.6 mmol, 5.0 equiv.), 4-dimethylaminopyridine (DMAP) (43 mg, 0.35 mmol, 0.10 equiv.), and acetic anhydride (1.0 mL, 1.08 g, 10.6 mmol, 3.0 equiv.) were added. The reaction was stirred overnight, and washed with water (5x5 mL) and brine (5 mL). The organic layer was dried over MgSO₄ and concentrated in vacuo.

Purification by MPLC (40 g silica) eluting with 0%→70% EtOAc/hexanes (25 column volumes) yielded the product as a white powder (1.01 g, 2.69 mmol, 76% yield over 2 steps).

**1H NMR:** (500 MHz, CDCl₃)

δ 8.49 (d, J = 1.9 Hz, 1H), 8.46 (dd, J = 4.7, 1.3 Hz, 1H), 7.55 (app d, J = 7.9 Hz, 1H), 7.27 (d, J = 8.9 Hz, 1H), 7.22 (dd, J = 7.8, 4.8 Hz, 1H), 6.83 (dd, J = 8.5, 2.3 Hz, 1H), 6.80 (d, J = 2.0 Hz, 1H), 2.92-2.85 (m, 2H), 2.78 (t, J = 9.8 Hz, 1H), 2.34-2.28 (m, 2H), 2.28 (s, 3H), 2.19-2.09 (m, 1H), 2.09-2.00 (m, 1H), 1.99-1.89 (m, 2H), 1.73-1.66 (m, 1H), 1.54-1.37 (m, 6H), 0.52 (s, 3H)

**13C NMR:** (126 MHz, CDCl₃)

δ 169.99, 150.54, 148.52, 147.72, 138.70, 138.13, 136.38, 135.75, 126.50, 122.89, 121.63, 118.68, 55.37, 54.68, 44.79, 44.24, 38.94, 37.56, 29.72, 27.70, 26.20, 26.06, 24.30, 21.27, 12.85

**HRMS:** (EI+)

m/z calculated for C₂₅H₂₉O₂N [M]+: 375.2198, found 375.2199.

**Figure 11.** Synthesis of dextromethorphan derivative.
(4bS,8aS,9S)-11-methyl-6,7,8a,9,10-hexahydro-5H-9,4b-(epiminoethano)phenanthren-3-yl trifluoromethanesulfonate [S49a]. To a 100 mL round-bottom flask containing dextromethorphan hydrobromide monohydrate (4.99 g, 13.5 mmol, 1.0 equiv.) was added hydrobromic acid (48 wt%, 29.5 mL, 21.1 g, 261 mmol, 19 equiv.). The reaction was refluxed overnight, poured on ice, and basified with saturated potassium carbonate solution. The aqueous layer was extracted with chloroform (3x50 mL). The organic layers were combined, dried over MgSO₄, filtered, and condensed through rotary evaporation to give the phenol intermediate as a white powder. In a 200 mL round-bottom flask carrying the intermediate were added CH₂Cl₂ (90 mL) and triethylamine (37.6 mL, 27.3 g, 270 mmol, 20 equiv.). The mixture was cooled to 0 °C in ice bath, and N-Phenyl-bis(trifluoromethanesulfonimide) (7.22 g, 20.2 mmol, 1.5 equiv.) was added in one portion. The reaction was allowed to warm to room temperature and stirred overnight. The reaction was then diluted with CH₂Cl₂, washed with sodium hydroxide (3x50 mL), and brine (50 mL). The organic layer was dried over MgSO₄, filtered, and condensed through rotary evaporation. Purification by flash chromatography on silica (250 mL) eluting with 2% → 5% → 10% (2 column volumes each) MeOH/CH₂Cl₂ doped with 2% NH₄OH yielded the product as an orange oil (4.49 g, 11.5 mmol, 86% yield).

¹H NMR: (500 MHz, CDCl₃)

δ 7.18 (d, J = 8.5 Hz, 1H), 7.12 (s, 1H), 7.03 (dd, J = 8.4, 1.6 Hz, 1H), 3.05 (d, J = 18.7 Hz, 1H), 2.86-2.80 (m, 1H), 2.62 (dd, J = 18.7, 5.7 Hz, 1H), 2.45 (dd, J = 12.0, 4.0 Hz, 1H), 2.39 (s, 3H), 2.30 (d, J = 14.1 Hz, 1H), 1.99 (td, J = 12.3, 2.6 Hz, 1H), 1.86 (app d, J = 12.7 Hz, 1H), 1.78 (td, J = 12.8, 4.7 Hz, 1H), 1.66 (d, J = 12.8 Hz, 1H), 1.56 (d, J = 13.1 Hz, 1H), 1.48–1.34 (m, 3H), 1.30 (d, J = 13.2 Hz, 1H), 1.19 (q, J = 13.3 Hz, 1H), 1.04 (qd, J = 12.8, 3.4 Hz, 1H)

(4bS,8aS,9S)-3-allyl-11-methyl-6,7,8a,9,10-hexahydro-5H-9,4b-(epiminoethano)phenanthrene [S49b]. To a flame-dried 200 mL round-bottom flask were added (4bS,8aS,9S)-11-methyl-6,7,8a,9,10-hexahydro-5H-9,4b-(epiminoethano)phenanthren-3-yl trifluoromethanesulfonate S49a (2.33 g, 5.99 mmol, 1.0 equiv.), LiCl (1.02 g, 24.0 mmol, 4.0 equiv), Pd(PPh₃)₄ (207.7 mg, 0.180 mmol, 0.030 equiv.), allylttributylstannane (2.1 mL, 2.18 g, 6.59 mmol, 1.1 equiv.), and DMF (24 mL, 0.25 M). The reaction was heated to 100 °C and stirred overnight. Upon cooling to room temperature, the reaction was washed with 10% ammonia solution (24 mL). The aqueous layer was extracted with ethyl acetate (3x30 mL). The organic layers were combined, dried over MgSO₄, filtered, and condensed via rotary evaporation.
Purification by flash chromatography on silica (200 mL) eluting with 2% (1.5 column volumes) → 5% (2.5 column volumes) MeOH/CH₂Cl₂ doped with 2% NH₄OH yielded the product as a yellow oil (1.41 g, 5.02 mmol, 84% yield).

¹H NMR: (500 MHz, CDCl₃)

δ 7.05 (s, 1H), 7.03 (d, J = 7.8 Hz, 1H), 6.94 (d, J = 7.7 Hz, 1H), 5.97 (ddt, J = 16.9, 1.0, 6.7 Hz, 1H), 5.10-5.01 (m, 2H), 3.35 (d, J = 6.6 Hz, 1H), 3.01 (d, J = 18.4 Hz, 1H), 2.84-2.78 (m, 1H), 2.62 (dd, J = 18.3, 5.6 Hz, 1H), 2.48-2.36 (m, 2H), 2.40 (s, 3H), 2.07 (td, J = 12.1, 2.6 Hz, 1H), 1.83 (app d, J = 12.5 Hz, 1H), 1.74 (td, J = 12.5, 4.6 Hz, 1H), 1.63 (d, J = 12.6 Hz, 1H), 1.51 (d, J = 12.4 Hz, 1H), 1.45–1.20 (m, 5H), 1.13 (qd, J = 12.4, 3.2 Hz, 1H)

(4bS,8aS,9S)-11-methyl-3-propyl-6,7,8a,9,10-hexahydro-5H-9,4b-(epiminoethano)phenanthrene [S49]. To a 100 mL round-bottom flask were added (4bS,8aS,9S)-3-allyl-11-methyl-6,7,8a,9,10-hexahydro-5H-9,4b-(epiminoethano)phenanthrene S49b (1.41 g, 5.02 mmol, 1.0 equiv.), palladium on carbon (5% wt, 141 mg, 0.066 mmol, 0.013 equiv.), and ethyl acetate (20 mL). Hydrogen gas was allowed to pass through the reaction mixture, which was stirred overnight. The reaction progress was monitored by crude NMR. Upon completion, the palladium catalyst was removed via filtration, and the filtrate was condensed via rotary evaporation to give the product as a yellow gel (1.40 g, 4.94 mmol, 98% yield).

¹H NMR: (500 MHz, CDCl₃)

δ 7.03 (d, J = 1.1 Hz, 1H), 7.01 (d, J = 7.7 Hz, 1H), 6.93 (dd, J = 7.7, 1.6 Hz, 1H), 6.00 (d, J = 18.3 Hz, 1H), 2.80 (dd, J = 5.4, 3.1 Hz, 1H), 2.60 (dd, J = 18.3, 5.7 Hz, 1H), 2.54 (dt, J = 8.2, 3.7 Hz, 2H), 2.46-2.38 (m, 2H), 2.39 (s, 3H), 2.07 (td, J = 12.2, 3.2 Hz, 1H), 1.82 (dt, J = 12.8, 3.0 Hz, 1H), 1.73 (td, J = 12.6, 4.8 Hz, 1H), 1.67-1.58 (m, 3H), 1.51 (app d, J = 12.0 Hz, 1H), 1.44–1.24 (m, 5H), 1.14 (qd, J = 12.1, 3.5 Hz, 1H), 0.93 (t, J = 7.3 Hz, 3H)

¹³C NMR: (126 MHz, CDCl₃)

δ 140.61, 139.99, 134.66, 127.63, 125.66, 125.46, 58.30, 47.48, 45.49, 42.86, 42.15, 38.17, 37.03, 36.60, 26.83, 26.71, 24.95, 24.00, 22.28, 14.02

HRMS: (ESI-TOF MS ES+)

m/z calculated for C₂₀H₃₀N [M+H]⁺: 284.2378, found 284.2372.

[α]D²⁴ = +59.0° (c = 1.08, CHCl₃)
For COSY see Supporting Information: Spectral Data

VIII. HPLC methods for the determination of product selectivity.

HPLC analysis was used to find the detection limit of these compounds to determine the selectivity of our reaction. As shown below, standards for both possible products were made using the reported rhodium catalyzed C—H amination procedure.\(^1\) A Zorbax CN 4.6 x 250 column with a 1.0 mL/min flow rate was used with a 95:5 hexanes:isopropanol mobile phase.

*Figure 12. Rh-catalyzed C—H amination of isopentylbenzene.*

The products were purified and isolated as inseparable mixtures. The purified mixture used for determining the HPLC detection limit contained a 10:1 ratio of benzylic to tertiary amination. A solution of 10 mg of the mixture in 1 mL of acetonitrile (0.0267 mmol/mL concentration) was then diluted by a factor of 10 to give 1 mg in 1 mL. This solution was again diluted to give a final sample containing 0.1 mg in 1 mL of acetonitrile. A 2 µL sample of this mixture was the concentration at which none of the tertiary product was detected by HPLC.

The manganese-catalyzed amination protocol was performed on isopentylbenzene and the crude reaction was analyzed by HPLC. No tertiary product was detected (see below). Due to the high detection limit of the HPLC, we concluded that the selectivity of our reaction is at least 100:1 in this case.
HPLC trace for the purified product standards from the rhodium catalyzed reaction

\[
\begin{array}{c}
\text{Rh}_2(\text{esp})_2 \rightarrow \text{TcesHN} \rightarrow \text{NHTces} \\
\text{major} \quad \text{minor}
\end{array}
\]
Likewise, the same approach was used to determine the detection limit of the minor mono-amination product in the following reaction.

**Figure 13.** Rh-catalyzed C–H amination of 6-methoxytetralin.
The purified mixture used from the rhodium reaction to determine the HPLC detection limit contained an 8:1 ratio of the major to minor products along with isolable diamination product. A solution of 5 mg of the major and minor product mixture in 1 mL of acetonitrile was then diluted by a factor of 10 to give 0.5 mg in 1 mL. This solution was again diluted to give a final sample containing 0.05 mg in 1 mL of acetonitrile. A 2 µL sample of this mixture was the concentration at which none of the minor product was detected by HPLC. A Zorbax CN 4.6 x 250 column with a 1.0 mL/min flow rate was used with a 95:5 hexanes/isopropanol mobile phase.

The diamination product from the rhodium reaction was also isolated and we did not detect any of this product in our own amination reaction by $^1$H NMR, however a minor peak was detected by HPLC.

We subjected the starting material of our manganese-catalyzed reaction, analyzed the crude reaction by HPLC, and detected none of the minor product. Due to the high detection limit of the HPLC, we concluded that the selectivity of our reaction is at least 20:1 in this case.
HPLC traces for the purified product standards from the rhodium catalyzed reaction

\[
\text{MeO} \quad \text{Rh}_2(\text{esp})_2 \quad \text{MeO} \quad \text{NHTces} \quad \text{MeO} \quad \text{NHTces} \quad \text{MeO} \quad \text{NHTces}
\]

Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=214, 4 Ref-off

| Peak RetTime | Type | Width | Area   | Height  | Area   |
|--------------|------|-------|--------|---------|--------|
| 17.638       | EV   | 0.4025| 9165.17773| 352.12317| 88.5141 |
| 18.623       | WV   | 0.4262| 1189.30896| 42.67750 | 11.4639 |

Totals: 1.03545e4 395.00067
Area Percent Report

Signal 1: DAD1 D, Sig=210.4 Ref-off

| # | RetTime | Type | Width | Area | Height | Area | Area |
|---|---------|------|-------|------|--------|------|------|
|   |         |      |       |      |        |      |      |
| 1 | 25.284  | BB   | 0.6242| 4.13164e4 | 1026.69141 | 100.0000 |

Totals: 4.13164e4 1026.69141
HPLC trace for the crude reaction under $[\text{Mn}^{III}(\text{ClPc})]\text{SbF}_6$ catalyzed conditions

---

**Area Percent Report**

**Sorted By** : Signal

**Multiplier** : 1.0000

**Dilution** : 1.0000

*Use Multiplier & Dilution Factor with ISTDs*

**Signal 1**:

| #  | RetTime | Type | Width | Area Height | Area [mAU] | %  |
|----|---------|------|-------|-------------|------------|----|
| 1  | 16.974  | BB   | 0.413 | 3.66413e4  | 1380.23132 | 95.9937 |
| 2  | 25.217  | VB   | 0.5752| 1529.21167 | 41.238023  | 4.0063 |

**Totals** : 3.81705e4 1421.51155
IX. Experimental kinetic data and methods for Figure 5

Figure 14. Mechanism of [Mn\textsuperscript{III}(ClPc)] catalyzed benzylic C–H amination.

**Method for KIE Determination:** The twice column-purified product mixture (ca. 30 mg in 800 µL CDCl\textsubscript{3}) was analyzed by \textsuperscript{13}C NMR (126 MHz instrument). Cr(acac)\textsubscript{3} (1.5 mg) was added directly to the solution in the NMR tube immediately prior to running the NMR study; this helps to significantly reduce delay times needed to obtain accurate integrations. The experiment was run under inverse-gated decoupling conditions without sample spinning. The KIE was reported as the area of the deuterated peak over that of the protonated peak. Three identical experiments were run and an average value was calculated with error reported as a standard deviation. Rh\textsubscript{2}(esp)\textsubscript{2} experiments were performed using the previously reported procedure on the same scale as the [Mn\textsuperscript{III}(ClPc)]Cl experiments.\textsuperscript{1}

[Mn\textsuperscript{III}(ClPc)]SbF\textsubscript{6}: C–H/C–D = 3.00 ± 0.08 (3.00, 2.92, 3.08)

Rh\textsubscript{2}(esp)\textsubscript{2}: C–H/C–D = 2.60 ± 0.03 (2.60, 2.62, 2.57)
**3-phenyl-3-((2,2,2-trichloroethoxy)sulfonyl)amino)propyl-3-d acetate.** According to the general procedure A on 1.5x scale, 3-phenylpropyl acetate (53.8 mg, 0.30 mmol, 1 equiv), benzene (0.60 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (34.6 mg, 0.030 mmol, 0.1 equiv), silver hexafluoroantimonate (10.3 mg, 0.030 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ3-iodanylidene)sulfamate (258.3 mg, 0.60 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8 h. After silica plug filtration using diethyl ether as the eluent (30 mL), the solvent was concentrated and the crude brown oil was loaded onto a silica gel column using dichloromethane to quantitatively transfer the product. Flash chromatography using gradient elution (500 mL of 100% dichloromethane then 300 mL of 2% diethyl ether in 98% dichloromethane followed by 300 mL of 5% diethyl ether in 95% dichloromethane) gave the product as a slightly yellow solid. The product was purified again to remove any trace impurities by flash chromatography using gradient elution (500 mL of 100% dichloromethane then 5%-15% ethyl acetate in hexanes) until the product elutes to give a pure white solid after solvent removal.

**Figure 15.** Determination of kinetic isotope effect via initial rate.

---

**General Procedure for Initial Rate Analysis:** *All reactions for rate analysis were run on 2x the normal scale.* In a 10 mL round bottom flask a Teflon stir bar was added and the flask was sealed with a Suba Seal rubber septum, placed under vacuum, flame-dried for 45 seconds, cooled under a purged and completely air-free argon balloon and wrapped in foil to exclude light. Once cooled, benzene (0.80 mL, 0.5 M to substrate), substrate (0.40 mmol, 1 equiv), and nitrobenzene (24.6 mg, 0.2 mmoles, 0.5 equiv) were added. Manganese (III) perchlorophthalocyanine chloride (46.2 mg, 0.040 mmol, 0.1 equiv) and silver hexafluoroantimonate (13.7 mg, 0.040 mmol, 0.1 equiv) were weighed in a foil wrapped 1-dram vial in the glove box and sealed with a Teflon cap. The vial was removed from the glove box and the contents added directly to the round bottom flask while maintaining an argon atmosphere. In a 1 dram vial
open to air, 2,2,2-trichloroethyl (phenyl-λ^3^-iodanylidene)sulfamate (344 mg, 0.80 mmol, 2 equiv) was weighed and added directly to the round bottom flask while maintaining an argon atmosphere and placed in a 40 °C oil bath. The Suba Seal septum and argon balloon were used to seal the flask throughout the duration of the experiments. Aliquots (50 µL) were taken every 2 minutes from the reaction flask for 14 minutes, and filtered through a silica pad with 1 mL of 80/20 Et_2O/CH_2Cl_2 for HPLC (Zorbax CN, 4.6 x 250 nm) analysis. The yield was determined by integration of the product peaks relative to the nitrobenzene internal standard and comparison to a standard curve. Yields are reported as the average of three runs with error bars denoting standard deviation. Error for kinetic isotopes was calculated via propagation of the standard error of the mean for each set of rates.

\[ \text{3-phenylpropyl-3,3-}^d \text{ acetate [1-}^d \text{].} \]

\[^1\text{H NMR: (400 MHz, Chloroform-}\text{d)} \]

\[ \delta 7.32 – 7.26 (m, 2H), 7.23 – 7.17 (m, 3H), 4.09 (t, J = 6.6 Hz, 2H), 2.06 (s, 3H), 1.95 (t, J = 6.6 Hz, 2H). \]

\[ [\text{Mn}^{III}(\text{ClPc})] \text{SbF}_6: \frac{k_H}{k_D} = 0.3491 / 0.1384 = 2.5 \pm 0.2 \]
Figure 16. Determination of $k_H$.

![Graph showing Mn(ClPc): H with the line equation $y = 0.3491x - 0.3614$ and $R^2 = 0.99359$.]

Figure 17. Determination of $k_D$.

![Graph showing Mn(ClPc): D with the line equation $y = 0.1384x - 0.2071$ and $R^2 = 0.99485$.]
Figure 18. Mechanistic probes for stereoretention and radical intermediates.

3-phenyl-3-(((2,2,2-trichloroethoxy)sulfonyl)amino)butyl acetate [53]. According to the general amination procedure B, 5Å powdered molecular sieves (40 mg), 3-phenylbutyl acetate (38.5 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ^3-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 8 h at 40 °C. After silica plug filtration using diethyl ether as the eluent (30 mL), the solvent was concentrated and the crude material was dry loaded onto a silica gel column. Flash chromatography using gradient elution (100 % hexanes to 10% ethyl acetate in hexanes) gave the pure product as a slightly discolored oil.

The enantiopure starting material was used for the analysis of stereoretention under [Mn^{III}(ClPc)] tetakis cation catalysis using the same procedure described above for the racemic material. Analysis of stereoretention under Rh_{2}(esp)_{2} catalysis was also performed using a previously reported procedure.1

^1H NMR: (500 MHz, CDCl₃)

δ 7.46 (d, J = 7.9 Hz, 2H), 7.39 (t, J = 7.8 Hz, 2H), 7.30 (t, J = 7.3 Hz, 1H), 5.75 (s, 1H), 4.55 (s, 2H), 4.20 (dt, J = 12.2, 6.3 Hz, 1H), 3.95 (dt, J = 11.7, 6.4 Hz, 1H), 2.40 (td, J = 6.4, 1.4 Hz, 2H), 1.93 (s, 3H), 1.89 (s, 3H).

^13C NMR: (126 MHz, CDCl₃)

δ 171.1, 143.2, 128.9, 128.0, 125.5, 93.6, 78.2, 62.0, 60.9, 49.0, 26.2, 20.9.

HRMS: (ESI-TOF MS ES+)

m/z calculated for C_{14}H_{18}NO_{5}SCl_{3}Na [M+Na]^+: 439.9869, found 439.9871

HPLC Analysis:

A Chiralcel OJ-H 4.6mm x 150mm column with a 1.0 mL/min flow rate was used with a 94:6 hexanes:isopropanol mobile phase.
HPLC trace for the racemic standard

Area Percent Report

Signal 1: DAD1 C, Sig=214,4 Ref=off

| #  | RetTime | Type | Width | Area [mAU*s] | Height [mAU] | Area [%] |
|----|---------|------|-------|--------------|--------------|----------|
| 1  | 18.768  | PV   | 0.7131| 2470.28296   | 51.39914     | 49.9244  |
| 2  | 20.986  | VBA  | 0.6336| 2477.76929   | 55.38854     | 50.0756  |

Totals: 4948.05225 106.78768
HPLC trace after intermolecular C—H amination with [Mn^{III}(ClPc)] 4
HPLC trace after C—H amination with Rh$_2$(esp)$_2$

Stereoretention study for the intramolecular [Mn(ClPc)] 4 catalyzed C—H amination

(R)-4-ethyl-4-methyl-1,2,3-oxathiazinane 2,2-dioxide [55]. The same procedure as previously reported$^4$ using manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv) instead of
[Mn(BuPc)]SbF$_6$ was performed. Similarly, the analysis was performed according to previously reported analytical procedures.$^4$

\[ \text{(S)-3-methylpentyl 4-nitrobenzoate [S50]} \]

To obtain the enantiopurity of the (S)-(−)-3-methyl-1-pentanol starting material, the alcohol converted to the \( p \)-NO$_2$-benzoate derivative and evaluated by HPLC analysis.

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

8.29 (d, \( J = 8.9 \) Hz, 2H), 8.20 (d, \( J = 8.8 \) Hz, 2H), 4.46 – 4.35 (m, 2H), 1.91 – 1.78 (m, 1H), 1.67 – 1.51 (m, 2H), 1.49 – 1.35 (m, 1H), 1.33 – 1.18 (m, 1H), 0.96 (d, \( J = 6.4 \) Hz, 3H), 0.91 (t, \( J = 7.4 \) Hz, 3H).

**HPLC trace of the racemic \( p \)-NO$_2$-benzoate protected starting material S50 for ee determination**

| mAU | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
|-----|----|----|----|----|----|----|----|----|----|----|----|
| Area Percent Report |

**Sorted By** : Signal  
**Multiplier** : 1.0000  
**Dilution** : 1.0000  
**Use Multiplier & Dilution Factor with ISTDs**

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

| Peak RetTime Type Width Area Height Area % |
|----|----|----|----|----|
| 1  | 17.004 | SM | 0.3949 | 1.50867e4 | 636.66479 | 49.2179 |
| 2  | 17.906 | SM | 0.4415 | 1.55662e4 | 587.61816 | 50.7821 |
| Totals | 3.06530e4 | 1224.28296 |
HPLC trace of the enantiopure $\rho$NO$_2$-benzoate protected starting material S50 for ee determination
GC trace of the racemic product 55 after the [Mn(ClPc)] 4 catalyzed intramolecular C—H amination with racemic 54

| Signal 1: FID1 A, |
|------------------|
| Peak RetTime Type Width Area Height Area % |
| #    [min]       [min] [pA] [pA] |  |
|------|--------|-------|-----|-----|-----|
| 1    20.965 EP  0.1918 2252.11914 138.87767 50.45201 |
| 2    21.547 EB  0.1934 2211.76440 151.39966 49.54799 |

Totals: 4463.89354 290.27733

Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Use Multiplier & Dilution Factor with ISTDs
GC trace of the enantiopure product after the [Mn(ClPc)] 4 catalyzed stereoretentive intramolecular C—H amination

\[
\text{Me}_2\text{H} \quad \text{OSO}_2\text{NH}_2 \quad \text{[Mn}^{II}\text{(ClPc)}\text{]}\text{Cl (10 mol\%)} \\
\text{AgSbF}_6 (10 \text{ mol\%}) \quad \text{Phl(OPiv)}_2 (2 \text{ equiv}) \\
\text{C}_8\text{H}_8, 40 \, ^\circ\text{C} \\
\text{ee} = 99\%, 54 \\
\text{ee} = 99\%, 55
\]
X. Site-selectivity probe for benzylic sites with different bond dissociation energies

**Figure 19.** Site-selectivity probe for benzylic sites with different bond dissociation energies.

2,2,2-trichloroethyl (1-(4-(2-oxopropyl)phenyl)ethyl)sulfamate [57]. According to the general amination procedure B, 5Å powdered molecular sieves (40 mg), freshly distilled 4-ethylphenylacetone 56 (32.4 mg, 0.20 mmol, 1 equiv), benzene (0.40 mL, 0.5M), manganese (III) perchlorophthalocyanine chloride (23.1 mg, 0.020 mmol, 0.1 equiv), silver hexafluoroantimonate (6.9 mg, 0.020 mmol, 0.1 equiv) and 2,2,2-trichloroethyl (phenyl-λ³-iodanylidene)sulfamate (172.2 mg, 0.40 mmol, 2 equiv) were combined in a 10 mL round-bottom flask and stirred for 24 h. After silica plug filtration using diethyl ether as the eluent (30 mL), the solvent was concentrated leaving a crude brown oil. A pipet tip of the crude material was diluted with diethyl ether to 0.8 mL in an HPLC vial. This solution was evaluated to determine the reaction selectivity (see HPLC traces below). The remaining crude material was dry loaded onto a silica gel column. Flash chromatography using gradient elution (400 mL of 5% ethyl acetate in 95% hexanes then 300 mL of 8% ethyl acetate in 92% hexanes, 300 mL of 10% ethyl acetate in 90% hexanes, 300 mL of 12% ethyl acetate in 88% hexanes, 200 mL of 14% ethyl acetate in 86% hexanes then 600 mL of 20% ethyl acetate in 80% hexanes) gave the pure product as a slightly discolored oil.

**Run 1** (44 mg, 0.113 mmol, 56% yield, 16.0:1 57:58 selectivity by HPLC)

**Run 2** (36 mg, 0.093 mmol, 47% yield, 17.5:1 57:58 selectivity by HPLC)

**Run 3** (42 mg, 0.108 mmol, 54% yield, 17.2:1 57:58 selectivity by HPLC)

**Average overall yield: 52% yield ± 4.7, 16.9:1 57:58 selectivity**

A slightly impure ¹H NMR spectrum is assigned and reported for compound 58 below in the spectra section as full characterization was hampered by inadequate amounts of product.

Characterization data for major regioisomer 57.
$^1$H NMR: (500 MHz, CDCl$_3$)

$^\delta$ 7.33 (d, $J = 8.1$ Hz, 2H), 7.21 (d, $J = 8.1$ Hz, 2H), 4.93 (d, $J = 7.1$ Hz, 1H), 4.73 (p, $J = 6.9$ Hz, 1H), 4.46 (d, $J = 10.8$ Hz, 1H), 4.45 (d, $J = 10.9$ Hz, 1H), 3.70 (s, 2H), 2.18 (s, 3H), 1.62 (d, $J = 6.9$ Hz, 3H)

$^{13}$C NMR: (126 MHz, CDCl$_3$)

$^\delta$ 206.0, 140.3, 134.4, 130.2, 126.8, 93.5, 78.3, 54.8, 50.5, 29.7, 22.9

HRMS: (ESI-TOF MS ES+)

$m/z$ calculated for C$_{13}$H$_{17}$NO$_4$SCl$_3$ [M+H]$^+$: 387.9944, found 387.993

HPLC Analysis:

A Zorbax CN 4.6 x 250 column with a 1.0 mL/min flow rate was used with an 88:12 hexanes:isopropanol mobile phase.

---

**Area Percent Report**

---

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTBs

Signal 1: DAD1 A, Sig=210.4 Ref=off

| Peak RetTime Type | Width | Area  | Height | Area  | %     |
|------------------|-------|-------|--------|-------|-------|
| 1 20.872 min PV  | 0.3395| 3732.22656 | 172.94319 | 100.000 |

Totals : 3732.22656 172.94319
Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=210,4 Ref=0ff

| # | RetTime | Type | Width [min] | Area [mAU*s] | Height [mAU] | %    |
|---|---------|------|-------------|--------------|--------------|------|
| 1 | 11.655  | HH   | 0.1894      | 214.56447    | 17.66770     | 100.0000 |

Totals: 214.56447 17.66770
HPLC trace corresponding to the crude mixture of Run 1

\[ \text{BDE} = 85.4 \text{ kcal/mol} \]

\[ \text{BDE} = 82.6 \text{ kcal/mol} \]

**Area Percent Report**

**Sorted By** : Signal
**Multiplier** : 1.0000
**Dilution** : 1.0000

Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=210,4 Ref=off

| Peak RetTime Type | Width | Area | Height | Area % |
|------------------|-------|------|--------|-------|
| 1 11.834 VB      | 0.1996| 324.71048 | 25.05017 | 5.8752 |
| 2 21.200 BB      | 0.3888| 5202.09131 | 201.42349 | 94.1248 |

**Totals** : 5526.80179 226.47366
XI. X-ray crystal structure characterization data

Figure 20. X-ray crystal structure analysis of citalopram (±)36.

Table 2. Crystal data and structure refinement for dm67bsa.

| Identification code     | dm67bsa          |
|-------------------------|------------------|
| Empirical formula       | C22 H23 Cl3 F N3 O4 S |
| Formula weight          | 550.84           |
| Temperature             | 173(2) K         |
| Wavelength              | 0.71073 Å        |
| Crystal system          | Triclinic        |
| Space group             | P-1              |
| Unit cell dimensions    | a = 9.0968(2) Å  |
|                         | a= 103.2330(9)°.|
|                         | b = 10.1411(2) Å |
|                         | b= 99.9696(10)°.|
|                         | c = 13.7748(3) Å |
|                         | g = 95.6757(9)°.|
| Volume                  | 1205.54(4) Å³   |
| Z                       | 2                |
| Density (calculated)    | 1.517 Mg/m³      |
| Absorption coefficient  | 0.510 mm⁻¹      |
| F(000)                  | 568              |
| Crystal size            | 0.485 x 0.332 x 0.312 mm³ |
| Theta range for data collection | 2.297 to 28.349°. |
Index ranges      -12≤h≤12, -13≤k≤13, -18≤l≤18
Reflections collected      26203
Independent reflections      6018 [R(int) = 0.0235]
Completeness to theta = 25.242°      99.9 %
Absorption correction      Integration
Max. and min. transmission      0.89495 and 0.86279
Refinement method      Full-matrix least-squares on F²
Data / restraints / parameters      6018 / 0 / 312
Goodness-of-fit on F²      1.047
Final R indices [I>2sigma(I)]      R1 = 0.0256, wR2 = 0.0674
R indices (all data)      R1 = 0.0272, wR2 = 0.0685
Extinction coefficient      n/a
Largest diff. peak and hole      0.432 and -0.365 e.Å⁻³

CCDC #1587014 (36) contains the supplementary crystallographic data for this structure. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk_structures.
Figure 21. X-ray crystal structure analysis of dopamine receptor agonist (+)-37

Table 3. Crystal data and structure refinement for dd59bsa.

| Identification code  | dd59bsa         |
|----------------------|-----------------|
| Empirical formula    | C17 H25 Cl3 N2 O4 S |
| Formula weight       | 459.80          |
| Temperature          | 100(2) K        |
| Wavelength           | 0.71073 Å       |
| Crystal system       | Orthorhombic    |
| Space group          | Pbca            |
| Unit cell dimensions | a = 13.2896(3) Å  
|                      | b = 17.4119(5) Å  
|                      | c = 17.5827(5) Å  |
|                      | a= 90°.         |
|                      | b= 90°.         |
|                      | g = 90°.        |
| Volume               | 4068.59(19) Å³  |
| Z                    | 8               |
| Density (calculated) | 1.501 Mg/m³     |
| Absorption coefficient | 0.579 mm⁻¹ |
| F(000)               | 1920            |
| Crystal size         | 0.474 x 0.22 x 0.084 mm³ |
| Theta range for data collection | 2.317 to 28.347°. |
| Index ranges         | -17<=h<=17, -22<=k<=23, -23<=l<=23 |
| Reflections collected| 46039           |
| Independent reflections | 5072 [R(int) = 0.0441] |
| Completeness to theta | 25.242°  |
| Absorption correction | Integration     |
| Parameter                                      | Value                        |
|-----------------------------------------------|------------------------------|
| Max. and min. transmission                    | 0.96329 and 0.820505         |
| Refinement method                             | Full-matrix least-squares on F² |
| Data / restraints / parameters                | 5072 / 3 / 259               |
| Goodness-of-fit on F²                          | 1.255                        |
| Final R indices [I>2σ(I)]                     | R1 = 0.0476, wR2 = 0.0924    |
| R indices (all data)                          | R1 = 0.0534, wR2 = 0.0944    |
| Extinction coefficient                        | 0.0044(2)                    |
| Largest diff. peak and hole                   | 0.466 and -0.333 eÅ⁻³        |

CCDC #1587015 (37) contains the supplementary crystallographic data for this structure. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

One B-level alert: D-H Without Acceptor O4 -- >H4D is present. This is because there are no good acceptors for the second H atom on the water molecule, causing it to disorders over 2 sites.
Figure 22. X-ray crystal structure analysis of glucocorticoid receptor agonist (-)38.

Table 4. Crystal data and structure refinement for dd95bs.

| Property                      | Value                                                  |
|-------------------------------|--------------------------------------------------------|
| Identification code           | dd95bs                                                 |
| Empirical formula             | C24.23 H26.81 Cl13.64 N O4 S                           |
| Formula weight                | 556.99                                                 |
| Temperature                   | 100(2) K                                               |
| Wavelength                    | 0.71073 Å                                              |
| Crystal system                | Orthorhombic                                           |
| Space group                    | P2₁2₁2₁                                                |
| Unit cell dimensions          | a = 10.0255(5) Å b = 11.1165(5) Å c = 45.894(2) Å     |
| Volume                        | 5114.9(4) Å³                                           |
| Z                             | 8                                                      |
| Density (calculated)          | 1.447 Mg/m³                                            |
| Absorption coefficient        | 0.539 mm⁻¹                                             |
| F(000)                        | 2312                                                   |
| Crystal size                  | 0.274 x 0.239 x 0.118 mm³                              |
| Theta range for data collection| 2.217 to 25.402°.                                     |
| Index ranges                  | -12<=h<=12, -13<=k<=13, -55<=l<=55                     |
Reflections collected: 134204
Independent reflections: 9363 [R(int) = 0.0426]
Completeness to theta = 25.242°: 99.9 %
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 0.7452 and 0.6793
Refinement method: Full-matrix least-squares on F^2
Data / restraints / parameters: 9363 / 225 / 735
Goodness-of-fit on F^2: 1.256
Final R indices [I>2sigma(I)]: R1 = 0.0453, wR2 = 0.1036
R indices (all data): R1 = 0.0462, wR2 = 0.1039
Absolute structure parameter: 0.12(8)
Extinction coefficient: n/a
Largest diff. peak and hole: 0.283 and -0.350 e.Å^-3

CCDC #1587016 (38) contains the supplementary crystallographic data for this structure. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

A B-level alert: PLAT934_ALERT_3_B Number of (Iobs-Icalc)/SigmaW > 10 Outliers… 2 Check is present. This is because a significant amount of disorders is modeled in the crystal structure. This alert recognizes that there are 10 reflections where the observed data is above the limit when compared to the calculated structure factors. There is no valid scientific reason to omit the outlying data, so it was left in the refinements. These 10 outliers do not significantly impact the validity of the modeled structure when comparing to the other 9353 unique reflections.
Figure 23. X-ray crystal structure analysis of leelamine (-)44.

Table 5. Crystal data and structure refinement for dd26bs_sq.

| Property                              | Value                                      |
|---------------------------------------|--------------------------------------------|
| Identification code                   | dd26bs_sq                                  |
| Empirical formula                     | C24 H32 Cl3 F3 N2 O4 S                     |
| Formula weight                        | 607.92                                     |
| Temperature                           | 100(2) K                                   |
| Wavelength                            | 0.71073 Å                                  |
| Crystal system                        | Monoclinic                                 |
| Space group                           | P2₁                                        |
| Unit cell dimensions                  | a = 15.0450(10) Å                         |
|                                       | a = 90°.                                   |
|                                       | b = 28.349(2) Å                           |
|                                       | b = 105.373(2)°.                          |
|                                       | c = 15.0499(10) Å                         |
|                                       | g = 90°.                                   |
| Volume                                | 6189.3(7) Å                                |
| Z                                     | 8                                          |
| Density (calculated)                  | 1.305 Mg/m³                                |
| Absorption coefficient                | 0.412 mm⁻¹                                 |
| F(000)                                | 2528                                       |
| Crystal size                          | 0.334 x 0.326 x 0.162 mm³                  |
| Theta range for data collection       | 2.227 to 25.397°.                          |
| Index ranges                          | -18<=h<=18, -34<=k<=34, -18<=l<=18         |
Reflections collected: 149726
Independent reflections: 22702 [R(int) = 0.0387]
Completeness to theta = 25.242°: 99.9%
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 0.7452 and 0.6921
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 22702 / 643 / 1501
Goodness-of-fit on F²: 1.033
Final R indices [I>2σ(I)]: R1 = 0.0566, wR2 = 0.1524
R indices (all data): R1 = 0.0579, wR2 = 0.1541
Absolute structure parameter: -0.014(9)
Extinction coefficient: 0.0098(7)
Largest diff. peak and hole: 1.110 and -0.650 e.A⁻³

CCDC #1587017 (44) contains the supplementary crystallographic data for this structure. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.
XII. References:

1. Fiori, K. W.; Du Bois, J. J. Am. Chem. Soc. 2007, 129, 562.
2. Safari, N. et. al. J. Porphyrins Phthalocyanines. 2005, 9, 256.
3. Uchida, H.; Yoshiyama, H.; Reddy, P. Y.; Nakamura, S.; Toru, T.; Synlett, 2003, 13, 2083.
4. Paradine, S. M. et al. Nat. Chem., 2015, 7, 987.
5. Dauban, P.; Dodd, R. H.; J. Org. Chem. 1999, 64, 5304.
6. Roesner, S.; Casatejada, J. M.; Elford, T. G.; Sonawane, R. P.; Aggarwal, V. K. Org. Lett., 2011, 13, 5740.
7. Lu, P.; Hou, T.; Gu, X.; Li, P. Org. Lett. 2015, 17, 1954.
8. Procopiou, P. A.; Baugh, S. P. D.; Flack, S. S.; Inglis, G. G. J. Org. Chem. 1998, 63, 2342.
9. Aymamí Bofarull, J.; Nicolas Chevalier, F. C.; Soler López, M.; Luque G., M. T.; Martinell P.; M. Carboxylic derivatives for use in the treatment of cancer. WO2009080722 A2, July 2, 2009.
10. Davis, H.; Genov, G. R.; Phipps, R. J. Angew. Chem. Int. Ed. 2017, 56, 13351.
11. Bess, E. N.; DeLuca, R. J.; Tindall, D. J.; Oderinde, M. S.; Roizen, J. L.; DuBois, J.; Sigman, M. S.; J. Am. Chem. Soc. 2014, 136, 5783.
12. Pallavicini, M.; Budriesi, R.; Fumagalli, L.; Ioan, P.; Chiarini, A.; Bolchi, C.; Ugenti, M. P.; Colleoni, S.; Gobbi, M.; Valoti, E. J. Med. Chem. 2006, 49, 7140.
13. Skov, A. B.; Broman, S. L.; Gertsen, A. S.; Elm, J.; Jevric, M.; Cacciarini, M.; Kadziola, A.; Mikkelsen, K.; Nielsen, M. B. Chem. Eur. J. 2016, 22, 14567.
14. Deiters, A.; Young, D. D.; Small molecule modifiers of microRNA MIR-122. WO2011091209 A1, July 28, 2011.
15. Chakrabarti, A.; Biswas, G. K.; Chakraborty, D. P. Tetrahedron 1989, 45, 5059.
16. Patrick, G. L.; J. Chem. Soc. Perkin Trans. 1. 1995, 1273.
17. Ward, R. S.; Davies, J.; Hodges, G.; Roberts, D. W. Synthesis. 2002, 16, 2431.
18. Pinto-Bazuco Mendiesta, M. A. E.; Negri, M.; Jagusz, C.; Müller-Vieira, U.; Lauterbach, T.; Hartmann, R. W. J. Med. Chem. 2008, 51, 5009.
19. Kokotos, C. G.; Baskakis, C.; Kokotos, G. J. Org. Chem. 2008, 73, 8623.
20. Albert, S.; Santelli-Rouvier, C.; Castaing, M.; Berthelot, M.; Spengler, G.; Molnar, J.; Barbe, J. Eur. J. Med. Chem. 2003, 38, 253.
21. Petersen, H.; Bögesö, K. P.; Holm, P. Crystalline base of citalopram and hydrochloride or hydrobromide salt thereof. EP1227088 A1, July 31, 2002.
22. Tagmataarchis, N.; Katerinopoulos, H. E. J. Heterocyclic Chem. 1996, 33, 983.
23. Robinson, R. P. et al. J. Med. Chem., 2009, 52, 1731.
24. McNeill, E.; Du Bois, J. Chem. Sci. 2012, 3, 1810.
25. Jin, Z.; Yang, R.; Du, Y.; Tiwari, B.; Ganguly, R.; Chi, Y. R. Org. Lett. 2012, 14, 3226.
26. Jiang, X.; Song, Z.; Xu, C.; Yao, Q.; Zhang, A. Eur. J. Org. Chem. 2014, 418.
Parameter | Value
--- | ---
1 Origin | Varian
2 Spectrometer | Inova
3 Solvent | CD3OD
4 Temperature | 20.0
5 Pulse Sequence | s2pul
6 Experiment | 1D
7 Probe | QUADG
8 Number of Scans | 8
9 Receiver Gain | 56
10 Relaxation Delay | 10.0000
11 Pulse Width | 12.1250
12 Spectrometer Frequency | 499.43
13 Spectral Width | 8000.0
14 Lowest Frequency | -1508.8
15 Nucleus | 1H
16 Acquired Size | 32768
17 Spectral Size | 65536

- 4.86 H2O
- 3.31 CD3OD
| Parameter         | Value            |
|-------------------|------------------|
| 1 Origin          | Varian           |
| 2 Spectrometer    | inova            |
| 3 Solvent         | CD3OD            |
| 4 Temperature     | 20.0             |
| 5 Pulse Sequence  | s2pul            |
| 6 Experiment      | 1D               |
| 7 Probe           | QUAOG            |
| 8 Number of Scans | 608              |
| 9 Receiver Gain   | 60               |
| 10 Relaxation Delay| 2.0000          |
| 11 Pulse Width    | 6.1250           |
| 12 Spectrometer Frequency | 126.60          |
| 13 Spectral Width | 32000.0          |
| 14 Lowest Frequency| -10000.0         |
| 15 Nucleus        | 13C              |
| 16 Acquired Size  | 32768            |
| 17 Spectral Size  | 65536            |
| Parameter          | Value        |
|--------------------|--------------|
| Origin             | Varian       |
| Spectrometer       | Inova        |
| Solvent            | CDCl3        |
| Pulse Sequence     | s2pul        |
| Experiment         | 1D           |
| Probe              | QUAO         |
| Number of Scans    | 544          |
| Receiver Gain      | 60           |
| Relaxation Delay   | 1.0000       |
| Pulse Width        | 0.0000       |
| Acquisition Time   | 1.0863       |
| Spectrometer Frequency | 125.66   |
| Spectral Width     | 30165.9      |
| Lowest Frequency   | -1276.8      |
| Nucleus            | 13C          |
| Acquired Size      | 32768        |
| Spectral Size      | 65536        |

![Spectroscopy Graph](image)
| Parameter          | Value          |
|--------------------|----------------|
| Origin             | Varian         |
| Spectrometer       | Inova          |
| Solvent            | CDCl3          |
| Temperature        | 20.0           |
| Pulse Sequence     | s2pul          |
| Experiment         | 1D             |
| Probe              | hcn            |
| Number of Scans    | 16             |
| Receiver Gain      | 42             |
| Relaxation Delay   | 10.0000        |
| Pulse Width        | 7.0000         |
| Acquisition Time   | 4.0960         |
| Spectrometer Frequency | 500.07      |
| Spectral Width     | 8000.0         |
| Lowest Frequency   | -1521.1        |
| Nucleus            | 1H             |
| Acquired Size      | 32768          |
| Spectral Size      | 65536          |

![Chemical Structure](image)

-7.26 CDCl3

-1.57 H2O

Grease
| Parameter       | Value            |
|----------------|------------------|
| Origin         | Varian           |
| Spectrometer   | inova            |
| Solvent        | CDCl3            |
| Temperature    | 20.0             |
| Pulse Sequence | s2pul            |
| Experiment     | 1D               |
| Probe          | QUADG            |
| Number of Scans| 256              |
| Receiver Gain  | 60               |
| Relaxation Delay| 2.0000          |
| Pulse Width    | 6.1250           |
| Acquisition Time| 1.0240          |
| Spectrometer Frequency | 125.60  |
| Spectral Width | 32000.0          |
| Lowest Frequency| -2188.2          |
| Nucleus        | 13C              |
| Acquired Size  | 32768            |
| Spectral Size  | 65536            |
| Parameter       | Value                                                                 |
|-----------------|----------------------------------------------------------------------|
| Origin          | Bruker BioSpin GmbH                                                  |
| Spectrometer    | spect                                                                |
| Solvent         | CDCl3                                                                |
| Temperature     | 298.1                                                                |
| Pulse Sequence  | zg30                                                                 |
| Experiment      | 1D                                                                   |
| Probe           | Z127784_0002 (CP BBO 50051 BBF-H-D-05 Z)                             |
| Number of Scans | 32                                                                   |
| Receiver Gain   | 137.4                                                                |
| Relaxation Delay| 1.0000                                                              |
| Pulse Width     | 12.0000                                                              |
| Acquisition Time| 3.2768                                                               |
| Spectrometer Frequency | 500.35                        |
| Spectral Width  | 100000.0                                                             |
| Lowest Frequency| -1910.3                                                              |
| Nucleus         | 1H                                                                   |
| Acquired Size   | 32768                                                                |
| Spectral Size   | 65536                                                                |
| Parameter                | Value                                                                 |
|--------------------------|-----------------------------------------------------------------------|
| Origin                   | Bruker BioSpin GmbH                                                   |
| Spectrometer             | spect                                                                |
| Solvent                  | CDC13                                                                |
| Temperature              | 298.1                                                                |
| Pulse Sequence           | zgpg30                                                               |
| Experiment               | 1D                                                                   |
| Probe                    | Z127784_0002 (CP BBO 50051 B8F–H–D–05 Z)                             |
| Number of Scans          | 2560                                                                 |
| Receiver Gain            | 190.5                                                                |
| Relaxation Delay         | 2.0000                                                               |
| Pulse Width              | 10.0000                                                              |
| Acquisition Time         | 1.0398                                                               |
| Spectrometer Frequency   | 125.83                                                               |
| Spectral Width           | 31512.6                                                              |
| Lowest Frequency         | -1916.9                                                              |
| Nucleus                  | 13C                                                                  |
| Acquired Size            | 32768                                                                |
| Spectral Size            | 65536                                                                |
| Parameter          | Value       |
|--------------------|-------------|
| Origin             | Varian      |
| Spectrometer       | Inova       |
| Solvent            | CDCl3       |
| Pulse Sequence     | s2pul       |
| Experiment         | 1D          |
| Probe              | QUAD        |
| Number of Scans    | 256         |
| Receiver Gain      | 60          |
| Relaxation Delay   | 1.0000      |
| Pulse Width        | 0.0000      |
| Acquisition Time   | 1.0863      |
| Spectrometer Frequency | 125.66    |
| Spectral Width     | 30165.9     |
| Lowest Frequency   | -1275.3     |
| Nucleus            | 13C         |
| Acquired Size      | 32768       |
| Spectral Size      | 65536       |

![Chemical Structure](image)

-77.2 CDCl3

```
f1 (ppm)
```

220  210  200  190  180  170  160  150  140  130  120  110  100  90  80  70  60  50  40  30  20  10  0  -1

140
-7.26 CDCl3

![](image)

-1.25 Grease

| Parameter   | Value       |
|-------------|-------------|
| Origin      | Varian      |
| Spectrometer| inova       |
| Solvent     | CDCl3       |
| Pulse Sequence | t2pul     |
| Experiment  | 1D          |
| Probe       | QUAD        |
| Number of Scans | 8           |
| Receiver Gain | 41         |
| Relaxation Delay | 5.00000   |
| Pulse Width  | 0.00000     |
| Acquisition Time | 4.6645   |
| Spectrometer Frequency | 499.69   |
| Spectral Width | 7024.9    |
| Lowest Frequency | -1011.9   |
| Nucleus     | 1H          |
| Acquired Size | 32768     |
| Spectral Size | 65536     |
| Parameter            | Value          |
|----------------------|----------------|
| Origin               | Varian         |
| Spectrometer         | Inova          |
| Solvent              | CDC13          |
| Pulse Sequence       | z2pul          |
| Experiment           | 1D             |
| Probe                | QUAD           |
| Number of Scans      | 8              |
| Receiver Gain        | 54             |
| Relaxation Delay     | 2.0000         |
| Pulse Width          | 0.0000         |
| Acquisition Time     | 4.6645         |
| Spectrometer Frequency| 499.69        |
| Spectral Width       | 7024.9         |
| Lowest Frequency     | -1011.9        |
| Nucleus              | 1H             |
| Acquired Size        | 32768          |
| Spectral Size        | 65536          |

![Chemical Structure](image)

-1.25 Grease

-1.67 H2O

$\text{Br}$

$\text{OAc}$

$\text{CCl}_3$

$\text{H}$

$\text{S}$

$\text{N}$
| Parameter          | Value  |
|--------------------|--------|
| Origin             | Varian |
| Spectrometer       | Inova  |
| Solvent            | CDCl3  |
| Pulse Sequence     | sZauli |
| Experiment         | 1D     |
| Probe              | QUAD   |
| Number of Scans    | 290    |
| Receiver Gain      | 60     |
| Relaxation Delay   | 10.0000|
| Pulse Width        | 0.0000 |
| Acquisition Time   | 1.0863 |
| Spectrometer Frequency | 125.66 |
| Spectral Width     | 30165.9|
| Lowest Frequency   | -1260.2|
| Nucleus            | 13C    |
| Acquired Size      | 32768  |
| Spectral Size      | 65536  |

![Chemical Structure](image)
| Parameter          | Value           |
|--------------------|-----------------|
| Origin             | Varian          |
| Spectrometer       | Inova           |
| Solvent            | CDCl₃           |
| Temperature        | 20.0            |
| Pulse Sequence     | s2pul           |
| Experiment         | 1D              |
| Probe              | QUAD            |
| Number of Scans    | 8               |
| Receiver Gain      | 48              |
| Relaxation Delay   | 1.0000          |
| Pulse Width        | 0.0000          |
| Acquisition Time   | 4.6645          |
| Spectrometer Frequency | 499.69   |
| Spectral Width     | 7024.9          |
| Lowest Frequency   | -1011.9         |
| Nucleus            | 1H              |
| Acquired Size      | 32768           |
| Spectral Size      | 65536           |
| Parameter         | Value                                                                 |
|-------------------|----------------------------------------------------------------------|
| 1 Origin          | Bruker BioSpin GmbH                                                  |
| 2 Spectrometer    | spect                                                               |
| 3 Solvent         | CDCl₃                                                               |
| 4 Temperature     | 298.0                                                               |
| 5 Pulse Sequence  | zgpg30                                                              |
| 6 Experiment      | 1D                                                                  |
| 7 Probe           | Z127784_0002 (CP BBO 500ST1 BBF-H-D-05 Z)                           |
| 8 Number of Scans | 256                                                                 |
| 9 Receiver Gain   | 190.5                                                               |
| 10 Relaxation Delay| 2.0000                                                             |
| 11 Pulse Width    | 10.0000                                                             |
| 12 Spectrometer Frequency| 126.83                                                              |
| 13 Spectral Width | 29761.9                                                             |
| 14 Lowest Frequency| -2284.9                                                             |
| 15 Nucleus        | 13C                                                                 |
| 16 Acquired Size  | 32768                                                               |
| 17 Spectral Size  | 65536                                                               |

![Chemical Structure](image)

![Spectrum Graph](image)
| Parameter          | Value            |
|-------------------|------------------|
| Origin            | Varian           |
| Spectrometer      | Inova            |
| Solvent           | CDCl3            |
| Pulse Sequence    | d2pul            |
| Experiment        | 1D               |
| Probe             | QUAD             |
| Number of Scans   | 496              |
| Receiver Gain     | 60               |
| Relaxation Delay  | 2.0000           |
| Pulse Width       | 0.0000           |
| Acquisition Time  | 1.0863           |
| Spectrometer Frequency | 125.66    |
| Spectral Width    | 10165.9          |
| Lowest Frequency  | -1278.4          |
| Nucleus           | 13C              |
| Acquired Size     | 32768            |
| Spectral Size     | 65536            |

![Chemical Structure](image)

![NMR Spectrum](image)
| Parameter          | Value   |
|--------------------|---------|
| Origin             | Varian  |
| Spectrometer       | Inova   |
| Solvent            | CDCl3   |
| Pulse Sequence     | s2pul   |
| Experiment         | 1D      |
| Probe              | QUAD    |
| Number of Scans    | 128     |
| Receiver Gain      | 60      |
| Relaxation Delay   | 0.0000  |
| Pulse Width        | 0.0000  |
| Acquisition Time   | 0.3277  |
| Spectrometer Frequency | 470.15 |
| Spectral Width     | 100000.0|
| Lowest Frequency   | -79538.0|
| Nucleus            | 19F     |
| Acquired Size      | 32768   |
| Spectral Size      | 65536   |
| Parameter     | Value          |
|--------------|----------------|
| Origin       | Varian         |
| Spectrometer | INEVA          |
| Solvent      | CDCl3          |
| Temperature  | 20.0           |
| Pulse Sequence | s2pul     |
| Experiment   | 1D             |
| Probe        | QUAD           |
| Number of Scans | 576       |
| Receiver Gain | 60            |
| Relaxation Delay | 5.0000  |
| Pulse Width  | 0.0000         |
| Acquisition Time | 1.0863 |
| Spectrometer Frequency | 125.66   |
| Spectral Width | 10165.9     |
| Lowest Frequency | -1260.2 |
| Nucleus      | 13C            |
| Acquired Size | 32768         |
| Spectral Size | 65536        |

![Chemical Structure](image)

-77.16 CDCl3
-65.98 Et2O
-29.84 grease
-15.39 Et2O

f1 (ppm)
| Parameter               | Value                                                                                                                                 |
|-------------------------|---------------------------------------------------------------------------------------------------------------------------------------|
| Title                   | ASH191:protonf19.10.fid                                                                                                             |
| Origin                  | Bruker BioSpin GmbH                                                                                                                 |
| Owner                   | user1d                                                                                                                               |
| Spectrometer            | spect                                                                                                                                |
| Solvent                 | CDCl3                                                                                                                                |
| Temperature             | 298.0                                                                                                                                |
| Pulse Sequence          | zgflaq                                                                                                                               |
| Experiment              | 1D                                                                                                                                     |
| Probe                   | Z127784_0002 (CP BBQ 500S1 BBF-H-D-05 Z)                                                                                           |
| Number of Scans         | 16                                                                                                                                     |
| Receiver Gain           | 191                                                                                                                                   |
| Relaxation Delay        | 1.0000                                                                                                                               |
| Pulse Width             | 15.0000                                                                                                                               |
| Acquisition Time        | 0.5767                                                                                                                               |
| Acquisition Date        | 2017-04-05T21:19:11                                                                                                                   |
| Modification Date       | 2017-04-05T21:19:11                                                                                                                   |
| Spectrometer Frequency  | 470.75                                                                                                                               |
| Spectral Width          | 113636.4                                                                                                                             |
| Lowest Frequency        | -101898.1                                                                                                                            |
| Nucleus                 | 19F                                                                                                                                   |
| Acquired Size           | 65536                                                                                                                                |
| Spectral Size           | 131072                                                                                                                               |
| Parameter      | Value                        |
|---------------|------------------------------|
| Origin        | Varian                       |
| Spectrometer  | inova                        |
| Solvent       | CDCl3                        |
| Pulse Sequence| s2pul                        |
| Experiment    | 1D                           |
| Probe         | hcm                          |
| Number of Scans| 8                            |
| Receiver Gain | 26                           |
| Relaxation Delay| 1.0000                      |
| Pulse Width   | 0.0000                       |
| Acquisition Time| 4.0960                      |
| Spectrometer Frequency| 500.07           |
| Spectral Width | 8000.0                      |
| Lowest Frequency| −1499.6                    |
| Nucleus       | 1H                           |
| Acquired Size | 32768                        |
| Spectral Size | 65536                        |
| Parameter          | Value     |
|--------------------|-----------|
| Origin             | Varian    |
| Spectrometer       | Inova     |
| Solvent            | CDCl3     |
| Pulse Sequence     | 12pul     |
| Experiment         | 1D        |
| Probe              | QUAD      |
| Number of Scans    | 144       |
| Receiver Gain      | 60        |
| Relaxation Delay   | 10.0000   |
| Pulse Width        | 0.0000    |
| Acquisition Time   | 1.0863    |
| Spectrometer Frequency | 125.66 |
| Spectral Width     | 30165.9   |
| Lowest Frequency   | -1260.2   |
| Nucleus            | 13C       |
| Acquired Size      | 32768     |
| Spectral Size      | 65536     |

![Chemical Structure Image]
| Parameter   | Value   |
|-------------|---------|
| Origin      | Varian  |
| Spectrometer| inova   |
| Solvent     | CDC13   |
| Pulse Sequence | s2pul  |
| Experiment  | 1D      |
| Probe       | quadbp  |
| Number of Scans | 16     |
| Receiver Gain | 54     |
| Relaxation Delay | 1.0000 |
| Pulse Width | 0.0000  |
| Acquisition Time | 4.0960 |
| Spectrometer Frequency | 399.74 |
| Spectral Width | 8000.0 |
| Lowest Frequency | -2426.7 |
| Nucleus     | 1H      |
| Acquired Size | 32768  |
| Spectral Size | 65536  |
| Parameter          | Value       |
|--------------------|-------------|
| Origin             | Varian      |
| Spectrometer       | Inova       |
| Solvent            | CDCl₃       |
| Pulse Sequence     | s2paul      |
| Experiment         | 1D          |
| Probe              | QUAD        |
| Number of Scans    | 976         |
| Receiver Gain      | 60          |
| Relaxation Delay   | 1.0000      |
| Pulse Width        | 0.0000      |
| Acquisition Time   | 1.0863      |
| Spectrometer Frequency | 125.66  |
| Spectral Width     | 10161.9     |
| Lowest Frequency   | -1275.5     |
| Nucleus            | 13C         |
| Acquired Size      | 32768       |
| Spectral Size      | 65536       |

```
-77.2 CDCl₃
```

```
\begin{align*}
\text{HN} & \quad \text{SO}_3 \\
\text{H} & \quad  \text{CH}_2 \\
\text{C}_6 & \quad \text{H}_6
\end{align*}
```

```
\text{OAc}
```

```
-1 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220
```

```
f1 (ppm)
```

```
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
```

```
163
```
| Parameter       | Value        |
|-----------------|--------------|
| Origin          | Varian       |
| Spectrometer    | inova        |
| Solvent         | CDCl3        |
| Pulse Sequence  | s2pul        |
| Experiment      | 1D           |
| Probe           | QUAD         |
| Number of Scans | 8            |
| Receiver Gain   | 52           |
| Relaxation Delay| 0.0000       |
| Pulse Width     | 0.0000       |
| Acquisition Time| 4.6645       |
| Spectrometer Frequency | 499.69  |
| Spectral Width  | 7024.9       |
| Lowest Frequency| -1021.4      |
| Nucleus         | 1H           |
| Acquired Size   | 32768        |
| Spectral Size   | 65536        |
| Parameter     | Value   |
|---------------|---------|
| Origin        | Varian  |
| Spectrometer  | inova   |
| Solvent       | CDCl3   |
| Pulse Sequence| s2pul   |
| Experiment    | 1D      |
| Probe         | QUAO    |
| Number of Scans| 640    |
| Receiver Gain | 60      |
| Relaxation Delay | 1.0000 |
| Pulse Width   | 0.0000  |
| Acquisition Time | 1.0835 |
| Spectrometer Frequency | 125.66 |
| Spectral Width | 30165.9 |
| Lowest Frequency | -1273.9 |
| Nucleus       | 13C     |
| Acquired Size | 32768   |
| Spectral Size | 65536   |
| Parameter         | Value         |
|-------------------|---------------|
| Origin            | Varian        |
| Spectrometer      | Inova         |
| Solvent           | CDCl₃         |
| Temperature       | 29.0          |
| Pulse Sequence    | s2pul         |
| Experiment        | 1D            |
| Probe             | QUAD          |
| Number of Scans   | 8             |
| Receiver Gain     | 60            |
| Relaxation Delay  | 1.0000        |
| Pulse Width       | 0.0000        |
| Acquisition Time  | 4.6645        |
| Spectrometer Frequency | 499.69        |
| Spectral Width    | 7024.9        |
| Lowest Frequency  | -1011.9       |
| Nucleus           | 1H            |
| Acquired Size     | 32768         |
| Spectral Size     | 61536         |
| Parameter          | Value                                      |
|--------------------|--------------------------------------------|
| Origin             | Bruker BioSpin GmbH                        |
| Spectrometer       | spect                                      |
| Solvent            | CDCl3                                      |
| Temperature        | 298.0                                      |
| Pulse Sequence     | zgpg90                                     |
| Experiment         | 1D                                         |
| Probe              | 2127784_0002 (CP BBD 500ST BBF-H-D-06 Z)   |
| Number of Scans    | 256                                        |
| Receiver Gain      | 190.5                                      |
| Relaxation Delay   | 3.00000                                    |
| Pulse Width        | 10.0000                                    |
| Spectrometer Frequency | 126.83                                  |
| Spectral Width     | 31512.6                                    |
| Lowest Frequency   | -1899.0                                    |
| Nucleus            | 13C                                        |
| Acquired Size      | 32768                                      |
| Spectral Size      | 65536                                      |

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
| Parameter | Value |
|-----------|-------|
| Origin    | Varian|
| Spectrometer | Inova |
| Solvent   | CDCl3 |
| Temperature | 50.3  |
| Pulse Sequence | s2pul |
| Experiment | 1D    |
| Probe     | QUAD  |
| Number of Scans | 230  |
| Receiver Gain | 60   |
| Relaxation Delay | 10.0000 |
| Pulse Width | 0.0000 |
| Acquisition Time | 1.0883 |
| 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
Spectrometer | spect
Solvent | DMSO
Temperature | 298.0
Pulse Sequence | zgflq
Experiment | 10
Probe | 2127784_0002 (CP BRD 50051 B8F-H.D.05 Z)
Number of Scans | 16
Receiver Gain | 190.5
Relaxation Delay | 1.0000
Pulse Width | 15.0000
Spectrometer Frequency | 470.75
Spectral Width | 113636.4
Lowest Frequency | -103898.1
Nucleus | 19F
Acquired Size | 65536
Spectral Size | 131072
| Parameter       | Value     |
|-----------------|-----------|
| Origin          | Varian    |
| Spectrometer    | Inova     |
| Solvent         | CDCl3     |
| Pulse Sequence  | s2pul     |
| Experiment      | 1D        |
| Probe           | QUAD      |
| Number of Scans | 304       |
| Receiver Gain   | 60        |
| Relaxation Delay| 2.00000   |
| Pulse Width     | 0.00000   |
| Acquisition Time| 1.0863    |
| Spectrometer Frequency | 125.66 |
| Spectral Width  | 30165.9   |
| Lowest Frequency| -1274.8   |
| Nucleus         | 13C       |
| Acquired Size   | 32768     |
| Spectral Size   | 65536     |
| Parameter     | Value   |
|---------------|---------|
| Origin        | Varian  |
| Spectrometer  | inova   |
| Solvent       | CDC13   |
| Pulse Sequence| 2pul    |
| Experiment    | 1D      |
| Probe         | QUAD    |
| Number of Scans| 480    |
| Receiver Gain | 60      |
| Relaxation Delay | 5.0000 |
| Pulse Width   | 0.0000  |
| Acquisition Time | 1.0863 |
| Spectrometer Frequency | 125.66 |
| Spectral Width | 30165.9|
| Lowest Frequency | -1260.2|
| Nucleus       | 13C     |
| Acquired Size | 32768   |
| Spectral Size | 65536   |
-7.26 CDCl3

$\text{O} = \text{N} - \text{S} - \text{O} - \text{CCl}_3$

-1.25 Grease

| Parameter       | Value       |
|-----------------|-------------|
| Origin          | Varian      |
| Spectrometer    | inova       |
| Solvent         | CDCl3       |
| Temperature     | 20.0        |
| Pulse Sequence  | s2pul       |
| Experiment      | 1D          |
| Probe           | hcn         |
| Number of Scans | 16          |
| Receiver Gain   | 42          |
| Relaxation Delay| 2.0000      |
| Pulse Width     | 0.0000      |
| Acquisition Time| 4.0960      |
| Spectrometer Frequency | 500.07   |
| Spectral Width  | 80000.0     |
| Lowest Frequency| -1499.6     |
| Nucleus         | 1H          |
| Acquired Size   | 32768       |
| Spectral Size   | 65536       |
| Parameter       | Value                                                                 |
|-----------------|-----------------------------------------------------------------------|
| Origin          | Bruker BioSpin GmbH                                                   |
| Spectrometer    | spect                                                                |
| Solvent         | CDCl3                                                                |
| Temperature     | 298.0                                                                |
| Pulse Sequence  | zgpg30                                                               |
| Experiment      | 1D                                                                   |
| Probe           | Z127784_0002 (CP BBO S0051 BBF-H-D-05 Z)                              |
| Number of Scans | 512                                                                  |
| Receiver Gain   | 190.5                                                                |
| Relaxation Delay| 2.00000                                                              |
| Pulse Width     | 10.00000                                                             |
| Spectrometer Frequency | 125.83                                                    |
| Spectral Width  | 29761.9                                                              |
| Lowest Frequency| -2284.9                                                              |
| Nucleus         | 13C                                                                  |
| Acquired Size   | 32768                                                                |
| Spectral Size   | 65636                                                                |

![Chemical Structure](image)
| Parameter       | Value   |
|-----------------|---------|
| Origin          | Varian  |
| Spectrometer    | Inova   |
| Solvent         | CDCl3   |
| Pulse Sequence  | s2pul   |
| Experiment      | 1D      |
| Probe           | QUAD    |
| Number of Scans | 8       |
| Receiver Gain   | 52      |
| Relaxation Delay| 2.0000  |
| Pulse Width     | 0.0000  |
| Acquisition Time| 4.6645  |
| Spectrometer Frequency | 499.69 |
| Spectral Width  | 7024.9  |
| Lowest Frequency| -1011.9 |
| Nucleus         | 1H      |
| Acquired Size   | 32768   |
| Spectral Size   | 65536   |

![Chemical Structure](image)

183
| Parameter          | Value   |
|--------------------|---------|
| Origin             | Varian  |
| Spectrometer       | Inova   |
| Solvent            | CDCl3   |
| Temperature        | 20.0    |
| Pulse Sequence     | s2pul   |
| Experiment         | 1D      |
| Probe              | QUAD    |
| Number of Scans    | 624     |
| Receiver Gain      | 60      |
| Relaxation Delay   | 2.0000  |
| Pulse Width        | 0.0000  |
| Acquisition Time   | 1.0383  |
| Spectrometer Frequency | 125.66 |
| Spectral Width     | 30165.9 |
| Lowest Frequency   | -1275.0 |
| Nucleus            | 1H      |
| Acquired Size      | 32768   |
| Spectral Size      | 65536   |
| Parameter      | Value         |
|----------------|---------------|
| Origin         | Varian        |
| Spectrometer   | Inova         |
| Solvent        | CDC13         |
| Temperature    | 29.0          |
| Pulse Sequence | 42ms          |
| Experiment     | 1D            |
| Probe          | QUAD          |
| Number of Scans| 16            |
| Receiver Gain  | 50            |
| Relaxation Delay| 0.0000       |
| Pulse Width    | 0.0000        |
| Acquisition Time| 4.6645       |
| Spectrometer Frequency | 499.69     |
| Spectral Width | 7024.9        |
| Lowest Frequency| -1021.8      |
| Nucleus        | 1H            |
| Acquired Size  | 32768         |
| Spectral Size  | 65536         |
| Parameter               | Value       |
|------------------------|-------------|
| Origin                 | Varian      |
| Spectrometer           | Inova       |
| Solvent                | CDCl3       |
| Temperature            | 22.0        |
| Pulse Sequence         | s2pul       |
| Experiment             | 1D          |
| Probe                  | QUAD        |
| Number of Scans        | 96          |
| Receiver Gain          | 60          |
| Relaxation Delay       | 2.0000      |
| Pulse Width            | 0.0000      |
| Acquisition Time       | 1.0863      |
| Spectrometer Frequency | 125.06      |
| Spectral Width         | 30165.9     |
| Lowest Frequency       | -1275.4     |
| Nucleus                | 13C         |
| Acquired Size          | 32768       |
| Spectral Size          | 65536       |

![NHTces NMe2 Chemical Structure]
| Parameter               | Value       |
|-------------------------|-------------|
| Origin                  | Varian      |
| Spectrometer            | Inova       |
| Solvent                 | CDCl3       |
| Temperature             | 20.0        |
| Pulse Sequence          | s2pul       |
| Experiment              | 1D          |
| Probe                   | QUAD        |
| Number of Scans         | 144         |
| Receiver Gain           | 60          |
| Relaxation Delay        | 2.0000      |
| Pulse Width             | 0.0000      |
| Acquisition Time        | 1.0863      |
| Spectrometer Frequency  | 125.66      |
| Spectral Width          | 30165.9     |
| Lowest Frequency        | -1272.6     |
| Nucleus                 | 13C         |
| Acquired Size           | 32768       |
| Spectral Size           | 65536       |
| Parameter       | Value          |
|-----------------|----------------|
| Origin          | Varian         |
| Spectrometer    | Inova          |
| Solvent         | CDCl3          |
| Temperature     | 20.0           |
| Pulse Sequence  | $\text{s2pul}$|
| Experiment      | 1D             |
| Probe           | quadbp         |
| Number of Scans | 16             |
| Receiver Gain   | 52             |
| Relaxation Delay| 0.0000         |
| Pulse Width     | 0.0000         |
| Acquisition Time| 4.0960         |
| Spectrometer Frequency | 399.74 |
| Spectral Width  | 80000.0        |
| Lowest Frequency| -2425.0        |
| Nucleus         | 1H             |
| Acquired Size   | 32768          |
| Spectral Size   | 65536          |

![Chemical Structure](image)
| Parameter         | Value  |
|-------------------|--------|
| Title             |        |
| Origin            | Varian |
| Spectrometer      | inertia |
| Solvent           | CDCl3  |
| Temperature       | 36.0   |
| Pulse Sequence    | s2pul  |
| Experiment        | 10     |
| Probe             | quad94 |
| Number of Scans   | 944    |
| Receiver Gain     | 60     |
| Relaxation Delay  | 2.0000 |
| Pulse Width       | 0.0000 |
| Acquisition Time  | 1.3107 |
| Spectrometer Frequency | 100.58 |
| Spectral Width    | 25000.0|
| Lowest Frequency  | -1029.7|
| Nucleus           | 13C    |
| Acquired Size     | 32768  |
| Spectral Size     | 65536  |

![NHTces](image)
| Parameter           | Value          |
|---------------------|----------------|
| Origin              | Varian         |
| Spectrometer        | Inova          |
| Solvent             | CD3CN          |
| Temperature         | 29.0           |
| Pulse Sequence      | z2pul          |
| Experiment          | 1D             |
| Probe               | quad94         |
| Number of Scans     | 208            |
| Receiver Gain       | 60             |
| Relaxation Delay    | 2.0000         |
| Pulse Width         | 0.0000         |
| Acquisition Time    | 1.3107         |
| Spectrometer Frequency | 100.58       |
| Spectral Width      | 25000.0        |
| Lowest Frequency    | -950.0         |
| Nucleus             | 13C            |
| Acquired Size       | 32768          |
| Spectral Size       | 65536          |

![Chemical Structure](image)
| Parameter          | Value            |
|--------------------|------------------|
| Origin             | Varian           |
| Spectrometer       | 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        | 0.0000           |
| Acquisition Time   | 0.3277           |
| Spectrometer Frequency | 470.15    |
| Spectral Width     | 1000.00          |
| Lowest Frequency   | -79541.0         |
| Nucleus            | 19F              |
| Acquired Size      | 32768            |
| Spectral Size      | 65536            |

- The chemical structure shown is that of a molecule with the formula NHTces. The molecule contains a benzene ring connected to a chain with a nitrogen atom at the end, bearing a BF$_3$ group.

- The 1D NMR spectrum is presented with the f1 (ppm) axis ranging from -160 to 40. There is a peak at around -79541.0 ppm.
| Parameter            | Value       |
|----------------------|-------------|
| Origin               | Varian      |
| Spectrometer         | Inova       |
| Solvent              | CDCl3       |
| Pulse Sequence       | s2pul       |
| Experiment           | 1D          |
| Probe                | QUAD        |
| Number of Scans      | 480         |
| Receiver Gain        | 60          |
| Relaxation Delay     | 2.0000      |
| Pulse Width          | 0.0000      |
| Acquisition Time     | 1.0863      |
| Spectrometer Frequency| 125.66      |
| Spectral Width       | 30165.9     |
| Lowest Frequency     | -1273.6     |
| Nucleus              | 13C         |
| Acquired Size        | 32768       |
| Spectral Size        | 65536       |

![Chemical Structure](image)
| Parameter       | Value                  |
|-----------------|------------------------|
| Origin          | Varian                 |
| Spectrometer    | Inova                  |
| Solvent         | CDCl3                  |
| Pulse Sequence  | s2pul                  |
| Experiment      | 1D                     |
| Probe           | QUAD                   |
| Number of Scans | 128                    |
| Receiver Gain   | 46                     |
| Relaxation Delay| 0.0000                 |
| Pulse Width     | 0.0000                 |
| Acquisition Time| 0.3277                 |
| Spectrometer Frequency | 470.15         |
| Spectral Width  | 1000000.0              |
| Lowest Frequency| -79541.0               |
| Nucleus         | 19F                    |
| Acquired Size   | 32768                  |
| Spectral Size   | 65536                  |
| Parameter      | Value   |
|----------------|---------|
| Origin         | Varian  |
| Spectrometer   | Inova   |
| Solvent        | CDCl3   |
| Pulse Sequence | s2pul   |
| Experiment     | 1D      |
| Probe          | QUAD    |
| Number of Scans| 224     |
| Receiver Gain  | 60      |
| Relaxation Delay| 1.0000  |
| Pulse Width    | 0.0000  |
| Acquisition Time| 1.0863  |
| Spectrometer Frequency| 125.66 |
| Spectral Width | 30165.9 |
| Lowest Frequency| -1279.0 |
| Nucleus        | 13C     |
| Acquired Size  | 32768   |
| Spectral Size  | 65536   |
Parameter | Value
--- | ---
1 Origin | Varian
2 Spectrometer | Innova
3 Solvent | CDCl3
4 Pulse Sequence | z2pul
5 Experiment | 1D
6 Probe | quad94
7 Number of Scans | 8
8 Receiver Gain | 48
9 Relaxation Delay | 2.0000
10 Pulse Width | 0.0000
11 Acquisition Time | 4.0960
12 Spectrometer Frequency | 399.95
13 Spectral Width | 8000.0
14 Lowest Frequency | -2424.5
15 Nucleus | 1H
16 Acquired Size | 32768
17 Spectral Size | 65536
| Parameter          | Value     |
|--------------------|-----------|
| Origin             | Varian    |
| Spectrometer       | Inova     |
| Solvent            | CDC13     |
| Pulse Sequence     | s2pul     |
| Experiment         | 1D        |
| Probe              | e64094    |
| Number of Scans    | 144       |
| Receiver Gain      | 60        |
| Relaxation Delay   | 2.0000    |
| Pulse Width        | 0.0000    |
| Acquisition Time   | 1.3107    |
| Spectrometer Frequency | 100.58 |
| Spectral Width     | 250000.0  |
| Lowest Frequency   | -1034.6   |
| Nucleus            | 13C       |
| Acquired Size      | 32768     |
| Spectral Size      | 65516     |
| Parameter          | Value       |
|--------------------|-------------|
| Origin             | Varian      |
| Spectrometer       | Inova       |
| Solvent            | CDC13       |
| Temperature        | 20.0        |
| Pulse Sequence     | s2pul       |
| Experiment         | 1D          |
| Probe              | QUAD        |
| Number of Scans    | 240         |
| Receiver Gain      | 60          |
| Relaxation Delay   | 2.0000      |
| Pulse Width        | 6.0000      |
| Acquisition Time   | 1.0863      |
| Spectrometer Frequency | 125.66    |
| Spectral Width     | 30165.9     |
| Lowest Frequency   | -1278.9     |
| Nucleus            | 13C         |
| Acquired Size      | 32768       |
| Spectral Size      | 63536       |
| Parameter       | Value          |
|-----------------|----------------|
| Origin          | Varian         |
| Spectrometer    | Inova          |
| Solvent         | CDCl3          |
| Pulse Sequence  | s2pul          |
| Experiment      | 1D             |
| Probe           | quad94         |
| Number of Scans | 1232           |
| Receiver Gain   | 60             |
| Relaxation Delay| 2.0000         |
| Pulse Width     | 0.0000         |
| Acquisition Time| 1.3107         |
| Spectrometer Frequency | 100.58 |
| Spectral Width  | 25000.0        |
| Lowest Frequency| -1029.8        |
| Nucleus         | 13C            |
| Acquired Size   | 32768          |
| Spectral Size   | 65536          |

![NMR Spectrum](image)
| Parameter      | Value         |
|---------------|---------------|
| Origin        | Varian        |
| Spectrometer  | Inova         |
| Solvent       | CDCl3         |
| Pulse Sequence| s2pul         |
| Experiment    | 1D            |
| Probe         | QUAD          |
| Number of Scans| 128          |
| Receiver Gain | 60            |
| Relaxation Delay | 0.0000     |
| Pulse Width   | 0.0000        |
| Acquisition Time | 0.3277    |
| Spectrometer Frequency | 470.15 |
| Spectral Width | 100000.0   |
| Lowest Frequency | -79538.0 |
| Nucleus       | 19F           |
| Acquired Size | 32768         |
| Spectral Size | 65536         |
| Parameter          | Value   |
|--------------------|---------|
| Origin             | Varian  |
| Spectrometer       | inova   |
| Solvent            | CDC13   |
| Temperature        | 20.0    |
| Pulse Sequence     | s2pul   |
| Experiment         | 1D      |
| Probe              | hcn     |
| Number of Scans    | 16      |
| Receiver Gain      | 26      |
| Relaxation Delay   | 10.0000 |
| Pulse Width        | 7.0000  |
| Acquisition Time   | 4.0960  |
| Spectrometer Frequency | 500.07 |
| Spectral Width     | 8000.0  |
| Lowest Frequency   | -1518.7 |
| Nucleus            | 1H      |
| Acquired Size      | 32768   |
| Spectral Size      | 65536   |
| Parameter          | Value   |
|-------------------|---------|
| Origin            | Varian  |
| Spectrometer      | Inova   |
| Solvent           | CDCl3   |
| Temperature       | 20.0    |
| Pulse Sequence    | z2pul   |
| Experiment        | 1D      |
| Probe             | QUAD    |
| Number of Scans   | 240     |
| Receiver Gain     | 60      |
| Relaxation Delay  | 2.0000  |
| Pulse Width       | 6.0000  |
| Acquisition Time  | 1.0863  |
| Spectrometer Freq | 125.66  |
| Spectral Width    | 30165.9 |
| Lowest Frequency  | -1276.9 |
| Nucleus           | 13C     |
| Acquired Size     | 32768   |
| Spectral Size     | 65536   |

![NMR Spectrum](image)
| Parameter        | Value          |
|------------------|----------------|
| Origin           | Varian         |
| Spectrometer     | Inova          |
| Solvent          | CDCl3          |
| Temperature      | 20.0           |
| Pulse Sequence   | s2paul         |
| Experiment       | 1D             |
| Probe            | QUAD           |
| Number of Scans  | 160            |
| Receiver Gain    | 52             |
| Relaxation Delay | 0.0000         |
| Pulse Width      | 6.2500         |
| Acquisition Time | 0.3277         |
| Spectrometer Frequency | 470.15 |
| Spectral Width   | 1000000.0      |
| Lowest Frequency | -79544.1       |
| Nucleus          | 19F            |
| Acquired Size    | 32768          |
| Spectral Size    | 65536          |

![Chemical Structure](image)
| Parameter          | Value |
|--------------------|-------|
| Origin             | Varian|
| Spectrometer       | Inova |
| Solvent            | CDCl3 |
| Temperature        | 20.0  |
| Pulse Sequence     | s2pul |
| Experiment         | 1D    |
| Probe              | hcn   |
| Number of Scans    | 16    |
| Receiver Gain      | 42    |
| Relaxation Delay   | 0.0000|
| Pulse Width        | 0.0000|
| Acquisition Time   | 4.0560|
| Spectrometer Frequency | 500.07|
| Spectral Width     | 8000.0|
| Lowest Frequency   | -1520.9|
| Nucleus            | 1H    |
| Acquired Size      | 32768 |
| Spectral Size      | 65536 |
| Parameter            | Value  |
|----------------------|--------|
| Origin               | Varian |
| Spectrometer         | Inova  |
| Solvent              | CDCl3  |
| Temperature          | 29.0   |
| Pulse Sequence       | s2pul  |
| Experiment           | 1D     |
| Probe                | quad94 |
| Number of Scans      | 224    |
| Receiver Gain        | 60     |
| Relaxation Delay     | 2.0000 |
| Pulse Width          | 0.0000 |
| Acquisition Time     | 1.3107 |
| Spectrometer Frequency| 100.58 |
| Spectral Width       | 25000.0|
| Lowest Frequency     | -1026.8|
| Nucleus              | 13C    |
| Acquired Size        | 32768  |
| Spectral Size        | 65536  |
| Parameter          | Value          |
|--------------------|----------------|
| Origin             | Varian         |
| Spectrometer       | inova          |
| Solvent            | CDCl3          |
| Pulse Sequence     | x2pul          |
| Experiment         | 1D             |
| Probe              | quad94         |
| Number of Scans    | 688            |
| Receiver Gain      | 60             |
| Relaxation Delay   | 1.0000         |
| Pulse Width        | 0.0000         |
| Acquisition Time   | 1.3107         |
| Spectrometer Frequency | 100.58   |
| Spectral Width     | 25000.0        |
| Lowest Frequency   | -1029.3        |
| Nucleus            | 13C            |
| Acquired Size      | 32768          |
| Spectral Size      | 65536          |

![Chemical Structure Image]
| Parameter       | Value                                      |
|-----------------|--------------------------------------------|
| Origin          | Bruker BioSpin GmbH                        |
| Spectrometer    | spect                                      |
| Solvent         | CDCl3                                      |
| Temperature     | 298.0                                      |
| Pulse Sequence  | zgpg30                                     |
| Experiment      | 1D                                         |
| Probe           | Z127784.0002 (CP880 S0051 BBF-H-D-05 Z)    |
| Number of Scans | 768                                        |
| Receiver Gain   | 190.5                                      |
| Relaxation Delay| 2.0000                                    |
| Pulse Width     | 10.0000                                    |
| Spectrometer Frequency | 125.83                                  |
| Spectral Width  | 29761.9                                    |
| Lowest Frequency| -2288.7                                    |
| Nucleus         | 13C                                        |
| Acquired Size   | 32768                                      |
| Spectral Size   | 65536                                      |

Syn Diastereomer
| Parameter         | Value                                                |
|------------------|------------------------------------------------------|
| Origin           | Bruker BioSpin GmbH                                  |
| Spectrometer     | spect                                                |
| Solvent          | CDCl₃                                                |
| Temperature      | 298.0                                                |
| Pulse Sequence   | zg30                                                 |
| Experiment       | 1D                                                   |
| Probe            | Z127784_0002 (CP BBO 500S1 BBF-H-O-05 Z)             |
| Number of Scans  | 16                                                   |
| Receiver Gain    | 61.8                                                 |
| Relaxation Delay | 5.0000                                               |
| Pulse Width      | 12.0000                                              |
| Spectrometer Frequency | 560.35                     |
| Spectral Width   | 10000.0                                               |
| Lowest Frequency | -1922.9                                               |
| Nucleus          | 1H                                                   |
| Acquired Size    | 32768                                                 |
| Spectral Size    | 65536                                                 |

Anti diastereomer
| Parameter                  | Value                                                                 |
|----------------------------|-----------------------------------------------------------------------|
| Origin                     | Bruker BioSpin GmbH                                                   |
| 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            | 640                                                                   |
| Receiver Gain              | 190.5                                                                 |
| Relaxation Delay           | 2.0000                                                                |
| Pulse Width                | 10.0000                                                               |
| Spectrometer Frequency     | 125.83                                                                |
| Spectral Width             | 29761.9                                                               |
| Lowest Frequency           | -2283.8                                                               |
| Nucleus                    | 13C                                                                   |
| Acquired Size              | 32768                                                                 |
| Spectral Size              | 65538                                                                 |

![Chemical structure](image)

Anti Diastereomer
Parameter | Value
---|---
Origin | Bruker BioSpin GmbH
Spectrometer | spect
Solvent | CDCl3
Temperature | 298.0
Pulse Sequence | zg30
Experiment | 1D
Probe | Z127784_00002 (CP 880 50051 BBF-H-00-05 Z)
Number of Scans | 32
Receiver Gain | 29.7
Relaxation Delay | 10.0000
Pulse Width | 12.0000
Spectrometer Frequency | 500.36
Spectral Width | 10000.0
Lowest Frequency | -1922.8
Nucleus | 1H
Acquired Size | 32768
Spectral Size | 65536
| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| 1. Origin          | Bruker BioSpin GmbH                                                  |
| 2. Spectrometer    | spect                                                               |
| 3. Solvent         | CDCl3                                                                |
| 4. Temperature     | 298.0                                                               |
| 5. Pulse Sequence  | zpgg30                                                              |
| 6. Experiment      | 1D                                                                  |
| 7. Probe           | 2127784_0002 (CP BOO 50051 8BF-H-D-05 Z)                            |
| 8. Number of Scans | 512                                                                 |
| 9. Receiver Gain   | 190.5                                                               |
| 10. Relaxation Delay| 2.0000                                                              |
| 11. Pulse Width    | 10.0000                                                             |
| 12. Spectrometer Frequency | 125.83               |
| 13. Spectral Width | 31512.6                                                             |
| 14. Lowest Frequency| -1901.5                                                            |
| 15. Nucleus        | 13C                                                                 |
| 16. Acquired Size  | 32768                                                               |
| 17. Spectral Size  | 66536                                                               |

![Chemical Structure](image.png)
| Parameter          | Value      |
|--------------------|------------|
| Origin             | Varian     |
| Spectrometer       | Inova      |
| Solvent            | CDCl3      |
| Temperature        | 20.0       |
| Pulse Sequence     | s2pul      |
| Experiment         | 1D         |
| Probe              | QUAD       |
| Number of Scans    | 16         |
| Receiver Gain      | 50         |
| Relaxation Delay   | 2.00000    |
| Pulse Width        | 0.00000    |
| Acquisition Time   | 4.6645     |
| Spectrometer Frequency | 499.69   |
| Spectral Width     | 7024.9     |
| Lowest Frequency   | -1011.9    |
| Nucleus            | 1H         |
| Acquired Size      | 32768      |
| Spectral Size      | 65536      |

![NMR Spectrum](image)

-7.26 CDCl3

-1.25 Grease
Parameter | Value
---|---
1 Origin | Varian
2 Spectrometer | inova
3 Solvent | CDCl3
4 Temperature | 20.0
5 Pulse Sequence | s2pul
6 Experiment | 1D
7 Probe | QUAD
8 Number of Scans | 384
9 Receiver Gain | 60
10 Relaxation Delay | 2.0000
11 Pulse Width | 0.0000
12 Acquisition Time | 1.0863
13 Spectrometer Frequency | 125.66
14 Spectral Width | 30165.9
15 Lowest Frequency | -1260.2
16 Nucleus | 13C
17 Acquired Size | 32768
18 Spectral Size | 65536
| Parameter        | Value     |
|------------------|-----------|
| Origin           | Varian    |
| Spectrometer     | inova     |
| Solvent          | CDCl3     |
| Temperature      | 20.0      |
| Pulse Sequence   | s2pul     |
| Experiment       | 1D        |
| Probe            | QUAD      |
| Number of Scans  | 690       |
| Receiver Gain    | 60        |
| Relaxation Delay | 2.0000    |
| Pulse Width      | 0.0000    |
| Acquisition Time | 1.0863    |
| Spectrometer Frequency | 125.66 |
| Spectral Width   | 30165.9   |
| Lowest Frequency | -1260.2   |
| Nucleus          | 13C       |
| Acquired Size    | 32758     |
| Spectral Size    | 65536     |

![Chemical Structure Image](image_url)
| Parameter          | Value         |
|--------------------|---------------|
| Origin             | Varian        |
| Spectrometer       | ineva         |
| Solvent            | CDC13         |
| Temperature        | 20.0          |
| Pulse Sequence     | s2pu1         |
| Experiment         | 1D            |
| Probe              | hcn           |
| Number of Scans    | 16            |
| Receiver Gain      | 42            |
| Relaxation Delay   | 0.0000        |
| Pulse Width        | 7.0000        |
| Acquisition Time   | 4.0960        |
| Spectrometer Frequency | 500.07     |
| Spectral Width     | 8000.0        |
| Lowest Frequency   | -1521.1       |
| Nucleus            | 1H            |
| Acquired Size      | 32768         |
| Spectral Size      | 65536         |

---

![Chemical Structure](image)

-7.26 CDC13
-1.26 Crease
-0.00 TMS

---

![NMR Spectrum](image)
| Parameter       | Value                                                                 |
|-----------------|-----------------------------------------------------------------------|
| Origin          | Bruker BioSpin GmbH                                                   |
| Spectrometer    | spect                                                                |
| Solvent         | CDC13                                                                |
| Temperature     | 298.0                                                                |
| Pulse Sequence  | zapg30                                                               |
| Experiment      | 1D                                                                   |
| Probe           | Z1277745_0002 (CP BBO 50051 E8F-H-D-05 Z)                            |
| Number of Scans | 1280                                                                 |
| Receiver Gain   | 190.5                                                                |
| Relaxation Delay| 2.0000                                                               |
| Pulse Width     | 10.0000                                                              |
| Acquisition Time| 1.0398                                                               |
| Spectrometer Frequency | 125.83                 |
| Spectral Width  | 31512.6                                                              |
| Lowest Frequency| -1899.0                                                              |
| Nucleus         | 13C                                                                  |
| Acquired Size   | 32768                                                                |
| Spectral Size   | 65536                                                                |

![Chemical Structure](image)
### Parameters

| Parameter         | Value          |
|-------------------|----------------|
| Origin            | Varian         |
| Spectrometer      | Inova          |
| Solvent           | CDC13          |
| Pulse Sequence    | z2pul          |
| Experiment        | 1D             |
| Probe             | QUAD           |
| Number of Scans   | 8              |
| Receiver Gain     | 40             |
| Relaxation Delay  | 0.0000         |
| Pulse Width       | 0.0000         |
| Acquisition Time  | 4.6645         |
| Spectrometer Frequency | 499.69          |
| Spectral Width    | 7024.9         |
| Lowest Frequency  | -1021.4        |
| Nucleus           | 1H             |
| Acquired Size     | 32768          |
| Spectral Size     | 65536          |
| Parameter          | Value         |
|--------------------|---------------|
| Origin             | Varian        |
| Spectrometer       | Inova         |
| Solvent            | CDCl3         |
| Pulse Sequence     | s2pul         |
| Experiment         | 1D            |
| Probe              | quad94        |
| Number of Scans    | 1072          |
| Receiver Gain      | 60            |
| Relaxation Delay   | 1.0000        |
| Pulse Width        | 0.0000        |
| Acquisition Time   | 1.3107        |
| Spectrometer Frequency | 100.58      |
| Spectral Width     | 25000.0       |
| Lowest Frequency   | -1027.8       |
| Nucleus            | 13C           |
| Acquired Size      | 32768         |
| Spectral Size      | 65536         |
| Parameter       | Value          |
|-----------------|----------------|
| Origin          | Varian         |
| Spectrometer    | inova          |
| Solvent         | CDCl3          |
| Pulse Sequence  | s2pul          |
| Experiment      | 1D             |
| Probe           | QUAD           |
| Number of Scans | 128            |
| Receiver Gain   | 60             |
| Relaxation Delay| 0.0000         |
| Pulse Width     | 0.0000         |
| Acquisition Time| 0.3277         |
| Spectrometer Frequency | 470.15         |
| Spectral Width  | 1000000.0      |
| Lowest Frequency| -79538.0       |
| Nucleus         | 19F            |
| Acquired Size   | 32768          |
| Spectral Size   | 65536          |
| Parameter                  | Value                                                            |
|----------------------------|------------------------------------------------------------------|
| Origin                     | Bruker BioSpin GmbH                                              |
| Spectrometer               | spect                                                            |
| Solvent                    | CDC13                                                            |
| Temperature                | 298.0                                                           |
| Pulse Sequence             | zg30                                                             |
| Experiment                 | 1D                                                               |
| Probe                      | Z127784_00052 (CP BBO 50091 BBF-H-D-05 2)                       |
| Number of Scans            | 16                                                               |
| Receiver Gain              | 55.0                                                             |
| Relaxation Delay           | 10.0000                                                         |
| Pulse Width                | 12.0000                                                         |
| Spectrometer Frequency     | 500.35                                                           |
| Spectral Width             | 10000.0                                                         |
| Lowest Frequency           | -1922.8                                                          |
| Nucleus                    | 1H                                                               |
| Acquired Size              | 32768                                                            |
| Spectral Size              | 65536                                                            |

![NMR Spectrum](image)

![Chemical Structure](image)
| Parameter       | Value                                                                 |
|-----------------|----------------------------------------------------------------------|
| Origin          | Bruker BioSpin GmbH                                                   |
| Spectrometer    | spect                                                                |
| Solvent         | CDCl₃                                                                |
| Temperature     | 298.0                                                                |
| Pulse Sequence  | zgflip                                                               |
| Experiment      | 1D                                                                   |
| Probe           | Z127784_0,0002 (CP BBD 50051 BFF-D-05 Z)                              |
| Number of Scans | 128                                                                  |
| Receiver Gain   | 190.5                                                                |
| Relaxation Delay| 1.0000                                                               |
| Pulse Width     | 15.0000                                                              |
| Spectrometer Frequency | 470.75                  |
| Spectral Width  | 113636.4                                                             |
| Lowest Frequency| -103898.1                                                            |
| Nucleus         | 19F                                                                  |
| Acquired Size   | 65536                                                                |
| Spectral Size   | 131072                                                               |

[Chemical structure image]

f1 (ppm): -200 to 244
| Parameter       | Value         |
|-----------------|---------------|
| Origin          | Varian        |
| Spectrometer    | Inova         |
| Solvent         | DMSO          |
| Temperature     | 20.0          |
| Pulse Sequence  | s2pal         |
| Experiment      | 1D            |
| Probe           | hcn           |
| Number of Scans | 16            |
| Receiver Gain   | 28            |
| Relaxation Delay| 0.00000       |
| Pulse Width     | 7.00000       |
| Acquisition Time| 4.0960        |
| Spectrometer Frequency | 500.07 |
| Spectral Width  | 8000.0        |
| Lowest Frequency| -1498.1       |
| Nucleus         | 1H            |
| Acquired Size   | 32768         |
| Spectral Size   | 65516         |

![Chemical Structure](image)

-3.34 H2O  -2.50 DMSO-d6  -1.23 Grease  -0.85 Grease

Plot of 1D NMR spectrum with chemical shifts labeled.
| Parameter       | Value                  |
|-----------------|------------------------|
| 1 Origin        | Varian                 |
| 2 Spectrometer  | inova                  |
| 3 Solvent       | DMSO                   |
| 4 Temperature   | 20.0                   |
| 5 Pulse Sequence| s2pul                  |
| 6 Experiment    | 1D                     |
| 7 Probe         | QUAD                   |
| 8 Number of Scans| 352                   |
| 9 Receiver Gain | 60                     |
| 10 Relaxation Delay| 2.0000               |
| 11 Pulse Width  | 6.0000                 |
| 12 Acquisition Time| 1.0863                |
| 13 Spectrometer Frequency | 125.66         |
| 14 Spectral Width| 30165.9               |
| 15 Lowest Frequency | -1346.2              |
| 16 Nucleus      | 13C                    |
| 17 Acquired Size| 32768                  |
| 18 Spectral Size| 63336                  |
| Parameter            | Value  |
|----------------------|--------|
| Origin               | Varian |
| Spectrometer         | inova  |
| Solvent              | CDCl3  |
| Temperature          | 29.0   |
| Pulse Sequence       | s2pul  |
| Experiment           | 1D     |
| Probe                | hcn    |
| Number of Scans      | 16     |
| Receiver Gain        | 26     |
| Relaxation Delay     | 5.0000 |
| Pulse Width          | 7.0000 |
| Acquisition Time     | 4.0960 |
| Spectrometer Frequency| 500.07 |
| Spectral Width       | 8000.0 |
| Lowest Frequency     | -1520.9|
| Nucleus              | 1H     |
| Acquired Size        | 32768  |
| Spectral Size        | 65536  |

![NMR Spectroscopy Graph](image)
| Parameter      | Value          |
|---------------|---------------|
| Origin        | Varian        |
| Spectrometer  | Innova        |
| Solvent       | CDCl3         |
| Temperature   | 22.0          |
| Pulse Sequence| s2pul         |
| Experiment    | 1D            |
| Probe         | QUAD          |
| Number of Scans| 304          |
| Receiver Gain | 60            |
| Relaxation Delay| 2.00000      |
| Pulse Width   | 6.00000       |
| Acquisition Time| 1.0863       |
| Spectrometer Frequency| 125.66     |
| Spectral Width | 30165.9     |
| Lowest Frequency | -1279.2    |
| Nucleus       | 13C           |
| Acquired Size | 32768         |
| Spectral Size | 65536         |
| Parameter          | Value          |
|--------------------|----------------|
| Origin             | Varian         |
| Spectrometer       | Inova          |
| Solvent            | CDCl3          |
| Pulse Sequence     | s2pul          |
| Experiment         | 1D             |
| Probe              | QUAD           |
| Number of Scans    | 502            |
| Receiver Gain      | 60             |
| Relaxation Delay   | 2.0000         |
| Pulse Width        | 0.0000         |
| Acquisition Time   | 1.0863         |
| Spectrometer Frequency | 125.66  |
| Spectral Width     | 30185.9        |
| Lowest Frequency   | -1260.2        |
| Nucleus            | 13C            |
| Acquired Size      | 32768          |
| Spectral Size      | 65536          |
| Parameter    | Value |
|--------------|-------|
| Origin       | Bruker BioSpin GmbH |
| Spectrometer | spec  |
| Solvent      | CDCl3 |
| Temperature  | 298.0 |
| Pulse Sequence | zgpg30 |
| Experiment   | 1D    |
| Probe        | Z127784_0002 (CP BBO 500ST 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 | -2292.7 |
| Nucleus      | 13C   |
| Acquired Size | 32768 |
| Spectral Size | 65536 |

![Chemical Structure Image](attachment:image.png)
| Parameter     | Value |
|--------------|-------|
| Origin       | Varian |
| Spectrometer | Inova  |
| Solvent      | CDCl3  |
| Temperature  | 20.0   |
| Pulse Sequence | z2pul |
| Experiment   | 1D     |
| Probe        | QUAD   |
| Number of Scans | 16    |
| Receiver Gain | 54    |
| Relaxation Delay | 5.0000 |
| Pulse Width  | 6.5000 |
| Acquisition Time | 4.6645 |
| Spectrometer Frequency | 599.69 |
| Spectral Width | 7024.9 |
| Lowest Frequency | -1022.7 |
| Nucleus      | 1H     |
| Acquired Size | 32768  |
| Spectral Size | 65536  |
| Parameter      | Value |
|---------------|-------|
| Origin        | Varian|
| Spectrometer  | Inova |
| Solvent       | CDCl3 |
| Temperature   | 20.0  |
| Pulse Sequence| z2pul |
| Experiment    | 3D    |
| Probe         | QUAD  |
| Number of Scans| 544  |
| Receiver Gain | 60    |
| Relaxation Delay| 2.0000|
| Pulse Width   | 6.0000|
| Acquisition Time| 1.0863|
| Spectrometer Frequency| 125.66|
| Spectral Width | 30163.9 |
| Lowest Frequency | -1274.1 |
| Nucleus       | 13C   |
| Acquired Size | 32768 |
| Spectral Size | 65536 |

![NMR Spectrum](image)
Parameter | Value
--- | ---
1 Origin | Varian
2 Spectrometer | ineva
3 Solvent | CDCl3
4 Temperature | 20.0
5 Pulse Sequence | s2pul
6 Experiment | 1D
7 Probe | QUAD
8 Number of Scans | 16
9 Receiver Gain | 60
10 Relaxation Delay | 5.0000
11 Pulse Width | 6.5000
12 Acquisition Time | 4.6645
13 Spectrometer Frequency | 499.69
14 Spectral Width | 7024.9
15 Lowest Frequency | −1022.5
16 Nucleus | 1H
17 Acquired Size | 32768
18 Spectral Size | 65536
| Parameter        | Value                                                                 |
|------------------|----------------------------------------------------------------------|
| Origin           | Bruker BioSpin GmbH                                                   |
| Spectrometer     | spect                                                                |
| Solvent          | CDC/3                                                                |
| Temperature      | 298.0                                                                |
| Pulse Sequence   | zgpp30                                                               |
| Experiment       | 1D                                                                   |
| Probe            | Z127794_0002 (CP BBO 50051 88F-H-D-05 Z)                             |
| Number of Scans  | 2560                                                                 |
| Receiver Gain    | 190.5                                                                |
| Relaxation Delay | 2.0000                                                               |
| Pulse Width      | 10.0000                                                              |
| Acquisition Time | 1.1010                                                               |
| Spectrometer Frequency | 125.83                  |
| Spectral Width   | 29761.9                                                             |
| Lowest Frequency | -2264.2                                                              |
| Nucleus          | 13C                                                                  |
| Acquired Size    | 32768                                                                |
| Spectral Size    | 65536                                                                |

![Chemical Structure Image]
| Parameter       | Value          |
|-----------------|----------------|
| Origin          | Varian         |
| Spectrometer    | Inova          |
| Solvent         | CDCl3          |
| Temperature     | 20.0           |
| Pulse Sequence  | s2pul          |
| Experiment      | 1D             |
| Probe           | hcn            |
| Number of Scans | 16             |
| Receiver Gain   | 32             |
| Relaxation Delay| 10.0000        |
| Pulse Width     | 7.0000         |
| Acquisition Time| 4.0960         |
| Spectrometer Frequency | 500.07       |
| Spectral Width  | 8000.0         |
| Lowest Frequency| -1521.4        |
| Nucleus         | 1H             |
| Acquired Size   | 32768          |
| Spectral Size   | 65536          |

![Chemical Structure](image)
| Parameter          | Value                                      |
|--------------------|--------------------------------------------|
| Origin             | Bruker BioSpin GmbH                        |
| Spectrometer       | spect                                      |
| Solvent            | CDCl3                                      |
| Temperature        | 298.0                                      |
| Pulse Sequence     | zgpa30                                     |
| Experiment         | 1D                                         |
| Probe              | 2127764_0002 (CP 880 50056 88F-H-D-D-S Z) |
| Number of Scans    | 1280                                       |
| Receiver Gain      | 190.5                                      |
| Relaxation Delay   | 2.0000                                    |
| Pulse Width        | 10.0000                                    |
| Acquisition Time   | 1.0398                                     |
| Spectrometer Frequency | 125.83                                    |
| Spectral Width     | 31512.6                                    |
| Lowest Frequency   | -1899.4                                    |
| Nucleus            | 13C                                        |
| Acquired Size      | 32768                                      |
| Spectral Size      | 65536                                      |
| Parameter          | Value                                      |
|--------------------|--------------------------------------------|
| Origin             | Bruker BioSpin GmbH                        |
| Spectrometer       | spect                                      |
| Solvent            | CDC13                                      |
| Temperature        | 298.0                                      |
| Pulse Sequence     | zg30                                       |
| Experiment         | 1D                                         |
| Probe              | Z127784_0002 (CP BBO S051 BBF-H-D-05 Z)   |
| Number of Scans    | 16                                         |
| Receiver Gain      | 62                                         |
| Relaxation Delay   | 1.0000                                     |
| Pulse Width        | 12.0000                                    |
| Acquisition Time   | 3.2768                                     |
| Spectrometer Frequency | 500.35                                    |
| Spectral Width     | 10000.0                                    |
| Lowest Frequency   | -1910.3                                    |
| Nucleus            | 1H                                         |
| Acquired Size      | 32768                                      |
| Spectral Size      | 65536                                      |

![NMR Spectrum](attachment:image)
| Parameter            | Value                                                                 |
|----------------------|----------------------------------------------------------------------|
| 1 Origin             | Bruker BioSpin GmbH                                                  |
| 2 Spectrometer       | spect                                                                |
| 3 Solvent            | CDCl3                                                                |
| 4 Temperature        | 298.0                                                                |
| 5 Pulse Sequence     | zgpg30                                                               |
| 6 Experiment         | 1D                                                                   |
| 7 Probe              | Z127784_0002 (CP 880 50051 88f-H-D-05 Z)                             |
| 8 Number of Scans    | 256                                                                  |
| 9 Receiver Gain      | 191                                                                  |
| 10 Relaxation Delay  | 2.0000                                                               |
| 11 Pulse Width       | 10.0000                                                              |
| 12 Acquisition Time  | 1.0398                                                               |
| 13 Spectrometer Frequency | 125.83                                                           |
| 14 Spectral Width    | 31512.6                                                              |
| 15 Lowest Frequency  | -1916.9                                                              |
| 16 nucleus           | 13C                                                                  |
| 17 Acquired Size     | 32768                                                                |
| 18 Spectral Size     | 65536                                                                |
| Parameter         | Value                                      |
|-------------------|--------------------------------------------|
| Origin            | Bruker BioSpin GmbH                         |
| Spectrometer      | spect                                      |
| Solvent           | CDCl3                                      |
| Temperature       | 298.0                                      |
| Pulse Sequence    | zgfpn                                      |
| Experiment        | 1D                                         |
| Probe             | Z127784_0002 (CP 880 50051 BBB-H-D-05 Z)    |
| Number of Scans   | 16                                         |
| Receiver Gain     | 191                                        |
| Relaxation Delay  | 1.0000                                    |
| Pulse Width       | 15.0000                                    |
| Acquisition Time  | 0.5767                                     |
| 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             | Bruker BioSpin GmbH                        |
| Spectrometer       | spect                                      |
| Solvent            | CDCl3                                      |
| Temperature        | 298.0                                      |
| Pulse Sequence     | zg10                                       |
| Experiment         | 1D                                         |
| Probe              | Z127784_0002 (CP BBO 500S1 BBF-H-D-03 Z)   |
| Number of Scans    | 16                                         |
| Receiver Gain      | 69                                         |
| Relaxation Delay   | 1.0000                                     |
| Pulse Width        | 12.0000                                    |
| Acquisition Time   | 3.2768                                     |
| Spectrometer Frequency | 500.35                                   |
| Spectral Width     | 10000.0                                    |
| Lowest Frequency   | -1910.3                                    |
| Nucleus            | 1H                                         |
| Acquired Size      | 32768                                      |
| Spectral Size      | 65536                                      |

![Chemical structure image](image)
| Parameter          | Value          |
|-------------------|----------------|
| Origin            | Varian         |
| Spectrometer      | inova          |
| Solvent           | CDCl₃          |
| Temperature       | 20.0           |
| Pulse Sequence    | s2pul          |
| Experiment        | 1D             |
| Probe             | QUAD           |
| Number of Scans   | 16             |
| Receiver Gain     | 50             |
| Relaxation Delay  | 0.0000         |
| Pulse Width       | 6.5000         |
| Acquisition Time  | 4.6645         |
| Spectrometer Frequency | 499.69     |
| Spectral Width    | 7024.9         |
| Lowest Frequency  | -1022.2        |
| Nucleus           | 1H             |
| Acquired Size     | 32768          |
| Spectral Size     | 65536          |
| Parameter            | Value                  |
|----------------------|------------------------|
| Origin               | Varian                 |
| Spectrometer         | inova                  |
| Solvent              | CDCl₃                  |
| Temperature          | 20.0                   |
| Pulse Sequence       | s2pul                  |
| Experiment           | 1D                     |
| Probe                | QUAD                   |
| Number of Scans      | 160                    |
| Receiver Gain        | 60                     |
| Relaxation Delay     | 2.00000                |
| Pulse Width          | 6.00000                |
| Acquisition Time     | 1.0863                 |
| Spectrometer Frequency| 125.66                |
| Spectral Width       | 30165.9                |
| Lowest Frequency     | -1275.4                |
| Nucleus              | 13C                    |
| Acquired Size        | 32768                  |
| Spectral Size        | 65536                  |
| Parameter      | Value                                                                 |
|----------------|-----------------------------------------------------------------------|
| Origin         | Bruker BioSpin GmbH                                                   |
| Spectrometer   | spect                                                                |
| Solvent        | CDC13                                                                 |
| Temperature    | 298.0                                                                |
| Pulse Sequence | zg30                                                                  |
| Experiment     | 1D                                                                   |
| Probe          | Z127784_0002 (CP 800S1 BBF-N-D-05 Z)                                  |
| Number of Scans| 16                                                                    |
| Receiver Gain  | 94                                                                    |
| Relaxation Delay| 1.0000                                                              |
| Pulse Width    | 12.0000                                                              |
| Acquisition Time| 3.2768                                                             |
| Spectrometer Frequency | 500.35              |
| Spectral Width | 10000.0                                                              |
| Lowest Frequency| –1910.3                                                             |
| Nucleus        | 1H                                                                   |
| Acquired Size  | 32768                                                                |
| Spectral Size  | 65536                                                                |

![NMR Spectrum](image)
| Parameter       | Value                                      |
|-----------------|--------------------------------------------|
| Origin          | Bruker BioSpin GmbH                         |
| Spectrometer    | spect                                      |
| Solvent         | CDCl3                                      |
| Temperature     | 298.0                                      |
| Pulse Sequence  | zgpg3D                                     |
| Experiment      | 1D                                         |
| Probe           | Z1277844_0002 (CP BN 50051 BBF-H-D-05 Z)   |
| Number of Scans | 256                                        |
| Receiver Gain   | 191                                        |
| Relaxation Delay| 2.0000                                     |
| Pulse Width     | 10.0000                                    |
| Acquisition Time| 1.0398                                     |
| Spectrometer Frequency | 125.83                             |
| Spectral Width  | 31512.6                                    |
| Lowest Frequency| -1916.9                                    |
| Nucleus         | 13C                                        |
| Acquired Size   | 32768                                      |
| Spectral Size   | 65536                                      |

![](image)
| Parameter       | Value          |
|-----------------|----------------|
| Origin          | Varian         |
| Spectrometer    | inova          |
| Solvent         | CDCl3          |
| Temperature     | 36.0           |
| Pulse Sequence  | s2pul          |
| Experiment      | 1D             |
| Probe           | quad94         |
| Number of Scans | 8              |
| Receiver Gain   | 54             |
| Relaxation Delay| 1.0000         |
| Pulse Width     | 0.0000         |
| Acquisition Time| 4.0960         |
| Spectrometer Frequency | 399.95 |
| Spectral Width  | 8000.0         |
| Lowest Frequency| -2424.5        |
| Nucleus         | 1H             |
| Acquired Size   | 32768          |
| Spectral Size   | 65536          |
| Parameter   | Value                                                                 |
|-------------|-----------------------------------------------------------------------|
| Origin      | Bruker BioSpin Corp.                                                  |
| 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 | 32                                                                  |
| Receiver Gain | 28                                                                  |
| Relaxation Delay | 2.0000                                                                |
| Pulse Width | 12.0000                                                              |
| Acquisition Time | 3.2768                                                             |
| Spectrometer Frequency | 500.35                                              |
| Spectral Width | 10000.0                                                          |
| Lowest Frequency | -1910.3                                                             |
| Nucleus     | 1H                                                                   |
| Acquired Size | 32768                                                                |
| Spectral Size | 65536                                                              |

![Chemical Structure](image-url)
| Parameter   | Value                                                                 |
|------------|----------------------------------------------------------------------|
| Origin     | Bruker BioSpin Gmbh                                                 |
| Spectrometer| spect                                                               |
| Solvent    | CDC13                                                               |
| Temperature| 298.0                                                               |
| Pulse Sequence | zggg10                                                            |
| Experiment | 1D                                                                  |
| Probe      | Z127784_0002 (CP BBO SD051 BBF-H-D-05 2)                            |
| Number of Scans | 256                                                                |
| Receiver Gain | 30                                                                |
| Relaxation Delay | 2.00000                                                              |
| Pulse Width | 10.00000                                                           |
| Acquisition Time | 1.0398                                                               |
| Spectrometer Frequency | 125.83                                                             |
| Spectral Width | 31512.6                                                              |
| Lowest Frequency | -1916.9                                                              |
| Nucleus    | 13C                                                                |
| Acquired Size | 32768                                                              |
| Spectral Size | 65536                                                              |

![NMR spectrum graph](image-url)
Parameter | Value
--- | ---
Origin | Varian
Spectrometer | ineova
Solvent | CDC13
Temperature | 20.0
Pulse Sequence | s2pul
Experiment | 1D
Probe | quad94
Number of Scans | 16
Receiver Gain | 36
Relaxation Delay | 0.0000
Pulse Width | 0.0000
Acquisition Time | 4.0960
Spectrometer Frequency | 199.95
Spectral Width | 8000.0
Lowest Frequency | ~2425.0
Nucleus | 1H
Acquired Size | 32768
Spectral Size | 65536
| Parameter          | Value       |
|--------------------|-------------|
| Origin             | Varian      |
| Spectrometer       | inova       |
| Solvent            | CDCl3       |
| Temperature        | 20.0        |
| Pulse Sequence     | s2pul       |
| Experiment         | 1D          |
| Probe              | quad94      |
| Number of Scans    | 48          |
| Receiver Gain      | 60          |
| Relaxation Delay   | 2.0000      |
| Pulse Width        | 0.0000      |
| Acquisition Time   | 1.3107      |
| Spectrometer Frequency | 100.58   |
| Spectral Width     | 25000.0     |
| Lowest Frequency   | -1036.7     |
| Nucleus            | 13C         |
| Acquired Size      | 32768       |
| Spectral Size      | 65536       |
Parameter | Value
--- | ---
Origin | Varian
Spectrometer | Inova
Solvent | CDC13
Temperature | 20.0
Pulse Sequence | z2pul
Experiment | 1D
Probe | quad94
Number of Scans | 16
Receiver Gain | 52
Relaxation Delay | 0.0000
Pulse Width | 0.0000
Acquisition Time | 4.0960
Spectrometer Frequency | 399.95
Spectral Width | 8000.0
Lowest Frequency | -2424.3
Nucleus | 1H
Acquired Size | 32768
Spectral Size | 65536
| Parameter        | Value         |
|------------------|---------------|
| Origin           | Varian        |
| Spectrometer     | Inova         |
| Solvent          | CDCl3         |
| Temperature      | 20.0          |
| Pulse Sequence   | s2pul         |
| Experiment       | 1D            |
| Probe            | QUAD          |
| Number of Scans  | 96            |
| Receiver Gain    | 60            |
| Relaxation Delay | 2.0000        |
| Pulse Width      | 6.0000        |
| Acquisition Time | 1.0863        |
| Spectrometer Frequency | 125.66 |
| Spectral Width   | 30165.9       |
| Lowest Frequency | -1279.3       |
| Nucleus          | 13C           |
| Acquired Size    | 32768         |
| Spectral Size    | 65336         |

![Chemical structure image]
| Parameter            | Value       |
|----------------------|-------------|
| Origin               | Varian      |
| Spectrometer         | Inova       |
| Solvent              | CDCl3       |
| Temperature          | 29.0        |
| Pulse Sequence       | s2pul       |
| Experiment           | 1D          |
| Probe                | quad94      |
| Number of Scans      | 112         |
| Receiver Gain        | 60          |
| Relaxation Delay     | 2.0000      |
| Pulse Width          | 0.0000      |
| Acquisition Time     | 1.1107      |
| Spectrometer Frequency| 100.58      |
| Spectral Width       | 25000.0     |
| Lowest Frequency     | -1030.4     |
| Nucleus              | 13C         |
| Acquired Size        | 32768       |
| Spectral Size        | 65536       |
| Parameter          | Value                  |
|--------------------|------------------------|
| Origin             | Varian                 |
| Spectrometer       | Inova                  |
| Solvent            | CD3CN                  |
| Temperature        | 20.0                   |
| Pulse Sequence     | s2pul                  |
| Experiment         | 1D                     |
| Probe              | QUAD                   |
| Number of Scans    | 16                     |
| Receiver Gain      | 44                     |
| Relaxation Delay   | 0.0000                 |
| Pulse Width        | 0.0000                 |
| Acquisition Time   | 4.6645                 |
| Spectrometer Frequency | 499.70                |
| Spectral Width     | 7024.9                 |
| Lowest Frequency   | -1024.2                |
| Nucleus            | 1H                     |
| Acquired Size      | 32768                  |
| Spectral Size      | 65536                  |
| Parameter           | Value       |
|---------------------|-------------|
| Origin              | Varian      |
| Spectrometer        | Inova       |
| Solvent             | CD3CN       |
| Temperature         | 20.0        |
| Pulse Sequence      | s2pul       |
| Experiment          | 1D          |
| Probe               | QUAD        |
| Number of Scans     | 192         |
| Receiver Gain       | 60          |
| Relaxation Delay    | 0.0000      |
| Pulse Width         | 0.0000      |
| Acquisition Time    | 1.0863      |
| Spectrometer Frequency | 125.66  |
| Spectral Width      | 30165.9     |
| Lowest Frequency    | -1176.7     |
| Nucleus             | 13C         |
| Acquired Size       | 32768       |
| Spectral Size       | 65536       |

![Chemical Structure](image1.png)
| Parameter          | Value       |
|--------------------|-------------|
| Origin             | Varian      |
| Spectrometer       | Inova       |
| Solvent            | CDC13       |
| Temperature        | 20.0        |
| Pulse Sequence     | s2pul       |
| Experiment         | 1D          |
| Probe              | QUAD        |
| Number of Scans    | 32          |
| Receiver Gain      | 52          |
| Relaxation Delay   | 0.0000      |
| Pulse Width        | 0.0000      |
| Acquisition Time   | 0.3277      |
| Spectrometer Frequency | 470.15  |
| Spectral Width     | 1000000.0   |
| Lowest Frequency   | -79341.0    |
| Nucleus            | 19F         |
| Acquired Size      | 32768       |
| Spectral Size      | 65536       |
| Parameter         | Value          |
|-------------------|----------------|
| Origin            | Varian         |
| Spectrometer      | inova          |
| Solvent           | CDCl3          |
| Temperature       | 20.0           |
| Pulse Sequence    | s2pul          |
| Experiment        | 1D             |
| Probe             | QUAD           |
| Number of Scans   | 16             |
| Receiver Gain     | 60             |
| Relaxation Delay  | 0.0000         |
| Pulse Width       | 0.0000         |
| Acquisition Time  | 4.6645         |
| Spectrometer Frequency | 499.69 |
| Spectral Width    | 7024.9         |
| Lowest Frequency  | -1021.9        |
| Nucleus           | 1H             |
| Acquired Size     | 32768          |
| Spectral Size     | 65536          |

-7.26 CDC3

[Chemical structure image]
| Parameter          | Value               |
|--------------------|---------------------|
| Origin             | Varian              |
| Spectrometer       | inova               |
| Solvent            | CDCl₃               |
| Temperature        | 20.0                |
| Pulse Sequence     | s2pul               |
| Experiment         | 1D                  |
| Probe              | quad94              |
| Number of Scans    | 48                  |
| Receiver Gain      | 60                  |
| Relaxation Delay   | 2.0000              |
| Pulse Width        | 0.0000              |
| Acquisition Time   | 1.3107              |
| Spectrometer Frequency | 100.58          |
| Spectral Width     | 250000.0            |
| Lowest Frequency   | -1027.8             |
| Nucleus            | 13C                 |
| Acquired Size      | 32768               |
| Spectral Size      | 65536               |

- 77.16 CDCl₃

![Chemical Structure Image]
| Parameter        | Value |
|------------------|-------|
| Origin           | Varian|
| Spectrometer     | inova |
| Solvent          | CDCl3 |
| Temperature      | 20.0  |
| Pulse Sequence   | s2psl |
| Experiment       | 1D    |
| Probe            | QUAD  |
| Number of Scans  | 16    |
| Receiver Gain    | 46    |
| Relaxation Delay | 5.0000|
| Pulse Width      | 6.5000|
| Acquisition Time | 4.6645|
| Spectrometer Frequency | 499.69 |
| Spectral Width   | 7024.9|
| Lowest Frequency | -1022.7|
| Nucleus          | 1H    |
| Acquired Size    | 32768 |
| Spectral Size    | 65536 |
| Parameter                  | Value          |
|----------------------------|----------------|
| Origin                     | Varian         |
| Spectrometer               | Innova         |
| Solvent                    | CDCl3          |
| Temperature                | 20.0           |
| Pulse Sequence             | s2pul          |
| Experiment                 | 1D             |
| Probe                      | QUAD           |
| Number of Scans            | 328            |
| Receiver Gain              | 60             |
| Relaxation Delay           | 2.0000         |
| Pulse Width                | 6.0000         |
| Acquisition Time           | 1.0863         |
| Spectrometer Frequency     | 125.66         |
| Spectral Width             | 30165.9        |
| Lowest Frequency           | -1278.2        |
| Nucleus                    | 13C            |
| Acquired Size              | 32768          |
| Spectral Size              | 65536          |
| Parameter       | Value    |
|-----------------|----------|
| Origin          | Varian   |
| Spectrometer    | inova    |
| Solvent         | CDCl3    |
| Pulse Sequence  | z2pul    |
| Experiment      | 1D       |
| Probe           | quad94   |
| Number of Scans | 8        |
| Receiver Gain   | 52       |
| Relaxation Delay| 0.0000   |
| Pulse Width     | 0.0000   |
| Acquisition Time| 4.0960   |
| Spectrometer Frequency | 399.95    |
| Spectral Width  | 8000.0   |
| Lowest Frequency| -2424.5  |
| Nucleus         | 1H       |
| Acquired Size   | 32768    |
| Spectral Size   | 65536    |
| Parameter      | Value       |
|----------------|-------------|
| Origin         | Varian      |
| Spectrometer   | Inova       |
| Solvent        | CDC13       |
| Temperature    | 20.0        |
| Pulse Sequence | s2pul       |
| Experiment     | 1D          |
| Probe          | quadbp      |
| Number of Scans| 16          |
| Receiver Gain  | 54          |
| Relaxation Delay | 0.0000   |
| Pulse Width    | 5.8250      |
| Acquisition Time | 4.0960   |
| Spectrometer Frequency | 399.74    |
| Spectral Width | 8000.0      |
| Lowest Frequency | -2428.2  |
| Nucleus        | 1H          |
| Acquired Size  | 32768       |
| Spectral Size  | 65536       |
| Parameter        | Value  |
|------------------|--------|
| Origin           | Varian |
| Spectrometer     | Inova  |
| Solvent          | CDC13  |
| Temperature      | 20.0   |
| Pulse Sequence   | s2pul  |
| Experiment       | 1D     |
| Probe            | quad94 |
| Number of Scans  | 688    |
| Receiver Gain    | 60     |
| Relaxation Delay | 2.0000 |
| Pulse Width      | 0.0000 |
| Acquisition Time | 1.3107 |
| Spectrometer Frequency | 100.58 |
| Spectral Width   | 25000.0|
| Lowest Frequency | -1026.5|
| Nucleus          | 13C    |
| Acquired Size    | 32768  |
| Spectral Size    | 65536  |
| Parameter       | Value  |
|-----------------|--------|
| Origin          | Varian |
| Spectrometer    | Inova  |
| Solvent         | CDCl3  |
| Pulse Sequence  | t2pul  |
| Experiment      | 1D     |
| Probe           | QUAD   |
| Number of Scans | 48     |
| Receiver Gain   | 60     |
| Relaxation Delay| 2.0000 |
| Pulse Width     | 0.0000 |
| Acquisition Time| 1.0863 |
| Spectrometer Frequency | 125.66 |
| Spectral Width  | 30165.9 |
| Lowest Frequency| -1285.2 |
| Nucleus         | 13C    |
| Acquired Size   | 32768  |
| Spectral Size   | 65536  |

2-propanol
### Parameter Table

| Parameter   | Value       |
|-------------|-------------|
| Origin      | Varian      |
| Spectrometer| inova       |
| Solvent     | CDCl3       |
| Pulse Sequence | s2pul       |
| Experiment  | 1D          |
| Probe       | QUAD        |
| Number of Scans | 4           |
| Receiver Gain | 41          |
| Relaxation Delay | 2.00000     |
| Pulse Width | 0.00000     |
| Acquisition Time | 4.6645      |
| Spectrometer Frequency | 499.69      |
| Spectral Width | 7024.9      |
| Lowest Frequency | -1021.4     |
| Nucleus     | 1H          |
| Acquired Size | 32768       |
| Spectral Size | 65536       |

**Dichloromethane**
Parameter | Value
---|---
1. Origin | Varian
2. Spectrometer | Inova
3. Solvent | CDC13
4. Pulse Sequence | szpul
5. Experiment | 1D
6. Probe | QUAD
7. Number of Scans | 8
8. Receiver Gain | 41
9. Relaxation Delay | 0.0000
10. Pulse Width | 0.0000
11. Acquisition Time | 4.6645
12. Spectrometer Frequency | 499.69
13. Spectral Width | 7024.9
14. Lowest Frequency | -1021.4
15. Nucleus | 1H
16. Acquired Size | 32768
17. Spectral Size | 65536
| Parameter       | Value          |
|-----------------|----------------|
| Origin          | Varian         |
| Spectrometer    | evoa           |
| Solvent         | CDCl3          |
| Pulse Sequence  | s2pul          |
| Experiment      | 1D             |
| Probe           | QUAD           |
| Number of Scans | 96             |
| Receiver Gain   | 60             |
| Relaxation Delay| 1.0000         |
| Pulse Width     | 0.0000         |
| Acquisition Time| 1.0863         |
| Spectrometer Frequency | 125.66     |
| Spectral Width  | 30165.9        |
| Lowest Frequency| -1277.3        |
| Nucleus         | 13C            |
| Acquired Size   | 32768          |
| Spectral Size   | 65536          |

\[ 77.2 \text{ CDCl3} \]
| Parameter               | Value                                                                 |
|------------------------|----------------------------------------------------------------------|
| Origin                 | Bruker BioSpin GmbH                                                   |
| Spectrometer           | spect                                                                |
| Solvent                | CDCl3                                                                |
| Temperature            | 298.0                                                                |
| Pulse Sequence         | zg30                                                                 |
| Experiment             | 1D                                                                   |
| Probe                  | Z127784_0002 (CP BBO 500S1 88F-H-D-05 Z)                             |
| Number of Scans        | 16                                                                   |
| Receiver Gain          | 191                                                                  |
| Relaxation Delay       | 2.0000                                                               |
| Pulse Width            | 12.0000                                                              |
| Acquisition Time       | 3.2768                                                               |
| Spectrometer Frequency | 500.35                                                               |
| Spectral Width         | 10000.0                                                               |
| Lowest Frequency       | -1922.8                                                              |
| Nucleus                | 1H                                                                   |
| Acquired Size          | 32768                                                                |
| Spectral Size          | 65536                                                                |

![NMR Spectrogram](image)
| Parameter         | Value |
|-------------------|-------|
| Origin            | Bruker BioSpin GmbH |
| Spectrometer      | spect |
| Solvent           | CDCl3 |
| Temperature       | 298.0 |
| Pulse Sequence    | zgpg30 |
| Experiment        | 1D    |
| Probe             | Z127784_0002 (CP BBO 500S1 EBF-H-D-05 Z) |
| Number of Scans   | 256   |
| Receiver Gain     | 191   |
| Relaxation Delay  | 2.0000|
| Pulse Width       | 10.0000|
| Acquisition Time  | 1.0398|
| Spectrometer Frequency | 125.83 |
| Spectral Width    | 31512.6|
| Lowest Frequency  | -1900.0|
| Nucleus           | 13C   |
| Acquired Size     | 32768 |
| Spectral Size     | 65536 |
| Parameter       | Value                                                                 |
|-----------------|----------------------------------------------------------------------|
| Origin          | Bruker BioSpin GmbH                                                  |
| Spectrometer    | spect                                                               |
| Solvent         | CDC13                                                               |
| Temperature     | 298.0                                                               |
| Pulse Sequence  | zg30                                                                 |
| Experiment      | 10                                                                  |
| Probe           | Z127784_0002 (CP BBO 50051 BBF-H-D-05 Z)                            |
| Number of Scans | 16                                                                  |
| Receiver Gain   | 30                                                                  |
| Relaxation Delay| 5.0000                                                             |
| Pulse Width     | 12.0000                                                             |
| Acquisition Time| 3.2768                                                              |
| Spectrometer Frequency | 500.35                      |
| Spectral Width  | 100000.0                                                            |
| Lowest Frequency| -1910.3                                                             |
| Nucleus         | 1H                                                                  |
| Acquired Size   | 32768                                                               |
| Spectral Size   | 65536                                                               |

![Chemical Structure](image)
| Parameter            | Value                                      |
|----------------------|--------------------------------------------|
| Origin               | Bruker BioSpin GmbH                        |
| Spectrometer         | spect                                      |
| Solvent              | CDCl3                                      |
| Temperature          | 298.0                                      |
| Pulse Sequence       | zgpg30                                     |
| Experiment           | 1D                                         |
| Probe                | Z127784_0002 (CP BBO 500S1 BRF-H-D-05 Z)   |
| Number of Scans      | 256                                        |
| Receiver Gain        | 191                                        |
| Relaxation Delay     | 2.0000                                     |
| Pulse Width          | 10.0000                                    |
| Acquisition Time     | 1.0398                                     |
| Spectrometer Frequency| 125.83                                     |
| Spectral Width       | 31512.6                                    |
| Lowest Frequency     | -1916.9                                    |
| Nucleus              | 13C                                        |
| Acquired Size        | 32768                                      |
| Spectral Size        | 65536                                      |
|   | Parameter          | Value                                                                 |
|---|--------------------|----------------------------------------------------------------------|
| 1 | Origin             | Bruker BioSpin GmbH                                                  |
| 2 | Spectrometer       | spect                                                                |
| 3 | Solvent            | CDC13                                                               |
| 4 | Temperature        | 298.0                                                               |
| 5 | Pulse Sequence     | zg30                                                                |
| 6 | Experiment         | 1D                                                                  |
| 7 | Probe              | 2127784_0002 (CP 880 S0051 88F-10-D-15 Z)                          |
| 8 | Number of Scans    | 16                                                                  |
| 9 | Receiver Gain      | 151                                                                 |
| 10| Relaxation Delay   | 5.0000                                                              |
| 11| Pulse Width        | 12.0000                                                             |
| 12| Acquisition Time   | 3.2768                                                              |
| 13| Spectrometer Frequency | 500.35                 |
| 14| Spectral Width     | 10000.0                                                             |
| 15| Lowest Frequency   | -1910.3                                                             |
| 16| Nucleus            | 1H                                                                  |
| 17| Acquired Size      | 32768                                                               |
| 18| Spectral Size      | 65536                                                               |

![Chemical Structure](image-url)
| Parameter            | Value                                                                 |
|----------------------|----------------------------------------------------------------------|
| Origin               | Bruker BioSpin GmbH                                                  |
| Spectrometer         | spect                                                                |
| Solvent              | CDC13                                                               |
| Temperature          | 298.0                                                               |
| Pulse Sequence       | zpgg30                                                              |
| Experiment           | 1D                                                                   |
| Probe                | Z127784_0002 (CP BRO 30051 BBF-H-D-05 Z)                            |
| Number of Scans      | 256                                                                 |
| Receiver Gain        | 191                                                                 |
| Relaxation Delay     | 2.0000                                                              |
| Pulse Width          | 10.0000                                                             |
| Acquisition Time     | 1.0398                                                              |
| Spectrometer Frequency| 125.83                                                               |
| Spectral Width       | 31512.6                                                              |
| Lowest Frequency     | -1916.9                                                              |
| Nucleus              | 13C                                                                 |
| Acquired Size        | 32768                                                                |
| Spectral Size        | 65336                                                               |

![NMR spectrum](image)
| Parameter       | Value         |
|-----------------|---------------|
| Origin          | Varian        |
| Spectrometer    | Inova         |
| Solvent         | CDCl3         |
| Temperature     | 20.0          |
| Pulse Sequence  | 2s2pul        |
| Experiment      | 1D            |
| Probe           | hcn           |
| Number of Scans | 4             |
| Receiver Gain   | 42            |
| Relaxation Delay| 2.0000        |
| Pulse Width     | 7.0000        |
| Acquisition Time| 4.0960        |
| Spectrometer Frequency | 500.07    |
| Spectral Width  | 8000.0        |
| Lowest Frequency| -1520.6       |
| Nucleus         | 1H            |
| Acquired Size   | 32768         |
| Spectral Size   | 65536         |
| Parameter          | Value                                                                 |
|-------------------|----------------------------------------------------------------------|
| Origin            | Bruker BioSpin GmbH                                                  |
| Spectrometer      | spect                                                               |
| Solvent           | CDC13                                                                |
| Temperature       | 298.0                                                                |
| Pulse Sequence    | zgpg30                                                              |
| Experiment        | 1D                                                                   |
| Probe             | Z127784_0002 (CP BBO S0051 BBF-H-D-05 Z)                             |
| Number of Scans   | 368                                                                  |
| Receiver Gain     | 190.5                                                                |
| Relaxation Delay  | 2.0000                                                              |
| Pulse Width       | 10.0000                                                             |
| Acquisition Time  | 1.0398                                                              |
| Spectrometer Frequency | 125.83                                                        |
| Spectral Width    | 31512.6                                                             |
| Lowest Frequency  | -1901.6                                                             |
| Nucleus           | 13C                                                                 |
| Acquired Size     | 32768                                                               |
| Spectral Size     | 65536                                                               |
| Parameter       | Value          |
|-----------------|----------------|
| Origin          | Varian         |
| Spectrometer    | Inova          |
| Solvent         | CDCl₃          |
| Temperature     | 20.0           |
| Pulse Sequence  | s2pul          |
| Experiment      | 1D             |
| Probe           | QUAD           |
| Number of Scans | 16             |
| Receiver Gain   | 58             |
| Relaxation Delay| 5.0000         |
| Pulse Width     | 6.5000         |
| Acquisition Time| 4.6645         |
| Spectrometer Frequency | 499.69       |
| Spectral Width  | 7024.9         |
| Lowest Frequency| -1022.5        |
| Nucleus         | 1H             |
| Acquired Size   | 32768          |
| Spectral Size   | 65536          |
| Parameter       | Value |
|-----------------|-------|
| Origin          | Varian |
| Spectrometer    | Inova |
| Solvent         | CDC3 |
| Temperature     | 20.0 |
| Pulse Sequence  | s2pui |
| Experiment      | 1D |
| Probe           | hcn |
| Number of Scans | 16 |
| Receiver Gain   | 32 |
| Relaxation Delay| 5.0000 |
| Pulse Width     | 7.0000 |
| Acquisition Time| 4.0960 |
| Spectrometer Frequency | 500.07 |
| Spectral Width  | 8000.0 |
| Lowest Frequency| -1521.1 |
| Nucleus         | 1H |
| Acquired Size   | 32768 |
| Spectral Size   | 65536 |

![Chemical Structure](image)

![NMR Spectrum](image)
| Parameter      | Value          |
|---------------|----------------|
| Origin        | Varian         |
| Spectrometer  | Inova          |
| Solvent       | CDCl3          |
| Temperature   | 21.0           |
| Pulse Sequence| s2pul          |
| Experiment    | 1D             |
| Probe         | QUAD           |
| Number of Scans| 320           |
| Receiver Gain | 60             |
| Relaxation Delay| 2.0000        |
| Pulse Width   | 6.0000         |
| Acquisition Time| 1.0863        |
| Spectrometer Frequency| 125.66 |
| Spectral Width | 30165.9       |
| Lowest Frequency | -1274.5      |
| Nucleus       | 13C            |
| Acquired Size | 32768          |
| Spectral Size | 65536          |

![Chemical structure](image)
| Parameter          | Value  |
|--------------------|--------|
| 1 Origin           | Varian |
| 2 Spectrometer     | INOVA  |
| 3 Solvent          | CDCl3  |
| 4 Temperature      | 20.0   |
| 5 Pulse Sequence   | s2pul  |
| 6 Experiment       | 1D     |
| 7 Probe            | quad94 |
| 8 Number of Scans  | 16     |
| 9 Receiver Gain    | 54     |
| 10 Relaxation Delay | 1.0000 |
| 11 Pulse Width     | 0.0000 |
| 12 Acquisition Time | 4.0960 |
| 13 Spectrometer Frequency | 399.95 |
| 14 Spectral Width  | 8000.0 |
| 15 Lowest Frequency | -2424.5|
| 16 Nucleus         | 1H     |
| 17 Acquired Size   | 32768  |
| 18 Spectral Size   | 65536  |

![NMR Spectrum](image)
| Parameter          | Value   |
|--------------------|---------|
| Origin             | Varian  |
| Spectrometer       | inova   |
| Solvent            | CDCl3   |
| Temperature        | 30.0    |
| Pulse Sequence     | s2pul   |
| Experiment         | 1D      |
| Probe              | QUAD    |
| Number of Scans    | 69      |
| Receiver Gain      | 60      |
| Relaxation Delay   | 10.0000 |
| Pulse Width        | 0.0000  |
| Acquisition Time   | 1.0863  |
| Spectrometer Frequency | 125.66 |
| Spectral Width     | 30165.9 |
| Lowest Frequency   | -1274.8 |
| Nucleus            | 13C     |
| Acquired Size      | 32768   |
| Spectral Size      | 65336   |
| Parameter          | Value  |
|--------------------|--------|
| Origin             | Varian |
| Spectrometer       | inova  |
| Solvent            | CDC13  |
| Temperature        | 30.0   |
| Pulse Sequence     | s2pul  |
| Experiment         | 1D     |
| Probe              | QUAD   |
| Number of Scans    | 16     |
| Receiver Gain      | 60     |
| Relaxation Delay   | 0.0000 |
| Pulse Width        | 0.0000 |
| Acquisition Time   | 4.664S |
| Spectrometer Frequency | 499.69 |
| Spectral Width     | 7024.9 |
| Lowest Frequency   | -1021.8 |
| Nucleus            | 1H     |
| Acquired Size      | 32768  |
| Spectral Size      | 65536  |
| Parameter          | Value    |
|--------------------|----------|
| Origin             | Varian   |
| Spectrometer       | inova    |
| Solvent            | CDCl3    |
| Temperature        | 20.0     |
| Pulse Sequence     | s2pul    |
| Experiment         | 1D       |
| Probe              | quadbp   |
| Number of Scans    | 16       |
| Receiver Gain      | 5.8      |
| Relaxation Delay   | 0.0000   |
| Pulse Width        | 0.0000   |
| Acquisition Time   | 4.0960   |
| Spectrometer Frequency | 399.74  |
| Spectral Width     | 8000.0   |
| Lowest Frequency   | -2426.0  |
| Nucleus            | 1H       |
| Acquired Size      | 32768    |
| Spectral Size      | 65536    |
| Parameter       | Value |
|-----------------|-------|
| Origin          | Varian|
| Spectrometer    | Inova |
| Solvent         | CDCl3 |
| Temperature     | 20.0  |
| Pulse Sequence  | s2pul |
| Experiment      | 1D    |
| Probe           | hcn   |
| Number of Scans | 16    |
| Receiver Gain   | 28    |
| Relaxation Delay| 0.0000|
| Pulse Width     | 7.0000|
| Acquisition Time| 4.0960|
| Spectrometer Frequency | 500.07 |
| Spectral Width  | 8000.0|
| Lowest Frequency| -1518.7|
| Nucleus         | 1H    |
| Acquired Size   | 32768 |
| Spectral Size   | 65536 |
| Parameter          | Value         |
|--------------------|---------------|
| 1 Origin           | Varian        |
| 2 Spectrometer     | Innova        |
| 3 Solvent          | CDCl$_3$      |
| 4 Temperature      | 20.0          |
| 5 Pulse Sequence   | $szpul$       |
| 6 Experiment       | 1D            |
| 7 Probe            | QUAO          |
| 8 Number of Scans  | 96            |
| 9 Receiver Gain    | 60            |
| 10 Relaxation Delay| 2.0000        |
| 11 Pulse Width     | 6.0000        |
| 12 Acquisition Time| 1.0863        |
| 13 Spectrometer Frequency | 125.66 |
| 14 Spectral Width  | 30165.9       |
| 15 Lowest Frequency| $-1275.4$     |
| 16 Nucleus         | 13C           |
| 17 Acquired Size   | 32768         |
| 18 Spectral Size   | 65536         |
| Parameter       | Value     |
|-----------------|-----------|
| Origin          | Varian    |
| Spectrometer    | inova     |
| Solvent         | CDCl3     |
| Temperature     | 50.0      |
| Pulse Sequence  | z2pul     |
| Experiment      | 1D        |
| Probe           | QUAD      |
| Number of Scans | 16        |
| Receiver Gain   | 58        |
| Relaxation Delay| 0.0000    |
| Pulse Width     | 5.8230    |
| Acquisition Time| 4.0960    |
| Spectrometer Frequency | 399.74 |
| Spectral Width  | 8000.0    |
| Lowest Frequency| -2428.0   |
| Nucleus         | 1H        |
| Acquired Size   | 32768     |
| Spectral Size   | 65536     |
| Parameter     | Value   |
|---------------|---------|
| Origin        | Varian  |
| Spectrometer  | Inova   |
| Solvent       | CDC13   |
| Temperature   | 20.0    |
| Pulse Sequence| 90pul   |
| Experiment    | 1D      |
| Probe         | hcn     |
| Number of Scans | 4      |
| Receiver Gain | 38      |
| Relaxation Delay | 0.0000 |
| Pulse Width   | 7.0000  |
| Acquisition Time | 4.0960 |
| Spectrometer Frequency | 500.07 |
| Spectral Width | 8000.0 |
| Lowest Frequency | -1521.1 |
| Nucleus       | 1H      |
| Acquired Size | 32768   |
| Spectral Size | 65536   |
| Parameter       | Value          |
|-----------------|----------------|
| Origin          | Varian         |
| Spectrometer    | Inova          |
| Solvent         | CDCl3          |
| Temperature     | 20.0           |
| Pulse Sequence  | s2pul          |
| Experiment      | 1D             |
| Probe           | hcn            |
| Number of Scans | 16             |
| Receiver Gain   | 50             |
| Relaxation Delay| 10.0000        |
| Pulse Width     | 7.0000         |
| Acquisition Time| 4.0960         |
| Spectrometer Frequency | 500.07 |
| Spectral Width  | 8000.0         |
| Lowest Frequency| -1520.6        |
| Nucleus         | 1H             |
| Acquired Size   | 32768          |
| Spectral Size   | 65536          |
| Parameter       | Value                                                                 |
|-----------------|----------------------------------------------------------------------|
| 1 Origin        | Bruker BioSpin GmbH                                                  |
| 2 Spectrometer  | spect                                                               |
| 3 Solvent       | CDCl3                                                               |
| 4 Temperature   | 298.1                                                               |
| 5 Pulse Sequence| zg30                                                                |
| 6 Experiment    | 1D                                                                  |
| 7 Probe         | Z127784_0002 (CP BBO 500S1 BF-H-D-05 Z)                              |
| 8 Number of Scans| 16                                                                 |
| 9 Receiver Gain | 86.0                                                                |
| 10 Relaxation Delay | 10.000000              |
| 11 Pulse Width  | 12.000000                                                           |
| 12 Spectrometer Frequency | 500.35                      |
| 13 Spectral Width | 100000.0                |
| 14 Lowest Frequency | -1922.3                     |
| 15 Nucleus      | 1H                                                                  |
| 16 Acquired Size | 32768                        |
| 17 Spectral Size  | 65536                                                                 |
| Parameter     | Value                                                                 |
|---------------|----------------------------------------------------------------------|
| Origin        | Bruker BioSpin GmbH                                                   |
| Spectrometer  | spect                                                                |
| Solvent       | CDCl3                                                                 |
| Temperature   | 298.1                                                                |
| Pulse Sequence| zgpg30                                                                |
| Experiment    | 1D                                                                   |
| Probe         | Z1277B4_0002 (CP BBO 500S1 B9F-H-D-05 2)                              |
| Number of Scans| 560                                                                 |
| Receiver Gain | 190.5                                                                |
| Relaxation Delay | 1.0000                                                            |
| Pulse Width   | 10.0000                                                              |
| Spectrometer Frequency | 125.83                                                           |
| Spectral Width | 31512.6                                                           |
| Lowest Frequency | -1898.9                                                           |
| Nucleus       | 13C                                                                  |
| Acquired Size | 32768                                                                |
| Spectral Size | 65536                                                                |

![NMR Spectrum Image](image_url)
| Parameter      | Value                                                                 |
|---------------|----------------------------------------------------------------------|
| Origin        | Bruker BioSpin GmbH                                                  |
| Spectrometer  | spec                                                                 |
| Solvent       | CDCl3                                                                |
| Temperature   | 298.2                                                                |
| Pulse Sequence| zg30                                                                 |
| Experiment    | 1D                                                                   |
| Probe         | Z127784_0002 (CP BBF 500S1 BBF-H-D-05 Z)                             |
| Number of Scans| 16                                                                  |
| Receiver Gain | 122.8                                                                |
| Relaxation Delay | 10.00000              |
| Pulse Width   | 12.00000                                                             |
| Spectrometer Frequency | 500.35                         |
| Spectral Width  | 10000.0                                                               |
| Lowest Frequency | -1887.7                         |
| Nucleus       | 1H                                                                   |
| Acquired Size | 32768                                                                 |
| Spectral Size | 65536                                                                 |

![Chemical Structure](image.png)
| Parameter | Value |
|-----------|-------|
| Origin    | Bruker BioSpin GmbH |
| Spectrometer | spect |
| Solvent   | CDCl3 |
| Temperature | 298.1 |
| Pulse Sequence | zg30 |
| Experiment | 1D |
| Probe     | Z127784_0002 (CP 880 500.31 BBF-H-D-D5 Z) |
| Number of Scans | 16 |
| Receiver Gain | 76.2 |
| Relaxation Delay | 10.0000 |
| Pulse Width  | 12.0000 |
| Spectrometer Frequency | 500.35 |
| Spectral Width | 10000.0 |
| Lowest Frequency | -1922.3 |
| Nucleus    | 1H |
| Acquired Size | 32768 |
| Spectral Size | 66536 |

![NMR Spectrum](image)
| Parameter       | Value                                                                 |
|-----------------|----------------------------------------------------------------------|
| Origin          | Bruker BioSpin GmbH                                                  |
| Spectrometer    | spect                                                               |
| Solvent         | CDC13                                                               |
| Temperature     | 298.2                                                               |
| Pulse Sequence  | zgpg30                                                              |
| Experiment      | 1D                                                                  |
| Probe           | Z127784_0002 (CP 5B51 BBF-H-D-05 Z)                                  |
| Number of Scans | 256                                                                 |
| Receiver Gain   | 190.5                                                               |
| Relaxation Delay| 2.00000                                                             |
| Pulse Width     | 10.00000                                                            |
| Spectrometer Frequency | 129.83                                    |
| Spectral Width  | 31512.6                                                             |
| Lowest Frequency| -1900.3                                                             |
| Nucleus         | 13C                                                                 |
| Acquired Size   | 32768                                                               |
| Spectral Size   | 65636                                                               |

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

![NMR Spectrogram](attachment:image.png)
| Parameter              | Value |
|------------------------|-------|
| Origin                 | Varian|
| Spectrometer           | inova |
| Solvent                | CDCl3 |
| Temperature            | 20.0  |
| Pulse Sequence         | s2pul |
| Experiment             | 1D    |
| Probe                  | quadbp|
| Number of Scans        | 4     |
| Receiver Gain          | 48    |
| Relaxation Delay       | 2.0000|
| Pulse Width            | 5.8250|
| Acquisition Time       | 4.0960|
| Spectrometer Frequency | 399.74|
| Spectral Width         | 8000.0|
| Lowest Frequency       | -2426.7|
| Nucleus                | 1H    |
| Acquired Size          | 32768 |
| Spectral Size          | 65536 |

![NMR Spectrum](image)

- 7.26 CDCl3
- 5.30 CH2Cl2