# Catalytic Cyclooligomerization of Enones with Three Methylene Equivalents

Conner M. Farley, You-Yun Zhou, Nishit Banka and Christopher Uyeda

*Department of Chemistry, Purdue University, West Lafayette, IN 47907, United States*

Correspondence: cuyeda@purdue.edu

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1. General Information

**General considerations.** Solvents were degassed and stored over activated 3 Å molecular sieves prior to use. Commercially available anhydrous \( N,N \)-dimethylacetamide (DMA) subjected to additional drying over activated 3 Å molecular sieves prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories, degassed, and stored over activated 3 Å molecular sieves. All other reagents and starting materials were purchased from commercial vendors and used without further purification unless otherwise noted. Liquid reagents were degassed and stored over activated 3 Å molecular sieves prior to use. Zn powder (325 mesh, 99.9%) was purchased from Strem Chemicals, stored under inert atmosphere, and used without further purification. The \( [\text{9}^{\text{th}}\text{NDI}]\text{Ni}_2(\text{C}_6\text{H}_6) \) complex was prepared according to previously reported procedures. The \( \text{Ni(Ph,Me-acac)}_2 \) and \( \text{Ni(Ph}_2\text{-acac)}_2 \) complexes were prepared according to previously reported procedures.

**Physical methods.** \(^1\text{H}, \(^1\text{9F} \) and \(^1\text{3C}\{^1\text{H}\} \) NMR spectra were collected at room temperature on a Varian INOVA 300 MHz or a Bruker AV-III-800 NMR spectrometer. \(^1\text{H} \) and \(^1\text{3C}\{^1\text{H}\} \) NMR spectra are reported in parts per million relative to tetramethylsilane, using the residual solvent resonances as an internal standard. High-resolution mass data were obtained using a Thermo Scientific LTQ Orbitrap XL mass spectrometer or a Thermo Electron Corporation MAT 95XP-Trap mass spectrometer. ATR-IR data were collected on a Thermo Scientific Nicolet Nexus spectrometer containing a MCT* detector and KBr beam splitter with a range of 350–7400 cm\(^{-1}\).

**X-Ray Crystallography.** Single crystals of \( \text{4} \) were coated with Fomblin oil and quickly transferred to the goniometer head of a Bruker Quest diffractometer with a fixed chi angle, a sealed tube fine focus X-ray tube, single crystal curved graphite incident beam monochromator, a Photon100 CMOS area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Mo Kα radiation (\( \lambda = 0.71073 \) Å) at 150 K. Single crystals of \( \text{23} \) were also coated with Fomblin oil and quickly transferred to the goniometer head of a Bruker Quest diffractometer with kappa geometry, an I-μ-S microsource X-ray tube, laterally graded multilayer (Goebel) mirror single crystal for monochromatization, a Photon2 CMOS area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Cu Kα radiation (\( \lambda = 1.54178 \) Å) at 150 K.

For both, data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX3. The space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs and refined by full matrix least squares against \( F^2 \) with all reflections using Shelxl2018 using the graphical interface Shelxle. If not specified otherwise H atoms attached to carbon and nitrogen atoms and hydroxyl hydrogens were positioned geometrically and constrained to ride on their parent atoms, with carbon hydrogen bond distances of 0.95 Å for and aromatic C-H, 1.00, 0.99 and 0.98 Å for aliphatic C-H, CH2 and CH3 moieties, respectively. Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. \( U_{iso}(H) \) values were set to a multiple of \( U_{eq}(C) \) with 1.5 for CH3, and 1.2 for C-H units, respectively. Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1854302–1854303.
contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

In the structure of 4, a toluene molecule was refined as three fold disordered. The benzene rings were constrained to resemble ideal hexagons with C-C bond distances of 1.39 Å. The three disordered moieties were restrained to have similar geometries. $U_{ij}$ components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy rates refined to 0.485(3), 0.342(3) and 0.173(3).
2. Reaction Optimization Studies

General Procedure for metal source comparison study. In an N₂-filled glovebox, a 5-mL vial was charged with the metal source, (0.01 mmol, 0.15 equiv), (±)-t-Bu-Quinox **L10** (2.62 mg, 0.01 mmol, 0.15 equiv), Zn Powder (27 mg, 0.41 mmol, 6 equiv), and a magnetic stir bar. A solution of (E)-1,5-diphenylpent-2-en-1-one (1) (0.3 mL of a 0.23 M stock solution in 1.25:1 CH₂Cl₂:DMA containing 0.24 M mesitylene, 0.07 mmol, 1.0 equiv) was added. The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, opened to ambient atmosphere, and diluted with CH₂Cl₂. An aliquot was analyzed by GC.

| Entry | Metal Source | Conversion | Yield A | Yield B |
|-------|--------------|------------|---------|---------|
| 1     | Ni(acac)₂    | 95%        | 70%     | 12%     |
| 2     | Ni(DME)Br₂   | 85%        | 42%     | 21%     |
| 3     | Ni(DME)Cl₂   | 93%        | 31%     | 13%     |
| 4     | Ni(hfacac)₂ · xH₂O | 24% | 0% | 18% |
| 5     | Ni(Ph,Me-acac)₂ | 95% | 66% | 10% |
| 6     | Ni(Ph₂-acac)₂ | 95%        | 70%     | 12%     |
| 7     | Ni(COD)₂     | 77%        | 23%     | 36%     |
| 8     | Ni(PPPh₃)₂Cl₂ | 85%        | 24%     | 41%     |
| 9     | Co(DME)Br₂   | 51%        | 0%      | 12%     |
| 10    | Fe(acac)₂    | 46%        | 0%      | 0%      |
| 11    | Cu(acac)₂    | < 1%       | 0%      | 0%      |
| 12    | NiI₂         | 83%        | 9%      | 19%     |
| 13ᵃ   | NiI₂         | 92%        | < 1%    | 17%     |
| 14ᵃ   | [iprNDI]Ni₂(C₆H₆) | 86% | 8% | 39% |

ᵃNo **L10** was added to the reaction
**General Procedure for ligand comparison study.** In an N₂-filled glovebox, a 5-mL vial was charged with Ni(acac)₂ (2.65 mg, 0.01 mmol, 0.15 equiv), ligand (0.01 mmol, 0.15 equiv), Zn powder (27 mg, 0.41 mmol, 6.0 equiv), and a magnetic stir bar. A solution of \((E)\)-1,5-diphenylpent-2-en-1-one (1) (0.3 mL of a 0.23 M stock solution in 1.25:1 CH₂Cl₂:DMA containing 0.24 M mesitylene, 0.07 mmol, 1.0 equiv) was added. The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox and diluted with CH₂Cl₂. An aliquot was used for GC analysis.

\[
\text{Entry} \quad \text{Ligand} \quad \text{Conversion} \quad \text{Yield A} \quad \text{Yield B}
\]
\begin{tabular}{|c|c|c|c|c|}
\hline
1 & L1 & 38\% & 2\% & 36\% \\
2 & L2 & 40\% & 6\% & 26\% \\
3 & L3 & 38\% & 6\% & 27\% \\
4 & L4 & 85\% & 9\% & 16\% \\
5 & L5 & 93\% & 17\% & 26\% \\
6 & L6 & 92\% & 30\% & 32\% \\
7 & L7 & 92\% & 29\% & 18\% \\
8 & L8 & 85\% & 60\% & 25\% \\
9 & L9 & 89\% & 62\% & 21\% \\
10 & L10 & 95\% & 70\% & 12\% \\
11 & L11 & 36\% & 11\% & 7\% \\
12 & L12 & 2\% & 0\% & 0\% \\
13 & L13 & 85\% & 6\% & 29\% \\
14 & L14 & 92\% & 19\% & 39\% \\
15 & L15 & 12\% & 6\% & 1\% \\
16 & L16 & 82\% & 12\% & 20\% \\
\hline
\end{tabular}
General Procedure for control experiments. In an N₂-filled glovebox, a 5-mL vial was charged with Ni(acac)₂, (2.65 mg, 0.01 mmol, 0.15 equiv), (±)-t-Bu-Quinox L₁₀ (2.62 mg, 0.01 mmol, 0.15 equiv), Zn Powder (27 mg, 0.41 mmol, 6 equiv), and a magnetic stir bar. A solution of (E)-1,5-diphenylpent-2-en-1-one (1) (0.3 mL of a 0.23 M stock solution in 1.25:1 CH₂Cl₂:DMA containing 0.24 M mesitylene, 0.07 mmol, 1.0 equiv) was added. The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, exposed to ambient atmosphere, and diluted with CH₂Cl₂. An aliquot was used for GC analysis.

| Entry | Deviation from Standard Conditions | Conversion | Yield A | Yield B |
|-------|-----------------------------------|------------|---------|---------|
| 1     | None                              | 95%        | 70%     | 12%     |
| 2     | No Ni(acac)₂ was added             | 0%         | 0%      | 0%      |
| 3     | No (±)-t-Bu-Quinox was added       | 10%        | 0%      | 0%      |
| 4     | No Zn was added                    | 0%         | 0%      | 0%      |
| 5     | No DMA was added                   | 11%        | 0%      | 0%      |
**General Procedure for CH$_2$Cl$_2$ equivalence study.** In an N$_2$-filled glovebox, a 5-mL vial was charged with Ni(acac)$_2$, (3.98 mg, 0.015 mmol, 0.15 equiv), (±)-t-Bu-Quinox L10 (3.94 mg, 0.015 mmol, 0.15 equiv), Zn Powder (40.5 mg, 0.60 mmol, 6 equiv), and a magnetic stir bar. A solution of (E)-1,5-diphenylpent-2-en-1-one (1) (24.4 mg, 0.10 mmol, 1.0 equiv.) and mesitylene (12.5 µL) in DCM (X µL) was added. The reaction mixture was diluted up to a total volume of 0.45 mL with DMA (Y µL). The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, exposed to ambient atmosphere, and diluted with CH$_2$Cl$_2$. An aliquot was used for GC analysis.

![Chemical structure](image)

| Entry | X              | Y               | Conversion | Yield A | Yield B |
|-------|----------------|-----------------|------------|---------|---------|
| 1     | 19.7 µL (3.0 equiv.) | 430.2 µL | 77%        | 33%     | 9%      |
| 2     | 62.5 µL (9.5 equiv.) | 387.5 µL | 70%        | 34%     | 13%     |
| 3     | 125 µL (19 equiv.) | 325 µL  | 72%        | 38%     | 14%     |
| 4     | 250 µL (38 equiv.) | 200 µL   | 96%        | 70%     | 14%     |

Under suboptimal reaction conditions, masses corresponding to the enone bearing 1, 2, 3, and 4 additional CH$_2$ equivalents were detected by GC/MS analysis using (E)-chalcone as a substrate.

**Procedure for characterization of the crude product mixture profile.** In an N$_2$-filled glovebox, a 5-mL vial was charged with Ni(DME)Br$_2$, (3.18 mg, 0.01 mmol, 0.05 equiv), (±)-t-Bu-Quinox L10 (3.14 mg, 0.012 mmol, 0.06 equiv), Zn Powder (67.5 mg, 1.0 mmol, 5.0 equiv), and a magnetic stir bar. A solution of (E)-chalcone (43.0 mg, 0.21 mmol, 1.0 equiv.) in DCM (0.5 mL) and DMA (50 µL) was added. The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, exposed to ambient atmosphere, and diluted with CH$_2$Cl$_2$. An aliquot was used for GC/MS analysis.
Figure S1. GC/MS spectrum of the crude reaction mixture using (E)-chalcone.

| Peak | Ret. Time   | m/z     |
|------|-------------|---------|
| A    | 7.033 min   | 222.05  |
| B    | 7.233 min   | 236.05  |
| C    | 7.792 min   | 250.05  |
| D    | 8.167 min   | 264.10  |
3. Synthesis and Characterization of Enone Substrates

**General procedure for the synthesis of Wittig reagents.** A round-bottom flask was charged with a magnetic stir bar, the appropriate bromoketone (1 equiv) and toluene (1 M). A solution of PPh₃ (1 equiv) in toluene (0.5 M) was added dropwise. After 16 h, the precipitated triphenylphosphonium bromide salt was isolated by filtration, washed with Et₂O, and dried under vacuum. The crude triphenylphosphonium bromide salt was dissolved in CH₂Cl₂ (1 M), and 2 M aqueous NaOH (1 equiv) was added. After stirring for 16 h, the phases were separated, and the aqueous phase was extracted 3x with CH₂Cl₂. The combined organic phases were dried over MgSO₄ and filtered. The filtrate was evaporated to dryness under reduced pressure to provide the ylide as a solid, which was carried forward without purification.

**General procedure for the synthesis of enone substrates.** A round-bottom flask was charged with a stir bar, the Wittig reagent (2 equiv), the aldehyde (1 equiv), and CH₂Cl₂ (0.5 M). The mixture was heated at reflux. After 16 h, the crude reaction mixture was concentrated under reduced pressure. The residue was loaded directly onto a SiO₂ column for purification.

(E)-1-(4-fluorophenyl)-5-phenylpent-2-en-1-one (S1). The reaction was conducted according to the general procedure without modification using 3-phenylpropanal (500 mg, 3.72 mmol, 1.0 equiv) and 4-fluorophenacyltriphenylphosphorane (2.96 g, 7.44 mmol, 2.0 equiv). Purification by column chromatography (SiO₂, 10% EtOAc in hexanes) provided (E)-1-(4-fluorophenyl)-5-phenylpent-2-en-1-one as a colorless oil (662 mg, 70% yield).

**¹H NMR (300 MHz, CDCl₃) δ 8.00 – 7.85 (m, 2H), 7.37 – 7.28 (m, 2H), 7.26 – 7.18 (m, 3H), 7.17 – 7.10 (m, 2H), 7.10 – 7.02 (m, 1H), 6.83 (dq, J = 15.4, 1.3 Hz, 1H), 2.86 (t, J = 7.6 Hz, 2H), 2.74 – 2.57 (m, 2H).**

**¹³C{¹H} NMR (201 MHz, CDCl₃) δ 189.14, 165.53 (d, ¹J_CF = 254.3 Hz), 148.57, 140.73, 134.18 (d, ¹J_CF = 3.0 Hz), 131.12 (d, ¹J_CF = 9.2 Hz), 128.53, 128.42, 126.23, 126.18, 115.61 (d, ¹J_CF = 21.7 Hz), 34.50, 34.48.**

**¹⁹F NMR (282 MHz, CDCl₃) δ -107.36.**

**HRMS(ESI) [m/z]: [M + H]⁺ Calcd for C₁₇H₁₅FO: 255.1178; found: 255.1177.**
(E)-4-(5-phenylpent-2-enoyl)benzonitrile (S2). The reaction was conducted according to the general procedure without modification using 3-phenylpropanal (473 mg, 3.52 mmol, 1.0 equiv) and 4-cyanophenacyltriphenylphosphorane (2.85 g, 7.04 mmol, 2.0 equiv). Purification by column chromatography (SiO2, 10% EtOAc in hexanes) provided (E)-4-(5-phenylpent-2-enoyl)benzonitrile as a white solid (561 mg, 61% yield).

$^1$H NMR (300 MHz, CDCl3) $\delta$ 7.92 (d, $J = 8.0$ Hz, 2H), 7.75 (d, $J = 8.3$ Hz, 2H), 7.32 (dd, $J = 7.9$, 6.4 Hz, 2H), 7.24 – 7.16 (m, 3H), 7.15 – 7.03 (m, 1H), 6.79 (dt, $J = 15.5$, 1.5 Hz, 1H), 2.86 (t, $J = 7.5$ Hz, 2H), 2.67 (td, $J = 8.3$, 7.9, 6.2 Hz, 2H).

$^{13}$C$^{1}$H NMR (201 MHz, CDCl3) $\delta$ 189.51, 150.57, 141.10, 140.48, 132.41, 128.93, 128.60, 128.42, 126.35, 126.04, 118.09, 115.84, 34.62, 34.34.

HRMS(ESI) (m/z): [M + H]$^+$ Calcd for C$_{18}$H$_{16}$NO: 262.1226; found: 262.1229

(E)-1-(4-(methylthio)phenyl)-5-phenylpent-2-en-1-one (S3). The reaction was conducted according to the general procedure without modification using 3-phenylpropanal (539 mg, 4.02 mmol, 1.0 equiv) and 4-(methylthio)phenacyltriphenylphosphorane (3.43 g, 8.04 mmol, 2.0 equiv). Purification by column chromatography (SiO2, 10% EtOAc in hexanes) provided (E)-1-(4-(methylthio)phenyl)-5-phenylpent-2-en-1-one (3) as a yellow solid (851 mg, 81% yield).

$^1$H NMR (300 MHz, CDCl3) $\delta$ 7.85 – 7.76 (m, 2H), 7.35 – 7.27 (m, 3H), 7.25 – 7.18 (m, 4H), 7.08 (dt, $J = 15.3$, 6.7 Hz, 1H), 6.90 – 6.79 (m, 1H), 2.85 (t, $J = 7.7$ Hz, 2H), 2.64 (q, $J = 7.8$, 7.3, 7.3 Hz, 2H), 2.53 (s, 3H).

$^{13}$C$^{1}$H NMR (201 MHz, CDCl3) $\delta$ 189.51, 147.96, 145.43, 140.84, 134.11, 128.98, 128.51, 128.42, 126.19, 125.03, 34.54, 34.53, 14.84.

HRMS(ESI) (m/z): [M + H]$^+$ Calcd for C$_{18}$H$_{18}$OS: 283.1151; found: 283.1155

(E)-1-(4-chlorophenyl)-5-phenylpent-2-en-1-one (S4). The reaction was conducted according to the general procedure without modification using 3-phenylpropanal (300 mg, 2.23 mmol, 1.0 equiv) and 4-chlorophenacyltriphenylphosphorane (1.87 g, 4.47 mmol, 2.0 equiv).
Purification by column chromatography (SiO2, 8% EtOAc in hexanes) provided (E)-1-(4-chlorophenyl)-5-phenylpent-2-en-1-one as a yellow oil (278 mg, 46% yield).

\[
{^1}H\text{ NMR (300 MHz, CDCl}_3\) 8 7.86 – 7.78 (m, 2H), 7.47 – 7.39 (m, 2H), 7.36 – 7.29 (m, 2H), 7.25 – 7.18 (m, 3H), 7.15 – 7.02 (m, 1H), 6.82 (ddt, J = 15.4, 1.5, 0.7 Hz, 1H), 2.86 (t, J = 7.6 Hz, 2H), 2.72 – 2.55 (m, 2H).
\]

\[
{^{13}}C\{^1H\text{ NMR (201 MHz, CDCl}_3\) 8 189.49, 148.94, 140.69, 139.08, 136.16, 129.96, 128.82, 128.54, 128.41, 126.25, 126.15, 34.52, 34.46.
\]

HRMS(ESI) (m/z): [M + H]⁺ Calcd for C_{17}H_{15}ClO: 271.0084; found: 271.0086

(E)-1-(4-methoxyphenyl)-5-phenylpent-2-en-1-one (S5). The reaction was conducted according to the general procedure without modification using 3-phenylpropanal (435 mg, 3.25 mmol, 1.0 equiv) and 4-methoxyphenacyltriphenylphosphorane (2.67 g, 6.50 mmol, 2.0 equiv). Purification by column chromatography (SiO2, 10% EtOAc in hexanes) provided (E)-1-(4-methoxyphenyl)-5-phenylpent-2-en-1-one as a yellow oil (761 mg, 88% yield).

\[
{^1}H\text{ NMR (300 MHz, CDCl}_3\) 8 7.98 – 7.81 (m, 2H), 7.36 – 7.28 (m, 2H), 7.25 – 7.17 (m, 3H), 7.07 (dt, J = 15.3, 6.8 Hz, 1H), 6.98 – 6.82 (m, 3H), 3.88 (s, 3H), 2.85 (t, J = 7.6 Hz, 2H), 2.73 – 2.54 (m, 2H).
\]

\[
{^{13}}C\{^1H\text{ NMR (201 MHz, CDCl}_3\) 8 189.05, 163.31, 147.32, 140.93, 130.84, 130.76, 128.50, 128.42, 126.21, 126.16, 113.73, 55.47, 34.59, 34.51.
\]

HRMS(ESI) (m/z): [M + H]⁺ Calcd for C_{18}H_{18}O_{2}: 267.1380; found: 267.1382

(E)-1-(naphthalen-2-yl)-5-phenylpent-2-en-1-one (S6). The reaction was conducted according to the general procedure without modification using 3-phenylpropanal (500 mg, 3.72 mmol, 1.0 equiv) and [(p-napthylbenzyl)methylene]triphenylphosphorane (2.13 g, 7.44 mmol, 2.0 equiv). Purification by column chromatography (SiO2, 10% EtOAc in hexanes) provided (E)-1-(naphthalen-2-yl)-5-phenylpent-2-en-1-one as a yellow solid (887 mg, 83% yield).

\[
{^1}H\text{ NMR (300 MHz, CDCl}_3\) 8 8.37 (s, 1H), 8.05 – 7.85 (m, 4H), 7.65 – 7.52 (m, 2H), 7.37 – 7.29 (m, 2H), 7.24 (dd, J = 5.9, 2.4 Hz, 3H), 7.19 – 7.09 (m, 1H), 7.02 (dt, J = 15.4, 1.2 Hz, 1H), 2.90 (dd, J = 8.6, 6.6 Hz, 2H), 2.77 – 2.61 (m, 2H).
\]

\[
{^{13}}C\{^1H\text{ NMR (201 MHz, CDCl}_3\) 8 190.62, 148.27, 140.86, 135.43, 135.20, 132.51, 130.03, 129.47, 128.54, 128.46, 128.45, 128.31, 127.80, 126.71, 126.62, 126.22, 124.52, 34.57.
\]

HRMS(ESI) (m/z): [M + Na]⁺ Calcd for C_{21}H_{18}O: 309.1250; found: 309.1252
(E)-1-(3-methoxyphenyl)-5-phenylpent-2-en-1-one (S7). The reaction was conducted according to the general procedure without modification using 3-phenylpropanal (435 mg, 3.25 mmol, 1.0 equiv) and 3-methoxyphenacyltriphenylphosphorane (2.67 g, 6.50 mmol, 2.0 equiv). Purification by column chromatography (SiO2, 5% Et2O in hexanes) provided (E)-1-(3-methoxyphenyl)-5-phenylpent-2-en-1-one as a yellow oil (383 mg, 44% yield).

1H NMR (300 MHz, CDCl3) δ 7.47 – 7.40 (m, 2H), 7.40 – 7.27 (m, 3H), 7.25 - 7.17 (m, 3H), 7.15 – 7.02 (m, 2H), 6.85 (dt, J = 15.3, 1.4 Hz, 1H), 3.86 (s, 3H), 2.86 (t, J = 7.6 Hz, 2H), 2.65 (td, J = 7.8, 6.2 Hz, 2H).

13C{1H} NMR (201 MHz, CDCl3) δ 190.54, 159.80, 148.46, 140.81, 139.27, 129.45, 128.52, 126.56, 126.20, 121.14, 119.23, 112.82, 55.46, 34.52, 34.50.

HRMS(ESI) (m/z): [M + H]^+ Calcd for C18H18O2: 267.1380; found: 267.1385

(E)-5-phenyl-1-(4-(trifluoromethyl)phenyl)pent-2-en-1-one (S8). The reaction was conducted according to the general procedure without modification using 3-phenylpropanal (500 mg, 3.72 mmol, 1.0 equiv) and 4-trifluoromethylphenacyltriphenylphosphorane (3.34 g, 7.44 mmol, 2.0 equiv). Purification by column chromatography (SiO2, 5% Et2O in hexanes) provided (E)-5-phenyl-1-(4-(trifluoromethyl)phenyl)pent-2-en-1-one as a white solid (691 mg, 61% yield).

1H NMR (300 MHz, CDCl3) δ 7.94 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.24 – 7.19 (m, 3H), 7.10 (dt, J = 15.5, 6.8 Hz, 1H), 6.82 (dt, J = 15.5, 1.4 Hz, 1H), 2.87 (dd, J = 8.4, 6.7 Hz, 2H), 2.67 (dtt, J = 8.0, 6.8, 1.2 Hz, 2H).

13C{1H} NMR (201 MHz, CDCl3) δ 190.00, 150.00, 140.68, 140.60, 133.91 (q, J_{CF} = 32.6 Hz), 128.84, 128.59, 128.44, 126.33, 125.57 (q, J_{CF} = 3.8 Hz), 123.66 (q, J_{CF} = 272.7 Hz), 34.61, 34.39.

19F NMR (282 MHz, CDCl3) δ -64.57.

HRMS(ESI) (m/z): [M + H]^+ Calcd for C18H15F3O: 305.1148; found: 305.1145

(E)-5-(benzyloxy)-1-phenylpent-2-en-1-one (S9). The reaction was conducted according to the general procedure without modification using 3-(benzyloxy)propanal (500 mg,
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3.0 mmol, 1 equiv) and phenacyltriphenylphosphorane (2.31 g, 6.0 mmol, 2 equiv). Purification by column chromatography (SiO2, 10% EtO in hexanes) provided (E)-5-(benzyloxy)-1-phenylpent-2-en-1-one as a colorless oil (720 mg, 89% yield).

\[ \text{1H NMR (300 MHz, CDCl}_3\text{)} \delta 7.98 - 7.84 (m, 2H), 7.60 - 7.51 (m, 1H), 7.51 - 7.42 (m, 2H), 7.37 - 7.26 (m, 5H), 7.14 - 7.00 (m, 1H), 7.00 - 6.90 (m, 1H), 4.55 (s, 2H), 3.66 (t, \text{J} = 6.4 \text{ Hz}, 2H), 2.64 (qd, \text{J} = 6.4, 1.1 \text{ Hz}, 2H). \]

13C\{1H\} NMR (201 MHz, CDCl3) \( \delta \) 190.73, 146.06, 138.10, 137.85, 132.66, 128.59, 128.51, 128.45, 127.73, 127.72, 127.47, 73.14, 68.39, 33.25.

HRMS(ESI) (m/z): [M + H]+ Calcd for C18H18O2: 267.1380; found: 267.1376 (2E,6Z)‐1‐(4‐fluorophenyl)dodeca‐2,6‐dien‐1‐one (S10). The reaction was conducted according to the general procedure without modification using cis-4-decenal (573 mg, 3.72 mmol, 1.0 equiv) and 4-fluorophenacyltriphenylphosphorane (2.96 g, 7.44 mmol, 2.0 equiv). Purification by column chromatography (SiO2, 5% EtO in hexanes) provided (2E,6Z)-1-(4-fluorophenyl)dodeca-2,6-dien-1-one as a colorless oil (602 mg, 59% yield).

\[ \text{1H NMR (300 MHz, CDCl}_3\text{)} \delta 8.37 (s, 1H), 8.05 - 7.85 (m, 4H), 7.65 - 7.52 (m, 2H), 7.37 - 7.29 (m, 2H), 7.24 (dd, \text{J} = 5.9, 2.4 \text{ Hz}, 3H), 7.19 - 7.09 (m, 1H), 7.02 (dt, \text{J} = 15.4, 1.2 \text{ Hz}, 1H), 2.90 (dd, \text{J} = 8.6, 6.6 \text{ Hz}, 2H), 2.77 - 2.61 (m, 2H). \]

13C\{1H\} NMR (201 MHz, CDCl3) \( \delta \) 189.17, 165.50 (d, \text{J}_{CF} = 254.1 \text{ Hz}), 149.42, 134.29 (d, \text{J}_{CF} = 3.0 \text{ Hz}), 131.46, 131.10 (d, \text{J}_{CF} = 9.2 \text{ Hz}), 127.73, 125.78, 115.60 (d, \text{J}_{CF} = 21.7 \text{ Hz}), 32.94, 31.51, 29.30, 27.28, 25.88, 22.56, 14.06.

19F NMR (282 MHz, CDCl3) \( \delta \) -107.50.

HRMS(ESI) (m/z): [M + H]+ Calcd for C18H23FO: 275.1806; found: 275.1812

(2E,6Z)-1-(4-fluorophenyl)dodeca-2,6-dien-1-one (S10). The reaction was conducted according to the general procedure without modification using cis-4-decenal (573 mg, 3.72 mmol, 1.0 equiv) and 4-fluorophenacyltriphenylphosphorane (2.96 g, 7.44 mmol, 2.0 equiv). Purification by column chromatography (SiO2, 5% EtO in hexanes) provided (2E,6Z)-1-(4-fluorophenyl)dodeca-2,6-dien-1-one as a colorless oil (602 mg, 59% yield).

\[ \text{1H NMR (300 MHz, CDCl}_3\text{)} \delta 8.37 (s, 1H), 8.05 - 7.85 (m, 4H), 7.65 - 7.52 (m, 2H), 7.37 - 7.29 (m, 2H), 7.24 (dd, \text{J} = 5.9, 2.4 \text{ Hz}, 3H), 7.19 - 7.09 (m, 1H), 7.02 (dt, \text{J} = 15.4, 1.2 \text{ Hz}, 1H), 2.90 (dd, \text{J} = 8.6, 6.6 \text{ Hz}, 2H), 2.77 - 2.61 (m, 2H). \]

13C\{1H\} NMR (201 MHz, CDCl3) \( \delta \) 189.17, 165.50 (d, \text{J}_{CF} = 254.1 \text{ Hz}), 149.42, 134.29 (d, \text{J}_{CF} = 3.0 \text{ Hz}), 131.46, 131.10 (d, \text{J}_{CF} = 9.2 \text{ Hz}), 127.73, 125.78, 115.60 (d, \text{J}_{CF} = 21.7 \text{ Hz}), 32.94, 31.51, 29.30, 27.28, 25.88, 22.56, 14.06.

19F NMR (282 MHz, CDCl3) \( \delta \) -107.50.

HRMS(ESI) (m/z): [M + H]+ Calcd for C18H23FO: 275.1806; found: 275.1812

(E)-2-(5-oxo-5-phenylpent-3-en-1-yl)isoindoline-1,3-dione (S11). The reaction was conducted according to the general procedure without modification using 3-(1,3-dioxoisindolin-2-yl)propanal (200 mg, 0.98 mmol, 1.0 equiv) and phenacyltriphenylphosphorane (897 mg, 1.96 mmol, 2.0 equiv). Purification by column chromatography (SiO2, 20% EtOAc in hexanes) provided (E)-2-(5-oxo-5-phenylpent-3-en-1-yl)isoindoline-1,3-dione as a white solid (252 mg, 84% yield).

\[ \text{1H NMR (300 MHz, CDCl}_3\text{)} \delta 7.95 - 7.81 (m, 4H), 7.73 (dt, \text{J} = 5.2, 2.1 \text{ Hz}, 2H), 7.61 - 7.50 (m, 1H), 7.45 (tt, \text{J} = 7.8, 1.2 \text{ Hz}, 2H), 7.07 - 6.85 (m, 2H), 3.92 (t, \text{J} = 7.1 \text{ Hz}, 2H), 2.74 (q, \text{J} = 6.9 \text{ Hz}, 2H). \]

13C\{1H\} NMR (201 MHz, CDCl3) \( \delta \) 190.40, 168.13, 144.34, 137.54, 134.08, 132.75, 131.96, 128.60, 128.53, 128.12, 123.35, 36.43, 31.68.
(E)-5-(1-benzyl-1H-indol-3-yl)-1-(2,3-difluorophenyl)pent-2-en-1-one (S12). The reaction was conducted according to the general procedure with the following modification: CHCl₃ was used instead of CH₂Cl₂, and the reaction was heated at 70 °C for 16 h using 3-(1-benzyl-1H-indol-3-yl)propanal¹¹ (254 mg, 0.97 mmol, 1.0 equiv) and 2,3-difluorophenacyltriphenylphosphorane (1.21 g, 2.90 mmol, 3.0 equiv). Purification by column chromatography (SiO₂, 15% EtOAc in hexanes) provided (E)-5-(1-benzyl-1H-indol-3-yl)-1-(2,3-difluorophenyl)pent-2-en-1-one as a viscous dark-yellow oil (356 mg, 92% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.76 – 7.49 (m, 3H), 7.32 – 7.21 (m, 3H), 7.21 – 7.03 (m, 6H), 6.94 (s, 1H), 6.85 – 6.71 (m, 1H), 5.28 (s, 2H), 3.02 (t, $J = 7.4$ Hz, 2H), 2.75 (q, $J = 7.1$ Hz, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 153.31 (dd, $J = 256.3$, 12.9 Hz), 150.34 (dd, $J = 250.6$, 13.0 Hz), 150.33, 137.63, 136.74, 134.88, 128.75, 127.87, 127.59, 126.73, 125.75, 125.46, 121.93, 119.12, 118.97, 117.86 (dd, $J = 17.6$, 1.1 Hz), 117.44, 117.35, 114.19, 109.84, 49.88, 33.53, 23.92.

HRMS(ESI) (m/z): [M + H]⁺ Calcd for C₂₆H₂₁F₂NO: 402.1664; found: 402.1661

(E)-1-(4-fluorophenyl)-5-methylhex-2-en-1-one (S13). The reaction was conducted according to the general procedure without modification using isovaleraldehyde (400 mg, 4.68 mmol, 1.0 equiv) and 4-fluorophenacyltriphenylphosphorane (3.7 g, 9.2 mmol, 2.0 equiv). Purification by column chromatography (SiO₂, 10% Et₂O in hexanes) provided (E)-1-(4-fluorophenyl)-5-methylhex-2-en-1-one as a light yellow oil (878 mg, 91% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.03 – 7.92 (m, 2H), 7.19 – 7.09 (m, 2H), 7.11 – 6.97 (m, 2H), 6.92 – 6.76 (m, 1H), 2.28 – 2.13 (m, 2H), 1.83 (dp, $J = 13.3$, 6.7 Hz, 1H), 0.96 (dd, $J = 6.7$, 0.5 Hz, 7H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 189.10, 165.49 (d, $4J_{CF} = 254.0$ Hz), 149.11, 134.33 (d, $4J_{CF} = 3.0$ Hz), 131.08 (d, $3J_{CF} = 9.2$ Hz), 126.50, 115.60 (d, $3J_{CF} = 21.8$ Hz), 42.13, 28.00, 22.47.

¹⁹F NMR (282 MHz, CDCl₃) δ -107.55.

HRMS(ESI) (m/z): [M + H]⁺ Calcd for C₁₅H₁₅FO: 207.1180; found: 207.1179
methyl (E)-8-(4-chlorophenyl)-8-oxooct-6-enoate (S14). The reaction was conducted according to the general procedure without modification using methyl-6-oxohexanoate (250 mg, 1.73 mmol, 1.0 equiv) and 4-chlorophenacyltriphenylphosphorane (1.44 g, 3.47 mmol, 2.0 equiv). Purification by column chromatography (SiO2, 20% EtOAc in hexanes) provided methyl (E)-8-(4-chlorophenyl)-8-oxooct-6-enoate as a yellow oil (152 mg, 31% yield).

$^1$H NMR (300 MHz, CDCl₃) δ 7.93 – 7.80 (m, 2H), 7.49 – 7.38 (m, 2H), 7.05 (dt, J = 15.3, 6.8 Hz, 1H), 6.85 (dt, J = 15.3, 1.4 Hz, 1H), 3.68 (s, 3H), 2.34 (qd, J = 6.8, 1.7 Hz, 4H), 1.78 – 1.64 (m, 2H), 1.57 (dq, J = 9.6, 6.8 Hz, 2H).

$^{13}$C{¹H} NMR (201 MHz, CDCl₃) δ 189.41, 173.82, 149.64, 139.08, 136.20, 129.95, 128.85, 125.71, 51.58, 33.75, 32.46, 27.57, 24.48.

HRMS(ESI) (m/z): [M + H]$^+$ Calcd for C₁₅H₁₈ClO₃: 281.0939; found: 281.0937

 tert-butyl (E)-4-(5-(3-methoxyphenyl)-5-oxopent-3-en-1-yl)piperidine-1-carboxylate (S15). The reaction was conducted according to the general procedure without modification using tert-butyl 4-(3-oxopropyl)piperidine-1-carboxylate (250 mg, 1.03 mmol, 1.0 equiv) and 3-methoxyphenacyltriphenylphosphorane (850 mg, 2.07 mmol, 2.0 equiv). Purification by column chromatography (SiO2, 20% EtOAc in hexanes) provided methyl (tert-butyl (E)-4-(5-(3-methoxyphenyl)-5-oxopent-3-en-1-yl)piperidine-1-carboxylate as a light yellow oil (339 mg, 88% yield).

$^1$H NMR (300 MHz, CDCl₃) δ 7.52 – 7.44 (m, 2H), 7.38 (t, J = 7.9 Hz, 1H), 7.15 – 7.09 (m, 1H), 7.09 – 7.00 (m, 1H), 6.87 (dt, J = 15.3, 1.4 Hz, 1H), 4.11 (bs, 2H), 3.87 (s, 3H), 2.66 (q, J = 10.9, 8.9 Hz, 2H), 2.35 (q, J = 6.9 Hz, 2H), 1.68 (d, J = 12.8 Hz, 2H), 1.49 (s, 12H), 1.22 – 1.03 (m, 2H).

$^{13}$C{¹H} NMR (201 MHz, CDCl₃) δ 190.46, 159.82, 154.86, 149.56, 139.30, 129.48, 125.99, 121.08, 119.15, 112.91, 79.28, 77.22, 55.47, 35.54, 34.88, 29.91, 28.48.

HRMS(ESI) (m/z): [M + H]$^+$ Calcd for C₂₂H₁₃NO₄: 374.2310; found: 374.2318
4. Synthesis of the (±)-t-Bu-Quinox ligand

(±)-t-Bu-Quinox (L10). To a 500 mL round bottom flask were added quinoline-2-carboxaldehyde (3.4 g, 21.7 mmol, 1 equiv.), t-BuOH (100 mL), (±)-t-leucinol (2.8 g, 23.9 mmol, 1.1 equiv) and a magnetic stir bar. The mixture was stirred at 30 °C for 2 h under an N₂ atmosphere. K₂CO₃ (9.01 g, 65.2 mmol, 3.0 equiv) and I₂ (11.0 g, 43.5 mmol, 2.0 equiv) were added, and the mixture was heated at 70 °C for 16 h. After cooling to ambient temperature, the reaction mixture was quenched with a saturated aqueous solution of Na₂S₂O₃ (~50 mL), which resulted in the solution turning from dark red to light yellow. Water was added (100 mL), and the solution was extracted with CH₂Cl₂ (5 x 100 mL). The combined organic phases were washed with brine (100 mL), dried over MgSO₄, and concentrated under reduced pressure. The crude material was loaded directly onto a SiO₂ column for purification (15% EtOAc in hexanes), providing (±)-t-Bu-Quinox (3.92 g, 71% yield) as a white crystalline solid. The spectral data match those previously reported.¹²

¹H NMR (300 MHz, CDCl₃) δ 8.32 – 8.19 (m, 3H), 7.86 (d, J = 8.2 Hz, 1H), 7.76 (dd, J = 8.3, 7.1 Hz, 1H), 7.61 (dd, J = 8.0, 6.9 Hz, 1H), 4.55 (ddd, J = 10.1, 8.7, 0.9 Hz, 1H), 4.48 – 4.35 (m, 1H), 4.26 – 4.10 (m, 1H), 1.02 (s, 9H).

Figure S2. ¹H NMR of L10 (CDCl₃, 273K)
5. Synthesis of the (±)-t-Bu-QuinoxNi(acac)₂ Complex

(±)-(t-Bu-Quinox)Ni(acac)₂ (4). In an N₂-filled glovebox, a 5 mL vial was charged with (±)-t-Bu-Quinox (L₁₀) (10.0 mg, 0.039 mmol, 1.0 equiv.), Ni(acac)₂ (10.1 mg, 0.039 mmol, 1.0 equiv.), C₆H₆ (1 mL) and a magnetic stir bar. An immediate color change to dark green was observed. After stirring for 5 min, the mixture was lyophilized to yield (±)-(t-Bu-Quinox)Ni(acac)₂ as a green solid (19.5 mg, 98% yield). Single crystals of 4 suitable for x-ray diffraction analysis were obtained by slow evaporation of a concentrated solution in toluene at room temperature. Complex 4 is NMR silent.

μₑff = 3.3 μB (Evans method, 293 K, C₆D₆)
Anal. Cald. for (C₃₆H₃₂N₂NiO₅): C 61.03, H 6.31, N 5.48; found: C 60.86, H 6.42, N 5.24.
UV-Vis-NIR (THF, nm (M⁻¹cm⁻¹)): 235 {60391}, 294 {41422}, 389 (sh)

Figure S3. FT-IR of 4.
Figure S4. UV-Vis-NIR spectrum of 4 in THF (0.0078 mM).
6. Substrate Scope Studies and Cyclopentane Characterization

**General Procedure for the synthesis of cyclopentanes from enones.** In an N₂-filled glovebox, a 5-mL vial was charged with Ni(acac)₂ (7.9 mg, 0.031 mmol, 0.15 equiv), (±)-t-Bu-Quinox (L10) (7.9 mg, 0.031 mmol, 0.15 equiv), Zn powder (81 mg, 1.23 mmol, 6.0 equiv), and a magnetic stir bar. To this mixture was added a solution of the substrate (0.21 mmol, 1.0 equiv) dissolved in CH₂Cl₂ (0.5 mL) and DMA (0.4 mL). The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, opened to ambient atmosphere, and loaded directly onto a SiO₂ column for purification.

The ratios of C₅:C₃ were determined by ¹H NMR integration from aliquots of the crude reaction mixtures. Reported yields are of the purified cyclopentane product. In all cases, the products were isolated exclusively with the *trans* relative stereochemistry.

**[2-phenethylcyclopentyl](phenyl)methanone (3).** The reaction was conducted according to the general procedure without modification using (E)-1,5-diphenylpent-2-en-1-one (1)¹³ (48.8 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 20% CH₂Cl₂ in hexanes).

- Ratio of C₅:C₃ = 5.8 : 1
- Run 1: 40.1 mg isolated (70% yield), yellow oil
- Run 2: 40.7 mg isolated (71% Yield), yellow oil

**¹H NMR (300 MHz, CDCl₃) δ 8.08 – 7.83 (m, 2H), 7.61 – 7.50 (m, 1H), 7.49 – 7.38 (m, 2H), 7.26 – 7.19 (m, 2H), 7.14 (td, J = 7.1, 6.5, 1.5 Hz, 3H), 3.41 (ddd, J = 11.0, 7.9, 6.0 Hz, 1H), 2.77 – 2.39 (m, 3H), 2.07 (dddd, J = 13.8, 12.1, 7.1, 3.2 Hz, 2H), 1.87 – 1.49 (m, 5H), 1.46 – 1.30 (m, 1H).

**¹³C{¹H} NMR (201 MHz, CDCl₃) δ 203.12, 142.53, 137.35, 132.82, 128.57, 128.38, 128.28, 128.24, 125.66, 52.95, 42.86, 37.48, 35.03, 32.71, 31.78, 25.14.

HRMS(ESI) (m/z): [M + H]⁺ Calcd for C₂₀H₂₂O: 279.1743; found: 279.1746
(4-fluorophenyl)(2-phenethylcyclopentyl)methanone (5). The reaction was conducted according to the general procedure without modification using (E)-1-(4-fluorophenyl)-5-phenylpent-2-en-1-one (S1) (52.5 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 0.5% Et₂O in hexanes).

Ratio of C₅ : C₃ = 5.9 : 1
Run 1: 43.3 mg isolated (71% yield), yellow oil
Run 2: 39.1 mg isolated (64% Yield), yellow oil

¹H NMR (300 MHz, CDCl₃) δ 8.02 – 7.91 (m, 2H), 7.25 – 7.19 (m, 2H), 7.18 – 7.05 (m, 5H), 3.34 (q, J = 8.0 Hz, 1H), 2.58 (dddd, J = 39.0, 14.7, 9.8, 5.6 Hz, 3H), 2.15 – 1.95 (m, 2H), 1.71 (d, J = 5.5 Hz, 4H), 1.67 – 1.56 (m, 1H), 1.38 (dd, J = 12.1, 8.1 Hz, 1H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 201.45, 165.61 (d, J_CF = 254.3 Hz), 142.43, 133.69 (d, J_CF = 3.0 Hz), 130.96 (d, J_CF = 9.3 Hz), 128.29, 128.22, 125.70, 115.62 (d, J_CF = 21.7 Hz), 52.89, 42.84, 37.44, 35.00, 32.66, 31.73, 25.10.

¹⁹F NMR (282 MHz, CDCl₃) δ -107.37.

HRMS(ESI) (m/z): [M + H]+ Calcd for C₂₀H₂₁FO: 297.1649; found: 297.1651

(2-phenethylcyclopentyl)(4-(trifluoromethyl)phenyl)methanone (6). The reaction was conducted according to the general procedure without modification using (E)-5-phenyl-1-(4-(trifluoromethyl)phenyl)pent-2-en-1-one (S8) (62.6 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 0.5% Et₂O in hexanes).

Ratio of C₅ : C₃ = 9.1 : 1
Run 1: 51.4 mg isolated (72% yield), yellow oil
Run 2: 49.9 mg isolated (70% Yield), yellow oil

¹H NMR (300 MHz, CDCl₃) δ 8.04 (d, J = 9.4 Hz, 2H), 7.73 (d, J = 9.4 Hz, 2H), 7.26 – 7.19 (m, 2H), 7.18 – 7.05 (m, 3H), 3.37 (dd, J = 23.9, 7.5 Hz, 1H), 2.70 – 2.58 (m, 1H), 2.52 (dddd, J = 13.1, 10.3, 5.9 Hz, 2H), 2.20 – 1.90 (m, 2H), 1.86 – 1.56 (m, 5H), 1.46 – 1.33 (m, 1H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 202.03, 142.27, 139.97, 134.12 (q, J_CF = 32.6 Hz), 128.66, 128.31, 128.20, 125.74, 125.63 (q, J_CF = 3.7 Hz), 123.64 (q, J_CF = 271.9 Hz), 53.27, 42.70, 37.36, 34.95, 32.62, 31.51, 25.11.

¹⁹F NMR (300 MHz, CDCl₃) δ -64.6
**4-(2-phenethylcyclopentane-1-carbonyl)benzonitrile (7).** The reaction was conducted according to the general procedure without modification using (E)-4-(5-phenylpent-2-enoyl)benzonitrile (S2) (54.0 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 0.5% Et₂O in hexanes).

- Ratio of C₅ : C₃ = >20 : 1
- Run 1: 39.4 mg isolated (63% yield), yellow oil
- Run 2: 38.2 mg isolated (61% Yield), yellow oil

**¹H NMR (300 MHz, CDCl₃)** δ 7.99 (d, J = 9.9 Hz, 2H), 7.75 (d, J = 9.9 Hz, 2H), 7.25 – 7.20 (m, 2H), 7.18 – 7.08 (m, 3H), 3.34 (td, J = 9.3, 8.5, 6.6 Hz, 1H), 2.65 (ddd, J = 15.4, 10.3, 5.6 Hz, 1H), 2.58 – 2.42 (m, 2H). 2.20 – 1.92 (m, 2H), 1.86 – 1.50 (m, 5H), 1.46 – 1.32 (m, 1H).

**¹³C{¹H} NMR (201 MHz, CDCl₃)** δ 201.62, 142.17, 140.26, 132.46, 128.74, 128.33, 128.20, 125.79, 118.01, 116.08, 53.28, 42.69, 37.32, 34.93, 32.59, 31.45, 25.09.

**HRMS(ESI) [m/z]:** [M + Na]⁺ Calcd for C₂₁H₂₁NO: 326.1515; found: 326.1514

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**4-(methylthio)phenyl)(2-phenethylcyclopentyl)methanone (8).** The reaction was conducted according to the general procedure without modification using (E)-1-(4-methylthio)-5-phenylpent-2-en-1-one (S3) (58.3 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 0.5% Et₂O in hexanes).

- Ratio of C₅ : C₃ = 5.4 : 1
- Run 1: 35.3 mg isolated (53% yield), yellow oil
- Run 2: 32.7 mg isolated (49% Yield), yellow oil

**¹H NMR (300 MHz, CDCl₃)** δ 7.94 – 7.81 (m, 2H), 7.28 – 7.19 (m, 4H), 7.14 (td, J = 7.4, 6.8, 1.7 Hz, 3H), 3.35 (q, J = 8.0 Hz, 1H), 2.72 – 2.42 (m, 6H), 2.18 – 1.96 (m, 2H), 1.86 – 1.50 (m, 5H), 1.43 – 1.30 (m, 1H).

**¹³C{¹H} NMR (201 MHz, CDCl₃)** δ 202.09, 145.49, 142.53, 133.64, 128.82, 128.27, 128.23, 125.66, 125.05, 52.71, 42.93, 37.49, 35.03, 32.71, 31.81, 25.12, 14.83.

**HRMS(ESI) [m/z]:** [M + H]⁺ Calcd for C₂₁H₂₄OS: 325.1621; found: 325.1623
(4-methoxyphenyl)(2-phenethylcyclopentyl)methanone (9). The reaction was conducted according to the general procedure without modification using (E)-1-(4-methoxyphenyl)-5-phenylpent-2-en-1-one (S5) (54.9 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO2, 40% CH2Cl2 in hexanes).

- Ratio of C5 : C3 = 3.8 : 1
- Run 1: 26.3 mg isolated (41% yield), yellow oil
- Run 2: 28.2 mg isolated (44% Yield), yellow oil

1H NMR (300 MHz, CDCl3) δ 7.99 – 7.90 (m, 2H), 7.27 – 7.20 (m, 2H), 7.20 – 7.09 (m, 3H), 6.97 – 6.90 (m, 2H), 3.87 (s, 3H), 3.36 (td, J = 8.9, 7.1 Hz, 1H), 2.72 – 2.40 (m, 3H), 2.19 – 1.95 (m, 2H), 1.86 – 1.68 (m, 4H), 1.67 – 1.51 (m, 1H), 1.46 – 1.30 (m, 1H).

13C{1H} NMR (201 MHz, CDCl3) δ 201.70, 163.31, 142.62, 130.63, 130.40, 128.26, 128.24, 125.63, 113.71, 55.47, 52.59, 43.00, 37.52, 35.06, 32.73, 31.91, 25.13.

HRMS(ESI) (m/z): [M + H]+ Calcd for C21H24O2: 309.1849; found: 309.1851

(4-chlorophenyl)(2-phenethylcyclopentyl)methanone (10). The reaction was conducted according to the general procedure without modification using (E)-1-(4-chlorophenyl)-5-phenylpent-2-en-1-one (S4) (55.8 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO2, 30% CH2Cl2 in hexanes).

- Ratio of C5 : C3 = 6.7 : 1
- Run 1: 43.1 mg isolated (67% yield), clear oil
- Run 2: 47.2 mg isolated (74% Yield), clear oil

1H NMR (300 MHz, CDCl3) δ 7.93 – 7.84 (m, 2H), 7.47 – 7.39 (m, 2H), 7.29 – 7.21 (m, 2H), 7.20 – 7.09 (m, 3H), 3.34 (dt, J = 9.2, 7.1 Hz, 1H), 2.65 (ddd, J = 13.6, 10.7, 5.5 Hz, 1H), 2.58 – 2.43 (m, 2H), 2.20 – 1.96 (m, 2H), 1.86 – 1.68 (m, 4H), 1.68 – 1.55 (m, 1H), 1.48 – 1.30 (m, 1H).

13C{1H} NMR (201 MHz, CDCl3) δ 201.81, 142.39, 139.25, 135.60, 129.79, 128.87, 128.30, 128.22, 125.71, 52.94, 42.81, 37.42, 35.00, 32.66, 31.67, 25.11.

HRMS(ESI) (m/z): [M + H]+ Calcd for C20H21ClO: 313.1354; found: 313.1352
naphthalen-2-yl(2-phenethylcyclopentyl)methanone (11). The reaction was conducted according to the general procedure without modification using (E)-1-(naphthalen-2-yl)-5-phenylpent-2-en-1-one (S6) (59.1 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 0.5% Et₂O in hexanes).

Ratio of C₅ : C₃ = 5.6 : 1
Run 1: 34.3 mg isolated (51% yield), yellow oil
Run 2: 37.9 mg isolated (56% Yield), yellow oil

¹H NMR (300 MHz, CDCl₃) δ 8.47 (d, J = 1.7 Hz, 1H), 8.06 (dd, J = 8.6, 1.8 Hz, 1H), 7.98 (dd, J = 7.6, 1.8 Hz, 1H), 7.96 – 7.84 (m, 2H), 7.67 – 7.50 (m, 2H), 7.34 – 7.18 (m, 2H), 7.18 – 7.09 (m, 3H), 3.59 (dt, J = 9.5, 7.4 Hz, 1H), 2.82 – 2.43 (m, 3H), 2.14 (dddd, J = 19.8, 12.3, 9.4, 5.0 Hz, 2H), 1.94 – 1.56 (m, 5H), 1.50 – 1.38 (m, 1H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 203.08, 142.51, 135.52, 134.71, 132.60, 129.88, 129.60, 128.46, 128.41, 128.34, 128.27, 128.24, 127.76, 126.73, 126.70, 125.66, 124.35, 53.00, 42.99, 37.49, 35.05, 32.77, 31.99, 25.19.

HRMS(ESI) (m/z): [M + H]⁺ Calcd for C₂₄H₂₅O: 329.1900; found: 329.1899

(2-(2-(benzyloxy)ethyl)cyclopentyl)(phenyl)methanone (12). The reaction was conducted according to the general procedure without modification using (E)-5-(benzyloxy)-1-phenylpent-2-en-1-one (S9) (55.0 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 6% Et₂O in hexanes).

Ratio of C₅ : C₃ = >20 : 1
Run 1: 44.5 mg isolated (70% yield), yellow oil
Run 2: 46.9 mg isolated (74% Yield), yellow oil

¹H NMR (300 MHz, CDCl₃) δ 8.01 – 7.90 (m, 2H), 7.54 (ddt, J = 8.2, 6.6, 1.4 Hz, 1H), 7.44 (ddt, J = 8.5, 7.6, 0.8 Hz, 2H), 7.35 – 7.16 (m, 5H), 4.36 (d, J = 2.9 Hz, 2H), 3.56 – 3.30 (m, 3H), 2.55 (h, J = 7.8 Hz, 1H), 2.15 – 1.89 (m, 2H), 1.83 – 1.59 (m, 5H), 1.41 – 1.28 (m, 1H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 202.91, 138.45, 137.31, 132.71, 128.51, 128.40, 128.26, 127.63, 127.39, 72.85, 69.71, 52.73, 40.14, 35.20, 33.09, 31.69, 25.06.

HRMS(APCI) (m/z): [M + H]⁺ Calcd for C₂₁H₂₄O₂: 309.1849; found: 309.1847
(3-methoxyphenyl)(2-phenethylcyclopentyl)methanone (13). The reaction was conducted according to the general procedure without modification using (E)-1-(3-methoxyphenyl)-5-phenylpent-2-en-1-one (S7) (55.0 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO2, 1% Et2O in hexanes).

- **Ratio of C5 : C3 = 7.7 : 1**
- Run 1: 47.7 mg isolated (75% yield), yellow oil
- Run 2: 49.8 mg isolated (78% Yield), yellow oil

1H NMR (300 MHz, CDCl3) δ 7.60 – 7.46 (m, 2H), 7.43 – 7.33 (m, 1H), 7.31 – 7.20 (m, 2H), 7.20 – 7.00 (m, 4H), 3.86 (s, 3H), 3.39 (ddd, J = 10.3, 7.9, 6.1 Hz, 1H), 2.72 – 2.42 (m, 3H), 2.24 – 1.92 (m, 2H), 1.85 – 1.50 (m, 5H), 1.46 – 1.31 (m, 1H).

13C{1H} NMR (201 MHz, CDCl3) δ 202.94, 159.85, 142.52, 138.76, 129.52, 128.27, 128.24, 125.66, 120.99, 119.27, 112.72, 55.44, 53.07, 42.92, 37.45, 35.02, 32.70, 31.85, 25.13.

HRMS(ESI) (m/z): [M + H]⁺ Calcd for C21H24O2: 309.1849; found: 309.1852

HRMS(APCI) (m/z): [M + H]⁺ Calcd for C21H21F3O: 347.1617; found: 347.1622

(2-(2-(1-benzyl-1H-indol-3-yl)ethyl)cyclopentyl)(2,3-difluorophenyl)methanonene (14). The reaction was conducted according to the general procedure without modification using (E)-5-(1-benzyl-1H-indol-3-yl)-1-(2,3-difluorophenyl)pent-2-en-1-one (S12) (82.9 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO2, 20% CH2Cl2 in hexanes).

- **Ratio of C5 : C3 = 5.7 : 1**
- Run 1: 51.6 mg isolated (57% yield), yellow oil
- Run 2: 52.1 mg isolated (57% Yield), yellow oil

1H NMR (300 MHz, CDCl3) δ 7.75 (ddd, J = 11.1, 7.7, 2.2 Hz, 1H), 7.65 (ddd, J = 7.8, 4.0, 2.2 Hz, 1H), 7.53 (dd, J = 7.9, 1.2 Hz, 1H), 7.27 (d, J = 5.8 Hz, 2H), 7.24 – 7.14 (m, 3H), 7.08 (dddd, J = 8.1, 6.8, 2.9, 1.2 Hz, 4H), 6.84 (s, 1H), 5.21 (s, 2H), 3.31 (q, J = 7.6 Hz, 1H), 2.80 (ddd, J = 15.2, 9.9, 5.6 Hz, 1H), 2.67 (td, J = 9.2, 8.5, 4.9 Hz, 1H), 2.56 (q, J = 7.4 Hz, 1H), 2.16 – 1.96 (m, 2H), 1.92 – 1.63 (m, 5H), 1.50 – 1.38 (m, 1H).
$^{13}$C\{\textsuperscript{1}H\} NMR (201 MHz, CDCl\textsubscript{3}) $\delta$ 200.51, 153.37 (dd, $^1$J\textsubscript{CF} = 256.2, $^2$J\textsubscript{CF} = 13.0 Hz), 150.38 (dd, $^1$J\textsubscript{CF} = 250.8, $^2$J\textsubscript{CF} = 13.0 Hz), 137.76, 136.68, 134.36 (ap t, $^4$J\textsubscript{CF} = 3.5 Hz), 128.69, 128.01, 127.49, 126.75, 125.25, 125.21 (dd, $^3$J\textsubscript{CF} = 7.3, $^4$J\textsubscript{CF} = 3.4 Hz), 121.65, 117.62 (d, $^2$J\textsubscript{CF} = 17.9 Hz), 117.31 (d, $^2$J\textsubscript{CF} = 17.7 Hz), 115.69, 109.59, 52.82, 49.78, 42.95, 35.98, 32.68, 31.56, 25.14, 24.18.

$^{19}$F NMR (282 MHz, CDCl\textsubscript{3}) $\delta$ -132.07, -137.83.

HRMS(APCI) (m/z): [M + H]$^+$ Calcd for C\textsubscript{29}H\textsubscript{27}F\textsubscript{2}NO: 444.2133; found: 444.2136

(2-hexylcyclopentyl)(phenyl)methanone (15). The reaction was conducted according to the general procedure without modification using (E)-1-phenyldec-2-en-1-one \textsuperscript{16} (47.6 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO\textsubscript{2}, 10% CH\textsubscript{2}Cl\textsubscript{2} in hexanes).

Ratio of C\textsubscript{5} : C\textsubscript{3} = 6.3 : 1
Run 1: 34.6 mg isolated (65% yield), yellow oil
Run 2: 32.5 mg isolated (61% Yield), yellow oil

$^1$H NMR (300 MHz, CDCl\textsubscript{3}) $\delta$ 8.00 – 7.93 (m, 2H), 7.60 – 7.50 (m, 1H), 7.51 – 7.41 (m, 2H), 3.35 (q, $J$ = 8.2, 7.4 Hz, 1H), 2.52 – 2.26 (m, 1H), 2.15 – 1.87 (m, 2H), 1.85 – 1.61 (m, 3H), 1.52 – 1.06 (m, 13H), 0.90 – 0.80 (m, 3H).

$^{13}$C\{\textsuperscript{1}H\} NMR (201 MHz, CDCl\textsubscript{3}) $\delta$ 203.42, 137.48, 132.70, 128.51, 128.37, 52.91, 43.09, 35.53, 32.71, 31.82, 31.70, 29.76, 29.24, 28.56, 25.14, 22.64, 14.09.

HRMS(ESI) (m/z): HRMS(ESI) (m/z): [M + H]$^+$ Calcd for C\textsubscript{19}H\textsubscript{28}O: 273.2213; found: 273.2215

$^{t}$ert-butyl-4-(2-(2-(3-methoxybenzoyl)cyclopentyl)ethyl)piperidine-1-carboxylate (16). The reaction was conducted according to the general procedure without modification using $^{t}$ert-butyl-(E)-4-(5-(3-methoxyphenyl)-5-oxopent-3-en-1-yl)piperidine-1-carboxylate (S\textsubscript{15}) (77.0 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO\textsubscript{2}, 15% Et\textsubscript{2}O in hexanes).

Ratio of C\textsubscript{5} : C\textsubscript{3} = 3.8 : 1
Run 1: 42.3 mg isolated (50% yield), yellow oil
Run 2: 44.9 mg isolated (52% Yield), yellow oil
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.56 – 7.47 (m, 2H), 7.37 (ddd, $J = 8.1, 7.6, 0.4$ Hz, 1H), 7.10 (ddd, $J = 8.2, 2.7, 1.0$ Hz, 1H), 4.03 (br s, 2H), 3.86 (s, 3H), 3.29 (m, 1 H), 2.62 (t, $J = 12.5$ Hz, 2H), 2.39 (dq, $J = 15.7, 8.0$ Hz, 1H), 2.12 – 1.91 (m, 2H), 1.82 – 1.66 (m, 3H), 1.57 (d, $J = 13.1$ Hz, 2H), 1.44 (d, $J = 2.8$ Hz, 12H), 1.34 – 1.10 (m, 4H), 1.01 (tq, $J = 10.8, 5.7, 5.0$ Hz, 2H).

$^{13}$C{${^1}_H$} NMR (201 MHz, CDCl$_3$) $\delta$ 203.03, 159.83, 154.88, 138.78, 129.53, 120.94, 119.17, 112.76, 79.11, 55.43, 53.08, 42.93, 36.01, 35.28, 32.68, 32.32, 31.84, 30.32, 28.48, 28.47, 25.07.

HRMS(ESI) (m/z): [M + H]$^+$ Calcd for C$_{25}$H$_{37}$NO$_4$: 416.2795; found: 416.2792

(4-fluorophenyl)(2-isobutylcyclopentyl)methanone (17). The reaction was conducted according to the general procedure without modification using (E)-1-(4-fluorophenyl)-5-methylhex-2-en-1-one (S13) (42.6 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO$_2$, 15% CH$_2$Cl$_2$ in hexanes).

Ratio of C$_5$ : C$_3$ = 7.1 : 1
Run 1: 32.8 mg isolated (64% yield), colorless oil
Run 2: 31.8 mg isolated (62% yield), colorless oil

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.02 – 7.94 (m, 2H), 7.17 – 7.08 (m, 2H), 3.28 (dt, $J = 9.1, 7.0$ Hz, 1H), 2.58 – 2.41 (m, 1H), 2.12 – 1.89 (m, 2H), 1.82 – 1.61 (m, 3H), 1.53 – 1.41 (m, 1H), 1.33 – 1.13 (m, 3H), 0.84 (d, $J = 6.6$ Hz, 6H).

$^{13}$C{${^1}_H$} NMR (201 MHz, CDCl$_3$) $\delta$ 201.70, 165.57 (d, $J = 254.3$ Hz), 133.83 (d, $J = 3.0$ Hz), 130.94 (d, $J = 9.3$ Hz), 115.57 (d, $J = 22.0$ Hz), 53.21, 45.15, 40.90, 32.78, 31.66, 26.93, 25.12, 23.39, 22.16.

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -107.60.

HRMS(ESI) (m/z): [M + H]$^+$ Calcd for C$_{16}$H$_{21}$FO: 249.1649; found: 249.1646

2-(2-(2-benzoylcyclopentyl)ethyl)isooindoline-1,3-dione (18). The reaction was conducted according to the general procedure without modification using (E)-2-(5-oxo-5-phenylpent-3-en-1-yl)isooindoline-1,3-dione (S11) (63.0 mg, 0.21 mmol, 1 equiv). Isolated yields were determined following column chromatography (SiO$_2$, CH$_2$Cl$_2$).

Ratio of C$_5$ : C$_3$ = 2.9 : 1
Run 1: 27.2 mg isolated (38% yield), yellow oil
Run 2: 32.1 mg isolated (45% Yield), yellow oil

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.01 – 7.88 (m, 2H), 7.80 (dd, $J = 5.5, 3.1$ Hz, 2H), 7.68 (dd, $J = 5.4, 3.1$ Hz, 2H), 7.59 – 7.49 (m, 1H), 7.44 (dd, $J = 8.2, 6.6$ Hz, 2H), 3.73 – 3.54 (m, 2H), 3.47 – 3.34 (m, 1H), 2.63 – 2.36 (m, 1H), 2.19 – 1.95 (m, 2H), 1.93 – 1.58 (m, 5H), 1.50 – 1.33 (m, 1H).

$^{13}$C{H} NMR (201 MHz, CDCl$_3$) $\delta$ 202.51, 168.27, 137.06, 133.81, 132.86, 132.15, 128.56, 128.40, 123.15, 52.74, 40.02, 37.16, 34.06, 32.50, 31.75, 25.15.

HRMS(ESI) (m/z): [M + H]$^+$ Calcd for C$_{22}$H$_{21}$O$_3$: 348.1594; found: 348.1596

**(Z)-(4-fluorophenyl)(2-(non-3-en-1-yl)cyclopentyl)methanone** (19). The reaction was conducted according to the general procedure without modification using (2E,6Z)-1-(4-fluorophenyl)dodeca-2,6-dien-1-one (S10) (56.7 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO$_2$, 0.2% Et$_2$O in hexanes).

Ratio of C$_5$ : C$_3$ = >20 : 1

Run 1: 50.7 mg isolated (78% yield), yellow oil

Run 2: 50.8 mg isolated (78% Yield), yellow oil

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.05 – 7.93 (m, 2H), 7.21 – 7.05 (m, 2H), 5.43 – 5.15 (m, 2H), 3.32 (q, $J = 7.8, 7.4$ Hz, 1H), 2.43 (dq, $J = 15.3, 8.2$ Hz, 1H), 2.16 – 1.85 (m, 5H), 1.83 – 1.62 (m, 3H), 1.53 – 1.15 (m, 10H), 0.91 – 0.82 (m, 3H).

$^{13}$C{H} NMR (201 MHz, CDCl$_3$) $\delta$ 201.60, 165.59 (d, $^1$J$_{CF} = 254.1$ Hz), 133.77 (d, $^4$J$_{CF} = 3.0$ Hz), 130.95 (d, $^3$J$_{CF} = 9.1$ Hz), 130.16, 129.31, 115.59 (d, $^2$J$_{CF} = 21.4$ Hz), 52.79, 42.92, 35.62, 31.69, 31.50, 29.37, 27.15, 26.31, 25.11, 22.70, 14.06.

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -107.53.

HRMS(APCI) (m/z): [M + H]$^+$ Calcd for C$_{21}$H$_{29}$FO: 317.2275; found: 317.2281

**methyl 5-(2-(4-chlorobenzoyl)cyclopentyl)pentanoate** (20). The reaction was conducted according to the general procedure without modification using (E)-8-(4-chlorophenyl)-8-oxooct-6-enoate (S14) (57.9 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO$_2$, 60% CH$_2$Cl$_2$ in hexanes).

Ratio of C$_5$ : C$_3$ = 4.3 : 1

Run 1: 46.1 mg isolated (69% yield), yellow oil

Run 2: 42.6 mg isolated (64% Yield), yellow oil
1H NMR (300 MHz, CDCl₃) δ 7.93 – 7.86 (m, 2H), 7.47 – 7.41 (m, 2H), 3.63 (s, 3H), 3.34 – 3.21 (m, 1H), 2.41 (q, J = 7.5 Hz, 1H), 2.30 – 2.21 (m, 2H), 2.15 – 1.88 (m, 2H), 1.78 – 1.65 (m, 2H), 1.65 – 1.50 (m, 2H), 1.49 – 1.11 (m, 6H).

13C{1H} NMR (201 MHz, CDCl₃) δ 201.92, 174.12, 139.24, 135.62, 129.80, 128.86, 52.89, 51.44, 42.72, 35.02, 33.97, 32.61, 31.66, 28.06, 25.08, 25.05.

HRMS(ESI) (m/z): [M + H]+ Calcd for C₁₈H₂₄ClO₃: 323.1409; found: 323.1412

(2-methylcyclopentyl)(phenyl)methanone (21) [100611-76-5]. The reaction was conducted according to the general procedure without modification using (Z)-1-phenylbut-2-en-1-one (30.2 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 10% CH₂Cl₂ in hexanes). The spectral data matched those previously reported.¹⁵

Ratio of C₅ : C₃ = 6.1 : 1
Run 1: 19.0 mg isolated (49% yield), yellow oil
Run 2: 19.4 mg isolated (50% Yield), yellow oil

¹H NMR (300 MHz, CDCl₃) δ 8.01 – 7.91 (m, 2H), 7.61 – 7.51 (m, 1H), 7.51 – 7.41 (m, 2H), 3.29 (q, J = 8.1 Hz, 1H), 2.41 (tt, J = 14.3, 6.8 Hz, 1H), 2.14 – 2.00 (m, 1H), 2.00 – 1.88 (m, 1H), 1.88 – 1.66 (m, 3H), 1.37 – 1.29 (m, 1H), 1.03 (dd, J = 6.7, 0.6 Hz, 3H).

1-(2-(6-methoxynaphthalen-2-yl)cyclopentyl)ethan-1-one (22). The reaction was conducted according to the general procedure without modification using (E)-4-(6-methoxynaphthalen-2-yl)but-3-en-2-one (46.7 mg, 0.21 mmol, 1.0 equiv). Isolated yields were determined following column chromatography (SiO₂, 7% Et₂O in hexanes).

Ratio of C₅ : C₃ = 1.4 : 1
Run 1: 21.3 mg isolated (39% yield), yellow oil
Run 2: 18.6 mg isolated (34% Yield), yellow oil

¹H NMR (800 MHz, CDCl₃) δ 7.71 (dd, J = 13.8, 8.7 Hz, 2H), 7.64 – 7.59 (m, 1H), 7.37 (dd, J = 8.5, 1.8 Hz, 1H), 7.15 (dd, J = 8.8, 2.5 Hz, 1H), 7.13 (d, J = 2.5 Hz, 1H), 3.93 (s, 3H), 3.42 (q, J = 9.1, 8.7 Hz, 1H), 3.14 (q, J = 8.8 Hz, 1H), 2.27 – 2.20 (m, 1H), 2.17 – 2.09 (m, 1H), 2.02 (s, 3H), 1.99 (ddd, J = 15.6, 8.0, 4.0 Hz, 1H), 1.97 – 1.91 (m, 1H), 1.91 – 1.81 (m, 2H).
$^{13}$C{${}^1$H} NMR (201 MHz, CDCl$_3$) $\delta$ 210.73, 157.37, 139.56, 133.32, 129.06, 128.98, 127.17, 126.14, 125.48, 118.84, 105.62, 60.27, 55.31, 48.99, 35.87, 30.08, 29.87, 25.43.

HRMS(ESI) (m/z): [M + H]$^+$ Calcd for C$_{18}$H$_{20}$O$_2$: 269.1536; found: 269.1539

**phenyl(2-phenylcyclopentyl)methanone (23).** The reaction was conducted according to the general procedure without modification using (E)-chalcone (43.0 mg, 0.21 mmol, 1 equiv). Isolated yields were determined following column chromatography (SiO$_2$, 50% CH$_2$Cl$_2$ in hexanes). Single crystals of 23 suitable for X-ray diffraction analysis were obtained by cooling a saturated Et$_2$O solution to -5 °C.

Ratio of C$_5 : C_3 = 2.2 : 1$

Run 1: 23.7 mg isolated (45% yield), white solid
Run 2: 22.0 mg isolated (42% Yield), white solid

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.86 – 7.77 (m, 2H), 7.56 – 7.42 (m, 1H), 7.44 – 7.32 (m, 2H), 7.26 – 7.24 (m, 4H), 7.20 – 7.11 (m, 1H), 3.90 – 3.75 (m, 1H), 3.66 (q, $J = 8.4$ Hz, 1H), 2.25 (td, $J = 6.8, 6.3, 3.1$ Hz, 2H), 2.03 – 1.76 (m, 4H).

$^{13}$C{${}^1$H} NMR (201 MHz, CDCl$_3$) $\delta$ 202.19, 144.72, 136.95, 132.79, 128.46, 128.42, 127.36, 126.16, 109.32, 54.72, 48.32, 35.30, 32.01, 25.84.

HRMS(APCI) (m/z): [M + H]$^+$ Calcd for C$_{18}$H$_{18}$O: 251.1430; found: 251.1433

**Other classes of electron-deficient alkenes that were examined but provided no cyclopentanation under catalytic conditions:**
7. Synthesis and Characterization of Representative Cyclopropanes

**General procedure for the synthesis of cyclopropanes from enones.** A flame-dried 100 mL flask was charged with solid NaH (60% in mineral oil, 1.2 equiv), trimethylsulfoxonium iodide (1.2 equiv), and a magnetic stir bar. The flask was placed under N₂ atmosphere, and DMSO (0.35 M) was added dropwise with stirring. After hydrogen evolution ceased, the reaction mixture was stirred for an additional 15 min, during which time the solution became clear. The enone (1.0 equiv) was added by syringe. The reaction was allowed to stir at room temperature. After 24 h, the reaction was quenched with water, and the mixture was extracted with Et₂O (3 x 10 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product was loaded onto a SiO₂ column for purification.

**2-(phenethylcyclopropyl)(phenyl)methanone (2).** The reaction was conducted according to the general procedure without modification using (E)-1,5-diphenylpent-2-en-1-one (1) (250 mg, 1.05 mmol, 1.0 equiv). (2-phenethylcyclopropyl)(phenyl)methanone (2) was isolated by column chromatography (SiO₂, 10% Et₂O in hexanes) as a light yellow oil (78.8 mg, 30% yield).

\[
{^1}H\text{ NMR (300 MHz, CDCl}_3\text{)} \delta 8.00 \text{–} 7.83 (m, 2H), 7.61 \text{–} 7.51 (m, 1H), 7.45 (dtt, J = 8.3, 6.6, 1.2 Hz, 2H), 7.25 \text{–} 7.20 (m, 2H), 7.20 \text{–} 7.12 (m, 3H), 2.77 (ddd, J = 10.8, 9.2, 5.4 Hz, 2H), 2.40 (dt, J = 8.1, 4.2 Hz, 1H), 1.88 \text{–} 1.70 (m, 2H), 1.68 \text{–} 1.59 (m, 1H), 1.53 \text{–} 1.39 (m, 1H), 0.91 (ddd, J = 7.8, 6.1, 3.5 Hz, 1H).
\]

\[
{^{13}}C\{^1H\} \text{ NMR (201 MHz, CDCl}_3\text{)} \delta 199.95, 141.66, 138.00, 132.61, 128.44, 128.41, 128.38, 127.97, 125.88, 35.60, 35.38, 26.58, 25.26, 18.75.
\]

HRMS(ESI) (m/z): [M + H]⁺ Calcd for C₁₈H₁₉O: 251.1430; found: 251.1431

**2-(phenethylcyclopropyl)(phenyl)methanone (S16).** The reaction was conducted according to the general procedure without modification using (E)-4-(6-methoxynaphthalen-2-yl)but-3-en-2-one (100 mg, 0.44 mmol, 1.0 equiv). 1-(2-(6-methoxynaphthalen-2-
(4-fluorophenyl)(2-isobutylcyclopropyl)methanone (S17). The reaction was conducted according to the general procedure without modification using (E)-1-(4-fluorophenyl)-5-methylhex-2-en-1-one (S13) (255 mg, 1.24 mmol, 1.0 equiv). (4-fluorophenyl)(2-isobutylcyclopropyl)methanone (S17) was isolated by column chromatography (SiO$_2$, 10% Et$_2$O in hexanes) as a light yellow oil (95.0 mg, 35% yield).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.09 – 7.92 (m, 2H), 7.20 – 7.09 (m, 2H), 2.37 (dt, $J = 8.1, 4.3$ Hz, 1H), 1.66 – 1.54 (m, 1H), 1.54 – 1.45 (m, 1H), 1.45 – 1.19 (m, 3H), 0.93 (dd, $J = 6.6, 1.4$ Hz, 6H).

$^{13}$C{$^1$H} NMR (201 MHz, CDCl$_3$) $\delta$ 198.54, 165.53 (d, $^1$J$_{CF} = 254.0$ Hz), 134.48 (d, $^4$J$_{CF} = 3.0$ Hz), 130.50 (d, $^3$J$_{CF} = 9.2$ Hz), 115.53 (d, $^2$J$_{CF} = 21.7$ Hz), 42.74, 28.59, 25.73, 25.15, 22.61, 22.50, 19.26.

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -107.85.

HRMS(ESI) (m/z): [M + H]$^+$ Calcd for C$_{14}$H$_{17}$FO: 221.1336; found: 221.1338
8. Assignment of Ratios Between the Cyclopentane and Cyclopropane Products

The assignment of the ratios between the cyclopentane and cyclopropane products were made using a combination of \(^1\)H NMR analysis and GC analysis of the crude reaction mixtures. Two product classes are discussed below. The remainder of the substrate classes were assigned by analogy.

Top spectrum (3): Isolated 22
Middle spectrum (2): Crude reaction mixture with ratio of 22 : S16 indicated
Bottom Spectrum (1): Isolated S16

Figure S5. \(^1\)H NMR of isolated 22 (Top spectrum), crude reaction mixture (Middle spectrum), and isolated S16 (Bottom Spectrum). (CDCl\(_3\), 273 K).
Top spectrum (3): Isolated 17
Middle spectrum (2): Crude reaction mixture with ratio of 17 : S17 indicated
Bottom Spectrum (1): Isolated S17

Figure S6. $^1$H NMR of isolated 17 (Top spectrum), crude reaction mixture (Middle spectrum), and isolated S17 (Bottom Spectrum). (CDCl$_3$, 273 K).
9. Mechanistic Studies

\[(2\text{-phenethylcyclopentyl-3,3,4,4,5,5-}\text{d}_6)(\text{phenyl})\text{methanone (3-d}_6)\]. In an N\textsubscript{2}-filled glovebox, a 5-mL vial was charged with Ni(acac\textsubscript{2}) (7.9 mg, 0.031 mmol, 0.15 equiv), (±)-t-Bu-Quinox (L\textbf{10}) (7.9 mg, 0.031 mmol, 0.15 equiv), Zn powder (81 mg, 1.23 mmol, 6.0 equiv), and a magnetic stir bar. To this mixture was added a solution of (E)-1,5-diphenylpent-2-en-1-one (1) (48.8 mg, 0.21 mmol, 1 equiv) in CD\textsubscript{2}Cl\textsubscript{2} (0.5 mL) and DMA (0.4 mL). The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, opened to ambient atmosphere, and loaded directly onto a SiO\textsubscript{2} column for purification (SiO\textsubscript{2}, 20% CH\textsubscript{2}Cl\textsubscript{2} in hexanes) to provide (2-phenethylcyclopentyl-3,3,4,4,5,5-\text{d}_6)(\text{phenyl})methanone as a colorless oil (34.9 mg, 60% yield, > 99% deuterium incorporation).

\begin{align*}
1^H\text{NMR (300 MHz, CDCl}_3) & \delta 8.01 - 7.89 \text{ (m, 2H), } 7.61 - 7.51 \text{ (m, 1H), } 7.51 - 7.39 \text{ (m, 2H), } 7.26 - 7.18 \text{ (m, 2H), } 7.18 - 7.08 \text{ (m, 3H), } 3.39 \text{ (d, } J = 7.9 \text{ Hz, 1H), } 2.72 - 2.44 \text{ (m, 3H), } 1.77 \text{ (ddt, } J = 13.1, 11.1, 5.8 \text{ Hz, 1H), } 1.68 - 1.56 \text{ (m, 1H).}
\end{align*}

\begin{align*}
13^C\{{^1H}\text{NMR (201 MHz, CDCl}_3) & \delta 203.17, 142.53, 137.35, 132.80, 128.55, 128.37, 128.27, 128.22, 125.65, 52.81, 42.72, 37.42, 35.02. \\
\text{HRMS(ESI) (m/z): } [M + H]^+ \text{ Calcd for C}_{20}H_{16}D_6O: 285.2120; \text{ found: 285.2122}
\end{align*}

In an N\textsubscript{2}-filled glovebox, a 5-mL vial was charged with Ni(acac\textsubscript{2}) (2.65 mg, 0.01 mmol, 0.15 equiv), (±)-t-Bu-Quinox (L\textbf{10}) (2.7 mg, 0.01 mmol, 0.15 equiv), Zn Powder (27 mg, 0.41 mmol, 6.0 equiv), and a magnetic stir bar. To this mixture was added a solution of (2-phenethylcyclopropyl)(phenyl)methanone (2) (17.2 mg, 0.07 mmol, 1.0 equiv) in CH\textsubscript{2}Cl\textsubscript{2} (0.17 mL) and DMA (0.13 mL). The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, and an aliquot was used for GC analysis. The conversion of 2 was determined by integration against mesitylene (< 2% conversion). Compound 3 was not detected in the mixture.
In an N2-filled glovebox, a 5-mL vial was charged with Ni(acac)2 (2.65 mg, 0.01 mmol, 0.15 equiv), (±)-t-Bu-Quinox (2.65 mg, 0.01 mmol, 0.15 equiv), Zn Powder (27 mg, 0.41 mmol, 6.0 equiv), and a magnetic stir bar. To this mixture was added a solution of (2-phenethylcyclopropyl)(phenyl)methanone (2) (17.2 mg, 0.07 mmol, 1.0 equiv) and (E)-5-phenyl-1-(4-(trifluoromethyl)phenyl)pent-2-en-1-one (S8) (20.9 mg, 0.07 mmol, 1.0 equiv) in CH2Cl2 (0.17 mL) and DMA (0.13 mL). The reaction was stirred at room temperature. After 16 h, the crude reaction mixture was removed from the glovebox, and an aliquot was used for GC analysis. The conversions and yields were determined by integration against mesitylene.

In an N2-filled glovebox, a 10 mL Schenk tube was charged with Ni(acac)2 (7.9 mg, 0.031 mmol, 0.15 equiv), (±)-t-Bu-Quinox (L10) (7.9 mg, 0.031 mmol, 0.15 equiv), Zn powder (81 mg, 1.23 mmol, 6.0 equiv), and a magnetic stir bar. To this mixture was added a solution of (E)-1,5-diphenylpent-2-en-1-one (1) (48.8 mg, 0.21 mmol, 1.0 equiv) in CD2Cl2 (0.5 mL) and DMA (0.4 mL). The reaction mixture was removed the glovebox and immediately placed in liquid N2. The Schlenk tube was connected to a Schlenk line, the N2 atmosphere was evacuated, and the reaction vessel was back-filled with ethylene (1 atm). The reaction was stirred at room temperature. After 4 days, an aliquot of the crude reaction mixture was filtered through silica gel and used for NMR analysis (CDCl3). Spectra of the pure 3-d6 and 3 are shown for comparison to indicate complete d6-incorporation.
Top spectrum (3): Crude ethylene experiment mixture
Middle spectrum (2): Isolated 3-d$_6$
Bottom Spectrum (1): Isolated 3

Figure S7. $^1$H NMR of crude ethylene experiment mixture (Top spectrum), isolated 3-d$_6$, (Middle spectrum), and isolated 3 (Bottom Spectrum). (CDCl$_3$, 273 K)
10. Cyclopentane Product Derivatization

**4-methoxyphenyl 2-phenethylcyclopentane-1-carboxylate (24).** A flame-dried microwave vial was charged with mCPBA (>77%, 95 mg, 0.55 mmol, 6.0 equiv), a solution of (4-methoxyphenyl)(2-phenethylcyclopentyl)methanone (9) (28.2 mg, 0.09 mmol, 1.0 equiv) dissolved in CH₂Cl₂ (2 mL), and a magnetic stir bar. The vial was sealed, evacuated and backfilled three times with N₂, and cooled to 0 °C in an ice bath. Trifluoroacetic acid (14 μL, 0.18 mmol, 2.0 equiv) was added by syringe, and the vial was then wrapped in aluminum foil. The reaction was stirred at room temperature. After 48 h, the crude reaction mixture was loaded directly onto a SiO₂ column for purification (40% CH₂Cl₂ in hexanes) to provide 4-methoxyphenyl 2-phenethylcyclopentane-1-carboxylate as a colorless oil (23.6 mg, 81% yield, 14:1 selectivity).

\[ ^1H \text{NMR (300 MHz, CDCl}_3 \delta 7.33 - 7.26 (m, 2H), 7.23 - 7.15 (m, 3H), 7.00 - 6.92 (m, 2H), 6.91 - 6.84 (m, 2H), 3.80 (s, 3H), 2.80 - 2.52 (m, 2H), 2.29 (pd, J = 8.4, 5.6 Hz, 1H), 2.16 - 1.90 (m, 4H), 1.84 - 1.62 (m, 3H), 1.43 - 1.24 (m, 1H).} \]

\[ ^{13}C\{^1H\} \text{NMR (201 MHz, CDCl}_3 \delta 175.43, 157.13, 144.36, 142.32, 128.36, 128.33, 125.77, 122.28, 114.40, 55.61, 50.38, 44.29, 37.32, 34.63, 32.68, 30.39, 24.91.} \]

HRMS(ESI) (m/z): [M + H]^+ Calcd for C₂₁H₂₄O₃: 325.1798; found: 325.1802

**2-phenethylcyclopentyl 4-(trifluoromethyl)benzoate (25).** A flame-dried microwave vial was charged with mCPBA (>77%, 124 mg, 0.72 mmol, 6.0 equiv), a solution of (2-phenethylcyclopentyl)(4-(trifluoromethyl)phenyl)methanone (6) (41.4 mg, 0.12 mmol, 1.0 equiv) in CH₂Cl₂ (2 mL), and a magnetic stir bar. The vial was sealed, evacuated and backfilled three times with N₂, and cooled to 0 °C with an ice bath. Trifluoroacetic acid (18 μL, 0.24 mmol, 2.0 equiv) was added by syringe, and the vial was then wrapped in aluminum foil. The reaction was stirred at 45 °C. After 48 h, the crude reaction mixture was loaded directly onto a SiO₂ column for purification (20% CH₂Cl₂ in hexanes) to provide 2-phenethylcyclopentyl 4-(trifluoromethyl)benzoate as a colorless oil (27.9 mg, 65% Yield, >20:1 selectivity).
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.13 (dd, $J = 8.0$, 0.9 Hz, 2H), 7.70 (dd, $J = 8.1$, 0.7 Hz, 2H), 7.31 – 7.23 (m, 3H), 7.23 – 7.10 (m, 3H), 5.12 (dt, $J = 6.5$, 3.8 Hz, 1H), 2.68 (ddq, $J$ = 13.9, 9.4, 7.0, 6.6 Hz, 2H), 2.21 – 1.96 (m, 3H), 1.96 – 1.70 (m, 4H), 1.69 – 1.57 (m, 1H), 1.47 – 1.29 (m, 1H).

$^{13}$C($^1$H) NMR (201 MHz, CDCl$_3$) $\delta$ 165.18, 142.14, 134.28 (q, $^2$J$_{CF}$ = 32.7 Hz), 133.96, 129.92, 128.33, 125.79, 125.33 (q, $^3$J$_{CF}$ = 3.8 Hz), 123.67 (q, $^1$J$_{CF}$ = 275.1 Hz), 82.63, 45.12, 35.44, 34.31, 32.01, 30.31, 22.82.

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -64.61.

HRMS(ESI) (m/z): [M + Na]$^+$ Calcd for C$_{21}$H$_{21}$F$_3$O$_2$: 385.1386; found: 385.1391
11. NMR Data for Enone Substrates

![Figure S8. $^1$H NMR of S1 (CDCl$_3$, 295 K).](image)

![Figure S9. $^{13}$C($^1$H) NMR of S1 (CDCl$_3$, 295 K).](image)
Figure S10. $^{19}$F NMR of S1 (CDCl$_3$, 295 K).
Figure S11. $^1$H NMR of S2 (CDCl$_3$, 295 K).

Figure S12. $^{13}$C{^1}H NMR of S2 (CDCl$_3$, 295 K).
Figure S13. $^1$H NMR of S3 (CDCl$_3$, 295 K).

Figure S14. $^{13}$C($^1$H) NMR of S3 (CDCl$_3$, 295 K).
Figure S15. $^1$H NMR of S4 (CDCl$_3$, 295 K).

Figure S16. $^{13}$C($^1$H) NMR of S4 (CDCl$_3$, 295 K).
Figure S17. $^1$H NMR of S5 (CDCl$_3$, 295 K).

Figure S18. $^{13}$C{$^1$H} NMR of S5 (CDCl$_3$, 295 K).
Figure S19. $^1$H NMR of S6 (CDCl$_3$, 295 K).

Figure S20. $^{13}$C($^1$H) NMR of S6 (CDCl$_3$, 295 K).
Figure S21. $^1$H NMR of S7 (CDCl$_3$, 295 K).

Figure S22. $^{13}$C($^1$H) NMR of S7 (CDCl$_3$, 295 K).
Figure S23. $^1$H NMR of S8 (CDCl$_3$, 295 K).

Figure S24. $^{13}$C{$^1$H} NMR of S8 (CDCl$_3$, 295 K).
Figure S25. $^{19}$F NMR of S8 (CDCl$_3$, 295 K).
Figure S26. $^1$H NMR of S9 (CDCl$_3$, 295 K).

Figure S27. $^{13}$C($^1$H) NMR of S9 (CDCl$_3$, 295 K).
Figure S28. $^1$H NMR of S10 (CDCl$_3$, 295 K).

Figure S29. $^{13}$C{$^1$H} NMR of S10 (CDCl$_3$, 295 K).
Figure S30. $^{19}$F NMR of S10 (CDCl₃, 295 K).
Figure S31. $^1$H NMR of S11 (CDCl$_3$, 295 K).

Figure S32. $^{13}$C($^1$H) NMR of S11 (CDCl$_3$, 295 K).
Figure S33. $^1$H NMR of S12 (CDCl$_3$, 295 K).

Figure S34. $^{13}$C($^1$H) NMR of S12 (CDCl$_3$, 295 K).
Figure S35. $^{19}$F NMR of S12 (CDCl$_3$, 295 K).
Figure S36. $^1\text{H}$ NMR of S13 (CDCl$_3$, 295 K).

Figure S37. $^{13}\text{C}$($^1\text{H}$) NMR of S13 (CDCl$_3$, 295 K).
Figure S38. $^{19}$F NMR of S13 (CDCl$_3$, 295 K).
Figure S39. $^1$H NMR of S14 (CDCl$_3$, 295 K).

Figure S40. $^{13}$C{$^1$H} NMR of S14 (CDCl$_3$, 295 K).
Figure S41. $^1$H NMR of S15 (CDCl$_3$, 295 K).

Figure S42. $^{13}$C($^1$H) NMR of S15 (CDCl$_3$, 295 K).
15. NMR Data for Cyclopentanes

Figure S43. $^1$H NMR of 3 (CDCl$_3$, 295 K).

Figure S44. $^{13}$C($^1$H) NMR of 3 (CDCl$_3$, 295 K).
**Figure S45.** $^1$H NMR of 5 (CDCl$_3$, 295 K).

**Figure S46.** $^{13}$C($^1$H) NMR of 5 (CDCl$_3$, 295 K).
Figure S47. $^{19}$F NMR of 5 (CDCl$_3$, 295 K).
Figure S48. $^1$H NMR of 6 (CDCl$_3$, 295 K).

Figure S49. $^{13}$C($^1$H) NMR of 6 (CDCl$_3$, 295 K).
Figure S50. $^{19}$F NMR of $6$ (CDCl$_3$, 295 K).
Figure S51. $^1$H NMR of 7 (CDCl$_3$, 295 K).

Figure S52. $^{13}$C($^1$H) NMR of 7 (CDCl$_3$, 295 K).
Figure S53. $^1$H NMR of 8 (CDCl$_3$, 295 K).

Figure S54. $^{13}$C{$^1$H} NMR of 8 (CDCl$_3$, 295 K).
Figure S55. $^1$H NMR of 9 (CDCl$_3$, 295 K).

Figure S56. $^{13}$C($^1$H) NMR of 9 (CDCl$_3$, 295 K).
Figure S57. $^1$H NMR of 10 (CDCl₃, 295 K).

Figure S58. $^{13}$C{$^1$H} NMR of 10 (CDCl₃, 295 K).
Figure S59. $^1$H NMR of 11 (CDCl3, 295 K).

Figure S60. $^{13}$C{$^1$H} NMR of 11 (CDCl3, 295 K).
Figure S61. $^1$H NMR of 12 (CDCl$_3$, 295 K).

Figure S62. $^{13}$C{$_1$H} NMR of 12 (CDCl$_3$, 295 K).
Figure S63. $^1$H NMR of 13 (CDCl$_3$, 295 K).

Figure S64. $^{13}$C($^1$H) NMR of 13 (CDCl$_3$, 295 K).
Figure S65. $^1$H NMR of 14 (CDCl$_3$, 295 K).

Figure S66. $^{13}$C($^1$H) NMR of 14 (CDCl$_3$, 295 K).
Figure S67. $^{19}$F NMR of 14 (CDCl$_3$, 295 K).
Figure S68. $^1$H NMR of 15 (CDCl$_3$, 295 K).

Figure S69. $^{13}$C{$^1$H} NMR of 15 (CDCl$_3$, 295 K).
Figure S70. $^1$H NMR of 16 (CDCl$_3$, 295 K).

Figure S71. $^{13}$C{$^1$H} NMR of 16 (CDCl$_3$, 295 K).
Figure S72. $^1$H NMR of 17 (CDCl$_3$, 295 K).

Figure S73. $^{13}$C{$^1$H} NMR of 17 (CDCl$_3$, 295 K).
Figure S74. $^{19}$F NMR of 17 (CDCl$_3$, 295 K).
Figure S75. $^1$H NMR of 18 (CDCl$_3$, 295 K).

Figure S76. $^{13}$C($^1$H) NMR of 18 (CDCl$_3$, 295 K).
Figure S77. $^1$H NMR of 19 (CDCl$_3$, 295 K).

Figure S78. $^{13}$C($^1$H) NMR of 19 (CDCl$_3$, 295 K).
Figure S79. $^{19}$F NMR of 19 (CDCl$_3$, 295 K).
Figure S80. $^1$H NMR of 20 (CDCl$_3$, 295 K).

Figure S81. $^{13}$C($^1$H) NMR of 20 (CDCl$_3$, 295 K).
Figure S82. $^1$H NMR of 21 (CDCl$_3$, 295 K).
Figure S83. $^1$H NMR of 22 (CDCl$_3$, 295 K).

Figure S84. $^{13}$C{$^1$H} NMR of 22 (CDCl$_3$, 295 K).
Figure S85. $^1$H NMR of 23 (CDCl$_3$, 295 K).

Figure S86. $^{13}$C($^1$H) NMR of 23 (CDCl$_3$, 295 K).
Figure S87. $^1$H NMR of 2 (CDCl$_3$, 295 K).

Figure S88. $^{13}$C($^1$H) NMR of 2 (CDCl$_3$, 295 K).
Figure S89. $^1$H NMR of S16 (CDCl$_3$, 295 K).

Figure S90. $^{13}$C($^1$H) NMR of S16 (CDCl$_3$, 295 K).
Figure S91. $^1$H NMR of S17 (CDCl$_3$, 295 K).

Figure S92. $^{13}$C($^1$H) NMR of S17 (CDCl$_3$, 295 K).
Figure S93. $^{19}$F NMR of S17 (CDCl$_3$, 295 K).
Figure S94. $^1$H NMR of 3-$d_6$ (CDCl$_3$, 295 K).

Figure S95. $^{13}$C($^1$H) NMR of 3-$d_6$ (CDCl$_3$, 295 K).
Figure S96. $^1$H NMR of 24 (CDCl$_3$, 295 K).

Figure S97. $^{13}$C($^1$H) NMR of 24 (CDCl$_3$, 295 K).
Figure S98. $^1$H NMR of 25 (CDCl$_3$, 295 K).

Figure S99. $^{13}$C($^1$H) NMR of 25 (CDCl$_3$, 295 K).
Figure S100. $^{19}$F NMR of 25 (CDCl$_3$, 295 K).
13. IR Data for Enones and Cyclopentanes

**Figure S101.** FT-IR of S1.

**Figure S102.** FT-IR of S2.
Figure S103. FT-IR of S3.

Figure S104. FT-IR of S4.
Figure S105. FT-IR of S5.

Figure S106. FT-IR of S6.
Figure S107. FT-IR of S7.

Figure S108. FT-IR of S8.
Figure S109. FT-IR of S9.

Figure S110. FT-IR of S10.
Figure S111. FT-IR of S11.

Figure S112. FT-IR of S12.
Figure S113. FT-IR of S13.

Figure S114. FT-IR of S14.
Figure S115. FT-IR of S15.

Figure S116. FT-IR of 3.
Figure S117. FT-IR of 5.

Figure S118. FT-IR of 6.
Figure S119. FT-IR of 7.

Figure S120. FT-IR of 8.
Figure S121. FT-IR of 9.

Figure S122. FT-IR of 10.
Figure S123. FT-IR of 11.

Figure S124. FT-IR of 12.
Supporting Information

Figure S125. FT-IR of 13.

Figure S126. FT-IR of 14.
Figure S127. FT-IR of 15.

Figure S128. FT-IR of 16.
Figure S129. FT-IR of 17.

Figure S130. FT-IR of 18.
Figure S131. FT-IR of 19.

Figure S132. FT-IR of 20.
Figure S133. FT-IR of 22.

Figure S134. FT-IR of 23.
Figure S135. FT-IR of 24.

Figure S136. FT-IR of 25.
Figure S137. FT-IR of 2.

Figure S138. FT-IR of S16.
Figure S139. FT-IR of S17.

Figure S140. FT-IR of 3-\(d_6\).
14. X-Ray Diffraction Data

Supporting Information

**Compound 4**

| Crystal data                        |                             |
|-------------------------------------|------------------------------|
| Chemical formula                    | C₅₉H₇₂N₄Ni₂O₁₀              |
| Mr                                  | 1114.62                      |
| Crystal system, space group         | Triclinic, P1               |
| Temperature (K)                     | 150                          |
| a, b, c (Å)                         | 8.8726 (5), 10.2560 (5), 32.4162 (17) |
| α, β, γ (°)                         | 83.7260 (17), 82.6157 (18), 75.5173 (16) |
| V (Å³)                              | 2823.2 (3)                   |
| Z                                    | 2                            |
| F(000)                              | 1180                         |
| Dₐ (Mg m⁻³)                         | 1.311                        |
| Radiation type                      | Mo Kα                        |
| No. of reflections for cell         | 9434                         |
| measurement                         |                              |
| θ range (°) for cell measurement    | 2.9–28.3                     |
| μ (mm⁻¹)                            | 0.73                         |
| Crystal shape                       | Plate                        |
| Colour       | Green                        |
|--------------|------------------------------|
| Crystal size (mm) | $0.19 \times 0.18 \times 0.05$ |

**Data collection**

| Diffractometer          | Bruker AXS D8 Quest CMOS diffractometer |
|-------------------------|----------------------------------------|
| Radiation source        | sealed tube X-ray source               |
| Monochromator           | Triumph curved graphite crystal         |
| Scan method             | $\phi$ and phi scans                   |
| Absorption correction   | Multi-scan                              |
| $T_{\text{min}}$, $T_{\text{max}}$ | 0.656, 0.746                           |
| No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections | 37118, 13147, 10377 |
| $R_{\text{int}}$        | 0.039                                   |
| $\theta$ values (°)     | $\theta_{\text{max}} = 28.3$, $\theta_{\text{min}} = 2.9$ |
| $(\sin \theta/\lambda)_{\text{max}}$ (Å$^{-1}$) | 0.668 |
| Range of $h$, $k$, $l$  | $h = -11 \text{ to } 10$, $k = -13 \text{ to } 12$, $l = -43 \text{ to } 43$ |

**Refinement**

| Refinement on           | $F^2$                                  |
|-------------------------|----------------------------------------|
| $R[F^2 > 2\sigma(F^2)]$, wR($F^2$), $S$ | 0.039, 0.089, 1.04                     |
| No. of reflections      | 13147                                   |
| No. of parameters       | 787                                     |
| No. of restraints       | 568                                     |
| H-atom treatment        | H-atom parameters constrained          |
| Weighting scheme        | $w = 1/[\sigma^2(F_c^2) + (0.0222P)^2 + 2.0196P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $(\Delta/\sigma)_{\text{max}}$ | 0.002                                 |
| $\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å$^{-3}$) | 0.34, -0.41 |
| Extinction method       | SHEXL2018/3 (Sheldrick 2018), $Fc^*=kFc[1+0.001xFc^2\text{sin}^2(\theta)/\text{sin}(2\theta)]^{-1/4}$ |
| Extinction coefficient  | 0.0042 (3)                              |
### Compound 23

| **Crystal data** |  |
|------------------|------------------|
| **Chemical formula** | C_{18}H_{18}O |
| **$M_r$** | 250.32 |
| **Crystal system, space group** | Triclinic, $P\overline{1}$ |
| **Temperature (K)** | 150 |
| **$a, b, c$ (Å)** | 5.6796 (6), 13.8004 (18), 17.618 (2) |
| **$\alpha, \beta, \gamma$ (°)** | 98.691 (8), 91.838 (9), 93.043 (7) |
| **$V$ (Å$^3$)** | 1362.0 (3) |
| **$Z$** | 4 |
| **$F(000)$** | 536 |
| **$D_r$ (Mg m$^{-3}$)** | 1.221 |
| **Radiation type** | Cu $K\alpha$ |
| **No. of reflections for cell measurement** | 9724 |
| **$\theta$ range (°) for cell measurement** | 2.5–80.3 |
| **$\mu$ (mm$^{-1}$)** | 0.57 |
| **Crystal shape** | Fragment |
| **Colour** | Colourless |
| **Crystal size (mm)** | $0.40 \times 0.23 \times 0.21$ |

**Data collection**

| **Diffractometer** | Bruker AXS D8 Quest CMOS diffractometer |
|---------------------|----------------------------------------|
| **Radiation source** | I-mu-S microsource X-ray tube |
| **Monochromator** | Laterally graded multilayer (Goebel) mirror |
| **Scan method** | $\omega$ and phi scans |
| **Absorption correction** | Multi-scan SADABS 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10 |

$T_{\text{min}}$, $T_{\text{max}}$ | 0.474, 0.754 |
### Supporting Information

| No. of measured, independent and observed \([I > 2\sigma(I)]\) reflections | 27448, 5832, 5311 |
|---|---|
| \(R_{int}\) | 0.083 |
| \(\theta\) values (°) | \(\theta_{\text{max}} = 80.8, \theta_{\text{min}} = 2.5\) |
| \((\sin \theta/\lambda)_{\text{max}}\) (Å\(^{-1}\)) | 0.640 |
| Range of \(h, k, l\) | \(h = -7 \rightarrow 7, k = -16 \rightarrow 17, l = -22 \rightarrow 22\) |

### Refinement

| Refinement on | \(F^2\) |
|---|---|
| \(R[F^2 > 2\sigma(F^2)], wR(F^2), S\) | 0.051, 0.144, 1.06 |
| No. of reflections | 5832 |
| No. of parameters | 343 |
| No. of restraints | 0 |
| H-atom treatment | H-atom parameters constrained |
| Weighting scheme | 
\[
w = \frac{1}{\sigma^2(F_o) + (0.0665P)^2 + 0.2621P} \]
where \(P = (F_o^2 + 2F_c^2)/3\) |
| \((\Delta/\sigma)_{\text{max}}\) | \(< 0.001\) |
| \(\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}\) (e Å\(^{-3}\)) | 0.35, -0.26 |
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