Catalytic Ring-Opening of Cyclic Alcohols Enabled by PCET Activation of Strong O-H Bonds

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Supporting Information

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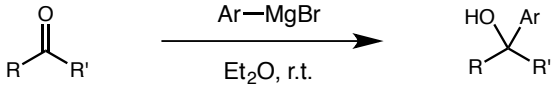
General Information

Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] All solvents were purified according to the method of Grubbs.[2] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath. Chromatographic purification of products was accomplished by flash chromatography on a Biotage Isolera One with cartridges containing Fluka 230–400 mesh silica gel or Acros Brockmann I 70–290 mesh neutral alumina. Thin-layer chromatography (TLC) was performed on Silicycle 250 μm silica gel plates or Sorbent Technologies 250 μm neutral alumina plates. Visualization of the developed chromatogram was performed by irradiation with UV light or treatment with a solution of potassium permanganate, ceric ammonium molybdate, or 2,4-dinitrophenylhydrazine stain followed by heating. Yields refer to purified compounds unless otherwise noted.

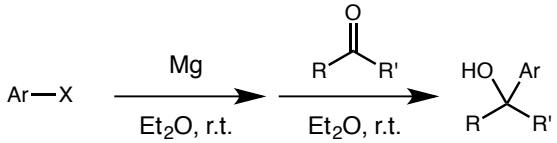
All ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance II 500 (500 and 126 MHz for ^{1}H and ^{13}C respectively), Bruker Avance III 300 (75 MHz for ^{13}C), or Bruker Avance III HD 800 (800 MHz for ^{1}H) instruments, and are internally referenced to residual protio-solvent signals: $CDCl_3$ at δ 7.26 and 77.16 ppm and C_6D_6 at δ 7.16 and 128.06 ppm. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), broad peak (b), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, m = multiplet), coupling constant (Hz) and integration; data for ^{13}C NMR are reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra were obtained at Princeton University Mass Spectrometry Facility using an Agilent 6210 TOF LC/MS (Electrospray Ionization) or an Agilent 7200 Q-TOF GC/MS (Electron Ionization); low-resolution ones were obtained on an Agilent 6120 LC/MS (Electrospray Ionization) or an Agilent 5975C GC/MSD (Electron Ionization). Cyclic voltammograms were acquired on a CH Instruments 600E potentiostat. Stern-Volmer experiments and measurement of the emission spectrum of photocatalyst were conducted on an Agilent Cary Eclipse Fluorescence Spectrophotometer.

Synthesis of Starting Materials



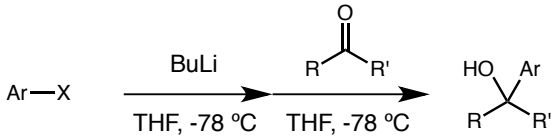
Procedure A (Grignard solution):

A flame-dried 250 mL round bottom flask was charged with a stir bar and degassed. Commercial 4-methoxyphenylmagnesium bromide solution (2.0 equiv, 0.5 M THF solution) was syringed into the flask. The relevant ketone (1.0 equiv) was added dropwise into the solution. The reaction was stirred at room temperature and consumption of starting material was monitored by TLC. Upon completion, the reaction mixture was quenched by slow addition of ice water. The aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, concentrated and purified by neutral alumina flash column chromatography (hexanes/EtOAc) to obtain the pure alcohol.



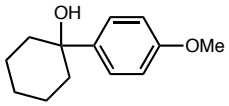
Procedure B (Grignard):

A flame-dried 250 mL round bottom flask was charged with a stir bar, catalytical amount of iodine, 1-iodo-4-methoxybenzene (1.5 equiv), and magnesium (1.75 equiv). The flask was then evacuated and carefully refilled with argon. Et_2O was added to make a 0.5 M solution of the aryl iodide, and the mixture was stirred at room temperature under Ar for 45 minutes to allow complete formation of the aryl Grignard reagent. The solution was cooled to 0 °C in an ice bath, and the ketone (1.0 equiv, 1.0 M Et_2O or THF solution) was added in dropwise. The reaction was allowed to warm to room temperature and consumption of ketone was monitored by TLC. Upon completion, dropwise addition of H_2O quenched the reaction. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, concentrated, and purified by neutral alumina flash column chromatography (hexanes/EtOAc) to afford the pure alcohol.



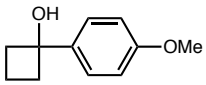
Procedure C (Lithiation):

Aryl bromide or the parental arene (1.0 equiv) was added into a flame-dried 100 mL round bottom flask containing a stir bar, and dissolved in anhydrous THF. The solution was purged with argon and cooled to –78 °C. Then *n*-BuLi (1.1 equiv) or *t*-BuLi (2.0 equiv) was added slowly into the solution. The reaction mixture was stirred at –78 °C and lithiation monitored by GC. When the aryl bromide was fully consumed, the ketone (1.0 equiv) was added dropwise via syringe. The reaction was allowed to warm up to room temperature and the consumption of ketone was monitored by TLC. Upon completion, the reaction mixture was quenched by slow addition of 30 mL saturated ammonium chloride. Organics were extracted three times with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, concentrated, and purified by neutral alumina flash column chromatography (hexanes/EtOAc) to obtain the pure alcohol.



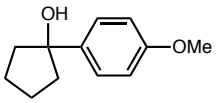
1-(4-methoxyphenyl)cyclohexan-1-ol

The titled compound was prepared according to a literature procedure.[3] Spectra are consistent with reported literature values. $E_{p/2}$ **(vs. Fc/Fc$^+$)** = 1.22 V.



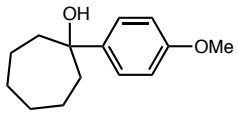
1-(4-methoxyphenyl)cyclobutan-1-ol

Prepared following the general procedure A with cyclobutanone to afford the titled compound as a colorless oil (2.1 g, 88%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.32 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 3.33 (s, 3H), 2.37 (dddd, *J* = 11.6, 9.2, 5.3, 2.7 Hz, 2H), 2.25 – 2.14 (m, 2H), 1.83 (tdd, *J* = 9.4, 5.9, 4.5 Hz, 1H), 1.51 (dddd, *J* = 16.4, 11.1, 8.8, 7.6 Hz, 1H). **^{13}C NMR (126 MHz, C_6D_6)** δ 158.9, 139.0, 126.2, 113.6, 76.2, 54.5, 37.2, 13.0. **IR (neat):** 3392, 2984, 2940, 2836, 1611, 1512, 1299, 1177, 1030, 828 cm^{-1}. **HRMS (EI):** exact mass calculated for [M•]$^+$ ($C_{11}H_{14}O_2$) requires *m/z* 178.0988, found *m/z* 178.0992.



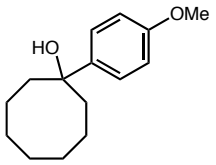
1-(4-methoxyphenyl)cyclopentan-1-ol

Prepared following the general procedure A with cyclopentanone to afford the titled compound as a colorless oil (2.8 g, 64%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.32 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.35 (d, *J* = 2.1 Hz, 3H), 1.99 – 1.84 (m, 2H), 1.79 (ddd, *J* = 11.5, 5.4, 2.4 Hz, 4H), 1.62 (ddd, *J* = 10.6, 5.2, 1.9 Hz, 2H). **^{13}C NMR (126 MHz, C_6D_6)** δ 158.6, 139.6, 126.3, 113.4, 82.5, 54.5, 41.7, 23.8. **IR (neat)**: 3405, 2955, 2872, 2836, 1611, 1581, 1511, 1463, 1442, 1365, 1297, 1240, 1177, 1114, 1093, 1033, 1000, 961, 904, 883, 795, 732 cm^{-1}. **HRMS (ESI):** exact mass calculated for [M-H_2O+H]$^+$ ($C_{12}H_{15}O$) requires *m/z* 175.11175, found *m/z* 175.11164.

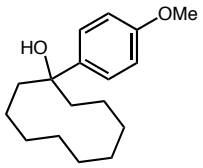


1-(4-methoxyphenyl)cycloheptan-1-ol

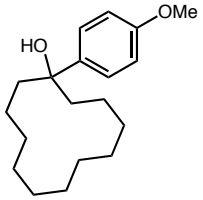
Prepared following the general procedure A with cycloheptan-1-one to afford the titled compound as a colorless oil (1.38 g, 74%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.37 (d, *J* = 8.8 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 3.36 (s, 1H), 1.88 (ddd, *J* = 14.4, 10.6, 1.8 Hz, 1H), 1.82 – 1.68 (m, 2H), 1.63 – 1.54 (m, 1H), 1.52 – 1.36 (m, 2H). **^{13}C NMR (126 MHz, C_6D_6)** δ 158.4, 143.5, 125.7, 113.4, 75.8, 54.5, 43.3, 28.9, 22.4. **IR (neat):** 3421, 2922, 2856, 1609, 1510, 1460, 1245, 1178, 1033, 799 cm^{-1}. **HRMS (EI):** exact mass calculated for [M•]$^+$ ($C_{14}H_{20}O_2$) requires *m/z* 220.1458, found *m/z* 220.1459.



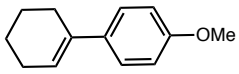
1-(4-methoxyphenyl)cyclooctan-1-ol
Prepared following the general procedure A with cyclooctan-1-one to afford the titled compound as a colorless oil (2.97 g, 76%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.39 (d, *J* = 8.9 Hz, 2H), 6.84 (d, *J* = 8.9 Hz, 2H), 3.36 (s, 2H), 1.92 (ddd, *J* = 14.9, 8.5, 1.8 Hz, 2H), 1.83 (ddd, *J* = 14.8, 9.8, 2.2 Hz, 2H), 1.76 – 1.64 (m, 2H), 1.63 – 1.50 (m, 3H), 1.48 – 1.35 (m, 5H). **^{13}C NMR (126 MHz, C_6D_6)** δ 158.5, 141.8, 126.3, 113.3, 75.6, 54.5, 37.9, 28.4, 24.4, 21.9. **IR (neat):** 3414, 2919, 2851, 1609, 1510, 1301, 1243, 1178, 1038, 830, 804 cm^{-1}. **HRMS (EI):** exact mass calculated for $[M\bullet]^+$ ($C_{15}H_{22}O_2$) requires *m/z* 234.1614, found *m/z* 234.1612.



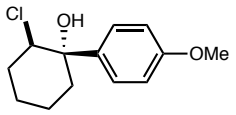
1-(4-methoxyphenyl)cyclodecan-1-ol
Prepared following the general procedure A with cyclodecan-1-one to afford the titled compound as a white solid (1.86 g, 39%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.41 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 3.37 (s, 3H), 1.95 (dt, *J* = 14.4, 6.1 Hz, 2H), 1.83 (dt, *J* = 14.2, 6.7 Hz, 2H), 1.60 – 1.36 (m, 14H). **^{13}C NMR (126 MHz, C_6D_6)** δ 158.5, 141.4, 126.3, 113.2, 76.5, 54.4, 35.5, 26.6, 26.0, 23.7, 21.6. **IR (neat):** 3363, 2920, 2845, 1610, 1582, 1510, 1483, 1442, 1297, 1245, 1178, 1038, 830 cm^{-1}. **MS (EI):** exact mass calculated for $[M\text{-}H_2O]^+$ ($C_{17}H_{24}O$) requires *m/z* 244.2, found *m/z* 244.2.



1-(4-methoxyphenyl)cyclododecan-1-ol
Prepared following the general procedure A with cyclododecanone to afford the titled compound as a white solid (2.93 g, 77%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.38 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.38 (s, 3H), 1.75 (ddt, *J* = 25.0, 13.4, 7.0 Hz, 4H), 1.30 (tt, *J* = 18.8, 9.8 Hz, 18H). **^{13}C NMR (126 MHz, C_6D_6)** δ 158.5, 141.1, 126.5, 113.2, 75.4, 54.5, 35.6, 26.4, 26.2, 22.5, 22.2, 20.0. **IR (neat):** 3334, 2933, 2848, 1609, 1509, 1470, 1178, 1038, 826, 737 cm^{-1}. **MS (EI):** exact mass calculated for $[M\text{-}H_2O]^+$ ($C_{19}H_{28}O$) requires *m/z* 272.2, found *m/z* 272.1.

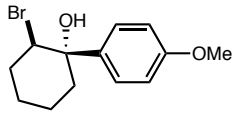


4′-methoxy-2,3,4,5-tetrahydro-1,1′-biphenyl
The titled compound was prepared according to a literature procedure.[3] Spectra are consistent with reported literature values.



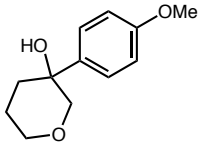
()-2-chloro-1-(4-methoxyphenyl)cyclohexan-1-ol
Trichloroisocyanuric acid (0.460 g, 1.8 mmol) was added in small portions to a stirred solution

of 4′-methoxy-2,3,4,5-tetrahydro-1,1′-biphenyl (1.000 g, 5.3 mmol) in a degassed mixture of acetone (12 mL) and water (3 mL). Upon completion, aqueous sodium bicarbonate (30 mL, saturated) and CH_2Cl_2 (30 mL) was added to the solution. The mixture was extracted with CH_2Cl_2 (2 × 30 mL) and the combined organic layers were washed with brine, drived over Na_2SO_4 and concentrated. The crude mixture was purified on silica gel to afford the titled compound as a pale lilac solid as a single diastereomer (0.95 g, 74%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.30 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 4.14 (q, *J* = 2.8 Hz, 1H), 3.32 (s, 3H), 2.40 (td, *J* = 13.1, 4.0 Hz, 1H), 2.30 (ddt, *J* = 14.8, 13.4, 4.3 Hz, 1H), 1.86 – 1.71 (m, 2H), 1.65 (qt, *J* = 12.6, 3.6 Hz, 1H), 1.49 – 1.29 (m, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 159.1, 138.5, 127.0, 113.3, 73.7, 65.4, 54.4, 30.6, 30.2, 20.7, 19.2. **IR (neat):** 3451, 2938, 2864, 1610, 1514, 1443, 1295, 1249, 1180, 1148, 1035, 973, 827, 812, 795, 719 cm^{-1}. **MS (EI):** exact mass calculated for $[M\text{-}HCl]^+$ ($C_{13}H_{16}O_2$) requires *m/z* 204.1, found *m/z* 204.1.



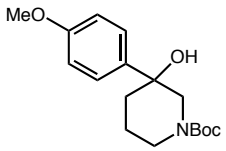
2-bromo-1-(4-methoxyphenyl)cyclohexan-1-ol

4′-methoxy-2,3,4,5-tetrahydro-1,1′-biphenyl (1.000 g, 5.3 mmol) was dissolved in degassed acetone (10 mL) and water (5 mL) with *N*-bromosuccinimide (0.947 g, 5.3 mmol). The mixture was stirred at 0 °C for an hour, then allowed to reach room temperature. Upon completion, 30 mL water was added to the reaction mixture and was extracted with ethyl acetate (4 × 30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. The crude mixture was purified on silica gel to afford the titled compound as an off-white solid as a single diastereomer (0.8 g, 53%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.27 (d, *J* = 8.9 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 4.31 (td, *J* = 3.7, 3.3, 2.0 Hz, 1H), 3.31 (s, 2H), 2.53 – 2.44 (m, 1H), 2.35 (ddt, *J* = 14.2, 12.3, 3.5 Hz, 1H), 1.95 – 1.87 (m, 1H), 1.81 (qt, *J* = 12.7, 3.7 Hz, 1H), 1.72 – 1.60 (m, 1H), 1.45 (dqd, *J* = 12.7, 4.4, 3.7, 2.1 Hz, 1H), 1.35 (dt, *J* = 13.4, 3.9 Hz, 1H). **^{13}C NMR (126 MHz, C_6D_6)** δ 159.1, 139.0, 126.8, 113.3, 73.5, 60.6, 54.4, 33.5, 31.0, 20.8, 20.2. **IR (neat):** 3451, 2937, 2862, 2837, 1612, 1513, 1444, 1293, 1180, 1036, 968, 826, 809, 700, 673 cm^{-1}. **MS (EI):** exact mass calculated for $[M\text{-}HBr\text{-}H_2O]^+$ ($C_{13}H_{14}O$) requires m/z 186.1, found m/z 186.2.



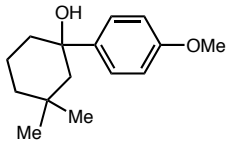
3-(4-methoxyphenyl)tetrahydro-2*H*-pyran-3-ol

Prepared following the general procedure B with dihydro-2*H*-pyran-3(4*H*)-one to afford the titled compound as a white solid (3.03 g, 58%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.44 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 3.73 – 3.65 (m, 1H), 3.62 (dd, *J* = 11.4, 2.3 Hz, 1H), 3.40 (d, *J* = 11.5 Hz, 1H), 3.32 (s, 3H), 3.11 (td, *J* = 11.2, 2.6 Hz, 1H), 3.02 (bs, 1H), 1.85 – 1.62 (m, 3H), 1.16 – 1.04 (m, 1H). **^{13}C NMR (126 MHz, C_6D_6)** δ 158.9, 136.8, 126.5, 113.5, 76.9, 70.3, 67.5, 54.5, 35.5, 22.2. **IR (neat):** 3431, 2949, 2843, 1609, 1512, 1302, 1246, 1177, 1082, 1034, 1016, 916, 827, 793, 731 cm^{-1}. **HRMS (EI)**: exact mass calculated for $[M\bullet]^+$ ($C_{12}H_{16}O_3$) requires *m/z* 208.1094, found *m/z* 208.1093.



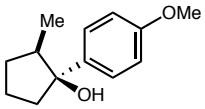
***tert*-butyl 3-hydroxy-3-(4-methoxyphenyl)piperidine-1-carboxylate**

Prepared following the general procedure B with *tert*-butyl 3-oxopiperidine-1-carboxylate to afford the titled compound as a colorless oil (2.01 g, 43%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.33 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 4.24 – 3.96 (m, 2H), 3.32 (s, 3H), 2.97 (d, *J* = 13.6 Hz, 1H), 2.56 (t, *J* = 12.6 Hz, 1H), 1.76 (t, *J* = 6.7 Hz, 1H), 1.61 – 1.49 (m, 1H), 1.45 (s, 9H), 1.18 – 1.07 (m, 2H). **^{13}C NMR (75 MHz, C_6D_6, 50 ºC)** δ 159.4, 156.0, 138.7, 126.6, 114.1, 79.5, 71.7, 55.4, 54.9, 44.5, 37.4, 28.6, 21.8. **IR (neat):** 3441, 2947, 1678, 1513, 1419, 1365, 1244, 1148, 1035, 827, 733 cm^{-1}. **MS (ESI):** exact mass calculated for $[M\text{-Boc-}H_2O+2H]^+$ ($C_{12}H_{16}NO$) requires *m/z* 190.1, found *m/z* 190.1.



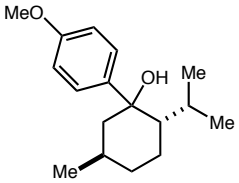
1-(4-methoxyphenyl)-3,3-dimethylcyclohexan-1-ol

Prepared following the general procedure A with 3,3-dimethylcyclohexan-1-one to afford the titled compound as a colorless oil (0.74 g, 43%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.31 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.36 (s, 3H), 2.04 – 1.91 (m, 1H), 1.65 – 1.39 (m, 6H), 1.25 (s, 3H), 1.10 (td, *J* = 13.3, 12.2, 4.0 Hz, 1H), 0.86 (s, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 158.5, 142.7, 125.8, 113.3, 73.6, 54.5, 51.0, 38.8, 34.1, 31.0, 27.2, 19.0. **IR (neat):** 3476, 2996, 2940, 2865, 2839, 1610, 1510, 1458, 1298, 1179, 1036, 989, 825, 795 cm^{-1}. **HRMS (EI):** exact mass calculated for $[M\bullet]^+$ ($C_{15}H_{22}O_2$) requires *m/z* 234.1614, found *m/z* 234.1612.



1-(4-methoxyphenyl)-2-methylcyclopentanol

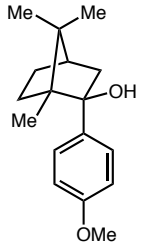
Prepared following general procedure A with 2-methylcyclopentanone to afford the titled compound as a colorless oil as a single diastereomer (0.9 g, 29%). Spectra are consistent with reported literature values.[4]



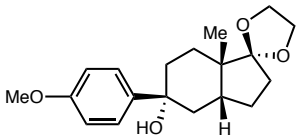
(2*S*,5*R*)-2-isopropyl-1-(4-methoxyphenyl)-5-methylcyclohexan-1-ol

Prepared following the general procedure B with menthone to afford the titled compound as a colorless oil as an ~ 3:1 mixture of diastereomers (1.3 g, 48%), which was carried on together to the next step without further separation. Characterization of this mixture is given herein. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.35 (d, *J* = 8.9 Hz, 2H), 6.88 (d, *J* = 9.1 Hz, 2H), 3.81 (s, 3H), 1.89 – 1.84 (m, 1H), 1.83 – 1.77 (m, 1H), 1.68 – 1.59 (m, 3H), 1.56 – 1.49 (m, 1H), 1.45 – 1.39 (m, 1H), 1.23 (d, *J* = 7.3 Hz, 1H), 1.07 – 0.98 (m, 1H), 0.89 (d, *J* = 6.5 Hz, 3H), 0.82 (d, *J* = 6.9 Hz,

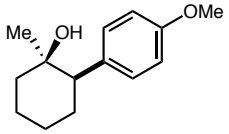
3H), 0.73 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 158.3, 140.9, 125.8, 113.4, 77.6, 54.4, 51.7, 50.2, 35.2, 28.2, 26.7, 23.6, 22.2, 21.2, 18.3. **IR (neat):** 3521, 2949, 2868, 1732, 1609, 1509, 1243, 1175, 1037, 826 cm^{-1}. **MS (ESI):** exact mass calculated for $[M\text{-}H_2O+H]^+$ ($C_{17}H_{25}O$) requires *m/z* 245.2, found *m/z* 245.2.



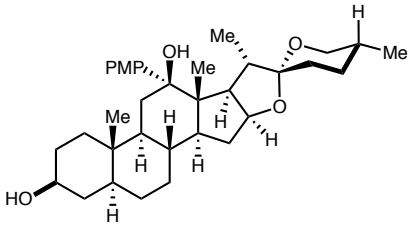
(1*R*,2*S*,4*R*)-2-(4-methoxyphenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol
The titled compound was prepared according to a literature procedure.[5] Spectra are consistent with reported literature values.



(3a*R*,7a*S*)-5-(4-methoxyphenyl)-7a-methyloctahydrospiro[indene-1,2′-[1,3]dioxolan]-5-ol
Prepared following the general procedure B with (3a*R*,7a*S*)-7a-methylhexahydrospiro[indene-1,2′-[1,3]dioxolan]-5(4*H*)-one (prepared according to a literature procedure[6]) to afford the titled compound as a colorless oil as a single diastereomer (0.701 g, 45%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.32 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.58 – 3.50 (m, 4H), 3.36 (s, 3H), 2.64 – 2.54 (m, 1H), 2.25 (td, *J* = 12.1, 11.1, 5.0 Hz, 1H), 2.19 – 2.10 (m, 2H), 2.04 – 1.93 (m, 1H), 1.90 – 1.80 (m, 3H), 1.79 – 1.71 (m, 1H), 1.63 – 1.48 (m, 2H), 1.14 (s, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 158.6, 142.6, 125.8, 120.5, 113.4, 72.9, 64.9, 63.8, 54.5, 44.1, 41.5, 37.4, 34.3, 32.9, 25.8, 24.8, 17.2. **IR (neat):** 3483, 2956, 1608, 1507, 1248, 1175, 1016, 1034, 947, 831 cm^{-1}. **MS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{19}H_{27}O_4$) requires *m/z* 319.2, found *m/z* 319.1.

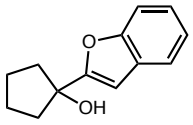


2-(4-methoxyphenyl)-1-methylcyclohexan-1-ol
Prepared following the general procedure A with methylmagnesium bromide (3.0 M in Et_2O) and 2-(4-methoxyphenyl)cyclohexan-1-one (racemic starting material prepared according to a literature procedure[7]) to afford the titled compound as a colorless oil as a single diastereomer (0.59 g, 99%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.14 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.35 (s, 3H), 2.24 (dd, *J* = 12.9, 3.4 Hz, 1H), 2.10 (qd, *J* = 12.9, 3.6 Hz, 1H), 1.86 (qt, *J* = 13.4, 3.8 Hz, 1H), 1.76 (dq, J = 13.0, 2.9 Hz, 1H), 1.68 (dt, J = 12.2, 3.4 Hz, 1H), 1.62 – 1.54 (m, 1H), 1.54 – 1.46 (m, 1H), 1.31 – 1.15 (m, 2H), 0.86 (s, 3H), 0.82 (s, 1H). **^{13}C NMR (126 MHz, C_6D_6)** δ 158.5, 135.2, 129.9, 113.4, 70.1, 54.4, 52.3, 40.3, 29.9, 29.0, 26.7, 22.0. **IR (neat):** 3499, 2928, 2856, 1609, 1510, 1448, 1243, 1178, 1035, 826, 800 cm^{-1}. **MS (ESI):** exact mass for $[M\text{-}H_2O+H]^+$ ($C_{14}H_{19}O$) requires *m/z* 203.1, found *m/z* 203.1.



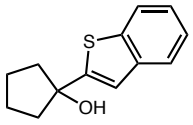
(2a*S*,4*S*,5′*R*,6a*S*,6b*S*,8a*S*,8b*R*,9*S*,10*R*,11a*S*,12a*S*)-8-(4-methoxyphenyl)-5′,6a,8a,9-tetramethyldocosahydrospiro[naphtho[2′,1′:4,5]indeno[2,1-*b*]furan-10,2′-pyran]-4,8-diol

Prepared following the general procedure B with hecogenin acetate (1 equiv), 1-iodo-4-methoxybenzene (8 equiv), and Mg (8.4 equiv) to afford the titled compound as a white solid as a single diastereomer (2.02 g, 89%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.43 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 4.69 (ddd, *J* = 8.7, 7.4, 6.2 Hz, 1H), 3.59 – 3.51 (m, 2H), 3.42 – 3.31 (m, 1H), 3.35 (s, 3H), 2.93 (dd, *J* = 8.7, 6.6 Hz, 1H), 2.24 (ddd, *J* = 14.0, 10.9, 6.0 Hz, 1H), 2.18 – 2.05 (m, 2H), 1.60 – 1.35 (m, 11H), 1.33 – 1.24 (m, 2H), 1.24 – 1.16 (m, 2H), 1.16 – 1.07 (m, 3H), 1.03 (ddd, *J* = 12.4, 10.7, 4.1 Hz, 1H), 0.95 (s, 3H), 0.85 (d, *J* = 7.0 Hz, 3H), 0.73 (s, 3H), 0.69 – 0.61 (m, 1H), 0.59 (d, *J* = 6.4 Hz, 4H), 0.51 (bs, 1H). **^{13}C NMR (126 MHz, C_6D_6)** δ 158.7, 139.1, 128.3, 112.6, 108.7, 80.7, 76.4, 70.7, 66.7, 54.5, 53.0, 49.9, 49.5, 49.1, 44.7, 42.5, 38.4, 36.8, 35.6, 35.1, 34.6, 31.8, 31.8, 31.7, 31.5, 30.3, 28.9, 28.6, 17.0, 15.3, 14.5, 12.2. **IR (neat):** 3424, 2927, 2859, 1609, 1510, 1457, 1296, 1247, 1179, 1178, 1044, 981, 899, 865, 832, 737 cm^{-1}. **MS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{34}H_{51}O_5$) requires *m/z* 539.4, found *m/z* 539.4.



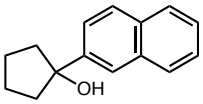
1-(benzofuran-2-yl)cyclopentanol

Prepared following general procedure C with benzofuran and cyclopentanone to afford the titled compound as a white solid (1.6 g, 54%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.40 (d, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.12 – 7.05 (m, 2H), 6.36 (s, 1H), 2.06 – 1.98 (m, 2H), 1.86 – 1.77 (m, 4H), 1.60 – 1.53 (m, 2H), 1.28 (s, 1H). **^{13}C NMR (126 MHz, C_6D_6)** δ 162.5, 155.0, 128.7, 123.8, 122.7, 120.8, 111.1, 101.0, 79.4, 39.8, 23.8. **IR (neat):** 3372, 2960, 2874, 1451, 1251, 1170, 1009, 985, 806, 750, 741 cm^{-1}. **MS (EI):** exact mass calculated for $[M\bullet]^+$ ($C_{13}H_{14}O_2$) requires *m/z* 202.1, found *m/z* 202.1. $\boldsymbol{E_{p/2}}$ **(vs. Fc/Fc$^+$)** = 1.27 V.



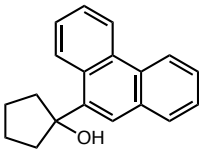
1-(benzo[*b*]thiophen-2-yl)cyclopentanol

Prepared following general procedure C with benzo[*b*]thiophene and cyclopentanone to afford the titled compound as a pale-yellow solid (1.9 g, 58%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.57 – 7.54 (m, 2H), 7.20 – 7.17 (m, 1H), 7.08 – 7.05 (m, 1H), 6.92 (s, 1H), 1.91 – 1.78 (m, 6H), 1.59 – 1.53 (m, 2H), 1.29 (s, 1H). **^{13}C NMR (126 MHz, C_6D_6)** δ 153.5, 140.1, 139.6, 124.1, 123.8, 123.2, 122.3, 118.5, 81.3, 42.5, 23.6. **IR (neat):** 3369, 2957, 2872, 1457, 1435, 1304, 1068, 1000, 828, 743, 726 cm^{-1}. **HRMS (EI):** exact mass calculated for $[M\bullet]^+$ ($C_{13}H_{14}OS$) requires *m/z* 218.0760, found *m/z* 218.0758. $\boldsymbol{E_{p/2}}$ **(vs. Fc/Fc$^+$)** = 1.18 V.



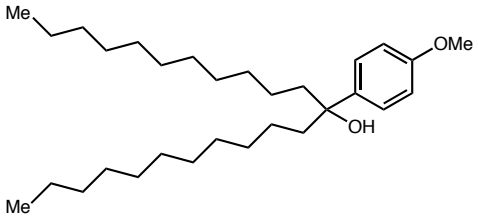
1-(naphthalen-2-yl)cyclopentanol

Prepared following general procedure C with 2-bromonaphthalene and cyclopentanone to afford the titled compound as a white solid (1.5 g, 35%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.90 (s, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.67 (t, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 1H), 7.30 (p, *J* = 7.0 Hz, 2H), 1.97 – 1.79 (m, 6H), 1.68 – 1.62 (m, 2H), 0.99 (s, 1H). **^{13}C NMR (126 MHz, C_6D_6)** δ 144.9, 133.5, 132.6, 128.1, 128.0, 127.8, 125.9, 125.5, 124.3, 123.2, 82.9, 41.9, 24.1. **IR (neat):** 3380, 2957, 2871, 1350, 1274, 1193, 1004, 856, 816, 745 cm^{-1}. **MS (EI):** exact mass calculated for $[M\bullet]^+$ ($C_{15}H_{16}O$) requires *m/z* 212.1, found *m/z* 212.1. $\boldsymbol{E_{p/2}}$ **(vs. Fc/Fc$^+$)** = 1.24 V.



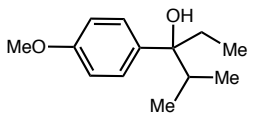
1-(phenanthren-9-yl)cyclopentanol

Prepared following general procedure C with 9-bromophenanthrene and cyclopentanone to afford the titled compound as a viscous oil (1.1 g, 41%). **^{1}H NMR (500 MHz, C_6D_6)** δ 8.96 (d, *J* = 8.5 Hz, 1H), 8.58 (d, *J* = 8.1 Hz, 1H), 8.49 – 8.47 (m, 1H), 7.73 – 7.70 (m, 1H), 7.66 (s, 1H), 7.50 – 7.41 (m, 4H), 2.16 – 2.04 (m, 4H), 2.00 – 1.91 (m, 2H), 1.64 – 1.56 (m, 2H), 1.24 (s, 1H). **^{13}C NMR (126 MHz, C_6D_6)** δ 140.3, 131.7, 131.4, 131.2, 130.5, 128.8, 128.6, 126.6, 126.5, 125.9, 125.8, 123.6, 123.1, 122.5, 83.4, 40.4, 23.7. **IR (neat):** 3554, 3377, 2953, 2871, 1449, 1185, 1000, 889, 767, 746, 726 cm^{-1}. **MS (EI):** exact mass calculated for $[M\bullet]^+$ ($C_{19}H_{18}O$) requires *m/z* 262.1, found *m/z* 262.1. $\boldsymbol{E_{p/2}}$ **(vs. Fc/Fc$^+$)** = 1.22 V.



12-(4-methoxyphenyl)tricosan-12-ol

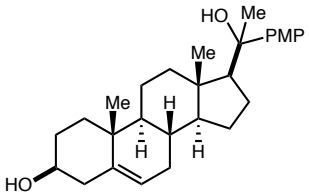
Prepared following general procedure A with tricosan-12-one to afford the titled compound as a colorless liquid (2.6 g, 38%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.34 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 3.33 (s, 3H), 1.82 – 1.68 (m, 4H), 1.43 – 1.16 (m, 37H), 0.91 (t, *J* = 6.9 Hz, 6H). **^{13}C NMR (126 MHz, C_6D_6)** δ 158.3, 138.7, 126.5, 113.4, 76.2, 54.4, 43.6, 32.0, 30.3, 29.79, 29.76, 29.74, 29.5, 23.6, 22.8, 14.0. **IR (neat):** 3475, 2922, 2852, 1612, 1511, 1464, 1247, 1178, 1039, 830 cm^{-1}. **HRMS (EI):** exact mass calculated for $[M\text{-}H_2O]^+$ ($C_{30}H_{52}O$) requires *m/z* 428.4013, found *m/z* 428.4023.



3-(4-methoxyphenyl)-2-methylpentan-3-ol

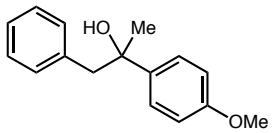
Prepared following general procedure B with 2-methylpentan-3-one to afford the titled compound as a colorless oil (1.1 g, 55%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.23 (d, *J* = 8.8 Hz, 2H),

6.83 (d, *J* = 8.8 Hz, 2H), 3.34 (s, 3H), 1.83 (p, *J* = 6.8 Hz, 1H), 1.65 (q, *J* = 7.4 Hz, 2H), 1.06 (s, 1H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.74 (d, *J* = 6.9 Hz, 3H), 0.67 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 158.2, 137.1, 127.1, 113.1, 78.5, 54.4, 37.8, 32.2, 17.4, 16.5, 7.8. **IR (neat):** 3513, 2965, 2937, 2877, 1611, 1510, 1463, 1295, 1245, 1177, 1036, 973, 826 cm^{-1}. **MS (EI):** exact mass calculated for $[M\bullet]^+$ ($C_{13}H_{20}O_2$) requires *m/z* 208.1, found *m/z* 208.1.



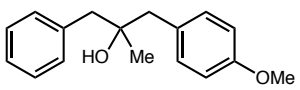
(3*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-(1-hydroxy-1-(4-methoxyphenyl)ethyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-ol

Prepared following the general procedure C with pregnenolone (1 equiv), 1-bromo-4-methoxybenzene (4 equiv), and *t*-BuLi (4 equiv) to afford the titled compound as a white solid as an ~ 2:1 mixture of diastereomers (0.95 g, 35%). The mixture of diastereomers was carried on together to the next step (characterization is given for the major diastereomer, which was separated by preparative SFC). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.35 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.37 – 5.32 (m, 1H), 3.37 (s, 3H), 2.28 – 2.15 (m, 2H), 1.98 – 1.89 (m, 2H), 1.74 – 1.49 (m, 6H), 1.43 – 1.31 (m, 2H), 1.29 (s, 3H), 1.26 (bs, 1H), 1.19 – 1.02 (m, 3H), 0.90 (s, 3H), 0.89 – 0.84 (m, 2H), 0.82 (s, 3H), 0.82 – 0.75 (m, 2H), 0.67 – 0.53 (m, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 158.7, 141.5, 141.3, 126.6, 121.5, 113.3, 75.5, 71.7, 60.7, 57.2, 54.8, 50.6, 43.1, 42.9, 39.3, 37.7, 36.8, 32.8, 32.3, 32.1, 31.7, 24.1, 23.3, 21.1, 19.5, 13.7. **IR (neat):** 3569, 3456, 2968, 2933, 2903, 2823, 1610, 1510, 1441, 1295, 1179, 1055, 1030, 839, 819, 736 cm^{-1}. **MS (ESI):** exact mass calculated for $[M\text{-}H_2O+H]^+$ ($C_{28}H_{39}O_2$) requires *m/z* 407.3, found *m/z* 407.1.



2-(4-methoxyphenyl)-1-phenylpropan-2-ol

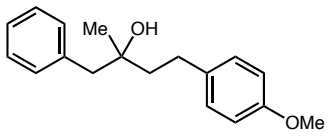
The titled compound was prepared according to a literature procedure,[8] using 1-(4-methoxyphenyl)ethan-1-one. **^{1}H NMR (500 MHz, C_6D_6)** δ 7.22 (d, *J* = 8.9 Hz, 2H), 7.10 – 7.01 (m, 3H), 6.98 – 6.94 (m, 2H), 6,79 (d, *J* = 8.9 Hz, 2H), 3.32 (s, 3H), 2.98 (d, *J* = 13.2 Hz, 1H), 2.89 (d, *J* = 13.2 Hz, 1H), 1.44 (s, 1H), 1.37 (s, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 158.9, 140.4, 137.7, 131.0, 128.2, 126.7, 126.7, 113.6, 74.1, 54.8, 51.1, 29.7. **IR (neat):** 3455, 2971, 2932, 1611, 1511, 1454, 1298, 1247, 1178, 1090, 1032, 832, 703 cm^{-1}. **HRMS (EI)**: exact mass calculated for $[M\text{-}H_2O]^+$ ($C_{16}H_{16}O$) requires *m/z* 224.1196, found *m/z* 224.1199. ***E*$_{p/2}$ (vs. Fc/Fc$^+$)** = 1.14V.



1-(4-methoxyphenyl)-2-methyl-3-phenylpropan-2-ol

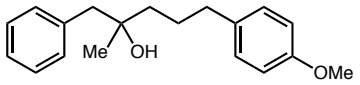
The titled compound was prepared in an analogous fashion as the above compound, using 1-(4-methoxyphenyl)propan-2-one. **^{1}H NMR (500 MHz, C_6D_6)** δ 7.18 – 7.13 (m, 4H), 7.13 – 7.07 (m, 1H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 3.32 (s, 3H), 2.69 (dd, *J* = 21.2, 13.3

Hz, 2H), 2.58 (dd, J = 16.7, 13.4 Hz, 2H), 0.91 (s, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 158.6, 138.0, 131.6, 130.8, 129.6, 128.2, 126.2, 113.5, 72.0, 54.4, 48.3, 47.5, 26.1. **IR (neat):** 3475, 3028, 2925, 2836, 1610, 1510, 1453, 1376, 1242, 1177, 1112, 1033, 832, 761, 735, 700 cm^{-1}. **HRMS (EI)**: exact mass calculated for $[M\text{-}H_2O]^+$ ($C_{17}H_{18}O$) requires *m/z* 238.1352, found *m/z* 238.1353. **$E_{p/2}$ (vs. Fc/Fc$^+$)** = 1.13 V.



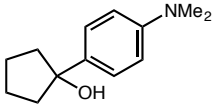
4-(4-methoxyphenyl)-2-methyl-1-phenylbutan-2-ol

The titled compound was prepared in an analogous fashion as the above compound, using 4-(4-methoxyphenyl)butan-2-one. **^{1}H NMR (500 MHz, C_6D_6)** δ 7.18 – 7.12 (m, 4H), 7.11 – 7.06 (m, 1H), 7.01 (d, J = 8.5 Hz, 2H), 6.80 (d, J = 8.6 Hz, 2H), 3.34 (s, 3H), 2.74 – 2.50 (m, 4H), 1.73 – 1.59 (m, 2H), 1.00 (s, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 158.1, 137.8, 134.6, 130.6, 129.2, 128.2, 126.3, 113.9, 71.7, 54.5, 48.2, 44.2, 29.5, 26.3. **IR (neat):** 3449, 3028, 2935, 2835, 1612, 1511, 1457, 1300, 1243, 1177, 1033, 821, 726, 701 cm^{-1}. **HRMS (EI)**: exact mass calculated for $[M\text{-}H_2O]^+$ ($C_{18}H_{20}O$) requires *m/z* 252.1509, found *m/z* 252.1511. **$E_{p/2}$ (vs. Fc/Fc$^+$)** = 1.16 V.



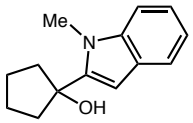
5-(4-methoxyphenyl)-2-methyl-1-phenylpentan-2-ol

Prepared following the general procedure B with 1-phenylpropan-2-one (from oxidation of 1-phenylpropan-2-ol) and 1-(3-bromopropyl)-4-methoxybenzene to afford the titled compound as a colorless oil (0.48 g, 48%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.17 – 7.06 (m, 5H), 7.01 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 3.35 (s, 3H), 2.54 (dd, J = 49.1, 13.1 Hz, 2H), 2.44 (t, J = 7.6 Hz, 2H), 1.65 (dddd, J = 22.5, 13.0, 9.4, 5.5 Hz, 2H), 1.43 – 1.29 (m, 2H), 0.93 (s, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 158.2, 137.9, 134.4, 130.6, 129.3, 128.2, 126.2, 113.8, 71.7, 54.5, 48.0, 41.4, 35.5, 26.4, 26.2. **IR (neat):** 3451, 3028, 2938, 1612, 1512, 1454, 1245, 1177, 1115, 1035, 927, 830, 729, 702 cm^{-1}. **HRMS (EI)**: exact mass calculated for $[M\text{-}H_2O]^+$ ($C_{19}H_{22}O$) requires *m/z* 266.1665, found *m/z* 266.1665. **$E_{p/2}$ (vs. Fc/Fc$^+$)** = 1.16 V.



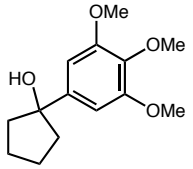
1-(4-(dimethylamino)phenyl)cyclopentanol

Prepared following general procedure A with 1-(4-(dimethylamino)phenyl)magnesium bromide (0.5 M in THF, 2.1 equiv) and cylcopentanone to afford the titled compound as a pale-yellow powder (0.8 g, 66%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.41 (d, J = 8.8 Hz, 2H), 6.66 (d, J = 8.8 Hz, 2H), 2.56 (s, 6H), 1.98 – 1.88 (m, 6H), 1.69 – 1.62 (m, 2H), 0.99 (s, 1H). **^{13}C NMR (126 MHz, C_6D_6)** δ 149.6, 135.7, 126.0, 112.5, 82.6, 41.5, 40.1, 23.8. **IR (neat):** 3353, 2964, 2948, 2851, 1612, 1521, 1329, 1208, 1134, 997, 835, 814 cm^{-1}. **MS (EI):** exact mass calculated for $[M\text{-}H_2O]^+$ ($C_{13}H_{17}N$) requires *m/z* 187.1, found *m/z* 187.2. **$E_{p/2}$ (vs. Fc/Fc$^+$)** = 0.39 V.



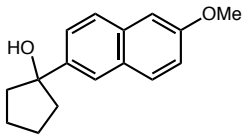
1-(1-methyl-1*H*-indol-2-yl)cyclopentanol

Prepared following general procedure C with 1-methyl-1*H*-indole and cyclopentanone to afford the titled compound as a yellow solid (0.7 g, 27%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.27 (dt, *J* = 21.1, 7.3 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 1H), 6.28 (s, 1H), 3.49 (s, 3H), 1.91 – 1.76 (m, 6H), 1.56 – 1.50 (m, 2H), 0.74 (s, 1H). **^{13}C NMR (126 MHz, C_6D_6)** δ 143.9, 138.9, 127.3, 121.6, 120.7, 119.5, 109.0, 98.6, 79.0, 39.8, 30.9, 23.6. **IR (neat):** 3378, 2951, 2872, 1468, 1385, 1313, 993, 779, 749, 732 cm^{-1}. **HRMS (EI):** exact mass calculated for $[M\bullet]^+$ ($C_{14}H_{17}NO$) requires *m/z* 215.1305, found *m/z* 215.1301. $\boldsymbol{E_{p/2}}$ **(vs. Fc/Fc$^+$)** = 0.69 V.



1-(3,4,5-trimethoxyphenyl)cyclopentan-1-ol

Prepared following the general procedure C with 5-bromo-1,2,3-trimethoxybenzene to afford the titled compound as an off-white solid (1.6 g, 78%). **^{1}H NMR (500 MHz, C_6D_6)** δ 6.73 (s, 2H), 3.87 (s, 3H), 3.48 (s, 6H), 1.98 – 1.88 (m, 2H), 1.88 – 1.79 (m, 4H), 1.72 – 1.60 (m, 2H). **^{13}C NMR (126 MHz, C_6D_6)** δ 153.5, 142.9, 138.1, 103.3, 83.0, 60.2, 55.7, 42.0, 23.9. **IR (neat):** 3440, 2945, 2872, 2836, 1587, 1509, 1451, 1410, 1236, 1003, 831, 731, 652 cm^{-1}. **HRMS (EI)**: exact mass calculated for $[M\bullet]^+$ ($C_{14}H_{20}O_4$) requires *m/z* 252.1356, found *m/z* 252.1352. $\boldsymbol{E_{p/2}}$ **(vs. Fc/Fc$^+$)** = 0.92 V.



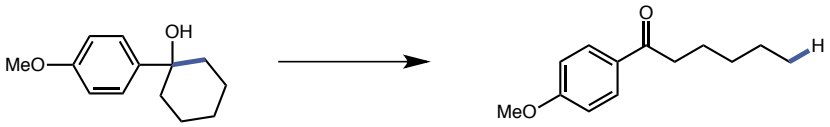
1-(6-methoxynaphthalen-2-yl)cyclopentan-1-ol

Prepared following the general procedure C with 2-bromo-6-methoxynaphthalene to afford the titled compound as a white solid (1.5 g, 73%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.84 (d, *J* = 1.8 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.59 (d, *J* = 8.9 Hz, 1H), 7.52 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.24 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 3.41 (s, 3H), 2.02 – 1.81 (m, 4H), 1.72 – 1.62 (m, 2H). **^{13}C NMR (126 MHz, C_6D_6)** δ 157.8, 142.6, 133.8, 129.6, 128.9, 126.7, 124.8, 123.3, 119.0, 105.6, 82.9, 54.5, 41.8, 24.0. **IR (neat):** 3443, 3052, 3007, 2953, 2870, 2843, 1603, 1484, 1387, 1265, 1202, 1028, 986, 854, 814, 671 cm^{-1}. **HRMS (EI)**: exact mass calculated for $[M\text{-}H_2O]^+$ ($C_{16}H_{16}O$) requires *m/z* 224.1196, found *m/z* 224.1196. $\boldsymbol{E_{p/2}}$ **(vs. Fc/Fc$^+$)** = 0.96 V.

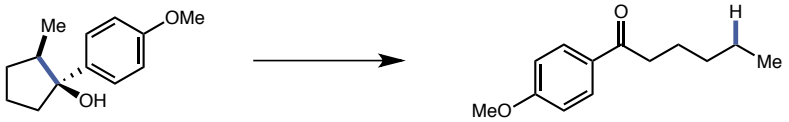
Synthesis of Products

General procedure:

A screw cap culture tube (16 × 125 mm) outfitted with a PTFE/silicone septa was charged with the relevant alcohol (1 mmol, 1 equiv),[9] $[Ir(dF(CF_3)ppy)_2(5,5'd(CF_3)bpy)](PF_6)$ (0.01 mmol, 0.01 equiv, 11 mg) and redistilled collidine (3 mmol, 3 equiv, 396 μL). The sealed culture tube was then evacuated and backfilled with argon three times. Redistilled thiophenol (0.25 mmol, 0.25 equiv, 26 μL) and 10 mL of degassed anhydrous CH_2Cl_2 were added via syringe. The reaction was irradiated by four blue LED lamps (Kessil H150B LED Grow Light), and let stir under an inert atmosphere at room temperature with a fan to cool the reaction setup. After 12–24 hours, the reaction was concentrated then purified by flash column chromatography (hexanes/EtOAc) to obtain the product. All scale-ups were run in duplicates and average yields are reported.



or

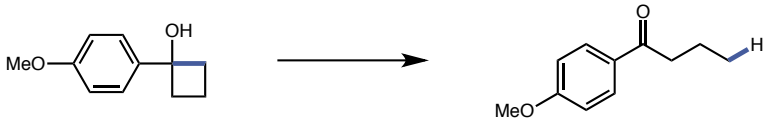


1-(4-methoxyphenyl)hexan-1-one

Prepared on 1 mmol scale following the general procedure with 1-(4-methoxyphenyl)cyclohexan-1-ol. The crude material was purified by silica gel column chromatography to afford the titled compound as a pale yellow solid (183 mg, 89%).

Alternatively, prepared on 1 mmol scale following the general procedure with 1-(4-methoxyphenyl)-2-methylcyclopentanol. The crude is purified by silica gel column chromatography to afford the titled compound as a pale yellow oil (201 mg, 97%).

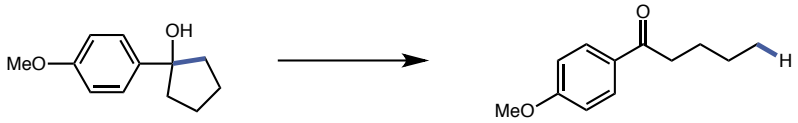
^{1}H NMR (500 MHz, C_6D_6) δ 7.89 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 8.9 Hz, 2H), 3.18 (s, 3H), 2.58 (t, *J* = 7.3 Hz, 2H), 1.73 (p, *J* = 7.3 Hz, 2H), 1.26-1.23 (m, 4H), 0.84 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 197.2, 163.1, 130.6, 130.2, 113.5, 54.5, 37.9, 31.6, 24.1, 22.6, 13.9. **IR (neat):** 2956, 2933, 1676, 1600, 1510, 1254, 1170, 1031, 830 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{13}H_{19}O_2$) requires *m/z* 207.13796, found *m/z* 207.13784.



1-(4-methoxyphenyl)butan-1-one

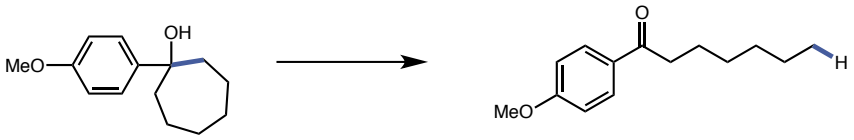
Prepared on 1 mmol scale following the general procedure with 1-(4-methoxyphenyl)cyclobutan-1-ol. The crude material was purified by silica gel column chromatography to afford the titled compound as a pale yellow oil (126 mg, 71%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.86 (d, *J* = 8.9 Hz, 2H), 6.65 (d, *J* = 8.9 Hz, 2H), 3.19 (s, 3H), 2.52 (t, *J* = 7.2 Hz, 2H), 1.72 (h, *J* = 7.4 Hz, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 197.0, 163.1, 130.6, 130.1, 113.5, 54.5,

39.8, 17.7, 13.7. **IR (neat):** 2963, 1676, 1600, 1258, 1170, 1030, 832 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{11}H_{15}O_2$) requires *m/z* 179.10666, found *m/z* 179.10692.



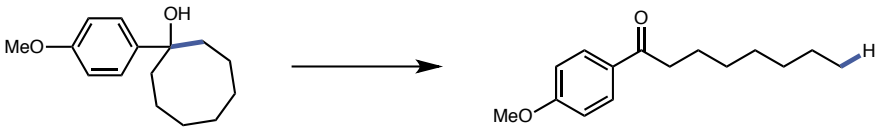
1-(4-methoxyphenyl)pentan-1-one

Prepared on 1 mmol scale following the general procedure with 1-(4-methoxyphenyl)cyclopentan-1-ol. The crude material was purified by silica gel column chromatography to afford the titled compound as a pale yellow oil (166 mg, 86%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.86 (d, *J* = 8.9 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 3.24 (s, 3H), 2.58 (t, *J* = 7.4 Hz, 2H), 1.68 (p, *J* = 7.4 Hz, 2H), 1.26 (h, *J* = 7.4 Hz, 2H), 0.84 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 197.2, 163.1, 130.5, 130.1, 113.5, 54.6, 37.6, 26.5, 22.5, 13.8. **IR (neat):** 2958, 2934, 2872, 1676, 1600, 1255, 1170, 1030, 840 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{12}H_{17}O_2$) requires *m/z* 193.12231, found *m/z* 193.12267.



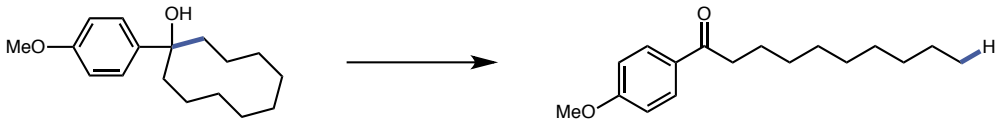
1-(4-methoxyphenyl)heptan-1-one

Prepared on 1 mmol scale following the general procedure with 1-(4-methoxyphenyl)cycloheptan-1-ol. The crude material was purified by silica gel column chromatography to afford the titled compound as a pale yellow solid (199 mg, 90%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.88 (d, *J* = 8.9 Hz, 2H), 6.67 (d, *J* = 8.9 Hz, 2H), 3.24 (s, 3H), 2.61 (t, *J* = 7.3 Hz, 2H), 1.71 (p, *J* = 7.4 Hz, 2H), 1.35 – 1.09 (m, 6H), 0.86 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 197.2, 163.1, 130.6, 130.1, 113.5, 54.6, 37.9, 31.8, 29.1, 24.4, 22.6, 14.0. **IR (neat):** 3004, 2950, 2933, 2858, 1670, 1604, 1509, 1407, 1249, 1179, 1035, 837 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{14}H_{21}O_2$) requires *m/z* 221.15361, found *m/z* 221.15353.



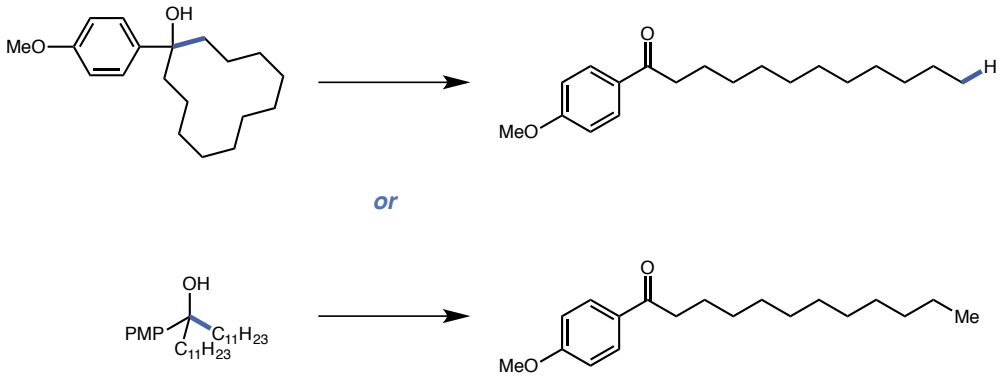
1-(4-methoxyphenyl)octan-1-one

Prepared on 1 mmol scale following the general procedure with 1-(4-methoxyphenyl)cyclooctan-1-ol. The crude material was purified by silica gel column chromatography to afford the titled compound as a pale yellow solid (189 mg, 81%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.90 (d, *J* = 8.9 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 3.19 (s, 3H), 2.61 (t, *J* = 7.3 Hz, 2H), 1.75 (p, *J* = 7.3 Hz, 2H), 1.42 – 1.09 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 197.2, 163.1, 130.6, 130.2, 113.5, 54.5, 38.0, 31.8, 29.4, 29.3, 24.5, 22.7, 14.0. **IR (neat):** 2927, 2855, 1676, 1600, 1509, 1256, 1169, 1032, 812 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{15}H_{23}O_2$) requires *m/z* 235.16926, found *m/z* 235.16923.



1-(4-methoxyphenyl)decan-1-one

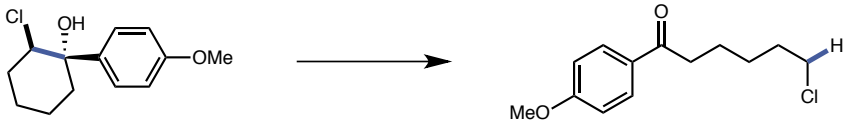
Prepared on 1 mmol scale following the general procedure with 1-(4-methoxyphenyl)cyclodecan-1-ol. The crude material was purified by silica gel column chromatography to afford the titled compound as a pale yellow solid (241 mg, 92%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.90 (d, *J* = 8.9 Hz, 2H), 6.66 (d, *J* = 8.9 Hz, 2H), 3.19 (s, 3H), 2.63 (t, *J* = 7.3 Hz, 2H), 1.77 (p, *J* = 7.3 Hz, 2H), 1.26 (d, *J* = 9.8 Hz, 12H), 0.91 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 197.2, 163.1, 130.6, 130.2, 113.5, 54.5, 38.0, 32.0, 29.7, 29.6, 29.5, 29.4, 24.5, 22.8, 14.0. **IR (neat):** 2954, 2915, 2849, 1678, 1605, 1579, 1254, 1178, 1031, 842, 811 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{17}H_{27}O_2$) requires *m/z* 263.20056, found *m/z* 263.20044.



1-(4-methoxyphenyl)dodecan-1-one

Prepared on 1 mmol scale following the general procedure with 1-(4-methoxyphenyl)cyclododec-1-ol. The crude material was purified by silica gel column chromatography to afford the titled compound as a pale yellow solid (245 mg, 85%).

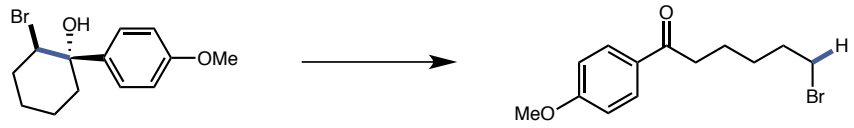
Alternatively, prepared on 1 mmol scale following the general procedure with 12-(4-methoxyphenyl)tricosan-12-ol. The crude is purified by silica gel column chromatography to afford the titled compound as a pale yellow powder (243 mg, 84%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.91 (d, *J* = 8.7 Hz, 2H), 6.66 (d, *J* = 8.7 Hz, 2H), 3.18 (s, 3H), 2.63 (t, *J* = 7.3 Hz, 2H), 1.78 (p, *J* = 7.2 Hz, 2H), 1.33-1.28 (m, 16H), 0.91 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 197.2, 163.1, 130.7, 130.2, 113.5, 54.5, 38.0, 32.0, 29.77, 29.75, 29.68, 29.5, 24.5, 22.8, 14.0. **IR (neat):** 2954, 2915, 2849, 1678, 1606, 1580, 1464, 1256, 1179, 1031, 841, 810 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{19}H_{31}O_2$) requires *m/z* 291.23186, found *m/z* 291.23176.



6-chloro-1-(4-methoxyphenyl)hexan-1-one

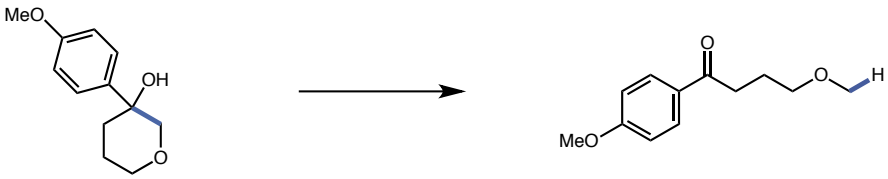
Prepared on 1 mmol scale following the general procedure with 2-chloro-1-(4-methoxyphenyl)cyclohexan-1-ol. The product was purified by silica gel column chromatography to afford the titled compound as a colorless oil (181 mg, 75%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.85 (d, *J* = 8.9 Hz, 2H), 6.68 (d, *J* = 8.9 Hz, 2H), 3.24 (s, 3H), 3.10 (t, *J* = 6.7 Hz, 2H), 2.49 (t, *J*

= 7.3 Hz, 2H), 1.54 (dt, *J* = 15.1, 7.3 Hz, 2H), 1.42 (dq, *J* = 9.1, 6.8 Hz, 2H), 1.25 – 1.13 (m, 2H). **^{13}C NMR (126 MHz, C_6D_6)** δ 196.9, 163.2, 130.4, 130.1, 113.6, 54.6, 44.5, 37.6, 32.4, 26.5, 23.4. **IR (neat):** 2938, 2865, 1674, 1599, 1575, 1509, 1418, 1309, 1256, 1169, 1029, 970, 834, 811, 718 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{13}H_{18}ClO_2$) requires *m/z* 241.09899, found *m/z* 241.09935.



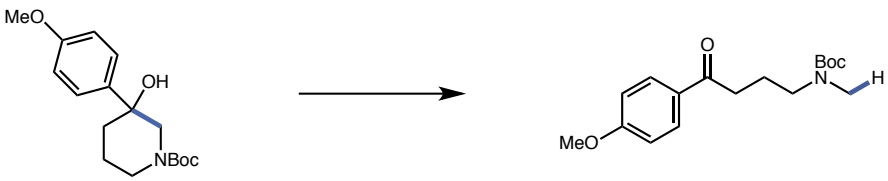
6-bromo-1-(4-methoxyphenyl)hexan-1-one

Prepared on 1 mmol scale following the general procedure with 2-bromo-1-(4-methoxyphenyl)cyclohexan-1-ol. The product was purified by silica gel column chromatography to afford the titled compound as a colorless oil (179 mg, 63%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.85 (d, *J* = 8.9 Hz, 2H), 6.68 (d, *J* = 8.9 Hz, 2H), 3.23 (s, 3H), 2.94 (t, *J* = 6.8 Hz, 2H), 2.47 (t, *J* = 7.2 Hz, 2H), 1.58 – 1.44 (m, 4H), 1.17 (tdd, *J* = 9.9, 8.4, 4.7 Hz, 2H). **^{13}C NMR (126 MHz, C_6D_6)** δ 196.8, 163.2, 130.4, 130.1, 113.6, 54.6, 37.5, 33.3, 32.6, 27.7, 23.3. **IR (neat):** 2936, 2839, 1673, 1598, 1575, 1509, 1418, 1362, 1252, 1217, 1168, 1028, 832, 810, 734 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{13}H_{18}BrO_2$) requires *m/z* 285.04847, found *m/z* 285.04882.



4-methoxy-1-(4-methoxyphenyl)butan-1-one

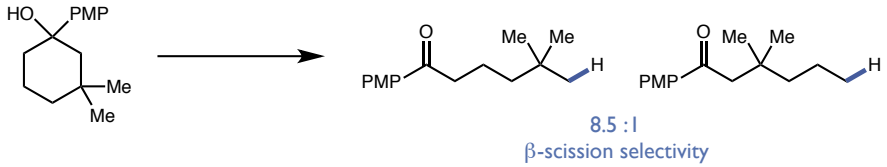
Prepared on 1 mmol scale following the general procedure with 3-(4-methoxyphenyl)tetrahydro-2*H*-pyran-3-ol. The crude material was first washed with 1.0 M HCl and then purified by alumina column chromatography to afford the titled compound as a brown solid (203 mg, 98%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.88 (d, *J* = 8.8 Hz, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 3.24 (t, *J* = 6.1 Hz, 2H), 3.20 (s, 3H), 3.08 (s, 3H), 2.79 (t, *J* = 7.2 Hz, 2H), 2.02 (p, *J* = 6.6 Hz, 2H). **^{13}C NMR (126 MHz, C_6D_6)** δ 197.1, 163.2, 130.4, 130.1, 113.5, 71.6, 57.9, 54.6, 34.5, 24.4. **IR (neat):** 2929, 1677, 1601, 1577, 1510, 1257, 1171, 1117, 1030, 836 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{12}H_{17}O_3$) requires *m/z* 209.11722, found *m/z* 209.11708.



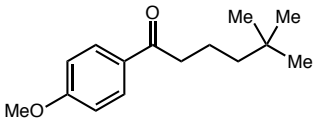
***tert*-butyl (4-(4-methoxyphenyl)-4-oxobutyl)(methyl)carbamate**

Prepared on 1 mmol scale following the general procedure with *tert*-butyl 3-hydroxy-3-(4-methoxyphenyl)piperidine-1-carboxylate. The crude material was purified by silica gel column chromatography to afford the titled compound as a colorless oil (269 mg, 88%). **^{1}H NMR (500 MHz, C_6D_6, 50 °C)** δ 7.87 (d, *J* = 8.9 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 3.24 (s, 3H), 3.21 – 3.15 (m, 2H), 2.67 (s, 3H), 2.62 (t, *J* = 6.5 Hz, 2H), 1.92 – 1.85 (m, 2H), 1.42 (s, 9H). **^{13}C NMR (75**

MHz, C_6D_6, 50 ºC) δ 196.9, 163.7, 155.8, 131.0, 130.5, 114.0, 78.8, 55.0, 48.4, 35.1, 34.0, 28.6, 22.7. **IR (neat):** 2972, 1681, 1599, 1392, 1364, 1256, 1163, 1028, 983, 830, 770 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M\text{-Boc}+2H]^+$ ($C_{12}H_{18}NO_2$) requires *m/z* 208.13321, found 208.13327.

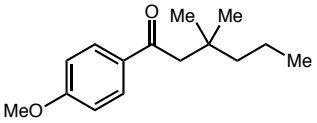


Prepared on 1 mmol scale following the general procedure with 1-(4-methoxyphenyl)-3,3-dimethylcyclohexan-1-ol. The crude material was purified by silica gel column chromatography to afford an 8.5:1 mixture of regioisomers as a pale yellow oil (220 mg, 94%). The isomers were separated by preparative SFC on a Chiralpak AD-H column (3 × 25 cm, conditions: 60 mL/min, 30% methanol, 220 nm, 10 mg/mL, 1 mL/injection) for final characterization.



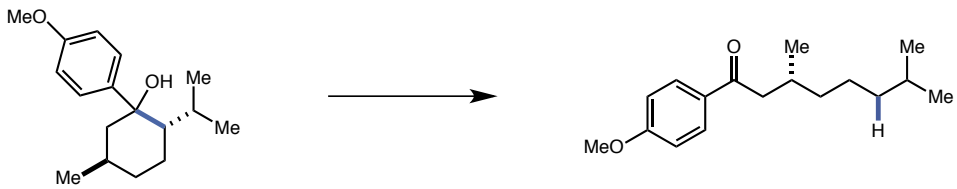
1-(4-methoxyphenyl)-5,5-dimethylhexan-1-one (major isomer)

^{1}H NMR (500 MHz, C_6D_6) δ 7.91 (d, *J* = 8.9 Hz, 2H), 6.67 (d, *J* = 8.9 Hz, 2H), 3.20 (s, 3H), 2.57 (t, *J* = 7.3 Hz, 2H), 1.85 – 1.62 (m, 2H), 1.27 – 1.07 (m, 2H), 0.88 (s, 9H). **^{13}C NMR (126 MHz, C_6D_6)** δ 197.1, 163.1, 130.7, 130.1, 113.5, 54.5, 43.8, 38.7, 30.1, 29.1, 19.5. **IR (neat):** 3000, 2954, 2901, 2865, 1668, 1601, 1577, 1420, 1256, 1182, 1033, 978, 826, 819 cm^{-1}. **HRMS (ESI)** exact mass calculated for $[M+H]^+$ ($C_{15}H_{23}O_2$) requires *m/z* 235.16926, found *m/z* 235.16884.



1-(4-methoxyphenyl)-3,3-dimethylhexan-1-one (minor isomer)

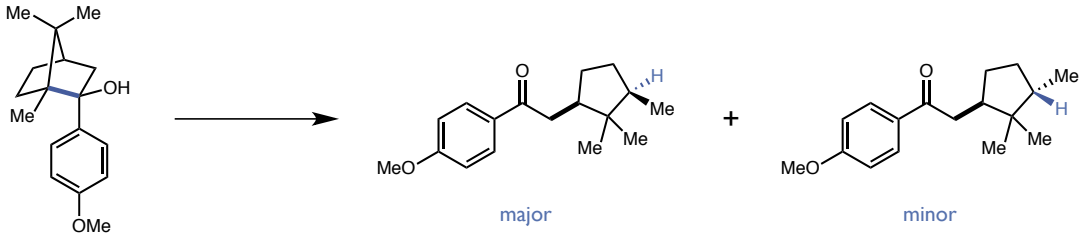
^{1}H NMR (500 MHz, C_6D_6) δ 7.90 (d, *J* = 8.9 Hz, 2H), 6.65 (d, *J* = 8.9 Hz, 2H), 3.18 (s, 3H), 2.62 (s, 2H), 1.43 – 1.35 (m, 2H), 1.29 – 1.16 (m, 2H), 1.06 (s, 6H), 0.87 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 197.2, 163.0, 132.1, 130.3, 113.4, 54.5, 47.3, 45.0, 33.6, 27.6, 17.4, 14.8. **IR (neat):** 2957, 2871, 1667, 1600, 1509, 1463, 1257, 1170, 1034, 1019, 844 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{15}H_{23}O_2$) requires *m/z* 235.16926, found *m/z* 235.16921.



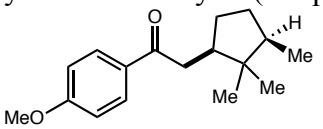
(*R*)-1-(4-methoxyphenyl)-3,7-dimethyloctan-1-one

Prepared on 1 mmol scale following the general procedure with (2*S*,5*R*)-2-isopropyl-1-(4-

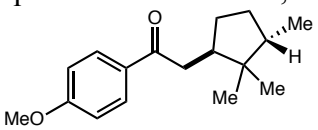
methoxyphenyl)-5-methylcyclohexanol. The crude material was purified by silica gel column chromatography to afford the titled compound as a colorless oil (235 mg, 90%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H), 2.89 (dd, *J* = 15.4, 5.7 Hz, 1H), 2.69 (dd, *J* = 15.4, 8.0 Hz, 1H), 2.21 – 2.08 (m, 1H), 1.52 (dp, *J* = 13.2, 6.8 Hz, 1H), 1.38 – 1.32 (m, 2H), 1.31 – 1.25 (m, 1H), 1.24 – 1.19 (m, 1H), 1.19 – 1.10 (m, 2H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.86 (dd, *J* = 6.6, 1.7 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 199.2, 163.3, 130.6, 130.4, 113.6, 55.5, 45.7, 39.1, 37.5, 30.1, 28.0, 24.8, 22.7, 22.6, 20.1. **IR (neat):** 2954, 2926, 1673, 1599, 1576, 1509, 1257, 1168, 1031, 828, 808 cm-1; **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{17}H_{27}O_2$) requires *m/z* 263.20056, found *m/z* 263.20097.



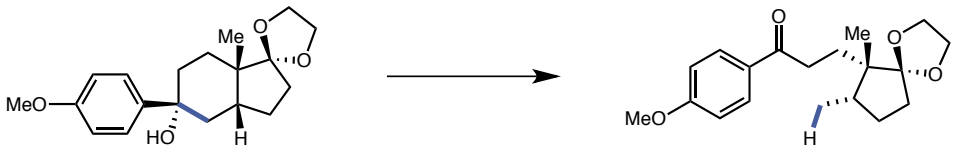
Prepared on 1 mmol scale following the general procedure with (1*R*,2*S*,4*R*)-2-(4-methoxyphenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol. The crude material was purified by silica gel column chromatography to afford a 6:1 mixture of diastereomers as a colorless oil (238 mg, 91%). The diastereomers were separated via preparative SFC on a Chiralpak AD-H column (2 × 25 cm, conditions: 70 mL/min, 15% methanol, 220 nm, 7 mg/mL, 1 mL/injection) and their stereochemistries were determined by NOESY analysis (see product NMR section).



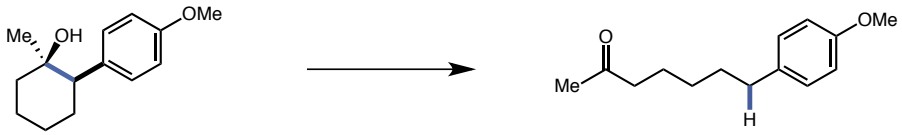
1-(4-methoxyphenyl)-2-((1*R*,3*R*)-2,2,3-trimethylcyclopentyl)ethan-1-one (major isomer)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H), 2.99 (dd, *J* = 15.1, 3.2 Hz, 1H), 2.66 (dd, *J* = 15.1, 10.8 Hz, 1H), 2.06 – 1.97 (m, 1H), 1.89 – 1.81 (m, 1H), 1.79 – 1.71 (m, 1H), 1.58 – 1.51 (m, 1H), 1.27 – 1.11 (m, 2H), 0.94 (s, 3H), 0.85 (d, *J* = 6.9 Hz, 3H), 0.61 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 199.5, 163.3, 130.4, 127.3, 113.6, 55.5, 46.8, 44.6, 42.5, 39.6, 30.1, 28.3, 25.5, 14.8, 14.0. **IR (neat):** 2952, 2869, 1673, 1598, 1575, 1509, 1313, 1210, 1166, 1029, 991, 824, 807 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{17}H_{25}O_2$) requires *m/z* 261.18491, found *m/z* 261.18505.



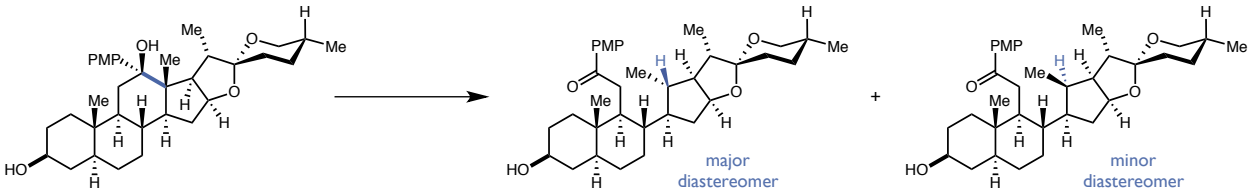
1-(4-methoxyphenyl)-2-((1*R*,3*S*)-2,2,3-trimethylcyclopentyl)ethan-1-one (minor isomer)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 2.97 (dd, *J* = 15.2, 4.0 Hz, 1H), 2.68 (dd, *J* = 15.3, 10.5 Hz, 1H), 2.18 (dtd, *J* = 10.2, 7.9, 3.9 Hz, 1H), 1.93 – 1.87 (m, 1H), 1.87 – 1.82 (m, 1H), 1.66 (h, *J* = 7.0 Hz, 1H), 1.27 – 1.13 (m, 2H), 0.89 (s, 3H), 0.87 (s, 3H), 0.86 (d, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 199.6, 163.2, 130.5, 130.4, 113.7, 55.5, 44.4, 43.5, 42.3, 40.1, 31.4, 29.5, 24.3, 23.6, 16.4. **IR (neat):** 2952, 2869, 1673, 1598, 1575, 1509, 1313, 1210, 1166, 1029, 991, 824, 807 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{17}H_{25}O_2$) requires *m/z* 261.18491, found *m/z* 261.18505.



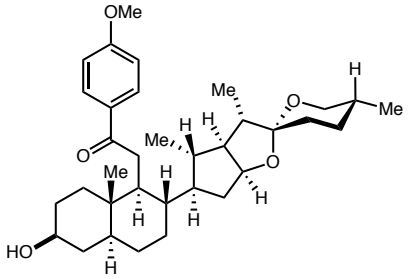
3-((6*S*,7*S*)-6,7-dimethyl-1,4-dioxaspiro[4.4]nonan-6-yl)-1-(4-methoxyphenyl)-propan-1-one
Prepared on 1 mmol scale following the general procedure with (3a′*R*,7a′*S*)-5′-(4-methoxyphenyl)-7a′-methyloctahydrospiro[[1,3]dioxolane-2,1′-inden]-5′-ol. The crude material was purified by silica gel column chromatography to afford the titled compound as a colorless oil (195 mg, 61%). **^{1}H NMR (500 MHz, C_6D_6)** δ 8.09 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.9 Hz, 2H), 3.50 – 3.39 (m, 4H), 3.34 (ddd, *J* = 16.2, 11.1, 5.1 Hz, 1H), 3.18 (s, 3H), 2.88 (ddd, *J* = 16.2, 11.0, 5.2 Hz, 1H), 2.08 – 2.02 (m, 1H), 2.02 – 1.94 (m, 2H), 1.89 – 1.84 (m, 1H), 1.82 – 1.74 (m, 2H), 1.28 – 1.20 (m, 1H), 1.05 (s, 3H), 0.96 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 198.3, 163.0, 130.8, 130.3, 120.1, 113.6, 64.7, 63.3, 54.5, 47.0, 41.8, 34.0, 32.8, 27.4, 25.8, 18.9, 15.5. **IR (neat):** 2958, 2876, 1673, 1599, 1575, 1509, 1306, 1255, 1169, 1028, 986, 839 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{19}H_{27}O_4$) requires *m/z* 319.19039, found *m/z* 319.19003.



7-(4-methoxyphenyl)heptan-2-one
Prepared on 1 mmol scale following the general procedure with 2-(4-methoxyphenyl)-1-methylcyclohexanol. The crude material was purified by silica gel column chromatography to afford the titled compound as a colorless oil (200 mg, 91%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.08 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 2.58 – 2.49 (m, 2H), 2.41 (t, *J* = 7.5 Hz, 2H), 2.12 (s, 3H), 1.64 – 1.54 (m, 4H), 1.35 – 1.27 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 209.3, 157.6, 134.6, 129.2, 113.7, 55.3, 43.7, 34.8, 31.5, 29.9, 28.7, 23.7. **IR (neat):** 2930, 2855, 1712, 1611, 1510, 1242, 1175, 1034, 822 cm^{-1}. **HRMS (EI):** exact mass calculated for $[M\bullet]^+$ ($C_{14}H_{20}O_2$) requires *m/z* 220.1458, found *m/z* 220.1454.

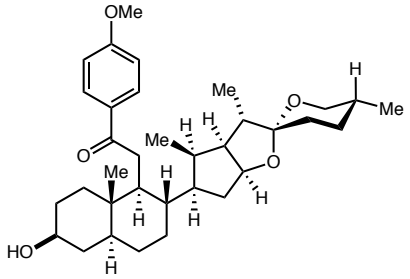


Prepared on 0.5 mmol scale following the general procedure with (2a*S*,4*S*,5′*R*,6a*S*,6b*S*,8*R*,8b*R*,9*S*,10*R*,11a*S*,12a*S*,12b*R*)-8-(4-methoxyphenyl)-5′,6a,8a,9-tetramethyldocosahydrospiro[naphtho[2′,1′:4,5]indeno[2,1-*b*]furan-10,2′-pyran]-4,8-diol (269 mg). The crude material was purified by silica gel column chromatography to afford an 8:1 mixture of diastereomers as a colorless oil (220 mg, 81%). The diastereomer were separated via preparative SFC on a Chiralpak AD-H column (3 × 25 cm, conditions: 60 mL/min, 30% isopropanol, 220 nm, 7 mg/mL, 1 mL/injection) and their stereochemistries were determined by NOESY analysis (see product NMR section).



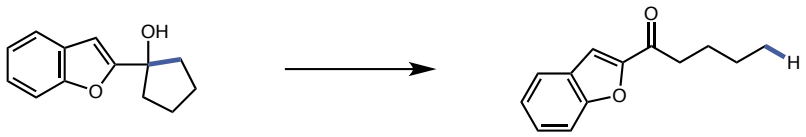
2-((1*S*,2*S*,4a*S*,6*S*,8a*S*)-6-hydroxy-8a-methyl-2-((2*R*,3*S*,3a*S*,4*S*,5*R*,5′*R*,6a*S*)-3,4,5′-trimethyldecahydrospiro[cyclopenta[*b*]furan-2,2′-pyran]-5-yl)decahydronaphthalen-1-yl)-1-(4-methoxyphenyl)ethan-1-one (major isomer)

^{1}H NMR (500 MHz, C_6D_6) δ 7.96 (d, *J* = 8.9 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 4.39 (dt, *J* = 8.8, 7.1 Hz, 1H), 3.57 – 3.41 (m, 2H), 3.34 (tt, *J* = 10.7, 4.9 Hz, 1H), 3.16 (s, 3H), 2.74 (dd, *J* = 18.1, 5.9 Hz, 1H), 2.60 (dd, *J* = 18.0, 3.0 Hz, 1H), 2.38 (ddd, *J* = 12.5, 7.1, 5.5 Hz, 1H), 2.16 (ddd, *J* = 11.3, 5.9, 3.0 Hz, 1H), 1.75 – 1.65 (m, 3H), 1.65 – 1.39 (m, 11H), 1.39 – 1.31 (m, 1H), 1.31 – 1.24 (m, 2H), 1.24 – 1.14 (m, 4H), 1.11 (d, *J* = 6.8 Hz, 3H), 1.00 – 0.89 (m, 2H), 0.87 (d, *J* = 6.5 Hz, 3H), 0.69 (s, 3H), 0.64 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 196.3, 163.2, 130.6, 130.0, 113.7, 108.3, 80.4, 70.3, 66.6, 57.6, 54.5, 50.4, 50.1, 45.3, 43.8, 42.6, 38.4, 37.7, 37.1, 36.8, 36.6, 32.7, 31.9, 31.4, 30.5, 28.9, 28.4, 25.6, 17.9, 17.0, 13.7, 12.1. **IR (neat):** 3405, 2925, 2862, 1676, 1599, 1575, 1510, 1456, 1255, 1169, 1032, 1052, 978, 828, 812, 755 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{34}H_{51}O_5$) requires *m/z* 539.37310, found *m/z* 539.37341.



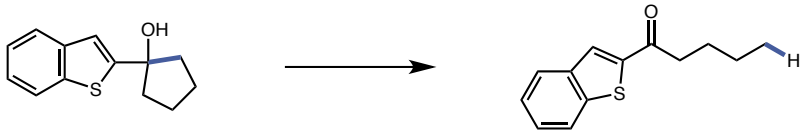
2-((1*S*,2*S*,4a*S*,6*S*,8a*S*)-6-hydroxy-8a-methyl-2-((2*R*,3*S*,3a*S*,4*R*,5*R*,5′*R*,6a*S*)-3,4,5′-trimethyldecahydrospiro[cyclopenta[*b*]furan-2,2′-pyran]-5-yl)decahydronaphthalen-1-yl)-1-(4-methoxyphenyl)ethan-1-one (minor isomer)

^{1}H NMR (800 MHz, C_6D_6) δ 7.97 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 4.43 – 4.37 (m, 1H), 3.51 – 3.44 (m, 2H), 3.41 – 3.36 (m, 1H), 3.18 (s, 3H), 2.79 (dd, *J* = 18.5, 2.8 Hz, 1H), 2.71 (dd, *J* = 18.6, 5.7 Hz, 1H), 2.26 – 2.20 (m, 2H), 2.17 (dq, *J* = 11.6, 5.7 Hz, 1H), 1.88 (h, *J* = 7.5 Hz, 1H), 1.84 – 1.76 (m, 2H), 1.71 – 1.60 (m, 6H), 1.57 – 1.43 (m, 4H), 1.34 – 1.26 (m, 2H), 1.24 – 1.11 (m, 5H), 1.04 (td, *J* = 14.2, 13.7, 3.8 Hz, 1H), 1.01 – 0.95 (m, 4H), 0.83 (dd, *J* = 7.4, 2.2 Hz, 3H), 0.72 (s, 3H), 0.63 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 197.2, 163.6, 130.9, 130.3, 114.1, 108.9, 81.0, 70.8, 67.1, 54.9, 53.2, 47.2, 46.4, 44.2, 43.2, 38.7, 38.6, 38.3, 37.6, 37.5, 37.4, 31.9, 31.71, 31.69, 31.5, 30.8, 29.3, 29.0, 17.4, 14.2, 12.9, 12.6. **IR (neat):** 3413, 2926, 2860, 1677, 1599, 1575, 1455, 1258, 1243, 1169, 1057, 978, 899, 812 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{34}H_{51}O_5$) requires *m/z* 539.37310, found *m/z* 539.37331.



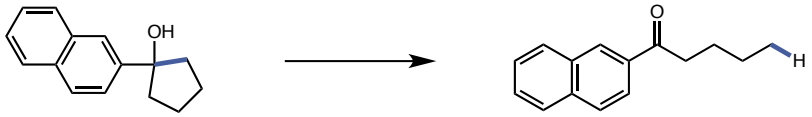
1-(benzofuran-2-yl)pentan-1-one

Prepared on 1 mmol scale following the general procedure with 1-(benzofuran-2-yl)cyclopentanol. The crude material was purified by silica gel column chromatography to afford the titled compound as a white solid (169 mg, 84%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.28 – 7.26 (m, 2H), 7.08 – 7.04 (m, 2H), 6.99 – 6.96 (m, 1H), 2.61 (t, *J* = 7.3 Hz, 2H), 1.65 (p, *J* = 7.4 Hz, 2H), 1.23 (h, *J* = 7.4 Hz, 2H), 0.81 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 190.1, 155.4, 153.3, 128.2, 127.3, 123.5, 123.0, 112.1, 111.2, 38.4, 25.8, 22.3, 13.7. **IR (neat):** 2959, 2932, 2872, 1682, 1556, 1280, 1159, 1141, 1027, 755 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{13}H_{15}O_2$) requires *m/z* 203.10666, found *m/z* 203.10638.



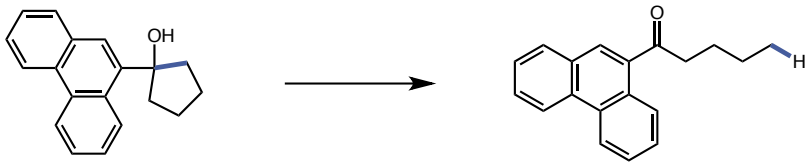
1-(benzo[*b*]thiophen-2-yl)pentan-1-one

Prepared on 1 mmol scale following the general procedure with 1-(benzo[*b*]thiophen-2-yl)cyclopentanol. The crude material was purified by silica gel column chromatography to afford the titled compound as an off-white powder (188 mg, 86%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.51 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.35 (m, 2H), 7.10 – 7.07 (m, 1H), 7.03 – 7.00 (m, 1H), 2.52 (t, *J* = 7.3 Hz, 2H), 1.64 (p, *J* = 7.4 Hz, 2H), 1.23 (h, *J* = 7.4 Hz, 2H), 0.82 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 193.3, 144.5, 142.4, 139.3, 128.1, 126.9, 125.5, 124.6, 122.9, 38.5, 26.4, 22.3, 13.7. **IR (neat):** 2961, 2951, 2929, 2871, 1658, 1519, 1407, 1177, 744, 727 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{13}H_{15}OS$) requires *m/z* 219.08381, found *m/z* 219.08372.



1-(naphthalen-2-yl)pentan-1-one

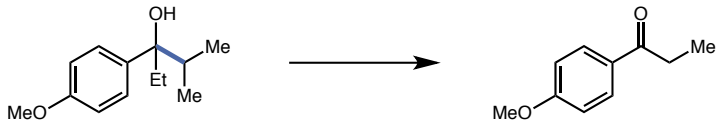
Prepared on 1 mmol scale following the general procedure with 1-(naphthalen-2-yl)cyclopentanol. The crude material was purified by silica gel column chromatography to afford the titled compound as a yellow solid (88 mg, 41%). Spectra are consistent with reported literature values.[10]



1-(phenanthren-9-yl)pentan-1-one

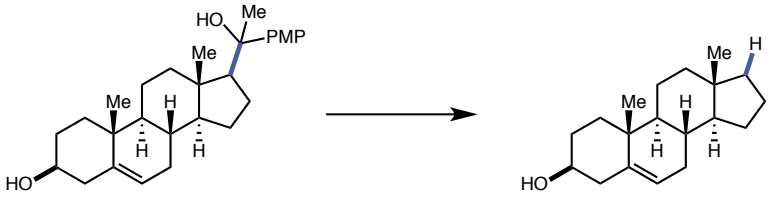
Prepared on 1 mmol scale following the general procedure with 1-(phenanthren-9-yl)cyclopentanol. The crude material was purified by silica gel column chromatography to afford the titled compound as a yellow solid (215 mg, 82%). **^{1}H NMR (500 MHz, C_6D_6)** δ 8.92 (d, *J* =

8.2 Hz, 1H), 8.43 (d, *J* = 8.2 Hz, 1H), 8.36 (d, *J* = 8.3 Hz, 1H), 7.73 (s, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.45 – 7.32 (m, 4H), 2.71 (t, *J* = 7.3 Hz, 2H), 1.73 (p, *J* = 7.5 Hz, 2H), 1.29 (h, *J* = 7.4 Hz, 2H), 0.85 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 203.2, 135.9, 131.8, 130.9, 130.2, 129.5, 128.9, 128.7, 128.2, 127.4, 127.0, 126.9, 126.7, 122.8, 122.7, 41.6, 26.6, 22.4, 13.8. **IR (neat):** 2957, 2929, 2871, 1678, 1448, 1249, 1130, 1085, 747, 725 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{19}H_{19}O$) requires *m/z* 263.14304, found *m/z* 263.14316.



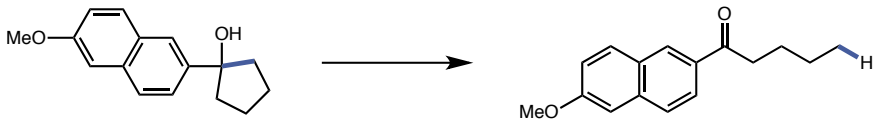
1-(4-methoxyphenyl)propan-1-one

Prepared on 1 mmol scale following the general procedure with 3-(4-methoxyphenyl)-2-methylpentan-3-ol. The crude material was purified by silica gel column chromatography to afford the titled compound as a yellow oil (152 mg, 93%). Spectra are consistent with reported literature values.[11]



(3*S*,8*S*,9*S*,10*R*,13*S*,14*S*)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-ol

Prepared on 0.5 mmol scale following the general procedure from (3*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-(1-hydroxy-1-(4-methoxyphenyl)ethyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-ol. The product was purified by silica gel column chromatography to afford the titled compound as a colorless oil (98 mg, 72%). **^{1}H NMR (500 MHz, C_6D_6)** δ 5.34 (dt, *J* = 4.8, 2.1 Hz, 1H), 3.39 (tt, *J* = 11.1, 4.8 Hz, 1H), 2.24 (dtdd, *J* = 16.0, 13.3, 5.3, 2.3 Hz, 2H), 1.95 (dtd, *J* = 17.5, 5.3, 2.6 Hz, 1H), 1.76 – 1.70 (m, 1H), 1.69 – 1.49 (m, 6H), 1.48 – 1.30 (m, 5H), 1.12 (dddd, *J* = 17.2, 11.9, 7.6, 4.3 Hz, 3H), 1.00 – 0.86 (m, 3H), 0.92 (s, 3H), 0.84 – 0.74 (m, 1H), 0.68 (s, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 140.9, 121.3, 71.3, 54.7, 50.4, 42.6, 40.5, 40.3, 38.7, 37.4, 36.6, 32.2, 32.1, 31.8, 25.6, 21.2, 20.6, 19.2, 17.1. **IR (neat):** 3242, 2930, 2858, 1610, 1453, 1376, 1232, 1110, 1019, 954, 812, 795, 739, 677 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M-H_2O+H]^+$ ($C_{19}H_{29}$) requires *m/z* 257.22638, found *m/z* 257.22619.

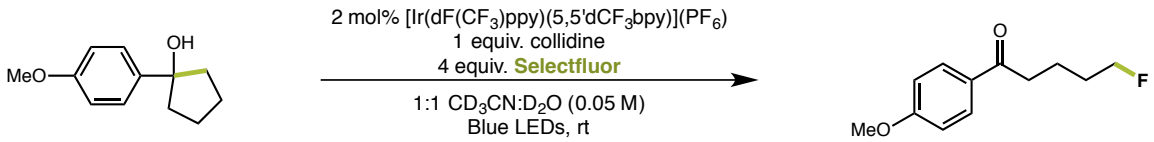


1-(6-methoxynaphthalen-2-yl)pentan-1-one

Prepared on 1 mmol scale in a single run, following the general procedure with 1-(6-methoxynaphthalen-2-yl)cyclopentanol. The crude material was purified by silica gel column chromatography to afford the titled compound as a yellow solid (18 mg, 7%). **^{1}H NMR (500 MHz, C_6D_6)** δ 8.27 (s, 1H), 8.20 (d, *J* = 8.6 Hz, 1H), 7.51 (dd, *J* = 19.3, 8.7 Hz, 2H), 7.12 (d, *J* = 2.5 Hz, 1H), 6.83 (d, *J* = 2.6 Hz, 1H), 3.33 (s, 3H), 2.72 (t, *J* = 7.3 Hz, 2H), 1.76 (p, *J* = 7.4 Hz, 2H), 1.31 (h, *J* = 7.4 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (126 MHz, C_6D_6)** δ 198.2,

159.6, 137.2, 133.0, 131.0, 129.4, 128.1, 127.0, 124.9, 119.6, 105.7, 54.5, 37.8, 26.5, 22.5, 13.9. **IR (neat):** 2955, 2936, 2871, 1675, 1623, 1603, 1482, 1266, 1164, 1030, 852, 811 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{16}H_{19}O_2$) requires *m/z* 243.13796, found *m/z* 243.13762.

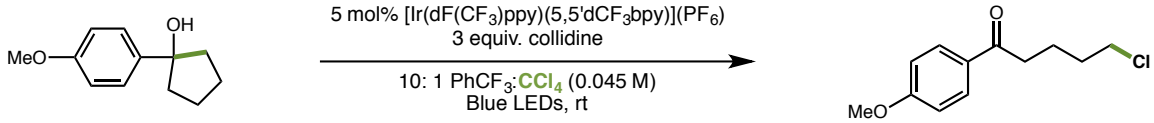
Protocol for forming distally fluorinated ketones via PCET-mediated ring-opening of cyclic alcohols



5-fluoro-1-(4-methoxyphenyl)pentan-1-one

A screw cap culture tube (16 × 125 mm) outfitted with a PTFE/silicone septa was charged with 1-(4-methoxyphenyl)cyclopentan-1-ol (0.5 mmol, 1 equiv, 96 mg), redistilled collidine (0.5 mmol, 1 equiv, 66 µL), $[Ir(dF(CF_3)ppy)_2(5,5'd(CF_3)bpy)](PF_6)$ (0.01 mmol, 0.02 equiv, 11 mg), and Selectfluor (2 mmol, 4 equiv, 709 mg). The vial was then evacuated and backfilled with nitrogen three times. Degassed acetonitrile-d_3 (5 mL) and water-d_2 (5 mL) were added to form a suspension. The mixture was sparged with nitrogen for 20 minutes. The reaction was irradiated with blue LEDs strips set inside a beaker, and let stir at room temperature with a fan to cool the reaction setup. After 3 hour, the reaction was concentrated, washed with water, extracted with EtOAc, then purified by silica gel column chromatography to afford the titled compound as a white solid (55 mg, 52%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.84 (d, J = 8.9 Hz, 2H), 6.66 (d, J = 8.9 Hz, 2H), 4.14 (t, J = 6.0 Hz, 1H), 4.05 (t, J = 6.0 Hz, 1H), 3.20 (s, 3H), 2.49 (t, J = 7.2 Hz, 2H), 1.71 (dt, J = 15.00, 7.3 Hz, 2H), 1.50 – 1.39 (m, 2H). **^{13}C NMR (126 MHz, C_6D_6)** δ 197.0, 163.6, 130.8, 130.5, 113.9, 83.7 (d, J = 166 Hz), 54.9, 37.5, 30.1, 20.3. **IR (neat):** 2940, 1675, 1599, 1576, 1510, 1256, 1207, 1169, 1029, 815 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{12}H_{16}FO_2$) requires *m/z* 211.11288, found *m/z* 211.11271.

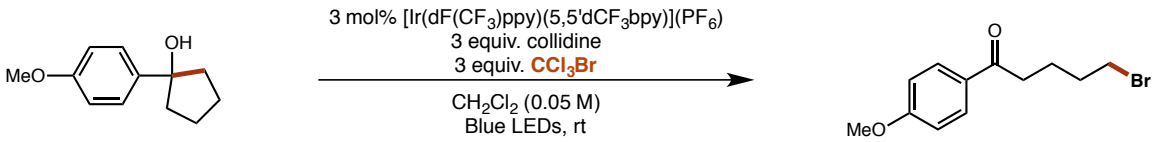
Protocol for forming distally chlorinated ketones via PCET-mediated ring-opening of cyclic alcohols



5-chloro-1-(4-methoxyphenyl)pentan-1-one

A screw cap culture tube (16 × 125 mm) outfitted with a PTFE/silicone septa was charged with 1-(4-methoxyphenyl)cyclopentan-1-ol (0.5 mmol, 1.0 equiv, 96 mg), redistilled collidine (1.5 mmol, 3 equiv, 198 µL), and $[Ir(dF(CF_3)ppy)_2(5,5'd(CF_3)bpy)](PF_6)$ (0.025 mmol, 0.05 equiv, 26 mg) in dry trifluorotoluene (10 mL). The mixture was sparged with argon for 20 minutes. Carbon tetrachloride (10 mmol, 20 equiv, 1 mL) was then added. The reaction was irradiated with four blue LEDs lamps (Kessil H150B LED Grow Light), and let stir at room temperature with a fan to cool the reaction setup. After 18 hours, the reaction was concentrated then purified by silica gel column chromatography to obtain the titled compound as a white solid(112 mg, 98%). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.83 (d, J = 8.8 Hz, 2H), 6.66 (d, J = 8.9 Hz, 2H), 3.19 (s, 3H), 3.09 (t, J = 6.7 Hz, 2H), 2.40 (t, J = 7.2 Hz, 2H), 1.67 (dt, J = 15.0, 7.2 Hz, 2H), 1.47 (dt, J = 14.0, 6.8 Hz, 2H). **^{13}C NMR (126 MHz, C_6D_6)** δ 196.5, 163.2, 130.3, 130.1, 113.5, 54.5, 44.4, 36.7, 32.0, 21.4. **IR (neat):** 2952, 1666, 1600, 1576, 1510, 1460, 1443, 1418, 1375, 1309, 1293, 1261, 1240, 1171, 1114, 1027, 980, 836, 786, 736, 704 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{12}H_{16}ClO_2$) requires *m/z* 227.08334, found *m/z* 227.08298.

Protocol for forming distally brominated ketones via PCET-mediated ring-opening of cyclic alcohols

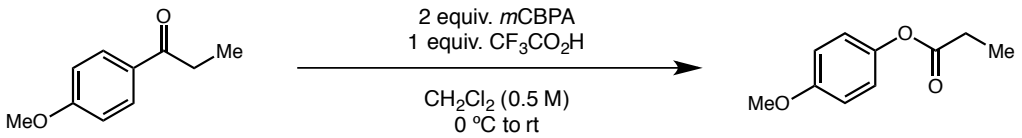


5-bromo-1-(4-methoxyphenyl)pentan-1-one

A screw cap culture tube (16 × 125 mm) outfitted with a PTFE/silicone septa was charged with 1-(4-methoxyphenyl)cyclopentan-1-ol (0.5 mmol, 1 equiv, 96 mg), redistilled collidine (1.5 mmol, 3 equiv, 198 µL), and $[Ir(dF(CF_3)ppy)_2(5,5'd(CF_3)bpy)](PF_6)$ (0.015 mmol, 0.03 equiv, 16 mg),. The vial was then evacuated and backfilled with argon three times. Bromotrichloromethane (1.5 mmol, 3 equiv, 147 µL) and dry CH_2Cl_2 (10 mL) were added. The reaction was irradiated with four blue LEDs lamps (Kessil H150B LED Grow Light), and let stir at room temperature with a fan to cool the reaction setup. After 24 hours, the reaction was concentrated then purified by silica gel column chromatography to obtain the titled compound (129 mg, 95% yield). **^{1}H NMR (500 MHz, C_6D_6)** δ 7.83 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 3.19 (s, 3H), 2.93 (t, *J* = 6.8 Hz, 2H), 2.38 (t, *J* = 7.1 Hz, 2H), 1.65 (p, *J* = 7.1 Hz, 2H), 1.54 (p, *J* = 6.8 Hz, 2H). **^{13}C NMR (126 MHz, C_6D_6)** δ 196.4, 163.2, 130.3, 130.1, 113.5, 54.5, 36.6, 33.0. 32.1, 22.7. **IR (neat):** 2949, 1665, 1600, 1513, 1459, 1438, 1406, 1375, 1309, 1266, 1226, 1186, 1172, 1115, 1027, 982, 834, 778, 737 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{12}H_{16}BrO_2$) requires *m/z* 271.03282, found *m/z* 271.03285.

Protocol for Baeyer-Villiger oxidation of ketone product

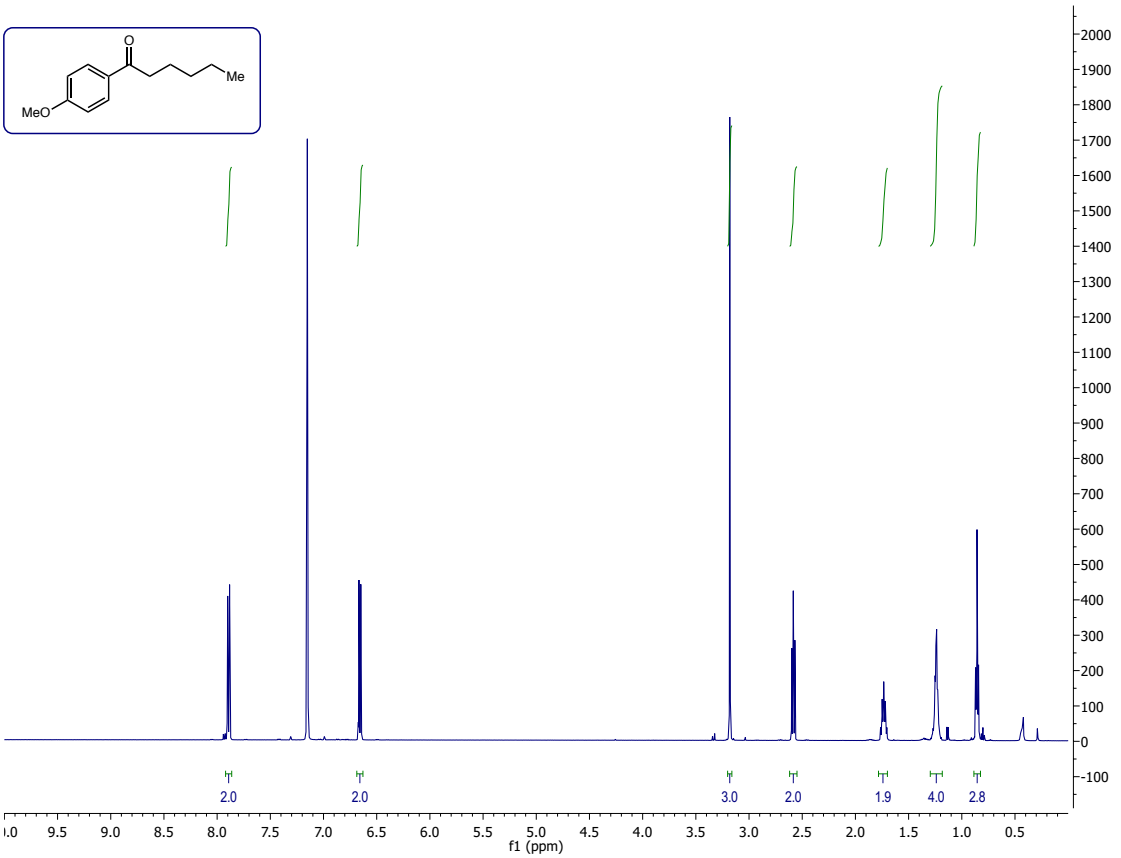
To verify that the PMP-ketone products can be easily derivatized via Baeyer-Villiger oxidation to furnish free carboxylic acid, 1-(4-methoxyphenyl)propan-1-one was subjected to classical Baeyer-Villiger conditions, the procedure and result of which are outlined below.

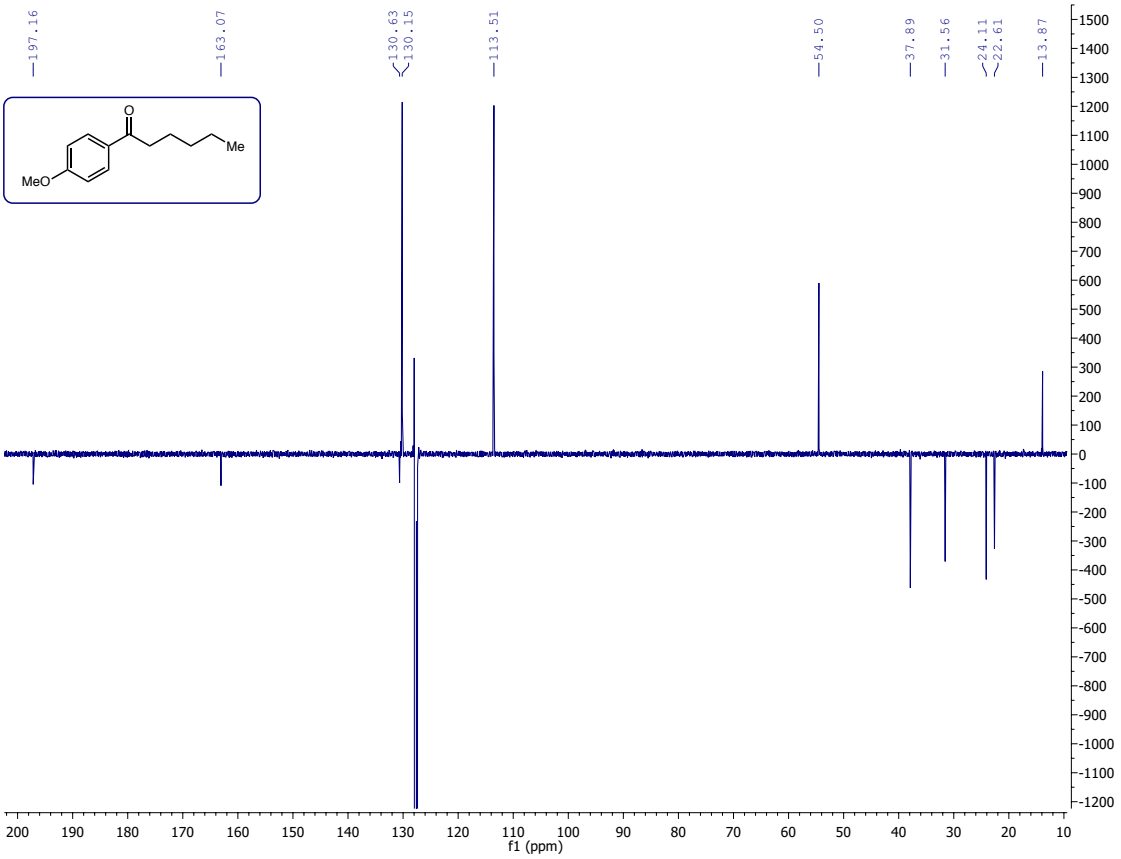


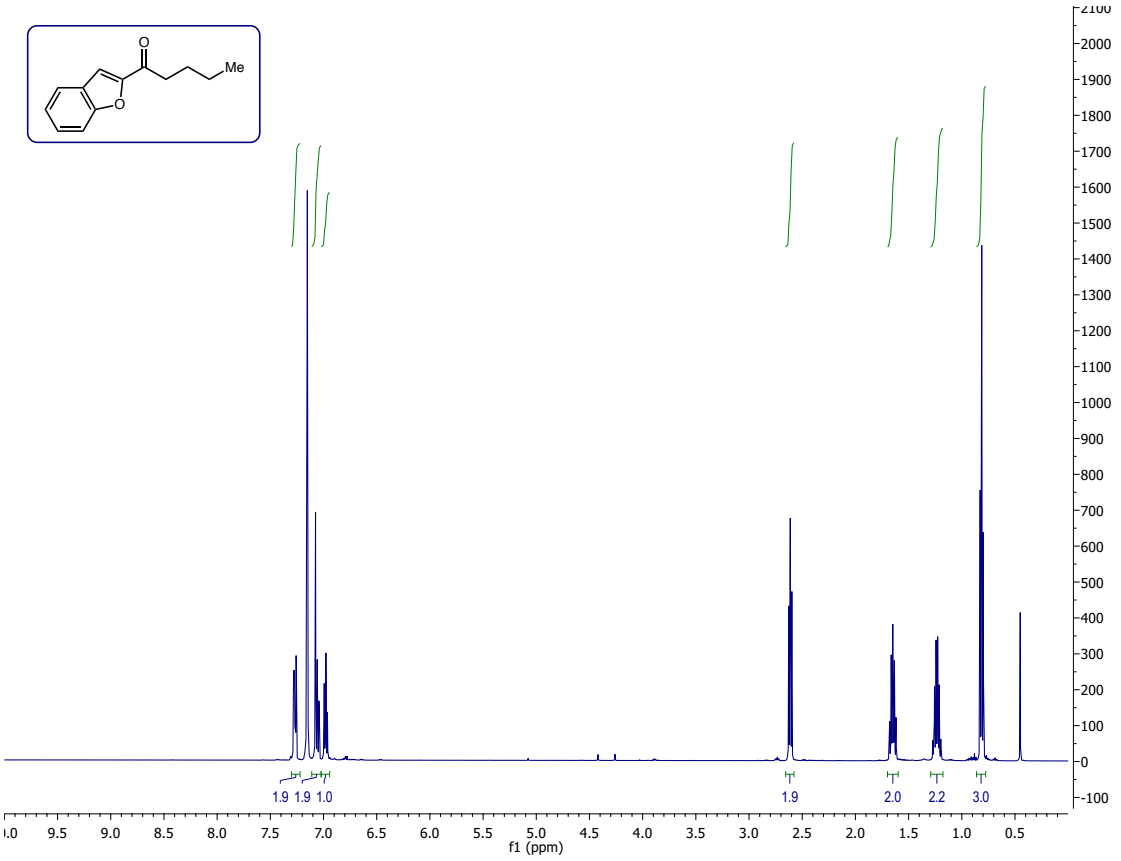
4-methoxyphenyl propionate

A screw-cap 2-dram vial was charged with 1-(4-methoxyphenyl)propan-1-one (1.0 mmol, 1.0 equiv, 164 mg) and 3-chlorobenzoperoxoic acid (~ 70% purity, 493 mg; 2.0 mmol, 2.0 equiv in pure *m*CPBA). The solids were dissolved in 2 mL of CH_2Cl_2 to form a suspension, which was stirred vigorouly while cooled with an ice bath. Trifluoroacetic acid (1.0 mmol, 1.0 equiv, 75 μL) was added slowly via syringe. The vial was left in the ice bath overnight, during which time the reaction warmed up to room tempurature. The crude material was washed in saturated $NaHCO_3$, extracted with CH_2Cl_2, concentrate to small volume, and purified by silica gel column chromatography to afford the titled compound as a colorless liquid (147 mg, 81%). Spectra are consistent with reported literature values.[12]

^{1}H and ^{13}C NMR Spectra of Products



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Me
O
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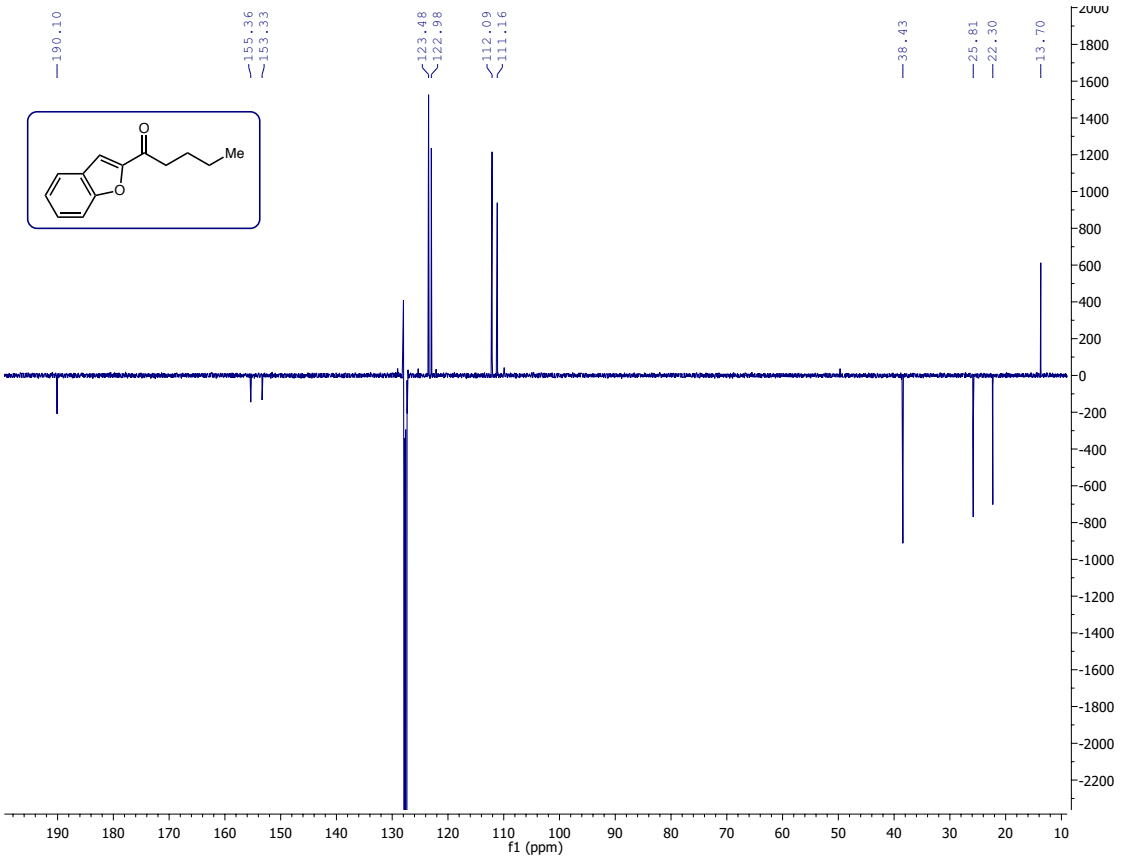
1.9
2.0
2.2
3.0
f1 (ppm)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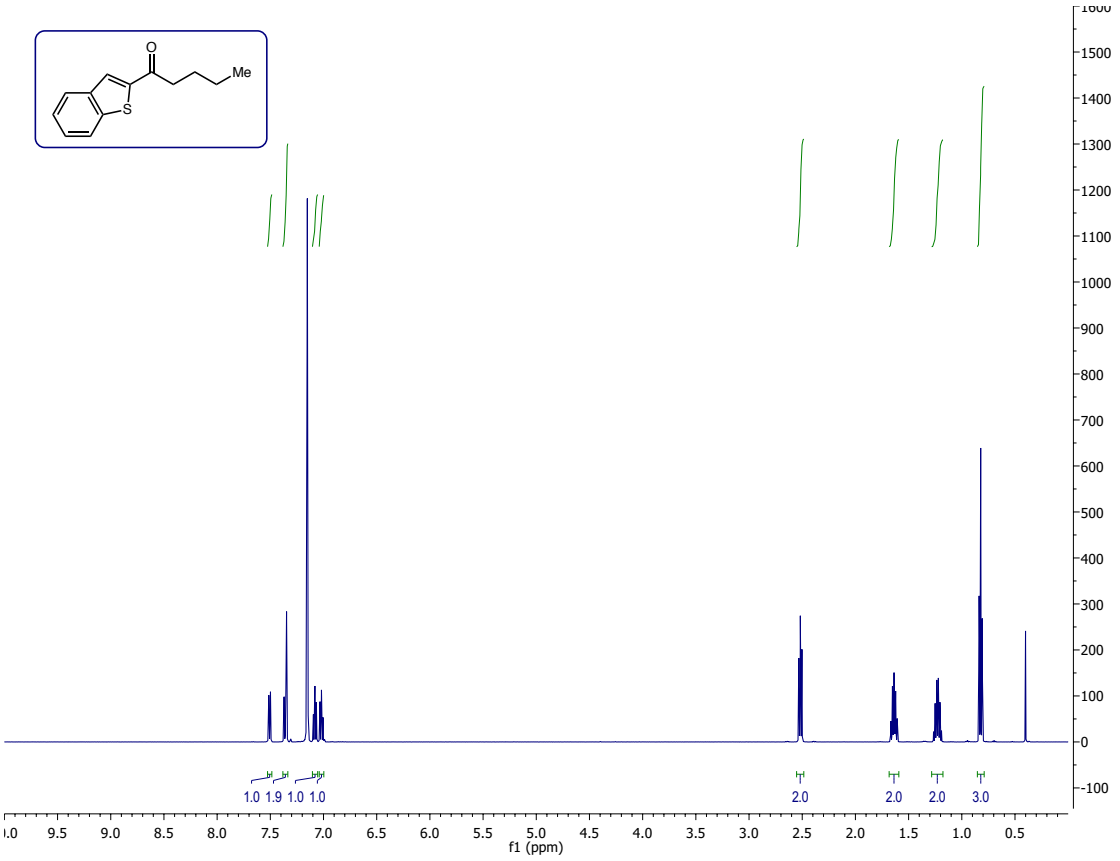
22.30
13.70
O
Me
O
f1 (ppm)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Me
S
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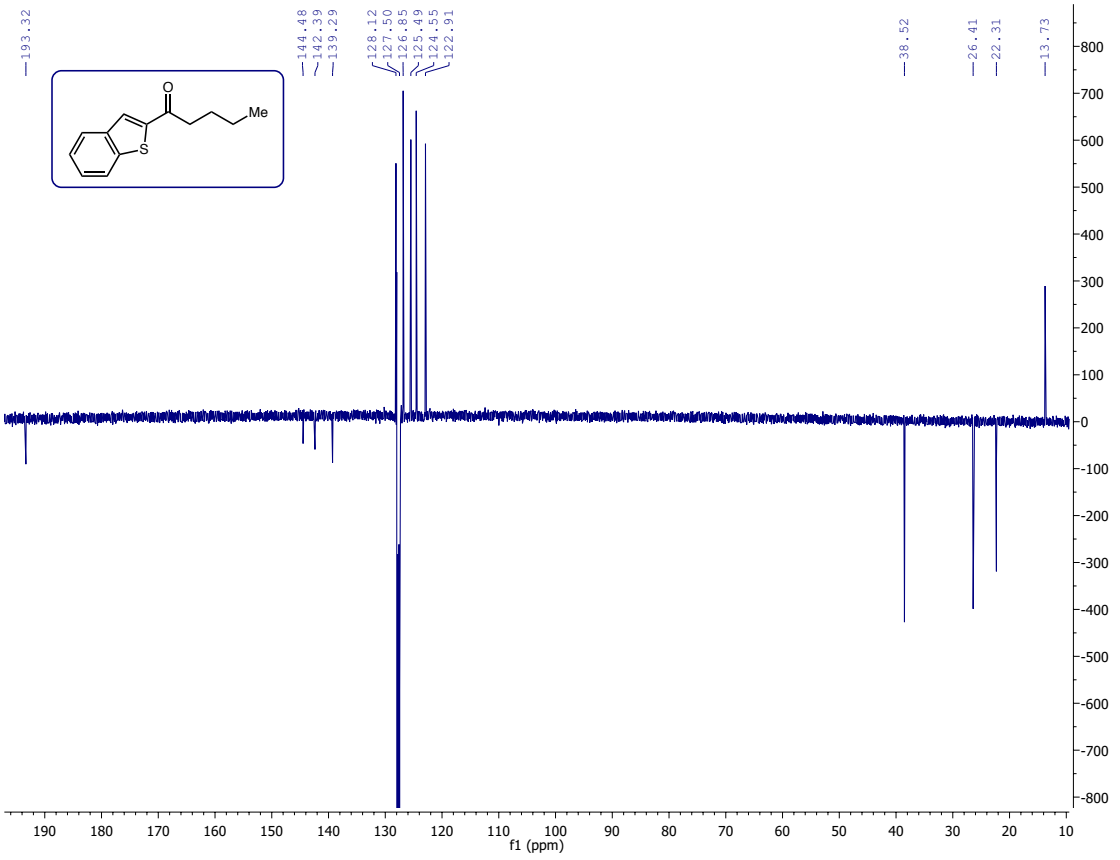
2.0
2.0
2.0
3.0
f1 (ppm)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Me
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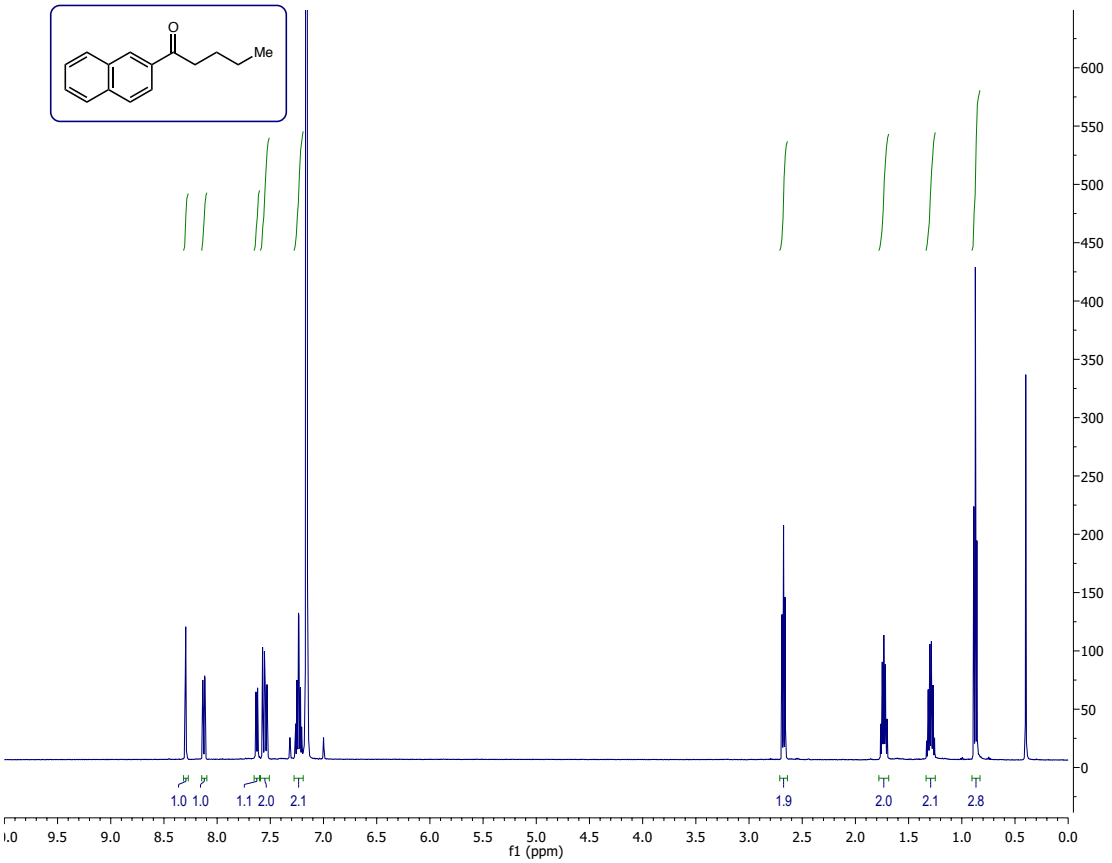
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Me
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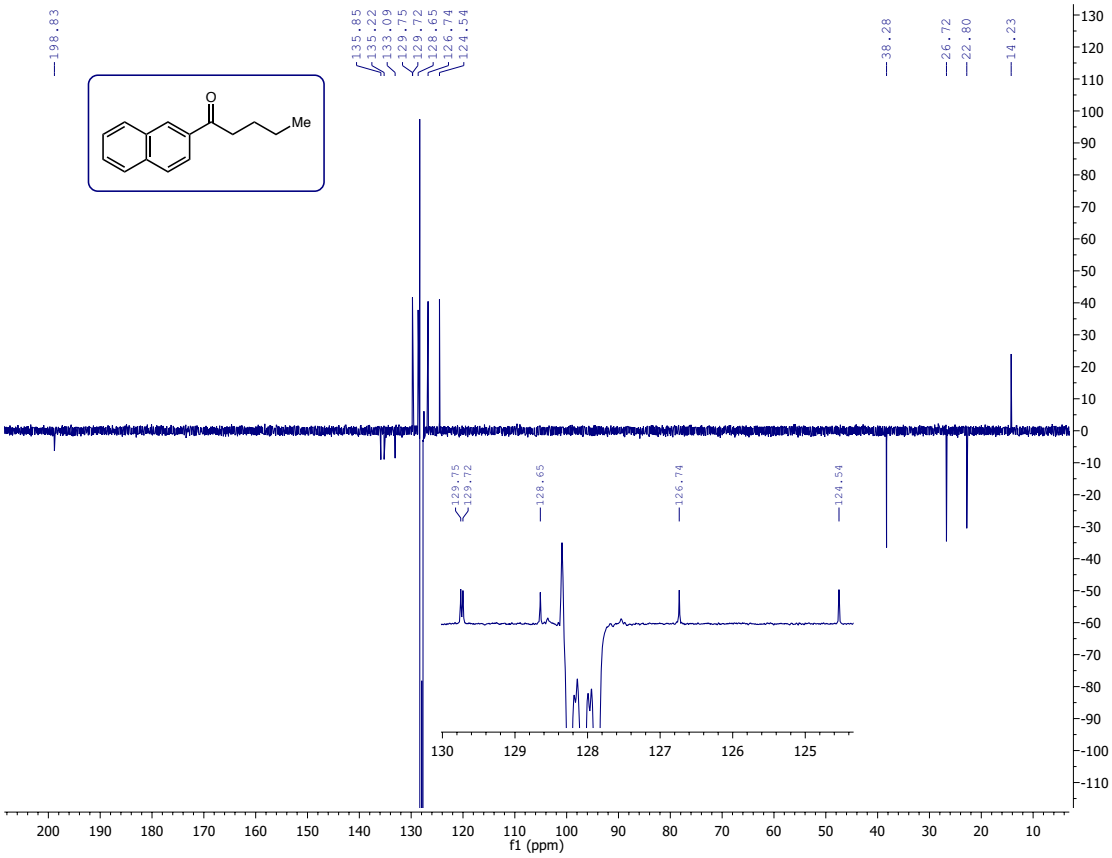
f1 (ppm)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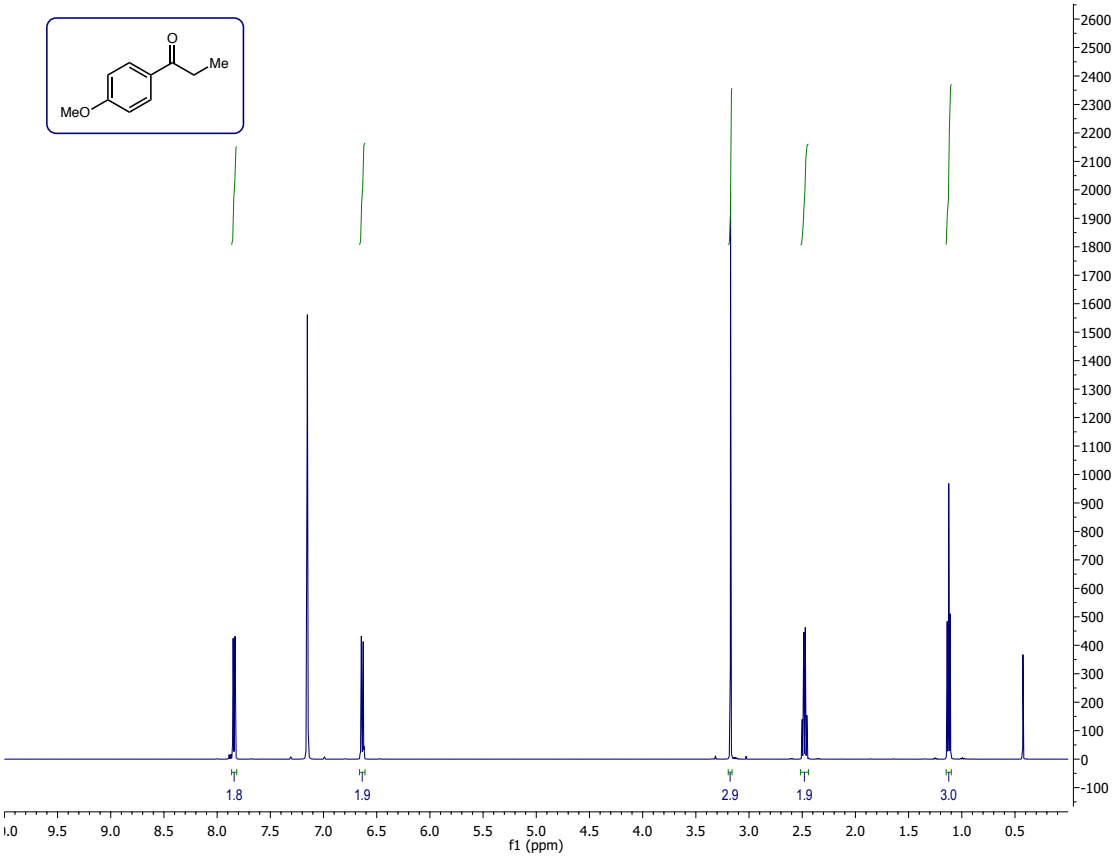
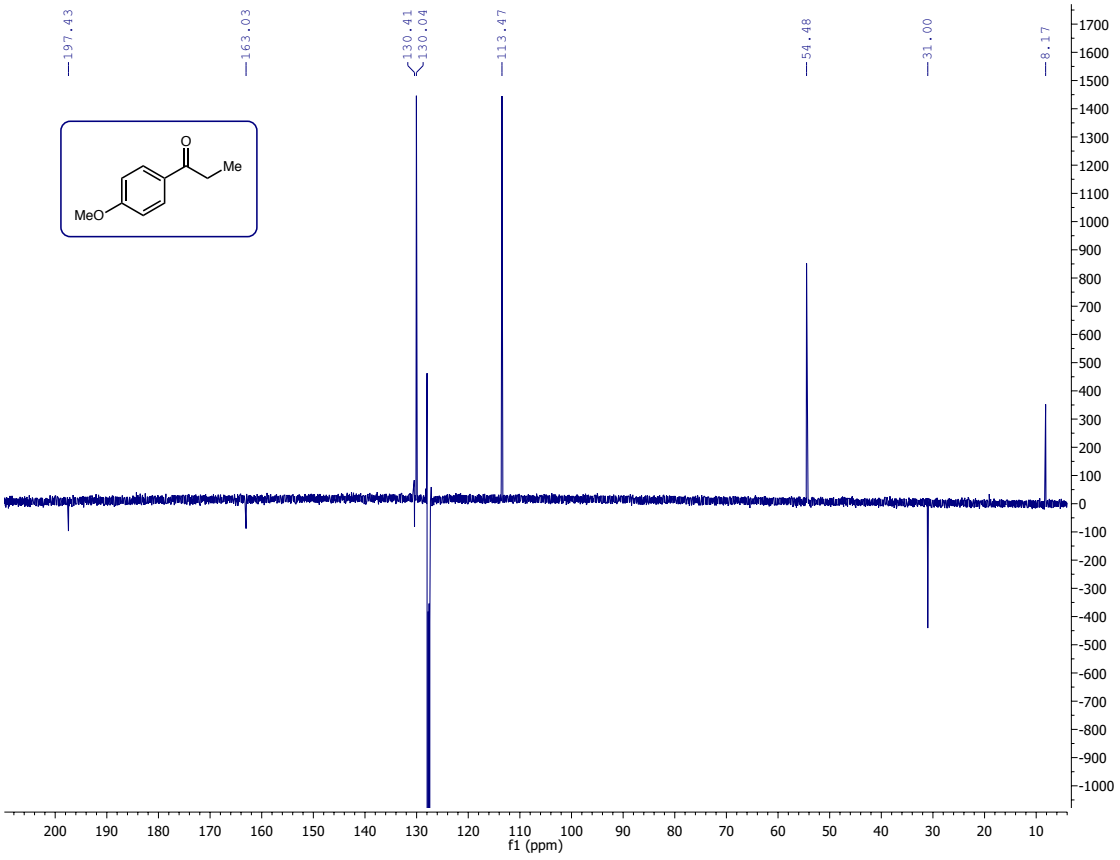
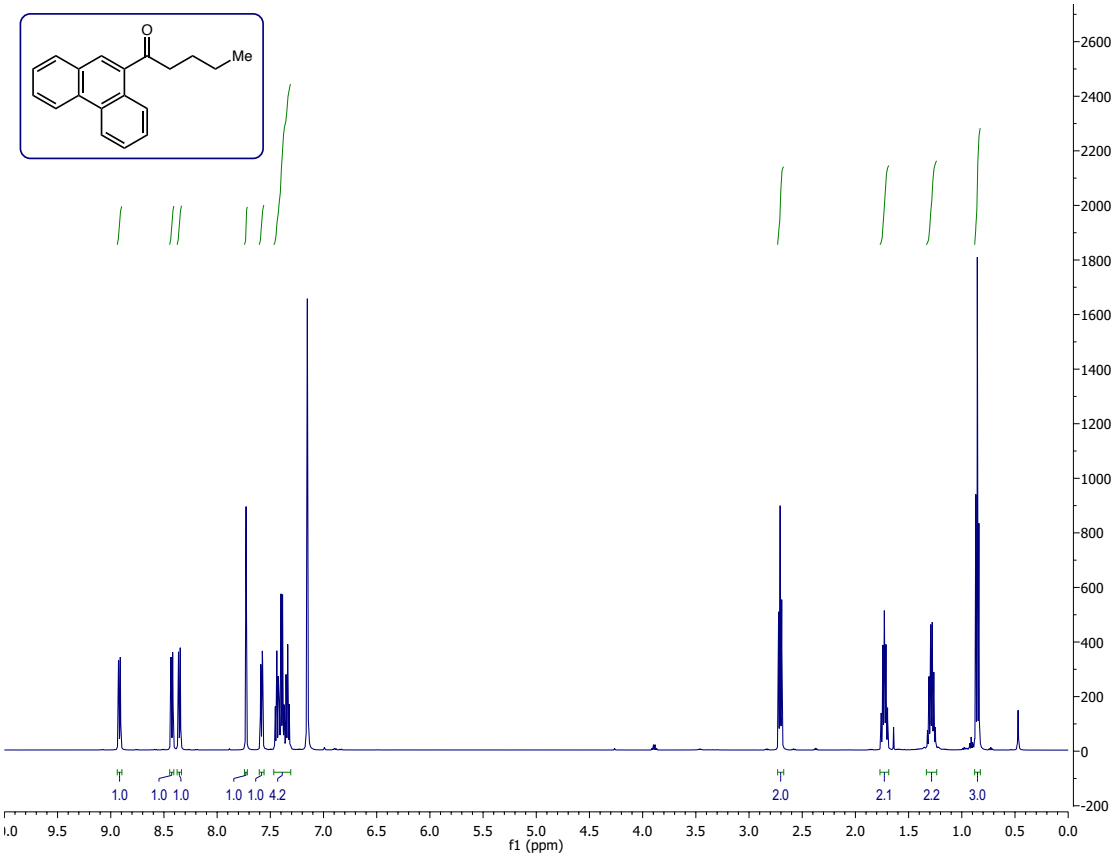
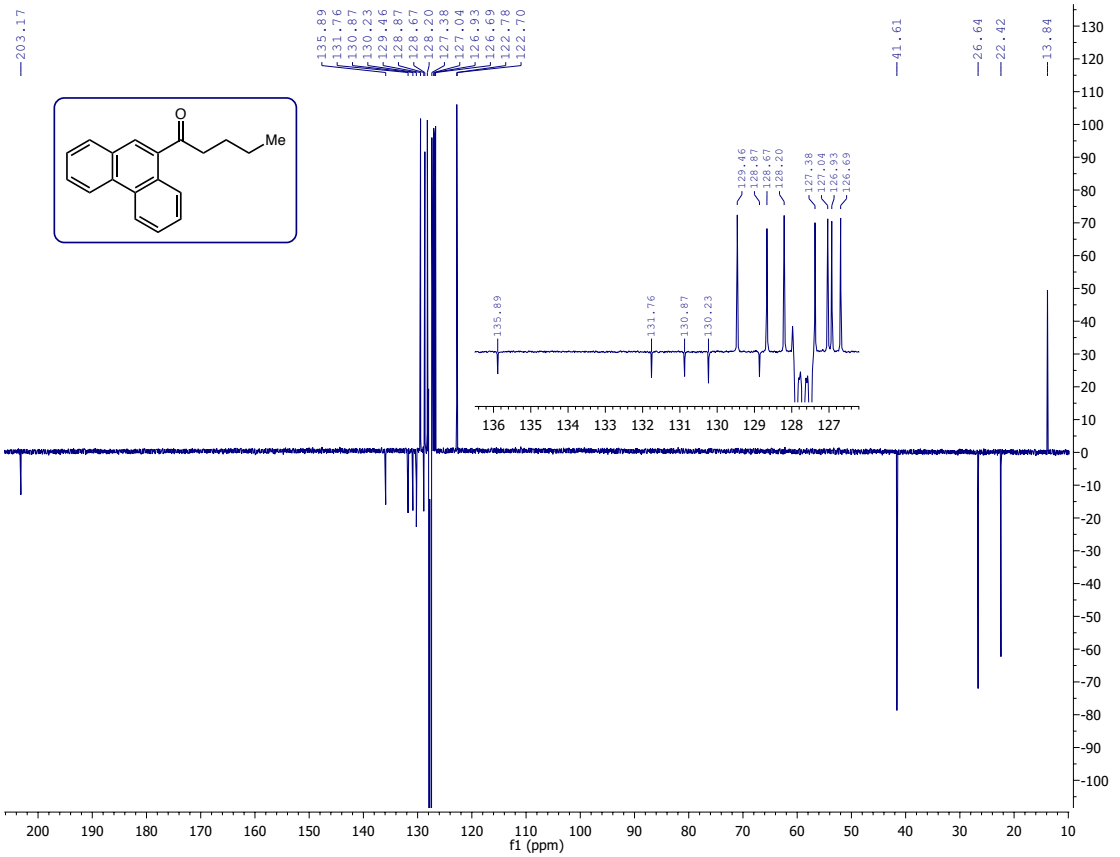
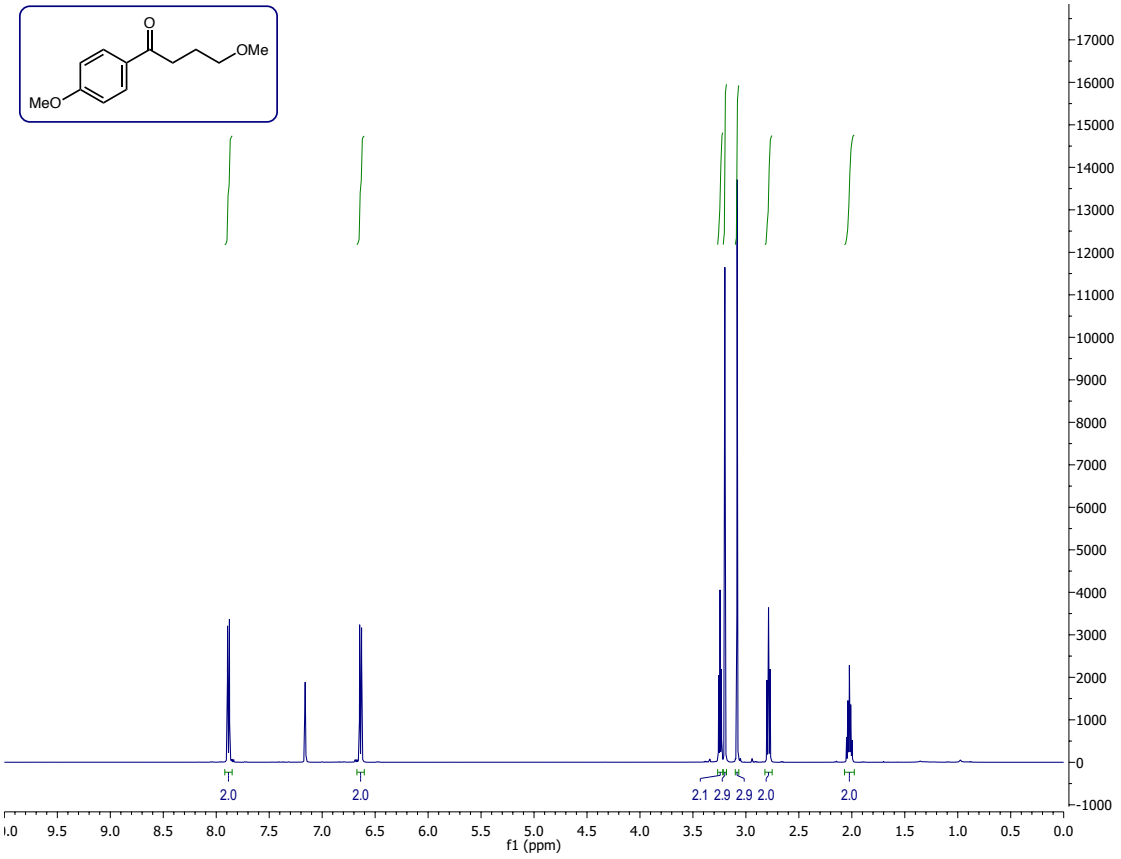
126.74
124.54
38.28
26.72
22.80
14.23
O
Me
f1 (ppm)

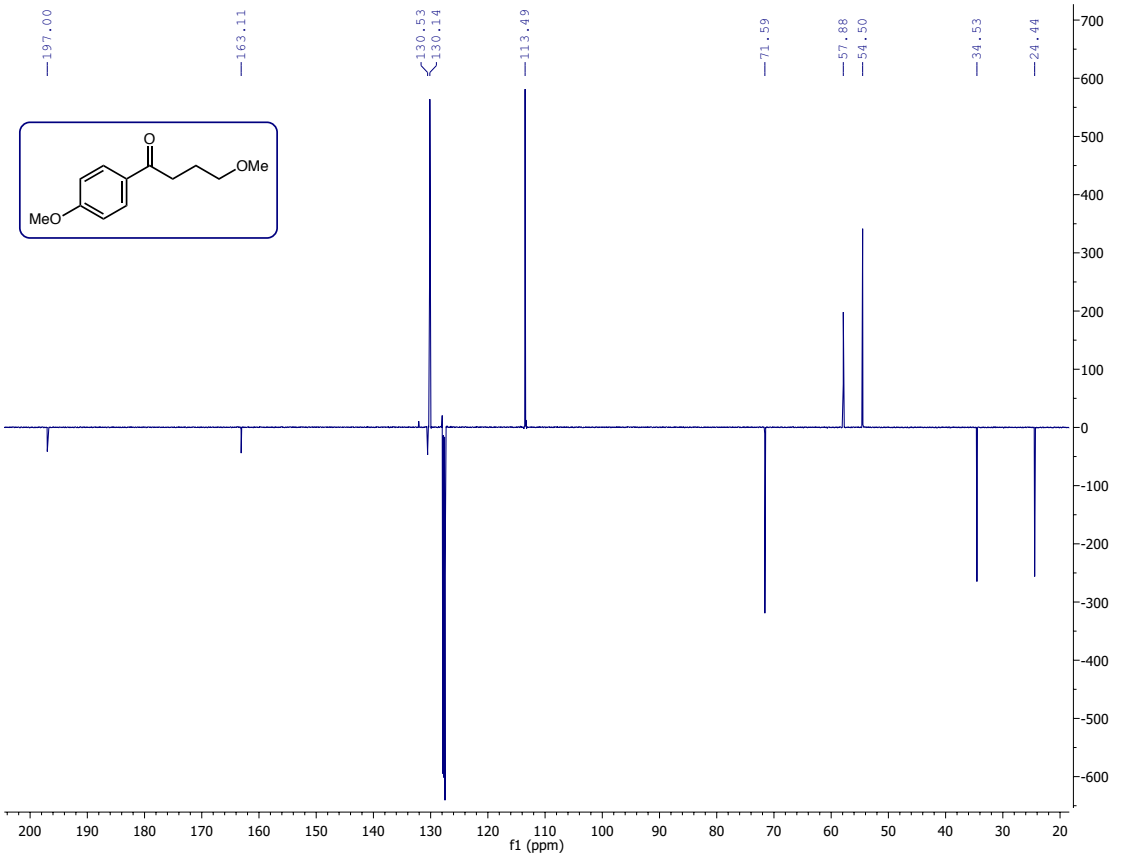

O
Me
MeO
1.8
1.9
2.9
1.9
3.0
f1 (ppm)

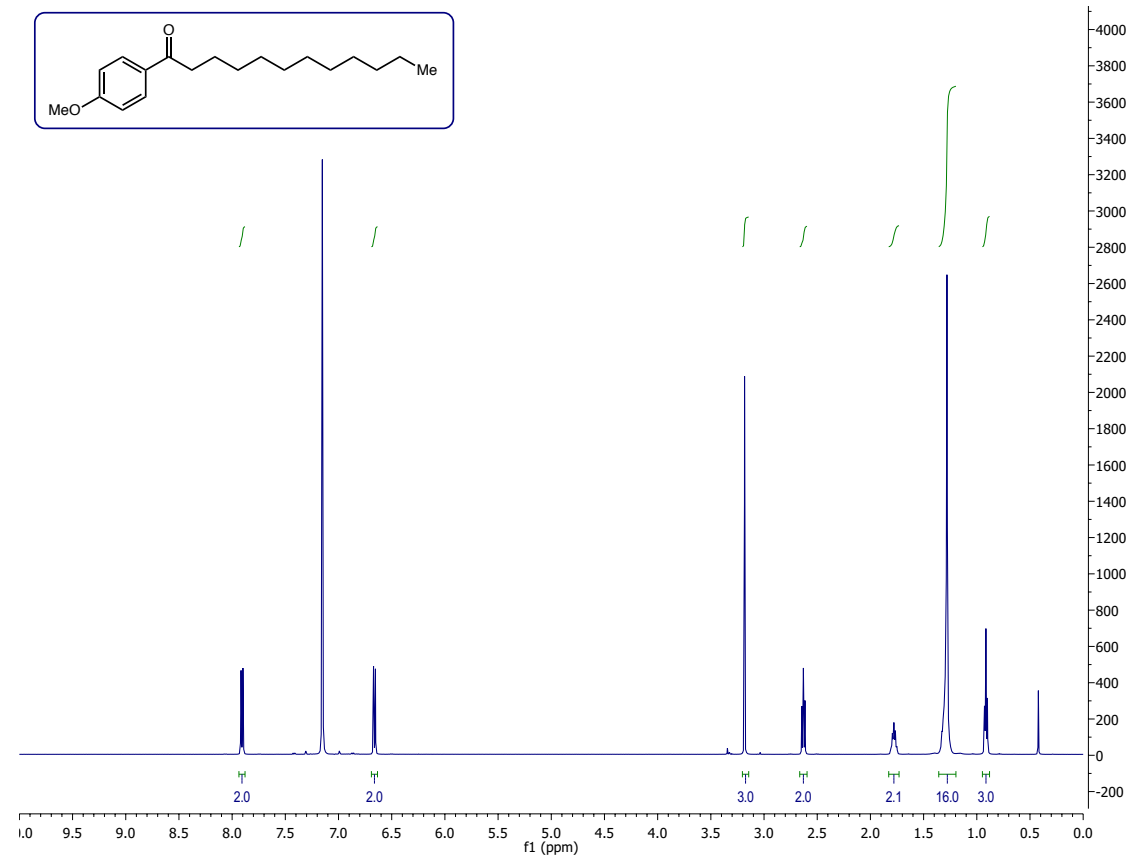

197.43
163.03
130.41
130.04
113.47
54.48
31.00
8.17
O
Me
MeO
f1 (ppm)

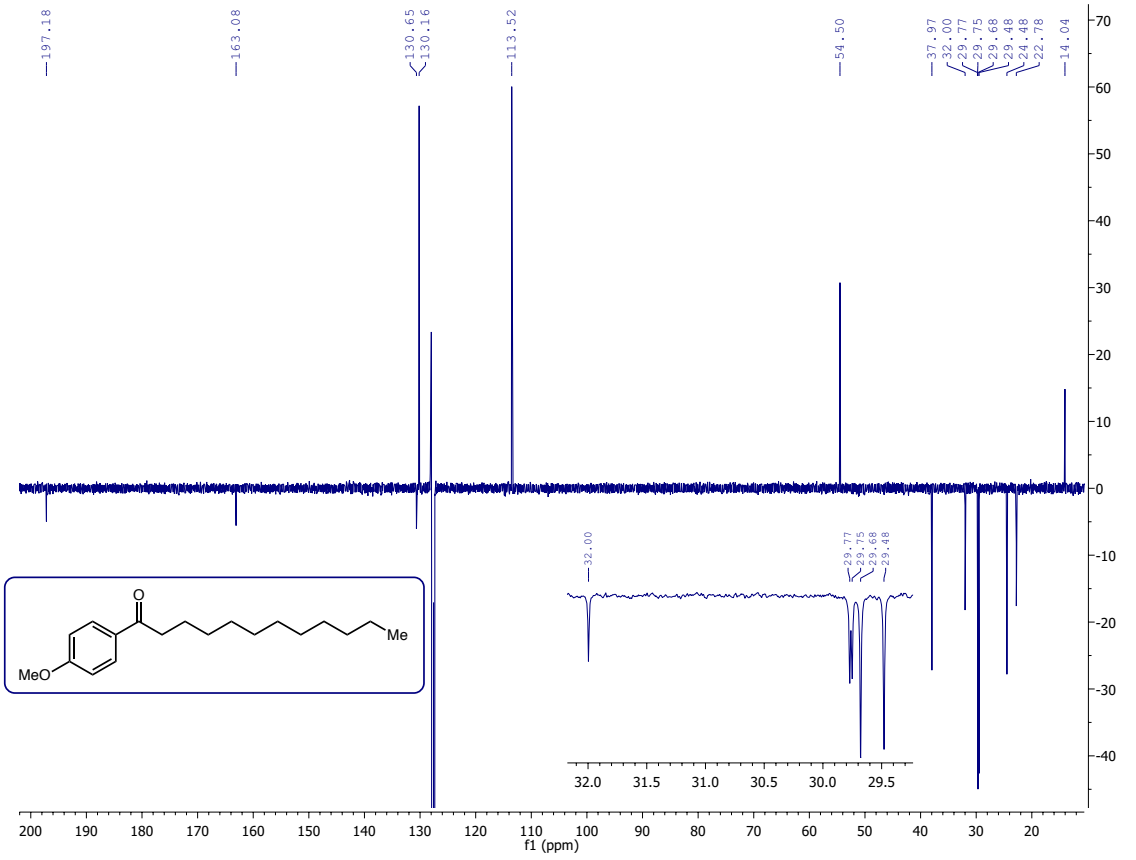

O
Me
1.0
1.0 1.0
1.0 1.0 4.2
2.0
2.1
2.2
3.0
f1 (ppm)

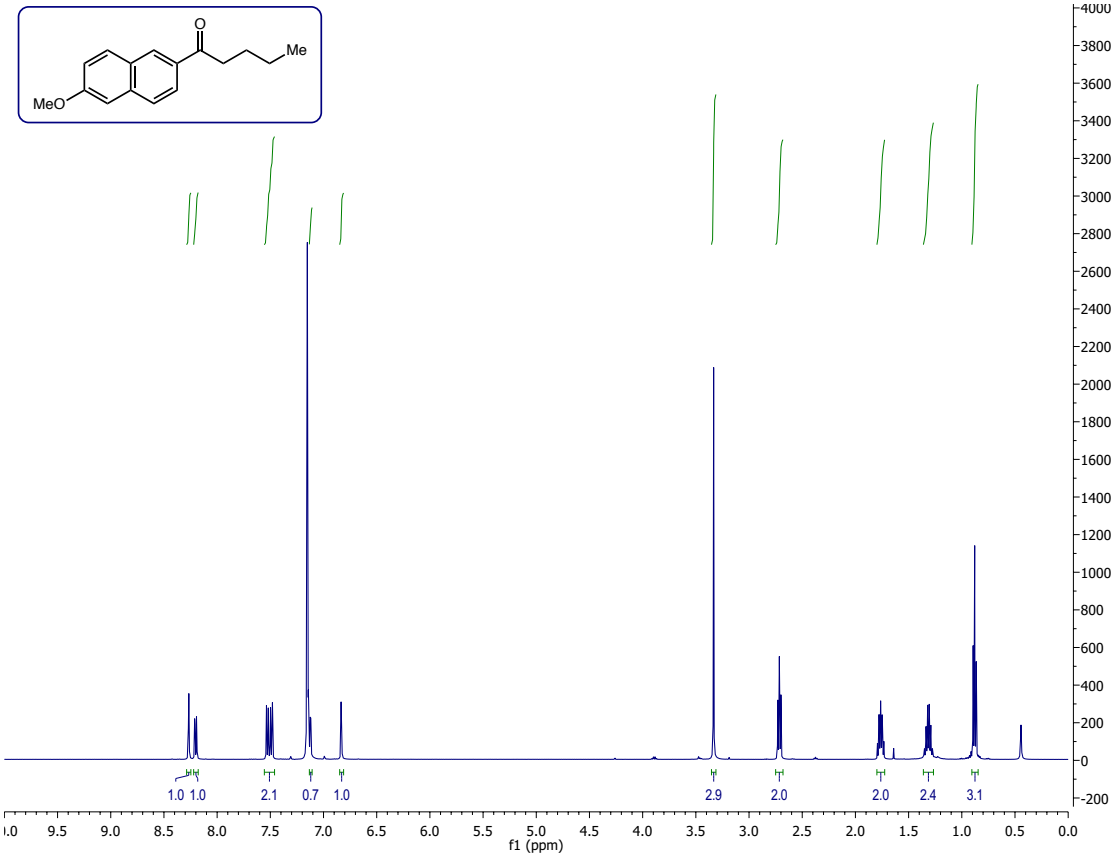

203.17
135.89
131.76
130.87
130.23
129.46
128.87
128.67
128.20
127.38
127.04
126.93
126.69
122.78
122.70
41.61
26.64
22.42
13.84
O
Me
f1 (ppm)

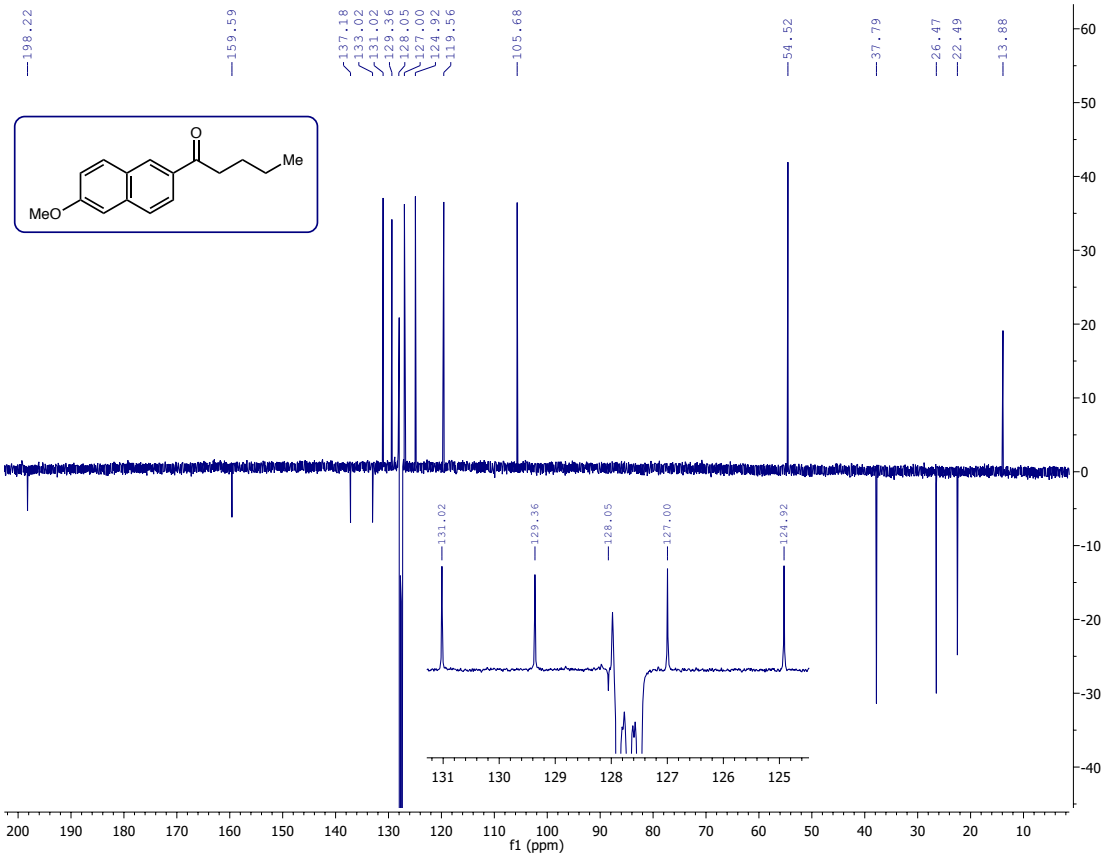

O
OMe
MeO
2.0
2.0
2.1 2.9 2.9 2.0
2.0
f1 (ppm)

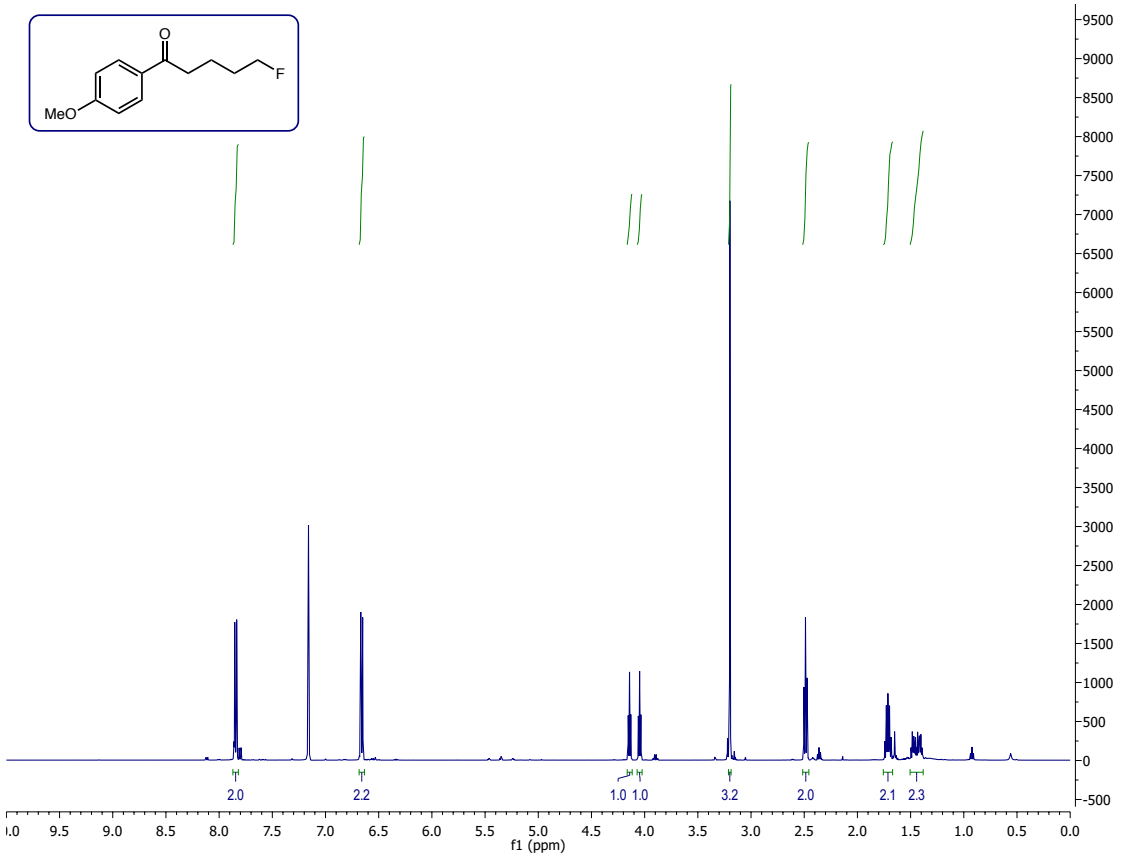

197.00
163.11
130.53
130.14
113.49
71.59
57.88
54.50
34.53
24.44
O
OMe
MeO
f1 (ppm)

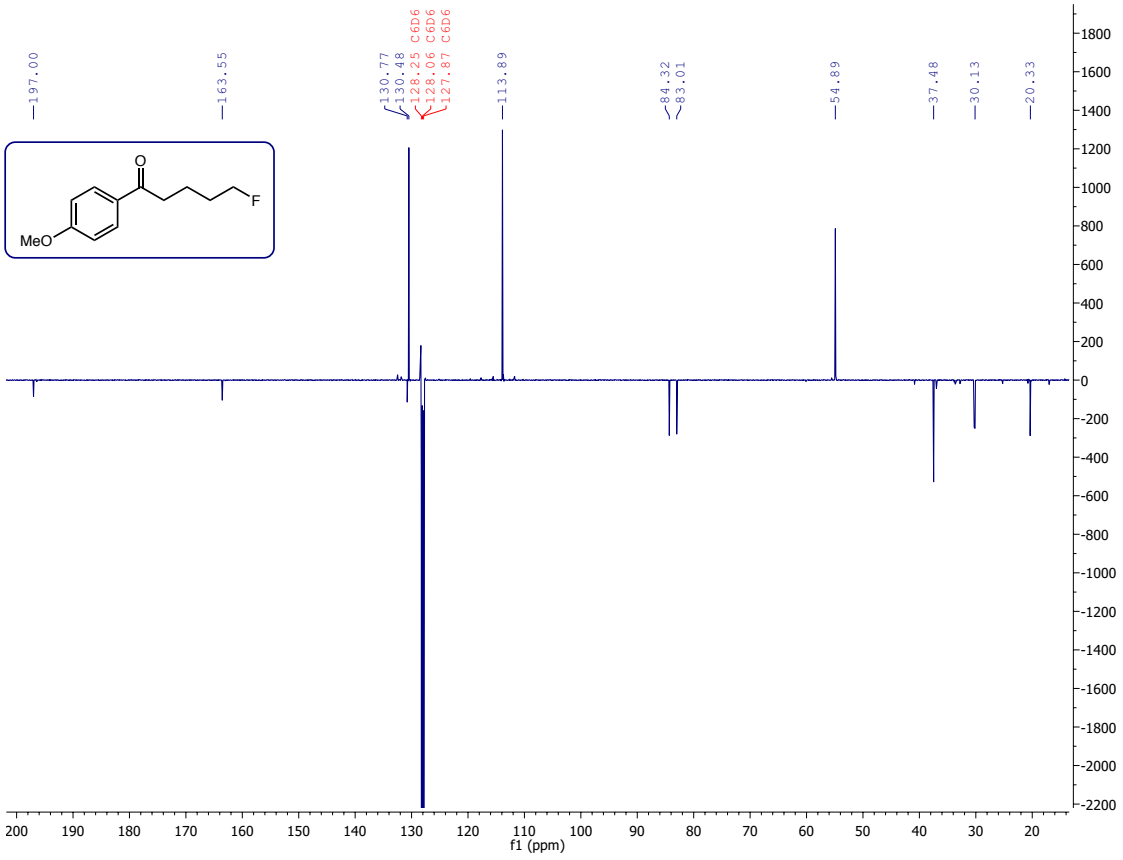

O
Me
MeO
2.0
2.0
3.0
2.0
2.1
16.0
3.0
f1 (ppm)

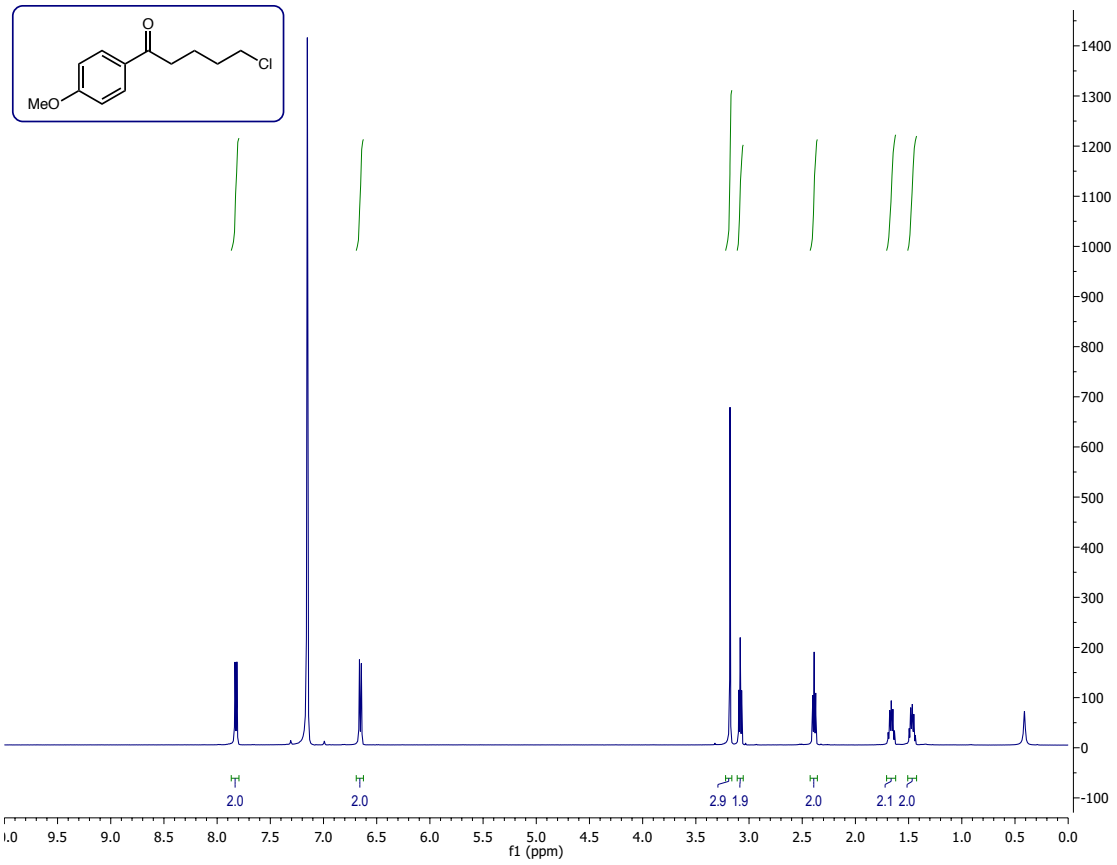

197.18
163.08
130.65
130.16
113.52
54.50
37.97
32.00
29.77
29.75
29.68
29.48
24.48
22.78
14.04
O
Me
MeO
f1 (ppm)

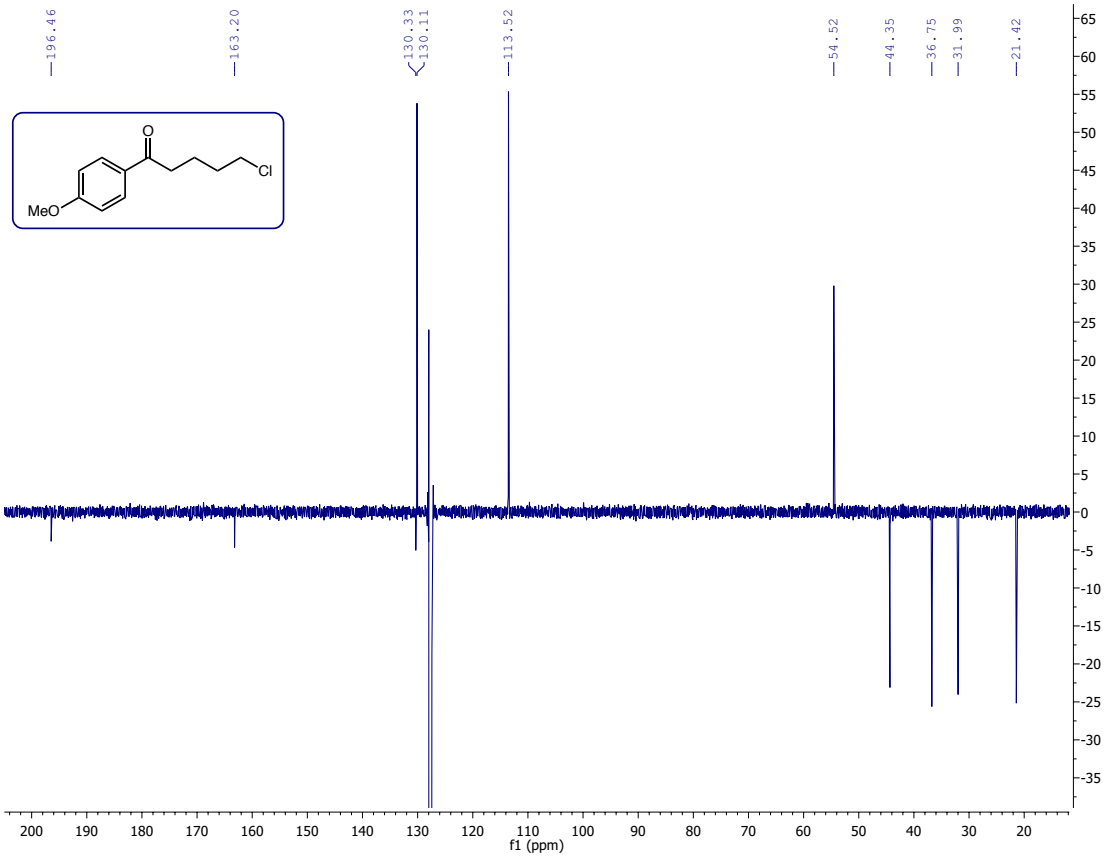

O
Me
MeO
1.0 1.0
2.1
0.7
1.0
2.9
2.0
2.0
2.4
3.1
f1 (ppm)

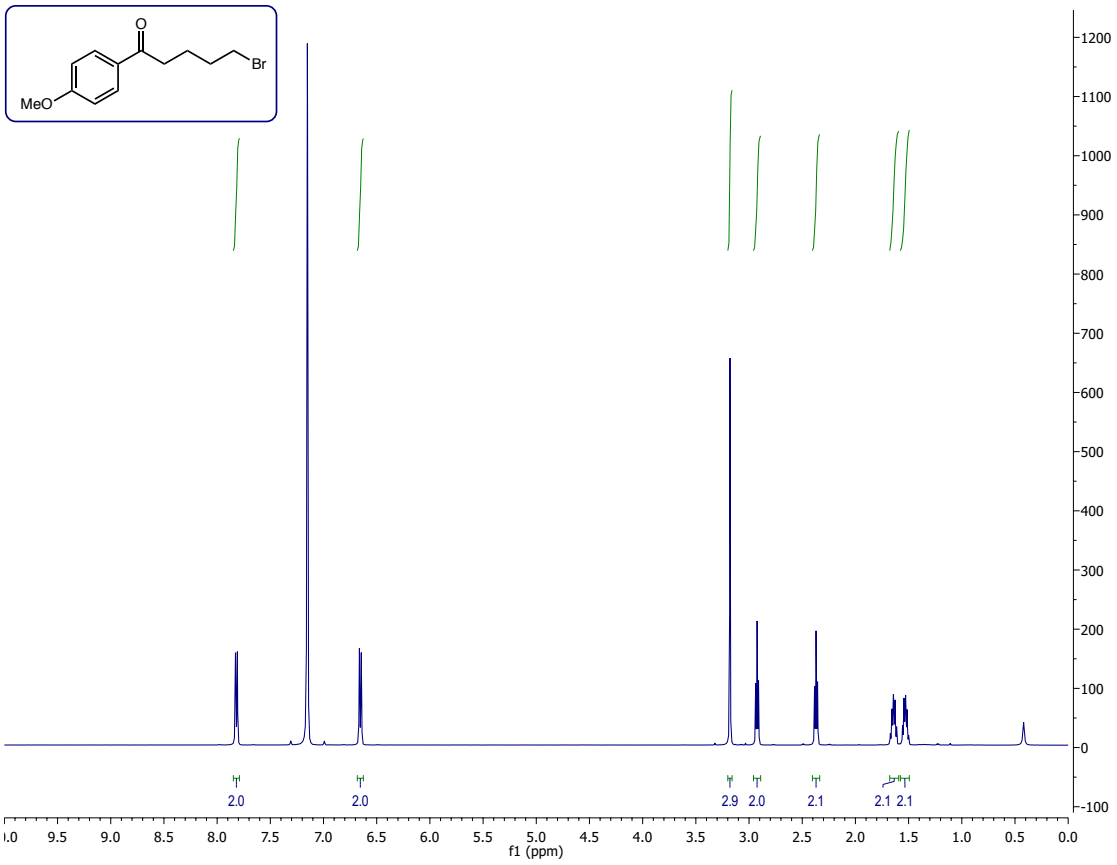

198.22
159.59
137.18
133.02
131.02
129.36
128.05
127.00
124.92
119.56
105.68
54.52
37.79
26.47
22.49
13.88
O
Me
MeO
131.02
129.36
128.05
127.00
124.92
f1 (ppm)

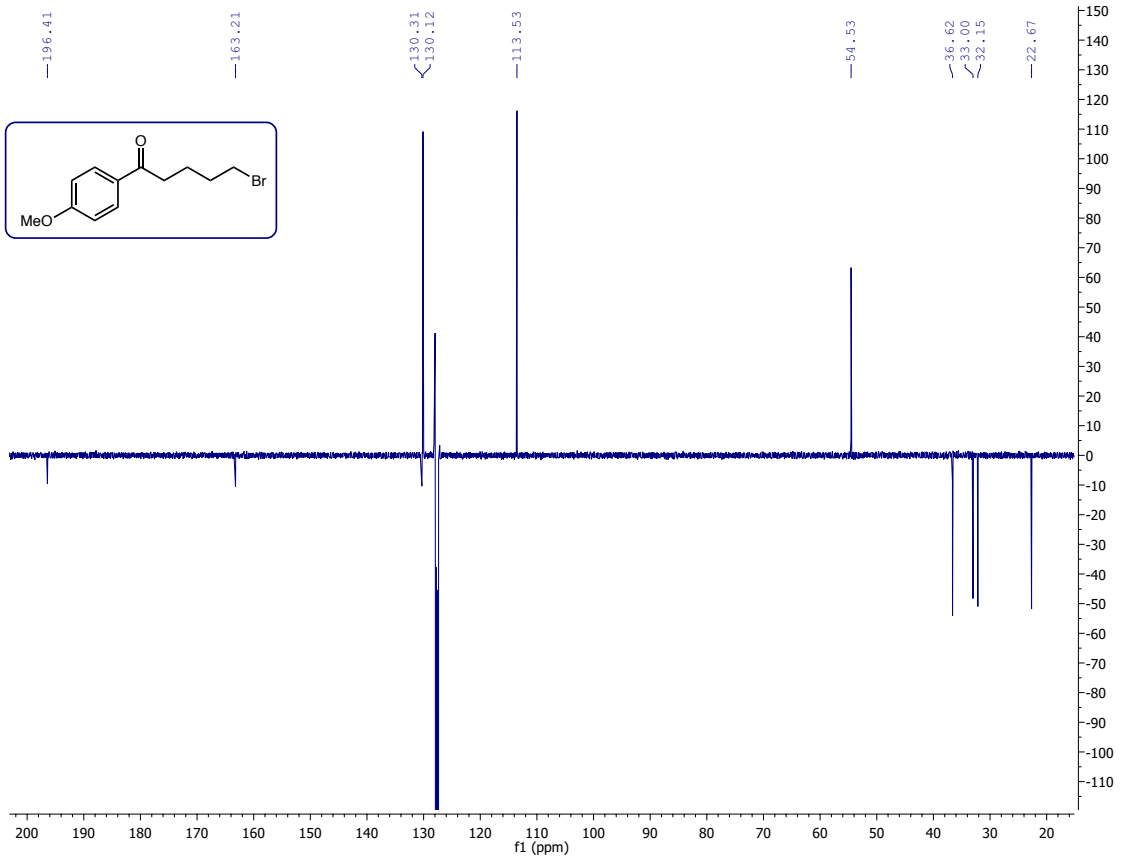

MeO
O
F
2.0
2.2
1.0 1.0
3.2
2.0
2.1 2.3
f1 (ppm)

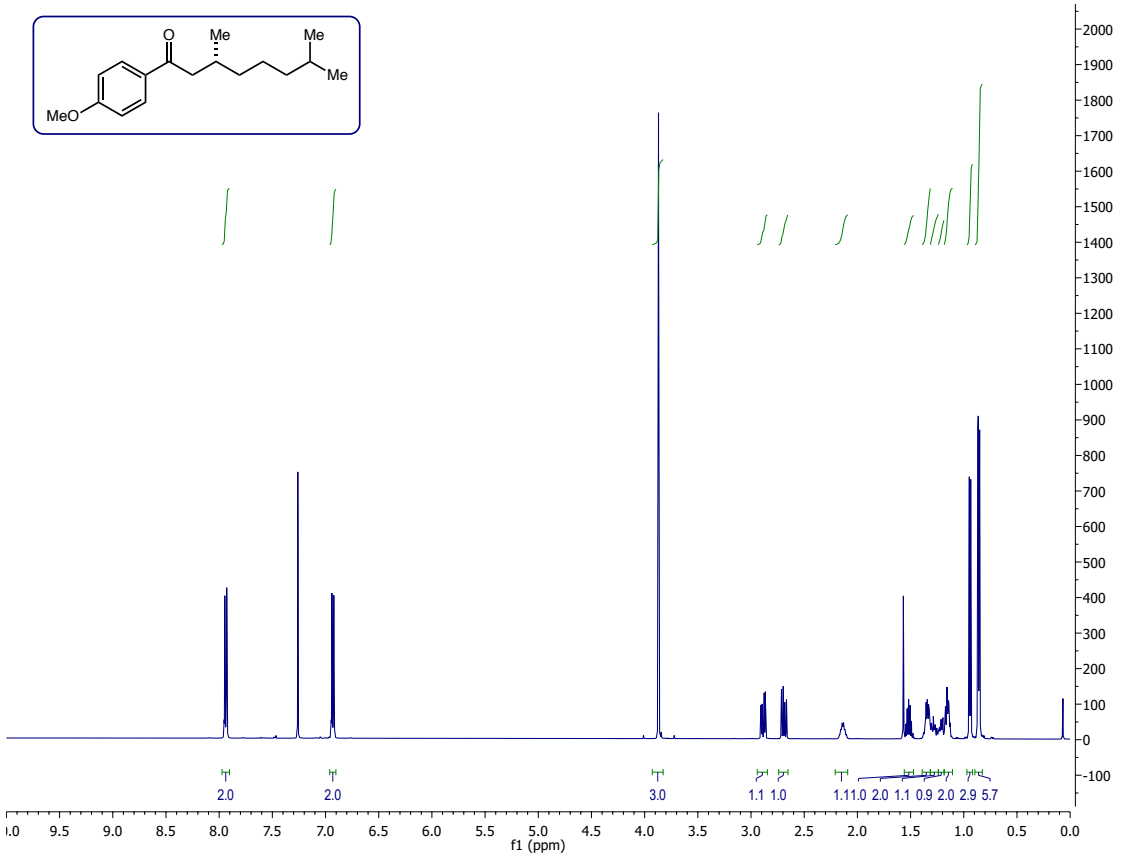

197.00
163.55
130.77
130.48
128.25 C6D6
128.06 C6D6
127.87 C6D6
113.89
84.32
83.01
54.89
37.48
30.13
20.33
MeO
O
F
f1 (ppm)

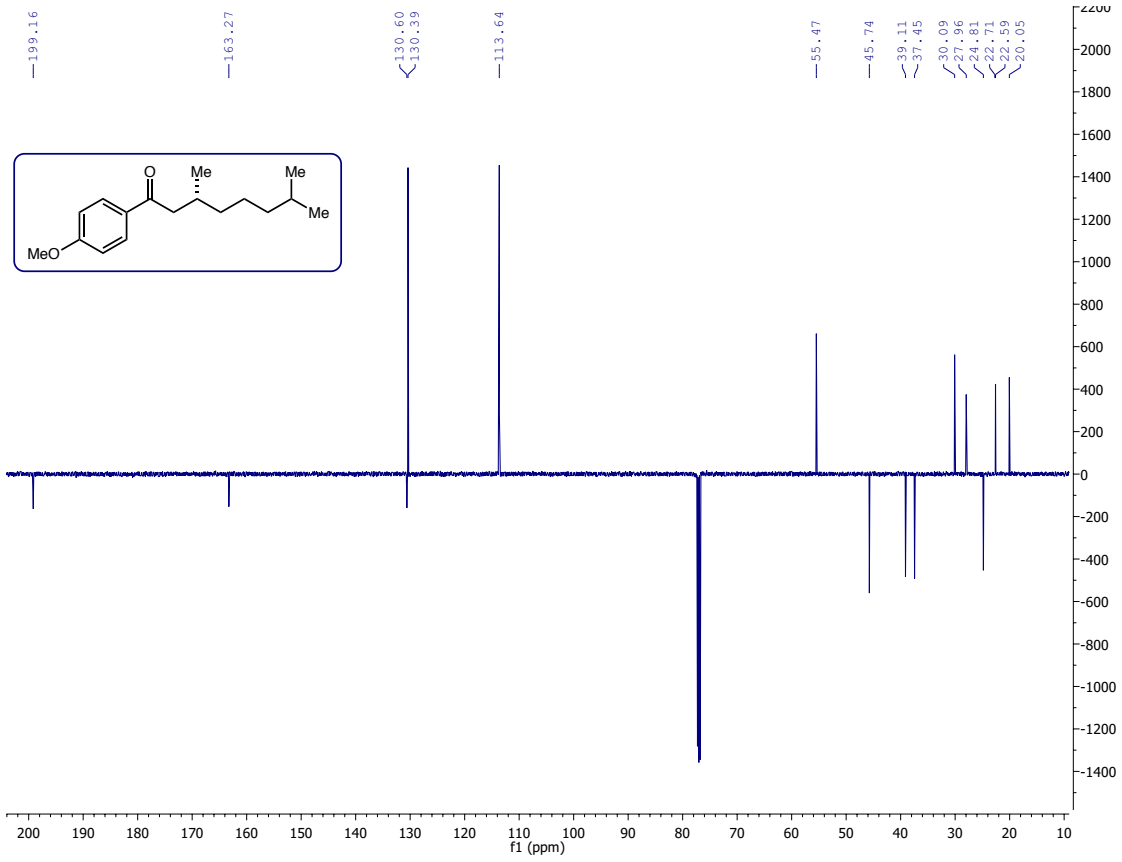

O
Cl
MeO
2.0
2.0
2.9
1.9
2.0
2.1
2.0
f1 (ppm)

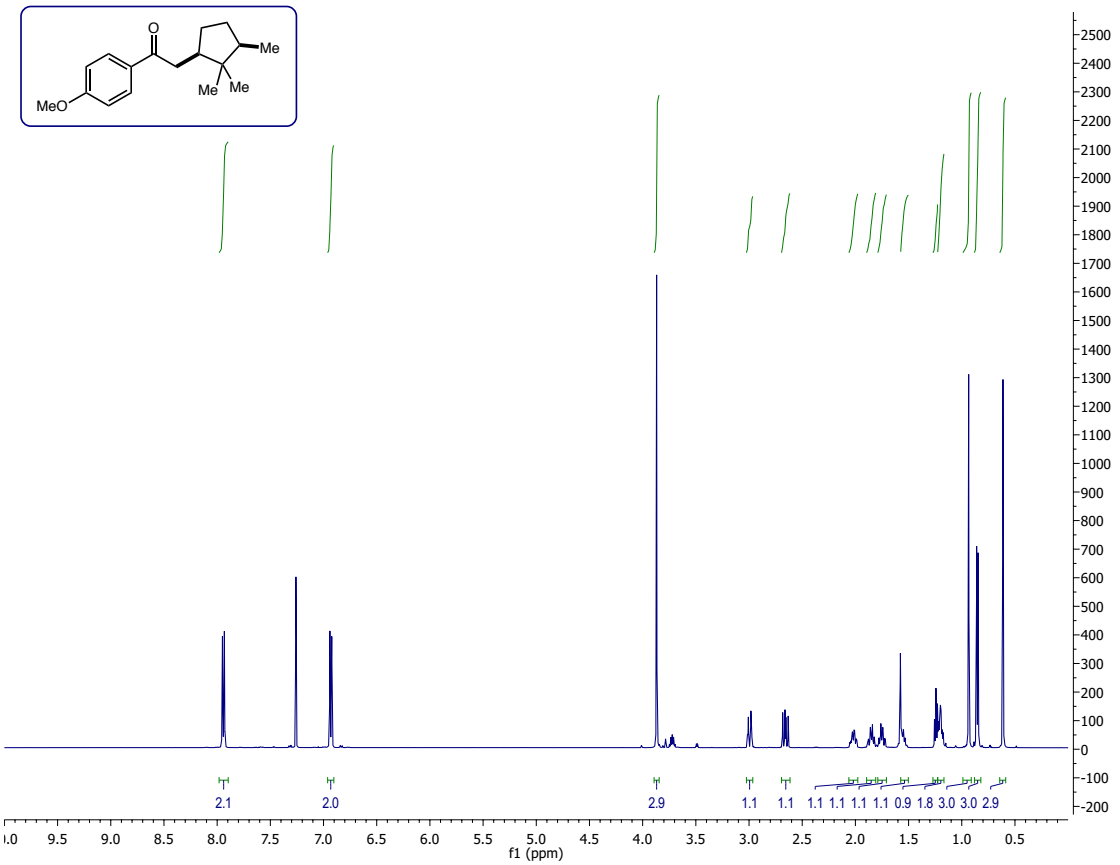

196.46
163.20
130.33
130.11
113.52
54.52
44.35
36.75
31.99
21.42
O
Cl
MeO
f1 (ppm)

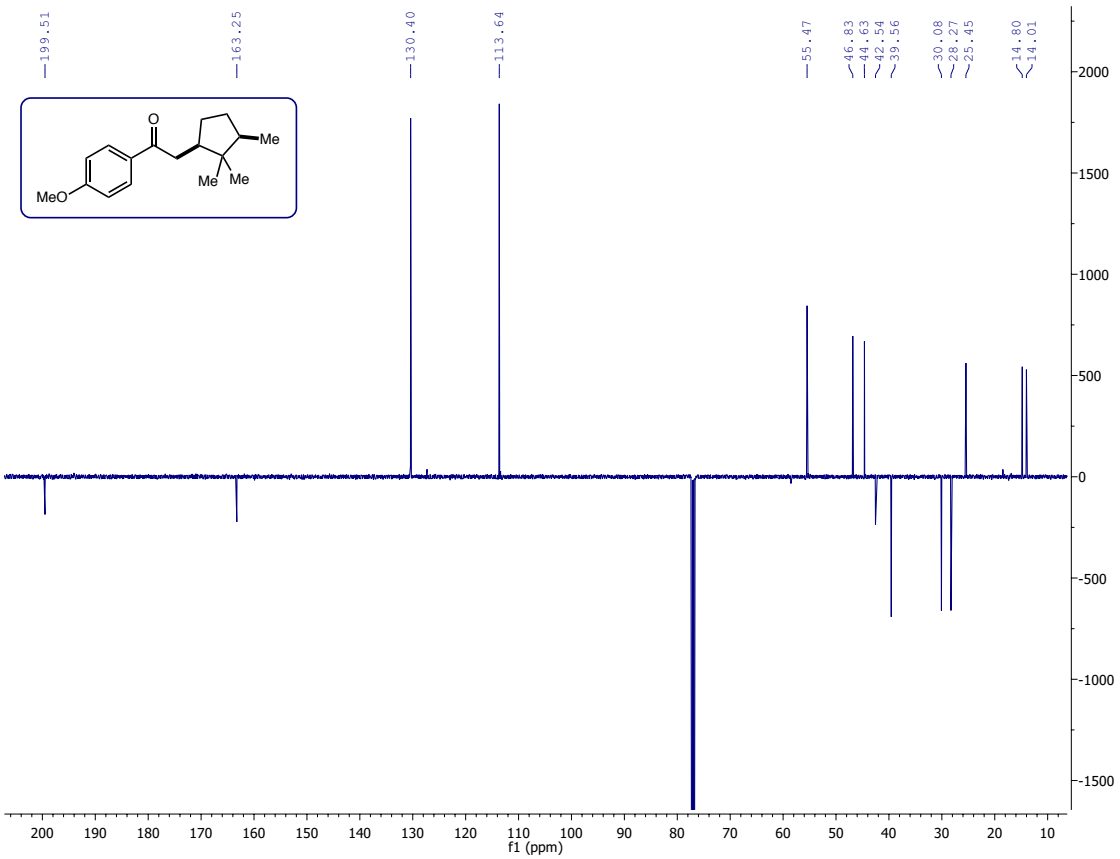

O
Br
MeO
2.0
2.0
2.9
2.0
2.1
2.1
2.1
f1 (ppm)

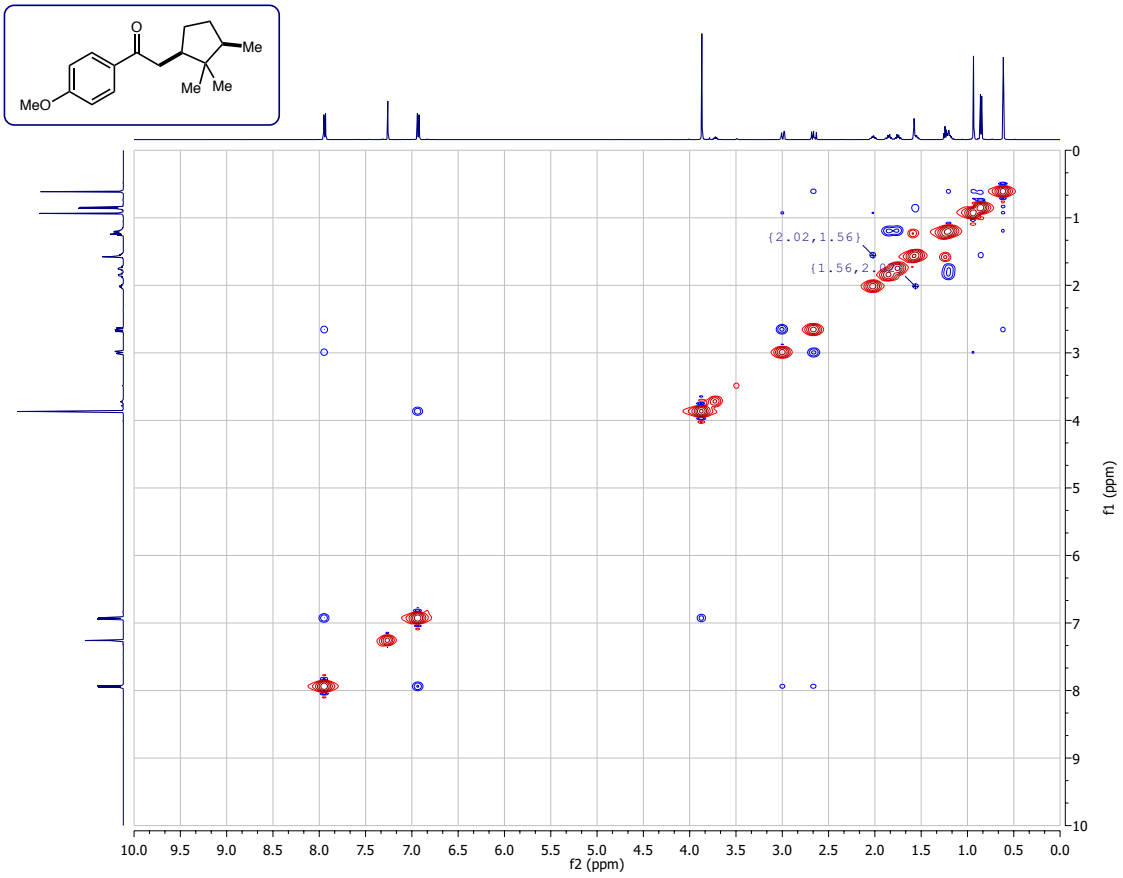

196.41
163.21
130.31
130.12
113.53
54.53
36.62
33.00
32.15
22.67
O
Br
MeO
f1 (ppm)

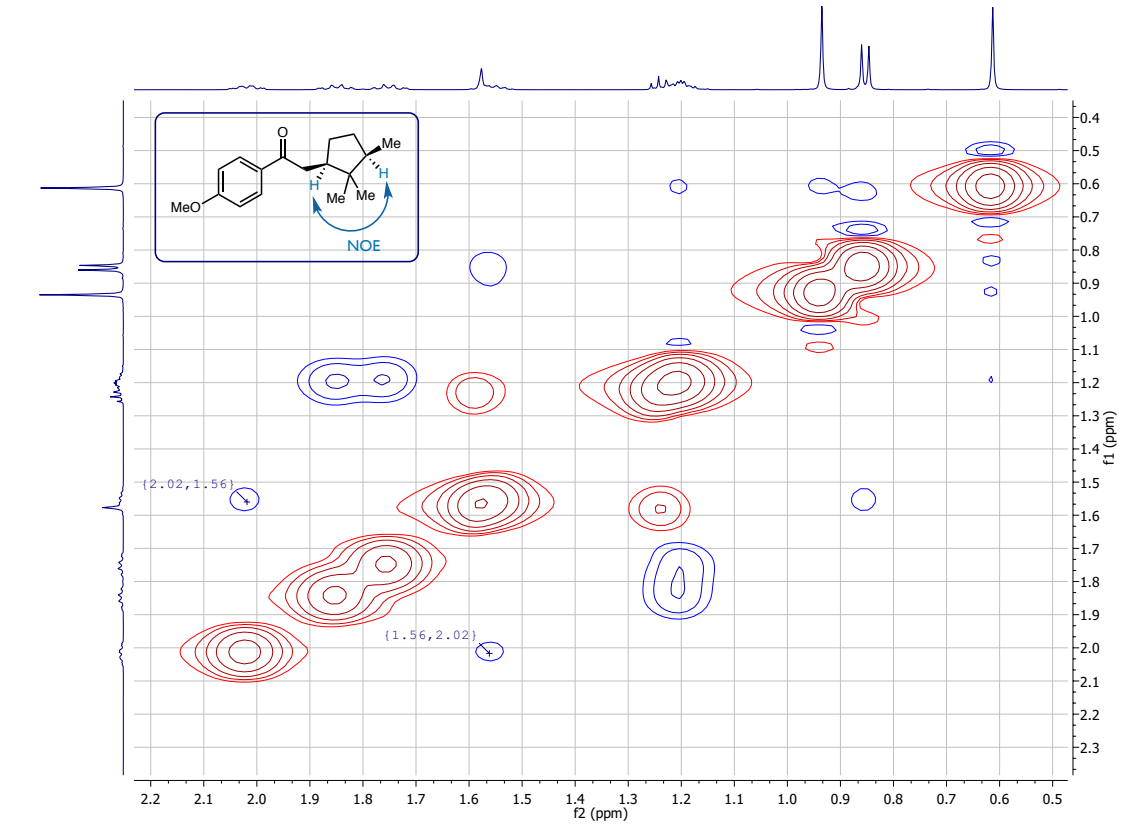

O
Me
Me
Me
MeO
2.0
2.0
3.0
1.1
1.0
1.1
1.0
2.0
1.1
0.9
2.0
2.9
5.7
f1 (ppm)

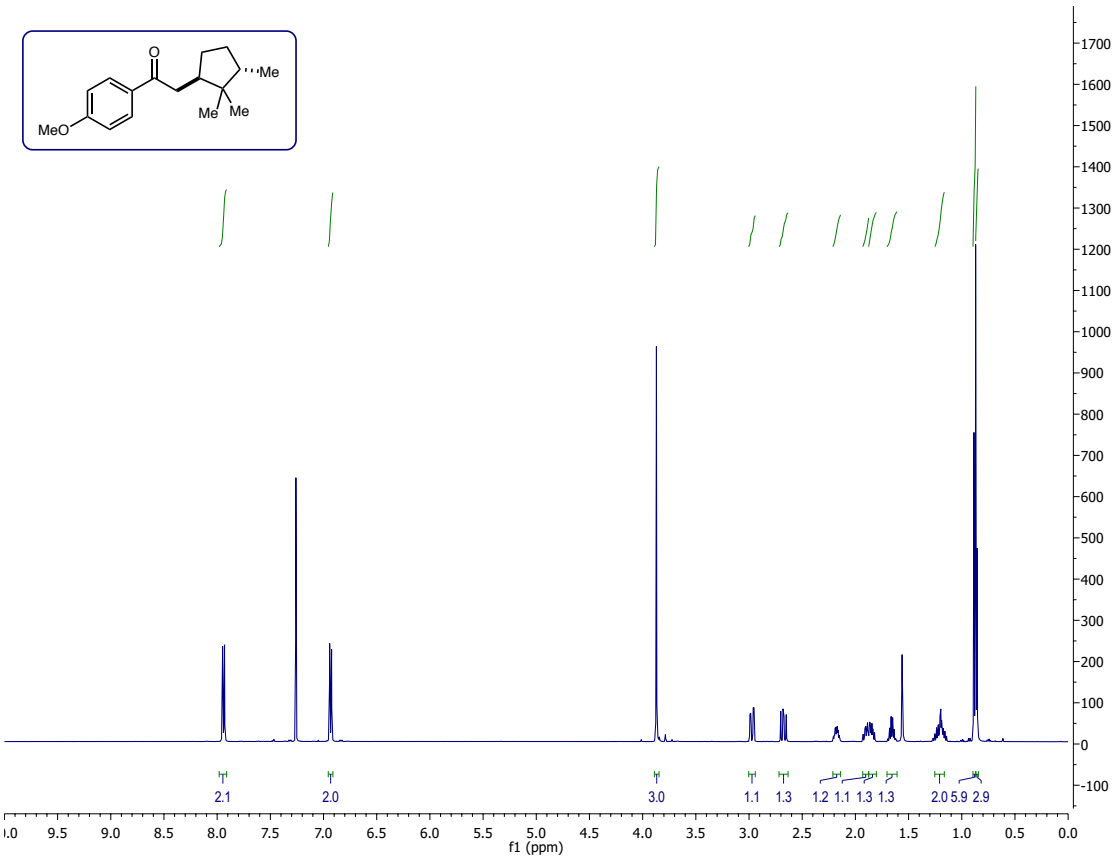

199.16
163.27
130.60
130.39
113.64
55.47
45.74
39.11
37.45
30.09
27.96
24.81
22.71
22.59
20.05
O
Me
Me
Me
MeO
f1 (ppm)


O
Me
Me
Me
MeO
2.1
2.0
2.9
1.1
1.1
1.1 1.1 1.1 1.1 0.9 1.8 3.0 3.0 2.9
f1 (ppm)

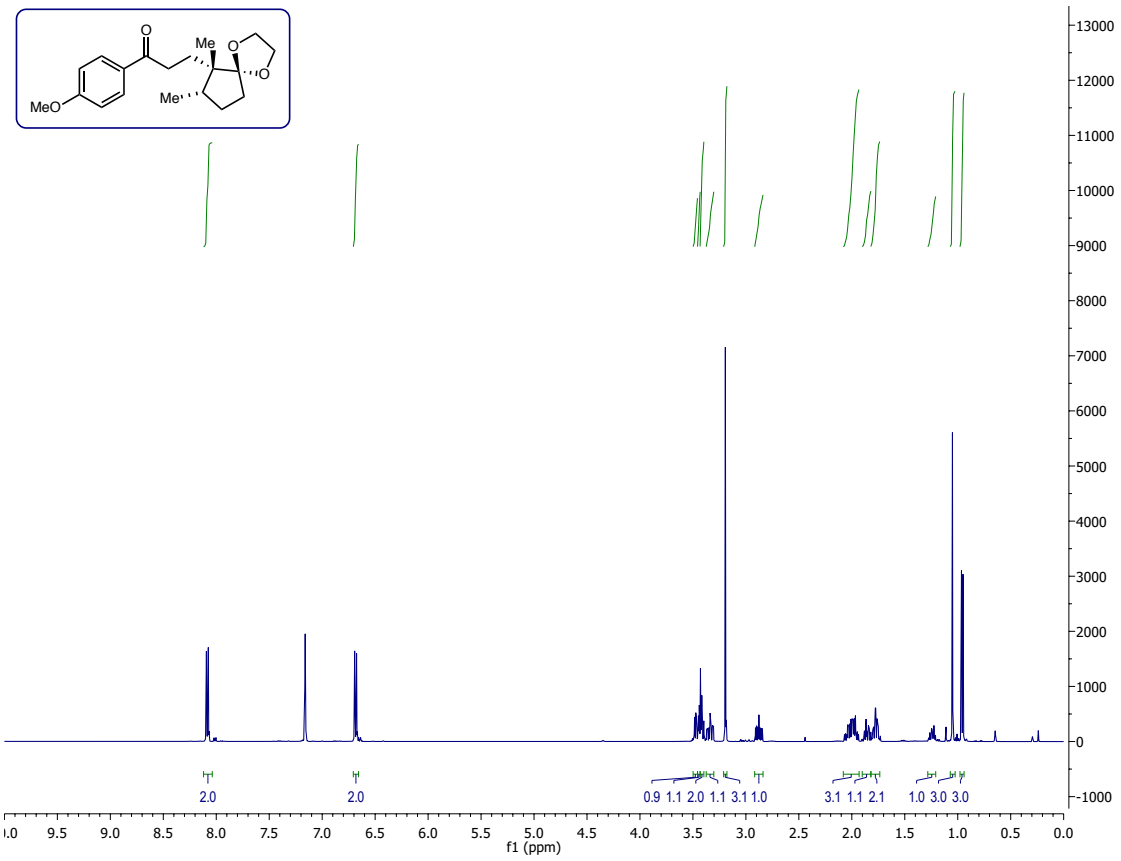

199.51
163.25
130.40
113.64
55.47
46.83
44.63
42.54
39.56
30.08
28.27
25.45
14.80
14.01
O
Me
Me
Me
MeO
f1 (ppm)

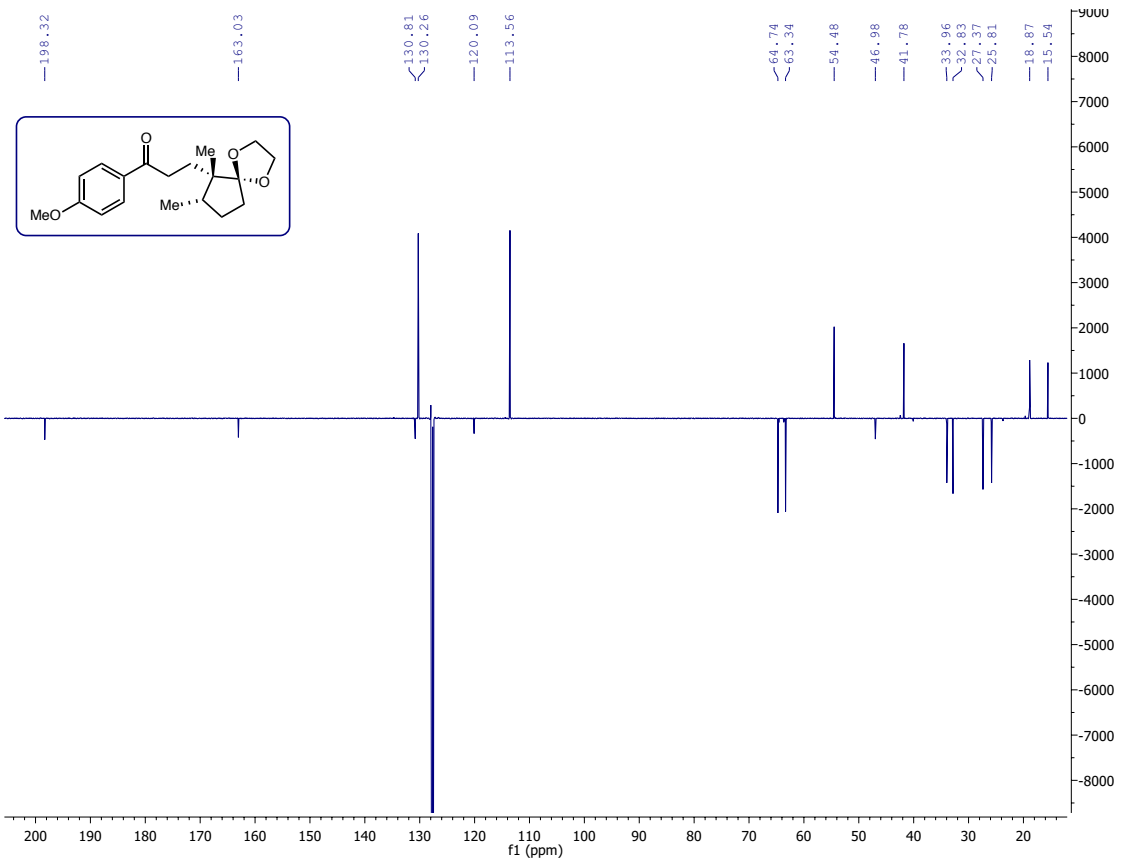

MeO
Me
Me
Me
{2.02,1.56}
{1.56,2.02}
f2 (ppm)
f1 (ppm)

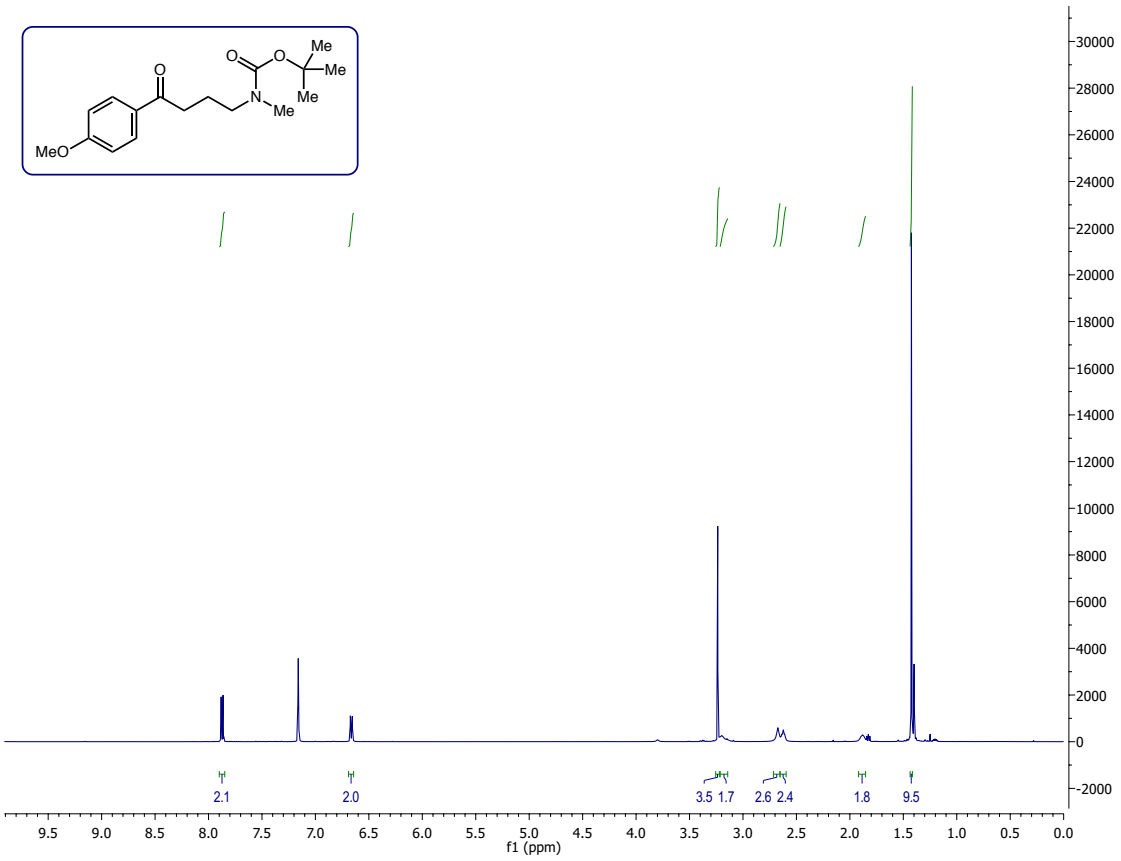

MeO
Me
Me
Me
H
H
NOE
{2.02,1.56}
{1.56,2.02}
f2 (ppm)
f1 (ppm)

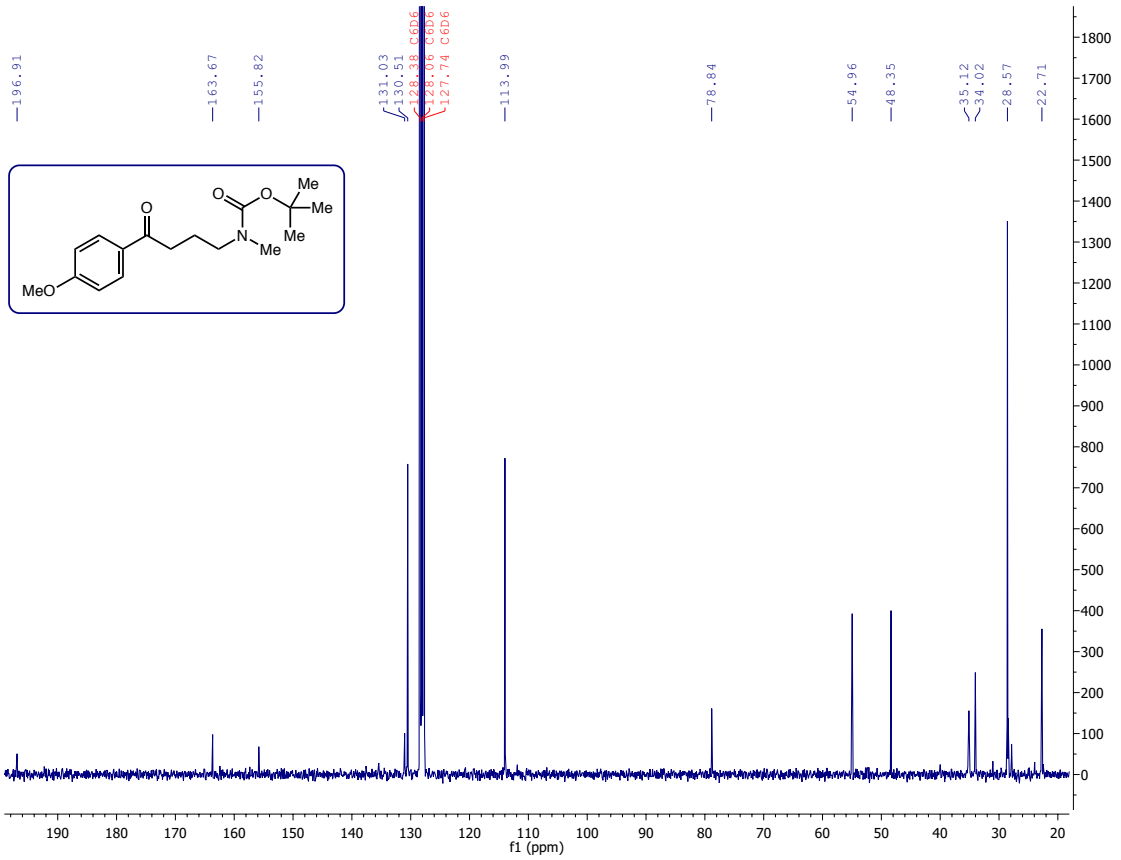

MeO
Me
Me
Me
2.1
2.0
3.0
1.1
1.3
1.2
1.1
1.3
1.3
2.0
5.9
2.9
f1 (ppm)

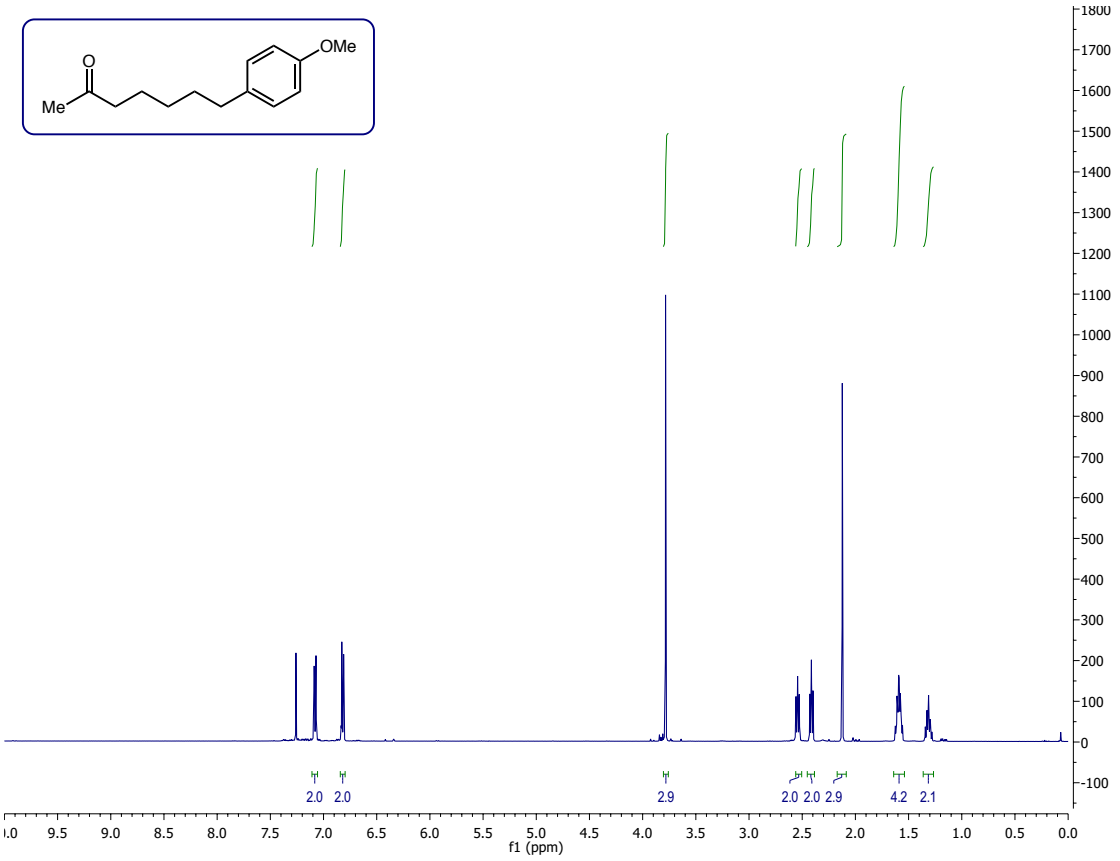

199.63
163.24
130.51
130.38
113.65
55.47
44.40
43.53
42.26
40.12
31.39
29.46
24.25
23.60
16.37
MeO
Me
Me
Me
f1 (ppm)

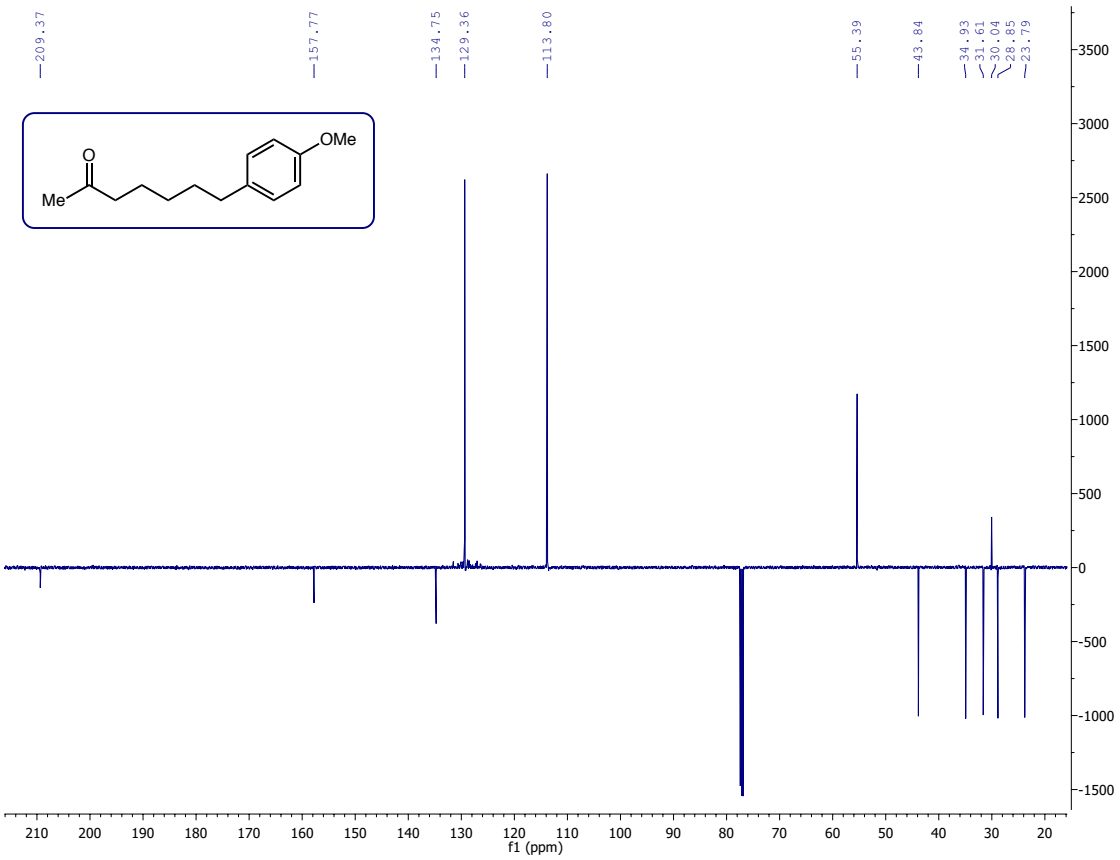

MeO
Me
Me
O
O
O
2.0
2.0
0.9 1.1 2.0 1.1 3.1 1.0
3.1 1.1 2.1
1.0 3.0 3.0
f1 (ppm)

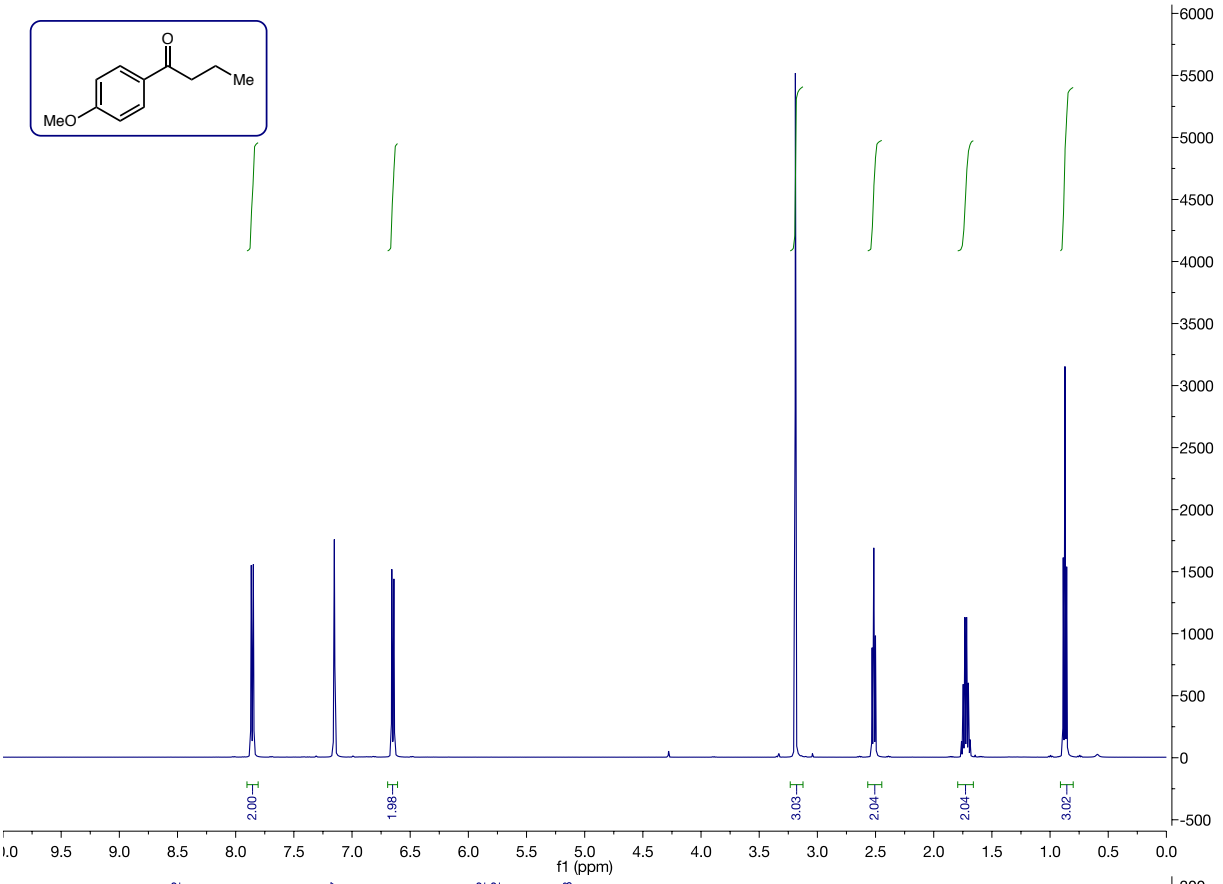

198.32
163.03
130.81
130.26
120.09
113.56
64.74
63.34
54.48
46.98
41.78
33.96
32.83
27.37
25.81
18.87
15.54
MeO
Me
Me
O
O
O
f1 (ppm)

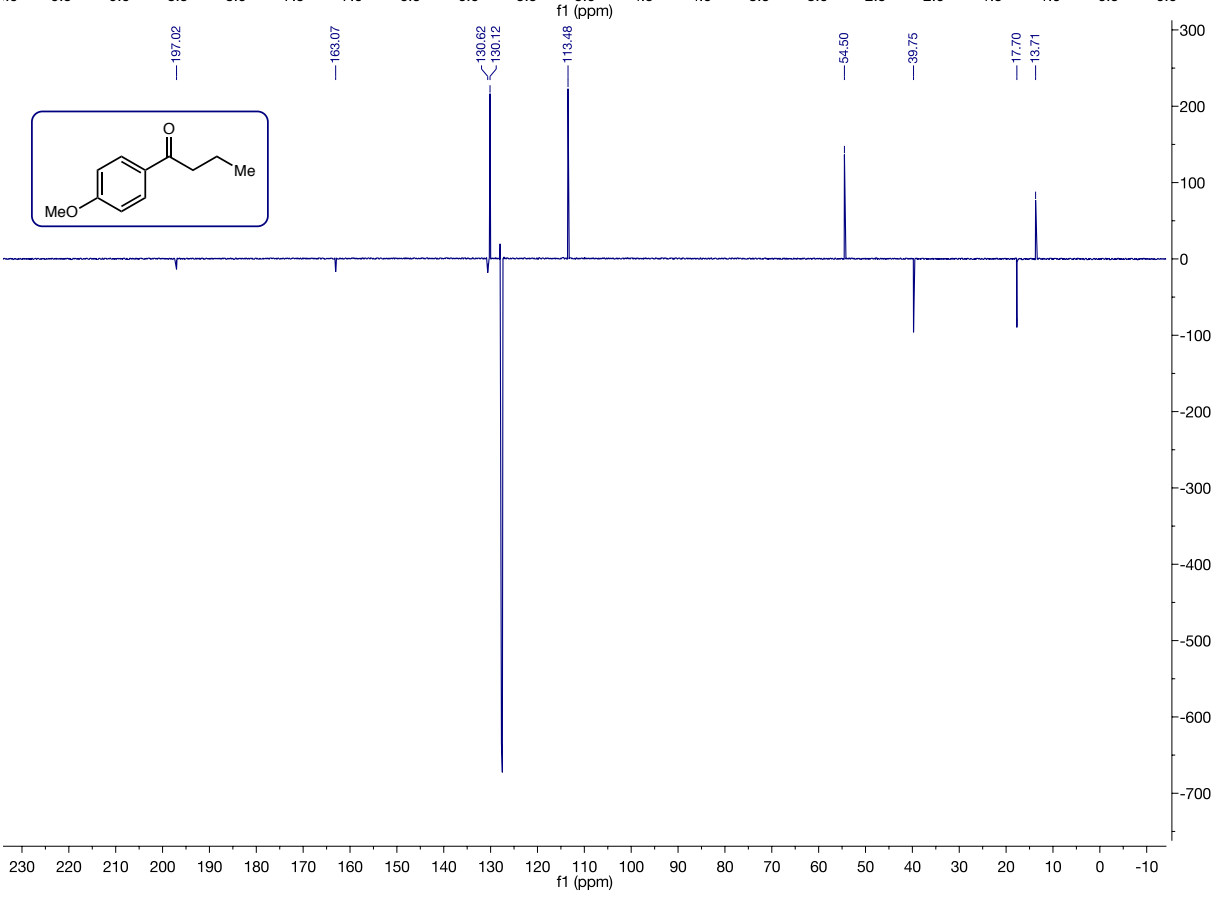

MeO
O
O
O
N
Me
Me
Me
Me
2.1
2.0
3.5 1.7
2.6 2.4
1.8
9.5
f1 (ppm)

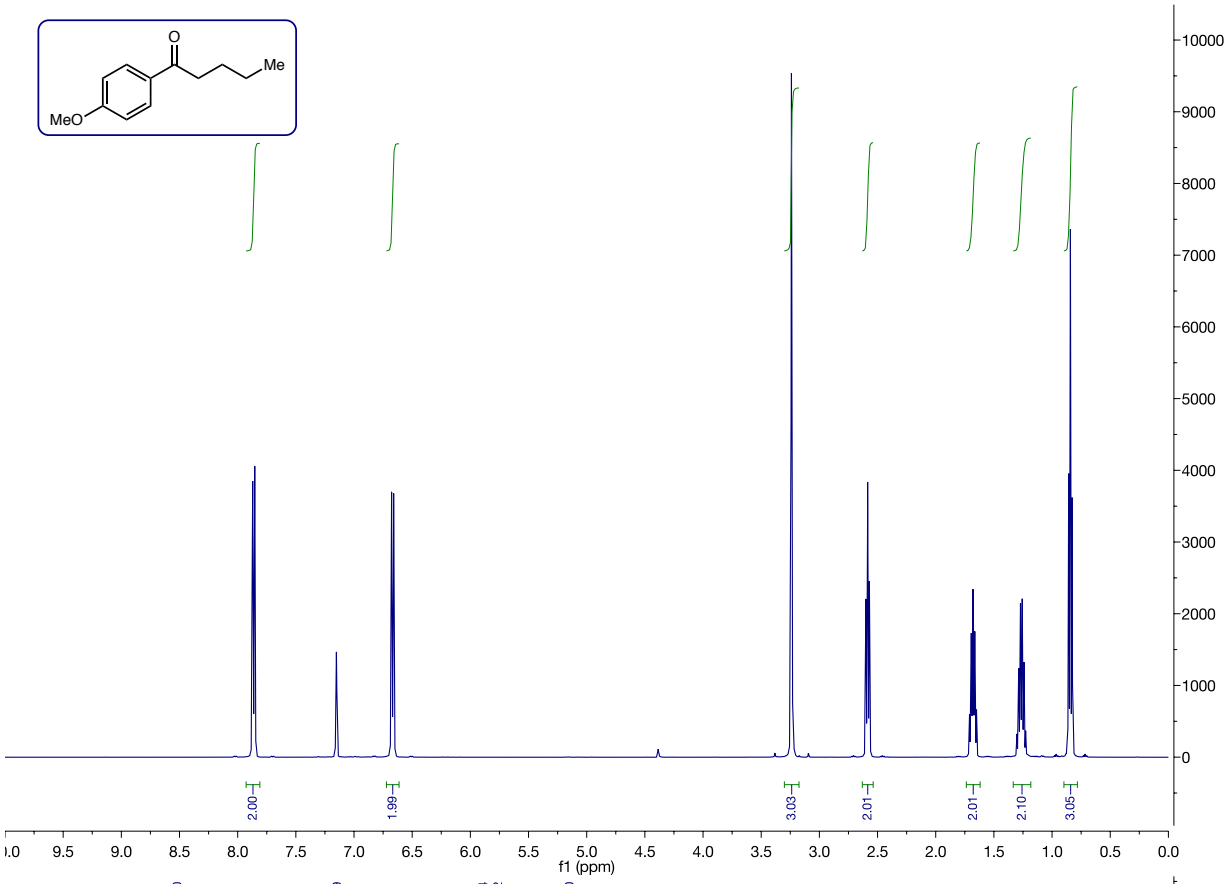

196.91
163.67
155.82
131.03
130.51
128.38 C6D6
128.06 C6D6
127.74 C6D6
113.99
78.84
54.96
48.35
35.12
34.02
28.57
22.71
MeO
f1 (ppm)

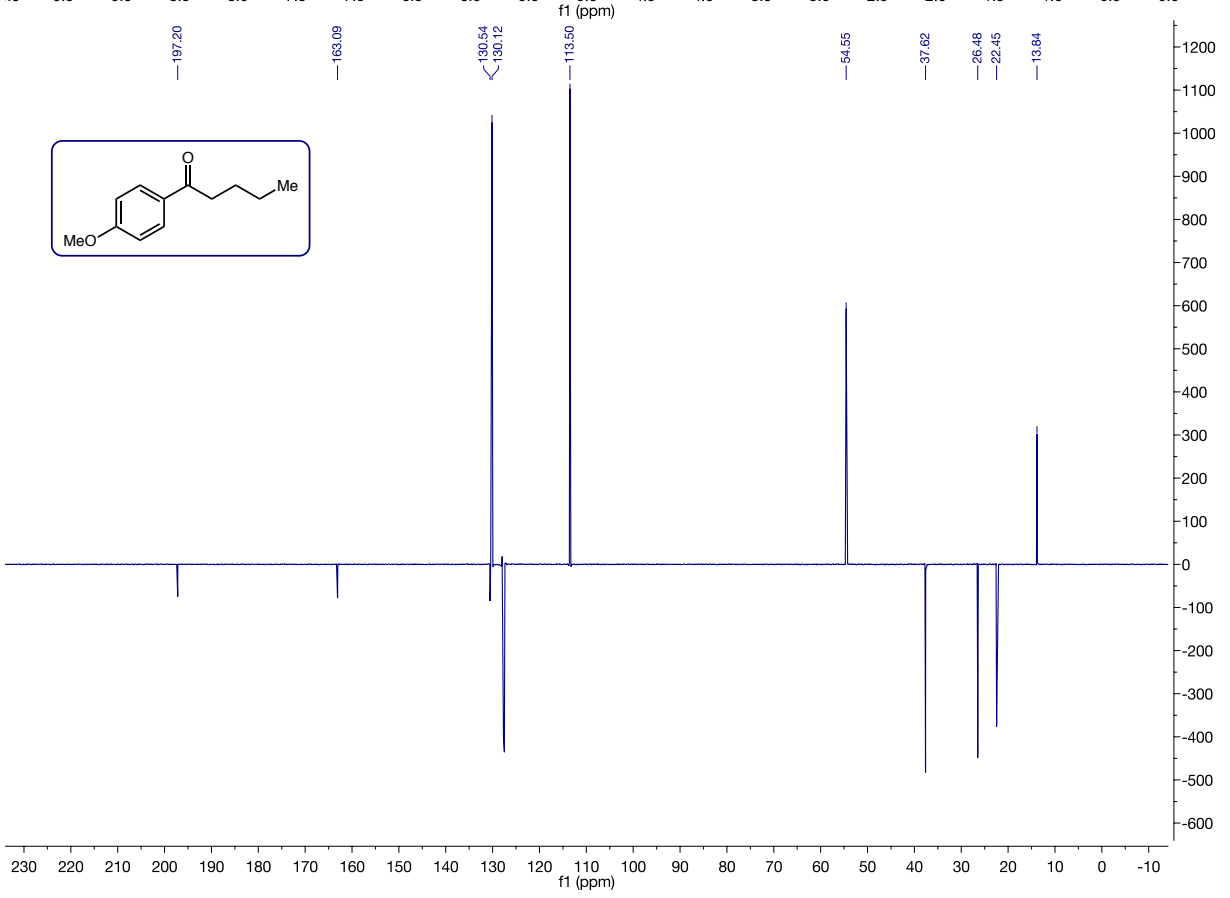

OMe
O
Me
2.0 2.0 2.9 2.0 2.0 2.9 4.2 2.1
f1 (ppm)

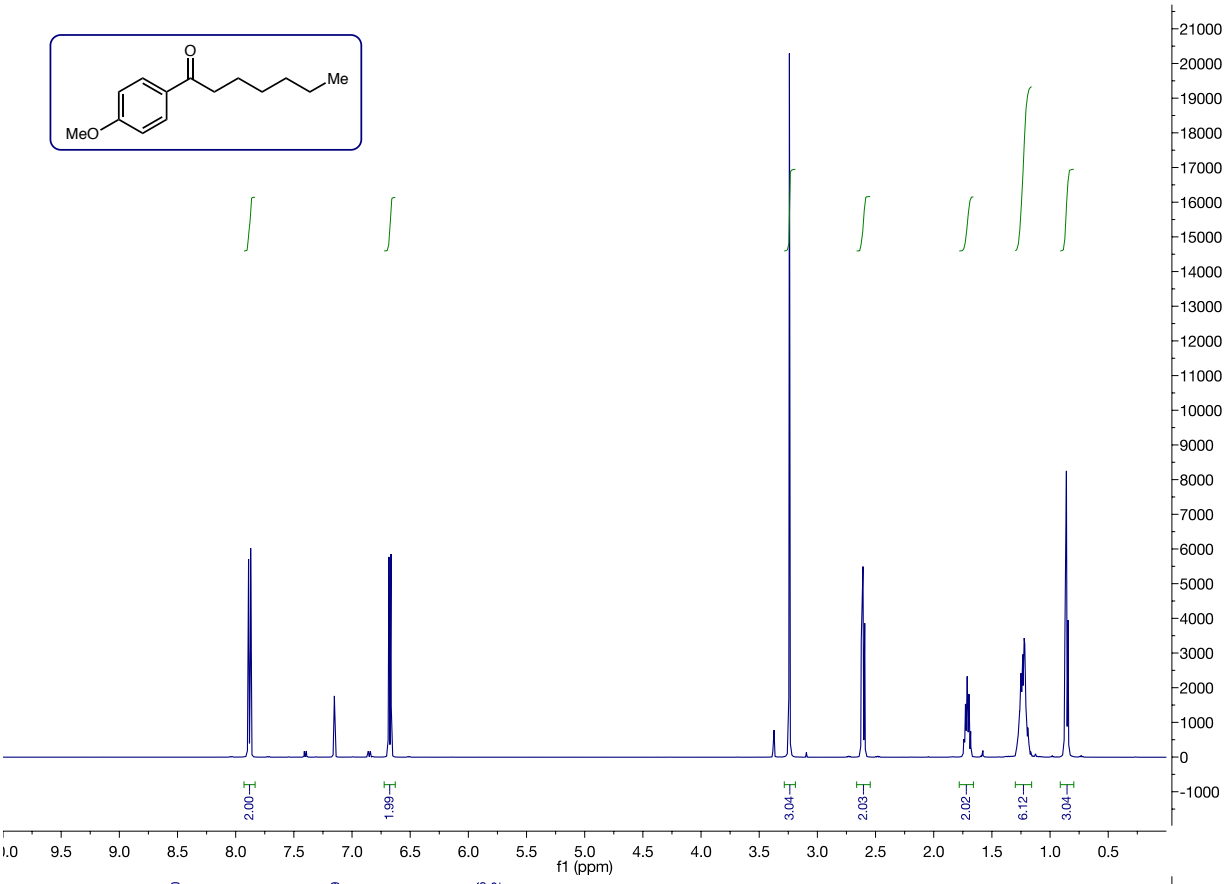

209.37
157.77
134.75
129.36
113.80
55.39
43.84
34.93
31.61
30.04
28.85
23.79
OMe
O
Me
f1 (ppm)

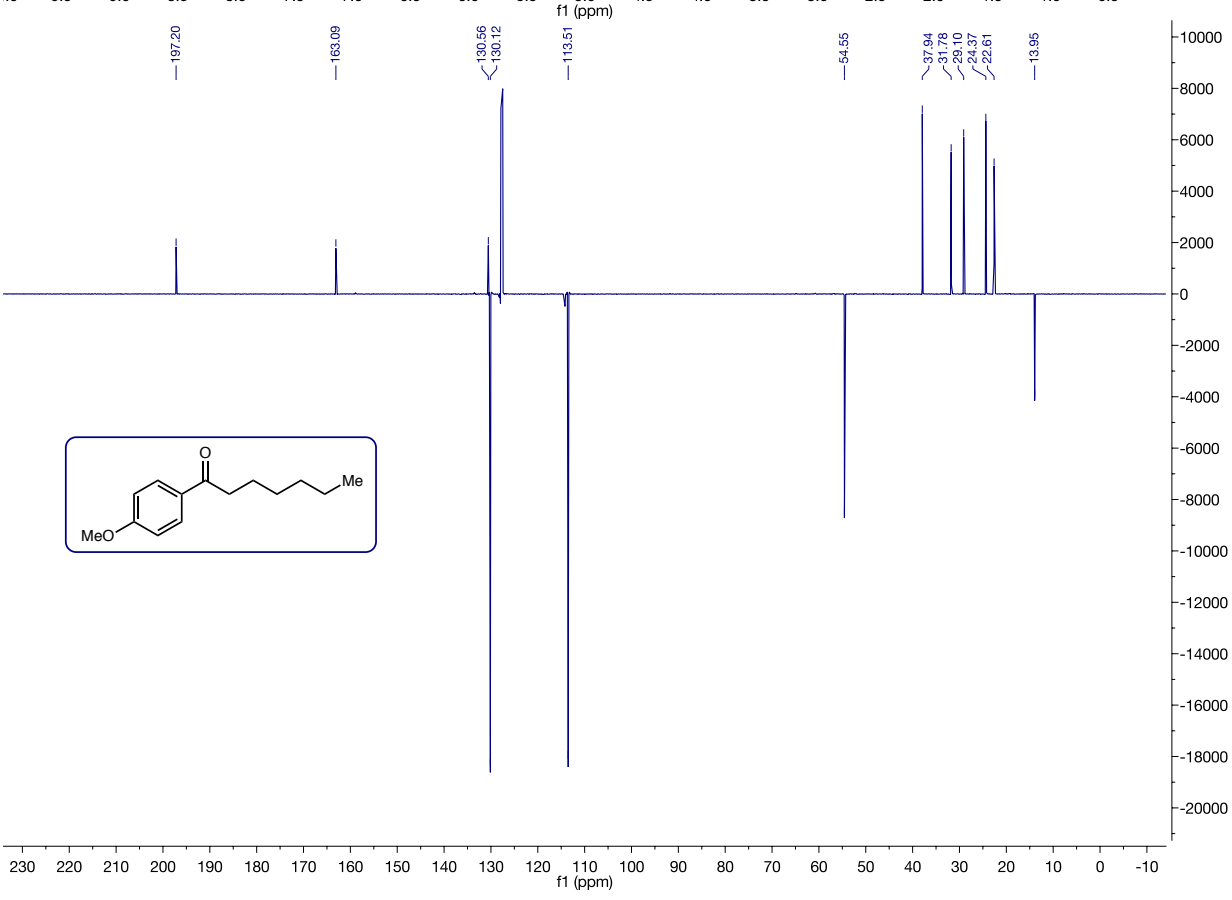

O
Me
MeO
2.00
1.98
3.03
2.04
2.04
3.02
f1 (ppm)

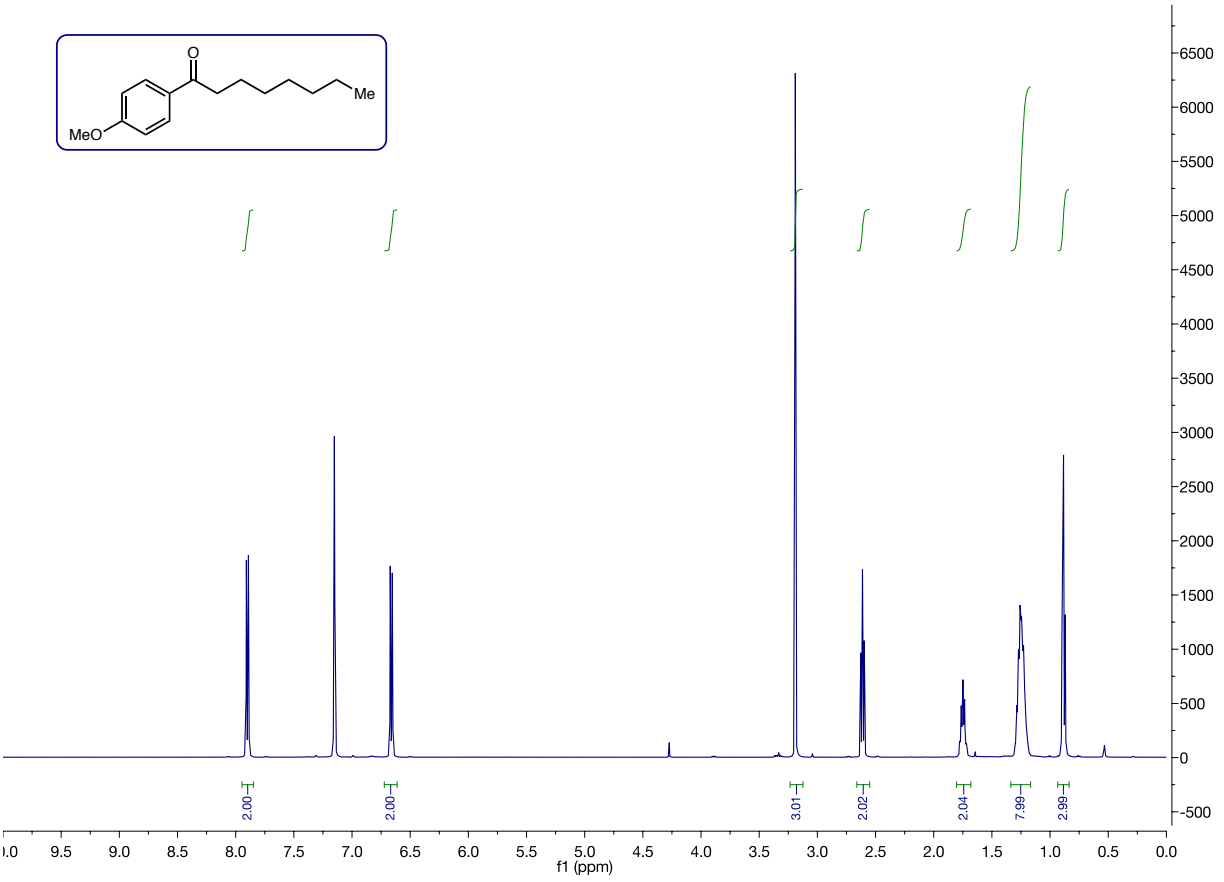

197.02
163.07
130.62
130.12
113.48
54.50
39.75
17.70
13.71
O
Me
MeO
f1 (ppm)

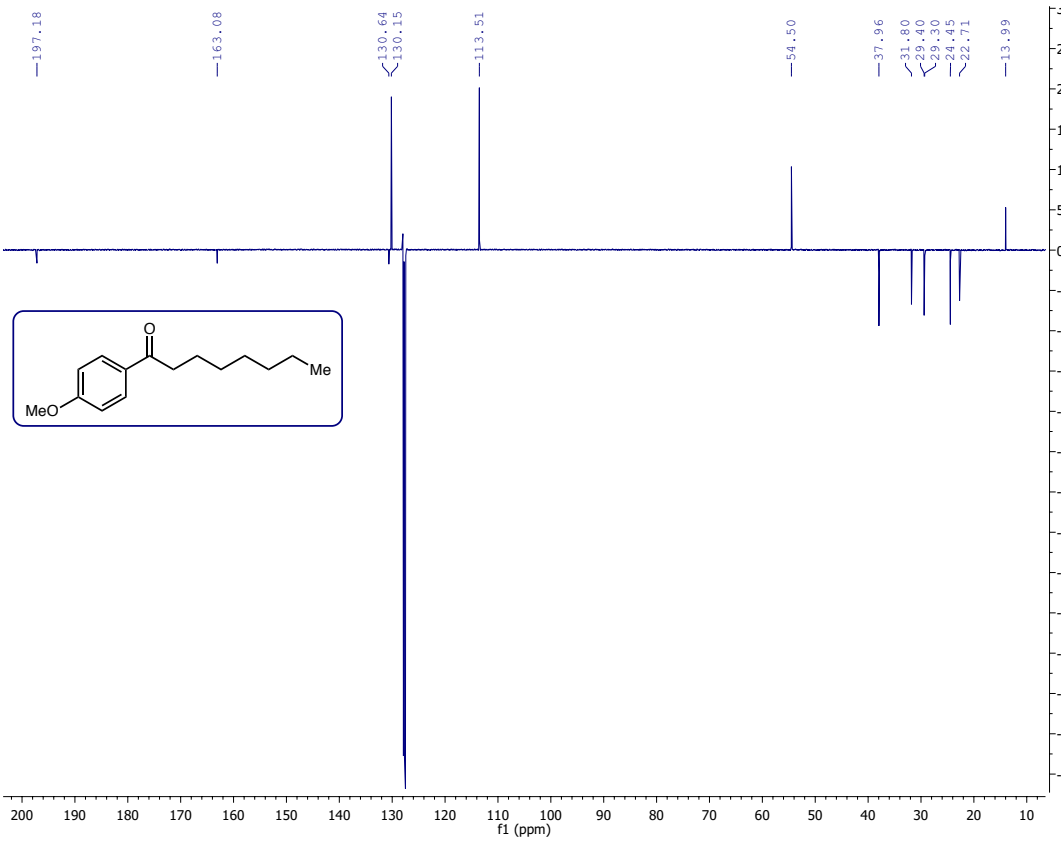

O
Me
MeO
2.00
1.99
3.03
2.01
2.01
2.10
3.05
f1 (ppm)

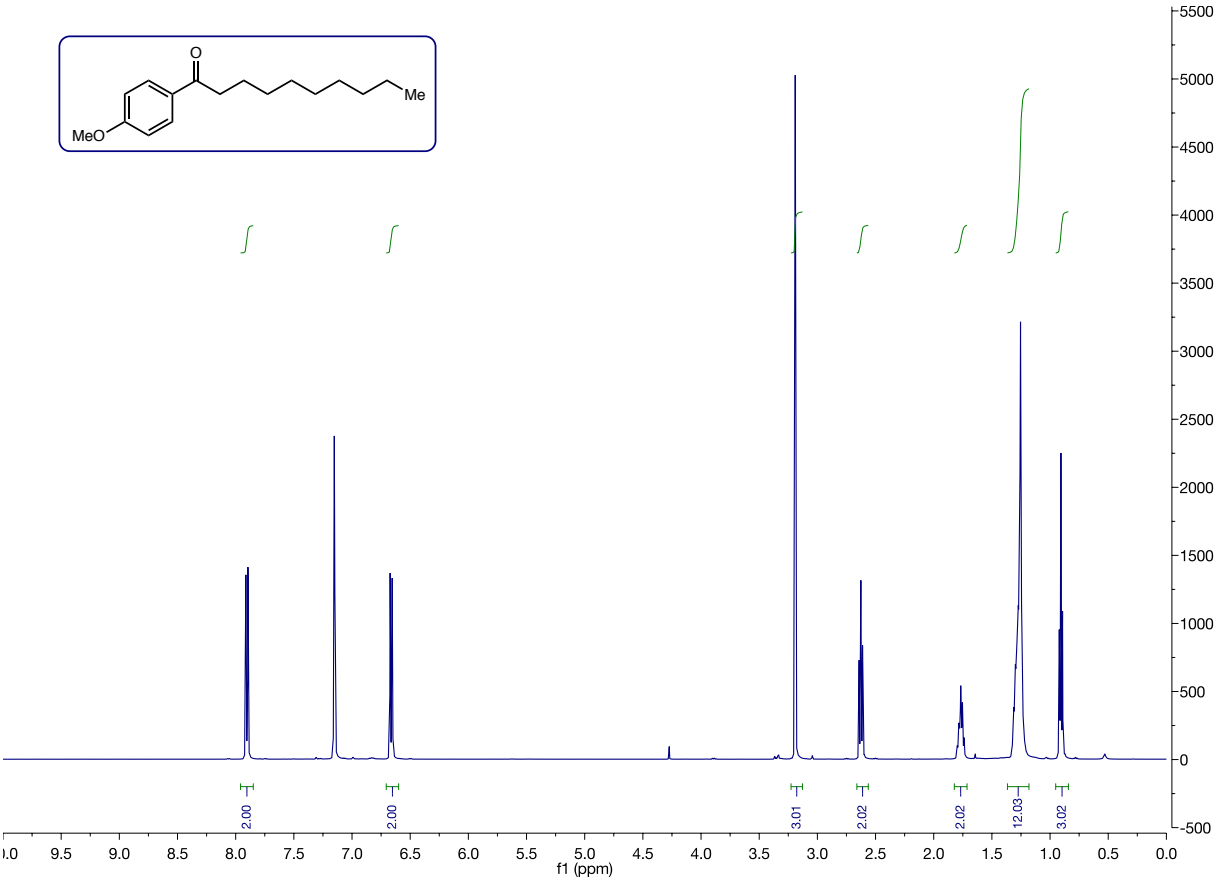

197.20
163.09
130.54
130.12
113.50
54.55
37.62
26.48
22.45
13.84
O
Me
MeO
f1 (ppm)

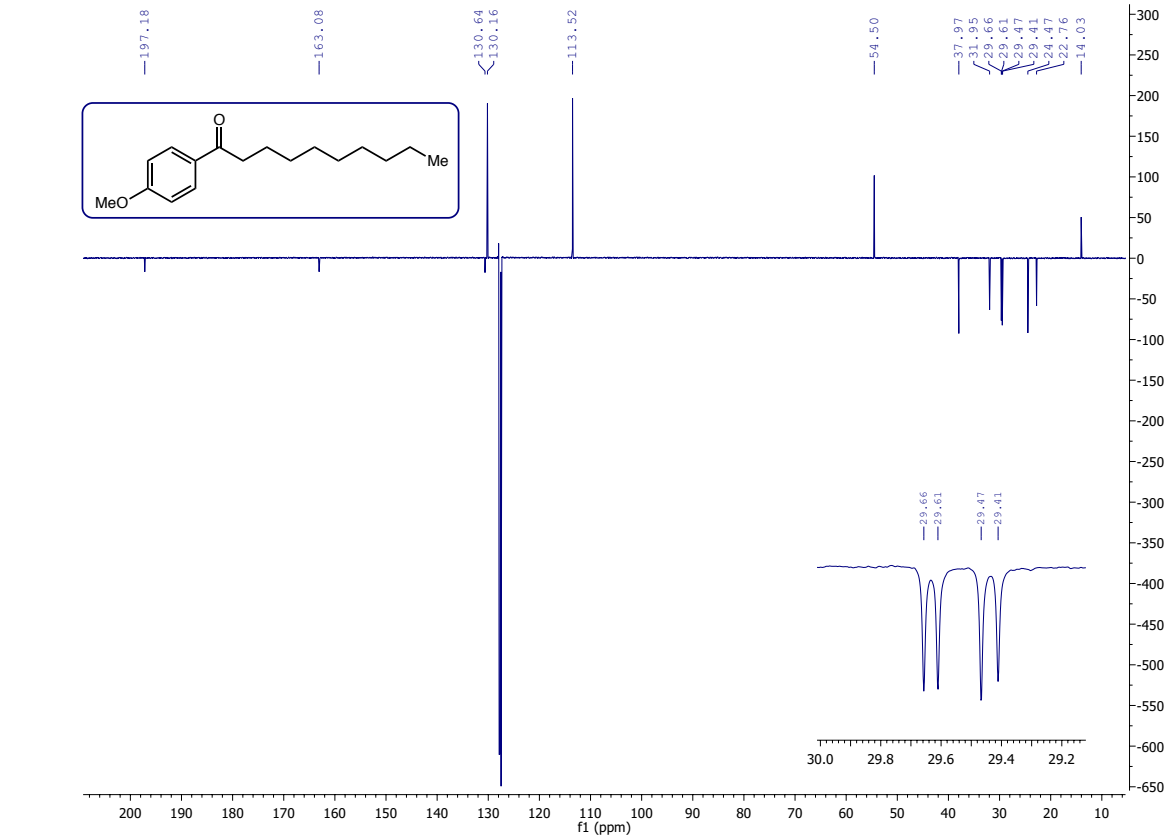

O
Me
MeO
2.00
1.99
3.04
2.03
2.02
6.12
3.04
f1 (ppm)

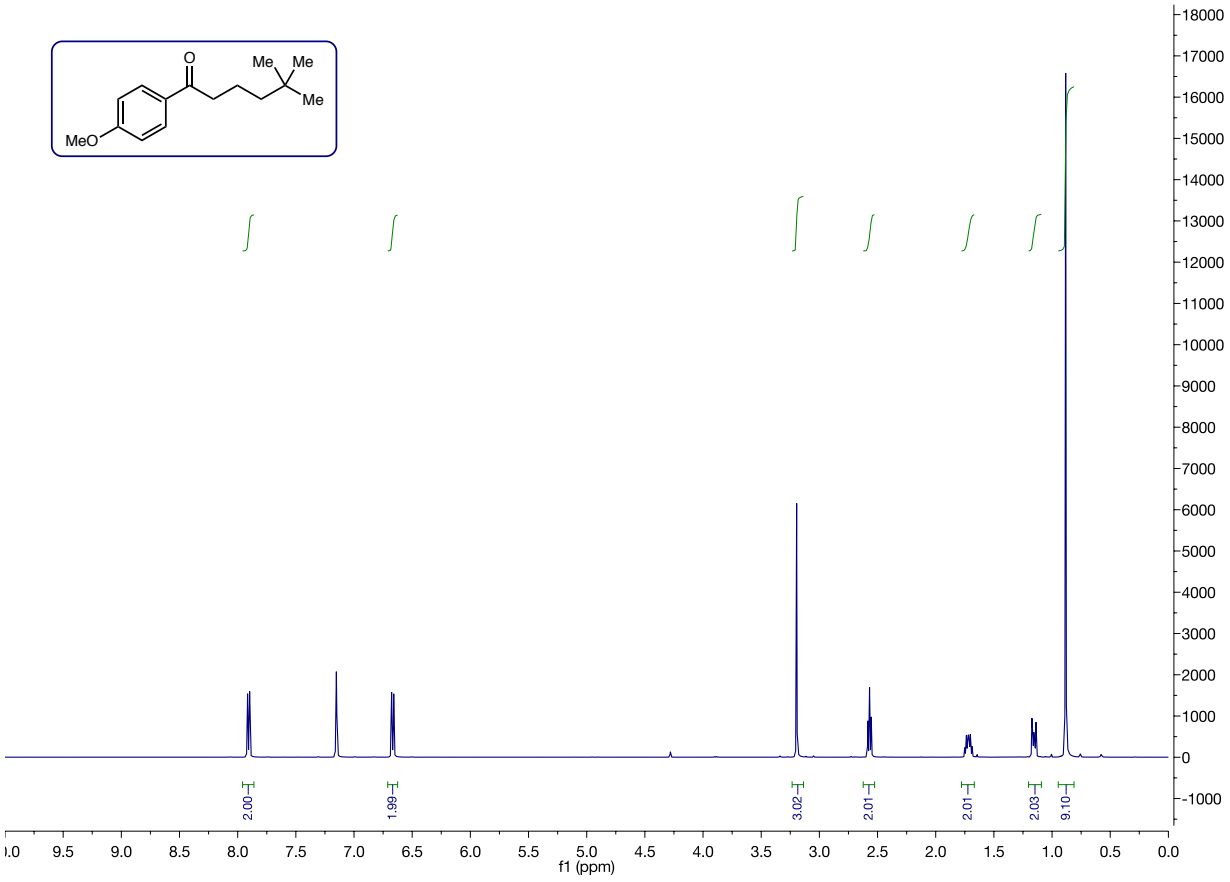

197.20
163.09
130.56
130.12
113.51
54.55
37.94
31.78
29.10
24.37
22.61
13.95
O
Me
MeO
f1 (ppm)


O
Me
MeO
2.00
2.00
3.01
2.02
2.04
7.99
2.99
f1 (ppm)


197.18
163.08
130.64
130.15
113.51
54.50
37.96
31.80
29.40
29.30
24.45
22.71
13.99
O
Me
MeO
f1 (ppm)


O
Me
MeO
2.00
2.00
3.01
2.02
2.02
12.03
3.02
f1 (ppm)


197.18
163.08
130.64
130.16
113.52
54.50
37.97
31.95
29.66
29.61
29.47
29.41
24.47
22.76
14.03
O
Me
MeO
29.66
29.61
29.47
29.41
f1 (ppm)


O
Me
Me
Me
MeO
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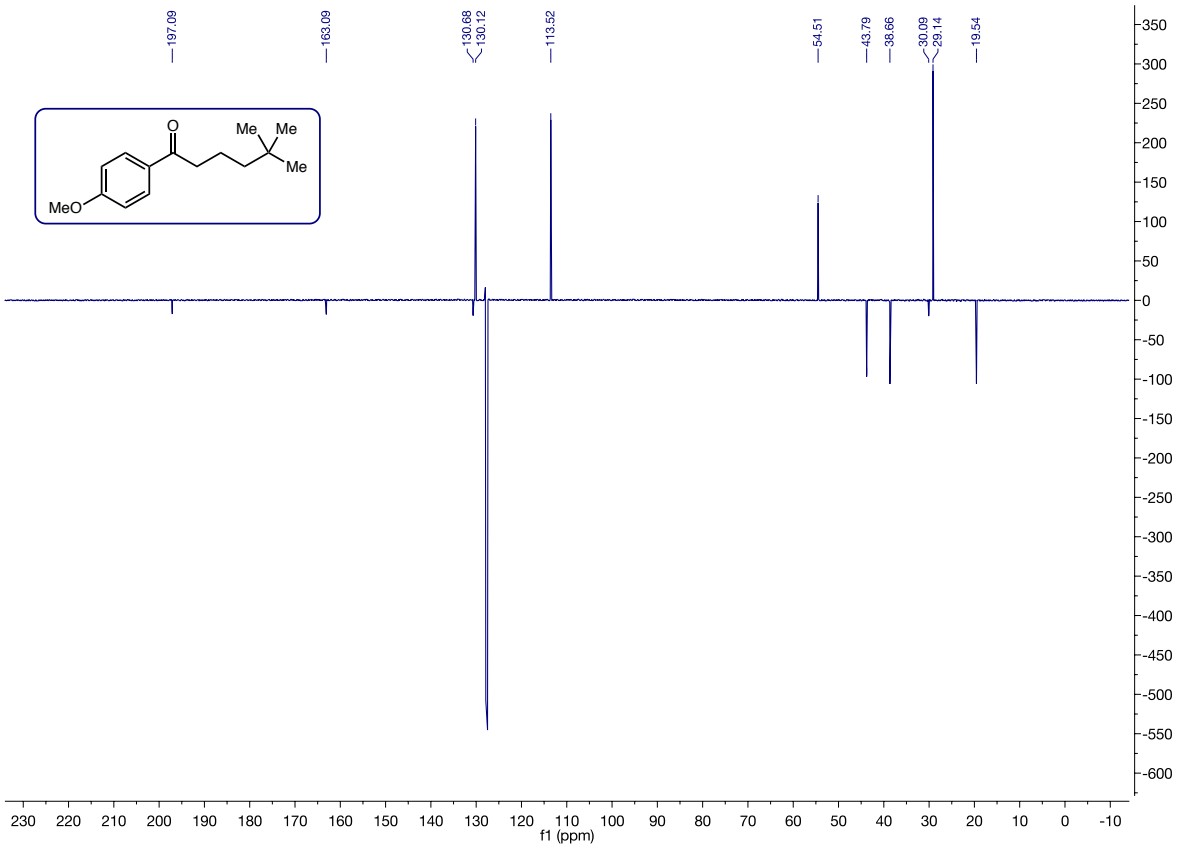
3.02
2.01
2.01
2.03
9.10
f1 (ppm)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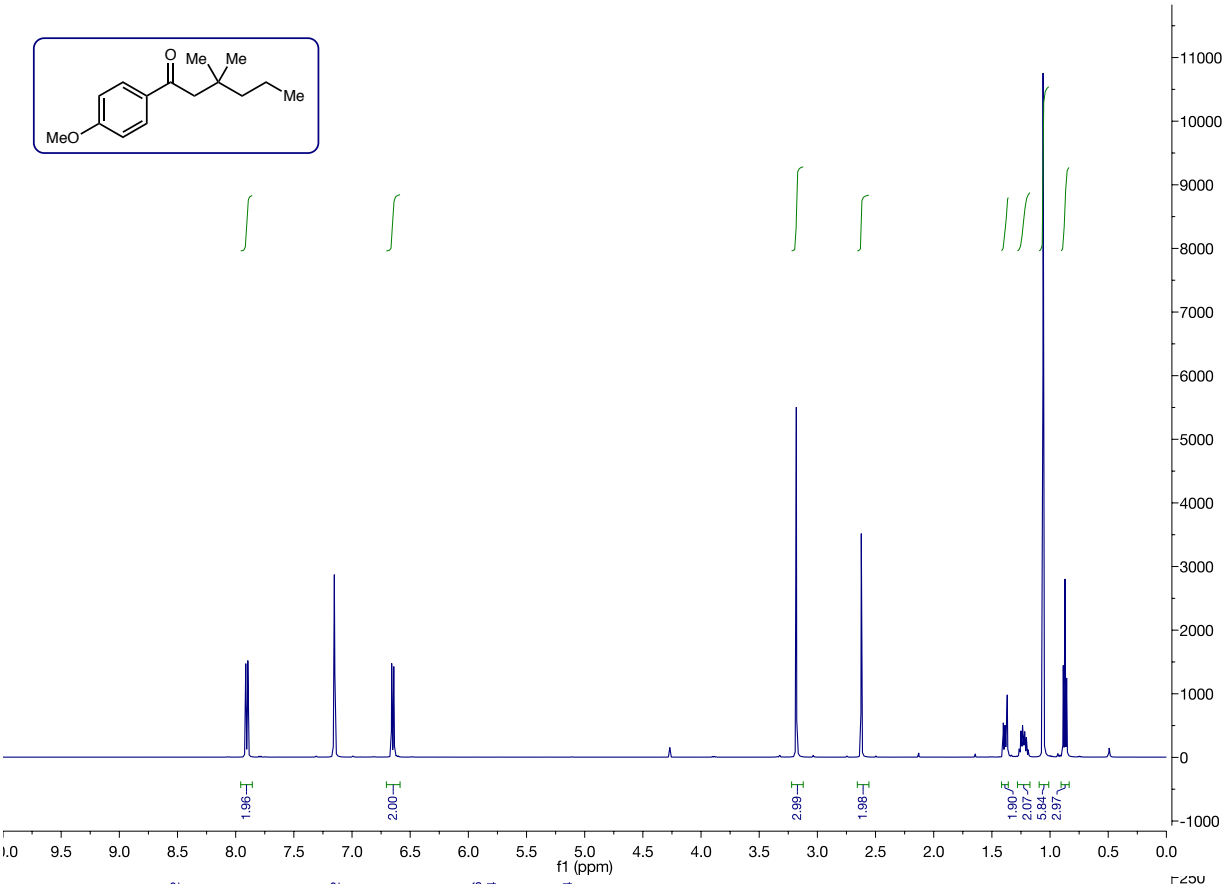
Me
Me
MeO
f1 (ppm)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Me
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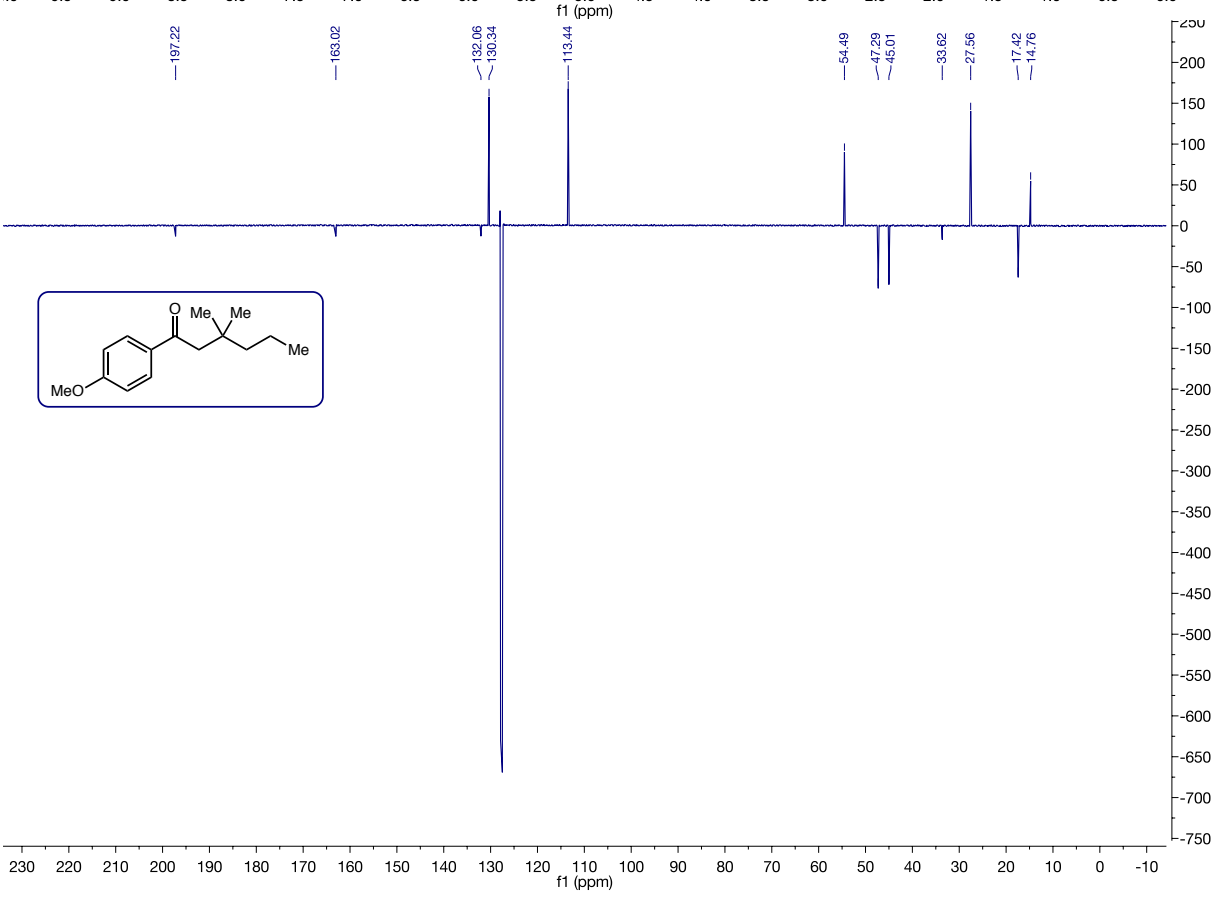
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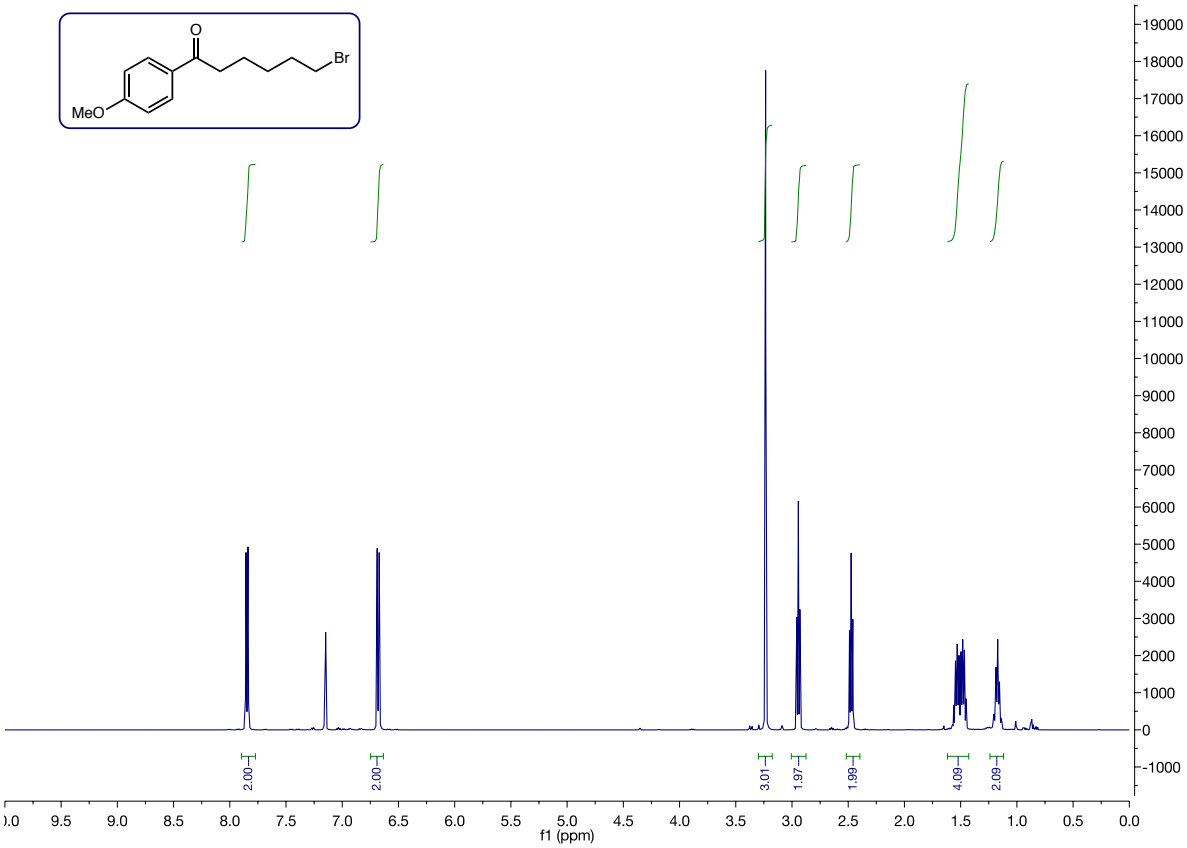
Me
Me
Me
MeO
f1 (ppm)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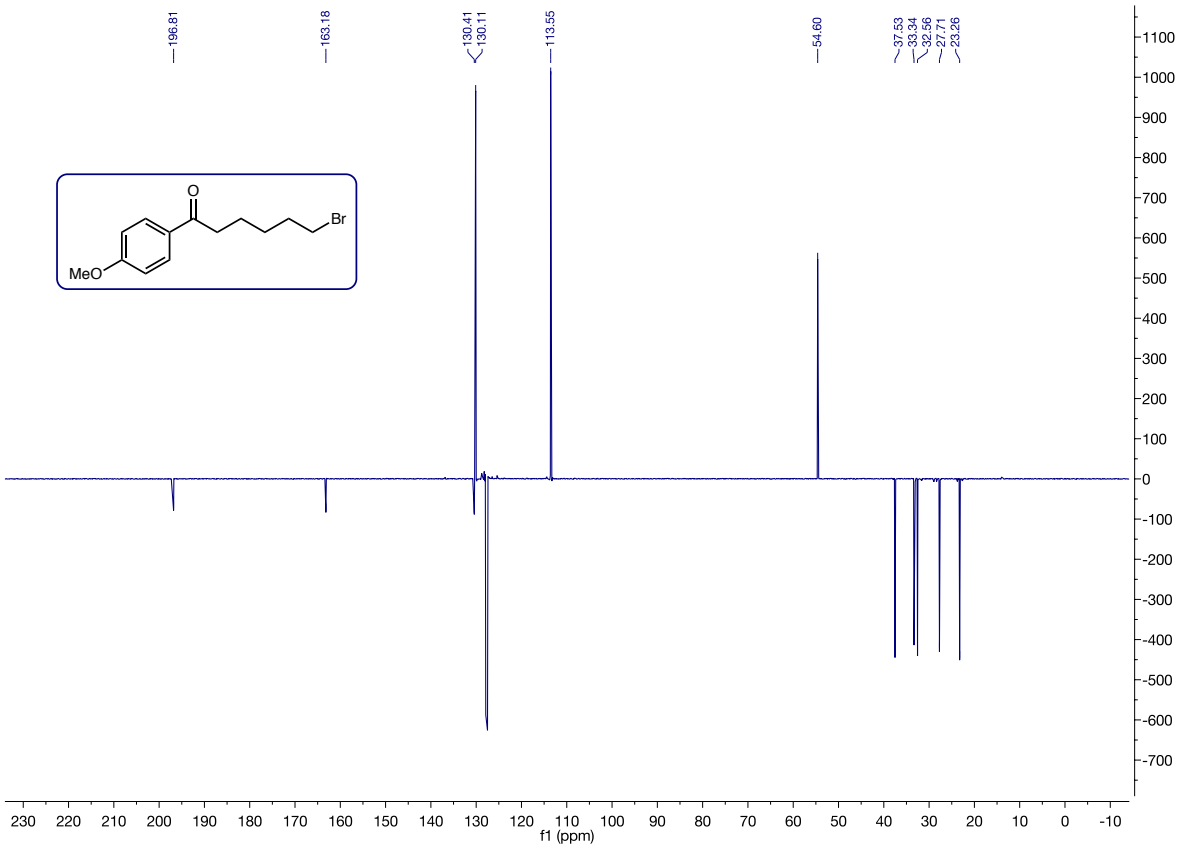
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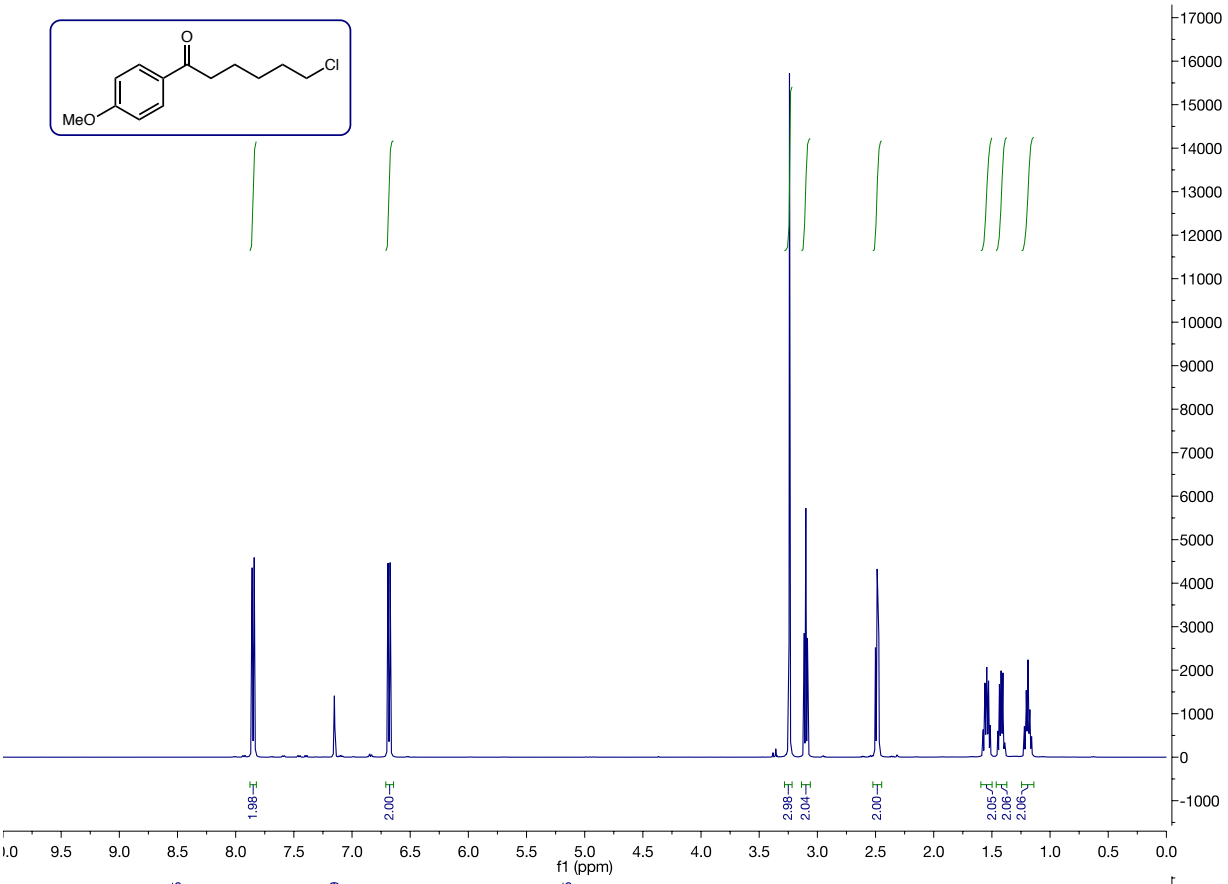
f1 (ppm)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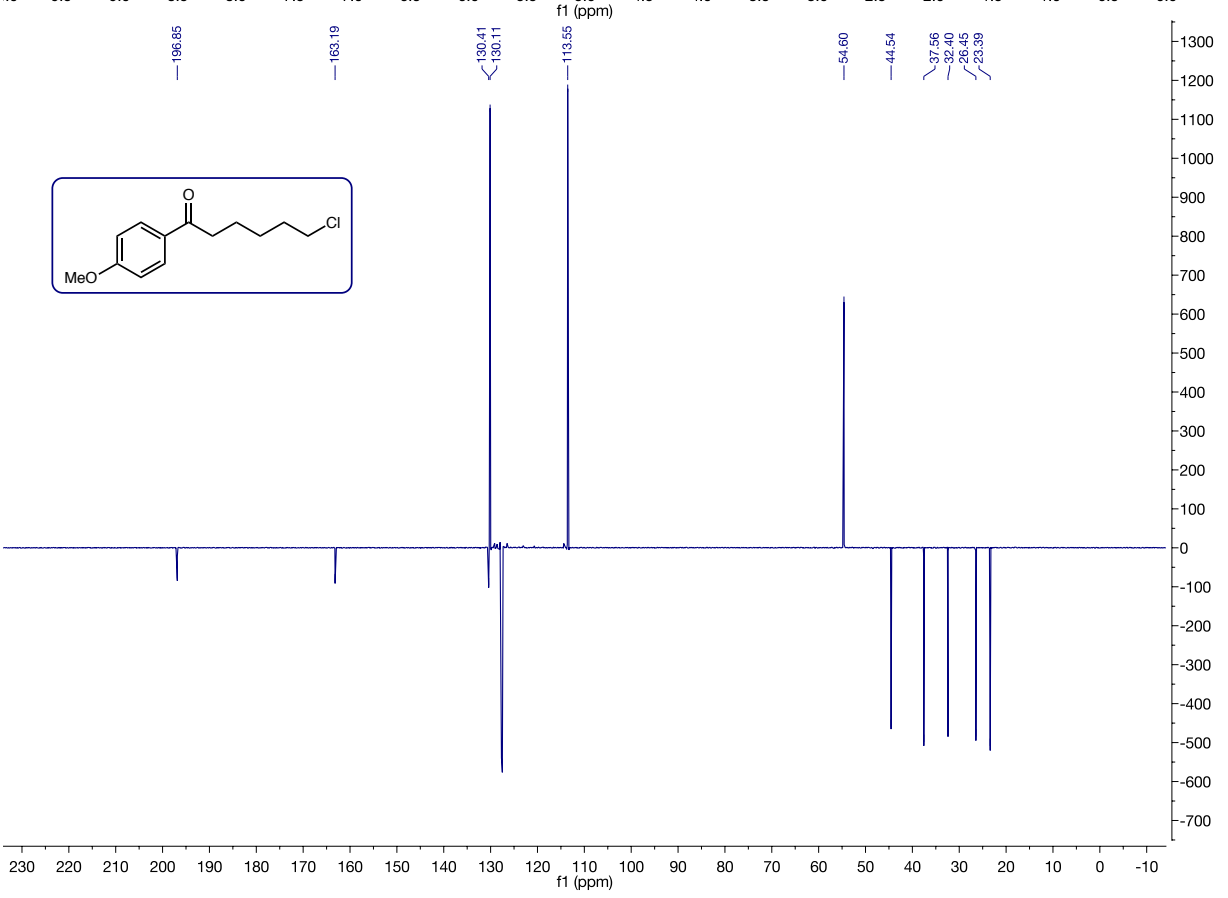
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26.45
23.39
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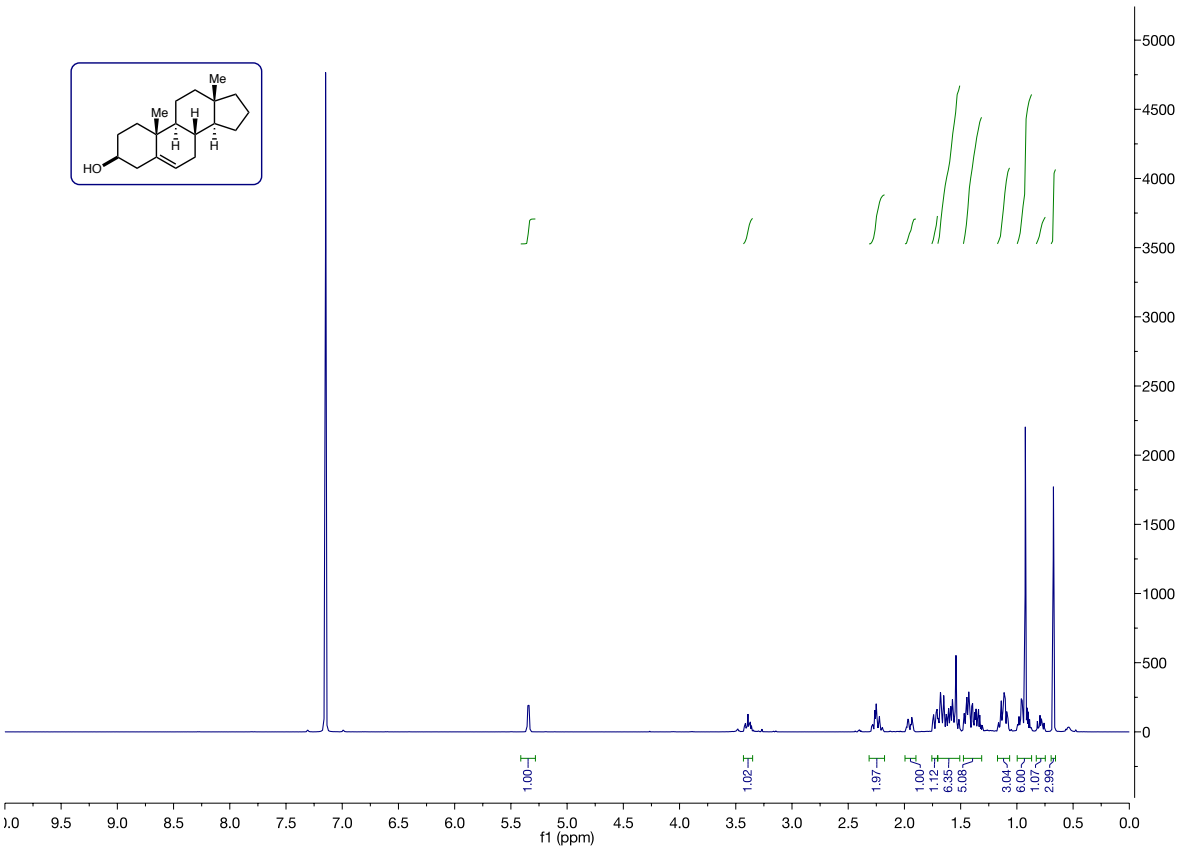
Cl
MeO
f1 (ppm)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Me
H
H
H
HO
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6.00
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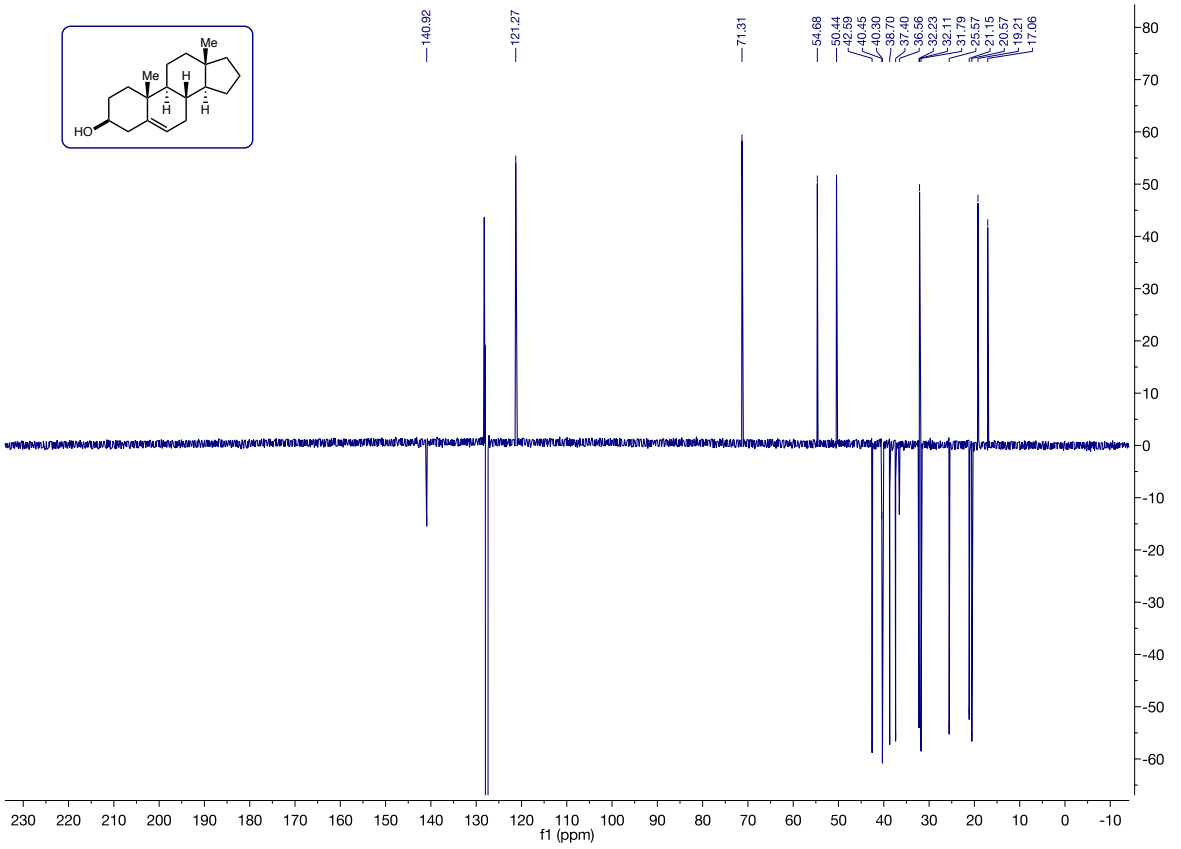
2.99
f1 (ppm)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H
H
HO
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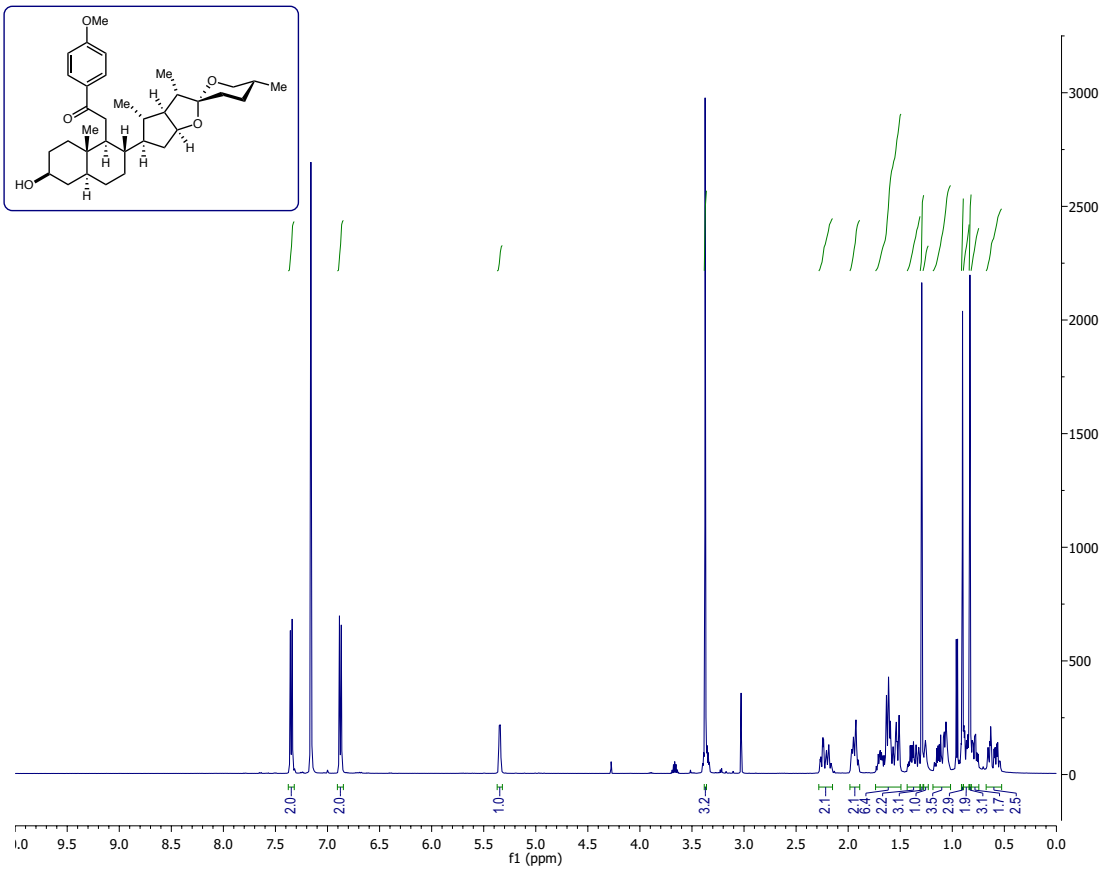
17.06
f1 (ppm)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Me
Me
Me
O
O
Me
H
H
H
H
H
H
HO
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2500
2000
1500
1000
500
0
2.0
2.0
1.0
3.2
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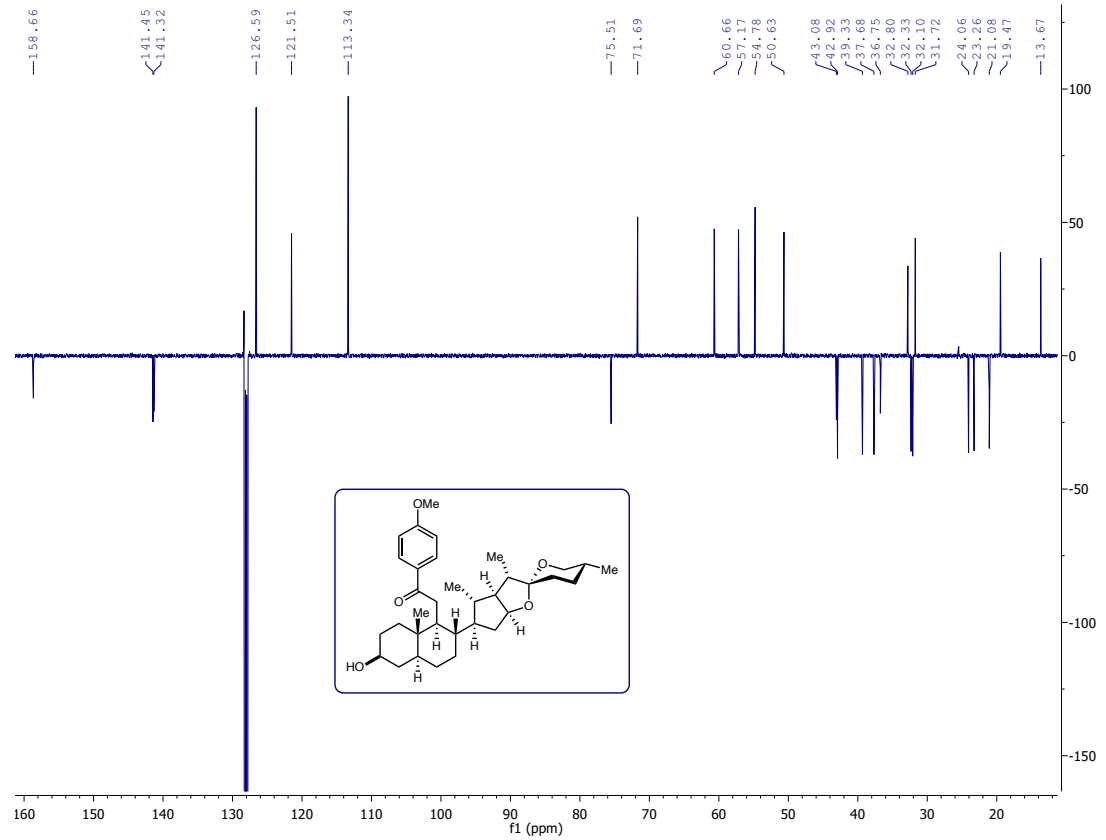
3.1
1.0
3.5
2.9
1.9
3.1
1.7
2.5
f1 (ppm)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141.32
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113.34
75.51
71.69
60.66
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42.92
39.33
37.68
36.75
32.80
32.33
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23.26
21.08
19.47
13.67
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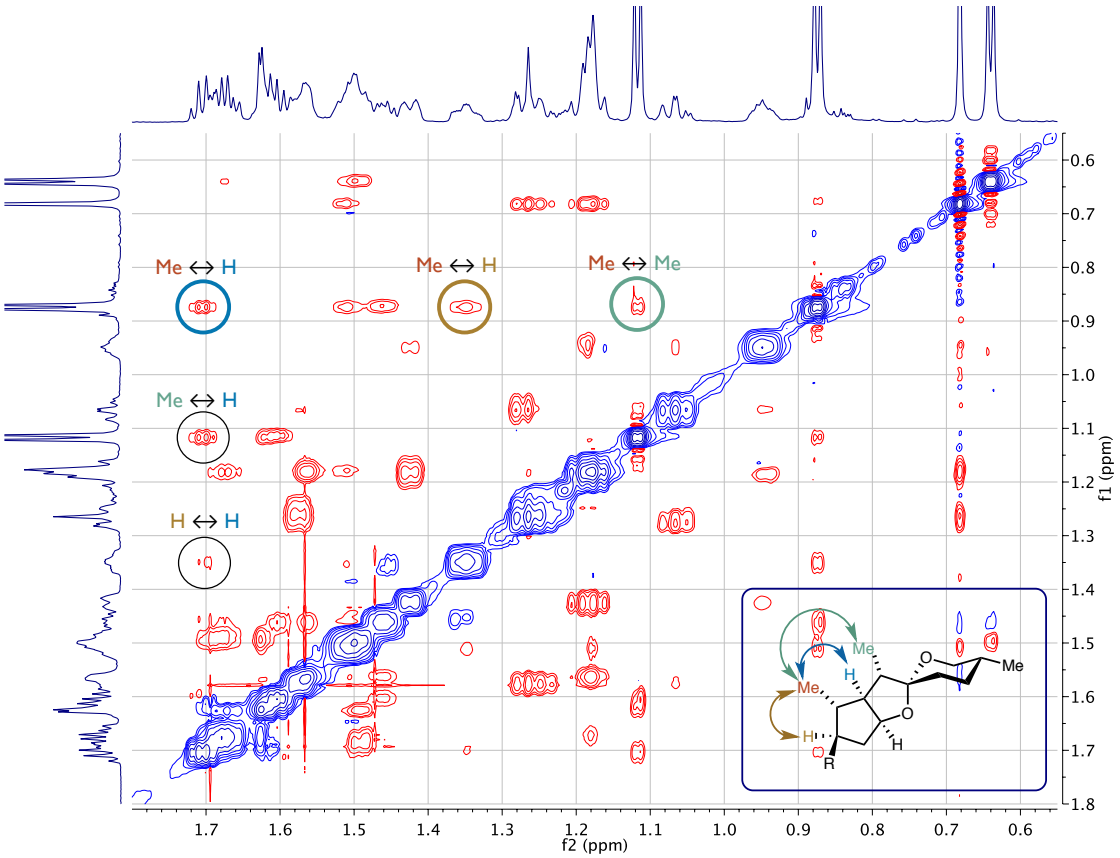
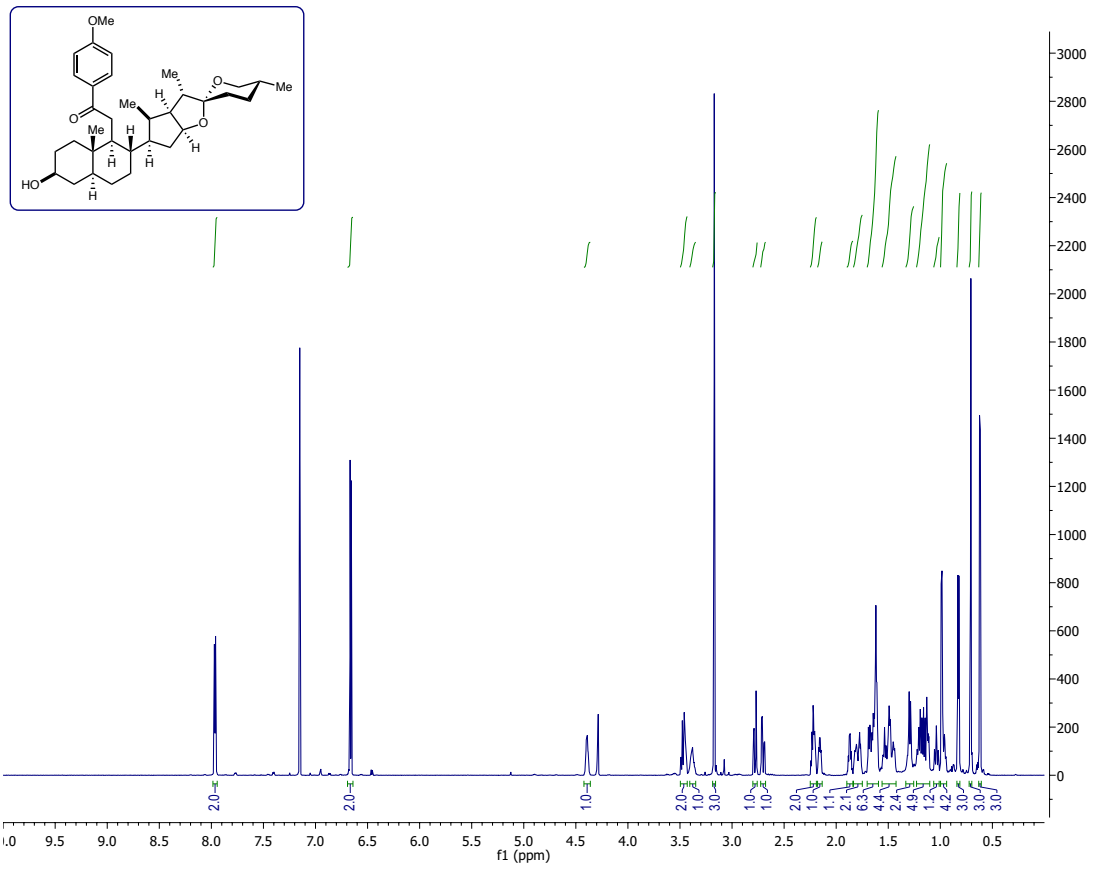
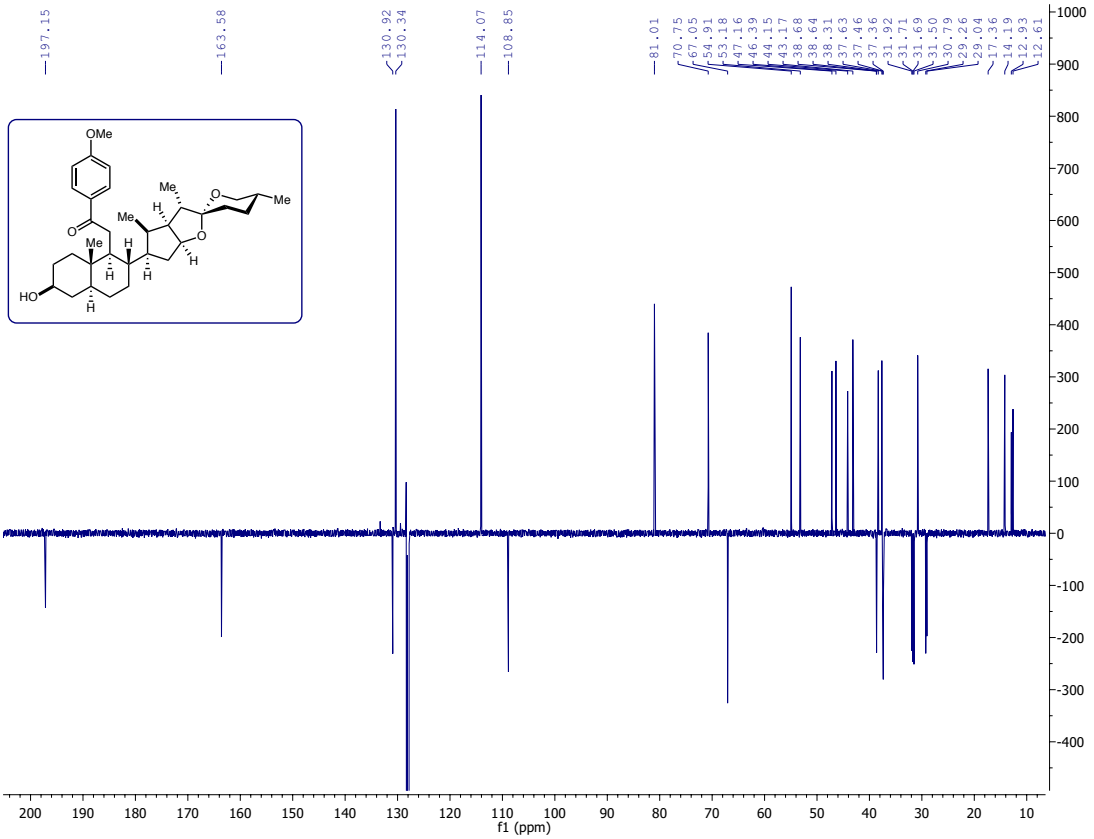
50
0
-50
-100
-150
f1 (ppm)



NOESY analysis of the *cis*-dimethyl product, annotated with important cross-peaks. Firstly, both methyls (Me and Me) show nuclear Overhauser effect to the center proton (H) of the same magnitude, signifying their similar spatial distance to H. Secondly, Me is observed to be spatially close to side proton (H), which is on the same face as the center proton H. Lastly, Me and Me also exhibits NOE against each other. This evidence, taken together, was determined to indicate that the two methyl groups in the major isomer are in a *cis* conformation.


OMe
Me
Me
Me
O
O
O
Me
H
H
H
H
H
HO
f1 (ppm)


197.15
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130.34
114.07
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81.01
70.75
67.05
54.91
53.18
47.16
46.39
44.15
43.17
38.68
38.64
38.31
37.63
37.46
37.36
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31.50
30.79
29.26
29.04
17.36
14.19
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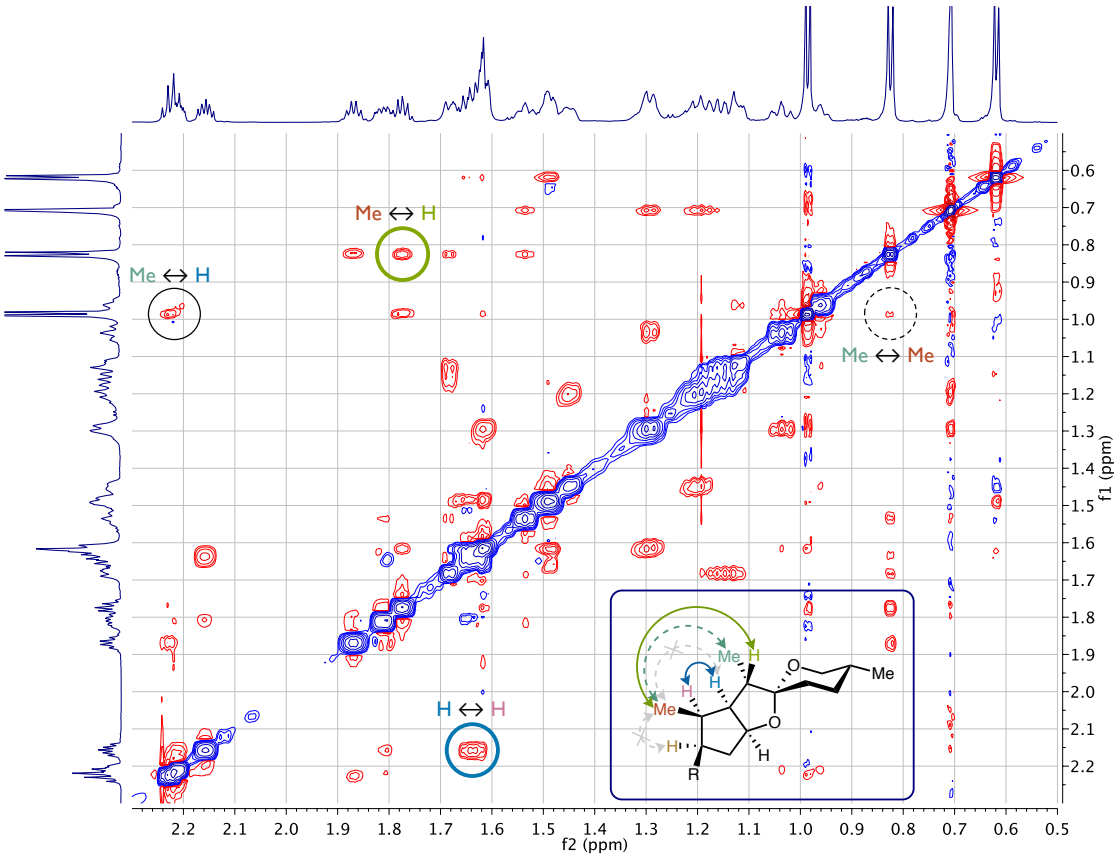
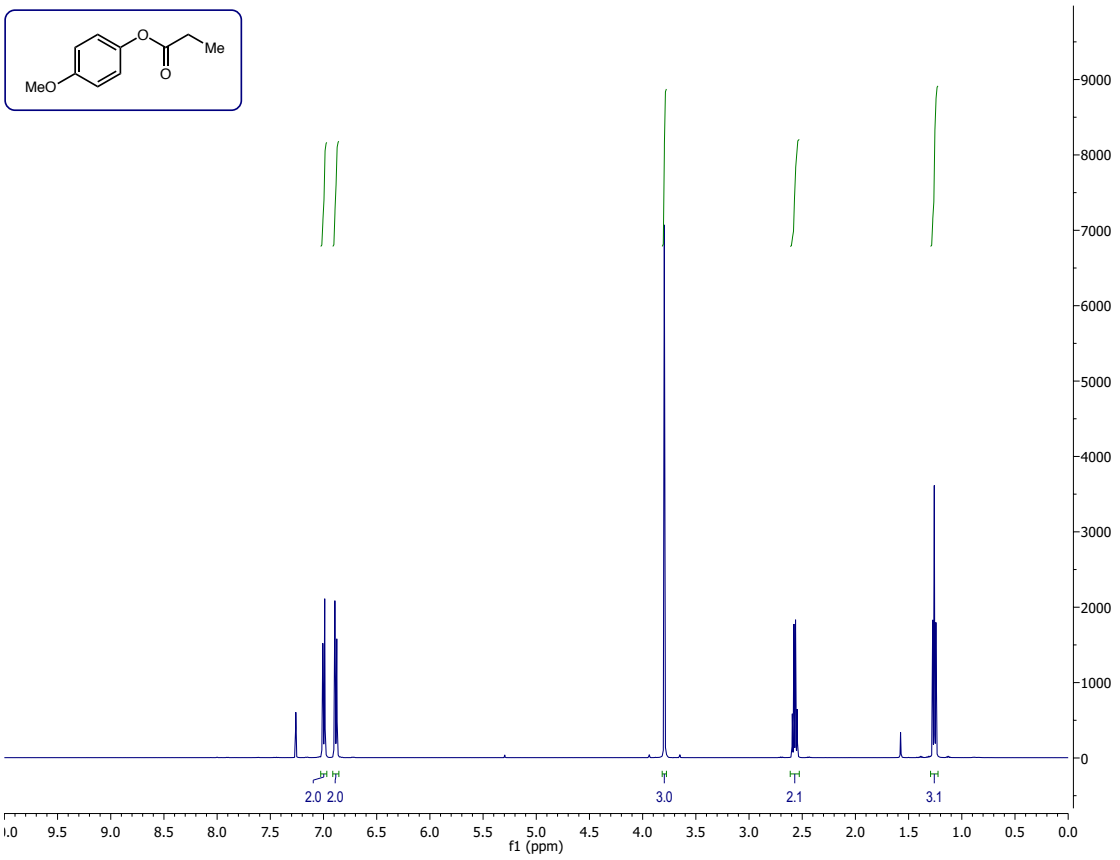
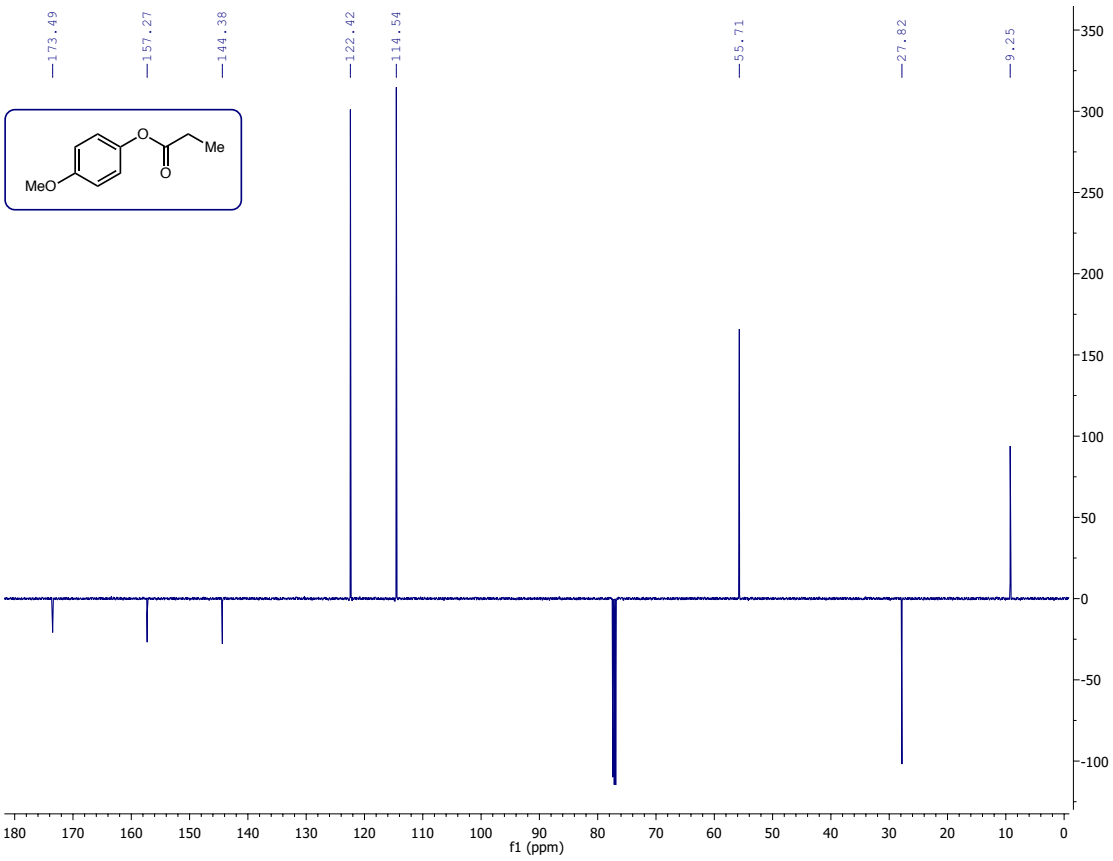
Me
H
H
H
H
H
HO
f1 (ppm)



NOESY analysis of the *trans*-dimethyl product, annotated with important cross-peaks. Firstly, comparing against the NOESY of the *cis* isomer, it is noted that there is only one methyl, namely the distant Me, in close contact with the center proton H. Secondly, the geminal proton H of Me is now proximal to the central H. Thirdly, a significantly weaker NOE is observed between Me and Me. Rather, Me shows strong NOE to the geminal proton H of the distant Me. This evidence suggests a *trans* conformation for this minor isomer.


MeO
O
O
Me
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
2.0 2.0
3.0
2.1
3.1
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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157.27
144.38
122.42
114.54
55.71
27.82
9.25
MeO
O
O
Me
350
300
250
200
150
100
50
0
-50
-100
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Stern-Volmer Studies

Stern-Volmer experiments tracking the quenching of the phosphorescence of $[Ir(dF(CF_3)ppy)_2(5,5'd(CF_3)bpy)](PF_6)$ (**C**) were conducted on an Agilent Cary Eclipse Fluorescence Spectrophotometer using the Cary Eclipse Scan Application. Fresh stock solutions of Ir photocatalyst **C**, 1-(4-methoxyphenyl)cyclooctan-1-ol (SM), and collidine were prepared in CH_2Cl_2 and mixed together at varying concentrations in volumetric flasks. All liquid transfers were done in the glovebox. The solutions were loaded into quartz cuvettes, sealed under inert atmosphere, and shielded from light exposure before sample collection. The samples were irradiated at 440 nm, and three-scan average emission intensities at 586 nm were recorded. Each concentration combination was repeated four times, and the final average slope of I_0/I to concentration is reported here as the K_{sv}.

Constant [collidine], varied alcohol substrate [SM]

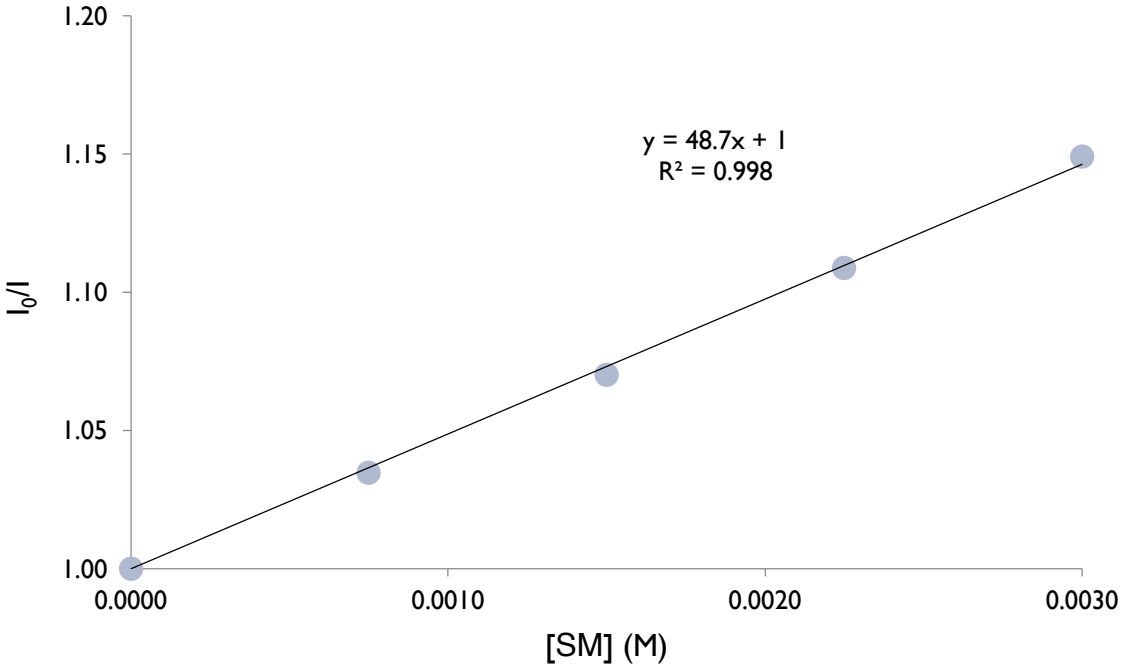


Figure S1. Stern-Volmer plot of [Ir(dF(CF_3)ppy)$_2$(5,5′d(CF_3)bpy)](PF_6) (244 μM) with varied [SM] in the presence of a constant concentration of collidine (7.22 mM) in CH_2Cl_2 at 23 °C.

Table S1. Individual results from Stern-Volmer quenching experiments with [Ir(dF(CF_3)ppy)$_2$(5,5′d(CF_3)bpy)](PF_6) (244 μM) with varied [SM] in the presence of collidine in CH_2Cl_2 at 23 °C.

		$I_{emission}$ (586 nm)					
[Colldine] (M)	[SM] (M)	run 1	run 2	run 3	run 4	mean $I_{emission}$	I_0/I
7.22E-03	0.00E+00	161.199	161.031	163.145	158.074	160.862	1.00
7.22E-03	7.50E-04	154.695	155.840	157.740	153.645	155.480	1.03
7.22E-03	1.50E-03	152.654	146.342	150.799	151.491	150.321	1.07
7.22E-03	2.25E-03	146.802	145.864	143.602	144.056	145.081	1.11
7.22E-03	3.00E-03	140.621	141.546	140.524	137.333	140.006	1.15

Constant [SM], varied [collidine]

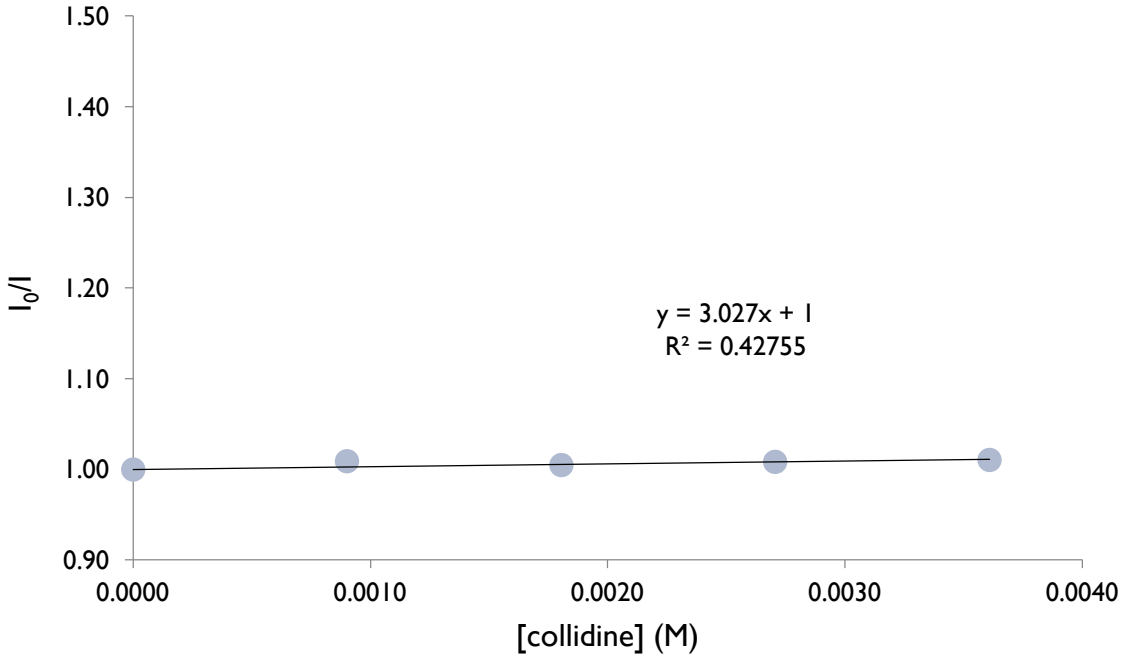
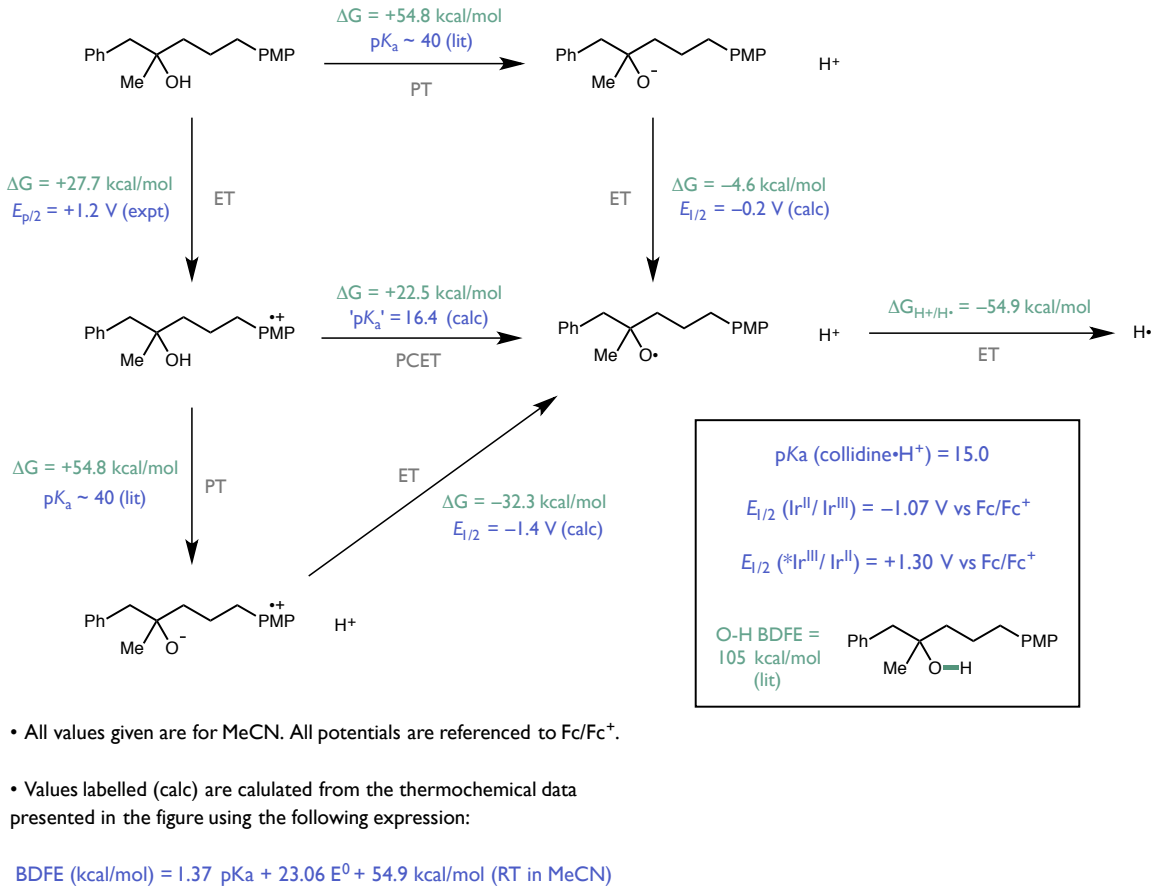


Figure S2. Stern-Volmer plot of [Ir(dF(CF_3)ppy)$_2$(5,5′d(CF_3)bpy)](PF_6) (244 μM) with varied [collidine] in the presence of a constant concentration of SM (15.0 mM) in CH_2Cl_2 at 23 °C.

Table S2. Individual results from Stern-Volmer quenching experiments with [Ir(dF(CF_3)ppy)$_2$(5,5′d(CF_3)bpy)](PF_6) (244 μM) with varied [collidine] in the presence of SM in CH_2Cl_2 at 23 °C.

		$I_{emission}$ (586 nm)					
[Colldine] (M)	[SM] (M)	run 1	run 2	run 3	run 4	mean $I_{emission}$	I_0/I
0.00E+00	1.50E-02	104.956	99.300	98.479	100.563	100.824	1.00
9.02E-04	1.50E-02	105.590	97.163	98.756	98.281	99.948	1.01
1.80E-03	1.50E-02	104.299	98.604	98.969	99.683	100.389	1.00
2.71E-03	1.50E-02	104.126	97.898	98.404	99.683	100.028	1.01
3.61E-03	1.50E-02	108.776	93.766	97.250	99.457	99.812	1.01

Experimental Details for Investigating Long-range PCET (Figure 3)



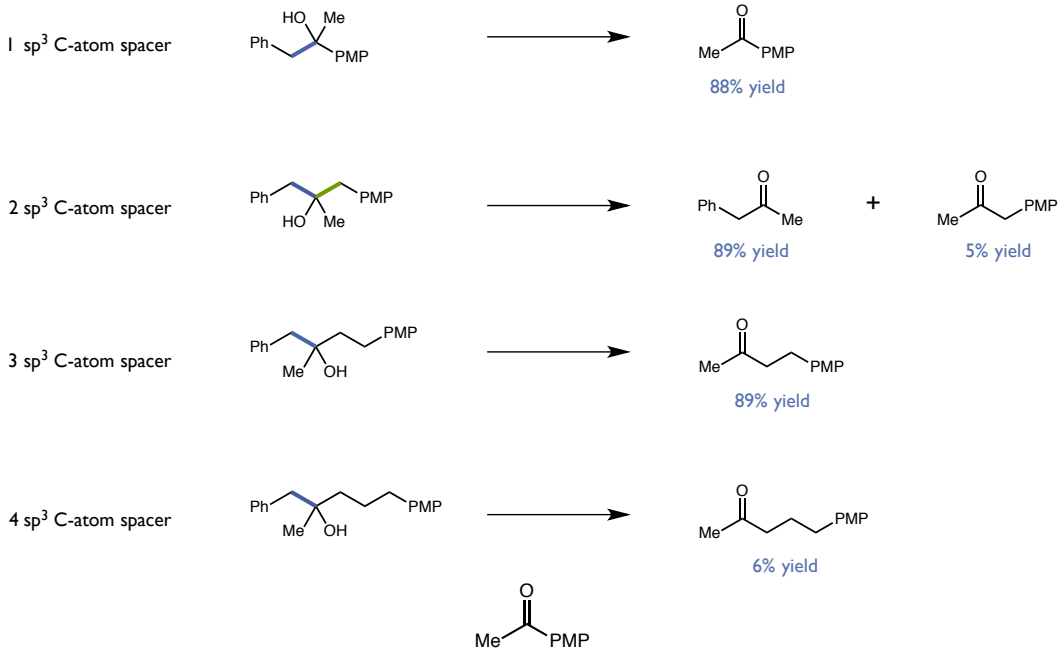
• All values given are for MeCN. All potentials are referenced to Fc/Fc^+.

• Values labelled (calc) are calulated from the thermochemical data presented in the figure using the following expression:

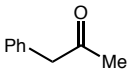
BDFE (kcal/mol) = 1.37 pKa + 23.06 E^0 + 54.9 kcal/mol (RT in MeCN)

Figure S3. Relationship and energy of different species and mechanistic pathways.

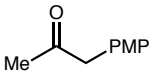
Screw-cap 2-dram vials outfitted with PTFE/silicone septa were charged with the relevant alcohol (0.05 mmol, 1.0 equiv), redistilled collidine (0.15 mmol, 3.0 equiv, 20 µL), and redistilled thiophenol (13 µmol, 0.25 equiv, 1.3 µL). A 1-mM stock solution of $[Ir(dF(CF_3)ppy)_2(5,5'd(CF_3)bpy)](PF_6)$ in degassed anhydrous CH_2Cl_2 was made, and 0.5 mL of this solution (0.5 µmol , 0.01 equiv in photocatalyst) was added to each vial via syringe. Thereafter, the vials were frozen in liquid nitrogen, evacuated, and let thaw in warm water bath; this process was repeated three times. The reactions were irradiated by strips of blue LED lights set inside a recrystallization dish, and let stir under a nitrogen atmosphere at room temperature with a fan to cool the setup. After 16–18 hours, the irradiation was stopped, and dibenzyl ether (0.05 mmol, 1.0 equiv, 9.5 µL) was introduced into each reaction as an internal standard. The crude reactions were concentrated, dissolved in benzene-d_6, and submitted for ^{1}H NMR. Percentage yields are calculated from integral ratio of ArCOC**H$_2$** peak to (PhC**H$_2$**)$_2$O peak. These yields were also confirmed by GC assays developed for the ketone products.



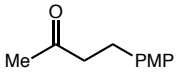
1-(4-methoxyphenyl)ethan-1-one
Spectra are consistent with reported literature values[13] and commercial samples.



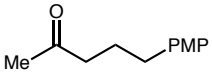
1-phenylpropan-2-one
Spectra are consistent with reported literature values.[14]



1-(4-methoxyphenyl)propan-2-one
Spectra are consistent with reported literature values[15] and commercial samples.



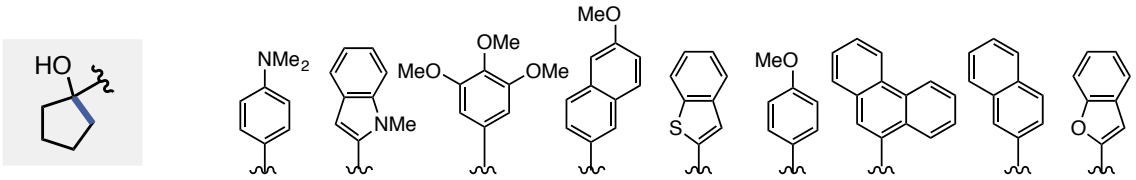
4-(4-methoxyphenyl)butan-2-one
Spectra are consistent with reported literature values[16] and commercial samples.



5-(4-methoxyphenyl)pentan-2-one
Spectra are consistent with reported literature values.[17]

Experimental Details for Investigating the Relationship Between Effective BDFE and Reaction Outcomes (Figure 4)

Setup for Brønsted bases 2-methoxypyridine, pyridine, and tetrabutylammonium trifluoroacetate followed the procedures outlined in the previous section. For $TBA^{+}TFA^{-}$, only 1 equiv (0.05 mmol) was used, and the weighing was carried out in a glovebox. Dibenzyl ether (0.05 mmol, 1.0 equiv, 9.5 μL) was used as an internal standard to calculate percentage yields, based on the ^{1}H NMR signal integral ratio of $ArCOCH_2$ peak to $(PhCH_2)_2O$ peak. Average isolated yields of 1-mmol reactions are reported for collidine reactions.



Base	$E_{p/2}$ (V)	0.39	0.69	0.92	0.96	1.18	1.22	1.22	1.24	1.27
2-MeO-pyridine	'BDFE'	77	84	90	91	96	97	97	97	98
pK_a = 9.9	Yield (%)	0	0	0	0	0	0	0	<5	8
pyridine	'BDFE'	81	88	93	94	99	100	100	101	101
pK_a = 12.5	Yield (%)	0	0	0	<5	6	16	14	5	19
CF_3COO^-	'BDFE'	81	88	93	94	99	100	100	101	101
pK_a = 12.5	Yield (%)	0	0	0	0	23	87	79	97	18
collidine	'BDFE'	84	91	97	98	103	104	104	104	105
pK_a =15	Yield (%)	0	0	<5	7	86	86	82	41	84

Figure S4. Effective BDFE and reaction outcome.

Cyclic Voltammograms of Starting Materials

All voltammograms were taken at room temperature using a saturated calomel (SCE) reference electrode, a mesh platinum (Pt) counter electrode, and a glassy carbon working electrode. The conditions of the experiments were the following: an acetonitrile solution of 100 mM tetrabutylammonium hexafluorophosphate (NBu_4PF_6) and 1 mM aryl alcohol, a scan rate of 0.1 V/s, and a positive initial scan direction. The reported potentials were averages over segments, and were taken at half-height of the cathodic peaks ($E_{p/2}$) of the compounds, since all oxidations were nonreversible. To convert the potentials from SCE to Fc/Fc^+ reference, 380 mV were subtracted from the measured values. The positive peaks on the return sweep of most substrates were thought to signify an ECE-type mechanism.[18]

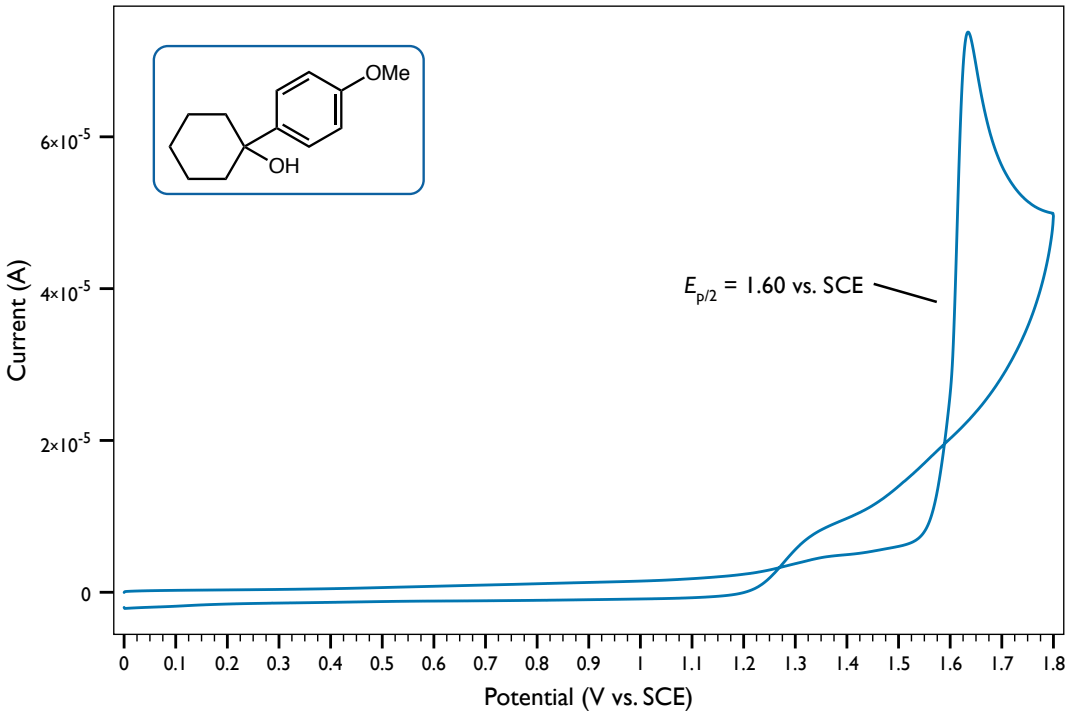


Figure S5. CV of 1-(4-methoxyphenyl)cyclohexan-1-ol in MeCN

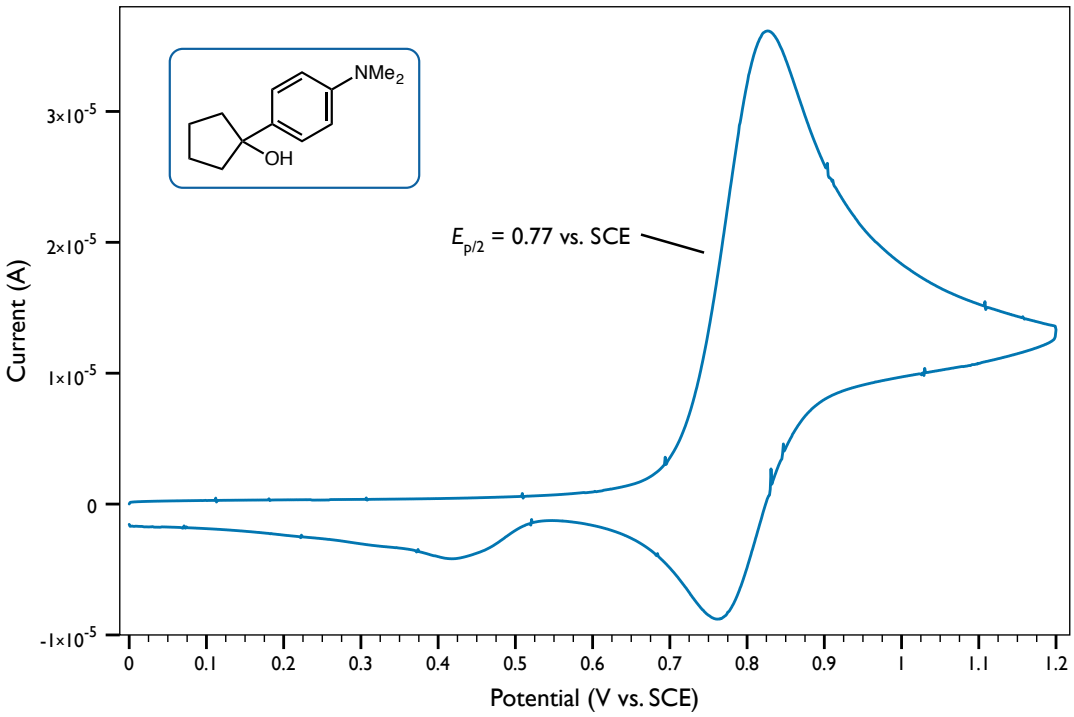


Figure S6. CV of 1-(4-(dimethylamino)phenyl)cyclopentanol in MeCN

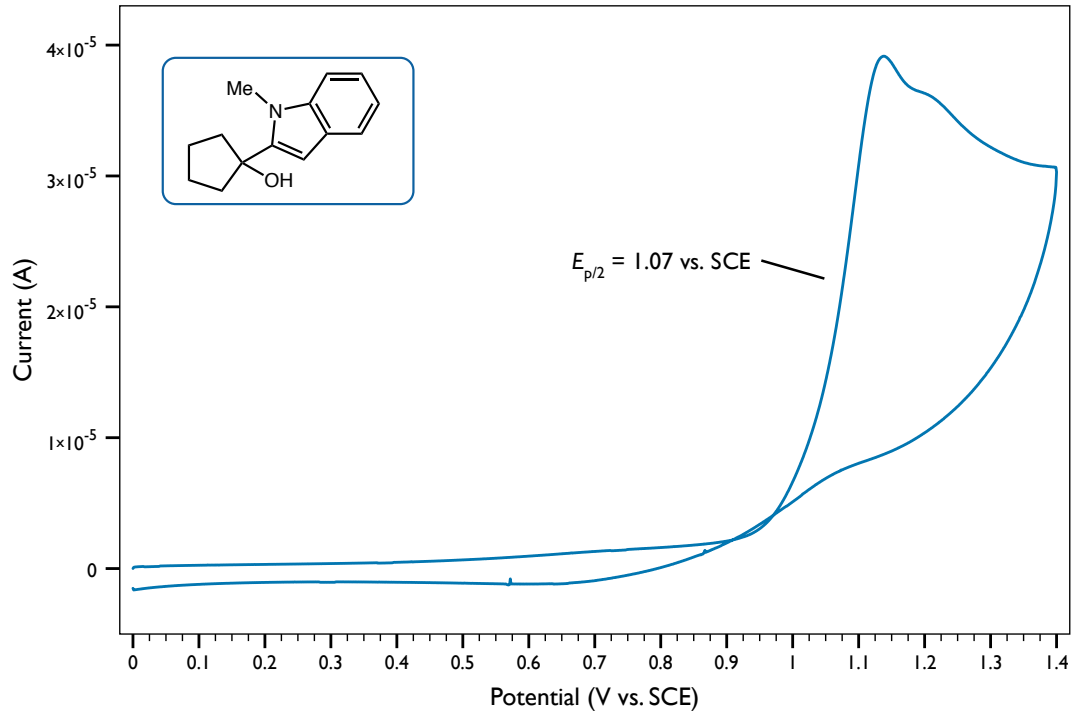


Figure S7. CV of 1-(1-methyl-1*H*-indol-2-yl)cyclopentanol in MeCN

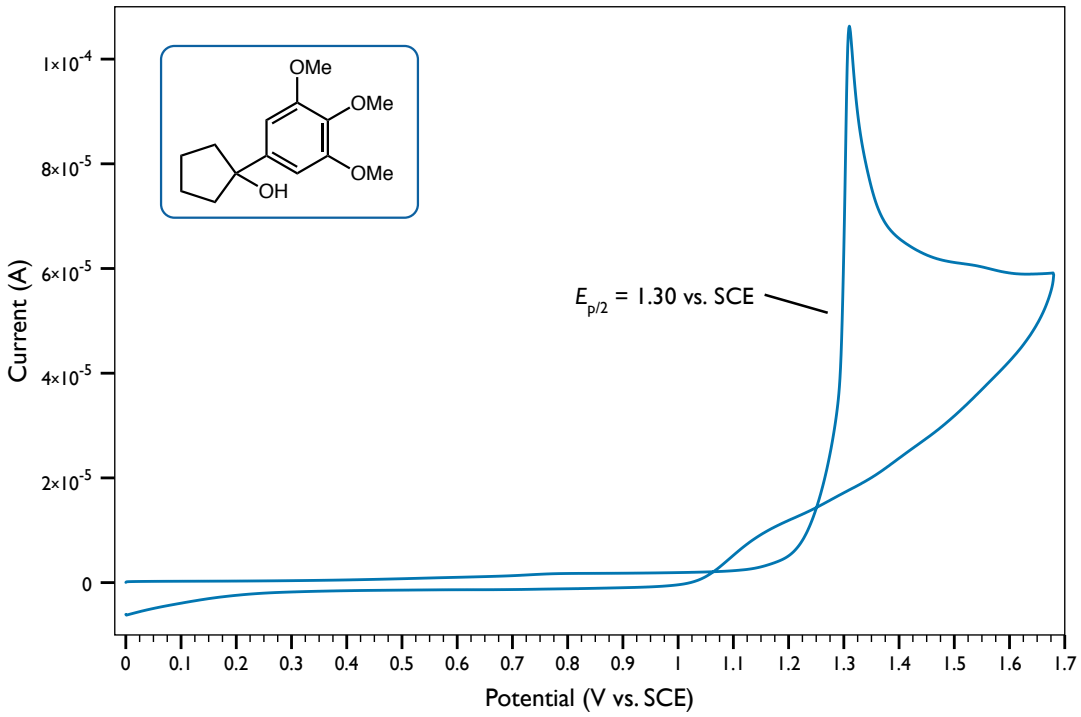


Figure S8. CV of 1-(3,4,5-trimethoxyphenyl)cyclopentan-1-ol in MeCN

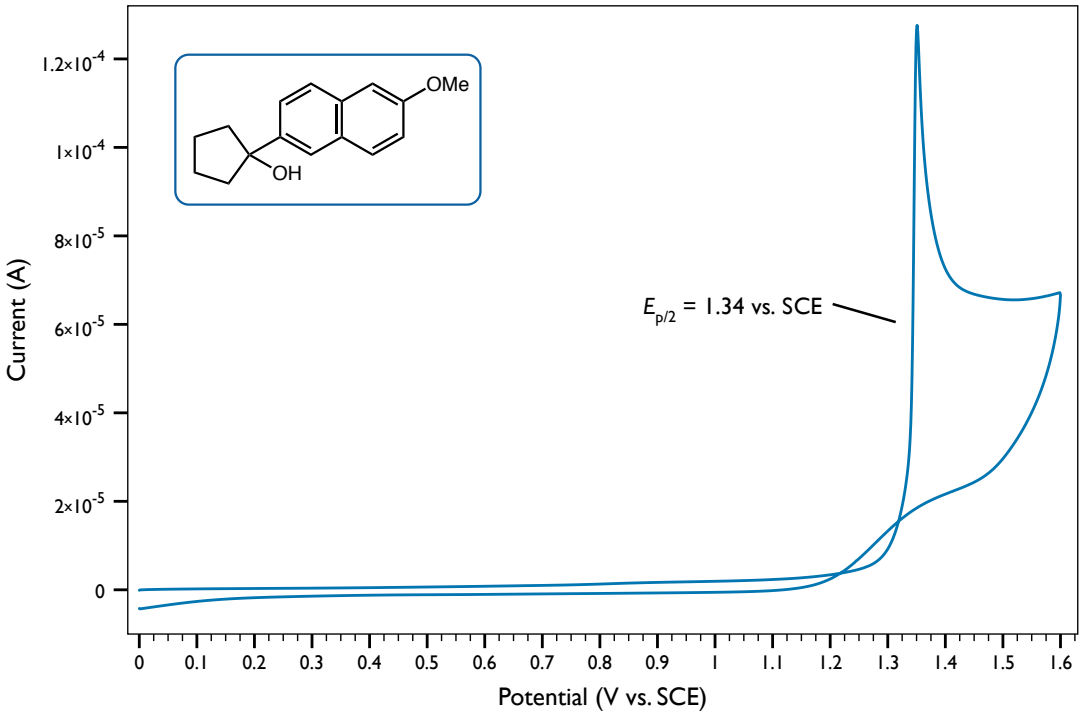


Figure S9. CV of 1-(6-methoxynaphthalen-2-yl)cyclopentan-1-ol in MeCN

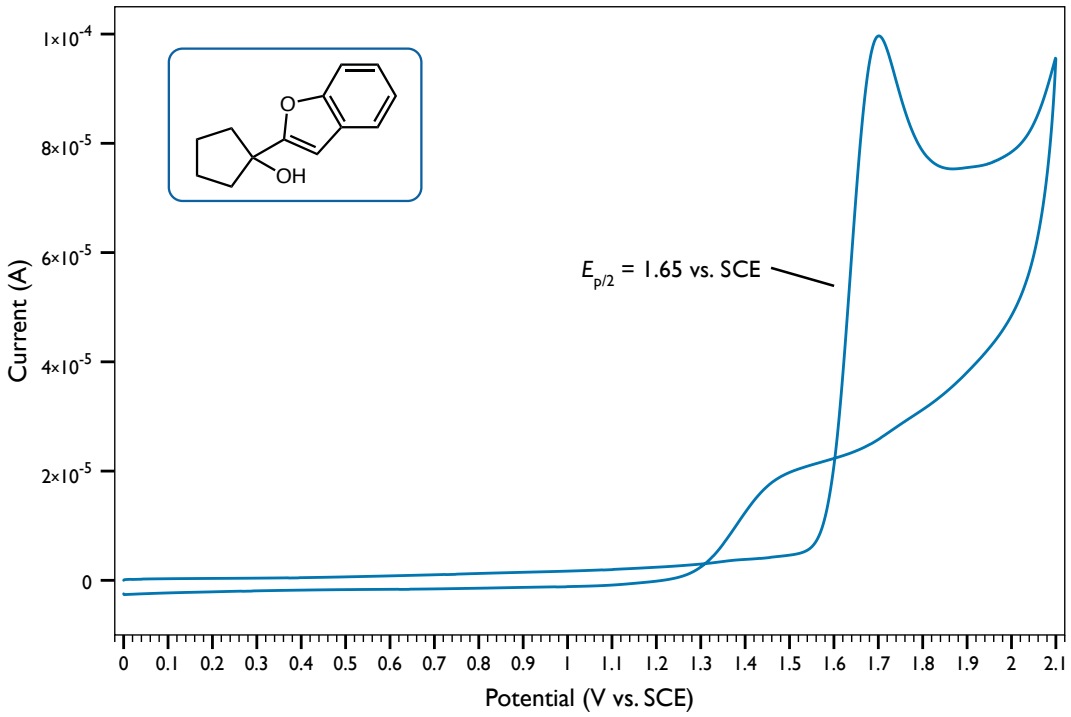


Figure S10. CV of 1-(benzofuran-2-yl)cyclopentanol in MeCN

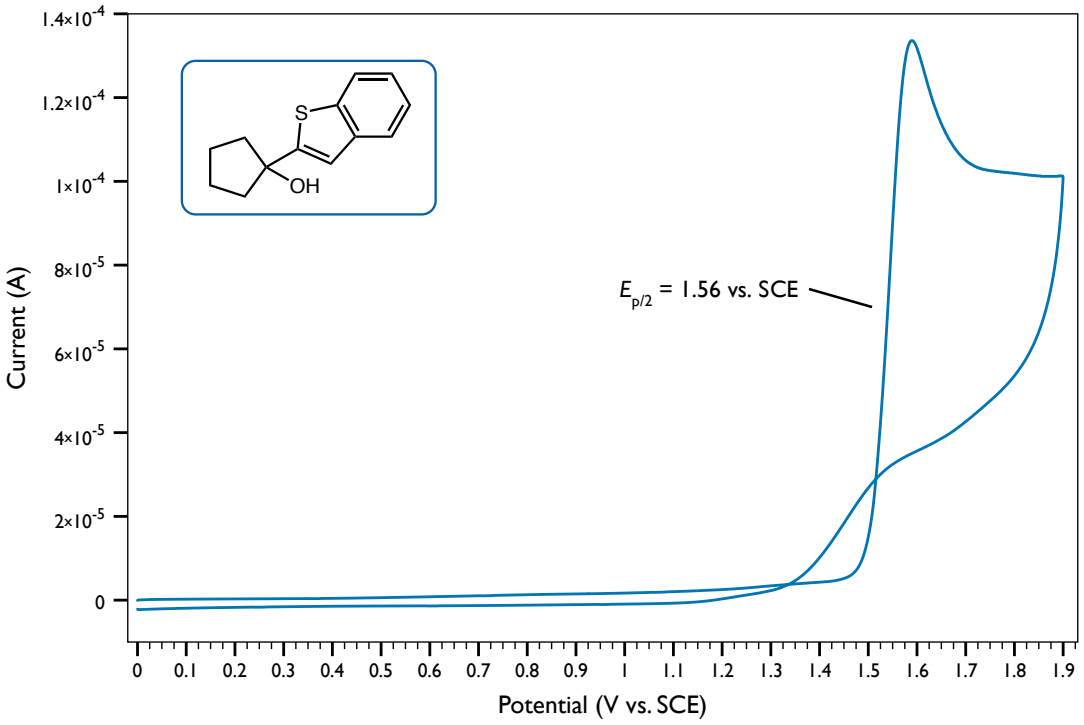


Figure S11. CV of 1-(benzo[*b*]thiophen-2-yl)cyclopentanol in MeCN

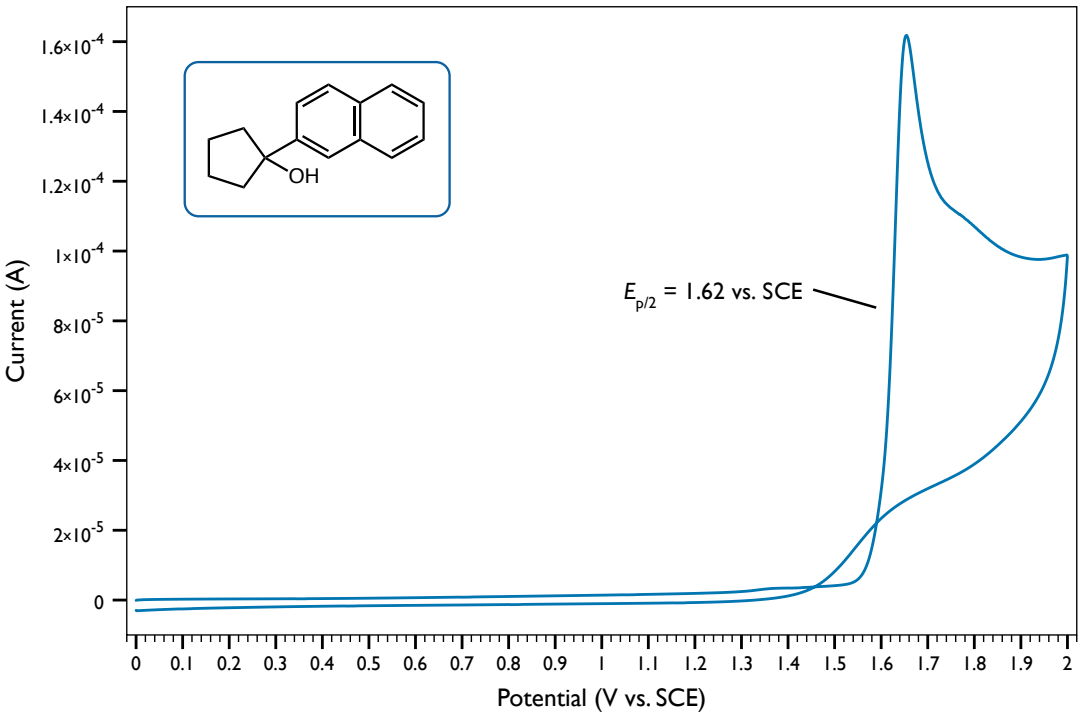


Figure S12. CV of 1-(naphthalen-2-yl)cyclopentanol in MeCN

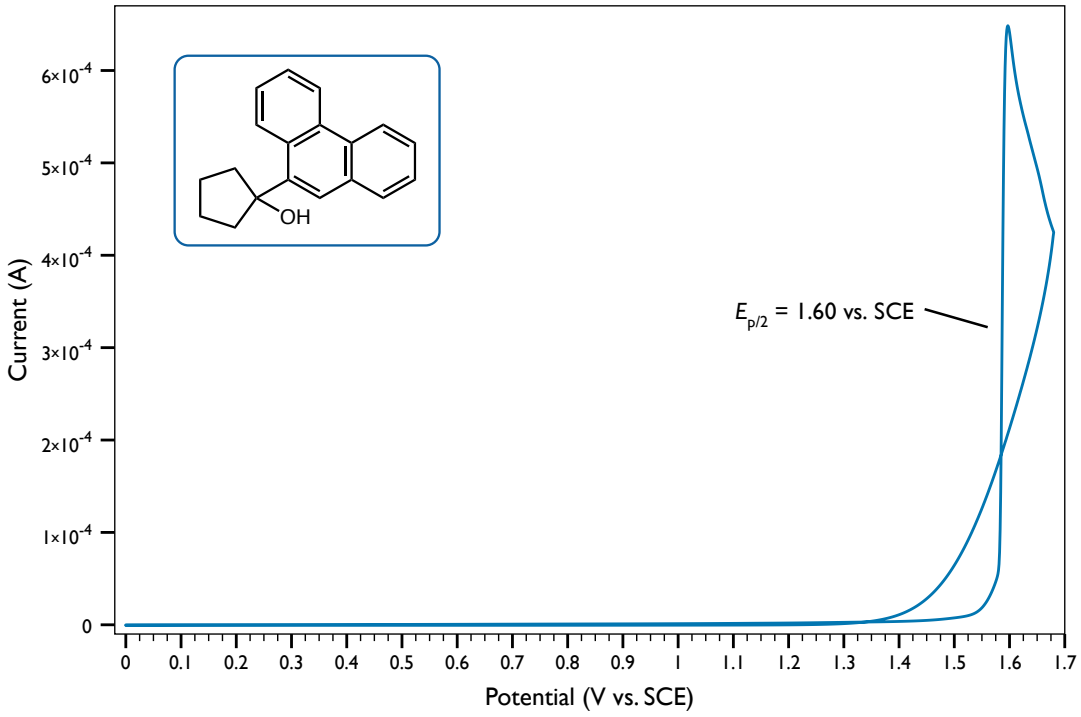


Figure S13. CV of 1-(phenanthren-9-yl)cyclopentanol in MeCN

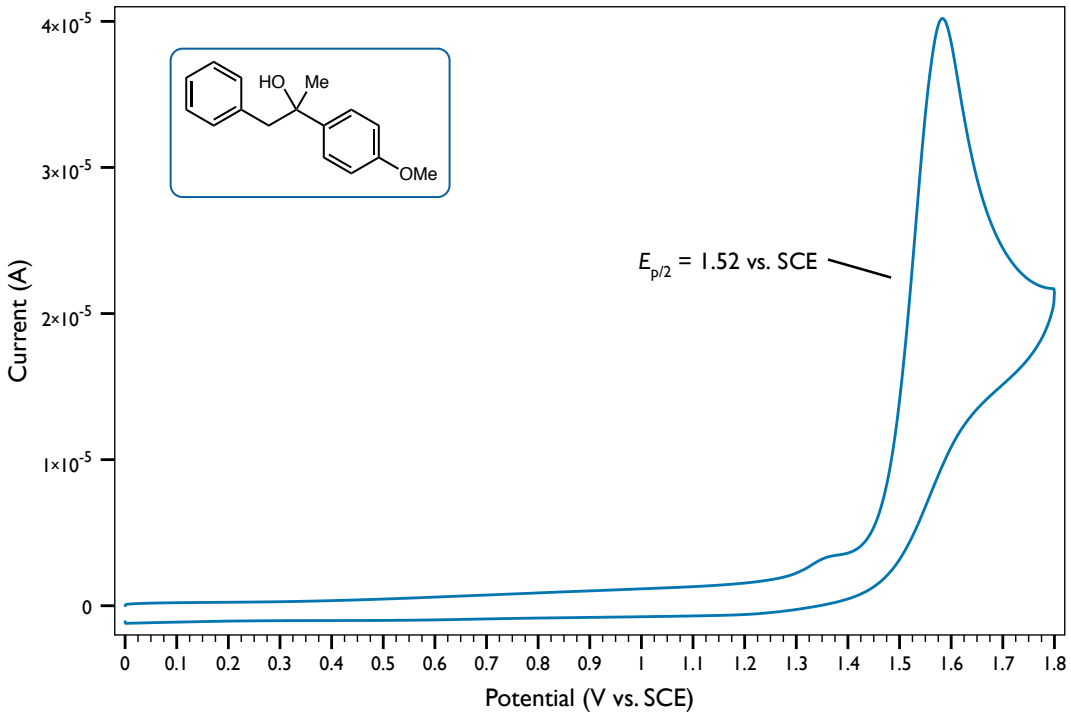


Figure S14. CV of 2-(4-methoxyphenyl)-1-phenylpropan-2-ol in MeCN

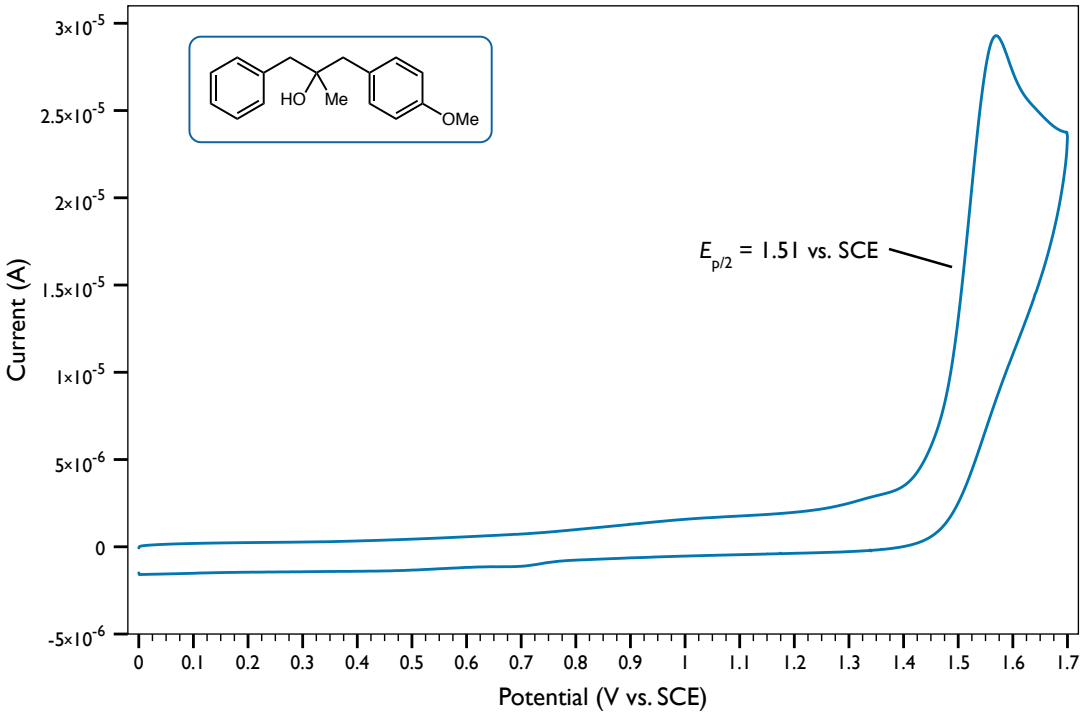


Figure S15. CV of 1-(4-methoxyphenyl)-2-methyl-3-phenylpropan-2-ol in MeCN

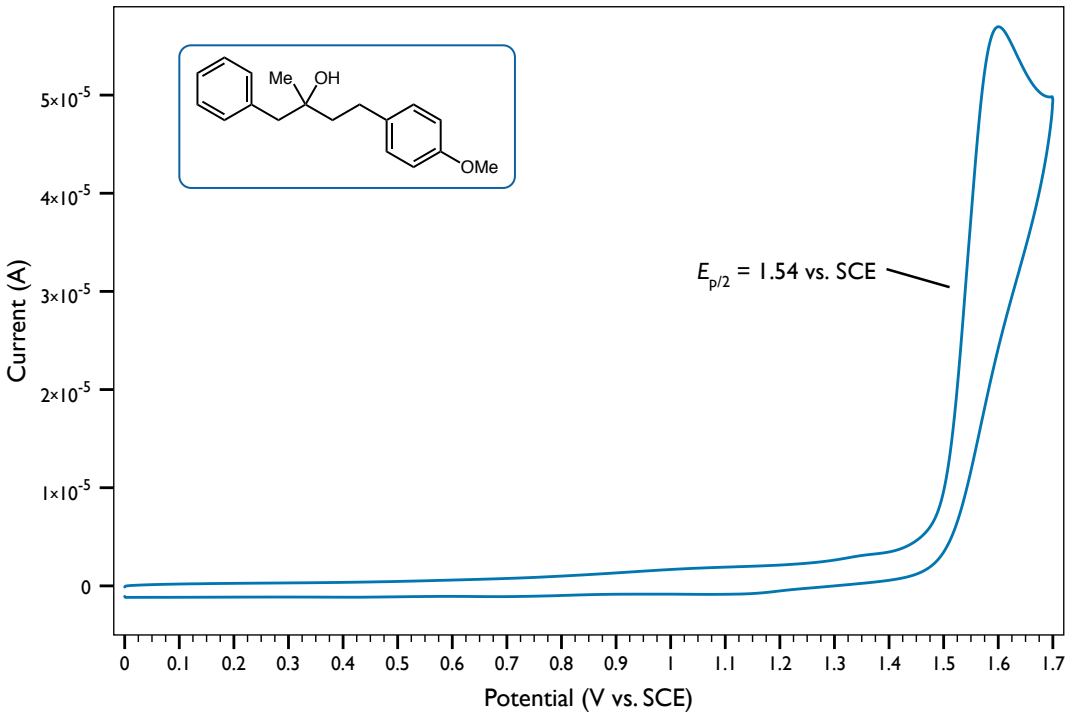


Figure S16. CV of 4-(4-methoxyphenyl)-2-methyl-1-phenylbutan-2-ol in MeCN

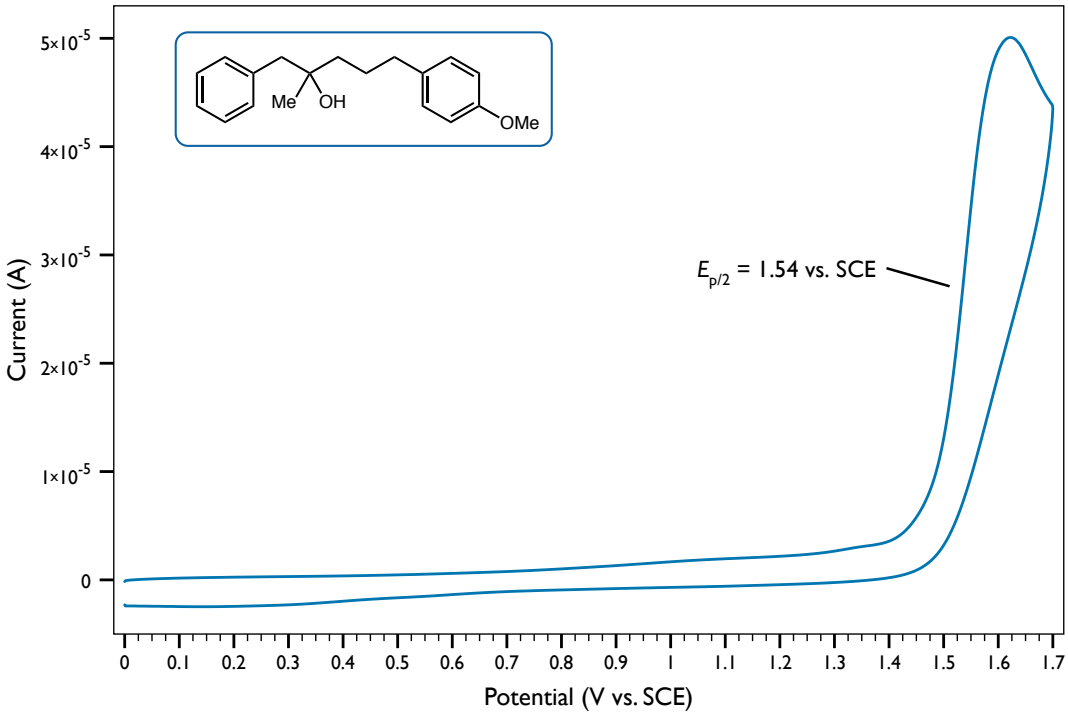
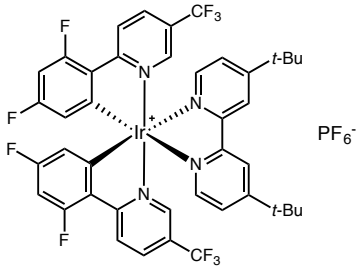
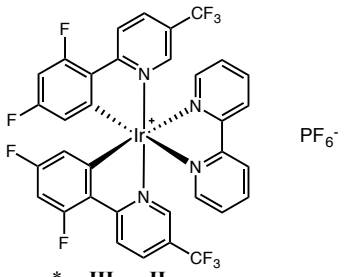


Figure S17. CV of 5-(4-methoxyphenyl)-2-methyl-1-phenylpentan-2-ol in MeCN

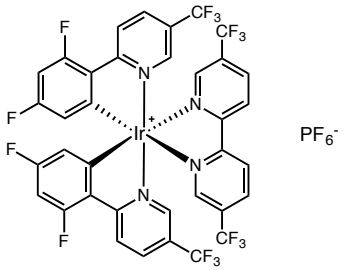
Structure and Potential Data of Photocatalysts



[Ir(dF(CF$_3$)ppy)(dtbbpy)](PF$_6$) (A). $E_{1/2}$(*Ir^{III}/Ir^{II}) = 1.21 V vs. SCE.[19]



[Ir(dF(CF$_3$)ppy)(bpy)](PF$_6$) (B). $E_{1/2}$(*Ir^{III}/Ir^{II}) = 1.32 V vs. SCE.[20]



[Ir(dF(CF$_3$)ppy)(5,5′d(CF$_3$)bpy)](PF$_6$) (C)

Ground state potentials were measured by CV in similar fashion to those in the previous section, at a 0.05 V/s scan rate with a negative initial direction. Excited state reduction potential was calculated using the Rehm-Weller equation:[21]

$$E°^*_{red} = E°_{red} + E^{0\text{-}0}$$

where $E°^*$ denotes the excited state reduction potential, $E°$ the ground state reduction potential, and $E^{0\text{-}0}$ the energy difference between the 0th vibration level of the ground state and that of the excited state. Due to the poor overlap between the absorption and emission spectra, $E^{0\text{-}0}$ is approximated as the high-energy onset of phosphorescence where the emission intensity is 10% of the obtained at the maximum emission wavelength, using the "10% rule."[22] These estimations were corroborated by approximating the HOMO-LUMO gap as the difference between the onset of oxidation and the onset of reduction.[23] $E_{1/2}$(Ir^{III}/Ir^{II}) = -0.69 V vs. SCE; $E_{1/2}$(*Ir^{III}/Ir^{II}) = 1.68 V vs. SCE.

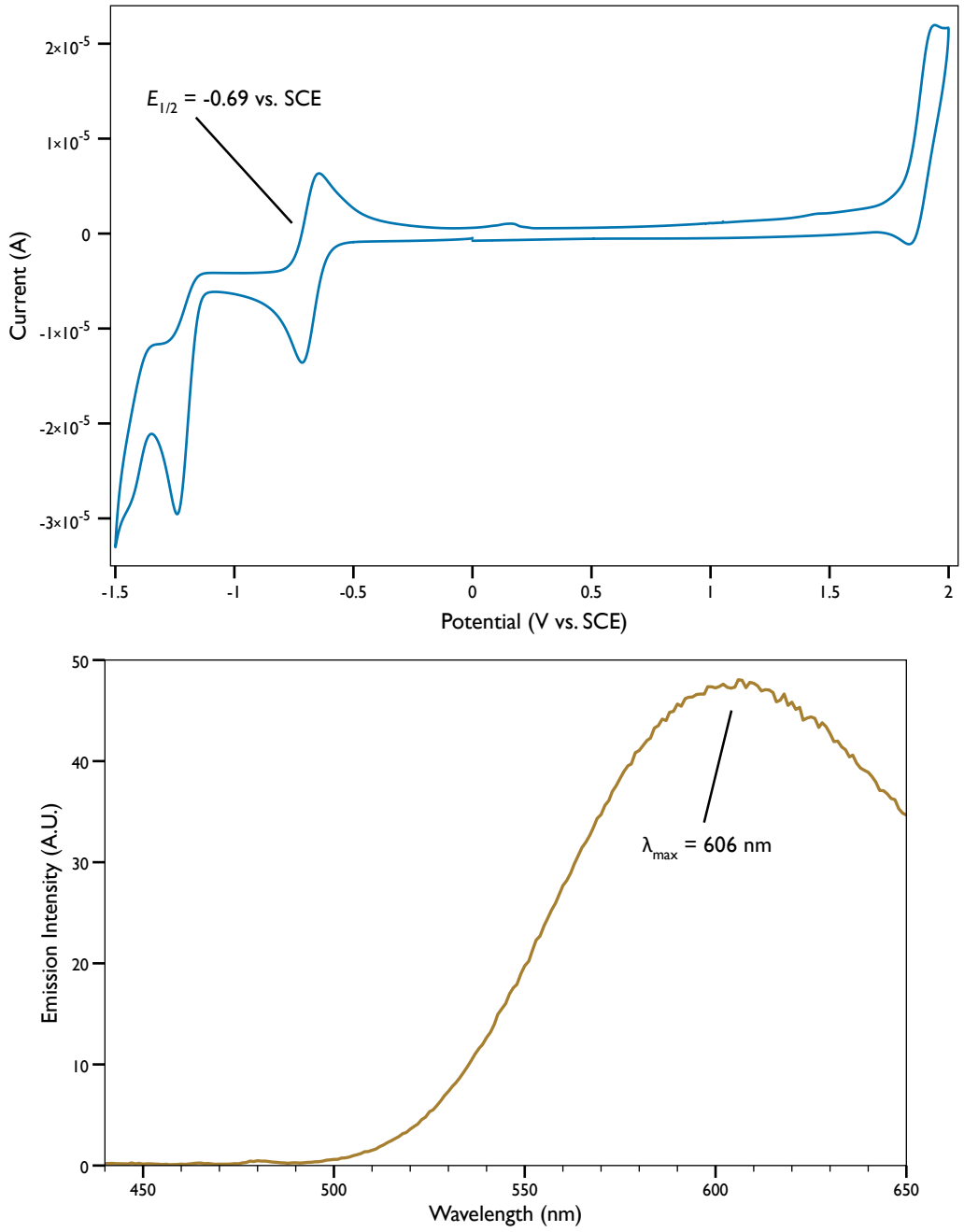


Figure S18. CV and phosphorescence spectrum of photocatalyst C in MeCN. The emission spectrum was taken with excitation wavelength of 420 nm. The emission maxima is at 606 nm, thus the 10% of the maxima is at 524 nm.

DFT Computations

All calculations used DFT methodology[24] as implemented in the Gaussian 09 series of computer programs.[25] We employed the unrestricted B3LYP functional[26] and the all-electron, valence triple-ζ plus polarization and diffuse function 6-311++G(2df,2p) basis sets.[27] Calculations were performed in the gas phase as well as with the CPCM polarizable conductor calculation model for acetonitrile.[28] All molecules underwent geometry optimization, and stationary points were subjected to normal mode analysis.

Calculation of O-H bond energies:

The bond energy was determined by calculating the energies of alcohol **4**, its corresponding alkoxy radical and an H-atom (Figure S19a). The O-H bond energy of the alcohol starting material was referenced to the O-H BDE of *t*-BuOH (106.3 kcal/mol) (Figure S19b).[29]

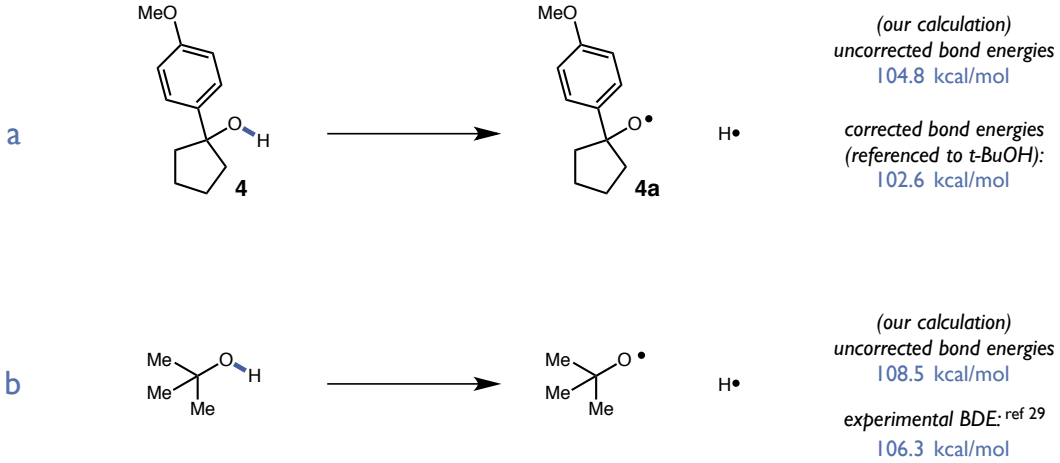


Figure S19. Chemical equations for themodynamic analysis

Table S3. Thermodynamic parameters: Geometries and frequencies were calculated with UB3LYP/6-311++G(2df,2p) with addition of the CPCM (solvent = acetonitrile) solvation model. Energies are given in hartrees particle^{-1}.

Entry	Job Name	E	G	H	S
1	tBuOH	-233.771051	-233.665141	-233.62844	77.251
2	tBuO-radical	-233.0959008	-233.003888	-232.96681	78.03
3	H-atom	-0.502283065	-0.512937	-0.499923	27.392
4	**4**	-617.5620333	-617.345275	-617.29049	115.298
5	**4a**	-616.8927875	-616.689505	-616.63494	114.853

Calculation of C-C bond energies:

The bond strengths of the scissile C-C bonds in 2-(4-methoxyphenyl)propan-2-ol (Figure S20a) and its corresponding alkoxy radical (Figure S20b) were estimated using DFT. To avoid the impact of ring strain on this BDE, 2-(4-methoxyphenyl)propan-2-ol was chosen as a model substrate to calculate the C-C bond energy. Furthermore, this substrate allowed us to reference all bond energies to experimental ethane C-C bond energies (Figure S20c).[30]

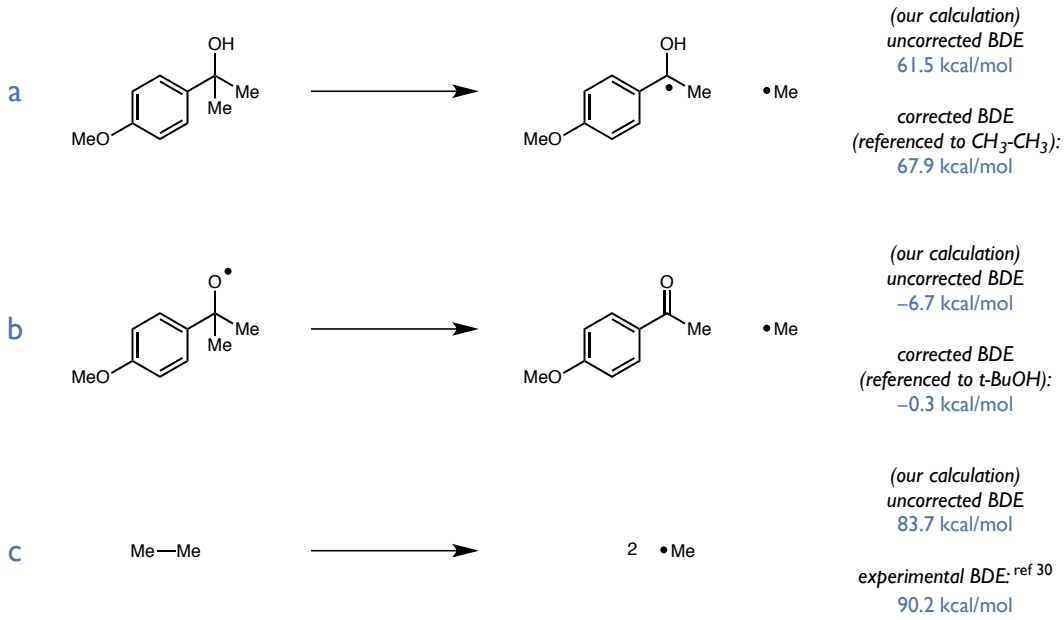


Figure S20. Chemical equations for themodynamic analysis

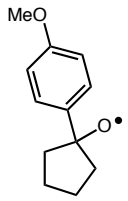
Table S4. Thermodynamic parameters: Geometries and frequencies were calculated with UB3LYP/6-311++G(2df,2p) with addition of the CPCM (solvent = acetonitrile) solvation model. Energies are given in hartrees particle^{-1}.

Entry	Job Name	E	G	H	S
1	2-(4-methoxyphenyl)propan-2-ol	-540.1276347	-539.945126	-539.89384	107.94
2	2-(4-methoxyphenyl)propan-2-ol ketyl	-500.1625304	-500.021591	-499.97093	106.63
3	2-(4-methoxyphenyl)propan-2-oxy radical	-539.4556213	-539.286322	-539.23474	108.57
4	1-(4-methoxyphenyl)ethan-1-one	-2.954782878	-499.468264	-499.42058	100.35
5	Me radical	-39.85846751	-39.846941	-39.824865	46.462
6	Ethane	-79.86192507	-79.809124	-79.783261	54.432

Optimized geometries:
Optimized geometries in Cartesian coordinates (Å) and energies (hartrees) for stationary points.

H•

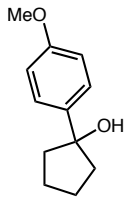
```
E(UB3LYP) =  -0.502283065410
Zero-point correction=                           0.000000 (Hartree/Particle)
Thermal correction to Energy=                    0.001416
Thermal correction to Enthalpy=                  0.002360
Thermal correction to Gibbs Free Energy=        -0.010654
Sum of electronic and zero-point Energies=             -0.502283
Sum of electronic and thermal Energies=                -0.500867
Sum of electronic and thermal Enthalpies=              -0.499923
Sum of electronic and thermal Free Energies=           -0.512937

Charge =  0 Multiplicity = 2
 Symbolic Z-Matrix:
 H                    -1.14243   0.26706   0.
```



E(UB3LYP) = -616.892787526
Zero-point correction= 0.243964 (Hartree/Particle)
Thermal correction to Energy= 0.256908
Thermal correction to Enthalpy= 0.257853
Thermal correction to Gibbs Free Energy= 0.203282
Sum of electronic and zero-point Energies= -616.648823
Sum of electronic and thermal Energies= -616.635879
Sum of electronic and thermal Enthalpies= -616.634935
Sum of electronic and thermal Free Energies= -616.689505

Charge = 0 Multiplicity = 2
Symbolic Z-Matrix:

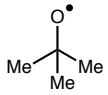
C	1.77789	-1.21227	0.26871
C	0.3934	-1.02284	0.17036
C	-0.1542	0.25719	0.09391
C	0.7226	1.35024	0.11671
C	2.10955	1.16739	0.21561
C	2.63199	-0.11091	0.29201
H	2.19545	-2.20804	0.33629
H	-0.25083	-1.89304	0.16119
H	0.31896	2.35151	0.0636
H	2.77782	2.01806	0.23941
O	3.98704	-0.30046	0.44403
C	4.73632	-0.28481	-0.77512
H	4.62908	0.67286	-1.2883
H	5.77749	-0.43545	-0.50263
H	4.41222	-1.08947	-1.43866
C	-1.66267	0.46922	-0.02877
C	-2.30756	-0.19161	-1.28514
C	-2.50433	-0.19325	1.18582
C	-3.7668	-0.42125	-0.90267
H	-1.80769	-1.14047	-1.48223
H	-2.1676	0.44605	-2.15762
C	-3.67833	-0.9463	0.5358
H	-2.8345	0.59867	1.85489
H	-1.82554	-0.83227	1.74427
H	-4.31378	0.52195	-0.92794
H	-4.27247	-1.11283	-1.57617
H	-4.60392	-0.80961	1.09316
H	-3.45888	-2.01533	0.52296
O	-2.03241	1.77079	0.06026



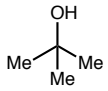
E(UB3LYP) = -617.562033269
Zero-point correction= 0.257203 (Hartree/Particle)
Thermal correction to Energy= 0.270596
Thermal correction to Enthalpy= 0.271540
Thermal correction to Gibbs Free Energy= 0.216758
Sum of electronic and zero-point Energies= -617.304830
Sum of electronic and thermal Energies= -617.291437
Sum of electronic and thermal Enthalpies= -617.290493
Sum of electronic and thermal Free Energies= -617.345275

Charge = 0 Multiplicity = 1
Symbolic Z-Matrix:

C	1.76675	-1.41568	-0.01356
C	0.40123	-1.19306	-0.00991
C	-0.13112	0.10313	0.00231
C	0.76869	1.16433	0.01074
C	2.14928	0.95883	0.00748
C	2.65573	-0.33714	-0.00496
H	2.16248	-2.42219	-0.02238
H	-0.25708	-2.05159	-0.01615
H	0.39437	2.17633	0.02035
H	2.807	1.81439	0.01596
O	3.98304	-0.65282	-0.00893
C	4.93447	0.40726	0.00506
H	4.8321	1.01944	0.90275
H	5.91106	-0.06726	0.00093
H	4.83577	1.03988	-0.87906
C	-1.6342	0.32071	0.00469
C	-2.36664	-0.30736	-1.20061
C	-2.36561	-0.32818	1.20057
C	-3.84886	-0.34509	-0.78408
H	-1.99347	-1.3194	-1.35858
H	-2.18107	0.2593	-2.11261
C	-3.84691	-0.43039	0.77124
H	-2.21375	0.25419	2.10877
H	-1.95469	-1.32171	1.37708
H	-4.3672	0.555	-1.11803
H	-4.37054	-1.18494	-1.24001
H	-4.43936	0.3765	1.20257
H	-4.29036	-1.36032	1.12328
O	-1.8544	1.74456	0.01529
H	-2.80118	1.91429	0.01042




```
E(UB3LYP) =  -233.095900814
 Zero-point correction=                           0.121585 (Hartree/Particle)
 Thermal correction to Energy=                    0.128143
 Thermal correction to Enthalpy=                  0.129087
 Thermal correction to Gibbs Free Energy=         0.092013
 Sum of electronic and zero-point Energies=           -232.974316
 Sum of electronic and thermal Energies=              -232.967758
 Sum of electronic and thermal Enthalpies=            -232.966814
 Sum of electronic and thermal Free Energies=         -233.003888

Charge =  0 Multiplicity = 2
 Symbolic Z-Matrix:
 C                    -1.40949   0.75671  -0.00002
 C                    -0.89618  -0.69522  -0.00022
 H                     0.17382  -0.69525  -0.0002
 H                    -1.25287  -1.19974   0.87336
 H                    -1.25285  -1.1995   -0.87395
 C                    -2.94949   0.75674  -0.00004
 H                    -3.30618   0.25222   0.87353
 H                    -3.30613   1.76555   0.00009
 H                    -3.30615   0.25247  -0.87377
 C                    -0.89616   1.48249   1.25749
 H                     0.17384   1.48247   1.25751
 H                    -1.25281   2.4913    1.25763
 H                    -1.25285   0.97797   2.13107
 O                    -0.93279   1.43098  -1.16751
```




```
E(UB3LYP) =  -233.771050974
 Zero-point correction=                           0.134914 (Hartree/Particle)
 Thermal correction to Energy=                    0.141670
 Thermal correction to Enthalpy=                  0.142614
 Thermal correction to Gibbs Free Energy=         0.105910
 Sum of electronic and zero-point Energies=           -233.636137
 Sum of electronic and thermal Energies=              -233.629381
 Sum of electronic and thermal Enthalpies=            -233.628437
 Sum of electronic and thermal Free Energies=         -233.665141

Charge =  0 Multiplicity = 1
 Symbolic Z-Matrix:
 C                    -1.40949   0.75671  -0.00002
 C                    -0.89618  -0.69522  -0.00022
 H                     0.17382  -0.69525  -0.0002
 H                    -1.25287  -1.19974   0.87336
 H                    -1.25285  -1.1995   -0.87395
 C                    -2.94949   0.75674  -0.00004
 H                    -3.30618   0.25222   0.87353
 H                    -3.30613   1.76555   0.00009
 H                    -3.30615   0.25247  -0.87377
 C                    -0.89616   1.48249   1.25749
 H                     0.17384   1.48247   1.25751
 H                    -1.25281   2.4913    1.25763
 H                    -1.25285   0.97797   2.13107
 O                    -0.93279   1.43098  -1.16751
 H                    -1.25277   2.33608  -1.16739
```

$H_3C—CH_3$

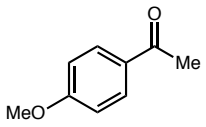
```
E(UB3LYP) =  -79.8619250703
 Zero-point correction=                           0.074226 (Hartree/Particle)
 Thermal correction to Energy=                    0.077720
 Thermal correction to Enthalpy=                  0.078664
 Thermal correction to Gibbs Free Energy=         0.052801
 Sum of electronic and zero-point Energies=           -79.787699
 Sum of electronic and thermal Energies=              -79.784206
 Sum of electronic and thermal Enthalpies=            -79.783261
 Sum of electronic and thermal Free Energies=         -79.809124

Charge =  0 Multiplicity = 1
 Symbolic Z-Matrix:
 C                    -2.19585   0.07418   0.
 H                    -1.83919  -0.93463   0.
 H                    -1.83917   0.57858  -0.87365
 H                    -3.26585   0.0742    0.
 C                    -1.6825    0.80014   1.2574
 H                    -0.6125    0.79996   1.2575
 H                    -2.039     1.80901   1.25731
 H                    -2.03934   0.29585   2.13106
```

•CH_3

E(UB3LYP) = -39.8584675068
Zero-point correction= 0.029612 (Hartree/Particle)
Thermal correction to Energy= 0.032658
Thermal correction to Enthalpy= 0.033602
Thermal correction to Gibbs Free Energy= 0.011527
Sum of electronic and zero-point Energies= -39.828856
Sum of electronic and thermal Energies= -39.825810
Sum of electronic and thermal Enthalpies= -39.824865
Sum of electronic and thermal Free Energies= -39.846941

Charge = 0 Multiplicity = 2
Symbolic Z-Matrix:

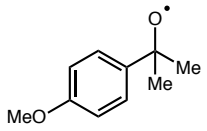
C	-2.28501	-0.05192	-0.21841
H	-1.78062	-0.94359	0.09047
H	-1.7806	0.66141	-0.83618
H	-3.29382	0.12643	0.09047



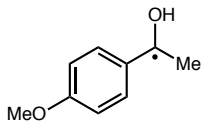
E(UB3LYP) = -499.601862578
 Zero-point correction= 0.169901 (Hartree/Particle)
 Thermal correction to Energy= 0.180335
 Thermal correction to Enthalpy= 0.181280
 Thermal correction to Gibbs Free Energy= 0.133599
 Sum of electronic and zero-point Energies= -499.431962
 Sum of electronic and thermal Energies= -499.421527
 Sum of electronic and thermal Enthalpies= -499.420583
 Sum of electronic and thermal Free Energies= -499.468264

Charge = 0 Multiplicity = 1
 Symbolic Z-Matrix:

C	-0.36127	0.67459	-0.52546
C	1.00707	0.90273	-0.72429
C	1.59008	2.0972	-0.28015
C	0.80476	3.06353	0.36281
C	-0.56357	2.83539	0.56165
C	-1.14659	1.64092	0.11751
H	-0.80641	-0.23741	-0.86457
H	1.60667	0.16492	-1.21521
H	1.2499	3.97554	0.70192
H	-1.16318	3.5732	1.05257
C	3.09374	2.34791	-0.49864
O	-2.54285	1.40812	0.32041
O	3.61727	3.4205	-0.09983
C	3.95673	1.28601	-1.2052
H	4.95943	1.3375	-0.83527
H	3.55474	0.31343	-1.01185
H	3.95564	1.46929	-2.25938
C	-2.73968	0.75689	1.5782
H	-3.78443	0.58269	1.73002
H	-2.21813	-0.17739	1.58159
H	-2.36376	1.37807	2.36415



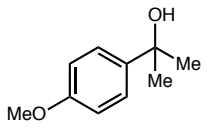

```
E(UB3LYP) =  -539.455621335
 Zero-point correction=                           0.207915 (Hartree/Particle)
 Thermal correction to Energy=                    0.219941
 Thermal correction to Enthalpy=                  0.220885
 Thermal correction to Gibbs Free Energy=         0.169299
 Sum of electronic and zero-point Energies=           -539.247706
 Sum of electronic and thermal Energies=              -539.235680
 Sum of electronic and thermal Enthalpies=            -539.234736
 Sum of electronic and thermal Free Energies=         -539.286322

Charge =  0 Multiplicity = 2
 Symbolic Z-Matrix:
 C                    -1.17387  -1.12313  -0.30006
 C                     0.21331  -1.00353  -0.14079
 C                     0.8017    0.26533  -0.05296
 C                     0.00292   1.41458  -0.1244
 C                    -1.38425   1.29497  -0.28366
 C                    -1.97264   0.02612  -0.3715
 H                    -1.62312  -2.09193  -0.36713
 H                     0.82319  -1.881    -0.08625
 H                     0.45218   2.38338  -0.05733
 H                    -1.99413   2.17245  -0.3382
 O                    -3.38813  -0.09593  -0.53401
 C                    -4.01182  -0.15891   0.75126
 H                    -5.07096  -0.25024   0.62966
 H                    -3.63987  -1.00716   1.28702
 H                    -3.79131   0.73353   1.29882
 C                     2.32607   0.39677   0.12206
 O                     2.62076   1.58947   0.85385
 C                     2.8614   -0.82407   0.89315
 H                     2.39472  -0.87119   1.85486
 H                     2.64089  -1.71651   0.34559
 H                     3.92054  -0.73274   1.01476
 C                     2.99774   0.46459  -1.26208
 H                     2.62579   1.31284  -1.79784
 H                     4.05688   0.55592  -1.14048
 H                     2.77723  -0.42785  -1.80964
```



E(UB3LYP) = -500.162591296
 Zero-point correction= 0.179385 (Hartree/Particle)
 Thermal correction to Energy= 0.190718
 Thermal correction to Enthalpy= 0.191662
 Thermal correction to Gibbs Free Energy= 0.141000
 Sum of electronic and zero-point Energies= -499.983207
 Sum of electronic and thermal Energies= -499.971874
 Sum of electronic and thermal Enthalpies= -499.970929
 Sum of electronic and thermal Free Energies= -500.021591

Charge = 0 Multiplicity = 2
 Symbolic Z-Matrix:

C	1.14635	0.98634	0.00759
C	-0.23458	1.10612	0.00812
C	-1.08567	-0.0285	0.01144
C	-0.44135	-1.30333	0.00665
C	0.93013	-1.41671	0.00352
C	1.74655	-0.27604	0.00483
H	1.74549	1.88464	0.01258
H	-0.65753	2.10033	0.00915
H	-1.04596	-2.19764	0.00822
H	1.40189	-2.39053	0.0043
O	3.09632	-0.49664	0.01766
C	3.96503	0.631	-0.02567
H	4.97612	0.23523	-0.00963
H	3.81604	1.21138	-0.93879
H	3.81853	1.27892	0.8409
C	-2.49081	0.07894	0.00725
O	-3.18979	-1.10252	-0.02588
C	-3.30029	1.32664	-0.00099
H	-3.82301	1.45798	-0.9551
H	-4.06671	1.2958	0.78004
H	-2.6946	2.21252	0.16966
H	-4.13459	-0.92216	0.00807



E(UB3LYP) = -540.127634724
 Zero-point correction= 0.220538 (Hartree/Particle)
 Thermal correction to Energy= 0.232848
 Thermal correction to Enthalpy= 0.233792
 Thermal correction to Gibbs Free Energy= 0.182508
 Sum of electronic and zero-point Energies= -539.907096
 Sum of electronic and thermal Energies= -539.894787
 Sum of electronic and thermal Enthalpies= -539.893843
 Sum of electronic and thermal Free Energies= -539.945126

Charge = 0 Multiplicity = 1
 Symbolic Z-Matrix:

C	-1.17387	-1.12313	-0.30006
C	0.21331	-1.00353	-0.14079
C	0.8017	0.26533	-0.05296
C	0.00292	1.41458	-0.1244
C	-1.38425	1.29497	-0.28366
C	-1.97264	0.02612	-0.3715
H	-1.62312	-2.09193	-0.36713
H	0.82319	-1.881	-0.08625
H	0.45218	2.38338	-0.05733
H	-1.99413	2.17245	-0.3382
O	-3.38813	-0.09593	-0.53401
C	-4.01182	-0.15891	0.75126
H	-5.07096	-0.25024	0.62966
H	-3.63987	-1.00716	1.28702
H	-3.79131	0.73353	1.29882
C	2.32607	0.39677	0.12206
O	2.62076	1.58947	0.85385
H	3.57102	1.67141	0.96295
C	2.8614	-0.82407	0.89315
H	2.39472	-0.87119	1.85486
H	2.64089	-1.71651	0.34559
H	3.92054	-0.73274	1.01476
C	2.99774	0.46459	-1.26208
H	2.62579	1.31284	-1.79784
H	4.05688	0.55592	-1.14048
H	2.77723	-0.42785	-1.80964

References

[1] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*. 4th ed.; Butterworth-Heinemann: Oxford, 1997.
[2] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics*, **1996**, *15*, 1518–1520.
[3] Rono, L. J.; Yayla, H. G.; Wang, D. Y.; Armstrong, M. F.; Knowles, R. R. *J. Am. Chem. Soc.*, **2013**, *135*, 17735–17738.
[4] Canonne, P.; Bernatchez, M. *J. Org. Chem.* **1987**, *52*, 4025–4031.
[5] Paramahamsan, H.; Pearson, A. J.; Pinkerton, A. A.; Zhurova, E. A. *Organometallics*, **2008**, *27*, 900–907.
[6] Baraldi, P. G.; Barco, A.; Benetti, S.; Pollini, G. P.; Polo, E.; Simoni, D. *J. Org. Chem.* **1985**, *50*, 23–29.
[7] Cheon, C. H.; Kanno, O.; Toste, F. D. *J. Am. Chem. Soc.* **2011**, *133*, 13248–13251.
[8] Baciocchi, E.; Bietti, M.; Manduchi, L.; Steenken, S. *J. Am. Chem. Soc.* **1999**, *121*, 6624–6629.
[9] In a few cases, the reaction was run on 0.5 mmol scale. Where it is the case, it will always be noted.
[10] Du, B.; Yuan, C.; Zhang, L.; Yang, L.; Liu, B. *Tetrahedron Lett.* **2013**, *54*, 2217–2220.
[11] Murata, R.; Hirano, K.; Uchiyama, M. *Chem. Asian J.* **2015**, *10*, 1286–1290.
[12] Iranpoor, N.; Firouzabadi, H.; Khalili, D.; Motevalli, S. *J. Org. Chem.* **2008**, *73*, 4882–4887.
[13] Wang, X.; Liu, M.; Xu, L.; Wang, Q.; Chen, J.; Ding, J.; Wu, H. *J. Org. Chem.* **2013**, *78*, 5273−5281.
[14] Morandi, B.; Wickens, Z. K.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2013**, *52*, 2944−2948.
[15] Morandi, B.; Wickens, Z. K.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2013**, *52*, 2944−2948.
[16] Hayashi, M.; Shibuya, M.; Iwabuchi, Y. *J. Org. Chem.* **2012**, *77*, 3005−3009.
[17] Yasu, Y.; Koike, T.; Akita, M. *Adv. Synth. Catal.* **2012***, 354*, 3414−3420.
[18] Houmam, A. *Chem. Rev.* **2008**, *108*, 2180–2237.
[19] Shaw, M. H.; Shurtleff, V. W.; Terret, J. A.; Cuthbertson, J. D.; MacMillan, D. W. C. *Science*, **2016**, *352*, 1304–1308.
[20] Hanss, D.; Freys, J. C.; Bernardinelli, G.; Wenger, O. S. *Eur. J. Inorg. Chem.* **2009**, 4850–4859.
[21] Brennan, J. L.; Keyes, T. E.; Forster, R. J. *Langmuir* **2006**, *22*, 10754–10761.
[22] (a) Dossing, A.; Ryu, C. K.; Kudo, S.; Ford, P. C. *J. Am. Chem. Soc.* **1993**, *115*, 5132–5137. (b) Bruner, B.; Walker, M. B.; Ghimire, M. M.; Zhang, D.; Selke, M.; Klausmeyer, K. K.; Omary, M. A.; Farmer, P. J. *Dalton Trans.* **2014**, *43*, 11548–11556. (c) McClure, L. J.; Ford, P. C. *J. Phys. Chem.* **1992**, *96*, 6640–6650. (d) Schlenker, C. W.; Thompson, M. E. *Top. Curr. Chem.* **2012**, *312*, 175–212.
[23] (a) Ye, C.; Li, M.; Luo, J.; Chen, L.; Tang, Z.; Pei, J.; Jiang, L.; Song, Y.; Zhu. D. *J. Mater. Chem.* **2012**, *22*, 4299–4305. (b) Singh, A.; Teegardin, K.; Kelly, M.; Prasad, K. S.; Krishnan, S.; Weaver, J. D. *J. Organomet. Chem.* **2015**, *776*, 51–59.
[24] Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*. University Press: Oxford, 1989.

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[25] Gaussian 09, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2010.
[26] (a) Parr, R. G.; Yang, W. *Annu. Rev. Phys. Chem.* **1995**, *46*, 701–728. (b) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623–11627. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789. (d) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100. (e) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
[27] (a) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639–5648. (b) Raghavachari, K.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650–654. (c) Blaudeau, J.-P.; McGrath, M. P.; Curtiss, L. A., Radom, L. *J. Chem. Phys.* **1997**, *107*, 5016–5021. (d) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033. (e) Hay, P. J. *J. Chem. Phys.* **1977**, *66*, 4377–4384. (f) Raghavachari, K.; Trucks, G. W. *J. Chem. Phys.* **1989**, *91*, 1062–1065. (g) Binning Jr., R. C.; Curtiss, L. A. *J. Comput. Chem.* **1990**, *11*, 1206–1216. (h) McGrath, M. P.; Radom, L. *J. Chem. Phys.* **1991**, *94*, 511–516. (i) Curtiss, L. A.; McGrath, M. P., Blaudeau, J.-P.; Davis, N. E.; Binning Jr., R. C.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 6104–6113. (j) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294–301. (k) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265–3269.
[28] (a) Barone, V.; Cossi, M. *J. Phys. Chem. A.*, **1998**, *102*, 1995–2001. (b) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.*, **2003**, *24*, 669–681.
[29] Luo, Y.-R. *Comprehensive Handbook of Chemical Bond Energies*; CRC Press: Boca Raton, FL, 2007, p 258.
[30] Luo, Y.-R. *Comprehensive Handbook of Chemical Bond Energies*; CRC Press: Boca Raton, FL, 2007, p 147.