Supporting Information

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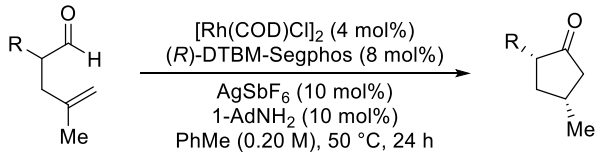
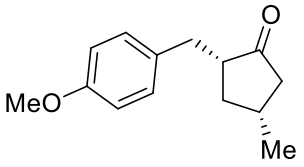
1. General Information

Commercially reagents were purchased from Sigma Aldrich, Strem, Acros Organics, TCI or Alfa Aesar and used without further purification. All experiments were performed in oven-dried or flame-dried glassware under an atmosphere of N_2. Tetrahydrofuran, diethyl ether, toluene, and dichloromethane were purified using an Innovative Technologies Pure Solv system, degassed by three freeze-pump-thaw cycles, and stored over 3A MS within a N_2 filled glove box. Reactions were monitored either via gas chromatography using an Agilent Technologies 7890A GC system equipped with an Agilent Technologies 5975C inert XL EI/CI MSD or by analytical thin-layer chromatography on EMD Silica Gel 60 F254 plates. Visualization of the developed plates was performed under UV light (254 nm) or using $KMnO_4$ stain. Purification and isolation of products were performed via silica gel chromatography (both column and preparative thin-layer chromatography). Column chromatography was performed with Silicycle Silia-P Flash Silica Gel using glass columns. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on a Bruker DRX-400 (400 MHz ^{1}H, 100 MHz ^{13}C, 376.5 MHz ^{19}F, 162 MHz ^{31}P), GN-500 (500 MHz ^{1}H, 125.7 MHz ^{13}C, 202 MHz ^{31}P), or CRYO-500 (500 MHz ^{1}H, 125.7 MHz ^{13}C) spectrometer. ^{1}H NMR spectra were internally referenced to the residual solvent signal or TMS. ^{13}C NMR spectra were internally referenced to the residual solvent signal. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm, δ 7.27 for $CDCl_3$), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ ppm, δ 77.16 for $CDCl_3$). Infrared spectra were obtained on a Thermo Scientific Nicolet iS5 FT-IR spectrometer equipped with an iD5 ATR accessory, and were reported in terms of frequency of absorption (cm^{-1}). Enantiomeric excesses for enantioselective reactions were determined by chiral SFC analysis using an Agilent Technologies HPLC (1200 series) system and Aurora A5 Fusion. High-resolution mass spectra (HRMS) were obtained on a micromass 70S-250 spectrometer (EI) or an ABI/Sciex QStar Mass Spectrometer (ESI), performed by the University of California, Irvine Mass Spectrometry Center. X-ray crystallography was performed by the X-ray Crystallography Facility of the University of California, San Diego.

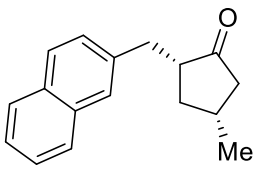
2. General Procedures for the Dynamic Kinetic Resolution using Hydroacylation



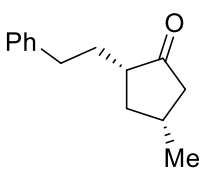
Method A: In a N_2-filled glovebox, $[Rh(COD)Cl]_2$ (2.0 mg, 0.0040 mmol, 4 mol%), (*R*)-DTBM-Segphos (10.7 mg, 0.0080 mmol, 8 mol%), and toluene (0.50 mL, 0.20 M) were added to a 1 dram vial equipped with a magnetic stir bar. The solution was stirred at 30 °C for 10 min. $AgSbF_6$ (3.4 mg, 0.010 mmol, 10 mol%), was added, and the resulting mixture was stirred at 30 °C for 30 min. Aldehyde **1** (0.10 mmol, 1.0 equiv) and 1-$AdNH_2$ (1.5 mg, 0.010 mmol, 10 mol%) were added. The vial was then sealed with a Teflon-lined screw cap and stirred at 50 °C for 24 h. The reaction mixture was cooled to rt, filtered through celite, and concentrated *in vacuo*. The diastereoselectivity was determined by ^{1}H NMR analysis of the unpurified reaction mixture. The ketone **2** was purified using preparative thin-layer chromatography.



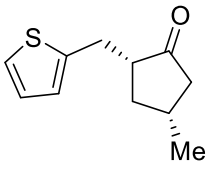
(2*R*,4*R*)-2-(4-methoxybenzyl)-4-methylcyclopentan-1-one (2a): The title compound was synthesized according to Method A and isolated by preparatory TLC (5% EtOAc in hexanes) as a white solid (20.5 mg, 94% yield, >20:1 *dr*, >99% *ee*, $[\alpha]^{24}_D$ = +151 (*c* 0.52, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 3.79 (s, 3H), 3.11 (dd, *J* = 13.8, 4.0 Hz, 1H), 2.56 – 2.45 (m, 2H), 2.40 (dtd, *J* = 12.4, 8.1, 4.1 Hz, 1H), 2.21 – 2.03 (m, 2H), 1.71 (dd, *J* = 18.4, 11.3 Hz, 1H), 1.21 – 1.11 (m, 1H), 1.10 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 219.8, 158.2, 132.2, 129.9, 114.0, 55.4, 53.1, 47.0, 38.3, 34.8, 29.7, 20.4. **IR** (ATR): 2952, 2934, 1721, 1610, 1319, 1181, 1037, 711 cm^{-1}. **HRMS** calculated for $C_{14}H_{18}O_2Na$ $[M+Na]^+$ 241.1205, found 241.1204. **Chiral SFC**: 100 mm CHIRALPAK AD-H, 1% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (major) = 6.1 min, t_{R2} (minor) = 8.3 min.



(2*R*,4*R*)-4-methyl-2-(naphthalen-2-ylmethyl)cyclopentan-1-one (2b): The title compound was synthesized according to Method A and isolated by preparatory TLC (5% EtOAc in hexanes) as a white solid (21.9 mg, 94% yield, >20:1 *dr*, 93% *ee*, $[\alpha]^{24}_D$ = +206 (*c* 0.93, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.73 (m, 3H), 7.62 (s, 1H), 7.50 – 7.40 (m, 2H), 7.31 (dd, *J* = 8.4, 1.4 Hz, 1H), 3.36 (dd, *J* = 13.8, 4.1 Hz, 1H), 2.72 (dd, *J* = 13.8, 9.5 Hz, 1H), 2.54 (ddd, *J* = 12.6, 9.1, 6.4 Hz, 2H), 2.21 – 2.05 (m, 2H), 1.76 (dd, *J* = 18.6, 11.3 Hz, 1H), 1.21 (q, *J* = 11.7 Hz, 1H), 1.10 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 219.6, 137.8, 133.7, 132.3, 128.2, 127.8, 127.59, 127.55, 127.2, 126.1, 125.5, 52.9, 46.9, 38.4, 35.9, 29.7, 20.3. **IR** (ATR): 2953, 1734, 1507, 1153, 775 cm^{-1}. **HRMS** calculated for $C_{17}H_{18}ONa$ $[M+Na]^+$ 261.1255, found 261.1255. **Chiral SFC**: 100 mm CHIRALPAK AD-H, 0.5% *i*-PrOH, 2.5 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (major) = 9.2 min, t_{R2} (minor) = 11.5 min.

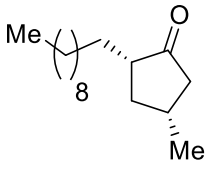


(2*S*,4*R*)-4-methyl-2-phenethylcyclopentan-1-one (2c): The title compound was synthesized according to Method A and isolated by preparatory TLC (5% EtOAc in hexanes) as a colorless oil (20.7 mg, 86% yield, >20:1 *dr*, 93% *ee*, $[\alpha]^{24}_D$ = +114 (*c* 0.41, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.19 (dd, *J* = 10.2, 4.3 Hz, 3H), 2.79 – 2.69 (m, 1H), 2.69 – 2.58 (m, 1H), 2.46 (dd, *J* = 18.3, 7.4 Hz, 1H), 2.41 – 2.30 (m, 1H), 2.22 – 2.05 (m, 3H), 1.76 (dd, *J* = 18.4, 11.6 Hz, 1H), 1.65 – 1.51 (m, 1H), 1.23 – 1.10 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 220.8, 141.8, 128.6, 128.5, 126.1, 50.3, 47.0, 38.8, 33.8, 31.6, 29.8, 20.5. **IR** (ATR): 2951, 2924, 1733, 1603, 1454, 906 cm^{-1}. **HRMS** calculated for $C_{14}H_{18}ONa$ $[M+Na]^+$ 225.1255, found 225.1250. **Chiral SFC**: 100 mm CHIRALPAK AD-H, 0% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 7.8 min, t_{R2} (major) = 8.6 min.

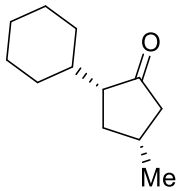


(2*R*,4*R*)-4-methyl-2-(thiophen-2-ylmethyl)cyclopentan-1-one (2d): The title compound was synthesized according to Method A and isolated by preparatory TLC (5% EtOAc in hexanes) as a colorless oil (18.3 mg, 94% yield, >20:1 *dr*, 93% *ee*, $[\alpha]^{24}_D$ = +173 (*c* 0.58, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.82 – 6.77 (m, 1H), 3.34 (dd, *J* = 15.0, 4.0 Hz, 1H), 2.84 (dd, *J* = 15.0, 8.9 Hz, 1H), 2.56 – 2.40 (m, 2H), 2.34 – 2.24 (m, 1H), 2.21 – 2.07 (m, 1H), 1.74 (dd, *J* = 18.5, 11.5 Hz, 1H), 1.26 – 1.16 (m, 1H), 1.12 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 219.1, 142.4, 126.9, 125.5, 123.7, 52.9, 46.9, 38.2,

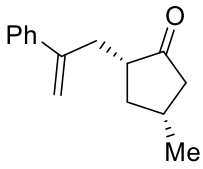
29.8, 29.6, 20.3. **IR** (ATR): 2953, 1736, 1455, 1437, 1245, 1154, 849 cm^{-1}. **HRMS** calculated for $C_{11}H_{14}OSNa$ $[M+Na]^+$ 217.0663, found 217.0658. **Chiral SFC**: 100 mm CHIRALPAK AD-H, 1% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (major) = 5.1 min, t_{R2} (minor) = 6.2 min.



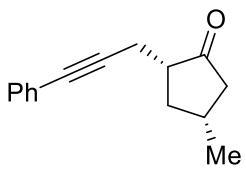
(2*S*,4*R*)-2-decyl-4-methylcyclopentan-1-one (2e): The title compound was synthesized according to Method A at 60 °C and isolated by preparatory TLC (5% EtOAc in hexanes) as a colorless oil (15.4 mg, 65% yield, >20:1 *dr*, 96% *ee*, $[\alpha]^{24}_D$ = +99 (*c* 1.0, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.46 (dd, *J* = 18.4, 7.4 Hz, 1H), 2.36 – 2.26 (m, 1H), 2.13 (qd, *J* = 12.4, 6.4 Hz, 2H), 1.76 (ddd, *J* = 24.5, 14.9, 8.1 Hz, 2H), 1.26 (s, 17H), 1.12 (dd, *J* = 11.6, 9.3 Hz, 4H), 0.89 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 221.3, 51.1, 47.0, 38.8, 32.1, 29.9, 29.84, 29.75, 29.7, 29.6, 29.5, 27.7, 22.8, 20.5, 14.3. **IR** (ATR): 2953, 2922, 2852, 1739, 1456, 1155, 720 cm^{-1}. **HRMS** calculated for $C_{16}H_{30}ONa$ $[M+Na]^+$ 261.2194, found 261.2184. **Chiral SFC** (of the corresponding tertiary alcohol after treatment with PhMgBr): 100 mm CHIRALPAK AD-H, 2% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 10.5 min, t_{R2} (major) = 12.0 min.



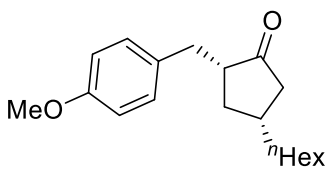
(2*R*,4*R*)-2-cyclohexyl-4-methylcyclopentan-1-one (2f): The title compound was synthesized according to Method A at 60 °C and isolated by preparatory TLC (5% EtOAc in hexanes) as a colorless oil (11.4 mg, 63% yield, >20:1 *dr*, >99% *ee*, $[\alpha]^{24}_D$ = +80 (*c* 0.94, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.50 – 2.36 (m, 1H), 2.18 – 1.99 (m, 3H), 1.86 – 1.56 (m, 6H), 1.47 – 1.36 (m, 1H), 1.35 – 1.19 (m, 3H), 1.18 – 1.00 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 220.8, 56.6, 48.2, 37.5, 34.4, 31.9, 29.7, 28.9, 26.7, 26.52, 26.48, 20.4. **IR** (ATR): 2922, 2851, 1733, 1449, 1152, 1076, 892 cm^{-1}. **HRMS** calculated for $C_{12}H_{20}OH$ $[M+H]^+$ 181.1592, found 181.1598. **Chiral SFC** (of the corresponding tertiary alcohol after treatment with PhMgBr): 100 mm CHIRALPAK AD-H, 1% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 14.2 min, t_{R2} (major) = 18.2 min.



(2*R*,4*R*)-4-methyl-2-(2-phenylallyl)cyclopentan-1-one (2g): The title compound was synthesized according to Method A and isolated by preparatory TLC (5% EtOAc in hexanes) as a colorless oil (16.5 mg, 69% yield, >20:1 *dr*, 94% *ee*, $[\alpha]^{24}_D$ = +85 (*c* 0.67, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.31 – 7.24 (m, 1H), 5.28 (s, 1H), 5.09 (s, 1H), 3.34 – 3.20 (m, 1H), 2.45 (dd, *J* = 18.3, 7.2 Hz, 1H), 2.31 – 2.10 (m, 3H), 2.04 (ddt, *J* = 18.1, 12.2, 6.2 Hz, 1H), 1.74 (dd, *J* = 18.4, 11.5 Hz, 1H), 1.16 – 0.99 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 220.2, 146.8, 140.4, 128.5, 127.8, 126.4, 113.8, 49.7, 46.8, 38.7, 36.2, 29.6, 20.4. **IR** (ATR): 2953, 1734, 1627, 1494, 1454, 1155 cm^{-1}. **HRMS** calculated for $C_{15}H_{18}ONa$ $[M+Na]^+$ 237.1255, found 237.1256. **Chiral SFC**: 250 mm CHIRALPAK AD, 1% *i*-PrOH, 2.5 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 9.4 min, t_{R2} (major) = 10.4 min.

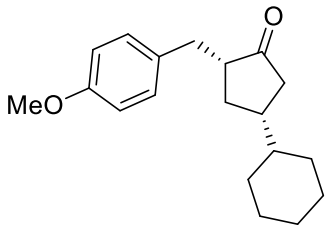


(2*R*,4*R*)-4-methyl-2-(3-phenylprop-2-yn-1-yl)cyclopentan-1-one (2h): The title compound was synthesized according to Method A at 60 °C and isolated by preparatory TLC (5% EtOAc in hexanes) as a colorless oil (14.5 mg, 68% yield, 11:1 *dr*, 95% *ee*, $[\alpha]^{24}_D$ = +212 (*c* 0.81, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 5.0 Hz, 2H), 7.28 (dd, *J* = 4.5, 2.3 Hz, 3H), 2.80 (dd, *J* = 16.8, 3.3 Hz, 1H), 2.63 – 2.36 (m, 4H), 2.21 (dt, *J* = 18.1, 5.9 Hz, 1H), 1.78 (dd, *J* = 18.4, 11.6 Hz, 1H), 1.49 (q, *J* = 15.1 Hz, 1H), 1.19 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 218.5, 131.7, 128.3, 127.9, 123.8, 87.5, 81.9, 49.8, 46.9, 37.8, 29.6, 20.4, 19.7. **IR** (ATR): 2954, 1738, 1498, 1455, 1339, 1156, 911 cm^{-1}. **HRMS** calculated for $C_{15}H_{16}ONa$ $[M+Na]^+$ 235.1099, found 235.1092. **Chiral SFC**: 100 mm CHIRALPAK AD-H, 1% *i*-PrOH, 3.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (major) = 4.4 min, t_{R2} (minor) = 5.3 min.

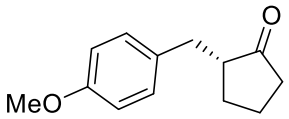


(2*R*,4*R*)-4-hexyl-2-(4-methoxybenzyl)cyclopentan-1-one (2i): The title compound was synthesized according to Method A and isolated by preparatory TLC (5% EtOAc in hexanes) as a yellow oil (18.9 mg, 66% yield, >20:1 *dr*, >99% *ee*, $[\alpha]^{24}_D$ = +82 (*c* 1.2, $CHCl_3$)). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 3.79 (s, 3H), 3.11 (dd, *J* = 13.9, 3.7 Hz,

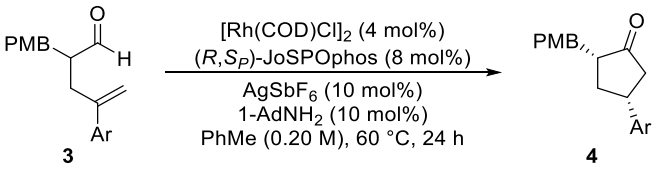
1H), 2.49 (dd, *J* = 14.3, 9.3 Hz, 2H), 2.38 (d, *J* = 9.1 Hz, 1H), 2.23 – 2.12 (m, 1H), 2.06 – 1.92 (m, 1H), 1.72 (dd, *J* = 18.5, 11.6 Hz, 1H), 1.38 (s, 2H), 1.27 (s, 8H), 1.14 (q, *J* = 12.1 Hz, 1H), 0.88 (t, *J* = 6.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 219.7, 158.1, 132.2, 129.9, 113.9, 55.4, 52.6, 45.6, 36.3, 36.0, 35.0, 34.8, 31.9, 29.5, 27.9, 22.8, 14.2. **IR** (ATR): 2954, 2922, 2853, 1737, 1611, 1512, 1464, 1245, 1176, 1036 cm^{-1}. **HRMS** calculated for $C_{19}H_{28}O_2Na$ $[M+Na]^+$ 311.1987, found 311.1980. **Chiral SFC**: 100 mm CHIRALPAK AD-H, 2% *i*-PrOH, 2.5 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (major) = 6.2 min, t_{R2} (minor) = 11.9 min.



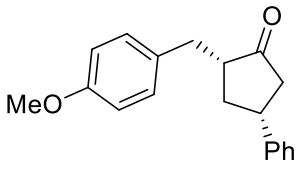
(2*R*,4*R*)-4-cyclohexyl-2-(4-methoxybenzyl)cyclopentan-1-one (2j): The title compound was synthesized according to Method A at 60 °C using (*R*, S_p)-JoSPOphos and isolated by preparatory TLC (5% EtOAc in hexanes) as a colorless oil (25.5 mg, 89% yield, >20:1 *dr*, >99% *ee*, $[\alpha]^{24}_D$ = +46 (*c* 0.39, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 3.12 (dd, *J* = 13.9, 4.0 Hz, 1H), 2.48 (dt, *J* = 21.9, 11.0 Hz, 2H), 2.41 – 2.27 (m, 1H), 2.24 – 2.12 (m, 1H), 1.83 – 1.59 (m, 7H), 1.28 – 1.05 (m, 5H), 1.00 – 0.79 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 219.6, 158.1, 132.2, 129.9, 114.0, 55.4, 52.7, 43.7, 43.6, 40.9, 34.8, 34.1, 32.0, 31.0, 26.6, 26.3, 26.2. **IR** (ATR): 2921, 2849, 1735, 1611, 1511, 1448, 1245, 1176, 1035, 831 cm^{-1}. **HRMS** calculated for $C_{19}H_{26}O_2H$ $[M+H]^+$ 287.2011, found 287.1998. **Chiral SFC**: 100 mm CHIRALPAK AD-H, 2% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (major) = 11.9 min, t_{R2} (minor) = 19.3 min.



(*R*)-2-(4-methoxybenzyl)cyclopentan-1-one (2k): The title compound was synthesized according to Method A and isolated by preparatory TLC (5% EtOAc in hexanes) as a colorless oil (10.6 mg, 52% yield, 82% *ee*, $[\alpha]^{24}_D$ = +107 (*c* 0.48, $CHCl_3$)). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 3.79 (s, 3H), 3.07 (dd, *J* = 14.0, 3.7 Hz, 1H), 2.53 (dd, *J* = 13.9, 9.3 Hz, 1H), 2.38 – 2.26 (m, 2H), 2.16 – 2.04 (m, 2H), 1.95 (d, *J* = 6.5 Hz, 1H), 1.79 – 1.67 (m, 1H), 1.57 (dd, *J* = 15.5, 7.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 220.5, 158.2, 132.1, 130.0, 114.0, 55.4, 51.3, 38.4, 34.8, 29.2, 20.7. **IR** (ATR): 2957, 1734, 1610, 1510, 1243, 1177 cm^{-1}. **HRMS** calculated for $C_{13}H_{16}O_2Na$ $[M+Na]^+$ 227.1048, found 227.1042. **Chiral SFC**: 100 mm CHIRALPAK AD-H, 1% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (major) = 6.4 min, t_{R2} (minor) = 7.8 min.

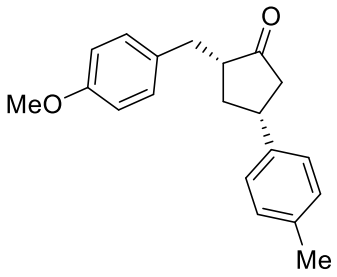


Method B: In a N_2-filled glovebox, $[Rh(COD)Cl]_2$ (2.0 mg, 0.0040 mmol, 4 mol%), (*R*,S_P)-JoSPOphos (4.4 mg, 0.0080 mmol, 8 mol%), and toluene (0.50 mL, 0.20 M) were added to a 1 dram vial equipped with a magnetic stir bar. The solution was stirred at 30 °C for 10 min. $AgSbF_6$ (3.4 mg, 0.010 mmol, 10 mol%), was added, and the resulting mixture was stirred at 30 °C for 30 min. Aldehyde **3** (0.10 mmol, 1.0 equiv) and 1-$AdNH_2$ (1.5 mg, 0.010 mmol, 10 mol%) were added. The vial was then sealed with a Teflon-lined screw cap and stirred at 60 °C for 24 h. The reaction mixture was cooled to rt, filtered through celite, and concentrated *in vacuo*. The diastereoselectivity was determined by ^{1}H NMR analysis of the unpurified reaction mixture. The ketone **4** was purified using preparative thin-layer chromatography.

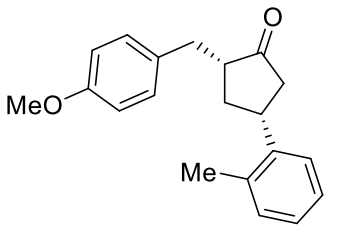


(2*R*,4*R*)-2-(4-methoxybenzyl)-4-phenylcyclopentan-1-one (4a): The title compound was synthesized according to Method B and isolated by preparatory TLC (5% EtOAc in hexanes) as a white solid (21.3 mg, 76% yield, >20:1 *dr*, >99% *ee*, $[\alpha]^{24}_D$ = +60.3 (*c* 1.0, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.18 (m, 3H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 3.35 – 3.23 (m, 1H), 3.19 (dd, *J* = 13.1, 3.2 Hz, 1H), 2.79 (dd, *J* = 19.0, 7.1 Hz,

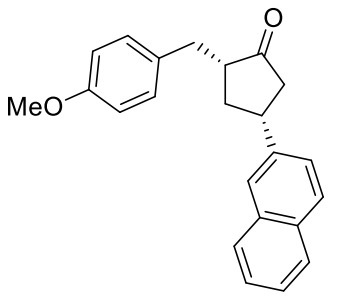
1H), 2.67 – 2.51 (m, 2H), 2.46 (ddd, *J* = 12.9, 7.7, 2.2 Hz, 1H), 2.30 (dd, *J* = 18.5, 12.2 Hz, 1H), 1.69 (q, *J* = 12.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 218.2, 158.3, 143.0, 131.9, 130.0, 128.8, 126.84, 126.83, 114.1, 55.4, 53.0, 45.9, 40.1, 37.7, 34.8. **IR** (ATR): 2921, 1724, 1608, 1510, 1441, 1242, 1028, 811, 758, 699 cm^{-1}. **HRMS** calculated for $C_{19}H_{20}O_2Na$ $[M+Na]^+$ 303.1361, found 303.1375. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 8% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} = 7.6 min, t_{R2} = 9.2 min, t_{R3} (major) = 10.7 min, t_{R4} (minor) = 12.0 min.



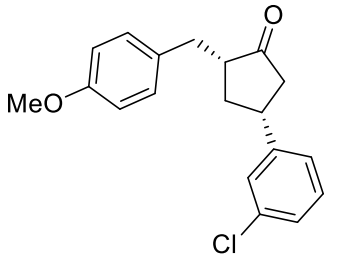
(2*R*,4*R*)-2-(4-methoxybenzyl)-4-(p-tolyl)cyclopentan-1-one (4b): The title compound was synthesized according to Method B and isolated by preparatory TLC (5% EtOAc in hexanes) as a white solid (26.5 mg, 90% yield, >20:1 *dr*, 95% *ee*, $[\alpha]^{24}_D$ = +67.8 (*c* 1.6, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 (dd, *J* = 15.5, 8.3 Hz, 6H), 6.84 (d, *J* = 8.5 Hz, 2H), 3.80 (s, 3H), 3.27 (dt, *J* = 11.9, 6.3 Hz, 1H), 3.18 (dt, *J* = 11.2, 5.7 Hz, 1H), 2.77 (dd, *J* = 18.5, 7.5 Hz, 1H), 2.67 – 2.51 (m, 2H), 2.44 (dt, *J* = 11.9, 3.8 Hz, 1H), 2.34 (s, 3H), 2.28 (dd, *J* = 18.5, 12.2 Hz, 1H), 1.66 (q, *J* = 12.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 218.3, 158.2, 140.0, 136.4, 131.9, 130.0, 129.4, 126.7, 114.0, 55.4, 53.0, 46.0, 39.7, 37.8, 34.8, 21.1. **IR** (ATR): 2923, 1721, 1608, 1510, 1440, 1242, 1170, 1031, 828, 811 cm^{-1}. **HRMS** calculated for $C_{20}H_{22}O_2Na$ $[M+Na]^+$ 317.1518, found 317.1511. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 5% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} = 6.9 min, t_{R2} = 9.5 min, t_{R3} (major) = 10.7 min, t_{R4} (minor) = 12.2 min.



(2*R*,4*R*)-2-(4-methoxybenzyl)-4-(*o*-tolyl)cyclopentan-1-one (4c): The title compound was synthesized according to Method B and isolated by preparatory TLC (5% EtOAc in hexanes) as a colorless oil (22.5 mg, 80% yield, >20:1 *dr*, >99% *ee*, $[\alpha]^{24}_D$ = +44.3 (*c* 1.4, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 7.14 (m, 4H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 3.80 (s, 3H), 3.54 – 3.40 (m, 1H), 3.21 (dd, *J* = 13.3, 3.3 Hz, 1H), 2.75 (dd, *J* = 18.5, 7.3 Hz, 1H), 2.68 – 2.53 (m, 2H), 2.41 – 2.31 (m, 4H), 2.26 (dd, *J* = 18.5, 12.2 Hz, 1H), 1.72 (q, *J* = 12.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 218.3, 158.2, 140.8, 136.1, 131.9, 130.7, 130.0, 126.58, 126.56, 124.9, 114.0, 55.4, 52.9, 45.6, 36.7, 36.3, 34.9, 19.8. **IR** (ATR): 2931, 1736, 1611, 1511, 1441, 1243, 1176, 1033, 835, 755 cm^{-1}. **HRMS** calculated for $C_{20}H_{22}O_2Na$ $[M+Na]^+$ 317.1518, found 317.1514. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 5% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} = 6.3 min, t_{R2} = 6.6 min, t_{R3} (major) = 8.3 min, t_{R4} (minor) = 12.5 min.

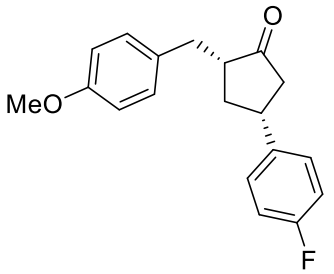


(2*R*,4*R*)-2-(4-methoxybenzyl)-4-(naphthalen-2-yl)cyclopentan-1-one (4d): The title compound was synthesized according to Method B and isolated by preparatory TLC (5% EtOAc in hexanes) as a colorless oil (29.1 mg, 88% yield, >20:1 *dr*, 96% *ee*, $[\alpha]^{24}_D$ = +65.0 (*c* 1.8, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (t, *J* = 7.9 Hz, 3H), 7.64 (s, 1H), 7.52 – 7.42 (m, 2H), 7.34 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 3.80 (s, 3H), 3.54 – 3.37 (m, 1H), 3.29 – 3.14 (m, 1H), 2.87 (dd, *J* = 18.9, 7.2 Hz, 1H), 2.72 – 2.59 (m, 2H), 2.59 – 2.48 (m, 1H), 2.41 (dd, *J* = 18.5, 12.2 Hz, 1H), 1.79 (q, *J* = 11.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 218.1, 158.3, 140.4, 133.6, 132.5, 131.9, 130.0, 128.5, 127.8, 127.7, 126.4, 125.8, 125.4, 125.0, 114.1, 55.4, 53.0, 45.9, 40.2, 37.6, 34.8. **IR** (ATR): 2930, 1736, 1610, 1511, 1300, 1243, 1177, 1033, 853, 817 cm^{-1}. **HRMS** calculated for $C_{23}H_{22}O_2Na$ $[M+Na]^+$ 353.1518, found 353.1534. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 7% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} = 29.5 min, t_{R2} = 49.4 min, t_{R3} (major) = 56.5 min, t_{R4} (minor) = 64.8 min.

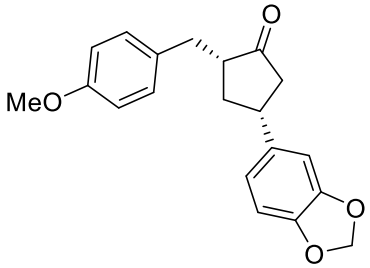


(2*R*,4*R*)-4-(3-chlorophenyl)-2-(4-methoxybenzyl)cyclopentan-1-one (4e): The title compound was synthesized according to Method B and isolated by preparatory TLC (5% EtOAc in hexanes) as a colorless oil (23.9 mg, 77% yield, >20:1 *dr*, 94% *ee*, $[\alpha]^{24}_D$ = +93.7 (*c* 1.4, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.17 (m, 3H), 7.09 (t, *J* = 7.8 Hz, 3H), 6.84 (d, *J* = 8.5 Hz, 2H), 3.79 (s, 3H), 3.32 – 3.14 (m, 2H), 2.78 (dd, *J* = 18.5, 7.4 Hz, 1H), 2.58 (ddt, *J* = 12.4, 9.0, 6.3 Hz, 2H), 2.49 – 2.39 (m, 1H), 2.25 (dd, *J* = 18.5, 12.2 Hz, 1H), 1.65 (q, *J* = 12.0 Hz, 1H). **^{13}C NMR** (101 MHz,

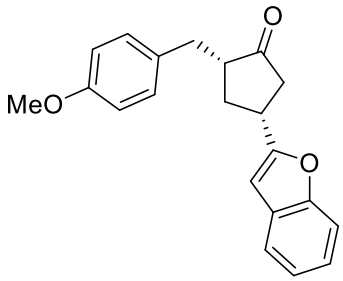
$CDCl_3$) δ 217.3, 158.3, 145.1, 134.6, 131.7, 130.02, 129.96, 127.1, 127.0, 125.1, 114.1, 55.4, 52.8, 45.7, 39.8, 37.4, 34.7. **IR** (ATR): 2931, 1737, 1597, 1511, 1243, 1176, 1033, 832, 784, 692 cm^{-1}. **HRMS** calculated for $C_{19}H_{19}ClO_2Na$ $[M+Na]^+$ 337.0971, found 337.0977. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 7% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} = 5.2 min, t_{R2} = 6.0 min, t_{R3} (major) = 6.3 min, t_{R4} (minor) = 7.3 min.



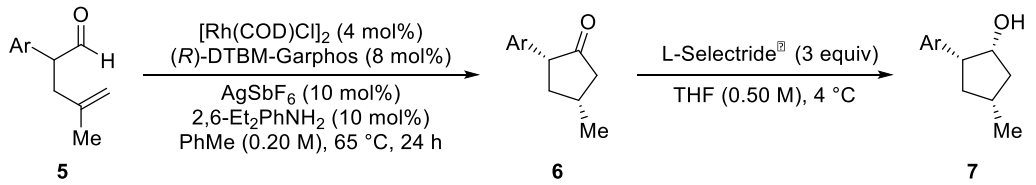
(2*R*,4*R*)-4-(4-fluorophenyl)-2-(4-methoxybenzyl)cyclopentan-1-one (4f): The title compound was synthesized according to Method B and isolated by preparatory TLC (5% EtOAc in hexanes) as a colorless oil (27.2 mg, 91% yield, >20:1 *dr*, >99% *ee*, $[\alpha]^{24}_D$ = +86.7 (*c* 1.6, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 8.4, 5.4 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 7.00 (t, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 3.79 (s, 3H), 3.27 (ddd, *J* = 18.9, 12.5, 6.6 Hz, 1H), 3.21 – 3.11 (m, 1H), 2.78 (dd, *J* = 18.7, 7.5 Hz, 1H), 2.67 – 2.50 (m, 2H), 2.43 (dt, *J* = 10.7, 5.4 Hz, 1H), 2.24 (dd, *J* = 18.5, 12.2 Hz, 1H), 1.69 – 1.57 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 217.8, 161.7 (d, *J* = 244.9 Hz), 158.3, 138.64 (d, *J* = 3.1 Hz), 131.7, 130.0, 128.3 (d, *J* = 7.8 Hz), 115.5 (d, *J* = 21.2 Hz), 114.1, 55.4, 52.9, 46.1, 39.4, 37.7, 34.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.5. **IR** (ATR): 2919, 1737, 1609, 1510, 1243, 1221, 1177, 1149, 1033, 865 cm^{-1}. **HRMS** calculated for $C_{19}H_{19}FO_2Na$ $[M+Na]^+$ 321.1267, found 321.1258. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 2% *i*-PrOH, 2.5 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} = 10.2 min, t_{R2} = 11.3 min, t_{R3} (major) = 12.6 min, t_{R4} (minor) = 15.9 min.



(2*R*,4*R*)-4-(benzo[*d*][1,3]dioxol-5-yl)-2-(4-methoxybenzyl)cyclopentan-1-one (4g): The title compound was synthesized according to Method B and isolated by preparatory TLC (10% EtOAc in hexanes) as a yellow solid (27.0 mg, 83% yield, >20:1 *dr*, 96% *ee*, $[\alpha]^{24}_D$ = +94.7 (*c* 1.5, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.75 (d, *J* = 7.9 Hz, 1H), 6.71 – 6.62 (m, 2H), 5.93 (s, 2H), 3.79 (s, 3H), 3.20 (ddd, *J* = 16.7, 12.8, 5.0 Hz, 2H), 2.74 (dd, *J* = 18.4, 7.6 Hz, 1H), 2.65 – 2.47 (m, 2H), 2.45 – 2.34 (m, 1H), 2.21 (dd, *J* = 18.5, 12.2 Hz, 1H), 1.62 (q, *J* = 12.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 218.0, 158.2, 148.0, 146.4, 136.9, 131.8, 130.0, 119.8, 114.0, 108.4, 107.2, 101.1, 55.4, 52.9, 46.2, 39.8, 37.8, 34.7. **IR** (ATR): 2925, 1717, 1511, 1439, 1239, 1177, 1030, 935, 836, 806 cm^{-1}. **HRMS** calculated for $C_{20}H_{20}O_4Na$ $[M+Na]^+$ 347.1259, found 347.1270. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 5% *i*-PrOH, 2.5 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (major) = 8.6 min, t_{R2} (minor) = 10.4 min.

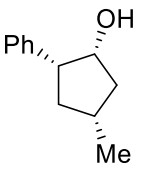


(2*R*,4*R*)-4-(benzofuran-2-yl)-2-(4-methoxybenzyl)cyclopentan-1-one (4h): The title compound was synthesized according to Method B and isolated by preparatory TLC (5% EtOAc in hexanes) as a yellow solid (17.1 mg, 53% yield, >20:1 *dr*, 74% *ee*, $[\alpha]^{24}_D$ = +134.6 (*c* 0.97, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 1H), 7.44 – 7.39 (m, 1H), 7.27 – 7.16 (m, 2H), 7.13 – 7.07 (m, 2H), 6.87 – 6.80 (m, 2H), 6.43 (s, 1H), 3.80 (s, 3H), 3.54 – 3.40 (m, 1H), 3.26 – 3.15 (m, 1H), 2.83 (dd, *J* = 18.6, 7.9 Hz, 1H), 2.64 – 2.42 (m, 4H), 1.91 – 1.79 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 216.9, 159.4, 158.3, 154.9, 131.6, 130.0, 128.5, 123.9, 122.9, 120.7, 114.1, 111.0, 101.7, 55.4, 52.3, 43.4, 34.9, 34.8, 34.1. **IR** (ATR): 2930, 1724, 1608, 1510, 1453, 1245, 1176, 1031, 805, 738 cm^{-1}. **HRMS** calculated for $C_{21}H_{20}O_3Na$ $[M+Na]^+$ 343.1310, found 343.1303. **Chiral SFC**: 100 mm CHIRALCEL OJ-H, 10% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 15.3 min, t_{R2} (major) = 22.9 min.

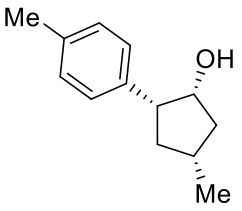


5 **6** **7**

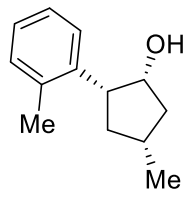
Method C: In a N_2-filled glovebox, $[Rh(COD)Cl]_2$ (2.0 mg, 0.0040 mmol, 4 mol%), (*R*)-DTBM-Segphos (10.7 mg, 0.0080 mmol, 8 mol%), and toluene (0.50 mL, 0.20 M) were added to a 1 dram vial equipped with a magnetic stir bar. The solution was stirred at 30 °C for 10 min. $AgSbF_6$ (3.4 mg, 0.010 mmol, 10 mol%), was added, and the resulting mixture was stirred at 30 °C for 30 min. Aldehyde **5** (0.10 mmol, 1.0 equiv) and 2,6-Et_2PhNH_2 (1.6 mL, 0.010 mmol, 10 mol%) were added. The vial was then sealed with a Teflon-lined screw cap and stirred at 65 °C for 24 h. The reaction mixture was cooled to rt, filtered through celite, and concentrated *in vacuo*. The hydroacylation yield and diastereoselectivity were determined by ^{1}H NMR analysis of the unpurified reaction mixture using triphenylmethane as an internal standard. The crude ketone **6** was dissolved in THF (0.50 M) and cooled to 4 °C. L-Selectride® (3 equiv, 1.0 M in THF) was added dropwise, and the resulting mixture was allowed to stirred at 4 °C for 16 h. The reaction mixture was quenched with 2 M aqueous NaOH and 30% aqueous H_2O_2, and the resulting mixture was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The alcohol **7** was purified using preparative thin-layer chromatography.



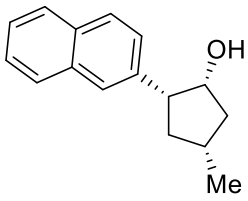
(1*R*,2*R*,4*R*)-4-methyl-2-phenylcyclopentan-1-ol (7a): The title compound was synthesized according to Method C and isolated by preparatory TLC (5% EtOAc in hexanes) as a colorless oil (12.7 mg, 76% yield over 2 steps, >20:1:1:1 *dr*, >99% *ee*, $[\alpha]^{24}_D$ = –25.1 (*c* 0.60, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.32 – 7.28 (m, 2H), 7.28 – 7.23 (m, 1H), 4.30 (dd, *J* = 7.5, 3.2 Hz, 1H), 3.16 – 3.02 (m, 1H), 2.43 – 2.26 (m, 1H), 2.21 – 2.09 (m, 1H), 2.05 (dt, *J* = 18.1, 6.3 Hz, 1H), 1.87 – 1.72 (m, 1H), 1.41 (ddd, *J* = 14.2, 7.2, 2.1 Hz, 1H), 1.19 (d, *J* = 6.6 Hz, 3H), 1.10 (d, *J* = 5.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.9, 128.8, 128.7, 126.8, 75.8, 52.7, 42.7, 36.9, 32.3, 21.8. **IR** (ATR): 3426, 2952, 2868, 1683, 1449, 1215, 1030, 1004, 754, 698 cm^{-1}. **HRMS** calculated for $C_{12}H_{16}ONa$ $[M+Na]^+$ 199.1099, found 199.1092. **Chiral SFC**: 250 mm CHIRALPAK AD, 5% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} = 6.2 min (minor), t_{R2} = 6.7 min, t_{R3} (major) = 7.5 min, t_{R4} = 9.2 min.



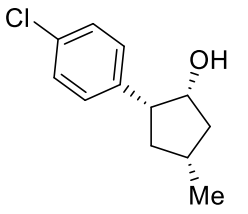
(1*R*,2*R*,4*R*)-4-methyl-2-(*p*-tolyl)cyclopentan-1-ol (7b): The title compound was synthesized according to Method C and isolated by preparatory TLC (5% EtOAc in hexanes) as a colorless oil (12.5 mg, 65% yield over 2 steps, >20:1:1:1 *dr*, >99% *ee*, $[\alpha]^{24}_D$ = –22.0 (*c* 0.68, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 4.28 (t, *J* = 4.5 Hz, 1H), 3.12 – 3.01 (m, 1H), 2.39 – 2.30 (m, 4H), 2.19 – 2.06 (m, 1H), 2.02 (dt, *J* = 12.5, 6.3 Hz, 1H), 1.78 (dd, *J* = 23.2, 12.0 Hz, 1H), 1.40 (ddd, *J* = 14.2, 7.3, 1.9 Hz, 1H), 1.18 (d, *J* = 6.6 Hz, 3H), 1.12 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.7, 136.4, 129.4, 128.6, 75.8, 52.3, 42.6, 37.0, 32.3, 21.8, 21.1. **IR** (ATR): 3449, 2951, 2926, 2868, 1515, 1455, 1129, 1103, 1002, 815 cm^{-1}. **HRMS** calculated for $C_{13}H_{18}ONa$ $[M+Na]^+$ 213.1255, found 213.1255. **Chiral SFC**: 100 mm CHIRALPAK AD-H, 3% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} = 4.5 min (minor), t_{R2} (major) = 7.5 min.



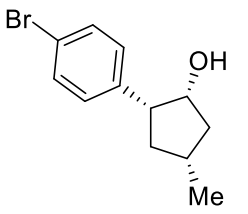
(1*R*,2*R*,4*R*)-4-methyl-2-(*o*-tolyl)cyclopentan-1-ol (7c): The title compound was synthesized according to Method C and isolated by preparatory TLC (5% EtOAc in hexanes) as a colorless oil (9.3 mg, 48% yield over 2 steps, >20:1:1:1 *dr*, 95% *ee*, $[\alpha]^{24}_D$ = –33.0 (*c* 0.53, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.2 Hz, 1H), 7.25 – 7.13 (m, 3H), 4.37 – 4.31 (m, 1H), 3.31 – 3.17 (m, 1H), 2.44 – 2.31 (m, 4H), 2.08 (dt, *J* = 16.9, 8.6 Hz, 1H), 1.91 (dd, *J* = 13.6, 5.6 Hz, 2H), 1.39 (ddd, *J* = 14.2, 7.9, 2.2 Hz, 1H), 1.20 (d, *J* = 6.6 Hz, 3H), 1.04 – 0.88 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.3, 136.8, 130.6, 128.2, 126.8, 126.1, 73.2, 49.1, 43.0, 37.1, 32.2, 21.4, 19.9. **IR** (ATR): 3439, 2951, 2927, 2868, 1489, 1457, 1130, 1004, 755, 726 cm^{-1}. **HRMS** calculated for $C_{13}H_{18}ONa$ $[M+Na]^+$ 213.1255, found 213.1255. **Chiral SFC**: 100 mm CHIRALPAK AD-H, 2% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} = 5.4 min (minor), t_{R2} (major) = 6.5 min.



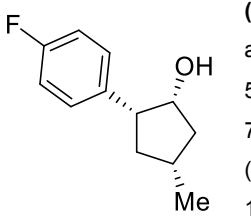
(1*R*,2*R*,4*R*)-4-methyl-2-(naphthalen-2-yl)cyclopentan-1-ol (7d): The title compound was synthesized according to Method C and isolated by preparatory TLC (5% EtOAc in hexanes) as a yellow solid (11.5 mg, 51% yield over 2 steps, >20:1:1:1 *dr*, 97% *ee*, $[\alpha]^{24}_{D}$ = –29.7 (*c* 0.75, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 3H), 7.75 (s, 1H), 7.47 (ddd, *J* = 16.9, 11.6, 6.6 Hz, 3H), 4.41 (t, *J* = 4.6 Hz, 1H), 3.32 – 3.21 (m, 1H), 2.47 – 2.34 (m, 1H), 2.26 – 2.07 (m, 2H), 1.95 (dd, *J* = 22.9, 11.6 Hz, 1H), 1.46 (ddd, *J* = 14.3, 7.0, 1.9 Hz, 1H), 1.24 (d, *J* = 6.4 Hz, 3H), 1.14 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.4, 133.7, 132.6, 128.2, 127.8, 127.7, 127.4, 127.1, 126.3, 125.7, 75.8, 52.8, 42.8, 36.9, 32.4, 21.8. **IR** (ATR): 3466, 2950, 2925, 2865, 1507, 1454, 1190, 1129, 1002, 829, 745 cm^{-1}. **HRMS** calculated for $C_{16}H_{18}ONa$ $[M+Na]^+$ 249.1255, found 249.1255. **Chiral SFC**: 100 mm CHIRALPAK AD-H, 3% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} = 18.4 min (minor), t_{R2} (major) = 20.7 min.



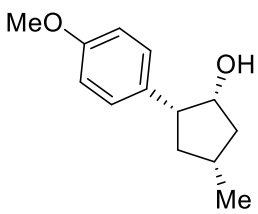
(1*R*,2*R*,4*R*)-2-(4-chlorophenyl)-4-methylcyclopentan-1-ol (7e): The title compound was synthesized according to Method C and isolated by preparatory TLC (5% EtOAc in hexanes) as a colorless oil (12.7 mg, 57% yield over 2 steps, >20:1:1:1 *dr*, 99% *ee*, $[\alpha]^{24}_{D}$ = –40.9 (*c* 0.30, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 4.32 – 4.25 (m, 1H), 3.09 – 2.98 (m, 1H), 2.42 – 2.29 (m, 1H), 2.12 (dtd, *J* = 13.6, 10.3, 6.8 Hz, 1H), 2.02 (dt, *J* = 12.5, 6.2 Hz, 1H), 1.75 (dd, *J* = 23.2, 11.9 Hz, 1H), 1.39 (ddd, *J* = 14.3, 7.2, 2.1 Hz, 1H), 1.18 (d, *J* = 6.6 Hz, 3H), 1.05 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.5, 132.6, 130.1, 128.7, 75.7, 52.0, 42.9, 37.1, 32.3, 21.7. **IR** (ATR): 3437, 2952, 2927, 2868, 1492, 1129, 1090, 1002, 831, 721 cm^{-1}. **HRMS** calculated for $C_{12}H_{15}ClO$ $[M]^+$ 210.0811, found 210.0817. **Chiral SFC**: 250 mm CHIRALPAK AD, 5% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} = 9.6 min (minor), t_{R2} = 10.4 min, t_{R3} (major) = 11.5 min, t_{R4} = 12.0 min.



(1*R*,2*R*,4*R*)-2-(4-bromophenyl)-4-methylcyclopentan-1-ol (7f): The title compound was synthesized according to Method C and isolated by preparatory TLC (5% EtOAc in hexanes) as a colorless oil (14.2 mg, 57% yield over 2 steps, >20:1:1:1 *dr*, 98% *ee*, $[\alpha]^{24}_{D}$ = –27.7 (*c* 0.33, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.14 (m, 2H), 4.29 (t, *J* = 4.5 Hz, 1H), 3.08 – 2.96 (m, 1H), 2.42 – 2.29 (m, 1H), 2.19 – 2.06 (m, 1H), 2.06 – 1.96 (m, 1H), 1.81 – 1.67 (m, 1H), 1.39 (ddd, *J* = 14.3, 7.2, 2.1 Hz, 1H), 1.18 (d, *J* = 6.6 Hz, 3H), 1.03 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.0, 131.7, 130.5, 120.6, 75.7, 52.1, 42.9, 37.1, 32.3, 21.7. **IR** (ATR): 3440, 2951, 2926, 2868, 1489, 1129, 1072, 1009, 818, 795 cm^{-1}. **HRMS** calculated for $C_{12}H_{15}BrO$ $[M]^+$ 254.0306, found 254.0297. **Chiral SFC**: 250 mm CHIRALPAK AD, 5% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} = 12.9 min (minor), t_{R2} (major) = 16.1 min.

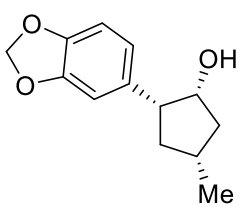


(1*R*,2*R*,4*R*)-2-(4-fluorophenyl)-4-methylcyclopentan-1-ol (7g): The title compound was synthesized according to Method C and isolated by preparatory TLC (5% EtOAc in hexanes) as a colorless oil (11.5 mg, 56% yield over 2 steps, >20:1:1:1 *dr*, >99% *ee*, $[\alpha]^{24}_{D}$ = –18.3 (*c* 0.26, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 7.0, 3.8 Hz, 2H), 7.07 – 6.99 (m, 2H), 4.28 (t, *J* = 4.5 Hz, 1H), 3.12 – 2.98 (m, 1H), 2.40 – 2.28 (m, 1H), 2.12 (dtd, *J* = 13.3, 10.0, 6.8 Hz, 1H), 2.02 (dt, *J* = 12.4, 6.3 Hz, 1H), 1.75 (dd, *J* = 22.9, 12.2 Hz, 1H), 1.39 (ddd, *J* = 14.4, 7.2, 2.1 Hz, 1H), 1.18 (d, *J* = 6.6 Hz, 3H), 1.05 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.9 (d, *J* = 244.7 Hz), 135.5 (d, *J* = 3.2 Hz), 130.1 (d, *J* = 7.8 Hz), 115.4 (d, *J* = 21.0 Hz), 75.7, 51.9, 42.8, 37.3, 32.3, 21.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.8. **IR** (ATR): 3469, 2955, 2929, 2871, 1598, 1509, 1222, 1157, 1004, 832 cm^{-1}. **HRMS** calculated for $C_{12}H_{15}FO$ $[M]^+$ 194.1107, found 194.1110. **Chiral SFC**: 100 mm CHIRALPAK AD-H, 2% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} = 4.6 min (minor), t_{R2} (major) = 5.8 min.

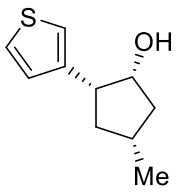


(1*R*,2*R*,4*R*)-2-(4-methoxyphenyl)-4-methylcyclopentan-1-ol (7h): The title compound was synthesized according to Method C and isolated by preparatory TLC (10% EtOAc in hexanes) as a colorless oil (10.4 mg, 50% yield over 2 steps, >20:1:1:1 *dr*, 99% *ee*, $[\alpha]^{24}_{D}$ = –39.1 (*c* 0.51, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 2H), 6.93 – 6.85 (m, 2H), 4.28 – 4.21 (m, 1H), 3.81 (s, 3H), 3.10 – 2.98 (m, 1H), 2.39 – 2.28 (m, 1H), 2.11 (ddt, *J* = 10.2, 9.5, 6.7 Hz, 1H), 2.01 (dt, *J* = 12.4, 6.4 Hz, 1H), 1.81 – 1.68 (m,

1H), 1.39 (ddd, *J* = 14.2, 7.3, 2.1 Hz, 1H), 1.18 (d, *J* = 6.6 Hz, 3H), 1.12 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 131.7, 129.7, 114.1, 75.8, 55.4, 51.8, 42.6, 37.2, 32.3, 21.8. **IR** (ATR): 3450, 2951, 2868, 1611, 1512, 1245, 1178, 1033, 1002, 830 cm^{-1}. **HRMS** calculated for $C_{13}H_{18}O_2Na$ $[M+Na]^+$ 229.1205, found 229.1204. **Chiral SFC**: 250 mm CHIRALPAK AD, 5% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} = 10.2 min (minor), t_{R2} = 11.3 min, t_{R3} (major) = 12.4 min, t_{R4} = 14.2 min.



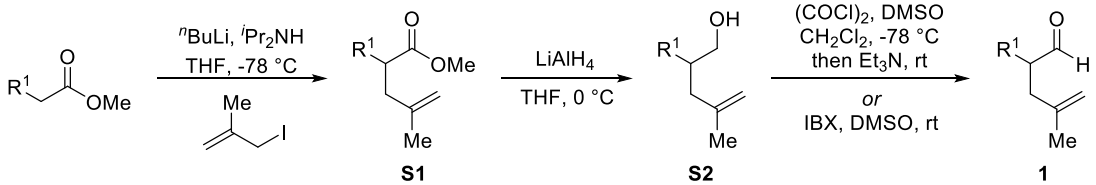
(1*R*,2*R*,4*R*)-2-(benzo[*d*][1,3]dioxol-5-yl)-4-methylcyclopentan-1-ol (7i): The title compound was synthesized according to Method C and isolated by preparatory TLC (10% EtOAc in hexanes) as a colorless oil (11.3 mg, 51% yield over 2 steps, >20:1:1:1 *dr*, 99% *ee*, $[\alpha]^{24}_D$ = –40.9 (*c* 0.58, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.82 – 6.76 (m, 2H), 6.74 (ddd, *J* = 8.0, 1.6, 0.6 Hz, 1H), 5.95 (s, 2H), 4.28 – 4.16 (m, 1H), 3.07 – 2.94 (m, 1H), 2.38 – 2.24 (m, 1H), 2.16 – 2.03 (m, 1H), 1.99 (dt, *J* = 12.4, 6.4 Hz, 1H), 1.77 – 1.64 (m, 1H), 1.38 (ddd, *J* = 14.2, 7.2, 2.0 Hz, 1H), 1.17 (d, *J* = 6.6 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.0, 146.4, 133.6, 121.5, 109.2, 108.4, 101.1, 75.8, 52.3, 42.6, 37.2, 32.2, 21.8. **IR** (ATR): 3557, 2951, 2868, 1503, 1489, 1440, 1250, 1229, 1037, 932 cm^{-1}. **HRMS** calculated for $C_{13}H_{16}O_3Na$ $[M+Na]^+$ 243.0997, found 243.1000. **Chiral SFC**: 250 mm CHIRALPAK AD, 10% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} = 7.0 min (minor), t_{R2} = 7.9 min, t_{R3} (major) = 11.6 min, t_{R4} = 14.4 min.

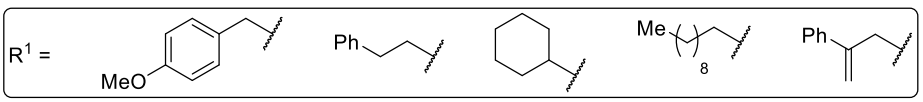


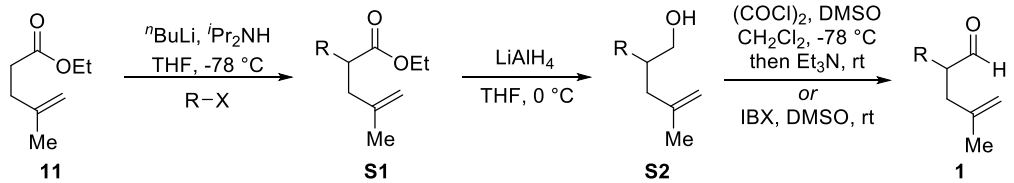
(1*R*,2*R*,4*R*)-4-methyl-2-(thiophen-3-yl)cyclopentan-1-ol (7j): The title compound was synthesized according to Method B and isolated by preparatory TLC (5% EtOAc in hexanes) as a colorless oil (9.3 mg, 51% yield, >20:1:1:1 *dr*, >99% *ee*, $[\alpha]^{24}_D$ = –26.1 (*c* 0.52, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.12 – 7.07 (m, 1H), 7.04 (d, *J* = 4.9 Hz, 1H), 4.27 (t, *J* = 4.4 Hz, 1H), 3.21 – 3.07 (m, 1H), 2.37 – 2.22 (m, 1H), 2.19 – 2.01 (m, 2H), 1.79 – 1.65 (m, 1H), 1.40 (ddd, *J* = 14.3, 6.5, 2.0 Hz, 1H), 1.19 (s, 1H), 1.17 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.1, 128.2, 126.0, 121.7, 75.3, 48.5, 42.5, 38.0, 32.2, 21.9. **IR** (ATR): 3440, 2951, 2926, 2867, 1455, 1128, 1002, 833, 778, 683 cm^{-1}. **HRMS** calculated for $C_{10}H_{14}OSNa$ $[M+Na]^+$ 205.0663, found 205.0658. **Chiral SFC**: 250 mm CHIRALPAK AD, 2% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} = 14.0 min (minor), t_{R2} (major) = 18.9 min.

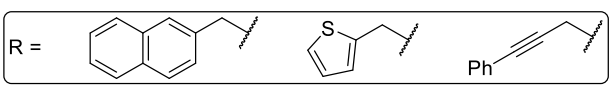
3. Preparation of Substrates

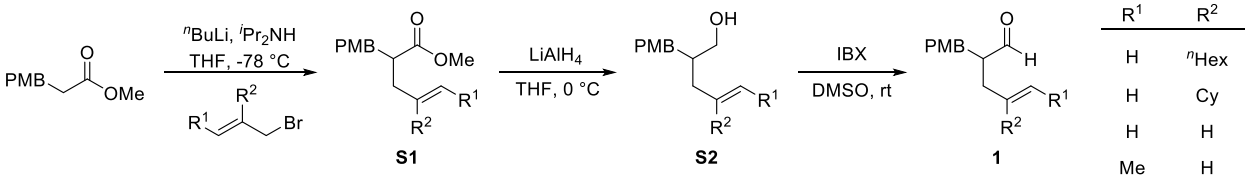
Preparation of Aldehydes 1











Preparation of methallyl iodide

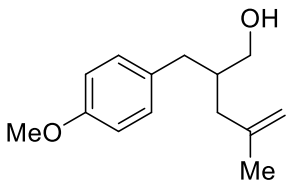
To a round bottom flask was added NaI (1.5 equiv) and acetone (1 M). Then, methallyl chloride (1.0 equiv) was added dropwise, and the resulting mixture was allowed to stir at rt for 3 h. The reaction was quenched with H_2O and extracted with pentanes. The combined organic layers were washed with 10% aqueous $Na_2S_2O_3$, dried with anhydrous $MgSO_4$, and concentrated *in vacuo* below rt. The crude methallyl iodide was used without further purification.

General Procedure for the Ester Alkylation

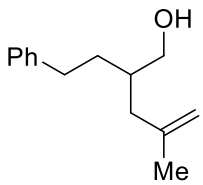
To an oven-dried round bottom flask was added ^{i}Pr$_2$NH (1.2 equiv) and THF (0.5 M), and the resulting solution was cooled to -78 °C. Then, ^{n}BuLi (1.1 equiv, 2.5 M in THF) was added dropwise, and the resulting mixture was stirred for 45 min. A solution of the ester (1 equiv) in THF (0.5 M) was added dropwise, and the resulting mixture was stirred for 1 h. The appropriate alkyl halide (1.2 equiv) was added, and the reaction mixture was stirred until full consumption of the ester was observed by GC-MS. The reaction was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and concentrated *in vacuo*. The alkylated ester was used without further purification.

General Procedure for the Reduction with LiAlH$_4$

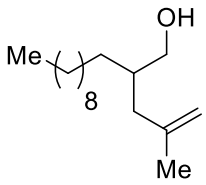
The crude alkylated ester was dissolved in THF (0.50 M), and the resulting solution was cooled to 0 °C. $LiAlH_4$ (1.5 equiv) was added portionwise, and the resulting mixture was allowed to stir for 30 min. The reaction was quenched using the Fieser method, filtered through celite, and concentrated *in vacuo*. The residue was purified by column chromatography to afford the pure alcohol **S2**.



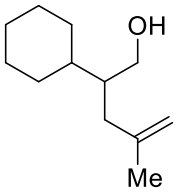
2-(4-methoxybenzyl)-4-methylpent-4-en-1-ol (S2a): The title compound was prepared using the general procedures for ester alkylation and ester reduction starting from methyl 3-(4-methoxyphenyl)propanoate (3.9 g, 20 mmol, 1 equiv), ^{i}Pr$_2$NH (3.4 mL, 24 mmol, 1.2 equiv), ^{n}BuLi (8.8 mL, 22 mmol, 1.1 equiv, 2.5 M in THF), methallyl iodide (4.4 g, 24 mmol, 1.2 equiv), and THF (80 mL, 0.25 M). Crude **S1a** (1 equiv) was reduced to **S2a** using $LiAlH_4$ (1.1 g, 30 mmol, 1.5 equiv) and THF (40 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S2a** as a colorless oil (2.27 g, 51% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 4.81 (s, 1H), 4.78 (s, 1H), 3.80 (s, 3H), 3.58 – 3.47 (m, 2H), 2.58 (d, *J* = 6.8 Hz, 2H), 2.13 (dd, *J* = 13.3, 7.9 Hz, 1H), 2.02 (dt, *J* = 12.6, 5.7 Hz, 2H), 1.74 (s, 3H), 1.43 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 144.7, 132.7, 130.2, 113.9, 112.3, 65.2, 55.4, 40.6, 40.4, 36.9, 22.4. **IR** (ATR): 3368, 2923, 2853, 1511, 1244, 887 cm^{-1}. **HRMS** calculated for $C_{14}H_{20}O_2Na$ $[M+Na]^+$ 243.1361, found 243.1360.



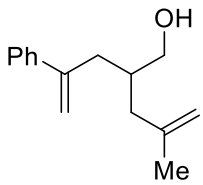
4-methyl-2-phenethylpent-4-en-1-ol (S2c): The title compound was prepared using the general procedures for ester alkylation and ester reduction starting from methyl 4-phenylbutanoate (2.0 g, 11.2 mmol, 1 equiv), ^{i}Pr$_2$NH (1.9 mL, 13.4 mmol, 1.2 equiv), ^{n}BuLi (4.9 mL, 12.3 mmol, 1.1 equiv, 2.5 M in THF), methallyl iodide (2.4 g, 13.4 mmol, 1.2 equiv), and THF (45 mL, 0.25 M). Crude **S1c** (1 equiv) was reduced to **S2c** using $LiAlH_4$ (637 mg, 16.8 mmol, 1.5 equiv) and THF (22 mL, 0.51 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S2c** as a colorless oil (1.30 g, 57% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.23 – 7.16 (m, 3H), 4.83 – 4.78 (m, 1H), 4.78 – 4.73 (m, 1H), 3.61 (s, 2H), 2.73 – 2.62 (m, 2H), 2.16 – 2.06 (m, 2H), 1.81 – 1.59 (m, 6H), 1.34 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.8, 142.6, 128.5, 125.9, 112.2, 65.8, 40.7, 38.0, 33.4, 33.0, 22.4. **IR** (ATR): 3335, 2920, 1648, 1453, 1029, 667 cm^{-1}. **HRMS** calculated for $C_{14}H_{20}ONa$ $[M+Na]^+$ 227.1412, found 227.1412.



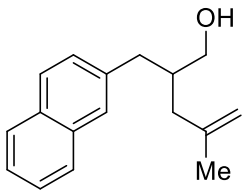
2-(2-methylallyl)dodecan-1-ol (S2e): The title compound was prepared using the general procedures for ester alkylation and ester reduction starting from methyl dodecanoate (2.1 g, 8.5 mmol, 1 equiv), $^{i}Pr_2NH$ (1.4 mL, 10.2 mmol, 1.2 equiv), ^{n}BuLi (3.7 mL, 9.4 mmol, 1.1 equiv, 2.5 M in THF), methallyl iodide (1.9 g, 10.2 mmol, 1.2 equiv), and THF (34 mL, 0.25 M). Crude **S1e** (1 equiv) was reduced to **S2e** using $LiAlH_4$ (484 mg, 12.8 mmol, 1.5 equiv) and THF (17 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S2e** as a colorless oil (1.48 g, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.78 (s, 1H), 4.74 (s, 1H), 3.55 (dd, *J* = 5.3, 2.3 Hz, 2H), 2.10 – 2.00 (m, 2H), 1.74 (s, 3H), 1.73 – 1.56 (m, 2H), 1.27 (s, 18H), 0.89 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.2, 111.9, 66.1, 40.9, 38.5, 32.1, 31.3, 30.1, 29.80, 29.77, 29.5, 27.1, 22.8, 22.4, 14.3. **IR** (ATR): 3343, 2921, 2852, 1455, 1375, 886 cm^{-1}. **HRMS** calculated for $C_{16}H_{32}O$ $[M]^+$ 240.2453, found 240.2458.



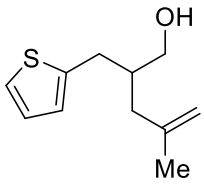
2-cyclohexyl-4-methylpent-4-en-1-ol (S2f): The title compound was prepared using the general procedures for ester alkylation and ester reduction starting from methyl 2-cyclohexylacetate (1.5 g, 9.7 mmol, 1 equiv), $^{i}Pr_2NH$ (1.6 mL, 11.7 mmol, 1.2 equiv), ^{n}BuLi (4.3 mL, 10.7 mmol, 1.1 equiv, 2.5 M in THF), methallyl iodide (2.1 g, 11.7 mmol, 1.2 equiv), and THF (39 mL, 0.25 M). Crude **S1f** (1 equiv) was reduced to **S2f** using $LiAlH_4$ (552 mg, 14.6 mmol, 1.5 equiv) and THF (19 mL, 0.51 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S2f** as a colorless oil (1.25 g, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.78 (s, 1H), 4.75 (s, 1H), 3.65 – 3.53 (m, 2H), 2.07 (ddd, *J* = 23.0, 13.8, 7.4 Hz, 2H), 1.74 (s, 4H), 1.67 (d, *J* = 10.3 Hz, 3H), 1.61 – 1.55 (m, 1H), 1.45 (d, *J* = 11.8 Hz, 2H), 1.32 – 1.16 (m, 3H), 1.08 (dt, *J* = 24.3, 12.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.8, 111.9, 64.1, 43.8, 39.0, 37.9, 30.2, 30.1, 27.0, 26.91, 26.87, 22.3. **IR** (ATR): 3335, 2910, 2850, 1647, 1447, 1069 cm^{-1}. **HRMS** calculated for $C_{12}H_{22}OH$ $[M+H]^+$ 183.1749, found 183.1753.



4-methyl-2-(2-phenylallyl)pent-4-en-1-ol (S2g): The title compound was prepared using the general procedures for ester alkylation and ester reduction starting from methyl 4-phenylpent-4-enoate[1] (1.6 g, 8.3 mmol, 1 equiv), $^{i}Pr_2NH$ (1.4 mL, 10.0 mmol, 1.2 equiv), ^{n}BuLi (3.6 mL, 9.1 mmol, 1.1 equiv, 2.5 M in THF), methallyl iodide (1.8 g, 10.0 mmol, 1.2 equiv), and THF (33 mL, 0.25 M). Crude **S1g** (1 equiv) was reduced to **S2g** using $LiAlH_4$ (472 mg, 12.5 mmol, 1.5 equiv) and THF (17 mL, 0.49 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S2g** as a yellow oil (1.23 g, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.38 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 5.32 (d, *J* = 1.7 Hz, 1H), 5.12 (m, 1H), 4.83 – 4.77 (m, 1H), 4.77 – 4.70 (m, 1H), 3.54 (d, *J* = 5.0 Hz, 2H), 2.55 (dd, *J* = 4.8, 3.5 Hz, 2H), 2.16 – 2.01 (m, 2H), 1.88 – 1.75 (m, 1H), 1.63 (dd, *J* = 1.4, 0.9 Hz, 3H), 1.45 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.5, 144.7, 141.1, 128.5, 127.6, 126.4, 114.4, 112.3, 65.6, 40.5, 37.7, 36.7, 22.3. **IR** (ATR): 3391, 2930, 1682, 1446, 1027 cm^{-1}. **HRMS** calculated for $C_{15}H_{20}O$ $[M]^+$ 216.1514, found 216.1507.

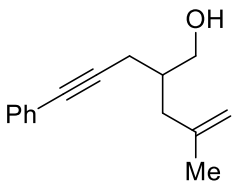


4-methyl-2-(naphthalen-2-ylmethyl)pent-4-en-1-ol (S2b): The title compound was prepared using the general procedures for ester alkylation and ester reduction starting from ethyl 4-methylpent-4-enoate[2] (**11**) (1.7 g, 12 mmol, 1 equiv), $^{i}Pr_2NH$ (2.0 mL, 14.4 mmol, 1.2 equiv), ^{n}BuLi (5.3 mL, 13.2 mmol, 1.1 equiv, 2.5 M in THF), 2-(bromomethyl)naphthalene (3.2 g, 14.4 mmol, 1.2 equiv), and THF (48 mL, 0.25 M). Crude **S1b** (1 equiv) was reduced to **S2b** using $LiAlH_4$ (683 mg, 18 mmol, 1.5 equiv) and THF (24 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S2b** as a yellow oil (1.64 g, 57% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 16.1, 7.8 Hz, 3H), 7.64 (s, 1H), 7.51 – 7.42 (m, 2H), 7.36 (dd, *J* = 8.3, 1.4 Hz, 1H), 4.84 (s, 1H), 4.82 (s, 1H), 3.63 – 3.53 (m, 2H), 2.88 – 2.75 (m, 2H), 2.27 – 2.04 (m, 3H), 1.76 (s, 3H), 1.46 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.6, 138.3, 133.7, 132.2, 128.1, 127.9, 127.7, 127.6, 126.1, 125.4, 112.4, 65.1, 62.9, 40.4, 37.9, 29.9, 22.4. **IR** (ATR): 3355, 2923, 1600, 1444, 1077 cm^{-1}. **HRMS** calculated for $C_{17}H_{20}ONa$ $[M+Na]^+$ 263.1412, found 263.1418.

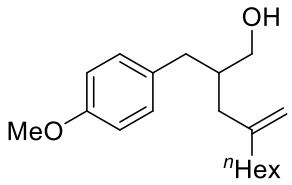


4-methyl-2-(thiophen-2-ylmethyl)pent-4-en-1-ol (S2d): The title compound was prepared using the general procedures for ester alkylation and ester reduction starting from ethyl 4-methylpent-4-enoate[2] (**11**) (3.5 g, 25 mmol, 1 equiv), $^{i}Pr_2NH$ (4.2 mL, 30 mmol, 1.2 equiv), ^{n}BuLi (11 mL, 27.5 mmol, 1.1 equiv, 2.5 M in THF), 2-(bromomethyl)thiophene[3] (5.3 g, 30 mmol, 1.2 equiv), and THF (100 mL, 0.25 M). Crude **S1d** (1 equiv) was reduced to **S2d** using $LiAlH_4$ (1.4 g, 38 mmol, 1.5 equiv) and THF (50 mL, 0.50 M). The crude material was

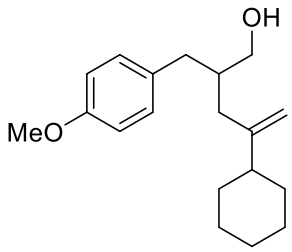
purified by column chromatography (10% EtOAc in hexanes) to afford **S2d** as a yellow oil (3.73 g, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 5.1 Hz, 1H), 6.94 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.82 (d, *J* = 3.4 Hz, 1H), 4.83 (s, 1H), 4.79 (s, 1H), 3.58 (d, *J* = 4.6 Hz, 2H), 2.95 – 2.79 (m, 2H), 2.18 – 1.99 (m, 3H), 1.75 (s, 3H), 1.43 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.3, 143.2, 126.9, 125.6, 123.6, 112.5, 64.9, 40.7, 40.0, 31.5, 22.4. **IR** (ATR): 3341, 2919, 1648, 1439, 1032, 888 cm^{-1}. **HRMS** calculated for $C_{11}H_{16}OSNa$ $[M+Na]^+$ 219.0820, found 219.0814.



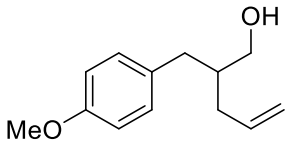
4-methyl-2-(3-phenylprop-2-yn-1-yl)pent-4-en-1-ol (S2h): The title compound was prepared using the general procedures for ester alkylation and ester reduction starting from ethyl 4-methylpent-4-enoate[2] (**11**) (2.6 g, 18 mmol, 1 equiv), ^{i}Pr$_2$NH (3.1 mL, 21.6 mmol, 1.2 equiv), ^{n}BuLi (7.9 mL, 19.8 mmol, 1.1 equiv, 2.5 M in THF), (3-bromoprop-1-yn-1-yl)benzene[4] (4.2 g, 21.6 mmol, 1.2 equiv), and THF (72 mL, 0.25 M). Crude **S1h** (1 equiv) was reduced to **S2h** using $LiAlH_4$ (1.0 g, 27 mmol, 1.5 equiv) and THF (36 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S2h** as a yellow oil (2.57 g, 67% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 7.33 – 7.26 (m, 3H), 4.84 (s, 1H), 4.81 (s, 1H), 3.79 – 3.67 (m, 2H), 2.55 (dd, *J* = 17.0, 5.3 Hz, 1H), 2.46 (dd, *J* = 17.0, 6.6 Hz, 1H), 2.25 – 2.13 (m, 2H), 2.11 – 1.99 (m, 1H), 1.81 (s, 1H), 1.78 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7, 131.7, 128.4, 127.8, 123.9, 112.6, 88.1, 82.3, 65.4, 39.5, 38.0, 22.4, 21.1. **IR** (ATR): 3334, 2928, 1649, 1489, 1069, 945 cm^{-1}. **HRMS** calculated for $C_{15}H_{18}ONa$ $[M+Na]^+$ 237.1255, found 237.1243.



2-(4-methoxybenzyl)-4-methylenedecan-1-ol (S2i): The title compound was prepared using the general procedures for ester alkylation and ester reduction starting from methyl 3-(4-methoxyphenyl)propanoate (971 mg, 5.0 mmol, 1 equiv), ^{i}Pr$_2$NH (0.85 mL, 6.0 mmol, 1.2 equiv), ^{n}BuLi (2.2 mL, 5.5 mmol, 1.1 equiv, 2.5 M in THF), 2-(bromomethyl)oct-1-ene[5] (1.2 g, 6.0 mmol, 1.2 equiv), and THF (20 mL, 0.25 M). Crude **S1i** (1 equiv) was reduced to **S2i** using $LiAlH_4$ (285 mg, 7.5 mmol, 1.5 equiv) and THF (10 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S2i** as a yellow oil (717 mg, 49% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.2 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 2H), 4.81 (s, 1H), 4.80 (s, 1H), 3.80 (s, 3H), 3.53 (s, 2H), 2.58 (t, *J* = 11.3 Hz, 2H), 2.16 – 1.91 (m, 5H), 1.35 (s, 3H), 1.27 (s, 6H), 0.89 (t, *J* = 6.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.0, 148.8, 132.7, 130.2, 113.9, 111.0, 65.3, 55.4, 40.7, 38.5, 37.0, 35.8, 31.9, 29.2, 27.7, 22.8, 14.2. **IR** (ATR): 3351, 2925, 2855, 1612, 1511, 1441, 1244, 1176, 1035, 890 cm^{-1}. **HRMS** calculated for $C_{19}H_{30}O_2Na$ $[M+Na]^+$ 313.2144, found 313.2131.

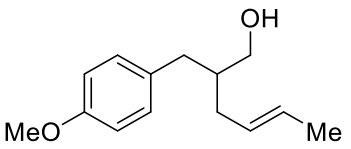


4-cyclohexyl-2-(4-methoxybenzyl)pent-4-en-1-ol (S2j): The title compound was prepared using the general procedures for ester alkylation and ester reduction starting from methyl 3-(4-methoxyphenyl)propanoate (311 mg, 1.6 mmol, 1 equiv), ^{i}Pr$_2$NH (0.27 mL, 1.9 mmol, 1.2 equiv), ^{n}BuLi (0.70 mL, 1.8 mmol, 1.1 equiv, 2.5 M in THF), (3-bromoprop-1-en-2-yl)cyclohexane[6] (488 mg, 2.4 mmol, 1.5 equiv), and THF (6.4 mL, 0.25 M). Crude **S1j** (1 equiv) was reduced to **S2j** using $LiAlH_4$ (91.1 mg, 2.4 mmol, 1.5 equiv) and THF (3.2 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S2j** as a colorless oil (239 mg, 52% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 4.83 (s, 1H), 4.79 (s, 1H), 3.80 (s, 3H), 3.57 – 3.48 (m, 2H), 2.63 – 2.52 (m, 2H), 2.15 – 2.03 (m, 2H), 2.03 – 1.93 (m, 1H), 1.86 – 1.64 (m, 6H), 1.34 (s, 1H), 1.29 – 1.02 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 154.0, 132.8, 130.2, 113.9, 109.0, 65.3, 55.4, 43.6, 41.1, 37.8, 37.0, 32.8, 32.5, 27.0, 26.9, 26.5. **IR** (ATR): 3357, 2922, 2850, 1611, 1511, 1447, 1244, 1176, 1034, 885 cm^{-1}. **HRMS** calculated for $C_{19}H_{28}O_2Na$ $[M+Na]^+$ 311.1987, found 311.1990.



2-(4-methoxybenzyl)pent-4-en-1-ol (S2k): The title compound was prepared using the general procedures for ester alkylation and ester reduction starting from methyl 3-(4-methoxyphenyl)propanoate (1.9 g, 9.8 mmol, 1 equiv), ^{i}Pr$_2$NH (1.7 mL, 11.8 mmol, 1.2 equiv), ^{n}BuLi (4.3 mL, 10.8 mmol, 1.1 equiv, 2.5 M in THF), allyl bromide (1.0 mL, 11.8 mmol, 1.2 equiv), and THF (39 mL, 0.25 M). Crude **S1k** (1 equiv) was reduced to **S2k** using $LiAlH_4$ (558 mg, 14.7 mmol, 1.5 equiv) and THF (20 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S2k** as a colorless oil (1.76 g, 87%

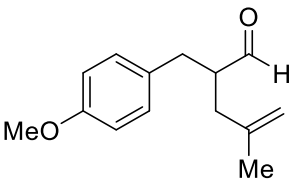
yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 5.84 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.12 – 5.04 (m, 2H), 3.80 (s, 3H), 3.59 – 3.51 (m, 2H), 2.60 (dd, *J* = 7.2, 2.5 Hz, 2H), 2.13 (t, *J* = 6.9 Hz, 2H), 1.93 – 1.84 (m, 1H), 1.31 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.0, 137.1, 132.6, 130.2, 116.7, 113.9, 64.9, 55.4, 42.7, 36.5, 35.6. **IR** (ATR): 3353, 2913, 1510, 1243, 1176 cm^{-1}. **HRMS** calculated for $C_{13}H_{18}O_2Na$ $[M+Na]^+$ 229.1205, found 229.1203.



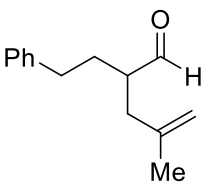
(*E*)-2-(4-methoxybenzyl)hex-4-en-1-ol (S2l): The title compound was prepared using the general procedures for ester alkylation and ester reduction starting from methyl 3-(4-methoxyphenyl)propanoate (1.2 g, 6.0 mmol, 1 equiv), ^{i}Pr$_2$NH (1.0 mL, 7.2 mmol, 1.2 equiv), ^{n}BuLi (2.6 mL, 6.6 mmol, 1.1 equiv, 2.5 M in THF), crotyl bromide (1.2 g, 9.0 mmol, 1.5 equiv), and THF (24 mL, 0.25 M). Crude **S1l** (1 equiv) was reduced to **S2l** using $LiAlH_4$ (342 mg, 9.0 mmol, 1.5 equiv) and THF (12 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S2l** as a light yellow oil (613 mg, 46% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.54 – 5.40 (m, 2H), 3.80 (s, 3H), 3.54 (dd, *J* = 5.0, 2.6 Hz, 2H), 2.57 (d, *J* = 7.2 Hz, 2H), 2.09 – 2.01 (m, 2H), 1.89 – 1.77 (m, 1H), 1.68 (d, *J* = 4.8 Hz, 3H), 1.29 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 132.8, 130.2, 129.3, 127.2, 113.9, 65.1, 55.4, 43.0, 36.6, 34.4, 18.1. **IR** (ATR): 3358, 2915, 1611, 1511, 1244, 1177, 1034, 967 cm^{-1}. **HRMS** calculated for $C_{14}H_{20}O_2Na$ $[M+Na]^+$ 243.1361, found 243.1369.

General Procedure for Swern Oxidation of Alcohols S2

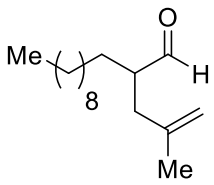
To an oven-dried round bottom flask was added oxalyl chloride (1.3 equiv) and CH_2Cl_2 (0.60 M). The mixture was cooled -78 °C, and DMSO (3 equiv) was added. The resulting mixture was stirred for 30 min. Alcohol **S2** (1 equiv) was added as a solution in CH_2Cl_2 (0.60 M), and the resulting mixture was stirred for 30 min. Et_3N (5 equiv) was added, and the resulting mixture was allowed to warm to rt and stirred for 30 min. The reaction mixture was quenched with H_2O and extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography to afford aldehyde **1**.



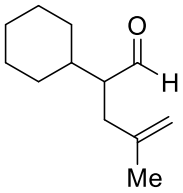
2-(4-methoxybenzyl)-4-methylpent-4-enal (1a): The title compound was prepared following the general procedure for Swern oxidation using **S2a** (2.3 g, 10.3 mmol, 1 equiv), oxalyl chloride (1.1 mL, 13.3 mmol, 1.3 equiv), DMSO (2.2 mL, 31 mmol, 3 equiv), Et_3N (7.2 mL, 51.5 mmol, 5 equiv), and CH_2Cl_2 (34.3 mL, 0.30 M). The crude material was purified by column chromatography (5% EtOAc in hexanes) to afford **1a** as a colorless oil (2.0 g, 88% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.66 (d, *J* = 2.6 Hz, 1H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.84 (d, *J* = 1.4 Hz, 1H), 4.75 (d, *J* = 0.5 Hz, 1H), 3.79 (s, 3H), 2.90 (dd, *J* = 13.4, 7.4 Hz, 1H), 2.79 (dddd, *J* = 13.4, 7.0, 6.2, 2.5 Hz, 1H), 2.71 (dd, *J* = 13.4, 6.0 Hz, 1H), 2.39 (dd, *J* = 14.8, 7.7 Hz, 1H), 2.15 (dd, *J* = 14.8, 6.2 Hz, 1H), 1.73 (d, *J* = 0.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.6, 158.4, 142.3, 130.8, 130.1, 114.1, 113.0, 55.4, 51.5, 37.2, 34.3, 22.6. **IR** (ATR): 2932, 2835, 1724, 1338, 1245, 907 cm^{-1}. **HRMS** calculated for $C_{14}H_{18}O_2Na$ $[M+Na]^+$ 241.1205, found 241.1195.



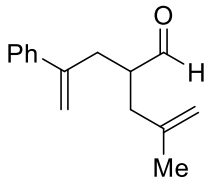
4-methyl-2-phenethylpent-4-enal (1c): The title compound was prepared following the general procedure for Swern oxidation using **S2c** (1.2 g, 6.1 mmol, 1 equiv), oxalyl chloride (0.68 mL, 8.0 mmol, 1.3 equiv), DMSO (1.3 mL, 18.3 mmol, 3 equiv), Et_3N (4.3 mL, 30.6 mmol, 5 equiv), and CH_2Cl_2 (20.4 mL, 0.30 M). The crude material was purified by column chromatography (5% EtOAc in hexanes) to afford **1c** as a light yellow oil (1.07 g, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.63 (d, *J* = 2.7 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.20 (dd, *J* = 14.1, 7.3 Hz, 3H), 4.82 (s, 1H), 4.73 (s, 1H), 2.75 – 2.57 (m, 2H), 2.57 – 2.47 (m, 1H), 2.42 (dd, *J* = 14.3, 7.6 Hz, 1H), 2.19 (dd, *J* = 14.3, 6.9 Hz, 1H), 2.03 – 1.90 (m, 1H), 1.82 – 1.72 (m, 1H), 1.69 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.7, 142.2, 141.5, 128.62, 128.56, 126.3, 113.1, 49.1, 37.5, 33.3, 30.5, 22.5. **IR** (ATR): 2927, 1727, 1651, 1495, 1454, 892 cm^{-1}. **HRMS** calculated for $C_{14}H_{18}ONa$ $[M+Na]^+$ 225.1255, found 225.1250.



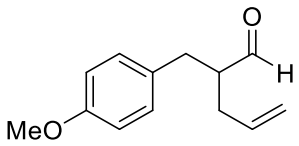
2-(2-methylallyl)dodecanal (1e): The title compound was prepared following the general procedure for Swern oxidation using **S2e** (1.5 g, 6.1 mmol, 1 equiv), oxalyl chloride (0.68 mL, 7.9 mmol, 1.3 equiv), DMSO (1.3 mL, 18.2 mmol, 3 equiv), Et_3N (4.2 mL, 30.3 mmol, 5 equiv), and CH_2Cl_2 (20 mL, 0.30 M). The crude material was purified by column chromatography (3% EtOAc in hexanes) to afford **1e** as a light yellow oil (1.38 g, 95% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.57 (d, *J* = 3.1 Hz, 1H), 4.80 (s, 1H), 4.72 (s, 1H), 2.45 (ddd, *J* = 11.1, 7.2, 3.1 Hz, 1H), 2.37 (dd, *J* = 14.4, 7.9 Hz, 1H), 2.13 (dd, *J* = 14.3, 6.3 Hz, 1H), 1.72 (s, 3H), 1.26 (s, 18H), 0.89 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.2, 142.6, 112.7, 49.9, 37.5, 32.0, 29.8, 29.72, 29.70, 29.6, 29.5, 29.1, 27.1, 22.8, 22.6, 14.2. **IR** (ATR): 2922, 2853, 1726, 1456, 1054, 891 cm^{-1}. **HRMS** calculated for $C_{16}H_{30}ONH_4$ $[M+NH_4]^+$ 256.2640, found 256.2633.



2-cyclohexyl-4-methylpent-4-enal (1f): The title compound was prepared following the general procedure for Swern oxidation using **S2f** (1.2 g, 6.6 mmol, 1 equiv), oxalyl chloride (0.73 mL, 8.5 mmol, 1.3 equiv), DMSO (1.4 mL, 19.7 mmol, 3 equiv), Et_3N (4.6 mL, 32.8 mmol, 5 equiv), and CH_2Cl_2 (22 mL, 0.30 M). The crude material was purified by column chromatography (3% EtOAc in hexanes) to afford **1f** as a light yellow oil (1.13 g, 95% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.60 (d, *J* = 3.5 Hz, 1H), 4.77 (s, 1H), 4.69 (s, 1H), 2.40 (dd, *J* = 13.9, 9.6 Hz, 1H), 2.31 (dt, *J* = 9.4, 3.9 Hz, 1H), 2.21 (dd, *J* = 14.0, 4.1 Hz, 1H), 1.81 – 1.59 (m, 9H), 1.32 – 1.18 (m, 2H), 1.18 – 1.03 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.6, 143.2, 112.4, 55.4, 38.7, 34.7, 30.6, 30.5, 26.60, 26.55, 26.4, 22.7. **IR** (ATR): 2923, 2852, 2705, 1724, 889 cm^{-1}. **HRMS** calculated for $C_{12}H_{20}O$ $[M]^+$ 180.1514, found 180.1521.



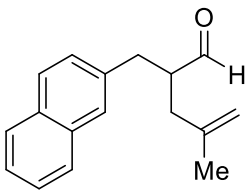
4-methyl-2-(2-phenylallyl)pent-4-enal (1g): The title compound was prepared following the general procedure for Swern oxidation using **S2g** (1.2 g, 5.5 mmol, 1 equiv), oxalyl chloride (0.61 mL, 7.1 mmol, 1.3 equiv), DMSO (1.2 mL, 16.4 mmol, 3 equiv), Et_3N (3.8 mL, 27.4 mmol, 5 equiv), and CH_2Cl_2 (18 mL, 0.30 M). The crude material was purified by column chromatography (5% EtOAc in hexanes) to afford **1g** as a light yellow oil (911 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.61 (d, *J* = 2.5 Hz, 1H), 7.42 – 7.28 (m, 5H), 5.34 (s, 1H), 5.12 (d, *J* = 1.0 Hz, 1H), 4.82 (s, 1H), 4.71 (s, 1H), 2.86 (dd, *J* = 14.2, 7.5 Hz, 1H), 2.61 (ddd, *J* = 14.1, 10.1, 4.4 Hz, 2H), 2.36 (dd, *J* = 14.4, 7.5 Hz, 1H), 2.18 (dd, *J* = 14.4, 6.1 Hz, 1H), 1.64 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.5, 145.6, 142.2, 140.5, 128.6, 127.9, 126.4, 115.2, 113.3, 47.6, 37.3, 35.0, 22.5. **IR** (ATR): 2934, 1723, 1627, 1443, 1376, 1302 cm^{-1}. **HRMS** calculated for $C_{15}H_{18}ONH_4$ $[M+NH_4]^+$ 232.1701, found 232.1703.



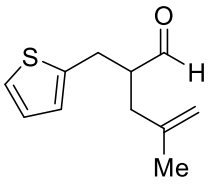
2-(4-methoxybenzyl)pent-4-enal (1k): The title compound was prepared following the general procedure for Swern oxidation using **S2k** (1.04 g, 5.0 mmol, 1 equiv), oxalyl chloride (0.56 mL, 6.5 mmol, 1.3 equiv), DMSO (1.1 mL, 15.1 mmol, 3 equiv), Et_3N (3.5 mL, 25 mmol, 5 equiv), and CH_2Cl_2 (17 mL, 0.30 M). The crude material was purified by column chromatography (5% EtOAc in hexanes) to afford **1k** as a colorless oil (929 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 5.83 – 5.71 (m, 1H), 5.12 – 5.06 (m, 2H), 3.79 (s, 3H), 2.95 (dd, *J* = 13.1, 6.2 Hz, 1H), 2.75 – 2.66 (m, 2H), 2.46 – 2.35 (m, 1H), 2.28 (dd, *J* = 13.2, 7.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.4, 158.4, 134.9, 130.7, 130.1, 117.7, 114.1, 55.4, 53.1, 33.8, 32.8. **IR** (ATR): 2913, 2835, 1723, 1511, 1244 cm^{-1}. **HRMS** calculated for $C_{13}H_{16}O_2Na$ $[M+Na]^+$ 227.1048, found 227.1044.

General Procedure for Oxidation of Alcohols with IBX

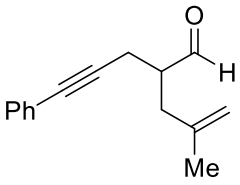
To a round bottom flask was added alcohol **S2** (1 equiv) and DMSO (0.25 M). IBX[7] (1.1–1.2 equiv) was added, and the resulting mixture was stirred at rt for 2 h. The reaction mixture was quenched with H_2O and filtered. The filtrate was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography to afford aldehyde **1**.



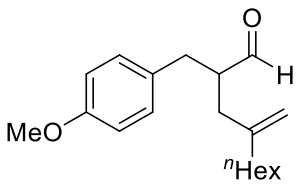
4-methyl-2-(naphthalen-2-ylmethyl)pent-4-enal (1b): The title compound was prepared following the general oxidation procedure with IBX using **S2b** (889 mg, 3.7 mmol, 1 equiv), IBX (1.2 g, 4.4 mmol, 1.2 equiv), and DMSO (15 mL, 0.25 M). The crude material was purified by column chromatography (5% EtOAc in hexanes) to afford **1b** as a colorless oil (758 mg, 86% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.72 (d, *J* = 2.4 Hz, 1H), 7.85 – 7.75 (m, 3H), 7.63 (s, 1H), 7.51 – 7.41 (m, 2H), 7.31 (dd, *J* = 8.4, 1.8 Hz, 1H), 4.87 (s, 1H), 4.78 (s, 1H), 3.14 (td, *J* = 9.9, 3.7 Hz, 1H), 3.00 – 2.88 (m, 2H), 2.49 – 2.40 (m, 1H), 2.21 (dd, *J* = 14.8, 5.7 Hz, 1H), 1.74 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 204.4, 142.2, 136.4, 133.7, 132.4, 128.4, 127.8, 127.66, 127.65, 127.5, 126.3, 125.7, 113.2, 51.2, 37.3, 35.3, 22.6. **IR** (ATR): 2932, 1723, 1599, 1507, 891 cm^{-1}. **HRMS** calculated for $C_{17}H_{18}ONa$ $[M+Na]^+$ 261.1255, found 261.1258.



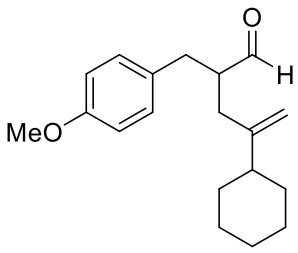
4-methyl-2-(thiophen-2-ylmethyl)pent-4-enal (1d): The title compound was prepared following the general oxidation procedure with IBX using **S2d** (766 mg, 3.9 mmol, 1 equiv), IBX (1.31 g, 4.7 mmol, 1.2 equiv), and DMSO (16 mL, 0.25 M). The crude material was purified by column chromatography (5% EtOAc in hexanes) to afford **1d** as a colorless oil (705 mg, 93% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.71 (d, *J* = 2.1 Hz, 1H), 7.15 (d, *J* = 5.1 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.81 (d, *J* = 3.3 Hz, 1H), 4.88 (s, 1H), 4.78 (s, 1H), 3.19 (dd, *J* = 15.1, 7.7 Hz, 1H), 3.01 (dd, *J* = 15.1, 5.8 Hz, 1H), 2.85 (qd, *J* = 7.7, 2.1 Hz, 1H), 2.43 (dd, *J* = 14.7, 7.6 Hz, 1H), 2.22 (dd, *J* = 14.7, 7.1 Hz, 1H), 1.75 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.8, 141.9, 141.2, 127.1, 126.0, 124.1, 113.5, 51.3, 37.1, 28.9, 22.5. **IR** (ATR): 3074, 2915, 1723, 1438, 893 cm^{-1}. **HRMS** calculated for $C_{11}H_{14}OSNa$ $[M+Na]^+$ 217.0663, found 217.0669.



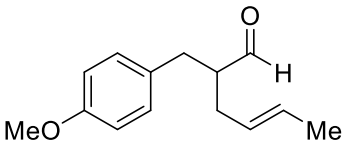
4-methyl-2-(3-phenylprop-2-yn-1-yl)pent-4-enal (1h): The title compound was prepared following the general oxidation procedure with IBX using **S2h** (310 mg, 1.5 mmol, 1 equiv), IBX (508 mg, 1.8 mmol, 1.2 equiv), and DMSO (6 mL, 0.25 M). The crude material was purified by column chromatography (5% EtOAc in hexanes) to afford **1h** as a yellow oil (258 mg, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.81 (d, *J* = 1.6 Hz, 1H), 7.39 (ddd, *J* = 7.0, 4.9, 3.5 Hz, 2H), 7.32 – 7.27 (m, 3H), 4.91 – 4.87 (m, 1H), 4.85 – 4.81 (m, 1H), 2.75 (dddd, *J* = 7.9, 7.2, 5.1, 1.6 Hz, 1H), 2.71 – 2.64 (m, 2H), 2.54 (dd, *J* = 14.4, 6.5 Hz, 1H), 2.39 (dd, *J* = 14.6, 7.3 Hz, 1H), 1.79 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.3, 141.7, 131.7, 128.4, 128.1, 123.5, 113.6, 86.3, 82.9, 48.5, 36.6, 22.5, 19.0. **IR** (ATR): 3076, 2932, 1726, 1650, 1598, 1375, 1069 cm^{-1}. **HRMS** calculated for $C_{15}H_{16}ONa$ $[M+Na]^+$ 235.1099, found 235.1105.



2-(4-methoxybenzyl)-4-methylenedecanal (1i): The title compound was prepared following the general oxidation procedure with IBX using **S2i** (500 mg, 1.7 mmol, 1 equiv), IBX (560 mg, 2.0 mmol, 1.1 equiv), and DMSO (7 mL, 0.25 M). The crude material was purified by column chromatography (5% EtOAc in hexanes) to afford **1i** as a light yellow oil (229 mg, 46% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.65 (d, *J* = 2.4 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 4.84 (s, 1H), 4.76 (s, 1H), 3.79 (s, 3H), 2.90 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.78 (s, 1H), 2.71 (dd, *J* = 13.7, 5.9 Hz, 1H), 2.38 (dd, *J* = 14.8, 8.2 Hz, 1H), 2.14 (dd, *J* = 14.8, 5.9 Hz, 1H), 1.99 (t, *J* = 7.4 Hz, 2H), 1.38 (s, 2H), 1.27 (s, 6H), 0.89 (t, *J* = 6.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 204.7, 158.4, 146.4, 130.8, 130.1, 114.1, 111.7, 55.4, 51.6, 36.1, 35.4, 34.4, 31.9, 29.1, 27.7, 22.7, 14.2. **IR** (ATR): 2927, 2855, 1725, 1612, 1512, 1442, 1246, 1177, 1036, 895 cm^{-1}. **HRMS** calculated for $C_{19}H_{28}O_2Na$ $[M+Na]^+$ 311.1987, found 311.1985.

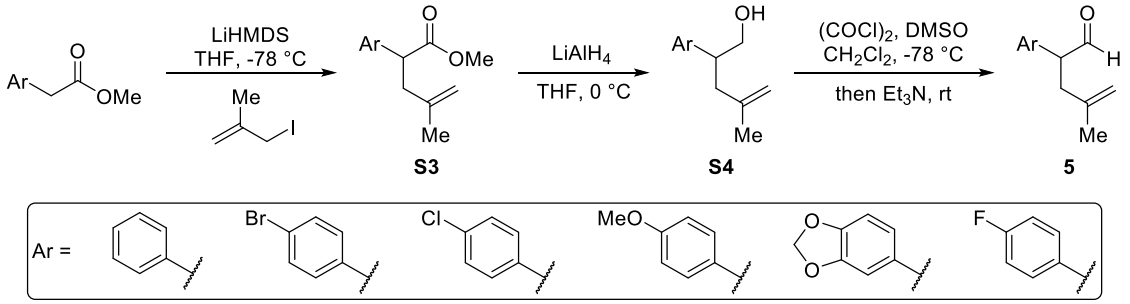


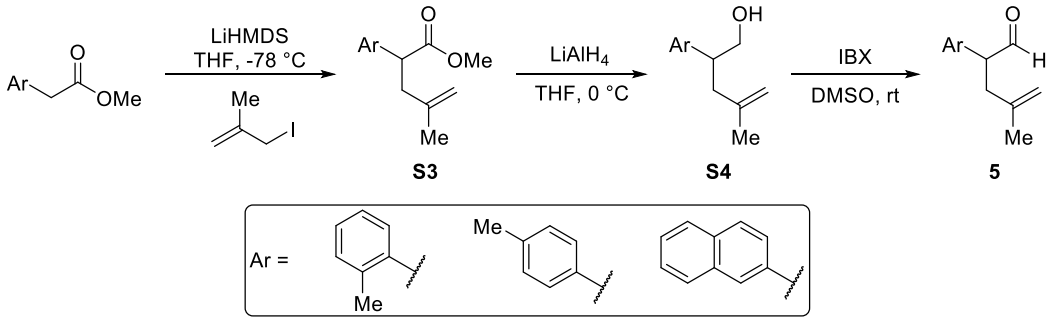
4-cyclohexyl-2-(4-methoxybenzyl)pent-4-enal (1j): The title compound was prepared following the general oxidation procedure with IBX using **S2j** (238 mg, 0.83 mmol, 1 equiv), IBX (254 mg, 0.91 mmol, 1.1 equiv), and DMSO (3.3 mL, 0.25 M). The crude material was purified by column chromatography (5% EtOAc in hexanes) to afford **1j** as a colorless oil (165 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.64 (d, *J* = 2.6 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.85 (s, 1H), 4.74 (s, 1H), 3.79 (s, 3H), 2.89 (dd, *J* = 13.3, 7.5 Hz, 1H), 2.80 (tdd, *J* = 13.5, 7.1, 2.6 Hz, 1H), 2.72 (dd, *J* = 13.3, 5.9 Hz, 1H), 2.41 (dd, *J* = 15.3, 7.9 Hz, 1H), 2.16 (dd, *J* = 15.3, 6.0 Hz, 1H), 1.83 – 1.64 (m, 6H), 1.32 – 1.06 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.9, 158.4, 151.7, 130.8, 130.1, 114.1, 109.7, 55.4, 51.8, 44.2, 34.6, 34.5, 32.52, 32.48, 26.87, 26.85, 26.4. **IR** (ATR): 2924, 2851, 1724, 1612, 1512, 1446, 1245, 1177, 1035, 887 cm^{-1}. **HRMS** calculated for $C_{19}H_{26}O_2Na$ $[M+Na]^+$ 309.1830, found 309.1817.



(*E*)-2-(4-methoxybenzyl)hex-4-enal (1l): The title compound was prepared following the general oxidation procedure with IBX using **S2l** (613 mg, 2.8 mmol, 1 equiv), IBX (856 mg, 3.1 mmol, 1.1 equiv), and DMSO (12 mL, 0.25 M). The crude material was purified by column chromatography (5% EtOAc in hexanes) to afford **1l** as a colorless oil (340 mg, 56% yield, 10:1 *E*:*Z*). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.68 (d, *J* = 2.1 Hz, 1H), 7.08 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 5.51 (dq, *J* = 13.8, 6.3 Hz, 1H), 5.37 (dtd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 3.79 (s, 3H), 2.93 (dd, *J* = 13.8, 7.0 Hz, 1H), 2.74 – 2.58 (m, 2H), 2.32 (dt, *J* = 14.2, 7.0 Hz, 1H), 2.26 – 2.16 (m, 1H), 1.66 (dd, *J* = 6.3, 1.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.8, 158.3, 131.0, 130.1, 128.4, 127.2, 114.1, 55.4, 53.6, 33.8, 31.8, 18.1. **IR** (ATR): 2916, 2836, 1723, 1612, 1512, 1441, 1244, 1177, 1034, 967 cm^{-1}. **HRMS** calculated for $C_{14}H_{18}O_2Na$ $[M+Na]^+$ 241.1205, found 241.1220.

Preparation of Aldehydes 5



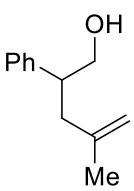


General Procedure for Ester Alkylation

To an oven-dried round bottom flask was added the appropriate ester and THF (0.25 M), and the resulting solution was cooled to -78 °C. Then, LiHMDS (1.1 equiv, 1.0 M in THF) was added dropwise, and the resulting mixture was stirred for 1 h. A solution of the methallyl iodide (1.2 equiv) was added dropwise, and the resulting mixture was stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and concentrated *in vacuo*. The alkylated ester **S3** was used without further purification.

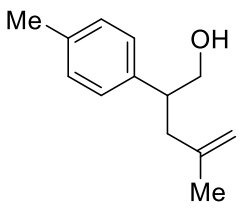
General Procedure for Ester Reduction

The crude alkylated ester **S3** was dissolved in THF (0.25 M), and the resulting solution was cooled to 0 °C. $LiAlH_4$ (1.5 equiv) was added portionwise, and the resulting mixture was stirred for 30 min. The reaction was quenched using the Fieser method, filtered through celite, and concentrated *in vacuo*. The residue was purified by column chromatography to afford alcohol **S4**.

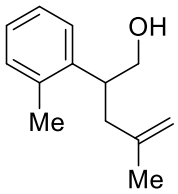


4-methyl-2-phenylpent-4-en-1-ol (S4a): The title compound was prepared using the general procedures for ester alkylation and ester reduction starting from methyl 2-phenylacetate (3.0 g, 20 mmol, 1 equiv), LiHMDS (1.0 M in THF, 22 mL, 22 mmol, 1.1 equiv), methallyl iodide (4.4 g, 24 mmol, 1.2 equiv), and THF (80 mL, 0.25 M). Crude **S3a** (1 equiv) was reduced to **S4a** using $LiAlH_4$ (1.1 g, 30 mmol, 1.5 equiv) and THF (40 mL, 0.50 M). The crude material

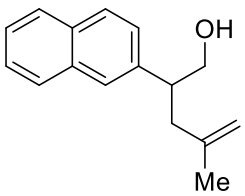
was purified by column chromatography (10% EtOAc in hexanes) to afford **S4a** as a colorless oil (2.33 g, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 9.7, 5.5 Hz, 2H), 7.28 – 7.19 (m, 3H), 4.73 (s, 1H), 4.68 (s, 1H), 3.76 (ddd, *J* = 18.3, 10.9, 6.6 Hz, 2H), 3.10 – 2.98 (m, 1H), 2.48 (dd, *J* = 14.1, 7.3 Hz, 1H), 2.35 (dd, *J* = 14.1, 7.9 Hz, 1H), 1.72 (s, 3H), 1.51 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.5, 142.3, 128.7, 128.1, 126.9, 112.5, 67.4, 46.4, 40.9, 22.5. **IR** (ATR): 3355, 3073, 2928, 1649, 1494, 1452, 1066, 1030, 886, 756 cm^{-1}. **HRMS** calculated for $C_{12}H_{16}ONH_4$ $[M+NH_4]^+$ 194.1545, found 194.1537.



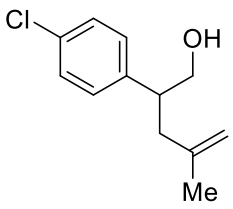
4-methyl-2-(*p*-tolyl)pent-4-en-1-ol (S4b): The title compound was prepared using the general procedures for ester alkylation and ester reduction starting from methyl 2-(*p*-tolyl)acetate (1.6 g, 10 mmol, 1 equiv), LiHMDS (1.0 M in THF, 11 mL, 11 mmol, 1.1 equiv), methallyl iodide (2.2 g, 12 mmol, 1.2 equiv), and THF (40 mL, 0.25 M). Crude **S3b** (1 equiv) was reduced to **S4b** using LiAlH4 (569 mg, 15 mmol, 1.5 equiv) and THF (20 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S4b** as a colorless oil (1.42 g, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 – 7.09 (m, 4H), 4.75 – 4.71 (m, 1H), 4.68 (dd, *J* = 2.0, 0.9 Hz, 1H), 3.77 (dd, *J* = 10.8, 5.6 Hz, 1H), 3.70 (dd, *J* = 10.8, 7.6 Hz, 1H), 3.01 (qd, *J* = 7.6, 5.7 Hz, 1H), 2.46 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.38 – 2.28 (m, 4H), 1.72 (s, 3H), 1.42 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7, 139.1, 136.4, 129.5, 128.0, 112.4, 67.5, 45.9, 40.9, 22.5, 21.2. **IR** (ATR): 3356, 2922, 1650, 1514, 1445, 1374, 1066, 1034, 885, 811 cm^{-1}. **HRMS** calculated for $C_{13}H_{18}ONa$ $[M+Na]^+$ 213.1255, found 213.1245.



4-methyl-2-(*o*-tolyl)pent-4-en-1-ol (S4c): The title compound was prepared using the general procedures for ester alkylation and ester reduction starting from methyl 2-(*o*-tolyl)acetate (1.6 g, 10 mmol, 1 equiv), LiHMDS (1.0 M in THF, 11 mL, 11 mmol, 1.1 equiv), methallyl iodide (2.2 g, 12 mmol, 1.2 equiv), and THF (40 mL, 0.25 M). Crude **S3c** (1 equiv) was reduced to **S4c** using LiAlH4 (569 mg, 15 mmol, 1.5 equiv) and THF (20 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S4c** as a colorless oil (1.15 g, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 3H), 7.16 – 7.09 (m, 1H), 4.76 – 4.72 (m, 1H), 4.70 (dd, *J* = 2.0, 0.9 Hz, 1H), 3.77 (qd, *J* = 10.9, 6.5 Hz, 2H), 3.45 – 3.32 (m, 1H), 2.50 – 2.42 (m, 1H), 2.39 (s, 3H), 2.33 (dd, *J* = 14.1, 7.3 Hz, 1H), 1.74 (s, 3H), 1.45 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.9, 140.5, 136.8, 130.8, 126.49, 126.45, 126.1, 112.4, 67.0, 41.0, 40.9, 22.6, 19.9. **IR** (ATR): 3353, 3072, 2936, 1648, 1461, 1374, 1033, 886, 757, 726 cm^{-1}. **HRMS** calculated for $C_{13}H_{18}ONH_4$ $[M+ NH_4]^+$ 208.1701, found 208.1694.

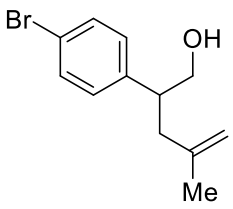


4-methyl-2-(naphthalen-2-yl)pent-4-en-1-ol (S4d): The title compound was prepared using the general procedures for ester alkylation and ester reduction starting from methyl 2-(naphthalen-2-yl)acetate (2.0 g, 10 mmol, 1 equiv), LiHMDS (1.0 M in THF, 11 mL, 11 mmol, 1.1 equiv), methallyl iodide (2.2 g, 12 mmol, 1.2 equiv), and THF (40 mL, 0.25 M). Crude **S3d** (1 equiv) was reduced to **S4d** using LiAlH4 (569 mg, 15 mmol, 1.5 equiv) and THF (20 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S4d** as a yellow oil (962 mg, 43% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.78 (m, 3H), 7.69 (s, 1H), 7.47 (dqd, *J* = 8.4, 6.8, 1.6 Hz, 2H), 7.39 (dd, *J* = 8.5, 1.7 Hz, 1H), 4.75 – 4.64 (m, 2H), 3.85 (qd, *J* = 10.9, 6.6 Hz, 2H), 3.30 – 3.14 (m, 1H), 2.56 (dd, *J* = 14.1, 7.2 Hz, 1H), 2.46 (dd, *J* = 14.1, 8.0 Hz, 1H), 1.75 (s, 3H), 1.41 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.5, 139.7, 133.7, 132.7, 128.5, 127.8, 127.0, 126.2, 126.1, 125.7, 112.7, 67.4, 46.6, 40.8, 22.6. **IR** (ATR): 3352, 2929, 1648, 1442, 1373, 1061, 1027, 887, 854, 815, 745 cm^{-1}. **HRMS** calculated for $C_{16}H_{18}ONa$ $[M+Na]^+$ 249.1255, found 249.1257.

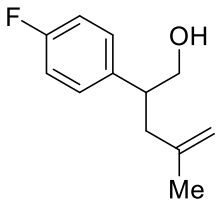


2-(4-chlorophenyl)-4-methylpent-4-en-1-ol (S4e): The title compound was prepared using the general procedures for ester alkylation and ester reduction starting from methyl 2-(4-chlorophenyl)acetate (1.43 g, 7.8 mmol, 1 equiv), LiHMDS (1.0 M in THF, 8.5 mL, 8.5 mmol, 1.1 equiv), methallyl iodide (1.70 g, 9.3 mmol, 1.2 equiv), and THF (31 mL, 0.25 M). Crude **S3e** (1 equiv) was reduced to **S4e** using $LiAlH_4$ (442 mg, 11.6 mmol, 1.5 equiv) and THF (15.5 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S4e** as a colorless oil (1.31 g, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.19 – 7.13 (m, 2H), 4.75 – 4.68 (m, 1H), 4.65 (dd, *J* = 2.0, 0.9 Hz, 1H), 3.77 (dd, *J* = 10.9, 5.6 Hz, 1H), 3.70 (dd,

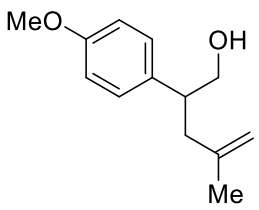
J = 10.9, 7.4 Hz, 1H), 3.09 – 2.94 (m, 1H), 2.46 (dd, *J* = 14.1, 7.0 Hz, 1H), 2.36 – 2.24 (m, 1H), 1.70 (s, 3H), 1.46 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 140.8, 132.6, 129.5, 128.8, 112.8, 67.3, 45.8, 40.7, 22.5. **IR** (ATR): 3342, 2931, 1649, 1491, 1444, 1091, 1035, 1014, 889, 821 cm^{-1}. **HRMS** calculated for $C_{12}H_{15}ClONH_4$ $[M+NH_4]^+$ 228.1155, found 228.1146.



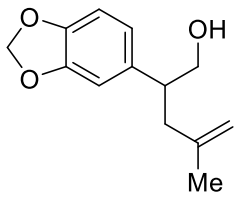
2-(4-bromophenyl)-4-methylpent-4-en-1-ol (S4f): The title compound was prepared using the general procedures for ester alkylation and ester reduction starting from methyl 2-(4-bromophenyl)acetate (1.83 g, 8.0 mmol, 1 equiv), LiHMDS (1.0 M in THF, 8.8 mL, 8.8 mmol, 1.1 equiv), methallyl iodide (1.75 g, 9.6 mmol, 1.2 equiv), and THF (32 mL, 0.25 M). Crude **S3f** (1 equiv) was reduced to **S4f** using $LiAlH_4$ (455 mg, 12.0 mmol, 1.5 equiv) and THF (16 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S4f** as a colorless oil (1.74 g, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 2H), 7.14 – 7.07 (m, 2H), 4.72 (d, *J* = 1.5 Hz, 1H), 4.65 (dd, *J* = 1.9, 0.9 Hz, 1H), 3.77 (dd, *J* = 10.9, 5.6 Hz, 1H), 3.69 (dd, *J* = 10.9, 7.3 Hz, 1H), 3.07 – 2.91 (m, 1H), 2.46 (dd, *J* = 14.1, 7.0 Hz, 1H), 2.30 (dd, *J* = 14.1, 8.3 Hz, 1H), 1.70 (s, 3H), 1.45 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 141.4, 131.8, 129.9, 120.6, 112.8, 67.2, 45.9, 40.7, 22.5. **IR** (ATR): 3345, 2930, 1649, 1444, 1487, 1374, 1073, 1009, 889, 817 cm^{-1}. **HRMS** calculated for $C_{12}H_{15}BrONH_4$ $[M+NH_4]^+$ 272.0650, found 272.0645.



2-(4-fluorophenyl)-4-methylpent-4-en-1-ol (S4g): The title compound was prepared using the general procedures for ester alkylation and ester reduction starting from methyl 2-(4-fluorophenyl)acetate (1.27 g, 7.6 mmol, 1 equiv), LiHMDS (1.0 M in THF, 8.3 mL, 8.3 mmol, 1.1 equiv), methallyl iodide (1.65 g, 9.1 mmol, 1.2 equiv), and THF (30 mL, 0.25 M). Crude **S3g** (1 equiv) was reduced to **S4g** using $LiAlH_4$ (429 mg, 11.3 mmol, 1.5 equiv) and THF (15.2 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S4g** as a colorless oil (1.29 g, 88% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 7.14 (m, 2H), 7.06 – 6.96 (m, 2H), 4.76 – 4.69 (m, 1H), 4.65 (dd, *J* = 2.0, 0.9 Hz, 1H), 3.77 (dd, *J* = 10.8, 5.6 Hz, 1H), 3.69 (dd, *J* = 10.8, 7.4 Hz, 1H), 3.09 – 2.94 (m, 1H), 2.46 (dd, *J* = 14.1, 7.0 Hz, 1H), 2.36 – 2.25 (m, 1H), 1.70 (s, 3H), 1.44 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.8 (d, *J* = 244.6 Hz), 143.3, 137.9 (d, *J* = 3.2 Hz), 129.5 (d, *J* = 7.8 Hz), 115.5 (d, *J* = 21.1 Hz), 112.7, 67.4, 45.7, 41.0, 22.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.6. **IR** (ATR): 3353, 2930, 1650, 1508, 1445, 1221, 1159, 1028, 889, 830 cm^{-1}. **HRMS** calculated for $C_{12}H_{15}FONH_4$ $[M+NH_4]^+$ 212.1451, found 212.1455.

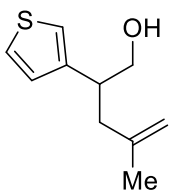


2-(4-methoxyphenyl)-4-methylpent-4-en-1-ol (S4h): The title compound was prepared using the general procedures for ester alkylation and ester reduction starting from methyl 2-(4-methoxyphenyl)acetate (1.33 g, 7.4 mmol, 1 equiv), LiHMDS (1.0 M in THF, 8.1 mL, 8.1 mmol, 1.1 equiv), methallyl iodide (1.61 g, 8.9 mmol, 1.2 equiv), and THF (30 mL, 0.25 M). Crude **S3h** (1 equiv) was reduced to **S4h** using $LiAlH_4$ (421 mg, 11.1 mmol, 1.5 equiv) and THF (14.8 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S4h** as a colorless oil (1.29 g, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.72 (s, 1H), 4.67 (s, 1H), 3.80 (s, 3H), 3.70 (dd, *J* = 24.8, 17.2 Hz, 2H), 3.06 – 2.93 (m, 1H), 2.44 (dd, *J* = 14.0, 7.1 Hz, 1H), 2.31 (dd, *J* = 14.1, 8.1 Hz, 1H), 1.71 (s, 3H), 1.37 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 143.7, 134.1, 129.0, 114.2, 112.5, 67.6, 55.4, 45.6, 41.0, 22.5. **IR** (ATR): 3377, 2932, 1611, 1511, 1442, 1245, 1178, 1033, 887, 827 cm^{-1}. **HRMS** calculated for $C_{13}H_{18}O_2NH_4$ $[M+NH_4]^+$ 224.1651, found 224.1665.



2-(benzo[*d*][1,3]dioxol-5-yl)-4-methylpent-4-en-1-ol (S4i): The title compound was prepared using the general procedures for ester alkylation and ester reduction starting from methyl 2-(benzo[*d*][1,3]dioxol-5-yl)acetate (1.04 g, 5.4 mmol, 1 equiv), LiHMDS (1.0 M in THF, 5.9 mL, 5.9 mmol, 1.1 equiv), methallyl iodide (1.17 g, 6.4 mmol, 1.2 equiv), and THF (21 mL, 0.25 M). Crude **S3i** (1 equiv) was reduced to **S4i** using $LiAlH_4$ (305 mg, 8.0 mmol, 1.5 equiv) and THF (10.8 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S4i** as a colorless oil (942 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.75 (dd, *J* = 15.4, 4.8 Hz, 2H), 6.68 (dd, *J* = 7.9, 1.5 Hz, 1H), 5.94 (d, *J* = 0.5 Hz, 2H), 4.73 (d, *J* = 1.5 Hz, 1H), 4.67 (dd, *J* = 2.0, 0.9 Hz, 1H), 3.74 (dd, *J* = 10.8, 5.5 Hz, 1H), 3.65 (dd, *J* = 10.8, 7.7 Hz, 1H), 2.96 (qd, *J* = 7.6, 5.6 Hz, 1H), 2.41 (dd, *J* = 14.1, 7.0 Hz, 1H), 2.27 (dd, *J* = 14.1, 8.2 Hz, 1H), 1.70 (s, 3H), 1.48 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.0, 146.4,

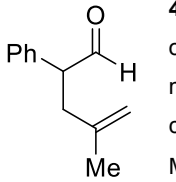
143.4, 136.0, 121.3, 112.6, 108.5, 108.1, 101.0, 67.5, 46.2, 41.0, 22.5. **IR** (ATR): 3362, 2894, 1504, 1486, 1439, 1243, 1036, 935, 888, 808 cm^{-1}. **HRMS** calculated for $C_{13}H_{16}O_3NH_4$ $[M+NH_4]^+$ 238.1443, found 238.1442.



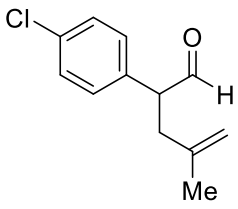
4-methyl-2-(thiophen-3-yl)pent-4-en-1-ol (S4j): The title compound was prepared using the general procedures for ester alkylation and ester reduction starting from methyl 2-(thiophen-3-yl)acetate (1.08 g, 6.4 mmol, 1 equiv), LiHMDS (1.0 M in THF, 7.0 mL, 7.0 mmol, 1.1 equiv), methallyl iodide (1.39 g, 7.6 mmol, 1.2 equiv), and THF (25 mL, 0.25 M). Crude **S3j** (1 equiv) was reduced to **S4j** using $LiAlH_4$ (363 mg, 9.6 mmol, 1.5 equiv) and THF (12.8 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S4j** as a colorless oil (1.11 g, 96% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 4.9, 2.9 Hz, 1H), 7.06 (dd, *J* = 2.9, 0.9 Hz, 1H), 7.01 (dd, *J* = 5.0, 1.3 Hz, 1H), 4.76 (d, *J* = 1.4 Hz, 1H), 4.70 (d, *J* = 1.0 Hz, 1H), 3.77 (dd, *J* = 10.8, 5.3 Hz, 1H), 3.68 (dd, *J* = 10.8, 7.1 Hz, 1H), 3.18 (qd, *J* = 7.4, 5.4 Hz, 1H), 2.45 (dd, *J* = 14.0, 7.5 Hz, 1H), 2.34 (dd, *J* = 14.0, 7.7 Hz, 1H), 1.72 (s, 3H), 1.56 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.5, 143.1, 127.0, 126.0, 121.3, 112.5, 66.9, 41.8, 40.8, 22.4. **IR** (ATR): 3361, 2929, 1647, 1444, 1374, 1064, 1027, 888, 775, 648 cm^{-1}. **HRMS** calculated for $C_{10}H_{14}OSNH_4$ $[M+NH_4]^+$ 200.1109, found 200.1109.

General Procedure for Swern Oxidation of Alcohols

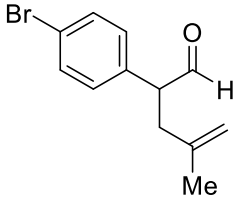
To an oven-dried round bottom flask was added oxalyl chloride (1.3 equiv) and CH_2Cl_2 (0.60 M). The mixture was cooled to -78 °C, and DMSO (3 equiv) was added. The resulting mixture was stirred for 30 min. Alcohol **S4** (1 equiv) was added as a solution in CH_2Cl_2 (0.60 M), and the resulting mixture was stirred for 30 min. Et_3N (5 equiv) was added, and the resulting mixture was allowed to warm to rt and stirred for 30 min. The reaction mixture was quenched with H_2O and extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography to afford aldehyde **5**.



4-methyl-2-phenylpent-4-enal (5a): The title compound was prepared following the general procedure for Swern oxidation using **S4a** (2.27 g, 13.0 mmol, 1 equiv), oxalyl chloride (1.4 mL, 16.9 mmol, 1.3 equiv), DMSO (2.8 mL, 39 mmol, 3 equiv), Et_3N (9.1 mL, 65 mmol, 5 equiv), and CH_2Cl_2 (43 mL, 0.30 M). The crude material was purified by column chromatography (3% EtOAc in hexanes) to afford **5a** as a colorless oil (1.93 g, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.69 (d, *J* = 2.2 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 7.24 – 7.20 (m, 2H), 4.78 – 4.72 (m, 1H), 4.69 – 4.61 (m, 1H), 3.76 (td, *J* = 7.5, 2.1 Hz, 1H), 2.87 (dd, *J* = 14.8, 7.2 Hz, 1H), 2.46 (dd, *J* = 14.9, 7.7 Hz, 1H), 1.72 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.4, 142.1, 136.1, 129.2, 128.9, 127.8, 113.0, 57.3, 37.8, 22.8. **IR** (ATR): 2936, 2714, 1720, 1650, 1492, 1453, 1076, 891, 755, 698 cm^{-1}. **HRMS** calculated for $C_{12}H_{14}ONa$ $[M+Na]^+$ 197.0942, found 197.0946.

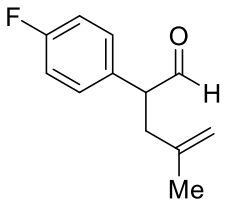


2-(4-chlorophenyl)-4-methylpent-4-enal (5e): The title compound was prepared following the general procedure for Swern oxidation using **S4e** (1.27 g, 6.0 mmol, 1 equiv), oxalyl chloride (0.67 mL, 7.8 mmol, 1.3 equiv), DMSO (1.3 mL, 18 mmol, 3 equiv), Et_3N (4.2 mL, 30 mmol, 5 equiv), and CH_2Cl_2 (20 mL, 0.30 M). The crude material was purified by column chromatography (3% EtOAc in hexanes) to afford **5e** as a light yellow oil (539 mg, 43% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.66 (d, *J* = 2.0 Hz, 1H), 7.39 – 7.30 (m, 2H), 7.18 – 7.10 (m, 2H), 4.76 (d, *J* = 1.4 Hz, 1H), 4.65 (s, 1H), 3.79 – 3.68 (m, 1H), 2.83 (dd, *J* = 14.8, 6.9 Hz, 1H), 2.43 (ddd, *J* = 14.8, 8.2, 0.8 Hz, 1H), 1.70 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.8, 141.7, 134.6, 133.8, 130.2, 129.3, 113.3, 56.6, 37.8, 22.7. **IR** (ATR): 2936, 1722, 1650, 1491, 1445, 1376, 1093, 1014, 893, 820 cm^{-1}. **HRMS** calculated for $C_{12}H_{13}ClONH_4$ $[M+NH_4]^+$ 226.0999, found 226.0988.

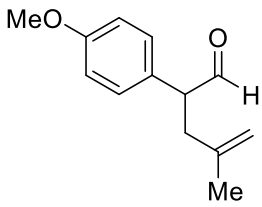


2-(4-bromophenyl)-4-methylpent-4-enal (5f): The title compound was prepared following the general procedure for Swern oxidation using **S4f** (1.70 g, 6.7 mmol, 1 equiv), oxalyl chloride (0.74 mL, 8.7 mmol, 1.3 equiv), DMSO (1.4 mL, 20 mmol, 3 equiv), Et_3N (4.6 mL, 33 mmol, 5 equiv), and CH_2Cl_2 (22 mL, 0.30 M). The crude material was purified by column chromatography (3% EtOAc in hexanes) to afford **5f** as a light yellow oil (1.15 g, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.66 (d, *J* = 2.0 Hz, 1H), 7.55 – 7.44 (m, 2H), 7.13 – 7.02 (m, 2H), 4.76 (s, 1H), 4.65 (s, 1H), 3.77 – 3.67 (m, 1H), 2.83 (dd, *J* = 14.8, 6.9 Hz, 1H), 2.43 (dd, *J* = 14.8, 8.2 Hz, 1H), 1.70 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.7, 141.6, 135.1, 132.3, 130.6, 121.9, 113.4, 56.7,

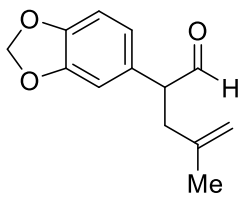
37.8, 22.7. **IR** (ATR): 2936, 2819, 2719, 1721, 1650, 1488, 1073, 1010, 892, 816 cm^{-1}. **HRMS** calculated for $C_{12}H_{13}BrONH_4$ $[M+NH_4]^+$ 270.0493, found 270.0505.



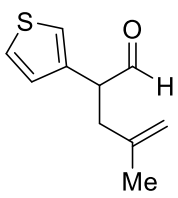
2-(4-fluorophenyl)-4-methylpent-4-enal (5g): The title compound was prepared following the general procedure for Swern oxidation using **S4g** (1.29 g, 6.6 mmol, 1 equiv), oxalyl chloride (0.74 mL, 8.6 mmol, 1.3 equiv), DMSO (1.4 mL, 20 mmol, 3 equiv), Et_3N (4.6 mL, 33 mmol, 5 equiv), and CH_2Cl_2 (22 mL, 0.30 M). The crude material was purified by column chromatography (3% EtOAc in hexanes) to afford **5g** as a colorless oil (1.13 g, 89% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.67 (d, *J* = 2.1 Hz, 1H), 7.21 – 7.15 (m, 2H), 7.10 – 7.03 (m, 2H), 4.76 (d, *J* = 1.4 Hz, 1H), 4.67 – 4.61 (m, 1H), 3.79 – 3.70 (m, 1H), 2.84 (dd, *J* = 14.8, 7.0 Hz, 1H), 2.42 (ddd, *J* = 14.8, 8.1, 0.8 Hz, 1H), 1.70 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.1 (d, *J* = 0.9 Hz), 162.4 (d, *J* = 246.5 Hz), 141.8, 131.8 (d, *J* = 3.3 Hz), 130.4 (d, *J* = 8.1 Hz), 116.1 (d, *J* = 21.4 Hz), 113.2, 56.5, 37.9, 22.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.9. **IR** (ATR): 2938, 2722, 1722, 1650, 1508, 1445, 1223, 1160, 893, 831 cm^{-1}. **HRMS** calculated for $C_{12}H_{13}FONH_4$ $[M+NH_4]^+$ 210.1294, found 210.1291.



2-(4-methoxyphenyl)-4-methylpent-4-enal (5h): The title compound was prepared following the general procedure for Swern oxidation using **S4h** (1.24 g, 6.0 mmol, 1 equiv), oxalyl chloride (0.67 mL, 7.8 mmol, 1.3 equiv), DMSO (1.3 mL, 18 mmol, 3 equiv), Et_3N (4.2 mL, 30 mmol, 5 equiv), and CH_2Cl_2 (20 mL, 0.30 M). The crude material was purified by column chromatography (3% EtOAc in hexanes) to afford **5h** as a light yellow oil (432 mg, 35% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.64 (d, *J* = 2.2 Hz, 1H), 7.17 – 7.09 (m, 2H), 6.94 – 6.87 (m, 2H), 4.78 – 4.72 (m, 1H), 4.69 – 4.63 (m, 1H), 3.81 (s, 3H), 3.70 (td, *J* = 7.6, 2.2 Hz, 1H), 2.82 (dd, *J* = 14.8, 7.1 Hz, 1H), 2.46 – 2.36 (m, 1H), 1.71 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.4, 159.2, 142.3, 129.9, 127.9, 114.6, 112.9, 56.5, 55.4, 37.8, 22.8. **IR** (ATR): 2936, 2836, 1720, 1609, 1511, 1248, 1178, 1032, 891, 827 cm^{-1}. **HRMS** calculated for $C_{13}H_{16}O_2NH_4$ $[M+NH_4]^+$ 222.1494, found 222.1496.



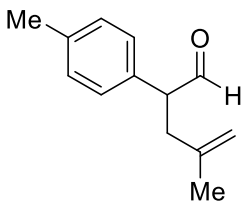
2-(benzo[*d*][1,3]dioxol-5-yl)-4-methylpent-4-enal (5i): The title compound was prepared following the general procedure for Swern oxidation using **S4i** (903 mg, 4.1 mmol, 1 equiv), oxalyl chloride (0.46 mL, 5.3 mmol, 1.3 equiv), DMSO (0.87 mL, 12.3 mmol, 3 equiv), Et_3N (2.9 mL, 20.5 mmol, 5 equiv), and CH_2Cl_2 (13.7 mL, 0.30 M). The crude material was purified by column chromatography (3% EtOAc in hexanes) to afford **5i** as a light yellow oil (303 mg, 34% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.63 (d, *J* = 2.1 Hz, 1H), 6.81 (dd, *J* = 7.8, 0.5 Hz, 1H), 6.71 – 6.65 (m, 2H), 5.97 (s, 2H), 4.76 (d, *J* = 1.4 Hz, 1H), 4.67 (d, *J* = 0.5 Hz, 1H), 3.70 – 3.62 (m, 1H), 2.80 (dd, *J* = 15.1, 6.8 Hz, 1H), 2.40 (dd, *J* = 14.8, 8.0 Hz, 1H), 1.71 (d, *J* = 0.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.1, 148.4, 147.3, 142.1, 129.7, 122.3, 113.0, 109.0, 108.9, 101.3, 56.9, 37.8, 22.7. **IR** (ATR): 2898, 1721, 1504, 1485, 1441, 1244, 1037, 934, 895, 808 cm^{-1}. **HRMS** calculated for $C_{13}H_{14}O_3NH_4$ $[M+NH_4]^+$ 236.1287, found 236.1287.



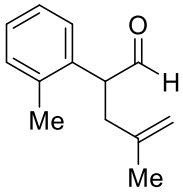
4-methyl-2-(thiophen-3-yl)pent-4-enal (5j): The title compound was prepared following the general procedure for Swern oxidation using **S4j** (1.07 g, 5.9 mmol, 1 equiv), oxalyl chloride (0.65 mL, 7.6 mmol, 1.3 equiv), DMSO (1.2 mL, 17.5 mmol, 3 equiv), Et_3N (4.1 mL, 29.2 mmol, 5 equiv), and CH_2Cl_2 (19.5 mL, 0.30 M). The crude material was purified by column chromatography (3% EtOAc in hexanes) to afford **5j** as a light yellow oil (777 mg, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.61 (d, *J* = 2.5 Hz, 1H), 7.36 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.14 (d, *J* = 2.2 Hz, 1H), 6.99 (d, *J* = 4.9 Hz, 1H), 4.79 (s, 1H), 4.71 (s, 1H), 3.89 (td, *J* = 7.4, 2.2 Hz, 1H), 2.82 (dd, *J* = 14.6, 7.6 Hz, 1H), 2.48 (dd, *J* = 14.7, 7.2 Hz, 1H), 1.73 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.7, 142.0, 136.3, 127.4, 126.6, 122.9, 113.0, 52.5, 37.7, 22.7. **IR** (ATR): 2936, 2818, 2718, 1723, 1650, 1376, 1076, 892, 777, 642 cm^{-1}. **HRMS** calculated for $C_{10}H_{12}SONH_4$ $[M+NH_4]^+$ 198.0953, found 198.0947.

General Procedure for Oxidation of Alcohols with IBX

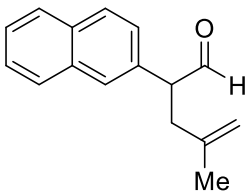
To a round bottom flask was added alcohol **S4** (1 equiv) and DMSO (0.25 M). IBX[7] (1.1 equiv) was added, and the resulting mixture was stirred at rt for 2 h. The reaction mixture was quenched with H_2O and filtered. The filtrate was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography to afford aldehyde **5**.



4-methyl-2-(*p*-tolyl)pent-4-enal (5b): The title compound was prepared following the general oxidation procedure with IBX using **S4b** (380 mg, 2.0 mmol, 1 equiv), IBX (616 mg, 2.2 mmol, 1.1 equiv), and DMSO (8 mL, 0.25 M). The crude material was purified by column chromatography (3% EtOAc in hexanes) to afford **5b** as a colorless oil (311 mg, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.66 (d, *J* = 2.2 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 4.76 (d, *J* = 1.7 Hz, 1H), 4.67 (d, *J* = 0.5 Hz, 1H), 3.72 (td, *J* = 7.5, 2.2 Hz, 1H), 2.84 (dd, *J* = 14.8, 7.1 Hz, 1H), 2.44 (dd, *J* = 14.8, 7.9 Hz, 1H), 2.35 (s, 3H), 1.71 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.5, 142.3, 137.5, 133.0, 129.9, 128.8, 112.9, 56.9, 37.7, 22.8, 21.2. **IR** (ATR): 2921, 2716, 1721, 1650, 1513, 1445, 1376, 1021, 890, 810 cm^{-1}. **HRMS** calculated for $C_{13}H_{16}O$ $[M]^+$ 188.1201, found 188.1208.

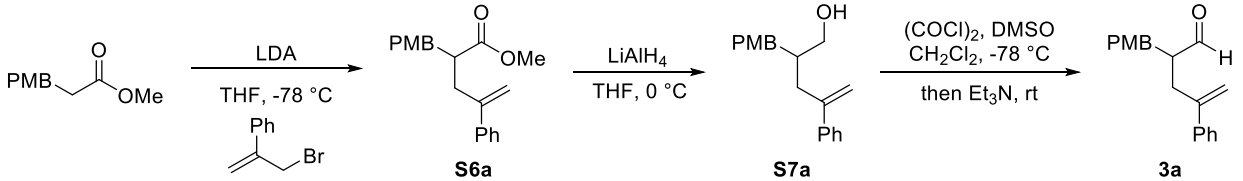


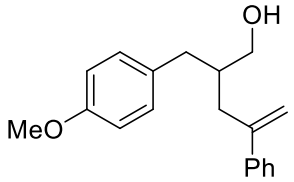
4-methyl-2-(*o*-tolyl)pent-4-enal (5c): The title compound was prepared following the general oxidation procedure with IBX using **S4c** (380 mg, 2.0 mmol, 1 equiv), IBX (616 mg, 2.2 mmol, 1.1 equiv), and DMSO (8 mL, 0.25 M). The crude material was purified by column chromatography (3% EtOAc in hexanes) to afford **5c** as a colorless oil (346 mg, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.63 (d, *J* = 2.1 Hz, 1H), 7.26 – 7.19 (m, 3H), 7.14 – 7.10 (m, 1H), 4.80 – 4.73 (m, 1H), 4.69 (dd, *J* = 1.7, 0.8 Hz, 1H), 4.01 (td, *J* = 7.3, 2.1 Hz, 1H), 2.89 (dd, *J* = 14.7, 7.5 Hz, 1H), 2.47 – 2.34 (m, 4H), 1.73 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.2, 142.4, 137.2, 134.7, 131.1, 128.0, 127.6, 126.7, 112.8, 53.4, 37.5, 22.9, 20.0. **IR** (ATR): 2935, 2717, 1720, 1650, 1490, 1445, 1377, 891, 755, 724 cm^{-1}. **HRMS** calculated for $C_{13}H_{16}ONa$ $[M+Na]^+$ 211.1099, found 211.1106.



4-methyl-2-(naphthalen-2-yl)pent-4-enal (5d): The title compound was prepared following the general oxidation procedure with IBX using **S4d** (453 mg, 2.0 mmol, 1 equiv), IBX (616 mg, 2.2 mmol, 1.1 equiv), and DMSO (8 mL, 0.25 M). The crude material was purified by column chromatography (3% EtOAc in hexanes) to afford **5d** as a colorless oil (212.6 mg, 47% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.76 (d, *J* = 2.1 Hz, 1H), 7.89 – 7.80 (m, 3H), 7.70 (s, 1H), 7.54 – 7.46 (m, 2H), 7.34 (dd, *J* = 8.4, 1.8 Hz, 1H), 4.77 (s, 1H), 4.71 (s, 1H), 3.94 (td, *J* = 7.6, 2.1 Hz, 1H), 2.96 (dd, *J* = 15.0, 6.9 Hz, 1H), 2.58 (dd, *J* = 14.9, 7.9 Hz, 1H), 1.75 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.3, 142.1, 133.7, 133.5, 132.9, 129.0, 128.0, 127.89, 127.86, 126.6, 126.3, 113.1, 57.5, 37.8, 22.8. **IR** (ATR): 2935, 2716, 1720, 1650, 1507, 1441, 891, 857, 816, 746 cm^{-1}. **HRMS** calculated for $C_{16}H_{16}ONa$ $[M+Na]^+$ 247.1099, found 247.1096.

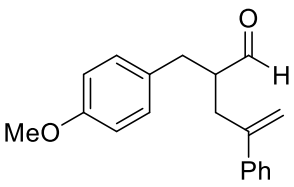
Preparation of Aldehyde 3a





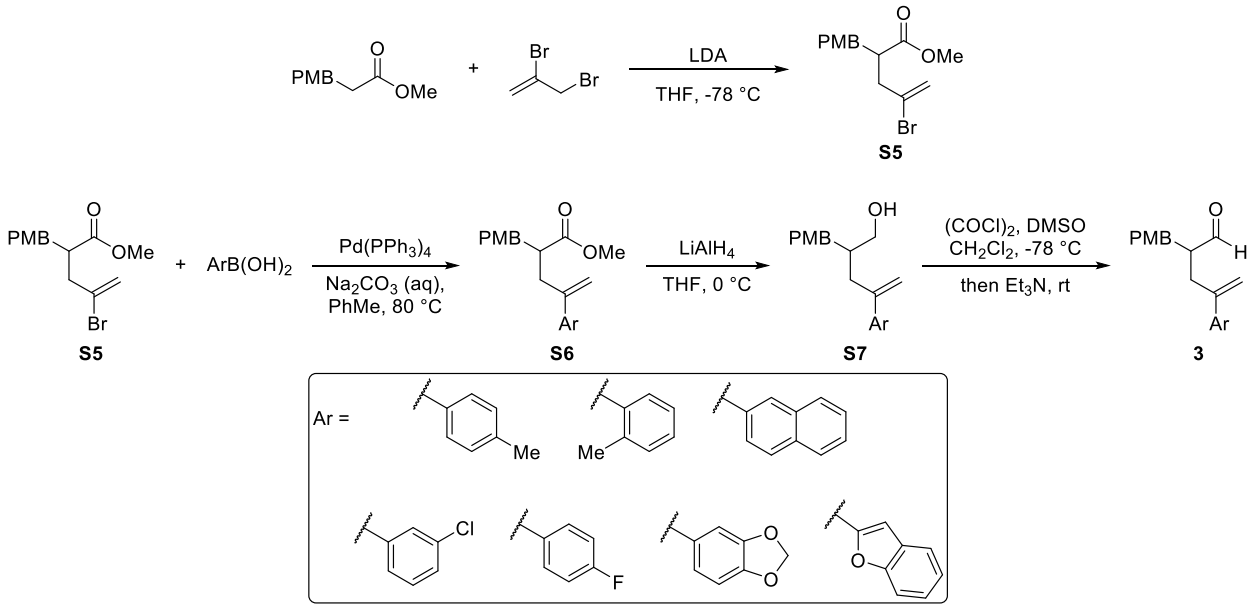
2-(4-methoxybenzyl)-4-phenylpent-4-en-1-ol (S7a): To an oven-dried round bottom flask was added ^{i}Pr$_2$NH (2.1 mL, 15 mmol, 1.3 equiv) and THF (25 mL), and the resulting solution was cooled to -78 °C. Then, ^{n}BuLi (5.8 mL, 14.4 mmol, 1.2 equiv, 2.5 M in THF) was added dropwise, and the resulting mixture was stirred for 1 hr. A solution of methyl 3-(4-methoxyphenyl)propanoate (2.33 g, 12 mmol, 1.0 equiv) in THF (10 mL) was added dropwise, and the resulting mixture was stirred for 1 h. Next, (3-bromoprop-1-en-2-yl)benzene[8] (3.55 g, 18 mmol, 1.5 equiv) was added, and the reaction mixture was stirred for 3 h. The reaction was quenched with saturated aqueous NH_4Cl and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and concentrated *in vacuo*. The ester **S6a** was used without further purification. Crude **S6a** was dissolved in THF (24 mL, 0.50 M), and the solution was cooled to 0 °C. $LiAlH_4$ (683 mg, 18 mmol, 1.5 equiv) was

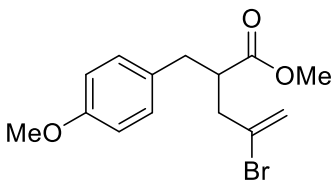
added portionwise, and the resulting mixture was stirred at 0 °C for 30 min. The reaction was quenched using the Fieser method, filtered through celite, and concentrated *in vacuo*. The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S7a** as a colorless oil (1.74 g, 52% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 5H), 7.06 – 7.00 (m, 2H), 6.85 – 6.79 (m, 2H), 5.34 (d, *J* = 1.6 Hz, 1H), 5.13 (d, *J* = 1.4 Hz, 1H), 3.80 (s, 3H), 3.57 – 3.45 (m, 2H), 2.66 – 2.51 (m, 4H), 1.93 – 1.81 (m, 1H), 1.27 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 147.4, 140.9, 132.6, 130.2, 128.5, 127.6, 126.4, 114.4, 113.9, 64.7, 55.4, 41.1, 37.2, 36.7. **IR** (ATR): 3360, 2930, 1611, 1511, 1442, 1300, 1244, 1177, 1027, 897, 779 cm^{-1}. **HRMS** calculated for $C_{19}H_{22}O_2Na$ $[M+Na]^+$ 305.1518, found 305.1505.



2-(4-methoxybenzyl)-4-phenylpent-4-enal (3a): To an oven-dried round bottom flask was added oxalyl chloride (1.1 mL, 12.4 mmol, 2 equiv) and CH_2Cl_2 (14 mL). The mixture was cooled to -78 °C, and DMSO (1.3 mL, 18.6 mmol, 3 equiv) was added. The resulting mixture was stirred for 10 min. Alcohol **S7a** (1.7 g, 6.2 mmol, 1.0 equiv) was added dropwise as a solution in CH_2Cl_2 (14 mL), and the resulting mixture was stirred for 15 min. Et_3N (5.2 mL, 37.2 mmol, 6 equiv) was added, and the resulting mixture was allowed to warm to rt and stirred for 10 min. The reaction mixture was quenched with H_2O and extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and concentrated *in vacuo*. The crude material was purified by column chromatography (50% CH_2Cl_2 in hexanes) to afford **3a** as a light yellow oil (1.27 g, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.67 (d, *J* = 2.0 Hz, 1H), 7.36 – 7.28 (m, 5H), 7.05 – 6.97 (m, 2H), 6.84 – 6.79 (m, 2H), 5.36 (d, *J* = 1.2 Hz, 1H), 5.13 (d, *J* = 1.2 Hz, 1H), 3.79 (s, 3H), 2.90 (ddd, *J* = 9.2, 3.6, 1.6 Hz, 2H), 2.78 – 2.68 (m, 2H), 2.66 – 2.58 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.3, 158.4, 145.6, 140.4, 130.6, 130.2, 128.6, 127.9, 126.4, 115.2, 114.1, 55.4, 51.7, 34.8, 34.2. **IR** (ATR): 2933, 2835, 1723, 1611, 1511, 1245, 1178, 1034, 901, 779, 704 cm^{-1}. **HRMS** calculated for $C_{19}H_{20}O_2Na$ $[M+Na]^+$ 303.1361, found 303.1367.

Preparation of Aldehydes 3b-h





methyl 4-bromo-2-(4-methoxybenzyl)pent-4-enoate (S5): To an oven-dried round bottom flask was added ^{i}Pr$_2$NH (3.4 mL, 24 mmol, 1.2 equiv) and THF (60 mL, 0.33 M), and the resulting solution was cooled to -78 °C. Then, ^{n}BuLi (8.8 mL, 22 mmol, 1.1 equiv, 2.5 M in THF) was added dropwise, and the resulting mixture was stirred for 45 min. A solution of methyl 3-(4-methoxyphenyl)propanoate (3.88 g, 20 mmol, 1 equiv) in THF (10 mL) was added dropwise, and the resulting mixture was allowed to stir for 1 h. Next, 2,3-dibromoprop-1-ene (5.33 g, 1.2 equiv, 90 wt%) was added, and the reaction mixture was stirred for 2 h. The reaction was quenched with saturated aqueous NH_4Cl and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and

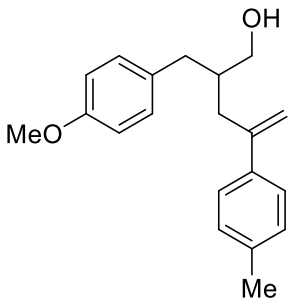
concentrated *in vacuo*. The residue was purified by column chromatography (3% EtOAc in hexanes) to afford **S5** as a colorless oil (4.74 g, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 5.64 (s, 1H), 5.47 (d, *J* = 1.5 Hz, 1H), 3.79 (s, 3H), 3.61 (s, 3H), 3.12 – 3.01 (m, 1H), 2.92 – 2.73 (m, 3H), 2.55 (dd, *J* = 14.6, 6.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.8, 158.5, 131.2, 130.5, 130.0, 119.1, 114.0, 55.4, 51.8, 46.4, 43.4, 36.8. **IR** (ATR): 2951, 1733, 1628, 1612, 1512, 1435, 1246, 1176, 1034, 893 cm^{-1}. **HRMS** calculated for $C_{14}H_{17}BrO_3Na$ $[M+Na]^+$ 335.0259, found 335.0275.

General Procedure for Suzuki Cross-coupling

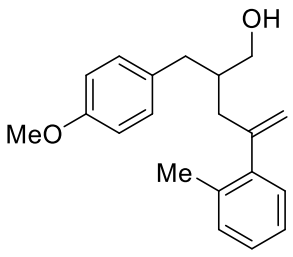
To a round bottom flask was charged $Pd(PPh_3)_4$ (1 mol%), the appropriate arylboronic acid (1.2 equiv), **S5** (1 equiv), Na_2CO_3 (3.0 equiv, 2 M in H_2O), and PhMe (0.20 M). The resulting mixture was stirred at 80 °C overnight. The reaction was cooled to rt and quenched with saturated aqueous NH_4Cl and extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and concentrated *in vacuo*. The ester **S6** was used without further purification.

General Procedure for Ester Reduction

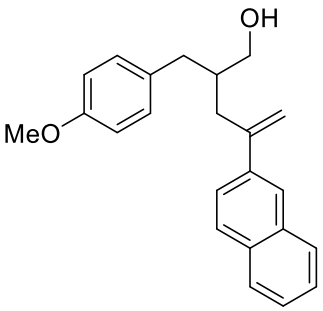
The crude ester **S6** was dissolved in THF (0.50 M), and the resulting solution was cooled to 0 °C. $LiAlH_4$ (1.5 equiv) was added portionwise, and the resulting mixture was stirred for 30 min. The reaction was quenched using the Fieser method, filtered through celite, and concentrated *in vacuo*. The residue was purified by column chromatography to afford alcohol **S7**.



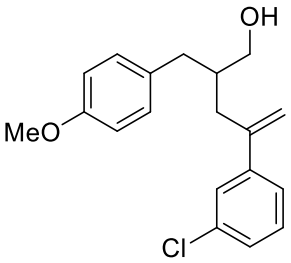
2-(4-methoxybenzyl)-4-(*p*-tolyl)pent-4-en-1-ol (S7b): The title compound was prepared following the general procedures for Suzuki cross-coupling and ester reduction using **S5** (940 mg, 3.0 mmol, 1 equiv), *p*-tolylboronic acid (490 mg, 3.6 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (34.7 mg, 0.030 mmol, 1 mol%), Na_2CO_3 (4.5 mL, 9.0 mmol, 3.0 equiv, 2 M in H_2O), and PhMe (15 mL, 0.20 M). Crude **S6b** (1 equiv) was reduced to **S7b** using $LiAlH_4$ (171 mg, 4.5 mmol, 1.5 equiv) and THF (6.0 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S7b** as a colorless oil (787 mg, 89% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 5.32 (s, 1H), 5.09 (s, 1H), 3.81 (s, 3H), 3.51 (s, 2H), 2.61 (dd, *J* = 7.2, 2.9 Hz, 2H), 2.56 (d, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 1.95 – 1.81 (m, 1H), 1.28 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 147.2, 137.9, 137.4, 132.6, 130.2, 129.2, 126.3, 113.9, 113.6, 64.7, 55.4, 41.1, 37.3, 36.8, 21.2. **IR** (ATR): 3369, 2920, 1611, 1510, 1442, 1244, 1177, 1031, 894, 825 cm^{-1}. **HRMS** calculated for $C_{20}H_{24}O_2H$ $[M+H]^+$ 297.1855, found 297.1856.



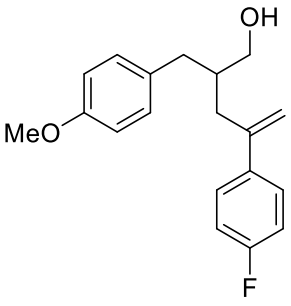
2-(4-methoxybenzyl)-4-(*o*-tolyl)pent-4-en-1-ol (S7c): The title compound was prepared following the general procedures for Suzuki cross-coupling and ester reduction using **S5** (940 mg, 3.0 mmol, 1 equiv), *o*-tolylboronic acid (490 mg, 3.6 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (34.7 mg, 0.030 mmol, 1 mol%), Na_2CO_3 (4.5 mL, 9.0 mmol, 3.0 equiv, 2 M in H_2O), and PhMe (15 mL, 0.20 M). Crude **S6c** (1 equiv) was reduced to **S7c** using $LiAlH_4$ (171 mg, 4.5 mmol, 1.5 equiv) and THF (6.0 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S7c** as a colorless oil (821 mg, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 – 7.13 (m, 3H), 7.11 (d, *J* = 6.7 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 5.27 (d, *J* = 1.0 Hz, 1H), 5.01 (d, *J* = 2.0 Hz, 1H), 3.79 (s, 3H), 3.57 – 3.45 (m, 2H), 2.66 (dd, *J* = 13.8, 6.2 Hz, 1H), 2.59 – 2.48 (m, 2H), 2.40 (dd, *J* = 14.4, 6.6 Hz, 1H), 2.29 (s, 3H), 1.84 – 1.73 (m, 1H), 1.22 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 148.6, 142.4, 135.0, 132.5, 130.5, 130.1, 128.6, 127.1, 125.7, 116.2, 113.9, 64.7, 55.4, 40.8, 39.2, 36.5, 20.1. **IR** (ATR): 3367, 2926, 1611, 1511, 1441, 1243, 1177, 1032, 903, 732 cm^{-1}. **HRMS** calculated for $C_{20}H_{24}O_2Na$ $[M+Na]^+$ 319.1674, found 319.1664.



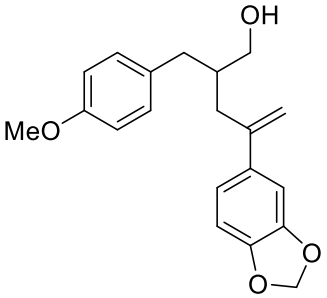
2-(4-methoxybenzyl)-4-(naphthalen-2-yl)pent-4-en-1-ol (S7d): The title compound was prepared following the general procedures for Suzuki cross-coupling and ester reduction using **S5** (940 mg, 3.0 mmol, 1 equiv), 2-naphthylboronic acid (619 mg, 3.6 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (34.7 mg, 0.030 mmol, 1 mol%), Na_2CO_3 (4.5 mL, 9.0 mmol, 3.0 equiv, 2 M in H_2O), and PhMe (15 mL, 0.20 M). Crude **S6d** (1 equiv) was reduced to **S7d** using $LiAlH_4$ (171 mg, 4.5 mmol, 1.5 equiv) and THF (6.0 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S7d** as a white solid (851 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.73 (m, 3H), 7.66 (s, 1H), 7.54 – 7.49 (m, 1H), 7.49 – 7.43 (m, 2H), 7.08 – 7.02 (m, 2H), 6.87 – 6.80 (m, 2H), 5.50 (d, *J* = 1.5 Hz, 1H), 5.24 (d, *J* = 1.2 Hz, 1H), 3.82 (s, 3H), 3.56 (d, *J* = 4.6 Hz, 2H), 2.75 – 2.56 (m, 4H), 1.93 (tt, *J* = 7.6, 4.2 Hz, 1H), 1.34 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.1, 147.1, 137.9, 133.5, 133.0, 132.6, 130.3, 128.3, 128.0, 127.6, 126.2, 126.0, 125.1, 124.8, 114.9, 113.9, 64.8, 55.4, 41.3, 37.0, 36.9. **IR** (ATR): 3306, 2931, 1610, 1509, 1243, 1023, 886, 828, 809, 751 cm^{-1}. **HRMS** calculated for $C_{23}H_{24}O_2Na$ $[M+Na]^+$ 355.1674, found 355.1680.



4-(3-chlorophenyl)-2-(4-methoxybenzyl)pent-4-en-1-ol (S7e): The title compound was prepared following the general procedures for Suzuki cross-coupling and ester reduction using **S5** (940 mg, 3.0 mmol, 1 equiv), 3-chlorophenylboronic acid (563 mg, 3.6 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (34.7 mg, 0.030 mmol, 1 mol%), Na_2CO_3 (4.5 mL, 9.0 mmol, 3.0 equiv, 2 M in H_2O), and PhMe (15 mL, 0.20 M). Crude **S6e** (1 equiv) was reduced to **S7e** using $LiAlH_4$ (171 mg, 4.5 mmol, 1.5 equiv) and THF (6.0 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S7e** as a colorless oil (732 mg, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.20 (m, 3H), 7.17 (dd, *J* = 4.5, 1.9 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 5.34 (s, 1H), 5.16 (s, 1H), 3.80 (s, 3H), 3.56 – 3.47 (m, 2H), 2.64 (dd, *J* = 13.8, 7.4 Hz, 1H), 2.60 – 2.45 (m, 3H), 1.90 – 1.78 (m, 1H), 1.27 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.1, 146.2, 142.8, 134.5, 132.4, 130.2, 129.7, 127.7, 126.6, 124.6, 115.4, 114.0, 64.6, 55.4, 41.0, 36.9, 36.7. **IR** (ATR): 3359, 2929, 1511, 1441, 1299, 1244, 1177, 1031, 804, 789 cm^{-1}. **HRMS** calculated for $C_{19}H_{21}ClO_2Na$ $[M+Na]^+$ 339.1128, found 339.1129.

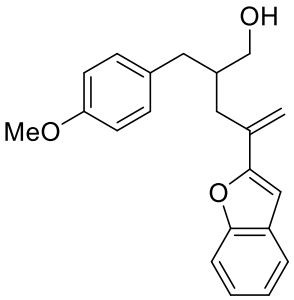


4-(4-fluorophenyl)-2-(4-methoxybenzyl)pent-4-en-1-ol (S7f): The title compound was prepared following the general procedures for Suzuki cross-coupling and ester reduction using **S5** (940 mg, 3.0 mmol, 1 equiv), 4-fluorophenylboronic acid (504 mg, 3.6 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (34.7 mg, 0.030 mmol, 1 mol%), Na_2CO_3 (4.5 mL, 9.0 mmol, 3.0 equiv, 2 M in H_2O), and PhMe (15 mL, 0.20 M). Crude **S6f** (1 equiv) was reduced to **S7f** using $LiAlH_4$ (171 mg, 4.5 mmol, 1.5 equiv) and THF (6.0 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S7f** as a colorless oil (808 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.21 (m, 2H), 7.00 (dd, *J* = 16.8, 8.5 Hz, 4H), 6.83 (d, *J* = 8.5 Hz, 2H), 5.28 (s, 1H), 5.11 (s, 1H), 3.80 (s, 3H), 3.56 – 3.42 (m, 2H), 2.67 – 2.45 (m, 4H), 1.89 – 1.75 (m, 1H), 1.35 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4 (d, *J* = 246.3 Hz), 158.1, 146.3, 136.9 (d, *J* = 3.3 Hz), 132.5, 130.2, 128.0 (d, *J* = 7.9 Hz), 115.3 (d, *J* = 21.3 Hz), 114.3 (d, *J* = 1.2 Hz), 113.9, 64.6, 55.4, 41.1, 37.3, 36.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.3. **IR** (ATR): 3344, 2929, 1601, 1508, 1244, 1177, 1030, 898, 839, 806 cm^{-1}. **HRMS** calculated for $C_{19}H_{21}FO_2Na$ $[M+Na]^+$ 323.1423, found 323.1409.



4-(benzo[*d*][1,3]dioxol-5-yl)-2-(4-methoxybenzyl)pent-4-en-1-ol (S7g): The title compound was prepared following the general procedures for Suzuki cross-coupling and ester reduction using **S5** (940 mg, 3.0 mmol, 1 equiv), 3,4-(methylenedioxy)phenylboronic acid (597 mg, 3.6 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (34.7 mg, 0.030 mmol, 1 mol%), Na_2CO_3 (4.5 mL, 9.0 mmol, 3.0 equiv, 2 M in H_2O), and PhMe (15 mL, 0.20 M). Crude **S6g** (1 equiv) was reduced to **S7g** using $LiAlH_4$ (171 mg, 4.5 mmol, 1.5 equiv) and THF (6.0 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S7g** as a yellow oil (880 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.07 – 7.01 (m, 2H), 6.85 – 6.76 (m, 4H), 6.74 (dd, *J* = 8.1, 0.5 Hz, 1H), 5.96 (dd, *J* = 1.4, 0.5 Hz, 1H), 5.95 (dd, *J* = 1.4, 0.4 Hz, 1H), 5.24 (d, *J* = 1.6 Hz, 1H), 5.04 (d, *J* = 1.1 Hz, 1H), 3.80 (s, 3H), 3.56 – 3.43 (m, 2H), 2.65 – 2.55 (m, 2H), 2.55 – 2.42 (m, 2H), 1.93 – 1.80 (m, 1H), 1.42 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 147.8,

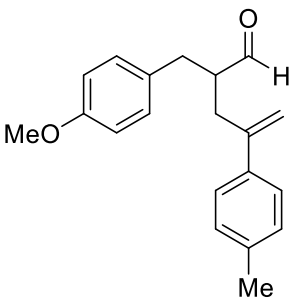
147.1, 146.8, 135.1, 132.6, 130.2, 119.9, 113.9, 113.4, 108.2, 107.0, 101.1, 64.6, 55.4, 41.1, 37.4, 36.7. **IR** (ATR): 3375, 2915, 1610, 1511, 1488, 1440, 1231, 1177, 1034, 935, 807 cm^{-1}. **HRMS** calculated for $C_{20}H_{22}O_4H$ $[M+H]^+$ 327.1596, found 327.1599.



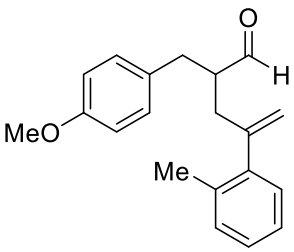
4-(benzofuran-2-yl)-2-(4-methoxybenzyl)pent-4-en-1-ol (S7h): The title compound was prepared following the general procedures for Suzuki cross-coupling and ester reduction using **S5** (940 mg, 3.0 mmol, 1 equiv), 2-benzofuranylboronic acid (583 mg, 3.6 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (34.7 mg, 0.030 mmol, 1 mol%), Na_2CO_3 (4.5 mL, 9.0 mmol, 3.0 equiv, 2 M in H_2O), and PhMe (15 mL, 0.20 M). Crude **S6h** (1 equiv) was reduced to **S7h** using $LiAlH_4$ (171 mg, 4.5 mmol, 1.5 equiv) and THF (6.0 mL, 0.50 M). The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S7h** as a yellow oil (379 mg, 39% yield). **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.48 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.44 (s, 1H), 5.87 (s, 1H), 5.21 (s, 1H), 3.77 (s, 3H), 3.59 – 3.48 (m, 2H), 2.65 (qd, *J* = 13.6, 7.2 Hz, 2H), 2.53 (dd, *J* = 14.2, 8.1 Hz, 1H), 2.42 (dd, *J* = 14.2, 5.9 Hz, 1H), 2.09 – 1.99 (m, 1H), 1.47 (s, 1H). **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 158.2, 156.4, 154.8, 136.3, 132.6, 130.3, 129.1, 124.7, 122.8, 121.1, 114.3, 113.8, 110.9, 103.2, 64.2, 55.3, 42.5, 36.8, 34.8. **IR** (ATR): 3387, 2930, 1611, 1511, 1452, 1244, 1176, 1031, 804, 743 cm^{-1}. **HRMS** calculated for $C_{21}H_{22}O_3Na$ $[M+Na]^+$ 345.1467, found 345.1482.

General Procedure for Swern Oxidation of Alcohols S7

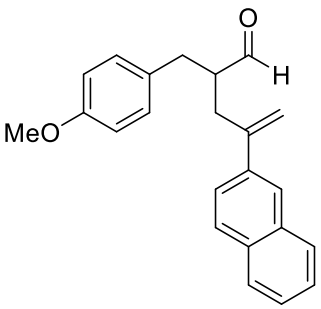
To an oven-dried round bottom flask was added oxalyl chloride (1.3 equiv) and CH_2Cl_2 (0.50 M). The mixture was cooled to -78 °C, and DMSO (3 equiv) was added. The resulting mixture was stirred for 30 min. Alcohol **S7** (1 equiv) was added as a solution in CH_2Cl_2 (0.50 M), and the resulting mixture was stirred for 30 min. Et_3N (5 equiv) was added, and the resulting mixture was allowed to warm to rt and stirred for 30 min. The reaction mixture was quenched with H_2O and extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography to afford aldehyde **3**.



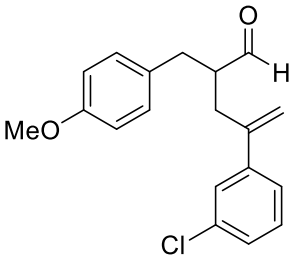
2-(4-methoxybenzyl)-4-(*p*-tolyl)pent-4-enal (3b): The title compound was prepared following the general procedure for Swern oxidation using **S7b** (754 mg, 2.5 mmol, 1 equiv), oxalyl chloride (0.28 mL, 3.3 mmol, 1.3 equiv), DMSO (0.54 mL, 7.6 mmol, 3 equiv), Et_3N (1.8 mL, 12.7 mmol, 5 equiv), and CH_2Cl_2 (10.2 mL, 0.25 M). The crude material was purified by column chromatography (3% EtOAc in hexanes) to afford **3b** as a light yellow oil (611 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.67 (d, *J* = 1.6 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 5.33 (s, 1H), 5.08 (s, 1H), 3.79 (s, 3H), 2.93 – 2.82 (m, 2H), 2.77 – 2.67 (m, 2H), 2.60 (dd, *J* = 14.4, 5.7 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.4, 158.4, 145.4, 137.7, 137.4, 130.7, 130.2, 129.3, 126.3, 114.4, 114.1, 55.4, 51.7, 34.8, 34.2, 21.2. **IR** (ATR): 2919, 2834, 1723, 1611, 1511, 1442, 1245, 1177, 1034, 825 cm^{-1}. **HRMS** calculated for $C_{20}H_{22}O_2NH_4$ $[M+ NH_4]^+$ 312.1964, found 312.1973.



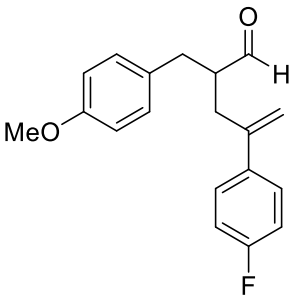
2-(4-methoxybenzyl)-4-(*o*-tolyl)pent-4-enal (3c): The title compound was prepared following the general procedure for Swern oxidation using **S7c** (763 mg, 2.6 mmol, 1 equiv), oxalyl chloride (0.29 mL, 3.3 mmol, 1.3 equiv), DMSO (0.55 mL, 7.7 mmol, 3 equiv), Et_3N (1.8 mL, 12.9 mmol, 5 equiv), and CH_2Cl_2 (10.3 mL, 0.25 M). The crude material was purified by column chromatography (3% EtOAc in hexanes) to afford **3c** as a colorless oil (713 mg, 94% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.63 (d, *J* = 2.3 Hz, 1H), 7.21 – 7.12 (m, 3H), 7.06 (d, *J* = 7.2 Hz, 1H), 7.03 – 6.96 (m, 2H), 6.83 – 6.76 (m, 2H), 5.26 (d, *J* = 1.5 Hz, 1H), 5.01 (d, *J* = 1.6 Hz, 1H), 3.79 (s, 3H), 2.88 (dd, *J* = 14.1, 7.7 Hz, 1H), 2.81 – 2.71 (m, 2H), 2.70 – 2.60 (m, 1H), 2.49 (dd, *J* = 14.7, 5.9 Hz, 1H), 2.26 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.3, 158.4, 146.9, 141.6, 135.1, 130.54, 130.48, 130.1, 128.7, 127.4, 125.8, 116.8, 114.1, 55.4, 51.5, 36.8, 34.4, 20.0. **IR** (ATR): 2931, 2835, 1724, 1611, 1512, 1245, 1178, 1034, 769, 732 cm^{-1}. **HRMS** calculated for $C_{20}H_{22}O_2Na$ $[M+ Na]^+$ 317.1518, found 317.1513.



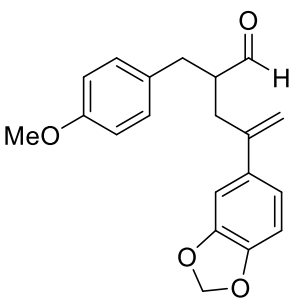
2-(4-methoxybenzyl)-4-(naphthalen-2-yl)pent-4-enal (3d): The title compound was prepared following the general procedure for Swern oxidation using **S7d** (807 mg, 2.4 mmol, 1 equiv), oxalyl chloride (0.27 mL, 3.2 mmol, 1.3 equiv), DMSO (0.52 mL, 7.3 mmol, 3 equiv), Et_3N (1.7 mL, 12.1 mmol, 5 equiv), and CH_2Cl_2 (9.7 mL, 0.25 M). The crude material was purified by column chromatography (3% EtOAc in hexanes) to afford **3d** as a white solid (685 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.72 (d, *J* = 1.5 Hz, 1H), 7.86 – 7.70 (m, 3H), 7.63 (s, 1H), 7.53 – 7.43 (m, 3H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 5.51 (s, 1H), 5.24 (s, 1H), 3.81 (s, 3H), 3.05 – 2.87 (m, 2H), 2.83 – 2.68 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.2, 158.4, 145.4, 137.4, 133.5, 133.1, 130.6, 130.2, 128.32, 128.27, 127.7, 126.4, 126.2, 125.1, 124.7, 115.7, 114.1, 55.4, 51.8, 34.6, 34.3. **IR** (ATR): 2929, 2834, 1717, 1611, 1511, 1245, 1177, 1031, 828, 816, 754 cm^{-1}. **HRMS** calculated for $C_{23}H_{22}O_2Na$ [M+ Na]$^+$ 353.1518, found 353.1518.



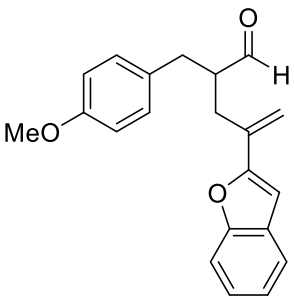
4-(3-chlorophenyl)-2-(4-methoxybenzyl)pent-4-enal (3e): The title compound was prepared following the general procedure for Swern oxidation using **S7e** (732 mg, 2.3 mmol, 1 equiv), oxalyl chloride (0.26 mL, 3.0 mmol, 1.3 equiv), DMSO (0.49 mL, 6.9 mmol, 3 equiv), Et_3N (1.6 mL, 11.6 mmol, 5 equiv), and CH_2Cl_2 (9.2 mL, 0.25 M). The crude material was purified by column chromatography (3% EtOAc in hexanes) to afford **3e** as a light yellow oil (710 mg, 98% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.68 (d, *J* = 1.9 Hz, 1H), 7.26 – 7.22 (m, 3H), 7.15 (dt, *J* = 6.4, 2.1 Hz, 1H), 7.04 – 6.99 (m, 2H), 6.85 – 6.81 (m, 2H), 5.36 (d, *J* = 0.5 Hz, 1H), 5.16 (d, *J* = 1.1 Hz, 1H), 3.80 (s, 3H), 2.96 – 2.82 (m, 2H), 2.74 – 2.65 (m, 2H), 2.61 – 2.54 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.9, 158.5, 144.5, 142.3, 134.6, 130.3, 130.2, 129.9, 128.0, 126.6, 124.6, 116.2, 114.2, 55.4, 51.6, 34.4, 34.2. **IR** (ATR): 2933, 2834, 1723, 1611, 1511, 1300, 1245, 1178, 1034, 790 cm^{-1}. **HRMS** calculated for $C_{19}H_{19}ClO_2Na$ [M+ Na]$^+$ 337.0971, found 337.0987.



4-(4-fluorophenyl)-2-(4-methoxybenzyl)pent-4-enal (3f): The title compound was prepared following the general procedure for Swern oxidation using **S7f** (773 mg, 2.6 mmol, 1 equiv), oxalyl chloride (0.29 mL, 3.0 mmol, 1.3 equiv), DMSO (0.55 mL, 7.7 mmol, 3 equiv), Et_3N (1.8 mL, 12.9 mmol, 5 equiv), and CH_2Cl_2 (10.3 mL, 0.25 M). The crude material was purified by column chromatography (3% EtOAc in hexanes) to afford **3f** as a colorless oil (721 mg, 94% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.67 (d, *J* = 2.0 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.00 (dd, *J* = 8.5, 8.0 Hz, 4H), 6.82 (d, *J* = 8.3 Hz, 2H), 5.29 (s, 1H), 5.11 (s, 1H), 3.79 (s, 3H), 2.94 – 2.82 (m, 2H), 2.74 – 2.64 (m, 2H), 2.58 (dd, *J* = 14.5, 4.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.1, 162.6 (d, *J* = 246.9 Hz), 158.5, 144.6, 136.4 (d, *J* = 3.3 Hz), 130.4, 130.2, 128.0 (d, *J* = 8.0 Hz), 115.5 (d, *J* = 21.4 Hz), 115.1 (d, *J* = 1.2 Hz), 114.1, 55.4, 51.7, 34.8, 34.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.8. **IR** (ATR): 2934, 2835, 1723, 1611, 1508, 1245, 1178, 1161, 1034, 839 cm^{-1}. **HRMS** calculated for $C_{19}H_{19}FO_2Na$ [M+ Na]$^+$ 321.1267, found 321.1264.

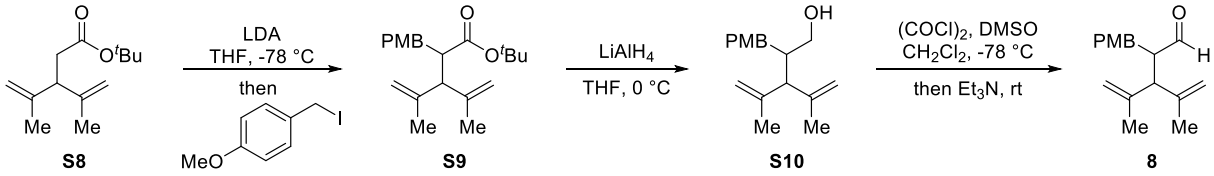


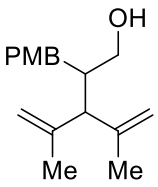
4-(benzo[*d*][1,3]dioxol-5-yl)-2-(4-methoxybenzyl)pent-4-enal (3g): The title compound was prepared following the general procedure for Swern oxidation using **S7g** (756 mg, 2.3 mmol, 1 equiv), oxalyl chloride (0.26 mL, 3.0 mmol, 1.3 equiv), DMSO (0.49 mL, 6.9 mmol, 3 equiv), Et_3N (1.6 mL, 11.6 mmol, 5 equiv), and CH_2Cl_2 (9.3 mL, 0.25 M). The crude material was purified by column chromatography (3% EtOAc in hexanes) to afford **3g** as a colorless oil (595 mg, 79% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.66 (d, *J* = 1.9 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.85 – 6.78 (m, 3H), 6.75 (d, *J* = 1.0 Hz, 2H), 5.98 – 5.93 (m, 2H), 5.25 (s, 1H), 5.04 (s, 1H), 3.79 (s, 3H), 2.86 (ddd, *J* = 21.6, 15.3, 8.3 Hz, 2H), 2.75 – 2.66 (m, 2H), 2.55 (dd, *J* = 14.3, 5.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.2, 158.4, 148.0, 147.4, 145.1, 134.6, 130.6, 130.2, 119.9, 114.3, 114.1, 108.3, 107.0, 101.3, 55.4, 51.7, 35.0, 34.2. **IR** (ATR): 2906, 2835, 1722, 1611, 1512, 1440, 1231, 1178, 1035, 809 cm^{-1}. **HRMS** calculated for $C_{20}H_{20}O_4Na$ [M+ Na]$^+$ 347.1259, found 347.1263.



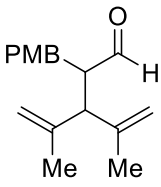
4-(benzofuran-2-yl)-2-(4-methoxybenzyl)pent-4-enal (3h): The title compound was prepared following the general procedure for Swern oxidation using **S7h** (379 mg, 1.2 mmol, 1 equiv), oxalyl chloride (0.13 mL, 1.5 mmol, 1.3 equiv), DMSO (0.25 mL, 3.5 mmol, 3 equiv), Et_3N (0.82 mL, 5.9 mmol, 5 equiv), and CH_2Cl_2 (4.8 mL, 0.25 M). The crude material was purified by column chromatography (3% EtOAc in hexanes) to afford **3h** as a yellow oil (297 mg, 79% yield). **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 9.70 (d, *J* = 1.9 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.43 (s, 1H), 5.87 (s, 1H), 5.21 (s, 1H), 3.76 (s, 3H), 2.93 (ddd, *J* = 20.4, 14.0, 7.0 Hz, 2H), 2.79 (ddd, *J* = 19.5, 13.9, 7.0 Hz, 2H), 2.53 (dd, *J* = 14.3, 5.2 Hz, 1H). **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 203.6, 158.6, 155.7, 154.8, 134.9, 130.5, 130.2, 128.9, 124.9, 122.9, 121.2, 114.9, 114.1, 111.0, 103.1, 55.3, 52.6, 34.5, 32.0. **IR** (ATR): 2933, 2834, 1723, 1611, 1511, 1452, 1245, 1176, 1034, 806, 743 cm^{-1}. **HRMS** calculated for $C_{21}H_{20}O_3Na$ [M+ Na]$^+$ 343.1310, found 343.1302.

Preparation of Aldehyde 8



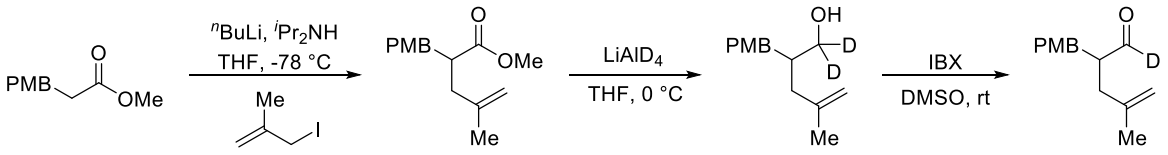


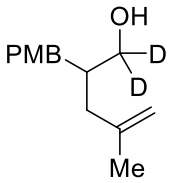
2-(4-methoxybenzyl)-4-methyl-3-(prop-1-en-2-yl)pent-4-en-1-ol (S10): To an oven-dried round bottom flask was added ^{i}Pr$_2$NH (3.5 mL, 25 mmol, 1.3 equiv) and THF (47 mL, 0.33 M), and the resulting solution was cooled to -78 °C. Then, ^{n}BuLi (9.6 mL, 24 mmol, 1.2 equiv, 2.5 M in THF) was added dropwise, and the resulting mixture was stirred for 1 hr. A solution of ester **S8**[9] (4.21 g, 20 mmol, 1.0 equiv) in THF (10 mL) was added dropwise, and the resulting mixture was stirred for 1 h. Then, 4-methoxybenzyl iodide[10] (7.44 g, 30 mmol, 1.5 equiv) was added, and the reaction mixture was stirred for 3 h. The reaction was quenched with saturated aqueous NH_4Cl and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and concentrated *in vacuo*. The ester **S9** was used without further purification. Crude **S9** was dissolved in THF (40 mL, 0.50 M), and the solution was cooled to 0 °C. $LiAlH_4$ (1.1 g, 30 mmol, 1.5 equiv) was added portionwise, and the resulting mixture was stirred at 60 °C for 12 h. The reaction was cooled to rt and quenched using the Fieser method. The resulting mixture was filtered through celite and concentrated *in vacuo*. The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S10** as a colorless oil (3.16 g, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 5.02 (s, 1H), 4.95 (s, 1H), 4.90 (s, 1H), 4.87 (s, 1H), 3.80 (s, 3H), 3.55 (dd, *J* = 11.3, 3.7 Hz, 1H), 3.48 (dd, *J* = 11.3, 3.1 Hz, 1H), 2.81 (dd, *J* = 13.9, 3.1 Hz, 1H), 2.72 (d, *J* = 11.4 Hz, 1H), 2.47 (dd, *J* = 13.8, 10.5 Hz, 1H), 2.04 (ddd, *J* = 14.3, 7.2, 3.4 Hz, 1H), 1.76 (s, 3H), 1.69 (s, 3H), 1.39 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 145.7, 144.5, 133.1, 130.2, 113.9, 112.8, 112.3, 61.8, 56.3, 55.4, 41.8, 34.0, 21.8, 20.2. **IR** (ATR): 3411, 2936, 1611, 1510, 1442, 1244, 1177, 1035, 890, 808 cm^{-1}. **HRMS** calculated for $C_{17}H_{24}O_2Na$ [M+Na]$^+$ 283.1674, found 283.1687.



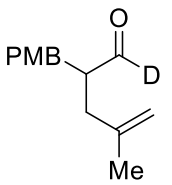
2-(4-methoxybenzyl)-4-methyl-3-(prop-1-en-2-yl)pent-4-enal (8): To an oven-dried round bottom flask was added oxalyl chloride (1.0 mL, 11.5 mmol, 1.3 equiv) and CH_2Cl_2 (18 mL, 0.50 M). The mixture was cooled to -78 °C, and DMSO (1.9 mL, 26.5 mmol, 3 equiv) was added. The resulting mixture was stirred for 30 min. Alcohol **S10** (2.30 g, 8.83 mmol, 1.0 equiv) was added as a solution in CH_2Cl_2 (18 mL, 0.50 M), and the resulting mixture was stirred for 30 min. Et_3N (6.2 mL, 44.2 mmol, 5 equiv) was added, and the resulting mixture was allowed to warm to rt and stirred for 30 min. The reaction mixture was quenched with H_2O and extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography (5% EtOAc in hexanes) to afford **8** as a colorless oil (1.71 g, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.50 (d, *J* = 3.1 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 5.05 (s, 1H), 4.97 (s, 1H), 4.91 (s, 1H), 4.80 (s, 1H), 3.78 (s, 3H), 3.01 – 2.92 (m, 2H), 2.89 – 2.82 (m, 1H), 2.70 (dd, *J* = 14.4, 8.7 Hz, 1H), 1.71 (s, 3H), 1.67 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.5, 158.3, 143.7, 142.6, 130.7, 130.1, 114.4, 114.1, 113.6, 55.4, 55.1, 53.2, 34.0, 21.6, 19.9. **IR** (ATR): 2938, 2835, 1727, 1612, 1512, 1245, 1178, 1035, 896, 827 cm^{-1}. **HRMS** calculated for $C_{17}H_{22}O_2Na$ [M+Na]$^+$ 281.1518, found 281.1515.

Preparation of Aldehyde 1a-d



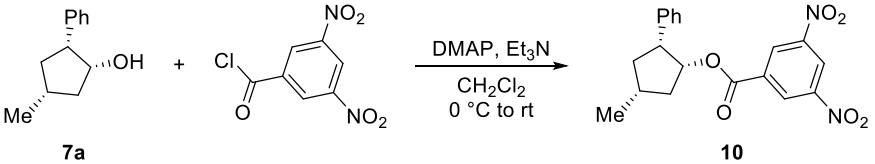


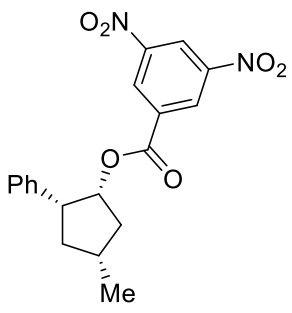
2-(4-methoxybenzyl)-4-methylpent-4-en-1,1-*d*$_2$-1-ol (S2a-*d*): To an oven-dried round bottom flask was added ^{i}Pr$_2$NH (0.85 mL, 6.0 mmol, 1.2 equiv) and THF (10 mL, 0.33 M), and the resulting solution was cooled to -78 °C. Then, ^{n}BuLi (2.2 mL, 5.5 mmol, 1.1 equiv, 2.5 M in THF) was added dropwise, and the resulting mixture was allowed to stir for 45 min. A solution of methyl 3-(4-methoxyphenyl)propanoate (971 mg, 5.0 mmol, 1.0 equiv) in THF (5 mL) was added dropwise, and the resulting mixture was allowed to stir for 1 h. Then, methallyl iodide (1.1 g, 6.0 mmol, 1.2 equiv) was added, and the reaction mixture was allowed to stir for 2 h. The reaction was quenched with saturated aqueous NH_4Cl and extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and concentrated *in vacuo*. The ester **S1a** was used without further purification. Crude **S1a** was dissolved in THF (10 mL, 0.50 M), and the solution was cooled to 0 °C. $LiAlD_4$ (315 mg, 7.5 mmol, 1.5 equiv) was added portionwise, and the resulting mixture was stirred for 1 h. The reaction was quenched using the Fieser method. The resulting mixture was filtered through celite and concentrated *in vacuo*. The crude material was purified by column chromatography (10% EtOAc in hexanes) to afford **S2a-*d*** as a colorless oil (478 mg, 43% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 4.81 (s, 1H), 4.78 (s, 1H), 3.80 (s, 3H), 2.58 (d, *J* = 6.8 Hz, 2H), 2.17 – 2.07 (m, 1H), 2.00 (ddd, *J* = 21.2, 13.9, 6.6 Hz, 2H), 1.73 (s, 3H), 1.37 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.0, 144.7, 132.7, 130.2, 113.9, 112.2, 65.1 – 63.7 (m), 55.4, 40.3, 40.3, 36.8, 22.4. **IR** (ATR): 3369, 2914, 1611, 1511, 1442, 1244, 1177, 1035, 888, 829 cm^{-1}. **HRMS** calculated for $C_{14}H_{18}D_2O_2Na$ $[M+Na]^+$ 245.1487, found 245.1489.



2-(4-methoxybenzyl)-4-methylpent-4-enal-1-*d* (1a-*d*): To a round bottom flask was added alcohol **S2a-*d*** (453 mg, 2.0 mmol, 1.0 equiv) and DMSO (8 mL, 0.25 M). IBX[7] (628 mg, 2.2 mmol, 1.1 equiv) was added, and the resulting mixture was stirred overnight at rt. The reaction mixture was quenched with H_2O (32 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography (5% EtOAc in hexanes) to afford **1a-*d*** as a colorless oil (365 mg, 82% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 4.84 (s, 1H), 4.75 (s, 1H), 3.79 (s, 3H), 2.90 (dd, *J* = 13.7, 7.5 Hz, 1H), 2.79 (dt, *J* = 13.9, 6.9 Hz, 1H), 2.71 (dd, *J* = 13.7, 6.1 Hz, 1H), 2.39 (dd, *J* = 14.8, 8.0 Hz, 1H), 2.15 (dd, *J* = 14.9, 6.3 Hz, 1H), 1.73 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.8 – 203.8 (m), 158.4, 142.3, 130.7, 130.1, 114.1, 113.0, 55.4, 51.4 – 51.2 (m), 37.2, 34.3, 22.6. **IR** (ATR): 2935, 2836, 1710, 1612, 1512, 1442, 1244, 1178, 1034, 830 cm^{-1}. **HRMS** calculated for $C_{14}H_{17}DO_2Na$ $[M+Na]^+$ 242.1267, found 242.1273.

4. Esterification of 7a

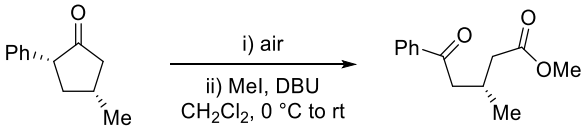




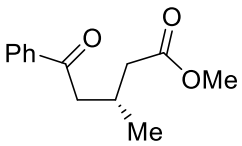
(1*R*,2*R*,4*R*)-4-methyl-2-phenylcyclopentyl 3,5-dinitrobenzoate (10): Alcohol **7a** (20.8 mg, 0.12 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (0.24 mL, 0.50 M) in a 1 dram vial equipped with a magnetic stir bar. Et_3N (33 mL, 0.24 mmol, 2.0 equiv) and DMAP (1.4 mg, 0.012 mmol, 10 mol%) were added. The resulting solution was cooled to 0 °C, and 3,5-dinitrobenzoyl chloride (40.8 mg, 0.18 mmol, 1.5 equiv) was added. The vial was then sealed with a Teflon-lined screw cap and stirred overnight. The reaction mixture was quenched with H_2O and extracted with CH_2Cl_2 (3 x 5 mL). The

combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and concentrated *in vacuo*. The title compound was isolated by preparative thin-layer chromatography (30% EtOAc in hexanes) as a yellow solid (37.3 mg, 85% yield, $[\alpha]^{24}_D$ = –112.2 (*c* 0.56, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.12 (t, *J* = 2.1 Hz, 1H), 8.78 (d, *J* = 2.1 Hz, 2H), 7.31 (dd, *J* = 12.6, 7.2 Hz, 4H), 7.15 (t, *J* = 7.1 Hz, 1H), 5.63 (td, *J* = 6.4, 3.6 Hz, 1H), 3.51 – 3.38 (m, 1H), 2.72 – 2.55 (m, 1H), 2.35 – 2.16 (m, 2H), 2.01 – 1.89 (m, 1H), 1.59 (ddd, *J* = 14.4, 8.3, 3.5 Hz, 1H), 1.32 – 1.11 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.0, 148.6, 139.0, 134.4, 129.2, 128.5, 128.4, 126.9, 122.1, 81.0, 50.3, 41.6, 38.5, 32.4, 21.0. **IR** (ATR): 3113, 2956, 1715, 1630, 1546, 1460, 1344, 1287, 1174, 754 cm^{-1}.

5. Oxidative Decomposition of 6a

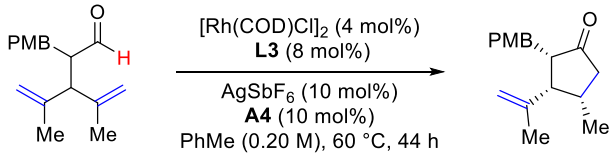


6a methyl ester of **6ab**

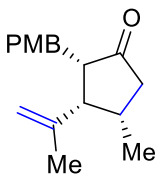


methyl (*R*)-3-methyl-5-oxo-5-phenylpentanoate: Ketone **6a** (12.0 mg, 0.069 mmol, 1.0 equiv) was allowed to stand in a 1 dram vial opened to air until full consumption of **6a** was observed by ^{1}H NMR (ca. 2 weeks). Then, CH_2Cl_2 (0.20 mL) and DBU (15 mL, 0.10 mmol, 1.5 equiv) was added to the crude material. The resulting mixture was cooled to 0 °C, and MeI (8.6 mL, 0.14 mmol, 2.0 equiv) was added. The vial was then sealed with a Teflon-lined screw cap and stirred overnight. The reaction mixture was concentrated *in vacuo*. The title compound was isolated by preparative thin-layer chromatography (5% EtOAc in hexanes) as a colorless oil (4.5 mg, 30% yield, $[\alpha]^{24}_D$ = +3.7 (*c* 0.30, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 3.68 (s, 3H), 3.11 (dd, *J* = 16.2, 5.9 Hz, 1H), 2.85 (dd, *J* = 16.3, 7.5 Hz, 1H), 2.69 (dq, *J* = 13.5, 6.7 Hz, 1H), 2.45 (dd, *J* = 15.3, 6.6 Hz, 1H), 2.33 (dd, *J* = 15.3, 7.0 Hz, 1H), 1.06 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 199.4, 173.2, 137.2, 133.2, 128.8, 128.3, 51.6, 45.0, 41.1, 27.0, 20.3. **IR** (ATR): 2954, 1732, 1682, 1448, 1368, 1211, 1159, 1002, 753, 690 cm^{-1}. **HRMS** calculated for $C_{13}H_{16}O_3Na$ $[M+Na]^+$ 243.0997, found 243.0996.

6. Hydroacylation of Aldehyde 8

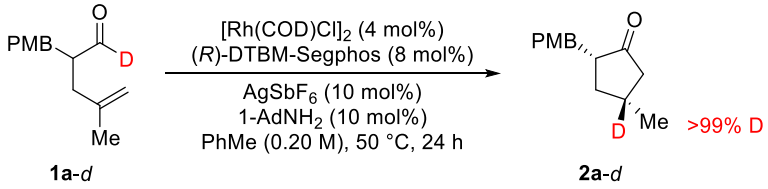


8 **9**

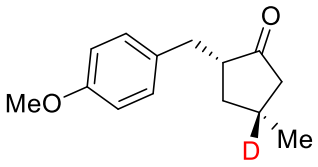


(2*S*,3*R*,4*S*)-2-(4-methoxybenzyl)-4-methyl-3-(prop-1-en-2-yl)cyclopentan-1-one (9): In a N_2-filled glovebox, $[Rh(COD)Cl]_2$ (2.0 mg, 0.0040 mmol, 4 mol%), (*R*)-DTBM-Segphos (10.7 mg, 0.0080 mmol, 8 mol%), and toluene (0.50 mL, 0.20 M) were added to a 1 dram vial equipped with a magnetic stir bar. The solution was stirred at 30 °C for 10 min. $AgSbF_6$ (3.4 mg, 0.010 mmol, 10 mol%), was added, and the resulting mixture was stirred 30 °C for 30 min. Aldehyde **8** (25.8 mg, 0.10 mmol, 1.0 equiv) and 1-$AdNH_2$ (1.5 mg, 0.010 mmol, 10 mol%) were added. The vial was then sealed with a Teflon-lined screw cap and stirred at 60 °C for 44 h. The reaction mixture was cooled to rt, filtered through celite, and concentrated *in vacuo*. The diastereoselectivity was determined by ^{1}H NMR analysis of the unpurified reaction mixture. The title compound was isolated by preparative thin-layer chromatography (5% EtOAc in hexanes) as a colorless oil (13.7 mg, 53% yield, >20:1:1:1 *dr*, >99% *ee*, $[\alpha]^{24}_D$ = +74.3 (*c* 0.56, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09 – 7.01 (m, 2H), 6.81 – 6.74 (m, 2H), 4.93 (dq, *J* = 2.9, 1.4 Hz, 1H), 4.83 (dd, *J* = 1.5, 0.6 Hz, 1H), 3.78 (s, 3H), 2.92 (dd, *J* = 14.1, 4.5 Hz, 1H), 2.72 (dd, *J* = 14.1, 5.5 Hz, 1H), 2.56 – 2.45 (m, 1H), 2.45 – 2.35 (m, 1H), 2.08 – 1.91 (m, 2H), 1.68 – 1.54 (m, 4H), 0.97 (d, *J* = 6.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 218.3, 158.1, 142.8, 131.4, 131.0, 115.1, 113.6, 57.2, 55.33, 55.26, 46.6, 32.9, 32.3, 17.88, 17.76. **IR** (ATR): 2954, 2915, 1738, 1611, 1511, 1441, 1244, 1177, 1035, 893 cm^{-1}. **HRMS** calculated for $C_{17}H_{22}O_2Na$ $[M+Na]^+$ 281.1518, found 281.1507. **Chiral SFC**: 250 mm CHIRALPAK IC, 3% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} = 13.6 min (minor), t_{R2} = 14.8 min (major).

7. Deuterium Labeling Experiment

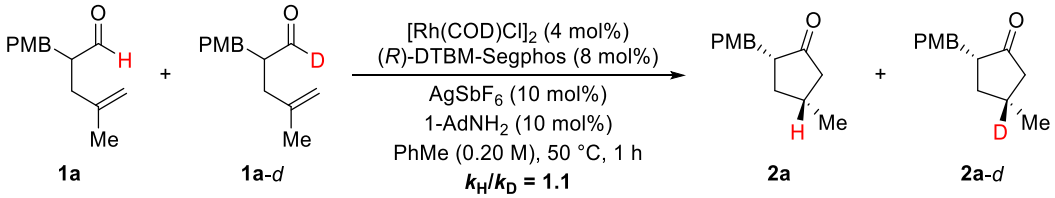


1a-*d* **2a**-*d*



(2*R*,4*R*)-2-(4-methoxybenzyl)-4-methylcyclopentan-1-one-4-*d* (2a-*d*): In a N_2-filled glovebox, $[Rh(COD)Cl]_2$ (2.0 mg, 0.0040 mmol, 4 mol%), (*R*)-DTBM-Segphos (10.7 mg, 0.0080 mmol, 8 mol%), and toluene (0.50 mL, 0.20 M) were added to a 1 dram vial equipped with a magnetic stir bar. The solution was stirred at 30 °C for 10 min. $AgSbF_6$ (3.4 mg, 0.010 mmol, 10 mol%), was added, and the resulting mixture was stirred 30 °C for 30 min. Aldehyde **1a**-*d* (21.9 mg, 0.10 mmol, 1.0 equiv) and 1-$AdNH_2$ (1.5 mg, 0.010 mmol, 10 mol%) were added. The vial was then sealed with a Teflon-lined screw cap and stirred at 50 °C for 24 h. The reaction mixture was cooled to rt, filtered through celite, and concentrated *in vacuo*. The diastereoselectivity was determined by ^{1}H NMR analysis of the unpurified reaction mixture. The title compound was isolated by preparative thin-layer chromatography (5% EtOAc in hexanes) as a white solid (18.2 mg, 83% yield, >20:1 *dr*, >99% *ee*, $[\alpha]^{24}_D$ = +71.2 (*c* 0.78, $CHCl_3$)). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 3.11 (dd, *J* = 13.8, 3.9 Hz, 1H), 2.56 – 2.44 (m, 2H), 2.44 – 2.35 (m, 1H), 2.20 – 2.10 (m, 1H), 1.71 (d, *J* = 18.5 Hz, 1H), 1.15 (t, *J* = 12.4 Hz, 1H), 1.09 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 219.9, 158.1, 132.2, 129.9, 114.0, 55.4, 53.1, 46.9, 38.2, 34.8, 29.3 (t, *J* = 19.6 Hz), 20.2. **IR** (ATR): 2953, 2867, 1736, 1611, 1511, 1455, 1243, 1177, 1034, 818 cm^{-1}. **HRMS** calculated for $C_{14}H_{17}DO_2Na$ $[M+Na]^+$ 242.1267, found 242.1278. **Chiral SFC**: 100 mm CHIRALPAK AD-H, 1% *i*-PrOH, 2.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} = 5.8 min (major), t_{R2} = 7.9 min (minor).

8. Kinetic Isotope Effect Experiment



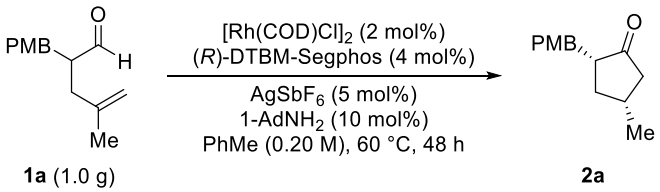
1a **1a**-*d* **2a** **2a**-*d*

In a N_2-filled glovebox, $[Rh(COD)Cl]_2$ (2.0 mg, 0.0040 mmol), (*R*)-DTBM-Segphos (10.7 mg, 0.0080 mmol), and toluene (0.25 mL) were added to a 1 dram vial equipped with a magnetic stir bar. The solution was stirred at 30 °C for 10 min. $AgSbF_6$ (3.4 mg, 0.010 mmol) was added, and the resulting mixture was stirred 30 °C for 30 min. Aldehydes **1a** (11.0 mg, 0.050 mmol) and **1a**-*d* (11.0 mg, 0.050 mmol) were added as a solution in toluene (0.25 mL). Then, 1-$AdNH_2$ (1.5 mg, 0.010 mmol) was added. The vial was then sealed with a Teflon-lined screw cap and stirred at 50 °C for 1 h. The reaction mixture was cooled to rt, filtered through celite, and concentrated *in vacuo*. The diastereoselectivity was determined by ^{1}H NMR analysis of the unpurified reaction mixture. The crude mixture was purified by preparative thin-layer chromatography (5% EtOAc in hexanes) to afford a mixture of **2a** and **2a**-*d* (3.9 mg, 18% yield). The ratio (1.1:1.0) of **2a** and **2a**-*d* was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 3.11 (dd, *J* = 13.7, 3.9 Hz, 1H), 2.55 – 2.45 (m, 2H), 2.44 – 2.35 (m, 1H), 2.16 (d, *J* = 12.1 Hz, 1H), 2.12 – 2.03 (m, **0.54H**), 1.77 – 1.66 (m, 1H), 1.22 – 1.12 (m, 1H), 1.10 (d, *J* = 6.3 Hz, 3H).

Recovered unreacted **1a** and **1a**-*d* (19.3 mg, 88% yield): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.66 (d, *J* = 2.5 Hz, **0.43H**), 7.09 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.84 (s, 1H), 4.75 (s, 1H), 3.79 (s, 3H), 2.90 (dd, *J* = 13.4, 7.4 Hz, 1H), 2.83 – 2.74 (m, 1H), 2.71 (dd, *J* = 13.4, 6.0 Hz, 1H), 2.39 (dd, *J* = 14.8, 7.9 Hz, 1H), 2.15 (dd, *J* = 14.7, 6.2 Hz, 1H), 1.72 (s, 3H).

9. Gram-scale Dynamic Kinetic Resolution of 1a

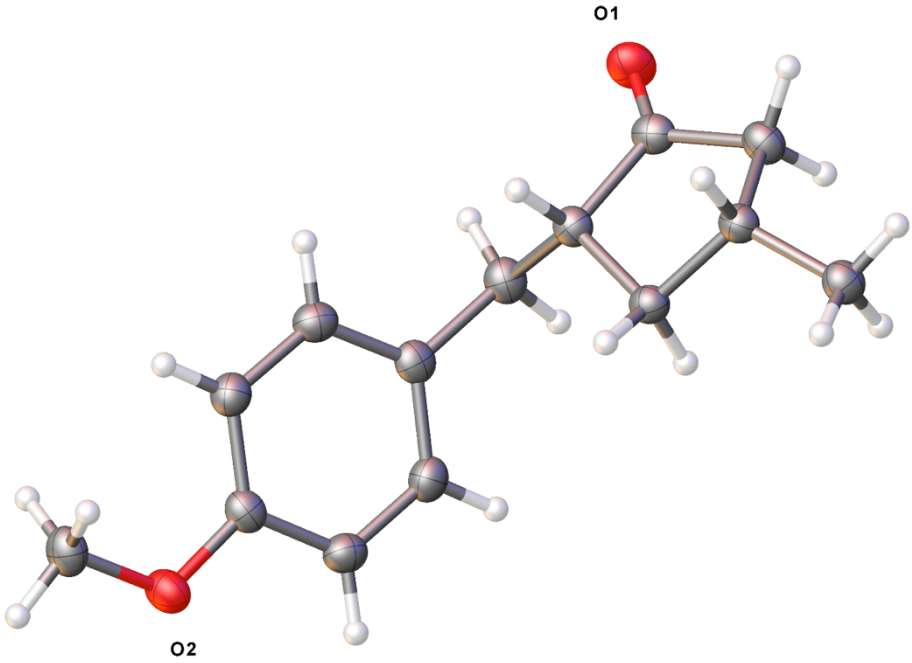


1a (1.0 g) **2a**

In a N_2-filled glovebox, $[Rh(COD)Cl]_2$ (45.2 mg, 0.092 mmol, 2 mol%), (*R*)-DTBM-Segphos (216 mg, 0.183 mmol, 4 mol%), and toluene (23 mL, 0.20 M) were added to an oven-dried round bottom flask equipped with a magnetic stir bar. The solution was stirred at 30 °C for 15 min. $AgSbF_6$ (78.7 mg, 0.229 mmol, 5 mol%) was added, and the resulting mixture was stirred 30 °C for 30 min. Aldehyde **1a** (1.0 g, 4.58 mmol, 1.0 equiv) and 1-$AdNH_2$ (69.3 mg, 0.458 mmol, 10 mol%) were added sequentially. The flask was then sealed with a rubber septum and removed from the glovebox. A N_2-filled balloon was attached, and the reaction was stirred at 60 °C for 48 h. The reaction mixture was cooled to rt, filtered through celite, and concentrated *in vacuo*. The diastereoselectivity was determined by ^{1}H NMR analysis of the unpurified reaction mixture. The crude mixture was purified by column chromatography (5% EtOAc in hexanes) to afford **2a** as a light yellow solid (891 mg, 89% yield, >20:1 *dr*, >99% *ee*). The ^{1}H NMR data matched those for **2a** obtained by following general Method A (page 4). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 3.79 (s, 3H), 3.11 (dd, *J* = 13.8, 4.0 Hz, 1H), 2.56 – 2.45 (m, 2H), 2.40 (dtd, *J* = 12.4, 8.1, 4.1 Hz, 1H), 2.21 – 2.03 (m, 2H), 1.71 (dd, *J* = 18.4, 11.3 Hz, 1H), 1.21 – 1.11 (m, 1H), 1.10 (d, *J* = 6.3 Hz, 3H).

10. X-ray Crystallographic Data

***X-ray Crystallographic Data for 2a* (CCDC 1869120)**



The single crystal X-ray diffraction studies were carried out on a Bruker Kappa APEX-II CCD diffractometer equipped with Cu K_a radiation (l = 1.5478). A 0.153 x 0.067 x 0.042 mm piece of a colorless block was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using f and v scans. Crystal-to-detector distance was 40 mm using variable exposure time (5s-20s) depending on q with a scan width of 2.0°. Data collection was 99.0% complete to 68.00° in *q*. A total of 12765 reflections were collected covering the indices, -5<=h<=6, -11<=k<=11, -14<=l<=14. 2136 reflections were found to be symmetry independent, with a R_{int} of 0.0286. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space

group was found to be $P2_1$. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. The absolute stereochemistry of the molecule was established by anomalous dispersion using the Parson's method with a Flack parameter of 0.022(64). Crystallographic data are summarized in Table S1.

Table S1. Crystal data and structure refinement for UCI_Dong_11-ZC-4.

Report date	2018-06-27	
Identification code	11-ZC-4	
Empirical formula	C14 H18 O2	
Molecular formula	C14 H18 O2	
Formula weight	218.28	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 5.1826(3) Å	α= 90°.
	b = 9.6599(5) Å	β= 93.160(2)°.
	c = 11.8510(6) Å	γ = 90°.
Volume	592.40(5) $Å^3$	
Z	2	
Density (calculated)	1.224 Mg/m^3	
Absorption coefficient	0.634 mm^{-1}	
F(000)	236	
Crystal size	0.153 x 0.067 x 0.042 mm^3	
Crystal color, habit	Colorless Block	
Theta range for data collection	3.735 to 68.149°.	
Index ranges	-5<=h<=6, -11<=k<=11, -14<=l<=14	
Reflections collected	12765	

Independent reflections	2136 [R(int) = 0.0286, R(sigma) = 0.0187]
Completeness to theta = 68.000°	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.3200 and 0.2284
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2136 / 1 / 147
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0264, wR2 = 0.0670
R indices (all data)	R1 = 0.0272, wR2 = 0.0674
Absolute structure parameter	0.02(6)
Extinction coefficient	n/a
Largest diff. peak and hole	0.114 and -0.130 e.$Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for UCI_Dong_11-ZC-4. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	10292(3)	2748(1)	5621(1)	32(1)
O(2)	976(3)	6936(1)	10207(1)	31(1)
C(1)	8554(3)	3506(2)	5284(2)	25(1)
C(2)	7910(4)	3901(2)	4069(2)	27(1)
C(3)	5249(3)	4593(2)	4073(1)	24(1)
C(4)	5314(4)	5292(2)	5244(1)	24(1)
C(5)	6663(3)	4229(2)	6033(1)	23(1)
C(6)	7990(4)	4765(2)	7133(2)	28(1)
C(7)	6116(4)	5325(2)	7949(1)	24(1)
C(8)	4598(3)	4437(2)	8553(2)	27(1)

C(9)	2833(4)	4918(2)	9306(2)	26(1)
C(10)	2584(3)	6336(2)	9469(1)	25(1)
C(11)	4082(4)	7246(2)	8871(2)	28(1)
C(12)	5821(4)	6744(2)	8123(2)	27(1)
C(13)	4690(4)	5572(2)	3088(2)	28(1)
C(14)	-674(4)	6038(2)	10795(2)	31(1)

Table S3. Bond lengths [Å] and angles [°] for UCI_Dong_11-ZC-4.

O(1)-C(1)	1.212(2)	C(2)-C(3)-C(4)	102.64(14)
O(2)-C(10)	1.370(2)	C(13)-C(3)-C(2)	113.76(15)
O(2)-C(14)	1.426(2)	C(13)-C(3)-C(4)	114.42(15)
C(1)-C(2)	1.509(3)	C(5)-C(4)-C(3)	104.03(14)
C(1)-C(5)	1.526(2)	C(1)-C(5)-C(4)	103.81(14)
C(2)-C(3)	1.533(3)	C(1)-C(5)-C(6)	112.14(14)
C(3)-C(4)	1.542(2)	C(4)-C(5)-C(6)	117.49(15)
C(3)-C(13)	1.518(3)	C(7)-C(6)-C(5)	113.12(14)
C(4)-C(5)	1.530(2)	C(8)-C(7)-C(6)	120.79(16)
C(5)-C(6)	1.531(2)	C(8)-C(7)-C(12)	117.44(17)
C(6)-C(7)	1.509(2)	C(12)-C(7)-C(6)	121.77(17)
C(7)-C(8)	1.389(3)	C(7)-C(8)-C(9)	122.31(17)
C(7)-C(12)	1.395(3)	C(10)-C(9)-C(8)	119.19(17)
C(8)-C(9)	1.392(3)	O(2)-C(10)-C(9)	124.77(16)
C(9)-C(10)	1.390(3)	O(2)-C(10)-C(11)	115.73(15)
C(10)-C(11)	1.392(3)	C(9)-C(10)-C(11)	119.49(16)
C(11)-C(12)	1.386(3)	C(12)-C(11)-C(10)	120.34(17)

C(11)-C(12)-C(7)	121.23(17)
C(10)-O(2)-C(14)	117.18(14)
O(1)-C(1)-C(2)	126.03(18)
O(1)-C(1)-C(5)	125.09(17)
C(2)-C(1)-C(5)	108.87(15)
C(1)-C(2)-C(3)	105.00(15)

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for UCI_Dong_11-ZC-4. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	26(1)	36(1)	35(1)	0(1)	1(1)	8(1)
O(2)	28(1)	32(1)	34(1)	-5(1)	8(1)	-1(1)
C(1)	18(1)	25(1)	31(1)	-2(1)	2(1)	-2(1)
C(2)	23(1)	31(1)	28(1)	-3(1)	3(1)	1(1)
C(3)	21(1)	24(1)	26(1)	-1(1)	2(1)	-1(1)
C(4)	22(1)	23(1)	26(1)	-1(1)	2(1)	1(1)
C(5)	19(1)	26(1)	25(1)	0(1)	2(1)	-1(1)
C(6)	22(1)	34(1)	26(1)	0(1)	-1(1)	-1(1)
C(7)	22(1)	29(1)	21(1)	0(1)	-4(1)	0(1)
C(8)	26(1)	25(1)	29(1)	-1(1)	-2(1)	0(1)
C(9)	24(1)	28(1)	26(1)	1(1)	0(1)	-3(1)
C(10)	20(1)	31(1)	23(1)	-2(1)	-1(1)	1(1)
C(11)	29(1)	24(1)	29(1)	0(1)	-1(1)	2(1)
C(12)	26(1)	30(1)	25(1)	4(1)	0(1)	-2(1)
C(13)	27(1)	31(1)	26(1)	-1(1)	1(1)	1(1)

C(14)	24(1)	40(1)	29(1)	1(1)	5(1)	1(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for UCI_Dong_11-ZC-4.

	x	y	z	U(eq)
H(2A)	7845	3070	3579	32
H(2B)	9213	4551	3795	32
H(3)	3895	3855	4049	28
H(4A)	6300	6169	5242	28
H(4B)	3543	5486	5476	28
H(5)	5341	3532	6237	28
H(6A)	8994	4002	7502	33
H(6B)	9221	5506	6952	33
H(8)	4770	3467	8449	32
H(9)	1813	4286	9703	31
H(11)	3912	8216	8976	33
H(12)	6831	7377	7721	32
H(13A)	2989	5998	3155	42
H(13B)	4706	5055	2377	42
H(13C)	6016	6296	3096	42
H(14A)	-1835	5550	10249	46
H(14B)	-1696	6584	11306	46
H(14C)	377	5364	11234	46

***X-ray Crystallographic Data for 4a* (CCDC 1869122)**

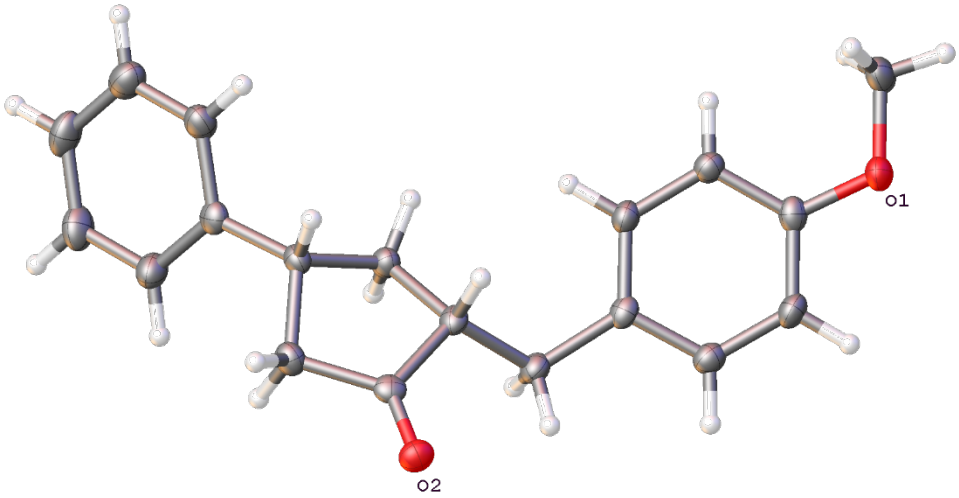


Table S6. Crystal data and structure refinement for UCIDong_16b_0m_a.

Identification code	ucidong_16b_0m_a	
Empirical formula	C19 H20 O2	
Formula weight	280.35	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 7.7848(5) Å	α= 90°.
	b = 6.8098(4) Å	β= 91.804(3)°.
	c = 14.0541(7) Å	γ = 90°.
Volume	744.68(7) $Å^3$	
Z	2	
Density (calculated)	1.250 Mg/m^3	
Absorption coefficient	0.626 mm^{-1}	
F(000)	300	
Crystal size	0.30 x 0.29 x 0.28 mm^3	
Theta range for data collection	3.146 to 68.286°.	
Index ranges	-9<=h<=9, -8<=k<=8, -16<=l<=16	
Reflections collected	8800	
Independent reflections	2712 [R(int) = 0.0327]	
Completeness to theta = 67.679°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3201 and 0.2289	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2712 / 1 / 191	
Goodness-of-fit on F^2	1.091	
Final R indices [I>2sigma(I)]	R1 = 0.0315, wR2 = 0.0768	
R indices (all data)	R1 = 0.0318, wR2 = 0.0771	
Absolute structure parameter	0.01(6)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.240 and -0.153 $e.Å^{-3}$	

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for UCIDong_16b_0m_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	574(2)	7987(2)	1024(1)	30(1)
O(2)	3074(2)	117(2)	5242(1)	29(1)
C(1)	1350(3)	9883(3)	982(1)	34(1)
C(2)	716(2)	7020(3)	1878(1)	25(1)
C(3)	1543(2)	7758(3)	2694(1)	25(1)
C(4)	1644(2)	6612(3)	3519(1)	26(1)
C(5)	942(2)	4738(3)	3553(1)	24(1)
C(6)	72(2)	4054(3)	2732(1)	27(1)
C(7)	-42(2)	5160(3)	1909(1)	29(1)
C(8)	1072(2)	3421(3)	4423(1)	25(1)
C(9)	2688(2)	3650(2)	5067(1)	23(1)
C(10)	3158(2)	1748(3)	5592(1)	23(1)
C(11)	3762(2)	2233(3)	6598(1)	27(1)
C(12)	4100(2)	4442(2)	6577(1)	23(1)
C(13)	2675(2)	5166(3)	5871(1)	25(1)
C(14)	4165(2)	5543(2)	7513(1)	24(1)
C(15)	5160(2)	7241(3)	7592(1)	31(1)
C(16)	5219(3)	8340(3)	8425(1)	36(1)
C(17)	4280(3)	7758(3)	9198(1)	36(1)
C(18)	3286(3)	6079(3)	9130(1)	36(1)
C(19)	3230(2)	4970(3)	8296(1)	31(1)

Table S8. Bond lengths [Å] and angles [°] for UCIDong_16b_0m_a.

O(1)-C(1)	1.428(2)
O(1)-C(2)	1.370(2)
O(2)-C(10)	1.215(2)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.392(2)
C(2)-C(7)	1.399(3)

C(3)-H(3)	0.9500
C(3)-C(4)	1.398(2)
C(4)-H(4)	0.9500
C(4)-C(5)	1.389(3)
C(5)-C(6)	1.399(2)
C(5)-C(8)	1.518(2)
C(6)-H(6)	0.9500
C(6)-C(7)	1.381(3)
C(7)-H(7)	0.9500
C(8)-H(8B)	0.9900
C(8)-H(8A)	0.9900
C(8)-C(9)	1.534(2)
C(9)-H(9)	1.0000
C(9)-C(10)	1.529(2)
C(9)-C(13)	1.531(2)
C(10)-C(11)	1.513(2)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(11)-C(12)	1.528(2)
C(12)-H(12)	1.0000
C(12)-C(13)	1.545(2)
C(12)-C(14)	1.514(2)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.394(3)
C(14)-C(19)	1.394(3)
C(15)-H(15)	0.9500
C(15)-C(16)	1.389(3)
C(16)-H(16)	0.9500
C(16)-C(17)	1.386(3)
C(17)-H(17)	0.9500
C(17)-C(18)	1.382(3)
C(18)-H(18)	0.9500
C(18)-C(19)	1.394(3)
C(19)-H(19)	0.9500

C(2)-O(1)-C(1)	116.63(13)
O(1)-C(1)-H(1A)	109.5
O(1)-C(1)-H(1B)	109.5

O(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
O(1)-C(2)-C(3)	124.83(16)
O(1)-C(2)-C(7)	116.10(15)
C(3)-C(2)-C(7)	119.07(15)
C(2)-C(3)-H(3)	120.2
C(2)-C(3)-C(4)	119.65(16)
C(4)-C(3)-H(3)	120.2
C(3)-C(4)-H(4)	119.0
C(5)-C(4)-C(3)	121.96(15)
C(5)-C(4)-H(4)	119.0
C(4)-C(5)-C(6)	117.28(16)
C(4)-C(5)-C(8)	123.63(15)
C(6)-C(5)-C(8)	119.09(16)
C(5)-C(6)-H(6)	119.1
C(7)-C(6)-C(5)	121.72(17)
C(7)-C(6)-H(6)	119.1
C(2)-C(7)-H(7)	119.9
C(6)-C(7)-C(2)	120.27(16)
C(6)-C(7)-H(7)	119.9
C(5)-C(8)-H(8B)	108.1
C(5)-C(8)-H(8A)	108.1
C(5)-C(8)-C(9)	116.63(14)
H(8B)-C(8)-H(8A)	107.3
C(9)-C(8)-H(8B)	108.1
C(9)-C(8)-H(8A)	108.1
C(8)-C(9)-H(9)	107.5
C(10)-C(9)-C(8)	112.19(14)
C(10)-C(9)-H(9)	107.5
C(10)-C(9)-C(13)	102.83(13)
C(13)-C(9)-C(8)	118.64(14)
C(13)-C(9)-H(9)	107.5
O(2)-C(10)-C(9)	124.77(15)
O(2)-C(10)-C(11)	126.05(16)
C(11)-C(10)-C(9)	109.18(14)
C(10)-C(11)-H(11A)	110.9
C(10)-C(11)-H(11B)	110.9

C(10)-C(11)-C(12)	104.20(14)
H(11A)-C(11)-H(11B)	108.9
C(12)-C(11)-H(11A)	110.9
C(12)-C(11)-H(11B)	110.9
C(11)-C(12)-H(12)	107.5
C(11)-C(12)-C(13)	101.89(14)
C(13)-C(12)-H(12)	107.5
C(14)-C(12)-C(11)	118.12(14)
C(14)-C(12)-H(12)	107.5
C(14)-C(12)-C(13)	113.77(14)
C(9)-C(13)-C(12)	103.72(13)
C(9)-C(13)-H(13A)	111.0
C(9)-C(13)-H(13B)	111.0
C(12)-C(13)-H(13A)	111.0
C(12)-C(13)-H(13B)	111.0
H(13A)-C(13)-H(13B)	109.0
C(15)-C(14)-C(12)	118.86(15)
C(19)-C(14)-C(12)	122.94(15)
C(19)-C(14)-C(15)	118.17(17)
C(14)-C(15)-H(15)	119.4
C(16)-C(15)-C(14)	121.13(18)
C(16)-C(15)-H(15)	119.4
C(15)-C(16)-H(16)	119.9
C(17)-C(16)-C(15)	120.15(19)
C(17)-C(16)-H(16)	119.9
C(16)-C(17)-H(17)	120.3
C(18)-C(17)-C(16)	119.39(18)
C(18)-C(17)-H(17)	120.3
C(17)-C(18)-H(18)	119.7
C(17)-C(18)-C(19)	120.57(18)
C(19)-C(18)-H(18)	119.7
C(14)-C(19)-C(18)	120.59(18)
C(14)-C(19)-H(19)	119.7
C(18)-C(19)-H(19)	119.7

Symmetry transformations used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for UCIDong_16b_0m_a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

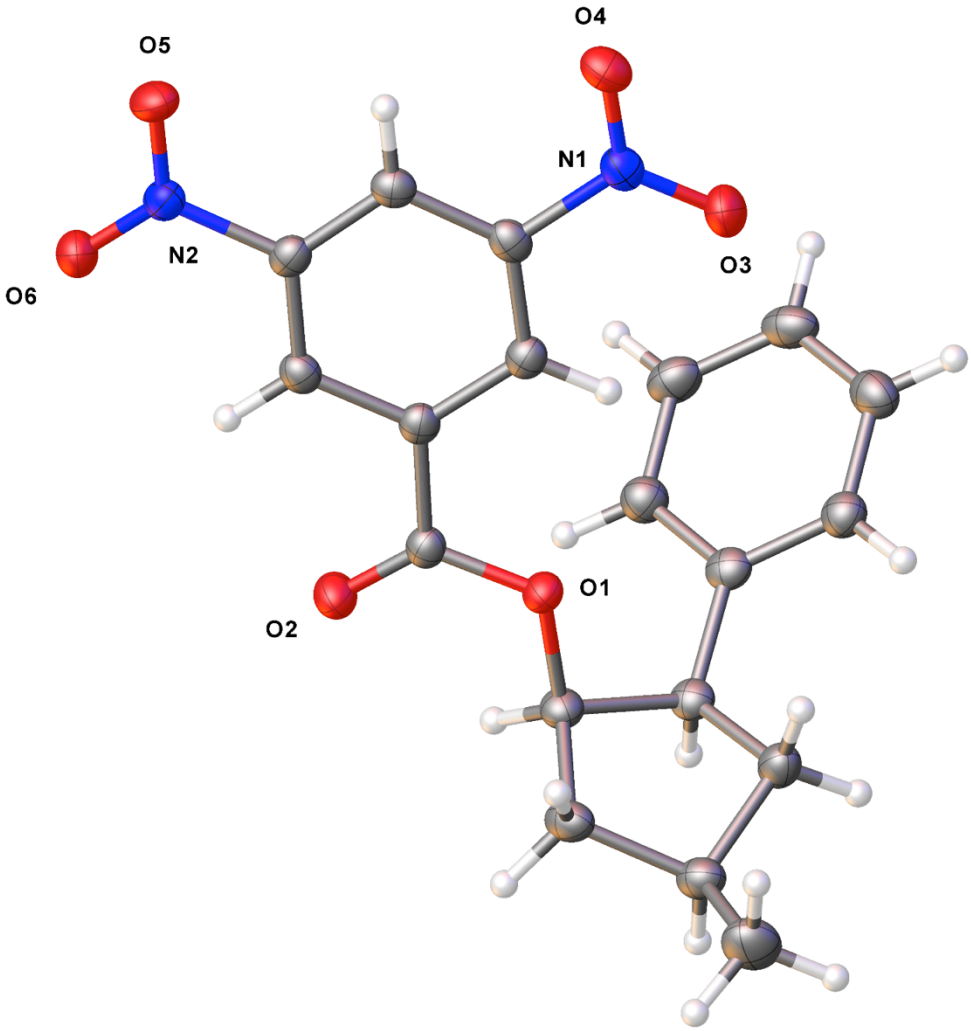
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	37(1)	32(1)	20(1)	1(1)	-2(1)	-1(1)
O(2)	32(1)	22(1)	32(1)	-4(1)	3(1)	0(1)
C(1)	44(1)	33(1)	24(1)	2(1)	1(1)	-2(1)
C(2)	24(1)	30(1)	21(1)	0(1)	2(1)	5(1)
C(3)	26(1)	25(1)	25(1)	-2(1)	0(1)	-2(1)
C(4)	26(1)	29(1)	22(1)	-3(1)	-2(1)	-2(1)
C(5)	21(1)	27(1)	23(1)	-2(1)	0(1)	1(1)
C(6)	28(1)	26(1)	26(1)	-3(1)	0(1)	-3(1)
C(7)	31(1)	32(1)	23(1)	-5(1)	-4(1)	-2(1)
C(8)	25(1)	26(1)	25(1)	0(1)	-1(1)	-3(1)
C(9)	23(1)	24(1)	23(1)	0(1)	1(1)	-1(1)
C(10)	19(1)	25(1)	27(1)	0(1)	5(1)	0(1)
C(11)	30(1)	24(1)	25(1)	3(1)	1(1)	2(1)
C(12)	23(1)	25(1)	22(1)	1(1)	1(1)	-1(1)
C(13)	28(1)	23(1)	25(1)	-1(1)	-1(1)	1(1)
C(14)	23(1)	26(1)	24(1)	1(1)	-3(1)	4(1)
C(15)	37(1)	28(1)	28(1)	3(1)	-1(1)	0(1)
C(16)	44(1)	29(1)	36(1)	-5(1)	-5(1)	-1(1)
C(17)	38(1)	41(1)	30(1)	-11(1)	-6(1)	9(1)
C(18)	34(1)	51(1)	24(1)	-3(1)	4(1)	5(1)
C(19)	28(1)	38(1)	26(1)	-1(1)	0(1)	-4(1)

Table S10. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for UCIDong_16b_0m_a.

	x	y	z	U(eq)
H(1A)	1155	10438	344	50
H(1B)	2588	9766	1118	50
H(1C)	840	10746	1454	50
H(3)	2037	9034	2691	31
H(4)	2209	7129	4073	31
H(6)	-454	2796	2741	32

H(7)	-639	4656	1362	34
H(8B)	1007	2040	4206	30
H(8A)	56	3668	4812	30
H(9)	3663	3985	4650	28
H(11A)	4824	1502	6775	32
H(11B)	2867	1910	7058	32
H(12)	5228	4648	6269	28
H(13A)	1545	5194	6176	30
H(13B)	2937	6496	5631	30
H(15)	5809	7654	7066	37
H(16)	5904	9493	8465	44
H(17)	4319	8506	9768	44
H(18)	2636	5677	9656	43
H(19)	2549	3813	8261	37

X-ray Crystallographic Data for 10 **(CCDC 1869121)**



The single crystal X-ray diffraction studies were carried out on a Bruker Kappa APEX-II CCD diffractometer equipped with Cu K_a radiation (l = 1.5478). Crystals of the subject compound were grown by dissolving approximately 1mg of sample in 350μL of Dichloromethane, which was then vapor diffused with Pentane over 2 days. A 0.357 x 0.046 x 0.023 mm piece of a colorless needle was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using f and v scans. Crystal-to-detector distance was 40 mm using variable exposure time (5s-20s) depending on q with a scan width of 2.0°. Data collection was 99.5% complete to 68.00° in *q*. A total of 25579 reflections were collected covering the indices, -12<=h<=12, -5<=k<=6, -19<=l<=19. 3089 reflections were found to be symmetry independent, with a R_{int} of 0.0376. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $P2_1$. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. The absolute stereochemistry of the molecule was established by anomalous dispersion using the Parson's method with a Flack parameter of 0.010(52). Crystallographic data are summarized in Table S11.

Table S11. Crystal data and structure refinement for UCI_Dong_ZC-11-16a.

Report date	2018-06-14	
Identification code	ZC-11-16a	
Empirical formula	C19 H18 N2 O6	
Molecular formula	C19 H18 N2 O6	
Formula weight	370.35	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 10.1670(3) Å	α= 90°.
	b = 5.5064(2) Å	β= 104.9590(10)°.
	c = 16.0224(5) Å	γ = 90°.
Volume	866.59(5) $Å^3$	
Z	2	
Density (calculated)	1.419 Mg/m^3	
Absorption coefficient	0.898 mm^{-1}	
F(000)	388	

Crystal size	0.357 x 0.046 x 0.023 mm^3
Crystal color, habit	Colorless Needle
Theta range for data collection	2.855 to 68.272°.
Index ranges	-12<=h<=12, -5<=k<=6, -19<=l<=19
Reflections collected	25579
Independent reflections	3089 [R(int) = 0.0376, R(sigma) = 0.0204]
Completeness to theta = 68.000°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.3200 and 0.2206
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3089 / 1 / 245
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0246, wR2 = 0.0649
R indices (all data)	R1 = 0.0251, wR2 = 0.0654
Absolute structure parameter	0.01(5)
Extinction coefficient	n/a
Largest diff. peak and hole	0.131 and -0.141 e.$Å^{-3}$

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for UCI_Dong_ZC-11-16a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	2372(1)	3438(2)	7378(1)	22(1)
O(2)	1314(1)	261(3)	6598(1)	29(1)
O(3)	4531(1)	9475(2)	5962(1)	32(1)
O(4)	3988(1)	9739(2)	4567(1)	29(1)

O(5)	1174(1)	3543(3)	2846(1)	30(1)
O(6)	566(1)	463(3)	3500(1)	29(1)
N(1)	3921(1)	8765(3)	5244(1)	24(1)
N(2)	1080(1)	2469(3)	3497(1)	23(1)
C(1)	2327(2)	2226(3)	8184(1)	23(1)
C(2)	1143(2)	3249(4)	8510(1)	27(1)
C(3)	1780(2)	4412(4)	9392(1)	27(1)
C(4)	3204(2)	5122(4)	9323(1)	27(1)
C(5)	3635(2)	2929(3)	8874(1)	22(1)
C(6)	4895(2)	3171(3)	8540(1)	24(1)
C(7)	5231(2)	1316(4)	8041(1)	28(1)
C(8)	6378(2)	1473(4)	7728(1)	32(1)
C(9)	7217(2)	3494(4)	7908(1)	32(1)
C(10)	6900(2)	5347(4)	8403(1)	32(1)
C(11)	5746(2)	5183(4)	8719(1)	27(1)
C(12)	960(2)	6497(5)	9617(2)	40(1)
C(13)	1853(2)	2217(3)	6649(1)	21(1)
C(14)	2050(2)	3547(3)	5874(1)	21(1)
C(15)	2866(2)	5603(3)	5939(1)	22(1)
C(16)	3038(2)	6624(3)	5184(1)	22(1)
C(17)	2440(2)	5701(3)	4371(1)	22(1)
C(18)	1654(2)	3641(3)	4339(1)	22(1)
C(19)	1440(2)	2552(3)	5069(1)	22(1)

Table S13. Bond lengths [Å] and angles [°] for UCI_Dong_ZC-11-16a.

O(1)-C(1)	1.4655(19)	C(4)-C(5)	1.526(3)
O(1)-C(13)	1.333(2)	C(5)-C(6)	1.517(2)
O(2)-C(13)	1.202(2)	C(6)-C(7)	1.393(3)
O(3)-N(1)	1.2223(19)	C(6)-C(11)	1.389(3)
O(4)-N(1)	1.2277(19)	C(7)-C(8)	1.386(3)
O(5)-N(2)	1.2252(19)	C(8)-C(9)	1.387(3)
O(6)-N(2)	1.223(2)	C(9)-C(10)	1.380(3)
N(1)-C(16)	1.470(2)	C(10)-C(11)	1.395(2)
N(2)-C(18)	1.472(2)	C(13)-C(14)	1.499(2)
C(1)-C(2)	1.537(2)	C(14)-C(15)	1.391(3)
C(1)-C(5)	1.544(2)	C(14)-C(19)	1.391(2)
C(2)-C(3)	1.535(2)	C(15)-C(16)	1.385(2)
C(3)-C(4)	1.532(2)	C(16)-C(17)	1.384(2)
C(3)-C(12)	1.516(3)	C(17)-C(18)	1.381(3)
C(18)-C(19)	1.381(2)	C(10)-C(9)-C(8)	119.39(17)
		C(9)-C(10)-C(11)	120.23(19)
C(13)-O(1)-C(1)	116.58(14)	C(6)-C(11)-C(10)	120.93(18)
O(3)-N(1)-O(4)	124.18(15)	O(1)-C(13)-C(14)	111.86(14)
O(3)-N(1)-C(16)	118.09(14)	O(2)-C(13)-O(1)	125.55(16)
O(4)-N(1)-C(16)	117.74(14)	O(2)-C(13)-C(14)	122.57(15)
O(5)-N(2)-C(18)	118.00(15)	C(15)-C(14)-C(13)	122.67(14)
O(6)-N(2)-O(5)	124.47(15)	C(15)-C(14)-C(19)	120.35(15)
O(6)-N(2)-C(18)	117.52(14)	C(19)-C(14)-C(13)	116.87(15)
O(1)-C(1)-C(2)	109.75(14)	C(16)-C(15)-C(14)	118.14(15)
O(1)-C(1)-C(5)	107.44(13)	C(15)-C(16)-N(1)	118.77(15)
C(2)-C(1)-C(5)	105.66(14)	C(17)-C(16)-N(1)	117.91(15)

C(3)-C(2)-C(1)	106.56(13)	C(17)-C(16)-C(15)	123.30(16)
C(4)-C(3)-C(2)	102.78(13)	C(18)-C(17)-C(16)	116.50(15)
C(12)-C(3)-C(2)	114.05(15)	C(17)-C(18)-N(2)	118.89(14)
C(12)-C(3)-C(4)	114.36(17)	C(17)-C(18)-C(19)	122.76(15)
C(5)-C(4)-C(3)	102.93(15)	C(19)-C(18)-N(2)	118.26(15)
C(4)-C(5)-C(1)	103.71(13)	C(18)-C(19)-C(14)	118.93(16)
C(6)-C(5)-C(1)	114.80(13)		
C(6)-C(5)-C(4)	117.89(15)		
C(7)-C(6)-C(5)	119.54(16)		
C(11)-C(6)-C(5)	122.37(16)		
C(11)-C(6)-C(7)	118.09(16)		
C(8)-C(7)-C(6)	121.08(18)		
C(7)-C(8)-C(9)	120.27(18)		

Table S14. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for UCI_Dong_ZC-11-16a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	24(1)	24(1)	18(1)	0(1)	4(1)	-3(1)
O(2)	34(1)	28(1)	25(1)	-1(1)	7(1)	-9(1)
O(3)	34(1)	31(1)	33(1)	-7(1)	8(1)	-9(1)
O(4)	28(1)	27(1)	34(1)	5(1)	11(1)	-2(1)
O(5)	30(1)	41(1)	21(1)	1(1)	9(1)	-5(1)
O(6)	29(1)	31(1)	27(1)	-5(1)	7(1)	-7(1)
N(1)	22(1)	22(1)	29(1)	-1(1)	8(1)	0(1)
N(2)	20(1)	29(1)	22(1)	-3(1)	6(1)	-1(1)
C(1)	25(1)	24(1)	20(1)	3(1)	5(1)	-1(1)

C(2)	21(1)	37(1)	24(1)	4(1)	6(1)	-1(1)
C(3)	23(1)	35(1)	24(1)	1(1)	8(1)	1(1)
C(4)	23(1)	34(1)	25(1)	-6(1)	6(1)	-2(1)
C(5)	22(1)	26(1)	19(1)	3(1)	4(1)	2(1)
C(6)	22(1)	29(1)	19(1)	3(1)	3(1)	3(1)
C(7)	26(1)	30(1)	28(1)	-1(1)	7(1)	1(1)
C(8)	29(1)	41(1)	28(1)	-2(1)	10(1)	7(1)
C(9)	23(1)	48(1)	28(1)	5(1)	9(1)	4(1)
C(10)	25(1)	39(1)	30(1)	2(1)	5(1)	-4(1)
C(11)	26(1)	31(1)	23(1)	-1(1)	5(1)	0(1)
C(12)	32(1)	44(1)	48(1)	-5(1)	19(1)	2(1)
C(13)	18(1)	23(1)	21(1)	-2(1)	4(1)	1(1)
C(14)	18(1)	22(1)	22(1)	-2(1)	6(1)	2(1)
C(15)	19(1)	24(1)	22(1)	-2(1)	4(1)	2(1)
C(16)	17(1)	21(1)	28(1)	0(1)	7(1)	2(1)
C(17)	19(1)	23(1)	24(1)	2(1)	7(1)	3(1)
C(18)	18(1)	26(1)	21(1)	-2(1)	4(1)	3(1)
C(19)	18(1)	23(1)	25(1)	0(1)	6(1)	0(1)

Table S15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for UCI_Dong_ZC-11-16a.

	x	y	z	U(eq)
H(1)	2250	424	8107	28
H(2A)	633	4477	8101	33
H(2B)	510	1933	8568	33
H(3)	1876	3134	9847	33
H(4A)	3175	6614	8973	33
H(4B)	3832	5382	9901	33
H(5)	3821	1583	9308	27
H(7)	4665	-78	7913	34
H(8)	6590	189	7388	39
H(9)	8002	3604	7692	39
H(10)	7469	6739	8529	38
H(11)	5539	6466	9060	32
H(12A)	867	7777	9181	59
H(12B)	1428	7149	10185	59
H(12C)	55	5912	9630	59
H(15)	3293	6287	6486	26
H(17)	2565	6445	3862	26
H(19)	884	1145	5022	26

11. References

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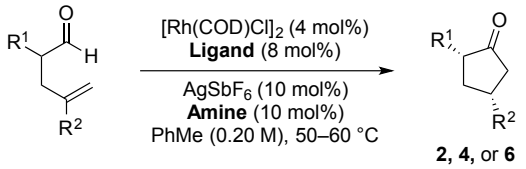
12. Ligand and Amine Combinations for Various Aldehydes



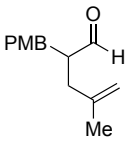
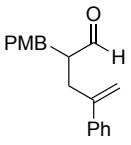
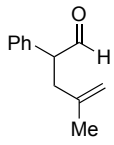
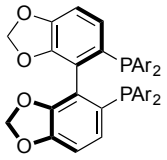
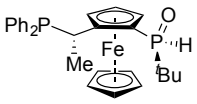
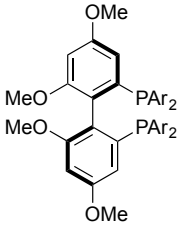
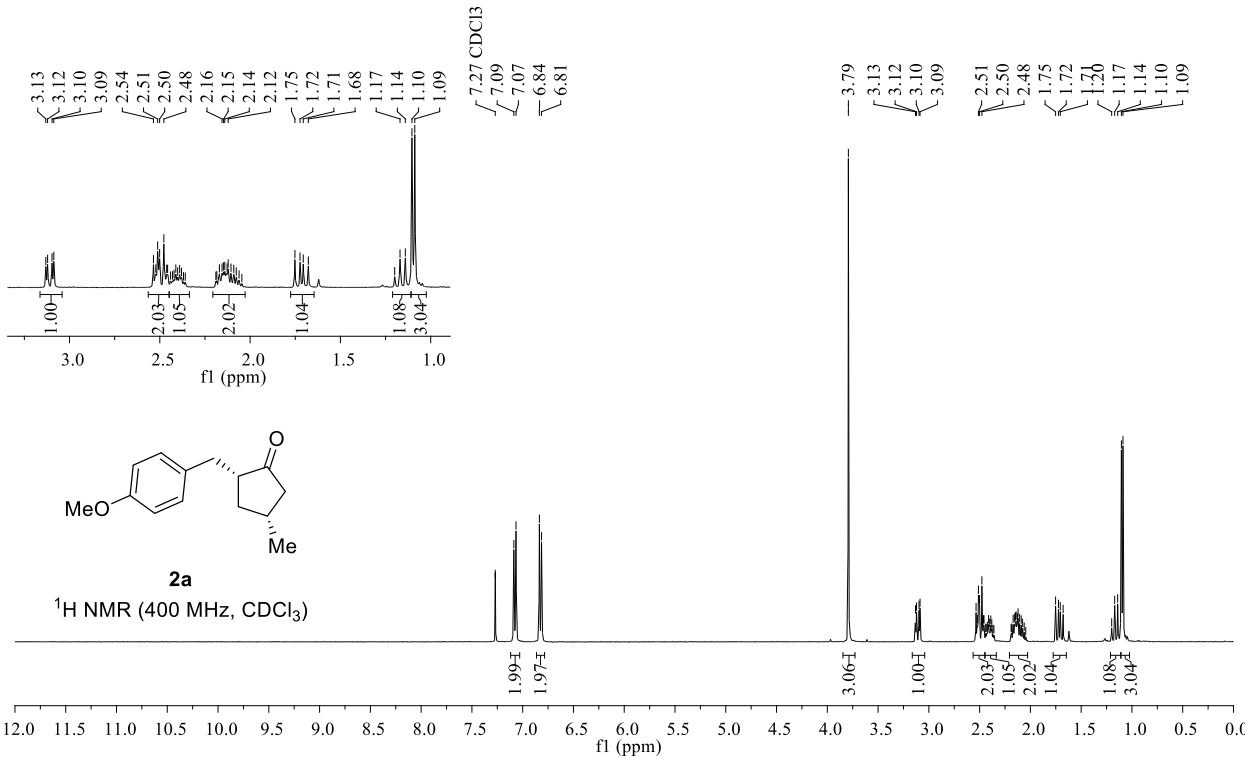
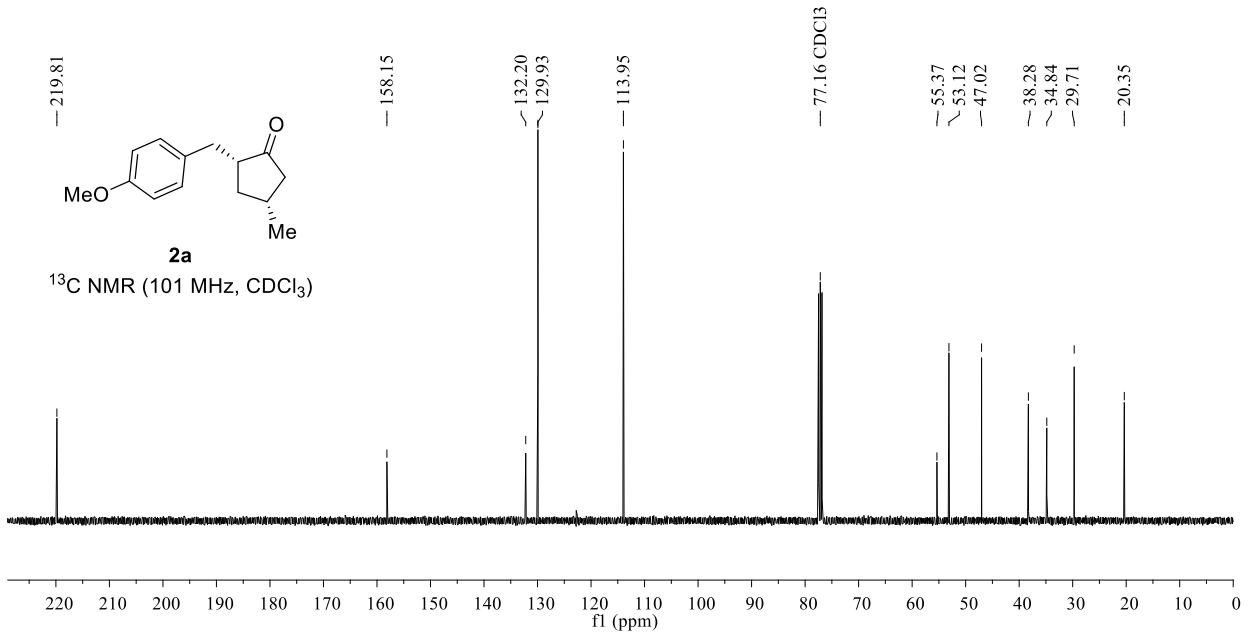
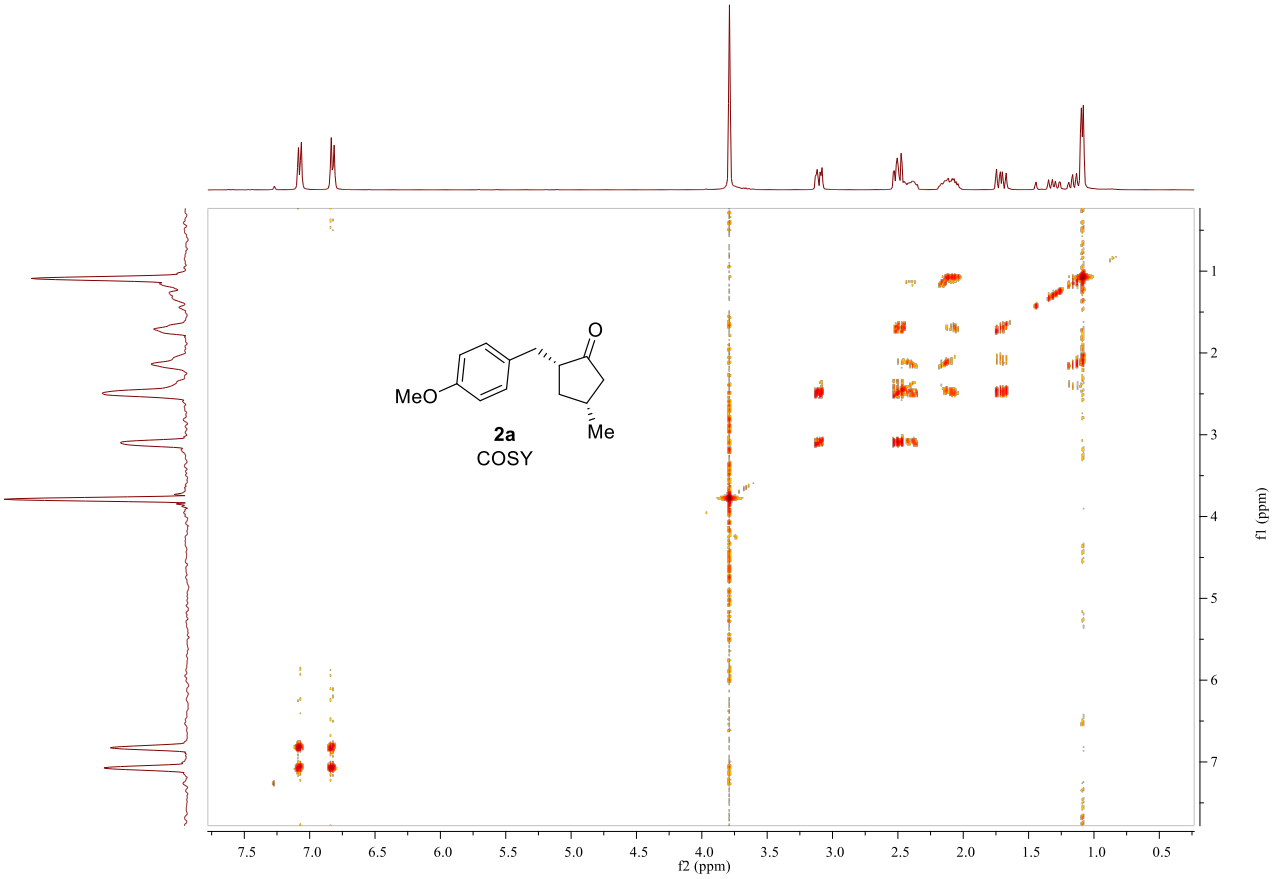
	 α–alkyl aldehyde with alkyl olefin (**1a**)	 α–alkyl aldehyde with styrenyl olefin (**3a**)	 α–aryl aldehyde with alkyl olefin (**5a**)
 (Ar = 3,5-^{t}Bu$_2$-4-OMePh) DTBM-Segphos (**L3**)/ 1-AdNH$_2$ (**A5**)	**2a**, 94% >20:1 *dr*, >99% *ee*	**4a**, <10% *dr* ND, *ee* ND	**6a**, 24% >20:1 *dr*, >99% *ee*
 JoSPOphos (**L4**)/ 1-AdNH$_2$ (**A5**)	**2a**, 78% >20:1 *dr*, >99% *ee*	**4a**, 76% >20:1 *dr*, >99% *ee*	**6a**, 54% 10:1 *dr*, 87% *ee*
 (Ar = 3,5-^{t}Bu$_2$-4-OMePh) DTBM-Garphos (**L5**)/ 2,6-Et$_2$PhNH$_2$ (**A8**)	**2a**, 83% >20:1 *dr*, 93% *ee*	**4a**, <10% *dr* ND, *ee* ND	**6a**, 87% >20:1 *dr*, >99% *ee*

Figure S1. Empirical Trend for Optimal Amine and Ligand.

13. NMR Spectra



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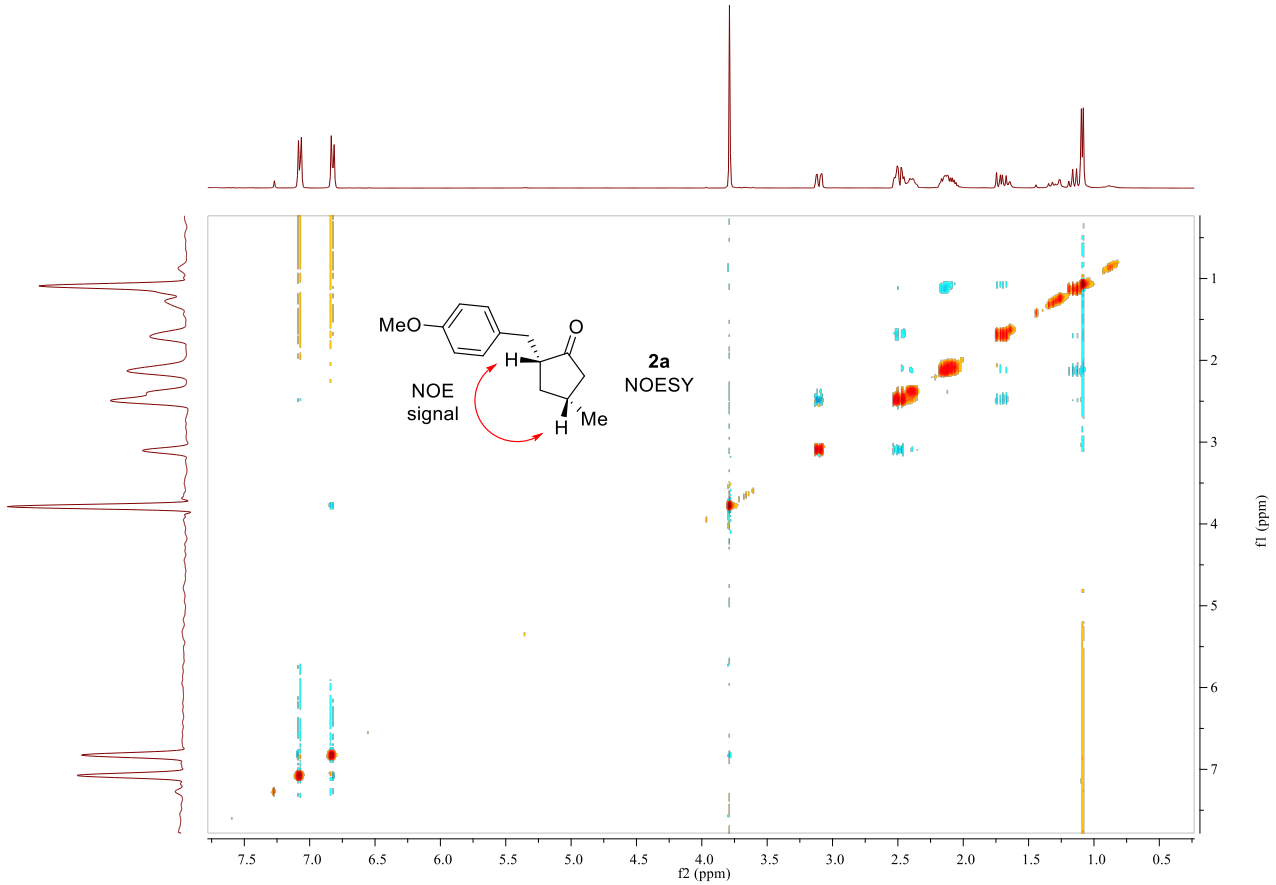
O
Me
2a
COSY
f1 (ppm)
f2 (ppm)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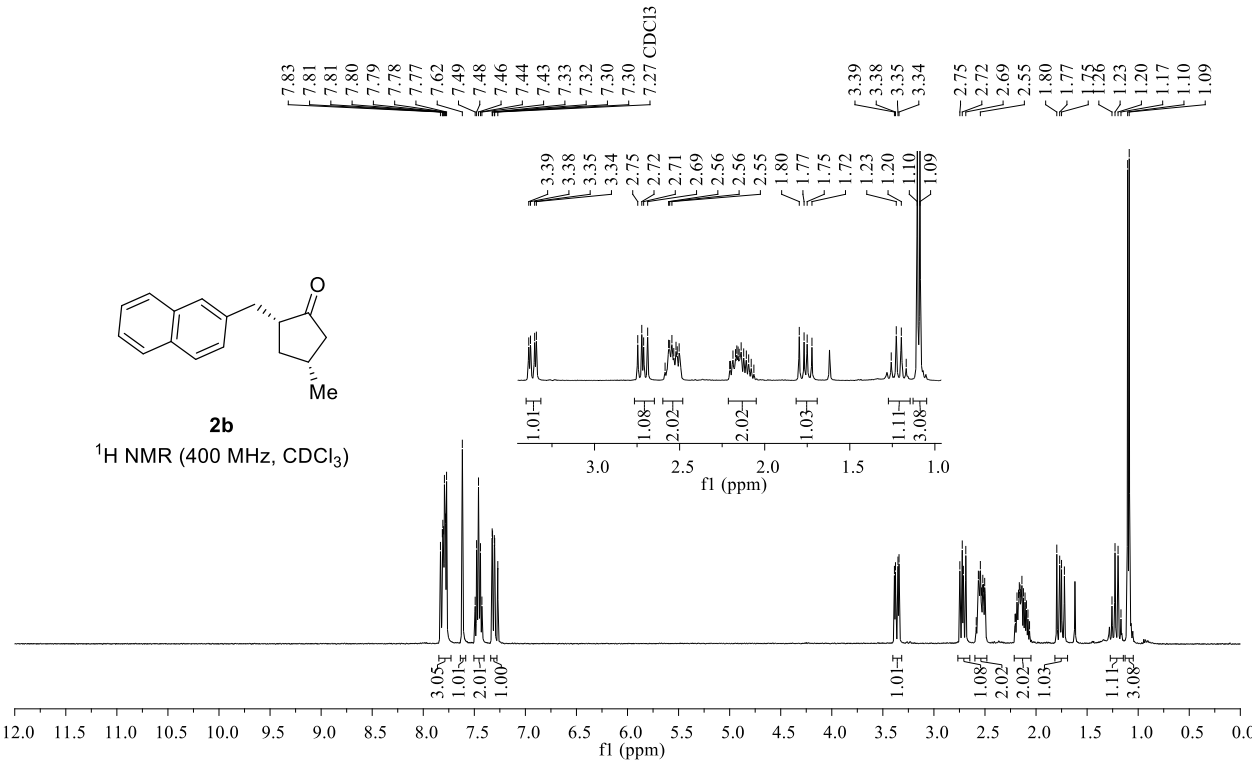
O
H
H
Me
NOE
signal
2a
NOESY
f1 (ppm)
f2 (ppm)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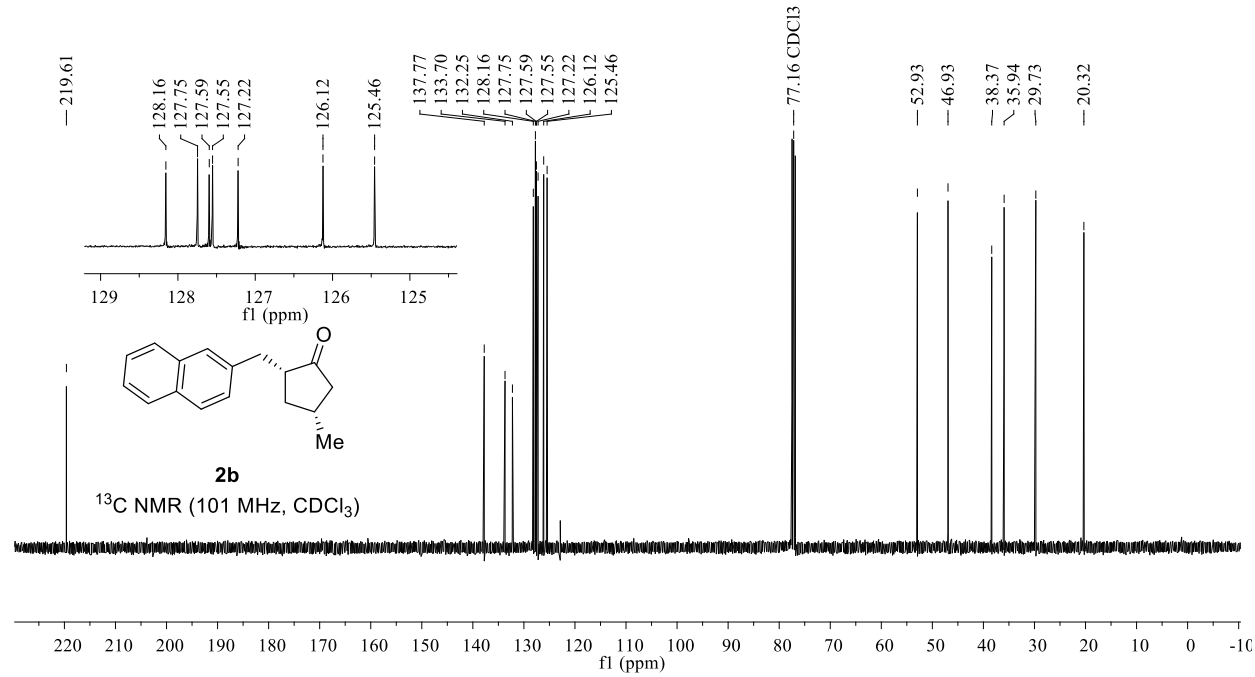
7.81
7.81
7.80
7.79
7.78
7.77
7.62
7.49
7.48
7.46
7.44
7.43
7.33
7.32
7.30
7.30
7.27 CDCl3
3.39
3.38
3.35
3.34
2.75
2.72
2.69
2.55
1.80
1.77
1.75
1.72
1.23
1.20
1.17
1.10
1.09
O
Me
2b
1H NMR (400 MHz, CDCl3)
3.05
1.01
2.01
1.00
1.01
1.08
2.02
2.02
1.03
1.11
3.08
f1 (ppm)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127.75
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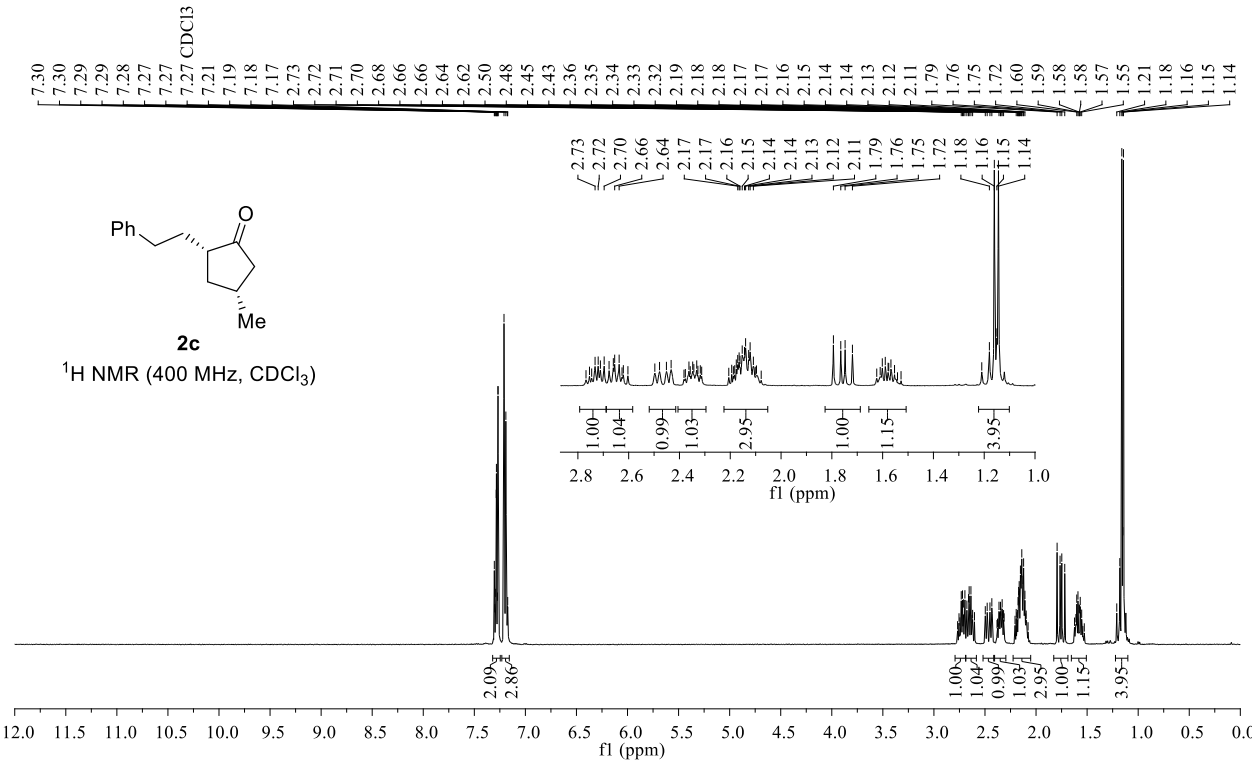
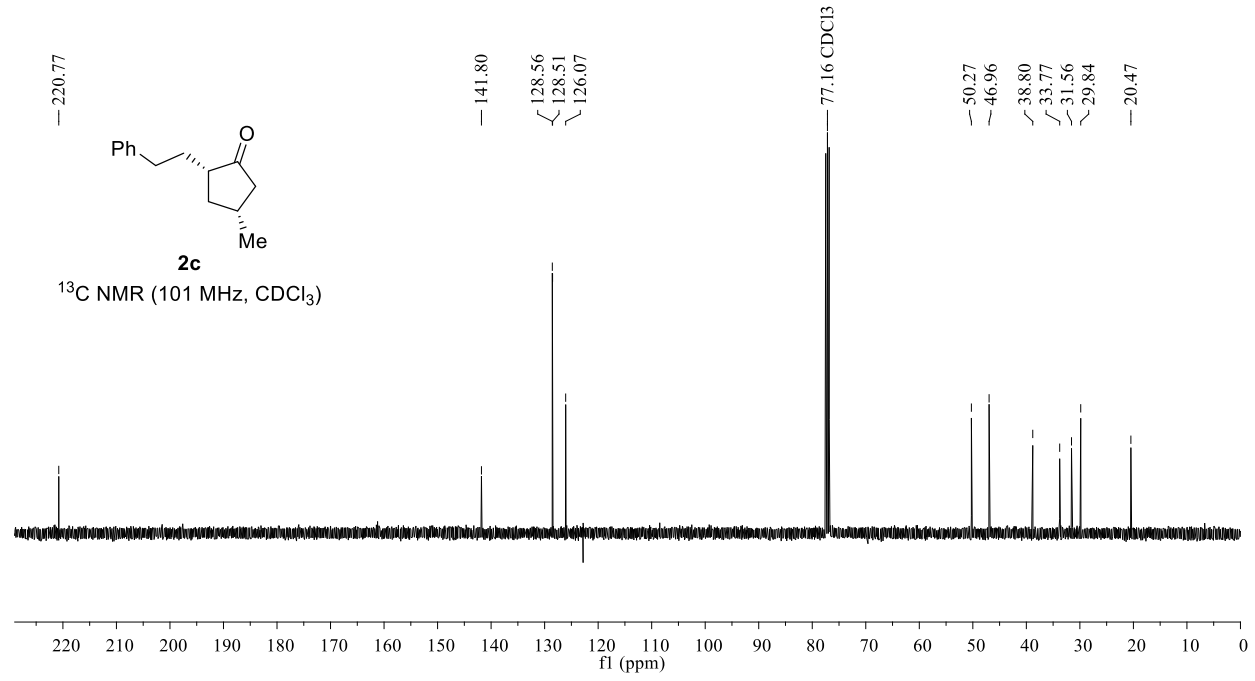
127.55
127.22
126.12
125.46
137.77
133.70
132.25
128.16
127.75
127.59
127.55
127.22
126.12
125.46
77.16 CDCl3
52.93
46.93
38.37
35.94
29.73
20.32
f1 (ppm)
O
Me
2b
13C NMR (101 MHz, CDCl3)
f1 (ppm)


Ph
O
Me
2c
1H NMR (400 MHz, CDCl3)
fl (ppm)


Ph
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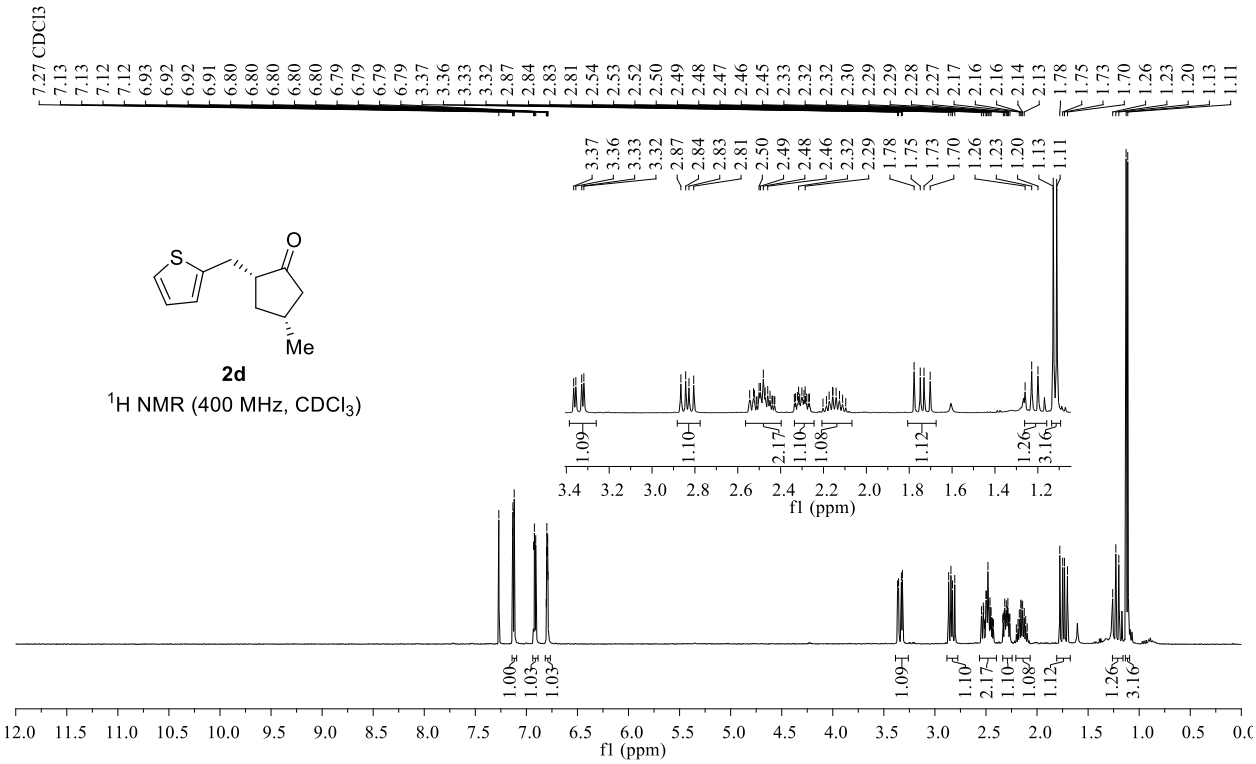
Me
2c
13C NMR (101 MHz, CDCl3)
fl (ppm)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7.12
7.12
7.12
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6.92
6.92
6.91
6.80
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6.80
6.80
6.80
6.79
6.79
6.79
6.79
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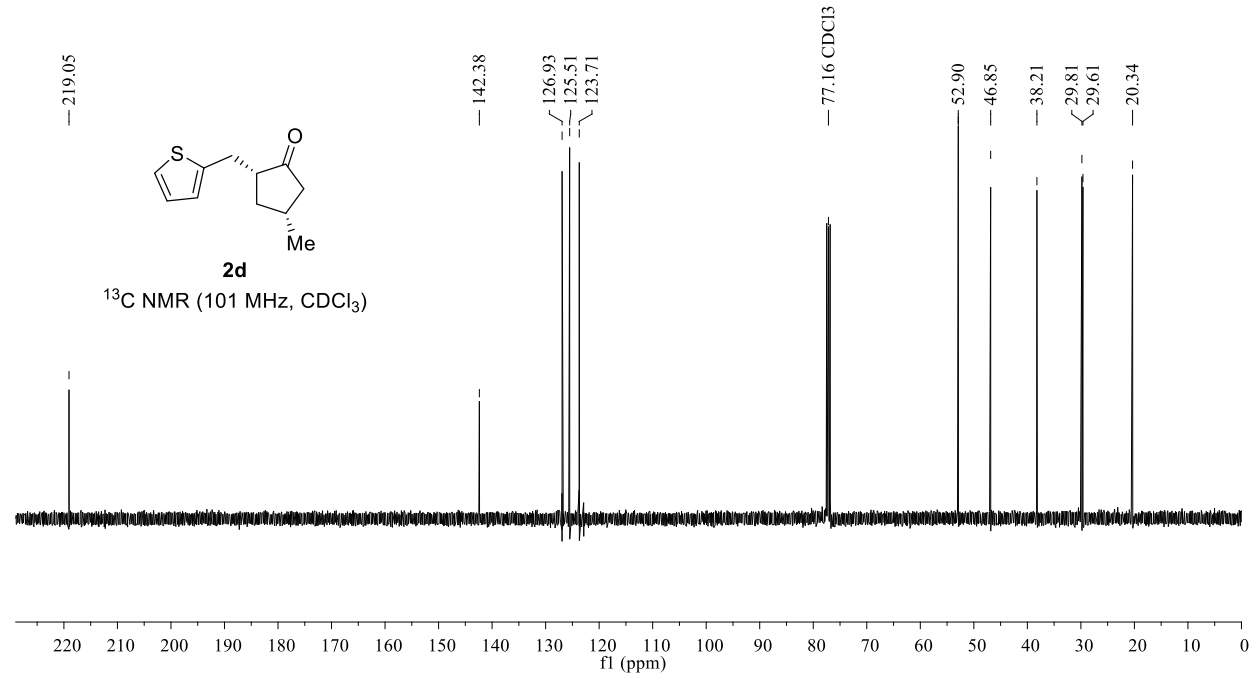
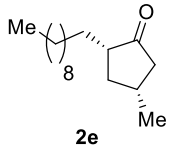
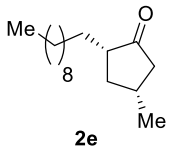
2.27
2.17
2.16
2.16
2.14
2.13
1.78
1.75
1.73
1.70
1.26
1.23
1.20
1.13
1.11
S
O
Me
2d
1H NMR (400 MHz, CDCl3)
1.00
1.03
1.03
1.09
1.10
2.17
1.10
1.08
1.12
1.26
3.16
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
f1 (ppm)


219.05
142.38
126.93
125.51
123.71
77.16 CDCl3
52.90
46.85
38.21
29.81
29.61
20.34
S
O
Me
2d
13C NMR (101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



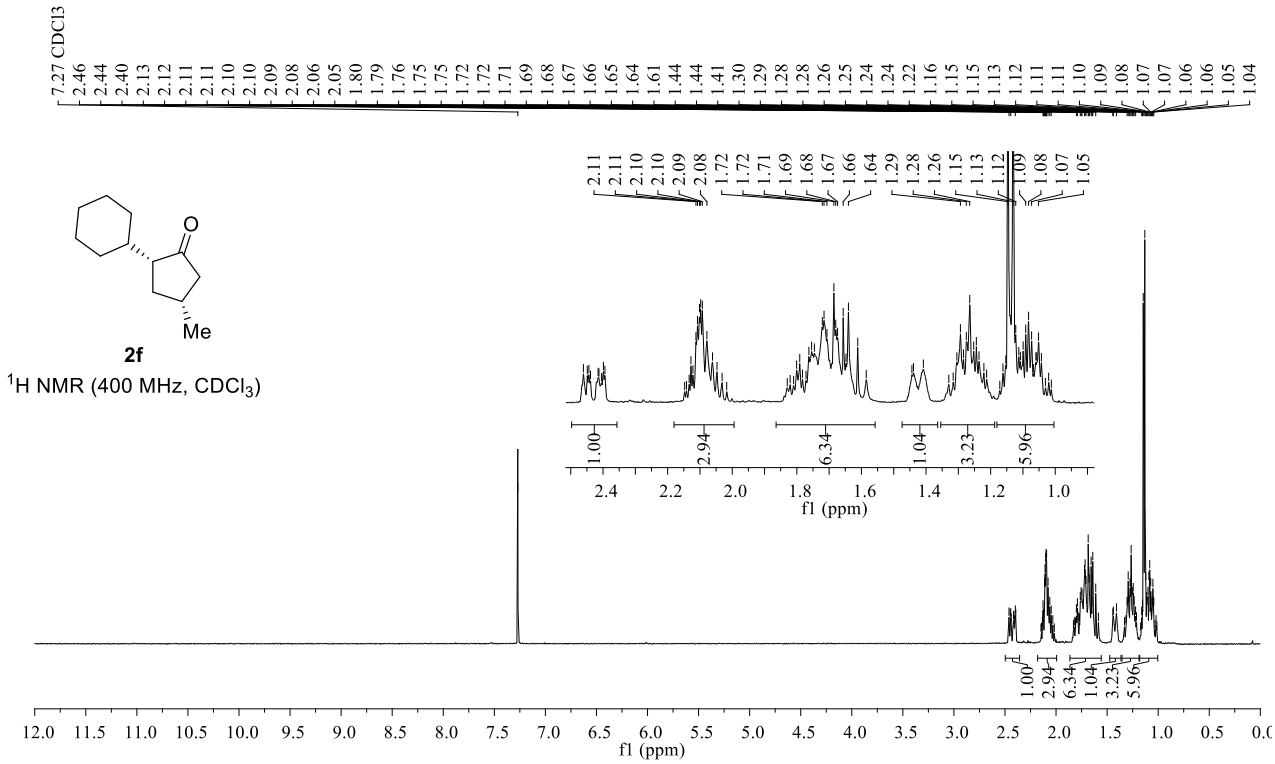
2e

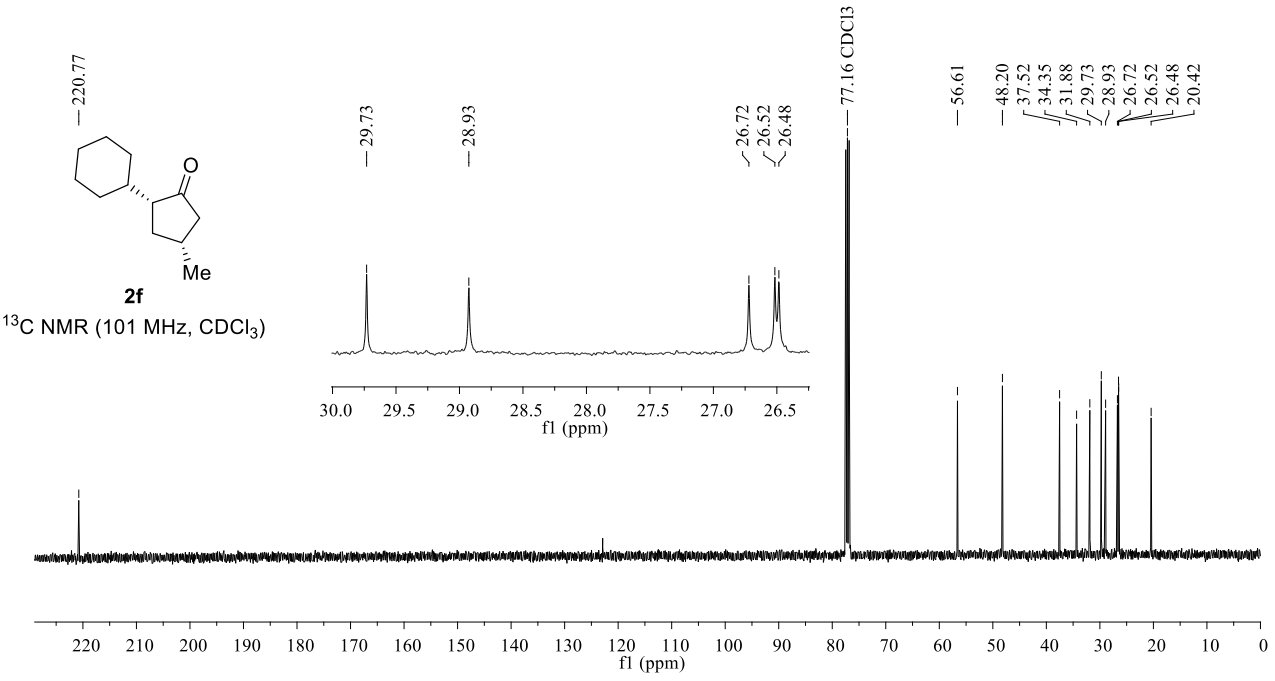
^{1}H NMR (400 MHz, $CDCl_3$)

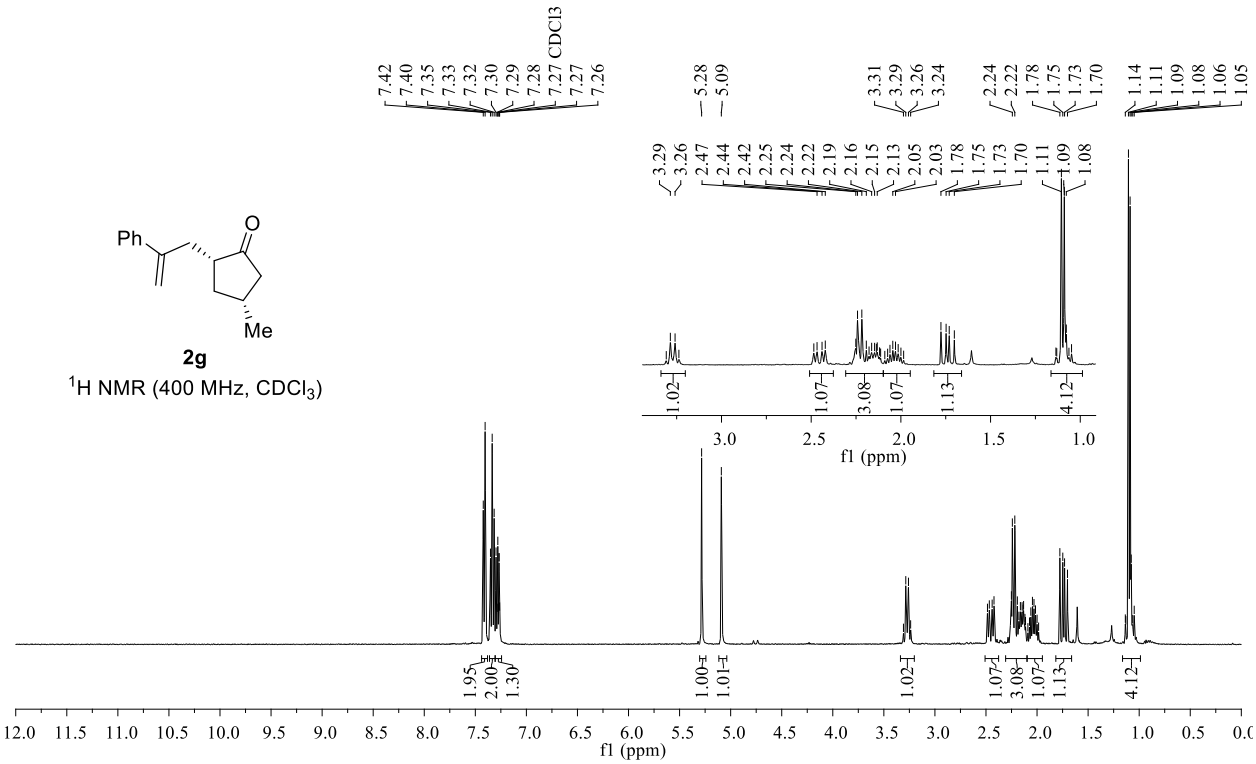


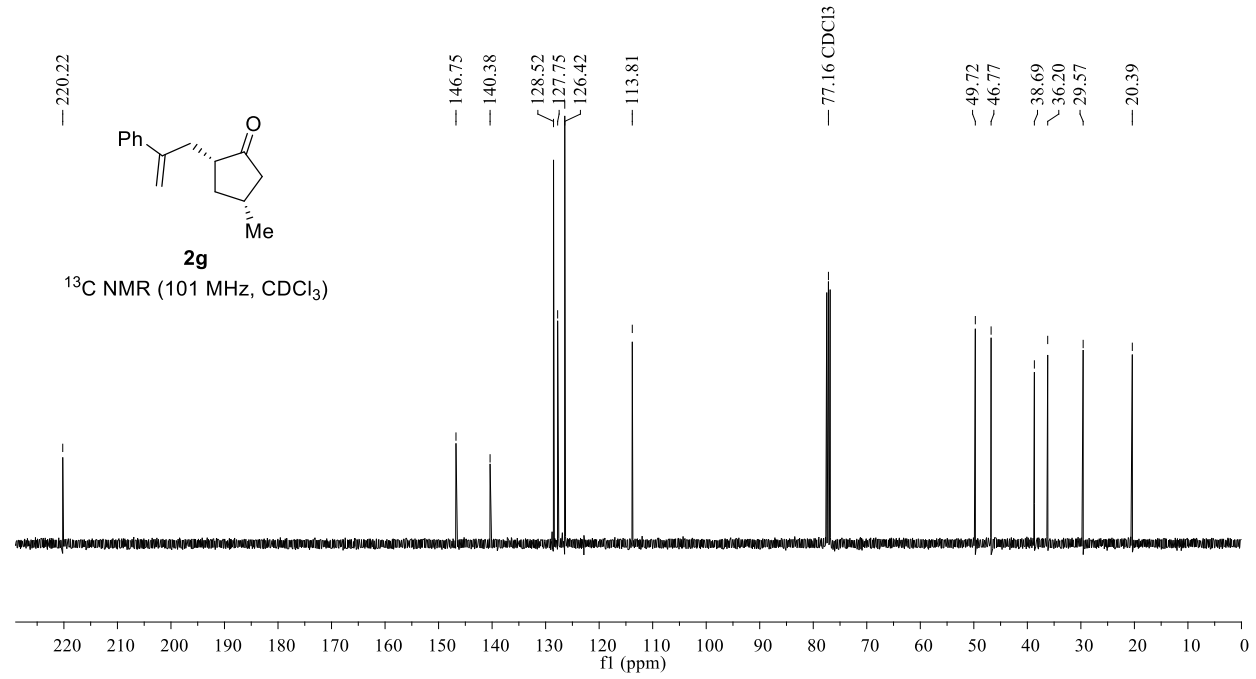
2e

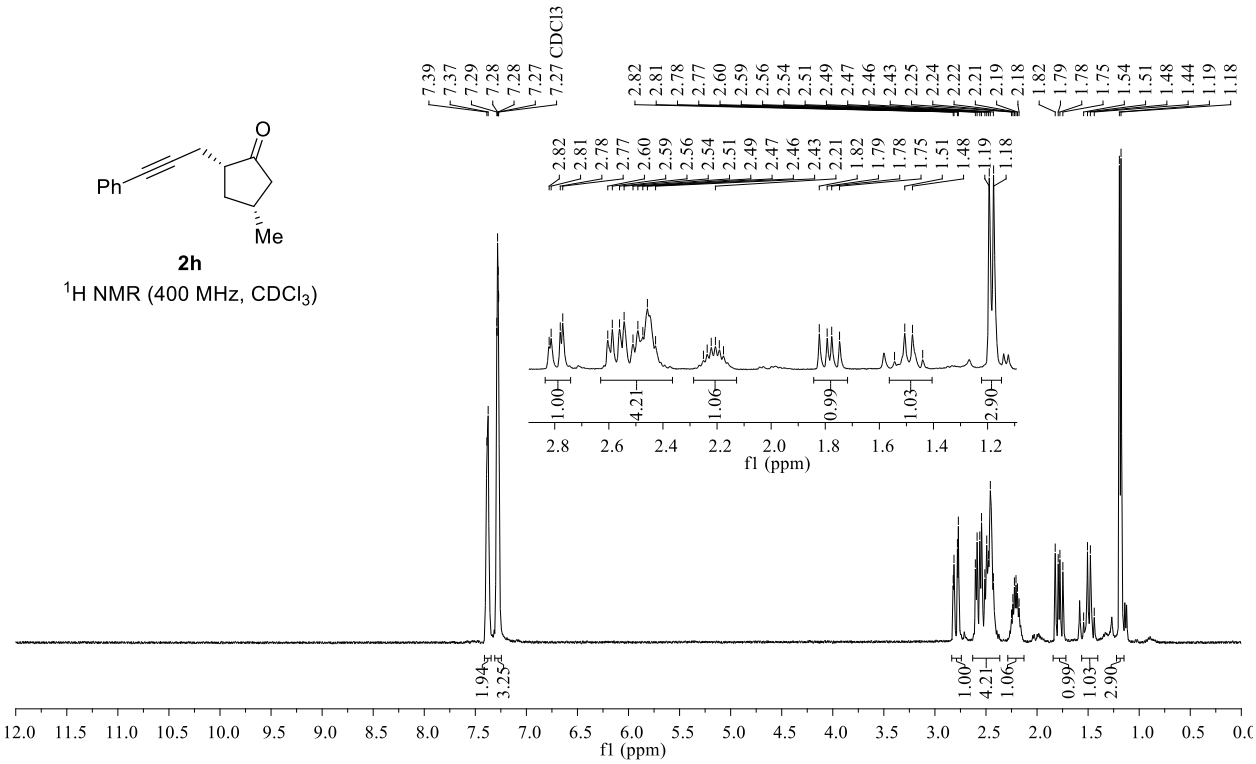
^{13}C NMR (126 MHz, $CDCl_3$)


7.27 CDCl3
2.46 2.44 2.40 2.13 2.12 2.11 2.11 2.10 2.10 2.09 2.08 2.06 2.05 1.80 1.79 1.76 1.75 1.75 1.72 1.72 1.71 1.69 1.68 1.67 1.66 1.65 1.64 1.61 1.44 1.44 1.41 1.30 1.29 1.28 1.28 1.26 1.25 1.24 1.24 1.22 1.16 1.15 1.15 1.13 1.12 1.11 1.11 1.10 1.09 1.08 1.07 1.07 1.06 1.06 1.05 1.04
O
Me
2f
1H NMR (400 MHz, CDCl3)
2.11 2.11 2.10 2.10 2.09 2.08 1.72 1.72 1.71 1.69 1.68 1.67 1.66 1.64 1.29 1.28 1.26 1.15 1.13 1.12 1.09 1.08 1.07 1.05
1.00 2.94 6.34 1.04 3.23 5.96
2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0
f1 (ppm)
1.00 2.94 6.34 1.04 3.23 5.96
12.0 11.5 11.0 10.5 10.0 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)


220.77
O
Me
2f
13C NMR (101 MHz, CDCl3)
29.73 28.93 26.72 26.52 26.48
77.16 CDCl3
56.61 48.20 37.52 34.35 31.88 29.73 28.93 26.72 26.52 26.48 20.42
30.0 29.5 29.0 28.5 28.0 27.5 27.0 26.5
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

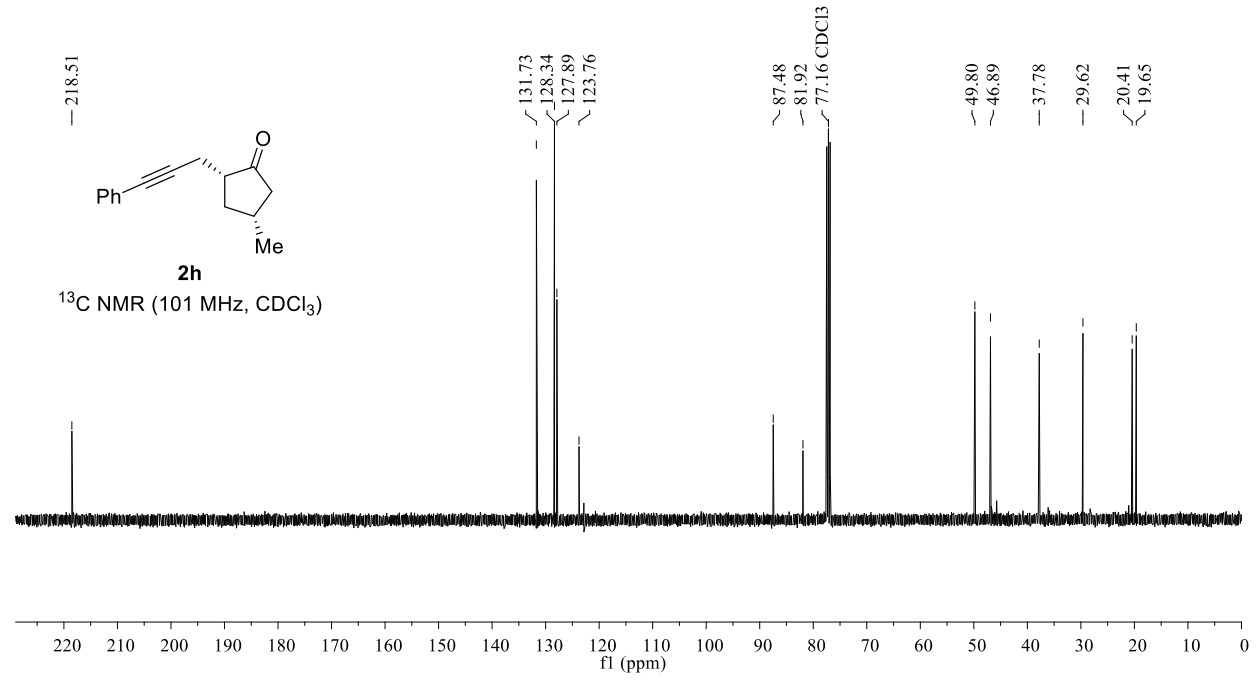

Ph
O
Me
2g
1H NMR (400 MHz, CDCl3)
fl (ppm)


Ph
O
Me
2g
13C NMR (101 MHz, CDCl3)
fl (ppm)



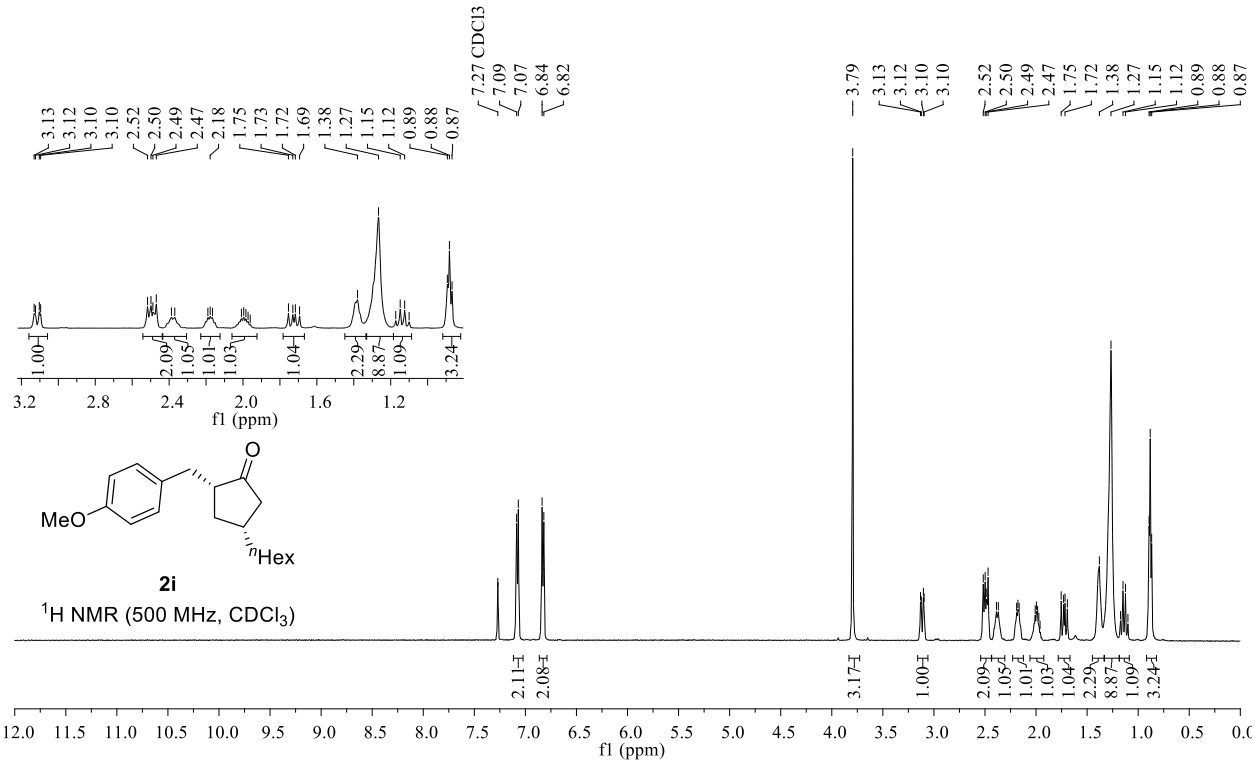
2h

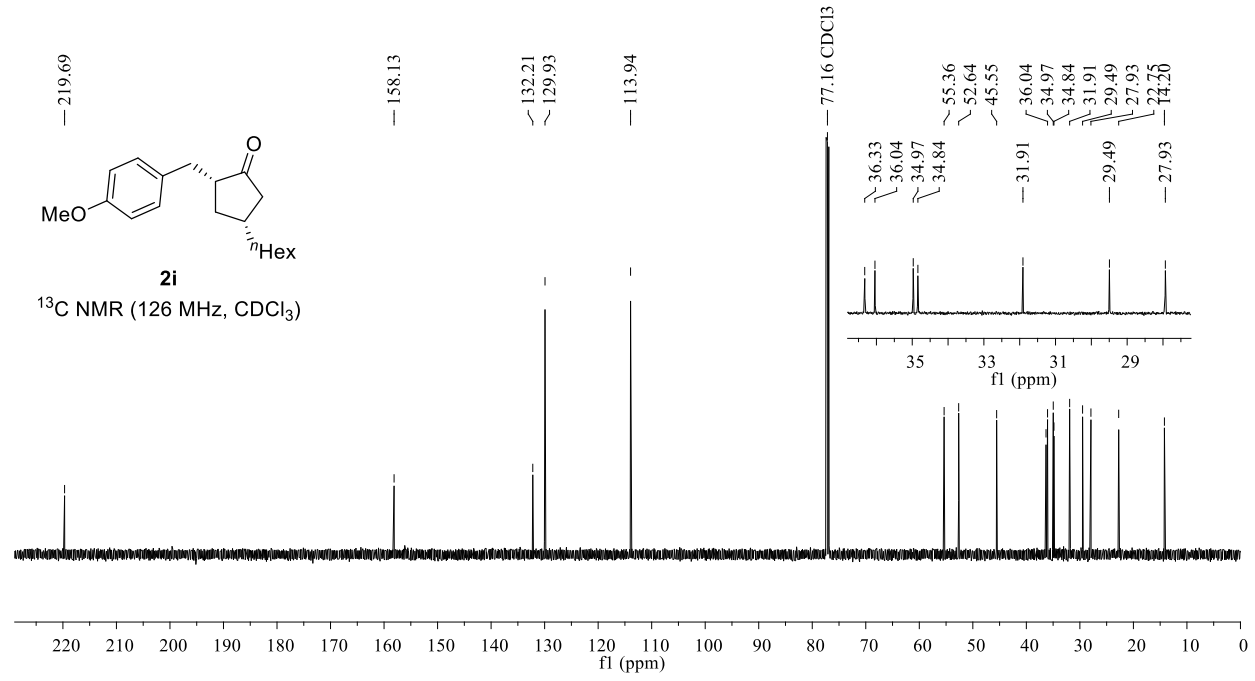
^{1}H NMR (400 MHz, $CDCl_3$)

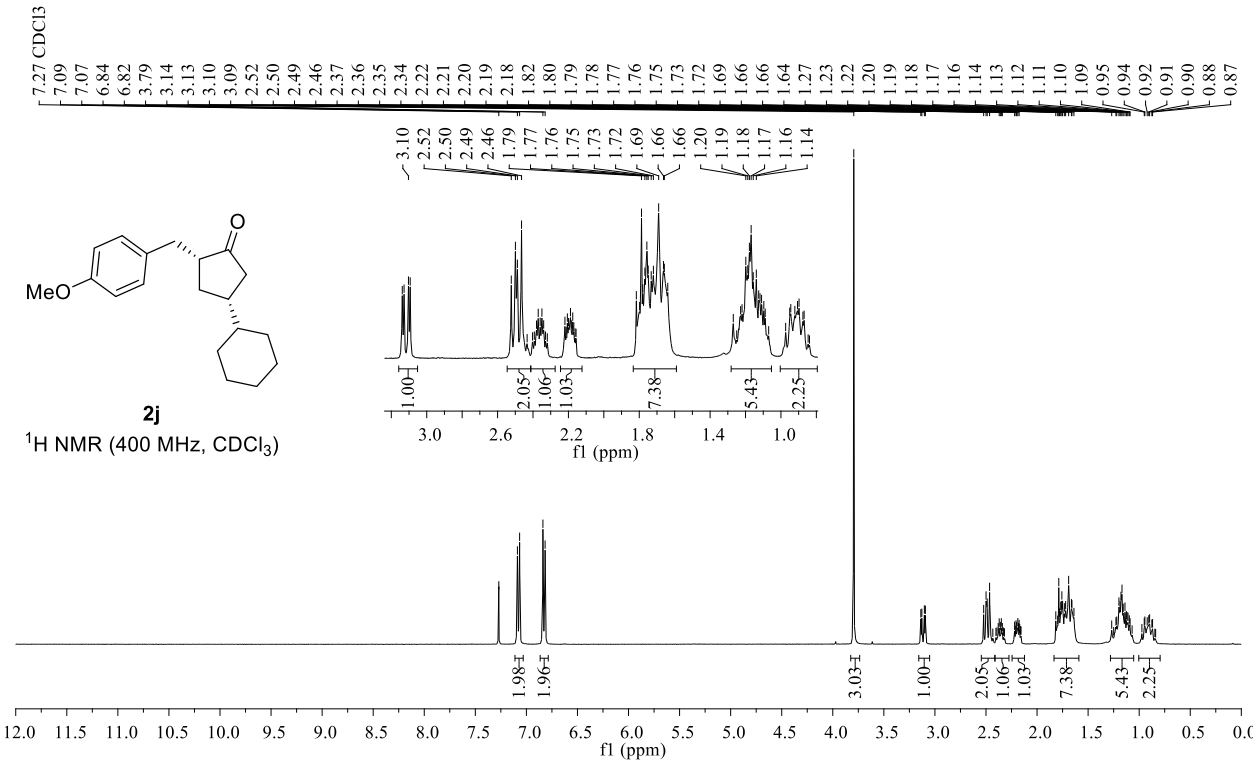


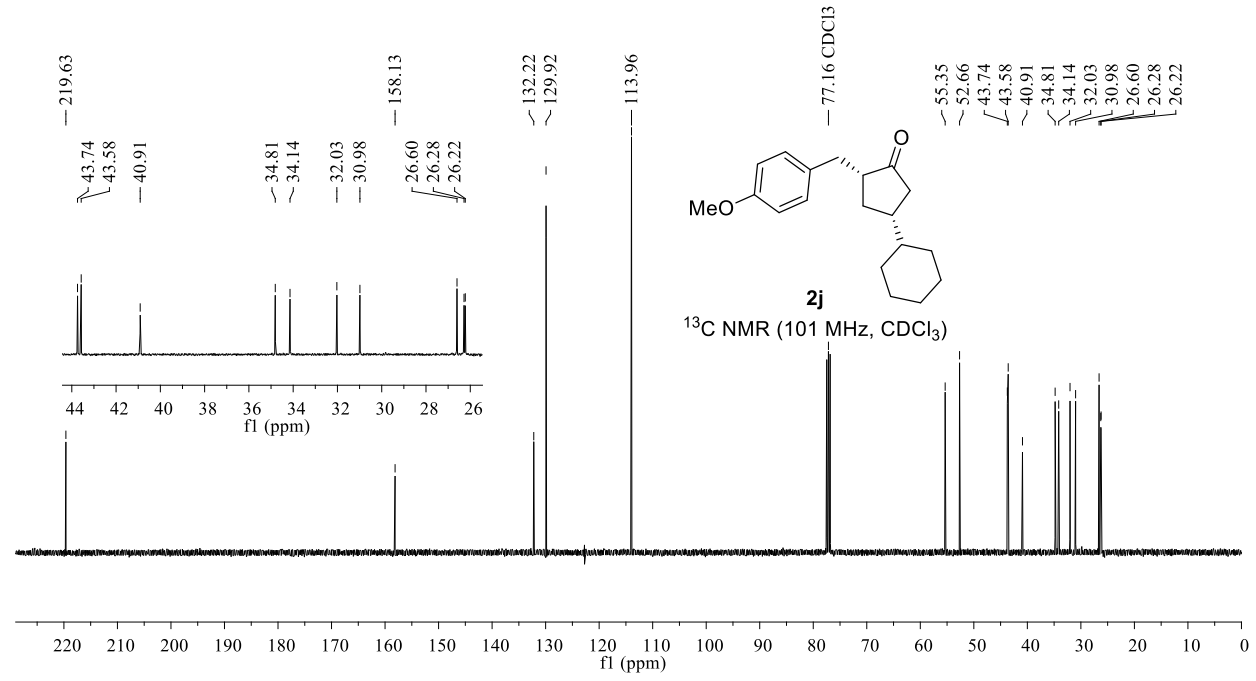
2h

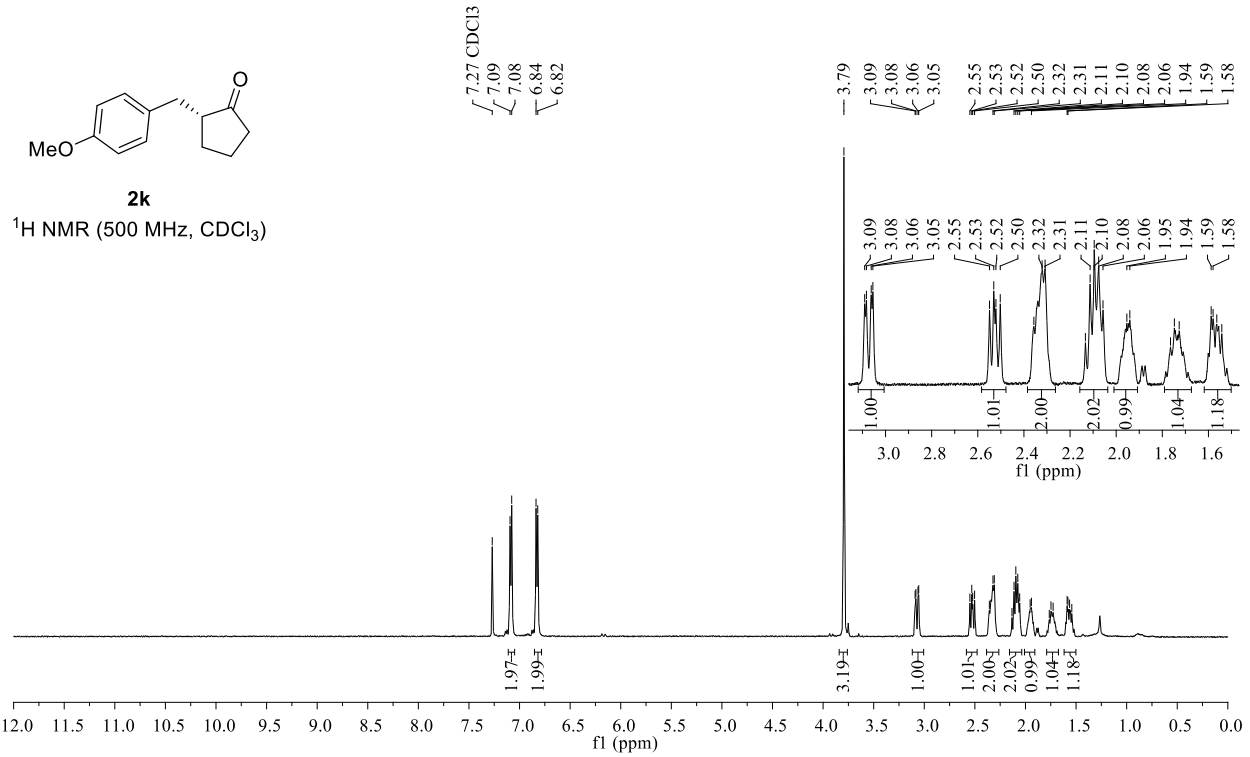
^{13}C NMR (101 MHz, $CDCl_3$)

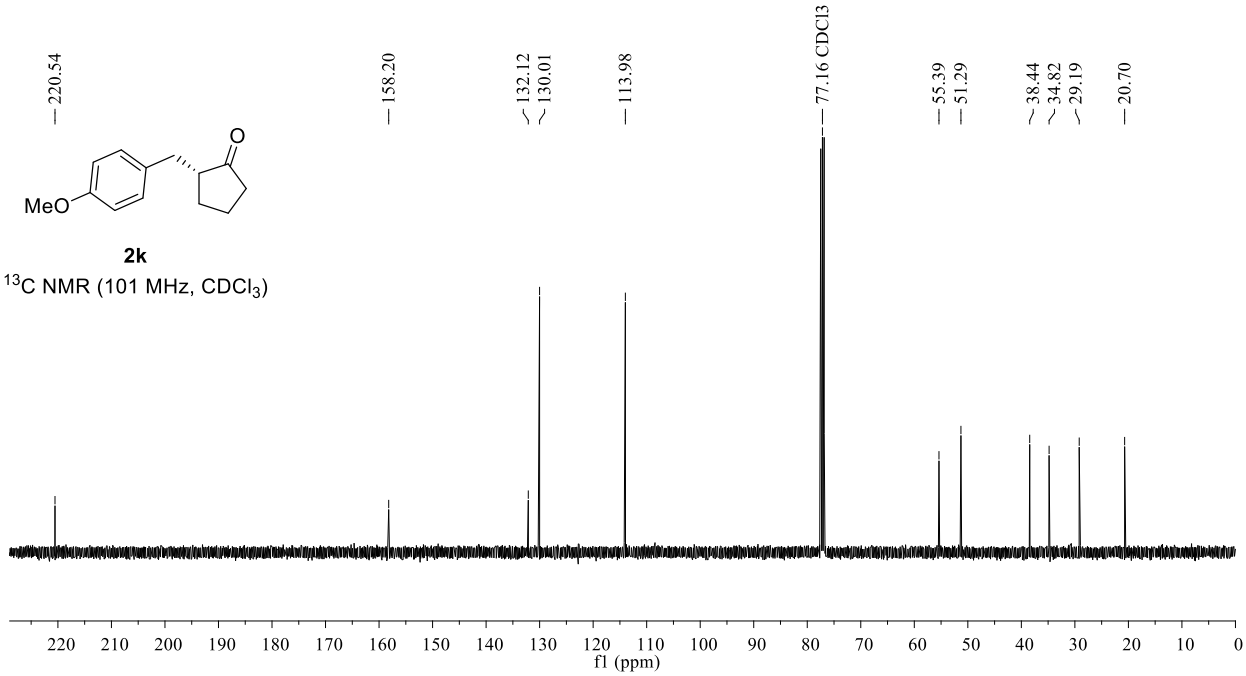

MeO
nHex
O
2i
1H NMR (500 MHz, CDCl3)
f1 (ppm)

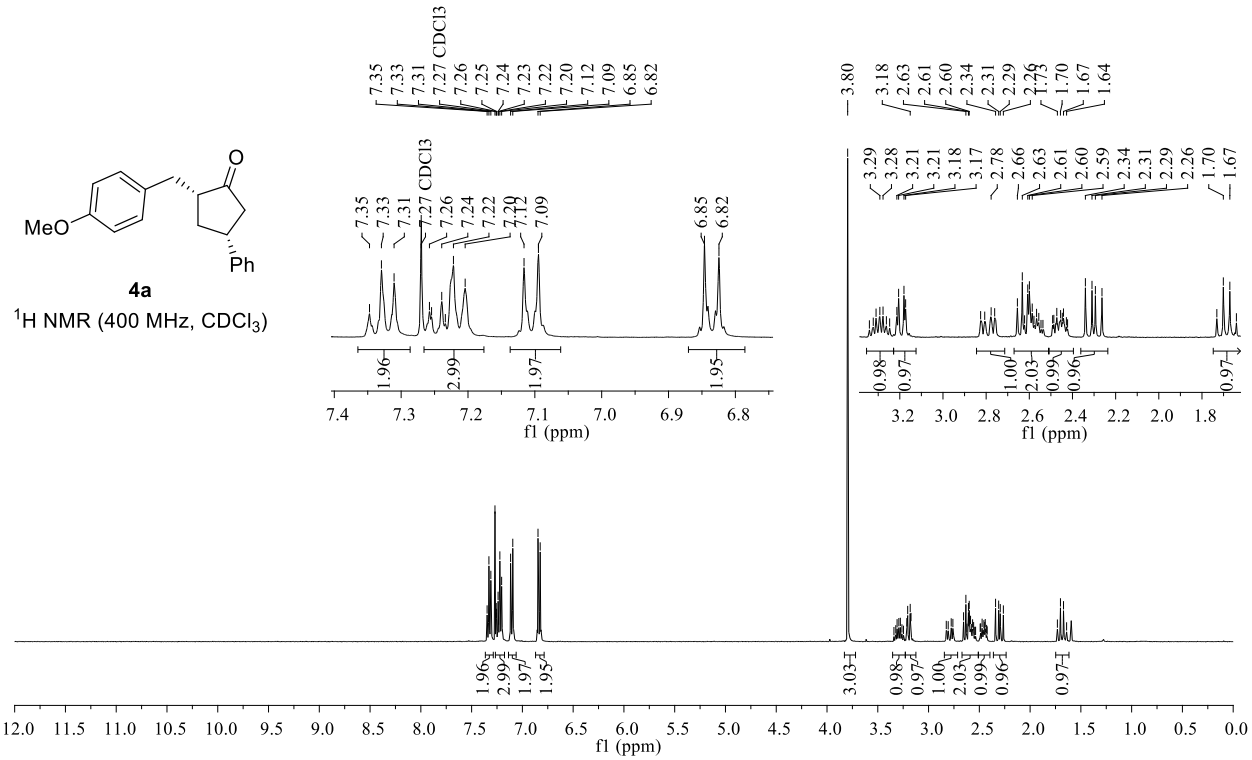

MeO
nHex
O
2i
13C NMR (126 MHz, CDCl3)
f1 (ppm)

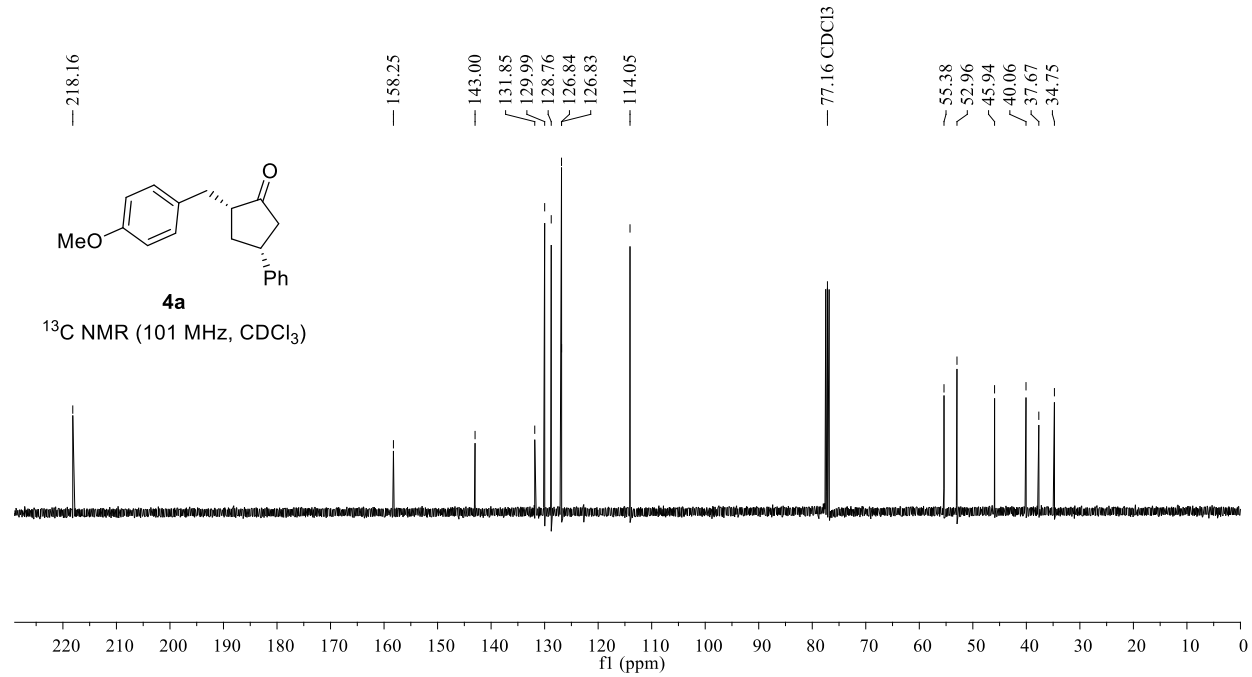

7.27 CDCl3
MeO
O
2j
1H NMR (400 MHz, CDCl3)
f1 (ppm)

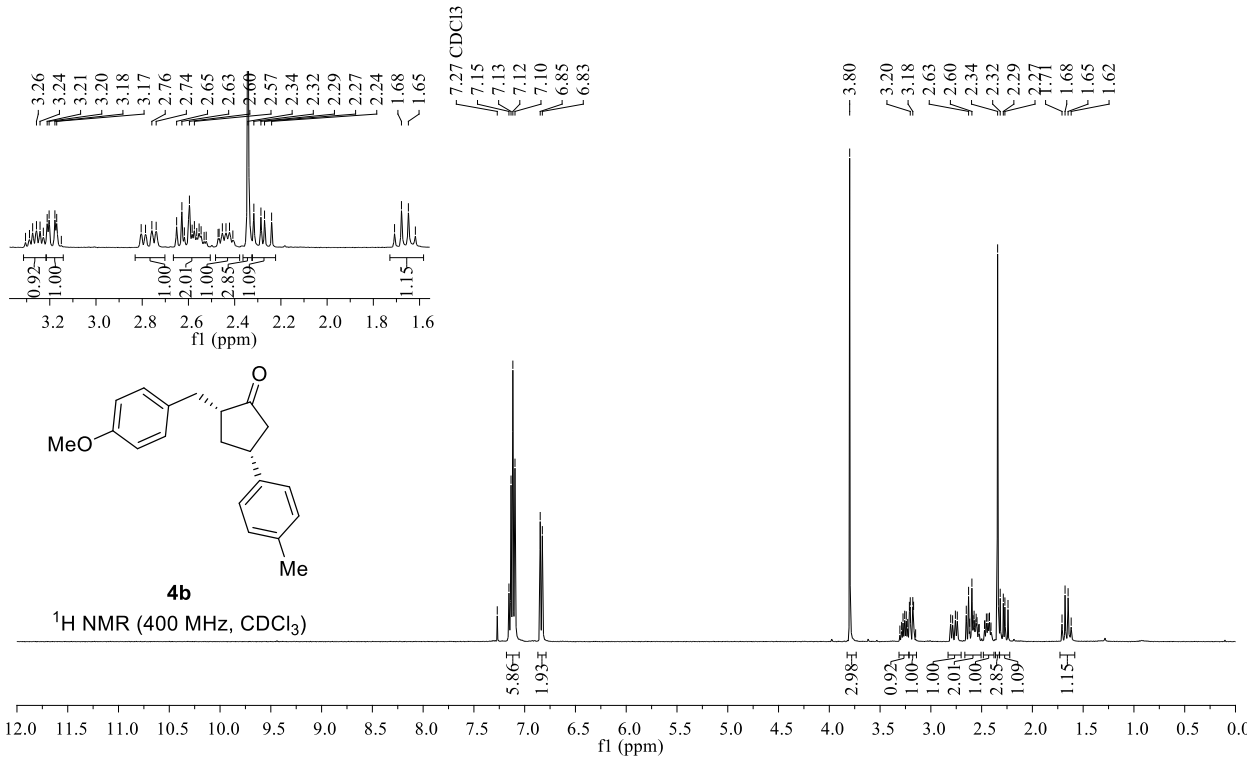

77.16 CDCl3
MeO
O
2j
13C NMR (101 MHz, CDCl3)
f1 (ppm)

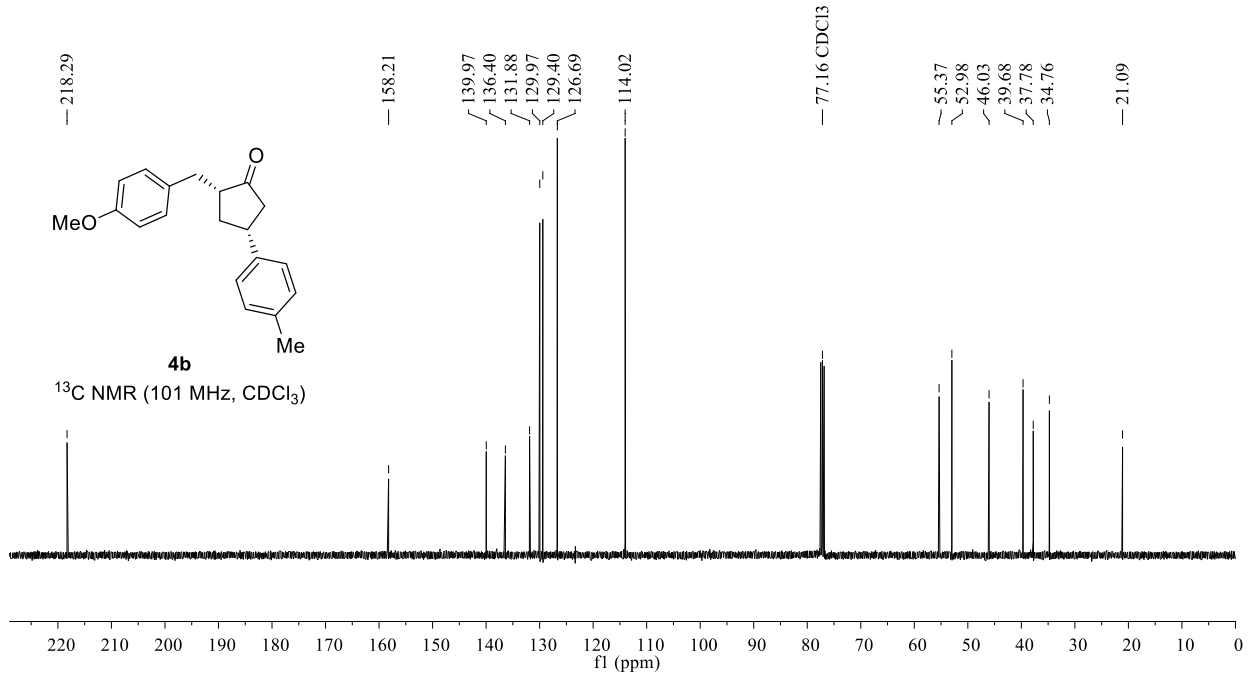

MeO
O
2k
1H NMR (500 MHz, CDCl3)
7.27 CDCl3
7.09
7.08
6.84
6.82
3.79
3.09
3.08
3.06
3.05
2.55
2.53
2.52
2.50
2.32
2.31
2.11
2.10
2.08
2.06
1.94
1.59
1.58
1.97
1.99
3.19
1.00
1.01
2.00
2.02
0.99
1.04
1.18
f1 (ppm)

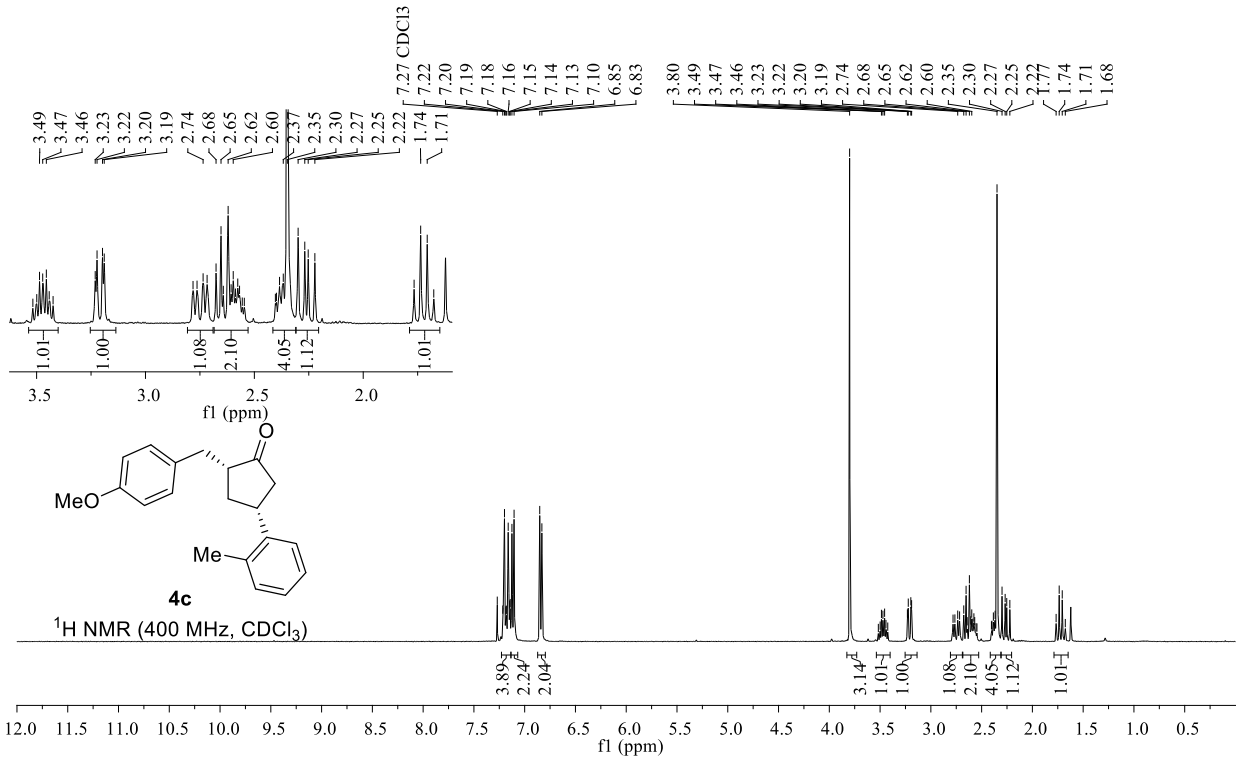

MeO
O
2k
13C NMR (101 MHz, CDCl3)
220.54
158.20
132.12
130.01
113.98
77.16 CDCl3
55.39
51.29
38.44
34.82
29.19
20.70
f1 (ppm)

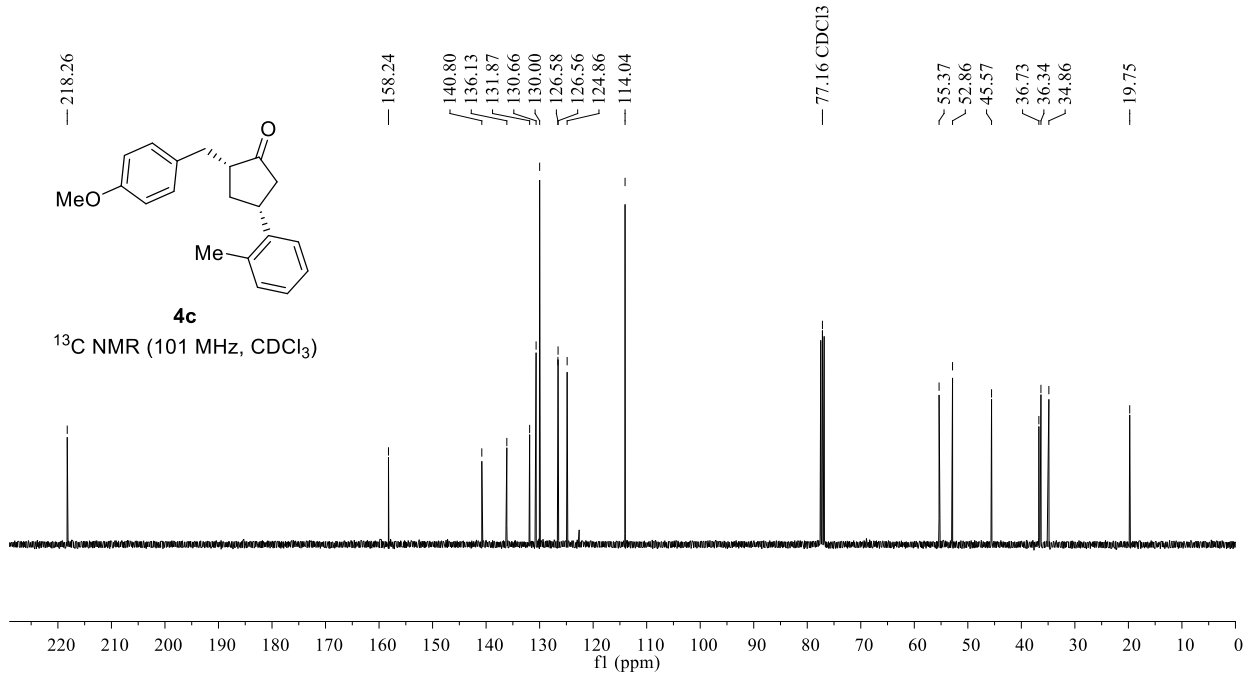

MeO
Ph
O
4a
^{1}H NMR (400 MHz, CDCl$_3$)
7.35 7.33 7.31 7.27 CDCl3 7.26 7.25 7.24 7.23 7.22 7.20 7.12 7.09 6.85 6.82
3.80
3.18 2.63 2.61 2.60 2.34 2.31 2.29 2.26 1.73 1.70 1.67 1.64
3.29 3.28 3.21 3.21 3.18 3.17 2.78 2.66 2.63 2.61 2.60 2.59 2.34 2.31 2.29 2.26 1.70 1.67
1.96 2.99 1.97 1.95
0.98 0.97 1.00 2.03 0.99 0.96 0.97
f1 (ppm)

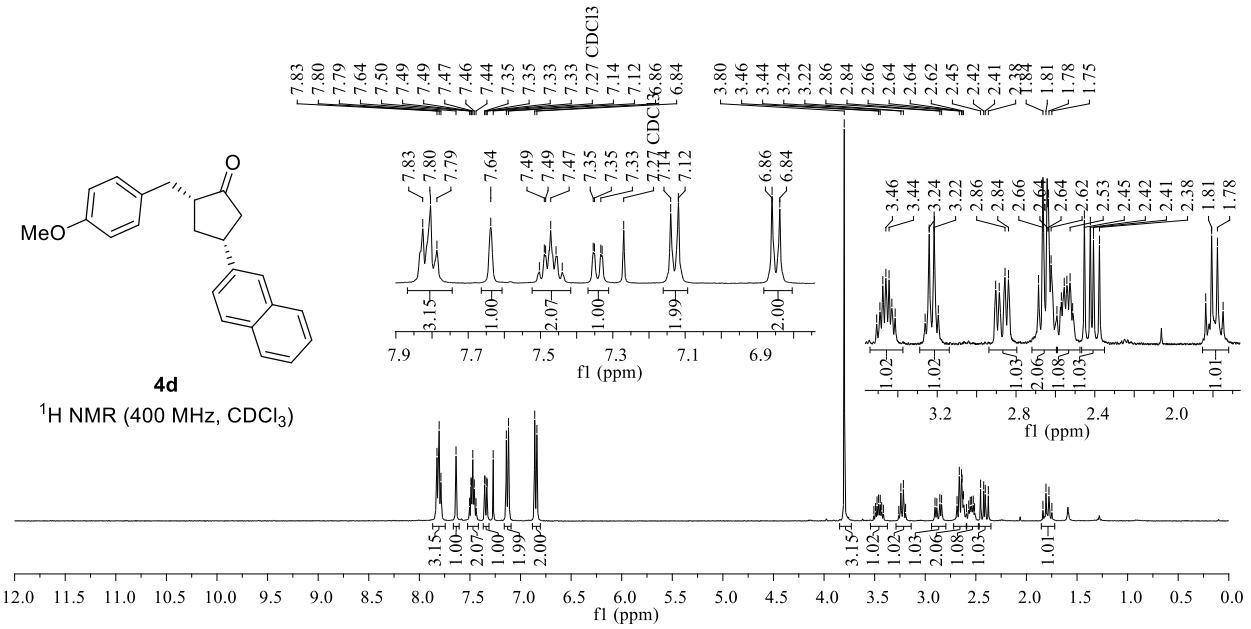

218.16
158.25
143.00
131.85 129.99 128.76 126.84 126.83
114.05
77.16 CDCl3
55.38 52.96 45.94 40.06 37.67 34.75
MeO
Ph
O
4a
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

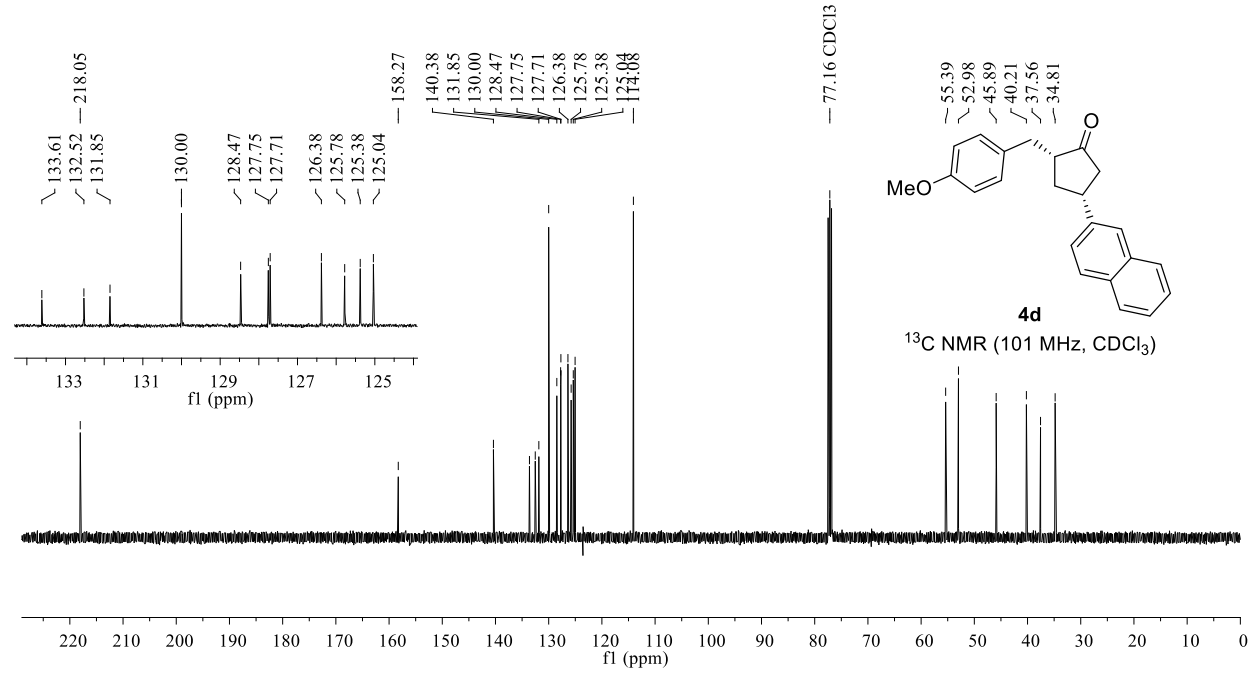

7.27 CDCl3
3.80
MeO
Me
O
4b
1H NMR (400 MHz, CDCl3)
f1 (ppm)

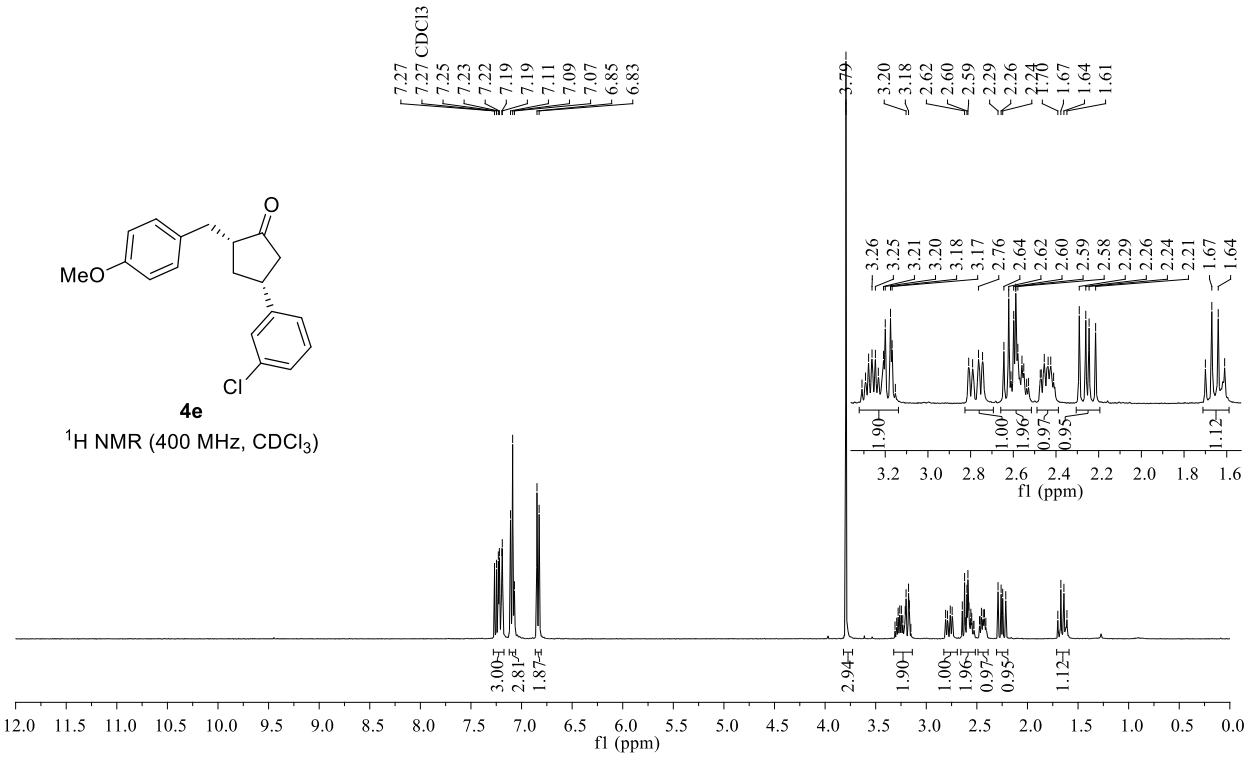

218.29
158.21
139.97
136.40
131.88
129.97
129.40
126.69
114.02
77.16 CDCl3
55.37
52.98
46.03
39.68
37.78
34.76
21.09
MeO
Me
O
4b
13C NMR (101 MHz, CDCl3)
f1 (ppm)

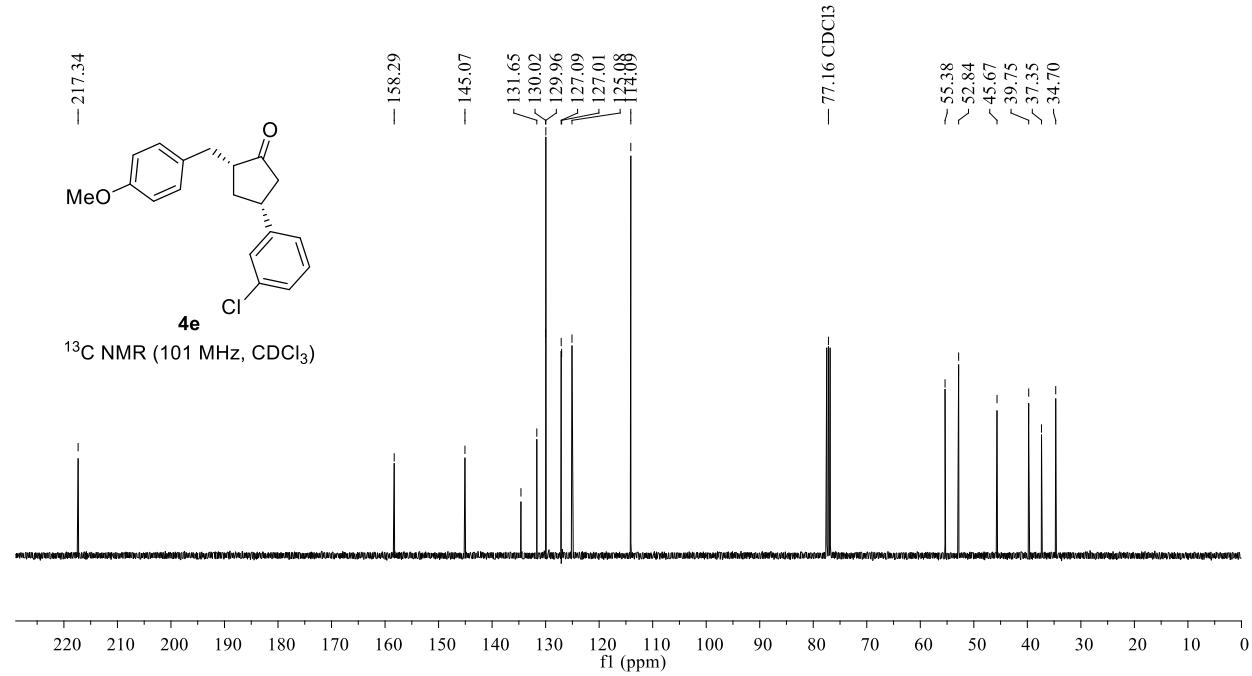

7.27 CDCl3
3.80
3.49
3.47
3.46
3.23
3.22
3.20
3.19
2.74
2.68
2.65
2.62
2.60
2.35
2.30
2.27
2.25
1.74
1.71
1.68
MeO
Me
O
4c
1H NMR (400 MHz, CDCl3)
f1 (ppm)

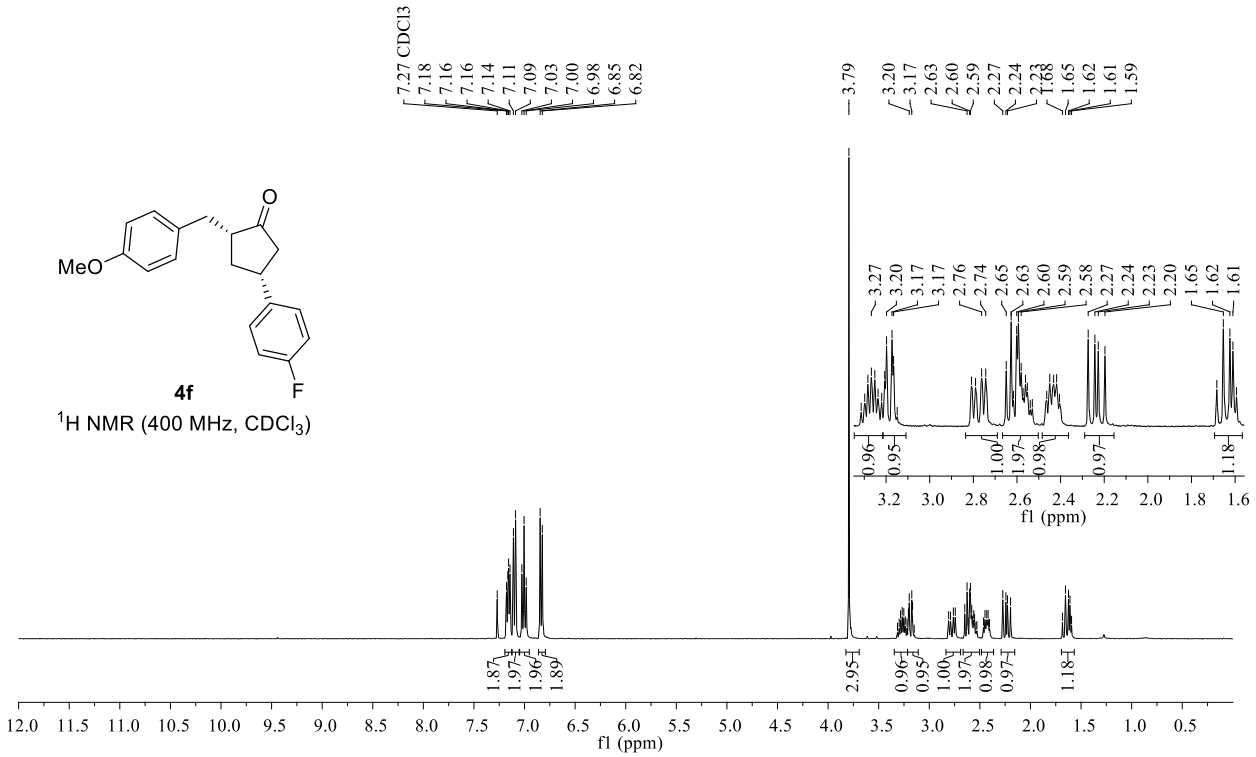

218.26
158.24
140.80
136.13
131.87
130.66
130.00
126.58
126.56
124.86
114.04
77.16 CDCl3
55.37
52.86
45.57
36.73
36.34
34.86
19.75
MeO
Me
O
4c
13C NMR (101 MHz, CDCl3)
f1 (ppm)

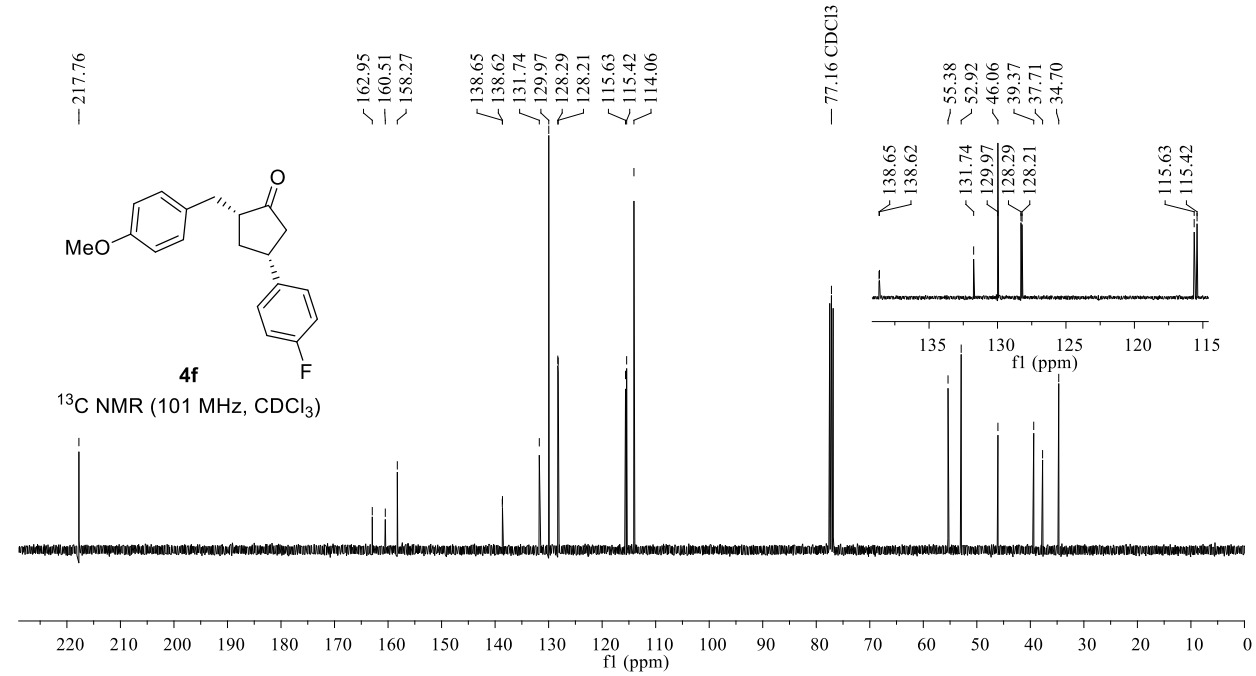

MeO
O
4d
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

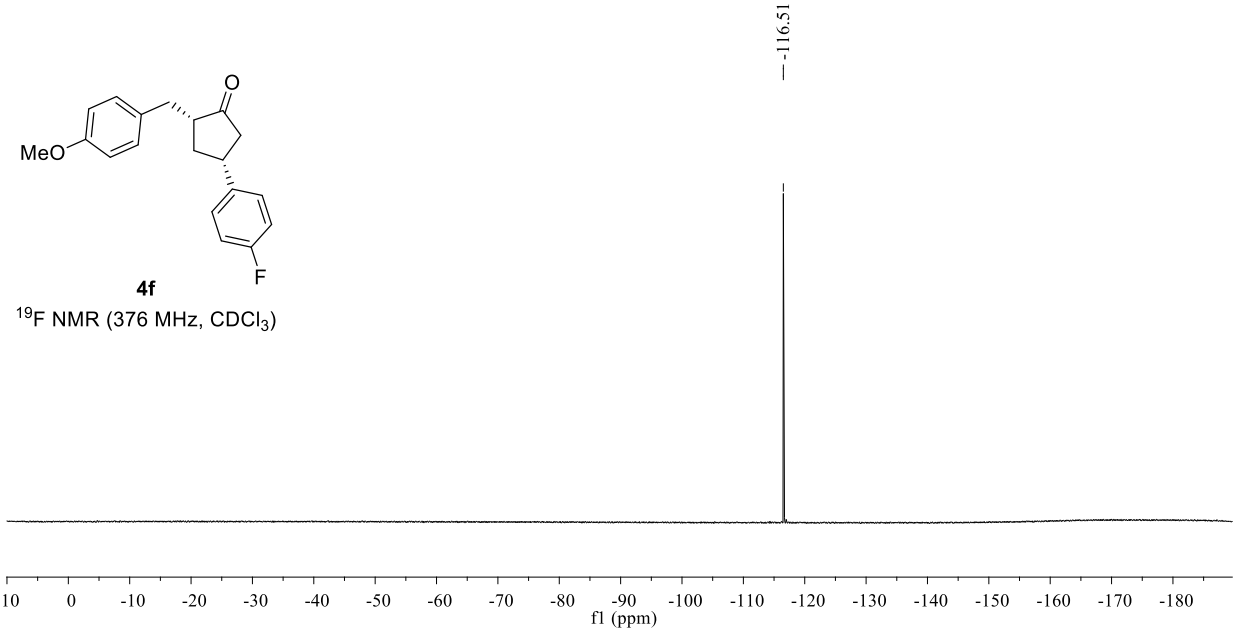

MeO
O
4d
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)


MeO
O
Cl
4e
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


MeO
O
Cl
4e
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

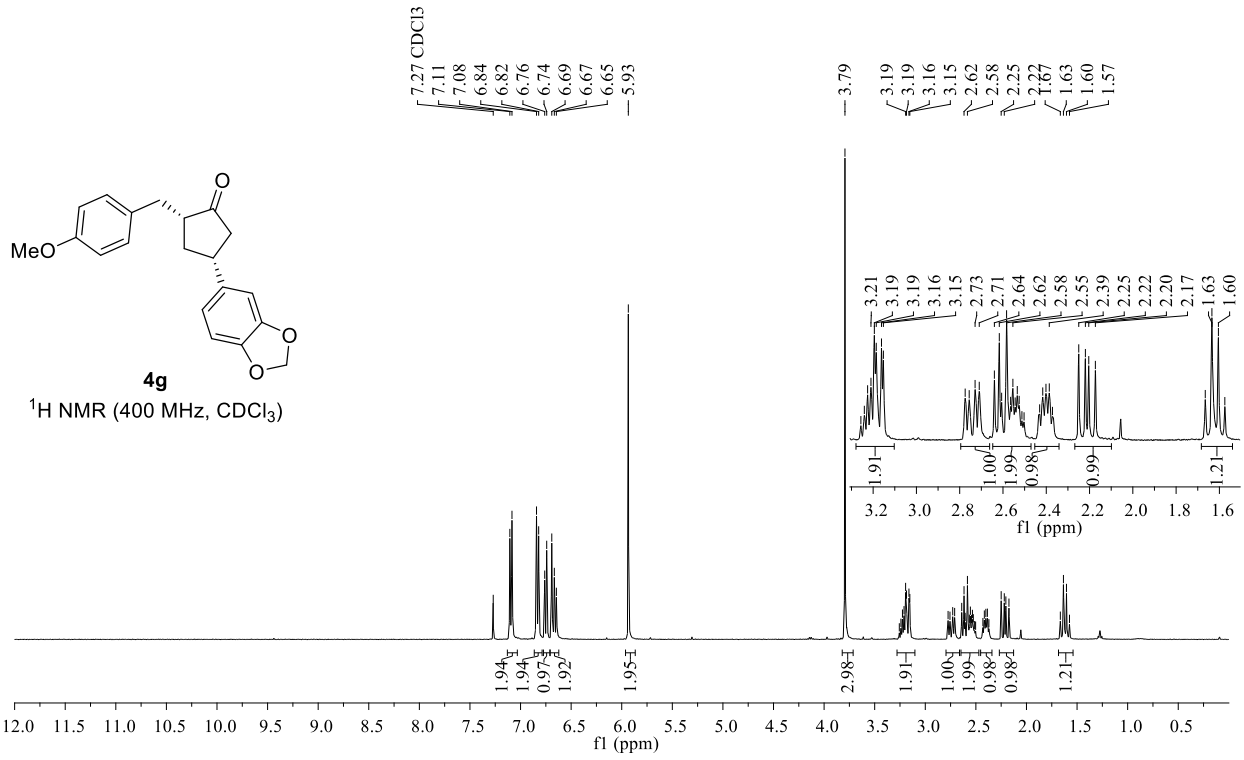

7.27 CDCl3
7.18
7.16
7.16
7.14
7.11
7.09
7.03
7.00
6.98
6.85
6.82
3.79
3.20
3.17
2.63
2.60
2.59
2.27
2.24
2.23
1.68
1.65
1.62
1.61
1.59
O
MeO
F
4f
1H NMR (400 MHz, CDCl3)
f1 (ppm)


217.76
162.95
160.51
158.27
138.65
138.62
131.74
129.97
128.29
128.21
115.63
115.42
114.06
77.16 CDCl3
55.38
52.92
46.06
39.37
37.71
34.70
O
MeO
F
4f
13C NMR (101 MHz, CDCl3)
f1 (ppm)



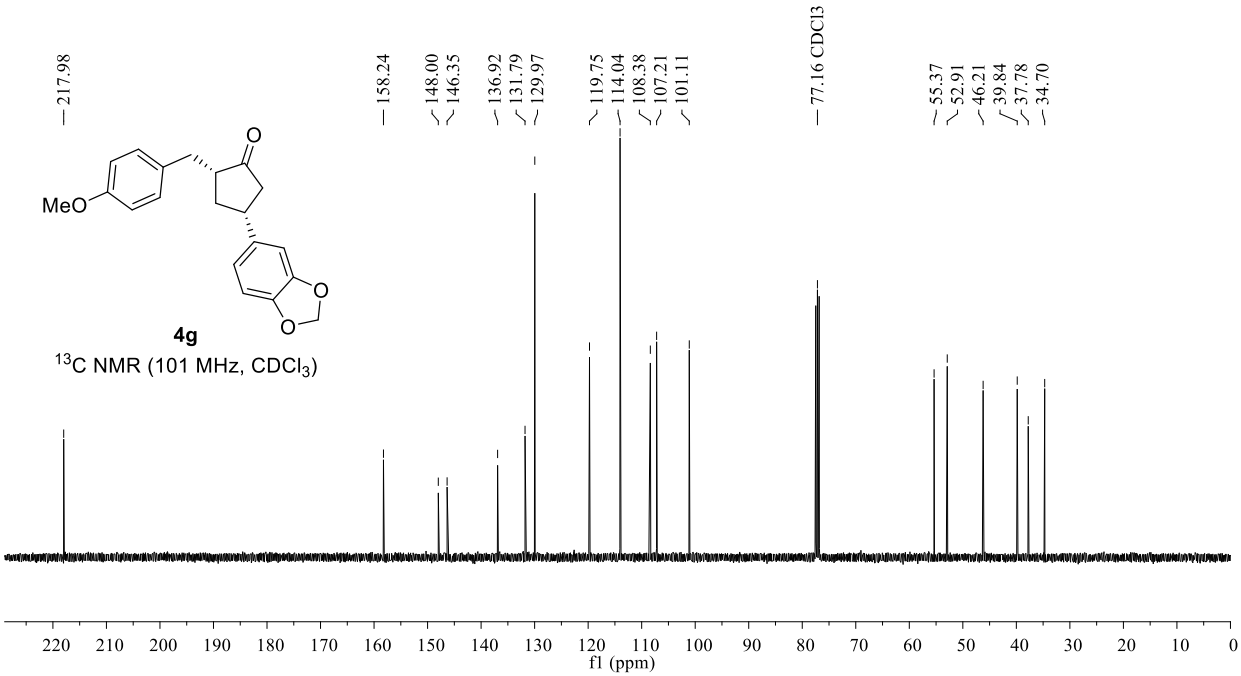
4f

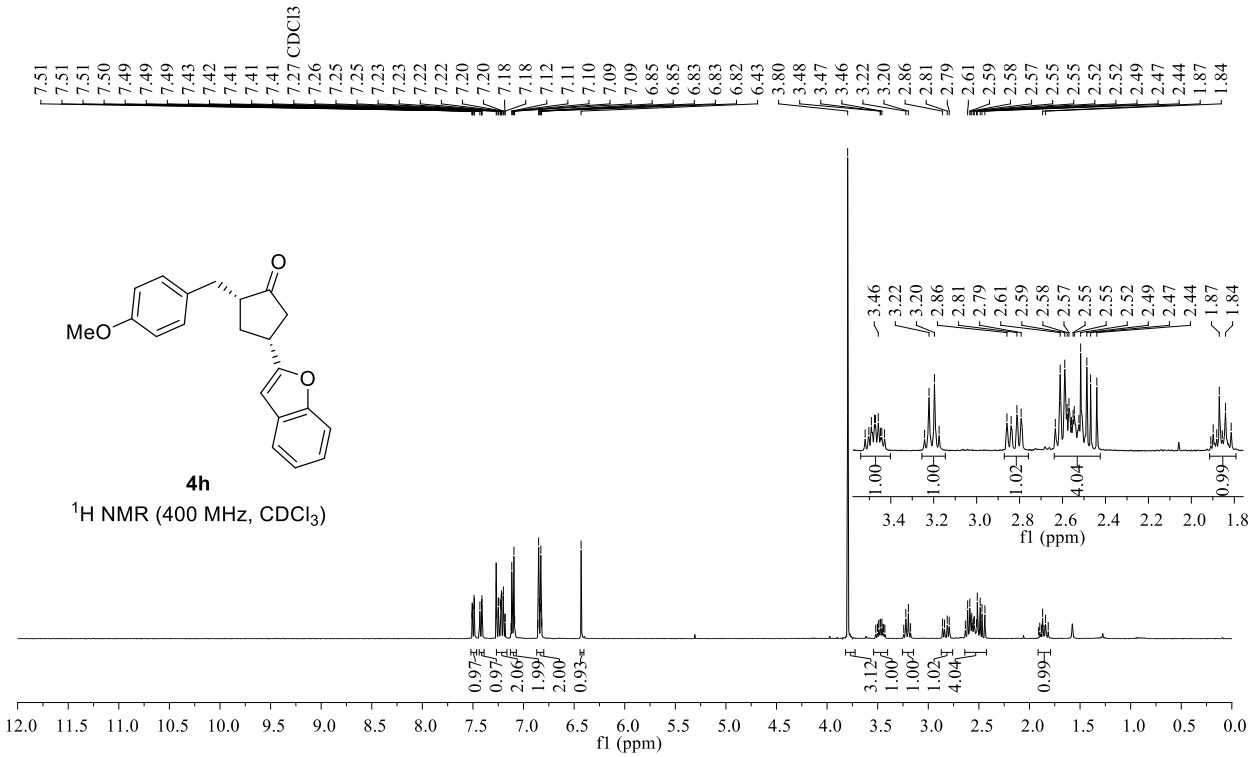
^{19}F NMR (376 MHz, $CDCl_3$)

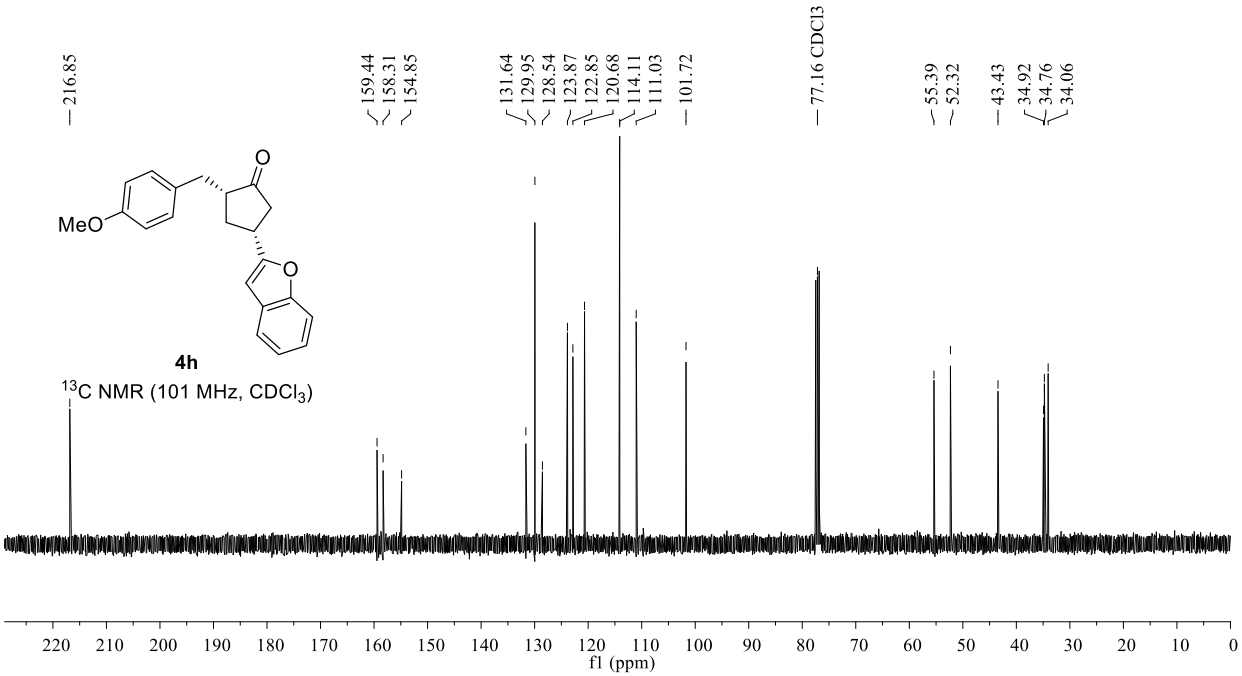


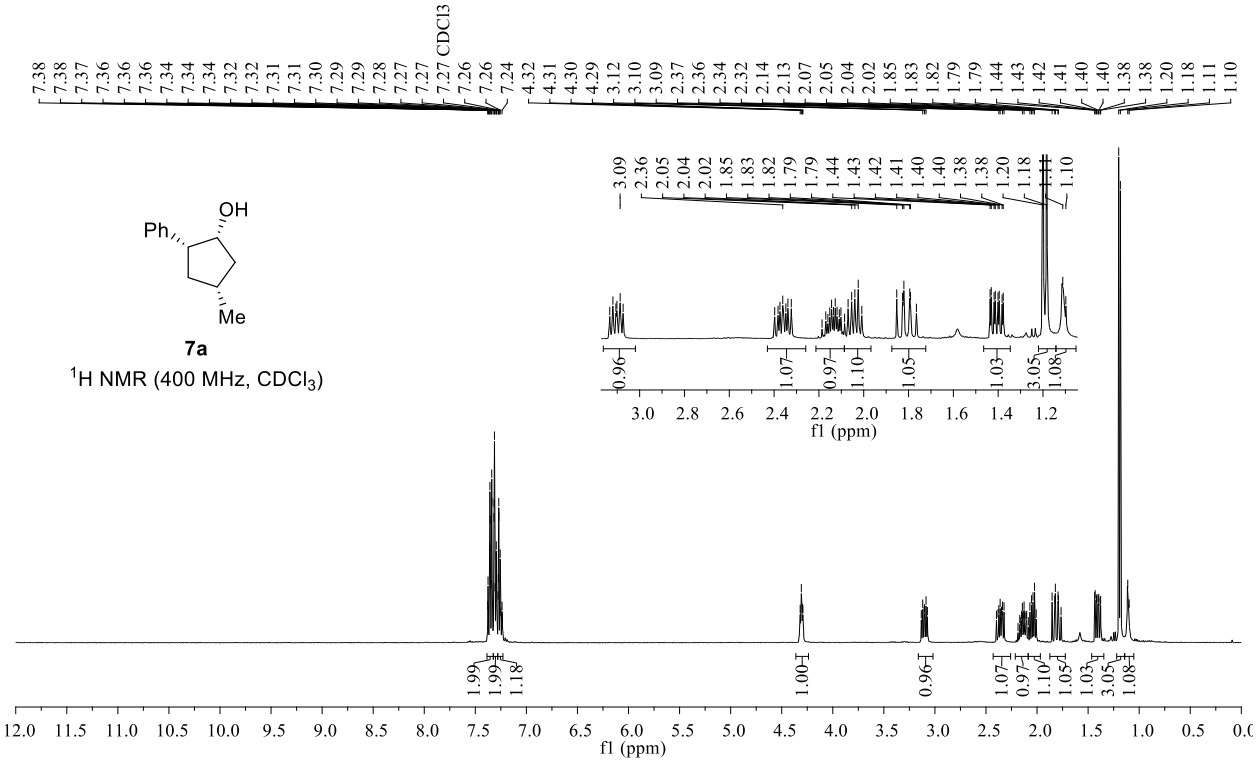
4g

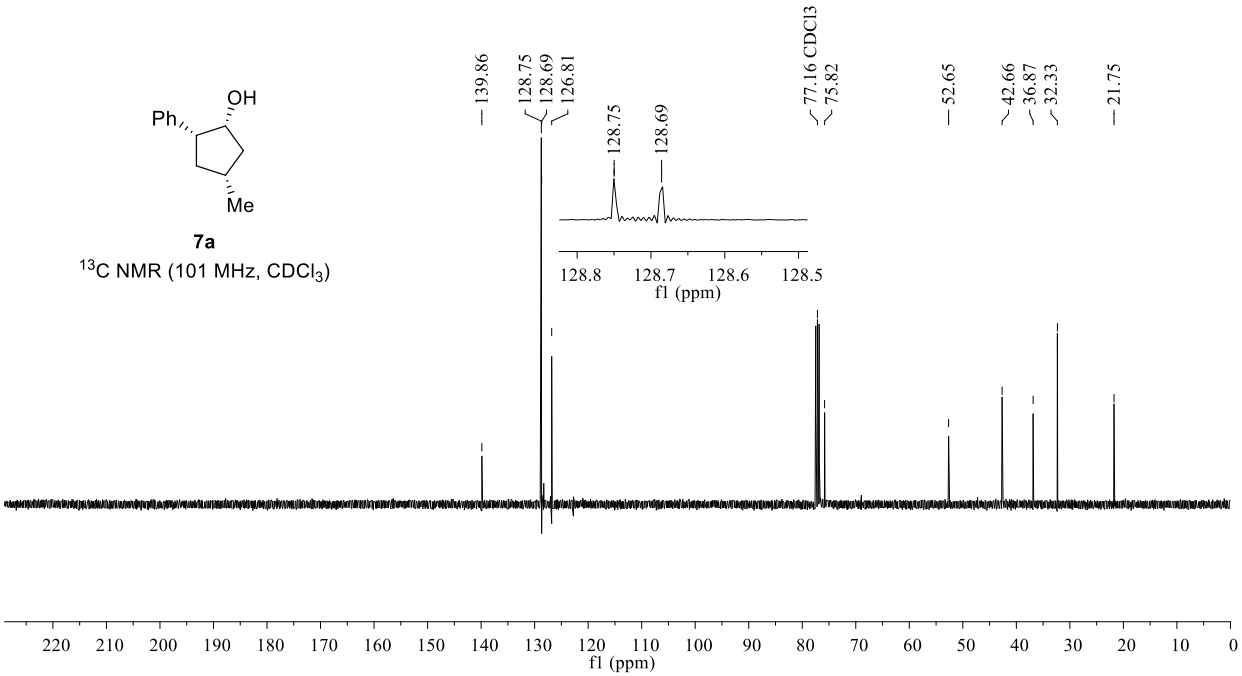
^{1}H NMR (400 MHz, $CDCl_3$)


217.98
158.24
148.00
146.35
136.92
131.79
129.97
119.75
114.04
108.38
107.21
101.11
77.16 CDCl3
55.37
52.91
46.21
39.84
37.78
34.70
MeO
O
O
O
4g
13C NMR (101 MHz, CDCl3)
f1 (ppm)


7.27 CDCl3
3.46
3.22
3.20
2.86
2.81
2.79
2.61
2.59
2.58
2.57
2.55
2.52
2.49
2.47
2.44
1.87
1.84
MeO
O
O
4h
1H NMR (400 MHz, CDCl3)
f1 (ppm)

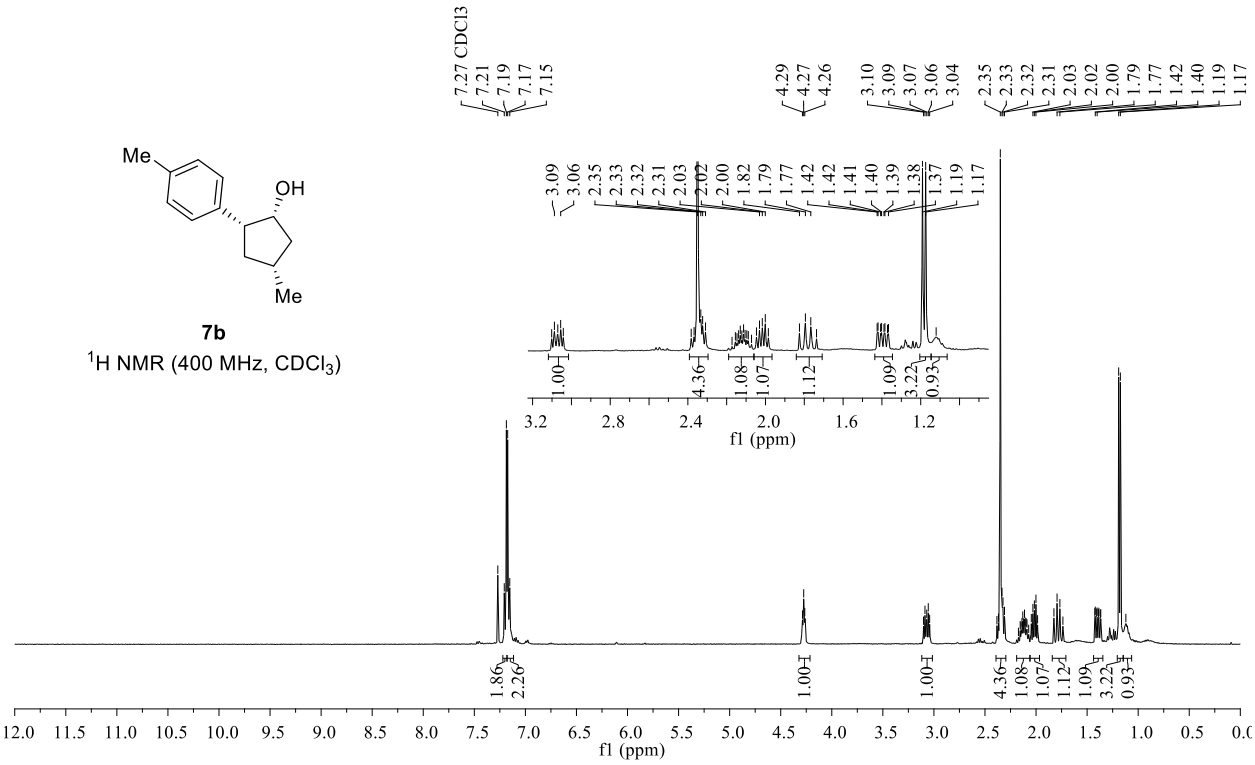

216.85
159.44
158.31
154.85
131.64
129.95
128.54
123.87
122.85
120.68
114.11
111.03
101.72
77.16 CDCl3
55.39
52.32
43.43
34.92
34.76
34.06
MeO
O
O
4h
13C NMR (101 MHz, CDCl3)
f1 (ppm)


7.27 CDCl3
OH
Ph
Me
7a
1H NMR (400 MHz, CDCl3)
f1 (ppm)



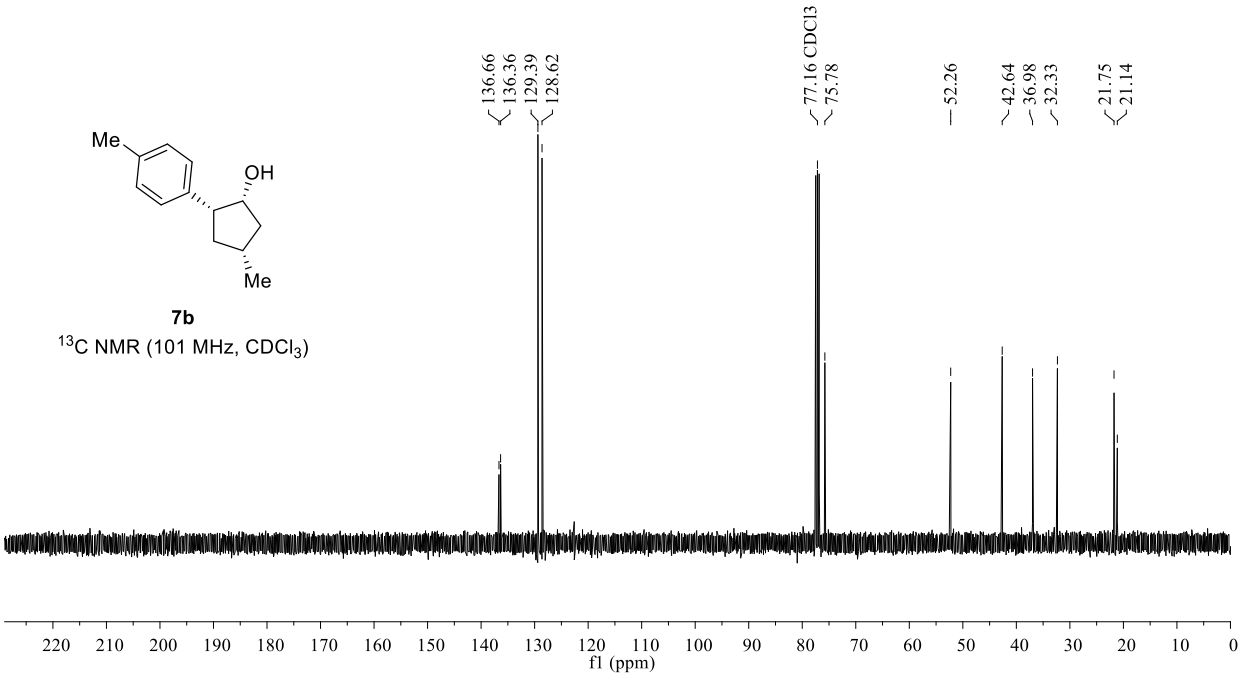
7a

^{13}C NMR (101 MHz, $CDCl_3$)



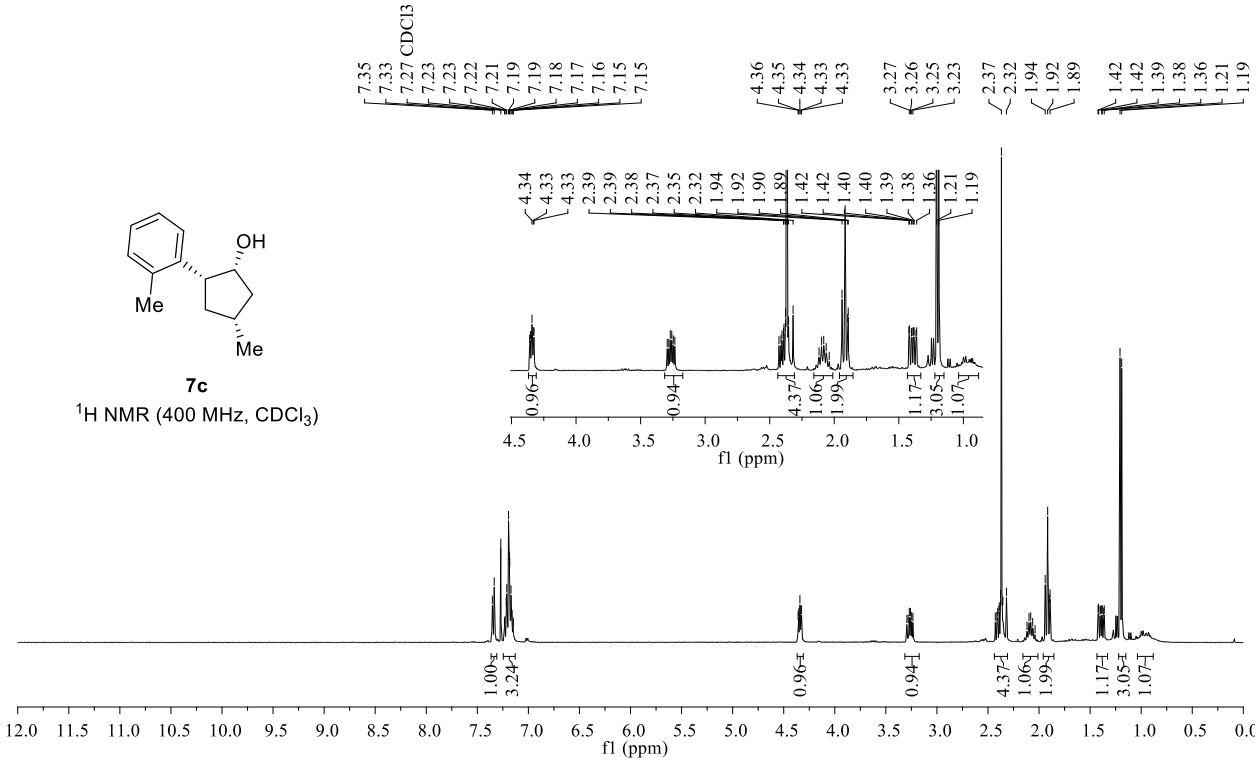
7b

^{1}H NMR (400 MHz, $CDCl_3$)



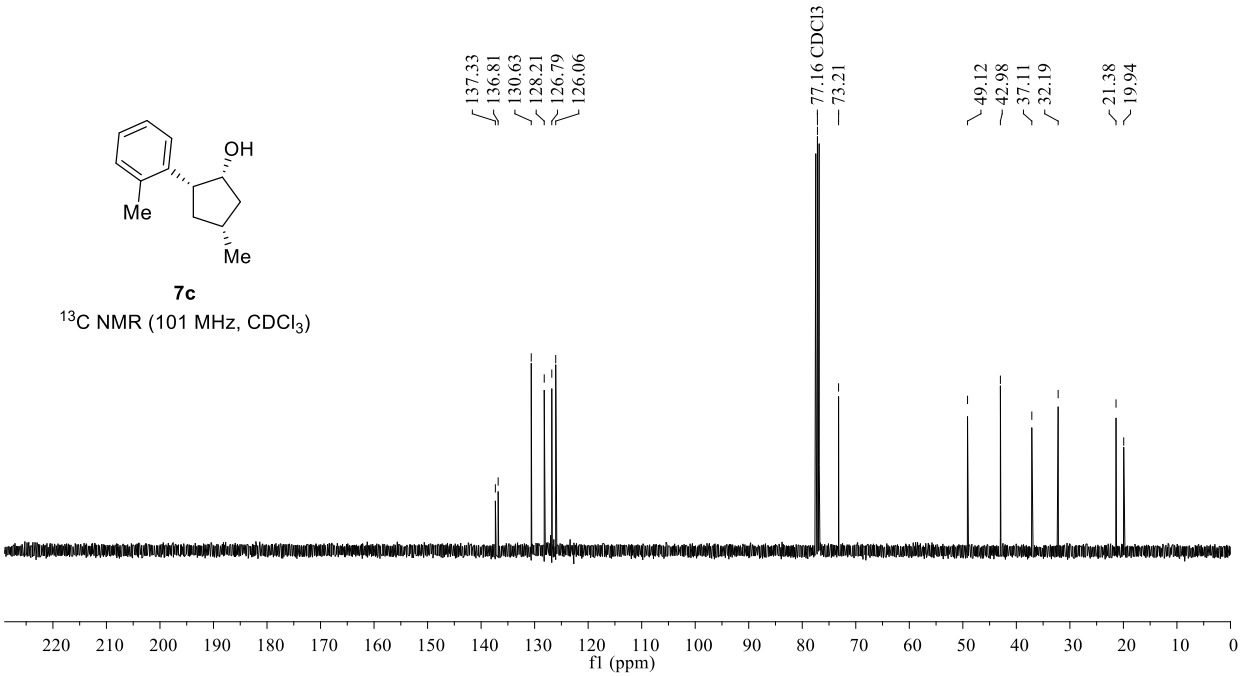
7b

^{13}C NMR (101 MHz, $CDCl_3$)



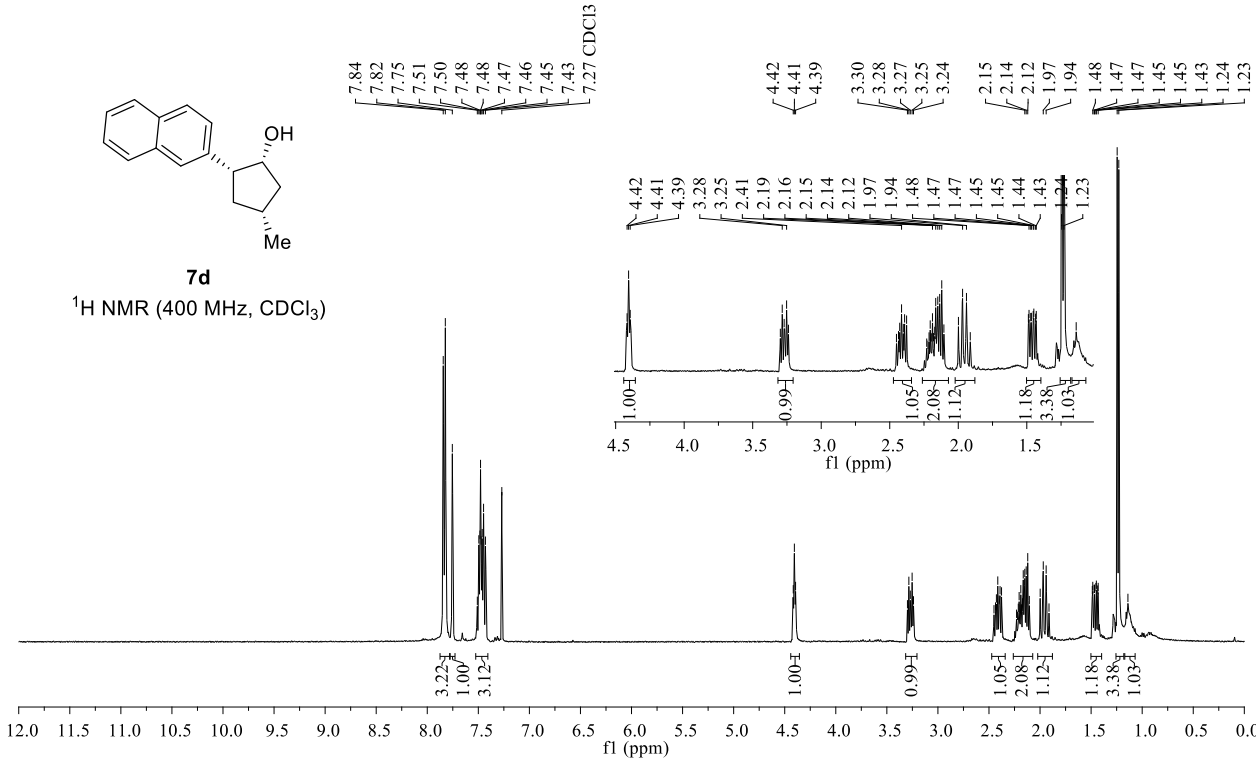
7c

^{1}H NMR (400 MHz, $CDCl_3$)



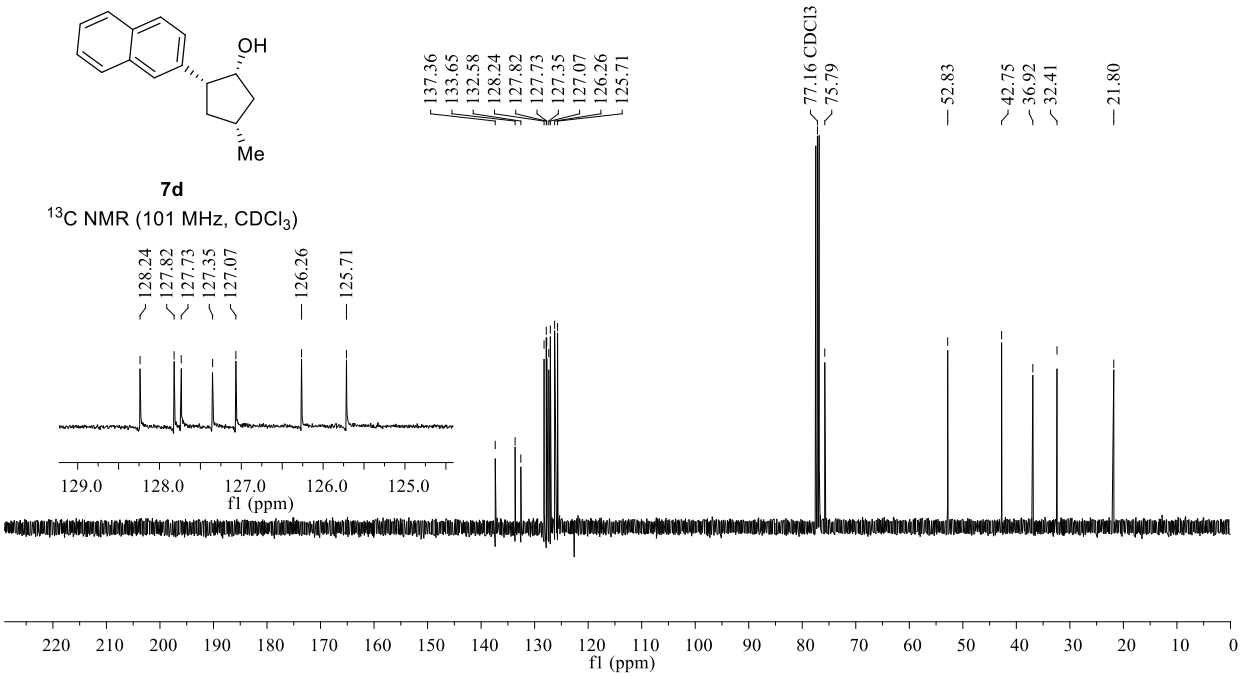
7c

^{13}C NMR (101 MHz, $CDCl_3$)



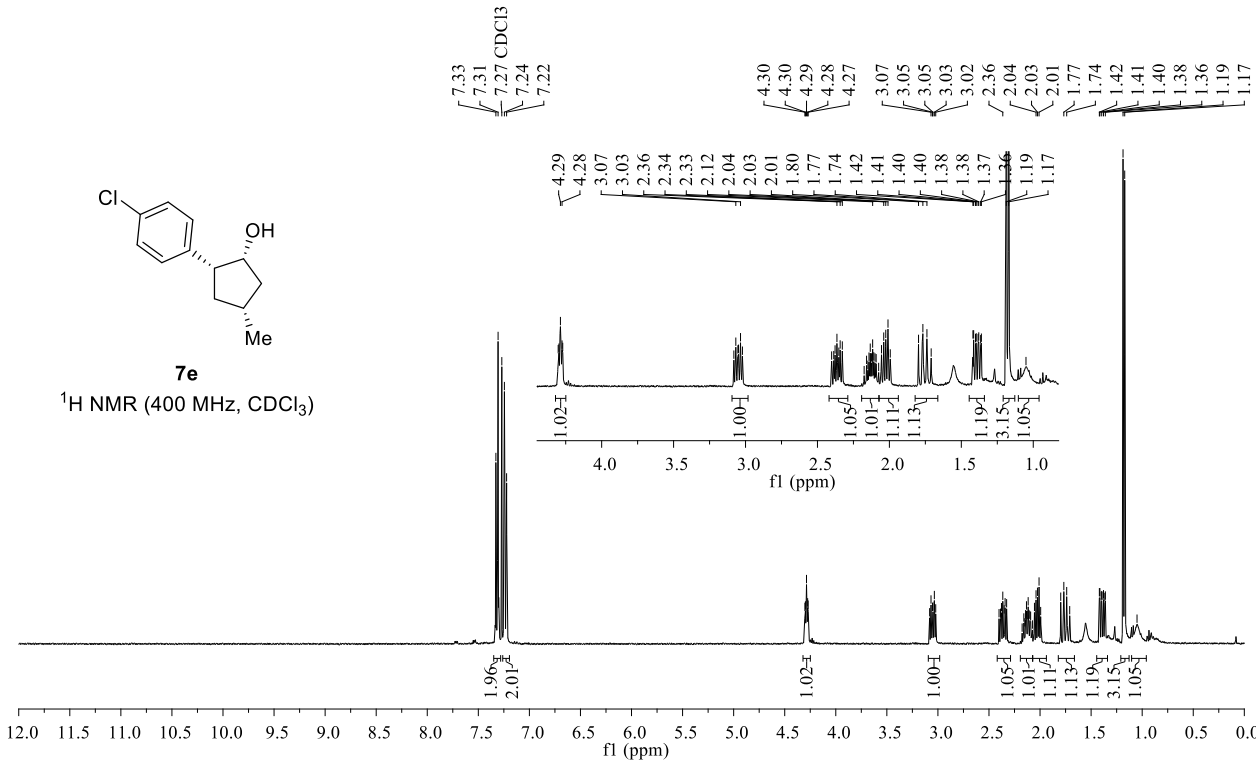
7d

^{1}H NMR (400 MHz, $CDCl_3$)



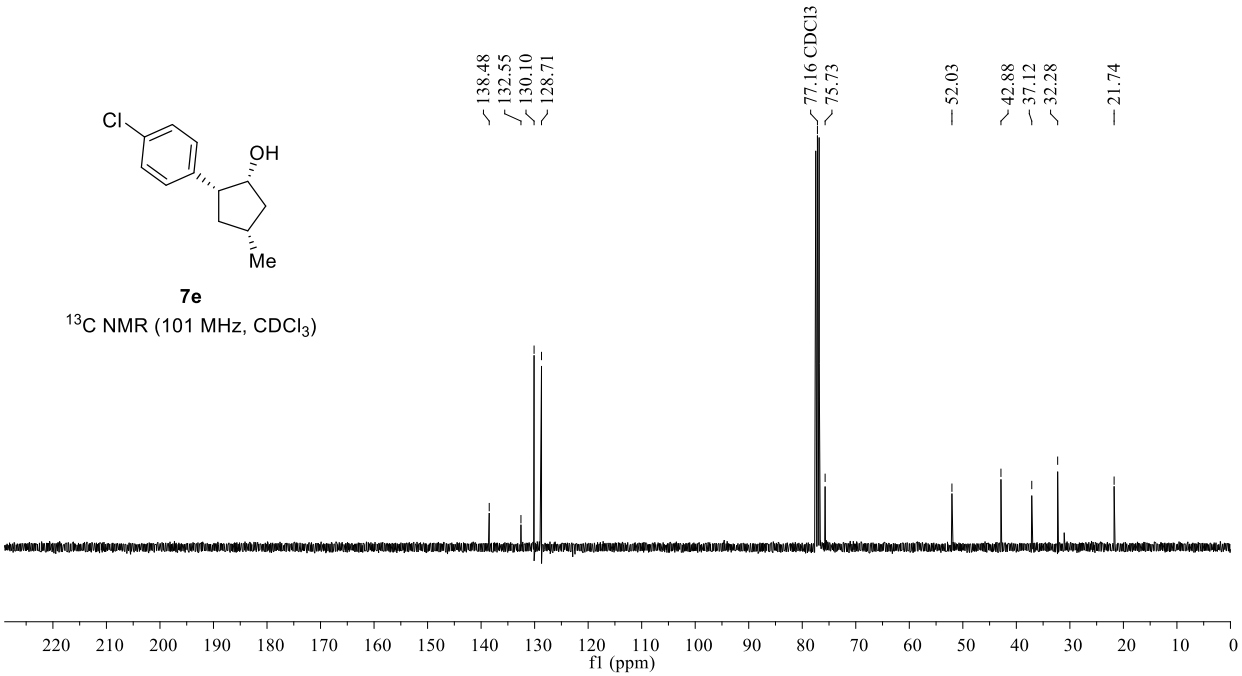
7d

^{13}C NMR (101 MHz, $CDCl_3$)



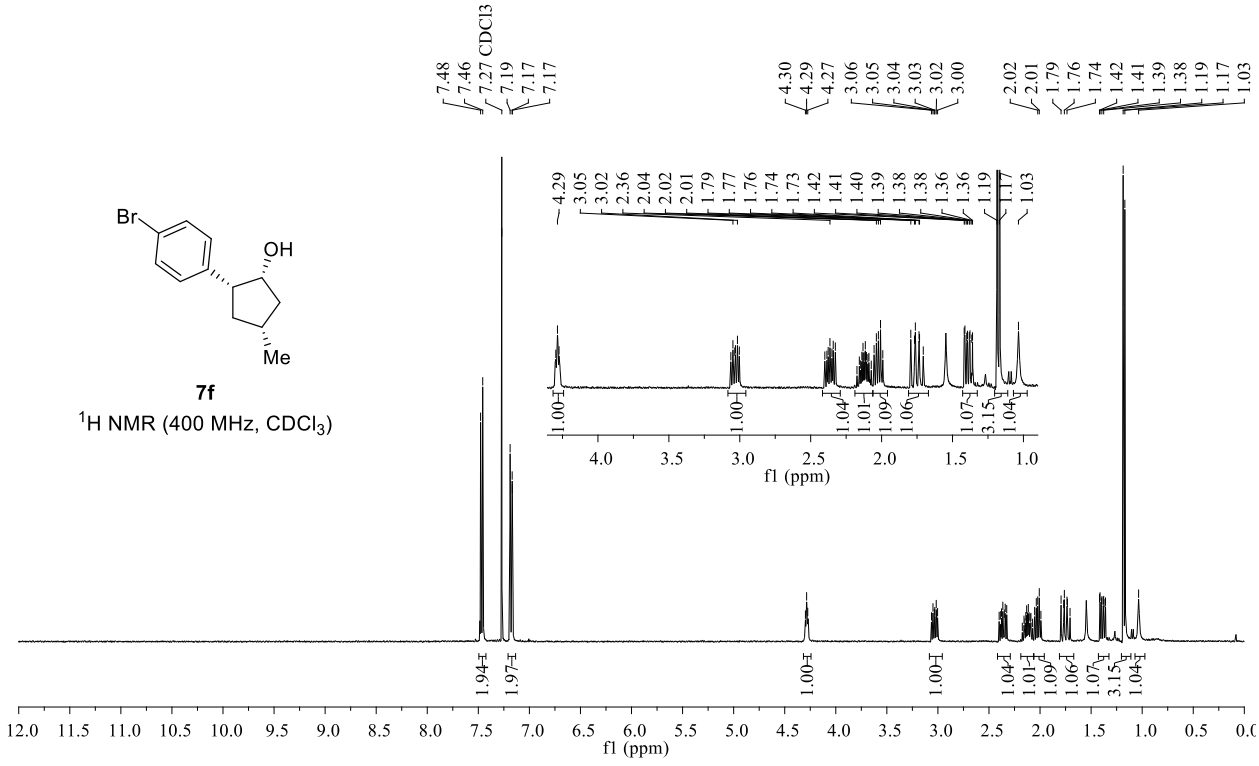
7e

^{1}H NMR (400 MHz, $CDCl_3$)



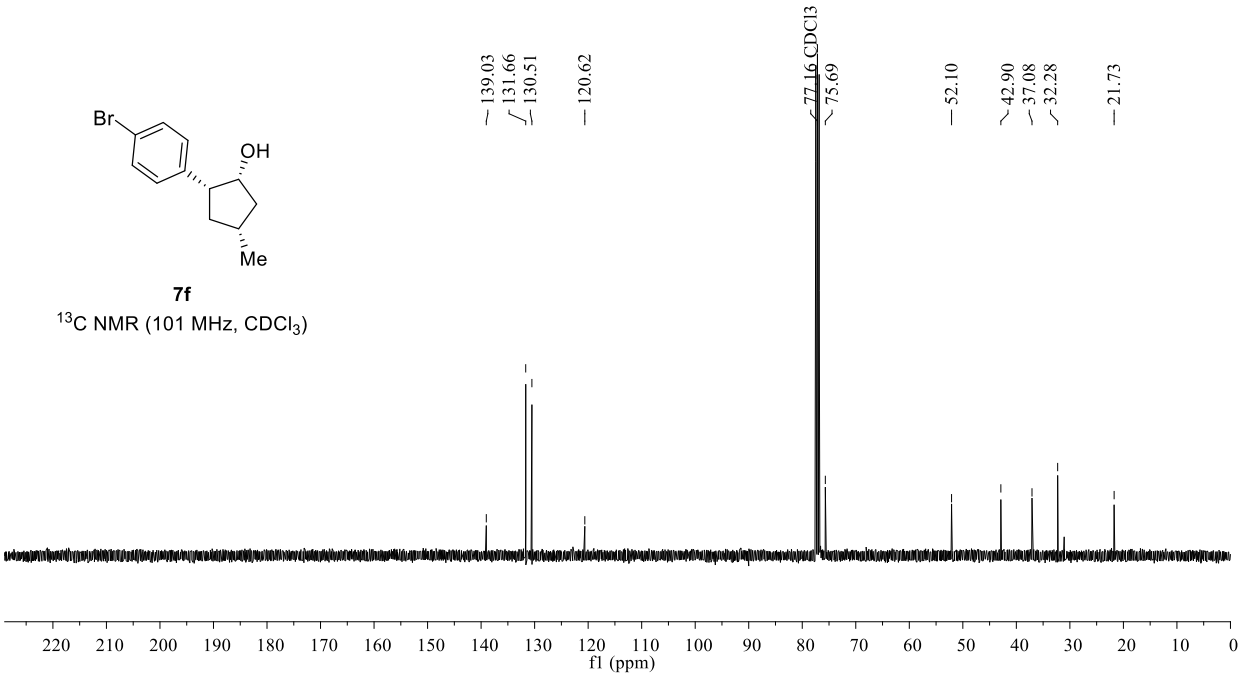
7e

^{13}C NMR (101 MHz, $CDCl_3$)



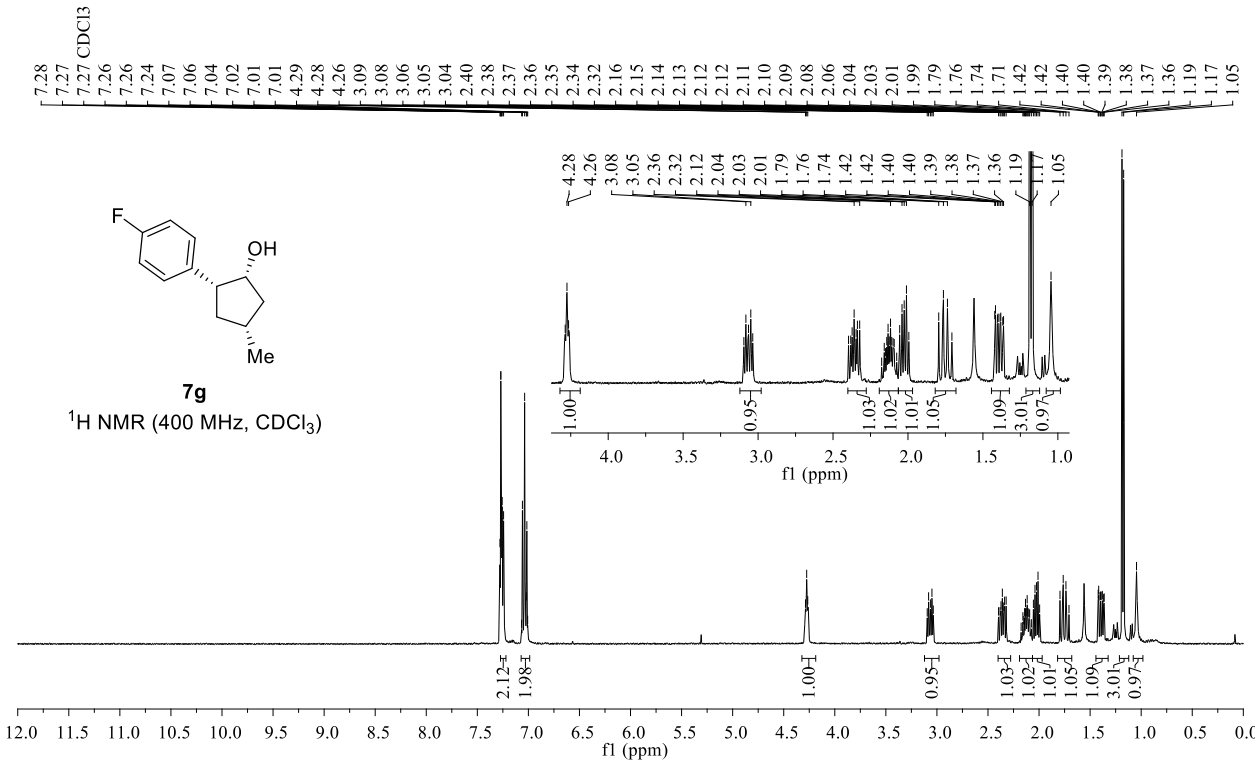
7f

^{1}H NMR (400 MHz, $CDCl_3$)



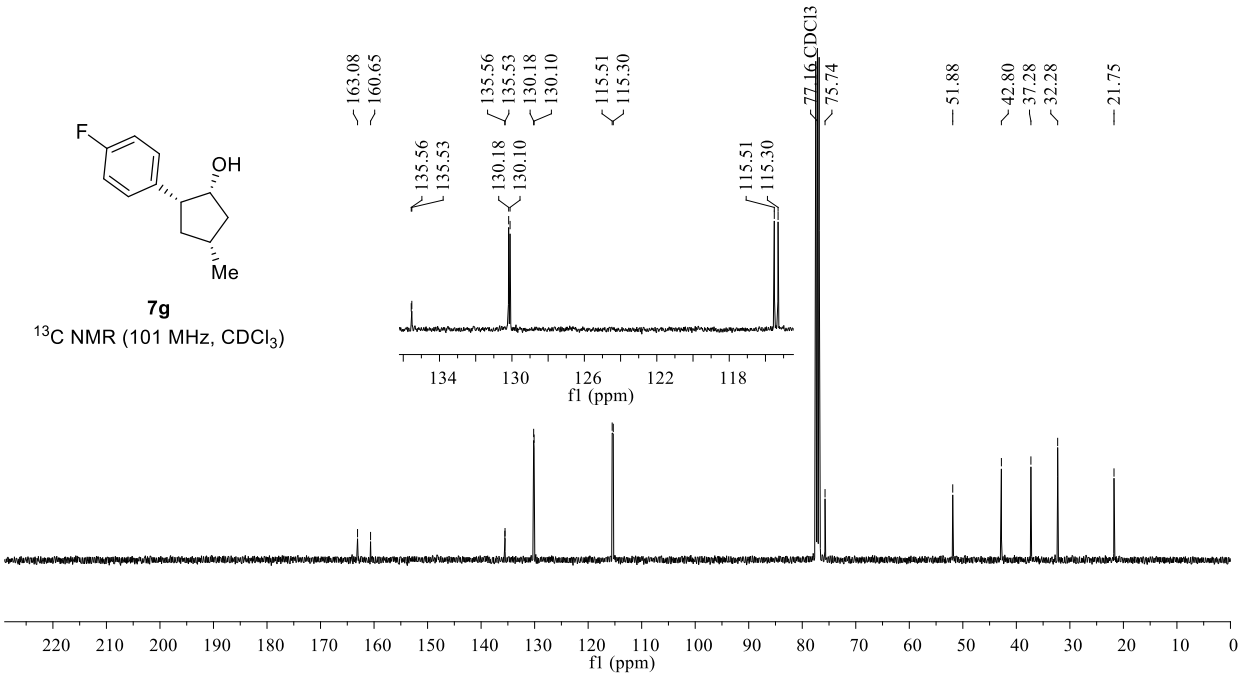
7f

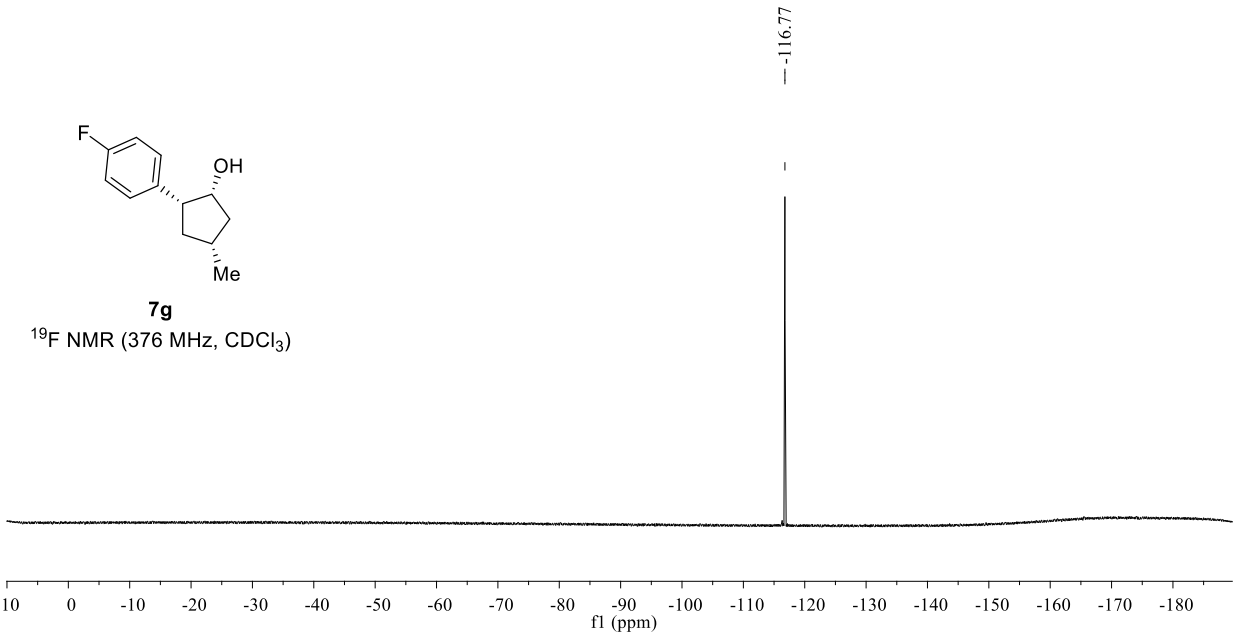
^{13}C NMR (101 MHz, $CDCl_3$)

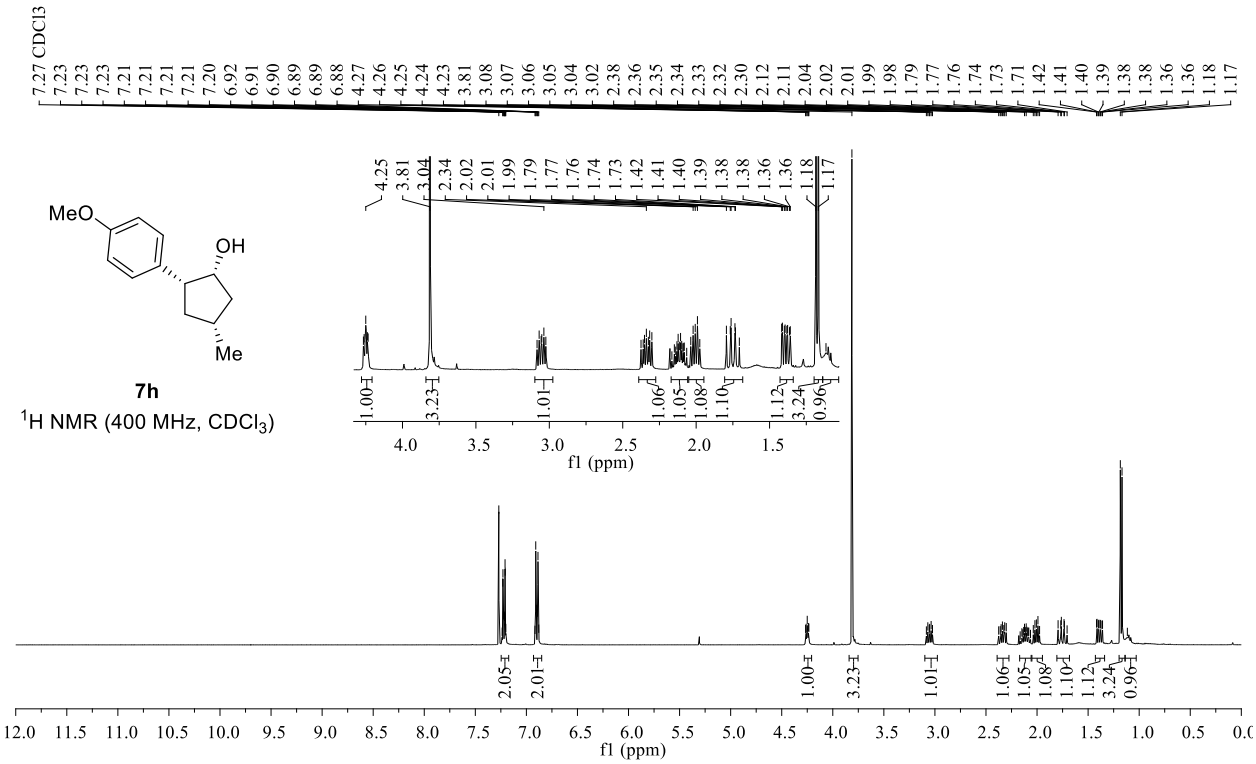


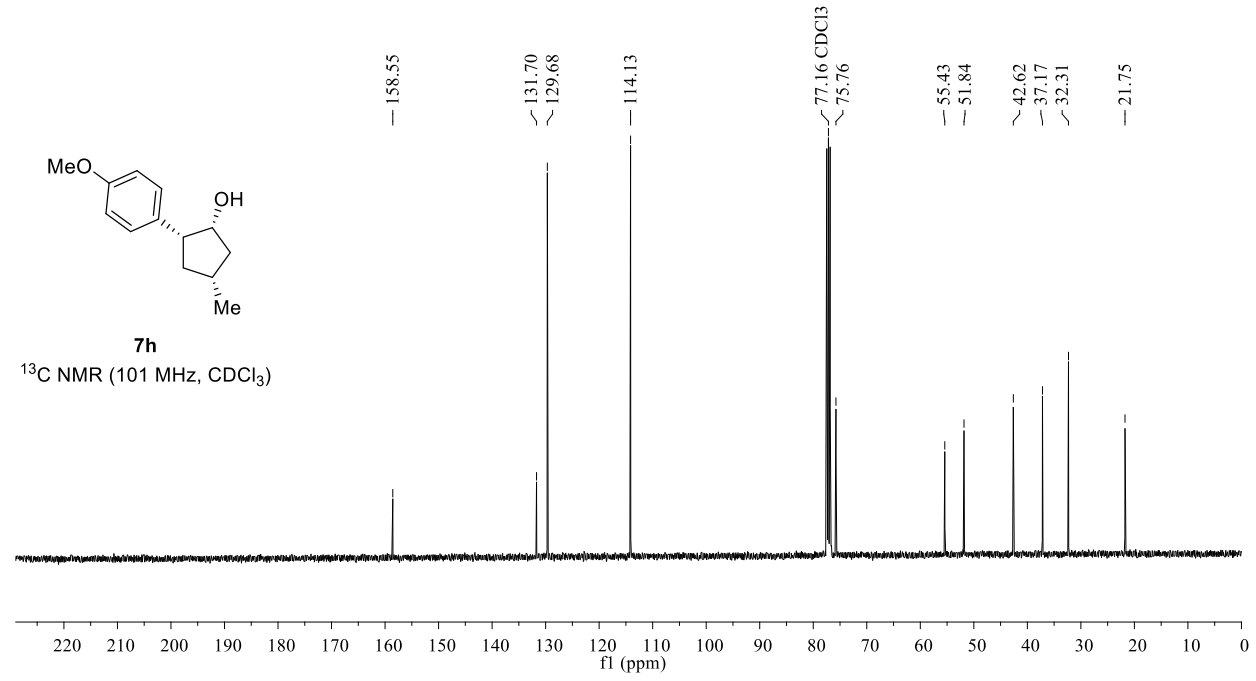
7g

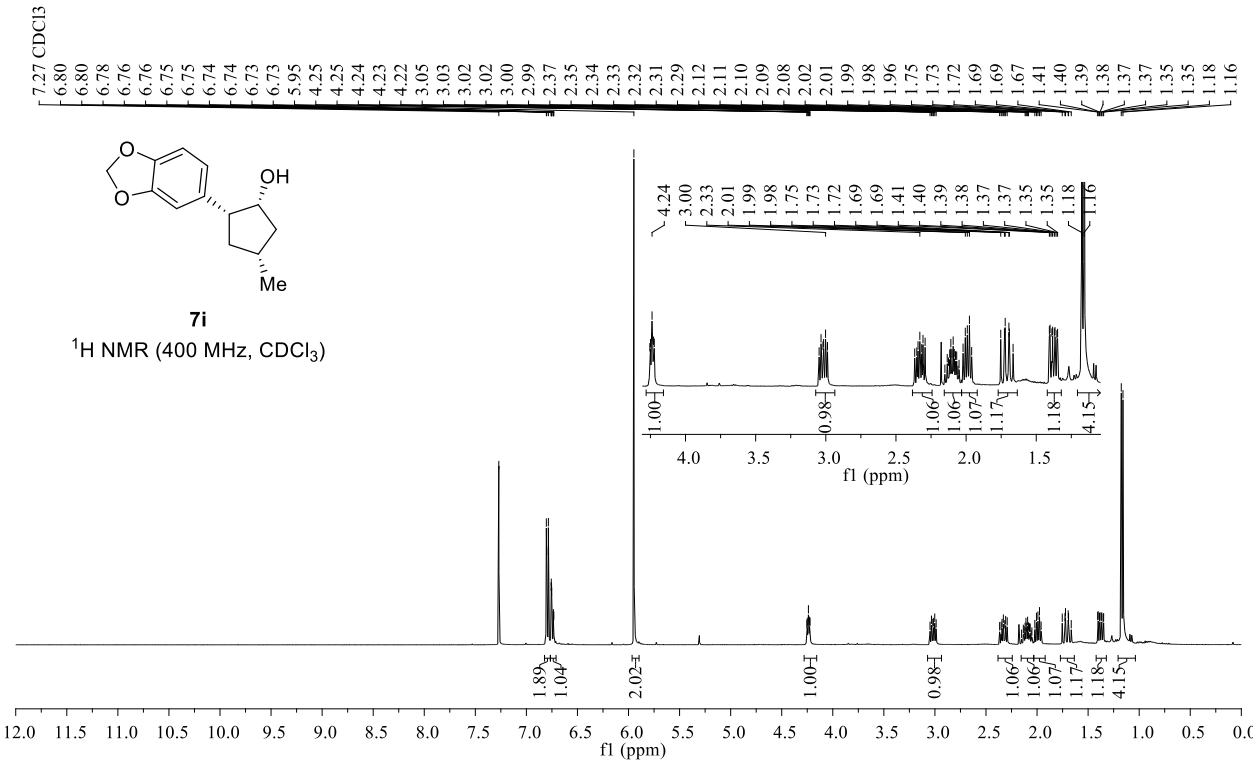
^{1}H NMR (400 MHz, $CDCl_3$)

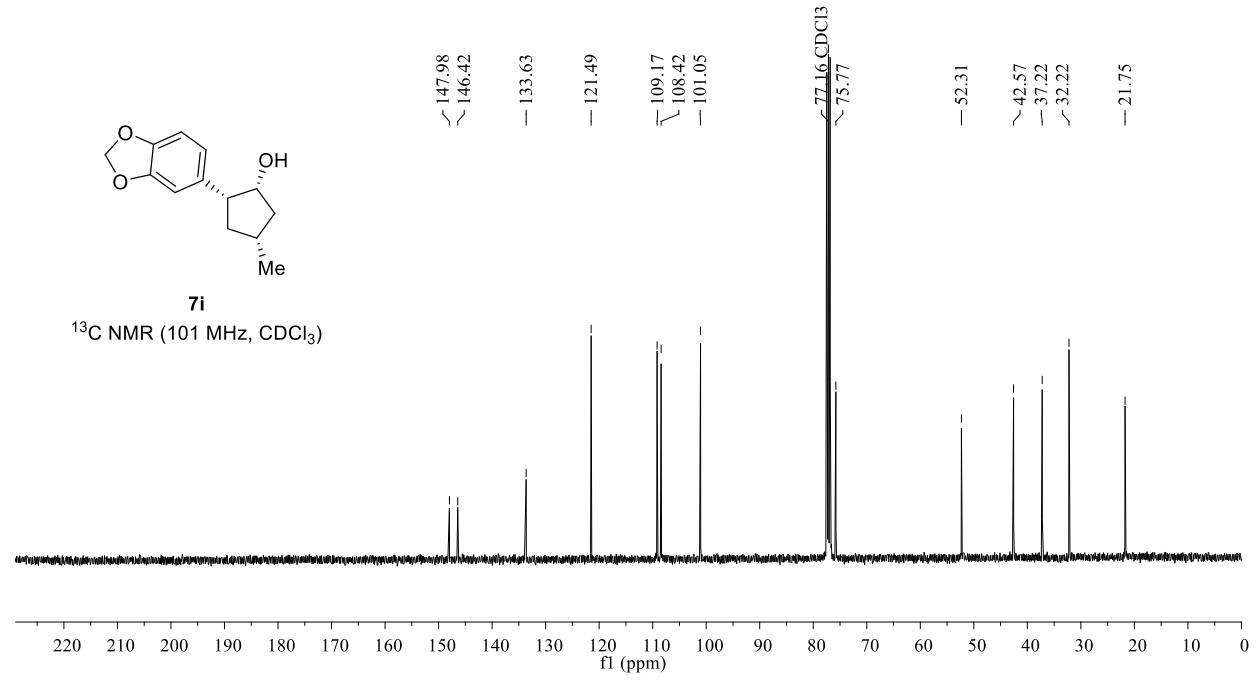

F
OH
Me
7g
13C NMR (101 MHz, CDCl3)
163.08
160.65
135.56
135.53
130.18
130.10
115.51
115.30
77.16 CDCl3
75.74
51.88
42.80
37.28
32.28
21.75
f1 (ppm)

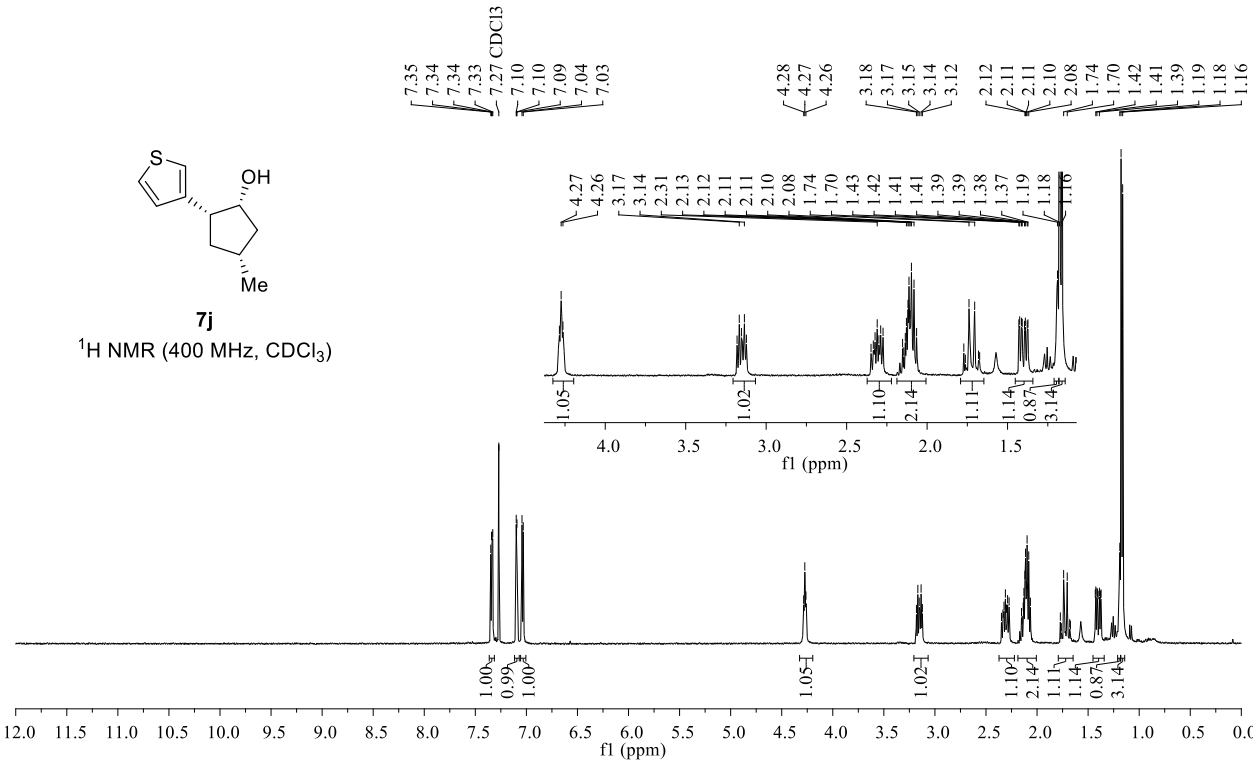

F
OH
Me
7g
19F NMR (376 MHz, CDCl3)
-116.77
f1 (ppm)

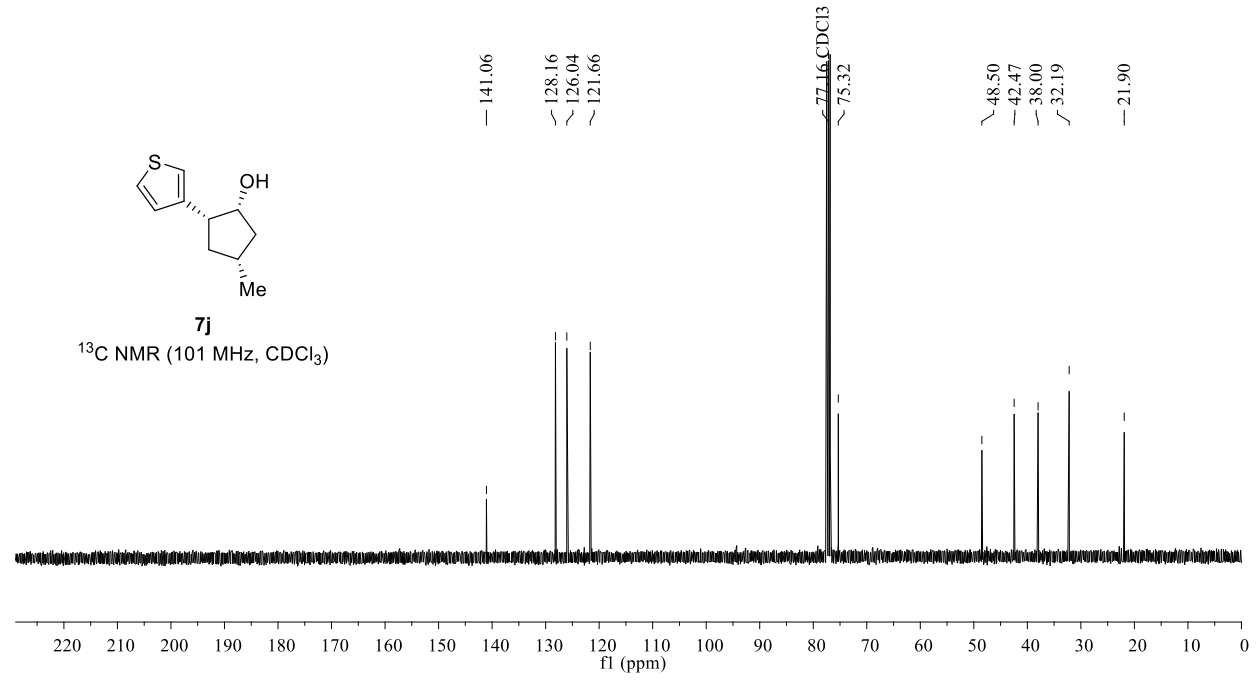

MeO
OH
Me
7h
1H NMR (400 MHz, CDCl3)
f1 (ppm)

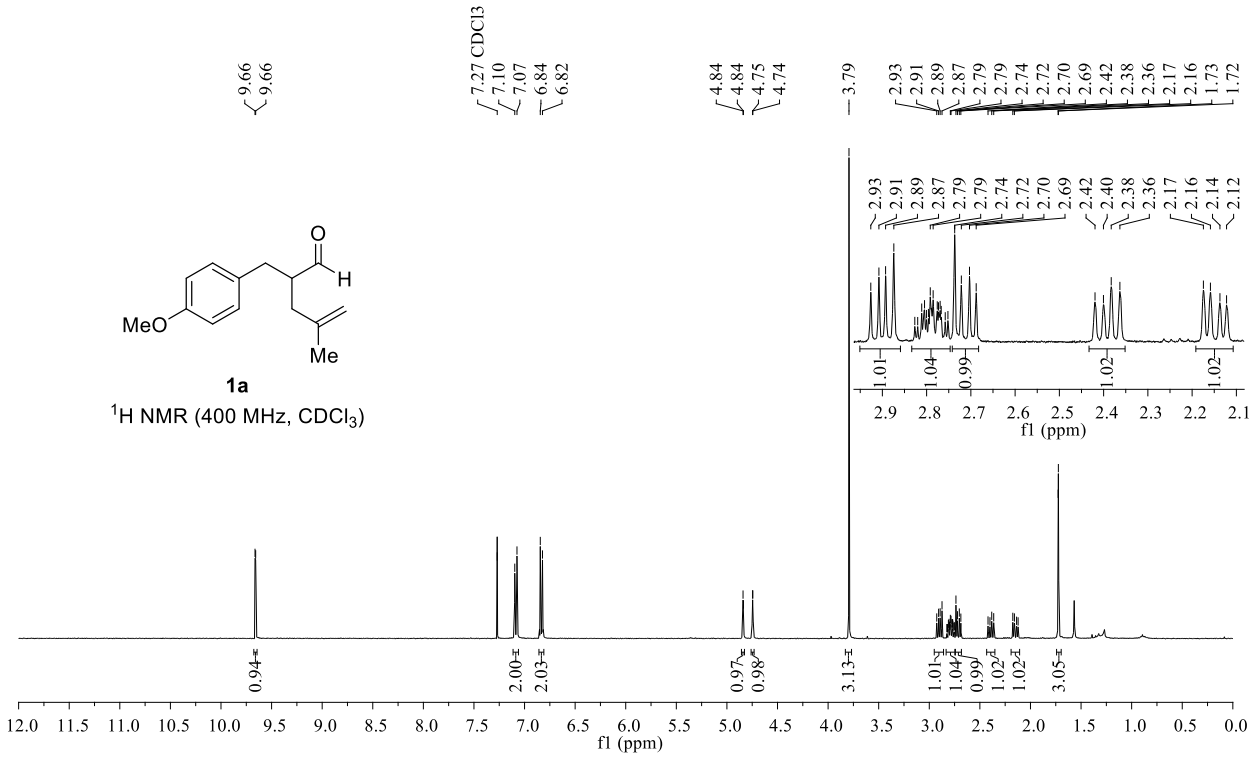

MeO
OH
Me
7h
13C NMR (101 MHz, CDCl3)
158.55
131.70
129.68
114.13
77.16 CDCl3
75.76
55.43
51.84
42.62
37.17
32.31
21.75
f1 (ppm)

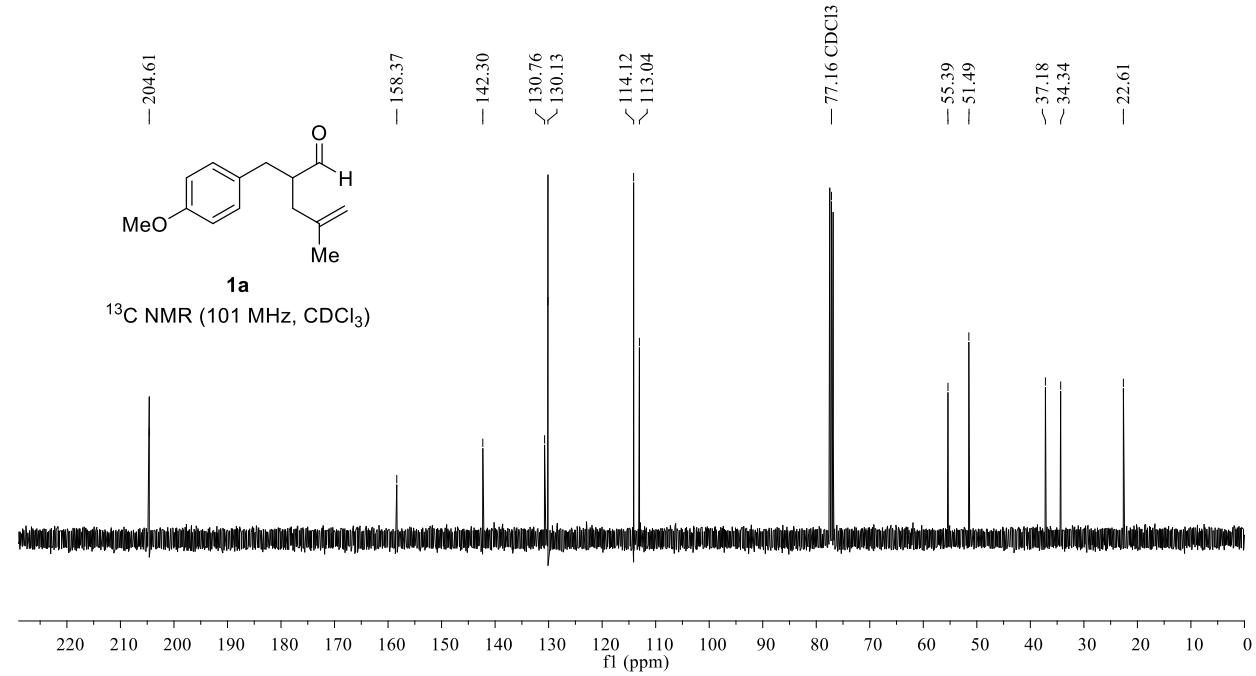

7.27 CDCl3
OH
Me
7i
1H NMR (400 MHz, CDCl3)
f1 (ppm)

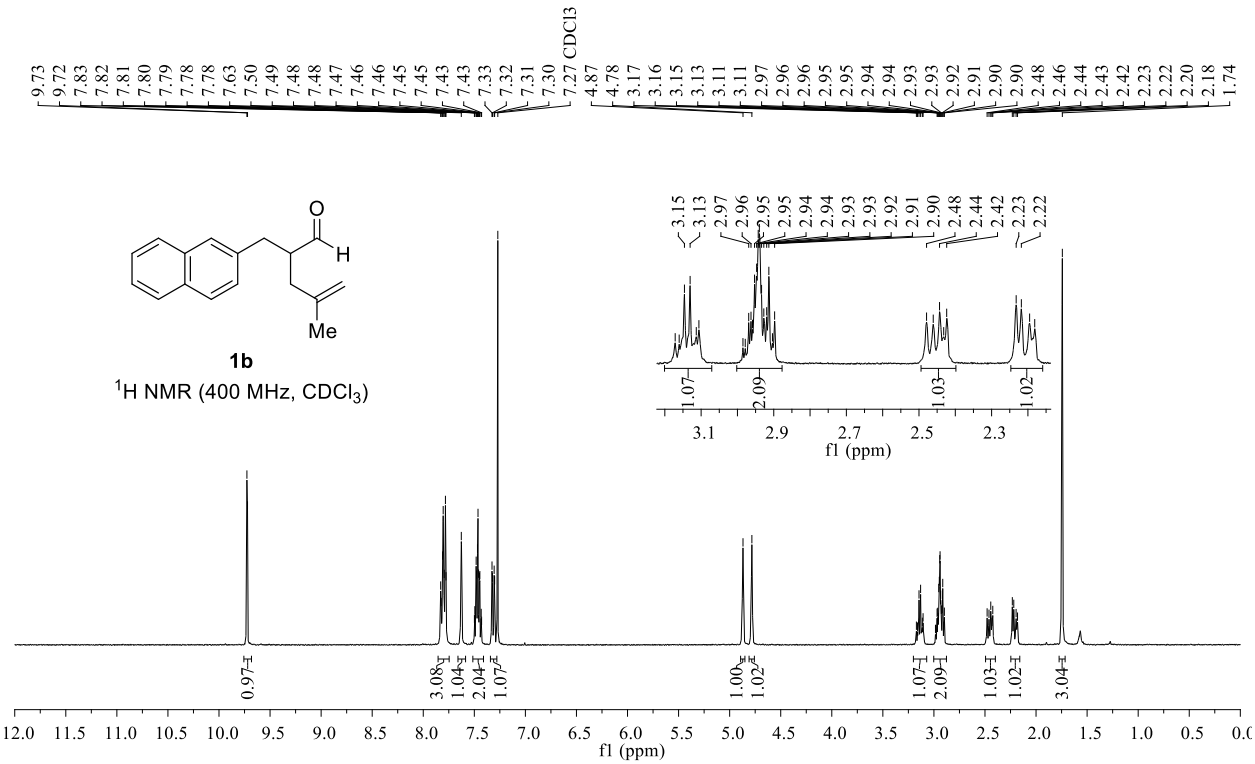

147.98
146.42
133.63
121.49
109.17
108.42
101.05
77.16 CDCl3
75.77
52.31
42.57
37.22
32.22
21.75
OH
Me
7i
13C NMR (101 MHz, CDCl3)
f1 (ppm)

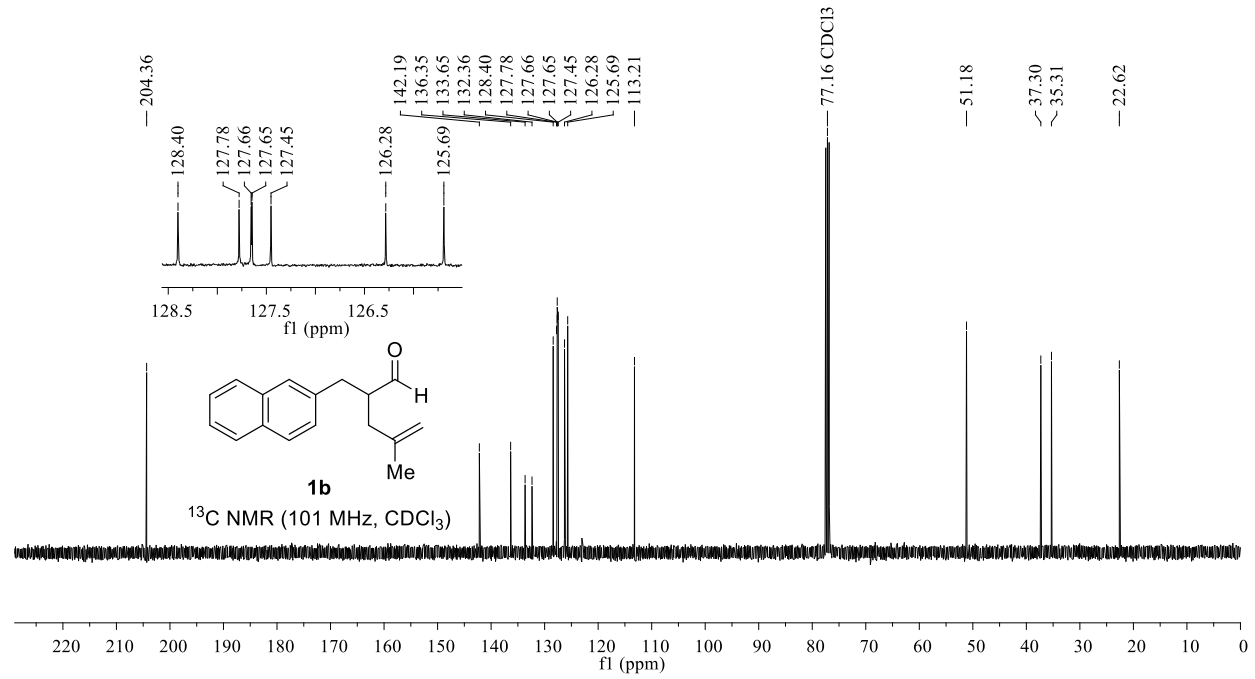

7.35
7.34
7.34
7.33
7.27 CDCl3
7.10
7.10
7.09
7.04
7.03
4.28
4.27
4.26
3.18
3.17
3.15
3.14
3.12
2.12
2.11
2.11
2.10
2.08
1.74
1.70
1.42
1.41
1.39
1.19
1.18
1.16
S
OH
Me
7j
1H NMR (400 MHz, CDCl3)
1.00
0.99
1.00
1.05
1.02
1.10
2.14
1.11
1.14
0.87
3.14
fl (ppm)

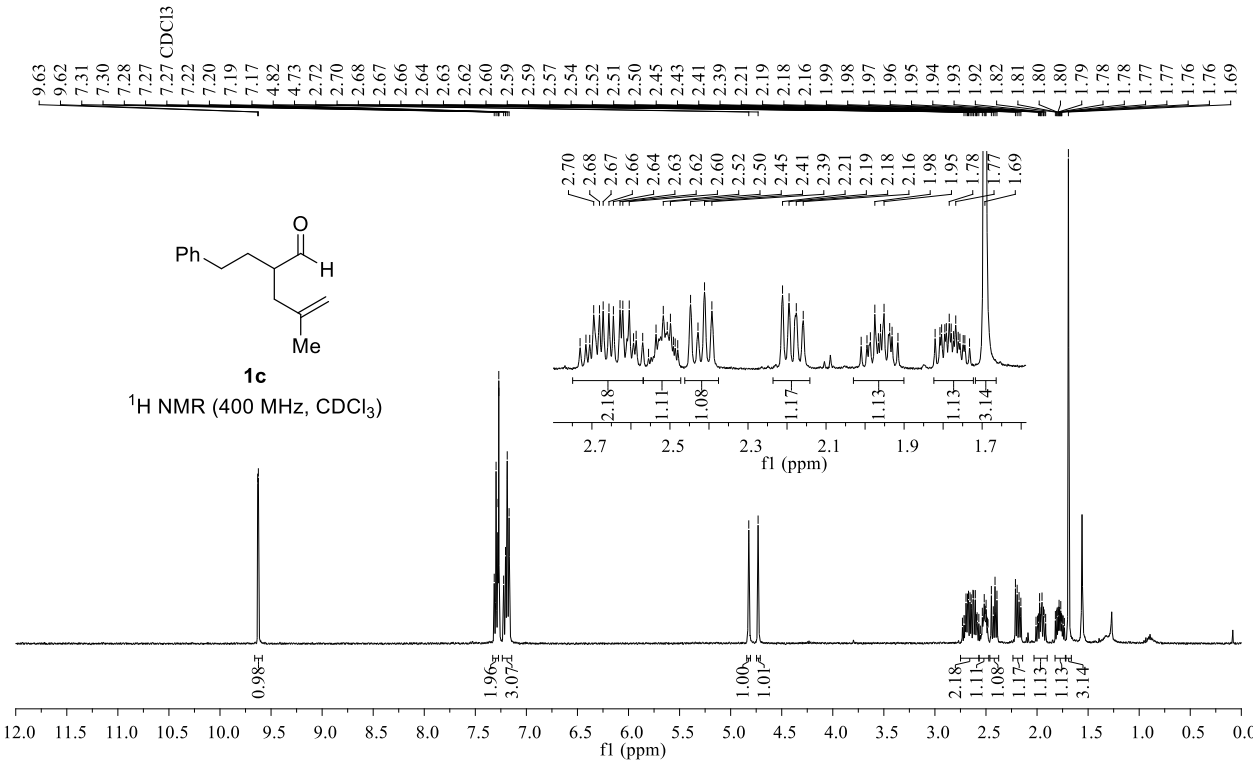

141.06
128.16
126.04
121.66
77.16 CDCl3
75.32
48.50
42.47
38.00
32.19
21.90
S
OH
Me
7j
13C NMR (101 MHz, CDCl3)
fl (ppm)

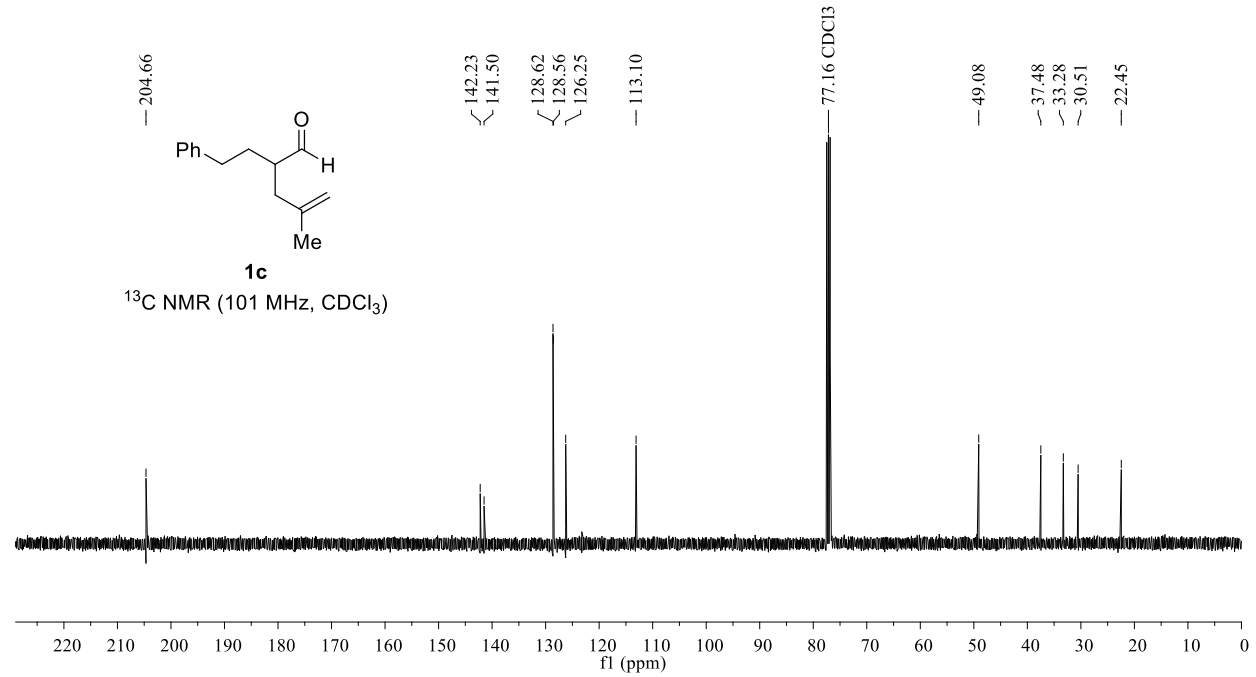

9.66
9.66
7.27 CDCl3
7.10
7.07
6.84
6.82
4.84
4.84
4.75
4.74
3.79
2.93
2.91
2.89
2.87
2.79
2.79
2.74
2.72
2.70
2.69
2.42
2.38
2.36
2.17
2.16
1.73
1.72
2.93
2.91
2.89
2.87
2.79
2.79
2.74
2.72
2.70
2.69
2.42
2.40
2.38
2.36
2.17
2.16
2.14
2.12
1.01
1.04
0.99
1.02
1.02
2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1
f1 (ppm)
O
H
MeO
Me
1a
1H NMR (400 MHz, CDCl3)
0.94
2.00
2.03
0.97
0.98
3.13
1.01
1.04
0.99
1.02
1.02
3.05
12.0 11.5 11.0 10.5 10.0 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)

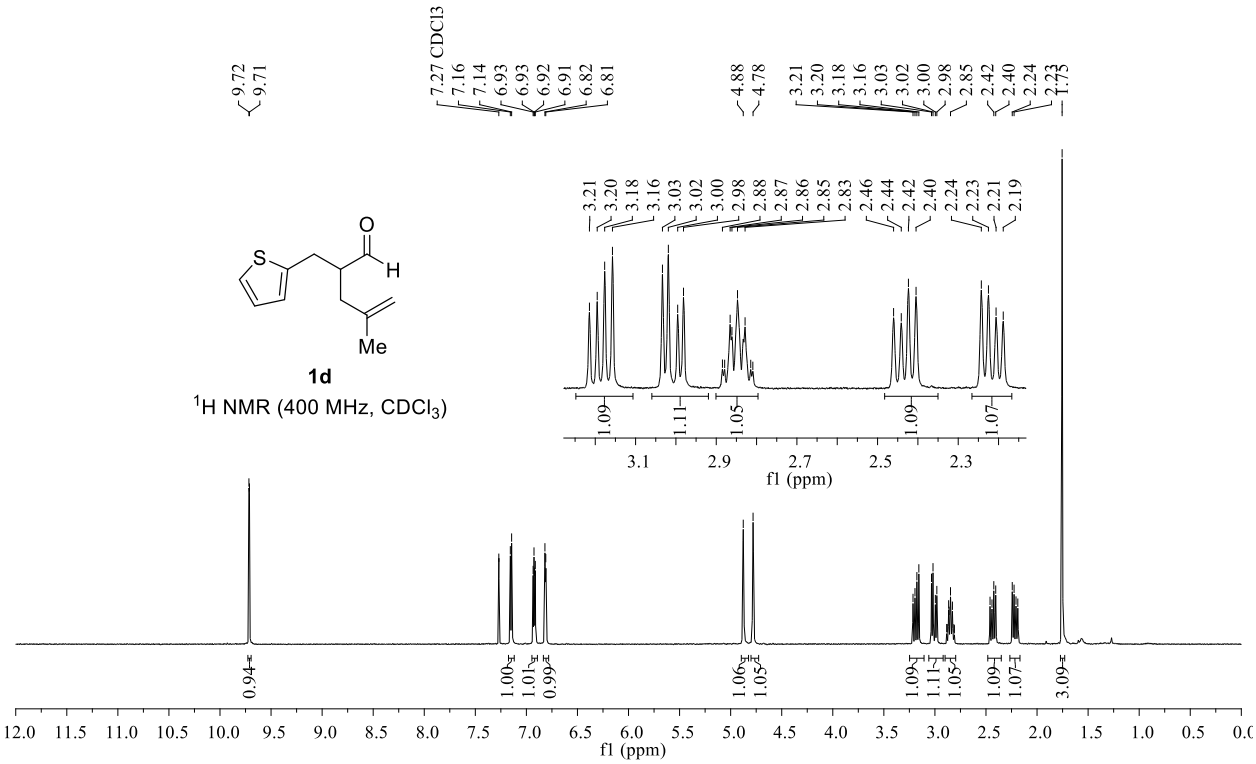

204.61
158.37
142.30
130.76
130.13
114.12
113.04
77.16 CDCl3
55.39
51.49
37.18
34.34
22.61
O
H
MeO
Me
1a
13C NMR (101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

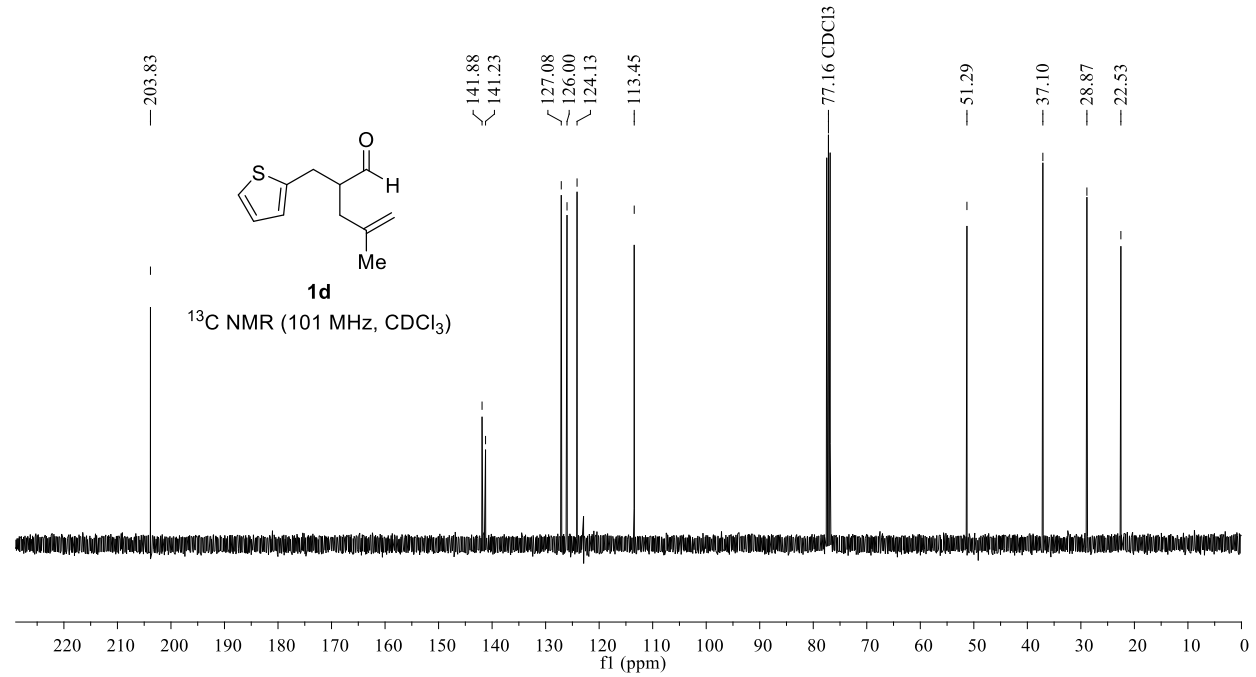

9.73 9.72 7.83 7.82 7.81 7.80 7.79 7.78 7.78 7.63 7.50 7.49 7.48 7.48 7.47 7.46 7.46 7.45 7.45 7.43 7.43 7.33 7.32 7.31 7.30 7.27 CDCl3 4.87 4.78 3.17 3.16 3.15 3.13 3.11 3.11 2.97 2.96 2.96 2.95 2.95 2.94 2.94 2.93 2.93 2.92 2.91 2.90 2.90 2.48 2.46 2.44 2.43 2.42 2.23 2.22 2.20 2.18 1.74
O
H
Me
1b
^{1}H NMR (400 MHz, $CDCl_3$)
3.15 3.13 2.97 2.96 2.95 2.95 2.94 2.94 2.93 2.93 2.92 2.91 2.90 2.48 2.44 2.42 2.23 2.22
1.07 2.09 1.03 1.02
3.1 2.9 2.7 2.5 2.3
f1 (ppm)
0.97 3.08 1.04 2.04 1.07 1.00 1.02 1.07 2.09 1.03 1.02 3.04
12.0 11.5 11.0 10.5 10.0 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)

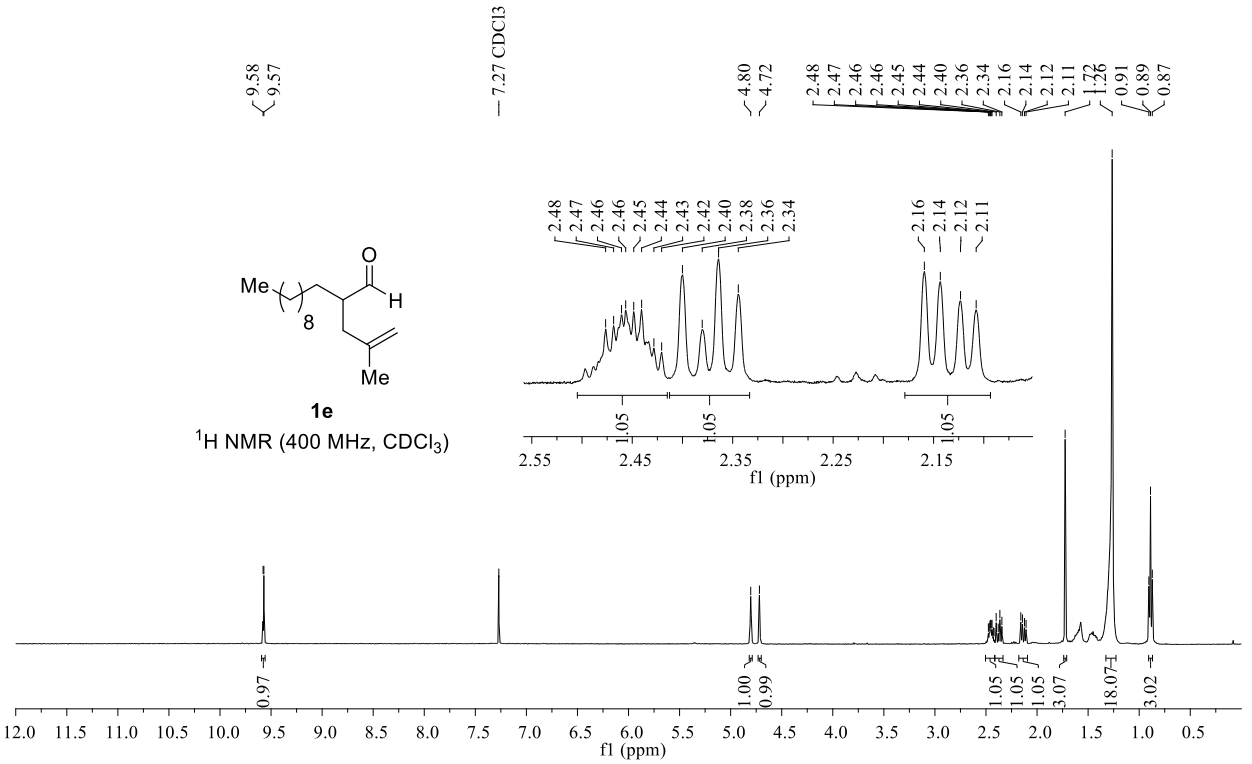

204.36
128.40 127.78 127.66 127.65 127.45 126.28 125.69
142.19 136.35 133.65 132.36 128.40 127.78 127.66 127.65 127.45 126.28 125.69 113.21
77.16 CDCl3
51.18
37.30 35.31
22.62
128.5 127.5 126.5
f1 (ppm)
O
H
Me
1b
^{13}C NMR (101 MHz, $CDCl_3$)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

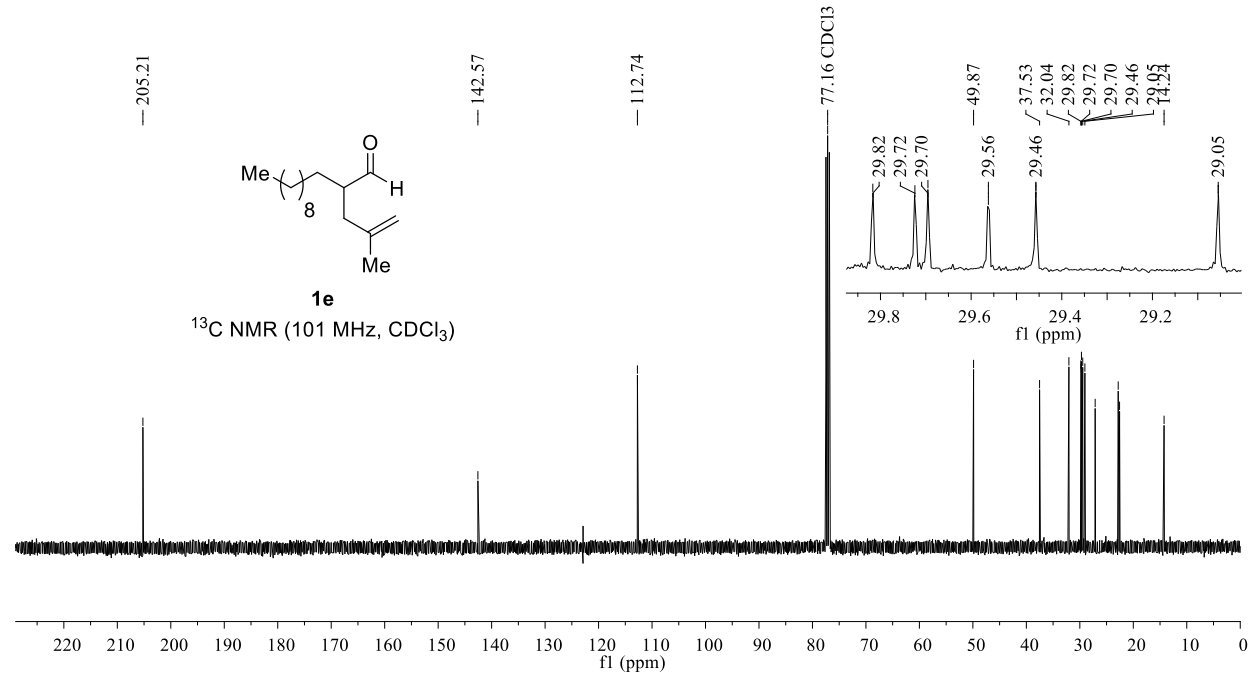

9.63 9.62 7.31 7.30 7.28 7.27 7.27 CDCl3 7.22 7.20 7.19 7.17 4.82 4.73 2.72 2.70 2.68 2.67 2.66 2.64 2.63 2.62 2.60 2.59 2.59 2.57 2.54 2.52 2.51 2.50 2.45 2.43 2.41 2.39 2.21 2.19 2.18 2.16 1.99 1.98 1.97 1.96 1.95 1.94 1.93 1.92 1.82 1.81 1.80 1.80 1.79 1.78 1.78 1.77 1.77 1.76 1.76 1.69
Ph
O
H
Me
1c
1H NMR (400 MHz, CDCl3)
2.70 2.68 2.67 2.66 2.64 2.63 2.62 2.60 2.52 2.50 2.45 2.41 2.39 2.21 2.19 2.18 2.16 1.98 1.95 1.78 1.77 1.69
2.18 1.11 1.08 1.17 1.13 1.13 3.14
f1 (ppm)
0.98 1.96 3.07 1.00 1.01 2.18 1.11 1.08 1.17 1.13 1.13 3.14
f1 (ppm)

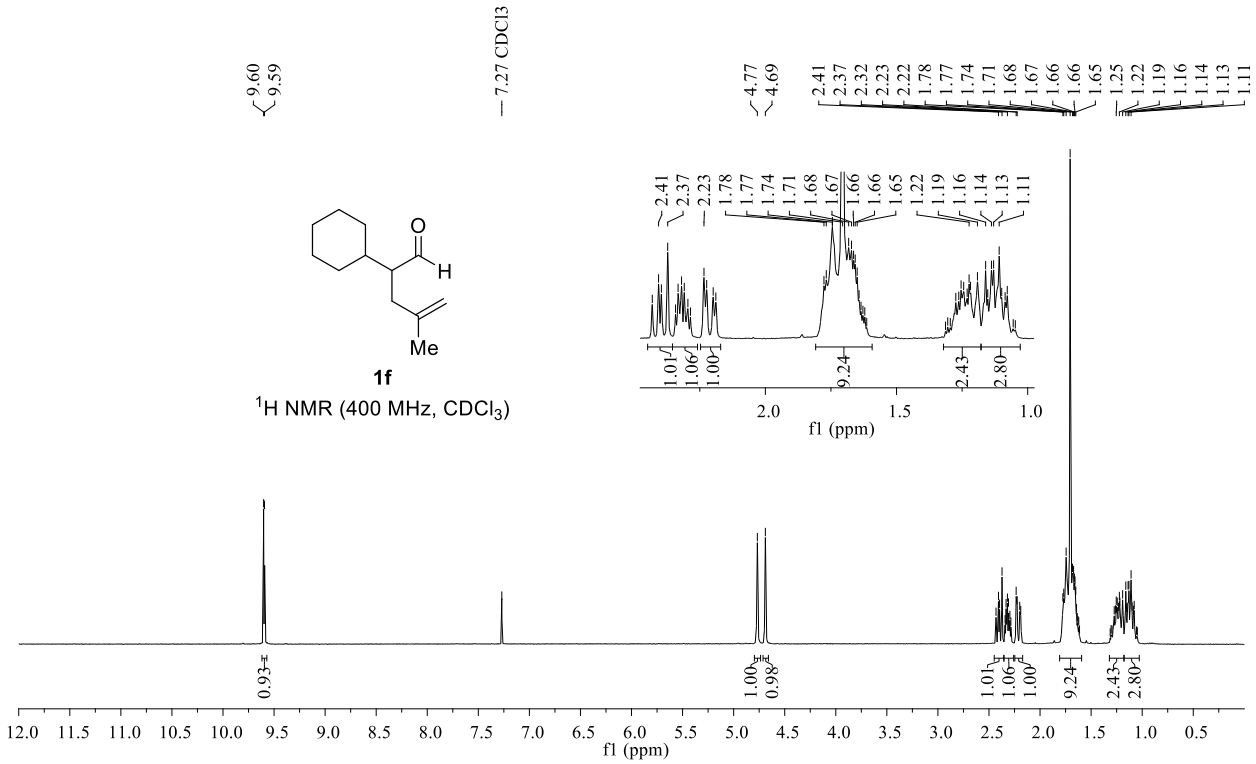

204.66
142.23 141.50 128.62 128.56 126.25 113.10 77.16 CDCl3 49.08 37.48 33.28 30.51 22.45
Ph
O
H
Me
1c
13C NMR (101 MHz, CDCl3)
f1 (ppm)

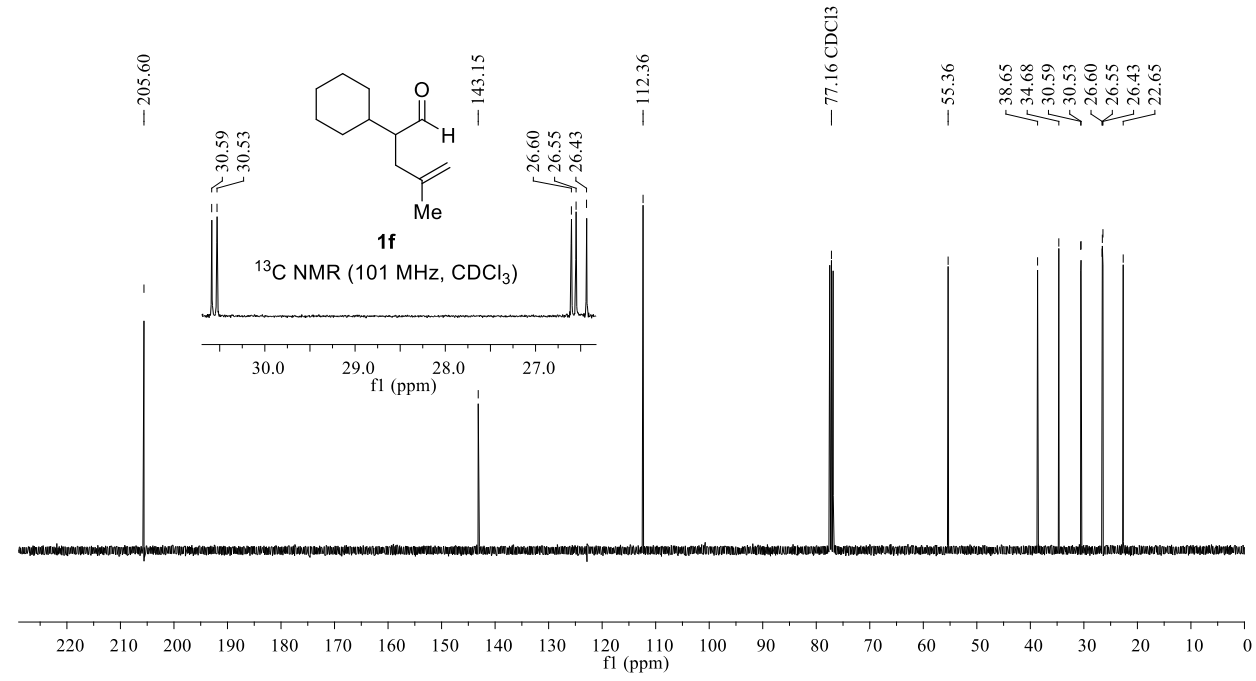

9.72
9.71
7.27 CDCl3
7.16
7.14
6.93
6.93
6.92
6.91
6.82
6.81
4.88
4.78
3.21
3.20
3.18
3.16
3.03
3.02
3.00
2.98
2.85
2.42
2.40
2.24
2.23
1.75
O
S
H
Me
1d
1H NMR (400 MHz, CDCl3)
fl (ppm)

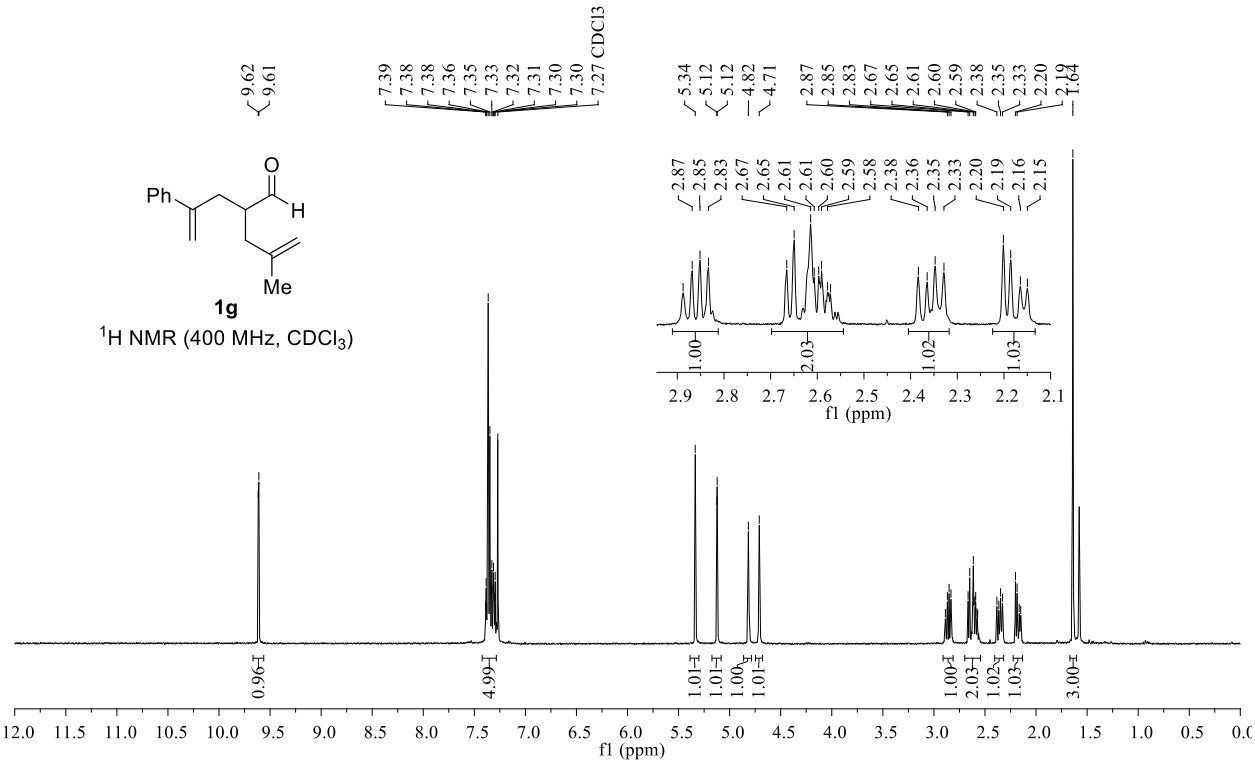

203.83
141.88
141.23
127.08
126.00
124.13
113.45
77.16 CDCl3
51.29
37.10
28.87
22.53
O
S
H
Me
1d
13C NMR (101 MHz, CDCl3)
fl (ppm)

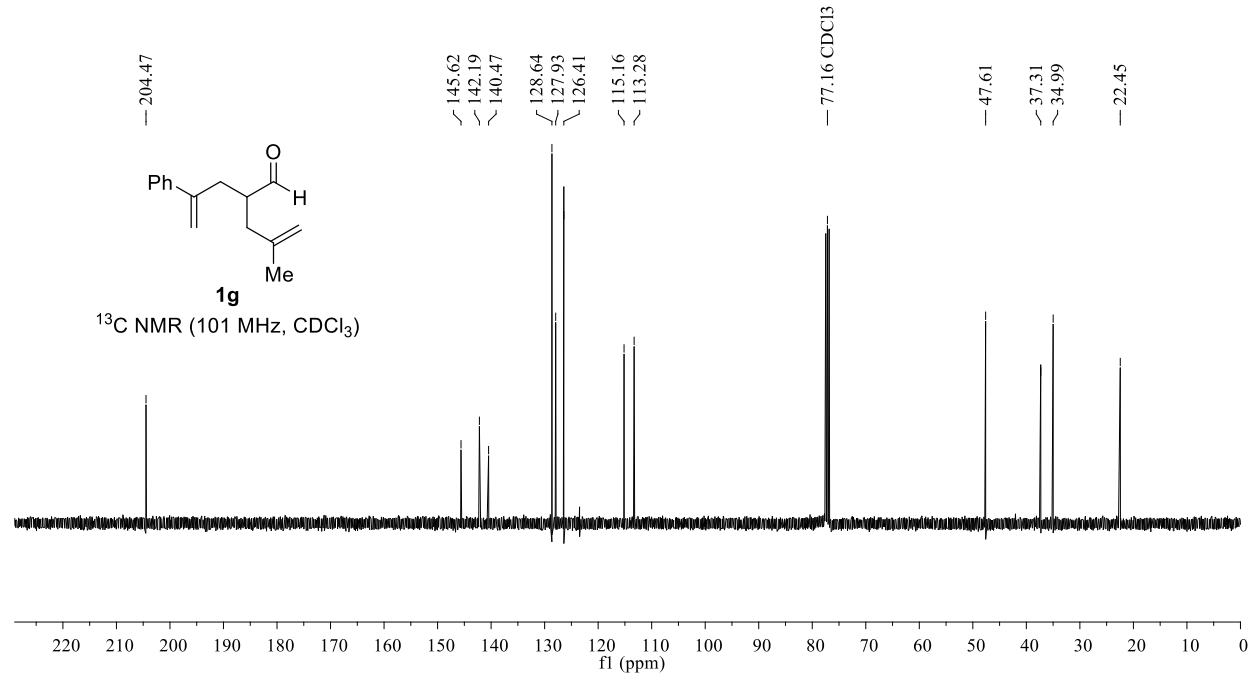

9.58
9.57
7.27 CDCl3
4.80
4.72
2.48
2.47
2.46
2.46
2.45
2.44
2.40
2.36
2.34
2.16
2.14
2.12
2.11
1.72
1.26
0.91
0.89
0.87
Me
8
O
H
Me
1e
1H NMR (400 MHz, CDCl3)
1.05
1.05
1.05
2.55
2.45
2.35
2.25
2.15
f1 (ppm)
0.97
1.00
0.99
1.05
1.05
1.05
3.07
18.07
3.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 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
f1 (ppm)

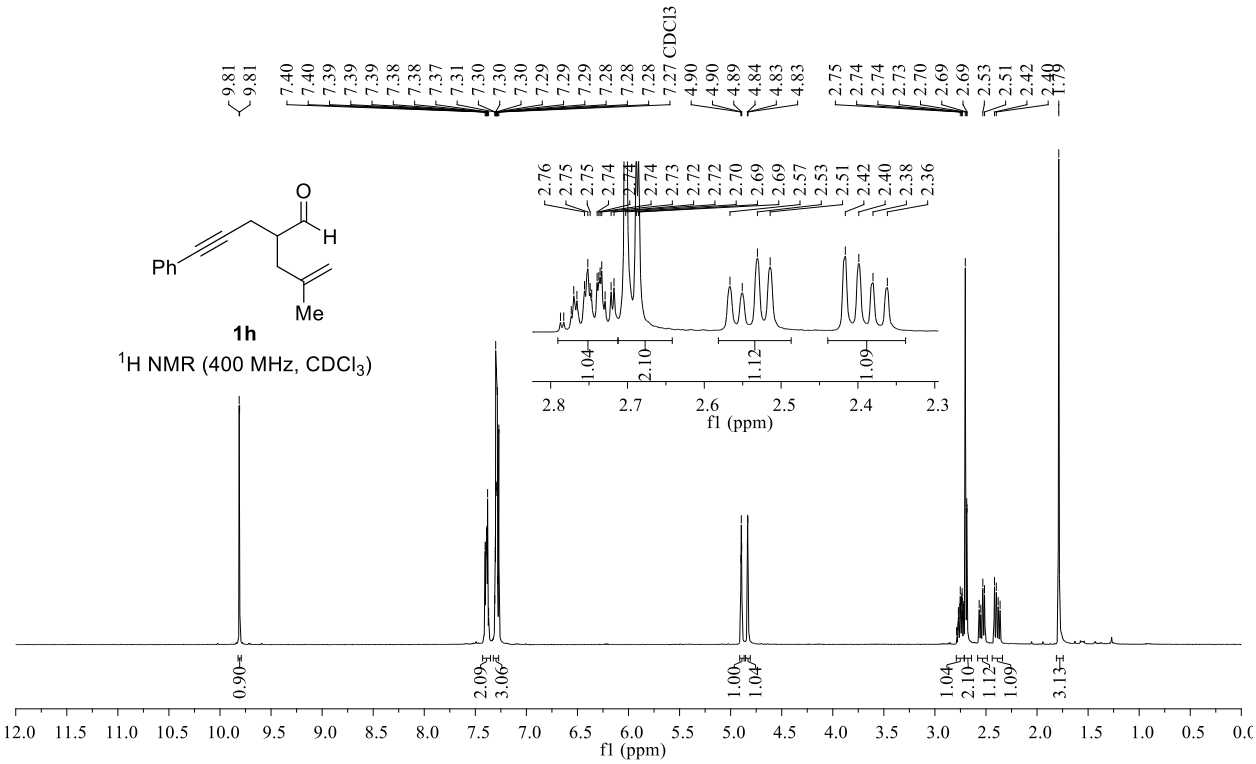

205.21
142.57
112.74
77.16 CDCl3
49.87
37.53
32.04
29.82
29.72
29.70
29.46
29.05
14.24
Me
8
O
H
Me
1e
13C NMR (101 MHz, CDCl3)
29.8
29.6
29.4
29.2
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

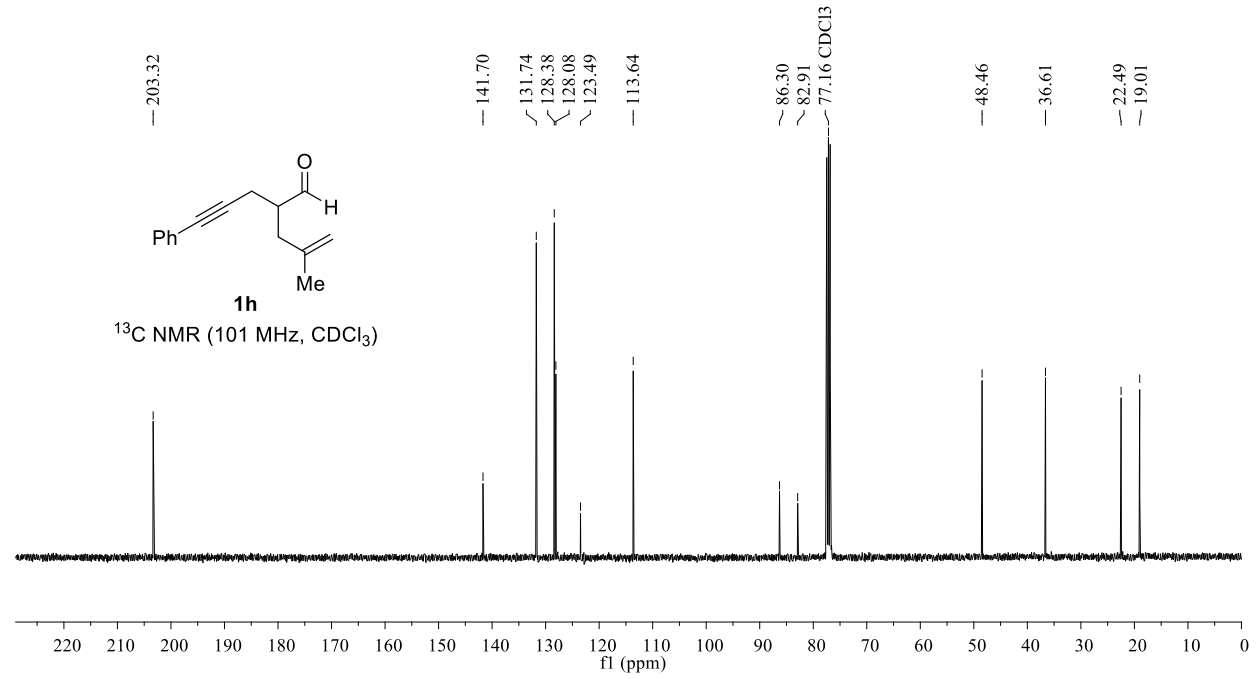

9.60
9.59
7.27 CDCl3
4.77
4.69
2.41
2.37
2.32
2.23
2.22
1.78
1.77
1.74
1.71
1.68
1.67
1.66
1.65
1.25
1.22
1.19
1.16
1.14
1.13
1.11
O
H
Me
1f
1H NMR (400 MHz, CDCl3)
1.01
1.06
1.00
9.24
2.43
2.80
2.0
1.5
1.0
f1 (ppm)
0.93
1.00
0.98
1.01
1.06
1.00
9.24
2.43
2.80
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 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
f1 (ppm)

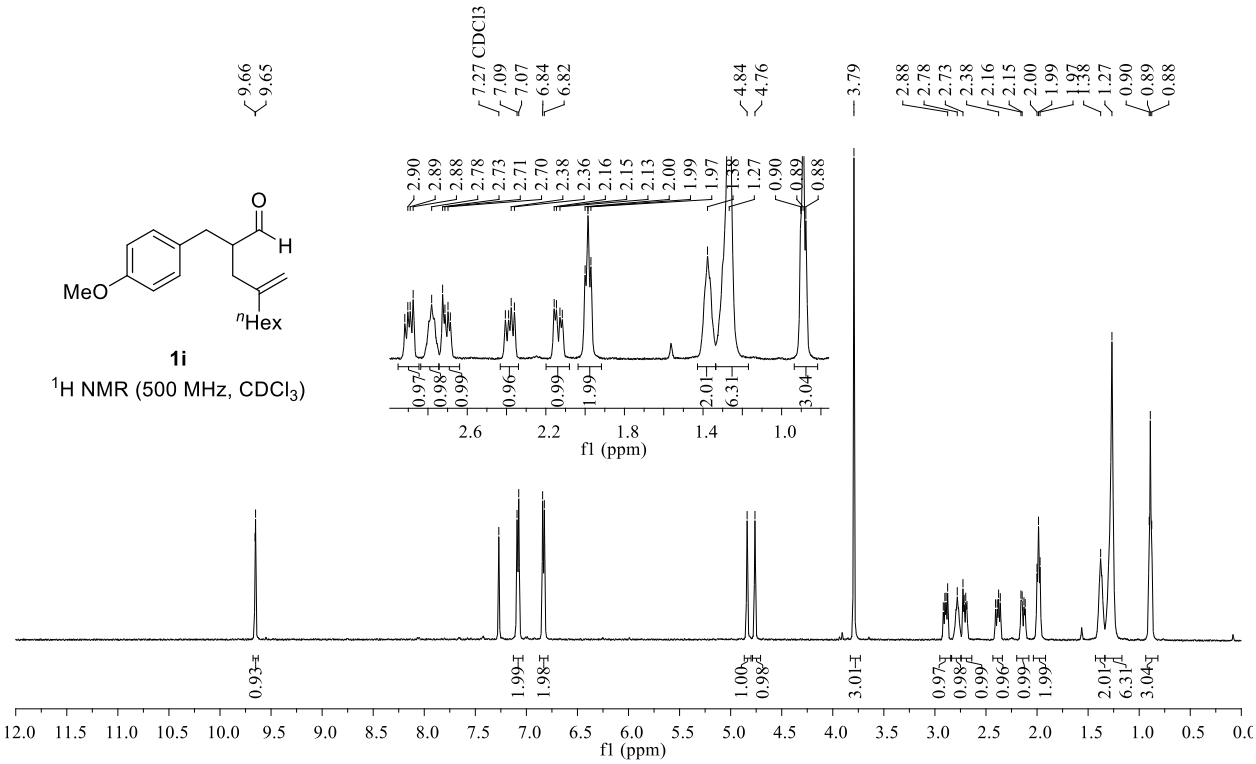

205.60
143.15
112.36
77.16 CDCl3
55.36
38.65
34.68
30.59
30.53
26.60
26.55
26.43
22.65
30.59
30.53
26.60
26.55
26.43
O
H
Me
1f
13C NMR (101 MHz, CDCl3)
30.0
29.0
28.0
27.0
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

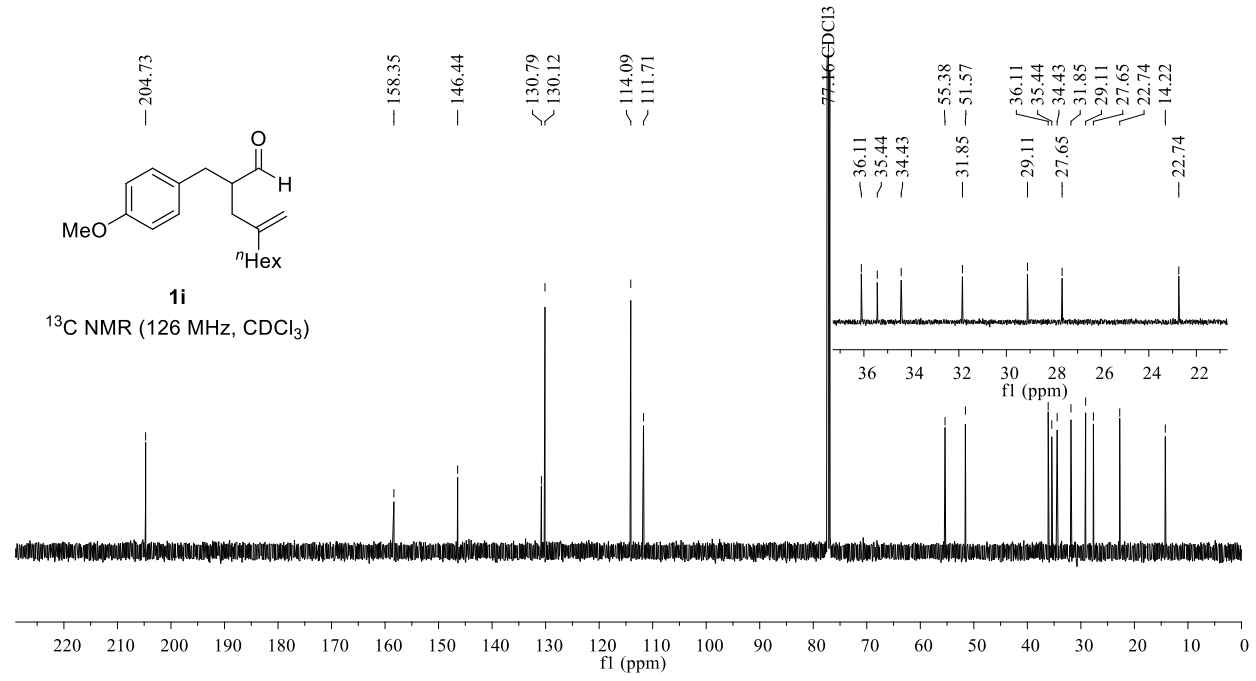

9.62
9.61
7.39
7.38
7.38
7.36
7.35
7.33
7.32
7.31
7.30
7.30
7.27 CDCl3
5.34
5.12
5.12
4.82
4.71
2.87
2.85
2.83
2.67
2.65
2.61
2.60
2.59
2.38
2.35
2.33
2.20
2.19
1.64
Ph
O
H
Me
1g
1H NMR (400 MHz, CDCl3)
0.96
4.99
1.01
1.01
1.00
1.01
1.00
2.03
1.02
1.03
3.00
fl (ppm)

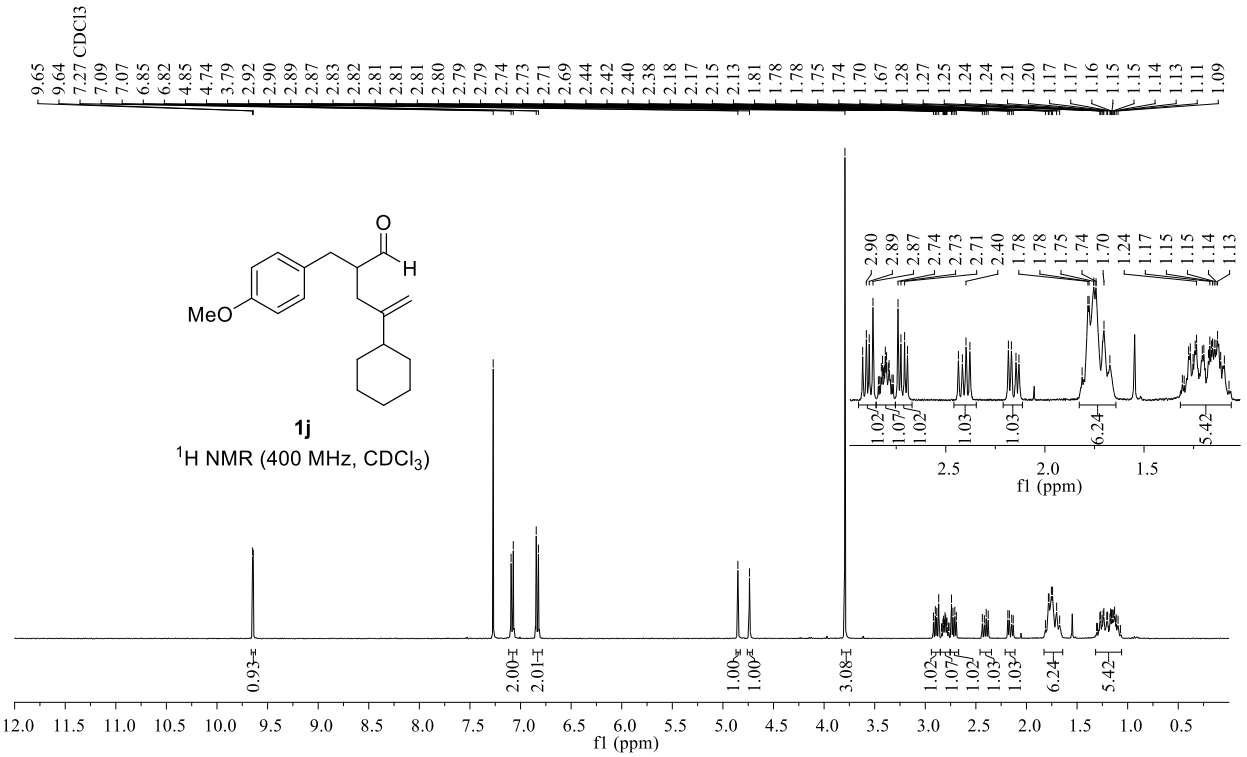

204.47
145.62
142.19
140.47
128.64
127.93
126.41
115.16
113.28
77.16 CDCl3
47.61
37.31
34.99
22.45
Ph
O
H
Me
1g
13C NMR (101 MHz, CDCl3)
fl (ppm)

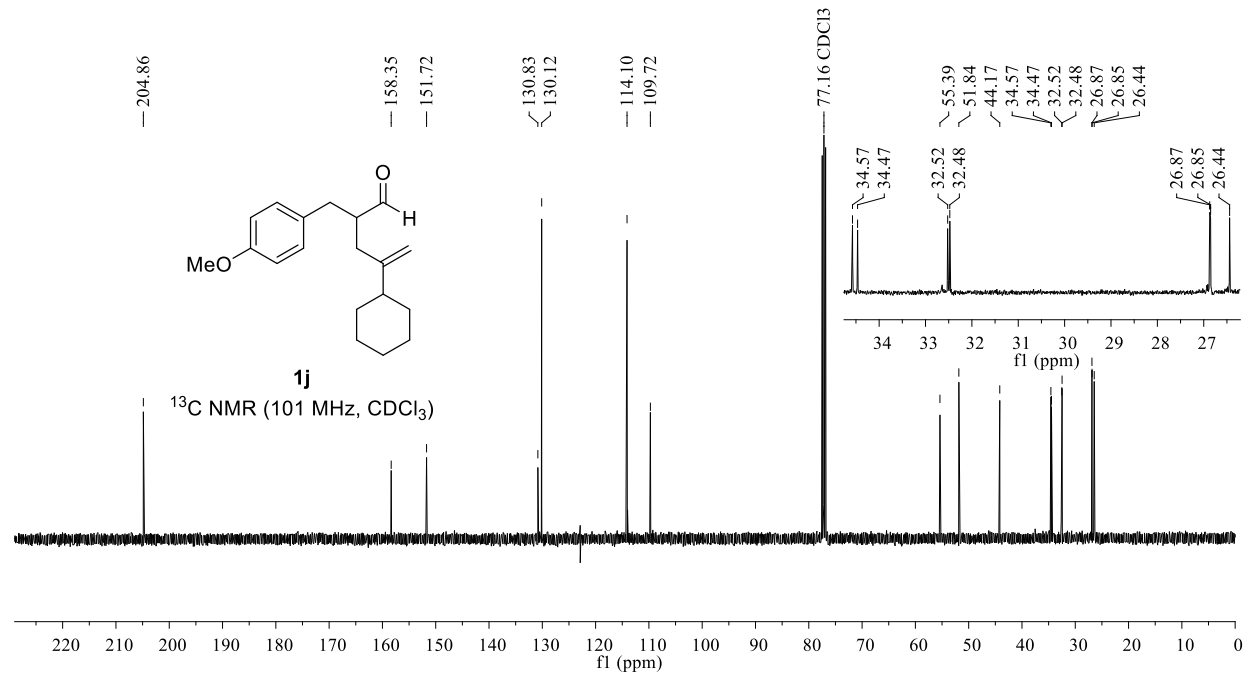

9.81
9.81
7.40
7.40
7.39
7.39
7.39
7.38
7.38
7.37
7.31
7.30
7.30
7.30
7.29
7.29
7.29
7.28
7.28
7.27 CDCl3
4.90
4.90
4.89
4.84
4.83
4.83
2.75
2.74
2.74
2.73
2.70
2.69
2.69
2.53
2.51
2.42
2.40
1.79
O
H
Ph
Me
1h
1H NMR (400 MHz, CDCl3)
2.76
2.75
2.75
2.74
2.74
2.73
2.72
2.72
2.70
2.69
2.69
2.57
2.53
2.51
2.42
2.40
2.38
2.36
1.04
2.10
1.12
1.09
2.8
2.7
2.6
2.5
2.4
2.3
f1 (ppm)
0.90
2.09
3.06
1.00
1.04
1.04
2.10
1.12
1.09
3.13
12.0
11.5
11.0
10.5
10.0
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
f1 (ppm)

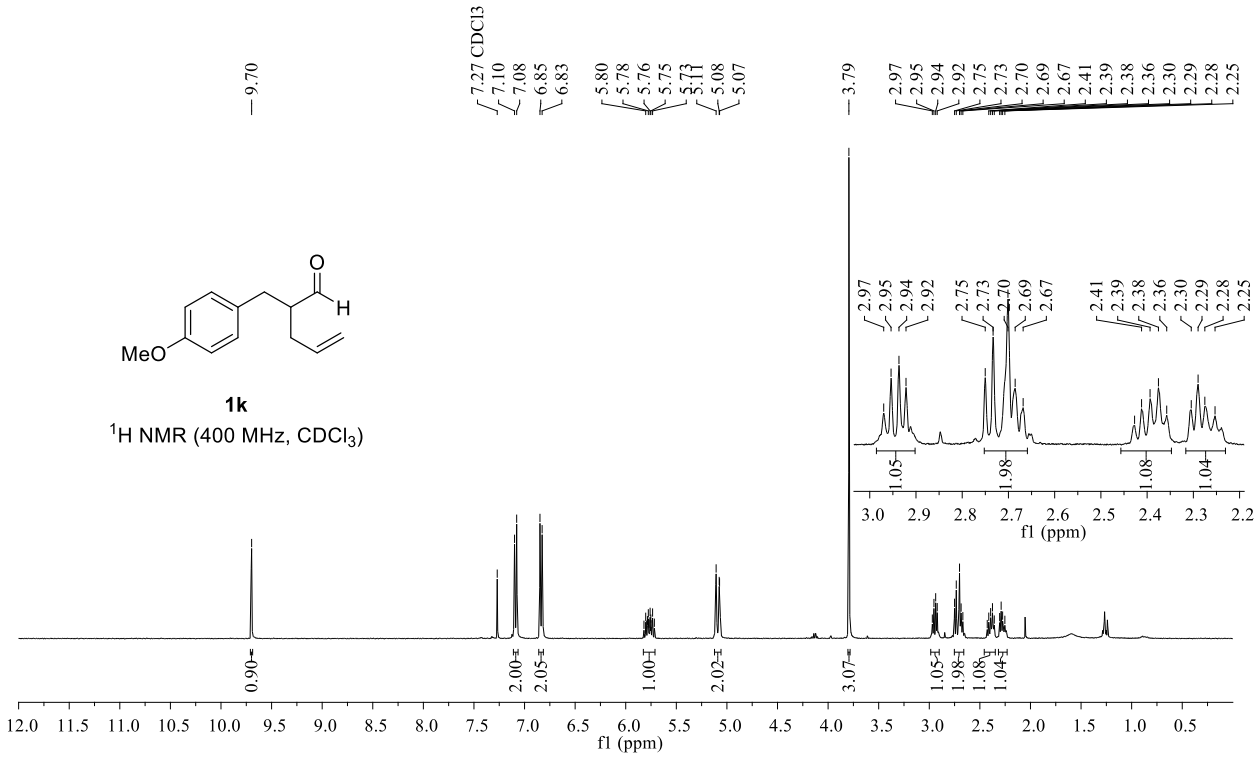

203.32
141.70
131.74
128.38
128.08
123.49
113.64
86.30
82.91
77.16 CDCl3
48.46
36.61
22.49
19.01
O
H
Ph
Me
1h
13C NMR (101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

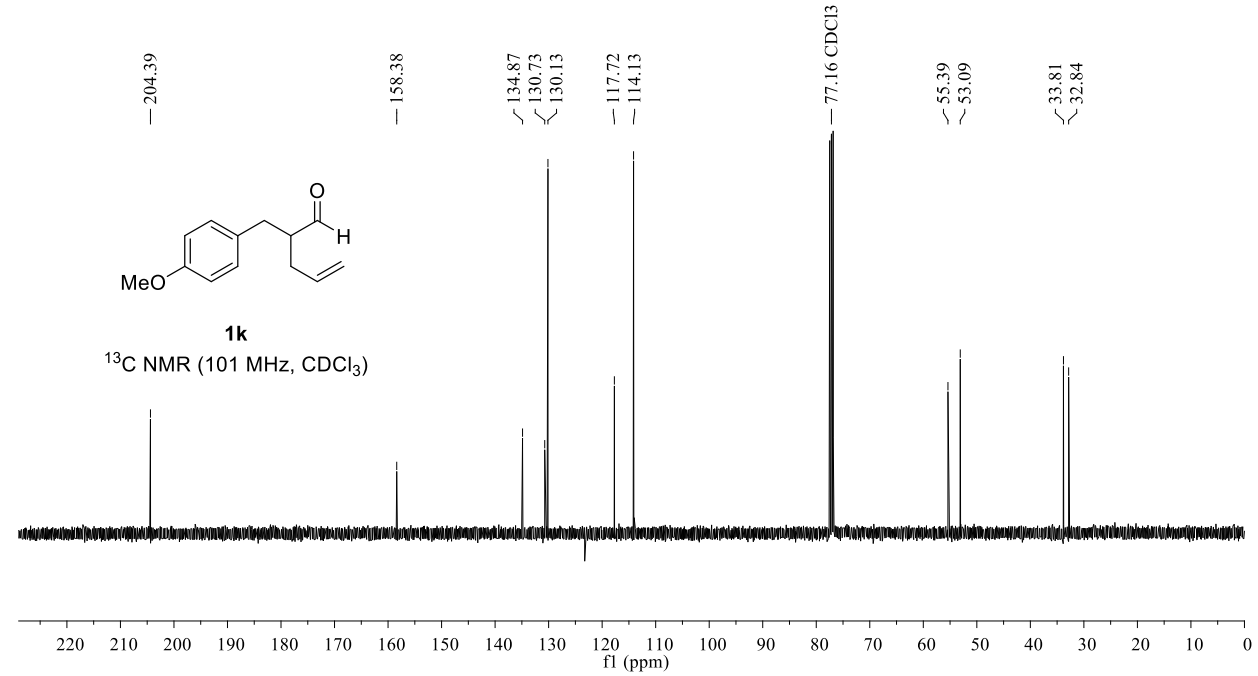

MeO
O
H
nHex
1i
1H NMR (500 MHz, CDCl3)
f1 (ppm)

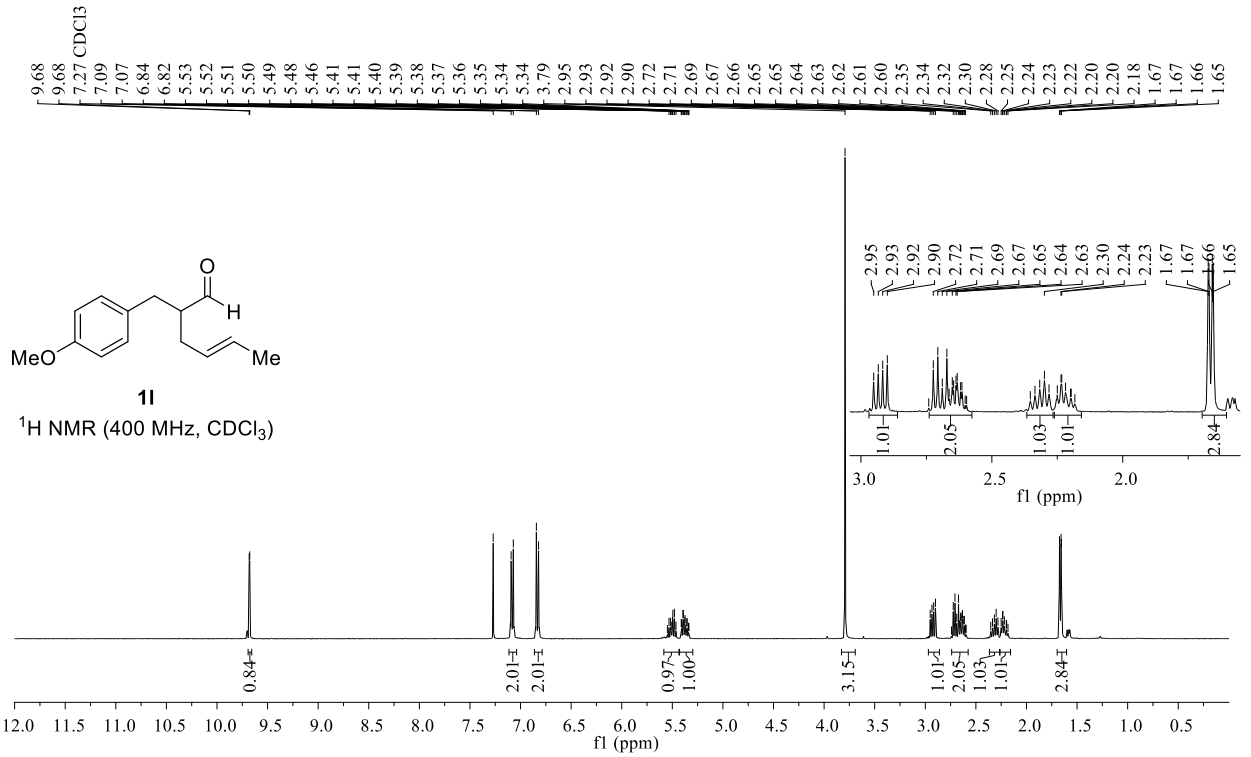

MeO
O
H
nHex
1i
13C NMR (126 MHz, CDCl3)
f1 (ppm)

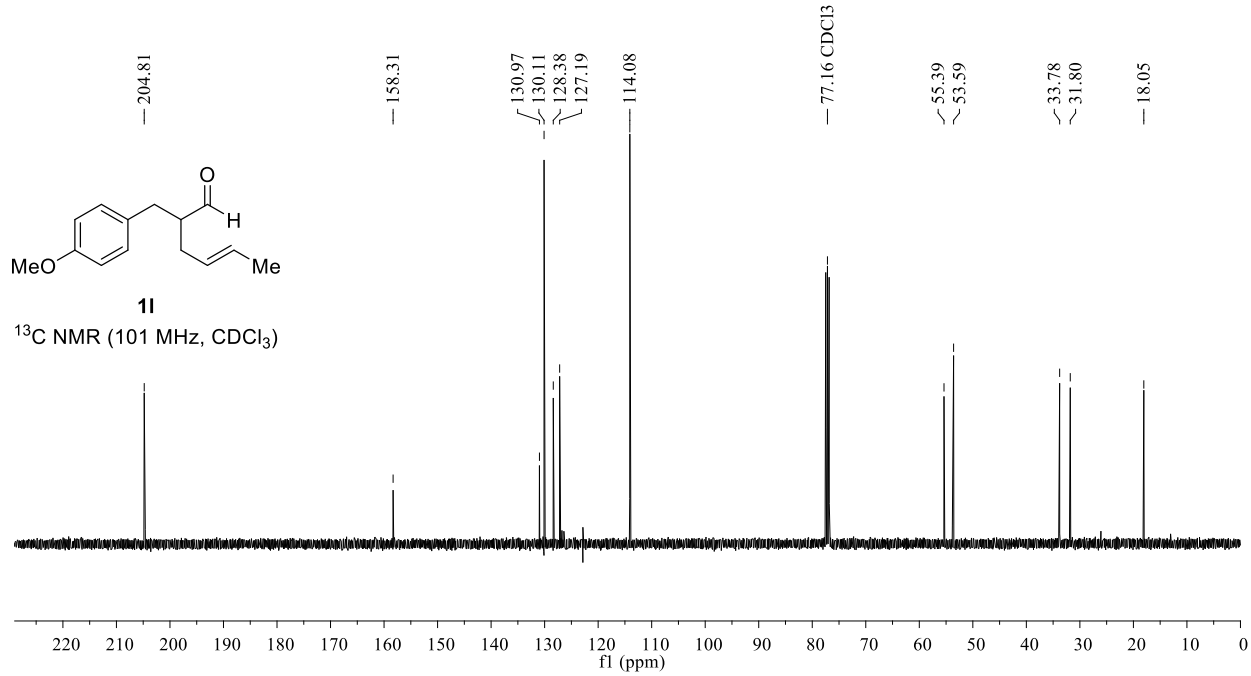

MeO
O
H
1j
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

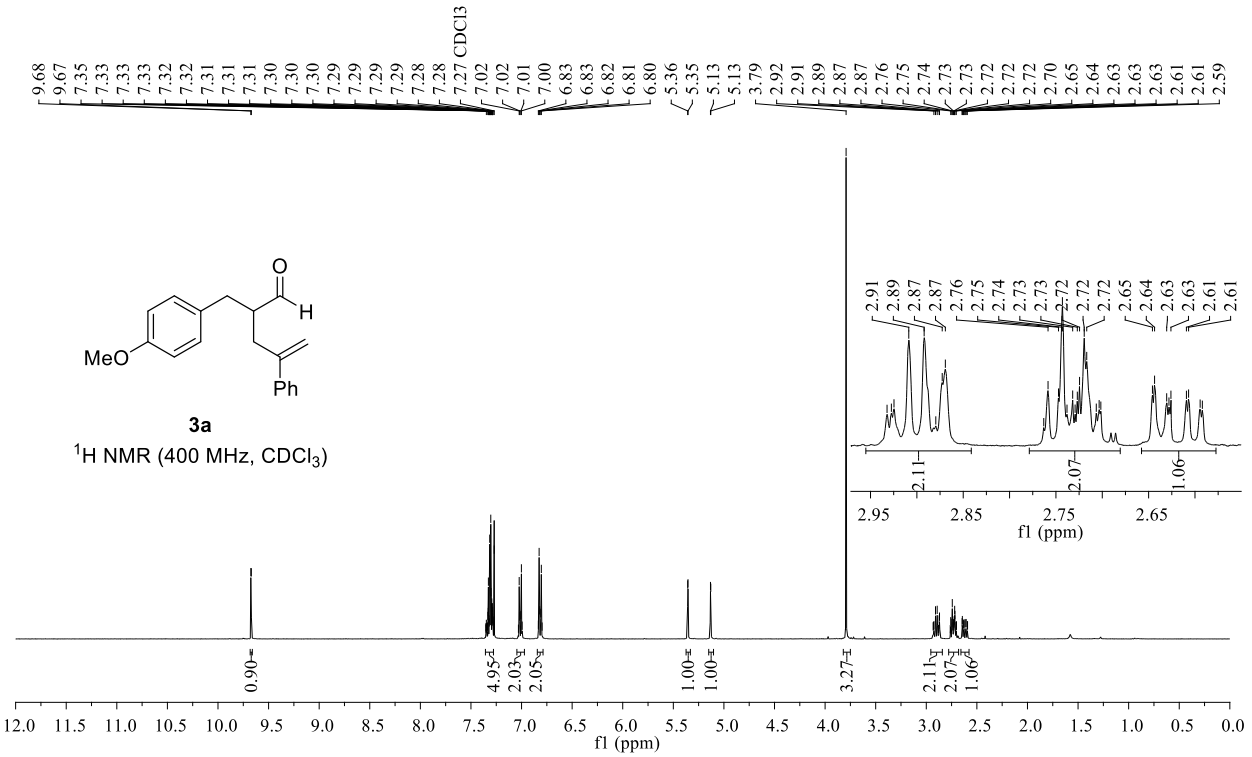

MeO
O
H
1j
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

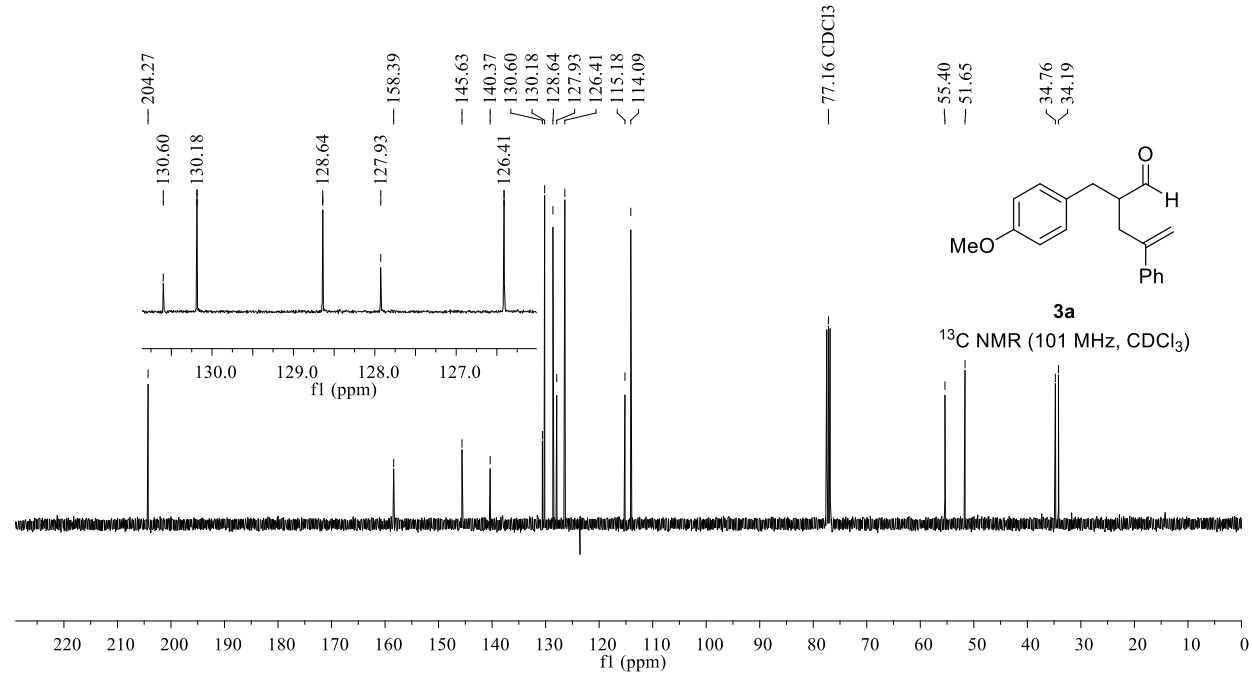

9.70
7.27 CDCl3
7.10
7.08
6.85
6.83
5.80
5.78
5.76
5.75
5.73
5.11
5.08
5.07
3.79
2.97
2.95
2.94
2.92
2.75
2.73
2.70
2.69
2.67
2.41
2.39
2.38
2.36
2.30
2.29
2.28
2.25
O
H
MeO
1k
1H NMR (400 MHz, CDCl3)
0.90
2.00
2.05
1.00
2.02
3.07
1.05
1.98
1.08
1.04
f1 (ppm)

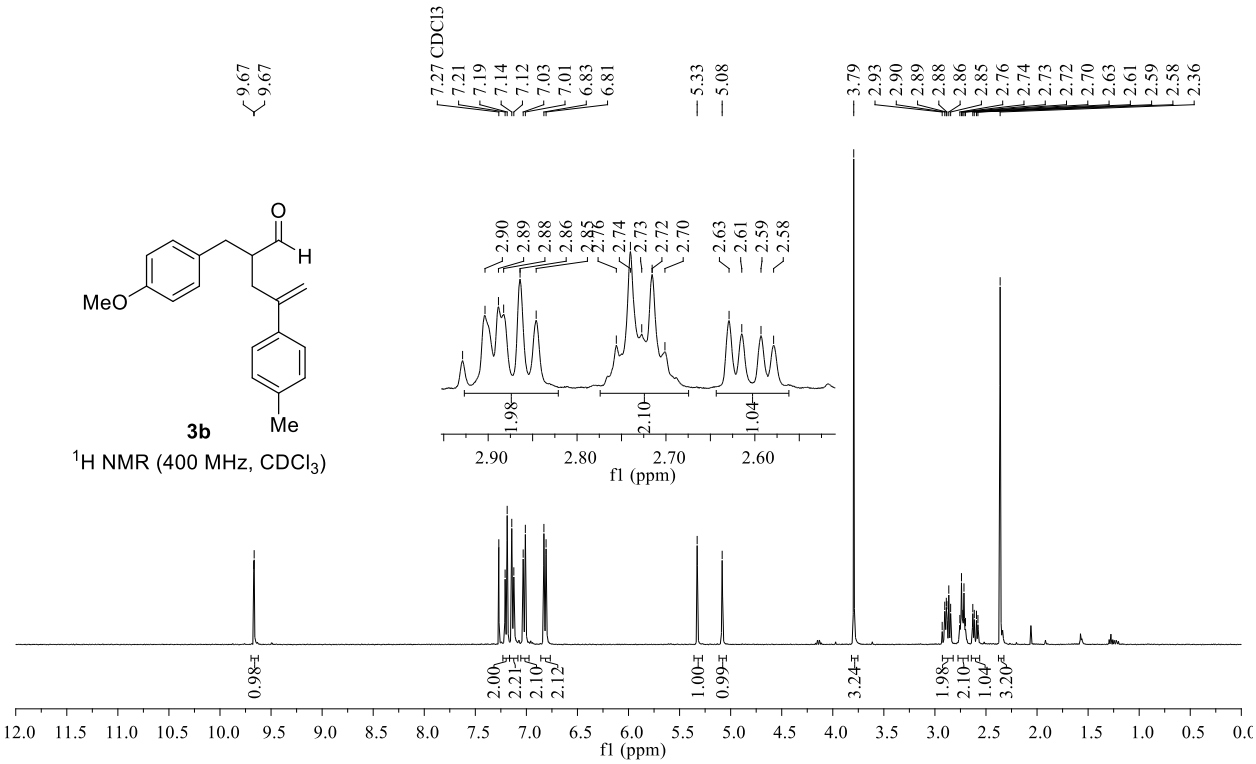

204.39
158.38
134.87
130.73
130.13
117.72
114.13
77.16 CDCl3
55.39
53.09
33.81
32.84
O
H
MeO
1k
13C NMR (101 MHz, CDCl3)
f1 (ppm)

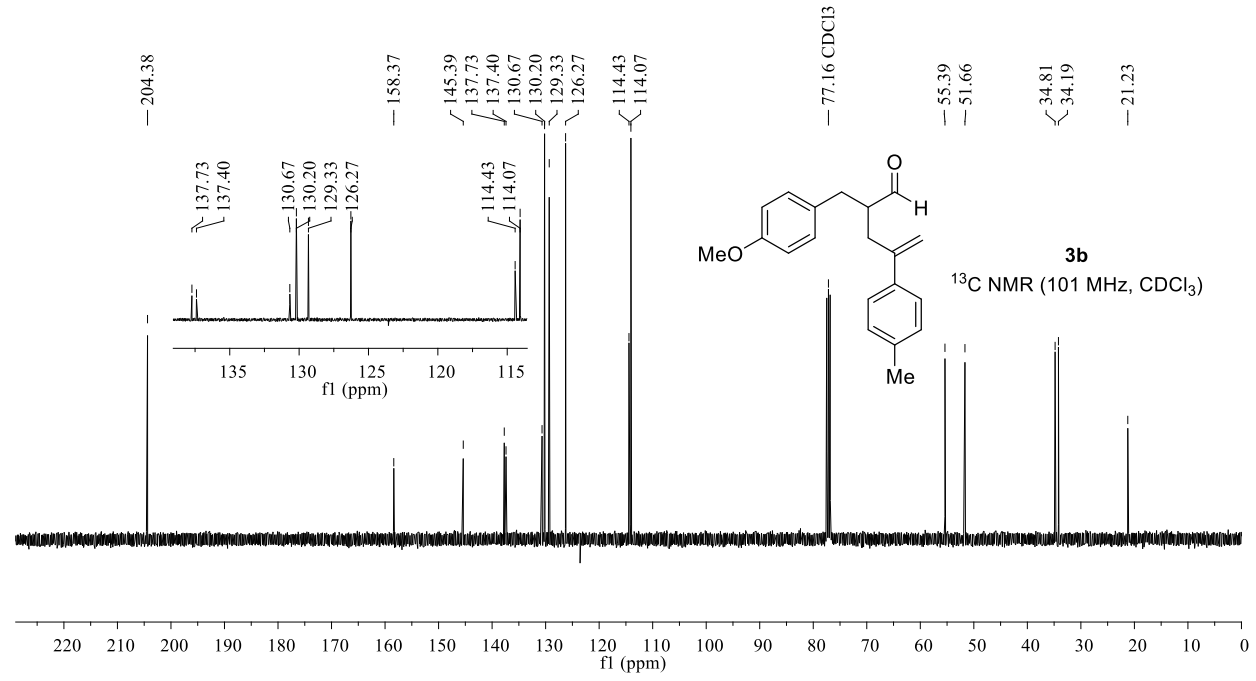

9.68
9.68
7.27 CDCl3
7.09
7.07
6.84
6.82
5.53
5.52
5.51
5.50
5.49
5.48
5.46
5.41
5.41
5.40
5.39
5.38
5.37
5.36
5.35
5.34
5.34
3.79
2.95
2.93
2.92
2.90
2.72
2.71
2.69
2.67
2.66
2.65
2.65
2.64
2.63
2.62
2.61
2.60
2.35
2.34
2.32
2.30
2.28
2.25
2.24
2.23
2.22
2.20
2.20
2.18
1.67
1.67
1.66
1.65
O
H
MeO
Me
1l
1H NMR (400 MHz, CDCl3)
1.01
2.05
1.03
1.01
2.84
3.0
2.5
2.0
f1 (ppm)
0.84
2.01
2.01
0.97
1.00
3.15
1.01
2.05
1.03
1.01
2.84
12.0 11.5 11.0 10.5 10.0 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
f1 (ppm)

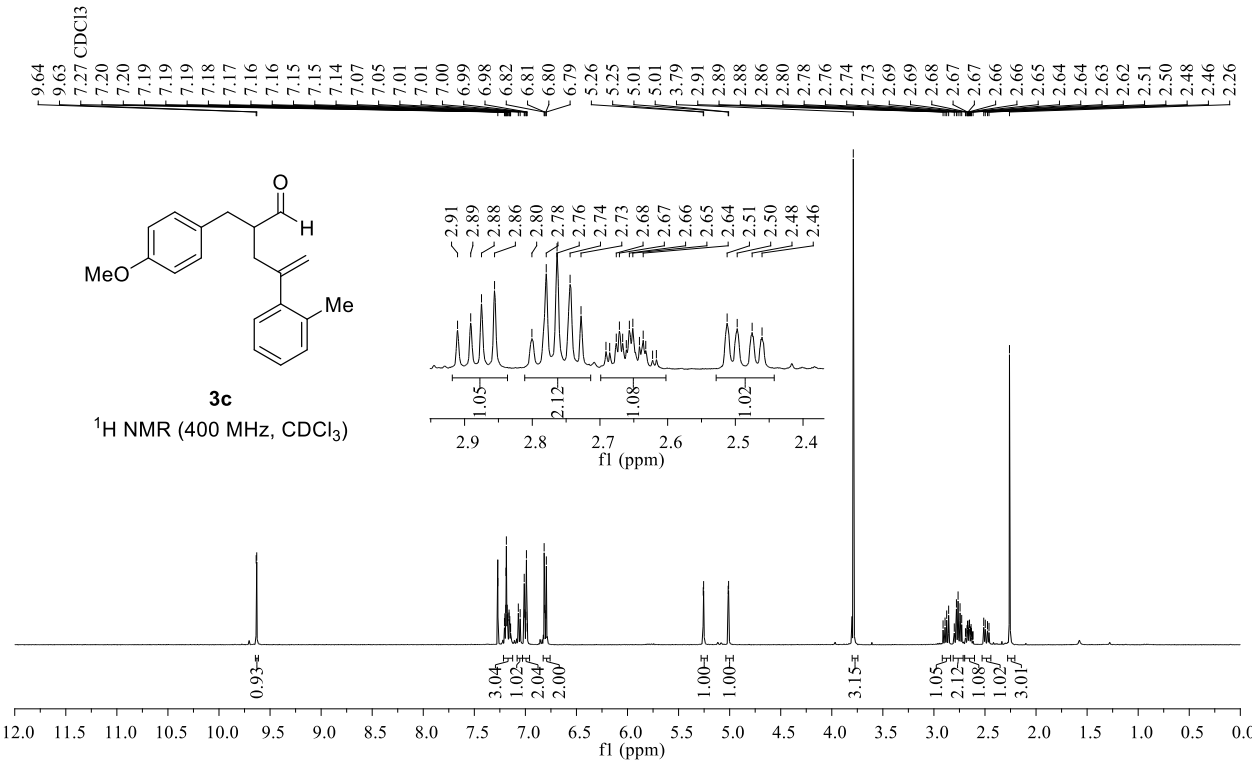

204.81
158.31
130.97
130.11
128.38
127.19
114.08
77.16 CDCl3
55.39
53.59
33.78
31.80
18.05
O
H
MeO
Me
1l
13C NMR (101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

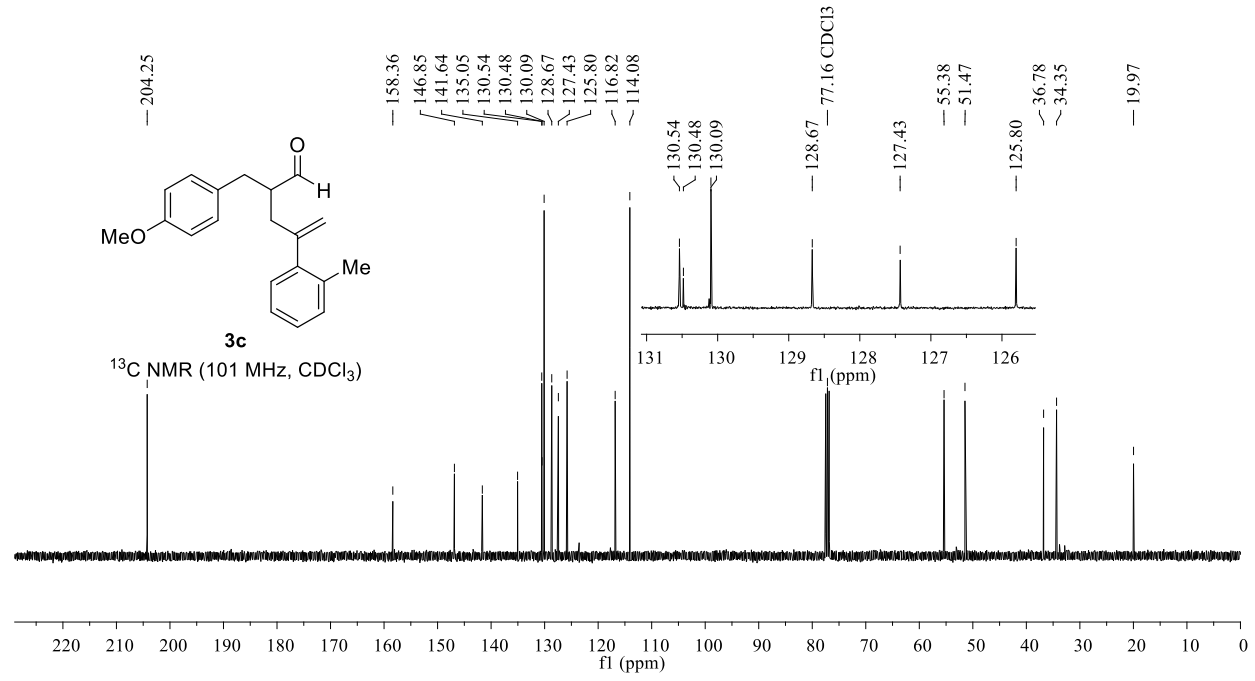

MeO
O
H
Ph
3a
1H NMR (400 MHz, CDCl3)
f1 (ppm)

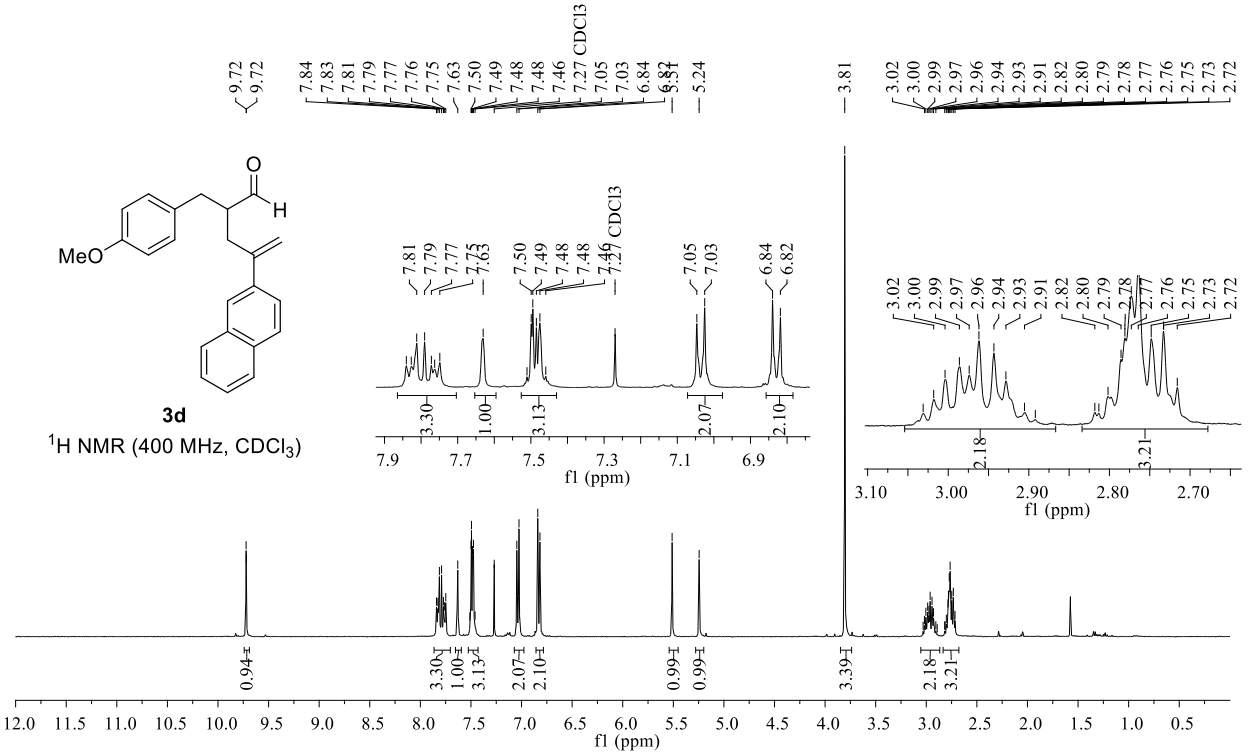

MeO
O
H
Ph
3a
13C NMR (101 MHz, CDCl3)
f1 (ppm)

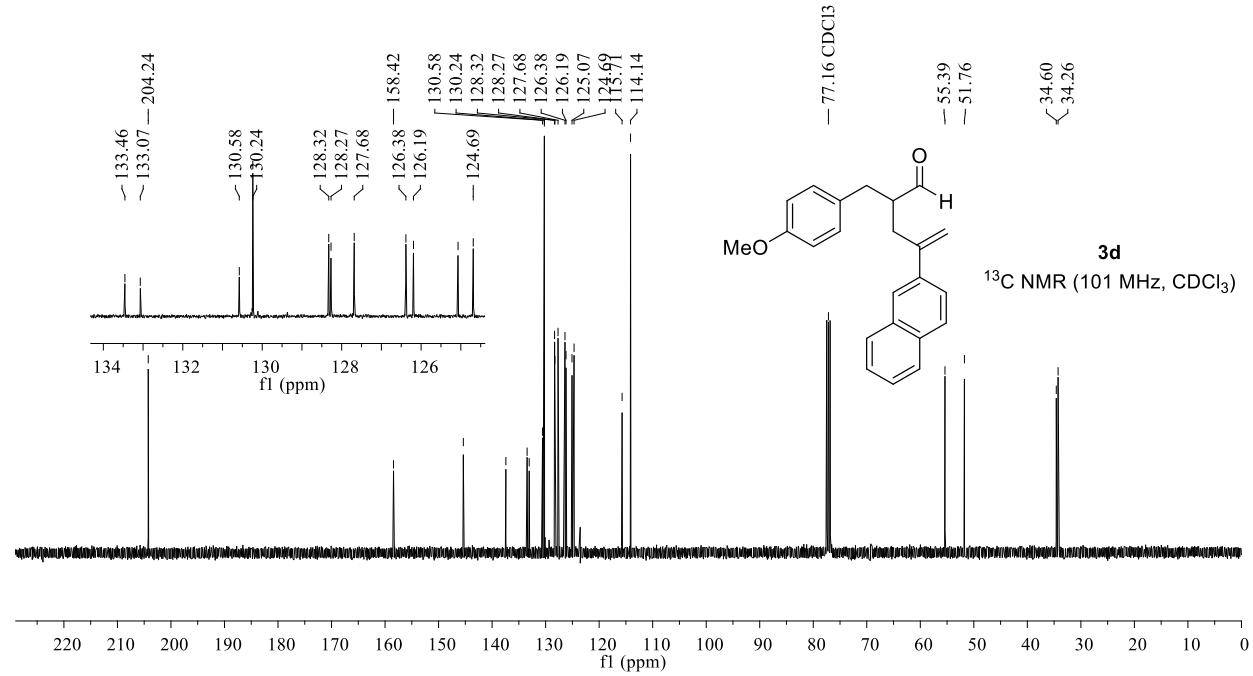

9.67
9.67
7.27 CDCl3
7.21
7.19
7.14
7.12
7.03
7.01
6.83
6.81
5.33
5.08
3.79
2.93
2.90
2.89
2.88
2.86
2.85
2.76
2.74
2.73
2.72
2.70
2.63
2.61
2.59
2.58
2.36
O
H
MeO
Me
3b
1H NMR (400 MHz, CDCl3)
1.98
2.10
1.04
f1 (ppm)
0.98
2.00
2.21
2.10
2.12
1.00
0.99
3.24
1.98
2.10
1.04
3.20
f1 (ppm)

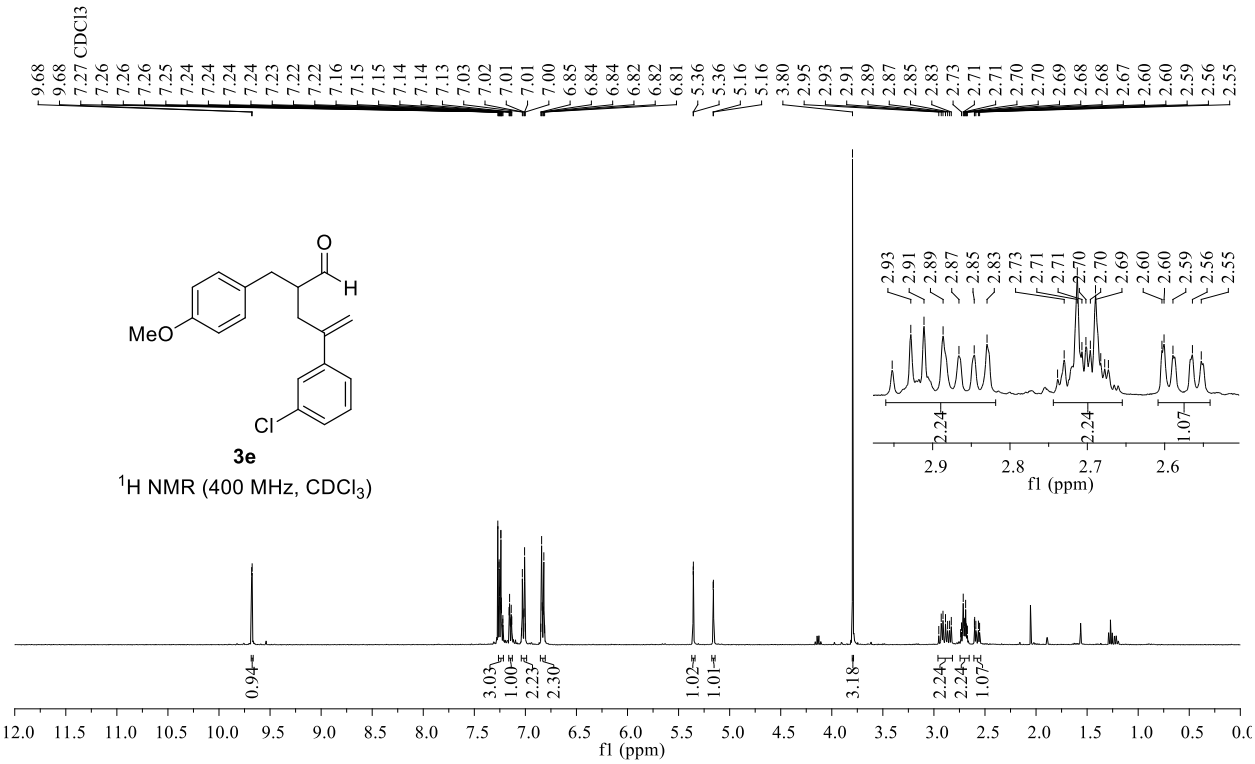

204.38
158.37
145.39
137.73
137.40
130.67
130.20
129.33
126.27
114.43
114.07
77.16 CDCl3
55.39
51.66
34.81
34.19
21.23
137.73
137.40
130.67
130.20
129.33
126.27
114.43
114.07
f1 (ppm)
O
H
MeO
Me
3b
13C NMR (101 MHz, CDCl3)
f1 (ppm)

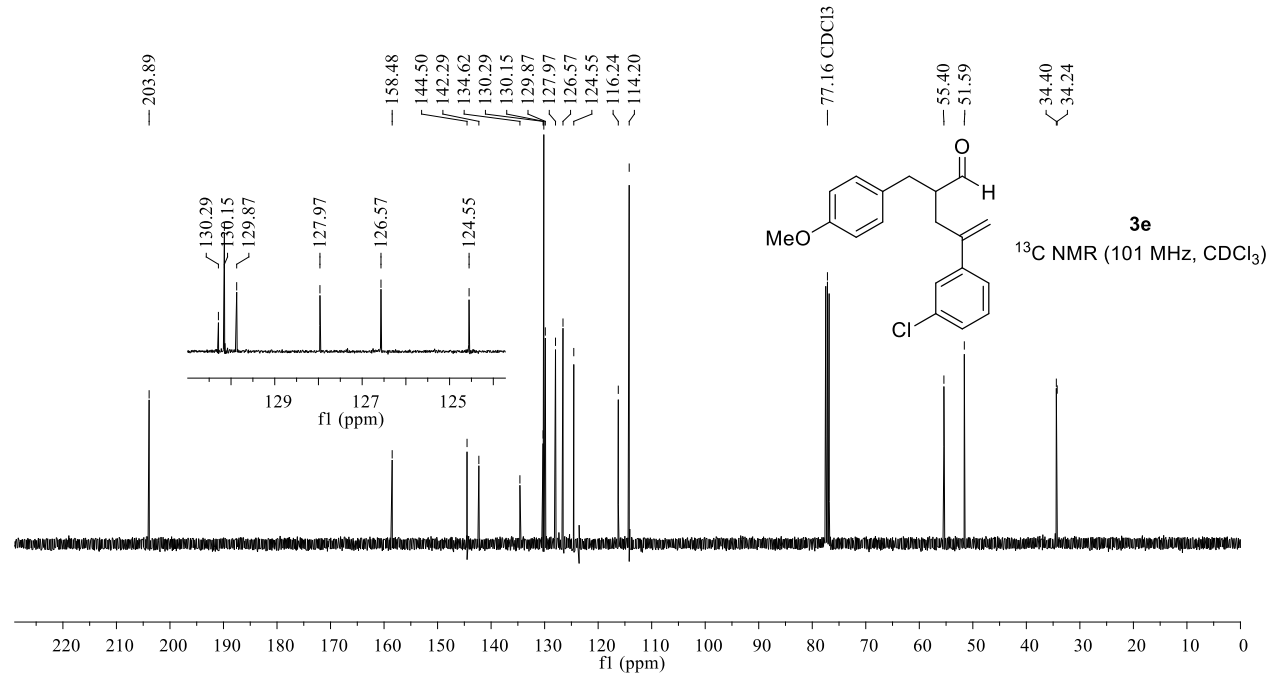

9.64 9.63 7.27 CDCl3 7.20 7.20 7.19 7.19 7.19 7.18 7.17 7.16 7.16 7.15 7.15 7.14 7.07 7.05 7.01 7.01 7.00 6.99 6.98 6.82 6.81 6.80 6.79
5.26 5.25 5.01 5.01 3.79 2.91 2.89 2.88 2.86 2.80 2.78 2.76 2.74 2.73 2.69 2.69 2.68 2.67 2.67 2.66 2.66 2.65 2.64 2.64 2.63 2.62 2.51 2.50 2.48 2.46 2.26
O
H
MeO
Me
3c
1H NMR (400 MHz, CDCl3)
2.91 2.89 2.88 2.86 2.80 2.78 2.76 2.74 2.73 2.68 2.67 2.66 2.65 2.64 2.51 2.50 2.48 2.46
1.05 2.12 1.08 1.02
2.9 2.8 2.7 2.6 2.5 2.4
f1 (ppm)
0.93 3.04 1.02 2.04 2.00 1.00 1.00 3.15 1.05 2.12 1.08 1.02 3.01
12.0 11.5 11.0 10.5 10.0 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)

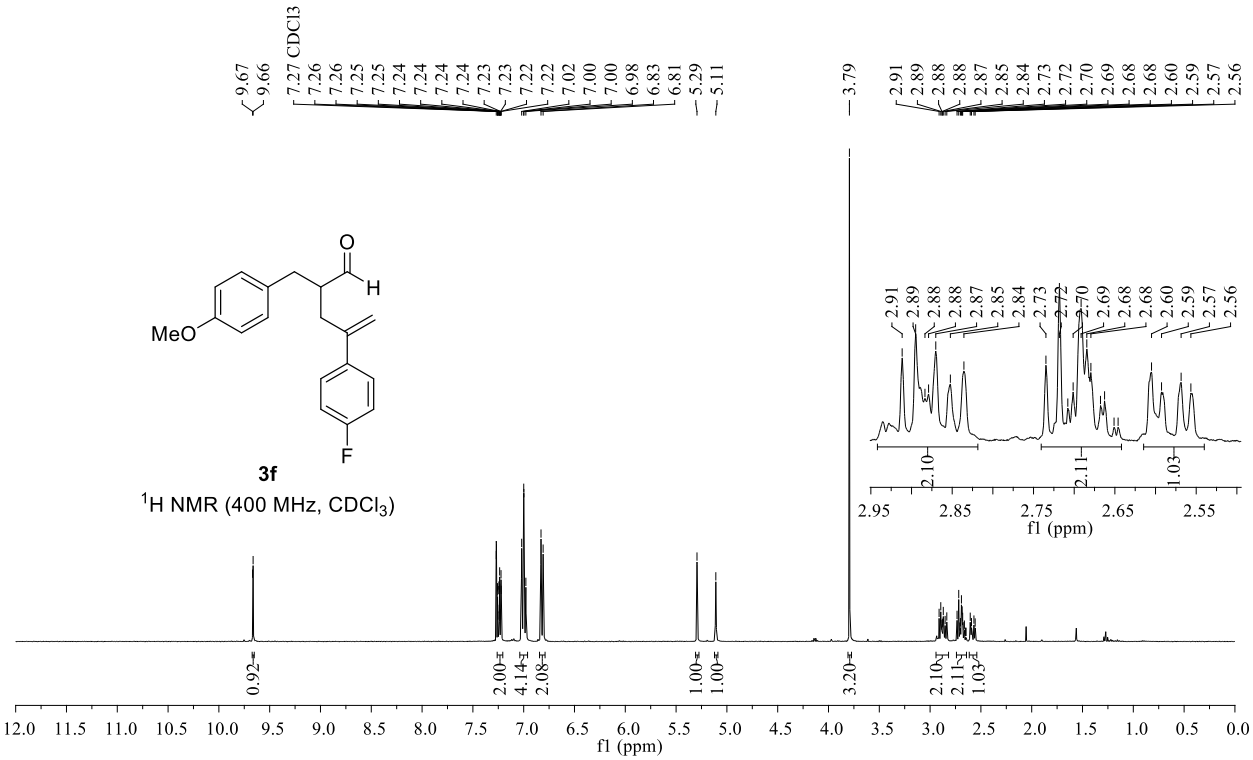

204.25
158.36 146.85 141.64 135.05 130.54 130.48 130.09 128.67 127.43 125.80 116.82 114.08
77.16 CDCl3
55.38 51.47 36.78 34.35 19.97
130.54 130.48 130.09 128.67 127.43 125.80
O
H
MeO
Me
3c
13C NMR (101 MHz, CDCl3)
131 130 129 128 127 126
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

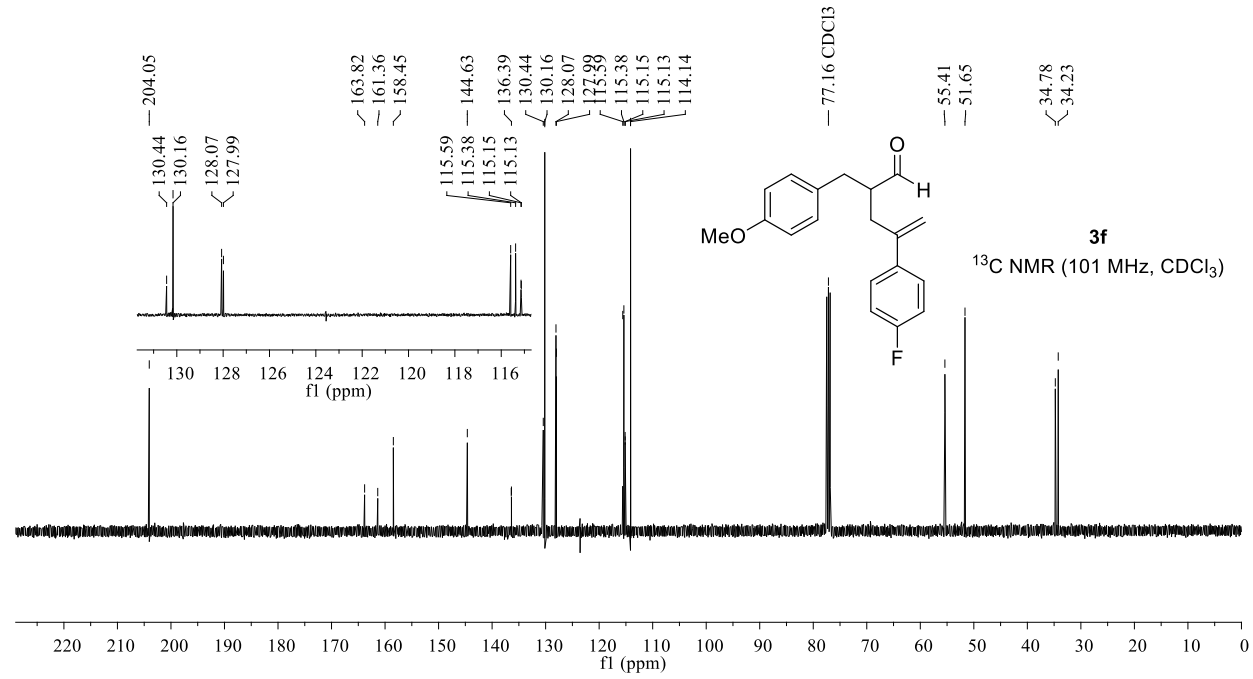

MeO
O
H
3d
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

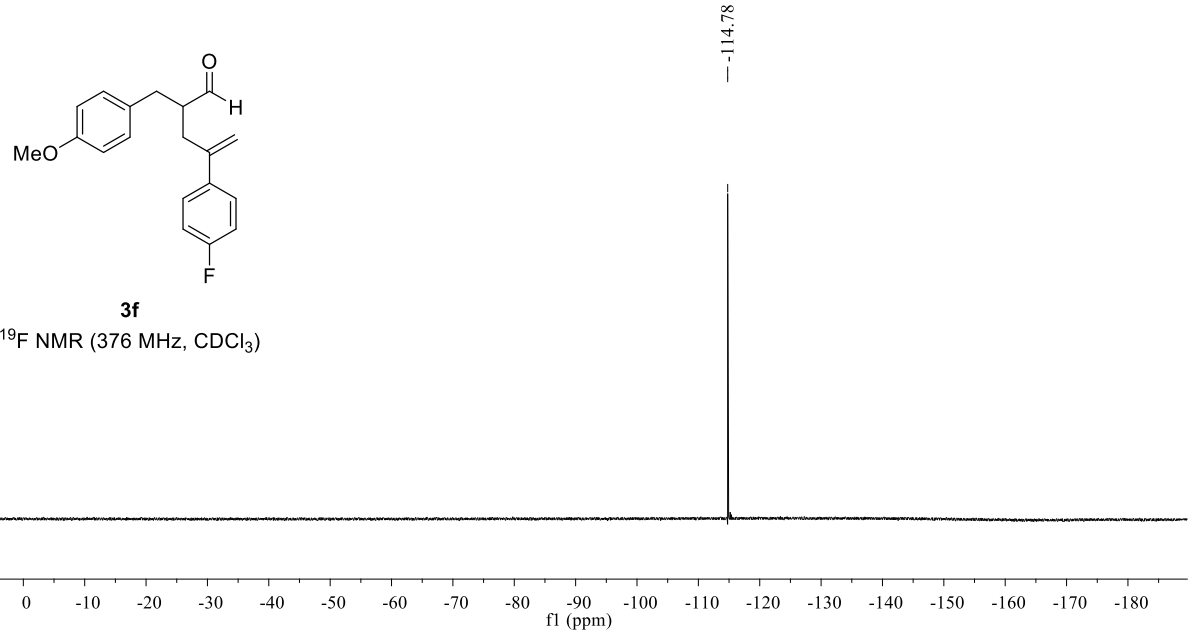

MeO
O
H
3d
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)


9.68 9.68 7.27 CDCl3 7.26 7.26 7.26 7.25 7.24 7.24 7.24 7.24 7.23 7.22 7.22 7.16 7.15 7.15 7.14 7.14 7.13 7.03 7.02 7.01 7.01 7.00 6.85 6.84 6.84 6.82 6.82 6.81 5.36 5.36 5.16 5.16 3.80 2.95 2.93 2.91 2.89 2.87 2.85 2.83 2.73 2.71 2.71 2.70 2.70 2.69 2.68 2.68 2.67 2.60 2.60 2.59 2.56 2.55
O
H
MeO
Cl
3e
1H NMR (400 MHz, CDCl3)
2.93 2.91 2.89 2.87 2.85 2.83 2.73 2.71 2.71 2.70 2.70 2.69 2.60 2.60 2.59 2.56 2.55
2.24 2.24 1.07
2.9 2.8 2.7 2.6
f1 (ppm)
0.94 3.03 1.00 2.23 2.30 1.02 1.01 3.18 2.24 2.24 1.07
12.0 11.5 11.0 10.5 10.0 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)


203.89
158.48 144.50 142.29 134.62 130.29 130.15 129.87 127.97 126.57 124.55 116.24 114.20
77.16 CDCl3
55.40 51.59
34.40 34.24
130.29 130.15 129.87 127.97 126.57 124.55
129 127 125
f1 (ppm)
O
H
MeO
Cl
3e
13C NMR (101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

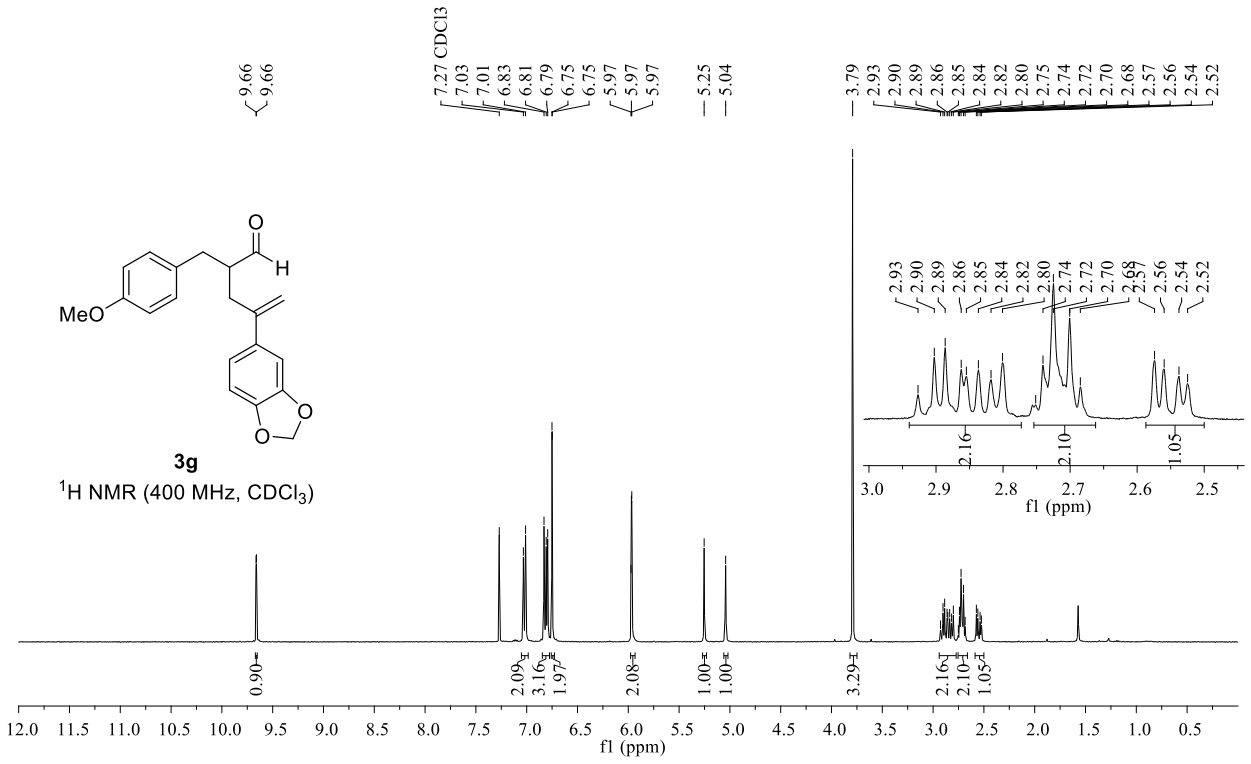

9.67
9.66
7.27 CDCl3
7.26
7.26
7.25
7.25
7.24
7.24
7.24
7.24
7.23
7.23
7.22
7.22
7.02
7.00
7.00
6.98
6.83
6.81
5.29
5.11
3.79
2.91
2.89
2.88
2.88
2.87
2.85
2.84
2.73
2.72
2.70
2.69
2.68
2.68
2.60
2.59
2.57
2.56
O
H
MeO
F
3f
1H NMR (400 MHz, CDCl3)
0.92
2.00
4.14
2.08
1.00
1.00
3.20
2.10
2.11
1.03
f1 (ppm)


204.05
163.82
161.36
158.45
144.63
136.39
130.44
130.16
128.07
127.99
115.59
115.38
115.15
115.13
77.16 CDCl3
55.41
51.65
34.78
34.23
O
H
MeO
F
3f
13C NMR (101 MHz, CDCl3)
f1 (ppm)



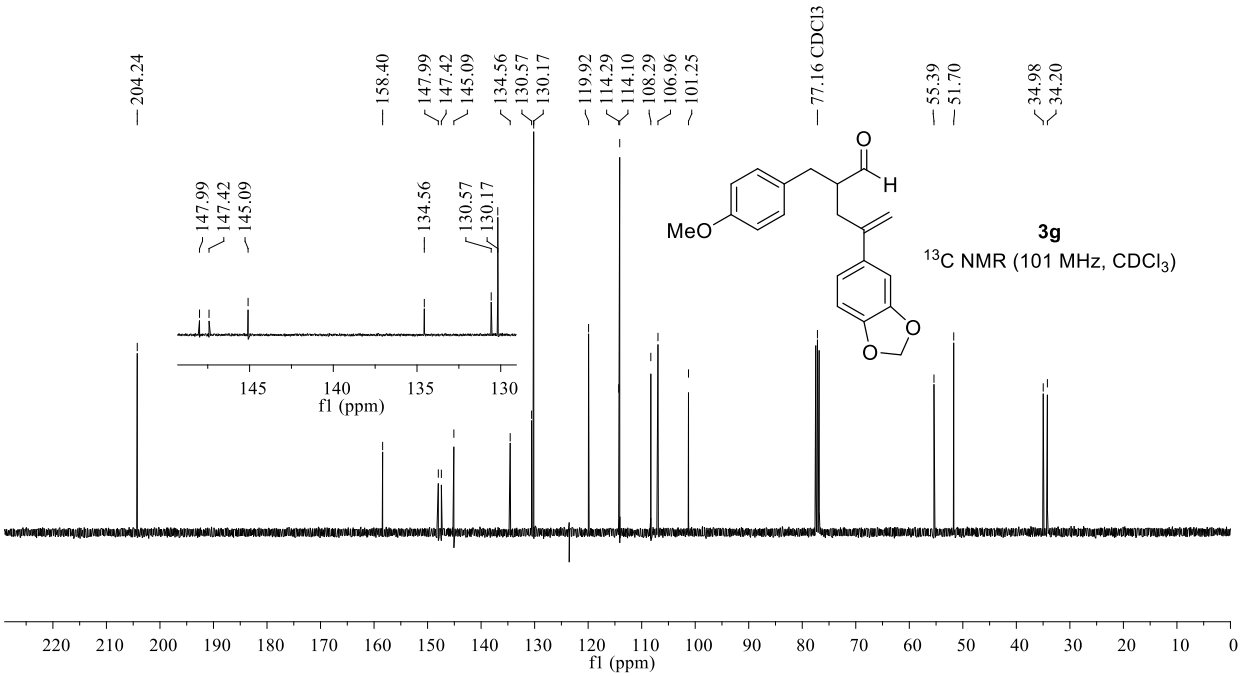
3f

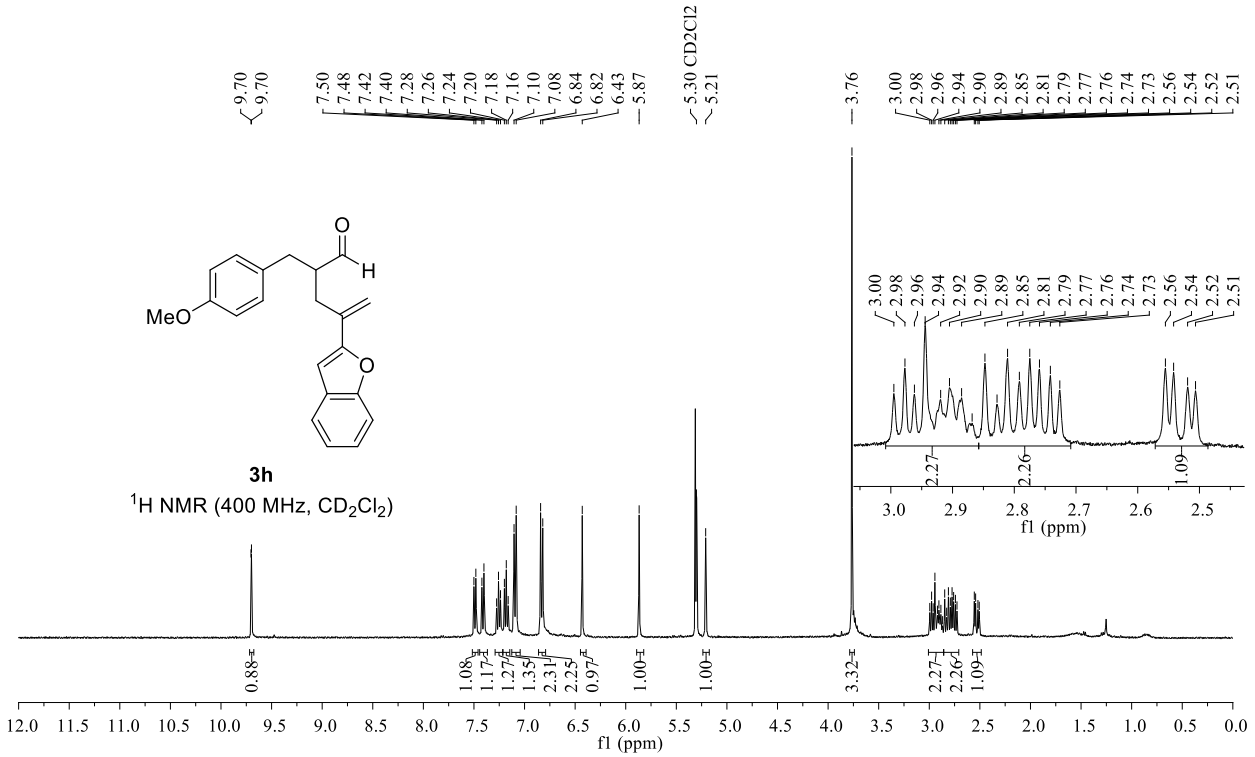
^{19}F NMR (376 MHz, $CDCl_3$)

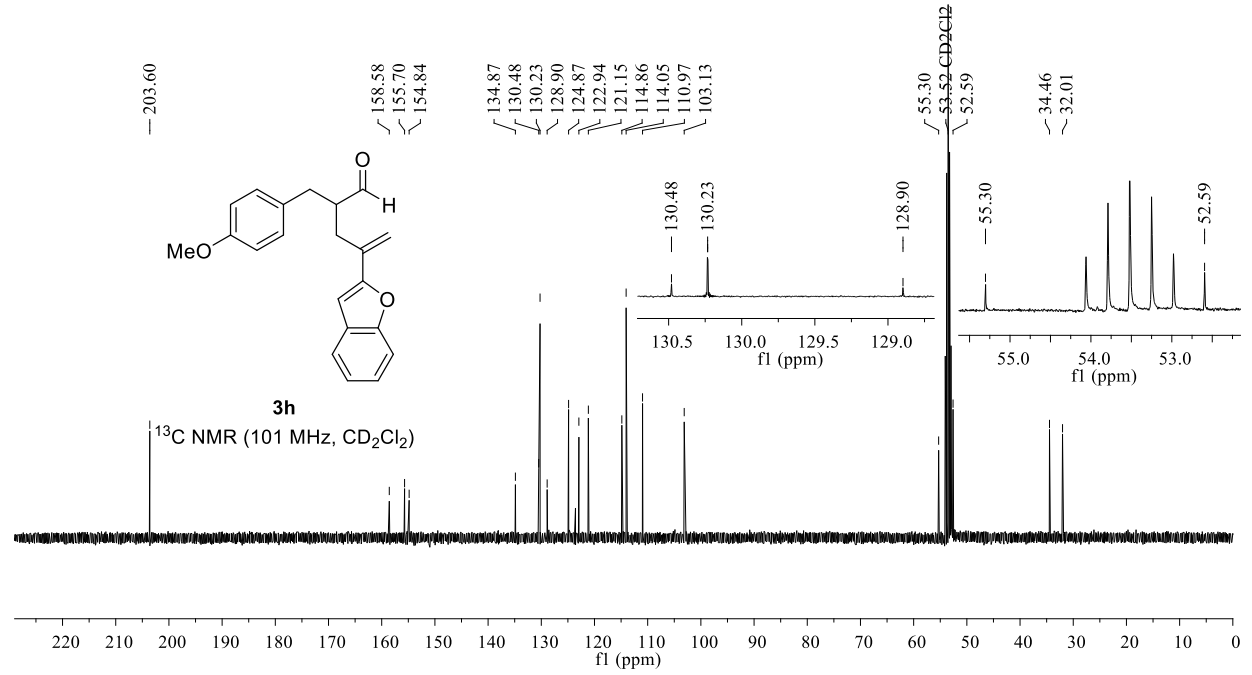


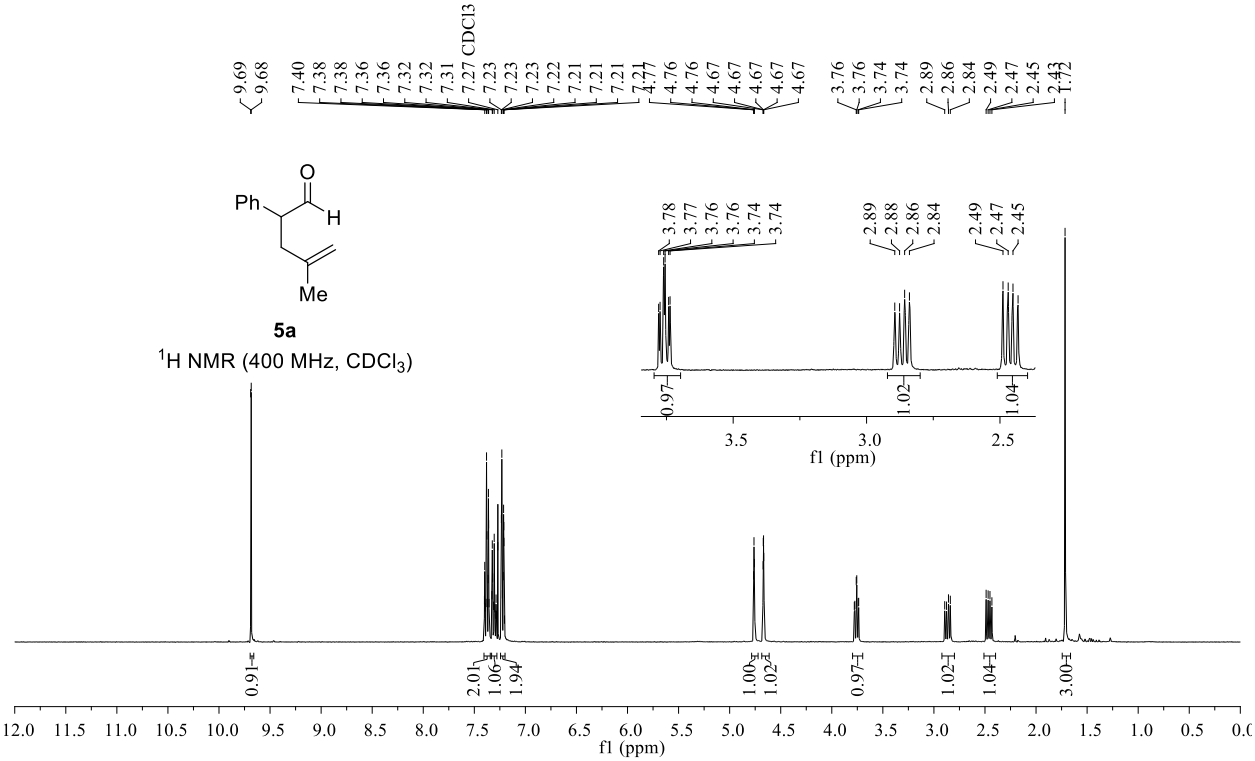
3g

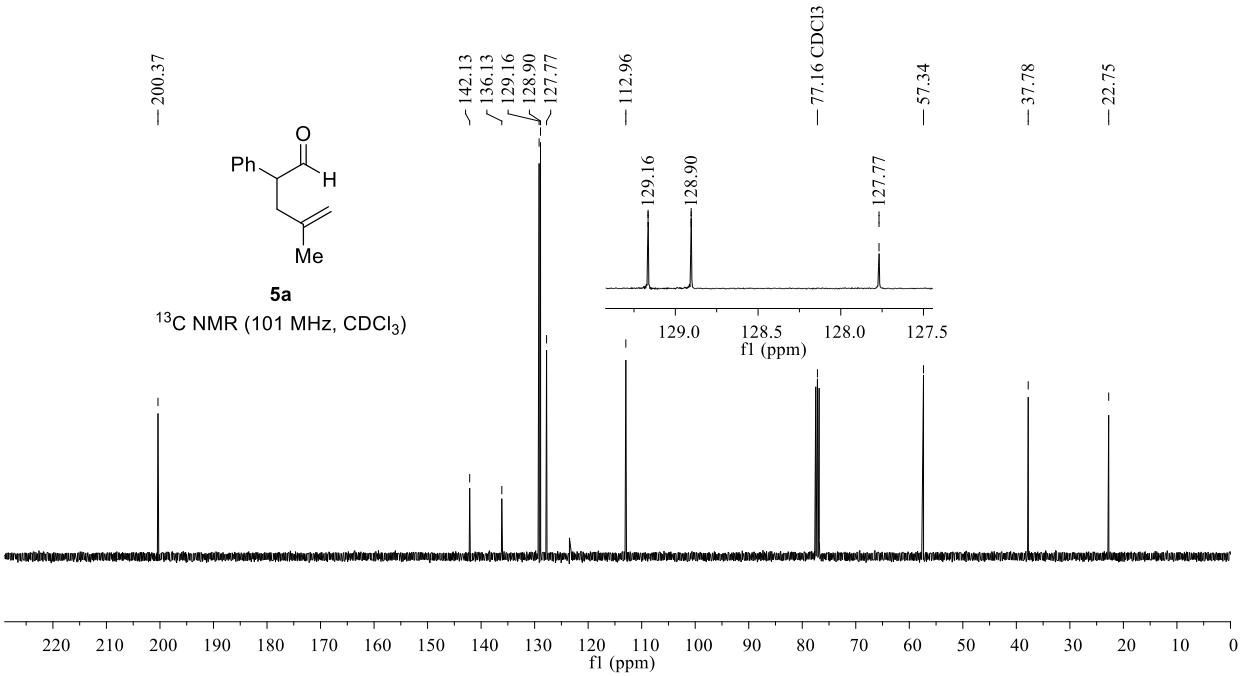
^{1}H NMR (400 MHz, $CDCl_3$)

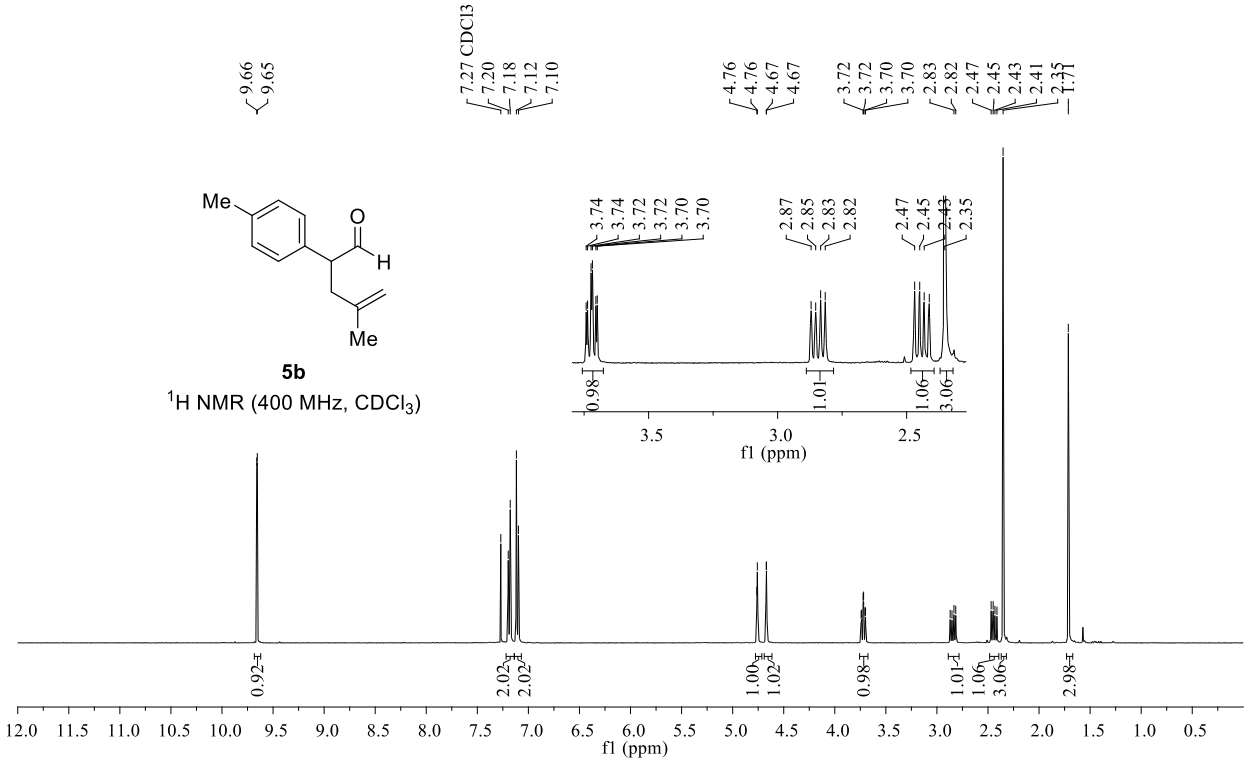

204.24
158.40
147.99
147.42
145.09
134.56
130.57
130.17
119.92
114.29
114.10
108.29
106.96
101.25
77.16 CDCl3
55.39
51.70
34.98
34.20
MeO
O
H
O
O
3g
13C NMR (101 MHz, CDCl3)
f1 (ppm)

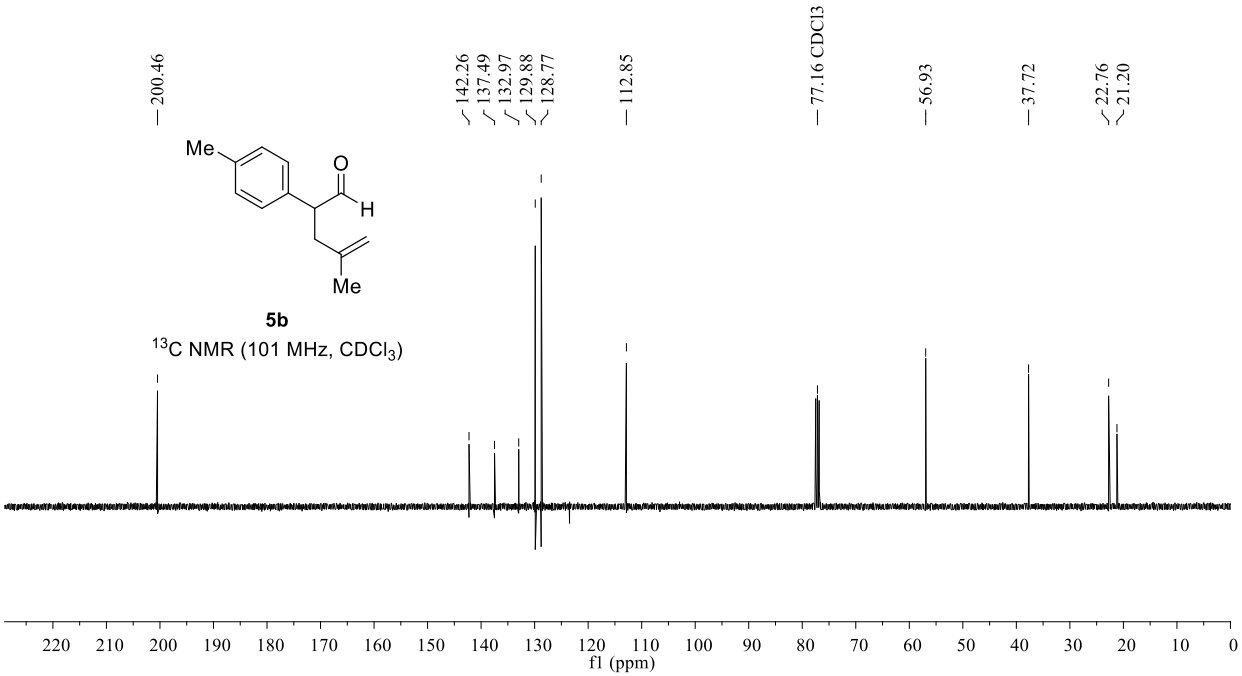

9.70
9.70
7.50
7.48
7.42
7.40
7.28
7.26
7.24
7.20
7.18
7.16
7.10
7.08
6.84
6.82
6.43
5.87
5.30 CD2Cl2
5.21
3.76
3.00
2.98
2.96
2.94
2.92
2.90
2.89
2.85
2.81
2.79
2.77
2.76
2.74
2.73
2.56
2.54
2.52
2.51
MeO
O
H
O
3h
1H NMR (400 MHz, CD2Cl2)
2.27
2.26
1.09
f1 (ppm)
0.88
1.08
1.17
1.27
1.35
2.31
2.25
0.97
1.00
1.00
3.32
2.27
2.26
1.09
f1 (ppm)


203.60
158.58
155.70
154.84
134.87
130.48
130.23
128.90
124.87
122.94
121.15
114.86
114.05
110.97
103.13
55.30
53.52 CD2Cl2
52.59
34.46
32.01
MeO
O
H
O
3h
13C NMR (101 MHz, CD2Cl2)
f1 (ppm)


9.69
9.68
7.40
7.38
7.38
7.36
7.36
7.32
7.32
7.31
7.27 CDCl3
7.23
7.23
7.23
7.22
7.21
7.21
7.21
4.76
4.76
4.67
4.67
4.67
4.67
3.76
3.76
3.74
3.74
2.89
2.86
2.84
2.49
2.47
2.45
1.72
Ph
O
H
Me
5a
1H NMR (400 MHz, CDCl3)
f1 (ppm)

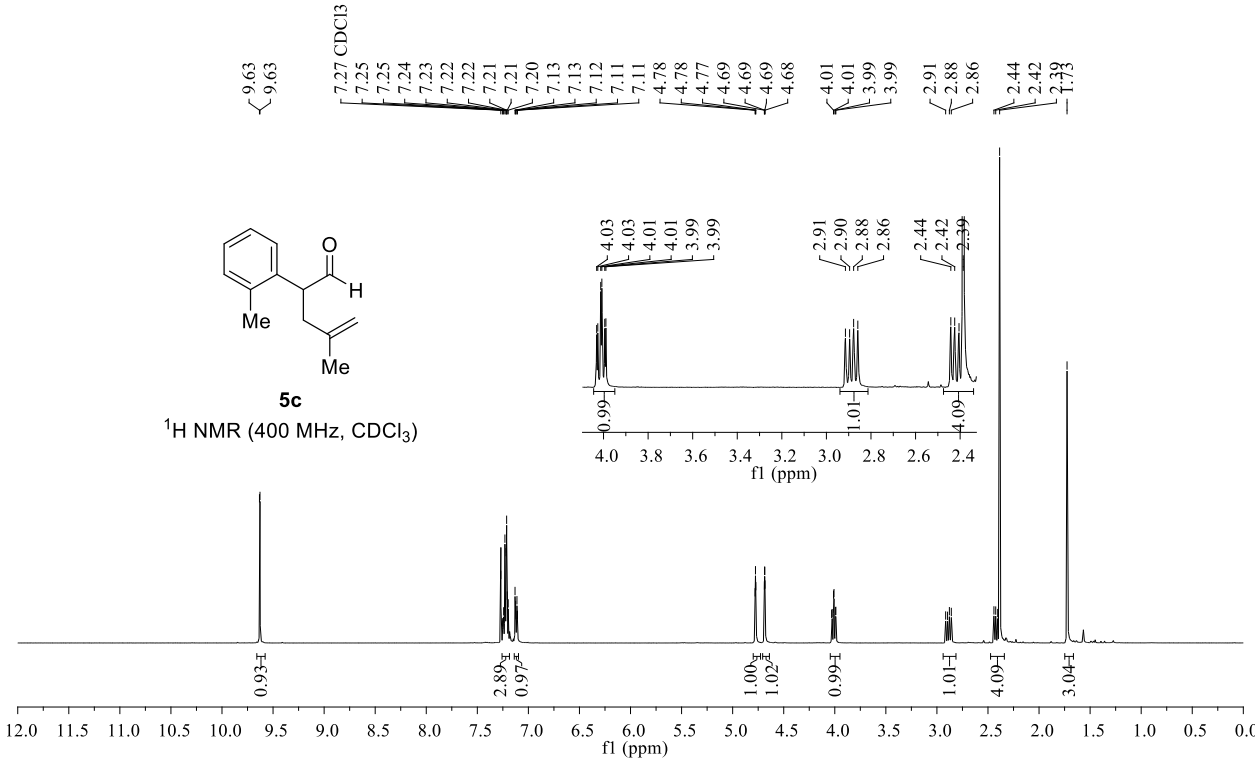

200.37
142.13
136.13
129.16
128.90
127.77
112.96
77.16 CDCl3
57.34
37.78
22.75
Ph
O
H
Me
5a
13C NMR (101 MHz, CDCl3)
129.16
128.90
127.77
129.0
128.5
128.0
127.5
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.66
9.65
7.27 CDCl3
7.20
7.18
7.12
7.10
4.76
4.76
4.67
4.67
3.72
3.72
3.70
3.70
2.83
2.82
2.47
2.45
2.43
2.41
2.35
1.71
Me
O
H
Me
5b
1H NMR (400 MHz, CDCl3)
3.74
3.74
3.72
3.72
3.70
3.70
2.87
2.85
2.83
2.82
2.47
2.45
2.43
2.35
0.98
1.01
1.06
3.06
3.5
3.0
2.5
f1 (ppm)
0.92
2.02
2.02
1.00
1.02
0.98
1.01
1.06
3.06
2.98
12.0 11.5 11.0 10.5 10.0 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
f1 (ppm)



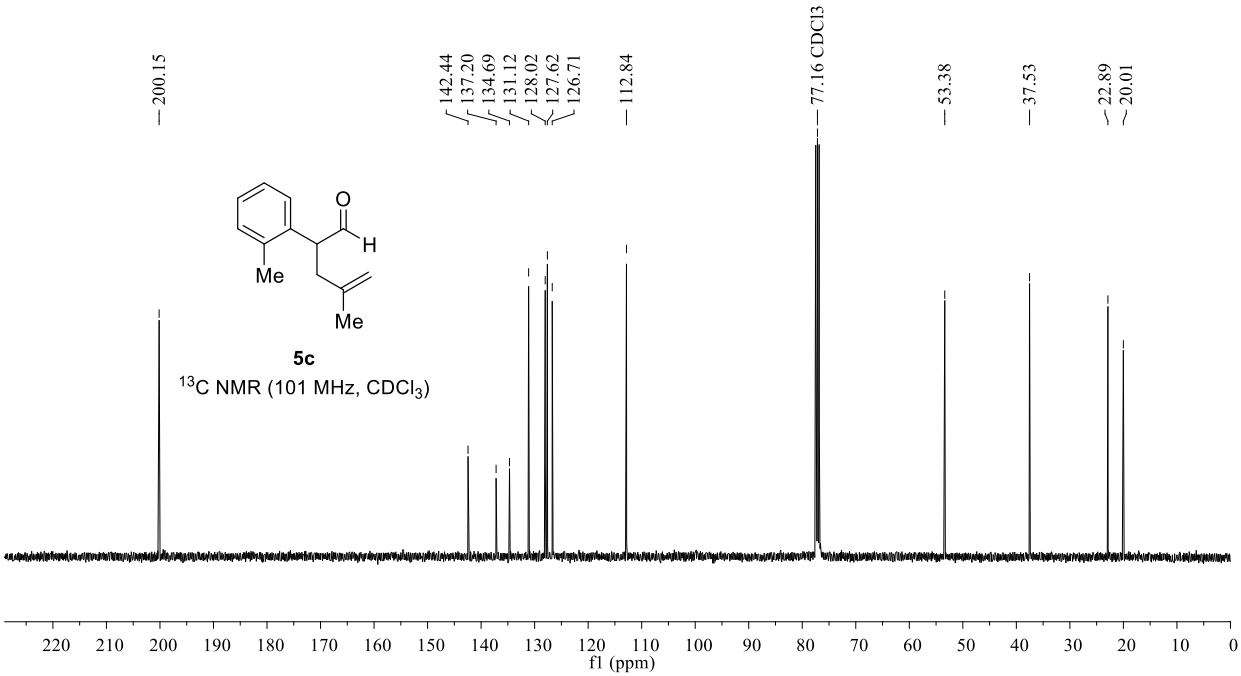
5b

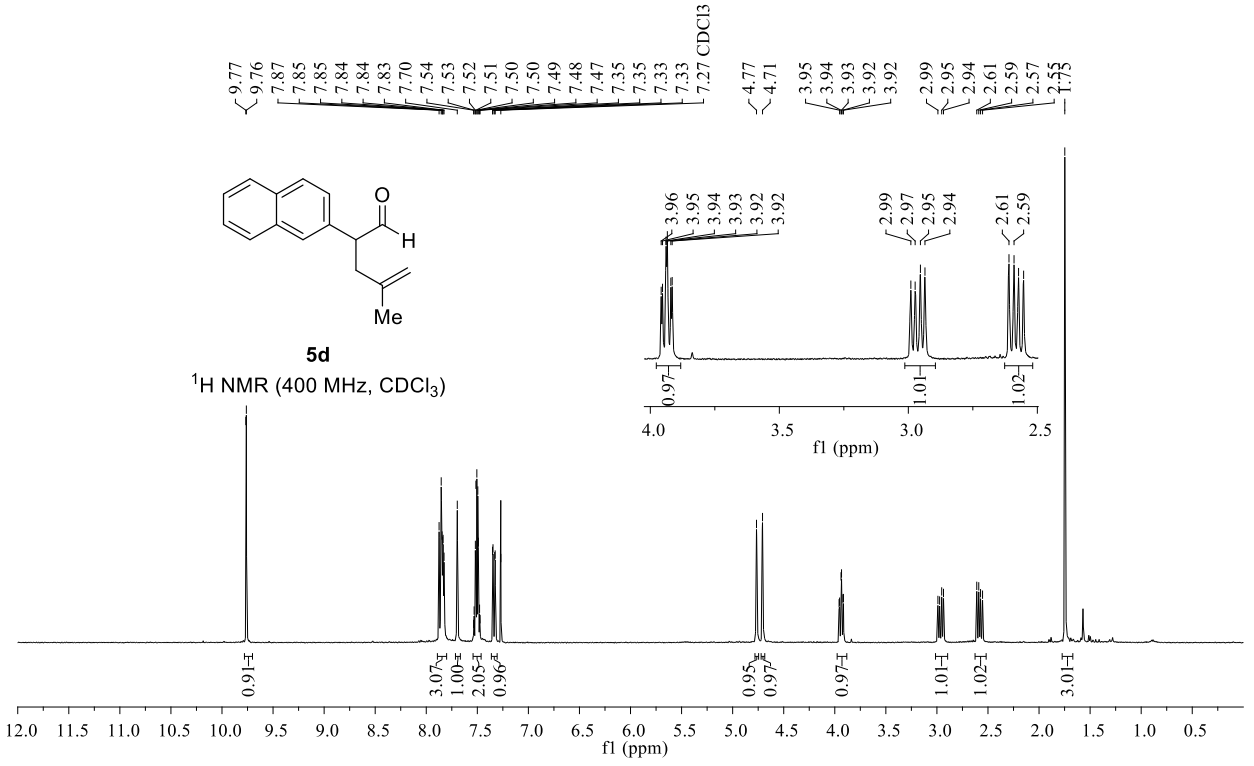
^{13}C NMR (101 MHz, $CDCl_3$)

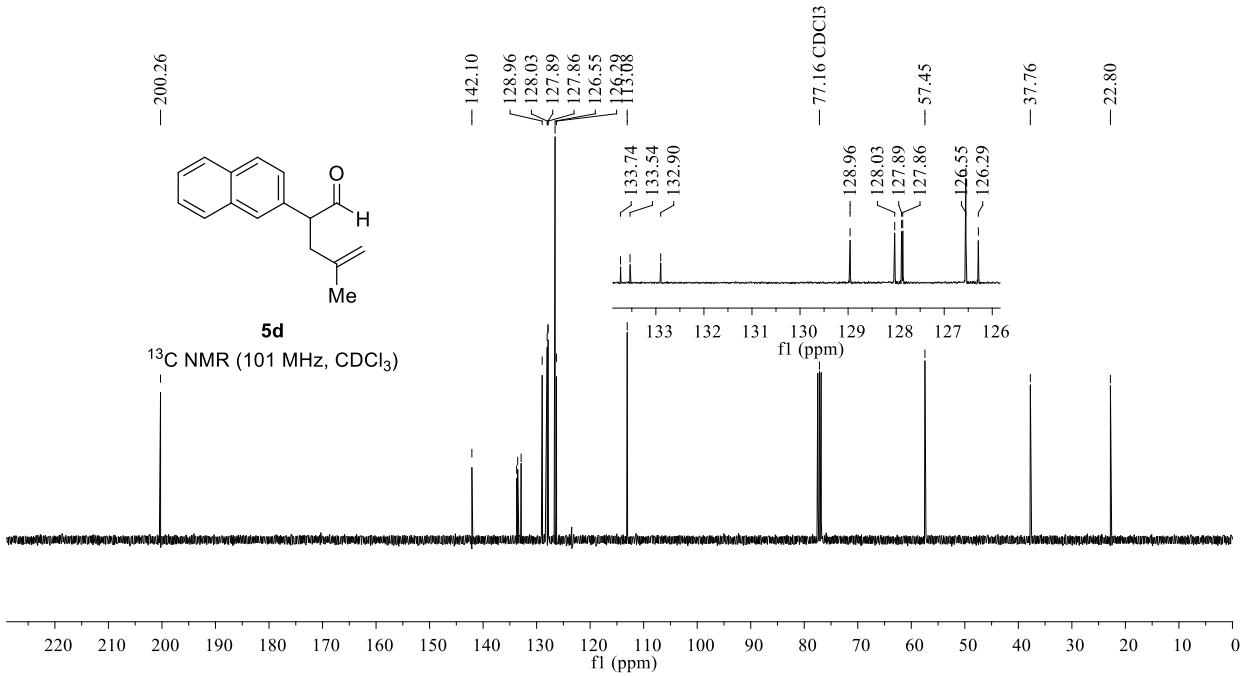


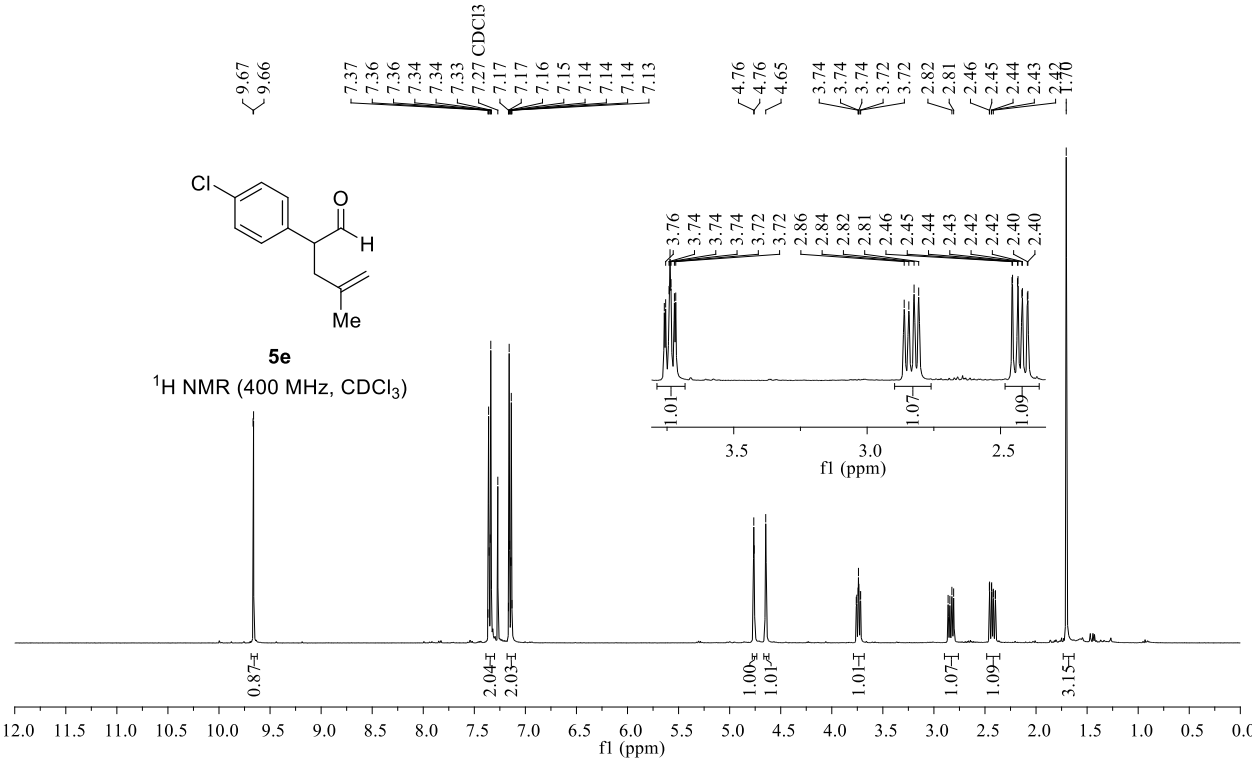
5c

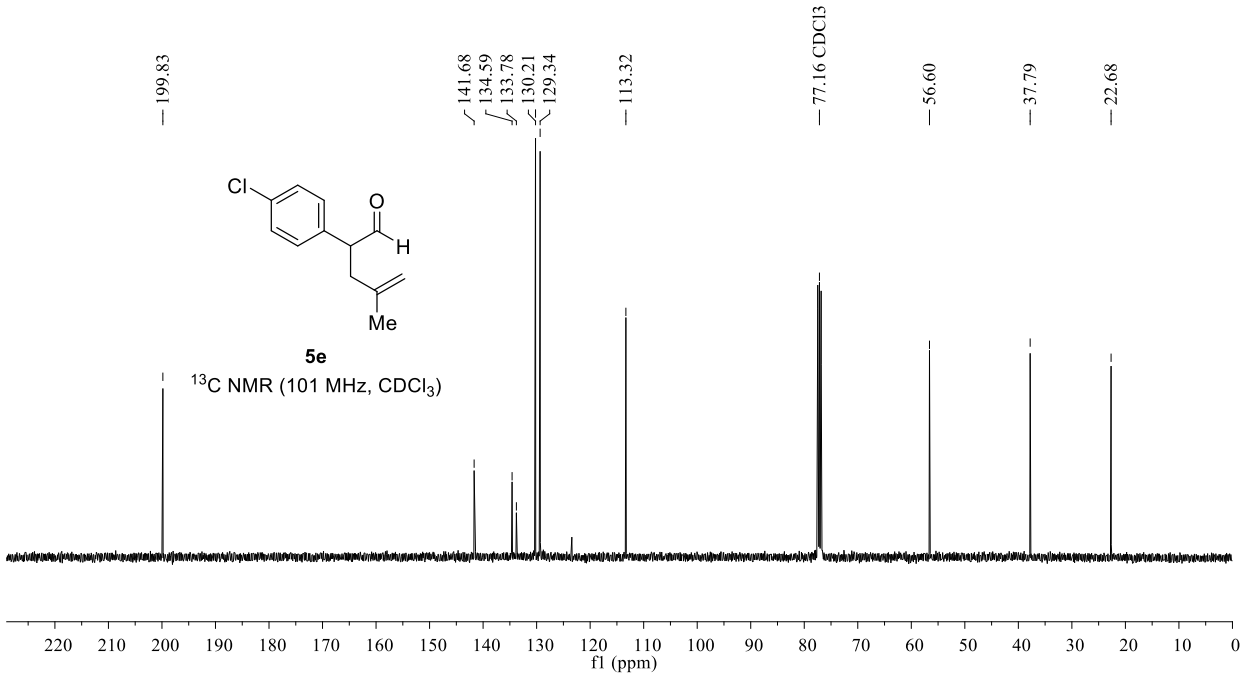
^{1}H NMR (400 MHz, $CDCl_3$)

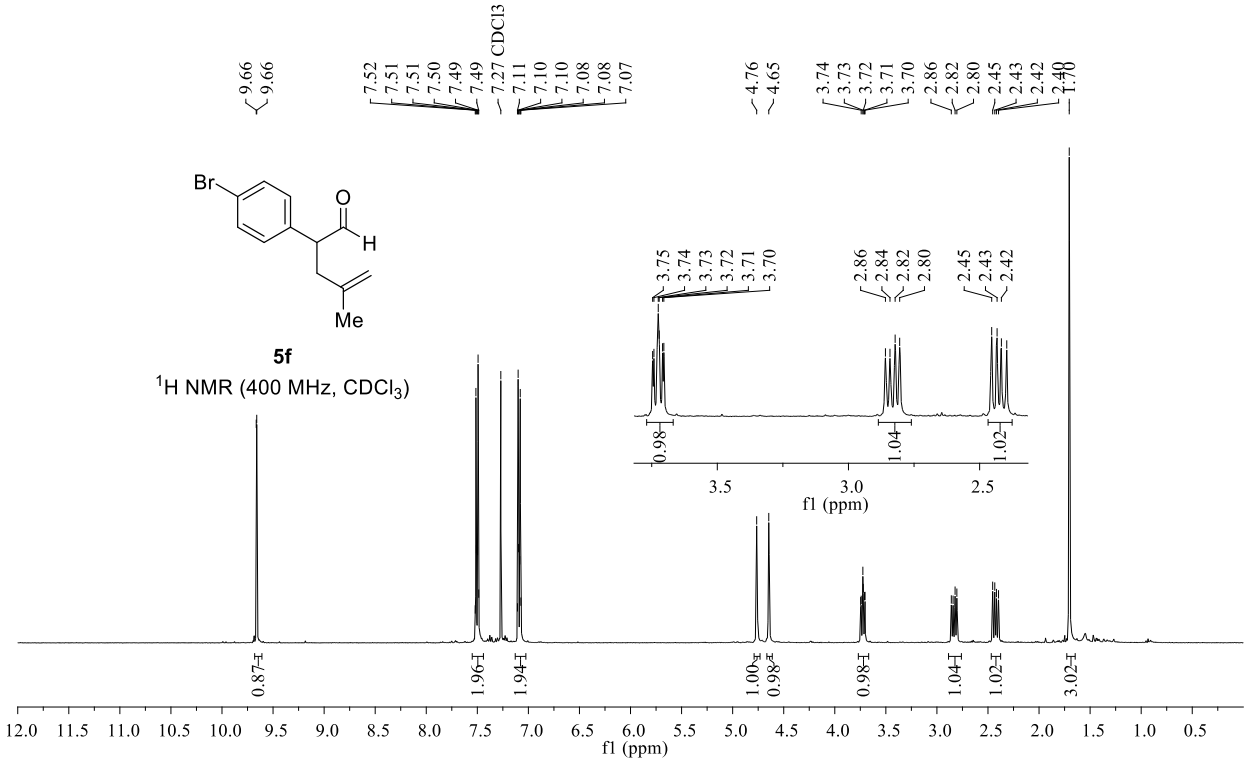

200.15
142.44
137.20
134.69
131.12
128.02
127.62
126.71
112.84
77.16 CDCl3
53.38
37.53
22.89
20.01
O
H
Me
Me
5c
13C NMR (101 MHz, CDCl3)
f1 (ppm)

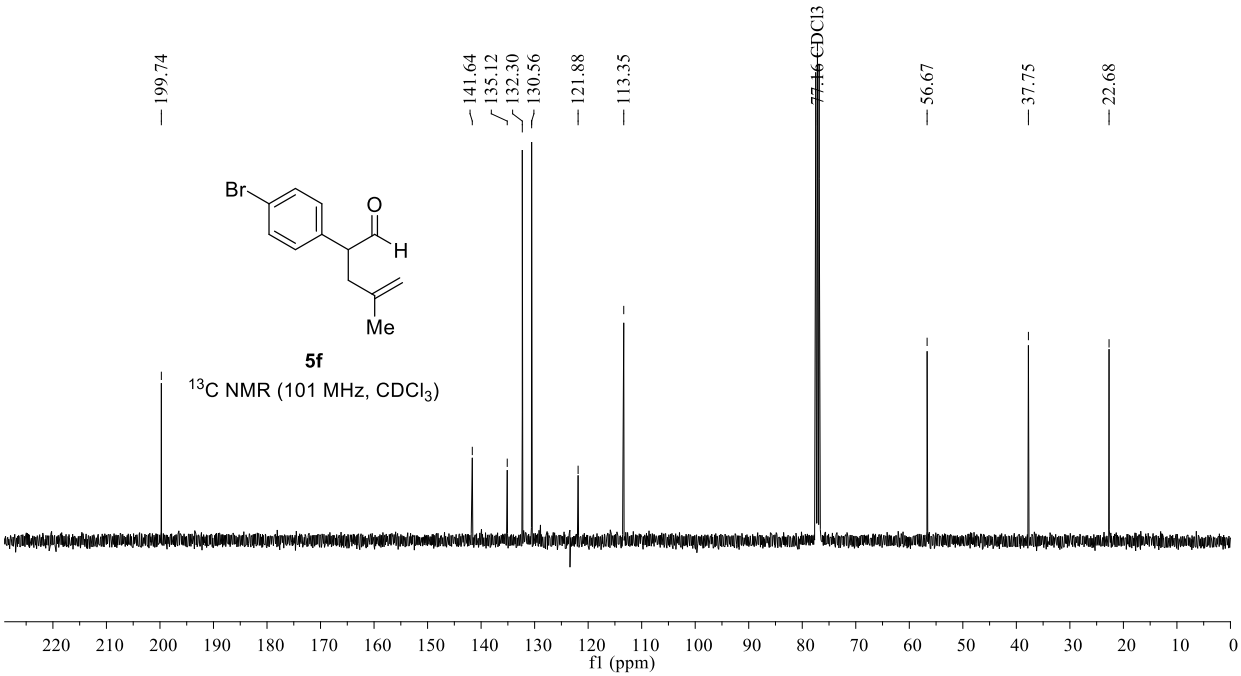

9.77
9.76
7.87
7.85
7.85
7.84
7.84
7.83
7.70
7.54
7.53
7.52
7.51
7.50
7.50
7.49
7.48
7.47
7.35
7.35
7.33
7.33
7.27 CDCl3
4.77
4.71
3.95
3.94
3.93
3.92
3.92
2.99
2.95
2.94
2.61
2.59
2.57
2.55
1.75
O
H
Me
5d
1H NMR (400 MHz, CDCl3)
0.91
3.07
1.00
2.05
0.96
0.95
0.97
0.97
1.01
1.02
3.01
f1 (ppm)

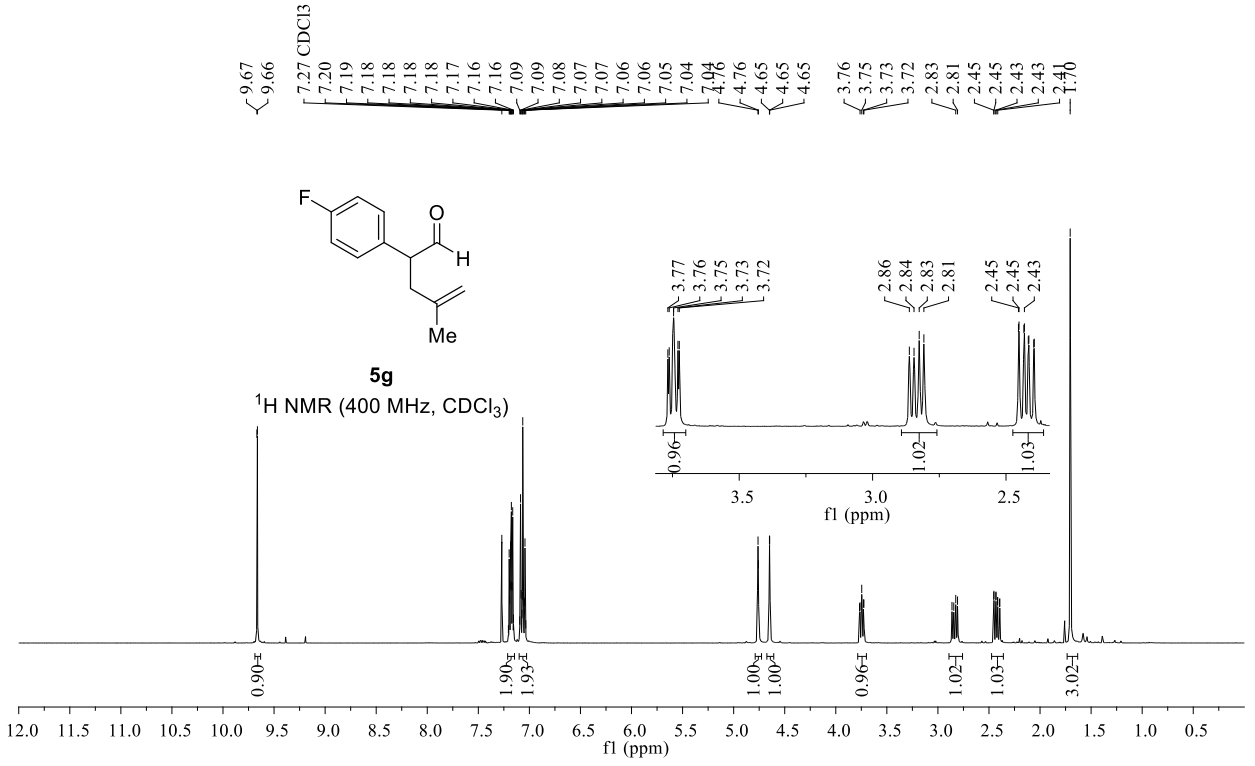

200.26
142.10
128.96
128.03
127.89
127.86
126.55
126.29
113.08
77.16 CDCl3
57.45
37.76
22.80
133.74
133.54
132.90
O
H
Me
5d
13C NMR (101 MHz, CDCl3)
f1 (ppm)

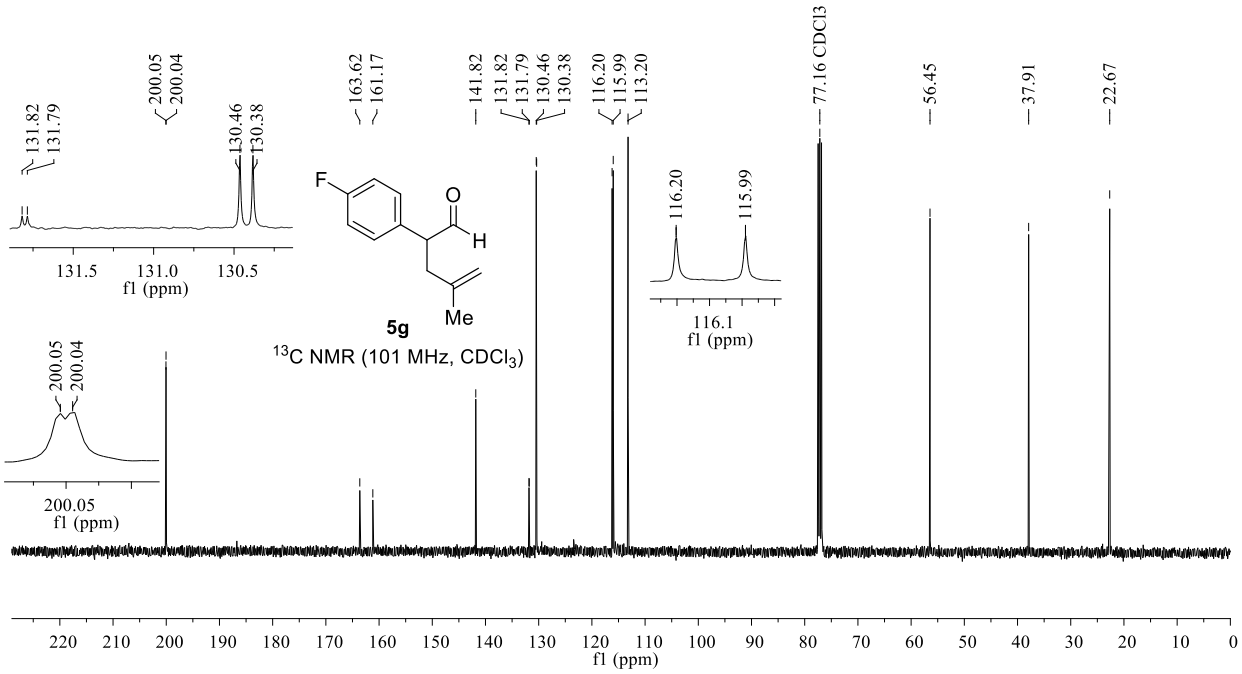

9.67
9.66
7.37
7.36
7.36
7.34
7.34
7.33
7.27 CDCl3
7.17
7.17
7.16
7.15
7.14
7.14
7.14
7.13
4.76
4.76
4.65
3.74
3.74
3.74
3.72
3.72
2.82
2.81
2.46
2.45
2.44
2.43
1.70
Cl
O
H
Me
5e
1H NMR (400 MHz, CDCl3)
f1 (ppm)

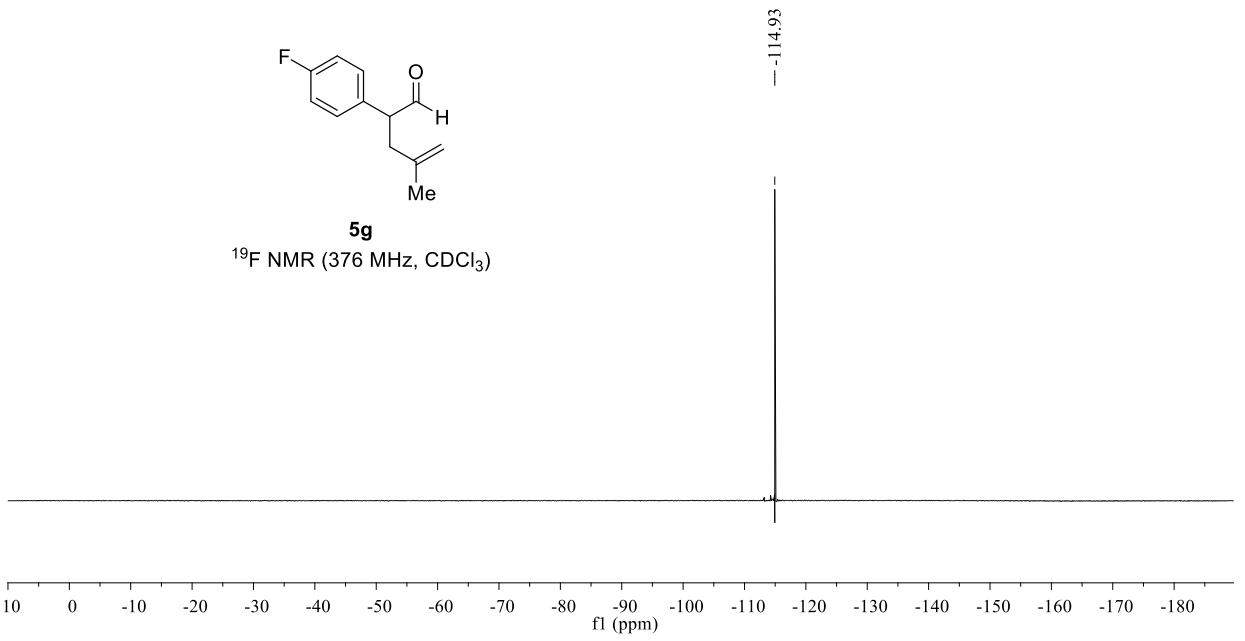

199.83
141.68
134.59
133.78
130.21
129.34
113.32
77.16 CDCl3
56.60
37.79
22.68
Cl
O
H
Me
5e
13C NMR (101 MHz, CDCl3)
f1 (ppm)

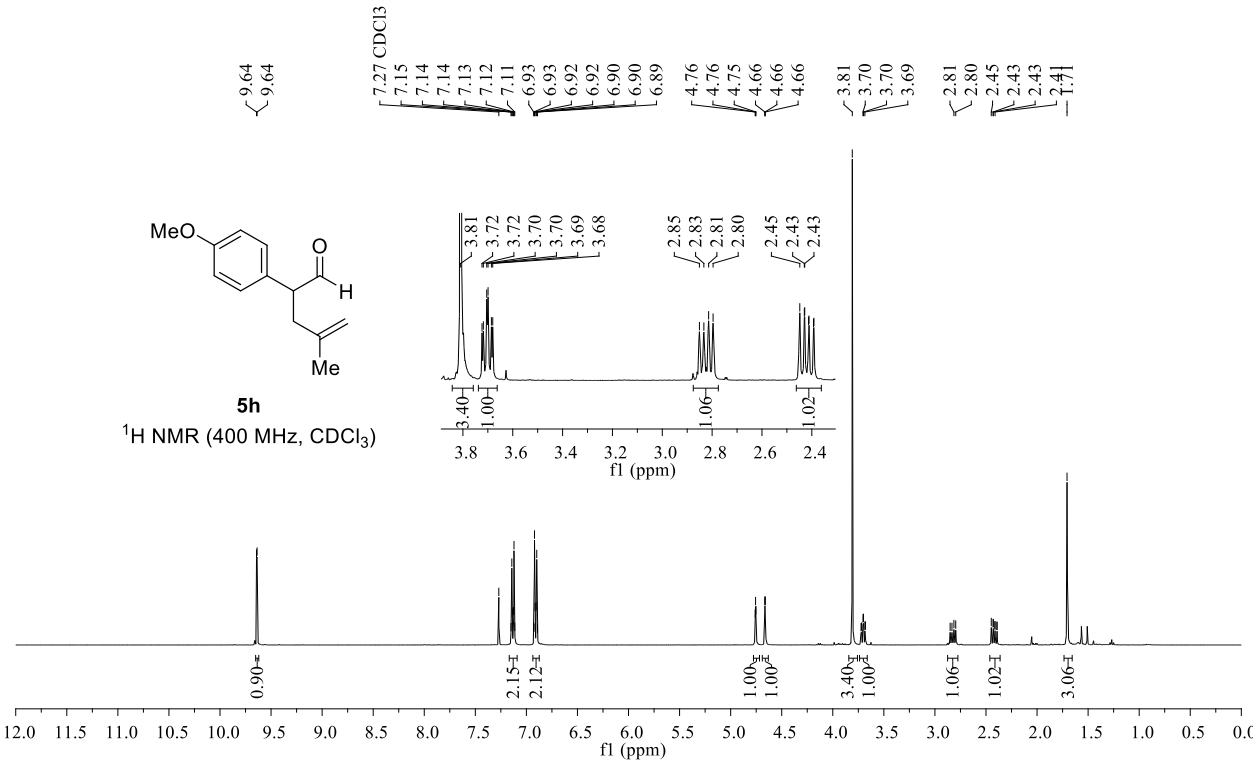

9.66
9.66
7.52
7.51
7.51
7.50
7.49
7.49
7.27 CDCl3
7.11
7.10
7.10
7.08
7.08
7.07
4.76
4.65
3.74
3.73
3.72
3.71
3.70
2.86
2.82
2.80
2.45
2.43
2.42
1.70
Br
O
H
Me
5f
1H NMR (400 MHz, CDCl3)
0.98
1.04
1.02
f1 (ppm)
0.87
1.96
1.94
1.00
0.98
0.98
1.04
1.02
3.02
f1 (ppm)

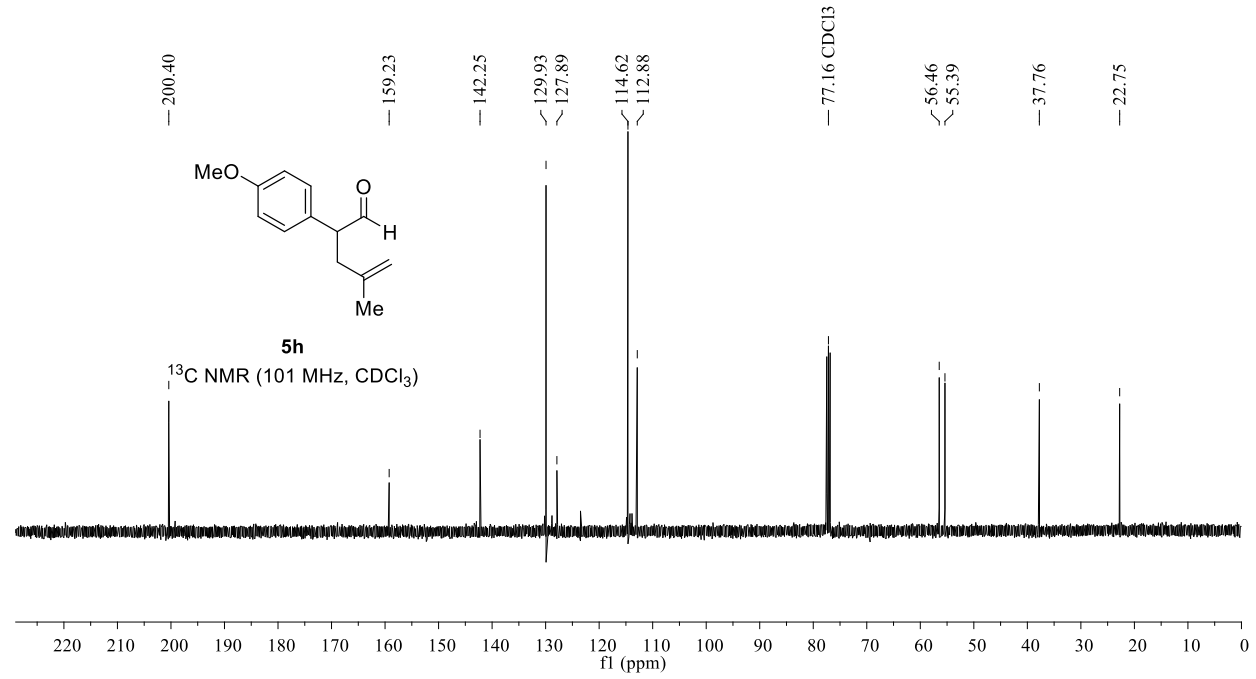

199.74
141.64
135.12
132.30
130.56
121.88
113.35
77.16 CDCl3
56.67
37.75
22.68
Br
O
H
Me
5f
13C NMR (101 MHz, CDCl3)
f1 (ppm)

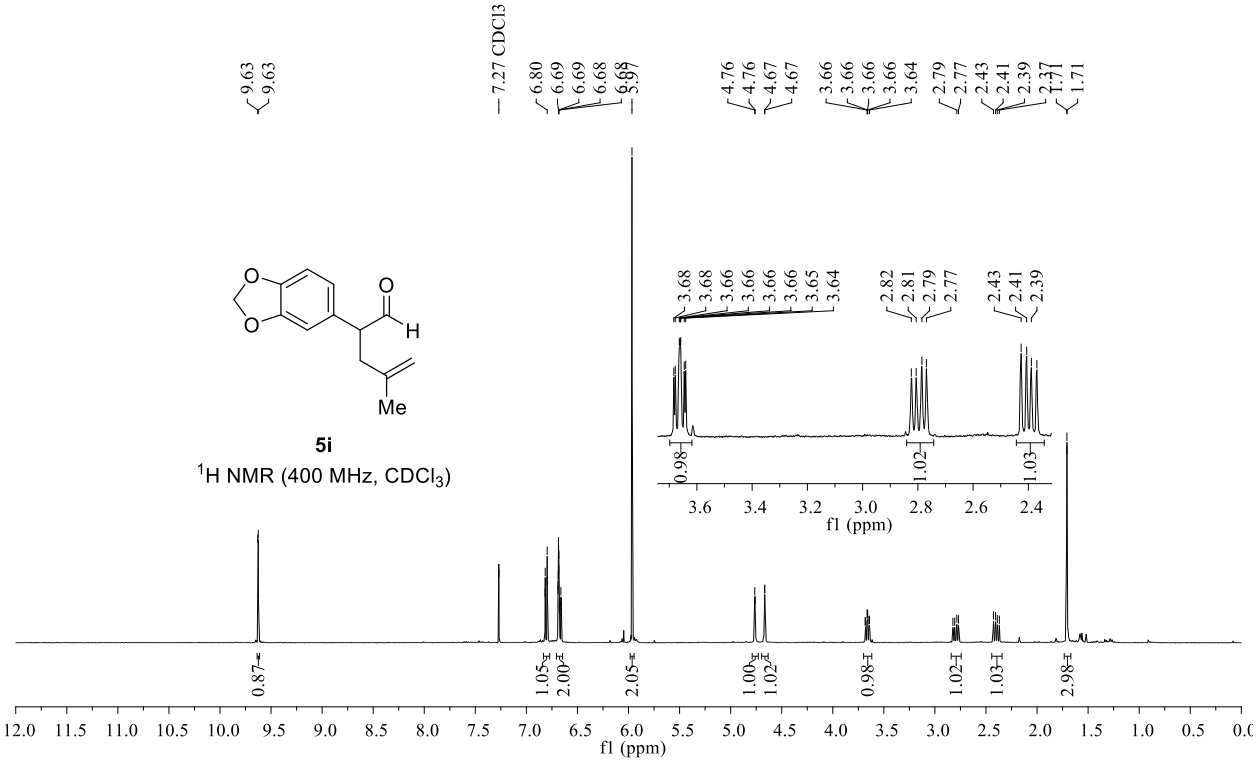

9.67
9.66
7.27 CDCl3
7.20
7.19
7.18
7.18
7.18
7.18
7.17
7.16
7.16
7.09
7.09
7.08
7.07
7.07
7.06
7.06
7.05
7.04
4.76
4.65
4.65
4.65
3.76
3.75
3.73
3.72
2.83
2.81
2.45
2.45
2.43
2.43
1.70
F
O
H
Me
5g
1H NMR (400 MHz, CDCl3)
3.77
3.76
3.75
3.73
3.72
2.86
2.84
2.83
2.81
2.45
2.45
2.43
0.96
1.02
1.03
f1 (ppm)
0.90
1.90
1.93
1.00
1.00
0.96
1.02
1.03
3.02
f1 (ppm)

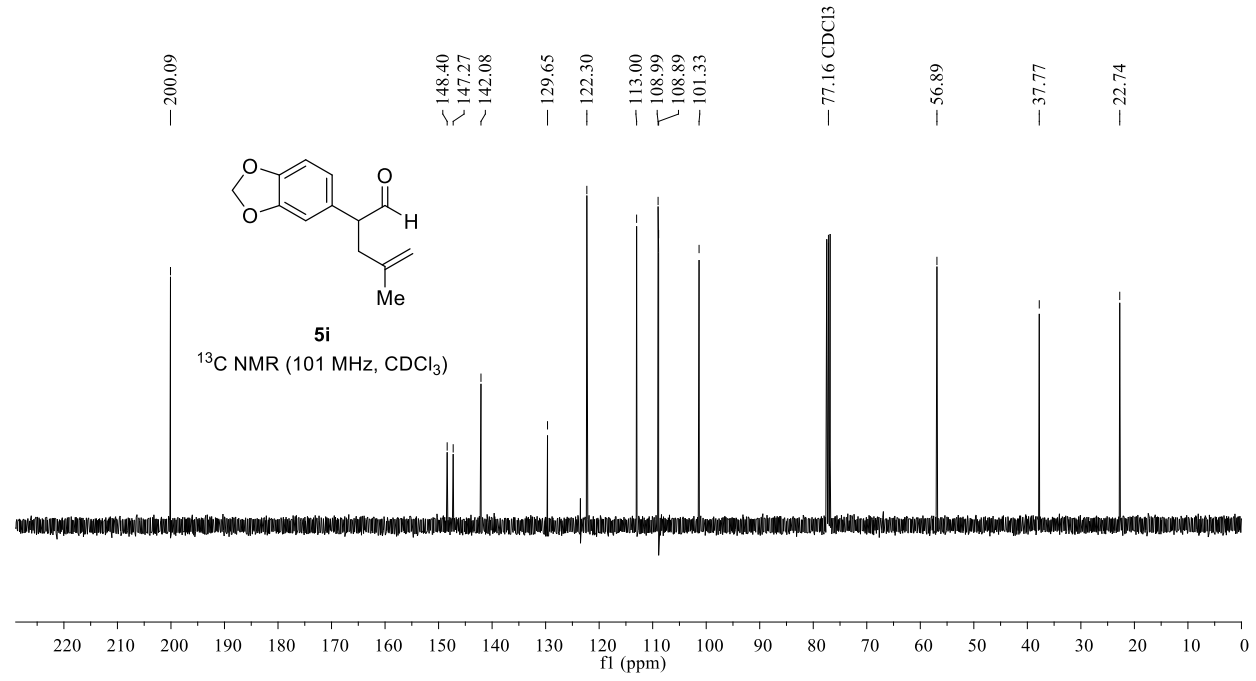

131.82
131.79
200.05
200.04
130.46
130.38
131.5
131.0
130.5
f1 (ppm)
163.62
161.17
141.82
131.82
131.79
130.46
130.38
116.20
115.99
113.20
77.16 CDCl3
56.45
37.91
22.67
F
O
H
Me
5g
13C NMR (101 MHz, CDCl3)
116.20
115.99
116.1
f1 (ppm)
200.05
200.04
200.05
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

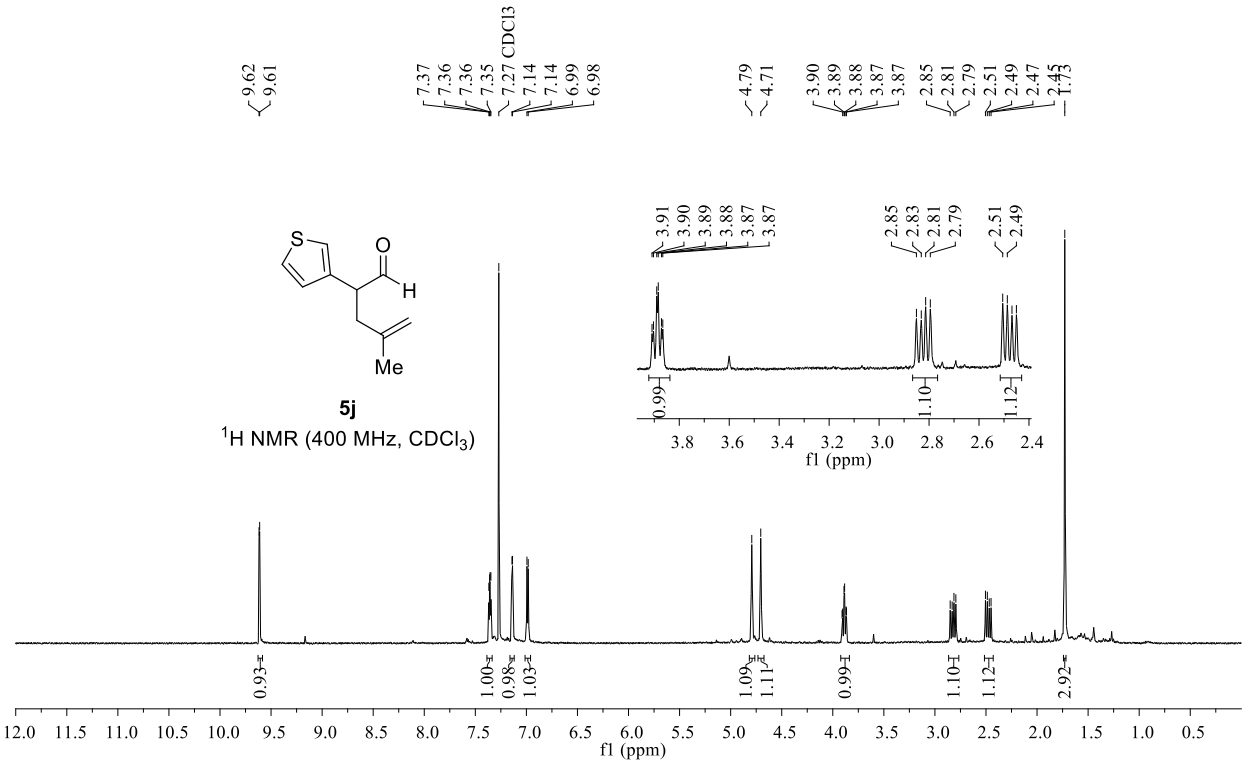

F
O
H
Me
5g
19F NMR (376 MHz, CDCl3)
-114.93
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

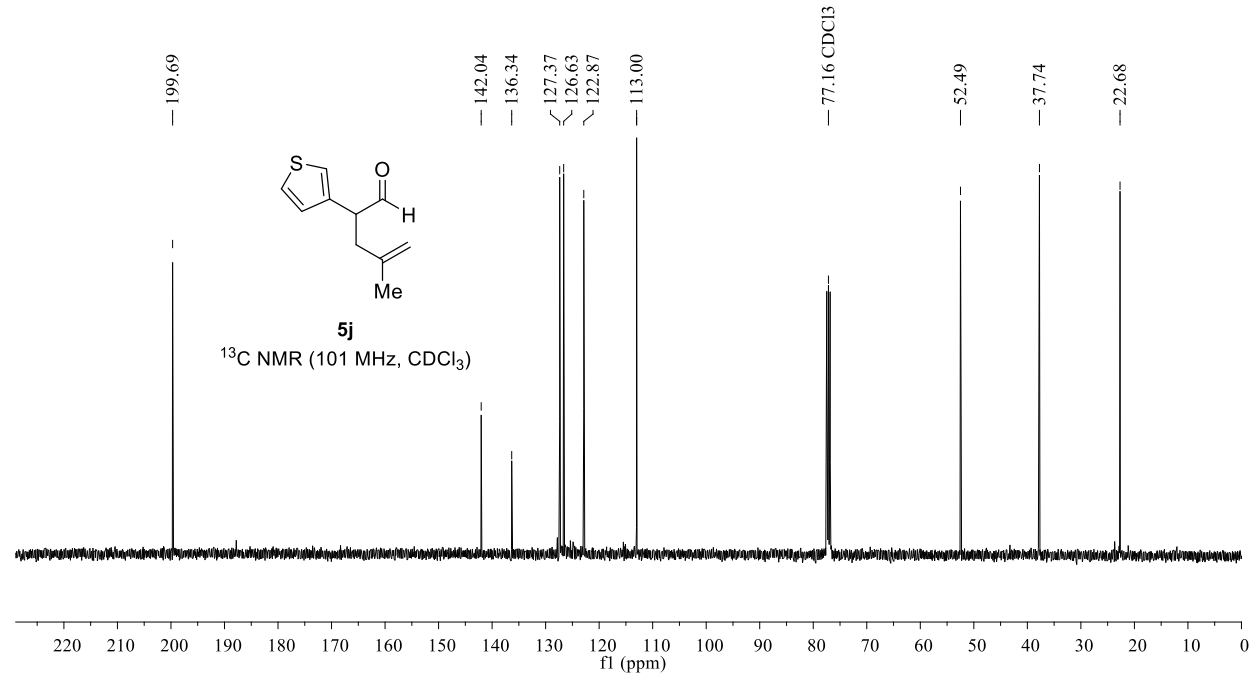

MeO
O
H
Me
5h
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

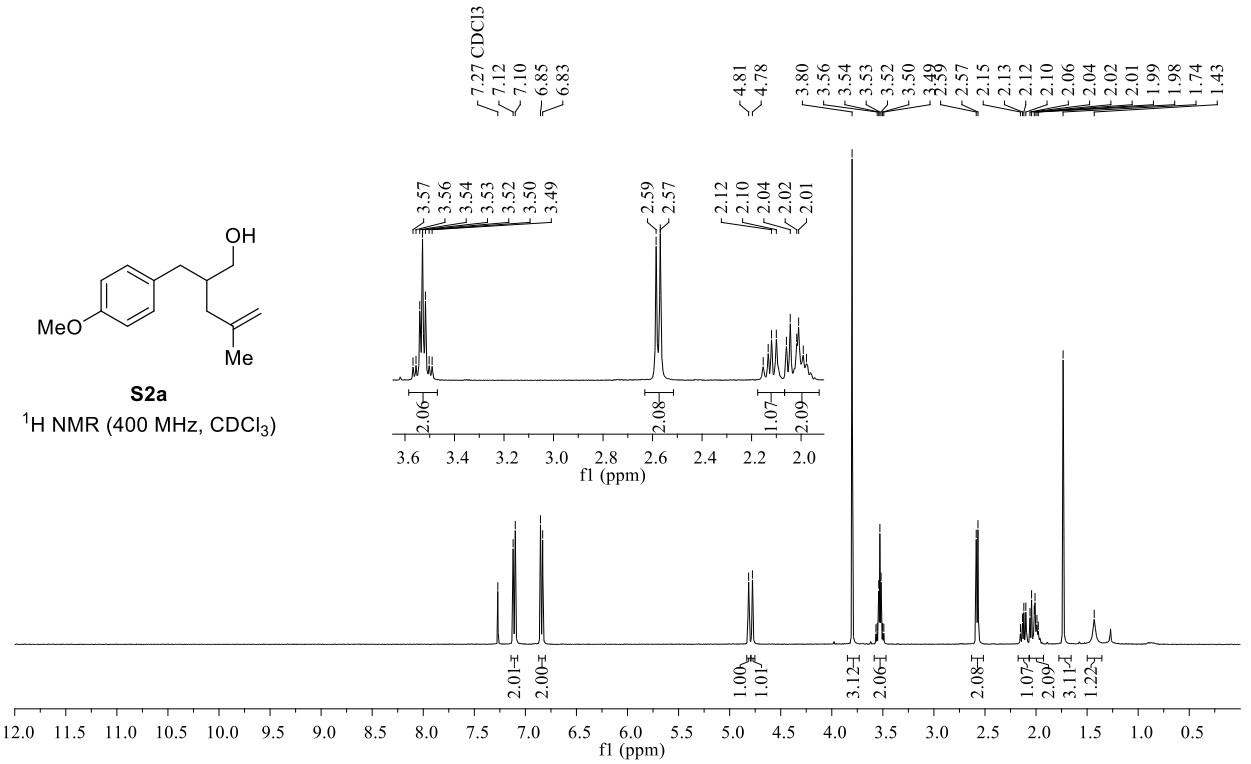

MeO
O
H
Me
5h
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

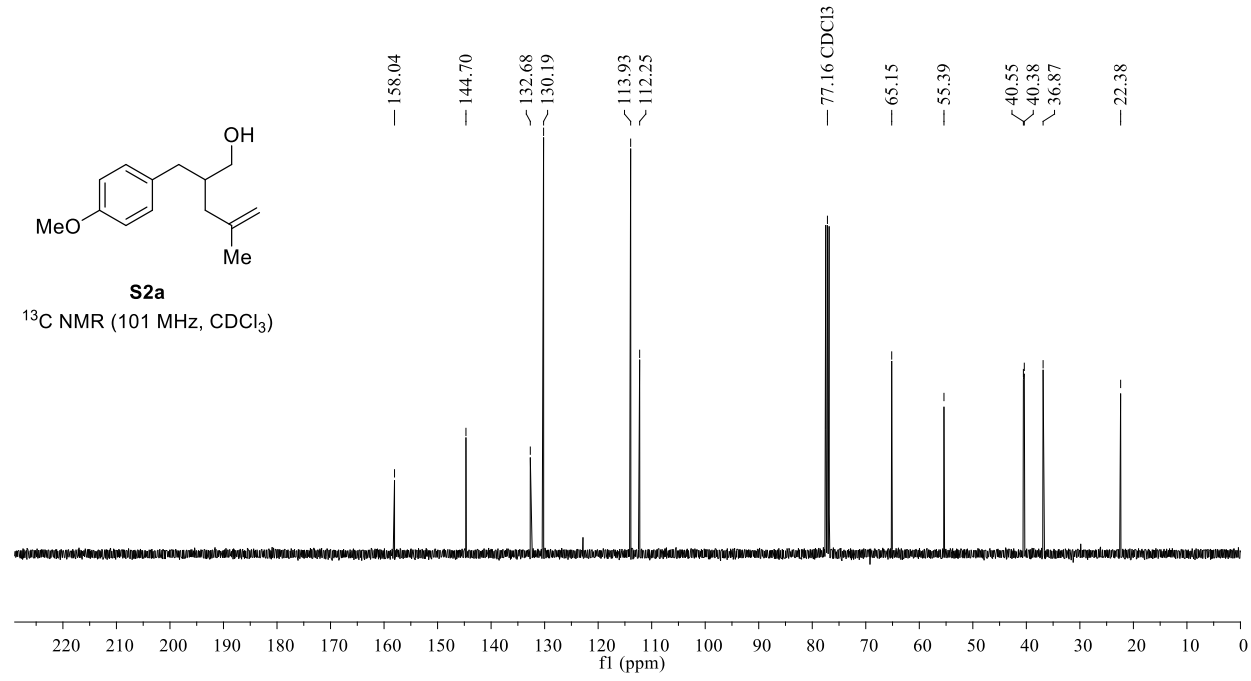

9.63
9.63
7.27 CDCl3
6.80
6.69
6.69
6.68
6.68
3.97
4.76
4.76
4.67
4.67
3.66
3.66
3.66
3.66
3.64
2.79
2.77
2.43
2.41
2.39
2.37
1.71
1.71
O
O
O
H
Me
5i
1H NMR (400 MHz, CDCl3)
3.68
3.68
3.66
3.66
3.66
3.66
3.65
3.64
2.82
2.81
2.79
2.77
2.43
2.41
2.39
0.98
1.02
1.03
3.6 3.4 3.2 3.0 2.8 2.6 2.4
f1 (ppm)
0.87
1.05
2.00
2.05
1.00
1.02
0.98
1.02
1.03
2.98
12.0 11.5 11.0 10.5 10.0 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)

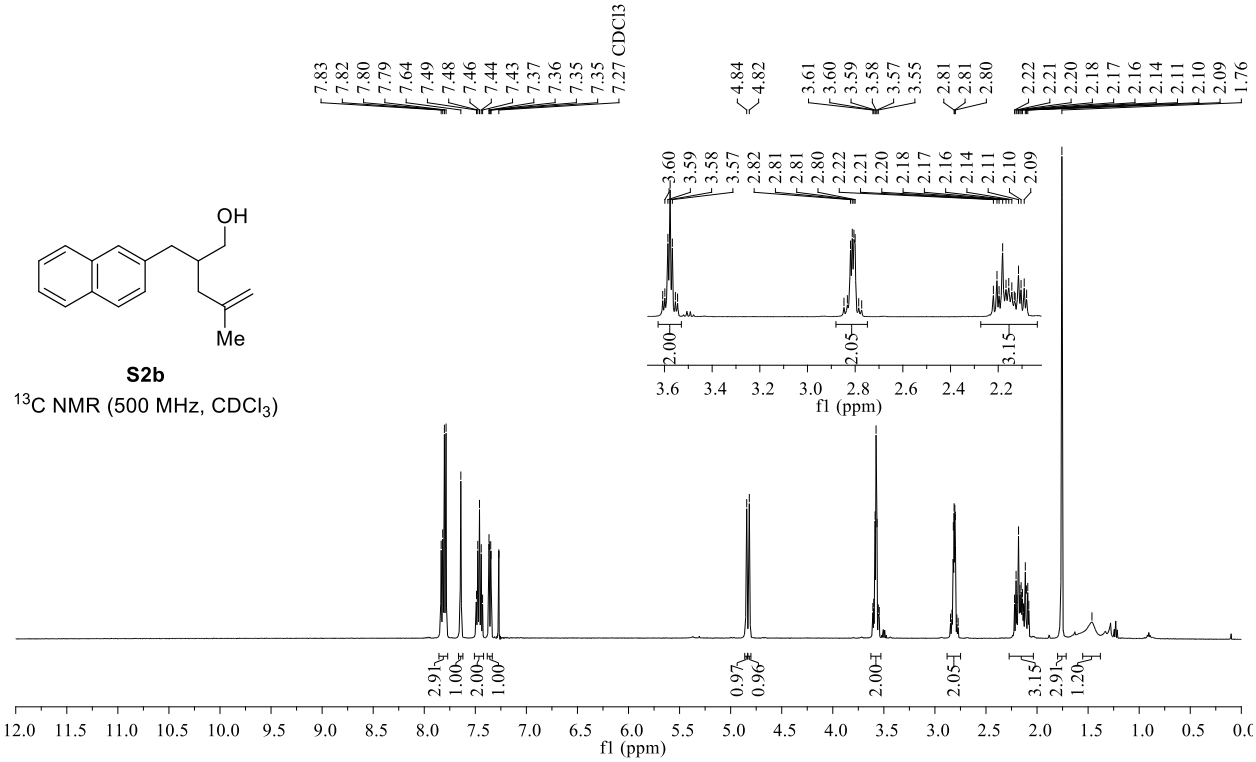

200.09
148.40
147.27
142.08
129.65
122.30
113.00
108.99
108.89
101.33
77.16 CDCl3
56.89
37.77
22.74
O
O
O
H
Me
5i
13C NMR (101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

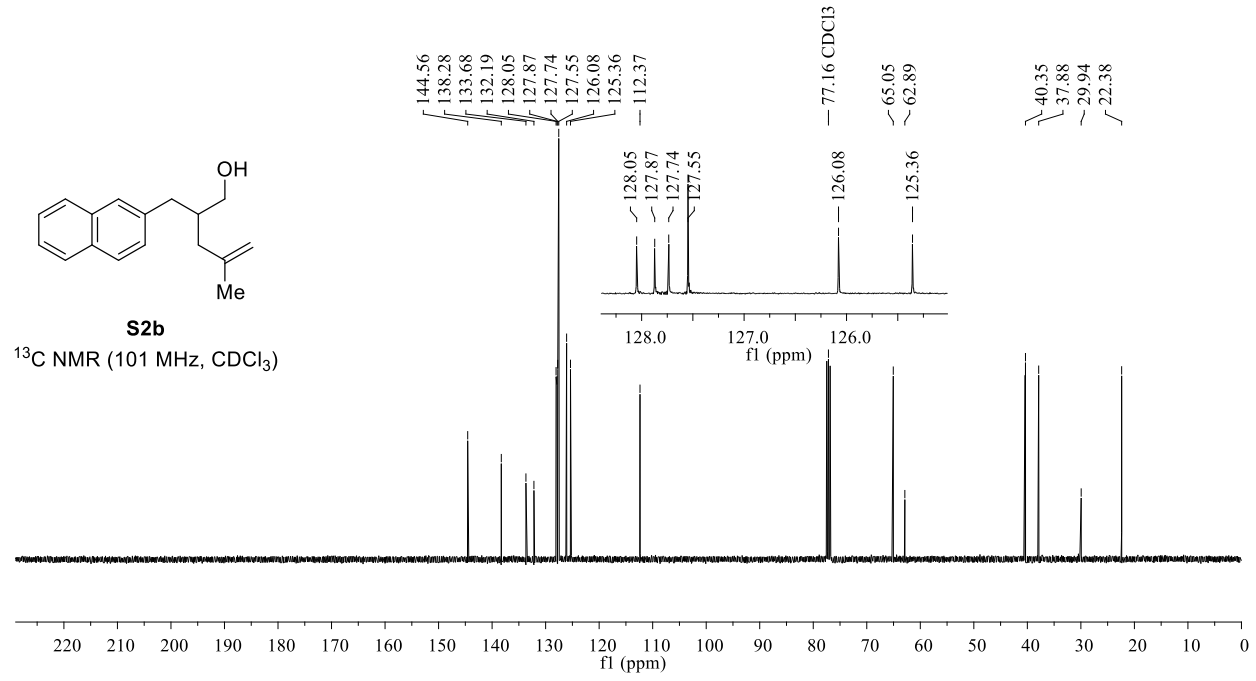

9.62
9.61
7.37
7.36
7.36
7.35
7.27 CDCl3
7.14
7.14
6.99
6.98
4.79
4.71
3.90
3.89
3.88
3.87
3.87
2.85
2.81
2.79
2.51
2.49
2.47
1.73
S
O
H
Me
5j
1H NMR (400 MHz, CDCl3)
0.93
1.00
0.98
1.03
1.09
1.11
0.99
1.10
1.12
2.92
fl (ppm)

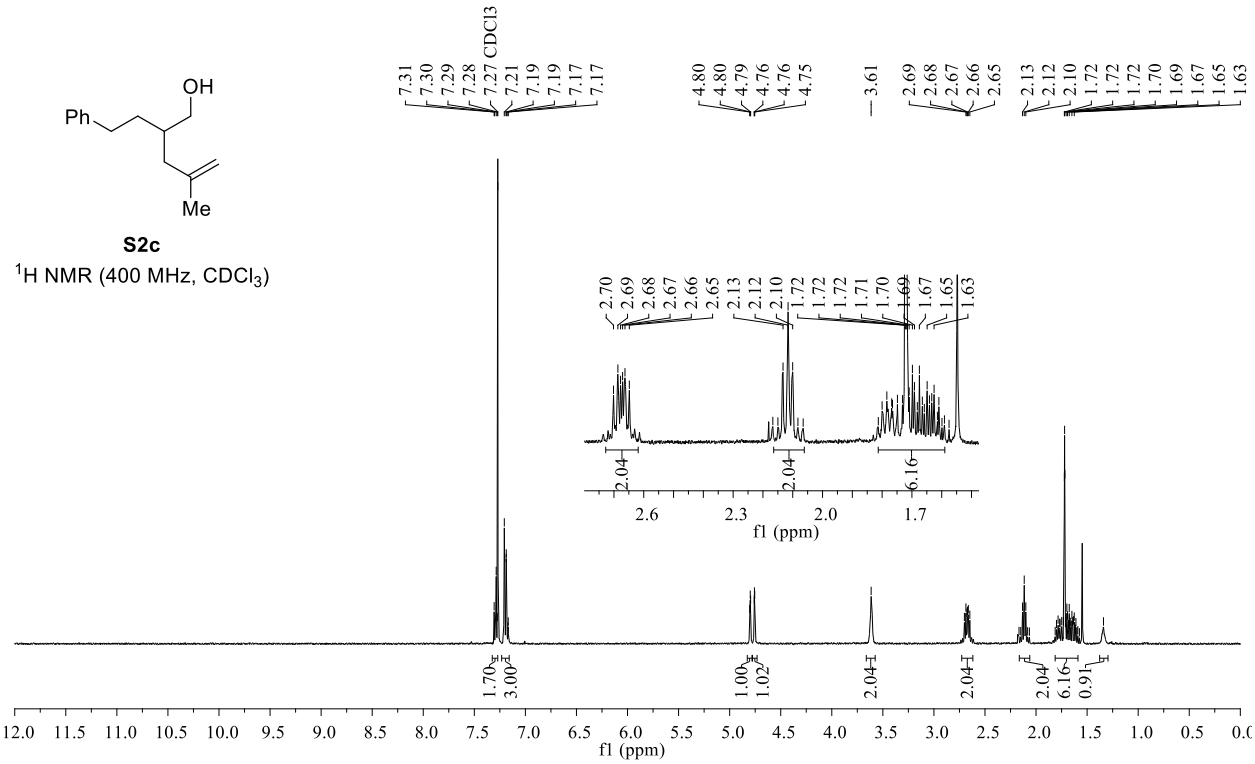

199.69
142.04
136.34
127.37
126.63
122.87
113.00
77.16 CDCl3
52.49
37.74
22.68
S
O
H
Me
5j
13C NMR (101 MHz, CDCl3)
fl (ppm)


OH
MeO
Me
S2a
1H NMR (400 MHz, CDCl3)
7.27 CDCl3
7.12
7.10
6.85
6.83
4.81
4.78
3.80
3.56
3.54
3.53
3.52
3.50
2.59
2.57
2.15
2.13
2.12
2.10
2.06
2.04
2.02
2.01
1.99
1.98
1.74
1.43
2.06
2.08
1.07
2.09
2.01
2.00
1.00
1.01
3.12
2.06
2.08
1.07
2.09
3.11
1.22
fl (ppm)


OH
MeO
Me
S2a
13C NMR (101 MHz, CDCl3)
158.04
144.70
132.68
130.19
113.93
112.25
77.16 CDCl3
65.15
55.39
40.55
40.38
36.87
22.38
fl (ppm)

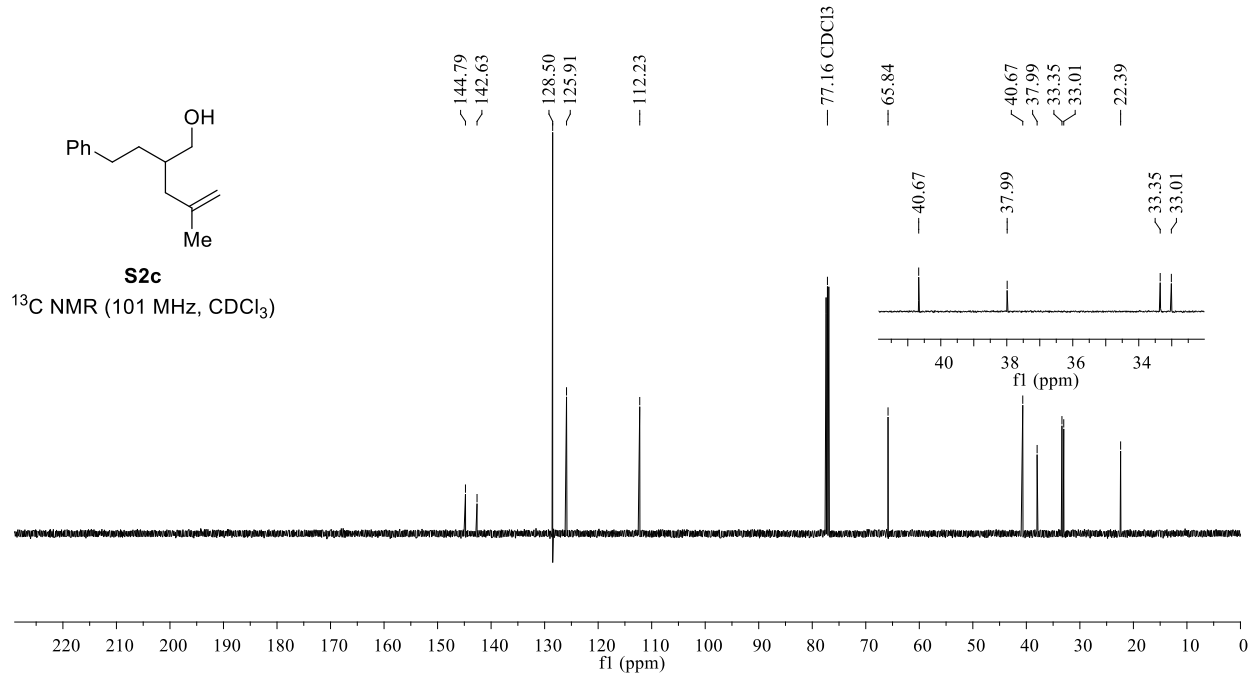

OH
Me
S2b
13C NMR (500 MHz, CDCl3)
f1 (ppm)


OH
Me
S2b
13C NMR (101 MHz, CDCl3)
f1 (ppm)



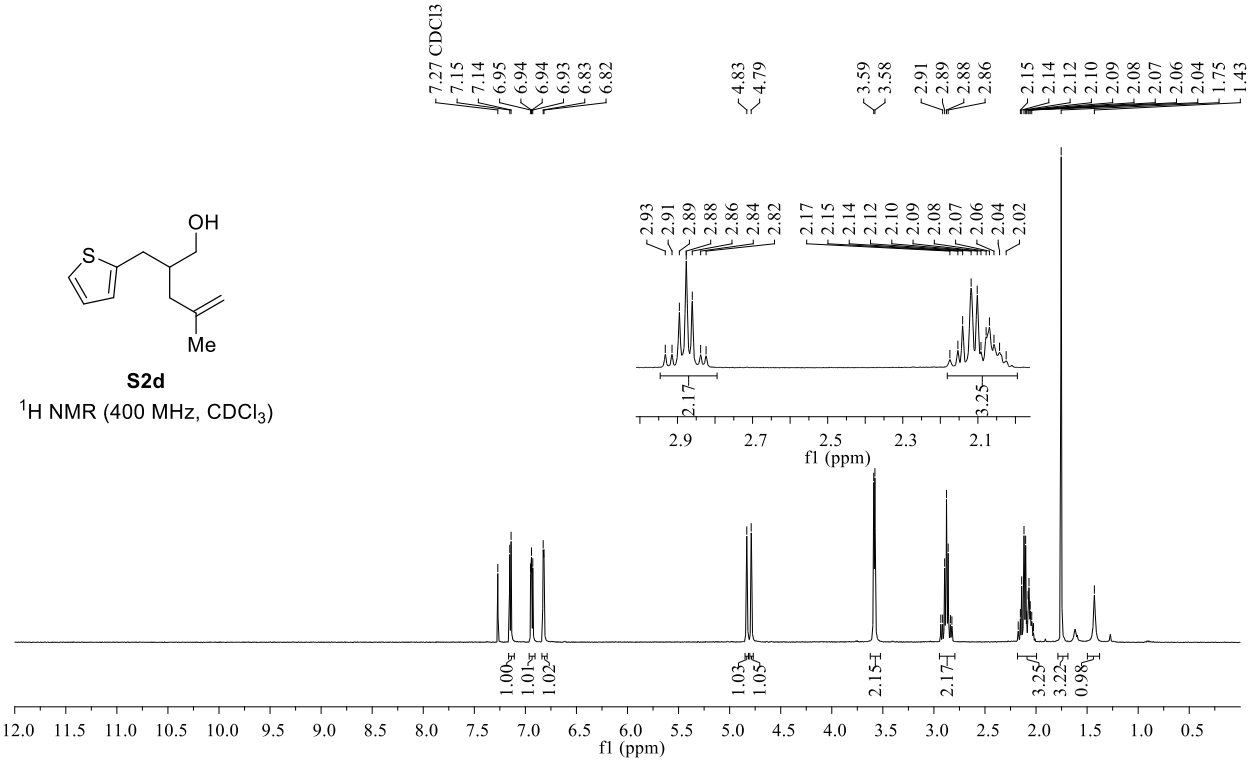
S2c

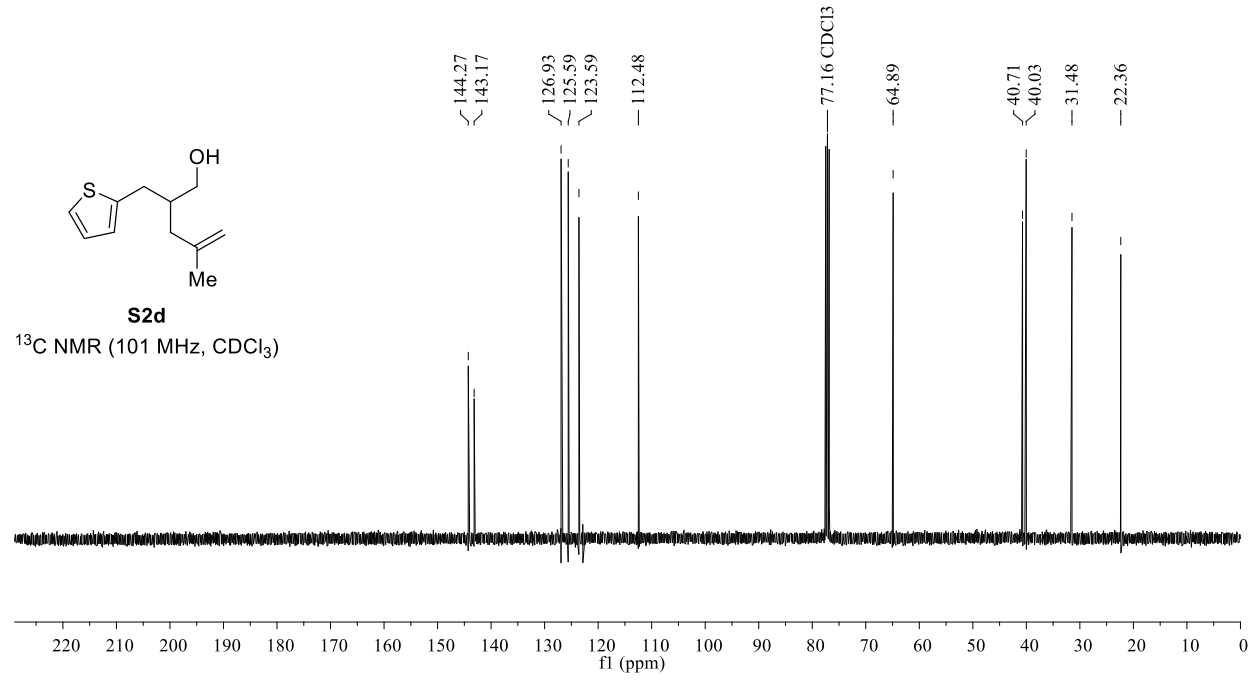
^{1}H NMR (400 MHz, $CDCl_3$)

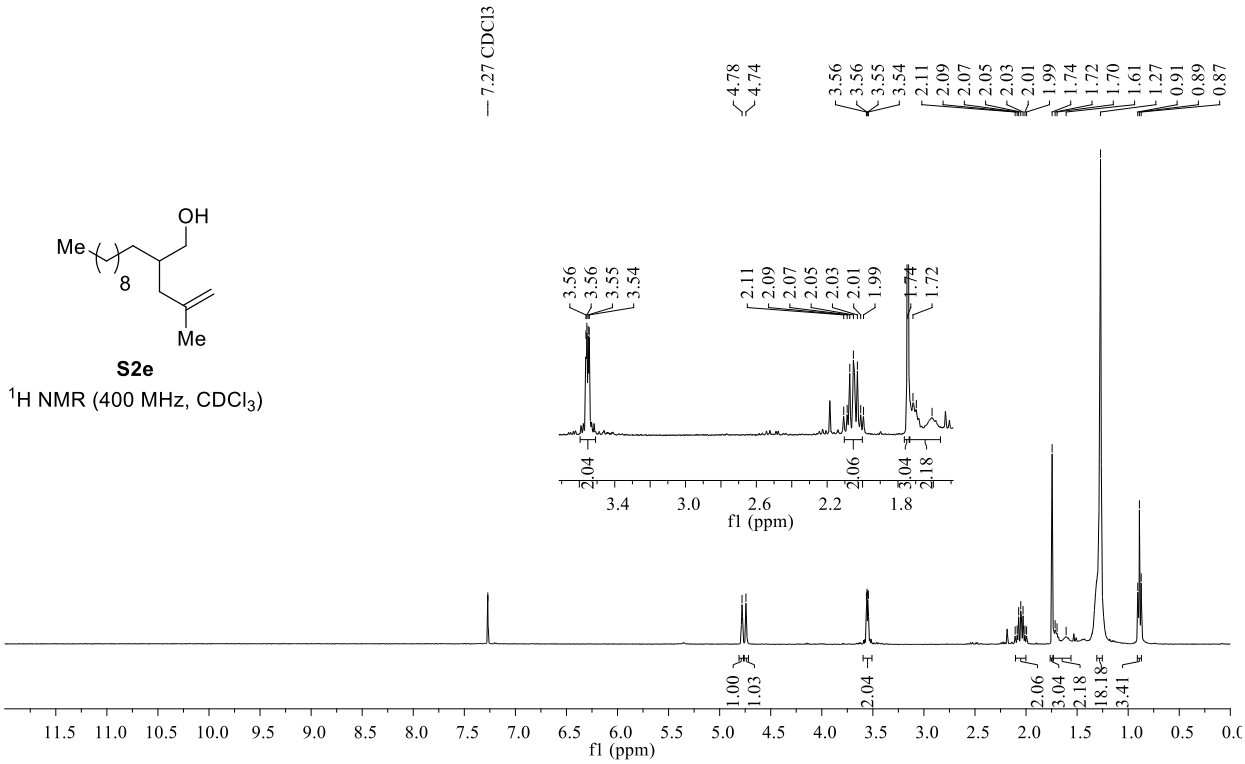


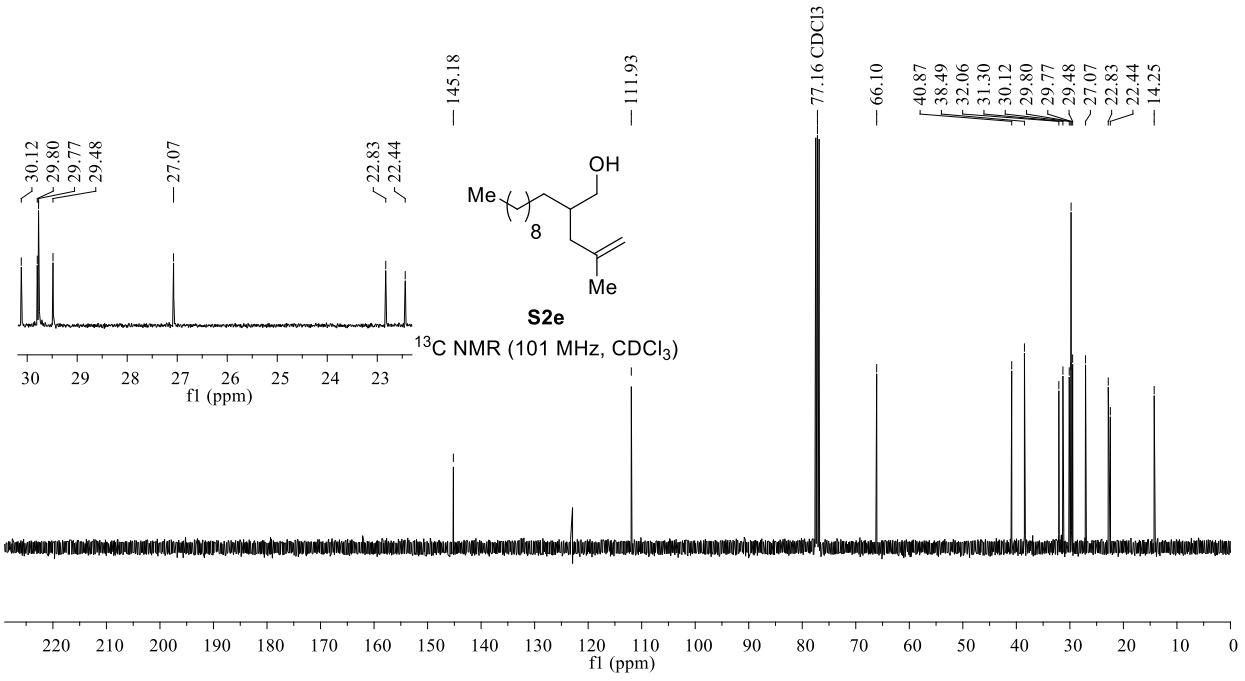
S2c

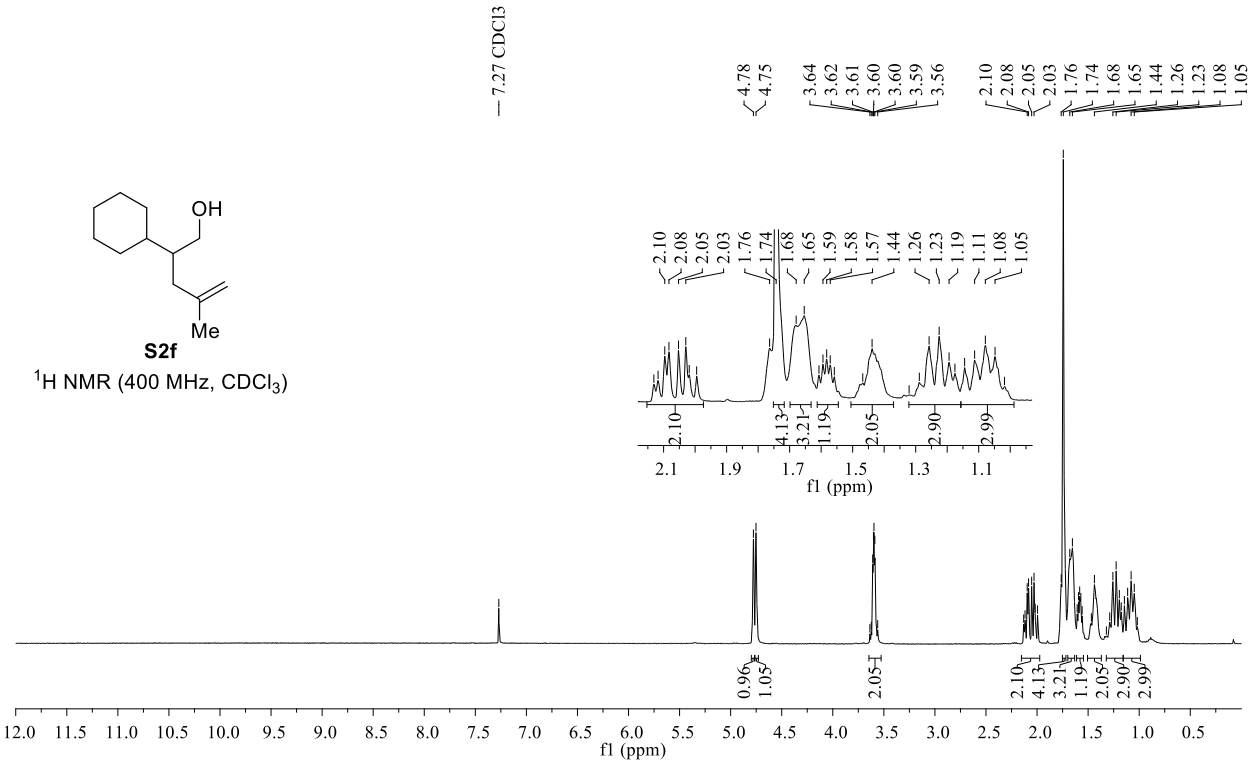
^{13}C NMR (101 MHz, $CDCl_3$)

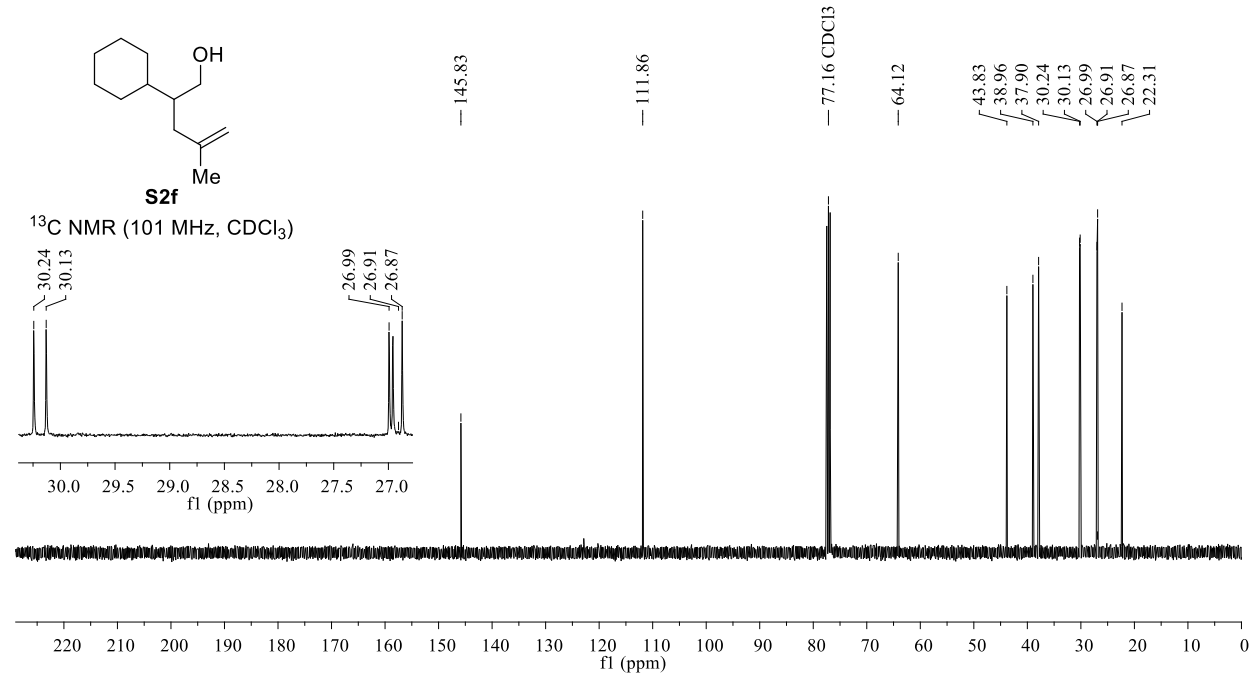

OH
S
Me
S2d
1H NMR (400 MHz, CDCl3)
7.27 CDCl3
7.15
7.14
6.95
6.94
6.94
6.93
6.83
6.82
4.83
4.79
3.59
3.58
2.91
2.89
2.88
2.86
2.15
2.14
2.12
2.10
2.09
2.08
2.07
2.06
2.04
1.75
1.43
2.93
2.91
2.89
2.88
2.86
2.84
2.82
2.17
2.15
2.14
2.12
2.10
2.09
2.08
2.07
2.06
2.04
2.02
2.17
3.25
2.9
2.7
2.5
2.3
2.1
f1 (ppm)
1.00
1.01
1.02
1.03
1.05
2.15
2.17
3.25
3.22
0.98
12.0 11.5 11.0 10.5 10.0 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
f1 (ppm)

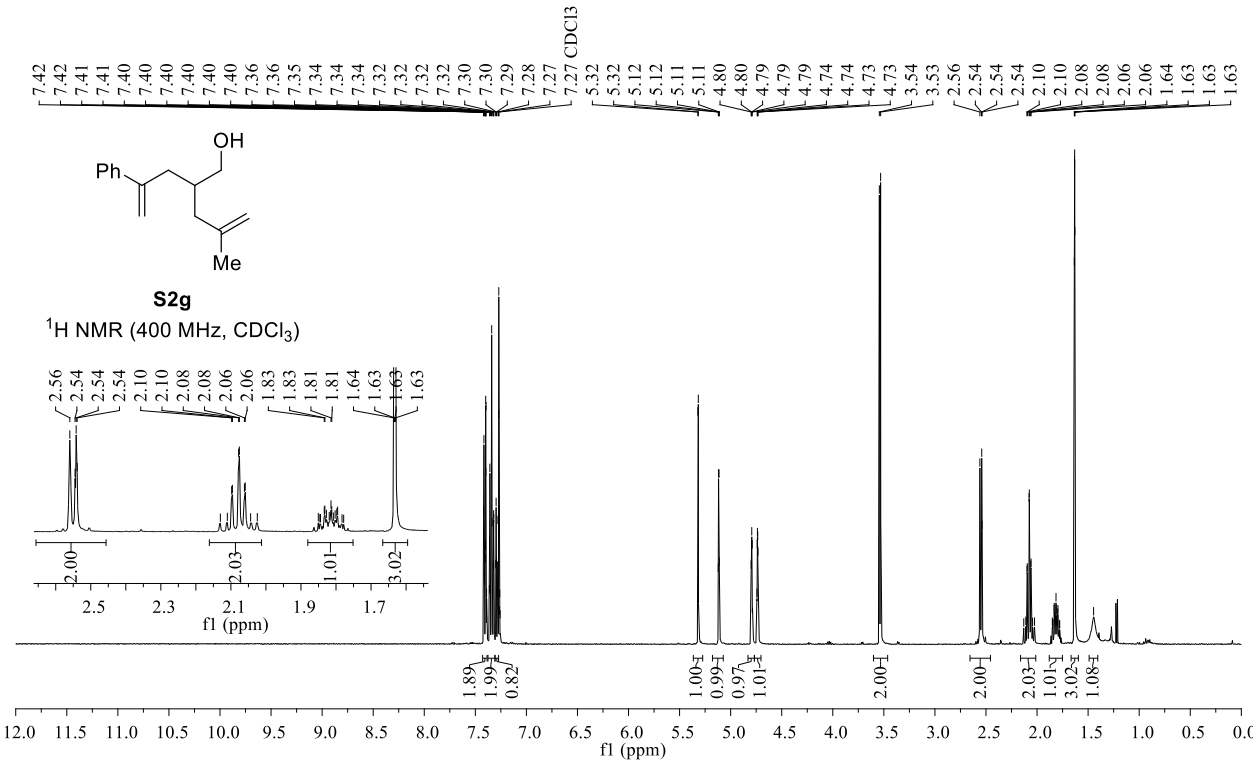

OH
S
Me
S2d
13C NMR (101 MHz, CDCl3)
144.27
143.17
126.93
125.59
123.59
112.48
77.16 CDCl3
64.89
40.71
40.03
31.48
22.36
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

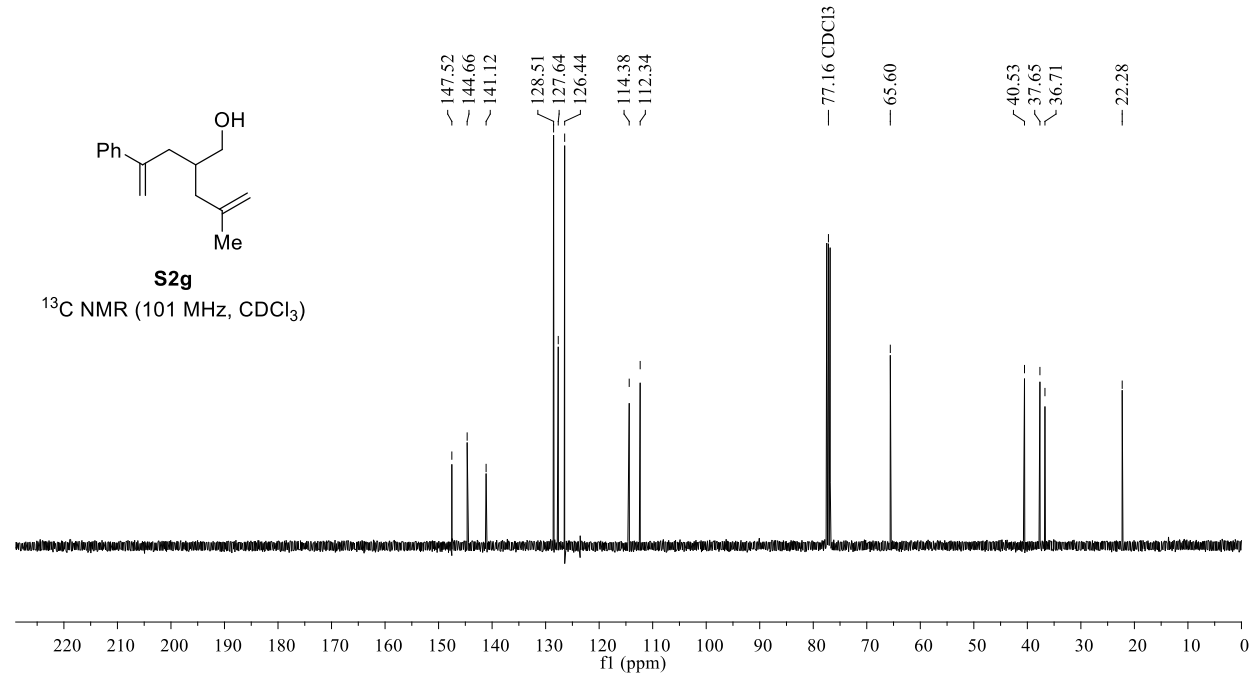

7.27 CDCl3
4.78
4.74
3.56
3.56
3.55
3.54
2.11
2.09
2.07
2.05
2.03
2.01
1.99
1.74
1.72
1.70
1.61
1.27
0.91
0.89
0.87
OH
Me
8
Me
S2e
1H NMR (400 MHz, CDCl3)
2.04
2.06
3.04
2.18
fl (ppm)
1.00
1.03
2.04
2.06
3.04
2.18
18.18
3.41
fl (ppm)

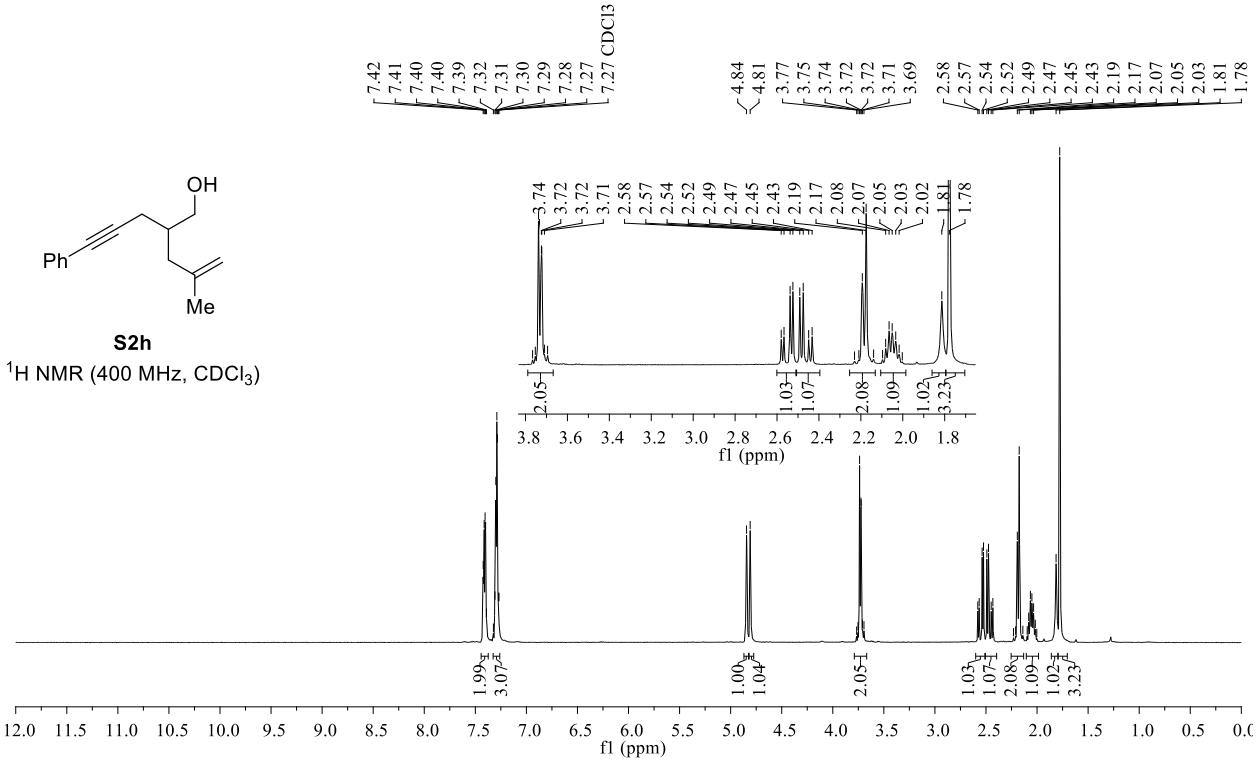

145.18
111.93
77.16 CDCl3
66.10
40.87
38.49
32.06
31.30
30.12
29.80
29.77
29.48
27.07
22.83
22.44
14.25
30.12
29.80
29.77
29.48
27.07
22.83
22.44
OH
Me
8
Me
S2e
13C NMR (101 MHz, CDCl3)
fl (ppm)
fl (ppm)


OH
Me
S2f
^{1}H NMR (400 MHz, $CDCl_3$)
7.27 CDCl3
4.78
4.75
3.64
3.62
3.61
3.60
3.59
3.56
2.10
2.08
2.05
2.03
1.76
1.74
1.68
1.65
1.59
1.58
1.57
1.44
1.26
1.23
1.19
1.11
1.08
1.05
0.96
1.05
2.05
2.10
4.13
3.21
1.19
2.05
2.90
2.99
f1 (ppm)


OH
Me
S2f
^{13}C NMR (101 MHz, $CDCl_3$)
145.83
111.86
77.16 CDCl3
64.12
43.83
38.96
37.90
30.24
30.13
26.99
26.91
26.87
22.31
f1 (ppm)

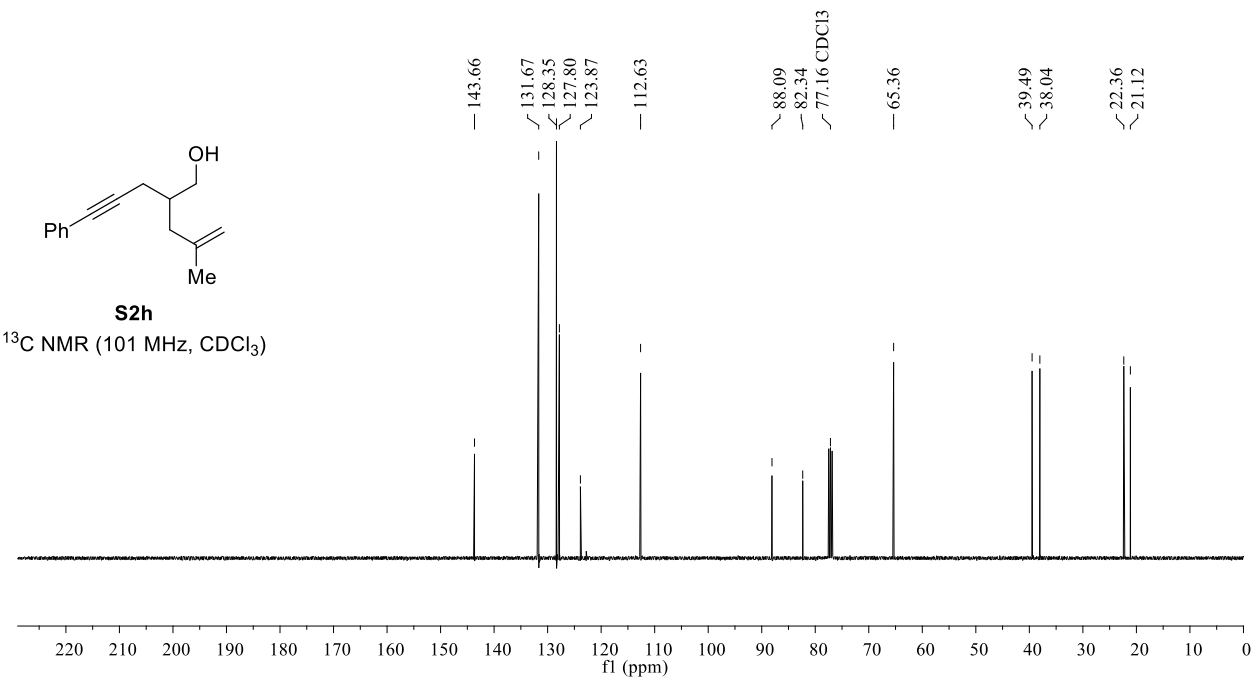

OH
Ph
Me
S2g
1H NMR (400 MHz, CDCl3)
7.27 CDCl3
f1 (ppm)


OH
Ph
Me
S2g
13C NMR (101 MHz, CDCl3)
77.16 CDCl3
f1 (ppm)



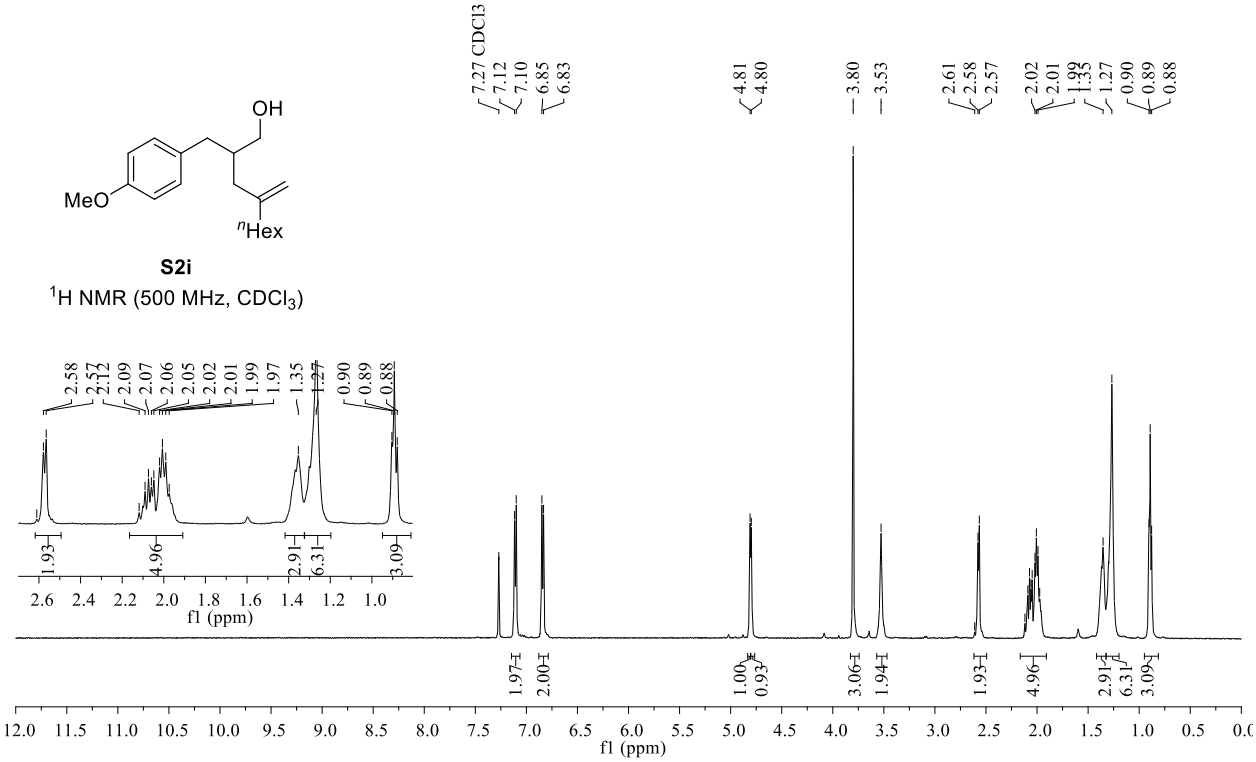
S2h

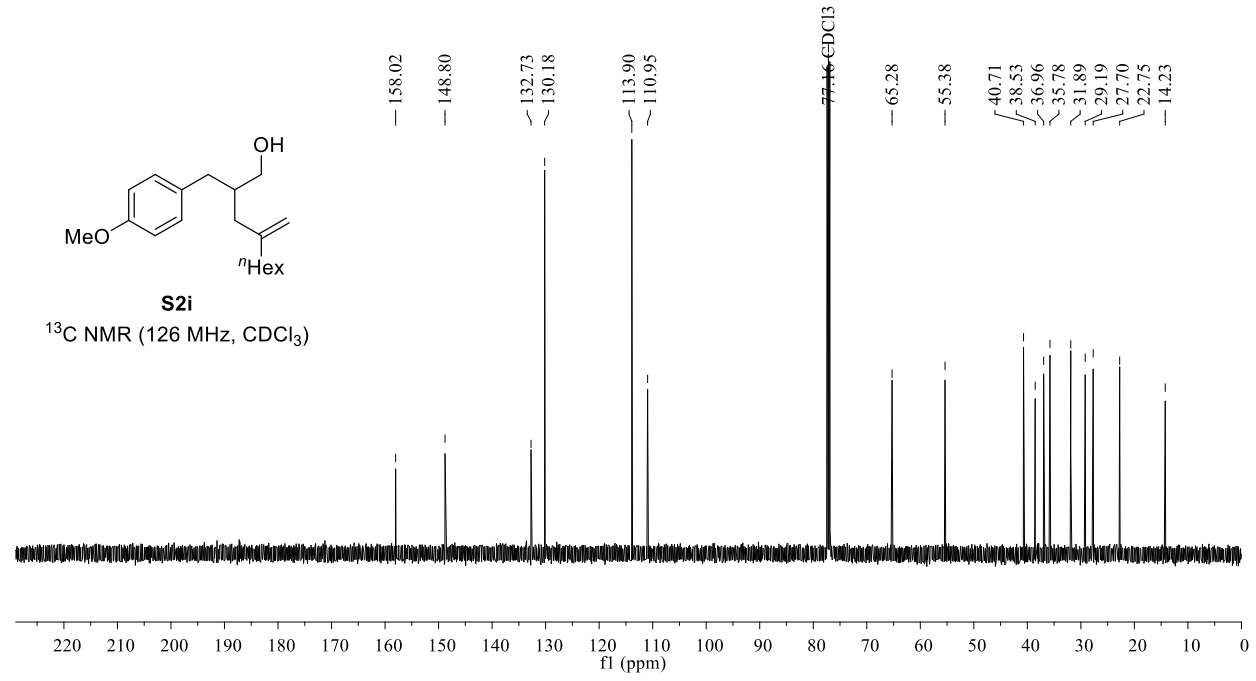
^{1}H NMR (400 MHz, $CDCl_3$)

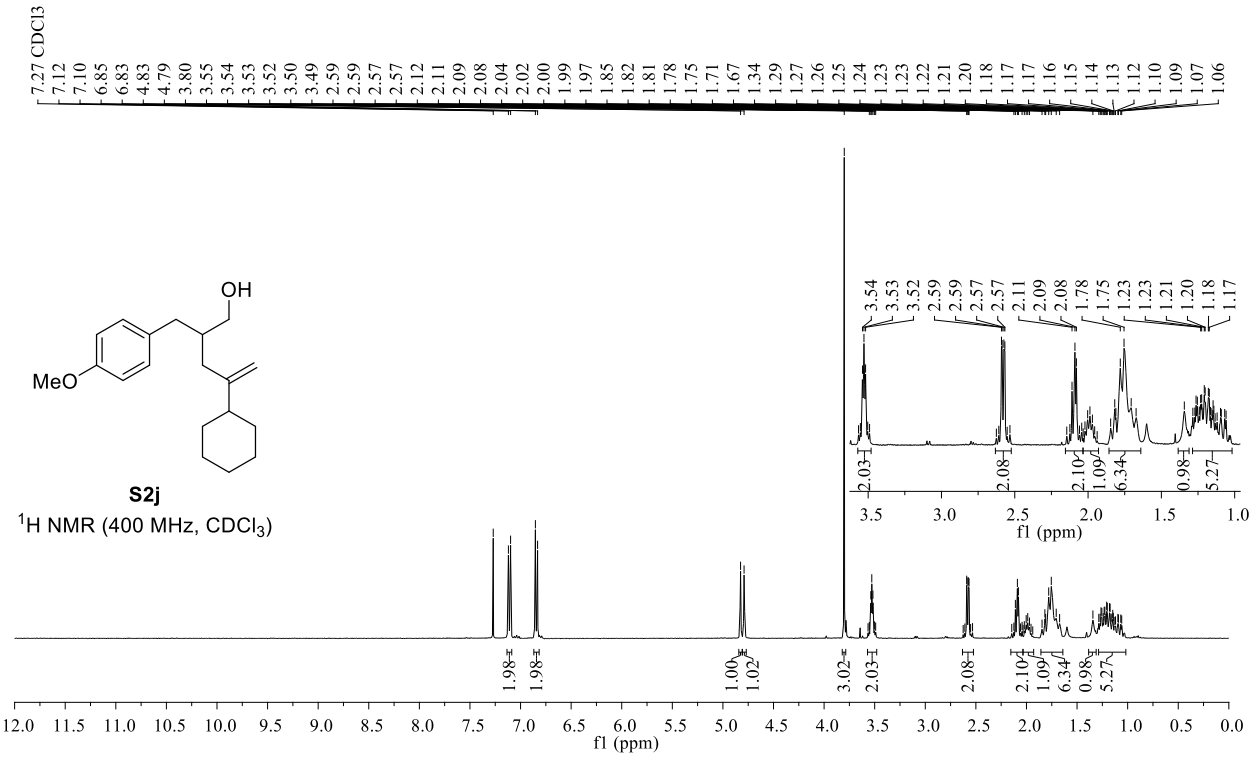


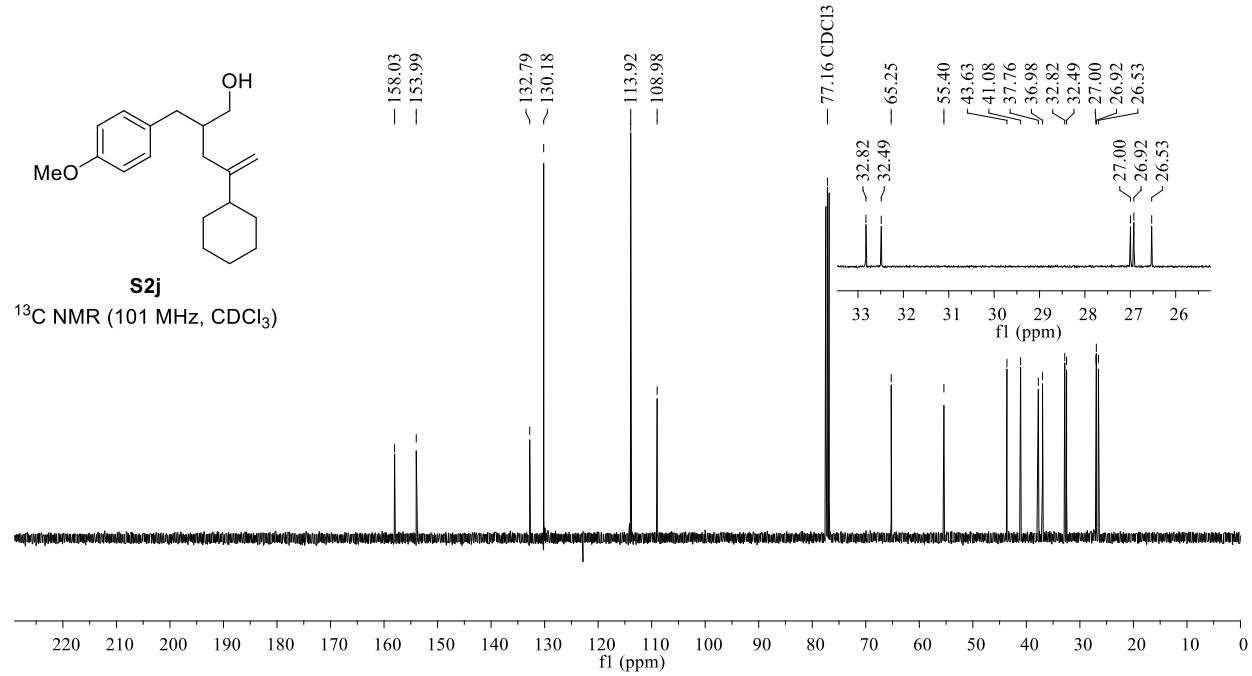
S2h

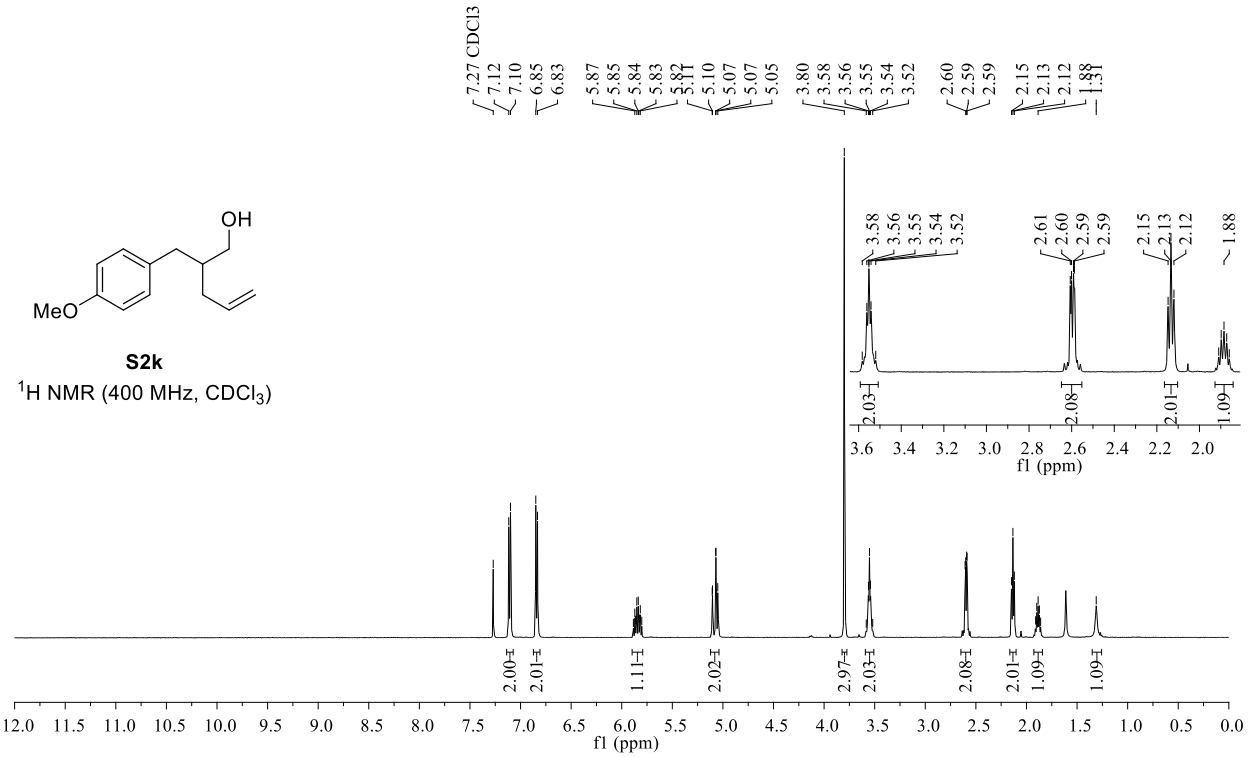
^{13}C NMR (101 MHz, $CDCl_3$)

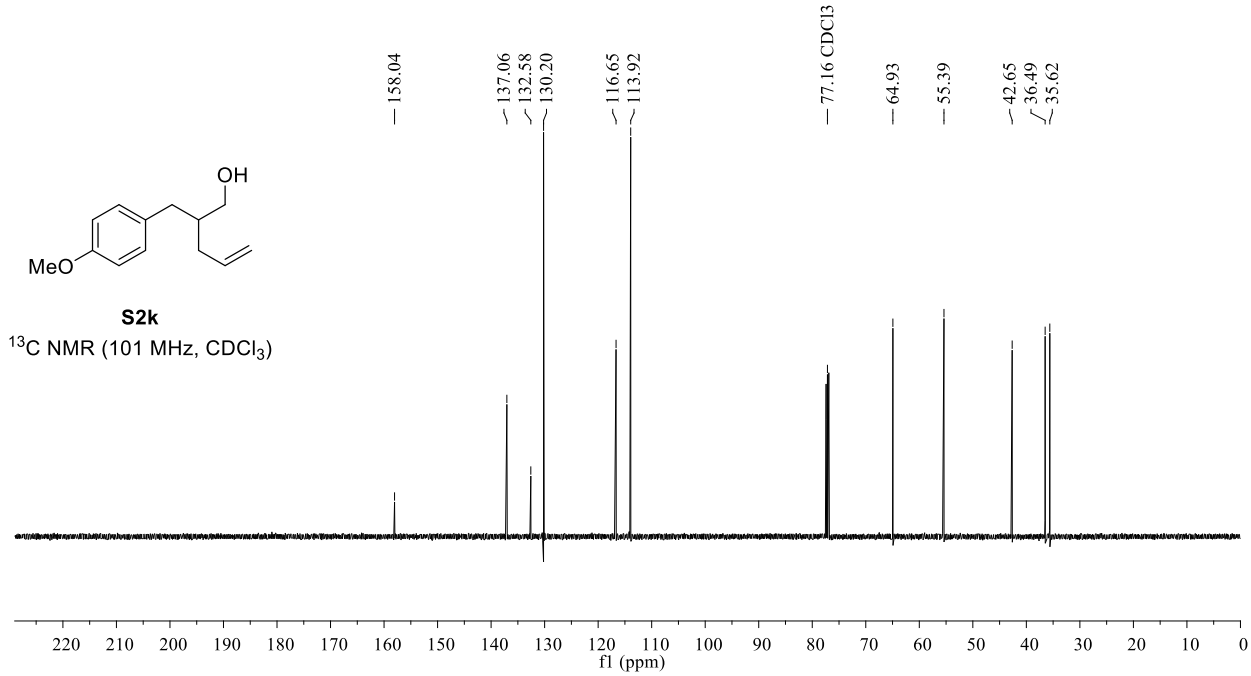

OH
MeO
nHex
S2i
1H NMR (500 MHz, CDCl3)
7.27 CDCl3
7.12
7.10
6.85
6.83
4.81
4.80
3.80
3.53
2.61
2.58
2.57
2.02
2.01
1.99
1.35
1.27
0.90
0.89
0.88
1.97
2.00
1.00
0.93
3.06
1.94
1.93
4.96
2.91
6.31
3.09
fl (ppm)

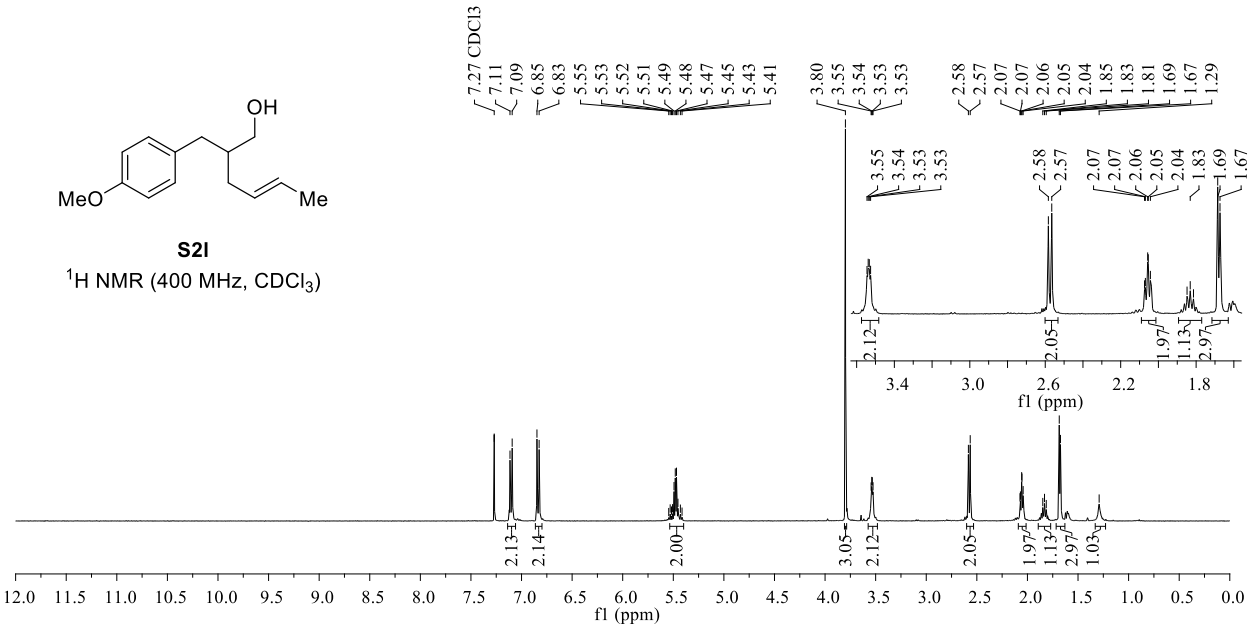

OH
MeO
nHex
S2i
13C NMR (126 MHz, CDCl3)
158.02
148.80
132.73
130.18
113.90
110.95
77.16 CDCl3
65.28
55.38
40.71
38.53
36.96
35.78
31.89
29.19
27.70
22.75
14.23
fl (ppm)


OH
MeO
S2j
1H NMR (400 MHz, CDCl3)
f1 (ppm)


OH
MeO
S2j
13C NMR (101 MHz, CDCl3)
f1 (ppm)

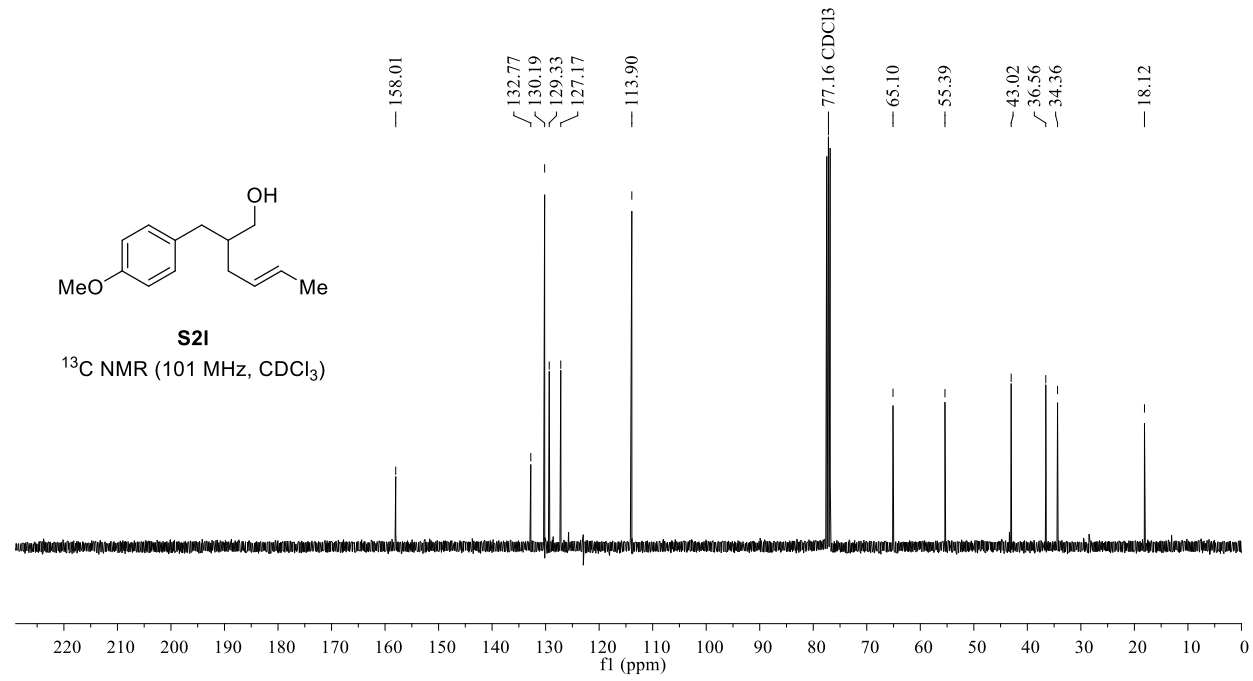

OH
MeO
S2k
1H NMR (400 MHz, CDCl3)
7.27 CDCl3
7.12
7.10
6.85
6.83
5.87
5.85
5.84
5.83
5.82
5.11
5.10
5.07
5.07
5.05
3.80
3.58
3.56
3.55
3.54
3.52
2.60
2.59
2.59
2.15
2.13
2.12
1.88
1.31
2.00
2.01
1.11
2.02
2.97
2.03
2.08
2.01
1.09
1.09
f1 (ppm)


OH
MeO
S2k
13C NMR (101 MHz, CDCl3)
158.04
137.06
132.58
130.20
116.65
113.92
77.16 CDCl3
64.93
55.39
42.65
36.49
35.62
f1 (ppm)



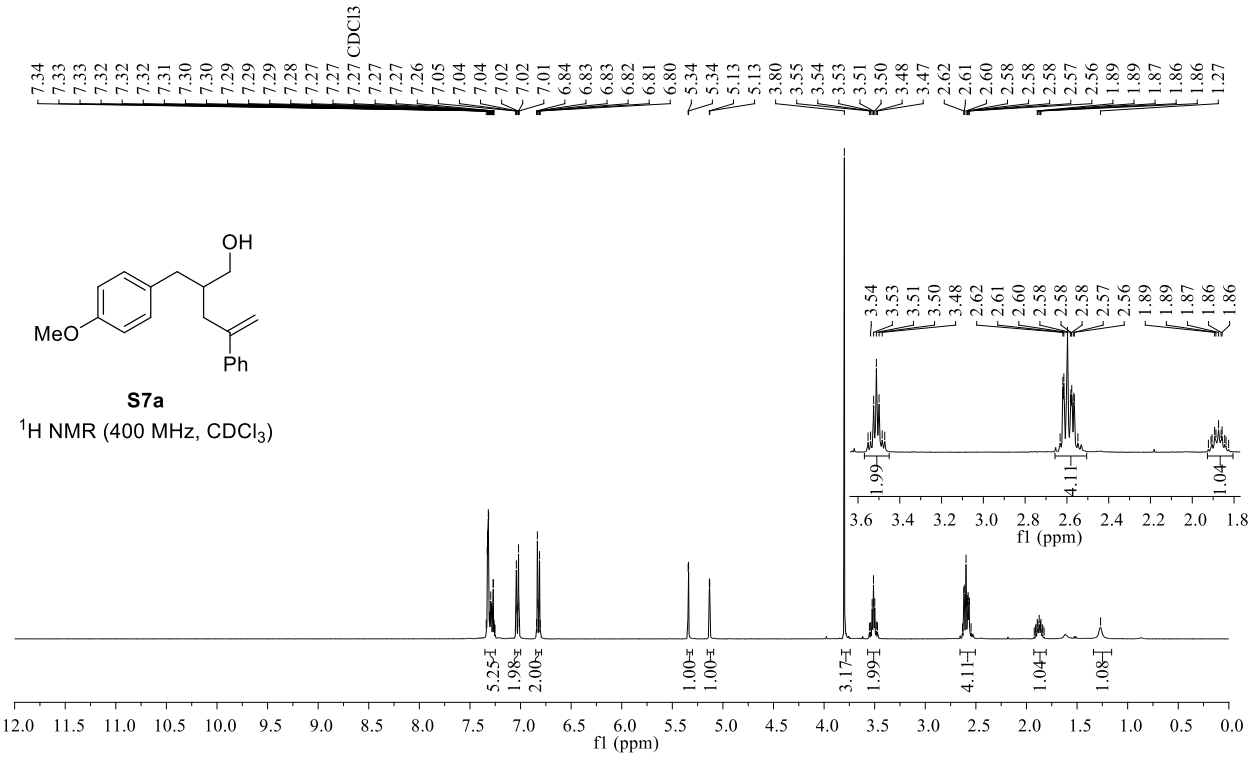
S2l

^{1}H NMR (400 MHz, $CDCl_3$)



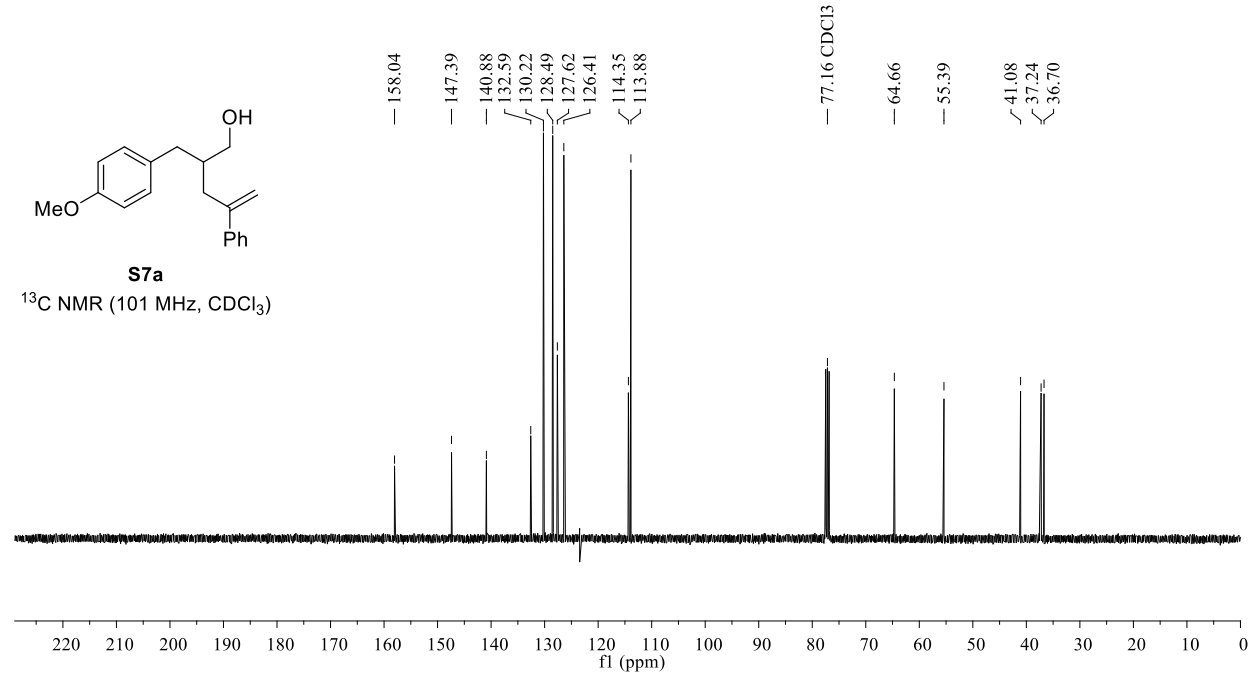
S2l

^{13}C NMR (101 MHz, $CDCl_3$)



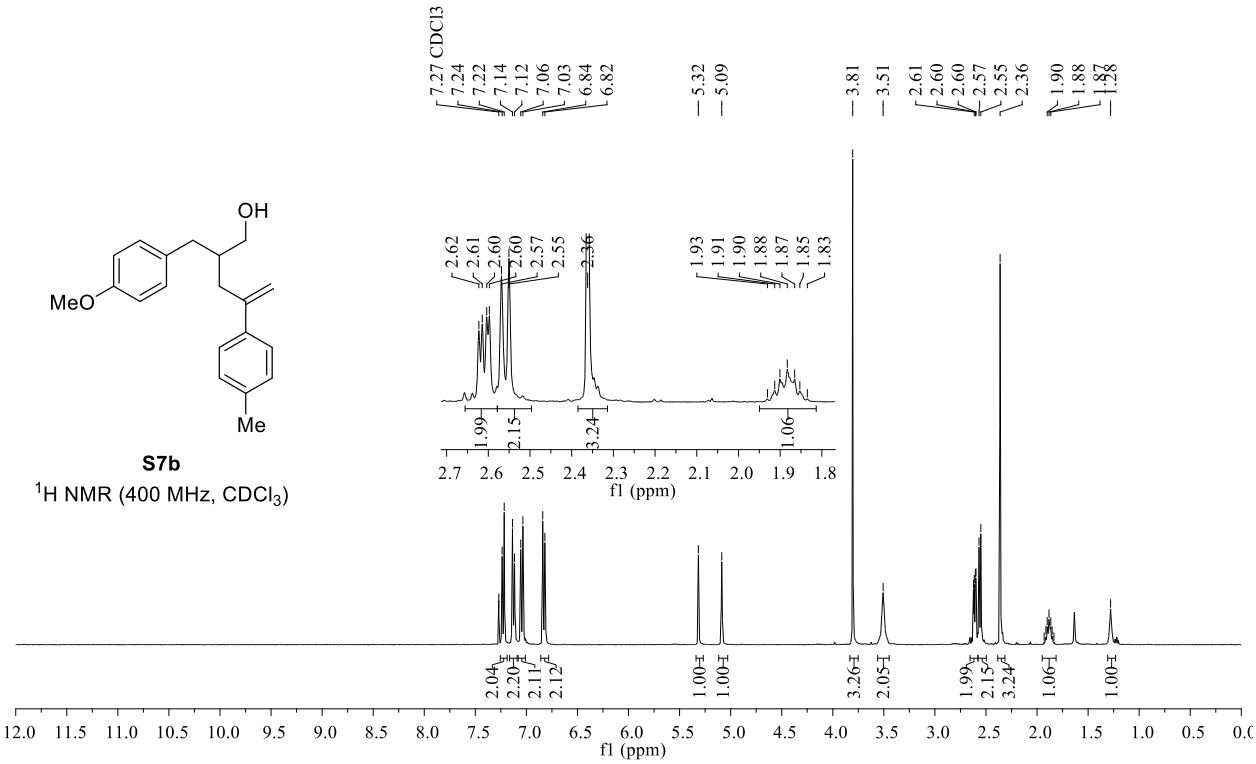
S7a

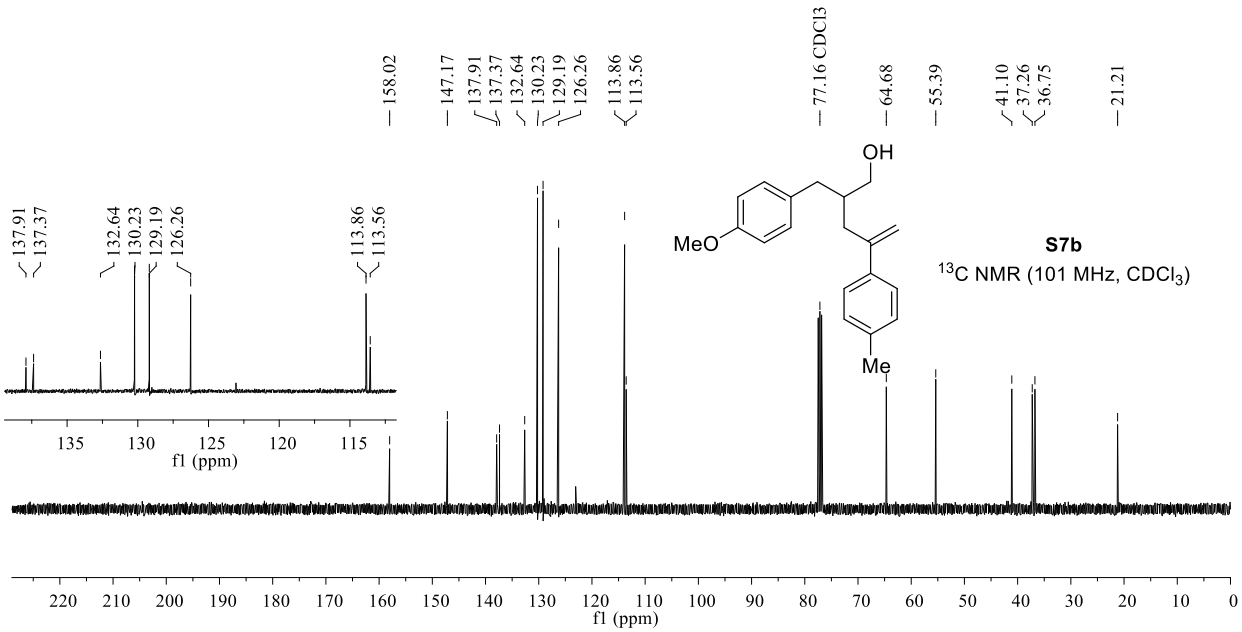
^{1}H NMR (400 MHz, $CDCl_3$)

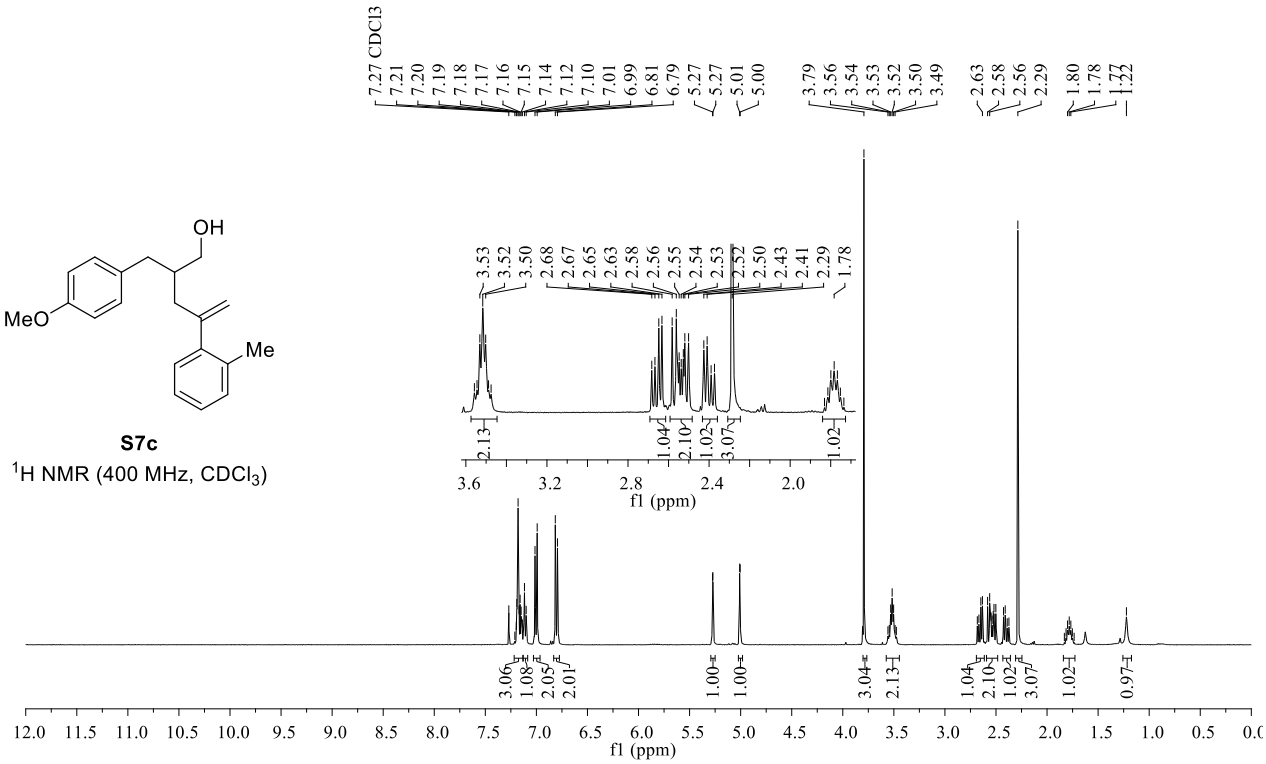


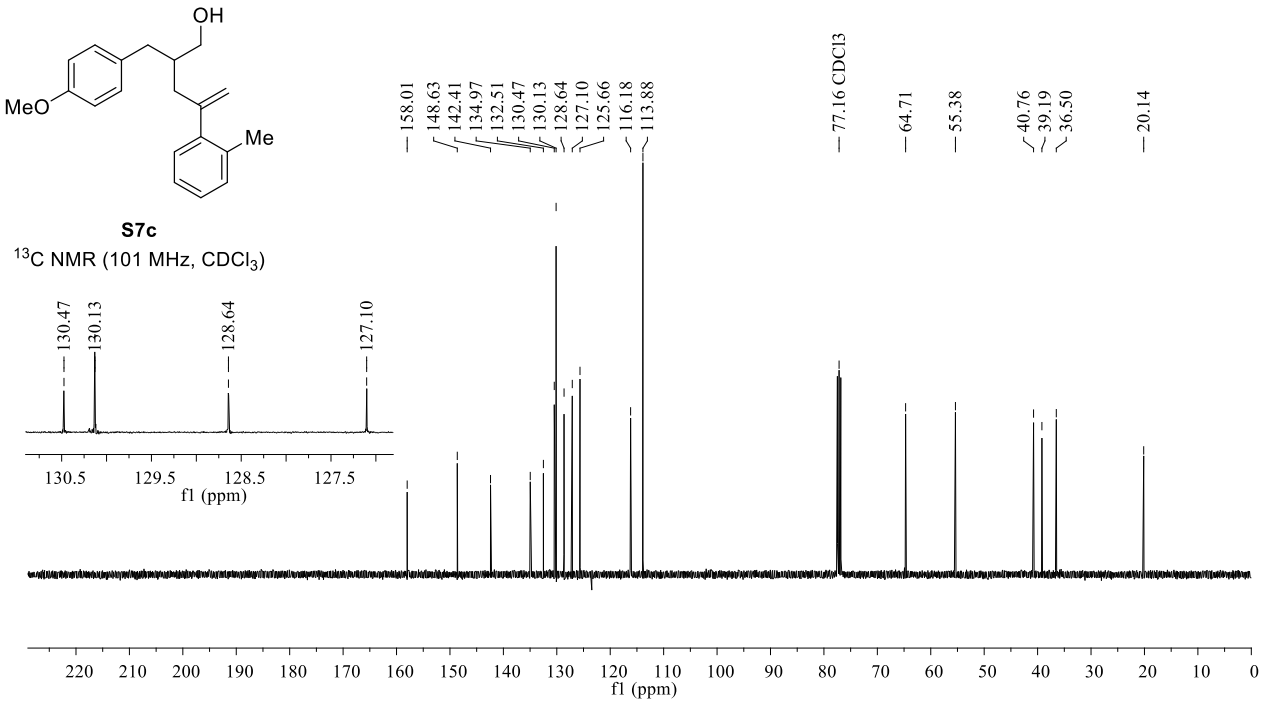
S7a

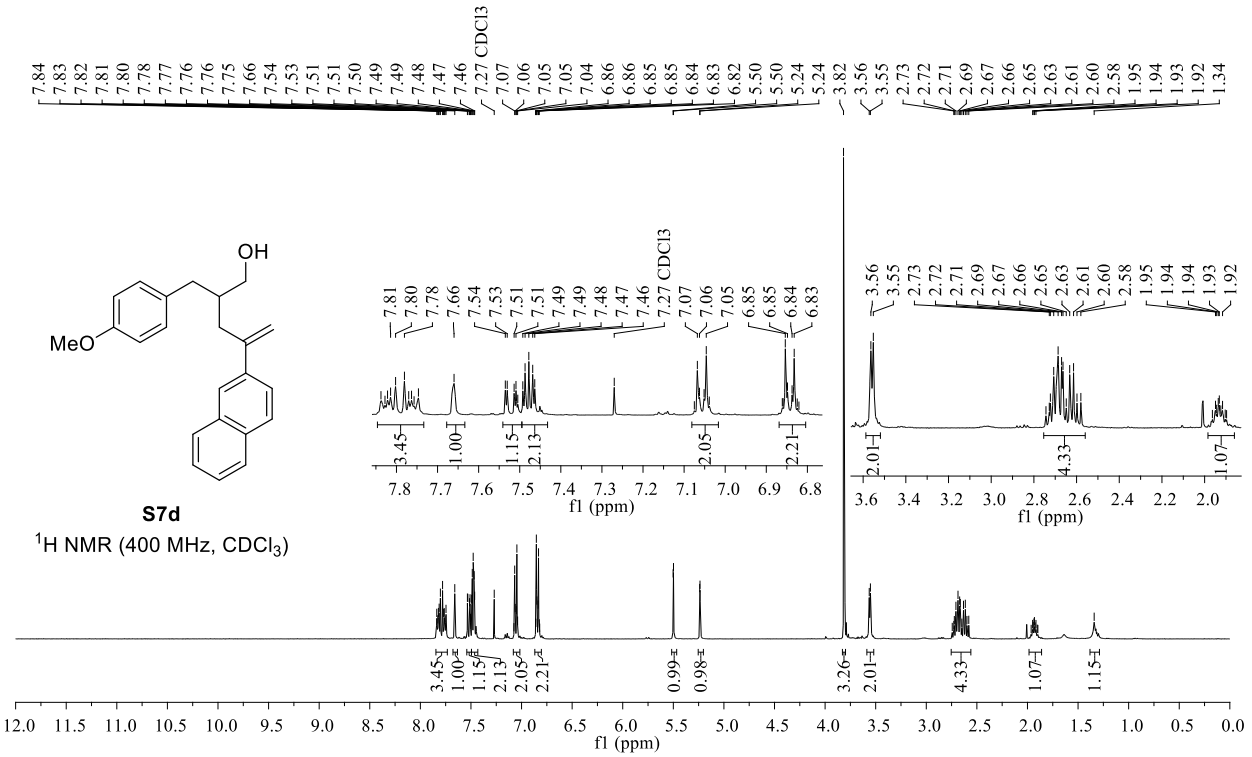
^{13}C NMR (101 MHz, $CDCl_3$)

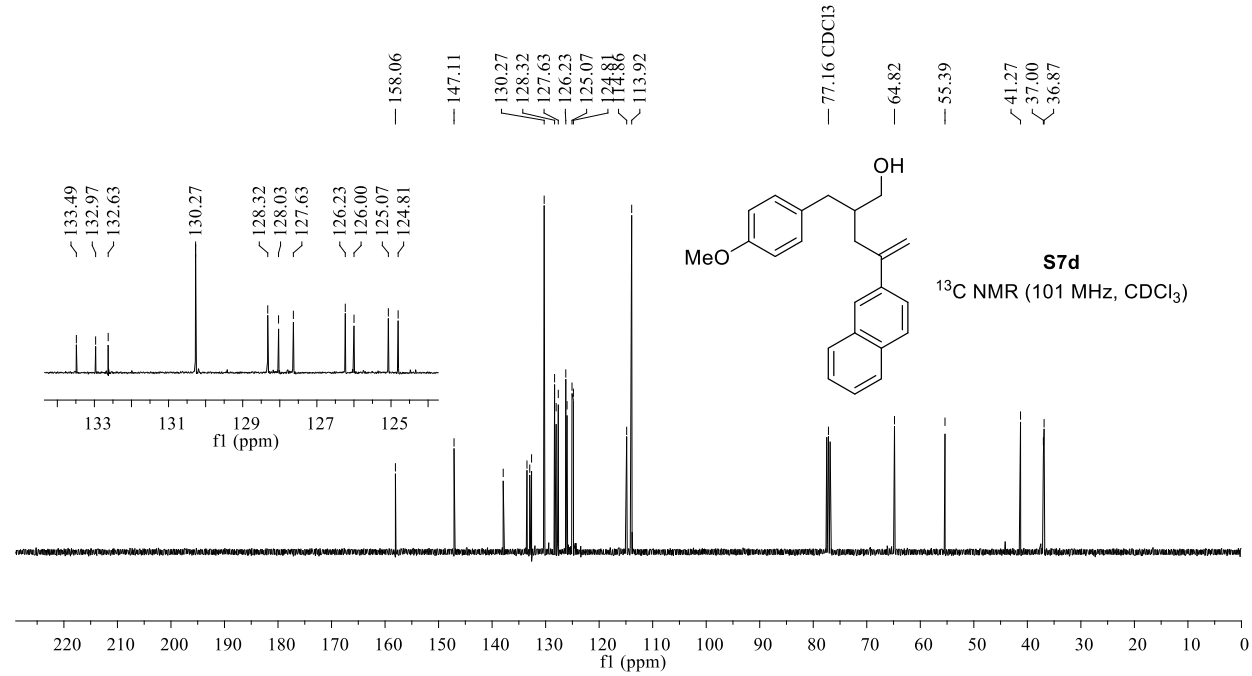

OH
MeO
Me
S7b
1H NMR (400 MHz, CDCl3)
fl (ppm)

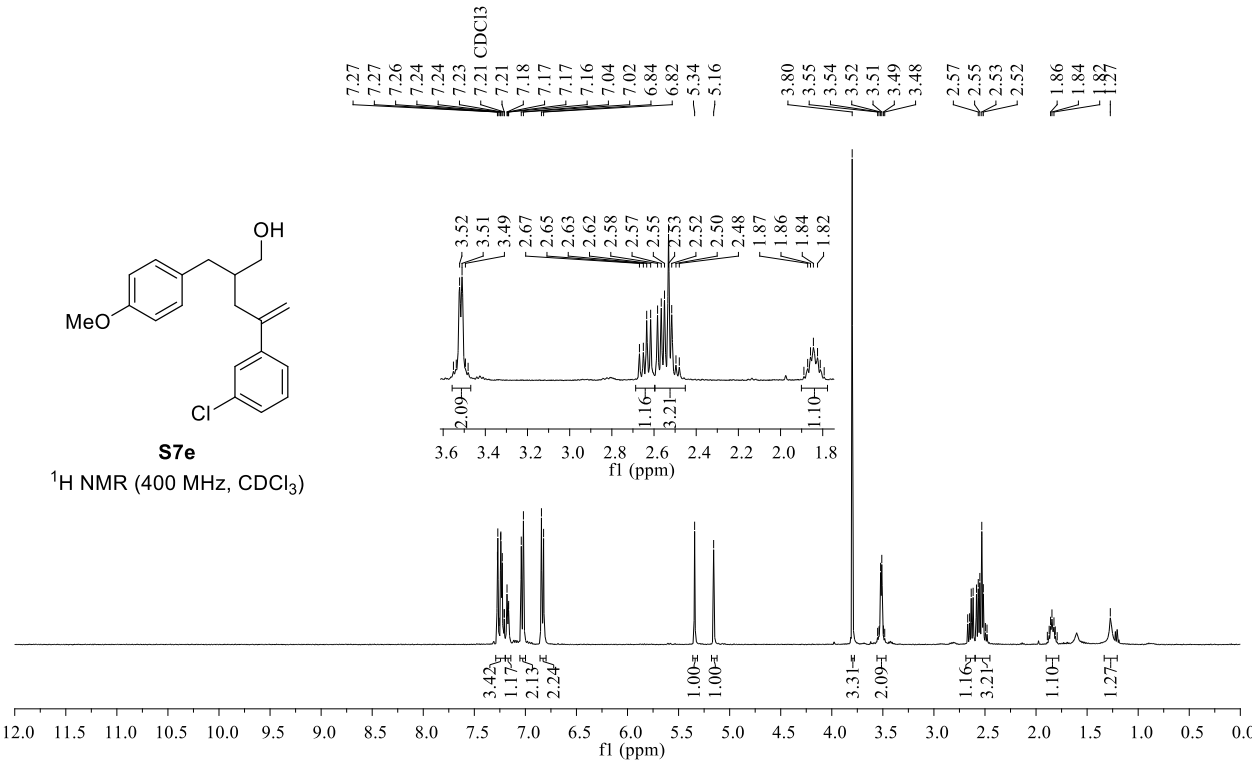

OH
MeO
Me
S7b
13C NMR (101 MHz, CDCl3)
fl (ppm)

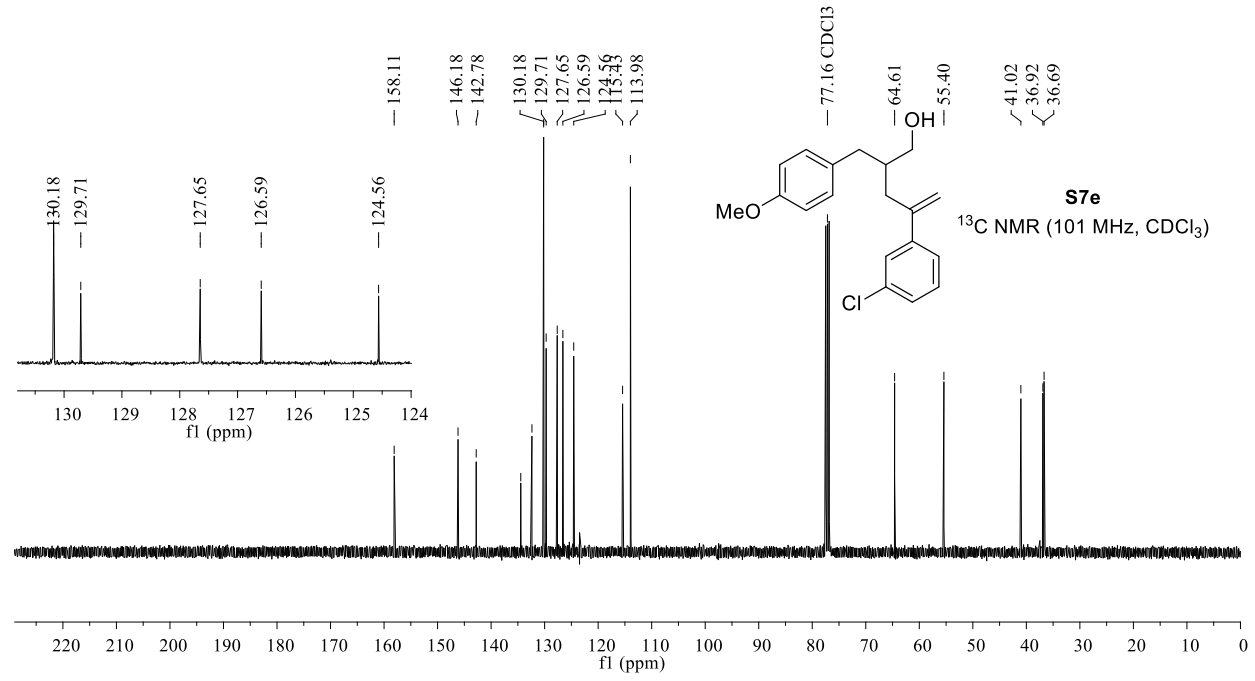

OH
MeO
Me
S7c
1H NMR (400 MHz, CDCl3)
7.27 CDCl3
7.21
7.20
7.19
7.18
7.17
7.16
7.15
7.14
7.12
7.10
7.01
6.99
6.81
6.79
5.27
5.27
5.01
5.00
3.79
3.56
3.54
3.53
3.52
3.50
3.49
2.63
2.58
2.56
2.29
1.80
1.78
1.77
1.22
3.53
3.52
3.50
2.68
2.67
2.65
2.63
2.58
2.56
2.55
2.54
2.53
2.52
2.50
2.43
2.41
2.29
1.78
2.13
1.04
2.10
1.02
3.07
1.02
3.6
3.2
2.8
2.4
2.0
f1 (ppm)
3.06
1.08
2.05
2.01
1.00
1.00
3.04
2.13
1.04
2.10
1.02
3.07
1.02
0.97
12.0
11.5
11.0
10.5
10.0
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
f1 (ppm)

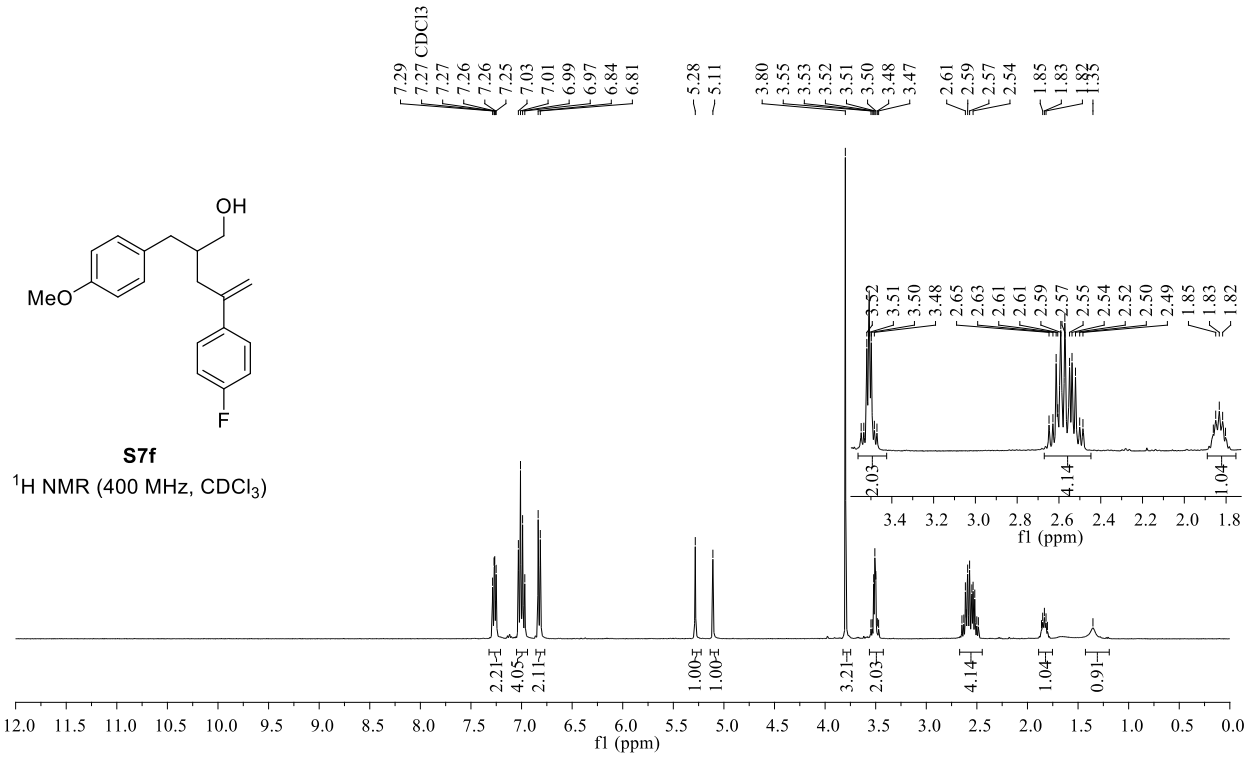

OH
MeO
Me
S7c
13C NMR (101 MHz, CDCl3)
158.01
148.63
142.41
134.97
132.51
130.47
130.13
128.64
127.10
125.66
116.18
113.88
77.16 CDCl3
64.71
55.38
40.76
39.19
36.50
20.14
130.47
130.13
128.64
127.10
130.5
129.5
128.5
127.5
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

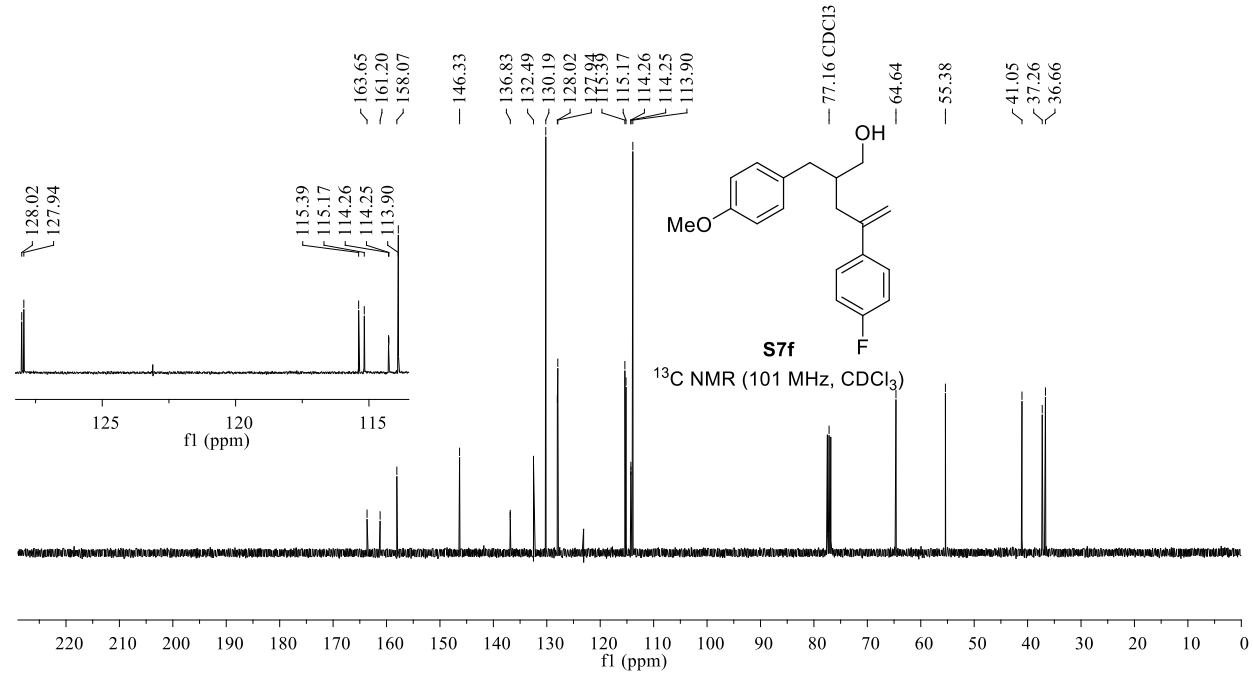

OH
MeO
S7d
1H NMR (400 MHz, CDCl3)
f1 (ppm)

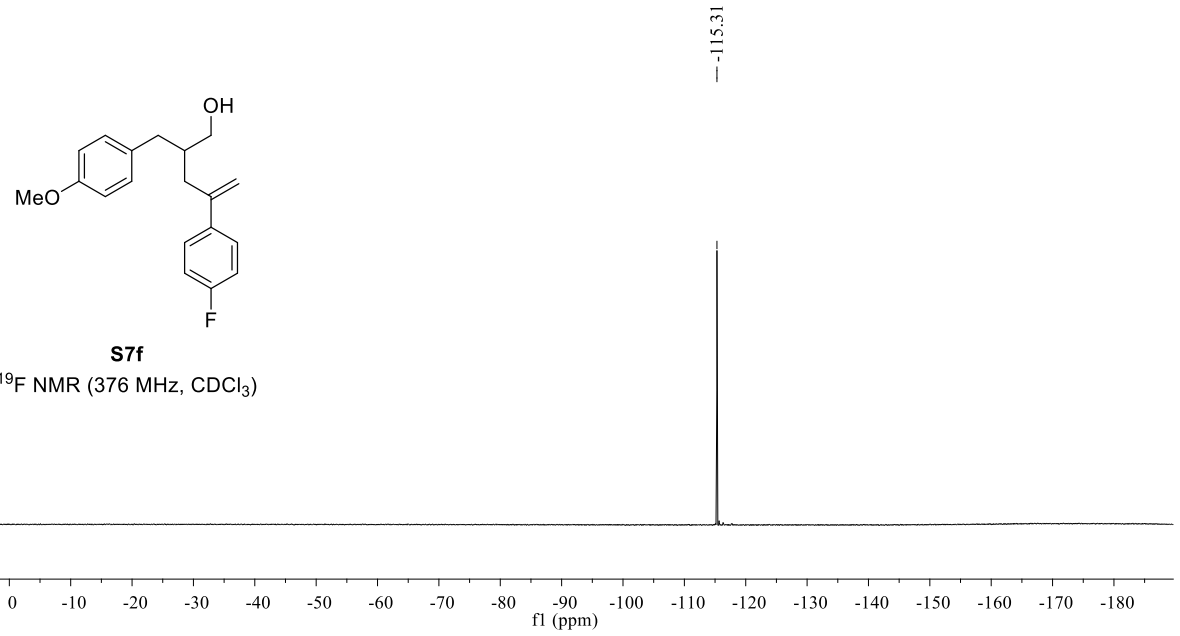

OH
MeO
S7d
13C NMR (101 MHz, CDCl3)
f1 (ppm)


OH
MeO
Cl
S7e
1H NMR (400 MHz, CDCl3)
CDCl3
fl (ppm)


OH
MeO
Cl
S7e
13C NMR (101 MHz, CDCl3)
CDCl3
fl (ppm)

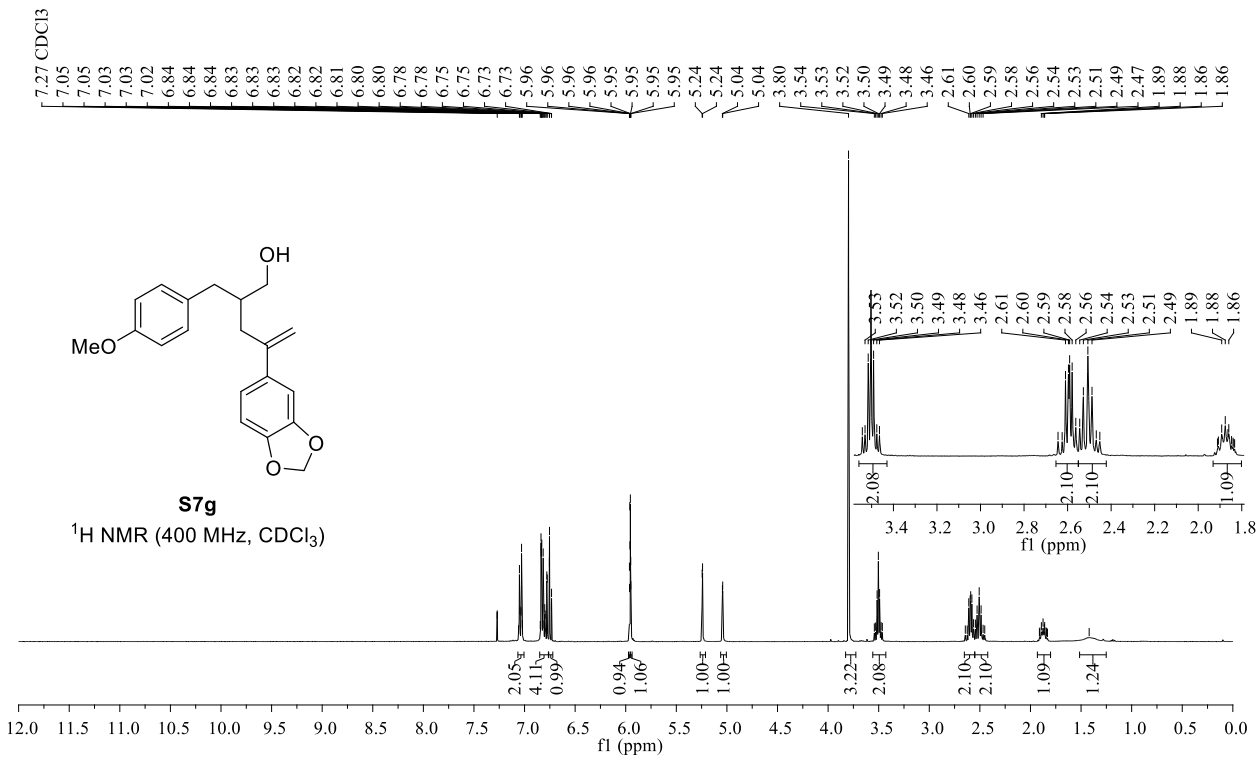

OH
MeO
F
S7f
1H NMR (400 MHz, CDCl3)
7.29
7.27 CDCl3
7.27
7.26
7.26
7.25
7.03
7.01
6.99
6.97
6.84
6.81
5.28
5.11
3.80
3.55
3.53
3.52
3.51
3.50
3.48
3.47
2.61
2.59
2.57
2.54
1.85
1.83
1.82
1.35
2.21
4.05
2.11
1.00
1.00
3.21
2.03
4.14
1.04
0.91
f1 (ppm)


163.65
161.20
158.07
146.33
136.83
132.49
130.19
128.02
127.94
115.39
115.17
114.26
114.25
113.90
77.16 CDCl3
64.64
55.38
41.05
37.26
36.66
OH
MeO
F
S7f
13C NMR (101 MHz, CDCl3)
f1 (ppm)



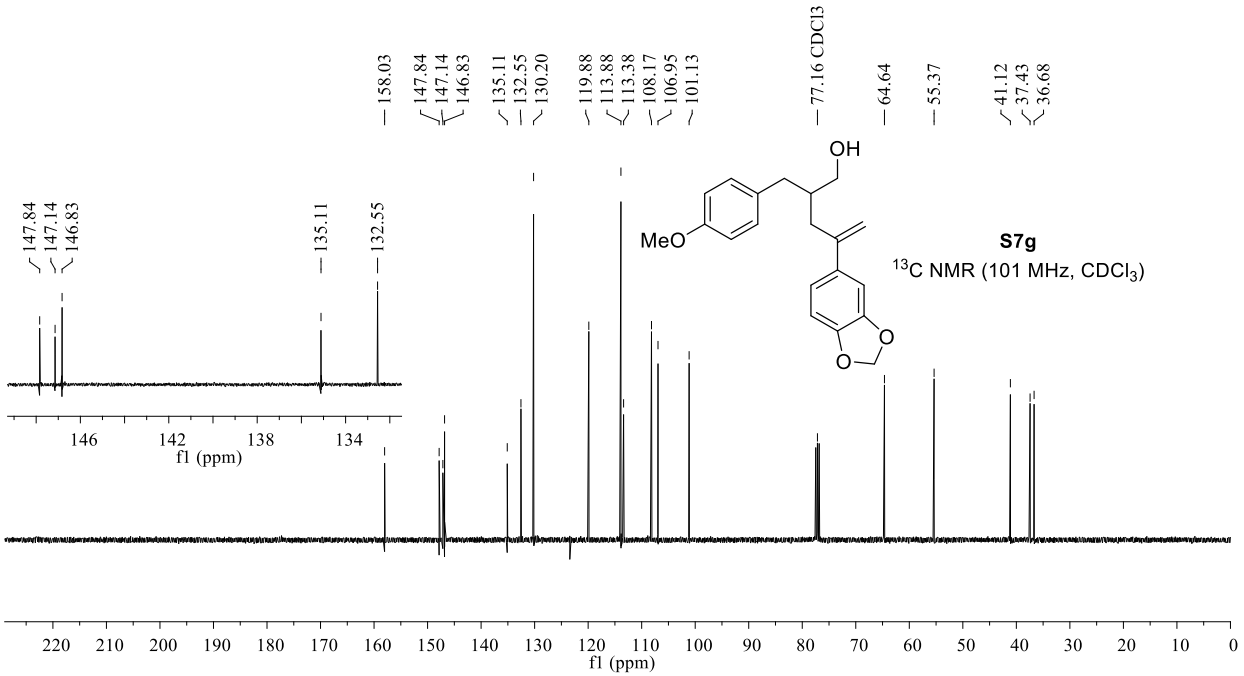
S7f

^{19}F NMR (376 MHz, $CDCl_3$)



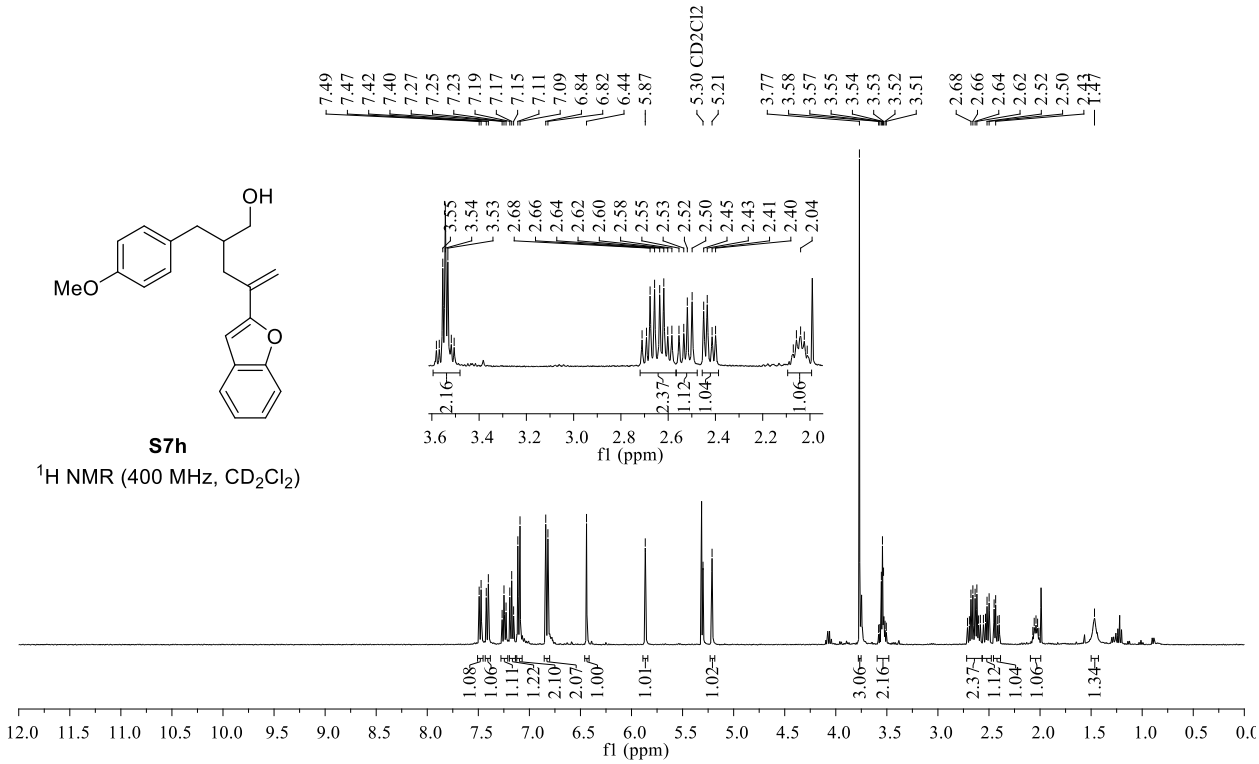
S7g

^{1}H NMR (400 MHz, $CDCl_3$)



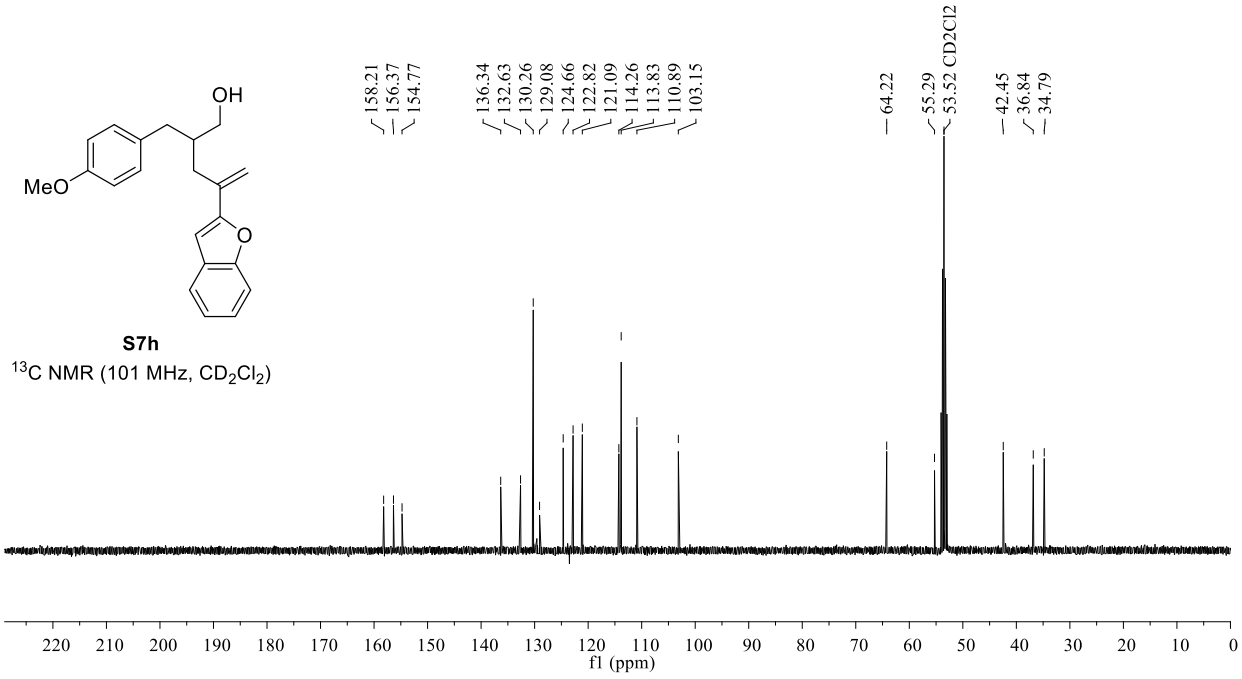
S7g

^{13}C NMR (101 MHz, $CDCl_3$)



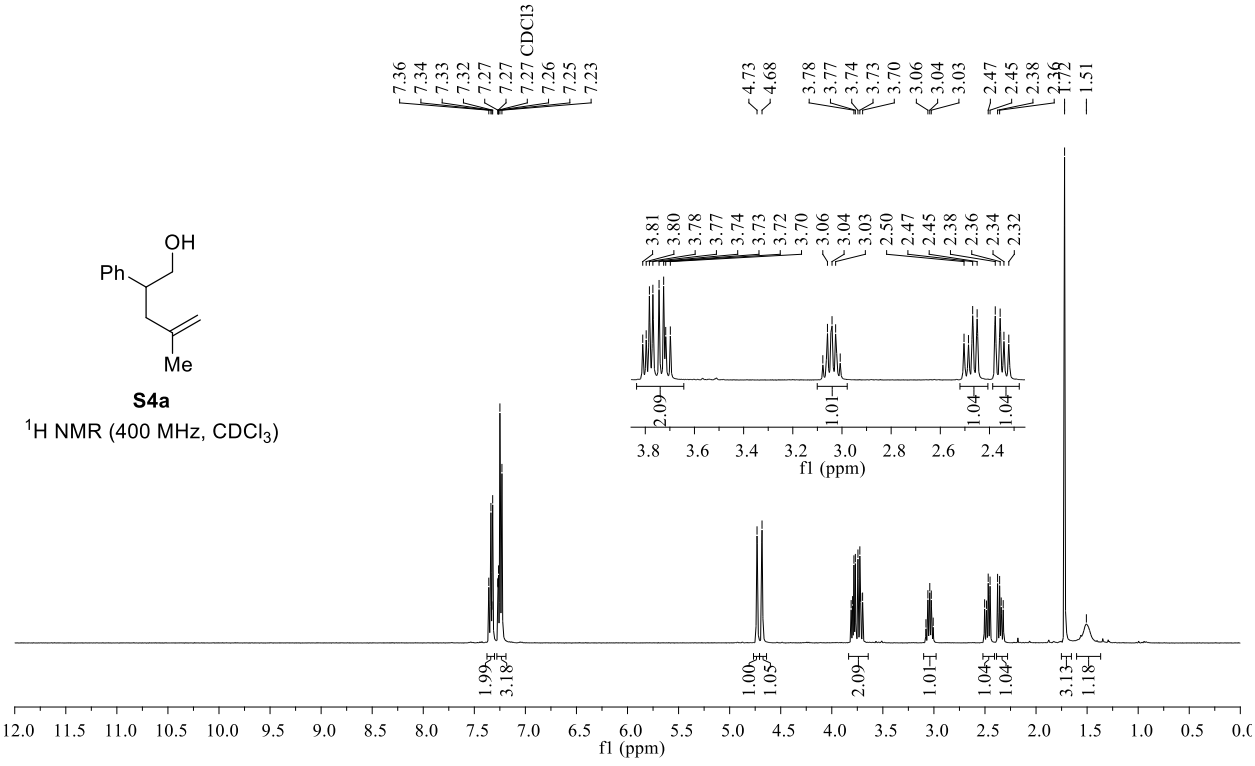
S7h

^{1}H NMR (400 MHz, CD_2Cl_2)



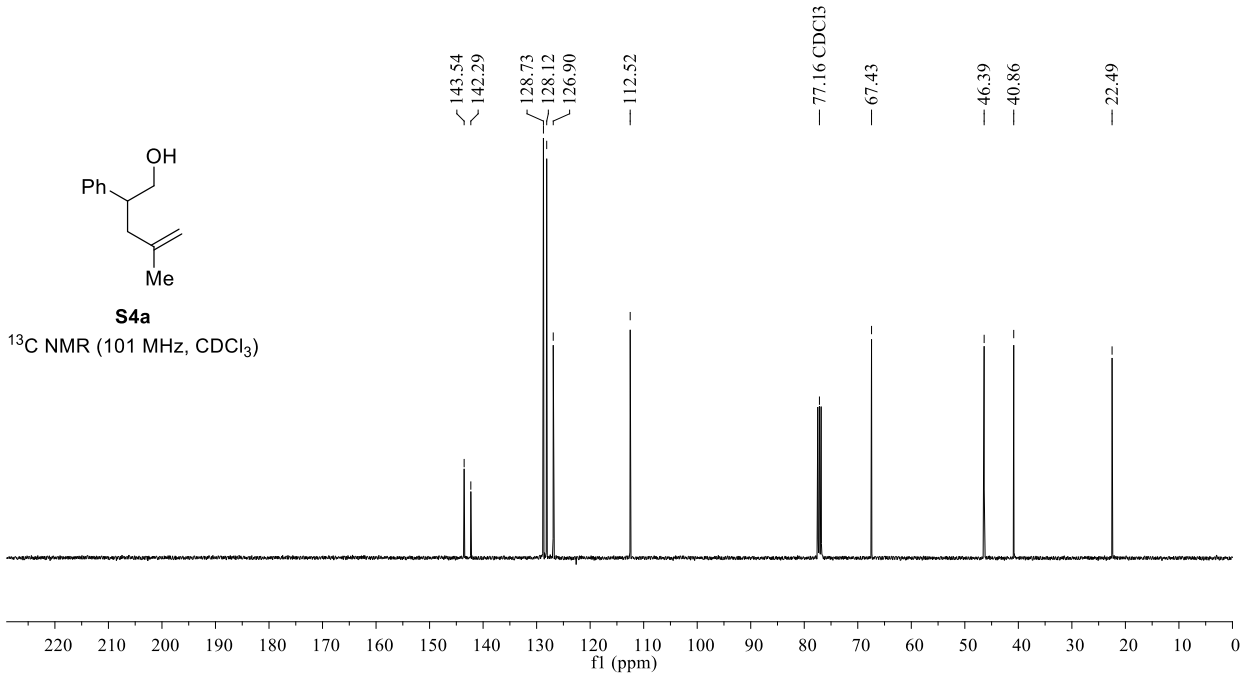
S7h

^{13}C NMR (101 MHz, CD_2Cl_2)



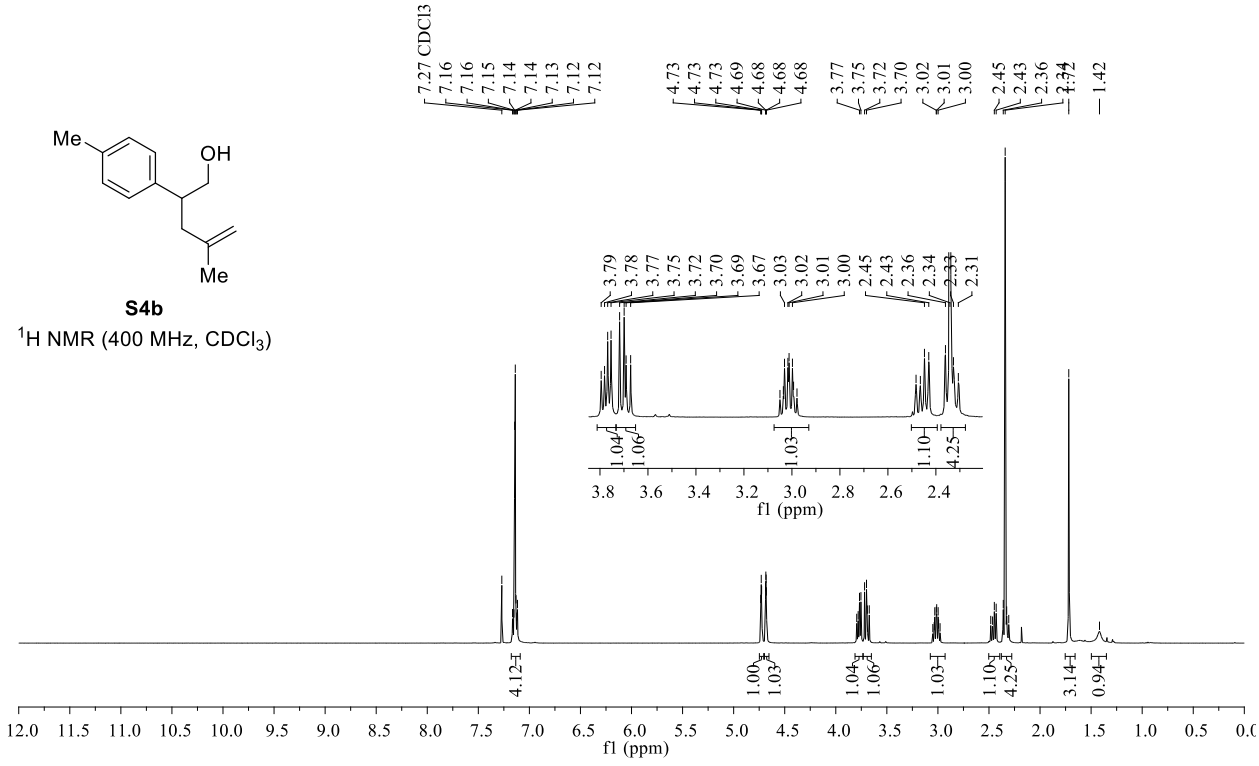
S4a

^{1}H NMR (400 MHz, $CDCl_3$)



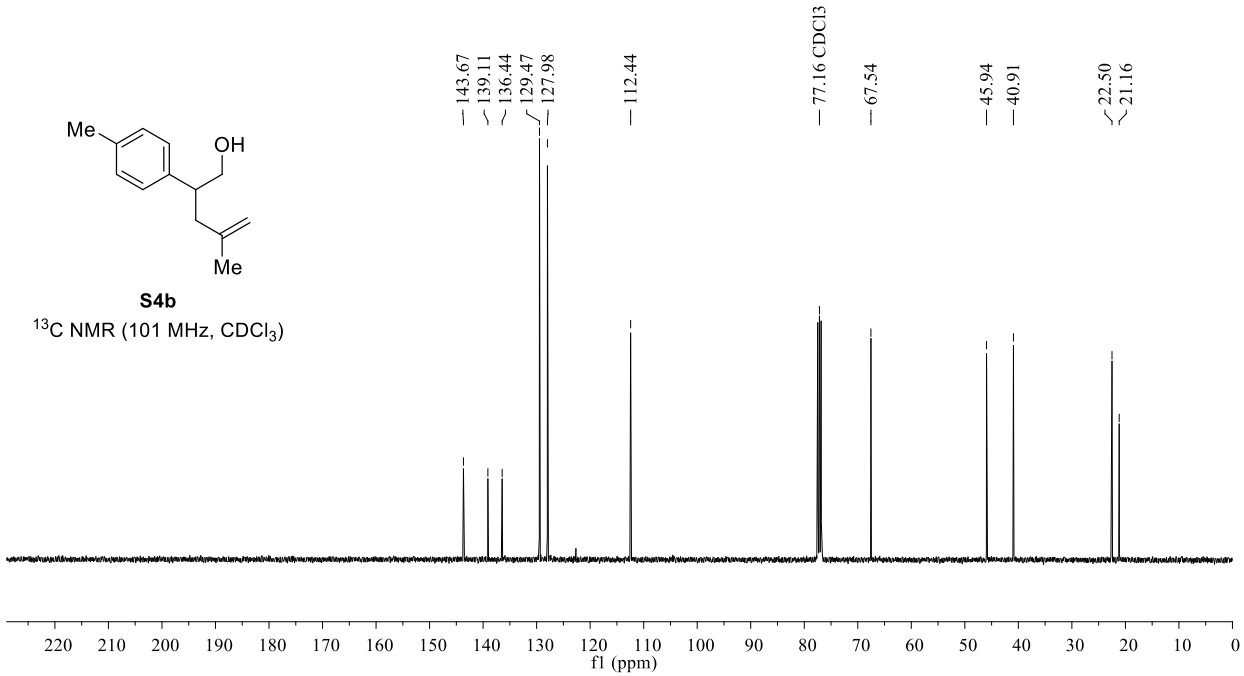
S4a

^{13}C NMR (101 MHz, $CDCl_3$)



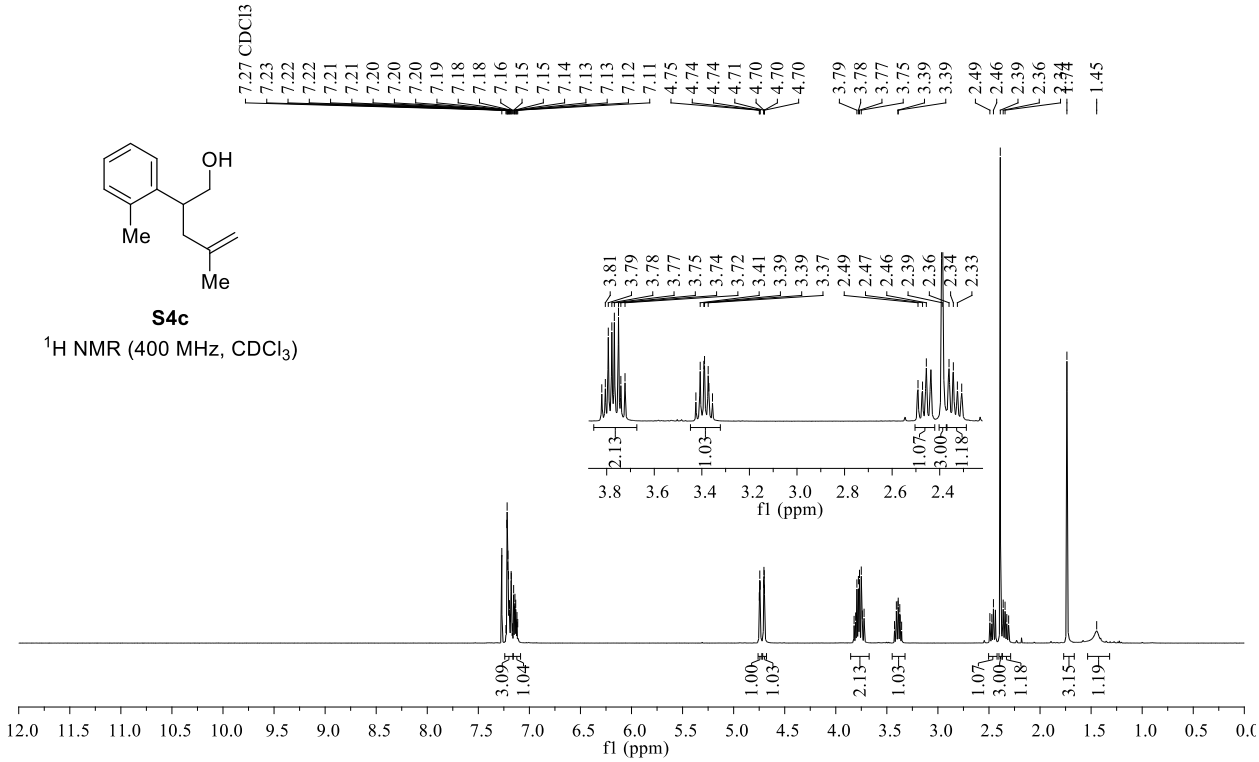
S4b

^{1}H NMR (400 MHz, $CDCl_3$)



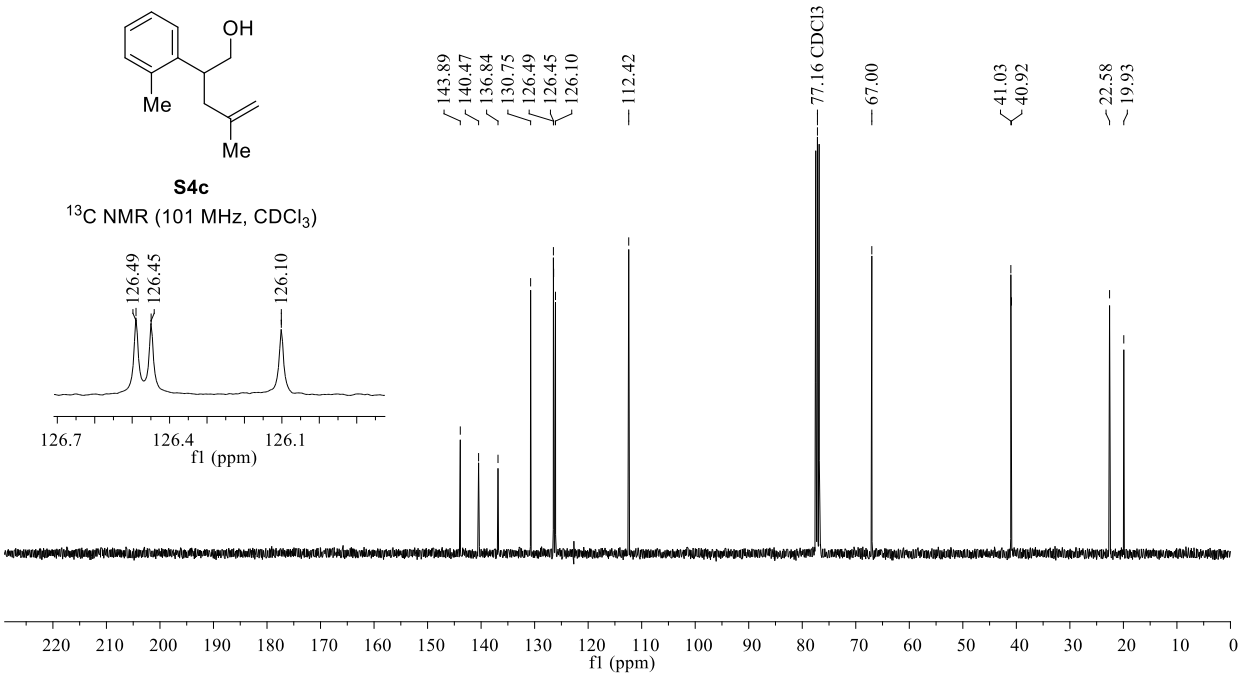
S4b

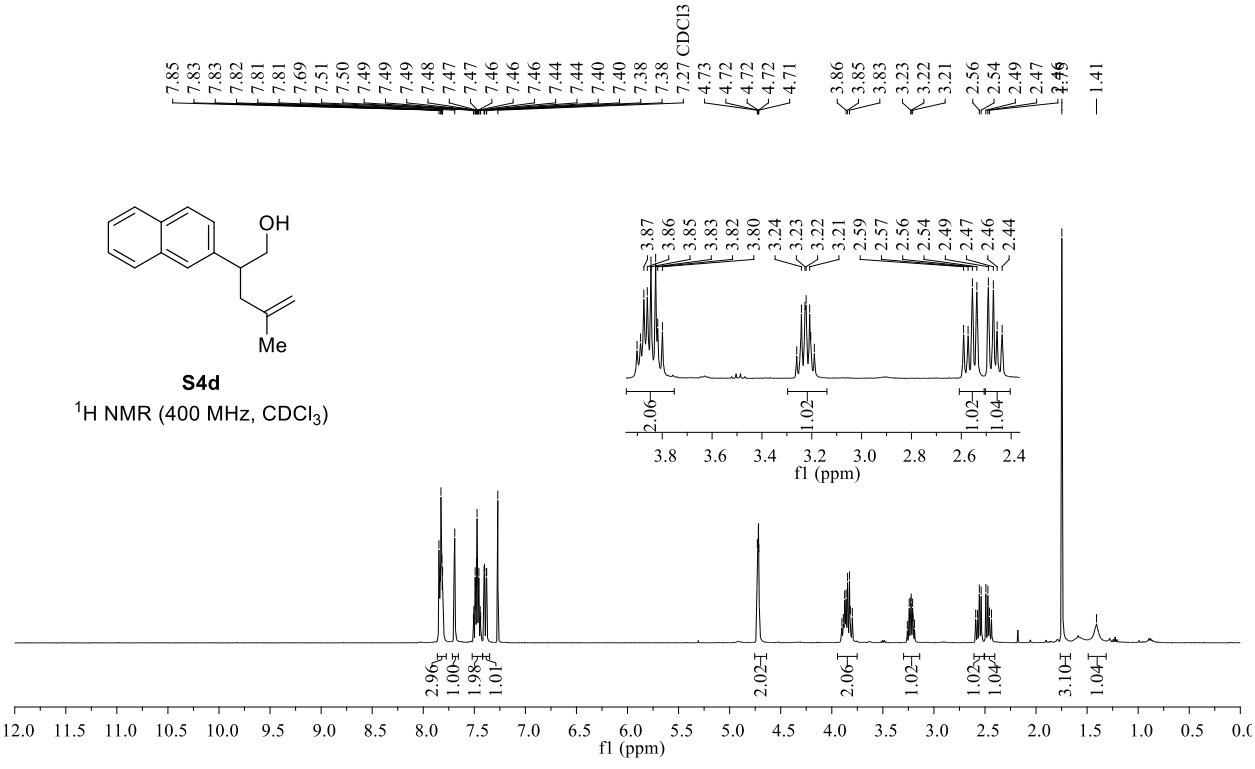
^{13}C NMR (101 MHz, $CDCl_3$)

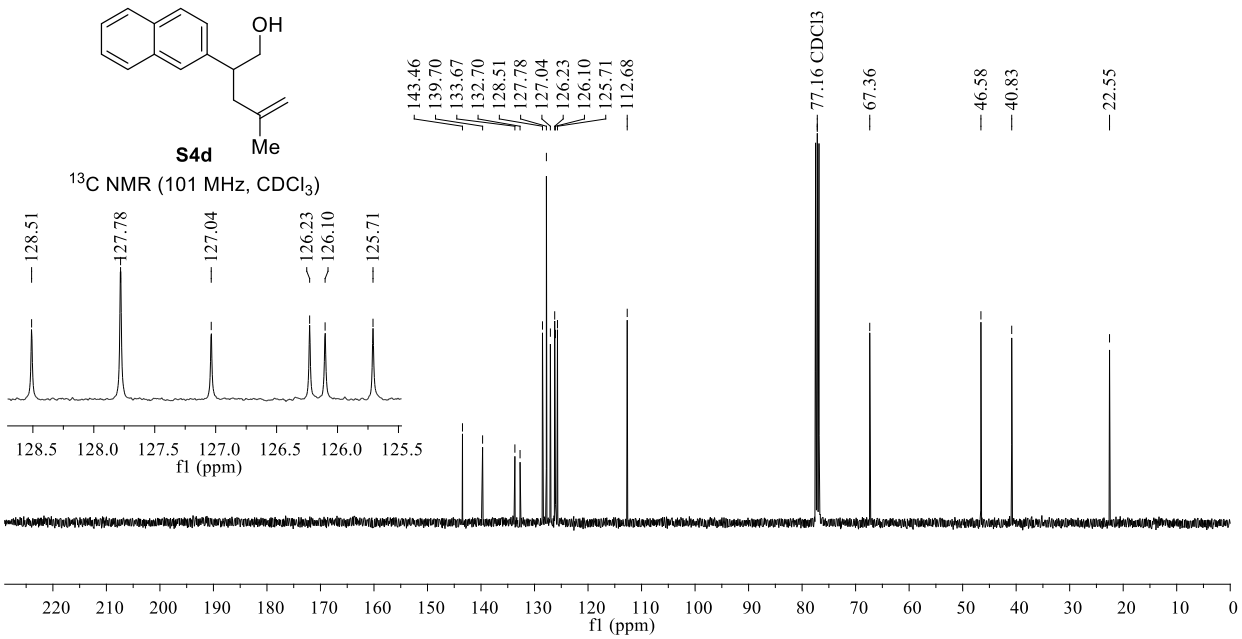


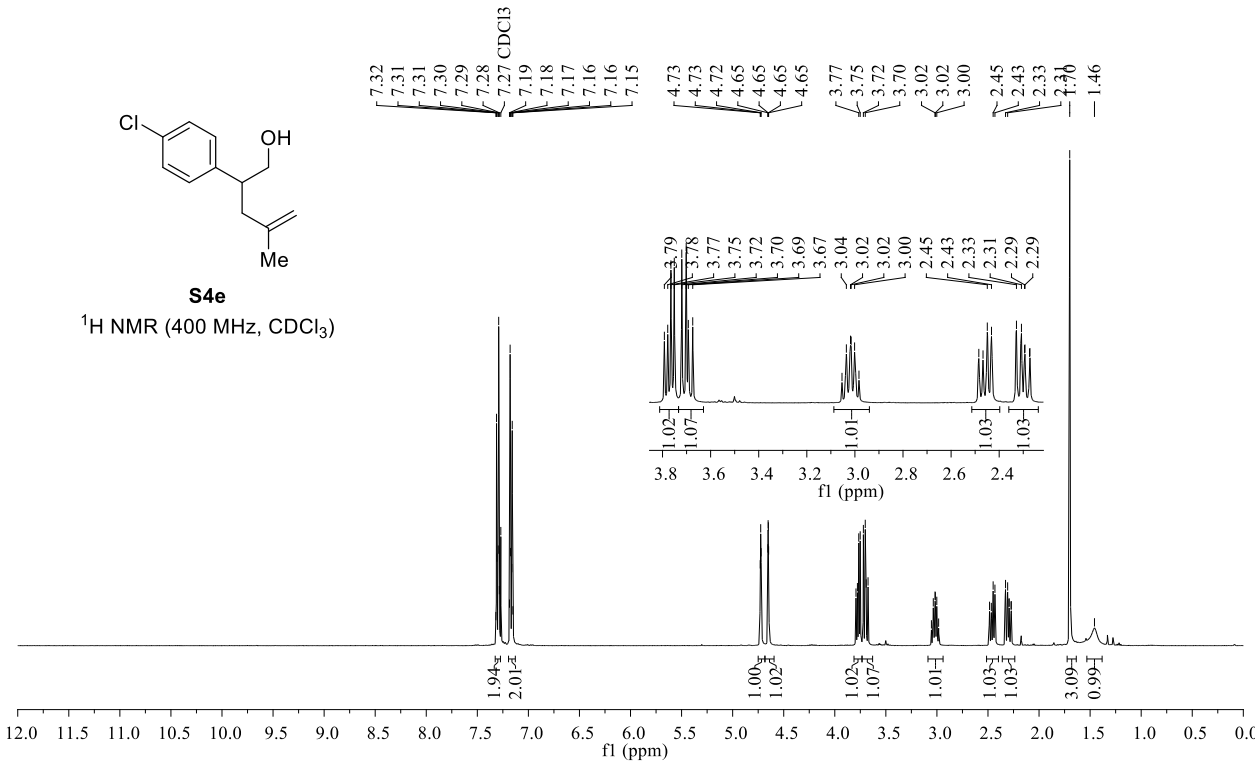
S4c

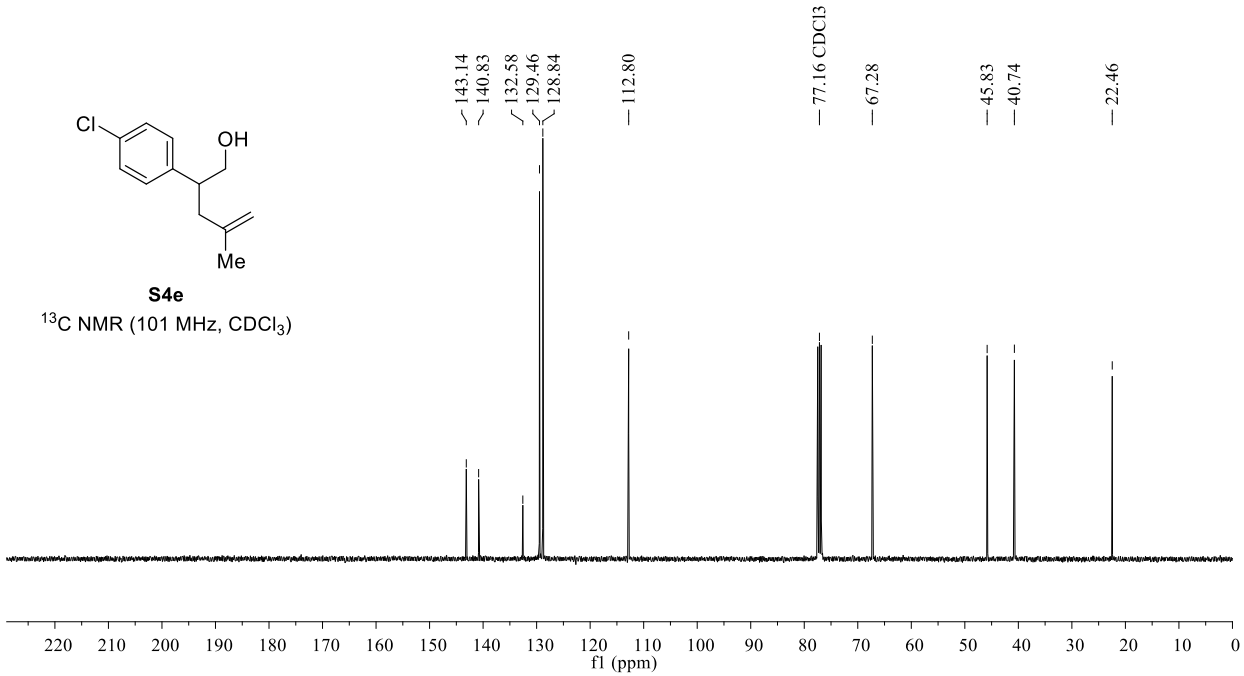
^{1}H NMR (400 MHz, $CDCl_3$)


OH
Me
Me
S4c
13C NMR (101 MHz, CDCl3)
143.89
140.47
136.84
130.75
126.49
126.45
126.10
112.42
77.16 CDCl3
67.00
41.03
40.92
22.58
19.93
126.49
126.45
126.10
126.7
126.4
126.1
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.85 7.83 7.83 7.82 7.81 7.81 7.69 7.51 7.50 7.49 7.49 7.49 7.48 7.47 7.47 7.46 7.46 7.46 7.44 7.44 7.40 7.40 7.38 7.38
7.27 CDCl3
4.73 4.72 4.72 4.72 4.71
3.86 3.85 3.83
3.23 3.22 3.21
2.56 2.54 2.49 2.47
1.41
OH
Me
S4d
1H NMR (400 MHz, CDCl3)
3.87 3.86 3.85 3.83 3.82 3.80 3.24 3.23 3.22 3.21 2.59 2.57 2.56 2.54 2.49 2.47 2.46 2.44
2.06 1.02 1.02 1.04
3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4
f1 (ppm)
2.96 1.00 1.98 1.01 2.02 2.06 1.02 1.02 1.04 3.10 1.04
12.0 11.5 11.0 10.5 10.0 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)

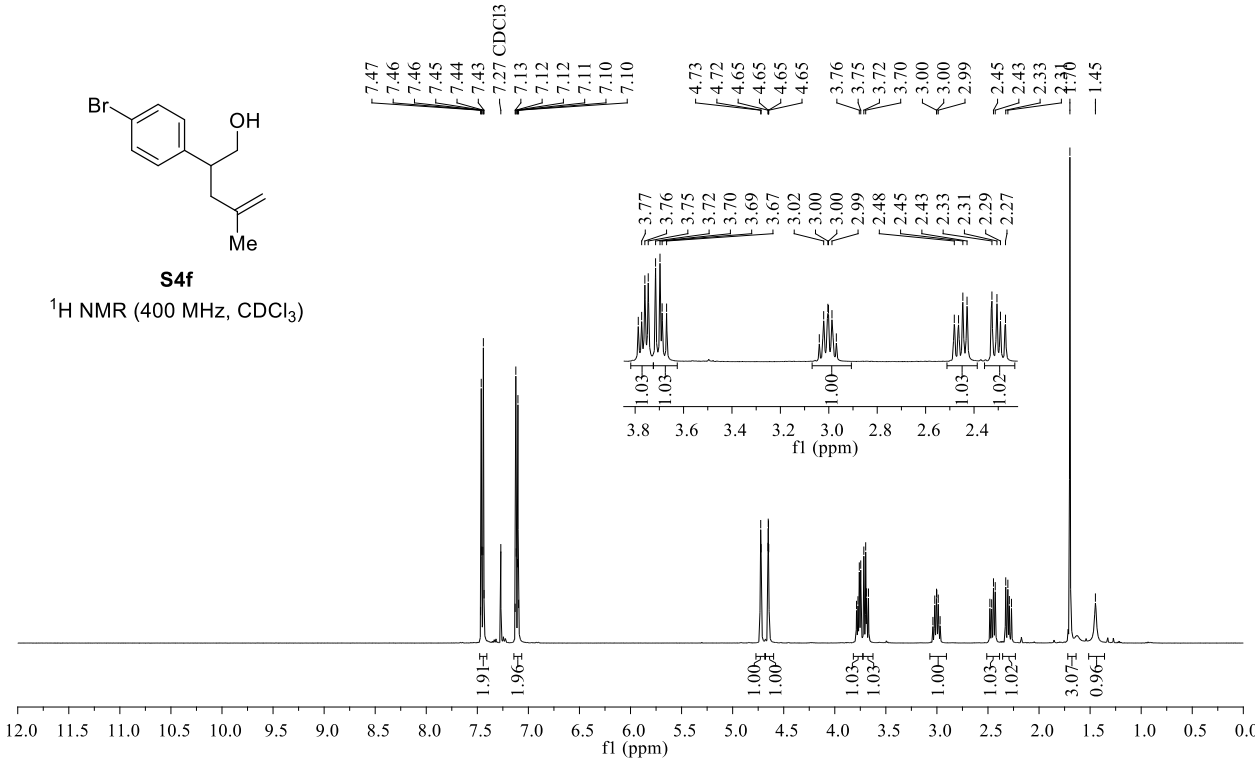

OH
Me
S4d
^{13}C NMR (101 MHz, CDCl$_3$)
143.46
139.70
133.67
132.70
128.51
127.78
127.04
126.23
126.10
125.71
112.68
77.16 CDCl3
67.36
46.58
40.83
22.55
128.51
127.78
127.04
126.23
126.10
125.71
f1 (ppm)


Cl
OH
Me
S4e
^{1}H NMR (400 MHz, CDCl$_3$)
7.27 CDCl3
4.73
4.72
4.65
3.77
3.75
3.72
3.70
3.02
3.00
2.45
2.43
2.33
2.31
1.46
f1 (ppm)



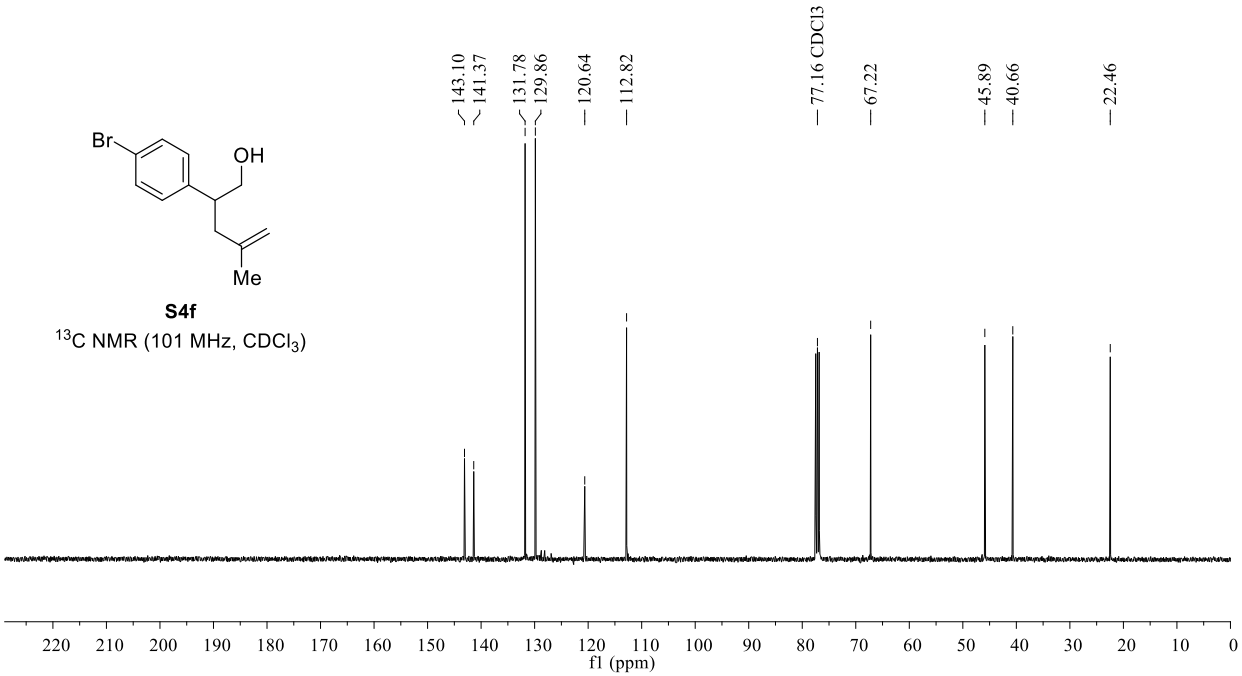
S4e

^{13}C NMR (101 MHz, $CDCl_3$)



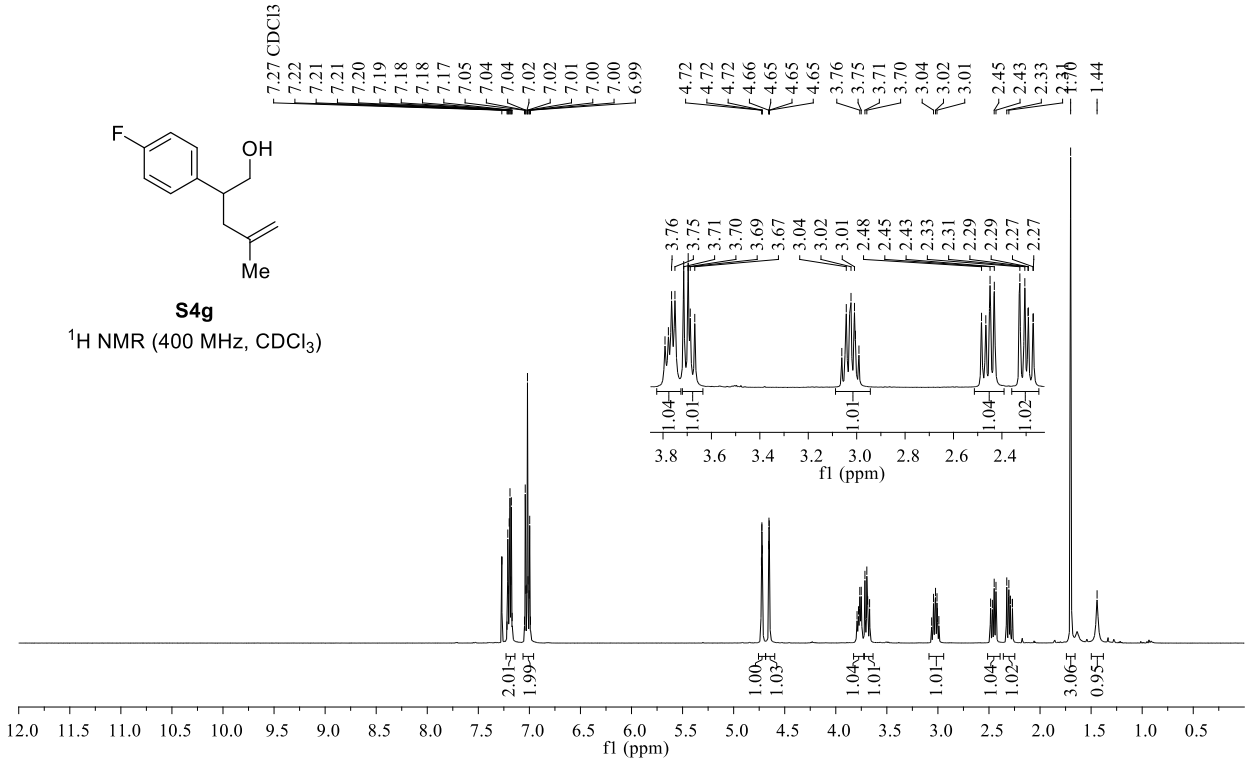
S4f

^{1}H NMR (400 MHz, $CDCl_3$)



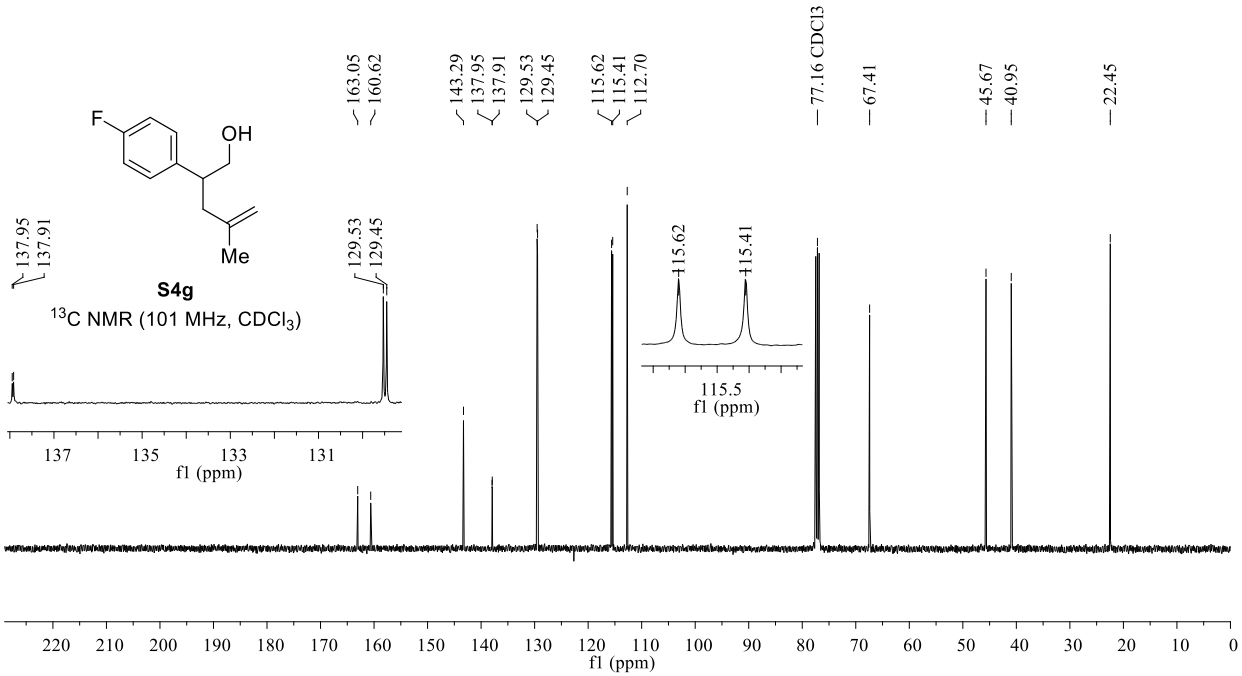
S4f

^{13}C NMR (101 MHz, $CDCl_3$)



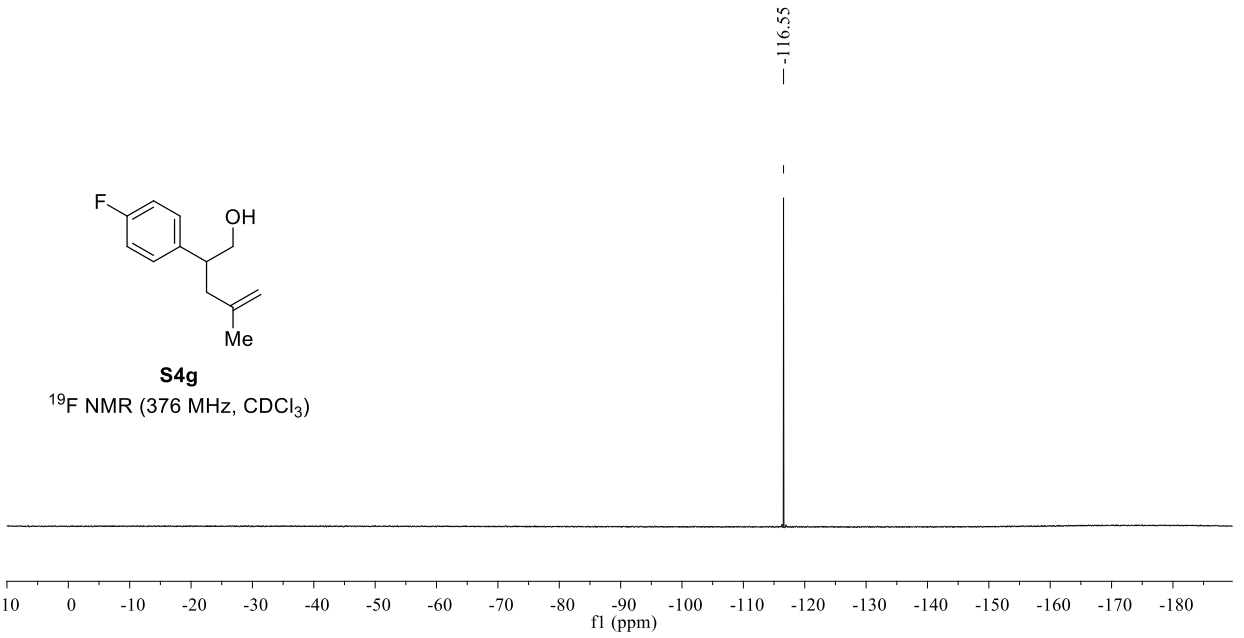
S4g

^{1}H NMR (400 MHz, $CDCl_3$)



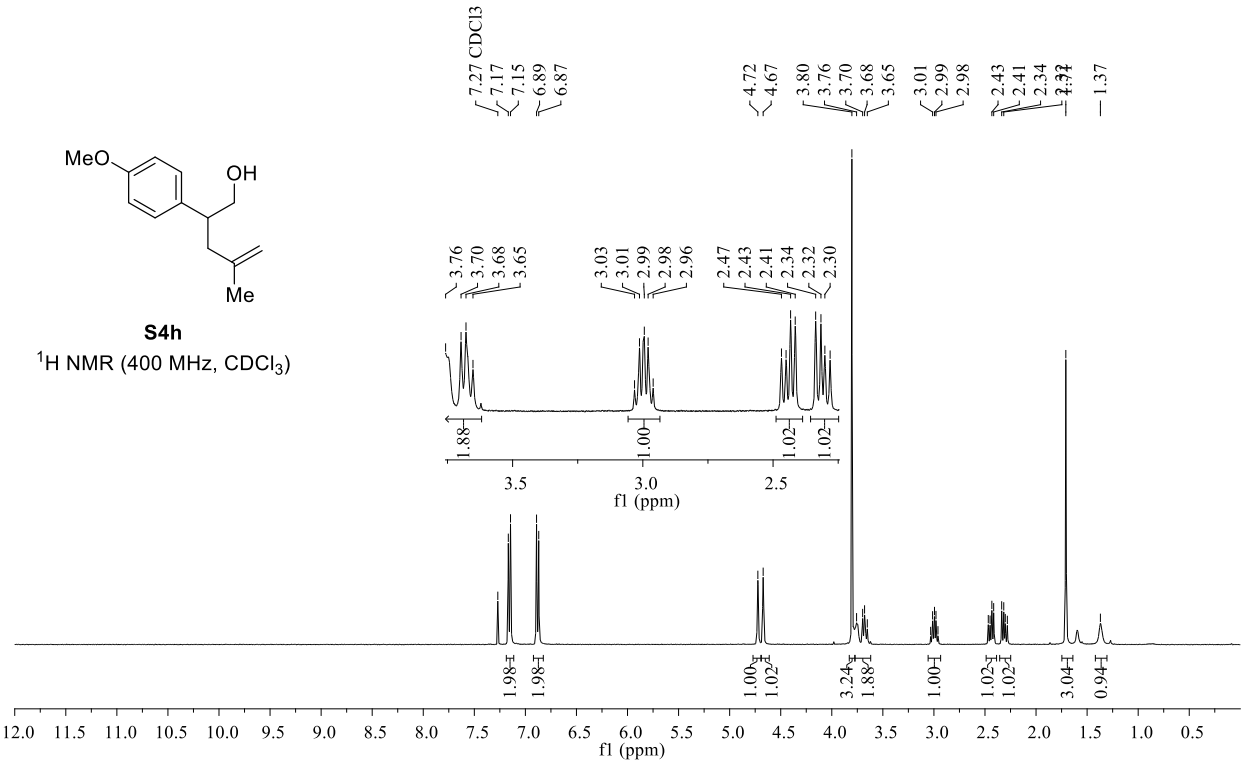
S4g

^{13}C NMR (101 MHz, $CDCl_3$)



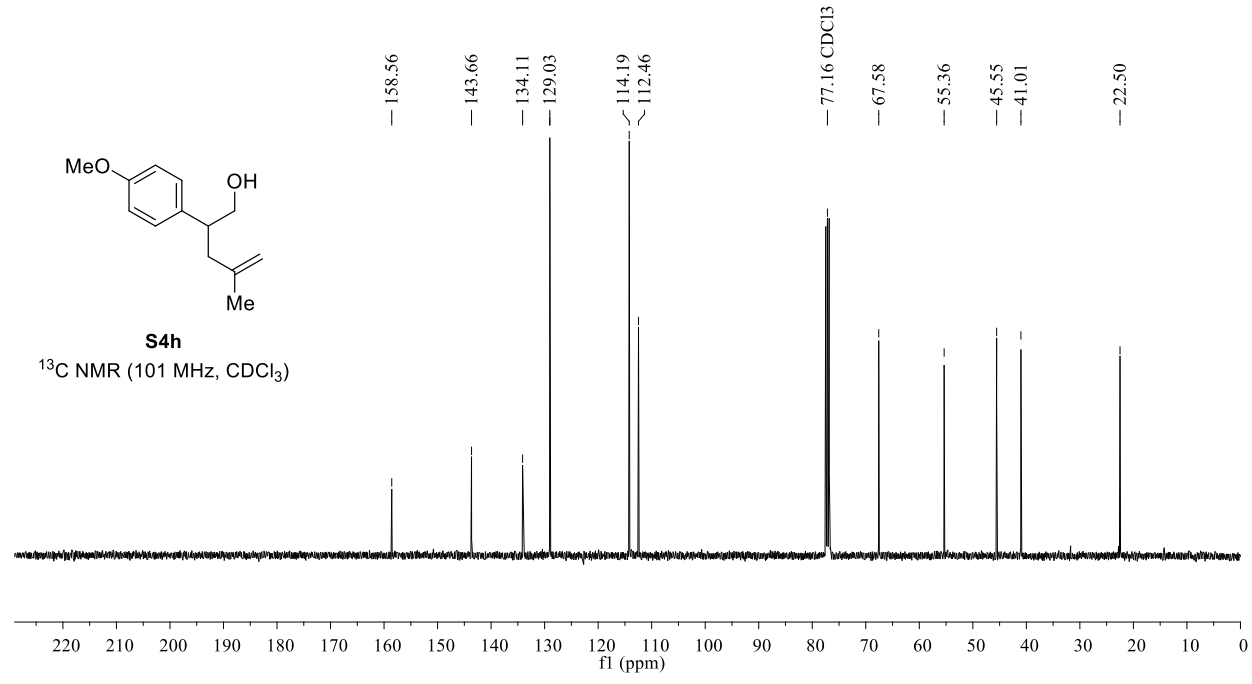
S4g

^{19}F NMR (376 MHz, $CDCl_3$)



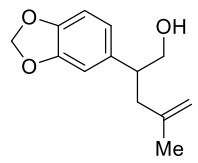
S4h

^{1}H NMR (400 MHz, $CDCl_3$)



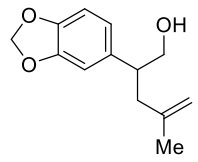
S4h

^{13}C NMR (101 MHz, $CDCl_3$)



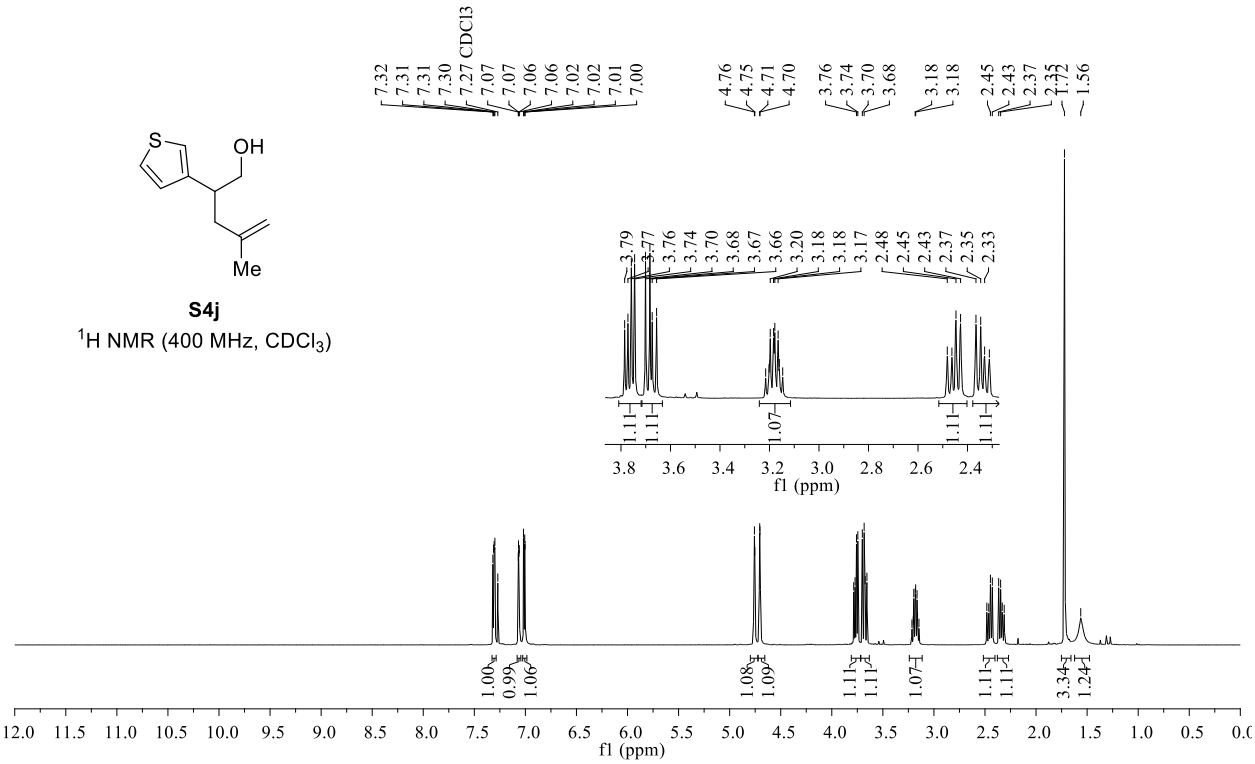
S4i

^{1}H NMR (400 MHz, $CDCl_3$)



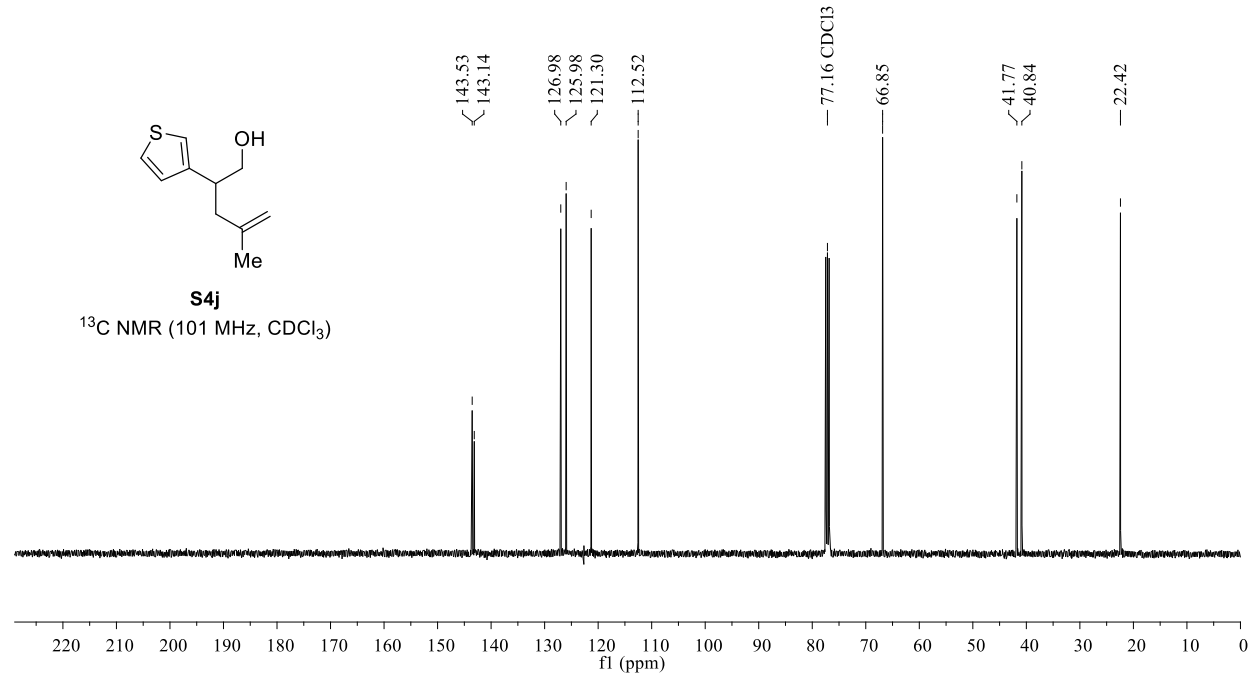
S4i

^{13}C NMR (101 MHz, $CDCl_3$)



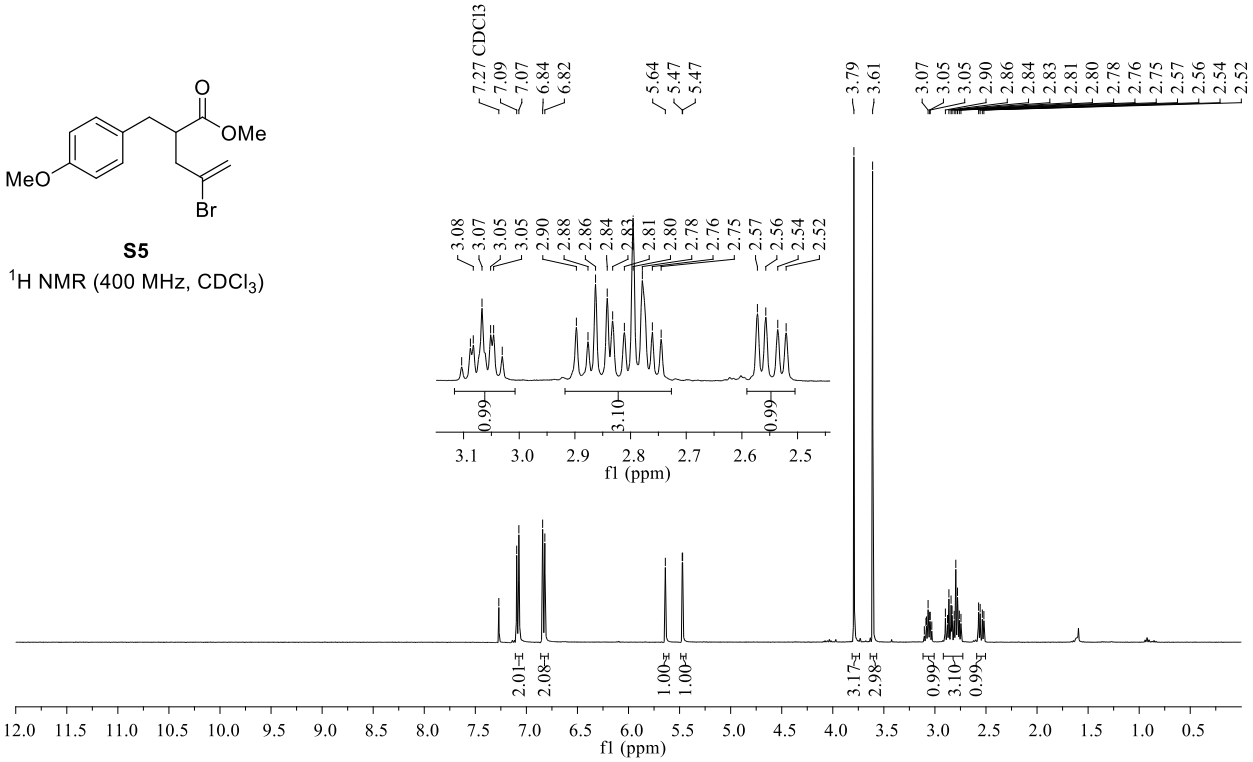
S4j

^{1}H NMR (400 MHz, $CDCl_3$)



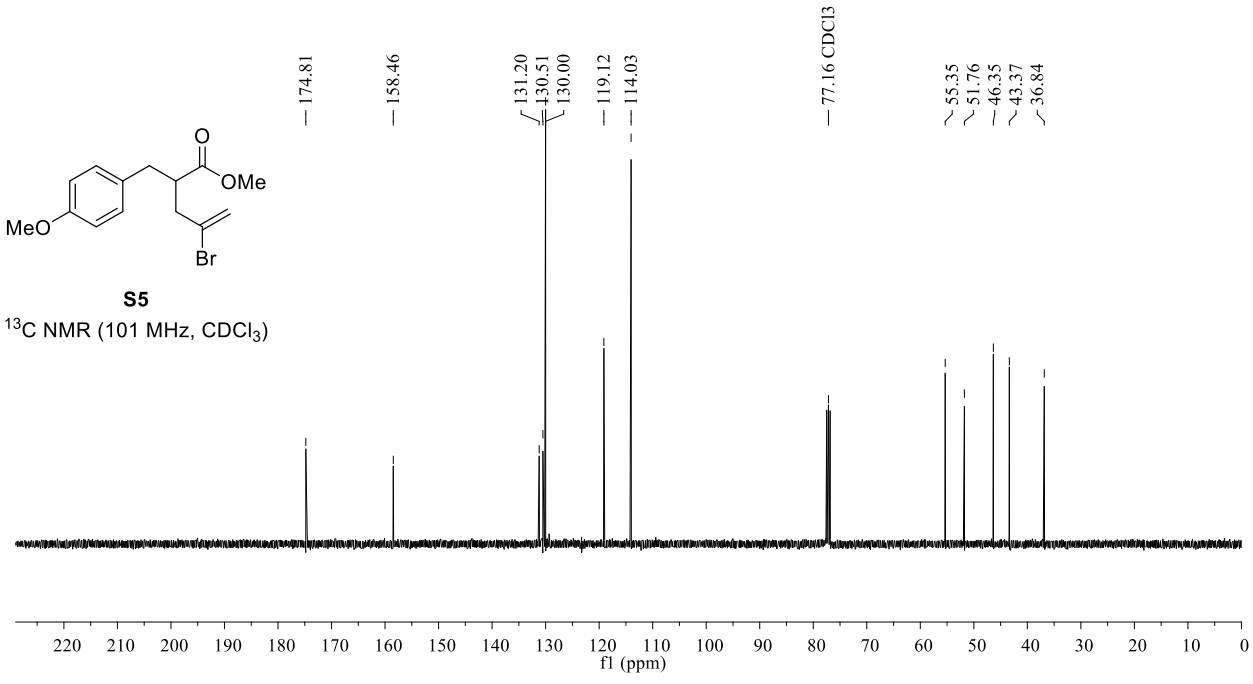
S4j

^{13}C NMR (101 MHz, $CDCl_3$)



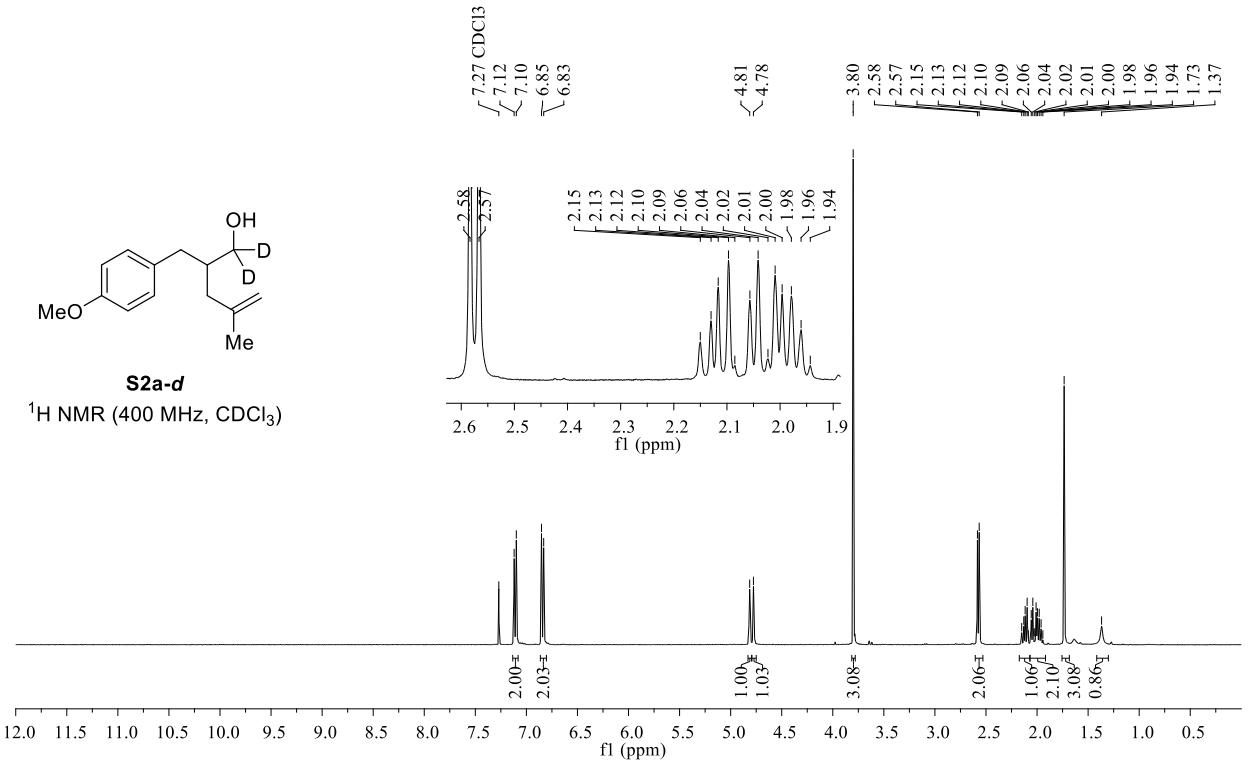
S5

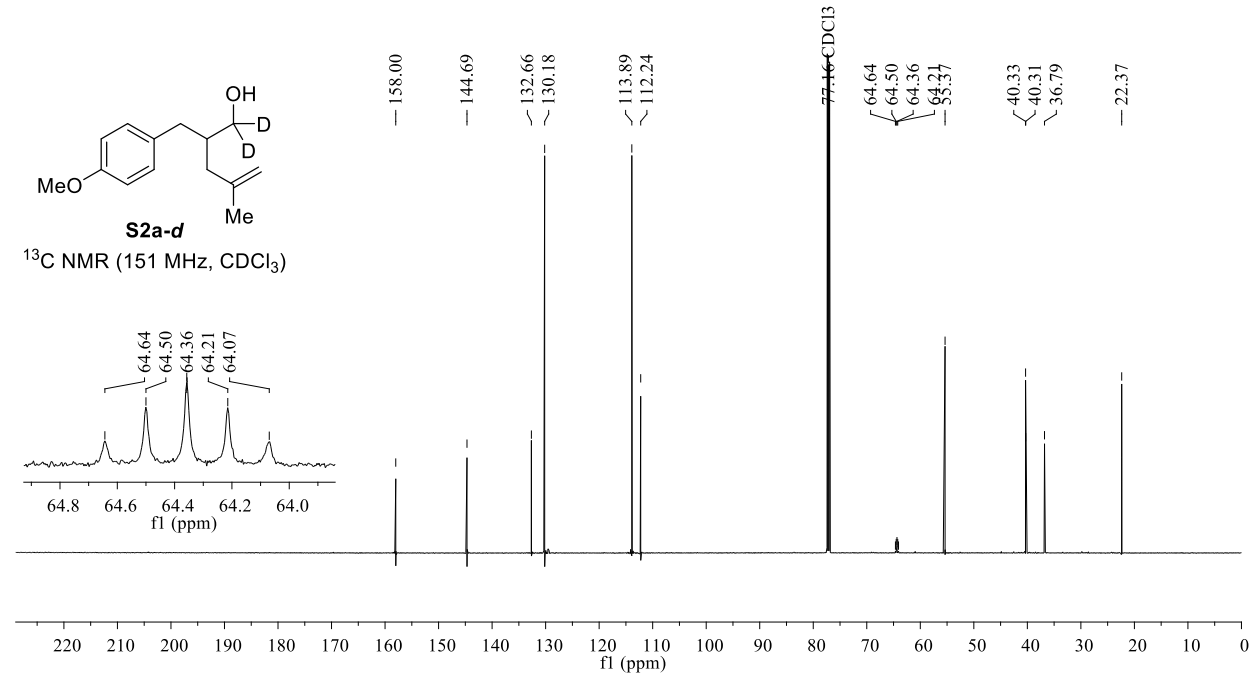
^{1}H NMR (400 MHz, $CDCl_3$)

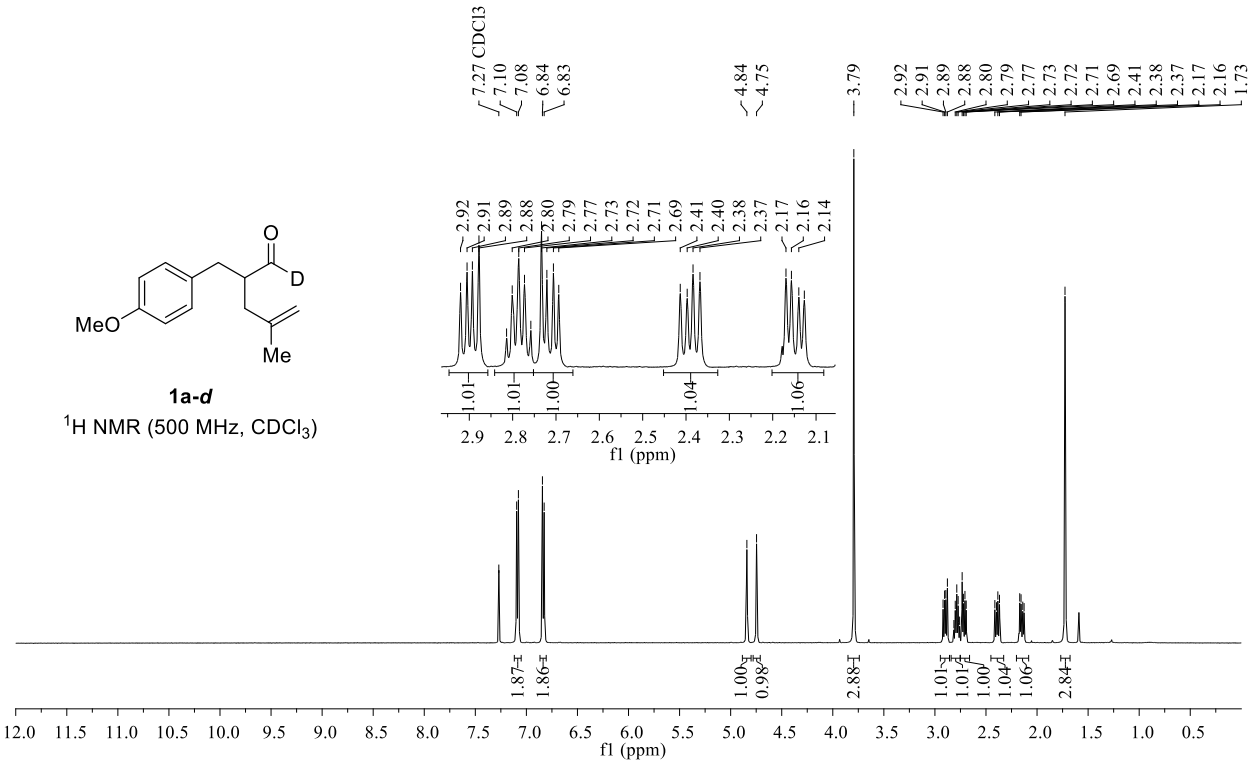


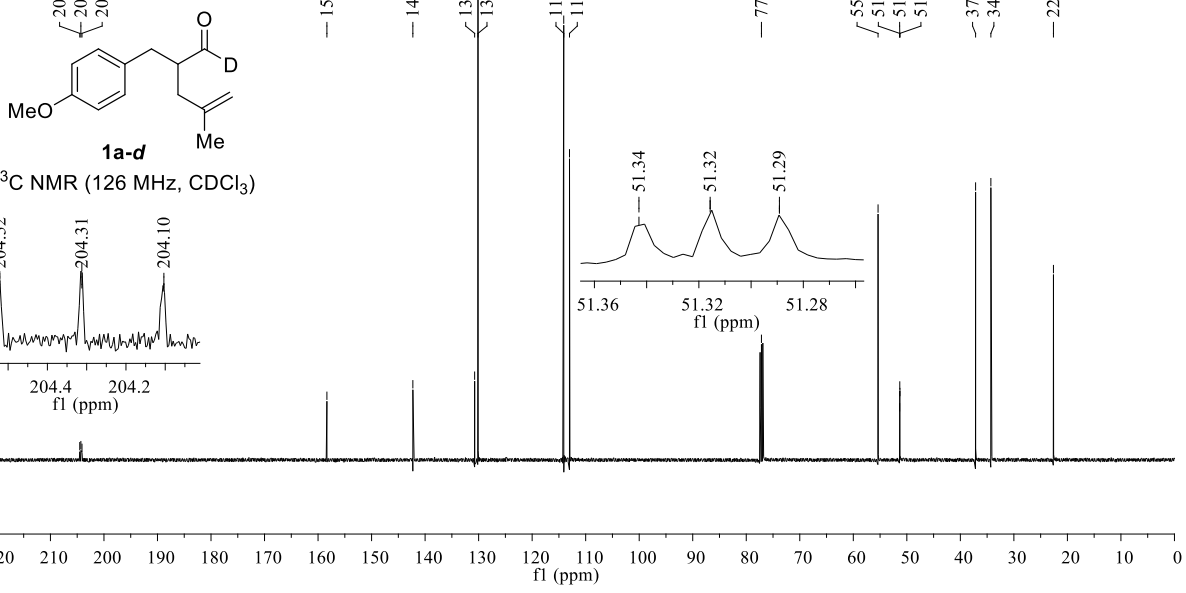
S5

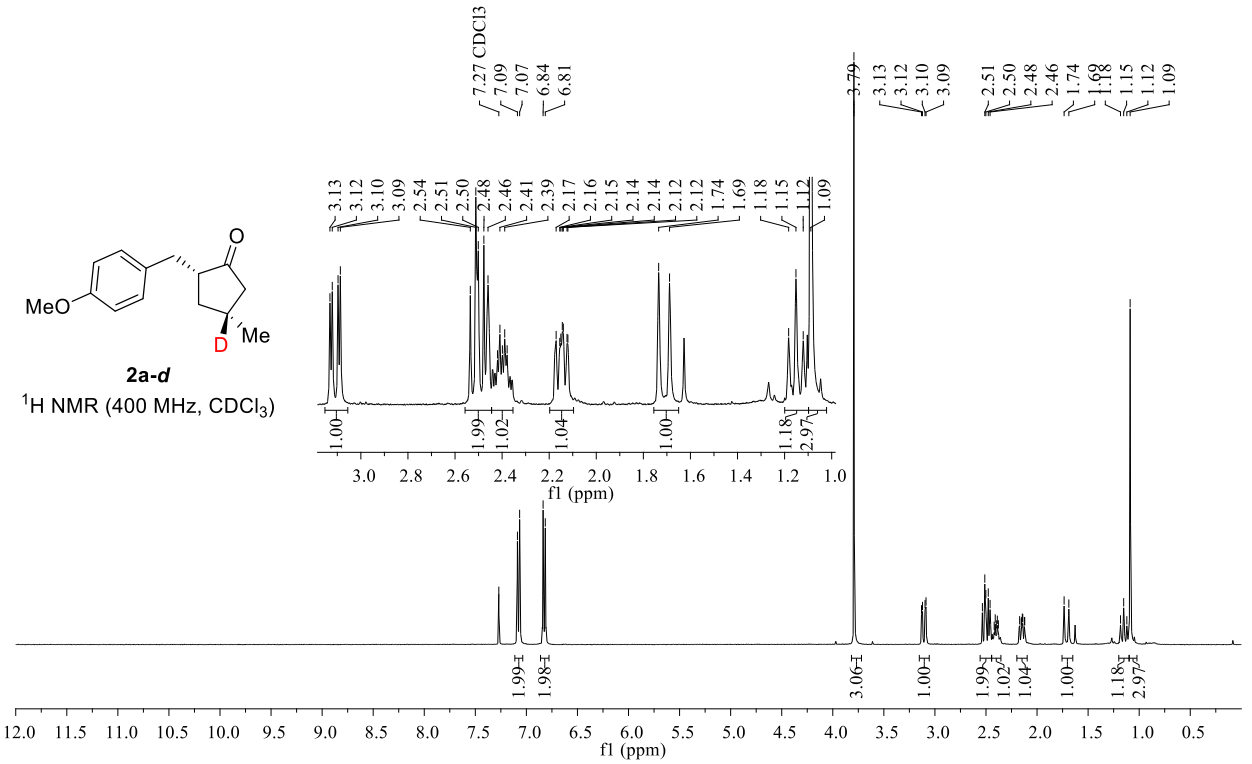
^{13}C NMR (101 MHz, $CDCl_3$)

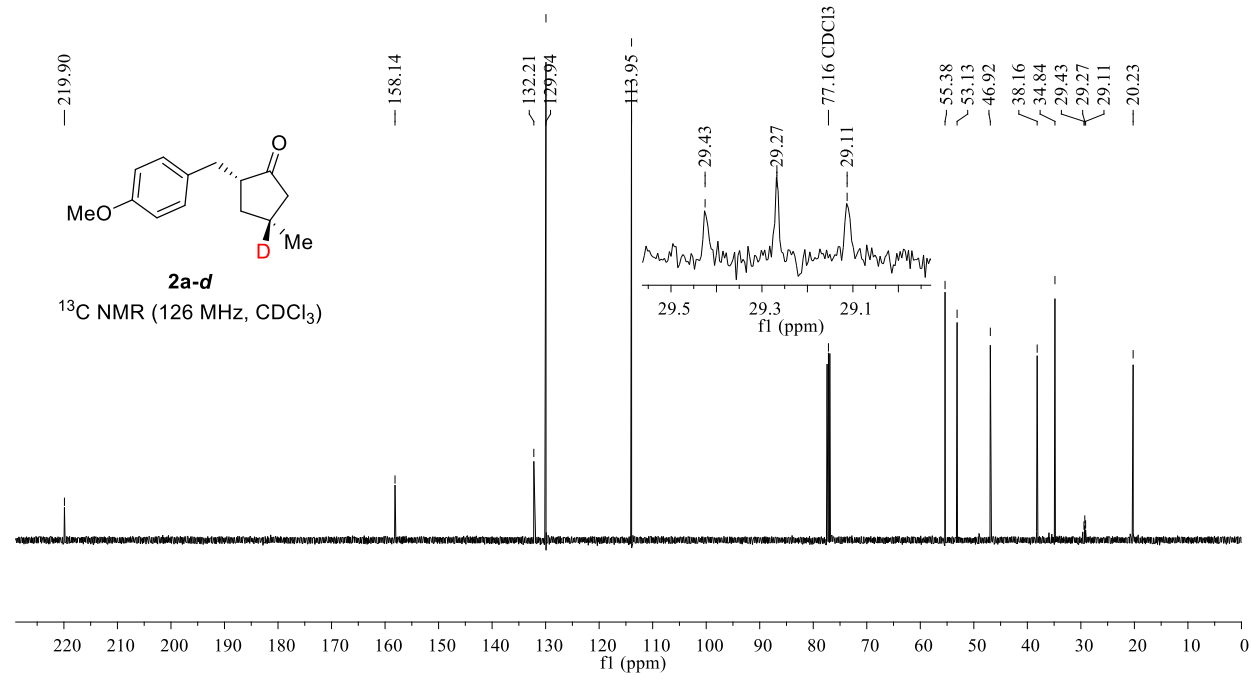

OH
D
D
MeO
Me
S2a-d
1H NMR (400 MHz, CDCl3)
7.27 CDCl3
7.12
7.10
6.85
6.83
4.81
4.78
3.80
2.58
2.57
2.15
2.13
2.12
2.10
2.09
2.06
2.04
2.02
2.01
2.00
1.98
1.96
1.94
1.73
1.37
2.00
2.03
1.00
1.03
3.08
2.06
1.06
2.10
3.08
0.86
f1 (ppm)

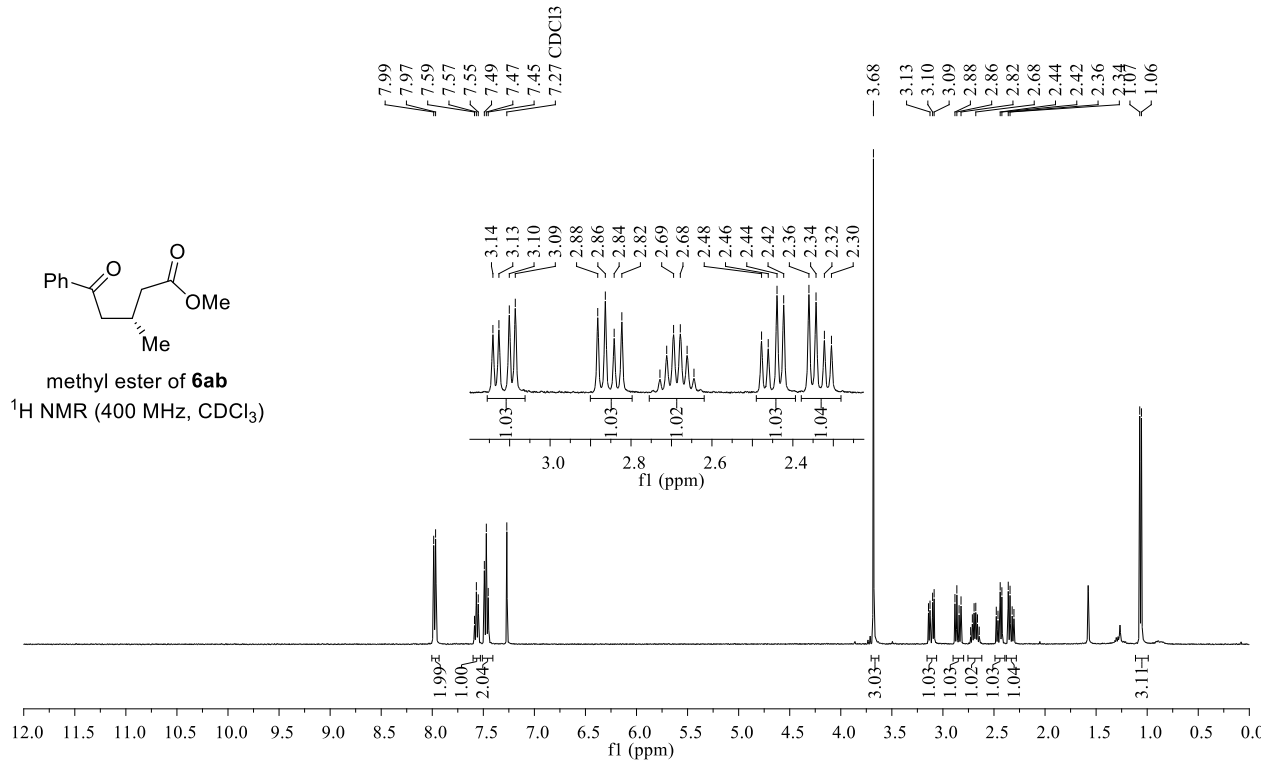

OH
D
D
MeO
Me
S2a-d
13C NMR (151 MHz, CDCl3)
158.00
144.69
132.66
130.18
113.89
112.24
77.16 CDCl3
64.64
64.50
64.36
64.21
55.37
40.33
40.31
36.79
22.37
f1 (ppm)

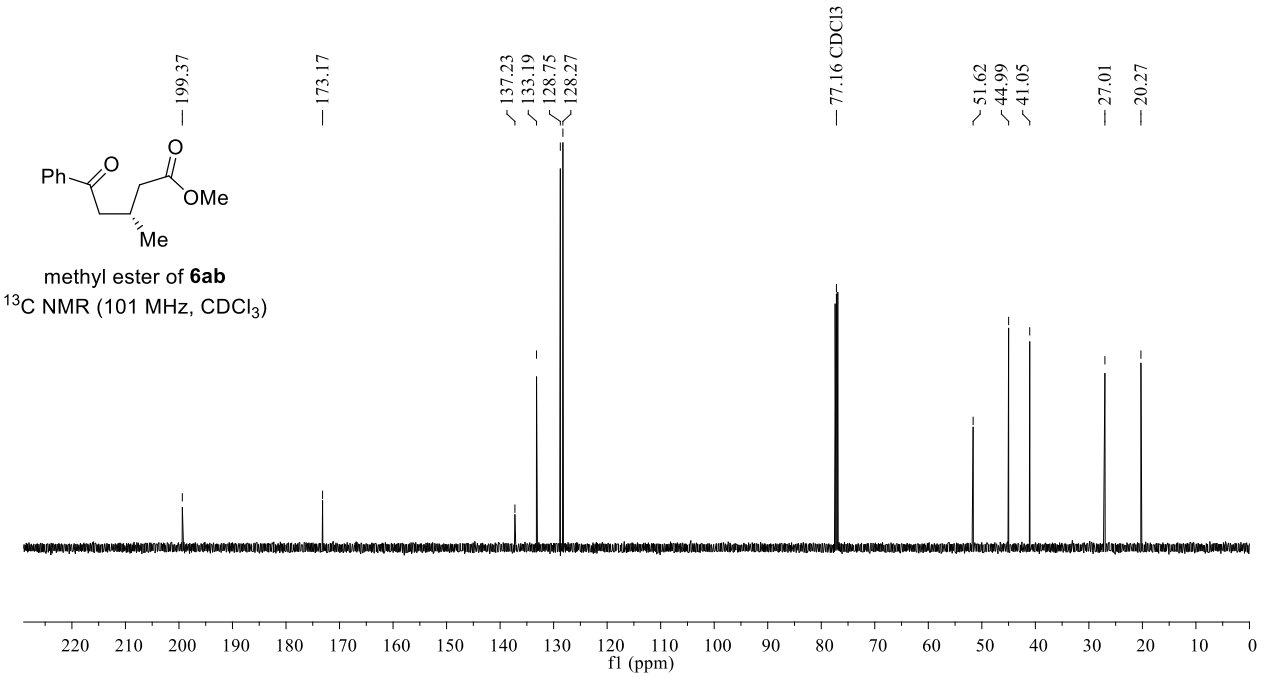

7.27 CDCl3
7.10
7.08
6.84
6.83
4.84
4.75
3.79
2.92
2.91
2.89
2.88
2.80
2.79
2.77
2.73
2.72
2.71
2.69
2.41
2.40
2.38
2.37
2.17
2.16
2.14
1.73
1.01
1.01
1.00
1.04
1.06
1.87
1.86
1.00
0.98
2.88
1.01
1.01
1.00
1.04
1.06
2.84
f1 (ppm)

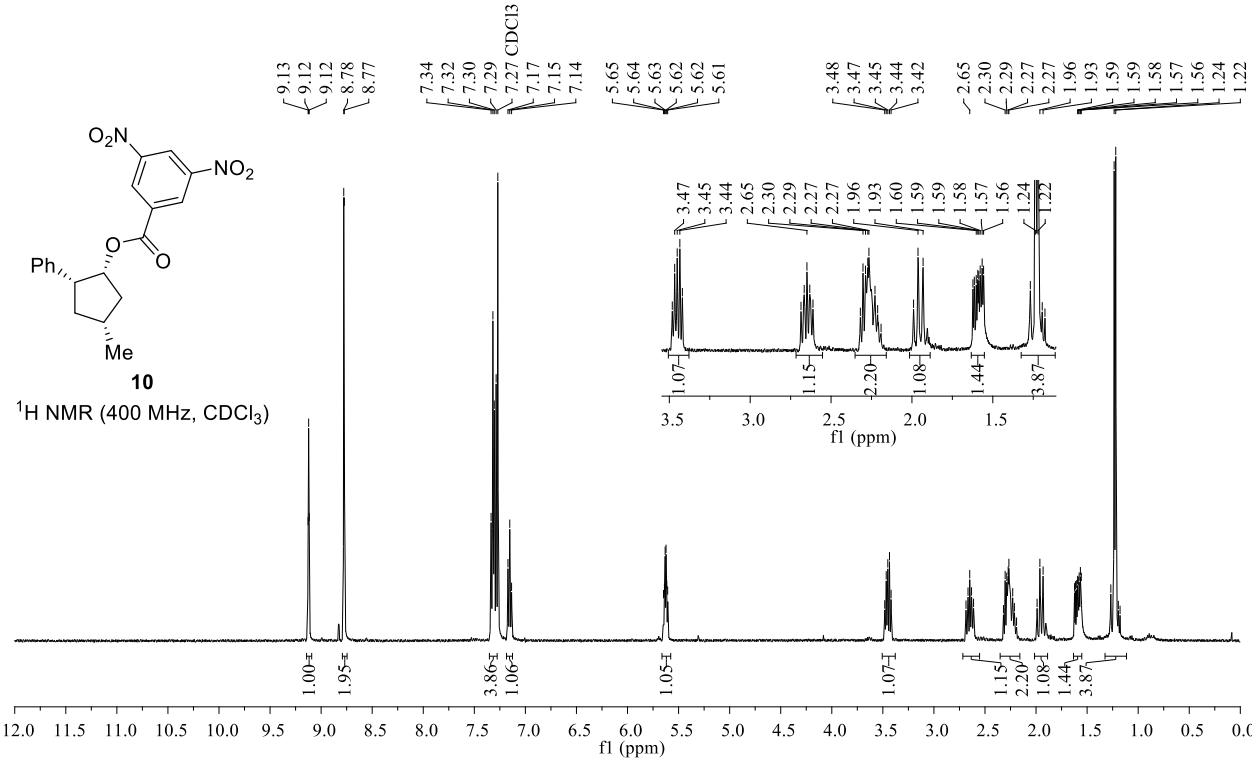

204.52
204.31
204.10
158.35
142.29
130.74
130.11
114.10
113.02
77.16 CDCl3
55.37
51.34
51.32
51.29
37.15
34.30
22.60
51.34
51.32
51.29
f1 (ppm)
f1 (ppm)

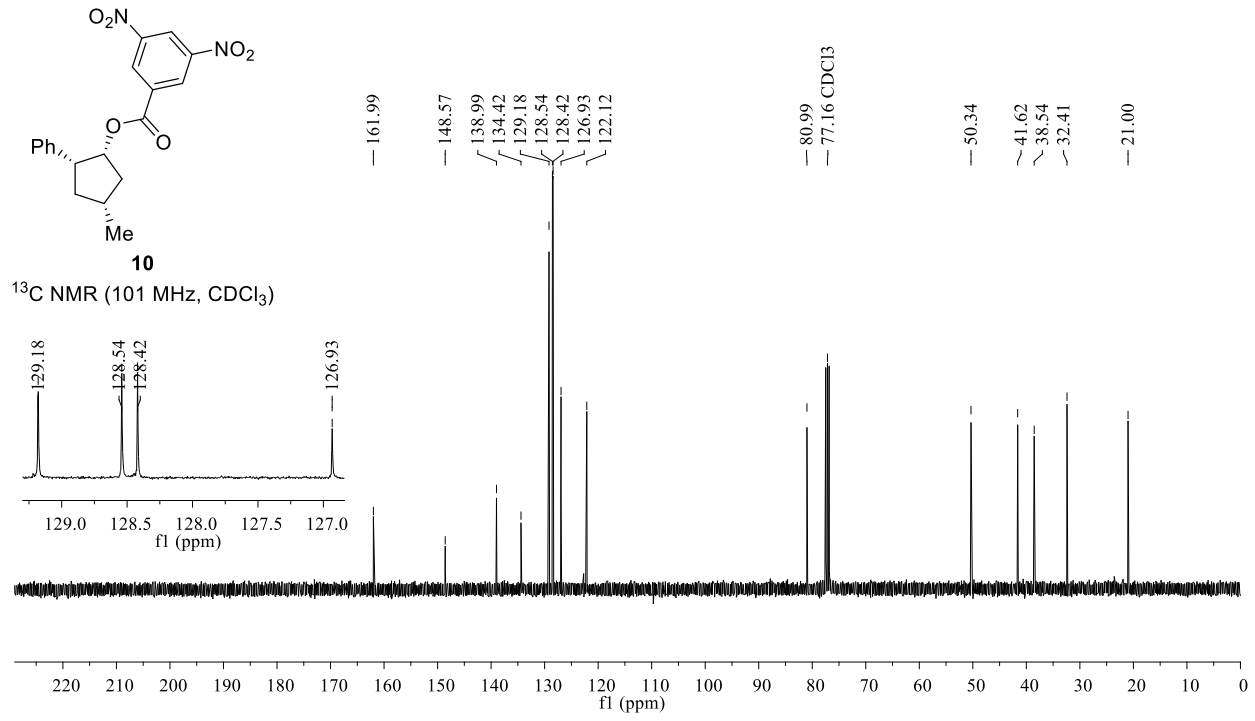

MeO
O
D
Me
2a-d
1H NMR (400 MHz, CDCl3)
7.27 CDCl3
7.09
7.07
6.84
6.81
3.79
3.13
3.12
3.10
3.09
2.51
2.50
2.48
2.46
1.74
1.68
1.18
1.15
1.12
1.09
fl (ppm)

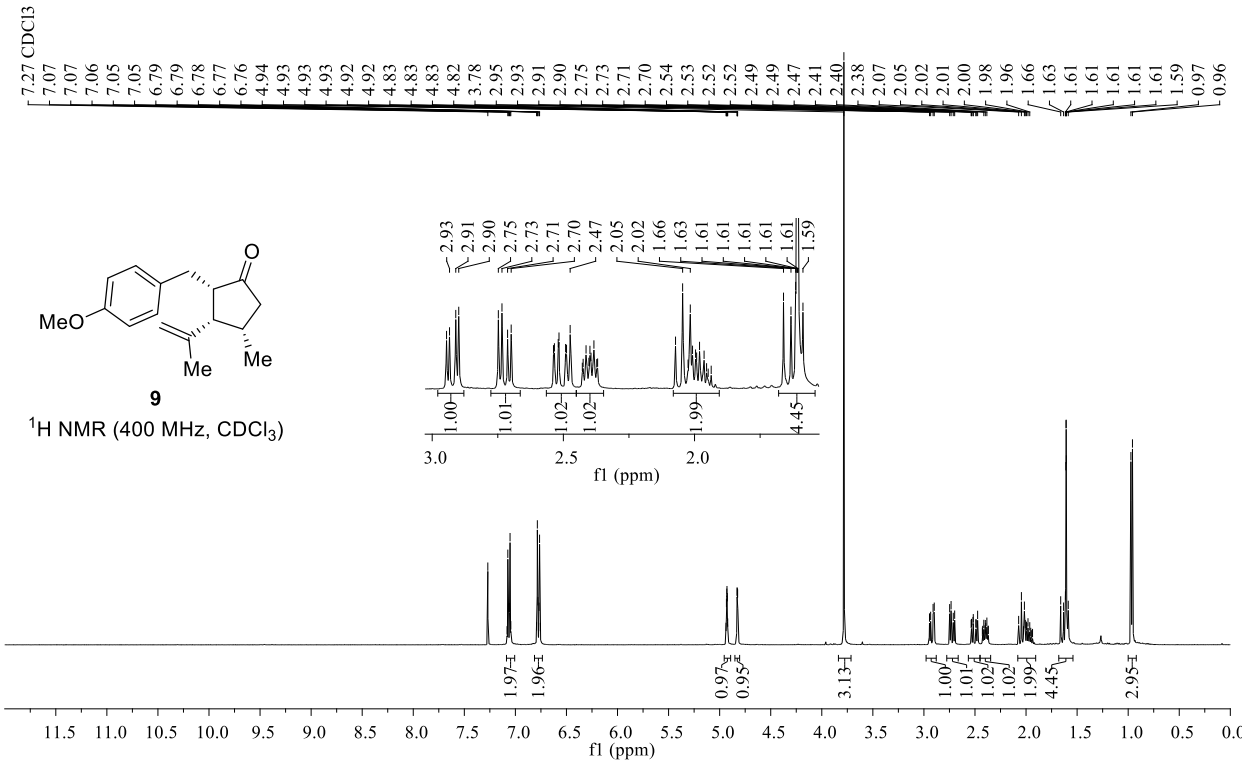

MeO
O
D
Me
2a-d
13C NMR (126 MHz, CDCl3)
219.90
158.14
132.21
129.94
113.95
77.16 CDCl3
55.38
53.13
46.92
38.16
34.84
29.43
29.27
29.11
20.23
fl (ppm)

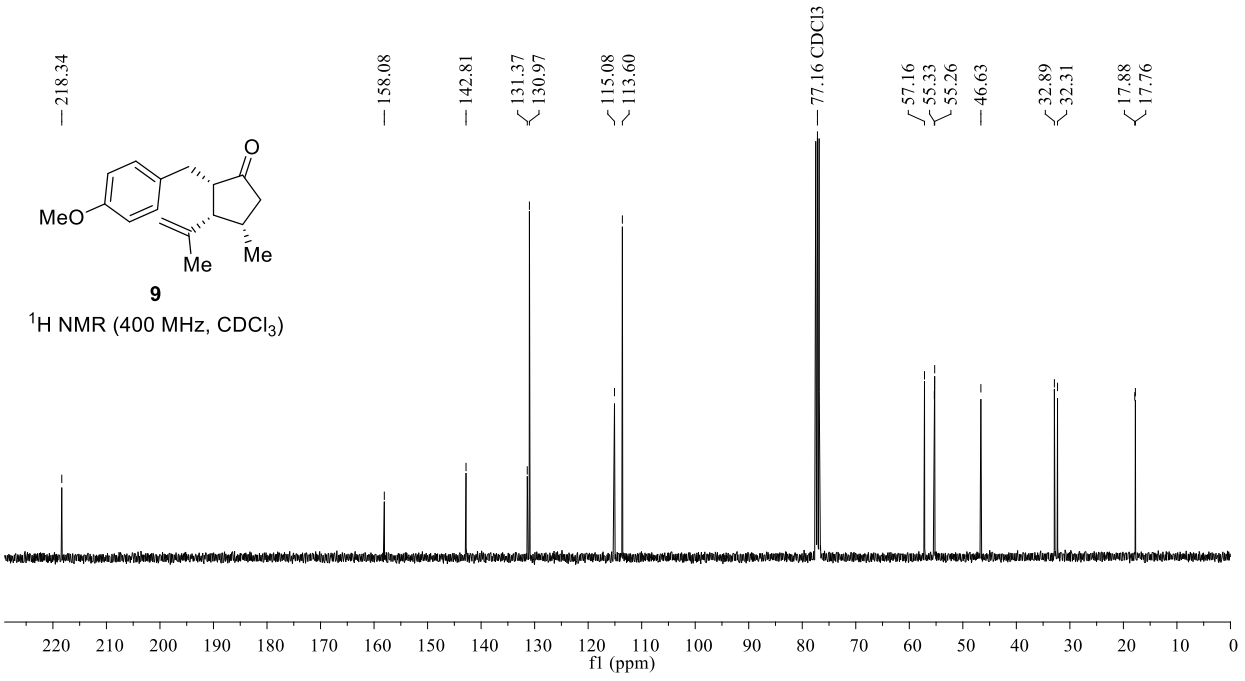

methyl ester of 6ab
1H NMR (400 MHz, CDCl3)
f1 (ppm)

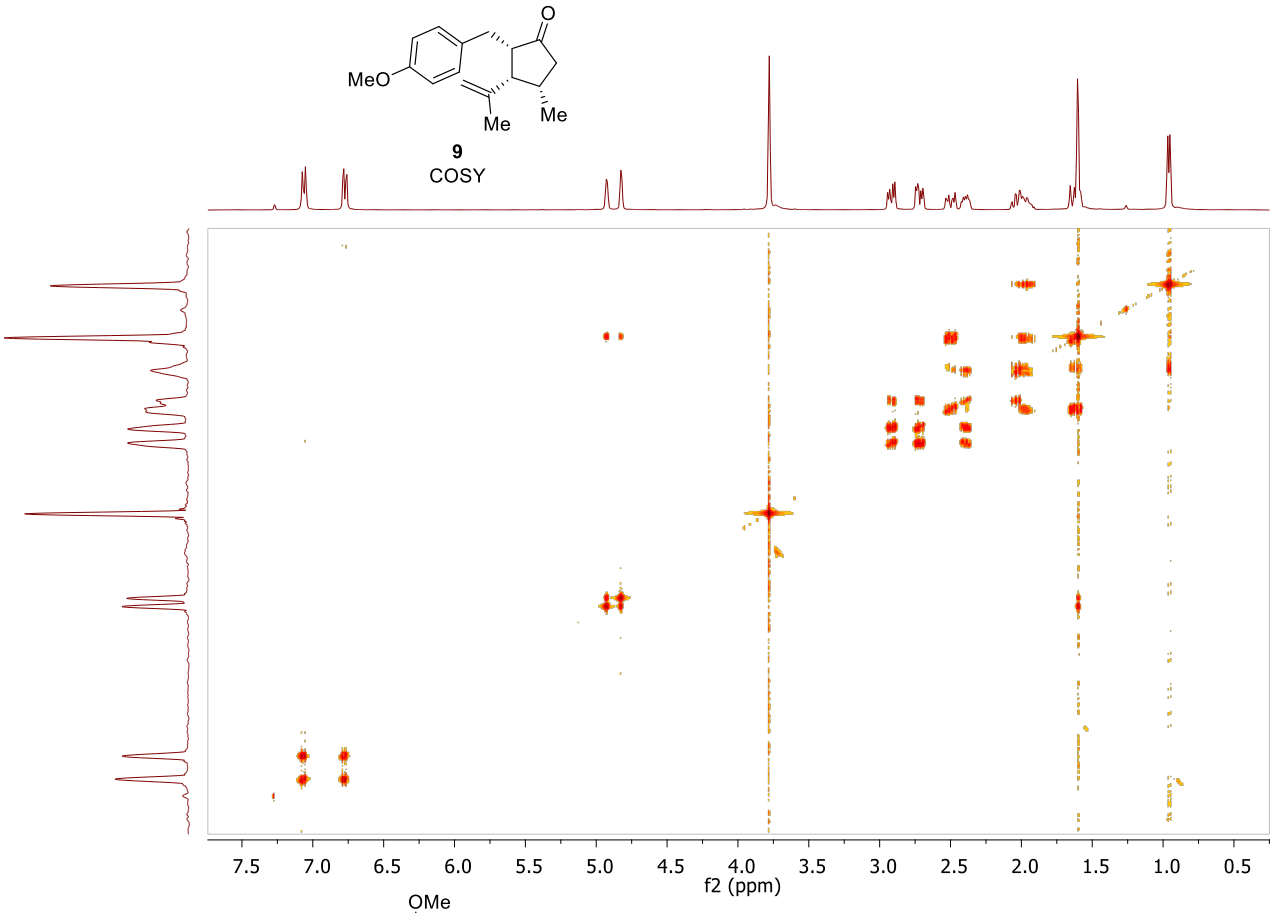

methyl ester of 6ab
13C NMR (101 MHz, CDCl3)
f1 (ppm)

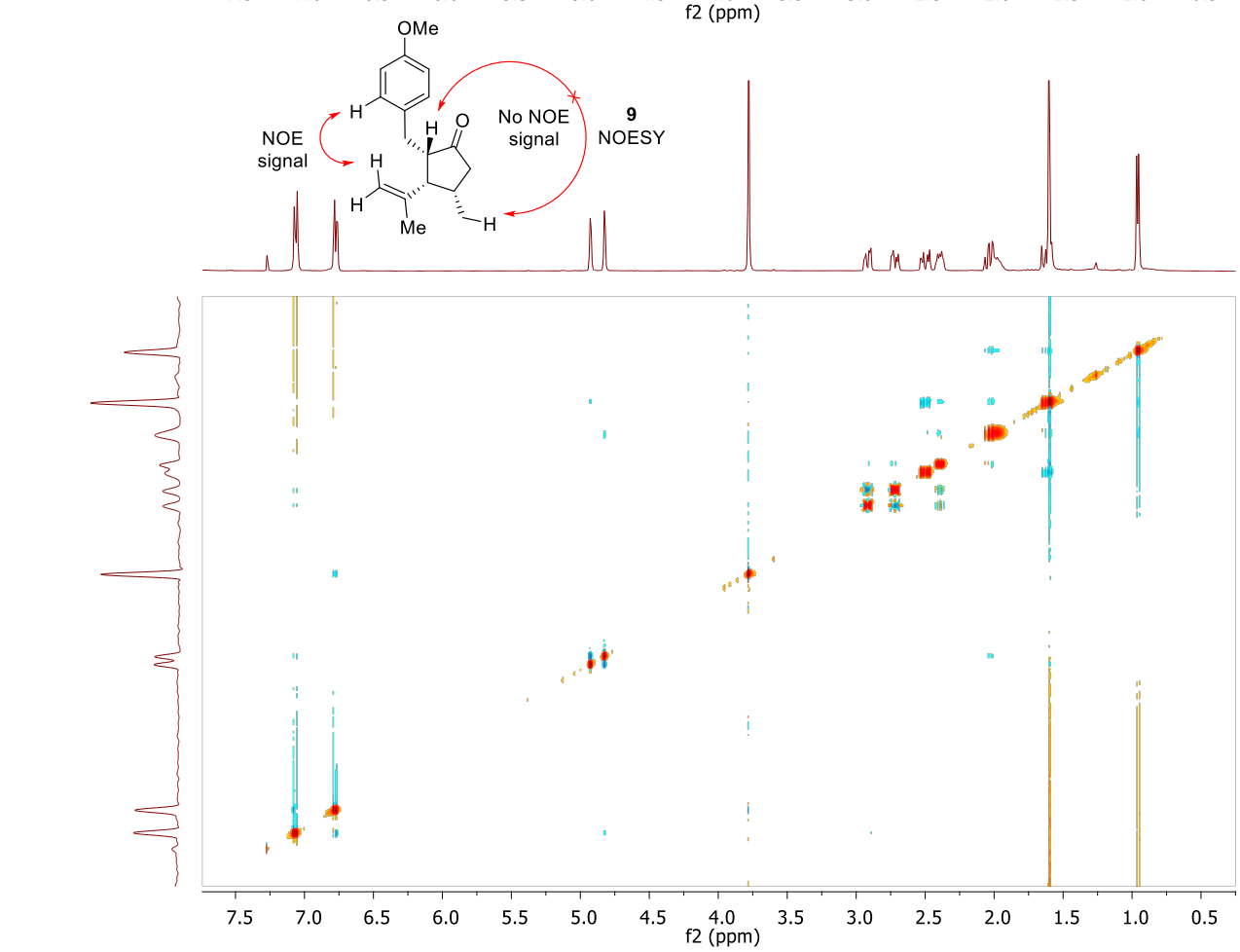

10
1H NMR (400 MHz, CDCl3)
fl (ppm)

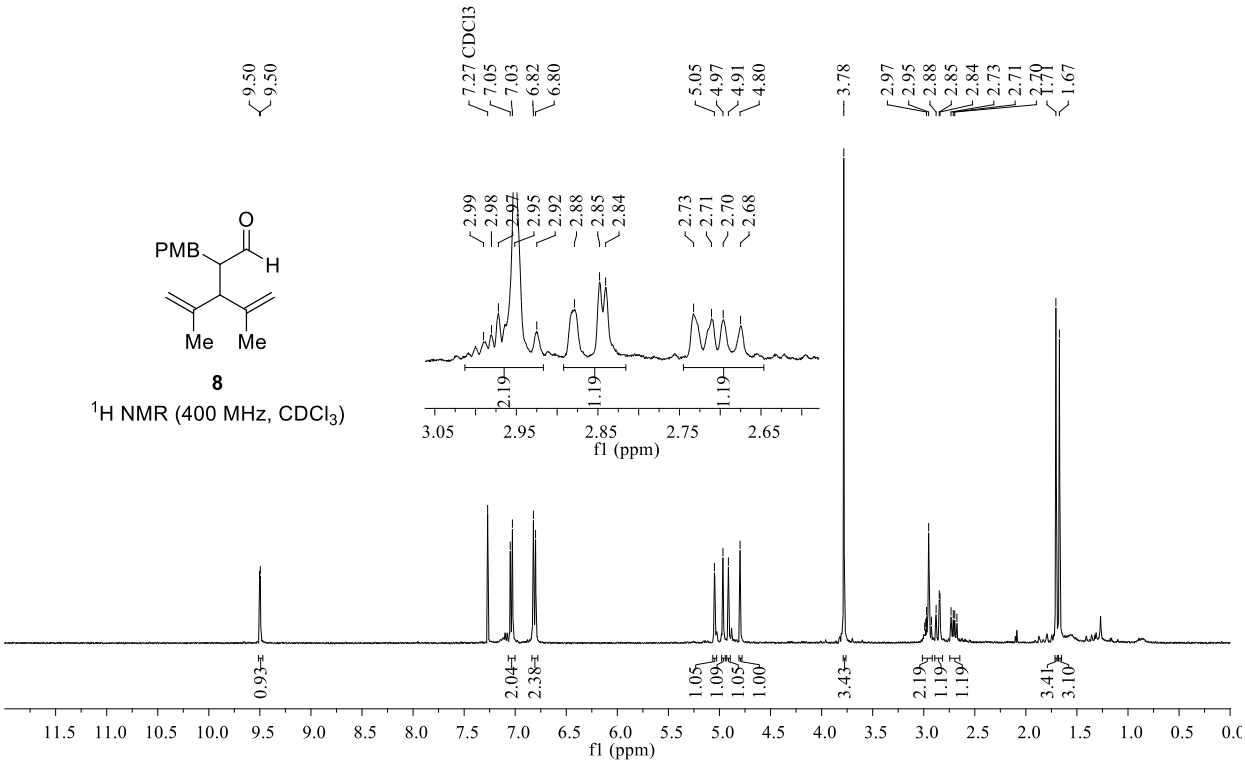

10
13C NMR (101 MHz, CDCl3)
fl (ppm)

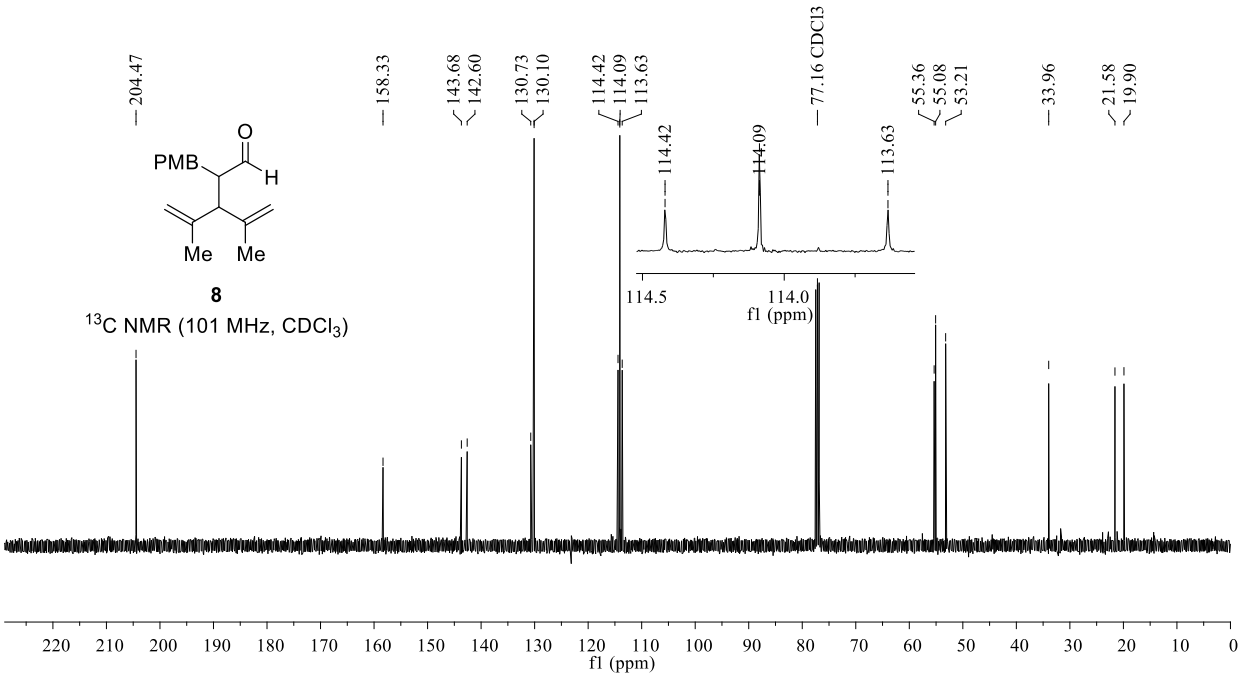

7.27 CDCl3
7.07
7.07
7.06
7.05
7.05
6.79
6.79
6.78
6.77
6.76
4.94
4.93
4.93
4.93
4.92
4.92
4.83
4.83
4.83
4.82
3.78
2.95
2.93
2.91
2.90
2.75
2.73
2.71
2.70
2.54
2.53
2.52
2.52
2.49
2.49
2.47
2.41
2.40
2.38
2.07
2.05
2.02
2.01
2.00
1.98
1.96
1.66
1.63
1.61
1.61
1.61
1.61
1.61
1.59
0.97
0.96
MeO
Me
Me
O
9
1H NMR (400 MHz, CDCl3)
2.93
2.91
2.90
2.75
2.73
2.71
2.70
2.47
2.05
2.02
1.66
1.63
1.61
1.61
1.61
1.61
1.59
1.00
1.01
1.02
1.02
1.99
4.45
3.0
2.5
2.0
f1 (ppm)
1.97
1.96
0.97
0.95
3.13
1.00
1.01
1.02
1.02
1.99
4.45
2.95
11.5 11.0 10.5 10.0 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
f1 (ppm)

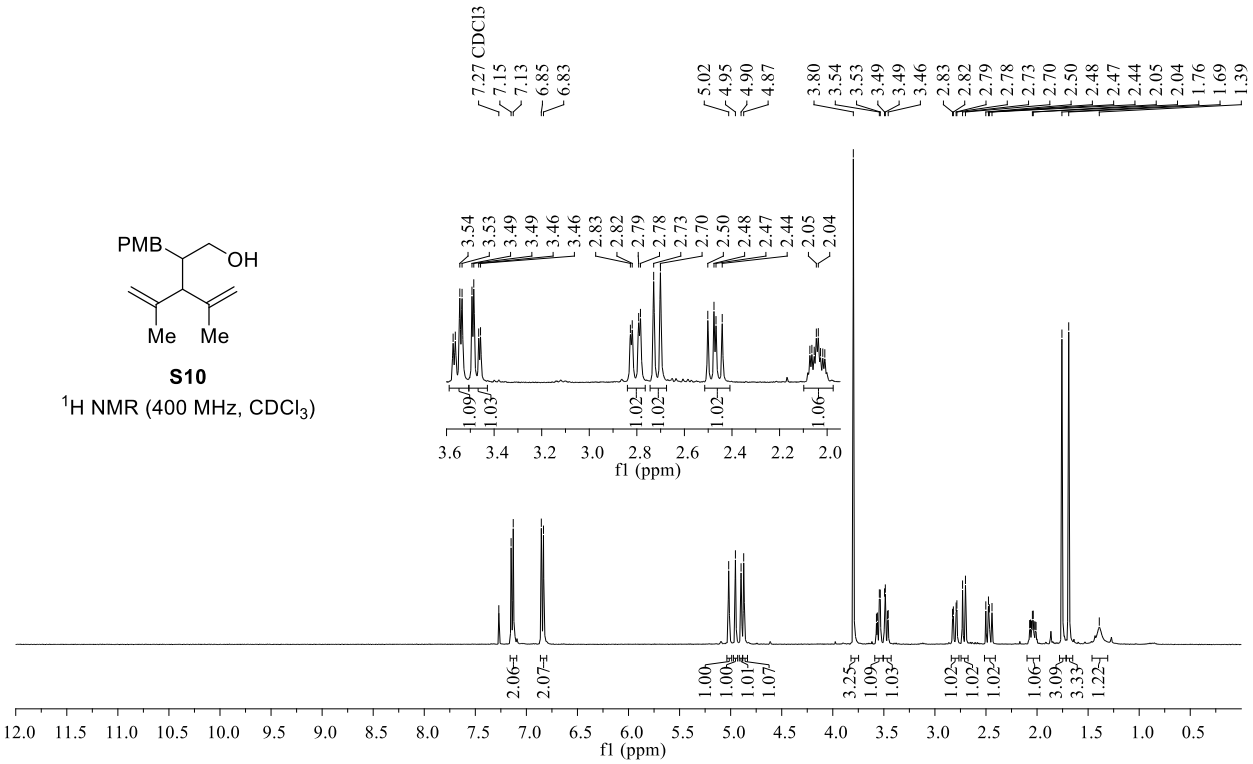

218.34
158.08
142.81
131.37
130.97
115.08
113.60
77.16 CDCl3
57.16
55.33
55.26
46.63
32.89
32.31
17.88
17.76
MeO
Me
Me
O
9
1H NMR (400 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

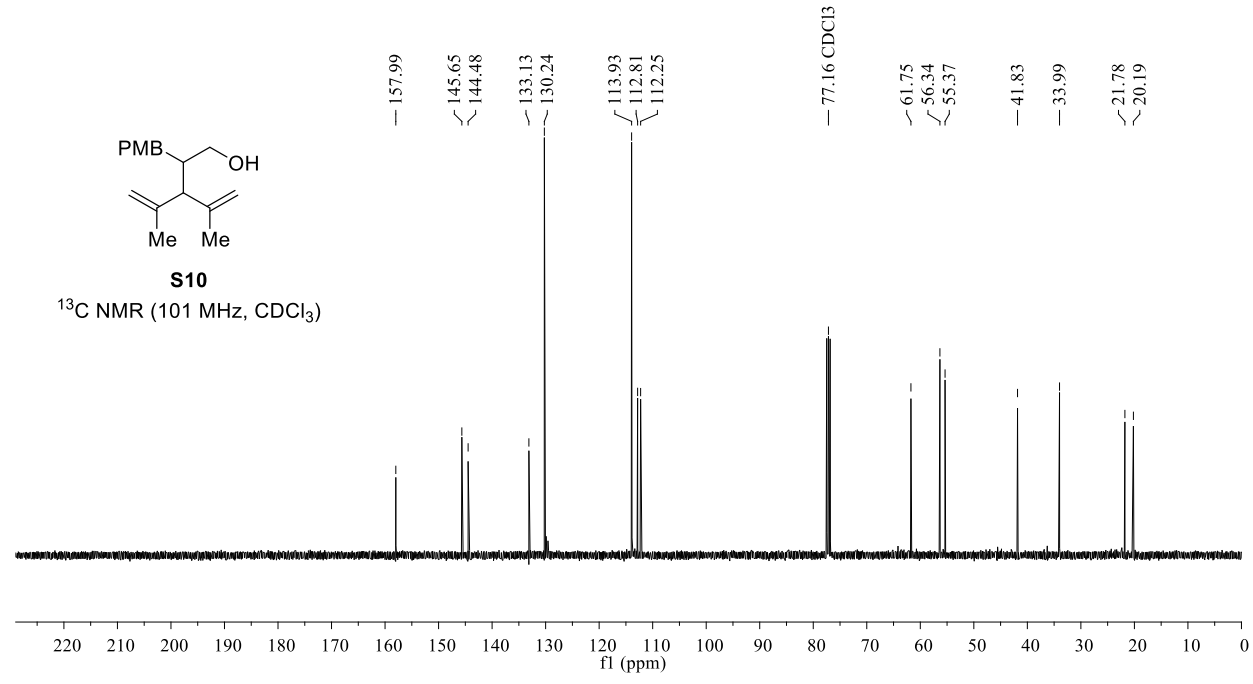

MeO
O
Me
Me
9
COSY
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f2 (ppm)


OMe
H
H
O
H
H
Me
H
NOE signal
No NOE signal
9
NOESY
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
f2 (ppm)

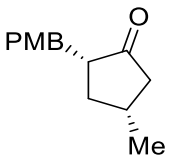

PMB
O
H
Me
Me
8
1H NMR (400 MHz, CDCl3)
f1 (ppm)


PMB
O
H
Me
Me
8
13C NMR (101 MHz, CDCl3)
f1 (ppm)

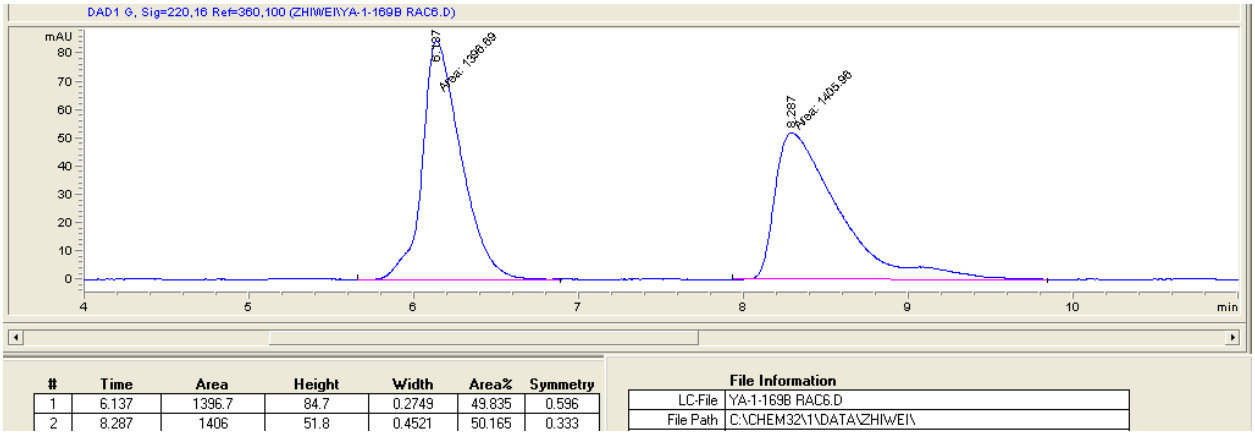

PMB
OH
Me Me
S10
1H NMR (400 MHz, CDCl3)
7.27 CDCl3
7.15
7.13
6.85
6.83
5.02
4.95
4.90
4.87
3.80
3.54
3.53
3.49
3.49
3.46
2.83
2.82
2.79
2.78
2.73
2.70
2.50
2.48
2.47
2.44
2.05
2.04
1.76
1.69
1.39
f1 (ppm)


PMB
OH
Me Me
S10
13C NMR (101 MHz, CDCl3)
157.99
145.65
144.48
133.13
130.24
113.93
112.81
112.25
77.16 CDCl3
61.75
56.34
55.37
41.83
33.99
21.78
20.19
f1 (ppm)

14. SFC Spectra



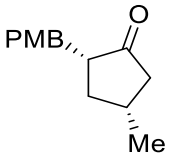
(±)-**2a**



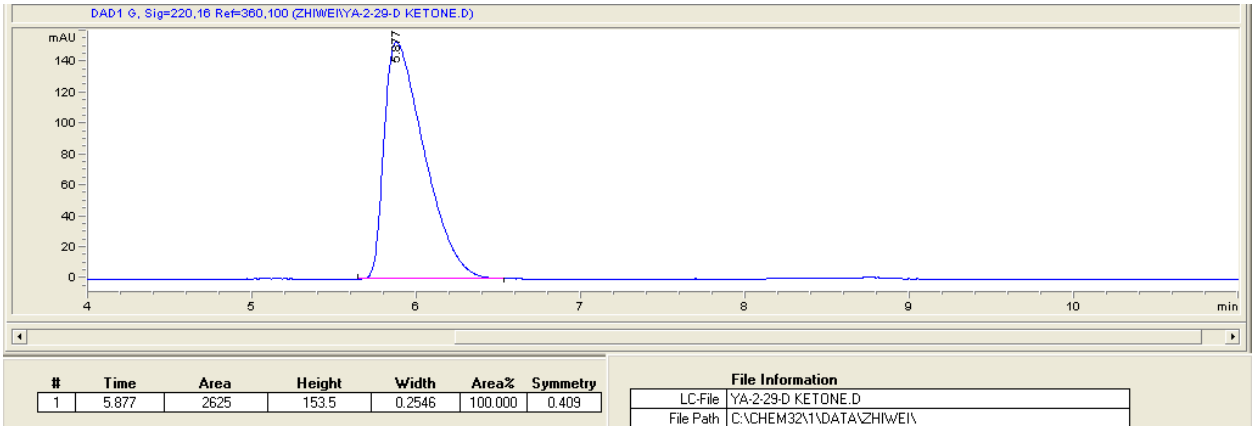
#	Time	Area	Height	Width	Area%	Symmetry
1	6.137	1396.7	84.7	0.2749	49.835	0.596
2	8.287	1406	51.8	0.4521	50.165	0.333

File Information

LC-File	YA-1-169B RAC6.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\



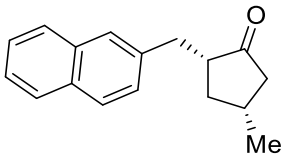
(+)-**2a**



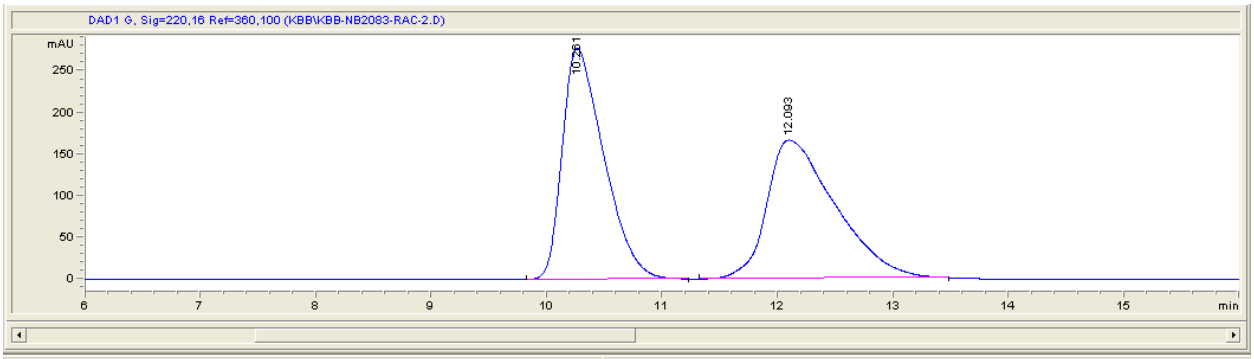
#	Time	Area	Height	Width	Area%	Symmetry
1	5.877	2625	153.5	0.2546	100.000	0.409

File Information

LC-File	YA-2-29-D KETONE.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\

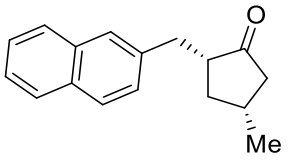


(±)-**2b**

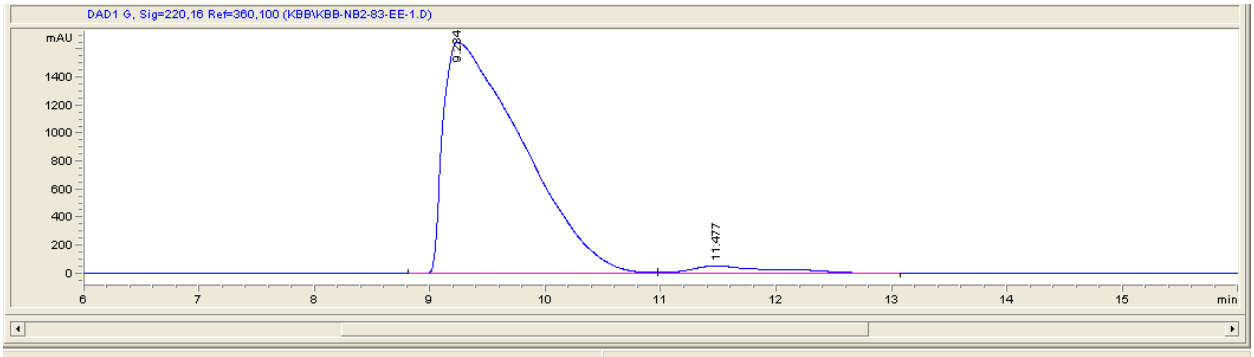


#	Time	Area	Height	Width	Area%	Symmetry
1	10.261	6941.6	277.5	0.3558	50.179	0.534
2	12.093	6892.1	166.4	0.5433	49.821	0.454

File Information	
LC-File	KBB-NB2083-RAC-2.D
File Path	C:\CHEM32\1\DATA\KBB\

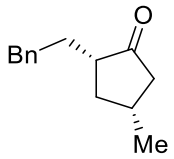


(+)-**2b**

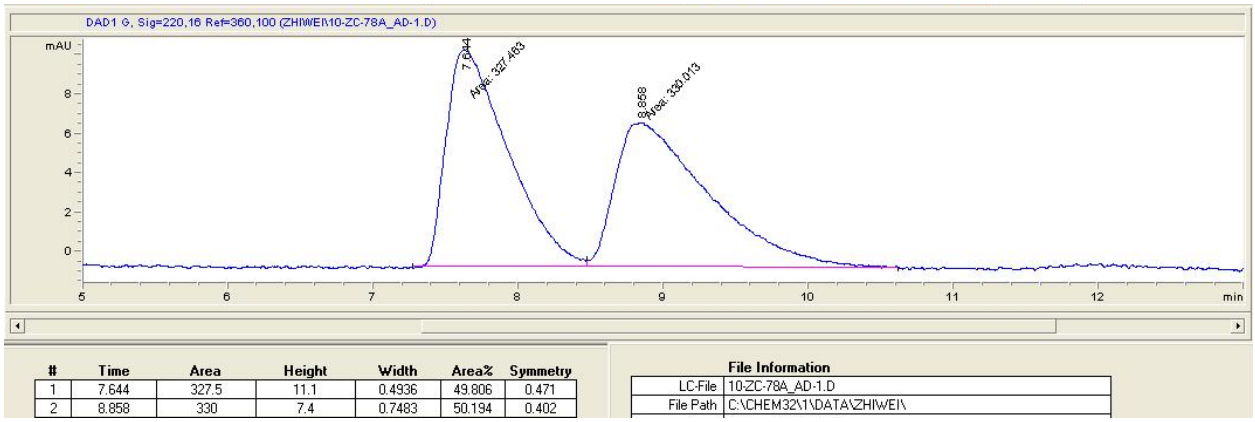


#	Time	Area	Height	Width	Area%	Symmetry
1	9.234	78823.5	1652.9	0.6134	96.567	0.202
2	11.477	2802.4	53.1	0.6358	3.433	0.388

File Information	
LC-File	KBB-NB2-83-EE-1.D
File Path	C:\CHEM32\1\DATA\KBB\

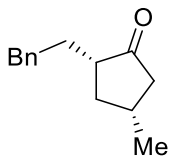


(±)-**2c**

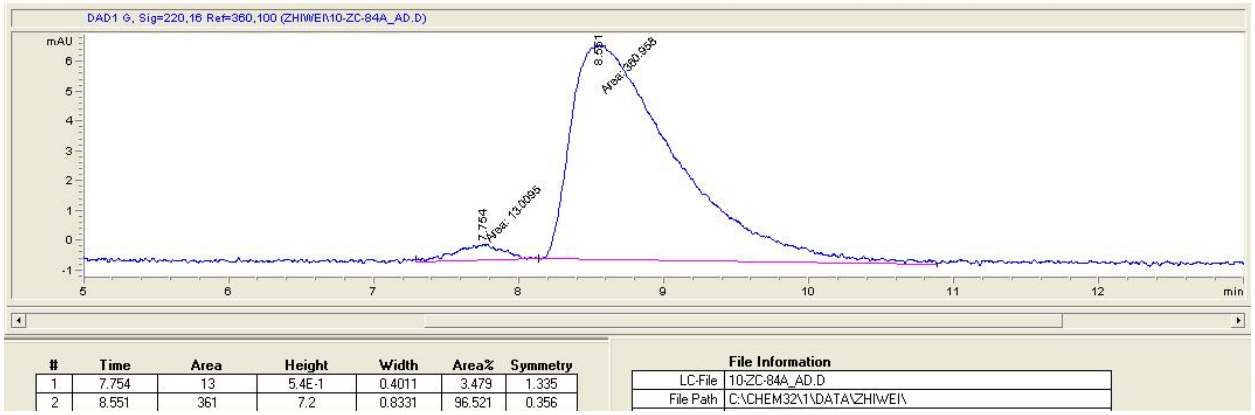


#	Time	Area	Height	Width	Area%	Symmetry
1	7.644	327.5	11.1	0.4936	49.806	0.471
2	8.858	330	7.4	0.7483	50.194	0.402

File Information	
LC-File	10-ZC-78A_AD-1.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\

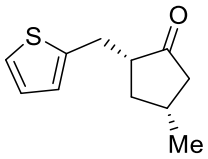


(+)-**2c**

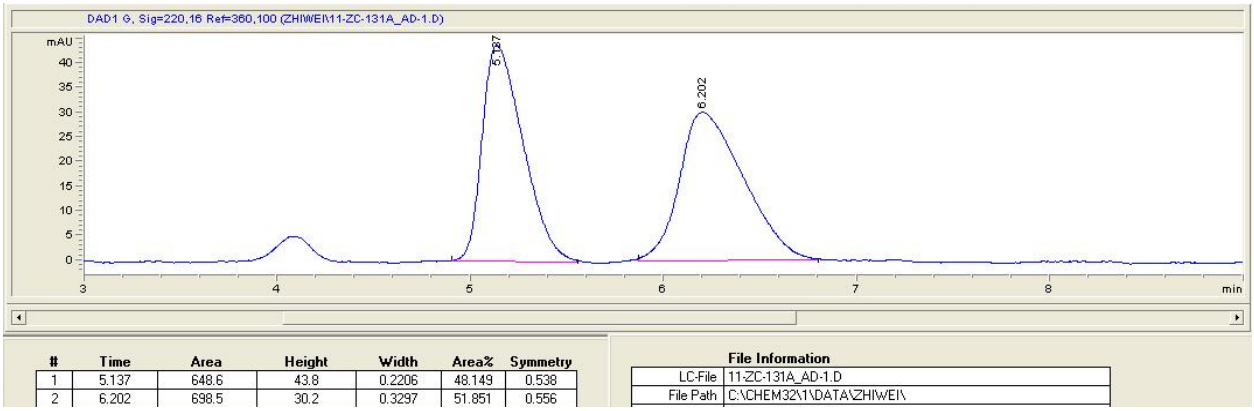


#	Time	Area	Height	Width	Area%	Symmetry
1	7.754	13	5.4E-1	0.4011	3.479	1.335
2	8.551	361	7.2	0.8331	96.521	0.356

File Information	
LC-File	10-ZC-84A_AD.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\



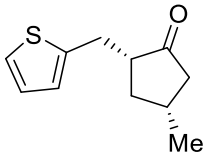
(±)-**2d**



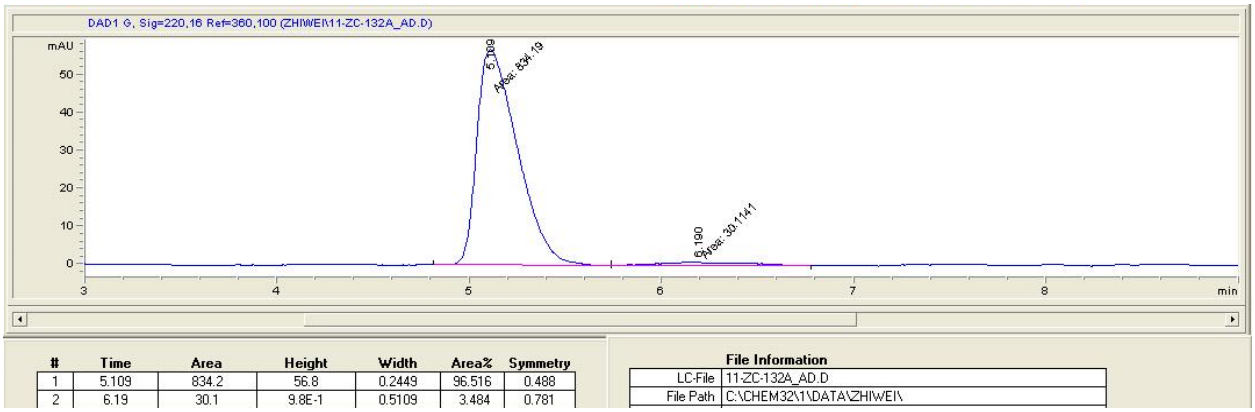
#	Time	Area	Height	Width	Area%	Symmetry
1	5.137	648.6	43.8	0.2206	48.149	0.538
2	6.202	698.5	30.2	0.3297	51.851	0.556

File Information	
LC-File	11-ZC-131A_AD-1.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\

* the peak at 4.1 min correspond to the *trans* diastereomer that was not separated from the product

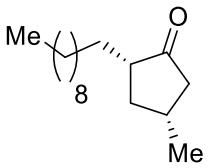


(+)-**2d**

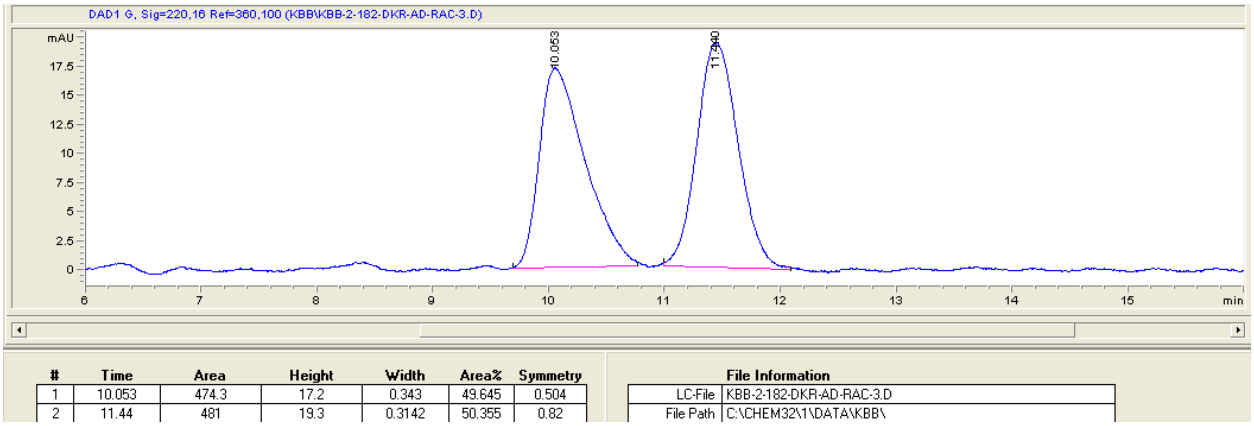


#	Time	Area	Height	Width	Area%	Symmetry
1	5.109	834.2	56.8	0.2449	96.516	0.488
2	6.19	30.1	9.8E-1	0.5109	3.484	0.781

File Information	
LC-File	11-ZC-132A_AD.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\

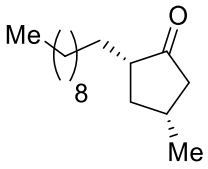


(±)-**2e**

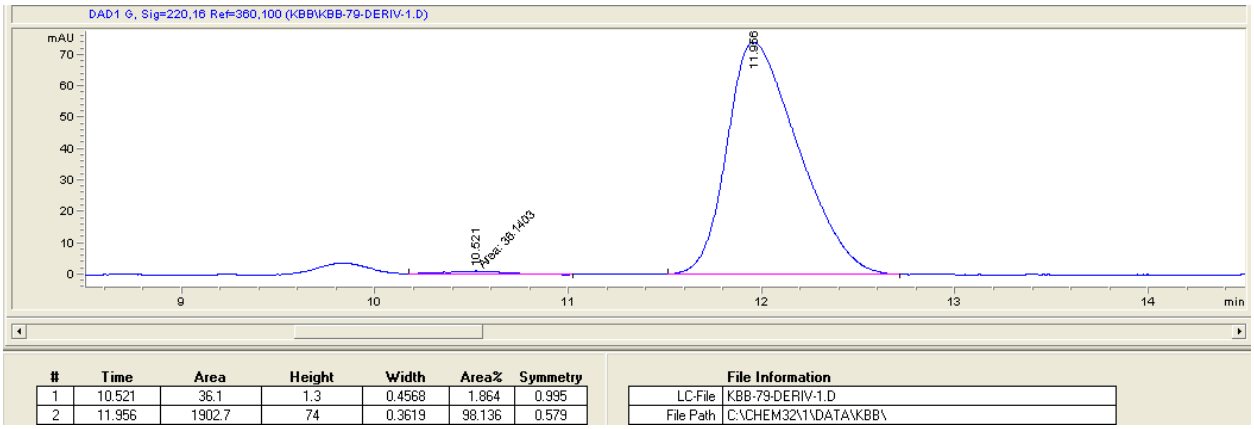


#	Time	Area	Height	Width	Area%	Symmetry
1	10.053	474.3	17.2	0.343	49.645	0.504
2	11.44	481	19.3	0.3142	50.355	0.82

File Information	
LC-File	KBB-2-182-DKR-AD-RAC-3.D
File Path	C:\CHEM32\1\DATA\KBB\

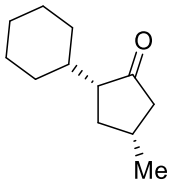


(+)-**2e**

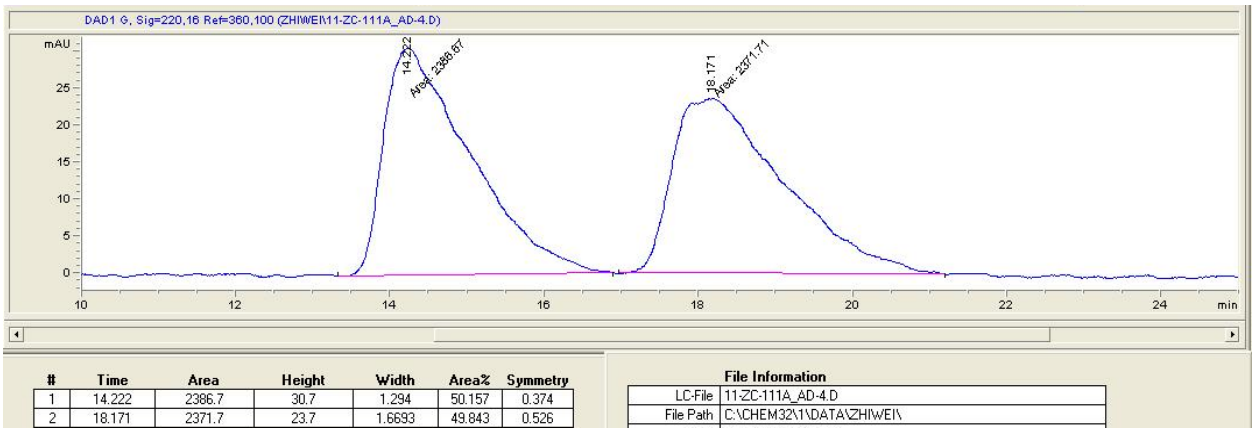


#	Time	Area	Height	Width	Area%	Symmetry
1	10.521	36.1	1.3	0.4568	1.864	0.995
2	11.956	1902.7	74	0.3619	98.136	0.579

File Information	
LC-File	KBB-79-DERIV-1.D
File Path	C:\CHEM32\1\DATA\KBB\

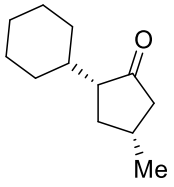


(±)-**2f**

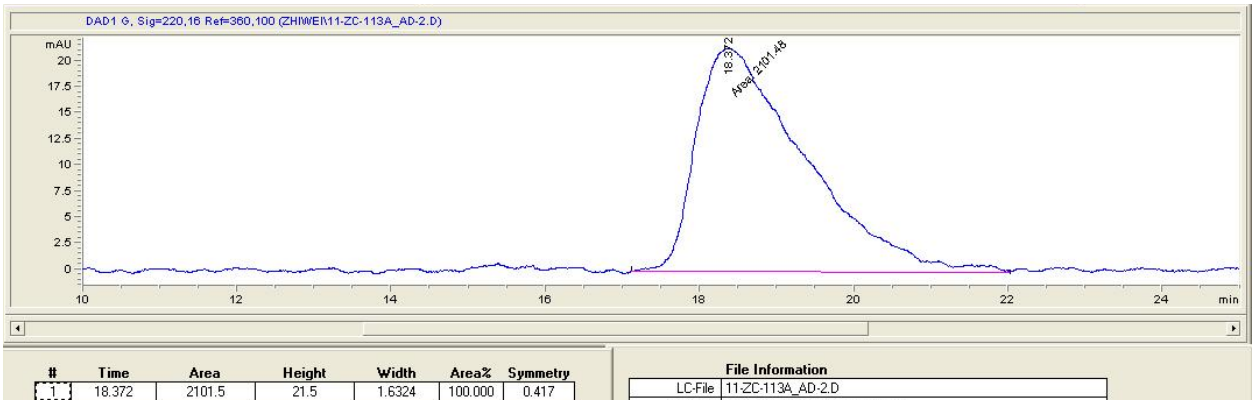


#	Time	Area	Height	Width	Area%	Symmetry
1	14.222	2386.7	30.7	1.294	50.157	0.374
2	18.171	2371.7	23.7	1.6693	49.843	0.526

File Information	
LC-File	11-ZC-111A_AD-4.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\

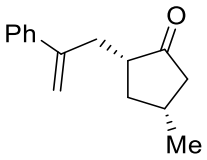


(+)-**2f**

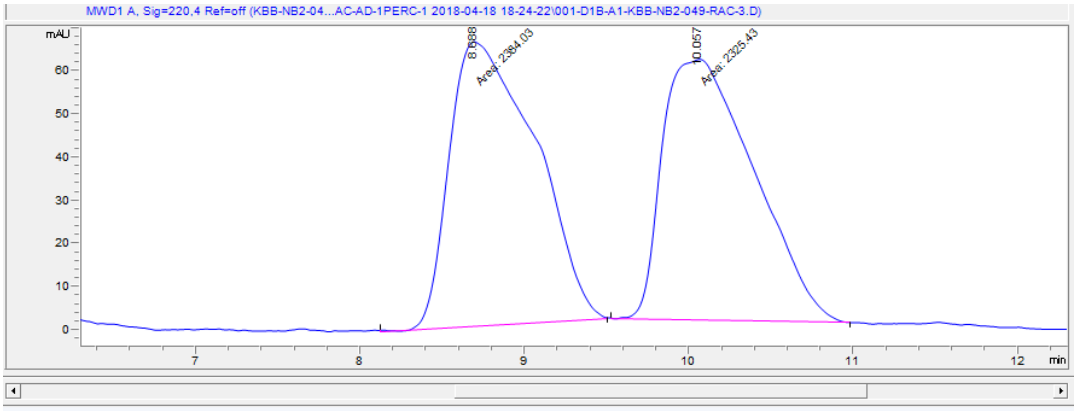


#	Time	Area	Height	Width	Area%	Symmetry
1	18.372	2101.5	21.5	1.6324	100.000	0.417

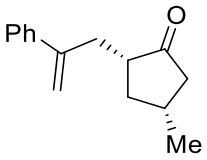
File Information	
LC-File	11-ZC-113A_AD-2.D



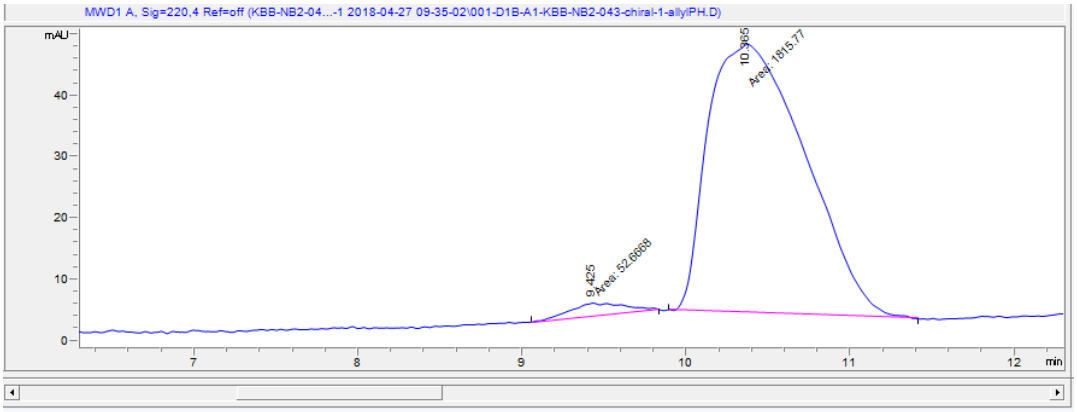
(±)-**2g**



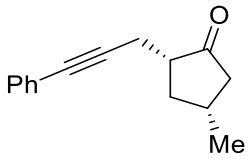
File Information		#	Time	Type	Area	Height	Width	Area%	Symmetry
LC-File	001-D1B-A1-KBB-NB2-049-RAC-3.D	1	8.688	MM	2384	65.9	0.6028	50.622	0.413
File Path	C:\Chem32\1\Data\KBB-NB2-049-RAC-AD-1PERC-1	2	10.057	MM	2325.4	60.3	0.6424	49.378	0.653



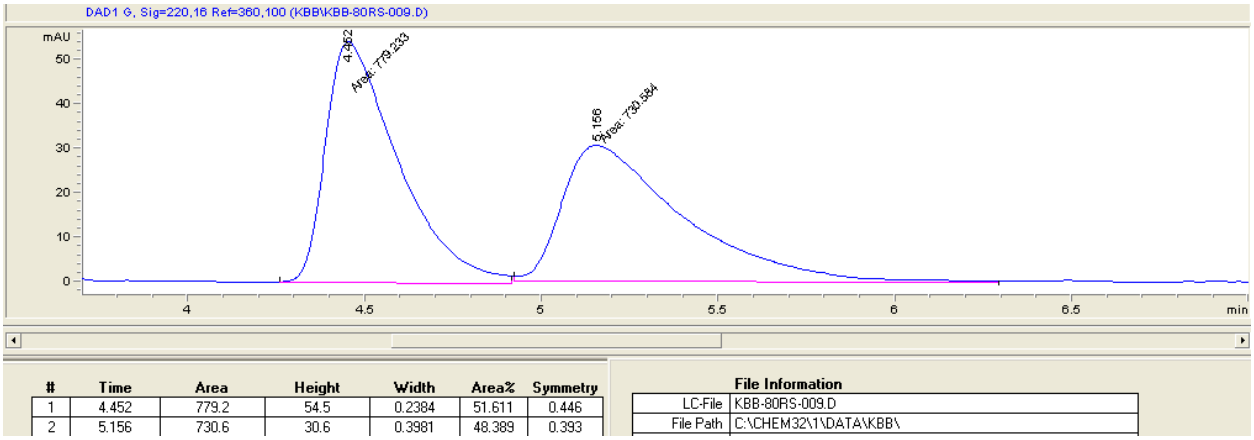
(±)-**2g**



File Information		#	Time	Type	Area	Height	Width	Area%	Symmetry
LC-File	001-D1B-A1-KBB-NB2-043-chiral-1-allylPH.D	1	9.425	MM	52.7	2.2	0.394	2.819	0.837
File Path	C:\Chem32\1\Data\KBB-NB2-043-allylPH-chiral-AD-1	2	10.365	MM	1815.8	44	0.6879	97.181	0.657

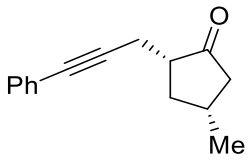


(±)-**2h**

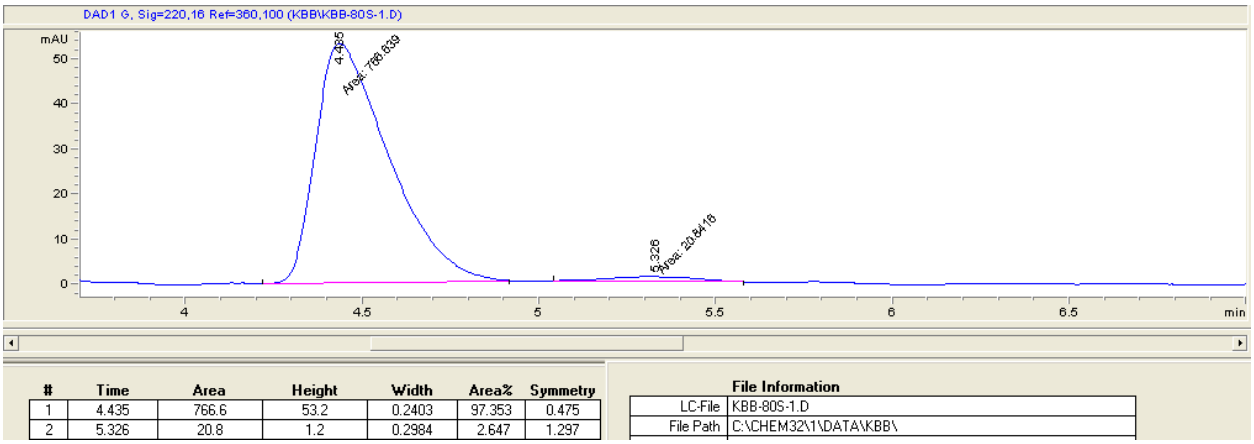


#	Time	Area	Height	Width	Area%	Symmetry
1	4.452	779.2	54.5	0.2384	51.611	0.446
2	5.156	730.6	30.6	0.3981	48.389	0.393

File Information	
LC-File	KBB-80RS-009.D
File Path	C:\CHEM32\1\DATA\KBB\

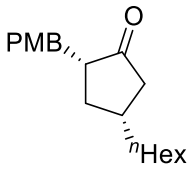


(+)-**2h**

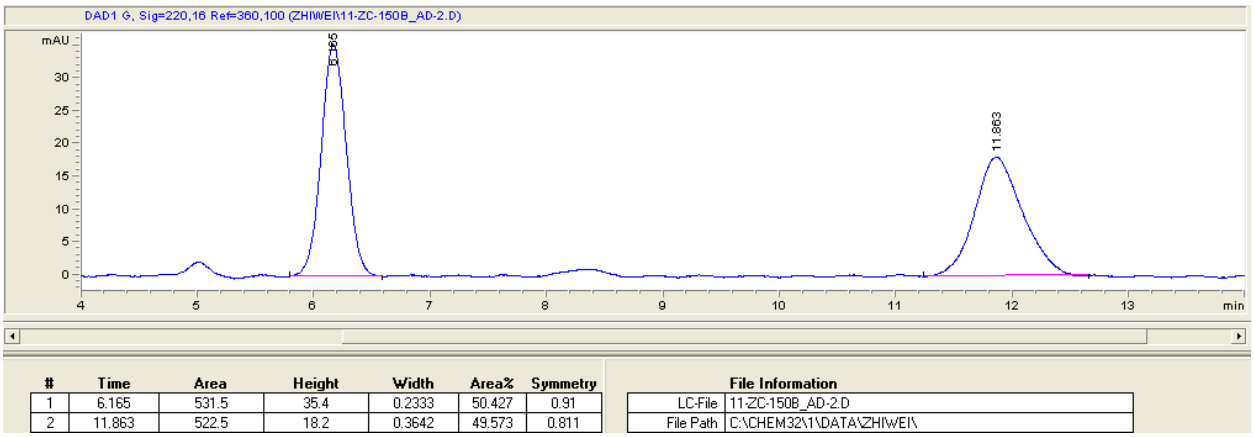


#	Time	Area	Height	Width	Area%	Symmetry
1	4.435	766.6	53.2	0.2403	97.353	0.475
2	5.326	20.8	1.2	0.2984	2.647	1.297

File Information	
LC-File	KBB-80S-1.D
File Path	C:\CHEM32\1\DATA\KBB\

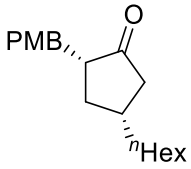


(±)-**2i**

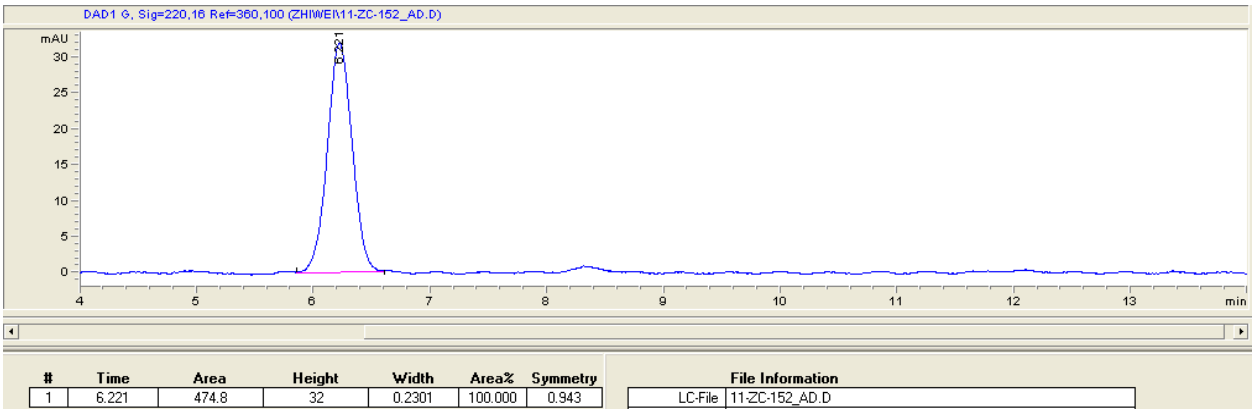


#	Time	Area	Height	Width	Area%	Symmetry
1	6.165	531.5	35.4	0.2333	50.427	0.91
2	11.863	522.5	18.2	0.3642	49.573	0.811

File Information	
LC-File	11-ZC-150B_AD-2.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\

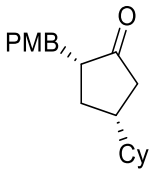


(+)-**2i**

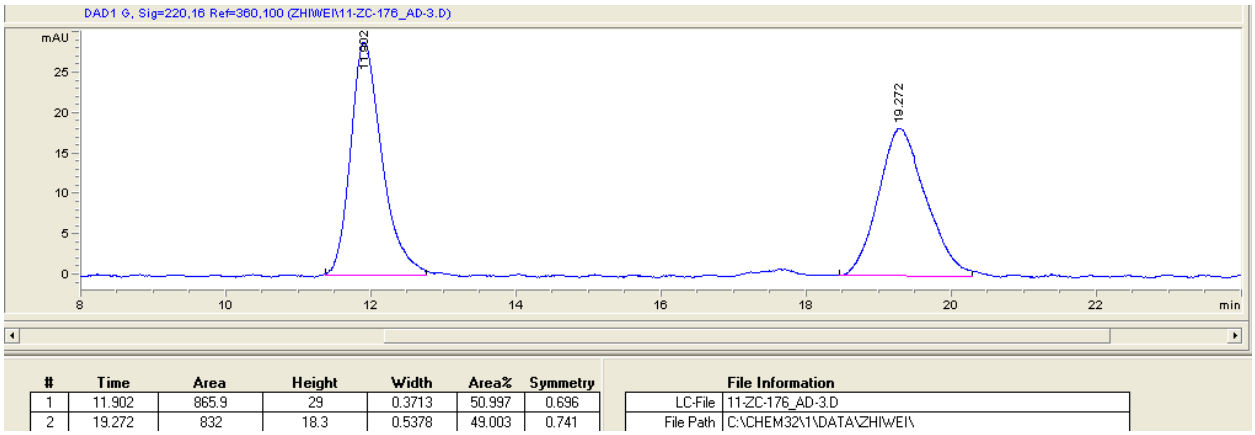


#	Time	Area	Height	Width	Area%	Symmetry
1	6.221	474.8	32	0.2301	100.000	0.943

File Information	
LC-File	11-ZC-152_AD.D

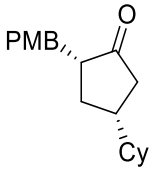


(±)-**2j**

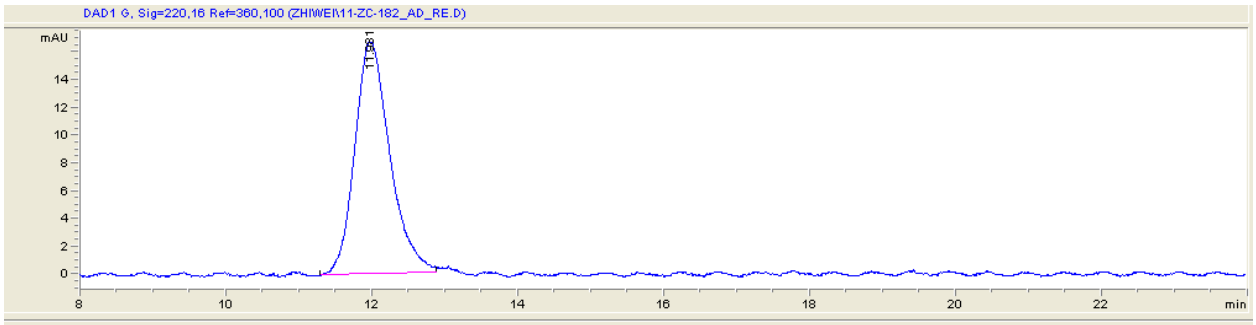


#	Time	Area	Height	Width	Area%	Symmetry
1	11.902	865.9	29	0.3713	50.997	0.696
2	19.272	832	18.3	0.5378	49.003	0.741

File Information	
LC-File	11-ZC-176_AD-3.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\

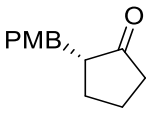


(+)-**2j**

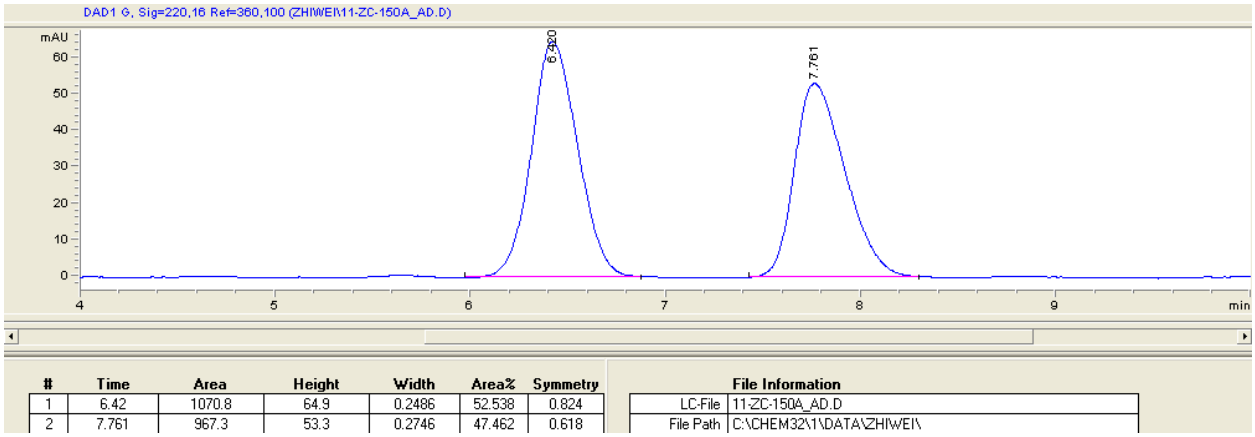


#	Time	Area	Height	Width	Area%	Symmetry
1	11.981	556.9	16.7	0.3934	100.000	0.795

File Information	
LC-File	11-ZC-182_AD_RE.D

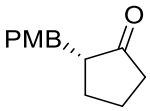


(±)-**2k**

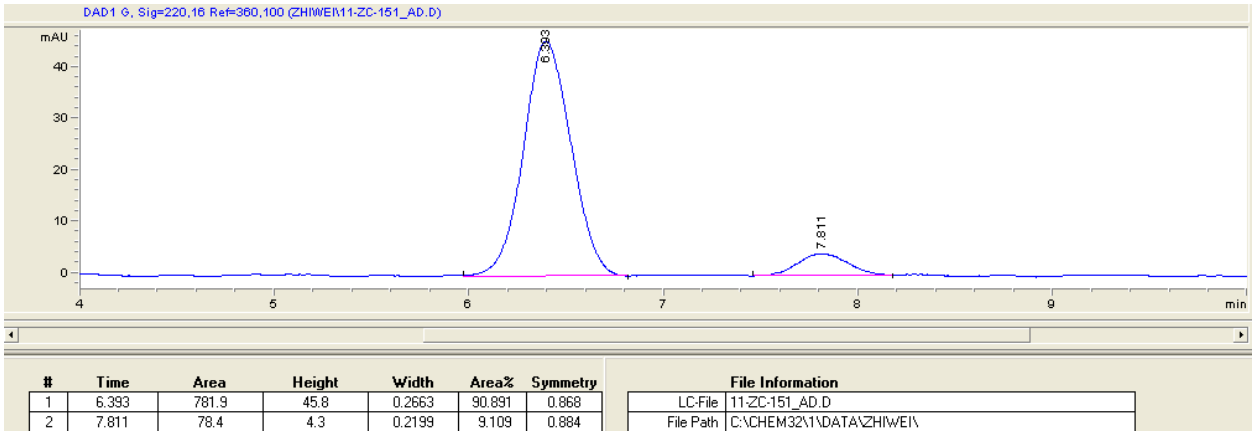


#	Time	Area	Height	Width	Area%	Symmetry
1	6.42	1070.8	64.9	0.2486	52.538	0.824
2	7.761	967.3	53.3	0.2746	47.462	0.618

File Information	
LC-File	11-ZC-150A_AD.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\

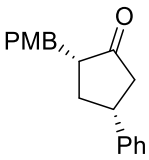


(+)-**2k**

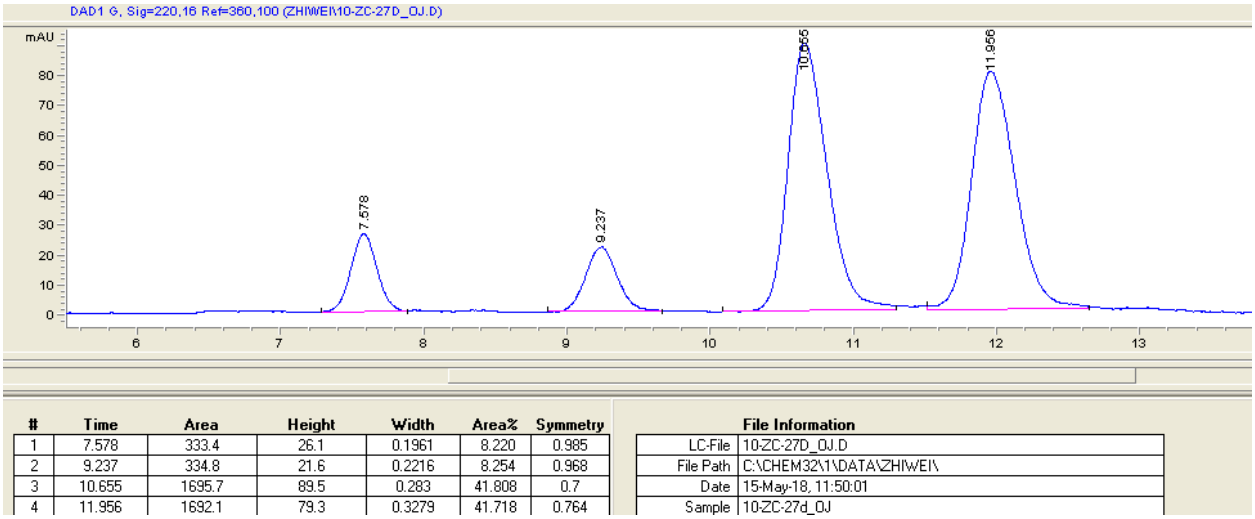


#	Time	Area	Height	Width	Area%	Symmetry
1	6.393	781.9	45.8	0.2663	90.891	0.868
2	7.811	78.4	4.3	0.2199	9.109	0.884

File Information	
LC-File	11-ZC-151_AD.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\



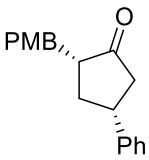
(±)-**4a**



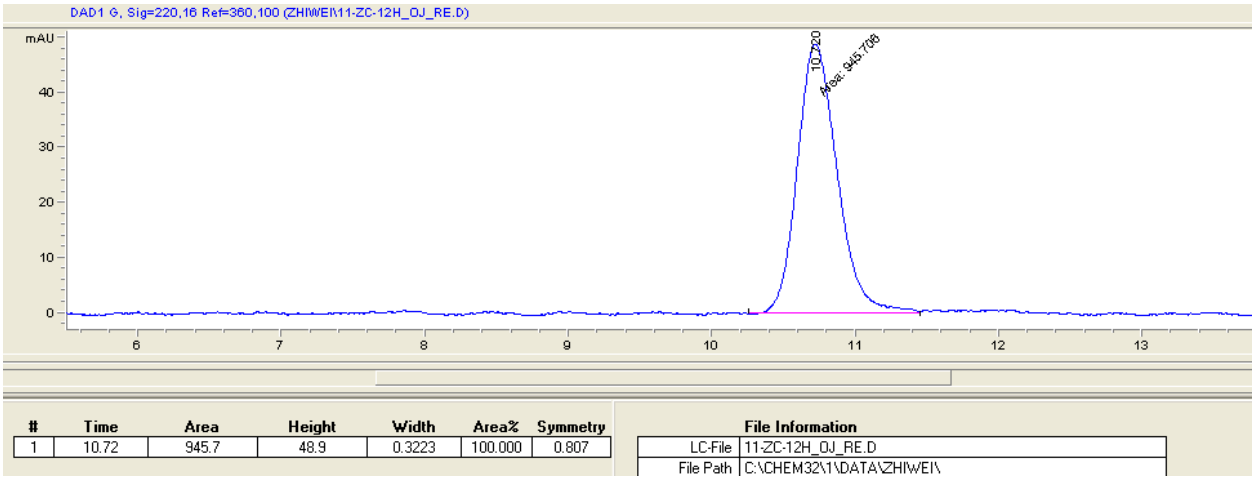
#	Time	Area	Height	Width	Area%	Symmetry
1	7.578	333.4	26.1	0.1961	8.220	0.985
2	9.237	334.8	21.6	0.2216	8.254	0.968
3	10.655	1695.7	89.5	0.283	41.808	0.7
4	11.956	1692.1	79.3	0.3279	41.718	0.764

File Information	
LC-File	10-ZC-27D_OJ.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\
Date	15-May-18, 11:50:01
Sample	10-ZC-27d_OJ

* peaks at 7.6 and 9.2 min correspond to the *trans* diastereomer that was not separated from the product

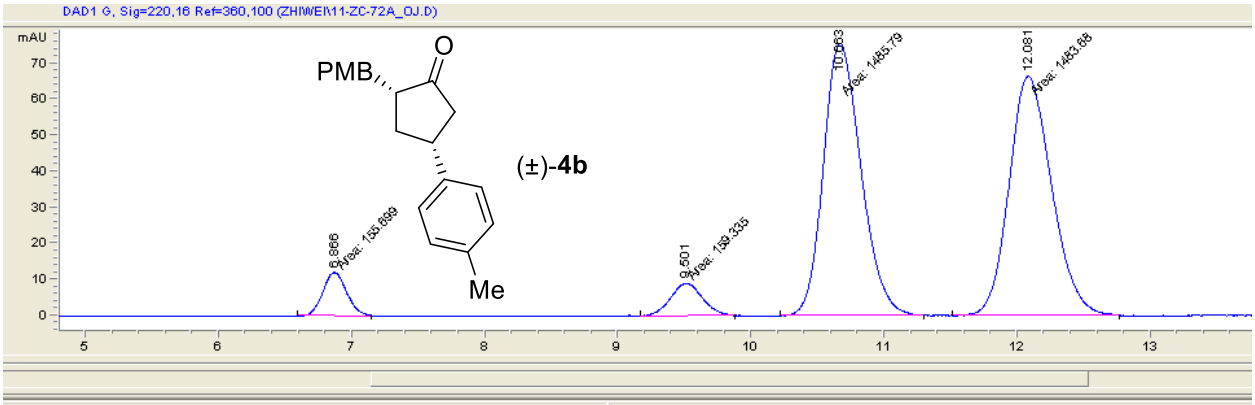


(+)-**4a**



#	Time	Area	Height	Width	Area%	Symmetry
1	10.72	945.7	48.9	0.3223	100.000	0.807

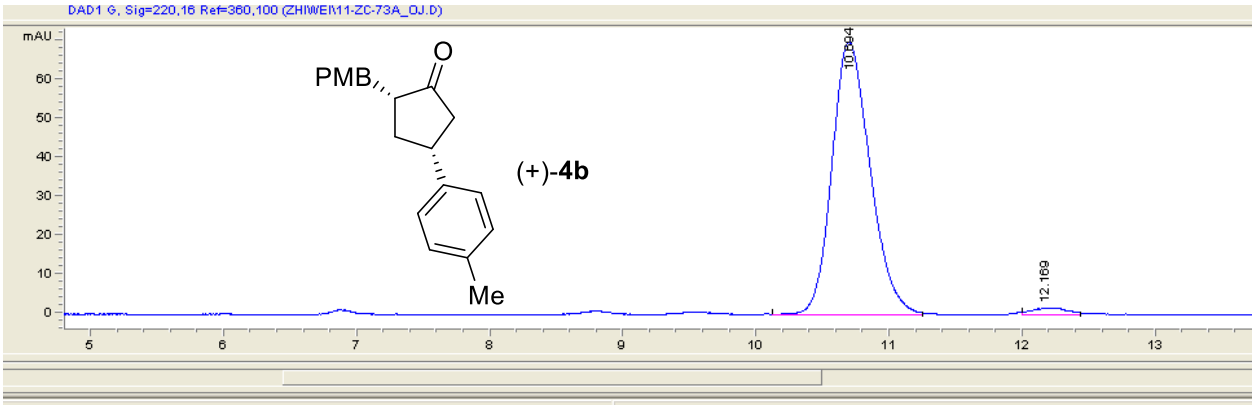
File Information	
LC-File	11-ZC-12H_OJ_RE.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\



#	Time	Area	Height	Width	Area%	Symmetry
1	6.866	155.7	12.2	0.2124	4.740	0.856
2	9.501	159.3	9.3	0.2861	4.851	0.87
3	10.663	1485.8	75.7	0.3273	45.236	0.737
4	12.081	1483.7	66.5	0.3716	45.172	0.797

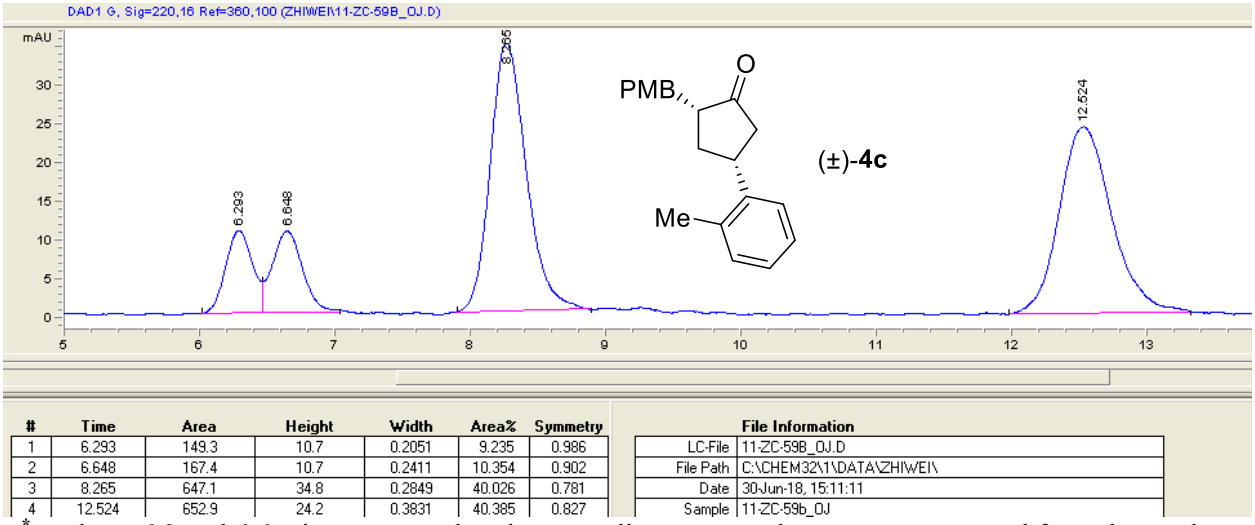
File Information	
LC-File	11-ZC-72A_OJ.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\
Date	13-Jul-18, 14:50:32
Sample	11-ZC-72a_OJ

* peaks at 6.9 and 9.5 min correspond to the *trans* diastereomer that was not separated from the product



#	Time	Area	Height	Width	Area%	Symmetry
1	10.694	1407.2	70.3	0.2885	97.518	0.765
2	12.169	35.8	1.9	0.2239	2.482	0.612

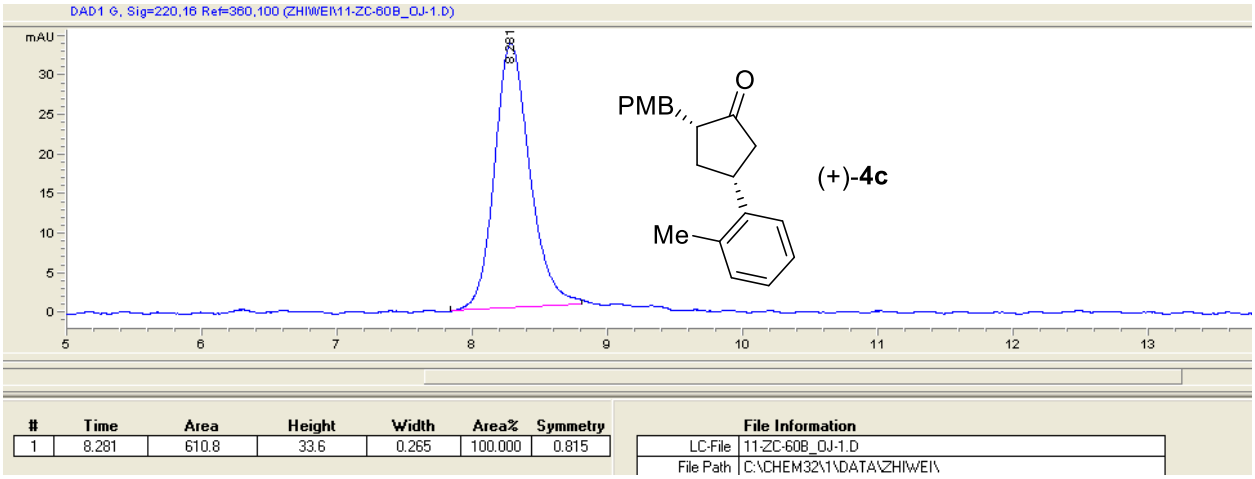
File Information	
LC-File	11-ZC-73A_OJ.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\



#	Time	Area	Height	Width	Area%	Symmetry
1	6.293	149.3	10.7	0.2051	9.235	0.986
2	6.648	167.4	10.7	0.2411	10.354	0.902
3	8.265	647.1	34.8	0.2849	40.026	0.781
4	12.524	652.9	24.2	0.3831	40.385	0.827

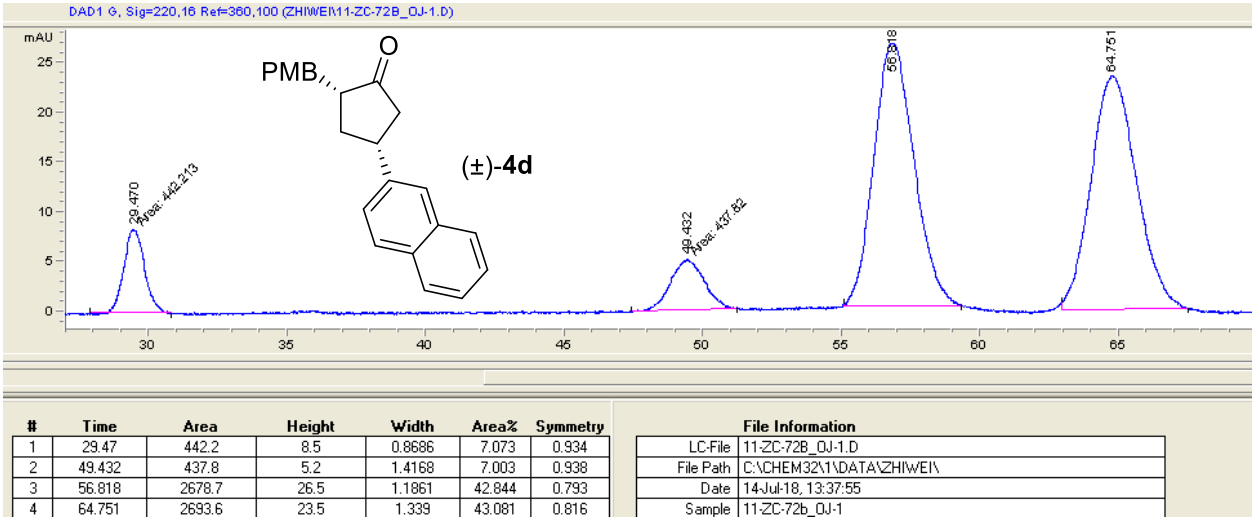
File Information	
LC-File	11-ZC-59B_OJ.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\
Date	30-Jun-18, 15:11:11
Sample	11-ZC-59b_OJ

* peaks at 6.3 and 6.6 min correspond to the *trans* diastereomer that was not separated from the product



#	Time	Area	Height	Width	Area%	Symmetry
1	8.281	610.8	33.6	0.265	100.000	0.815

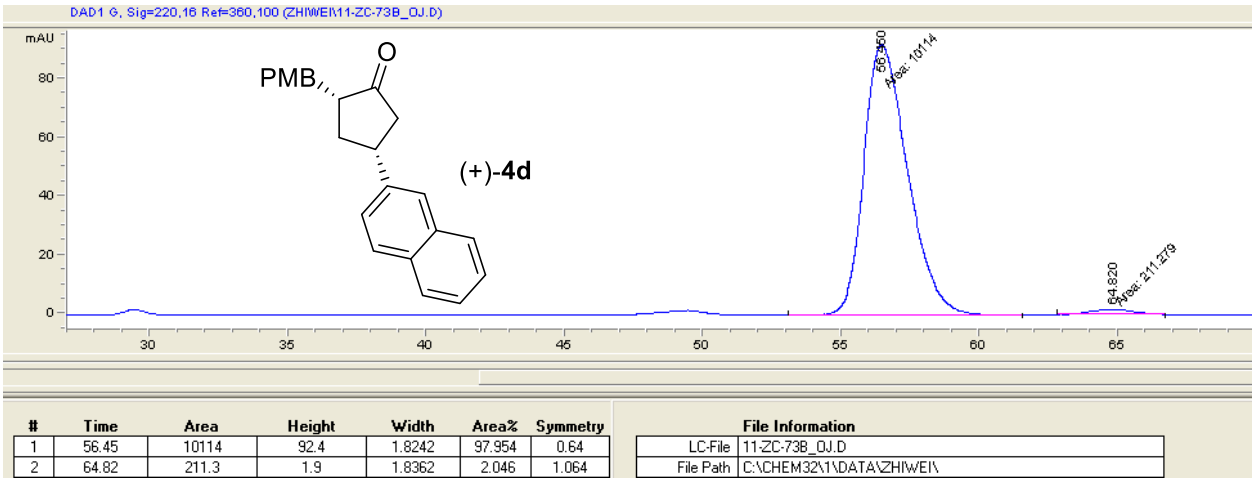
File Information	
LC-File	11-ZC-60B_OJ-1.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\



#	Time	Area	Height	Width	Area%	Symmetry
1	29.47	442.2	8.5	0.8686	7.073	0.934
2	49.432	437.8	5.2	1.4168	7.003	0.938
3	56.818	2678.7	26.5	1.1861	42.844	0.793
4	64.751	2693.6	23.5	1.339	43.081	0.816

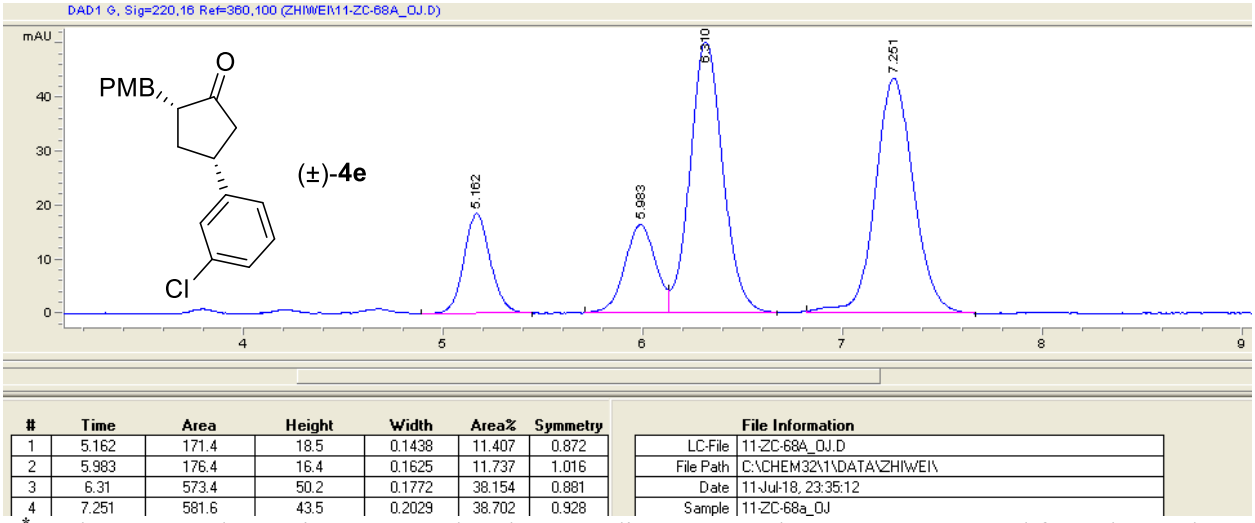
File Information	
LC-File	11-ZC-72B_OJ-1.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\
Date	14-Jul-18, 13:37:55
Sample	11-ZC-72b_OJ-1

* peaks at 29.5 and 49.4 min correspond to the *trans* diastereomer that was not separated from the product



#	Time	Area	Height	Width	Area%	Symmetry
1	56.45	10114	92.4	1.8242	97.954	0.64
2	64.82	211.3	1.9	1.8362	2.046	1.064

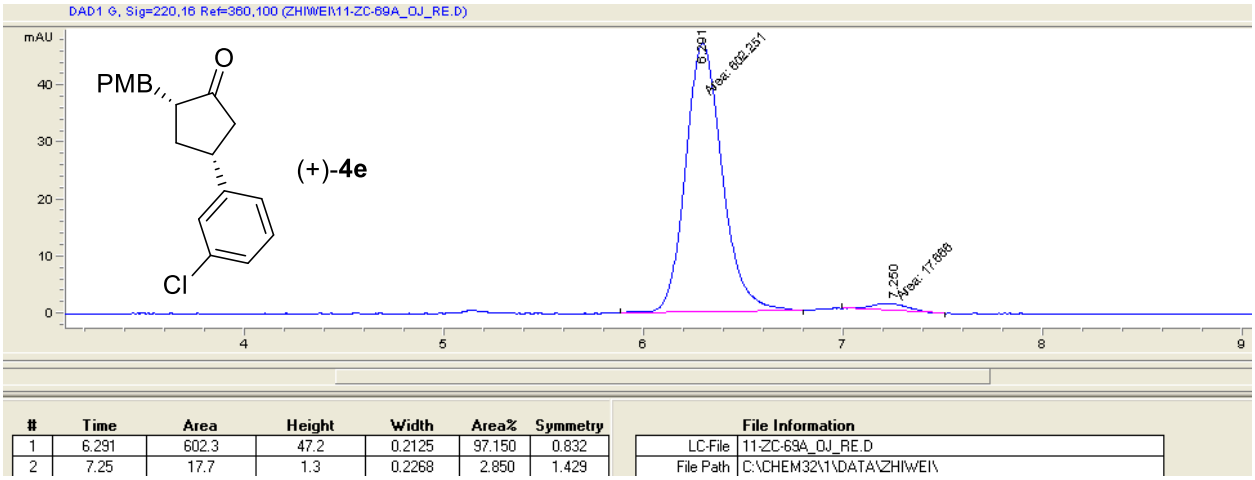
File Information	
LC-File	11-ZC-73B_OJ.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\



#	Time	Area	Height	Width	Area%	Symmetry
1	5.162	171.4	18.5	0.1438	11.407	0.872
2	5.983	176.4	16.4	0.1625	11.737	1.016
3	6.31	573.4	50.2	0.1772	38.154	0.881
4	7.251	581.6	43.5	0.2029	38.702	0.928

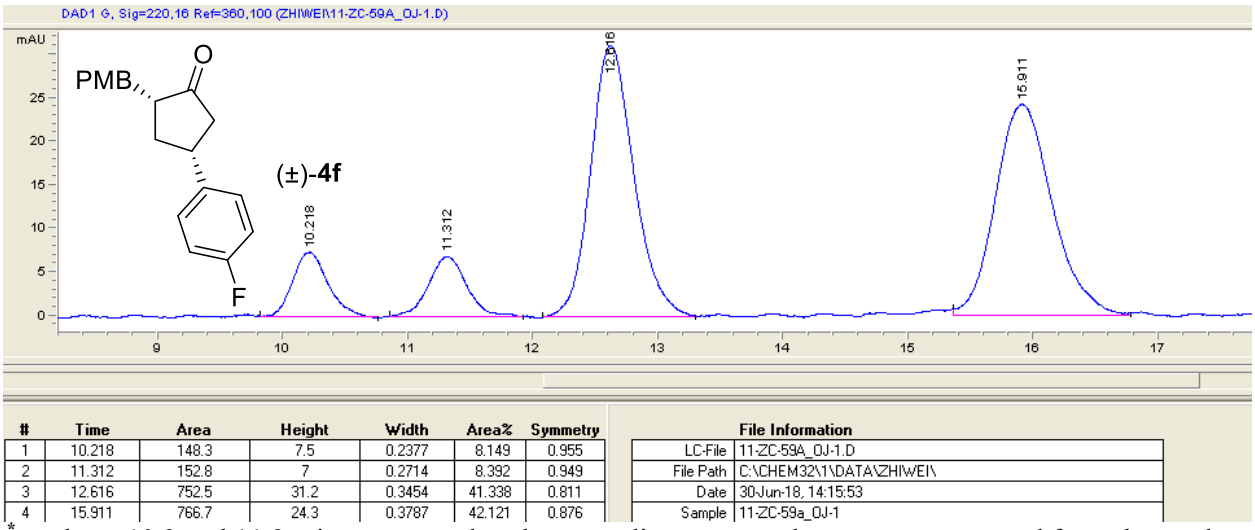
File Information	
LC-File	11-ZC-68A_OJ.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\
Date	11-Jul-18, 23:35:12
Sample	11-ZC-68a_OJ

* peaks at 5.2 and 6.0 min correspond to the *trans* diastereomer that was not separated from the product



#	Time	Area	Height	Width	Area%	Symmetry
1	6.291	602.3	47.2	0.2125	97.150	0.832
2	7.25	17.7	1.3	0.2268	2.850	1.429

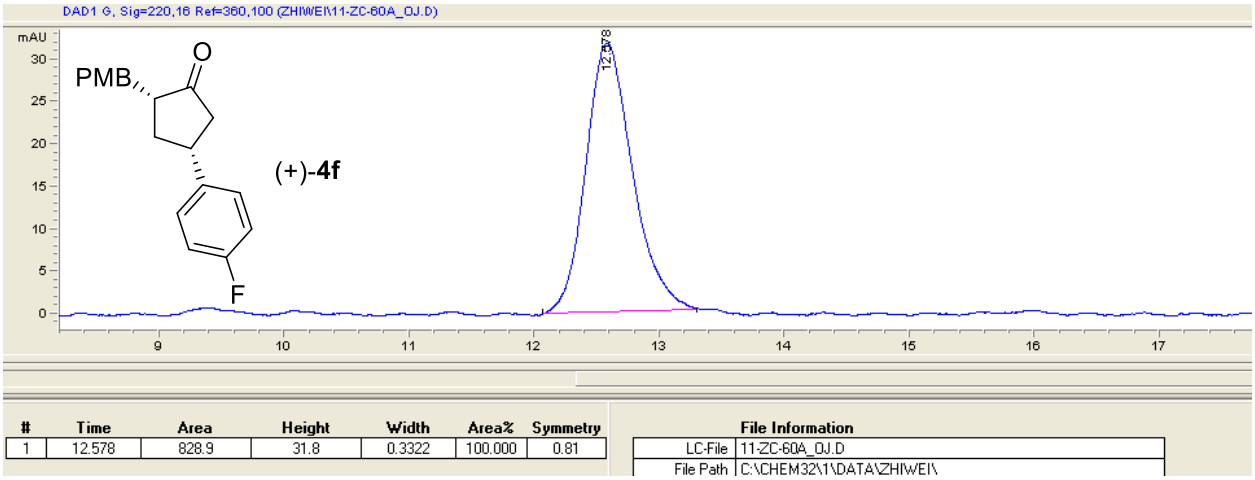
File Information	
LC-File	11-ZC-69A_OJ_RE.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\



#	Time	Area	Height	Width	Area%	Symmetry
1	10.218	148.3	7.5	0.2377	8.149	0.955
2	11.312	152.8	7	0.2714	8.392	0.949
3	12.616	752.5	31.2	0.3454	41.338	0.811
4	15.911	766.7	24.3	0.3787	42.121	0.876

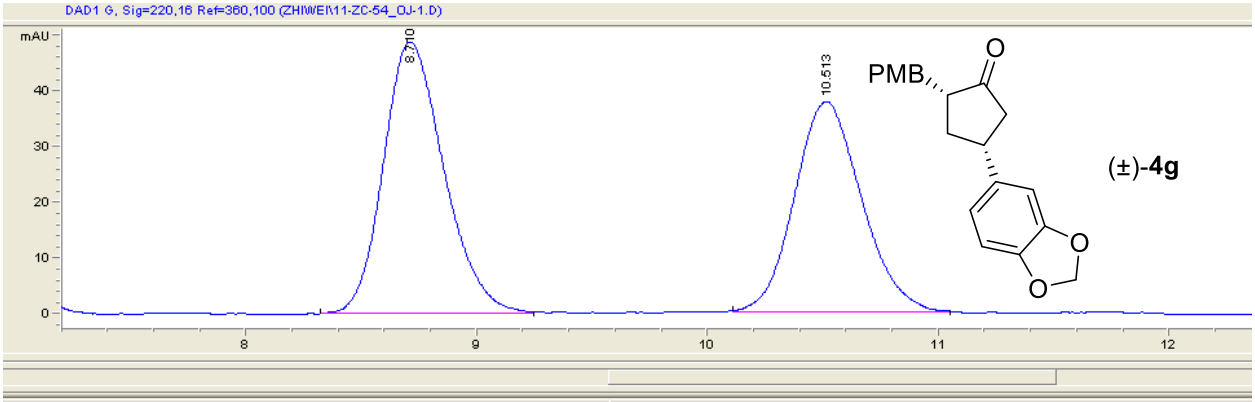
File Information	
LC-File	11-ZC-59A_OJ-1.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\
Date	30-Jun-18, 14:15:53
Sample	11-ZC-59a_OJ-1

* peaks at 10.2 and 11.3 min correspond to the *trans* diastereomer that was not separated from the product



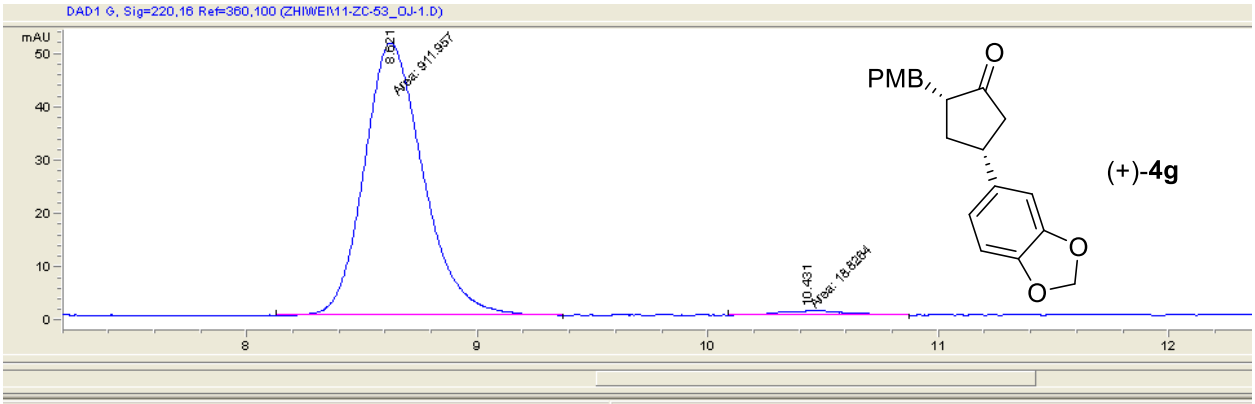
#	Time	Area	Height	Width	Area%	Symmetry
1	12.578	828.9	31.8	0.3322	100.000	0.81

File Information	
LC-File	11-ZC-60A_OJ.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\



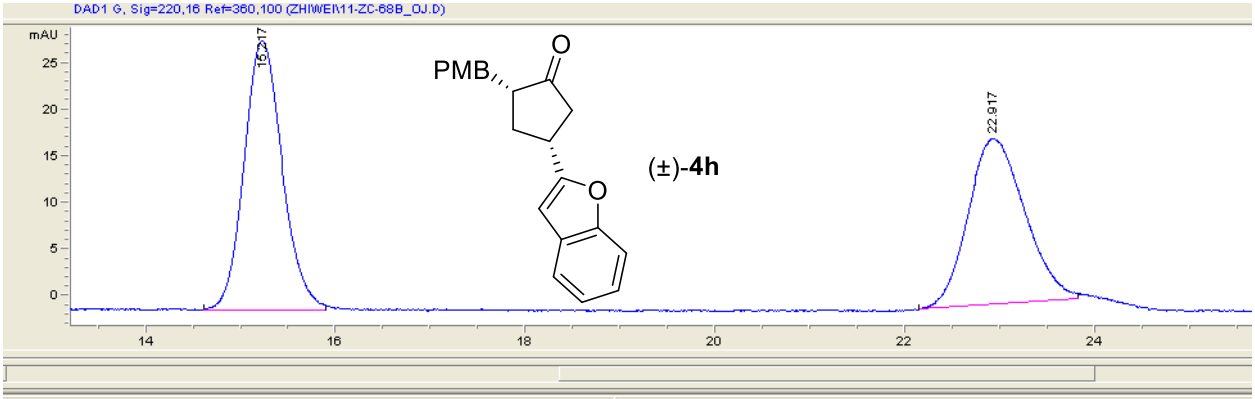
#	Time	Area	Height	Width	Area%	Symmetry
1	8.71	890.2	48.8	0.279	53.582	0.762
2	10.513	771.2	37.9	0.2966	46.418	0.86

File Information	
LC-File	11-ZC-54_OJ-1.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\



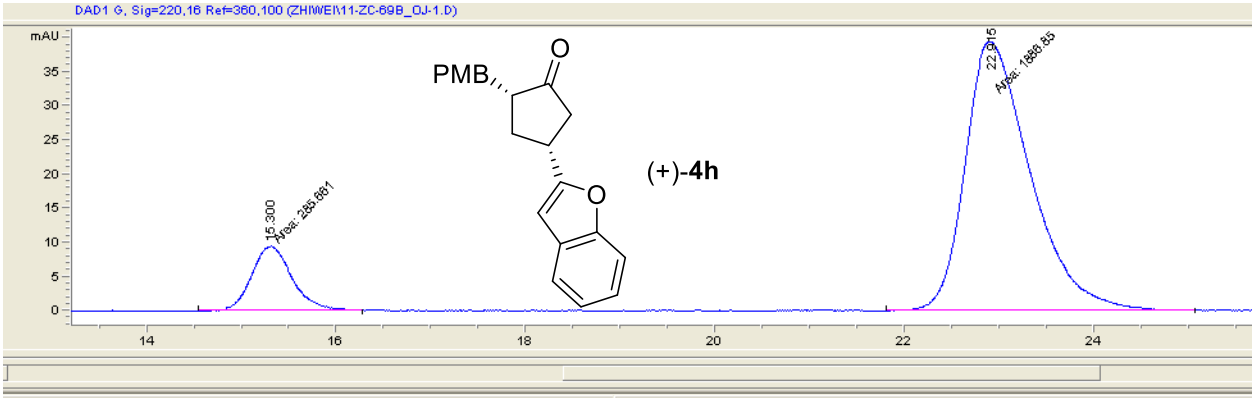
#	Time	Area	Height	Width	Area%	Symmetry
1	8.621	912	51.1	0.2973	97.977	0.788
2	10.431	18.8	8.4E-1	0.3748	2.023	0.73

File Information	
LC-File	11-ZC-53_OJ-1.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\



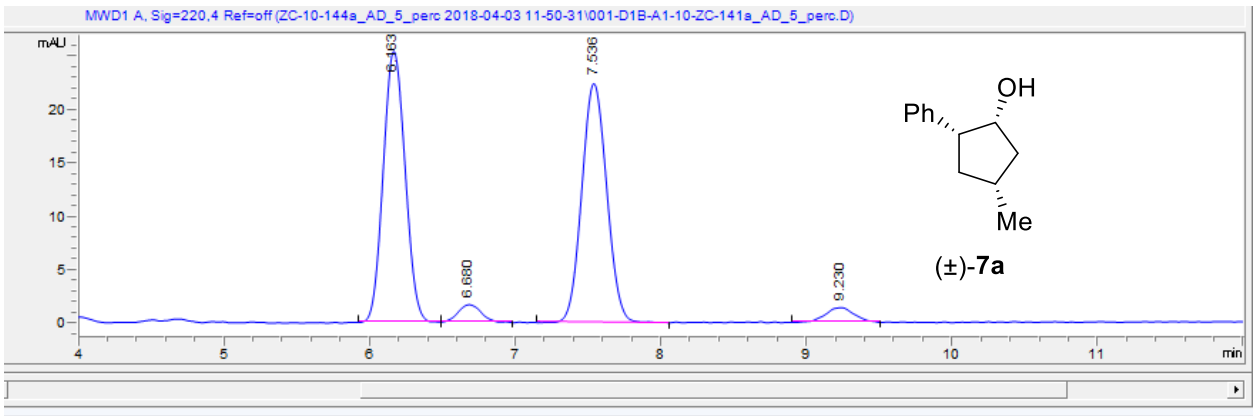
#	Time	Area	Height	Width	Area%	Symmetry
1	15.217	813.7	29	0.3332	52.265	0.852
2	22.917	743.1	17.9	0.4897	47.735	0.747

File Information	
LC-File	11-ZC-68B_OJ.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\



#	Time	Area	Height	Width	Area%	Symmetry
1	15.3	285.7	9.5	0.5001	13.149	0.838
2	22.915	1886.9	39.4	0.7972	86.851	0.658

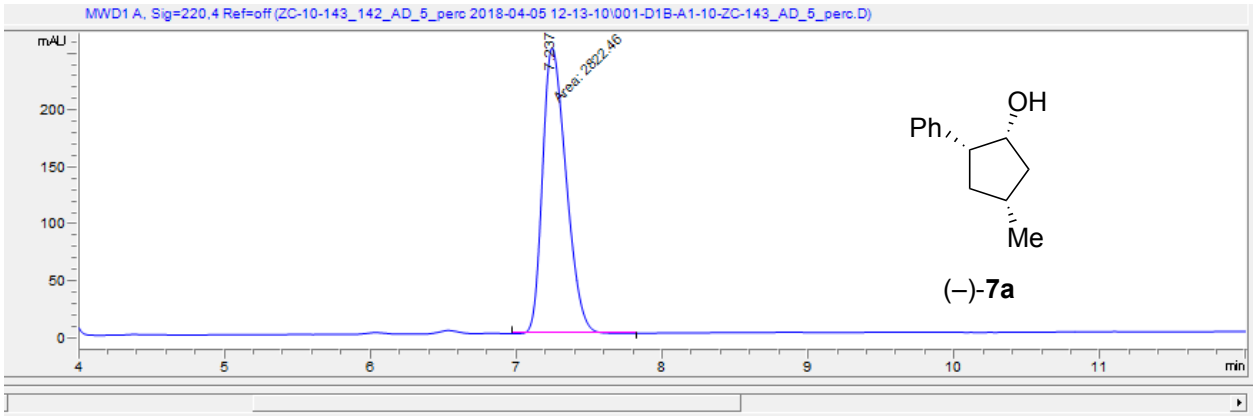
File Information	
LC-File	11-ZC-69B_OJ-1.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\



File Information	
LC-File	001-D1B-A1-10-ZC-141a_AD_5_perc.D
File Path	C:\Chem32\1\Data\ZC-10-144a_AD_5_perc 2018-0
Date	03-Apr-18, 11:51:27
Sample	10-ZC-141a_AD_5_perc

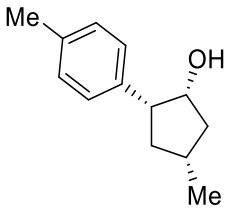
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.163	BV	267.6	25.6	0.166	46.514	0.896
2	6.68	VB	19.2	1.7	0.1803	3.339	0.886
3	7.536	BB	268.7	22.6	0.189	46.713	0.907
4	9.23	BB	19.8	1.4	0.2069	3.434	1.089

* peaks at 6.7 and 9.2 min correspond to another diastereomer that was not separated from the product

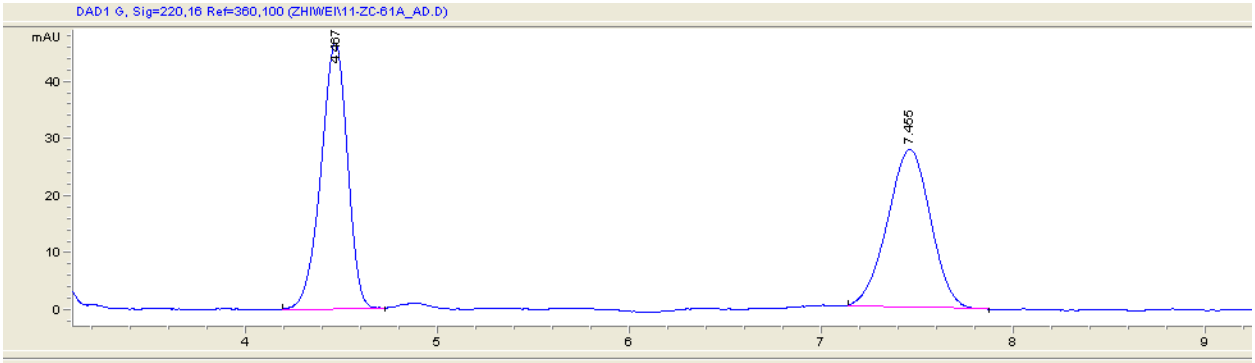


File Information	
LC-File	001-D1B-A1-10-ZC-143_AD_5_perc.D
File Path	C:\Chem32\1\Data\ZC-10-143_142_AD_5_perc 201

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.237	MM	2822.5	251.1	0.1874	100.000	0.665

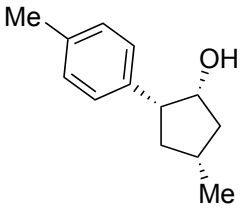


(±)-**7b**

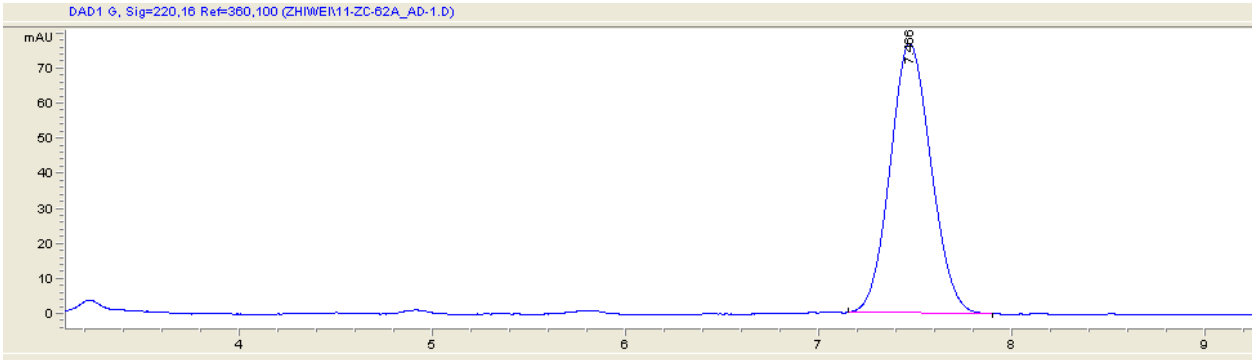


#	Time	Area	Height	Width	Area%	Symmetry
1	4.467	451.5	46.7	0.1497	51.057	1.154
2	7.455	432.8	27.7	0.2326	48.943	1.04

File Information	
LC-File	11-ZC-61A_AD.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\

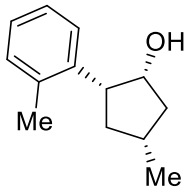


(–)-**7b**

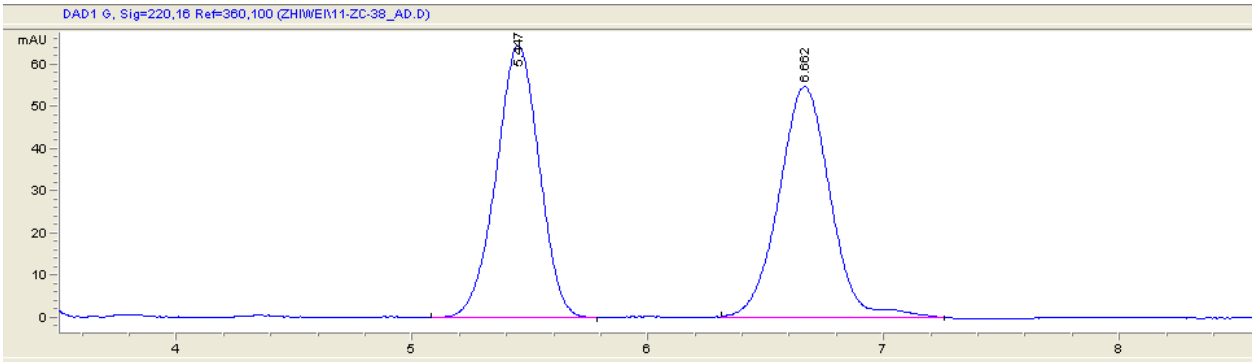


#	Time	Area	Height	Width	Area%	Symmetry
1	7.466	1134.9	77.1	0.2267	100.000	0.884

File Information	
LC-File	11-ZC-62A_AD-1.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\

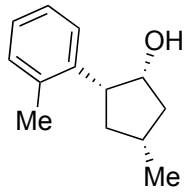


(±)-**7c**

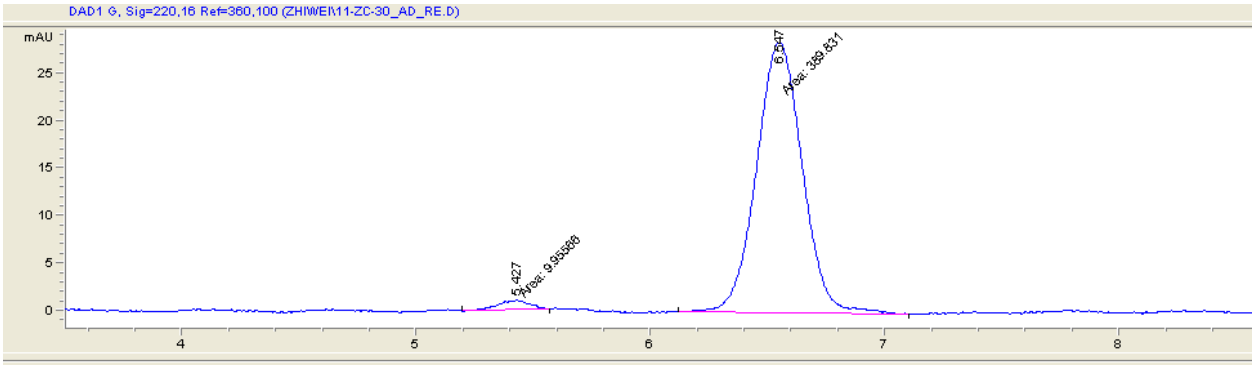


#	Time	Area	Height	Width	Area%	Symmetry
1	5.447	822.3	64.6	0.1886	49.559	1.04
2	6.662	836.9	54.9	0.2309	50.441	0.934

File Information	
LC-File	11-ZC-38_AD.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\

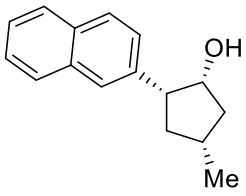


(–)-**7c**

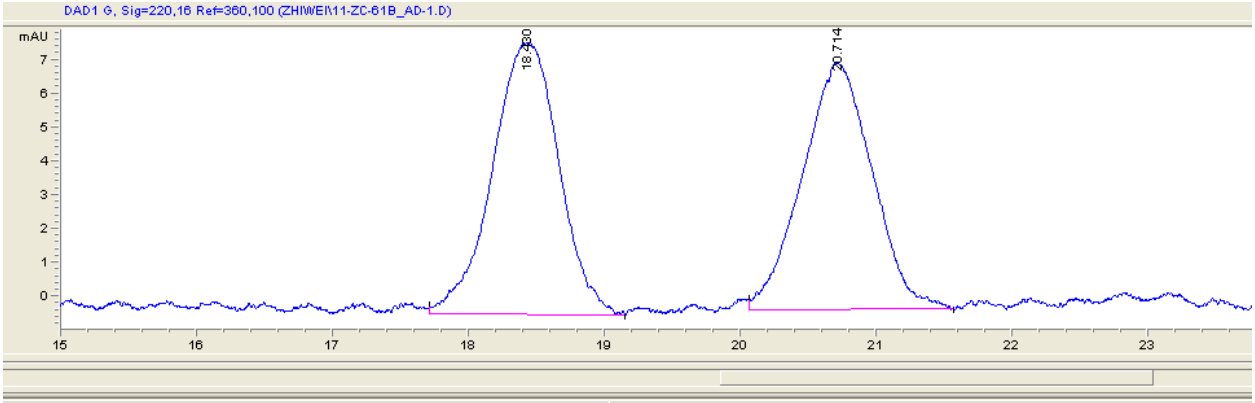


#	Time	Area	Height	Width	Area%	Symmetry
1	5.427	10	1	0.1647	2.490	1.472
2	6.547	389.8	28.4	0.2284	97.510	0.945

File Information	
LC-File	11-ZC-30_AD_RE.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\

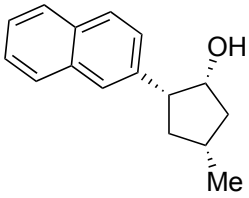


(±)-**7d**

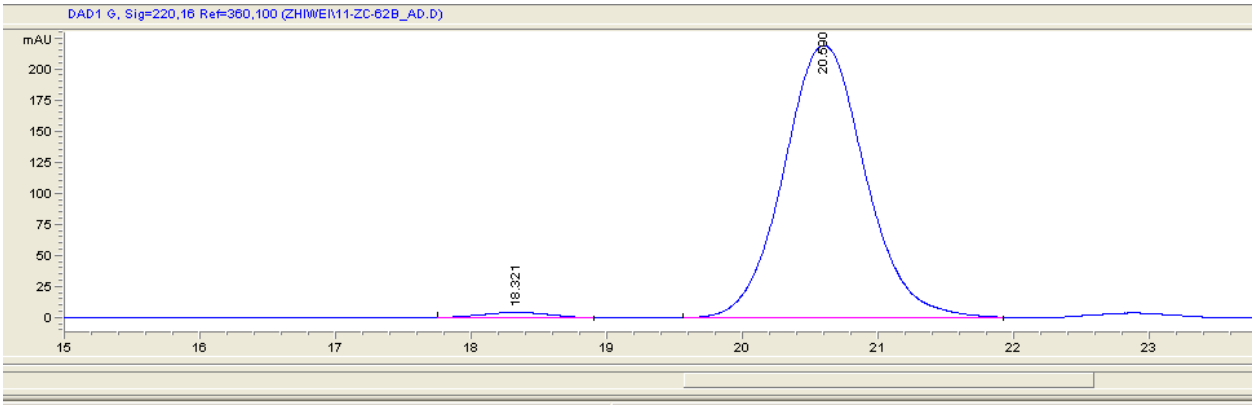


#	Time	Area	Height	Width	Area%	Symmetry
1	18.43	273.7	8.1	0.4012	50.950	1.065
2	20.714	263.5	7.3	0.4237	49.050	1.009

File Information	
LC-File	11-ZC-61B_AD-1.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\

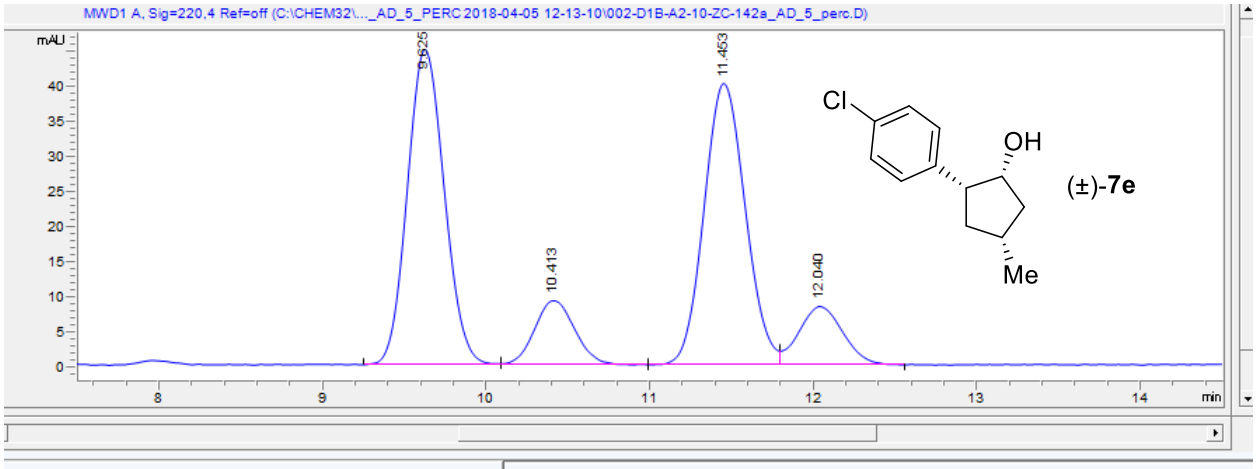


(–)-**7d**



#	Time	Area	Height	Width	Area%	Symmetry
1	18.321	161.3	4.8	0.398	1.730	1.01
2	20.59	9162.7	219.2	0.6096	98.270	0.915

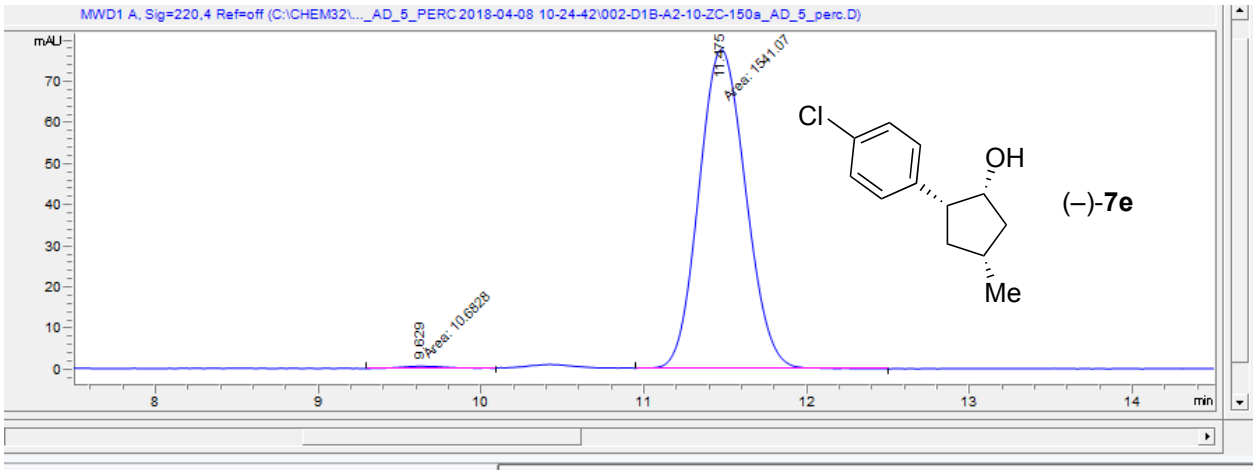
File Information	
LC-File	11-ZC-62B_AD.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\



File Information	
LC-File	002-D1B-A2-10-ZC-142a_AD_5_perc.D
File Path	C:\CHEM32\1\DATA\ZC-10-143_142_AD_5_PERC 2018
Date	05-Apr-18, 12:34:52
Sample	10-ZC-142a_AD_5_perc

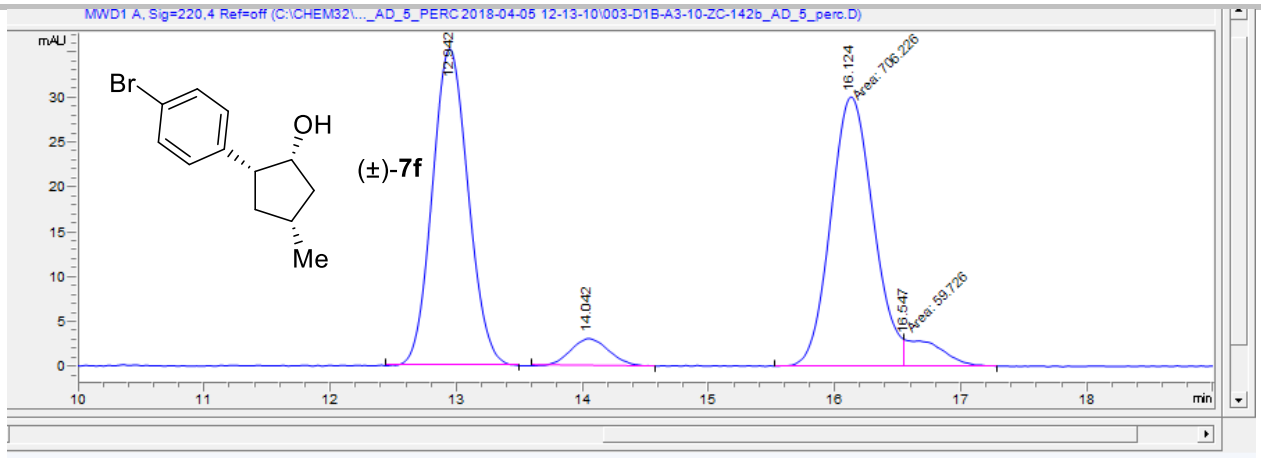
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.625	BV	706.1	45	0.2472	40.981	0.88
2	10.413	VV R	156.3	9.1	0.2597	9.074	0.875
3	11.453	BV	705	40.1	0.2749	40.918	0.884
4	12.04	VV R	155.5	8.3	0.2902	9.027	0.879

* peaks at 10.4 and 12.0 min correspond to another diastereomer that was not separated from the product



File Information	
LC-File	002-D1B-A2-10-ZC-150a_AD_5_perc.D
File Path	C:\CHEM32\1\DATA\ZC-10-150A_151_AD_5_PERC 201
Date	08-Apr-18, 10:56:33

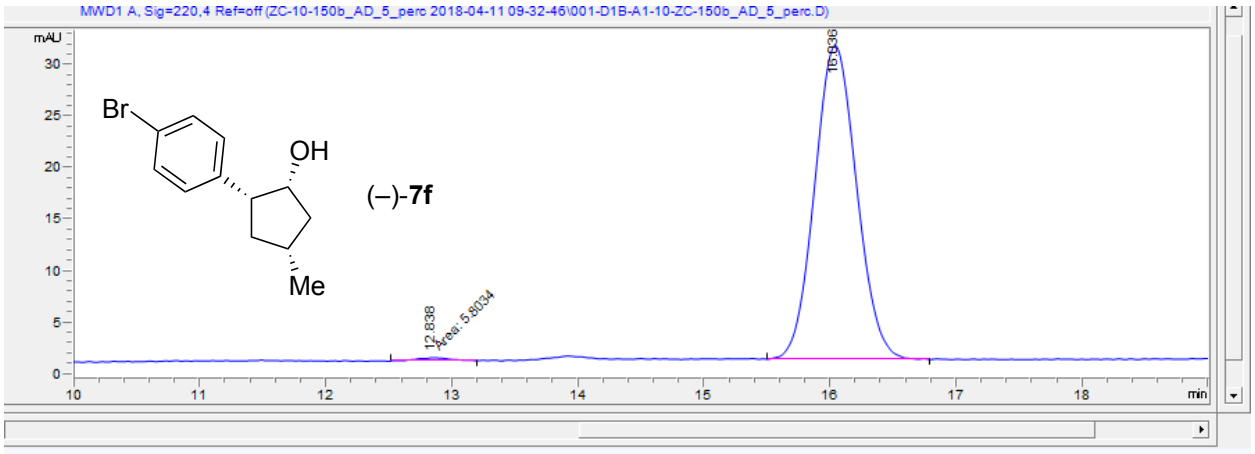
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.629	MM	10.7	5.5E-1	0.3234	0.688	0.879
2	11.475	MM	1541.1	77.4	0.3316	99.312	0.89



File Information	
LC-File	003-D1B-A3-10-ZC-142b_AD_5_perc.D
File Path	C:\CHEM32\1\DATA\ZC-10-143_142_AD_5_PERC 2018
Date	05-Apr-18, 12:55:41
Sample	10-ZC-142b_AD_5_perc

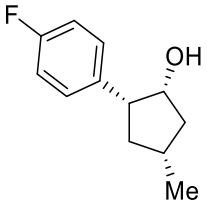
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.942	VB	698.2	35.3	0.309	45.661	0.9
2	14.042	BB	65	3	0.2728	4.249	0.878
3	16.124	MM	706.2	30	0.3928	46.185	0.893
4	16.547	MM	59.7	3	0.2428	3.906	0

* peaks at 14.0 and 16.5 min correspond to another diastereomer that was not separated from the product

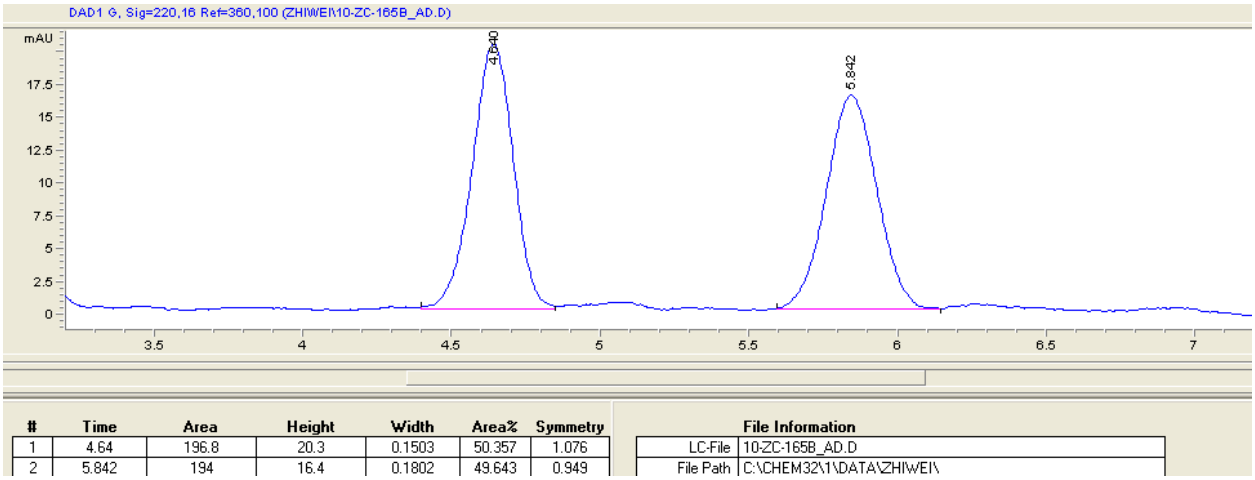


File Information	
LC-File	001-D1B-A1-10-ZC-150b_AD_5_perc.D
File Path	C:\Chem32\1\Data\ZC-10-150b_AD_5_perc 2018-04-1

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.838	MM	5.8	3E-1	0.3228	0.818	0.755
2	16.036	BV R	703.7	30.4	0.3582	99.182	0.921

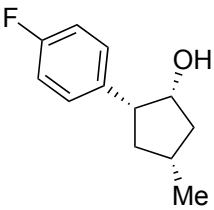


(±)-**7g**

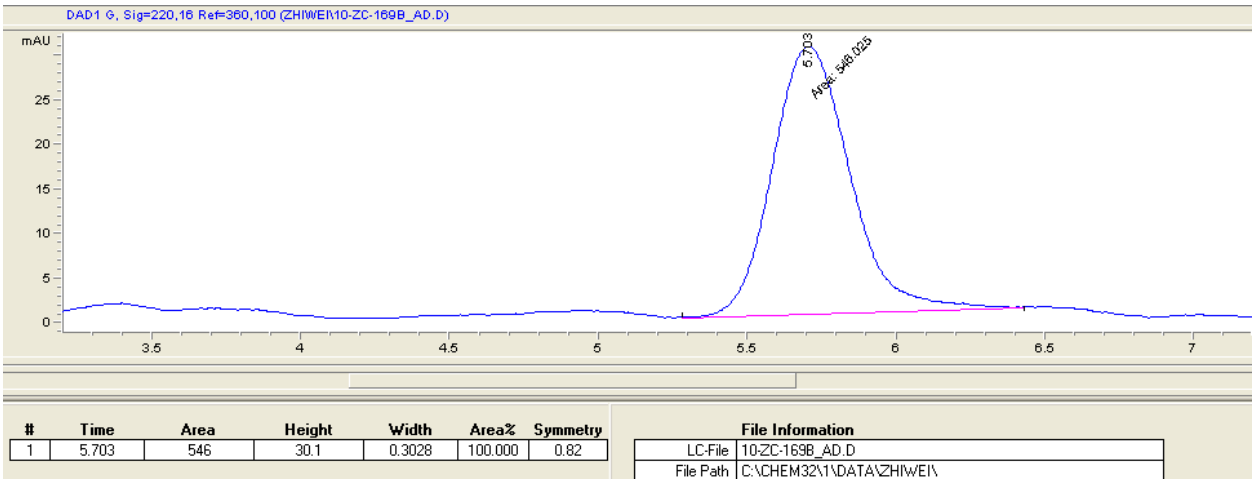


#	Time	Area	Height	Width	Area%	Symmetry
1	4.64	196.8	20.3	0.1503	50.357	1.076
2	5.842	194	16.4	0.1802	49.643	0.949

File Information	
LC-File	10-ZC-165B_AD.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\

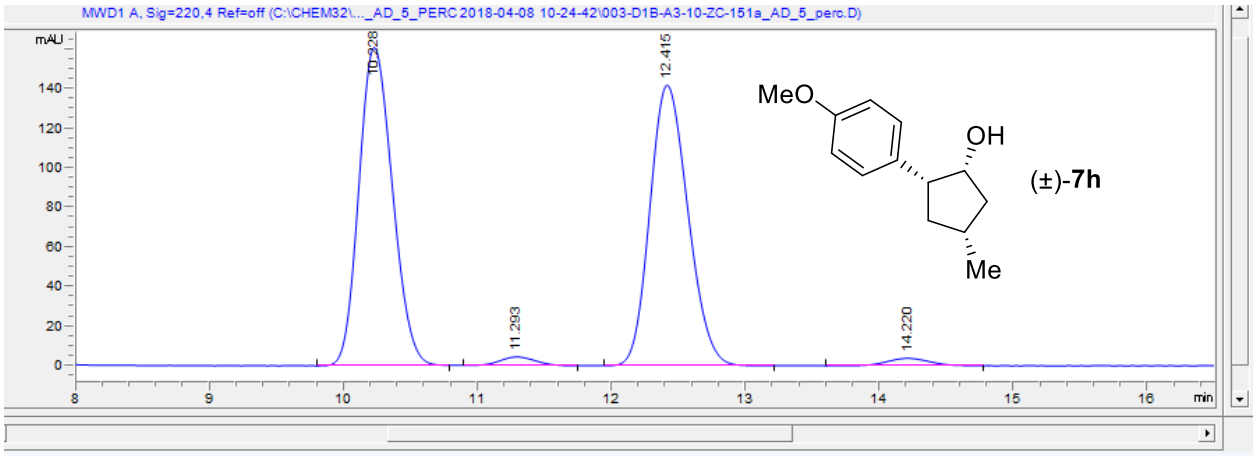


(–)-**7g**



#	Time	Area	Height	Width	Area%	Symmetry
1	5.703	546	30.1	0.3028	100.000	0.82

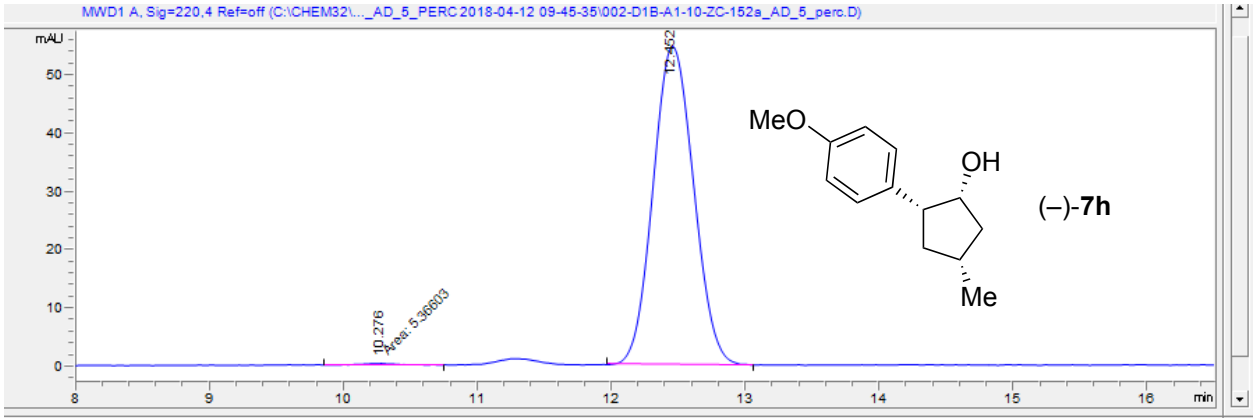
File Information	
LC-File	10-ZC-169B_AD.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\



File Information	
LC-File	003-D1B-A3-10-ZC-151a_AD_5_perc.D
File Path	C:\CHEM32\1\DATA\ZC-10-150A_151_AD_5_PERC 201
Date	08-Apr-18, 11:27:26
Sample	10-ZC-151a_AD_5_perc

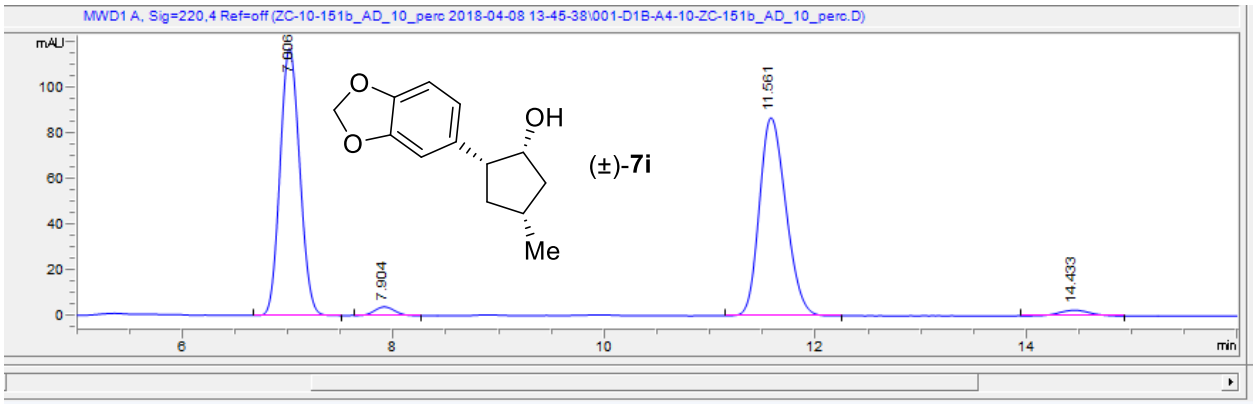
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.228	BB	2787.3	160.4	0.2747	48.523	0.811
2	11.293	BB	79.5	4.3	0.2695	1.384	0.895
3	12.415	BV R	2793	141.5	0.3063	48.622	0.8
4	14.22	BB	84.5	3.7	0.3152	1.471	1.013

* peaks at 11.3 and 14.2 min correspond to another diastereomer that was not separated from the product



File Information	
LC-File	002-D1B-A1-10-ZC-152a_AD_5_perc.D
File Path	C:\CHEM32\1\DATA\ZC-10-152A_AD_5_PERC 2018-04

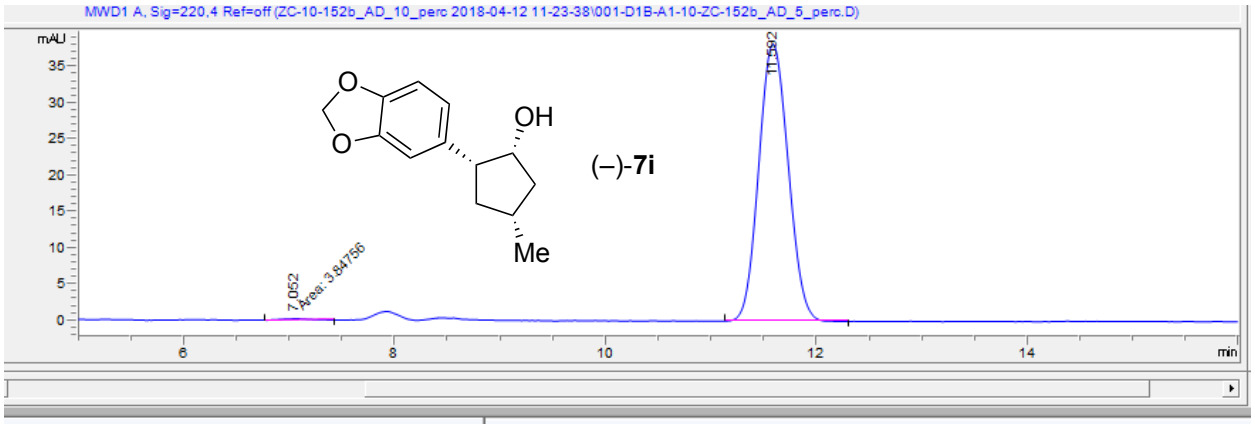
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	10.276	MM	5.4	2.8E-1	0.3155	0.465	1.099
2	12.452	BB	1147.9	54.5	0.3339	99.535	0.896



File Information	
LC-File	001-D1B-A4-10-ZC-151b_AD_10_perc.D
File Path	C:\Chem32\1\Data\ZC-10-151b_AD_10_perc 2018-
Date	08-Apr-18, 13:46:38
Sample	10-ZC-151b_AD_10_perc

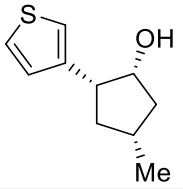
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.006	BB	1509.6	117.1	0.2044	48.359	0.879
2	7.904	BB	51.4	3.8	0.2121	1.648	0.902
3	11.561	BB	1509.3	86.8	0.2728	48.349	0.755
4	14.433	BB	51.3	2.5	0.3042	1.645	0.978

* peaks at 7.9 and 14.4 min correspond to another diastereomer that was not separated from the product

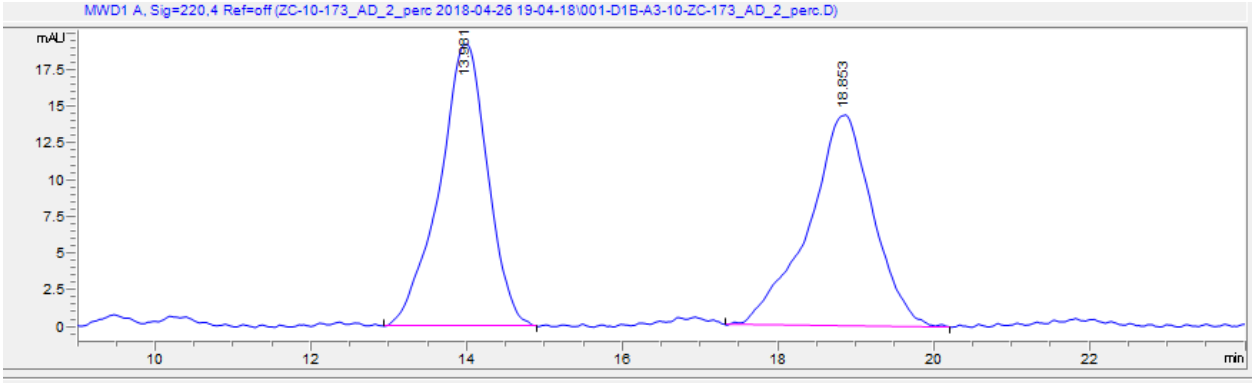


File Information	
LC-File	001-D1B-A1-10-ZC-152b_AD_5_perc.D
File Path	C:\Chem32\1\Data\ZC-10-152b_AD_10_perc 2018-

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.052	MM	3.8	2.3E-1	0.2848	0.516	0.976
2	11.592	BB	741.7	38.1	0.3113	99.484	0.886

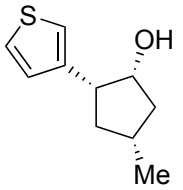


(±)-**7j**

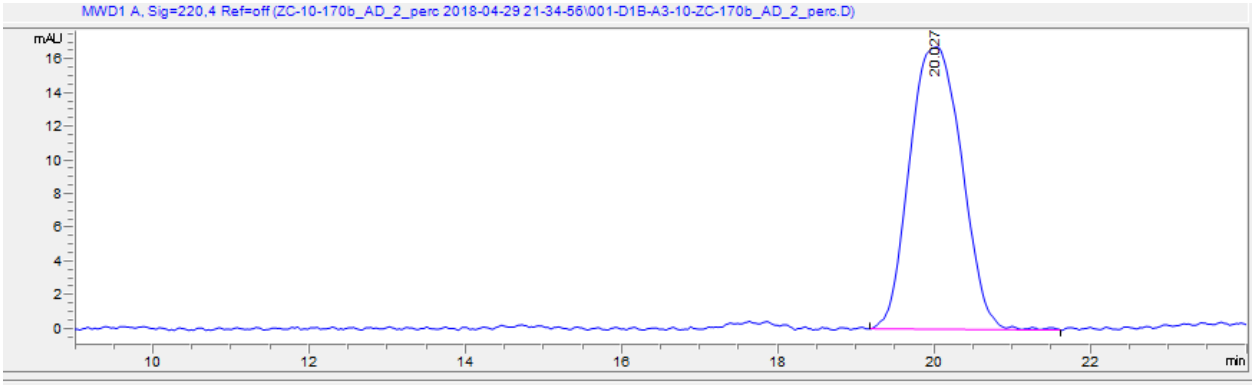


File Information	
LC-File	001-D1B-A3-10-ZC-173_AD_2_perc.D
File Path	C:\Chem32\1\Data\ZC-10-173_AD_2_perc 2018-04

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	13.981	BV	830.2	19.2	0.5943	49.933	1.216
2	18.853	VV R	832.4	14.4	0.7056	50.067	1.32

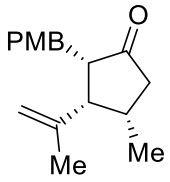


(–)-**7j**

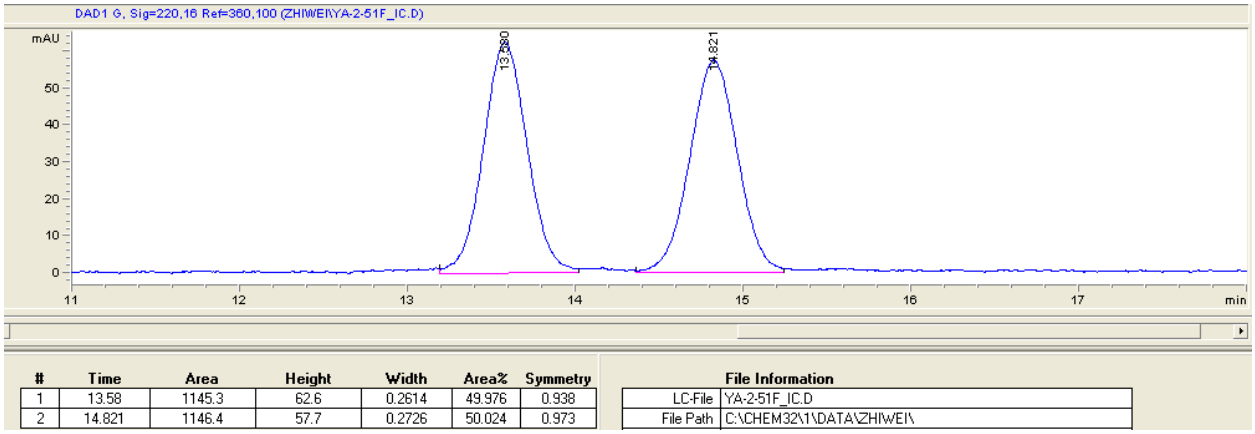


File Information	
LC-File	001-D1B-A3-10-ZC-170b_AD_2_perc.D
File Path	C:\Chem32\1\Data\ZC-10-170b_AD_2_perc 2018-0

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	20.027	BV R	785.2	16.9	0.5732	100.000	1.069

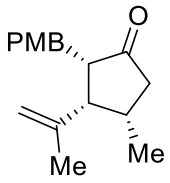


(±)-**9**

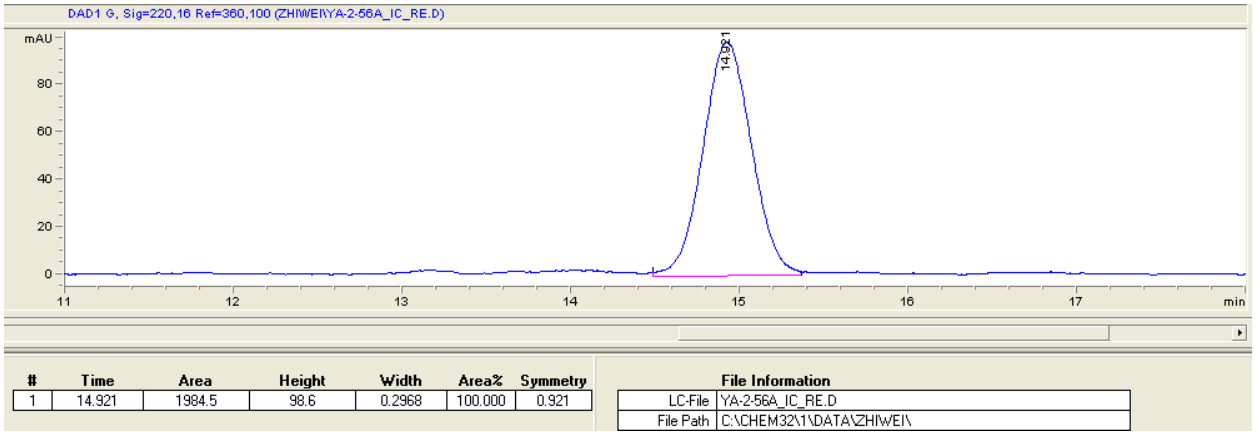


#	Time	Area	Height	Width	Area%	Symmetry
1	13.58	1145.3	62.6	0.2614	49.976	0.938
2	14.821	1146.4	57.7	0.2726	50.024	0.973

File Information	
LC-File	YA-2-51F_IC.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\

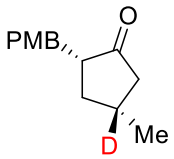


(+)-**9**

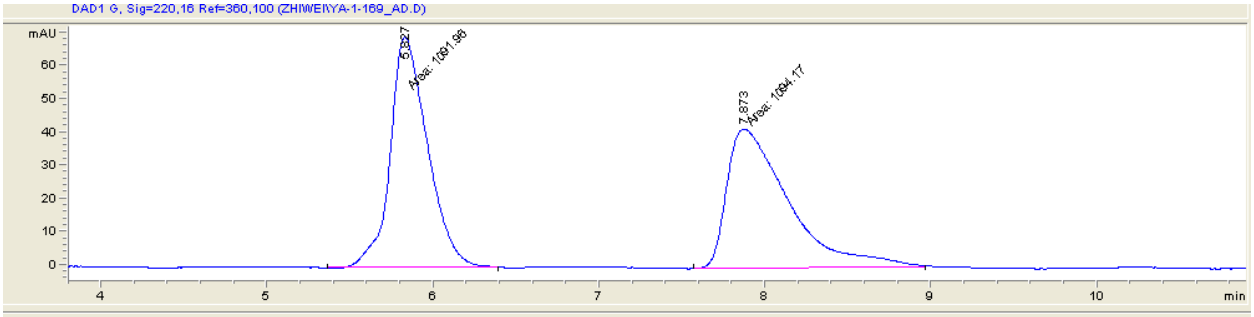


#	Time	Area	Height	Width	Area%	Symmetry
1	14.921	1984.5	98.6	0.2968	100.000	0.921

File Information	
LC-File	YA-2-56A_IC_RE.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\

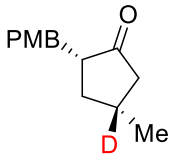


(±)-**2a**-*d*

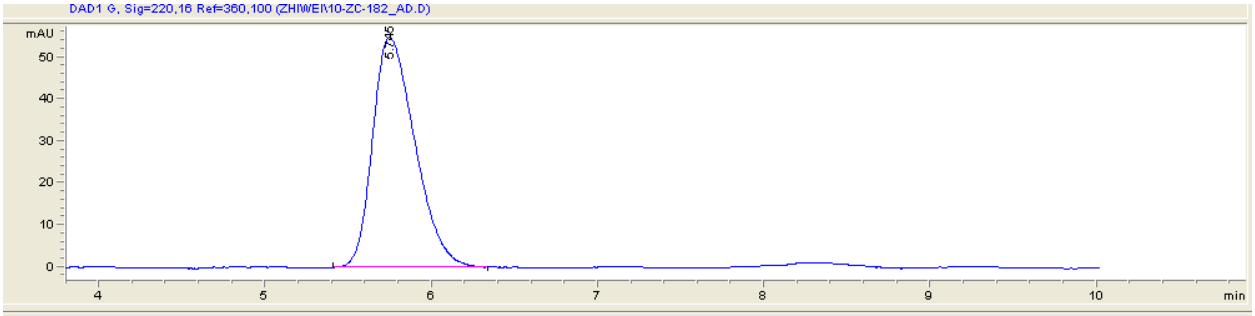


#	Time	Area	Height	Width	Area%	Symmetry
1	5.827	1092	69.4	0.2624	49.950	0.64
2	7.873	1094.2	42	0.4338	50.050	0.379

File Information	
LC-File	YA-1-169_AD.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\



(+)-**2a**-*d*



#	Time	Area	Height	Width	Area%	Symmetry
1	5.745	973.5	54.9	0.2599	100.000	0.632

File Information	
LC-File	10-ZC-182_AD.D
File Path	C:\CHEM32\1\DATA\ZHIWEI\