Palladium-Catalyzed Asymmetric Trimethylenemethane [3+2] Cycloaddition Reactions

Barry M. Trost*, James P. Stambuli, Steven M. Silverman, and Ulrike Schwörer
Department of Chemistry, Stanford University, Stanford, CA 94305-5080

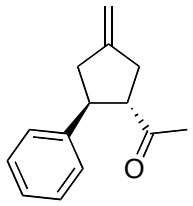
Supporting Information

General Methods. All reactions were carried out under an inert atmosphere. All solvents were dried by passing through an Alumina column except for tetrahydrofuan, which was distilled over sodium/benzophenone. All compounds were purchased from commercial sources unless listed. The following compounds were prepared according to known literature procedures: $Pd(dba)_2$,[1] **1**,[2] **L1**,[3] **L2**-**L3**,[4] **L4**,[3] **L5**,[5] and **L6**.[6]

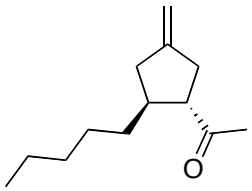
Flash chromatography was performed with 0.040-0.063 μm Silica Gel. Melting points were obtained on a Thomas-Hoover apparatus in open capillary tubes. ^1H and ^{13}C NMR spectroscopy was performed on a Mercury NMR at 400 (^1H) or 100 (^{13}C) MHz. Chemical shifts are reported in ppm relative to tetramethylsilane or residual protiated solvent. All ^{13}C NMR spectra were proton decoupled. Infrared Spectroscopic data was recorded on sodium chloride plates as thin films on a Perkin-Elmer Paragon 500 FT-IR spectrometer. Chiral GC analysis was performed on an HP 6850 Series GC System using a CycloSil-B column. Chiral HPLC analysis was performed on a Thermo Separation Products Spectra Series P-100 using Chiralcel® columns. Optical rotations were measured on a Jasco DIP-1000 digital polarimeter using 5 cm cells with a Na 589 nm filter.

Representative Procedure for Asymmetric [3+2] Trimethylenemethane Cycloaddition Reactions (Table 1, Entry 1). A vial containing $Pd(dba)_2$ (8 mg, 0.01 mmol) and **L6** (16 mg, 0.030 mmol) is evacuated and purged with nitrogen (three times) and 1.0 mL of toluene is added. The mixture is stirred for 2 min while a separate vial containing **1** (100 μL, 0.483 mmol) and (*E*)- 4-phenyl-3-buten-2-one (44 mg, 0.30 mmol) is evacuated and purged with nitrogen (three times) and 1.0 mL of toluene is added. The latter solution is added to the catalyst solution and the reaction is stirred at -25 °C until the ketone is completely consumed, as determined by GC. Toluene is removed on a

rotary evaporator and the crude residue is dissolved in methylene chloride and adsorbed onto a silica gel column eluting with 10-20% ethyl acetate in petroleum ether to give 63% yield (38 mg, 0.19 mmol) of a colorless oil.

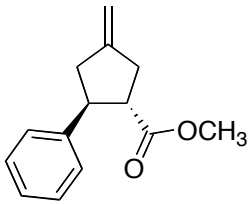


Starting from 44 mg (0.30 mmol) of *(E)*-4-phenyl-3-buten-2-one, 63% yield (38 mg, 0.19 mmol) of the above product was obtained as a colorless oil.[2] R_f = 0.50 (20% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.95 (s, 3H), 2.50-2.88 (m, 4H), 3.17 (dq, *J* = 2.4, 8.8 Hz, 1H), 3.32 (dq, *J* = 2.0, 9.0 Hz, 1H), 4.93 (br s, 2H), 7.20-7.33 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.3, 36.3, 41.8, 48.8, 59.6, 106.5, 126.7, 127.2, 128.6, 143.0, 148.8, 209.8; IR (neat): ν_{max}(cm^{-1}) = 3070, 2917, 1707, 1655, 1493, 1428, 1357, 1172, 877; $[\alpha]_D$ = -91.2 (*c* = 0.69, $CHCl_3$); Chiral GC: CycloSil-B column, 140 °C isothermal, 50:1 split ratio, 15.0 split flow, 1.2 flow rate, t_R = 40.44 (minor), 43.43 (major).

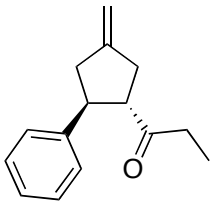


Starting from 50 μL (0.30 mmol) of *(E)*-3-nonen-2-one, 79% yield (46 mg, 0.24 mmol) of the above product was obtained as a colorless oil. R_f = 0.63 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3H), 1.22-1.28 (m, 7H), 1.40-1.43 (m, 1H), 1.90-1.98 (m, 1H), 2.14-2.22 (m, 4H), 2.38-.244 (m, 1H), 2.58-2.62 (m, 3H), 4.84 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =14.0, 22.6, 27.8, 29.3, 32.0, 34.8, 36.3, 38.9, 42.5, 58.3, 106.0, 149.6, 210.8; IR (film): ν_{max}(cm^{-1}) = 2927, 2859, 1711, 1456, 1360, 1165; $[\alpha]_D$ = -55.3 (*c* = 0.84, $CHCl_3$); Chiral GC:

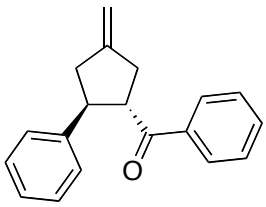
CycloSil-B column, 130 °C isothermal, 50:1 split ratio, 15.0 split flow, 1.2 flow rate, t_R = 24.13 (minor), 24.41 (major); HRMS calcd. for $C_{13}H_{22}O$ m/z 194.1671, found 194.1669.



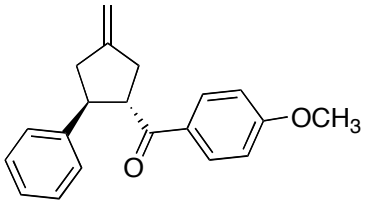
Starting from 26 mg (0.16 mmol) of methyl cinnamate, 81% yield (29 mg, 0.13 mmol) of the above product was obtained as a colorless oil.[2] R_f = 0.40 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.49-2.56 (m, 1H), 2.67-2.72 (m, 1H), 2.80-2.88 (m, 2H), 2.94-3.00 (m, 1H), 3.02-3.48 (m, 1H), 3.59 (s, 3H), 4.94 (br s, 2H), 7.19-7.32 (m, 5H); Chiral GC: CycloSil-B column, 140 °C isothermal, 50:1 split ratio, 15.0 split flow, 1.5 flow rate, t_R = 30.97 (major), 32.28 (minor).



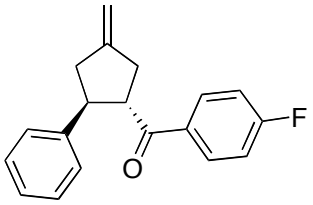
Starting from 48 mg (0.30 mmol) of *(E)*-phenyl-penten-3-one, 72% yield (46 mg, 0.22 mmol) of the above product was obtained as a colorless oil. R_f = 0.50 (20% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 5.2 Hz, 3H), 2.05-2.13 (m, 1H), 2.24-2.32 (m, 1H), 2.51-2.87 (m, 4H), 3.16 (dq, *J* = 2.0, 9.2 Hz, 1H), 3.33 (dq, *J* = 2.4, 9.2 Hz, 1 H), 4.92 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =14.0, 22.6, 27.8, 29.3, 32.0, 34.8, 36.3, 38.9, 42.5, 58.3, 106.0, 149.6, 210.8; IR (film): ν_{max}(cm^{-1}) = 3063, 2968, 2940, 1709, 1654, 1493, 1374, 1115, 1018; $[\alpha]_D$ = -100.6 (*c* = 0.78, $CHCl_3$); Chiral GC: CycloSil-B column, 140 °C isothermal, 50:1 split ratio, 15.0 split flow, 1.2 flow rate, t_R = 52.98 (minor), 55.78 (major); HRMS calcd. for $C_{15}H_{18}O$ m/z 214.1358, found 214.1354.



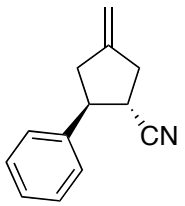
Starting from 61 mg (0.29 mmol) of *(E)*-chalcone, 83% yield (62 mg, 0.24 mmol) of the above product was obtained as a viscous oil.[2] R_f = 0.70 (50% ethyl acetate/petroleum ether);^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.62-2.71 (m, 2H), 2.88-2.97 (m, 2H), 3.73 (dq, *J* = 1.2, 9.4 Hz, 1H), 3.97 (vq, *J* = 9.2Hz, 1H), 4.94 (s, 1H), 4.98 (s, 1H), 7.13-7.22 (m, 1H), 7.23-7.28 (m, 4H), 7.37-7.40 (m, 2H), 7.48-7.50 (m, 1H), 7.82-7.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 38.4, 40.8, 47.9, 54.2, 106.5, 126.5, 127.3, 128.3, 128.5, 133.0, 143.4, 149.3, 201.2; δ =; IR (film): ν_{max}(cm^{-1}) = 3061, 2926, 1680, 1597, 1493, 1448, 1233; $[\alpha]_D$ = -70.6 (*c* = 0.57, $CHCl_3$); Chiral HPLC: Chiralcel® AD column, 10% isopropanol in heptane, 0.5 mL/min, λ = 254 nm; t_1 = 11.18 (minor), 12.80 (major).



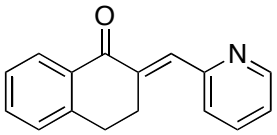
Starting from 72 mg (0.30 mmol) of *(E)*-4'-methoxychalcone, 73% yield (65 mg, 0.22 mmol) of the above product was obtained as a viscous oil. R_f = 0.64 (50% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.62-2.70 (m, 2H), 2.85-2.96 (m, 2H), 3.67-3.74 (m, 1H), 3.81 (s, 3H), 3.89-3.96 (m, 1H), 4.93 (s, 1H), 4.97 (s, 1H), 6.82-6.86 (m, 2H), 7.12-7.16 (m, 1H), 7.21-7.27 (m, 4H), 7.79-7.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 38.4, 40.9, 47.9, 53.7, 55.4, 106.3, 113.6, 126.4, 127.2, 128.4, 129.8, 130.6, 143.4, 149.4, 163.3, 199.6; δ =; IR (film): ν_{max}(cm^{-1}) = 3073, 2940, 2836, 1670, 1600, 1260, 1171, 1030; $[\alpha]_D$ = -58.28 (*c* = 0.47, $CHCl_3$); Chiral HPLC: Chiralcel® AD column, 10% isopropanol in heptane, 1.0 mL/min, λ = 254 nm; t_1 = 11.24 (minor), 13.07 (major); HRMS calcd. for $C_{20}H_{20}O_2$ m/z 292.1463, found 292.1476.



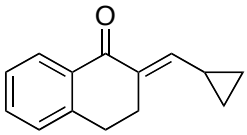
Starting from 69 mg (0.30 mmol) of *(E)*-4'-fluorochalcone, 80% yield (68 mg, 0.24 mmol) of the above product was obtained as a viscous oil. R_f = 0.56 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.57-2.69 (m, 2H), 2.89-2.95 (m, 2H), 3.67-3.74 (m, 1H), 3.88-3.95 (m, 1H), 4.94 (br s, 1H), 4.99 (br s, 1H), 6.90-6.94 (m, 2H), 7.20-7.23 (m, 2H), 7.38-7.42 (m, 2H), 7.49-7.54 (m, 1H), 7.82-7.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 38.4, 41.0, 47.1, 54.3, 106.7, 115.2, 115.3, 128.3, 128.5, 128.6, 18.7, 133.1, 136.7, 148.9, 201.0; δ =; IR (film): ν_{max}(cm^{-1}) = 3063, 2945, 1677, 1597, 1510, 1448, 1222, 1159, 1015; $[\alpha]_D$ = -71.7 (*c* = 0.74, $CHCl_3$); Chiral HPLC: Chiralcel® AD column, 2% isopropanol in heptane, 1.0 mL/min, λ = 254 nm; t_1 = 8.75 (minor), 10.94 (major); Anal. calcd. for $C_{19}H_{17}FO$: C, 81.40; H, 6.11. Found C, 81.24, H, 6.31.



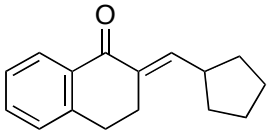
Starting from 40 μL (41 mg, 0.32 mmol) of cinnamonitrile, 78% yield (45 mg, 0.25 mmol) of the above product was obtained as a fluffy white solid. R_f = 0.40 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.52-2.61 (m, 1H), 2.71-3.00 (m, 4H), 3.34-3.41 (m, 1H), 5.00-5.03 (m, 2H), 7.25-7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.4, 37.3, 39.6, 50.0, 108.3, 122.2, 126.9, 127.5, 128.8, 139.8, 145.8; IR (film): ν_{max}(cm^{-1}) = 3071, 3032, 2917, 2241, 1654, 1456, 1429, 1260, 1228, 1144, 1076; mp: 86.0-88.0 °C; $[\alpha]_D$ = -61.8 (*c* = 0.96, $CHCl_3$); Chiral GC: CycloSil-B column, 140 °C isothermal, 50:1 split ratio, 15.0 split flow, 1.6 flow rate, t_R = 47.84 (minor), 50.09 (major); Anal. calcd. for $C_{13}H_{13}N$: C, 85.21; H, 7.15; N, 7.64. Found C, 85.10; H, 7.31; N, 7.82.



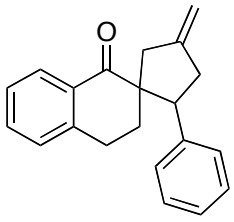
Representative Procedure for the Synthesis of α, β Unsaturated Ketone Substrates (Table 3). α-Tetralone (1.012 g, 6.922 mmol) is dissolved in 2.5 mL of ethanol and 4.2 mL of aqueous NaOH (10 wt%) is added. Pyridine carboxaldehyde (0.92 mL, 9.7 mmol) is added and the reaction is heated to 50 °C for 16 h. After this time, 20 mL of ether is added, the organic layer is separated and the remaining aqueous layer is extracted with ether (2 x 20 mL). The ethereal layer is washed with water (20 mL) and brine (20 mL), and dried over $MgSO_4$. The ethereal solution was removed on a rotary evaporator until approximately 10 mL remained. The solution was cooled to –20 °C for 12 h, which gave 39.4% yield (642 mg, 2.73 mmol) of a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.96-2.99 (m, 2H), 3.09-3.11 (m, 2H), 7.25-7.39 (m, 3H), 7.49-7.53 (m, 1H), 7.72-7.80 (m, 2H), 8.12-8.14 (m, 1H), 8.58 (br s, 1H), 8.69 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.1, 28.6, 123.2, 127.0, 128.2, 131.6, 132.4, 133.0, 133.4, 136.6, 137.4, 143.0, 149.1, 150.5, 187.2; IR (film): ν_{max}(cm^{-1}) = 3028, 2939, 2845, 1670, 1606, 1412, 1298, 1137, 1024, 949; mp: 73.0-74.0 °C; HRMS calcd. for $C_{16}H_{13}NO$ m/z 235.0997, found 235.0977.



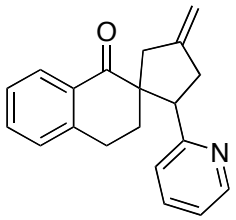
Starting from 982 mg (6.72 mmol) of α-tetralone, 45.2% yield (843 mg, 4.25 mmol) of the above product was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.70-0.73 (m, 2H), 0.99-1.04 (m, 2H), 1.65-1.74 (m, 1H), 2.89-2.99 (m, 4H), 6.32-6.36 (m, 1H), 7.22-7.24 (m, 1H), 7.25-7.34 (m, 1H), 7.45-7.47 (m, 1H), 8.07-8.09 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.0, 11.8, 25.4, 28.9, 126.8, 128.0, 128.1, 132.5, 132.8, 133.6, 143.5, 145.6, 186.7; IR (film): ν_{max}(cm^{-1}) = 3005, 2938, 2844, 1672, 1611, 1455, 1318, 1244, 914; mp: 60.5-61.0 °C; HRMS calcd. for $C_{14}H_{14}NO$ m/z 198.1045, found 198.1042.



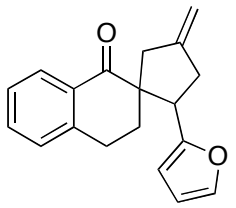
Starting from 878 mg (6.00 mmol) of α-tetralone, 38.3% yield (520 mg, 2.30 mmol) of the above product was obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39-1.44 (m, 2H), 1.60-1.88 (m, 8H), 2.78-2.84 (m, 3H), 2.92-2.94 (m, 2H), 6.87 (dt, *J* = 9.6, 1.6 Hz, 1H), 7.21-7.24 (m, 1H), 7.30-7.34 (m, 1H), 7.44 (td, *J* = 1.6, 7.6, 1H), 8.07-8.10 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.5, 25.7, 29.1, 33.3, 38.8, 126.8, 128.0, 128.1, 132.9, 133.5, 133.6, 143.6, 145.2, 187.7; IR (film): ν_{max}(cm^{-1}) = 2916, 2860, 1672, 1618, 1453, 1297, 1240, 1128, 1023; HRMS calcd. for $C_{16}H_{18}O$ m/z 226.1358, found 226.1350.



Starting from 19 mg (0.083 mmol) of benzylidene tetralone, 94% yield (22 mg, 0.078 mmol) of the above product was obtained as a viscous oil. R_f = 0.65 (10% ethyl aceate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.70-1.74 (m, 2H), 2.56-2.61 (m, 1H), 2.74-2.97 (m, 5H), 4.23 (m, 1), 4.98 (br s, 1H), 5.03 (br s, 1H), 7.13-7.28 (m, 7H), 7.39-7.44 (m, 1H), 8.05 (dd, *J* = 1.4, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.7, 27.5, 36.3 41.8, 49.0, 56.5, 107.3, 126.4, 126.6, 128.0, 128.1, 128.5, 128.7, 132.2, 133.2, 140.7, 143.3, 148.5, 200.8; IR (film): ν_{max}(cm^{-1}) = 3065, 2926, 1678, 1600, 1453, 1229; $[\alpha]_D$ = -91.9 (*c* = 0.40, $CHCl_3$); Chiral HPLC: Chiralcel® OD column, 1% isopropanol in heptane, 0.8 mL/min, λ = 254 nm; t_1 = 9.27 (minor), 9.82 (major); HRMS calcd. for $C_{21}H_{20}O$ m/z 288.1514, found 288.1514.

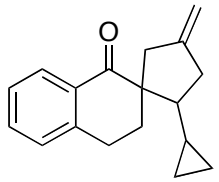


Starting from 71 mg (0.30 mmol) of 2-pyrilidine tetralone, 87% yield (76 mg, 0.26 mmol) of the above product was obtained as a viscous oil. R_f = 0.30 (30% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.61-1.72 (m, 2H), 1.77-1.82 (m, 1H), 2.56-2.60 (m, 1H), 2.78-3.01 (m, 4H), 4.25 (t, *J* = 8.4 Hz, 1H), 5.01 (br s, 1H), 5.05 (br s, 1H), 7.16-7.19 (m, 2H), 7.26-7.32 (m, 1H), 7.42-7.46 (m, 1H), 7.54-7.58 (m, 1H), 8.04-8.06 (m, 1H), 8.42-8.44 (m, 1H), 8.51 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.6, 27.2, 35.7, 41.4, 46.6, 56.4, 108.0, 123.1, 126.7, 128.0, 128.6, 131.9, 133.4, 136.0, 136.3, 143.1, 147.5, 148.0, 150.1, 200.2; IR (film): ν_{max}(cm^{-1}) = 3066, 2931, 1673, 1599, 1425, 1225, 1026; $[\alpha]_D$ = -88.6 (*c* = 0.52, $CHCl_3$); Chiral HPLC: Chiralcel® AD column, 10% isopropanol in heptane, 1.0 mL/min, λ = 254 nm; t_1 = 9.29 (minor), 11.31 (major); HRMS calcd. for $C_{20}H_{19}NO$ m/z 289.1467, found 289.1467.

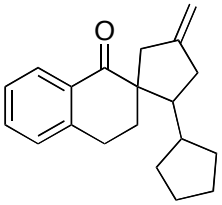


Starting from 67 mg (0.30 mmol) of 2-furylidine tetralone, 60% yield (49 mg, 0.18 mmol) of the above product was obtained as a viscous oil. R_f = 0.62 (5% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.63-1.81 (m, 2H), 2.52-2.57 (m, 1H), 2.68-3.01 (m, 5H), 4.21 (t, *J* = 9.2 Hz, 1H), 4.96 (br s, 1H), 5.00 (br s, 1H), 6.05 (d, *J* = 3.2 Hz, 1H), 6.24 (dd, *J* = 2.0, 3.2 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.24-7.26 (m, 1H), 7.31 (vt, *J* = 7.6 Hz, 1H), 7.43-7.45 (m, 1H), 8.08 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.7, 27.5, 34.5, 41.5, 43.3, 56.2, 106.6, 1-7.6, 109.9, 126.6, 128.0, 128.5, 132.0, 133.2, 141.3, 143.4, 147.9, 155.2, 158.1, 200.3; IR (film): ν_{max}(cm^{-1}) = 2927, 1678, 1600, 1453, 1226; $[\alpha]_D$ = -71.6 (*c* = 0.66, $CHCl_3$); Chiral HPLC:

Chiralcel® OD column, 1% isopropanol in heptane, 0.5 mL/min, λ = 230 nm; t_1 = 19.07 (minor), 20.12 (major); HRMS calcd. for $C_{19}H_{18}O_2$ m/z 278.1307, found 278.1308.



Starting from 60 mg (0.30 mmol) of cyclopropylidene tetralone, 70% yield (53 mg, 0.21 mmol) of the above product was obtained as a viscous oil. R_f = 0.74 (5% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.15-0.18 (m, 2H), 0.25-0.28 (m, 1H), 0.40-0.46 (m, 1H), 0.58-0.61 (m, 1H), 1.96-2.01 (m, 1H), 2.21-2.42 (m, 4H), 2.59-2.70 (m, 2H), 2.95-3.06 (m, 2H), 4.86-4.88 (m, 2H), 7.18-7.32 (m, 2H), 7.45-7.48 (m, 1H), 8.03 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 3.6, 3.9, 11.6, 25.9, 26.9, 36.7, 42.2, 49.4, 55.2, 106.8, 126.5, 127.1, 127.8, 128.5, 132.5, 133.1, 143.5, 148.9, 149.1, 201.8; IR (film): ν_{max}(cm^{-1}) = 3073, 2928, 1678, 1601, 1454, 1224; $[\alpha]_D$ = -64.1 (*c* = 0.45, $CHCl_3$); Chiral HPLC: Chiralcel® AD column, 0.5% isopropanol in heptane, 1.0 mL/min, λ = 254 nm; t_1 = 8.78 (minor), 9.90 (major); HRMS calcd. for $C_{18}H_{20}O$ m/z 252.1514, found 252.1508.



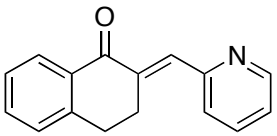
Starting from 68 mg (0.30 mmol) of cyclopentylidene tetralone, 53% yield (45 mg, 0.16 mmol) of the above product was obtained as a viscous oil. R_f = 0.62 (10% ethyl acetate/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.01-1.83 (m, 10H), 2.06-2.14 (m, 2H), 2.33-2.37 (m, 1H), 2.65-2.79 (m, 2H), 2.82-2.90 (m, 2H), 2.99-3.03 (m, 1H), 4.88 (br s, 2H), 7.18-7.33 (m, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 8.03 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.4, 24.9, 25.0, 25.6, 31.4, 32.2, 36.6, 42.5, 43.3, 50.3, 54.7, 106.7, 126.6, 127.9, 128.4, 133.1, 143.3, 149.4, 201.8; IR (film): ν_{max}(cm^{-1}) = 3069, 2946, 2866, 1676, 1600, 1454, 1230; $[\alpha]_D$ = -33.4 (*c* = 0.45, $CHCl_3$); Chiral HPLC:

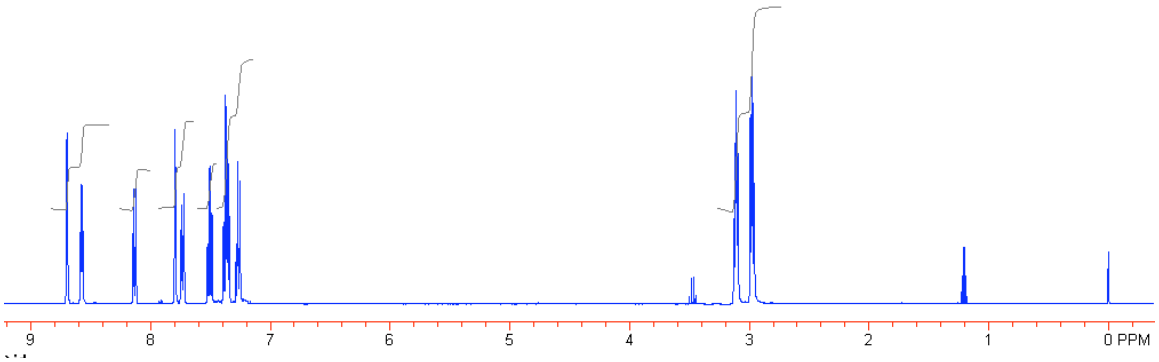
Chiralcel® AD column, 0.5% isopropanol in heptane, 1.0 mL/min, λ = 230 nm; t_1 = 7.37 (minor), 9.43 (major); HRMS calcd. for $C_{20}H_{24}O$ m/z 280.1827, found 280.1835.

References

(1) Komiya, S. *Synthesis of Organometallic Compounds. A Practical Guide*; John Wiley & Sons: New York, 1997.
(2) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1979**, *101*, 6429.
(3) Duursma, A.; Boiteau, J.-G.; Lefort, L.; Boogers, J. A. F.; DeVries, A. H. M.; DeVries, J. G.; Minnaard, A. J.; Feringa, B. L. *J. Org. Chem.* **2004**, *69*, 8045.
(4) Rimkus, A.; Sewald, N. *Org. Lett* **2003**, *5*, 79.
(5) Hartwig, J. F.; Shu, C. *Angew. Chem. Int. Ed.* **2004**, *43*, 4794.
(6) Choi, Y. H.; Choi, J. Y.; Yang, H. Y.; Kim, Y. H. *Tetrahedron: Asymmetry* **2002**, *13*, 801.

Table 3, Entry 2





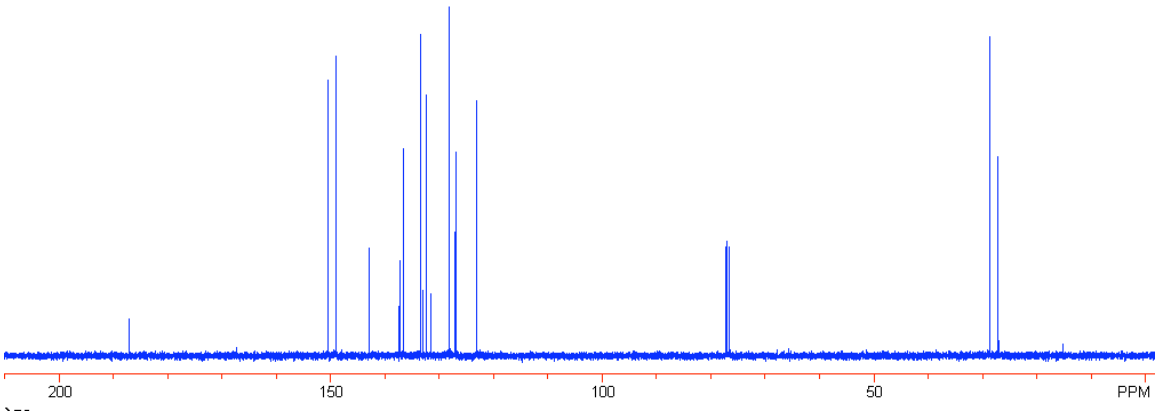
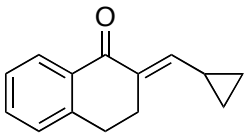
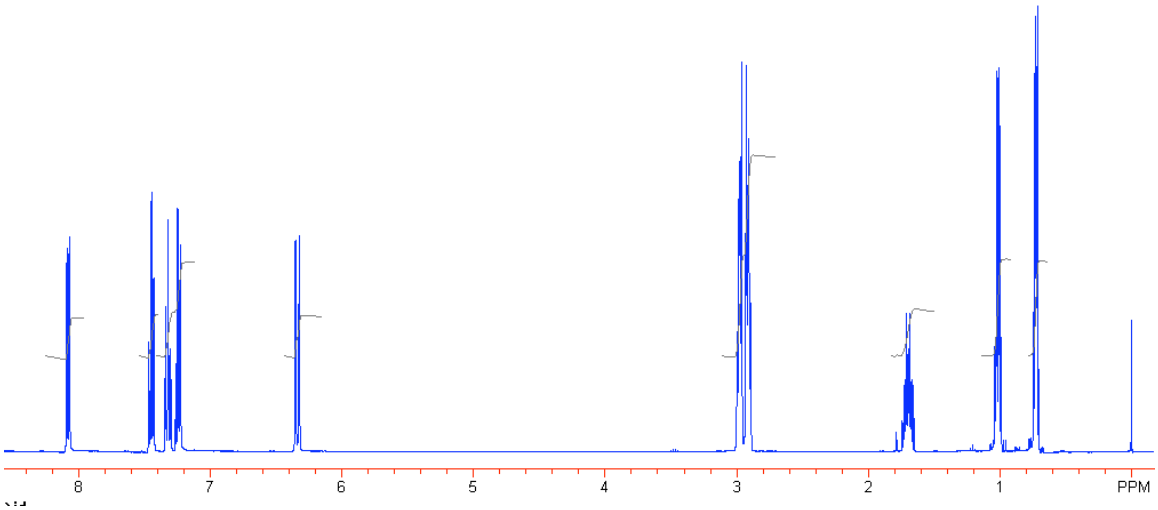


Table 3, Entry 4





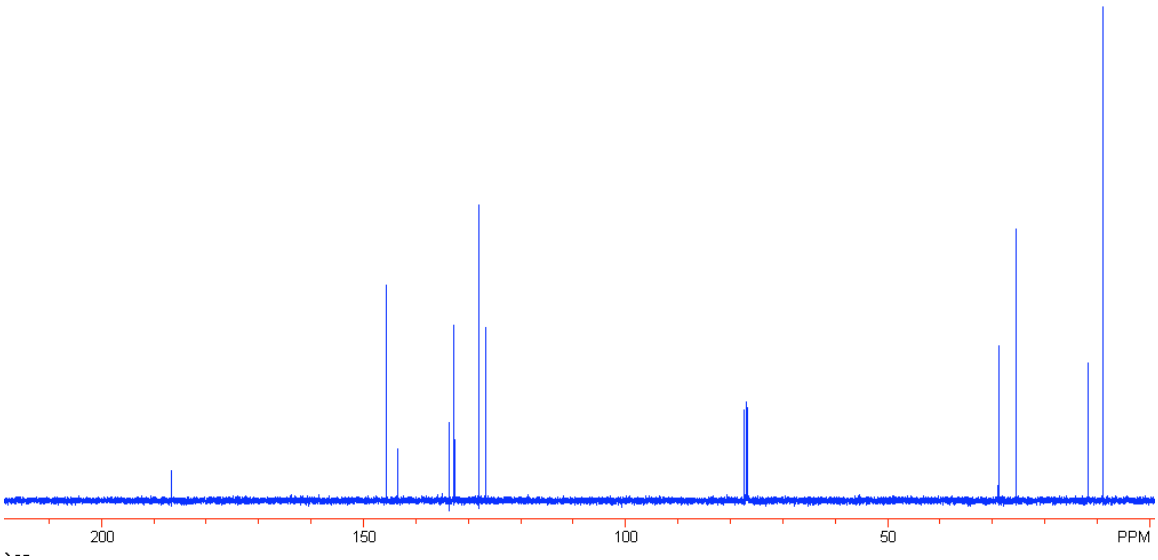
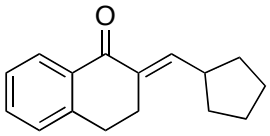
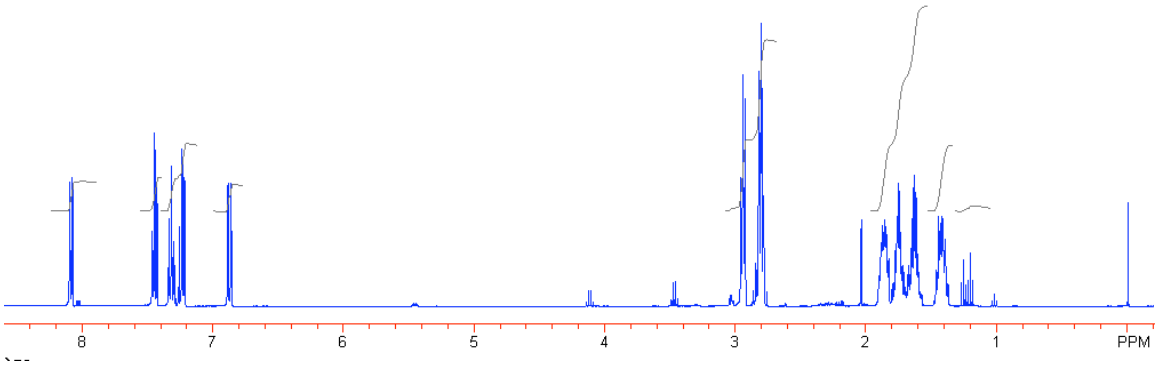


Table 3, Entry 5





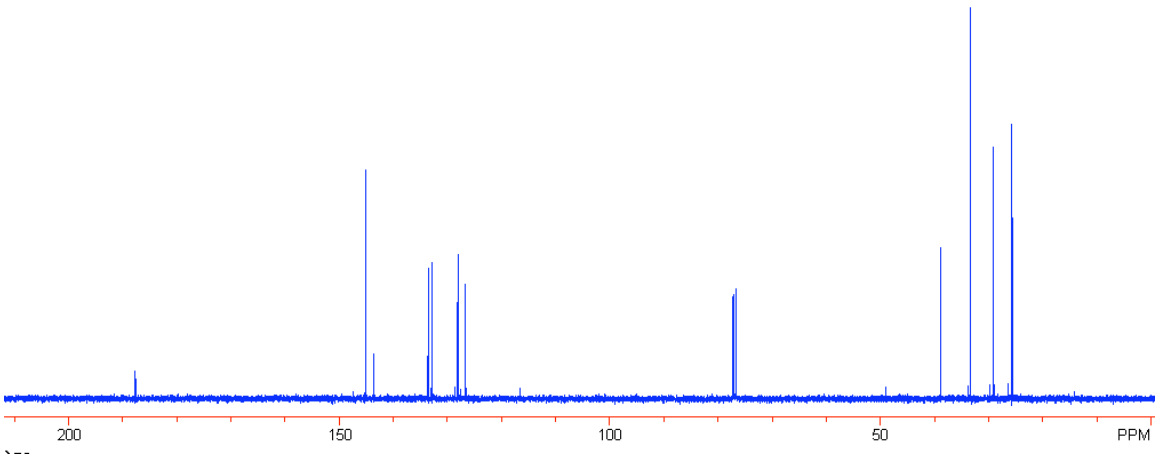
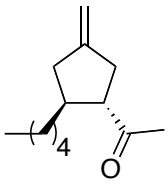
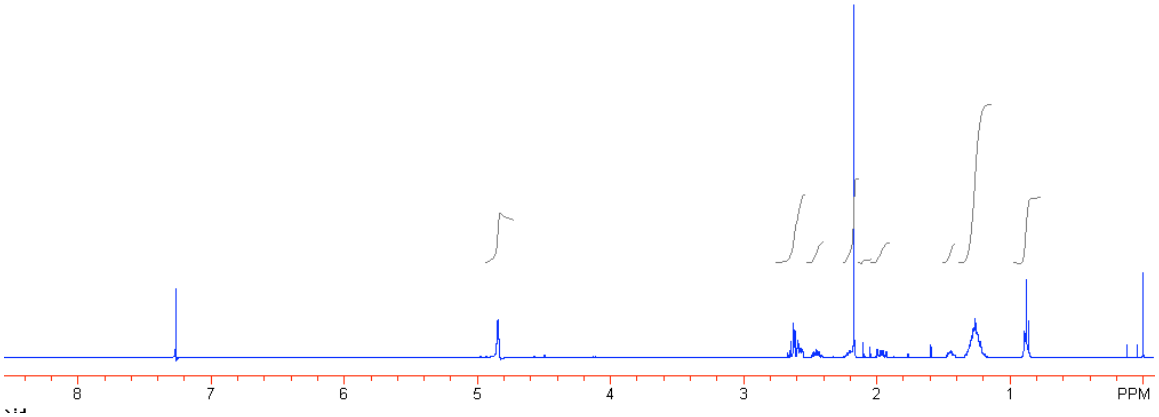


Table 2, Product 3





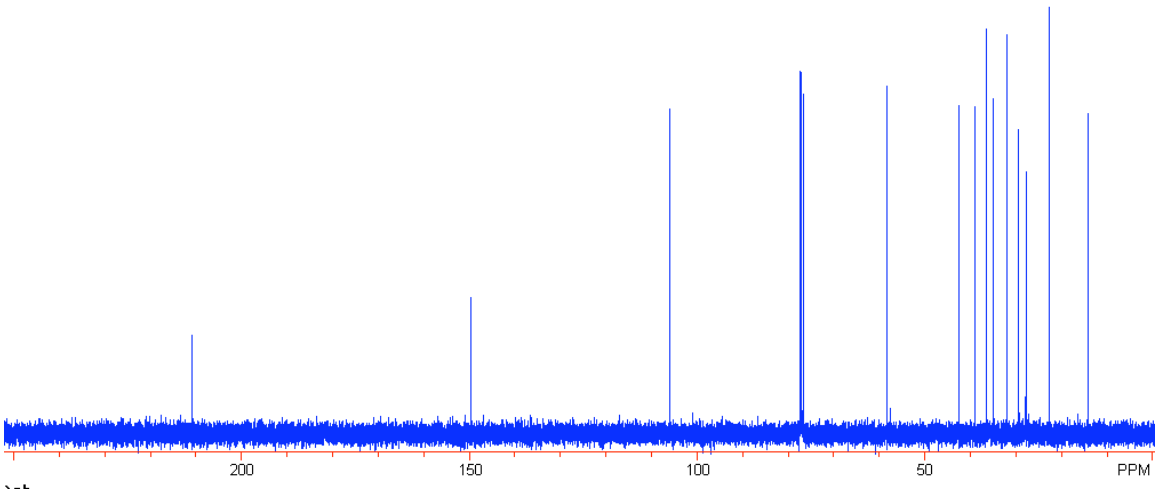
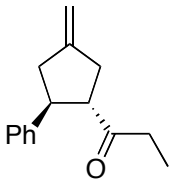
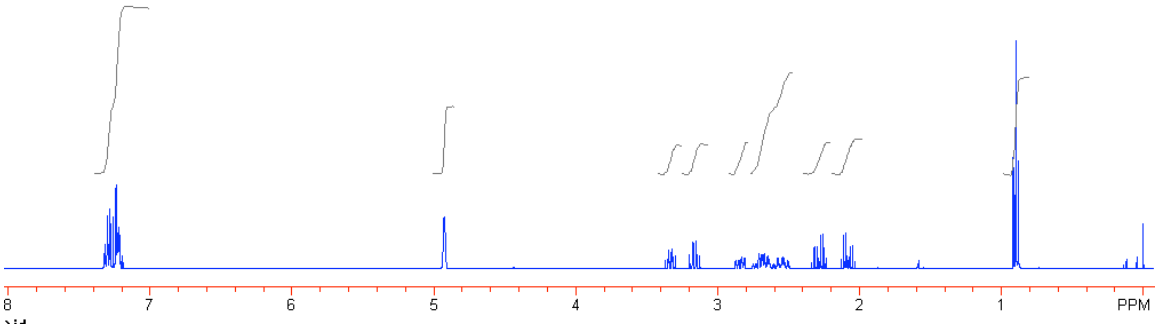


Table 2, Product 4





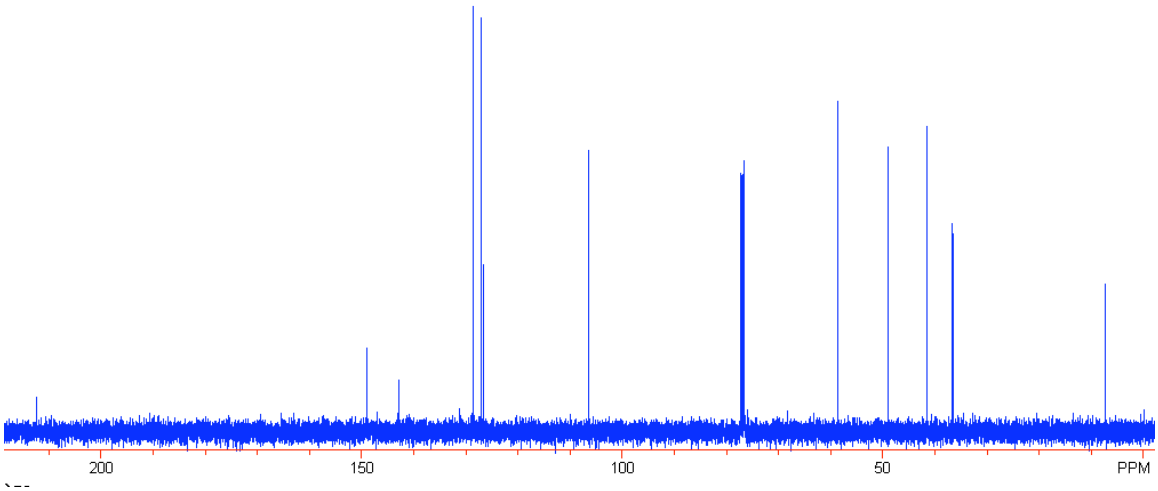
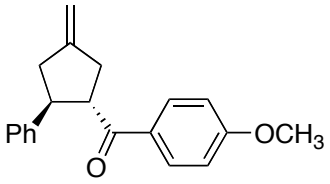
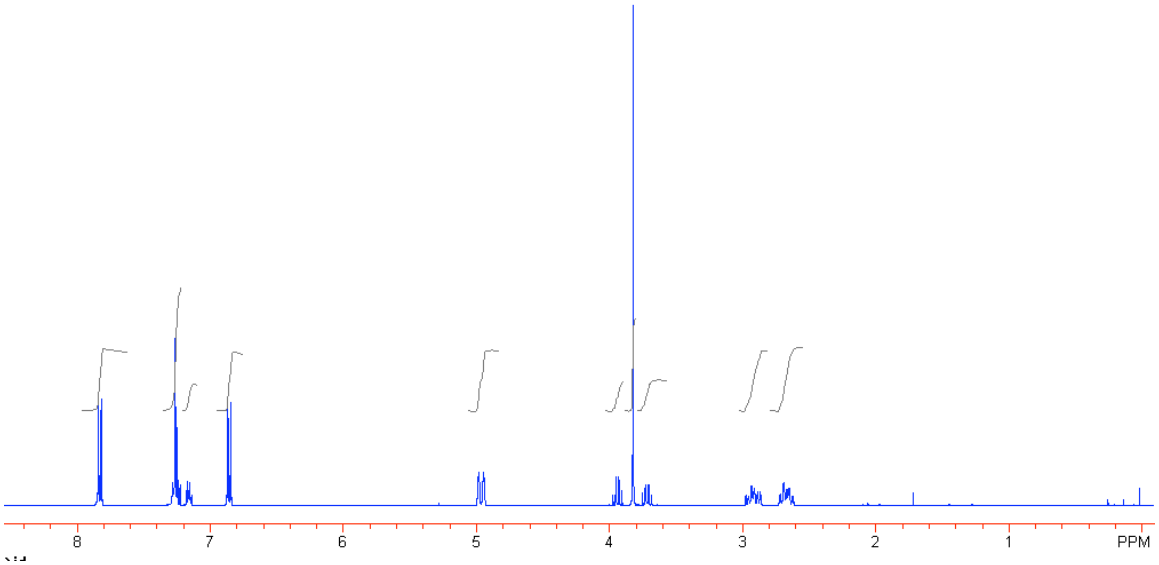


Table 2, Product 6a





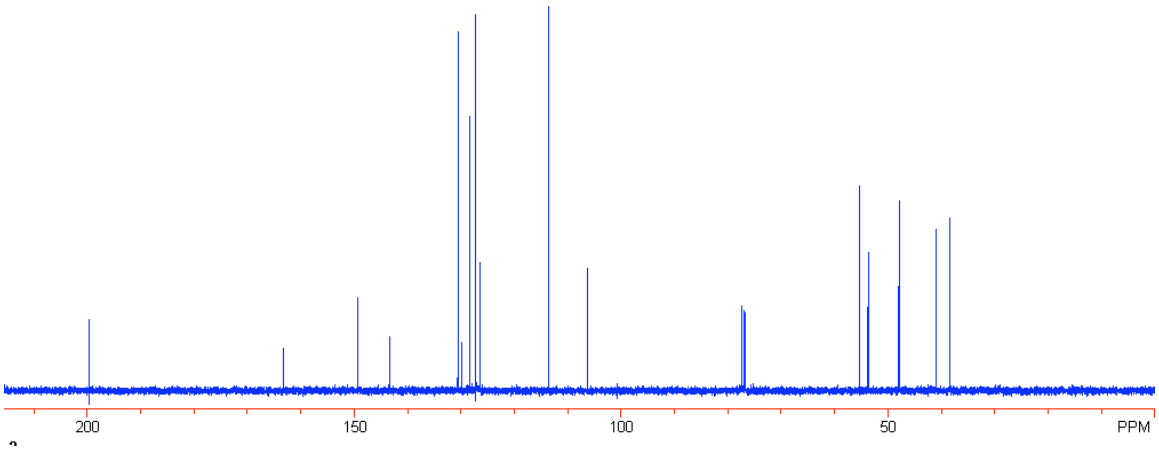
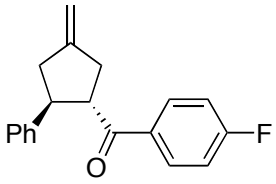
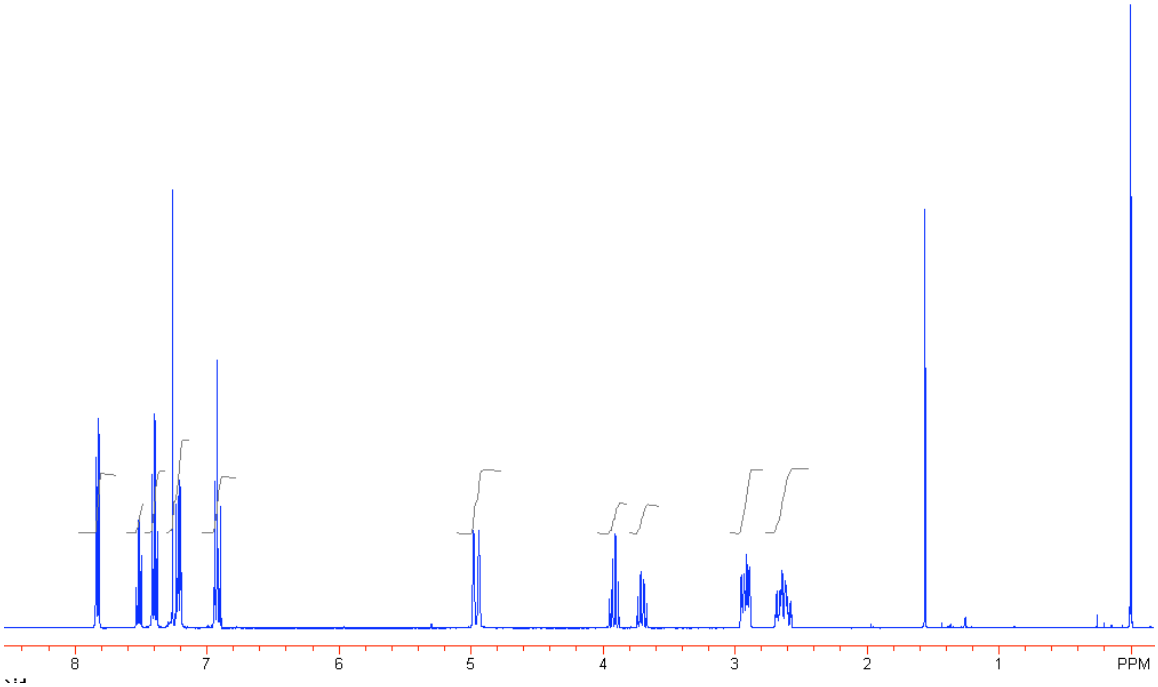


Table 2, Product 6b





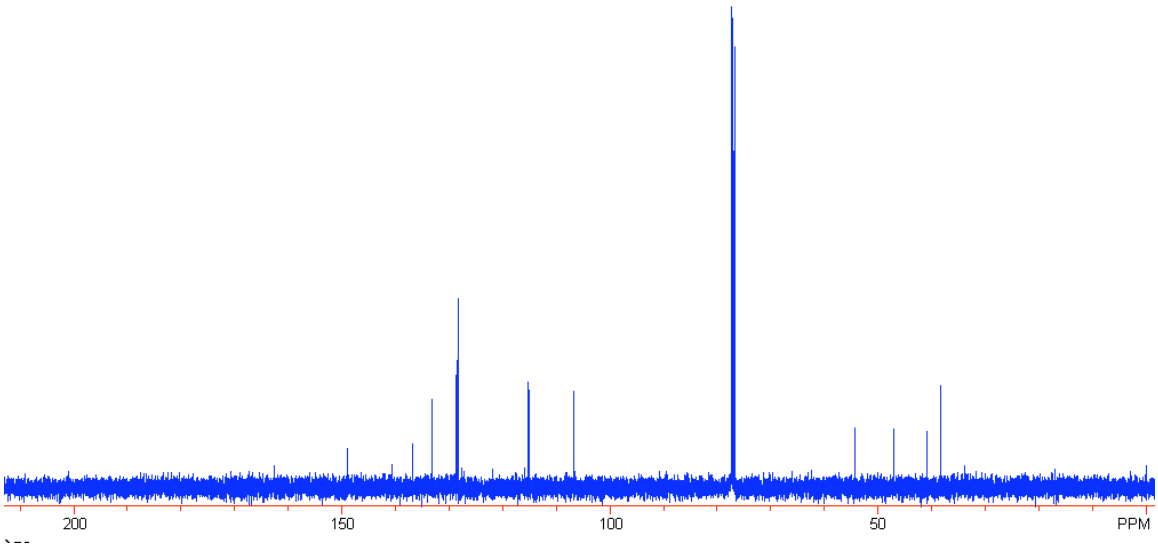
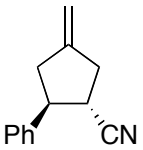
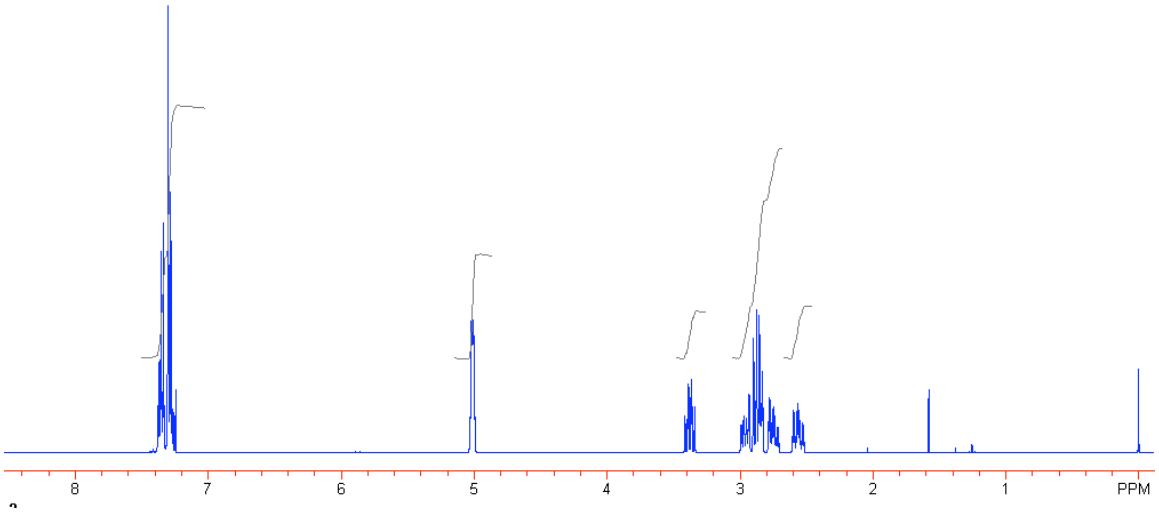


Table 2, Product 7





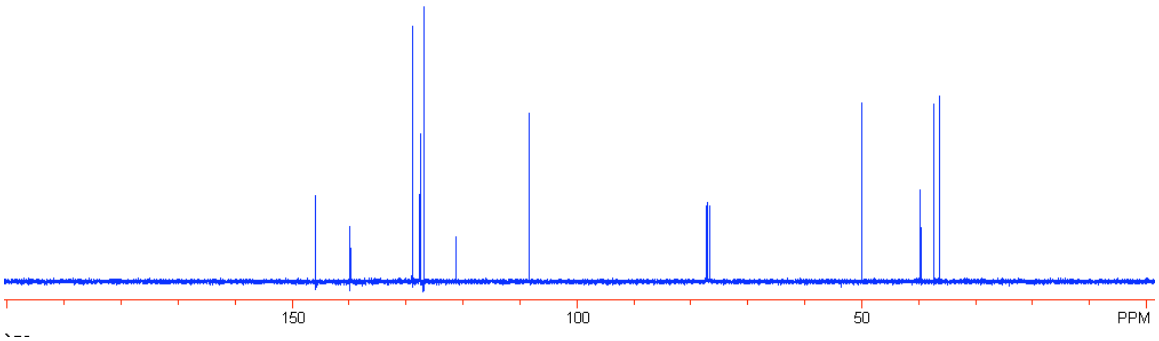
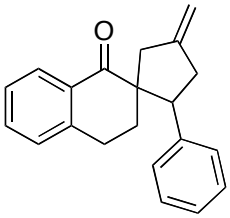
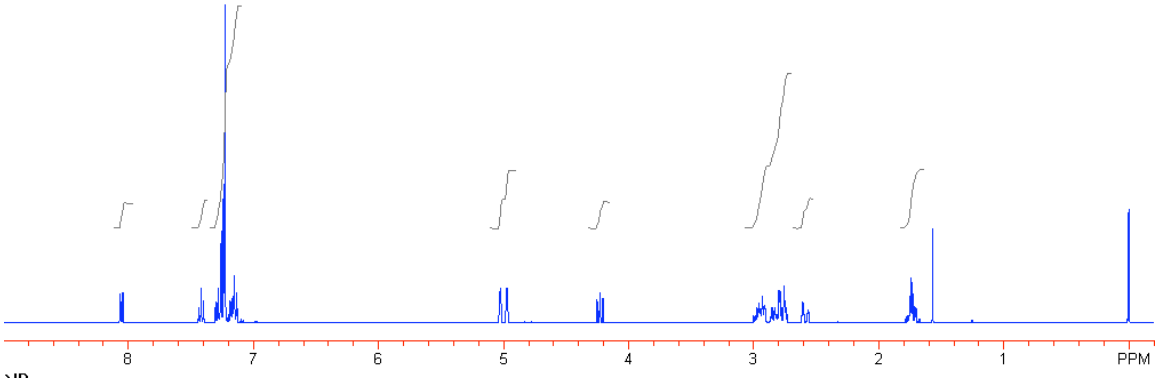


Table 3, Product 1





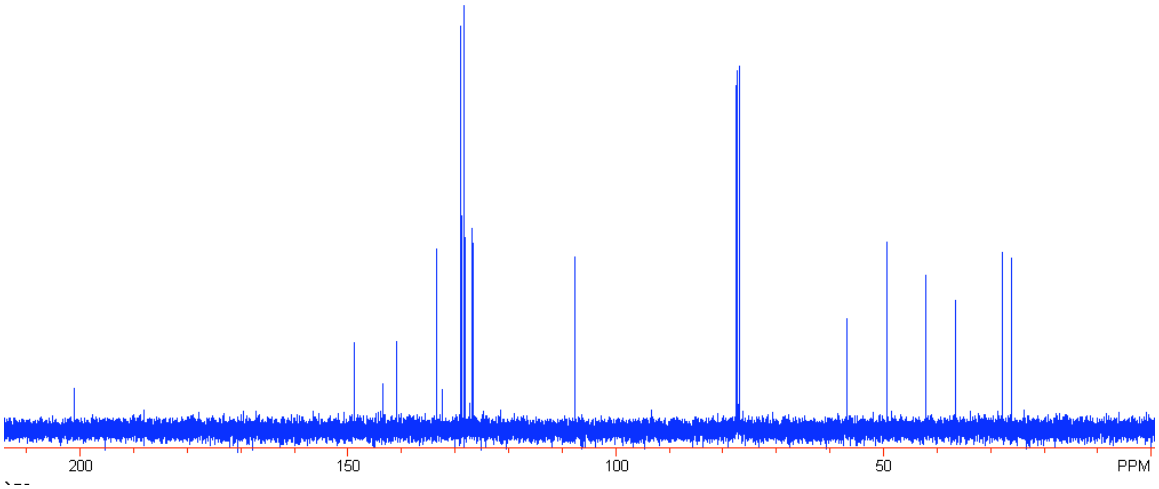
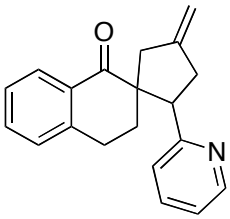
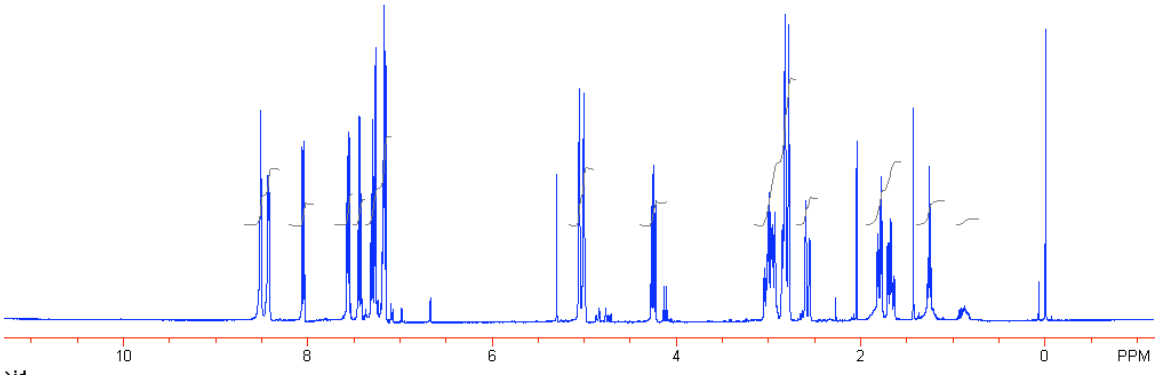


Table 3, Product 2





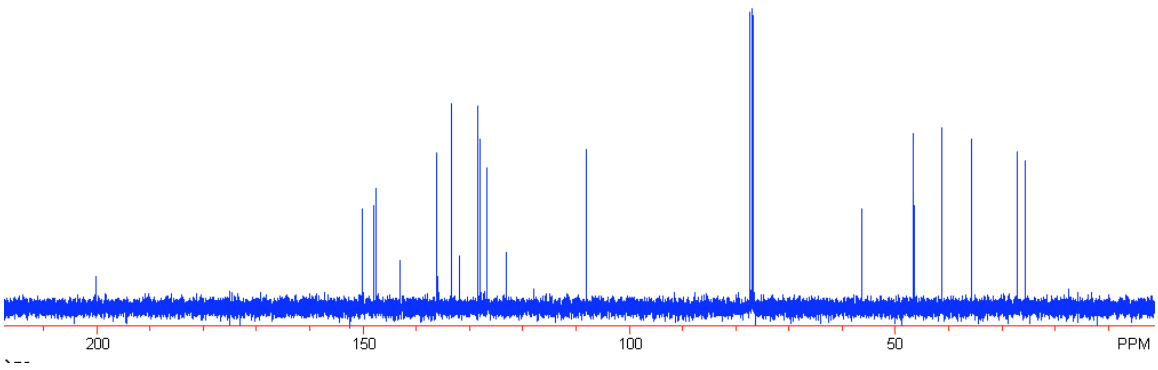
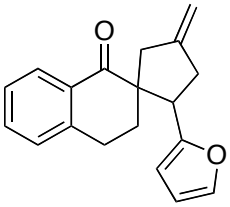
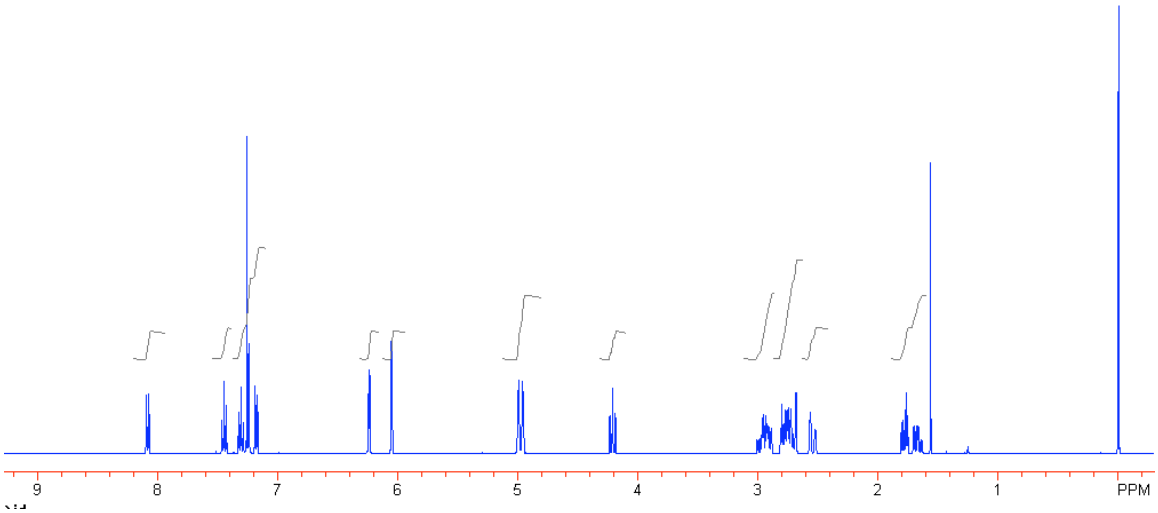


Table 3, Product 3





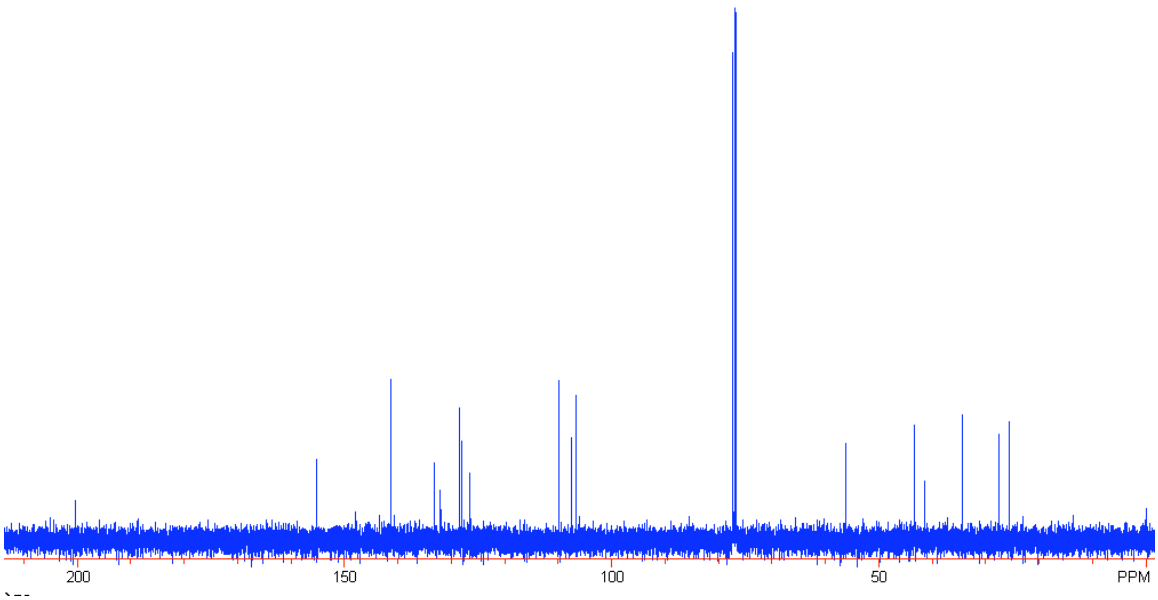
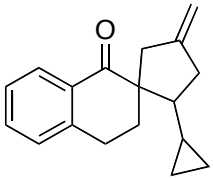
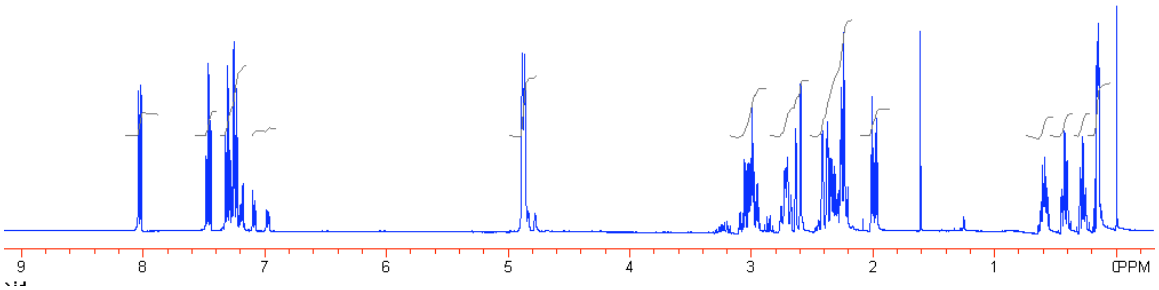


Table 3, Product 4





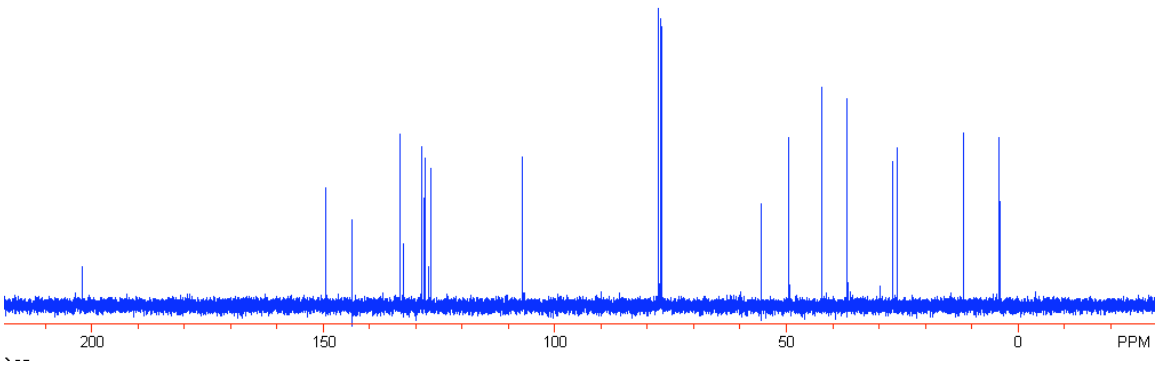


Table 3, Product 5