Supporting Information

Diastereoselective Synthesis of Diquinanes and Triquinanes Bearing Vicinal Quaternary Carbon Stereocenters from Acyclic Allene-based Precursors *via* a Cascade Reaction

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Part 1. General Information

All reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. All the chemicals were purchased commercially, and used without further purification. Anhydrous THF was distilled from sodium-benzophenone. Anhydrous tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium-benzophenone, acetonitrile (CH_3CN), 1, 2-dichloroethane (DCE), dichloromethane (DCM), carbon tetrachloride (CCl_4) were distilled from calcium hydride. Toluene and EtOH was distilled from sodium. All other solvents were purchased as ACS reagents and used without further purification. Yields refer to chromatographically.

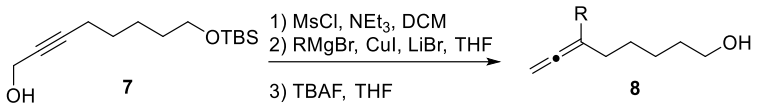
Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Tsingdao silica gel plates (GF-254) using UV light as visualizing agent and an ethanolic solution of phosphomolybdic acid and cerium sulfate, and heat as developing agents. Tsingdao silica gel (60, particle size 0.040-0.063 mm) was used for flash column chromatography.

NMR spectra were recorded on either a Brüker Advance 400 (^1H: 400 MHz, ^{13}C: 100 MHz) or Brüker Advance 500 (^1H: 500 MHz, ^{13}C: 125 MHz) and were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: ^1H NMR = 7.27 ppm, ^{13}C NMR = 77.0 ppm) The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

IR spectra were recorded on an IR Prestige-21 FTIR spectrometer with a KBr disc. Melting points (m.p.) are uncorrected and were recorded on a SGWX-4B apparatus.

Part 2: General procedure and characteristic data for substrates

General procedure A:

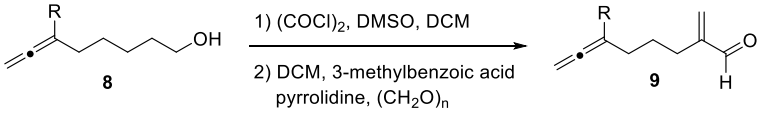


To a stirred solution of alcohol **7** [1] (5.12 g, 20 mmol, 1 equiv.) in DCM (50 mL) at 0 °C was added Et_3N (3.6 mL, 26 mmol, 1.3 equiv) and methanesulfonyl chloride (1.7 ml, 22 mmol, 1.1 equiv.) sequently. The resulting solution was stirred for 30 min at 0 °C and then diluted with Et_2O (50 ml). The reaction mixture was filtered through a plug of silica gel and washed with Et_2O. The filtrate was concentrated in *vacuo* and the crude product was used directly for the next step without further purification.

To a stirred solution of LiBr (3.48 g, 40 mmol, 2 equiv.), CuI (7.62 g, 40 mmol, 2 equiv.) in THF (150 mL) at -78 °C was added the corresponding Grignard reagent (1 M in THF, 40 mL, 2 equiv.) dropwise. Stirring was continued at -78 °C for 2 h followed by dropwise addition of a solution of previous product in THF (50 ml). The reaction mixture was further stirred for 1 h at -78 °C and then allowed to warm to room temperature for additional 3h. The mixture was quenched with saturated aqueous NH_4Cl (100 mL) and NH_4OH (100 mL). The organic layer was separated and the aqueous phase was extracted with EtOAc (2 × 150 mL). The combined organic layers were washed with NH_4OH (100 mL), brine (100 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was used directly for the next step without further purification.

To a stirred solution of the residue in THF (20 mL) was added TBAF (1 M in THF, 40 mL, 2 equiv) at room temperature. The reaction mixture was stirred for 4 h. After completion, the mixture was quenched with a saturated solution of NH_4Cl (40 mL) and extracted with EtOAc (3 × 100 mL). The combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 20:1 to 5:1) to give the desired product [2] **8a-8k**.

General procedure B:

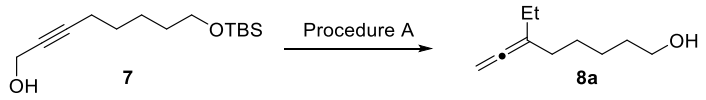


To a stirred solution of DMSO (2.1 mL, 30 mmol, 3 equiv.) in dry DCM (50 mL) at -78 °C was added oxalyl chloride (1.3 mL, 15 mmol, 1.5 equiv.) dropwise. The reaction mixture was stirred at -78 °C for 30 min and a solution of alcohol **8** (10 mmol, 1 equiv.) in dry DCM (15 mL) was added dropwise. The reaction mixture was stirred at -78 °C for 45 min followed by addition of Et_3N (8.3 mL, 60 mmol, 6 equiv.) at the same temperature. The cooling bath was then removed and the reaction was stirred at room temperature for 1 h. After completion, the mixture was quenched with a saturated solution of NH_4Cl (30 mL) and extracted with DCM (3 × 50 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (10 mL), brine (10 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the aldehyde product was used directly for the next step without further purification.

To a solution of the previous aldehyde in DCM (20 mL) was added pyrrolidine (0.08 ml, 1 mmol, 0.1 equiv.), 3-methylbenzoic acid (136 mg, 1 mmol, 0.1 equiv.) and formaldehyde (37% solution in H_2O, 0.97 mL, 1.2 equiv.) at room temperature. The reaction mixture was heated to 45 °C and stirred for 2h. After completion, the mixture was quenched with a saturated solution of $NaHCO_3$ (30 mL) and extracted with DCM (3 × 50 mL). The combined organic layers were washed

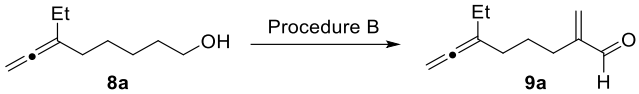
with brine and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 100:1 to 40:1) to give the desired product [3] **9a-9k**.

Synthesis of substrate **8a**:



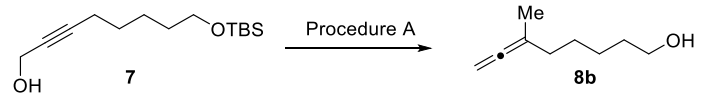
Substrate **8a** (1.45 g) was obtained in 47% yield as a colorless oil following general procedure A. HRMS (APCI) m/z calcd for $C_{10}H_{19}O$ $[M+H]^+$: 155.1430; found: 155.1428; IR ν_{max} (film): 2965, 2875, 2858, 1956, 1459, 1432, 1260, 1072, 1055, 844, 749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 4.66 – 4.63 (m, 2H), 3.59 (t, *J* = 6.7 Hz, 2H), 2.17 (s, 1H), 1.95 – 1.88 (m, 4H), 1.63 – 1.48 (m, 2H), 1.48 – 1.31 (m, 4H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.3, 104.8, 75.9, 62.7, 32.5, 32.0, 27.2, 25.4, 25.0, 12.1 ppm.

Synthesis of substrate **9a**:



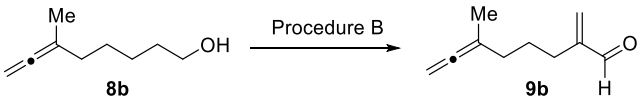
Substrate **9a** (1.05 g) was obtained in 64% yield as a colorless oil following general procedure B. HRMS (APCI) m/z calcd for $C_{11}H_{17}O$ $[M+H]^+$: 165.1274; found: 165.1273; IR ν_{max} (film): 2965, 2943, 2875, 1956, 1691, 1453, 1433, 1376, 1330, 1275, 945, 846, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.53 (s, 1H), 6.25 (d, *J* = 0.7 Hz, 1H), 5.99 (s, 1H), 4.76 – 4.59 (m, 2H), 2.26 (t, *J* = 7.7 Hz, 2H), 1.97 – 1.90 (m, 4H), 1.63 – 1.55 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.3, 194.6, 150.1, 134.1, 104.4, 76.2, 31.5, 27.3, 25.5, 25.0, 12.1 ppm.

Synthesis of substrate **8b**:



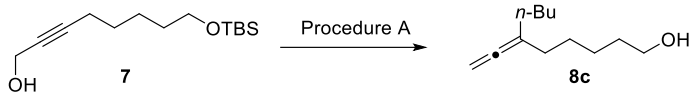
Substrate **8b** (1.82 g) was obtained in 65% yield as a colorless oil following general procedure A. HRMS (APCI) m/z calcd for $C_9H_{17}O$ $[M+H]^+$: 141.1274; found: 141.1274; IR ν_{max} (film): 2981, 2934, 1960, 1461, 1442, 1427, 1071, 1053, 844, 619 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 4.58 – 4.55 (m, 2H), 3.62 (t, *J* = 6.6 Hz, 2H), 1.95 – 1.90 (m, 2H), 1.79 (s, 1H), 1.66 (t, *J* = 3.1 Hz, 2H), 1.62 – 1.51 (m, 2H), 1.49 – 1.42 (m, 2H), 1.42 – 1.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.1, 98.2, 73.8, 62.8, 33.3, 32.5, 27.1, 25.3, 18.6 ppm.

Synthesis of substrate **9b**:



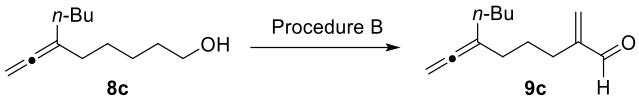
Substrate **9b** (0.95 g) was obtained in 63% yield as a colorless oil following general procedure B. HRMS (APCI) m/z calcd for $C_{10}H_{15}O$ $[M+H]^+$: 151.1117; found: 151.1121; IR ν_{max} (film): 2975, 2861, 1959, 1691, 1442, 1429, 1370, 1275, 1261, 944, 846, 763, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.54 (s, 1H), 6.26 (s, 1H), 6.00 (s, 1H), 4.62 – 4.55 (m, 2H), 2.27 (t, *J* = 7.7 Hz, 2H), 2.06 – 1.81 (m, 2H), 1.67 (t, *J* = 3.1 Hz, 3H), 1.63 – 1.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.1, 194.7, 150.1, 134.1, 97.8, 74.1, 32.8, 27.2, 25.4, 18.6 ppm.

Synthesis of substrate **8c**:



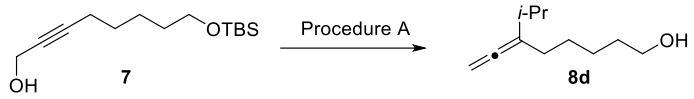
Substrate **8c** (2.22 g) was obtained in 61% yield as a colorless oil following general procedure A. HRMS (APCI) m/z calcd for $C_{12}H_{23}O$ $[M+H]^+$: 183.1743; found: 183.1743; IR ν_{max} (film): 2931,2871, 1957, 1456, 1431, 1378, 1071, 1054, 842, 729 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 4.65 – 6.62 (m, 2H), 3.64 (t, *J* = 6.6 Hz, 2H), 1.96 – 1.90(m, 4H), 1.67 – 1.52 (m, 2H), 1.51 – 1.25 (m, 9H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.6, 103.1, 75.3, 62.9, 32.6, 31.9, 31.8, 29.7, 27.2, 25.4, 22.4, 13.9 ppm.

Synthesis of substrate **9c**:



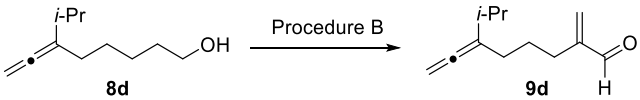
Substrate **9c** (1.41 g) was obtained in 73% yield as a colorless oil following general procedure B. HRMS (APCI) m/z calcd for $C_{13}H_{21}O$ $[M+H]^+$: 193.1587; found: 193.1586; IR ν_{max} (film): 2956, 2931, 2872, 1957, 1696, 1456, 1378, 1260, 945, 844, 741 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.53 (s, 1H), 6.26 (d, *J* = 0.9 Hz, 1H), 5.99 (d, *J* = 0.6 Hz, 1H), 4.64 (p, *J* = 3.2 Hz, 2H), 2.26 (t, *J* = 7.6 Hz, 2H), 1.99 – 1.84 (m, 4H), 1.68 – 1.51 (m, 2H), 1.43 – 1.35 (m, 2H), 1.35 – 1.25 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.6, 194.7, 150.1, 134.1, 102.6, 75.6, 31.7, 31.5, 29.6, 27.3, 25.5, 22.4, 13.9 ppm.

Synthesis of substrate **8d**:



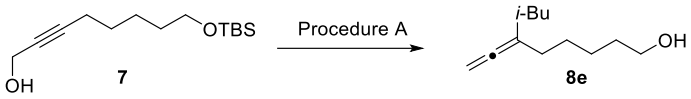
Substrate **8d** (1.88 g) was obtained in 56% yield as a colorless oil following general procedure A. HRMS (APCI) m/z calcd for $C_{11}H_{21}O$ $[M+H]^+$: 169.1587; found: 169.1587; IR ν_{max} (film): 3046, 2933, 2862, 1953, 1448, 1382, 1340, 1072, 1052, 842, 763, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 4.67 (dd, *J* = 6.1, 3.3 Hz, 2H), 3.61 (t, *J* = 6.7 Hz, 2H), 2.12 – 2.01 (m, 1H), 1.98 – 1.85 (m, 3H), 1.60 – 1.53 (m, 2H), 1.49 – 1.30 (m, 4H), 1.00 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.6, 109.5, 76.6, 62.8, 32.6, 30.3, 30.1, 27.4, 25.4, 21.5 ppm.

Synthesis of substrate **9d**:



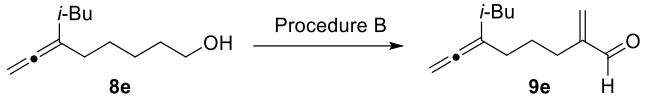
Substrate **9d** (1.03 g) was obtained in 59% yield as a colorless oil following general procedure B. HRMS (APCI) m/z calcd for $C_{12}H_{19}O$ $[M+H]^+$: 179.1430; found: 179.1433; IR ν_{max} (film): 2960, 2932, 2870, 1953, 1695, 1682, 1447, 1362, 1275, 1065, 946, 843 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.53 (s, 1H), 6.26 (d, *J* = 0.8 Hz, 1H), 5.99 (d, *J* = 0.8 Hz, 1H), 4.69 (dd, *J* = 6.0, 3.4 Hz, 2H), 2.27 (t, *J* = 7.7 Hz, 2H), 2.10 – 2.05 (m, 1H), 1.98 – 1.93 (m, 2H), 1.62 – 1.55 (m, 2H), 1.01 (t, *J* = 5.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.6, 194.6, 150.2, 134.0, 109.1, 76.9, 30.3, 29.6, 27.3, 25.7, 21.5 ppm.

Synthesis of substrate **8e**:



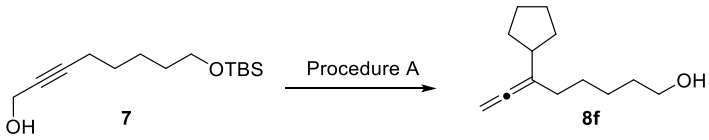
Substrate **8e** (1.76 g) was obtained in 48% yield as a colorless oil following general procedure A. HRMS (APCI) m/z calcd for $C_{12}H_{23}O$ $[M+H]^+$: 183.1743; found: 183.1743; IR ν_{max} (film): 2953, 2902, 2868, 1957, 1464, 1430, 1068, 1053, 841 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 4.61 (p, *J* = 3.0 Hz, 2H), 3.63 (t, *J* = 6.7 Hz, 2H), 1.93 – 1.88 (m, 2H), 1.82 – 1.79 (m, 2H), 1.76 – 1.70 (m, 2H), 1.62 – 1.54 (m, 2H), 1.47 – 1.33 (m, 4H), 0.89 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.2, 101.8, 74.8, 62.9, 41.9, 32.6, 31.9, 27.2, 26.4, 25.4, 22.5 ppm.

Synthesis of substrate **9e**:



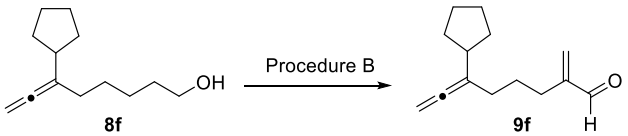
Substrate **9e** (1.14 g) was obtained in 59% yield as a colorless oil following general procedure B. HRMS (APCI) m/z calcd for $C_{13}H_{21}O$ $[M+H]^+$: 193.1587; found: 193.1590; IR ν_{max} (film): 2954, 2928, 2868, 1957, 1693, 1473, 1275, 1167, 1103, 943, 843 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.54 (s, 1H), 6.26 (d, *J* = 0.9 Hz, 1H), 6.00 (s, 1H), 4.63 (p, *J* = 3.1 Hz, 2H), 2.30 – 2.23 (m, 2H), 1.95 – 1.86 (m, 2H), 1.82 – 1.79 (m, 2H), 1.78 – 1.65 (m, 1H), 1.63 – 1.53 (m, 2H), 0.89 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 206.2, 194.7, 150.1, 134.1, 101.4, 75.1, 41.8, 31.4, 27.3, 26.4, 25.5, 22.5 ppm.

Synthesis of substrate **8f**:



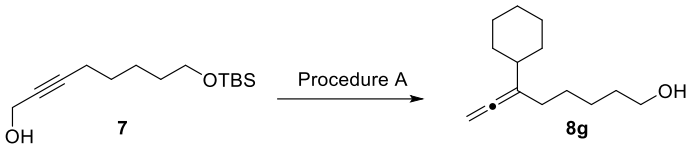
Substrate **8f** (2.64 g) was obtained in 68% yield as a colorless oil following general procedure A. HRMS (APCI) m/z calcd for $C_{13}H_{23}O$ $[M+H]^+$: 195.1743; found: 195.1745; IR ν_{max} (film): 2936, 2864, 1953, 1451, 1431, 1343, 1070, 1064, 843 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 4.67 (q, *J* = 3.2 Hz, 2H), 3.63 (t, *J* = 6.6 Hz, 2H), 2.29 – 2.24 (m, 1H), 2.06 – 1.88 (m, 2H), 1.82 – 1.71 (m, 2H), 1.65 – 1.56 (m, 7H), 1.48 – 1.44 (m, 2H), 1.44 – 1.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.5, 107.4, 76.4, 62.9, 41.8, 32.6, 31.5, 31.2, 27.4, 25.5, 24.9 ppm.

Synthesis of substrate **9f**:



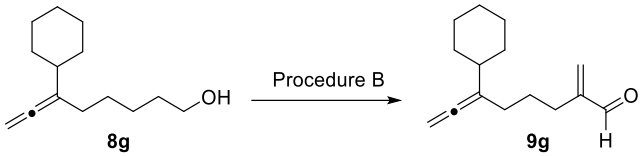
Substrate **9f** (1.17 g) was obtained in 57% yield as a colorless oil following general procedure B. HRMS (APCI) m/z calcd for $C_{14}H_{21}O$ $[M+H]^+$: 205.1587; found: 205.1587; IR ν_{max} (film): 2950, 2867, 1953, 1695, 1447, 1352, 1306, 1276, 1261, 943, 843, 751 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 9.53 (s, 1H), 6.26 (d, *J* = 0.9 Hz, 1H), 5.99 (d, *J* = 0.6 Hz, 1H), 4.68 (q, *J* = 3.3 Hz, 2H), 2.29 – 2.24 (m, 3H), 1.99 – 1.95 (m, 2H), 1.81 – 1.72 (m, 2H), 1.66 – 1.56 (m, 4H), 1.55 – 1.47 (m, 2H), 1.44 – 1.34 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 204.5, 194.7, 150.2, 134.1, 107.1, 76.7, 41.8, 31.5, 30.8, 27.4, 25.8, 25.0 ppm.

Synthesis of substrate **8g**:



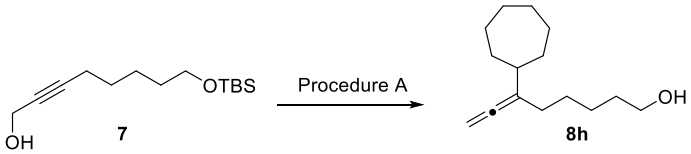
Substrate **8g** (2.48g) was obtained in 60% yield as a colorless oil following general procedure A. HRMS (APCI) m/z calcd for $C_{14}H_{25}O$ $[M+H]^+$: 209.1900; found: 209.1899; IR ν_{max} (film): 2926, 2852, 1952, 1448, 1417, 1070, 1053, 995, 889, 841 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 4.66 (dd, *J* = 5.9, 3.3 Hz, 2H), 3.63 (t, *J* = 6.6 Hz, 2H), 2.00 – 1.89 (m, 2H), 1.82 – 1.69 (m, 5H), 1.69 – 1.61 (m, 1H), 1.59 – 1.54 (m, 3H), 1.49 – 1.34 (m, 4H), 1.30 – 1.18 (m, 3H), 1.17 – 1.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.2, 108.6, 76.3, 62.9, 40.1, 32.6, 32.1, 30.2, 27.4, 26.5, 26.3, 25.4 ppm.

Synthesis of substrate **9g**:



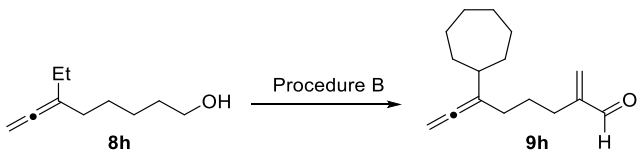
Substrate **9g** (1.35 g) was obtained in 62% yield as a colorless oil following general procedure B. HRMS (APCI) m/z calcd for $C_{15}H_{23}O$ $[M+H]^+$: 219.1743; found: 219.1741; IR ν_{max} (film): 2926, 2852, 2697, 1952, 1694, 1469, 1350, 1178, 1054, 941, 842, 750 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 9.53 (s, 1H), 6.25 (d, *J* = 0.8 Hz, 1H), 5.99 (s, 1H), 4.67 (dd, *J* = 5.9, 3.3 Hz, 2H), 2.26 (t, *J* = 7.7 Hz, 2H), 1.97 – 1.93 (m, 2H), 1.81 – 1.68 (m, 4H), 1.68 – 1.48 (m, 3H), 1.26 – 1.07 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 205.2, 194.6, 150.2, 134.0, 108.2, 76.7, 40.1, 32.1, 29.7, 27.4, 26.5, 26.3, 25.8 ppm.

Synthesis of substrate **8h**:



Substrate **8h** (2.17 g) was obtained in 49% yield as a colorless oil following general procedure A. HRMS (APCI) m/z calcd for $C_{15}H_{27}O$ $[M+H]^+$: 223.2056; found: 223.2058; IR ν_{max} (film): 2961, 2919, 2857, 1952, 1489, 1431, 1076, 1047, 846 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 4.65 (dd, *J* = 5.6, 3.3 Hz, 2H), 3.61 (t, *J* = 6.7 Hz, 2H), 1.97 – 1.86 (m, 4H), 1.82 – 1.74 (m, 2H), 1.71 – 1.62 (m, 2H), 1.60 – 1.53 (m, 4H), 1.53 – 1.45 (m, 2H), 1.46 – 1.32 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 205.1, 109.6, 76.4, 62.9, 42.3, 33.7, 32.6, 30.6, 28.3, 27.5, 26.5, 25.5 ppm.

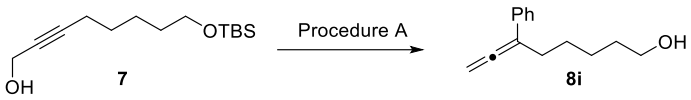
Synthesis of substrate **9h**:



Substrate **9h** (1.27 g) was obtained in 55% yield as a colorless oil following general procedure B. HRMS (APCI) m/z calcd for $C_{16}H_{25}O$ $[M+H]^+$: 233.1900; found: 233.1899; IR ν_{max} (film): 2944, 2879, 1956, 1673, 1468, 1355, 1285, 1241, 947, 841 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.54 (s, 1H), 6.26 (d, *J* = 0.8 Hz, 1H), 6.00 (s, 1H), 4.69 – 4.57 (m, 2H),

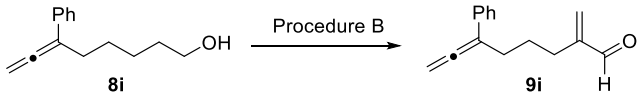
2.32 – 2.23 (m, 2H), 1.98 – 1.93 (m, 2H), 1.93 – 1.84 (m, 1H), 1.82 – 1.75 (m, 2H), 1.70 – 1.63 (m, 2H), 1.61 – 1.54 (m, 3H), 1.54 – 1.45 (m, 3H), 1.45 – 1.36 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.0, 194.7, 150.2, 134.1, 109.1, 76.7, 42.2, 33.6, 30.0, 28.3, 27.4, 26.4, 25.8 ppm.

Synthesis of substrate **8i**:



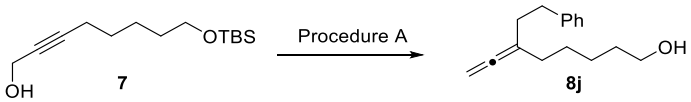
Substrate **8i** (1.71 g) was obtained in 42% yield as a colorless oil following general procedure A. HRMS (APCI) m/z calcd for $C_{14}H_{19}O$ $[M+H]^+$: 203.1430; found: 203.1431; IR ν_{max} (film): 2994, 1935, 1759, 1448, 1374, 1147, 1241, 1053, 750, 689 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.43 (d, *J* = 7.6 Hz, 2H), 7.34 (dd, *J* = 10.6, 4.9 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 5.09 (t, *J* = 3.3 Hz, 2H), 3.66 (t, *J* = 6.6 Hz, 2H), 2.47 – 2.43 (m, 2H), 1.72 (s, 1H), 1.68 – 1.55 (m, 4H), 1.55 – 1.43 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 208.6, 136.4, 128.4, 126.6, 126.0, 104.9, 78.2, 62.9, 32.6, 29.4, 27.6, 25.5 ppm.

Synthesis of substrate **9i**:



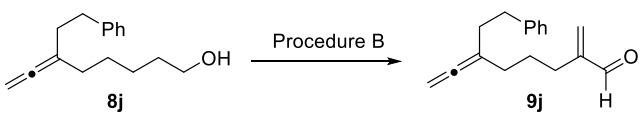
Substrate **9i** (1.21 g) was obtained in 57% yield as a colorless oil following general procedure B. HRMS (APCI) m/z calcd for $C_{15}H_{17}O$ $[M+H]^+$: 213.1274; found: 213.1275; IR ν_{max} (film): 2955, 2876, 1953, 1752, 1710, 1618, 1393, 1301, 1106, 948, 849, 751 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.56 (s, 1H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.33 (dd, *J* = 10.4, 5.0 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.28 (d, *J* = 0.5 Hz, 1H), 6.02 (s, 1H), 5.10 (t, *J* = 3.3 Hz, 2H), 2.48 – 2.43 (m, 2H), 2.37 (t, *J* = 7.7 Hz, 2H), 1.79 – 1.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 208.5, 194.6, 150.0, 136.2, 134.2, 128.4, 126.6, 125.9, 104.5, 78.4, 28.9, 27.4, 25.9 ppm.

Synthesis of substrate **8j**:



Substrate **8j** (2.81 g) was obtained in 61% yield as a colorless oil following general procedure A. HRMS (APCI) m/z calcd for $C_{16}H_{23}O$ $[M+H]^+$: 231.1743; found: 231.1744; IR ν_{max} (film): 2999, 2858, 1939, 1769, 1759, 1448, 1247, 1241, 1053, 750, 681 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 – 7.28 (m, 2H), 7.25 – 7.17 (m, 3H), 4.72 (p, *J* = 3.3 Hz, 2H), 3.64 (t, *J* = 6.6 Hz, 2H), 2.76 (dd, *J* = 9.2, 7.0 Hz, 2H), 2.31 – 2.19 (m, 2H), 2.06 – 1.94 (m, 2H), 1.68 – 1.56 (m, 2H), 1.53 – 1.46 (m, 2H), 1.43 – 1.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.7, 142.3, 128.4, 128.3, 125.7, 102.8, 76.2, 62.9, 34.0, 33.9, 32.6, 32.2, 27.2, 25.4 ppm.

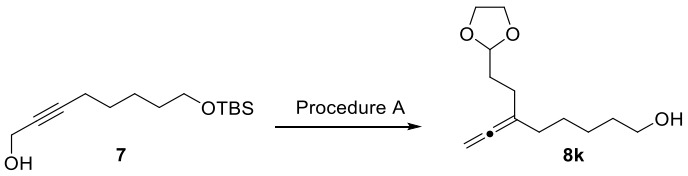
Synthesis of substrate **9j**:



Substrate **9j** (1.34 g) was obtained in 56% yield as a colorless oil following general procedure B. HRMS (APCI) m/z calcd for $C_{17}H_{21}O$ $[M+H]^+$: 241.1587; found: 241.1587; IR ν_{max} (film): 2934, 2859, 1956, 1714, 1690, 1602, 1453, 1276, 1076,

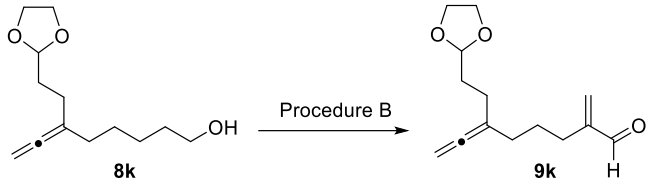
945, 850, 763 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 9.55 (s, 1H), 7.30 – 7.18 (m, 5H), 6.26 (d, *J* = 0.7 Hz, 1H), 6.01 (s, 1H), 4.72 (p, *J* = 3.3 Hz, 2H), 2.96 – 2.68 (m, 2H), 2.30 – 2.23 (m, 4H), 2.01 – 1.98 (m, 2H), 1.73 – 1.53 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 205.8, 194.6, 150.1, 142.2, 134.1, 128.4, 128.3, 125.8, 102.4, 76.5, 34.0, 33.8, 31.8, 27.3, 25.6 ppm.

Synthesis of substrate **8k**:



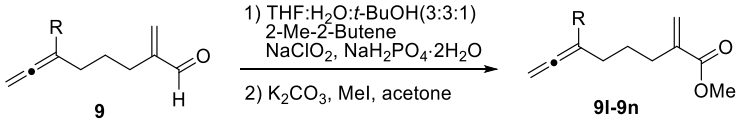
Substrate **8k** (2.88 g) was obtained in 64% yield as a colorless oil following general procedure A. HRMS (APCI) m/z calcd for $C_{13}H_{23}O_3$ $[M+H]^+$: 227.1642; found: 227.1640; IR ν_{max} (film): 3181, 2930, 2883, 1956, 1423, 1410, 1141, 1053, 1034, 947, 848 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 4.88 (t, *J* = 4.8 Hz, 1H), 4.71 – 4.61 (m, 2H), 3.98 – 3.91 (m, 2H), 3.84 – 3.79 (m, 2H), 3.59 (t, *J* = 6.7 Hz, 2H), 2.04 – 1.98 (m, 2H), 1.95 – 1.90 (m, 2H), 1.81 – 1.72 (m, 2H), 1.60 – 1.50 (m, 2H), 1.48 – 1.40 (m, 2H), 1.39 – 1.31 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 205.4, 104.1, 102.6, 76.3, 64.9, 62.8, 32.6, 32.3, 31.9, 27.2, 26.1, 25.4 ppm.

Synthesis of substrate **9k**:



Substrate **9k** (1.29 g) was obtained in 55% yield as a colorless oil following general procedure B. HRMS (APCI) m/z calcd for $C_{14}H_{21}O_3$ $[M+H]^+$: 237.1485; found: 237.1484; IR ν_{max} (film): 2949, 2930, 1956, 1713, 1689, 1439, 1370, 1260, 1139, 1031, 945, 856, 741 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 9.51 (s, 1H), 6.23 (s, 1H), 5.98 (s, 1H), 4.87 (t, *J* = 4.7 Hz, 1H), 4.67 (p, *J* = 3.3 Hz, 2H), 3.93 (dd, *J* = 8.7, 5.1 Hz, 2H), 3.82 (dd, *J* = 8.7, 5.2 Hz, 2H), 2.24 (t, *J* = 7.7 Hz, 2H), 2.04 – 1.97 (m, 2H), 1.96 – 1,91 (m, 2H), 1.79 – 1.73 (m, 2H), 1.63 – 1.53 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 205.4, 194.6, 150.1, 134.2, 104.1, 102.2, 76.7, 64.9, 31.9, 31.8, 27.3, 26.1, 25.5 ppm.

General procedure C:

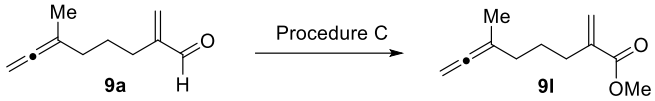


To a stirred solution of aldehyde **9** (1mmol, 1 equiv.) in THF (10 mL) was added water (10 mL), *t*-BuOH (3 mL), sodium dihydrogen phosphate dihydrate (312 mg, 2 mmol, 2 equiv.), 2-methyl-2-butene (1.7 mL, 20 mmol, 20 equiv.) and sodium chlorite (181 mg, 2 mmol, 2 equiv.) sequently. The reaction mixture was stirred for 2h at room temperature. After completion, the mixture was quenched with saturated aqueous NH_4Cl (10 ml) and extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine (5 mL), dried over Na_2SO_4. The solvent was removed under vacuum and the crude acid was used directly for the next step without further purification.

To a solution of the acid in dry acetone (20 mL) was added K_2CO_3 (276 mg, 2 mmol, 2 equiv.) and MeI (426 mg, 3 mmol, 3 equiv.) at room temperature. The mixture was stirred for 6h. After completion, it was quenched with saturated

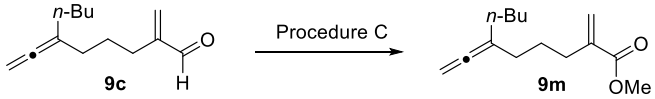
aqueous NH_4Cl (20 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 100:1 to 50 :1) to give product **9l-9n**.

Synthesis of substrate **9l**:



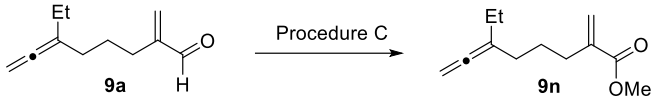
Substrate **9l** (113 mg) was obtained in 63% yield as a colorless oil following general procedure C. HRMS (APCI) m/z calcd for $C_{11}H_{17}O_2$ $[M+H]^+$: 181.1223; found: 181.1224; IR ν_{max} (film): 2950, 2938, 2858, 1722, 1438, 1275, 1196, 1167, 1135, 852, 749 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 6.32 – 5.93 (m, 1H), 5.54 (d, *J* = 1.4 Hz, 1H), 4.59 (dd, *J* = 6.3, 3.2 Hz, 2H), 3.75 (s, 3H), 2.32 (dd, *J* = 11.2, 4.0 Hz, 2H), 2.06 – 1.85 (m, 2H), 1.68 (t, *J* = 3.1 Hz, 3H), 1.62 (dd, *J* = 15.2, 7.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 206.2, 167.7, 140.5, 124.8, 97.9, 74.1, 51.7, 32.8, 31.4, 26.1, 18.7 ppm.

Synthesis of substrate **9m**:



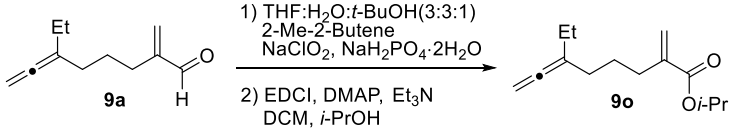
Substrate **9m** (115 mg) was obtained in 52% yield as a colorless oil following general procedure C. HRMS (APCI) m/z calcd for $C_{14}H_{23}O_2$ $[M+H]^+$: 223.1693; found: 223.1693; IR ν_{max} (film): 2956, 2931, 2872, 1957, 1696, 1456, 1378, 1354, 1260, 944, 845 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.14 (s, 1H), 5.54 (d, *J* = 1.2 Hz, 1H), 4.65 (p, *J* = 3.2 Hz, 2H), 3.75 (s, 3H), 2.46 – 2.23 (m, 2H), 1.97 – 1.90 (m, 4H), 1.71 – 1.50 (m, 2H), 1.50 – 1.21 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.6, 167.7, 140.5, 124.8, 102.8, 75.5, 51.7, 31.8, 31.4, 29.7, 26.2, 22.4, 13.9 ppm.

Synthesis of substrate **9n**:



Substrate **9n** (110 mg) was obtained in 57% yield as a colorless oil following general procedure C. HRMS (APCI) m/z calcd for $C_{12}H_{18}NaO_2$ $[M+Na]^+$: 217.1199; found: 217.1201; IR ν_{max} (film): 2961, 2927, 1951, 1724, 1636, 1412, 1306, 1108, 1081, 948, 846 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 6.13 (d, *J* = 0.8 Hz, 1H), 5.53 (d, *J* = 1.3 Hz, 1H), 4.67 (p, *J* = 3.4 Hz, 2H), 3.74 (s, 3H), 2.32 (t, *J* = 7.5 Hz, 2H), 1.96 – 1.92 (m, 4H), 1.67 – 1.47 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 205.4, 167.7, 140.5, 124.7, 104.5, 76.1, 51.7, 31.5, 26.2, 25.0, 12.1 ppm.

Synthesis of substrate **9o**:



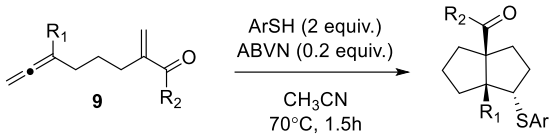
To a stirred solution of aldehyde **9a** (164 mg, 1mmol, 1 equiv.) in THF (10 mL) was added water (10 mL), *t*-BuOH (3 mL), sodium dihydrogen phosphate dihydrate (312 mg, 2 mmol, 2 equiv.), 2-methyl-2-butene (1.7 mL, 20 mmol, 20 equiv) and sodium chlorite (181 mg, 2 mmol, 2 equiv.) sequently. The reaction mixture was stirred for 2h at room

temperature. After completion, the mixture was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine (5 mL), dried over Na_2SO_4. The solvent was removed under vacuum and the crude acid was used directly for the next step without further purification.

To a stirred solution of the crude acid in DCM (5 mL) was added EDCI (229 mg, 1.2 mmol, 1.2 equiv.), DMAP (24 mg, 0.2 mmol, 0.2 equiv.), *i*-PrOH (120 mg, 2 mmol, 2 equiv.), Et_3N (0.42 mL, 3 mmol, 3 equiv.) sequently and the mixture was further stirred for 12h at room temperature. After completion, the mixture was diluted with DCM (25 mL) and washed with brine (2 × 10 mL), dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 100:1 to 50 :1) to give the desired product **9o** (99 mg) in 44% yield as a colorless oil. HRMS (APCI) m/z calcd for $C_{14}H_{22}NaO_2$ $[M+Na]^+$: 245.1512; found: 245.1511. IR ν_{max} (film): 2978, 2934, 1951, 1713, 1475, 1271, 1182, 1109, 913, 846, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.11 (d, *J* = 1.4 Hz, 1H), 5.49 (d, *J* = 1.4 Hz, 1H), 5.09 – 5.03 (m, 1H), 4.73 – 4.62 (m, 2H), 2.37 – 2.27 (m, 2H), 1.97 – 1.92 (m, 4H), 1.70 – 1.55 (m, 2H), 1.27 (d, *J* = 6.3 Hz, 6H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.4, 166.8, 141.2, 124.1, 104.5, 76.0, 67.8, 31.5, 31.4, 26.3, 25.0, 21.8, 12.1 ppm.

Part 3: General procedure and characteristic data for products

General procedure D:

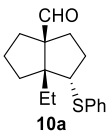


To a flame-dried flask containing **9** (0.2 mmol, 1 equiv) in dry CH_3CN (16 mL) was added a solution of ArSH (0.4 mmol, 2 equiv) and ABVN (9.9 mg, 0.4 mmol, 2 equiv) in dry CH_3CN (4 mL) dropwise by syringe pump in 1 h at 70°C under argon. The resultant reaction mixture was then stirred at 70 °C for additional 30 min. After cooled to ambient temperature, the solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 150:1 to 50:1) to give the desired products **10a-10o**, **11a-11e**.

General procedure E:

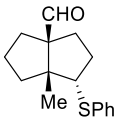
To a flame-dried flask containing 9a (32.8 mg, 0.2 mmol, 1 equiv.) in dry PhMe (16 mL) was added a solution of ArSH (0.6 mmol, 3 equiv) and AIBN (9.9 mg, 0.6 mmol, 3 equiv.) in dry PhMe (4 mL) at 90°C under argon. The reaction mixture was stirred at 90 °C for 3h. After cooled to ambient temperature, the solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 150:1 to 50:1) to give the desired product **11f-11i**.

Synthesis of product **10a**:



Product **10a** (38.4 mg) was obtained in 70% yield as a colorless oil following general procedure D. HRMS (APCI) m/z calcd for $C_{17}H_{23}OS$ $[M+H]^+$: 275.1464; found: 275.1465; IR ν_{max} (film): 2957, 2874, 1716, 1581, 1479, 1460, 1275, 1261, 1024, 749, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.65 (s, 1H), 7.43 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.30 (dd, *J* = 7.0, 1.6 Hz, 2H), 7.25 – 7.18 (m, 1H), 3.24 (dd, *J* = 11.4, 6.2 Hz, 1H), 2.30 – 2.14 (m, 2H), 2.14 – 1.92 (m, 2H), 1.84 – 1.64 (m, 5H), 1.59 – 1.39 (m, 3H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.1, 136.3, 131.4, 128.9, 126.7, 65.8, 62.6, 57.7, 36.2, 35.3, 33.6, 32.0, 29.5, 26.1, 10.4 ppm.

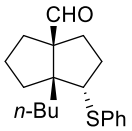
Synthesis of product **10b**:



10b

Product **10b** (33.7 mg) was obtained in 65% yield as a colorless oil following general procedure D. HRMS (APCI) m/z calcd for $C_{16}H_{21}OS$ $[M+H]^+$: 261.1308; found: 261.1308; IR ν_{max} (film): 2962, 2875, 1721, 1573, 1483, 1451, 1255, 1103, 1051, 743, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.56 (s, 1H), 7.43 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.25 – 7.18 (m, 1H), 3.10 (dd, *J* = 12.3, 5.7 Hz, 1H), 2.40 – 2.31 (m, 1H), 2.23 – 2.10 (m, 2H), 1.95 – 1.87 m, 1H), 1.84 – 1.70 (m, 3H), 1.54 – 1.40 (m, 3H), 1.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.1, 136.3, 131.3, 128.9, 126.6, 64.7, 59.6, 58.9, 37.7, 36.4, 32.6, 31.2, 25.7, 22.8.

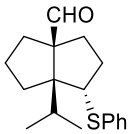
Synthesis of product **10c**:



10c

Product **10c** (35.1 mg) was obtained in 58% yield as a colorless oil following general procedure D. HRMS (APCI) m/z calcd for $C_{19}H_{27}OS$ $[M+H]^+$: 303.1777; found: 303.1774; IR ν_{max} (film): 2955, 2930, 2870, 1716, 1588, 1469, 1449, 1265, 1092, 1045, 747, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.64 (s, 1H), 7.42 (dd, *J* = 8.3, 1.0 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.24 – 7.20 (m, 1H), 3.24 (dd, *J* = 11.5, 6.2 Hz, 1H), 2.32 – 2.24 (m, 1H), 2.23 – 2.12 (m, 1H), 2.14 – 2.05 (m, 1H), 2.02 – 1.95 (m, 1H), 1.82 – 1.71 (m, 3H), 1.66 – 1.58 (m, 3H), 1.51 – 1.39 (m, 2H), 1.33 – 1.22 (m, 4H), 0.85 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.0, 136.3, 131.4, 128.9, 126.7, 65.8, 62.3, 58.0, 37.0, 36.2, 35.8, 33.5, 32.0, 28.0, 26.1, 23.5, 13.9.

Synthesis of product **10d**:

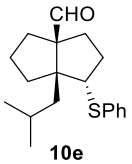


10d

Product **10d** (38.0 mg) was obtained in 66% yield as a colorless oil following general procedure D. HRMS (APCI) m/z calcd for $C_{18}H_{25}OS$ $[M+H]^+$: 289.1621; found: 289.1619; IR ν_{max} (film): 2957, 2875, 1713, 1583, 1478, 1460, 1391, 1264, 1173, 1084, 748, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.74 (s, 1H), 7.42 – 7.40 (m, 2H), 7.37 – 7.18 (m, 3H), 3.49 (dd, *J* = 10.5, 7.0 Hz, 1H), 2.32 – 2.16 (m, 3H), 2.06 – 1.93 (m, 2H), 1.85 – 1.76 (m, 3H), 1.75 – 1.65 (m, 1H), 1.58 – 1.45

(m, 2H), 0.94 (dd, J = 12.8, 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.4, 136.3, 131.6, 128.9, 126.8, 66.8, 65.6, 53.5, 36.9, 36.9, 34.8, 33.8, 32.9, 26.7, 20.1, 19.6 ppm.

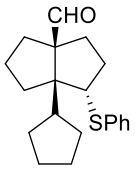
Synthesis of product **10e**:



10e

Product **10e** (38.8 mg) was obtained in 64% yield as a colorless oil following general procedure D. HRMS (APCI) m/z calcd for $C_{19}H_{27}OS$ $[M+H]^+$: 303.1777; found: 303.1778; IR ν_{max} (film): 2954, 2868, 1716, 1693, 1479, 1437, 1365, 1226, 1085, 1025, 748, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.60 (s, 1H), 7.45 – 7.38 (m, 2H), 7.32 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 3.30 (dd, J = 10.8, 6.4 Hz, 1H), 2.30 – 2.17 (m, 2H), 2.15 – 2.08 (m, 2H), 1.91 – 1.71 (m, 4H), 1.71 – 1.60 (m, 1H), 1.53 – 1.34 (m, 4H), 0.93 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.1, 136.2, 131.2, 128.9, 126.6, 66.9, 62.9, 57.0, 46.8, 36.5, 35.8, 34.1, 31.9, 26.5, 25.6, 25.4, 25.1 ppm.

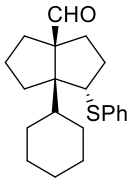
Synthesis of product **10f**:



10f

Product **10f** (45.7 mg) was obtained in 73% yield as a colorless oil following general procedure D. HRMS (APCI) m/z calcd for $C_{20}H_{27}OS$ $[M+H]^+$: 315.1777; found: 315.1775; IR ν_{max} (film): 2952, 2868, 1721, 1575, 1487, 1456, 1303, 1224, 1087, 1031, 738, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.72 (s, 1H), 7.49 – 7.36 (m, 2H), 7.34 – 7.18 (m, 3H), 3.42 (dd, J = 10.5, 6.7 Hz, 1H), 2.32 – 2.18 (m, 2H), 2.18 – 1.99 (m, 3H), 1.90 – 1.65 (m, 5H), 1.65 – 1.37 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.9, 136.4, 131.4, 128.9, 126.7, 67.4, 64.7, 56.2, 46.8, 36.1, 35.4, 34.9, 32.7, 29.4, 29.3, 26.5, 25.9, 25.4 ppm.

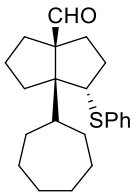
Synthesis of product **10g**:



10g

Product **10g** (36.2 mg) was obtained in 55% yield as a colorless oil following general procedure D. HRMS (APCI) m/z calcd for $C_{21}H_{29}OS$ $[M+H]^+$: 329.1934; found: 329.1929; IR ν_{max} (film): 2927, 2851, 1711, 1581,1487, 1436, 1279, 1092, 1031, 769, 702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.74 (s, 1H), 7.44 (dd, J = 5.2, 3.3 Hz, 2H), 7.36 – 7.17 (m, 3H), 3.54 (dd, J = 10.5, 6.9 Hz, 1H), 2.34 – 2.22 (m, 1H), 2.29 – 2.14 (m, 2H), 2.02 – 1.93 (m, 1H), 1.84 – 1.42 (m, 13H), 1.22 – 1.08 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.3, 136.3, 131.5, 128.9, 126.7, 66.7, 65.5, 53.7, 45.0, 36.8, 36.8, 34.5, 33.0, 30.1, 29.9, 27.1, 26.8, 26.7, 26.5 ppm.

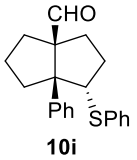
Synthesis of product **10h**:



10h

Product **10h** (25.4 mg) was obtained in 37% yield as a colorless oil following general procedure D. HRMS (APCI) m/z calcd for $C_{22}H_{31}OS$ $[M+H]^+$: 343.2090; found: 343.2093; IR ν_{max} (film): 2945, 2887, 1714, 1569, 1492, 1443, 1258, 1083, 1042, 765, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.70 (s, 1H), 7.44 – 7.42 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 – 7.20 (m, 1H), 3.51 (dd, *J* = 10.7, 6.9 Hz, 1H), 2.36 – 2.26 (m, 1H), 2.23 – 2.17 (m, 2H), 2.12 – 2.00 (m, 1H), 1.86 – 1.63 (m, 8H), 1.58 – 1.38 (m, 8H), 1.34 – 1.24 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.5, 136.3, 131.6, 128.9, 126.7, 67.0, 66.9, 54.2, 45.0, 37.6, 37.4, 34.8, 33.5, 31.9, 31.1, 28.0, 27.9, 27.0, 26.8 ppm.

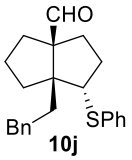
Synthesis of product **10i**:



10i

Product **10i** (25.9 mg) was obtained in 40% yield (dr =4:1) as a colorless oil following general procedure D. HRMS (APCI) m/z calcd for $C_{21}H_{23}OS$ $[M+H]^+$: 323.1464; found: 323.1466; IR ν_{max} (film): 2954, 2920, 1716, 1629, 1476, 1422, 1269, 1256, 1085, 1028, 749, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 0.23H), 8.82 (s, 1H), 7.34 – 7.28 (m, 1H), 7.26 – 7.20 (m, 6H), 7.19 – 7.14 (m, 4H), 3.93 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.46 (dd, *J* = 12.0, 6.7 Hz, 0.24H), 2.45 – 2.25 (m, 5H), 2.07 – 1.92 (m, 4H), 1.70 – 1.57 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 202.7, 201.2, 142.6, 140.1, 136.3, 135.5, 131.7, 131.7, 128.8, 128.8, 128.7, 128.5, 127.5, 127.2, 127.1, 126.7, 126.7, 126.6, 68.4, 67.6, 65.3, 64.5, 59.5, 59.3, 38.0, 37.7, 37.2, 36.3, 33.5, 32.6, 31.9, 30.8, 26.7, 23.9 ppm.

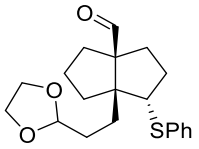
Synthesis of product **10j**:



10j

Product **10j** (37.7mg) was obtained in 54% yield as a colorless oil following general procedure D. HRMS (APCI) m/z calcd for $C_{23}H_{27}OS$ $[M+H]^+$: 351.1777; found: 351.1779; IR ν_{max} (film): 2952, 2923, 2869, 1714, 1585, 1479, 1452, 1396, 1224, 1025, 752, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.72 (s, 1H), 7.50 – 7.40 (m, 2H), 7.36 – 7.27 (m, 3H), 7.26 – 7.16 (m, 3H), 7.12 – 7.08 (m, 2H), 3.35 (dd, *J* = 11.5, 6.3 Hz, 1H), 2.73 – 2.56 (m, 2H), 2.38 – 2.33 (m, 1H), 2.29 – 2.23 (m, 1H), 2.18 – 2.08 (m, 2H), 1.96 – 1.87 (m, 2H), 1.84 – 1.77 (m, 3H), 1.56 – 1.48 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.9, 142.1, 136.1, 131.7, 129.1, 128.4, 128.2, 126.9, 125.9, 66.0, 62.3, 58.1, 39.7, 36.2, 35.8, 33.8, 32.3, 32.1, 26.2 ppm.

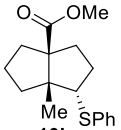
Synthesis of product **10k**:



10k

Product **10k** (41.6mg) was obtained in 60% yield as a colorless oil following general procedure D. HRMS (APCI) m/z calcd for $C_{20}H_{27}O_3S$ $[M+H]^+$: 347.1675; found: 347.1677; IR ν_{max} (film): 2954, 2870, 1714, 1584, 1456, 1362, 1274, 1141, 1088, 1025, 748, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.65 (s, 1H), 7.43 – 7.40 (m, 2H), 7.30 – 7.21 (m, 3H), 4.78 – 4.76 (m, 1H), 3.97 – 3.87 (m, 2H), 3.87 – 3.75 (m, 2H), 3.23 (dd, *J* = 11.3, 6.3 Hz, 1H), 2.34 – 2.15 (m, 2H), 2.15 – 1.96 (m, 2H), 1.86 – 1.72 (m, 4H), 1.70 – 1.57 (m, 4H), 1.52 – 1.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.8, 136.1, 131.4, 128.9, 126.7, 104.3, 66.0, 64.8, 61.5, 57.8, 36.0, 35.5, 33.8, 31.9, 31.1, 30.3, 26.1 ppm.

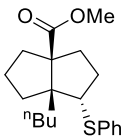
Synthesis of product **10l**:



10l

Product **10l** (35.9 mg) was obtained in 62% yield (dr =5:1) as a colorless oil following general procedure D**.** HRMS (APCI) m/z calcd for $C_{17}H_{23}O_2S$ $[M+H]^+$: 291.1413; found: 291.1415; IR ν_{max} (film): 2950, 2873, 1724, 1583, 1479, 1438, 1302, 1273, 1193, 1132, 1025, 738, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.31 – 7.27 (m, 2H), 7.22 – 7.17 (m, 1H), 3.69 (s, 0.6H), 3.68 (s, 3H), 3.26 (dd, *J* = 12.0, 6.3 Hz, 1H), 3.20 (dd, *J* = 11.1, 5.9 Hz, 0.22H), 2.51 – 2.44 (m, 1H), 2.36 – 2.28 (m, 1H), 2.24 – 2.15 (m, 1H), 1.89 – 1.84 (m, 1H), 1.82 – 1.76 (m, 1H), 1.73 – 1.65 (m, 2H), 1.58 – 1.46 (m, 3H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.0, 136.8, 131.4, 130.9, 128.9, 128.80, 126.5, 126.3, 62.6, 62.4, 58.8, 58.4, 58.3, 58.3, 51.5, 40.0, 38.5, 38.0, 37.1, 35.5, 34.8, 33.8, 32.9, 25.4, 24.1, 23.2, 20.4 ppm.

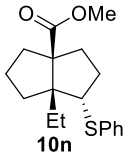
Synthesis of product **10m**:



10m

Product **10m** (37.1mg) was obtained in 56% yield as a colorless oil following general procedure D. HRMS (APCI) m/z calcd for $C_{20}H_{29}O_2S$ $[M+H]^+$: 333.1883; found: 333.1885; IR ν_{max} (film): 2954, 2872, 1723, 1578, 1465, 1436, 1274, 1243, 1171, 1023, 750, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.4 (dd, *J* = 5.2, 3.4 Hz, 2H), 7.32 – 7.25 (m, 2H), 7.23 – 7.17 (m, 1H), 3.67 (s, 3H), 3.39 (dd, *J* = 11.4, 6.4 Hz, 1H), 2.46 – 2.30 (m, 1H), 2.30 – 2.14 (m, 2H), 1.96 – 1.92 (m, 1H), 1.85 – 1.73 (m, 2H), 1.70 – 1.51 (m, 6H), 1.49 – 1.34 (m, 1H), 1.39 – 1.22 (m, 3H), 0.84 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.3, 136.8, 131.1, 128.8, 126.3, 62.7, 61.0, 57.6, 51.5, 38.4, 37.5, 35.5, 34.8, 33.7, 27.4, 25.5, 23.7, 14.0 ppm.

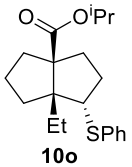
Synthesis of product **10n**:



10n

Product **10n** (44.3 mg) was obtained in 73% yield as a colorless oil following general procedure D. HRMS (APCI) m/z calcd for $C_{18}H_{24}NaO_2S$ $[M+Na]^+$: 327.1389; found: 327.1389; IR ν_{max} (film): 2950, 2875, 1721, 1578, 1465, 1442, 1271, 1236, 1192, 1172, 741, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.43 – 7.40 (m, 2H), 7.31 – 7.24 (m, 2H), 7.22 – 7.18 (m, 1H), 3.68 (s, 3H), 3.38 (dd, *J* = 11.3, 6.4 Hz, 1H), 2.43 – 2.30 (m, 1H), 2.25 – 2.19 (m, 2H), 2.01 – 1.86 (m, 1H), 1.85 – 1.42 (m, 8H), 0.89 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.2, 136.8, 131.0, 128.8, 126.3, 62.6, 61.3, 57.4, 51.6, 38.4, 35.5, 34.2, 33.8, 30.0, 25.5, 9.8 ppm.

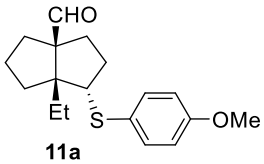
Synthesis of product **10o**:



10o

Product **10o** (34.4 mg) was obtained in 52% yield as a colorless oil following general procedure D. HRMS (APCI) m/z calcd for $C_{20}H_{28}NaO_2S$ $[M+Na]^+$: 355.1702; found: 355.1699; IR ν_{max} (film): 2962, 2923, 2876, 1713, 1581, 1483, 1436, 1273, 1242, 1180, 1109, 738, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.45 – 7.38 (m, 2H), 7.31 – 7.15 (m, 3H), 5.09 – 4.98 (m, 1H), 3.42 (dd, *J* = 11.1, 6.2 Hz, 1H), 2.39 – 2.29 (m, 1H), 2.28 – 2.12 (m, 2H), 1.98 – 1.84 (m, 1H), 1.81 – 1.63 (m, 5H), 1.60 – 1.52 (m, 3H), 1.25 (d, *J* = 6.3 Hz, 6H), 0.91 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.2, 137.0, 130.8, 128.8, 126.2, 67.7, 62.4, 61.0, 57.4, 38.5, 35.6, 34.2, 33.7, 29.9, 25.3, 21.8, 21.7, 9.9.ppm.

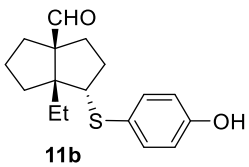
Synthesis of product **11a**:



11a

Product **11a** (38.2 mg) was obtained in 63% yield as a colorless oil following general procedure D. HRMS (APCI) m/z calcd for $C_{18}H_{24}NaO_2S$ $[M+Na]^+$: 327.1389; found: 327.1391; IR ν_{max} (film): 2938, 2849, 1717, 1650, 1492, 1275, 1241, 1031, 763, 749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.6 (s, 1H), 7.48 – 7.31 (m, 2H), 6.92 – 6.78 (m, 2H), 3.80 (s, 3H), 3.08 (dd, *J* = 11.4, 6.2 Hz, 1H), 2.30 – 2.23(m, 1H), 2.11 – 1.95 (m, 3H), 1.87 – 1.60 (m, 5H), 1.60 – 1.34 (m, 3H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.1, 159.3, 134.9, 126.4, 114.5, 65.9, 62.6, 59.5, 55.3, 36.2, 35.2, 33.6, 31.9, 29.6, 26.1, 10.5 ppm.

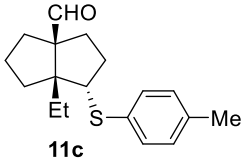
Synthesis of product **11b**:



11b

Product **11b** (32.6 mg) was obtained in 56% yield as a colorless oil following general procedure D. HRMS (APCI) m/z calcd for $C_{17}H_{22}NaO_2S$ $[M+Na]^+$: 313.1233; found: 313.1231; IR ν_{max} (film): 2957, 2932, 2927, 1695, 1582, 1494, 1263, 1221, 1095, 1014, 832, 745 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.63 (s, 1H), 7.35 (d, *J* = 8.3 Hz, 2H), 6.78 (d, *J* = 8.3 Hz, 2H), 3.08 (dd, *J* = 11.2, 6.0 Hz, 1H), 2.30 – 2.23 (m, 1H), 2.13 – 1.95 (m, 3H), 1.79 – 1.70 (m, 3H), 1.68 – 1.60 (m, 2H), 1.56 – 1.51 (m, 1H), 1.50 – 1.46 (m, 1H), 1.44 – 1.38 (m, 1H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.5, 155.6, 135.2, 126.4, 116.0, 66.0, 62.7, 59.5, 36.2, 35.2, 33.6, 31.9, 29.6, 26.1, 10.4 ppm.

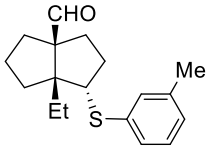
Synthesis of product **11c**:



11c

Product **11c** (38.6 mg) was obtained in 67% yield as a colorless oil following general procedure D. HRMS (APCI) m/z calcd for $C_{18}H_{24}NaOS$ $[M+Na]^+$: 311.1440; found: 311.1439; IR ν_{max} (film): 2957, 2920, 1716, 1632, 1490, 1463, 1279, 1255, 1088, 763, 749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.64 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 3.17 (dd, *J* = 11.4, 6.2 Hz, 1H), 2.33 (s, 3H), 2.31 – 2.23 (m, 1H), 2.19 – 1.94 (m, 3H), 1.87 – 1.63 (m, 5H), 1.59 – 1.39 (m, 3H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ = 205.1, 136.9, 132.5, 132.18, 129.7, 65.8, 62.6, 58.4, 36.2, 35.3, 33.6, 31.9, 29.6, 26.1, 21.0, 10.4 ppm.

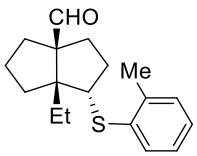
Synthesis of product **11d**:



11d

Product **11d** (23.6 mg) was obtained in 41% yield as a colorless oil following general procedure D. HRMS (APCI) m/z calcd for $C_{18}H_{24}NaOS$ $[M+Na]^+$: 311.1440; found: 311.1431; IR ν_{max} (film): 2957, 2937, 1715, 1469, 1452, 1273, 1259, 1052, 762, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.66 (s, 1H), 7.24 – 7.12 (m, 3H), 7.03 (d, *J* = 7.0 Hz, 1H), 3.23 (dd, *J* = 11.5, 6.3 Hz, 1H), 2.33 (s, 3H), 2.30 – 2.20(m, 2H), 2.14 – 2.06 (m, 1H), 2.03 – 1.90 (m, 2H), 1.86 – 1.71 (m, 2H), 1.72 – 1.65 (m, 2H), 1.63 – 1.40 (m, 3H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.1, 138.7, 136.0, 132.0, 128.7, 128.3, 127.5, 65.8, 62.6, 57.6, 36.2, 35.3, 33.6, 32.0, 29.5, 26.1, 21.3, 10.4 ppm.

Synthesis of product **11e**:

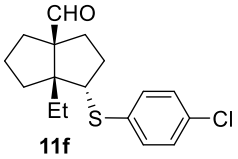


11e

Product **11e** (20.1 mg) was obtained in 35% yield as a colorless oil following general procedure D. HRMS (APCI) m/z calcd for $C_{18}H_{24}NaOS$ $[M+Na]^+$: 311.1440; found: 311.1430; IR ν_{max} (film): 2938, 2898, 1716, 1487, 1432, 1303, 1267, 1046, 766, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.66 (s, 1H), 7.43 – 7.38 (m, 1H), 7.23 – 7.17 (m, 1H), 7.16 – 7.10 (m, 2H), 3.22 (dd, *J* = 11.3, 6.1 Hz, 1H), 2.43 (s, 3H), 2.30 – 2.24 (m, 1H), 2.19 – 2.13 (m, 1H), 2.10 – 2.02 (m, 2H), 1.84

– 1.74 (m, 3H), 1.74 – 1.65 (m, 2H), 1.59 – 1.49 (m, 2H), 1.47 – 1.40 (m, 1H), 0.90 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.1, 139.2, 135.4, 131.3, 130.2, 126.6, 126.4, 65.8, 62.7, 56.8, 36.3, 35.3, 33.3, 32.1, 29.5, 26.1, 20.8, 10.4 ppm.

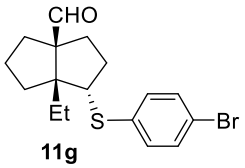
Synthesis of product **11f**:



11f

Product **11f** (32.5 mg) was obtained in 53% yield as a colorless oil following general procedure E. HRMS (APCI) m/z calcd for $C_{17}H_{21}ClNaOS$ $[M+Na]^+$: 331.0894; found: 331.0894; IR ν_{max} (film): 2957, 2921, 1716, 1565, 1473, 1282, 1266, 1092, 1010, 823, 765 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.64 (s, 1H), 7.37 – 7.31 (m, 2H), 7.27 – 7.23 (m, 2H), 3.19 (dd, J = 11.3, 6.2 Hz, 1H), 2.31 – 2.22 (m, 1H), 2.20 – 2.03 (m, 2H), 1.95 – 1.91 (m, 1H), 1.83 – 1.59 (m, 5H), 1.60 – 1.39 (m, 3H), 0.90 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.9, 134.8, 132.8, 132.7, 129.0, 65.8, 62.6, 58.0, 36.2, 35.2, 33.4, 31.9, 29.6, 26.1, 10.4 ppm.

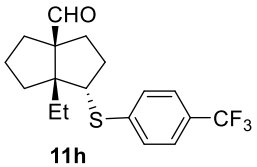
Synthesis of product **11g**:



11g

Product **11g** (36.6 mg) was obtained in 52% yield as a colorless oil following general procedure E. HRMS (APCI) m/z calcd for $C_{17}H_{21}BrNaOS$ $[M+Na]^+$: 375.0389; found: 375.0381; IR ν_{max} (film): 2962, 2929, 1710, 1646, 1456, 1384, 1273, 1255, 1085, 1000, 763, 731 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.65 (s, 1H), 7.40 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 6.7 Hz, 2H), 3.20 (dd, J = 11.3, 6.1 Hz, 1H), 2.31 – 2.25 (m, 1H), 2.19 – 2.15 (m, 1H), 2.11 – 2.06 (m, 1H), 1.98 – 1.92 (m, 1H), 1.80 – 1.74 (m, 3H), 1.68 – 1.61 (m, 2H), 1.56 – 1.41 (m, 3H), 0.90 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.9, 135.6, 132.8, 132.0, 120.7, 65.8, 62.6, 57.8, 36.2, 35.2, 33.4, 31.9, 29.5, 26.1, 10.4 ppm.

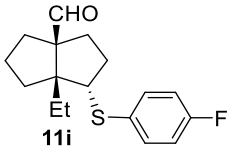
Synthesis of product **11h**:



11h

Product **11h** (30.7 mg) was obtained in 45% yield as a colorless oil following general procedure E. HRMS (APCI) m/z calcd for $C_{18}H_{21}F_3NaOS$ $[M+H]^+$: 365.1157; found: 227. 365.1157; IR ν_{max} (film): 2960, 2937, 1715, 1674, 1521, 1324, 1275, 1166, 1093, 1061, 1012, 834, 749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.67 (s, 1H), 7.52 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 8.2 Hz, 2H), 3.33 (dd, J = 11.3, 6.2 Hz, 1H), 2.32 – 2.24 (m, 2H), 2.21 – 2.11 (m, 1H), 1.98 – 1.90 (m, 1H), 1.85 – 1.74 (m, 3H), 1.71 – 1.65 (m, 2H), 1.58 – 1.47 (m, 3H), 0.91 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.8, 142.0, 136.6, 134.6, 129.4(q, ^2J = 35.3 Hz), 127.8 (q, ^1J = 233.6 Hz), 125.7 (q, ^3J = 7.5 Hz), 65.6, 62.6, 56.3, 36.2, 35.2, 33.3, 32.0, 29.5, 26.1, 10.4 ppm.

Synthesis of product **11i**:

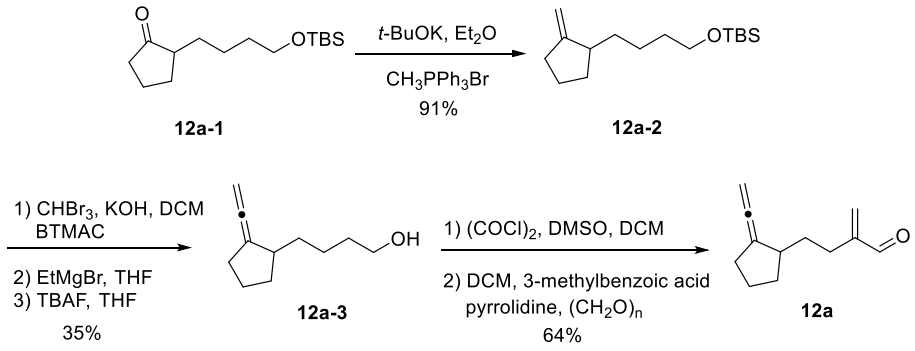


11i

Product **11i** (22.9 mg) was obtained in 39% yield as a colorless oil following general procedure E. HRMS (APCI) m/z calcd for $C_{17}H_{21}FNaOS$ $[M+Na]^+$: 315.1189; found: 315.1189; IR ν_{max} (film): 2940, 2875, 1714, 1589, 1489, 1307, 1265, 1223, 1087, 1012, 832, 816 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.63 (s, 1H), 7.46 – 7.37 (m, 2H), 7.02 – 6.96 (m, 2H), 3.13 (dd, J = 11.4, 6.1 Hz, 1H), 2.31 – 2.23 (m, 1H), 2.14 – 2.03 (m, 2H), 1.98 – 1.92 (m, 1H), 1.80 – 1.70 (m, 3H), 1.68 – 1.57 (m, 2H), 1.54 – 1.39 (m, 3H), 0.90 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.0, 162.17 (d, ^1J = 247.2 Hz), 134.41 (d, ^3J = 8.1 Hz), 131.12 (d, ^4J = 3.4 Hz), 115.98 (d, ^2J = 21.7 Hz). 65.85, 62.59, 58.89, 36.23, 35.21, 33.49, 31.86, 29.54, 26.11, 10.42 ppm.

Part 4: General procedure and characteristic data for tricyclic precursors

Synthesis of **12a**:



Synthesis of Compound **12a-2.**

To a stirred solution of methyl triphenylphosphonium bromide (4.28 g, 12 mmol, 1.2 equiv.) in dry Et_2O (50 mL) was added *t*-BuOK (1.34 g, 12 mmol, 1.2 equiv.) and the resulting mixture was stirred at room temperature for 1 h. Ketone [4] **12a-1** (2.70 g, 10 mmol, 1 equiv.) was dissolved in dry Et_2O (10 mL) and added dropwise to this solution. The reaction mixture was stirred at room temperature for additional 10 min and then refluxed for 6 h. After completion, the mixture was quenched with a saturated solution of NH_4Cl (30 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 50:1 to 20:1) to give product **12a-2** (2.43 g) in 91% yield as a colorless oil. HRMS (APCI) m/z calcd for $C_{16}H_{33}OSi$ $[M+H]^+$: 269.2295; found: 269.2294; IR ν_{max} (film): 2925, 2851, 2352, 1965, 1717, 1442, 1273, 1251, 1157, 1024, 841, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 4.87 (s, 1H), 4.78(s, 1H), 3.62 (t, J = 6.5 Hz, 2H), 2.41 – 2.22 (m, 3H), 1.97 – 1.82 (m, 1H), 1.75 – 1.65 (m, 1H), 1.64 – 1.46 (m, 4H), 1.42 – 1.32 (m, 2H), 1.30 – 1.17 (m, 2H), 0.91 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.1, 103.9, 63.2, 43.9, 34.3, 33.2, 33.0, 32.7, 26.0, 24.2, 24.1, 18.4, -5.3 ppm.

Synthesis of Compound **12a-3.**

To a stirred solution of **12a-2** (2.68 g, 10 mmol, 1 equiv.) in DCM (10 mL) was added crushed KOH (841 mg, 15 mmol, 1.5 equiv.) and benzyl triethyl ammonium chloride (114 mg, 0.5 mmol, 0.05 equiv.). Bromoform (1.10 ml, 12 mmol, 1.2 equiv.) was then added by syringe pump in 1 h at 40 °C. The reaction mixture was stirred for 24 h at room temperature. After completion, the mixture was then filtered through a plug of silica gel and washed with hexane. The solvent was removed under vacuum and the crude product was used directly for the next step without further purification.

To a stirred solution of the crude product in THF (20 mL) was added *n*-BuMgBr (1 M in THF, 13 mL, 1.3 equiv.) dropwise at room temperature. The reaction mixture was stirred for 2 h. After completion, the mixture was quenched with a saturated solution of NH_4Cl (30 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the allene product was used directly for the next step without further purification [5].

To a stirred solution of the allene product in THF (10 mL) was added TBAF (1 M in THF, 20 mL, 2 equiv.) at room temperature. The reaction mixture was stirred for 4 h. After completion, the mixture was quenched with a saturated solution of NH_4Cl (40 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 8:1 to 2:1) to give the desired product **12a-3** (581 mg) in 35% yield for 3 steps as a colorless oil.

HRMS (APCI) m/z calcd for $C_{11}H_{19}O$ $[M+H]^+$: 167.1430; found: 167.1433; IR ν_{max} (film): 2935, 2863, 2365, 1958, 1713, 1700, 1456, 1325, 1233, 1055, 1033, 764, 749 cm^{-1};

^1H NMR (500 MHz, $CDCl_3$) δ = 4.71 – 4.65 (m, 2H), 3.64 (t, *J* = 6.6 Hz, 2H), 2.54 – 2.47 (m, 1H), 2.47 – 2.34 (m, 2H), 1.92 – 1.86 (m, 1H), 1.80 – 1.69 (m, 1H), 1.60 – 1.55 (m, 4H), 1.50 – 1.36 (m, 3H), 1.36 – 1.18 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 202.3, 107.3, 76.3, 63.0, 42.8, 34.1, 33.2, 32.9, 30.9, 25.3, 24.0 ppm.

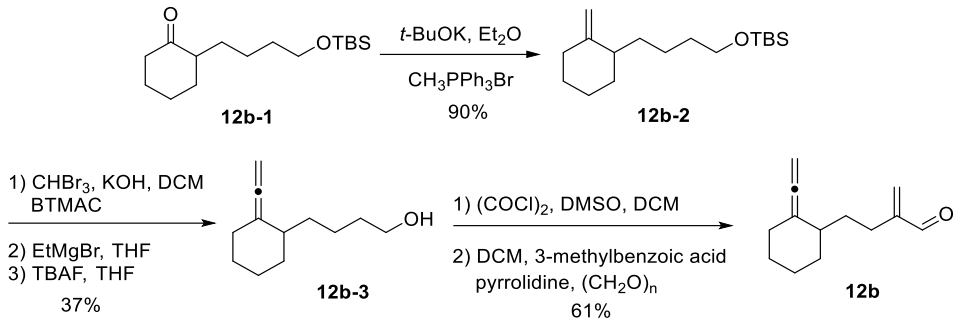
Synthesis of Compound **12a.**

To a stirred solution of DMSO (1 mL, 15 mmol, 3 equiv.) in dry DCM (50 mL) at -78 °C was added oxalyl chloride (0.65 mL, 7.5 mmol, 1.5 equiv.) dropwise. The reaction mixture was stirred at -78 °C for 30 min and a solution of **12a-3** (830mg, 5 mmol, 1 equiv.) in dry DCM (15 mL) was added dropwise. The reaction mixture was stirred at -78 °C for 45 min followed by addition of Et_3N (4.20 ml, 30 mmol, 6 equiv.) at the same temperature. The cooling bath was then removed and the reaction was stirred at room temperature for 1 h. After completion, the mixture was quenched with a saturated solution of NH_4Cl (20 mL) and extracted with DCM (3 × 50 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (10 mL), brine (10 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the aldehyde was used directly for the next step without further purification.

To a solution of the previous aldehyde in DCM (10 mL) was added pyrrolidine (0.04 mL, 0.5 mmol, 0.1 equiv.), 3-methylbenzoic acid (68 mg, 0.5 mmol, 0.1 equiv.) and formaldehyde (37% solution in H_2O, 0.49 mL, 1.2 equiv.) at room temperature. The reaction mixture was heated to 45 °C and stirred for 2h. After completion, the mixture was quenched with a saturated solution of $NaHCO_3$ (10 mL) and extracted with DCM (3 × 20 mL). The combined organic layers were washed with brine (5 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 80:1 to 20:1) to give the desired product **12a** (565 mg) in 64% yield for 2 steps as a colorless oil. HRMS (APCI) m/z calcd for $C_{12}H_{17}O$ $[M+H]^+$: 177.1274; found: 177.1275; IR ν_{max} (film): 2948, 2863, 1713, 1454, 1447, 1267, 1083, 1020, 847, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.54 (s, 1H), 6.28 (d, *J* = 0.5 Hz, 1H), 6.00 (s, 1H), 4.83 – 4.59 (m, 2H), 2.53 – 2.50 (m, 1H), 2.47 – 2.37 (m, 2H), 2.31 (t, *J* = 8.0 Hz, 2H), 1.99 – 1.87 (m, 1H), 1.81 – 1.65 (m, 2H), 1.60 – 1.55 (m, 1H), 1.48 – 1.44 (m, 1H), 1.36 – 1.23 (m, 1H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ = 202.3, 194.7, 150.4, 134.0, 106.9, 76.6, 42.4, 33.1, 32.3, 30.8, 25.9, 25.3 ppm.

Synthesis of **12b**:



Synthesis of Compound **12b-2.**

To a stirred solution of methyl triphenylphosphonium bromide (4.28 g, 12 mmol, 1.2 equiv.) in dry Et_2O (50 mL) was added *t*-BuOK (1.34 g, 12 mmol, 1.2 equiv.) and the resulting mixture was stirred at room temperature for 1 h. Ketone [6] **12b-1** (2.84 g, 10 mmol, 1 equiv.) was dissolved in dry Et_2O (10 mL) and added dropwise to the solution. The reaction mixture was stirred at room temperature for additional 10 min and then refluxed for 6 h. After completion, the mixture was quenched with a saturated solution of NH_4Cl (30 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 50:1 to 20:1) to give product **12b-2** (2.54 g) in 90% yield as a colorless oil. HRMS (APCI) m/z calcd for $C_{17}H_{35}OSi$ $[M+H]^+$: 283.2452; found: 283.2449; IR ν_{max} (film): 2930, 2856, 1457, 1446, 1364, 1255, 1101, 887, 835, 773, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 4.64 (s, 1H), 4.56 (s, 1H), 3.61 (t, *J* = 6.6 Hz, 2H), 2.28 – 2.16 (m, 1H), 2.04 – 1.97 (m, 2H), 1.84 – 1.74 (m, 1H), 1.69 – 1.39 (m, 6H), 1.39 – 1.18 (m, 5H), 0.90 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.0, 105.4, 63.2, 43.1, 34.7, 33.8, 33.1, 31.8, 28.8, 25.9, 24.2, 23.6, 18.3, -5.3 ppm.

Synthesis of Compound **12b-3.**

To a stirred solution of **12b-2** (2.82 g, 10 mmol, 1 equiv.) in DCM (10 ml) was added crushed KOH (841 mg, 15 mmol, 1.5 equiv.) and benzyl triethyl ammonium chloride (114 mg, 0.5 mmol, 0.05 equiv.). Bromoform (1.10 ml, 12 mmol, 1.2 equiv.) was then added by syringe pump in 1h at 40 °C. The reaction mixture was stirred for 24 h at room temperature. After completion, the mixture was then filtered through a plug of silica gel and washed with hexane. The solvent was removed under vacuum and the crude product was used directly for the next step without further purification.

To a solution of the crude product in THF (20 ml) was added *n*-BuMgBr (1 M in THF, 13 mL, 1.3 equiv.) dropwise at room temperature. The reaction mixture was stirred for 2 h. After completion, the mixture was quenched with a saturated solution of NH_4Cl (30 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the allene product was used directly for the next step without further purification.

To a solution of the allene product in THF (10 mL) was added TBAF (1 M in THF, 20 mL, 2 equiv.) at room temperature and the reaction mixture was stirred for 4 h. After completion, the mixture was quenched with a saturated solution of NH_4Cl (40 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 8:1 to 2:1) to give the desired product **12b-3** (663 mg) in 37% yield for 3

steps as a colorless oil.

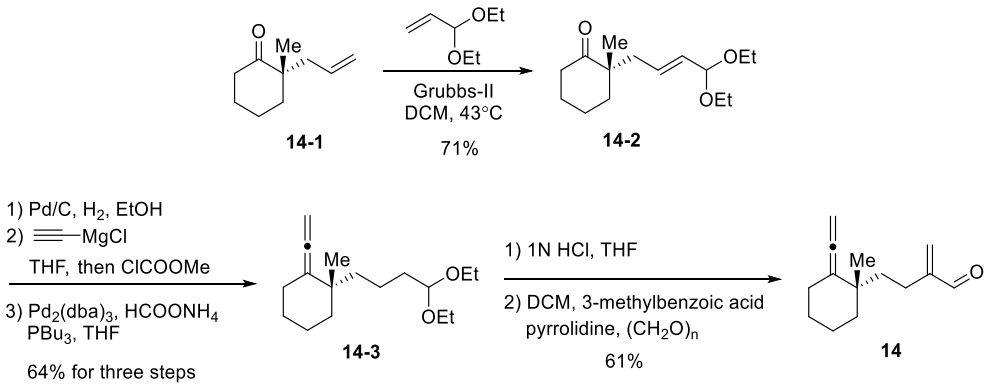
HRMS (APCI) m/z calcd for $C_{12}H_{21}O$ $[M+H]^+$: 181.1587; found: 181.1592; IR ν_{max} (film): 2927, 2852, 2359, 1957, 1701, 1438, 1275, 1260, 1030, 831, 763, 750 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 4.65 (dd, *J* = 5.6, 3.3 Hz, 2H), 3.61 (t, *J* = 6.7 Hz, 2H), 1.98 – 1.85 (m, 3H), 1.82 – 1.74 (m, 2H), 1.70 – 1.62 (m, 2H), 1.59 – 1.54 (m, 3H), 1.51 – 1.46 (m, 2H), 1.46 – 1.33 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 205.1, 109.6, 76.4, 62.9, 42.3, 33.7, 32.6, 30.6, 28.3, 27.5, 26.5, 25.5 ppm.

Synthesis of Compound **12b.**

To a stirred solution of DMSO (1.0 ml, 15 mmol, 3 equiv.) in dry DCM (50 mL) at -78 °C was added oxalyl chloride (0.65 ml, 7.5 mmol, 1.5 equiv.) dropwise. The reaction mixture was stirred at -78 °C for 30 min and a solution of **12b-3** (830mg, 5 mmol, 1 equiv.) in dry DCM (15 mL) was added dropwise. The reaction mixture was stirred at -78 °C for 45 min followed by addition of Et_3N (4.20 ml, 30 mmol, 6 equiv.) at the same temperature. The cooling bath was then removed and the reaction was stirred at room temperature for 1 h. After completion, the mixture was quenched with a saturated solution of NH_4Cl (20 mL) and extracted with DCM (3 × 50 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (10 mL), brine (10 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the aldehyde was used directly for the next step without further purification.

To a solution of the previous aldehyde in DCM (10 mL) was added pyrrolidine (0.04 mL, 0.5 mmol, 0.1 equiv.), 3-methylbenzoic acid (68 mg, 0.5 mmol, 0.1 equiv.) and formaldehyde (37% solution in H_2O, 0.49 mL, 1.2 equiv.) at room temperature. The reaction mixture was heated to 45 °C and stirred for 2h. After completion, the mixture was quenched with a saturated solution of $NaHCO_3$ (10 mL) and extracted with DCM (3 × 20 mL). The combined organic layers were washed with brine (5 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 80:1 to 20:1) to give the desired product **12b** (580 mg) in 61% yield for 2 steps as a colorless oil. HRMS (APCI) m/z calcd for $C_{13}H_{19}O$ $[M+H]^+$: 191.1430; found: 191.1434; IR ν_{max} (film): 2935, 2834, 2360, 1958, 1714, 1442, 1273, 1255, 1010, 941, 838, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.54 (s, 1H), 6.26 (d, *J* = 0.8 Hz, 1H), 5.99 (s, 1H), 4.64 (dd, *J* = 3.2, 2.7 Hz, 2H), 2.36 – 2.16 (m, 3H), 2.02 – 1.80 (m, 3H), 1.79 – 1.58 (m, 4H), 1.46 – 1.31 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 202.9, 194.8, 150.5, 133.9, 105.3, 74.9, 39.0, 33.4, 31.5, 31.4, 27.4, 25.5, 25.4 ppm.

Synthesis of Compound **14.**



Synthesis of Compound **14-2.**

To a stirred solution of ketone [7] **14-1** (2.28 g, 15 mmol, 1 equiv.) in DCM (75 mL) at room temperature was added acrolein diethyl acetal (3.91 g, 30 mmol, 2 equiv.) and Grubbs' catalyst II (382 mg, 0.45 mmol, 0.03 equiv.). The reaction mixture was then refluxed for 5 h. After cooled to ambient temperature, the solvent was removed under vacuum and the

residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 10:1 to 3:1) to give product **14-2** (2.70 g) in 71% yield as a light brown oil. HRMS (APCI) m/z calcd for $C_{15}H_{27}O_3$ $[M+H]^+$: 255.1955; found: 255.1955; IR ν_{max} (film): 2994, 1933, 1769, 1759, 1708, 1452, 1447, 1373, 1246, 1124, 1052, 987 cm^{-1}; ^1H NMR (400 MHz, Acetone) δ = 5.78 – 5.60 (m, 1H), 5.51 – 5.45 (m, 1H), 4.82 (d, *J* = 5.1 Hz, 1H), 3.60 – 3.54 (m, 2H), 3.45 – 3.40 (m, 2H), 2.42 – 2.32 (m, 3H), 2.23 (dd, *J* = 13.9, 7.5 Hz, 1H), 1.82 – 1.74 (m, 5H), 1.60 – 1.56 (m, 1H), 1.16 – 1.10 (m, 6H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, Acetone) δ = 213.0, 131.3, 129.0, 101.0, 60.1, 48.1, 39.9, 38.6, 38.3, 27.2, 22.1, 20.8, 14.7 ppm.
$[\alpha]_D^{20}$ = -34.8 (c = 0.50, MeOH)

Synthesis of Compound **14-3.**

To a stirred solution of **14-2** (1.27 g, 5 mmol, 1 equiv.) in dry EtOH (20 ml) at room temperature was added palladium on carbon (53 mg, 0.5 mmol, palladium 10% on carbon, 0.1 equiv.). The reaction mixture was degassed by hydrogen and the resultant mixture was stirred at room temperature for 18 h. After completion, the mixture was filtered through a plug of silica gel and the filtrate was concentrated under vacuum. The residue was used directly for the next step without further purification.

To a stirred solution of the residue in THF (5 mL) was added ethynylmagnesium chloride (0.6 M in THF, 12.5 mL, 1.5 equiv.) dropwise at room temperature. The mixture was stirred for 30 min and then warmed to 45°C for additional 4h. It was then recooled to room temperature and methyl chloroformate (0.78 mL, 10 mmol, 2 equiv.) was added dropwise to this solution. The reaction mixture was stirred for 12h at room temperature and then quenched with a saturated aqueous solution of $NaHCO_3$ (20 mL), extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was used directly for the next step without further purification.

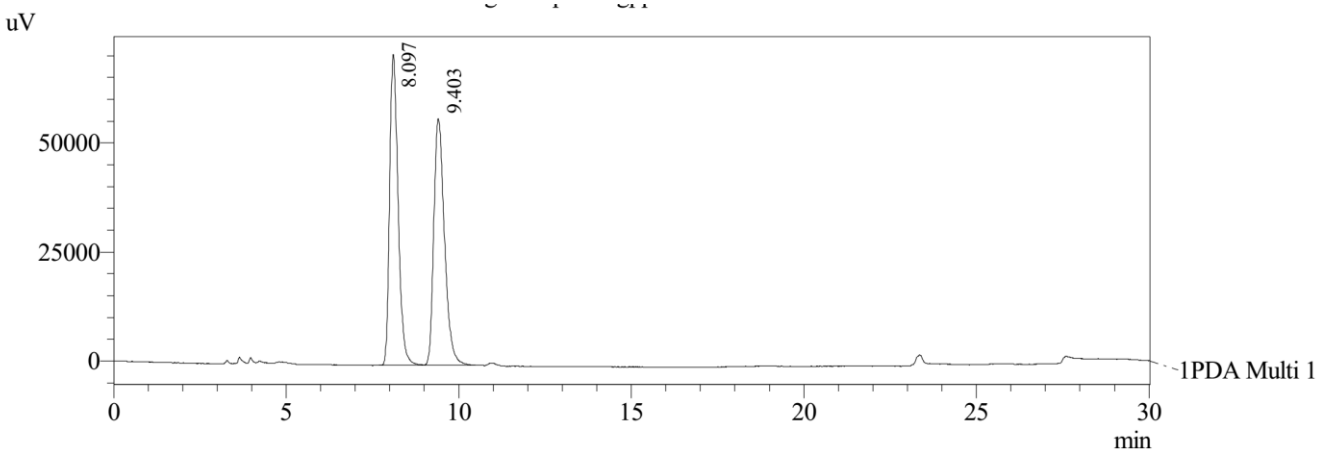
To a stirred solution of the previous residue in THF (20 mL) were added ammonium formate (0.95 g, 15 mmol, 3 equiv.), PBu_3 (101 mg, 0.5 mmol, 0.1 equiv.), $Pd_2(dba)_3$ (229 mg, 0.25 mmol, 0.05 equiv.) sequently. After stirring at 40 °C for 12 h, the reaction mixture was then filtered through a plug of silica gel and washed with EtOAc. The filtrate was concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel (hexane/EtOAc = 20:1 to 8:1) to give product [8] **14-3** (850 mg) in 64% yield for 3 steps as a colorless oil. HRMS (APCI) m/z calcd for $C_{17}H_{30}NaO_2$ $[M+Na]^+$: 289.2138; found: 289.2140; IR ν_{max} (film): 2976, 2930, 1955, 1769, 1758, 1373, 1247, 1241, 1126, 1104, 1097, 844 cm^{-1}; ^1H NMR (400 MHz, Acetone) δ = 4.64 – 4.54 (m, 2H), 4.47 (t, *J* = 5.7 Hz, 1H), 3.65 – 3.54 (m, 2H), 3.50 – 3.40 (m, 2H), 2.16 – 2.10 (m, 2H), 1.72 – 1.60 (m, 2H), 1.60 – 1.47 (m, 5H), 1.45 – 1.37 (m, 1H), 1.36 – 1.23 (m, 4H), 1.13 (dd, *J* = 9.5, 4.6 Hz, 6H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, Acetone) δ = 204.1, 107.6, 102.6, 73.5, 60.3, 39.1, 37.6, 35.6, 34.1, 28.1, 26.9, 25.6, 21.5, 19.1, 14.8 ppm; $[\alpha]_D^{20}$ = -106.7 (c = 0.50, MeOH)

Synthesis of Compound **14.**

To a stirred solution of **14-3** (533 mg, 2 mmol, 1 equiv.) in THF (20 mL) was added HCl (1N, 2 mL) and then stirred at room temperature for 1 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under vacuum to give the aldehyde which was used without further purification.

To stirred a solution of the aldehyde in DCM (4 mL) was added pyrrolidine (16 µl, 0.2 mmol, 0.1 equiv.), 3-methylbenzoic acid (27 mg, 0.2 mmol, 0.1 equiv.) and formaldehyde (37% solution in H_2O, 0.19 mL, 1.2 equiv.) at room temperature. The reaction mixture was heated to 45 °C and stirred for 2h. After completion, the mixture was quenched with a saturated solution of $NaHCO_3$ (10 mL) and extracted with DCM (3 × 15 mL). The combined organic layers were washed

with brine (5 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 80:1 to 20:1) to give product **14** (249 mg, 92% ee) in 61% yield for 3 steps as a colorless oil. HRMS (APCI) m/z calcd for $C_{14}H_{21}O$ $[M+H]^+$: 205.1587; found: 205.1588; IR ν_{max} (film): 2949, 2854, 1952, 1776, 1759, 1690, 1449, 1327, 1238, 1062, 941, 841cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.55 (s, 1H), 6.27 (s, 1H), 5.98 (s, 1H), 4.61 (d, J = 3.2 Hz, 2H), 2.23 – 2.09 (m, 4H), 1.8 – 1.67 (m, 1H), 1.71 – 1.62 (m, 1H), 1.60 – 1.49 (m, 3H), 1.42 – 1.28 (m, 3H), 1.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.1, 194.7, 151.1, 133.7, 107.4, 74.3, 39.2, 36.2, 35.8, 28.2, 26.9, 25.9, 22.7, 21.7 ppm; $[\alpha]_D^{20}$ = -85.8 (c = 0.30, MeOH). HPLC (DAICEL Chiralpak- AS column, 100% hexane, flow rate: 1.0 mL/min): t_{minor} = 7.945 min; t_{major} = 9.238 min.



1 PDA Multi 1 / 214nm 4nm

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PDA Ch1 214nm 4nm

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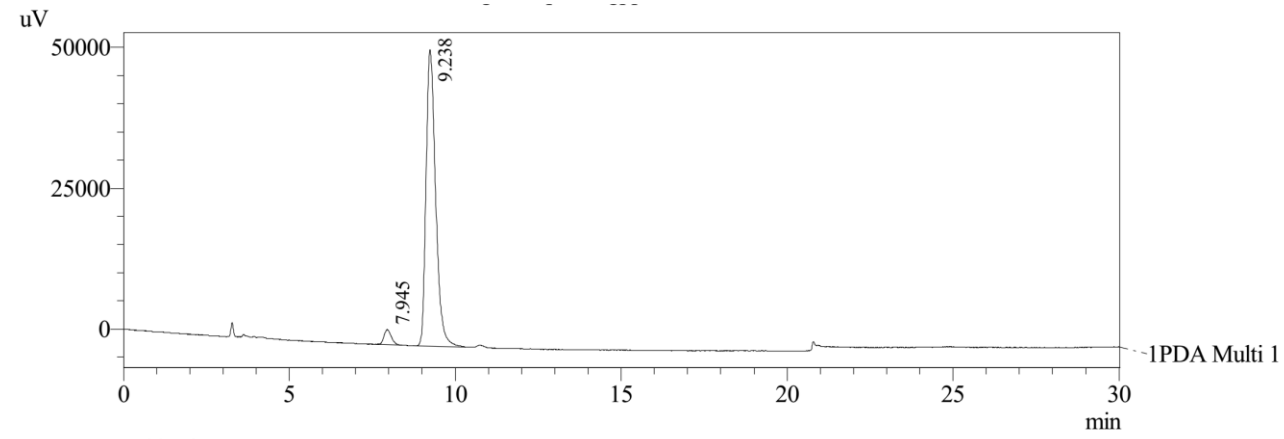

1 PDA Multi 1 / 214nm 4nm

PeakTable

PDA Ch1 214nm 4nm

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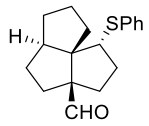
1	7.945	41810	2700	3.807	4.877
2	9.238	1056546	52661	96.193	95.123
Total		1098357	55361	100.000	100.000

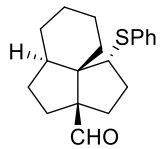
Part 5: General procedure and characteristic data for tricyclic products

Synthesis of Product **13a** and **13b.**



13a

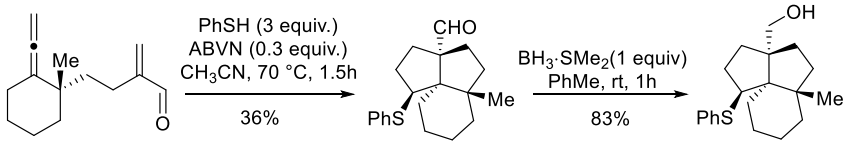
Product **13a** (42.3 mg) was obtained in 74% yield as a colorless oil following general procedure D. HRMS (APCI) m/z calcd for $C_{18}H_{23}OS$ $[M+H]^+$: 287.1464; found: 287.1468; IR ν_{max} (film): 2946, 2868, 1715, 1578, 1476, 1442, 1307, 1085, 1042, 743, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.62 (s, 1H), 7.42 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.24 – 7.20 (m, 1H), 3.33 (dd, *J* = 12.4, 5.5 Hz, 1H), 2.64 – 2.55 (m, 1H), 2.27 – 2.12 (m, 3H), 1.96 – 1.88 (m, 1H), 1.88 – 1.82 (m, 1H), 1.79 – 1.68 (m, 3H), 1.60 – 1.51 (m, 4H), 1.50 – 1.43 (m, 1H), 1.36 (dt, *J* = 12.0, 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.7, 136.3, 131.2, 129.0, 126.7, 69.0, 65.9, 59.6, 47.4, 34.3, 34.3, 34.1, 34.1, 32.5, 31.4, 26.8 ppm.



13b

Product **13b** (34.3 mg) was obtained in 57% yield as a colorless oil following general procedure D. HRMS (APCI) m/z calcd for $C_{19}H_{25}OS$ $[M+H]^+$: 301.1621; found: 301.1616; IR ν_{max} (film): 2933, 2861, 1710, 1566, 1442, 1279, 1266, 1107, 1056, 817, 751, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.69 (s, 1H), 7.48 – 7.43 (m, 2H), 7.33 – 7.28 (m, 2H), 7.27 – 7.20 (m, 1H), 3.21 (dd, *J* = 11.5, 6.7 Hz, 1H), 2.64 – 2.52 (m, 1H), 2.33 – 2.25 (m, 1H), 2.23 – 2.16 (m, 1H), 2.10 – 2.02 (m, 1H), 1.88 – 1.74 (m, 4H), 1.71 – 1.55 (m, 4H), 1.48-1.42 (m, 1H), 1.40 – 1.34 (m, 1H), 1.31 – 1.25 (m, 2H), 1.21 – 1.15 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 205.5, 136.4, 131.7, 128.9, 126.8, 66.4, 61.1, 61.0, 42.9, 34.4, 33.4, 32.8, 32.4, 32.0, 28.2, 23.7, 22.6 ppm.

Synthesis of **14-p** and **15:**



14 (92% ee)

14-P

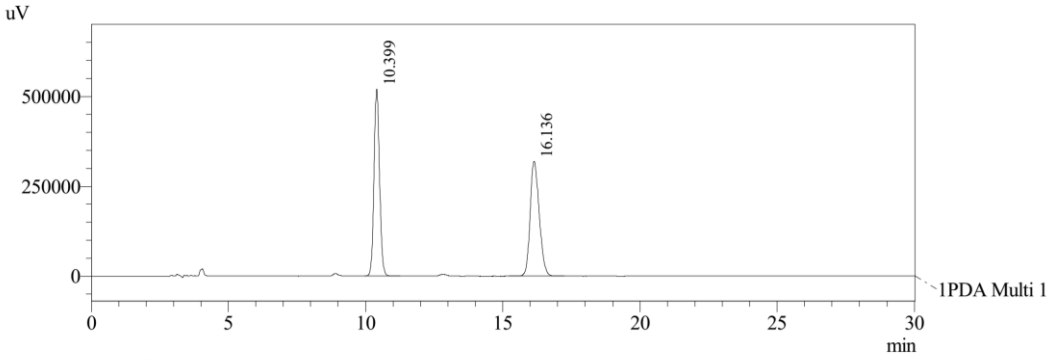
15 (92% ee)

To a flame-dried flask containing **14** (40.8 mg, 0.2 mmol, 1 equiv.) in dry CH_3CN (16 mL) was added a solution of PhSH (66.1 mg, 0.6 mmol, 3 equiv.) and ABVN (14.9 mg, 0.6 mmol, 3 equiv.) in dry CH_3CN (4 mL) at 70°C under argon. The reaction mixture was stirred at 70 °C for 1.5h. After cooled to ambient temperature, the solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 100:1 to 50:1) to give the desired product **14-p** (22.8 mg) in 36% yield as a colorless oil. HRMS (APCI) m/z calcd for $C_{20}H_{27}OS$ $[M+H]^+$: 315.1777; found: 315.1771; IR ν_{max} (film): 3044, 2942, 2888, 1675, 1507, 1449, 1286 1251, 1085, 1045, 817, 729, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.50 (s, 1H), 7.45 – 7.40 (m, 2H), 7.32 – 7.28 (m, 2H), 7.26 – 7.20 (m, 1H), 3.21 (dd, *J* = 11.1, 8.0 Hz, 1H), 2.52 (dd, *J* = 13.7, 11.3 Hz, 1H), 2.24 – 2.15 (m, 2H), 1.97 – 1.87 (m, 2H), 1.78 (dt, *J* = 8.9, 2.7 Hz, 2H), 1.69 – 1.63 (m, 1H), 1.59 – 1.52 (m, 3H), 1.46 – 1.41 (m, 1H), 1.33 (s, 3H), 1.30 – 1.36 (dd, *J* = 8.6, 5.7 Hz, 2H), 1.09

– 0.98 (m, 1H), 0.99 – 0.90 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.4, 137.5, 131.2, 128.9, 126.7, 58.9, 54.4, 51.5, 41.5, 39.1, 38.0, 36.6, 35.4, 32.9, 28.4, 25.4, 23.5, 21.2 ppm.

$[\alpha]_D^{20}$ = +116.2 (c = 0.30, MeOH)

To a stirred solution of **14-p** (15.7 mg, 0.05 mmol, 1 equiv.) in dry PhMe (2 mL) at room temperature under argon was added borane-dimethyl sulfide (2 M in THF, 25 µl, 1 equiv.). The reaction mixture was stirred for 1h. After completion, water (5 mL) was added dropwise and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ (5 mL), brine (5 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 25:1 to 5:1) to give product **15** (13.2 mg, 92% ee) in 83% yield as a colorless oil. HRMS (ESI) m/z calcd for $C_{20}H_{29}OS$ $[M+H]^+$: 317.1934; found: 317.1932; IR ν_{max} (film): 2956, 2868, 1487, 1449, 1360, 1261, 1142, 1087, 1025, 913, 800, 743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.29 – 7.27 (m, 1H), 7.26-7.23 (m, 1H), 7.21 – 7.17 (m, 1H), 3.44 (s, 2H), 3.17 (dd, *J* = 11.1, 8.1 Hz, 1H), 2.18 – 2.11 (m, 2H), 2.05 – 1.93 (m, 2H), 1.88 – 1.81 (m, 1H), 1.69 – 1.58 (m, 4H), 1.57 – 1.49 (m, 3H), 1.43 – 1.36 (m, 2H), 1.31 (s, 3H), 1.03 (dd, *J* = 11.7, 2.6 Hz, 1H), 0.95 – 0.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.2, 130.8, 128.8, 126.2, 70.4, 59.0, 51.3, 44.6, 42.8, 41.1, 38.0, 36.7, 36.2, 33.3, 31.8, 25.5, 23.6, 21.3; $[\alpha]_D^{20}$ = +79.5 (c = 0.10, MeOH). HPLC (DAICEL Chiralpak- AD column, 95: 5 hexane/ethanol, flow rate: 1.0 mL/min): t_{major} = 10.372 min; t_{minor} = 16.232 min.



1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

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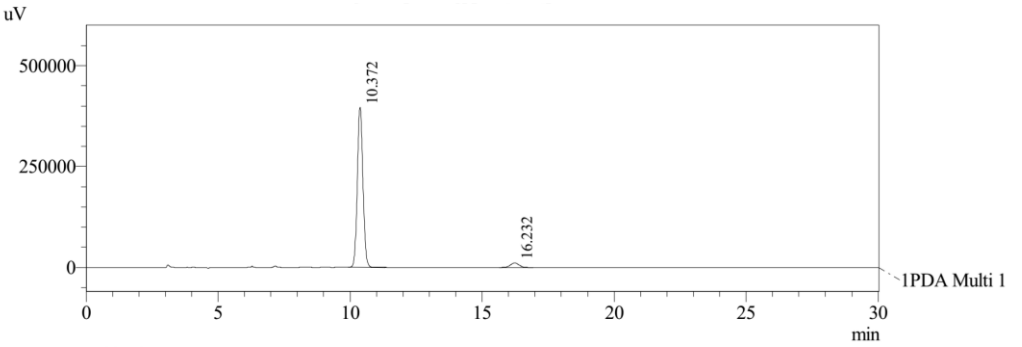

1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
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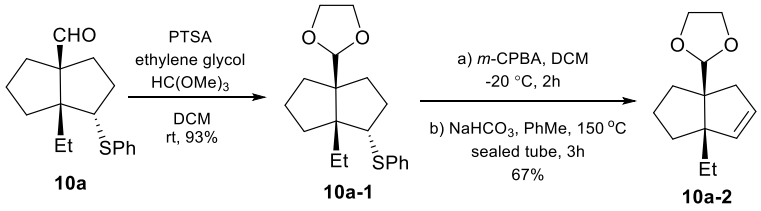
Total		6127171	408210	100.000	100.000

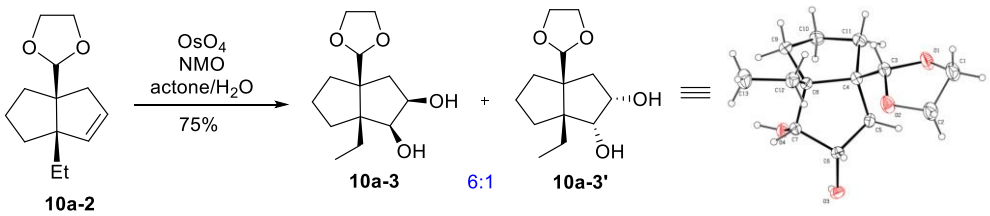
Part 6: X-ray Crystallographic data for 10a-3':



To a stirred solution of **10a** (82.2 mg, 0.3 mmol, 1 equiv) in PhMe (3 mL) were added ethylene glycol (186 mg, 3 mmol, 10 equiv), triethyl orthoformate (133.4 mg, 0.9 mmol, 1 equiv), and *p*-TsOH (5.2 mg, 0.03 mmol, 0.1 equiv) sequently. The reaction mixture was stirred for 12 h and then quenched with a saturated aqueous solution of $NaHCO_3$ (5 mL). The mixture was extracted with EtOAc (3 × 10 mL) and the combined organic layers were washed with brine (5 mL), dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 30:1 to 10:1) to give product **10a-1** (89.4 mg) in 93% yield as a colorless oil. HRMS (APCI) m/z calcd for $C_{19}H_{27}O_2S$ $[M+H]^+$: 319.1726; found: 319.1727. IR ν_{max} (film): 2957, 2874, 1715, 1583, 1479, 1437, 1275, 1260, 1099, 1046, 952, 913, 690 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.41 (dt, *J* = 3.1, 1.8 Hz, 2H), 7.32 – 7.24 (m, 2H), 7.22 – 7.12 (m, 1H), 4.81 (s, 1H), 4.02 – 3.90 (m, 2H), 3.89 – 3.84 (m, 2H), 3.44 – 3.33 (m, 1H), 2.17 – 2.10 (m, 1H), 2.02 – 1.94 (m, 1H), 1.92 – 1.83 (m, 1H), 1.80 – 1. 60 (m, 7H), 1.58 – 1.43 (m, 2H), 1.04 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.4, 130.7, 128.7, 126.0, 107.7, 65.2, 64.9, 58.9, 58.4, 57.6, 36.4, 34.1, 34.1, 32.0, 29.2, 24.9, 10.4 ppm.

To a stirred solution of **10a-1** (31.8 mg, 0.1 mmol, 1 equiv) in DCM (1.5 mL) at –20 °C was added a solution of *m*-CPBA (20.6 mg, 0.15 mmol, 2 equiv) in DCM (1.5 mL). The reaction mixture was stirred for 2h. After completion, it was quenched with a saturated aqueous solution of Na_2SO_3 (5 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (5 ml) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was used directly for the next step without further purification.

To a solution of the crude product in PhMe (2 mL) was added $NaHCO_3$ (25.2 mg, 0.3 mmol, 3 equiv) in a sealed tube. The reaction mixture was then heated to 160 °C for 3 h. After completion, the solution was concentrated in *vacuo* and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 15:1 to 5:1) to give product **10a-2** (14.2 mg) in 67% yield as a colorless oil. HRMS (APCI) m/z calcd for $C_{13}H_{21}O_2$ $[M+H]^+$: 209.1536; found: 209.1538. IR ν_{max} (film): 2935, 2848, 2359, 2345, 1667, 1463, 1384, 1266, 1085, 1024, 800, 745 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 5.65 – 5.59 (m, 1H), 5.58 – 5.46 (m, 1H), 4.84 (s, 1H), 3.99 – 3.94 (m, 2H), 3.93 – 3.80 (m, 2H), 2.67 (dt, *J* = 17.1, 2.1 Hz, 1H), 2.21 – 2.08 (m, 1H), 1.91 – 1.80 (m, 1H), 1.75 – 1.70 (m, 1H), 1.68 – 1.56 (m, 4H), 1.53 – 1.46 (m, 1H), 1.44 – 1.38 (m, 1H),, 0.93 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.0, 128.3, 108.1, 65.2, 65.0, 62.8, 55.7, 43.9, 37.7, 36.8, 29.1, 23.8, 10.3 ppm.



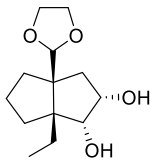
To a stirred solution of **10a-2** (100 mg, 0.5 mmol, 1 equiv) and 4-MethylMorpholine N-oxide (NMO, 176mg, 1.5 mmol, 3 equiv) in acetone (5 mL) at 0 °C was added a solution of OsO_4 (25.1 mg, 0.1 mmol, 0.2 equiv) in H_2O (1 mL). The reaction mixture was stirred for 3h. After completion, it was quenched with a saturated aqueous solution of Na_2SO_3

(5 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (5 mL) and dried over Na_2SO_4. The solution was concentrated in *vacuo* and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 6:1 to 3:1) to give product **10a-3** (90.7 mg) in 75% yield as a colorless oil, and **10a-3'** (15.1 mg) in 12.5% yield as a colorless crystal.

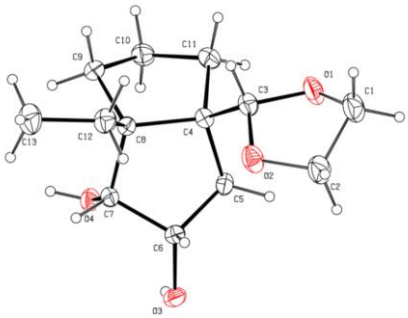
Compound **10a-3:** HRMS (APCI) m/z calcd for $C_{13}H_{22}O_4Na$ $[M+Na]^+$: 265.1410; found: 265.1411. IR ν_{max} (film): 2922, 2849, 1276, 1261, 765, 750 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 4.72 (s, 1H), 4.13 – 4.07 (m, 1H), 4.06 – 3.97 (m, 3H), 3.85 (dd, *J* = 14.9, 7.6 Hz, 1H), 3.63 (d, *J* = 3.6 Hz, 1H), 1.95 – 1.91 (m, 1H), 1.80 – 1.69 (m, 2H), 1.69 – 1.61 (m, 3H), 1.61 – 1.48 (m, 3H), 1.45 – 1.41 (m, 1H), 1.20 – 1.13 (m, 1H), 0.95 (t, *J* = 7.3 Hz, 3H), 0.90 – 0.82 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 107.6, 79.1, 77.3, 77.0, 76.7, 72.1, 65.4, 64.7, 57.6, 56.3, 38.5, 36.1, 32.0, 28.4, 23.7, 9.9 ppm.

Compound **10a-3':** HRMS (APCI) m/z calcd for $C_{13}H_{22}O_4Na$ $[M+Na]^+$: 265.1410; found: 265.1411. M.P. = 94.2–96.1 °C. IR ν_{max} (film): 2922, 2849, 1276, 1261, 765, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 4.71 (s, 1H), 4.22 – 4.12 (m, 1H), 3.98 – 3.92 (m, 2H), 3.91 – 3.88 (m, 1H), 3.87 – 3.79 (m, 2H), 2.24 (dd, *J* = 14.0, 7.1 Hz, 1H), 2.10 – 1.98 (m, 1H), 1.89 – 1.72 (m, 1H), 1.67 – 1.59 (m, 5H), 1.48 – 1.37 (m, 2H), 1.38 – 1.33 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 107.6, 79.4, 72.1, 65.4, 64.7, 57.6, 56.3, 38.5, 36.1, 32.0, 28.4, 23.7, 9.9 ppm.

Crystal data and structure refinement for **10a-3'**



10a-3'



Empirical formula	$C_{13}H_{22}O_4$
Formula weight	242.30
Temperature/K	298
Crystal system	triclinic
Space group	P-1
a/Å	9.8273(9)
b/Å	11.3792(11)
c/Å	11.6772(11)
α /°	75.657(5)
β /°	86.929(5)
γ /°	87.177(4)
Volume/$Å^3$	1262.4(2)
Z	4
ρ_{calc} g/cm^3	1.275
μ /mm^{-1}	0.760
F(000)	528.0
Crystal size/mm^3	0.43 × 0.36 × 0.28

Radiation	CuKα (λ = 1.54178)
2Θ range for data collectic	7.822 to 122.856
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, 0 ≤ 13
Reflections collected	3795
Independent reflections	3795 [R_{int} = 0.0413, R_{sigma} = 0.03(
Data/restraints/parameter	3795/28/328
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I	R_1 = 0.0433, wR_2 = 0.0961
Final R indexes [all data	R_1 = 0.0570, wR_2 = 0.1039
Largest diff. peak/hole / e	0.20/-0.16

Part 7: References

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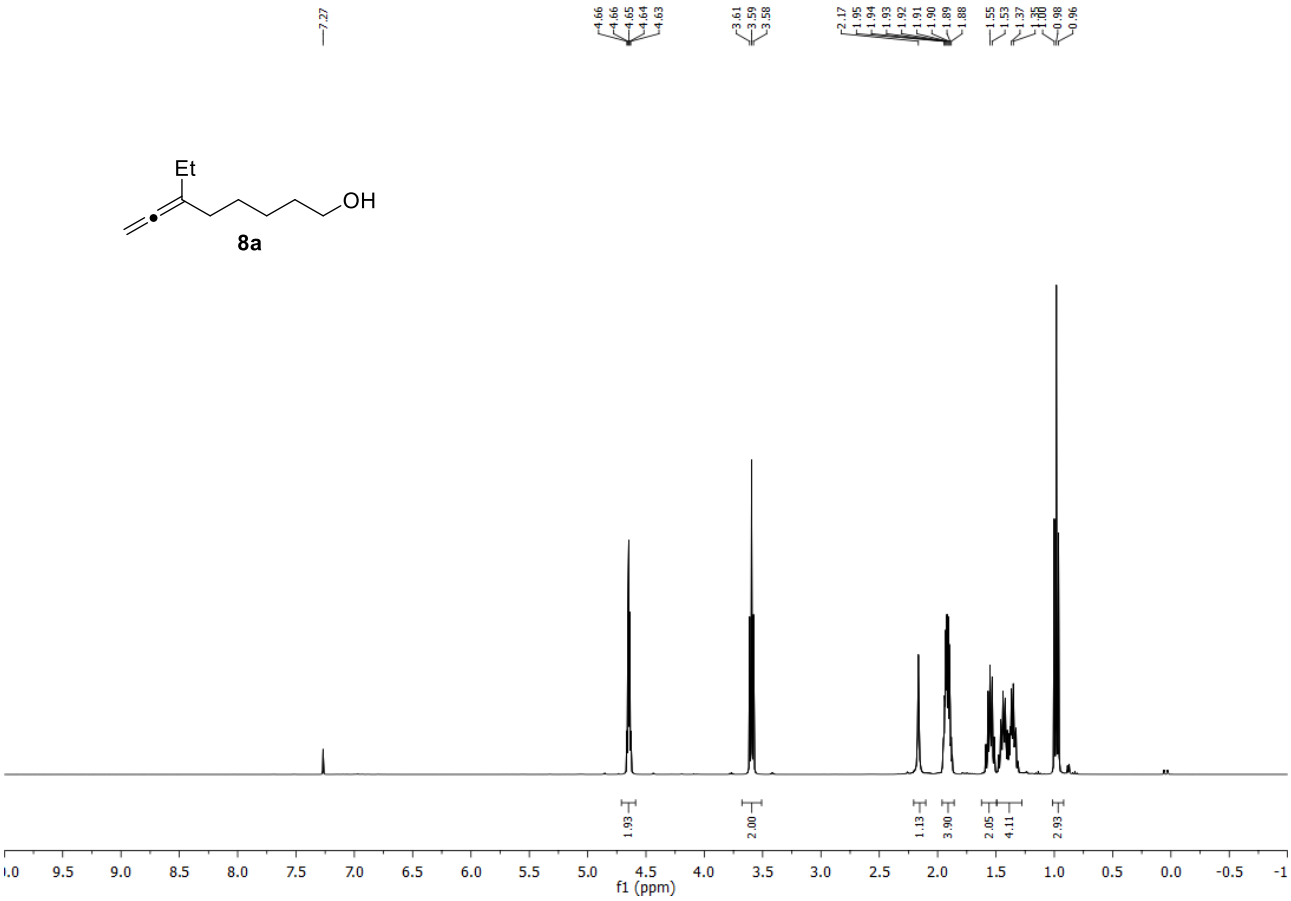
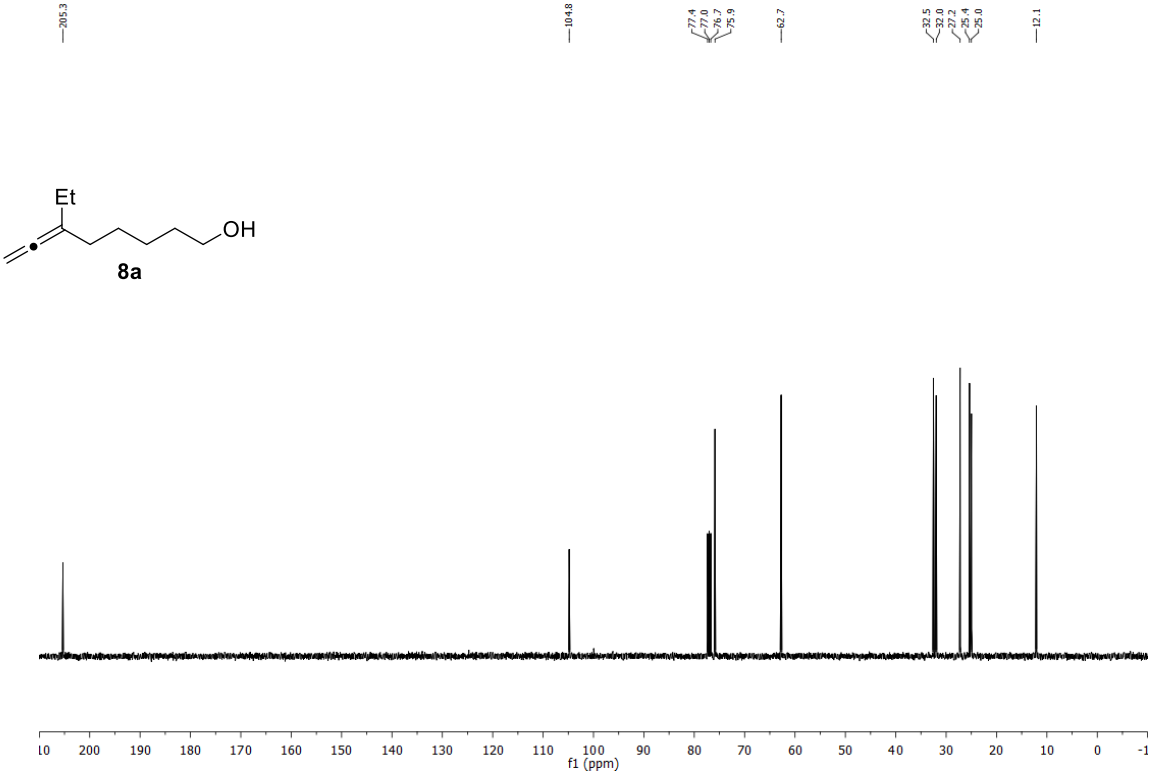
Part 8: NMR spectra

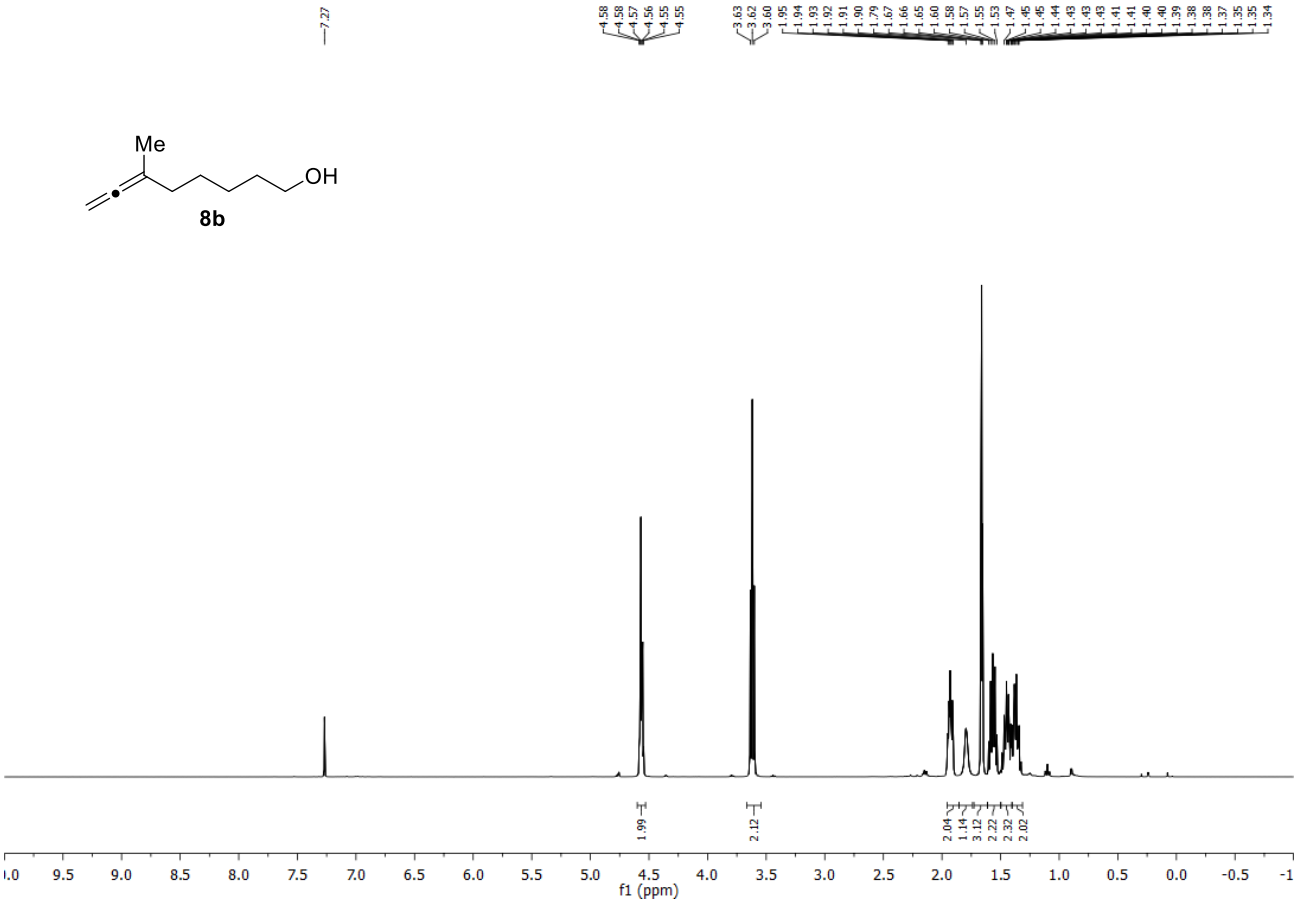
^{1}H NMR Spectra of **8a**



^{13}C NMR Spectra of **8a**



^{1}H NMR Spectra of **8b**



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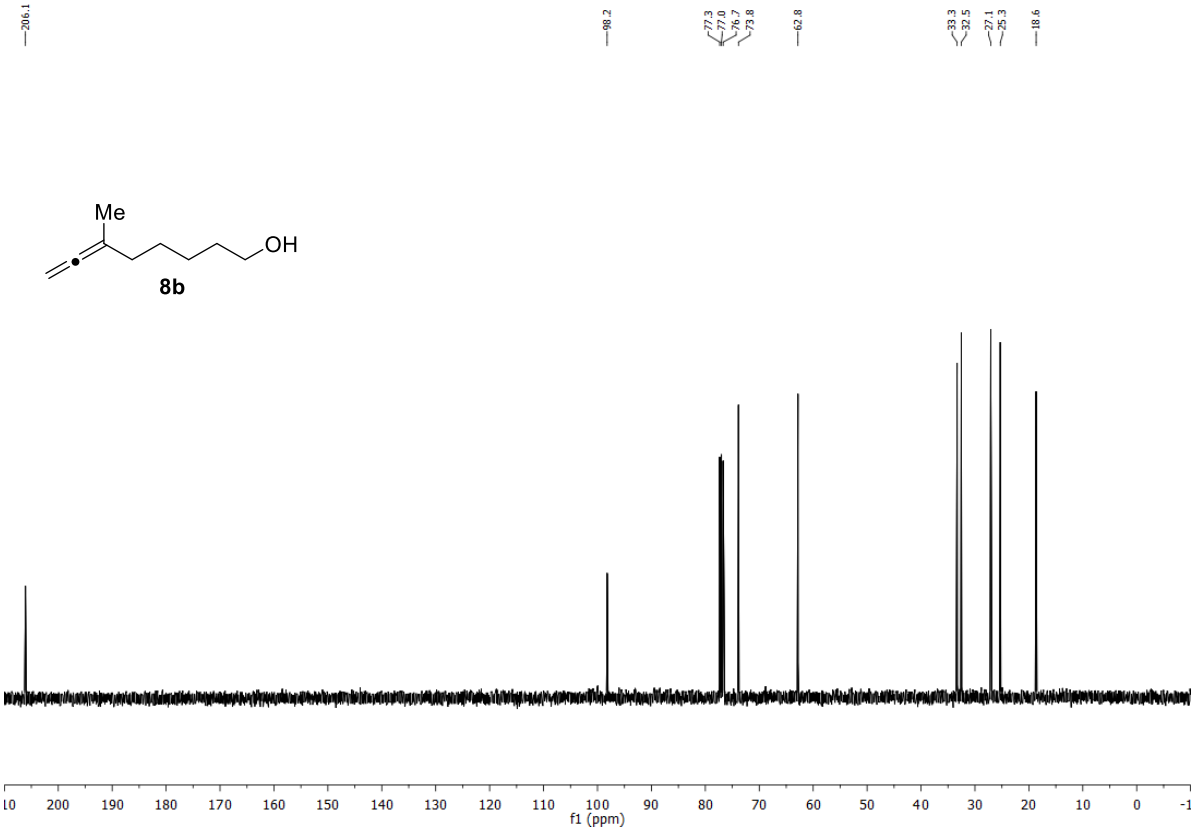
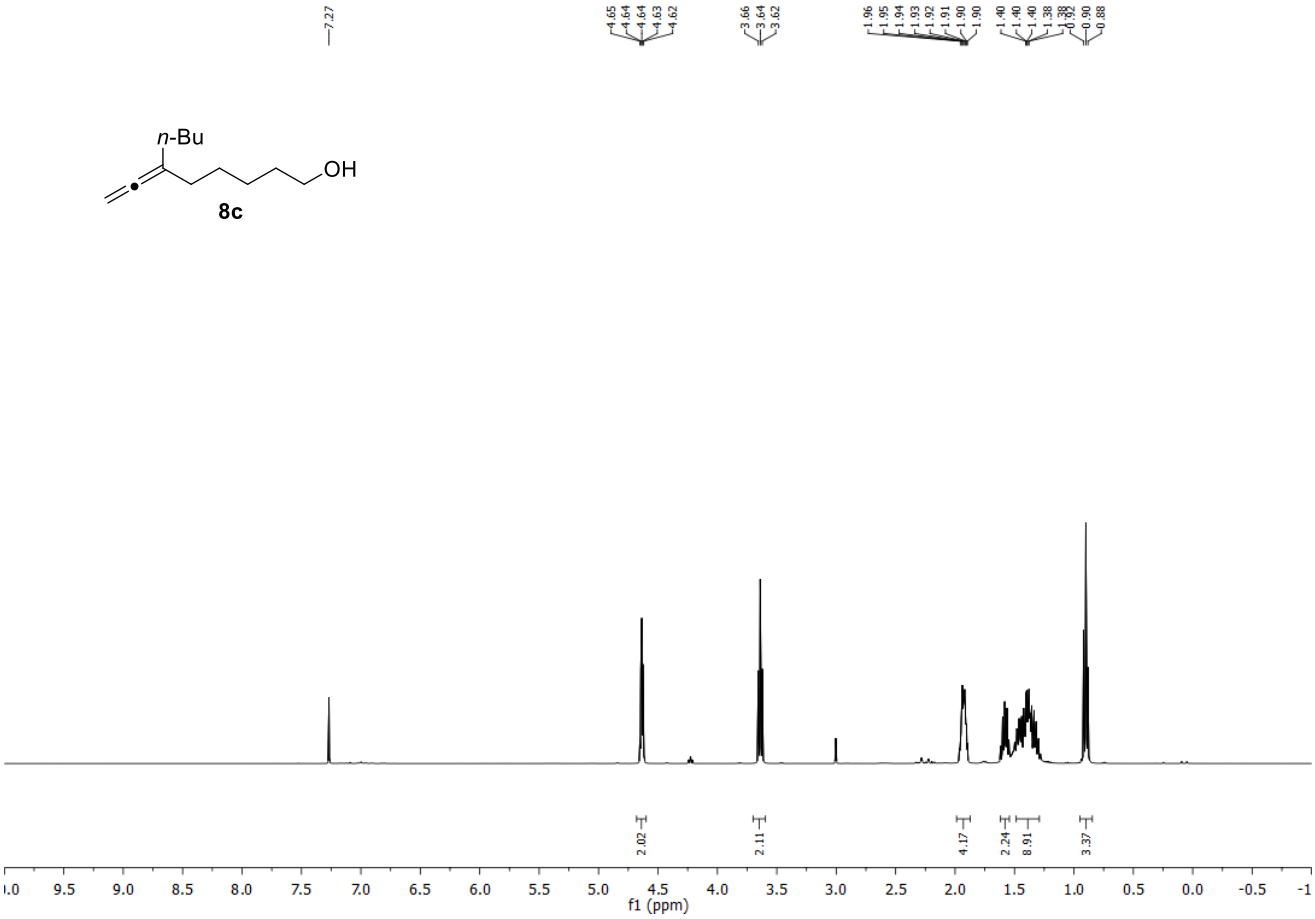


^{1}H NMR Spectra of **8c**



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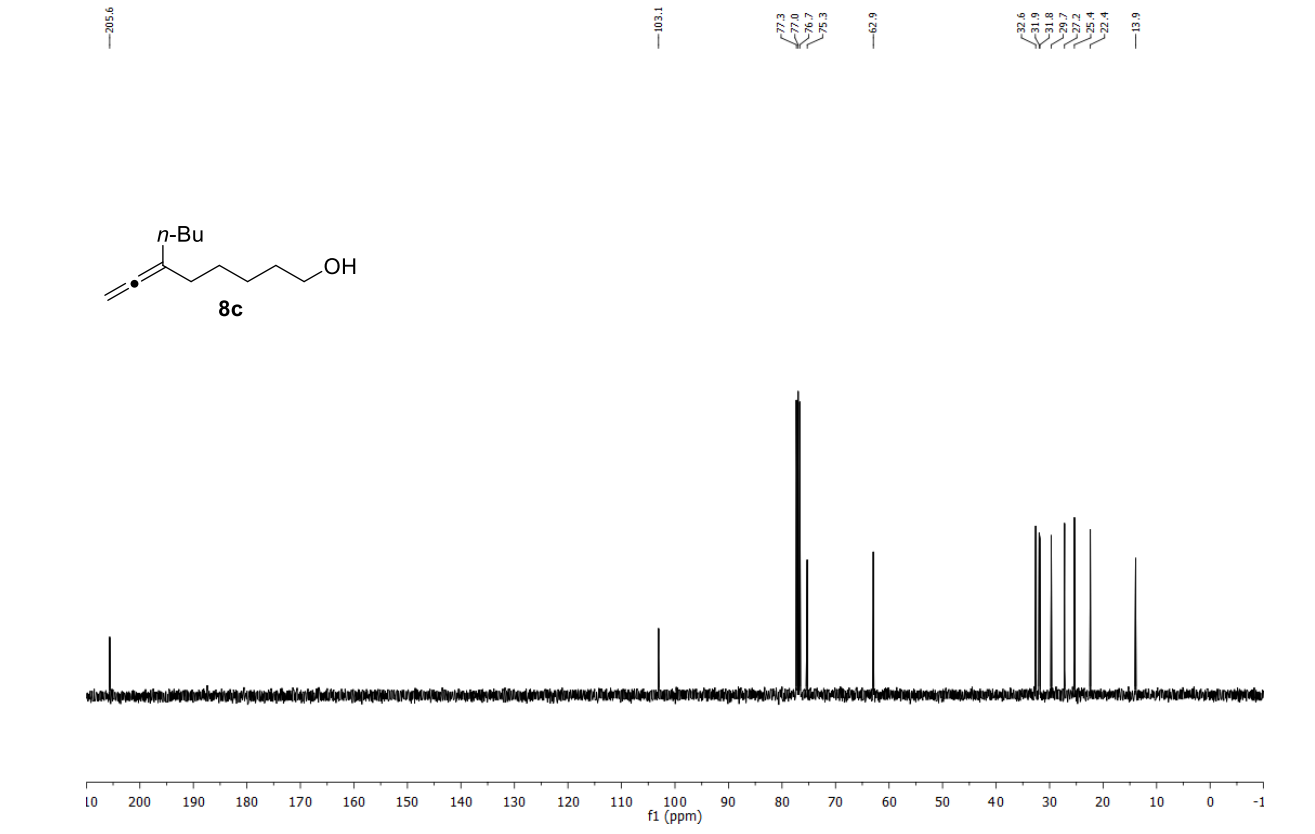

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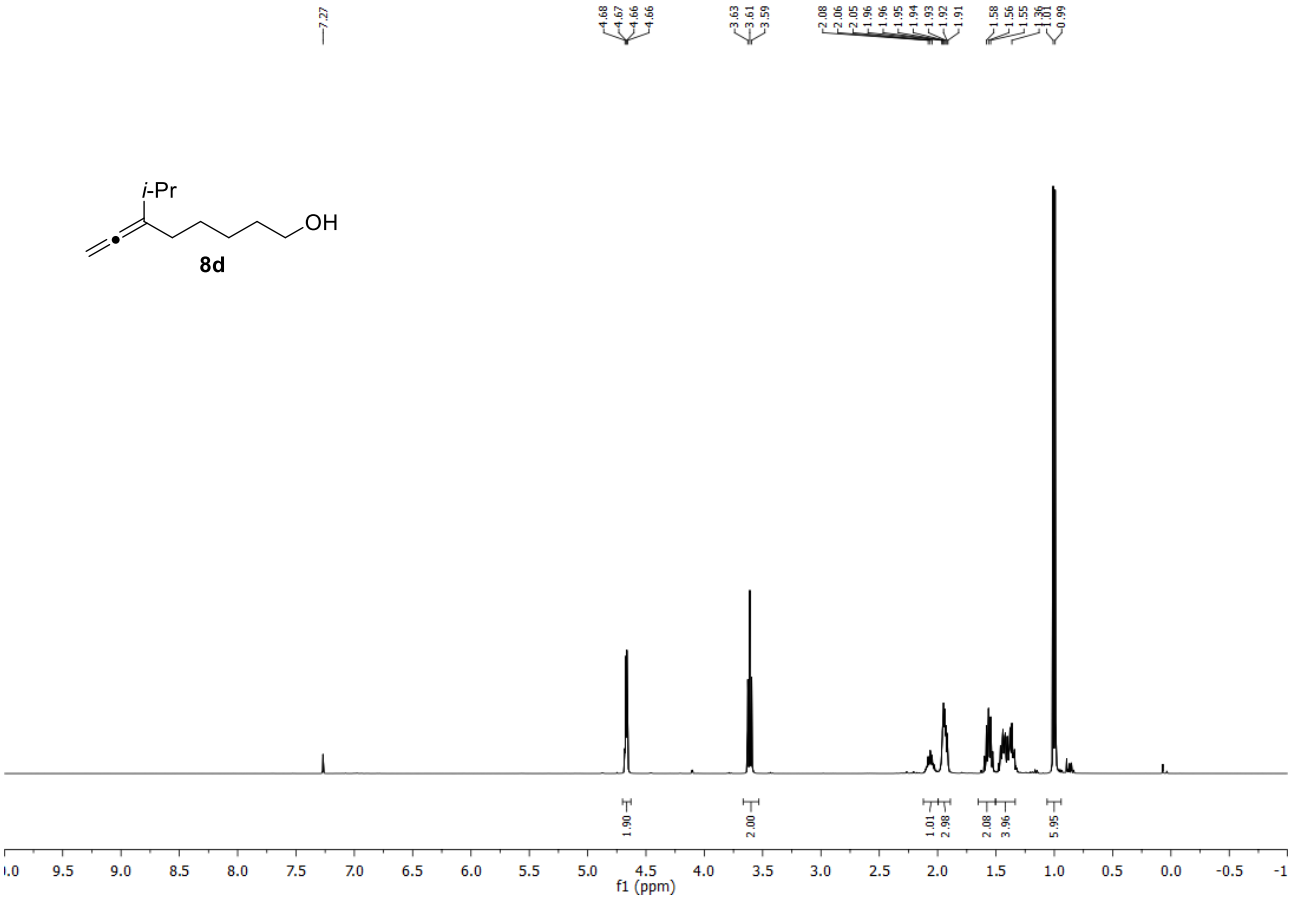

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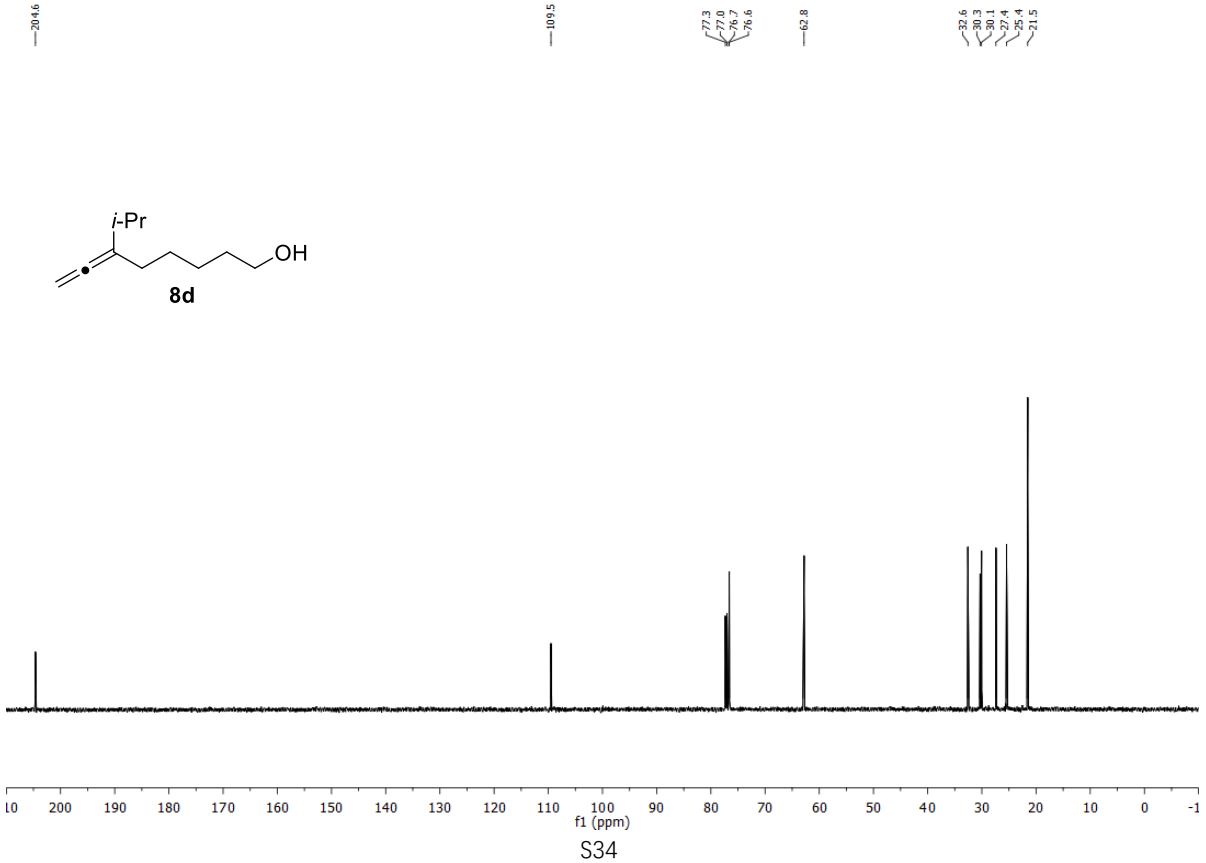

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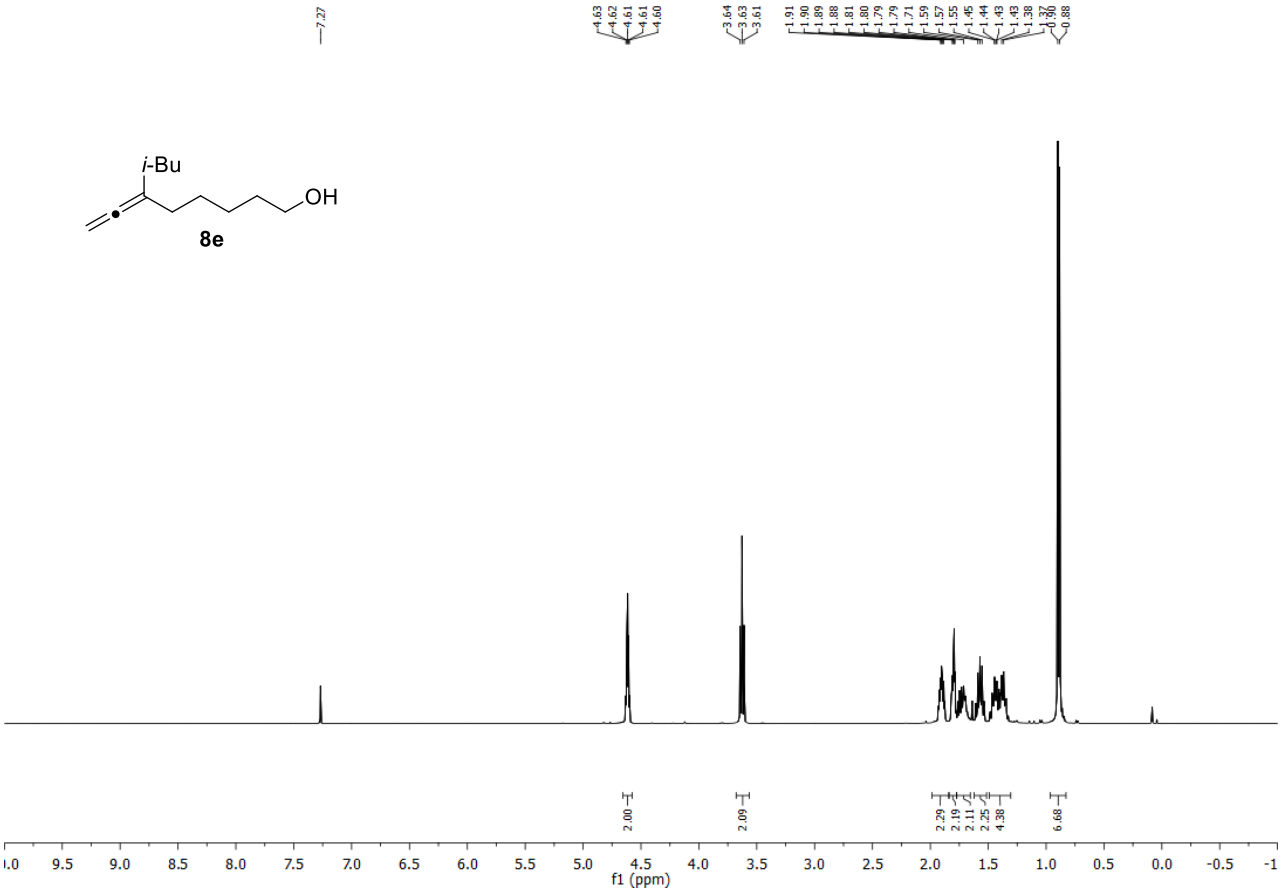

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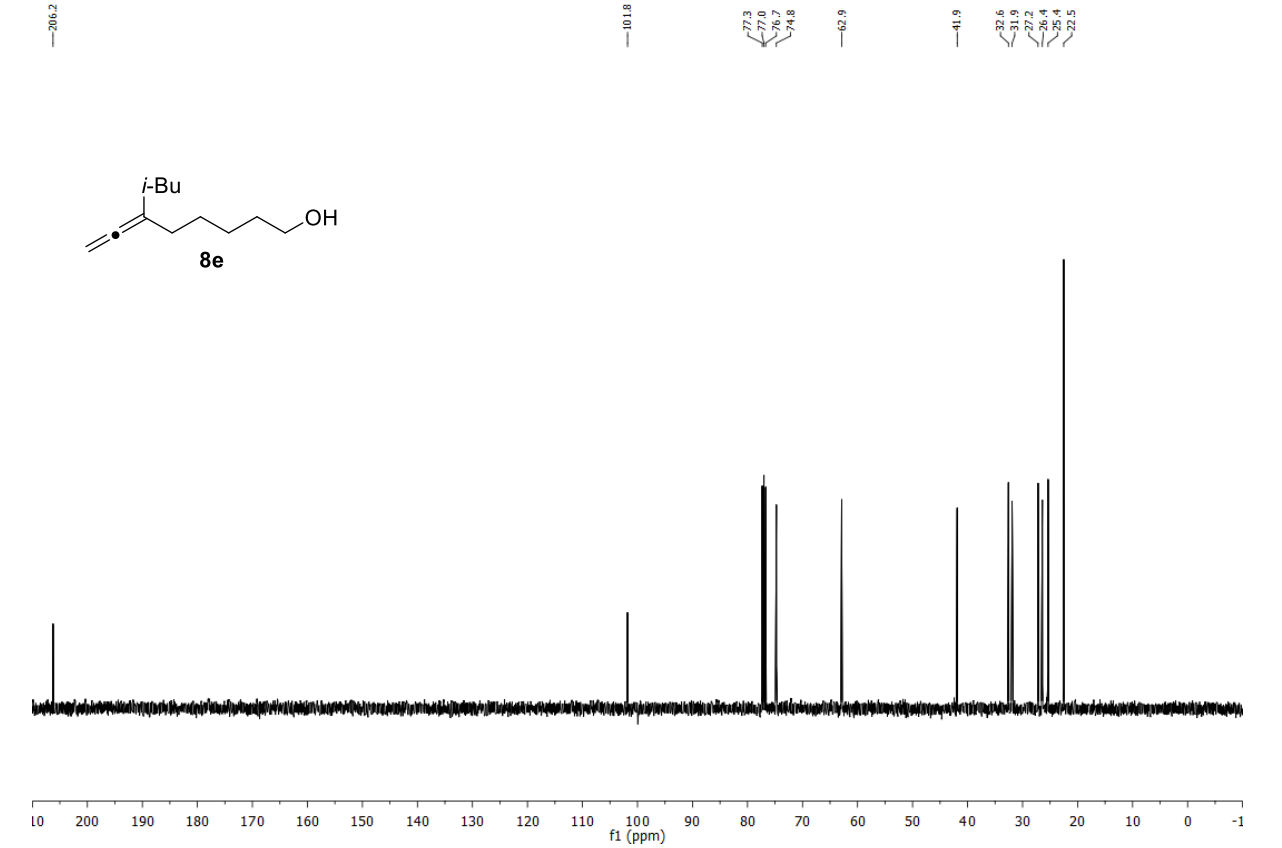
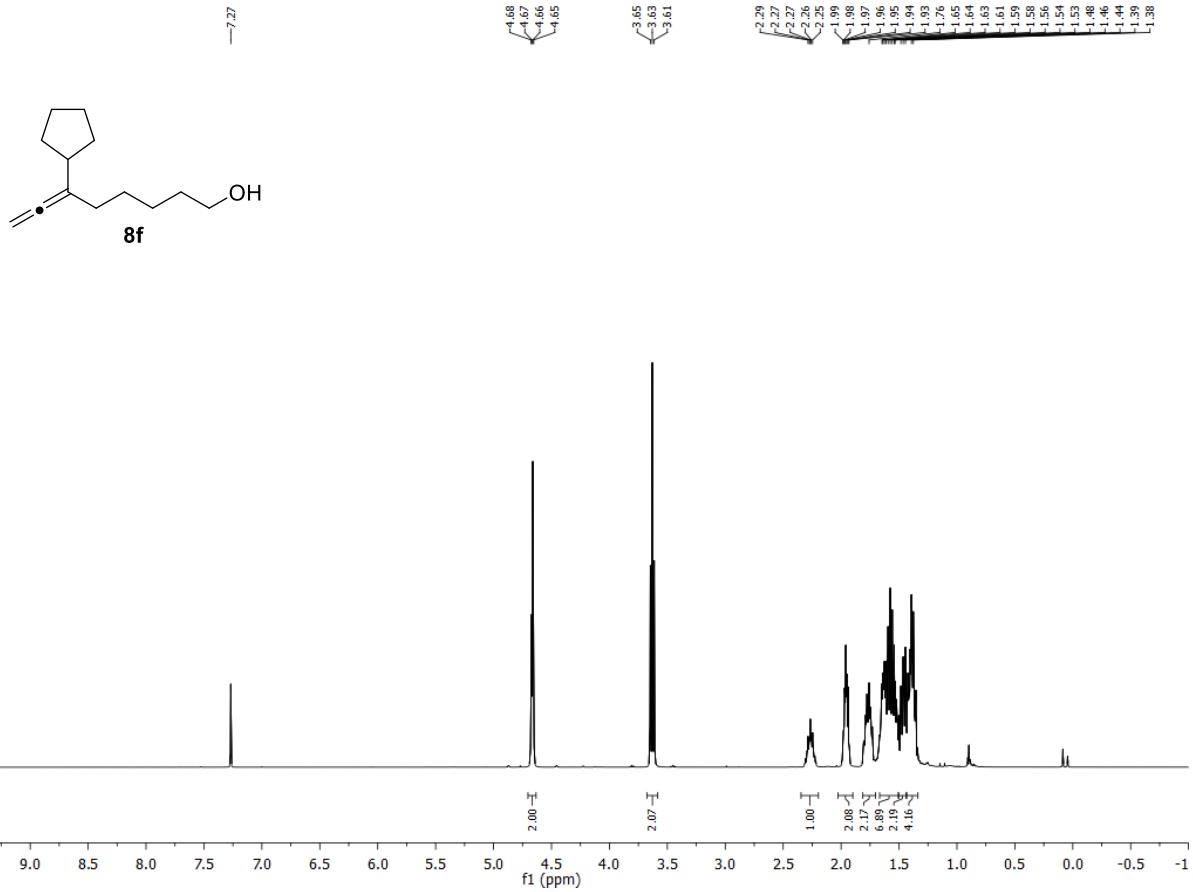


^{1}H NMR Spectra of **8f**



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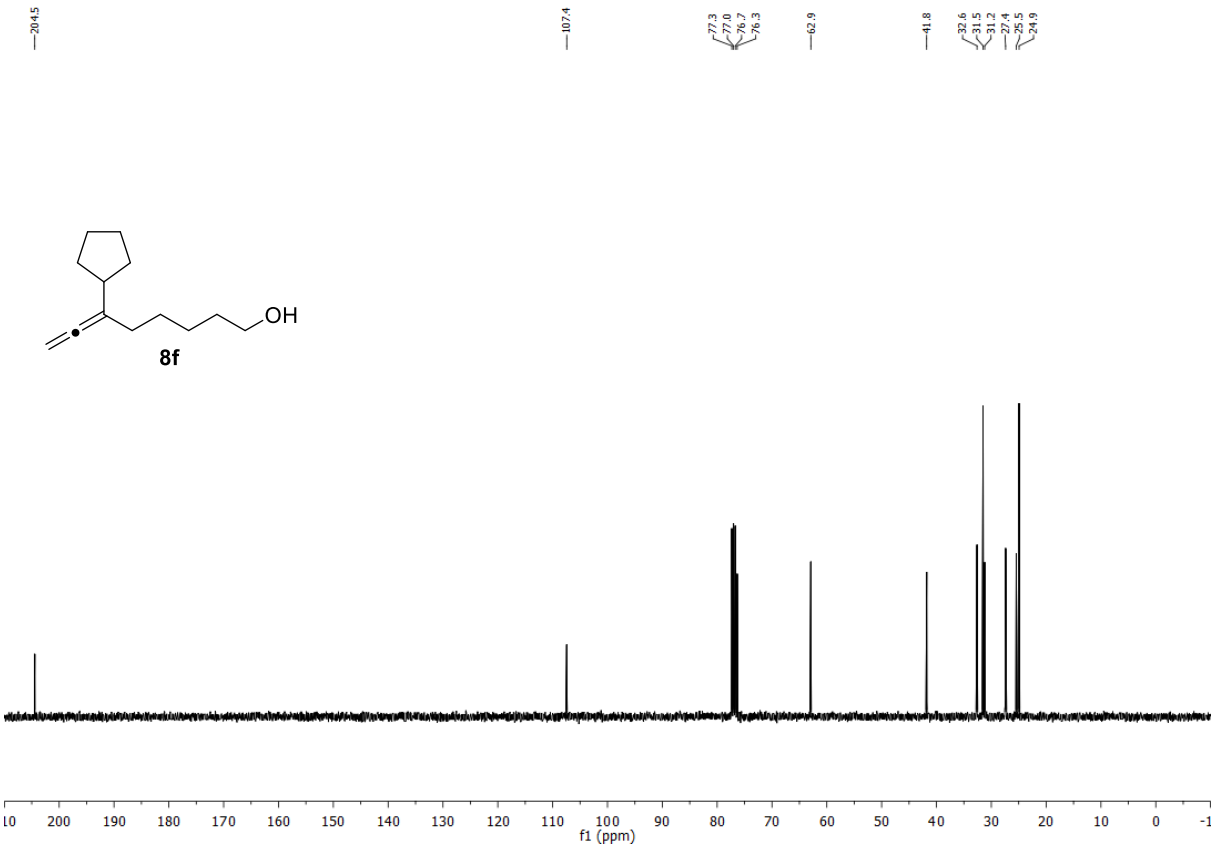

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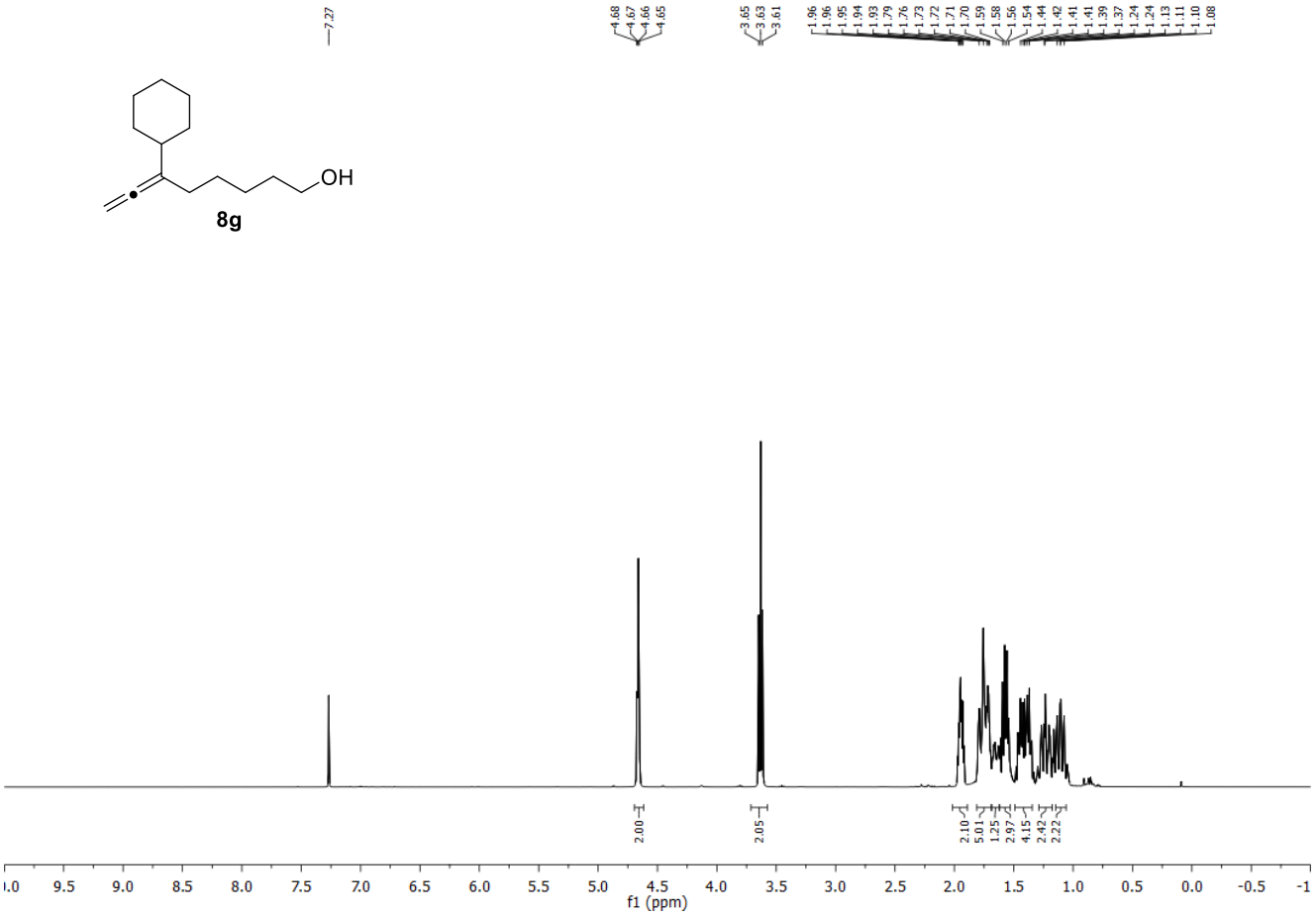

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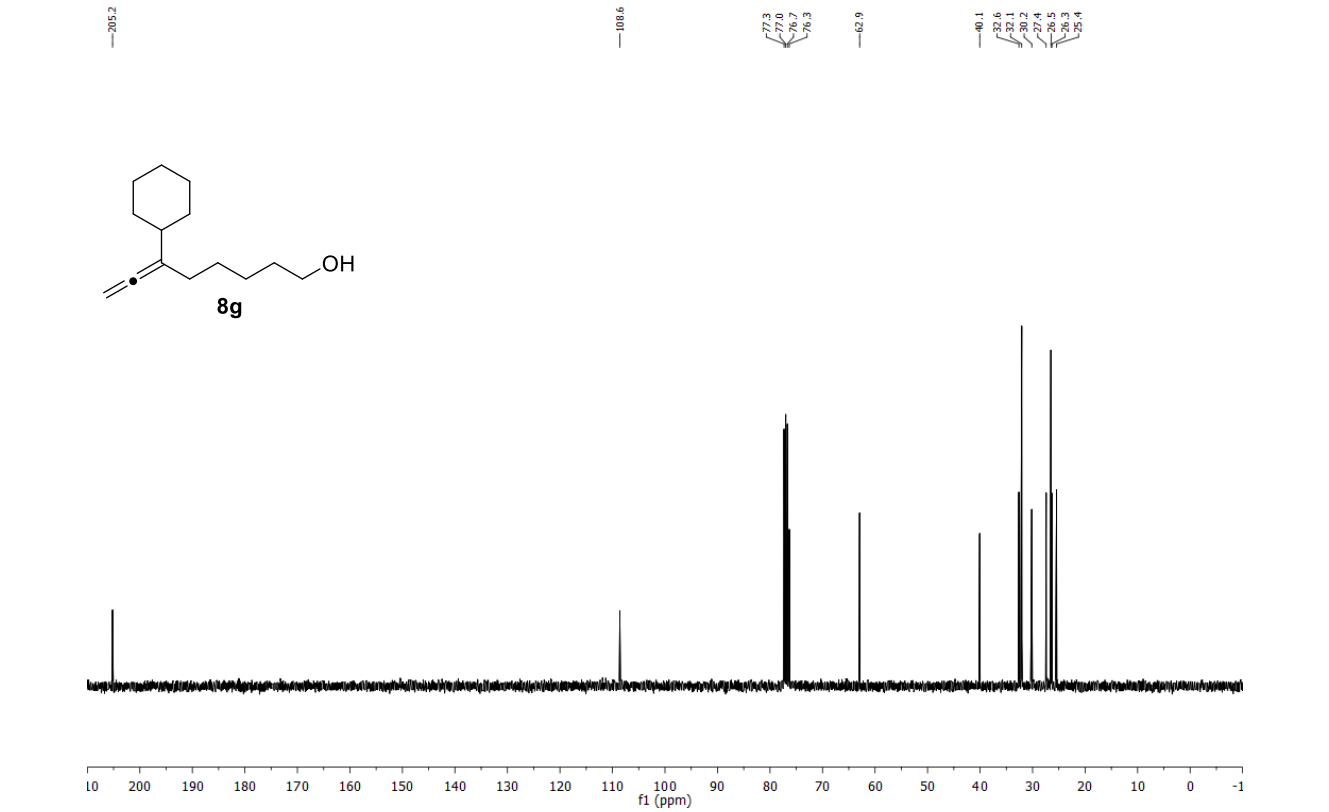

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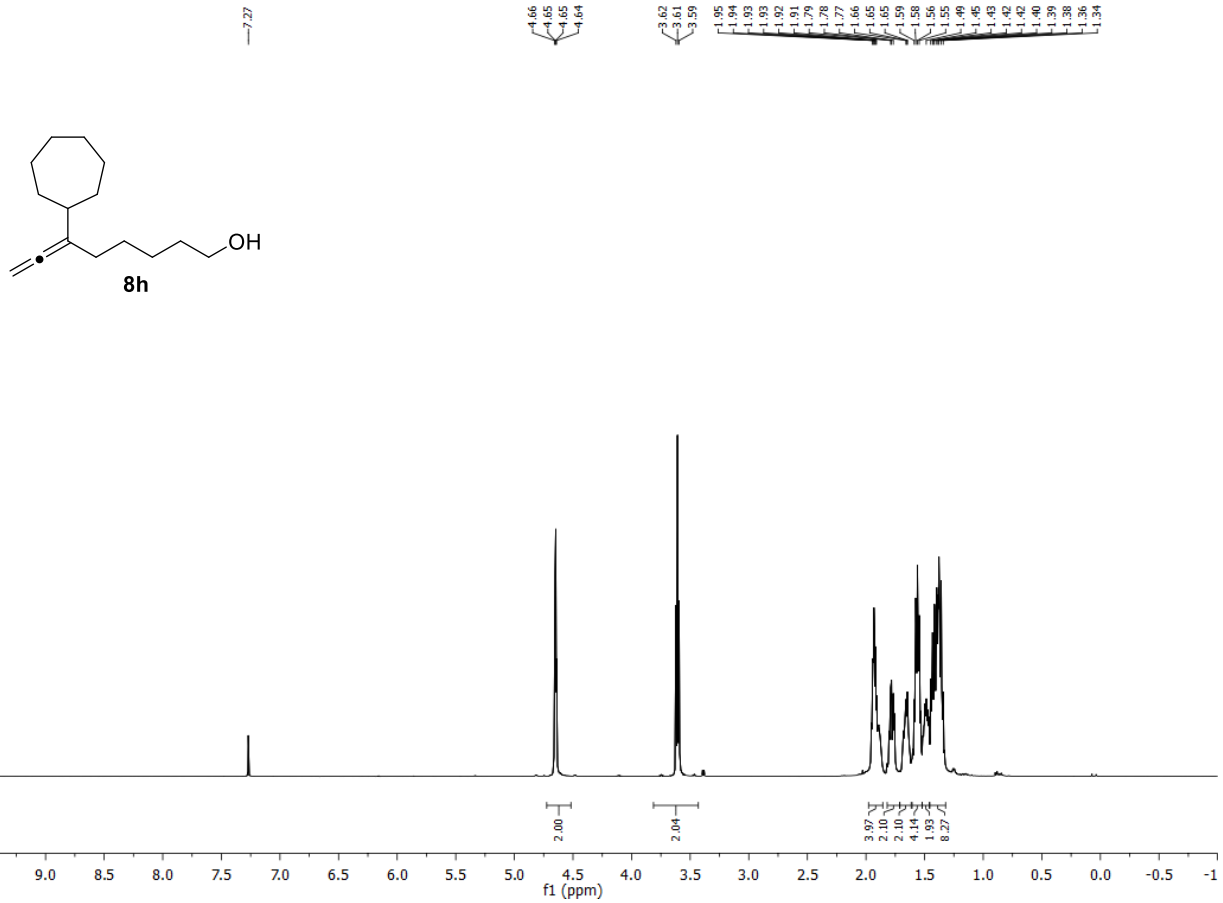
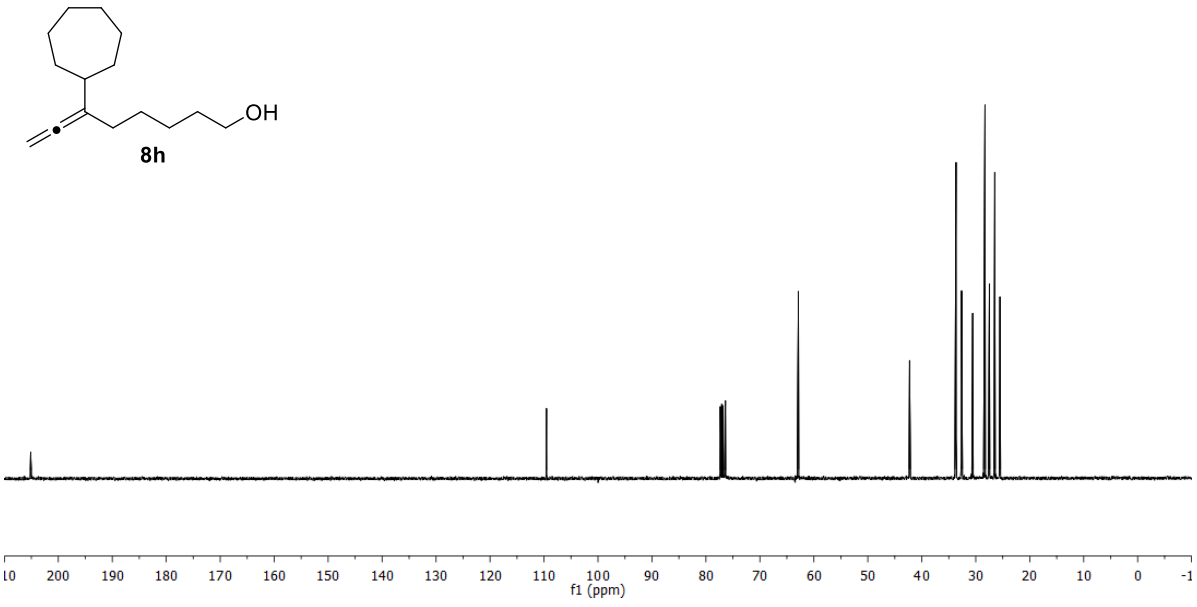
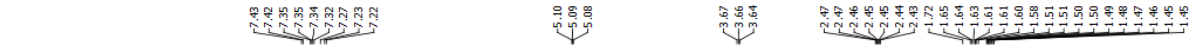
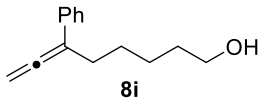


^{13}C NMR Spectra of **8h**



^{1}H NMR Spectra of **8i**





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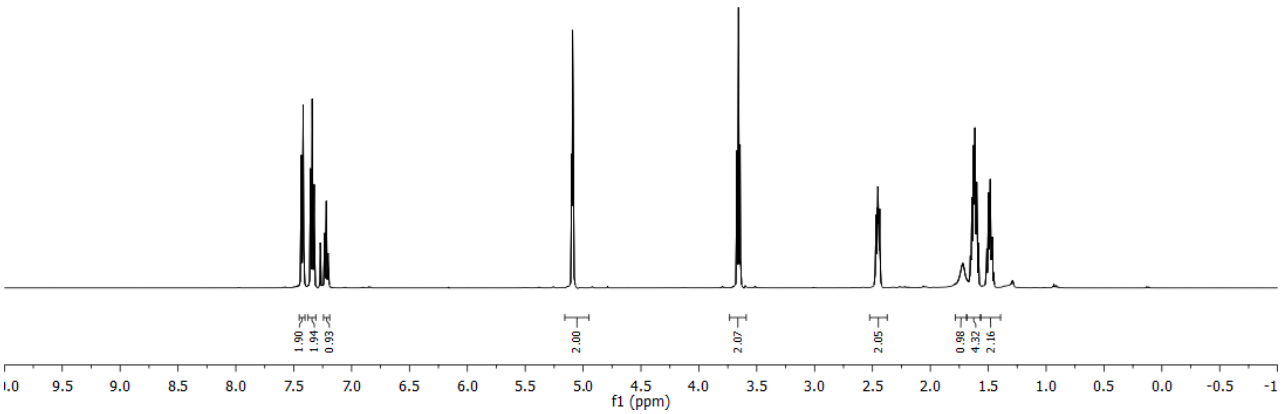

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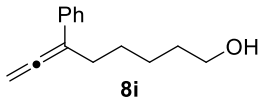

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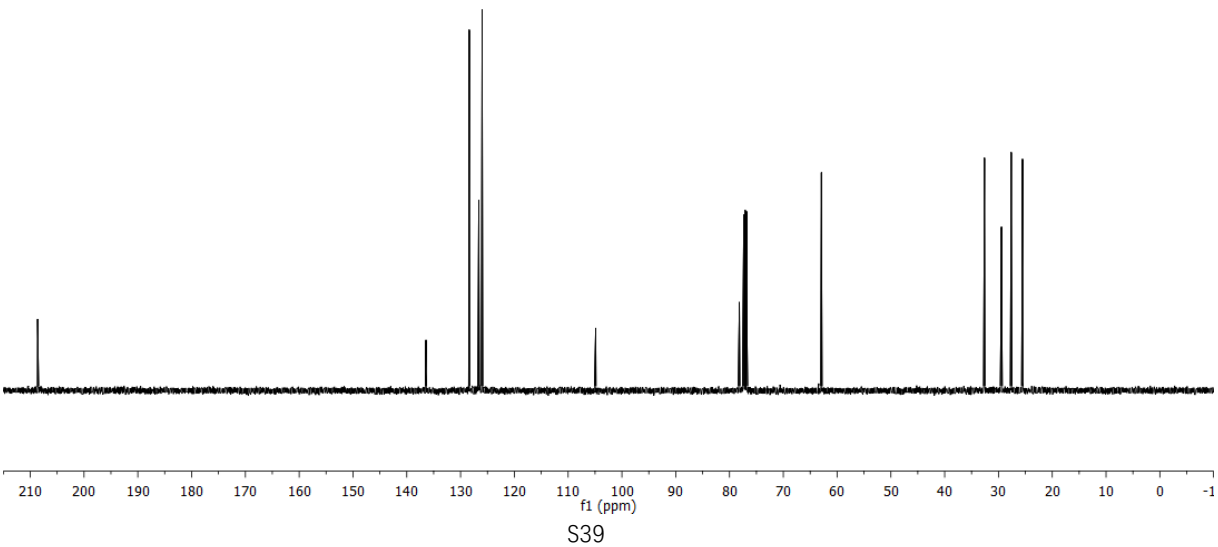

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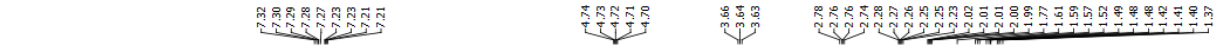
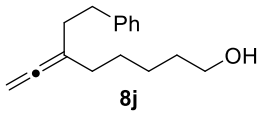
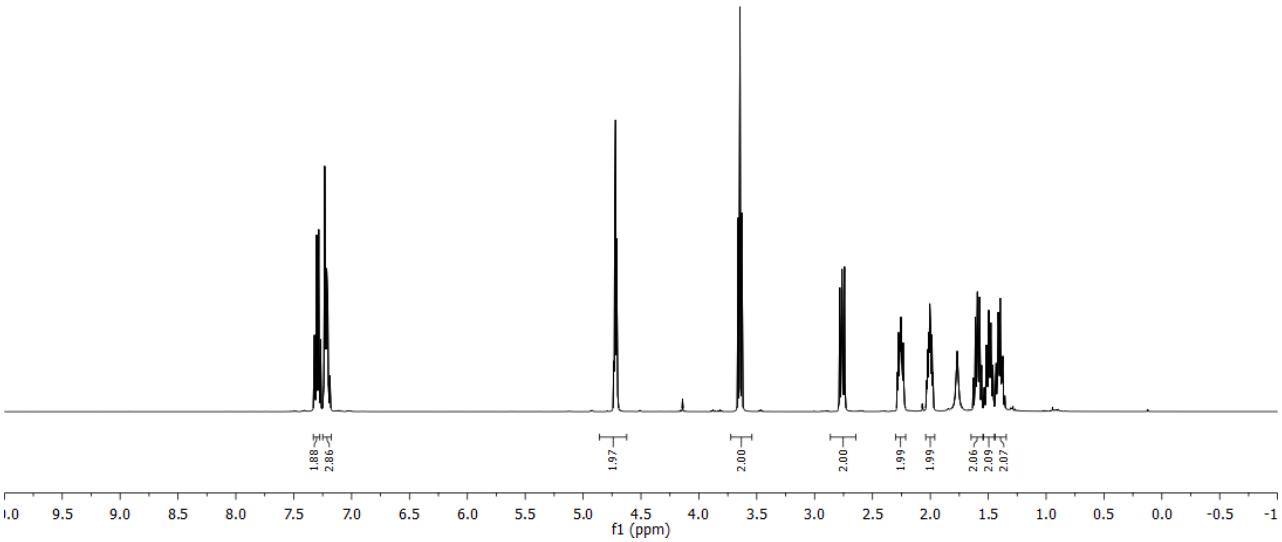




8j



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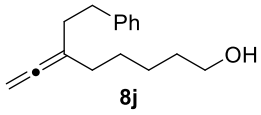
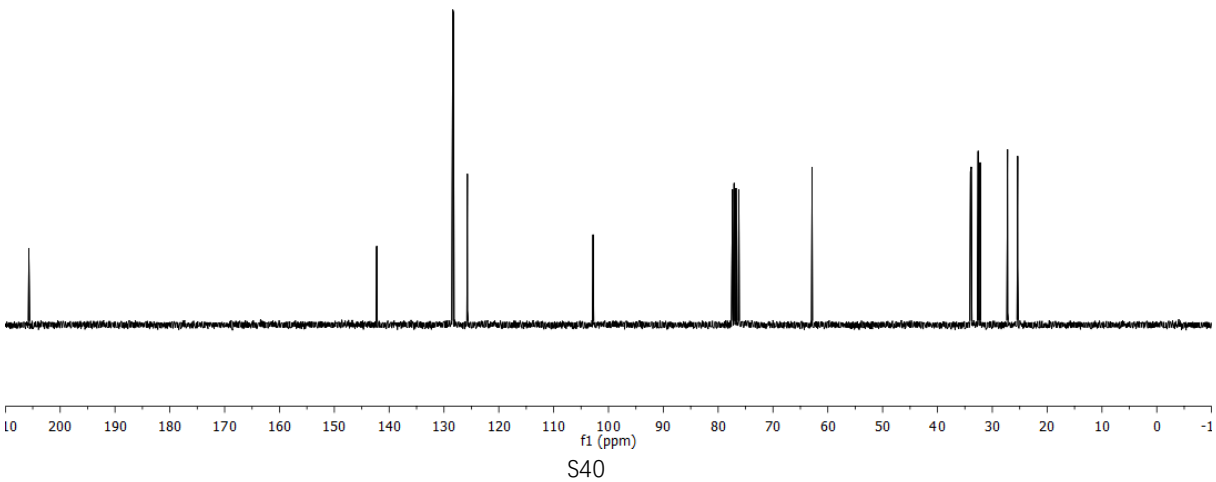


8j



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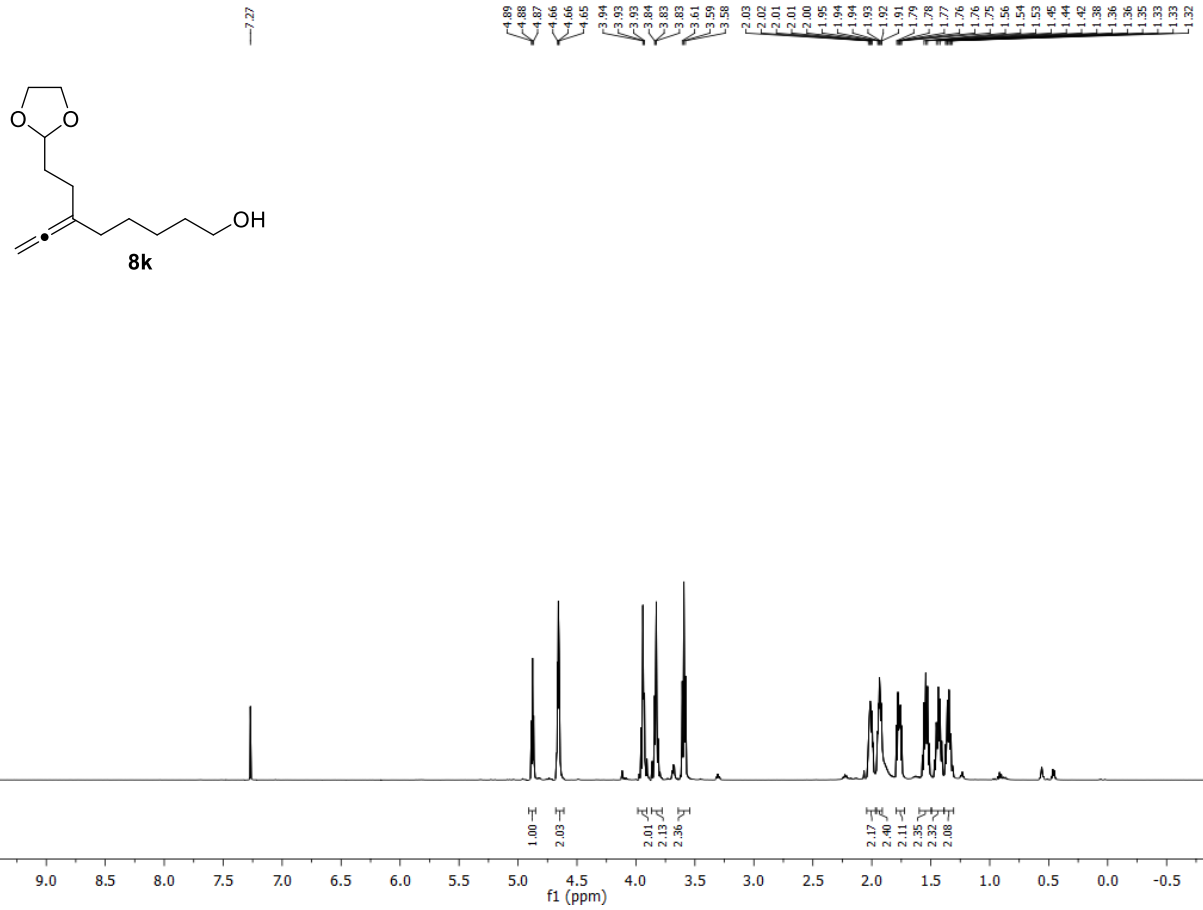

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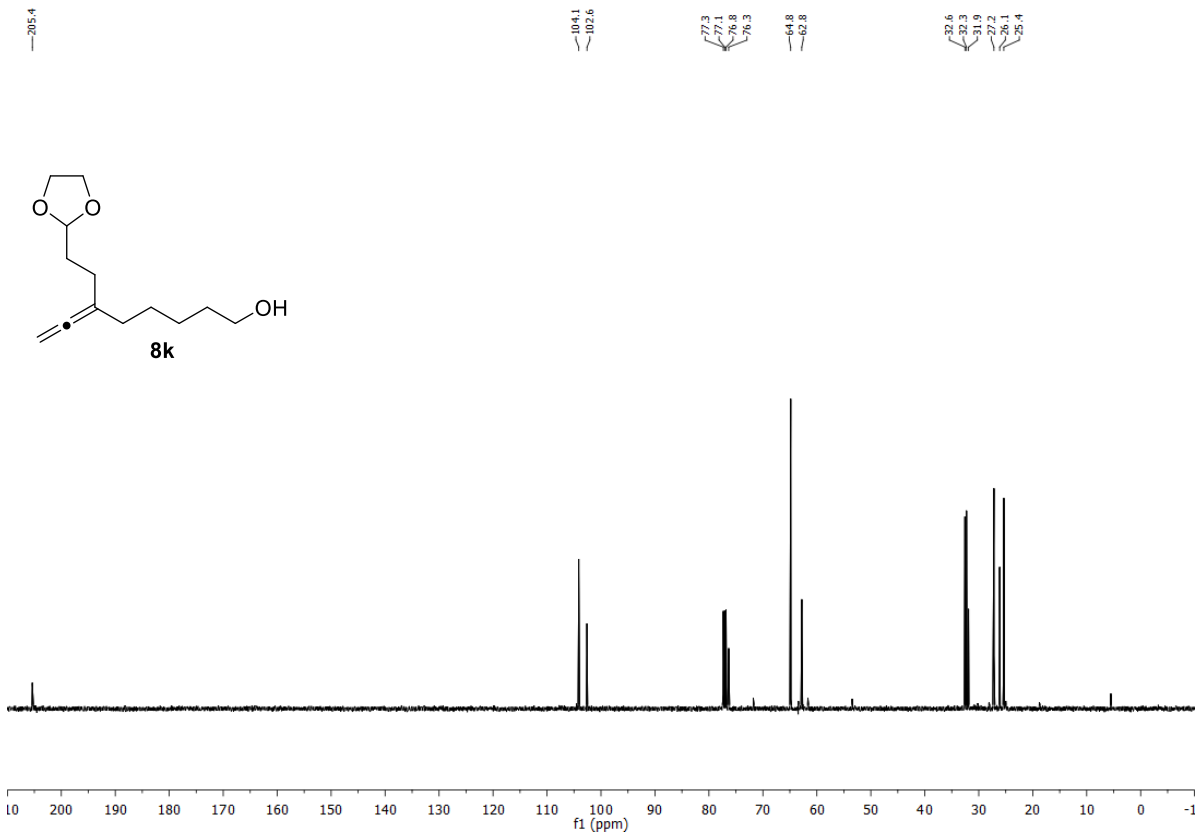

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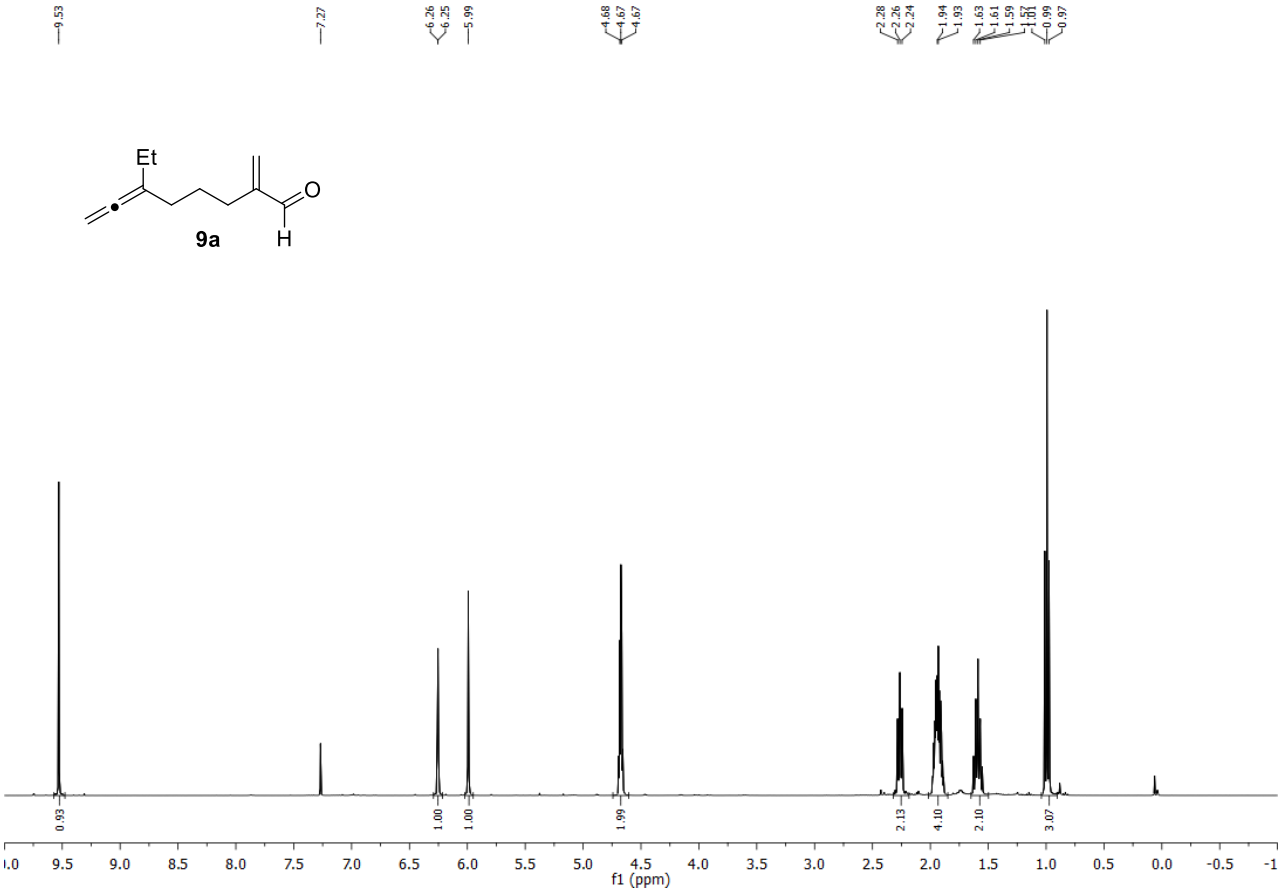
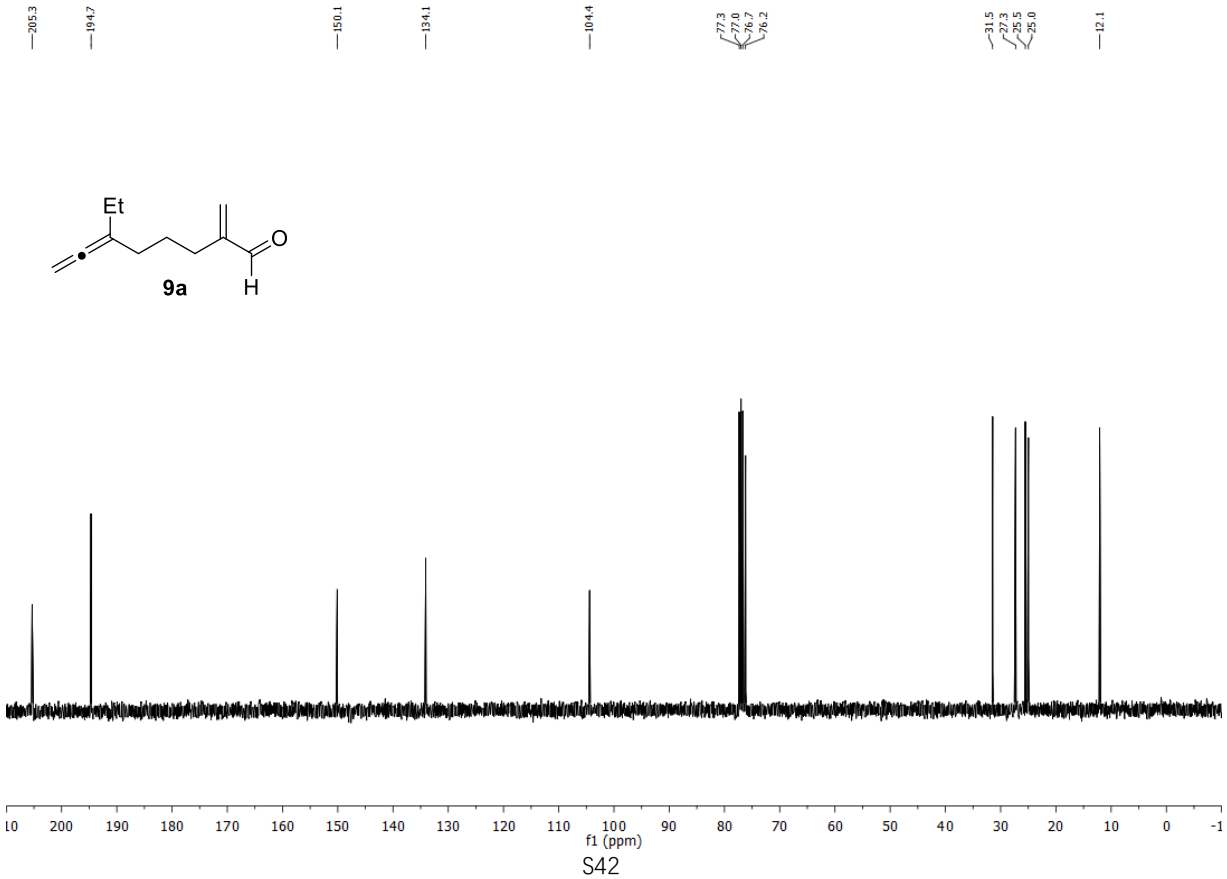


^{13}C NMR Spectra of **9a**



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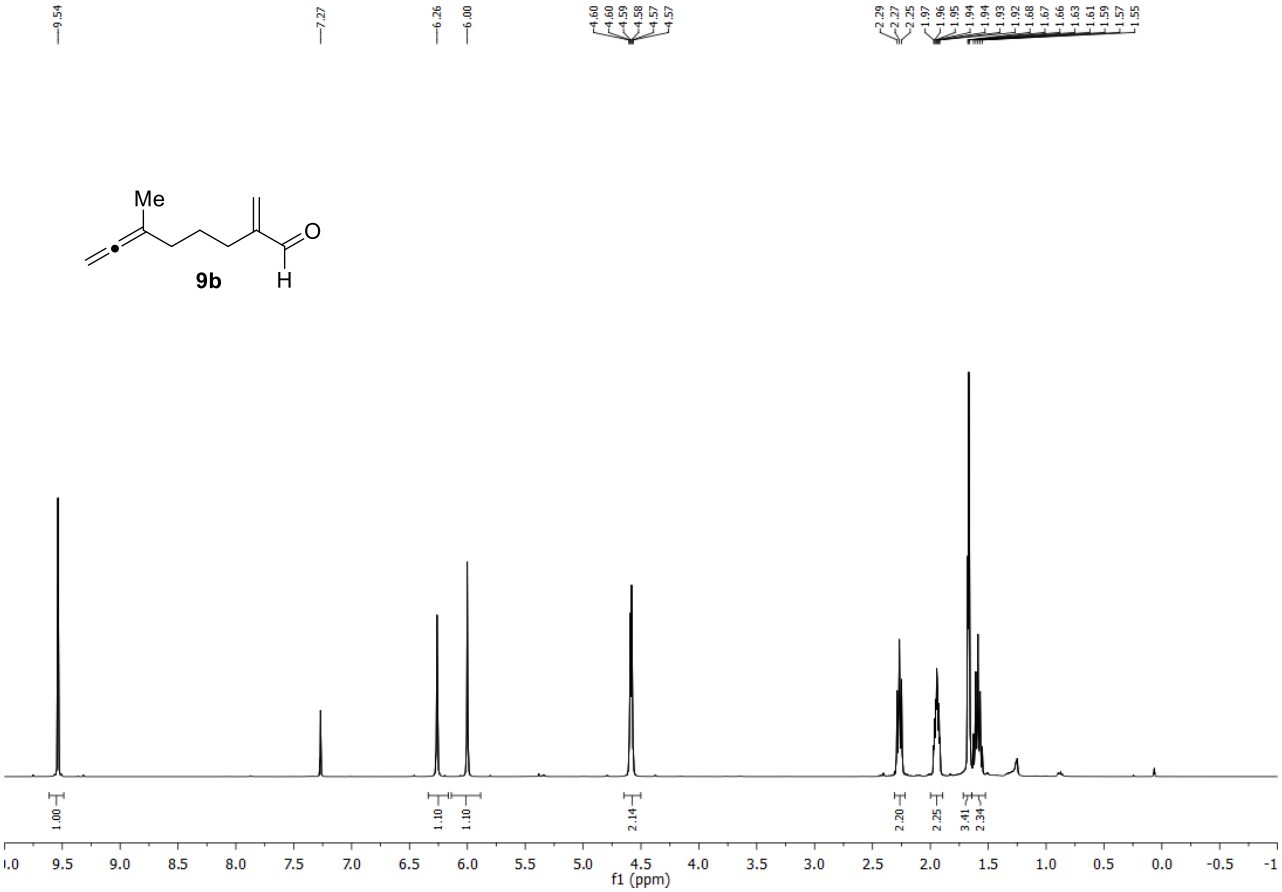
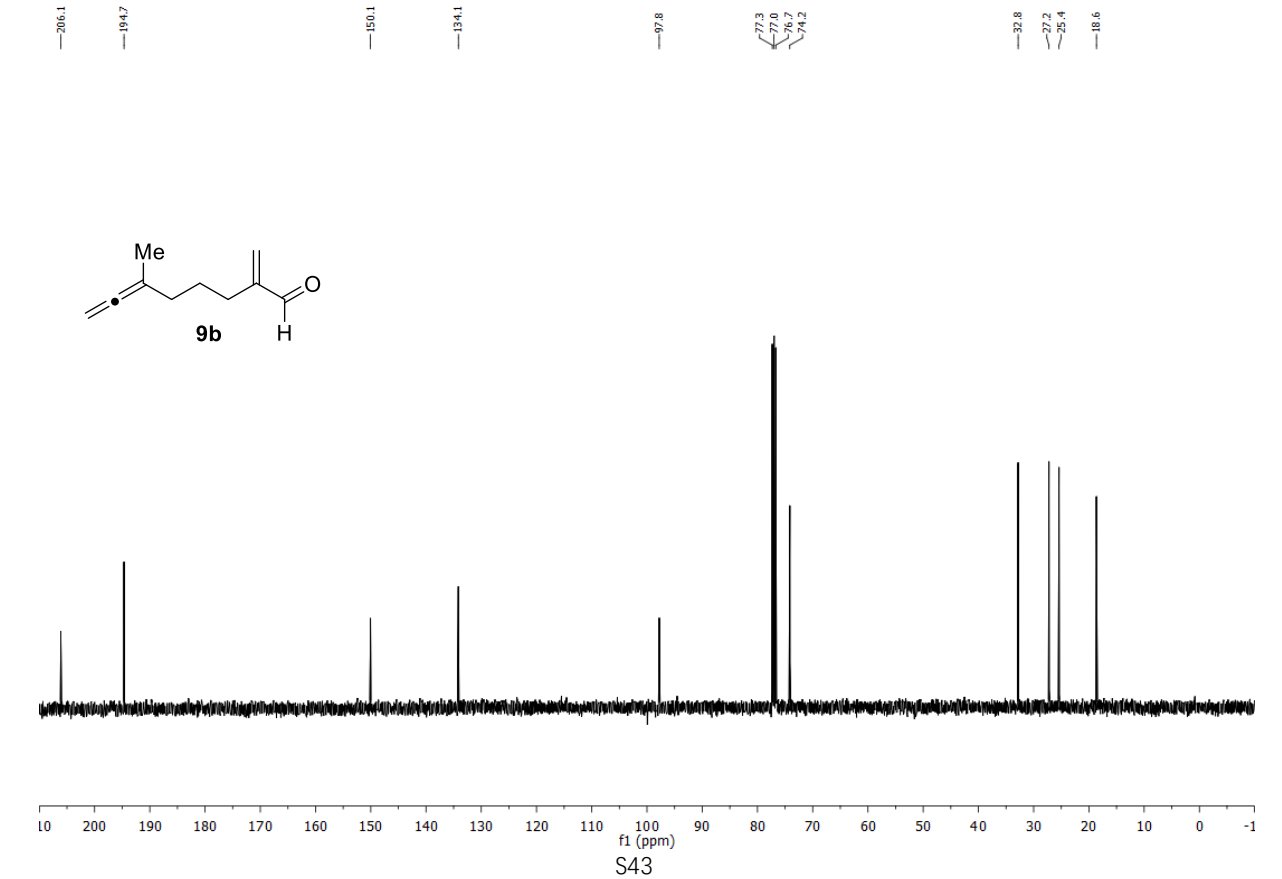
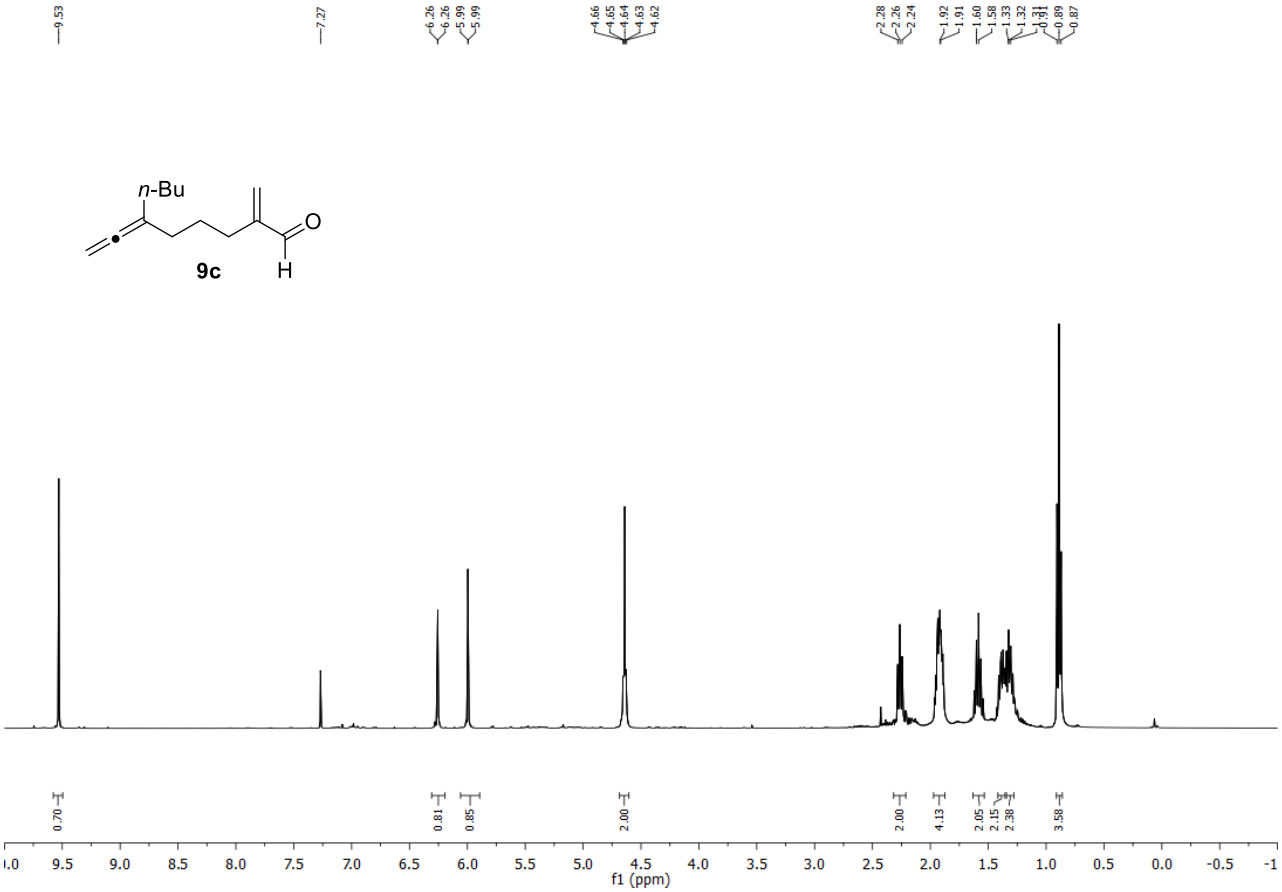


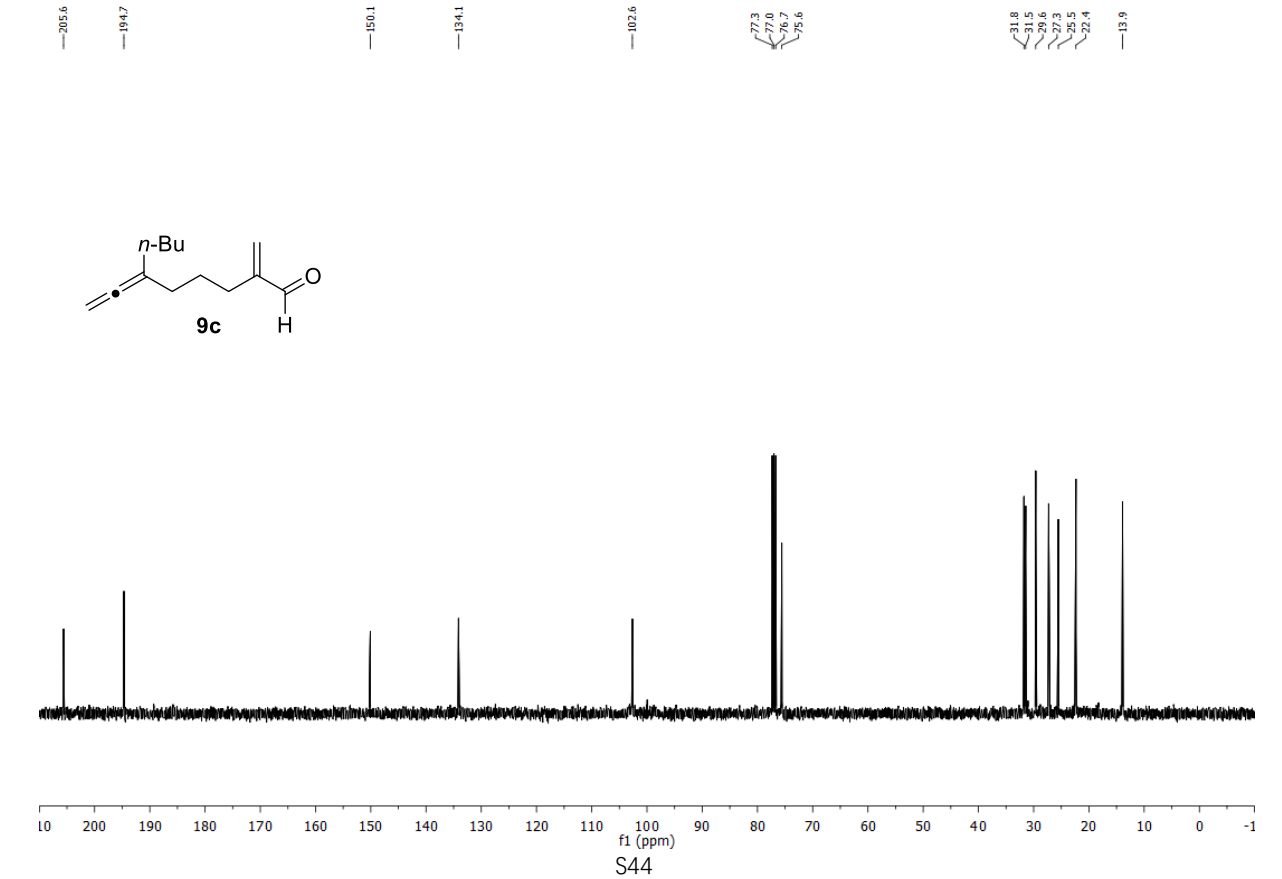
^{13}C NMR Spectra of **9b**



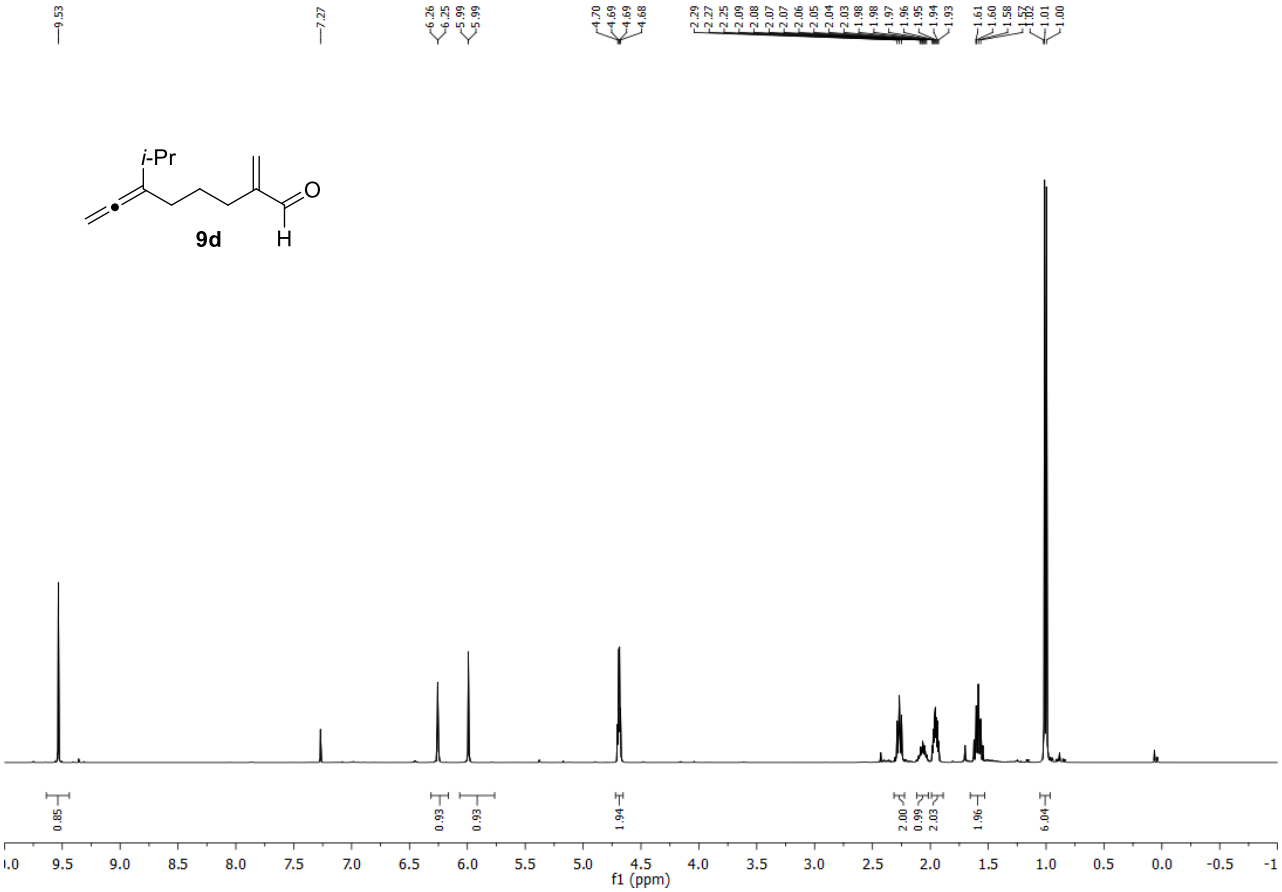
^{1}H NMR Spectra of **9c**



^{13}C NMR Spectra of **9c**



^{1}H NMR Spectra of **9d**



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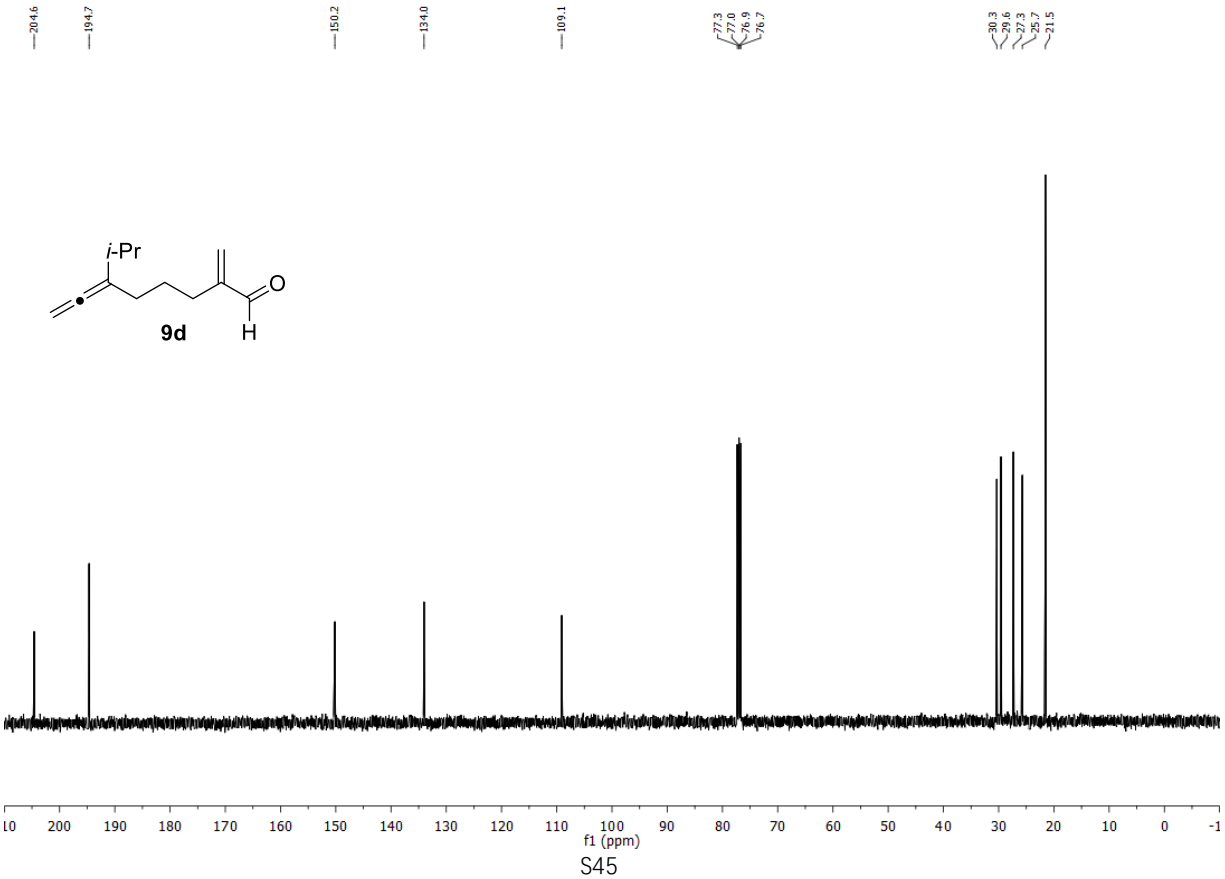
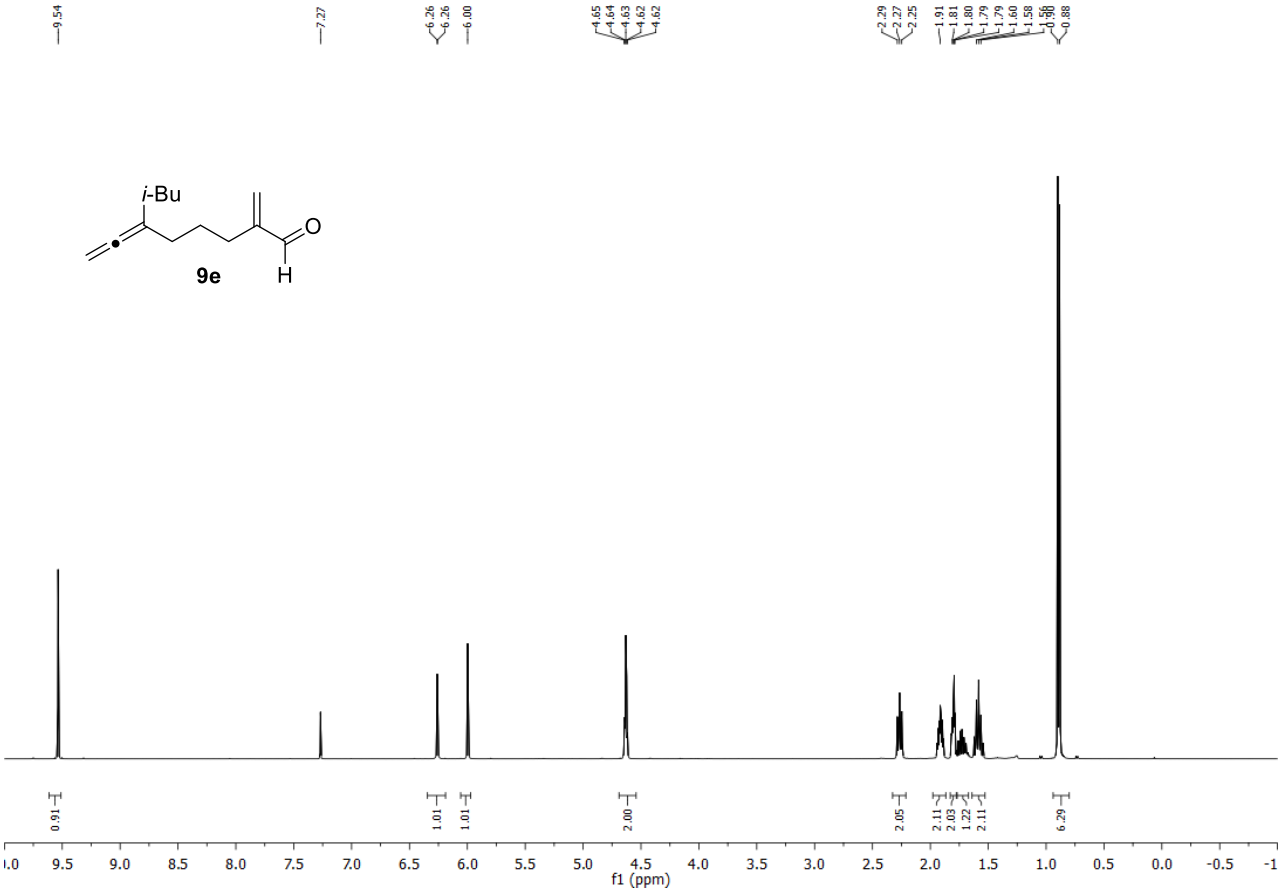
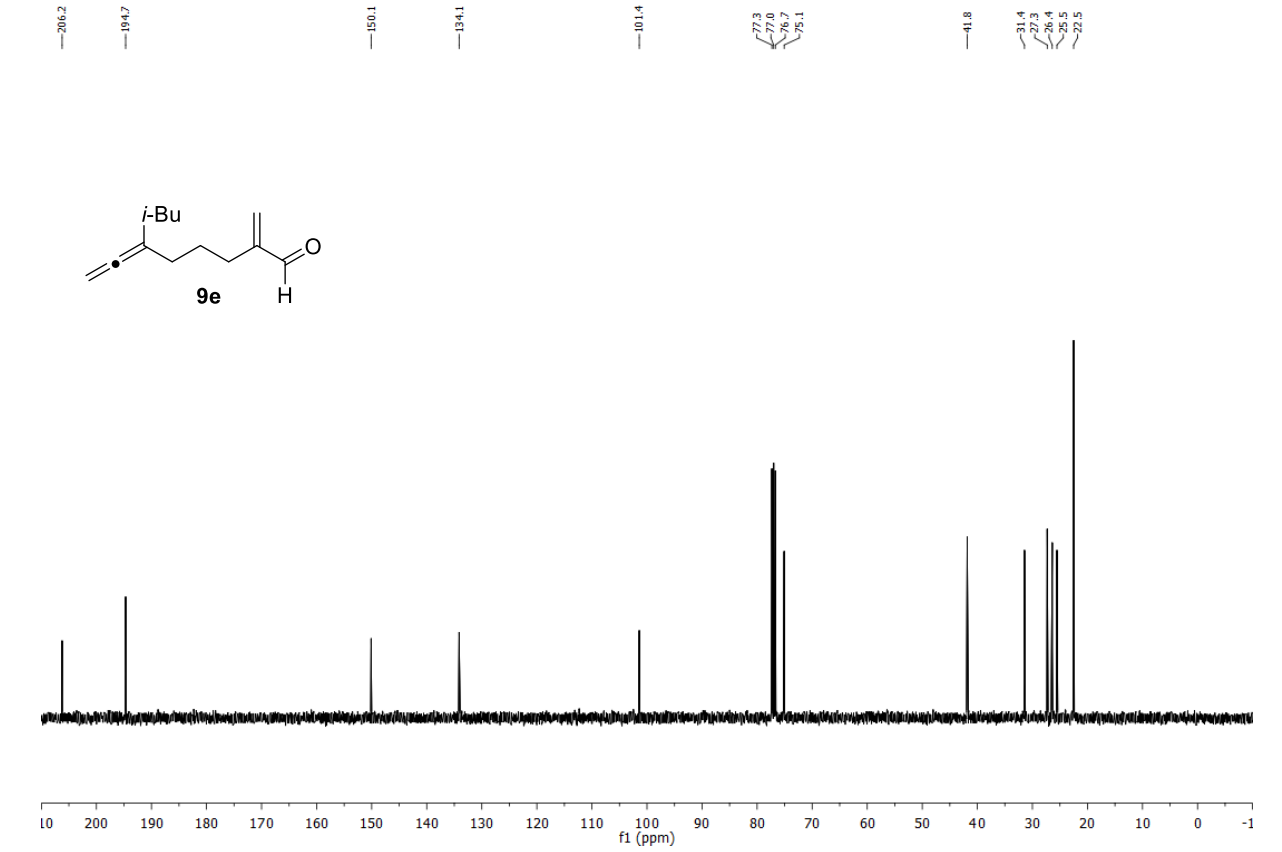


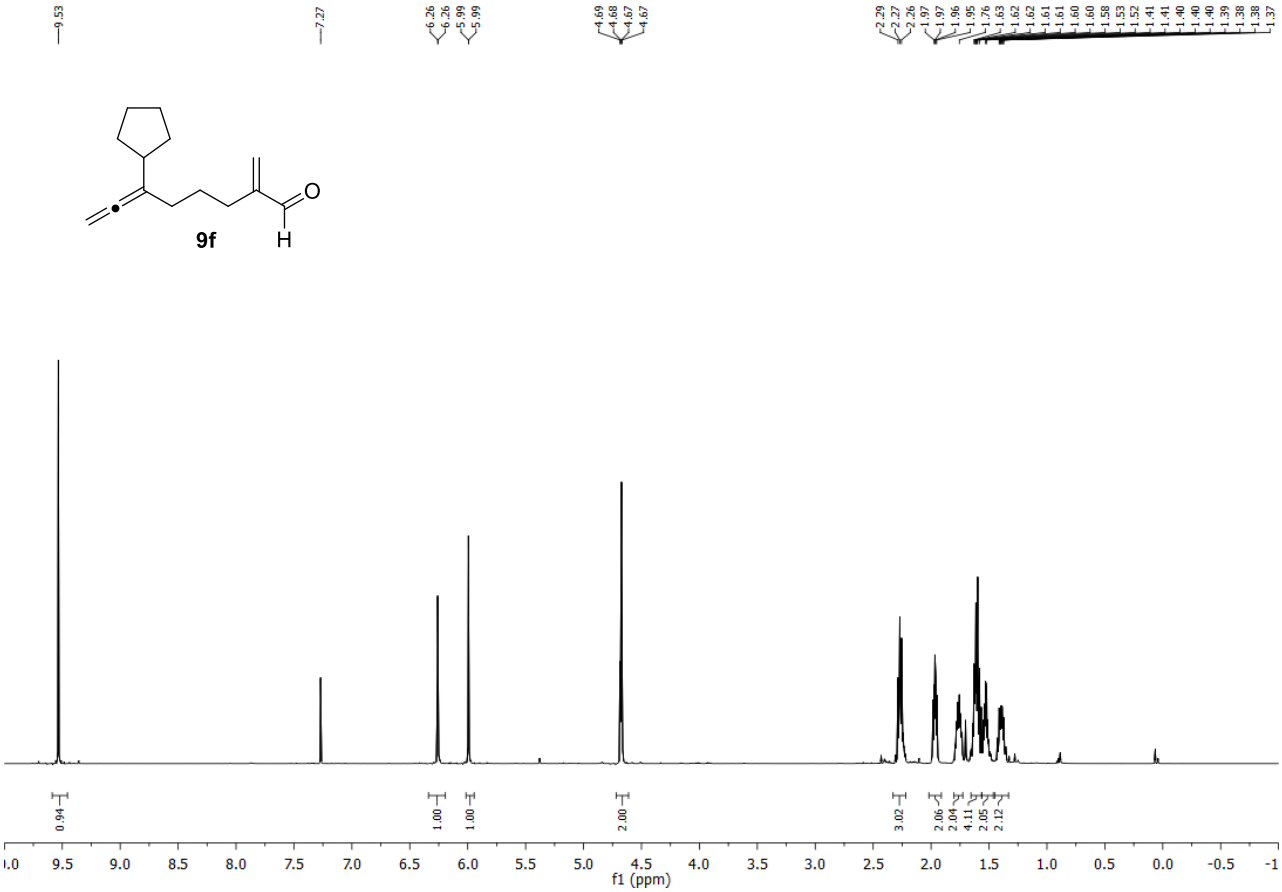
^{1}H NMR Spectra of **9e**



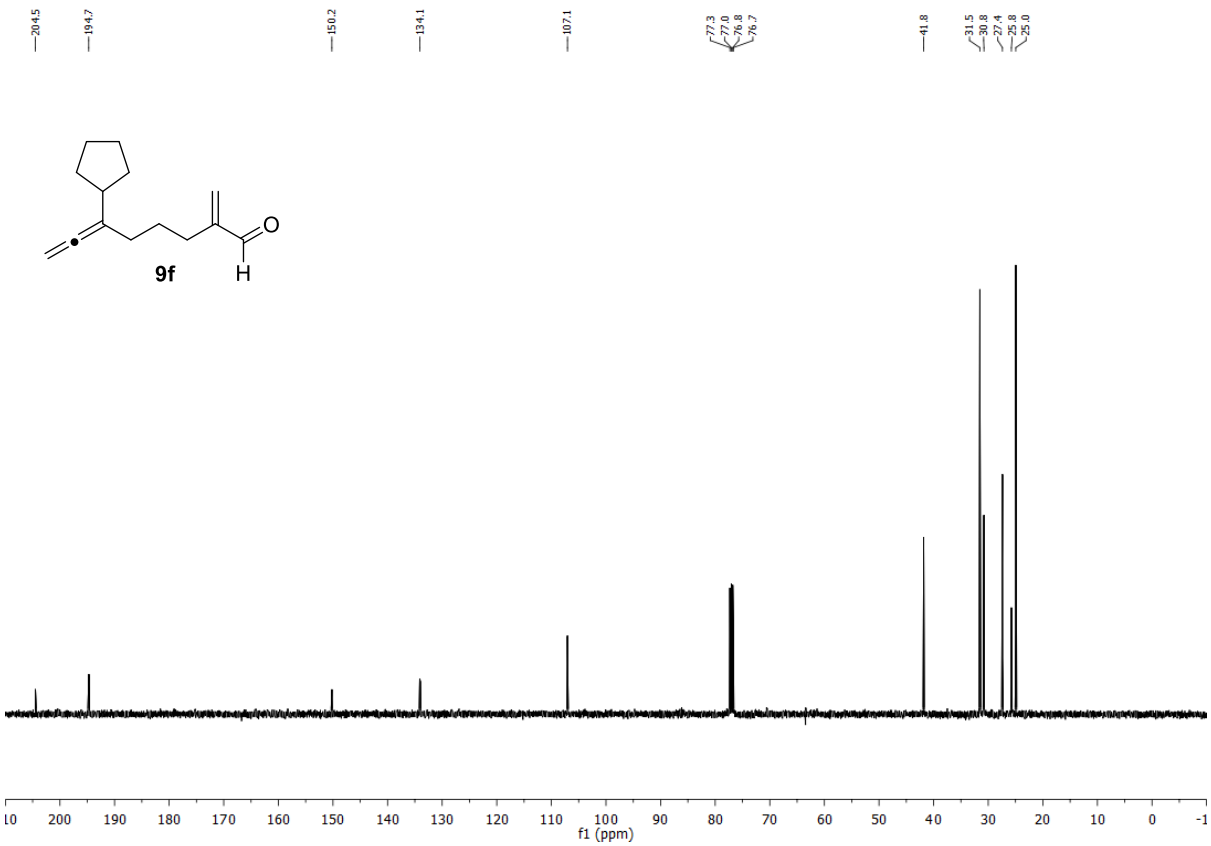
^{13}C NMR Spectra of **9e**



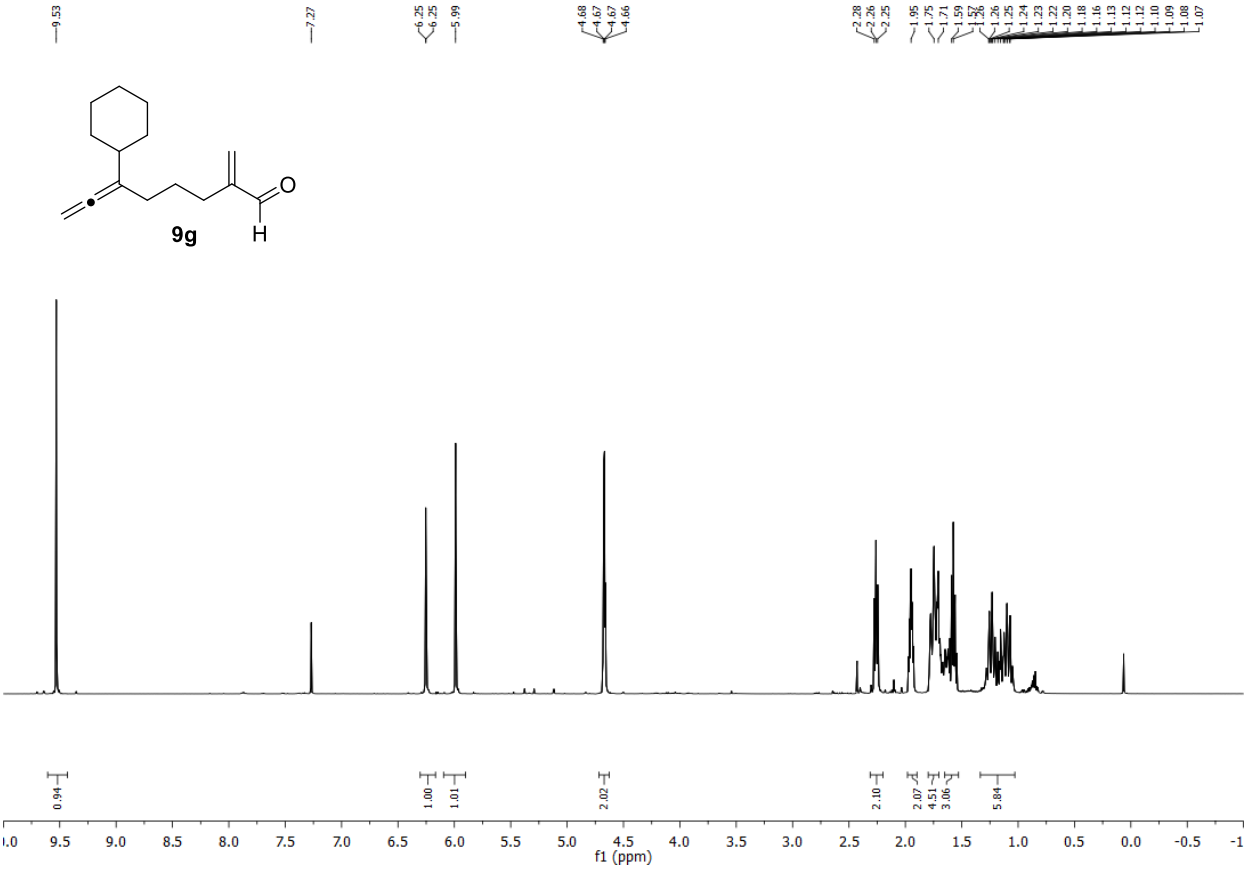
^{1}H NMR Spectra of **9f**



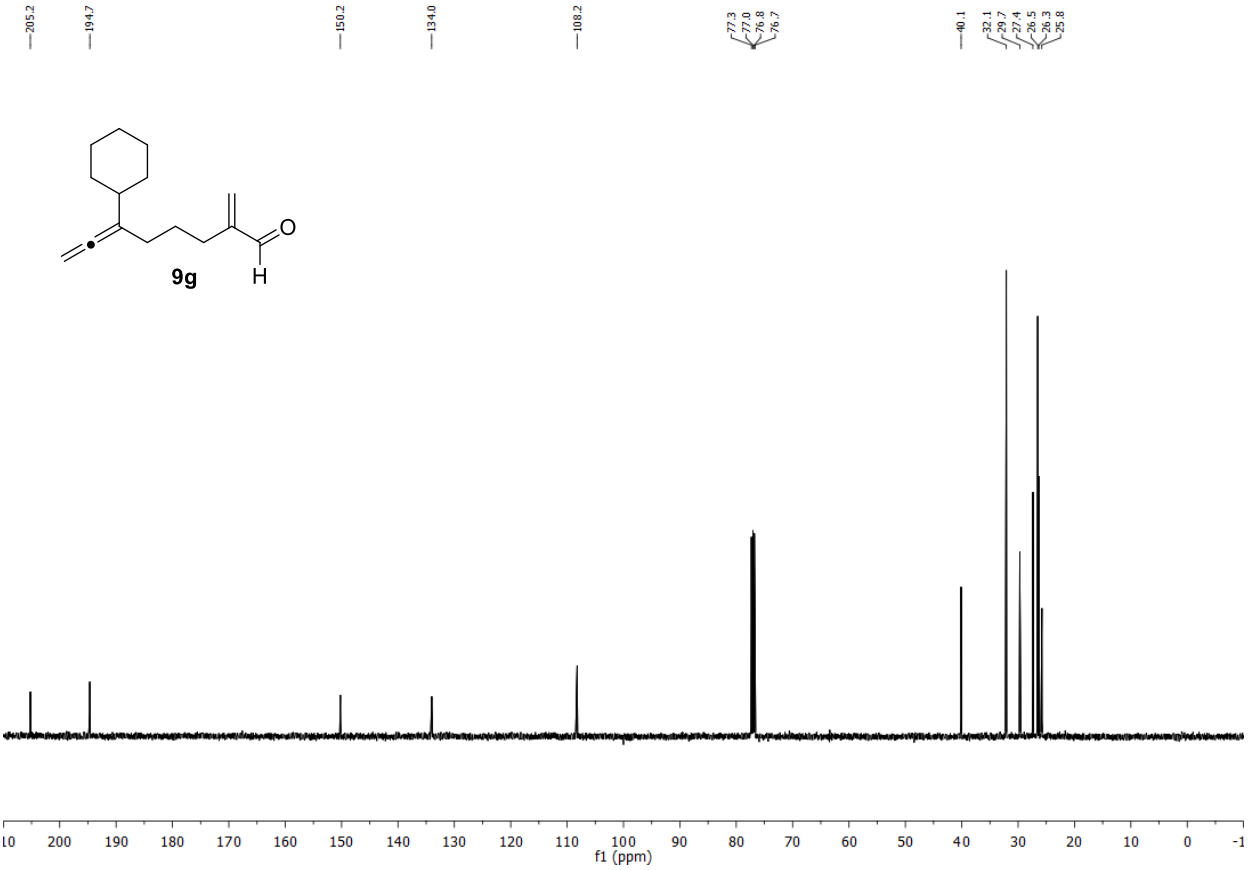
^{13}C NMR Spectra of **9f**



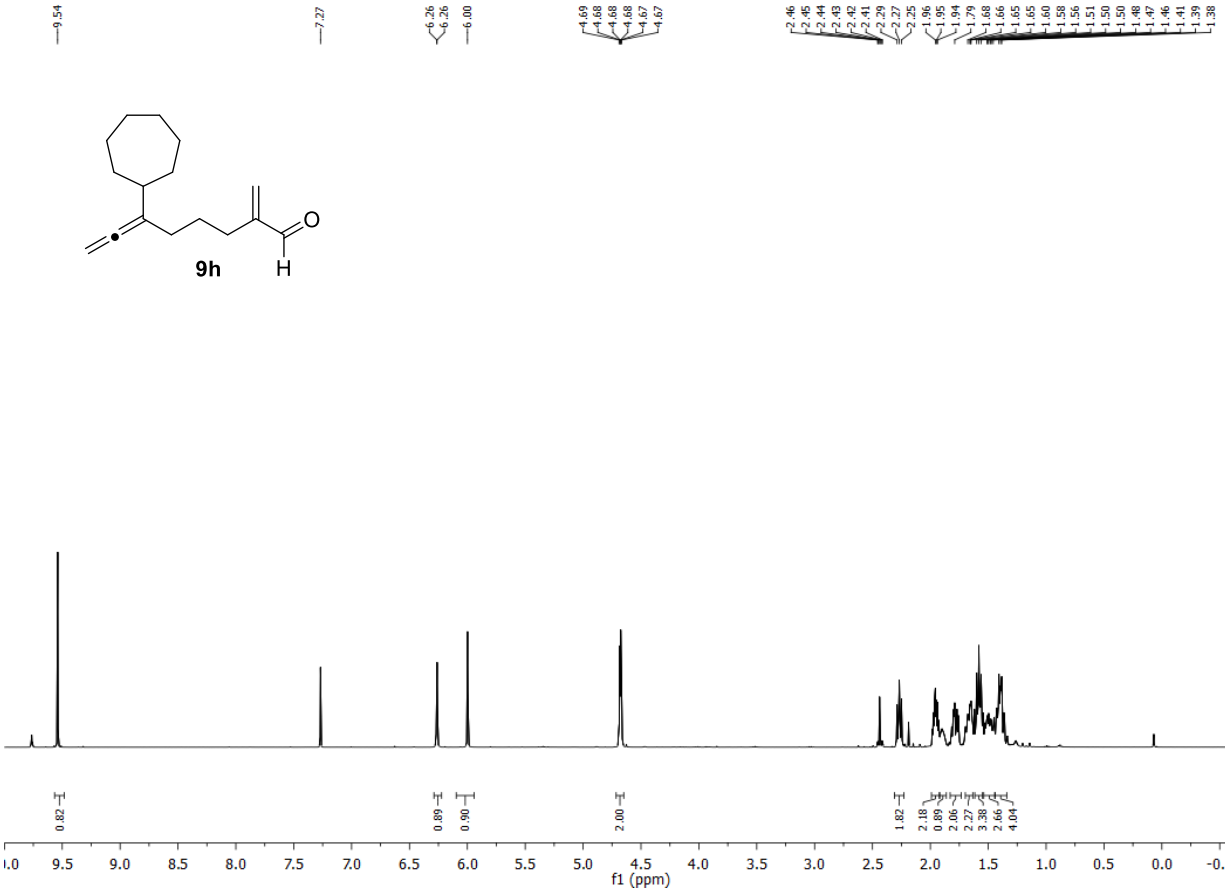
^{1}H NMR Spectra of **9g**



^{13}C NMR Spectra of **9g**



^{1}H NMR Spectra of **9h**



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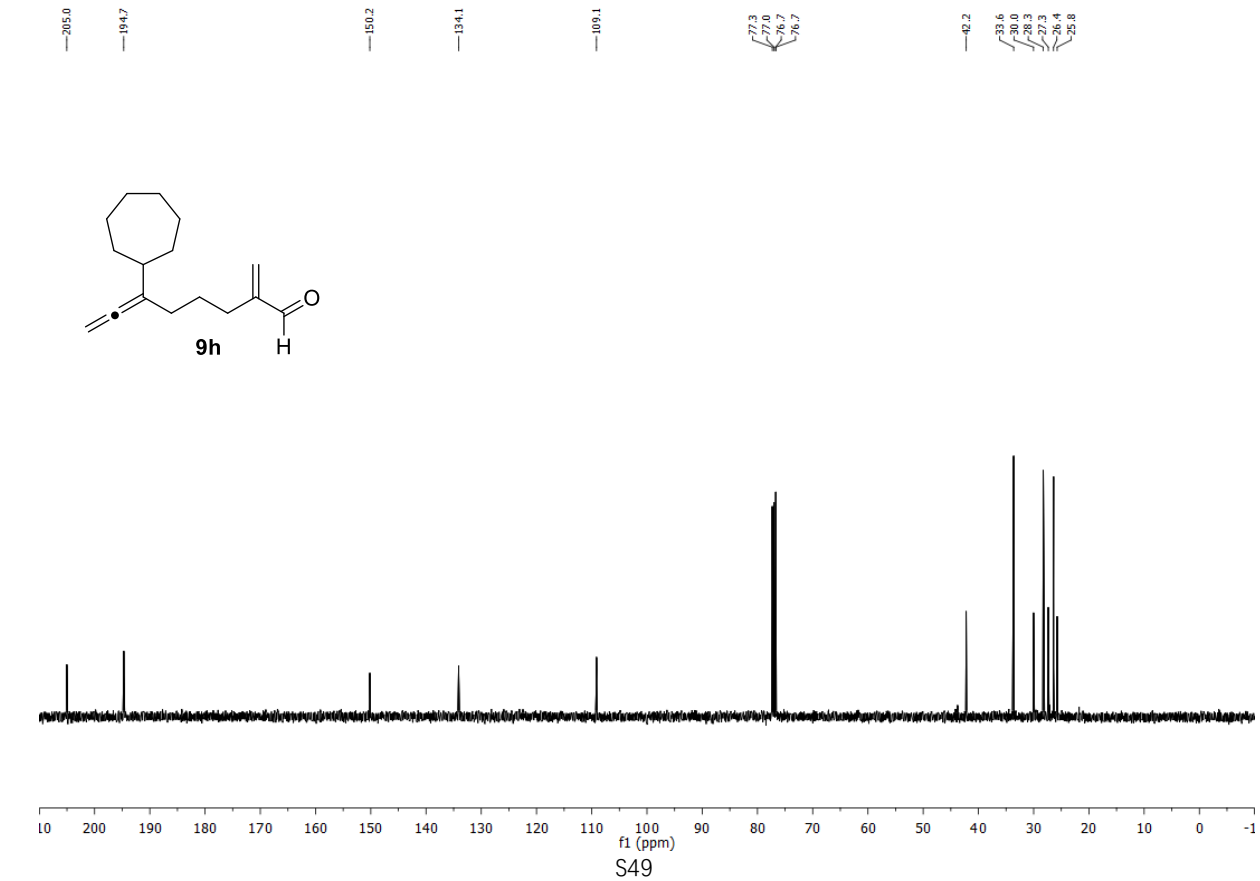
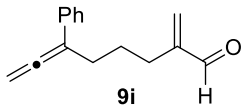
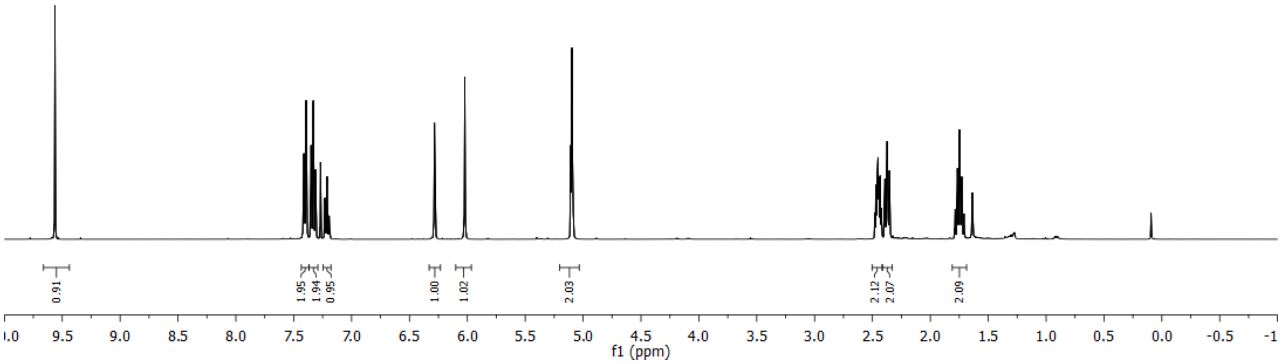


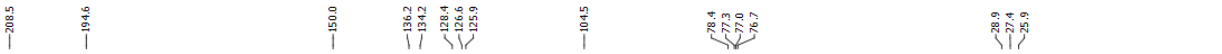
^{1}H NMR Spectra of **9i**

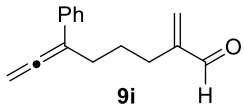


9i

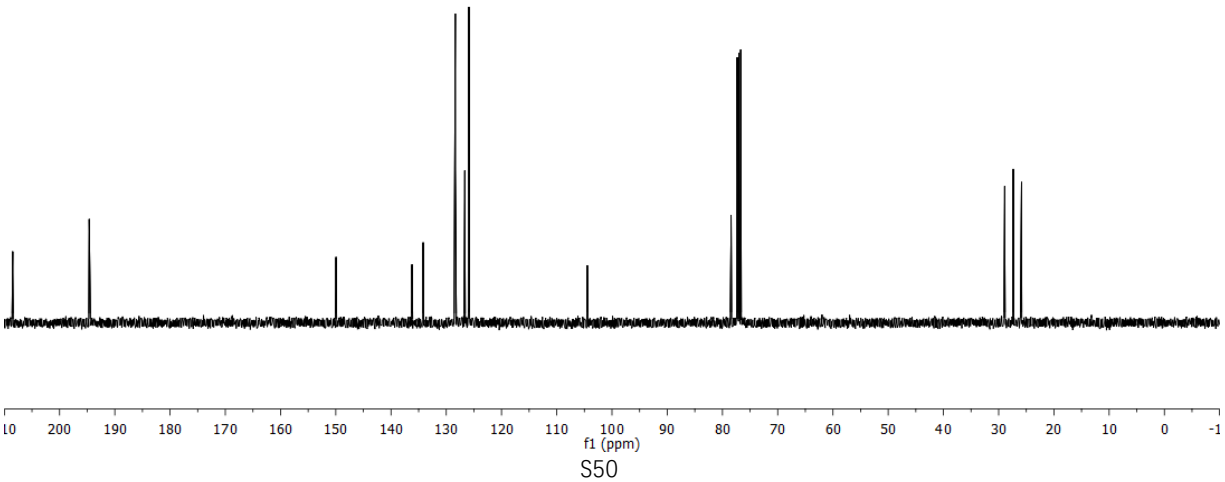


^{13}C NMR Spectra of **9i**





9i



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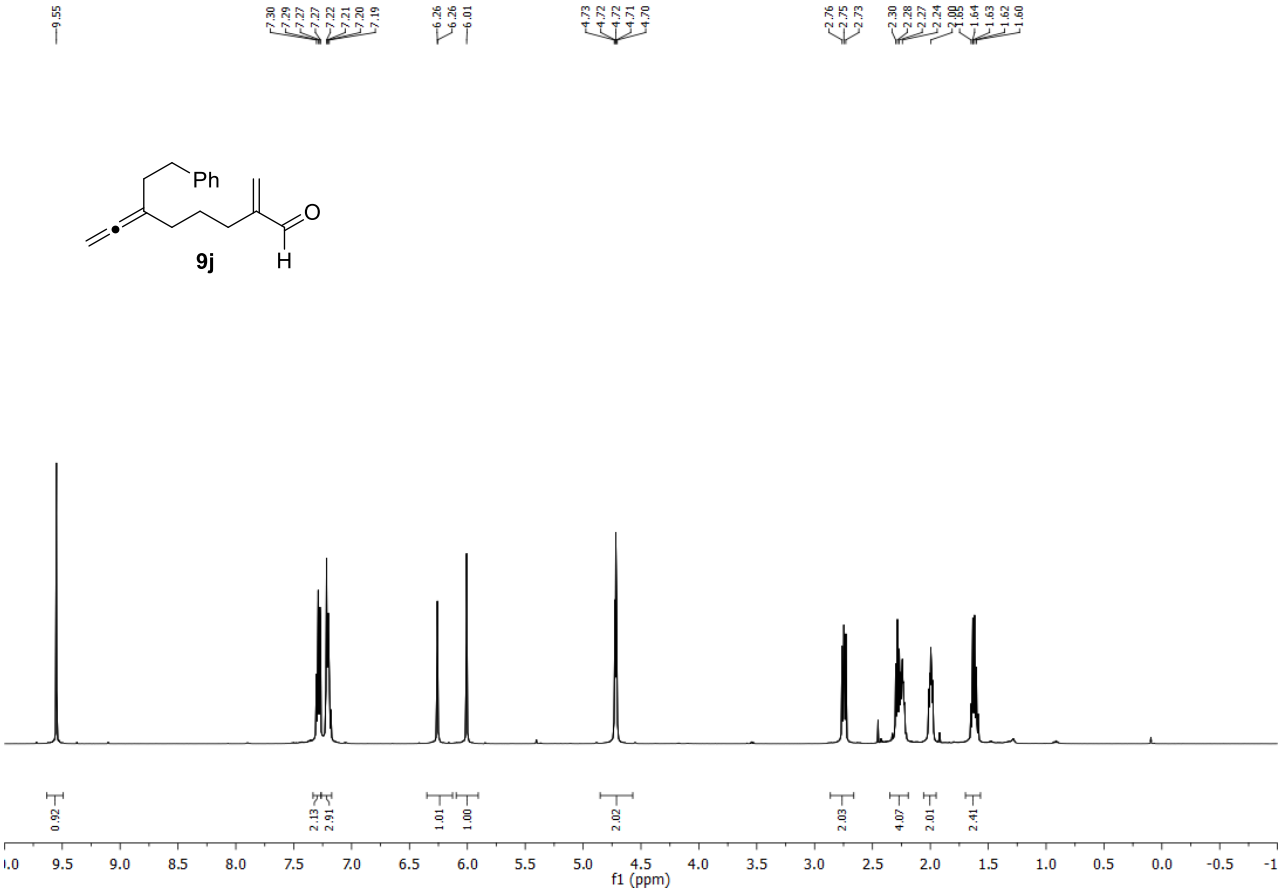

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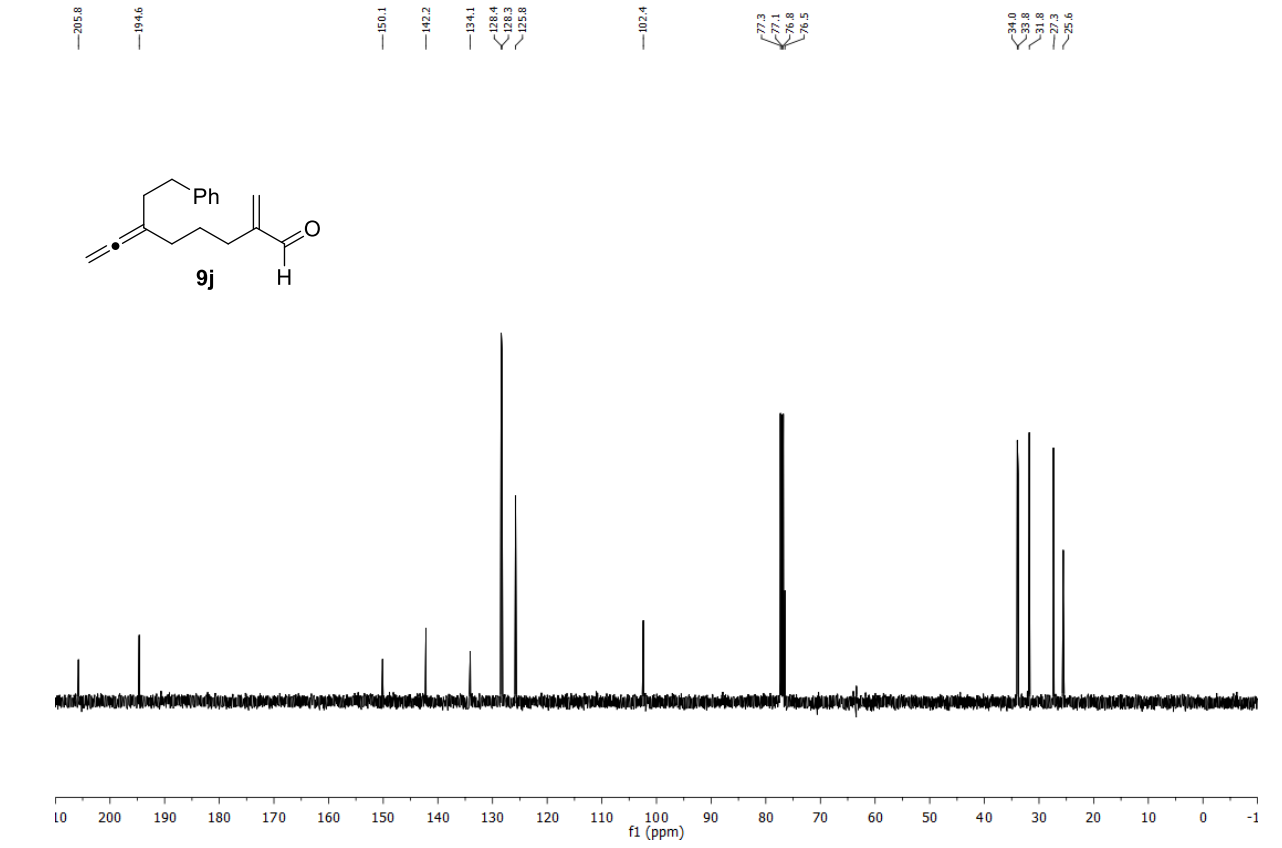
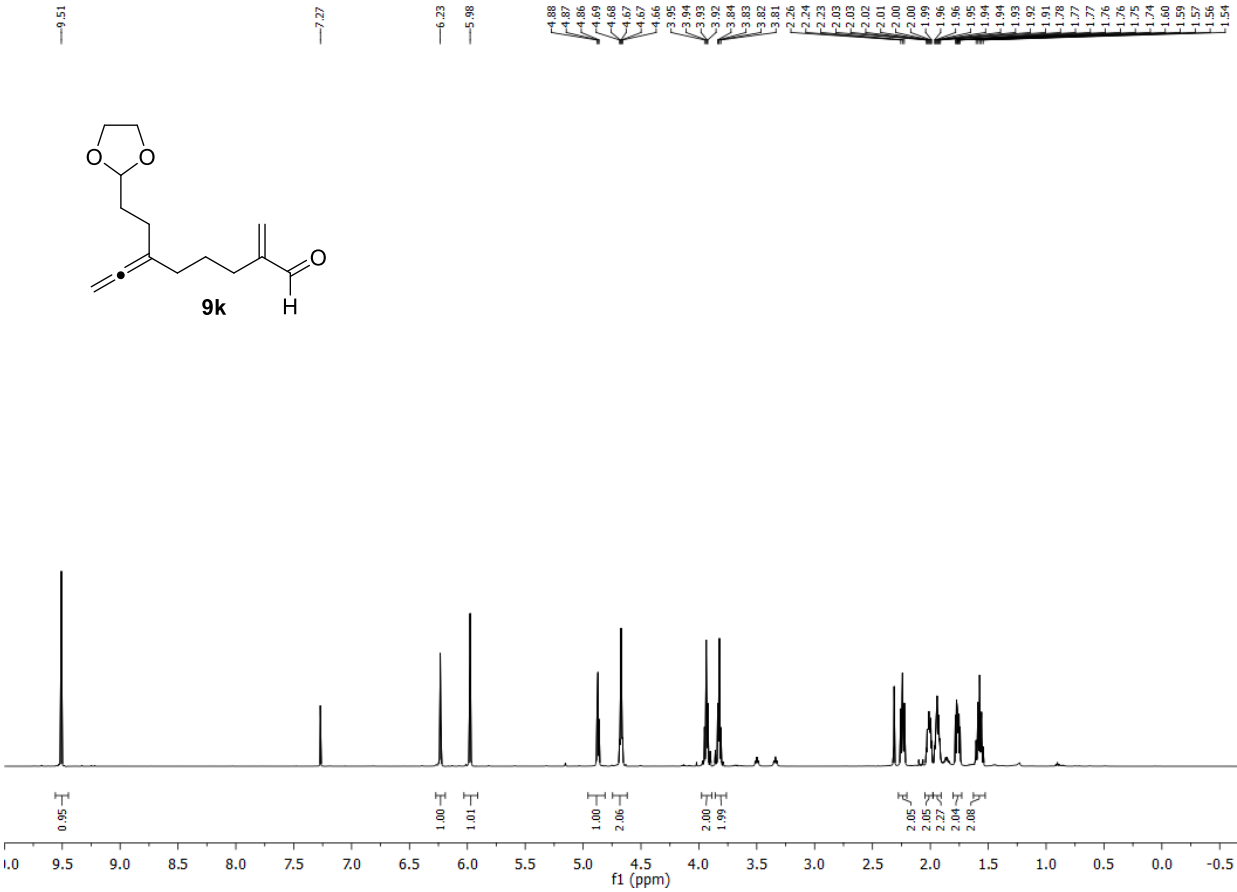
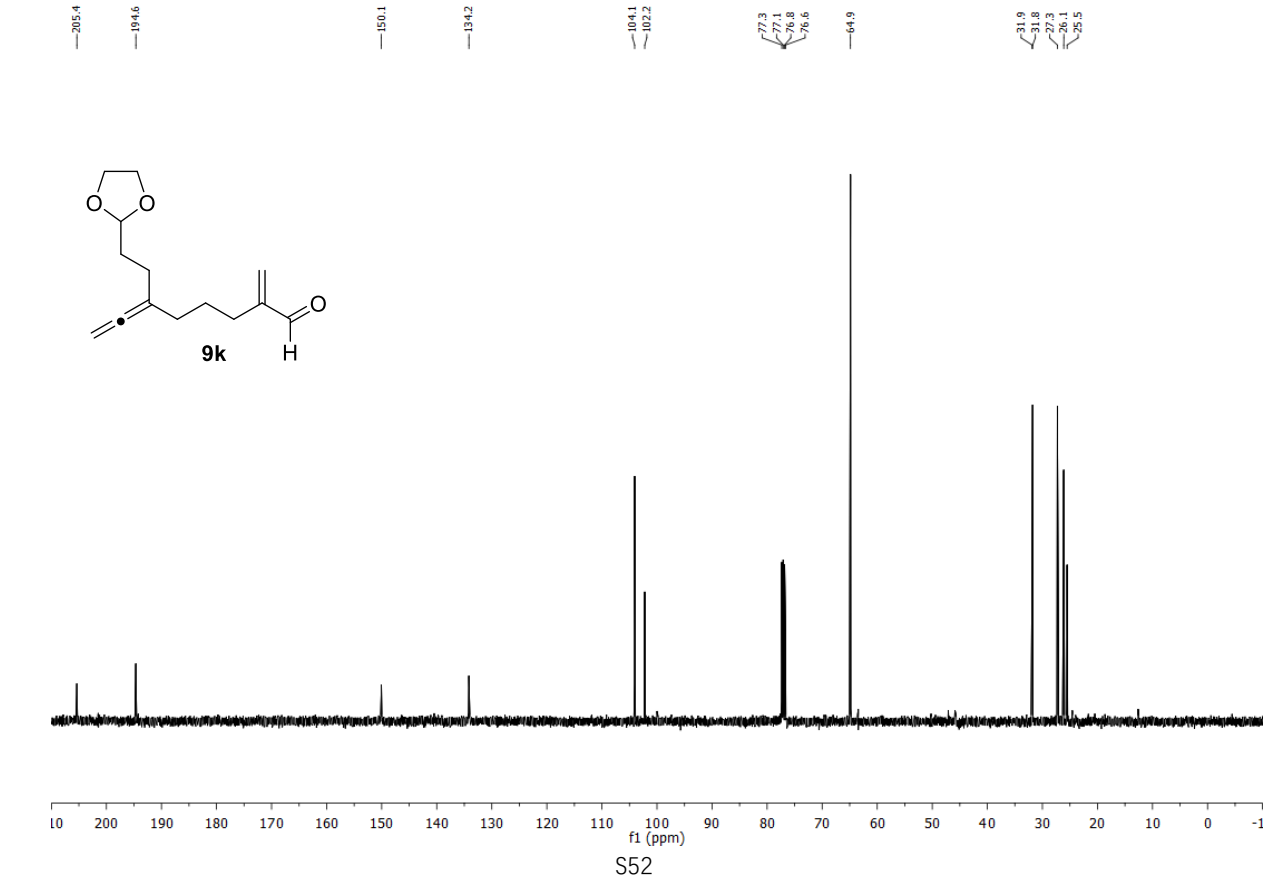


^{1}H NMR Spectra of **9k**



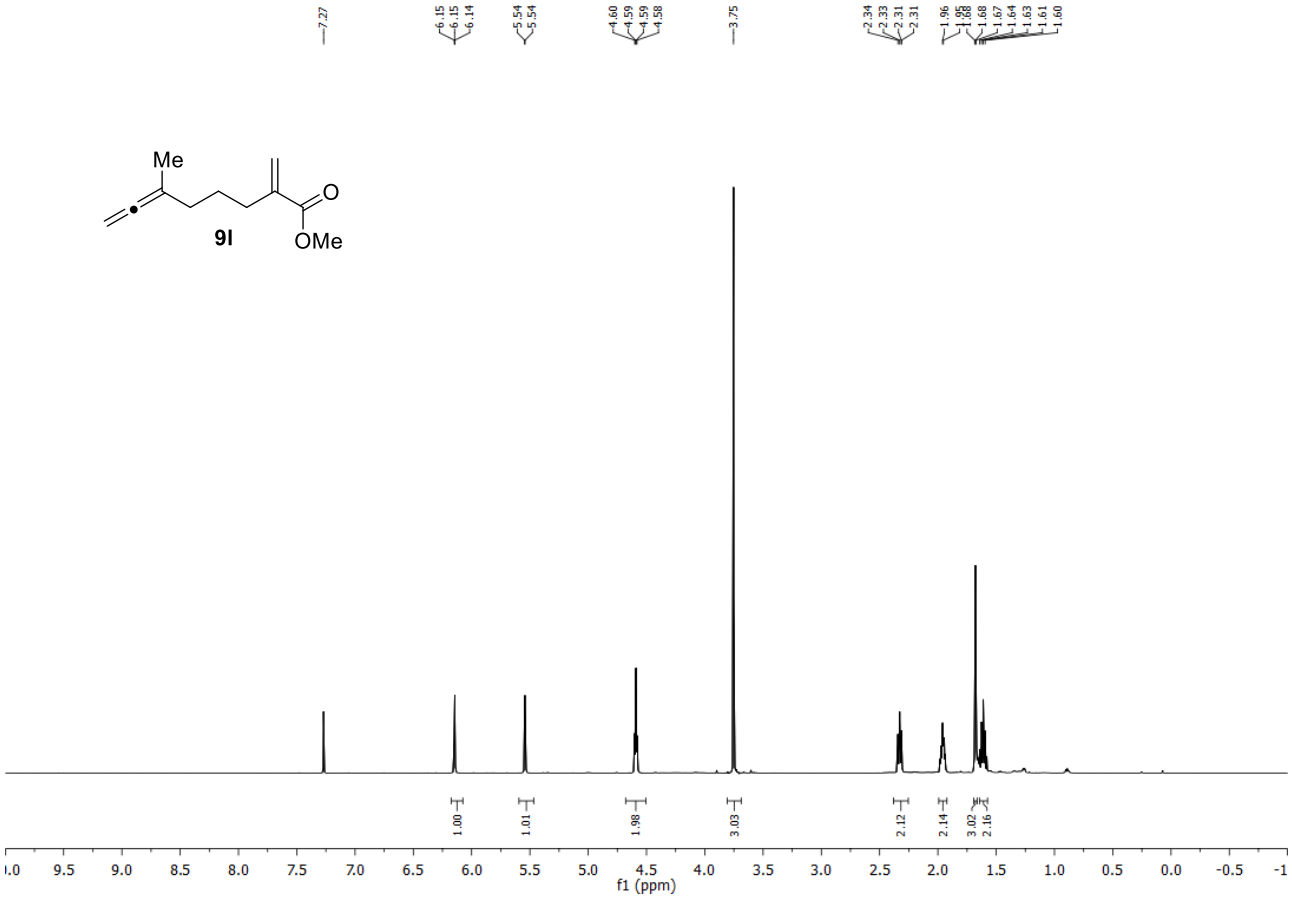
9k

^{13}C NMR Spectra of **9k**

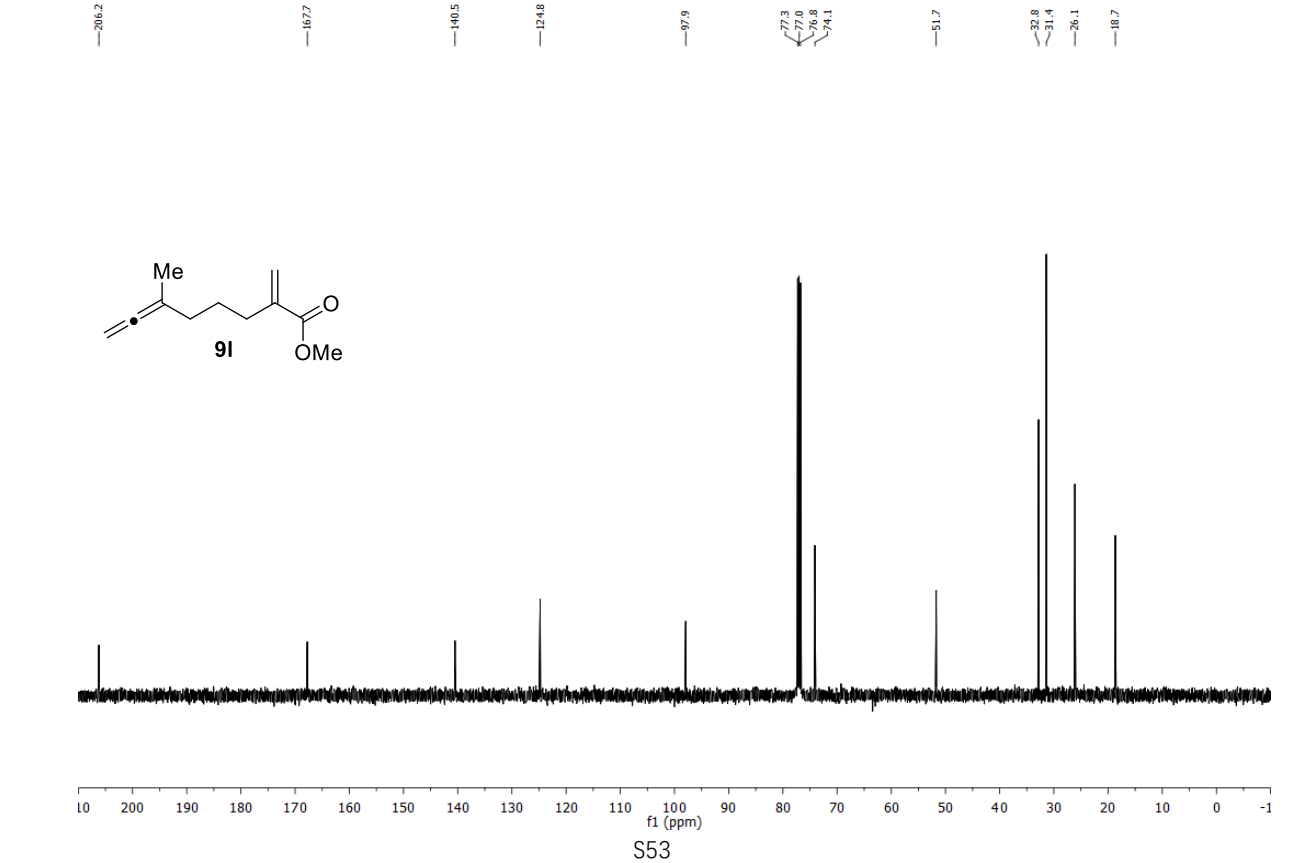


9k

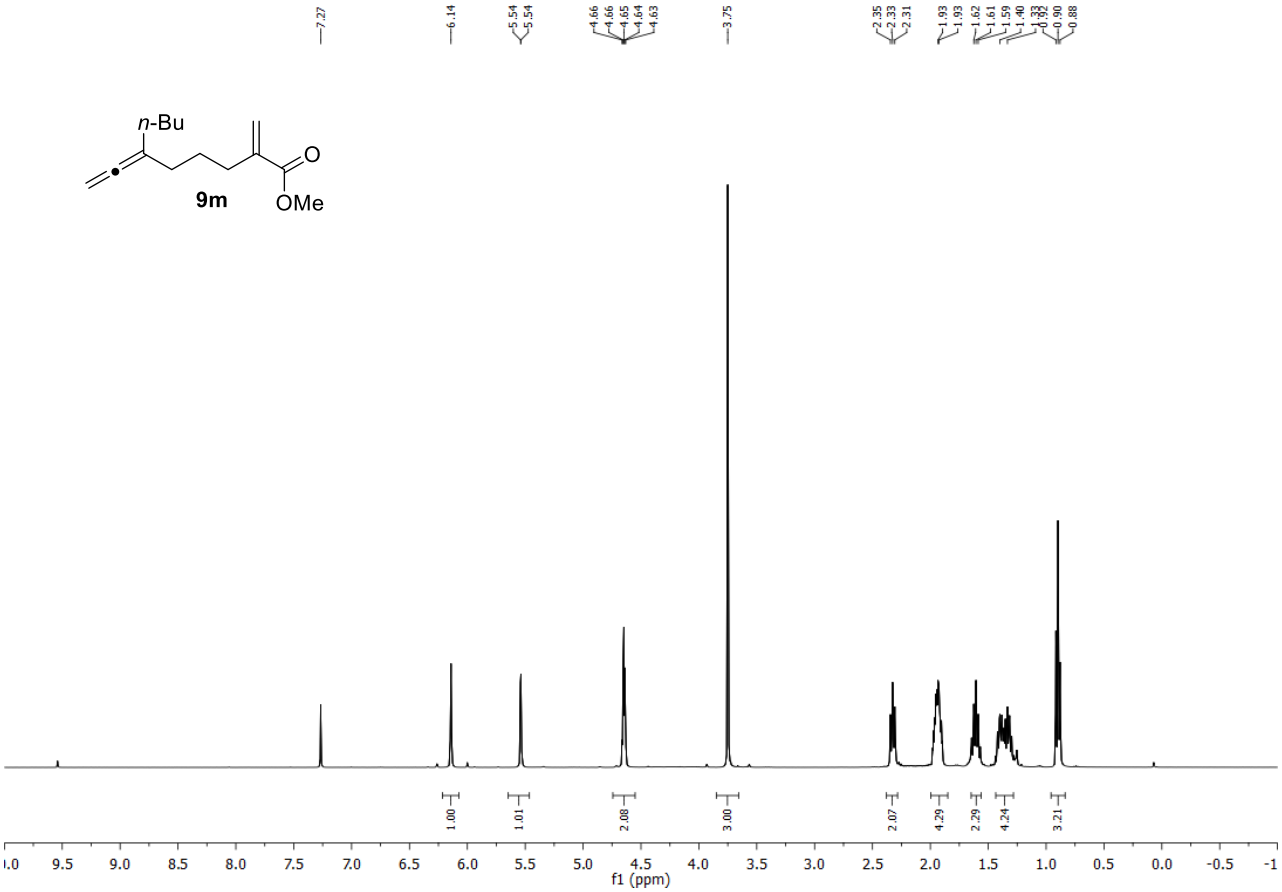
^{1}H NMR Spectra of **9l**



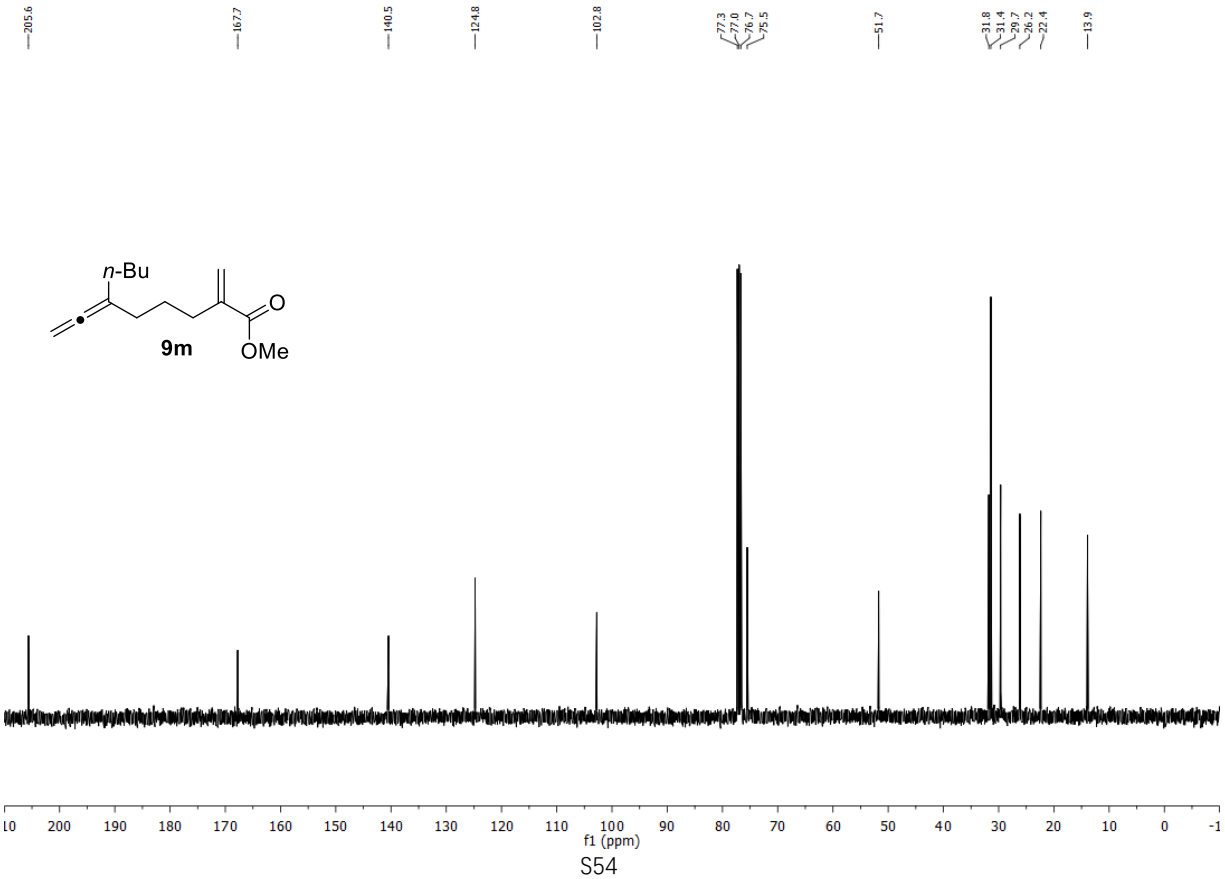
^{13}C NMR Spectra of **9l**



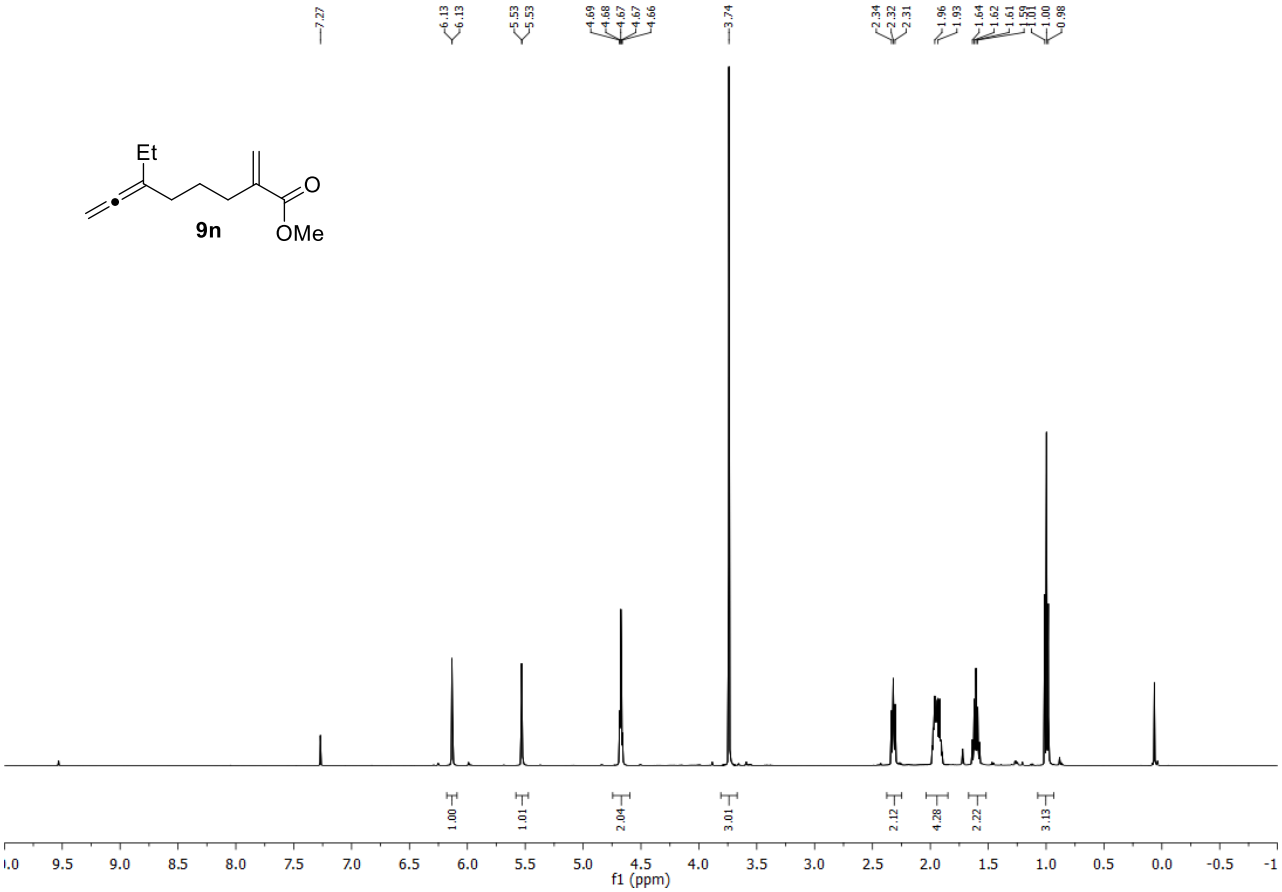
^{1}H NMR Spectra of **9m**



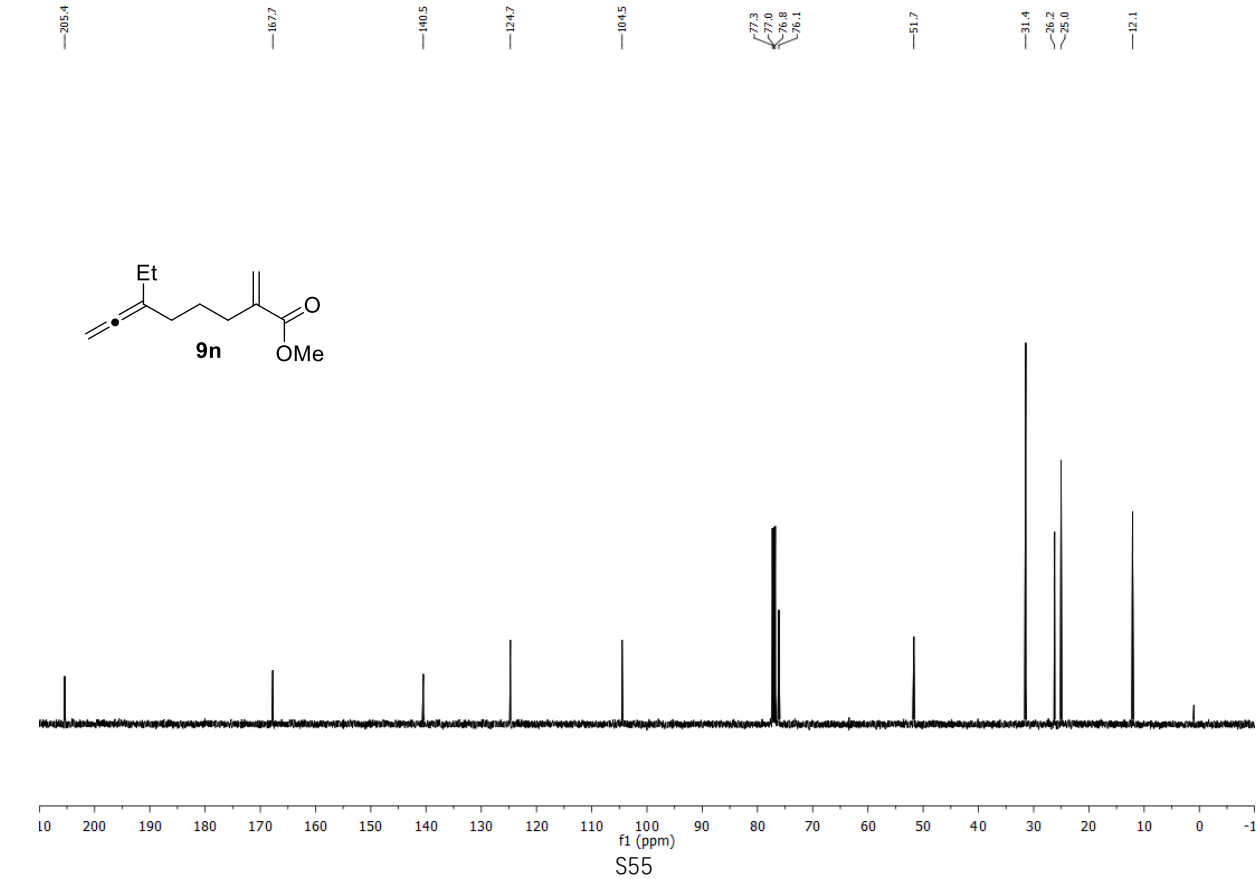
^{13}C NMR Spectra of **9m**



^{1}H NMR Spectra of **9n**



^{13}C NMR Spectra of **9n**



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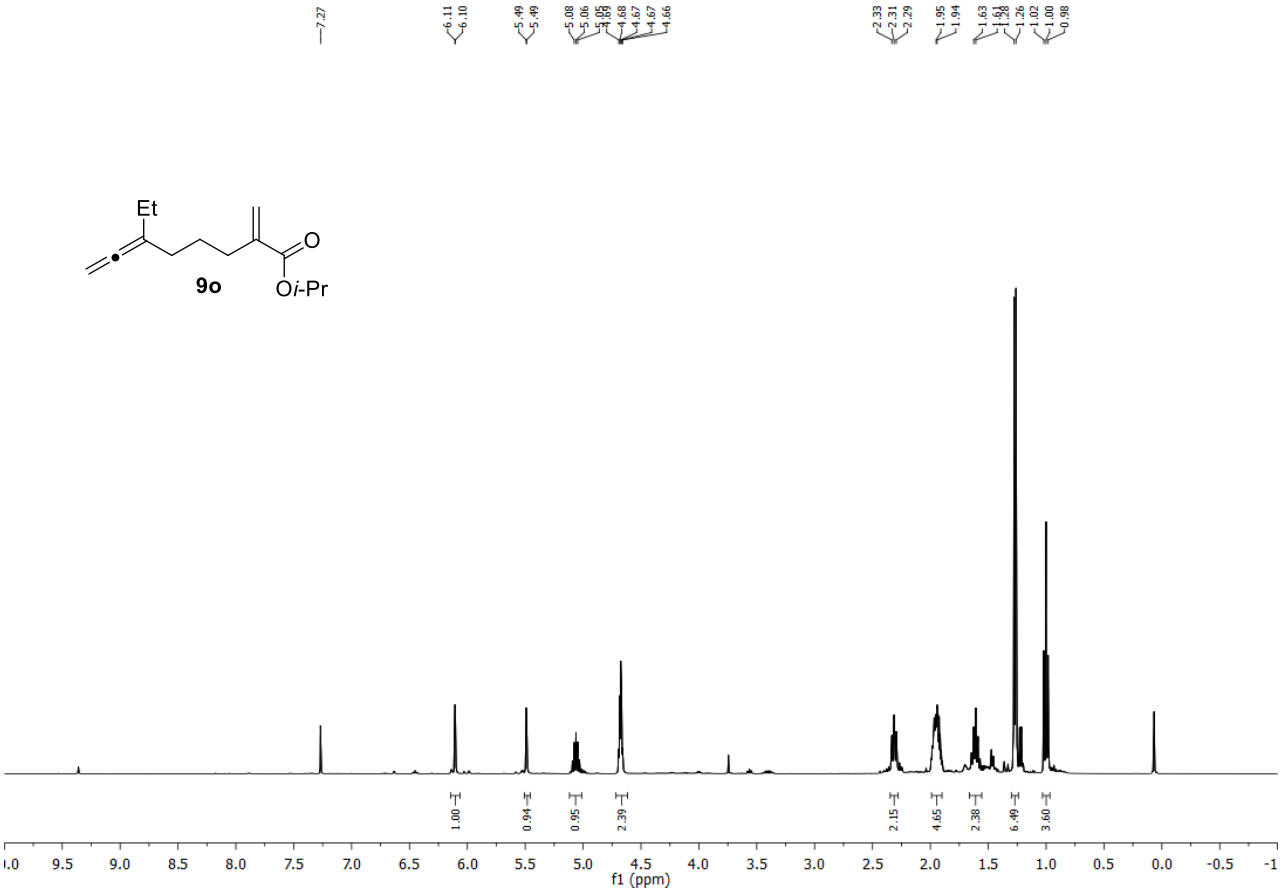

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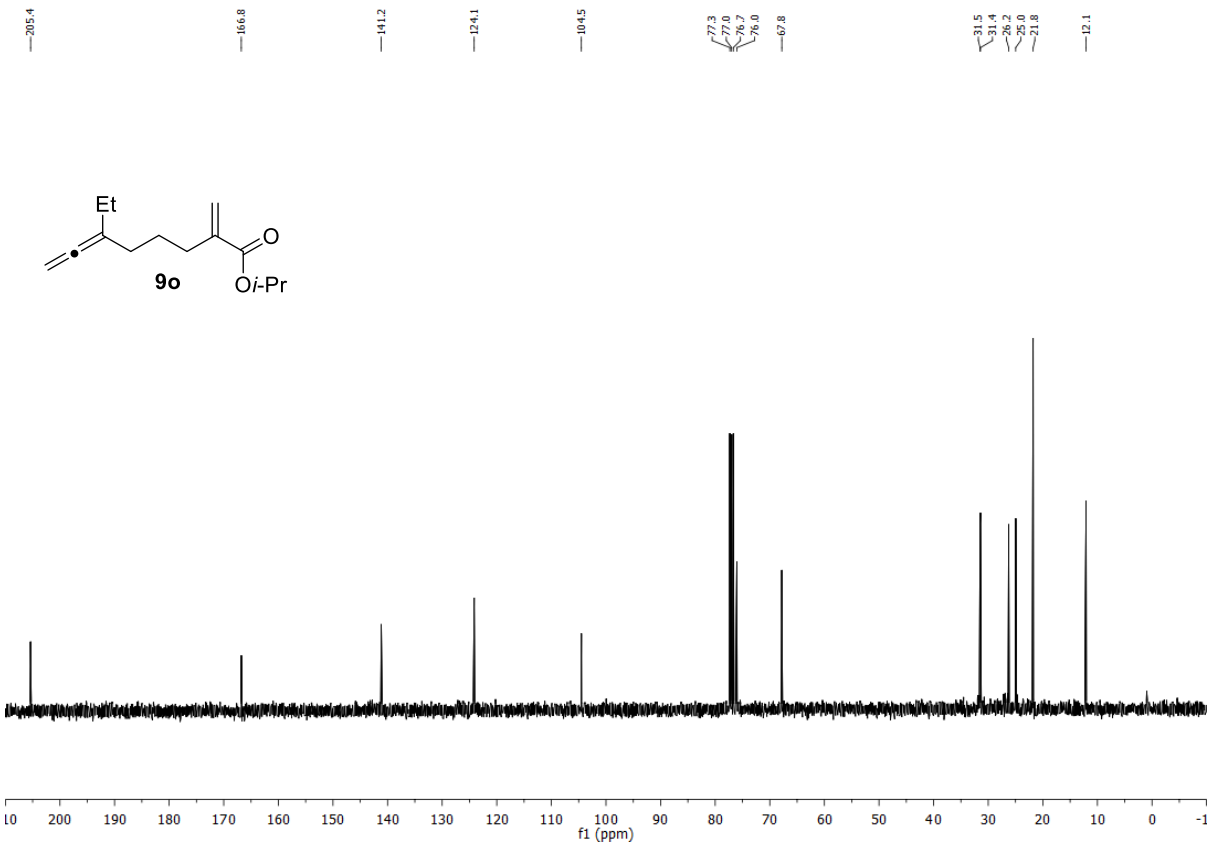
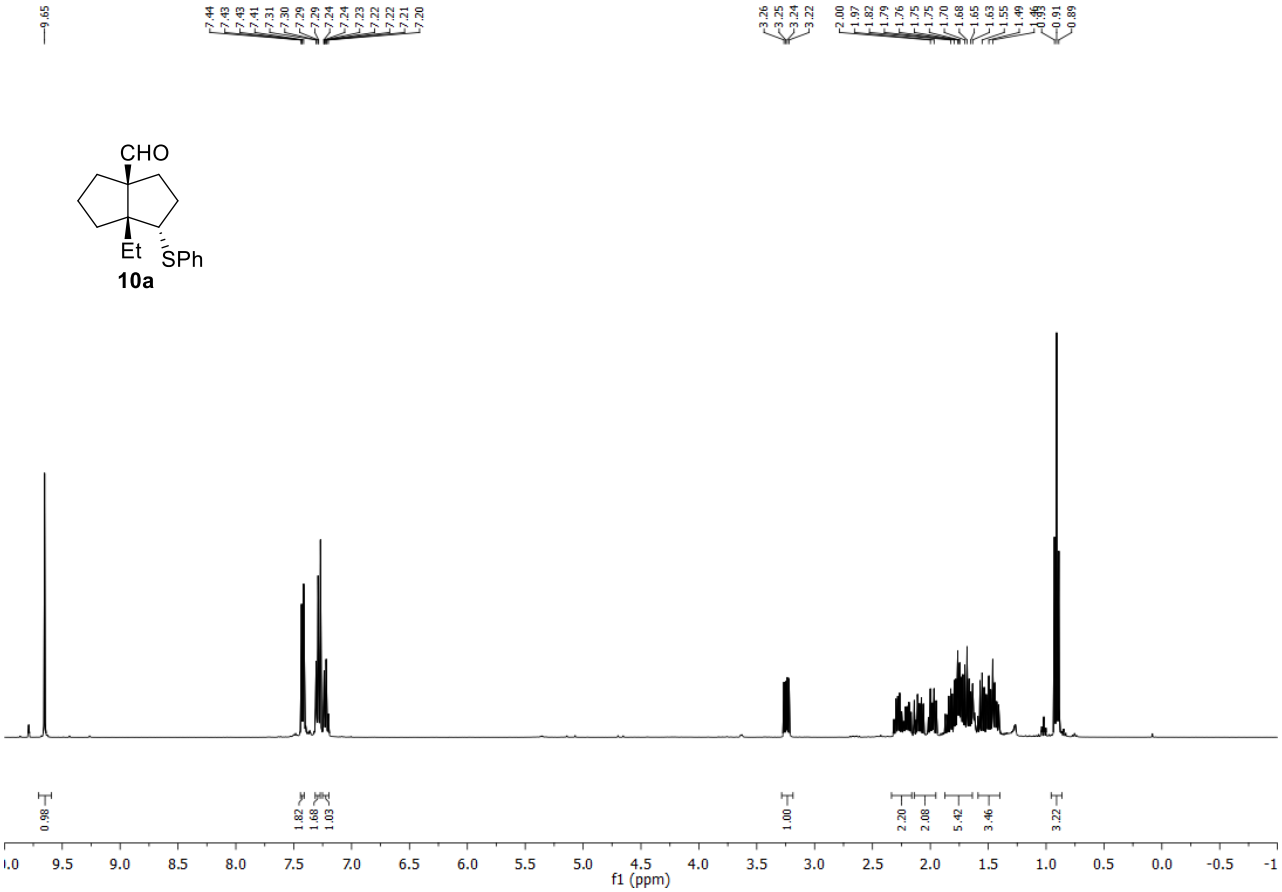
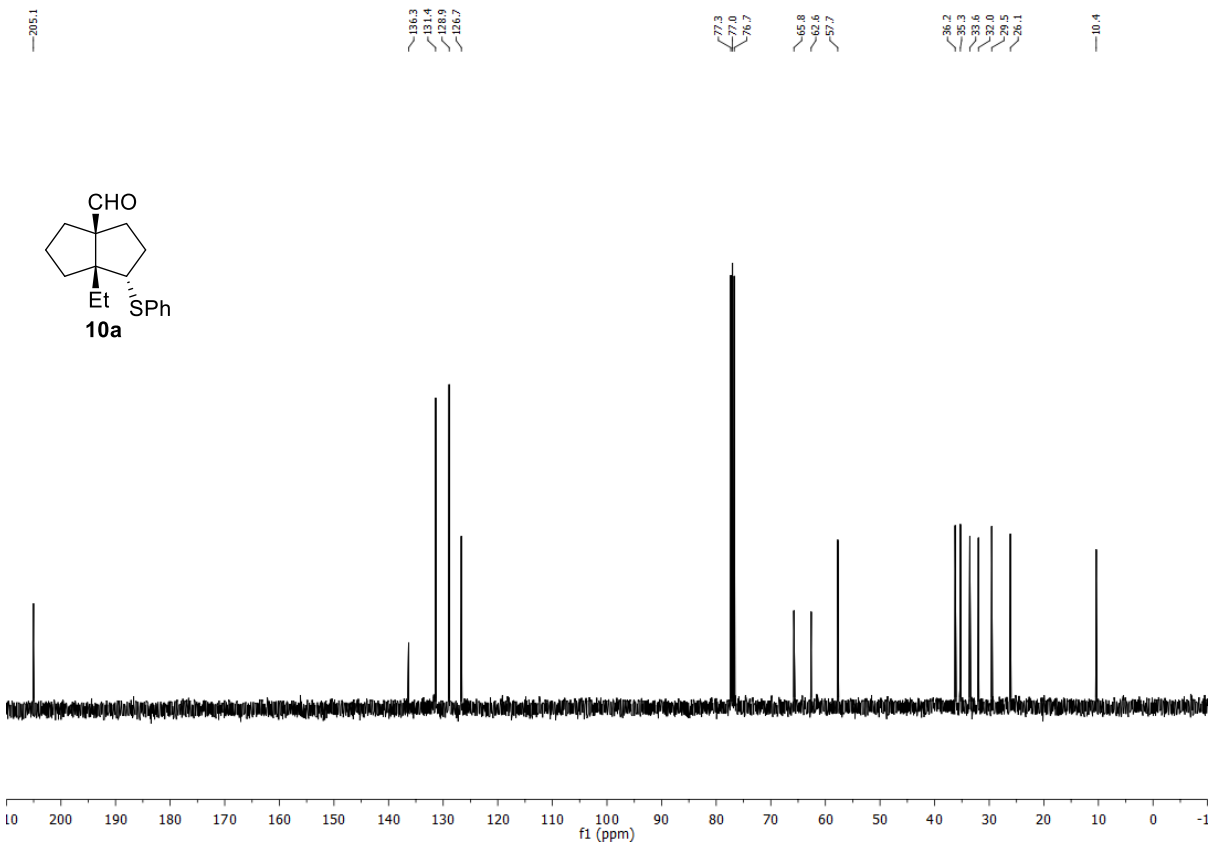


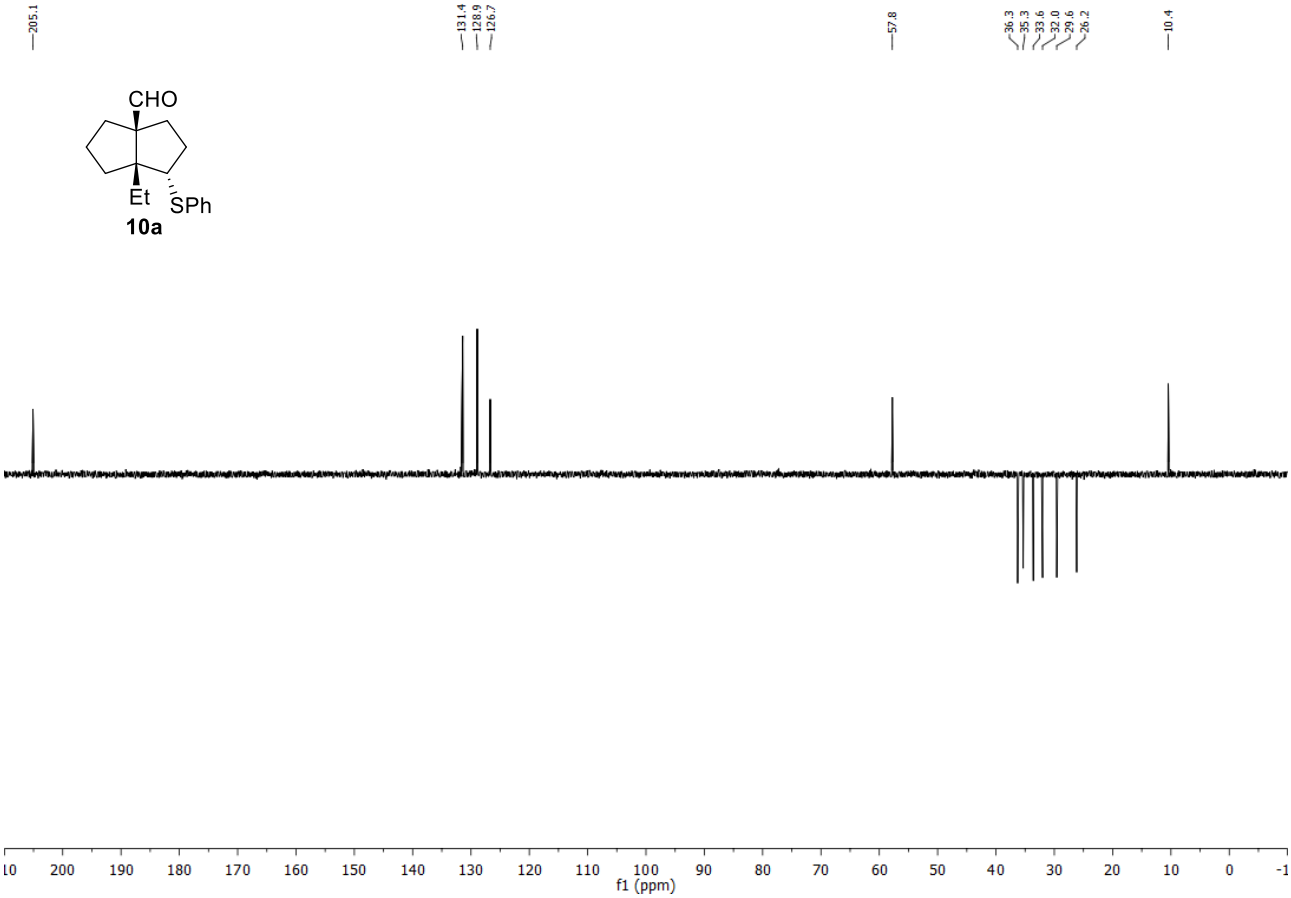
^{1}H NMR Spectra of **10a**



^{13}C NMR Spectra of **10a**



DEPT NMR Spectra of **10a**



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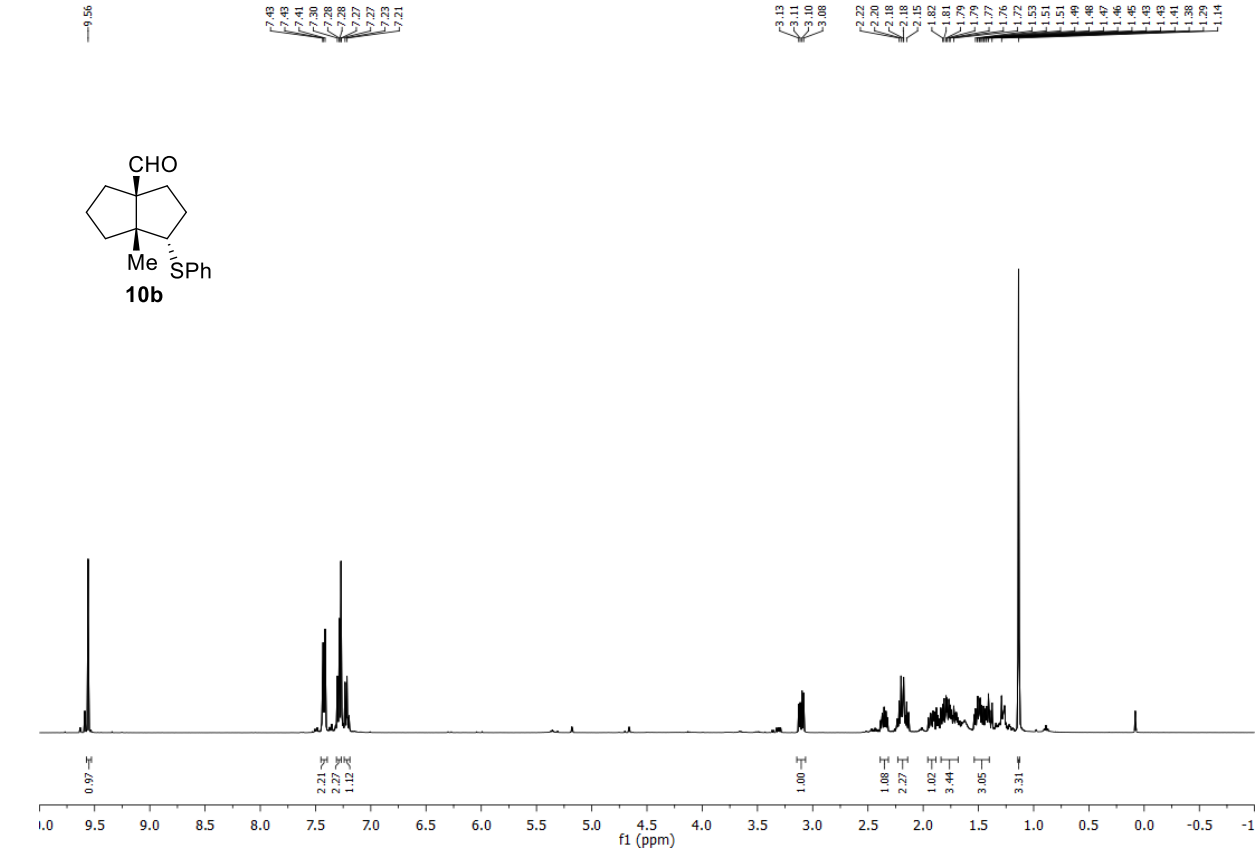
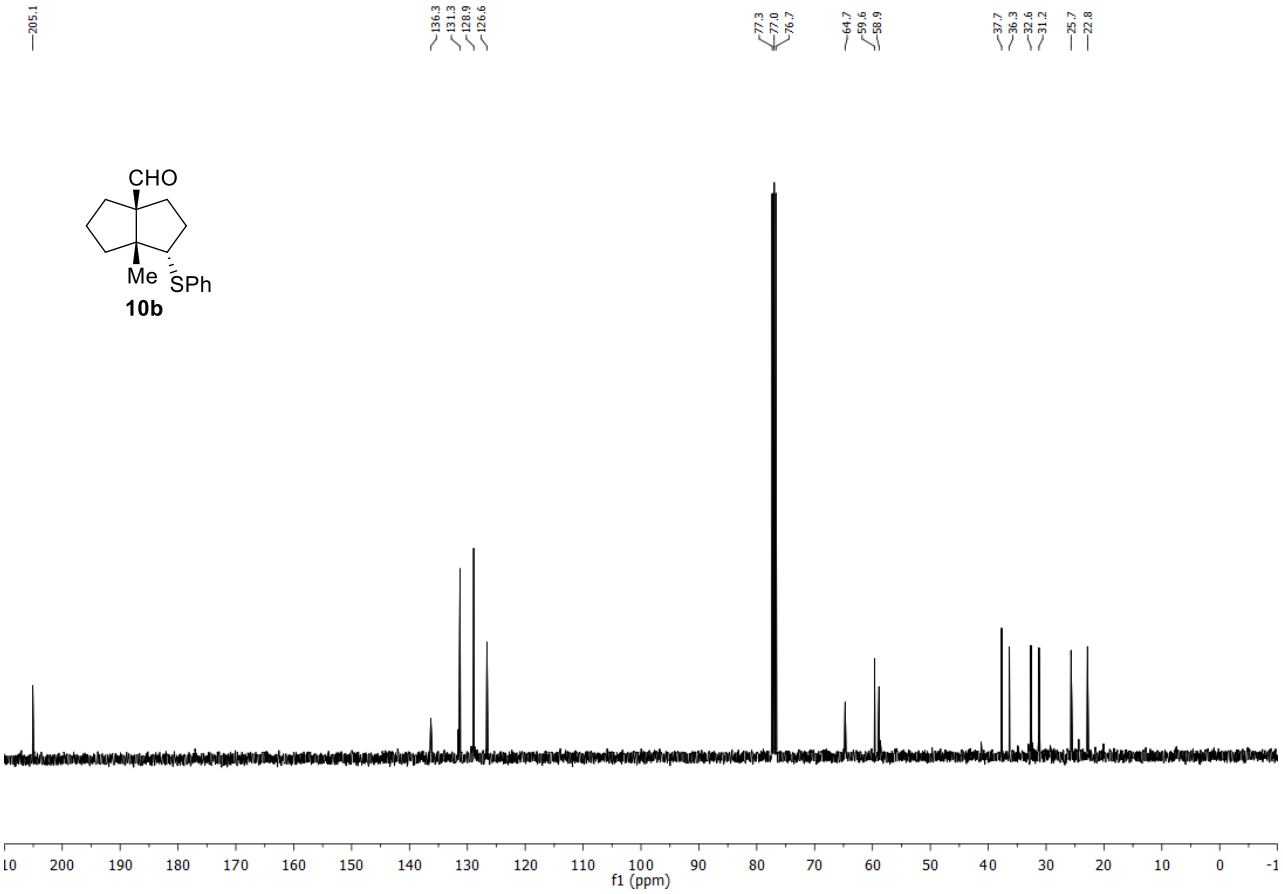
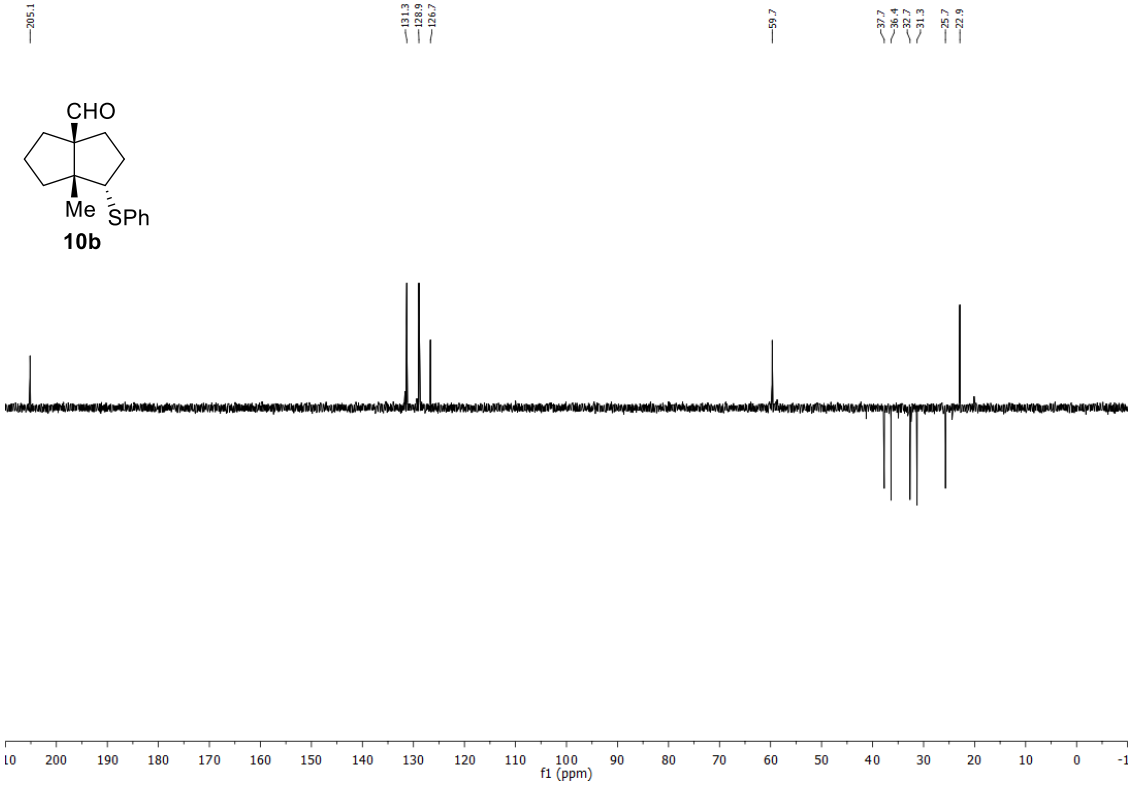


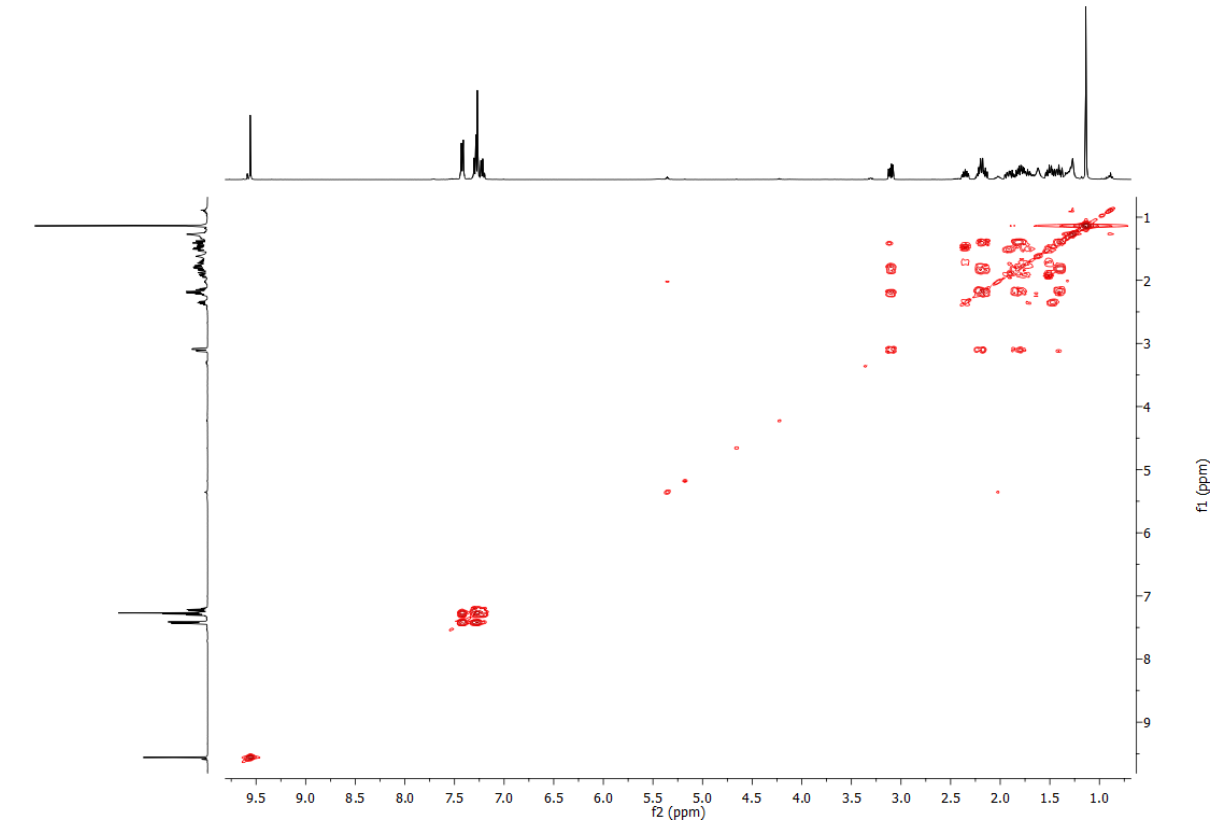
^{13}C NMR Spectra of **10b**



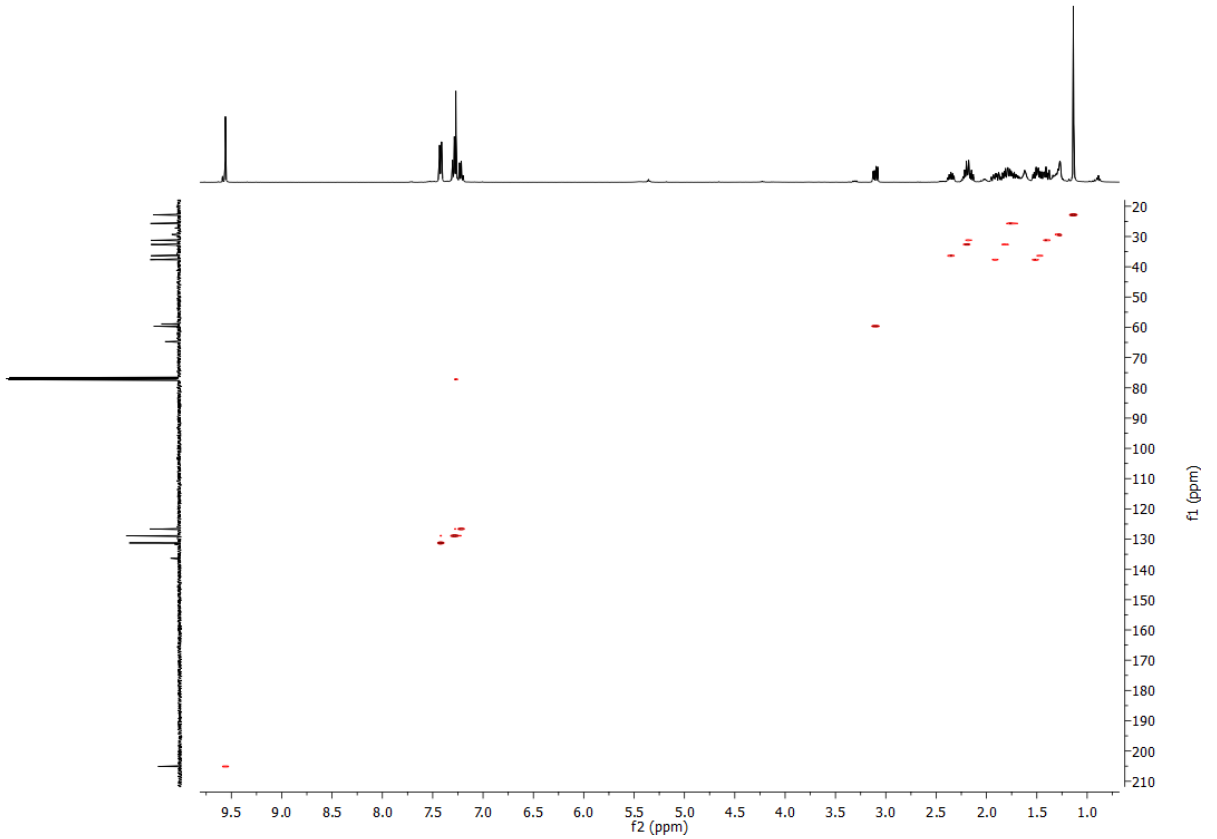
DEPT NMR Spectra of **10b**



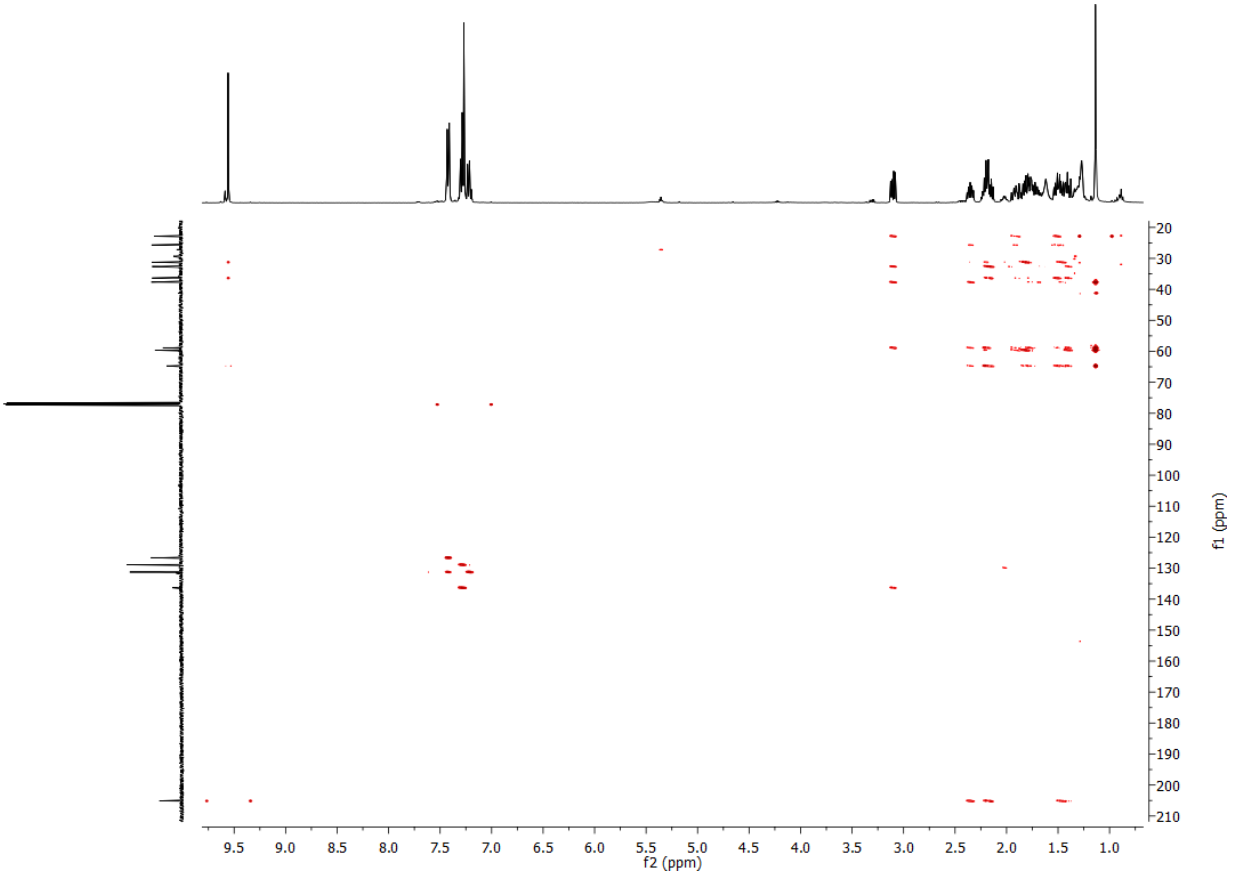
H-H COSY NMR Spectra of **10b**



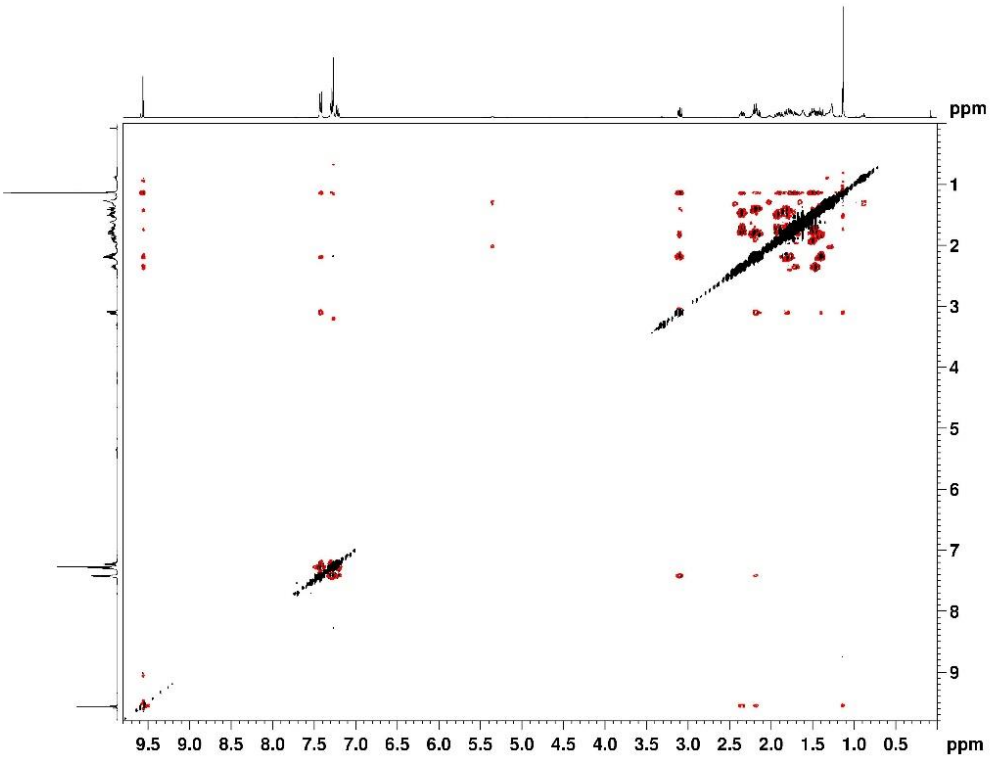
C-H HSQC NMR Spectra of **10b**



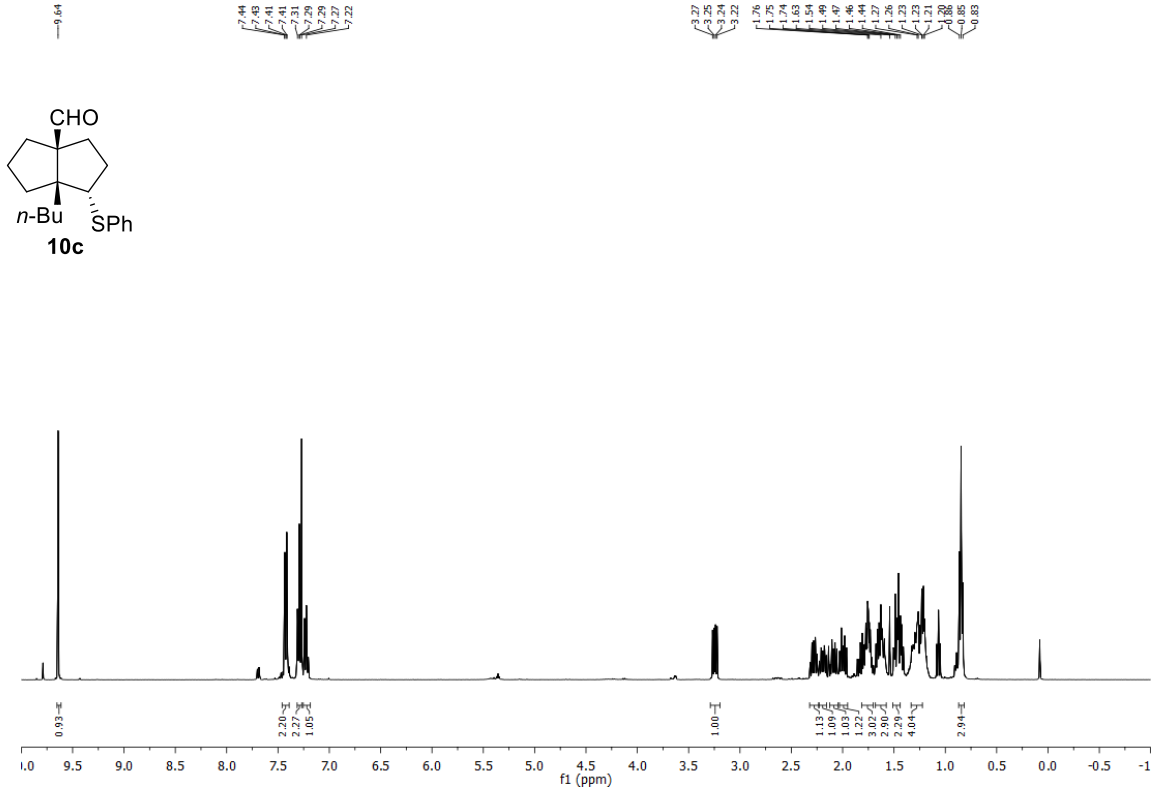
C-H HSBC NMR Spectra of **10b**



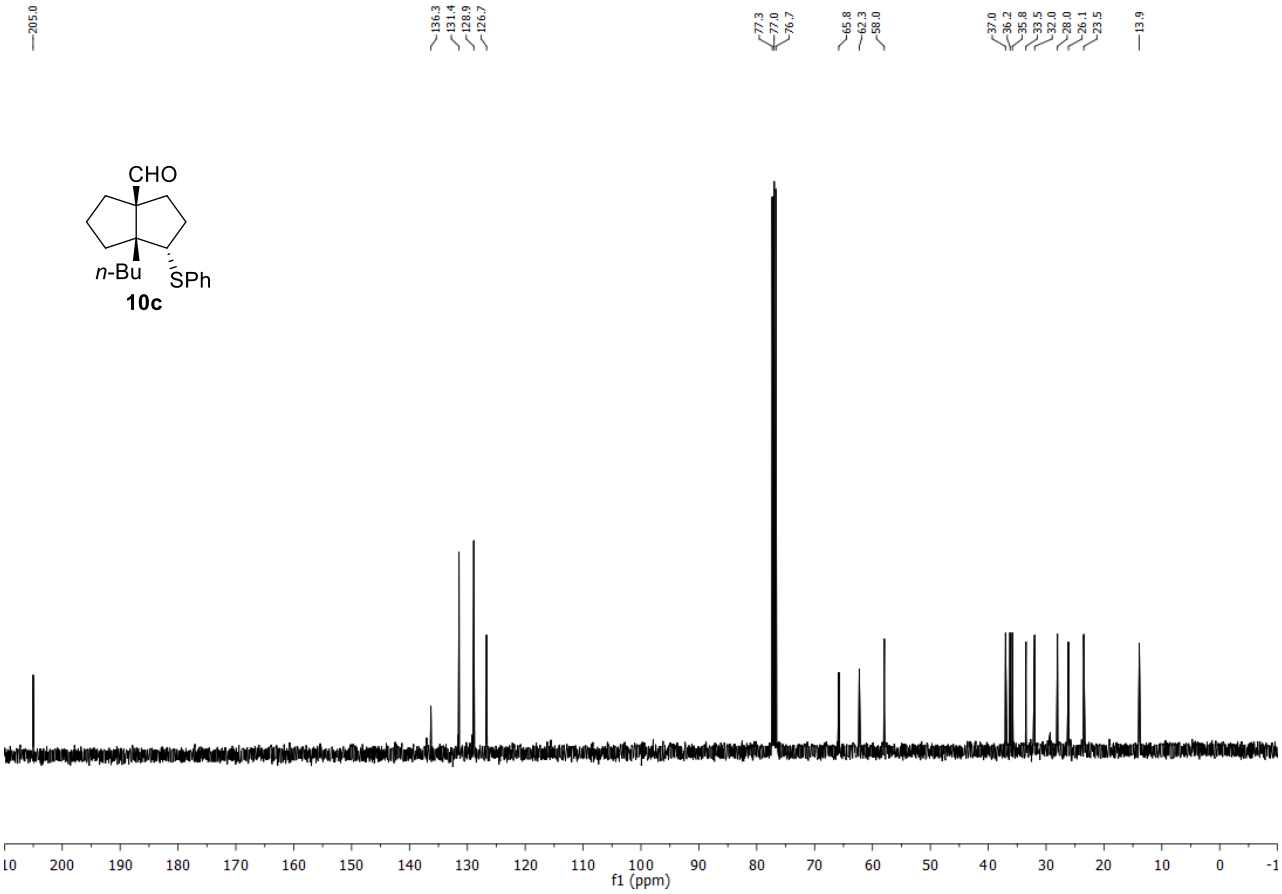
H-H NOESY NMR Spectra of **10b**



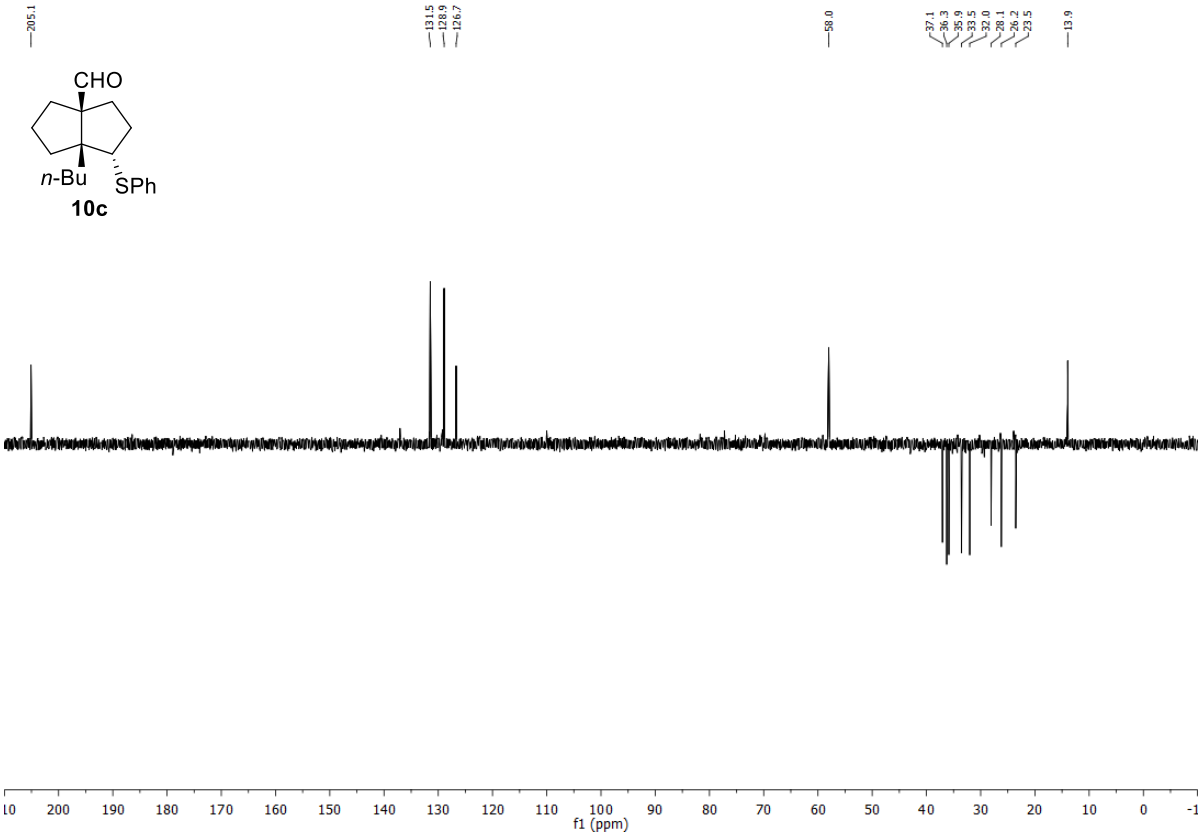
^{1}H NMR Spectra of **10c**



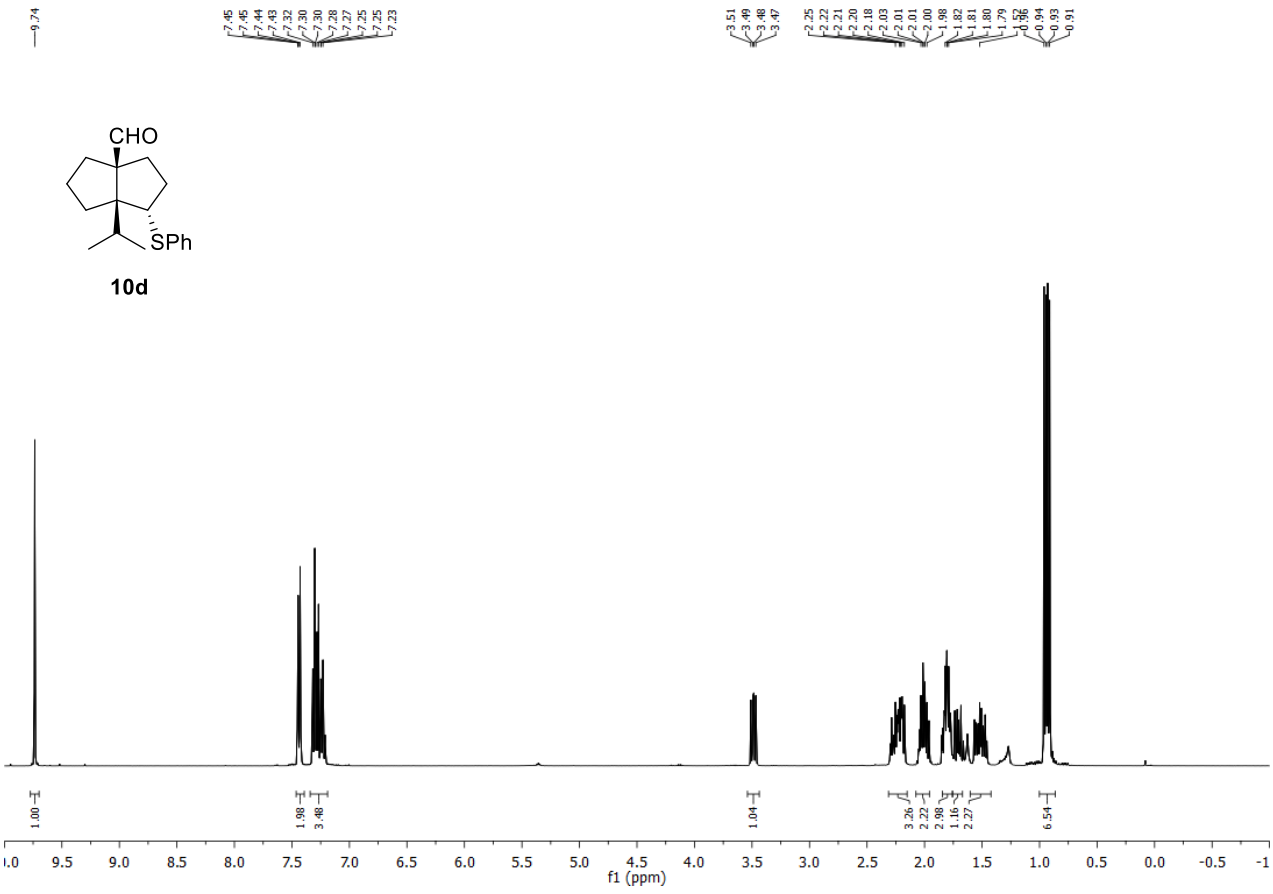
^{13}C NMR Spectra of **10c**



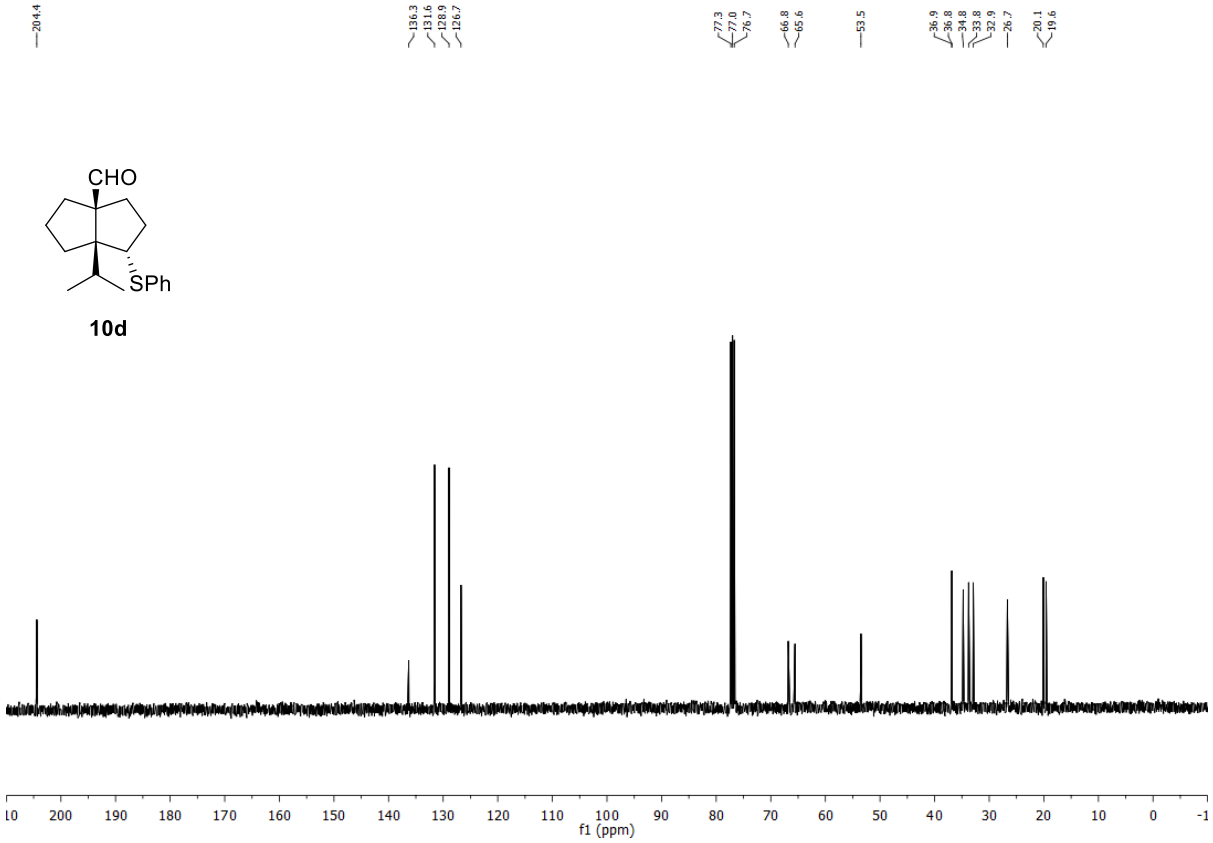
DEPT NMR Spectra of **10c**



^{1}H NMR Spectra of **10d**



^{13}C NMR Spectra of **10d**



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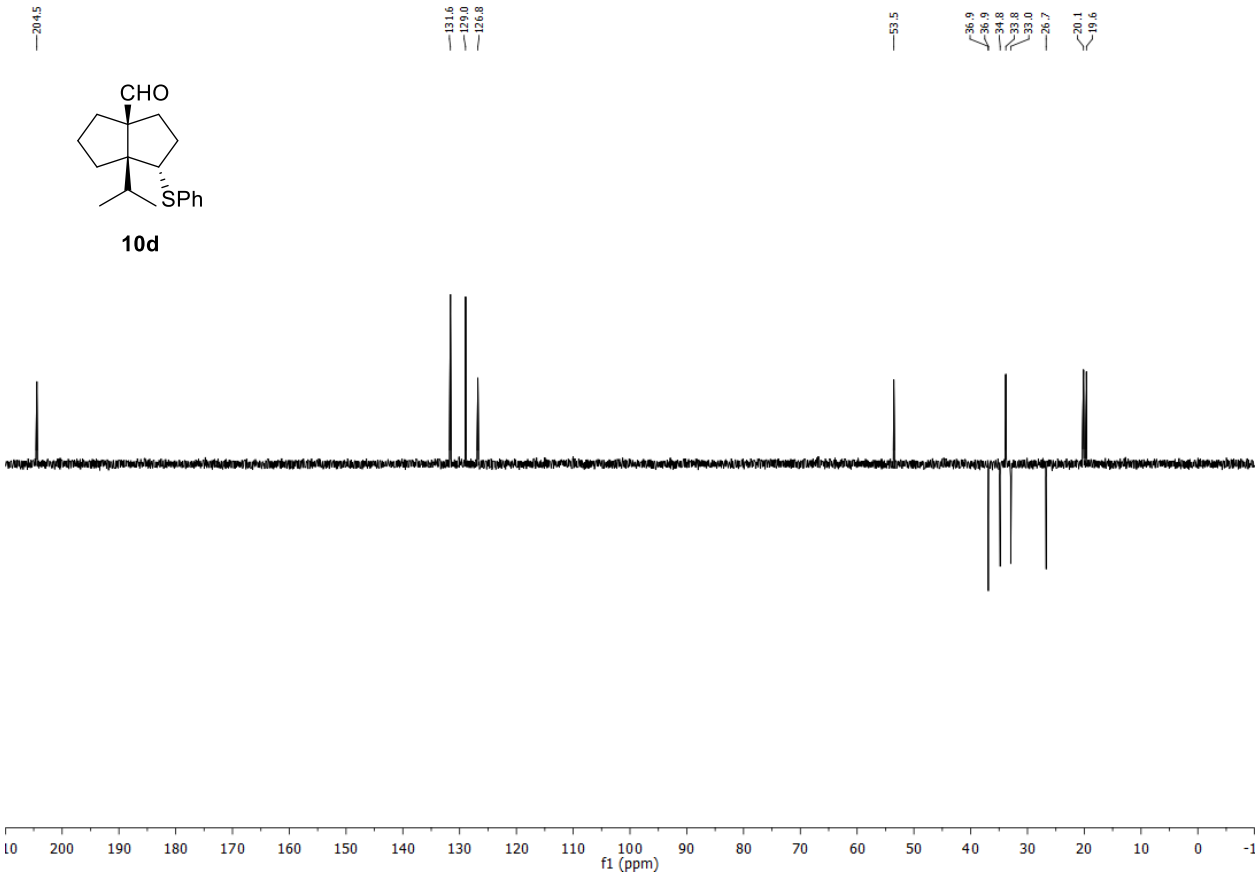

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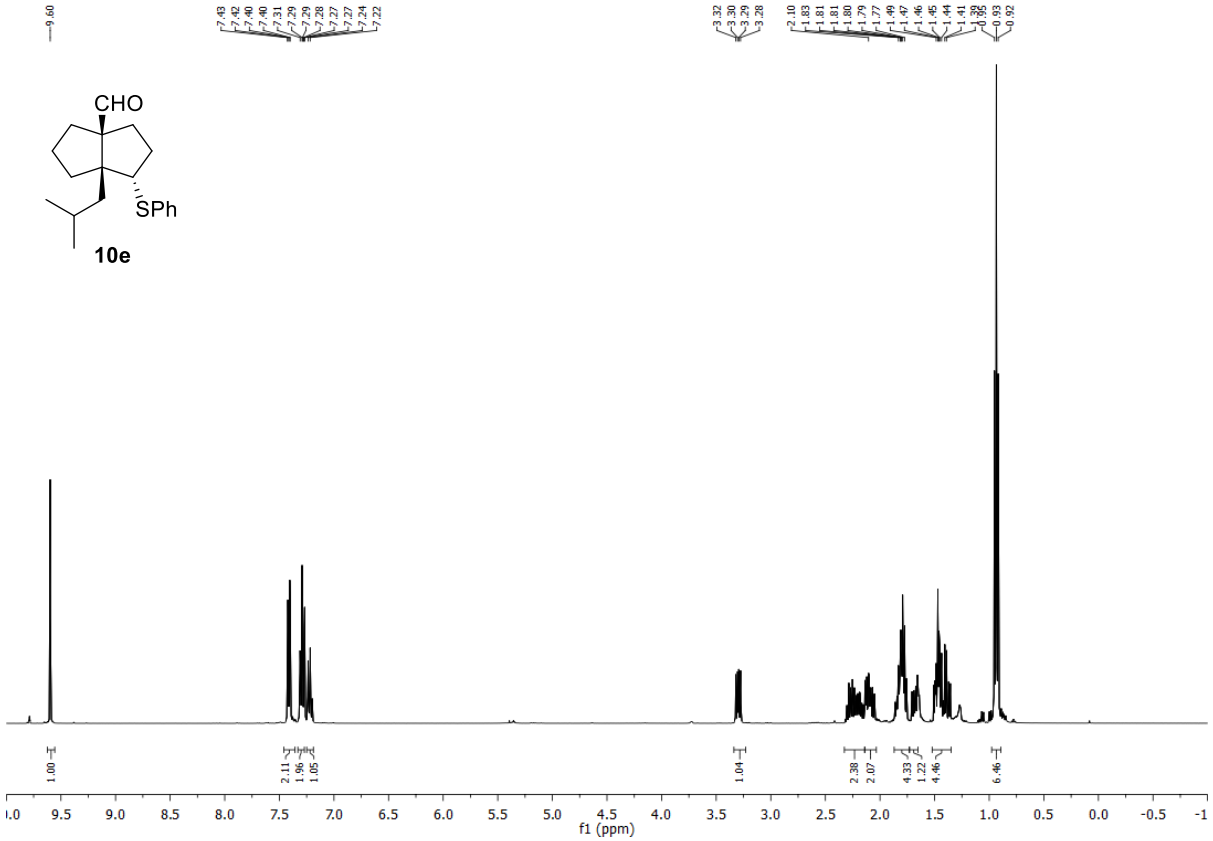
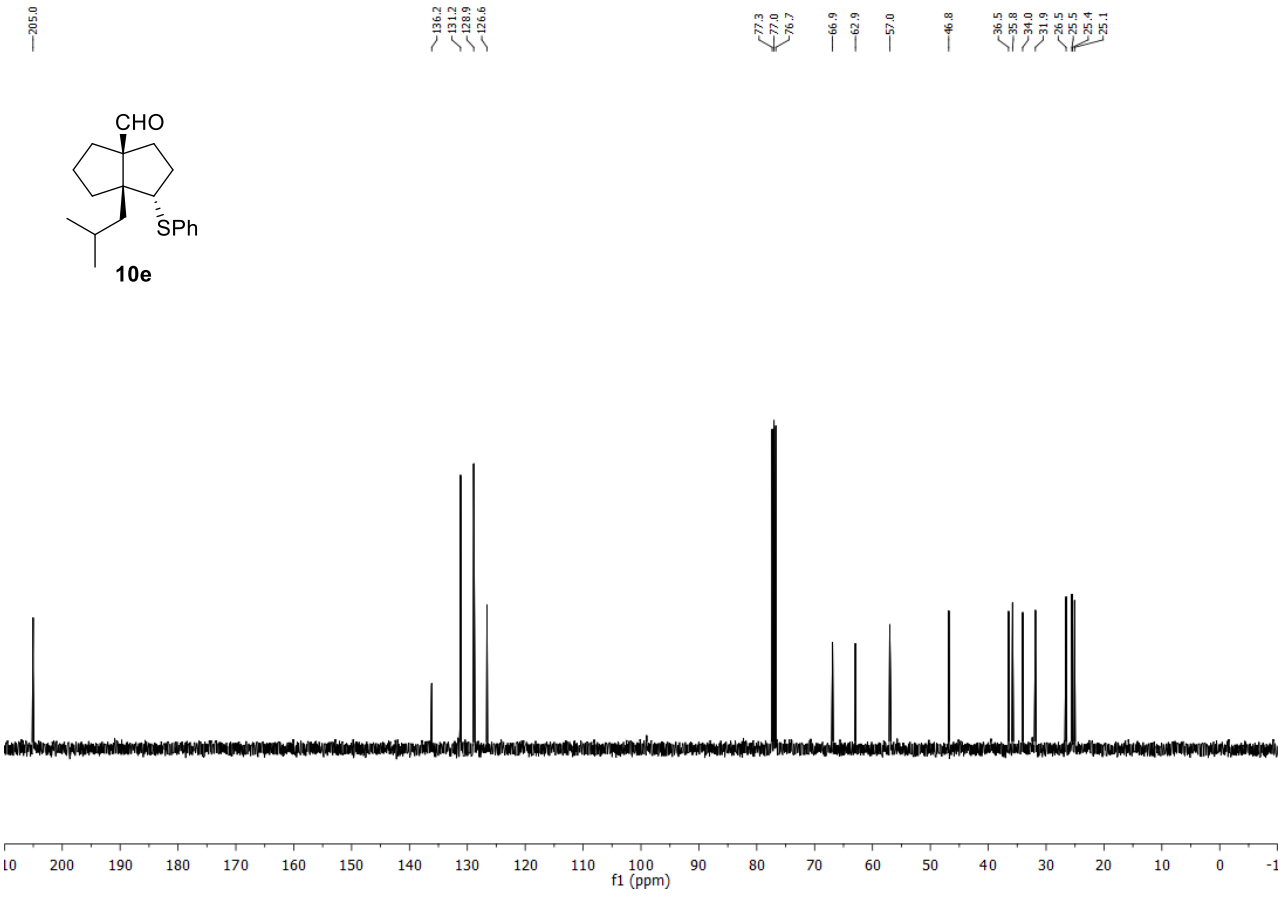
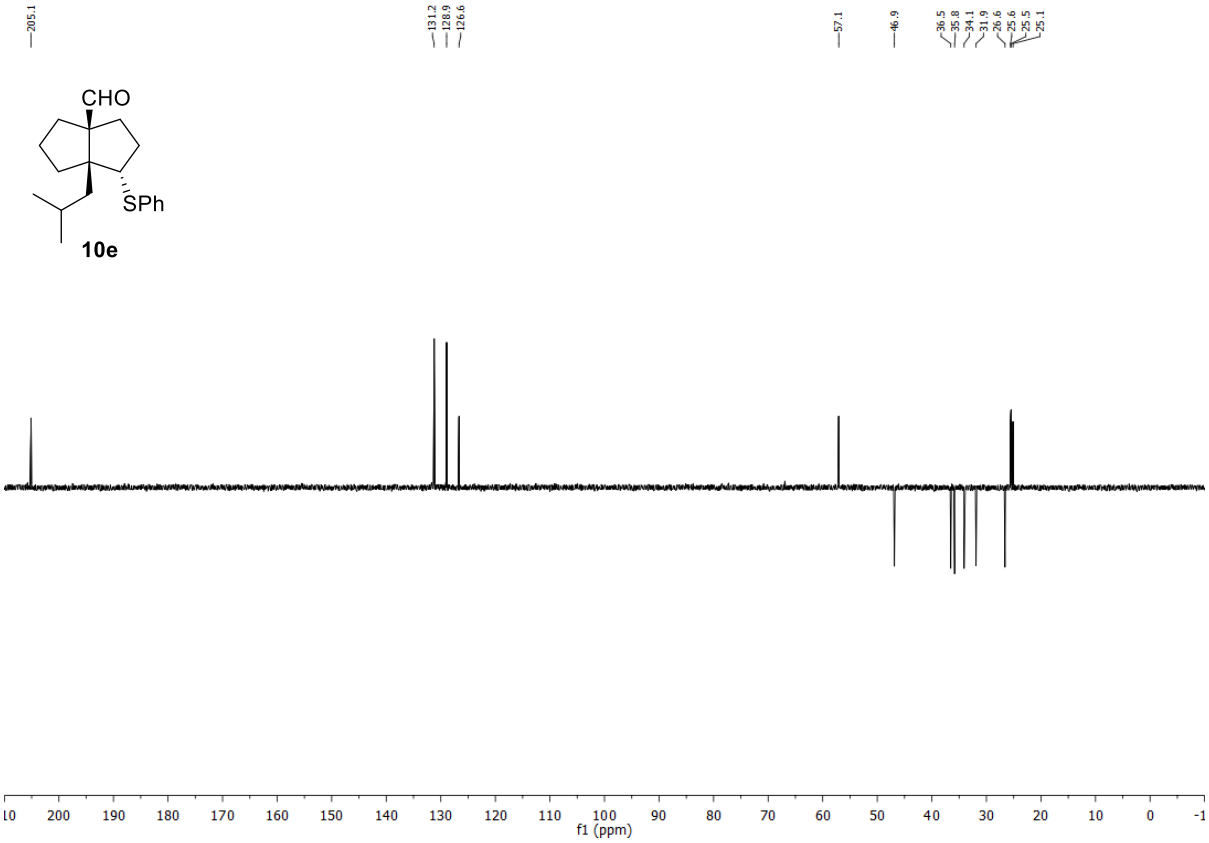


^{13}C NMR Spectra of **10e**



DEPT NMR Spectra of **10e**



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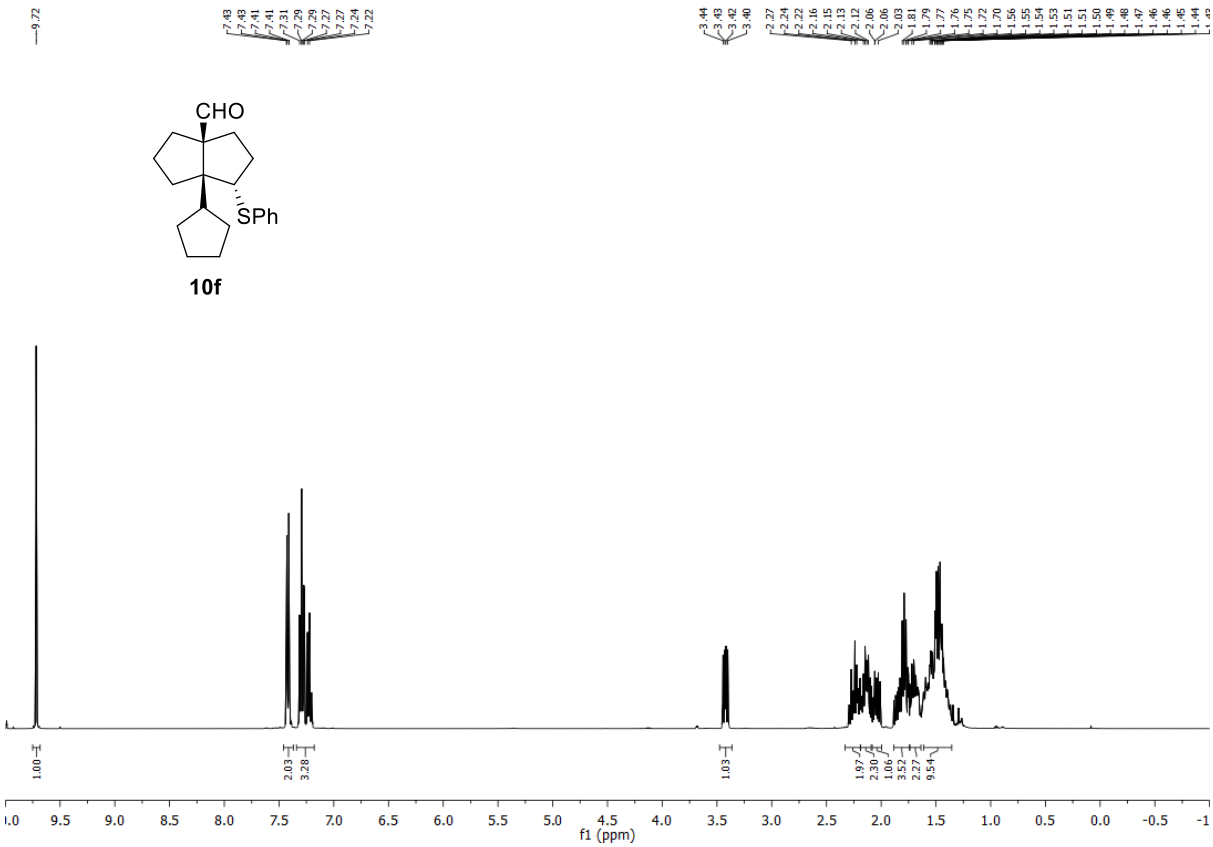

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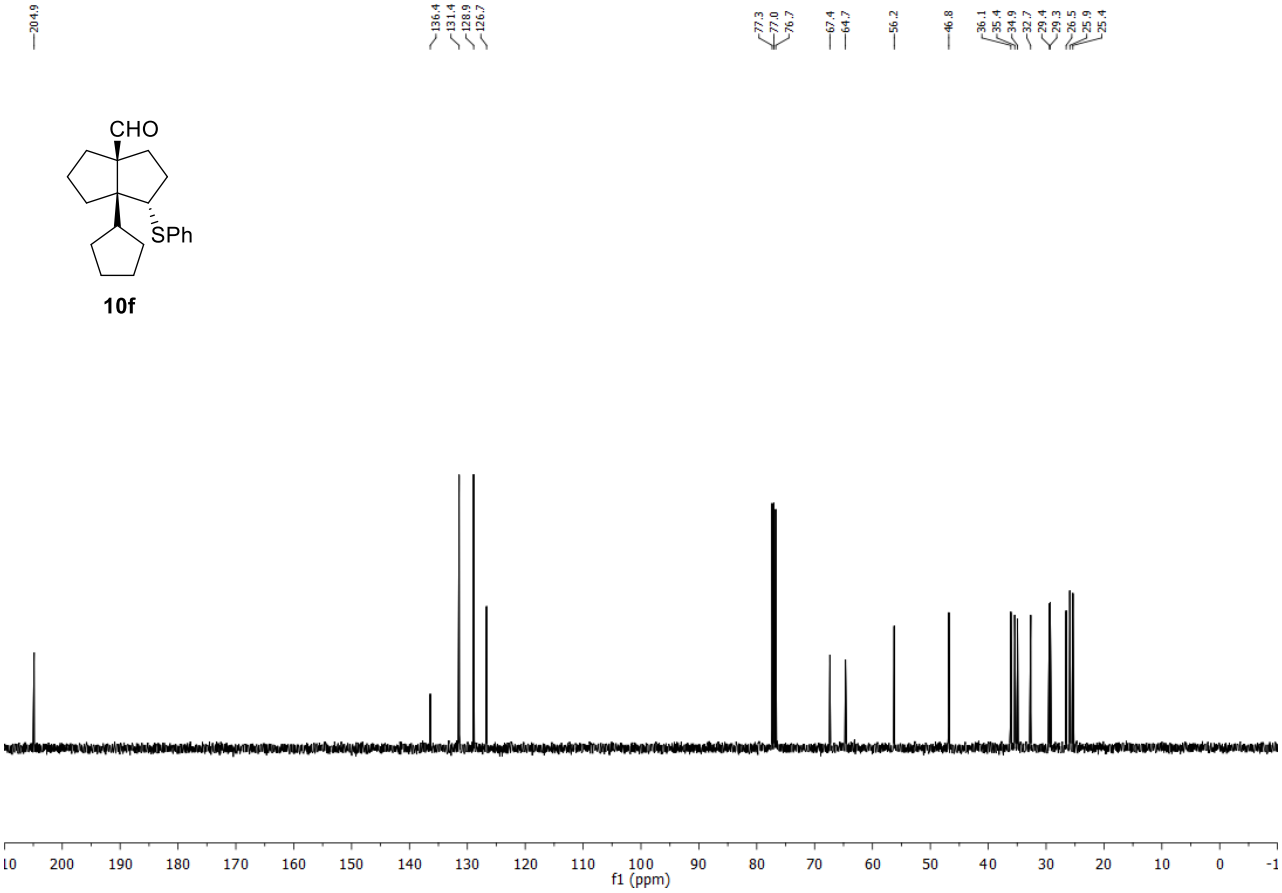
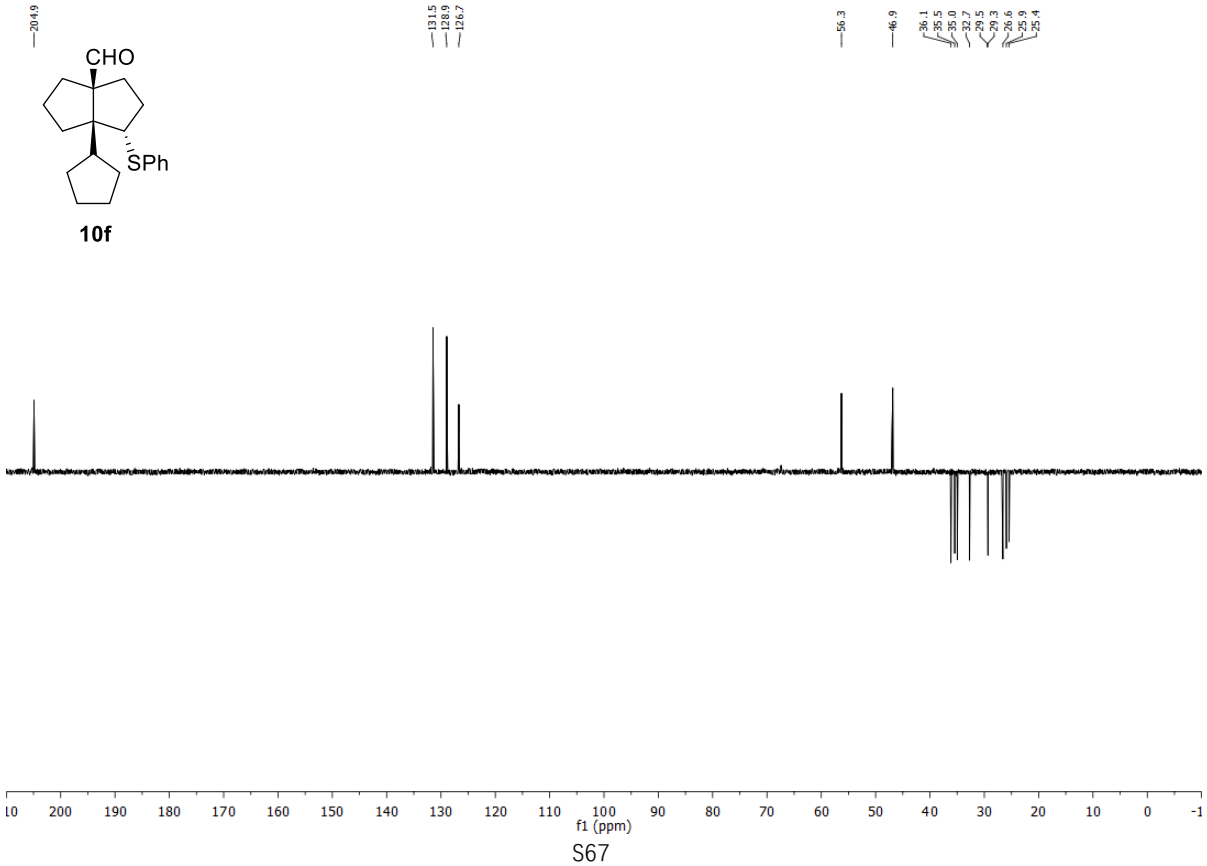
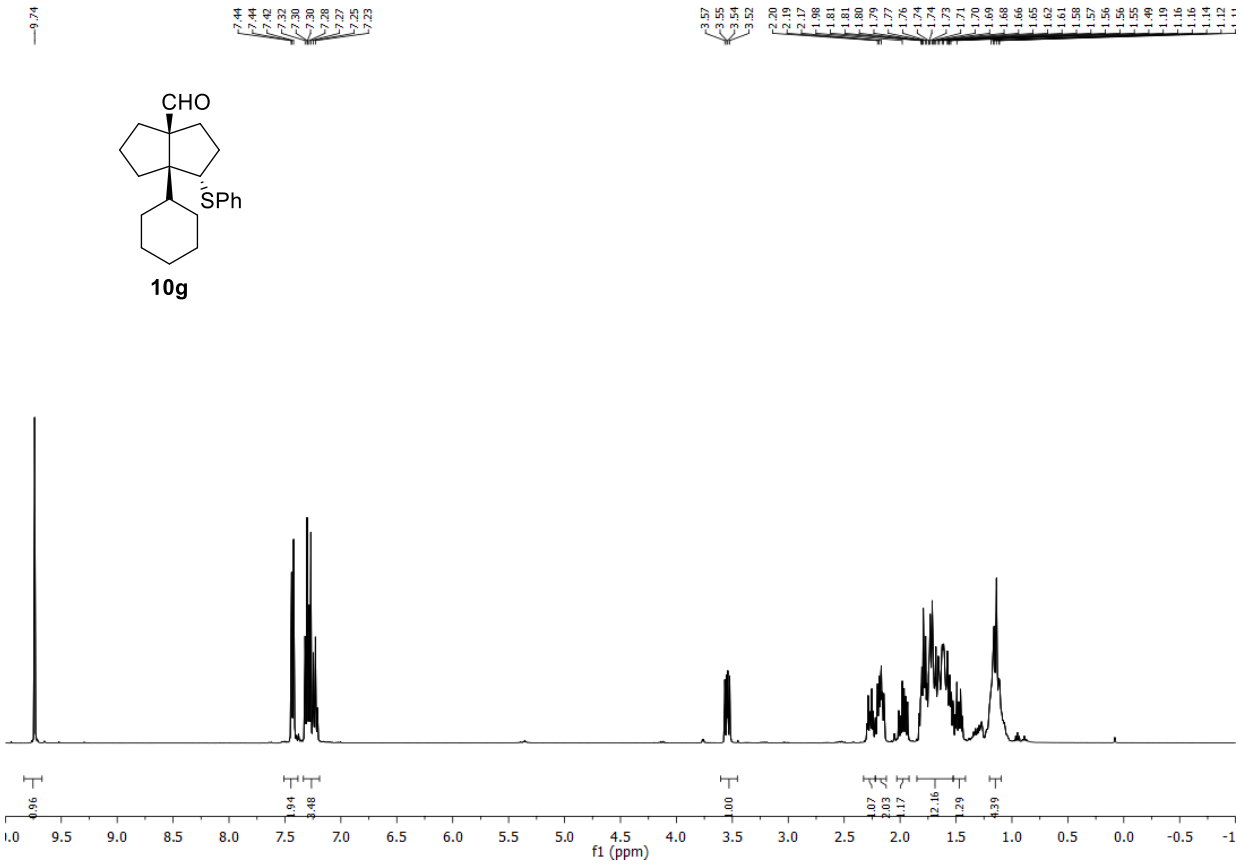


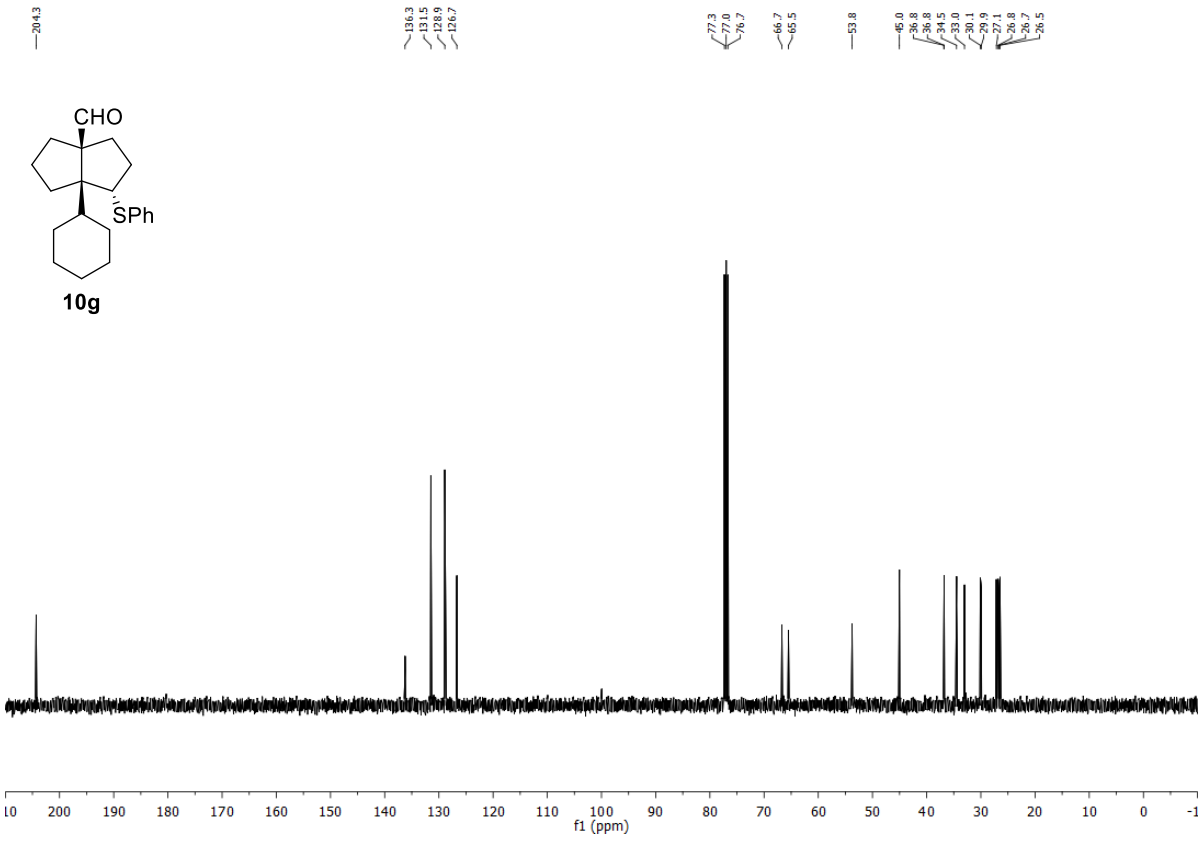
DEPT NMR Spectra of **10f**



^{1}H NMR Spectra of **10g**



^{13}C NMR Spectra of **10g**



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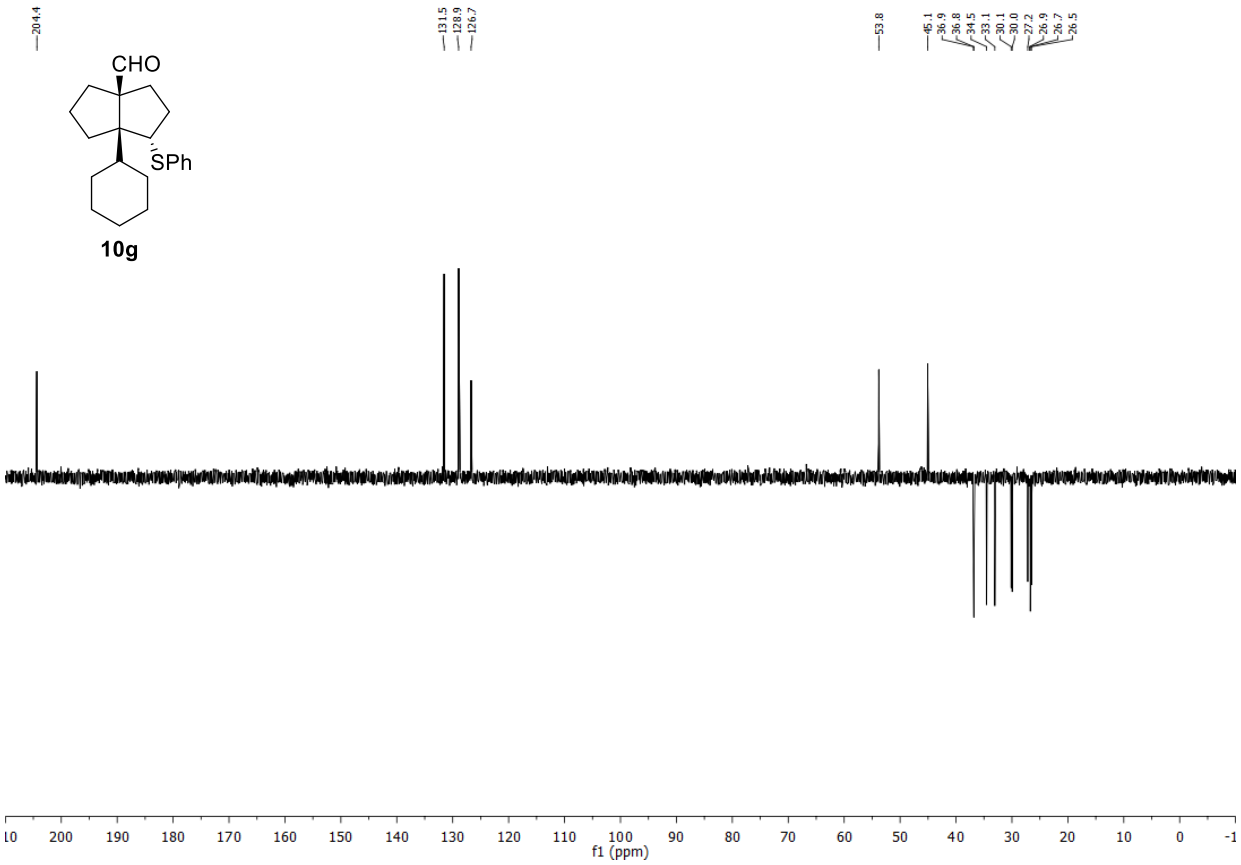

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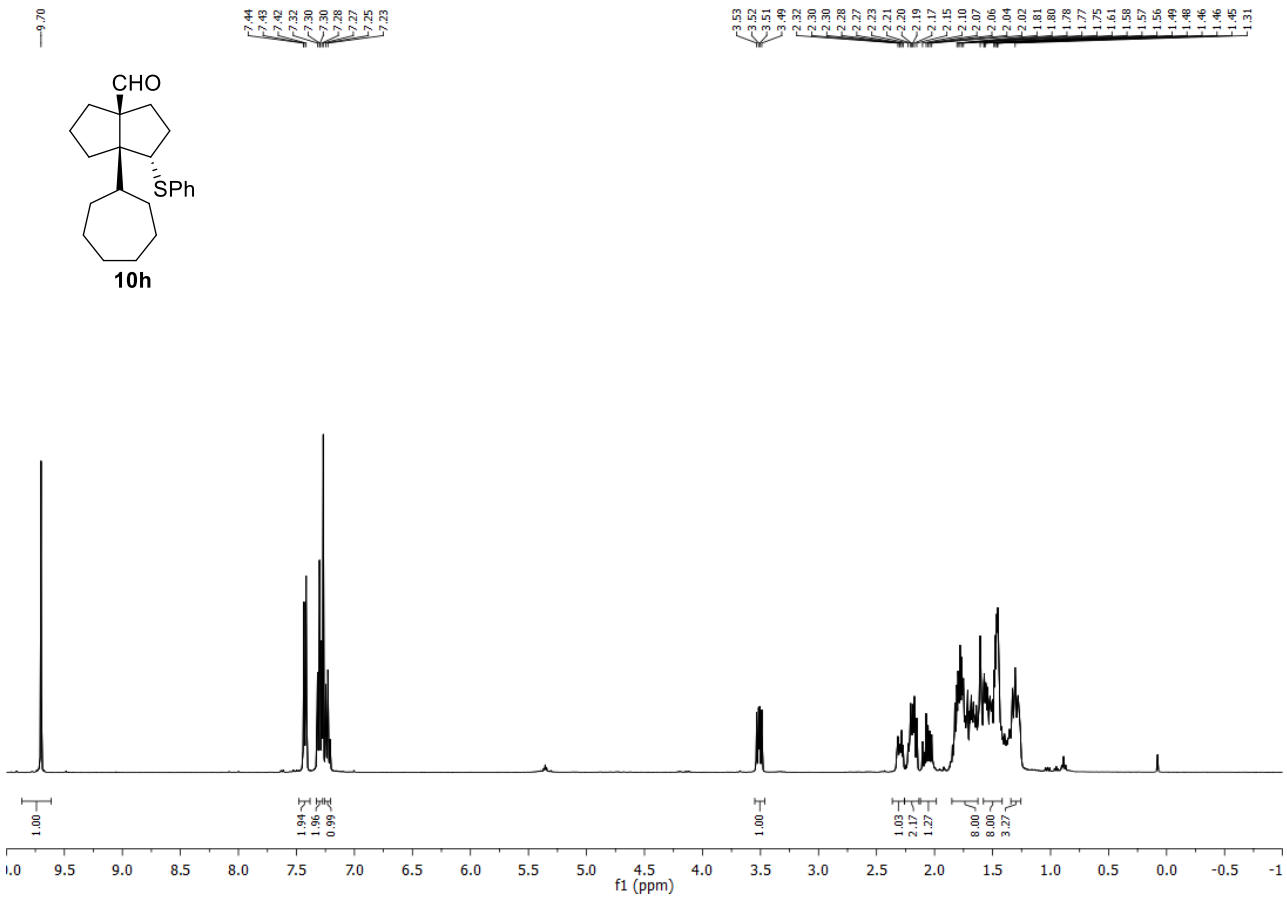
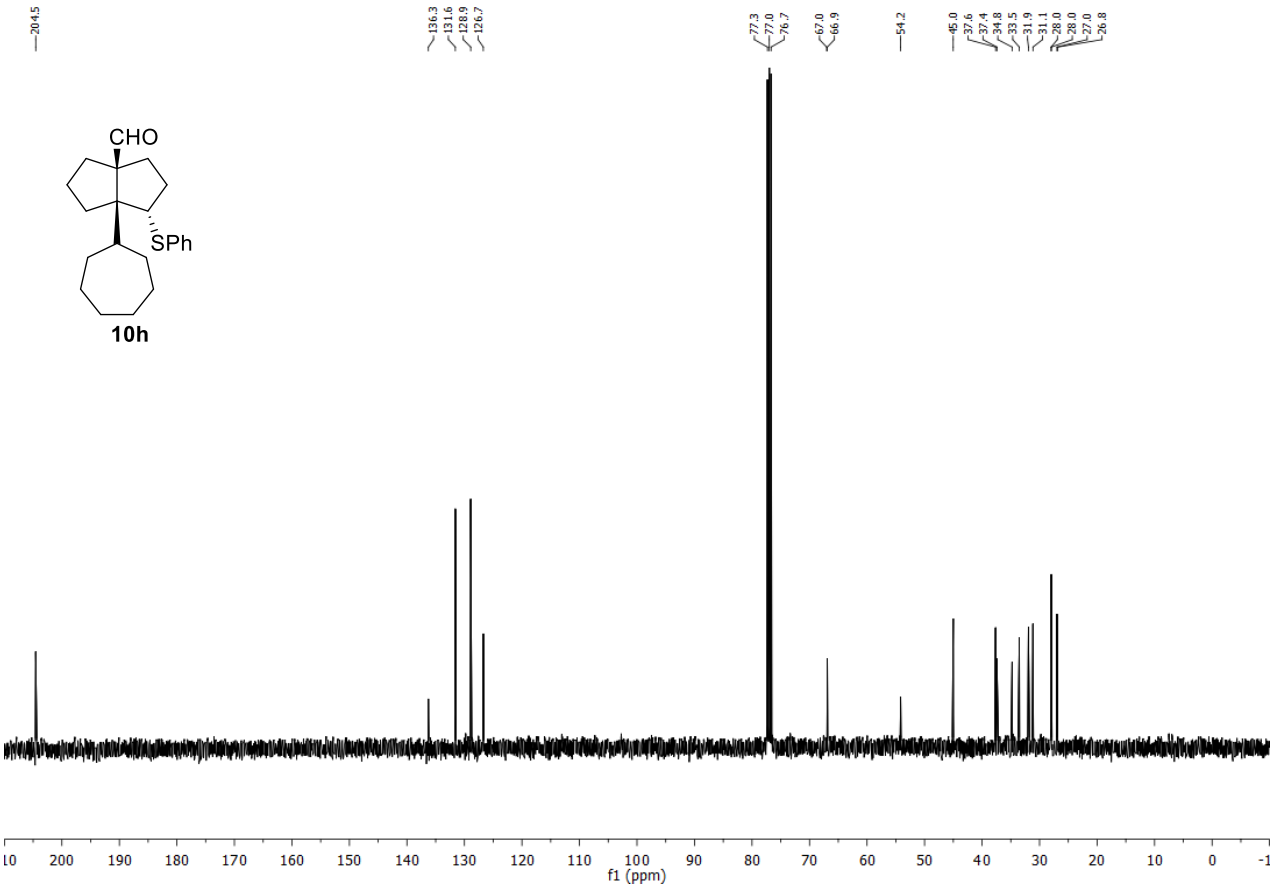
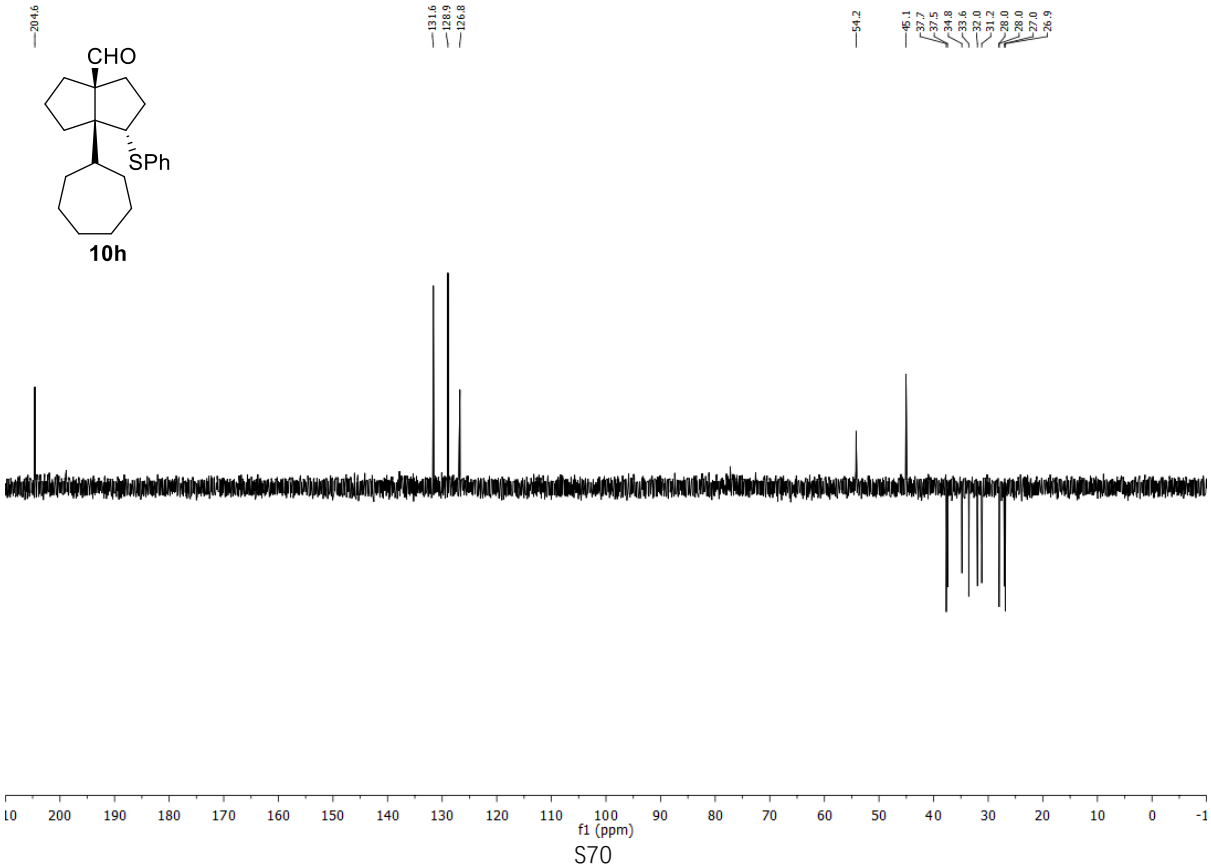


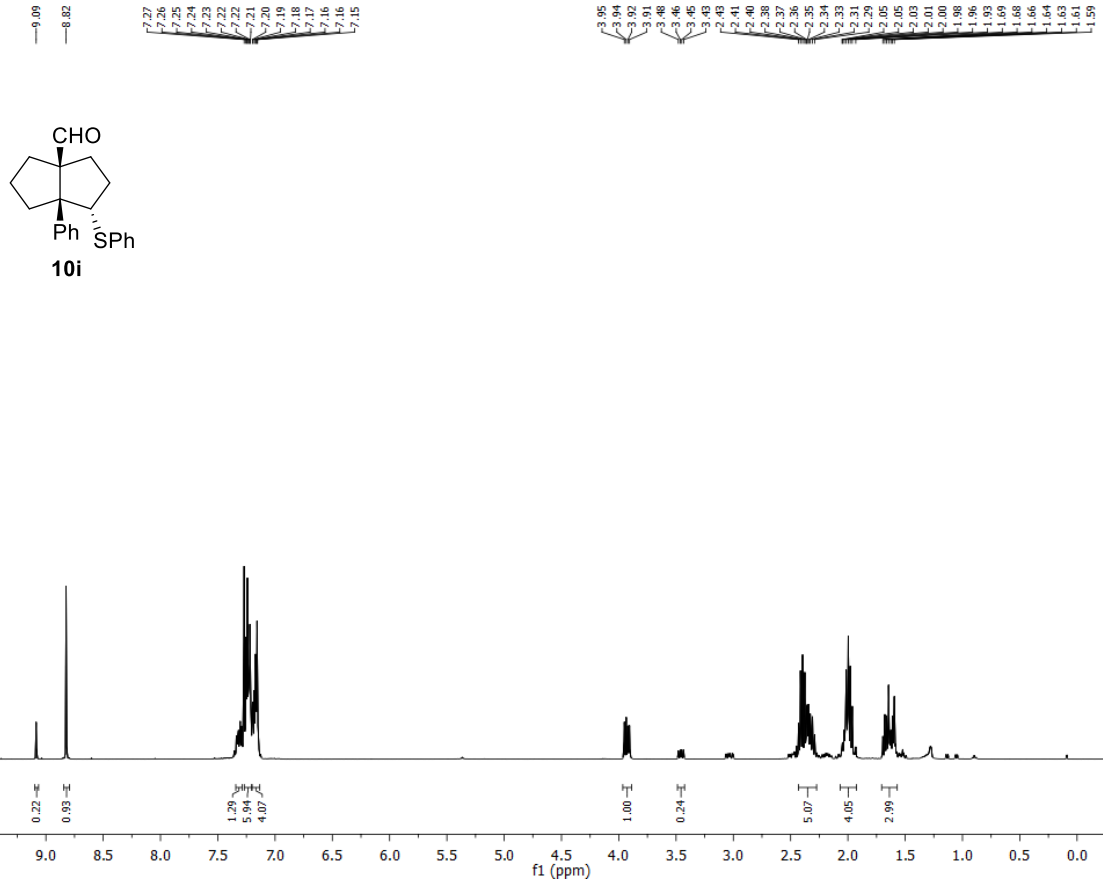
^{13}C NMR Spectra of **10h**



DEPT NMR Spectra of **10h**



^{1}H NMR Spectra of **10i**



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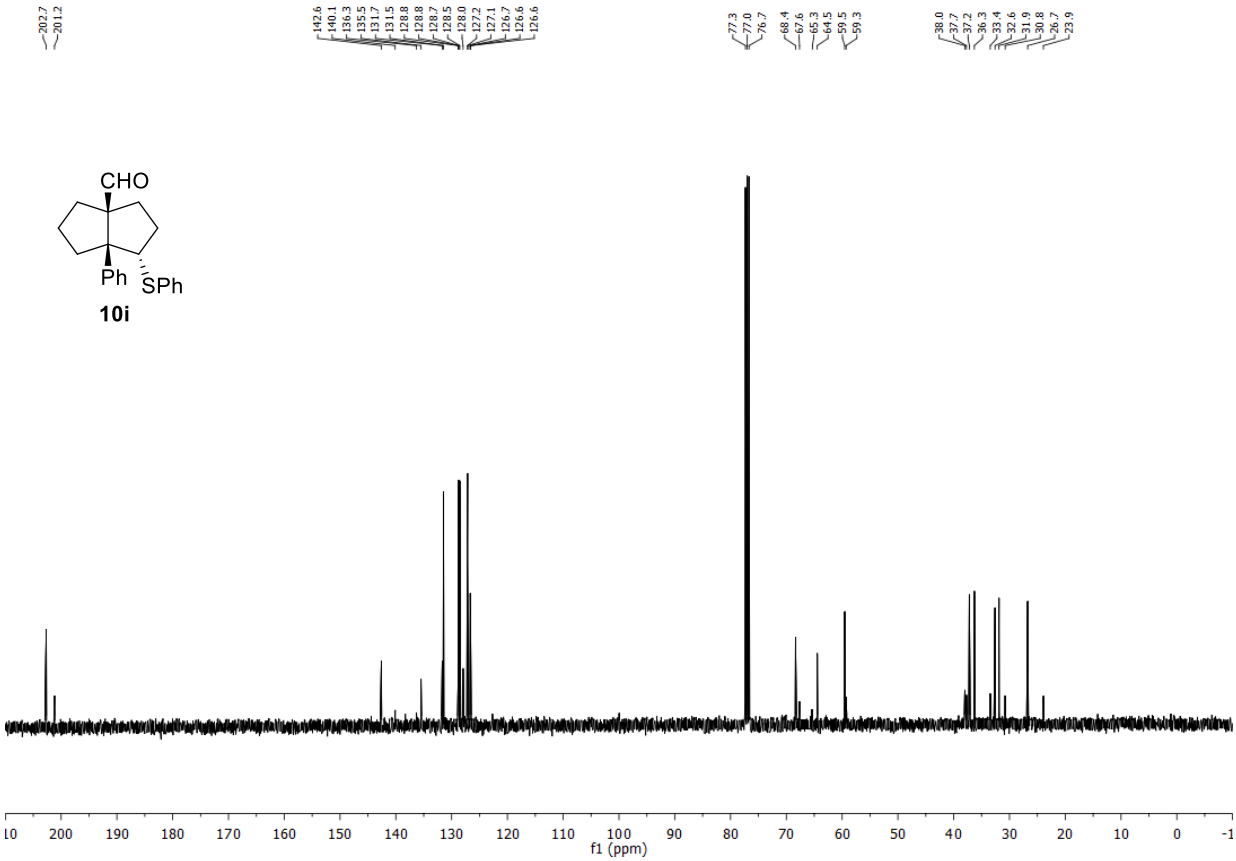
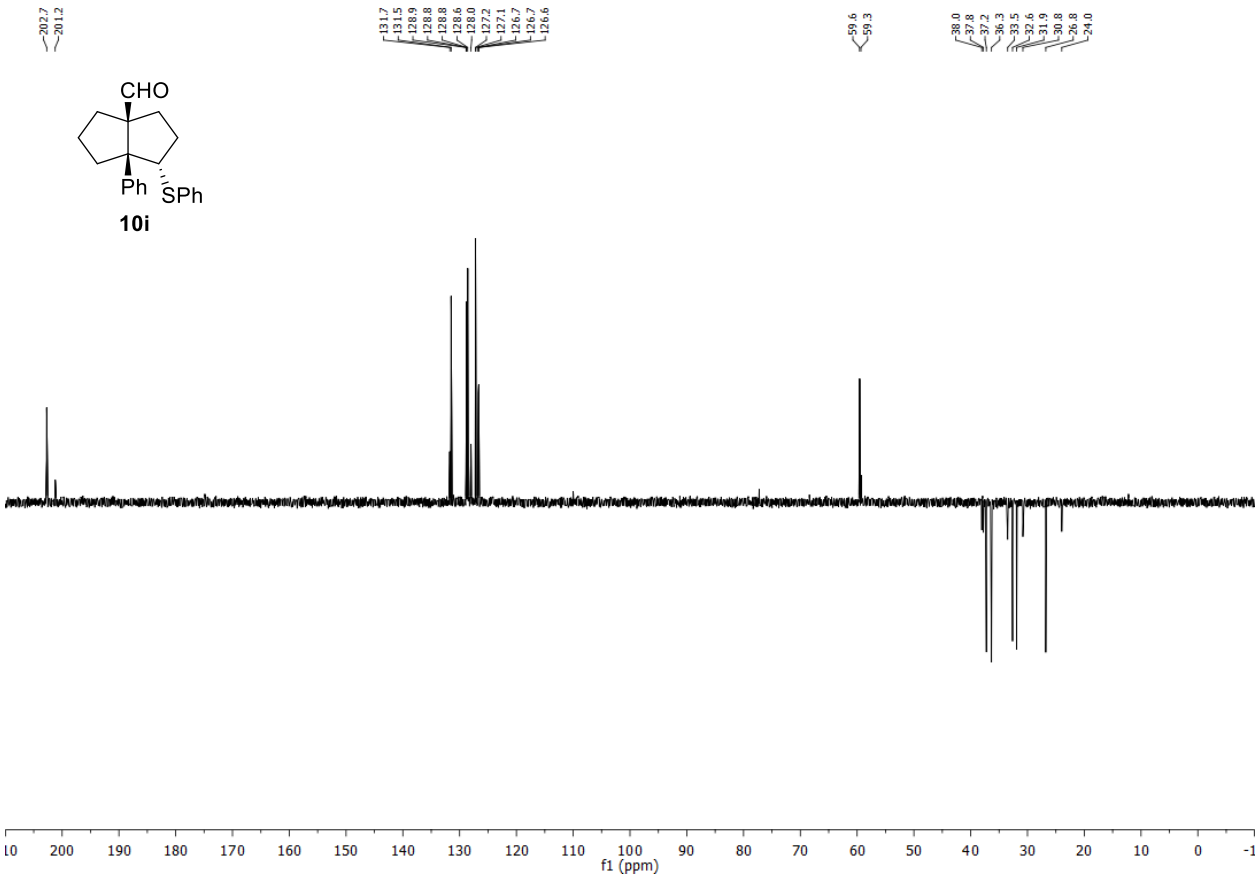
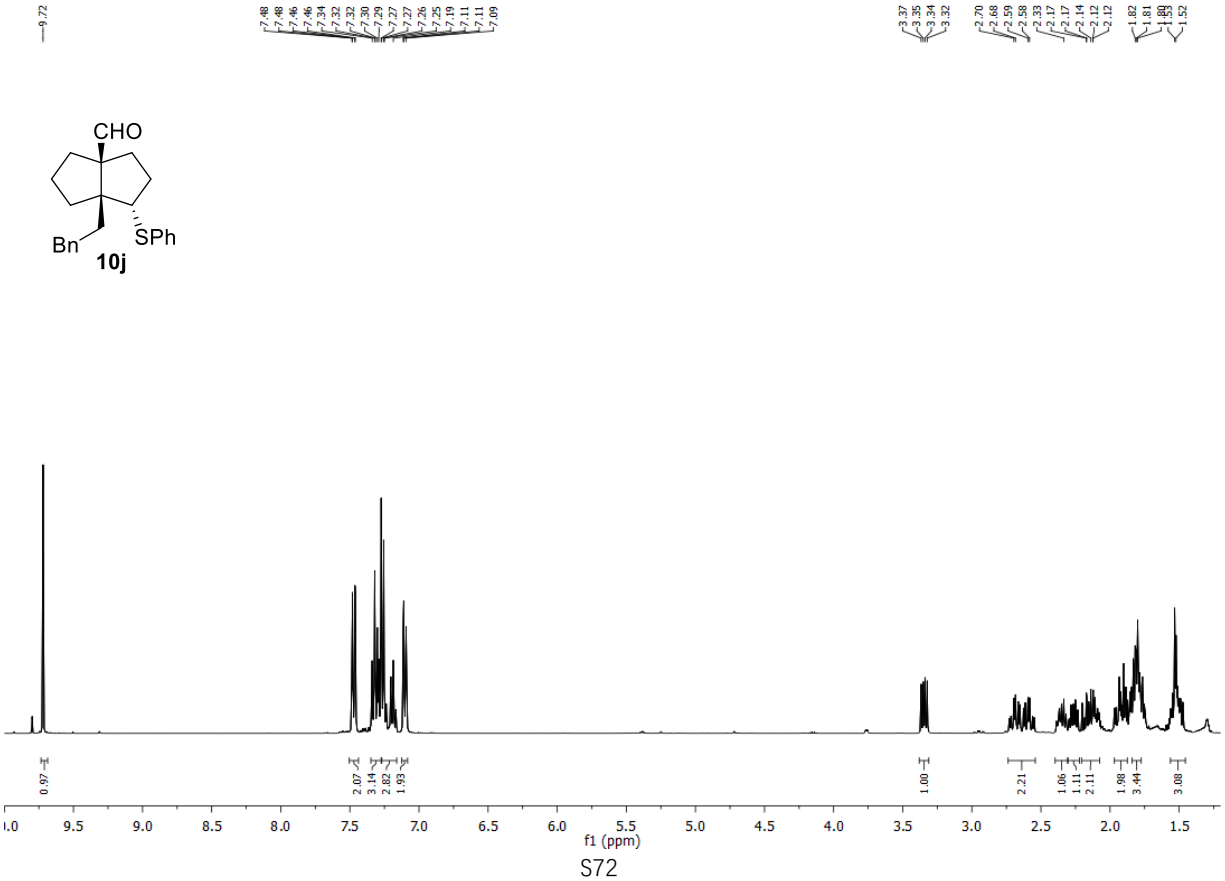


DEPT NMR Spectra of **10i**



^{1}H NMR Spectra of **10j**



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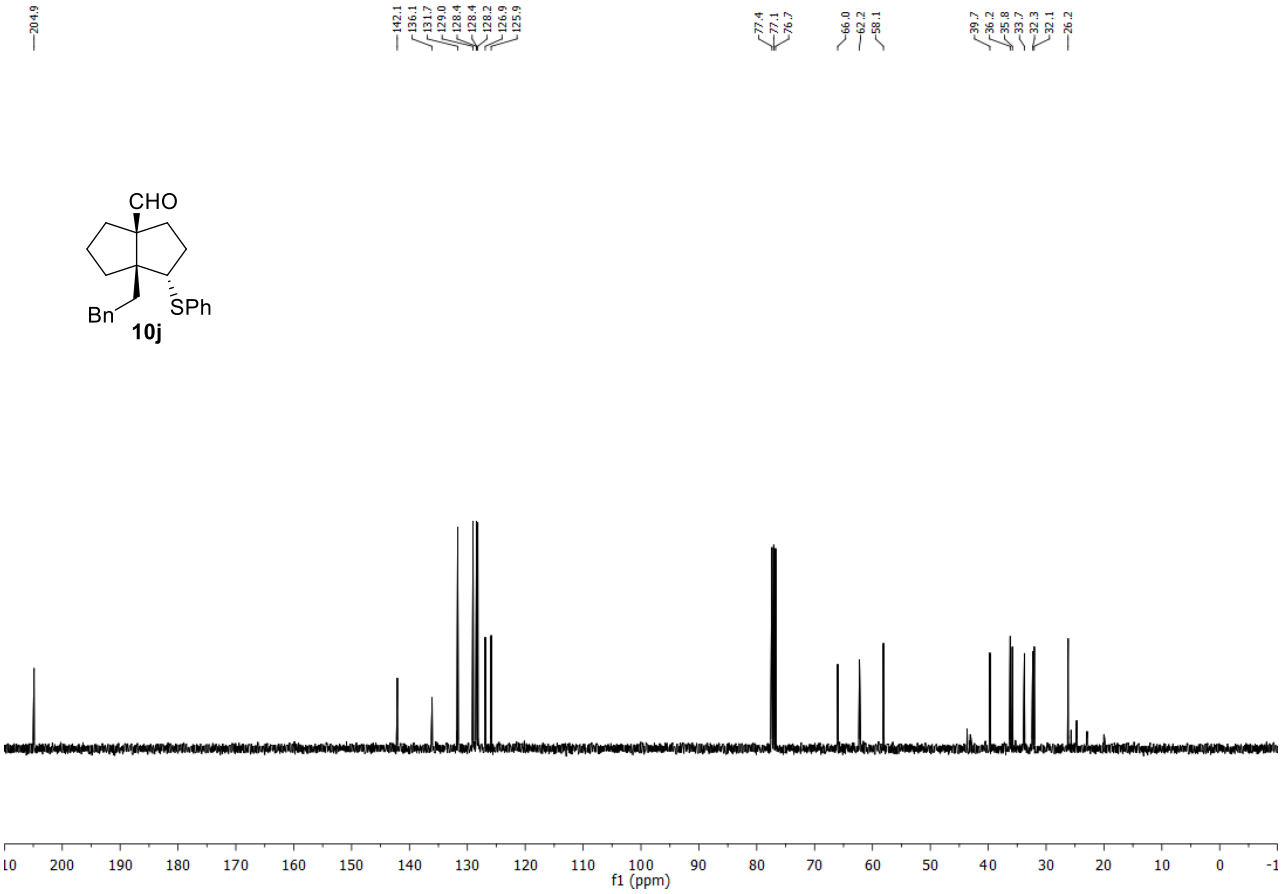
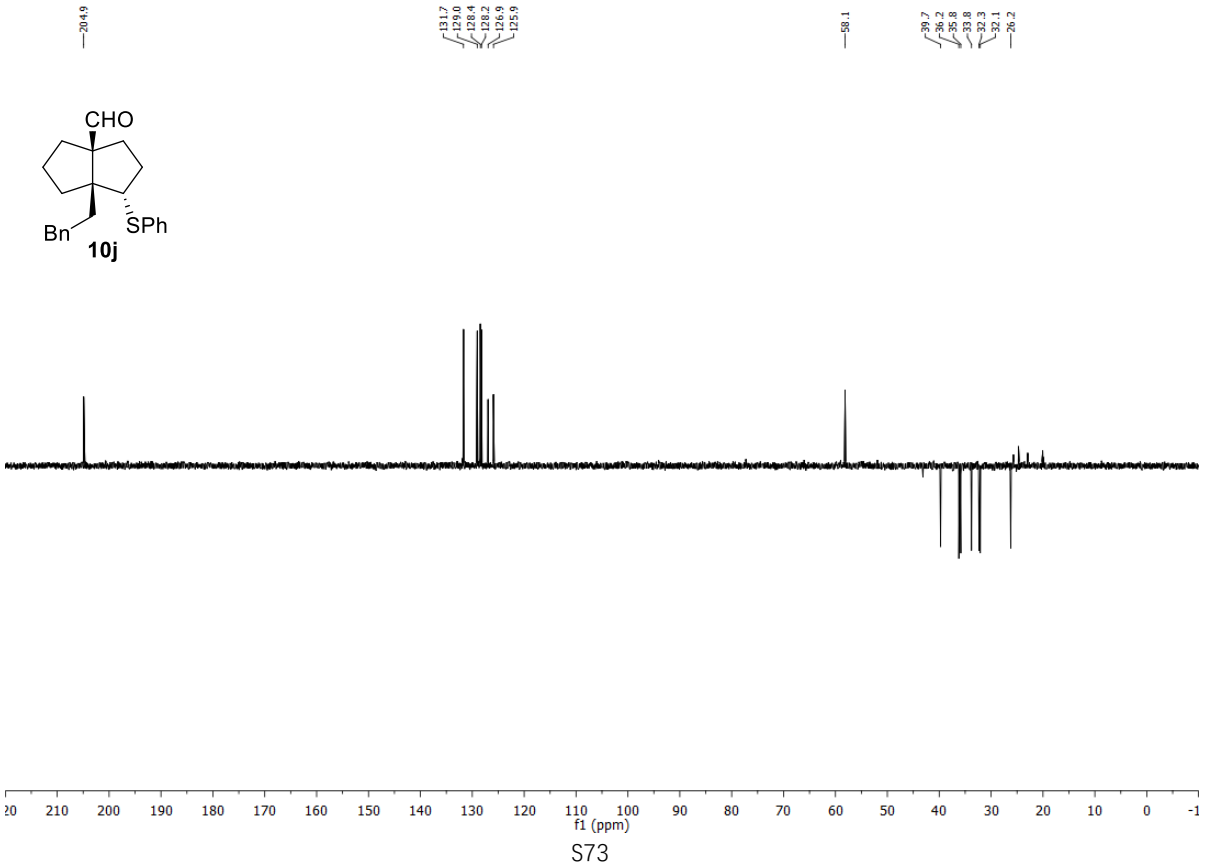
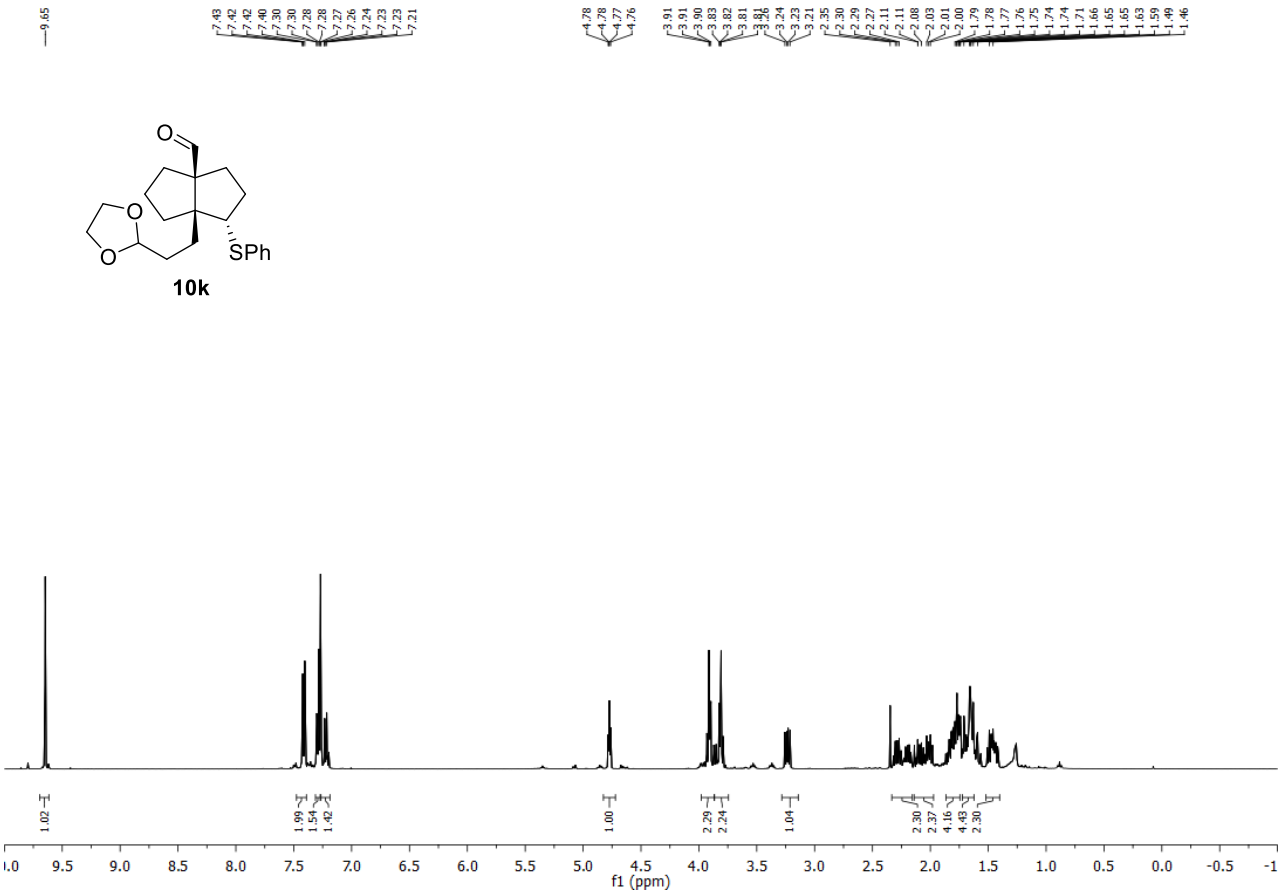


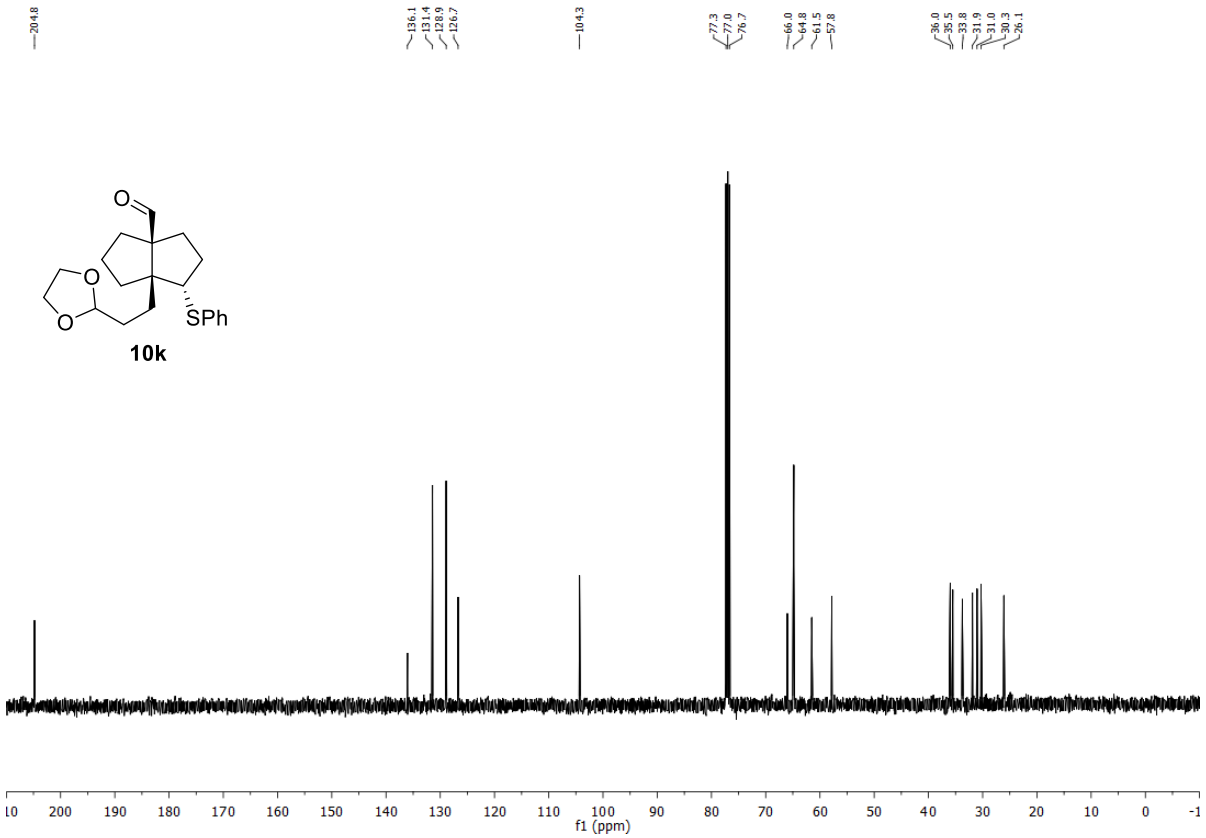
DEPT NMR Spectra of **10j**



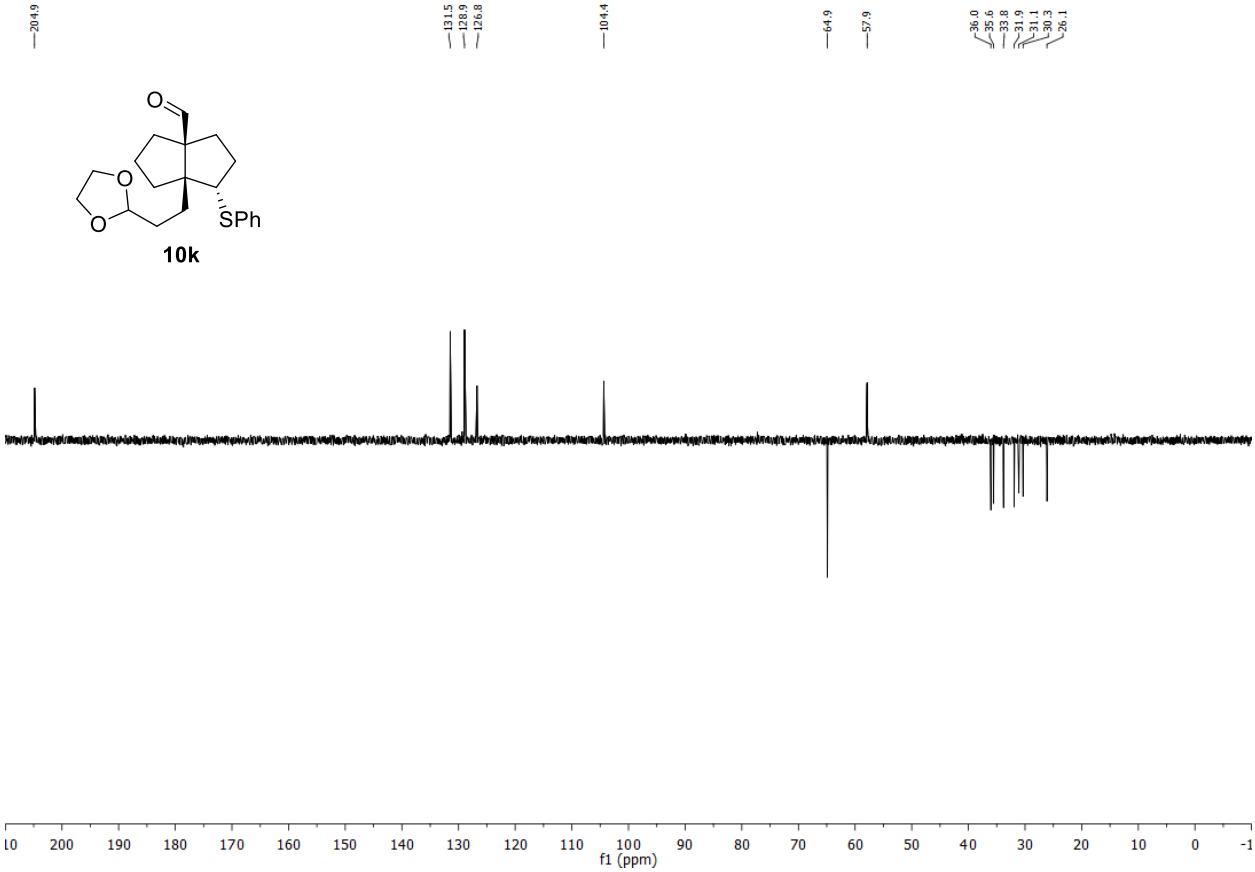
^{1}H NMR Spectra of **10k**



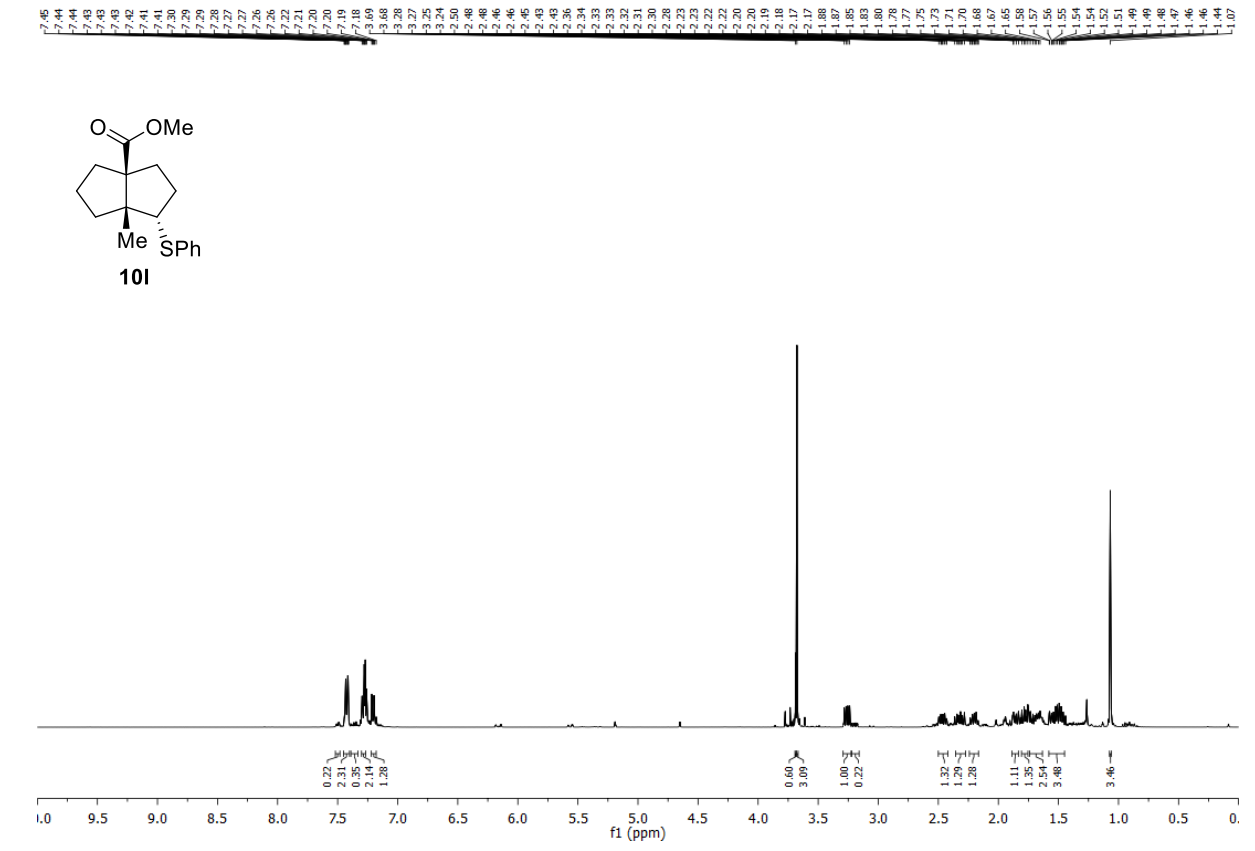
^{13}C NMR Spectra of **10k**



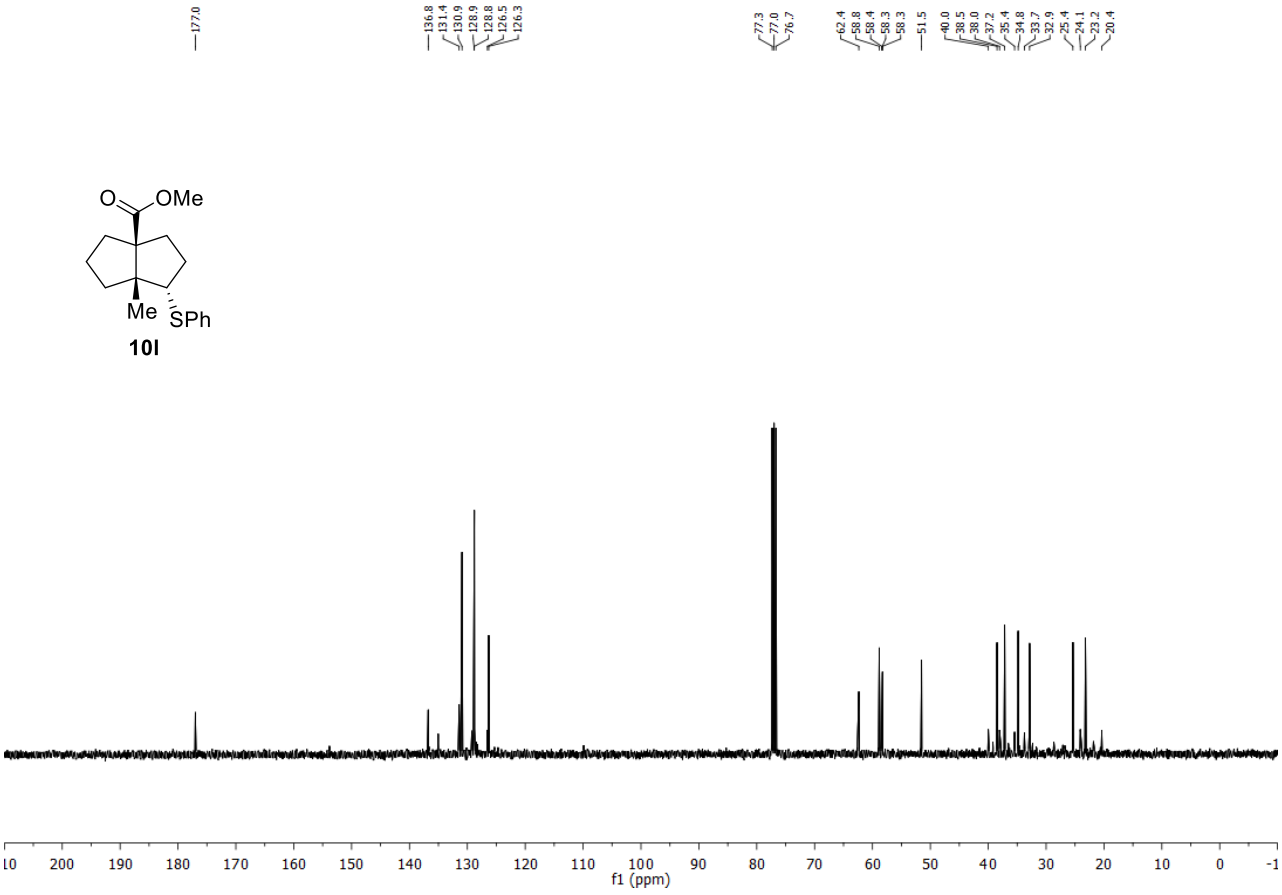
DEPT NMR Spectra of **10k**



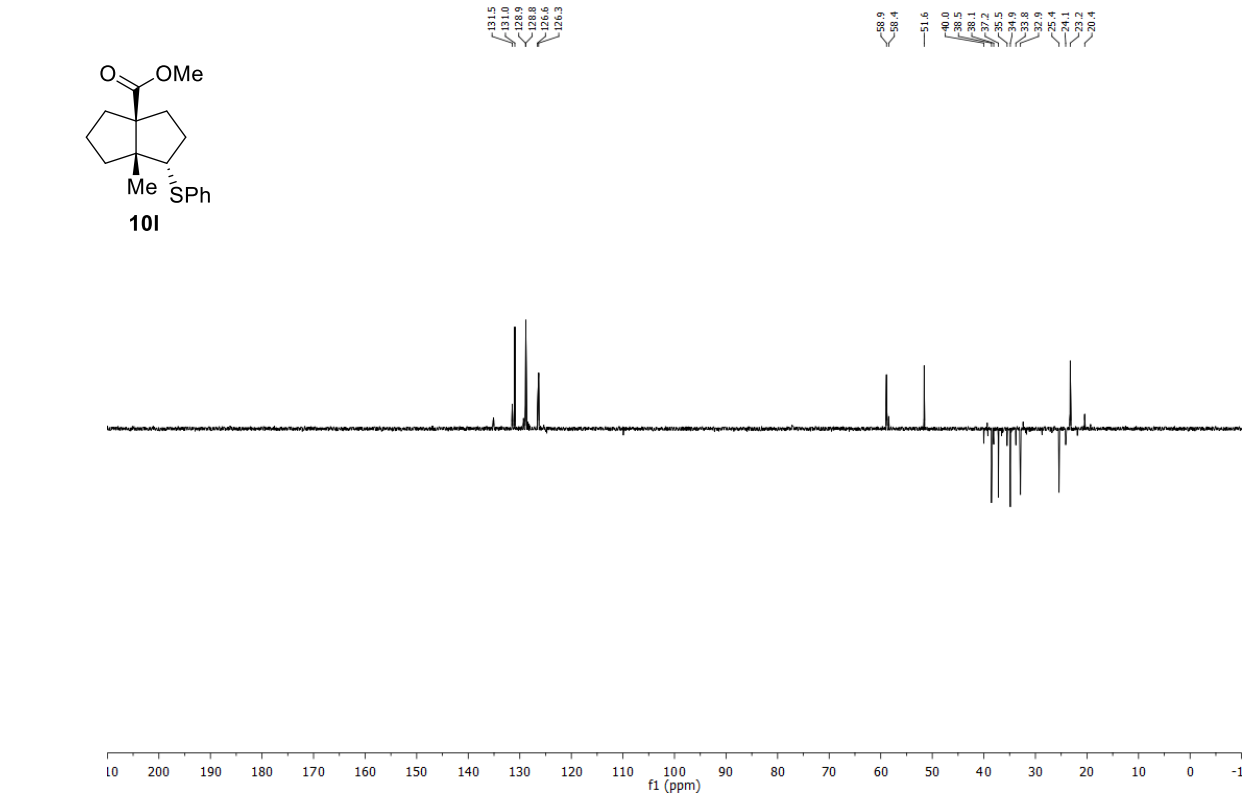
^{1}H NMR Spectra of **10l**



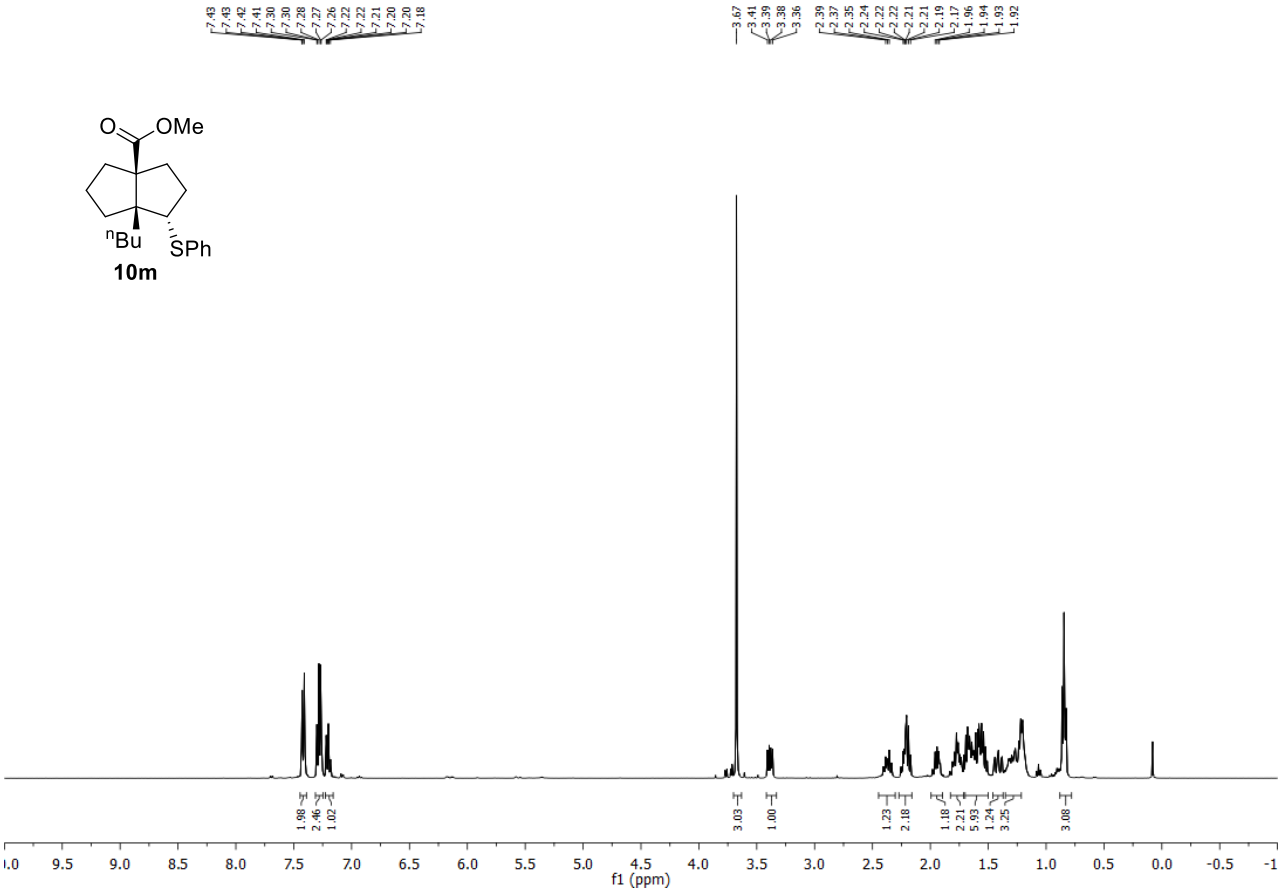
^{13}C NMR Spectra of **10l**



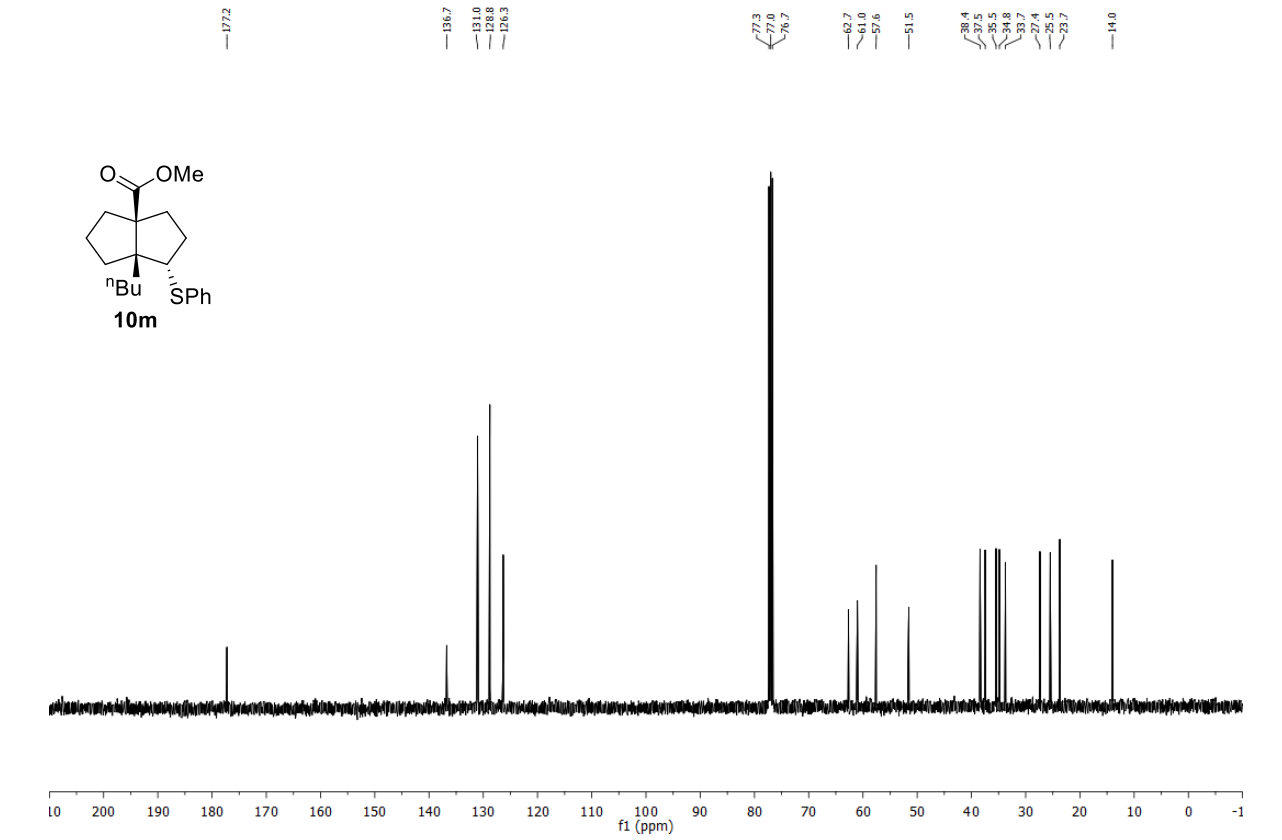
DEPT NMR Spectra of **10l**



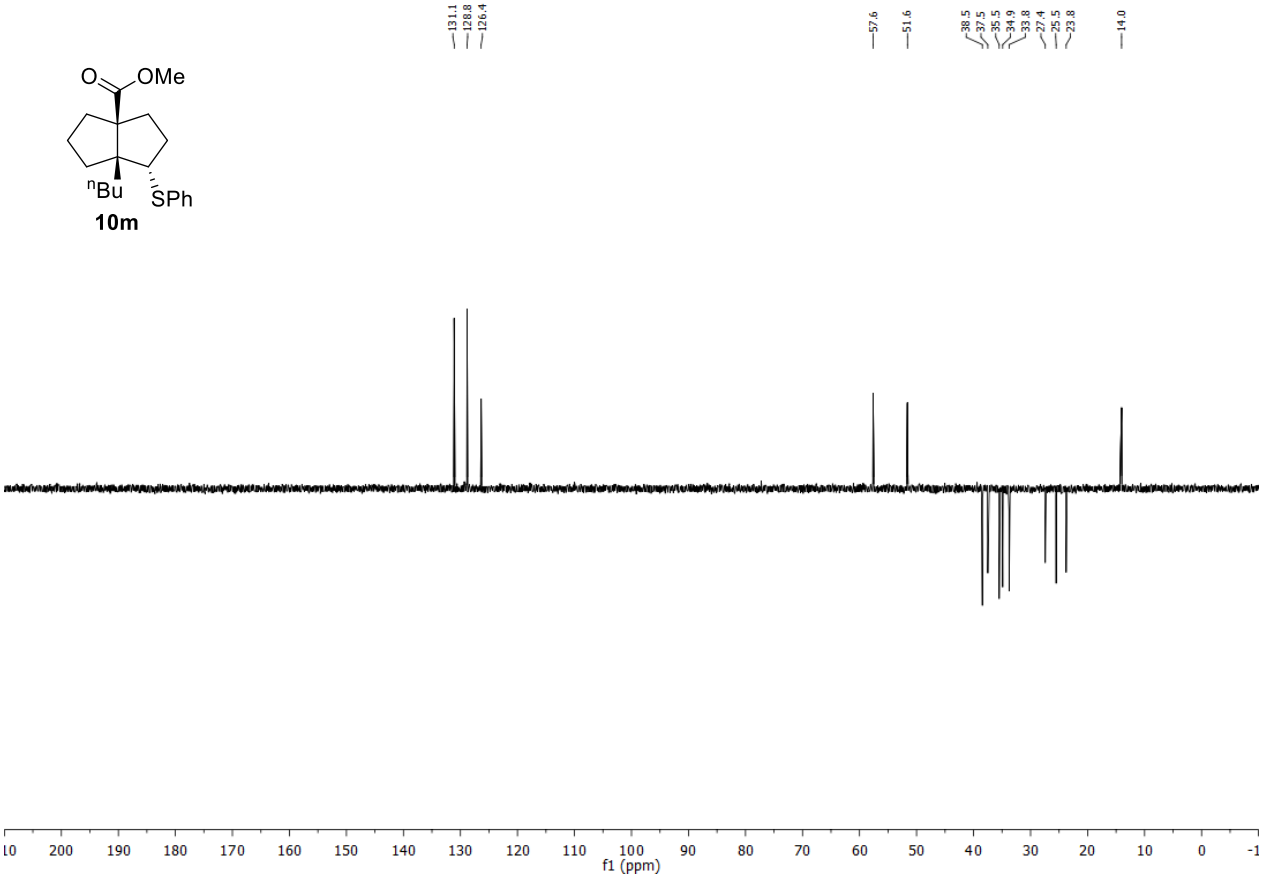
^{1}H NMR Spectra of **10m**



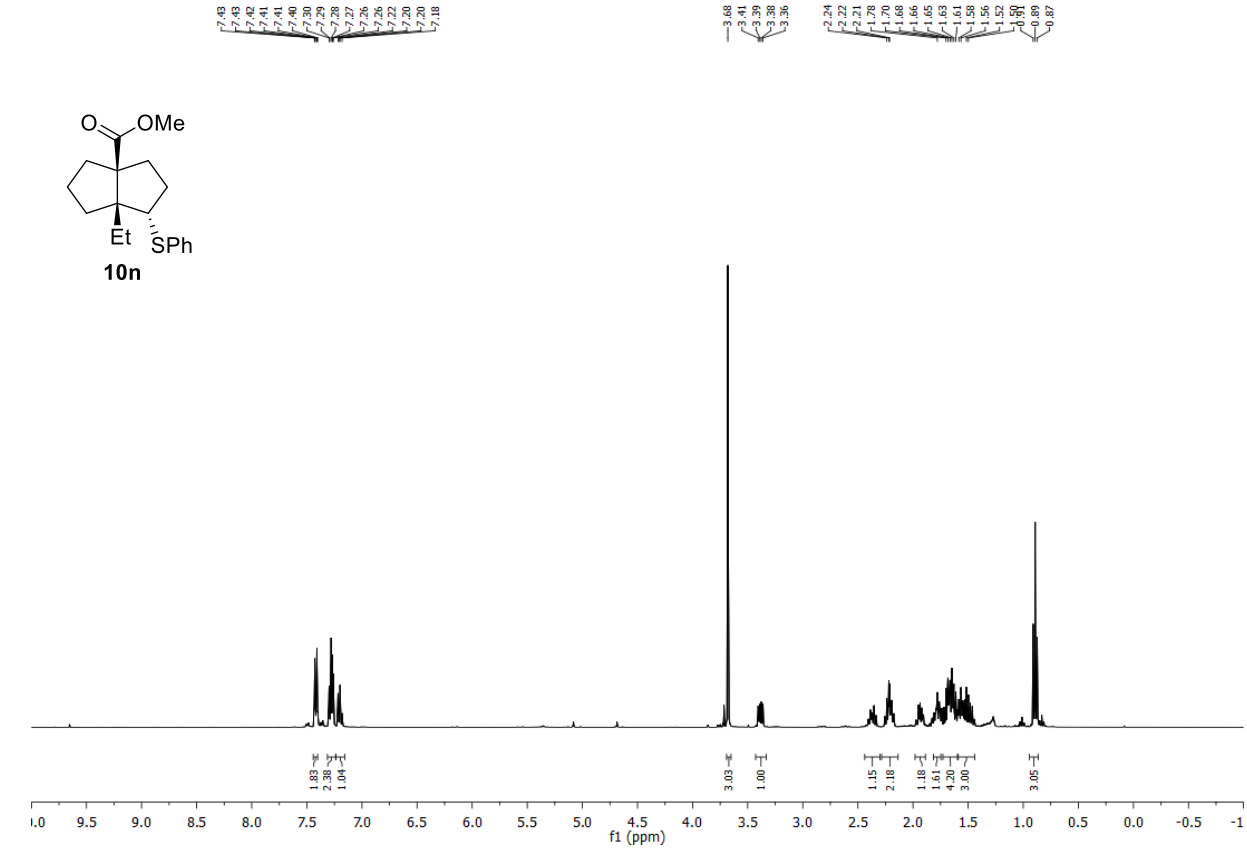
^{13}C NMR Spectra of **10m**



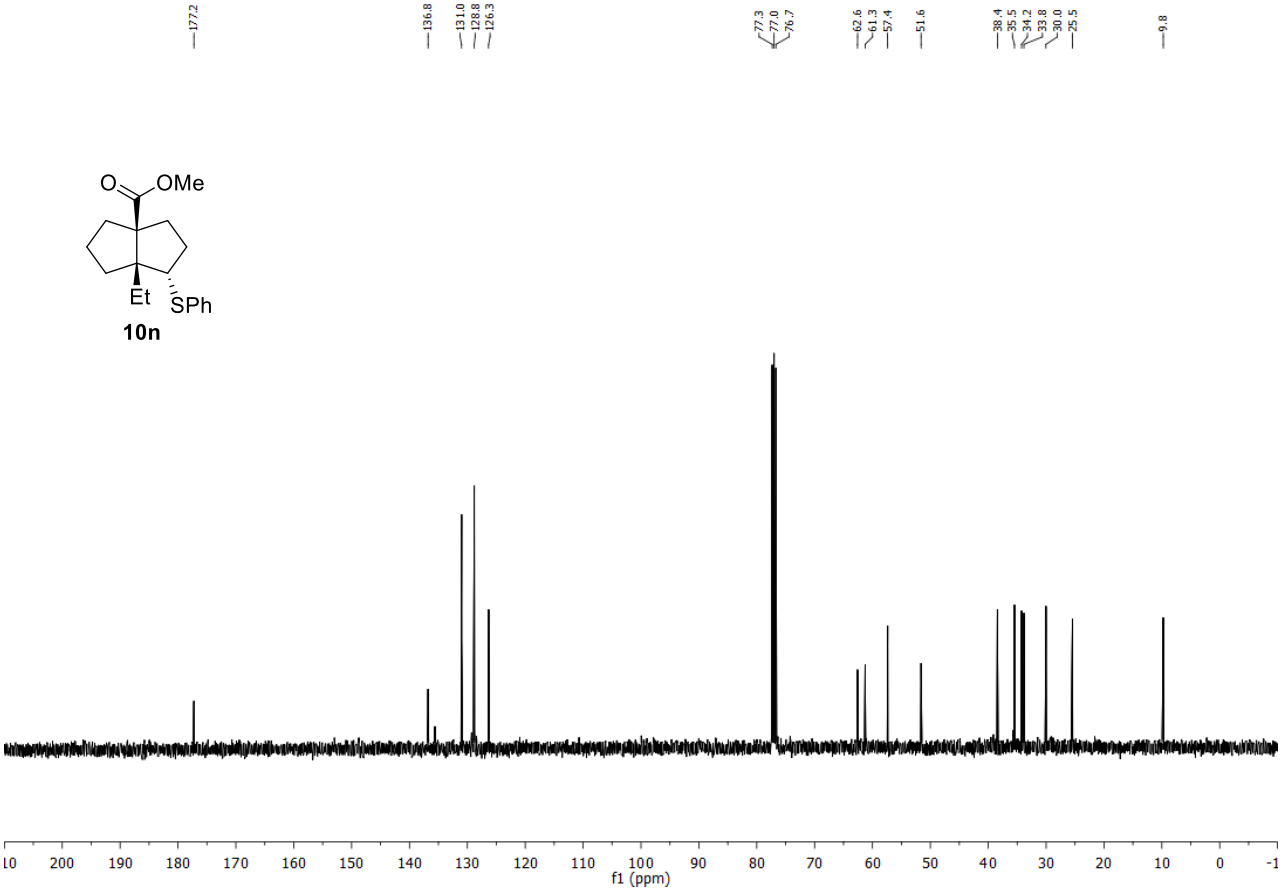
DEPT NMR Spectra of **10m**



^{1}H NMR Spectra of **10n**



^{13}C NMR Spectra of **10n**



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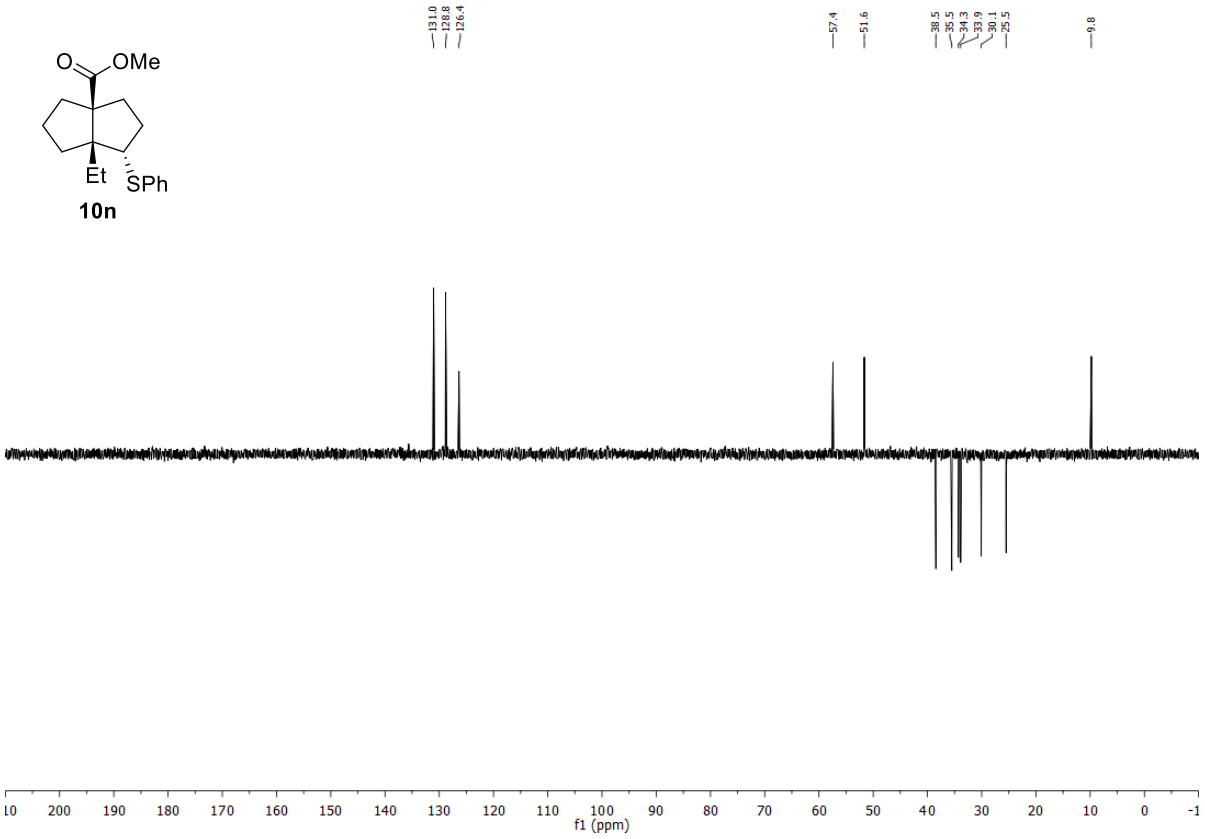
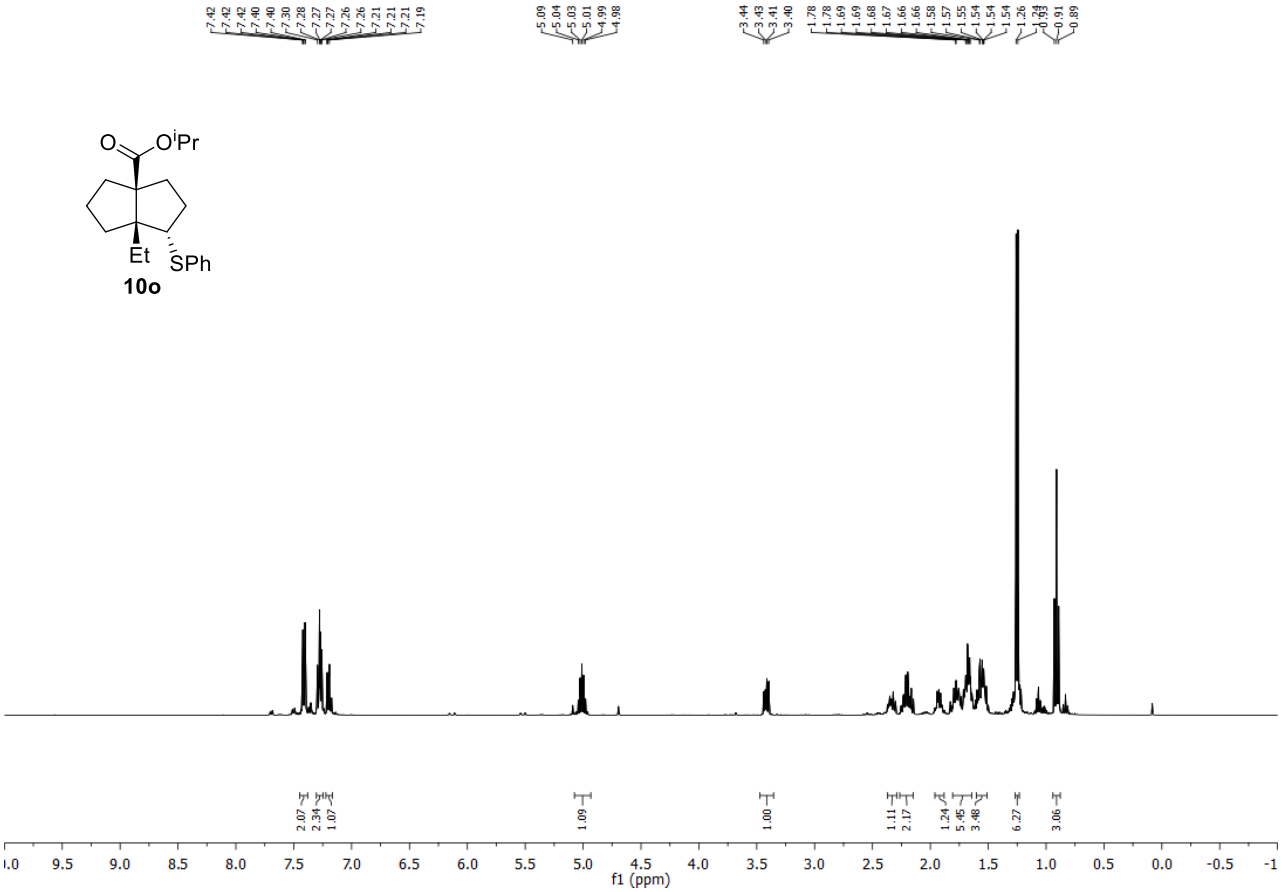


^{1}H NMR Spectra of **10o**



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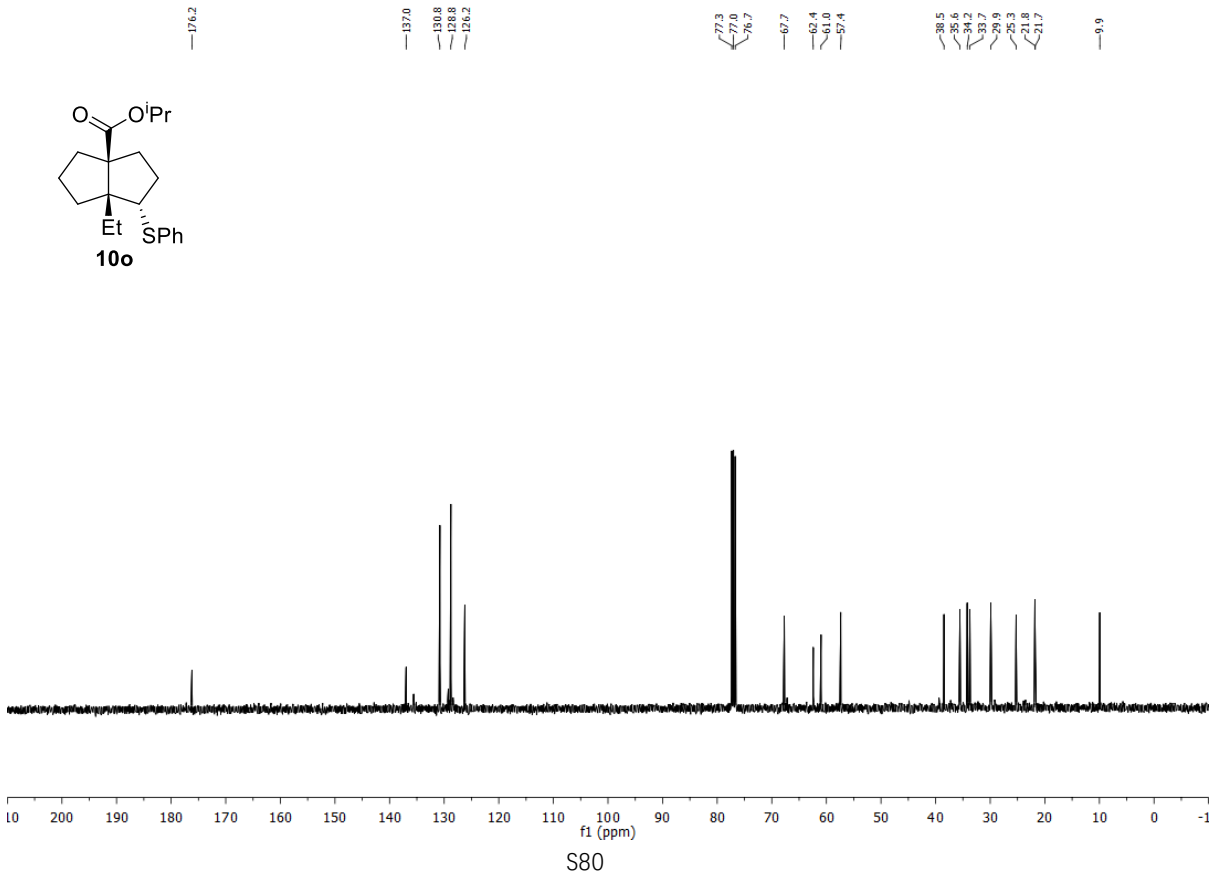
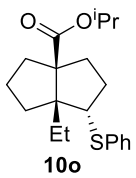
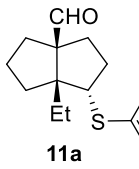


DEPT NMR Spectra of **10o**



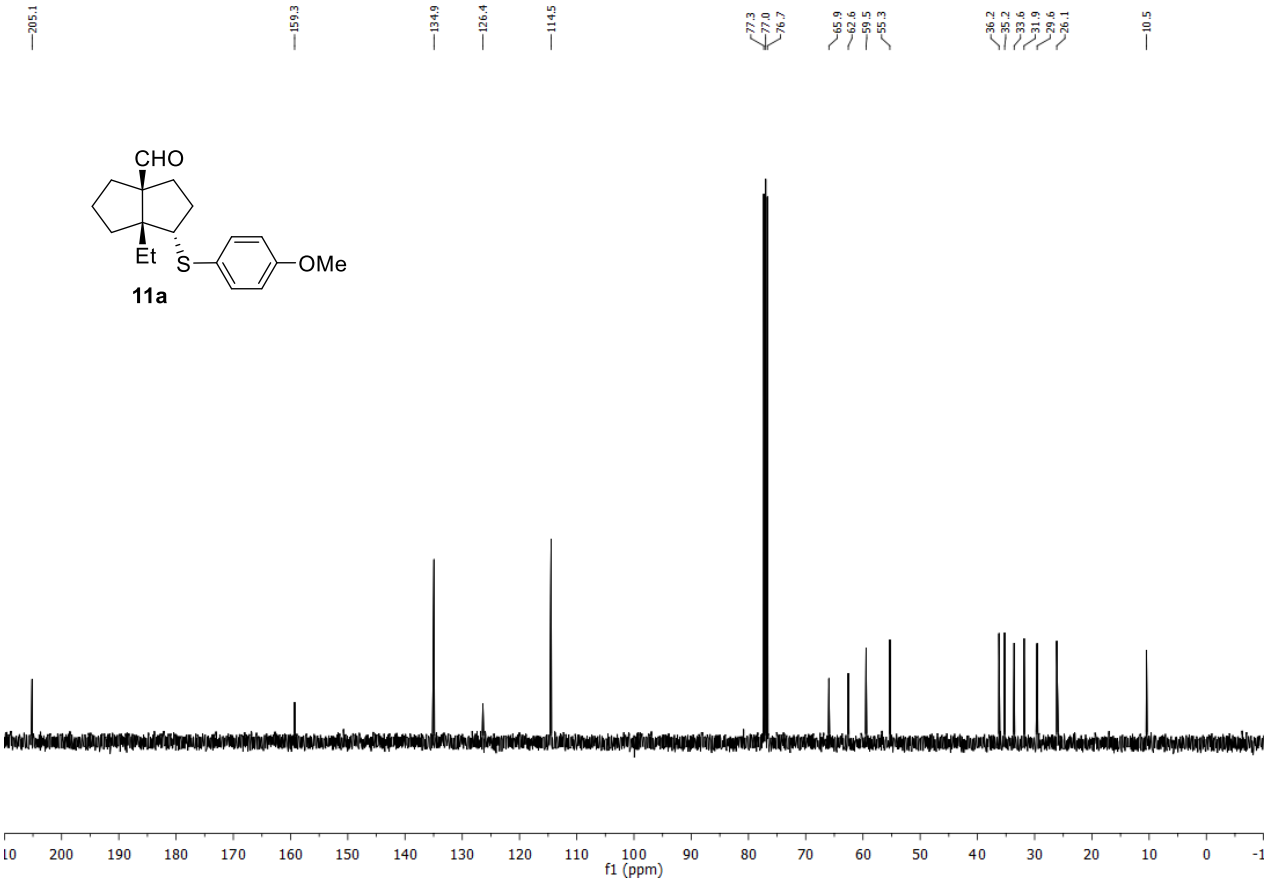
10o

^{1}H NMR Spectra of **11a**

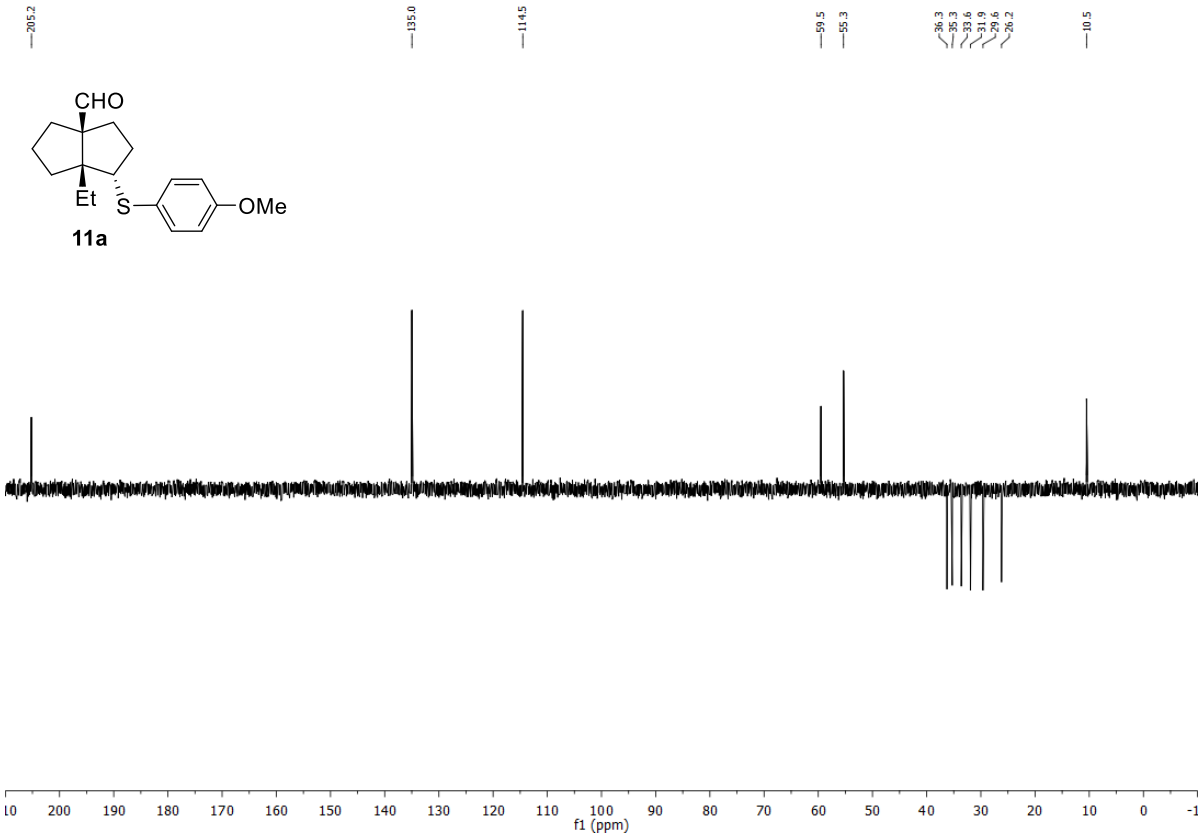


11a

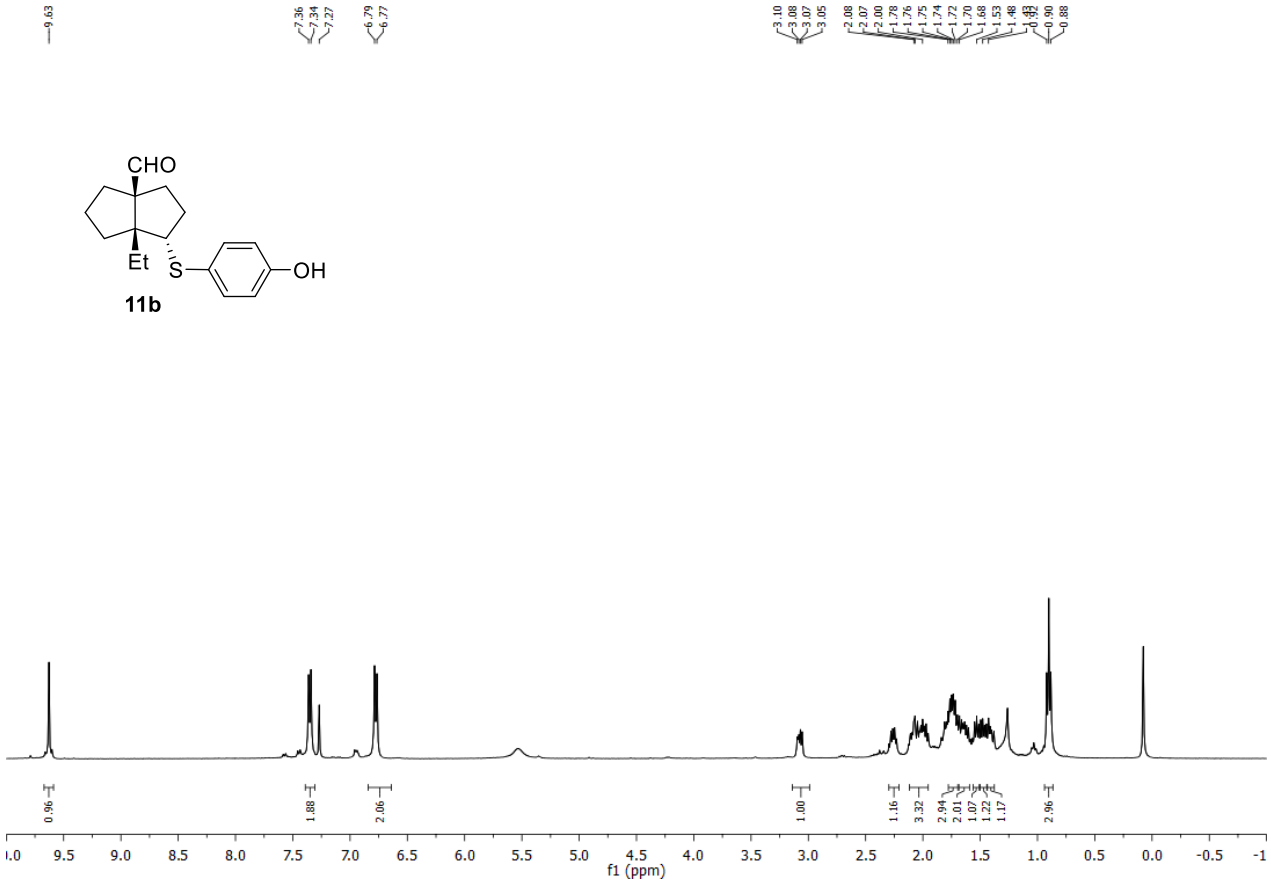
^{13}C NMR Spectra of **11a**



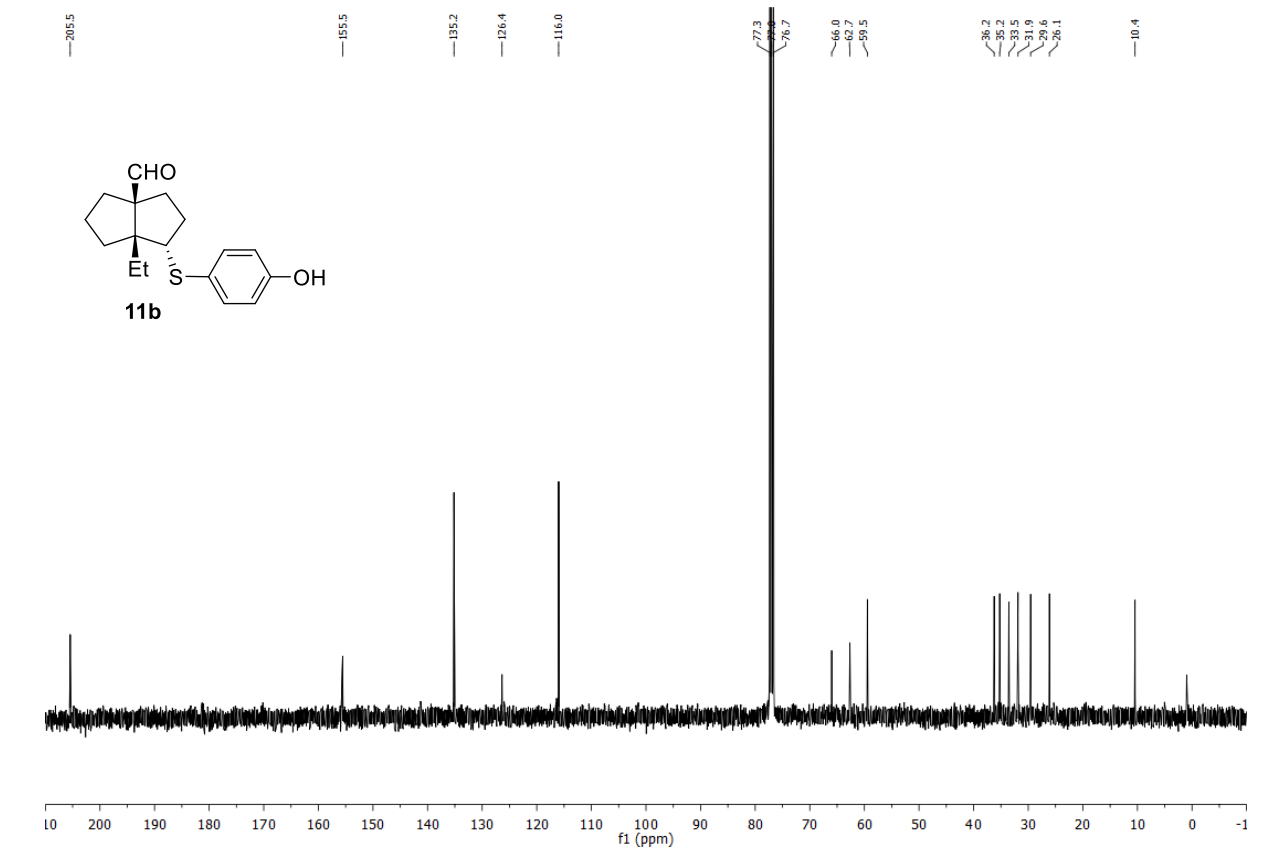
DEPT NMR Spectra of **11a**



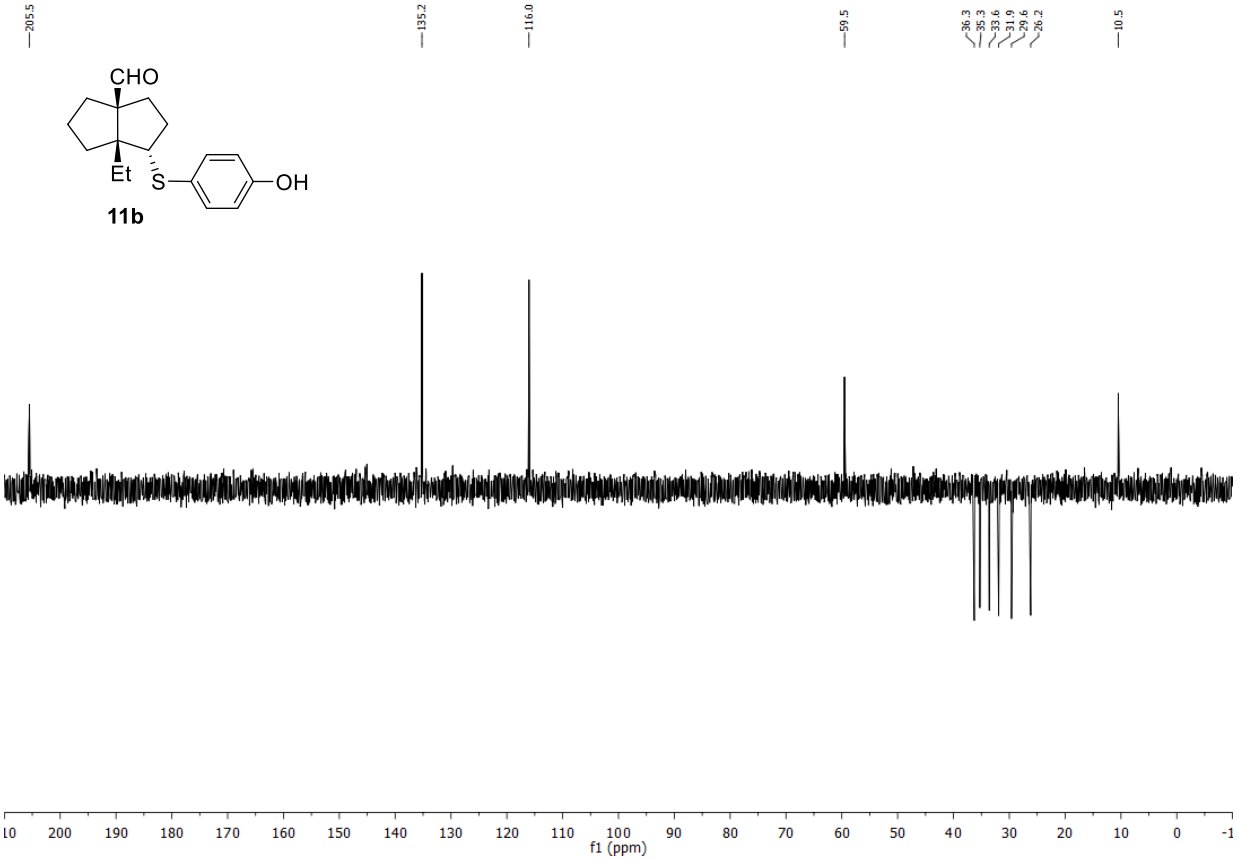
^{1}H NMR Spectra of **11b**



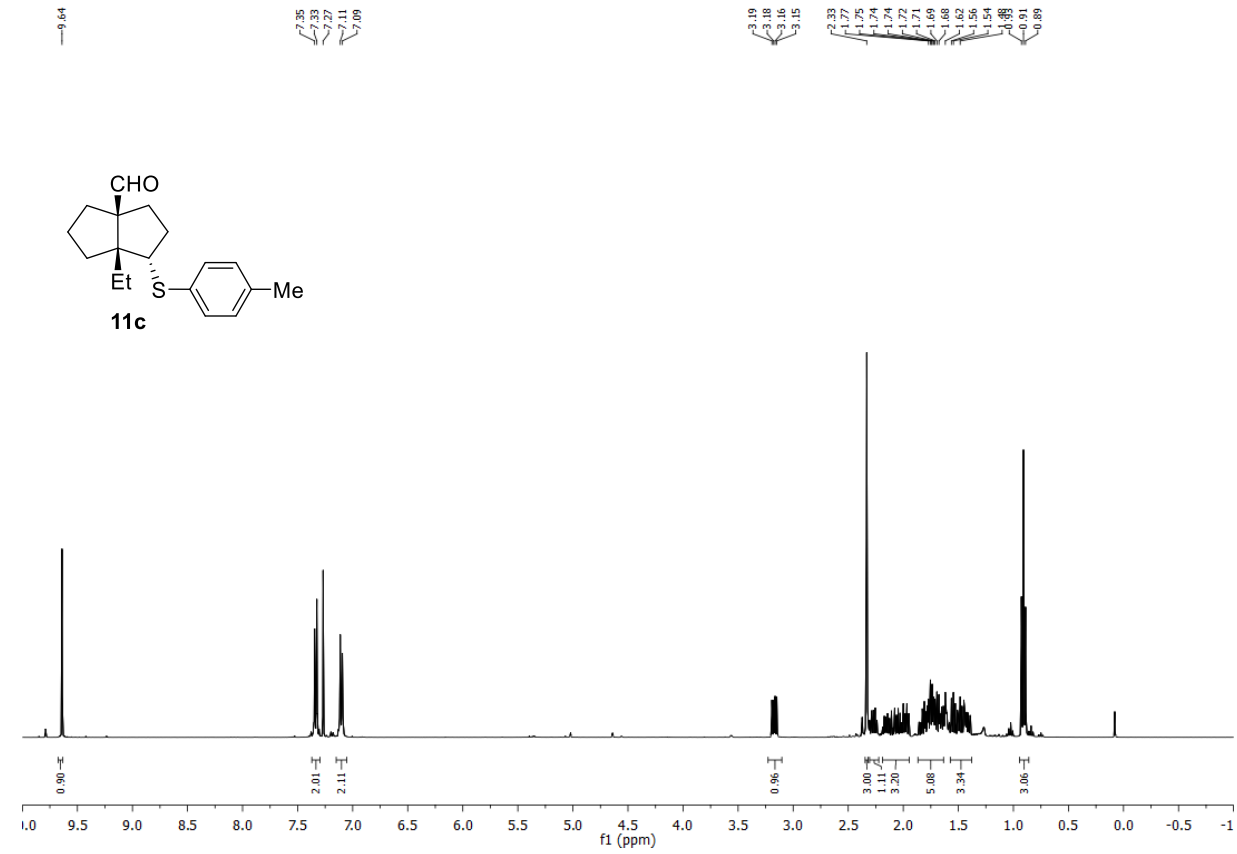
^{13}C NMR Spectra of **11b**



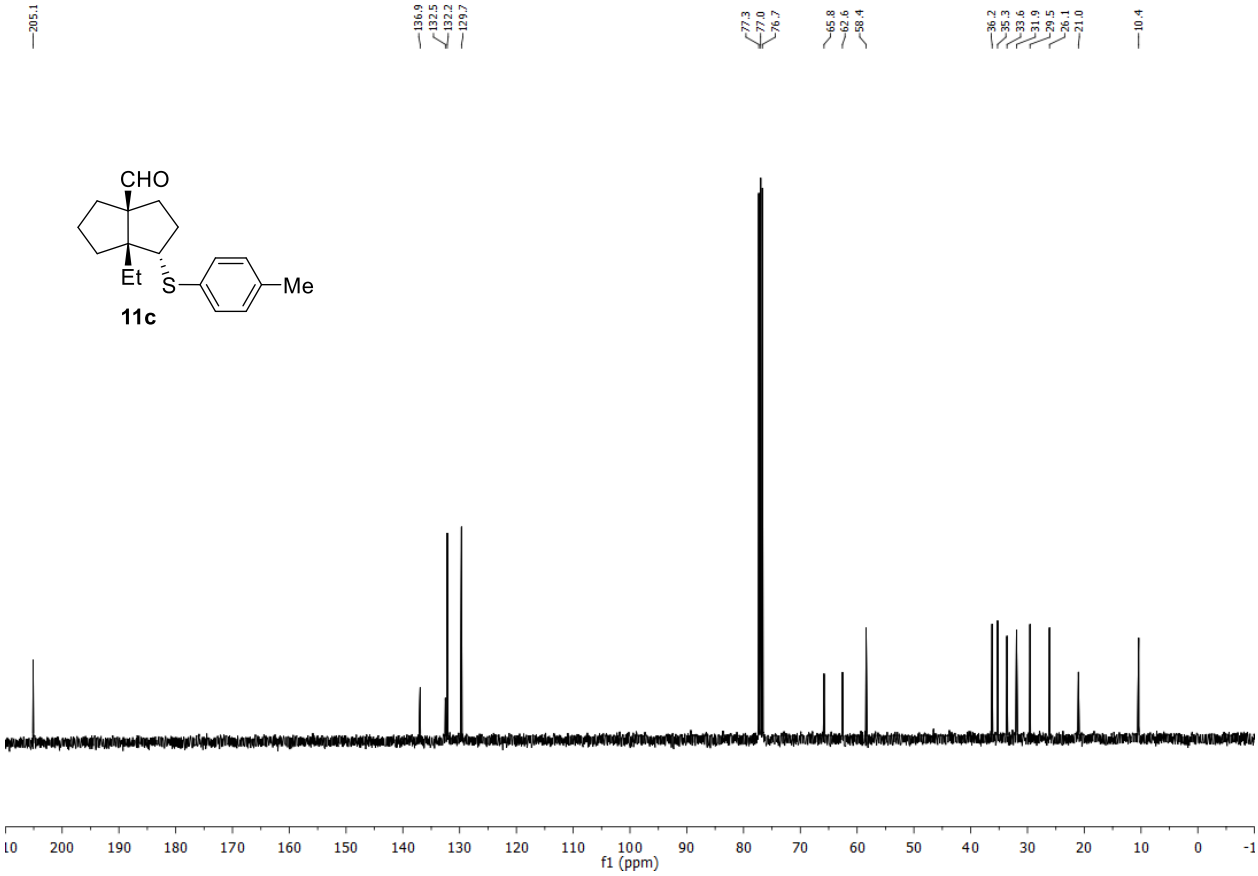
DEPT NMR Spectra of **11b**



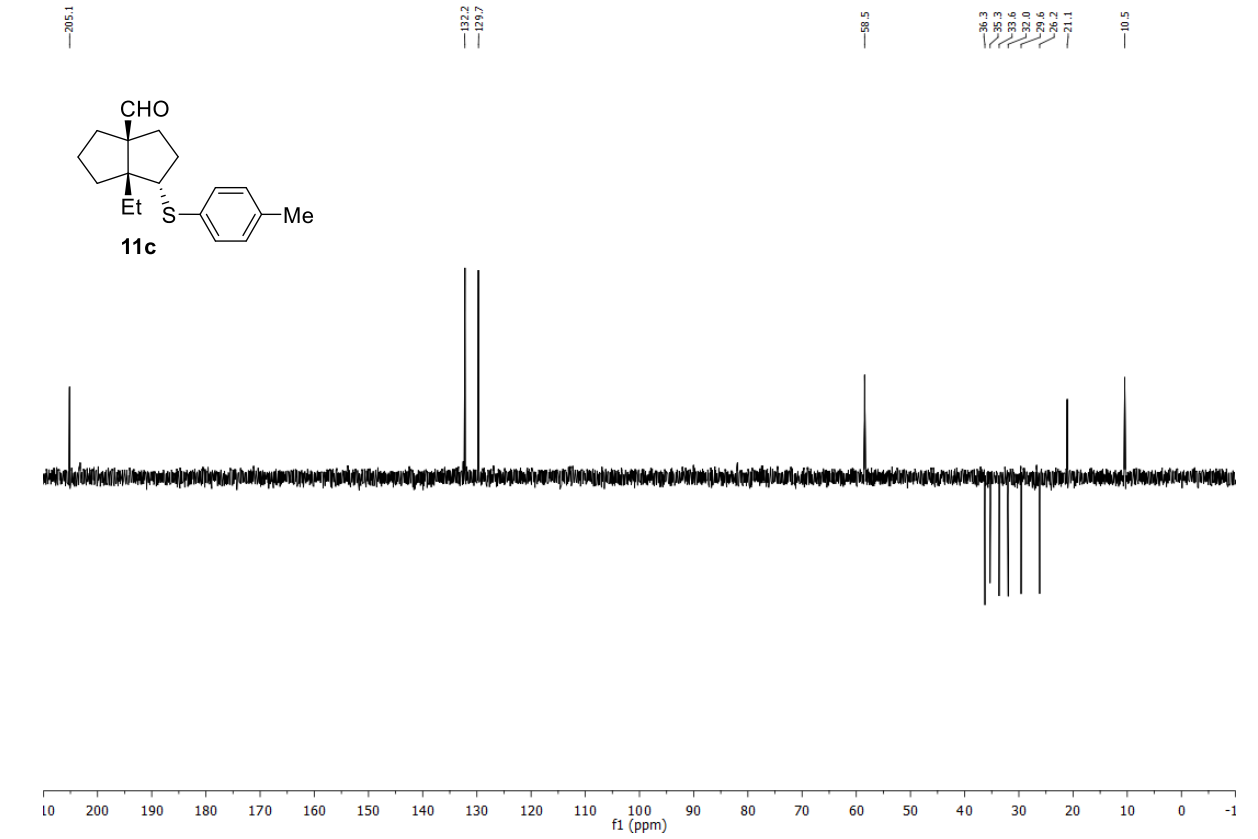
^{1}H NMR Spectra of **11c**



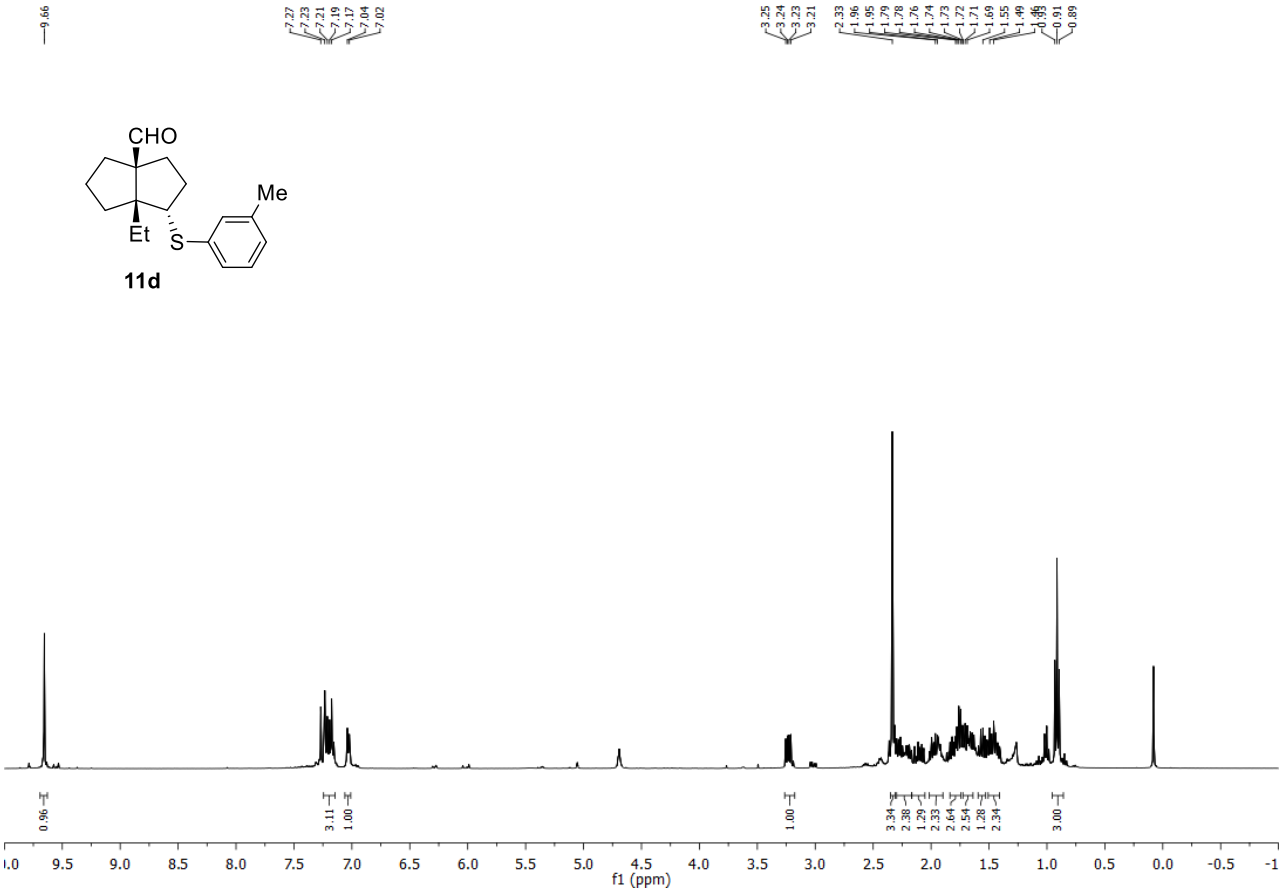
^{13}C NMR Spectra of **11c**



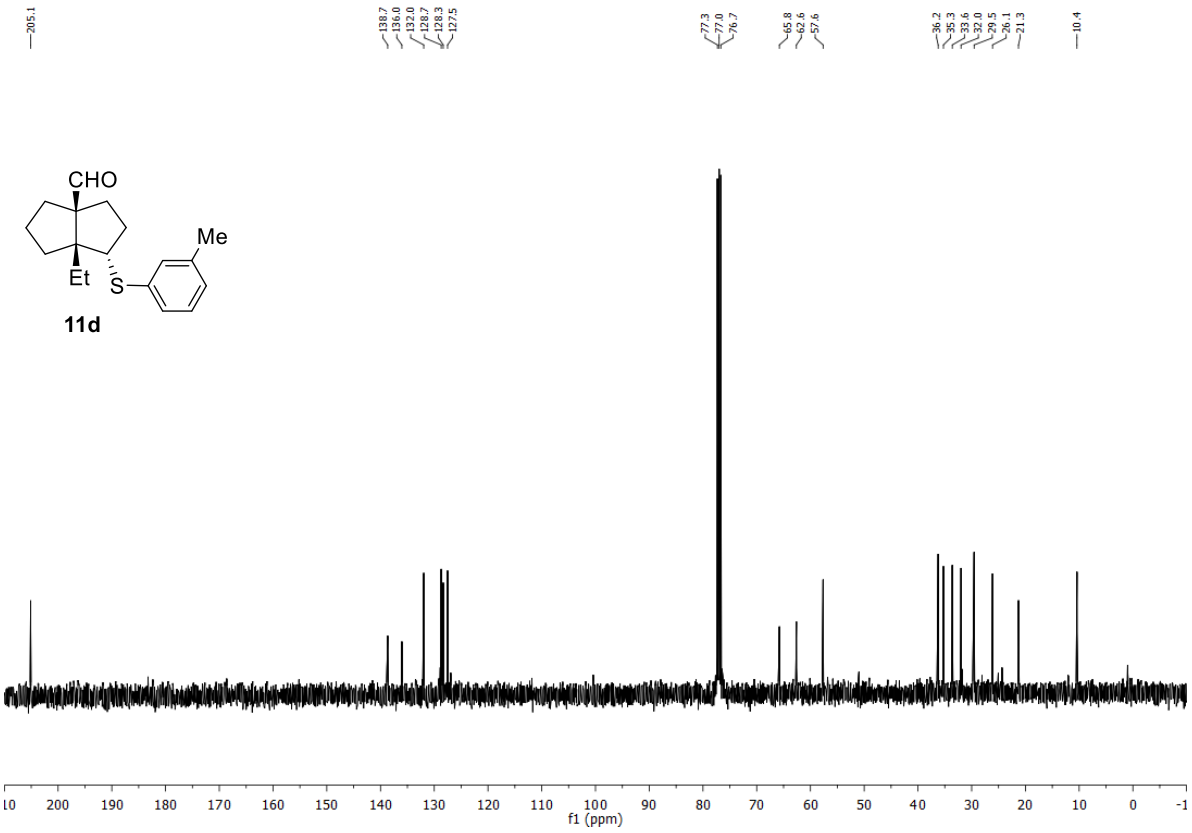
DEPT NMR Spectra of **11c**



^{1}H NMR Spectra of **11d**



^{13}C NMR Spectra of **11d**



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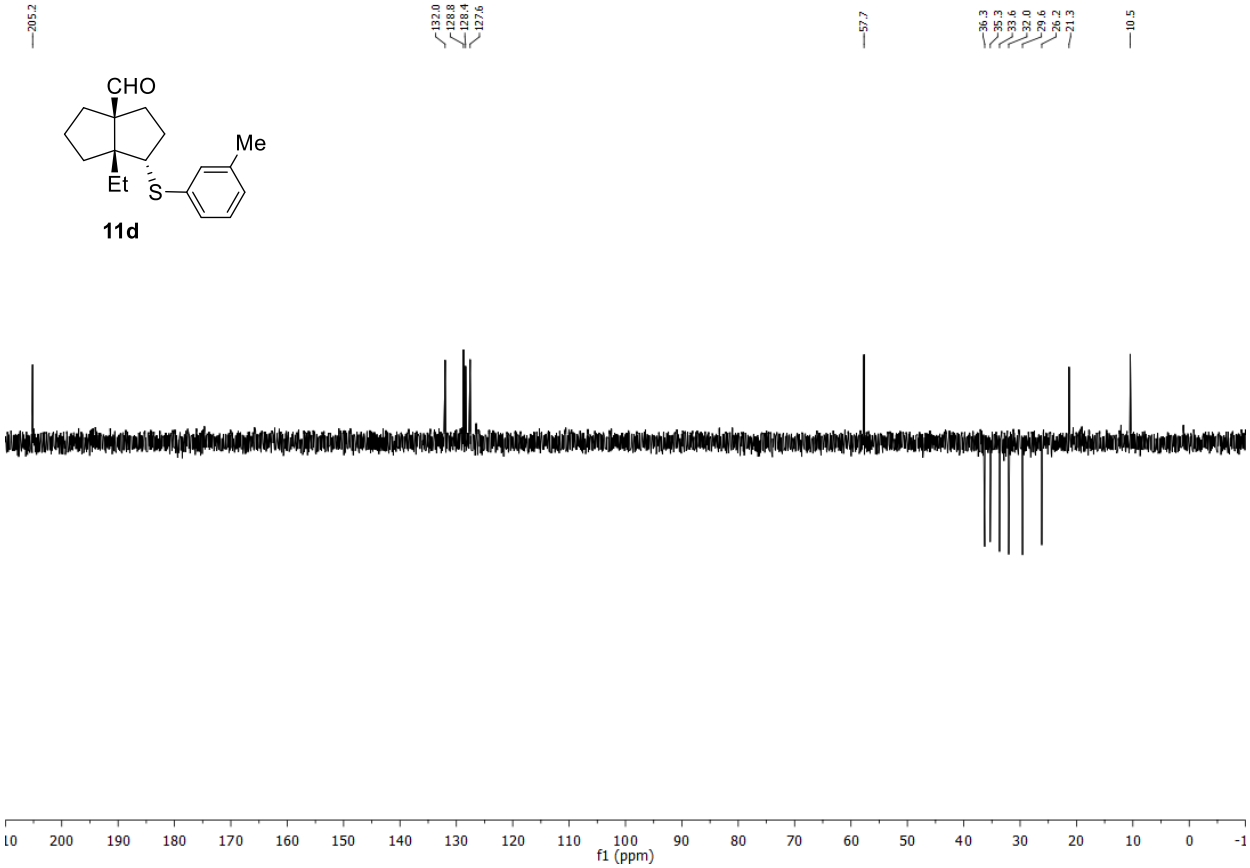

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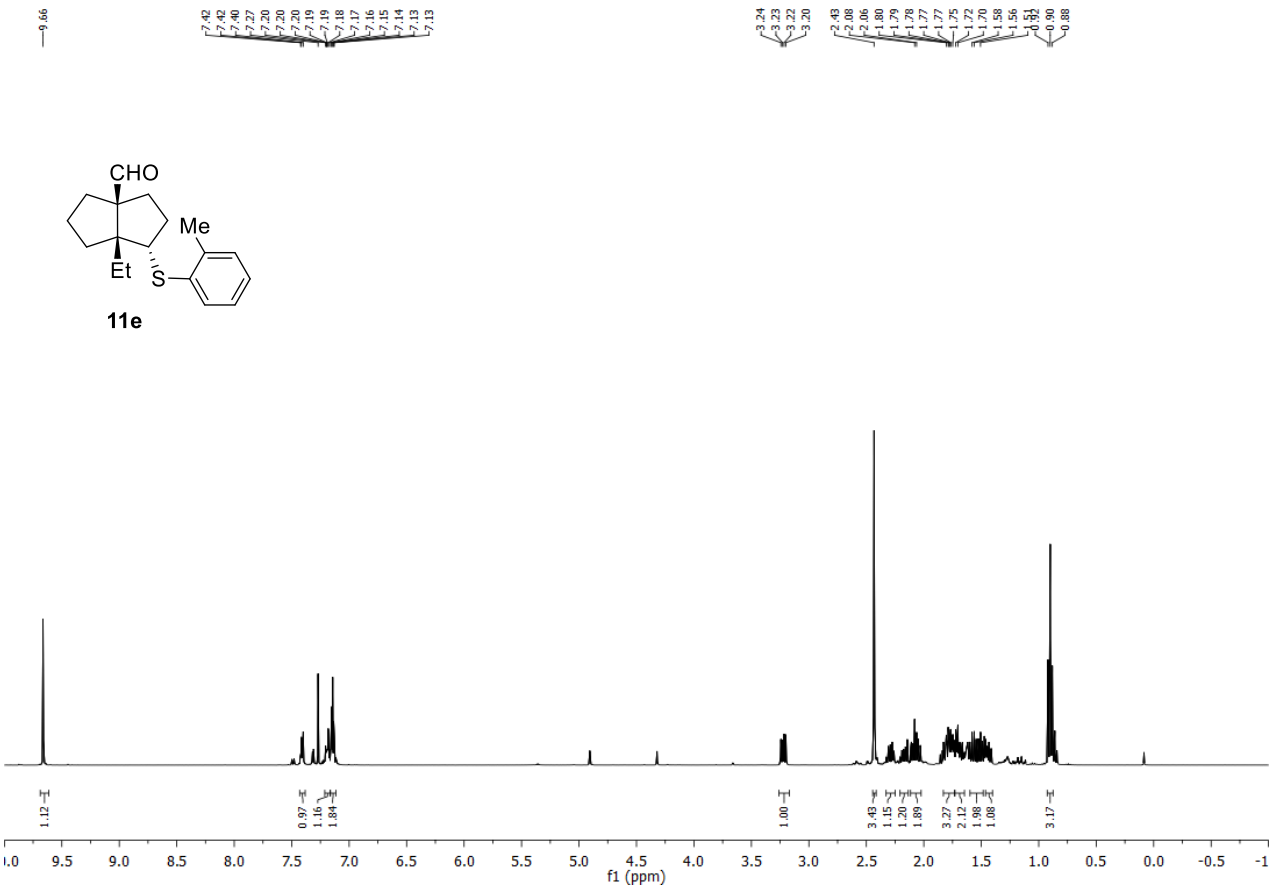
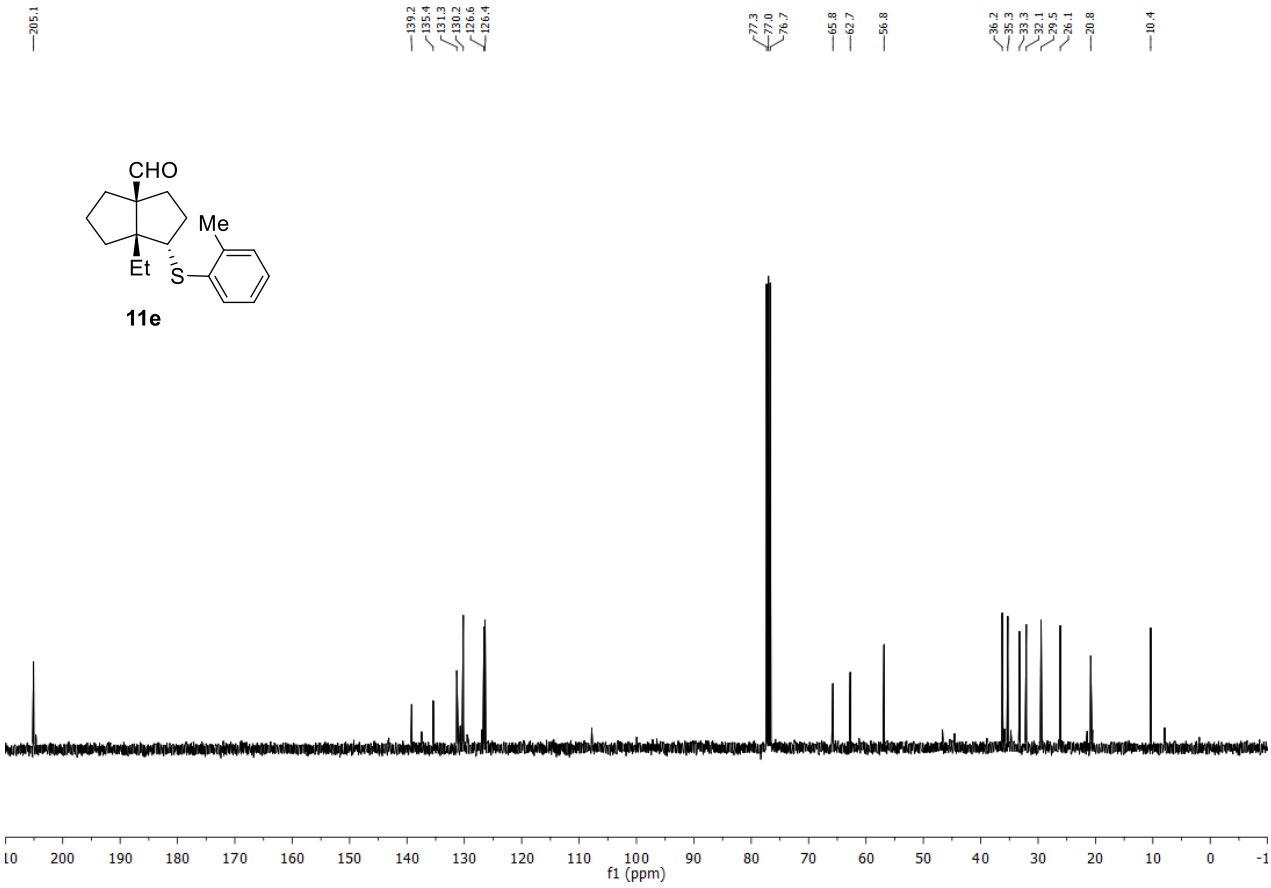
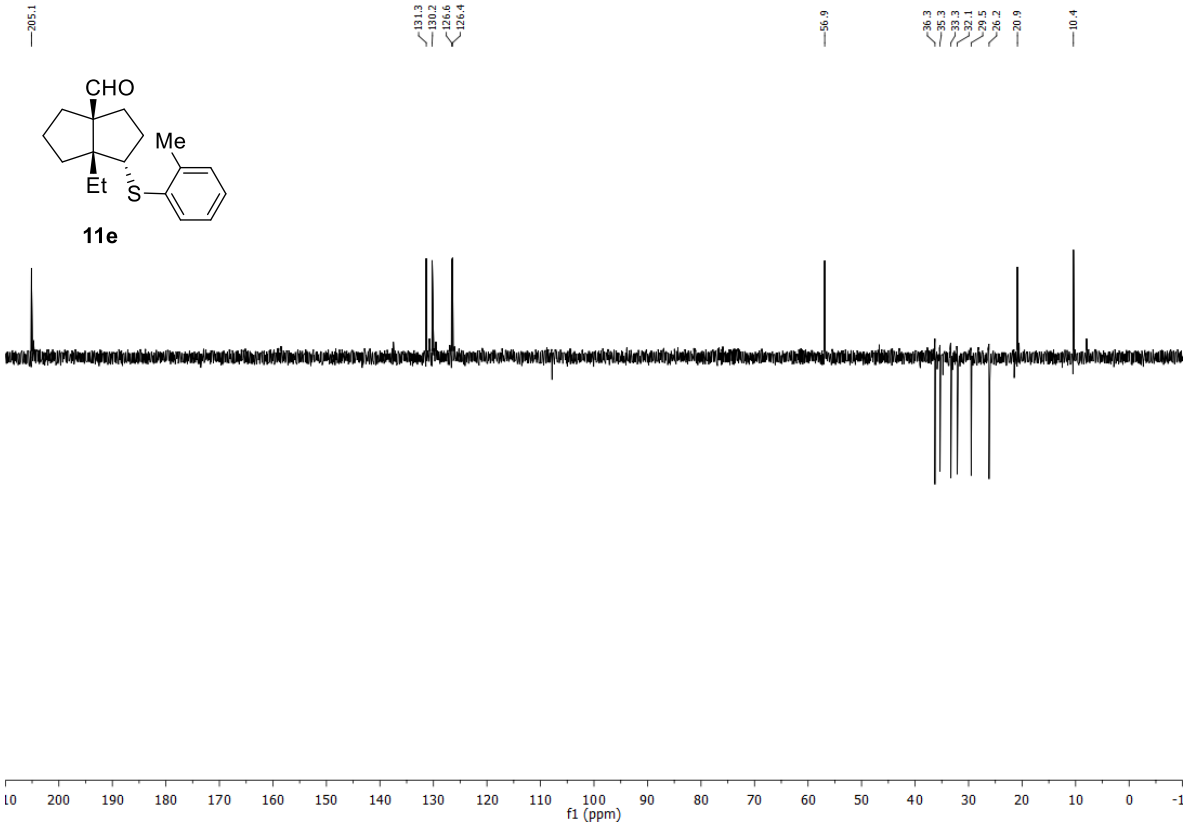


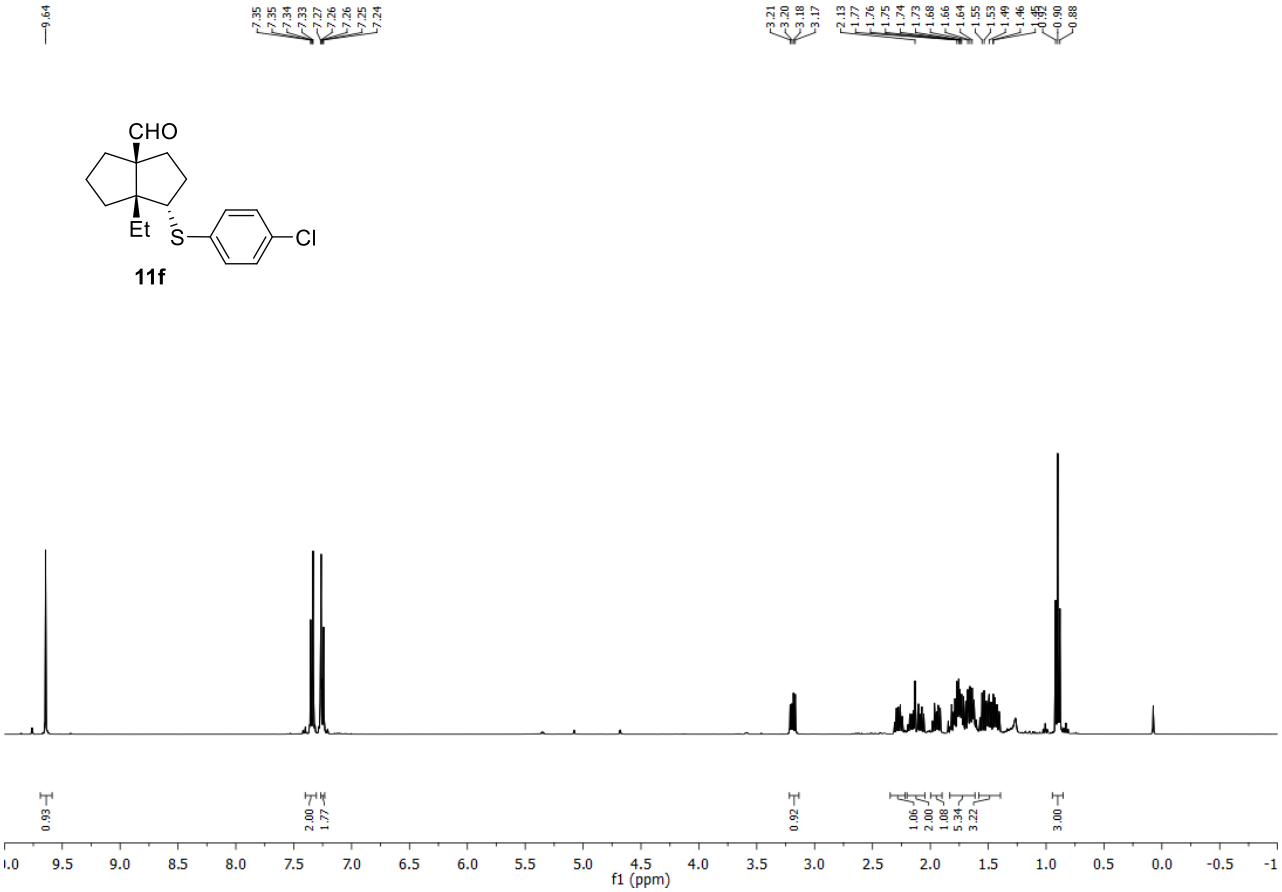
^{13}C NMR Spectra of **11e**



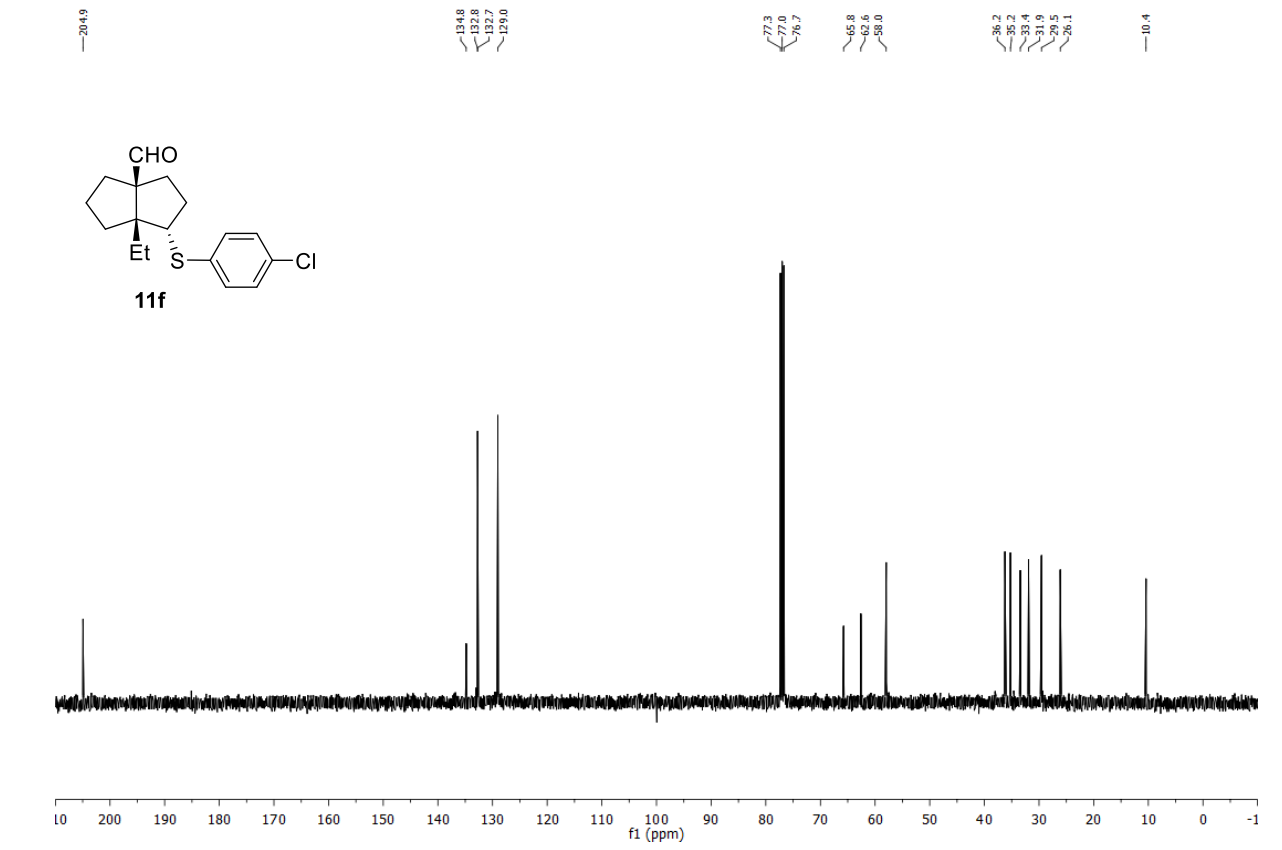
DEPT NMR Spectra of **11e**



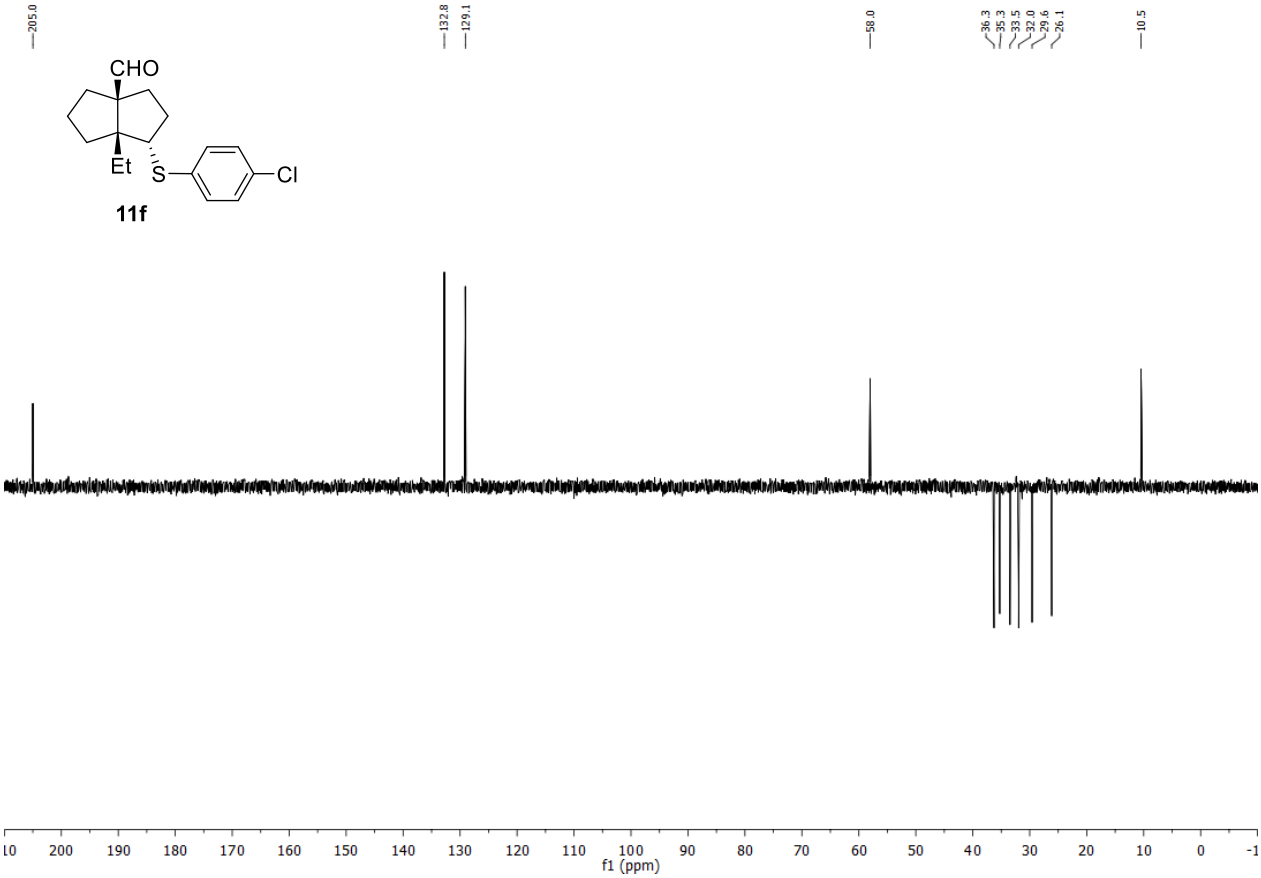
^{1}H NMR Spectra of **11f**



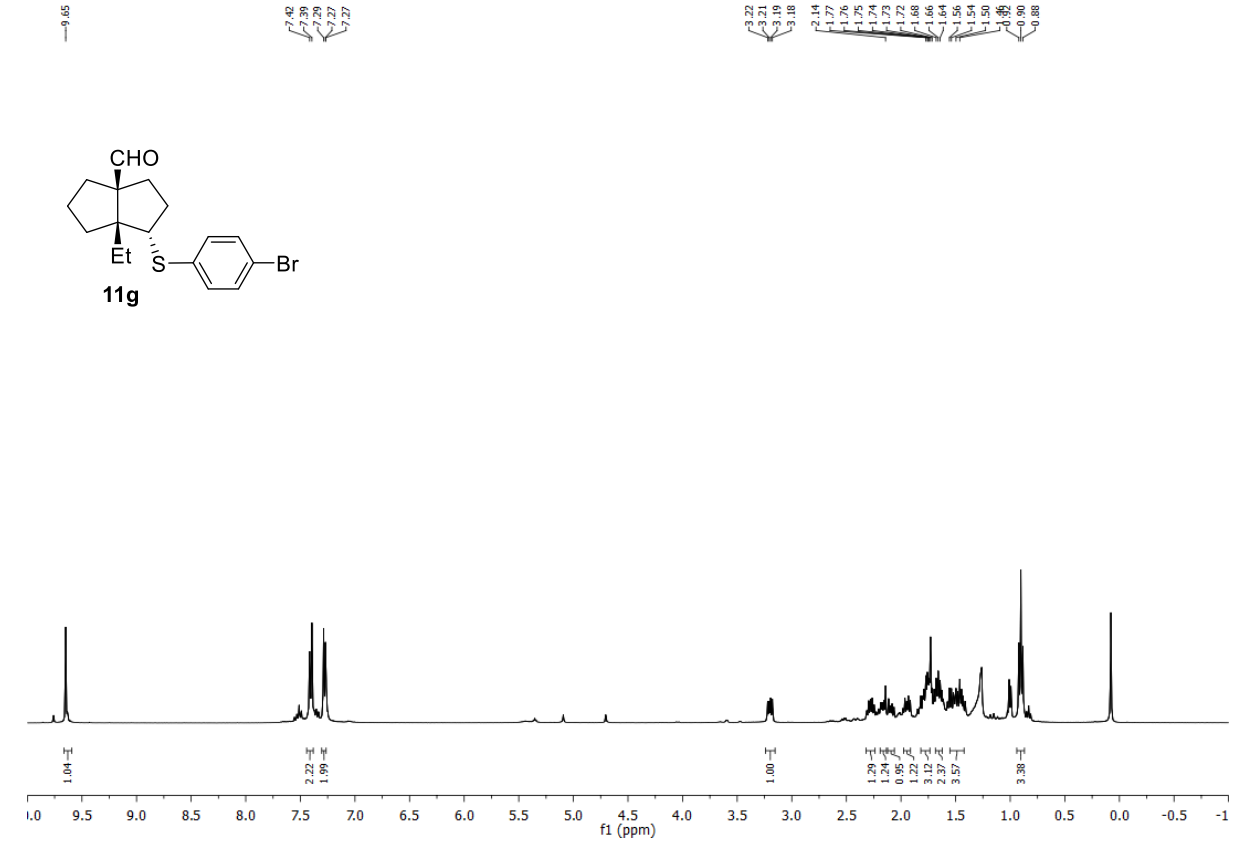
^{13}C NMR Spectra of **11f**



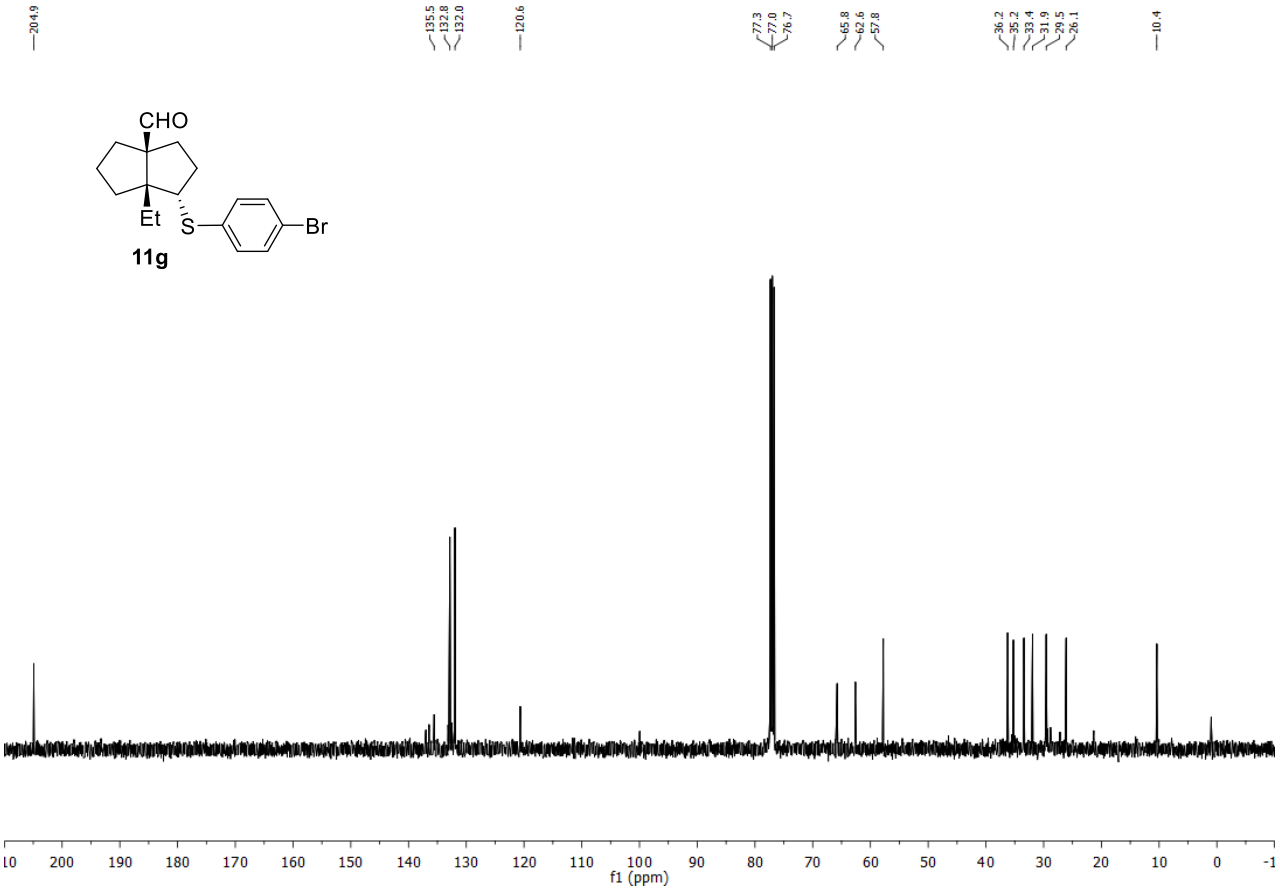
DEPT NMR Spectra of **11f**



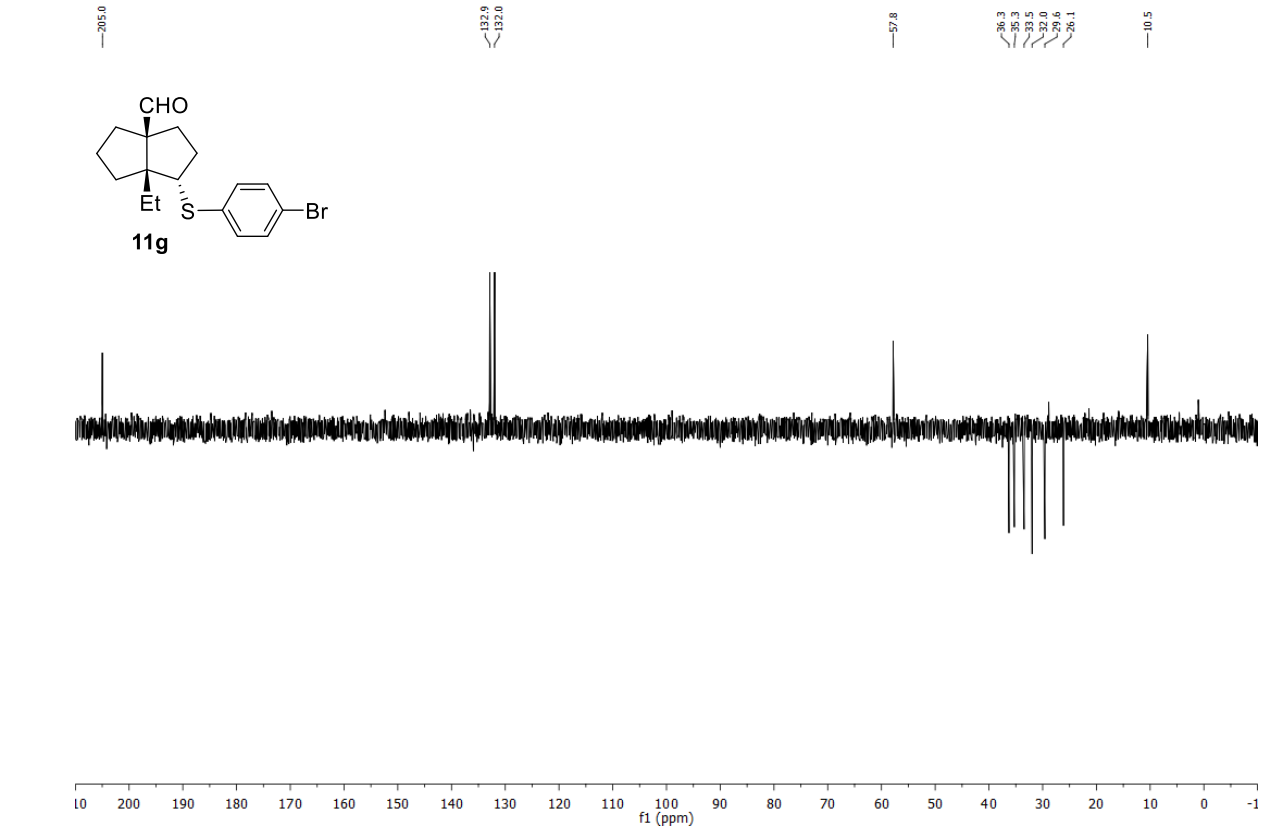
^{1}H NMR Spectra of **11g**



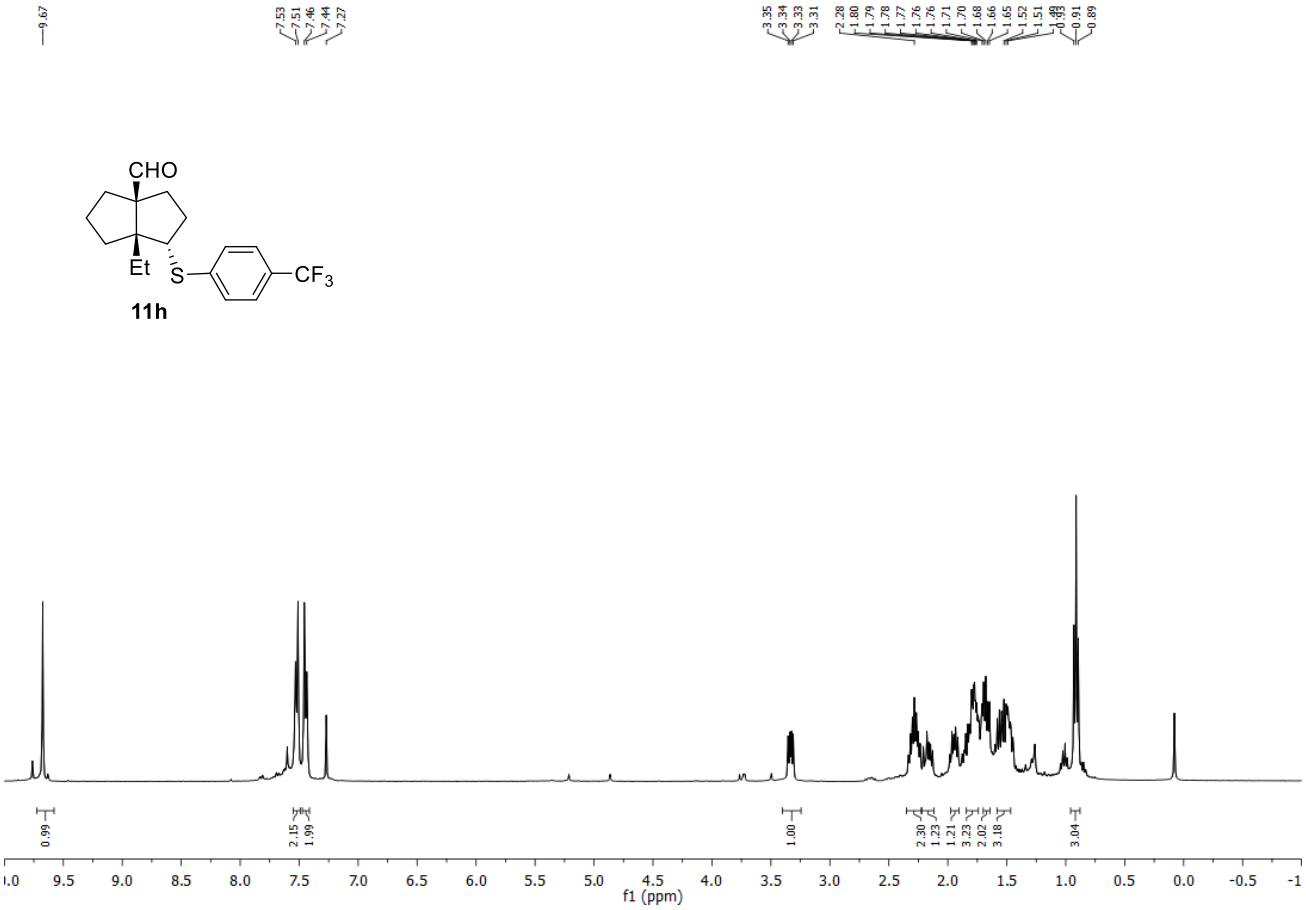
^{13}C NMR Spectra of **11g**



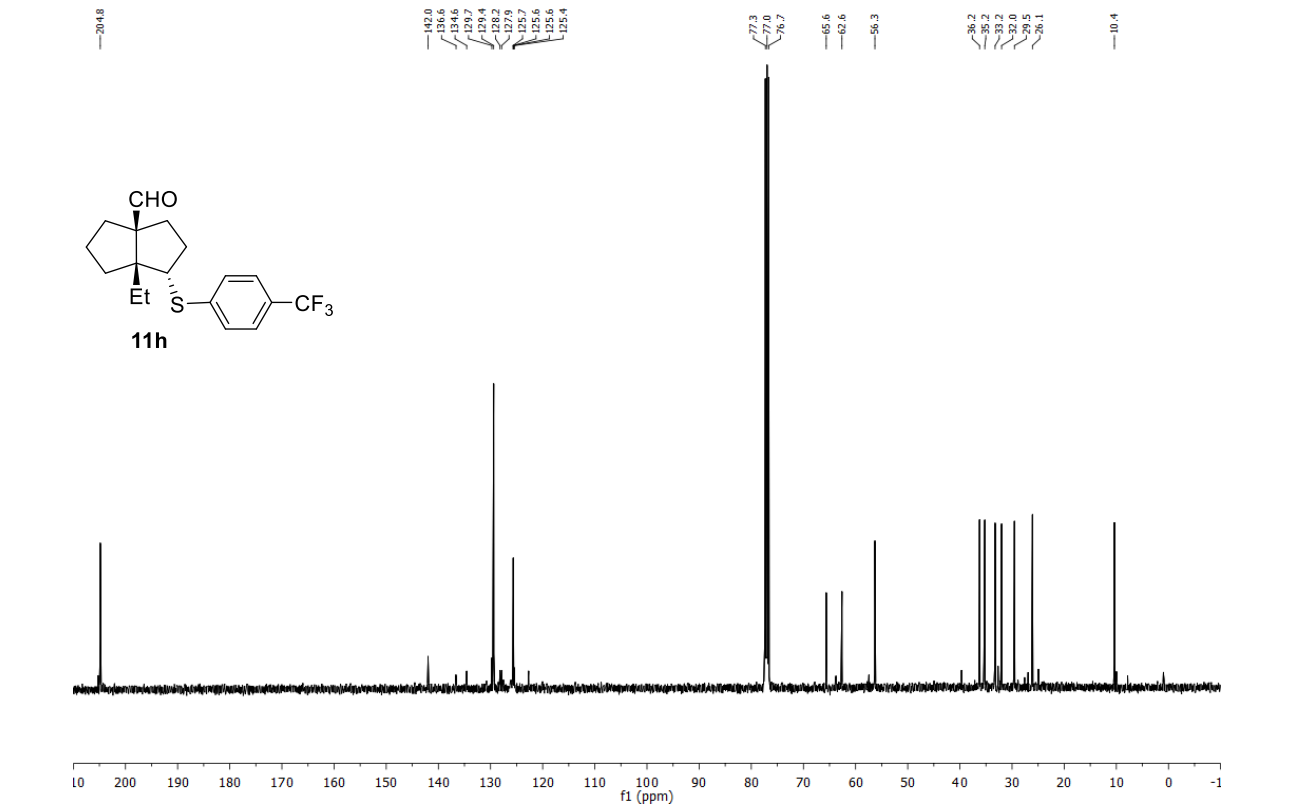
DEPT NMR Spectra of **11g**



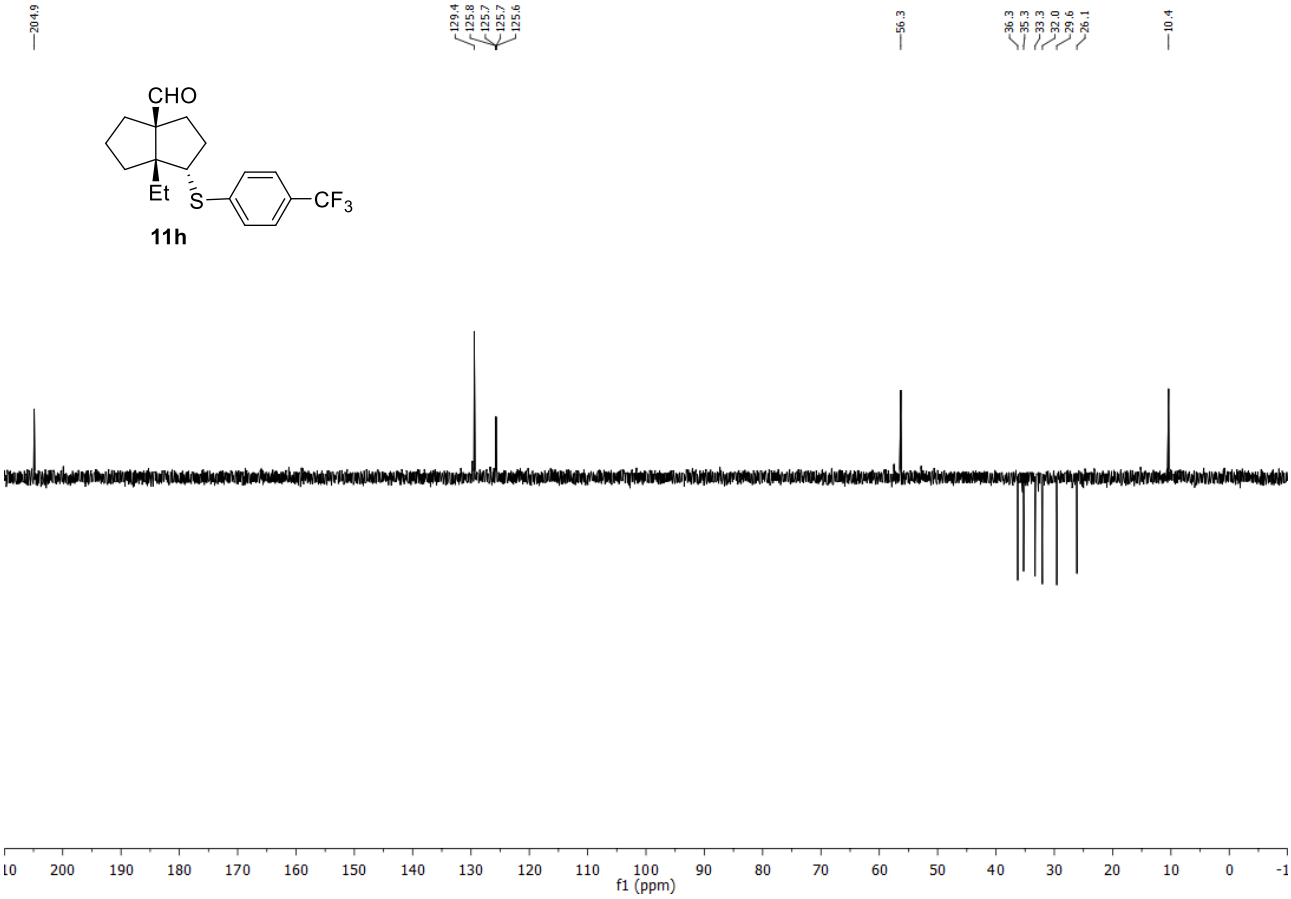
^{1}H NMR Spectra of **11h**



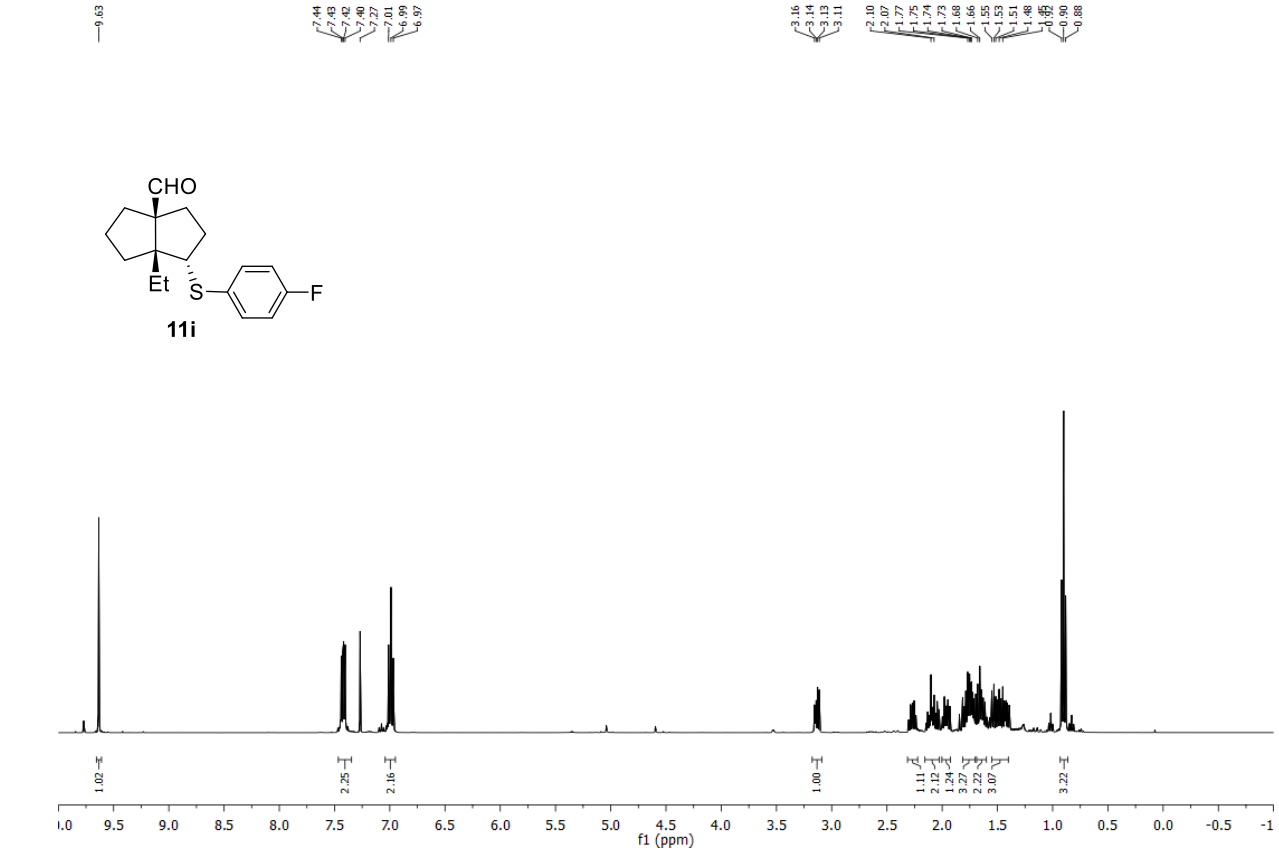
^{13}C NMR Spectra of **11h**



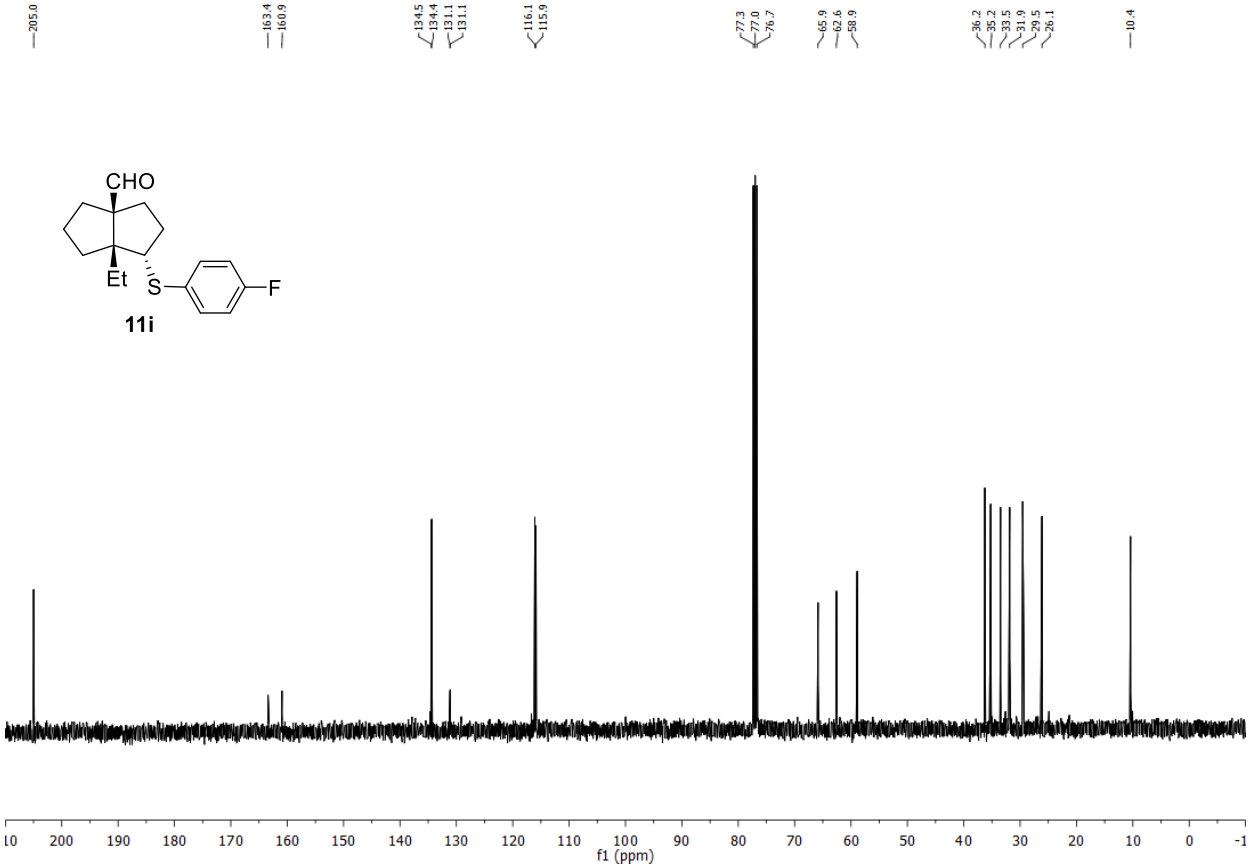
DEPT NMR Spectra of **11h**



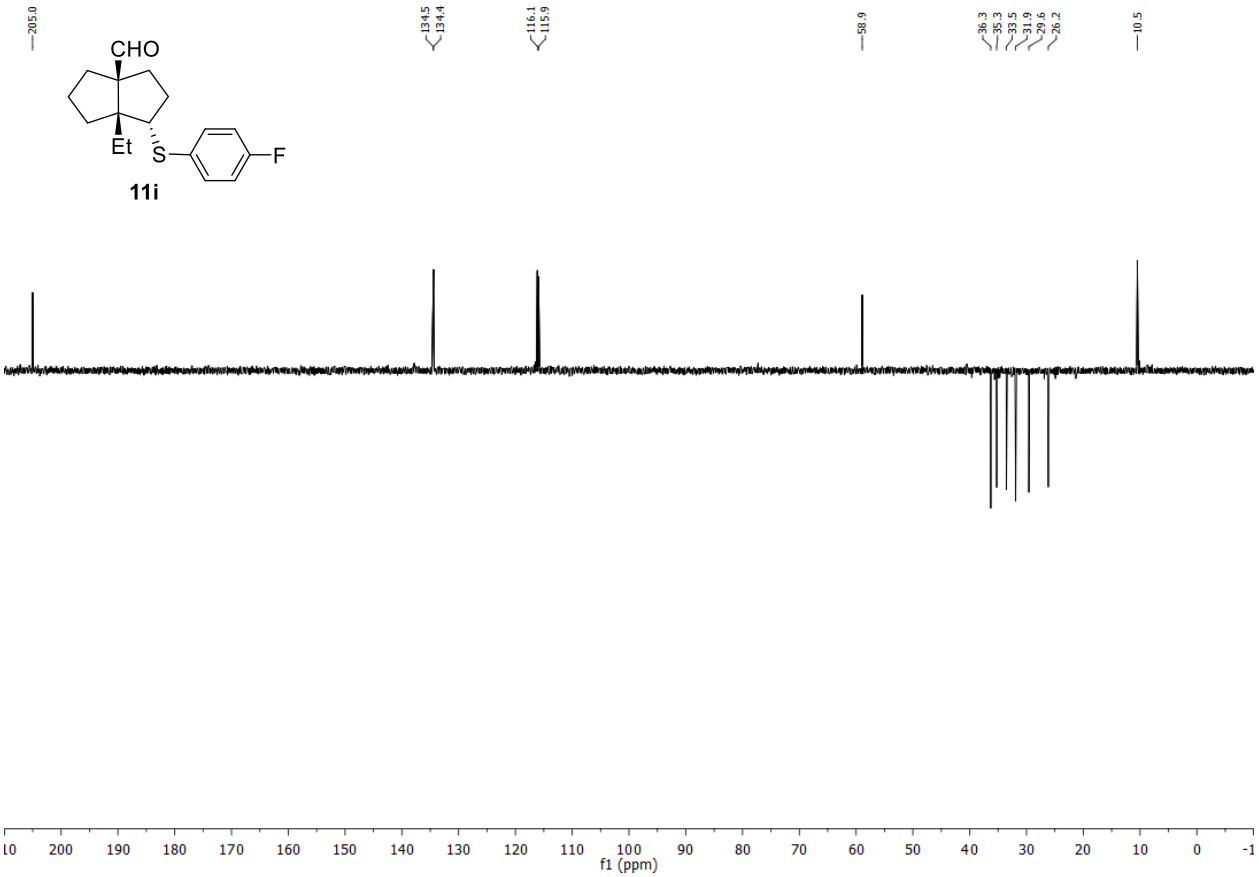
^{1}H NMR Spectra of **11i**



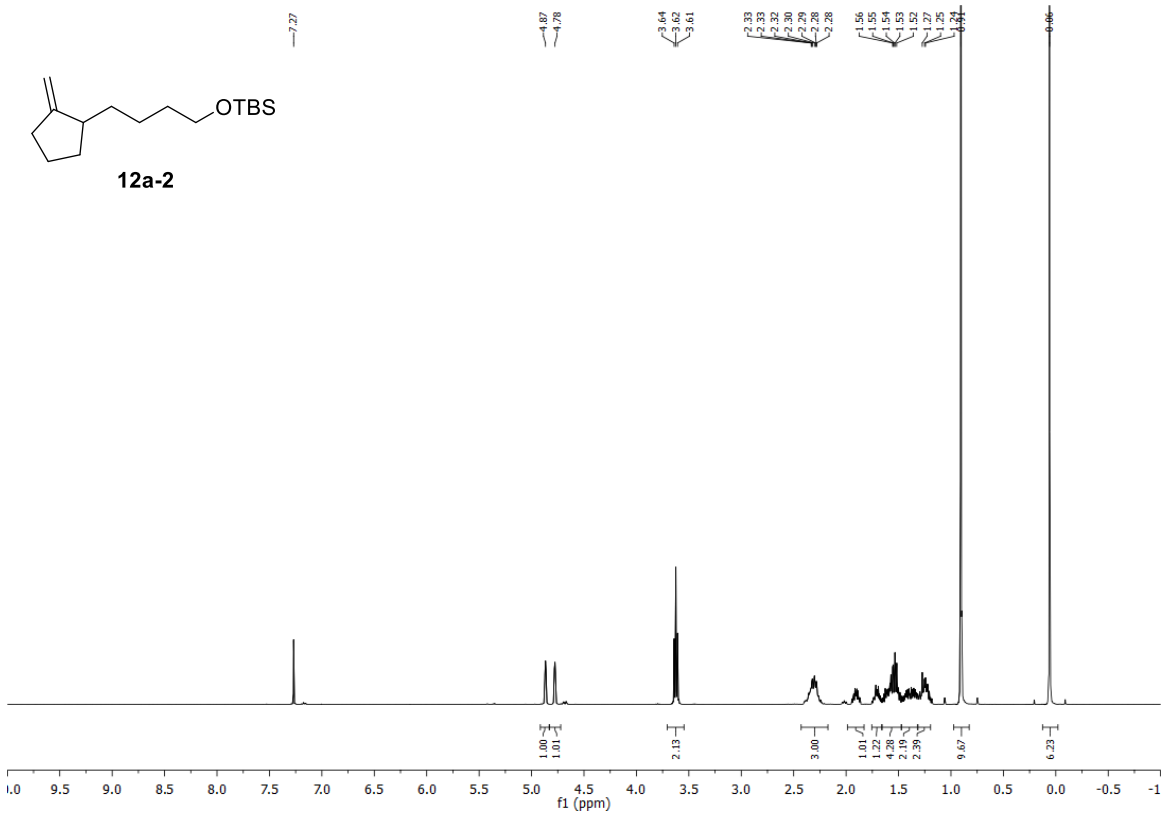
^{13}C NMR Spectra of **11i**



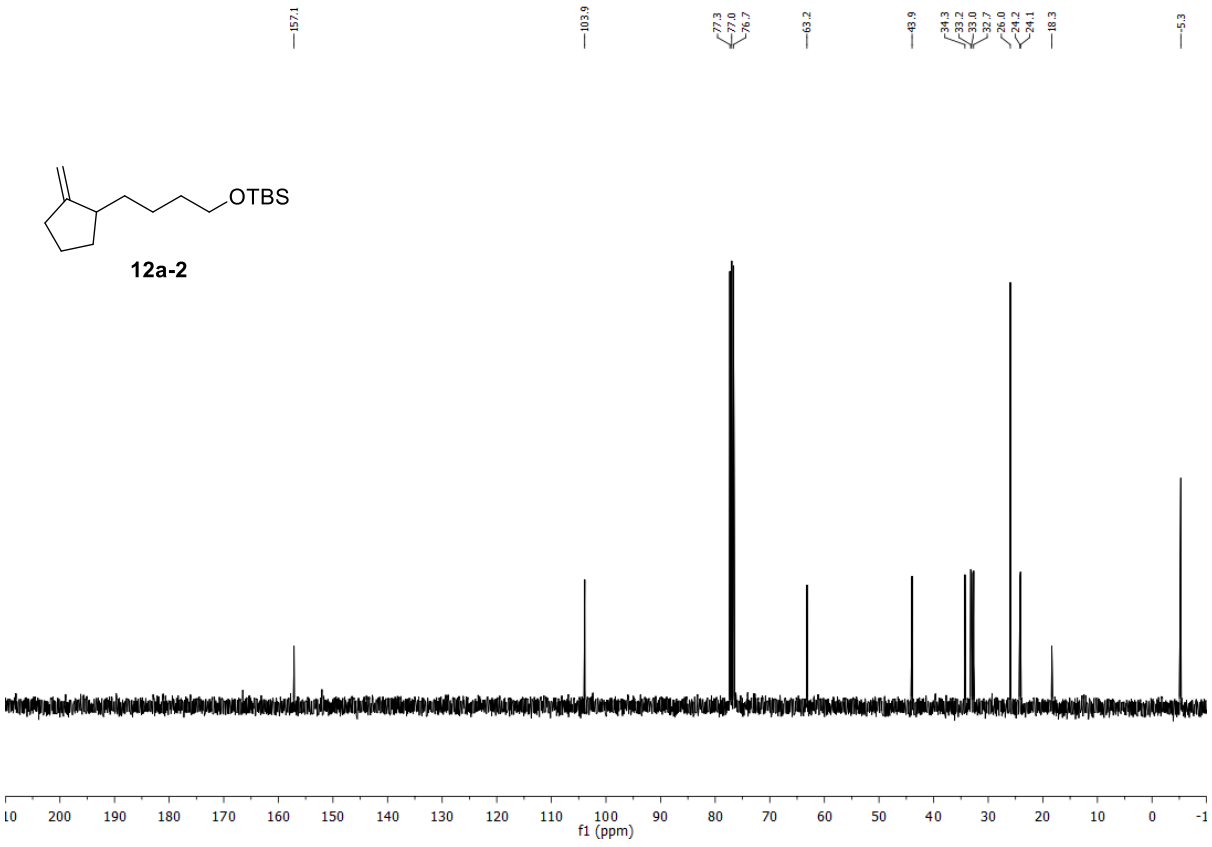
DEPT NMR Spectra of **11i**



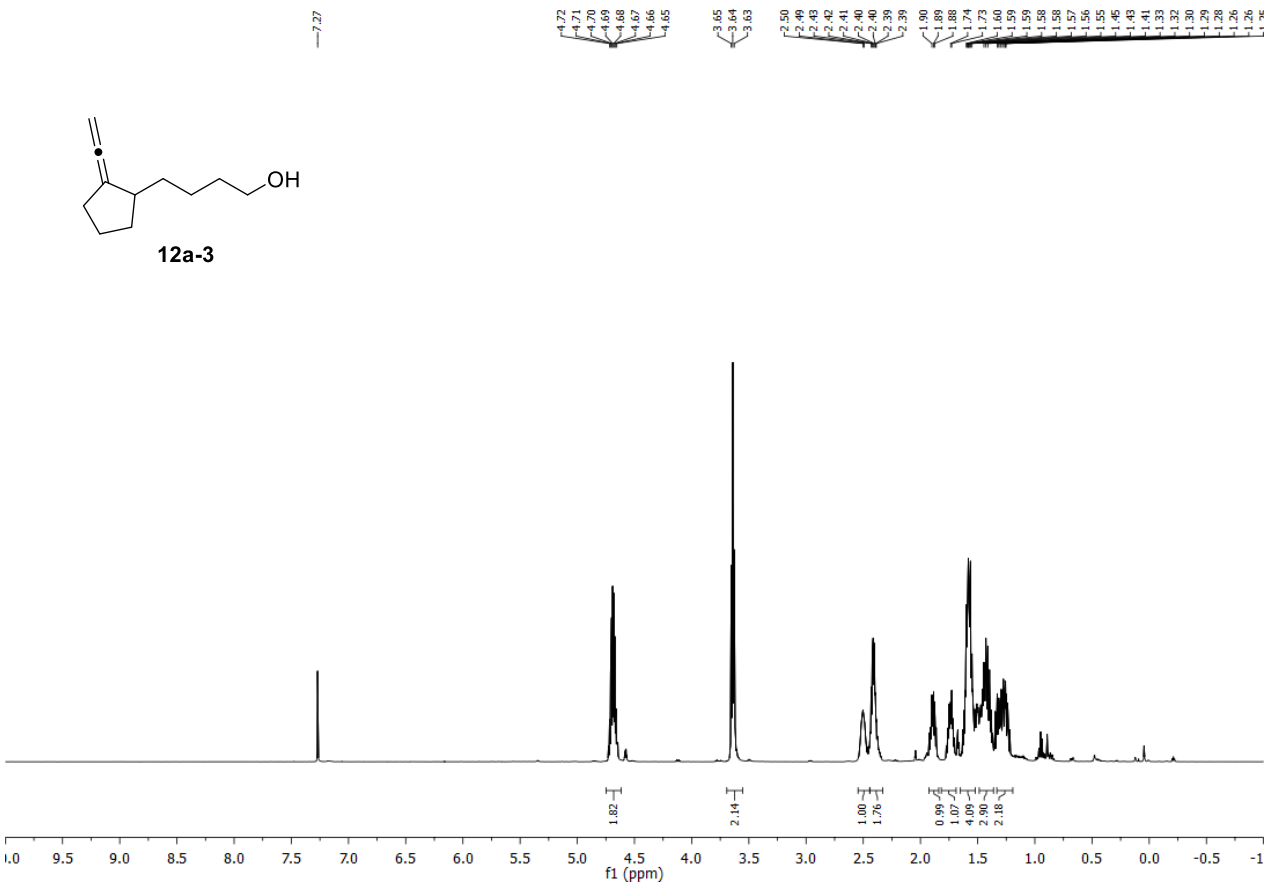
^{1}H NMR Spectra of **12a-2**



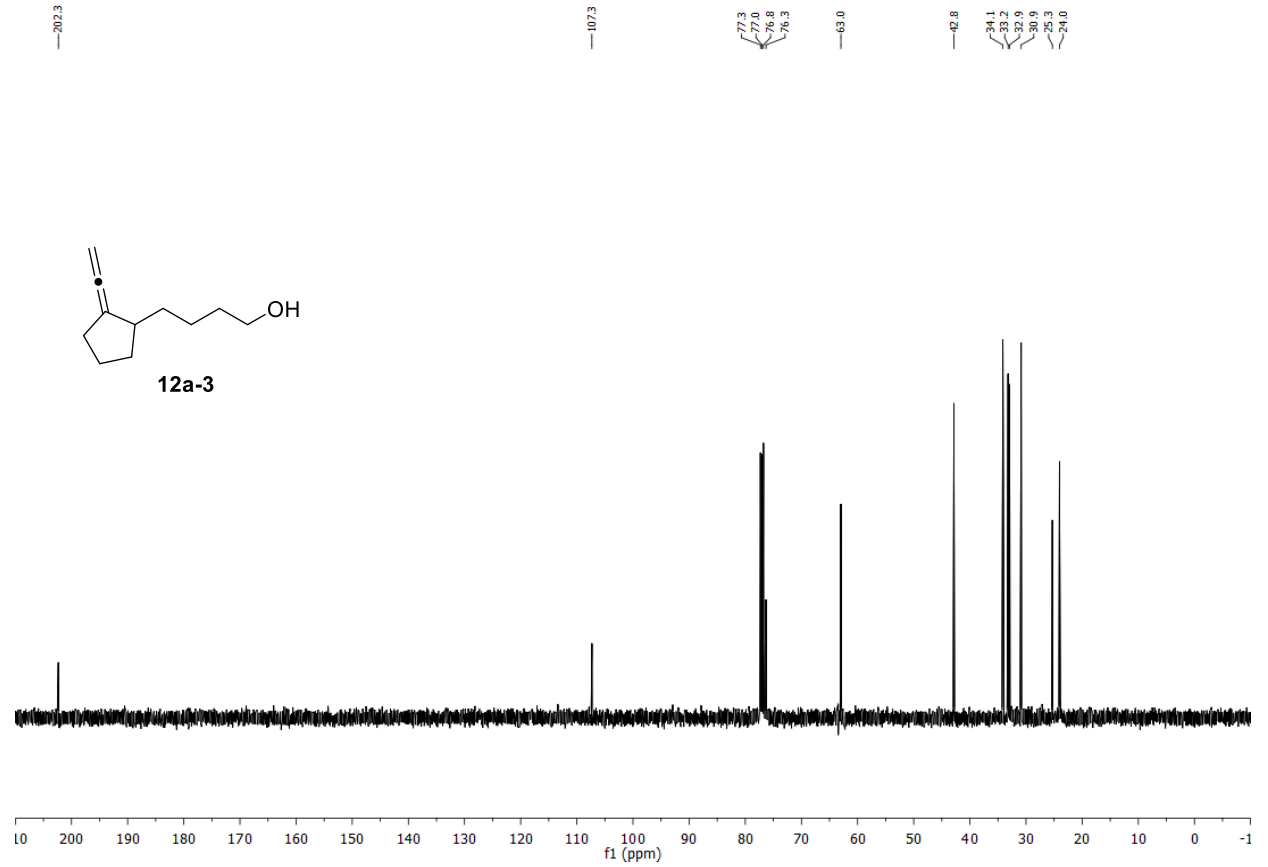
^{13}C NMR Spectra of **12a-2**



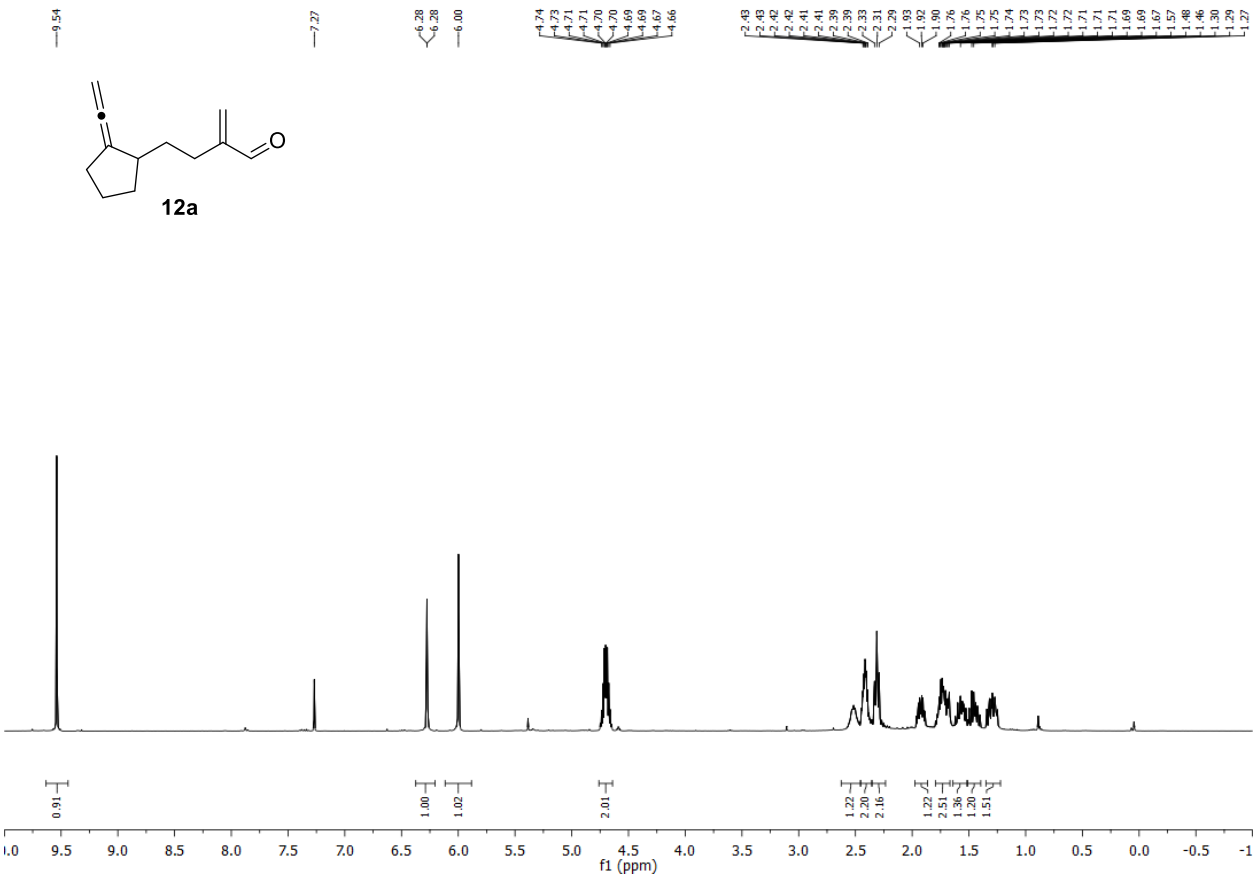
^{1}H NMR Spectra of **12a-3**



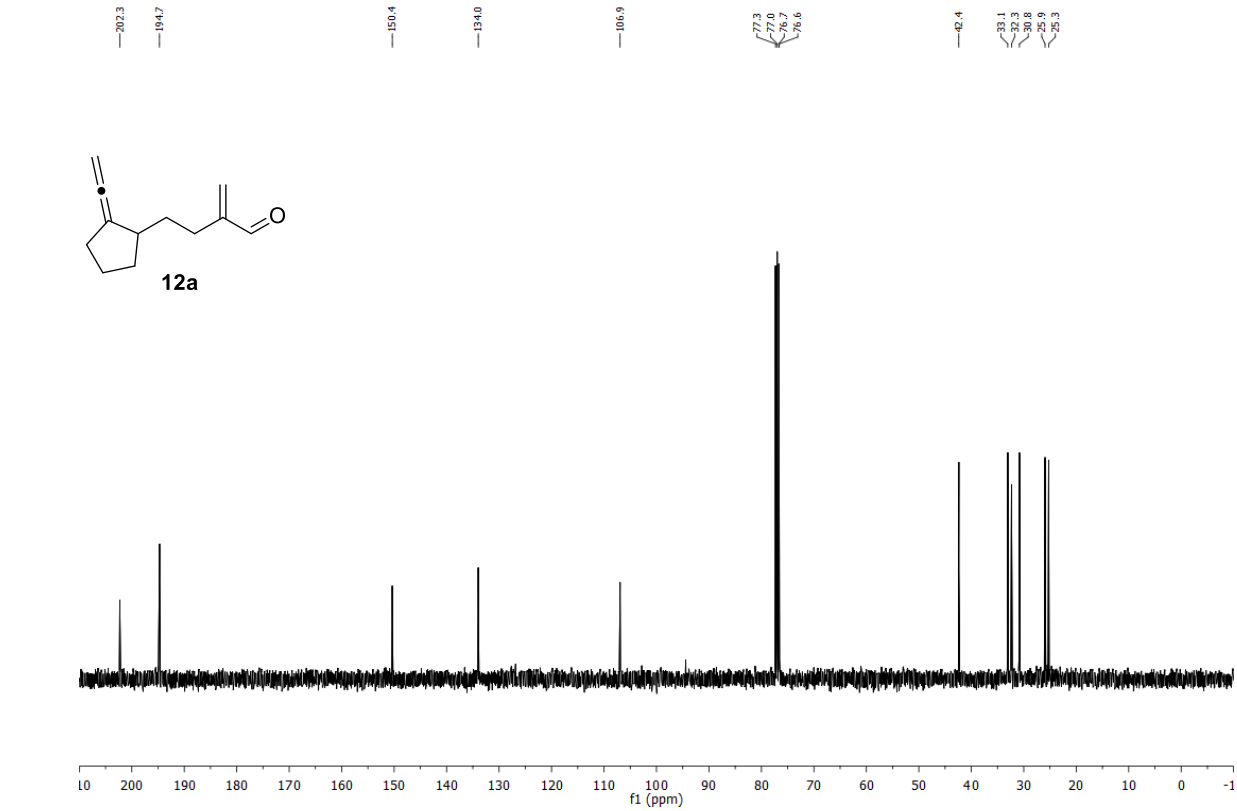
^{13}C NMR Spectra of **12a-3**



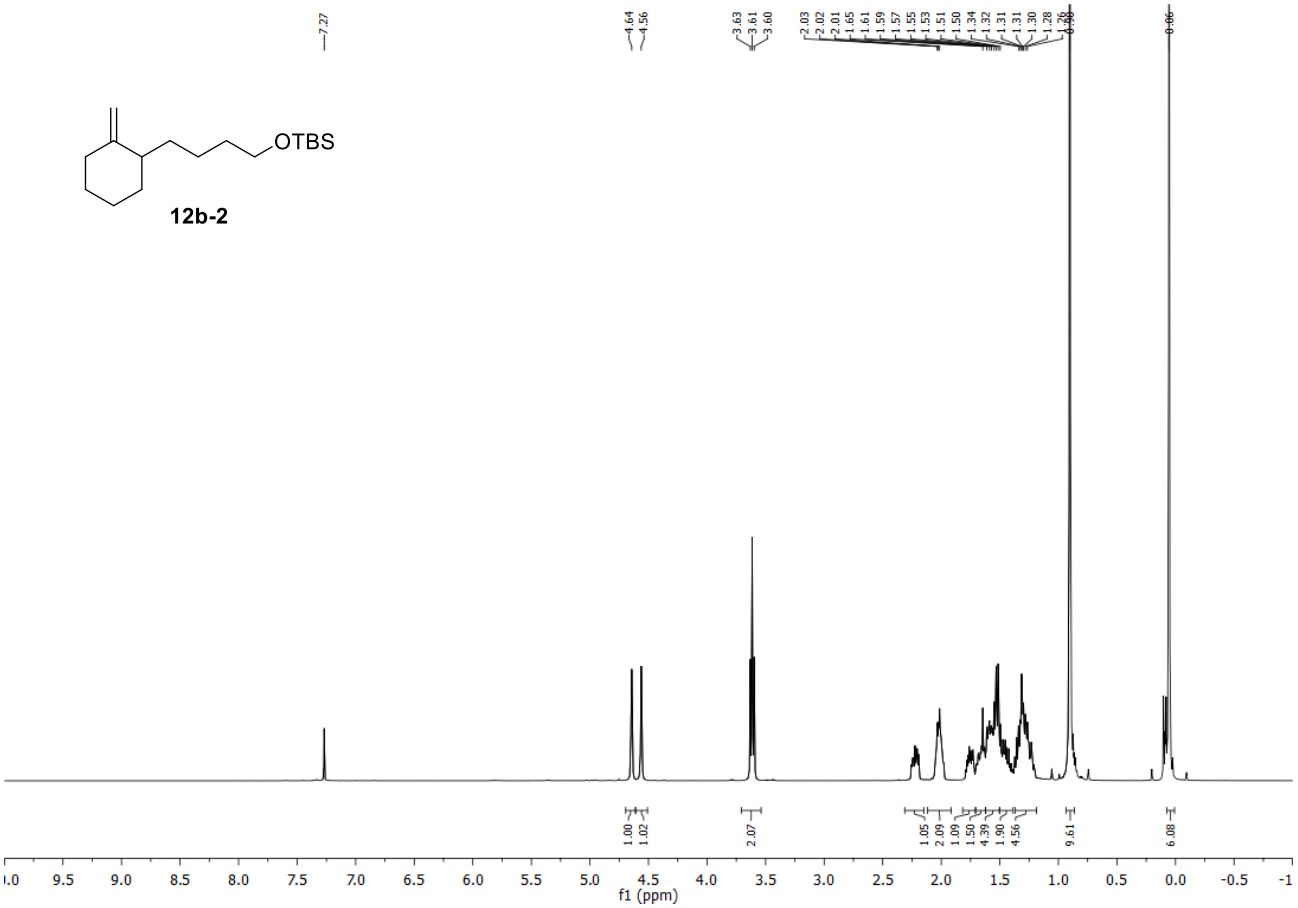
^{1}H NMR Spectra of **12a**



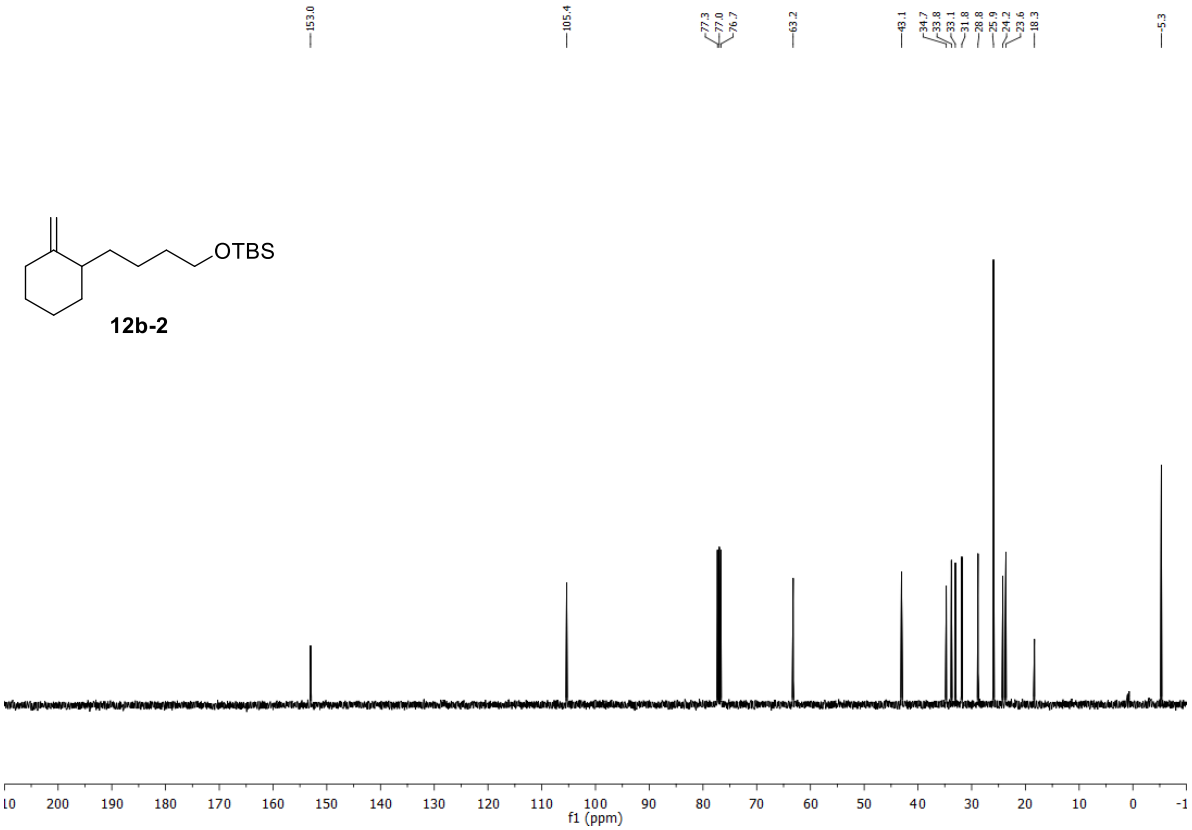
^{13}C NMR Spectra of **12a**



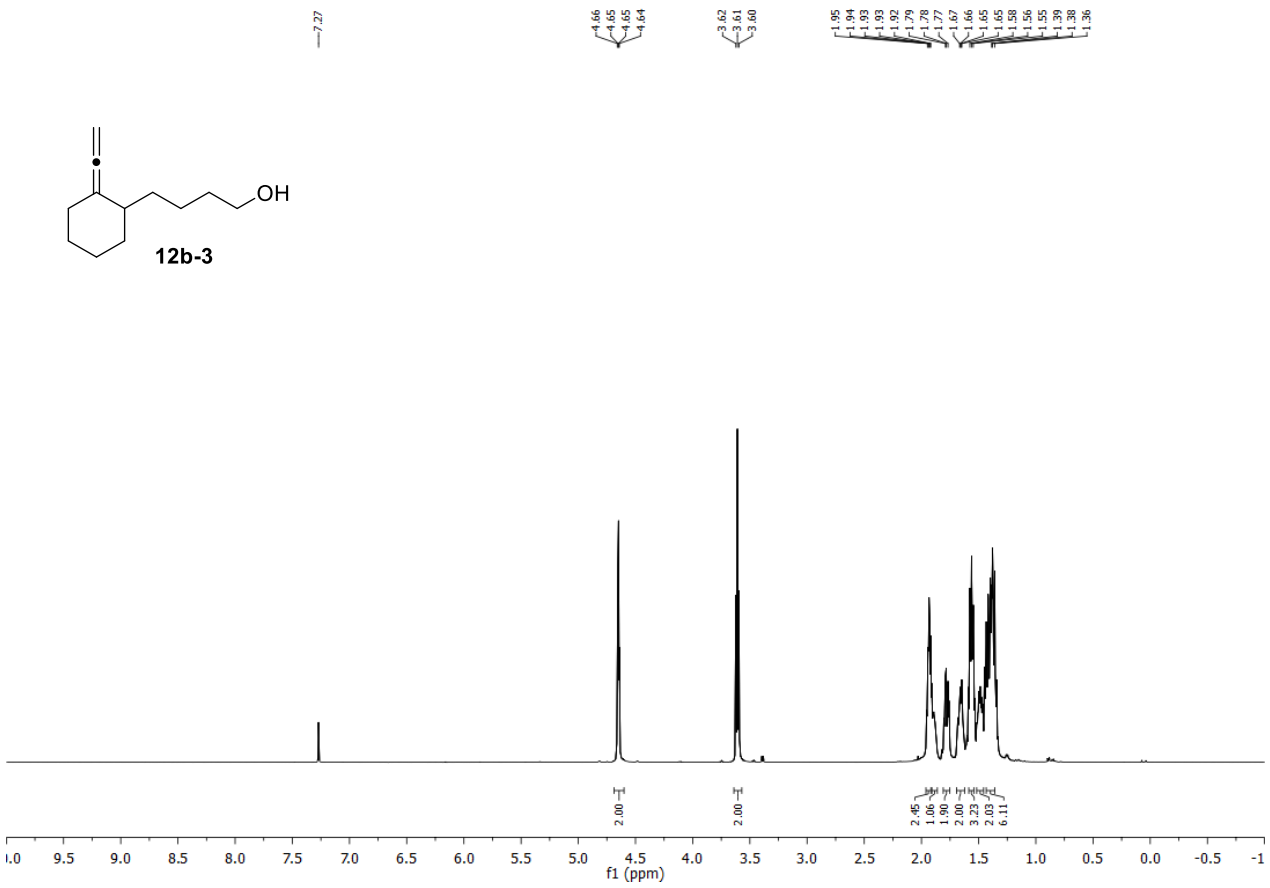
^{1}H NMR Spectra of **12b-2**



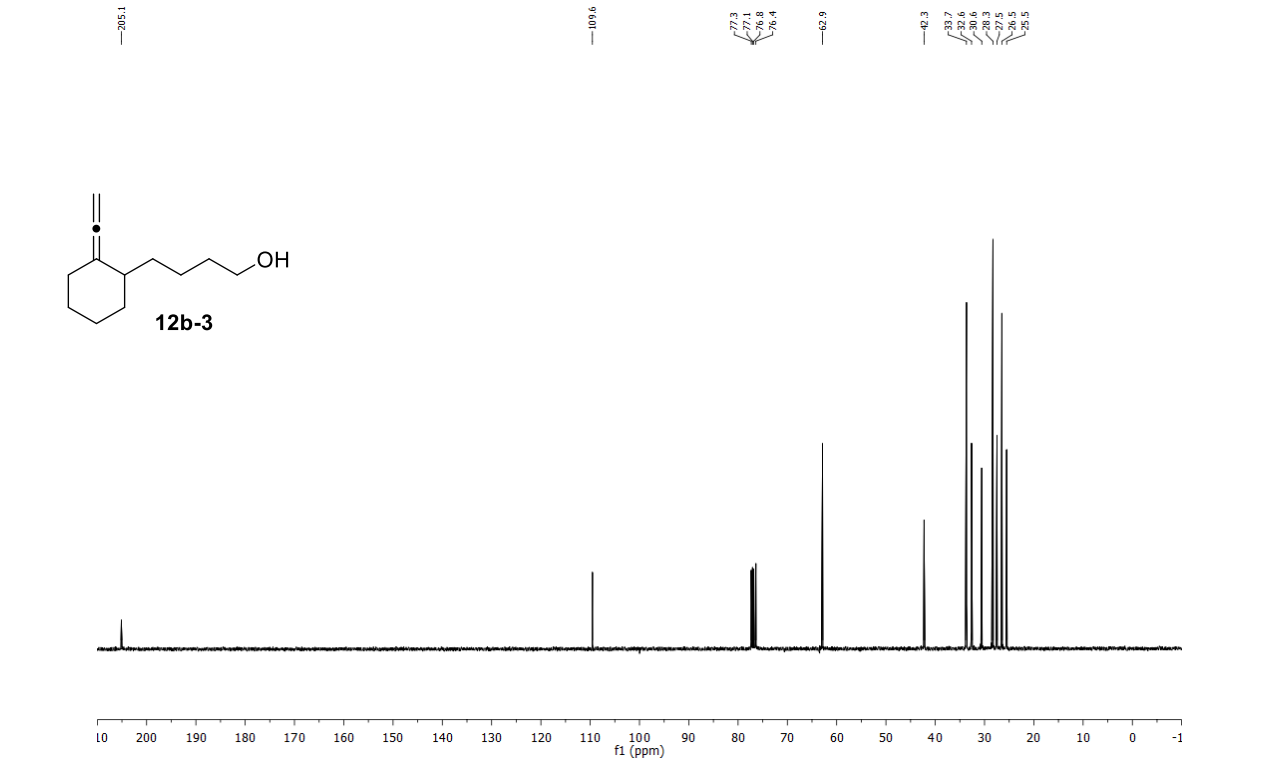
^{13}C NMR Spectra of **12b-2**



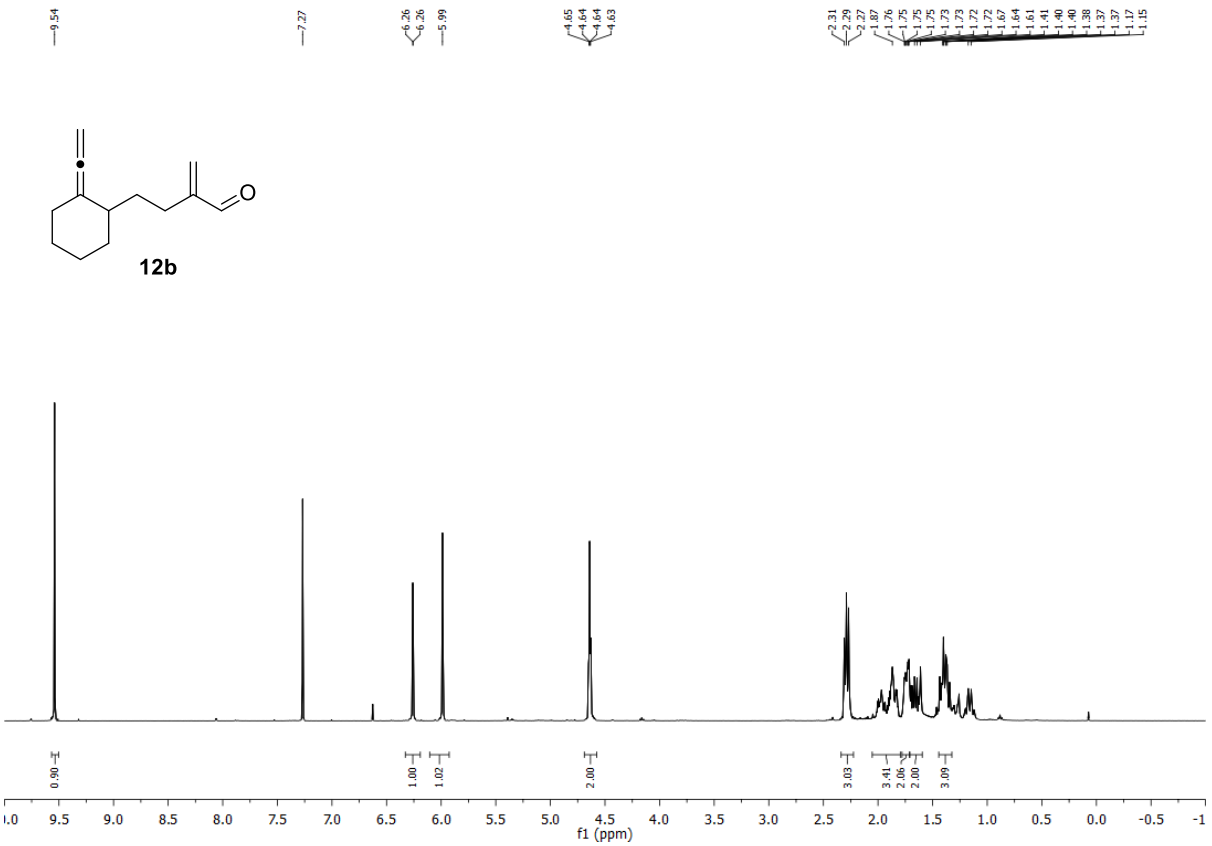
^{1}H NMR Spectra of **12b-3**



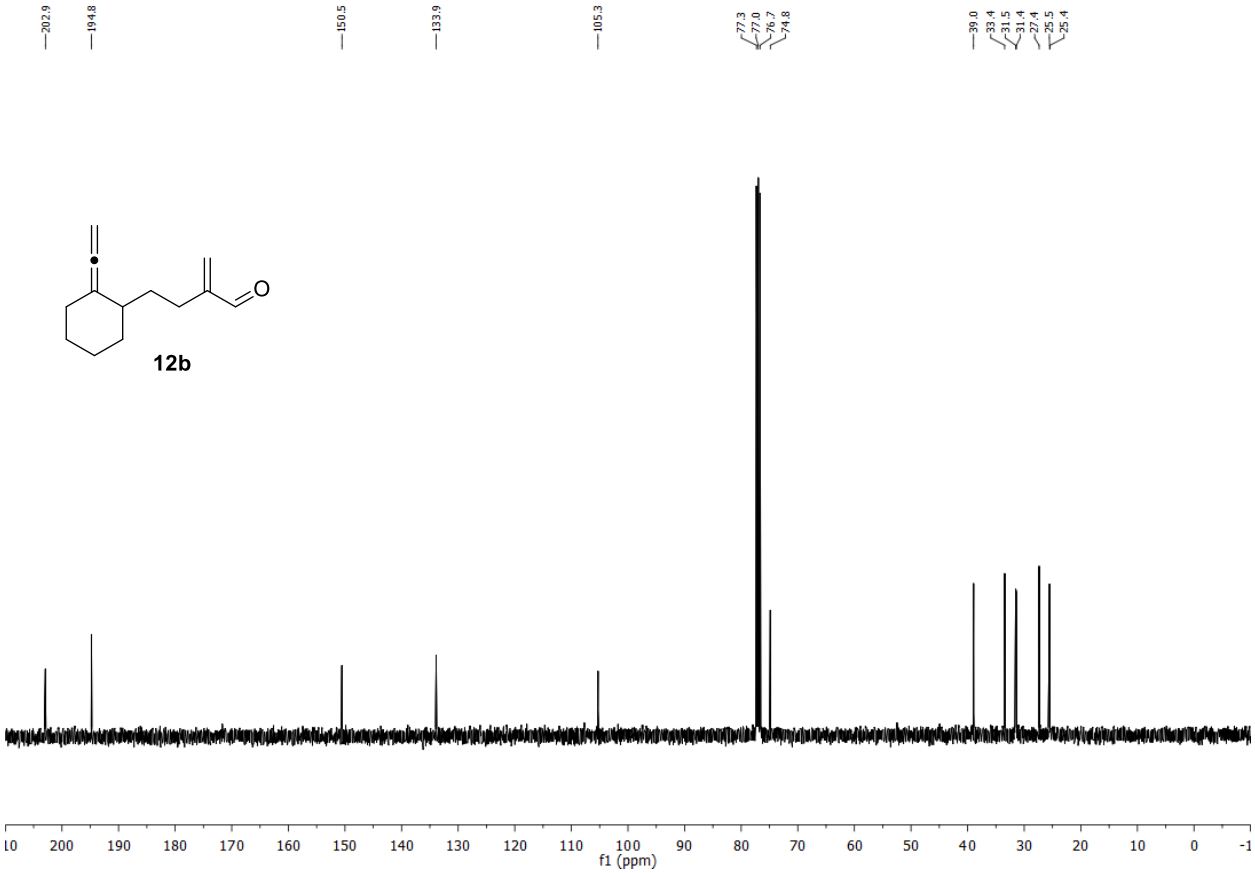
^{13}C NMR Spectra of **12b-3**



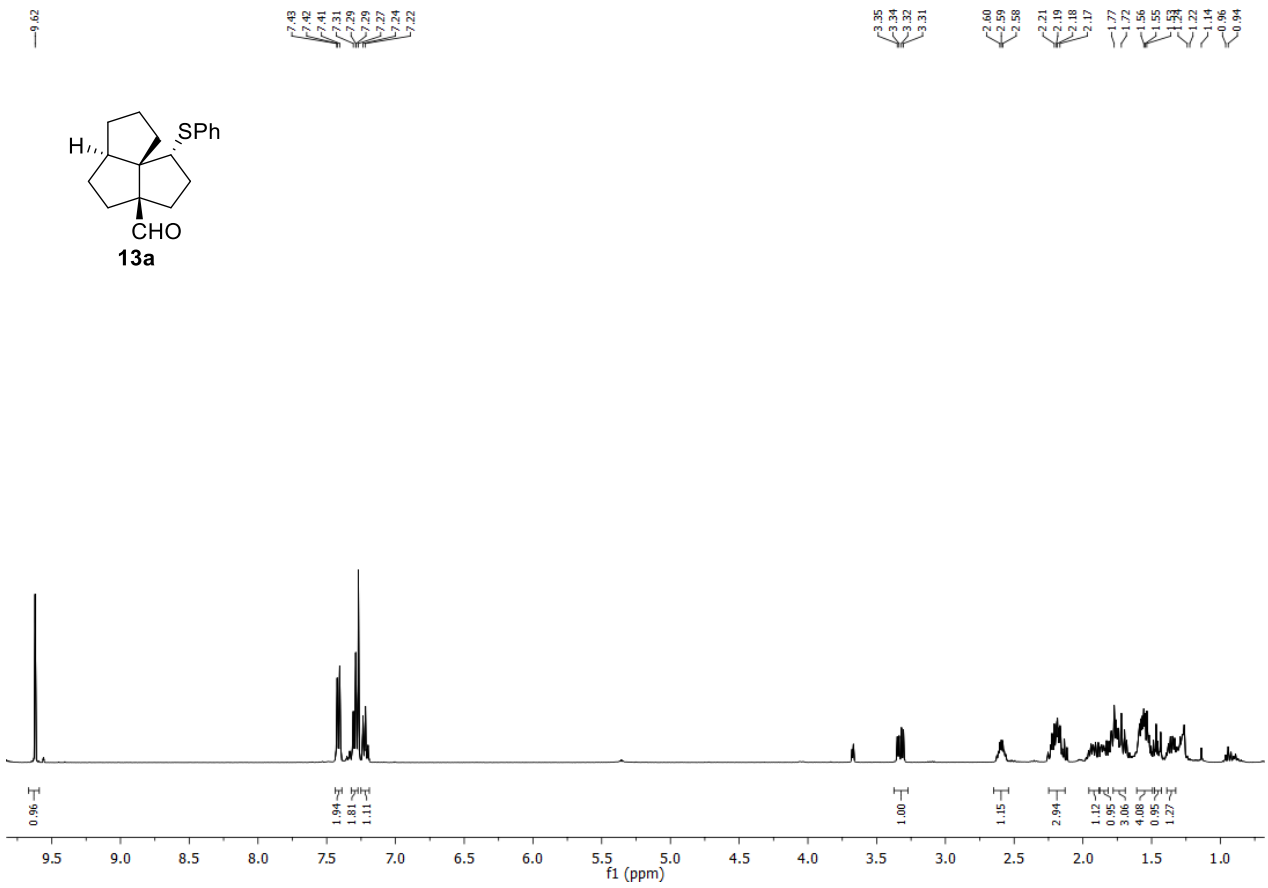
^{1}H NMR Spectra of **12b**



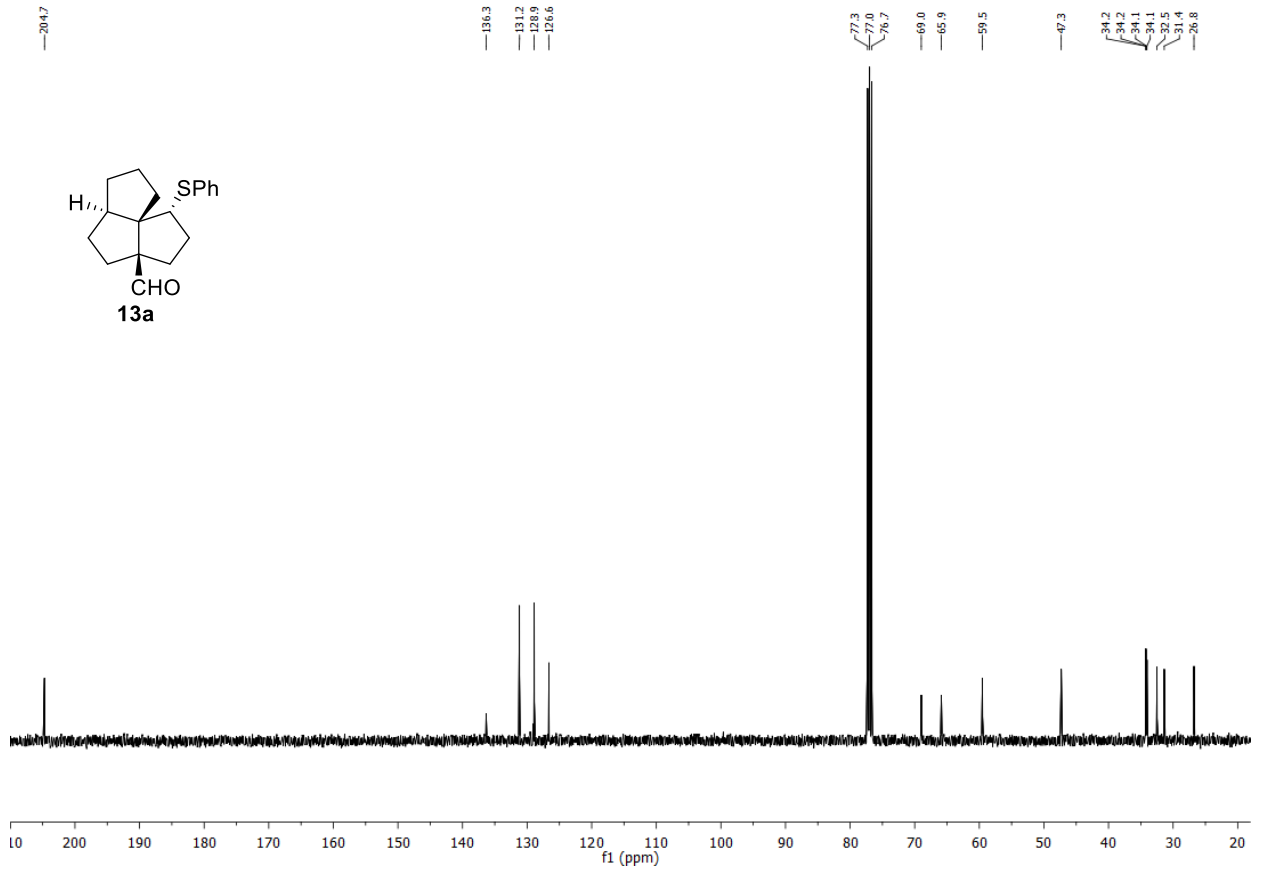
^{13}C NMR Spectra of **12b**



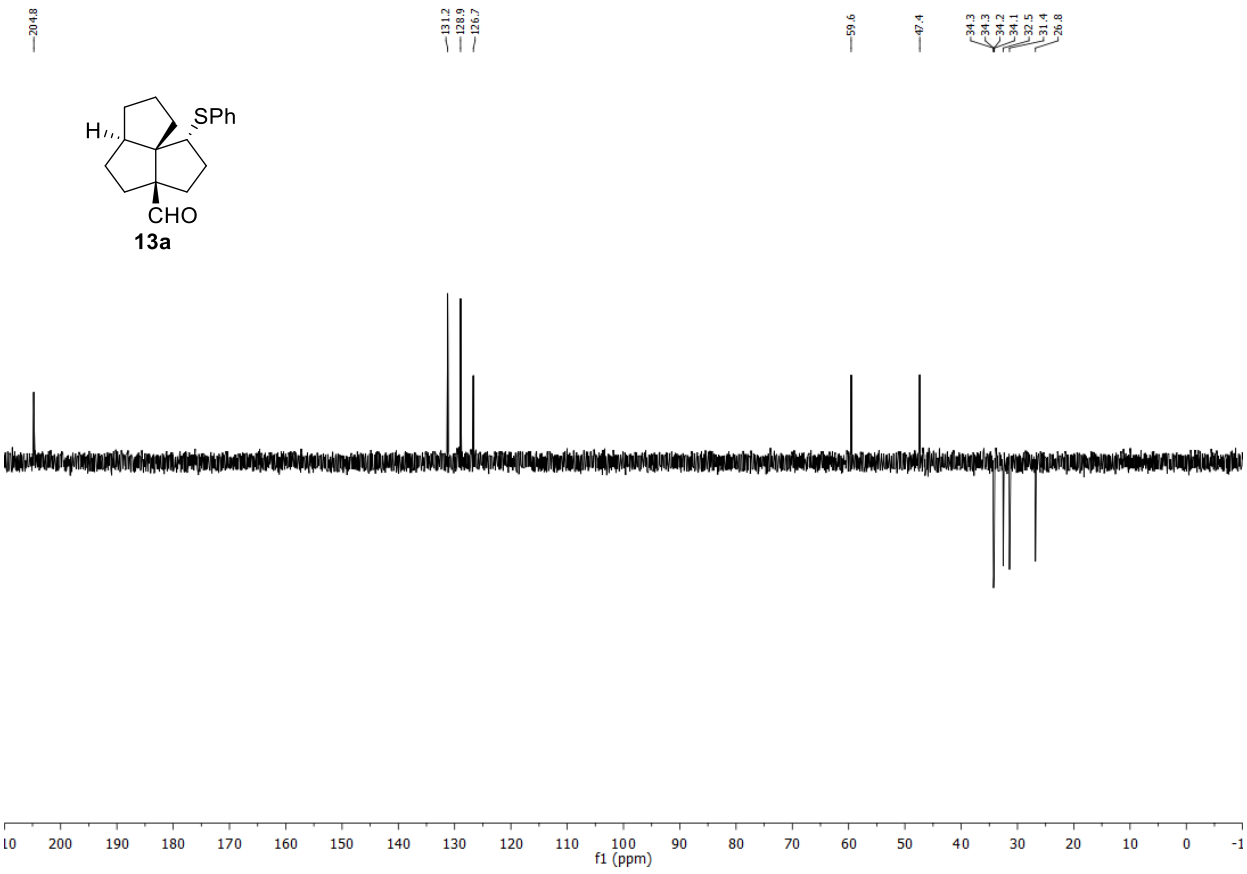
^{1}H NMR Spectra of **13a**



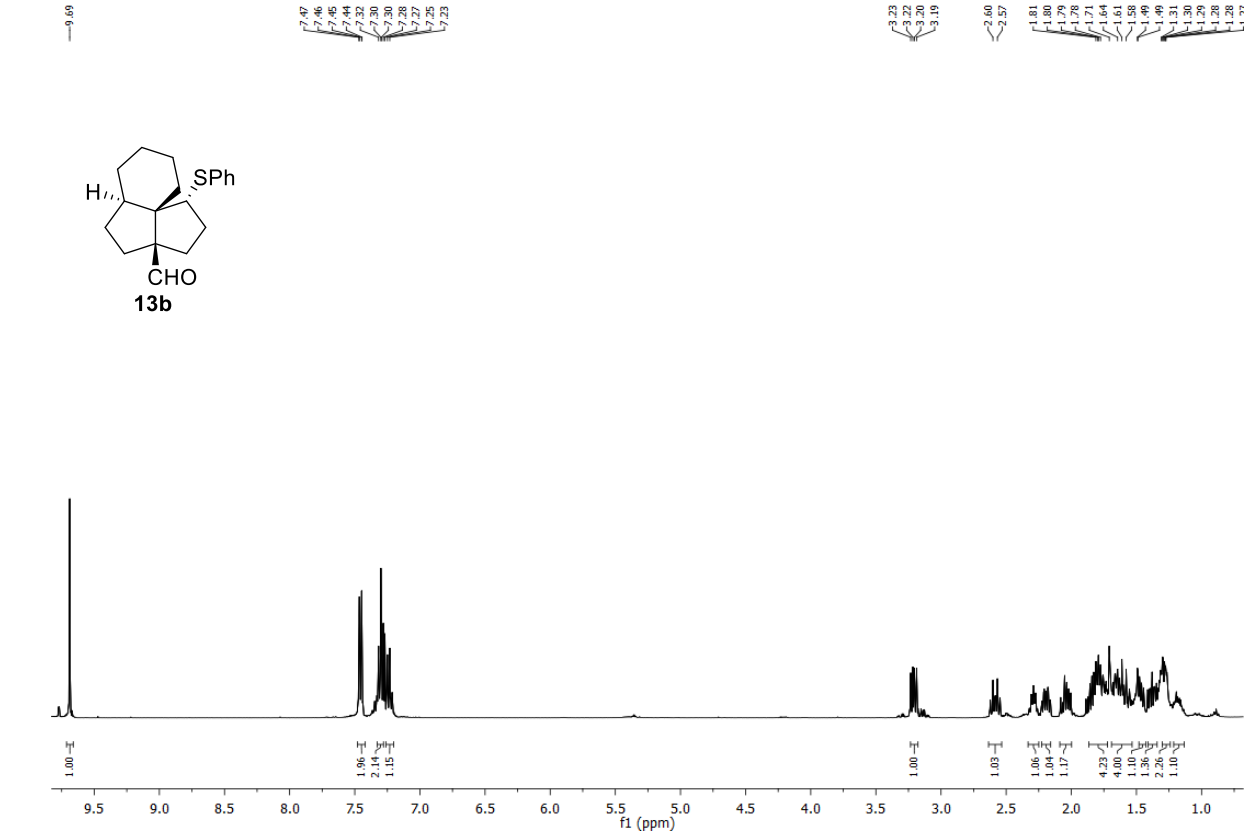
^{13}C NMR Spectra of **13a**



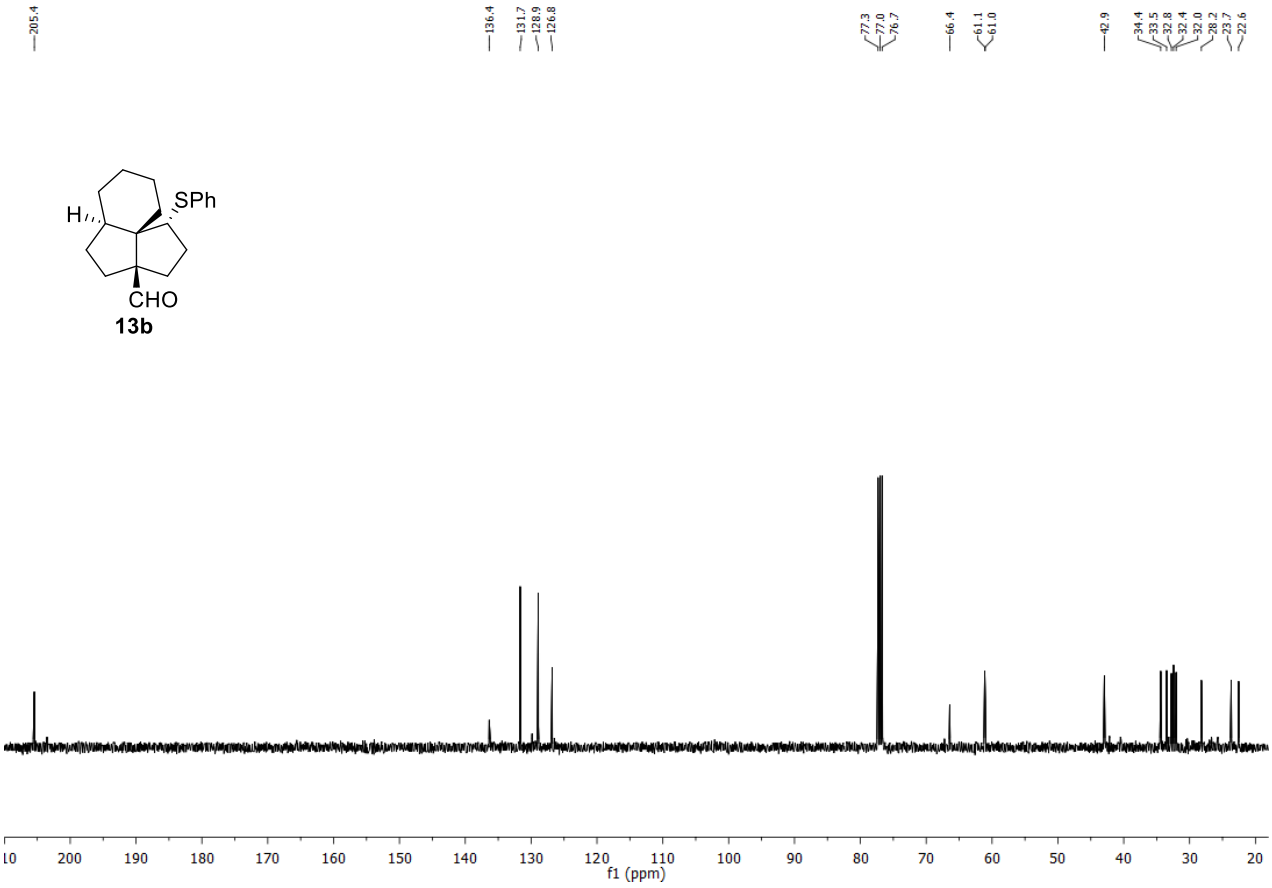
DEPT NMR Spectra of **13a**



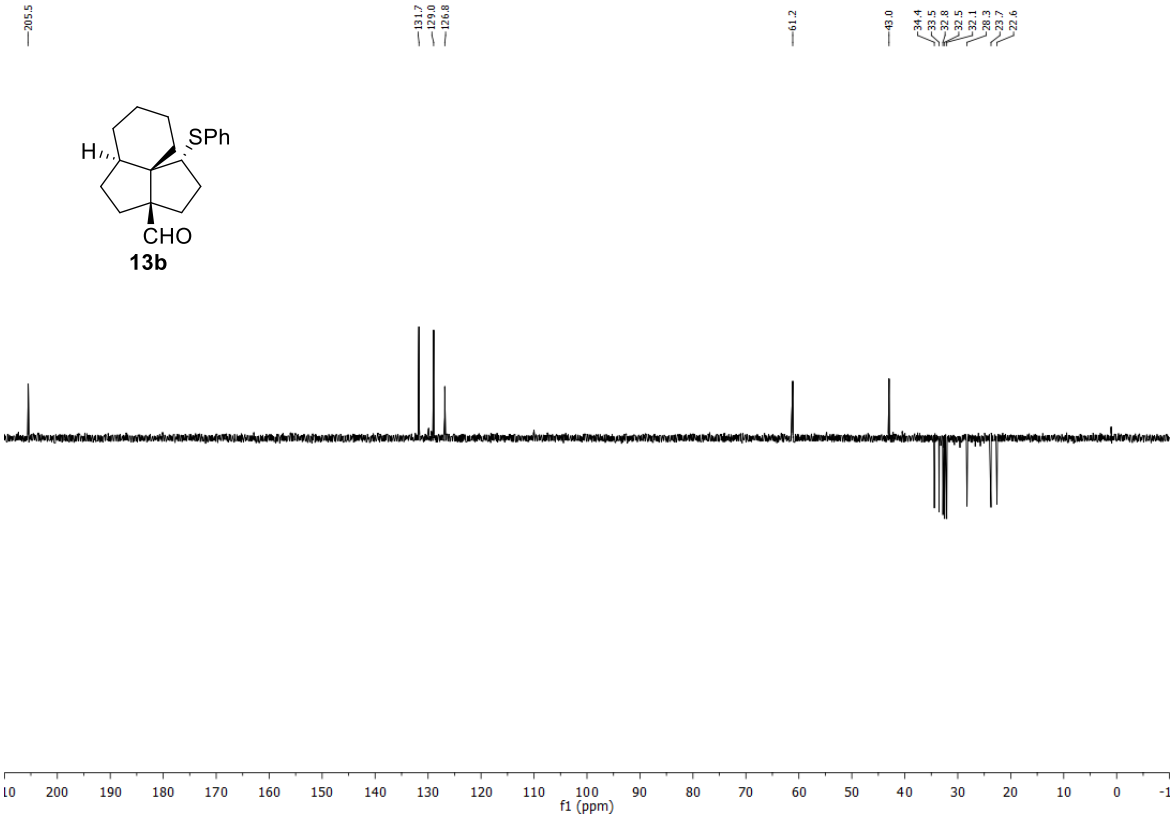
^{1}H NMR Spectra of **13b**



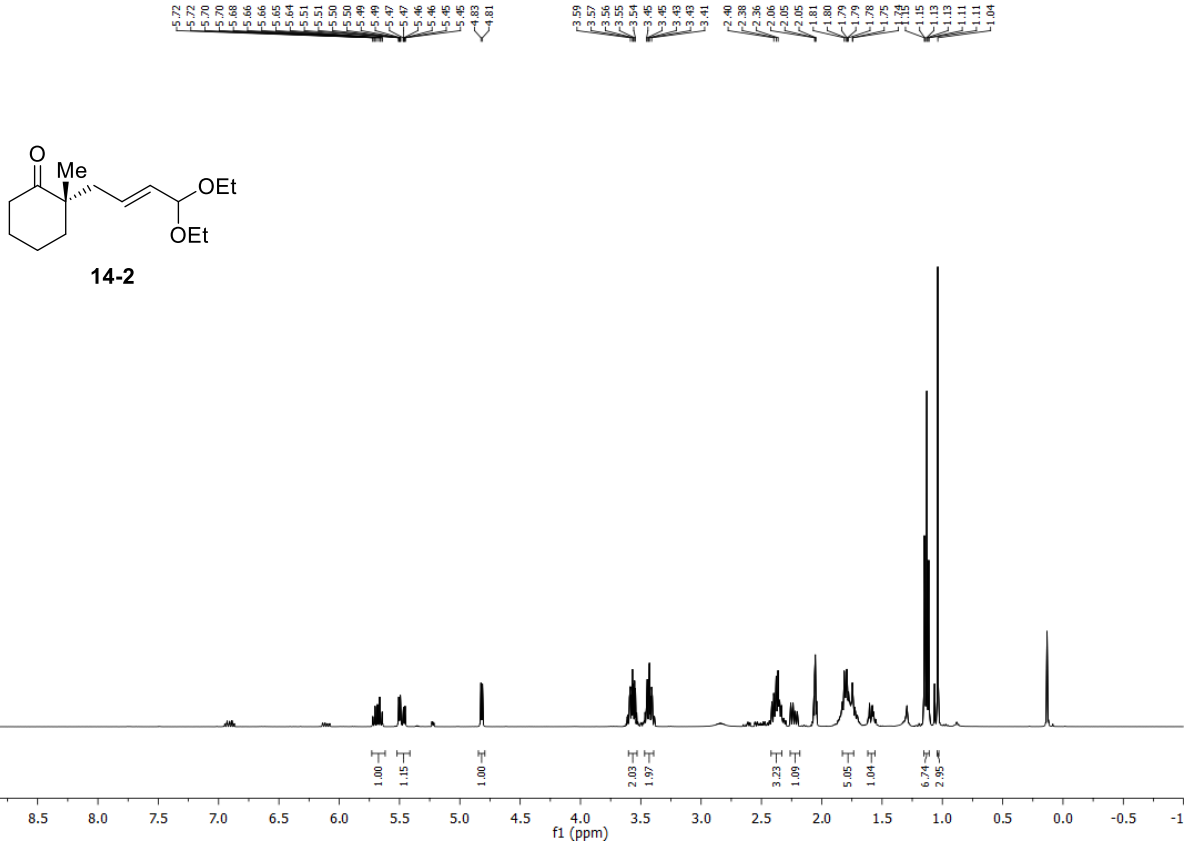
^{13}C NMR Spectra of **13b**



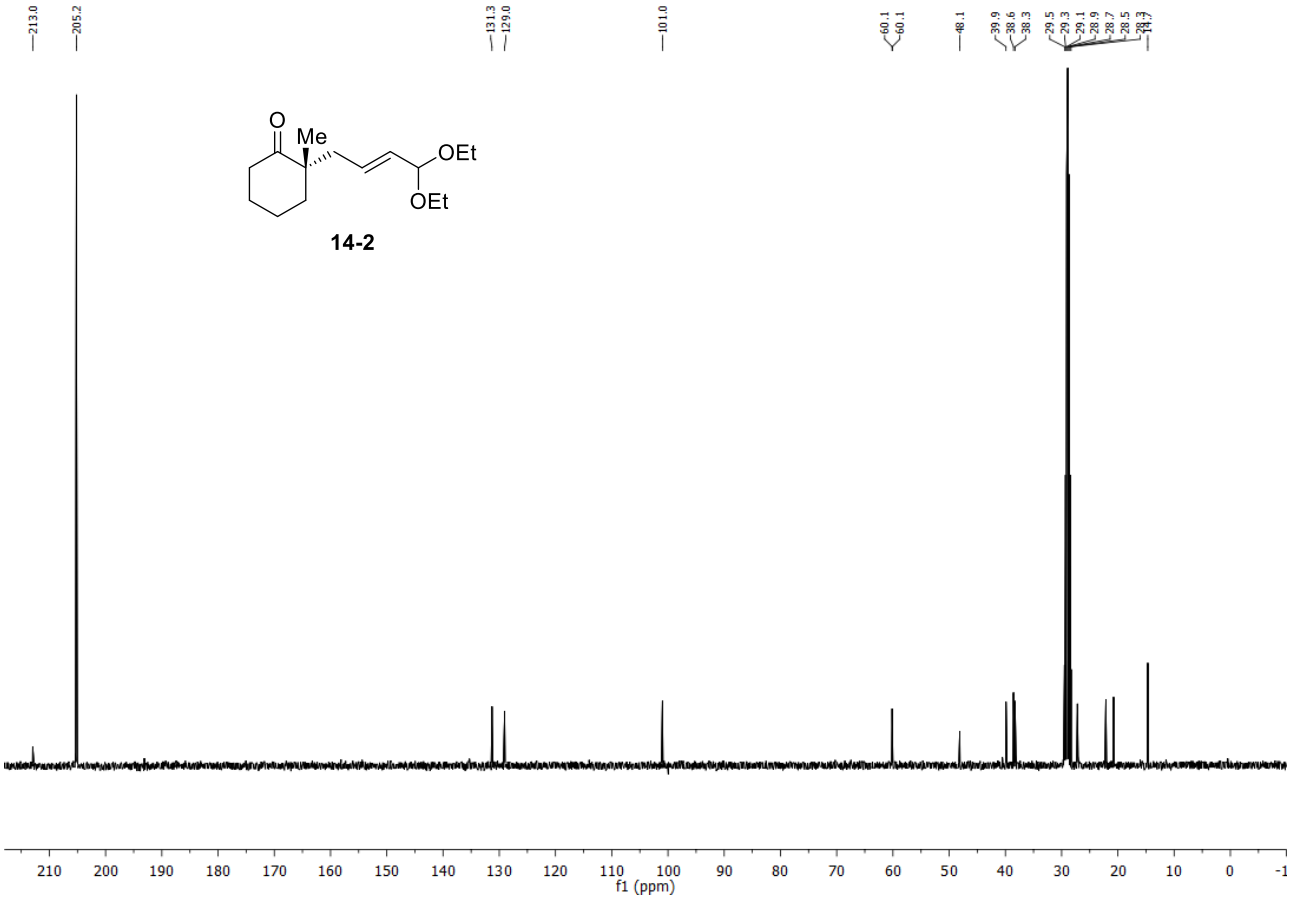
DEPT NMR Spectra of **13b**



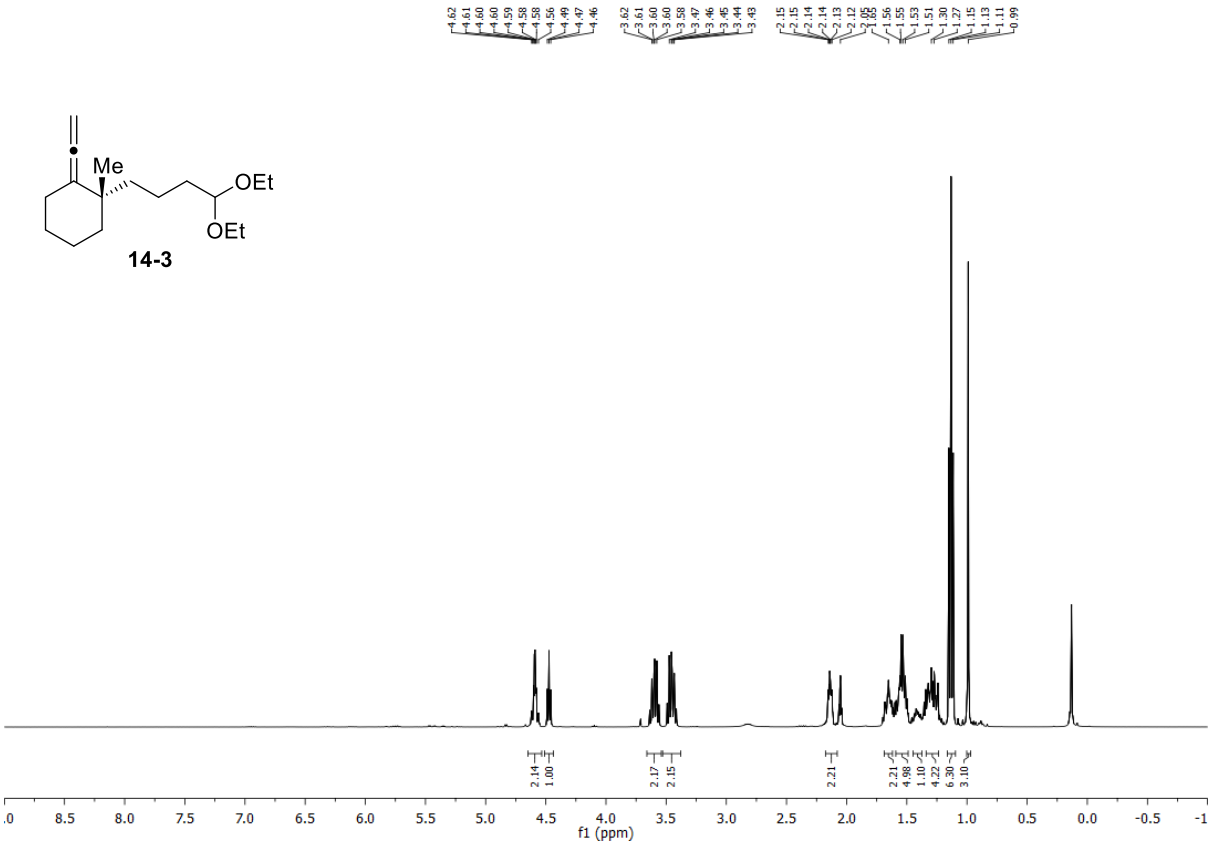
^{1}H NMR Spectra of **14-2**



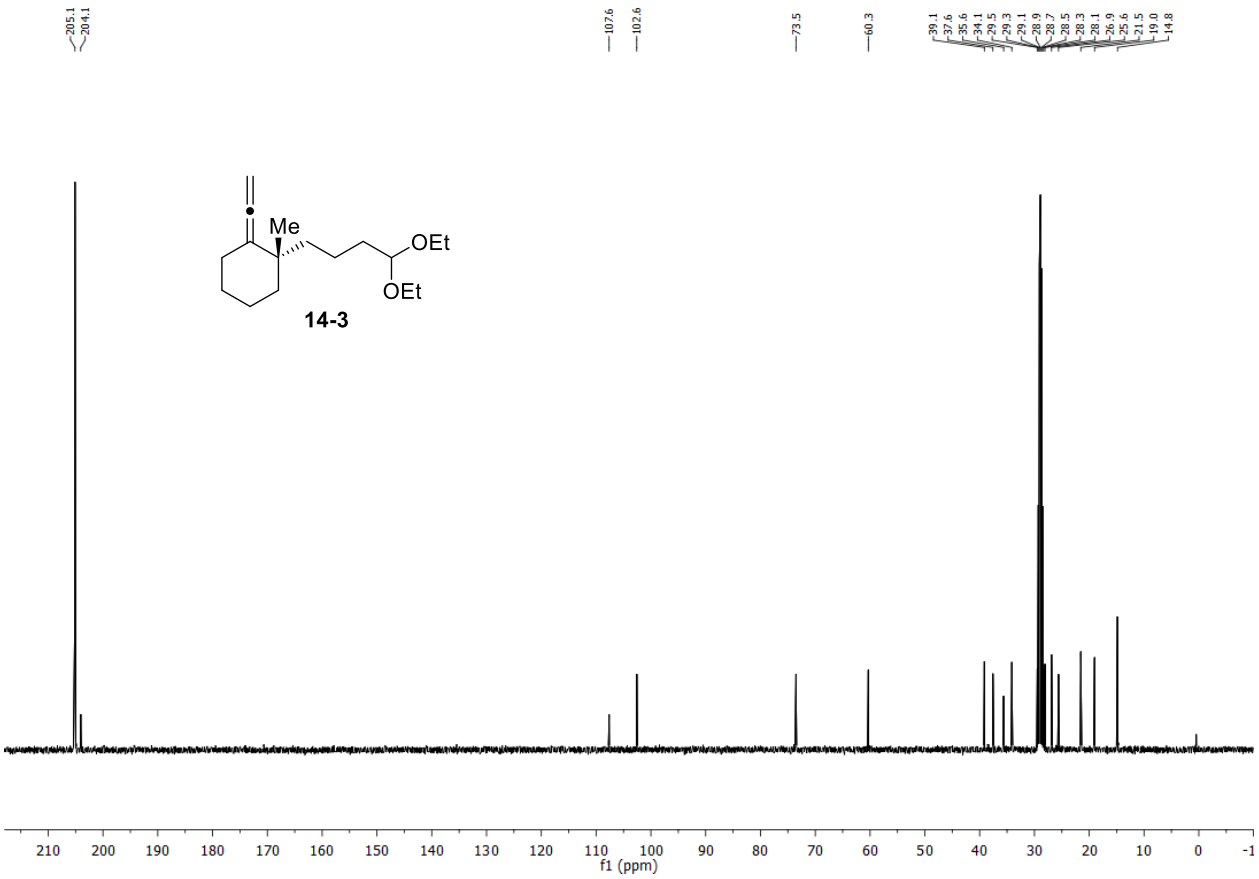
^{13}C NMR Spectra of **14-2**



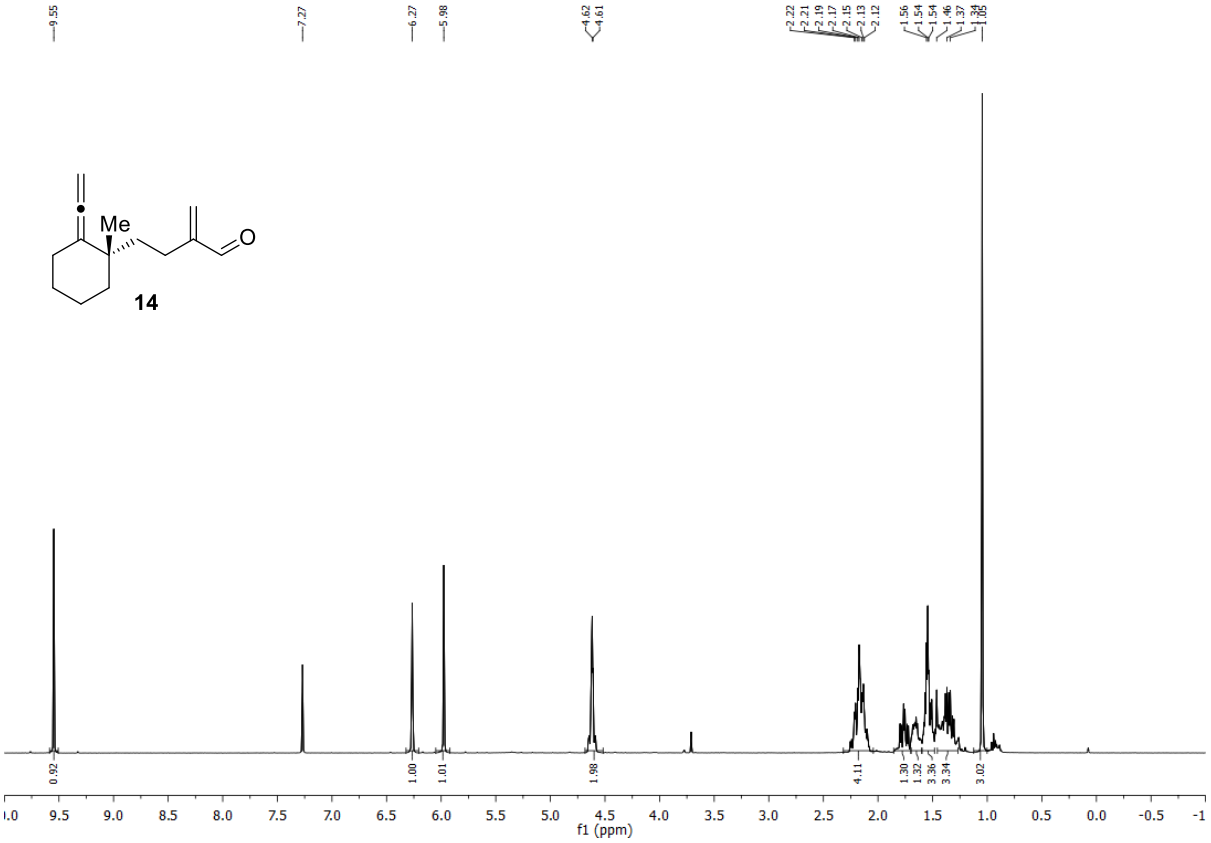
^{1}H NMR Spectra of **14-3**



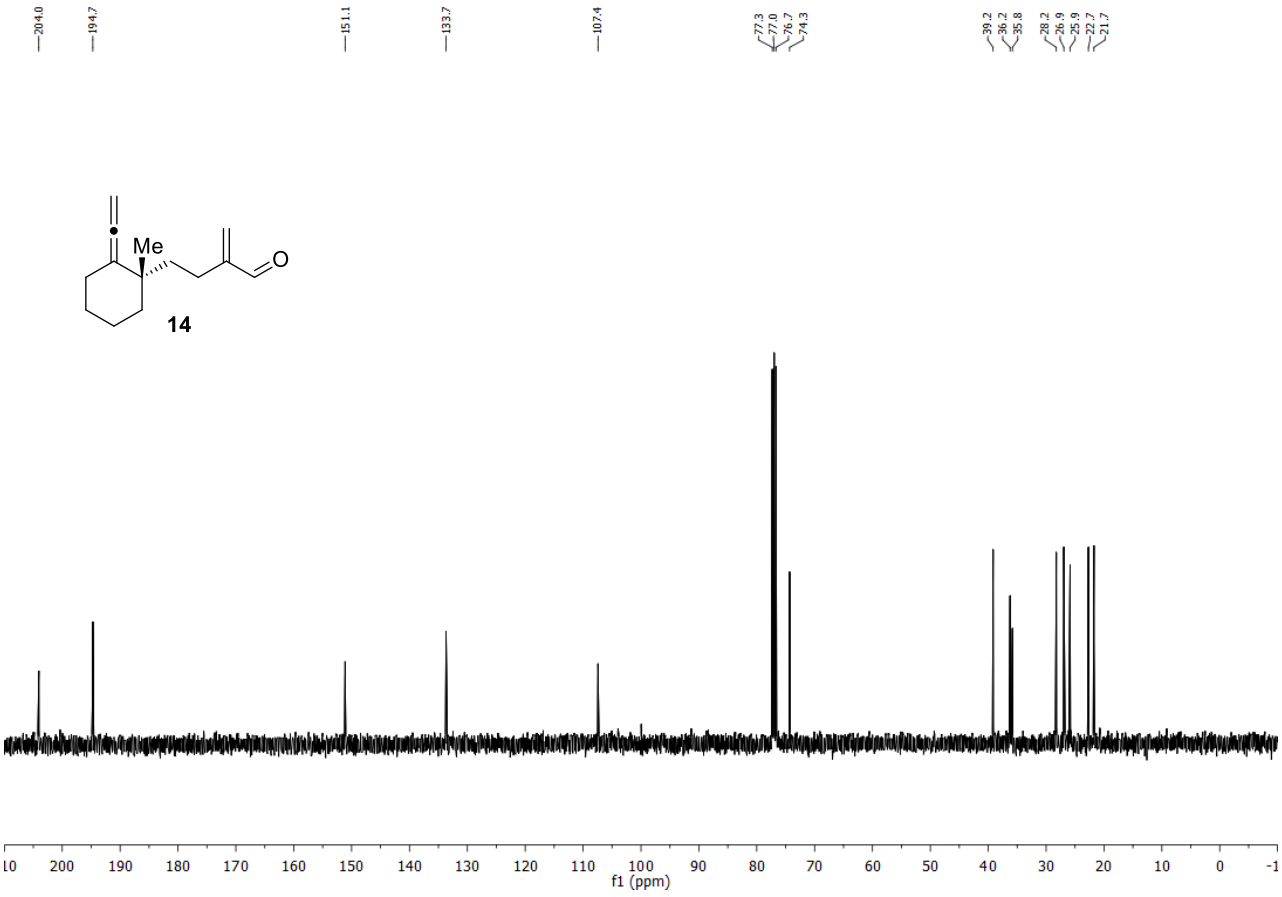
^{13}C NMR Spectra of **14-3**



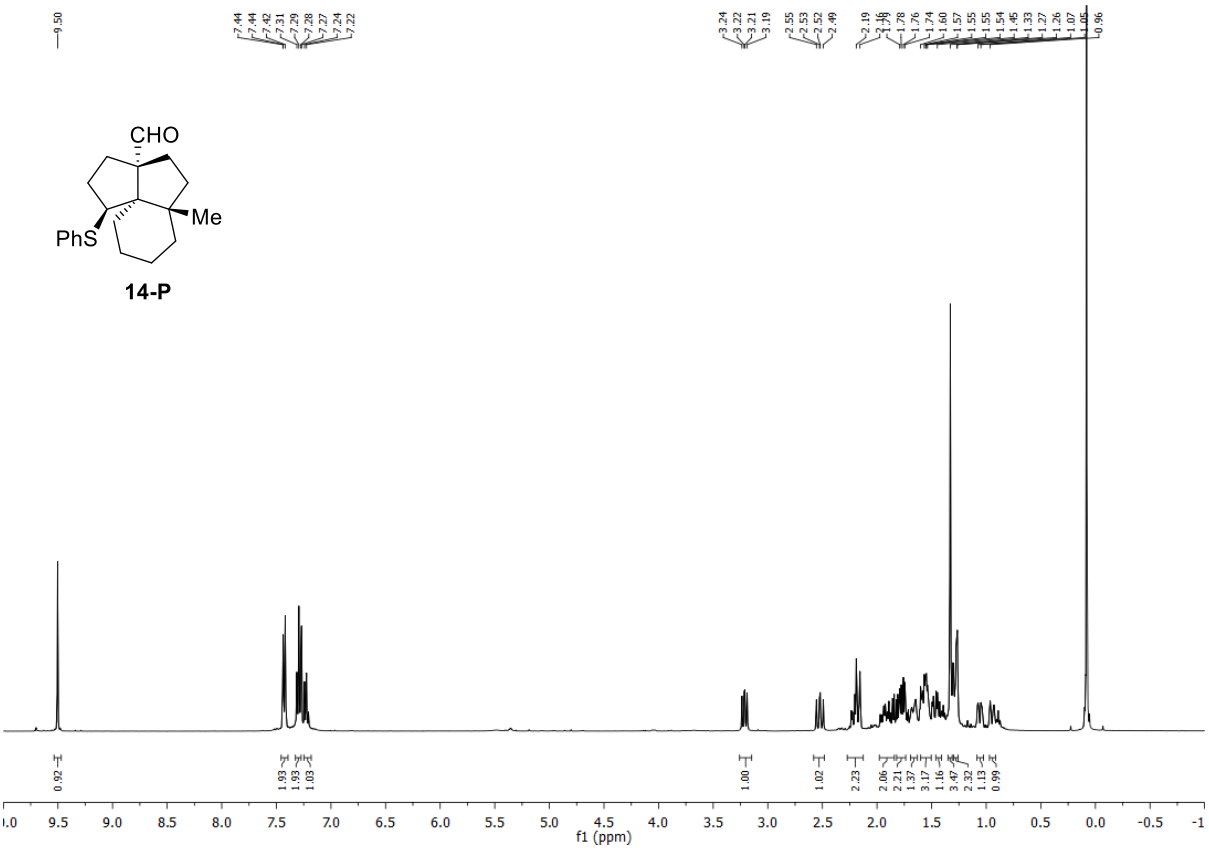
^{1}H NMR Spectra of **14**



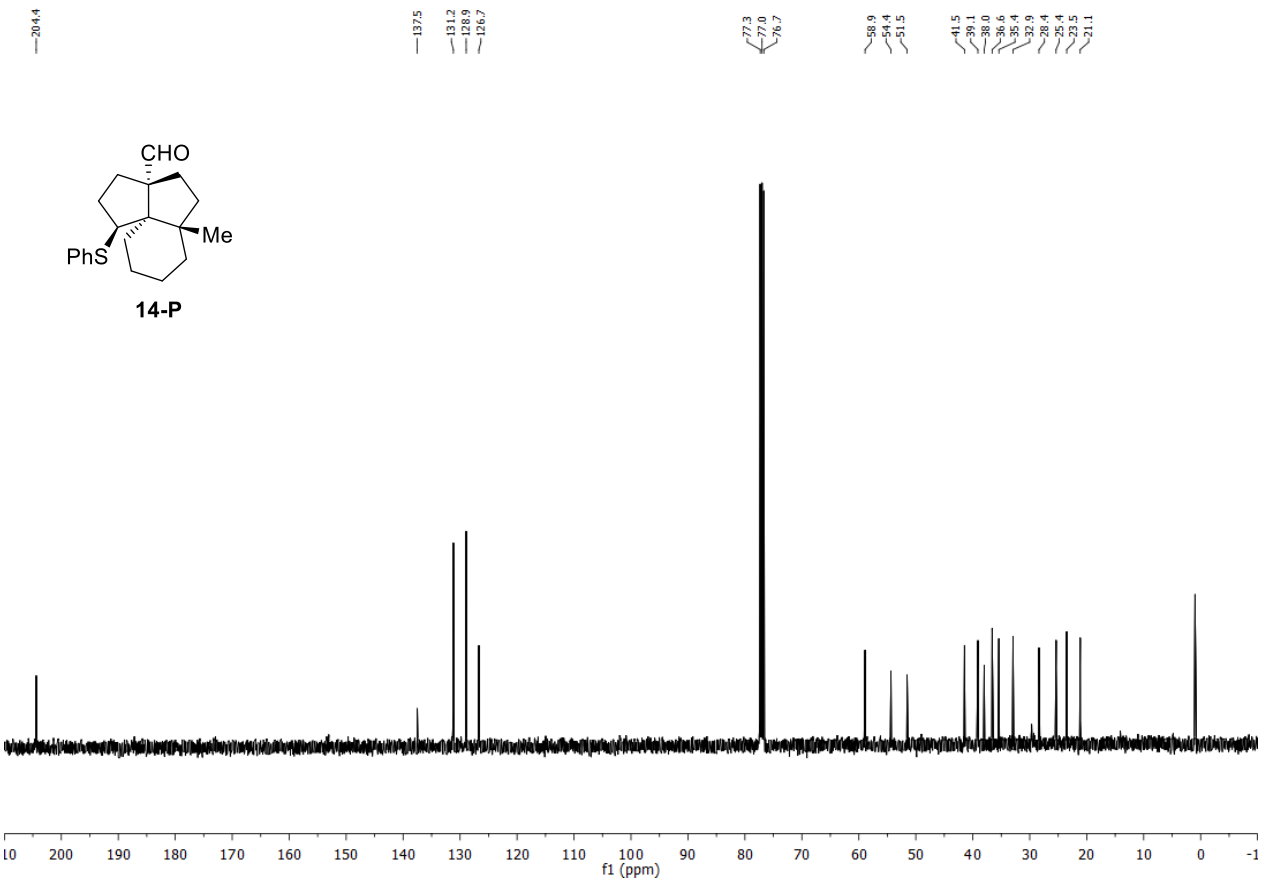
^{13}C NMR Spectra of **14**



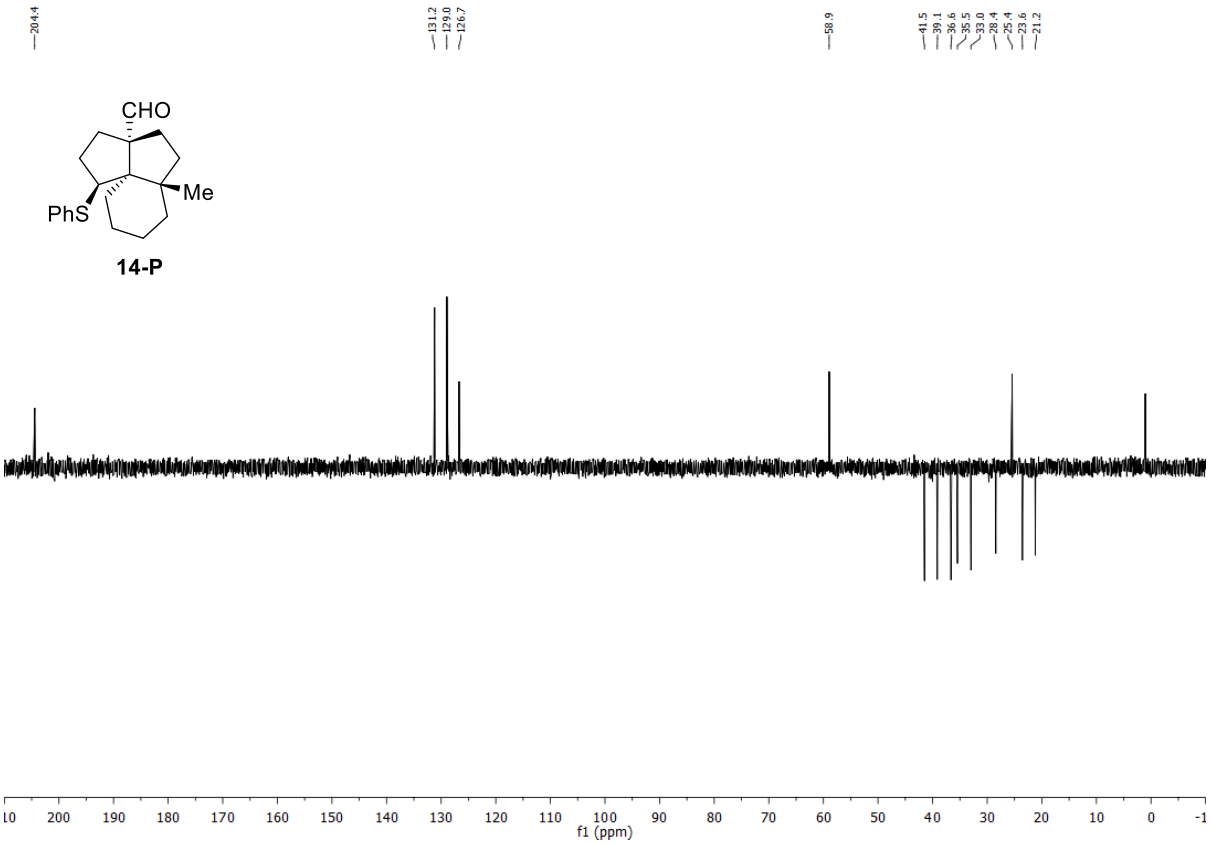
^{1}H NMR Spectra of **14-p**



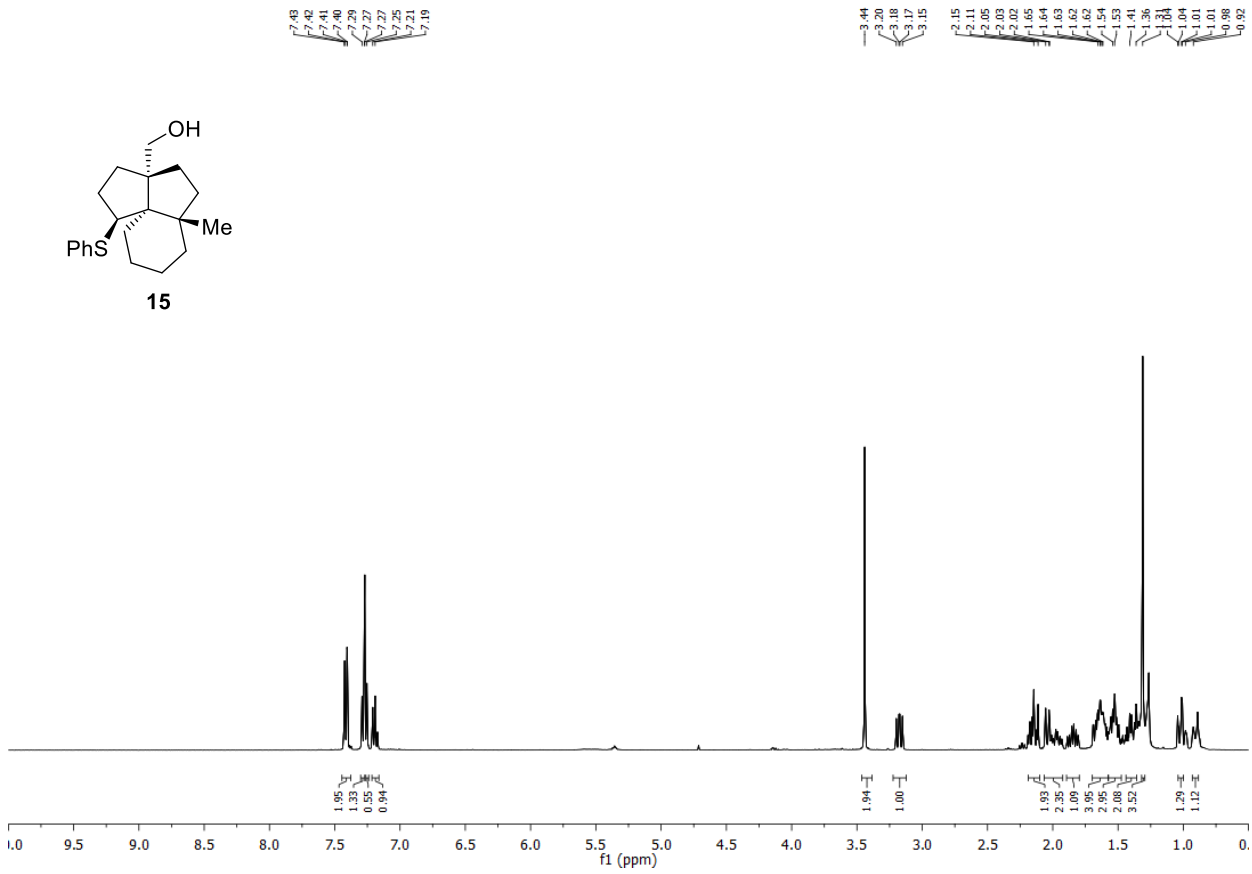
^{13}C NMR Spectra of **14-p**



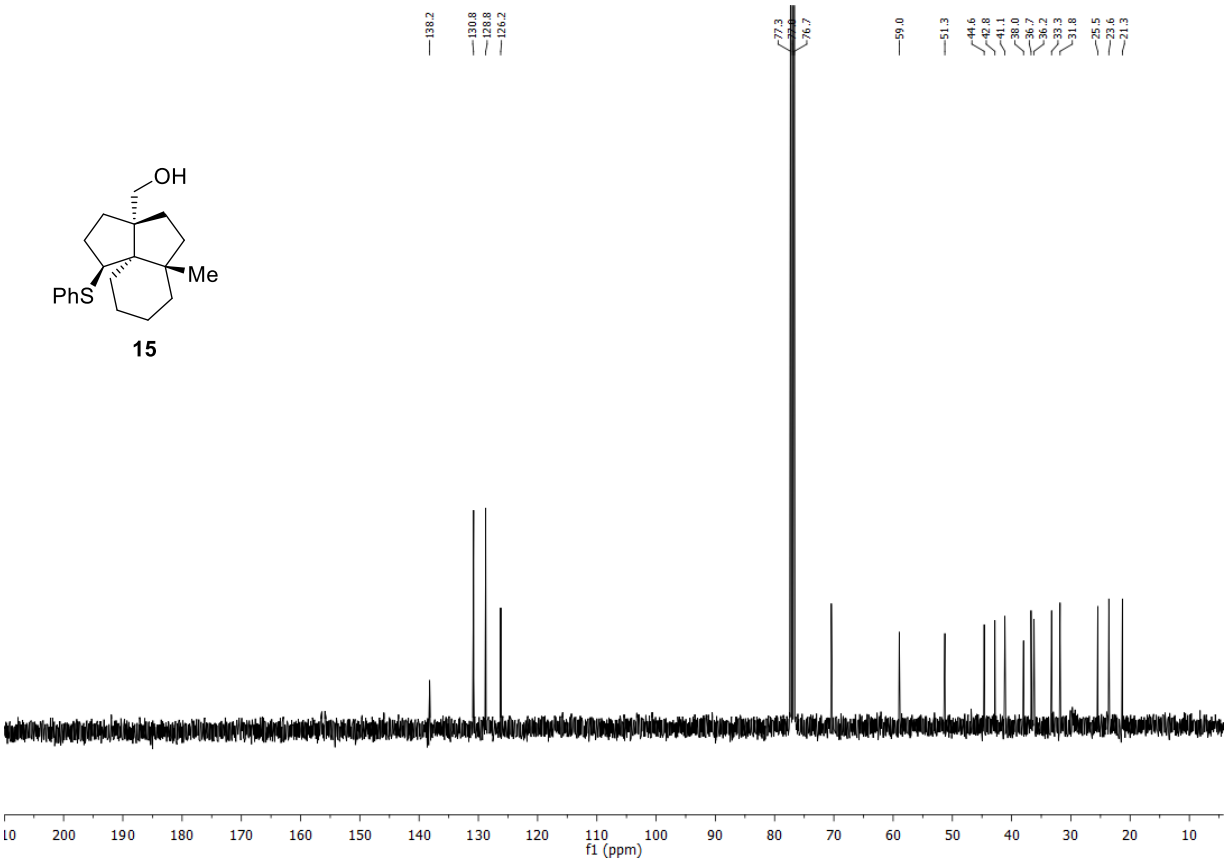
DEPT NMR Spectra of **14-p**



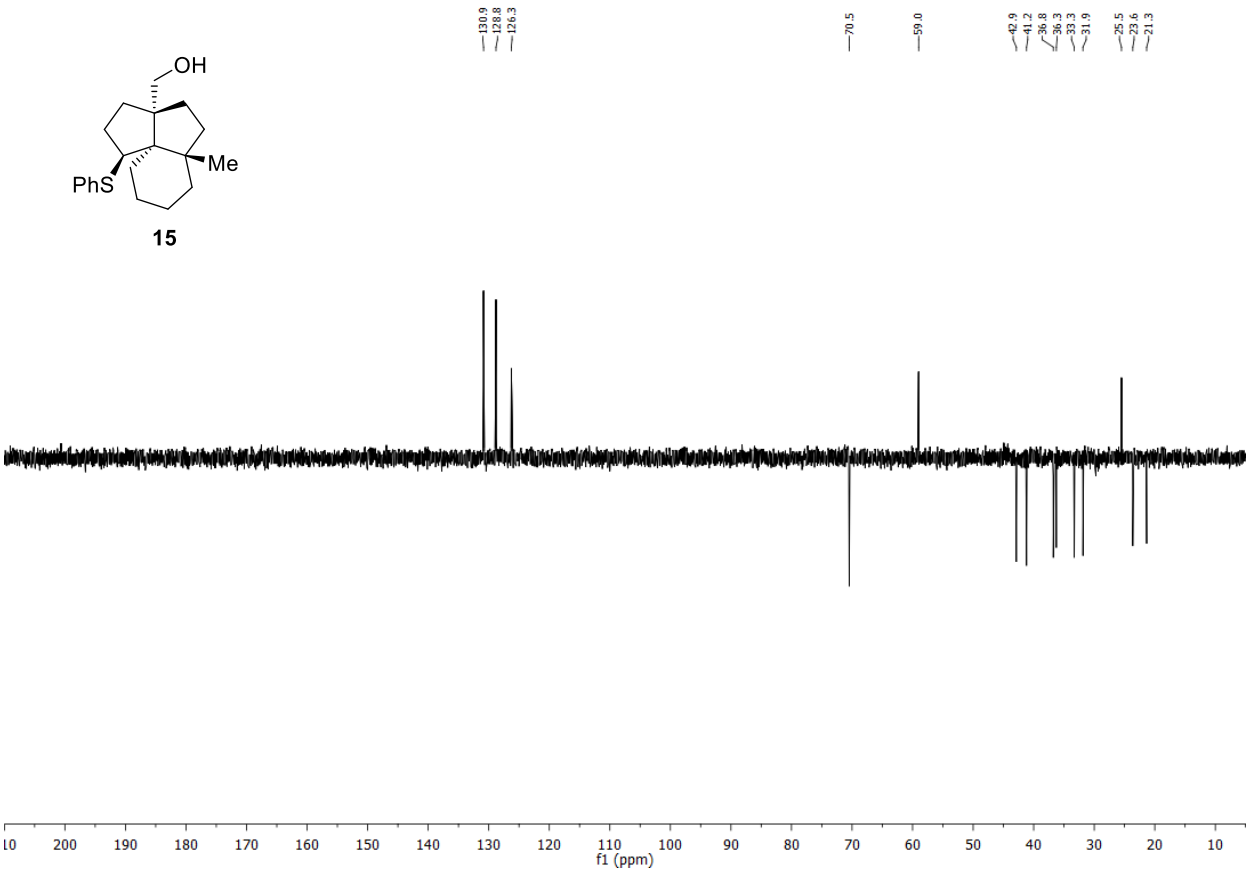
^{1}H NMR Spectra of **15**



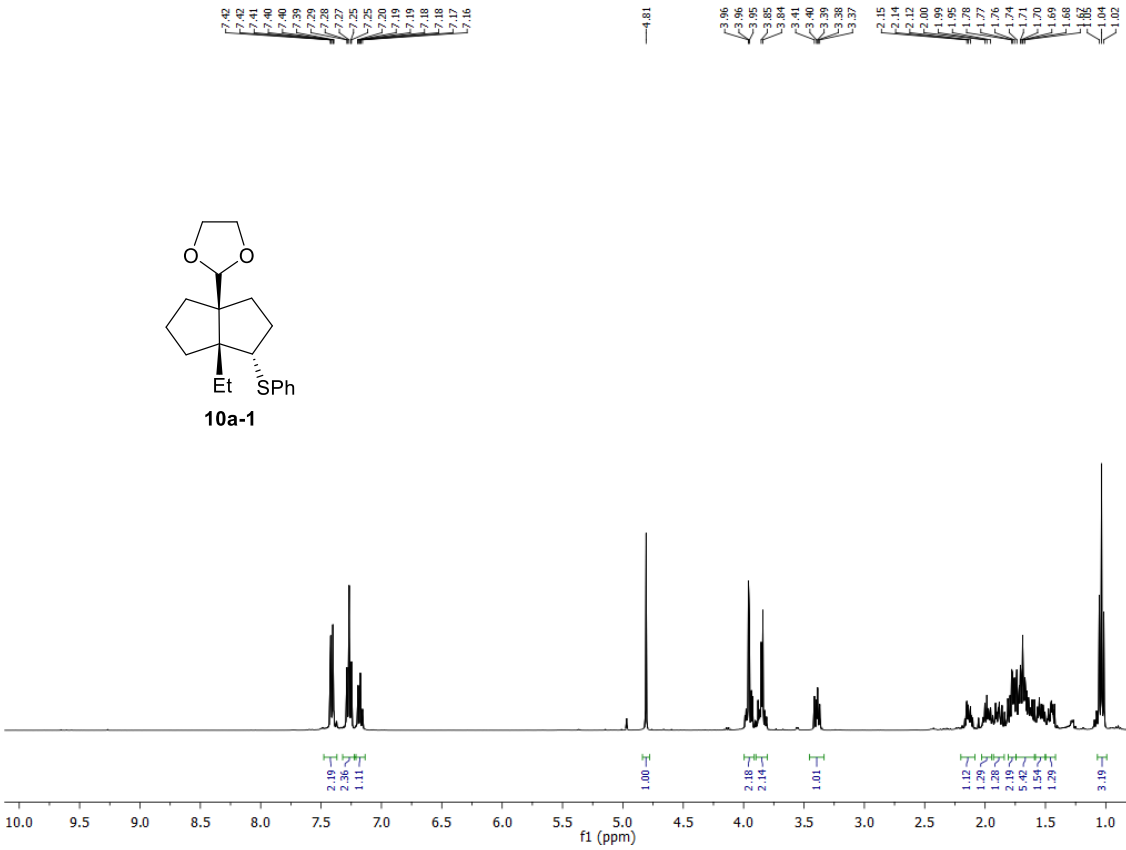
^{13}C NMR Spectra of **15**



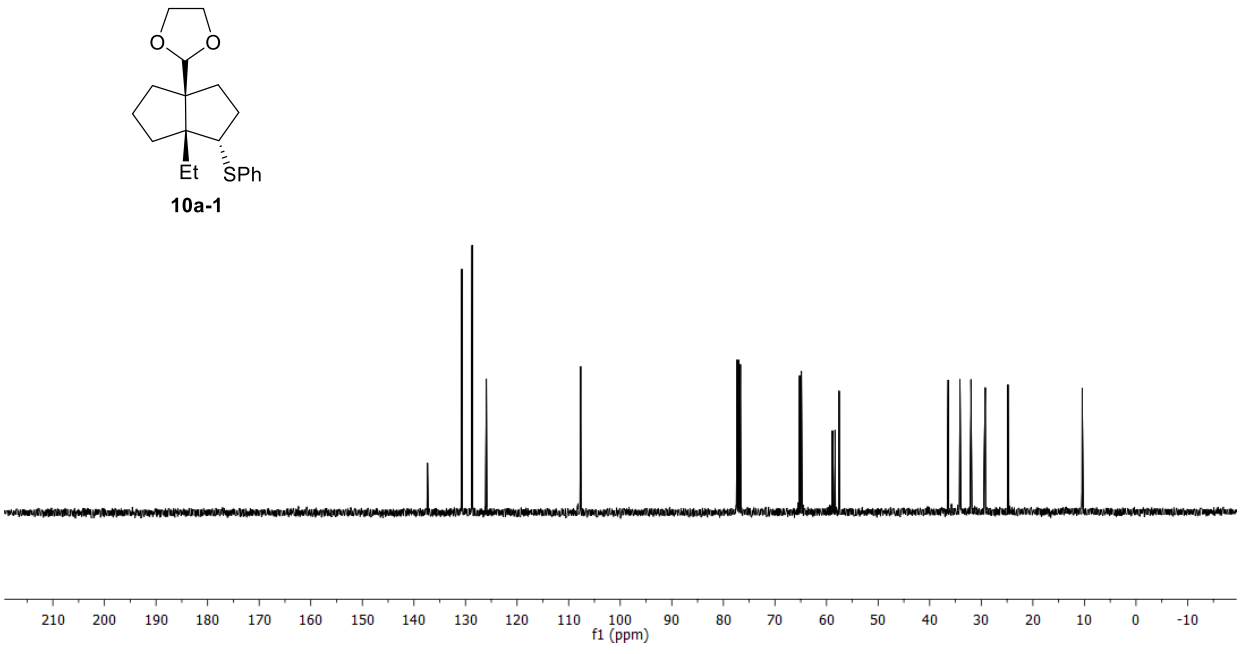
DEPT NMR Spectra of **15**



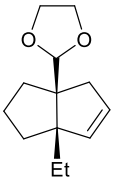
^{1}H NMR Spectra of **10a-1**



^{13}C NMR Spectra of **10a-1**

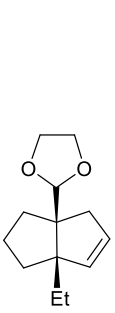


^{1}H NMR Spectra of **10a-2**



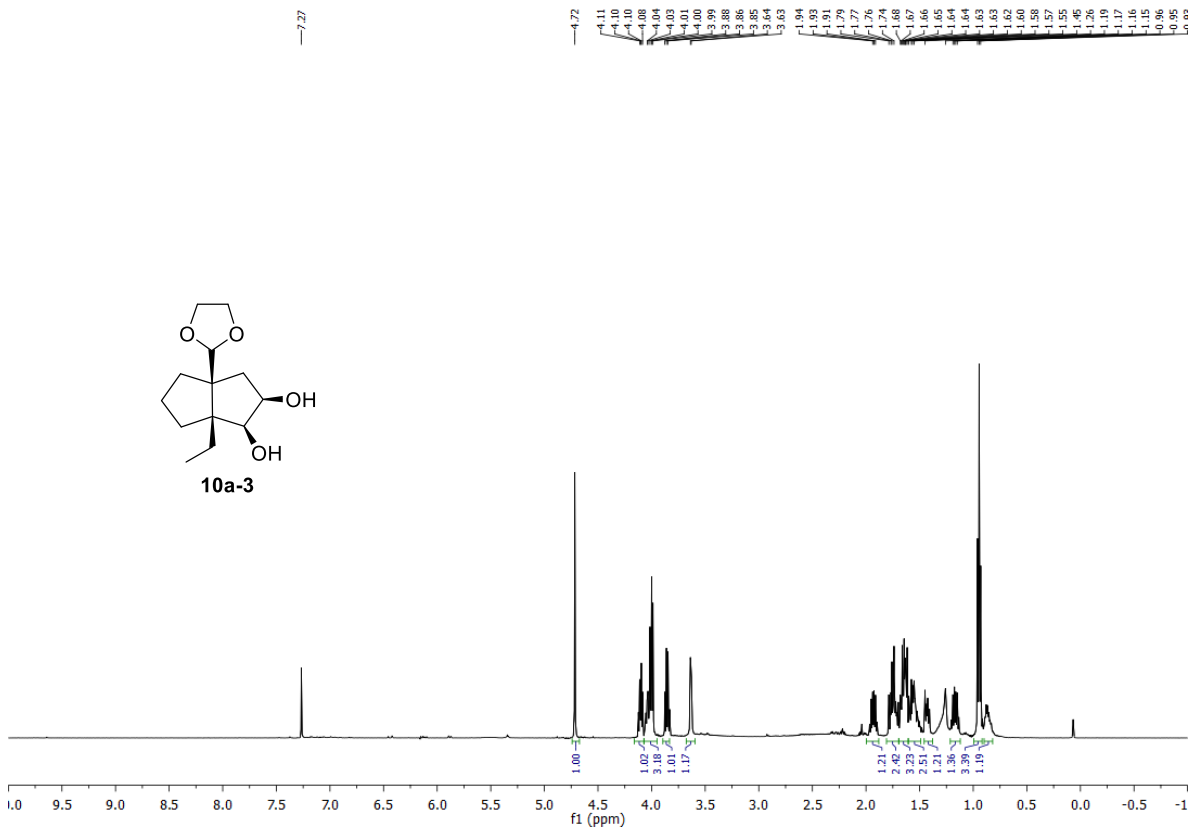
10a-2

^{13}C NMR Spectra of **10a-2**

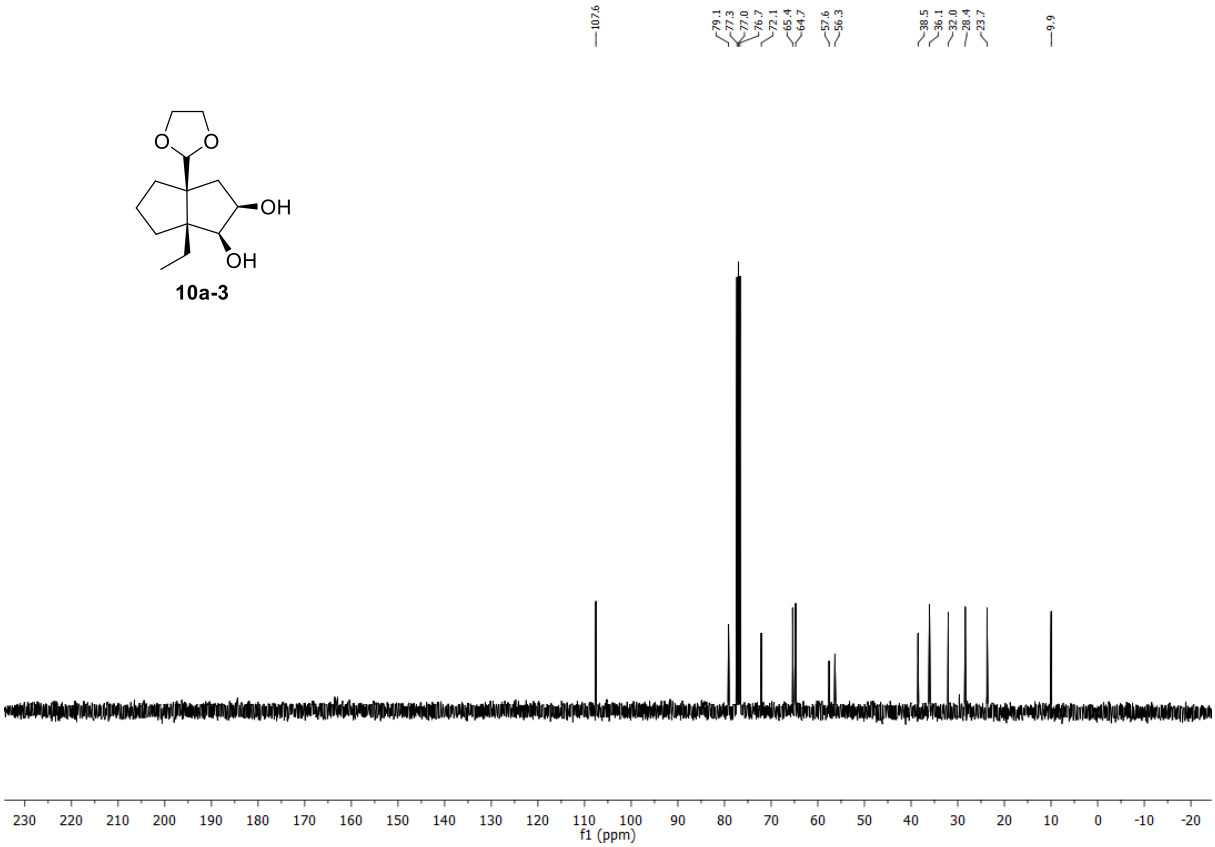


10a-2

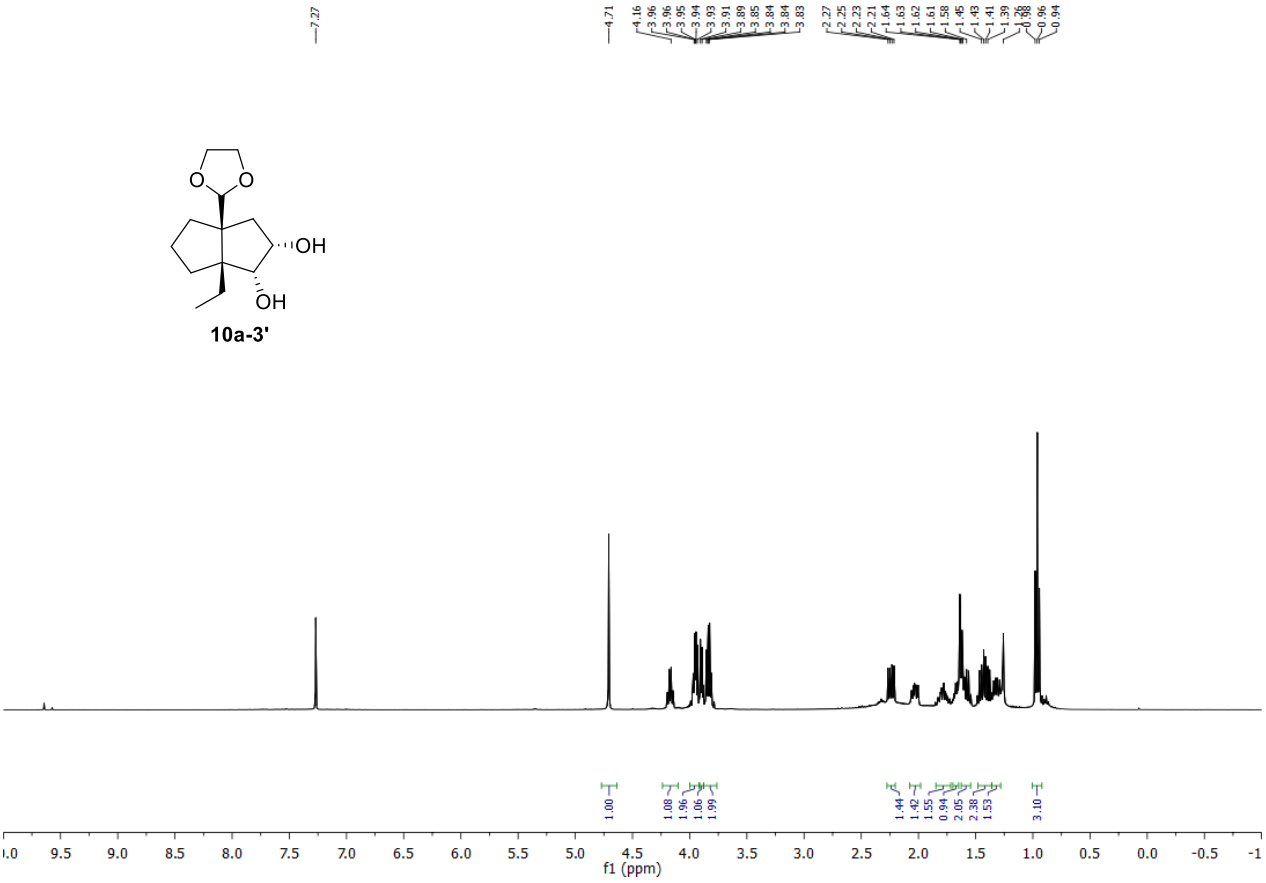
^{1}H NMR Spectra of **10a-3**



^{13}C NMR Spectra of **10a-3**



^{1}H NMR Spectra of **10a-3'**



^{13}C NMR Spectra of **10a-3'**