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Supporting Information

A Cyclic (Alkyl)(Amido)Carbene: Synthesis, Study and Utility as a Desulfurization Reagent

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General Considerations. All procedures were performed using standard Schlenk techniques under an atmosphere of nitrogen or in a nitrogen filled glove box unless otherwise noted. All compounds, except for **3**, were found to be air stable and all chromatographic separations were performed under ambient conditions. The compound 2,2,4,4-tetramethylglutaryl dichloride was prepared according to a literature procedure.[1] Carbonyl sulfide was purchased from Sigma Aldrich and passed through a drying tube packed with 3 Å molecular sieves to remove the residual moisture prior to use. Solvents were dried and degassed using a Vacuum Atmospheres Company solvent purification system and stored over 4 Å molecular sieves in a nitrogen filled glove box. Infrared (IR) spectra were recorded on a Thermo Scientific Nicolet iS5 spectrometer equipped with an iD3 attenuated total reflectance (ATR) attachment (diamond crystal) or using CaF_2 or KBr solution cells. High resolution mass spectra (HRMS) were obtained with a Waters Micromass Autospec-Ultima (CI) or Agilent 6530 QTOF (ESI) mass spectrometer. NMR spectra were recorded on a Varian 400, 500, or 600 MHz spectrometer. Chemical shifts (δ) are reported in ppm and are referenced to the residual solvent (^{1}H: THF-d_8, 1.72 ppm; $CDCl_3$, 7.26 ppm; C_6D_6, 7.15 ppm, C_7D_8, 2.08 ppm; ^{13}C: THF-d_8, 67.21 ppm; $CDCl_3$, 77.0 ppm, C_6D_6, 128.0 ppm). The ^{77}Se NMR data were referenced to an external 60% (v/v) Me_2Se standard in $CDCl_3$ set at δ 0.0 ppm. Elemental analyses were performed with a Thermo Scientific Flash 2000 Organic Elemental Analyzer. Melting points were measured using a Stanford Research Systems MPA100 OptiMelt automated melting point apparatus and are uncorrected.

1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylpiperidine-2,6-dione (1). The compound 2,6-di-*iso*-propyl aniline (1.81 mL, 9.59 mmol, 1 eq) was added to a stirred solution of 2,2,4,4-tetramethylglutaryl dichloride (2.16 g, 9.59 mmol) and triethylamine (4.01 mL, 28.75 mmol, 3 eq) in CH_2Cl_2 (10 mL). The resultant solution was stirred for 1.5 h at ambient temperature and then heated at 40 °C for 1 h. The volatiles were then removed under reduced pressure and the residue was washed with a mixture of hexanes/CH_2Cl_2 (2:1 v:v) (60 mL). The filtrate was collected and concentrated under reduced pressure. Purification via column chromatography (2:1 v/v CH_2Cl_2/hexanes, SiO_2) afforded the desired compound as a white solid (2.82 g, 8.56 mmol, 90% yield). m.p. = 141-143 °C. ^{1}H NMR ($CDCl_3$, 399.68 MHz): δ 1.13 (d, J = 7.05 Hz, 12H), 1.43 (s, 12H), 1.96 (s, 2H), 2.59 (sept., J = 7.1 Hz, 2H), 7.20 (d, J = 7.8 Hz, 2H), 7.36 (t, J = 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.50 MHz): δ 23.72, 28.62, 39.30, 45.59, 123.66, 128.96, 131.38, 145.28, 177.95. IR (ATR): $\nu_{C=O}$ = 1723, 1679 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd for $C_{21}H_{32}NO_2$: 330.2433; Found: 330.2433. Anal. Calcd for $C_{21}H_{31}NO_2$: C, 76.55; H, 9.48; N, 4.25. Found: C, 76.88; H, 9.42; N, 4.30.

1-(2,6-diisopropylphenyl)-6-hydroxy-3,3,5,5-tetramethylpiperidin-2-one (2). To a stirred solution of **1** (1.27 g, 3.85 mmol) in CH_2Cl_2 (10 mL), DIBAL-H (1.0 M in hexanes, 5.8 mL, 1.5 eq, 5.8 mmol) was added dropwise over the course of 10 min at -78 °C. The resultant solution was stirred at this temperature for 4 h, after which time H_2O (5.8 mL) was carefully added followed by 2 M aqueous NaOH (1.7 mL). After warming to room temperature, the mixture was poured into a saturated solution of Rochelle's salt (35 mL) and extracted with CH_2Cl_2 (5 × 20 mL). The combined organic layers were then washed with H_2O, followed by brine, and subsequently dried with Na_2SO_4. Removal of the volatiles

under reduced pressure afforded a crude white solid, which was purified via column chromatography (2:1 CH_2Cl_2/hexanes then CH_2Cl_2, SiO_2) to afford the desired compound as a white solid (0.61 g, 1.84 mmol, 48% yield). m.p. = 240-242 °C. ^{1}H NMR ($CDCl_3$, 399.68 MHz): δ 1.09-1.14 (m, 9H), 1.22 (d, *J* = 6.7 Hz, 3H), 1.25 (d, *J* = 7.0 Hz, 3H), 1.29 (s, 3H), 1.34 (s, 3H), 1.37 (s, 3H), 1.58 (d, *J* = 1.2 Hz, 1H), 2.14 (d, *J* = 14.1 Hz, 1H), 2.27 (d, *J* = 4.3 Hz, 1H), 3.03 (sept., *J* = 7.0 Hz, 1H), 3.17 (sept., *J* = 7.0 Hz, 1H), 4.56 (dd, J_1 = 1.18 Hz, J_2 = 4.3 Hz, 1H), 7.18-7.20 (m, 2H), 7.32 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.50 MHz): δ 23.34, 23.89, 24.25, 24.89, 25.62, 26.64, 28.09, 28.42, 30.09, 31.61, 35.08, 38.07, 44.23, 89.96, 124.22, 124.30, 128.53, 135.53, 145.80, 148.45, 176.26. IR (ATR): ν_{O-H} = 3383cm^{-1}; $\nu_{C=O}$ = 1618 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd for $C_{21}H_{34}NO_2$: 332.2590; Found: 332.2589. Anal. Calcd for $C_{21}H_{33}NO_2$: C, 76.09; H, 10.03; N, 4.23. Found: C, 76.03; H, 10.05; N, 4.19.

6-chloro-1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylpiperidin-2-one (3). To a Schlenk flask containing **2** (1.05 g, 3.17 mmol) and DMF (3 drops) in THF (10 mL), thionyl chloride (0.69 mL, 3 eq, 9.50 mmol) was added with stirring at ambient temperature. The resultant solution was stirred under an inert atmosphere for 12 h, after which the volatiles were removed under reduced pressure to afford the desired compound as an off-white solid (1.10 g, 3.14 mmol, 99% yield). Cooling a saturated solution of **3** in hexanes to -30 °C in a glove box freezer afforded colorless single crystals suitable for a single crystal X-ray diffraction analysis. m.p. = 186-189 °C (dec.). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 0.94 (s, 3H), 1.08 (d, *J* = 7.0 Hz, 3H), 1.12 (d, *J* = 7.0 Hz, 3H), 1.14-1.19 (m, 4H), 1.30 (s overlapping d, *J* = 6.7 Hz, 6H), 1.44 (s overlapping d, *J* = 6.7 Hz, 6H), 2.29 (d, *J* = 14.1 Hz, 1H), 3.01 (sept., *J* = 7.0 Hz, 1H), 3.31 (sept., *J* = 7.0 Hz, 1H), 5.42 (d, *J* = 2.4 Hz, 1H), 7.07 (dd, J_1 = 1.9 Hz, J_2 = 7.0, 1H), 7.17-7.24 (m, 2H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 22.63, 23.58, 24.00, 25.33, 26.23, 27.96, 29.18, 29.25, 29.98, 32.24, 36.97, 38.42, 43.74, 90.74, 124.33, 125.11, 129.14, 136.69, 145.21, 148.23, 175.38. IR (CH_2Cl_2, CaF_2): $\nu_{C=O}$ = 1666 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd for $C_{21}H_{33}ClNO$: 350.2251; Found: 350.2244. Anal. Calcd for $C_{21}H_{32}ClNO$: C, 72.08; H, 9.22; N, 4.00. Found: C, 71.67; H, 9.11; N, 3.81.

4-isopropyl-7,7,9,9,10,10-hexamethyl-8,9,9a,10-tetrahydropyrido[1,2-a]indol-6(7H)-one (5). A vial was charged with **3** (75 mg, 0.21 mmol), NaHMDS (47 mg, 0.26 mmol, 1.2 eq), benzene (5 mL), and a stir bar. After stirring at ambient temperature for 1 h, the mixture was passed through a PTFE filter and the remaining volatiles were removed under reduced pressure. Purification via column chromatography (2:1 v/v CH_2Cl_2/hexanes, SiO_2) afforded the desired compound as a colorless crystalline compound (63 mg, 0.20 mmol, 94% yield). Slow evaporation of a saturated solution of diethyl ether/n-pentane (1:1 v/v) afforded colorless single crystals suitable for a single crystal X-ray diffraction analysis. m.p. = 91-92 °C. ^{1}H NMR (C_6D_6, 399.68 MHz): δ 0.91 (d, *J* = 8.2 Hz, 6H), 0.95 (s, 3H), 1.13 (s, 3H), 1.18 (d, *J* = 7.0 Hz, 3H), 1.36 (d overlapping d, *J* = 6.7 Hz, 8H), 1.64 (d, *J* = 6.7 Hz, 3H), 3.42 (s, 1H), 3.58 (sept., *J* = 7.0 Hz, 1H), 6.78 (dd, J_1 = 1.2 Hz, J_2 = 7.4 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.19 (dd, J_1 = 1.2 Hz, J_2 = 7.8 Hz, 1H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 22.64, 24.61, 24.96, 25.46, 27.25, 28.48, 29.69, 30.67, 31.83, 34.08, 39.49, 45.88, 52.18, 81.03, 118.69, 125.45, 126.04, 139.53, 139.69, 144.39, 176.78. IR (ATR): $\nu_{C=O}$ = 1651 cm^{-1}. HRMS (CI): $[M]^+$ calcd for $C_{21}H_{31}NO$:

313.2405; Found: 313.2406. Anal. Calcd for $C_{21}H_{31}NO$: C, 80.46; H, 9.97; N, 4.47. Found: C, 80.69; H, 9.84; N, 4.46.

1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethyl-6-thioxopiperidin-2-one (6). A stirred solution of **3** (100 mg, 0.29 mmol) and S_8 (18 mg, 0.56 mmol, 2 eq) in toluene (8 mL) was cooled to 0 °C. To the colorless solution, NaHMDS (63 mg, 0.34 mmol, 1.2 eq) in toluene (1 mL) was added dropwise which immediately resulted in the formation of a bright yellow color. Stirring was continued at this temperature for 1 h, after which time the volatiles were removed under reduced pressure and the residue was purified by flash chromatography (1:1 v/v CH_2Cl_2/hexane, SiO_2) to yield the desired compound as a bright yellow, crystalline solid (20 mg, 0.06 mmol, 20% yield). m.p. = 133-135 °C. ^{1}H NMR ($CDCl_3$, 400.09 MHz): δ 1.09 (d, *J* = 6.7 Hz, 6H), 1.14 (d, *J* = 6.7 Hz, 6H), 1.46 (s, 6H), 1.56 (s, 6H), 2.04 (s, 2H), 2.55 (sept., *J* = 6.7 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 1H). ^{1}H NMR (THF-d_8, 399.77 MHz): δ 1.05 (d, *J* = 6.7 Hz, 6H), 1.10 (d, *J* = 6.7 Hz, 6H), 1.41 (s, 6H), 1.53 (s, 6H), 2.07 (s, 2H), 2.59 (sept., *J* = 6.7 Hz, 2H), 7.14 (d, *J* = 7.4 Hz, 2H), 7.26 (t, *J* = 7.4, 1H). ^{13}C NMR ($CDCl_3$, 100.60 MHz): δ 23.88, 24.07, 28.55, 29.15, 32.81, 39.47, 45.41, 46.05, 124.08, 128.97, 136.21, 144.59, 175.86, 219.02. ^{13}C NMR (THF-d_8, 100.52 MHz): δ 24.13, 24.44, 29.25, 29.33, 33.27, 40.15, 46.14, 46.38, 124.51, 129.24, 137.56, 145.51, 176.26, 220.08. IR (ATR): $\nu_{C=O}$ = 1713 cm^{-1}, $\nu_{C=S}$ = 1193 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd for $C_{21}H_{32}NOS$: 346.2205; Found: 346.2211. Anal. Calcd for $C_{21}H_{31}NOS$: C, 73.00; H, 9.04; N, 4.05; S, 9.28. Found: C, 72.88; H, 8.83; N, 4.27; S, 9.23.

4-(2,6-diisopropylphenyl)-1-ethyl-6,6,8,8-tetramethyl-2-phenyl-4-azaspiro[2.5]oct-1-en-5-one (7). A 10 mL Schlenk flask was charged with **3** (75 mg, 0.21 mmol), 1-phenyl-1-butyne (0.11 g, 12.2 µL, 0.86 mmol, 4 eq), toluene (5 mL), and a stir bar. The solution was cooled to 0 °C and NaHMDS (47 mg, 0.26 mmol, 1.2 eq) in toluene (1 mL) was added dropwise via syringe. After stirring at this temperature for 1 h, the cooling bath was removed and stirring was continued for 2 h at ambient temperature. The residual volatiles were then removed under reduced pressure and the crude mixture was purified via column chromatography (5:1 v/v hexane/EtOAc, SiO_2) to afford the desired compound as a white solid (51 mg, 0.11 mmol, 54% yield). Evaporation of a saturated pentane solution afforded colorless crystalline plates suitable for single crystal X-ray diffraction analysis. m.p.= 124-126 °C. ^{1}H NMR (C_6D_6, 399.68 MHz): δ 0.44 (d, *J* = 6.7 Hz, 3H), 0.60 (s, 3H), 0.74 (t, *J* = 7.4 Hz, 3H), 1.22 (dd, J_1 = 1.6 Hz, J_2 = 6.7 Hz, 3H), 1.29 (d, *J* = 6.7 Hz, 3H), 1.36-1.41 (m, 6H), 1.60 (d, *J* = 9.0 Hz, 6H), 3.43 (d, *J* = 14.1 Hz, 1H), 1.99 (qd, J_1 = 1.6 Hz, J_2 = 7.4, 2H), 2.19 (d, *J* = 14.1 Hz, 1H), 2.87 (sept., *J* = 7.0 Hz, 1H), 3.45 (sept., *J* = 7.0 Hz, 1H), 6.93 (dd, J_1 = 2.0 Hz, J_2 = 7.0 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 7.07-7.12 (m, 4H), 7.47 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 12.64, 19.25, 22.30, 22.48, 24.93, 25.53, 26.30, 28.63, 28.80, 29.46, 30.38, 32.47, 37.28, 38.38, 52.48, 58.47, 120.83, 123.19, 123.78, 128.12, 128.46, 128.92, 129.49, 129.80, 136.33, 147.03, 149.12, 177.02. IR (ATR): $\nu_{C=O}$ = 1637 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd for $C_{31}H_{42}NO$: 444.3266; Found: 444.3271. Anal. Calcd for $C_{31}H_{41}NO$: C, 83.92; H, 9.31; N, 3.16. Found: C, 83.53; H, 9.49; N, 2.96.

1-(2,6-diisopropylphenyl)-6-mercapto-3,3,5,5-tetramethylpiperidin-2-one (8). Method A: A solution of **3** (146 mg, 0.42 mmol) and CS_2 (95 mg, 75 µl, 3 eq) in toluene

(10 mL) was cooled to 0 °C with stirring. To the solution, NaHMDS (99 mg, 0.54 mmol, 1.3 eq) in toluene (1 mL) was added dropwise over a period of 5 min. The reaction solution gradually changed color from light orange to a dark purple color over the course of the addition. The reaction mixture was allowed to warm to room temperature overnight, after which time a yellow reaction mixture with visible precipitate was observed. The residue was purified via column chromatography (10:1 v/v hexane/EtOAc, SiO_2) to afford **8** (34 mg, 0.09 mmol, 23% yield) as an off-white solid as well as **6** (30 mg, 0.09 mmol, 21% yield). Method B: After cooling a Schlenk flask containing **3** (50 mg, 0.14 mmol) in toluene (10 mL) to 0 °C, the atmosphere was evacuated. The reaction vessel was then placed under an atmosphere of COS (g) (1 atm) and stirred. NaHMDS (37 mg, 0.20 mmol, 1.4 eq) in toluene (1 mL) was added slowly to the solution, which gradually turned yellow. After 1 h the cooling bath was removed and the reaction mixture was left stirring overnight. The residue was purified by column chromatography (10:1 v/v hexane/EtOAc, SiO_2) to afford **8** (28 mg, 0.08 mmol, 57% yield). m.p. = 157-159 °C. ^{1}H NMR ($CDCl_3$, 400.09 MHz): δ 1.11 (dd, J_1 = 1.2 Hz, J_2 = 5.1 Hz, 6H), 1.22 (s, 3H), 1.28 (t, J = 7.0 Hz, 6H), 1.34 (s, 3H), 1.40 (d, J = 5.1 Hz, 6H), 1.61 (d, J = 5.9 Hz, 1H), 1.67 (dd, J_1 = 1.6 Hz, J_2 = 14.5 Hz, 1H), 2.17 (d, J = 14.5, Hz, 1H), 2.98 (sept., J = 7.0 Hz, 1H), 3.07 (sept., J = 7.0 Hz, 1H), 4.77 (dd, J_1 = 1.6 Hz, J_2 = 5.9 Hz, 1H), 7.19 (t, J = 7.8 Hz, 2H), 7.32 (t, J = 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.60 MHz): δ 23.27, 23.35, 24.16, 24.99, 27.14, 28.02, 28.19, 28.89, 30.46, 31.22, 35.49, 38.24, 46.47, 71.73, 124.19, 124.28, 128.47, 136.23, 145.19, 148.07, 175.94. IR (ATR): $\nu_{C=O}$ = 1650 cm^{-1}. HRMS (ESI): $[M+H]^+$ calcd for $C_{21}H_{34}NOS$: 348.2356, Found: 348.2358. Anal. Calcd for $C_{21}H_{33}NOS$: C, 72.57; H, 9.57; N, 4.03; S, 9.22. Found: C, 72.24; H, 9.74; N, 3.98; S, 8.88.

1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethyl-keto-piperidinyl-iridium (I) (1,5-cyclooctadiene) chloride (9). A Schlenk flask which was completely covered with aluminum foil was charged with **3** (100 mg, 0.29 mmol) and $[Ir(COD)Cl]_2$ (95.9 mg, 0.14 mmol, 0.5 eq.) and toluene (10 mL). The solution was cooled to 0 °C and NaHMDS (68 mg, 0.37 mmol, 1.3 eq.) in toluene (1 mL) was added dropwise with stirring. The reaction mixture was left in the dark overnight and allowed to warm to ambient temperature. The solvent was then removed under reduced pressure and the residue was purified by column chromatography (2:1 v/v CH_2Cl_2/hexane, SiO_2) to afford the desired compound as a red-orange solid (16 mg, 0.02 mmol, 9% yield). Crystals suitable for a single crystal X-ray diffraction analysis were obtained by slow evaporation of a heptanes solution of **9** over 48 h. m.p. = 187-189 °C (dec.). ^{1}H NMR ($CDCl_3$, 399.68 MHz): δ 0.95 (d, J = 6.7 Hz, 3H), 1.08 (dd, J_1 = 3.1 Hz, J_2 = 6.7 Hz, 6H), 1.21 (s, 4H), 1.37 (d, J = 6.3 Hz, 3H), 1.41 (d, J = 6.3 Hz, 6H), 1.53 (bs, 3H), 1.69-1.83 (m, 3H), 2.01-2.07 (m, 1H), 2.2 (s, 3H), 2.31 (sept., J = 7.8 Hz, 1H), 2.45 (sept., J = 6.7 Hz, 1H), 2.56 (d overlapping d, J_1 = 12.3 Hz, J_2 = 12.3 Hz, 2H), 3.50-3.55 (m, 1H), 3.59 (sept., J = 6.7 Hz, 1H), 4.69-4.74 (m, 1H), 4.80-4.86 (m, 1H), 7.14 (dd, J_1 = 1.6 Hz, J_2 = 7.4 Hz, 1H), 7.33 (dd, J_1 = 1.6 Hz, J_2 = 7.8 Hz, 1H), 7.41 (t, J = 7.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.60 MHz): δ 22.51, 23.65, 25.16, 25.43, 26.26, 26.83, 28.29, 28.42, 28.50, 29.53, 31.50, 32.09, 32.91, 34.42, 39.08, 42.55, 53.32, 53.53, 56.78, 92.55, 93.17, 122.47, 124.96, 129.28, 139.25, 145.43, 146.81, 176.72, 287.65. IR (ATR): $\nu_{C=O}$ = 1713 cm^{-1}. HRMS (ESI): $[M-Cl]^+$ calcd for $C_{29}H_{43}IrNO$: 614.2970; Found: 614.2971. Anal. Calcd for $C_{29}H_{43}ClIrNO$: C, 53.64; H, 6.68; N, 2.16. Found: C, 53.99; H, 6.73; N, 2.01.

1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethyl-keto-piperidinyl-iridium (I) (dicarbonyl) chloride (10). Carbon monoxide was bubbled through a solution of **9** (20 mg, 0.03 mmol) in CH_2Cl_2 (3 mL) which immediately turned bright yellow. After the solvent had evaporated, hexanes (3 mL) was added and CO was continued to be bubbled through the solution until the solvent had evaporated; this process was repeated one more time. The bright yellow solid was dried under reduced pressure, washed with a minimal amount of hexanes, and dried under reduced pressure again to afford the desired compound **10** as a bright yellow solid (17 mg, 0.03 mmol, 94% yield). m.p. = 128-130 °C (dec.). ^{1}H NMR ($CDCl_3$ 399.77 MHz): δ 0.94 (d, *J* = 7.0 Hz, 3H), 1.03 (d, *J* = 6.7 Hz, 3H), 1.34 (d, *J* = 6.3 Hz, 3H), 1.40 (d, *J* = 6.7 Hz, 3H), 1.44 (s, 3H), 1.50 (s, 3H), 1.65 (s, 3H), 1.97 (d overlapping s, 4H), 2.19 (d, *J* = 14.5 Hz, 1H), 2.72 (sept., *J* = 6.7 Hz, 1H), 2.96 (sept., *J* = 6.7 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.49 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.52 MHz): δ 22.66, 23.34, 25.13, 25.19, 28.39, 28.86, 29.61, 31.78, 33.04, 38.86, 45.21, 49.79, 124.06, 124.81, 138.79, 143.96, 144.94, 169.57, 175.72, 181.51, 280.64. IR (CH_2Cl_2, KBr): $\nu_{C=O}$ = 1756 cm^{-1}, 1986 cm^{-1}, 2068 cm^{-1}. HRMS (ESI): $[M+Na]^+$ calcd for $C_{23}H_{31}ClIrNO_3Na$: 620.1506; Found: 620.1511. Anal. Calcd for $C_{23}H_{31}ClIrNO_3$: C, 46.26; H, 5.23; N, 2.35. Found: C, 46.61; H, 5.58; N, 2.01.

1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethyl-6-selenoxopiperidin-2-one (11). To a vial containing **3** (75 mg, 0.21 mmol) and selenium powder (51 mg, 0.65 mmol, 3 eq) in C_6D_6 (5 mL), NaHMDS (51 mg, 0.28 mmol, 1.3 eq) was added with stirring. The reaction mixture was left overnight after which time it was filtered through a PTFE filter. The resultant residue was purified via column chromatography (1:1 v/v CH_2Cl_2/hexane, SiO_2) to afford the desired compound as a magenta crystalline solid (46 mg, 0.12 mmol, 55% yield). m.p. = 128-130 °C. ^{1}H NMR ($CDCl_3$, 400.09 MHz): δ 1.10 (d, *J* = 7.0 Hz, 6H), 1.16 (d, *J* = 7.0 Hz, 6H), 1.46 (s, 6H), 1.62 (s, 6H), 2.07 (s, 2H), 2.59 (sept., *J* = 7.0 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125.60 MHz): δ 23.95, 24.09. 28.63, 29.03, 33.58, 39.61, 45.44, 48.96, 125.14, 128.99, 138.24, 144.34, 174.85, 228.01. ^{77}Se NMR (acetone-d_6, 144.44 MHz): δ 1179.71. IR (ATR): $\nu_{C=O}$ = 1715 cm^{-1}. HRMS (ESI): $[M+Na]^+$ calcd for $C_{21}H_{31}NOSeNa$: 416.1464; Found: 416.1470. Anal. Calcd for $C_{21}H_{31}NOS$: C, 64.27; H, 7.96; N, 3.57. Found: C, 64.44; H, 7.84; N, 3.32.

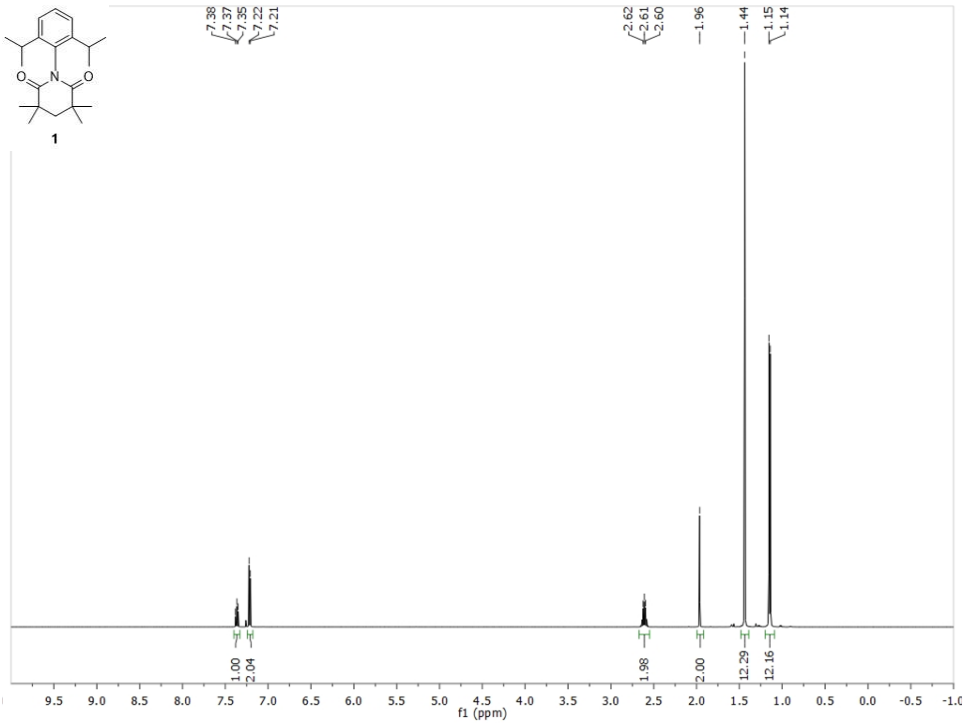
X-Ray Crystallography. Colorless, single crystals of **3** were obtained by cooling a saturated hexane solution of **3** to -30 °C; this compound crystallized in the orthorhombic $P2_12_12_1$ space group with four molecules of **3**. Colorless, single crystals of **5** were obtained by slow evaporation of a saturated solution of diethyl ether/n-pentane (1:1 v/v); this compound crystallized in the monoclinic $P2_1/c$ space group with four molecules of **5**. Colorless single crystals of **7** were grown by slow evaporation of a pentane solution; this compound crystallized in the monoclinic $P2_1/n$ space group with four molecules of **7** and four molecules of pentane, which was removed using SQUEEZE. Orange, single crystals of **9** were obtained by the slow evaporation of a heptane solution; this compound crystallized in the monoclinic $P2_1/c$ space group with four molecules of **9**. Crystallographic measurements were carried out on a Rigaku Mini CCD, Nonius Kappa CCD, or Rigaku AFC-12 with Saturn 724+ CCD area detector diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 100 K, 120 K, or 150 K using an Oxford Cryostream low temperature device. A sample of suitable size and quality was

selected and mounted onto a nylon loop. Data reductions were performed using DENZO-SMN.[2] The structures were solved by direct methods which successfully located most of the non-hydrogen atoms. Subsequent refinements on *F*2 using the SHELXTL/PC package (version 6)[3] allowed the location of the remaining non-hydrogen atoms. Key details of the crystal and structure refinement data are summarized in Table S1. Further crystallographic details may be found in the respective CIFs which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK. The CCDC reference numbers for **3**, **5**, **7**, and **9** were assigned as 1024535, 1024536, 1024537, and 1024538, respectively.

Table S1. Summary of crystal data, data collection, and structure refinement details.

	3	**5**	**7**[a]	**9**
Formula	$C_{21}H_{32}NOCl$	$C_{21}H_{31}NO$	$C_{31}H_{41}NO$	$C_{29}H_{43}ClIrNO$
M_r	349.9	313.5	443.7	649.3
crystal size	0.20 × 0.20 × 0.20	0.23 × 0.18 × 0.08	0.20 × 0.20 × 0.20	0.34 × 0.10 × 0.06
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a (Å)	11.6015(19)	8.9044(5)	8.6897(5)	15.8695(19)
b (Å)	12.822(2)	11.5431(6)	29.0766(18)	11.8315(13)
c (Å)	13.428(2)	17.7110(8)	10.8005(7)	14.6016(17)
α (°)	90.000(0)	90.000(0)	90.000(0)	90.000(0)
β (°)	90.000(0)	92.232(3)	106.809(3)	96.061(3)
γ (°)	90.000(0)	90.000(0)	90.000(0)	90.000(0)
V (Å^3)	1997.5(6)	1825.20(16)	2612.3(3)	2726.3(5)
Z	4	4	4	4
ρ_{calc} (g cm^{-3})	1.16	1.14	1.13	1.58
μ (mm^{-1})	0.199	0.069	0.066	5.016
F(000)	760	688	968	1304
T (K)	150(2)	120(2)	120(2)	100(2)
scan mode	ω	ω, φ	ω, φ	ω, φ
hkl range	-13 → 13 -15 → 15 -15 → 15	-10 → 10 -13 → 13 -21 → 20	-10 → 10 -34 → 34 -12 → 12	-18 → 18 -14 → 12 -17 → 17
measd reflns	17572	70507	141864	30408
unique reflns	3505 [0.067]	3217 [0.049]	4602 [0.069]	4778 [0.057]
refinement reflns	3505	3217	4602	4778
refined parameters	225	216	307	306
GOF on F^2	1.006	1.006	1.006	1.006
R1[b] (all data)	0.041 (0.044)	0.039 (0.046)	0.043 (0.055)	0.033(0.035)
wR2[c](all data)	0.107 (0.110)	0.098 (0.109)	0.119 (0.139)	0.090 (0.092)
ρ_{fin} (max/min) (e Å^{-3})	0.343 -0.213	0.287 -0.219	0.290 -0.234	1.732 -2.695

[a] A highly disordered molecule of pentane was removed using SQUEEZE. [b] R1 = Σ||Fo| − |Fc||/Σ|Fo|. [c] wR2 = {[Σ*w*(*F*o^2 − *F*c^2)^2]/[Σ*w*(*F*o^2)^2]}$^{1/2}$.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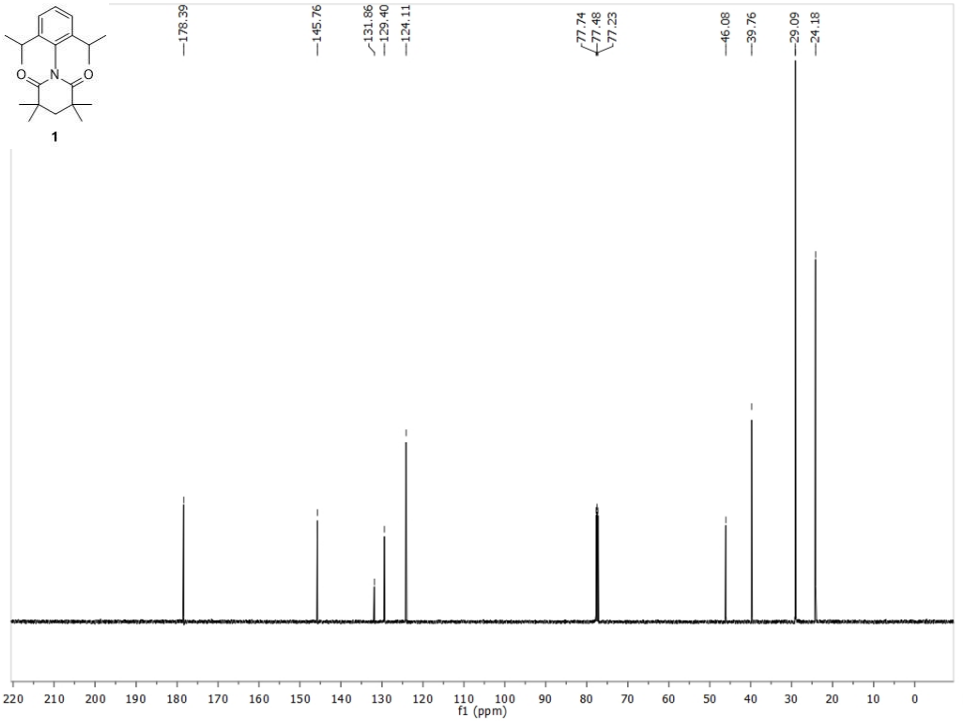
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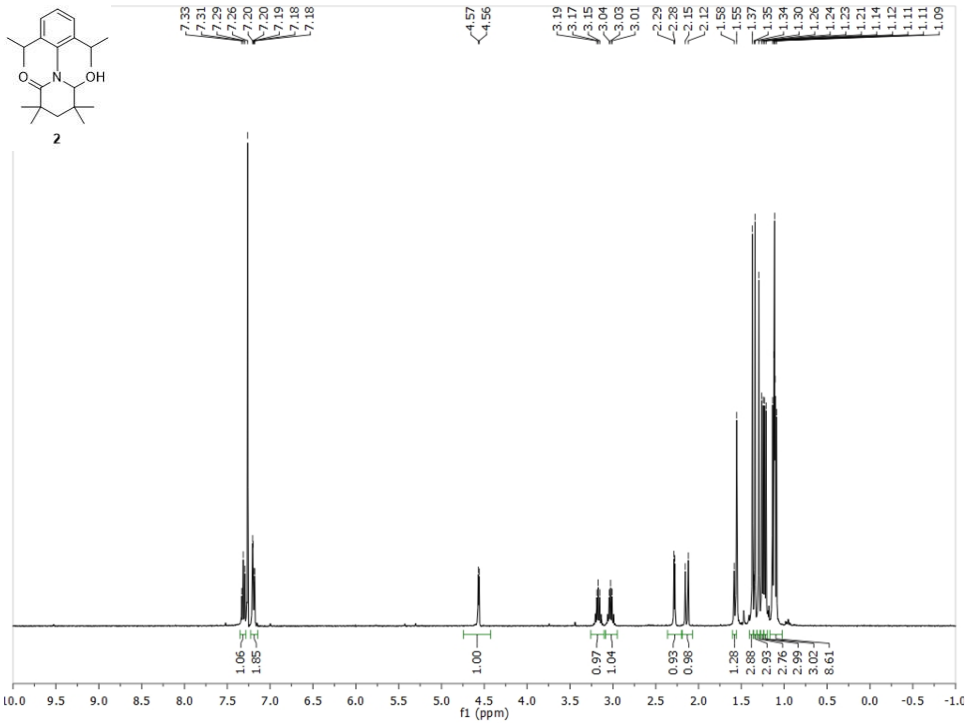
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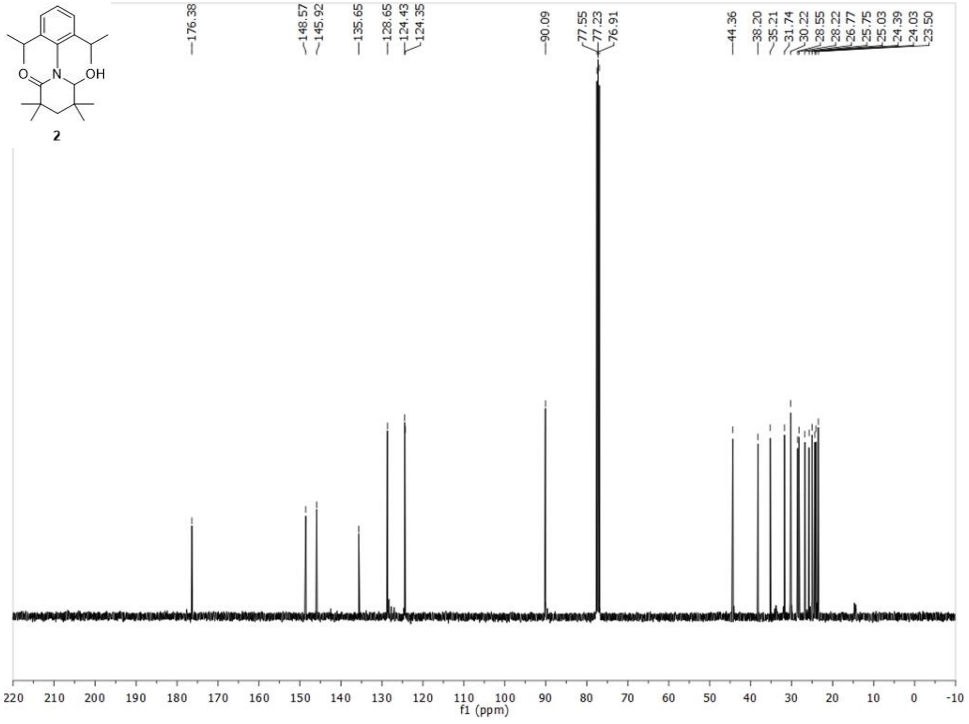
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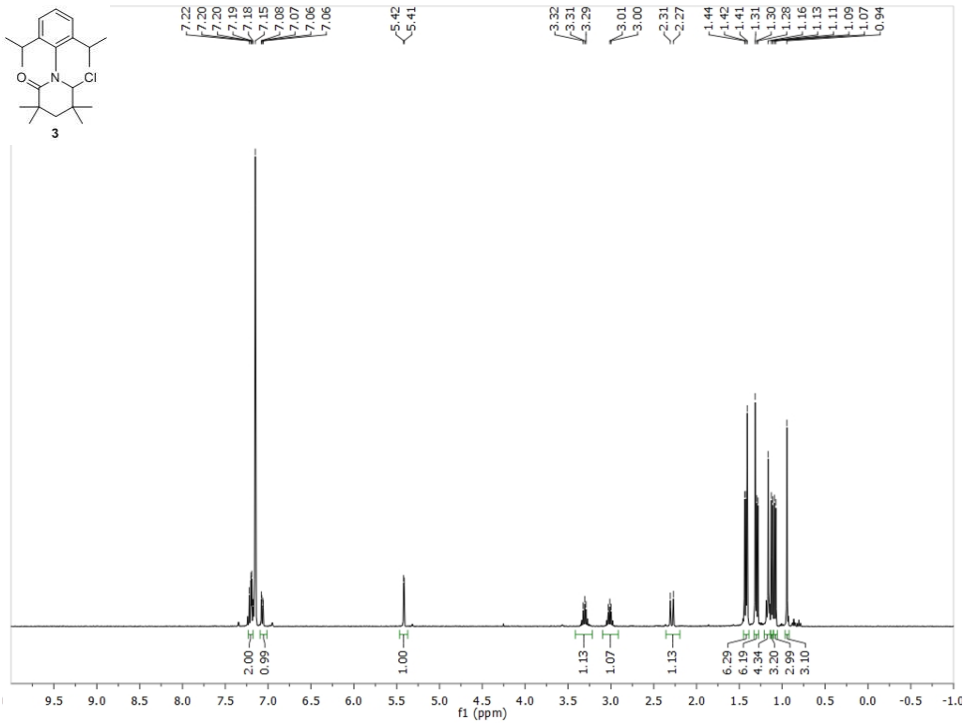
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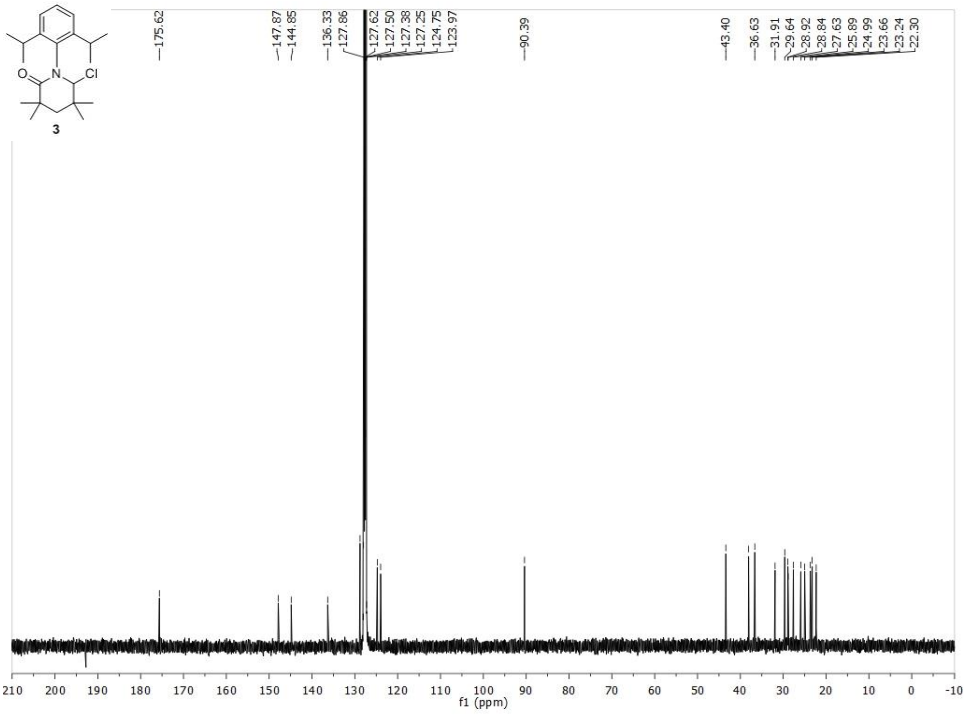
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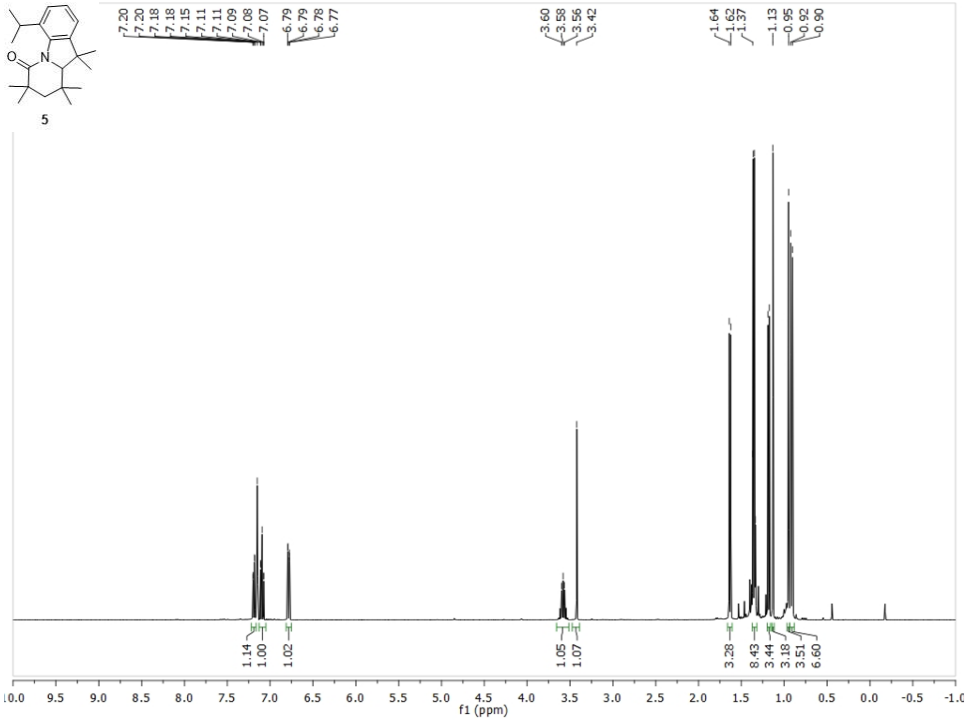
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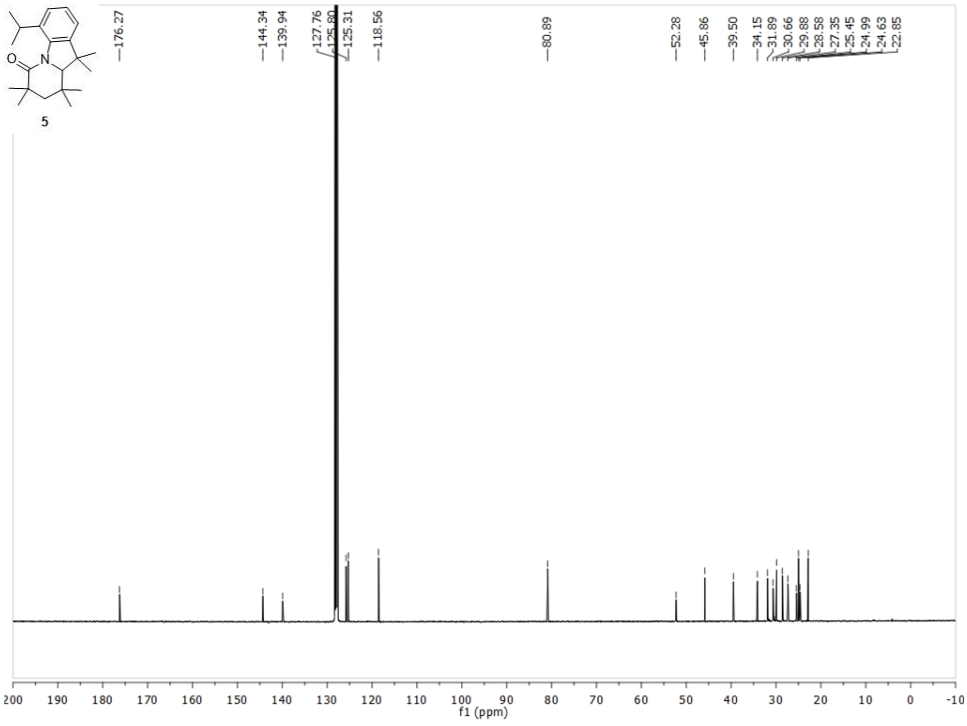
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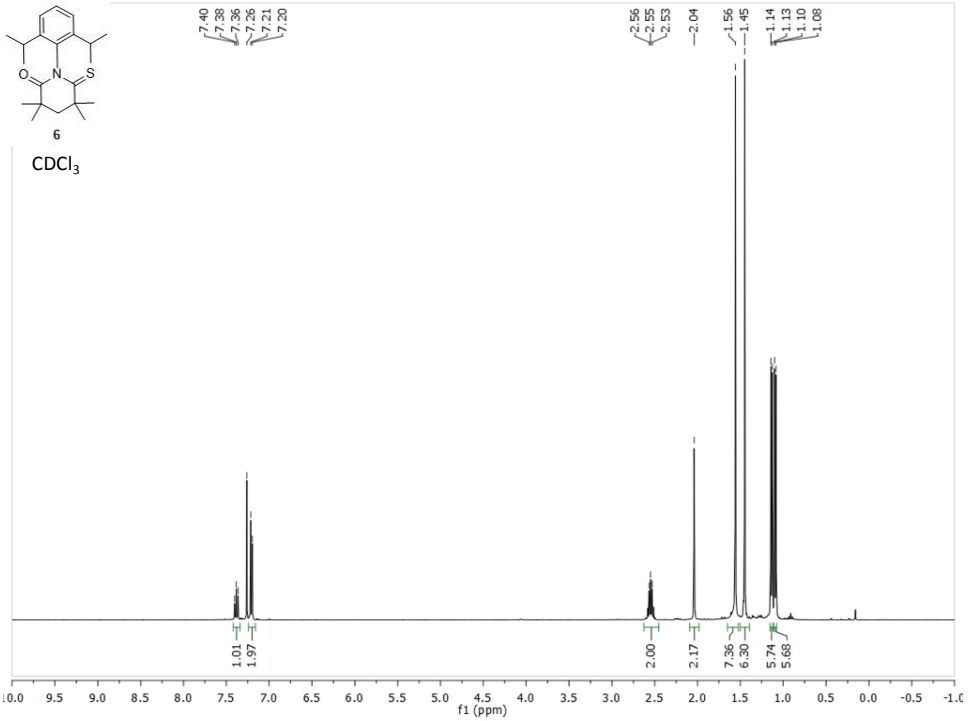
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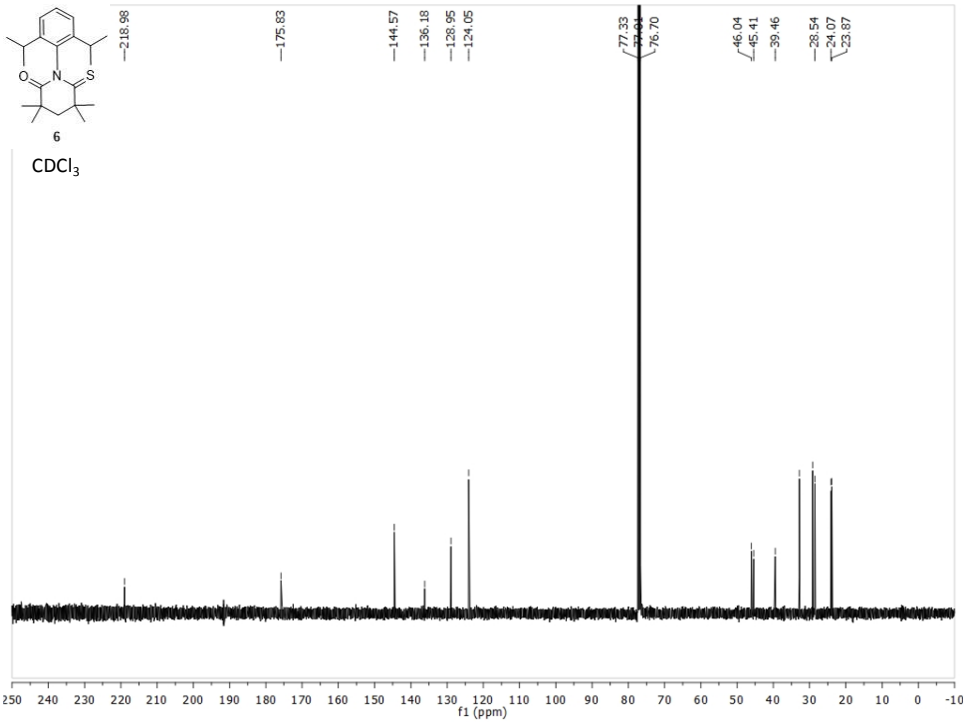
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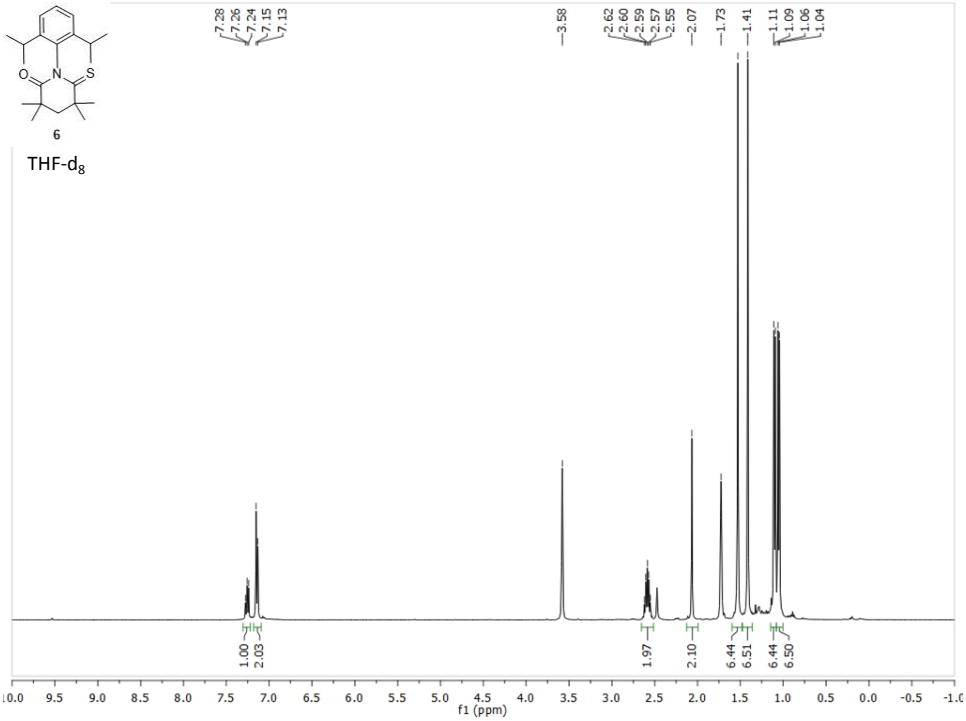
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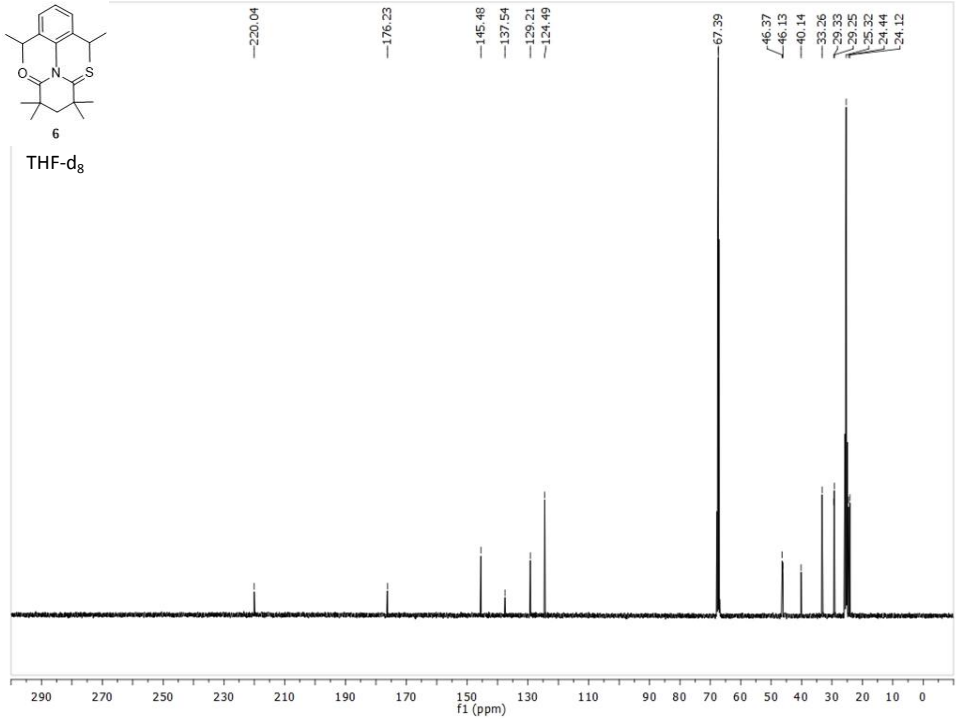
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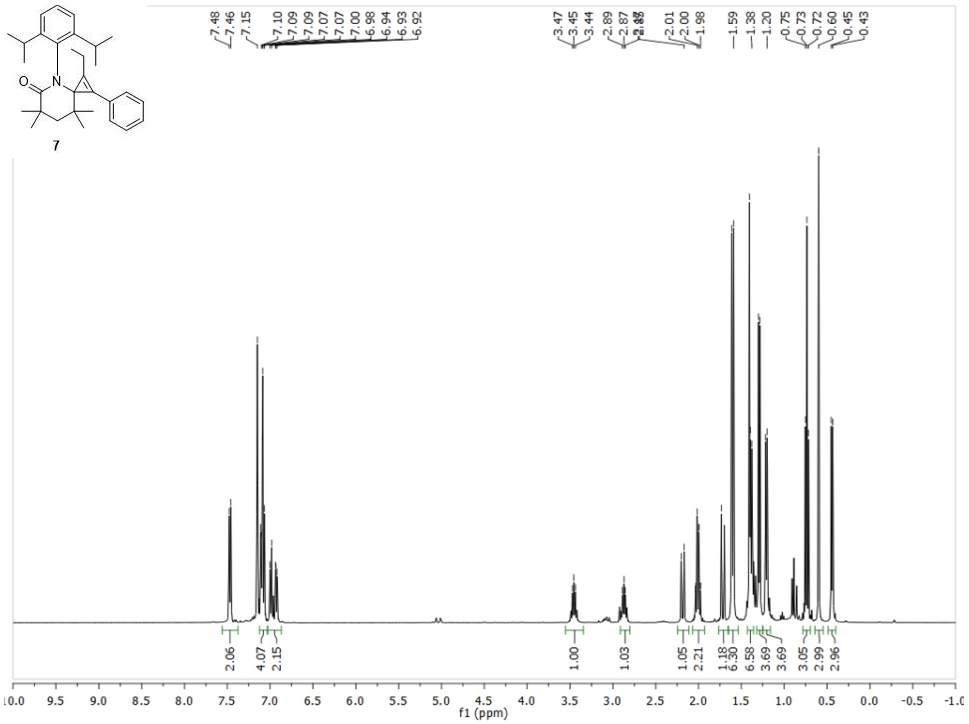
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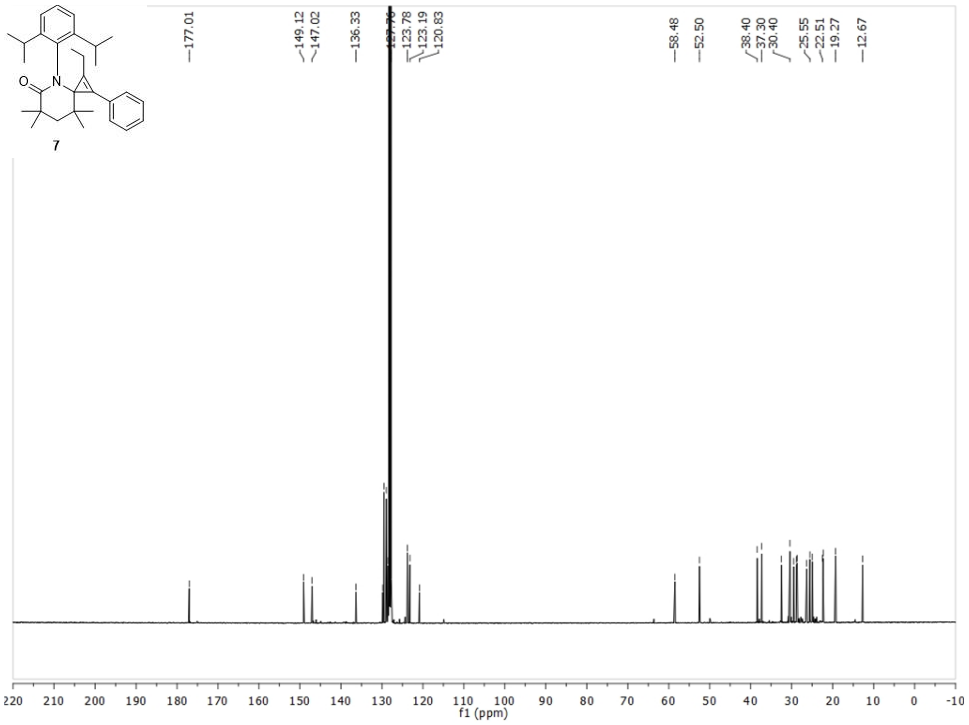
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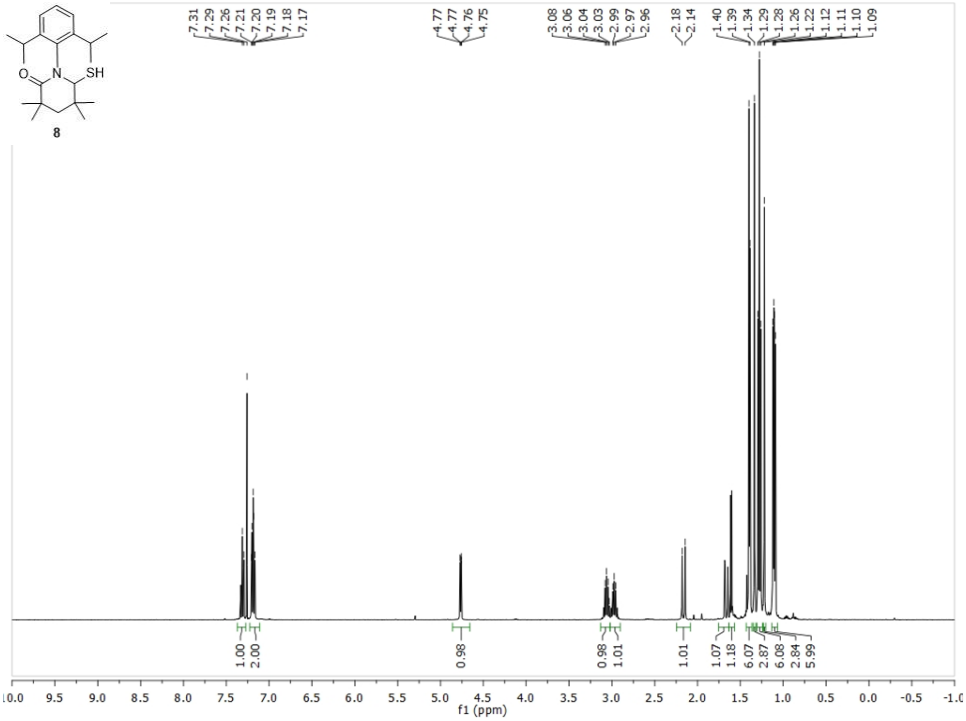
7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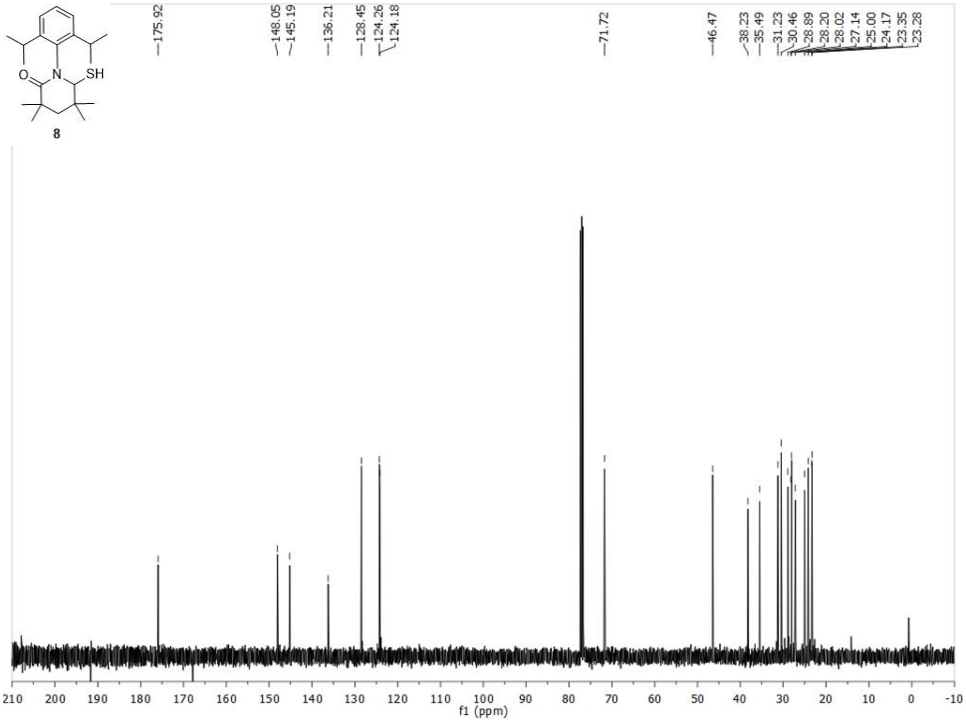
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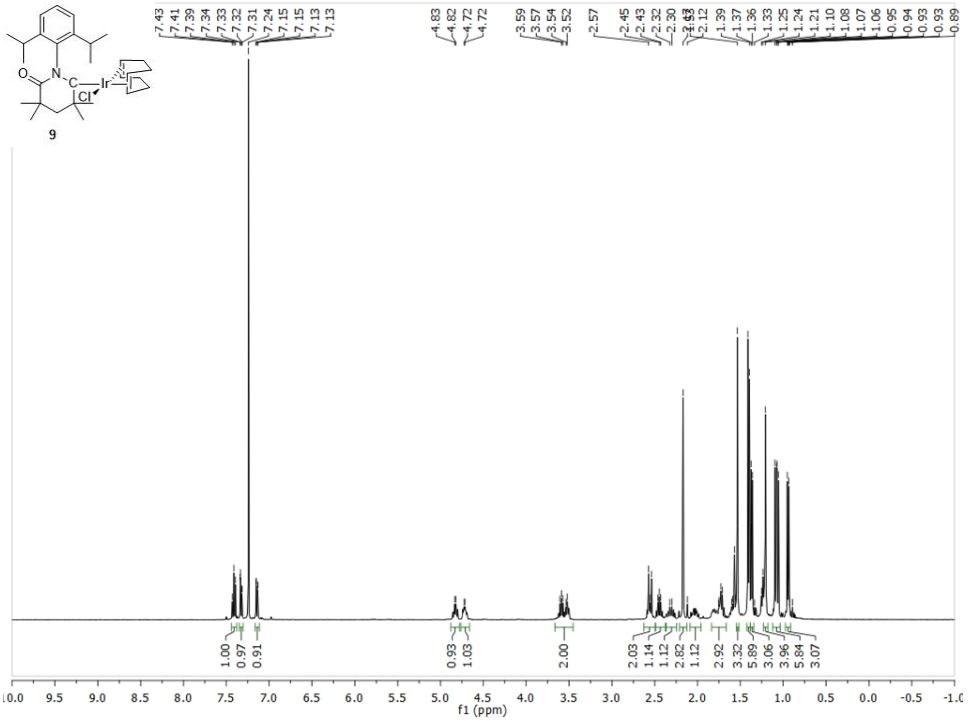
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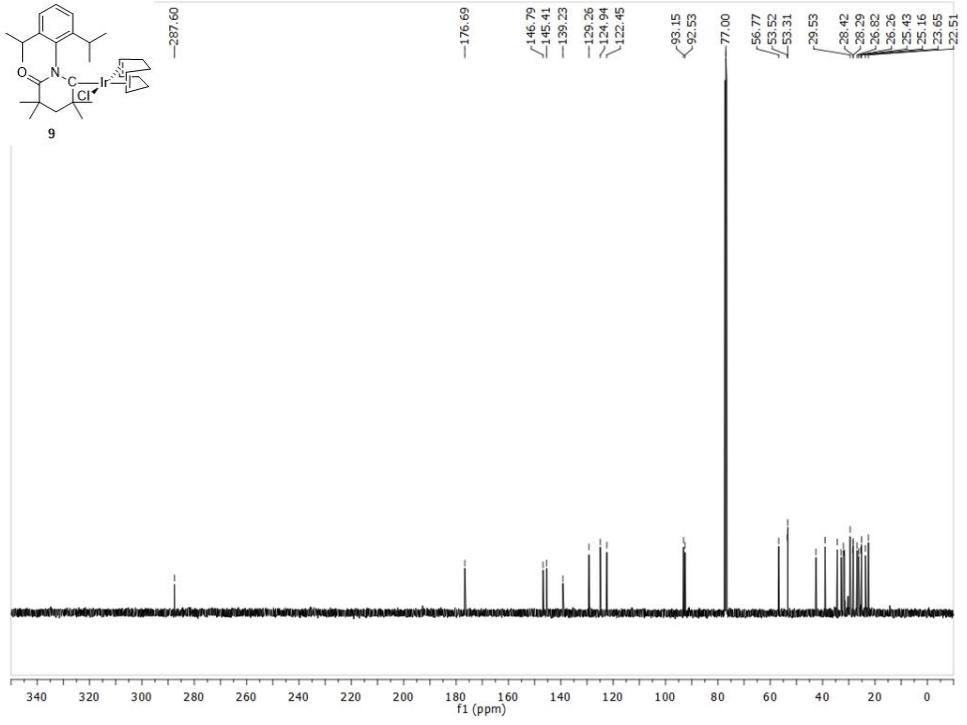
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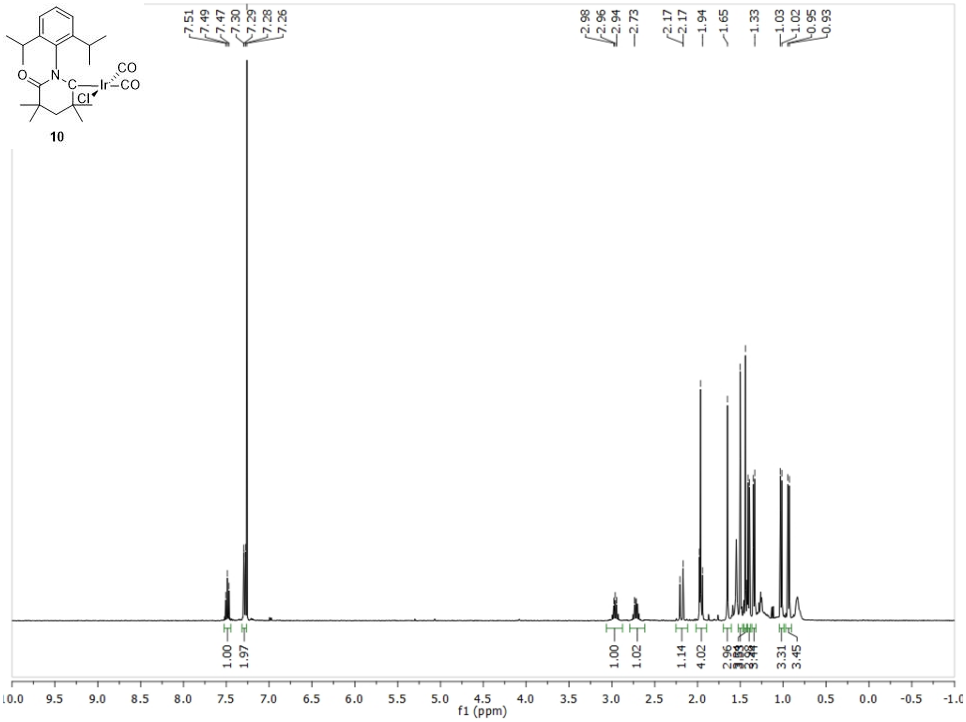
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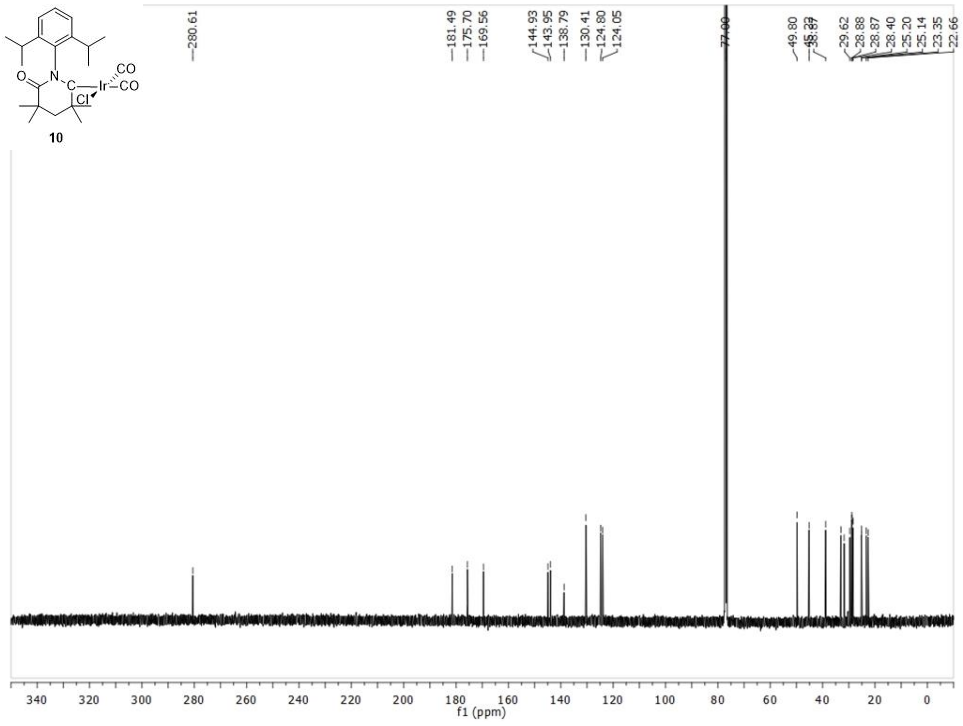
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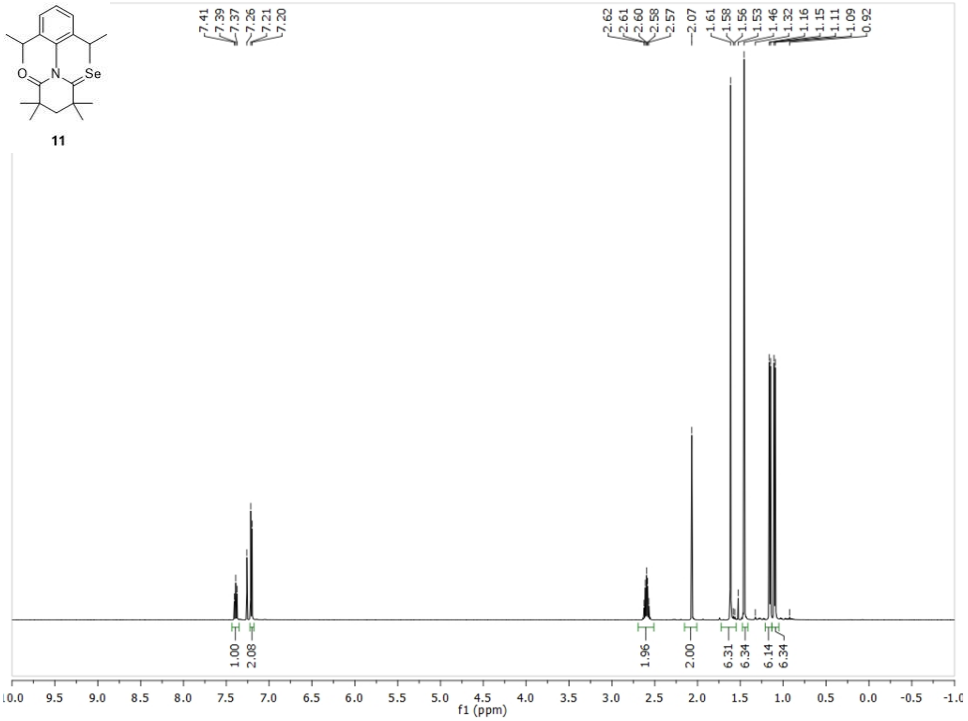
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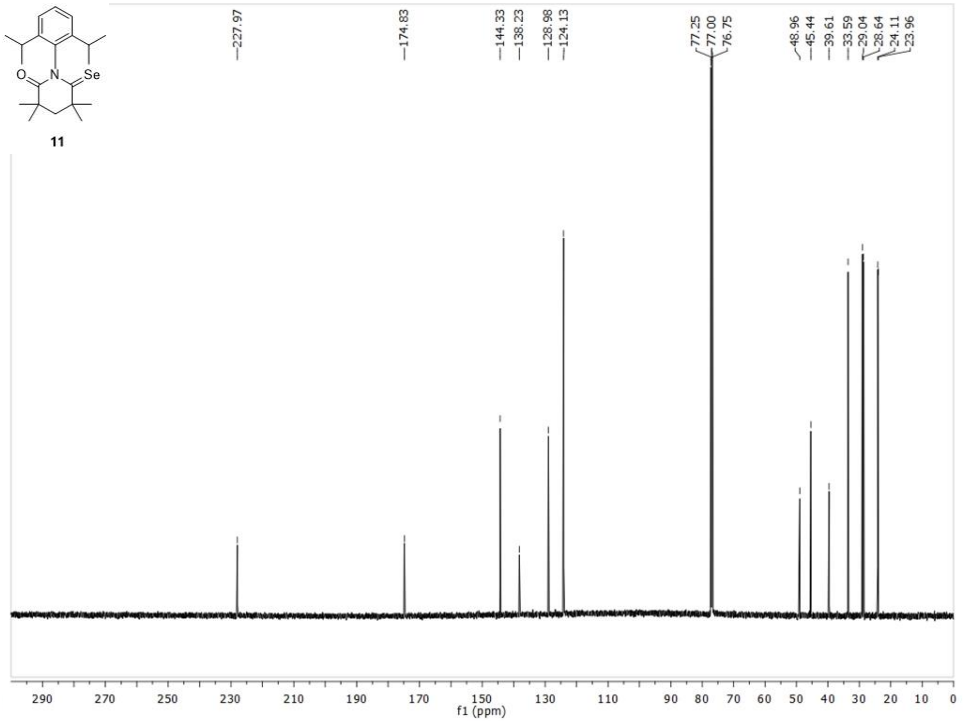
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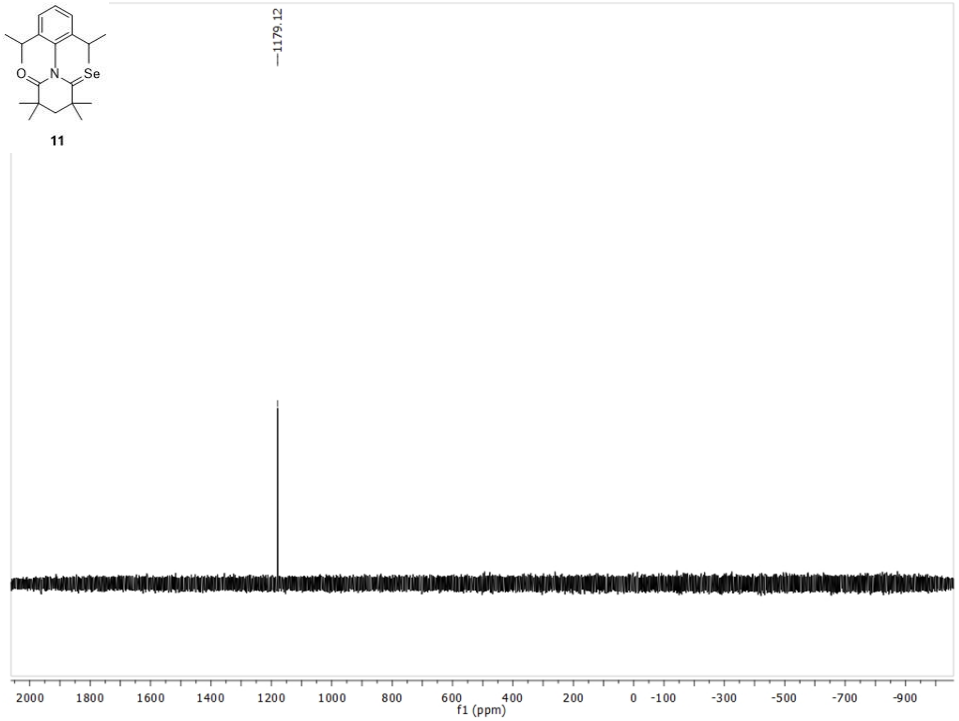
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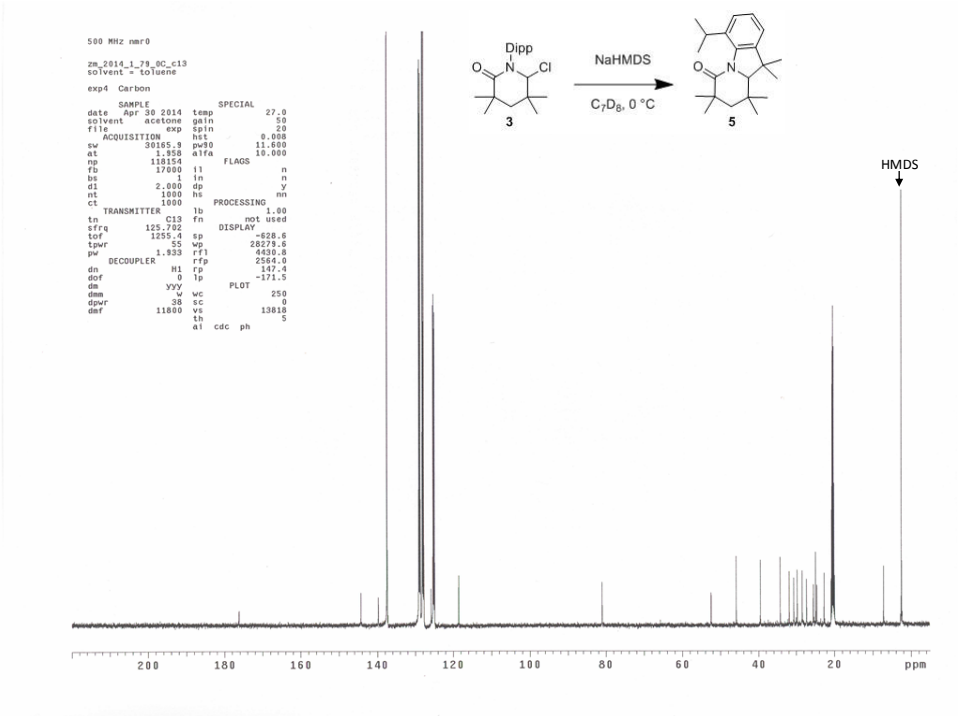
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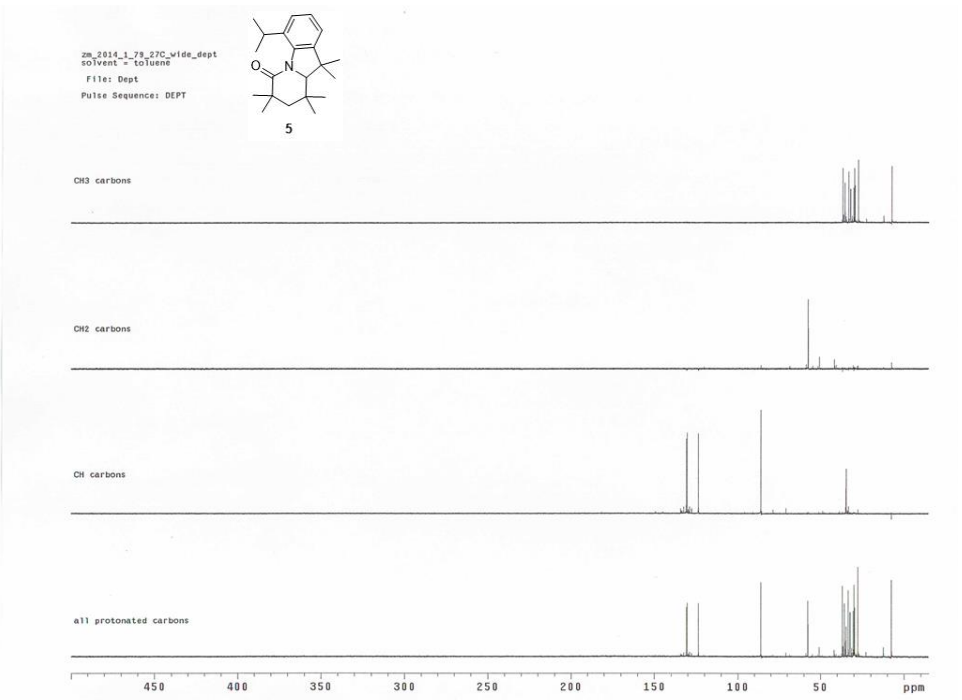
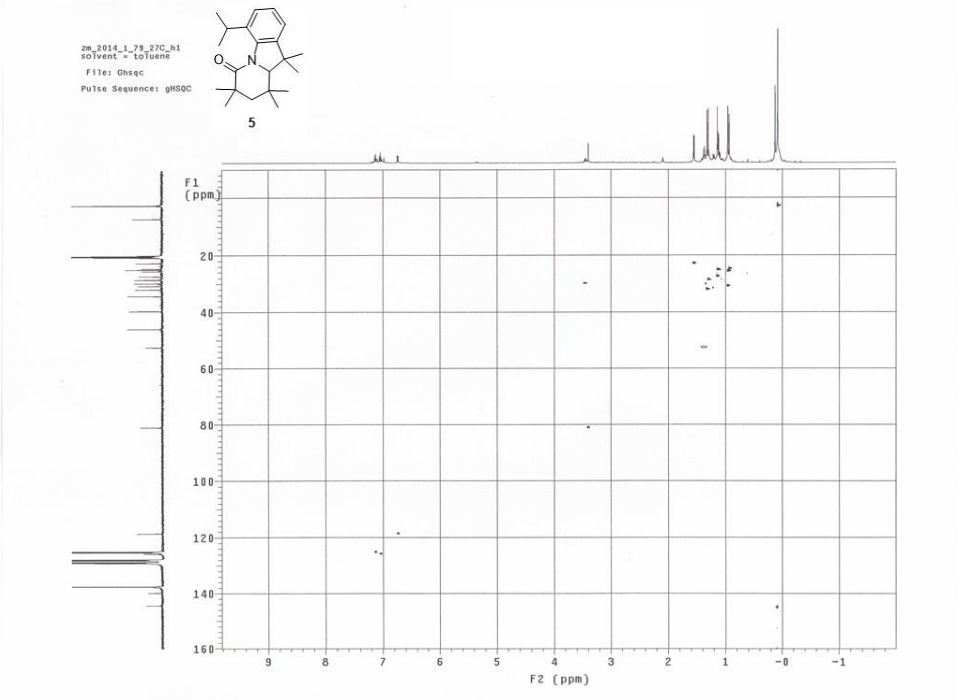
SAMPLE
date Apr 30 2014
solvent acetone
file exp
ACQUISITION
sw 30165.9
at 1.958
np 118154
fb 17000
bs 1
d1 2.000
nt 1000
ct 1000
TRANSMITTER
tn C13
sfrq 125.702
tof 1255.4
tpwr 55
pw 1.933
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 38
dmf 11800
SPECIAL
temp 27.0
gain 50
spin 20
hst 9.008
pw90 11.600
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -628.6
wp 28279.6
rf1 4430.8
rfp 2564.0
rp 147.4
lp -171.5
PLOT
wc 250
sc 0
vs 13818
th 5
al cdc ph
Dipp
Cl
3
NaHMDS
C7D8, 0 °C
5
HMDS
200 180 160 140 120 100 80 60 40 20 ppm


zm_2014_1_79_27C_wide_dept
solvent = toluene
File: Dept
Pulse Sequence: DEPT
5
CH3 carbons
CH2 carbons
CH carbons
all protonated carbons
450
400
350
300
250
200
150
100
50
ppm


zm_2014_1_79_27C_h1
solvent = toluene
File: Ghsqc
Pulse Sequence: gHSQC
5
F1 (ppm)
20
40
60
80
100
120
140
160
9
8
7
6
5
4
3
2
1
-0
-1
F2 (ppm)

References

(1) Renner, C. A.; Greene, F. D. *J. Org. Chem.* **1976**, *41*, 2813.

(2) DENZO-SMN. (1997): Z. Otwinowski, W. Minor in *Methods in Enzymology*, *276: Macromolecular Crystallography, part A*, (Eds.: C. W. Carter, Jr., R. M. Sweets) Academic Press, **1997**, 307.

(3) Sheldrick, G. M.; *Acta Cryst.* **2008,** *A64*, 112.