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Cyclic (Aryl)(Amido)carbenes: Pushing the π-Acidity of Amidocarbenes Through Benzannulation

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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. Benzene and THF were dried

over sodium, distilled and degassed. Chloroform and acetonitrile were dried over calcium hydride, distilled and degassed. All dried and degassed solvents were stored over 3 Å molecular sieves in a nitrogen filled glove box. NMR spectra were recorded on Bruker AscendTM 500 MHz or Bruker Avance400 MHz spectrometers at ambient probe temperatures, and chemical shifts are given in δ with positive values downfield of TMS (^{1}H: C_6D_6, δ 7.16; $CDCl_3$, δ 7.26; ^{13}C: C_6D_6, δ128.6). Melting points were obtained using a MEL-TEMP II laboratory device, USA apparatus and are uncorrected. Elemental analyses were performed at Midwest Microlab, LLC. FTIR measurements were performed on a Bruker Tensor II FTIR spectrophotometer in 1 mL Specac solution IR cells equipped with CaF_2 windows. High resolution mass spectrometry measurements were performed on a Thermo Scientific Velos Pro Ion Trap LC-MS.

SYNTHESIS

Synthesis of (*E*)-2-((mesitylimino)methyl)benzoic acid (**3a**):

To a solution of 2-carboxybenzaldehyde acid (compound **2**, 5.0 g, 33 mmol) in isopropanol (75 mL) was added 3 drops of acetic acid. The solution was stirred for 1 hour at room temperature followed by the addition of 4.5 g (33 mmol) of 2,4,6-trimethylaniline (**1a**). The resulting solution was then heated to reflux for 1 hour, was then cooled to room temperature then stirred overnight at which point a white, needle shaped precipitate formed. The solid was filtered and washed with cold methanol to give compound **3a** as a white crystalline solid (6.76 g recovered, 76% yield). M.P.: 122-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.0 Hz, 1H), 7.77 (dt, J = 14.7 Hz, 7.5 Hz, 2H), 7.63 (t, J = 7.3 Hz, 1H), 6.92 (s, 2H), 6.39 (s, 1H), 3.74 (s, 1H), 2.38 (s, 6H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.17, 146.09, 137.91, 134.36, 134.15, 132.02, 130.61, 129.63, 128.26, 125.41, 123.62, 93.44, 77.27, 20.74, 18.56.

Synthesis of (*E*)-2-(((2,6-diisopropylphenyl)imino)methyl)benzoic acid (**3b**):

To a solution of 2-carboxybenzaldehyde acid (compound **2**, 5.0 g, 33 mmol) in methanol (15 mL) was added 3 drops of acetic acid. The solution was stirred for 1 hour at room temperature followed by the addition of 5.9g (33.3 mmol) of 2,6-(diisopropyl)aniline (**1b**). The resulting solution was then heated to reflux for 1 hour, was then cooled to room temperature then stirred overnight. All volatiles were removed in vacuo to give **3b** as a yellow sticky, viscous oil (quantitative yield)

which was used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.51 (m, 4H), 7.21 (q, J = 4.3 Hz, 3H), 6.36 (s, 1H), 3.47 (s, 2H), 1.54 – 1.03 (m, 12H). ^{13}C NMR (101 MHz, CDCl3) δ 169.03, 146.03, 143.99, 137.05, 134.16, 130.68, 128.48, 126.25, 125.49, 123.83, 123.51, 94.87, 27.91, 24.03.

Synthesis of (*E*) – 2 - (((3,3",5,5" - tetrakis(trifluoromethyl) - [1,1':3',1" - terphenyl] - 2' - yl)imino) methyl)benzoic acid (**3c**):

To a solution of 2-carboxybenzaldehyde acid (compound **2**, 0.6g (4.00 mmol) in methanol (15 mL) was added 3 drops of acetic acid. The solution was stirred for 1 hour at room temperature followed by the addition of 2g (3.87 mmol) of 3,3",5,5"-tetrakis(trifluoromethyl)-[1,1':3',1"-terphenyl]-2'-amine (**1c**). The resulting solution was then heated to reflux for 1 hour, was then cooled to room temperature then stirred overnight at which point a white, needle shaped precipitate formed. The solid was filtered and washed with cold methanol to give compound **3c** as a white crystalline solid 1.70g, 2.62 mmol, 68% yield). M.P.: 130-132 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 4H), 7.87 (s, 2H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.59 (td, *J* = 7.5, 1.1 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 2.7 Hz, 3H), 7.24 (d, *J* = 7.6 Hz, 1H), 5.81 (d, *J* = 13.0 Hz, 1H), 3.81 (d, *J* = 13.0 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 167.84, 144.54, 141.33, 138.53, 134.56, 132.97, 132.73, 132.70, 132.44, 132.27, 131.08, 129.92, 127.49, 126.50, 125.81, 124.33, 122.81, 122.16, 121.94, 121.91, 90.04. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.78.

Synthesis of 3-chloro-2-mesitylisoindolin-1-one (**4a**):

To a Schlenk flask, 1.0 g (3.74 mmol) of **3a** dissolved in 20 mL of acetonitrile. Then 0.89 g (7.5 mmol) of thionyl chloride was added and refluxed for 3 hours. Volatiles were evaporated under reduced pressure overnight to afford the desired compound as an off white solid (1.07g, 3.74 mmol, 99% yield). M.P. = 146 – 148 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 7.81 (d, J = 7.5 Hz, 1H), 7.25 (d, J = 7.6 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.80 (s, 1H), 6.69 (s, 1H), 6.46 (s, 1H), 2.43 (s, 3H), 2.08 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 166.01, 144.08, 138.92, 138.50, 135.83, 132.70, 131.04, 130.96, 130.41, 130.13, 129.57, 124.34, 124.14, 73.98, 20.97, 19.22, 17.68. HRMS (ESI): $[M-Cl]^+$ calculated for: $C_{17}H_{16}NO$: 250.1232; Found: 250.1200

Synthesis of 3-chloro-2-(2,6-diisopropylphenyl)isoindolin-1-one (**4b**):

To a Schlenk flask, 5g (16.2 mmol) of **3b** dissolved in 15 mL of acetonitrile. Then 2.5 ml (32.4 mmol) of thionyl chloride was added and refluxed for 3 hours. Volatiles were evaporated under reduced pressure overnight to afford the desired compound as an off white solid (5.3g, 16.2 mmol, 99% yield). M.P.: 156 – 158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.78 – 7.68 (m, 2H), 7.68 – 7.60 (m, 1H), 7.50 – 7.39 (m, 1H), 7.33 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.26 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.57 (s, 1H), 3.10 (hept, *J* = 6.8 Hz, 1H), 2.57 (hept, *J* = 6.8 Hz, 1H), 1.38 – 1.18 (m, 9H), 1.13 (d, *J* = 6.8 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.55, 149.58, 146.98, 143.71, 133.18, 130.57, 130.29, 129.95, 129.63, 124.81, 124.60, 124.28, 124.21, 74.64, 29.25, 29.05, 25.14, 24.13, 23.69. HRMS (ESI): $[M-Cl]^+$ calculated for: $C_{20}H_{22}NO$: 292.1701; Found: 292.1450.

Synthesis of 3-chloro-2-((((3,3",5,5" - tetrakis(trifluoromethyl) - [1,1':3',1" - terphenyl] - 2' - yl))isoindolin-1-one (**4c**):

To a Schlenk flask, 0.5g (0.77 mmol) of **3c** dissolved in 5 mL of acetonitrile. Then 0.2 ml (2.75 mmol) of thionyl chloride was added and refluxed for 3 hours. Volatiles were evaporated under reduced pressure overnight to afford the desired compound as an off white solid (0.514g, 0.77 mmol, 99% yield). M.P.: 146 – 148 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 8.26 (s, 2H), 7.78 – 7.55 (m, 4H), 7.48 (s, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.67 (t, *J* = 7.4 Hz, 1H), 6.54 (d, *J* = 7.5 Hz, 1H), 5.51 (s, 1H). ^{13}C NMR (126 MHz, C_6D_6) δ 169.50, 142.74, 142.43, 141.63, 140.71, 139.38, 133.43, 132.50, 132.23, 132.02, 131.96, 131.83, 131.57, 131.46, 131.30, 131.04, 130.74, 130.52, 130.49, 130.11, 129.04, 129.01, 128.86, 128.59, 128.34, 125.01, 124.41, 124.35, 123.48, 122.84, 122.24, 121.91, 121.88, 121.85, 121.82, 121.79, 121.76, 121.73, 120.67, 120.06, 73.01. ^{19}F NMR (471 MHz, C_6D_6) δ -62.65, -62.93. HRMS (APCI): $[M+H]^+$ calculated for: $C_{30}H_{15}F_{12}ClNO$: 668.0651; Found: 668.0550.

Synthesis of (*E*)-2,2'-dimesityl-[1,1'-biisoindolinylidene]-3,3'-dione (**5a**):

Added 1.0 g (3.5 mmol) of **4a** to schlenk flask, dissolved in 25 mL of dry THF and cooled to -78 °C. A solution of 0.68 g (3.7 mmol) NaHMDS in 10 mL of THF was added dropwise over 30 minutes. After 2 hours the solution was allowed to warm to room temperature. Solution turns black/green. The solution was filtered over celite and volatiles were evaporated under reduced pressure. The product was purified by column chromatography (80:20 DCM: Hexane). Recovered

a yellow solid (0.75 g, 1.5 mmol, 86% yield). M.P.: 294-296 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 7.5 Hz, 1H), 7.55 (dt, J = 33.5, 7.2 Hz, 2H), 6.67 (s, 2H), 2.27 (s, 3H), 1.59 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.80, 137.80, 136.68, 132.63, 132.00, 129.37, 129.16, 127.97, 124.46, 124.29, 20.93, 18.15, 14.11. HRMS (ESI): $[M+H]^+$ calculated for: $C_{34}H_{31}N_2O_2$: 499.2386; Found: 499.2050. Elemental analysis: calculated for $C_{34}H_{30}N_2O_2$: C: 81.90% (found: 81.79%), H: 6.06% (found: 6.30%), N: 5.62% (found 5.53%).

Synthesis of (*E*)-2,2'-(2,6-diisopropylphenyl)-[1,1'-biisoindolinylidene]-3,3'-dione (**5b**):

2.0 g (6.1 mmol) of **4b** was added to a Schlenk flask, dissolved in 25 mL of dry THF and cooled to -78 °C. A solution of 1.34 g (7.3 mmol) NaHMDS in 10 mL of THF was added dropwise over 30 minutes. After 2 hours the solution was allowed to warm to room temperature. Solution turns black/green. The solution was filtered over celite and volatiles were evaporated under reduced pressure. The product was purified by column chromatography (80:20 DCM: Hexane). Recovered a yellow solid (1.72g, 2.95 mmol, 97% yield). M.P.: 256-260 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.85 – 7.78 (m, 2H), 7.49 – 7.43 (m, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 2.72 (hept, *J* = 6.9 Hz, 2H), 1.17 (d, *J* = 6.9 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.39, 147.45, 147.27, 134.48, 132.11, 130.36, 127.03, 124.40, 124.22, 124.12, 124.02, 123.54, 29.49, 24.13. HRMS (ESI): $[M+H]^+$ calculated for: $C_{40}H_{43}N_2O_2$: 583.3325; Found: 583.3500.

Synthesis of 2-mesityl-3-thioxoisoindolin-1-one (**6a**):

Added 1.0 g (3.5 mmol) of **4a** and 0.34 g (11 mmol) sulfur to a Schlenk flask and dissolved in 25 mL of THF. The flask was then cooled to -78 °C. A solution of 0.83 g (4.5 mmol) NaHMDS in 10 mL of THF was added dropwise over 30 minutes. The reaction was allowed to warm to room temperature and was stirred overnight. The solution was filtered over celite and volatiles were evaporated under reduced pressure. Purified by column chromatography (80:20 DCM: Hexane). Recovered a bright pink solid (0.49 g, 1.7 mmol, 49% yield). M.P.: 137-139 °C. ^{1}H NMR (400 MHz, C6D6) δ 7.88 (ddd, J = 3.5, 2.0, 0.7 Hz, 1H), 7.53 (ddd, J = 5.7, 2.1, 0.7 Hz, 1H), 7.05 – 6.92 (m, 2H), 6.72 (dd, J = 1.2, 0.6 Hz, 2H), 2.05 (s, 3H), 1.97 (s, 6H). ^{13}C NMR (101 MHz, C6D6) δ 196.80, 169.12, 139.17, 137.59, 136.68, 134.16, 133.32, 130.28, 129.48, 124.27, 123.07, 21.04, 17.80. HRMS (ESI): $[M+H]^+$ calculated for: $C_{17}H_{17}NOS$: 282.0953; Found: 282.0750.

Synthesis of 2-(2,6-diisopropylphenyl)-3-thioxoisoindolin-1-one (**6b**):

2.0 g (6.1 mmol) of **4b** and 0.587 g (18.31 mmol) sulfur were added to a Schlenk flask then dissolved in 25 mL of THF. The flask was then cooled to -78 °C followed by the dropwise addition of a solution of 1.34 g (7.3 mmol) NaHMDS in 10 mL of THF over 30 minutes. The reaction was allowed to warm to room temperature and was stirred overnight. The solution was filtered over celite and volatiles were evaporated under reduced pressure. Purified by column chromatography (80:20 DCM: Hexane). Recovered a bright pink solid (1.34 g, 4.14 mmol, 67% yield). M.P.: 106-110 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.17 – 8.03 (m, 1H), 8.00 – 7.88 (m, 1H), 7.88 – 7.77 (m, 2H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 2H), 2.65 (hept, *J* = 6.9 Hz, 2H), 1.17 (d, *J* = 6.9 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.16, 170.10, 147.26, 137.20, 134.53, 133.66, 130.48, 129.28, 127.31, 124.39, 124.21, 123.52, 29.39, 24.51, 24.10. HRMS (ESI): $[M+H]^+$ calculated for: $C_{20}H_{22}NOS$: 324.1422; Found: 324.1050.

Synthesis of 2-mesityl-3-selenoxoisoindolin-1-one (**7a**):

Added 100 mg (0.35 mmol) of **4a** and 83 mg (1.05 mmol) of red selenium to schlenk flask, dissolved in 5 mL of THF, and cooled to -78 °C. A solution of 83 mg (0.45 mmol) of NaHMDS in 2 mL of THF was added dropwise over 30 minutes. The reaction was allowed to warm to room temperature and was stirred overnight. The solution was filtered over celite and volatiles were evaporated under reduced pressure. Purified by column chromatography (80:20 DCM: Hexanes). Recovered a teal solid (35 mg, 0.11 mmol, 15% yield). M.P.: 130-132 °C. ^{1}H NMR (CDCl3, 400.13 MHz): δ 2.09 (s, 6H), 2.36 (s, 3H), 7.02 (s, 2H), 7.75 (t, J = 8.0 Hz, 2H), 7.87 (m, 2H), 8.09 (d, J = 8.0 Hz, 1H). 13C NMR (C6D6, 100.61 MHz): δ 18.05, 21.36, 123.55, 125.90, 126.52, 129.39, 130.66, 133.35, 134.50, 136.23, 139.66, 141.21, 169.93, 200.95. 77Se NMR (CDCl3, 76.31 MHz): δ 1240.9 (1204.5, acetone-d_6). Elemental analysis: calculated for $C_{17}H_{15}NOSe$: C: 62.2% (found: 62.31%), H: 4.61% (found: 4.97%), N: 4.27% (found 4.03%).

Synthesis of 2-mesityl-3-selenoxoisoindolin-1-one (**7b**):

2.0 g (6.1 mmol) of **4b** and 1.45 g (18.36 mmol) of red selenium were added to a Schlenk flask then dissolved in 15 mL of THF. The solution was then cooled to -78 °C followed by the dropwise addition of a solution of 1.34 g (7.3 mmol) of NaHMDS in 5 mL of THF was added dropwise over 30 minutes. The reaction was allowed to warm to room temperature and was stirred overnight. The

solution was filtered over celite and volatiles were evaporated under reduced pressure. Purified by column chromatography (80:20 DCM: Hexanes). Recovered a teal solid (0.635 g, 1.71 mmol, 28% yield). M.P.: 110-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dt, *J* = 7.6, 0.9 Hz, 1H), 7.96 – 7.83 (m, 2H), 7.77 (ddd, *J* = 7.6, 7.2, 1.4 Hz, 1H), 7.50 (dd, *J* = 8.1, 7.5 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 2H), 2.65 (hept, *J* = 6.8 Hz, 2H), 1.14 (dd, *J* = 6.9, 5.3 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.83, 170.69, 147.02, 141.21, 134.59, 133.45, 130.58, 130.51, 126.34, 126.06, 124.25, 123.73, 29.48, 24.60, 24.18. ^{77}Se NMR (76 MHz, $CDCl_3$) δ 1263.84. (1231.1, acetone-d_6). HRMS (ESI): $[M+H]^+$ calculated for: $C_{20}H_{22}NOSe$: 372.0867; Found: 372.0011.

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Synthesis of **Fa**-[Ir(cod)Cl] (**8a**):

Added 85 mg (0.30 mmol) of **4a** and 100 mg (0.15 mmol) of $[Ir(cod)Cl]_2$ to Schlenk flask and dissolved in THF in glovebox. The flask was cooled to -78°C and 65 mg (0.35 mmol) of NaHMDS in 2 mL of THF was added dropwise over 30 minutes. After 1 hour the solution was allowed to warm to room temperature then stirred overnight. The solution was filtered over celite and volatiles were evaporated under reduced pressure. Purified by column chromatography (80:20 DCM: Hexanes). Recovered an orange solid (18 mg, 0.031 mmol, 10% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 – 8.52 (m, 1H), 7.79 (ddd, J = 11.9, 5.5, 3.8 Hz, 2H), 7.75 – 7.67 (m, 1H), 7.09 (s, 1H), 6.97 (s, 1H), 5.56 – 5.42 (m, 1H), 5.13 (d, J = 4.8 Hz, 1H), 3.43 – 3.27 (m, 2H), 2.41 (d, J = 22.1 Hz, 7H), 2.22 (d, J = 5.1 Hz, 3H), 1.96 (s, 3H), 1.86 (ddd, J = 23.4, 16.2, 7.6 Hz, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 250.10, 169.55, 148.66, 138.96, 136.96, 135.55, 134.56, 133.90, 132.89, 132.72, 130.05, 128.27, 124.19, 123.23, 100.99, 99.17, 57.63, 56.72, 35.01, 32.01, 29.70, 27.29, 21.20, 19.66, 18.47.

Synthesis of **Fa**-[Ir$(CO)_2$Cl] (**9a**):

Inside of a nitrogen filled glovebox, an NMR equipped with a septum-lined cap was filled with 85 mg (0.30 mmol) of **8a** followed by the addition of 0.5 mL of $CDCl_3$ resulting in a deep red solution. The NMR tube was removed from the box and then carbon monoxide was bubbled into the solution for approximately 30 seconds which resulted in a color change of the solution to dark yellow. The complex was then characterized by ^{1}H and ^{13}C NMR spectroscopy (quantitative yield by ^{1}H NMR spectroscopy). To obtain an IR spectrum of **9a**, the NMR tube was returned to the glove box, and the solution was transferred to an air tight liquid IR cell equipped with CaF_2 windows. Over time

the compound will oxidized in solution to give phthalimide **10** with the visible deposition of iridium metal in the NMR tube (see discussion below for full analysis). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.94 – 7.75 (m, 3H), 7.05 (s, 2H), 5.68 – 5.47 (3H, free cod), 2.39 (s, 3H), 2.37 (s, 7H, free cod), 2.21 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 246.12, 168.53, 145.83, 140.46, 136.62, 135.49, 135.22, 134.96, 134.26, 132.80, 129.65, 129.30, 128.69 (free cod), 125.90, 123.74, 122.61, 77.26, 77.01, 76.76, 28.03 (free cod), 21.28, 18.72, 1.11. FTIR: ($CDCl_3$): $\nu_{Ir\text{-}CO}$: 2081.7, 2001.8 cm^{-1}, $\nu_{C=O\ (amide)}$: 1692.2 cm^{-1}.

Synthesis of *N*-mesitylphthalimide (method A) (**10**):

Phthalic anhydride (5.00 g, 33.8 mmol), 2,4,6-trimethylaniline (4.57 g, 33.8 mmol), and a few drops of glacial acetic acid were added to a round bottom flask equipped with a reflux condenser and heated to 150 °C for 2 hours. 100 mL of hexanes was added to the flask while still hot to precipitate the product as a white solid. The precipitate was filtered to isolate the product as a white solid (8.95 g, 33.7 mmol, 100% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, J = 5.5, 3.0 Hz, 1H), 7.82 (dd, J = 5.5, 3.0 Hz, 1H), 7.03 (d, J = 0.6 Hz, 1H), 2.36 (s, 2H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.29, 139.25, 136.35, 134.13, 131.97, 129.18, 126.97, 123.62, 77.21, 77.09, 76.89, 76.57, 53.28, 21.00, 17.84.

Synthesis of *N*-mesitylphthalimide (method B) (**10**):

Fa-[Ir(cod)Cl] (**8a**, 50 mg, 0.081 mmol) was dissolved in 5 mL of DCM in a Schlenk flask and wrapped in foil and covered with a rubber septum. Carbon monoxide was bubbled directly into the solution until all solvent had evaporated. Then 5 mL of hexanes was added, and carbon monoxide was bubbled into the solution until all solvent had evaporated, this was repeated 2 more times. The residue was dissolved in 5 mL of hexanes again and filtered over celite to afford an off-white solid 13mg, 0.047 mmol, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, J = 5.5, 3.0 Hz, 1H), 7.82 (dd, J = 5.5, 3.0 Hz, 1H), 7.03 (d, J = 0.6 Hz, 1H), 2.36 (s, 2H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.29, 139.25, 136.35, 134.13, 131.97, 129.18, 126.97, 123.62, 77.21, 77.09, 76.89, 76.57, 53.28, 21.00, 17.84.

NMR SPECTRA of COMPOUNDS

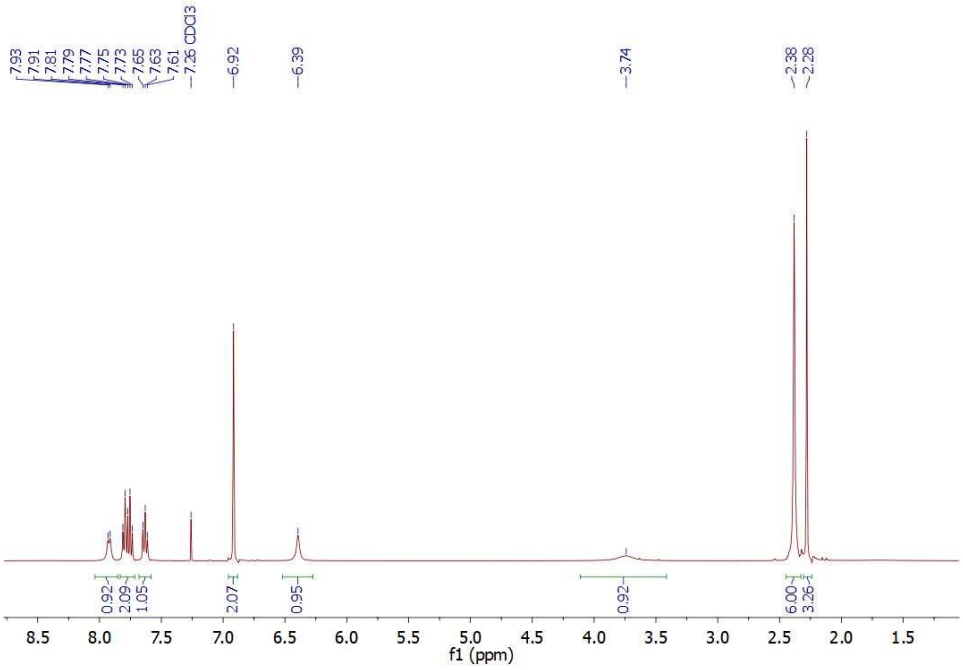

Figure S1 ^{1}H NMR of **3a** in $CDCl_3$**.**

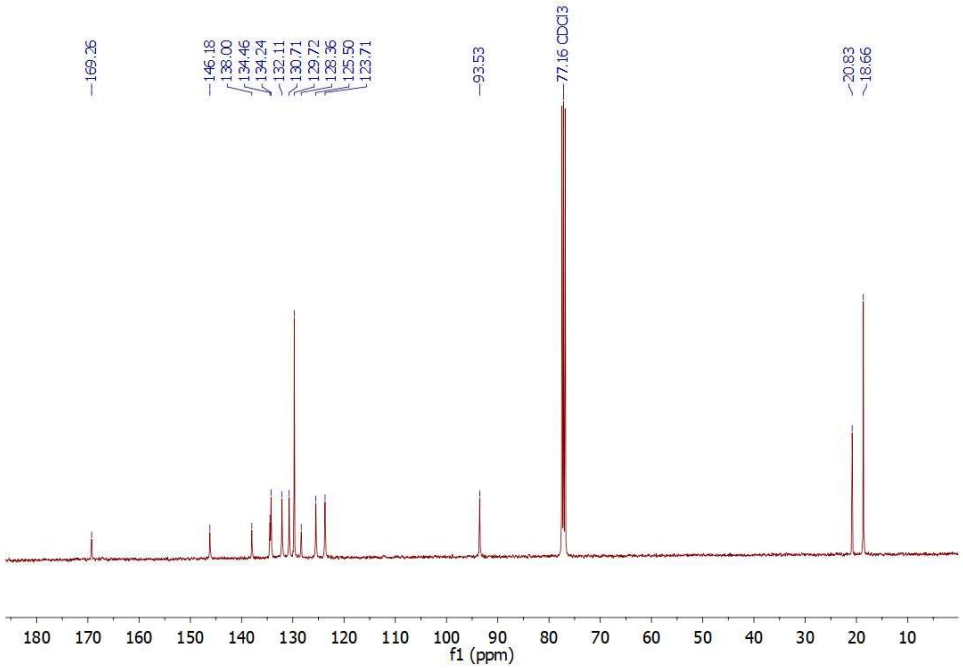

Figure S2 ^{13}C NMR of **3a** in $CDCl_3$**.**

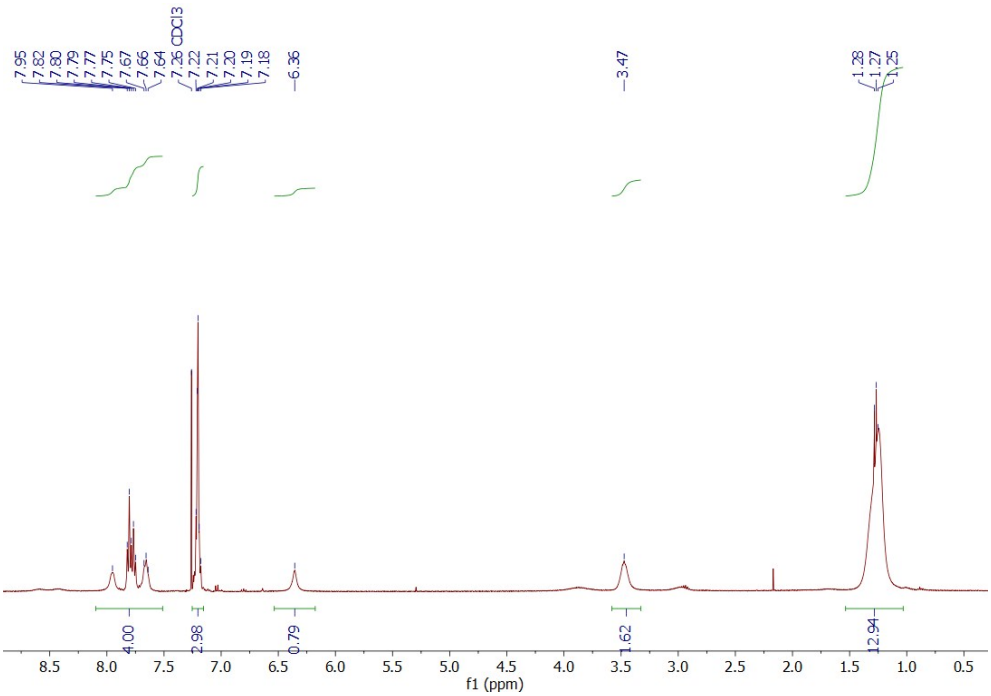

Figure S3 ^{1}H NMR of **3b** in $CDCl_3$**.**

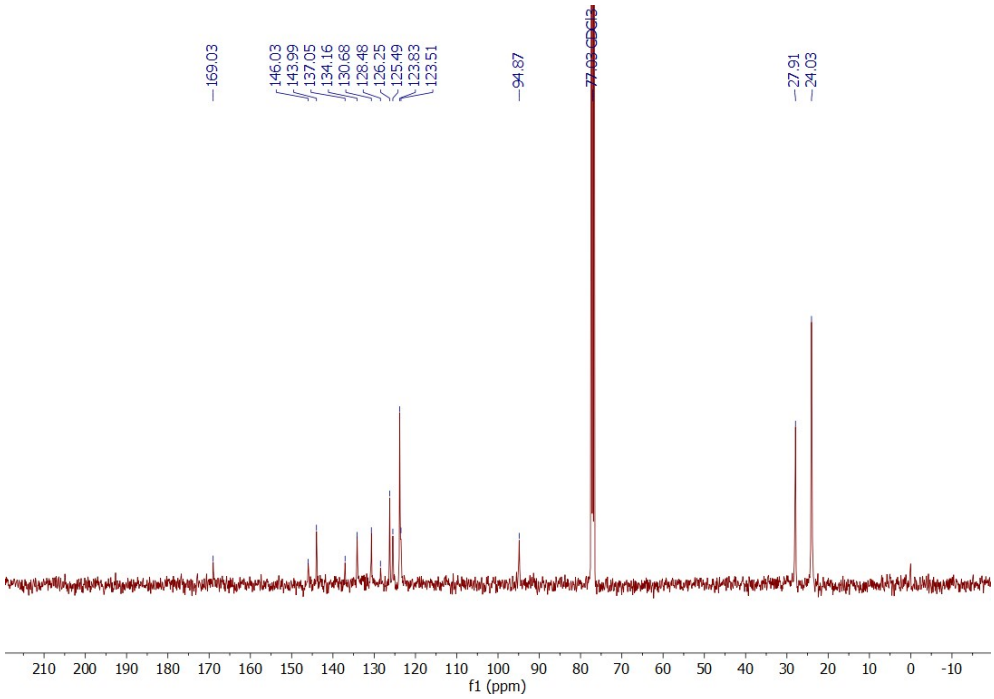

Figure S4 ^{13}C NMR of **3b** in $CDCl_3$.

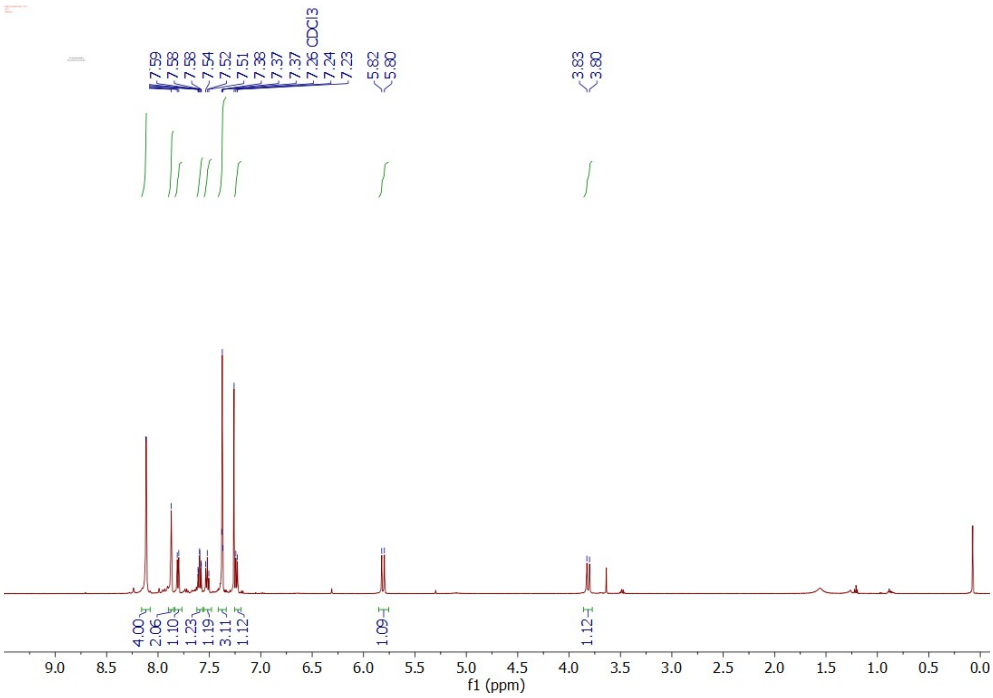

Figure S5 ^{1}H NMR of **3c** in $CDCl_3$.

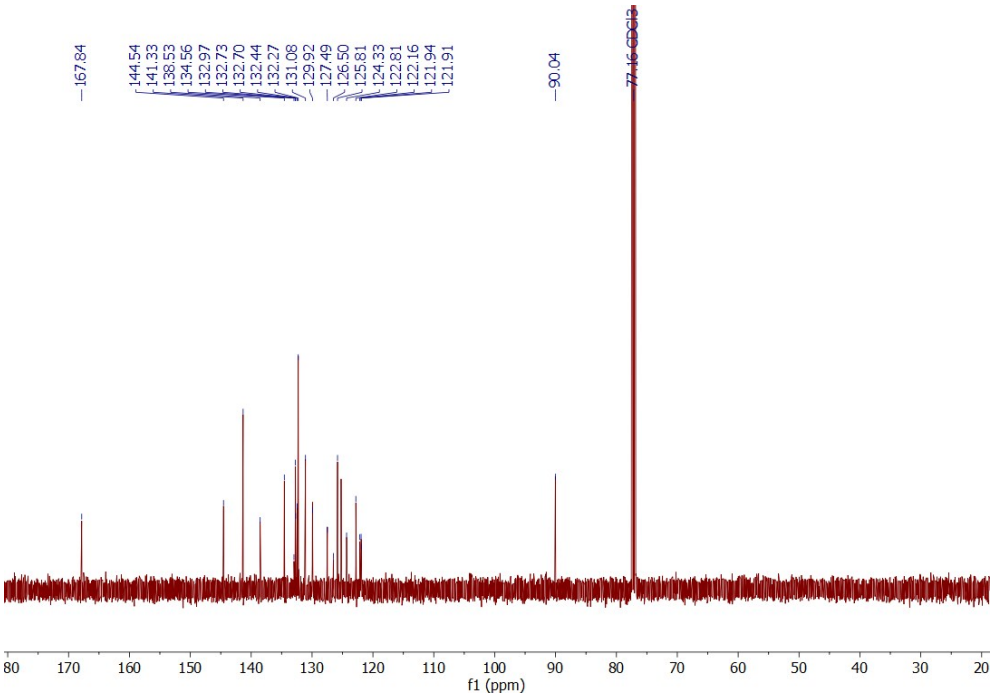

Figure S6 ^{13}C NMR of **3c** in $CDCl_3$.

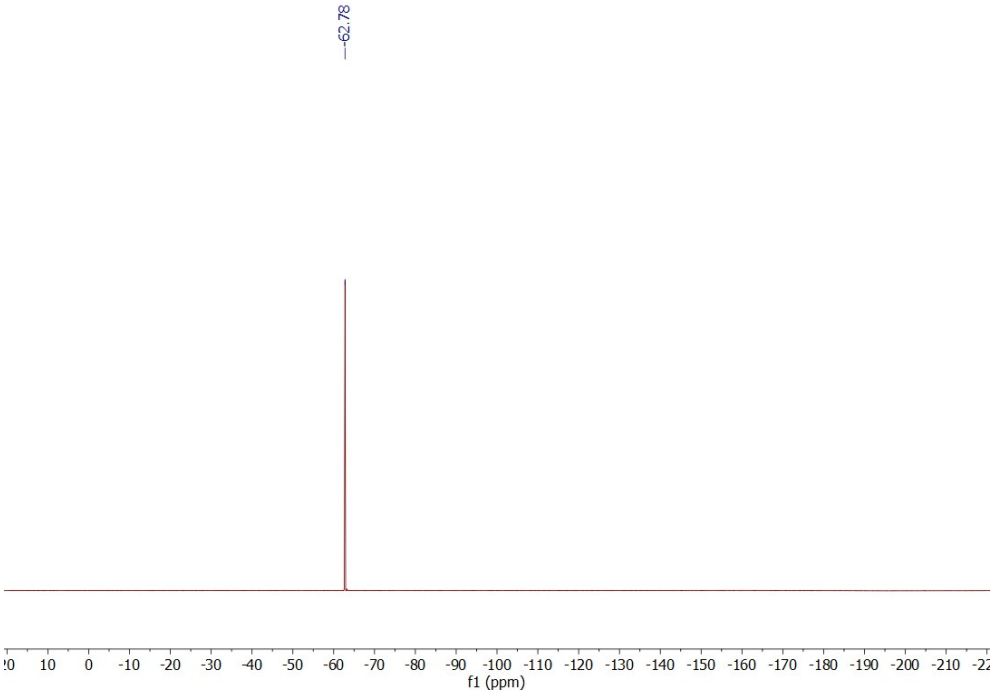

Figure S7 ^{19}F NMR of **3c** in $CDCl_3$.

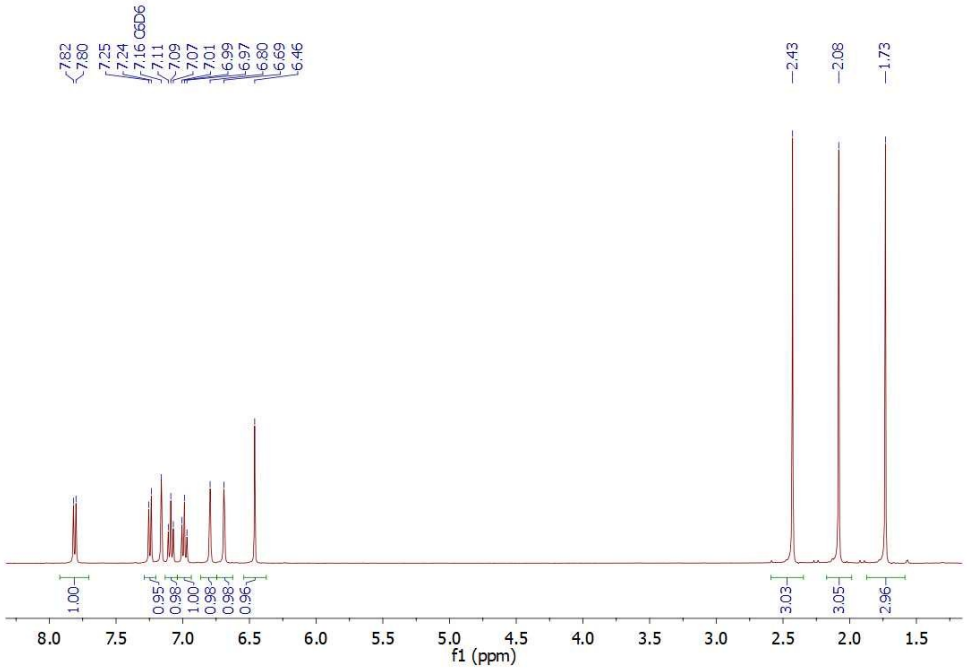

Figure S8 ^{1}H NMR of **4a** in C_6D_6.

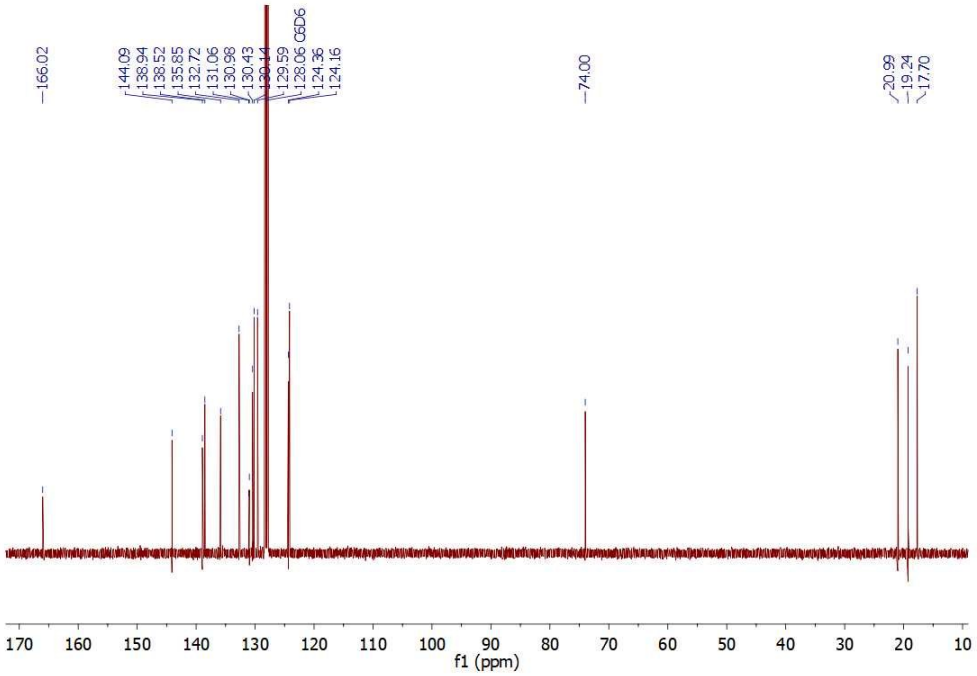

Figure S9 ^{13}C NMR of **4a** in C_6D_6.

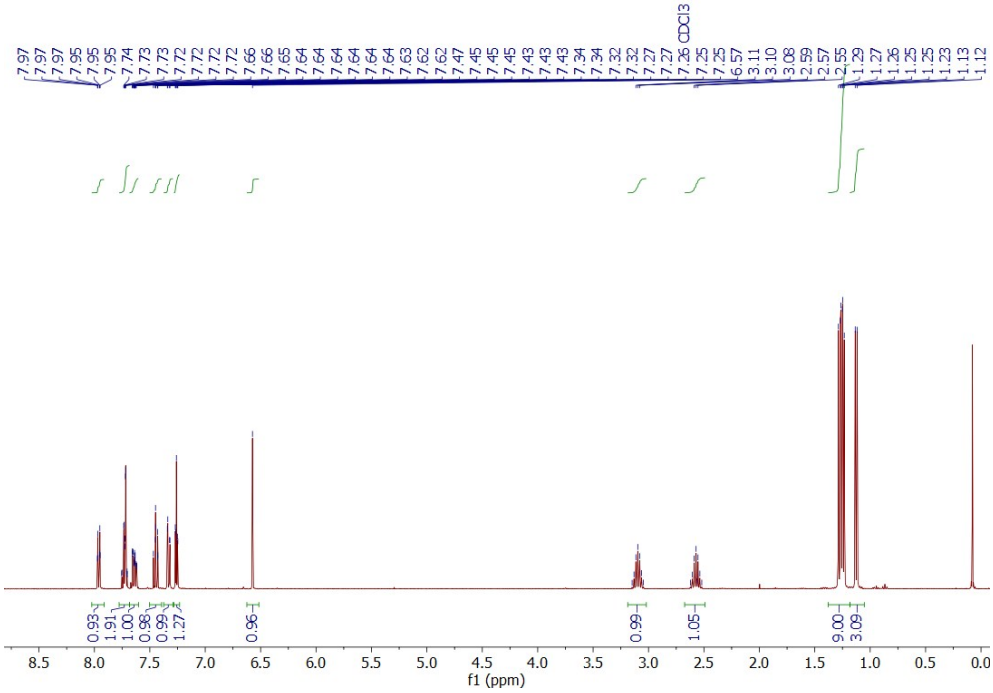

Figure S10 ^{1}H NMR of **4b** in $CDCl_3$.

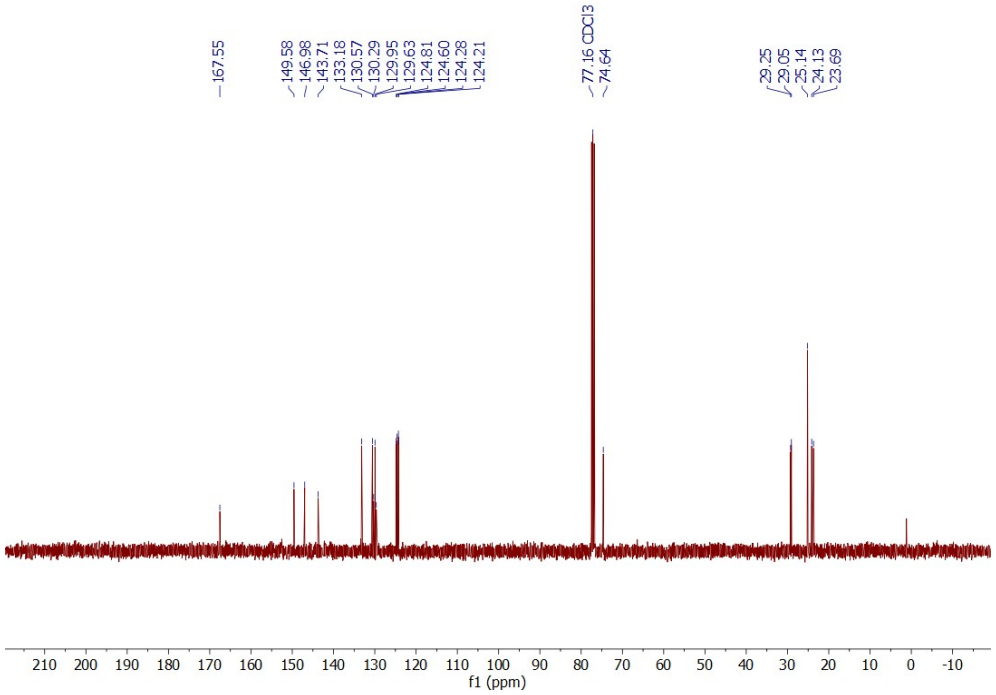

Figure S11 ^{13}C NMR of **4b** in $CDCl_3$.

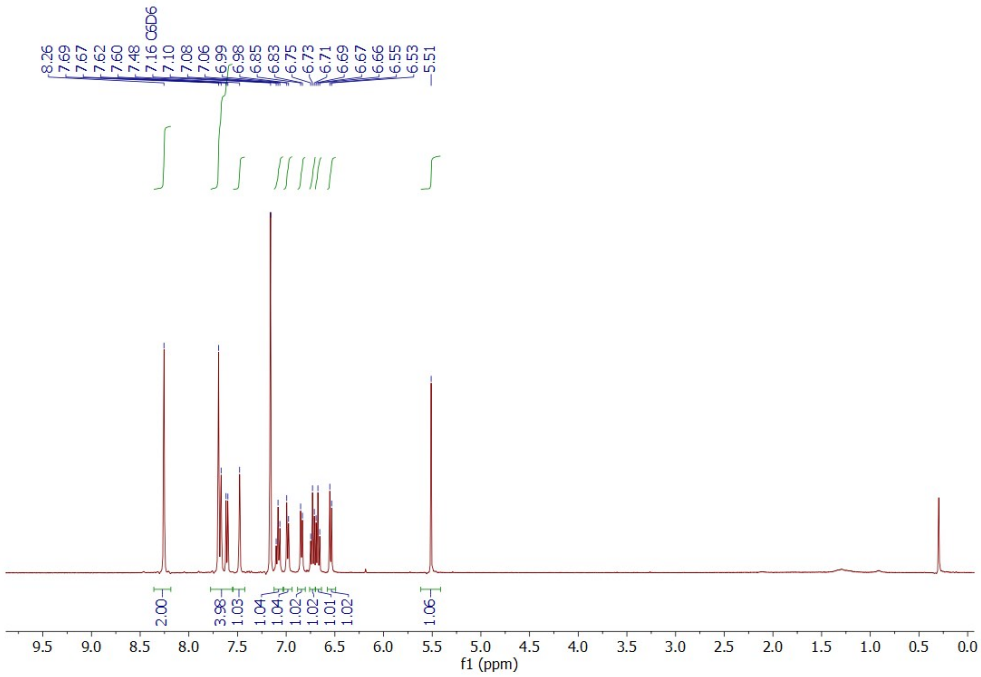

Figure S12 ^{1}H NMR of **4c** in C_6D_6.

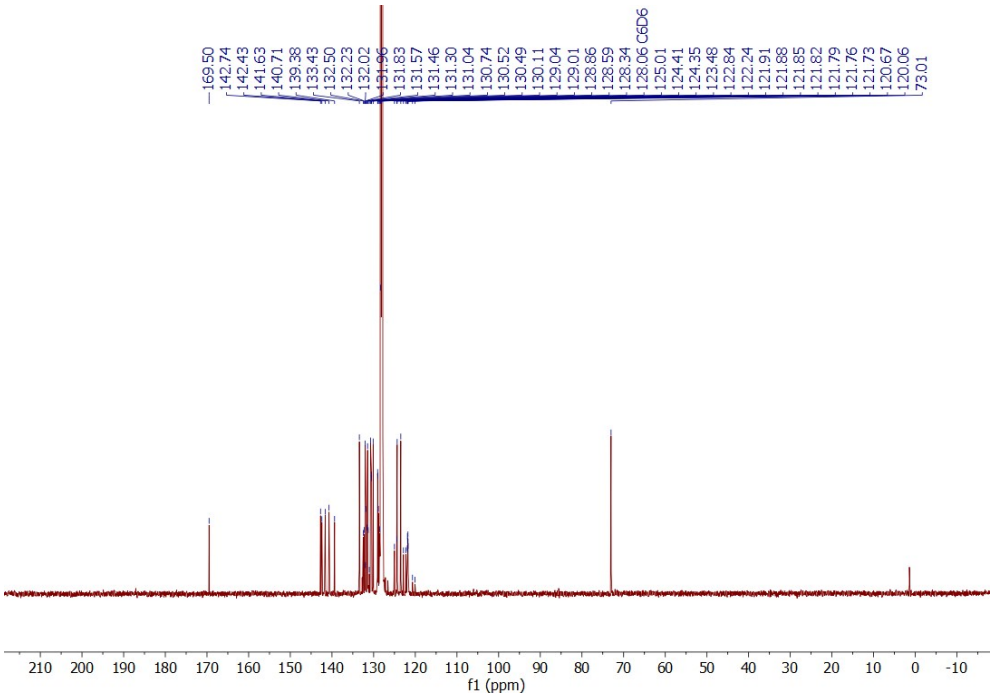

Figure S13 ^{13}C NMR of **4c** in C_6D_6.

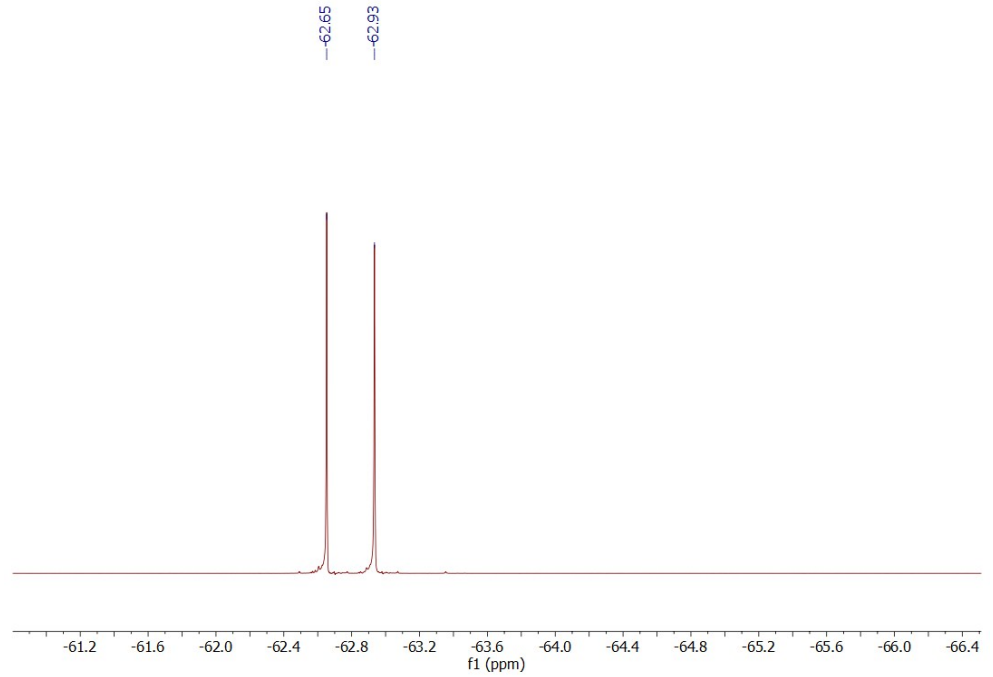

Figure S14 ^{19}F NMR of **4c** in C_6D_6.

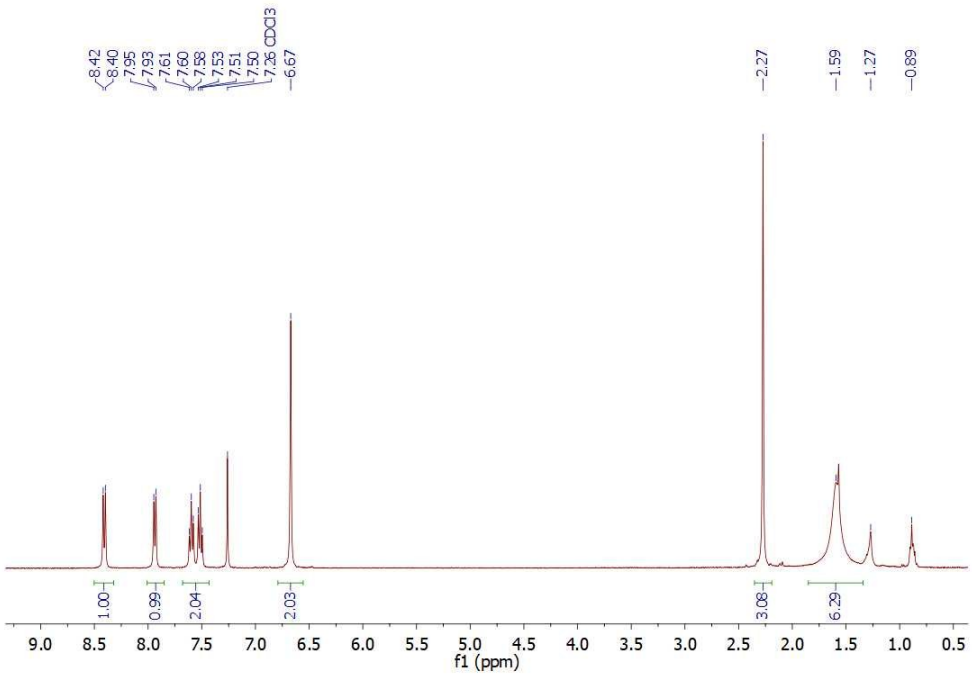

Figure S15 ^{1}H NMR of **5a** in $CDCl_3$.

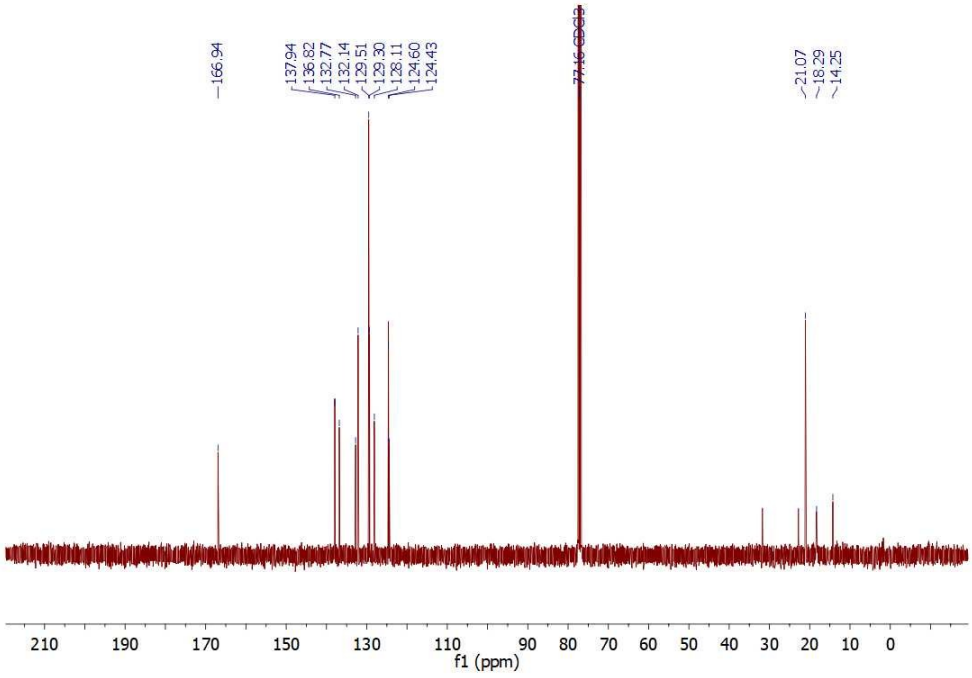

Figure S16 ^{13}C NMR of **5a** in $CDCl_3$.

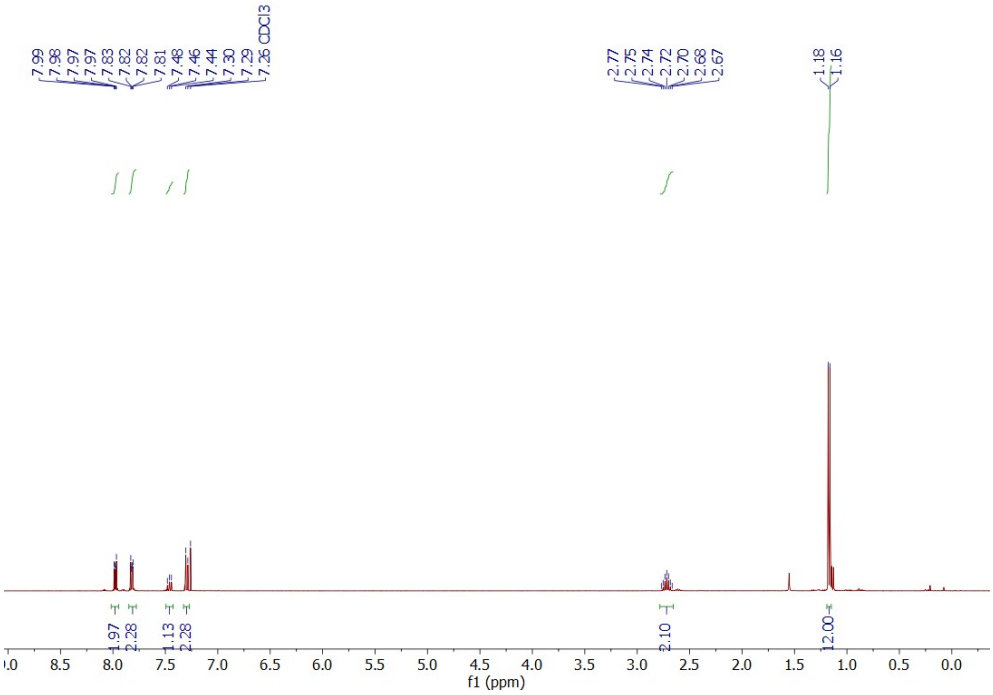

Figure S17 ^{1}H NMR of **5b** in $CDCl_3$.

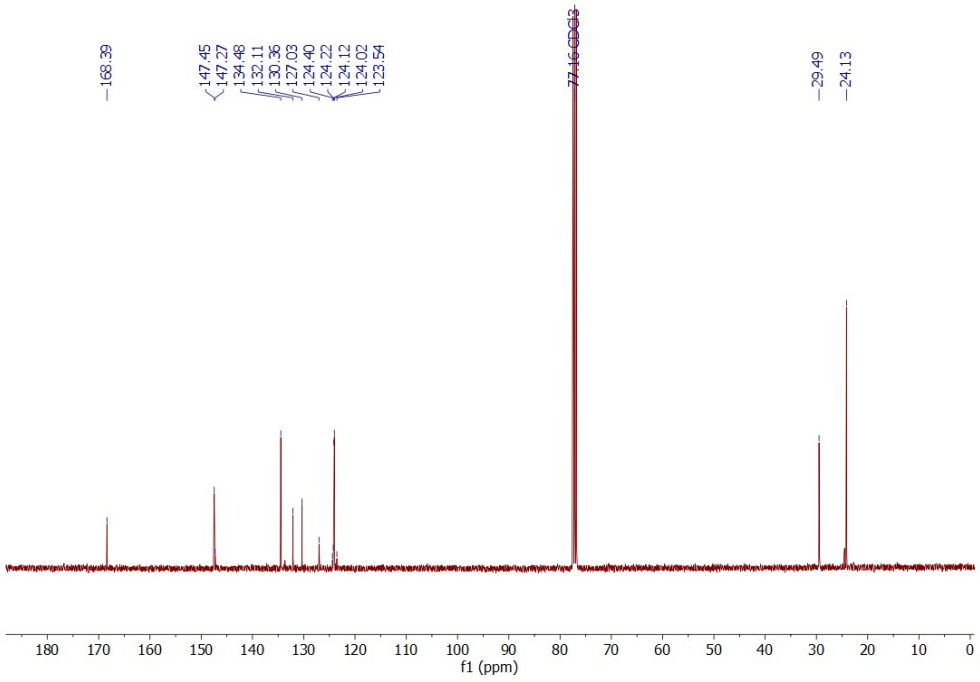

Figure S18 ^{13}C NMR of **5b** in $CDCl_3$.

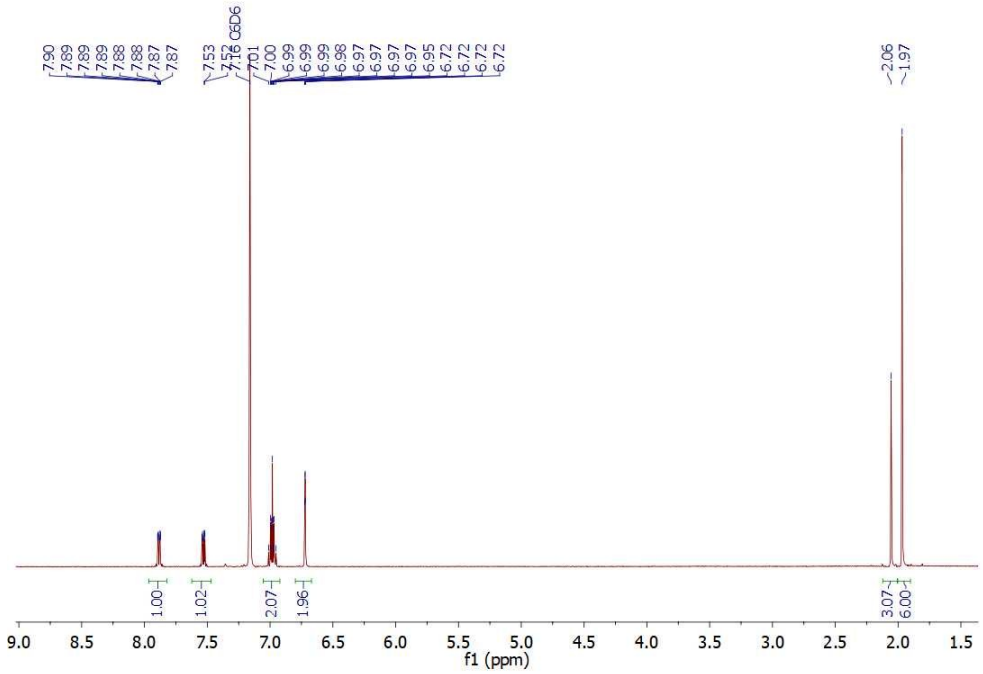

Figure S19 ^{1}H NMR of **6a** in C_6D_6.

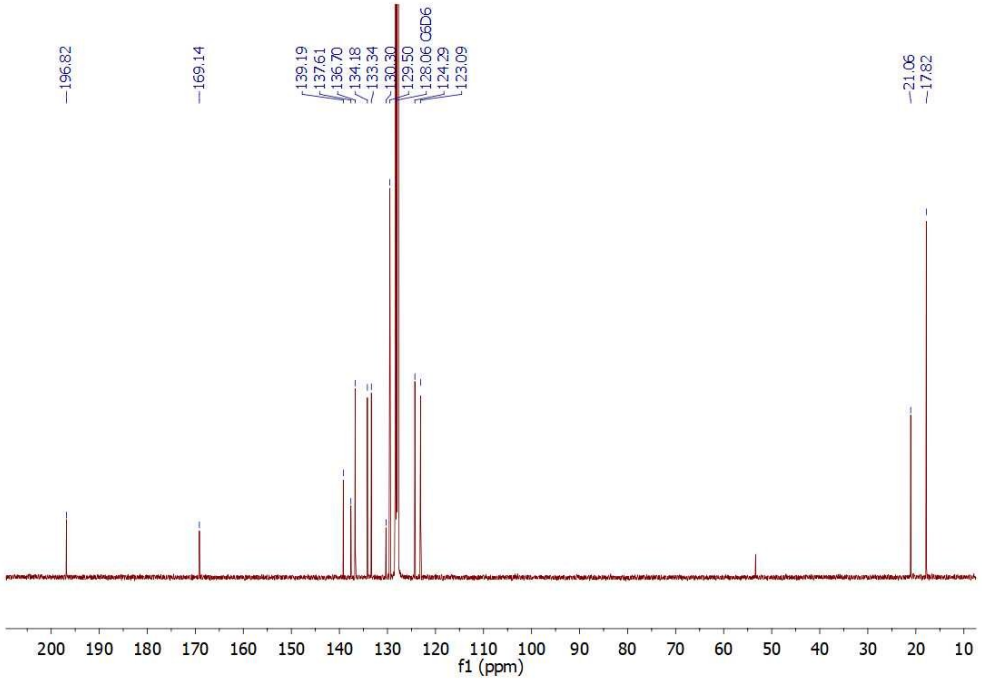

Figure S20 ^{13}C NMR of **6a** in C_6D_6.

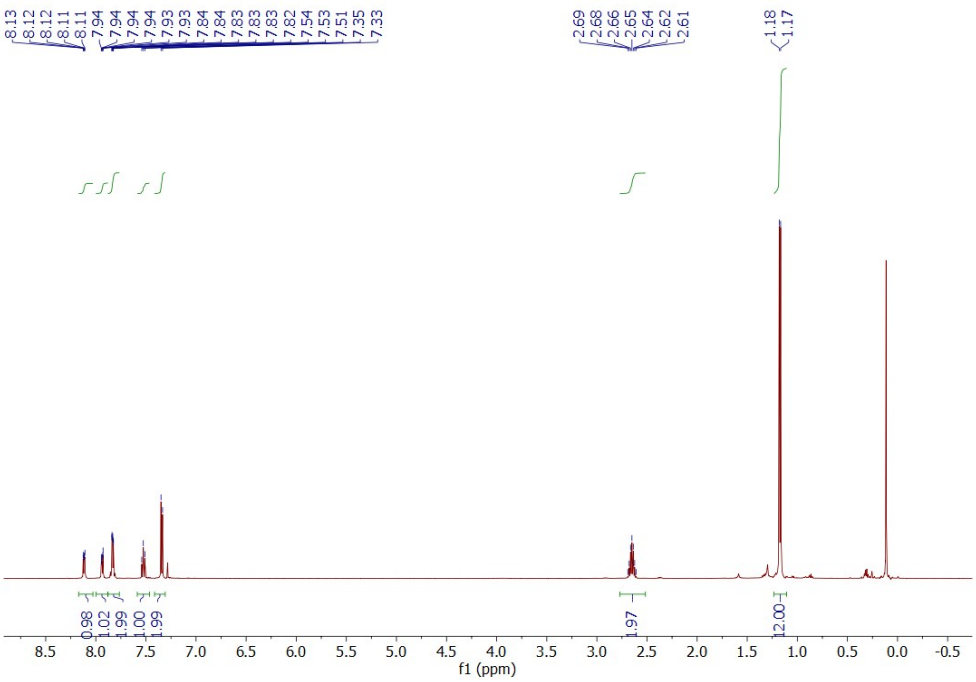

Figure S21 ^{1}H NMR of **6b** in $CDCl_3$.

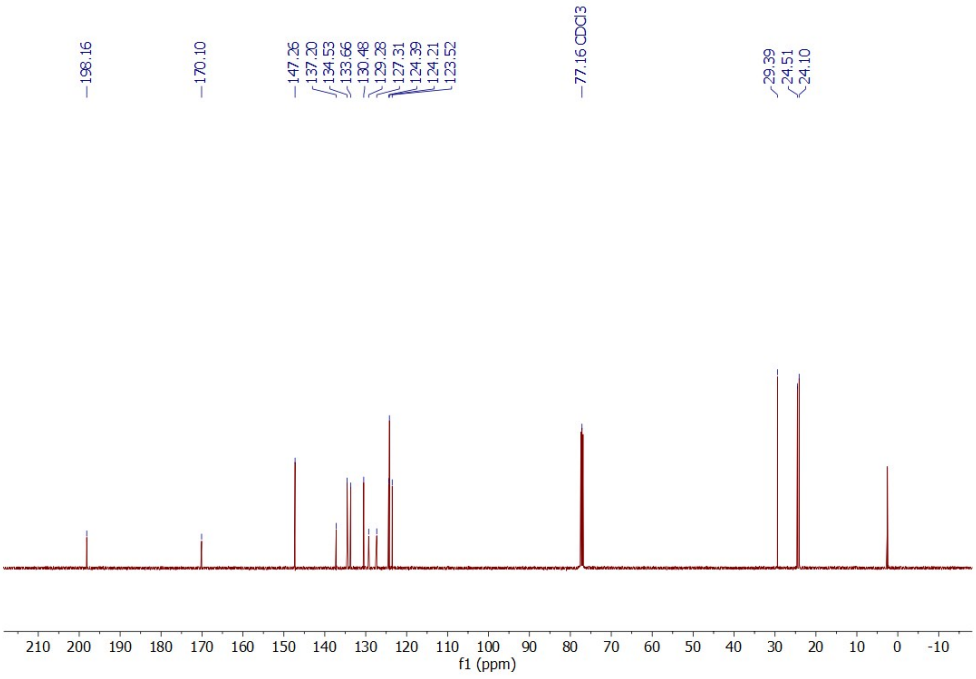

Figure S22 ^{13}C NMR of **6b** in $CDCl_3$.

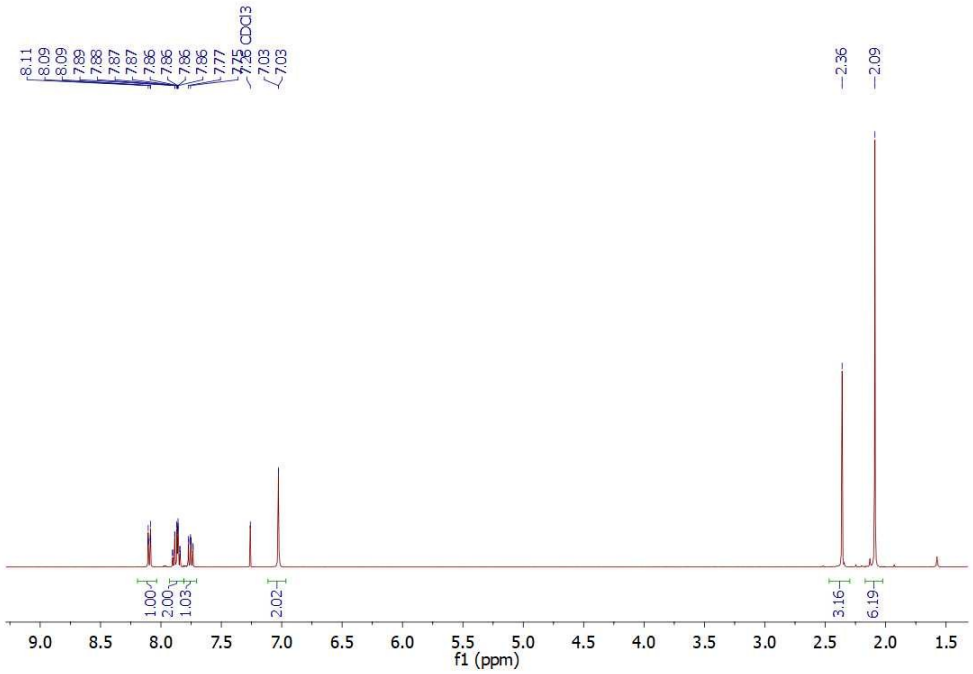

Figure S23 ^{1}H NMR of **7a** in $CDCl_3$.

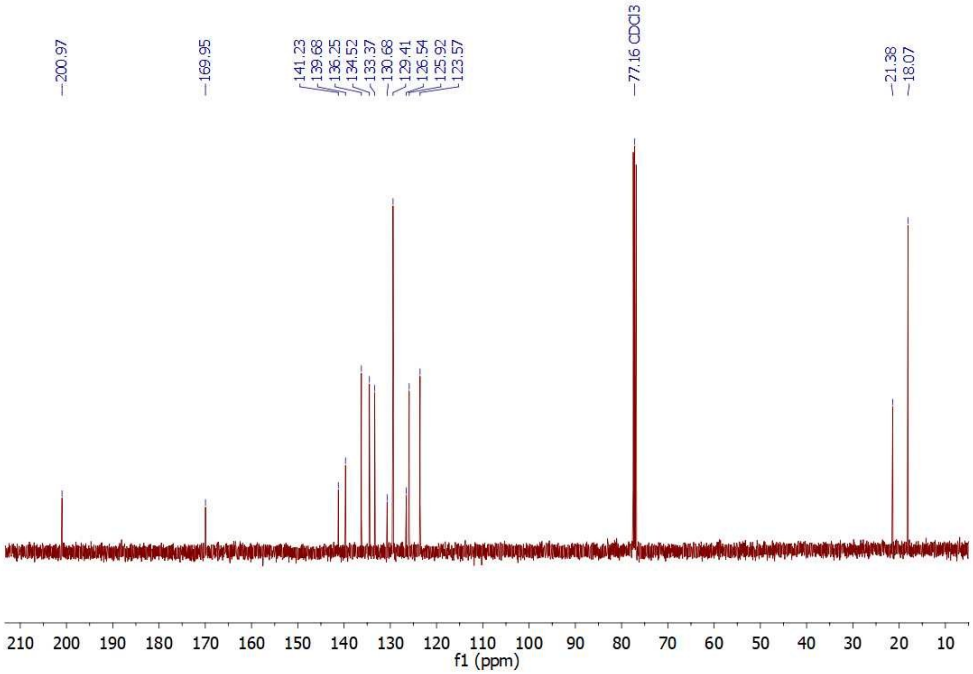

Figure S24 ^{13}C NMR of **7a** in $CDCl_3$.

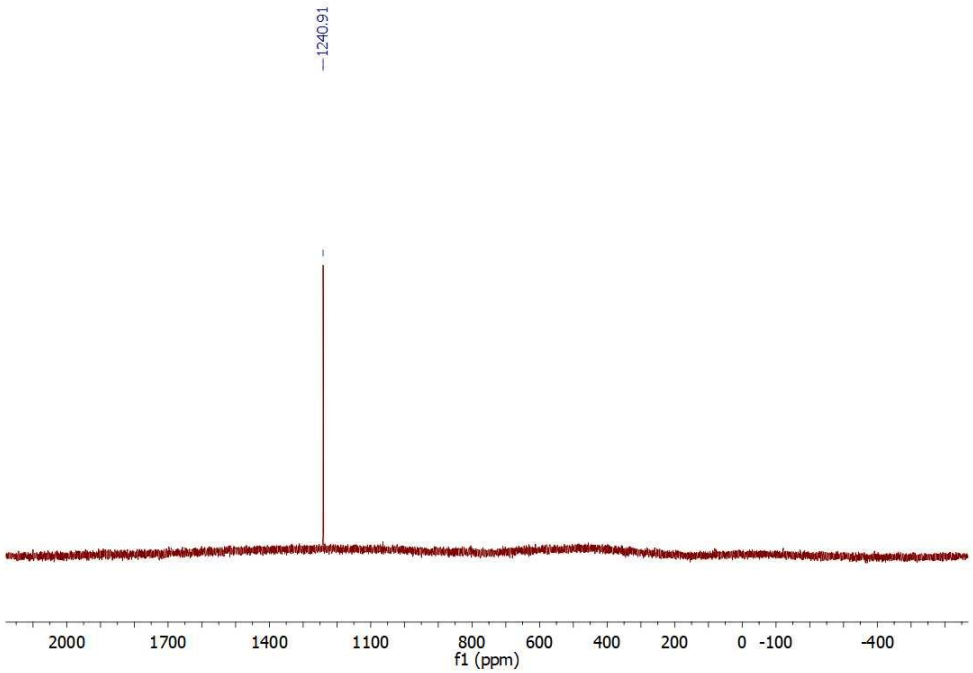

Figure S25 ^{77}Se NMR of **7a** in $CDCl_3$.

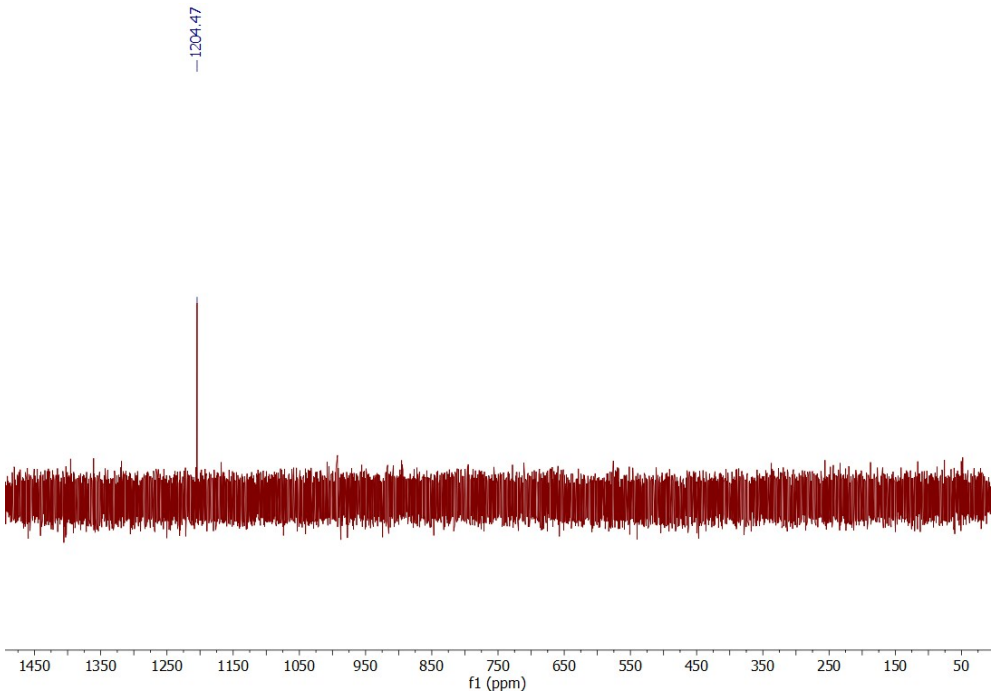

Figure S26 ^{77}Se NMR of **7a** in acetone-d_6.

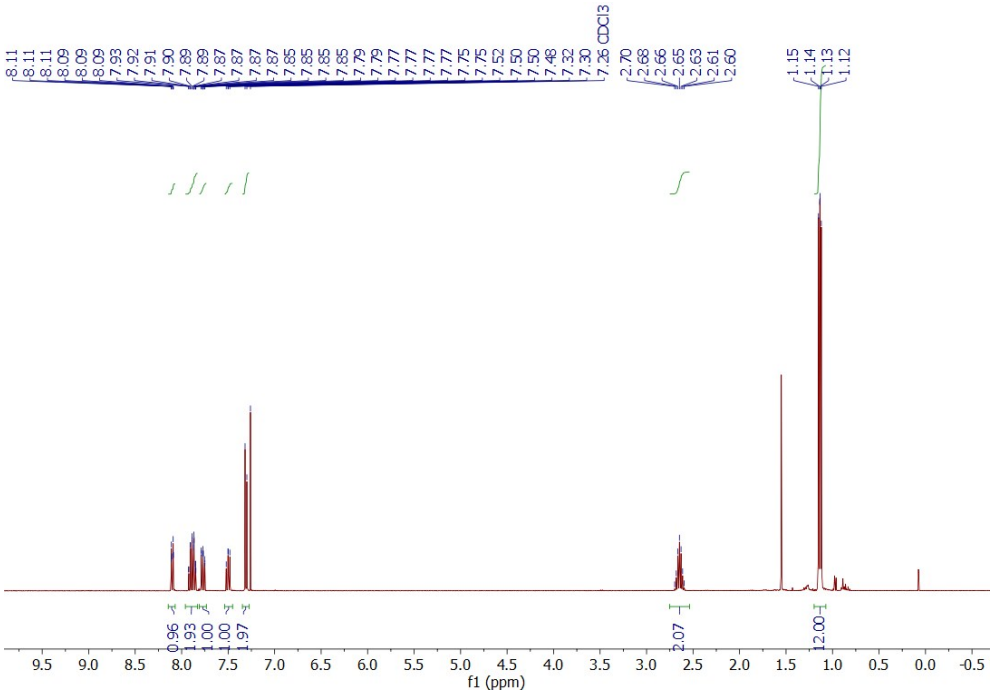

Figure S27 ^{1}H NMR of **7b** in $CDCl_3$.

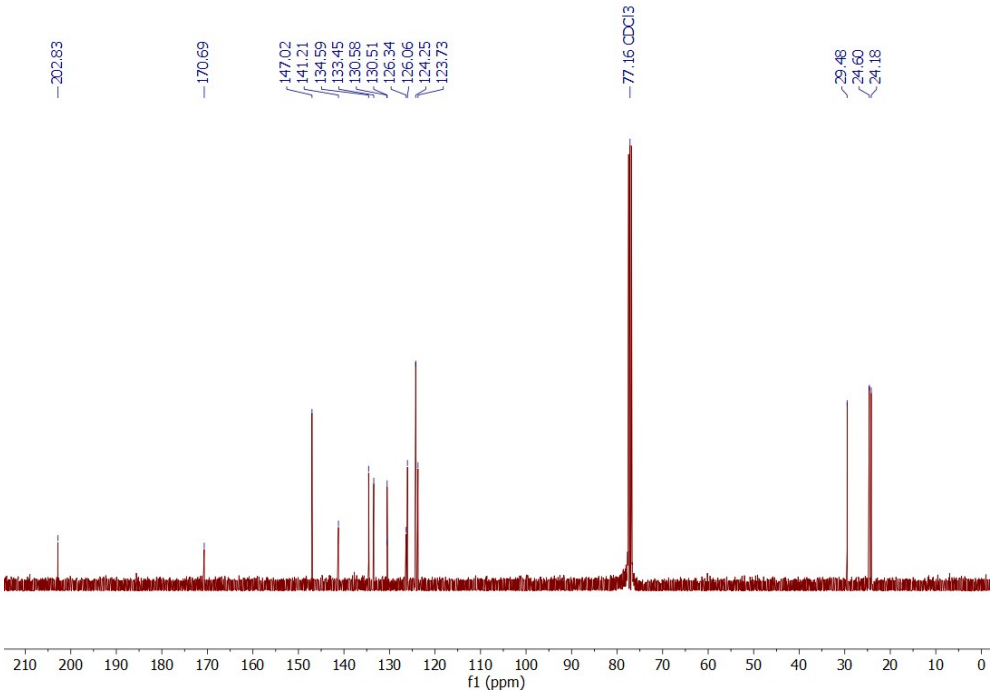

Figure S28 ^{13}C NMR of **7b** in $CDCl_3$.

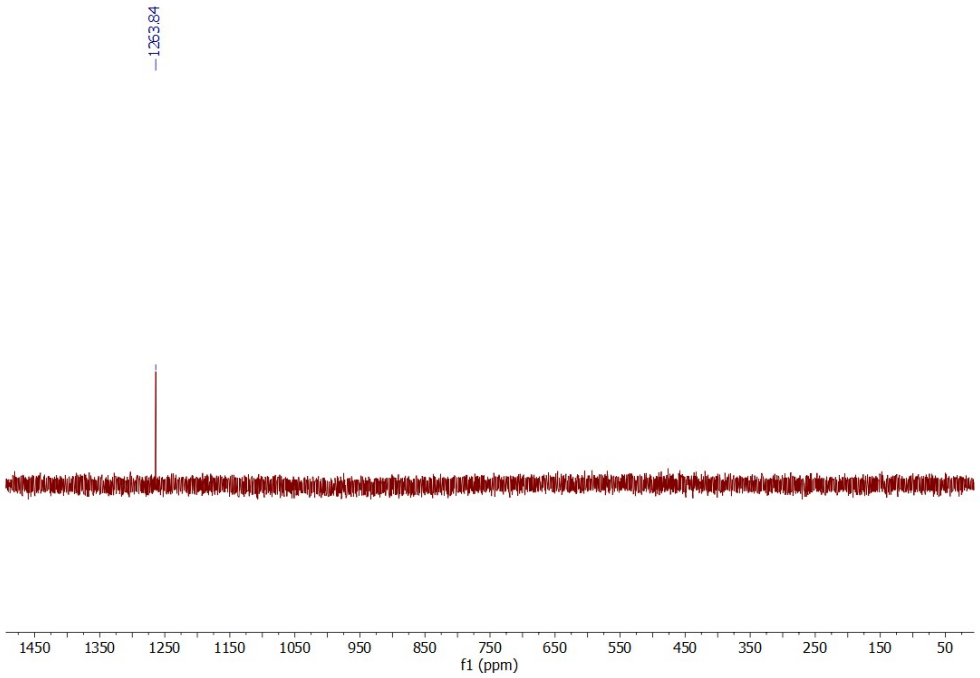

Figure S29 ^{77}Se NMR of **7b** in $CDCl_3$.

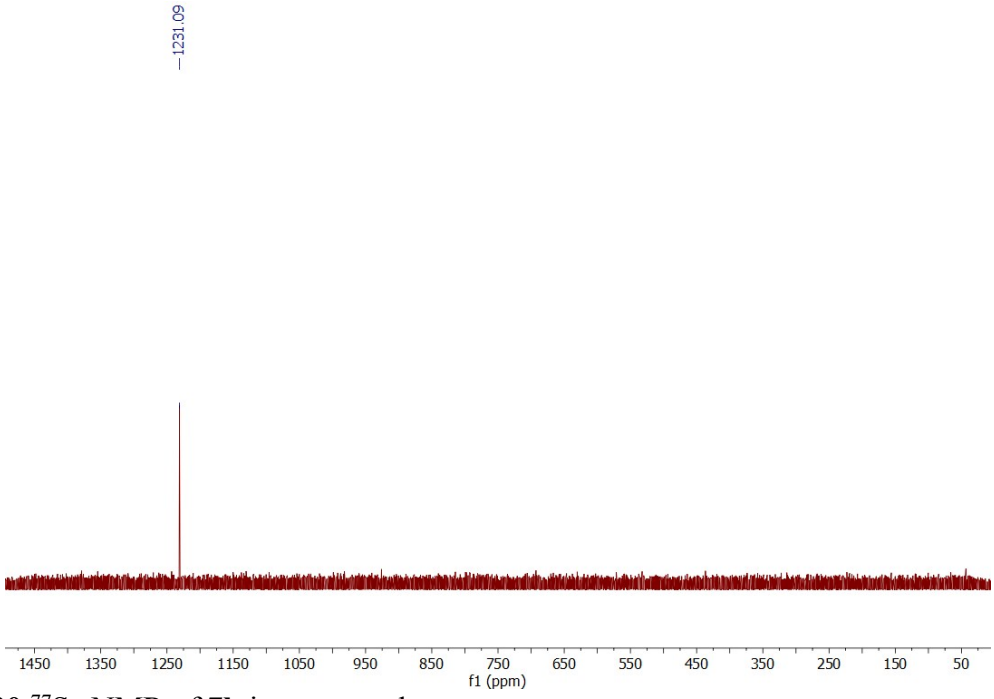

Figure S30 ^{77}Se NMR of **7b** in acetone-d_6.

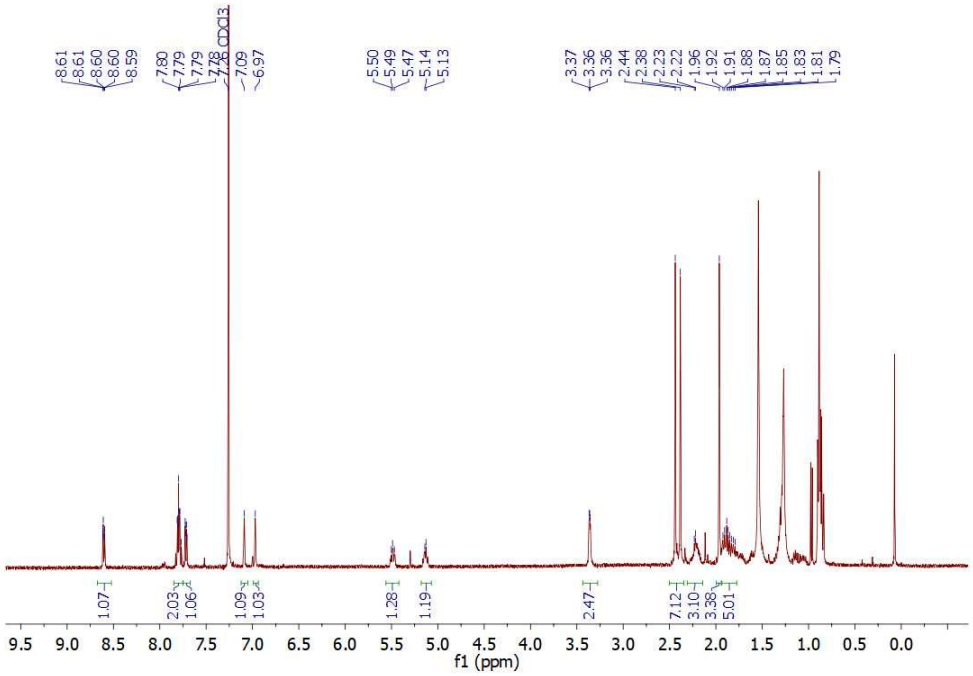

Figure S31 ^{1}H NMR of **8a** in $CDCl_3$.

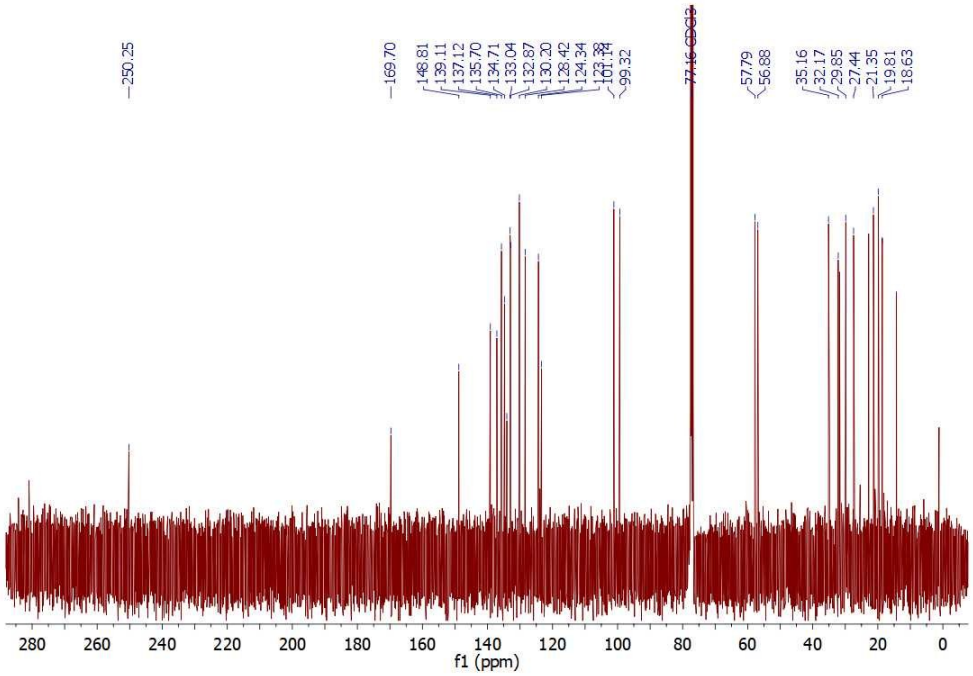

Figure S32 ^{13}C NMR of **8a** in $CDCl_3$.

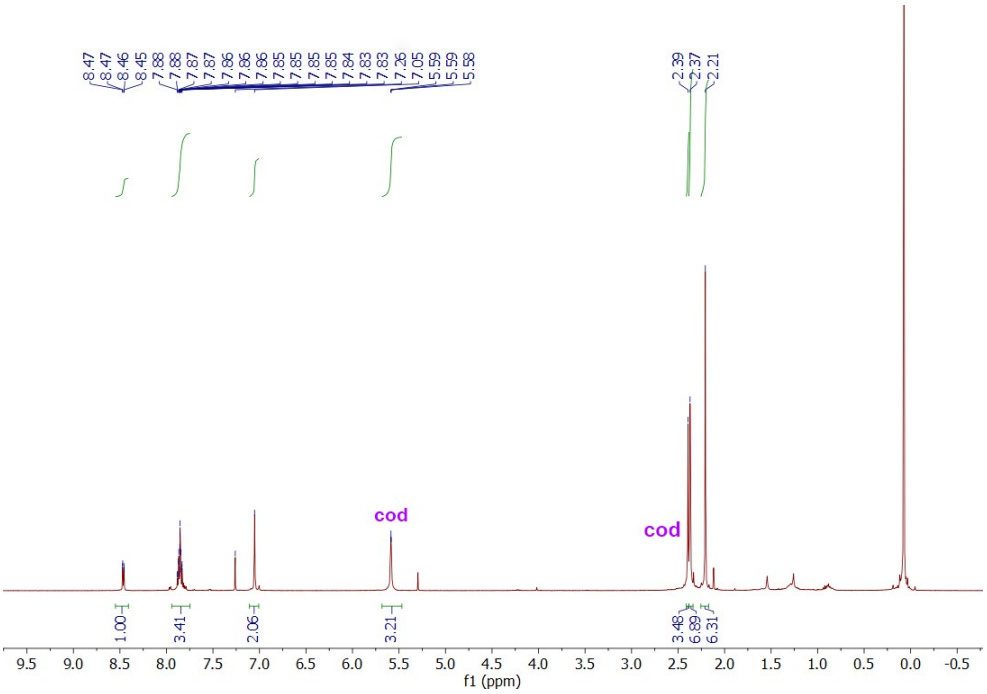

Figure S33 ^{1}H NMR of **9a** in $CDCl_3$.

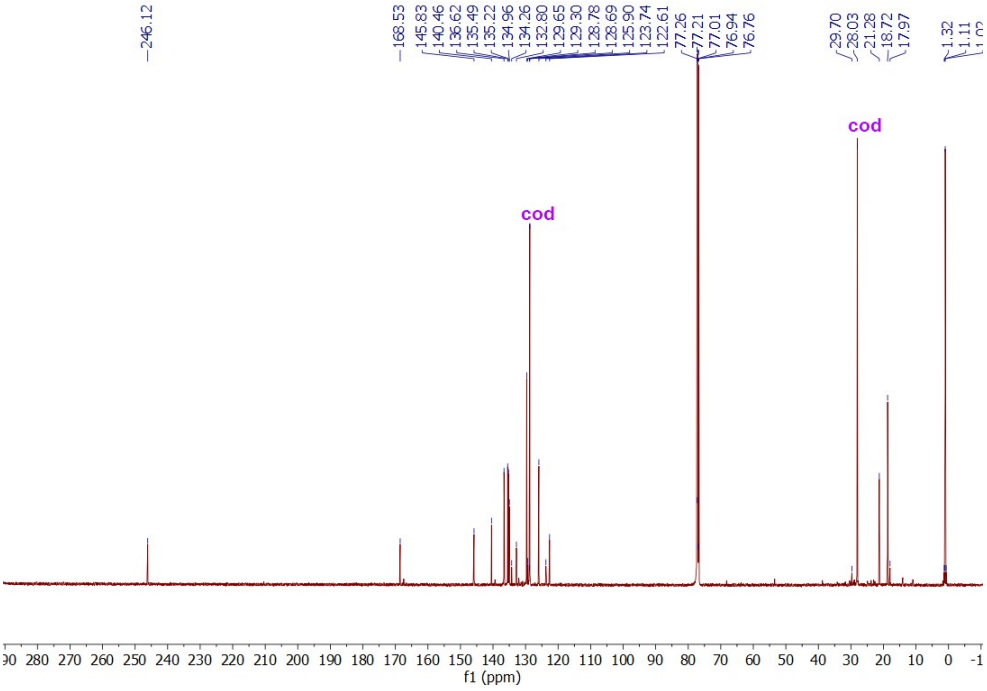

Figure S34 ^{13}C NMR of **9a** in $CDCl_3$.

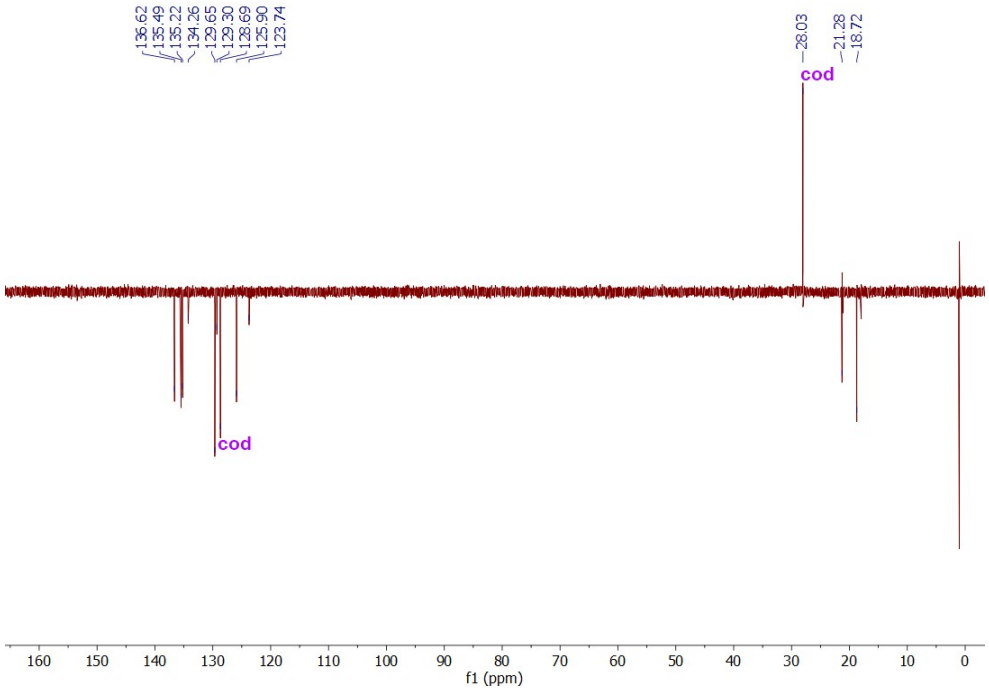

Figure S35 DEPT-135 spectra of **9a** in $CDCl_3$.

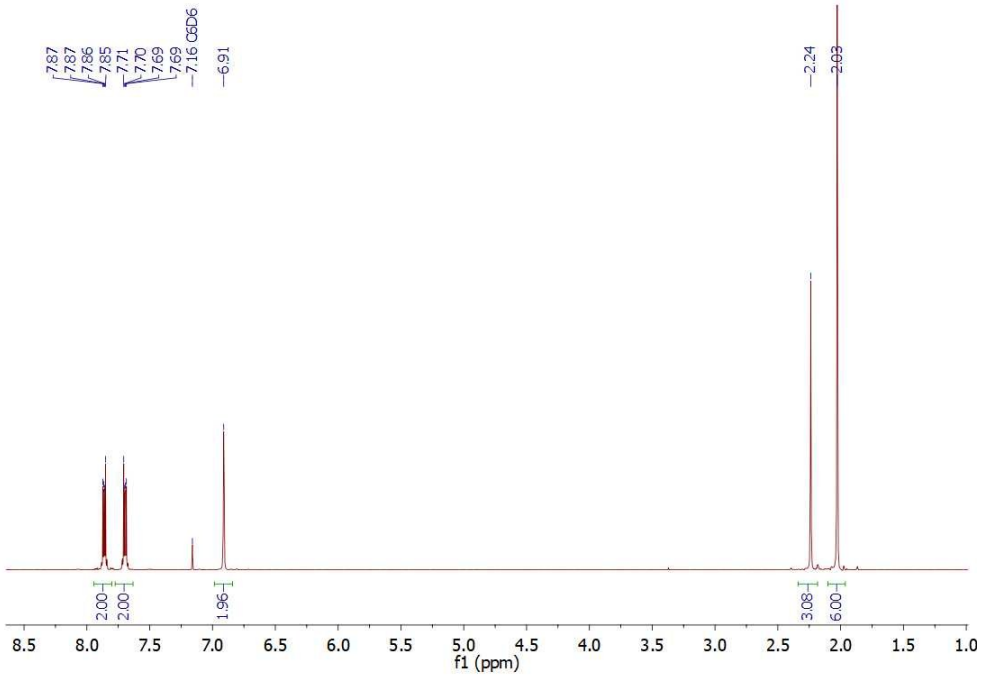

Figure S36 ^1H NMR of **10** in $CDCl_3$ (Method A Synthesis).

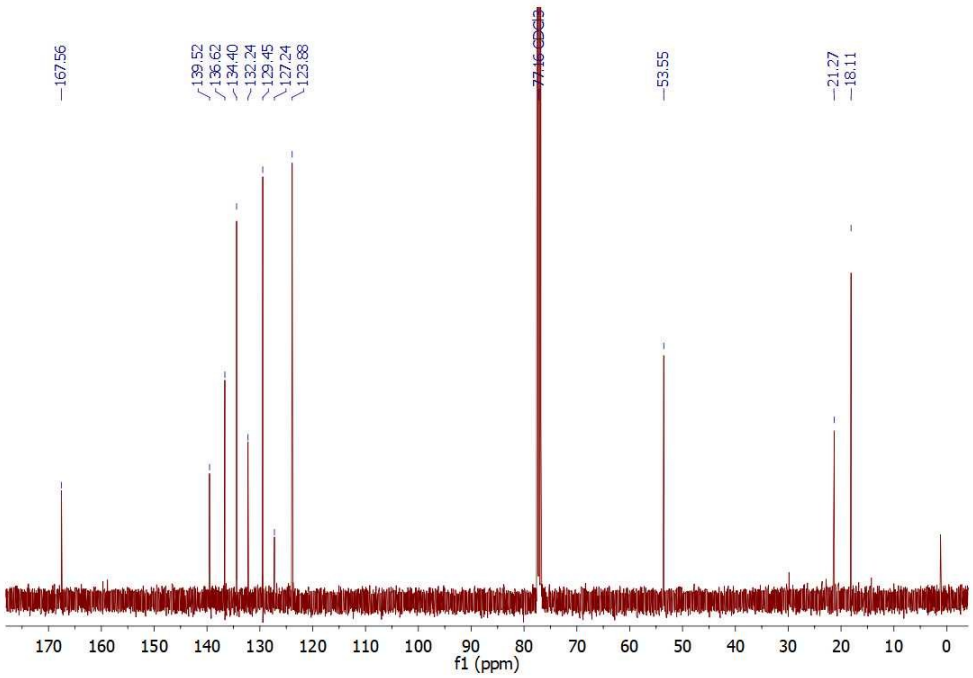

Figure S37 ^{13}C NMR of **10** in $CDCl_3$ (Method A Synthesis).

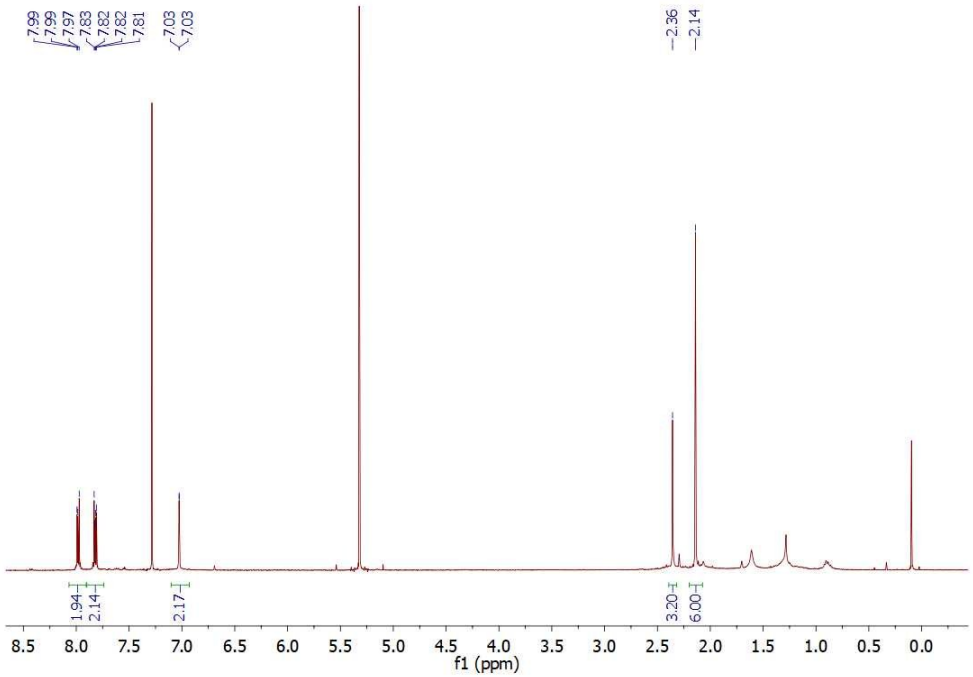

Figure S38 ^{1}H NMR of **10** in $CDCl_3$ (Method B Synthesis).

Figure S39 ^{13}C NMR of **10**in $CDCl_3$ (Method B Synthesis).

Oxidation of 9a: ^{13}C NMR DEPT-135 and FTIR DATA

To determine the Tolman Electronic Parameter (TEP), the carbonyl stretching frequencies for compound **9a** were measured using FTIR spectroscopy. A freshly prepared solution of **9a** in $CDCl_3$ was transferred inside of a nitrogen-filled glovebox into a 1 mL Specac solution IR cell equipped with CaF_2 windows. As expected, there were CO stretching modes observed for the amide carbonyl in the ligand at 1692.2 cm^{-1}, and for the metal carbonyls at 2001.8 and 2081.7 cm^{-1} (Figure S40). The metal carbonyl stretching frequencies allowed us to determine the TEP of **Fa** using Nolan's method,[1] which was found to be 2065 cm^{-1}. Importantly we also observed a peak at 2256.6 cm^{-1}, which corresponds to the $[Ir(CO)_6]^{3+}$ cation.[2, 3] In agreement with the presence of $[Ir(CO)_6]^{3+}$ in the solution, we note that the ^{13}C NMR spectrum of this mixture featured a peak at 122.6 ppm, a peak which is consistent with the iridium(III)carbonyl cation.[2] [3]To confirm the identity of this peak, a DEPT-135 NMR spectrum was acquired on the solution to remove all quaternary carbons from the ^{13}C NMR spectrum. Note: DEPT-135 places all CH and CH_3 groups in a negative phase with all CH_2 groups in a positive phase and all quaternary carbons are absent. Figure S41 displays

a stacked ^{13}C NMR spectrum and the corresponding DEPT-135 spectrum taken on the sample. As you can see the signal at 122.6 ppm is indeed a quaternary carbon, thus providing more evidence for the presence of $[Ir(CO)_6]^{3+}$ cation. Given the sensitive nature of the tricationic complex, which is known to readily decompose in air, we did not attempt isolation of $[Ir(CO)_6]^{3+}$.[3]

Based on this data, we propose that upon oxidation of **9a** to give the phthalimide **10**, the resulting $[Ir(CO)_2Cl]$ fragment disproportionates according to the balanced reaction shown below:

$$3\ [Ir^{1+}(CO)_2Cl] \rightarrow 2\ Ir^0 \ +\ [Ir^{3+}(CO)_6]Cl_3$$

As further evidence for this disproportionation reaction, we also note that during the oxidation of **9a** to give phthalimide **10**, the deposition of iridium metal is observed on the sides of the NMR tube or reaction flask (Figure S42).

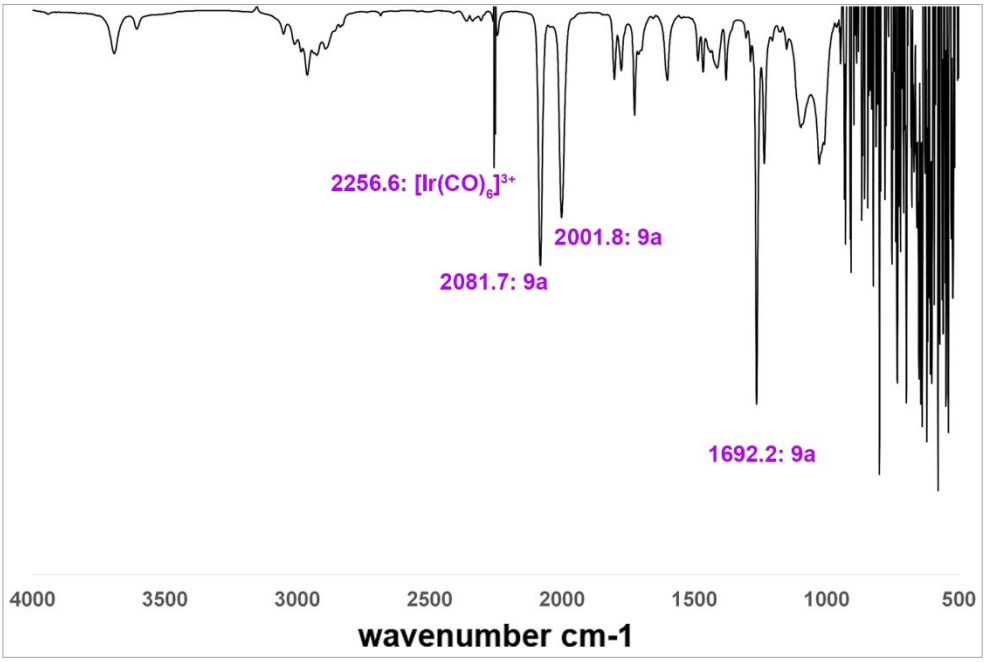

Figure S40 FTIR Data of **9a** in $CDCl_3$ using a liquid IR cell with CaF_2 windows.

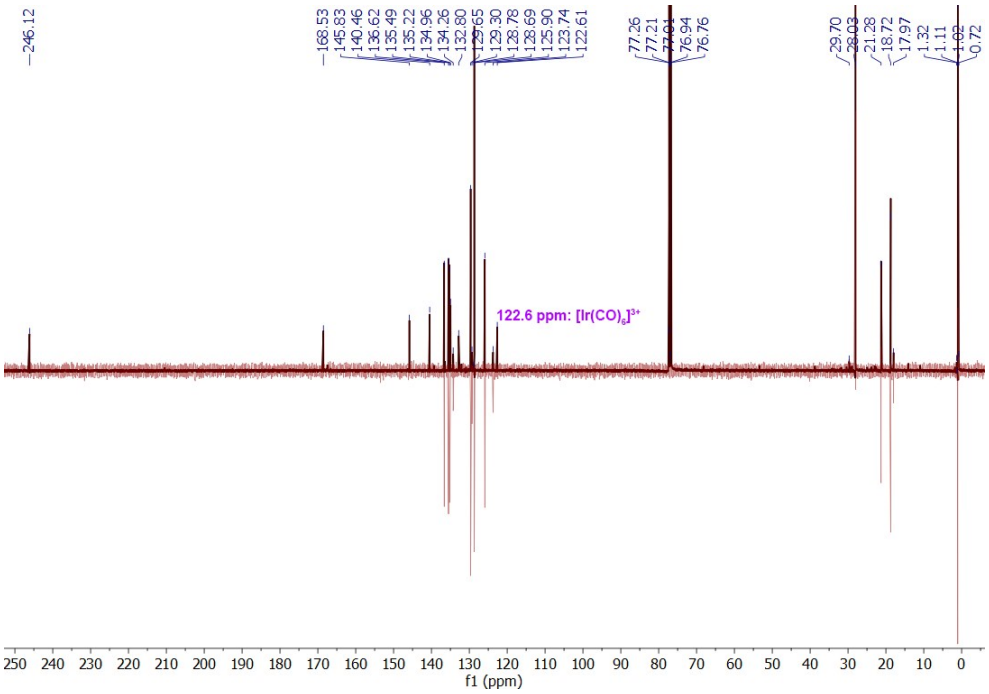

Figure S41 Stacked ^{13}C NMR and DEPT-135 spectra of **9a** in $CDCl_3$.

Figure S42 Reaction vial for the oxidation of **9a** to give **10**, note dark black iridium metal on sides of flask.

HIGH RESOLUTION MASS SPECTROMETRIC DATA

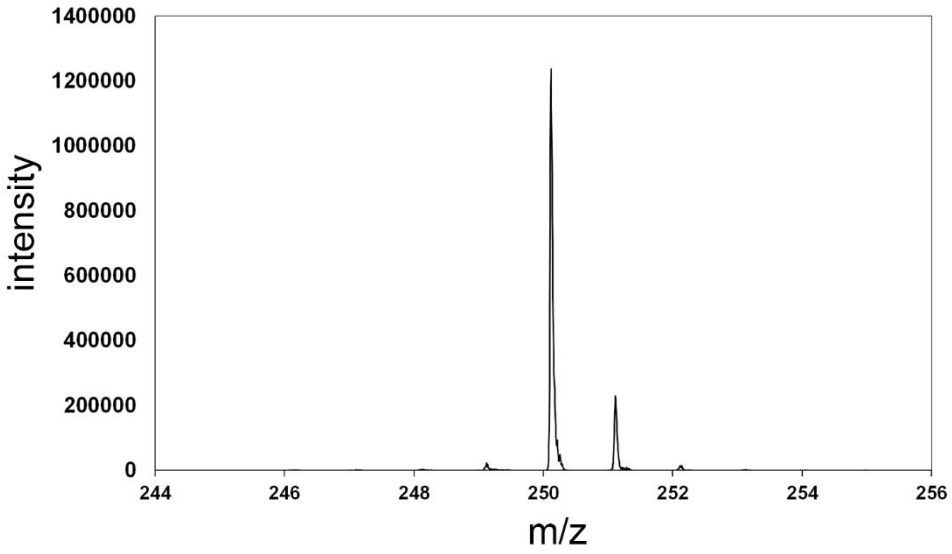

Figure S43. HRMS of spectrum of **4a.**

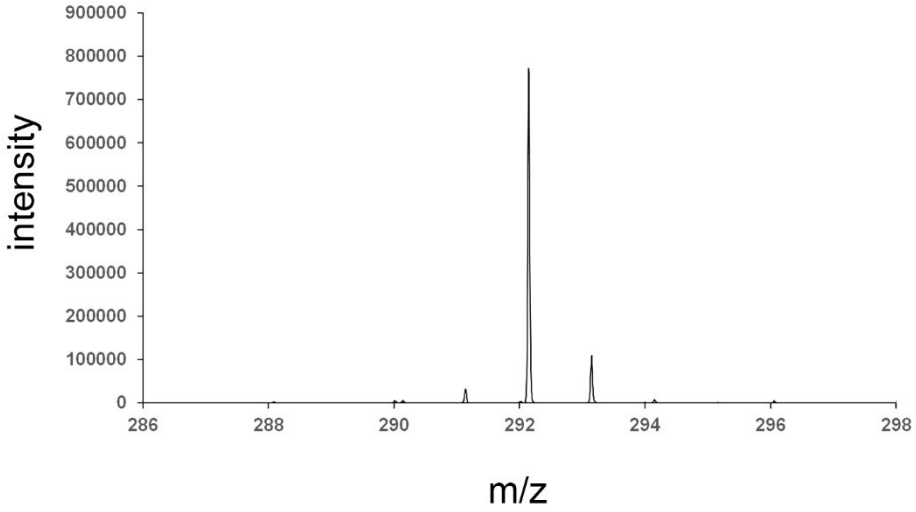

Figure S44. HRMS of spectrum of **4b.**

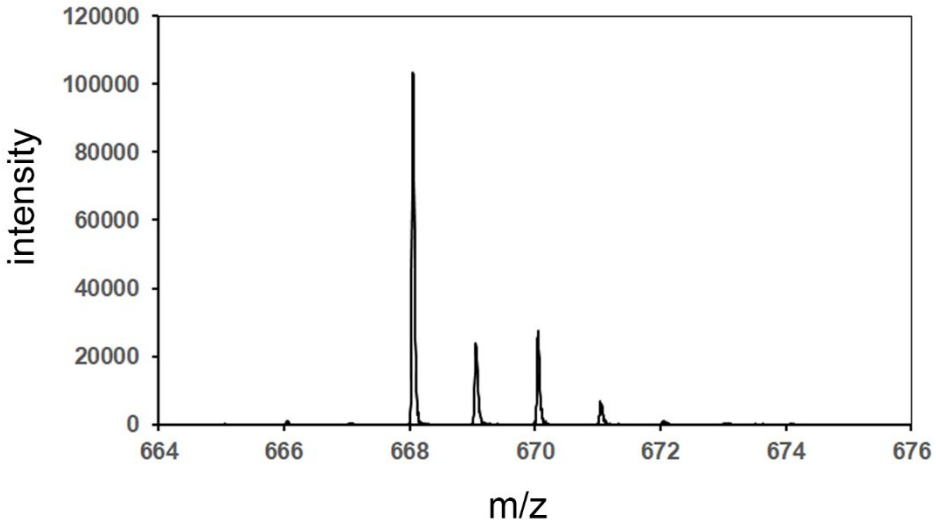

Figure S45. HRMS of spectrum of **4c.**

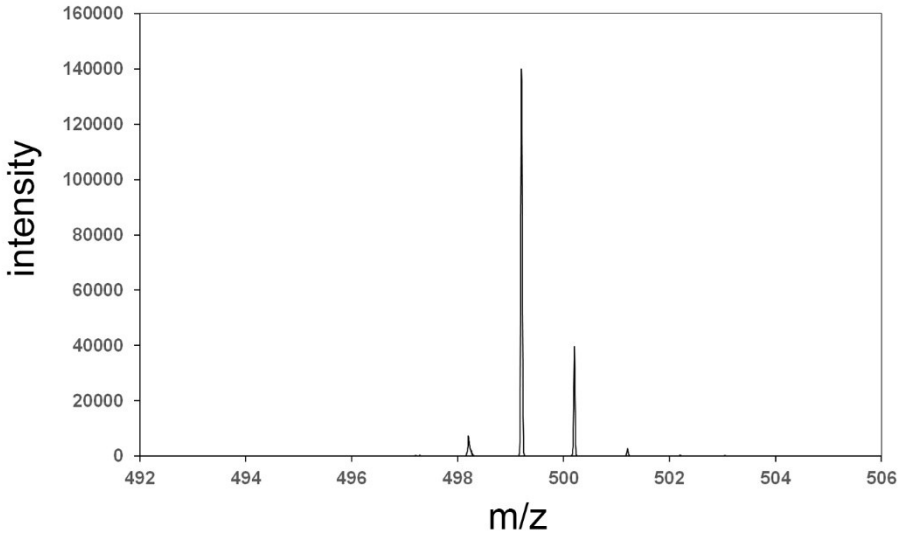

Figure S46. HRMS of spectrum of **5a.**

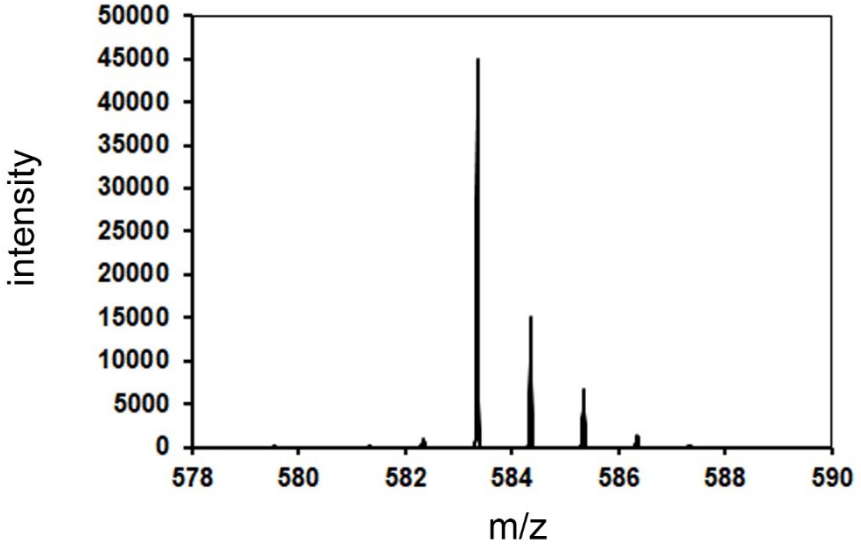

Figure S47. HRMS of spectrum of **5b.**

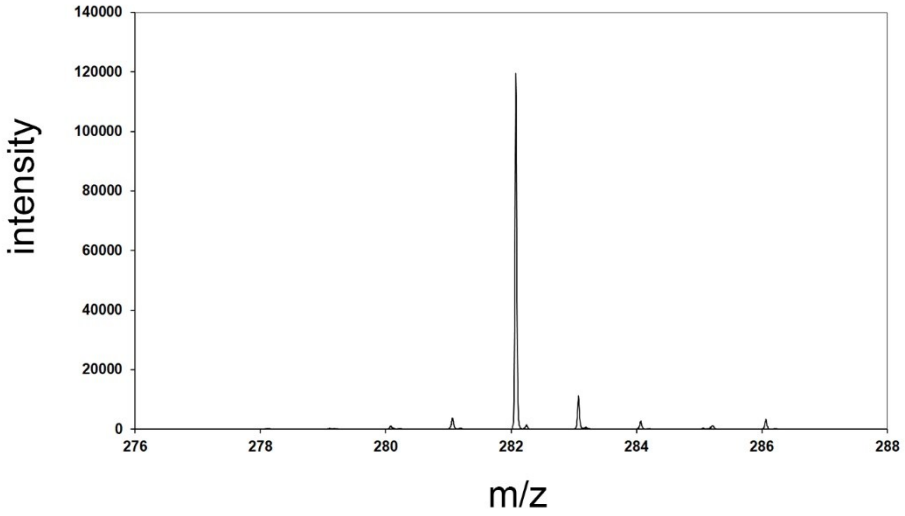

Figure S48. HRMS of spectrum of **6a.**

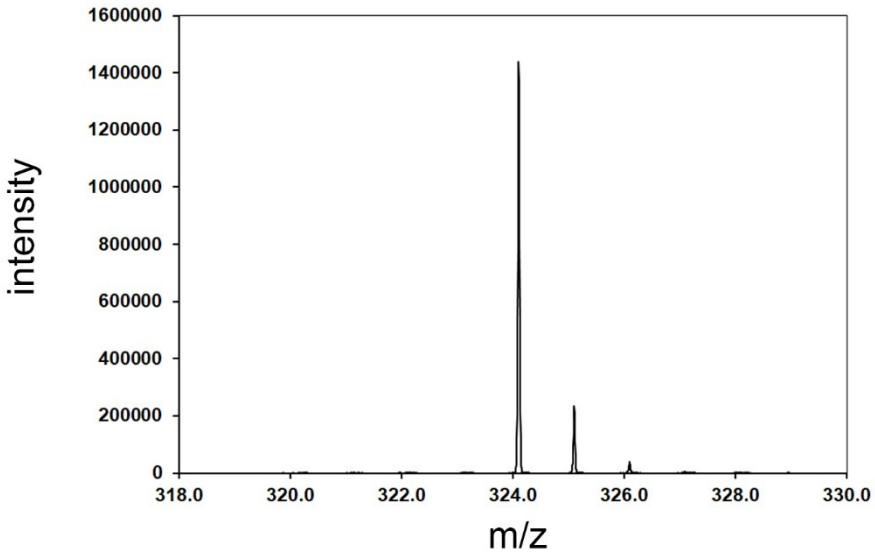

Figure S49. HRMS of spectrum of **6b.**

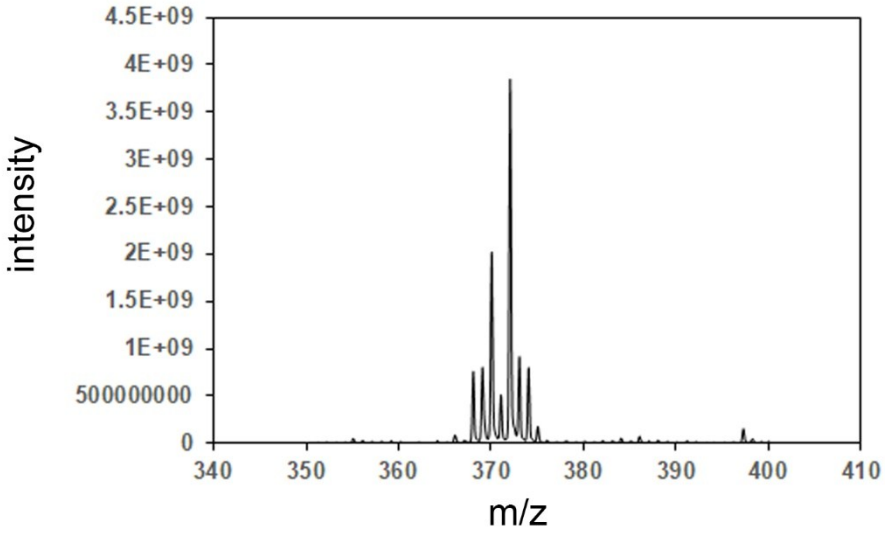

Figure S50. HRMS of spectrum of **7b.**

X-RAY CRYSTALLOGRAPHY

General Considerations: All crystallographic measurements were carried out on a Rigaku SCX Mini CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 223 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 CrysAlisPro 1.171.39.30d (Rigaku OD, 2017). 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 (ShelXL (Sheldrick, 2015) allowed location of the remaining non-hydrogen. Single crystals suitable for x-ray diffraction were all grown by slow evaporation of independent hexanes solutions saturated with the compounds. Compound **5a** crystallized as yellow prisms in the monoclinic space group $P2_{1/n}$, **6a** crystallized as pink prisms in the orthorhombic space group $P2_12_12_1$, and **7a** crystallized at teal prisms in the monoclinic space group $P2_{1/n}$. Key details of the crystal and structure refinement data are summarized in Table S1. Additional crystallographic details may be found in the respective CIF files which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK. The CCDC reference numbers for **5a**, **6a**, and **7a** were assigned as 1939286, 1939287, and 1939288, respectively.

Table S1. Crystal Data, Data Collection and Structure Refinement for **5a**, **6a**, and **7a**.

	5a		**6a**		**7a**	
Empirical Formula	$C_{34}H_{30}N_2O_2$		$C_{17}H_{15}NOS$		$C_{17}H_{15}NOSe$	
Formula Weight	498.60		281.36		328.26	
Temperature	223(2) K		223(2) K		223(2) K	
Wavelength	0.71075 Å		0.71073 Å		0.71073 Å	
Crystal System	Monoclinic		Orthorhombic		Monoclinic	
Space Group	*P*21/n		*P*212121		*P*21/n	
Unit Cell Dimensions	a = 10.941(2) Å	α= 90.0°	a = 8.0730(8) Å	α= 90°	a = 10.019(2) Å	α= 90°
	b = 16.435(3) Å	β=104.77(3)°	b = 11.6945(12) Å	β= 90°	b = 8.6626(17) Å	β= 101.67(3)°
	c = 15.416(4) Å	γ = 90.0°	c = 14.8493(13) Å	γ= 90°	c = 17.467(5) Å	γ= 90°
Volume	2680.3(10) $Å^3$		1401.9(2) $Å^3$		1484.7(6) $Å^3$	
Z	4		4		4	
Density (calculated)	1.236 Mg/m3		1.333 Mg/m3		1.469 Mg/m3	
Absorption coefficient	0.077 mm^{-1}		0.225 mm^{-1}		2.524 mm^{-1}	
F(000)	1056		592		664	
Crystal size	0.300 x 0.300 x 0.300 mm^3		0.300 x 0.200 x 0.200 mm^3		0.250 x 0.200 x 0.180 mm^3	
Theta range for data collections	6.002 to 50.000°		4.434 to 49.99°		4.348 to 49.988 °	
Index ranges	-13<=h<=13 -19<=k<=19 -18<=l<=18		-9<=h<9 -13<=k<=13 -17<=l<=17		-11<=h<=11 -10<=k<=10 -20<=l<=20	
Reflections collected	21657		11981		10958	
Independent reflections	4713 [R(int) = 0.0893]		2458 [R(int) = 0.0420]		2526 [R(int) = 0.0933]	
Completeness to theta = 26.00°	99.9 %		99.4 %		99.6 %	
Refinement method	Full-matrix least-squares on F^2		Full-matrix least-squares on F^2		Full-matrix least-squares on F^2	
Data/restraints/parameters	4713/ 0 / 349		2458 / 0 / 184		2526 / 0 / 184	
GooF on F^2	1.018		1.078		0.979	
Final R indices [I>2sigma(I)]	R1 = 0.0591, wR2 = 0.1173		R1 = 0.0503, wR2 = 0.1306		R1 = 0.0541, wR2 = 0.1220	
R indices (all data)	R1 = 0.1165, wR2 = 0.1403		R1 = 0.0686, wR2 = 0.1455		R1 = 0.0858, wR2 = 0.1488	
Largest diff. peak and hole	0.20 and -0.17 e.$Å^{-3}$		0.15 and -0.30 e.$Å^{-3}$		0.40 and -0.59 e.$Å^{-3}$	

References

1 R. A. Kelly, III, H. Clavier, S. Giudice, N. M. Scott, E. D. Stevens, J. Bordner, I. Samardjiev, C. D. Hoff, L. Cavallo and S. P. Nolan, *Organometallics*, 2008, **27**(2), 202-210.

2 C. Bach, H. Willner, F. Aubke, C. Wang, S. J. Rettig and J. Trotter, *Angew. Chem. Int. Ed.*, 1996, **35**(17), 1974-1976.

3 B. von Ahsen, M. Berkei, G. Henkel, H. Willner and F. Aubke, *J. Am. Chem. Soc.*, 2002, **124**(28), 8371-8379.