Supporting Information

Electrostatic Control of Regioselectivity via Ion Pairing in a Au(I)-Catalyzed Rearrangement

Vivian M. Lau, Craig F. Gorin, and Matthew W. Kanan*
*To whom correspondence should be addressed. E-mail: mkanan@stanford.edu

Experimental Methods

General methods

All reactions were carried out in oven- or flame-dried glassware, under an atmosphere of dry N_2 unless otherwise indicated. Organic reagents were purchased from Sigma-Aldrich, Acros Organics, Alfa Aesar or Matrix Scientific, and used as received. Toluene, CH_2Cl_2, THF and Et_2O were dried by passing through an activated alumina column on an Innovative Technology PureSolv solvent purification system; $CHCl_3$ (stabilized with amylenes) and $(CH_2Cl)_2$ were dried over activated 4 Å molecular sieves. All other solvents were reagent grade and used without purification. Thin layer chromatography was performed with silica gel-coated aluminum plates (Fluka, with fluorescent indicator) and visualized under UV light. Flash chromatography was performed with 230-400 mesh silica gel (Silicycle SiliaFlash P60).

IPrAuCl and $[XPhosAu(NCCH_3)]SbF_6$ were purchased from Sigma-Aldrich and used as received. IMesAuCl,[1] SIPrAuCl,[1] Ph_3PAuCl,[2] $(o\text{-tol})_3PAuCl$,[3] SPhosAuCl,[4] and XPhosAuCl[4] were synthesized as previously described, using $(tht)AuCl$[5] as the gold precursor. Cationic Au(I) complexes $[IPrAu(NCCH_3)]BF_4$,[6] $[IPrAu(NCCH_3)]SbF_4$,[6] $[IPrAu(NCPh)]B(Ar^F)_4$,[7] $[Ph_3PAu]NTf_2$,[2] and $Ph_3PAu(NCCH_3)SbF_6$[8] were synthesized according to the literature.

Routine NMR spectra were obtained on Varian spectrometers (300 MHz Inova, 400 MHz Mercury, 400 MHz Direct Drive or 500 MHz Inova). ^1H and ^{13}C spectra were referenced to residual solvent signal relative to trimethylsilane; ^{19}F spectra were referenced relative to CCl_3F; ^{31}P spectra were referenced relative to 85% H_3PO_4.

Low resolution mass spectrometry was performed on a Waters 2795 HPLC-MS using electrospray ionization with a micromass ZQ single quadrupole detector, or a HP 7890/5975 GC-MS using electron impact ionization with a single quadrupole detector.

X-ray characterization was carried out by Dr. Allen G. Oliver at the Molecular Structure Facility (University of Notre Dame). Data was collected on a Bruker APEX-II diffractometer using a Mo-Kα radiation source (λ=0.71073 Å).

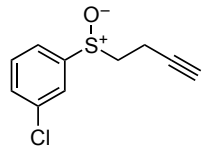
Synthesis of Aryl Alkynyl Sulfoxides

Representative procedure:

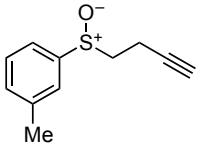
Synthesis of 1-(but-3-yn-1-ylsulfinyl)-3-chlorobenzene (1a)

To a solution of 3-chlorothiophenol (4.98 g, 4.0 mL, 34.4 mmol) in toluene (150 mL) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (5.76 g, 5.7 mL, 37.8 mmol). The mixture was stirred until it became turbid. A solution of 3-butynyl p-toluenesulfonate[9] (8.3 g, 37.0 mmol) in toluene (25 mL) was added *via* syringe. The reaction mixture was stirred at room temperature for 16 hours. The reaction was quenched with 1M HCl, and then extracted with Et_2O. The combined organic layers were washed with H_2O and brine, dried over $MgSO_4$, filtered, and evaporated to dryness to give a light yellow oil, which was used without further purification.

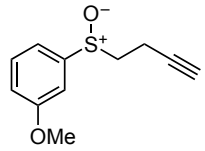
To a solution of the crude aryl alkynyl sulfide (6.4 g, 32.5 mmol) in CH_2Cl_2 (200 mL), cooled to 0 °C was added mCPBA (~70%, 7.89 g, 32 mmol) in one portion. The reaction was stirred at 0 °C for 15 minutes, then warmed to room temperature over 40 minutes. The reaction was quenched with aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic layers were combined and dried over $MgSO_4$, filtered, and evaporated to dryness to give a turbid white oil. The crude product was purified by flash chromatography on SiO_2 (4:1 hexanes/EtOAc) to give the product as a colorless clear oil that solidifies on standing (5.37 g, 25.2 mmol, 73% over 2 steps).



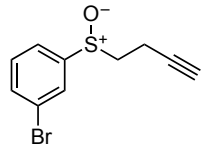
Cl-sulfoxide (1a). R_f = 0.11 (4:1 hexanes/EtOAc); **^1H NMR (400 MHz, $CDCl_3$)**: δ 7.64 (s, 1H), 7.51-7.43 (m, 3H), 3.07-2.98 (m, 1H), 2.96-2.87 (m, 1H), 2.78-2.68 (m, 1H), 2.49-2.38 (m, 1H), 2.05 (t, 1H, *J* = 2.8 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 145.3, 135.9, 131.5, 130.6, 124.2, 122.2, 80.4, 70.8, 55.3, 12.0. **LRMS (ESI-MS+)**: *m/z* (%) 235.4 (100), 213.4 [M + H^+] (90), 157.3 (100).



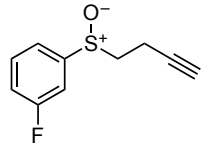
Me-sulfoxide (1b). Prepared from 3-methylthiophenol to yield the product (73%) as a colorless oil. $\mathbf{R_f}$ = 0.10 (3:1 hexanes/EtOAc); **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 7.45 (s, 1H), 7.42-7.29 (m, 3H), 3.03-2.88 (m, 1H), 2.77-2.66 (m, 1H), 2.45-2.37 (m, 4H), 2.03 (t, 1H, *J* = 2.7 Hz); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 142.9, 139.7, 132.1, 129.2, 124.3, 121.2, 80.7, 70.5, 55.2, 21.5, 12.1. **LRMS (ESI-MS+)**: *m/z* (%) 215.5 (17), 193.5 [M + H$^+$] (87), 137.4 (100).



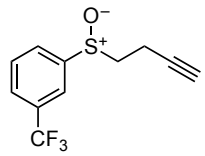
MeO-sulfoxide (1c). Prepared from 3-methoxythiophenol to yield the product (75%) as a pale yellow oil. $\mathbf{R_f}$ = 0.21 (3:2 hexanes/EtOAc); **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 7.41 (ddd, 1H, *J* = 8.2, 7.6, 0.4 Hz), 7.21 (dd, 1H, *J* = 2.6, 1.6 Hz), 7.12 (ddd, 1H, *J* = 7.6, 1.6, 0.9 Hz), 7.02 (ddd, 1H, *J* = 8.2, 2.6, 0.9 Hz), 3.86 (s, 3H), 3.04-2.89 (m, 2H), 2.77-2.68 (m, 1H), 2.46-2.37 (m, 1H). 2.04 (t, 1H, *J* = 2.6 Hz); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ160.6, 144.5, 130.4, 117.7, 116.0, 108.5, 80.7, 70.6, 55.7, 55.2, 12.1. **LRMS (ESI-MS+)**: *m/z* (%) 231.5 (55), 209.5 [M + H$^+$] (100), 153.4 (84).



Br-sulfoxide (1d). Prepared from 3-bromothiophenol to yield the product (50%) as a thick yellow oil that solidifies on standing. $\mathbf{R_f}$ = 0.16 (3:1 hexanes/EtOAc); **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 7.75 (t, 1H, *J* = 1.7 Hz), 7.60 (d, 1H, *J* = 7.8 Hz), 7.49 (d, 1H, *J* = 7.8 Hz), 7.37 (t, 1H, *J* = 7.8 Hz), 3.04-2.95 (m, 1H), 2.93-2.85 (m, 1H), 2.75-2.66 (m, 1H), 2.45-2.36 (m, 1H), 2.03 (t, 1H, *J* = 2.7 Hz); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 145.1, 133.9, 130.5, 126.6, 123.3, 122.3, 80.1, 70.7, 54.7, 11.6. **LRMS (ESI-MS+)**: *m/z* (%) 281.4 (29), 259.4 [M (^{81}Br) + H$^+$] (100), 203.4 (40).



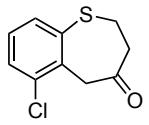
F-sulfoxide (1e). Prepared from 3-fluorothiophenol to yield the product (54%) as a pale yellow oil. $\mathbf{R_f}$ = 0.23 (3:2 hexanes/EtOAc); **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 7.54-7.49 (m, 1H), 7.42-7.37 (m, 2H), 7.21 (td, 1h, *J* = 8.3, 2.5 Hz), 3.07-2.90 (m, 2H), 2.79-2.70 (m, 1H), 2.48-2.39 (m, 1H), 2.05 (t, 1H, *J* = 2.7 Hz); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 163.2 (d, *J* = 252.4 Hz), 145.7 (d, *J* = 5.5 Hz), 131.1 (d, *J* = 7.6 Hz), 119.7 (d, *J* = 3.1 Hz), 118.4 (d, 22.1 Hz), 111.5 (d, *J* = 24.4 Hz), 80.4, 70.6, 55.2, 12.0; **^{19}F NMR (376 MHz, CDCl$_3$)**: δ −109.7-−109.8 (m). **LRMS (ESI-MS+)**: *m/z* (%) 219.5 (24), 197.5 [M + H$^+$] (78), 141.3 (100).



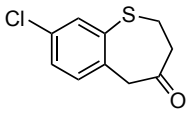
CF$_3$-sulfoxide (1f). Prepared from 3-(trifluoromethyl)thiophenol to yield the product (42%) as a colorless oil. $\mathbf{R_f}$ = 0.18 (3:1 hexanes/EtOAc); **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 7.92 (s, 1H), 7.83-7.77 (m, 2H), 7.69 (t, 1H, 7.8 Hz), 3.09-3.01 (m, 1H), 2.98-2.91 (m, 1H), 2.82-2.72 (m, 1H), 2.52-2.43 (m, 1H), 2.04 (t, 1H, 2.7 Hz); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 144.8, 132.3, 130.0, 128.1 (q), 127.4, 124.8, 121.2 (q), 80.2, 70.9, 55.4, 12.0; **^{19}F NMR (376 MHz, CDCl$_3$)**: δ −63.2. **LRMS (ESI-MS+)**: *m/z* (%) 247.5 [M + H$^+$] (100), 191.4 (75).

Synthesis of sulfoxide rearrangement products

To a solution of aryl alkynyl sulfoxide in CH_2Cl_2 (10 mM) was added Ph_3PAuCl, XPhosAuCl, or IPrAuCl (4 mol%). The mixture was stirred until fully dissolved, and $NaB(Ar^F)_4$ (4 mol%) was added. The reaction was stirred at room temperature until conversion was complete by TLC. The reaction was evaporated to dryness, dissolved in CH_2Cl_2 and eluted through a plug of Celite. The crude reaction mixture was analyzed by ^{1}H NMR to determine the product ratio, and purified by flash chromatography on SiO_2 to remove byproducts and catalyst and determine total yield. The regioisomeric products were then separated by flash chromatography on SiO_2 for characterization.



2a

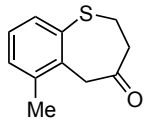


3a

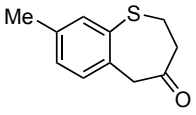
Synthesized using IPrAuCl in 75% yield, **2a**:**3a** = 0.8:1.

2a. White solid. $\mathbf{R_f}$ = 0.32 (4:1 hexanes/EtOAc); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.47 (d, 1H, *J* = 7.6 Hz), 7.37 (d, 1H, *J* = 8.1 Hz), 7.13 (t, 1H, *J* = 7.9 Hz), 4.26 (s, 2H), 3.08 (dd, 2H, *J* = 7.6, 5.5 Hz), 2.81 (dd, 2H, 7.6, 5.5 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 205.1, 137.0, 136.5, 134.7, 132.8, 130.2, 128.4, 47.2, 44.0, 31.4. **LRMS (ESI-MS+)**: *m/z* (%) 243.6 (41), 213.4 [M + H^+] (52), 152.3 (38), 150.3 (42), 106.2 (79), 102.3 (100).

3a. White solid. $\mathbf{R_f}$ = 0.27 (4:1 hexanes/EtOAc); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.53 (d, 1H, *J* = 1.6 Hz), 7.24-7.18 (m, 2H), 3.94 (s, 2H), 3.06 (dd, 2H, *J* = 7.6, 5.1 Hz), 2.85 (dd, 2H, 7.6, 5.1 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 205.6, 136.9, 136.7, 133.6, 133.1, 131.3, 128.9, 50.6, 45.0, 31.7. **LRMS (ESI-MS–)**: *m/z* (%) 275.4 (47), 257.1 (4), 213.3 [M + H^-] (4), 211.4 [M – H^+] (6), 113.2 (34), 91.2 (100).



2b

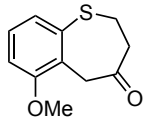


3b

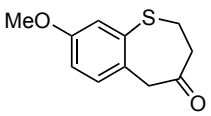
Synthesized using XPhosAuCl in 79% yield, **2b**:**3b** = 1:0.8.

2b. Pale yellow solid. $\mathbf{R_f}$ = 0.36 (1:4 hexanes/CH_2Cl_2); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.40 (d, 1H, *J* = 7.5 Hz), 7.14 (d, 1H, *J* = 7.5 Hz), 7.07 (t, 1H, *J* = 7.6 Hz), 4.11 (s, 2H), 3.06-3.03 (m, 2H), 2.84-2.80 (m, 2H), 2.43 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 206.4, 137.8, 136.9, 135.8, 131.8, 130.9, 127.2, 46.6, 45.0, 31.9, 21.2. **LRMS (ESI-MS+)**: *m/z* (%) 231.5 (66), 209.5 (97), 193.5 [M + H^+] (24), 191.5 [M – H^-] (28), 163.4 (49), 102.3 (100).

3b. White solid. $\mathbf{R_f}$ = 0.32 (1:4 hexanes/CH_2Cl_2); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.36 (s, 1H), 7.16 (d, 1H, *J* = 7.7 Hz), 7.06 (d, 1H, *J* = 7.7 Hz), 3.94 (s, 2H), 3.06-3.03 (m, 2H), 2.86-2.82 (m, 2H), 2.32 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 206.7, 137.8, 135.1, 134.7, 134.6, 130.2, 129.6, 50.8, 45.1, 31.7, 20.9. **LRMS (ESI-MS+)**: *m/z* (%) 231.5 (40), 209.5 (99), 193.5 [M + H^+] (8), 191.5 [M – H^-] (48), 163.4 (100), 102.3 (51).



2c

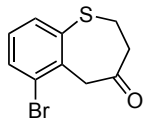


3c

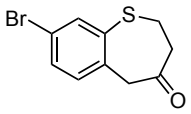
Synthesized from IPrAuCl in 80% yield, **2c**:**3c** = 1:5.

2c. White solid (could not be cleanly separated from **3b** after repeated flash chromatography). $\mathbf{R_f}$ = 0.22 (4:1 hexanes/EtOAc); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.18-7.14 (m, 2H), 6.87 (t, 1H, *J* = 4.4 Hz), 4.10 (s, 2H), 3.84 (s, 3H), 3.08-3.05 (m, 2H), 2.86-2.81 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 207.1, 157.5, 136.5, 128.1, 126.8, 126.0, 111.3, 56.1, 44.7, 42.5, 31.5. **LRMS (ESI-MS+)**: *m/z* (%) 231.4 (60), 209.4 [M + H^+] (68), 74.2 (29), 65.1 (100).

3c. Colorless oil. $\mathbf{R_f}$ = 0.22 (4:1 hexanes/EtOAc); **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.18 (d, 1H, *J* = 8.4 Hz), 7.10 (d, 1H, *J* = 2.7 Hz), 6.79 (dd, 1H, *J* = 8.4, 2.7 Hz), 3.91 (s, 2H), 3.79 (s, 3H), 3.09-3.05 (m, 2H), 2.87-2.83 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 206.8, 158.8, 136.0, 131.1, 130.1, 119.1, 114.4, 55.5, 50.2, 45.0, 31.7. **LRMS (ESI-MS+)**: *m/z* (%) 247.4 (37), 239.4 (21), 231.4 (31), 225.4 (88), 209.4 [M + H^+] (55), 195.4 (21), 65.1 (100).



2d

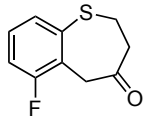


3d

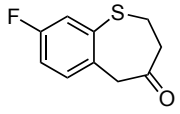
Synthesized using XPhosAuCl in 67% yield, **2d**:**3d** = 1:0.7.

2d. White oil. $\mathbf{R_f}$ = 0.30 (4:1 hexanes/EtOAc); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.55 (d, 1H, *J* = 8.1 Hz), 7.51 (d, 1H, *J* = 7.6 Hz), 7.05 (t, 1H, *J* = 7.9 Hz), 4.31 (s, 2H), 3.10-2.07 (m, 2H), 2.83-2.79 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 205.0, 138.3, 136.8, 133.62, 133.59, 128.8, 125.0, 50.2, 43.7, 31.3. **LRMS (EI-MS+)**: *m/z* (%) 257.90/255.80 [M^+] (38), 229.80/227.85 (74), 199.85/201.85 (75), 121.00 (100).

3d. White solid. $\mathbf{R_f}$ = 0.24 (4:1 hexanes/EtOAc); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.70 (d, 1H, *J* = 2.1 Hz), 7.38 (dd, 1H, *J* = 8.1, 2.1 Hz), 7.15 (d, 1H, *J* = 8.1 Hz), 3.93 (s, 2H), 3.01-3.06 (m, 2H), 2.88-2.84 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 205.4, 137.2 (overlapping), 136.4, 131.9, 131.6, 121.0, 50.7, 45.0, 31.7. **LRMS (ESI-MS–)**: *m/z* (%) 321.4/319.4 (20), 303.3/301.1 (5), 287.4/289.4 (8), 273.4/271.4 (5), 255.4/257.2 [M – H^+] (8), 237.3/235.3 (24), 113.2 (43), 91.1 (100), 81.0/79.0 (30).



2e

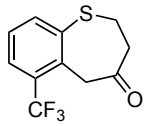


3e

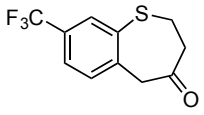
Synthesized using Ph_3PAuCl in 55% yield, **2e**:**3e** = 1:0.8.

2e. White oil. $\mathbf{R_f}$ = 0.29 (4:1 hexanes/EtOAc); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.34 (d, 1H, *J* = 7.7 Hz), 7.17 (dt, 1H, *J* = 7.7, 5.6 Hz), 7.04 (dt, 1H, *J* = 8.6, 1.2 Hz), 4.02 (s, 2H), 3.10-3.06 (m, 2H), 2.88-2.85 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 205.4, 160.5 (d), 137.3 (d), 129.5 (d), 128.6 (d), 125.5 (d), 116.1 (d), 44.7, 41.9 (d), 31.5; **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –114.43 (q, *J* = 5.6 Hz). **LRMS (ESI-MS+)**: *m/z* (%) 219.3 (26), 213.3 (21), 197.3 [M + H^+] (21), 102.3 (16), 65.1 (100).

3e. White solid. $\mathbf{R_f}$ = 0.24 (4:1 hexanes/EtOAc); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.29-7.22 (m, 2H), 6.96 (dt, 1H, *J* = 8.3, 2.7 Hz), 3.95 (s, 2H), 3.10-3.07 (m, 2H), 2.88-2.85 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 205.9, 161.4 (d), 136.9 (d), 134.0 (d), 131.5 (d), 120.8 (d), 115.7 (d), 50.4, 45.0, 31.7; **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –114.97 (q, *J* = 8.6 Hz). **LRMS (ESI-MS–)**: *m/z* (%) 259.4 (100), 249.4 (68), 229.3 (71), 227.4 (35), 211.4 (22), 209.3 (32), 195.4 [M – H^+] (53), 175.3 (76), 159.3 (34), 113.1 (62), 91.0 (86).



2f



3f

Synthesized using Ph_3PAuCl in 64% yield, **2f**:**3f** = 0.9:1.

2f. Yellow oil, solidifies on standing. $\mathbf{R_f}$ = 0.39 (4:1 hexanes/EtOAc); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.78 (d, 1H, *J* = 7.7 Hz), 7.66 (d, 1H, *J* = 7.7 Hz), 7.33 (t, 1H, 7.8 Hz), 4.20 (s, 2H), 3.10 (dd, 2H, 7.6, 5.6 Hz), 2.76 (dd, 2H, 7.6, 5.6 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 204.0, 138.2 (overlapping), 137.7 (d), 137.4, 127.8, 126.8 (q), 122.5, 46.5 (q), 43.0, 30.5.**^{19}F NMR (376 MHz, $CDCl_3$)**: δ −59.2. **LRMS (ESI-MS+)**: *m/z* (%) 269.4 [M + Na^+] (38), 263.4 (18), 247.4 [M + H^+] (5), 102.2 (30), 65.2 (100).

3f. White solid. $\mathbf{R_f}$ = 0.27 (4:1 hexanes/EtOAc); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.80 (s, 1H), 7.51 (d, 1H, *J* = 8.0 Hz), 7.40 (d, 1H, *J* = 8.0 Hz), 4.05 (s, 2H), 3.12-2.09 (m, 2H), 2.91-2.88 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ

204.9, 142.2 (d), 136.4, 130.75 (q), 130.68, 130.3 (d), 125.7 (q), 122.2, 51.2, 45.2, 31.7. **^{19}F NMR (376 MHz, $CDCl_3$)**: δ −63.1. **LRMS (ESI-MS–)**: *m/z* (%) 309.4 (92), 261.4 (21), 245.4 [M – H^+] (100), 225.3 (43).

Gold(I) complexes

$Ph_3PAu(NCCH_3)PF_6$

Ph_3PAuCl (50 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (4.5 mL) in a reaction flask covered in foil. The solution was cooled to 0 °C in an ice bath, and CH_3CN (10 μL, 0.19 mmol) and $AgPF_6$ (26 mg, 0.1 mmol) were added. The reaction was stirred at 0 °C for 1 hour, filtered through a Celite plug and a 0.2 μm PTFE syringe filter, while keeping the solution at < 0 °C. The solution was evaporated to ~0.5 mL volume, layered with hexanes at –20 °C and triturated gently to afford a pale pink precipitate. The supernatant was removed, and the solid washed with hexanes and dried *in vacuo* to yield the product (49.1 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.57 (m, 3H), 7.53-7.44 (m, 12 H), 2.51 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 134.2 (d), 133.0 (d), 129.9 (d), 2.8. (one signal was not observed).**^{19}F NMR (376 MHz, $CDCl_3$)**: δ –73.4 (d, *J* = 712.5 Hz); **^{31}P NMR (162 MHz, $CDCl_3$)**: δ 30.9 (br), –134.2 (quint). **LRMS (ESI-MS+)**: *m/z* (%) 459.3 [Ph_3PAu^+] (100), 500.2 [$Ph_3PAuNCCH_3^+$] (79). **LRMS (ESI-MS–)**: *m/z* (%) 145.1 [PF_6^-] (100).

[(*o*-tol)$_3$PAu(NCCH$_3$)]SbF$_6$

(*o*-tol)$_3$PAuCl (54 mg, 0.1 mmol) was dissolved in CH_3CN/CH_2Cl_2 (1:6 v/v, 5 mL). $AgSbF_6$ (34 mg, 0.1 mmol) was added quickly in one portion, resulting in immediate precipitation of AgCl. The reaction mixture was stirred for 15 minutes, and filtered through a Celite plug and a 0.2 μm PTFE syringe filter. The filtrate was evaporated to ~2 mL volume, then layered with hexanes and triturated at −78 °C to afford a white precipitate. The supernatant was decanted, and the solid washed with hexanes and dried *in vacuo* to yield the product as a fine white powder (74.7 mg, 96%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (t, 3H, *J* = 7.6 Hz), 7.41 (t, 3H, *J* = 5.6 Hz), 7.29-7.24 (t, 3H, *J* = 7.6 Hz), 6.92 (dd, 3H, *J* = 14.1, 7.6 Hz), 2.62 (br, 9H), 2.46 (br, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: 142.7 (d), 133.7 (d), 133.0 (d), 133.9 (d), 127.4 (d), 122.7 (d), 23.2 (d), 2.8; **^{31}P NMR (162 MHz, $CDCl_3$)**: δ 1.2 (br). **LRMS (ESI-MS+)**: *m/z* (%) 501.2 [(*o*-tol)$_3$PAu$^+$] (100), 542.2 [(*o*-tol)$_3$PAuNCCH$_3^+$] (50). **LRMS (ESI-MS–)**: *m/z* (%) 235.1, 237.1 [SbF_6^-] (100, 90).

[(*o*-tol)$_3$PAu(NCCH$_3$)]PF$_6$

(*o*-tol)$_3$PAuCl (107 mg, 0.2 mmol), $AgPF_6$ (51 mg, 0.2 mmol) and CH_3CN (20 μL, 0.38 mmol) were cooled to 0 °C in an ice bath and dissolved in CH_2Cl_2. The reaction mixture was stirred for 15 minutes, then filtered through a Celite plug and a 0.2 μm PTFE syringe filter. The filtrate was evaporated to dryness, yielding a white solid foam, cooled to −78 °C and triturated with Et_2O. The supernatant was decanted, and the solid was washed with Et_2O and dried *in vacuo* to yield the product as a white powder (113.0 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (t, 3H, *J* = 7.6 Hz), 7.42 (t, 3H, *J* = 6.1 Hz), 7.28-7.24 (m, 3H), 6.92 (dd, 3H, *J* = 14.3, 8.2 Hz), 2.65 (br, 9H), 2.52 (br, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: 142.7 (d), 133.7 (d), 132.9 (d, overlapping), 127.3 (d), 23.3 (d), 2.9 (one signal was not observed); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –73.6; **^{31}P NMR (162 MHz, $CDCl_3$)**: δ 0.95, −143.3 (quint., *J* = 711.7 Hz). **LRMS (ESI-MS+)**: *m/z* (%) 501.3 [(*o*-tol)$_3$PAu$^+$] (100), 542.3 [(*o*-tol)$_3$PAuNCCH$_3^+$] (78). **LRMS (ESI-MS–)**: *m/z* (%) 145.1 [PF_6^-] (100).

[XPhosAu(NCCH$_3$)]PF$_6$

XPhosAuCl (127.6 mg, 0.18 mmol) was dissolved in CH_2Cl_2 (10 mL) and cooled to 0 °C in an ice bath. $AgPF_6$ (45.5 mg, 0.18 mmol) was added in one portion, followed by CH_3CN (100 μL, 1.9 mmol). The reaction mixture was stirred for 30 minutes, and then filtered through a Celite plug and a 0.2 μm PTFE syringe filter. The filtrate was evaporated to dryness to give a white foam. The foam was gently triturated with Et_2O, and the supernatant was decanted. The solid was then washed with Et_2O and dried *in vacuo* to yield the product as a white powder (85.7 mg, 55%). Crystals suitable for x-ray analysis were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.61 (m, 1H), 7.60-7.55 (m, 2H), 7.28-7.24 (m, 1H), 7.14 (s, 2H), 2.96 (sept., 1H, *J* = 6.6 Hz), 2.41 (s, 3H), 2.25-2.03 (m, 6H), 1.95-1.66 (m, 8H), 1.50-1.19 (m, 22H), 0.95 (d, 6H, *J* = 6.6 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 149.9, 146.8 (overlapping), 133.7 (d), 132.0 (d), 131.5, 128.1 (d), 121.7, 36.9 (d), 34.1, 31.1 (d), 30.2, 27.0 (d), 26.6 (d), 25.6 (d), 23.3, 2.6 (2 signals were not observed); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –73.6 (d, *J* = 712.1 Hz); **^{31}P NMR (162 MHz, $CDCl_3$)**: δ 33.3, −143.3 (quint., *J* = 712.8 Hz). **LRMS (ESI-MS+)**: *m/z* (%) 673.6 [$XPhosAu^+$] (100), 714.5 [$XPhosAuNCCH_3^+$] (48). **LRMS (ESI-MS–)**: *m/z* (%) 145.0 [PF_6^-] (100).

[XPhosAu(NCCH$_3$)]BF$_4$
Synthesized analogous to [XPhosAu(NCCH$_3$)]PF$_6$, using AgBF$_4$. The product was isolated as a pale yellow powder in 54% yield.
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.66-7.51 (m, 3H), 7.28-7.21 (m, 1H), 7.14 (s, 2H), 2.96 (sept., 1H, *J* = 6.4 Hz), 2.48 (s, 3H), 2.23-2.02 (m, 6H), 1.94-1.65 (m, 8H), 1.49-1.08 (m, 22H), 0.95 (d, 6H, *J* = 6.4 Hz); **^{13}C NMR (125 MHz, CDCl$_3$)**: 149.9, 146.8 (overlapping), 135.6 (d), 144.7 (m), 133.7 (d), 132.1 (d), 131.5, 128.0 (d), 36.8 (d), 34.1, 31.1 (d), 30.2, 27.0 (d), 26.6 (d), 25.6 (d), 24.2, 23.3, 2.8; **^{19}F NMR (376 MHz, CDCl$_3$)**: δ –153.7, –153.8; **^{31}P NMR (162 MHz, CDCl$_3$)**: δ 33.2. **LRMS (ESI-MS+)**: *m/z* (%) 673.5 [XPhosAu$^+$] (100), 714.5 [XPhosAuNCCH$_3^+$] (65). **LRMS (ESI-MS–)**: *m/z* (%) 85.7, 86.8 [BF$_4^-$] (13, 100).

[IMesAu(NCCH$_3$)]SbF$_6$
IMesAuCl (54 mg, 0.1 mmol) was dissolved in CH$_3$CN/CH$_2$Cl$_2$ (1:6 v/v, 5 mL) at –20 °C. AgSbF$_6$ (34 mg, 0.1 mmol) was added, and the mixture stirred at –20 °C for 20 minutes. The reaction mixture was filtered through a Celite plug and a 0.2 μm PTFE syringe filter, then evaporated to ~1 mL volume. The solution was layered with hexanes and left at –20 °C to recrystallize over 2 days. A pale pink microcrystalline solid precipitated, which was collected by decanting the supernatant. The solid was washed with hexanes, and dried *in vacuo* to give the product as a pale pink powder (49.0 mg, 63%).
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.23 (s, 2H), 7.08 (s, 4H), 2.39 (s, 6H), 2.32 (s, 3H), 2.10 (s, 12H); **^{13}C NMR (125 MHz, CDCl$_3$)**: δ 140.7, 134.6, 133.8, 129.9, 123.6, 21.3, 17.7, 2.7 (carbene *C* was not observed). **LRMS (ESI-MS+)**: *m/z* (%) 501.3 [IMesAu$^+$] (99), 542.4 [IMesAuNCCH$_3^+$] (100). **LRMS (ESI-MS–)**: *m/z* (%) 235.1, 237.1 [SbF$_6^-$] (100, 86).

[SIPrAu(NCCH$_3$)]SbF$_6$
SIPrAuCl (62.2 mg, 0.1 mmol) and acetonitrile (10 μL, 0.19 mmol) were dissolved in CH$_2$Cl$_2$ (5 mL) at –78 °C. AgSbF$_6$ (34.3 mg, 0.1 mmol) was added in one portion, and the reaction mixture was allowed to warm to room temperature while stirring for 45 minutes. The reaction mixture was filtered through a Celite plug and evaporated to dryness, giving a white foam. The solid foam was cooled to –78 °C, layered with hexanes and triturated until a fine white powder formed. The supernatant was decanted, and the solid was washed with hexanes and dried *in vacuo* to give the product (66.4 mg, 77%).
^{1}H NMR (500 MHz, CDCl$_3$): δ 7.49 (t, 2H, *J* = 8.0 Hz), 7.29 (d, 4H, 8.0 Hz), 4.21 (s, 4H), 3.00 (sept., 4H, *J* = 7.0 Hz), 2.30 (s, 3H), 1.37 (d, 24H, *J* = 7 Hz); **^{13}C NMR (125 MHz, CDCl$_3$)**: δ 146.6, 133.0, 130.8, 125.0, 54.0, 29.1, 25.4, 24.1, 2.8 (carbene *C* was not observed). **LRMS (ESI-MS+)**: *m/z* (%) 587.4 [SIPrAu$^+$] (89), 628.5 [SIPrAuNCCH$_3^+$] (100). **LRMS (ESI-MS–)**: *m/z* (%) 235.1, 237.1 [SbF$_6^-$] (100, 73).

[IPrAu(NCPh)]SbF$_6$
IPrAuCl (62.0 mg, 0.1 mmol) was dissolved in CH$_2$Cl$_2$ (5 mL) and benzonitrile (12 μL, 12 mg, 0.12 mmol). AgSbF$_6$ (34.3 mg, 0.1 mmol) was added, and the mixture was stirred at room temperature for 30 minutes. The mixture was filtered through a short plug of Celite and a 0.2 μm PTFE syringe filter, and evaporated to dryness. Et$_2$O was added, and the residue triturated until a fine white precipitate formed. The supernatant was decanted, and the remaining solid was washed with pentane and dried *in vacuo* to yield 38 mg of white powder as the product (41%).
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.82-7.77 (m, 3H), 7.62-7.56 (m, 4H), 7.44 (s, 2H), 7.37 (d, 4H, *J* = 7.8 Hz), 2.50 (sept., 4H, *J* = 7.0 Hz), 1.33 (d, 12H, *J* = 7.0 Hz), 1.27 (d, 12H, *J* = 7.0 Hz); **^{13}C NMR (125 MHz, CDCl$_3$)**: δ 145.7, 136.6, 133.8, 133.2, 131.5, 130.0, 125.2, 124.7, 29.0, 24.9, 24.1 (carbene *C* was not observed). **LRMS (ESI-MS+)**: *m/z* (%) 585.7 [IPrAu$^+$] (100), 617.7 [IPrAu$^+$ + CH$_3$OH] (67), 658.7 [IPrAuNCCH$_3^+$ + CH$_3$OH] (60), 689.7 [IPrAuNCPh$^+$] (6). **LRMS (ESI-MS–)**: *m/z* (%) 235.1, 237.1 [SbF$_6^-$] (100, 80).

Catalytic experiments

Method A (Using LAuCl pre-catalysts with halide abstractor):

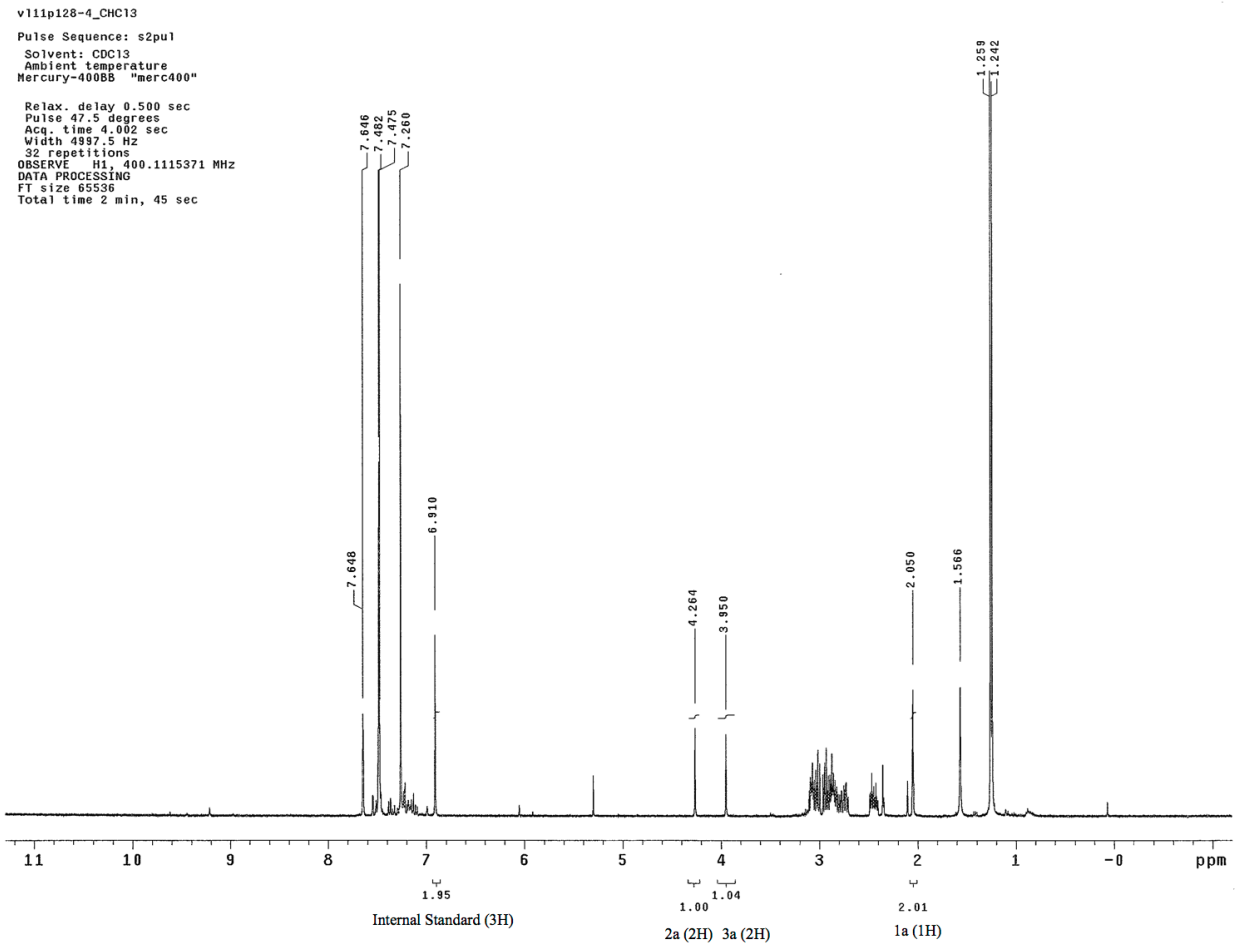
A scintillation vial was charged with a magnetic stir bar and 4.4 mL of CH_2Cl_2. Pre-catalyst (50 µL of a 10 mM stock solution in CH_2Cl_2, 0.5 µmol, 2 mol%) was added, followed by substrate **1a** (50 µL of a 0.5 M stock solution in CH_2Cl_2, 25 µmol). $NaB(Ar^F)_4$ (500 µL of a 2.5 mM stock solution in CH_2Cl_2, 0.5 µmol, 2 mol%) was added, and the reaction stirred at ambient temperature for 17 hours. The reaction was quenched by the addition of CH_3CN (1 mL), and then evaporated to dryness. The product was dissolved in $CDCl_3$ and analyzed by ^1H NMR with 1,3,5-Triisopropylbenzene (100 µL of a 25 mM solution in $CDCl_3$, 2.5 µmol) added as an internal standard. Reported product ratios and NMR yields are averages of duplicate reactions.

Method B (Using cationic Au(I) catalysts):

A septum-sealed, oven-dried 25 mL round-bottom flask was charged with a magnetic stir bar and 5 mL of solvent. The flask was charged with catalyst (25 µL of a 10 mM stock solution in $CHCl_3$, 0.25 µmol, 2 mol%), followed by substrate **1a-e** (25 µL of a 0.5 M stock solution in $CHCl_3$, 12.5 µmol). The reaction was stirred at ambient temperature for 4 hours, quenched by the addition of CH_3CN (1 mL), and evaporated to dryness. The product was dissolved in $CDCl_3$ and analyzed by ^1H NMR with 1,3,5-Triisopropylbenzene (100 µL of a 25 mM solution in $CDCl_3$, 2.5 µmol) added as an internal standard. Reported product ratios and NMR yields are averages of duplicate reactions.

Example crude ^1H NMR for product ratio and yield calculations:

Method B, rearrangement of **1a** catalyzed by $[IMesAu(NCMe)]SbF_6$ in $CHCl_3$



Diffusion NMR experiments

Diffusion measurements were obtained on a 600 MHz Varian Inova spectrometer equipped with a 5 mm $^{1}H\{^{13}C,^{15}N\}$ triple resonance Z-PFG probe. A standard pulsed gradient stimulated echo (PGSTE) pulse sequence was used with rectangular gradient pulses (δ = 1.5 ms), and temperature regulation (25 °C) without spinning. The pulse and delay times (δ, Δ) were kept constant during the experiment, and the gradient strength (G) was varied such that at least 90% attenuation of signal was achieved. The gradient strength was increased in 12 – 18 steps, with 32 scans per increment, and relaxation delays set to at least 5 × T_1. The gradient strength was calibrated by measuring the diffusion of HDO in D_2O. All samples were prepared as 5 mM solutions in 700 μL of deuterated solvent, in 5 mm diameter tubes.

Diffusion coefficients were obtained by applying the Stejskal-Tanner equation:

$$\ln\left(\frac{I}{I_0}\right) = -(\gamma\delta G)^2\left(\Delta - \frac{\delta}{3}\right)D$$

I and I_0 are the signal intensity and initial signal intensity, respectively, γ is the gyromagnetic ratio of the observed nucleus (^{1}H, 2.6753×10^{4} rad · $s^{-1}G^{-1}$), δ is the length of the gradient pulse, Δ is the time between the midpoint of the gradient pulses, G is the gradient strength, and D is the diffusion coefficient. All experiments yielded semi-log plots where standard linear regression gave *R* factors of 0.998 or better.

Hydrodynamic radii (r_H) were calculated from the diffusion coefficients using the Stokes-Einstein relationship:

$$D = \frac{kT}{c\pi\eta r_H}$$

The solvent viscosity (η) was taken as 0.41 cP and 0.54 cP for CD_2Cl_2 and $CDCl_3$, respectively. The numerical factor *c* was estimated semi-empirically using the method of Chen and Chen[10]:

$$c = \frac{6}{1 + 0.695\left(\frac{r_{solv}}{r_H}\right)^{2.234}}$$

Solvent radii (r_{solv}) were 2.49 Å and 2.60 Å for CD_2Cl_2 and $CDCl_3$, respectively.[11] Convergent values of *c* were reached within three iterations. Performing diffusion experiments with longer Δ indicated that convection effects[12] become detrimental at 231 ms for $CDCl_3$ and 181 ms for CD_2Cl_2. Reported diffusion coefficients and hydrodynamic radii are the averages of values obtained with $\Delta \leq 181$ ms in $CDCl_3$, and $\Delta \leq 151$ ms in CD_2Cl_2.

Figure S1. Stejskal-Tanner plots for the diffusion of [IPrAu(NCPh)]B(Ar^F)$_4$, [IPrAu(NCPh)]SbF$_6$ and [IPrAu(NCMe)]SbF$_6$

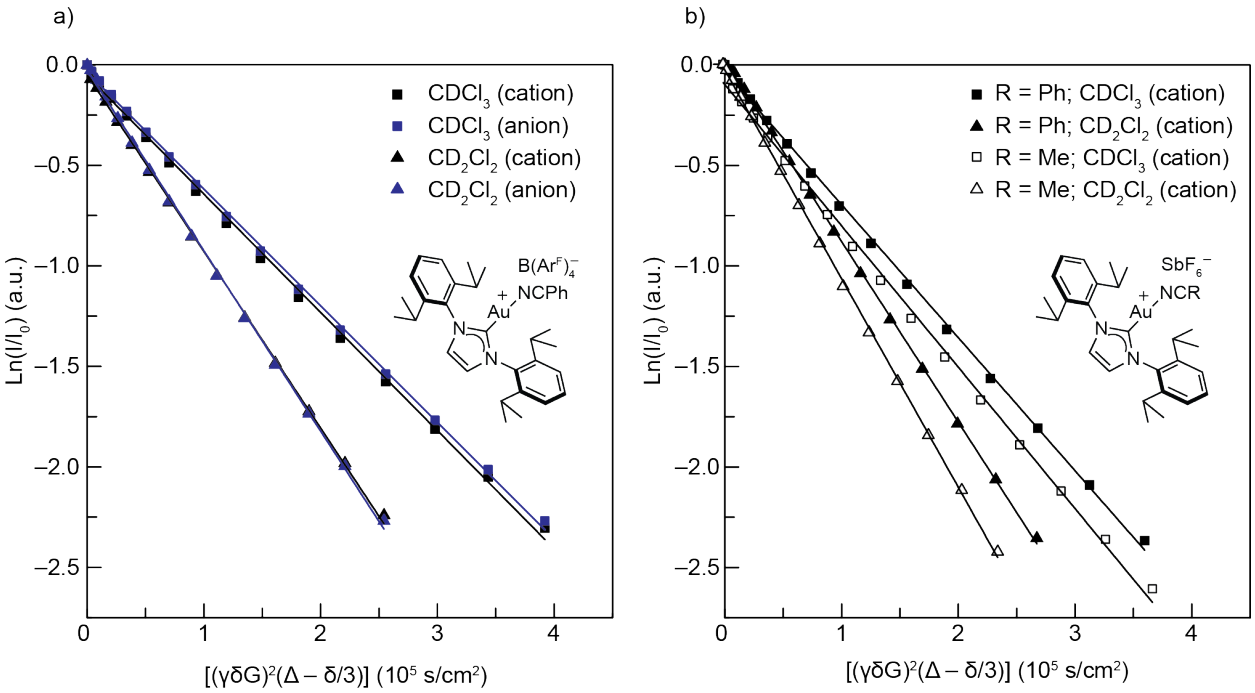
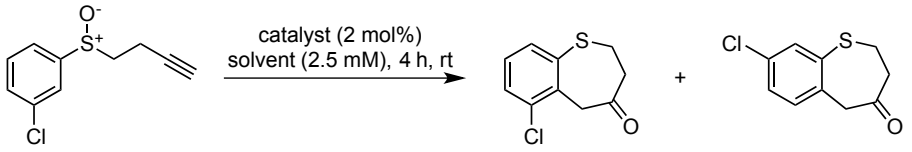


Table S1. Diffusion coefficients and hydrodynamic radii extracted from NMR experiments

Compound	Solvent	Δ (ms)	D (10^{-10} m^2 s^{-1})		r_H (Å)
[IPrAu(NCMe)]SbF_6	$CDCl_3$	131	Cation	7.03	6.31
		181	Cation	7.03	6.31
		231	Cation	7.32	6.10
	CD_2Cl_2	111	Cation	10.0	5.87
		131	Cation	10.5	5.65
		131	Cation	10.4	5.70
		181	Cation	12.9	4.83
[IPrAu(NCPh)]SbF_6	$CDCl_3$	111	Cation	6.62	6.64
		131	Cation	6.60	6.66
		181	Cation	6.73	6.55
	CD_2Cl_2	111	Cation	8.98	6.43
		131	Cation	9.32	6.23
		151	Cation	8.86	6.51
[IPrAu(NCPh)]$B(Ar^F)_4$	$CDCl_3$	131	Cation	6.19	7.03
			Anion	6.02	7.20
		181	Cation	5.88	7.35
			Anion	5.80	7.43
		231	Cation	6.73	6.54
			Anion	6.50	6.74
	CD_2Cl_2	111	Cation	8.81	6.54
			Anion	8.64	6.64
		131	Cation	8.78	6.55
			Anion	8.98	6.43
		151	Cation	8.56	6.70
			Anion	8.57	6.69
$[(nBu)_4N]B(Ar^F)_4$	CD_2Cl_2	131	Cation	10.9	5.48
			Anion	9.06	6.38

Table S2. Effect of counterion and ligand on regioselectivity of rearrangement of **1a** to **2a** and **3a**.[a]



1a **2a** **3a**

Catalyst	Solvent (ε)	2a : 3a	yield (%)
$[Ph_3PAu(NCMe)]PF_6$	Toluene (2.4)	1 : 1.4	17
	$CHCl_3$ (4.8)	1 : 1.1	17
	CH_2Cl_2 (8.9)	1 : 0.8	20
	$(CH_2Cl)_2$ (10.4)	1 : 0.8	21
$[Ph_3PAu]NTf_2$	Toluene	1 : 1.6	34
	$CHCl_3$	1 : 1.0	24
	CH_2Cl_2	1 : 0.7	20
	$(CH_2Cl)_2$	1 : 0.7	26
$[Ph_3PAu(NCMe)]SbF_6$	Toluene[b]	1 : 2.3	71
	$CHCl_3$	1 : 1.2	38
	CH_2Cl_2[b]	1 : 0.7	45
	$(CH_2Cl)_2$	1 : 0.8	24
$[(o\text{-}tol)_3PAu(NCMe)]PF_6$	Toluene	1 : 1.7	17
	$CHCl_3$	1 : 1.3	18
	CH_2Cl_2	1 : 0.9	19
	$(CH_2Cl)_2$	1 : 0.8	18
$[XPhosAu(NCMe)]PF_6$	Toluene	1 : 2.1	21
	Et_2O (4.3)	1 : 1.8	12
	$CHCl_3$	1 : 1.5	20
	EtOAc (6.0)	1 : 1.5	10
	CH_2Cl_2	1 : 0.9	20
	$(CH_2Cl)_2$	1 : 0.9	23
	Acetone (20.7)	1 : 0.7	10
$[XPhosAu(NCMe)]BF_4$	Toluene	1 : 2.4	17
	$CHCl_3$	1 : 1.5	13
	CH_2Cl_2	1 : 0.9	12
	$(CH_2Cl)_2$	1 : 0.8	13
$[IMesAu(NCMe)]SbF_6$	Toluene	1 : 2.0	57
	$CHCl_3$	1 : 1.0	32
	CH_2Cl_2	1 : 0.6	33
	$(CH_2Cl)_2$	1 : 0.6	38
$[IPrAu(NCMe)]BF_4$	Toluene	1 : 1.6	28
	$CHCl_3$	1 : 1.3	28
	CH_2Cl_2	1 : 1.1	25
	$(CH_2Cl)_2$	1 : 1.2	24
(tht)AuCl	Toluene	1 : 1.0	11
	CH_2Cl_2	1 : 0.8	13

[a] Method B used. [b] 4 mol% catalyst used.

Table S3. Accompaniment to Figure 1a.[a]

Catalyst	Solvent (ε)	2a : 3a	yield (%)
[IPrAu(NCPh)]B(Ar^F)$_4$	Toluene (2.4)	1 : 1.1	59
	Et_2O (4.3)	1 : 0.8	28
	$CHCl_3$ (4.8)	1 : 1.1	39
	EtOAc (6.0)	1 : 1.1	30
	CH_2Cl_2 (8.9)	1 : 1.1	44
	$(CH_2Cl)_2$ (10.4)	1 : 1.2	46
	Acetone (20.7)	1 : 0.8	25
[IPrAu(NCMe)]SbF_6	Toluene	1 : 2.6	88
	Et_2O	1 : 2.2	34
	$CHCl_3$	1 : 1.7	58
	EtOAc	1 : 1.5	30
	CH_2Cl_2	1 : 1.2	50
	$(CH_2Cl)_2$	1 : 1.3	48
	Acetone	1 : 1.1	35
[SIPrAu(NCMe)]SbF_6	Toluene	1 : 4.5	82
	$CHCl_3$	1 : 2.7	64
	CH_2Cl_2	1 : 1.9	48
	$(CH_2Cl)_2$	1 : 1.8	48

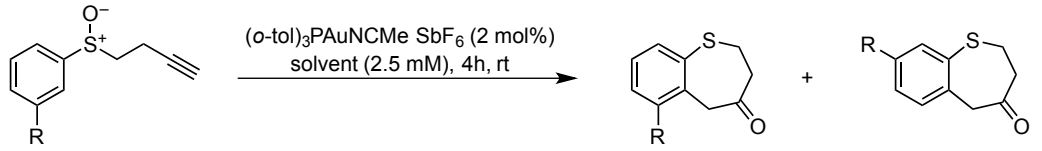
[a] Method B used.

Table S4. Accompaniment to Figure 1b.[a]

Catalyst	Solvent (ε)	2a : 3a	yield (%)
[XPhosAu(NCMe)]SbF_6	Benzene (2.3)	1 : 3.4	38
	Toluene (2.4)	1 : 3.3	43
	Et_2O (4.3)	1 : 2.7	31
	$CHCl_3$ (4.8)	1 : 1.8	23
	EtOAc (6.0)	1 : 1.6	25
	Toluene/CH_2Cl_2 1:1 v/v (6.4)	1 : 1.6	29
	THF (7.6)	1 : 1.1	21
	CH_2Cl_2 (8.9)	1 : 0.8	17
	$(CH_2Cl)_2$ (10.4)	1 : 0.8	18
	o-Difluorobenzene (13.8)	1 : 0.9	22
	Acetone (20.7)	1 : 0.9	20
	Nitromethane (35.9)	1 : 0.9	12
[(o-tol)$_3$PAu(NCMe)]SbF_6	Toluene	1 : 3.0	22
	$CHCl_3$	1 : 1.4	20
	CH_2Cl_2	1 : 0.6	32
	$(CH_2Cl)_2$	1 : 0.6	22

[a] Method B used.

Table S5. Accompaniment to Figure 2.[a]

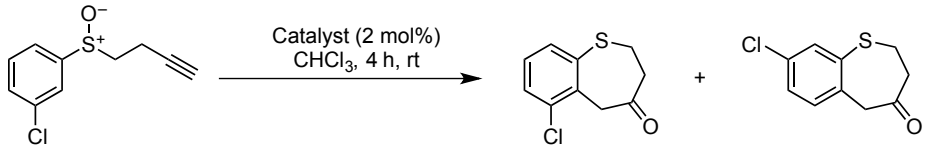


1a - f **2a - f** **3a - f**

Catalyst	Solvent (ε)	2x : 3x	yield (%)
1b (Me)	CH_2Cl_2 (8.9)	1 : 0.8	49
	$CHCl_3$ (4.8)	1 : 0.8	56
	Toluene (2.4)	1 : 0.7	55
1c (MeO)	CH_2Cl_2	1 : 2.0	38
	$CHCl_3$	1 : 2.5	40
	Toluene	1 : 2.6	31
1d (Br)	CH_2Cl_2	1 : 0.7	26
	$CHCl_3$	1 : 1.1	32
	Toluene	1 : 1.9	40
1a (Cl)	CH_2Cl_2	1 : 0.6	32
	$CHCl_3$	1 : 1.4	20
	Toluene	1 : 3.0	22
1e (F)	CH_2Cl_2	1 : 1.4	45
	$CHCl_3$	1 : 2.6	45
	Toluene	1 : 4.3	37
1f (CF_3)	CH_2Cl_2	1 : 1.1	31
	$CHCl_3$	1 : 3.2	42
	Toluene	1 : 6.9	47

[a] Method B used

Table S6. Variation of reaction concentration.[a]

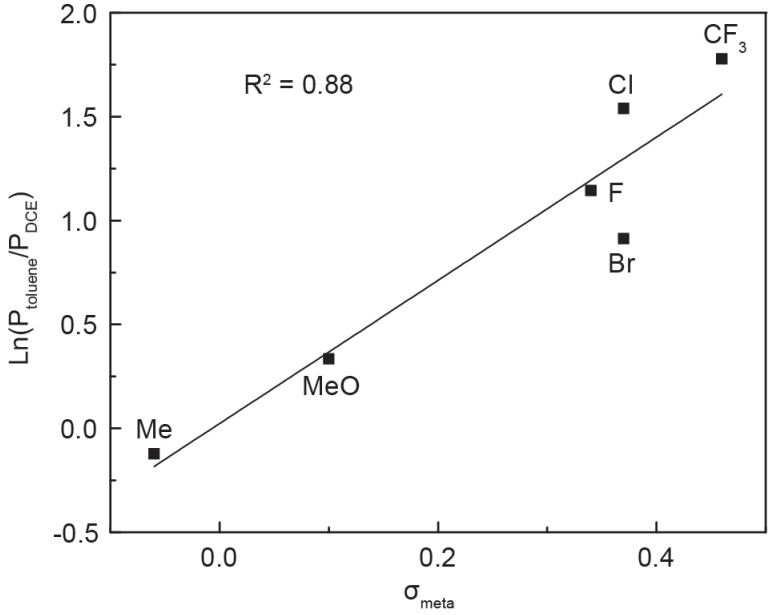


1a **2a** **3a**

Catalyst	[1a] (mM)	[catalyst] (mM)	2a : 3a	yield (%)
[XPhosAu(NCMe)]SbF_6	2.5	0.05	1 : 1.8	23
	5.0	0.1	1 : 1.8	21
	15	0.3	1 : 1.9	21
	25	0.5	1 : 1.9	24
	250	5.0	1 : 1.5	21
[IPrAu(NCPh)]$B(Ar^F)_4$	2.5	0.05	1 : 1.1	39
	25	0.5	1 : 1.0	22
	125	2.5	1 : 1.0	20
	250	5.0	1 : 1.1	19

[a] Method B used, the volume of solvent was varied.

Figure S2. Correlation of solvent-dependent change in selectivity with Hammett parameter σ_{meta} of the substrate substituent. $P_{toluene}$ and P_{DCE} are the product ratios (**3x**/**2x**) in toluene and 1,2-dichloroethane, respectively.



DFT studies of transition state charge distribution

Density functional theory (DFT) studies were performed with the GAUSSIAN09 program at the PBE1PBE/6-31+G**/SDD level. SDD was used only for Au Atoms. The structures were optimized to a transition state, with the starting coordinates modeled off the literature values.[13] Frequency calculations were run to ensure a single negative frequency was obtained. Dipole moments were calculated from the center of nuclear mass.

Coordinates and Dipole moments of transition state structures:

2a (TS):

SCF Done: E(RPBE1PBE) = -1915.55206754 A.U.
Charge= 1.0000 electrons
Dipole moment (field-independent basis, Debye):
X= -0.0136 Y= 0.1213 Z= 2.6359 Tot= 2.6422

Atom	X	Y	Z
C	2.810585	-2.059890	1.624312
C	0.543629	-0.849754	-0.927797
C	4.447787	0.886899	-0.743703
C	3.580060	0.167611	0.104878
H	5.336663	0.409758	-1.145542
C	1.377638	-2.297730	1.053043
C	1.402576	-1.796932	-0.357686
S	3.962555	-1.503010	0.343243
O	2.428491	-2.206148	-1.011845
C	2.415108	0.771024	0.615358
C	2.155549	2.107633	0.287266
C	3.007014	2.822431	-0.538353
C	4.155615	2.200910	-1.050702
H	1.777838	0.280483	1.340139
H	2.790287	3.859349	-0.772804
H	0.613674	-1.804439	1.658295
H	1.186928	-3.374834	1.060437
H	2.825492	-1.325333	2.433354
H	3.258345	-2.981069	2.002997
Au	-1.335778	-0.372476	-0.372982
H	0.936211	-0.487545	-1.882623
P	-3.545869	0.196512	0.184454
C	-3.981365	-0.078150	1.936016
H	-5.025416	0.194030	2.120051
H	-3.837413	-1.130925	2.192517
H	-3.336455	0.526423	2.579072
C	-3.958207	1.946396	-0.130772
H	-3.802373	2.177951	-1.187605
H	-5.001954	2.147777	0.129914
H	-3.308614	2.594733	0.462858
C	-4.789697	-0.751493	-0.757337
H	-4.668075	-1.820250	-0.563060
H	-5.800951	-0.447040	-0.469790
H	-4.654408	-0.579010	-1.828212
Cl	0.751470	2.868039	0.951703
H	4.823181	2.764801	-1.694471

3a (TS):

SCF Done: E(RPBE1PBE) = -1915.55023171 A.U.
Charge= 1.0000 electrons
Dipole moment (field-independent basis, Debye):
X= 3.9104 Y= 1.0154 Z= 4.3572 Tot= 5.9444

Atom	X	Y	Z
C	-1.974267	2.939042	1.148832
C	-0.172174	0.575747	-0.912497
C	-4.282115	-0.250342	-0.048798
C	-3.231145	0.520243	0.488709
H	-5.113462	0.223989	-0.561283
C	-0.581705	2.724212	0.476733
C	-0.814724	1.795509	-0.673991
S	-3.313021	2.218988	0.165811
O	-1.819582	2.142101	-1.394515
C	-2.143600	-0.099802	1.134911
C	-2.138993	-1.495029	1.260378
C	-3.170532	-2.256539	0.743184
C	-4.241881	-1.624575	0.087504
H	-1.374293	0.476844	1.633467
H	-1.318854	-1.979421	1.780547
H	-3.172324	-3.336429	0.848272
H	0.152566	2.336857	1.186671
H	-0.233391	3.692793	0.106530
H	-2.027230	2.513278	2.153652
H	-2.235301	3.996945	1.221104
Au	1.676588	0.012178	-0.329381
H	-0.702773	-0.009499	-1.669139
Cl	-5.523543	-2.583580	-0.549492
P	3.850464	-0.674087	0.242007
C	4.546283	0.138398	1.721533
H	5.560329	-0.224914	1.915673
H	4.578185	1.220597	1.570960
H	3.919636	-0.071839	2.592137
C	4.002522	-2.461553	0.581322
H	3.684641	-3.033278	-0.294439
H	5.039804	-2.717889	0.818790
H	3.364686	-2.738059	1.424790
C	5.067861	-0.350742	-1.079508
H	5.104915	0.719590	-1.298085
H	6.062655	-0.689324	-0.773057
H	4.774815	-0.878170	-1.990974

2b (TS):

SCF Done: E(RPBE1PBE) = -1495.39541421 A.U.

Charge= 1.0000 electrons

Dipole moment (field-independent basis, Debye):

X= -1.4344 Y= 1.2978 Z= 3.5844 Tot= 4.0731

Atom	X	Y	Z
C	2.861301	-2.067724	1.485561
C	0.609264	-0.606088	-0.912850
C	4.441764	1.091660	-0.631950
C	3.592613	0.296079	0.168729
H	5.331683	0.660466	-1.081027
C	1.432437	-2.271552	0.890765
C	1.453659	-1.632229	-0.463377
S	4.011667	-1.375521	0.272060
O	2.466125	-1.979946	-1.163655
C	2.423966	0.846493	0.733980
C	2.113630	2.206736	0.536394
C	2.966696	2.969775	-0.248908

C	4.122244	2.417608	-0.828361
H	1.823003	0.278751	1.436521
H	2.745883	4.021898	-0.407353
H	4.771035	3.042426	-1.434353
H	0.662393	-1.851213	1.541586
H	1.258408	-3.346653	0.789981
H	2.860363	-1.411694	2.359461
H	3.320423	-3.013841	1.779762
Au	-1.289358	-0.223657	-0.339279
H	1.001511	-0.145794	-1.824337
C	0.894121	2.795102	1.183422
H	-0.008409	2.256669	0.868588
H	0.954310	2.727456	2.275261
H	0.773776	3.848179	0.919460
P	-3.536579	0.199645	0.201555
C	-3.808839	1.712111	1.188887
H	-4.875280	1.847954	1.394614
H	-3.269654	1.640387	2.137065
H	-3.437581	2.583811	0.643666
C	-4.338013	-1.129153	1.163283
H	-5.383765	-0.877655	1.366196
H	-4.298625	-2.067056	0.603223
H	-3.814069	-1.271287	2.112016
C	-4.596887	0.411013	-1.268993
H	-5.633421	0.595773	-0.970047
H	-4.239940	1.253983	-1.866311
H	-4.557517	-0.489395	-1.887487

3b (TS):
SCF Done: E(RPBE1PBE) = -1495.39617189A.U.
Charge= 1.0000 electrons
Dipole moment (field-independent basis, Debye):
X= -1.0581 Y= 0.9788 Z= 3.6903 Tot= 3.9618

Atom	X	Y	Z
C	2.409076	-2.611213	1.212747
C	0.416255	-0.506631	-0.925179
C	4.390445	0.734207	-0.144943
C	3.422309	-0.114836	0.434407
H	5.258983	0.299858	-0.633916
C	1.001712	-2.557701	0.539872
C	1.149915	-1.665874	-0.653931
S	3.670909	-1.807001	0.193485
O	2.179480	-1.959209	-1.363803
C	2.277355	0.424906	1.054298
C	2.142448	1.819018	1.109248
C	3.101968	2.639508	0.547716
C	4.246042	2.109684	-0.091320
H	1.572210	-0.197688	1.591754
H	1.279805	2.248425	1.609017
H	2.986326	3.718724	0.608540
H	0.236705	-2.204554	1.235104
H	0.742383	-3.570295	0.217723
H	2.422070	-2.138636	2.197772
H	2.769805	-3.635349	1.328475
Au	-1.461891	-0.058616	-0.330891
H	0.888824	0.085332	-1.714175

C	5.271745	3.028319	-0.686531
H	6.103753	2.474319	-1.126495
H	4.828137	3.652607	-1.469378
H	5.677557	3.702732	0.074893
P	-3.672047	0.480315	0.253859
C	-4.195550	2.140591	-0.295971
H	-4.104367	2.216295	-1.382621
H	-5.234895	2.329764	-0.009682
H	-3.555463	2.902315	0.156642
C	-4.018566	0.456614	2.046705
H	-5.066643	0.707996	2.237578
H	-3.810941	-0.537135	2.451850
H	-3.379415	1.179984	2.559552
C	-4.906342	-0.654993	-0.468264
H	-5.917852	-0.358201	-0.173524
H	-4.831514	-0.638383	-1.558668
H	-4.718620	-1.676096	-0.126435

2c (TS):
SCF Done: E(RPBE1PBE) = –1570.52768171 A.U.
Charge= 1.0000 electrons
Dipole moment (field-independent basis, Debye):
X= -1.3032 Y= 2.2948 Z= 3.1366 Tot= 4.0968

Atom	X	Y	Z
C	2.729035	-2.169702	1.618844
C	0.527276	-0.846415	-0.915268
C	4.475278	0.735235	-0.725472
C	3.579113	0.043793	0.119019
H	5.344466	0.231224	-1.135879
C	1.294584	-2.364956	1.035919
C	1.343375	-1.841779	-0.366166
S	3.904009	-1.638662	0.348326
O	2.356938	-2.277254	-1.022415
C	2.437747	0.680175	0.633686
C	2.213000	2.039944	0.335762
C	3.101179	2.723979	-0.485871
C	4.222942	2.060391	-1.009539
H	1.784807	0.217507	1.363564
H	2.951643	3.771862	-0.718248
H	4.907295	2.609713	-1.648680
H	0.540636	-1.860878	1.644654
H	1.077760	-3.436988	1.024650
H	2.756888	-1.437835	2.429656
H	3.147819	-3.104296	1.997811
Au	-1.350997	-0.356251	-0.360694
H	0.933571	-0.479584	-1.862195
O	1.119893	2.574465	0.913325
C	0.867034	3.956165	0.713666
H	0.688935	4.177350	-0.345194
H	-0.031537	4.180098	1.288190
H	1.696446	4.567534	1.087164
P	-3.568118	0.181697	0.192651
C	-3.753801	1.725048	1.151721
H	-4.808476	1.914252	1.374872
H	-3.197659	1.648131	2.089594
H	-3.353112	2.565938	0.579795

C	-4.414298	-1.087414	1.196221
H	-5.444269	-0.784546	1.409513
H	-4.426016	-2.038267	0.657118
H	-3.881645	-1.232467	2.139634
C	-4.644577	0.409779	-1.264050
H	-4.654651	-0.504127	-1.863669
H	-5.667157	0.645852	-0.953292
H	-4.261326	1.223351	-1.885347

3c (TS):

SCF Done: E(RPBE1PBE) = –1570.52698887 A.U.

Charge= 1.0000 electrons

Dipole moment (field-independent basis, Debye):

X= 1.9769 Y= -1.7452 Z= 4.0571 Tot= 4.8388

Atom	X	Y	Z
C	2.858099	-2.054718	1.489345
C	0.572409	-0.671912	-0.954853
C	4.422919	1.139259	-0.587722
C	3.574238	0.320894	0.187446
H	5.324410	0.724870	-1.028680
C	1.433114	-2.274507	0.891287
C	1.450311	-1.647946	-0.468320
S	3.999422	-1.354195	0.271498
O	2.488752	-1.971377	-1.150319
C	2.391871	0.843445	0.746158
C	2.112112	2.193100	0.530265
C	2.932349	3.013693	-0.214581
C	4.098086	2.469233	-0.774210
H	1.756735	0.288685	1.425264
H	2.675402	4.059667	-0.344206
H	4.753951	3.104832	-1.360451
H	0.655204	-1.857159	1.534658
H	1.268847	-3.352154	0.800219
H	2.851643	-1.396151	2.361464
H	3.327363	-2.995127	1.785815
Au	-1.312769	-0.266283	-0.363546
H	0.958909	-0.220688	-1.873656
F	0.999839	2.693548	1.084944
P	-3.520249	0.261173	0.243047
C	-3.670002	1.804082	1.207230
H	-3.265818	2.641292	0.632430
H	-4.718944	2.005562	1.445991
H	-3.101159	1.718906	2.136670
C	-4.622194	0.498917	-1.192737
H	-4.651050	-0.413308	-1.794290
H	-5.636617	0.741805	-0.861138
H	-4.245481	1.311941	-1.818735
C	-4.350970	-1.006527	1.260515
H	-3.800092	-1.156055	2.192682
H	-5.374426	-0.697928	1.495757
H	-4.379757	-1.956086	0.719802

2d (TS):
SCF Done: E(RPBE1PBE) = -4026.60039425 A.U.
Charge= 1.0000 electrons
Dipole moment (field-independent basis, Debye):
X= -.1143 Y= -0.0547 Z= 2.3944 Tot= 2.4637

Atom	X	Y	Z
C	2.760583	-2.148695	1.763695
C	0.504298	-1.181959	-0.894011
C	4.390251	0.541040	-0.899966
C	3.527516	-0.085413	0.024141
H	5.277560	0.024669	-1.254054
C	1.323722	-2.429934	1.222366
C	1.351863	-2.073014	-0.231253
S	3.903544	-1.725950	0.423851
O	2.384415	-2.550755	-0.834530
C	2.364900	0.567709	0.476122
C	2.099275	1.858969	0.006161
C	2.944928	2.483144	-0.894423
C	4.093452	1.814022	-1.344147
H	1.734232	0.151749	1.250966
H	2.725648	3.487491	-1.240793
H	4.755971	2.308085	-2.047752
H	0.565600	-1.870627	1.775227
H	1.123367	-3.498965	1.339089
H	2.785662	-1.339270	2.497621
H	3.206220	-3.032061	2.225814
Au	-1.361063	-0.609774	-0.380879
H	0.895885	-0.926476	-1.883182
Br	0.574789	2.761845	0.644820
P	-3.557460	0.051558	0.120395
C	-3.673595	1.628703	1.033210
H	-3.224634	2.430782	0.441618
H	-4.719400	1.877360	1.239187
H	-3.131109	1.551293	1.979006
C	-4.484189	-1.144855	1.141733
H	-5.500806	-0.783846	1.326612
H	-4.535141	-2.108675	0.628579
H	-3.976840	-1.290016	2.098957
C	-4.593299	0.294561	-1.362619
H	-5.607618	0.592214	-1.078838
H	-4.156104	1.069921	-1.997045
H	-4.640504	-0.633856	-1.937658

3d (TS):
SCF Done: E(RPBE1PBE) = -4026.59789400 A.U.
Charge= 1.0000 electrons
Dipole moment (field-independent basis, Debye):
X= 6.0266 Y= 1.3337 Z= 4.3034 Tot= 7.5245

Atom	X	Y	Z
C	-1.139709	3.367335	1.067333
C	0.310446	0.700406	-0.902561
C	-3.837194	0.422526	0.072850
C	-2.690641	1.087573	0.553935
H	-4.615539	0.970261	-0.449036
C	0.200259	2.943941	0.388307
C	-0.171287	2.000442	-0.713121

S	-2.579023	2.766256	0.147864
O	-1.141188	2.435324	-1.433147
C	-1.670091	0.373487	1.212347
C	-1.828240	-1.004744	1.407726
C	-2.954986	-1.660359	0.946420
C	-3.957744	-0.937486	0.277612
H	-0.827973	0.878718	1.668818
H	-1.060153	-1.558700	1.937994
H	-3.079793	-2.725973	1.106666
H	0.892599	2.497335	1.105579
H	0.663316	3.841407	-0.032086
H	-1.222846	3.008523	2.096121
H	-1.267057	4.451811	1.081689
Au	2.090560	-0.058930	-0.327661
H	-0.304989	0.150873	-1.620756
Br	-5.482818	-1.839262	-0.340300
P	4.177697	-0.986530	0.225350
C	4.136976	-2.155641	1.627858
H	3.457255	-2.981529	1.402706
H	5.136509	-2.558573	1.819131
H	3.779537	-1.647667	2.527294
C	5.449530	0.240680	0.681740
H	6.399525	-0.256609	0.901065
H	5.597060	0.945145	-0.140920
H	5.127647	0.801137	1.563224
C	4.918903	-1.935419	-1.146558
H	5.887076	-2.349056	-0.847229
H	4.253166	-2.753054	-1.434669
H	5.060135	-1.285545	-2.014073

2e (TS):

SCF Done: E(RPBE1PBE) = -1555.28982476 A.U.
Charge= 1.0000 electrons
Dipole moment (field-independent basis, Debye):
X= -0.0498 Y= 0.3916 Z= 2.8744 Tot= 2.9014

Atom	X	Y	Z
C	2.858099	-2.054718	1.489345
C	0.572409	-0.671912	-0.954853
C	4.422919	1.139259	-0.587722
C	3.574238	0.320894	0.187446
H	5.324410	0.724870	-1.028680
C	1.433114	-2.274507	0.891287
C	1.450311	-1.647946	-0.468320
S	3.999422	-1.354195	0.271498
O	2.488752	-1.971377	-1.150319
C	2.391871	0.843445	0.746158
C	2.112112	2.193100	0.530265
C	2.932349	3.013693	-0.214581
C	4.098086	2.469233	-0.774210
H	1.756735	0.288685	1.425264
H	2.675402	4.059667	-0.344206
H	4.753951	3.104832	-1.360451
H	0.655204	-1.857159	1.534658
H	1.268847	-3.352154	0.800219
H	2.851643	-1.396151	2.361464
H	3.327363	-2.995127	1.785815

Au	-1.312769	-0.266283	-0.363546
H	0.958909	-0.220688	-1.873656
F	0.999839	2.693548	1.084944
P	-3.520249	0.261173	0.243047
C	-3.670002	1.804082	1.207230
H	-3.265818	2.641292	0.632430
H	-4.718944	2.005562	1.445991
H	-3.101159	1.718906	2.136670
C	-4.622194	0.498917	-1.192737
H	-4.651050	-0.413308	-1.794290
H	-5.636617	0.741805	-0.861138
H	-4.245481	1.311941	-1.818735
C	-4.350970	-1.006527	1.260515
H	-3.800092	-1.156055	2.192682
H	-5.374426	-0.697928	1.495757
H	-4.379757	-1.956086	0.719802

3e (TS):
SCF Done: E(RPBE1PBE) = -1555.26844087 A.U.
Charge= 1.0000 electrons
Dipole moment (field-independent basis, Debye):
X= -2.9883 Y= -0.7451 Z= 4.4644 Tot= 5.4236

Atom	X	Y	Z
C	2.471059	-2.557743	1.228707
C	0.403760	-0.494394	-0.913915
C	4.443080	0.754809	-0.213907
C	3.484479	-0.075883	0.400492
H	5.304753	0.349226	-0.734713
C	1.046527	-2.502215	0.593429
C	1.164282	-1.629883	-0.617316
S	3.711593	-1.776191	0.166665
O	2.180183	-1.926873	-1.345428
C	2.364314	0.479253	1.051203
C	2.231562	1.873591	1.106228
C	3.170089	2.698833	0.514041
C	4.263298	2.117305	-0.137946
H	1.665776	-0.137113	1.603418
H	1.385113	2.305983	1.629749
H	3.089283	3.780071	0.553050
H	0.302131	-2.134312	1.303226
H	0.771628	-3.517796	0.293953
H	2.514797	-2.076386	2.208617
H	2.828274	-3.583121	1.344869
Au	-1.478681	-0.067680	-0.322831
H	0.861965	0.088671	-1.718061
F	5.164707	2.919368	-0.705080
P	-3.696501	0.455467	0.252437
C	-4.061816	2.243833	0.235373
H	-5.112663	2.422116	0.484340
H	-3.429867	2.761064	0.961907
H	-3.854691	2.654579	-0.756192
C	-4.215109	-0.108087	1.909983
H	-5.257608	0.167139	2.098255
H	-4.114833	-1.194198	1.981487
H	-3.582405	0.349304	2.675031
C	-4.918773	-0.277703	-0.888418

H -4.831622 -1.367225 -0.877165
H -5.934199 0.004434 -0.592698
H -4.732358 0.071743 -1.907198

2f (TS):
SCF Done: E(RPBE1PBE) = -1792.86096491 A.U.
Charge= 1.0000 electrons
Dipole moment (field-independent basis, Debye):
X= 0.3271 Y= -1.0624 Z= 2.0860 Tot= 2.3637

Atom	X	Y	Z
C	2.720882	-2.180961	1.754489
C	0.443874	-1.193020	-0.907788
C	4.429549	0.452822	-0.912743
C	3.546666	-0.144574	0.011280
H	5.290535	-0.101182	-1.276206
C	1.273485	-2.418255	1.221509
C	1.297712	-2.081173	-0.236615
S	3.884098	-1.793549	0.423353
O	2.294044	-2.592447	-0.855957
C	2.421112	0.560709	0.473845
C	2.217439	1.873040	0.031268
C	3.091843	2.462452	-0.869639
C	4.198941	1.745163	-1.341951
H	1.773054	0.161887	1.243837
H	2.928826	3.485572	-1.194137
H	0.536393	-1.829776	1.772716
H	1.037666	-3.478781	1.350400
H	2.769085	-1.374936	2.491229
H	3.137992	-3.078183	2.216564
Au	-1.412207	-0.610635	-0.386139
H	0.834101	-0.946525	-1.899900
P	-3.566904	0.155149	0.153895
C	-3.920944	0.229766	1.943116
H	-3.204244	0.892279	2.435480
H	-4.933610	0.607574	2.115698
H	-3.832174	-0.766949	2.382919
C	-3.890480	1.844898	-0.454483
H	-3.797834	1.870422	-1.543350
H	-4.897406	2.168136	-0.172329
H	-3.157402	2.536503	-0.031073
C	-4.909516	-0.864110	-0.546318
H	-5.885042	-0.446995	-0.277231
H	-4.821665	-0.896111	-1.635362
H	-4.838810	-1.886065	-0.165057
C	1.028084	2.655039	0.524414
H	4.884144	2.210836	-2.042794
F	1.350396	3.925180	0.797888
F	0.500609	2.116917	1.640105
F	0.043936	2.687991	-0.398346

3f (TS):
SCF Done: E(RPBE1PBE) = -1792.85748160 A.U.
Charge= 1.0000 electrons
Dipole moment (field-independent basis, Debye):
X= 7.3726 Y= 2.2282 Z= 4.5996 Tot= 8.9708

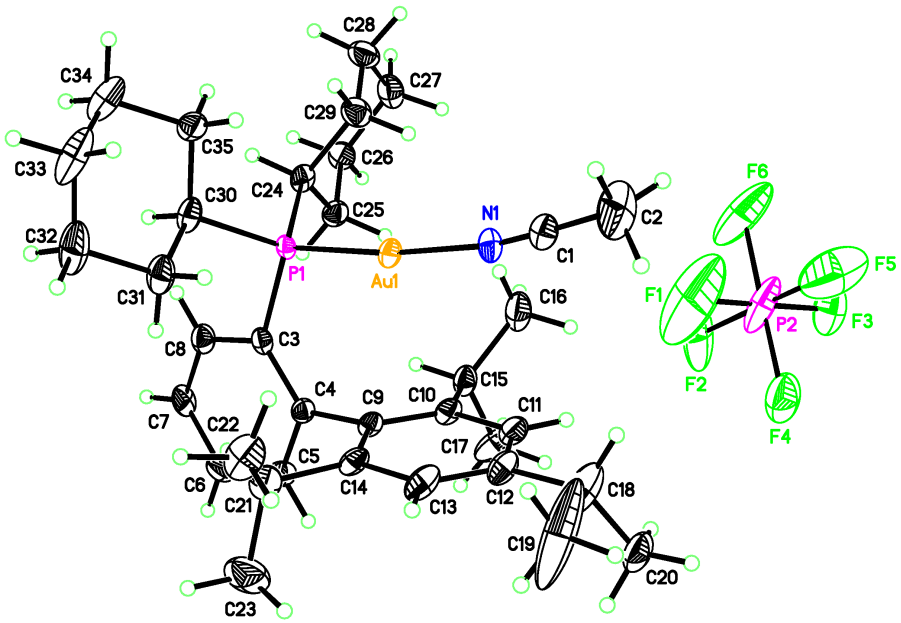
Atom	X	Y	Z

C	-1.229758	3.354846	1.069688
C	0.252480	0.689905	-0.885480
C	-3.879437	0.372066	0.059468
C	-2.748019	1.059070	0.550041
H	-4.665489	0.907810	-0.463969
C	0.116116	2.939205	0.396863
C	-0.241444	1.991739	-0.705632
S	-2.666744	2.741219	0.155909
O	-1.199508	2.413765	-1.440083
C	-1.721823	0.355023	1.209040
C	-1.853882	-1.028044	1.399522
C	-2.965855	-1.697217	0.927081
C	-3.977796	-0.988715	0.253785
H	-0.891347	0.872139	1.674574
H	-3.071018	-2.766576	1.082629
H	0.808962	2.499764	1.118112
H	0.574449	3.839089	-0.023569
H	-1.309957	3.000922	2.100640
H	-1.364110	4.438522	1.079263
Au	2.040325	-0.049316	-0.313510
H	-0.358597	0.132860	-1.601872
P	4.143933	-0.951927	0.223313
C	5.076127	-0.030274	1.493802
H	4.514857	-0.013557	2.431664
H	6.048906	-0.500284	1.669368
H	5.232722	1.000382	1.165076
C	4.080087	-2.666984	0.845661
H	3.611921	-3.314943	0.100137
H	5.088968	-3.035262	1.056641
H	3.486569	-2.709534	1.762571
C	5.263524	-1.018332	-1.216764
H	6.228877	-1.447864	-0.931215
H	4.818394	-1.629693	-2.005954
H	5.422603	-0.011052	-1.610352
H	-1.077330	-1.567109	1.932348
C	-5.179242	-1.751182	-0.248796
F	-4.805573	-2.712799	-1.109593
F	-5.821521	-2.351854	0.765706
F	-6.053636	-0.955016	-0.876345

References

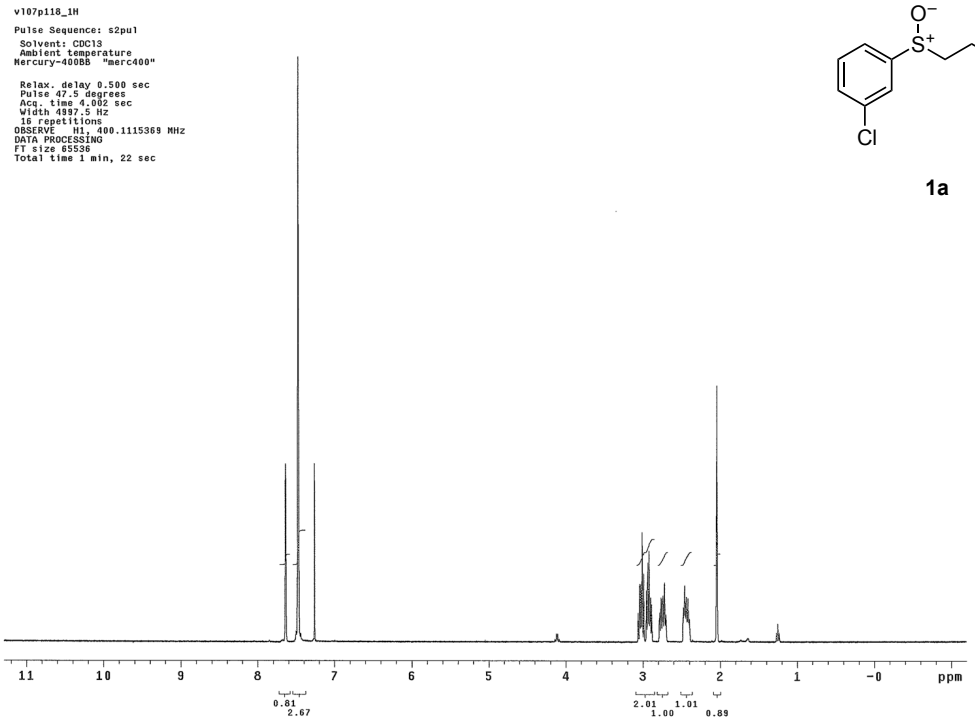
(1) de Frémont, P.; Scott, N. M.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 2411.
(2) Mézailles, N.; Ricard, L.; Gagosz, F. *Org. Lett.* **2005**, *7*, 4133.
(3) Weber, D.; Gagné, M. R. *Chem. Sci.* **2012**, *4*, 335.
(4) Nieto-Oberhuber, C.; López, S.; Echavarren, A. M. *J. Am. Chem. Soc.* **2005**, *127*, 6178.
(5) Uson, R.; Laguna, A.; Laguna, M.; Briggs, D. A.; Murray, H. H.; Fackler, J. P., Jr. Inorganic Syntheses; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 1989; Vol. 26, pp. 85–91.
(6) de Frémont, P.; Marion, N.; Nolan, S. P. *J. Organomet. Chem.* **2009**, *694*, 551.
(7) Huguet, N.; Lebœuf, D.; Echavarren, A. M. *Chem. Eur. J.* **2013**, *19*, 6581.
(8) Herrero-Gómez, E.; Nieto-Oberhuber, C.; López, S.; Benet-Buchholz, J.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2006**, *45*, 5455.
(9) Darses, B.; Michaelides, I. N.; Sladojevich, F.; Ward, J. W.; Rzepa, P. R.; Dixon, D. J. *Org. Lett.* **2012**, *14*, 1684.
(10) Chen, H. C.; Chen, S. H. *J. Phys. Chem.* **1984**, *88*, 5118.
(11) Zuccaccia, D.; Macchioni, A. *Organometallics* **2005**, *24*, 3476.
(12) Martínez-Viviente, E.; Pregosin, P. S. *Helv. Chim. Acta* **2003**, *86*, 2364.
(13) Lu, B.; Li, Y.; Wang, Y.; Aue, D. H.; Luo, Y.; Zhang, L. *J. Am. Chem. Soc.* **2013**, *135*, 8512.

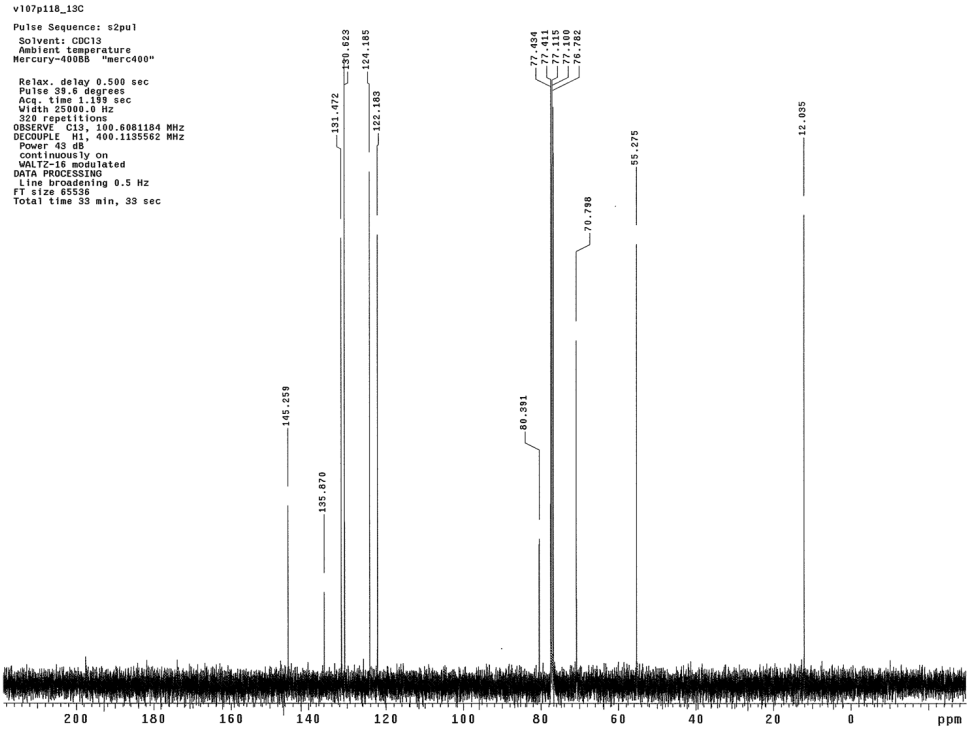
X-Ray structure of [XPhosAu(NCCH$_3$)]PF$_6$

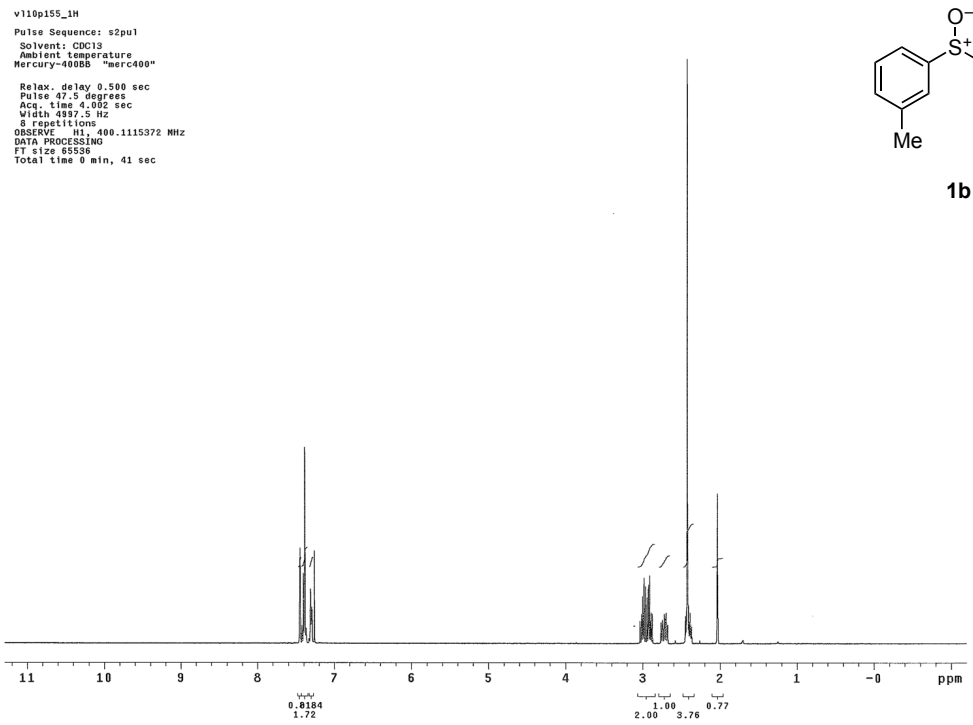


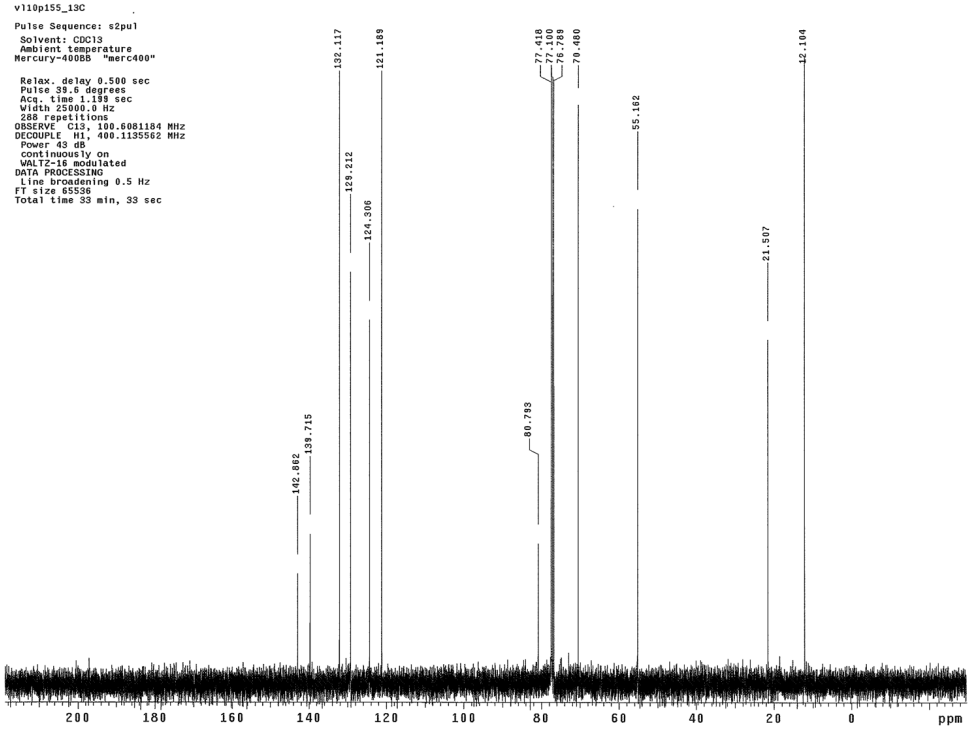
Empirical formula	$C_{35}H_{52}AuF_6NP_2$
Formula weight	859.68
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$Pna2_1$
Unit cell dimensions	a = 22.231(3) Å α = 90°
	b = 12.5844(17) Å β = 90°
	c = 12.8929(17) Å γ = 90°
Volume	3607.0(8) Å^3
Z	4
Density (calculated)	1.583 g.cm^{-3}
Absorption coefficient (μ)	4.223 mm^{-1}
F(000)	1728
Crystal color, habit	colorless, block
Crystal size	0.228 × 0.156 × 0.126 mm^3
θ range for data collection	1.832 to 28.468°
Index ranges	-29 ≤ h ≤ 29, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17
Reflections collected	91782
Independent reflections	9090 [R_{int} = 0.0492]
Completeness to θ = 25.242°	100.0 %
Absorption correction	Numerical
Max. and min. transmission	0.6552 and 0.4122
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9090 / 1 / 413
Goodness-of-fit on F^2	1.202
Final R indices [I>2σ(I)]	R_1 = 0.0313, wR_2 = 0.0669
R indices (all data)	R_1 = 0.0359, wR_2 = 0.0682
Absolute structure parameter	0.036(3)
Extinction coefficient	n/a
Largest diff. peak and hole	1.473 and -2.527 e$^-$.Å^{-3}

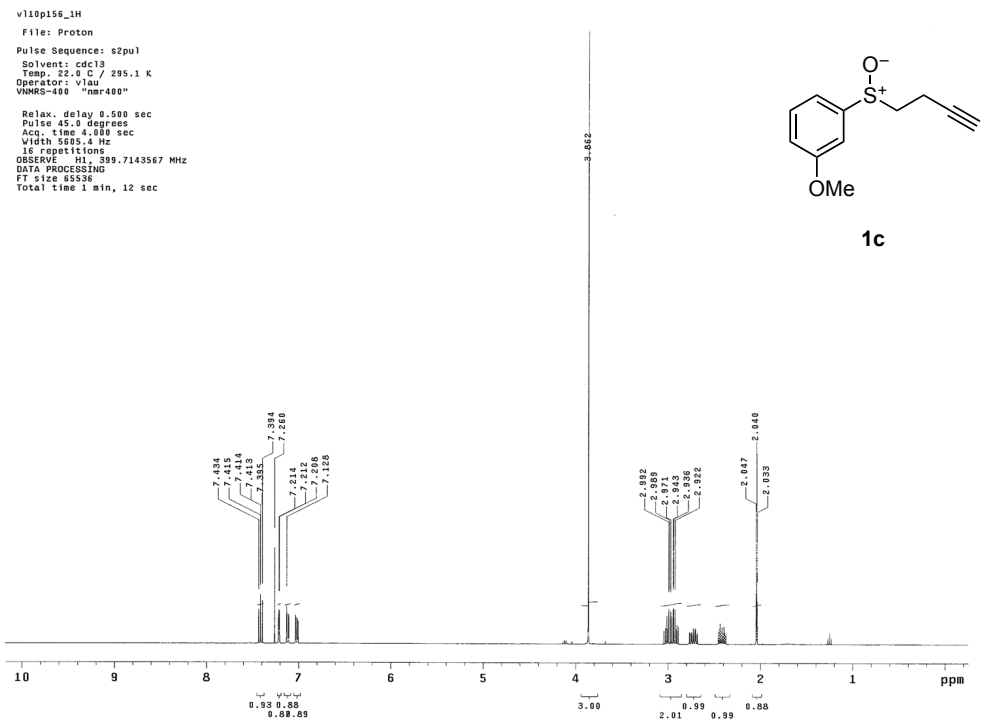
NMR Spectra


v107p118_1H
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 47.5 degrees
Acq. time 4.002 sec
Width 4987.5 Hz
16 repetitions
OBSERVE H1, 400.1115369 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 22 sec
O⁻
S⁺
Cl
1a
11 10 9 8 7 6 5 4 3 2 1 -0 ppm
0.81
2.67
2.01
1.00
1.01
0.89


v107p118_13C
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 39.6 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
320 repetitions
OBSERVE C13, 100.6081184 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
line broadening 0.5 Hz
FT size 65536
Total time 33 min, 33 sec
145.259
135.870
131.472
130.623
124.185
122.183
80.391
77.434
77.411
77.115
77.100
76.782
70.798
55.275
12.035
200 180 160 140 120 100 80 60 40 20 0 ppm

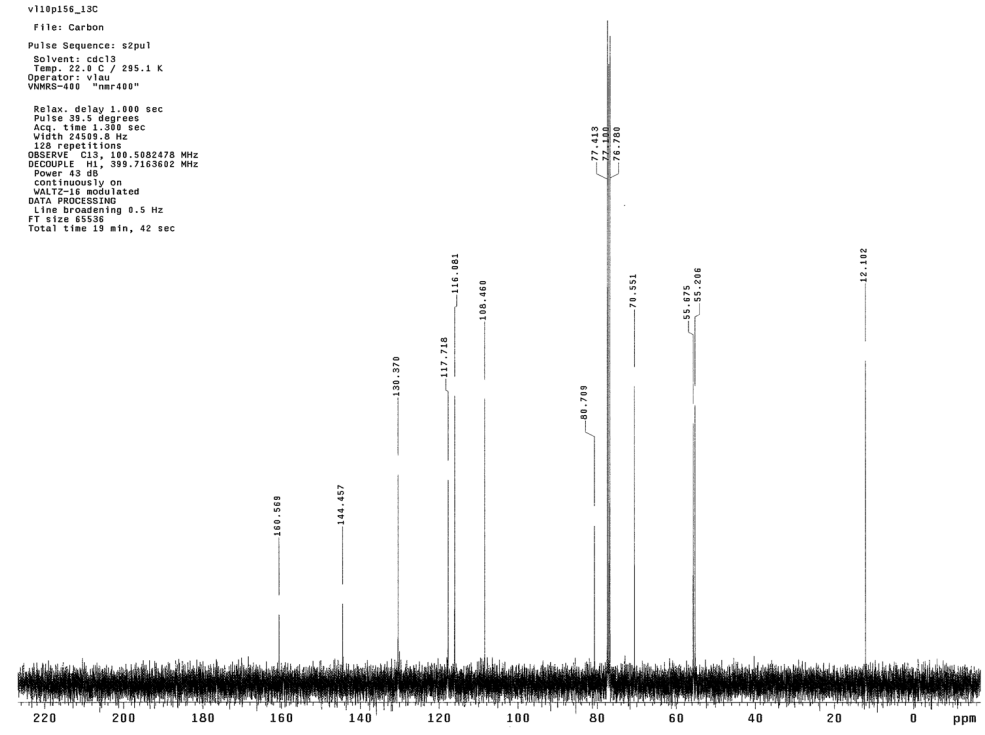

v110p155_1H
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 47.5 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
8 repetitions
OBSERVE H1, 400.1115372 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 41 sec
O⁻
S⁺
Me
1b
11 10 9 8 7 6 5 4 3 2 1 -0 ppm
0.8184
1.72
1.00
2.00
3.76
0.77

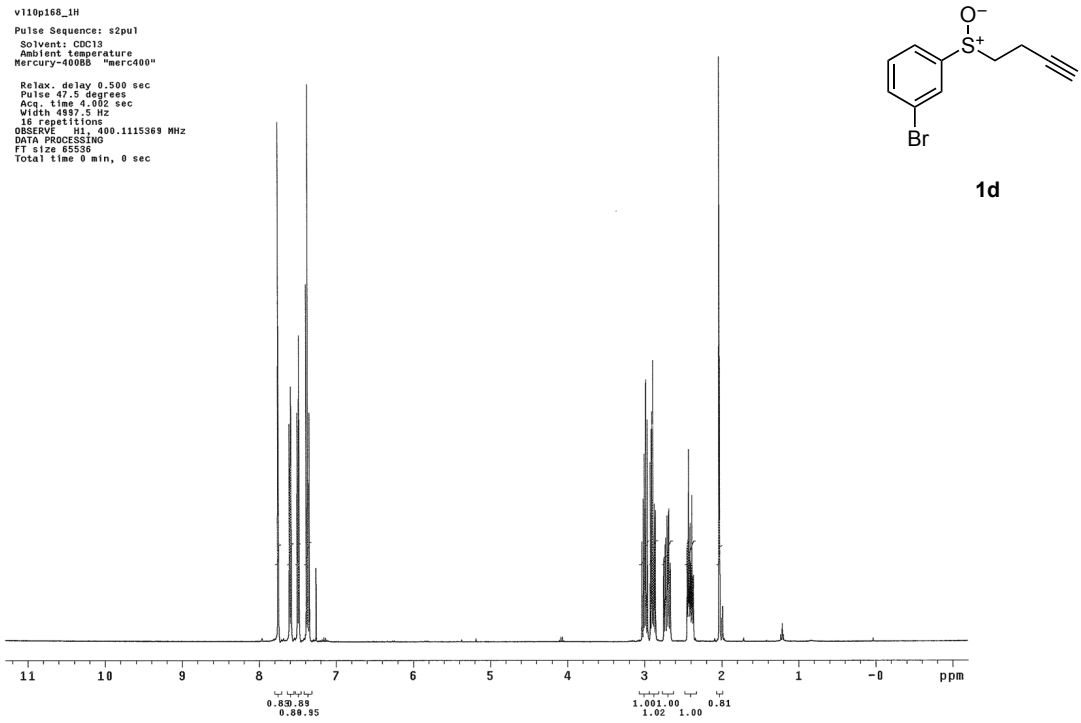

v110p155_13C
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 39.6 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
288 repetitions
OBSERVE C13, 100.6081184 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 33 min, 33 sec
142.862
139.715
132.117
129.212
124.306
121.189
80.793
77.418
77.100
76.788
70.480
55.162
21.507
12.104
200 180 160 140 120 100 80 60 40 20 0 ppm

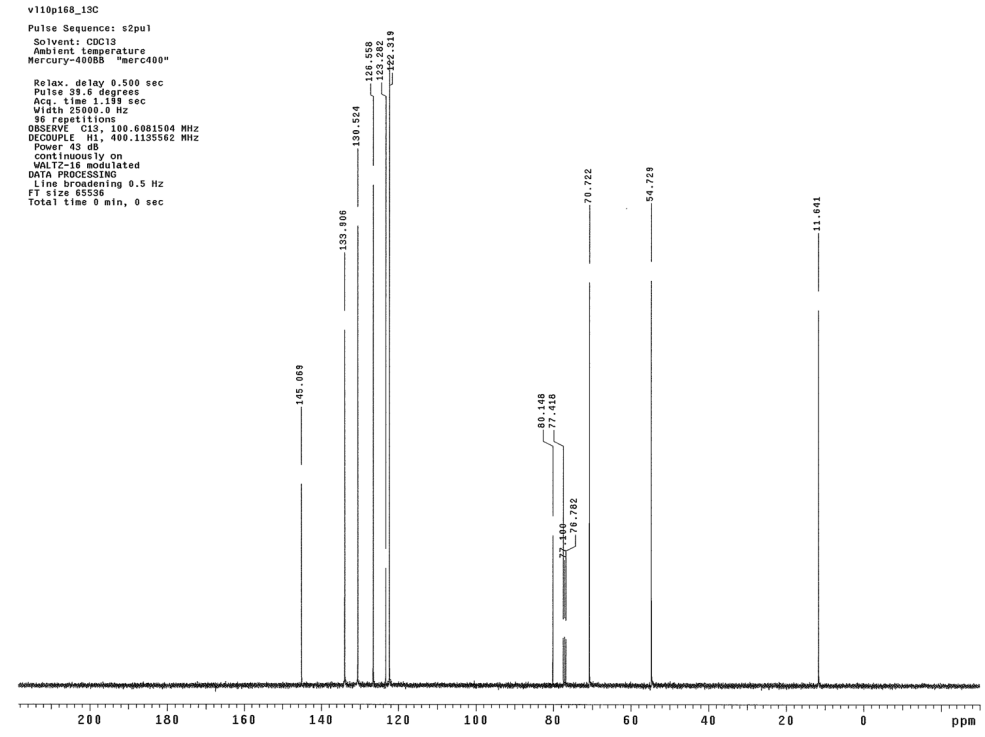

vl10p156_1H
File: Proton
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 22.0 C / 295.1 K
Operator: vlau
VNMRS-400 "nmr400"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 4.000 sec
Width 5685.4 Hz
16 repetitions
OBSERVE H1, 399.7143567 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 12 sec
7.434
7.415
7.414
7.413
7.355
7.394
7.260
7.214
7.212
7.208
7.128
3.662
2.992
2.989
2.971
2.943
2.936
2.922
2.047
2.033
2.040
10
9
8
7
6
5
4
3
2
1
ppm
0.93 0.88
0.88 0.89
3.00
2.01
0.99
0.99
0.88

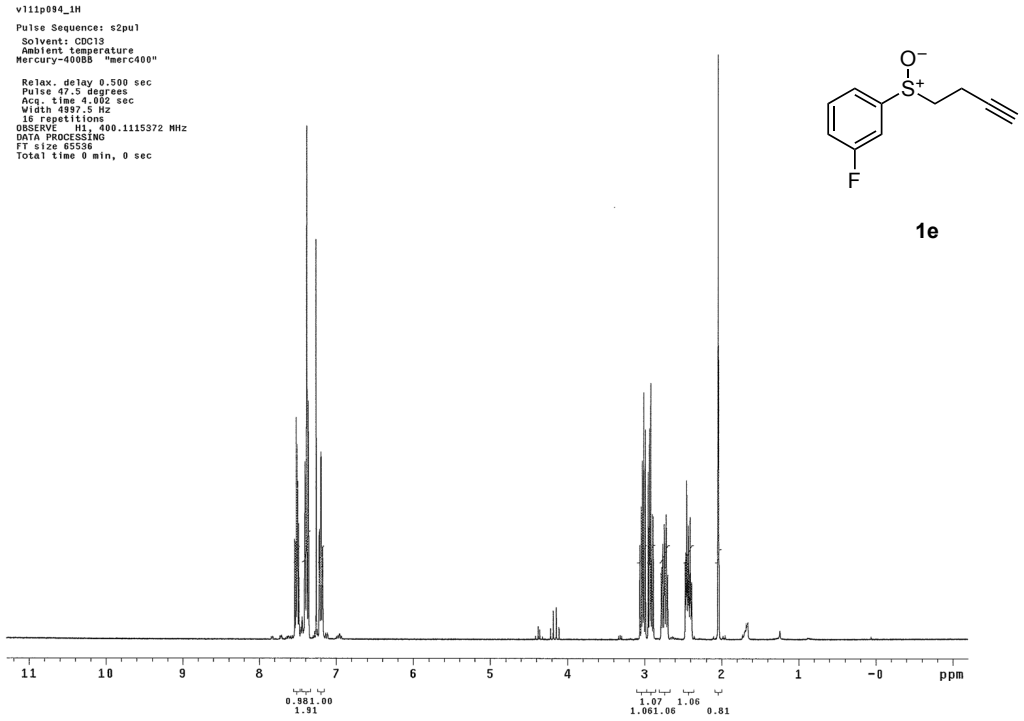
O⁻
S⁺
OMe

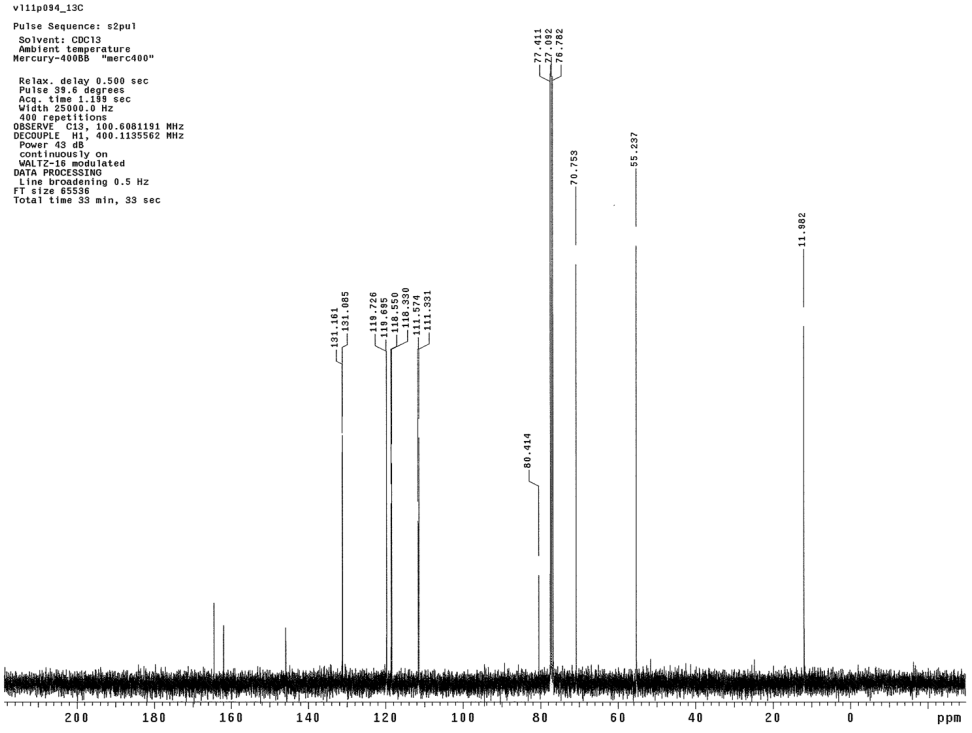
1c

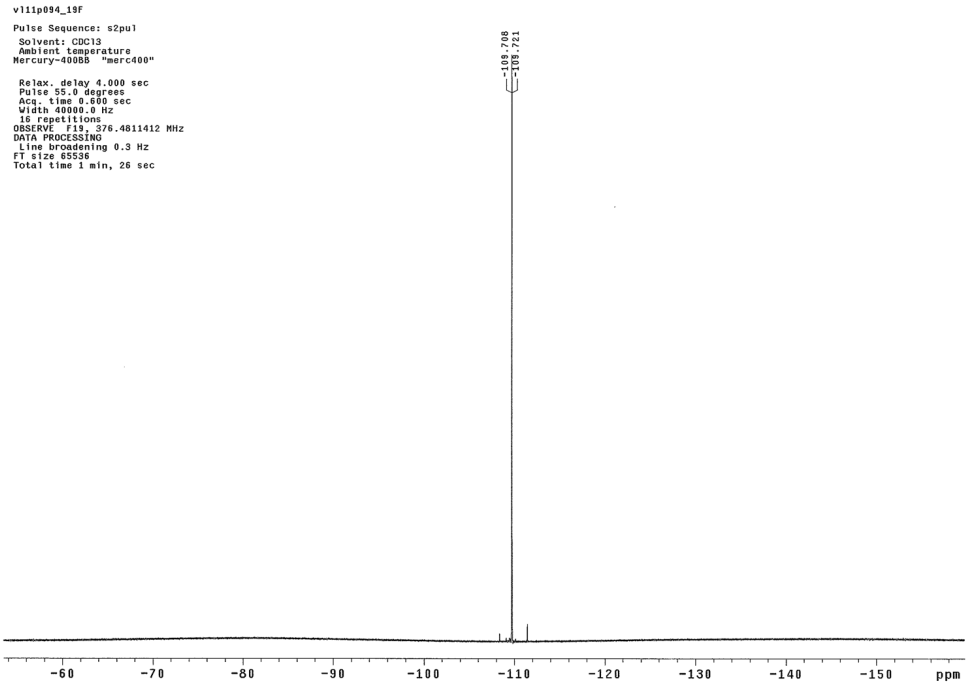

vl10p156_13C
File: Carbon
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 22.0 C / 295.1 K
Operator: vlau
VNMRS-400 "nmr400"
Relax. delay 1.000 sec
Pulse 39.5 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
128 repetitions
OBSERVE C13, 100.5082478 MHz
DECOUPLE H1, 399.7163602 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min, 42 sec
160.569
144.457
130.370
117.718
116.081
108.460
80.709
77.413
77.100
76.788
70.551
55.675
55.206
12.102
220
200
180
160
140
120
100
80
60
40
20
0
ppm

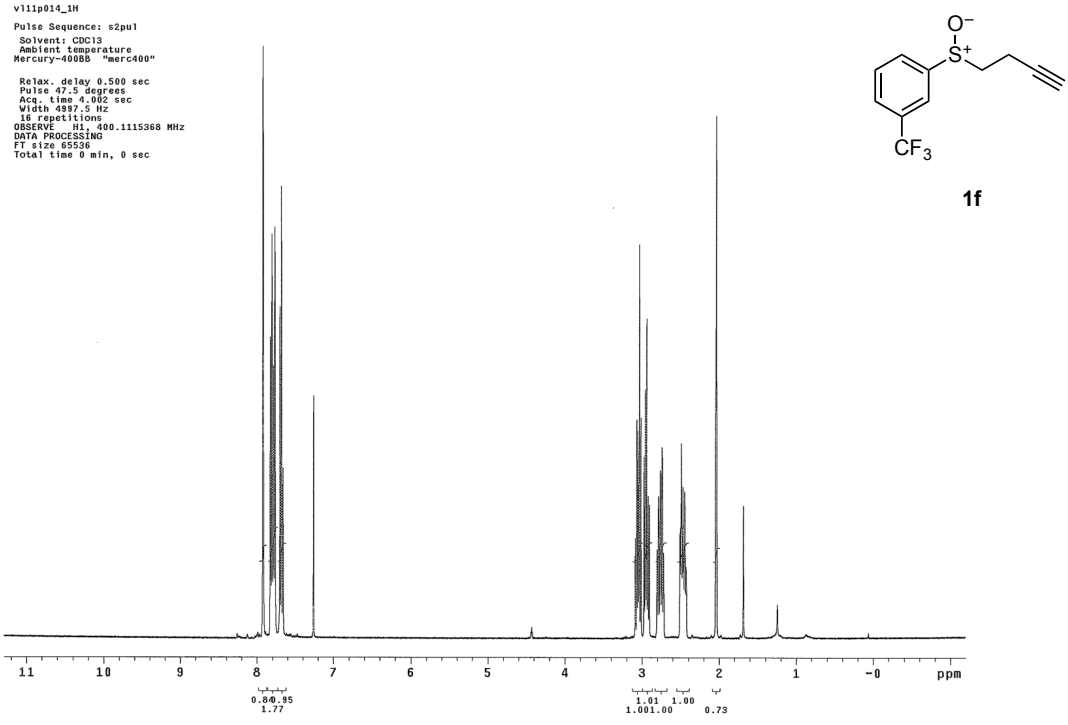

v110p168_1H
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 47.5 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
16 repetitions
OBSERVE H1, 400.1115369 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 0 sec
O⁻
S⁺
Br
1d
11 10 9 8 7 6 5 4 3 2 1 -0 ppm
0.83 0.89
0.80 0.95
1.001.00
1.02 1.00
0.81


v110p168_13C
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 39.6 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
96 repetitions
OBSERVE C13, 100.6081504 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 0 sec
145.069
133.806
130.524
126.558
123.282
122.319
80.148
77.418
77.100
76.782
70.722
54.729
11.641
200 180 160 140 120 100 80 60 40 20 0 ppm


v111p094_1H
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 47.5 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
16 repetitions
OBSERVE H1, 400.1115372 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 0 sec
O
S+
F
1e
11 10 9 8 7 6 5 4 3 2 1 -0 ppm
0.981.00
1.91
1.07 1.06
1.061.06 0.81

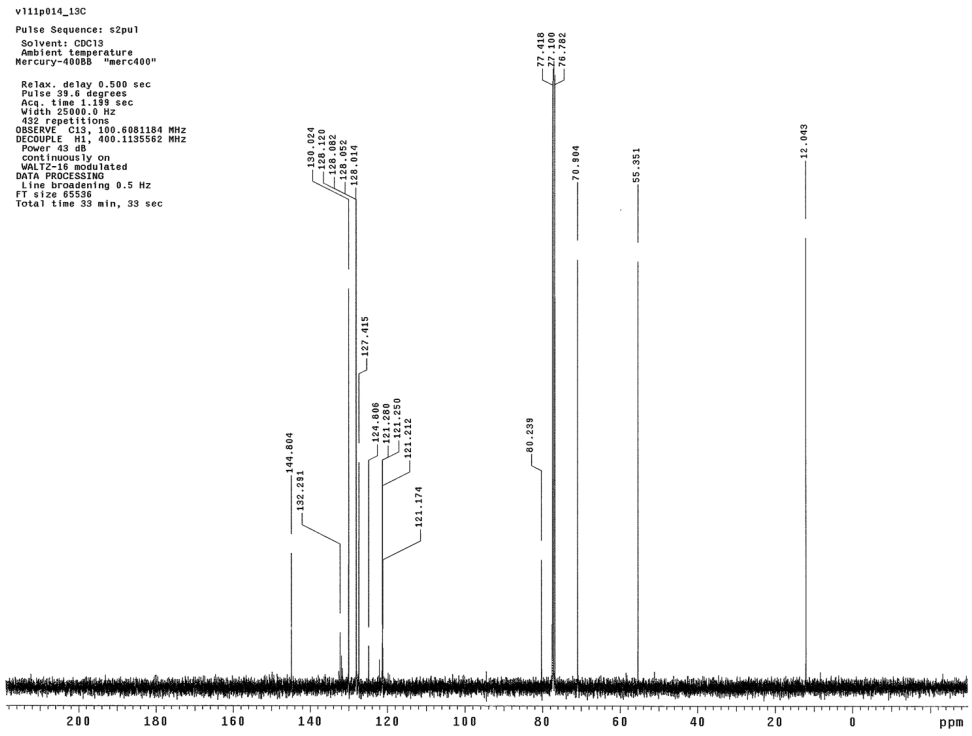

v111p094_13C
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 39.6 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
400 repetitions
OBSERVE C13, 100.6081191 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 33 min, 33 sec
77.411
77.092
76.782
70.753
55.237
11.982
131.161
131.085
119.726
119.695
118.559
118.330
111.574
111.531
80.414
200 180 160 140 120 100 80 60 40 20 0 ppm

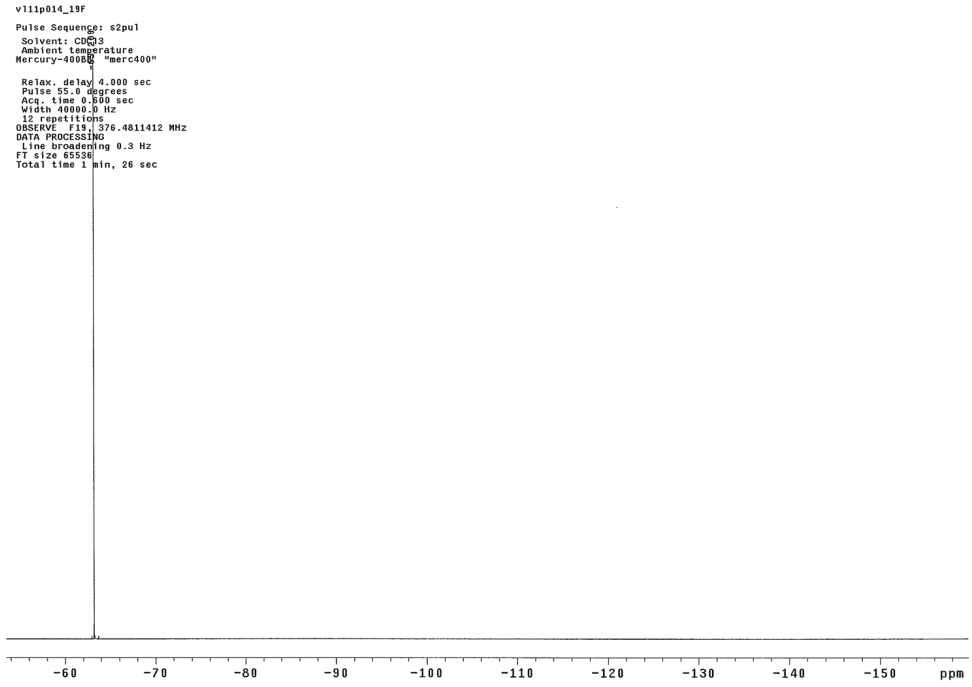

v111p094_19F
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 4.000 sec
Pulse 55.0 degrees
Acq. time 0.600 sec
Width 40000.0 Hz
16 repetitions
OBSERVE F19, 376.4811412 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min, 26 sec
-109.708
-109.721
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
ppm

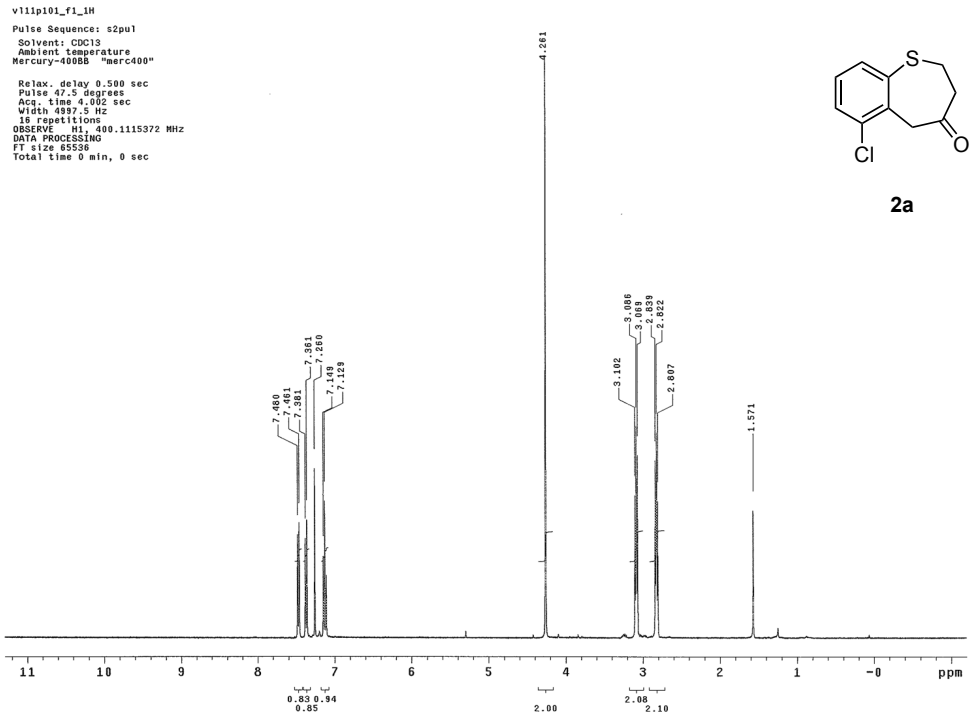

v111p014_1H
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 47.5 degrees
Acq. time 4.002 sec
Width 4987.5 Hz
16 repetitions
OBSERVE H1, 400.1115368 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 0 sec
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.84
0.95
1.77
1.01
1.00
1.001.00
0.73

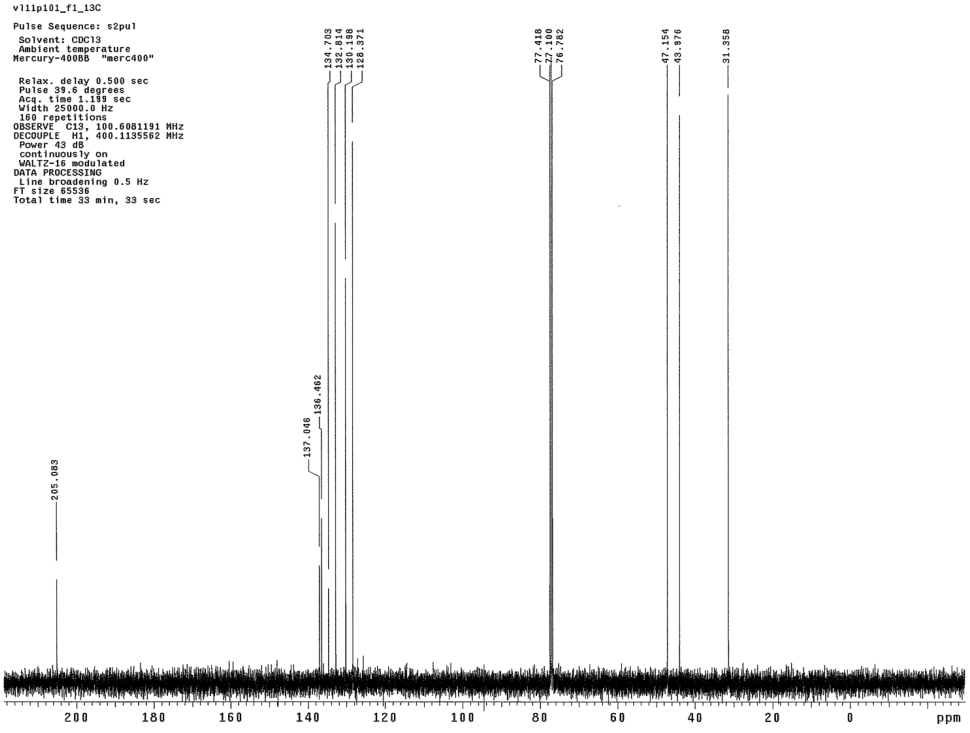
O⁻
S⁺
CF3

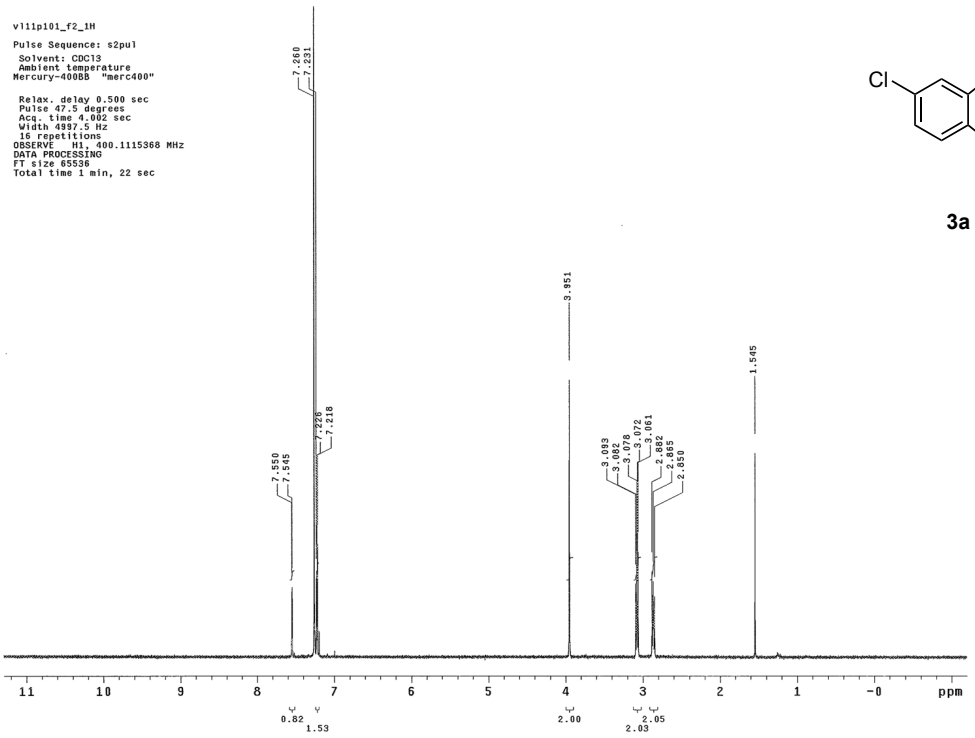
1f


v111p014_13C
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 39.6 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
432 repetitions
OBSERVE C13, 100.6081184 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 33 min, 33 sec
144.804
132.231
130.024
128.120
128.082
128.052
128.014
127.415
124.806
124.280
121.250
121.212
121.174
80.239
77.418
77.100
76.782
70.804
55.351
12.043
200
180
160
140
120
100
80
60
40
20
0
ppm


v111p014_19F
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 4.000 sec
Pulse 55.0 degrees
Acq. time 0.500 sec
Width 40000.0 Hz
12 repetitions
OBSERVE F19, 376.4811412 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min, 26 sec
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
ppm

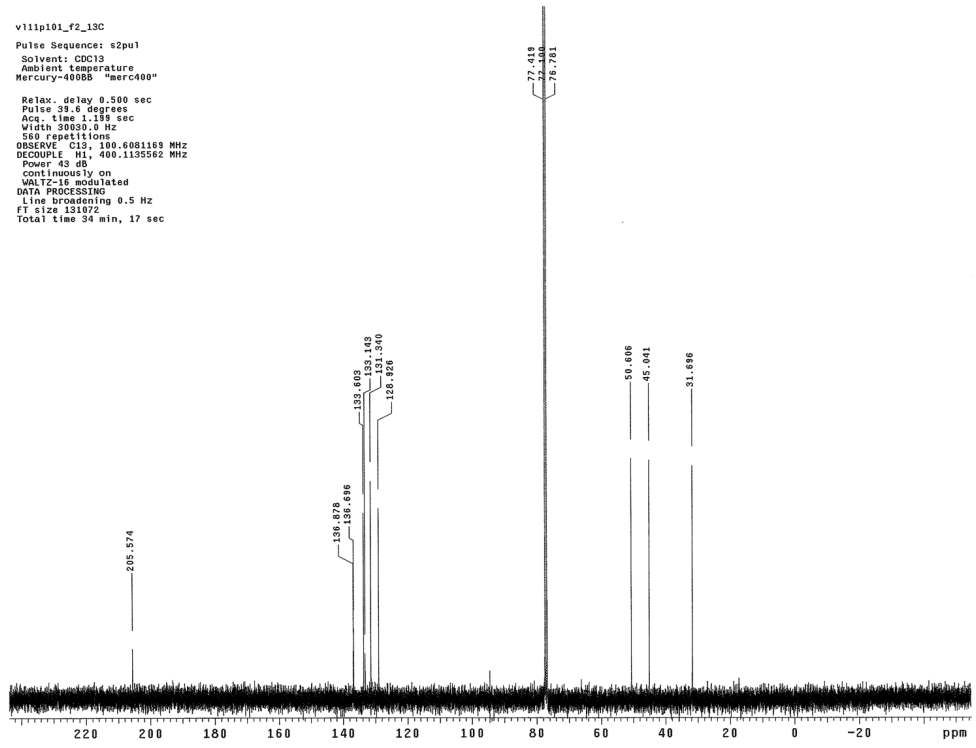

v111p101_f1_1H
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 47.5 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
16 repetitions
OBSERVE H1, 400.1115372 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 0 sec
4.261
3.086
3.069
3.053
2.832
3.102
2.807
1.571
7.460
7.461
7.361
7.260
7.149
7.129
S
Cl
O
2a
ppm
0.83 0.94
0.85
2.00
2.08
2.10

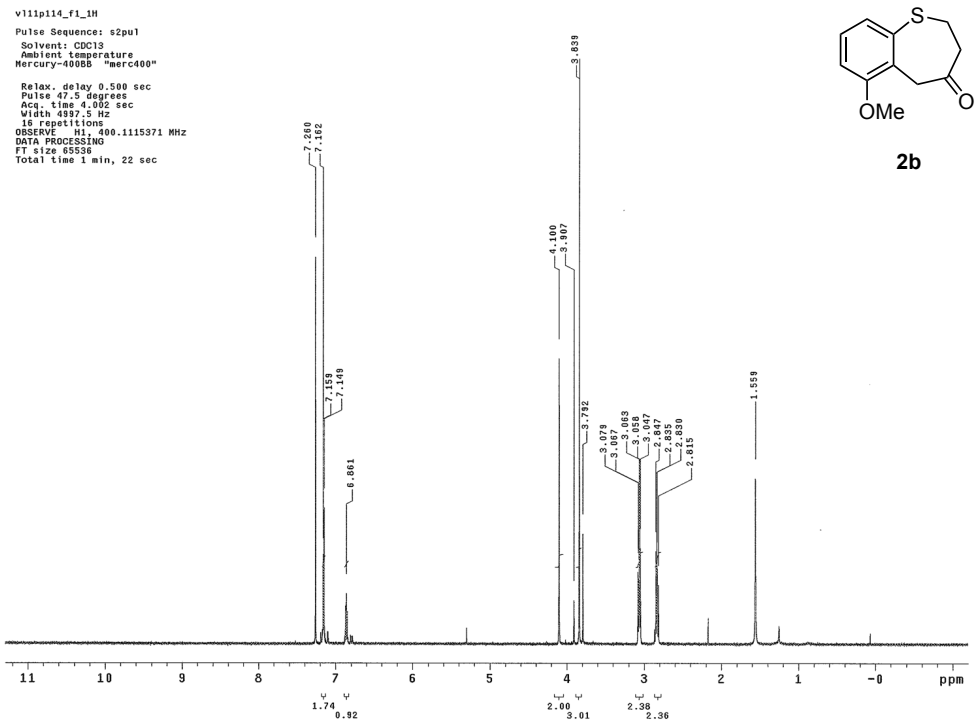

v111p101_f1_13C
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 39.6 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
160 repetitions
OBSERVE C13, 100.6081191 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 33 min, 33 sec
134.703
132.814
130.186
128.371
77.418
77.100
76.782
47.154
43.876
31.358
137.046
136.462
205.083
ppm

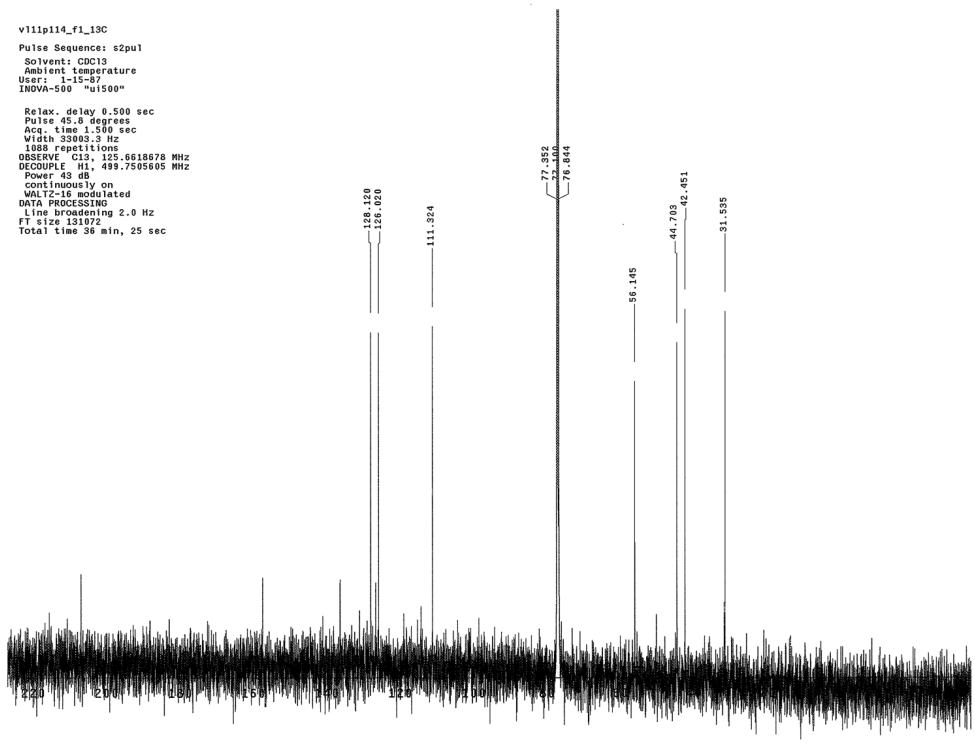

v111p101_f2_1H
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 47.5 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
16 repetitions
OBSERVE H1, 400.1115368 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 22 sec
7.260
7.231
7.550
7.545
7.228
7.218
3.951
3.093
3.082
3.078
3.072
3.061
2.882
2.865
2.850
1.545
11 10 9 8 7 6 5 4 3 2 1 -0 ppm
0.82
1.53
2.00
2.03
2.05

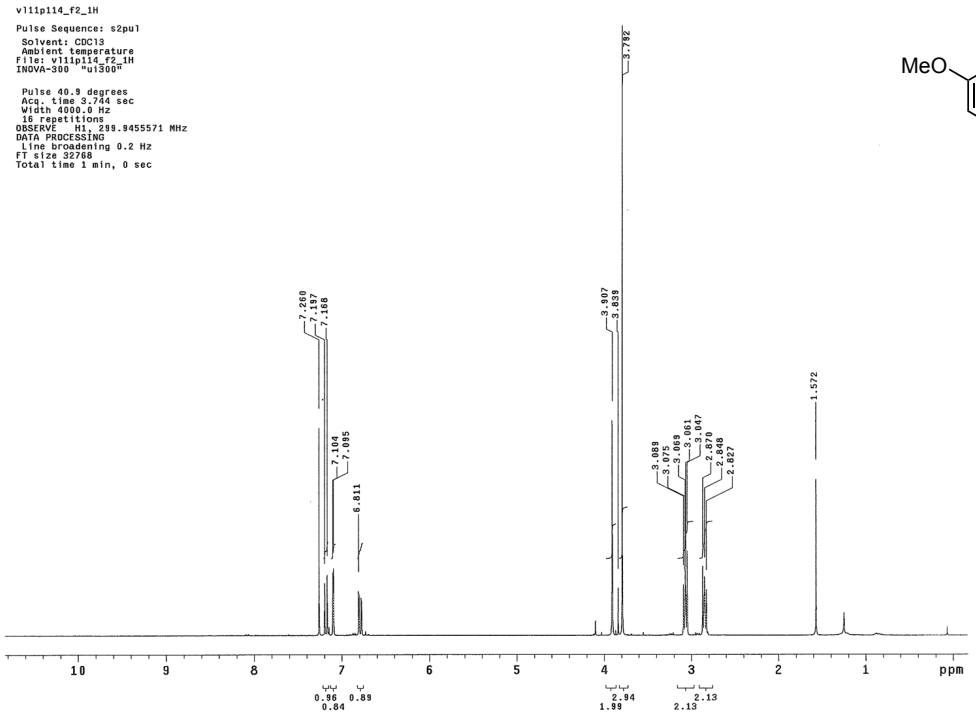
Cl
S
O

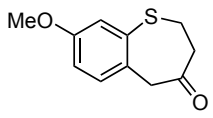
3a


v111p101_f2_13C
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 39.6 degrees
Acq. time 1.199 sec
Width 30030.0 Hz
560 repetitions
OBSERVE C13, 100.6081169 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 34 min, 17 sec
77.418
77.101
76.781
205.574
136.678
136.696
133.603
133.143
131.340
128.826
50.606
45.041
31.686
220 200 180 160 140 120 100 80 60 40 20 0 -20 ppm

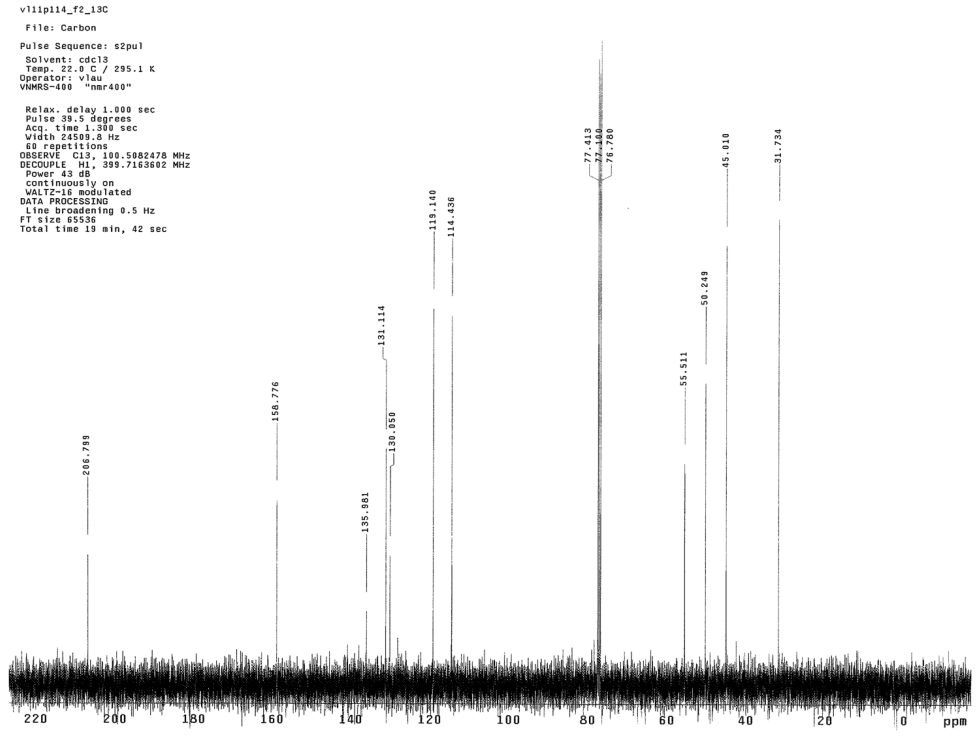

v111p114_f1_1H
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 47.5 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
16 repetitions
OBSERVE H1, 400.1115371 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 22 sec
7.280
7.162
7.159
7.149
6.861
4.100
3.907
3.839
3.792
3.079
3.067
3.063
3.058
3.047
2.847
2.835
2.830
2.815
1.559
S
OMe
O
2b
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.74
0.82
2.00
3.01
2.38
2.36

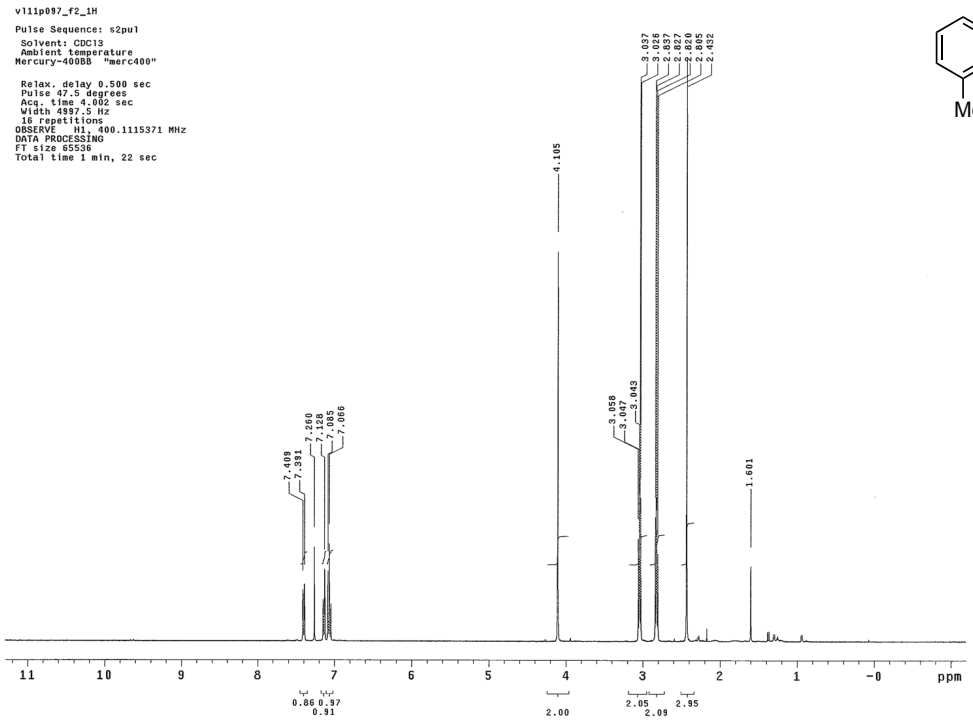

v111p114_f1_13C
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-15-87
INOVA-500 "ui500"
Relax. delay 0.500 sec
Pulse 45.8 degrees
Acq. time 1.500 sec
Width 33003.3 Hz
1088 repetitions
OBSERVE C13, 125.6618678 MHz
DECOUPLE H1, 499.7505605 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 36 min, 25 sec
128.120
126.020
111.324
77.352
77.148
76.944
56.145
44.703
42.451
31.535
220
200
180
160
140
120
100
80
60

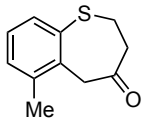

v11p114_f2_1H
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: v11p114_f2_1H
INOVA-300 "u1300"
Pulse 40.9 degrees
Acq. time 3.744 sec
Width 4000.0 Hz
16 repetitions
OBSERVE H1, 299.9455571 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min, 0 sec
7.260
7.197
7.168
7.104
7.095
6.811
3.897
3.859
3.792
3.089
3.075
3.069
3.061
3.047
2.870
2.848
2.827
1.572
ppm
0.96
0.84
0.89
2.84
1.99
2.13
2.13


MeO
S
O

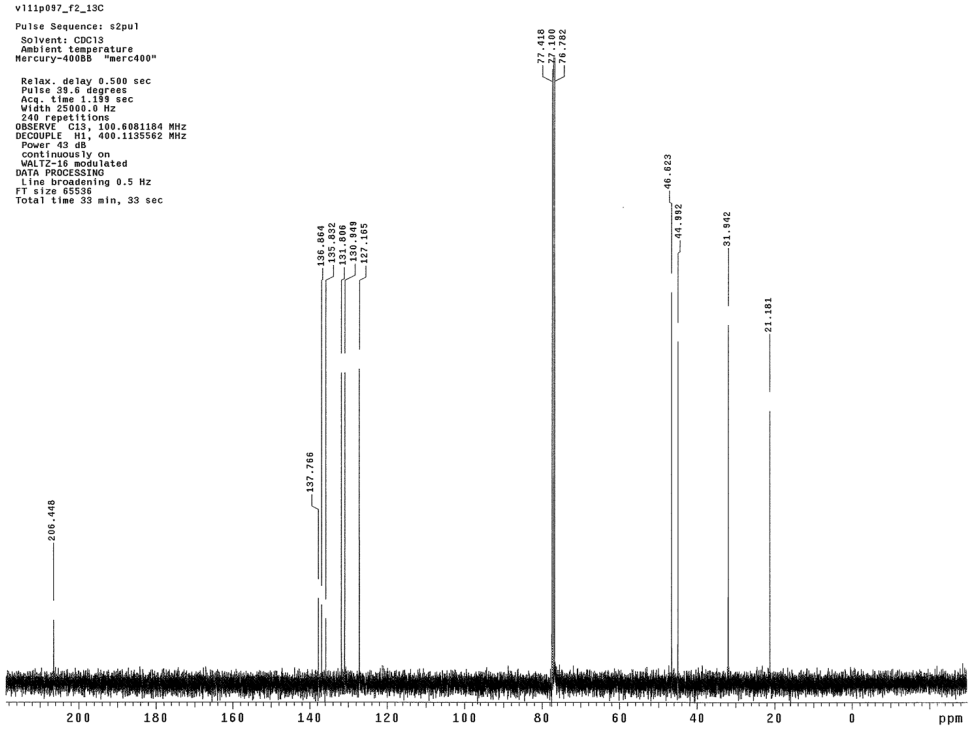
3b

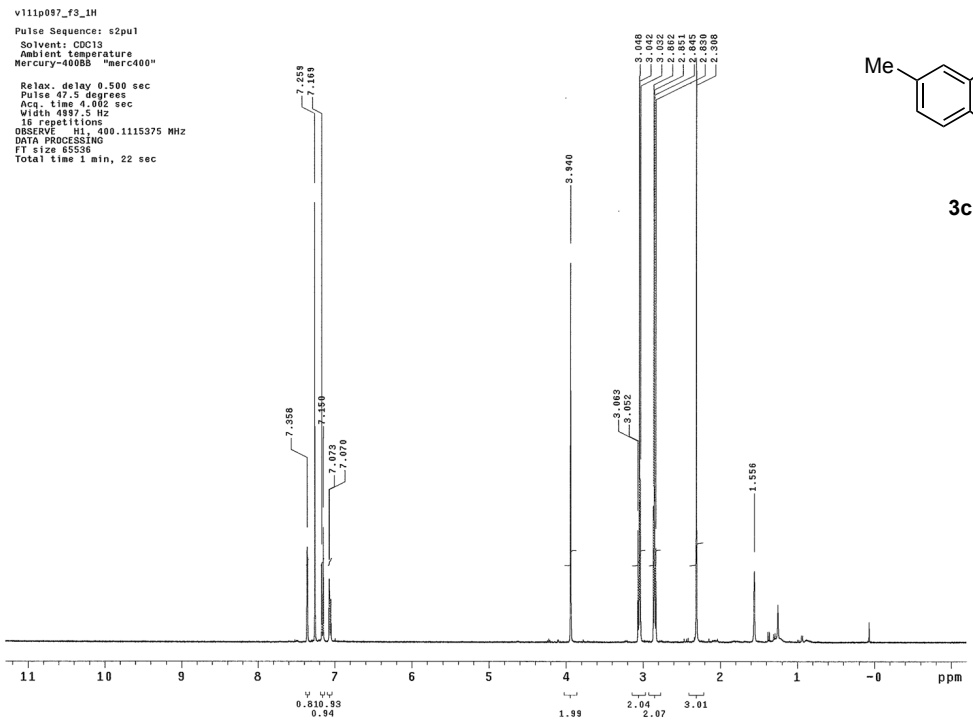

v11p114_f2_13C
File: Carbon
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 22.0 C / 295.1 K
Operator: vlau
VNMRS-400 "nmr400"
Relax. delay 1.000 sec
Pulse 39.5 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
60 repetitions
OBSERVE C13, 100.5082478 MHz
DECOUPLE H1, 399.7163602 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min, 42 sec
206.789
158.776
135.981
131.114
130.059
119.140
114.436
77.413
77.100
76.780
55.511
50.249
45.010
31.734
ppm


v111p097_f2_1H
Pulse Sequence: s2pul
Solvent: CDC13
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 47.5 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
16 repetitions
OBSERVE H1, 400.1115371 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 22 sec
7.409
7.391
7.260
7.128
7.105
7.066
4.105
3.058
3.047
3.043
3.037
3.026
3.017
2.827
2.820
2.805
2.452
1.601
0.86 0.97
0.91
2.00
2.05
2.09
2.95
ppm


S
Me
O

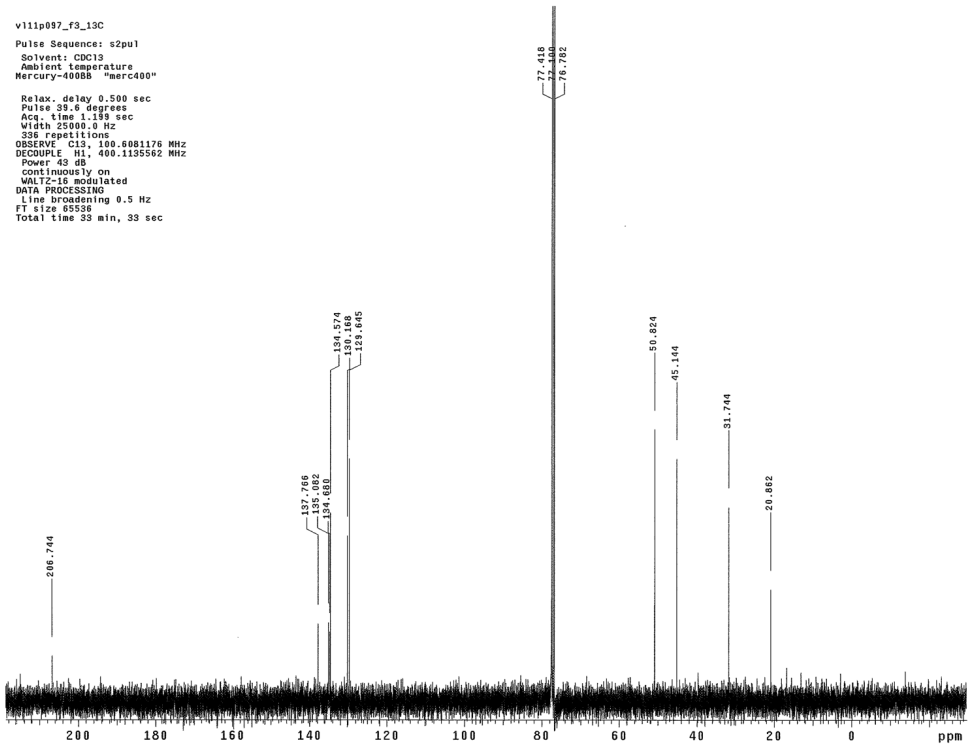
2c

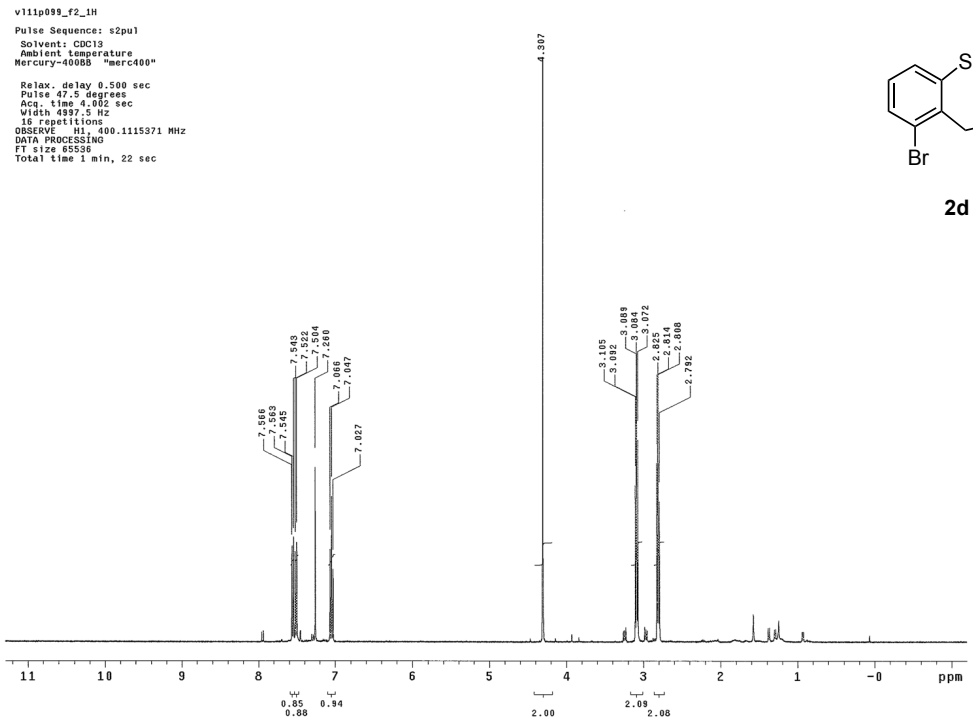

v111p097_f2_13C
Pulse Sequence: s2pul
Solvent: CDC13
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 39.6 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
240 repetitions
OBSERVE C13, 100.6081184 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
line broadening 0.5 Hz
FT size 65536
Total time 33 min, 33 sec
206.448
137.766
136.864
135.882
131.808
130.949
127.165
77.418
77.100
76.782
46.623
44.892
31.942
21.181
ppm


v111p097_f3_1H
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 47.5 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
16 repetitions
OBSERVE H1, 400.1115375 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 22 sec
7.358
7.259
7.169
7.160
7.073
7.070
3.940
3.063
3.052
3.048
3.042
3.032
2.862
2.851
2.845
2.830
2.308
1.556
0.810.93
0.94
1.99
2.04
2.07
3.01
ppm

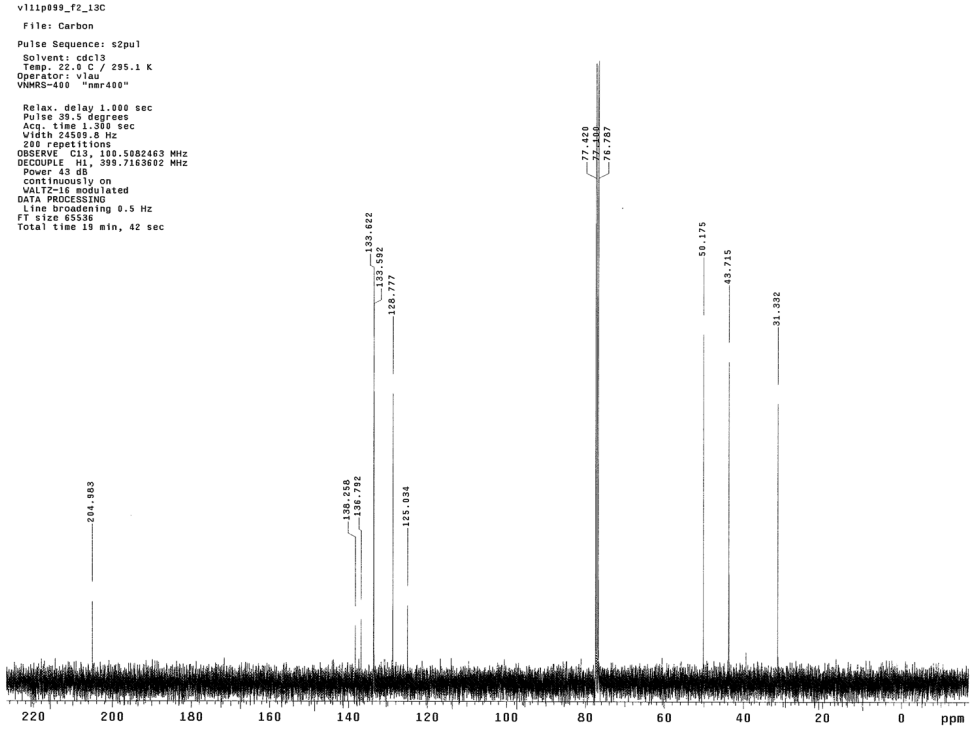
Me
S
O

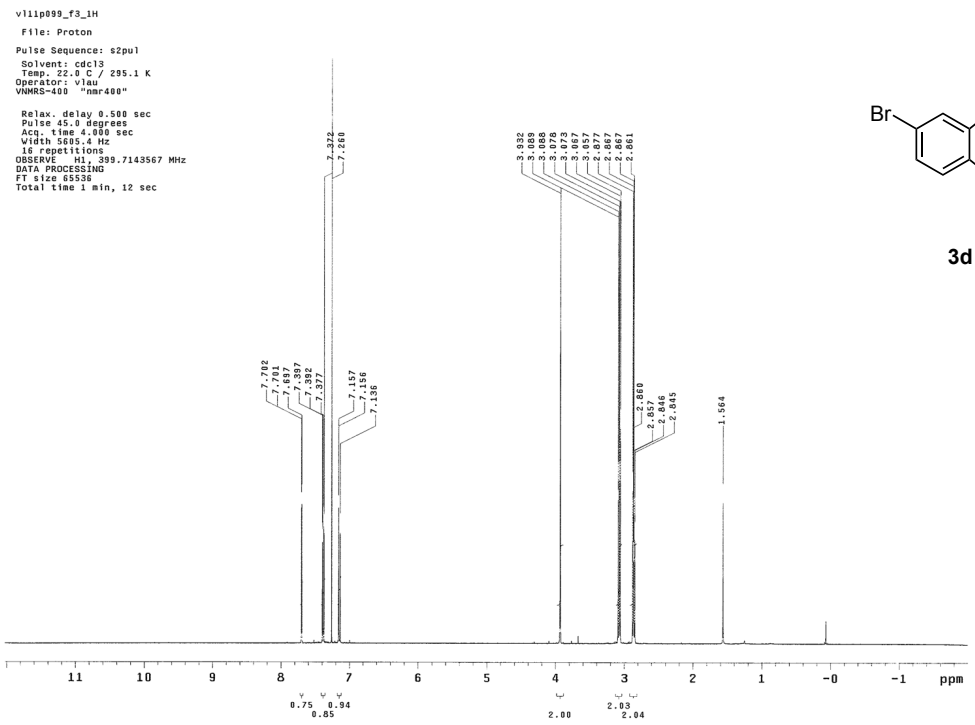
3c


v111p097_f3_13C
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 39.6 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
336 repetitions
OBSERVE C13, 100.6081176 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
line broadening 0.5 Hz
FT size 65536
Total time 33 min, 33 sec
206.744
197.756
135.082
134.680
134.574
130.188
129.645
77.418
77.100
76.782
50.824
45.144
31.744
20.862
ppm


v11p099_f2_1H
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 47.5 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
16 repetitions
OBSERVE H1, 400.1115371 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 22 sec
4.007
7.566
7.563
7.545
7.543
7.539
7.264
7.260
7.066
7.047
7.027
3.105
3.092
3.089
3.084
3.072
2.825
2.814
2.808
2.792
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.85
0.88
0.94
2.00
2.09
2.08
S
Br
O

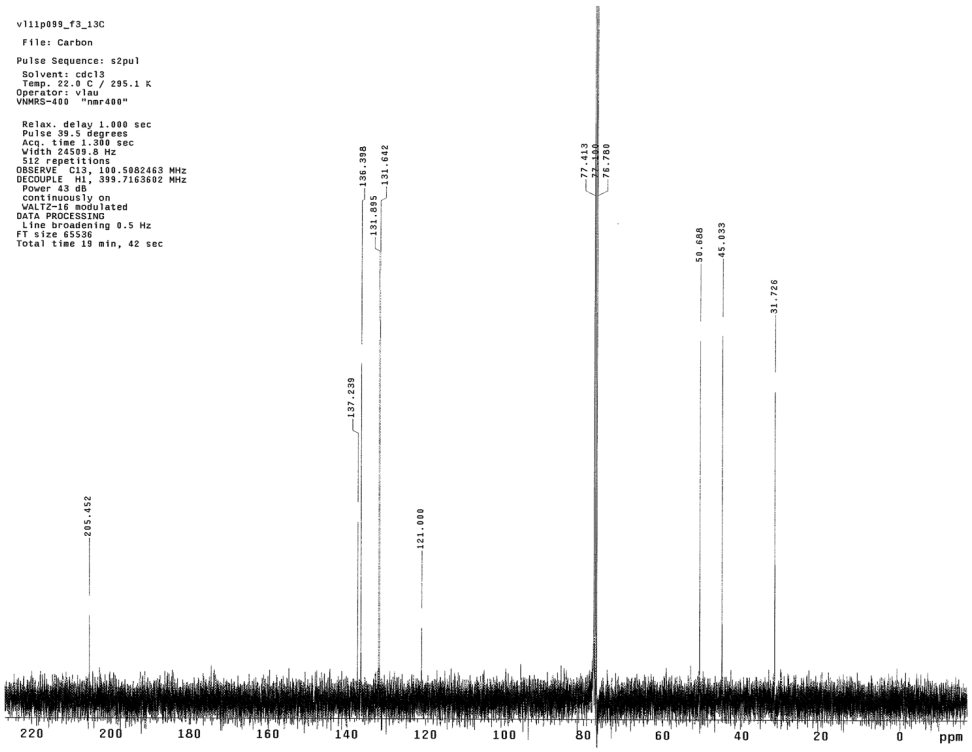
2d

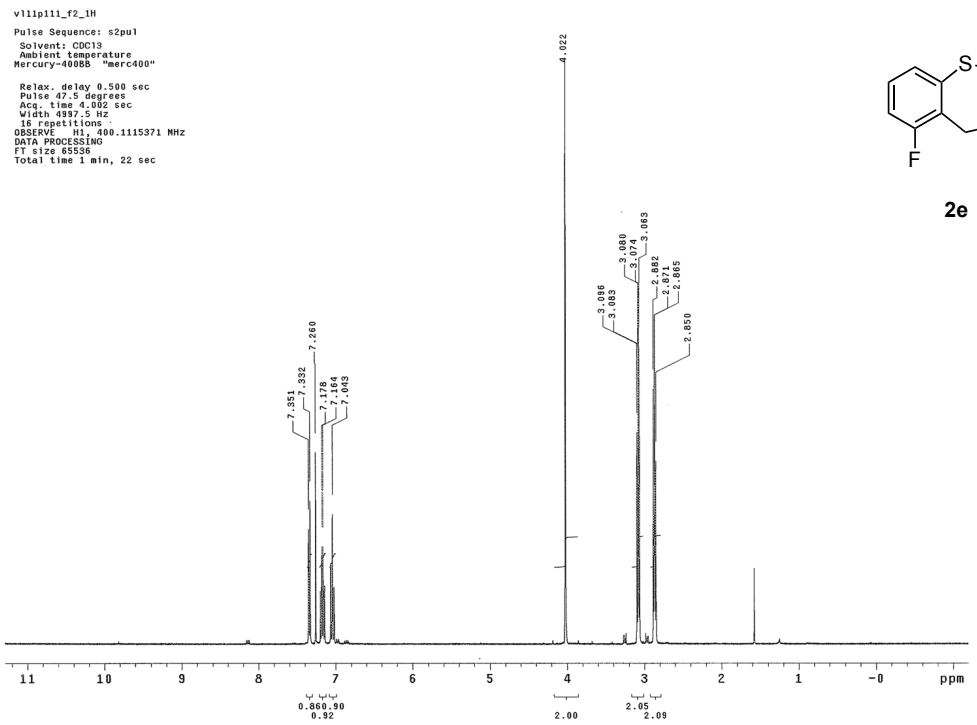

v11p099_f2_13C
File: Carbon
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 22.0 C / 295.1 K
Operator: vlau
VNMRS-400 "nmr400"
Relax. delay 1.000 sec
Pulse 39.5 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
200 repetitions
OBSERVE C13, 100.5882463 MHz
DECOUPLE H1, 399.7163602 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min, 42 sec
204.983
138.258
136.782
133.622
133.592
128.777
125.034
77.408
77.000
76.787
50.175
43.715
31.332
220
200
180
160
140
120
100
80
60
40
20
0
ppm


vl11p099_f3_1H
File: Proton
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 22.0 C / 295.1 K
Operator: vlau
VNMRS-400 "nmr400"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 4.000 sec
Width 5605.4 Hz
16 repetitions
OBSERVE H1, 399.7143567 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 12 sec
7.702
7.701
7.687
7.397
7.382
7.377
7.372
7.260
7.157
7.156
7.136
3.932
3.089
3.088
3.076
3.073
3.067
3.057
2.877
2.867
2.867
2.861
2.860
2.857
2.846
2.845
1.564
11 10 9 8 7 6 5 4 3 2 1 -0 -1 ppm
0.75 0.94
0.85
2.00
2.03
2.04

Br
S
O

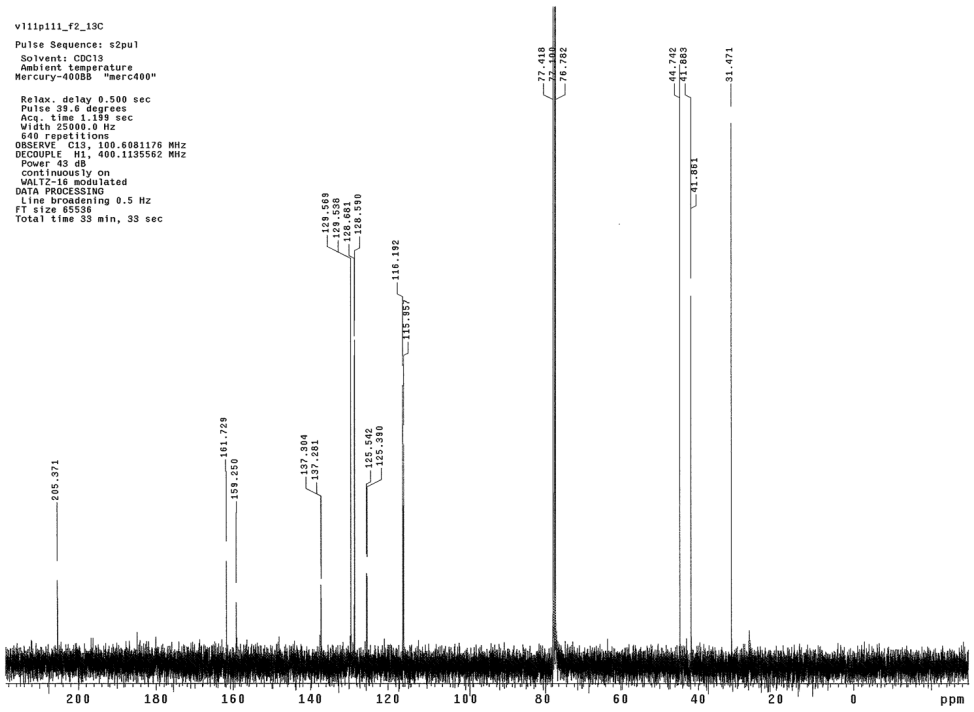
3d

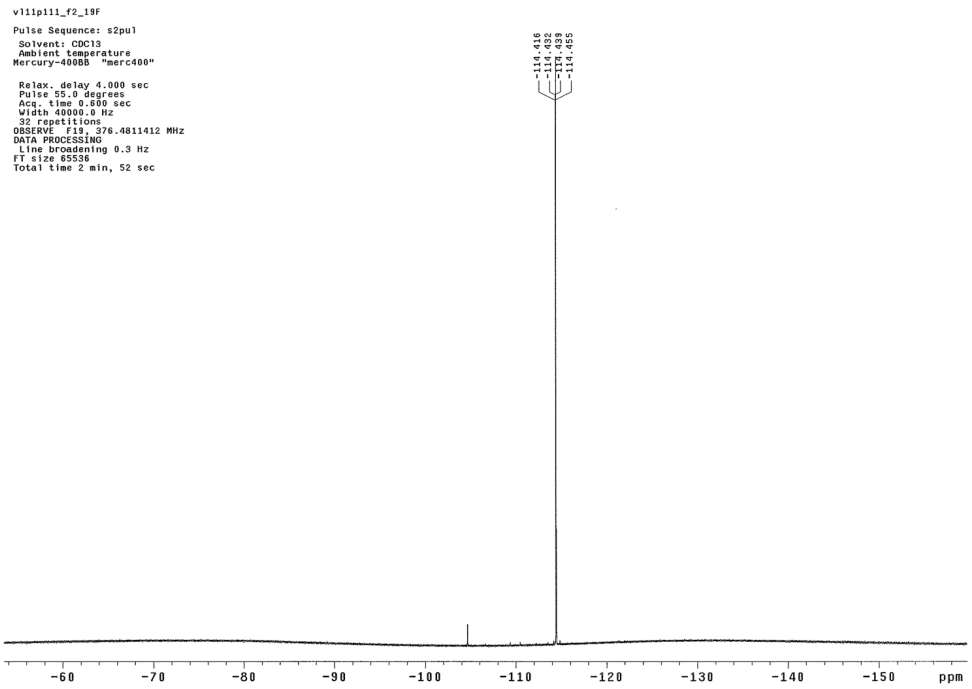

vl11p099_f3_13C
File: Carbon
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 22.0 C / 295.1 K
Operator: vlau
VNMRS-400 "nmr400"
Relax. delay 1.000 sec
Pulse 39.5 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
512 repetitions
OBSERVE C13, 100.5082463 MHz
DECOUPLE H1, 399.7163602 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min, 42 sec
136.398
131.642
131.595
77.413
77.100
76.788
59.688
45.033
31.726
137.239
121.000
205.452
220 200 180 160 140 120 100 80 60 40 20 0 ppm

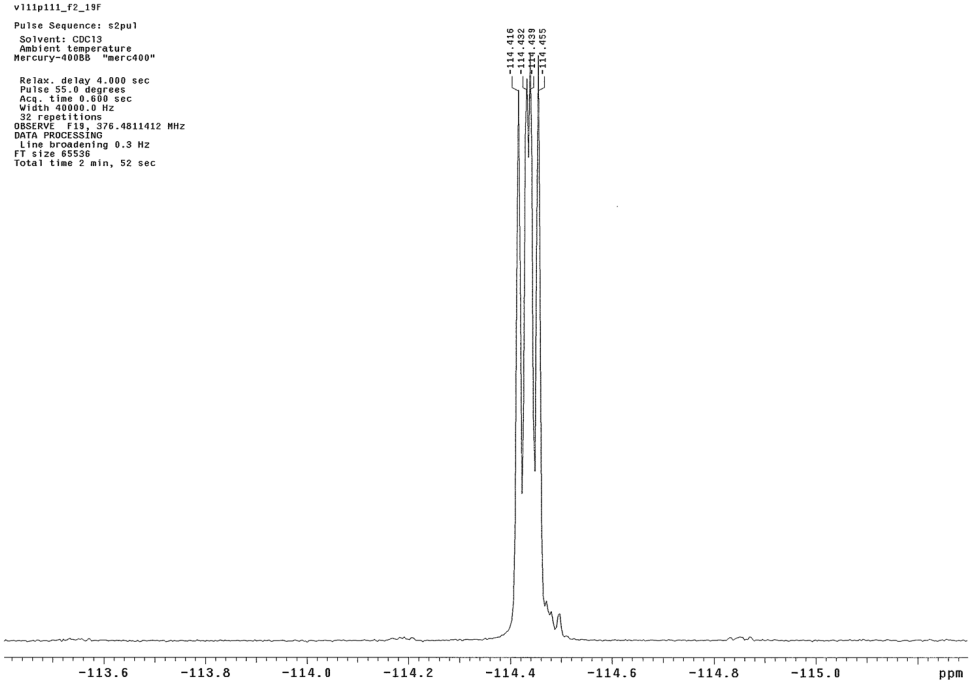

v111p111_f2_1H
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 47.5 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
16 repetitions
OBSERVE H1, 400.1115371 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 22 sec
4.022
3.086
3.083
3.080
3.074
3.063
2.882
2.871
2.865
2.850
7.351
7.332
7.260
7.178
7.164
7.045
0.860.90
0.92
2.00
2.05
2.09
ppm

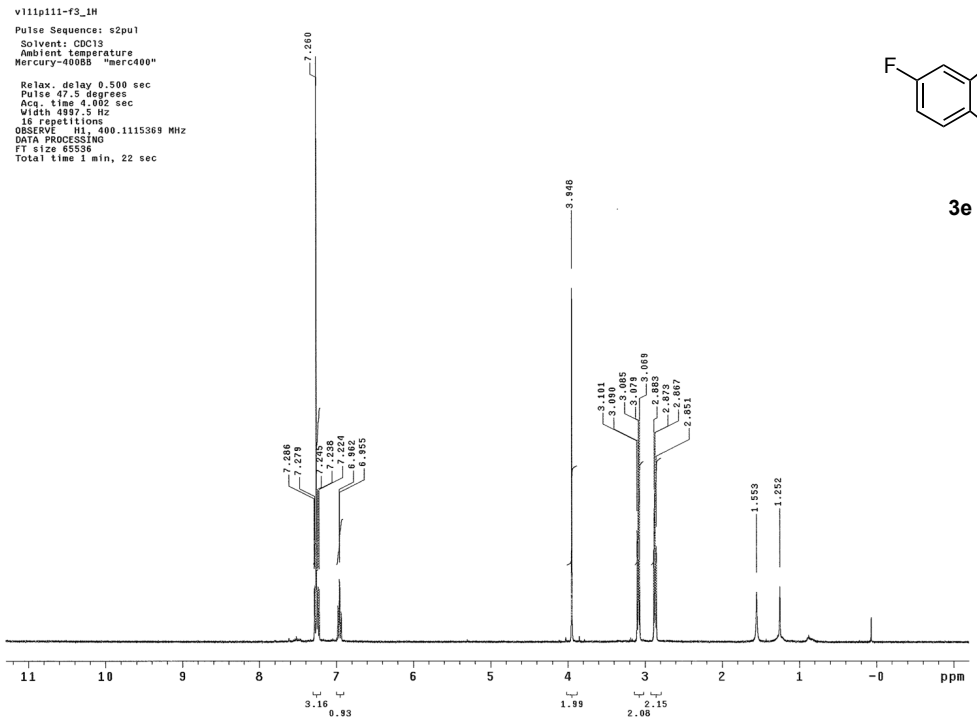
S
O
F

2e

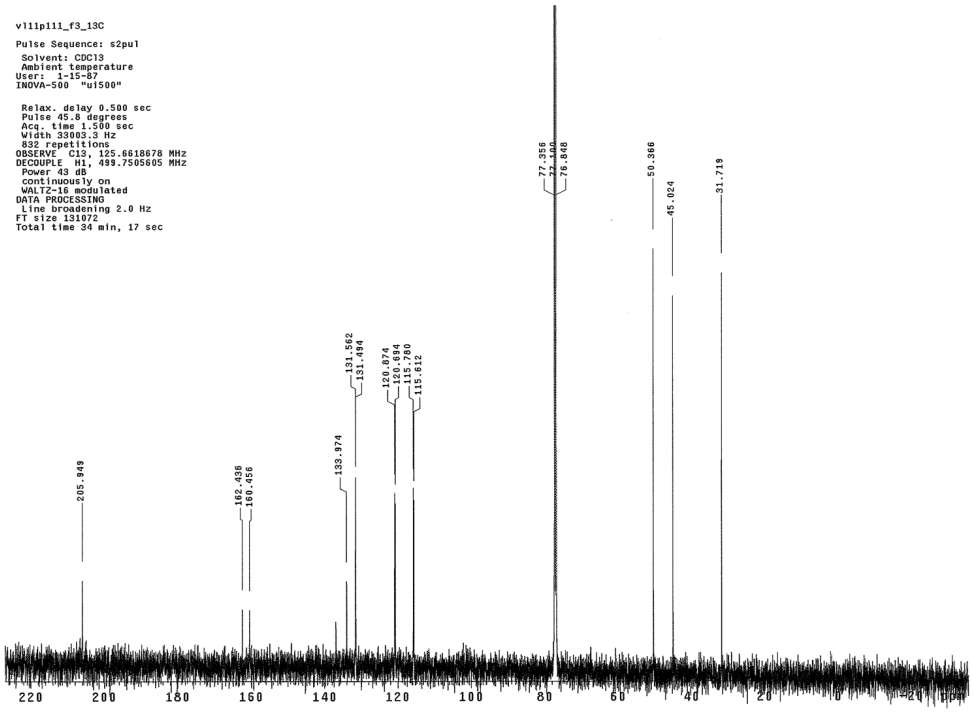

v111p111_f2_13C
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 39.6 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
640 repetitions
OBSERVE C13, 100.6081176 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 33 min, 33 sec
205.371
161.729
159.250
137.804
137.281
129.569
129.536
129.461
128.510
125.542
125.380
116.192
115.957
77.418
77.100
76.782
44.742
41.883
41.861
31.471
ppm

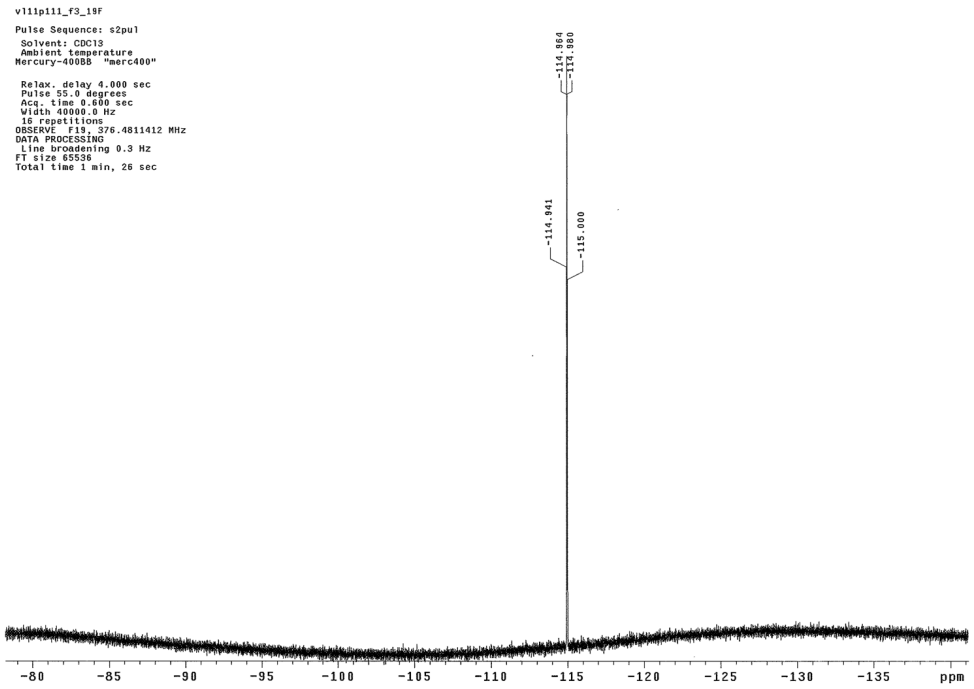

v111p111_f2_19F
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 4.000 sec
Pulse 55.0 degrees
Acq. time 0.600 sec
Width 40000.0 Hz
32 repetitions
OBSERVE F19, 376.4811412 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 2 min, 52 sec
-114.416
-114.432
-114.439
-114.455
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
ppm

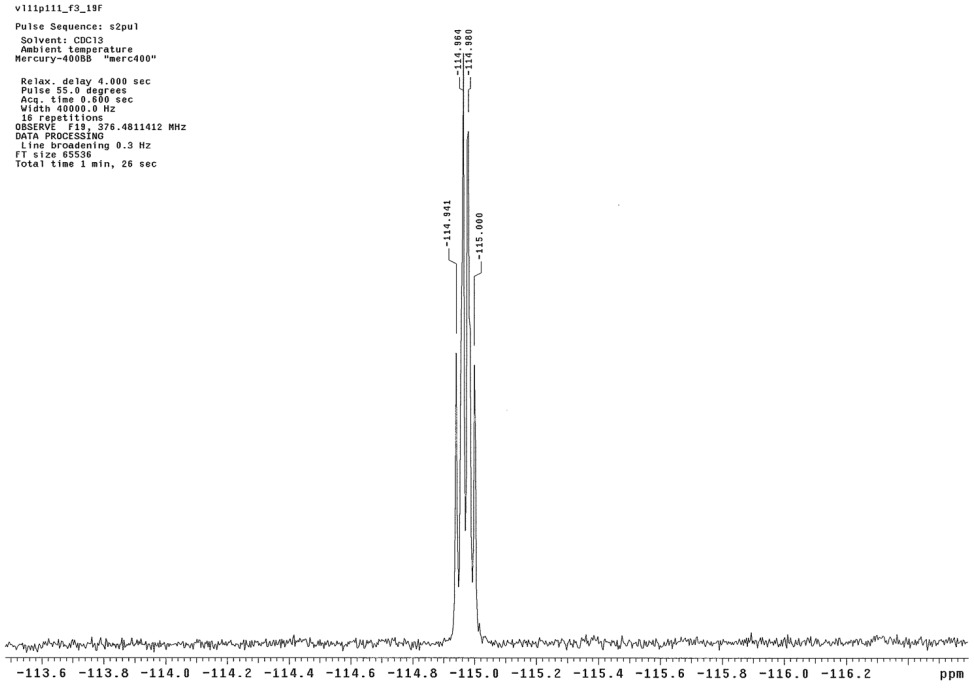

v111p111_f2_19F
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 4.000 sec
Pulse 55.0 degrees
Acq. time 0.600 sec
Width 40000.0 Hz
32 repetitions
OBSERVE F19, 376.4811412 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 2 min, 52 sec
-114.416
-114.432
-114.439
-114.455
-113.6
-113.8
-114.0
-114.2
-114.4
-114.6
-114.8
-115.0
ppm

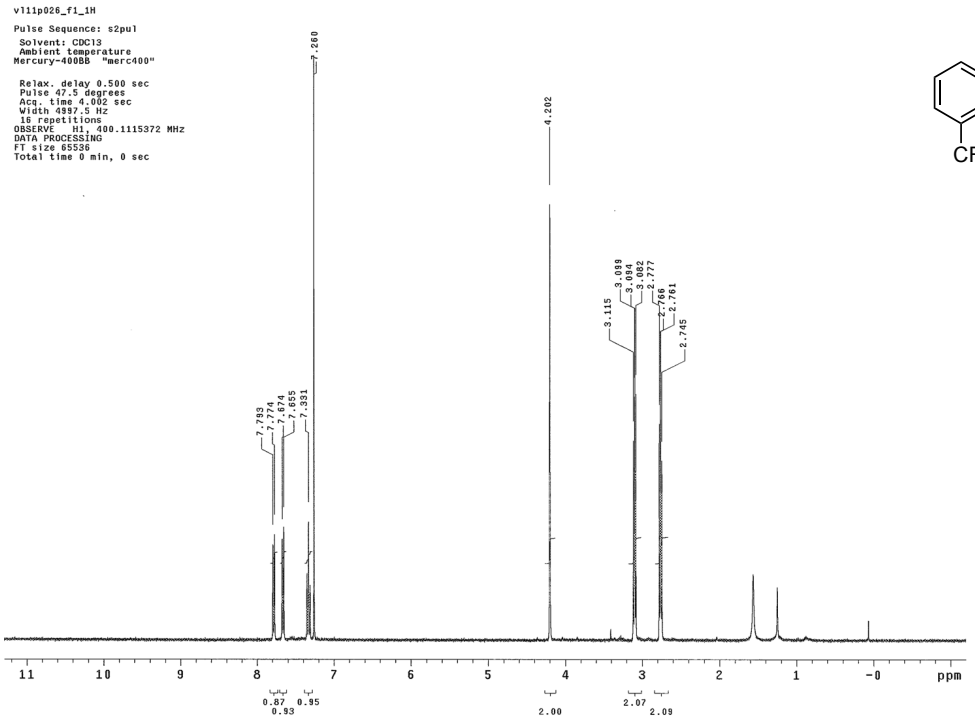

v111p111-f3_1H
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 47.5 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
16 repetitions
OBSERVE H1, 400.1115369 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 22 sec
7.260
7.286
7.279
7.245
7.238
7.224
6.962
6.955
3.946
3.101
3.088
3.085
3.079
3.069
2.883
2.873
2.867
2.851
1.553
1.252
3.16
0.93
1.99
2.15
2.08
ppm

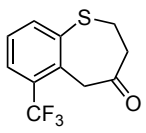
3e


v111p111_f3_13C
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-15-87
INOVA-500 "u1500"
Relax. delay 0.500 sec
Pulse 45.8 degrees
Acq. time 1.500 sec
Width 33003.3 Hz
832 repetitions
OBSERVE C13, 125.6618678 MHz
DECOUPLE H1, 499.7505605 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 34 min, 17 sec
205.949
162.436
160.456
133.974
131.562
131.494
120.674
120.634
115.780
115.612
77.356
77.148
76.848
50.366
45.024
31.719
ppm

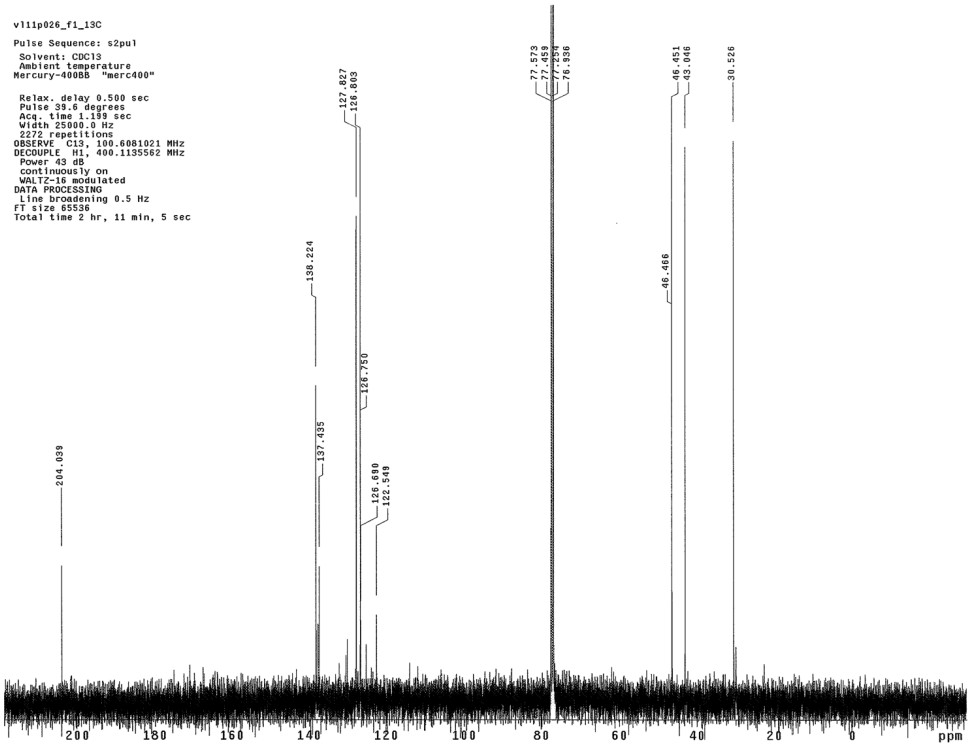

v111p111_f3_19F
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 4.000 sec
Pulse 55.0 degrees
Acq. time 0.600 sec
Width 40000.0 Hz
16 repetitions
OBSERVE F19, 376.4811412 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min, 26 sec
-114.864
-114.980
-114.941
-115.000
-80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 ppm

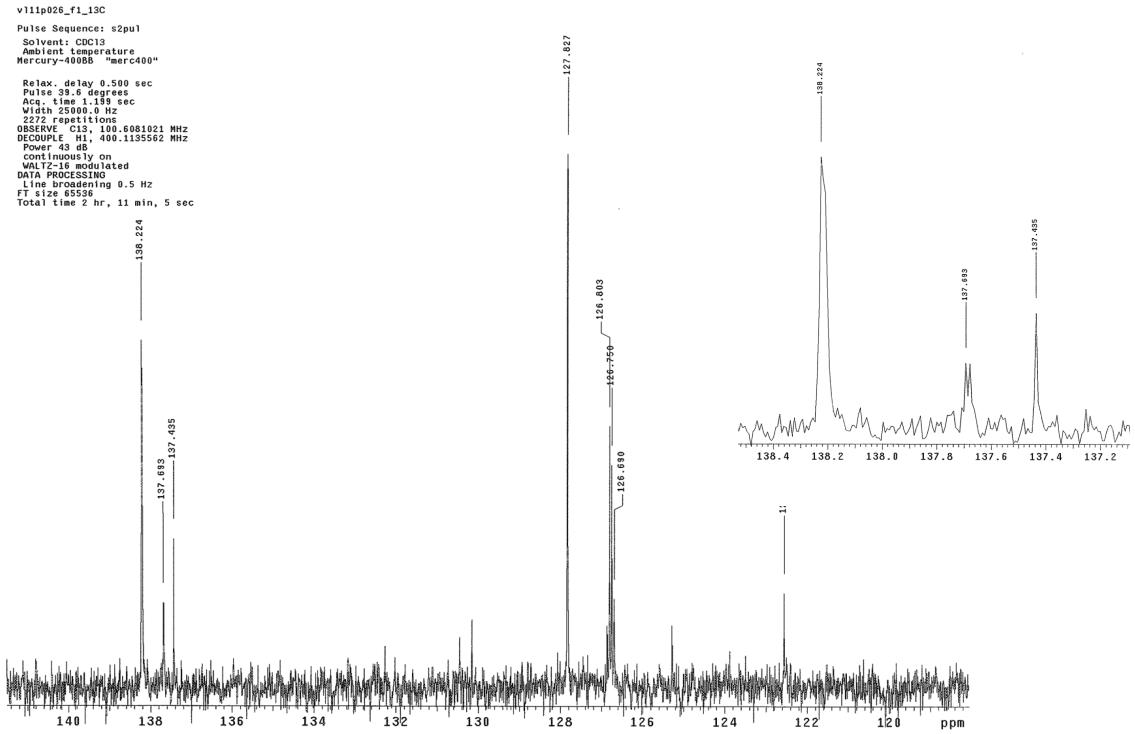

v111p111_f3_19F
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 4.000 sec
Pulse 55.0 degrees
Acq. time 0.600 sec
Width 40000.0 Hz
16 repetitions
OBSERVE F19, 376.4811412 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min, 26 sec
-114.864
-114.980
-114.941
-115.000
-113.6 -113.8 -114.0 -114.2 -114.4 -114.6 -114.8 -115.0 -115.2 -115.4 -115.6 -115.8 -116.0 -116.2 ppm

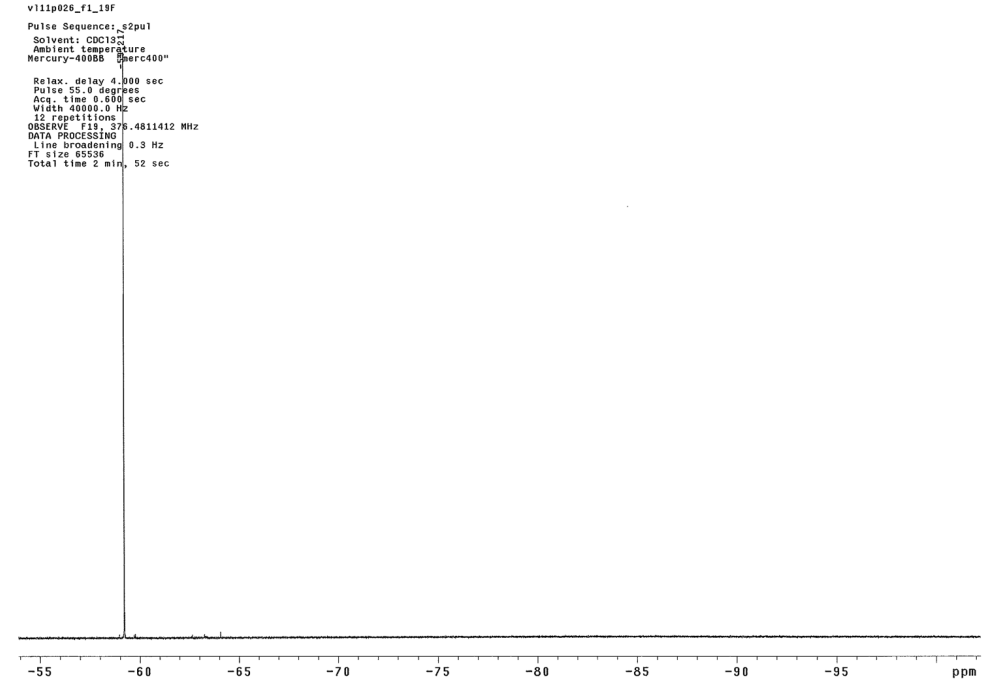

v111p026_f1_1H
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 47.5 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
16 repetitions
OBSERVE H1, 400.1115372 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 0 sec
7.260
4.202
3.115
3.099
3.084
3.062
2.777
2.766
2.761
2.745
7.788
7.774
7.674
7.655
7.331
0.87
0.93
0.95
2.00
2.07
2.09
ppm

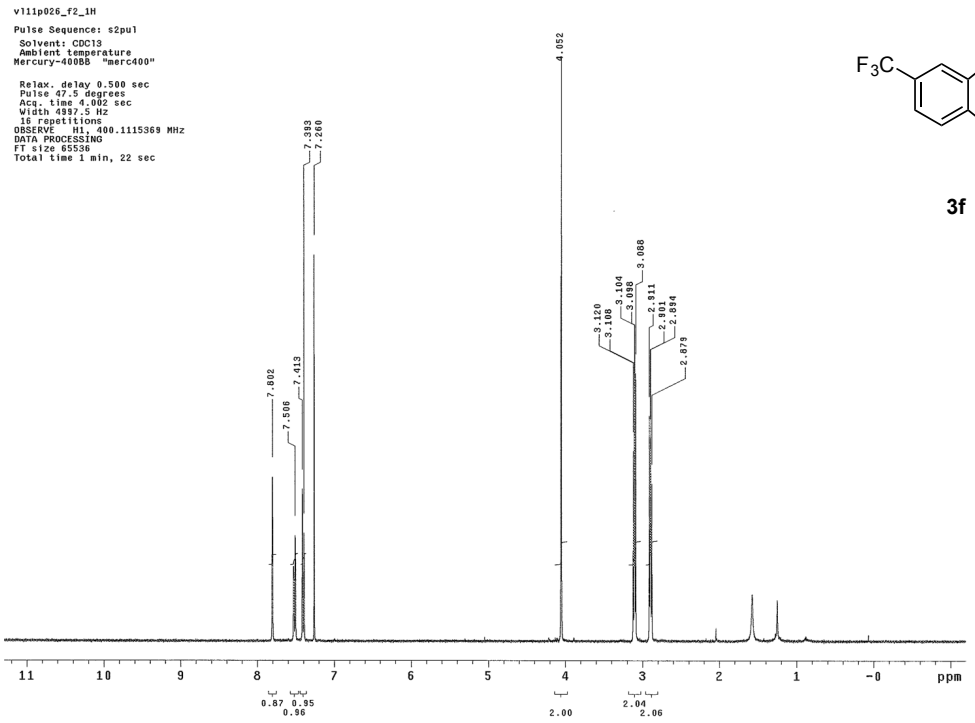

S
O
CF3

2f

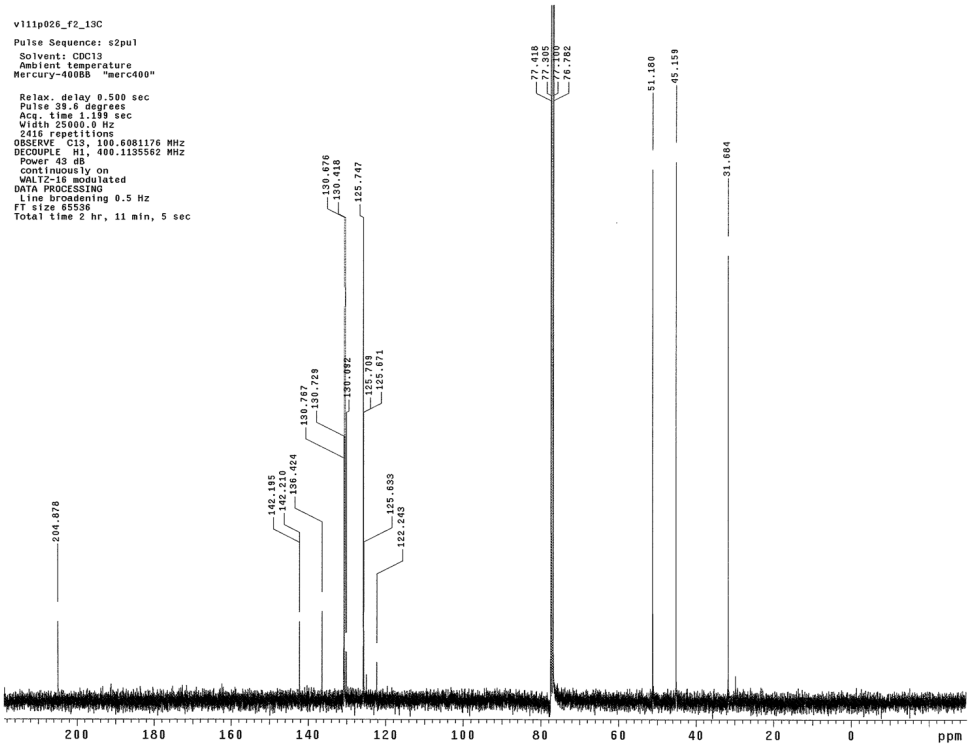

v111p026_f1_13C
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 39.6 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
2272 repetitions
OBSERVE C13, 100.6081021 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
line broadening 0.5 Hz
FT size 65536
Total time 2 hr, 11 min, 5 sec
204.039
138.224
137.435
127.827
126.803
126.750
126.680
122.548
77.573
77.459
77.256
76.938
46.451
46.466
43.046
30.526
ppm

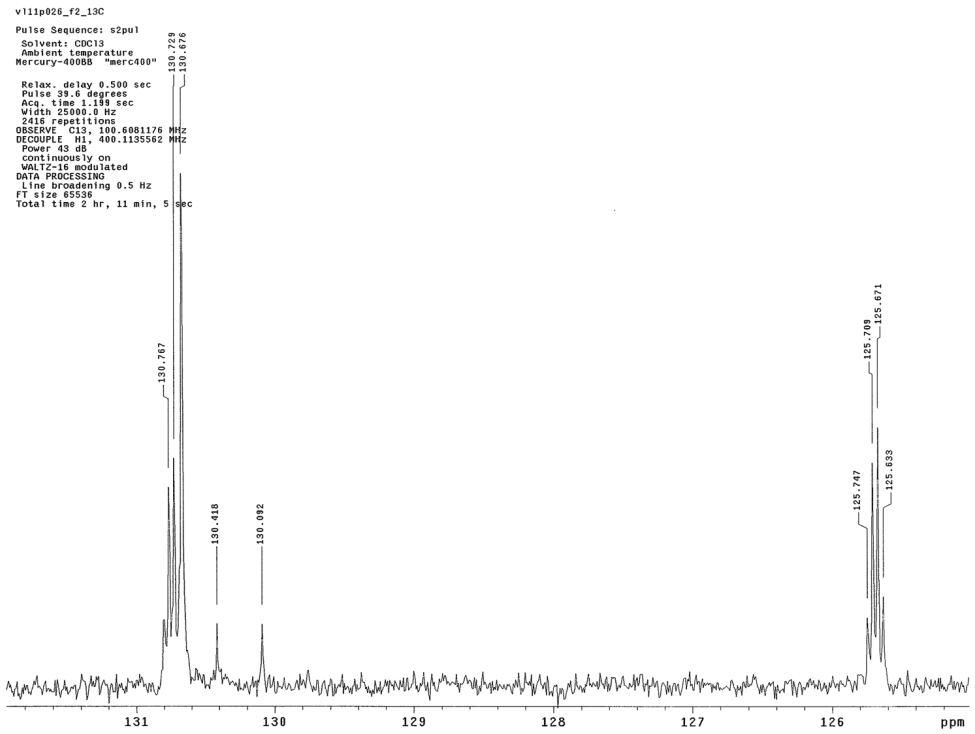

v111p026_f1_13C
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 39.6 degrees
Acq. time 1.189 sec
Width 25000.0 Hz
2272 repetitions
OBSERVE C13, 100.6081021 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 2 hr, 11 min, 5 sec
138.224
137.693
137.435
127.827
126.803
126.750
126.690
140
138
136
134
132
130
128
126
124
122
120
ppm
138.4
138.2
138.0
137.8
137.6
137.4
137.2

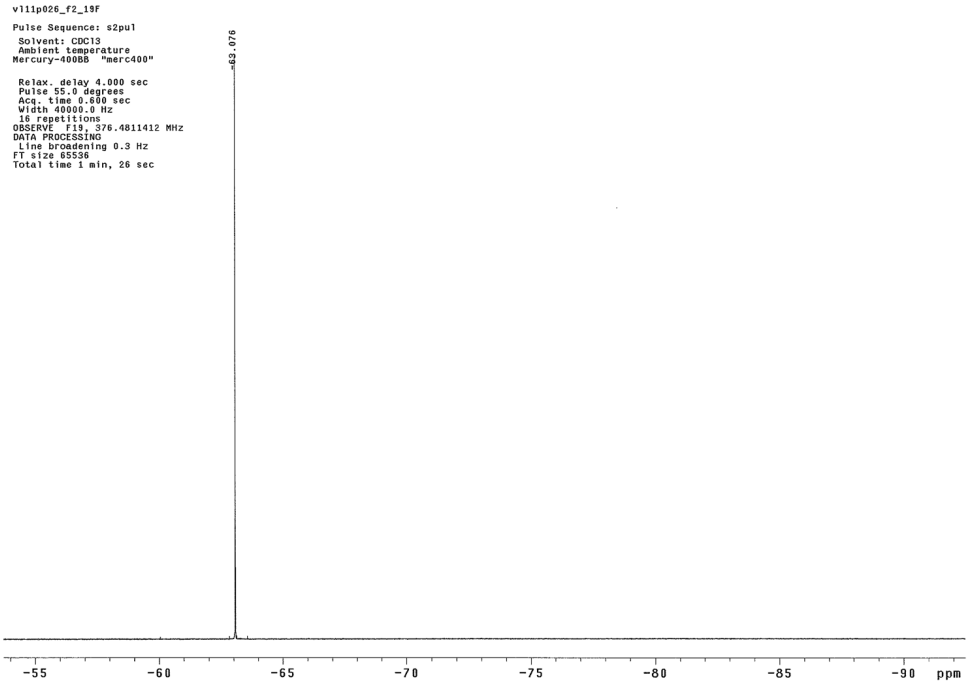

v111p026_f1_19F
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 4.000 sec
Pulse 55.0 degrees
Acq. time 0.600 sec
Width 40000.0 Hz
12 repetitions
OBSERVE F19, 376.4811412 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 2 min, 52 sec
-55
-60
-65
-70
-75
-80
-85
-90
-95
ppm

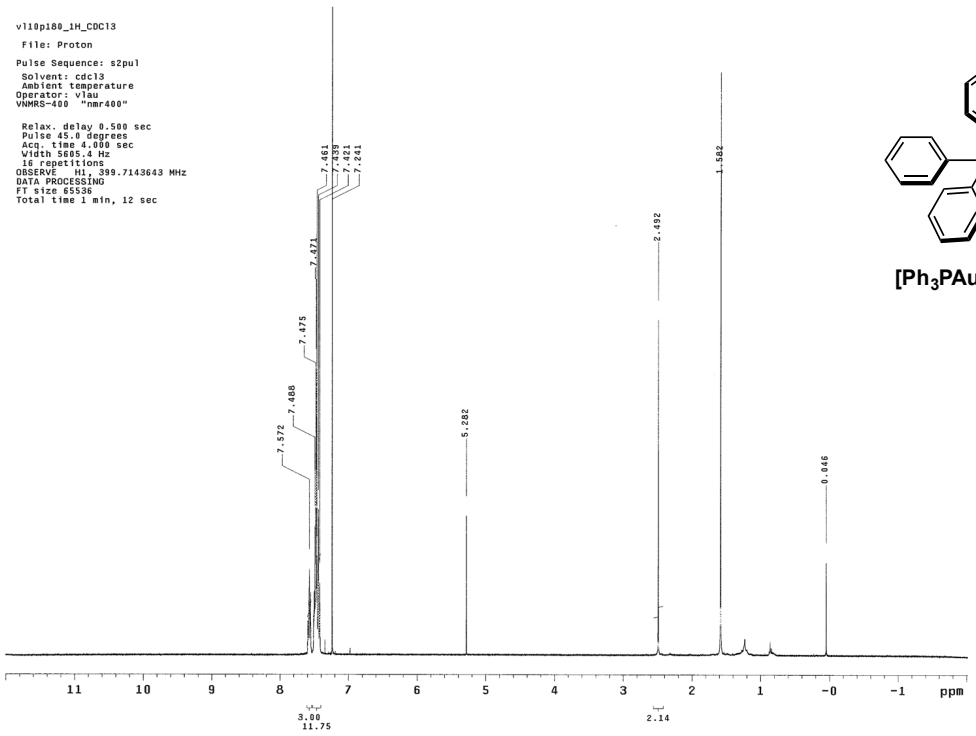

v111p026_f2_1H
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 47.5 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
16 repetitions
OBSERVE H1, 400.1115369 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 22 sec
7.802
7.506
7.413
7.393
7.260
4.052
3.120
3.108
3.104
3.088
3.088
2.911
2.901
2.894
2.879
0.87
0.95
0.96
2.00
2.04
2.06
ppm

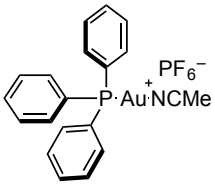
3f


v111p026_f2_13C
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 39.6 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
2416 repetitions
OBSERVE C13, 100.6081176 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 2 hr, 11 min, 5 sec
204.878
142.195
142.210
136.424
130.787
130.729
130.676
130.418
130.092
125.747
125.709
125.671
125.633
122.243
77.418
77.305
77.300
76.782
51.180
45.159
31.684
ppm

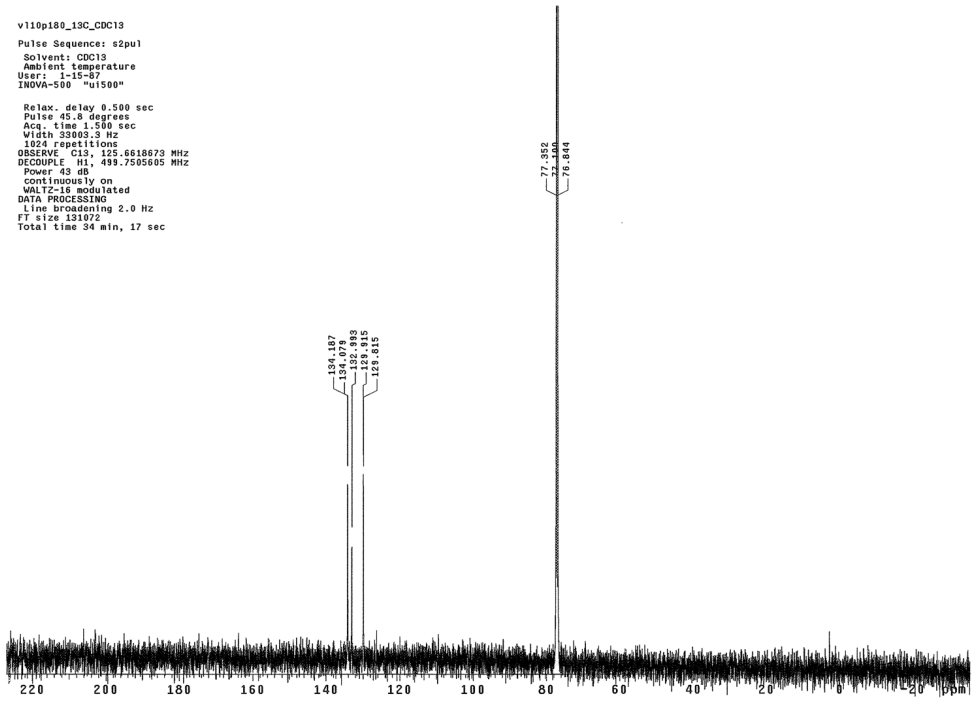

v111p026_f2_13C
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 39.6 degrees
Acq. time 1.189 sec
Width 25000.0 Hz
2416 repetitions
OBSERVE C13, 100.6081176 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 2 hr, 11 min, 5 sec
130.729
130.676
130.767
130.418
130.092
125.709
125.671
125.747
125.633
131
130
129
128
127
126
ppm

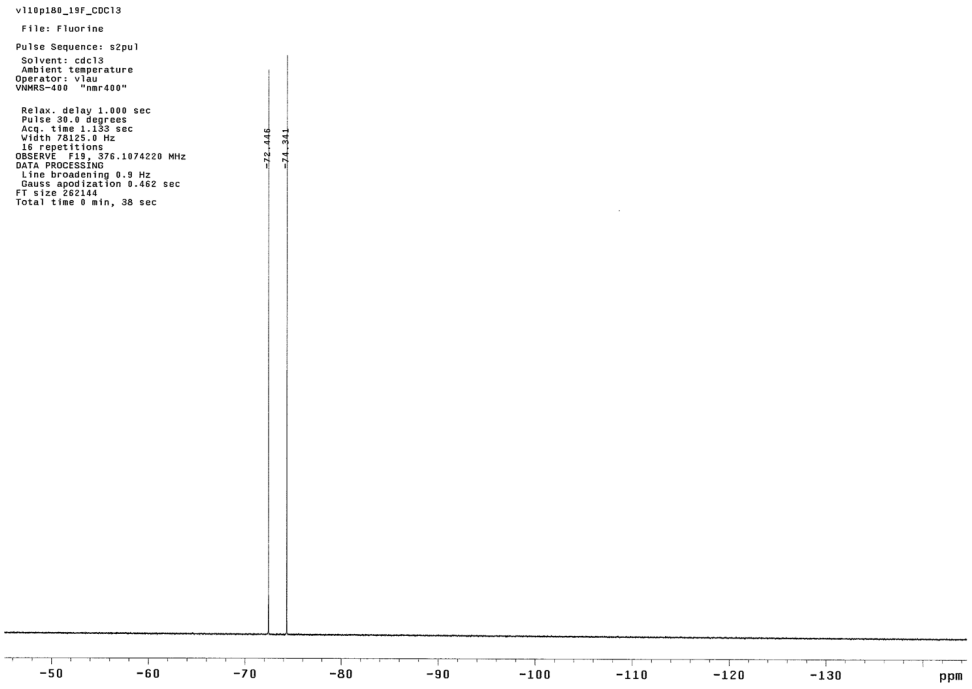

v111p026_f2_19F
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 4.000 sec
Pulse 55.0 degrees
Acq. time 0.600 sec
Width 40000.0 Hz
16 repetitions
OBSERVE F19, 376.4811412 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min, 26 sec
-63.076
-55
-60
-65
-70
-75
-80
-85
-90
ppm

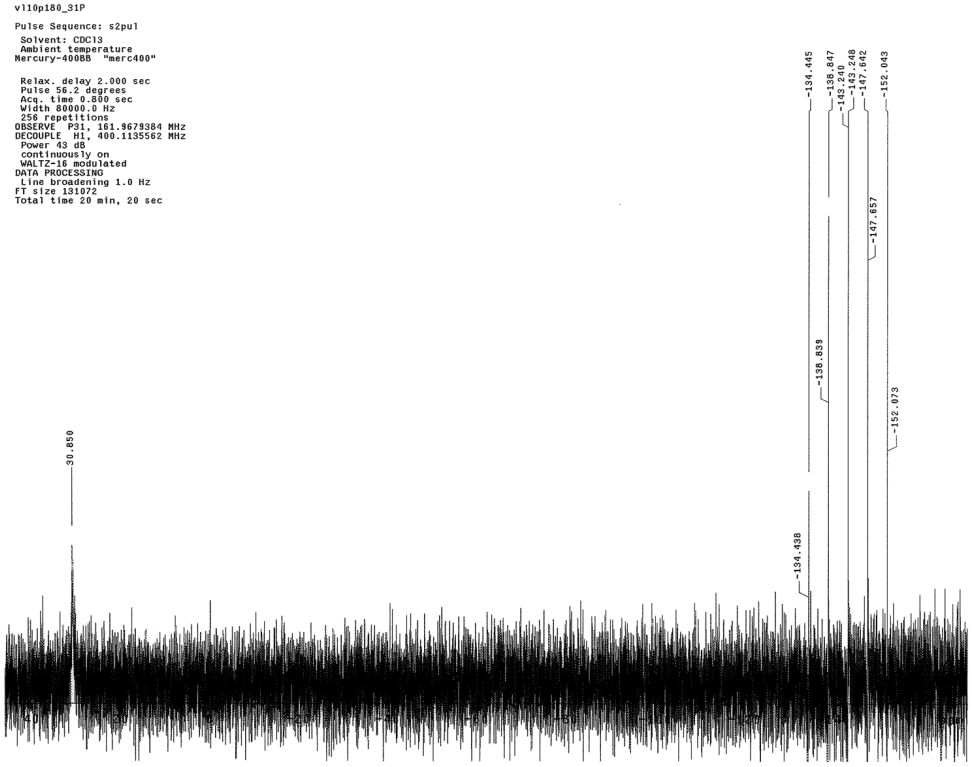


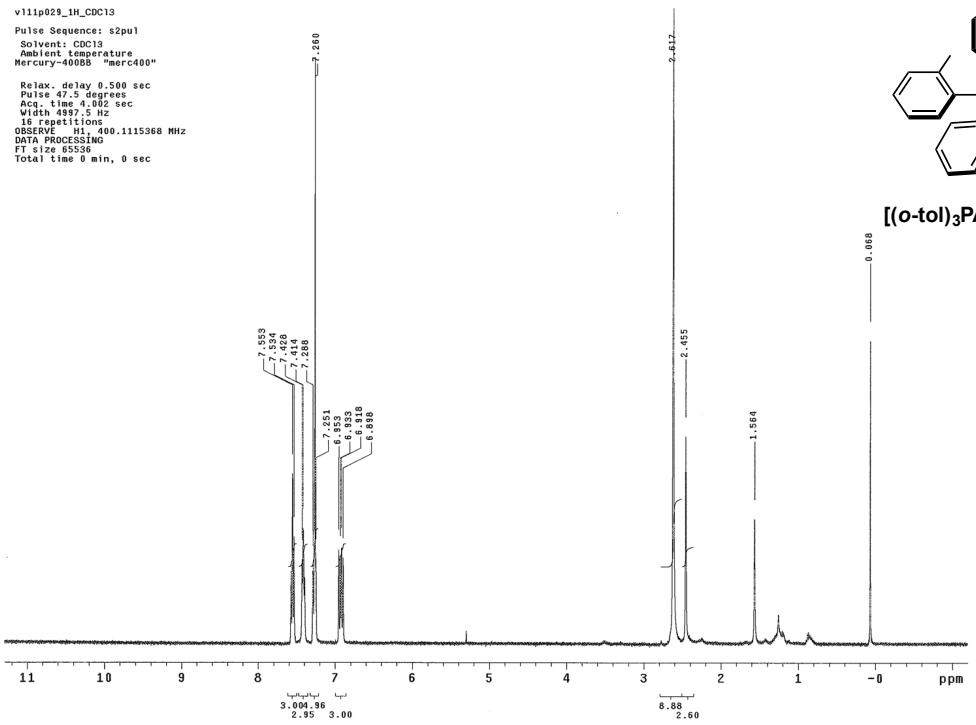


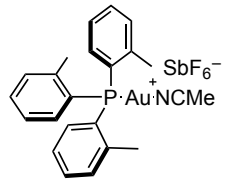
[$Ph_3PAu(NCCH_3)$]PF_6



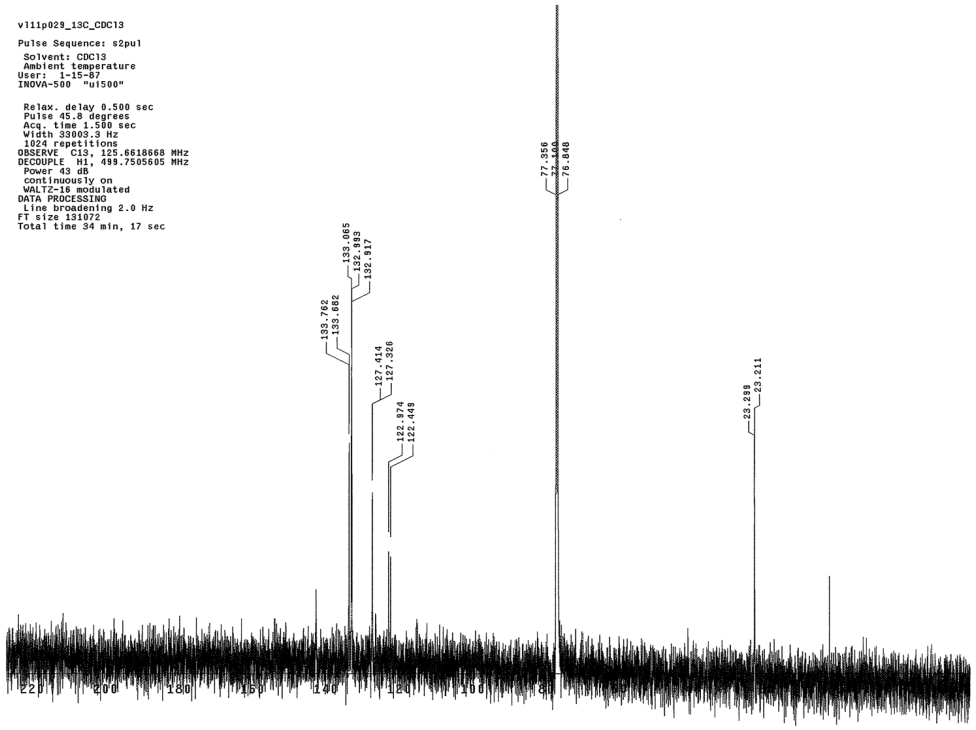

v110p180_19F_CDCl3
File: Fluorine
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vlau
VNMRS-400 "nmr400"
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 1.133 sec
Width 78125.0 Hz
16 repetitions
OBSERVE F19, 376.1074220 MHz
DATA PROCESSING
Line broadening 0.9 Hz
Gauss apodization 0.462 sec
FT size 262144
Total time 0 min, 38 sec
-72.446
-74.341
-50
-60
-70
-80
-90
-100
-110
-120
-130
ppm


v110p180_31P
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 2.000 sec
Pulse 56.2 degrees
Acq. time 0.800 sec
Width 80000.0 Hz
256 repetitions
OBSERVE P31, 161.9679384 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 20 min, 20 sec
30.650
-134.438
-136.839
-134.445
-138.847
-143.240
-143.248
-147.642
-147.657
-152.043
-152.073





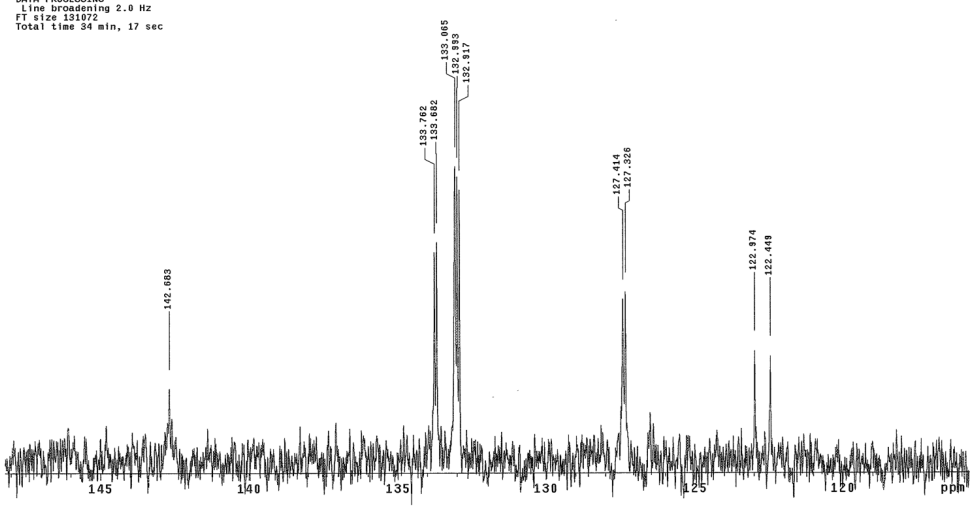
[(*o*-tol)$_3$PAu(NCCH$_3$)]SbF$_6$



v111p029_13C_CDCl3

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-15-87
INOVA-500 "ui500"

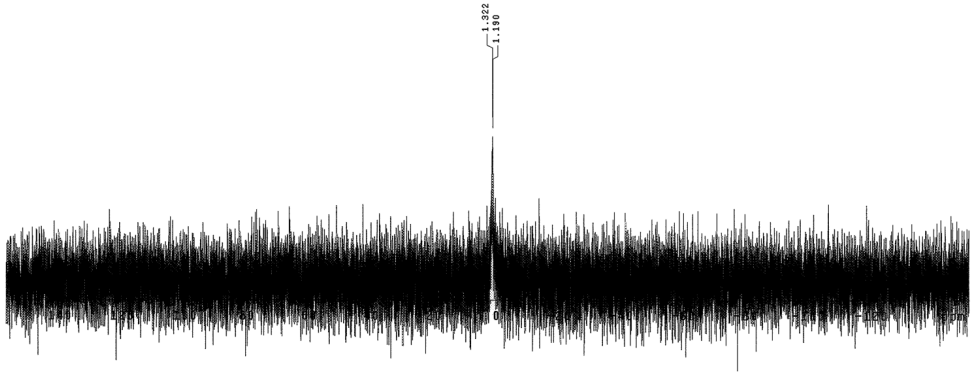
Relax. delay 0.500 sec
Pulse 45.8 degrees
Acq. time 1.500 sec
Width 33003.3 Hz
1024 repetitions
OBSERVE C13, 125.6618668 MHz
DECOUPLE H1, 499.7505605 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 34 min, 17 sec

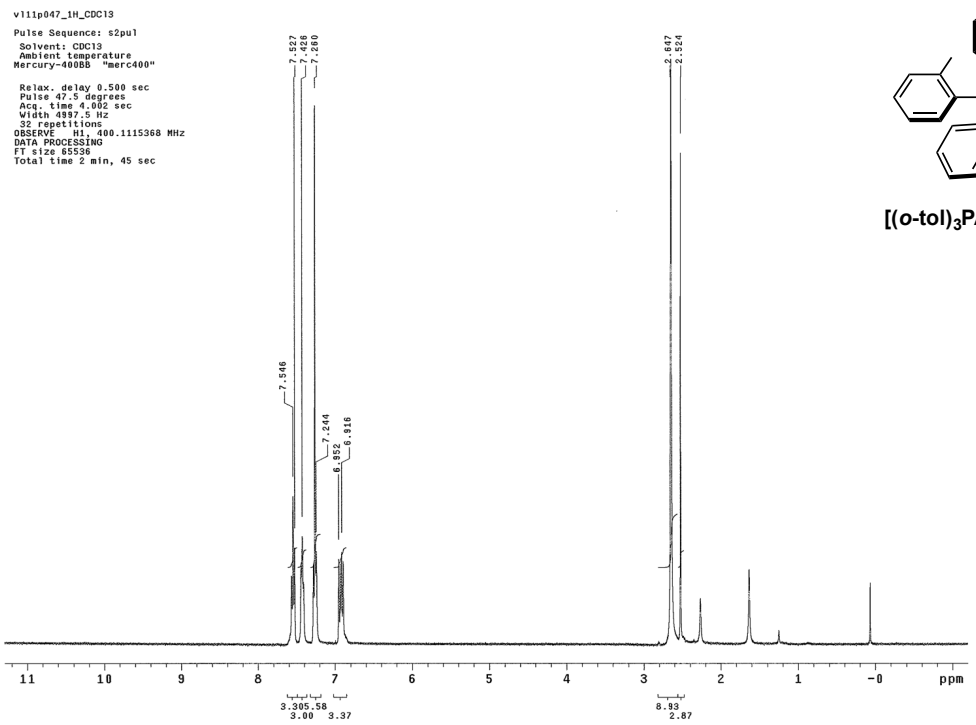


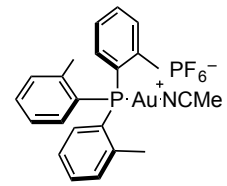
v111p029_31P_CDCl3

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"

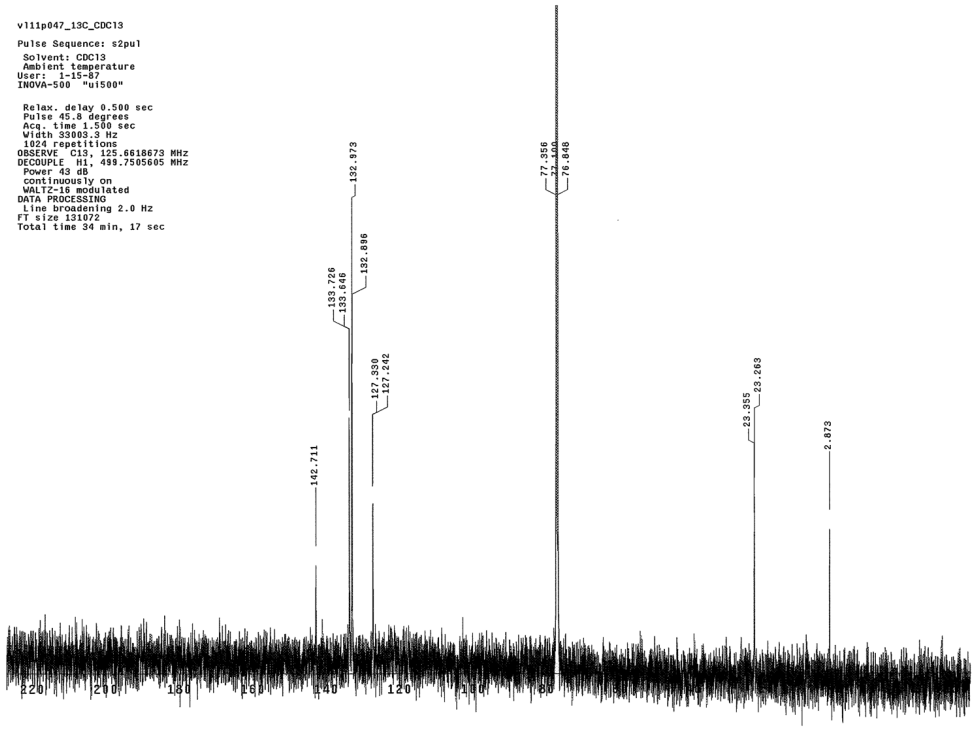
Relax. delay 2.000 sec
Pulse 56.2 degrees
Acq. time 0.800 sec
Width 50000.0 Hz
512 repetitions
OBSERVE P31, 161.9679384 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 34 min, 42 sec

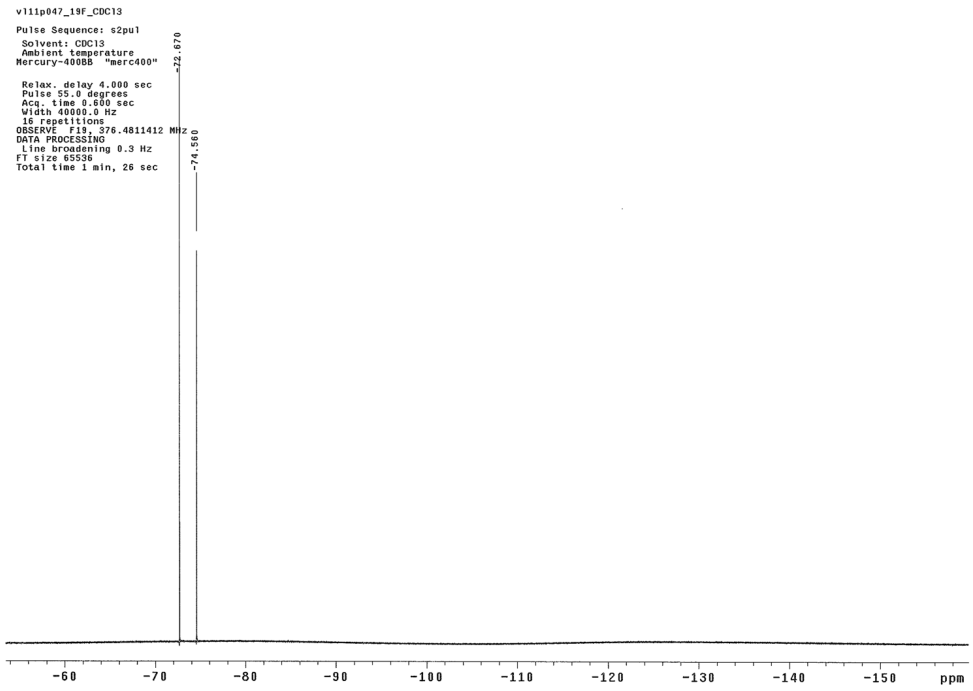


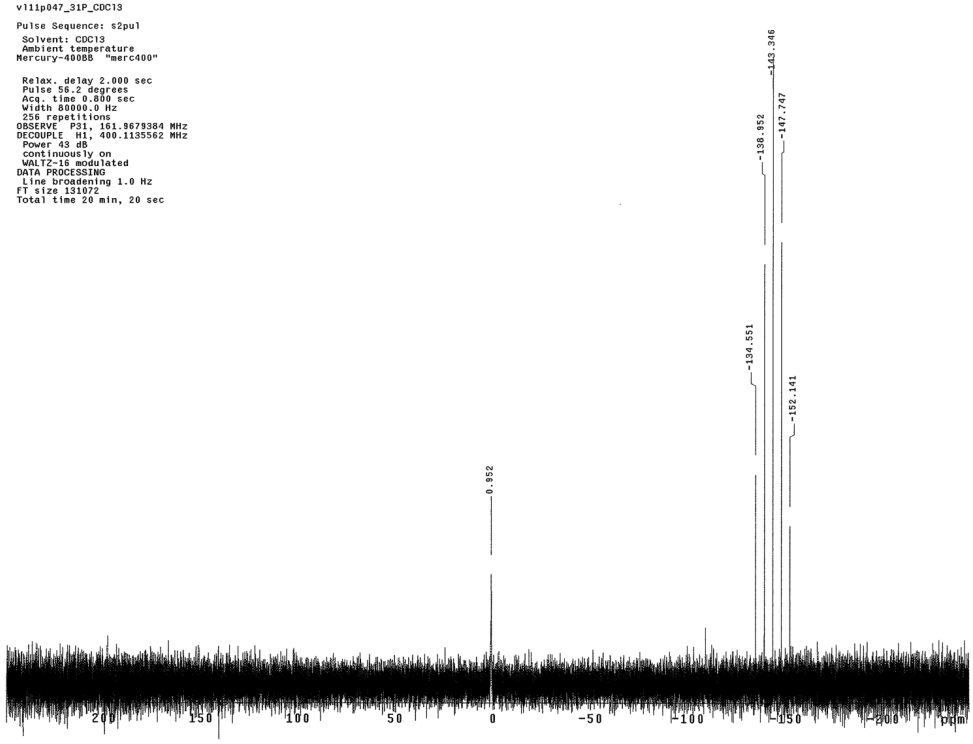


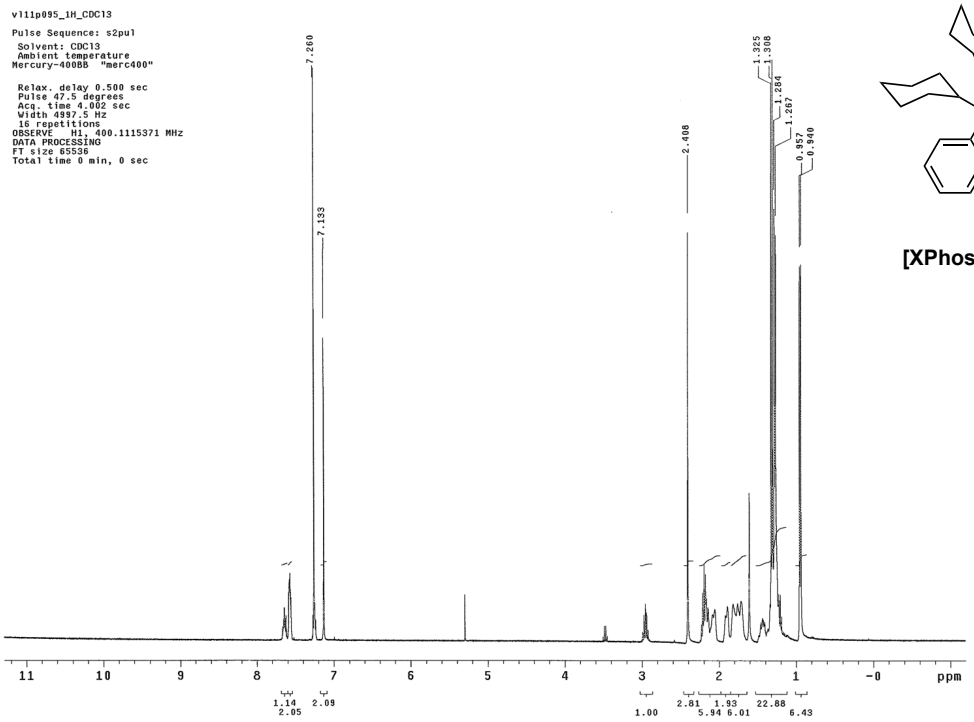


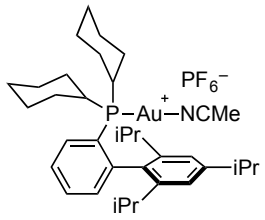
[(*o*-tol)$_3$PAu(NCCH$_3$)]PF$_6$



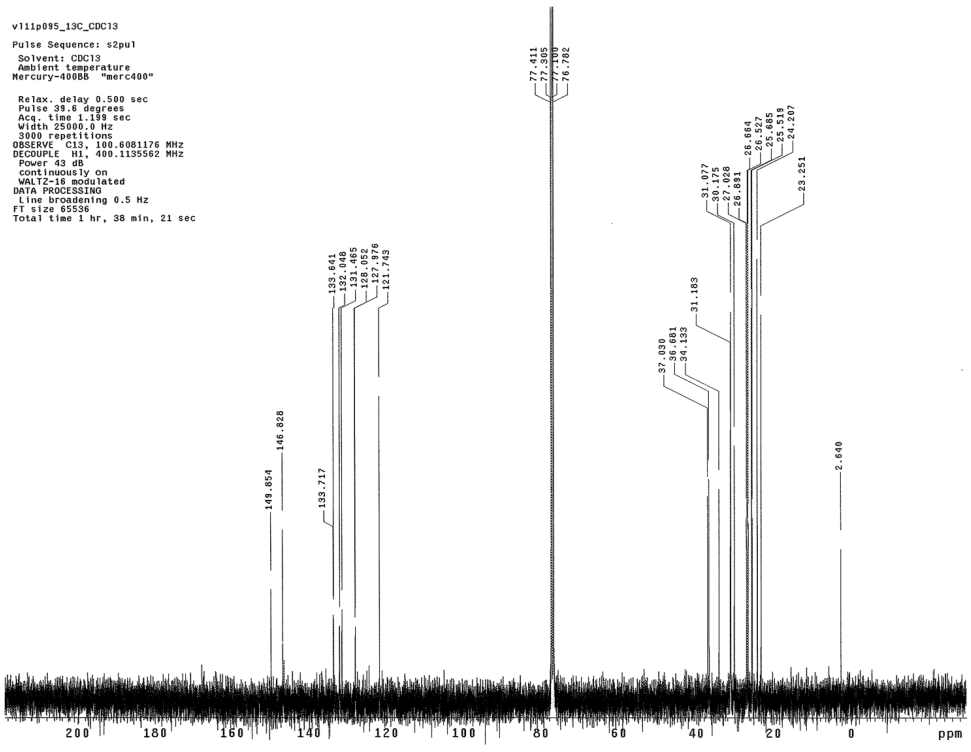

v111p047_19F_CDCl3
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 4.000 sec
Pulse 55.0 degrees
Acq. time 0.600 sec
Width 40000.0 Hz
16 repetitions
OBSERVE F19, 376.4811412 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min, 26 sec
-72.670
-74.560
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
ppm

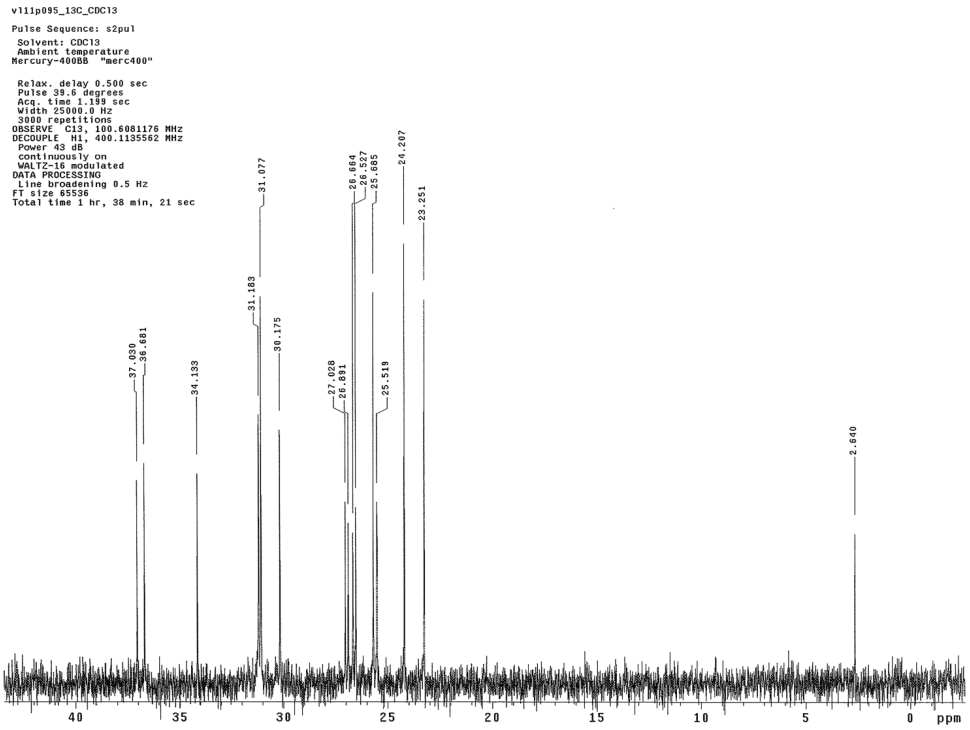

v111p047_31P_CDCl3
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 2.000 sec
Pulse 56.2 degrees
Acq. time 0.800 sec
Width 80000.0 Hz
256 repetitions
OBSERVE P31, 161.9679384 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 20 min, 20 sec
0.952
-134.551
-136.952
-143.346
-147.747
-152.141
200
150
100
50
0
-50
-100
-150
-200
ppm

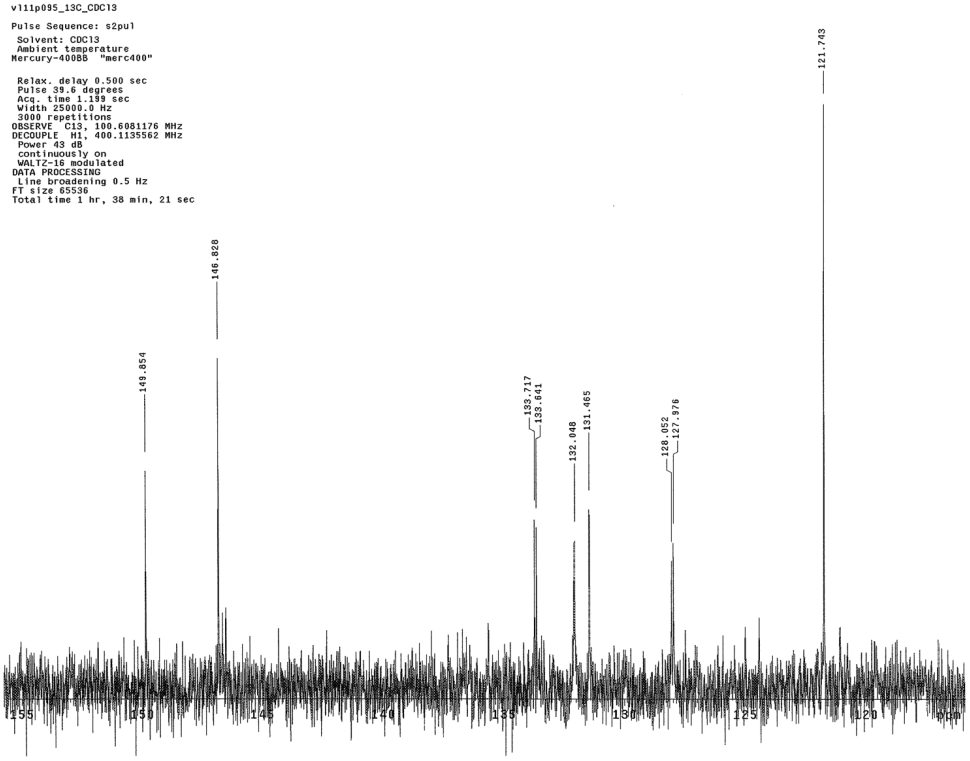


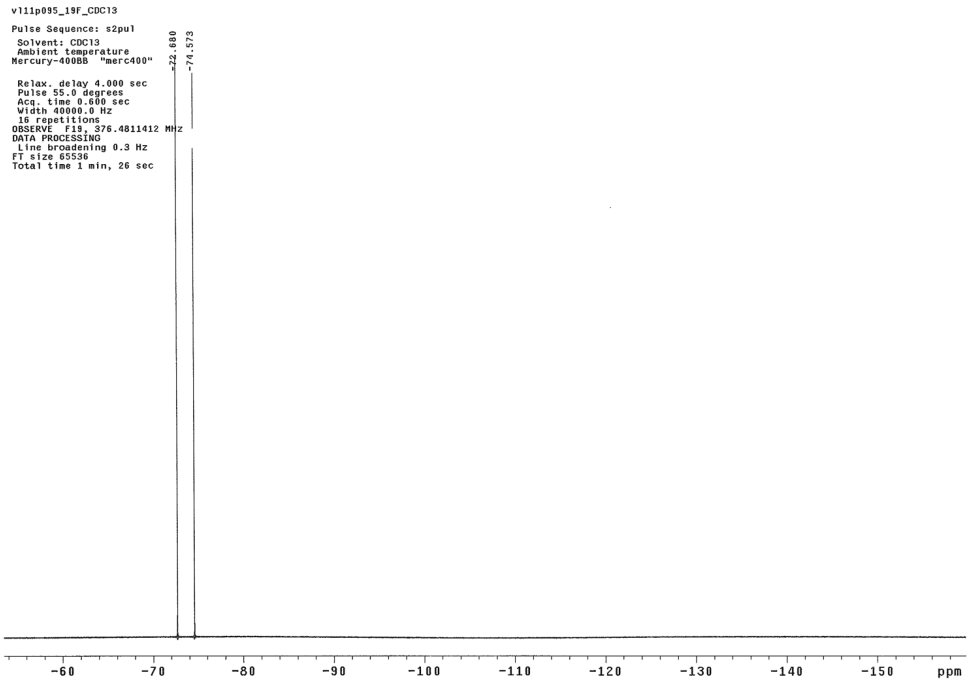


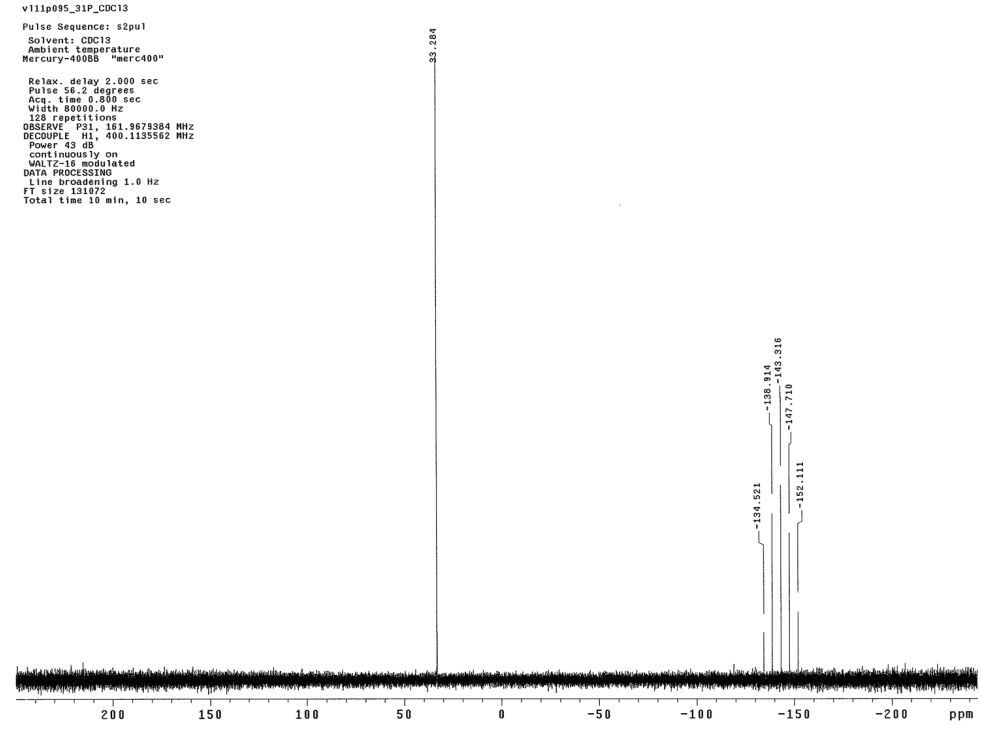
[XPhosAu(NCCH$_3$)]PF$_6$

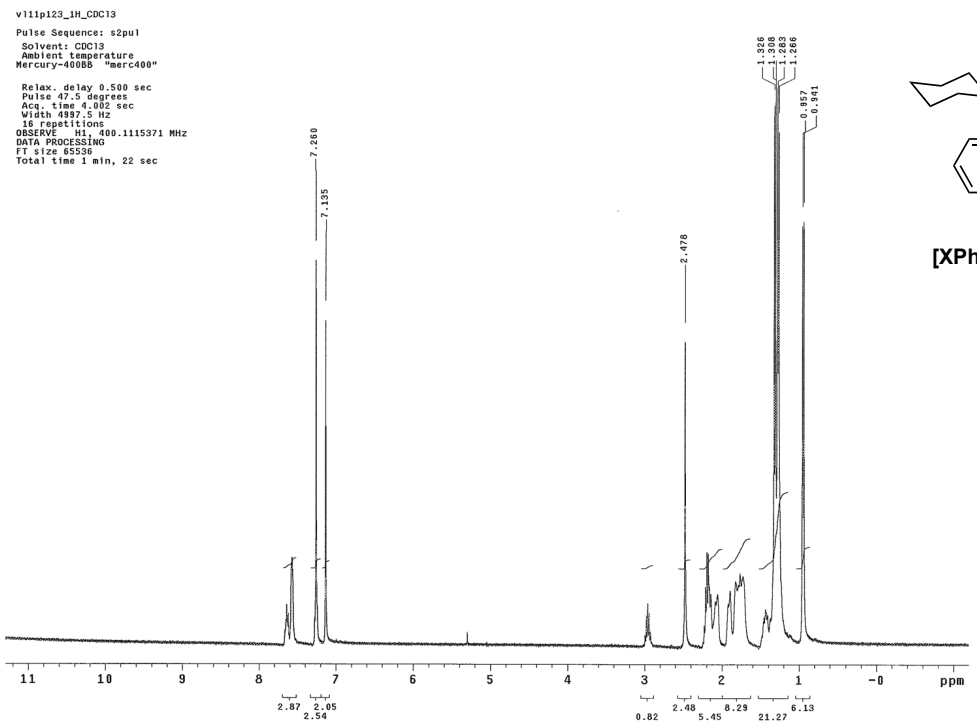


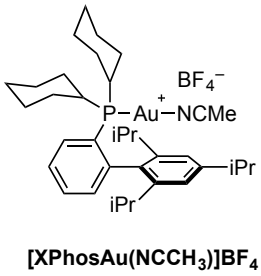

v111p095_13C_CDCl3
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 39.6 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
3000 repetitions
OBSERVE C13, 100.6081176 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 hr, 38 min, 21 sec
37.930
36.681
34.133
31.183
31.077
30.175
27.028
26.881
26.664
26.527
25.685
25.519
24.207
23.251
2.640
40
35
30
25
20
15
10
5
0
ppm


v111p095_13C_CDCl3
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 0.500 sec
Pulse 39.6 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
3000 repetitions
OBSERVE C13, 100.6081176 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 hr, 38 min, 21 sec
149.854
146.828
133.717
133.641
132.048
131.465
128.052
127.976
121.743
155
150
145
140
135
130
125
120
ppm

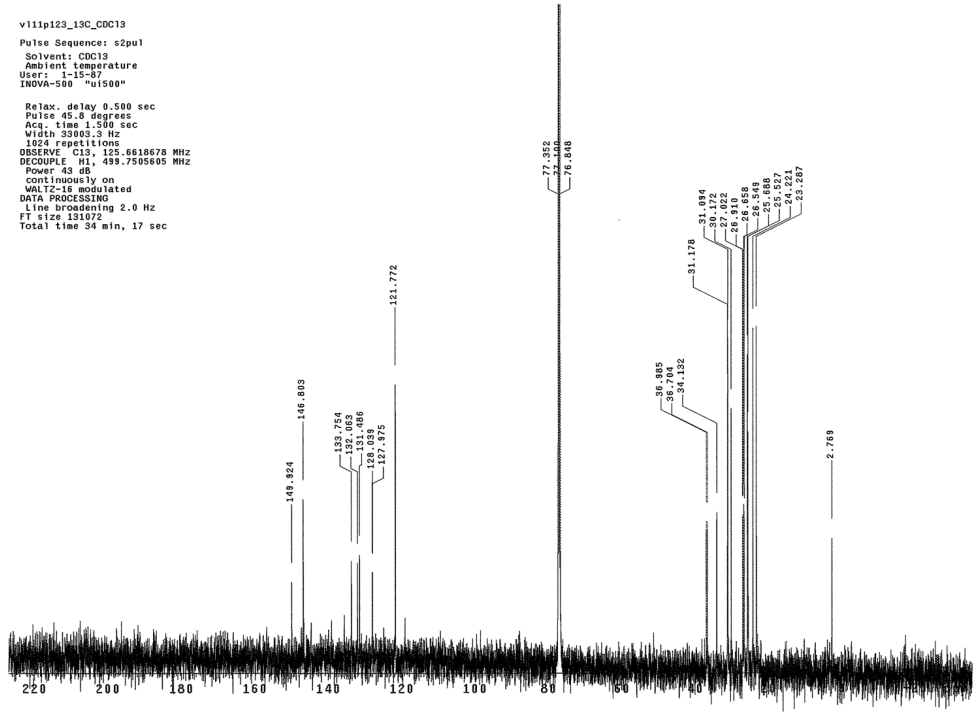

v111p095_19F_CDCl3
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 4.000 sec
Pulse 55.0 degrees
Acq. time 0.600 sec
Width 40000.0 Hz
16 repetitions
OBSERVE F19, 376.4811412 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min, 26 sec
-72.680
-74.573
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
ppm

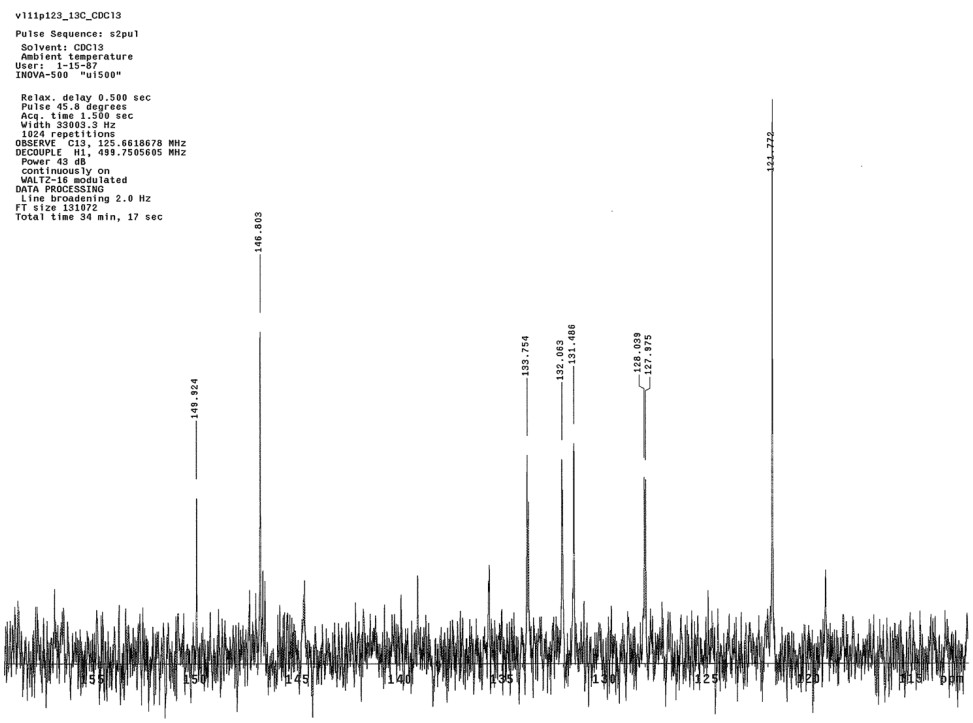

v111p095_31P_CDCl3
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 2.000 sec
Pulse 56.2 degrees
Acq. time 0.800 sec
Width 80000.0 Hz
128 repetitions
OBSERVE P31, 161.9675384 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously On
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 10 min, 10 sec
33.284
-134.521
-138.914
-143.316
-147.710
-152.111
200
150
100
50
0
-50
-100
-150
-200
ppm

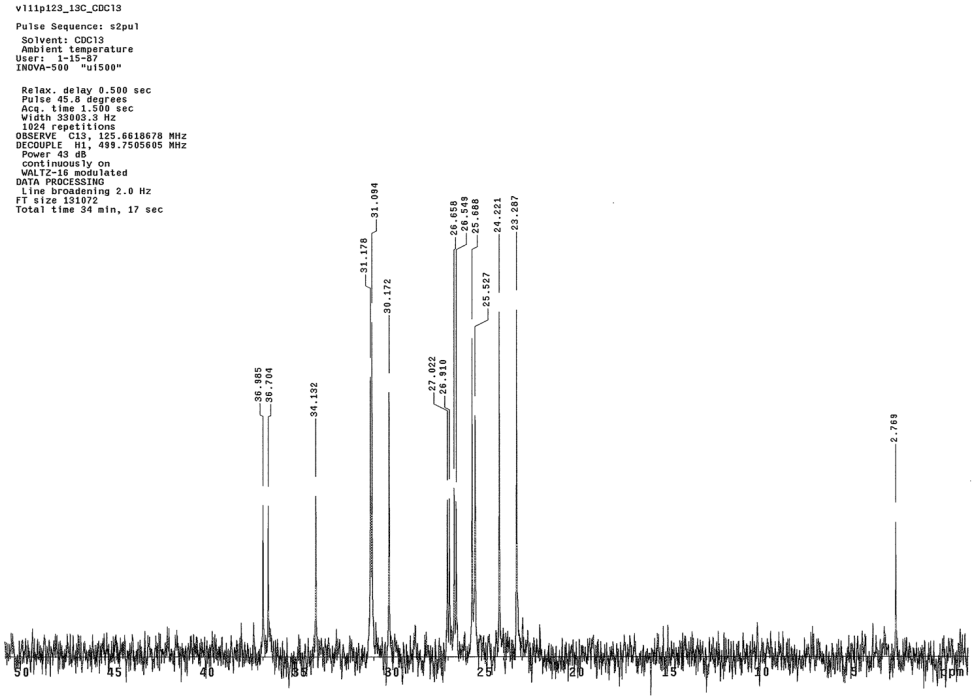


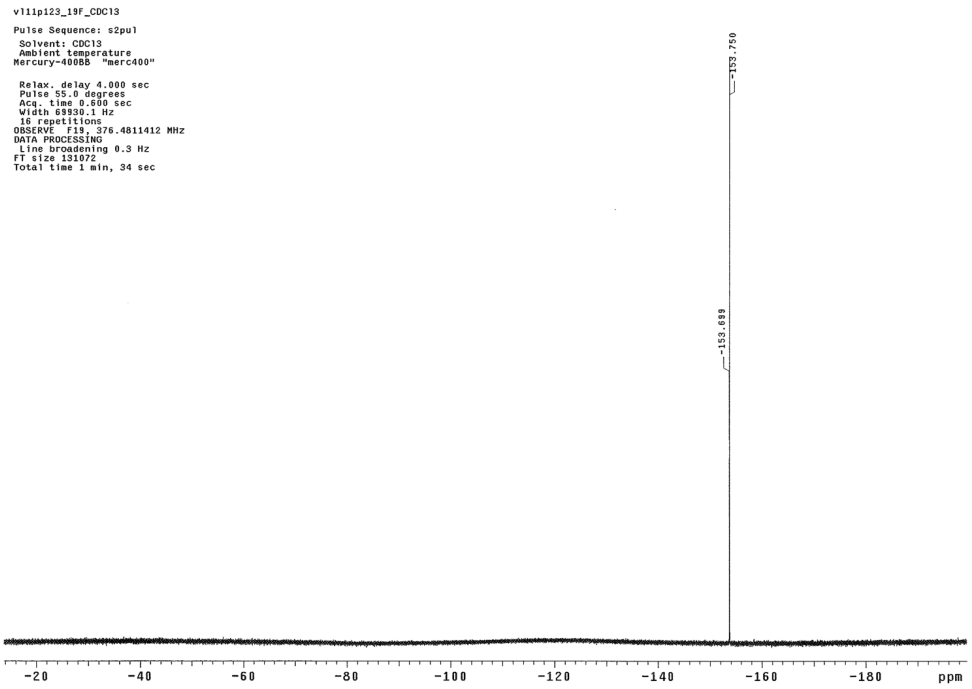


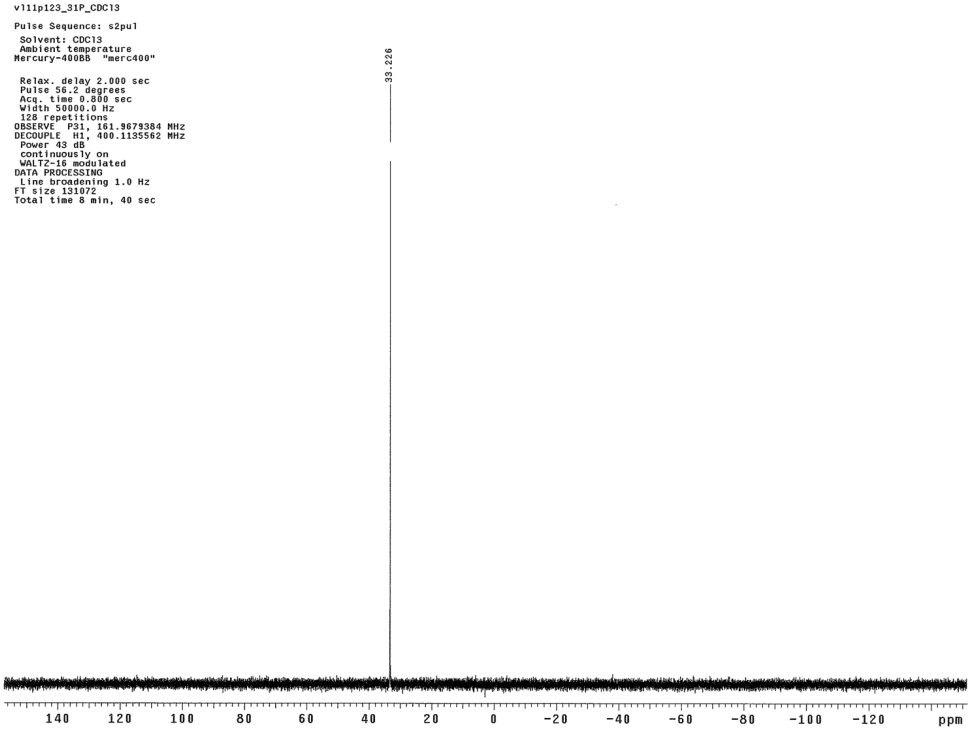
[XPhosAu(NCCH$_3$)]BF$_4$

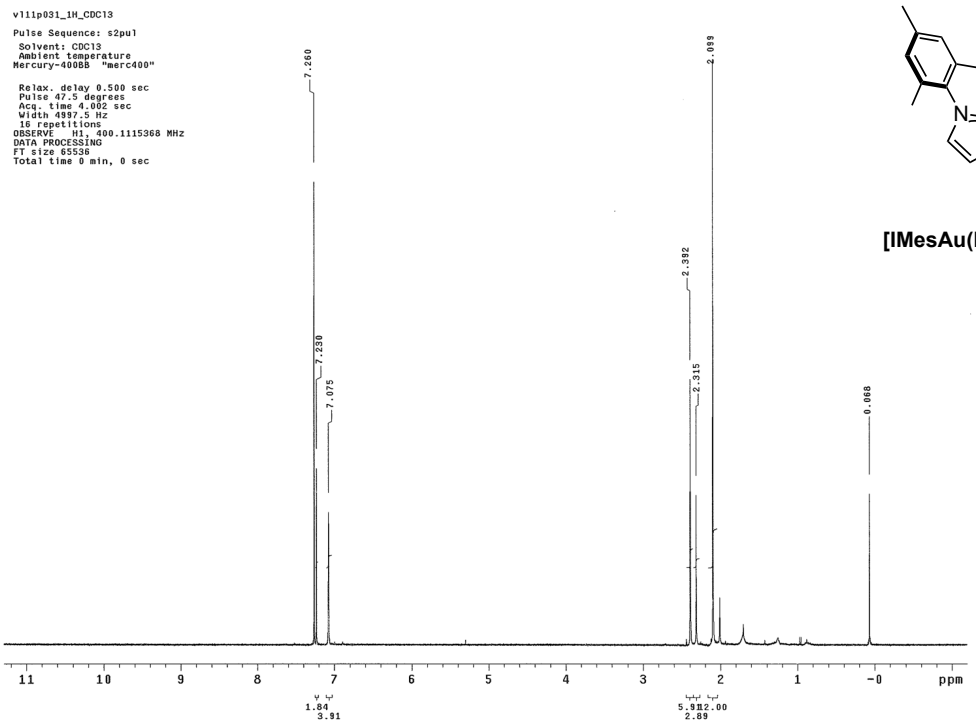


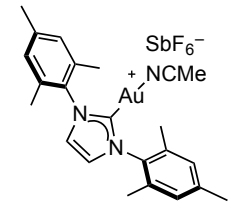

v111p123_13C_CDCl3
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-15-87
INOVA-500 "ui500"
Relax. delay 0.500 sec
Pulse 45.8 degrees
Acq. time 1.500 sec
Width 33003.3 Hz
1024 repetitions
OBSERVE C13, 125.6618678 MHz
DECOUPLE H1, 499.7505605 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 34 min, 17 sec
149.924
146.803
133.754
132.063
131.486
128.009
127.975
131.772
ppm


v111p123_13C_CDCl3
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-15-87
INOVA-500 "ui500"
Relax. delay 0.500 sec
Pulse 45.8 degrees
Acq. time 1.500 sec
Width 33003.3 Hz
1024 repetitions
OBSERVE C13, 125.6618678 MHz
DECOUPLE H1, 499.7505605 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 34 min, 17 sec
36.985
36.704
34.132
31.178
31.094
30.172
27.022
26.910
26.658
26.549
25.688
25.527
24.221
23.287
2.769
ppm

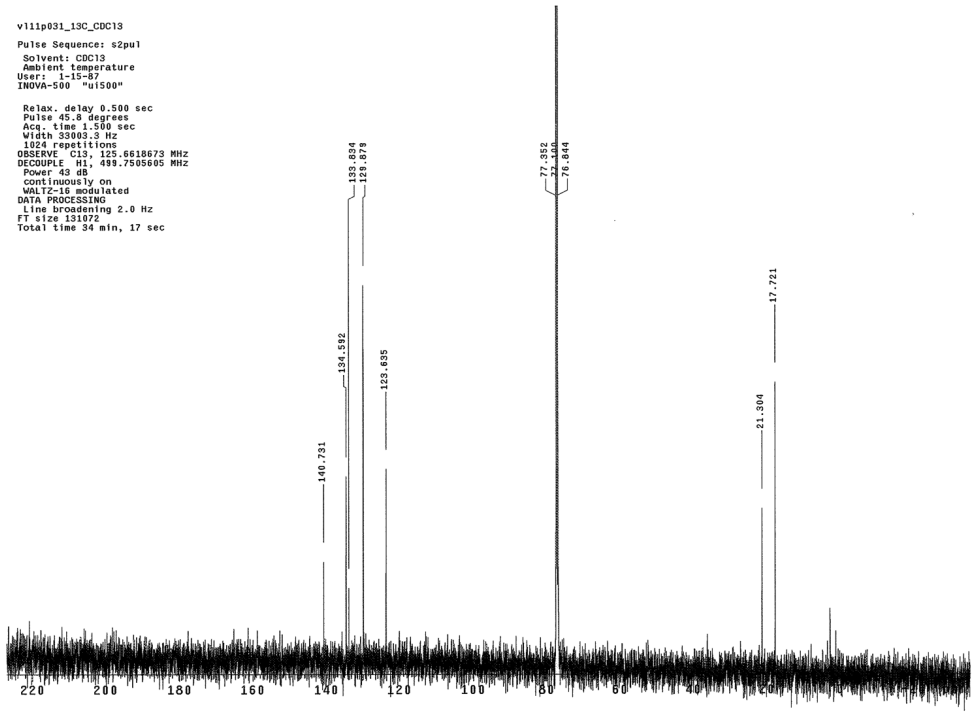

v111p123_19F_CDCl3
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 4.000 sec
Pulse 55.0 degrees
Acq. time 0.600 sec
Width 69930.1 Hz
16 repetitions
OBSERVE F19, 376.4811412 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 1 min, 34 sec
-153.750
-153.689
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

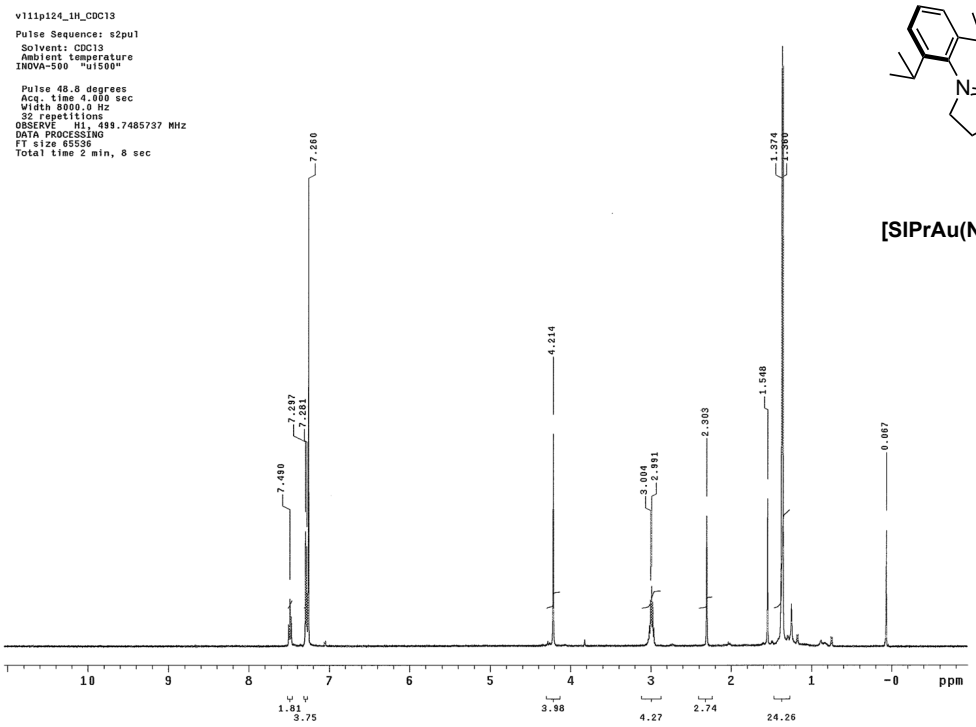

v111p123_31P_CDCl3
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "merc400"
Relax. delay 2.000 sec
Pulse 56.2 degrees
Acq. time 0.800 sec
Width 50000.0 Hz
128 repetitions
OBSERVE P31, 161.9679384 MHz
DECOUPLE H1, 400.1135562 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 8 min, 40 sec
33.226
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm

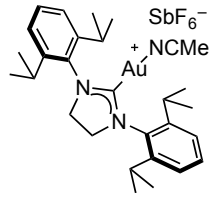




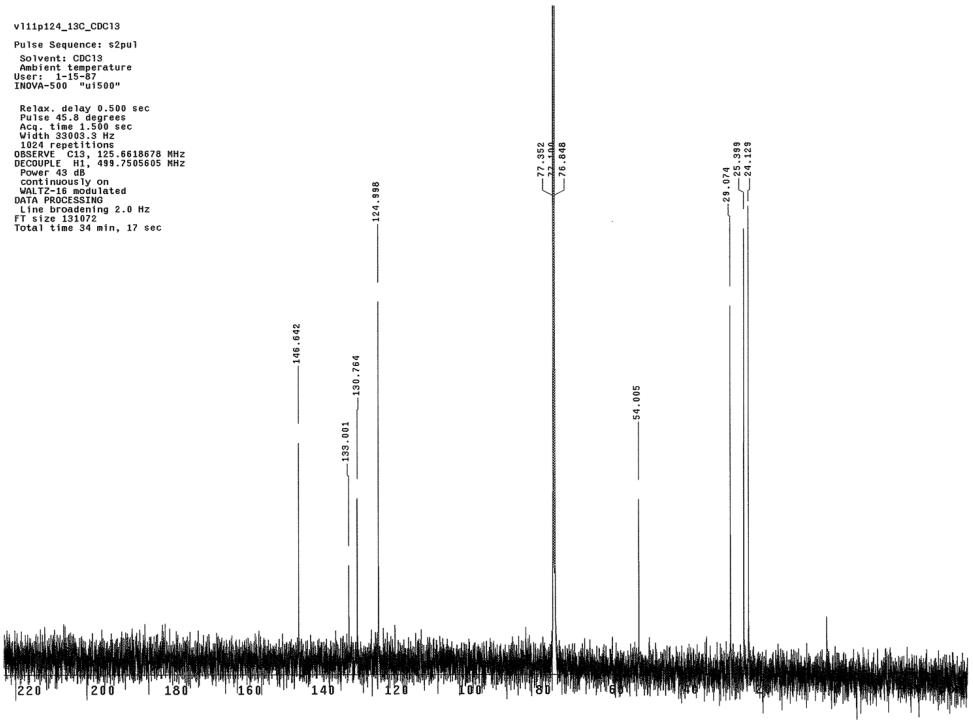
[IMesAu(NCCH$_3$)]SbF$_6$

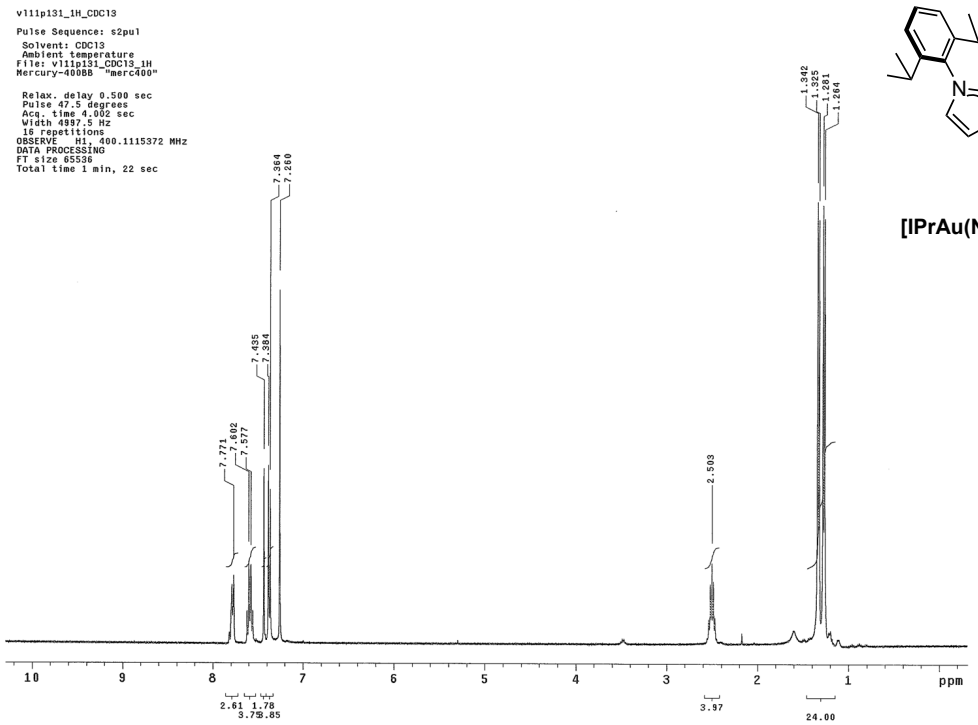


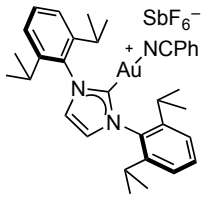




[SIPrAu(NCCH$_3$)]SbF$_6$







[IPrAu(NCPh)]SbF$_6$