Supporting Information for:

Well defined Au(III)-bisfluorides supported by N-ligands

Mohammad Albayer, Robert Corbo and Jason L. Dutton*[a]

EXPERIMENTAL DETAILS

Solvents used were obtained from Caledon Laboratories and dried using an Innovative Technologies Solvent Purification System with dual columns packed with solvent appropriate drying agents. The dried solvents were stored under an N_2 atmosphere over 3 Å molecular sieves in the glovebox. Solvents for NMR spectroscopy were purchased from Cambridge Isotope Laboratories and dried by stirring for three days over CaH_2, distilled prior to use, and stored in the glovebox over 3 Å molecular sieves. $[Au(4\text{-}DMAP)_2][OTf]$,[1] $[Au(4\text{-}DMAP)_2(4\text{-}cyanopyr)_2][OTf]_3$,[1] tht-AuCl,[2] $[Au(pyridine)_2][BF_4]$[3] and $[PhI(4\text{-}cyanopyridine)_2(OTf)_2]$[4] were synthesised via literature procedures. Gold powder was purchased from Precious Metals Online. All reactions involving XeF_2 were done in 15 mL polyethyelene centrifuge tubes. KF was dried under vacuum in the glovebox port overnight prior to use.

X-ray Crystallography Details

Single crystals were selected under n-paratone oil, mounted on nylon loops and placed into a cold stream (172 K) of N_2 on an Oxford CCD diffractometer using Cu Kα radiation. Structure solution and refinement were performed using the SHELXTL suite of software.

Synthesis of **4IM**

N-methylimidazole (175 µL, 2.20 mmol) was added to a dichloromethane solution (20 mL) containing tht-AuCl (350 mg, 1.09 mmol) and KOTf (210 mg, 1.12 mmol). The mixture was stirred for 24 hours in the dark. The solvent was removed under vacuum to give a light yellow solid. The solid was washed with diethyl ether and recrystallized from dichloromethane/ diethyl ether to give a white solid. Yield: 455 mg, 82%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.26 (s, 2 H), 7.13 (s, 2 H), 7.05 (s, 2 H), 3.84 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 141.00, 129.44, 121.71, 35.23. ESI-MS: *m/z* 361 [Au(N-methylimidazole)$_2$]$^+$.

Synthesis of **5NMe$_2$** using XeF_2

To a solution of [Au(4-DMAP)$_2$][OTf] (25 mg, 0.042 mmol) in 2 mL $CHCl_3$ was added XeF_2 (9 mg, 0.051 mmol). The mixture was stirred for 4 hours to give a yellow solid, which was filtered and washed with $CHCl_3$ (3 X 3 mL). Yield 21 mg, 78%.

Synthesis of **5NMe$_2$** using KF.

To a solution of **6NMe$_2$** (100 mg, 0.091 mmol) in 5 mL CH_3CN was added KF (10.6 mg, 0.182 mmol) and 18-crown-6 (145 mg, 0.547 mmol). The mixture was stirred for 30 minutes to give a yellow solution. Solvent was reduced to half in vacuo followed by the addition of 5 mL of diethyl ether to afford a yellow solid. The solid was washed with CH_2Cl_2 (2X3mL) and then recrystallized from CH_3CN/diethyl ether. Yield: 35 mg, 61%. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) = 7.94 (d, *J* = 8.0 *Hz*, 4H), 6.77 (d, *J* = 8.0 *Hz*, 4H), 3.14 (s, 12 H). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) = 157.47, 144.17, 108.34, 40.20. ^{19}F NMR (376 MHz, CD_3CN): δ (ppm) = -79.35 (s), -249.40 (s). ESI-MS: *m/z* 479 [Au(4-DMAP)$_2$F$_2$]$^+$. Elemental Analysis, % calc'd (found): C 28.67 (28.63), H 3.21 (3.32), N 8.92 (8.60).

Synthesis of **5IM** using XeF_2

To a solution of [Au(1-methylimidazole)$_2$][OTf] (25 mg, 0.049 mmol) in 2 mL $CHCl_3$ was added XeF_2 (10 mg, 0.059 mmol). The mixture was stirred for 4 hours to give a pale yellow solid, which was filtered and washed with $CHCl_3$ (3 X 3 mL). Yield: 20mg, 73%.

Synthesis of **5IM** using KF

To a solution of **6IM** (100 mg, 0.098 mmol) in 5 mL CH_3CN was added KF (11.5 mg, 0.197 mmol) and 18-crown-6 (156 mg, 0.59 mmol). The mixture was stirred for 30 minutes to give a pale yellow solution. Solvent was reduced to half in vacuo followed by the addition of 5 mL of diethyl ether to afford a pale yellow solid. The solid was washed with CH_2Cl_2 (2X3mL) and then recrystallized from CH_3CN/diethyl ether. Yield: 14 mg, 26%. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) = 8.18 (s, 2 H), 7.37 (s, 2 H), 7.21 (s, 2 H), 3.86 (s, 6 H). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) = 136.45, 123.43, 120.57, 36.59. ^{19}F NMR (376 MHz, CD_3CN): δ (ppm) = -79.30 (s), -284.03 (s). ESI-MS: *m/z* 399 [Au(1-methylimidazole)$_2$F$_2$]$^+$. Elemental Analysis, % calc'd (found): C 19.72 (19.93), H 2.21 (2.32), N 10.22 (10.05).

Synthesis of **5H** using XeF_2.

To a solution of [Au(pyridine)$_2$][BF_4] (55 mg, 0.12 mmol) in 2 mL dichloromethane was added XeF_2 (25 mg, 0.15 mmol). The mixture was stirred for 12 hours to give a beige solid, which was filtered and washed with dichloromethane (3 X 3 mL). Yield: 48 mg, 81%.

Synthesis of **5H** using KF

To a solution of **6H** (100 mg, 0.106 mmol) in 5 mL CH_3CN was added KF (12.4 mg, 0.213 mmol) and 18-crown-6 (169 mg, 0.64 mmol). The mixture was stirred for 30 minutes to give a pale yellow solution. Solvent was reduced to half in vacuo followed by the addition of 5 mL of diethyl ether to afford a beige solid. The solid was washed with CH_2Cl_2 (2X3mL) and then recrystallized from CH_3CN/diethyl ether. Yield: 26 mg, 51%. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) = 7.66 (d, *J* = 4.0 *Hz*, 4H), 8.38 (t, *J* = 8.0 *Hz*, 8H), 7.9 (t, *J* = 4.0 Hz 4H). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) = 147.53, 145.97, 128.67. ^{19}F NMR (376 MHz, CD_3CN): δ (ppm) = -151.72 (s), -237.28 (s). ESI-MS: *m/z* 393 [Au(pyridine)$_2$F$_2$]$^+$. Elemental Analysis, % calc'd (found): C 25.02 (26.23), H 2.10 (2.33), N 5.84 (5.82).

Synthesis of **6IM**

A solution of [PhI(4-cyanopyridine)$_2$(OTf)$_2$] (278 mg, 0.392 mmol) in CH_3CN (5 mL) was added drop wise to a solution of of **5IM** (200 mg, 0.392 mmol) in CH_3CN (5 mL). The mixture was then stirred for 10 min giving a yellow solution. The solvent was removed under reduced pressure to give a yellow solid. The solid was recrystallized from CH_3CN/diethyl ether Yield: 317 mg, 79%. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) = 8.95 (d, *J* = 7.0 *Hz*, 4H), 8.31 (s, 2H), 8.18 (d, *J* = 7.0 Hz 4H), 7.33 (s, 2H), 7.30 (s, 2H), 3.77 (s, 6H). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) = 152.19, 139.76, 133.15, 129.15, 125.98, 125.52, 114.76, 36.87. ESI-MS: *m/z* 361 [Au(N-methylimidazole)$_2$]$^+$.

Synthesis of **6H**

A solution of [PhI(4-cyanopyridine)$_2$(OTf)$_2$] (325 mg, 0.453 mmol) in CH_3CN (5 mL) was added drop wise to a solution of **4H** (200 mg, 0.453 mmol) in CH_3CN (5 mL). The mixture was then stirred for 10 min giving a brown-yellow solution. The solvent was removed under reduced pressure to give a beige solid. The solid was recrystallized from CH_3CN/diethyl ether. Yield: 356 mg 83 %. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) = 9.09 (d, *J* = 7.0 *Hz*, 4H), 8.88 (d, *J* = 5.5 Hz, 4H), 8.34 (t, *J* = 8.0 Hz 2H), 8.19 (d, *J* = 8.0 *Hz*, 4H), 7.86 (t, *J* = 8.0 Hz 2H). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) = 151.87, 150.52, 146.97, 133.97, 131.74, 129.49, 114.62. *m/z* 355 [Au(pyr)$_2$]$^+$.

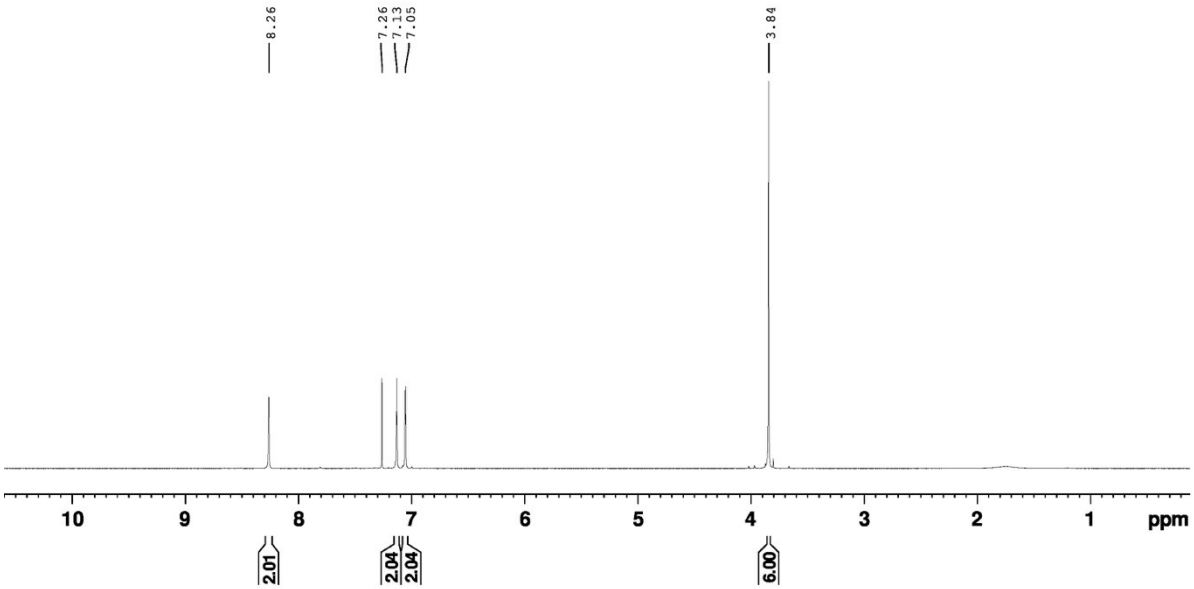

Figure S1. Proton-NMR spectrum of **4IM**.

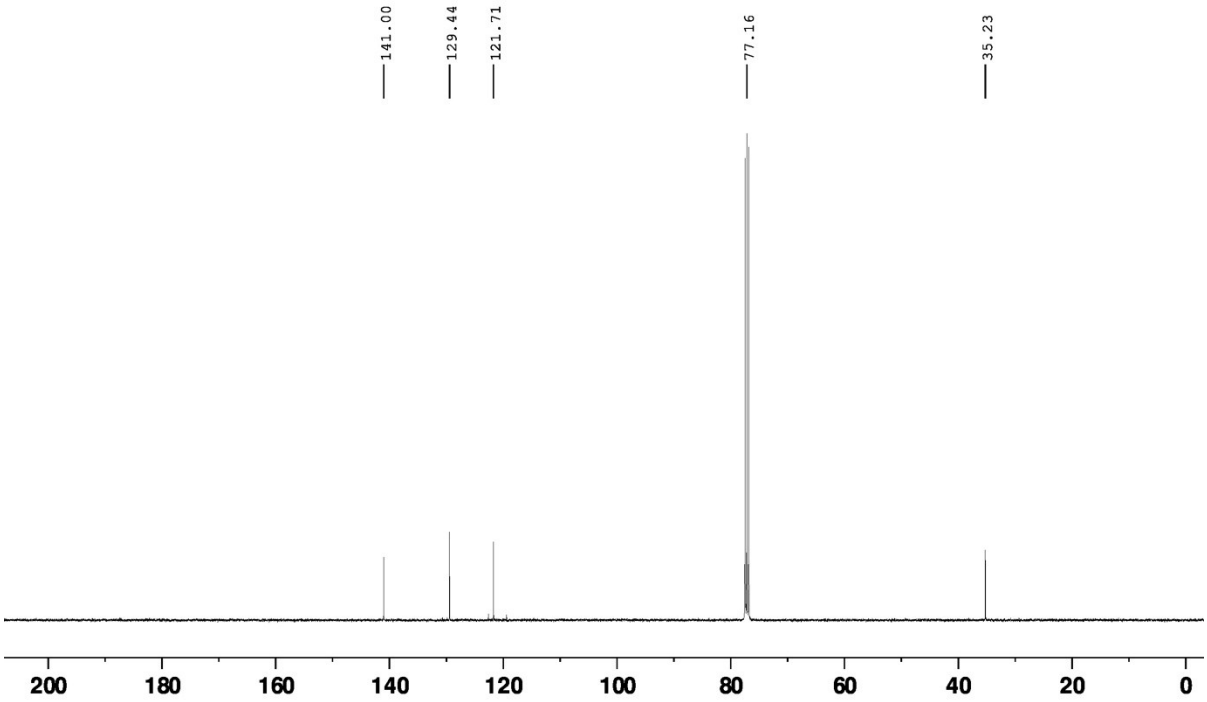

Figure S2. Carbon-13 NMR spectrum of **4IM**.

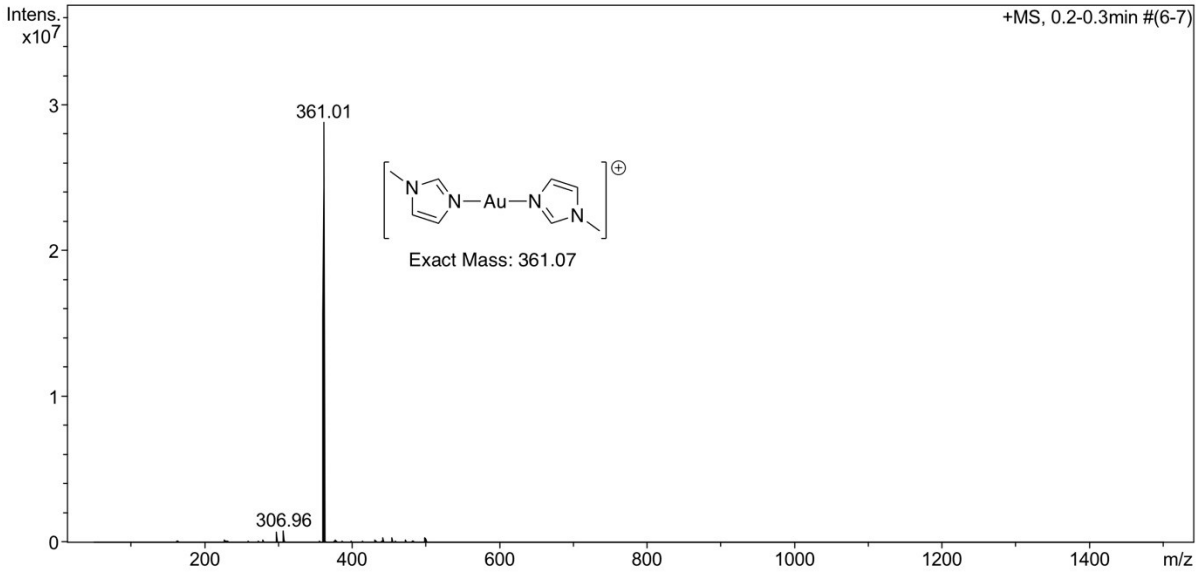

Figure S3. Positive ion mass spectrum of **4IM**.

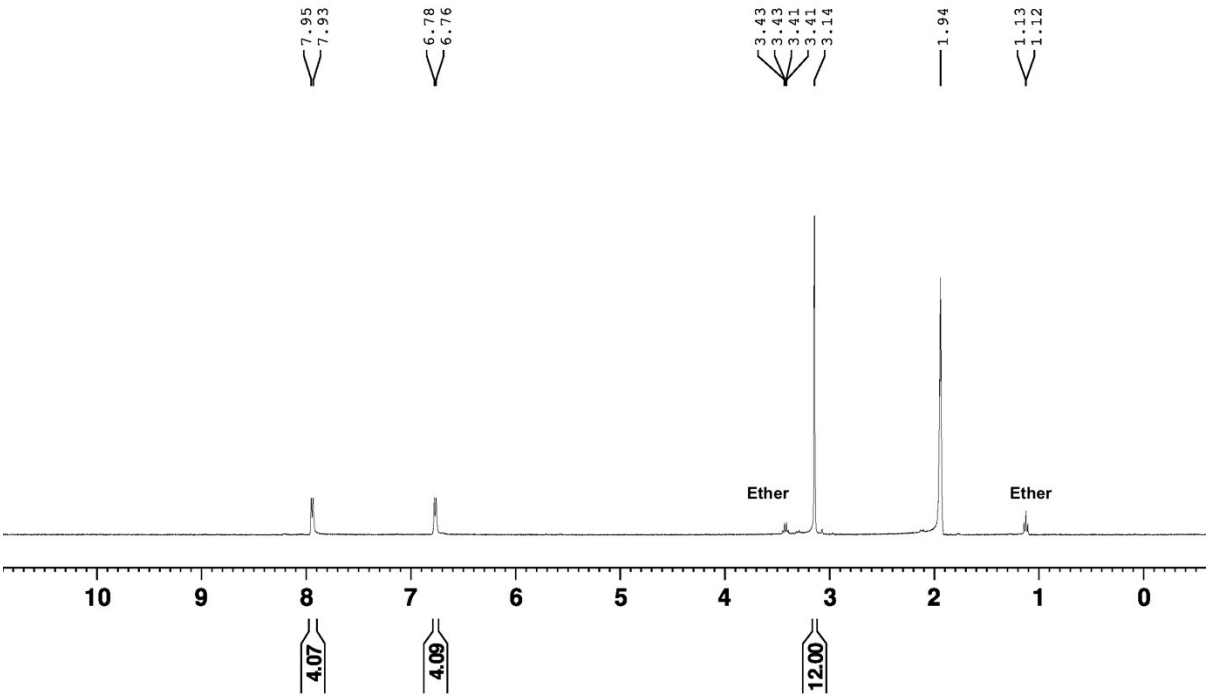

Figure S4. Proton-NMR spectrum of **5NMe$_2$**.

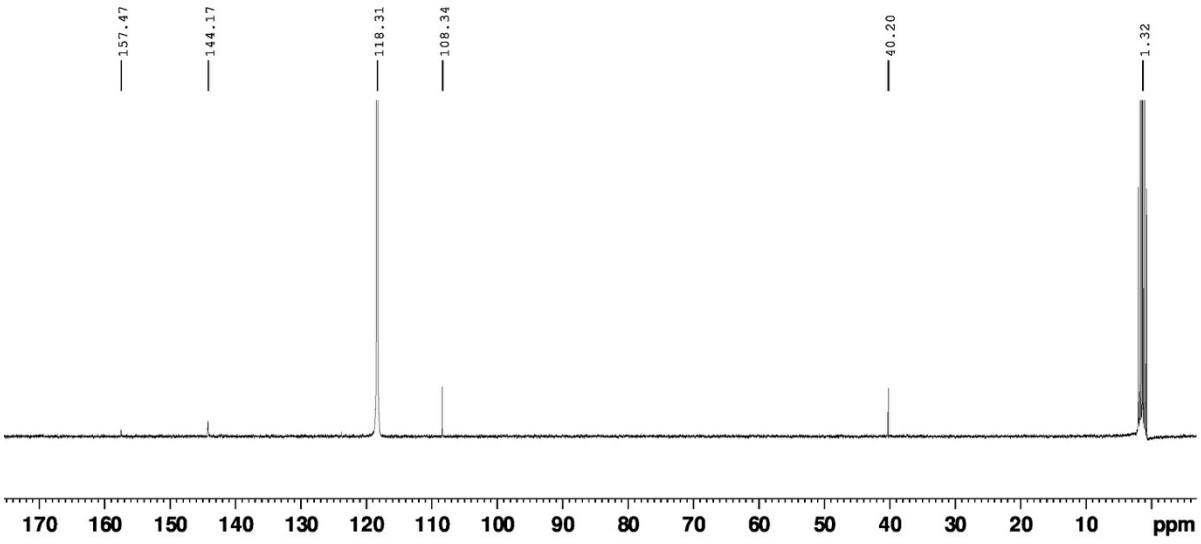

Figure S5. Carbon-13 NMR spectrum of **5NMe$_2$**.

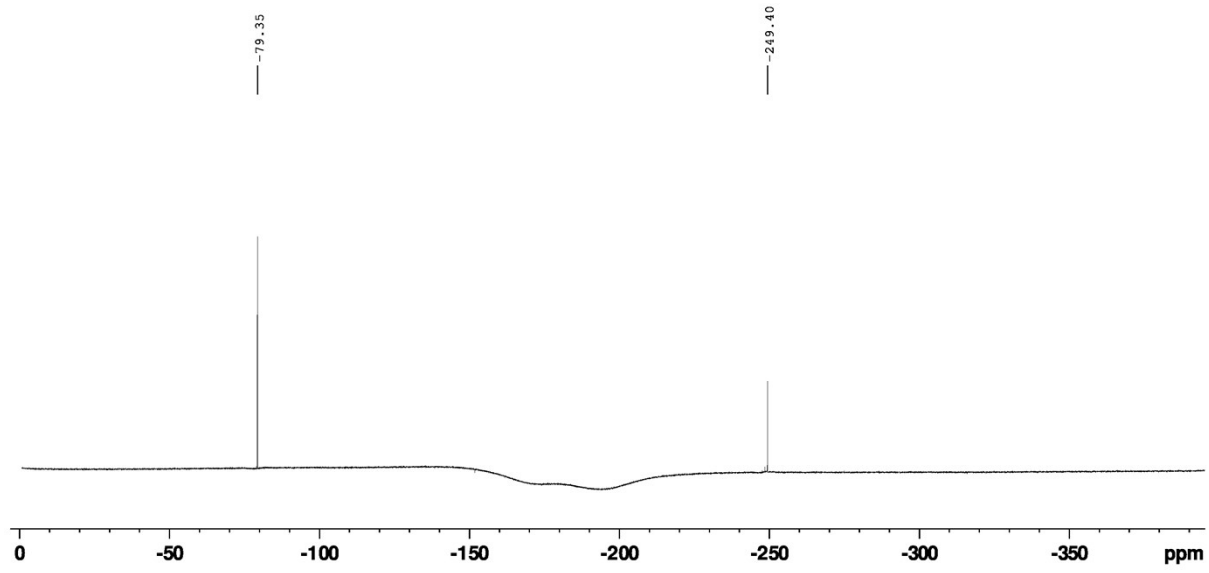

Figure S5. Fluorine-19 NMR spectrum of **5NMe$_2$**.

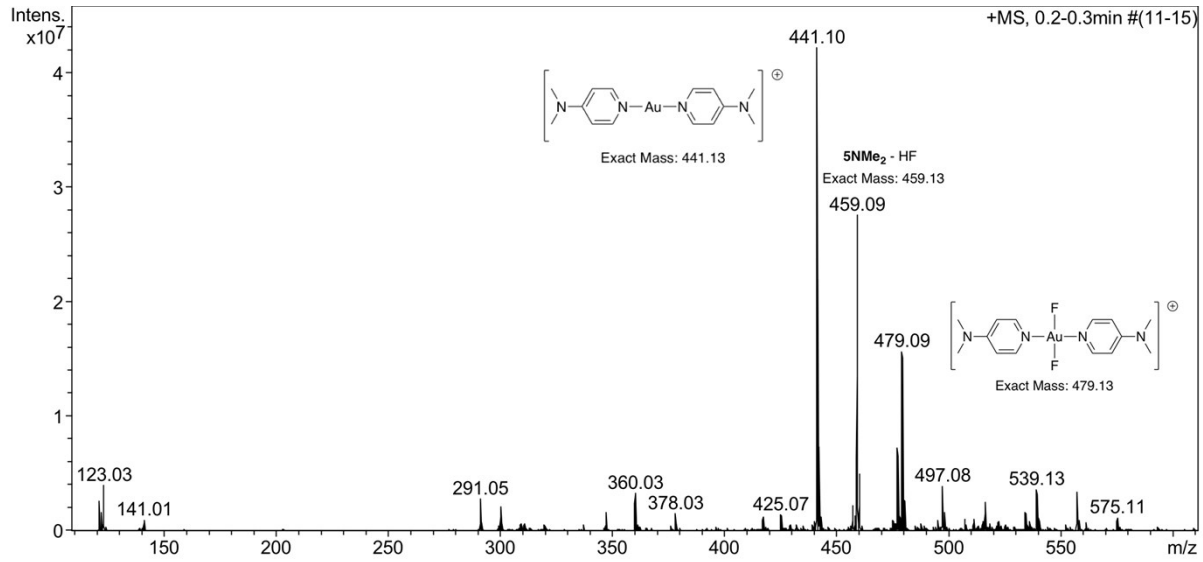

Figure S6. Positive ion mass spectrum of **5NMe$_2$**.

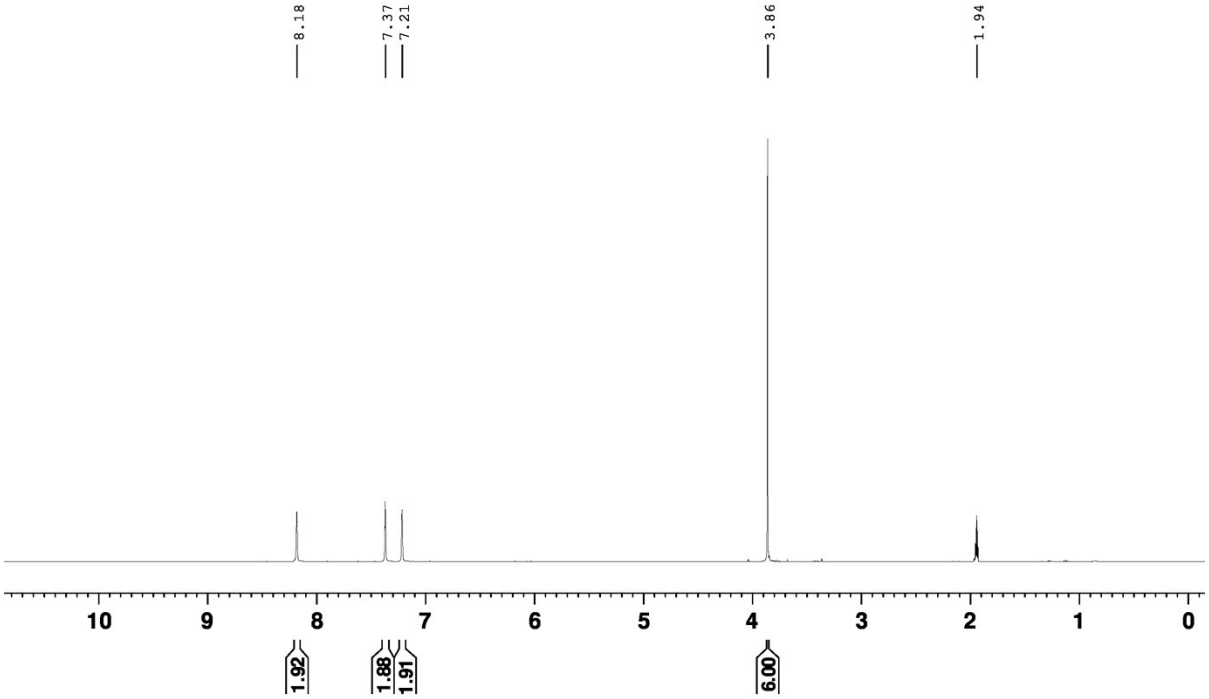

Figure S7. Proton-NMR spectrum of **5IM**.

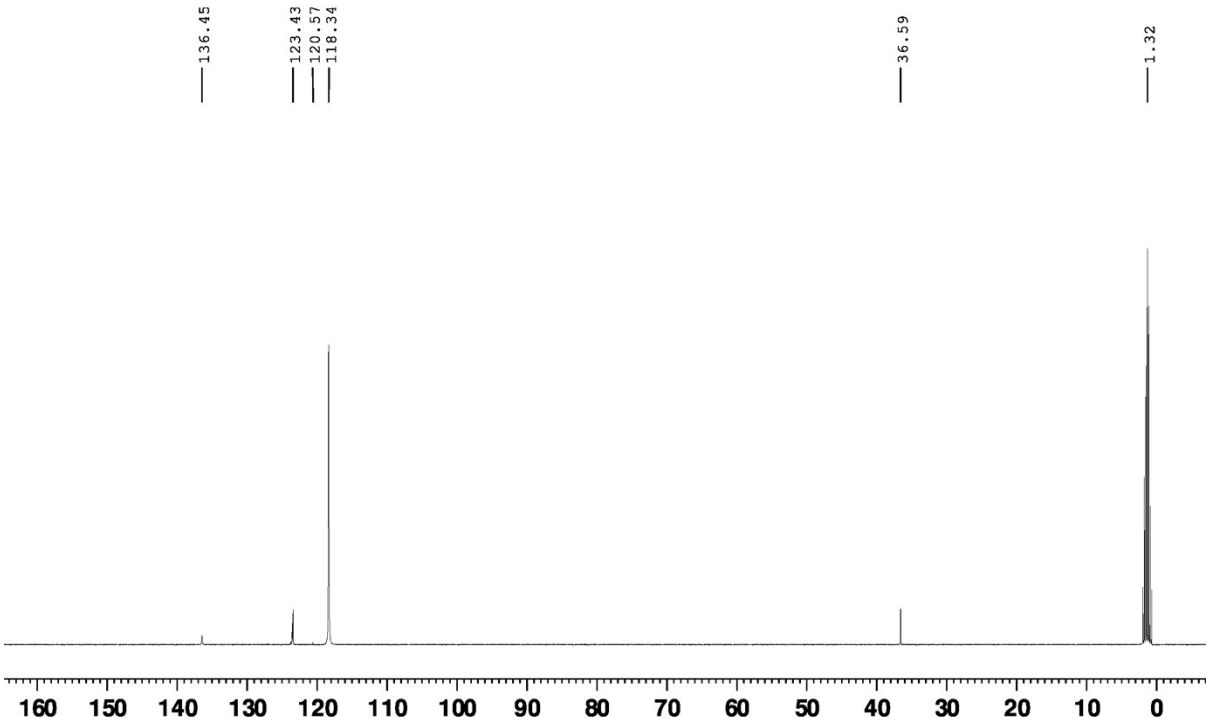

Figure S8. Carbon-13 NMR spectrum of **5IM**.

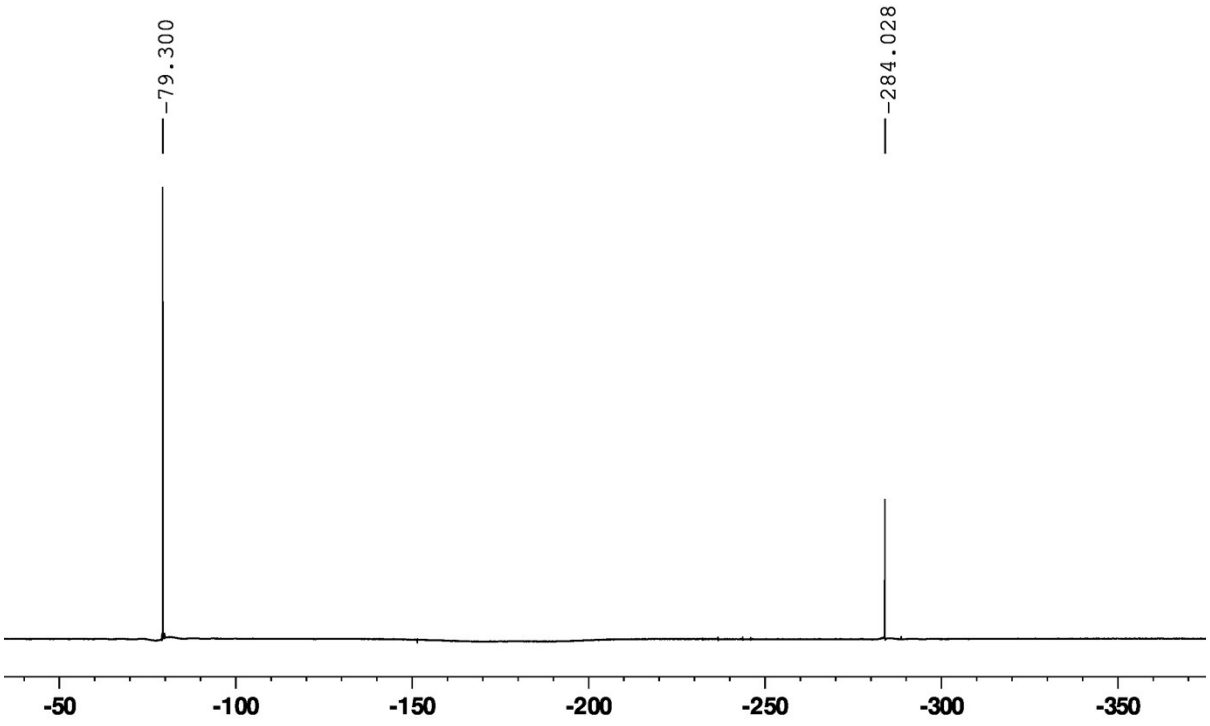

Figure S9. Fluorine-19 NMR spectrum of **5IM**.

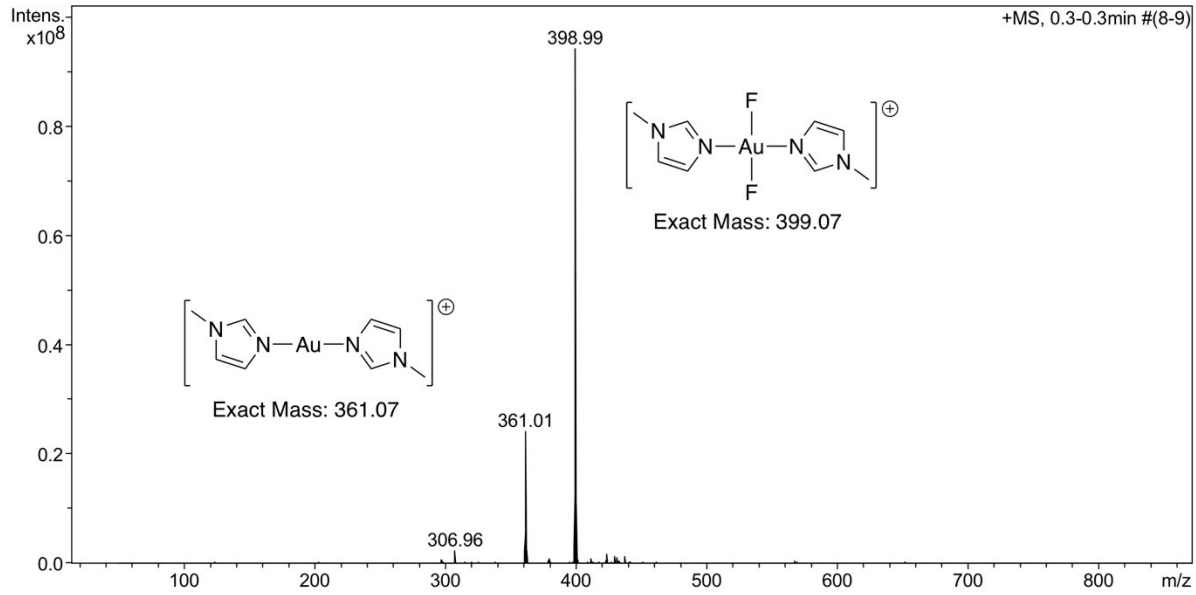

Figure S10. Positive ion mass spectrum of **5IM**.

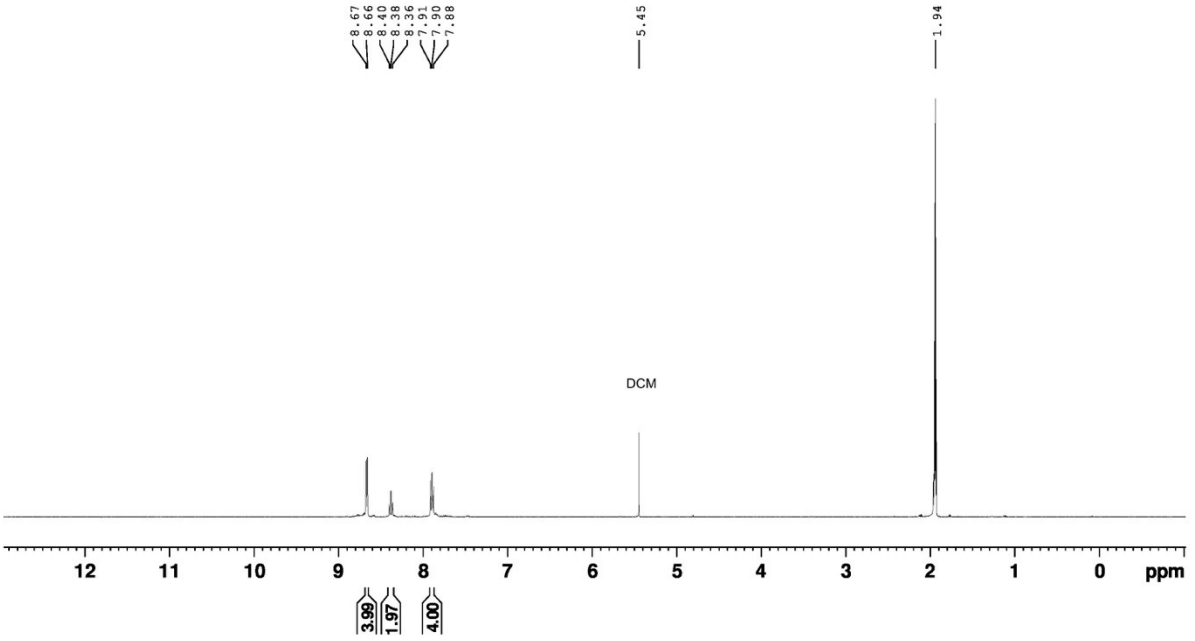

Figure S11. Proton-NMR spectrum of **5H**.

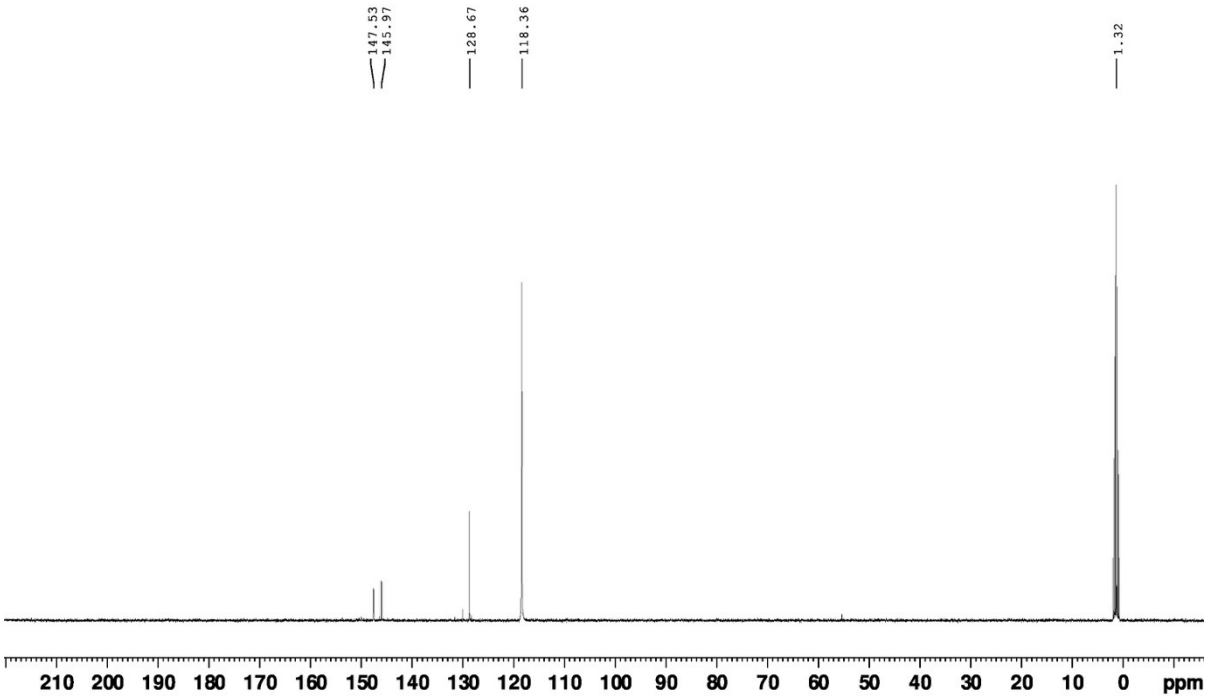

Figure S12. Carbon-13 NMR spectrum of **5H**.

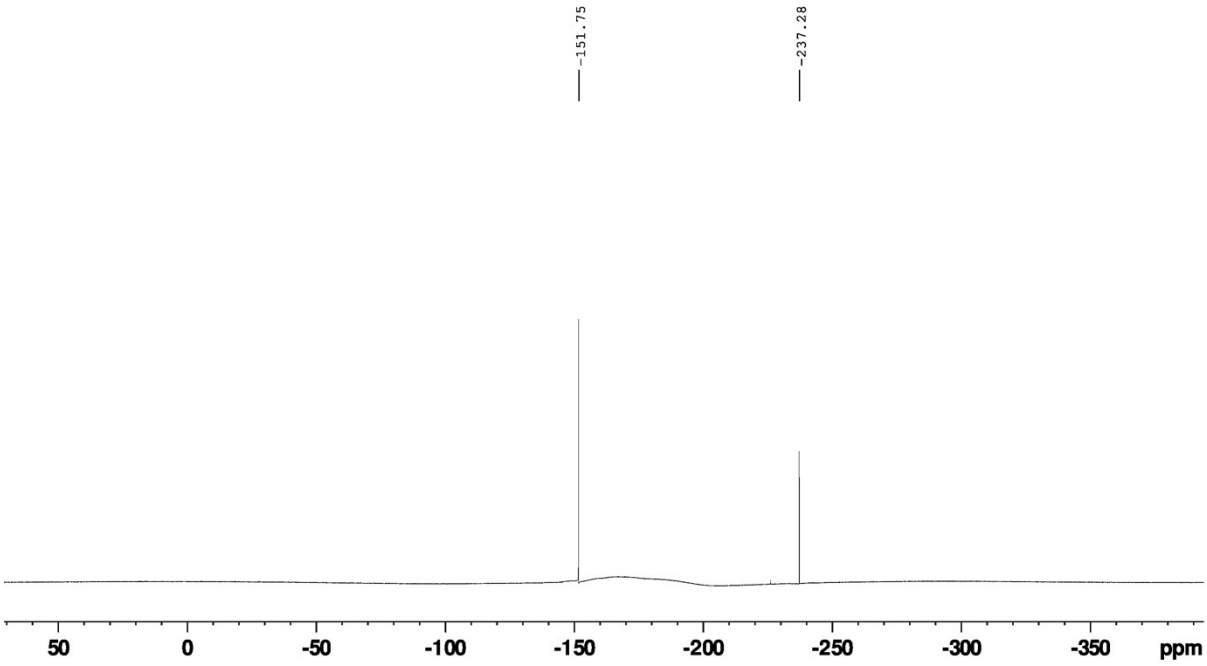

Figure S13. Fluorine-19 NMR spectrum of **5H**.

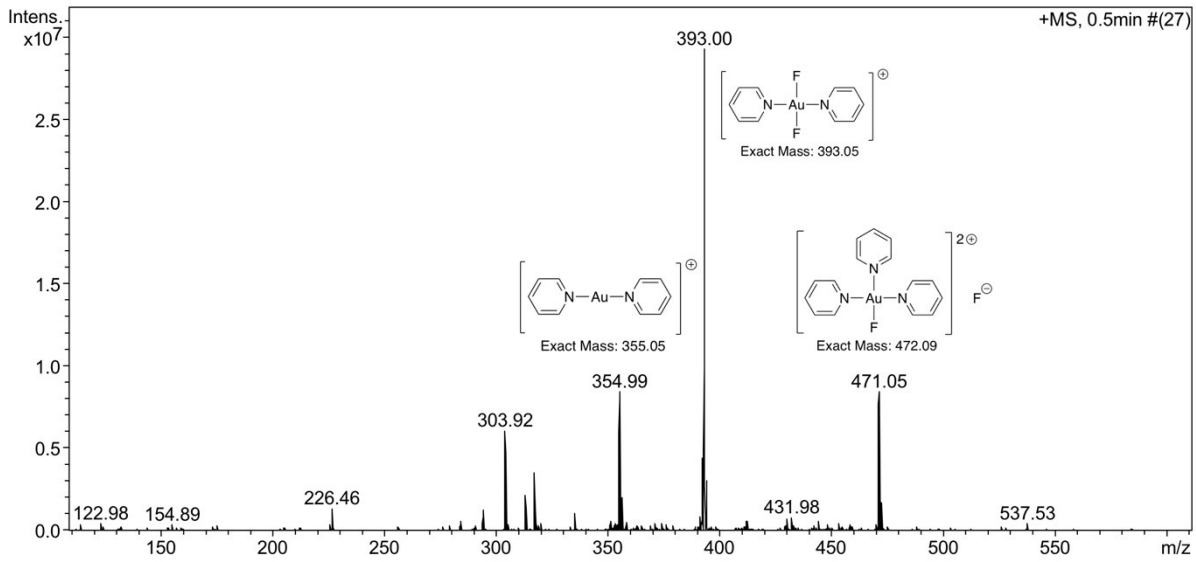

Figure S14. Positive ion mass spectrum of **5H**.

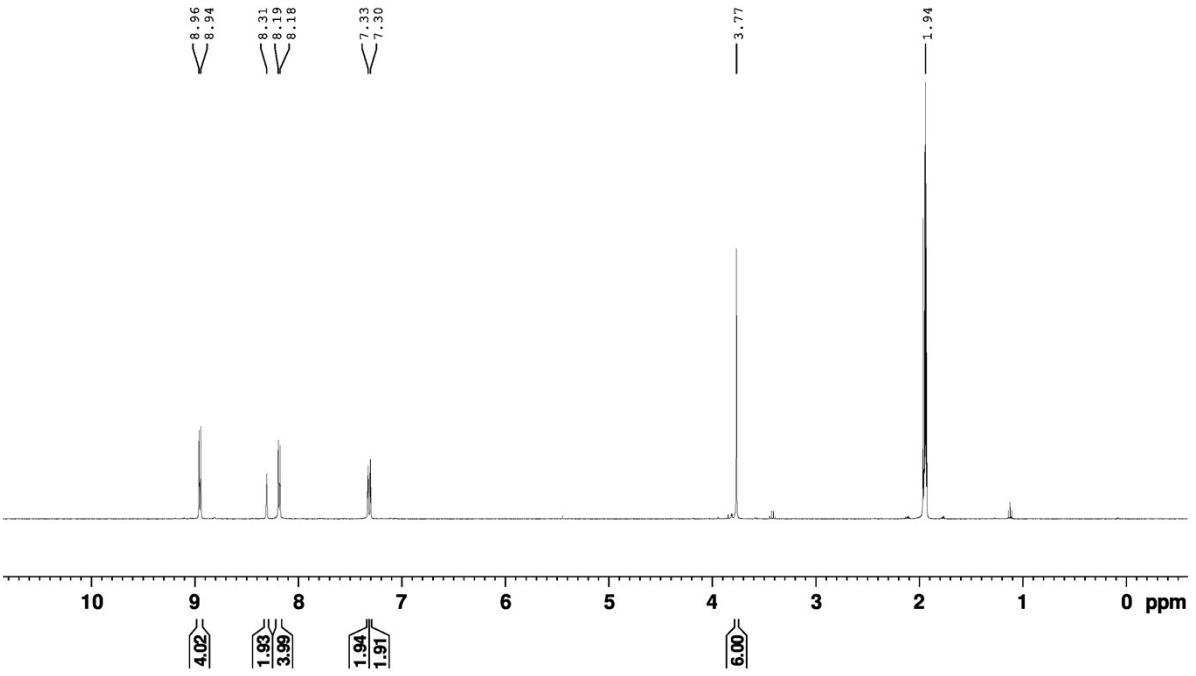

Figure S15. Proton-NMR spectrum of **6IM.**

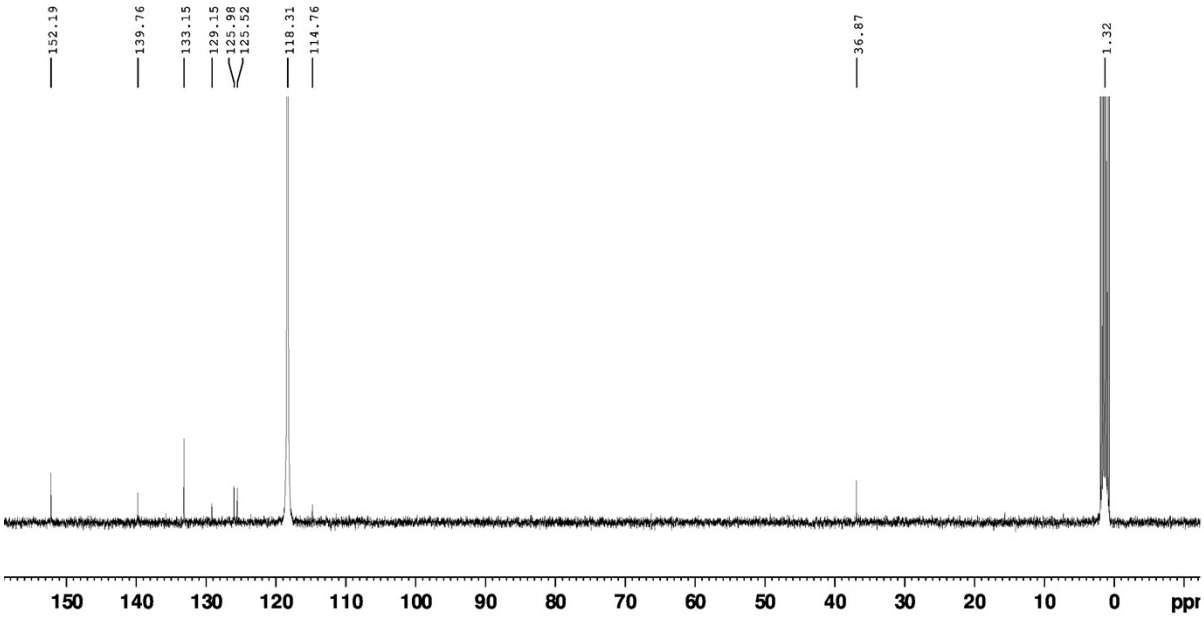

Figure S16. Carbon-13 NMR spectrum of **6IM.**

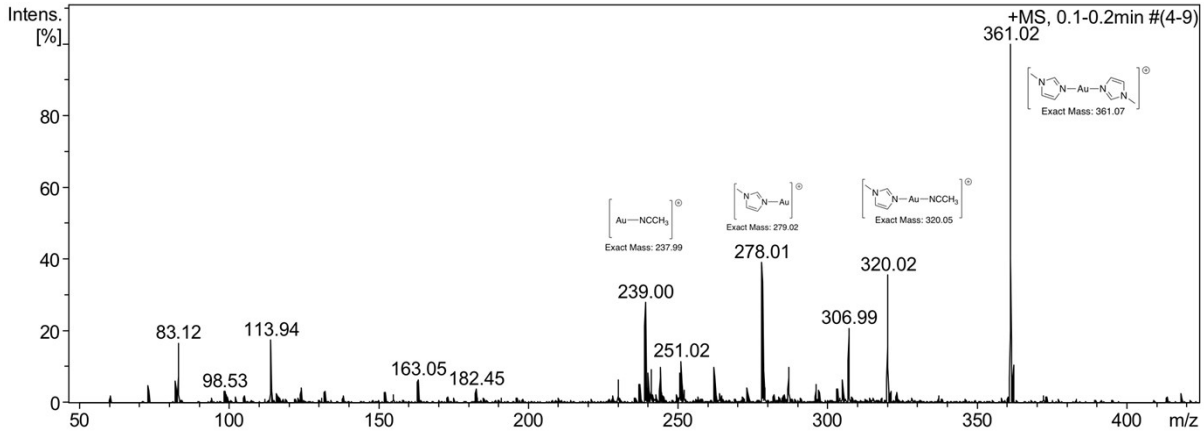

Figure S17. Positive ion mass spectrum of **6IM.**

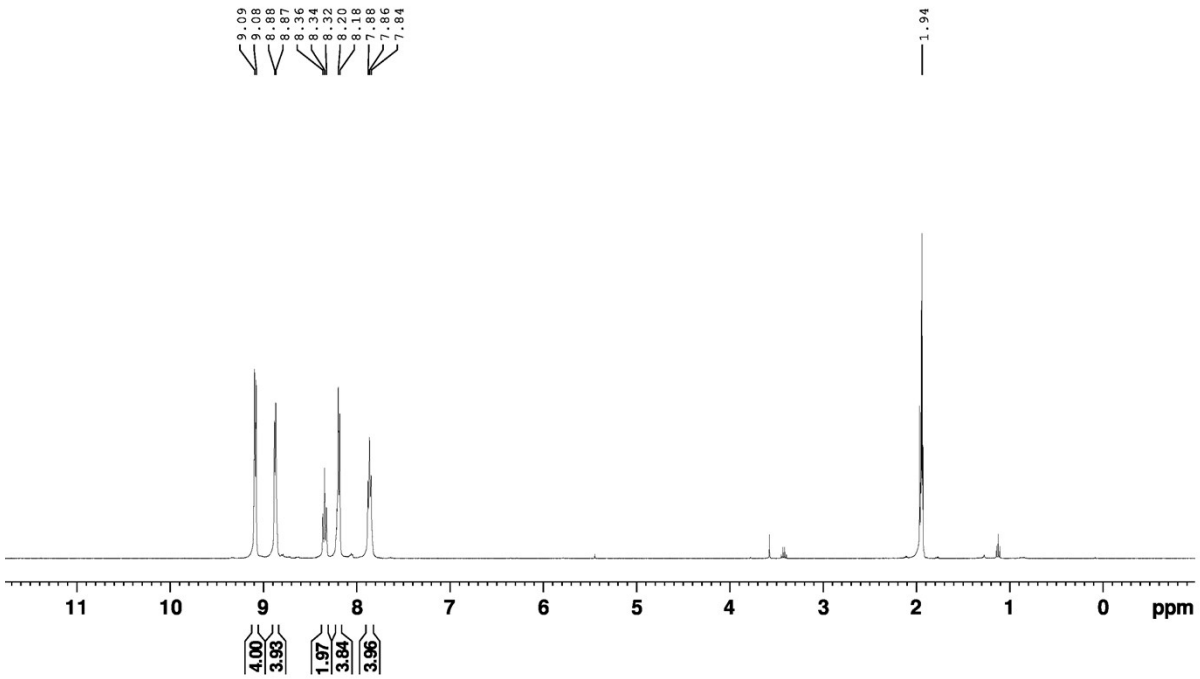

Figure S18. Proton-NMR spectrum of **6H.**

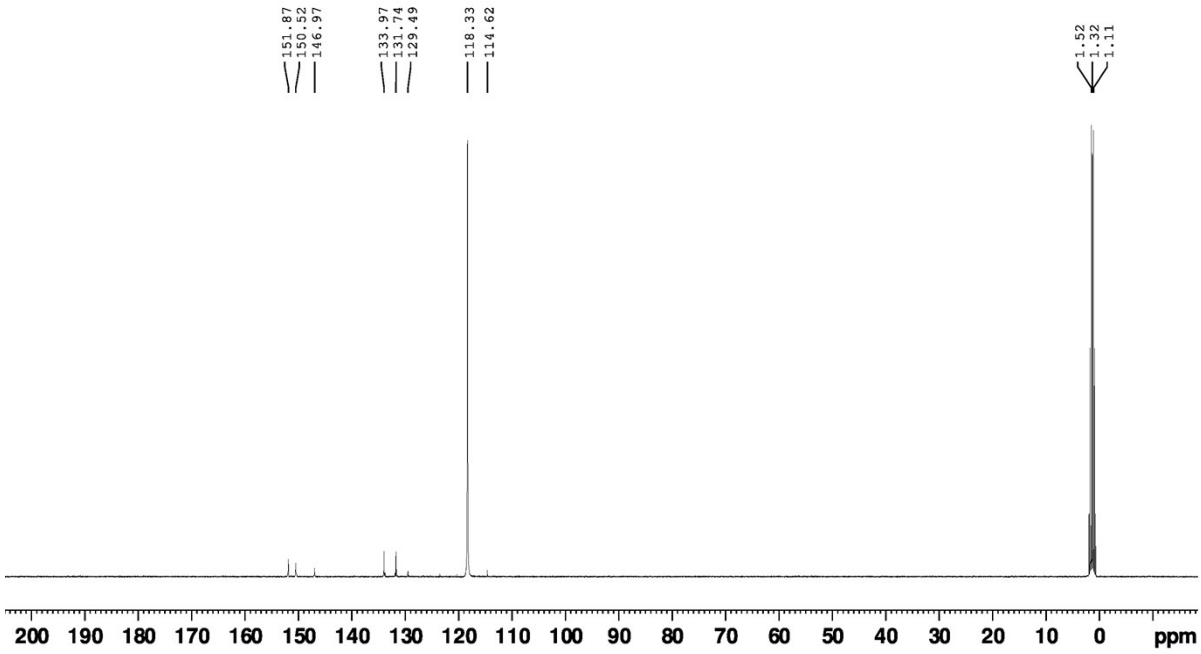

Figure S19. Carbon-13 NMR spectrum of **6H.**

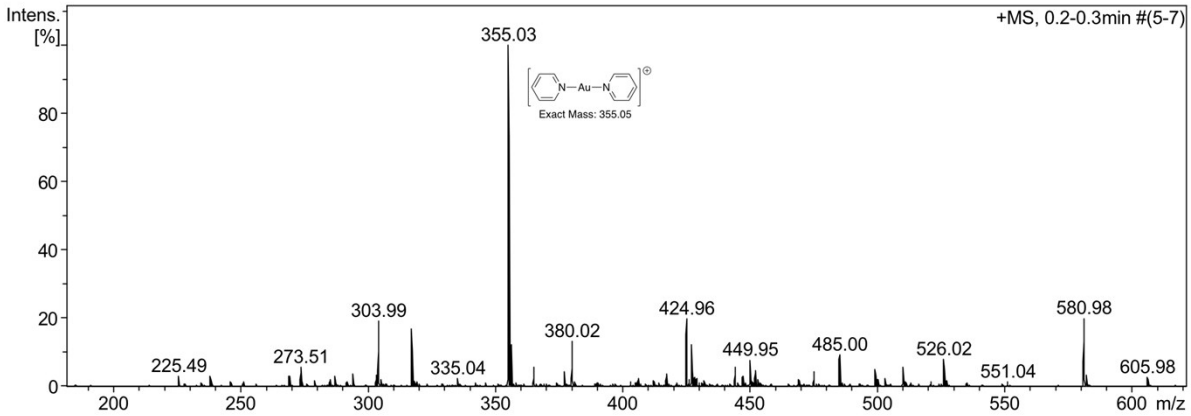

Figure S20. Positive ion mass spectrum of **6H.**

References:

(1) R. Corbo, T. P. Pell, B. D. Stringer, C. F. Hogan, D. J. D. Wilson, P. J. Barnard and J. L. Dutton, *J. Am. Chem. Soc.*, 2014, **136**, 12415-12421.

(2) R. Uson, A. Laguna, M. Laguna, D. A. Briggs, H. H. Murray and J. P. Fackler, *Inorg. Synth*. **1989**, *26*, 85-91.

(3) R. Corbo, G. F. Ryan, M. A. Haghighatbin, C. F. Hogan, D. J. D. Wilson, M. D. Hulett, P. J. Barnard and J. L. Dutton, *Inorg. Chem.* **2016**, *55*, 2830-2839.

(4) R. Weiss and J. Seubert, *J. Angew. Chem., Int. Ed*. **1994**, *33*, 891-893.