

# Anionic and Zwitterionic Carboranyl N-Heterocyclic Carbene Au(I) Complexes

Steven P. Fisher<sup>a</sup>, Ahmad El-Hellani<sup>b</sup>, Fook S. Tham<sup>a</sup>, Vincent Lavallo<sup>a</sup>

<sup>a</sup> Department of Chemistry University of California, Riverside, Riverside, CA 92521 United States.

[vincent.lavallo@ucr.edu](mailto:vincent.lavallo@ucr.edu)

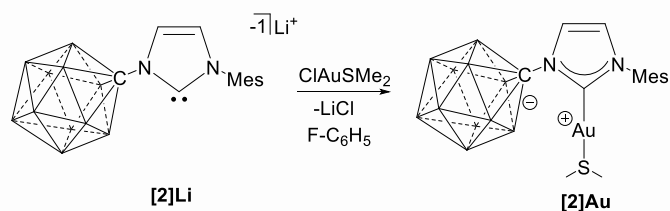
<sup>b</sup> Chemistry Department, Faculty of Arts and Sciences, American University of Beirut, Beirut, Lebanon.

## Supporting Information

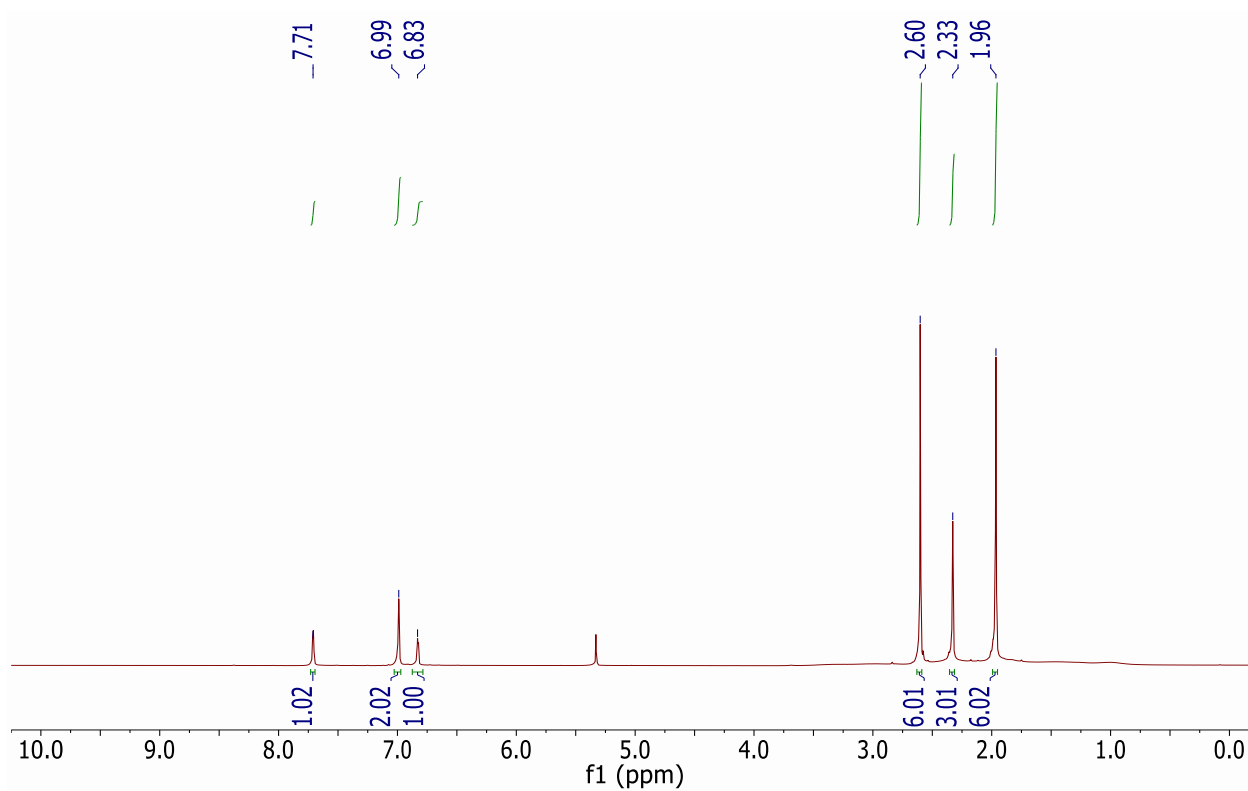
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**General Considerations:** All manipulations were carried out using standard Schlenk or glovebox techniques under a dinitrogen atmosphere unless otherwise stated. Dry solvents were obtained via distillation under argon from calcium hydride (acetonitrile), sodium-potassium alloy (diethyl ether), and potassium benzophenone ketyl (tetrahydrofuran). Benzene, methylene chloride and fluorobenzene were collected from a solvent purification system by SG Waters USA, LLC utilizing a fifteen minute argon sparge followed by passage through activated aluminum. Compounds **[2]Li** and **[3]Li<sub>2</sub>** were prepared according to the literature.<sup>(1,2)</sup> Unless specifically stated, reagents were purchased from commercial vendors and used without further purification. Nuclear magnetic resonance (NMR) spectroscopy was carried out using: Bruker Avance 300 MHz, Bruker Avance 600 MHz, and Varian Inova 300 MHz. NMR chemical shifts are reported in parts per million (ppm) with <sup>1</sup>H and <sup>13</sup>C chemical shifts referenced to the residual non-deutero solvent. The <sup>11</sup>B-<sup>1</sup>H coupling constants from <sup>11</sup>B spectra are reported when possible. Infrared spectroscopy was recorded on a Bruker ALPHA FTIR Spectrometer. High-resolution mass spectrometry (HRMS) was collected on an Agilent Technologies 6210 (TOF LC/MS) featuring electrospray ionization. Complete crystallographic data for compounds **[2]Au** and **[3]AuLi** are available free of charge from the Cambridge Crystallographic Data Center under reference numbers 1449175 and 1449174, respectively. These structures can be accessed at: <http://www.ccdc.cam.ac.uk/>.

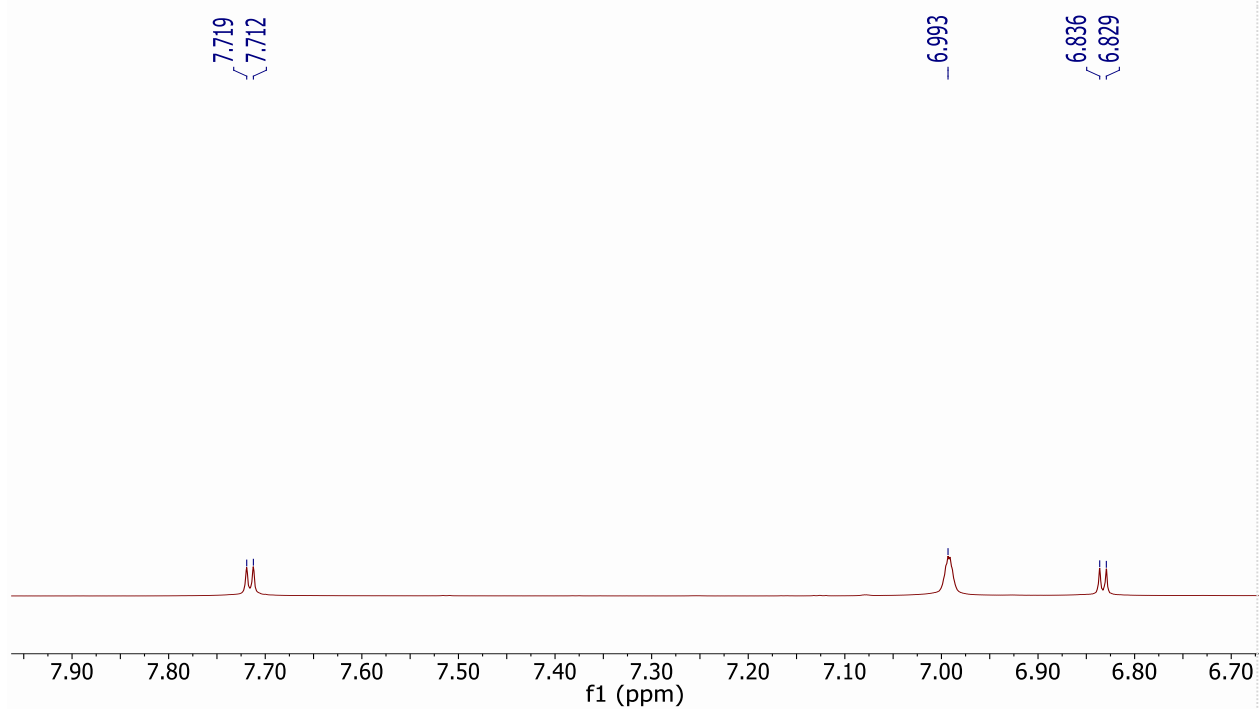
### Synthesis of **[2]Au**:



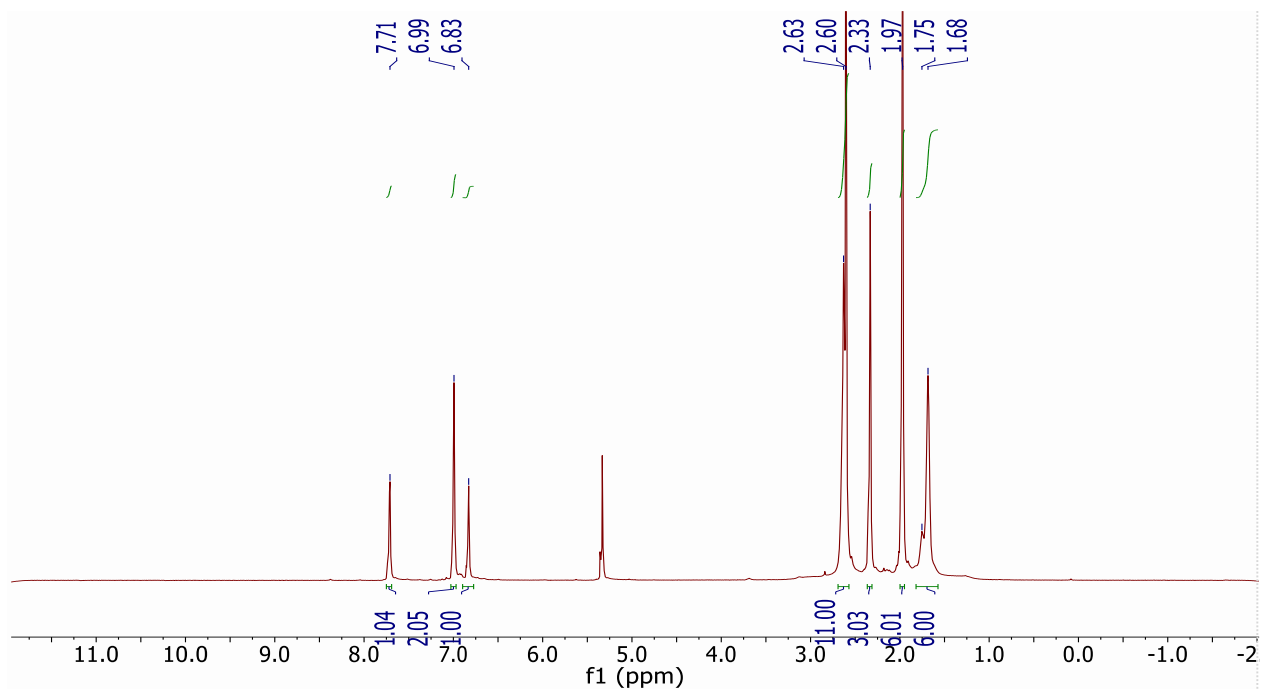
A 20 mL scintillation vial was equipped with a stir bar and loaded with **[2]Li** (50.0 mg, 126  $\mu\text{mol}$ ) and  $\text{ClAuSMe}_2$  (37.9 mg, 126  $\mu\text{mol}$ ). The vial was cooled to  $-40\text{ }^\circ\text{C}$  in a cold well before cold ( $-40\text{ }^\circ\text{C}$ )  $\text{F-C}_6\text{H}_5$  (5 mL) was added and the reaction stirred for 30 minutes at  $-40\text{ }^\circ\text{C}$ . After thirty minutes the reaction mixture was pumped down to dryness then methylene chloride (7 mL) was added, the mixture was stirred then filtered and the filtrate set aside. Methylene chloride (7 mL) was added and the mixture was stirred then filtered. The combined filtrate was pumped down to dryness furnishing **[2]Au** (69.4 mg, 82% yield). Single crystals for the X-ray diffraction study were obtained by preparative crystallization from THF and hexane at  $-30\text{ }^\circ\text{C}$  overnight. <sup>1</sup>H NMR (300 MHz, methylene chloride- $\text{d}_2$ ,  $25\text{ }^\circ\text{C}$ ):  $\delta$  = 7.71 (d, <sup>3</sup> $J(\text{H,H})$  = 2.1 Hz, 1H), 6.99 (m, 2H), 6.83 (d, <sup>3</sup> $J(\text{H,H})$  = 2.1 Hz, 1H), 2.60 (s, 6H), 2.33 (s, 3H), 1.96 (s, 6H), 3.8 – 0.75 (bm, 11H) ppm. <sup>1</sup>H[<sup>11</sup>B] NMR (192.5 MHz, methylene chloride- $\text{d}_2$ ,  $25\text{ }^\circ\text{C}$ ):  $\delta$  = 7.71 (d, 1H), 6.99 (m, 2H), 6.83 (d, 1H), 2.63 (s, 5H, B-H), 2.60 (s, 6H), 2.33 (s, 3H), 1.97 (s, 6H), 1.75 (s, 1H), 1.68 (s, 5H) ppm. <sup>13</sup>C[<sup>1</sup>H] (75 MHz, methylene chloride- $\text{d}_2$ ,  $25\text{ }^\circ\text{C}$ ):  $\delta$  = 175.2, 140.4, 135.9, 135.1, 129.6, 124.3, 121.6, 78.8, 24.4, 21.3, 17.9 ppm. <sup>11</sup>B[<sup>1</sup>H] NMR (96 MHz, methylene chloride- $\text{d}_2$ ,  $25\text{ }^\circ\text{C}$ ):  $\delta$  = -8.7, -13.6 ppm. <sup>11</sup>B NMR (96 MHz, methylene chloride- $\text{d}_2$ ,  $25\text{ }^\circ\text{C}$ ):  $\delta$  = -8.7 (<sup>1</sup> $J(\text{H,B})$  = 134.4 Hz), -13.6 (<sup>1</sup> $J(\text{H,B})$  = 144 Hz) ppm. IR (evaporated methylene chloride film, ATR,  $25\text{ }^\circ\text{C}$ ): 2533 (B-H). HRMS (negative mode ESI/APCI)  $[\text{M-H}]^{-1}$  m/z Calc:  $\text{C}_{15}\text{H}_{29}\text{B}_{22}\text{N}_2\text{Au}_1\text{S}_1$  = 585.2828 : Found = 585.2847.



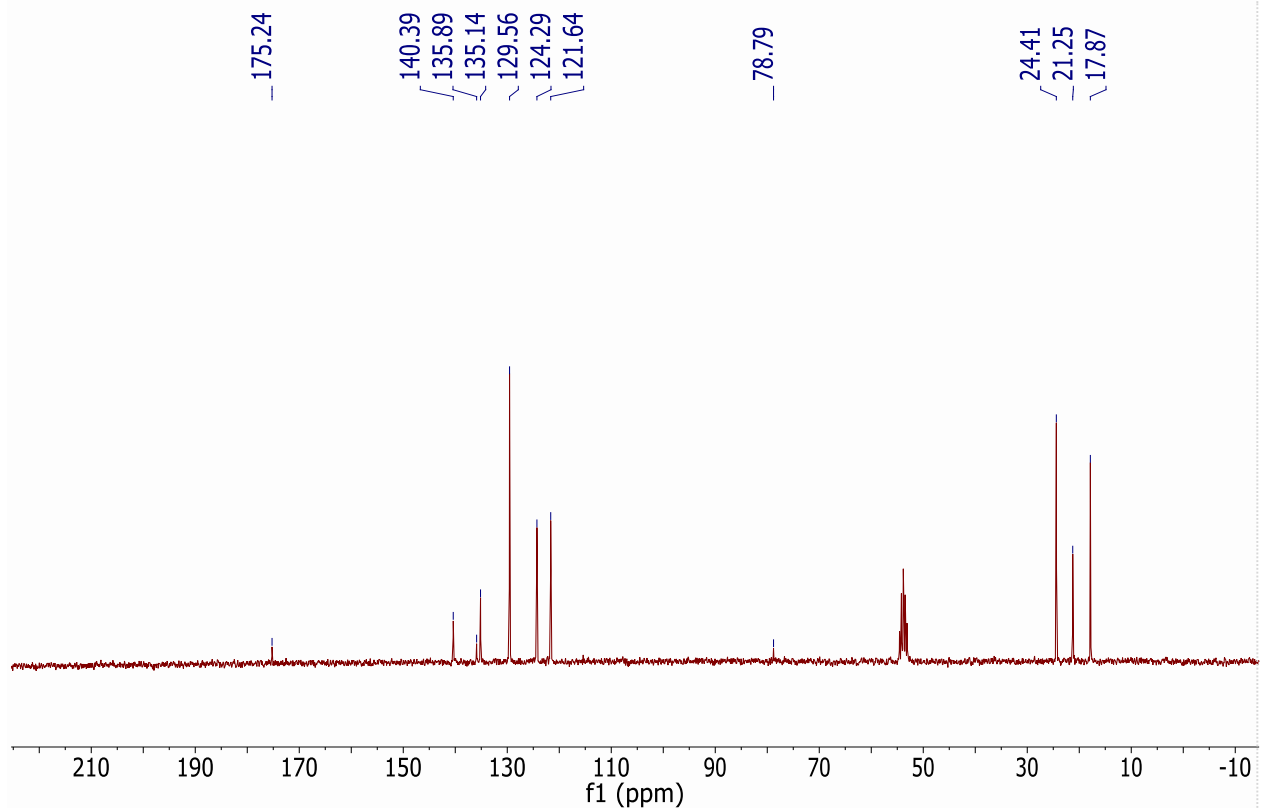
**Fig. S1.**  $^1\text{H}$ -NMR spectrum of **[2]Au** in methylene chloride- $\text{d}_2$ .



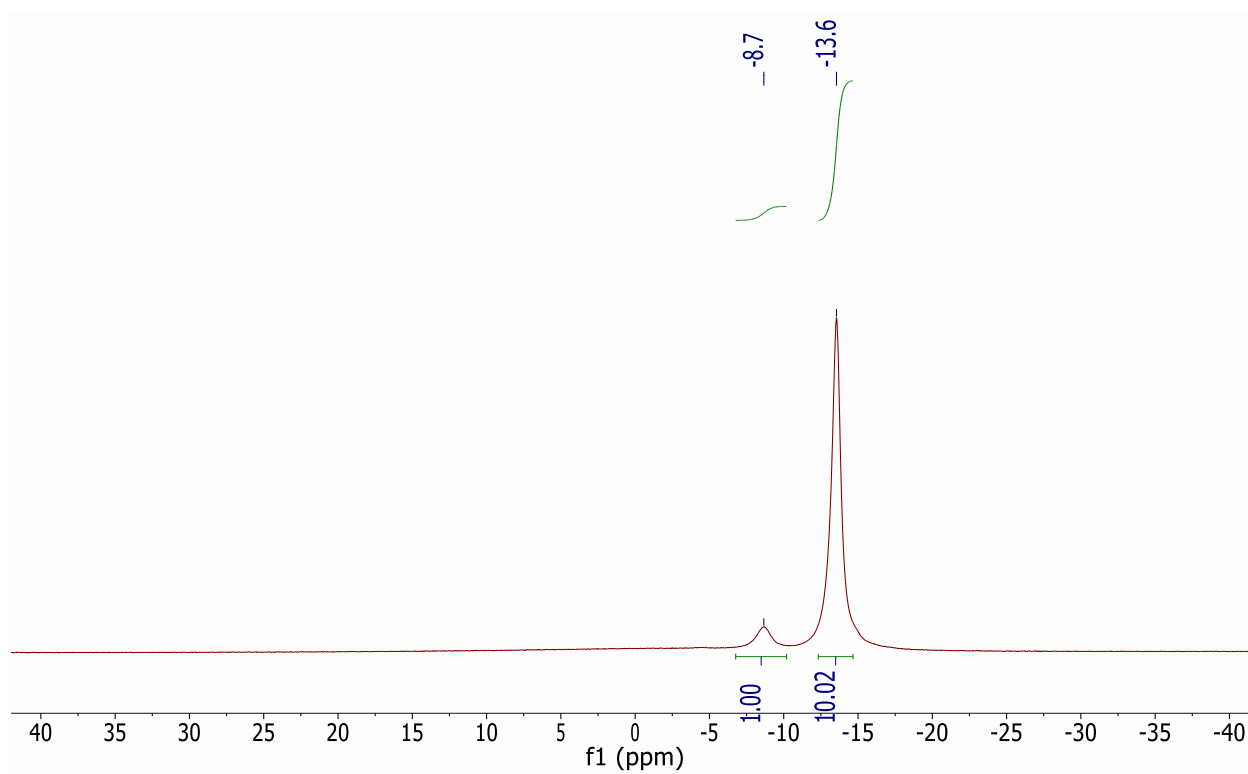
**Fig. S2.** An expanded view of the aromatic region of the  $^1\text{H}$ -NMR spectrum of **[2]Au** in methylene chloride- $\text{d}_2$  showing the small  $^3J(\text{H},\text{H})$  coupling of the imidazolylidene backbone protons.



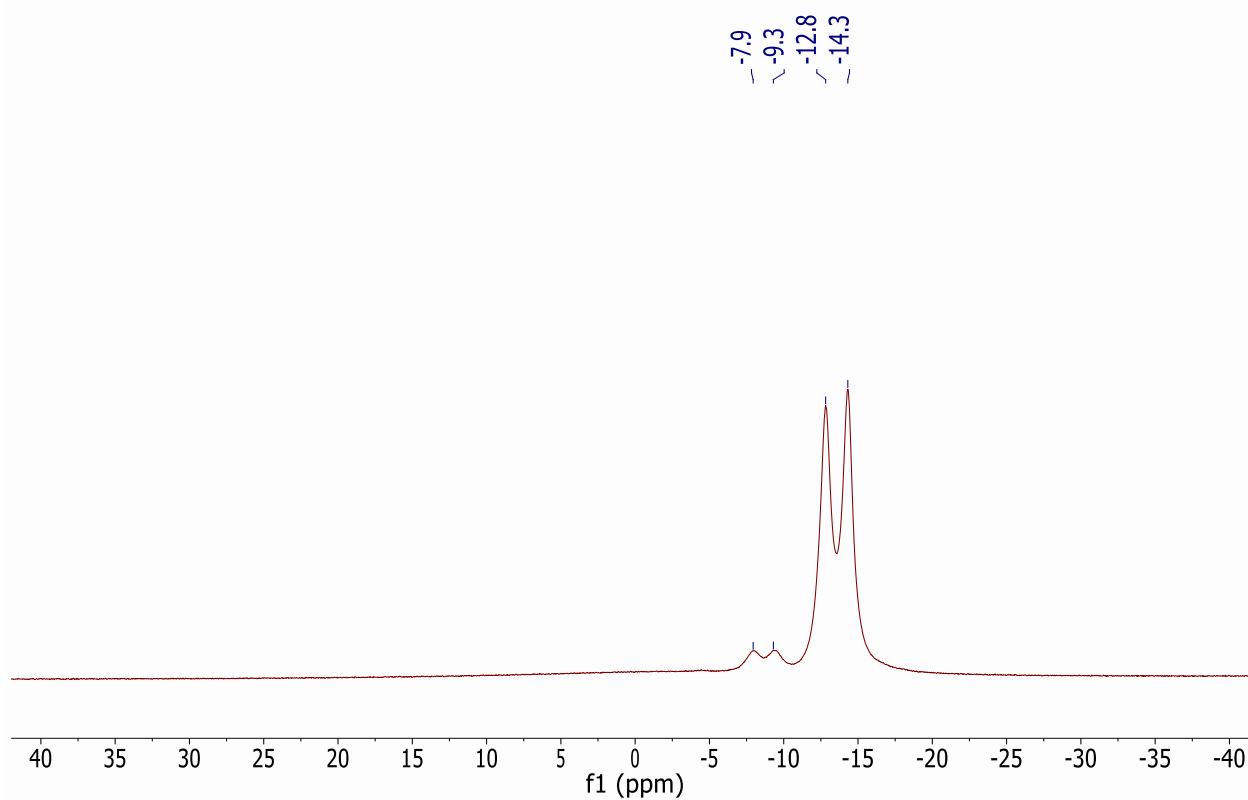
**Fig. S3.**  $^1\text{H}[^{11}\text{B}]$ -NMR spectrum of **[2]Au** in methylene chloride- $\text{d}_2$ . The boron hydrides appear at 2.63, 1.75, and 1.68 ppm.



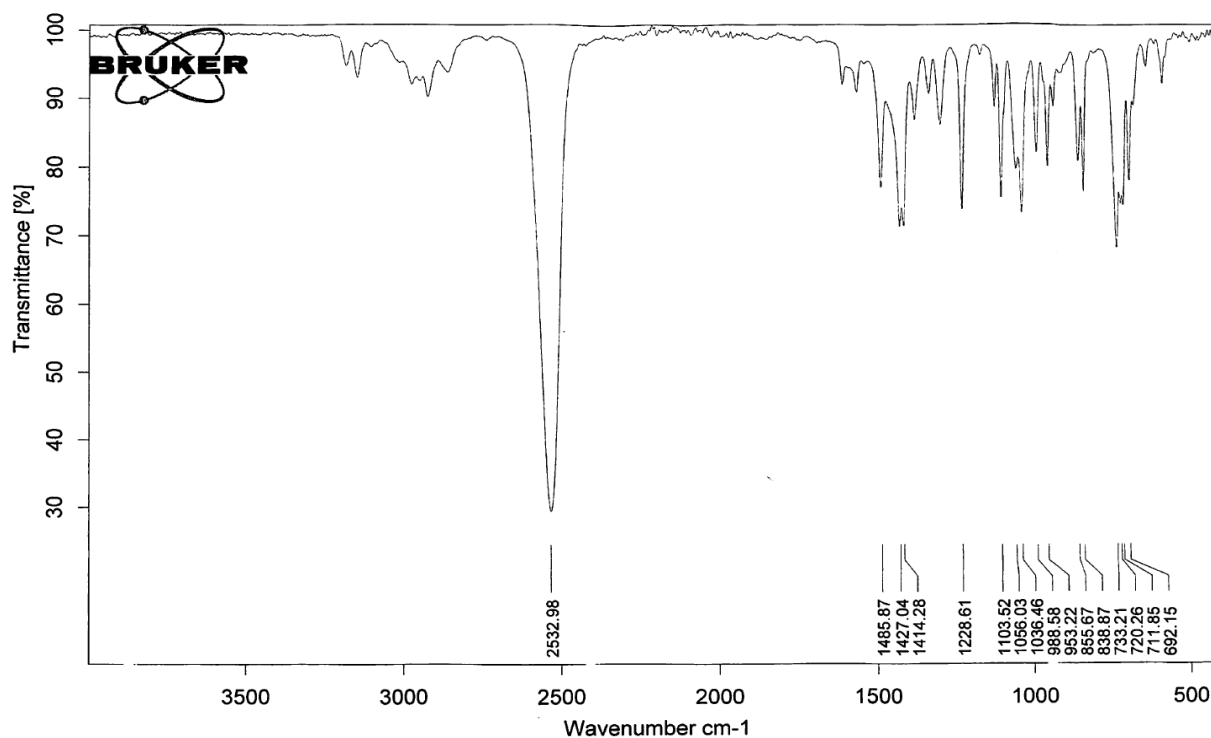
**Fig. S4.**  $^{13}\text{C}[^1\text{H}]$ -NMR spectrum of **[2]Au** in methylene chloride- $\text{d}_2$ .



**Fig. S5.**  $^{11}\text{B}[^1\text{H}]$ -NMR spectrum of  $[\mathbf{2}]\text{Au}$  in methylene chloride- $\text{d}_2$ .

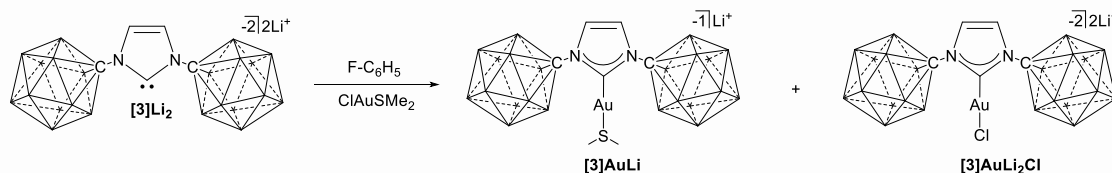


**Fig. S6.**  $^{11}\text{B}$ -NMR spectrum of  $[\mathbf{2}]\text{Au}$  in methylene chloride- $\text{d}_2$  showing the  $^1J(\text{B},\text{H})$  coupling.



**Fig. S7.** IR-spectrum of **[2]Au**, the B-H stretches appear at 2532 cm<sup>-1</sup>.

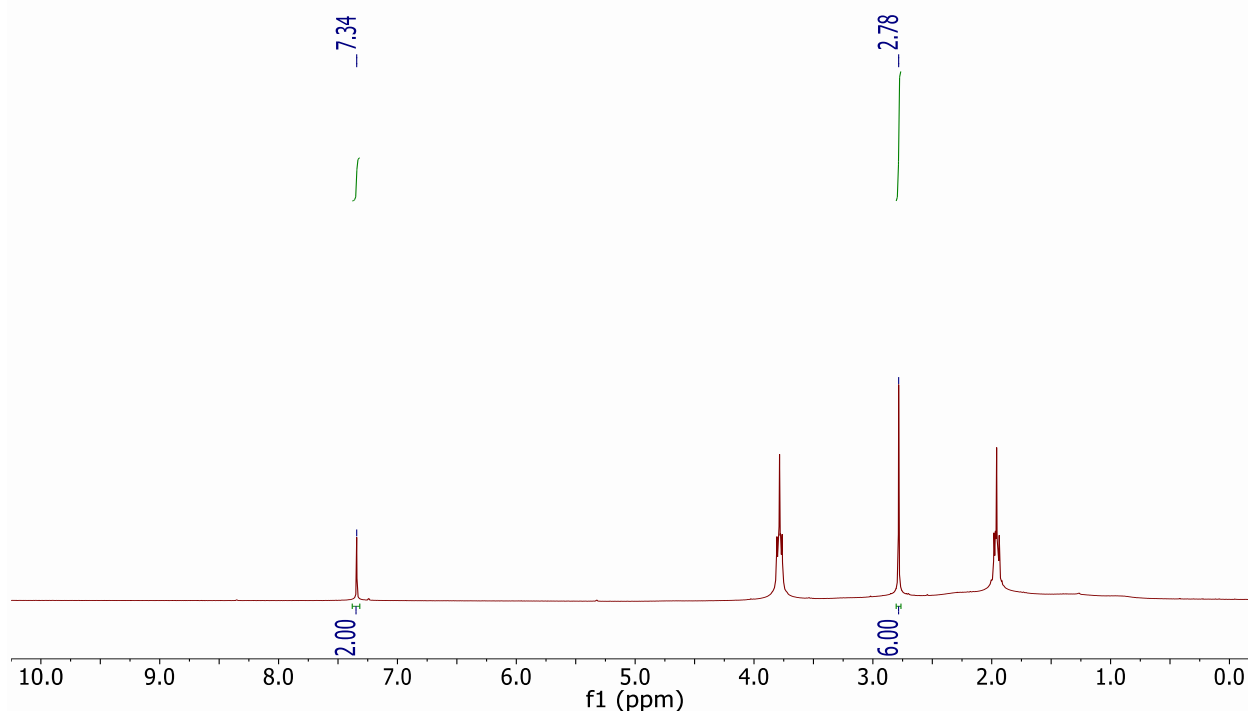
### **Synthesis of [3]AuLi and [3]AuLi<sub>2</sub>Cl:**



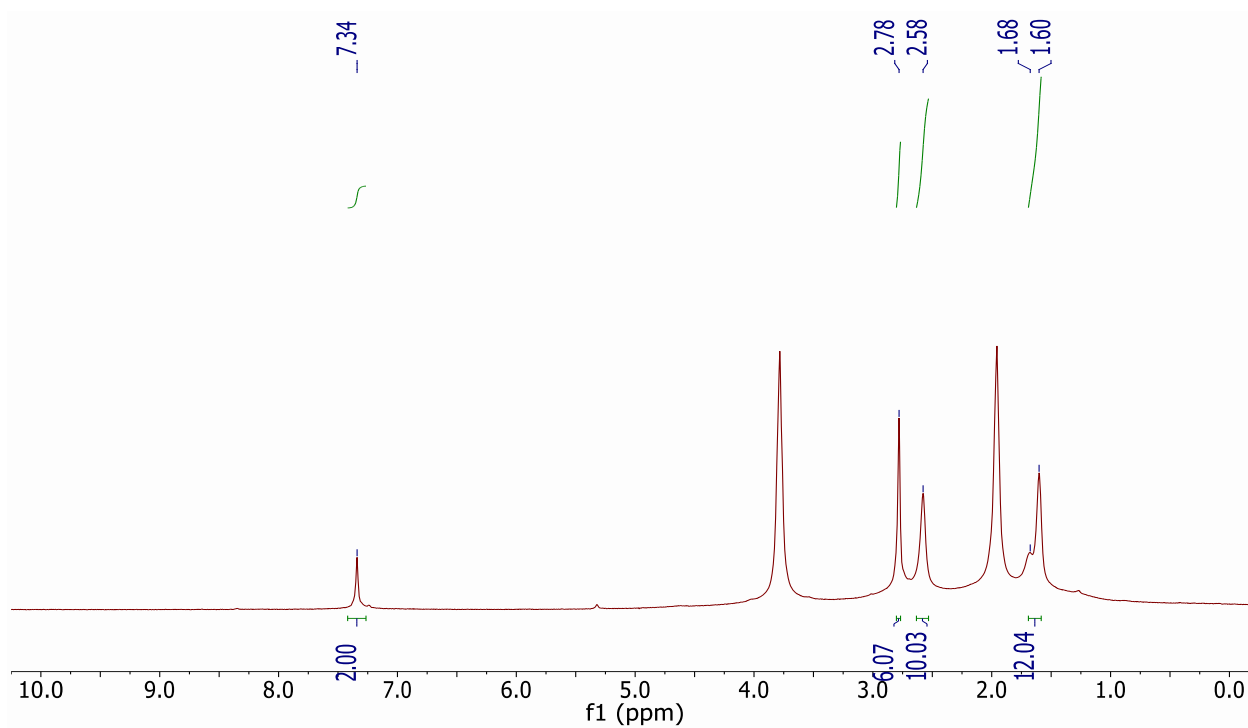
A 20 mL glass scintillation vial was equipped with a stir bar and loaded with **[3]Li<sub>2</sub>** (50.1 mg, 76 μmol) and ClAuSMe<sub>2</sub> (22.6 mg, 76 μmol). The vial was cooled to -40 °C in a cold well and cold (-40 °C) fluorobenzene (5 mL) was added. After 15 minutes any brown solid on the walls of the scintillation vial was scraped down into the reaction mixture and further stirred for 30 minutes at -40 °C. *Note: [3]Li<sub>2</sub> is not very soluble in F-C<sub>6</sub>H<sub>5</sub> and builds up on the vial walls.* More F-C<sub>6</sub>H<sub>5</sub> (5 mL) was added to the reaction mixture and the reaction was filtered while cold. The solvent was removed *in vacuo* giving **[3]AuLi** as a gold film (15.2 mg, 22% yield). A crystal of **[3]AuLi** was grown by cooling a solution of F-C<sub>6</sub>H<sub>5</sub> and hexane at -30 °C. <sup>1</sup>H NMR (300 MHz, methylene chloride-d<sub>2</sub>, 25 °C): δ = 7.34 (s, 2H), 2.78 (s, 6H) 3.38-0.60 (bm, 22H) ppm. <sup>1</sup>H[<sup>11</sup>B] NMR (192.5 MHz, methylene chloride-d<sub>2</sub>, 25 °C): δ = 7.34 (s, 2H), 2.78 (s, 6H), 2.58 (s, 5H), 1.68 (s, 1H), 1.60 (s, 5H) ppm. <sup>13</sup>C[<sup>1</sup>H] (150 MHz, methylene chloride-d<sub>2</sub>, 25 °C): δ = 174.3, 122.3, 79.9, 25.1 ppm. <sup>11</sup>B[<sup>1</sup>H] NMR (96 MHz, methylene chloride-d<sub>2</sub>, 25 °C): δ = -8.8, -13.8 ppm. <sup>11</sup>B NMR (96 MHz, methylene chloride-d<sub>2</sub>, 25 °C): δ = -8.8 (<sup>1</sup>J(H,B) = 134.4 Hz), -13.8 (<sup>1</sup>J(H,B) = 124.8 Hz) ppm. IR (evaporated methylene chloride film, ATR, 25 °C): 2532 (B-H). HRMS (negative mode ESI/APCI) [M]<sup>-</sup> m/z Calc: C<sub>7</sub>H<sub>30</sub>B<sub>22</sub>N<sub>2</sub>AuS<sub>1</sub> = 609.3999 : Found = 609.3996, [M-S(Me)<sub>2</sub>]<sup>-</sup> m/z Calc: C<sub>5</sub>H<sub>24</sub>B<sub>22</sub>N<sub>2</sub>Au<sub>1</sub> = 547.3807: Found = 547.3807.

To the insoluble residue, acetonitrile (4 mL) was added and the suspension was filtered. The remaining residue was extracted once more with acetonitrile (2 mL) and again filtered. The combined filtrate was pumped down to dryness containing **[3]AuLi<sub>2</sub>Cl**. <sup>1</sup>H NMR (300 MHz, acetonitrile-d<sub>3</sub>, 25 °C): δ = 7.35 (s, 2H), 3.5 – 0.65 (bm, 22H, B-H) ppm. <sup>1</sup>H[<sup>11</sup>B] NMR (192.5 MHz, acetonitrile-d<sub>3</sub>, 25 °C): δ = 7.34 (s, 2H), 2.57 (bs, 10H), 1.63 (bs, 2H), 1.54 (bs, 10H) ppm. <sup>13</sup>C[<sup>1</sup>H] (150 MHz, acetonitrile-d<sub>3</sub>, 25 °C): δ = 172.4, 122.9, 80.9 ppm. <sup>11</sup>B[<sup>1</sup>H] NMR (96 MHz, acetonitrile-d<sub>3</sub>, 25 °C): δ = -8.9, -13.9 ppm. <sup>11</sup>B NMR (96 MHz, acetonitrile-d<sub>3</sub>, 25 °C): δ = -8.9 (<sup>1</sup>J(H,B) = 139.2 Hz), -13.9 (<sup>1</sup>J(H,B) = 137 Hz) ppm. HRMS (negative mode ESI/APCI) [M]<sup>2-</sup> m/z Calc: C<sub>5</sub>H<sub>24</sub>B<sub>22</sub>N<sub>2</sub>Au<sub>1</sub>Cl<sub>1</sub> = 291.1754 : Found = 291.1753.

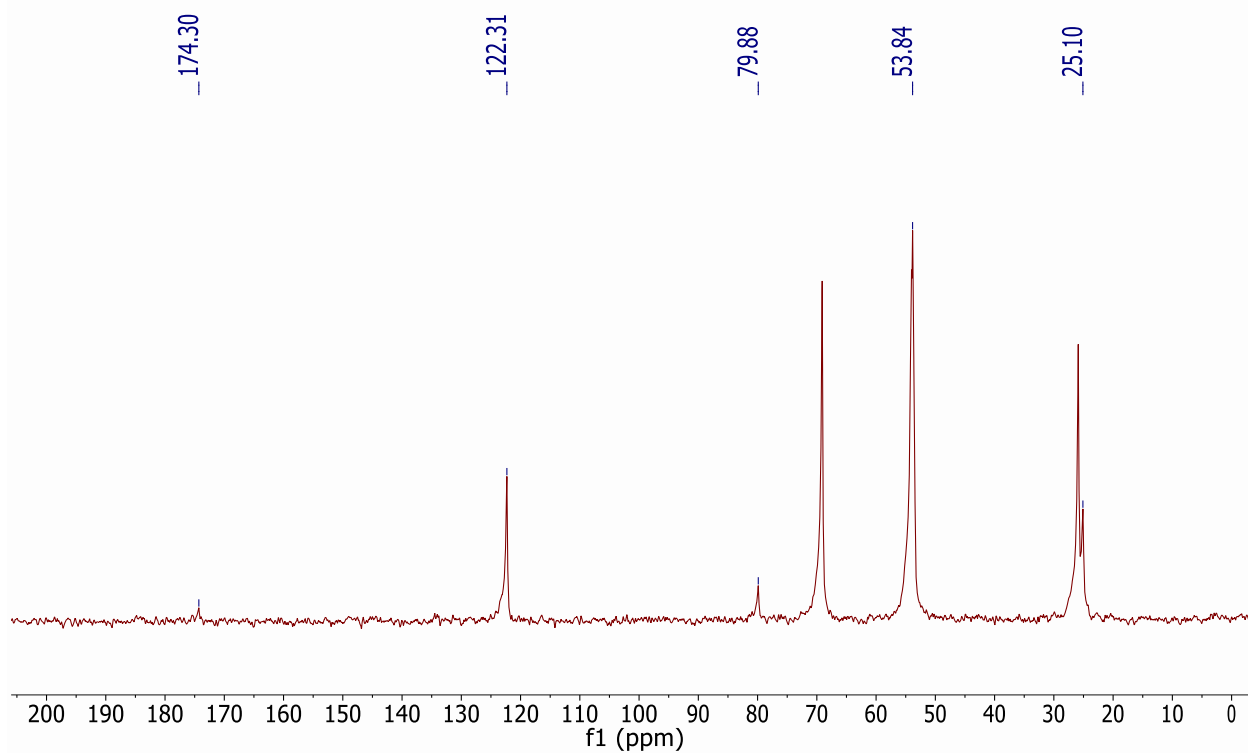
### Spectroscopic Data for **[3]AuLi**:



**Fig. S8.** <sup>1</sup>H-NMR spectrum of **[3]AuLi** in methylene chloride-d<sub>2</sub>. Note: THF(3.79 and 1.96 ppm) is coordinated to the lithium cation.

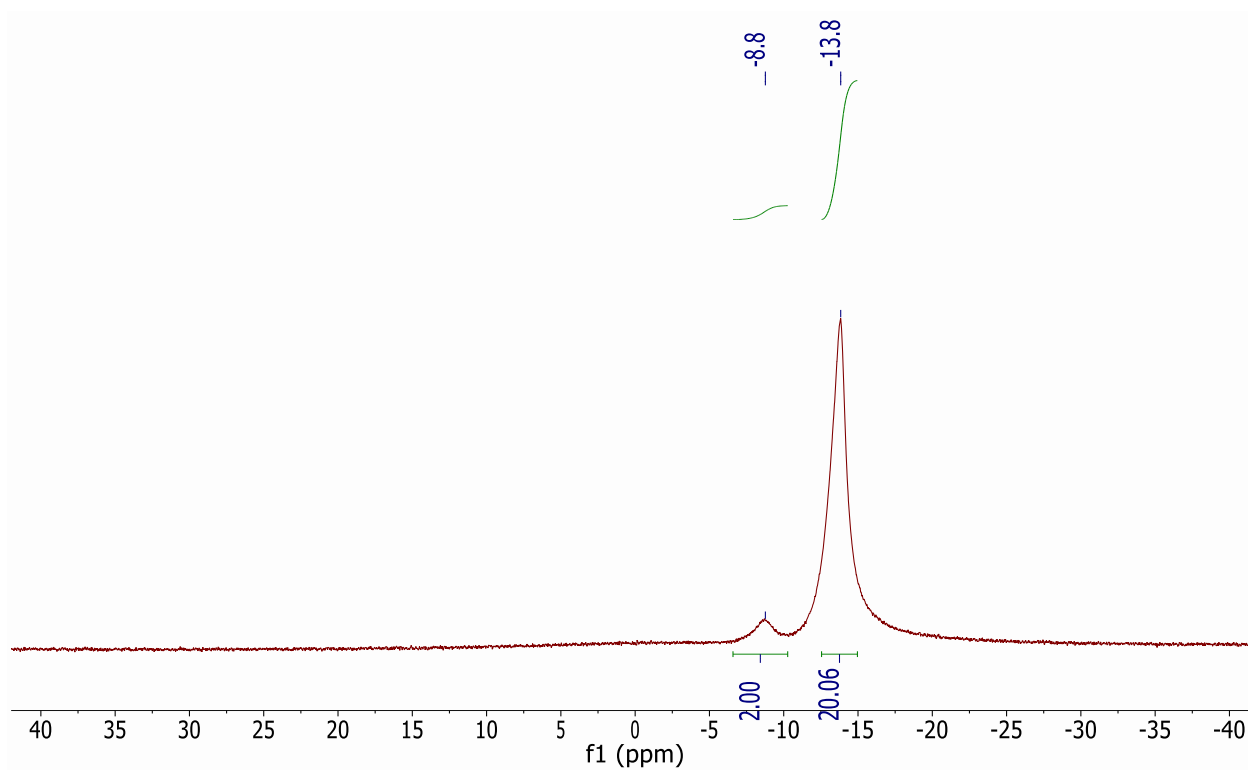


**Fig. S9.**  $^1\text{H}[^{11}\text{B}]$ -NMR spectrum of **[3]AuLi** in methylene chloride- $\text{d}_2$ . The boron hydrides appear at 2.58, 1.68 and 1.60 ppm.

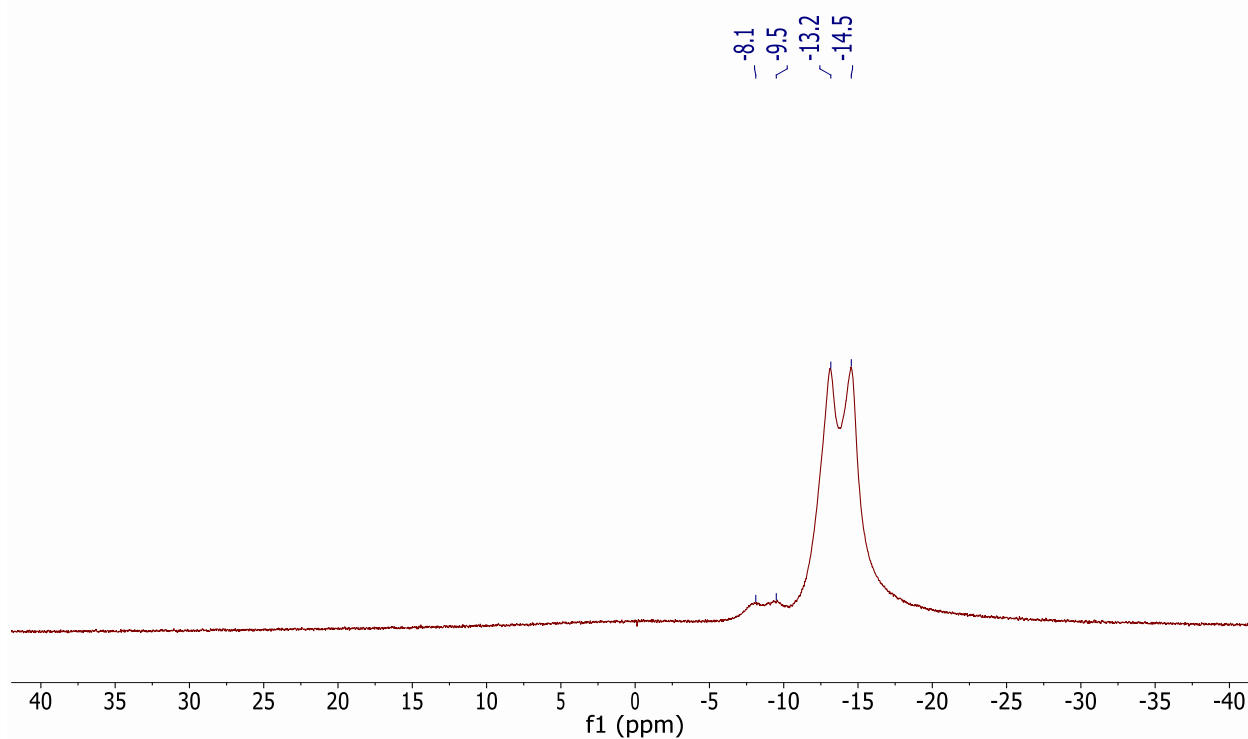


**Fig. S10.**  $^{13}\text{C}[^1\text{H}]$ -NMR spectrum of **[3]AuLi** in methylene chloride- $\text{d}_2$ . Note: THF(69.09 and 25.88 ppm) is coordinated to the lithium cation.

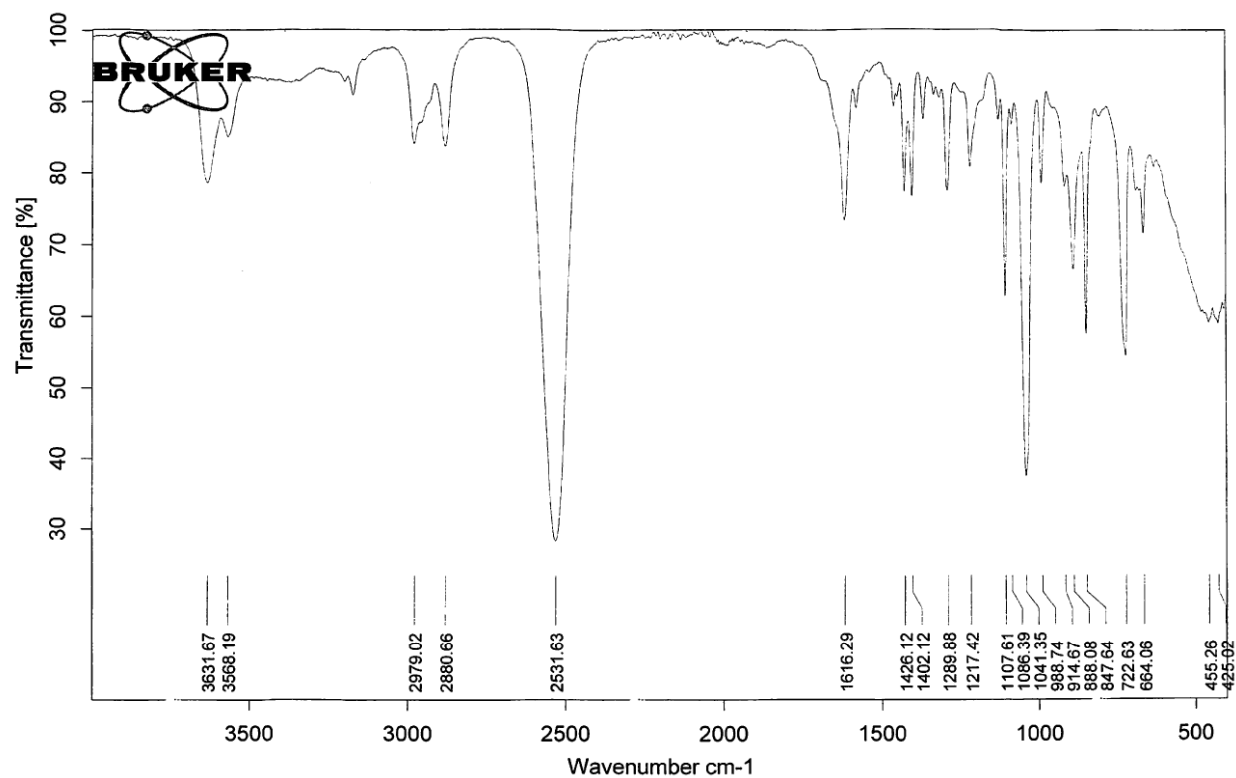




**Fig. S11.**  $^{11}\text{B}[^1\text{H}]$ -NMR spectrum of  $[\mathbf{3}]\text{AuLi}$ .

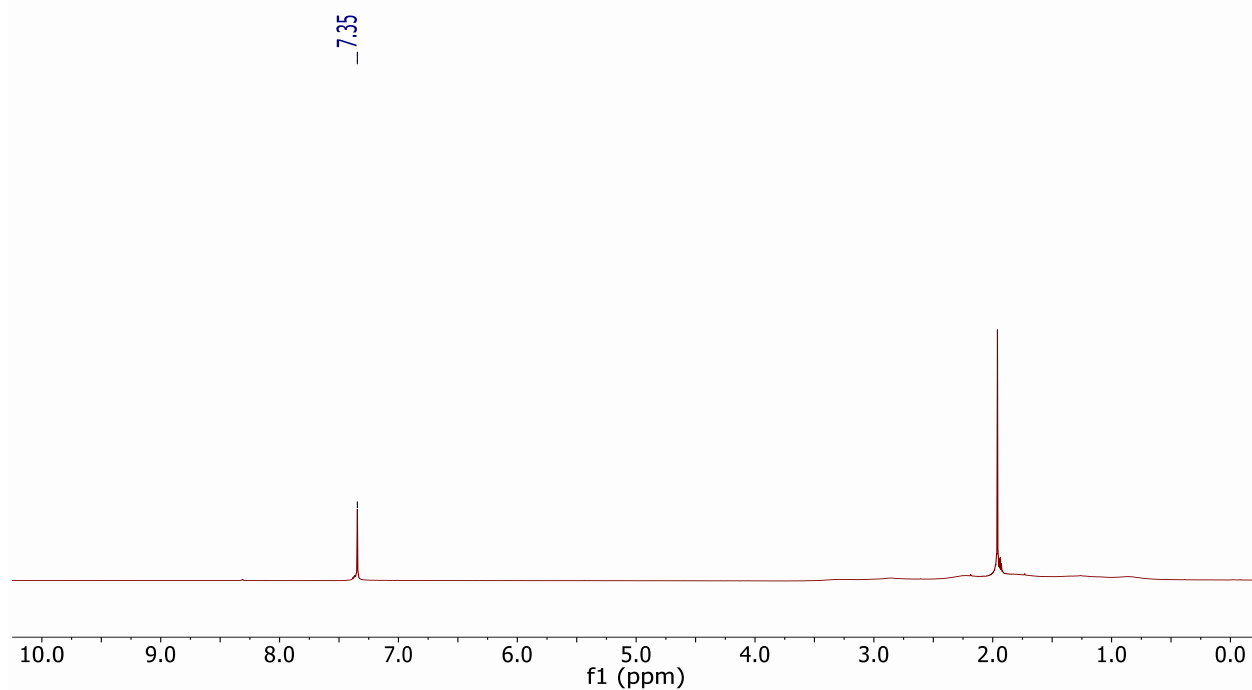


**Fig. S12.**  $^{11}\text{B}$ -NMR spectrum of  $[\mathbf{3}]\text{AuLi}$  showing the  $^1J(\text{B},\text{H})$  coupling.

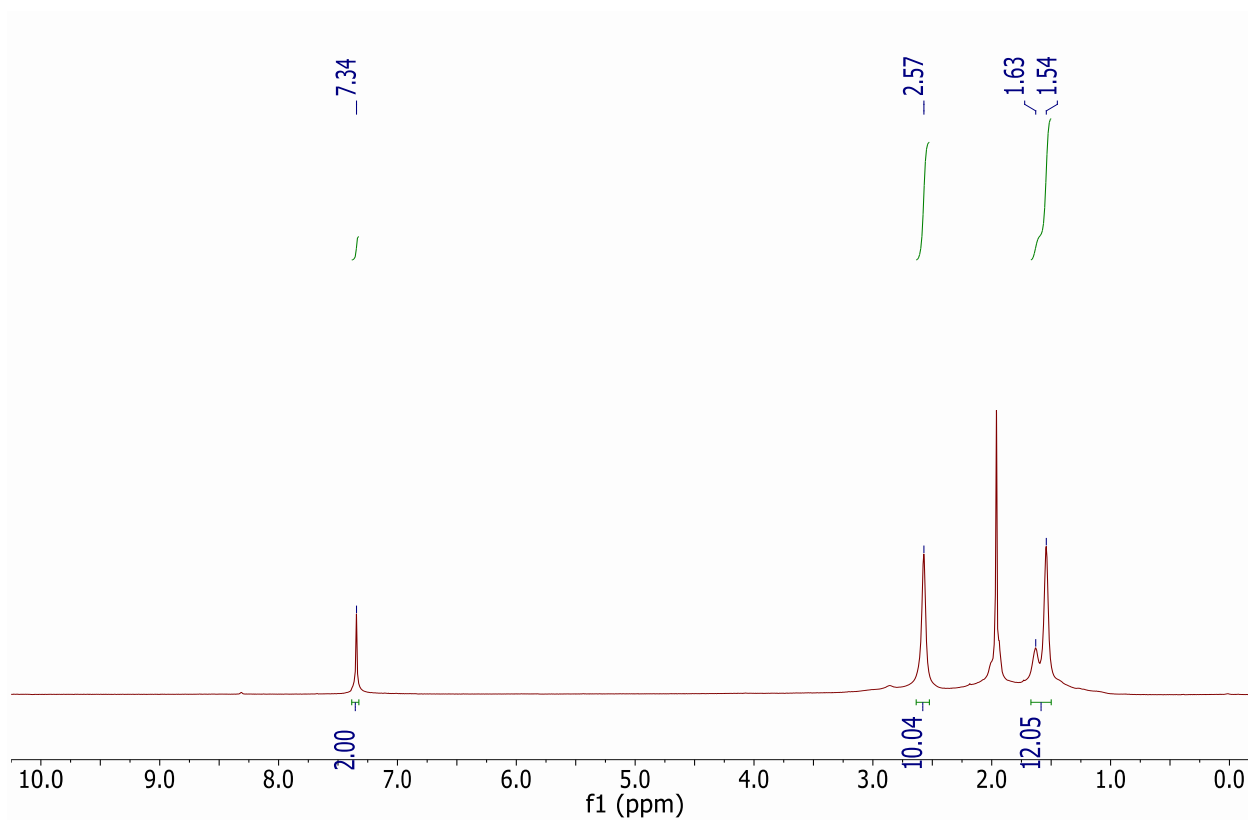


**Fig. S13.** IR spectrum of **[3]AuLi**. The B-H stretches appear at  $2532\text{ cm}^{-1}$ .

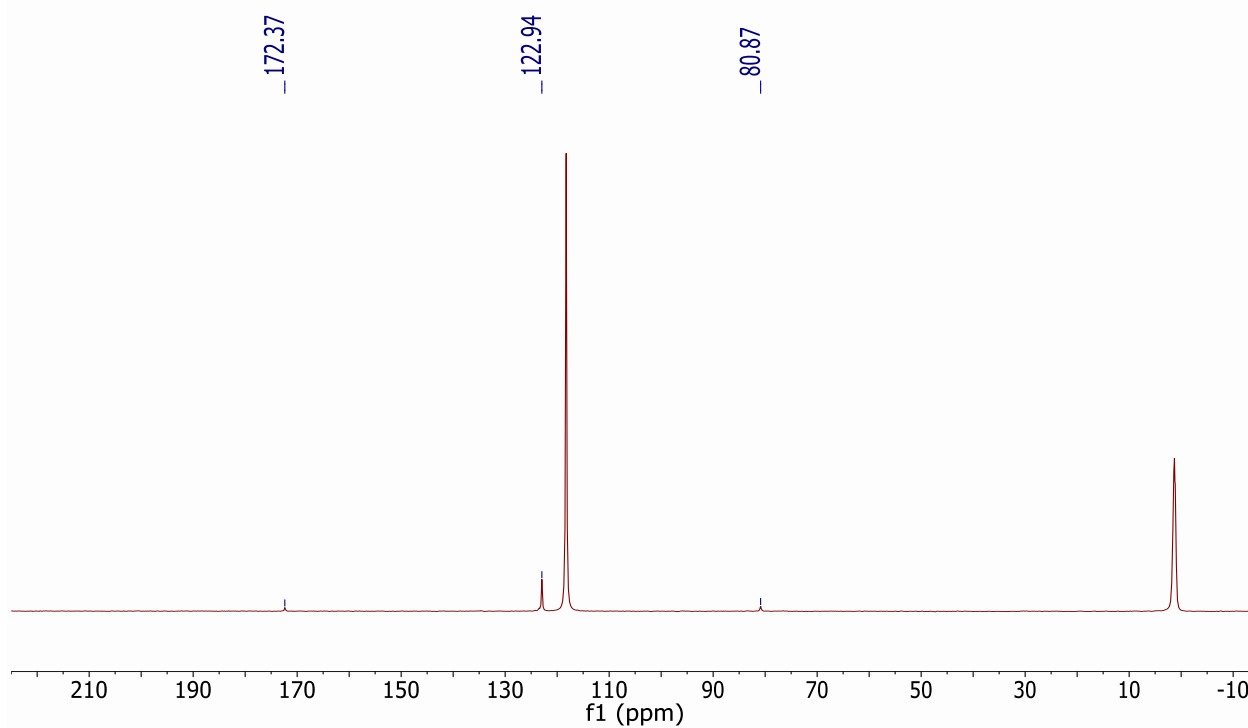
**Spectroscopic Data for **[3]AuLi<sub>2</sub>Cl**:**



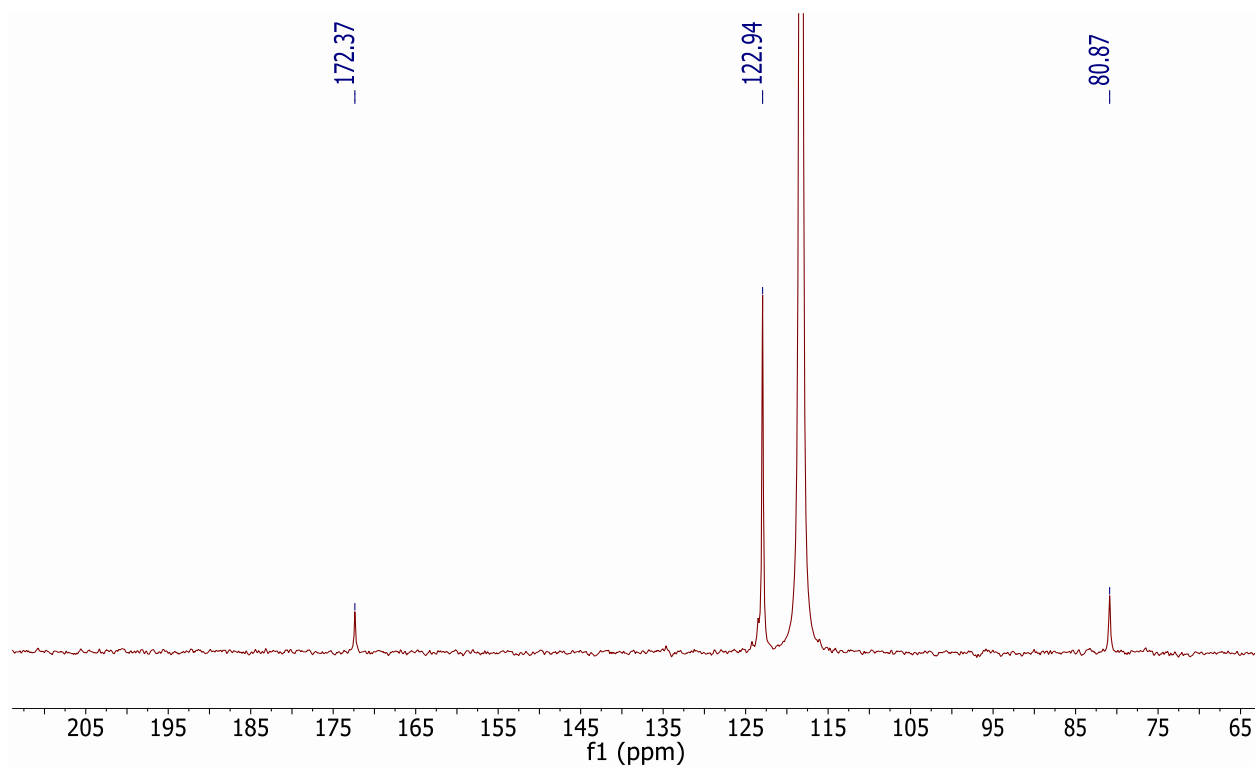
**Fig. S14.**  $^1\text{H}$ -NMR spectrum of the residue **[3]AuLi<sub>2</sub>Cl** in acetonitrile- $\text{d}_3$  showing the lack of coordinated dimethylsulfide. *Note: Acetonitrile is coordinated to the lithium cations at  $1.96\text{ ppm}$ .*



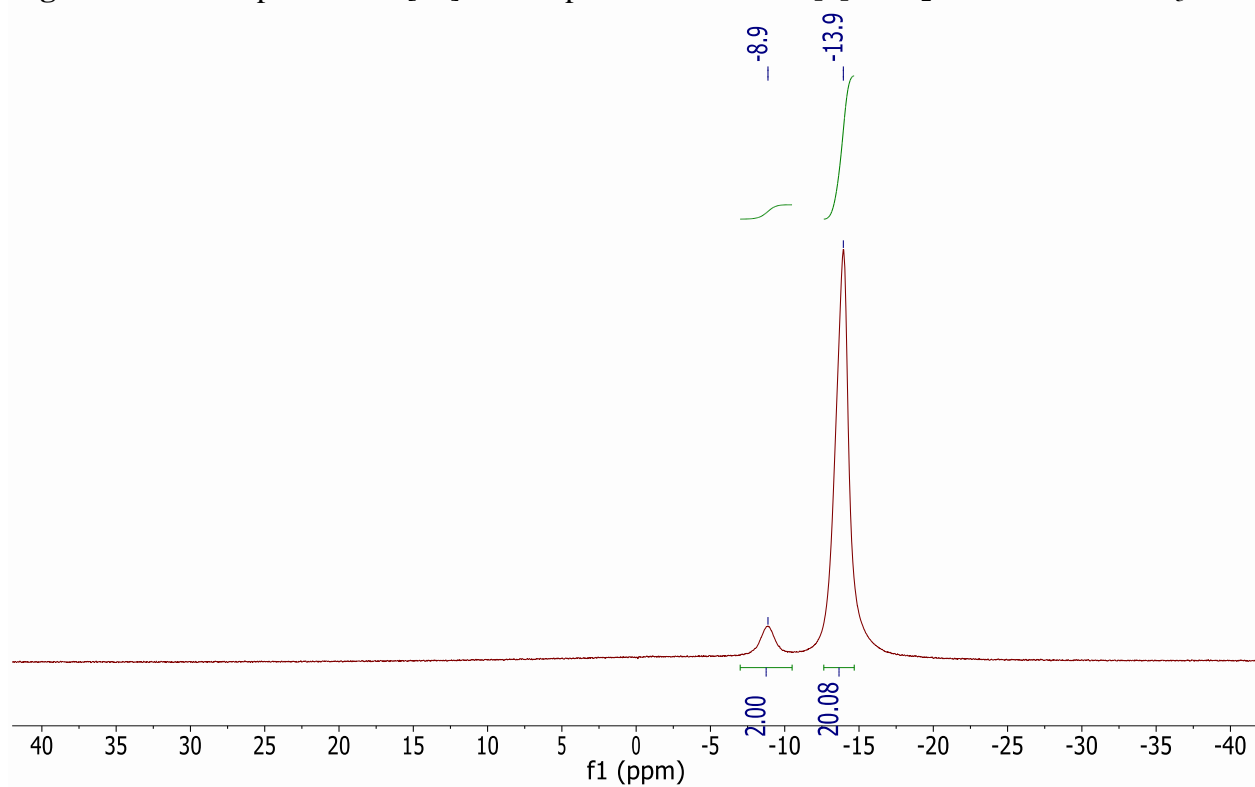
**Fig. S15.** <sup>1</sup>H[<sup>11</sup>B]-NMR spectrum of residue [3]AuLi<sub>2</sub>Cl in acetonitrile-d<sub>3</sub>. The boron hydrides appear at 2.57, 1.63, and 1.54 ppm.



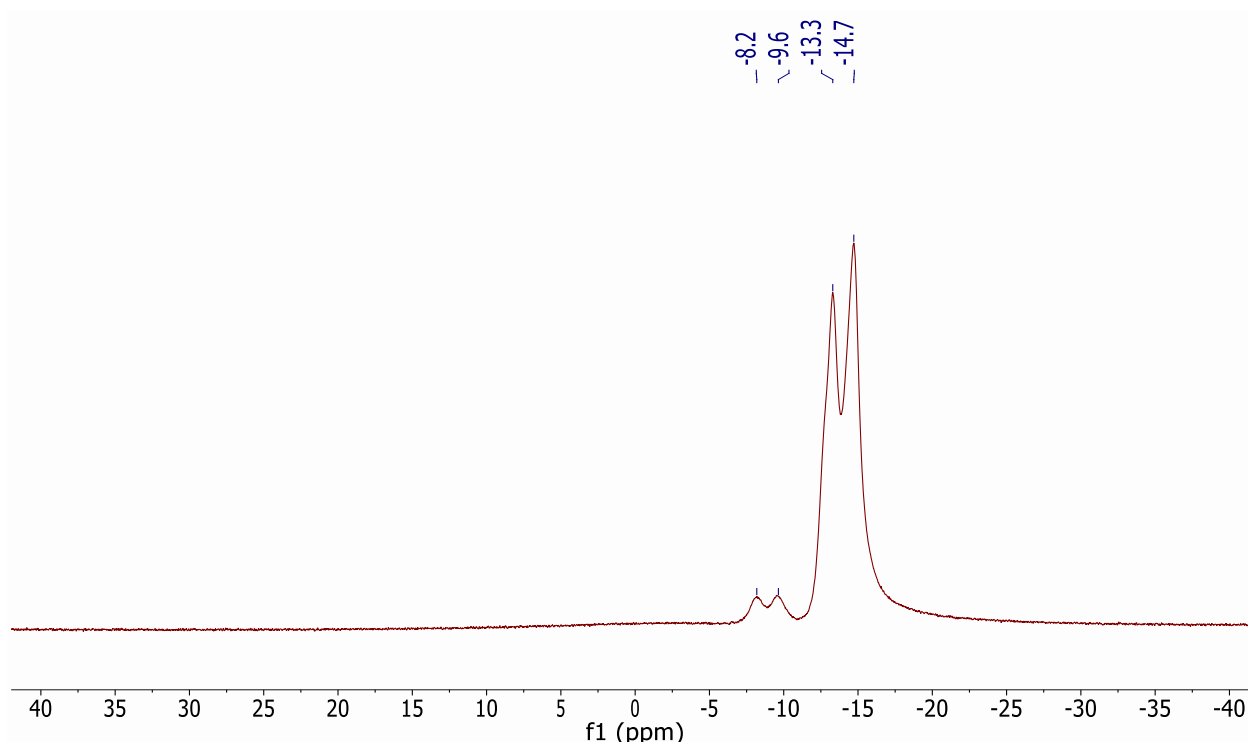
**Fig. S16.** <sup>13</sup>C[<sup>1</sup>H]-NMR spectrum of residue [3]AuLi<sub>2</sub>Cl in acetonitrile-d<sub>3</sub>.



**Fig. S17.** A blow up of the  $^{13}\text{C}[^1\text{H}]$ -NMR spectrum of residue **[3]AuLi<sub>2</sub>Cl** in acetonitrile- $\text{d}_3$ .

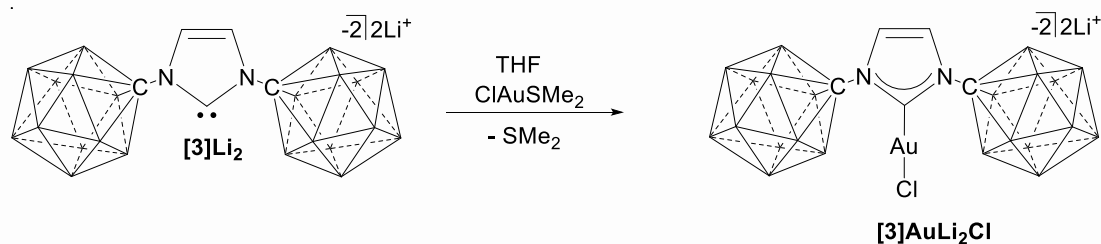


**Fig. S18.**  $^{11}\text{B}[^1\text{H}]$ -NMR spectrum of residue **[3]AuLi<sub>2</sub>Cl** in acetonitrile- $\text{d}_3$ .



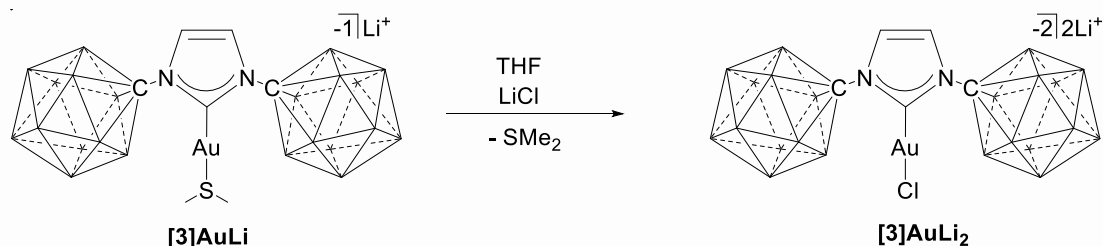
**Fig. S19.**  $^{11}\text{B}$ -NMR spectrum of residue  $[\mathbf{3}]\text{AuLi}_2\text{Cl}$  in acetonitrile- $\text{d}_3$  showing the  $^1J(\text{B},\text{H})$  coupling.

#### Direct Synthesis of $[\mathbf{3}]\text{AuLi}_2\text{Cl}$ :



A 20 mL scintillation vial was equipped with a stir bar and loaded with  $[\mathbf{3}]\text{Li}_2$  (50.6 mg, 77.3  $\mu\text{mol}$ ) and  $\text{ClAuSMe}_2$  (22.8 mg, 77.3  $\mu\text{mol}$ ). The solids were dissolved in THF (2 mL) and the solution was stirred for 2 hours at room temperature, then the high vacuum was applied for three minutes (*removes liquid dimethylsulfide*). After applying vacuum THF (1 mL) was added to the solution and the reaction was stirred for another two hours at room temperature then finally pumped down furnishing the title compound  $[\mathbf{3}]\text{AuLi}_2\text{Cl}$  quantitatively. The spectroscopic data matches that provided above.

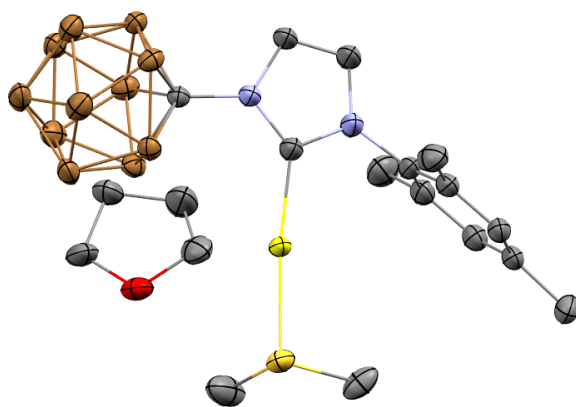
### Conversion of [3]AuLi to [3]AuLi<sub>2</sub>Cl:



A 20 mL scintillation vial was equip with a stir bar and **[3]AuLi** (34.3 mg) was dissolved in a minimal amount of THF. The THF was then saturated in LiCl and stirred at room temperature for two hours. After two hours the reaction was pumped on via high vacuum (1 minute) then THF (1 mL) was added and stirred for another two hours then pumped down to dryness. Acetonitrile (2 mL) was added and the reaction mixture filtered. The acetonitrile was pumped down giving to quantitatively afford **[3]AuLi<sub>2</sub>Cl**. The spectroscopic data matches that provided above

### X-Ray Structure Determination

#### Crystal Structure of [2]Au:



**Fig. S20.** Solid state structure of **[2]Au**. Hydrogen atoms are omitted for clarity. Color code: Au = yellow, B = brown, C = gray, N = blue, O = red, S = orange.

A brown fragment of a prism (0.325 x 0.288 x 0.168 mm<sup>3</sup>) was used for the single crystal x-ray diffraction study of C<sub>15</sub>H<sub>30</sub>N<sub>2</sub>B<sub>11</sub>SAu<sub>0.88</sub>CS<sub>0.12</sub>.C<sub>4</sub>H<sub>8</sub>O (sample vL156SF\_0m). The crystal was coated with paratone oil and mounted on to a cryo-loop glass fiber. X-ray intensity data were collected at 100(2) K on a Bruker APEX2 platform-CCD x-ray diffractometer system (fine focus Mo-radiation,  $\lambda = 0.71073 \text{ \AA}$ , 50KV/30mA power). The CCD detector was placed at a distance of 5.0600 cm from the crystal.

A total of 3600 frames were collected for a sphere of reflections (with scan width of  $0.3^\circ$  in  $\omega$ , starting  $\omega$  and  $2\theta$  angles at  $-30^\circ$ , and  $\phi$  angles of  $0^\circ$ ,  $90^\circ$ ,  $120^\circ$ ,  $180^\circ$ ,  $240^\circ$ , and  $270^\circ$  for every 600 frames, 10 sec/frame exposure time). The frames were integrated using the Bruker SAINT software package and using a narrow-frame integration algorithm. Based on an orthorhombic crystal system, the integrated frames yielded a total of 96913 reflections at a maximum  $2\theta$  angle of  $52.728^\circ$  ( $0.80 \text{ \AA}$  resolution), of which 5742 were independent reflections ( $R_{\text{int}} = 0.0304$ ,  $R_{\text{sig}} = 0.0108$ , redundancy = 16.9, completeness = 100%) and 4992 (86.9%) reflections were greater than  $2\sigma$  (I). The unit cell parameters were, **a** = 18.8223(7)  $\text{\AA}$ , **b** = 15.7649(6)  $\text{\AA}$ , **c** = 18.9175(7)  $\text{\AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 5613.4(4) \text{ \AA}^3$ ,  $Z = 8$ , calculated density  $D_c = 1.540 \text{ g/cm}^3$ . Absorption corrections were applied (absorption coefficient  $\mu = 4.867 \text{ mm}^{-1}$ ; max/min transmission = 0.495/0.301) to the raw intensity data using the SADABS program.

The Bruker SHELXTL software package was used for phase determination and structure refinement. The distribution of intensities ( $E^2 - 1 = 1.104$ ) and systematic absent reflections indicated one possible space group, Pbca. The space group Pbca (#61) was later determined to be correct. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetric unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified. There was one disordered molecule of  $\text{C}_{15}\text{H}_{30}\text{N}_2\text{B}_{11}\text{SAu}$  and one disordered THF solvent present in the asymmetric unit of the unit cell. The Au/Cs and THF disordered site occupancy ratios were 88%/12% and 55%/45%, respectively.

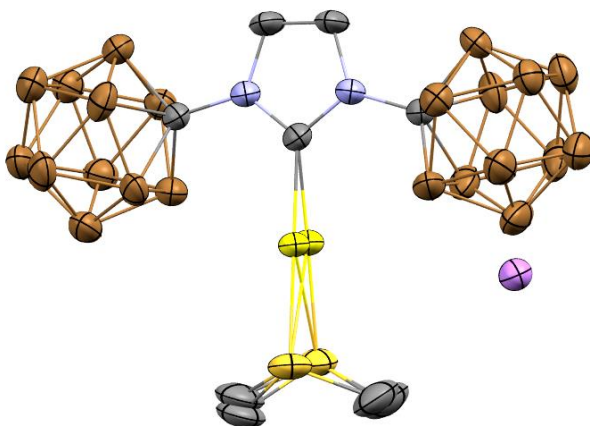
Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on  $F^2$ . The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. The refinement converged at  $R1 = 0.0165$ ,  $wR2 = 0.0395$ , with intensity,  $I > 2\sigma$  (I). The largest peak/hole in the final difference map was  $0.524/-0.425 \text{ e/\AA}^3$

**Table 1.** Crystal data and structure refinement for [2]Au.

Identification code	vL156SF_0m	
Empirical formula	$\text{C}_{19} \text{H}_{38} \text{Au}_{0.88} \text{B}_{11} \text{Cs}_{0.12} \text{N}_2 \text{O S}$	
Formula weight	650.84	
Temperature	100(2) K	
Wavelength	0.71073 $\text{\AA}$	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	$a = 18.8223(7) \text{ \AA}$	$\alpha = 90^\circ$ .
	$b = 15.7649(6) \text{ \AA}$	$\beta = 90^\circ$ .
	$c = 18.9175(7) \text{ \AA}$	$\gamma = 90^\circ$ .
Volume	$5613.4(4) \text{ \AA}^3$	

Z	8
Density (calculated)	1.540 Mg/m <sup>3</sup>
Absorption coefficient	4.867 mm <sup>-1</sup>
F(000)	2569
Crystal size	0.325 x 0.288 x 0.168 mm <sup>3</sup>
Theta range for data collection	2.000 to 26.364°.
Index ranges	-23<=h<=23, -19<=k<=19, -23<=l<=23
Reflections collected	96913
Independent reflections	5742 [R(int) = 0.0304]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	5742 / 28 / 371
Goodness-of-fit on F <sup>2</sup>	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0165, wR2 = 0.0395
R indices (all data)	R1 = 0.0219, wR2 = 0.0420
Extinction coefficient	n/a
Largest diff. peak and hole	0.524 and -0.425 e.Å <sup>-3</sup>

### Crystal Structure of [3]AuLi:



**Fig. S21.** Solid state structure of [3]AuLi. Hydrogen atoms and THFs are omitted for clarity. Color code: Au = yellow, B = brown, C = gray, Li = pink, N = blue, S = orange.

A colorless plate fragment (0.308 x 0.266 x 0.056 mm<sup>3</sup>) was used for the single crystal x-ray diffraction study of [Li[C<sub>4</sub>H<sub>8</sub>O]<sub>2</sub>]<sup>+</sup>. [C<sub>7</sub>H<sub>30</sub>B<sub>22</sub>N<sub>2</sub>SAu]<sup>-</sup> (sample vL163SF\_0m). The crystal was coated with paratone oil and mounted on to a cryo-loop glass fiber. X-ray intensity data were collected at 200(2) K on a Bruker APEX2 platform-CCD x-ray diffractometer system (fine focus



Mo-radiation,  $\lambda = 0.71073 \text{ \AA}$ , 50KV/30mA power). The CCD detector was placed at a distance of 5.0600 cm from the crystal.

A total of 3600 frames were collected for a sphere of reflections (with scan width of  $0.3^\circ$  in  $\omega$  and  $\phi$ , starting  $\omega$  and  $2\theta$  angles of  $-30^\circ$ , and  $\phi$  angles of  $0^\circ, 90^\circ, 120^\circ, 180^\circ, 240^\circ$ , and  $270^\circ$  for every 600 frames, 30 sec/frame exposure time). The frames were integrated using the Bruker SAINT software package and using a narrow-frame integration algorithm. Based on a monoclinic crystal system, the integrated frames yielded a total of 98237 reflections at a maximum  $2\theta$  angle of  $59.142^\circ$  ( $0.72 \text{ \AA}$  resolution), of which 12091 were independent reflections ( $R_{\text{int}} = 0.0477$ ,  $R_{\text{sig}} = 0.0287$ , redundancy = 8.1, completeness = 100%) and 10308 (85.3%) reflections were greater than  $2\sigma(I)$ . The unit cell parameters were,  $a = 11.1021(7) \text{ \AA}$ ,  $b = 14.8321(10) \text{ \AA}$ ,  $c = 26.1690(17) \text{ \AA}$ ,  $\beta = 90.0492(12)^\circ$ ,  $V = 4309.2(5) \text{ \AA}^3$ ,  $Z = 4$ , calculated density  $D_c = 1.394 \text{ g/cm}^3$ . Absorption corrections were applied (absorption coefficient  $\mu = 3.495 \text{ mm}^{-1}$ ; max/min transmission = 0.828/0.412) to the raw intensity data using the SADABS program.

The Bruker SHELXTL software package was used for phase determination and structure refinement. The distribution of intensities ( $E^2 - 1 = 0.812$ ) and systematic absent reflections indicated one possible space group,  $P2(1)/n$ . The space group  $P2(1)/n$  (#14) was later determined to be correct. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetric unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified. There was one disordered cation of  $[\text{Li}[\text{C}_4\text{H}_8\text{O}]_2]^+$  and one disordered anion of  $[\text{C}_7\text{H}_{30}\text{B}_{22}\text{N}_2\text{SAu}]^-$  present in the asymmetric unit of the unit cell. Three of the four THF molecules of the cation were modeled with disorder (disordered site occupancy ratios were 80%/20%, 77%/23%, and 55%/45%). The  $\text{AuSC}_2\text{H}_6$ -group of the anion was modeled with disorder (disordered site occupancy ratios were 81%/19%). The structure was refined as a pseudo-merohedral twin (twin law 1 0 0 0 -1 0 0 0 -1, and twin ratio of 59%/41%).

Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on  $F^2$ . The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. The refinement converged at  $R1 = 0.0314$ ,  $wR2 = 0.0704$ , with intensity  $I > 2\sigma(I)$ . The largest peak/hole in the final difference map was  $1.080/-0.861 \text{ e/\AA}^3$ .

**Table 2.** Crystal data and structure refinement for **[3]AuLi**.

Identification code	vL163SF_0m
Empirical formula	C23 H62 Au B22 Li N2 O4 S
Formula weight	904.53
Temperature	200(2) K

Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 11.1021(7) Å	$\alpha = 90^\circ$ .
	b = 14.8321(10) Å	$\beta = 90.0492(12)^\circ$ .
	c = 26.1690(17) Å	$\gamma = 90^\circ$ .
Volume	4309.2(5) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.394 Mg/m <sup>3</sup>	
Absorption coefficient	3.495 mm <sup>-1</sup>	
F(000)	1816	
Crystal size	0.308 x 0.266 x 0.056 mm <sup>3</sup>	
Theta range for data collection	1.373 to 29.571°.	
Index ranges	-15 ≤ h ≤ 15, -20 ≤ k ≤ 20, -36 ≤ l ≤ 36	
Reflections collected	98237	
Independent reflections	12091 [R(int) = 0.0477]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	12091 / 405 / 592	
Goodness-of-fit on F <sup>2</sup>	1.027	
Final R indices [I > 2σ(I)]	R1 = 0.0314, wR2 = 0.0704	
R indices (all data)	R1 = 0.0419, wR2 = 0.0745	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.080 and -0.861 e.Å <sup>-3</sup>	

### **References:**

1. A. El-Hellani, V. Lavallo, *Angew. Chem. Int. Ed.*, **2014**, 53, 4489-4493.
2. M. J. Asay, S. P. Fisher, S. E. Lee, F. S. Tham, D. Borchardt, V. Lavallo, *Chem. Commun.*, **2015**, 51, 5359-5362.