Supplementary Information

Ligand-based control of nuclearity in (NHC)gold(I) sulfides

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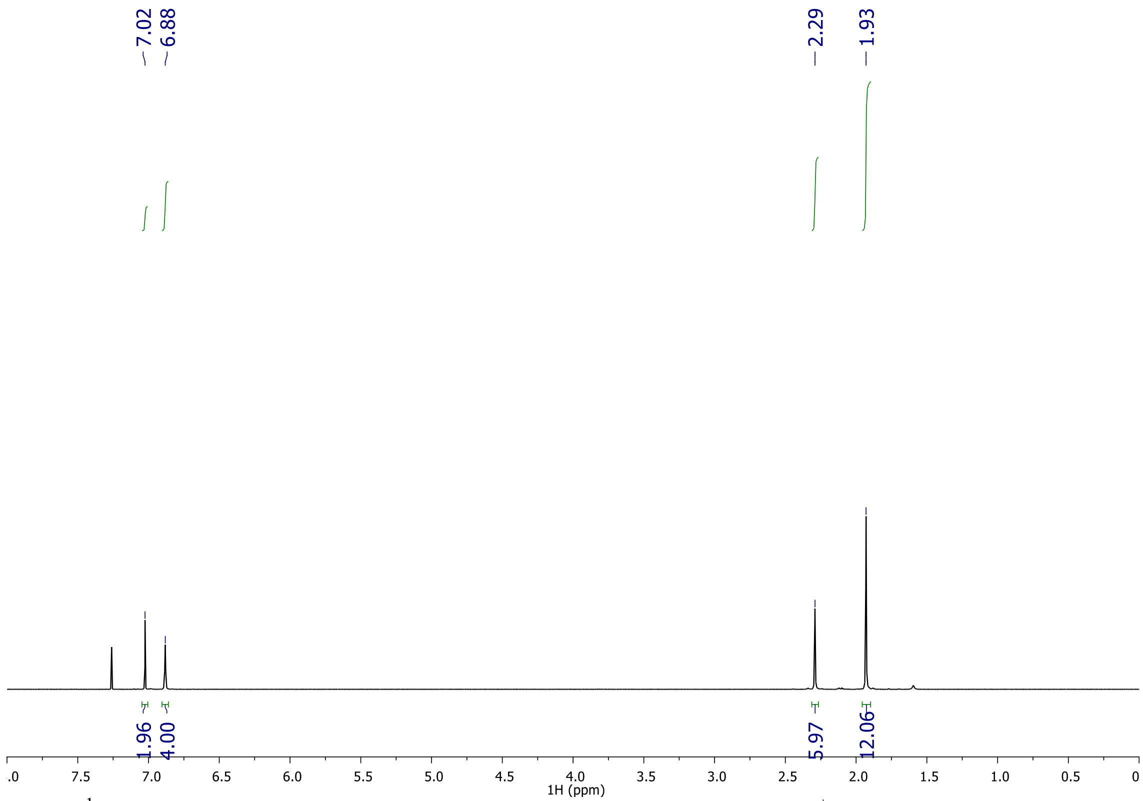

Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of $\{[(IMes)Au]_3(\mu_3\text{-}S)\}^+BF_4^-$, **[1]BF$_4$**.

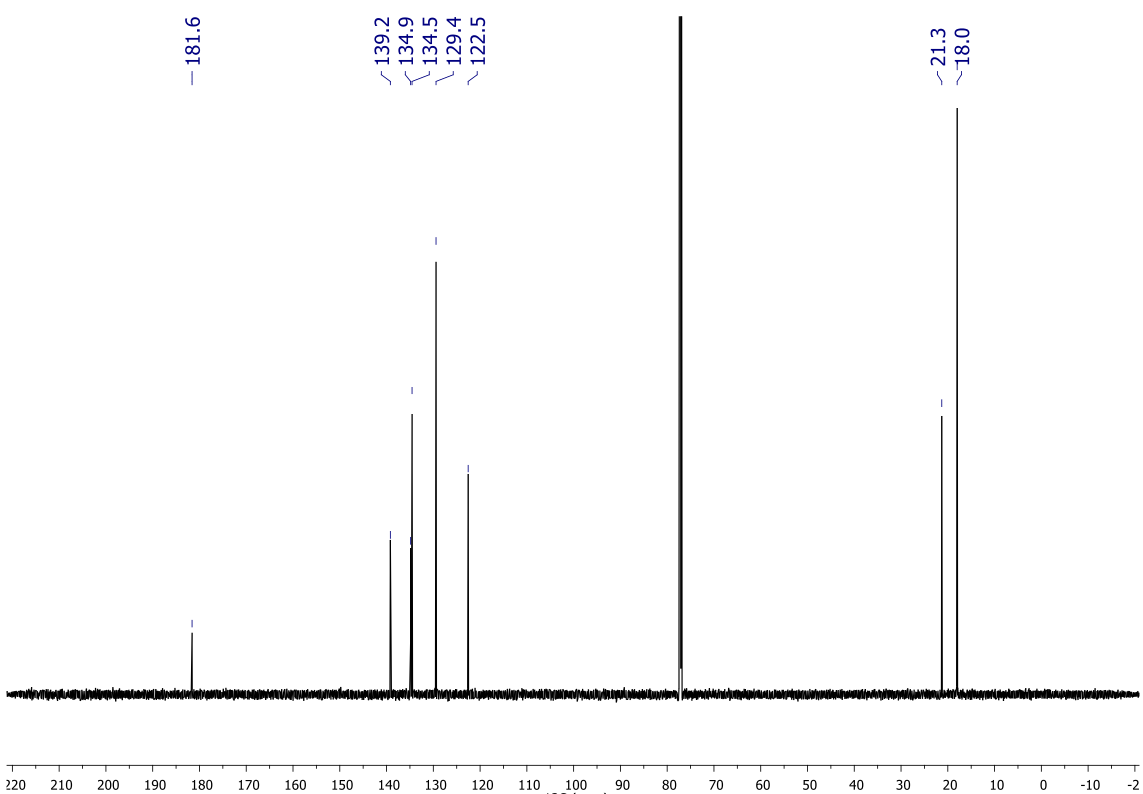

Figure S2. ^{13}C NMR (176 MHz, $CDCl_3$) spectrum of **[1]BF$_4$**.

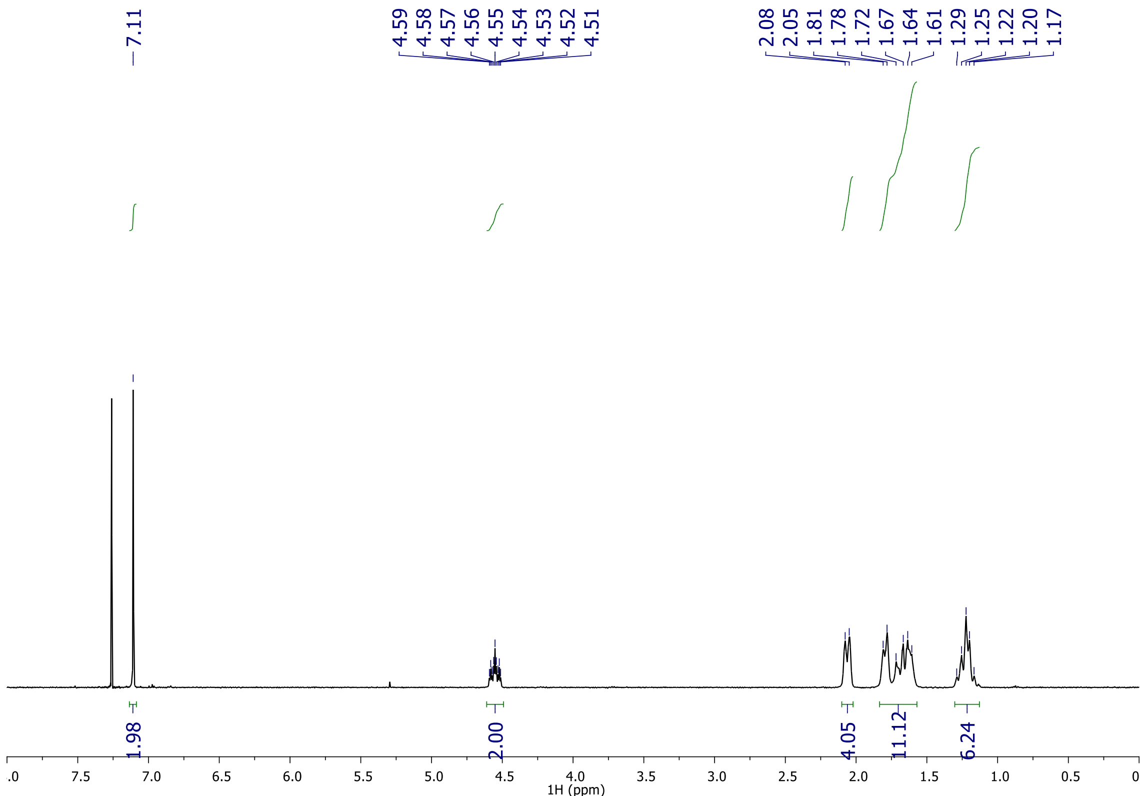

Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of $\{[(ICy)Au]_3(\mu_3\text{-}S)\}^+Cl^-$, **[2]Cl**.

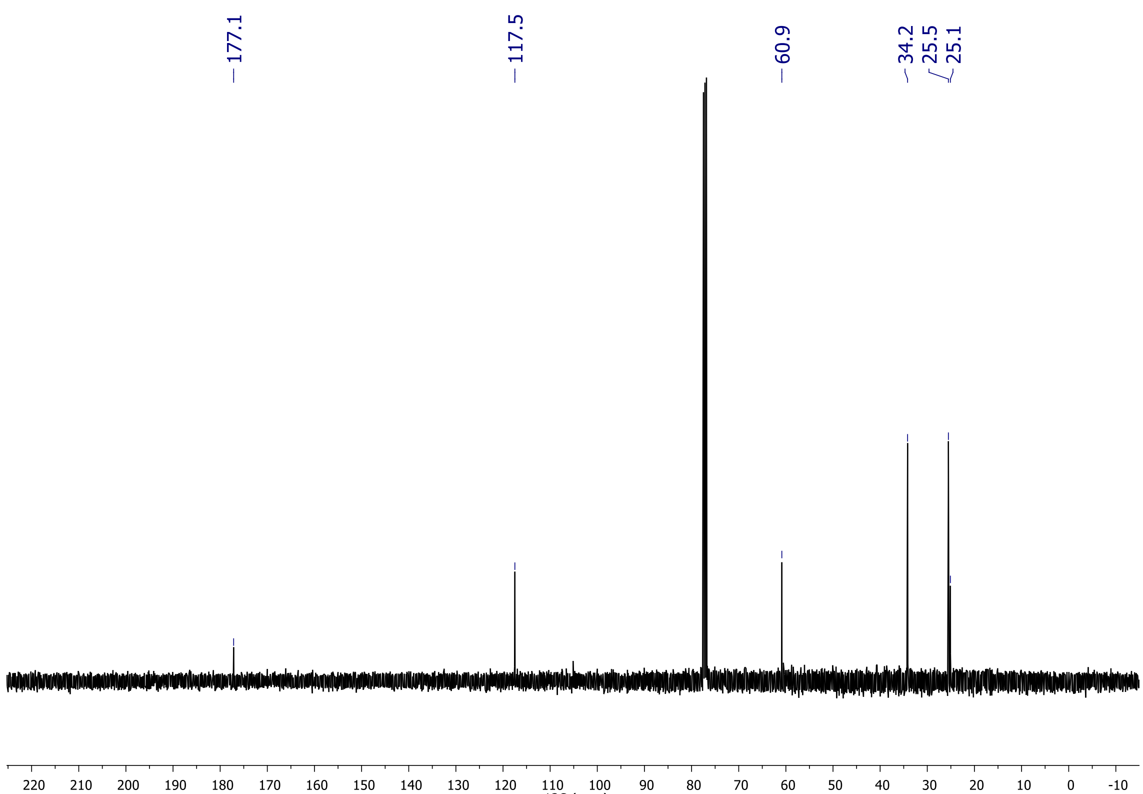

Figure S4. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **[2]Cl**.

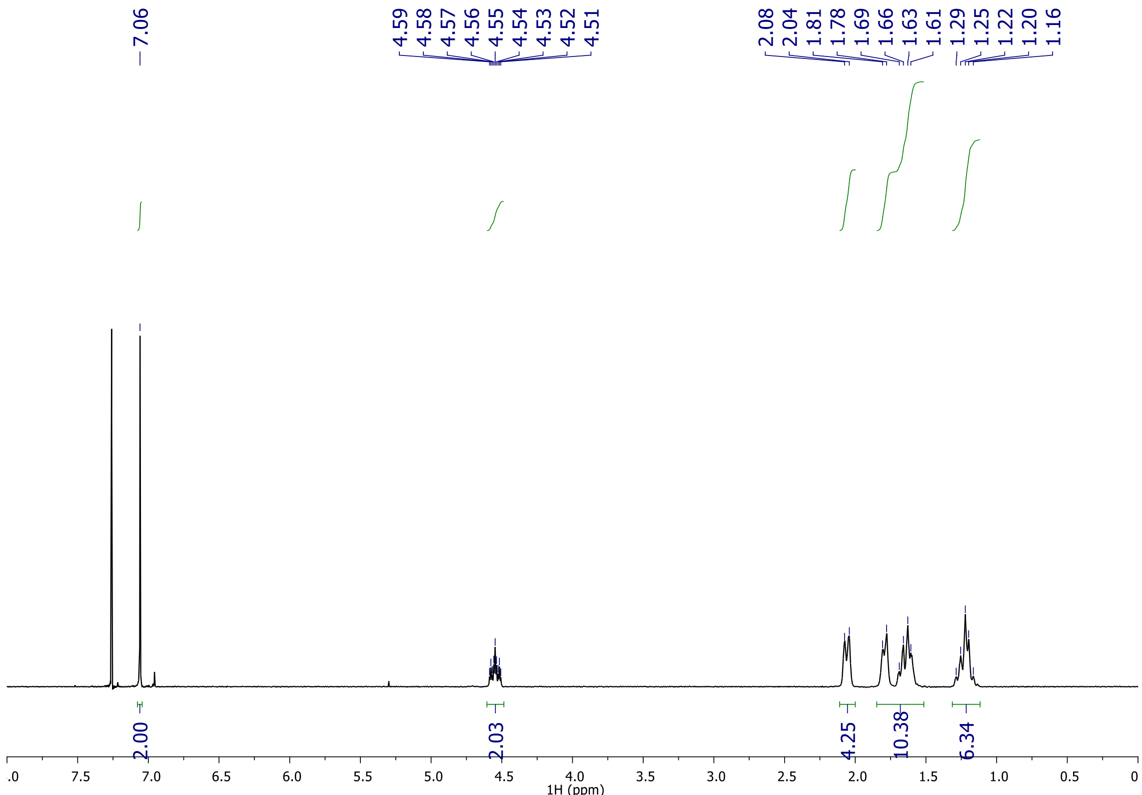

Figure S5. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of {[(ICy)Au]$_3$(μ_3-S)}$^{+}$BF$_4^{-}$, **[2]BF$_4$**.

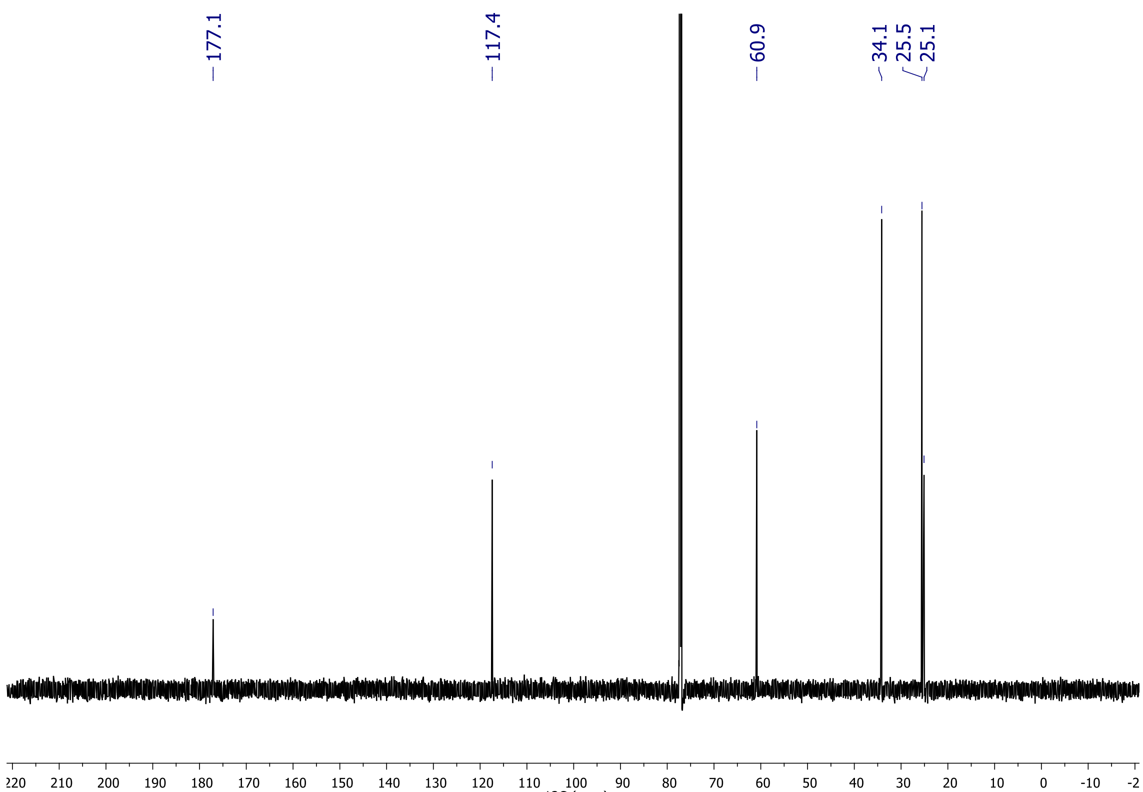

Figure S6. ^{13}C NMR (176 MHz, CDCl$_3$) spectrum of **[2]BF$_4$**.

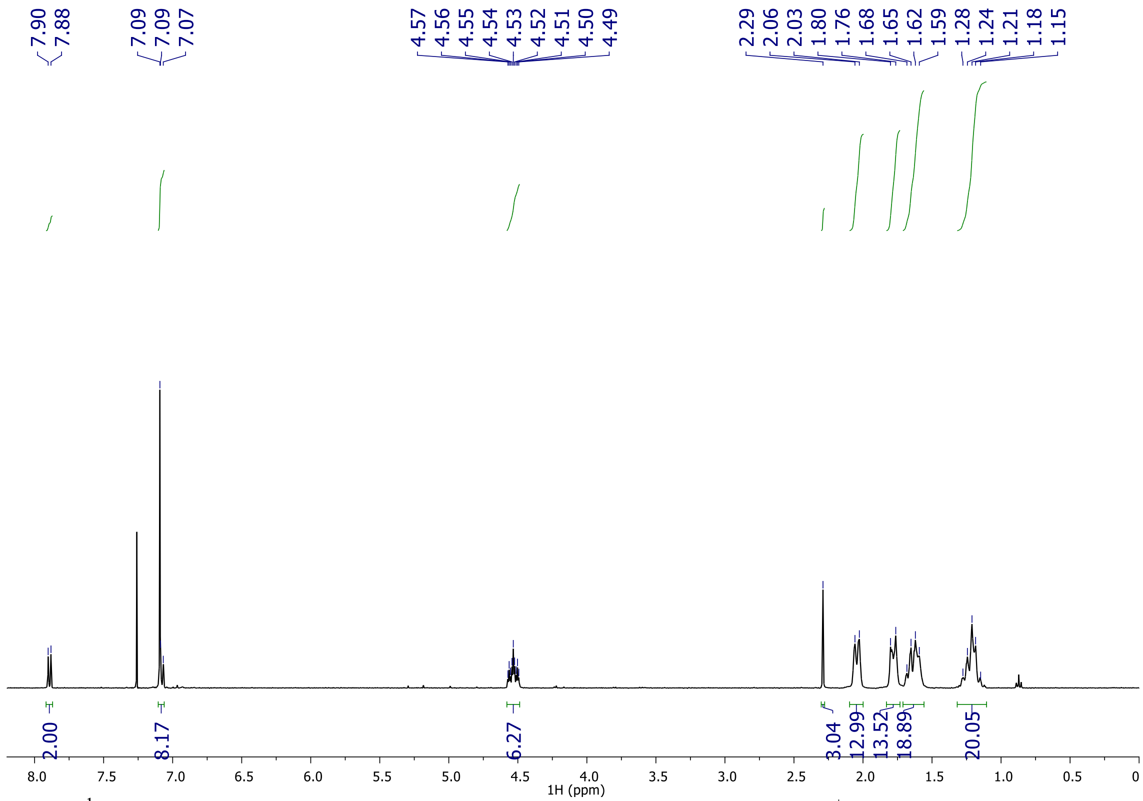

Figure S7. [1]H NMR of (400 MHz, $CDCl_3$) spectrum of $\{[(ICy)Au]_3(\mu_3\text{-}S)\}^+OTs^-$, **[2]OTs**. Trace of pentane at δ 0.87 ppm.[1]

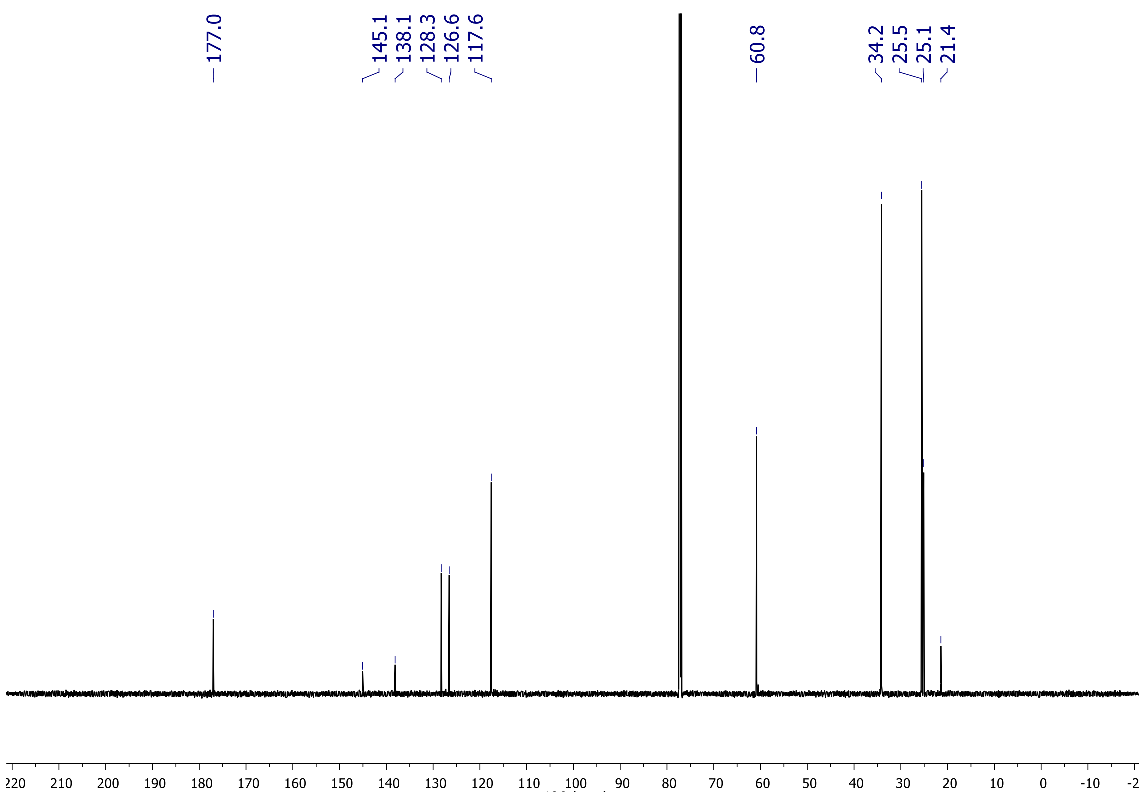

Figure S8. [13]C NMR (176 MHz, $CDCl_3$) spectrum of **[2]OTs**.

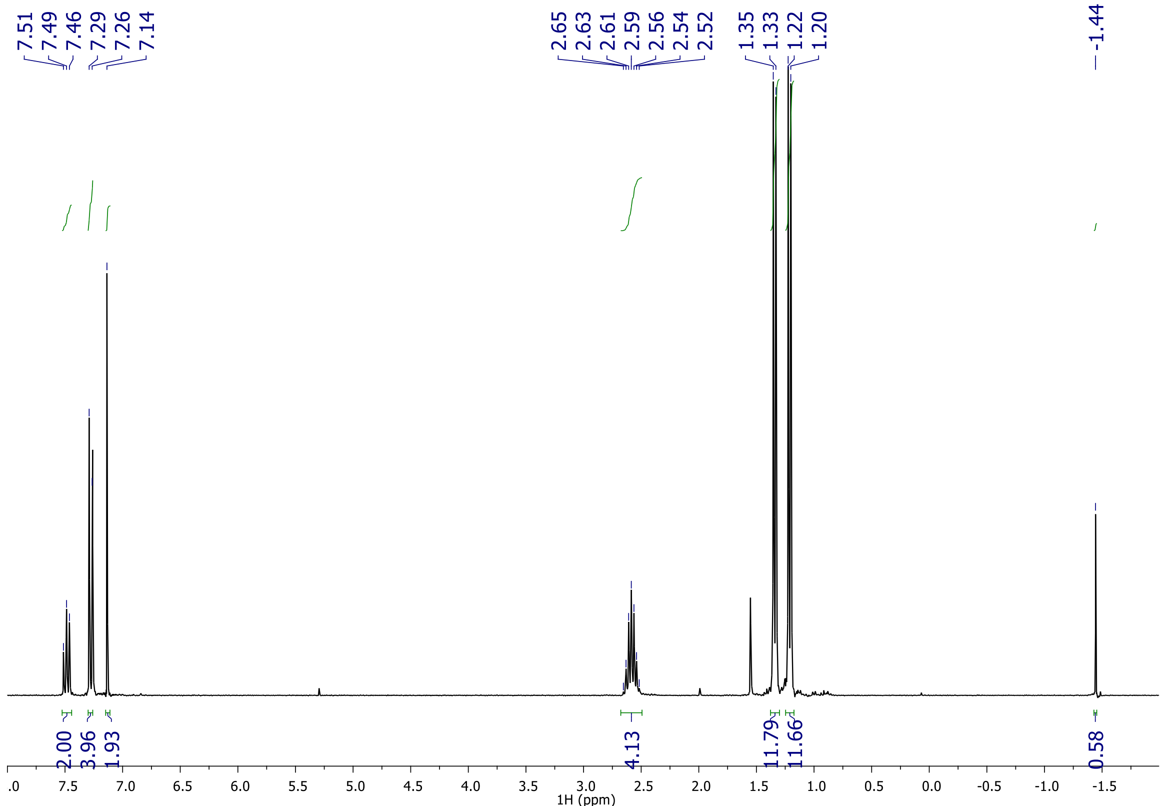

Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (IDipp)AuSH, **3**. Trace CH_2Cl_2 at δ 5.32 ppm.[1]

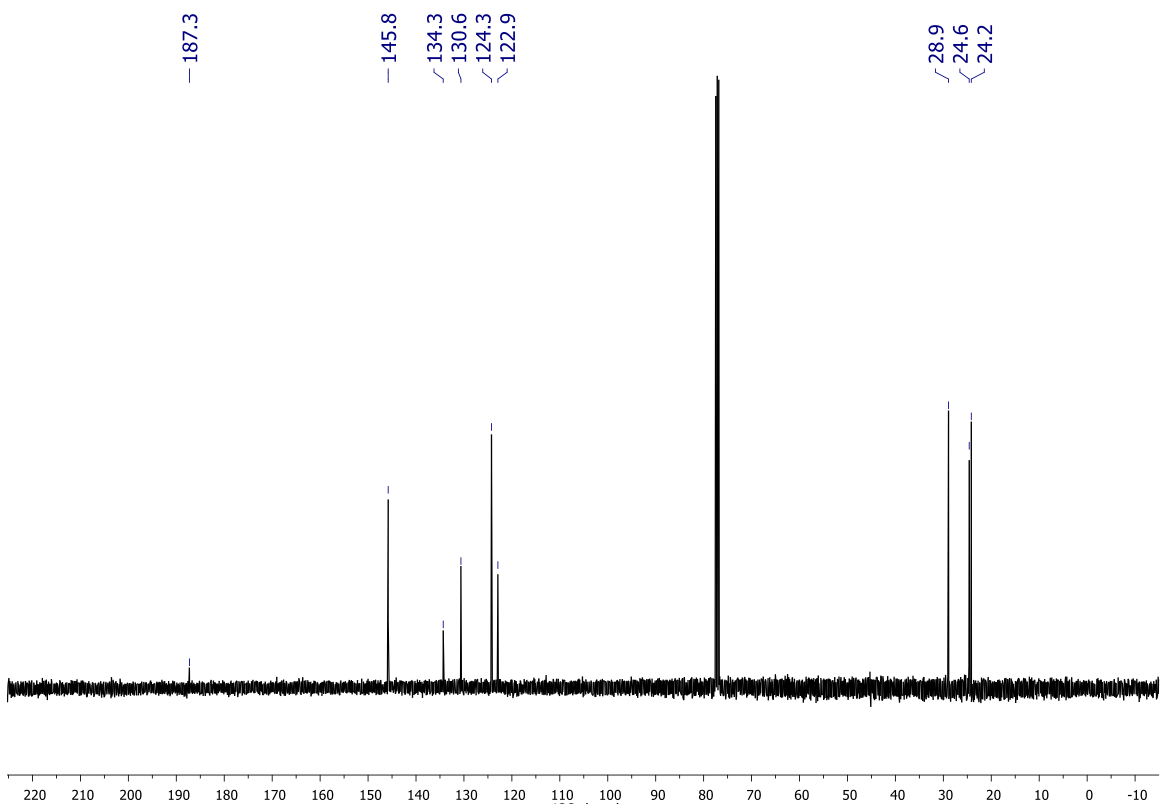

Figure S10. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3**.

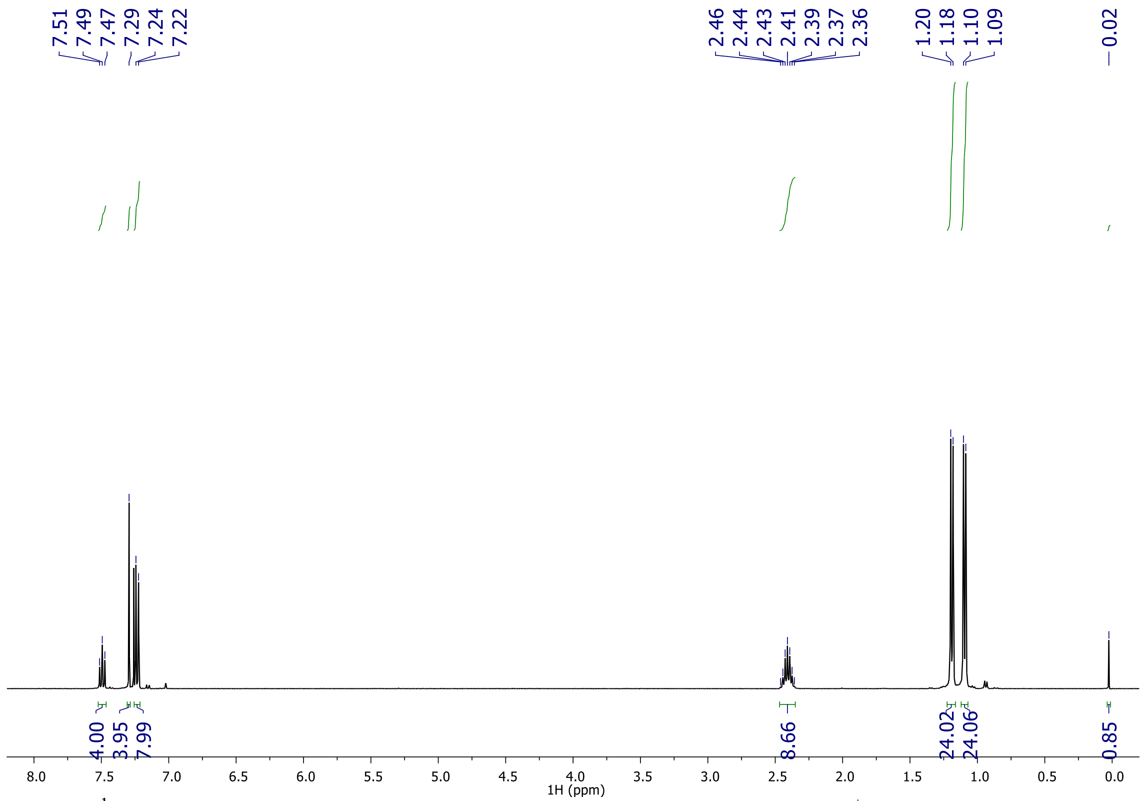

Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of $\{[(IDipp)Au]_2(\mu\text{-}SH)\}^+$ OTf^-, **[4]OTf**. Resonances for trace $\{[(IDipp)Au]_3(\mu_3\text{-}S)\}^+$ (see Figure S13) at δ 7.15, 7.02, and 0.94 ppm.

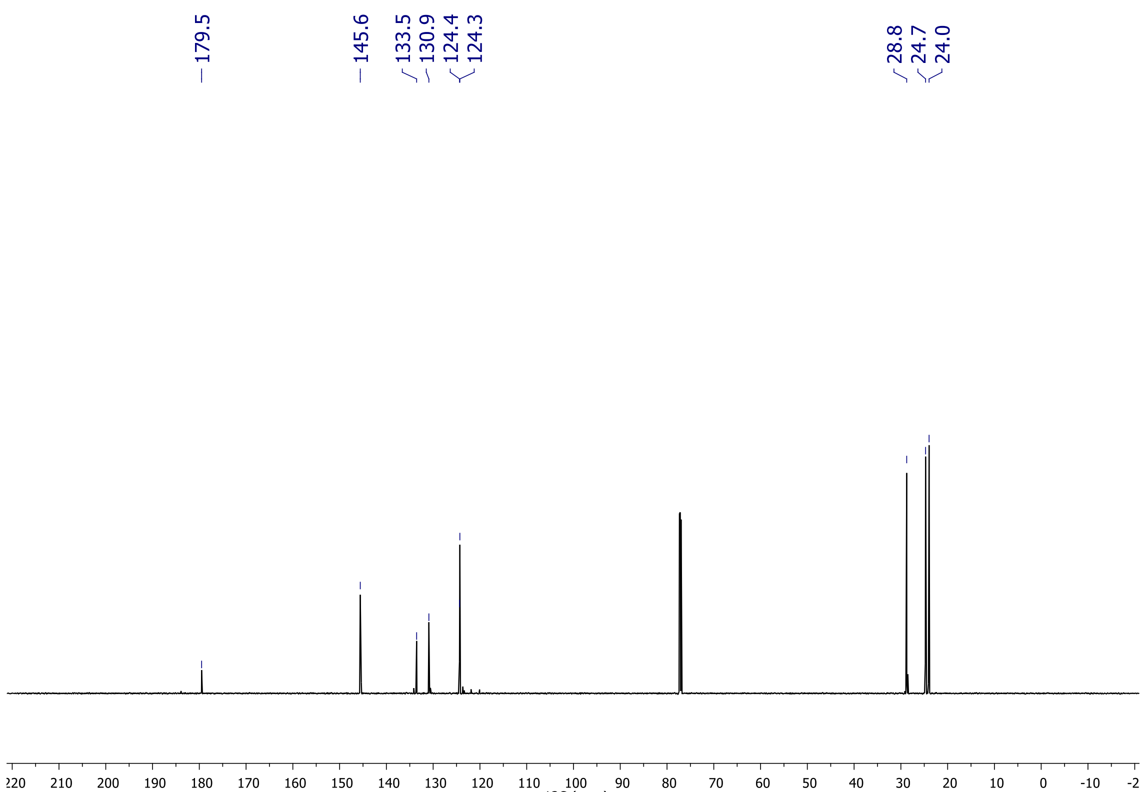

Figure S12. ^{13}C NMR (176 MHz, $CDCl_3$) spectrum of **[4]OTf**.

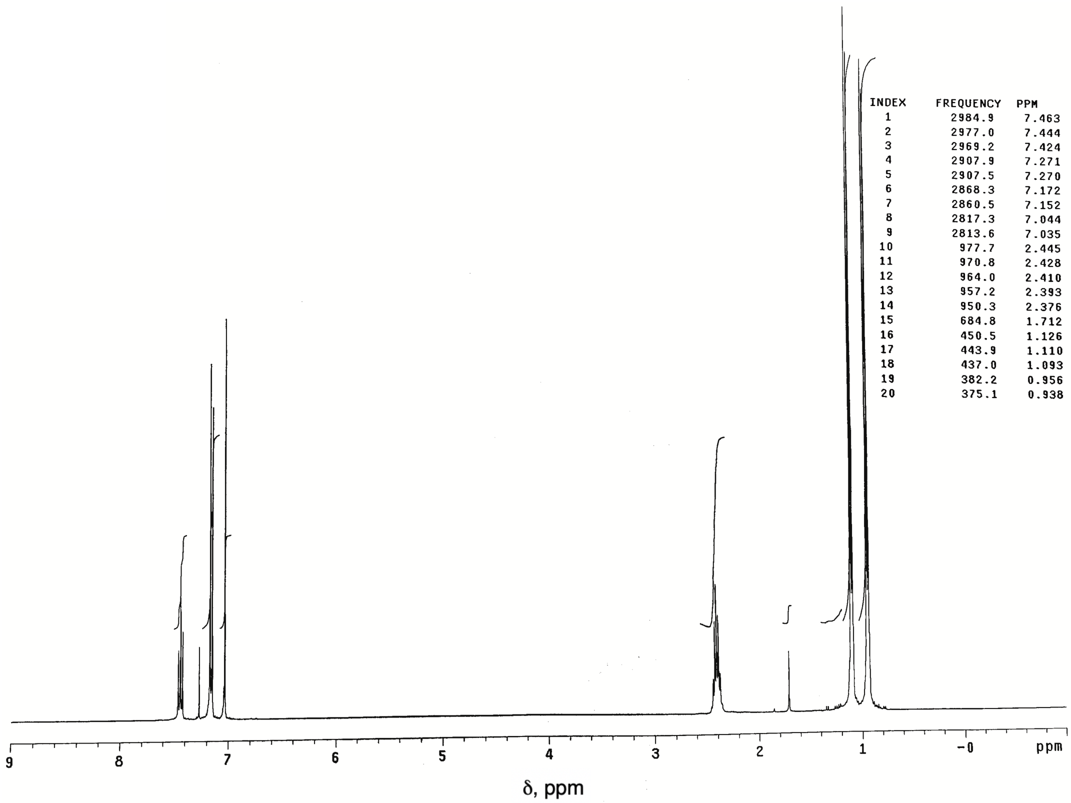

Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of $\{[(IDipp)Au]_3(\mu_3\text{-}S)\}^+$ OTf^-, **[5]OTf**.

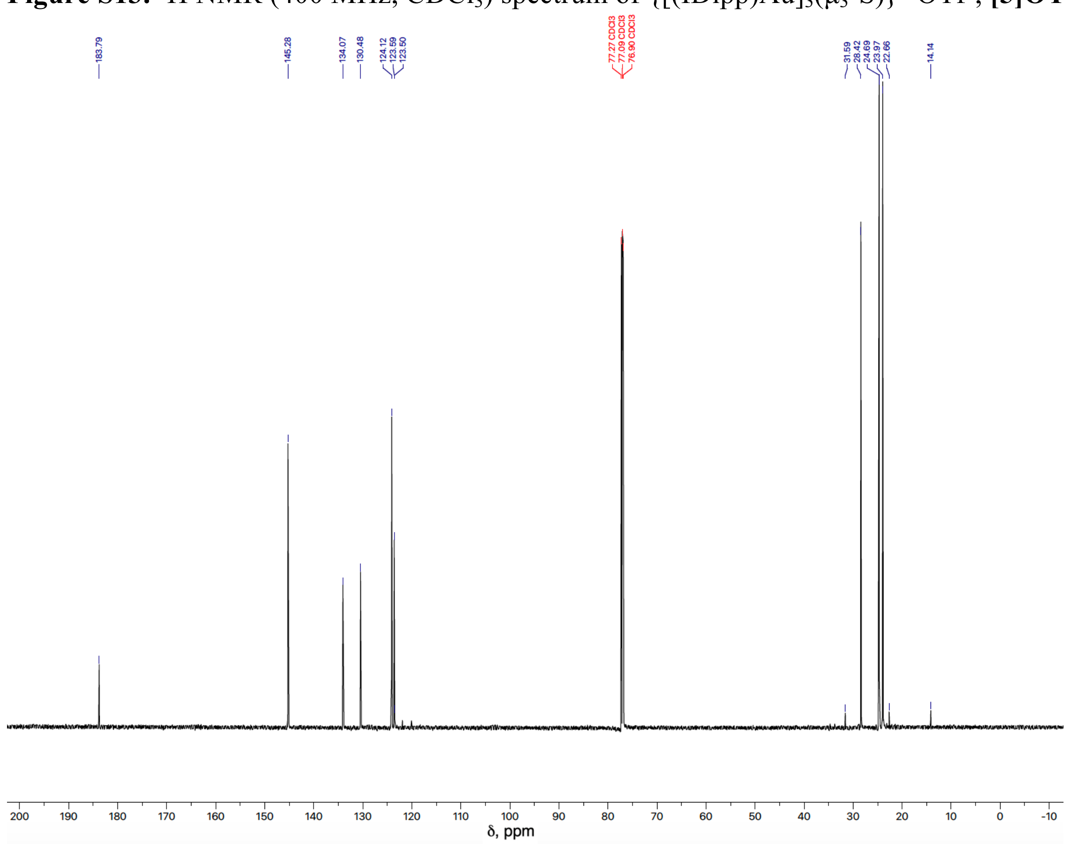

Figure S14. ^{13}C NMR (176 MHz, $CDCl_3$) spectrum of **[5]OTf**.

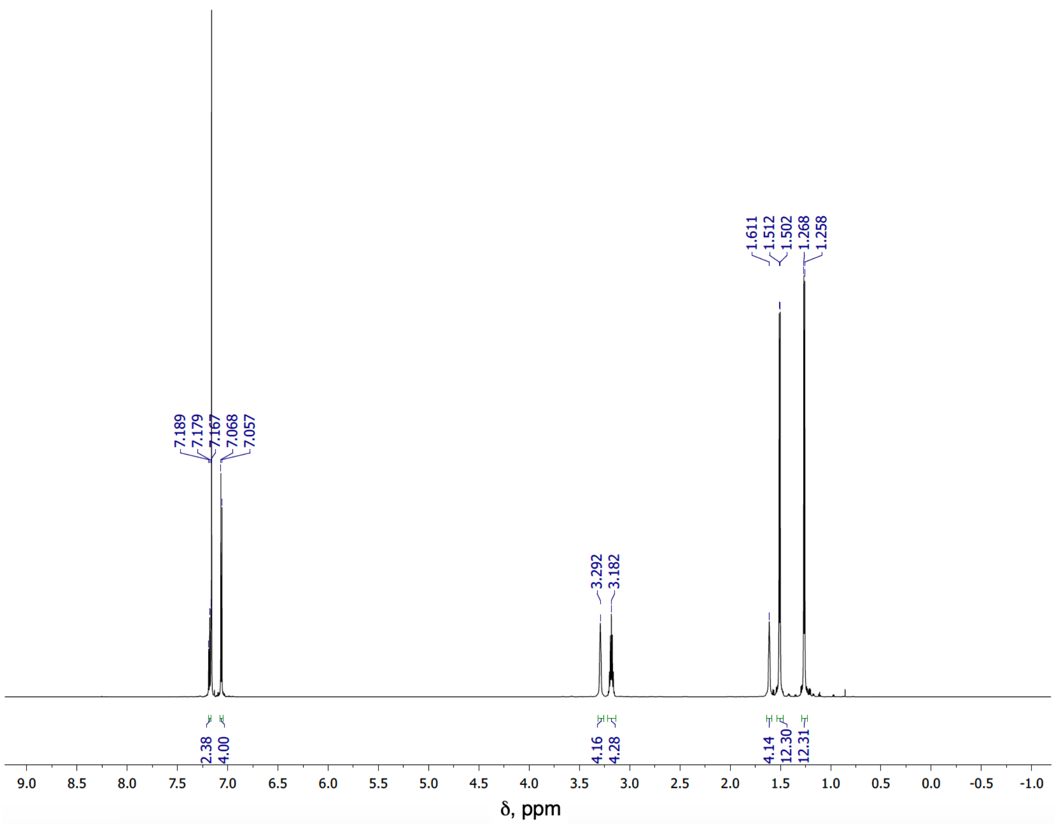

Figure S15. ^{1}H NMR (400 MHz, C_6D_6) spectrum of $[(7Dipp)Au]_2S$, **6**.

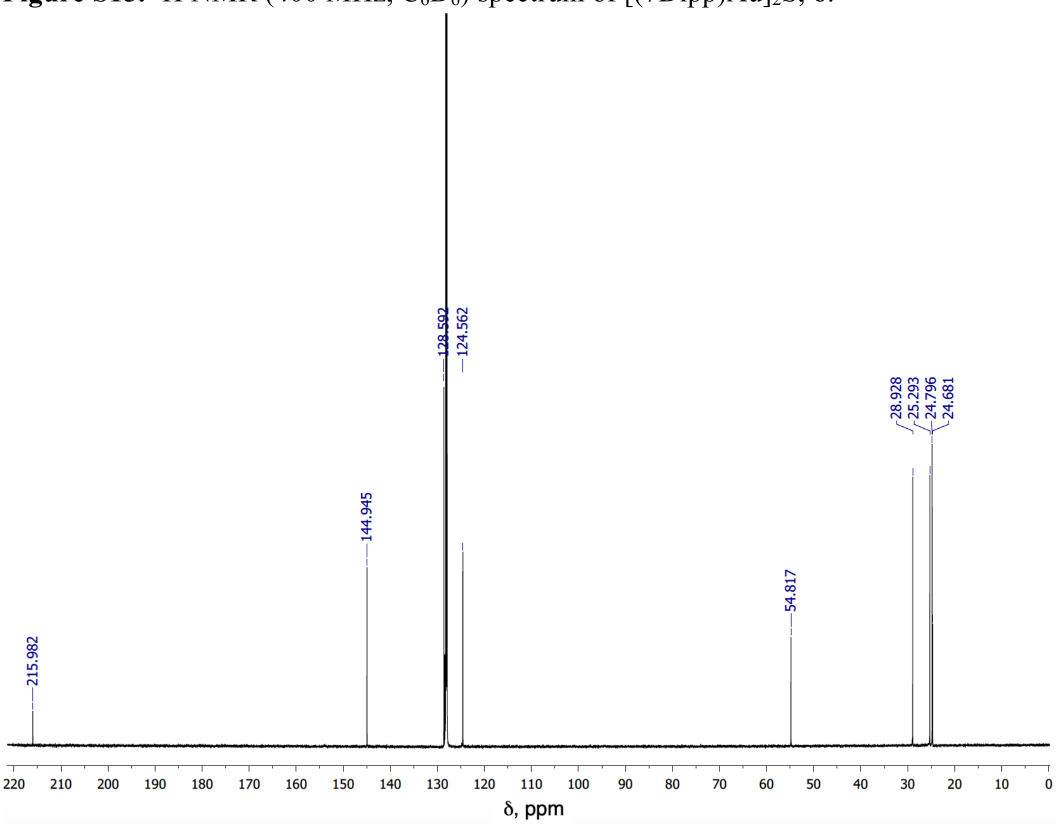

Figure S16. ^{13}C NMR (176 MHz, C_6D_6) spectrum of **6**.

Selected solid-state structures[2–5]

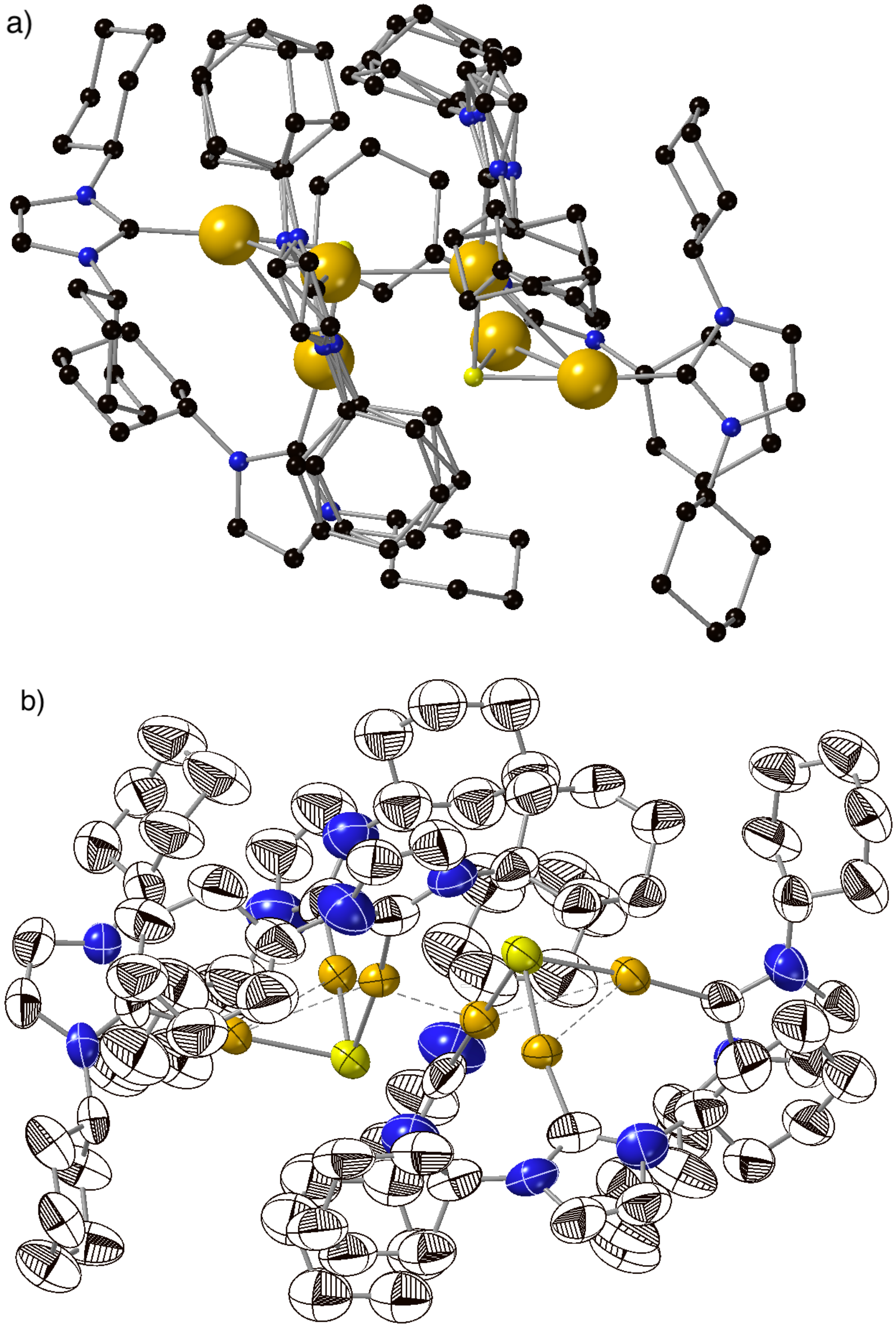

Figure S17 a) Solid-state structure of $\{[(ICy)Au]_3(\mu_3\text{-}S)\}_2^{2+}$ from **[2]OTs**, rendered as ball-and-stick representation, showing positional disorder. b) Solid-state structure of $\{[(ICy)Au]_3(\mu_3\text{-}S)\}_2^{2+}$, shown as 50% ellipsoids, using one set of positions. Anions and co-crystallised solvent omitted for clarity. Au•••Au distances less than 3.30 Å shown as dashed lines.

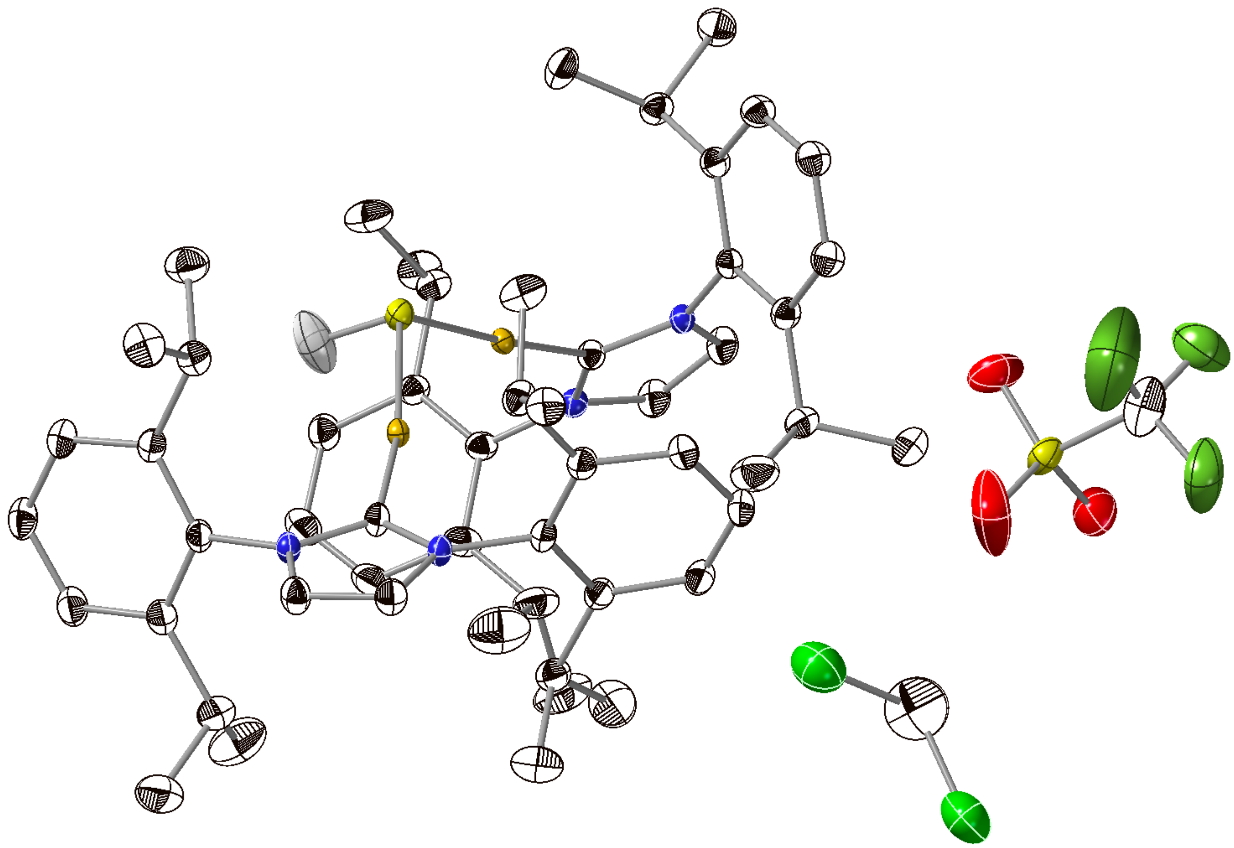

Figure S18. Solid-state structure of {[(IDipp)Au]$_2$(μ-SH)}$^+$ (CH_2Cl_2) OTf^-, **[4]OTf**•CH_2Cl_2.

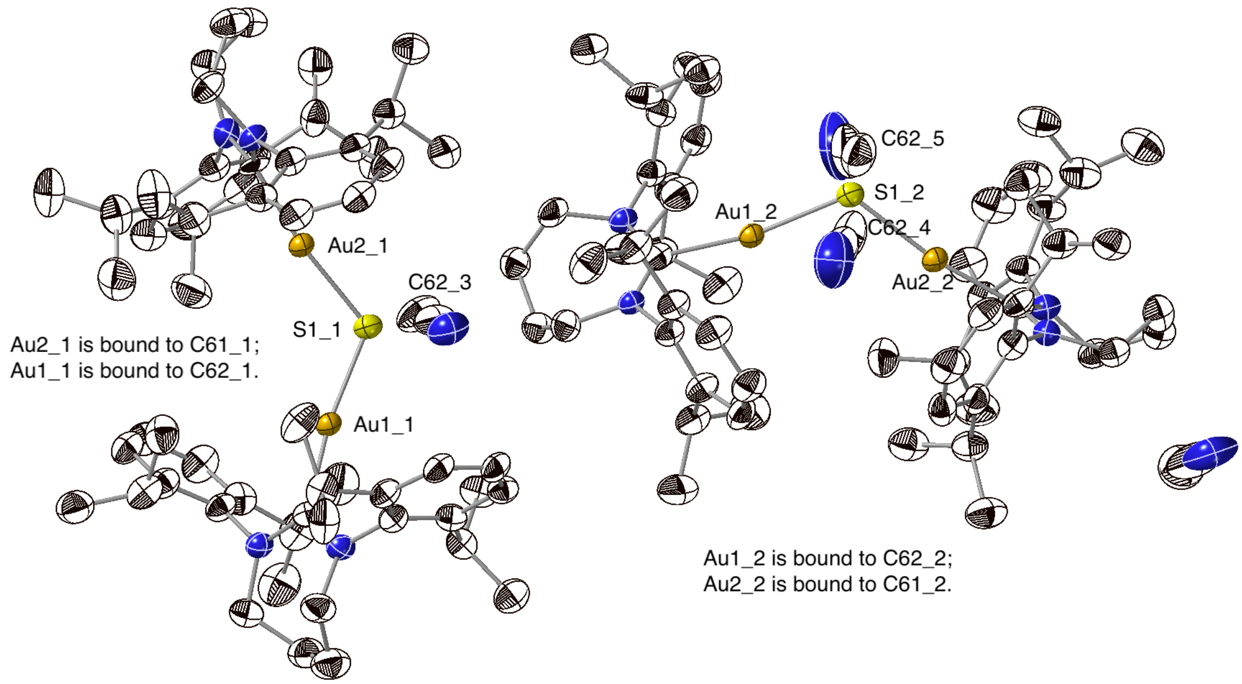

Figure S19. Asymmetric unit of **6**, including co-crystallised CH_3CN. Selected interatomic distances (Å) and angles (°):

Au1_1–S1_1 2.2805(11), Au2_1–S1_1 2.2891(11), Au1_1–Au2_1 3.8933(7), C62_1–Au1_1 2.026(4), Au2_1–C61_1 2.019(4); Au1_1–S1_1–Au2_1 116.88(6), C62_1–Au1_1–S1_1 172.04(11), C61_1–Au2_1–S1_1 171.30(11).

C_{Solv}–S distances: S1_1–C62_3 3.493 (6), C62_6–S1_1 3.383(10), C62_4–S1_2 3.413(7), C62_5–S1_2 3.525(7). [C62_6 is not shown but lies behind S1_1.]

References

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4. G. Sheldrick, *Acta Crystallogr. C*, 2015, **71**, 3-8.
5. G. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112-122.