Electronic Supplementary Material (ESI) for ChemComm.

A cationic gold-fluorenyl complex with a dative Au→C$^+$ bond: Synthesis, structure, and carbophilic reactivity.

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Supporting Information

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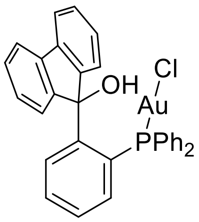
1 Experimental

1.1 General experimental

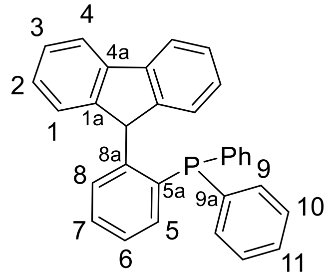
All reactions and manipulations were carried out under an atmosphere of dry, O_2-free nitrogen using standard a double-manifold or a nitrogen-filled glove box. All solvents were dried by passing through an alumina column (pentane and CH_2Cl_2) or by refluxing under N_2 over Na/K (Et_2O and THF). Deuterated solvents were distilled and/or dried over molecular sieves before use. Chemicals were purchased from commercial suppliers and used as received. 2-Bromophenyl-diphenylphosphine was synthesized as described in the literature.[1] ^1H, ^{13}C, ^{11}B, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker Avance II 400. Chemical shifts are expressed as parts per million (ppm, δ) downfield of tetramethylsilane (TMS) and are referenced to $CDCl_3$ (7.26/77.16 ppm) as internal standards. NMR spectra were referenced to $CFCl_3$ (^{19}F), $BF_3{\cdot}Et_2O/CDCl_3$ (^{11}B) and H_3PO_4 (^{31}P). All coupling constants are absolute values and are expressed in Hertz (Hz). Mass spectrometry analyses were performed in-house at the Center for Mass Spectrometry. Elemental analyses were performed by Atlantic Microlab (Norcross, GA).

1.2 Syntheses

Synthesis of **1**

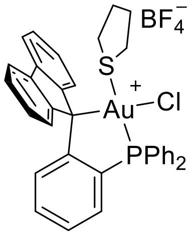


2-Bromophenyl-diphenylphosphine (500 mg, 1.46 mmol) was dissolved in Et_2O (20 mL), cooled to -78 °C and treated with *n*-butyllithium (2.5 M hexanes, 0.7 mL, 1.76 mmol, 1.2 equiv.). The resulting mixture was stirred at low temperature for 2 hours. To this cooled solution, freshly recrystallized fluorenone (290 mg, 1.61 mmol. 1.1 equiv.) was added as a solid. The resulting mixture was stirred and allowed to slowly warm to ambient temperature at which point a yellow/orange precipitate became visible. After stirring for a further 18 h, the reaction was quenched by addition of water. The aqueous phase was then extracted with Et_2O (3 x 20 mL) and the organic fractions were combined, dried over $MgSO_4$, and evacuated to dryness to afford a yellow residue. This residue was triturated in pentane, yielding a white powdery solid which was isolated by filtration and washed with a small amount of acetonitrile (1 mL) to yield 318 mg of impure **L**OH (Figure S1). A portion of this impure product (100 mg) was dissolved in CH_2Cl_2 (3 mL) and combined with (tht)AuCl (81 mg, 0.25 mmol). The resulting solution was stirred vigorously for 15 mins leading to the appearance of a white precipitate, which was augmented by addition of pentane (10 mL) to the solution. The precipitate was isolated by filtration, washed with pentane (3 x 3 mL) and dried *in vacuo* to yield the **1** (71 mg, 42% yield).



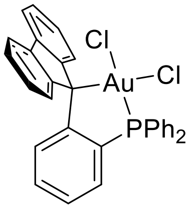
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.75 – 7.64 (m, 4H, H-9), 7.62 (d, $^2J_{HH}$ = 7.5 Hz, 2H, H-4 or H-1), 7.55 – 7.47 (m, 8H. H-10, H-11 and H-1 or H4), 7.36 (td, $^2J_{HH}$ = 7.5, $^3J_{HH}$ = 1.2 Hz, 2H, H-2 or H-3), 7.29 – 7.22 (m, 2H, H-2 or H-3), 7.14 (tt, $^{2}J_{HH}$ = 7.6 Hz, $^{3}J_{\mathrm{HH}}$ = 1.7 Hz, 1H, H-6), 7.09 (tt, $^{2}J_{HH}$ = 7.3 Hz, $^{3}J_{\mathrm{HH}}$ = 1.6 Hz, 1H, H-7), 6.89 (ddd, $^{3}J_{HP}$ = 13.9 Hz, $^{2}J_{\mathrm{HH}}$ = 7.9 Hz, $^{3}J_{\mathrm{HH}}$ = 1.6 Hz, 1H), 6.62 (ddd, $^{2}J_{HH}$ = 7.7Hz, $^{4}J_{\mathrm{HP}}$ = 5.0Hz, $^{3}J_{\mathrm{HH}}$ = 1.6 Hz, 1H, H-8), 2.65 (s, 1H, O-*H*). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 151.16 (s, C-1a or C-4a), 147.98 (d, *J* = 7.7 Hz, C-9a), 139.29 (s, C-1a or C-4a), 135.21 (d, *J* = 8.4 Hz, C-5), 134.19 (d, *J* = 14.2 Hz, C-9), 133.50 (s, C-10 or C-11), 133.00 (s, C-10 or C-11), 131.21 (d, *J* = 2.3 Hz, C-7), 130.36 (d, *J* = 8.9 Hz, C-8), 129.55 (s, C-2 or C-3), 129.08 (s, C-10 or C-11), 128.99 (s, C-10 or C-11), 128.85 (s, C-2 or C-3), 127.25 (d, *J* = 9.9 Hz, C-6), 126.27 (s C-10 or C-11), 125.83 (s C-16 or C-17), 125.70 (s, C-10 or C-11), 120.16 (s, C-1 or C-4), 87.09 (s, *C*-OH). **^{31}P NMR** (162 MHz, CD_3CN, 298 K) δ/ppm: 38.52 (s). **HRMS** (ESI$^+$) *m/z* calculated for $[M+NH_4]^+$ $[C_{31}H_{23}AuClOP]NH_4^+$: 692.1179, found: 692.1164. Because this compound was not used as a catalyst, we did not collect elemental analysis. The connectivity of **L**OH and **1** was confirmed by X-ray diffraction (see structure deposited in the Cambridge structural database under CCDC numbers 2172689 for **L**OH and 2172690 for **1**).

Synthesis of [**2**][BF_4]



Compound [**2**][BF_4] was synthesized by combining **L**OH (30.0 mg) and (tht)AuCl (21.8 mg, 0.068 mmol) in CH_2Cl_2 (1 mL) at room temperature followed by addition, after 15 min, of HBF_4 (52% w/w in Et_2O, 0.05 mL). Addition of Et_2O (5 mL) to the resulting solution led to the precipitation of a yellow powder which was isolated by filtration, washed with Et_2O (1 mL x 3) and dried *in vacuo* to yield [**2**][BF_4] (40.9 mg, yield 72.4%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 7.99 – 7.86 (m, 6H, H-9 and H-4), 7.87 – 7.71 (m, 6H, H-10 and H-11), 7.64 – 7.52 (m, 2H, H-6 or H-7 and H-5), 7.50 (td, $^{2}J_{HH}$ = 7.5 Hz, $^{3}J_{HH}$ = 1.0 Hz, 2H, H-6 or H-7).7.42 (tdd, $^{2}J_{HH}$ = 6.8 Hz, $^{4}J_{\mathrm{HP}}$ = 3.6 Hz, $^{3}J_{\mathrm{HH}}$ = 1.5 Hz, 1H, H-6 or H-7), 7.36 (td, $^{2}J_{HH}$ = 7.5 Hz, $^{3}J_{HH}$ = 1.1 Hz, 2H, H-2 or H-3), 7.08 (d, $^{2}J_{HH}$ = 7.6 Hz, 2H, H-1), 6.57 (dd, $^{2}J_{HH}$ = 8.1 Hz, $^{4}J_{Hp}$ = 3.4 Hz, 1H, H-8), 3.13 (br s, 2H, tht), 2.34 (br s, 2H, tht), 2.12 – 1.77 (m, 4H, tht). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm: 153.86 (d, *J* = 26.2 Hz), 150.83 (s), 147.91 (d, *J* = 2.0 Hz), 140.64 (s), 139.52 (s), 135.74 (s), 134.41 (d, *J* = 11.8 Hz), 133.94 (s), 132.60 (s), 130.55 (d, *J* = 13.1 Hz), 130.38 (s), 129.89 (d, *J* = 12.9 Hz), 129.43 (s), 128.68 (s), 127.84 (s), 126.61 (s), 125.74 (s), 124.71 (s), 124.17 (s), 121.15 (s), 88.16 (d, *J* = 7.2 Hz), 39.13 (s), 30.53 (s). **^{31}P NMR** (162 MHz, CD_3CN, 298 K) δ/ppm: 69.6 (s). **Elemental Analysis** of $C_{35}H_{30}AuBClF_4BPS$ calculated: C: 50.47, H: 3.63, found: C: 50.79, H: 3.73.

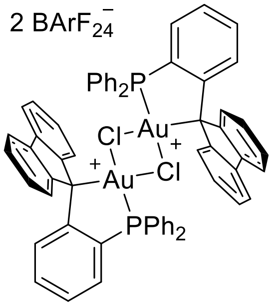
Synthesis of **3**



Compound **3** was synthesized by subsequent addition of HCl (1 N in Et_2O, 1.0 mL) and trifluoroacetic anhydride (1 mL) to **1** (38.0 mg, 0.056 mmol) dissolved in CH_2Cl_2 (3 mL). The resulting solution was stirred for 15 min, concentrated to 1 mL and combined with Et_2O to yield a yellow precipitate. The precipitate was isolated by filtration, washed with Et_2O (1 mL x 3) and dried *in vacuo* to yield **3** (23.0 mg, 59%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K) δ/ppm: 8.02 – 7.94 (m, 4H, H-9), 7.81 (dd, $^{2}J_{HH}$ = 7.6, $^{3}J_{HH}$ = 0.9 Hz, 2H, H-4), 7.76 – 7.69 (m, 2H, H-11), 7.67 – 7.63 (m, 4H, H-10), 7.53 – 7.43 (m, 1H, H-5), 7.41 – 7.33 (m, 3H, H-2 or H-3 and H-6 or H-7), 7.33 – 7.28 (m, 1H, H-6 or H-7), 7.18 (td, $^{2}J_{HH}$ = 7.5 Hz, $^{3}J_{HH}$ = 1.1 Hz, 2H, H-2 or H-3), 6.97 (d, $^{2}J_{HH}$ = 7.5 Hz, 2H, H-1), 6.58 (dd, $^{2}J_{HH}$ = 7.9 Hz, $^{3}J_{HH}$ 3.0 Hz, 1H, H-8). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ/ppm:

156.75 (d, *J* = 27.5 Hz), 150.86 (s), 140.65 (s), 134.70 (s, *J* = 2.71), 134.40 (d, *J* = 11.4 Hz), 133.91 (d, *J* = 3.3 Hz), 131.78 (d, *J* = 4.3 Hz), 131.12 (s), 130.60 (s), 130.10 (d, *J* = 19.2 Hz), , 129.88 (d, *J* = 12.8 Hz), 129.71 (d, *J* = 8.9 Hz), 128.68 (s), 127.82 (s), 126.03 (s), 125.74 (s), 125.48 (s), 120.54 (s), 85.61 (d, *J* = 7.3 Hz). **^{31}P NMR** (162 MHz, CD_3CN, 298 K) δ/ppm: 62.2 (s). **Elemental Analysis** of $C_{31}H_{22}AuCl_2P$ calculated: C: 53.70, H: 3.20, found: C: 53.98, H: 3.32.

Synthesis of [**4**$_2$][BArF$_{24}$]$_2$



Compound [**4**$_2$][BArF$_{24}$]$_2$ was synthesized by combining NaBArF$_{24}$ (BArF$_{24}$ = $B(3,5\text{-}C_6H_3(CF_3)_2)_4$) (83.1 mg, 0.094 mmol) and **3** (65.0 mg, 0.094 mmol) in *o*-difluorobenzene (2 mL). After being stirred briefly, the resulting orange solution was cooled to –40 °C and layered with hexanes (15 mL). Dark orange/red crystals suitable for X-ray diffraction formed over a period of 5 days at –40 °C. These crystals were isolated and analyzed to yield complex [**4**$_2$][BArF$_{24}$]$_2$ (106.1 mg, 67.4%). **^{1}H NMR** (400 MHz, CD_2Cl_2, 298 K) δ/ppm: 7.79 (td, *J* = 6.7, 3.2 Hz, 2H), 7.75 – 7.69 (m, 8H, Counter anion), 7.70 – 7.46 (m, 14H), 7.44 (dd, *J* = 8.1, 7.0 Hz, 2H), 7.24 – 7.14 (m, 2H), 7.14 – 7.05 (m, 3H), 6.88 (d, *J* = 7.6 Hz, 2H), 6.79 (dd, *J* = 7.9, 3.4 Hz, 1H).**^{13}C NMR** (126 MHz, CD_2Cl_2, 233 K) δ/ppm: 161.76 (dd, *J* = 99.5, 49.7 Hz), 151.26 (s), 150.32 (s), 149.17 (s), 144.71 (s), 140.77 (s), 136.18 (s), 135.41 (s), 134.68 (s), 134.07 (s), 133.77 (s), 133.63 (s), 130.96 (s), 130.59 (s), 129.68 (s), 129.16 – 128.20 (m), 127.54 (s), 126.56 (s), 128.03 – 120.83 (m), 124.33 (s), 122.08 (s), 121.53 (s), 117.91 (s), 117.26 (s), 116.84 (s), 102.39 (s). **^{31}P NMR** (162 MHz, CD_2Cl_2, 298 K) δ/ppm: 73.8 (s). The VT NMR measurement suggests that the spectra correspond to [**4**][BArF$_{24}$]. **Elemental Analysis** of $C_{126}H_{68}Au_2B_2Cl_2F_{48}P_2$ + 2NaCl calculated: C: 47.91, H: 2.17, found: C: 48.10, H: 2.14. The purification protocol did not involve a step during which NaCl was separated.

2 NMR spectra

2.1 NMR spectra of products

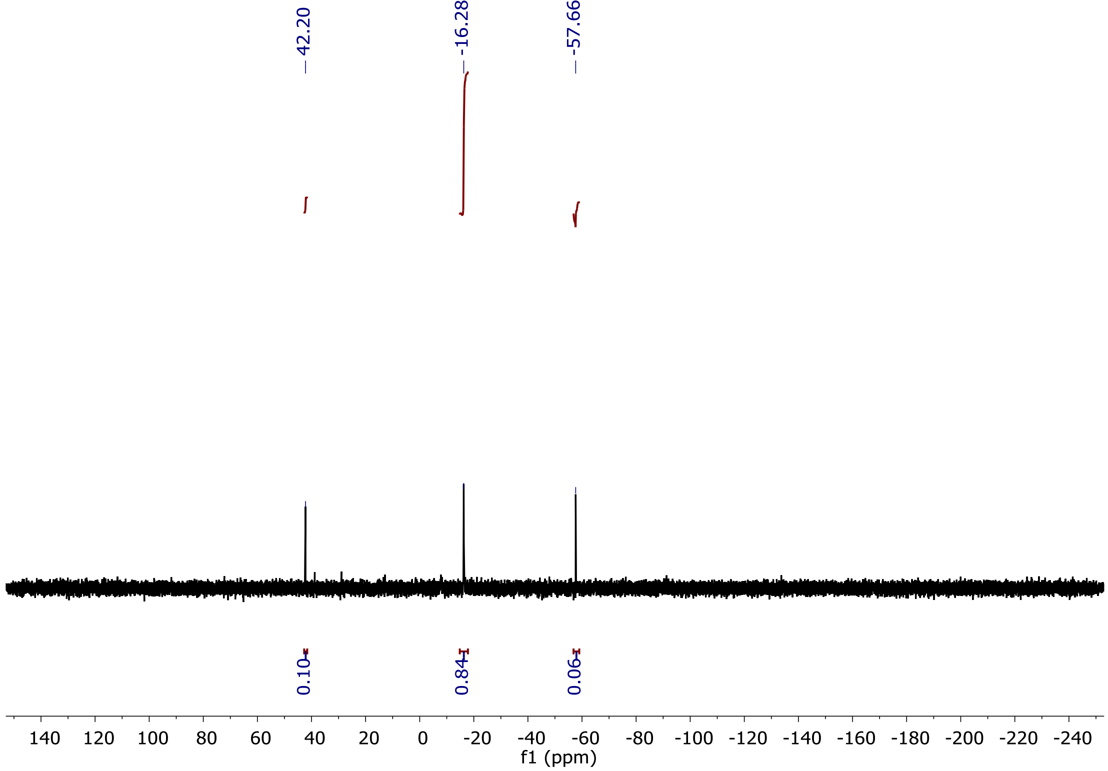


Figure S1. ^{31}P NMR (400 MHz, CD_3CN, 298 K) spectrum of crude **L**OH.

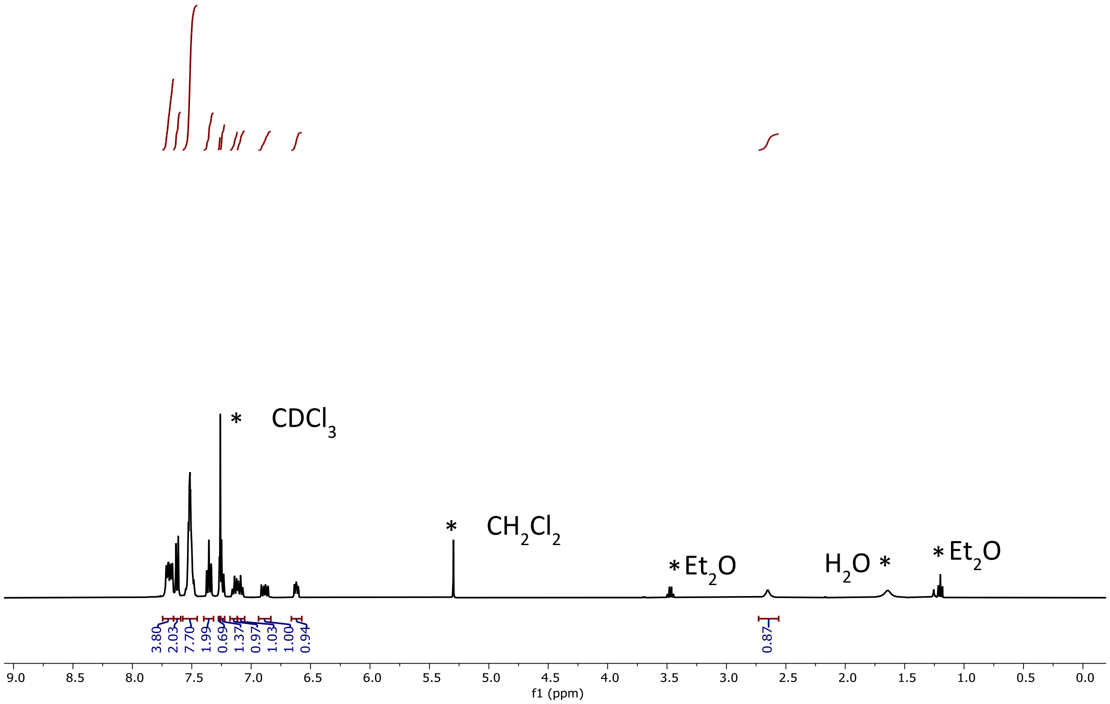


Figure S2. ^{1}H NMR (400 MHz, CD_3CN, 298 K) spectrum of **1**

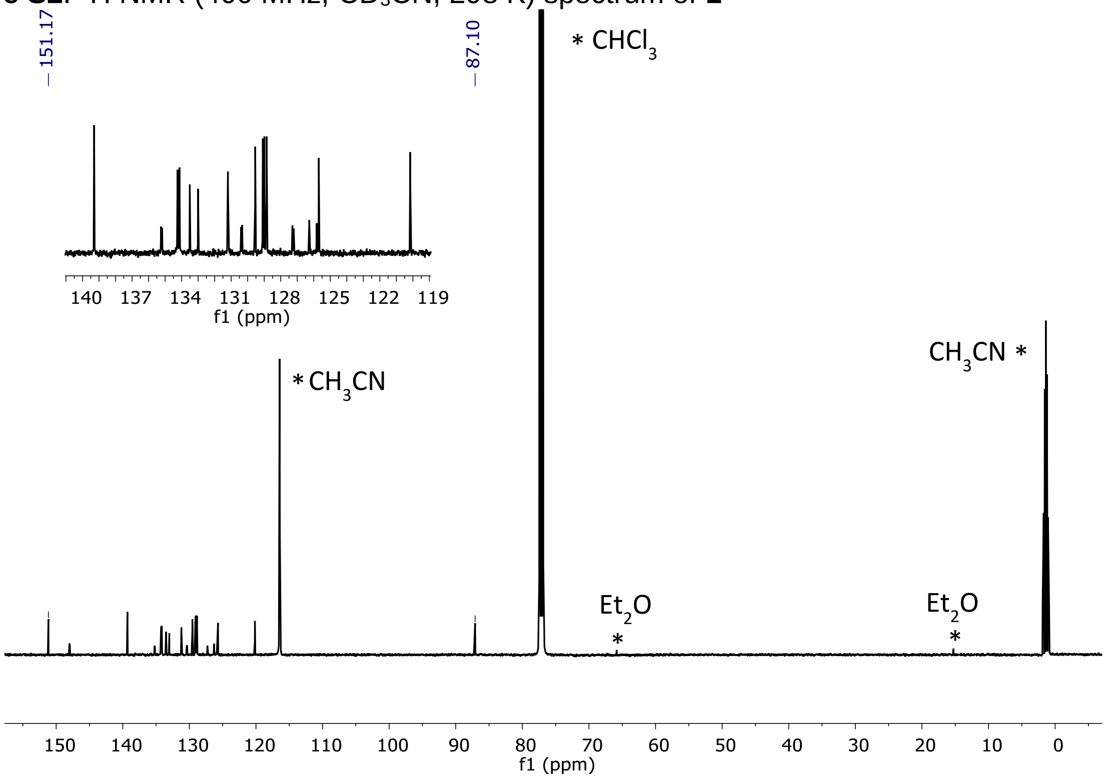


Figure S3. ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **1**

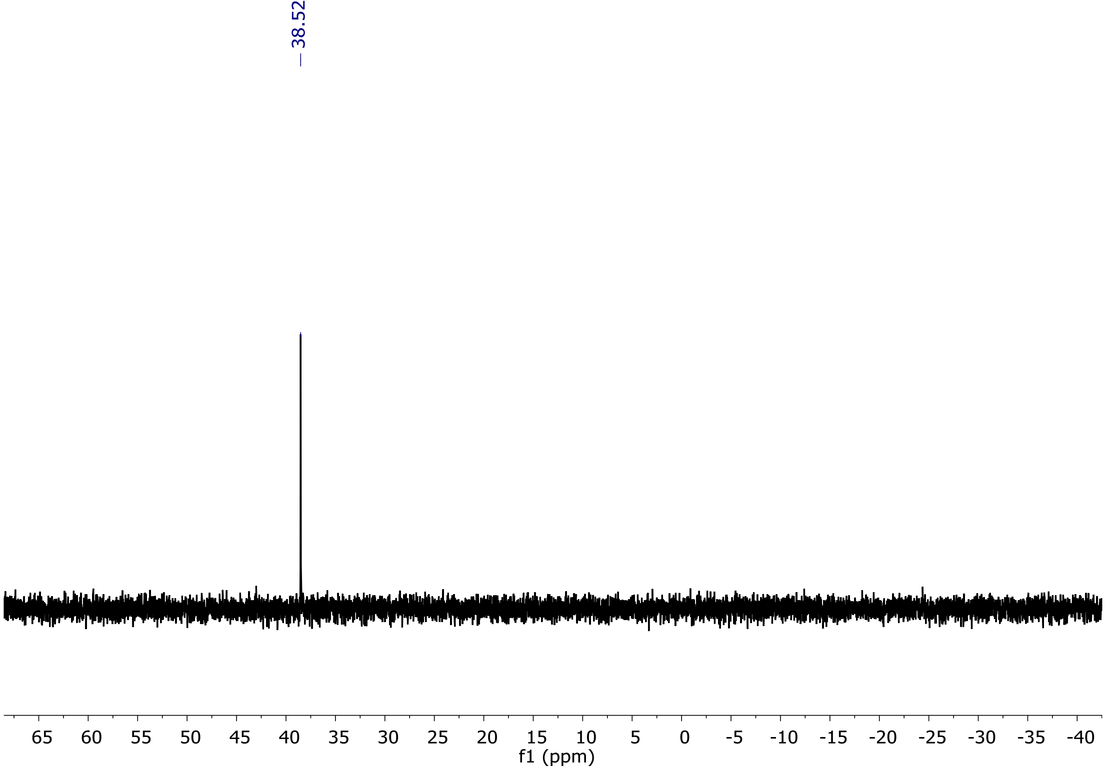


Figure S4. ^{31}P NMR (162 MHz, CD_3CN, 298 K) spectrum of **1**

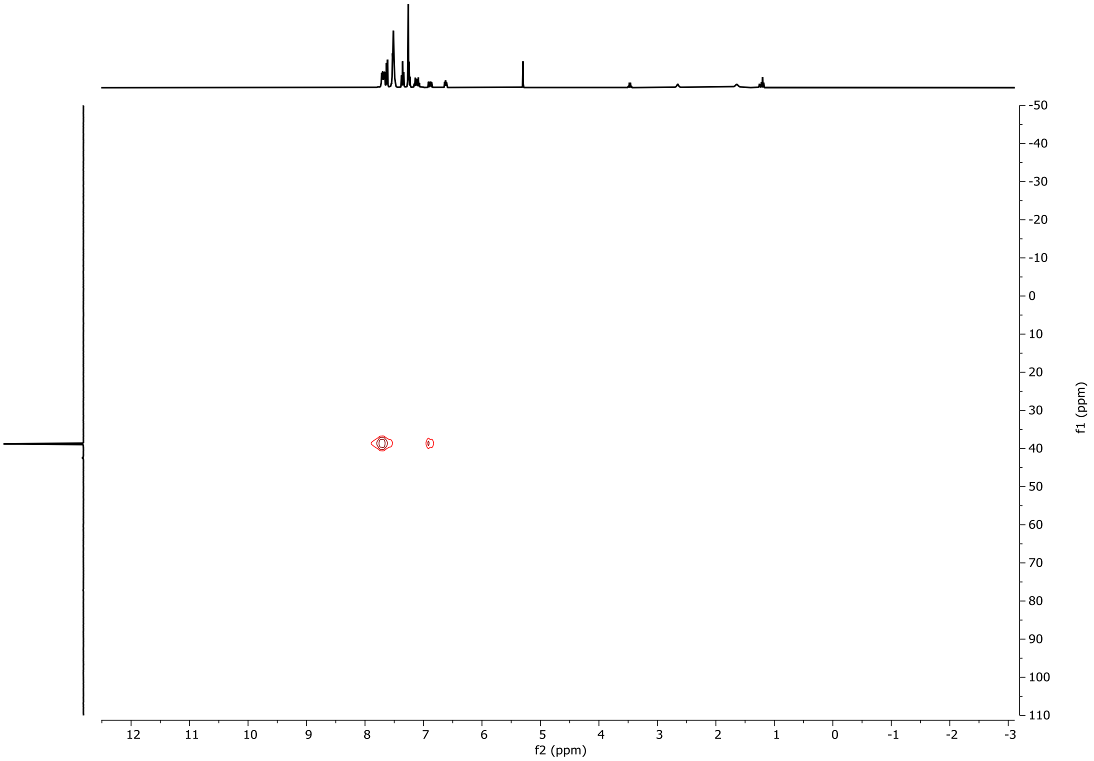


Figure S5. 2D-^{1}H, ^{31}P-HSQC NMR (162 MHz, CDCl$_3$, 298 K) spectrum of **1**. Both the ^{1}H and ^{31}P spectra are external projections.

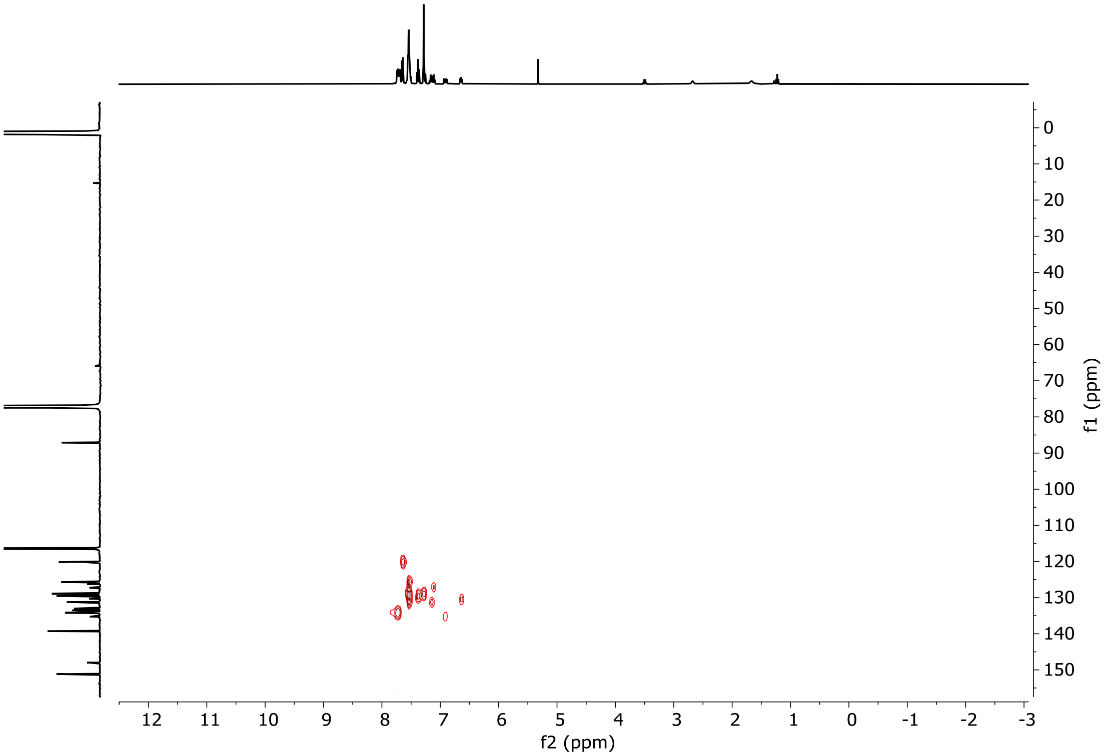


Figure S6. 2D-^{1}H, ^{13}C-HSQC NMR (162 MHz, CDCl$_3$, 298 K) spectrum of **1**. Both the ^{1}H and ^{13}C spectra are external projections.

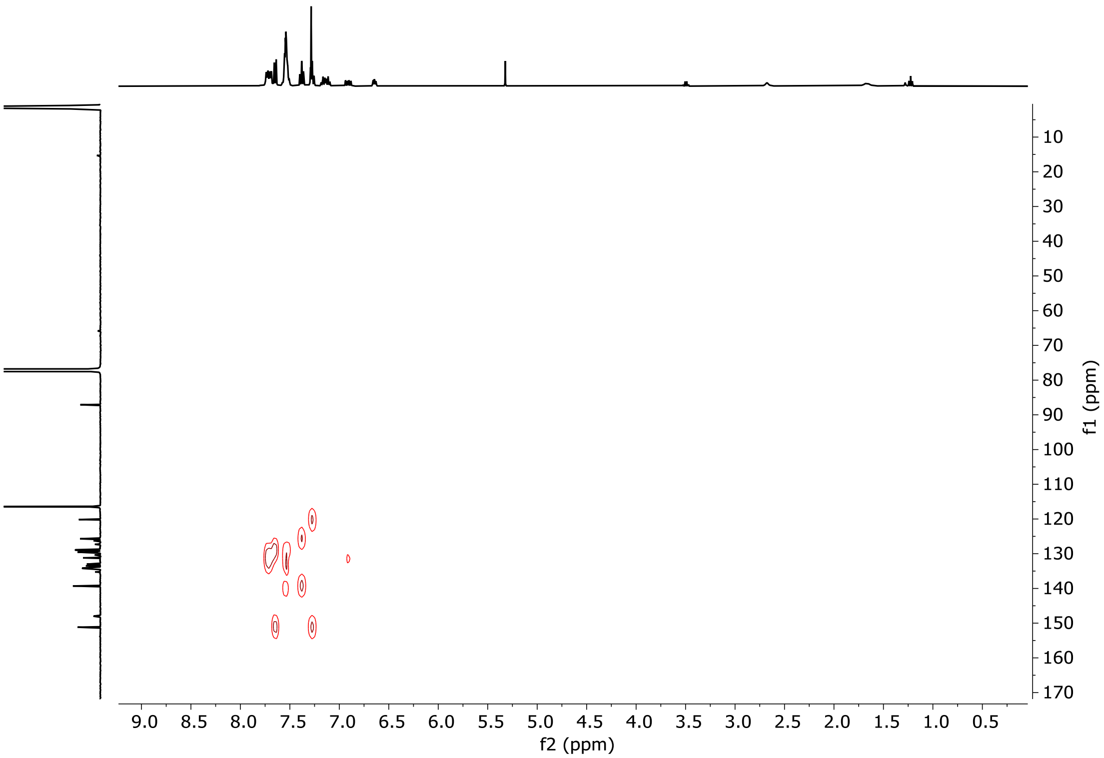


Figure S7. 2D-^{1}H, ^{13}C-HMBC NMR (162 MHz, CDCl$_3$, 298 K) spectrum of **1**. Both the ^{1}H and ^{13}C spectra are external projections.

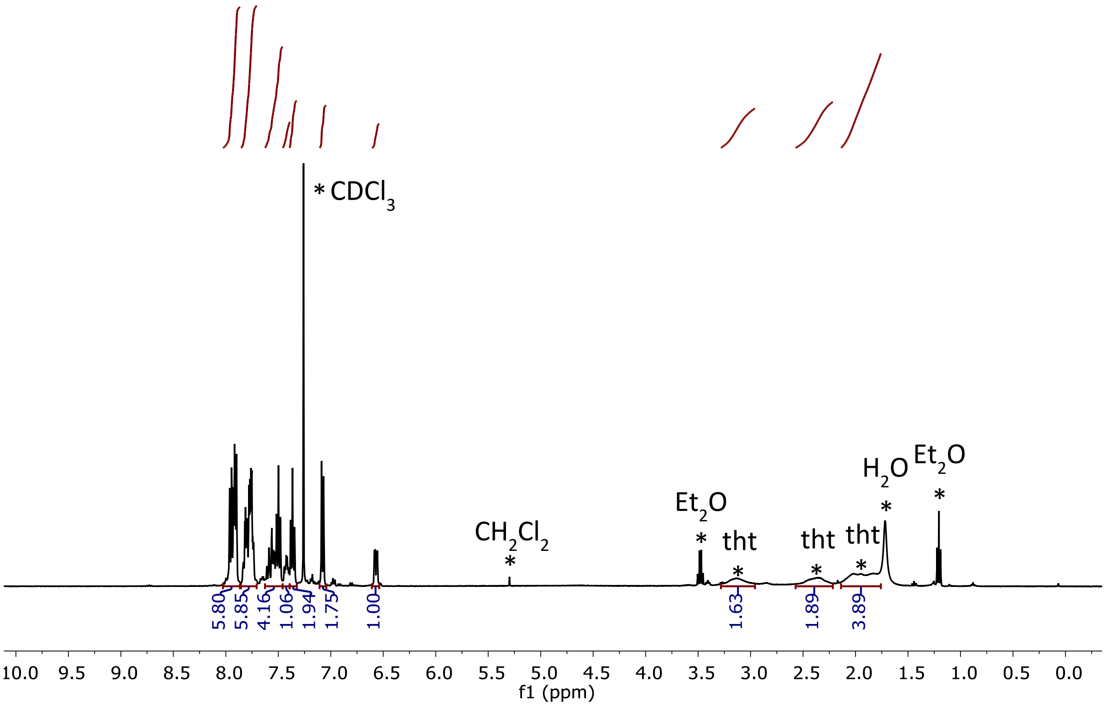


Figure S8. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of [**2**][BF$_4$]

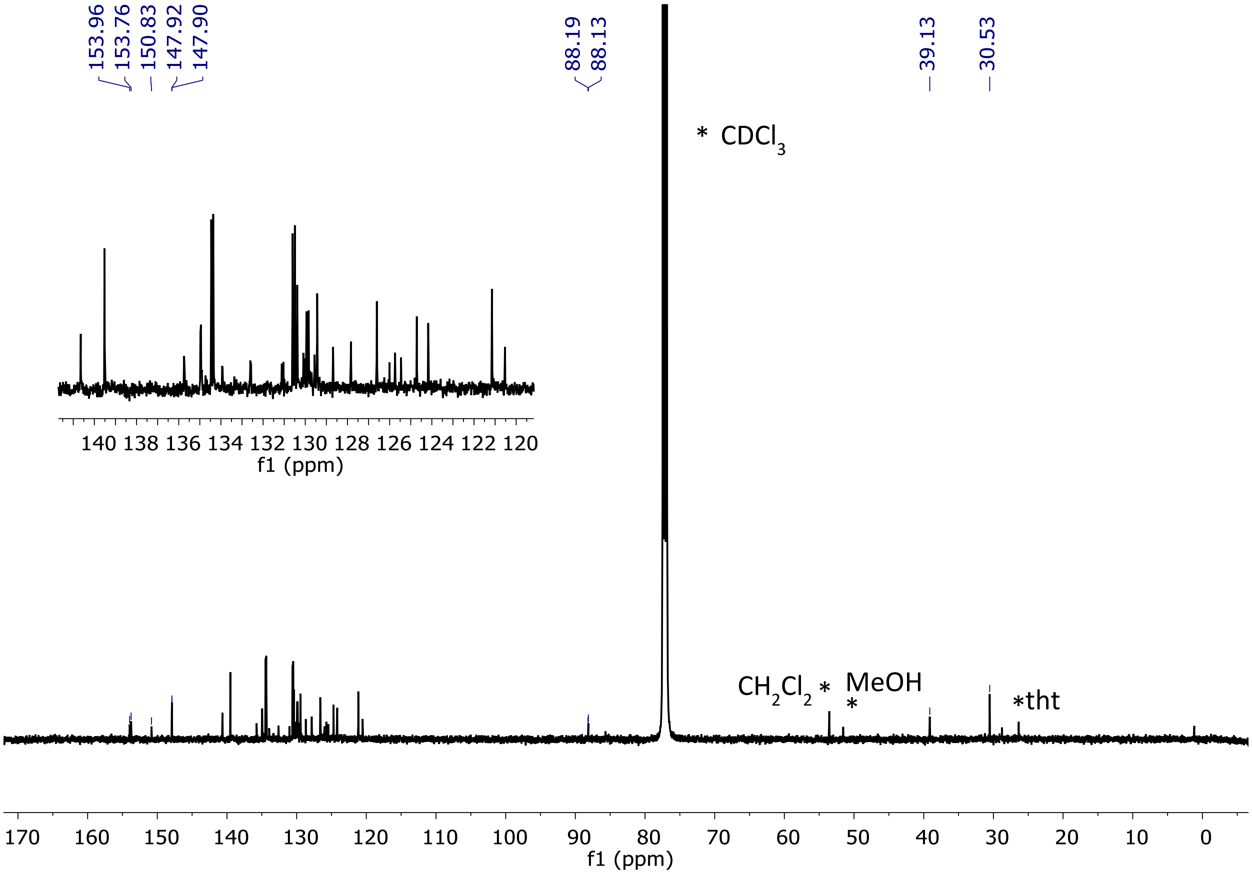


Figure S9. ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) spectrum of [**2**][BF$_4$]

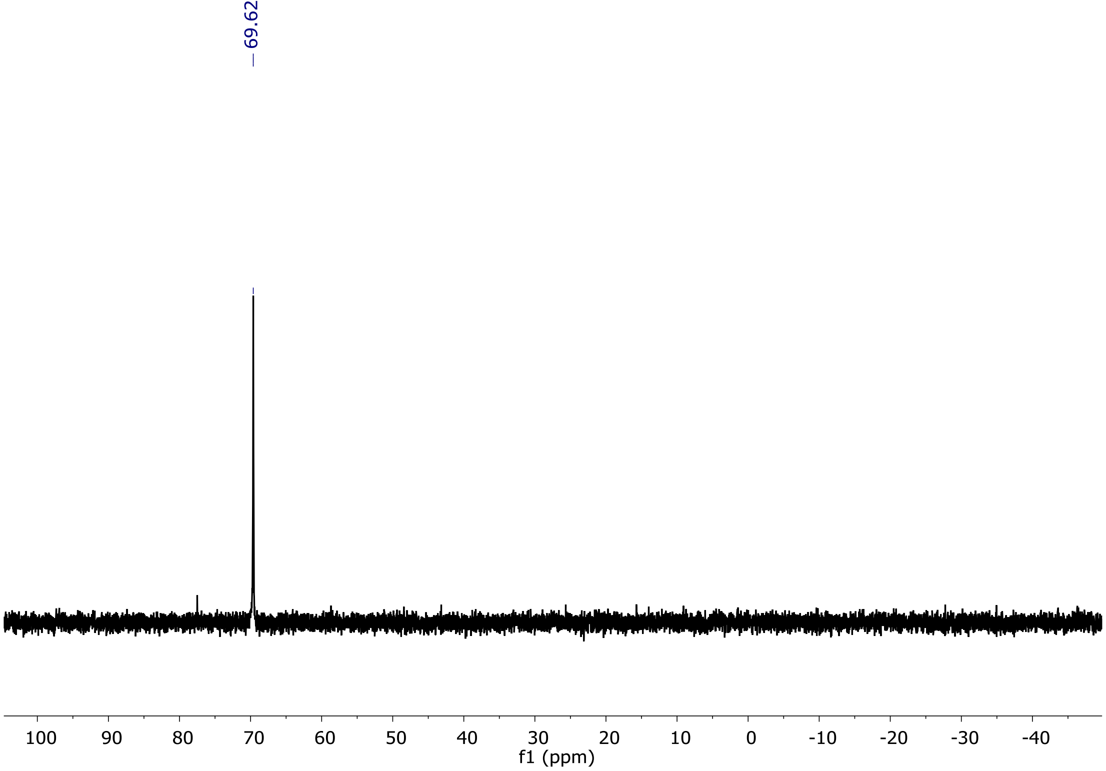


Figure S10. ^{31}P NMR (162 MHz, CD$_3$CN, 298 K) spectrum of [**2**][BF$_4$]

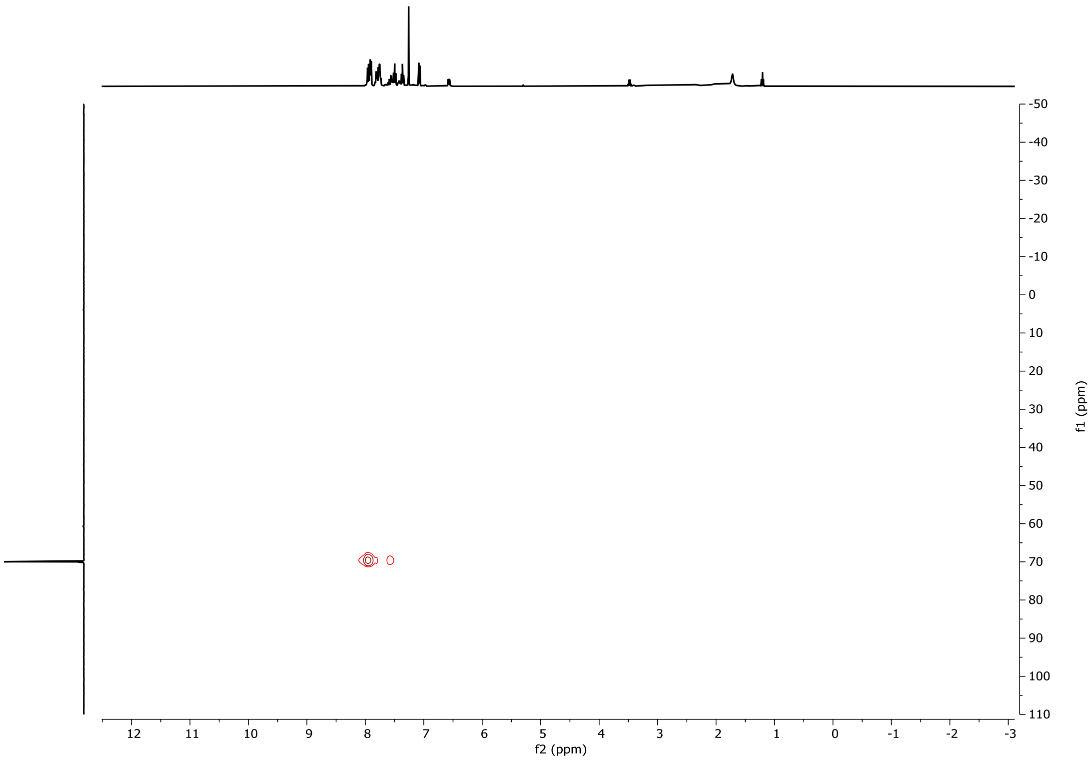


Figure S11. 2D-^{1}H, ^{31}P-HSQC NMR (162 MHz, CDCl$_3$, 298 K) spectrum of [**2**][BF$_4$] . Both the ^{1}H and ^{31}P spectra are external projections.

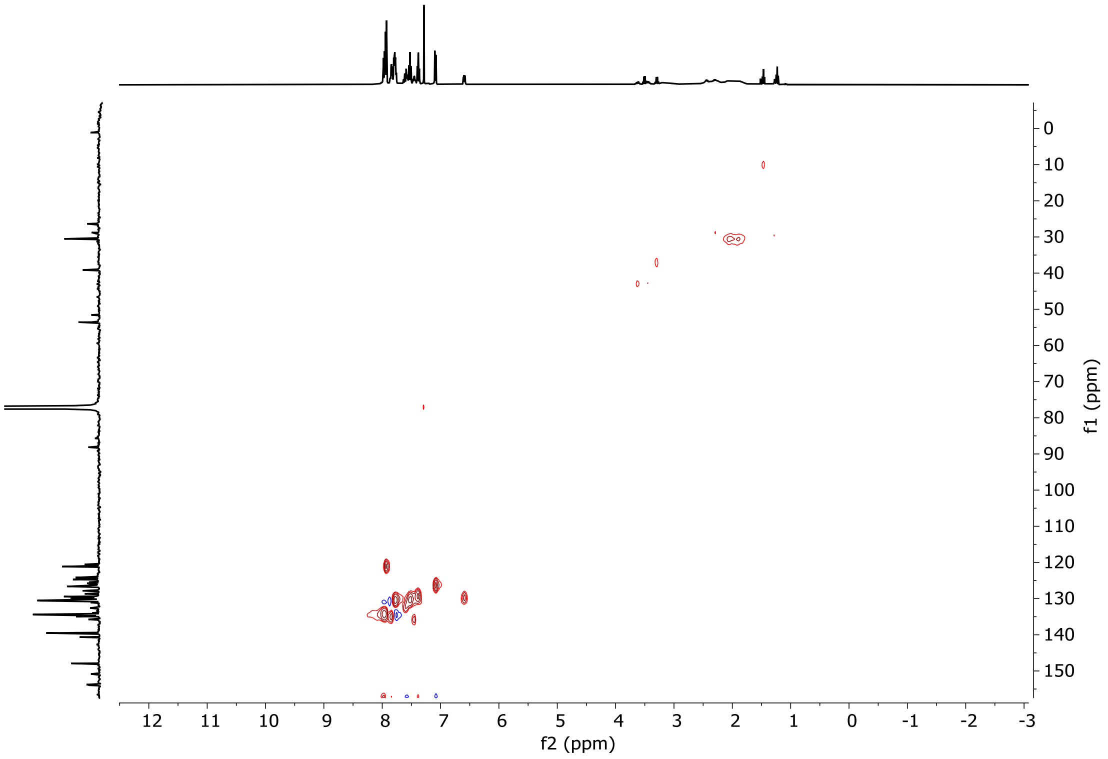


Figure S12. 2D-^{1}H, ^{13}C-HSQC NMR (162 MHz, $CDCl_3$, 298 K) spectrum of [**2**][BF_4] . Both the ^{1}H and ^{13}C spectra are external projections.

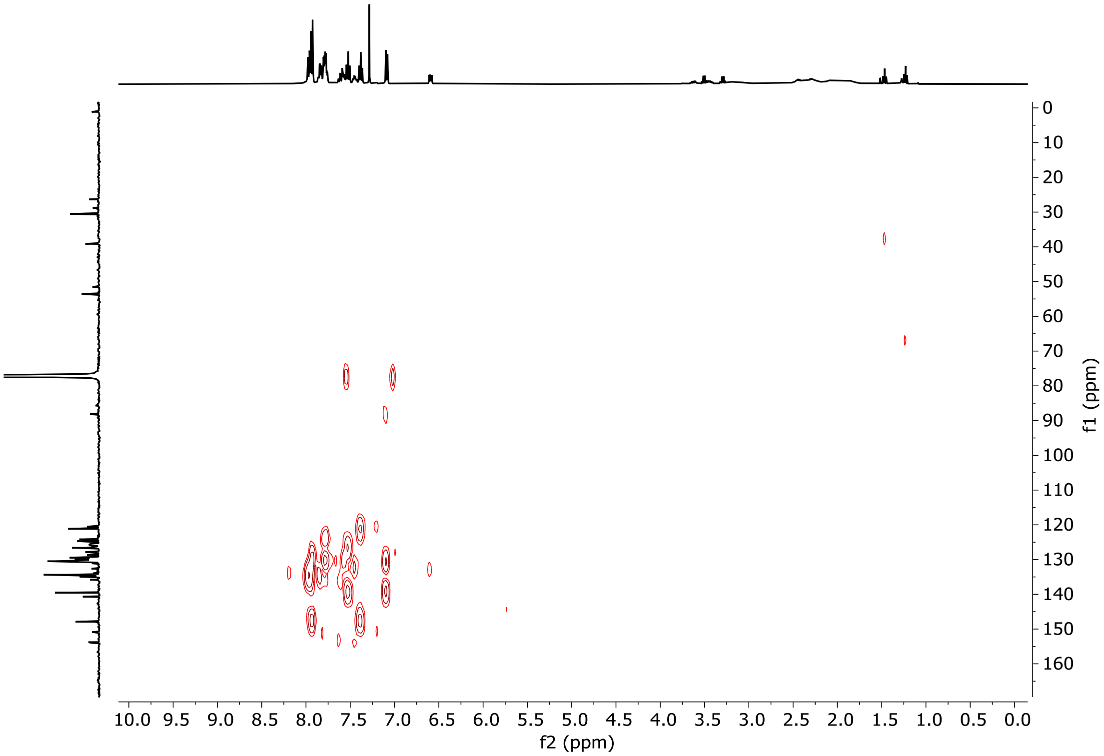


Figure S13. 2D-^{1}H, ^{13}C-HMBC NMR (162 MHz, $CDCl_3$, 298 K) spectrum of [**2**][BF_4] . Both the ^{1}H and ^{13}C spectra are external projections.

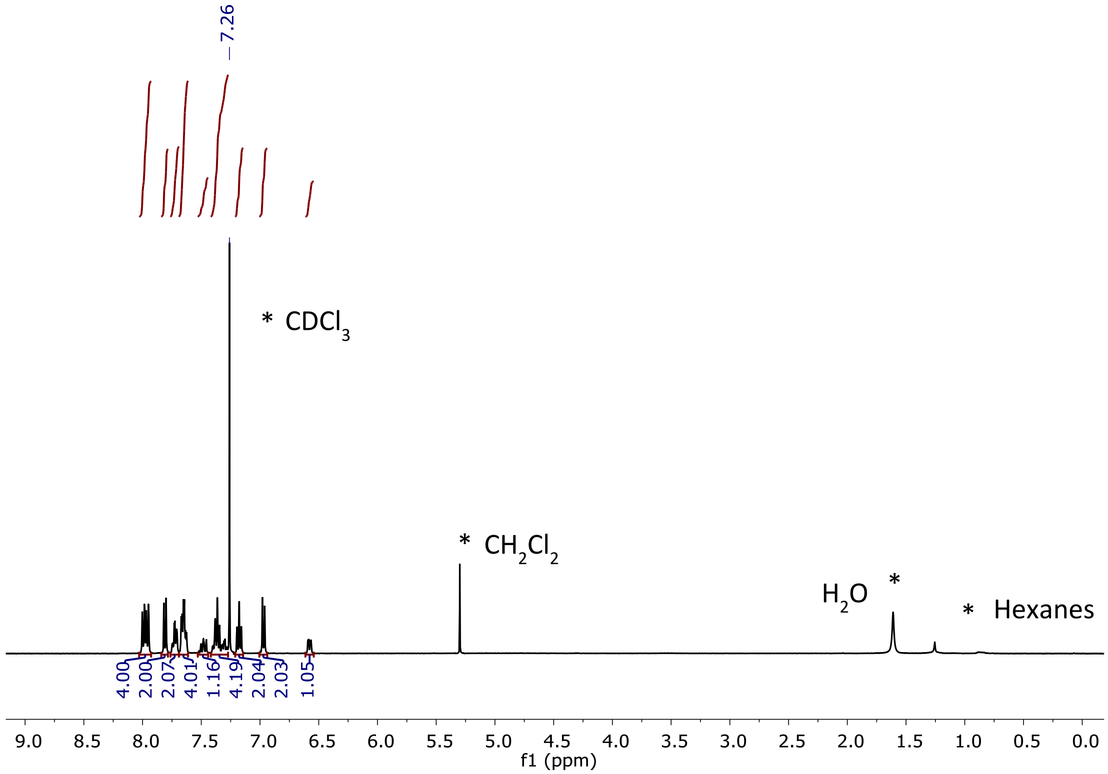


Figure S14. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of **3**.

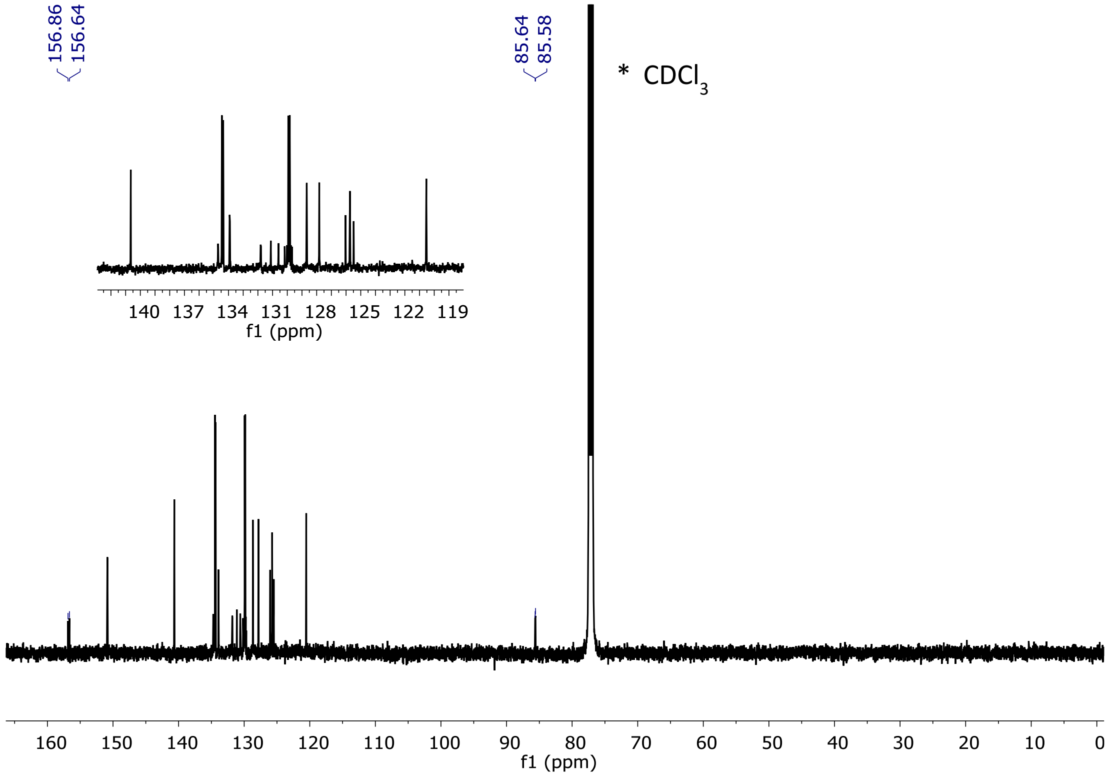


Figure S15. ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) spectrum of **3**

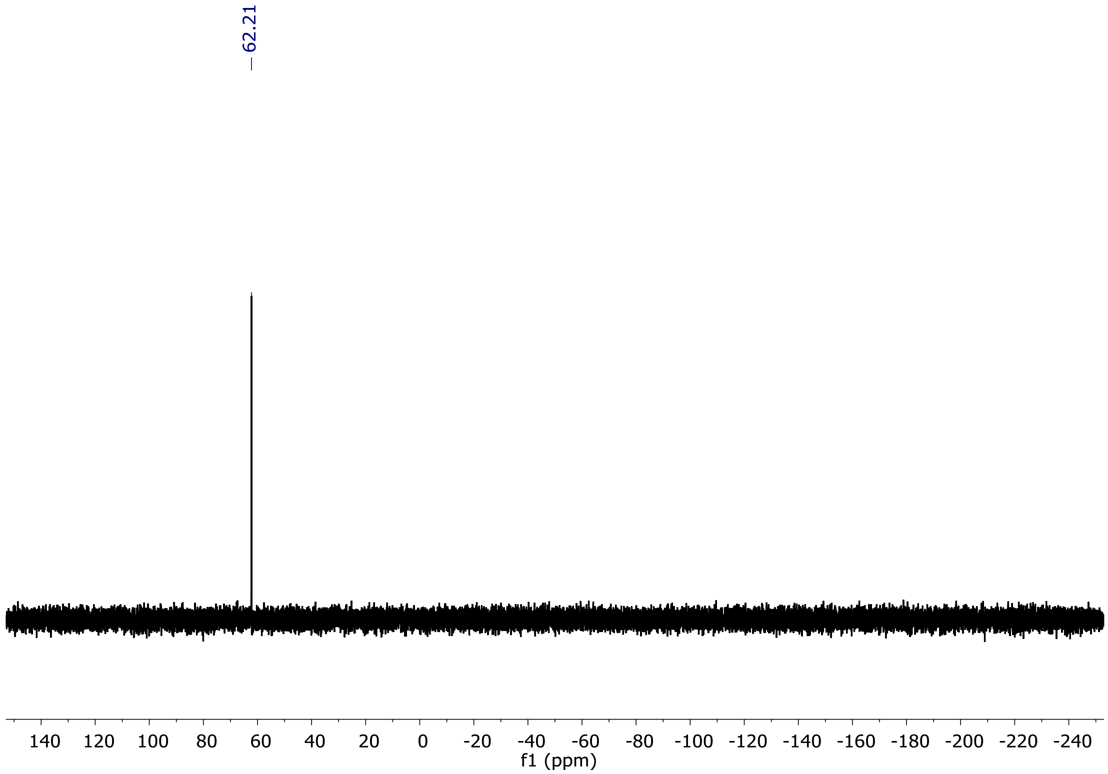


Figure S16. ^{31}P NMR (162 MHz, CD_3CN, 298 K) spectrum of **3**

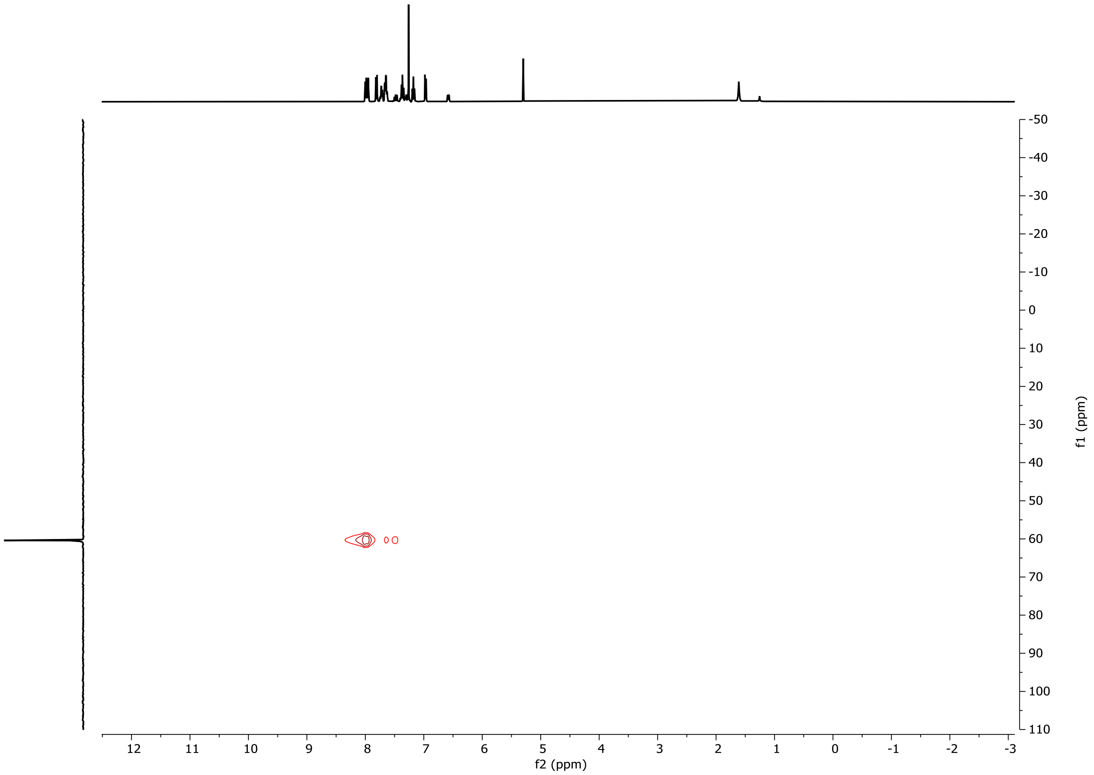


Figure S17. 2D-^{1}H, ^{31}P-HSQC NMR (162 MHz, $CDCl_3$, 298 K) spectrum of **3**. Both the ^{1}H and ^{31}P spectra are external projections.

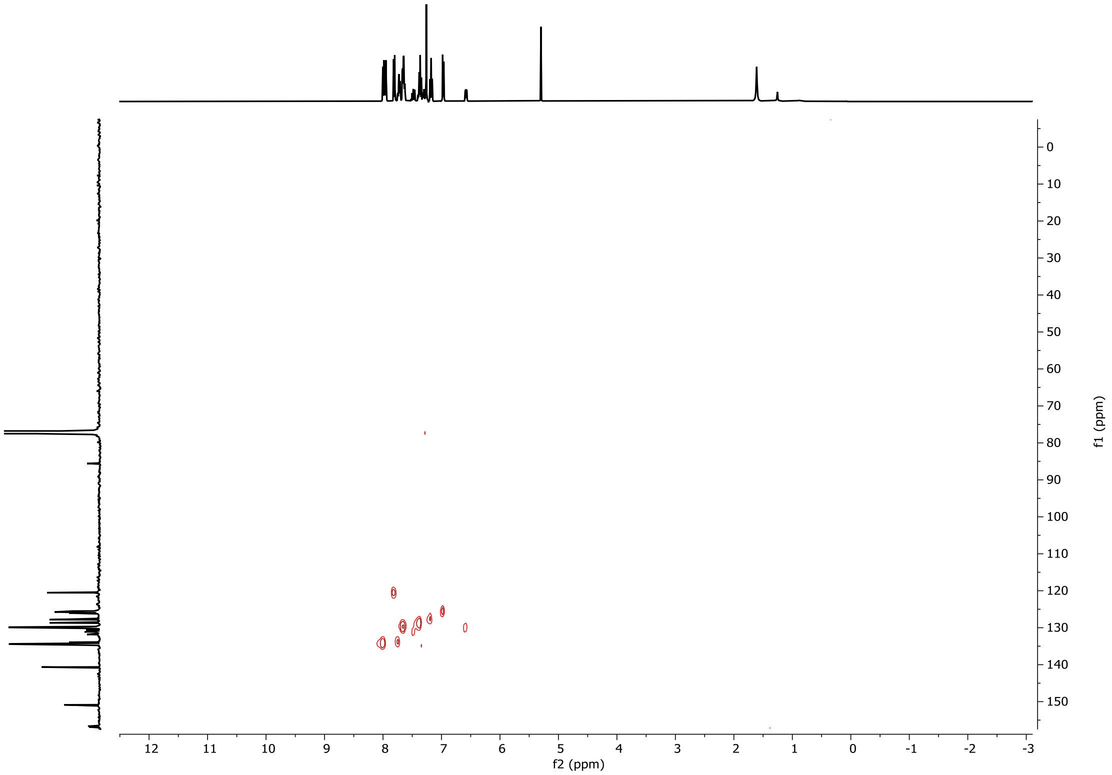


Figure S18. 2D-^{1}H, ^{13}C-HSQC NMR (162 MHz, CDCl$_3$, 298 K) spectrum of **3**. Both the ^{1}H and ^{13}C spectra are external projections.

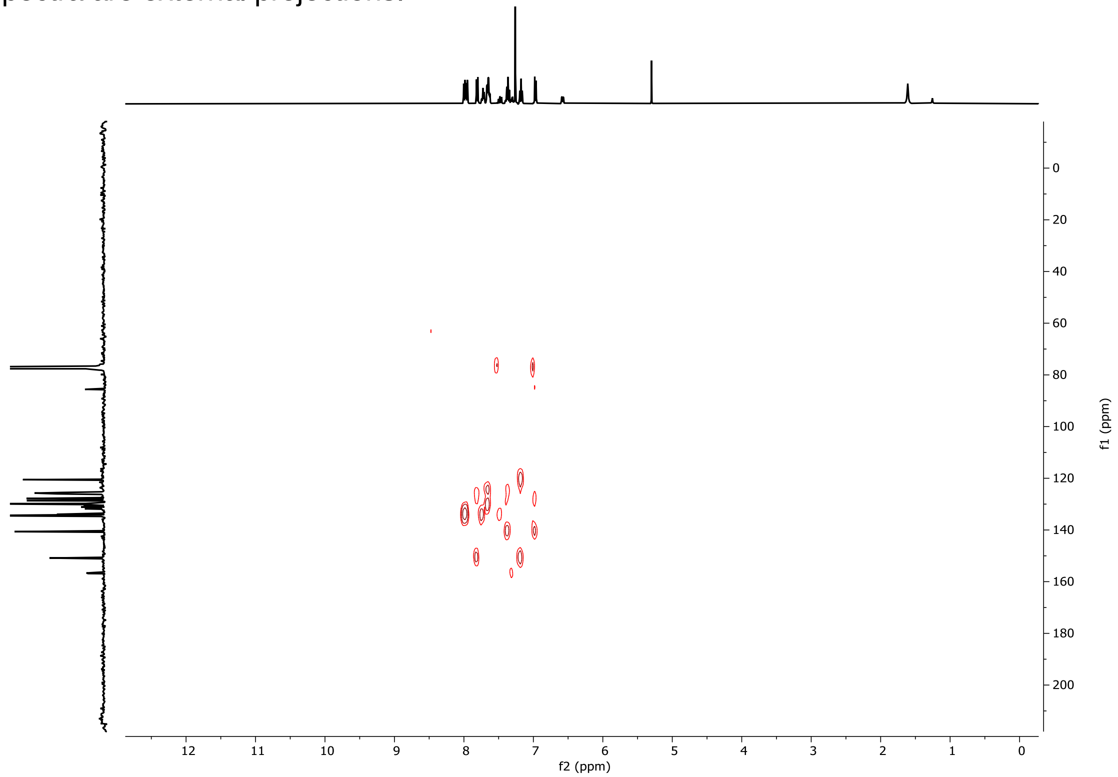


Figure S19. 2D-^{1}H, ^{13}C-HMBC NMR (162 MHz, CDCl$_3$, 298 K) spectrum of **3**. Both the ^{1}H and ^{13}C spectra are external projections.

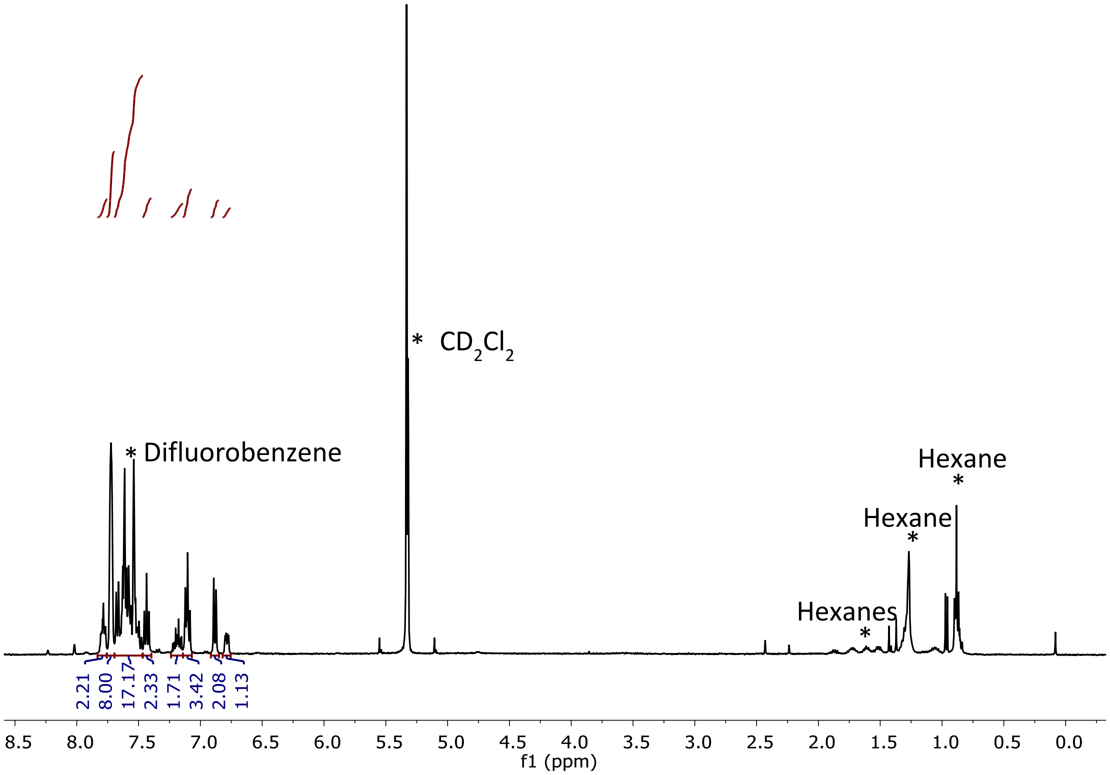


Figure S20. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 298 K) spectrum of [**4**$_2$][BArF$_{24}$]$_2$. ^{1}H NMR was collected from a batch of crystals which have hexanes and *o*-difluorobenzene in the crystal lattice. c

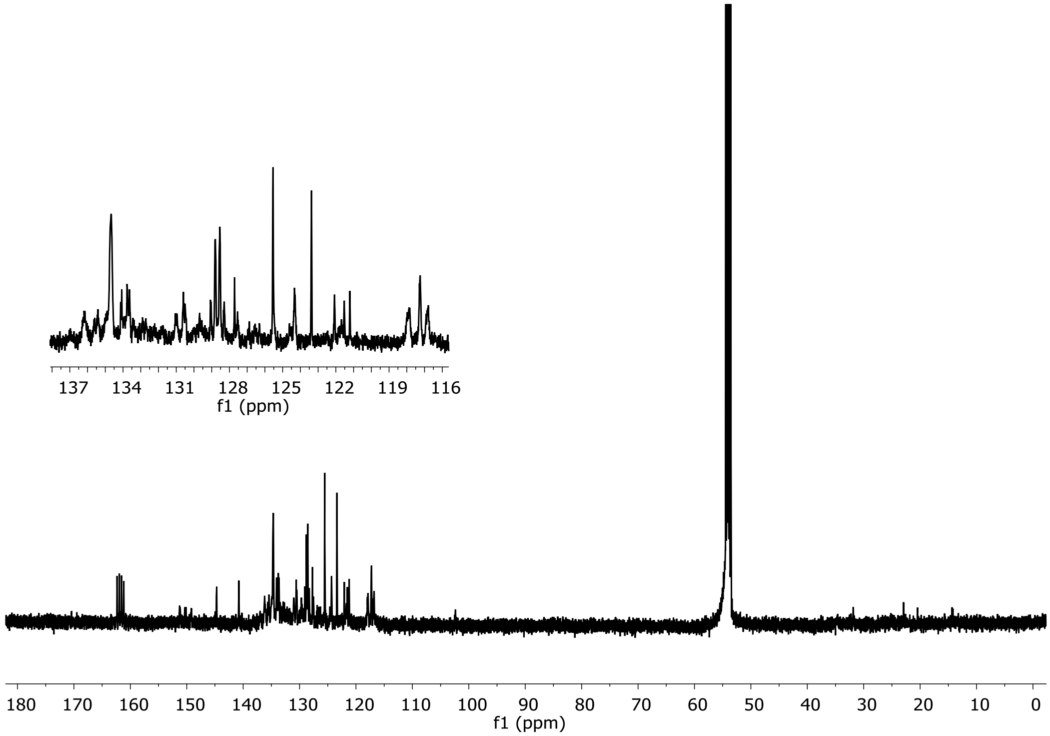


Figure S21. ^{13}C NMR (126 MHz, CD$_2$Cl$_2$, 298 K) spectrum of [**4**$_2$][BArF$_{24}$]$_2$ at –40 °C. The VT NMR measurement suggests that this spectrum is of [**4**][BArF$_{24}$].

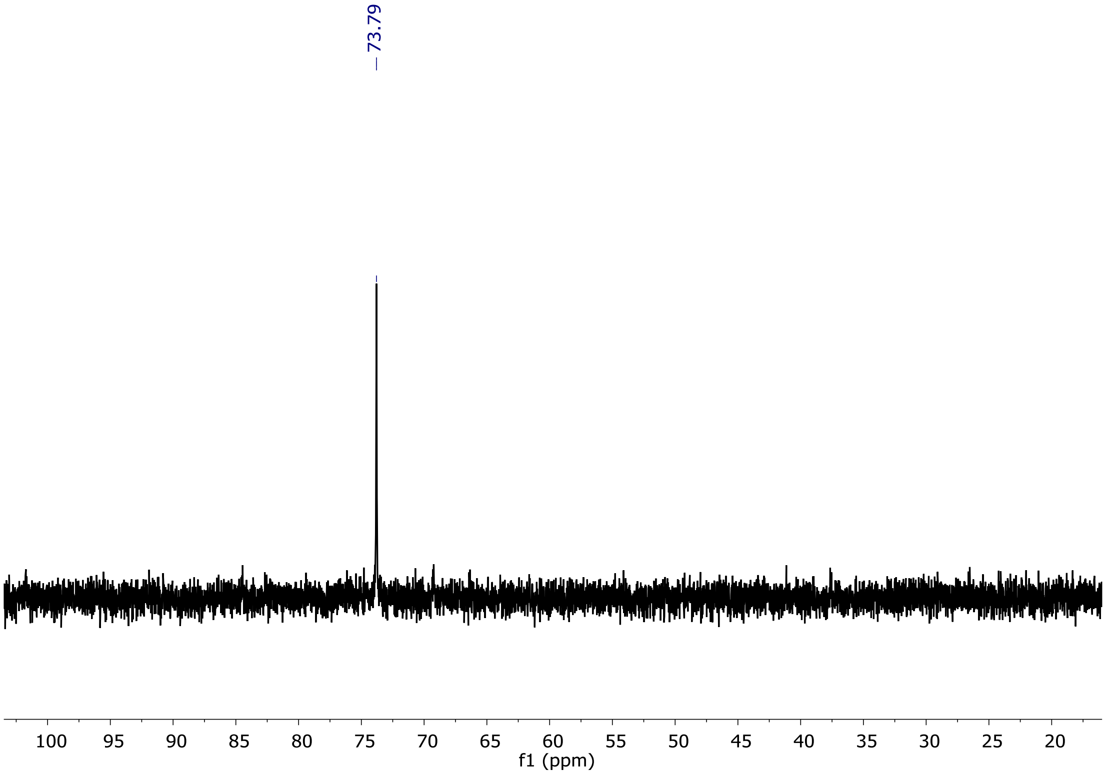


Figure S22. ^{31}P NMR (162 MHz, CD_2Cl_2, 298 K) spectrum of [**4**$_2$][BArF$_{24}$]$_2$. The VT NMR measurement suggests that this spectrum is of [**4**][BArF$_{24}$].

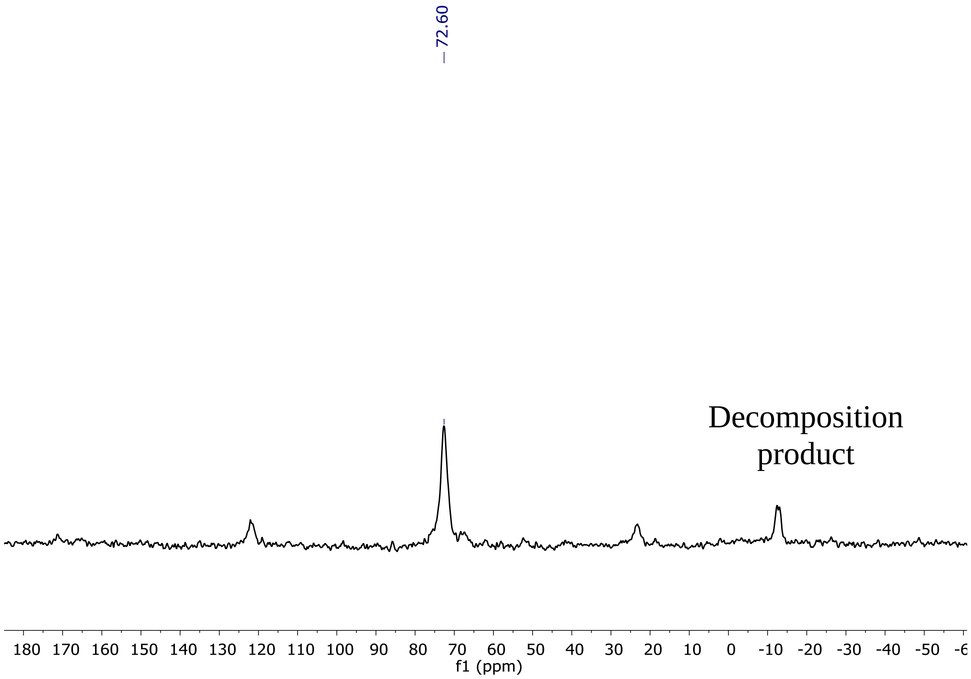


Figure S23. Solid-state ^{31}P NMR (162 MHz, 298 K) spectrum of [**4**$_2$][BArF$_{24}$]$_2$.

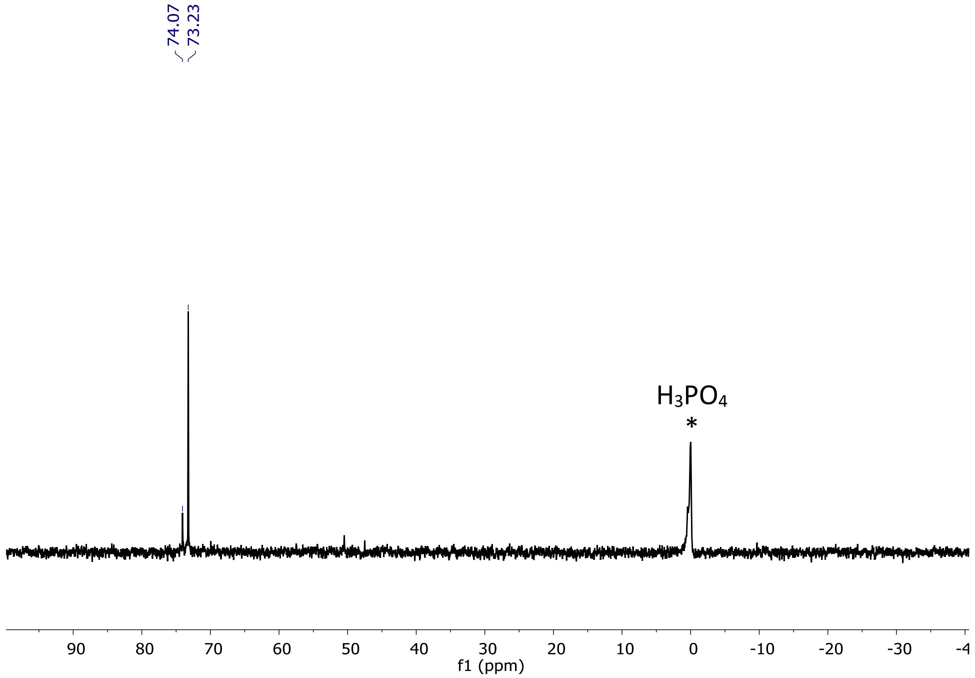


Figure S24. ^{31}P NMR (202 MHz, CD_2Cl_2, 258 K) spectrum of [**4**$_2$][BArF$_{24}$]$_2$/[**4**][BArF$_{24}$]. Referenced to H_3PO_4.

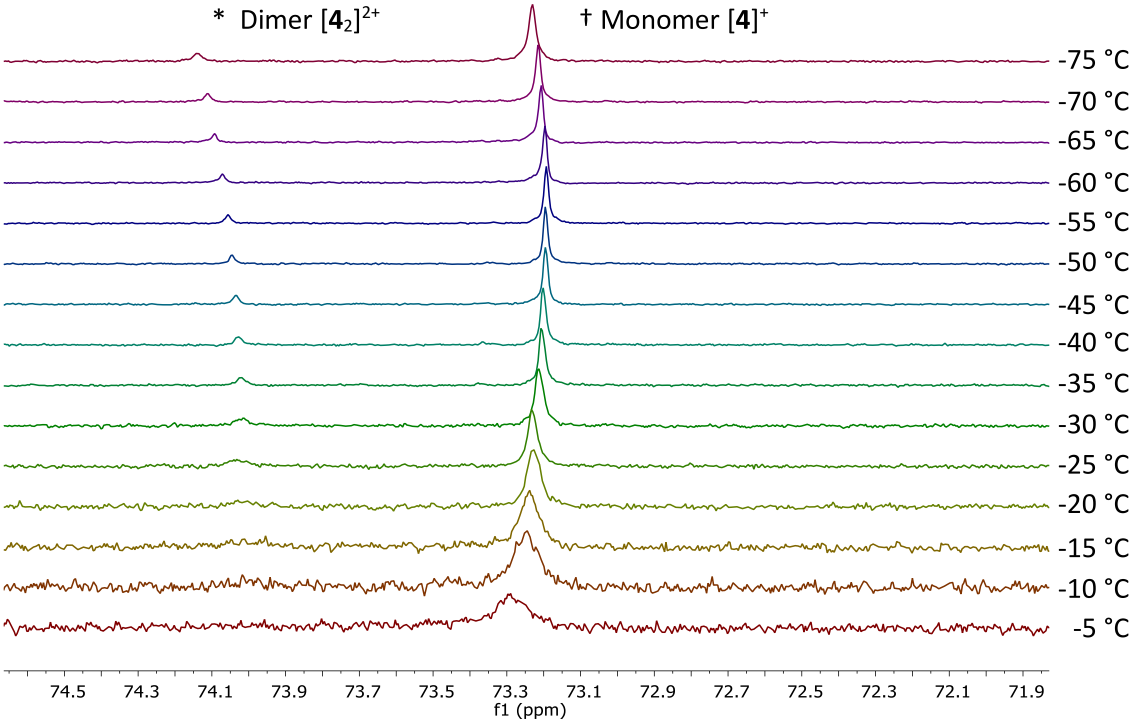


Figure S25. Variable temperature ^{31}P NMR (202 MHz, CD_2Cl_2) spectra of [**4**$_2$][BArF$_{24}$]$_2$/[**4**][BArF$_{24}$] from -75 °C to -5 °C showing two peaks attributed to the monomer and dimeric species coalesce at approximately -20 °C.

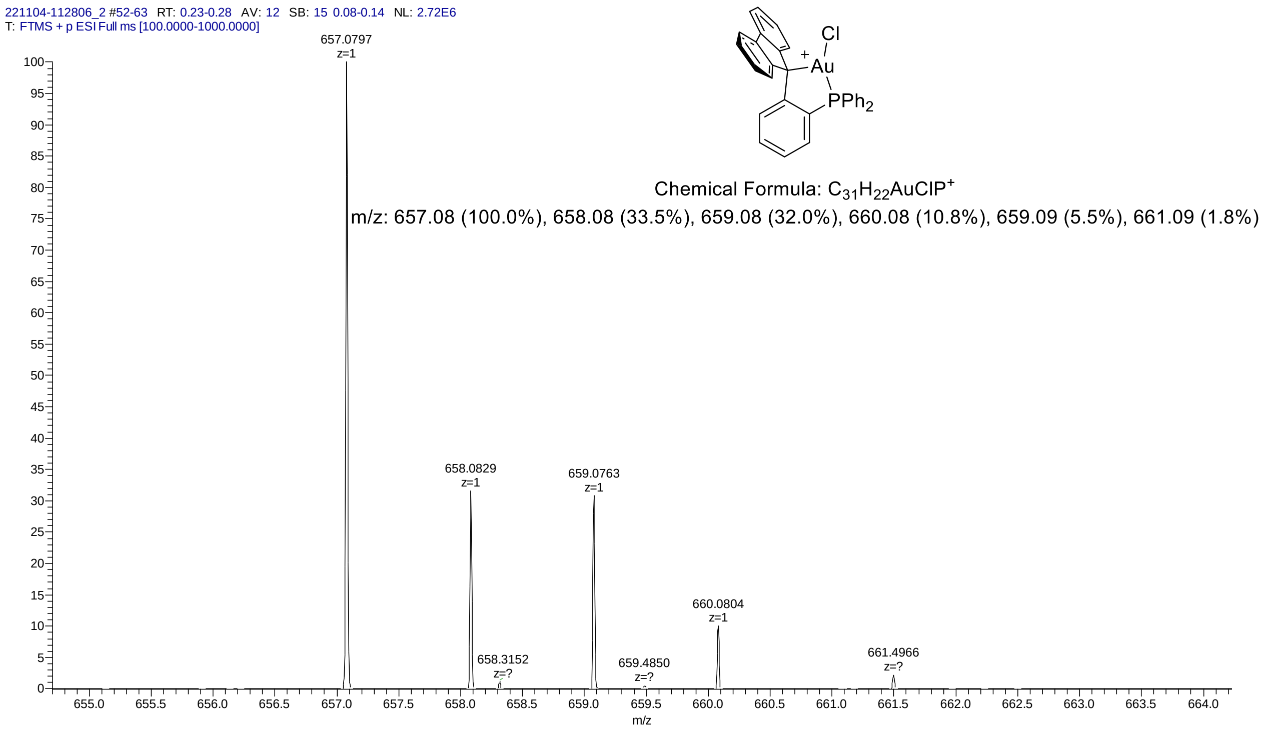


Figure S26. ESI(+) mass spectrum of [**4**][BArF$_{24}$].

2.2 Catalytic studies

For the catalytic studies, the eneyne (23.8 mg, 25 µl, 0.1 mmol) was loaded into an NMR tube. The freshly crystallized pre-catalyst (2 µmol, 2 mol%) was then weighed out and dissolved in CD_2Cl_2 (0.6 ml). The solution was then added to the NMR tube in the NMR room. Reaction progress was monitored in situ via ^1H NMR. Final conversion of the reaction was measured based on the integrated ^1H NMR spectra.[2] 6-Endo: ^1H NMR (500 MHz, CD_2Cl_2, 298 K) δ/ppm: 6.19 (d, J = 9.9 Hz, 1H), 5.91 – 5.76 (m, 1H), 5.02 – 4.94 (d, J = 16.1 Hz, 2H), 4.15 (m, 4H), 2.85 (t, J = 1.6 Hz, 2H), 2.68 (dd, J = 4.4, 2.1 Hz, 4H), 1.22 (m, 6H). 6-Exo: 1H NMR (500 MHz, CD_2Cl_2, 298 K) δ/ppm: 6.55 (dd, J = 17.6, 10.4 Hz, 1H), 5.62 (t, J = 2.4 Hz, 1H), 5.16 – 5.09 (m, 2H), 4.15 (m, 4H), 3.08 (dt, J = 11.2, 2.2 Hz, 4H), 1.22 (m, 6H). The results of these catalysis experiments are presented in the table in Scheme 4 of the main text.

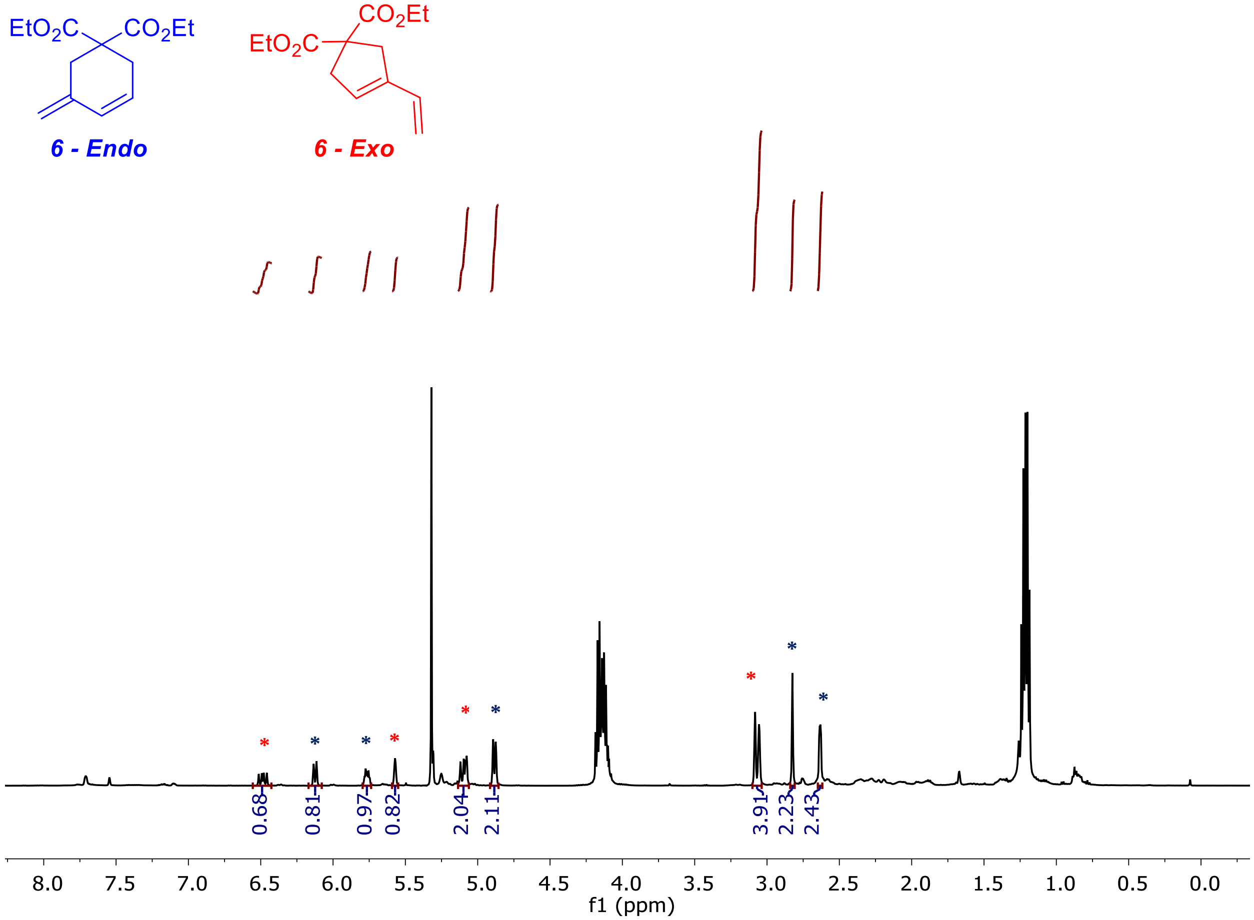


Figure S27. *In situ* ^1H NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of reaction outlined in scheme 4.

3 Computational studies

3.1 General methods

The structures of [**2**]$^+$, **3**, [**4**]$^+$, [**4**$_2$]$^{2+}$, [$Ph_3P(Me)Au(Cl)$]$^+$, and [$(Ph_3P(Me)Au(\mu_2\text{-}Cl))_2$]$^{2+}$ were optimized using DFT methods as implemented in Gaussian 16 using the MPW1PW91 functional and a mixed basis set defined as follows: Au cc-PVTZ-PP; P 6-31G(d',p'); C/N/O 6-31G(d'); H 6-31G. Frequency calculations, performed using the same level of theory on the optimized geometries, found no imaginary frequencies. Simulated NMR spectra using the GIAO method were calculated using the PBEPBE functional with the same mixed basis set. This NMR calculation afforded chemical shifts for [**4**]$^+$ and [**4**$_2$]$^{2+}$ separated by exactly 1 ppm which is close to the separation observed experimentally (see main text). The Pipek-Mezey orbitals were calculated using the multiwfn program.[3] The resulting optimized structures and Pipek-Mezey orbitals were visualized using the Avogadro program.[4]

3.2 Geometry optimized structures

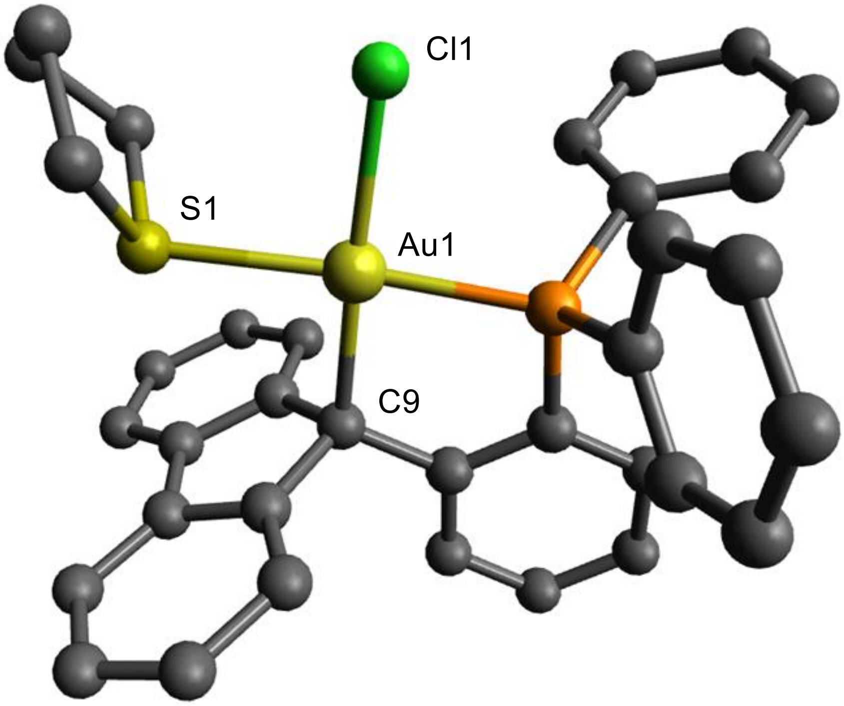


Figure S28. Optimized structure of compound [**2**]$^+$. Computed bond distances: Au1-C9 2.14 Å; Au1-Cl1 2.38 Å; Au1-S1 2.45 Å.

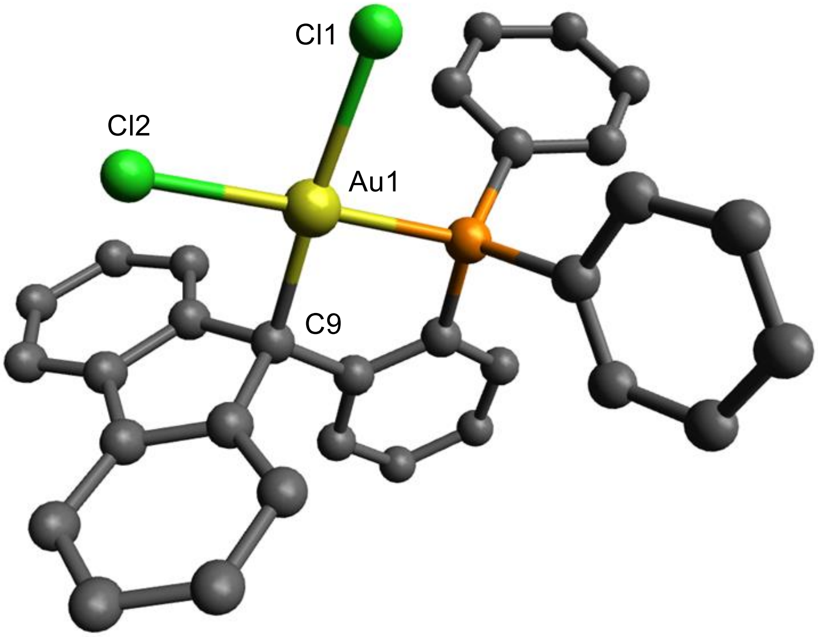


Figure S29. Optimized structure of compound **3**. Computed bond distances: Au1-C9 2.13 Å; Au1-Cl1 2.38 Å; Au1-Cl2 2.32 Å.

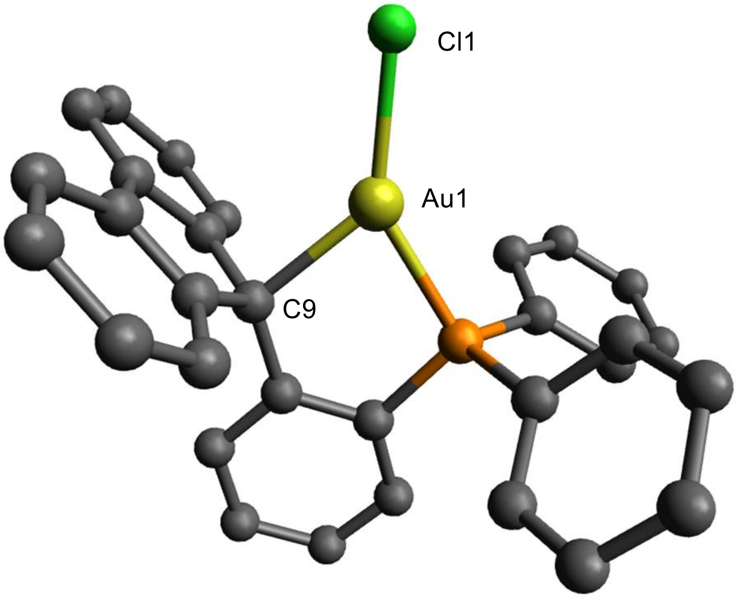


Figure S30. Optimized structure of compound [**4**]$^+$. Computed bond distances: Au1-C9 2.19 Å; Au1-Cl1 2.28 Å.

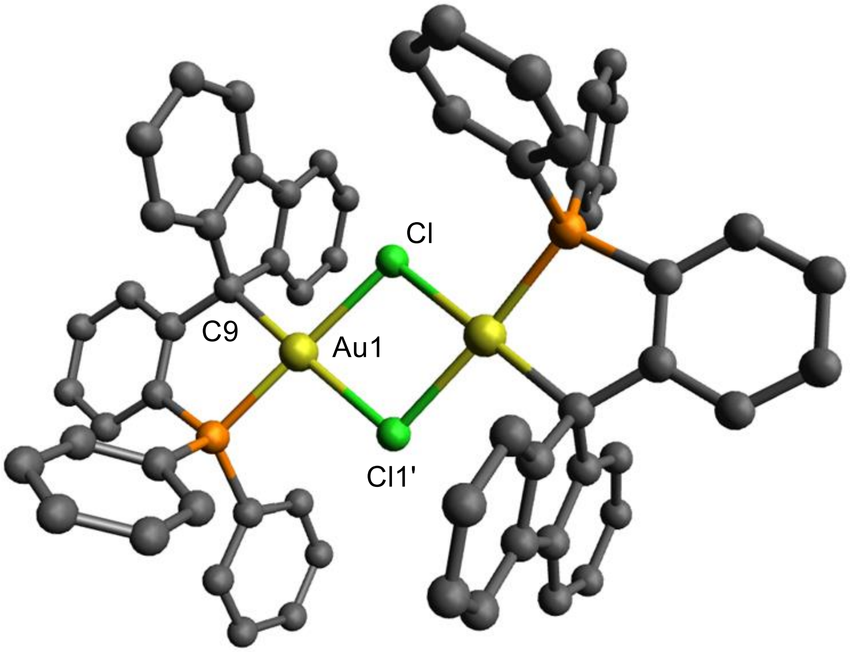


Figure S31. Optimized structure of compound [**4**$_2$]$^{2+}$. Computed bond distances: Au1-C9 2.15 Å; Au1-Cl1 2.45 Å; Au1-Cl1’ 2.51 Å, Average Au-Cl bond length 2.48 Å.

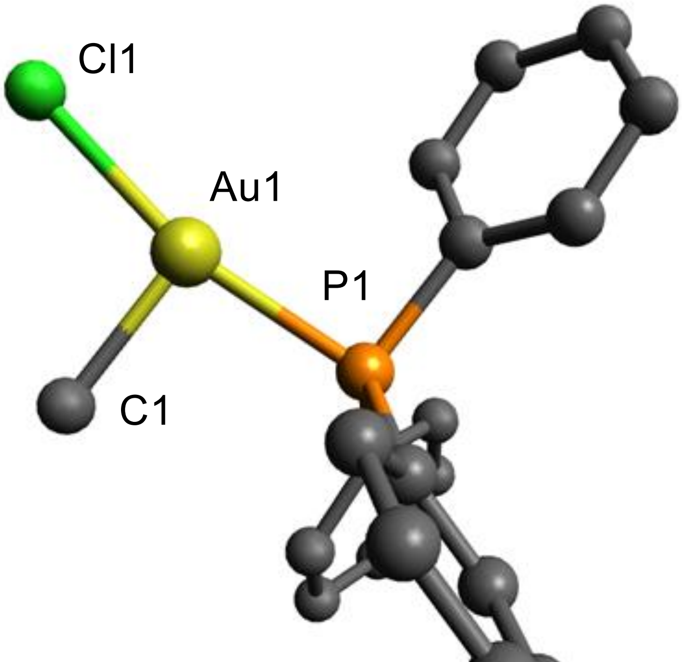


Figure S32. Optimized structure of compound [Ph$_3$P(Me)AuCl]$^+$. Computed bond distances: Au1-C1 2.06 Å; Au1-Cl1 2.27 Å.

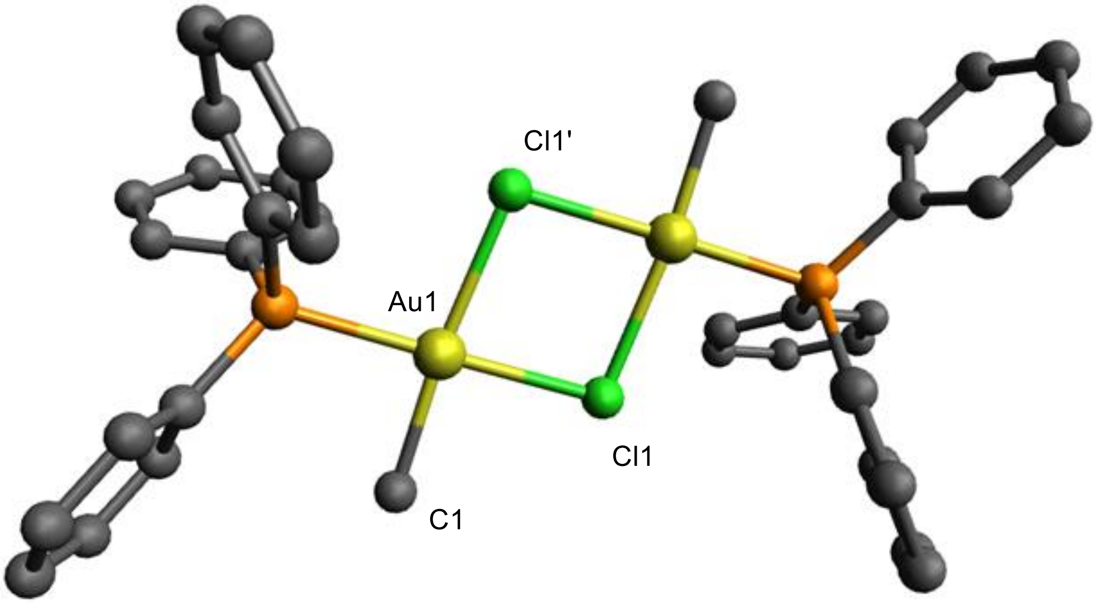


Figure S33. Optimized structure of compound $[(Ph_3P(Me)Au(\mu_2\text{-}Cl))_2]^{2+}$. Computed bond distances: Au1-C1 2.06 Å; Au1-Cl1 2.49 Å; Au1-Cl1’ 2.44 Å.

3.3 Pipek-Mezey orbitals

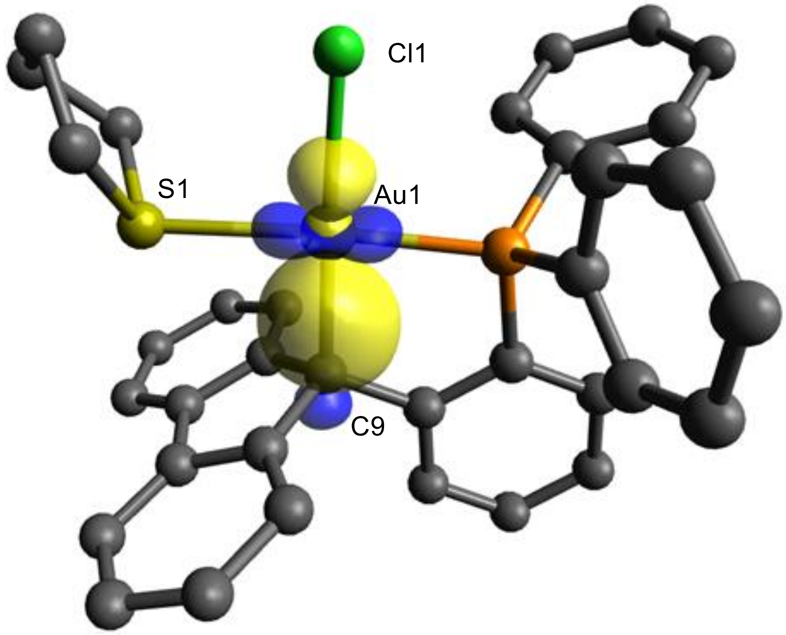


Figure S34. Pipek-Mezey orbital depicting the Au-C9 bond in complex [**2**]$^{+}$. Au: 54.0% C: 32.2%

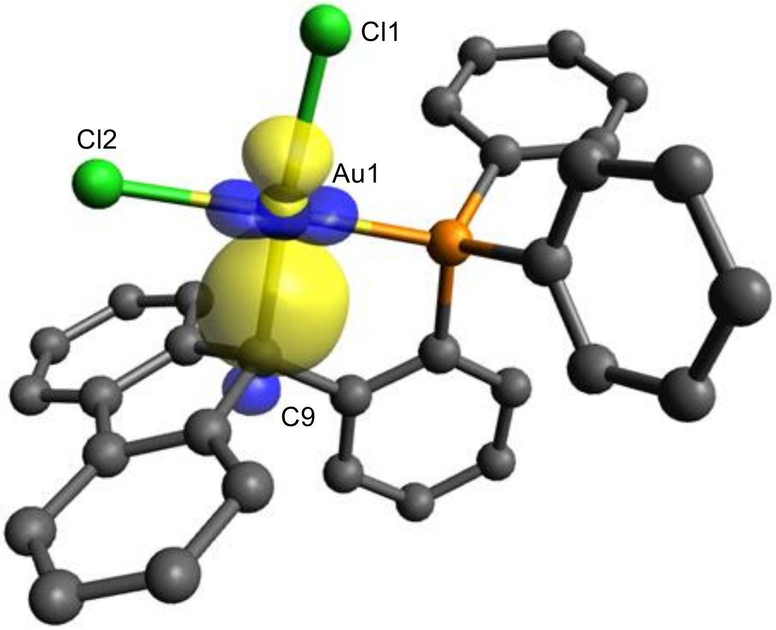


Figure S35. Pipek-Mezey orbital depicting the Au-C9 bond in complex **3**. Au: 50.1% C: 35.6%

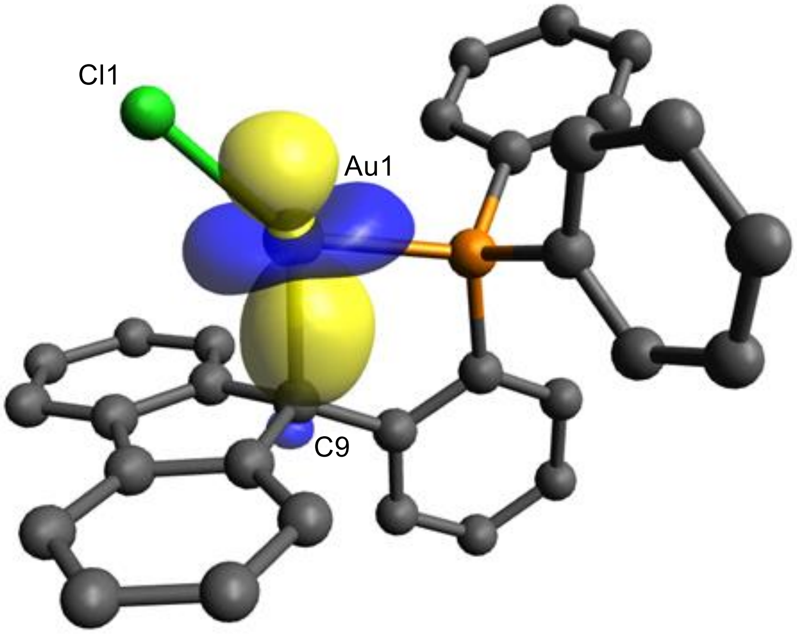


Figure S36. Pipek-Mezey orbital depicting the Au-C9 bond in complex [**4**]$^+$. Au: 72.5% C: 15.4%

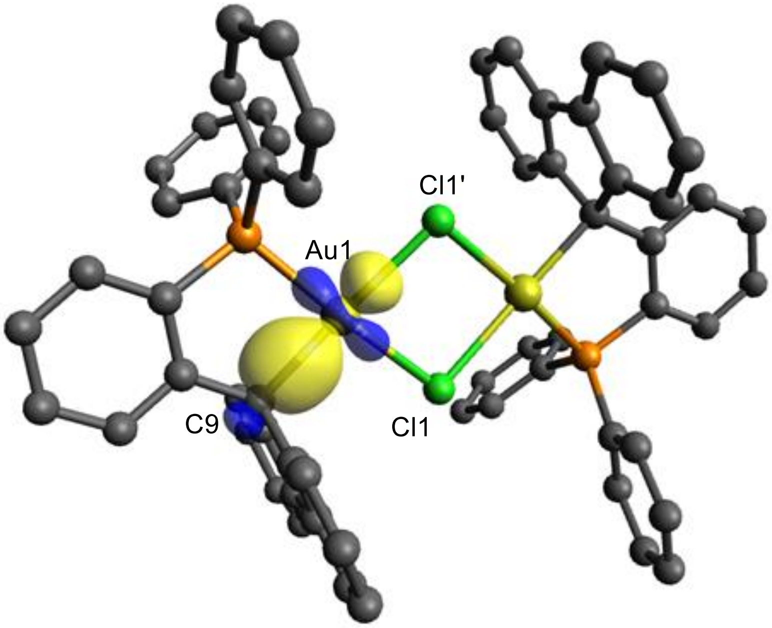


Figure S37. Pipek-Mezey orbital depicting the Au-C9 bond in complex [**4**$_2$]$^{2+}$. Au: 64.4% C: 23.4%

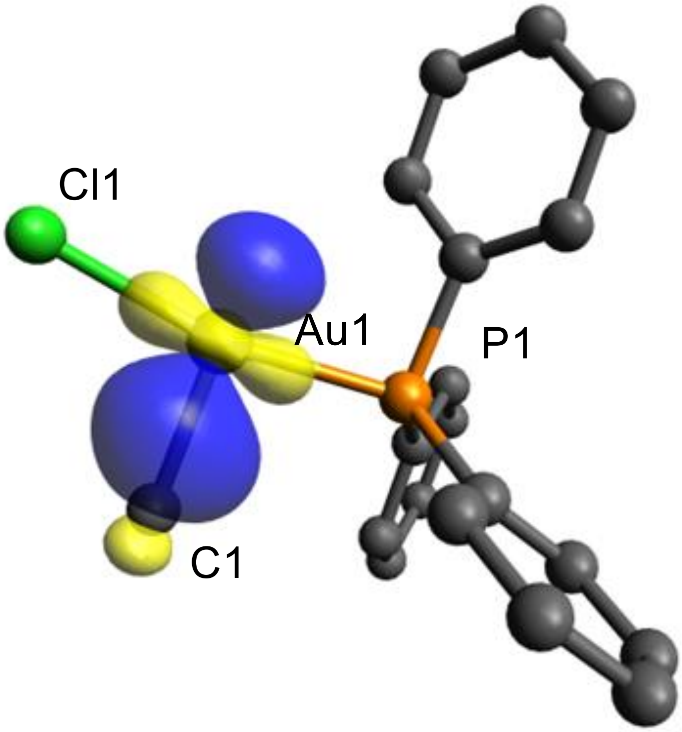


Figure S38. Pipek-Mezey orbital depicting the Au-C1 bond in complex $[Ph_3P(Me)AuCl]^+$. Au: 63.8% C: 28.1%

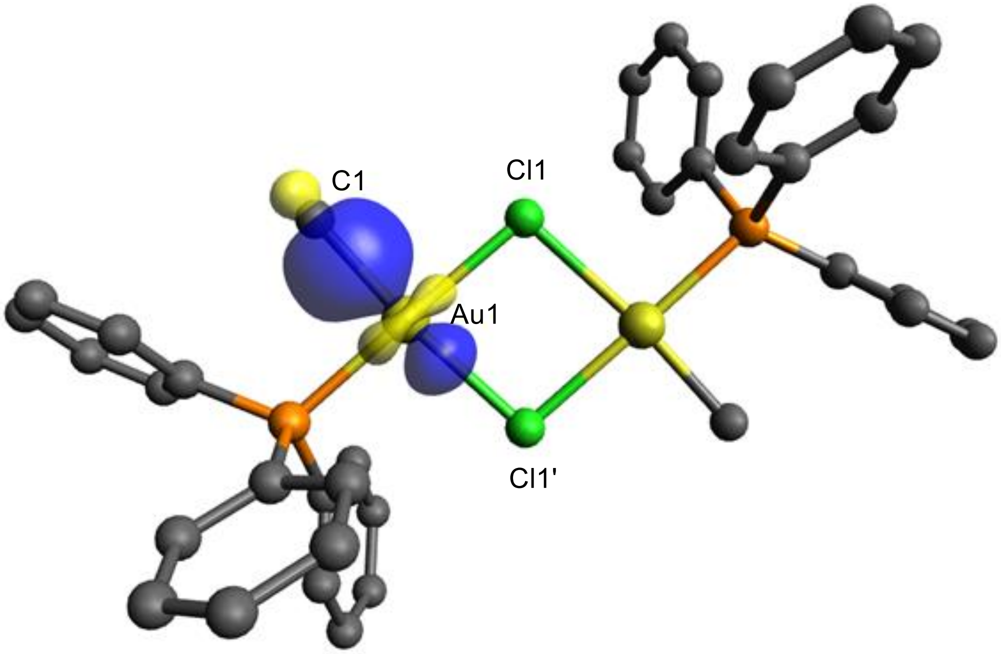


Figure S39. Pipek-Mezey orbital depicting the Au-C1 bond in complex $[(Ph_3P(Me)Au(\mu_2\text{-}Cl))_2]^{2+}$. Au: 55.6% C: 34.2%

3.5 Cartesian coordinates of geometry optimized structures

Atom Number	Coordinates		
	X	Y	Z
Au1	-0.19984	-0.66269	-0.16206
P2	0.69767	-2.81762	-0.63677
Cl3	1.89711	0.2431	0.14891
C4	-2.46779	-1.48326	-0.60114
C5	3.85934	-0.51657	-3.34048
C6	4.03422	0.75573	-3.88541
C7	2.92576	1.73794	-1.97897
C8	2.50076	2.72596	1.33931
C9	2.75454	0.46049	-1.42877
C10	2.12862	3.96993	1.82698
C11	-0.93557	1.26838	0.37858
C12	0.16256	2.20165	0.85836
C13	-0.19211	3.46683	1.34686
C14	1.51573	1.85575	0.84945
C15	0.77978	4.33773	1.82229
C16	-1.72648	1.79146	-0.79053
C17	5.17752	-1.30514	2.01909
C18	4.61608	-1.98215	3.09917
C19	-4.41054	1.14784	1.67417
C20	3.21922	-0.67199	-2.11596
C21	-3.27101	1.31165	0.88876
C22	4.35876	-0.6571	1.09781
C23	-4.26557	0.69155	2.98407
C24	3.56855	1.87947	-3.20609
C25	-1.99807	1.01158	1.41554
C26	-4.02959	2.24897	-1.41753
C27	-3.10153	1.79959	-0.48138
C28	-3.00078	0.41211	3.51136
C29	2.96846	-0.68639	1.26635
C30	3.23142	-2.01627	3.26424
C31	-2.61267	-4.03914	-1.51028
C32	-1.27307	2.24295	-2.02683
C33	-2.40506	-2.62256	-2.05331
C34	-3.57178	2.69142	-2.65815
C35	-3.4199	-3.93243	-0.21754
C36	-1.85648	0.57436	2.73031
C37	-2.76062	-2.83393	0.60913
C38	-2.20717	2.69127	-2.96074
C39	2.40605	-1.37171	2.35083
H40	4.20635	-1.3454	-3.84806
H41	4.51005	0.86488	-4.79464
H42	2.57718	2.56964	-1.47719
H43	3.49327	2.44322	1.33689
H44	2.84283	4.61988	2.19097
H45	-1.18348	3.75349	1.35328
H46	0.50314	5.26687	2.1761
H47	6.20256	-1.28375	1.90136
H48	5.22686	-2.46032	3.77986
H49	-5.34568	1.36055	1.293
H50	3.0866	-1.61361	-1.71497
H51	4.77387	-0.15813	0.29547
H52	-5.10302	0.5583	3.57225
H53	3.70026	2.81861	-3.61315
H54	-5.03776	2.25442	-1.19708
H55	-2.91338	0.08338	4.48569
H56	2.81975	-2.52044	4.0651
H57	-1.66521	-4.49457	-1.31079
H58	-3.13301	-4.64041	-2.22626
H59	-0.26509	2.24591	-2.24817
H60	-3.18036	-2.37683	-2.7486
H61	-1.47	-2.54039	-2.56694
H62	-4.24943	3.02335	-3.36217
H63	-3.39431	-4.86129	0.31299
H64	-4.44631	-3.70573	-0.41753
H65	-0.92194	0.37408	3.1196
H66	-3.4099	-2.50707	1.39431
H67	-1.86094	-3.16142	1.08687
H68	-1.88788	3.02582	-3.88332
H69	1.38142	-1.39787	2.47117

Table S1. Cartesian coordinates for compound [**2**]$^{+}$.

Atom	Coordinates		
Number	X	Y	Z
Au1	-0.18042	-0.2875	-1.09881
P2	1.56216	0.03151	0.3356
Cl3	-1.98248	-0.53914	-2.54682
Cl4	1.36567	-0.6953	-2.86664
C5	-0.65084	0.15643	1.88673
C6	-1.43805	0.04943	0.58729
C7	0.72087	0.30043	4.34647
C8	-2.46945	-1.04877	0.64603
C9	0.74502	0.13154	1.94104
C10	-1.3525	0.27646	3.09651
C11	1.43326	0.19185	3.16213
C12	-2.27501	1.27225	0.30795
C13	-4.8644	-1.36351	0.39993
C14	-3.62971	0.91401	0.17476
C15	-0.67633	0.34973	4.30596
C16	-3.75083	-0.52782	0.38847
C17	-1.87869	2.59979	0.19558
C18	-2.29835	-2.39652	0.93802
C19	-4.59047	1.88631	-0.08944
C20	-2.84475	3.57083	-0.06882
C21	-4.18784	3.21508	-0.21346
C22	-3.416	-3.23096	0.94739
C23	-4.68681	-2.71816	0.67566
C24	5.00172	-2.08775	0.98447
C25	4.63274	-3.38039	0.61825
C26	3.35124	-3.63089	0.13054
C27	2.43335	-2.59242	0.01267
C28	2.79754	-1.29512	0.39042
C29	4.08876	-1.0428	0.86948
C30	2.46173	1.58709	0.06246
C31	3.25833	1.7179	-1.08464
C32	3.93116	2.9114	-1.32352
C33	3.81304	3.97681	-0.43151
C34	3.01664	3.85082	0.70393
C35	2.33828	2.65988	0.95369
H36	1.21721	0.3445	5.25019
H37	-2.38388	0.31064	3.0863
H38	2.46449	0.15558	3.17862
H39	-5.8055	-0.98624	0.20751
H40	-1.20981	0.44155	5.18459
H41	-0.88682	2.86256	0.30585
H42	-1.36019	-2.7737	1.14446
H43	-5.58427	1.62759	-0.19176
H44	-2.56488	4.56012	-0.1583
H45	-4.88994	3.94426	-0.41441
H46	-3.30328	-4.2352	1.15673
H47	-5.5032	-3.34945	0.67912
H48	5.9526	-1.90461	1.34129
H49	5.30972	-4.15409	0.70829
H50	3.08285	-4.5889	-0.14371
H51	1.48614	-2.7782	-0.35243
H52	4.36317	-0.08452	1.13673
H53	3.34474	0.93224	-1.74819
H54	4.52067	3.00906	-2.16493
H55	4.31624	4.85935	-0.61297
H56	2.92879	4.64121	1.36164
H57	1.746	2.56858	1.79386

Table S2. Cartesian coordinates for compound **3**.

Atom	Coordinates		
Number	X	Y	Z
Au1	-0.36571	-0.2719	-1.01231
P2	1.52747	-0.01847	0.23533
Cl3	-1.1373	-0.65495	-3.12442
C4	-0.41837	0.066	2.09792
C5	-1.3424	0.07299	0.91482
C6	1.26542	0.01752	4.33836
C7	-2.3321	-1.01773	0.74522
C8	0.96907	0.00559	1.95047
C9	-0.96178	0.11656	3.38669
C10	1.81673	-0.0284	3.06361
C11	-2.06886	1.30897	0.52777
C12	-4.58244	-1.32874	-0.10397
C13	-3.35354	0.9637	0.04654
C14	-0.12044	0.09469	4.49455
C15	-3.51802	-0.49043	0.18097
C16	-1.65031	2.63726	0.5773
C17	4.34506	3.29136	0.27289
C18	4.49079	2.49133	-2.00672
C19	4.72715	-2.55968	1.68548
C20	4.64047	3.52024	-1.07348
C21	7.03795	-2.21441	0.15317
C22	5.85387	-3.34158	1.93588
C23	7.00713	-3.17362	1.16715
C24	0.9165	0.92996	-1.95824
C25	-3.92745	0.44176	2.32844
C26	0.91738	3.35146	-1.97233
C27	0.91043	-2.20319	1.92773
C28	-4.03308	-2.30543	1.83468
Au1	-0.36571	-0.2719	-1.01231
P2	1.52747	-0.01847	0.23533
Cl3	-1.1373	-0.65495	-3.12442
C4	-0.41837	0.066	2.09792
C5	-1.3424	0.07299	0.91482
C6	1.26542	0.01752	4.33836
C7	-2.3321	-1.01773	0.74522

Atom	Coordinates		
Number	X	Y	Z
C29	2.36143	1.5346	-0.15831
C30	2.86204	1.70839	-1.4589
C31	3.47767	2.90499	-1.80613
C32	3.59502	3.92968	-0.86624
C33	3.09625	3.75997	0.42374
C34	2.47409	2.56667	0.78211
H35	1.87873	-0.00536	5.16803
H36	-1.98438	0.16994	3.51496
H37	2.83952	-0.0869	2.93913
H38	-5.44944	-0.95639	-0.52195
H39	-0.52513	0.13599	5.44299
H40	-0.71689	2.88402	0.9418
H41	-1.35869	-2.748	1.4835
H42	-5.15106	1.70748	-0.76451
H43	-2.23582	4.61614	0.14867
H44	-4.41323	4.02646	-0.71083
H45	-3.23689	-4.21742	0.98613
H46	-5.23911	-3.33052	-0.03163
H47	5.97424	-2.04974	-0.02778
H48	5.13018	-4.27402	-0.48275
H49	2.74441	-4.66106	-0.66916
H50	1.19209	-2.82038	-0.39197
H51	4.43427	-0.1947	0.23958
H52	2.77312	0.95068	-2.15388
H53	3.8485	3.03588	-2.76027
H54	4.05306	4.81677	-1.12757
H55	3.18812	4.52046	1.11529
H56	2.09812	2.44342	1.73526
C29	2.36143	1.5346	-0.15831
C30	2.86204	1.70839	-1.4589
C31	3.47767	2.90499	-1.80613
C32	3.59502	3.92968	-0.86624
C33	3.09625	3.75997	0.42374
C34	2.47409	2.56667	0.78211
H35	1.87873	-0.00536	5.16803

Table S3. Cartesian coordinates for compound [**4**]$^+$.

Atom Number	Coordinates		
	X	Y	Z
Au1	-0.23062	-1.86562	-0.21016
Au2	0.23062	1.86562	-0.21016
P3	1.14753	-3.66361	0.14868
P4	-1.14753	3.66361	0.14868
Cl5	-1.60962	0.15793	-0.40904
Cl6	1.60962	-0.15793	-0.40904
C7	-1.82666	-3.30221	-0.16939
C8	2.50771	-3.76295	-1.03073
C9	-1.83121	-7.09247	-0.20724
C10	-0.47169	-7.4087	-0.13136
C11	-2.25595	-5.76906	-0.20759
C12	-1.32183	-4.72835	-0.12635
C13	0.03114	-5.05749	-0.02879
C14	-2.69777	-2.86845	0.97017
C15	2.28373	-3.406	-2.36848
C16	0.46662	-6.39038	-0.041
C17	-3.87653	-2.27856	0.46852
C18	3.2952	-3.57433	-3.30622
C19	3.74994	-4.28092	-0.63774
C20	4.75506	-4.44805	-1.58645
C21	4.52875	-4.09689	-2.9158
C22	-4.85304	-1.81951	1.34338
C23	-2.49173	-3.0091	2.33896
C24	-4.6397	-1.95302	2.71869
C25	-3.47385	-2.54099	3.21367
C26	-2.34551	-3.19483	-2.72621
C27	-3.27273	-2.79227	-3.68814
C28	-4.46109	-2.16609	-3.30576
C29	-4.75506	-1.93579	-1.9588
C30	-3.83269	-2.32797	-0.99721
C31	-2.62689	-2.94783	-1.38545
C32	2.8404	-3.50976	4.41436
C33	3.25821	-2.58092	3.46049
C34	2.75305	-2.63198	2.16657
C35	1.8209	-3.625	1.82391
C36	1.39621	-4.55312	2.78492
C37	1.91287	-4.4932	4.0765
C38	3.47385	2.54099	3.21367
C39	2.49173	3.0091	2.33896
C40	4.6397	1.95302	2.71869
C41	2.69777	2.86845	0.97017
C42	4.85304	1.81951	1.34338
C43	1.82666	3.30221	-0.16939
C44	3.87653	2.27856	0.46852
C45	1.32183	4.72835	-0.12635
C46	2.62689	2.94783	-1.38545
C47	3.83269	2.32797	-0.99721
C48	2.25595	5.76906	-0.20759
C49	-0.03114	5.05749	-0.02879
C50	2.34551	3.19483	-2.72621
C51	4.75506	1.93579	-1.9588
C52	-2.50771	3.76295	-1.03073
C53	-1.8209	3.625	1.82391
C54	1.83121	7.09247	-0.20724
C55	-0.46662	6.39038	-0.041
C56	3.27273	2.79227	-3.68814
C57	4.46109	2.16609	-3.30576
C58	-2.28373	3.406	-2.36848
C59	-3.74994	4.28092	-0.63774
C60	-2.75305	2.63198	2.16657
C61	-1.39621	4.55312	2.78492
C62	0.47169	7.4087	-0.13136
C63	-3.2952	3.57433	-3.30622
C64	-4.75506	4.44805	-1.58645
C65	-3.25821	2.58092	3.46049
C66	-1.91287	4.4932	4.0765
C67	-4.52875	4.09689	-2.9158
C68	-2.8404	3.50976	4.41436
H69	-2.52838	-7.85128	-0.26372
H70	-0.1673	-8.39473	-0.1425
H71	-3.26314	-5.55236	-0.26791
H72	1.37079	-3.01965	-2.65537
H73	1.47304	-6.61138	0.01655
H74	3.13412	-3.31286	-4.29147
H75	3.91804	-4.53648	0.34789
H76	5.6701	-4.83302	-1.30444
H77	5.2771	-4.2239	-3.61499
H78	-5.7194	-1.3882	0.98503
H79	-1.63129	-3.45003	2.69987
H80	-5.35559	-1.61141	3.37886
H81	-3.33739	-2.63006	4.23272
H82	-1.46982	-3.66563	-3.00286
H83	-3.0792	-2.95825	-4.68815
H84	-5.13347	-1.86842	-4.02987
H85	-5.64072	-1.48291	-1.68396
H86	3.21963	-3.4682	5.37326
H87	3.94438	-1.85384	3.71651
H88	3.06121	-1.9441	1.46167
H89	0.70411	-5.27715	2.53632
H90	1.60815	-5.17871	4.78519
H91	3.33739	2.63006	4.23272
H92	1.63129	3.45003	2.69987
H93	5.35559	1.61141	3.37886
H94	5.7194	1.3882	0.98503
H95	3.26314	5.55236	-0.26791
H96	1.46982	3.66563	-3.00286
H97	5.64072	1.48291	-1.68396
H98	2.52838	7.85128	-0.26372
H99	-1.47304	6.61138	0.01655
H100	3.0792	2.95825	-4.68815
H101	5.13347	1.86842	-4.02987
H102	-1.37079	3.01965	-2.65537
H103	-3.91804	4.53648	0.34789
H104	-3.06121	1.9441	1.46167
H105	-0.70411	5.27715	2.53632
H106	0.1673	8.39473	-0.1425
H107	-3.13412	3.31286	-4.29147
H108	-5.6701	4.83302	-1.30444
H109	-3.94438	1.85384	3.71651
H110	-1.60815	5.17871	4.78519
H111	-5.2771	4.2239	-3.61499
H112	-3.21963	3.4682	5.37326

Table S4. Cartesian coordinates for compound [**4**$_2$]$^{2+}$.

Atom Number	Coordinates		
	X	Y	Z
Au1	-1.48162	-0.05526	0.71206
P2	0.64791	-0.01054	-0.18223
Cl3	-3.72264	-0.0826	1.0759
C4	-0.09753	1.16211	-4.03162
C5	-1.00635	0.19346	-4.46064
C6	-1.37709	-0.84993	-3.61407
C7	-0.83921	-0.92732	-2.3329
C8	0.08077	0.04918	-1.89907
C9	0.44212	1.10173	-2.75129
C10	1.5919	1.47041	0.2221
C11	0.91399	2.65533	0.54793
C12	1.63589	3.81509	0.80787
C13	3.02943	3.79678	0.74713
C14	3.70497	2.62124	0.42321
C15	2.99286	1.45469	0.15998
C16	-0.81299	-0.08288	2.66078
C17	1.66796	-1.47047	0.11099
C18	1.89026	-2.41589	-0.89834
C19	2.23205	-1.655	1.38423
C20	2.66458	-3.54141	-0.62893
C21	3.0038	-2.78196	1.64094
C22	3.21576	-3.72728	0.63665
H23	0.17545	1.92731	-4.668
H24	-1.40619	0.25015	-5.41035
H25	-2.0491	-1.56362	-3.93668
H26	-1.11283	-1.69705	-1.70229
H27	1.10355	1.82632	-2.43111
H28	-0.11691	2.6659	0.59445
H29	1.14094	4.68889	1.0456
H30	3.56307	4.6581	0.94304
H31	4.73599	2.6159	0.37845
H32	3.49246	0.58397	-0.07932
H33	0.25692	-0.07302	2.67093
H34	-1.16614	-0.96846	3.14651
H35	-1.18252	0.7785	3.1769
H36	1.48245	-2.27906	-1.83642
H37	2.07387	-0.95588	2.12668
H38	2.83069	-4.24046	-1.36971
H39	3.42042	-2.91977	2.575
H40	3.78285	-4.56702	0.83227

Table S5. Cartesian coordinates for compound $[Ph_3P(Me)AuCl]^+$.

Atom	Coordinates		
Number	X	Y	Z
Au1	1.70476	-0.70414	0.0002
Au2	-1.70475	0.70416	-0.00011
P3	-3.89596	-0.12427	0.01562
P4	3.89598	0.12426	0.01554
Cl5	-0.58891	-1.52599	-0.03524
Cl6	0.58892	1.52601	-0.03595
C7	3.88077	1.44786	-1.21515
C8	3.35267	1.20373	-2.49332
C9	3.38662	2.20483	-3.45687
C10	4.4174	2.70349	-0.90303
C11	4.44191	3.69984	-1.87543
C12	3.93245	3.45169	-3.14807
C13	4.93226	1.90945	4.11903
C14	3.59667	1.6811	3.79252
C15	3.26378	1.1239	2.56194
C16	4.27557	0.78468	1.65332
C17	5.6221	1.01235	1.98621
C18	5.94184	1.57847	3.21607
C19	-3.88081	-1.44833	-1.21457
C20	-4.27546	-0.78406	1.65368
C21	-3.35263	-1.20476	-2.49281
C22	-4.41767	-2.70376	-0.90202
C23	-3.2636	-1.12286	2.56239
C24	-5.62195	-1.01159	1.98677
C25	-3.3867	-2.2062	-3.456
C26	-4.4423	-3.70047	-1.87407
C27	-3.59638	-1.67957	3.79321
C28	-5.94159	-1.57722	3.21689
C29	-3.93274	-3.45286	-3.14677
C30	-4.93194	-1.90783	4.11991
C31	-5.18189	1.07121	-0.40142
C32	-5.71385	1.13258	-1.69764
C33	-5.64581	1.95374	0.58997
C34	-6.69834	2.07042	-1.99522
C35	-6.63106	2.88401	0.28086
C36	-7.15452	2.94544	-1.01108
C37	5.18189	-1.07141	-0.40108
C38	5.71392	-1.13323	-1.69724
C39	5.64567	-1.95365	0.59063
C40	6.69836	-2.07124	-1.99446
C41	6.63087	-2.8841	0.28187
C42	7.15441	-2.94598	-1.01002
C43	2.43719	-2.62487	0.0354
C44	-2.43724	2.62487	0.03458
H45	2.91631	0.23724	-2.73832
H46	2.98542	2.01431	-4.4477
H47	4.81387	2.90493	0.08725
H48	4.86149	4.67204	-1.63537
H49	3.95613	4.23285	-3.90215
H50	5.18806	2.34418	5.08078
H51	2.81161	1.93673	4.49757
H52	2.21903	0.95961	2.31511
H53	6.41593	0.74829	1.29351
H54	6.98253	1.7553	3.47021
H55	-2.91612	-0.23843	-2.73815
H56	-4.8142	-2.90479	0.08831
H57	-2.21888	-0.9586	2.31544
H58	-6.41584	-0.74779	1.29404
H59	-2.98542	-2.0161	-4.44688
H60	-4.86204	-4.67251	-1.63366
H61	-2.81127	-1.93489	4.49831
H62	-6.98227	-1.75393	3.4712
H63	-3.95652	-4.23429	-3.90057
H64	-5.18768	-2.34217	5.08185
H65	-5.3832	0.44053	-2.46557
H66	-5.25918	1.89923	1.60421
H67	-7.11734	2.10815	-2.99613
H68	-6.99517	3.55776	1.05053
H69	-7.92639	3.67177	-1.24785
H70	5.38338	-0.4414	-2.46541
H71	5.25901	-1.89878	1.60484
H72	7.11743	-2.10931	-2.99532
H73	6.99488	-3.55764	1.05178
H74	7.92624	-3.67245	-1.2465
H75	3.09466	-2.76599	-0.82308
H76	2.97542	-2.77343	0.9727
H77	1.55565	-3.26591	-0.01992
H78	-3.09469	2.76572	-0.82397
H79	-2.97552	2.77369	0.97181
H80	-1.55571	3.26592	-0.0209

Table S6. Cartesian coordinates for compound $[(Ph_3P(Me)Au(\mu_2\text{-}Cl))_2]^{2+}$.

4 X-ray diffraction analysis

4.1 Experimental details

The crystallographic measurements were performed at 110(2) K using a three circle (Quest; Mo Kα radiation, λ = 0.71073 Å) and kappa (Venture; Cu Kα radiation, λ = 1.54178 Å) Bruker-AXS with IµS source and a Photon III area detector diffractometer. In each case, a specimen of suitable size and quality was selected and mounted onto a nylon loop and cooled to 110(2) K in a cold nitrogen stream (OXFORD Cryosystems). The data was collected and reduced using Bruker AXS APEX 3 software[5] and solved by direct methods. Semiempirical absorption corrections were applied using SADABS.[6] Subsequent refinement using a difference map on F^2 using the SHELXTL/PC package (version 6.1 & OLEX^2).[7, 8] Thermal parameters were refined anisotropically for all non-hydrogen atoms to convergence. H atoms were added at idealized positions using a riding model. The results of these X-ray measurements are provided as CIF files. CCDC 2172689-2172692 and 2210579 contain the supplementary crystallographic data for this paper.

4.2 CCDC numbers

Compound	CCDC
LOH	2172689
1	2172690
[**2**][BF_4]	2172691
3	2172692
[$\mathbf{4}_2$][$BArF_{24}$]$_2$	2210579

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