# Supporting Information

## Macrocyclic stibine-bridged [1.1.1] and [1.1.1.1]ferrocenophanes

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# Synthetic details

## General considerations:

AuI was obtained from Ambeed. AuCl(tht) (tht = tetrahydrothiophene), 1,1′-dilithioferrocene·(tmeda)[1] (tmeda = N,N,N′,N′-tetramethylethylenediamine) and $PhSbCl_2$[2] were prepared using existing synthetic methods. All preparations were carried out under an atmosphere of dry $N_2$ employing either glovebox or standard Schlenk techniques. Solvents were dried by refluxing under $N_2$ over Na ($Et_2O$), Na/K (THF) or $CaH_2$ ($CH_2Cl_2$). $CDCl_3$ was dried over 4Å molecular sieves. All solvents were ACS reagent grade and used as received. NMR spectra were recorded on a Bruker Ascend 400 NMR (399.51 MHz for $^1H$, 100.47 MHz for $^{13}C$) or Bruker Avance 500 NMR (499.42 MHz for $^1H$, 125.60 MHz for $^{13}C$) spectrometer at room temperature unless otherwise noted. Chemical shifts are given in ppm and are referenced to residual $^1H$ and $^{13}C$ solvent signals. Elemental analyses were performed at Atlantic Microlab (Norcross, GA). Electrospray ionization mass spectra were recorded on an Applied Biosystems PE SCIEX QSTAR instrument.

## Single crystal X-ray diffraction measurement:

Crystallographic measurements were performed at 110(2) K using Bruker D8 Quest (Mo source, λ = 0.71073 Å) equipped with a Photon III area detector, Bruker APEX 22 (Mo source, λ = 0.71073 Å), XtaLAB Synergy-ED (Cu source, λ = 1.54178 Å). In each case, a specimen of suitable size and quality was selected and mounted onto a loop and cooled to 110(2) K in a cold nitrogen stream (OXFORD Cryosystems). The data was collected and reduced using Bruker AXS APEX 4 software[3] and solved by direct methods with SHELXT. [4] Semiempirical absorption corrections were applied using SADABS.[5] Subsequent refinements were carried out using a difference Fourier map on $F^2$ using the SHELXL/PC package (version 6.1 & OLEX2).[4, 6] Thermal displacement parameters were refined anisotropically for all non-hydrogen atoms to convergence. H atoms were added at idealized positions and refined using a riding atom model. The results of these X-ray measurements are provided as CIF files. CCDC 2551732-2551734 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk

# Synthetic procedures and characterization

## Synthesis of **1** and **2**:

A solution of $PhSbCl_2$ (857.8 mg, 3.18 mmol) in THF (10 mL) was added dropwise to a suspension of 1,1′-dilithioferrocene·(tmeda) (1.04 g, 3.18 mmol) in a mixture of $Et_2O$ (15 mL) and THF (25 mL) at -78 °C. After stirring at this temperature for 30 min, the solution was slowly warmed to room temperature and was stirred for an additional 12 h. The solvent was removed *in vacuo*, and the resulting sticky oil was redissolved in $CH_2Cl_2$ (50 mL), washed with water (3 x 30 mL), and then with brine (30 mL). The collected $CH_2Cl_2$ fraction was dried over $MgSO_4$, filtered, and brought to dryness under reduced pressure to afford an orange sticky oil. The residue was washed with pentane (100 mL) to afford a yellow-orange solid comtaining a mixture of **1** and **2** along with other unidentified compounds. This solid was then subjected to flash column chromatography using 100-200 mesh silica gel and an eluent of hexanes/$CH_2Cl_2$ (1:4 v/v) to yield a mixture of compounds **1** and **2** as a yellow-orange solid. This mixture was characterized by elemental analysis (EA) prior to further purification (EA calculated (%) for $C_{48}H_{39}Sb_3Fe_3$ or $C_{64}H_{52}Sb_4Fe_4$: C, 50.19; H, 3.42; found C, 50.94; H, 3.31.) Preparative TLC was further performed on a silica gel-coated aluminum sheet to separate **1** and **2** with hexanes/$CH_2Cl_2$ (3:7 v/v) as the eluent. This afforded pure **1** (0.14 g, 0.126 mmol, 4% yield) and **2** (0.14 g, 0.095 mmol, 3% yield) as yellow-orange solids. Single crystals of **1** were obtained as yellow-orange blocks by diffusion of pentane into a $CH_2Cl_2$ solution of the compound at ambient temperature. Single crystals of **2** were obtained as yellow blocks by diffusion of pentane into a 1,2-dichlorobenzene solution of the compound at room temperature. The $^{13}C\{^1H\}$ NMR spectra of purified **1** and **2** exhibited accidentally overlapping signals, complicating precise assignment of the resonances.

**1: $^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.65-7.62 (m, 2H, $H_{Sb\text{-}phenyl}$), 7.60-7.56 (m, 4H, $H_{Sb\text{-}phenyl}$), 7.39-7.34 (m, 3H, $H_{Sb\text{-}phenyl}$), 7.34-7.29 (m, 6H, $H_{Sb\text{-}phenyl}$), 4.87-4.85 (m, 2H, $H_{Cp}$), 4.68-4.66 (m, 2H, $H_{Cp}$), 4.51-4.50 (m, 2H, $H_{Cp}$), 4.48-4.46 (m, 4H, $H_{Cp}$), 4.45-4.43 (m, 2H, $H_{Cp}$), 4.39-4.37 (m, 2H, $H_{Cp}$), 4.28-4.25 (m, 4H, $H_{Cp}$), 3.99-3.97 (m, 2H, $H_{Cp}$), 3.93-3.91 (m, 2H, $H_{Cp}$), 3.81-3.79 (m, 2H, $H_{Cp}$). **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) $\delta$ 139.6 (q), 138.4 (q), 137.0, 136.4, 128.8, 128.7, 128.6, 77.9, 77.7, 76.5, 75.6, 74.0, 73.9, 71.2, 71.1, 71.0, 70.8, 70.7, 70.6, 69.2 (q), 68.8 (q), 67.7 (q). **DEPT-135 NMR** (100 MHz, $CDCl_3$) $\delta$ 137.0, 136.4, 128.8, 128.7, 128.6, 77.9, 77.7, 77.4, 76.5,

75.6, 74.0, 73.9, 71.2, 71.1, 71.0, 70.8, 70.7, 70.6. **HRMS** (ESI-TOFMS, positive): *m/z* $[M]^+$ calculated. for $[C_{48}H_{39}Sb_3Fe_3]^+$ 1147.8213; found 1147.8227.

**2: $^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.66-7.61 (m, 2H, $H_{Sb\text{-}phenyl}$), 7.60-7.51 (m, 6H, $H_{Sb\text{-}phenyl}$), 7.39-7.34 (m, 3H, $H_{Sb\text{-}phenyl}$), 7.34-7.28 (m, 9H, $H_{Sb\text{-}phenyl}$), 4.86-4.84 (m, 2H, $H_{Cp}$), 4.66-4.65 (m, 2H, $H_{Cp}$), 4.51-4.49 (m, 2H, $H_{Cp}$), 4.49-4.45 (m, 7H, $H_{Cp}$), 4.45-4.43 (m, 2H, $H_{Cp}$), 4.43-4.41 (m, 1H, $H_{Cp}$), 4.38-4.36 (m, 2H, $H_{Cp}$), 4.32-4.31 (m, 2H, $H_{Cp}$), 4.28-4.25 (m, 4H, $H_{Cp}$), 4.08-4.04 (m, 1H, $H_{Cp}$), 4.01-4.0 (m, 1H, $H_{Cp}$), 3.98-3.97 (m, 2H, $H_{Cp}$), 3.92-3.90 (m, 2H, $H_{Cp}$), 3.80-3.79 (m, 2H, $H_{Cp}$). **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) $\delta$ 142.0 (q), 139.5 (q), 138.4 (q), 137.0,136.5, 136.3, 134.6, 134.4, 128.8, 128.7, 128.6, 128.4, 128.4, 127.8, 77.8, 77.7, 76.5, 75.7, 75.6, 75.3, 74.0, 73.8, 71.6, 71.2, 71.1, 70.9, 70.8, 70.7, 70.7, 70.6, 69.1 (q), 68.7 (q), 67.6 (q). **DEPT-135 NMR** (100 MHz, $CDCl_3$) $\delta$ 137.0, 136.3, 134.6, 128.8, 128.7, 128.6, 128.4, 127.8, 77.8, 77.7, 77.4, 76.5, 75.6, 75.3, 74.7, 74.0, 73.8, 71.6, 71.2, 71.1, 70.9, 70.8, 70.7, 70.6. **HRMS** (ESI-TOFMS, positive): *m/z* $[M]^+$ calculated. for $[C_{64}H_{52}Sb_4Fe_4]^+$ 1531.7622; found 1531.7647.

**Synthesis of 3**: **1** (30 mg, 0.026 mmol) was dissolved in $CH_2Cl_2$ (4 mL) in a 20 mL scintillation vial. AuI (9 mg, 0.028 mmol) was added, and the solution was stirred for 1 hour at room temperature, during which time a deep yellow color developed. The solution was filtered through a 0.4 μm PTFE membrane and concentrated under vacuum. Hexanes (10 mL) was then added in one portion to precipitate the product as a yellow powder. This precipitate was isolated on a glass frit and washed with hexanes (3 x 10 mL) to afford **3** (28 mg, 73 % yield). Orange-yellow block-shaped single crystals were obtained by vapor diffusion of hexanes into a $CHCl_3$ solution of **3**.
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.79-7.77 (m, 6H, $H_{Sb\text{-}phenyl}$), 7.38-7.36 (m, 9H, $H_{Sb\text{-}phenyl}$), 4.46-4.44 (m, 12H, $H_{Cp}$), 4.36-4.35 (m, 6H, $H_{Cp}$), 4.18-4.16 (m, 6H, $H_{Cp}$). **$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$) $\delta$ 136.5, 134.3, 130.0, 129.1, 75.1, 74.1, 71.6, 71.4, 70.5. **Elemental analysis** calculated (%) for $C_{48}H_{39}Sb_3Fe_3AuI$: C, 39.15; H, 2.67; found: C, 40.95; H, 3.01. **HRMS** (ESI-TOFMS, positive): *m/z* $[M\text{-}I]^+$ calculated. for $[C_{48}H_{39}Sb_3Fe_3Au]^+$: 1346.7879; found: 1346.7889.

2.2. NMR and mass spectra

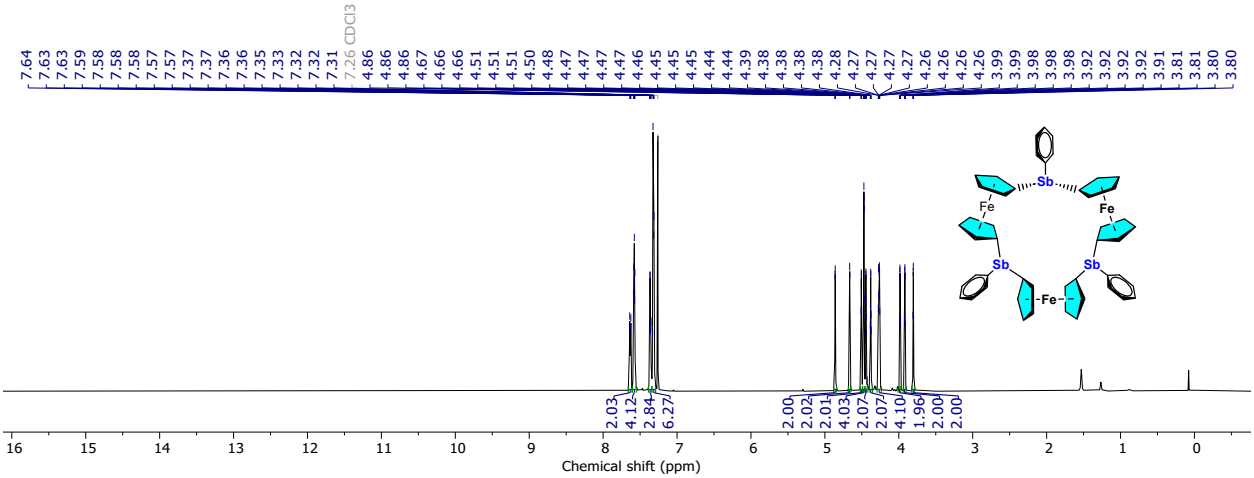


**Fig S1**. $^{1}H$ NMR spectrum of **1** in $CDCl_3$.

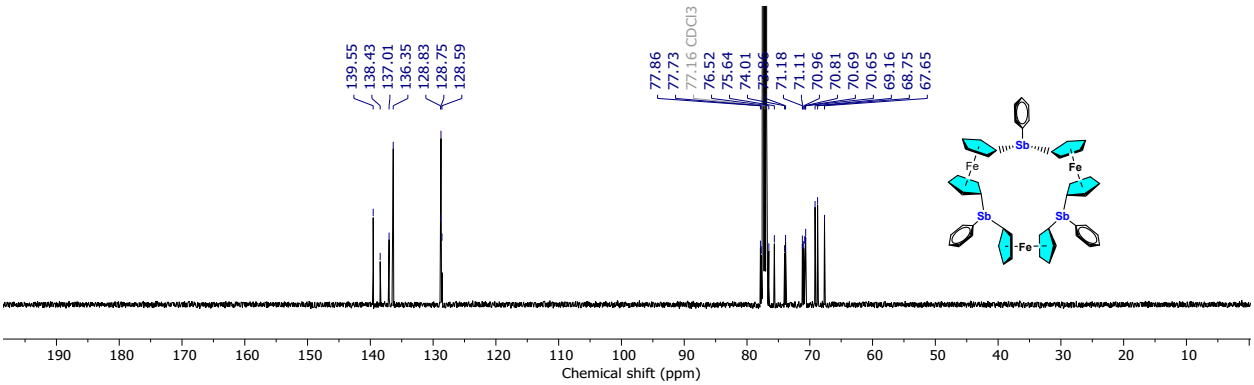


**Fig S2**. $^{13}C\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$.

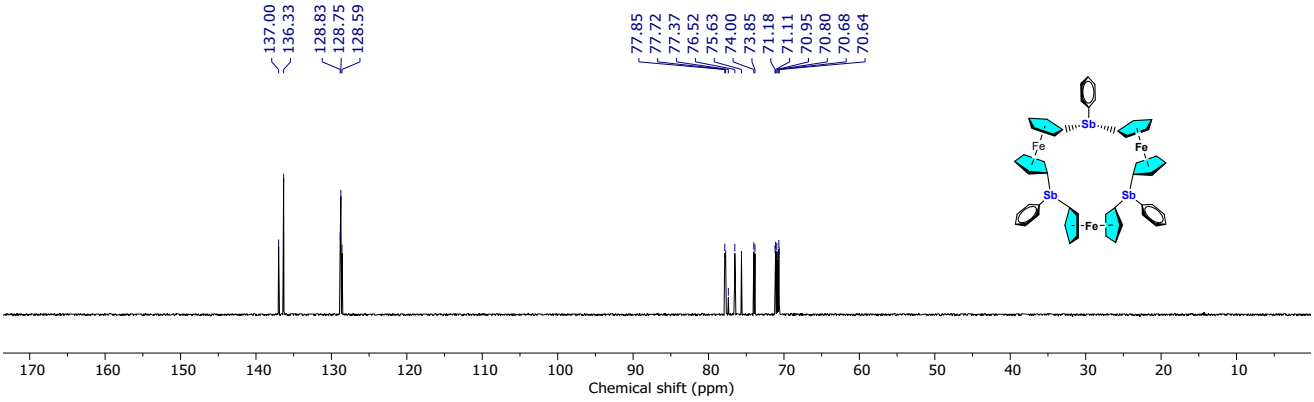


**Fig S3**. DEPT-135 spectrum of **1** in $CDCl_3$.

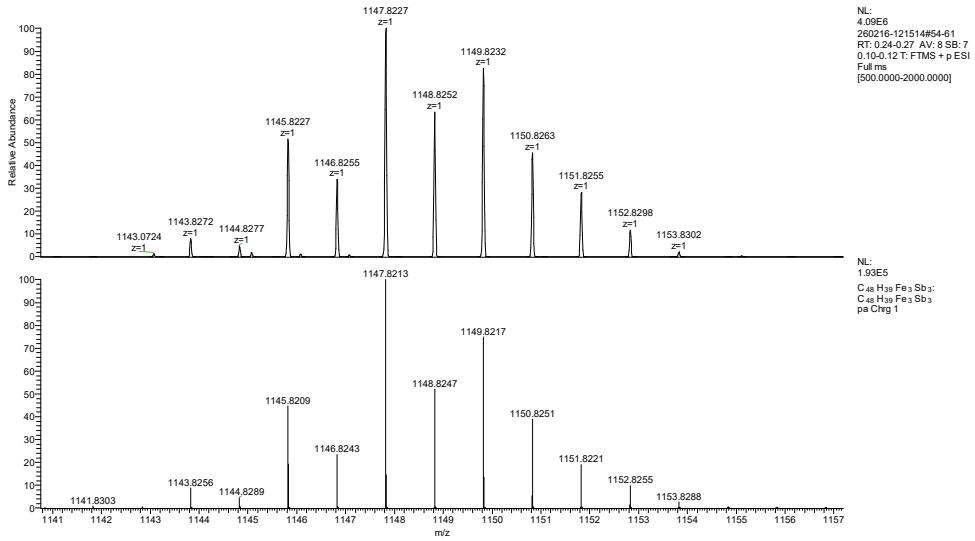


**Fig S4**. HRMS of **1**.

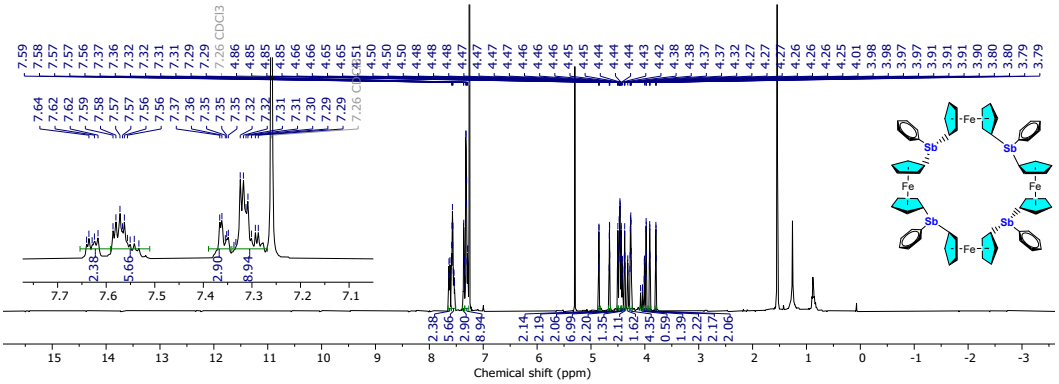


**Fig S5**. $^{1}H$ NMR spectrum of **2** in $CDCl_3$.

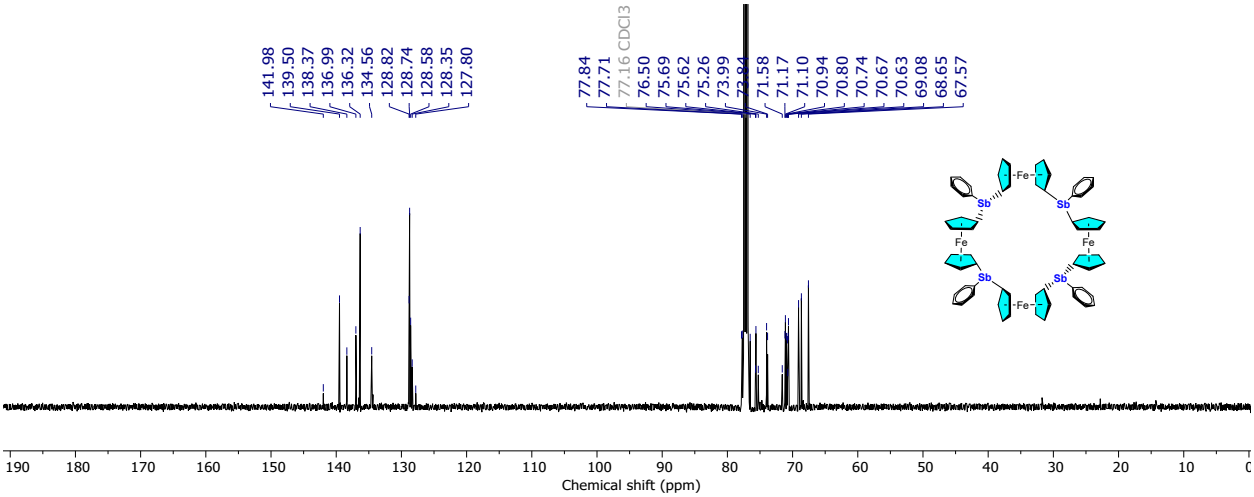


**Fig S6**. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$.

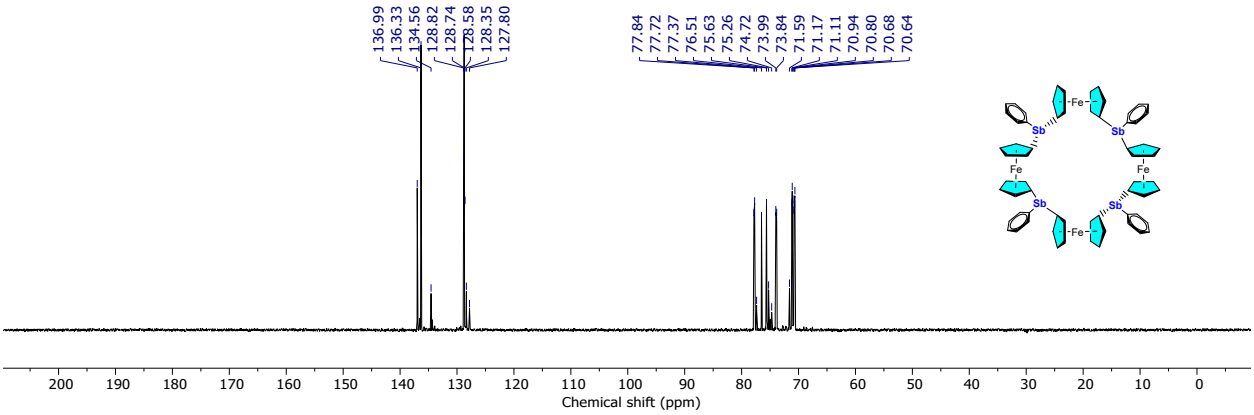


**Fig S7**. DEPT-135 NMR spectrum of **2** in $CDCl_3$.

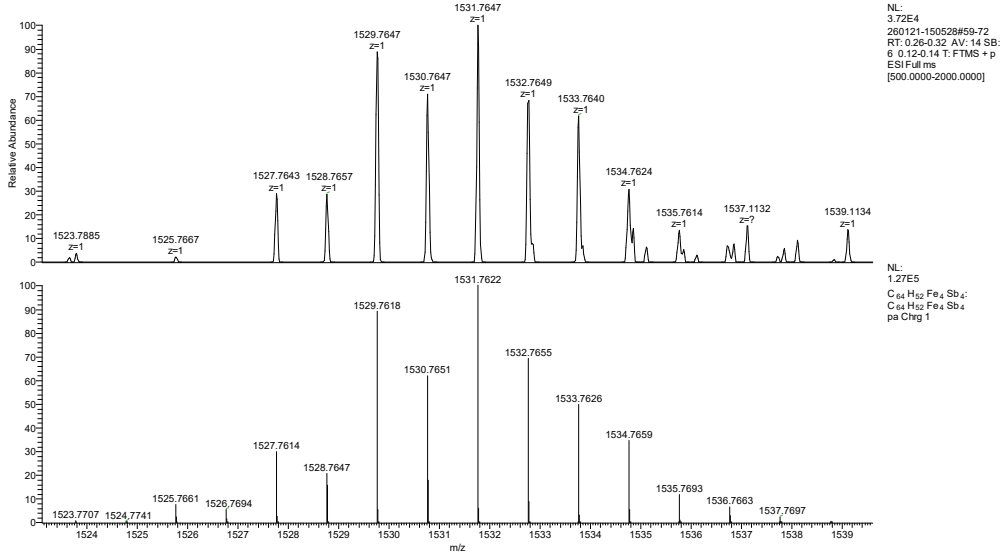


**Fig S8**. HRMS of **2**.

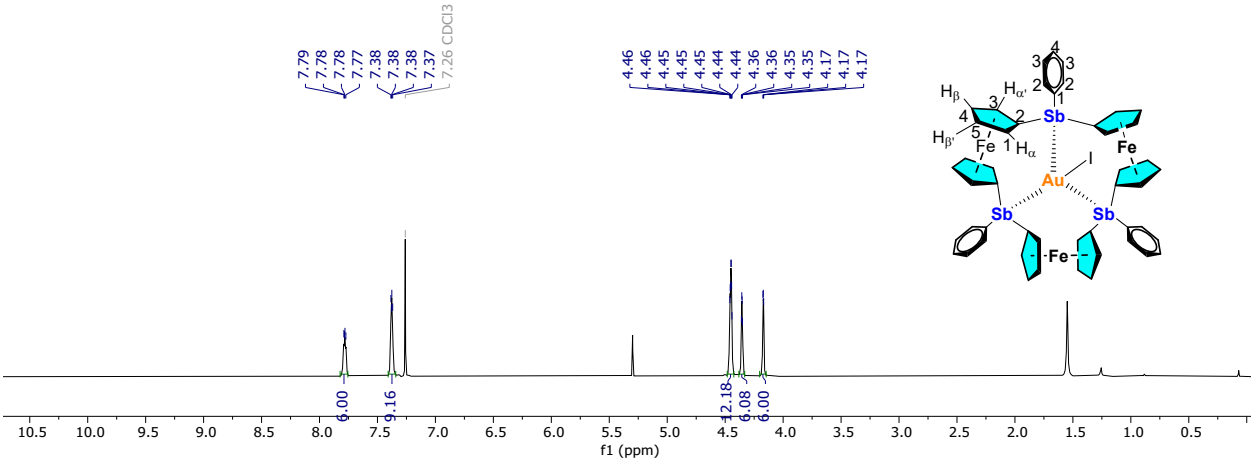


**Fig S9**. $^{1}$H NMR spectrum of **3** in $CDCl_3$.

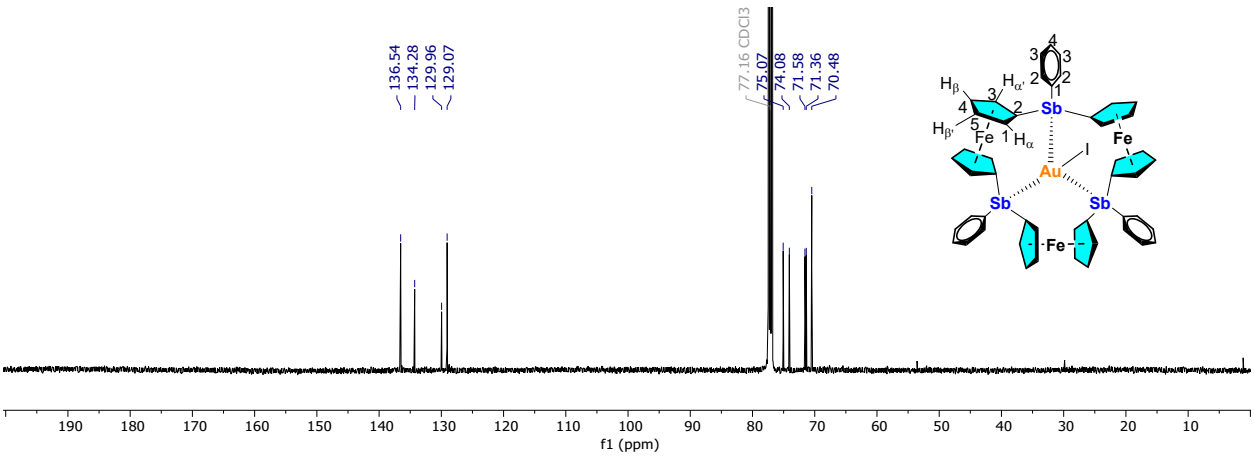


**Fig S10.** $^{13}$C{$^{1}$H} NMR spectrum of **3** in $CDCl_3$.

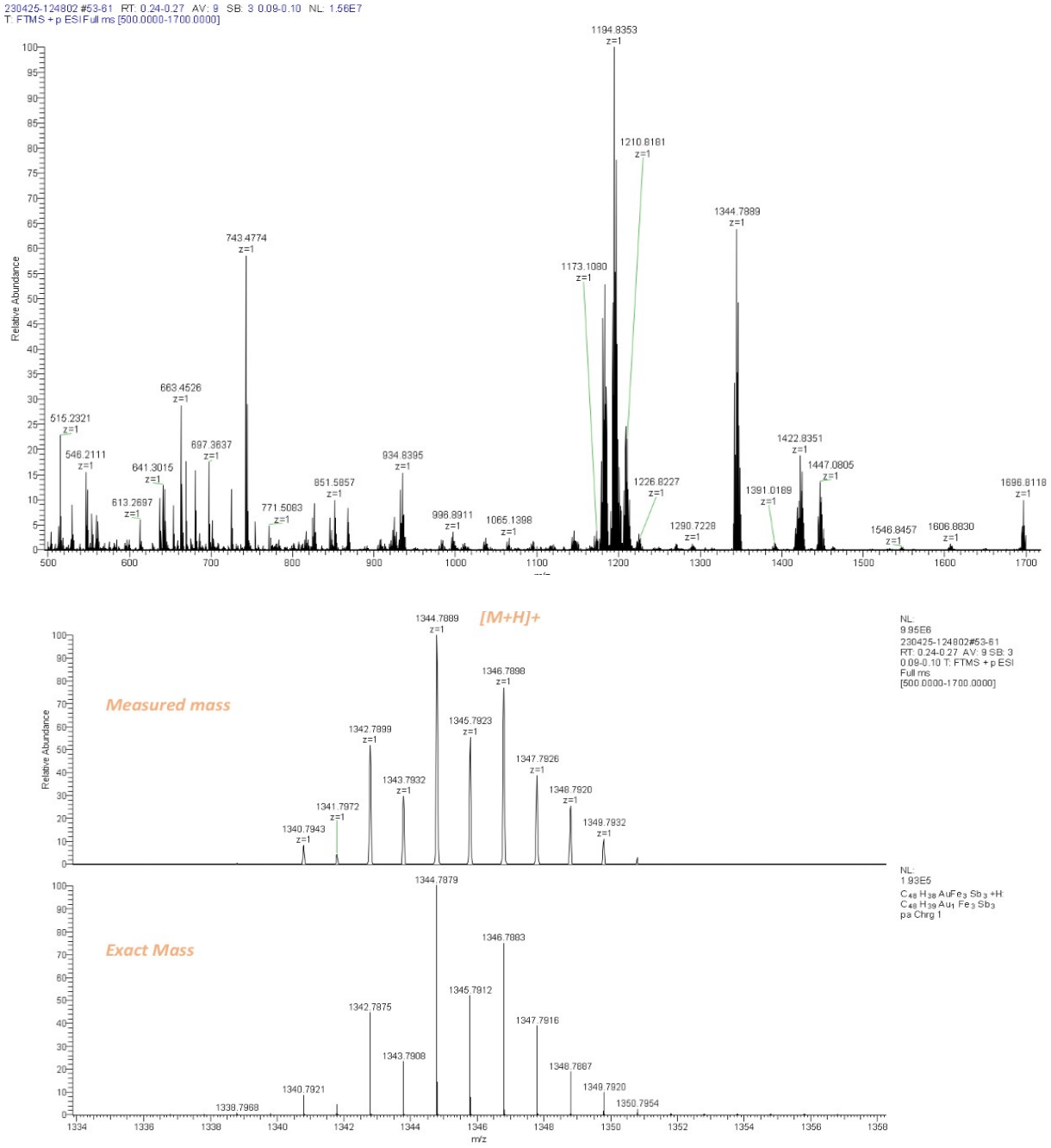


**Fig S11**. HRMS of **3**.

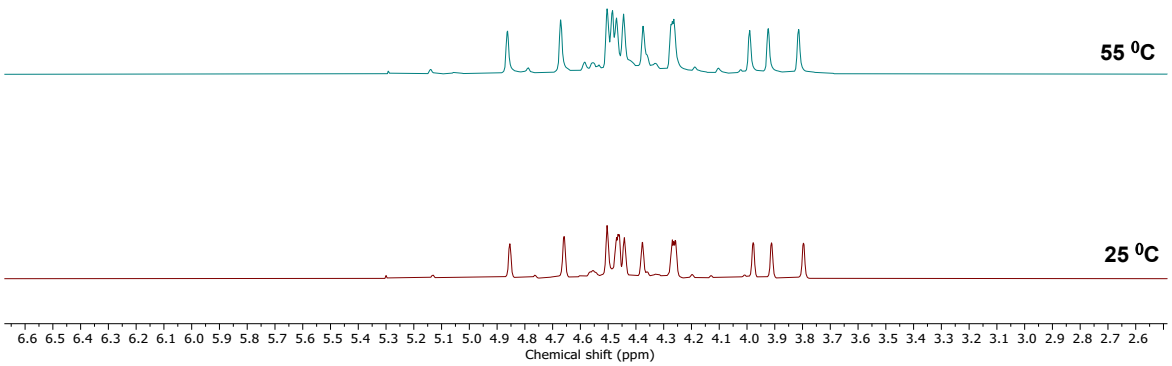


**Fig S12.** $^{1}H$ NMR spectra of **1** in $CDCl_3$ collected at 25 °C and 55 °C

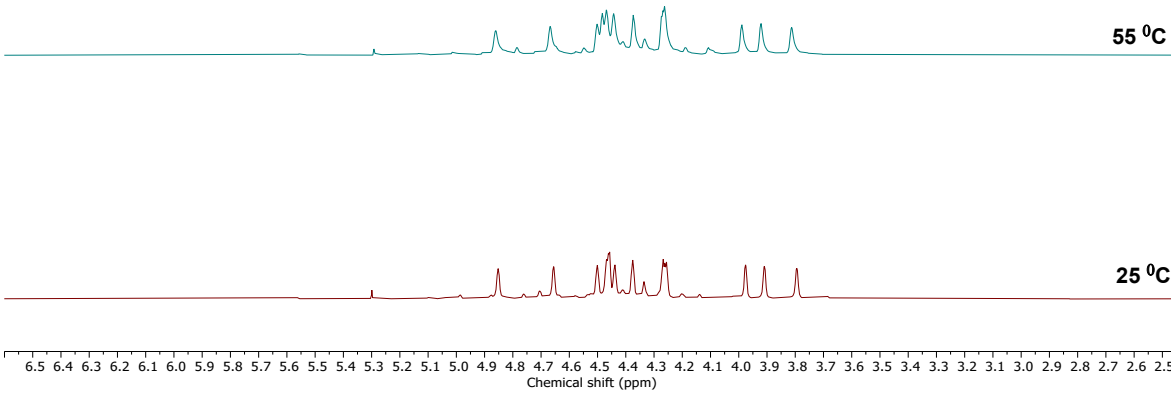


**Fig S13.** $^{1}H$ NMR spectra of **2** in $CDCl_3$ collected at 25 °C and 55 °C

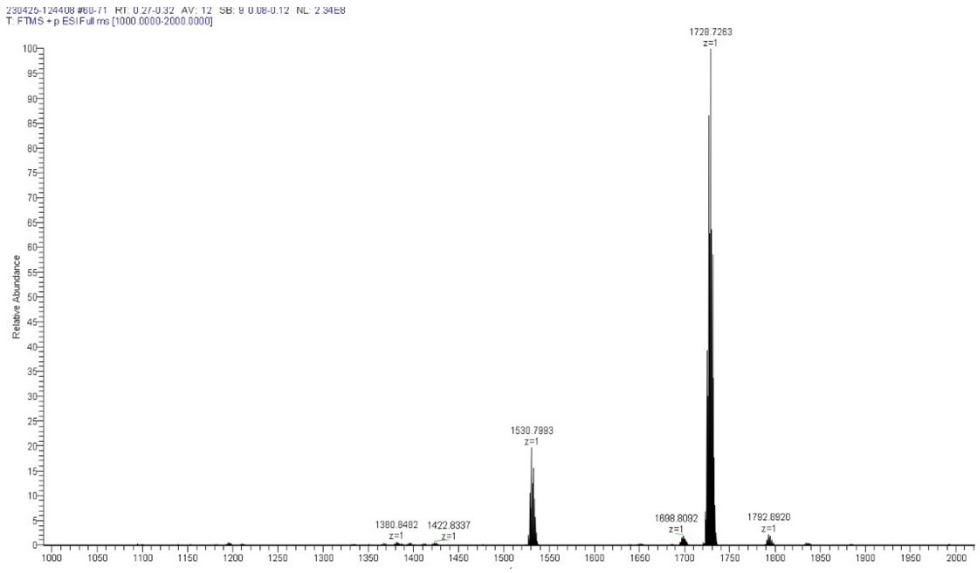


**Fig S14**. HRMS of [**2**-Au]$^{+}$ generated from the reaction of (**2**+AuI).

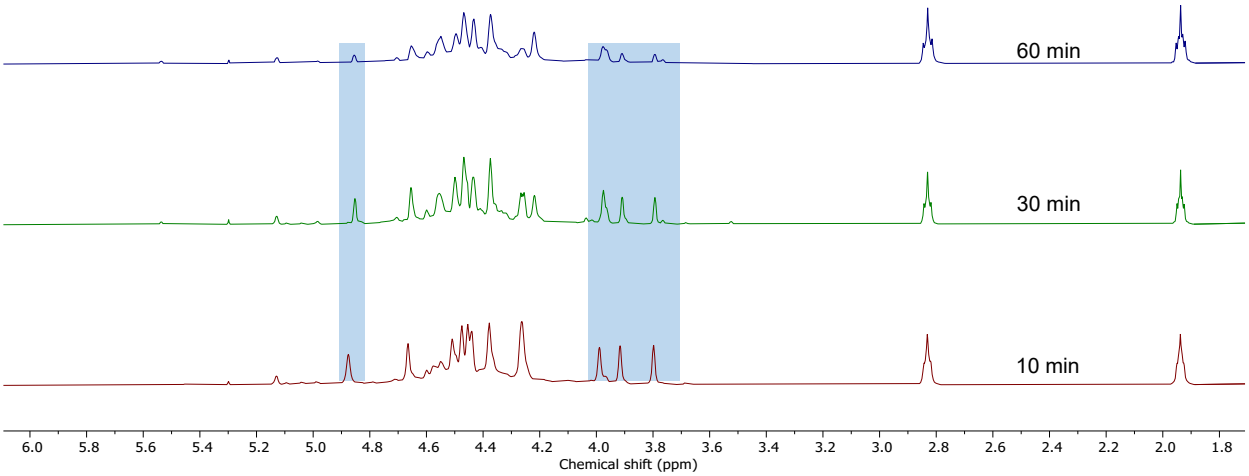


**Fig S15**. Stacked $^{1}$H NMR spectra of an equimolar mixture of **1** and AuCl(tht) in $CDCl_3$ recorded at different time points. The peak at 4.86 ppm, as well as the peaks in the range of 3.80 to 3.99 ppm diminished in intensity and characteristic peaks in the region of 4.46- 4.21 ppm appeared, suggesting the *in situ* formation of a symmetrical gold-chloride complex.

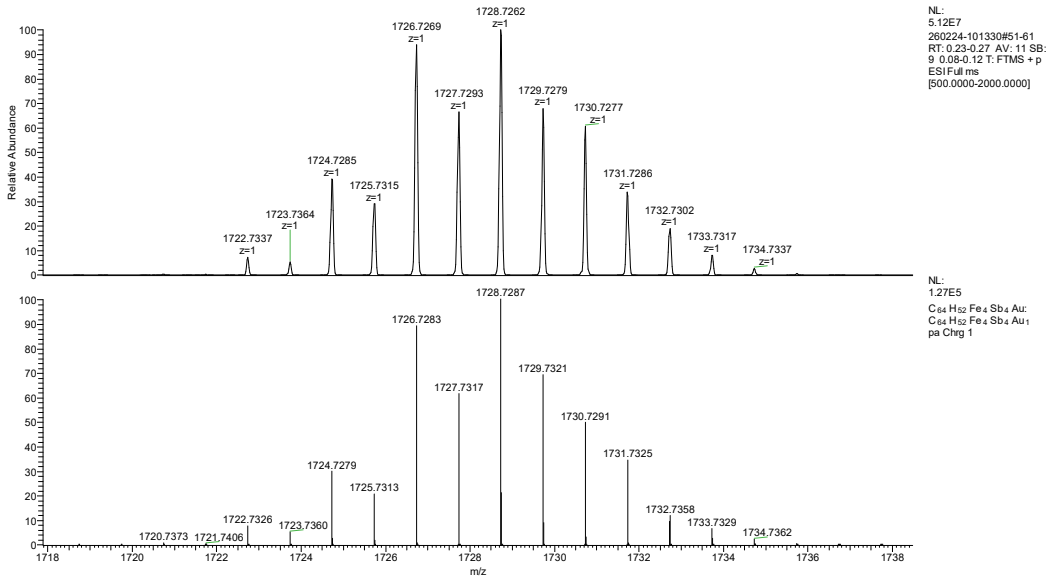


**Fig S16**. HRMS of [**2**-Au]$^+$ generated from the reaction of (**2**+(tht)AuCl).

## UV-vis spectroscopy

UV-Vis absorbance measurements were performed on a Shimadzu UV-2502PC UV-Vis spectrophotometer. Spectra were collected at a concentration of 1 x $10^{-3}$ M in $CH_2Cl_2$ using a 1 cm quartz cuvette.

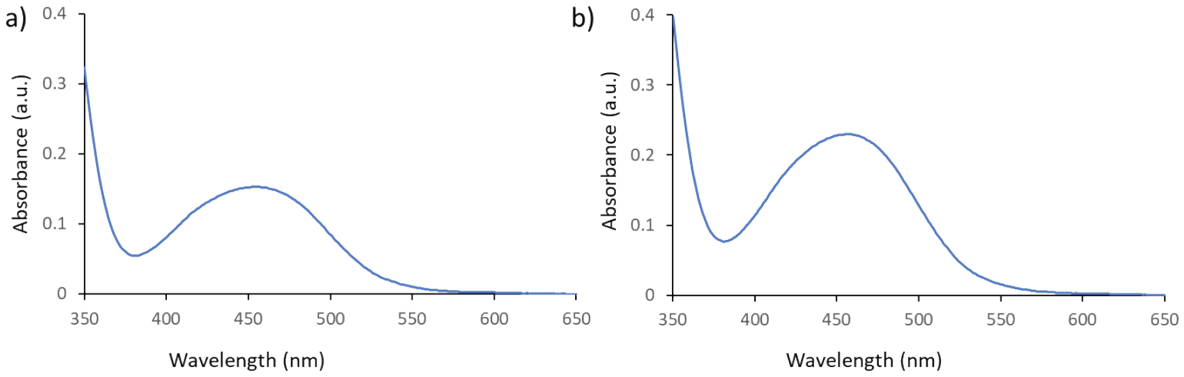


**Fig S17**. UV-vis spectra of **1** (a) and **2** (b) in $CH_2Cl_2$.

## Cyclic Voltammetry

Cyclic voltammetry measurements were recorded with a CH Instrument (Model 660 D) electrochemical analyzer, using a glassy carbon working electrode, an Ag/AgCl reference electrode, a platinum wire auxiliary electrode, and a solution of **1** and **2** in degassed $CH_2Cl_2$ with 0.1 M [$^n$Bu$_4$N][PF$_6$] as the supporting electrolyte. The voltammograms were collected at room temperature under $N_2$, with a scan rate of 100 mV/s. The voltammograms are referenced against $Fc/Fc^+$ in the same solvent.

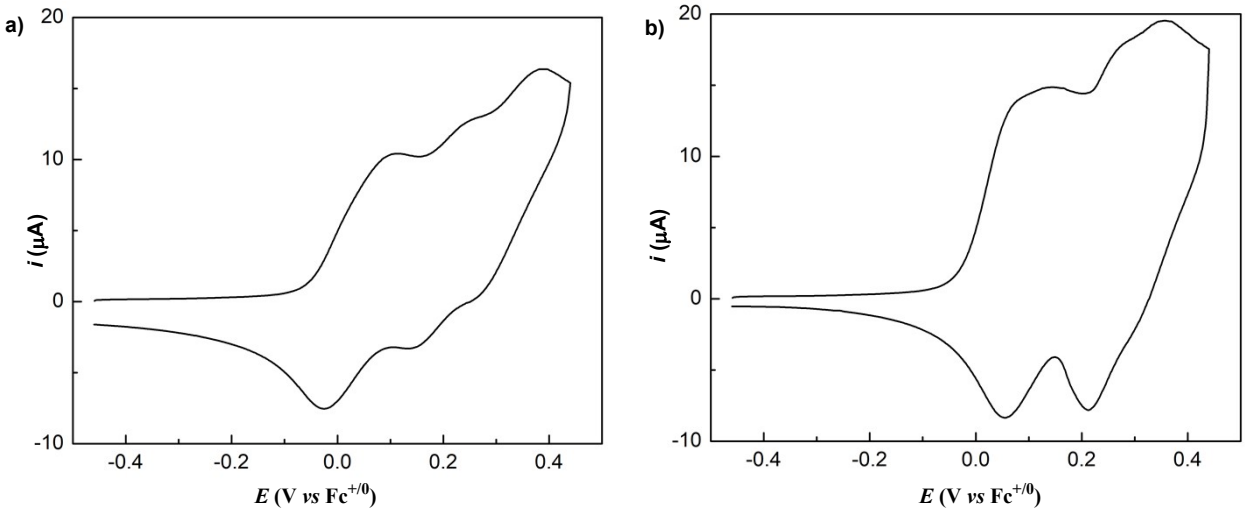


**Fig S18.** Cyclic voltammograms of (a) **1** ($3.0 \times 10^{-4}$ M) and (b) **2** ($1.0 \times 10^{-3}$ M) in $CH_2Cl_2$ recorded at a scan rate of 100 mV $s^{-1}$ with [$^n$Bu$_4$N][PF$_6$] (0.1 M) as the supporting electrolyte. Potentials are referenced to $Fc^{+/0}$.

## Catalysis

Compound **1** (5 mg, 0.0044 mmol), *N*-propalgyl-4-fluorobenzamide (15 mg, 0.087 mmol) and 0.6 mL of a $CDCl_3$ stock solution (0.007 M) of (tht)AuCl (0.0044 mmol) were added to an NMR tube. The reaction progress was monitored *in situ via* $^1$H NMR spectroscopy. Spectra were recorded every 5 min. The final conversion of the reaction was determined by integrating the peaks at 7.97 and 7.79 ppm.

Compound **3** (6.5 mg, 0.0044 mmol) and *N*-propalgyl-4-fluorobenzamide (15 mg, 0.087 mmol) were added to an NMR tube in 0.6 mL of $CDCl_3$. The reaction progress was monitored *in situ via* $^1$H NMR spectroscopy. Spectra were recorded every 5 min. The final conversion of the reaction was measured based on the integration of the peaks at 7.97 and 7.79 ppm.

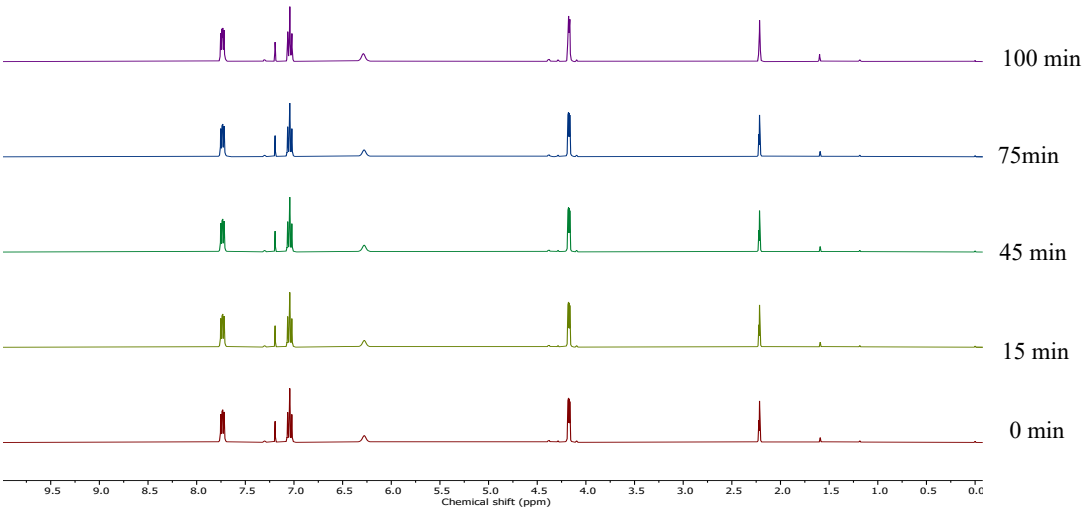


**Fig S19.** Stacked $^1$H NMR spectra recorded for the propargyl amide substrate **4** in $CDCl_3$ in the presence of 5 mol% of **3**. No conversion to **5** is observed.

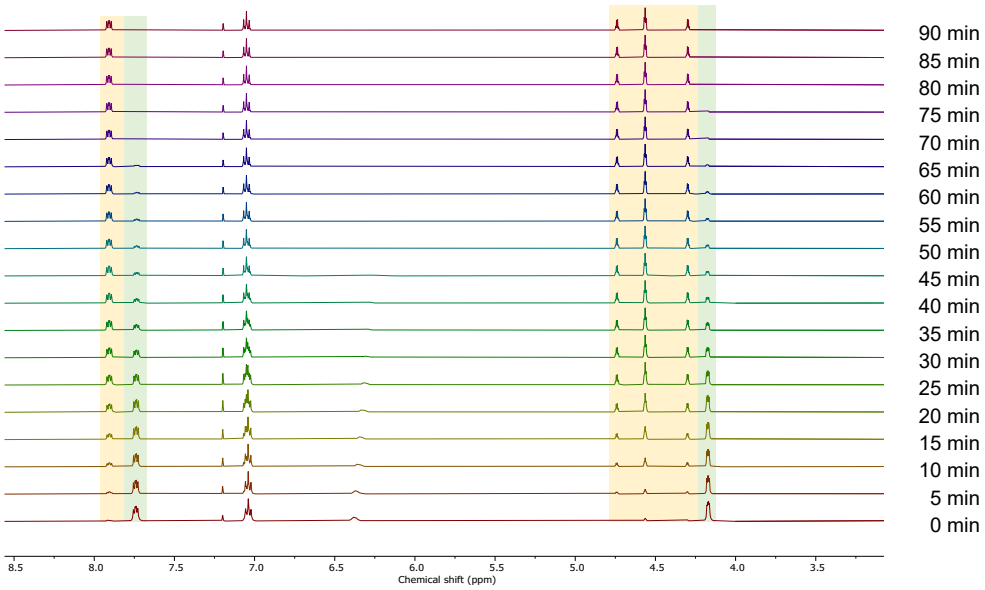


**Fig S20**. Stacked $^{1}$H NMR spectra recorded for the propargyl amide substrate **4** in $CDCl_3$ in the presence of **1** (5 mol%) and AuCl(tht) (5 mol%). The highlighted areas show the progressive disappearance of **4** (green highlight) and the progressive appearance of **5** (yellow highlight).

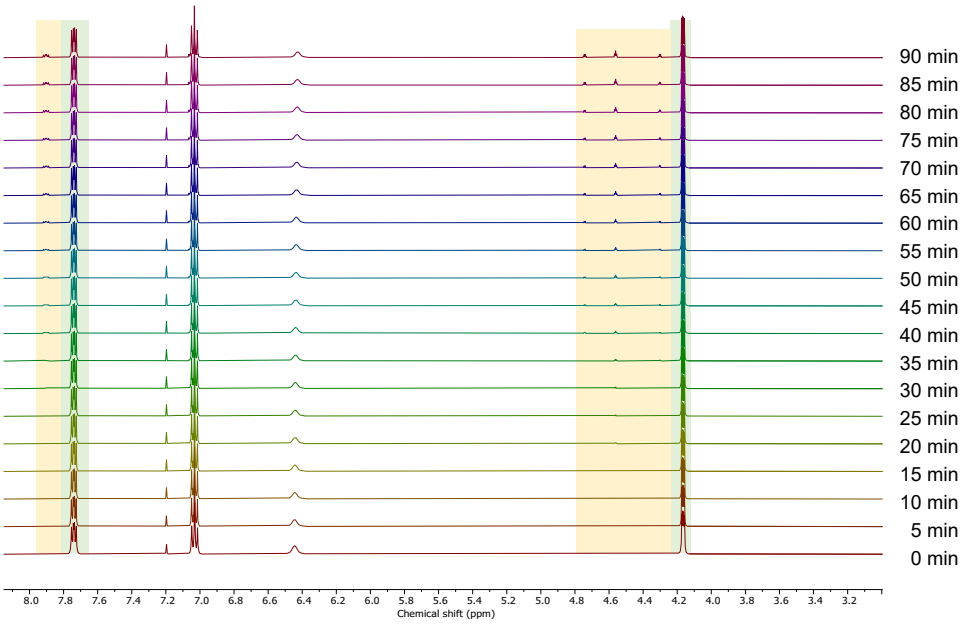


**Fig S21.** Stacked $^{1}$H NMR spectra recorded for the propargyl amide substrate **4** in $CDCl_3$ in the presence of AuCl(tht) (5 mol%). The highlighted areas show the progressive, yet slow disappearance of **4** (green highlight) and the progressive appearance of **5** (yellow highlight).

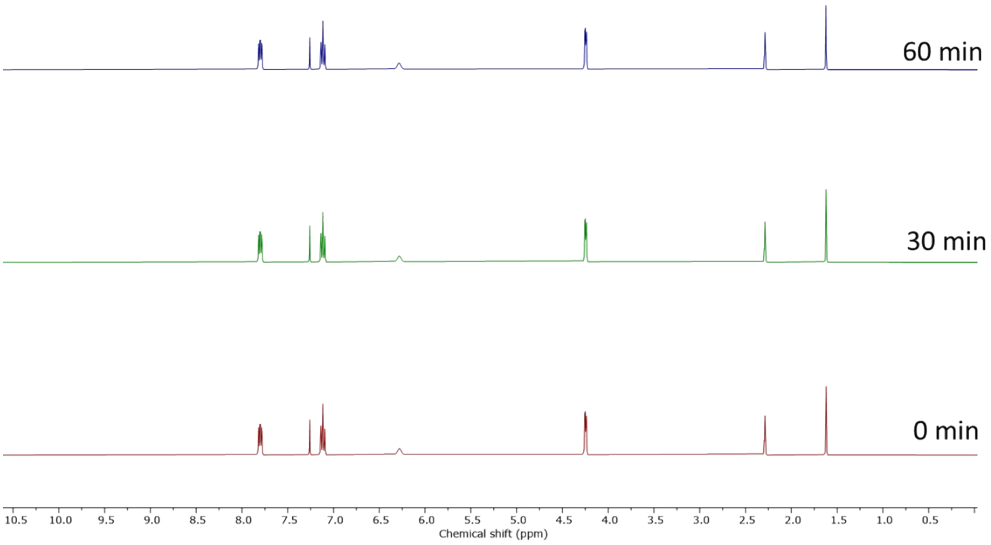


**Fig S22.** Stacked $^{1}$H NMR spectra recorded for the propargyl amide substrate **4** in $CDCl_3$ in the presence of **1** (5 mol%). No conversion is observed in the time window.

## References


1. J. J. Bishop, A. Davison, M. L. Katcher, D. W. Lichtenberg, R. E. Merrill and J. C. Smart, *J. Organomet. Chem.*, 1971, **27**, 241–249.
2. B. A. Chalmers, M. Bühl, K. S. Athukorala Arachchige, A. M. Z. Slawin and P. Kilian, *Chem. Eur. J.*, 2015, **21**, 7520–7531.
3. Bruker, 2019, APEX3 (v2019.2011–2010), Bruker AXS Inc., Madison, Wisconsin, USA.
4. G. M. Sheldrick, *Acta Crystallogr. A*, 2015, **71**, 3–8.
5. G. M. Sheldrick, *SADABS, Version 2007/4, Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA*, 2007.
6. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.