Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

Table of contents

General Methods

Reactions were performed under a nitrogen atmosphere in flame dried glassware. Glassware and NMR tubes used for generation of gold allyloxysulfonium complexes were silanized before use.[S1] NMR spectra were obtained on a Varian spectrometer operating at 400 or 500 MHz for ^{1}H, 125 MHz for ^{13}C, and 202 MHz for ^{31}P at 25 °C unless noted otherwise. ^{13}C NMR spectra were referenced relative to CD_2Cl_2 (δ 53.8) or $CDCl_3$ (δ 77.2), ^{1}H NMR spectra were referenced relative to residual $CHCl_3$ (δ 7.26) or $CHDCl_2$ (δ 5.32). ^{31}P NMR spectra was referenced to an external solution of triphenylphosphine oxide in CD_2Cl_2 (δ 26.9). Flash column chromatography was performed employing 200-400 mesh silica gel 60 (EM). Thin layer chromatography (TLC) was performed on silica gel 60 F254. CD_2Cl_2 was dried over CaH_2 and degassed prior to use. Ether, methylene chloride, and THF were purified by passage through columns of activated alumina under nitrogen. Reagents and other materials were obtained through major chemical suppliers and were used as received unless noted otherwise. Room temperature is 25 °C.

Gold vinyl carbene complexes were prepared following published procedures.[S2] Bis(4-chlorophenyl) sulfoxide[S3] and bis(4-methoxyphenyl) sulfoxide[S4] were prepared employing known procedures.

Synthesis of Gold Allyloxysulfonium Complexes

{(IPr)Au[η^1-C(H)(OSMe$_2$)C(H)=C(4-C$_6$H$_4$OMe)$_2$]}$^+$ OTf$^–$ (3a). A solution of DMSO (2.1 mg, 2.27 × 10^{-2} mmol) in CD_2Cl_2 (0.15 mL) was added dropwise to a freshly prepared solution of **1** (1.36 × 10^{-2} mmol) in CD_2Cl_2 (0.55 mL) with constant agitation at –95 °C to give a pale yellow solution of **3a** in 96 ± 5 % yield (^{1}H NMR). The yield of **3a** was determined by integrating the vinylic H_2 resonance of **3a** at δ 5.65 relative to the resonance of CH_2Br_2 at δ 4.96 in the ^{1}H NMR spectrum. ^{1}H NMR (500 MHz; CD_2Cl_2; 0 °C): δ 7.54 (t, *J* = 7.8 Hz, 2H), 7.41-7.35 (m, 4H), 7.33 (s, 2H), 7.29 (d, *J* = 7.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.9 Hz, 2H), 6.71 (d, *J* = 8.6 Hz, 2H), 6.54 (d, *J* = 8.5 Hz, 2H), 5.65 (d, *J* = 11.4 Hz, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 3.60 (d, *J* = 11.3 Hz, 1H), 3.05 (s, 3H), 2.80 (s, 3H), 2.46 (sept, *J* = 6.8 Hz, 4H), 1.28 – 1.17 (m, 24H). ^{13}C{^{1}H} NMR (125 MHz; CD_2Cl_2; –80 °C): δ 183.9, 158.0, 157.6, 145.2, 145.2, 145.0, 139.34, 133.2, 132.9, 130.2, 129.8, 127.7, 123.6, 123.6, 123.0, 121.0, 118.4, 113.6, 113.2, 112.4, 61.8, 54.9, 39.9, 39.0 (Me, partial overlap with free DMSO), 28.2 (IPr), 24.5 (IPr), 24.1 (IPr), 23.2 (IPr), 23.0 (IPr). The solution also contained resonances corresponding to TMSOMe at δ 49.7 and –1.9, TMSOTf at δ 1.1, and CH_2Br_2 at δ 21.1.

{(IPr)Au[η^1-^{13}C(H)(O-S(Me)$_2$)-^{13}C(H)=C(4-C$_6$H$_4$OMe)$_2$]}$^+$ OTf$^–$ (3a-^{13}C$_2$). ^{1}H NMR (–30 °C): δ 5.6 (dd, $^1J_{CH}$ = 156.8, $^3J_{HH}$ = 10.3 Hz, 1H). ^{13}C NMR (–95 °C): δ 113.6 (dd, $^1J_{CH}$ = 158.0, $^1J_{CC}$ = 42.3 Hz), 61.6 (dd, $^1J_{CH}$ = 139.8, $^1J_{CC}$ = 41.3 Hz).

{(IPr)Au[η^1-C(H)(O-SCH$_2$CH$_2$CH$_2$CH$_2$)-C(H)=C(4-C$_6$H$_4$OMe)$_2$]}$^+$ OTf$^–$ (3b). A solution of tetrahydrothiophene 1-oxide (1.6 mg, 1.49 × 10^{-2} mmol) in CD_2Cl_2 (0.15 mL) was added dropwise to a freshly prepared solution of **1** (1.24 × 10^{-2} mmol) in CD_2Cl_2 (0.55 mL) with constant agitation at –95 °C to give a pale yellow solution of **3b** in 95 ± 5 % yield (^{1}H NMR). The yield of **3b** was determined by

integrating the vinylic H_2 resonance of **3b** at δ 5.63 relative to the resonance of CH_2Br_2 at δ 4.96 in the ^1H NMR spectrum. ^1H NMR (500 MHz; CD_2Cl_2; –50 °C): δ 7.53 (d, *J* = 7.7 Hz, 2H), 7.42 – 7.29 (m, 6H), 7.25 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 6.69 (d, *J* = 8.2 Hz, 2H), 6.40 (d, *J* = 8.1 Hz, 2H), 5.63 (d, *J* = 11.5 Hz, 1H), 3.96 (d, *J* = 11.3 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.32 – 3.22 (m, 1H), 3.12 – 3.00 (m, 2H), 2.89 – 2.78 (m, 1H), 2.46 (sept, *J* = 6.8 Hz, 4H), 2.34 – 2.22 (m, 1H), 2.18 (d, J = 7.8 Hz, 1H), 1.87 – 1.76 (m, 1H), 1.72 – 1.57 (m, 1H), 1.28 – 1.17 (m, 24H). $^{13}C\{^1H\}$ NMR (125 MHz; CD_2Cl_2; –70 °C): δ 183.2, 158.3, 157.8, 145.3, 145.0, 133.0, 130.6, 130.0, 129.7, 128.0, 124.1, 123.9, 123.8, 123.4, 113.2, 112.6, 64.1, 55.0, 28.3, 28.2, 26.4, 26.0, 25.4, 24.9, 24.4, 24.2, 23.2, 23.1. The solution also contained resonances corresponding to TMSOMe at δ 49.7 and –1.9, TMSOTf at δ 1.1, and CH_2Br_2 at δ 21.1.

{(IPr)Au[η^1-C(H)(O-S(C_5H_6)$_2$)-C(H)=C(4-C_6H_4OMe)$_2$]}$^+$ OTf$^–$ (3c). A solution of diphenylsulfoxide (3.0 mg, 1.48 × 10^{-2} mmol) in CD_2Cl_2 (0.15 mL) was added dropwise to a freshly prepared solution of vinylcarbene (1.18 × 10^{-2} mmol) in CD_2Cl_2 (0.55 mL) was added dropwise with constant agitation at –95 °C to give a pale yellow solution of **3c** in 95 ± 5 % yield (^1H NMR). The yield of **3c** was determined by integrating the vinylic H_2 resonance of **3c** at δ 5.57 relative to the resonance of CH_2Br_2 at δ 4.96 in the ^1H NMR spectrum. ^1H NMR (500 MHz; CD_2Cl_2; –40 °C): δ 7.71 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 7.1 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 4H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.42 (d, *J* = 7.1 Hz, 2H), 7.36 (d, *J* = 7.36, 2H), 7.32 (s, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 7.01 (d, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 2H), 6.69 (d, *J* = 8.9 Hz, 2H), 6.64 (d, *J* = 8.9 Hz, 2H), 6.37 (d, *J* = 7.9 Hz, 2H), 5.57 (d, *J* = 11.8 Hz, 1H), 4.32 (d, *J* = 11.8 Hz, 1H), 3.81 (s, 3H), 3.73 (s, 3H), 2.55 – 2.23 (m, 4H; overlap of two septets), 1.34 - 1.02 (m, 24H). $^{13}C\{^1H\}$ NMR (125 MHz; CD_2Cl_2; –70 °C; aliphatic resonances only): δ 63.1, 55.0, 28.4, 28.2, 24.8, 24.5, 24.3, 23.5, 23.3, 23.3, 23.1. The solution also contained resonances corresponding to TMSOMe at δ 49.7 and –1.9, TMSOTf at δ 1.1, and CH_2Br_2 at δ 21.1.

{(IPr)Au[η^1-C(H)(O-S(4-C_6H_4Me)$_2$)-C(H)=C(4-C_6H_4OMe)$_2$]}$^+$ OTf$^–$ (3d). A solution of *p*-tolyl sulfoxide (5.0 mg, 2.17 × 10^{-2} mmol) in CD_2Cl_2 (0.10 mL) was added dropwise to a freshly prepared

solution of vinylcarbene (1.18×10^{-2} mmol) in CD_2Cl_2 (0.60 mL) was added dropwise with constant agitation at –95 °C to give a pale yellow solution of **3d** in 95 ± 5 % yield (^{1}H NMR). The yield of **3f** was determined by integrating the vinylic H_2 resonance of **3d** at δ 5.57 relative to the resonance of CH_2Br_2 at δ 4.96 in the ^{1}H NMR spectrum. ^{1}H NMR (500 MHz; CD_2Cl_2; –50 °C): δ 7.62 – 7.27 (m, 8H; aromatic peaks of IPr ligand, bound *p*-tolyl sulfoxide, and excess free *p*-tolyl sulfoxide overlap on top of each other), 7.19 (t, *J* = 7.9 Hz, 4H), 7.06 (dd, *J* = 7.7, 4.5 Hz, 4H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.75 (d, *J* = 8.2 Hz, 2H), 6.67 (d, *J* = 8.6 Hz, 2H) 6.36 (d, *J* = 8.1 Hz, 2H), 5.57 (d, *J* = 11.7 Hz, 1H), 4.27 (d, *J* = 11.6 Hz, 1H), 3.80 (s, 3H), 3.73 (s, 3H), 2.42 (4H; overlaps with excess free *p*-tolyl sulfoxide), 2.37 (s, 3H), 2.35 (s, 3H), 1.32 - 1.02 (m, 24H). ^{13}C{^{1}H} NMR (125 MHz; CD_2Cl_2; –60 °C): δ 65.7, 55.1, 28.5, 28.3, 24.5, 24.4, 23.5, 23.3, 21.4. The solution also contained resonances corresponding to TMSOMe at δ 49.8 and –1.7, TMSOTf at δ 1.4, and CH_2Br_2 at δ 21.4.

{(IPr)Au[η^1-C(H)(O-S(4-$C_6H_4Cl)_2$)-C(H)=C(4-$C_6H_4OMe)_2$]}$^+$ OTf$^-$ (3e). A solution of bis(4-chlorophenyl) sulfoxide (5.0 mg, 1.83×10^{-2} mmol) in CD_2Cl_2 (0.10 mL) was added dropwise to a freshly prepared solution of vinylcarbene (1.18×10^{-2} mmol) in CD_2Cl_2 (0.60 mL) was added dropwise with constant agitation at –95 °C to give a pale yellow solution of **3e** in 98 ± 5 % yield (^{1}H NMR). The yield of **3e** was determined by integrating the vinylic H_2 resonance of **3** at δ 5.56 relative to the resonance of CH_2Br_2 at δ 4.96 in the ^{1}H NMR spectrum. ^{1}H NMR (500 MHz; CD_2Cl_2; –30 °C): δ 7.67 – 6.96 (aromatic peaks of IPr ligand, bound bis(4-chlorophenyl) sulfoxide, and excess of sulfoxide overlaps), 5.56 (d, *J* = 11.5 Hz, 1H), 4.34 (d, *J* = 11.6 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 2.51 – 2.33 (m, 4H; overlap of two septets), 1.32 - 1.08 (m, 24H). ^{13}C{^{1}H} NMR (125 MHz; CD_2Cl_2; –60 °C): δ 65.7, 55.0, 28.3, 28.1, 24.5, 24.3, 23.5, 23.2, 23.0. The solution also contained resonances corresponding to TMSOMe at δ 49.7 and –1.9, TMSOTf at δ 1.2, and CH_2Br_2 at δ 21.0.

{(IPr)Au[η^1-C(H)(O-S(4-$C_6H_4OMe)_2$)-C(H)=C(4-$C_6H_4OMe)_2$]}$^+$ OTf$^-$ (3f). A solution of bis(4-methoxyphenyl) (5.5 mg, 2.01×10^{-2} mmol) in CD_2Cl_2 (0.10 mL) was added dropwise to a freshly prepared solution of vinylcarbene (1.18×10^{-2} mmol) in CD_2Cl_2 (0.60 mL) was added dropwise with

constant agitation at –95 °C to give a pale yellow solution of **3f** in 91 ± 5 % yield (^{1}H NMR). The yield of **3f** was determined by integrating the vinylic H_2 resonance of **3f** at δ 5.56 relative to the resonance of CH_2Br_2 at δ 4.96 in the ^{1}H NMR spectrum. ^{1}H NMR (500 MHz; CD_2Cl_2; –20 °C): δ 7.50 (d, *J* = 8.7 Hz, 5H), 7.41 (d, *J* = 7.9 Hz, 2H), 7.38 (d, *J* = 7.7 Hz, 2H), 7.31 (s, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 1H), 7.16 (d, *J* = 8.8 Hz, 6H), 7.00 – 6.90 (m, 5H), 6.79 – 6.68 (m, 9H), 6.42 (d, *J* = 8.2 Hz, 2H), 5.56 (d, *J* = 11.7 Hz, 1H), 4.27 (d, *J* = 11.7 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.77 (s, 3H), 3.15 (s, 3H), 2.55 – 2.35 (m, 4H; overlap of two septets), 1.33 - 1.07 (m, 24H). ^{13}C{^{1}H} NMR (125 MHz; CD_2Cl_2; –60 °C): δ 65.8, 56.1, 55.6, 55.1, 28.5, 28.4, 24.6, 24.3, 23.6, 23.3. The solution also contained resonances corresponding to TMSOMe at δ –1.7, TMSOTf at δ 1.4, and CH_2Br_2 at δ 20.1.

Kinetics of the Elimination of Gold Allyloxysulfonium Complexes

A freshly prepared solution of **3a** (11.8×10^{-3} mmol, 17 mM) and CH_2Br_2 (4.1 μmol; internal standard) in CD_2Cl_2 (0.70 mL) at –95 °C was placed in the probe of an NMR spectrometer at 33 °C and monitored periodically by ^{1}H NMR spectroscopy. The concentration of **3a** was determined by integration the vinylic H_2 resonance of **3a** at δ 5.65 relative to the resonance for CH_2Br_2 at δ 4.96. A plot of ln[**3a**] versus time was linear to >2 half-lives with a first-order rate constant of $11.7 \pm 0.6 \times 10^{-4}$ s^{-1} ($\Delta G^{\ddagger}$ = 22.0 kcal/mol) (Figure S1, Table 1). The kinetics of the thermal decomposition of gold allyloxysulfonium complexes **3b** and **3c** were analyzed employing similar procedures at the temperatures indicated in Table 1 (Figures S2 - S17). Hammett analyss of the first-order rate constants for the decomposition of gold allyloxydirarylsulfonium complexes **3c**-**3f** was achieved through a plot of log *k* versus $\Sigma\sigma$ gave acceptable fit (R^2 = 0.90) with a slope of ρ = 1.0 ± 0.2 (Figure 1). Eyring analysis of the first-order rate constants for the decomposition of **3b** (17 mM) as a function of temperature (–28 to –3 °C) were linear where ln(*k*/T) = (–10300 ± 280)/T + (26 ± 1) (Figure 1).

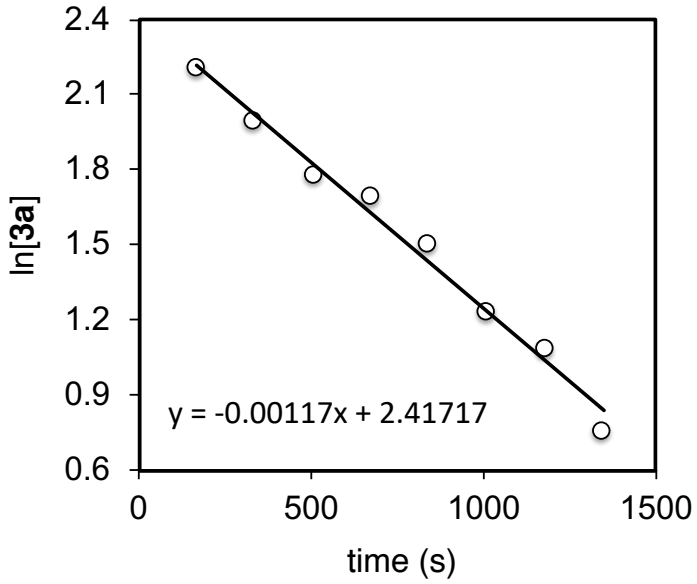

Figure S1 (Table 1, entry 1). First-order plot for the elimination of **3a** (17mM) in CD_2Cl_2 at 33 °C.

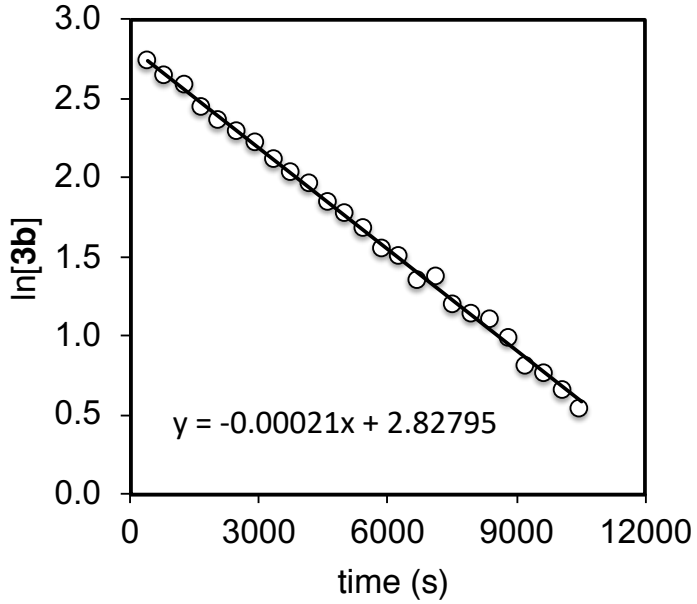

Figure S2 (Table 1, entry 2). First-order plot for the elimination of **3b** (17mM) in CD_2Cl_2 at –16 °C.

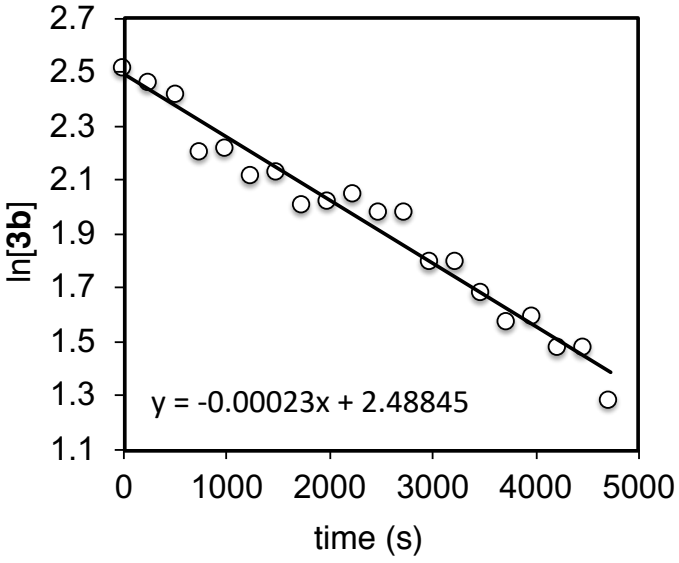

Figure S3 (Table 1, entry 3). First-order plot for the elimination of **3b** (17mM) in CD_2Cl_2 at –16 °C.

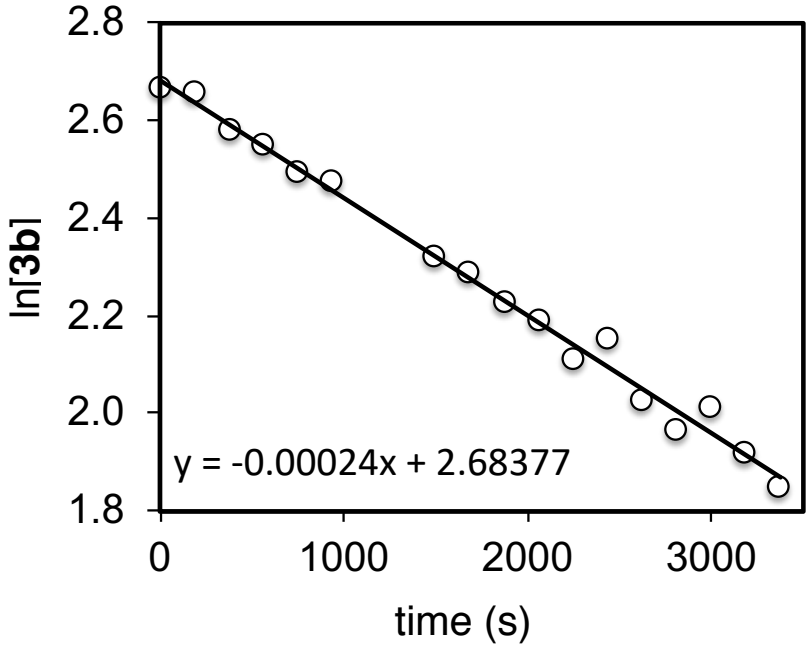

Figure S4 (Table 1, entry 4). First-order plot for the elimination of **3b** (17mM) in CD_2Cl_2 at –16 °C.

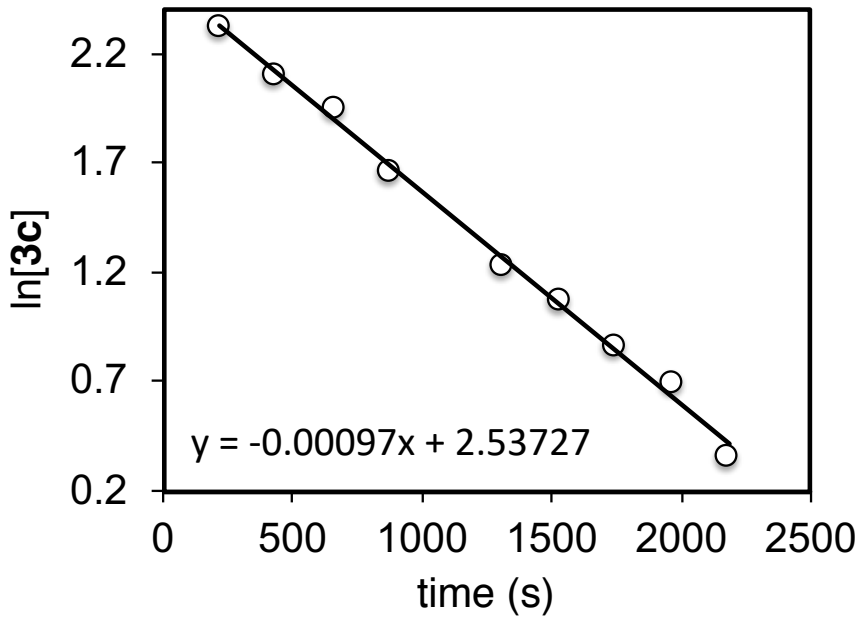

Figure S5 (Table 1, entry 5). First-order plot for the elimination of **3c** (17mM) in CD_2Cl_2 at –28 °C.

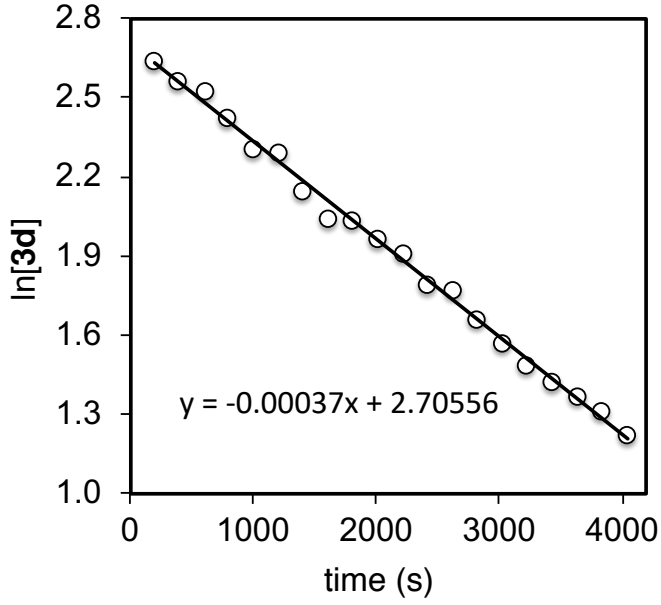

Figure S6 (Table 1, entry 6). First-order plot for the elimination of **3d** (17mM) in CD_2Cl_2 at –27 °C.

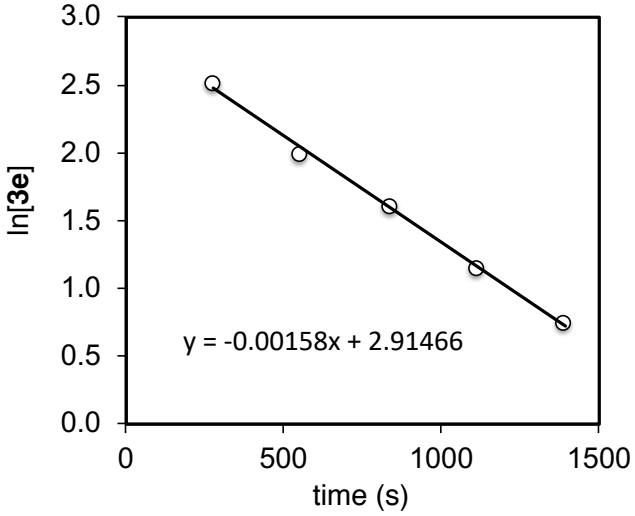

Figure S7 (Table 1, entry 7). First-order plot for the elimination of **3e** (17mM) in CD_2Cl_2 at –27 °C.

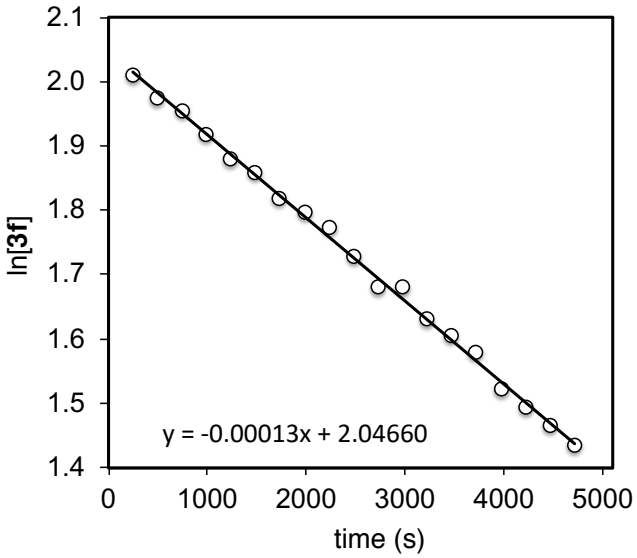

Figure S8 (Table 1, entry 8). First-order plot for the elimination of **3f** (17mM) in CD_2Cl_2 at –27 °C.

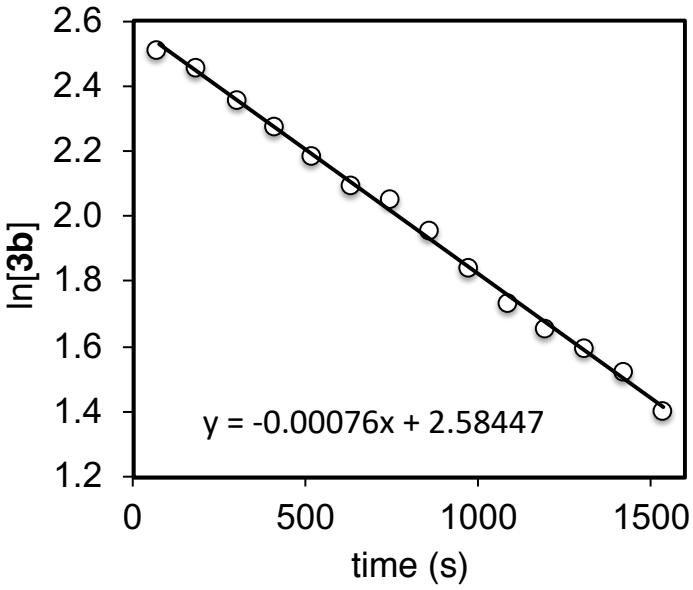

Figure S9 (Table 1, entry 9). First-order plot for the elimination of **3b** (17mM) in CD_2Cl_2 at –9 °C.

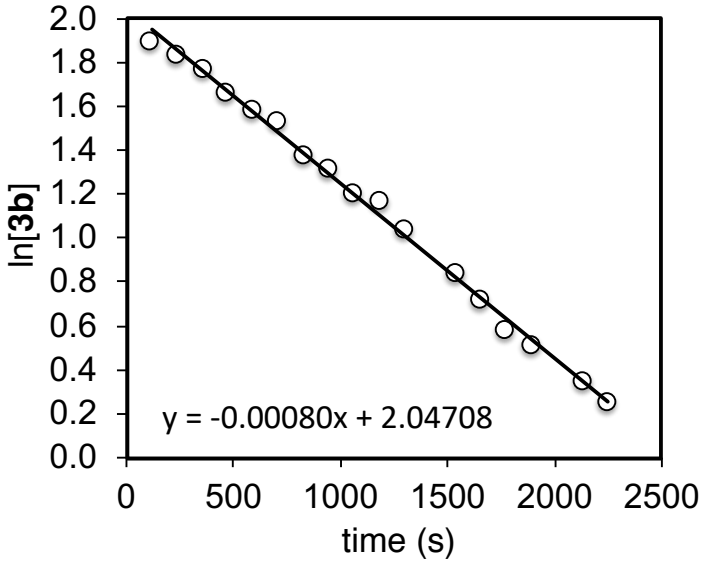

Figure S10 (Table 1, entry 10). First-order plot for the elimination of **3b** (17mM) in CD_2Cl_2 at –9 °C.

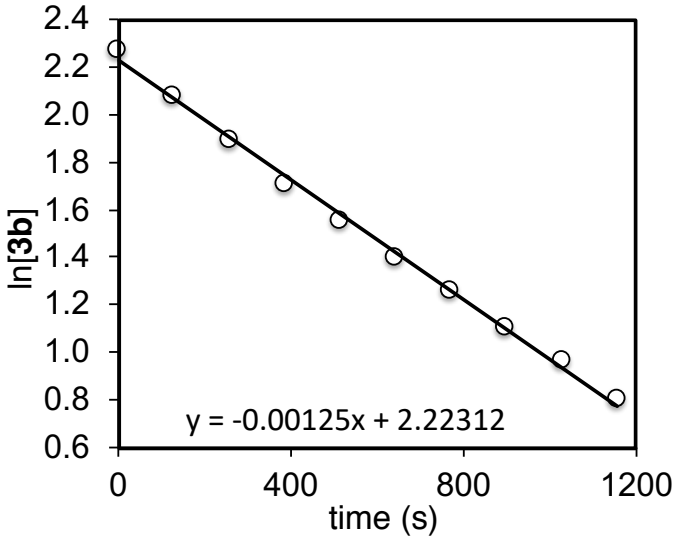

Figure S11 (Table 1, entry 11). First-order plot for the elimination of **3b** (17mM) in CD_2Cl_2 at –3 °C.

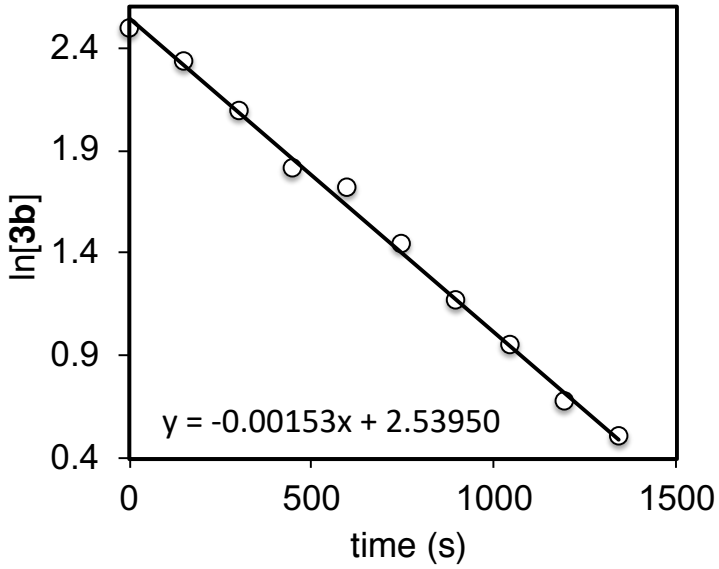

Figure S12 (Table 1, entry 12). First-order plot for the elimination of **3b** (18mM) in CD_2Cl_2 at –3 °C.

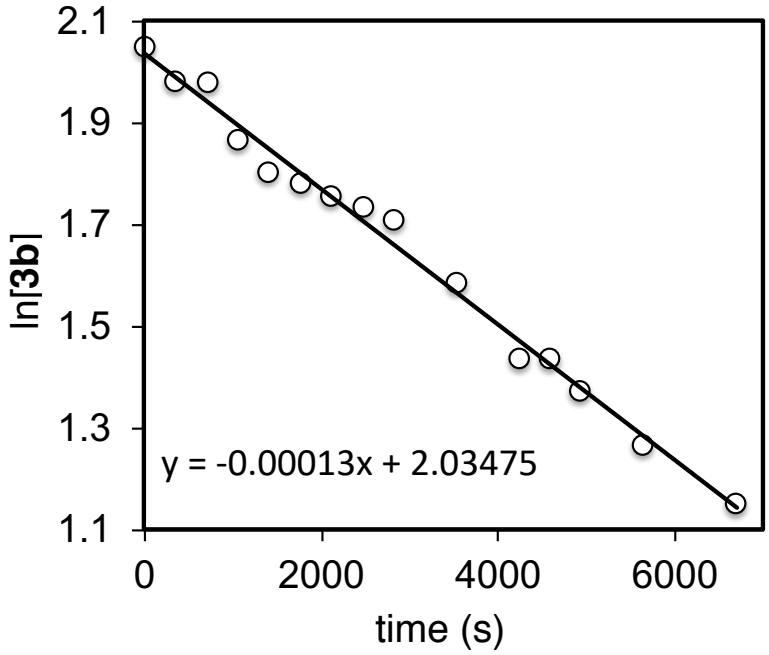

Figure S13 (Table 1, entry 13). First-order plot for the elimination of **3b** (17mM) in CD_2Cl_2 at –20 °C.

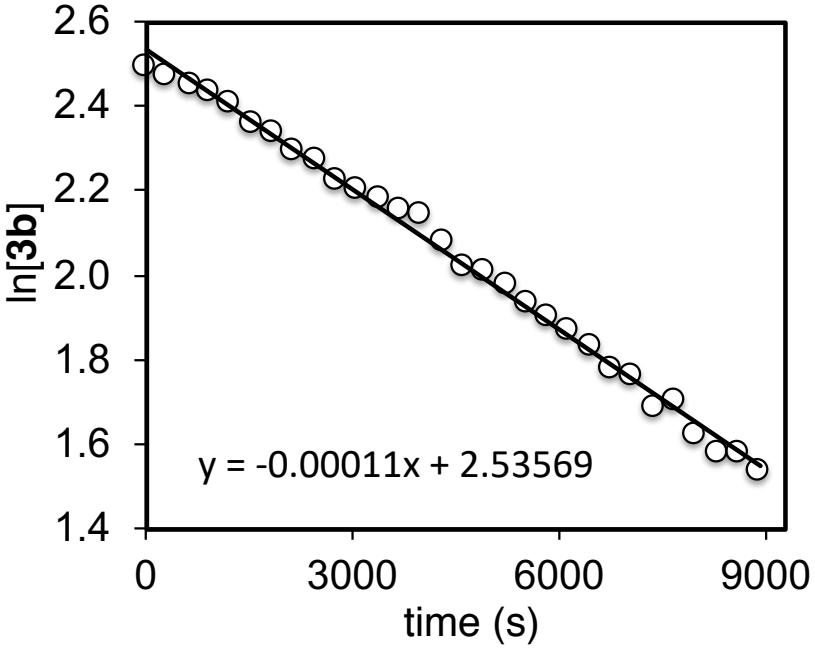

Figure S14 (Table 1, entry 14). First-order plot for the elimination of **3b** (17mM) in CD_2Cl_2 at –21 °C.

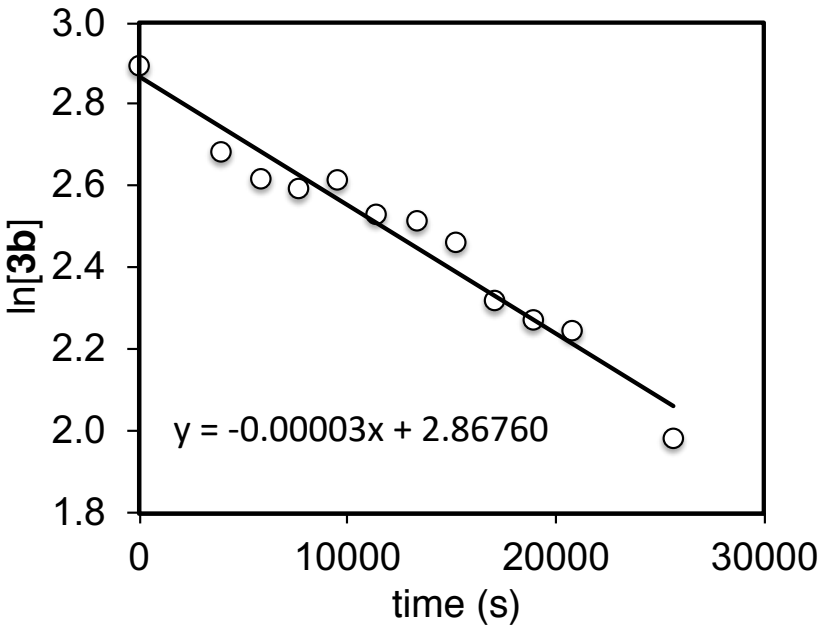

Figure S15 (Table 1, entry 15). First-order plot for the elimination of **3b** (17mM) in CD_2Cl_2 at –28 °C.

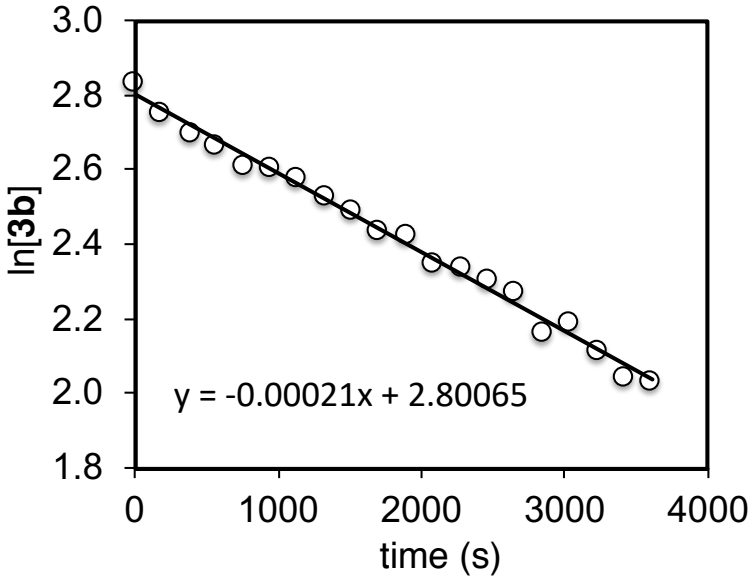

Figure S16 (Table 1, entry 16). First-order plot for the elimination of **3b** (17mM) in CD_2Cl_2 containing THTSO (51 mM) at –16 °C.

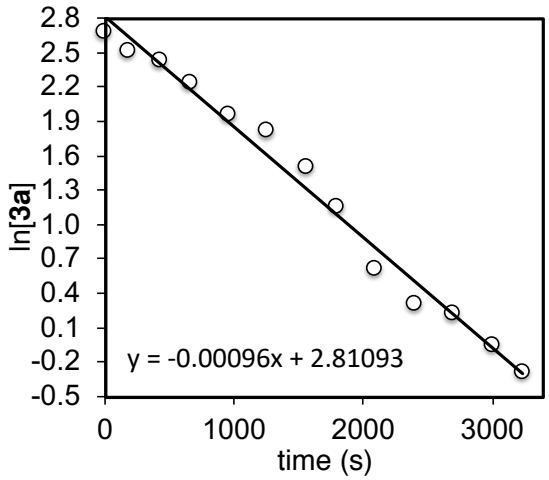

Figure S17 (Table 1, entry 17). First-order plot for the elimination of **3a** (23mM) in CD_2Cl_2/DMSO-d_6 (*v/v* = 3.7:1) at 33 °C.

Sulfoxide Exchange Experiments

Conversion of 3c to 3b in presence of THTSO. A solution of diphenylsulfoxide (2.6 mg, 1.29×10^{-2} mmol) in CD_2Cl_2 (0.15 mL) was added dropwise to a freshly prepared solution of **1** (1.18×10^{-2} mmol) in CD_2Cl_2 (0.50 mL) with constant agitation at –95 °C to give a pale yellow solution of **3c** in 82 % yield (^{1}H NMR). Then, THTSO (1.2 μL, 1.30×10^{-2} mmol) was added via syringe and washed with CD_2Cl_2 (0.05 mL) at –78 °C. The contents of the tube were mixed thoroughly and the tube was placed in the probe of an NMR spectrometer precooled at –80 °C and gradually warmed. The concentrations of **3b** and **3c** were determined by integrating the C2 proton of **3b** at δ 5.66 and the C2 proton of **3c** at δ 5.57 relative to the resonance for CH_2Br_2 at δ 4.96. ^{1}H NMR analysis of the solution at –32 °C (15 min.) revealed complete consumption of **3c** to form a mixture of **3b** (67%) and **2** (27%).

Conversion of 3b to 3a in presence of DMSO. A solution of DMSO (0.9 mg, 12 μmol) in CD_2Cl_2 (0.10 mL) was added to an NMR tube containing a freshly prepared solution of **3b** (1.2×10^{-2} mmol) in CD_2Cl_2 (0.7 mL) at –78 °C. The contents of the tube were mixed thoroughly and the tube was placed in the probe of an NMR spectrometer precooled at –80 °C. The probe was warmed at –21 °C and the

solution was monitored periodically by ^{1}H NMR spectroscopy. The concentrations of **3a** and **3b** were determined by integrating the C1 proton of **3a** at δ 3.60 and the C1 proton of **3b** at δ 3.96 relative to the resonance for CH_2Br_2 at δ 4.96. ^{1}H NMR analysis of the solution after 1 h revealed quantitative formation of **3a**.

Reaction of 3b with THT. Tetrahydrothiophene (1.0 mg, 11 μmol) in 0.1 mL CD_2Cl_2 was added to a solution of **3b** (1.2×10^{-2} mmol, 0.6 mL CD_2Cl_2) at –78 °C, mixed thoroughly, and placed in the probe of an NMR spectrometer precooled at –80 °C. The probe was warmed at –24 °C and the solution was monitored periodically by ^{1}H NMR spectroscopy. The concentrations of **3b** and {(IPr)Au[η^1-C(H)(S$(CH_2)_4$)C(H)=C(4-C_6H_4OMe)$_2$]}$^+$ OTf^- (**4**) were determined by integrating the C1 resonance of **3b** at δ 5.63 and the C1 resonance of **4** at δ 5.58 relative to the resonance for CH_2Br_2 at δ 4.96. A plot of ln[**3b**] versus time was linear to 3 half-lives with a first order rate constant of k = 7.22 ± 0.01 × 10^{-4} s^{-1} (Figure S18). ^{1}H NMR analysis of the solution after 1 h revealed quantitative formation of **4**.

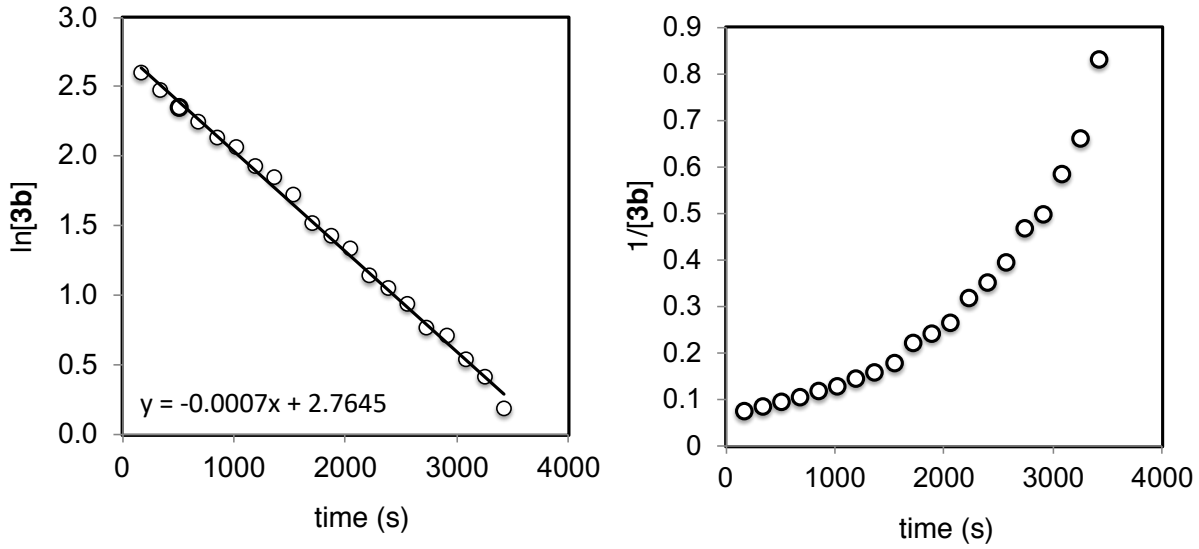

Figure S18. First-order (left) and second-order (right) plots of the disappearance of **3b** for the reaction of **3b** (16 mM) with THT (16 mM) to form **4** in CD_2Cl_2 at –24 °C.

Synthesis of gold sulfide complexes

{(IPr)Au(SMe$_2$)}$^+$ OTf$^-$. Dimethyl sulfide (7.1 μL, 9.7 $\times$ 10^{-2} mmol) and CH_2Cl_2 (3 mL) were added to a mixture of IPrAuCl (50 mg, 8.0 $\times$ 10^{-2} mmol) and AuOTf (22 mg, 8.5 $\times$ 10^{-2} mmol) at room temperature and stirred for 2 h. The crude mixture was filtered through Celite and concentrated under vacuum to give {(IPr)Au(SMe$_2$)}$^+$ OTf$^-$ (63 mg, 100 %) as a white solid. ^{1}H NMR (400 MHz; CD_2Cl_2): δ 7.59 (t, *J* = 7.8 Hz, 2H), 7.43 (s, 2H), 7.38 (d, *J* = 7.6 Hz, 4H), 2.48 (sept, *J* = 6.9 Hz, 4H), 2.27 (s, 6H), 1.29 (d, *J* = 6.8 Hz, 12H), 1.27 (d, *J* = 6.6 Hz, 12H).

Gold sulfide complexes {(IPr)Au(THT)}$^+$ OTf$^-$ and {(IPr)Au(SPh$_2$)}$^+$ OTf$^-$ were prepared employing a procedure similar to that used to synthesize {(IPr)Au(SMe$_2$)}$^+$ OTf$^-$.

{(IPr)Au(THT)}$^+$ OTf$^-$. ^{1}H NMR (400 MHz; CD_2Cl_2): δ 7.60 (t, *J* = 7.8 Hz, 2H), 7.43 (s, 2H), 7.38 (d, *J* = 7.8 Hz, 4H), 3.04 – 2.87 (m, 4H), 2.48 (sept, *J* = 6.9 Hz, 4H), 1.85 – 1.70 (m, 4H), 1.28 (d, *J* = 7.1 Hz, 12H), 1.26 (d, *J* = 7.2 Hz, 12H).

{(IPr)Au(SPh$_2$)}$^+$ OTf$^-$. ^{1}H NMR (400 MHz; CD_2Cl_2): δ 7.65 (t, *J* = 7.8 Hz, 2H), 7.46 (s, 2H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 7.8 Hz, 4H), 7.31 (t, *J* = 7.8 Hz, 4H), 7.03 (d, *J* = 7.8 Hz, 4H), 2.49 (h, *J* = 7.3 Hz, 4H), 1.25 (d, *J* = 6.8 Hz, 12H), 1.15 (d, *J* = 6.9 Hz, 12H).

References

S1) M. Hans, J. Lorkowski, A. Demonceau, L. Delaude, *Beilstein. J. Org. Chem.* **2015**, *11*, 2318–2325.

S2) N. Kim and R. A. Widenhoefer, *Chem. Sci.,* **2019**, *10*, 6149-6156.

S3) L. L. Baldassari, A. C. Mantovani, S. Senoner, B. Maryasin, N. Maulide, D. S. Lüdtke, *Org. Lett*, **2018**, *20*, 5881–5885.

S4) G. A. Olah, E. R. Marinez, G. K. S. Prakash, *Synlett*, **1999**, *9*, 1397–1398.

Figure S19. ^{1}H NMR spectrum of **3a** (CD_2Cl_2, 0 °C). Additional peaks observed at δ 4.96 (s, CH_2Br_2; internal standard), δ 3.30 (s, TMSOMe), δ 2.66 (free DMSO), δ 0.43 (s, TMSOTf), δ 0.02 (s, TMSOMe).

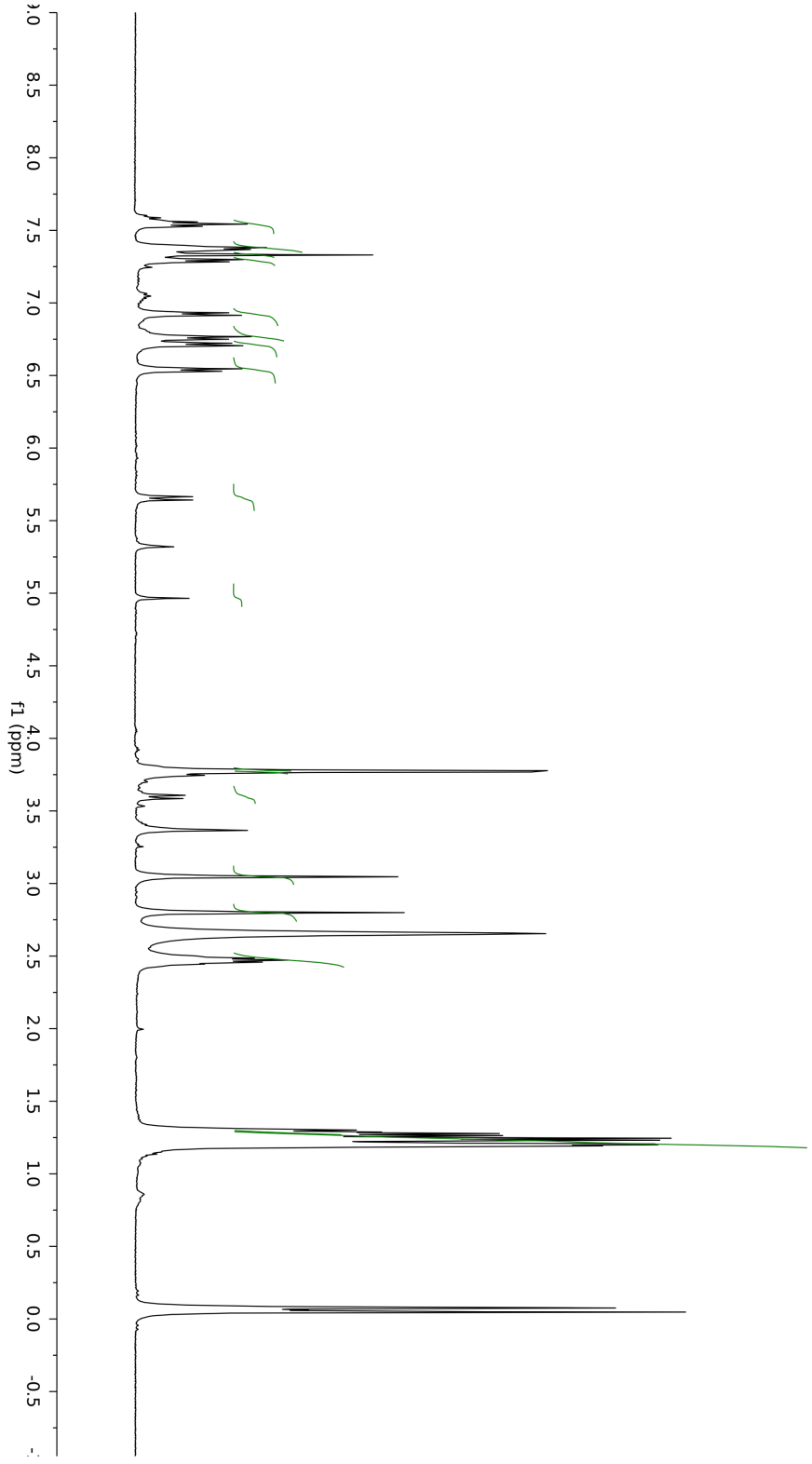

Figure 20. ^{13}C NMR spectrum of **3a** (CD_2Cl_2, –80 °C). Additional peaks observed at δ 49.7 (TMSOMe), 39.0 (free DMSO), δ 21.1 (CH_2Br_2; internal standard), δ 1.1 (TMSOTf), δ –1.90 (TMSOMe).

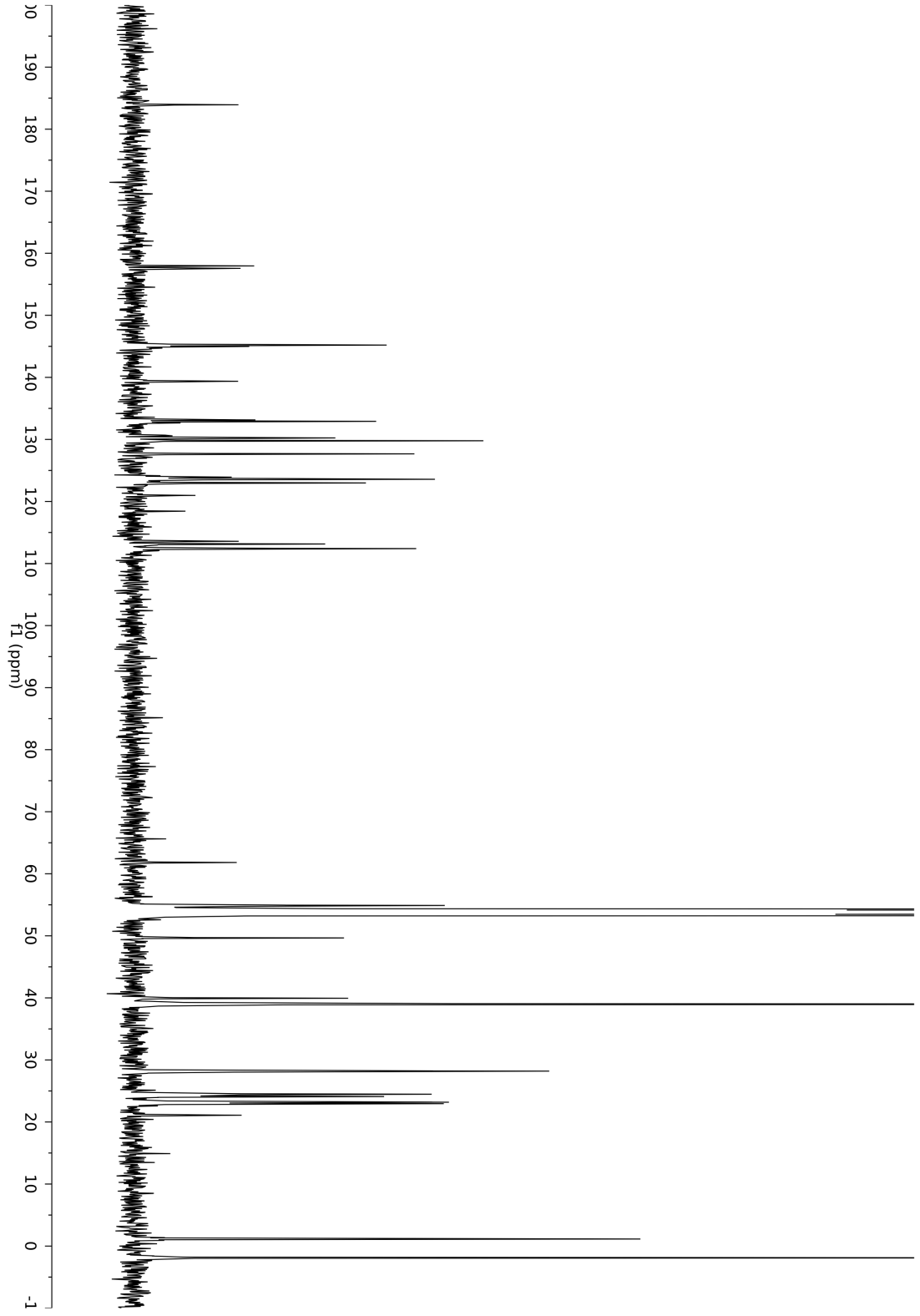

Figure S21. ^{1}H NMR spectrum of **3b** (CD_2Cl_2, –50 °C). Additional peaks observed at δ 4.96 (s, CH_2Br_2; internal standard), δ 3.30 (s, TMSOMe), δ 0.43 (s, TMSOTf), δ 0.02 (s, TMSOMe).

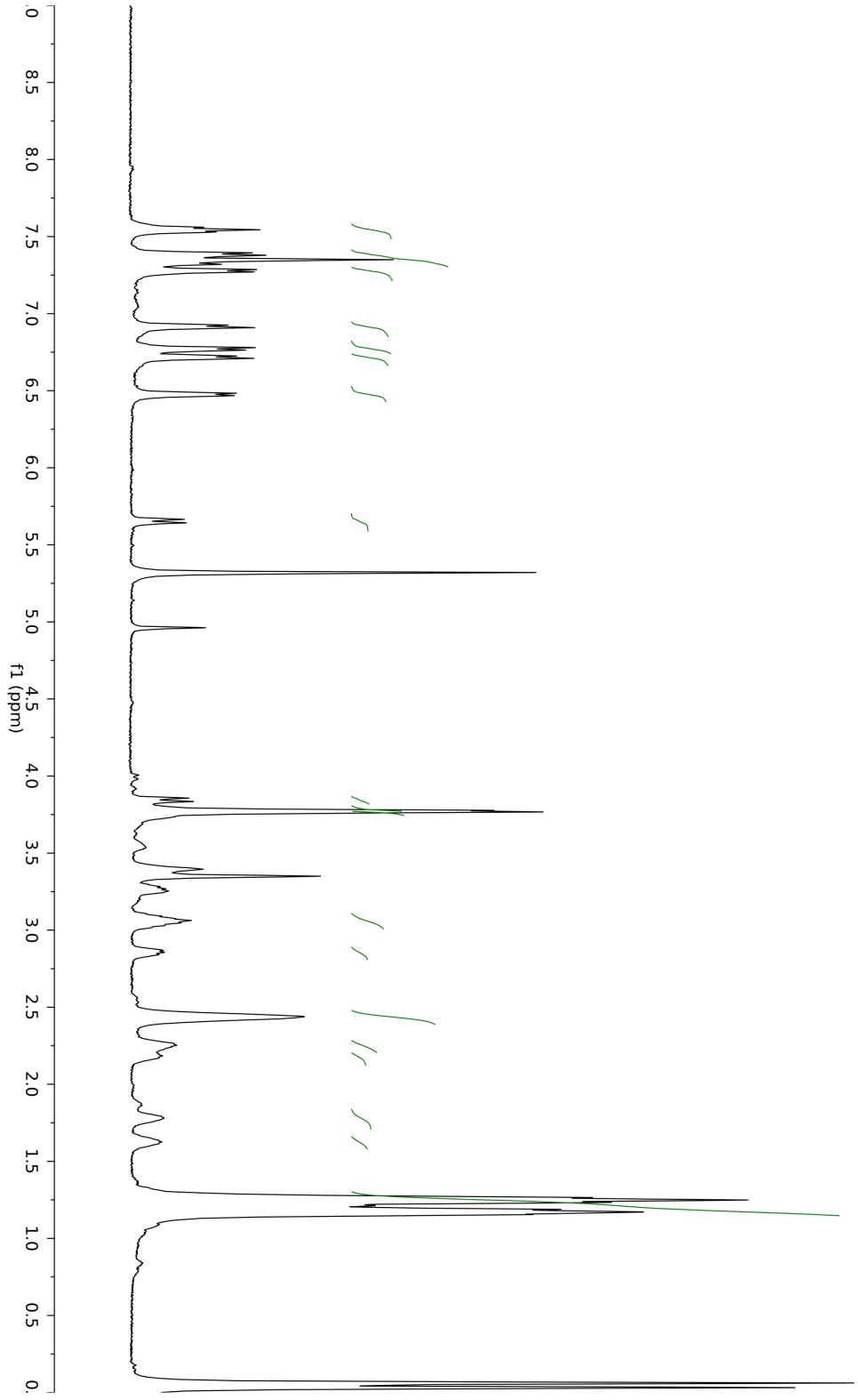

Figure S22. ^{13}C NMR spectrum of **3b** (CD_2Cl_2, –70 °C). Additional peaks observed at δ 49.7 (TMSOMe), δ 22.1 (CH_2Br_2; internal standard), δ 1.2 (TMSOTf), δ –1.8 (TMSOMe).

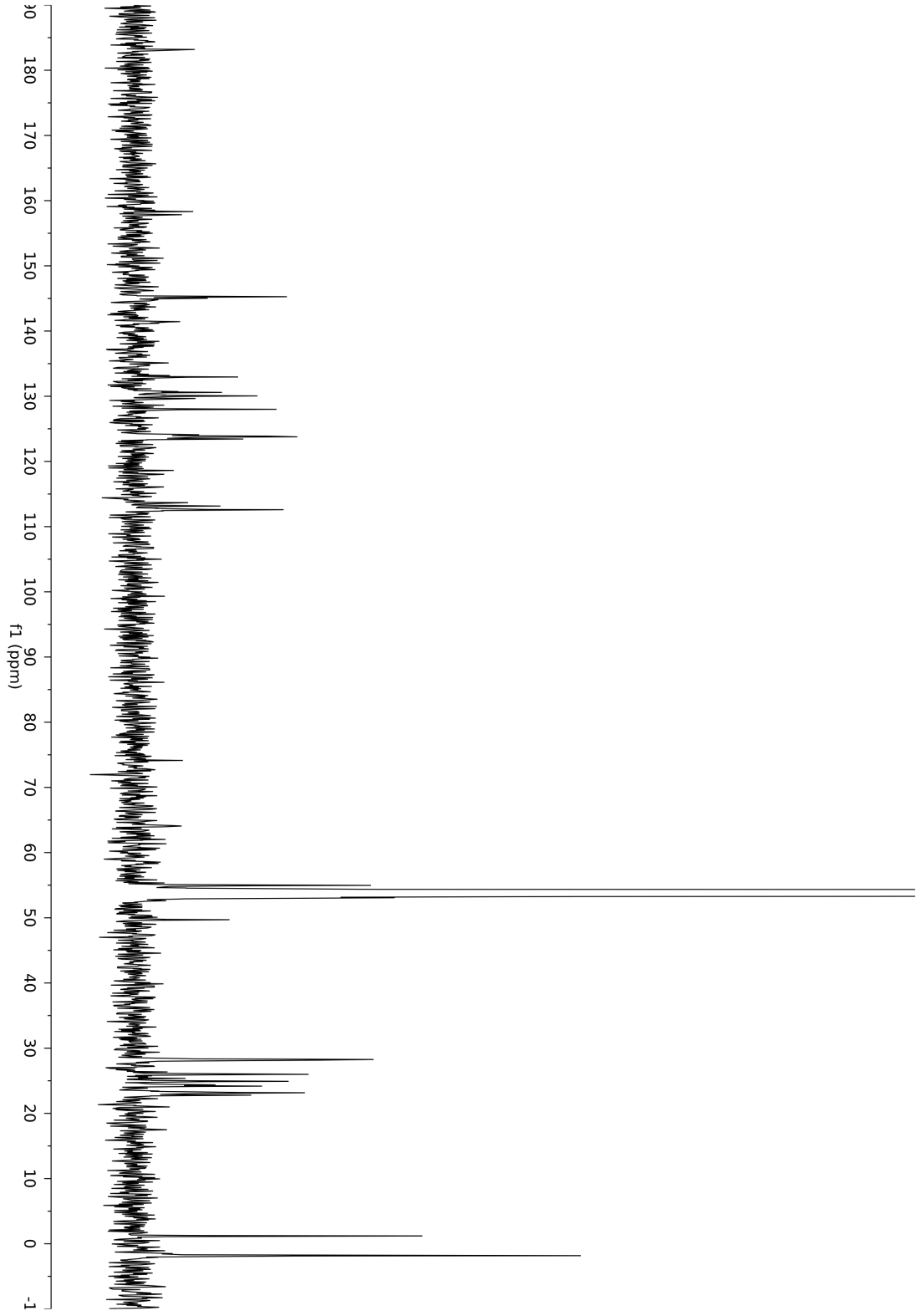

Figure S23. ^{1}H NMR spectrum of **3c** (CD_2Cl_2, –40 °C). Additional peaks observed at δ 4.96 (s, CH_2Br_2; internal standard), δ 3.30 (s, TMSOMe), δ 0.43 (s, TMSOTf), δ 0.02 (s, TMSOMe).

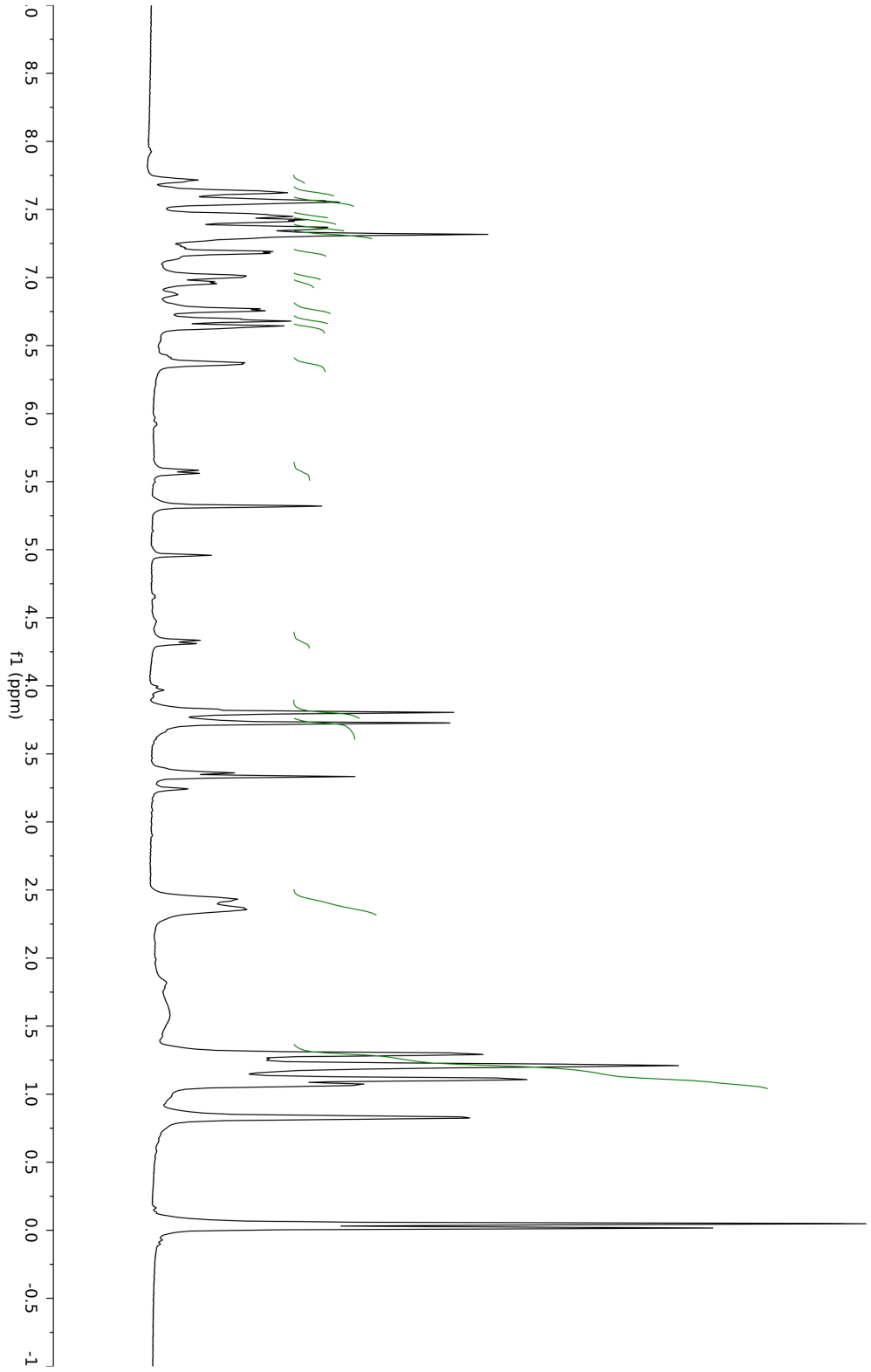

Figure S24. ^{13}C NMR spectrum of **3c** (CD_2Cl_2, –70 °C). Additional peaks observed at δ 49.7 (TMSOMe), δ 23.1 (CH_2Br_2; internal standard), δ 1.3 (TMSOTf), δ –1.8 (TMSOMe).

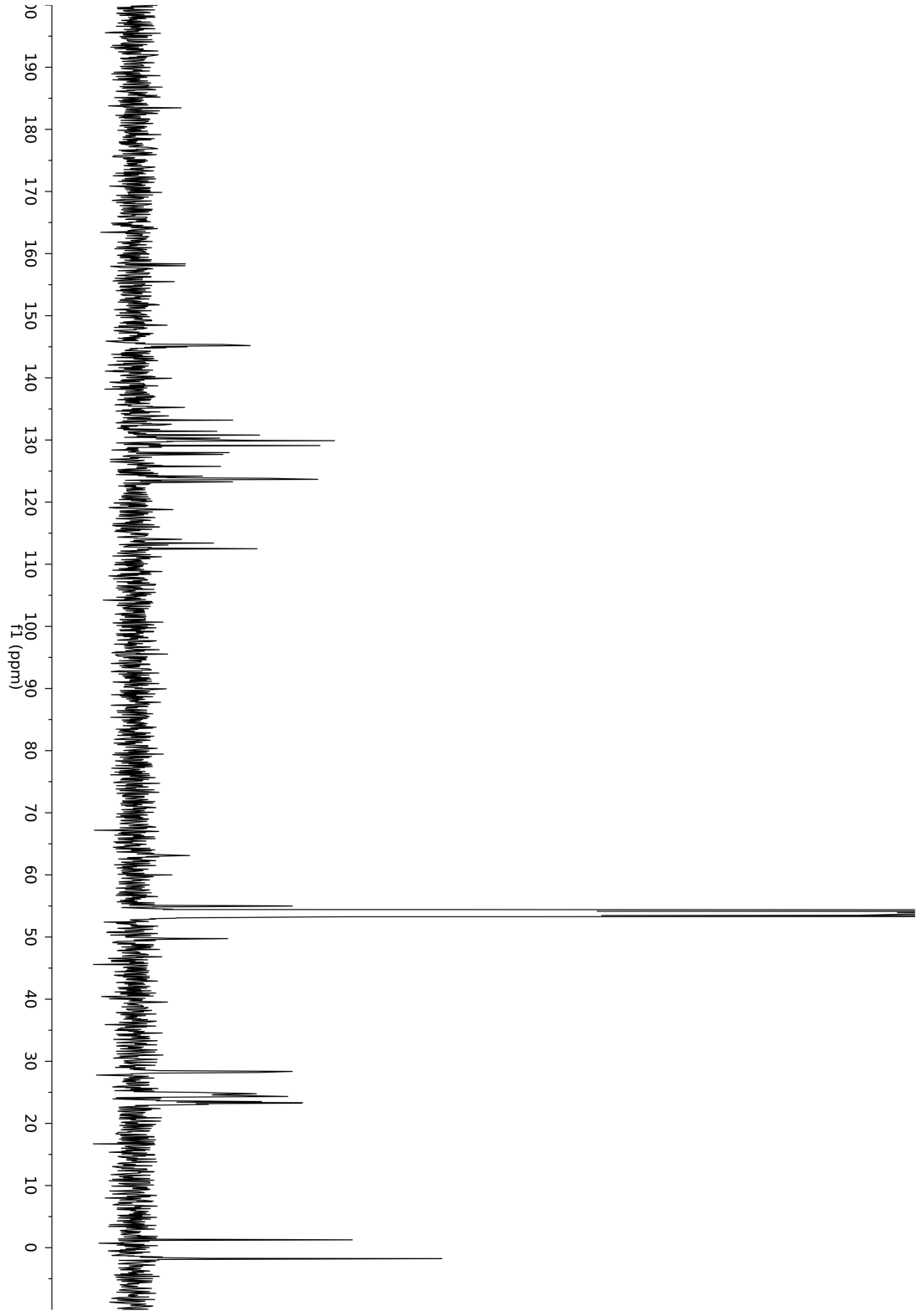

Figure S25. ^{1}H NMR spectrum of $\{(IPr)Au(SMe_2)\}^{+}$ OTf^{-} (CD_2Cl_2).

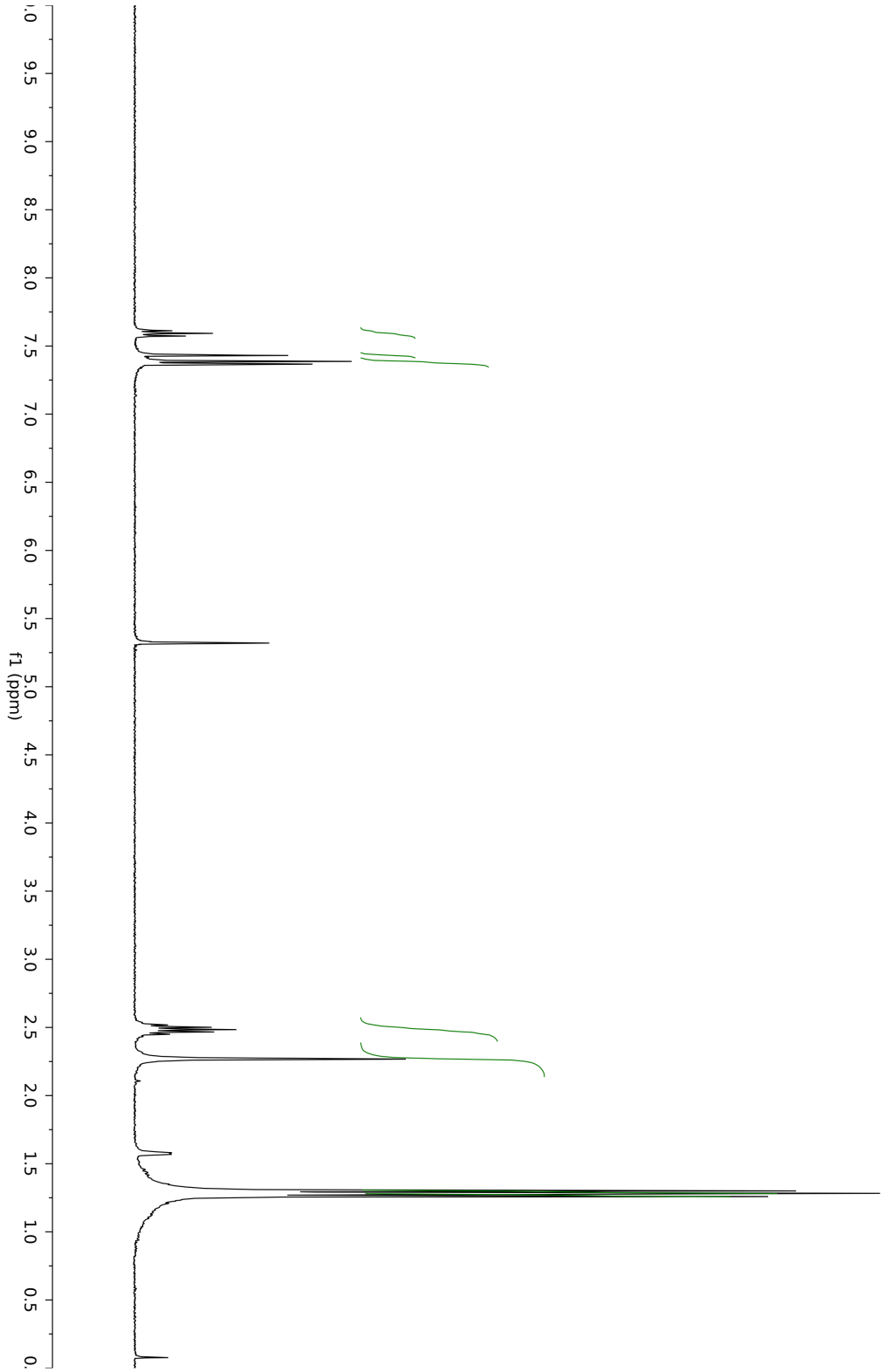

Figure S26. ^{1}H NMR spectrum of $\{(IPr)Au(THT)\}^{+}$ OTf^{-} (CD_2Cl_2).

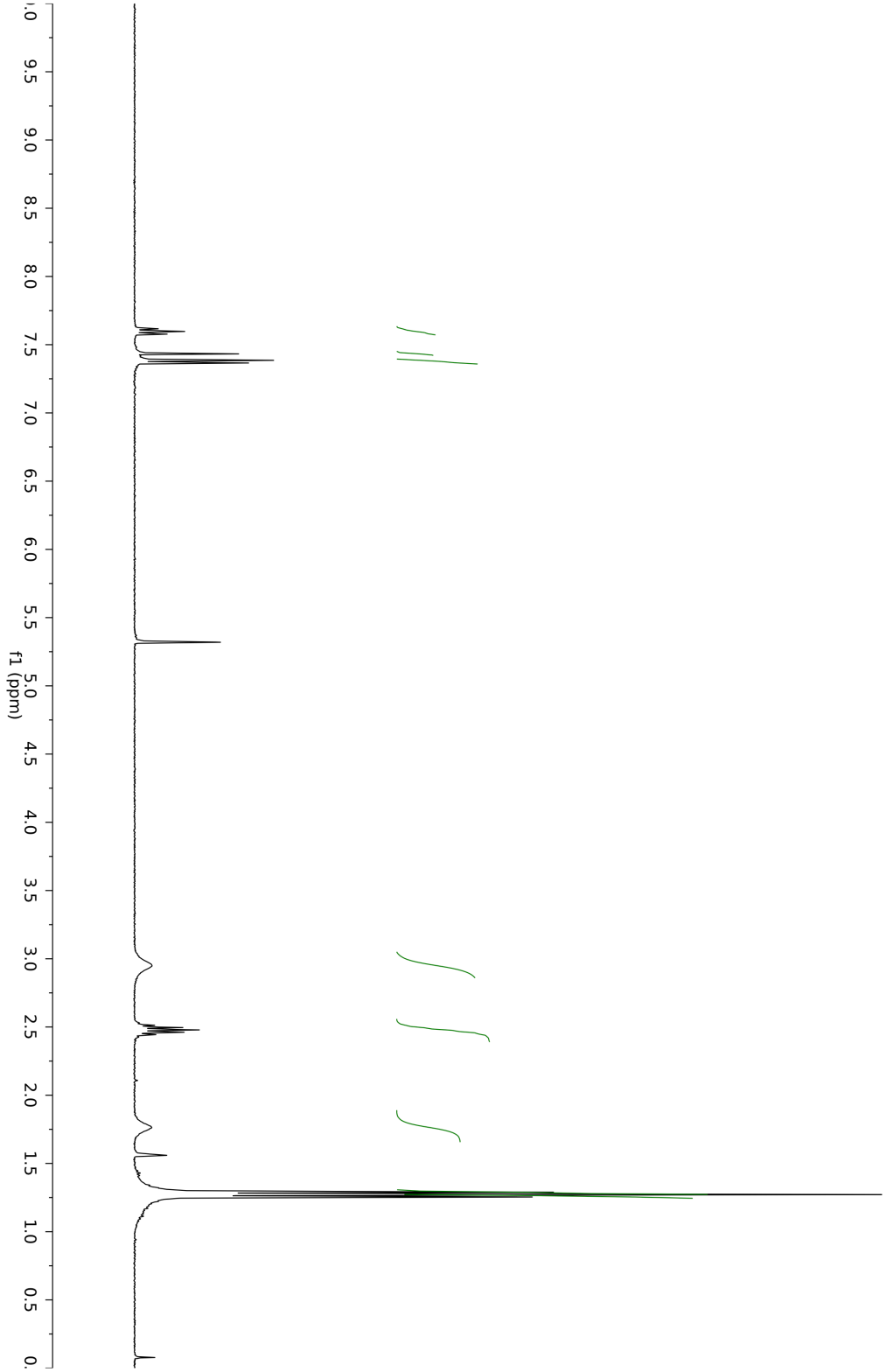

Figure S27. ^{1}H NMR spectrum of $\{(IPr)Au(SPh_2)\}^{+}$ OTf^{-} (CD_2Cl_2).