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Supporting Information

Gold(I) Carbenoids: On-Demand Access to Gold(I) Carbenes in Solution

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Supporting Information

1. General information

All reactions under a N_2 atmosphere were conducted after preparation in the glove box, reactions carried out under Ar atmosphere were performed using standard Schlenk techniques. Anhydrous solvents for synthesis were obtained by passing them through an activated alumina column on a PureSolvTM solvent purification system (Innovative Technologies, Inc., MA). Deuterated solvents were purchased from Sigma-Aldrich and, unless otherwise stated, distilled over a suitable drying agent[1] (Benzene-d_6, Toluene-d_8 and THF-d_8 over molten K, CD_2Cl_2 and $DCCl_3$ over CaH_2) under Ar before use. Analytical TLC was performed on precoated neutral aluminum oxide plates (0.2 mm thick, Gf234, Merck, Germany) and observed under UV light. Column chromatography was performed on neutral aluminum oxide Carlo Erba. NMR spectra were recorded either on a Bruker Avance 300, 400 or 500 Ultrashield instruments. Chemical shifts are reported in parts per million and referenced to residual solvent. Coupling constants (*J*) are reported in hertz (Hz). Mass spectra were recorded on a Water LCT Premier Spectrometer (ESI and APCI), on an Autoflex Bruker Daltonics (MALDI and LDI), or on an AgilentMSD-5975B (GC-MS).

2-(Di-*tert*-butylphosphino)biphenyl gold(I) chloride, 2-Di-*tert*-butylphosphino-2′,4′,6′-triisopropylbiphenyl gold(I) chloride, 1,3-Bis(2,6-diisopropylphenyl-imidazol-2-ylidene)gold(I) chloride, (Trimethylsilyl)diazomethane ($TMSCHN_2$) (2M in hexanes), Silver hexafluoroantimonate(VI), Silver bis(trifluoromethanesulfonyl)imide, Trimethylsilyl trifluoromethanesulfonate (TMSOTf), Trimethylsilyl trifluoroacetate ($TMSO_2CCF_3$), Trimethylsilyl mathanesulfonate ($TMSOSO_2CH_3$) and Norbornene were purchased from Sigma-Aldrich and used without further purification. Trimethylsilyl bis(trifluoromethanesulfonyl)imide ($TMSNTf_2$) was purchased from TCI and used without further purification. Cyclohexene was purchased from Acros and used without further purification

Unless otherwise stated, all other reagents were purchased from commercial sources and used without further purification.

2. Synthesis of gold carbenoid complexes

General Procedure

A solution of $TMSCHN_2$ (2 M in hexane, 1 to 2 equiv.) was added to a solution of gold chloride complex (1 equiv.) and MeOH (6 equiv.) in anhydrous C_6H_6 (6 mL). After a few seconds, N_2 evolution started and it stopped after 30 min. The mixture was filtered through a small pad of silica gel in order to quench the excess $TMSCHN_2$ and rinsed three times with 2 mL of CH_2Cl_2. After evaporation of the volatiles in a rotary evaporator the complexes were purified by either recrystallization or column chromatography on neutral aluminum oxide. Single crystals suitable for XRay diffraction were obtained by slow diffusion of pentane into a solution of the pure carbenoid compounds in CH_2Cl_2.

2.1. (Chloromethyl)(2-(di-*tert*-butylphosphino)biphenyl)gold (**1a**)

2-(Di-*tert*-butylphosphino)biphenyl gold(I) chloride (200 mg, 0.377 mmol), MeOH (91 µL, 2.26 mmol) and $TMSCHN_2$ (0.226 mL, 0.452 mmol) were used. Complex **1a** was purified by column chromatography on neutral aluminum oxide using a pentane/CH_2Cl_2/acetonitrile (100:10:2) mixture as eluent. Yield: 120 mg (58.5 %) of **1a** as a white solid.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.91 – 7.86 (m, 1H, H_{arom}), 7.52 – 7.44 (m, 2H, H_{arom}), 7.42 – 7.35 (m, 3H, H_{arom}), 7.26 – 7.22 (m, 1H, H_{arom}), 7.18 – 7.14 (m, 2H, H_{arom}), 2.96 (d, J_{H-P} = 3.6 Hz, 2H, CH_2Cl), 1.39 (d, J_{H-P} = 14.5 Hz, 18H, PC(CH_3)$_3$).

^{31}P NMR (162 MHz, CD_2Cl_2) δ 68.29 (s).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 150.67 (d, J_{C-P} = 16.2 Hz, C_{arom}), 143.98 (d, J_{C-P} = 5.6 Hz, C_{arom}), 135.58 (s, C_{arom}), 133.27 (d, J_{C-P} = 7.6 Hz, C_{arom}), 130.56 (d, J_{C-P} = 2.2 Hz, C_{arom}), 130.08 (s, C_{arom}), 129.22 (d, J_{C-P} = 33.5 Hz, C_{arom}), 128.63 (s, C_{arom}), 127.43 (s, C_{arom}), 127.17 (d, J_{C-P} = 5.3 Hz, C_{arom}), 53.58 (d, J_{C-P} = 112.6 Hz, Au*C*H$_2$Cl), 37.63 (d, J_{C-P} = 19.7 Hz, P*C*(CH$_3$)$_3$), 31.31 (d, J_{C-P} = 7.0 Hz, PC(*C*H$_3$)$_3$).

HRMS (ESI+) Calcd. for $C_{21}H_{29}AuPClNa$ $[M+Na]^+$: 567.1253 Found: 567.1274.

Anal. Calcd. for $C_{21}H_{29}AuClP$: C, 46.29; H, 5.37. Found: C, 46.23; H, 5.21.

2.2. (Chloromethyl-*d*)(2-(di-*tert*-butylphosphino)biphenyl)gold (**1a-*d*$_1$**)

2-(Di-*tert*-butylphosphino)biphenyl gold(I) chloride (200 mg, 0.377 mmol), CD_3OD (91 μL, 2.26 mmol) and $TMSCHN_2$ (0.226 mL, 0.452 mmol) were used. Complex **1a-*d*$_1$** was purified by column chromatography on neutral aluminum oxide using a pentane/ CH_2Cl_2/acetonitrile (100:10:2) mixture as eluent. Yield: 113 mg (54.9%) of **1a-*d*$_1$** as a white crystalline solid.

^{1}H NMR (400 MHz CD_2Cl_2) δ 7.91 – 7.85 (m, 1H, H_{arom}), 7.52 – 7.43 (m, 2H, H_{arom}), 7.42 – 7.36 (m, 3H, H_{arom}), 7.26 – 7.22 (m, 1H, H_{arom}), 7.19 – 7.13 (m, 2H, H_{arom}), 2.96 (d, J_{H-P} = 3.6 Hz, 2H, AuC*H*$_2$Cl), 2.94 (dt, J_{H-P} = 3.2, J_{H-D} = 1.4 Hz, 1H, AuC*H*DCl), 1.39 (d, J_{H-P} = 14.5 Hz, 18H, PC(C*H*$_3$)$_3$).

^{31}P NMR (162 MHz, CD_2Cl_2) δ 68.3.

^{13}C NMR (101 MHz, CD_2Cl_2) δ 150.1 (d, J_{C-P} = 16.1 Hz, C_{arom}), 143.4 (d, J_{C-P} = 5.7 Hz, C_{arom}), 135.0, 132.7 (d, J_{C-P} = 7.7 Hz, C_{arom}), 130.0 (d, J_{C-P} = 2.2 Hz, C_{arom}), 129.5, 128.6 (d, J_{C-P} = 33.6 Hz, C_{arom}), 128.0, 126.8, 126.6 (d, J_{C-P} = 5.3 Hz, C_{arom}), 53.0 (d, J_{C-P} = 112.7 Hz, Au*C*H$_2$Cl), 52.9 (dt, J_{C-P} = overlapping, J_{C-D} = 21.8 Hz, Au*C*HDCl) (d, J_{C-P} = 19.6 Hz, *C*(CH$_3$)$_3$), 30.7 (d, J_{C-P} = 7.0 Hz, C(*C*H$_3$)$_3$).

2.3. (Chloromethyl)(2-(di-*tert*-butylphosphino)-2′,4′,6′-triisopropylbiphenyl)gold (**1b**)

2-(Di-*tert*-butylphosphino)-2′,4′,6′-triisopropylbiphenyl gold(I) chloride (197 mg, 0.300 mmol), MeOH (73 μL, 1.80 mmol) and $TMSCHN_2$ (0.500 mL (0.6 M), 0.300 mmol) were used. Complex **1b** was purified by column chromatography on neutral aluminum oxide using a pentane/CH_2Cl_2/acetonitrile (100:10:2) mixture as eluent. Yield: 112 mg (55.9 %) of **1b** as a white solid.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.89 (m, 1H, H_{arom}), 7.51 – 7.42 (m, 2H, H_{arom}), 7.22 (m, 1H), 7.05 (m, 2H), 3.03 – 2.86 (m, 1H, C*H*(CH$_3$)$_2$), 2.94 (d, J_{H-P} = 3.8 Hz, 2H, CH_2Cl), 2.40 (hept, J_{H-H} = 6.7 Hz, 2H, C*H*(CH$_3$)$_2$), 1.41 (d, J_{H-P} = 14.4 Hz, 18H, PC(C*H*$_3$)$_3$), 1.33 (d, J_{H-H} = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.27 (d, J_{H-H} = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 0.90 (d, J_{H-H} = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$).

^{31}P NMR (162 MHz, CD_2Cl_2) δ 68.85 (s).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 149.3 (s, C_{arom}), 148.7 (d, $J_{C\text{-}P}$ = 16.9 Hz, C_{arom}), 147.0 (s, C_{arom}), 138.2 (d, $J_{C\text{-}P}$ = 4.3 Hz, C_{arom}), 136.5 (s, C_{arom}), 135.3 (d, $J_{C\text{-}P}$ = 8.4 Hz, C_{arom}), 131.6 (d, $J_{C\text{-}P}$ = 31.2 Hz, C_{arom}), 130.3 (d, $J_{C\text{-}P}$ = 2.2 Hz, C_{arom}), 126.8 (d, $J_{C\text{-}P}$ = 5.4 Hz, C_{arom}), 121.8 (s, C_{arom}), 53.9 (d, $J_{C\text{-}P}$ = 112.5 Hz, CH_2Cl), 38.3 (d, $J_{C\text{-}P}$ = 20.1 Hz, $PC(CH_3)_3$), 34.7 (s, $CH(CH_3)_2$), 31.8 (d, $J_{C\text{-}P}$ = 6.8 Hz, $PC(CH_3)_3$), 31.4 (s, $CH(CH_3)_2$), 26.4 (s, $CH(CH_3)_2$), 24.6 (s, $CH(CH_3)_2$), 23.3 (s, $CH(CH_3)_2$).

HRMS (ESI+) Calcd. for $C_{30}H_{47}AuPClNa$ $[M+Na]^+$: 693.2662 Found: 693.2688.

Anal. Calcd. for $C_{30}H_{47}AuClP$: C, 53.69; H, 7.06. Found: C, 53.69; H, 6.96.

2.4. (Chloromethyl)(1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene)gold (**1c**)

1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene gold(I) chloride (300 mg, 0.483 mmol), MeOH (117 μL, 2.90 mmol) and $TMSCHN_2$ (531 μL (2 M), 1.063 mmol) were used. Complex **3** was purified by column chromatography on neutral aluminum oxide using a pentane/EtOAc/acetonitrile (10:1:0.5) mixture as eluent. Yield: 180 mg (58.7 %) of **1c** as a white solid.

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.54 (t, $J_{H\text{-}H}$ = 7.7 Hz, 2H, H_{arom}), 7.34 (d, $J_{H\text{-}H}$ = 7.7 Hz, 4H, H_{arom}), 7.16 (s, 2H, H_{imid}), 3.34 (s, 2H, CH_2Cl), 2.60 (hept, $J_{H\text{-}H}$ = 7.0 Hz, 4H, $CH(CH_3)_2$), 1.34 (d, $J_{H\text{-}H}$ = 6.9 Hz, 12H, $CH(CH_3)_2$), 1.22 (d, $J_{H\text{-}H}$ = 6.9 Hz, 12H, $CH(CH_3)_2$).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 195.2 (s, C-Au), 146.5 (s, C_{arom}), 135.1 (s, C_{arom}), 130.8 (s, C_{arom}), 124.5 (s, C_{arom}), 123.6 (s, C_{imid}), 47.2 (s, CH_2Cl), 29.3 (s, $CH(CH_3)_2$), 24.7 (s, $CH(CH_3)_2$), 24.2 (s, $CH(CH_3)_2$).

HRMS (ESI+) Calcd. for $C_{28}H_{39}AuClN_2$ $[M+H]^+$: 635.2462 Found: 635.2475.

Anal. Calcd. for $C_{28}H_{38}AuClN_2$: C, 52.96; H, 6.03; N, 4.41. Found: C, 52.88; H, 6.09; N, 4.24.

2.5. (Chloromethyl)(tris(2,4-di-*tert*-butylphenyl)phosphite)gold (**1d**)

Tris(2,4-di-*tert*-butylphenyl)phosphite gold(I) chloride (300 mg, 0.341 mmol), MeOH (83 μL, 2.05 mmol) and $TMSCHN_2$ (341 μL (2 M), 0.682 mmol) were used. Complex **1d** could not be purified by conventional means as it would immediately decompose in the column. After $TMSCHN_2$ was consumed (as evidenced by the disappearance of the yellow color) the solvents were removed under reduced pressure and the residue redissolved in anhydrous Et_2O (2 mL) and filtered through 2 HPLC filters into a Schlenk flask. Anhydrous *n*-hexane (5 mL) were added over the solution and the solvents removed under vacuum. The off-white solid thus obtained was used without further purification.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.49 (dd, $J_{H,H}$ = 8.5, 1.5 Hz, 3H_{arom}), 7.46 (dd, $J_{H,H}$ = 2.6, 1.1 Hz, 3H_{arom}), 7.17 (dd, $J_{H,H}$ = 8.5, 2.6 Hz, 3H_{arom}), 3.62 (d, $J_{H,P}$ = 5.7 Hz, 2H, CH_2Cl), 1.45 (s, 27H, $C(CH_3)_3$), 1.30 (s, 27H, $C(CH_3)_3$).

^{31}P NMR (202 MHz, CD_2Cl_2) δ 143.2 (s).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 148.4 (s, C_{arom}), 148.1 (d, $J_{C,P}$ = 5.1 Hz, C_{arom}), 139.7 (d, $J_{C,P}$ = 5.8 Hz), 125.9 (s, C_{arom}), 124.5 (s, C_{arom}), 119.8 (d, $J_{C,P}$ = 9.5 Hz, C_{arom}), 49.1 (d, $J_{C,P}$ = 180.5 Hz, CH_2Cl), 35.6 (s, $C(CH_3)_3$), 35.1 (s, $C(CH_3)_3$), 31.7 (s, $C(CH_3)_3$), 30.8 (s, $C(CH_3)_3$).

2.6. ((Tetrahydro-1*H*-furan-1-ium-1-yl)methyl)(2-(di-*tert*-butylphosphino)biphenyl)gold hexafluoroantimonate (**8**)

Complex **8** was obtained as the product of an NMR scale experiment as follows: A solution of silver hexafluoroantimonate (16.40 mg, 0.048 mmol) in 0.4 mL of CD_2Cl_2 was added to a solution of **1a** (20 mg, 0.037 mmol) and tetrahydrofuran (30.0 μL, 0.367 mmol) in 0.6 mL of CD_2Cl_2 contained in an NMR tube at -78 ºC. The mixture was well mixed at this temperature and transferred to the NMR instrument. The reaction was monitored by multinuclear NMR as it was warmed up from -78 ºC to -20 ºC. At this temperature total conversion of **1a** into **8** was observed. Single crystals suitable for X-Ray diffraction were obtained by layering anhydrous *n*-hexane over the previously analyzed sample at -20 ºC. After one day crystals suitable for diffraction were found in the NMR tube.

^{1}H NMR (500 MHz, -20 ºC, CD_2Cl_2) δ 7.86 (m, 1H, H_{arom}), 7.55 – 7.48 (m, 2H, H_{arom}), 7.44 – 7.33 (m, 3H, H_{arom}), 7.23 (m, 1H, H_{arom}), 7.19 – 7.13 (m, 2H, H_{arom}), 4.66 (d, J_{H-P} = 3.5 Hz, 2H, $CH_2(OC_4H_8)$), 4.34 – 4.26 (m, 4H, $CH_2(OC_4H_8)$), 2.27 – 2.20 (m, 4H, $CH_2(OC_4H_8)$), 1.37 (d, J_{H-P} = 15.0 Hz, 18H, $PC(CH_3)_3$).

^{31}P NMR (202 MHz, -20 ºC, CD_2Cl_2) δ 64.4 (s).

^{13}C NMR (126 MHz, -20 ºC, CD_2Cl_2) δ 149.5 (d, J_{C-P} = 15.3 Hz, C_{arom}), 143.9 (d, J_{C-P} = 5.8 Hz, C_{arom}), 135.1 (s, C_{arom}), 133.0 (d, J_{C-P} = 7.6 Hz, C_{arom}), 130.9 (d, J_{C-P} = 2.3 Hz, C_{arom}), 130.0 (s, C_{arom}), 128.6 (s, C_{arom}), 127.5 (d, J_{C-P} = 38.8 Hz, C_{arom}), 127.5 (d, J_{C-P} = 5.9 Hz, C_{arom}), 127.1 (s, C_{arom}), 116.2 (d, J_{C-P} = 105.0 Hz, $CH_2(OC_4H_8)$), 87.5 (s, $CH_2(OC_4H_8)$), 37.6 (d, J_{C-P} = 21.6 Hz, $PC(CH_3)_3$), 30.9 (d, J_{C-P} = 6.6 Hz, $PC(CH_3)_3$), 25.0 (s, $CH_2(OC_4H_8)$).

2.7. (Chloro(phenyl)methyl)(2-(di-*tert*-butylphosphino)biphenyl)gold (**9**)

Phenyldiazomethane[2] (5 mL solution in benzene, approx. 1.8 mmol) was added directly over 2-(di-*tert*-butylphosphino)biphenyl gold(I) chloride (300 mg, 0.565 mmol) in a 25 mL Schlenk flask under Ar atmosphere (strict exclusion of oxygen and water are essential for the reproducibility of this reaction). The mixture was then stirred at 35 ºC while reaction progress was monitored by ^{31}P NMR. Once all the starting material has been consumed the heating was removed and the mixture concentrated to about 1 mL under reduced pressure. (**Attention!** Excess phenyldiazomethane is still present in the mixture, as evidenced by the intense red color, and a risk of explosion exists if all the solvent is removed) Anhydrous *n*-pentane (15 mL) is added over the mixture. The system is cooled down to -40 ºC with constant stirring for 30 minutes in order to induce precipitation of the product as a white solid. Filtration of the supernatant is performed with a cannula at -40 ºC. The product is washed with two portions of 2.5 mL anhydrous *n*-pentane at -40 ºC. The combined supernatant is treated with 1M HCl in MeOH until all the red color of the remaining phenyldiazomethane has faded and then safely discarded. The obtained white solid is dried on the high vacuum overnight at 0 ºC. Crystals suitable for X-Ray measurement were obtained by storing a solution of complex **9** in a mixture of toluene and pentane in a ratio of about 1:10 in the

freezer (-35 ºC) for several days. Due to the handling and final characteristics of the product an accurate determination of the reaction yield is not possible, however conversion is complete as evidenced by ^{31}P NMR evaluation during the synthesis.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.90 – 7.85 (m, 1H, H_{arom}), 7.57 – 7.36 (m, 4H, H_{arom}), 7.25 – 7.19 (m, 3H, H_{arom}), 7.16 (s, 2H, H_{arom}), 7.15 (s, 2H, H_{arom}), 7.09 – 7.05 (m, 1H, H_{arom}), 6.96 (m, 1H, H_{arom}), 4.04 (d, $J_{H\text{-}P}$ = 5.5 Hz, 1H, C*H*ClPh), 1.42 (d, $J_{H\text{-}P}$ = 14.7 Hz, 9H, PC(CH_3)$_3$), 1.30 (d, $J_{H\text{-}P}$ = 14.6 Hz, 9H, PC(CH_3)$_3$).

^{31}P NMR (162 MHz, CD_2Cl_2) δ 66.38 (s).

^{13}C NMR (100 MHz, CD_2Cl_2) δ 151.9 (d, $J_{C\text{-}P}$ = 2.6 Hz, C_{arom}), 150.7 (d, $J_{C\text{-}P}$ = 16.3 Hz, C_{arom}), 143.7 (d, $J_{C\text{-}P}$ = 5.7 Hz, C_{arom}), 135.4 (s, C_{arom}), 133.3 (d, $J_{C\text{-}P}$ = 7.5 Hz, C_{arom}), 130.6 (d, $J_{C\text{-}P}$ = 2.2 Hz), 130.1 (s, C_{arom}), 130.0 (s, C_{arom}), 128.8 (s, C_{arom}), 128.7 (d, $J_{C\text{-}P}$ = 33.6 Hz, C_{arom}), 128.6 (s, C_{arom}), 128.2 (d, $J_{C\text{-}P}$ = 2.4 Hz, C_{arom}), 128.0 (s, C_{arom}), 127.6 (s, C_{arom}), 127.2 (d, $J_{C\text{-}P}$ = 5.3 Hz, C_{arom}), 124.3 (s, C_{arom}), 76.0 (d, $J_{C\text{-}P}$ = 105.0 Hz, *C*HClPh), 37.6 (d, $J_{C\text{-}P}$ = 19.8 Hz, P*C*(CH$_3$)$_3$), 37.5 (d, $J_{C\text{-}P}$ = 20.0 Hz, P*C*(CH$_3$)$_3$), 31.3 (d, $J_{C\text{-}P}$ = 7.0 Hz, PC(*C*H$_3$)$_3$), 31.1 (d, $J_{C\text{-}P}$ = 7.0 Hz, PC(*C*H$_3$)$_3$).

3. **Activation of carbenoid complexes with chloride scavengers**

3.1. Formation of ethylene

In a glovebox, 0.018 mmol of carbenoid complex (either 10 mg **1a** or **1a-*d*$_1$**) was dissolved in 0.5 mL toluene-d_8 and transferred to a NMR tube capped with a rubber septum. Separately, TMSOTf (0.044 mmol, 8μL) was taken in a microsyringe and protected from air. Outside the glovebox TMSOTf was added over the mixture in the NMR tube and the sample transferred to the NMR instrument.

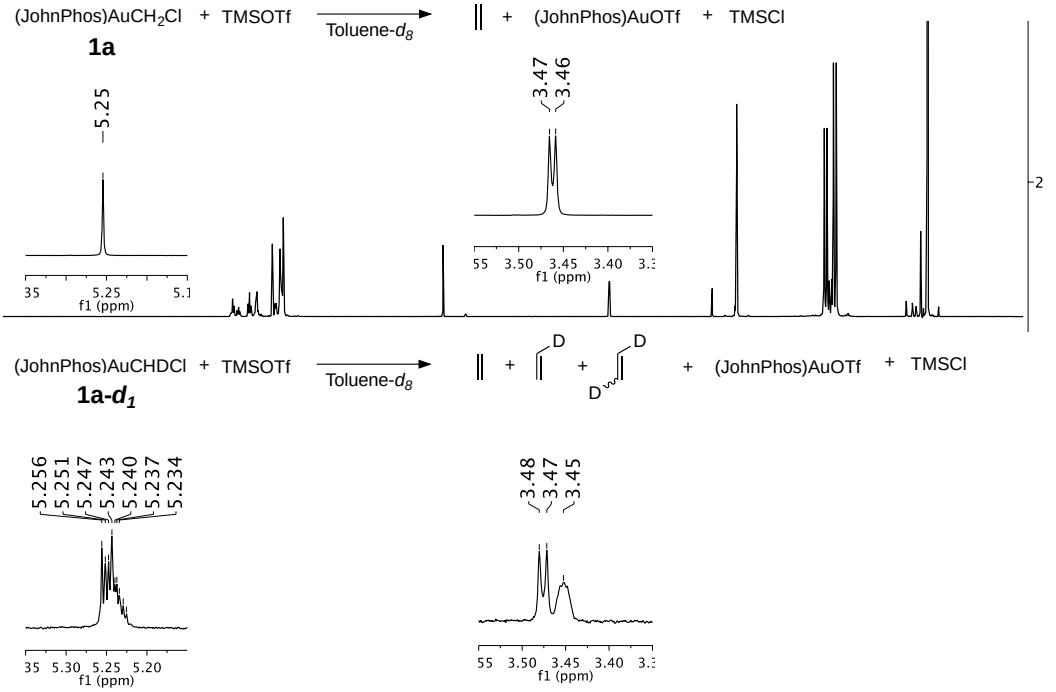


Figure S1. ^{1}H NMR spectra obtained after activation of complexes **1a** (top) and **1a-*d*$_1$** (bottom) with TMSOTf in toluene-d_8. The inserts show the signals corresponding to the starting carbenoid (around 3.45 ppm) and the formed ethylene (around 5.25 ppm).

3.2. Quantification of ethylene

Ethylene formation was quantified using a ManontheMoonTech X102 Gas Evolution device that monitors the gas evolution by measuring the pressure change versus time in closed reaction systems.

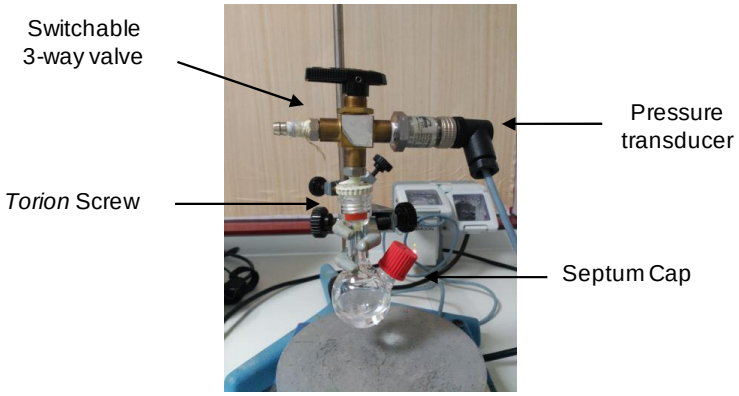


Figure S2. ManontheMoonTech X102 reaction flask.

Calibration Method

In a glass ampule, toluene was saturated in ethylene by bubbling the gas through anhydrous toluene for 15 minutes. The reaction flask was connected to the switchable 3-way valve via the *Torion* screw and capped with the septum cap. The closed reaction flask was filled with ethylene gas and 5.0 ml of the previously saturated toluene. The reaction flask was connected to the pressure transducer and controlled until the pressure reading stabilized at 0.390-0.400 bar. Separately, a high pressure reactor was charged with 1 bar of ethylene (total pressure = 1 bar + atmospheric pressure) and a known volume of gas was withdrawn using a Hamilton® SampleLock syringe. Ethylene was then injected through the septum cap and the change in pressure was determined. Applying the gas ideal equation SE1, the molar amount *n* of added ethylene was calculated which was then correlated to the observed change in pressure ΔP (bar).

$$PV = nRT \rightarrow n = \frac{PV}{RT}$$

Equation SE1. Ideal gas equation, where: P = pressure of the gas, V = volume of the gas, n = moles of the gas, R = the ideal gas constant, T = the absolute temperature of the gas.

Table S1. Calibration of the pressure response to ethylene.

Entry	$V_{ethylene}$ (ml)	T (K)	$P_{ethylene}$ (bar)	$n_{ethyelene}$ (mmol)	ΔP (bar)
1	2.50	298	2	0.2	0.128
2	2.50	298	2	0.2	0.123
				Average: $\Delta P_{0.2\ mmol}$	0.125
3	1.25	298	2	0.1	0.071
4	1.25	298	2	0.1	0.077
				Average: $\Delta P_{0.1\ mmol}$	0.074

Ethylene quantification

The reaction flask was filled with toluene (5.0 mL, anhydrous and saturated in ethylene), **1a** and ethylene gas. Then, it was connected to the pressure transducer and controlled until the pressure reading stabilized at 0.390-0.400 bar. TMSOTf (2 equiv) was injected through the septum cap and the pressure change measured over time. The yield of ethylene at any time was calculated using equation SE2.

$$Yield\ (\%) = \frac{\Delta P_t}{\Delta P_{max}} * 100$$

Equation SE2. Where: ΔP_t = pressure difference along the reaction. ΔP_{max} = maximum pressure change expected given the amount of **1a** used (see calibration).

Conditions A: **1a** (0.2 mmol, 109 mg), TMSOTf (0.4 mmol, 72 μL), ΔP_{max} = 0.074 bar.

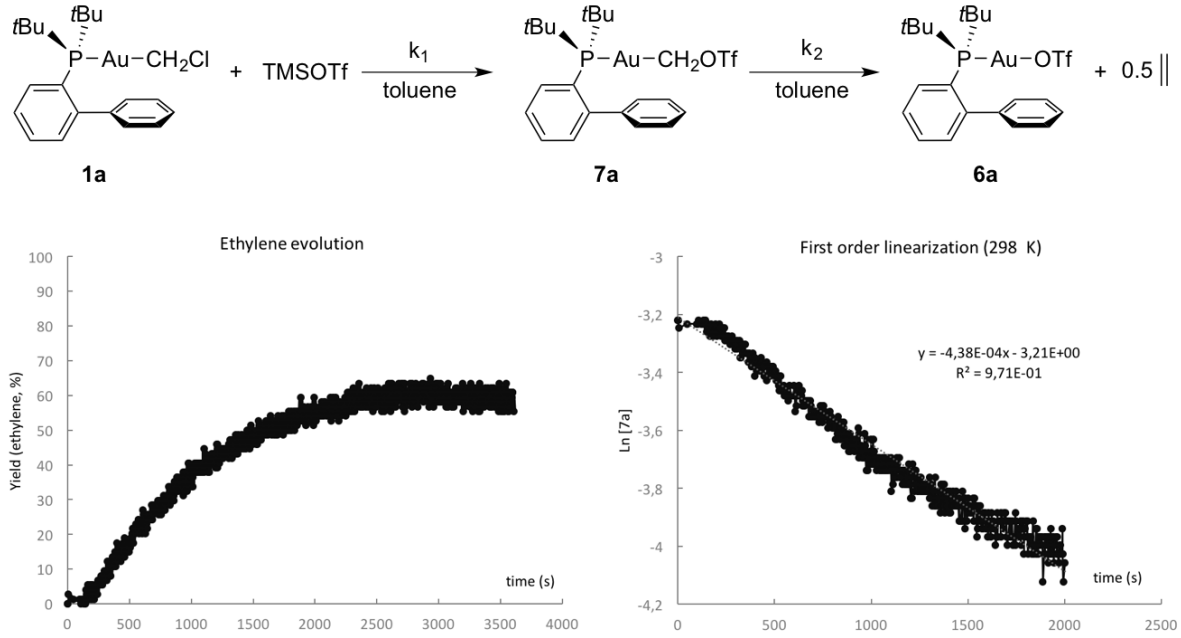


Figure S3. Left: yield profile measured for the reaction of **1a** (0.2 mmol) with TMSOTf. Right: corresponding first order linearization plot for the change of concentration of **7a** over time.

Conditions B: **1a** (0.4 mmol, 218 mg), TMSOTf (0.8 mmol, 144 μL), ΔP_{max} = 0.125 bar.

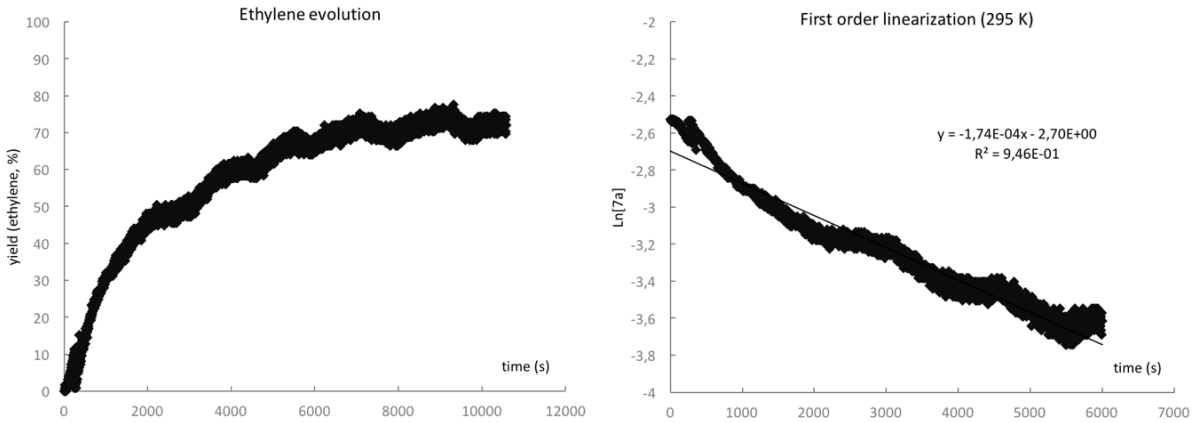


Figure S4. Left: yield profile measured for the reaction of **1a** (0.4 mmol) with TMSOTf. Right: corresponding first order linearization plot for the change of concentration of **7a** over time.

Gas phase analysis

In a closed reaction flask under argon, carbenoid **1a** (0.03 mmol, 16 mg) was dissolved in 0.5 mL of anhydrous toluene. In a glovebox, TMSOTf (0.06 mmol, 11 μL) was taken in a microsyringe and protected from air. Outside the glovebox TMSOTf was added over the solution. The mixture was then stirred at 25ºC for 30 minutes. A Hamilton® SampleLock syringe was filled with 250 μL of gas from the gas phase of the reaction. The gas was injected in a GC-MS instrument.

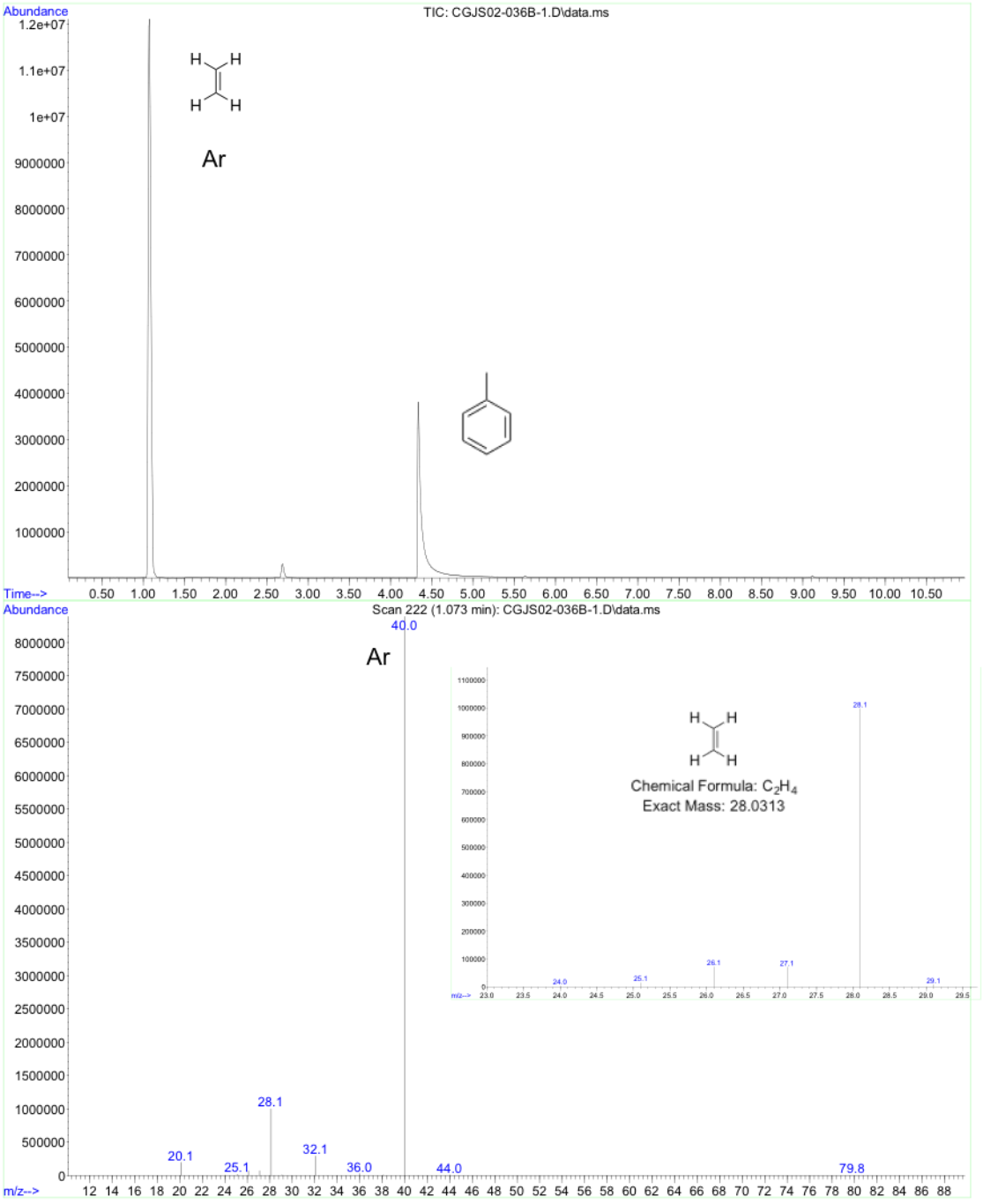


Figure S5. GC-MS trace and MS spectrum from the gas phase during the activation of **1a** with TMSOTf.

3.3. Effect of the anion in the decomposition of gold carbenoids

In a glovebox, carbenoid complex (0.018 mmol, 10 mg **1a** or 11 mg **1c**) was dissolved in 0.5 mL toluene-d_8 and transferred to a NMR tube capped with a rubber septum. Separately, 0.037 mmol of TMS-X compound (either 6.6 μL TMSOTf, 7.7 μL $TMSO_2CCF_3$, 8.4 μL $TMSNTf_2$, or 5.7 μL $TMSOSO_2CH_3$) was taken in a microsyringe and protected from air. Outside the glovebox TMSOTf was added over the mixture in the NMR tube at room temperature for **1a** or at 273 K for **1c** and the sample transferred to the NMR instrument.

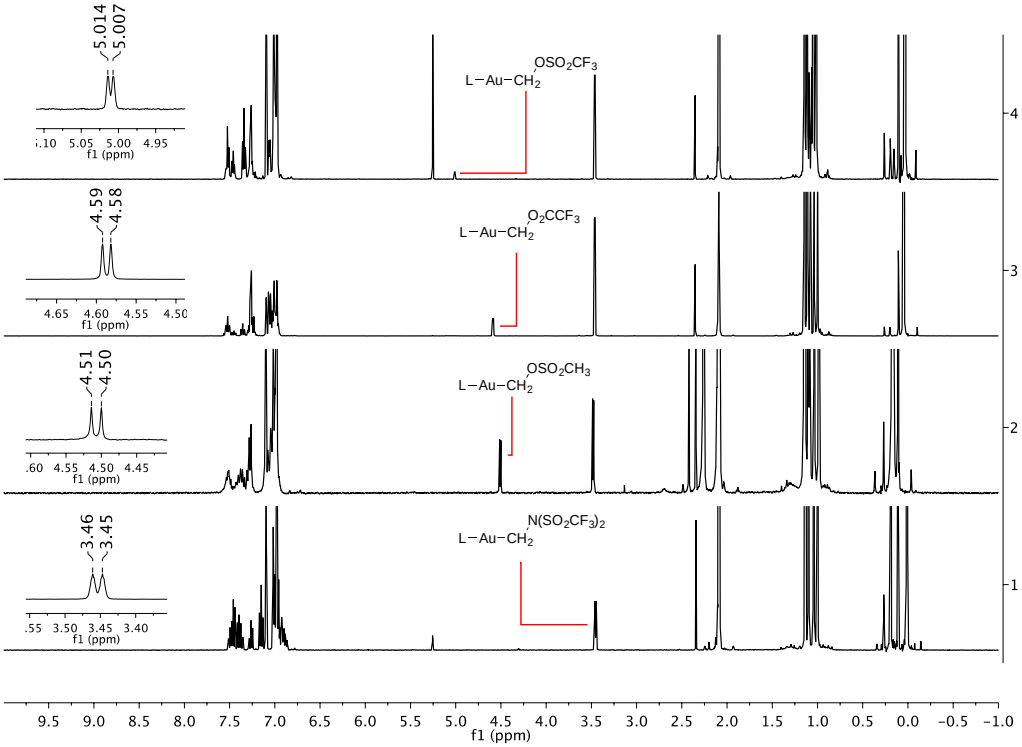


Figure S6. Observable intermediates of the type (JohnPhos)$AuCH_2X$ after the activation of complex **1a** with 1) $TMSNTf_2$, 2) $TMSOSO_2CH_3$, 3) $TMSOOCCF_3$ and 4) TMSOTf in toluene-d_8 at room temperature.

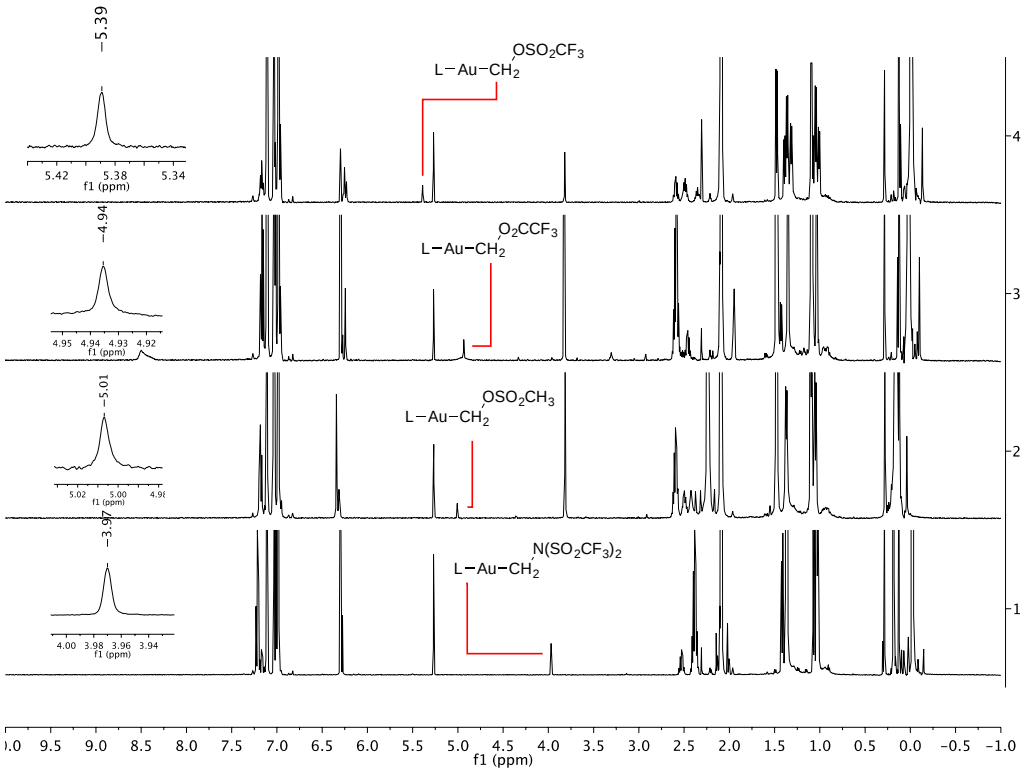


Figure S7. Observable intermediates of the type (IPr)AuCH$_2$X after the activation of complex **1c** with 1) TMSNTf$_2$, 2) TMSOSO$_2$CH$_3$, 3) TMSOOCCF$_3$ and 4) TMSOTf in toluene-d_8 at 273 K.

3.4. In presence of olefins, formation of cyclopropanes

General Procedure A, using silver salts:

In a glovebox, 0.017 mmol of carbenoid complex (either 9.3 mg **1a**, 10.5 mg **1c** or 15.2 mg **1d**) was put into a glass vial together with the corresponding olefin (20 equivalents, 0.340 mmol, 34.4 μL cyclohexene or 31.1 mg norbornene) and the internal standard 0.018 mmol, 3.0 μL diphenylmethane. The mixture was dissolved in 0.5 mL CD_2Cl_2 and transferred to a NMR tube capped with a rubber septum. Separately 0.020 mmol, 7.9 mg of $AgNTf_2$ was dissolved in 0.2 mL of toluene-d_8 and kept in a 1 mL plastic syringe protected from air. Outside the glovebox in a cooling bath kept at -40 ºC the silver solution was added over the mixture in the NMR tube. The tube was shaken and left warming up to room temperature. The yield was calculated by integration of the ^{1}H NMR signals of the cyclopropanes and the internal standard using equation SE1.

General Procedure B, using TMS compounds:

In a glovebox, 0.017 mmol of carbenoid complex (either 9.3 mg **1a**, 10.5 mg **1c** or 15.2 mg **1d**) was put into a glass vial together with the corresponding olefin (20 equivalents, 0.340 mmol, 34.4 μL cyclohexene or 31.1 mg norbornene) and the internal standard 0.018 mmol, 3.0 μL diphenylmethane. The mixture was dissolved in 0.5 mL CD_2Cl_2 and transferred to a NMR tube capped with a rubber septum. Separately 0.035 mmol, 8 μL of $TMSNTf_2$ were taken in a microsyringe protected from air. Outside the glovebox in a cooling bath kept at -80 ºC the $TMSNTf_2$ was added over the mixture in the NMR tube. The tube was shaken and immediately transferred to the NMR instrument where ^{1}H NMR spectra were measured at temperatures ranging -80 to 25 ºC. The yield was calculated by integration of the ^{1}H NMR

signals of the cyclopropanes and the internal standard at the temperature of maximum yield using equation SE3.

Chemical shifts of the formed cyclopropanes were in agreement to previously reported data.[3] Mass spectra obtained from CGMS analysis of the reaction mixtures confirmed formation of the expected products.

$$Yield(\%) = \frac{\left(\frac{N^{H}_{I.S.} * n_{I.S.} * I_{prod}}{I_{I.S.} * N^{H}_{prod.}}\right)}{n_{carbenoid}} * 100$$

Equation SE3. Where: $N^{H}_{I.S.}$ = number of protons corresponding to the integrated signal of the internal standard (for diphenylmethane $N^{H}_{I.S.}$ = 2), $n_{I.S.}$ = amount of internal standard used (0.017 mmol), I_{prod} = Measured integral of the product, $I_{I.S.}$ = Measured integral of the internal standard, $N^{H}_{prod.}$ = number of protons corresponding to the integrated signal of the products (for cyclopropanes $N^{H}_{prod.}$ = 1, for cycloheptatrienes $N^{H}_{prod.}$ = 2), $n_{carbenoid}$ = amount of starting carbenoid complex (0.018 mmol).

Representative analytical data

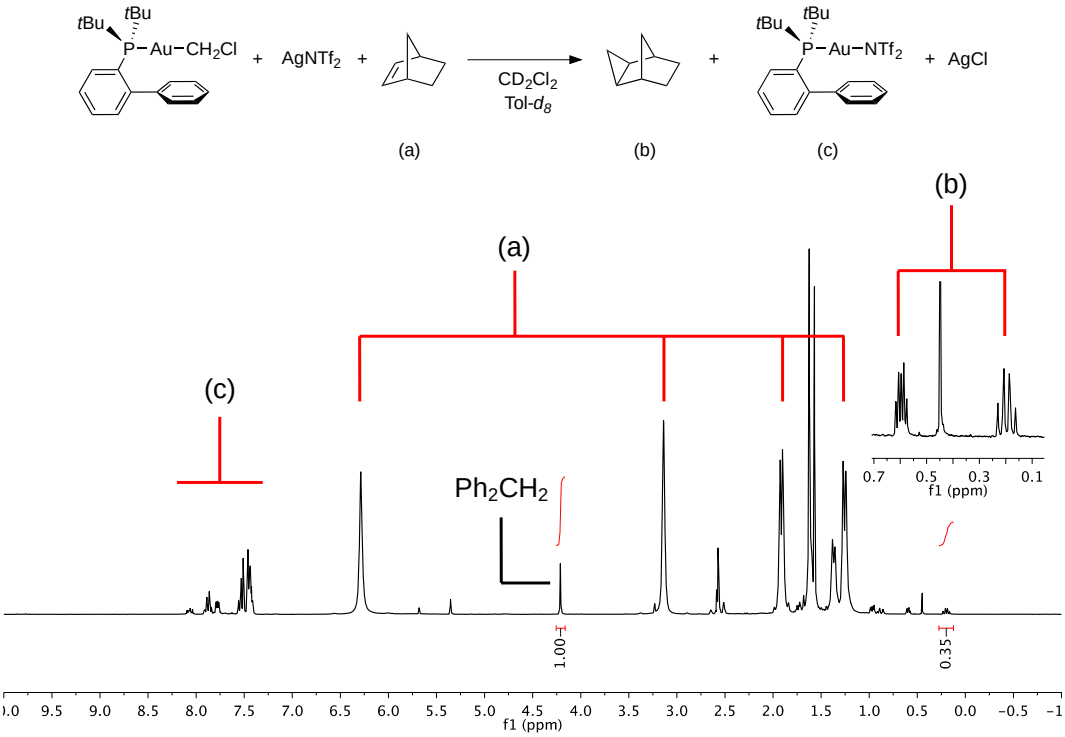


Figure S8. Typical ^{1}H NMR spectrum obtained during the cyclopropanation of norbornene with complex **1a** and $AgNTf_2$. Diphenylmethane as internal standard.

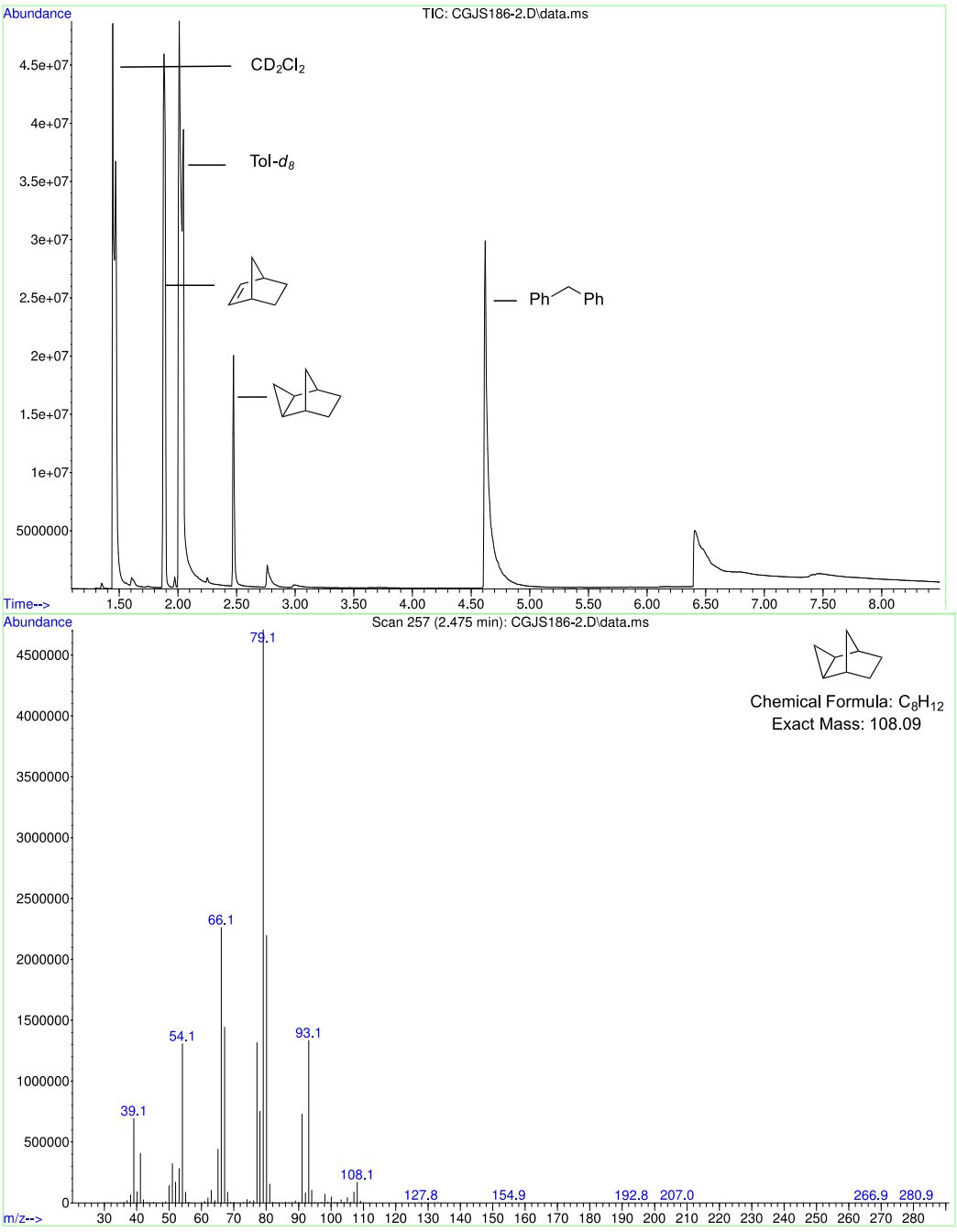


Figure S9. GC-MS trace and MS spectrum obtained during the cyclopropanation of norbornene with complex **1a** and $AgNTf_2$.

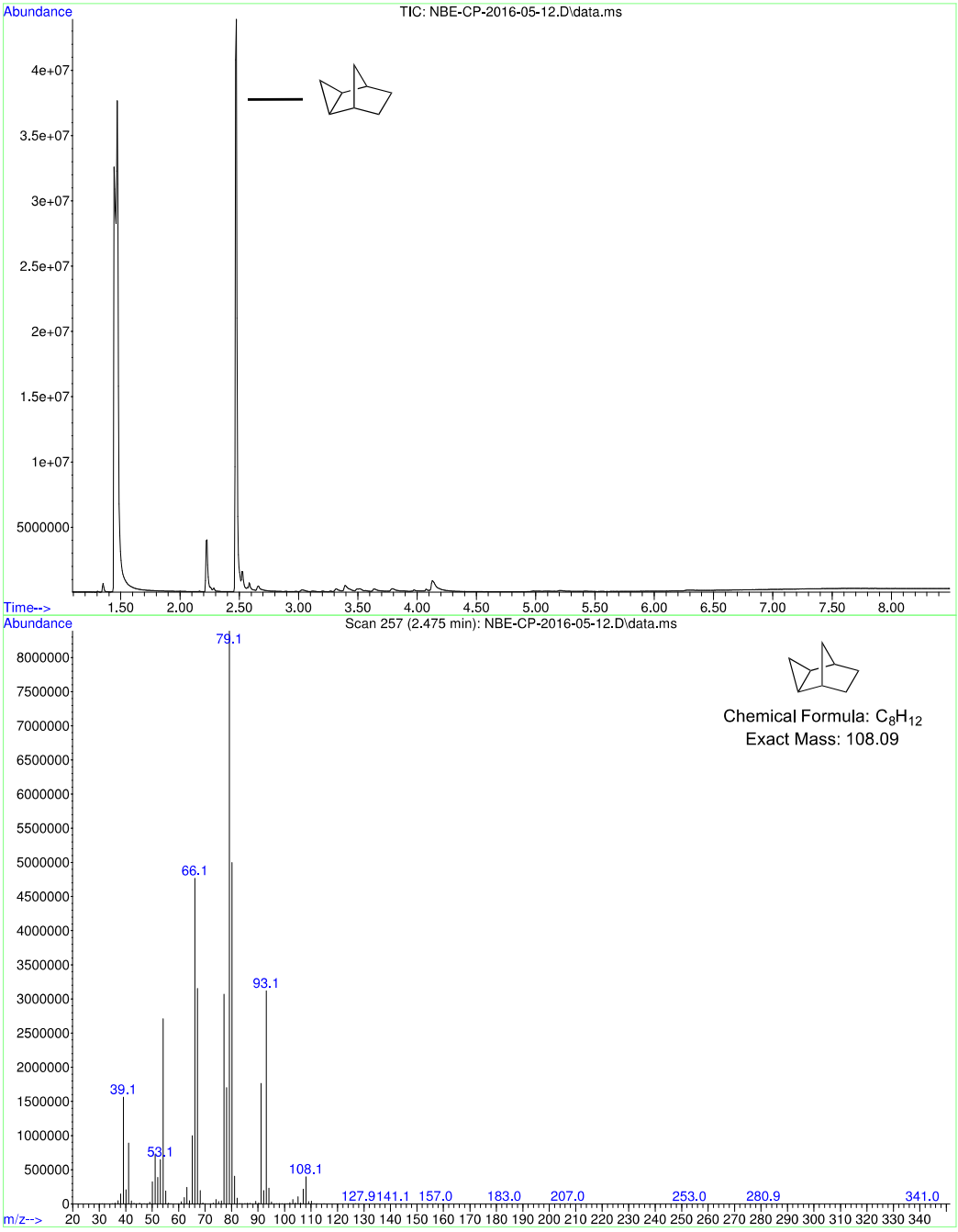


Figure S10. GC-MS trace and MS spectrum of an authentic sample of exo-tricyclo[3.2.1.$0^{2,4}$]octane.

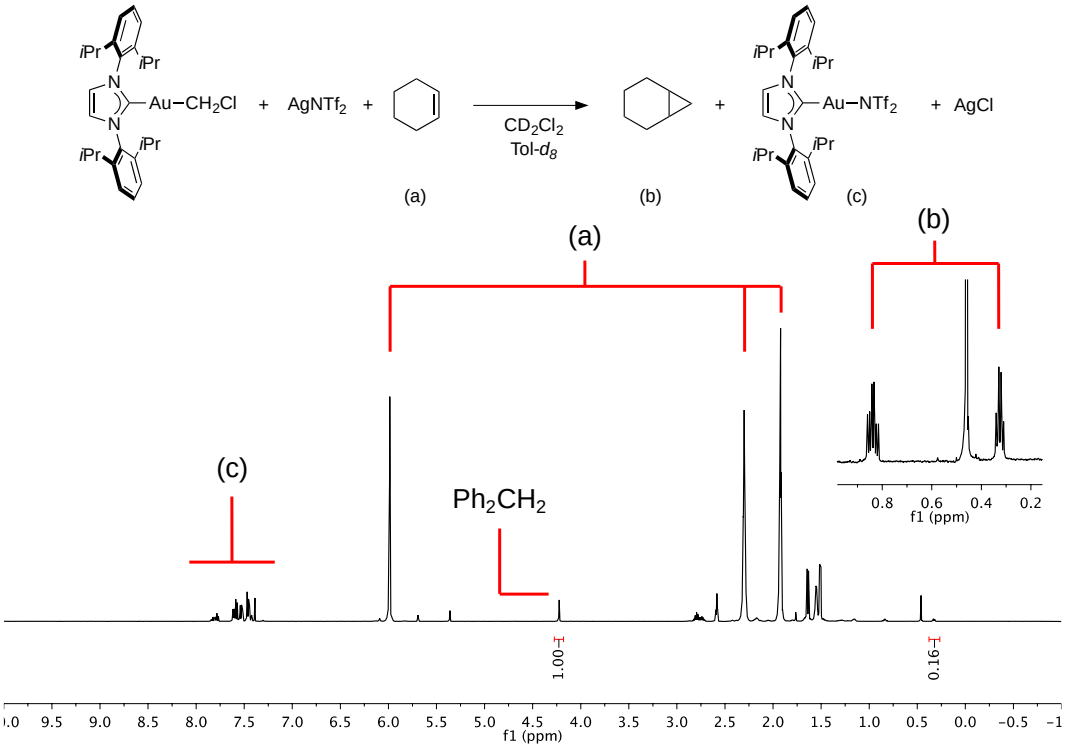


Figure S11. Typical ^{1}H NMR spectrum obtained during the cyclopropanation of cyclohexene with complex **1c** and $AgNTf_2$. Diphenylmethane as internal standard.

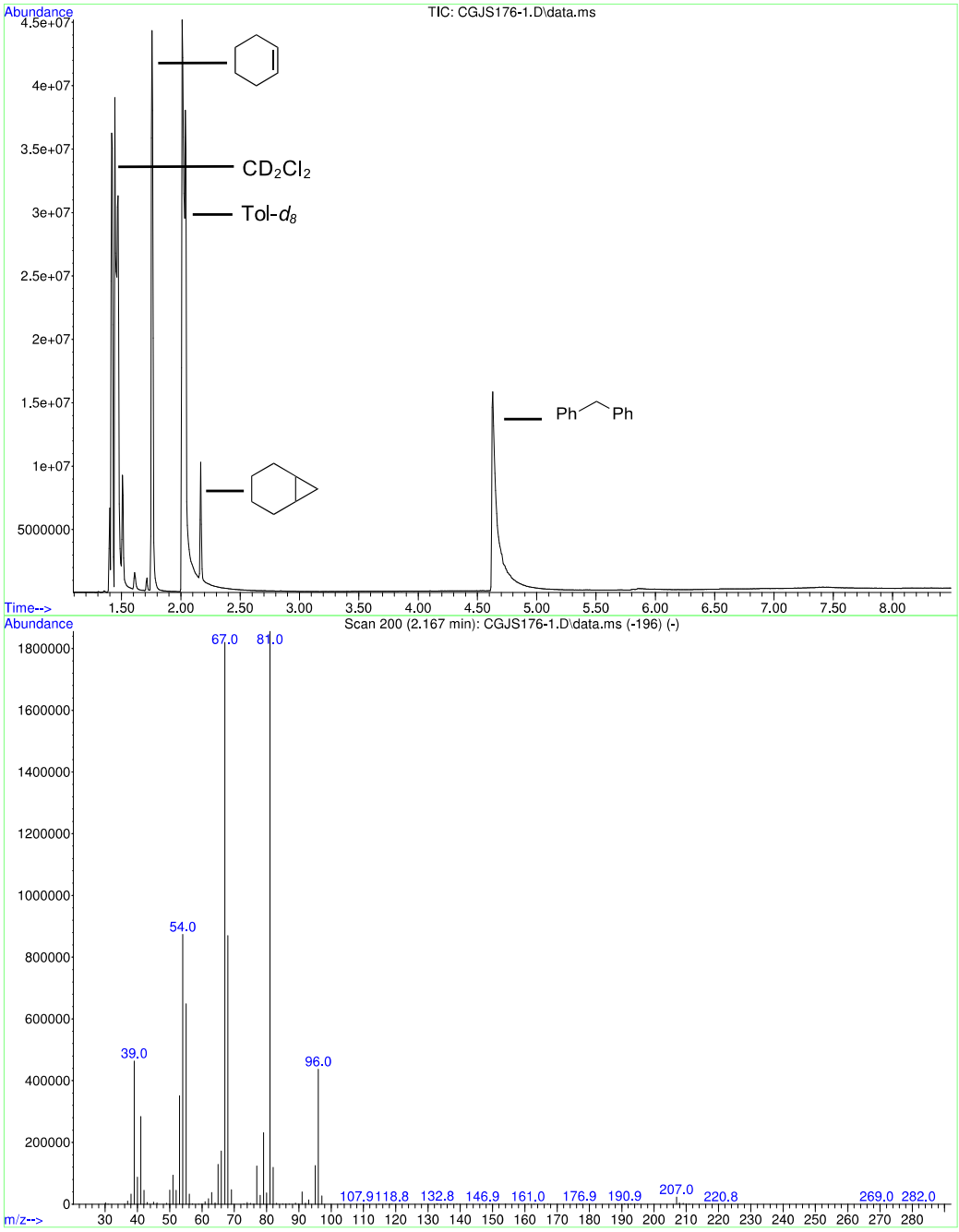


Figure S12. GC-MS trace and MS spectrum obtained during the cyclopropanation of cyclohexene with complex **1c** and $AgNTf_2$.

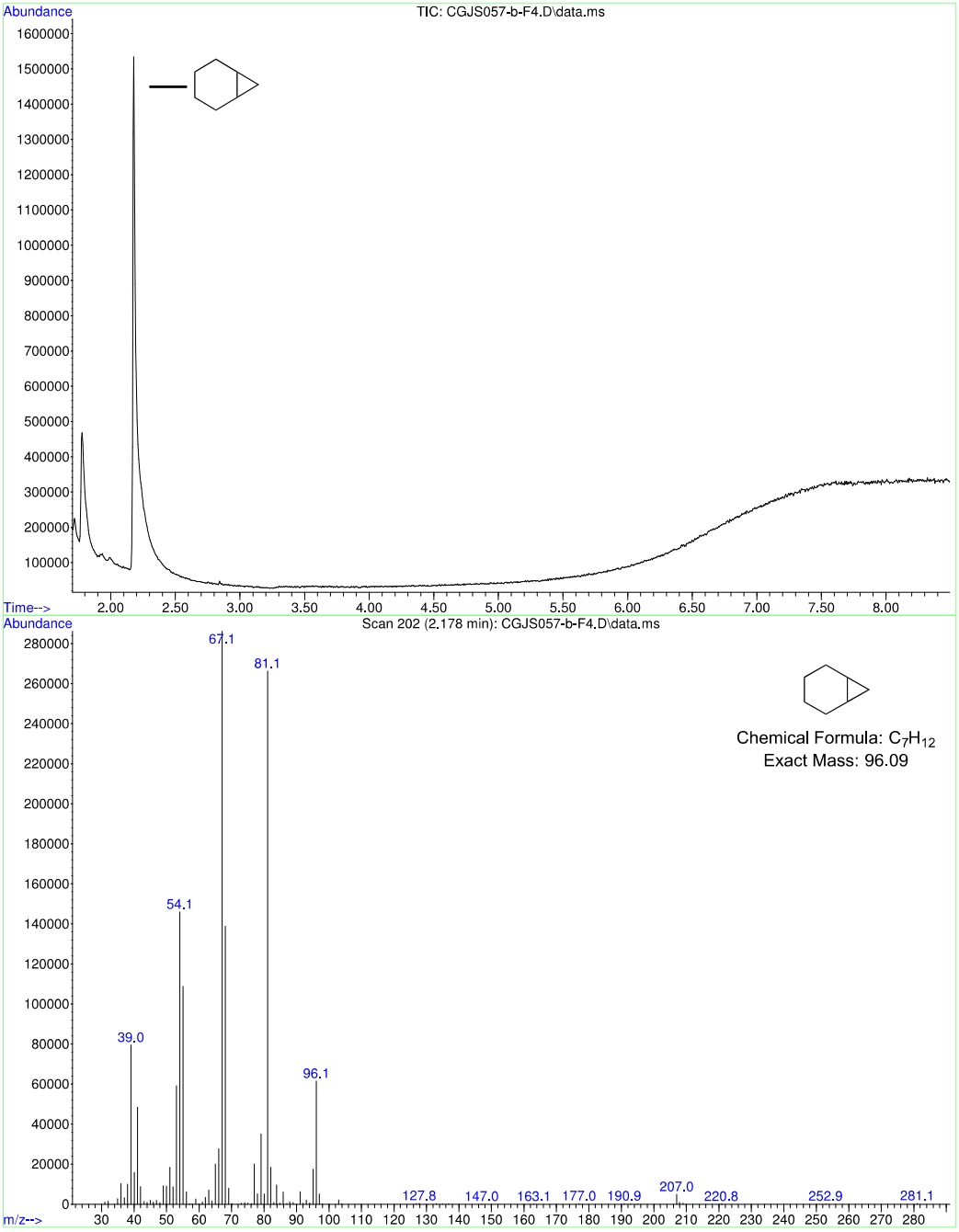


Figure S13. GC-MS trace and MS spectrum of an authentic sample of bicyclo[4.1.0]heptane.

Table S2. Yields for cyclopropanation of cyclohexene and norbornene with complexes **1a**, **1c** and **1d.** Procedure A.

Entry	Complex	Olefin	Integral I.S.	Integral Cyclop.	Yield (%)
1	**1a**	Cyclohexene	1145.05	280.25	51.82
2	**1a**	Cyclohexene	1107.57	355.89	68.04
				Average	59.93
3	**1a**	Norbornene	791.24	294.48	78.81
4	**1a**	Norbornene	2181.91	712.04	69.11
				Average	73.96
5	**1c**	Cyclohexene	1164.31	231.19	39.71

6	**1c**	Cyclohexene	950.15	225.84	50.33
				Average	45.02
7	**1c**	Norbornene	935.02	183.28	41.51
8	**1c**	Norbornene	2045.81	583.02	60.34
				Average	50.92
9	**1d**	Cyclohexene	989.72	38.91	8.28
10	**1d**	Cyclohexene	1000†	0	0
				Average	4.14
11	**1d**	Norbornene	1000†	0	0
12	**1d**	Norbornene	1000†	0	0
				Average	0

†Arbitrary integral assigned when no product could be detected.

Table S3. Yields for cyclopropanation of cyclohexene and norbornene with complexes **1a**, **1c** and **1d**. Procedure B.

Entry	Complex	Olefin	Integral I.S.	Integral Cyclop.	Yield (%)
1	**1a**	Cyclohexene	1551.35	367.39	50.15
2	**1a**	Cyclohexene	1101.78	270.75	52.04
				Average	51.10
3	**1a**	Norbornene	1174.46	550.38	99.23
4	**1a**	Norbornene	1012.27	454.01	94.97
				Average	97.10
5	**1c**	Cyclohexene	1310.17	462.89	74.81
6	**1c**	Cyclohexene	1787.82	496.93	58.86
				Average	66.84
7	**1c**	Norbornene	1409.69	428.74	64.40
8	**1c**	Norbornene	1399.73	570.28	86.27
				Average	75.34
9	**1d**	Cyclohexene	1000†	0	0
10	**1d**	Cyclohexene	1000†	0	0
				Average	0
11	**1d**	Norbornene	1000†	0	0
12	**1d**	Norbornene	1000†	0	0
				Average	0

†Arbitrary integral assigned when no product could be detected.

3.5. In benzene, formation of cycloheptatriene

General Procedure A:

In a glovebox, 0.017 mmol of carbenoid complex (either 9.3 mg **1a**, 10.5 mg **1c** or 15.2 mg **1d**) was put into a glass vial together with the internal standard 0.018 mmol, 3.0 μL diphenylmethane. The mixture was dissolved in 0.5 mL benzene-d_6 and transferred to a NMR tube capped with a rubber septum. Separately 0.020 mmol, 7.9 mg of $AgNTf_2$ was dissolved in 0.2 mL of benzene-d_6 and kept in a 1 mL plastic syringe protected from air. Outside the glovebox the silver solution was added over the mixture in the NMR tube at room temperature. The conversion was calculated by integration of the ^{1}H NMR signals of the cycloheptatriene and the internal standard.

General Procedure B:

In a glovebox, 0.017 mmol of carbenoid complex (either 9.3 mg **1a**, 10.5 mg **1c** or 15.2 mg **1d**) was put into a glass vial together with the internal standard 0.018 mmol, 3.0 μL diphenylmethane. The mixture was dissolved in 0.5 mL benzene-d_6 and transferred to a NMR tube capped with a rubber septum. Separately, 0.035 mmol, 8 μL of $TMSNTf_2$ was taken in a microsyringe and protected from air. Outside the glovebox at room temperature $TMSNTf_2$ was added over the mixture in the NMR tube. The conversion was calculated by integration of the ^1H NMR signals of the cycloheptatriene and the internal standard using equation SE1.

Chemical shift of the formed cyclopropanes were in agreement to previously reported data.[4] In order to confirm the identity of the product, the reaction was repeated in non-deuterated benzene and its proton spectrum acquired using an external C_6D_6 reference.

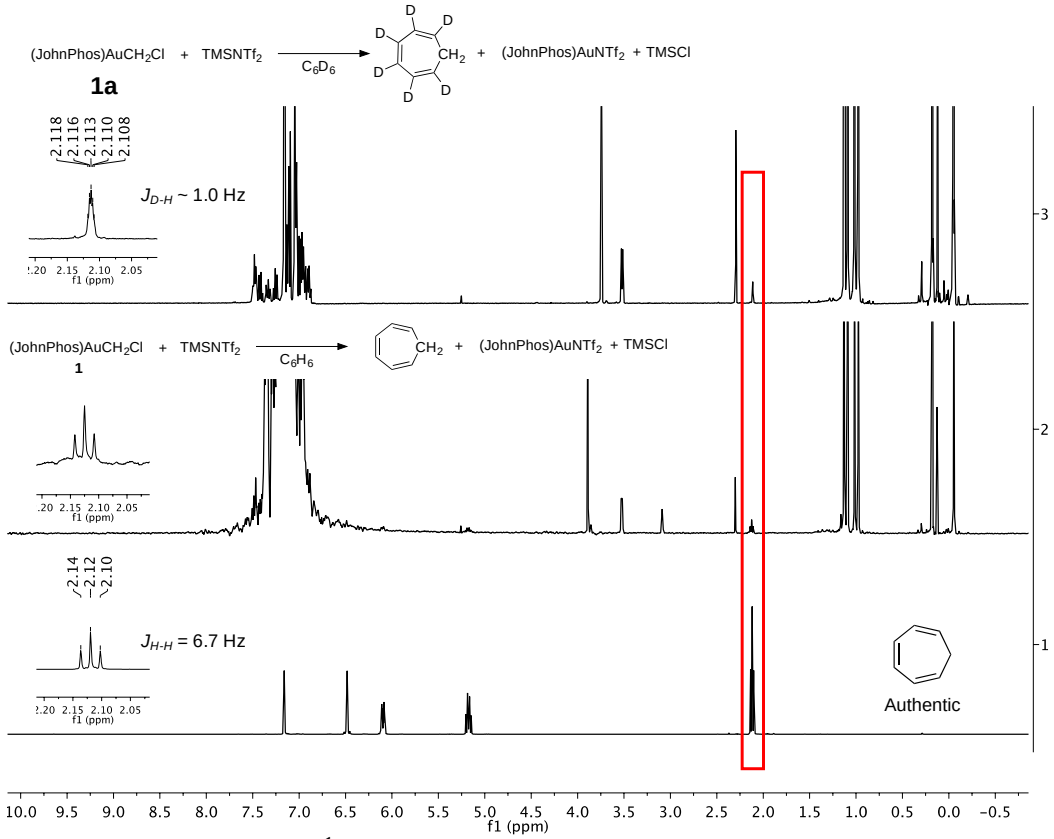


Figure S14. Comparison of ^1H NMR spectra of the reaction mixtures during ring expansion of C_6D_6 (top), C_6H_6 (middle) under conditions B and authentic cycloheptatriene (bottom).

Table S4. Yields for the ring expansion of C_6D_6 complexes **1**, **3** and **4**.

Entry	Complex	Procedure	Integral I.S.	Integral CHT	Yield (%)
1	**1a**	A	3062.93	229.33	7.93
2	**1a**	A	2036.54	106.18	5.52
				Average	6.72
3	**1a**	B	3231.52	360.02	11.79
4	**1a**	B	3411.11	404.24	12.54
				Average	12.16
5	**1c**	A	2456.09	322.26	13.89

6	**1c**	A	7337.91	675.81	9.75
				Average	11.82
7	**1c**	B	3050.78	795.20	27.60
8	**1c**	B	3006.99	780.7	27.49
				Average	27.56
9	**1d**	A	2331.99	32.99	1.41
10	**1d**	A	1000†	0	0
				Average	0.70
11	**1d**	B	2432.51	102.76	4.47
12	**1d**	B	1000†	0	0
				Average	2.23

†Arbitrary integral assigned when no product could be detected.

3.6. Kinetic measurements

Reaction of gold carbenoid **1a** with AgOTf in toluene-d_8 was monitored by ^{1}H NMR at various temperatures. The rate determined constants allowed the calculation of the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the initial exchange of chloride for triflate (**1a** to **7a**) and the subsequent decay of **7a** into **9a** and ethylene. In a typical experiment, inside the glovebox, 0.70 mL of a stock solution containing carbenoid complex **1a** (0.0262 mmol/mL) and diphenylmethane as internal standard (0.0262 mmol/mL) was put in a NMR tube and capped with a rubber septum. A syringe was loaded with 0.30 mL of a stock solution of AgOTf (0.613 mmol/mL) and protected from air. Outside the glovebox, either at room temperature (for runs at or above room temperature) or at 253 K (for all other cases), the solution of AgOTf was added over the mixture in the NMR tube and immediately transferred to the NMR instrument. ^{1}H NMR spectra were acquired every 3 minutes after the temperature of the sample had stabilized.

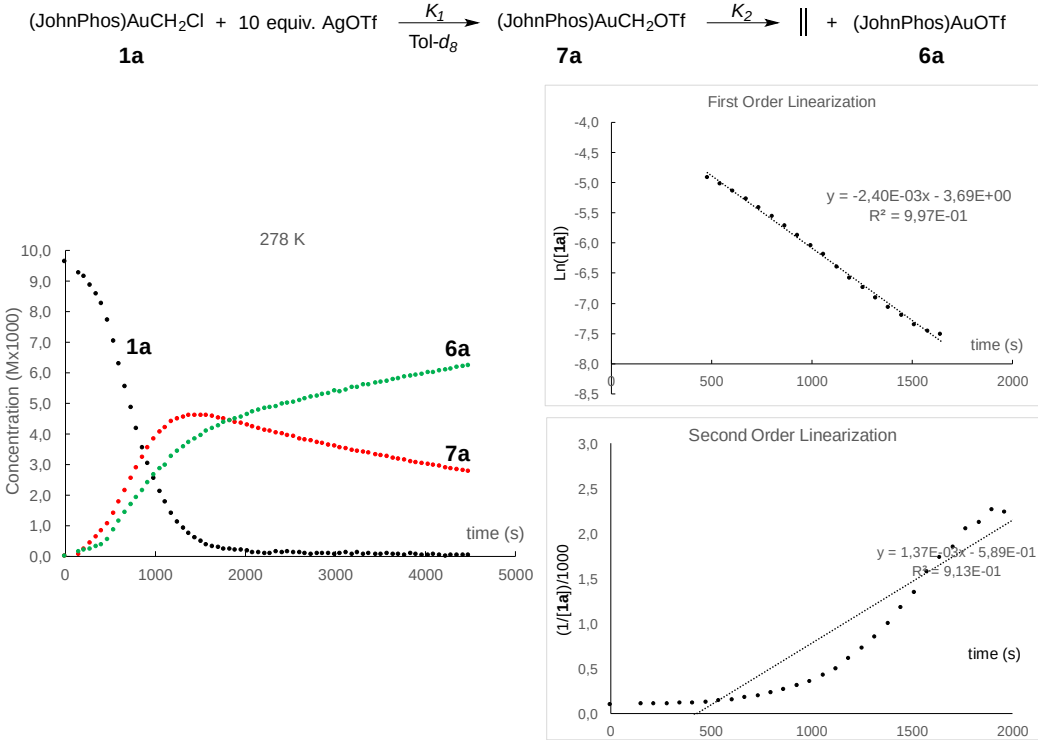


Figure S15. Left: typical concentration profiles measured for the reaction of **1a** with AgOTf at temperatures lower than room temperature. Right: corresponding first and second order linearization plots for the change of concentration of **1a** over time.

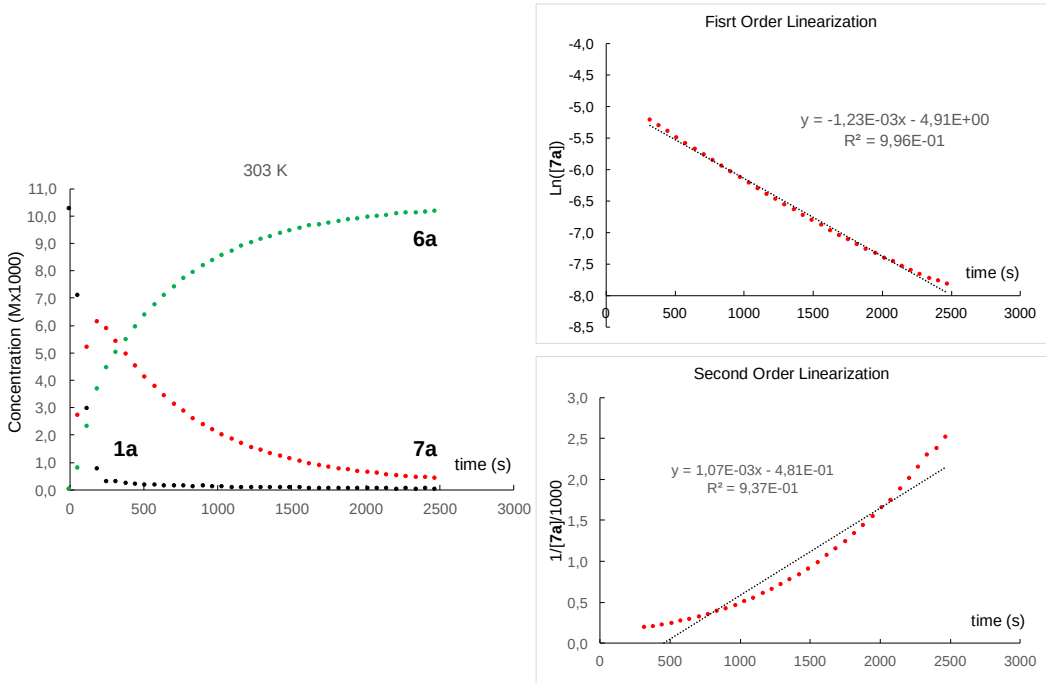


Figure S16. Left: typical concentration profiles measured for the reaction of **1a** with AgOTf at temperatures higher than room temperature. Right: corresponding first and second order linearization plots for the change of concentration of **7a** over time.

Table S5. Measured rate constants (average of two measurements).

T (K)	$k_{obs}(s^{-1})$	k_1 ($M^{-1}s^{-1}$)*	T (K)	k_2 (s^{-1})
263	5.44E-04	5.85E-03	288	3.13E-04
268	9.71E-04	1.04E-02	293	4.77E-04
273	1.29E-03	1.38E-02	296	7.47E-04
278	2.33E-03	2.50E-02	303	1.19E-03

*Under pseudofirst order conditions $k_1 = k_{obs}/[AgOTf]_0$ where $[AgOTf]_0$ = 0.09302 M

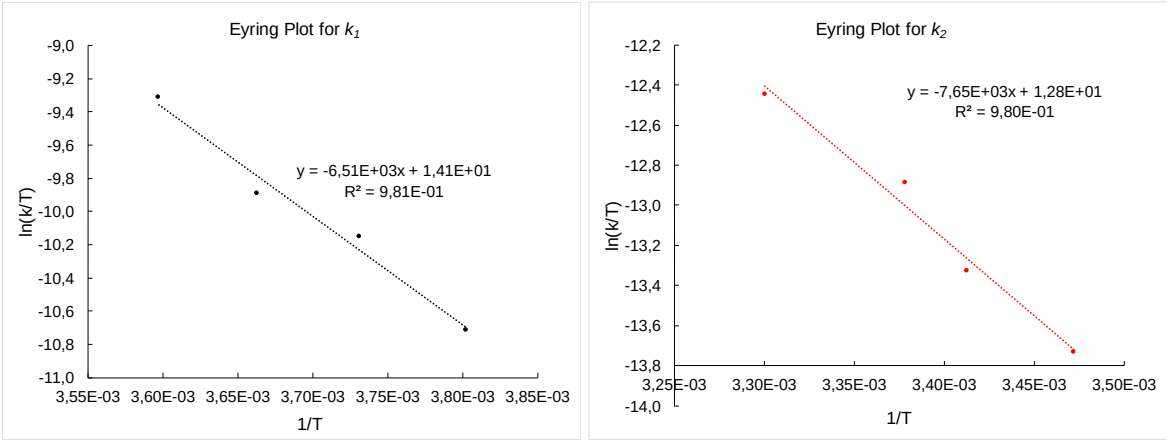


Figure S17. Eyring plots constructed with data from table S4.

Using the linearized Eyring equation[5] $ln\left(\frac{k}{T}\right) = \frac{-\Delta H^{\ddagger}}{R} \cdot \frac{1}{T} + ln\left(\frac{k_B}{h}\right) + ln\left(\frac{\Delta S^{\ddagger}}{R}\right)$ the activation parameters for the first (k_1: $\Delta H^{\ddagger}$ = 12.9 ± 0.5 kcal•mol^{-1} and $\Delta S^{\ddagger}$ = -19.2 ± 2 cal•mol^{-1}K^{-1}) and

second (k_2: $\Delta H^{\ddagger}$ = 15.0 ± 0.7 kcal•mol^{-1} and $\Delta S^{\ddagger}$ = -21.5 ± 2 cal•mol^{-1}K^{-1}) processes were calculated.

3.7. Activation of complex **9**

In a glovebox, complex **9** (0.016 mmol, 10.0 mg) was put into a glass vial together with the internal standard (diphenylmethane, 0.02 mmol, 3.4 μL), dissolved in 0.5 mL CD_2Cl_2 and transferred to a NMR tube capped with a rubber septum. Separately, TMSOTf (0.022 mmol, 4 μL) was taken in a microsyringe and protected from air. Outside the glovebox at room temperature TMSOTf was added over the mixture in the NMR tube. After NMR monitoring was finished, the mixture was filtered through a small pad of silica gel and rinsed with two portions of 0.5 mL CH_2Cl_2. The resulting solution was analyzed by GC-MS. The yield was calculated by integration of the GC-FID signals of the *cis*-stilbene, *trans*-stilbene, 1,2,3-triphenylcyclopropane and internal standard using equation SE4, the areas were correlated to the data obtained in an equimolar mixture of the products and the internal standard (0.02 mmol of every compound).

$$Yield(\%) = \frac{\left(\frac{A_{prod} * n_{I.S.} * A_{I.S.}^{eq.mix.}}{A_{I.S.} * A_{prod}^{eq.mix.}}\right)}{n_{prod}^{max}} * 100$$

Equation SE4. Where: A_{prod} = area corresponding to the integrated signal of the product, $n_{I.S.}$ = amount of internal standard used (0.02 mmol), $A^{eq.mix.}_{I.S.}$ = area corresponding to the integrated signal of the internal standard in the equimolar mixture used for the calibration, $A_{I.S.}$ = area corresponding to the integrated signal of the internal standard, $A^{eq.mix.}_{prod.}$ = area corresponding to the integrated signal of the product in the equimolar mixture used for the calibration, $n^{max}_{prod.}$ = maximum amount of product, 0.008 mmol for *cis* and *trans*-stilbene, 0.005 mmol for 1,2,3-triphenylcyclopropane.

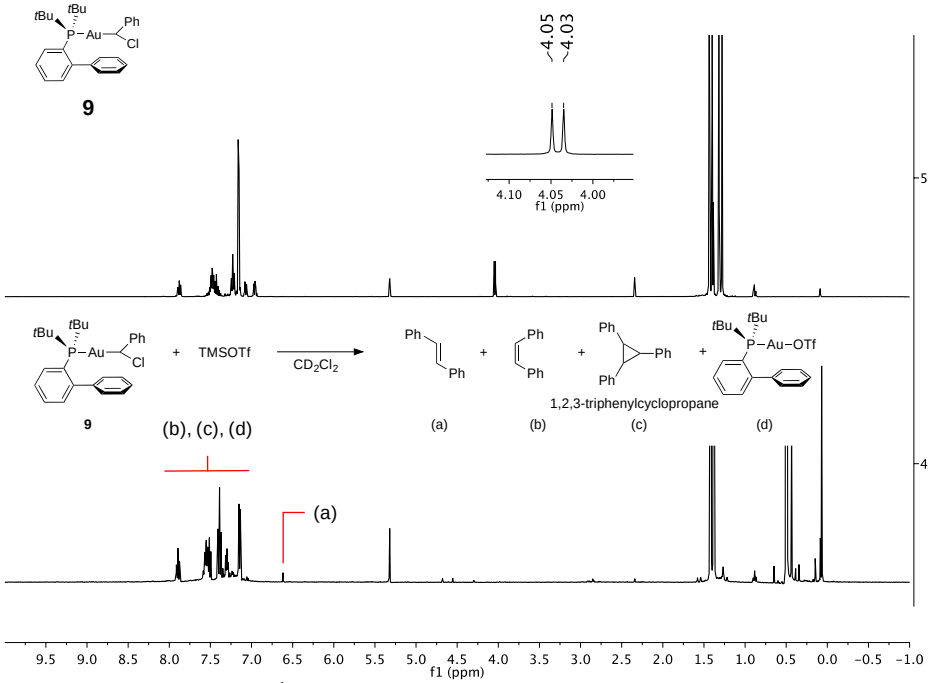


Figure S18. Comparison of ^{1}H NMR spectra of **9** before (top) and after activation with TMSOTf (bottom). Signal corresponding to *cis*-stilbene is clearly visible at 6.62 ppm. Other products were more reliably detected by GC-MS and GC-FID.

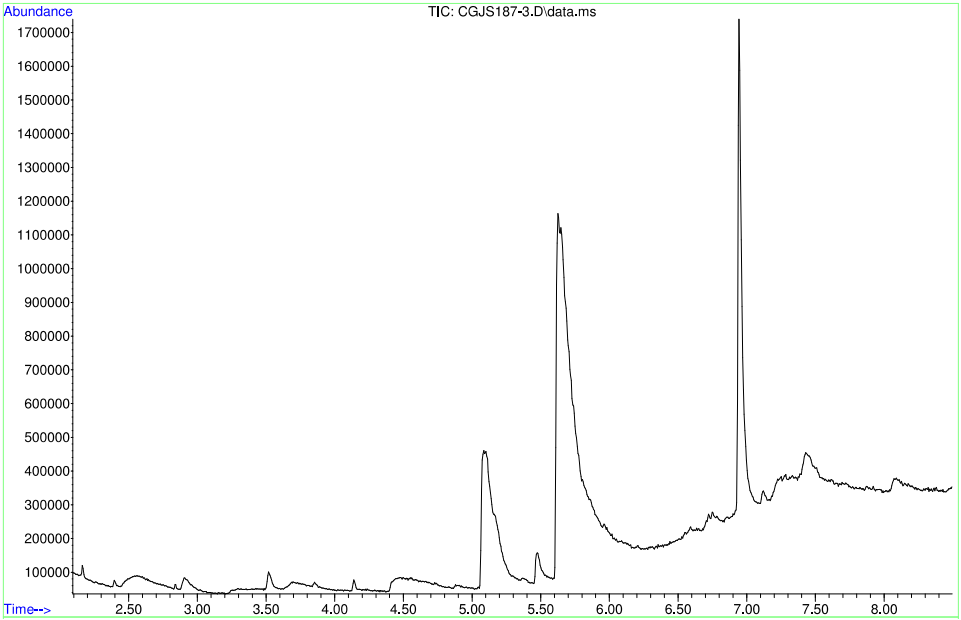


Figure S19. GC-MS chromatogram obtained after the activation of **9** with TMSOTf.

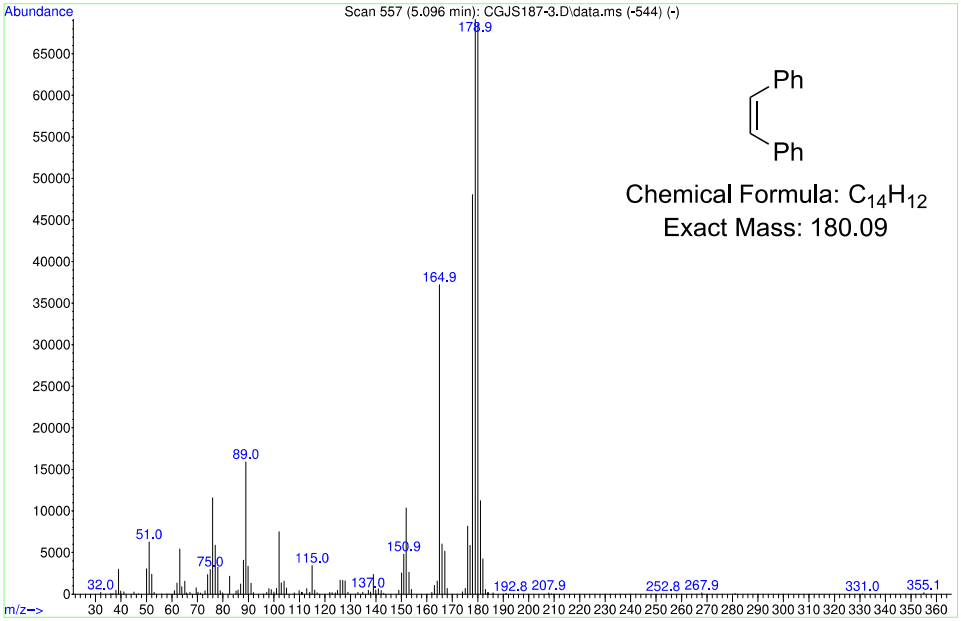


Figure S20. MS spectrum of peak at 5.096 min.

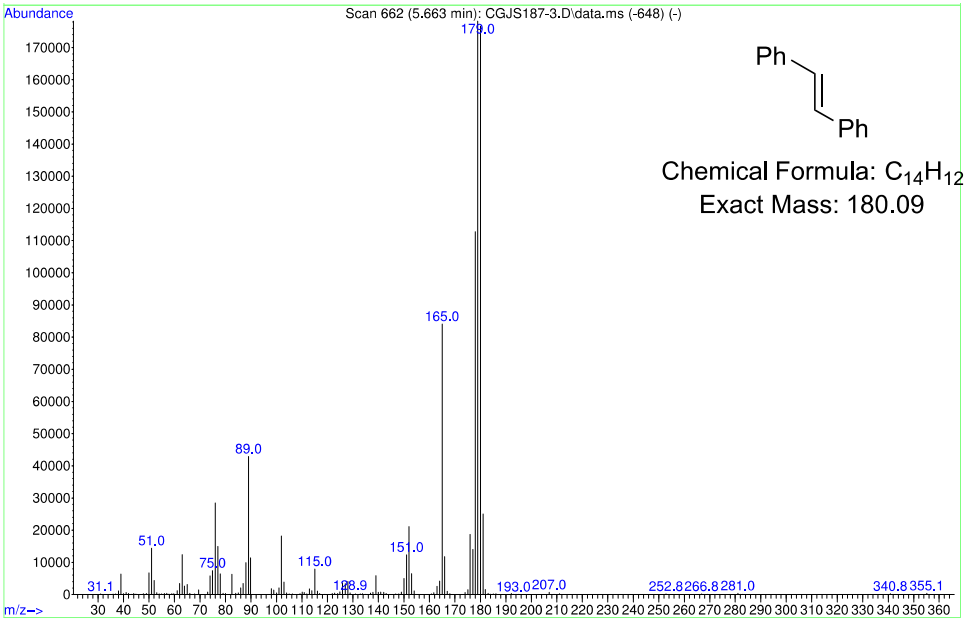


Figure S21. MS spectrum of peak at 5.663 min.

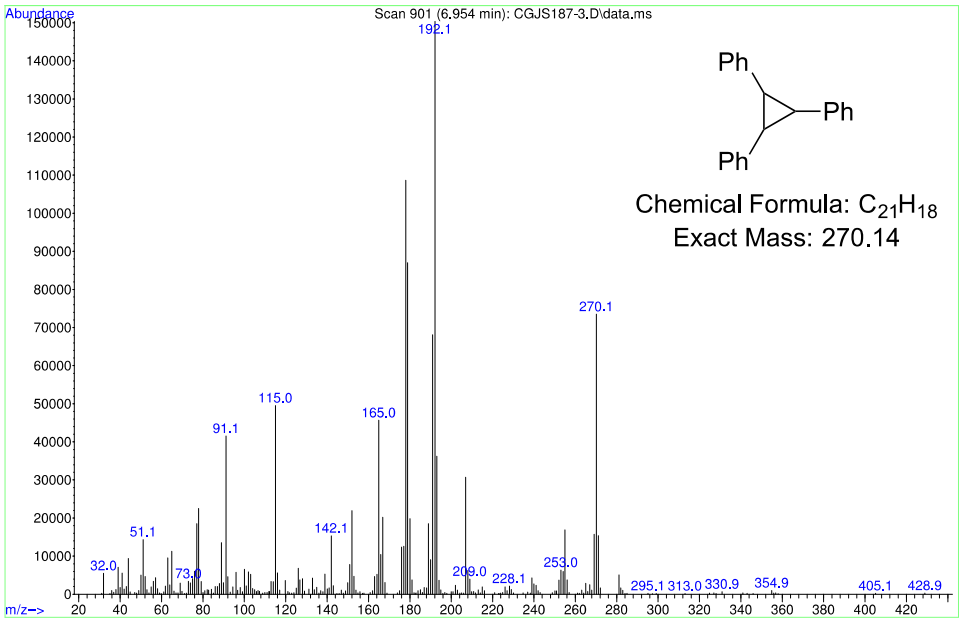


Figure S22. MS spectrum of peak at 6.954 min.

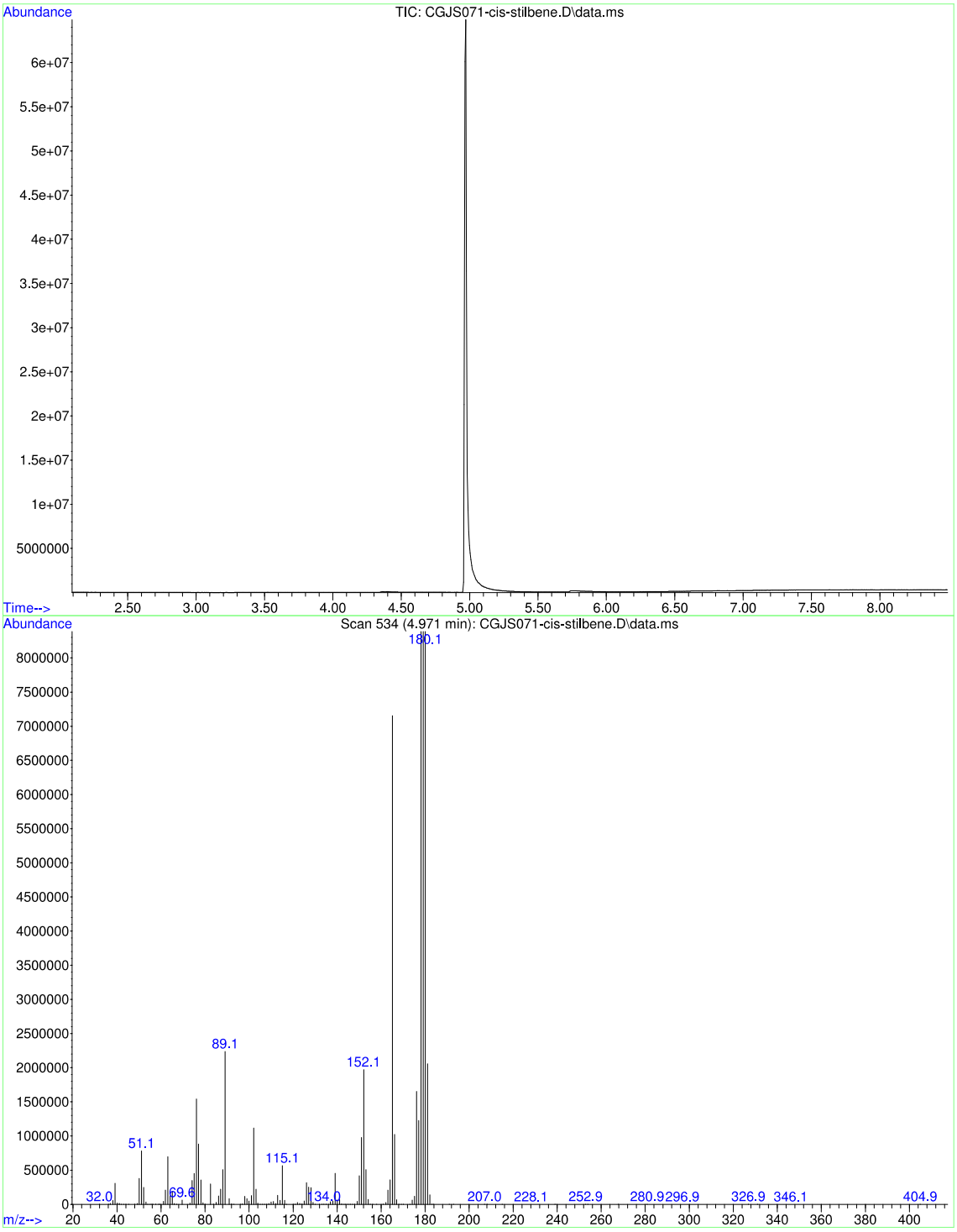


Figure S23. GC-MS trace and MS spectrum of authentic *cis*-stilbene.

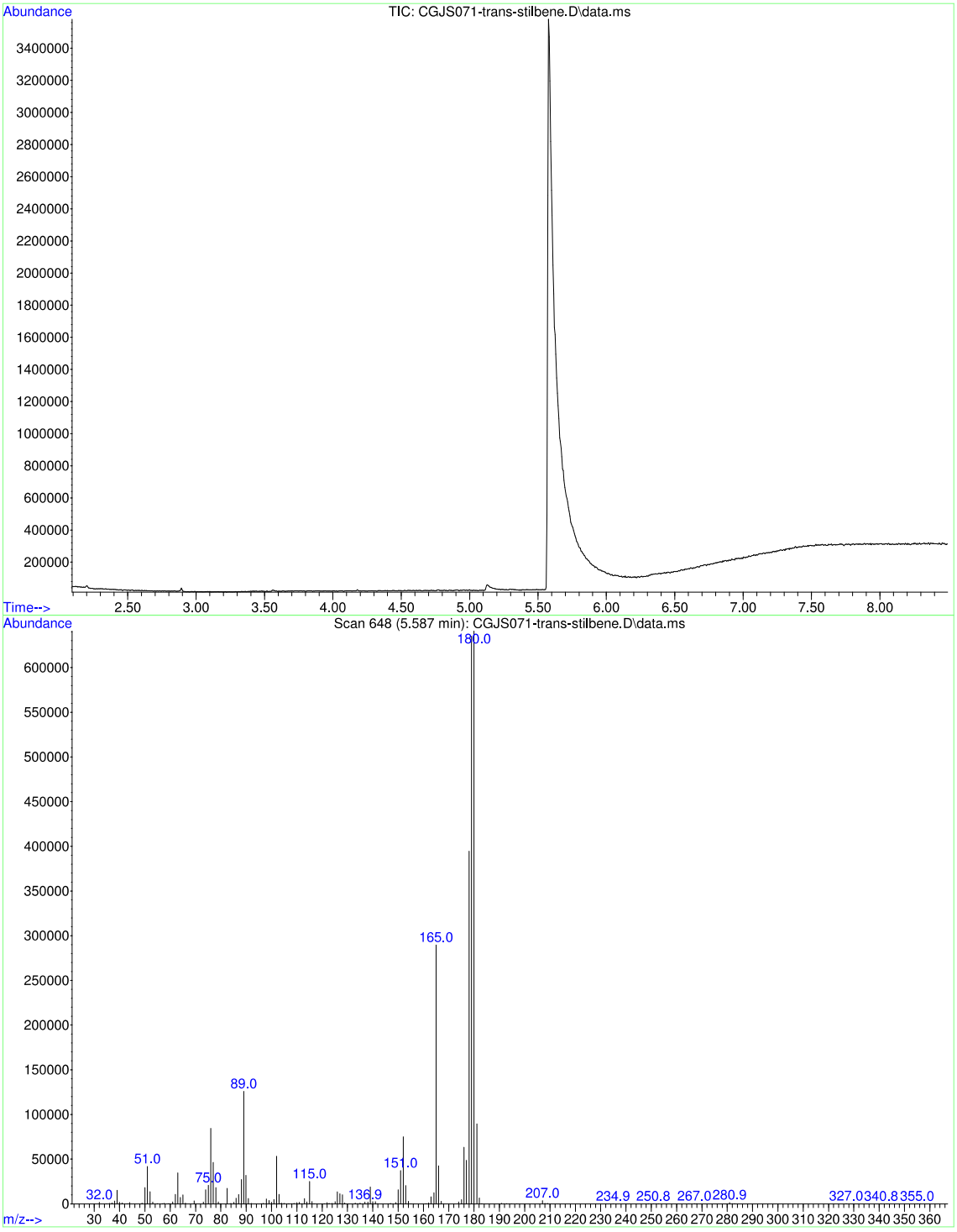


Figure S24. GC-MS trace and MS spectrum of authentic *trans*-stilbene.

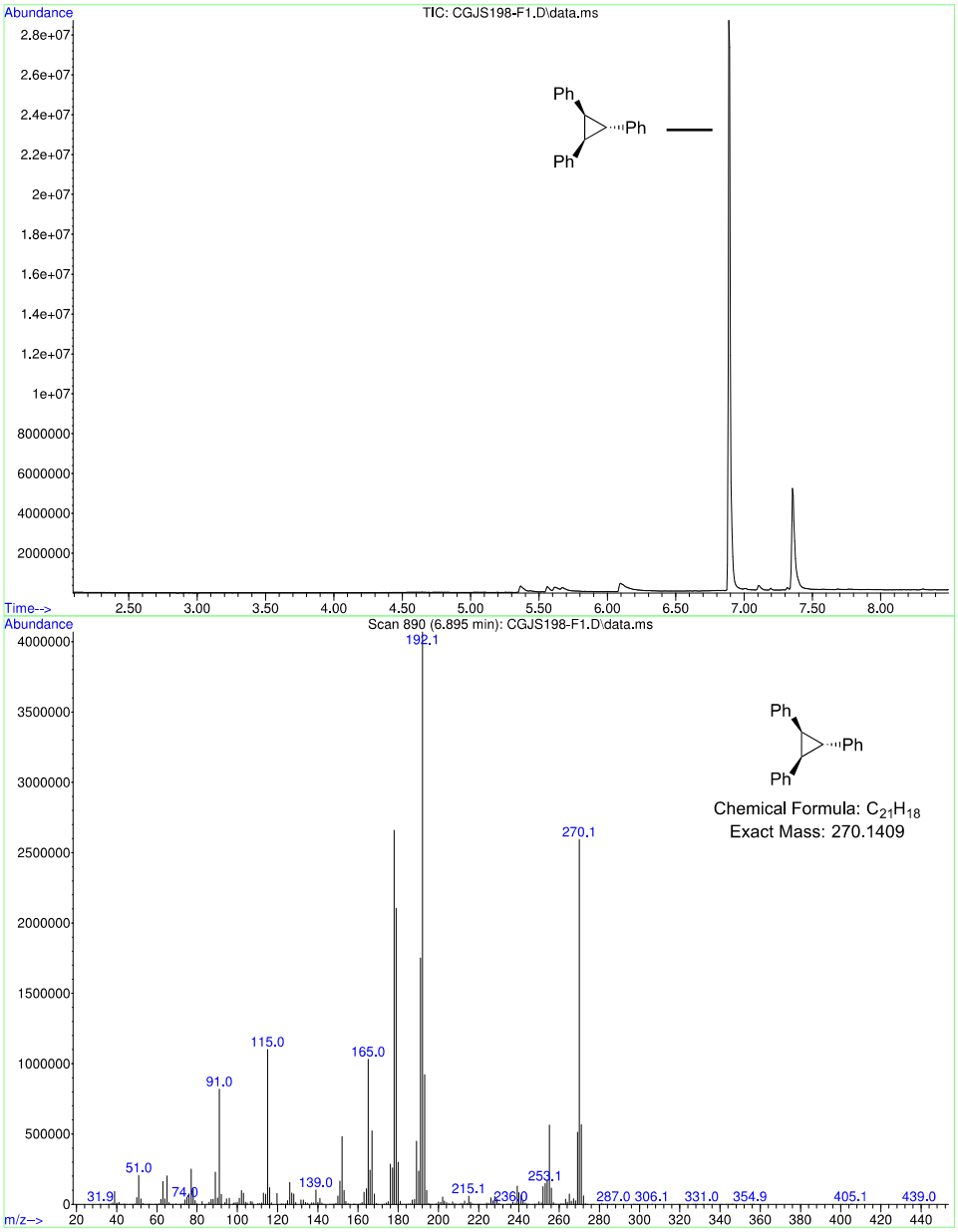


Figure S25. GC-MS trace and MS spectrum of authentic 1,2,3-triphenylcyclopropane.

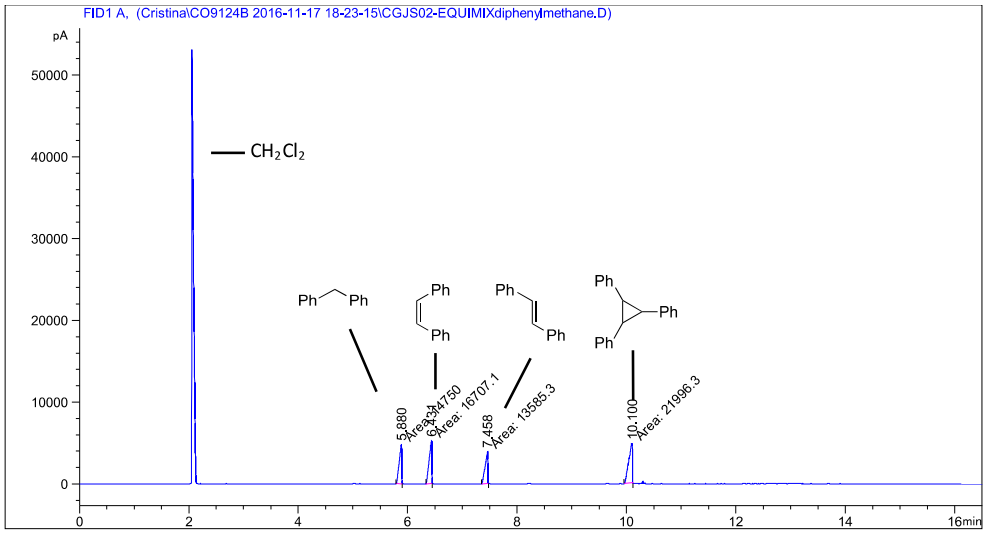


Figure S26. GC-FID chromatogram of the equimolar mixture of *cis*-stilbene, *trans*-stilbene, 1,2,3-triphenylcyclopropane and diphenylmethane.

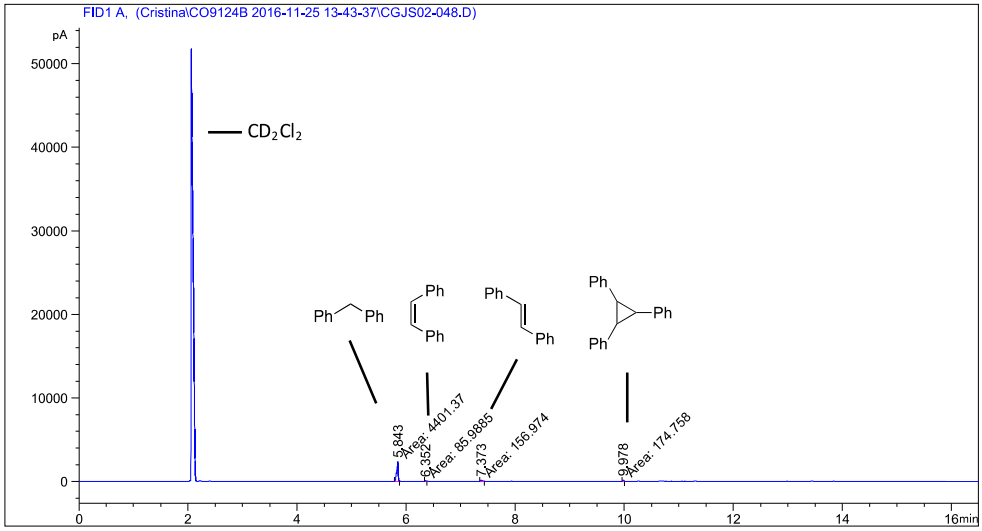


Figure S27. GC-FID chromatogram obtained after the activation of **9** with TMSOTf.

Table S6. Yields for *cis*-stilbene, *trans*-stilbene and 1,2,3-triphenylcyclopropane obtained after activation of **9** with TMSOTf.

Entry	Compound	Area I.S.	Area compound	Yield (%)
1	***cis*-stilbene**	5206.00	88.48	4.06
2		4401.37	85.99	4.31
			Average	4.19
3	***trans*-stilbene**	5206.00	197.12	11.11
4		4401.37	156.97	9.70
			Average	10.4
5	**1,2,3-triphenylcyclopropane**	5206.00	138.48	7.13
6		4401.37	174.76	9.70
			Average	8.41

4. X-Ray crystallography

4.1. Analysis of previously reported structures featuring a [MCH_2Cl] motif as per May 2016.

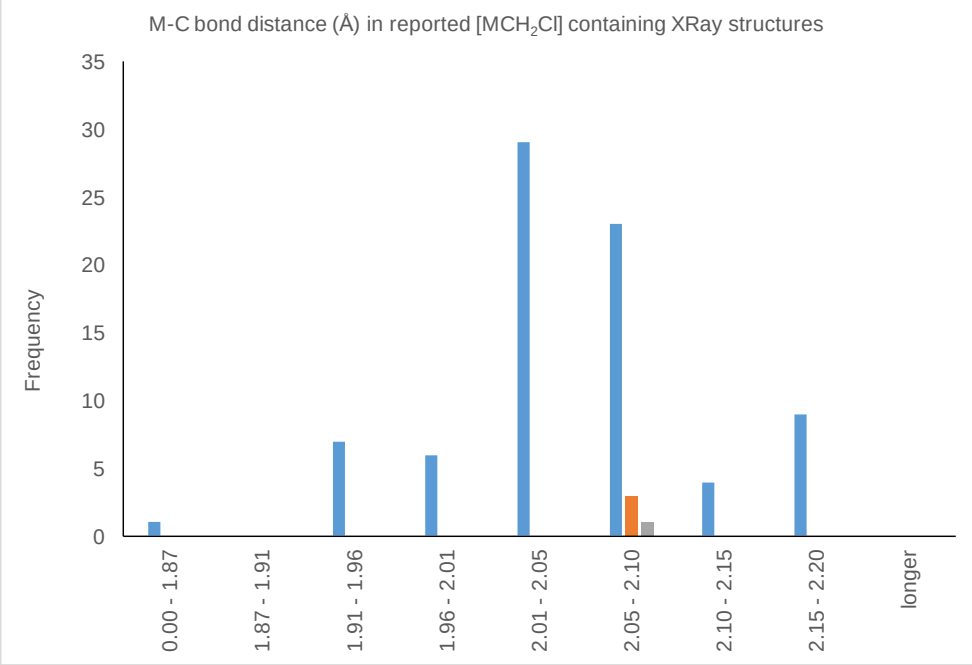


Figure S28. Histogram showing the distribution of M–C bond distances found in all currently published crystal structures featuring a [MCH_2Cl] (blue), new chloromethyl complexes **1a**, **1b** and **1c** (orange) and chloro(phenyl)methyl complex **9** (grey).

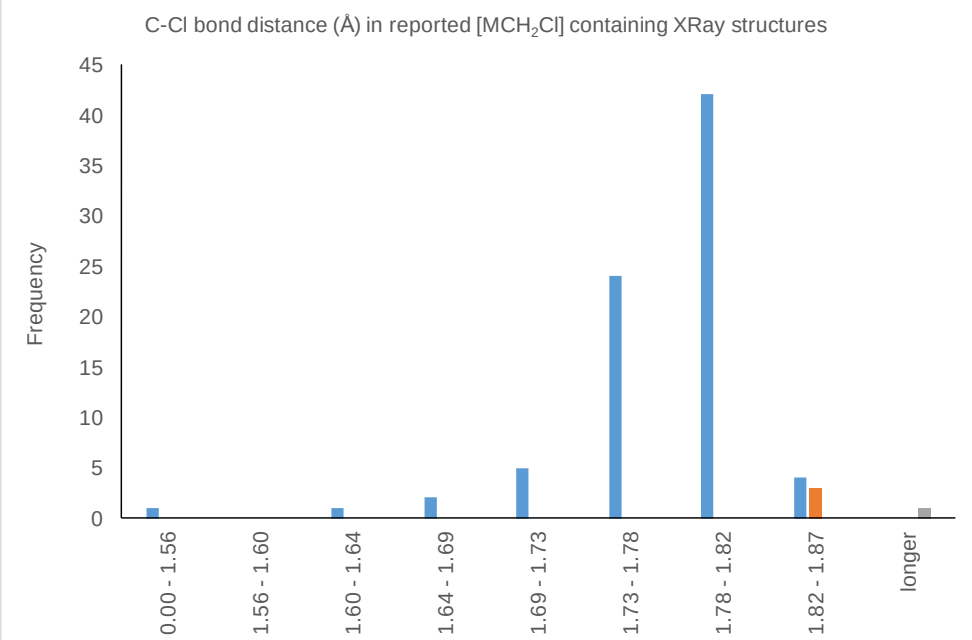


Figure S29. Histogram showing the distribution of C–Cl bond distances found in all currently published crystal structures featuring a [MCH_2Cl] (blue), new chloromethyl complexes **1a**, **1b** and **1c** (orange) and chloro(phenyl)methyl complex **9** (grey).

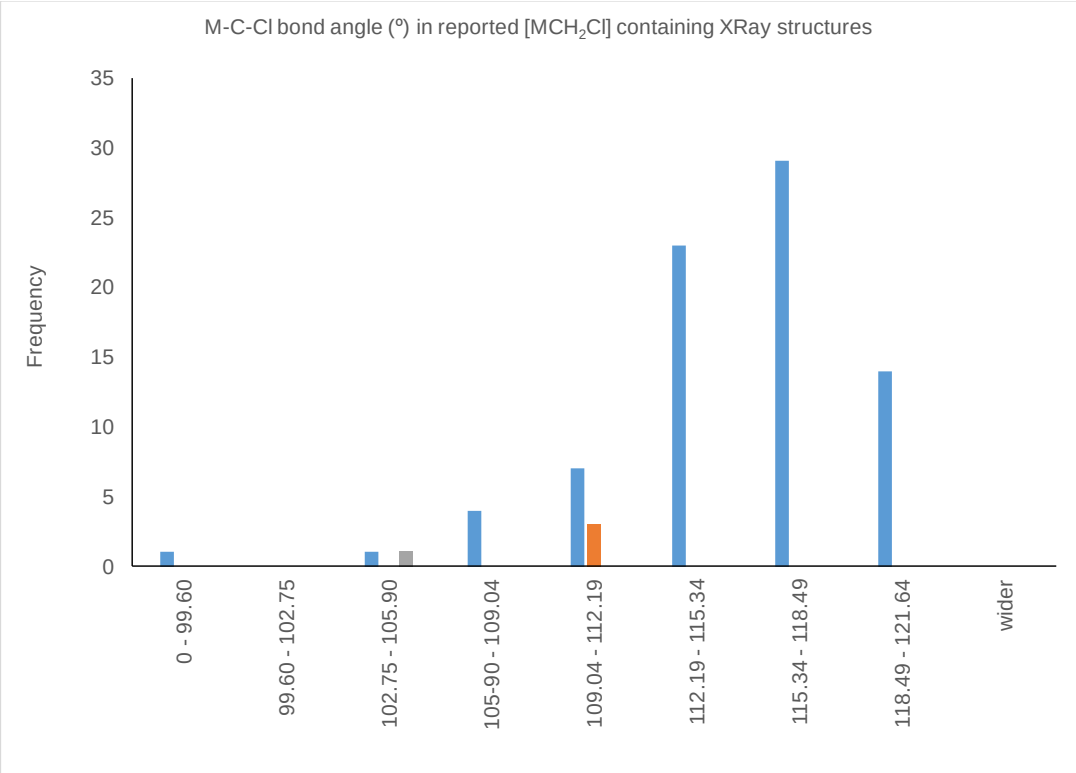
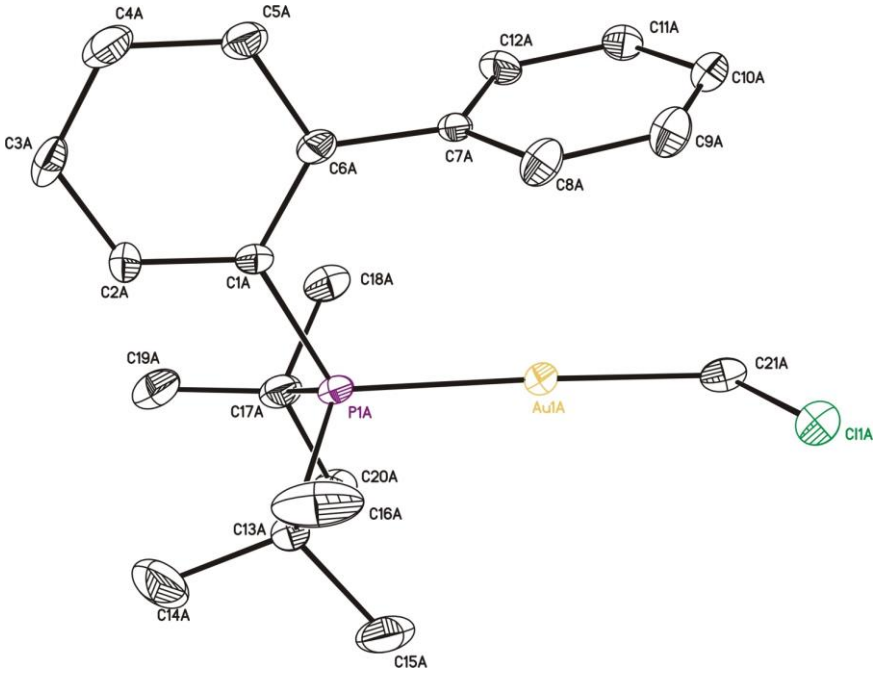


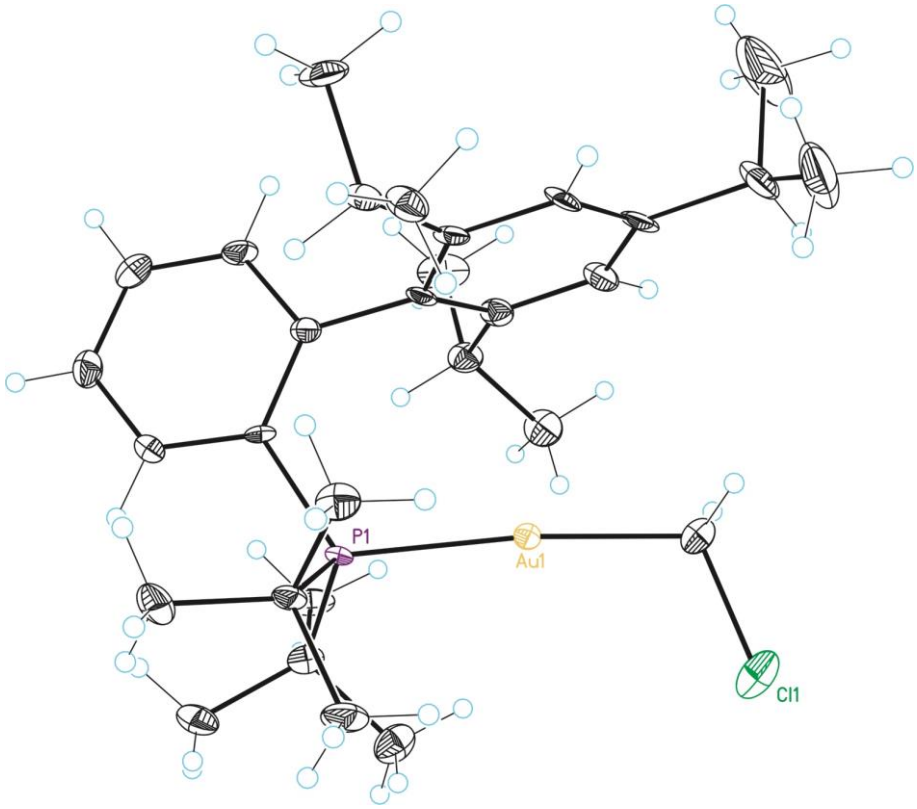
Figure S30. Histogram showing the distribution of M–C–Cl bond angles found in all currently published crystal structures featuring a [MCH_2Cl] (blue), new chloromethyl complexes **1a**, **1b** and **1c** (orange) and chloro(phenyl)methyl complex **9** (grey).

4.2. Crystal data and structure refinement for complex **1a**



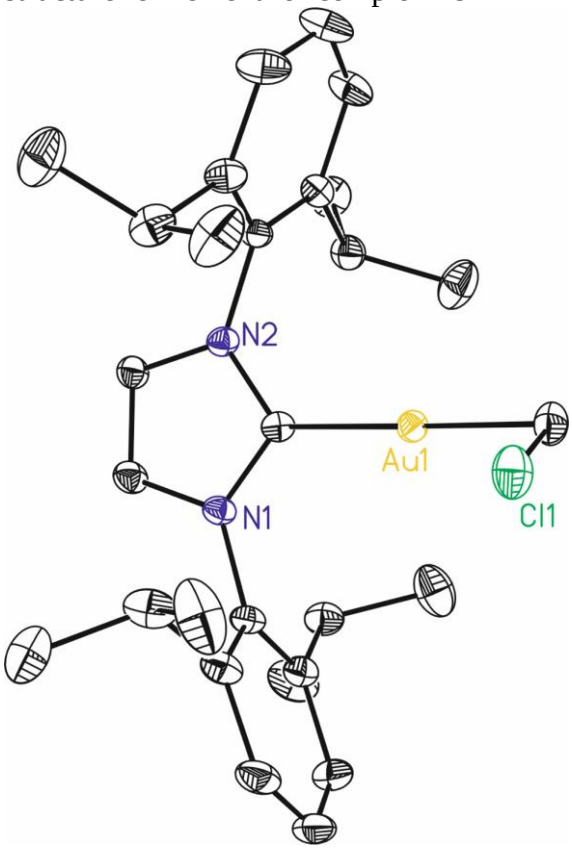
Empirical formula	C42 H58 Au2 Cl2 P2	
Formula weight	1089.66	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.4982(6) Å	α = 72.868(3) °.
	b = 13.6572(7) Å	β = 89.459(3) °.
	c = 15.1002(9) Å	γ = 88.404(3) °.
Volume	2068.1(2) Å^3	
Z	2	
Density (calculated)	1.750 Mg/m^3	
Absorption coefficient	7.320 mm^{-1}	
F(000)	1064	
Crystal size	0.20 x 0.20 x 0.10 mm^3	
Theta range for data collection	1.56 to1.56 °.	
Index ranges	-16 <=h<=16 ,-19 <=k<=21 ,0 <=l<=23	
Reflections collected	15820	
Independent reflections	13265 [R(int) = 0.0000]	
Completeness to theta =33.32 °	0.989 %	
Absorption correction	Empirical (TWINABS)	
Max. and min. transmission	0.5281 and 0.3222	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15820 / 0 / 446	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0729 , wR2 = 0.1911	
R indices (all data)	R1 = 0.0863 , wR2 = 0.2084	
Largest diff. peak and hole	11.419 and -6.610 e.Å^{-3}	

4.3. Crystal data and structure refinement for complex **1b**



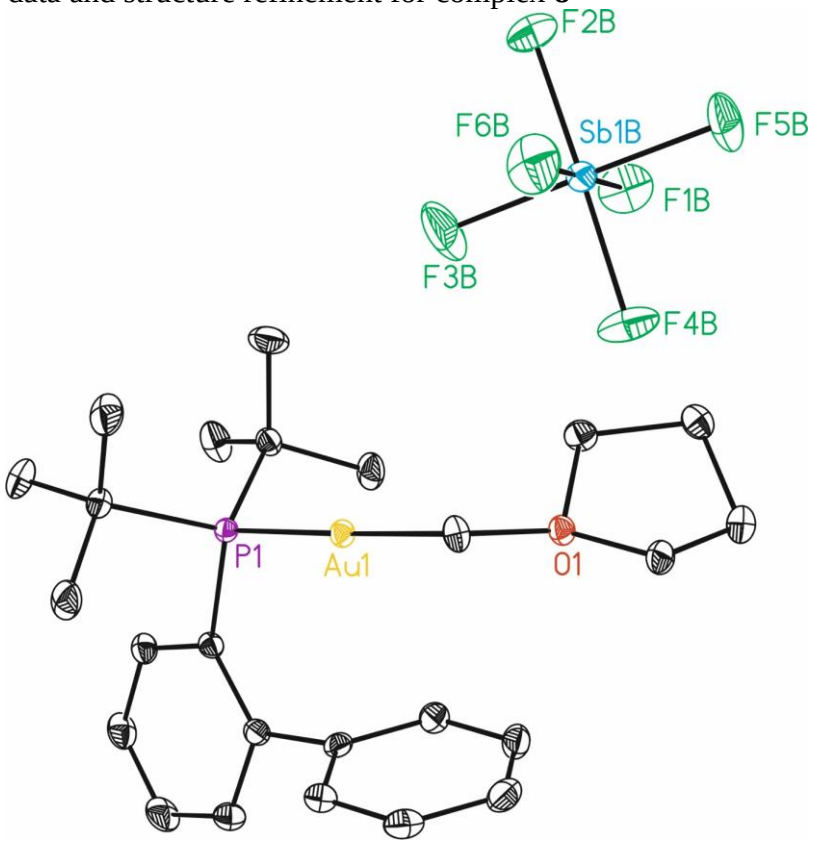
Empirical formula	C30 H47 Au Cl P	
Formula weight	671.06	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 20.5365(8) Å	α 90.00 °.
	b = 8.9497(4) Å	β = 104.0760(10) °.
	c = 16.4737(6) Å	γ = 90.00 °.
Volume	2936.9(2) $Å^3$	
Z	4	
Density (calculated)	1.518 Mg/m^3	
Absorption coefficient	5.170 mm^{-1}	
F(000)	1352	
Crystal size	0.30 x 0.30 x 0.30 mm^3	
Theta range for data collection	1.02 to 29.95 °.	
Index ranges	-25 <=h<=26 ,-12 <=k<=11 ,-22 <=l<=16	
Reflections collected	30282	
Independent reflections	7571 [R(int) = 0.0611]	
Completeness to theta =29.95 °	0.888 %	
Absorption correction	Empirical	
Max. and min. transmission	0.224 and 0.212	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7571 / 0 / 310	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R1 = 0.0512 , wR2 = 0.1431	
R indices (all data)	R1 = 0.0570 , wR2 = 0.1493	
Largest diff. peak and hole	5.340 and -3.785 $e.Å^{-3}$	

4.4. Crystal data and structure refinement for complex **1c**



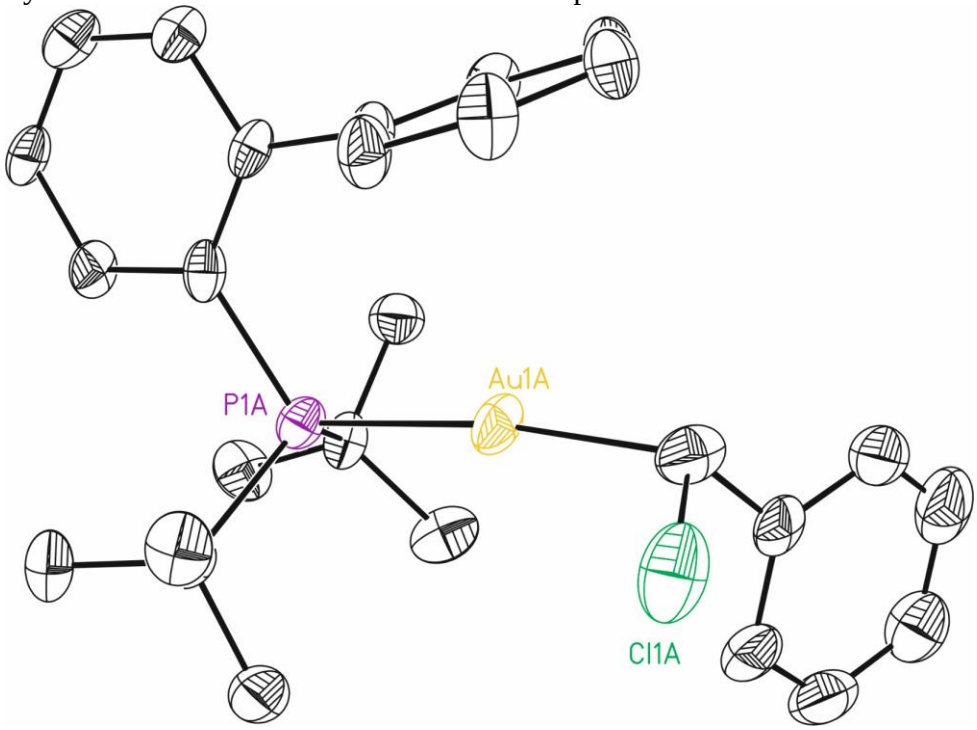
Empirical formula	C28 H38 Au Cl N2	
Formula weight	635.02	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.8883(11)Å	α= 88.838(3)°.
	b = 11.5073(13)Å	β = 88.638(3)°.
	c = 12.2747(14)Å	γ = 83.728(3)°.
Volume	1387.7(3) $Å^3$	
Z	2	
Density (calculated)	1.520 Mg/m^3	
Absorption coefficient	5.414 mm^{-1}	
F(000)	632	
Crystal size	0.30 x 0.20 x 0.20 mm^3	
Theta range for data collection	2.072 to 35.077°.	
Index ranges	-15<=h<=12,-14<=k<=18,-19<=l<=19	
Reflections collected	23948	
Independent reflections	11088[R(int) = 0.0177]	
Completeness to theta =35.077°	90.3%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.411 and 0.337	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11088/ 0/ 297	
Goodness-of-fit on F^2	1.073	
Final R indices [I>2sigma(I)]	R1 = 0.0190, wR2 = 0.0454	
R indices (all data)	R1 = 0.0216, wR2 = 0.0462	
Largest diff. peak and hole	2.151 and -1.303 e.$Å^{-3}$	

4.5. Crystal data and structure refinement for complex **8**



Empirical formula	C25 H37 Au F6 O P Sb	
Formula weight	817.23	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.6064(7)Å	α = 90°.
	b = 9.3096(5)Å	β = 105.7134(12)°.
	c = 23.0909(12)Å	γ = 90°.
Volume	2815.6(3) $Å^3$	
Z	4	
Density (calculated)	1.928 Mg/m^3	
Absorption coefficient	6.277 mm^{-1}	
F(000)	1576	
Crystal size	0.30 x 0.01 x 0.01 mm^3	
Theta range for data collection	1.832 to 34.453°.	
Index ranges	-20<=h<=21,-11<=k<=14,-28<=l<=36	
Reflections collected	42197	
Independent reflections	11560[R(int) = 0.0276]	
Completeness to theta =34.453°	97.2%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.940 and 0.647	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11560/ 0/ 322	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0216, wR2 = 0.0432	
R indices (all data)	R1 = 0.0307, wR2 = 0.0456	
Largest diff. peak and hole	1.766 and -0.676 $e.Å^{-3}$	

4.6. Crystal data and structure refinement for complex **9**



Empirical formula	C56.33 H68.67 Au2 Cl2 P2	
Formula weight	1272.55	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 20.8103(14)Å	α = 90°.
	b = 10.4355(6)Å	β = 103.897(2)°.
	c = 36.623(3)Å	γ = 90°.
Volume	7720.6(9) $Å^3$	
Z	6	
Density (calculated)	1.642 Mg/m^3	
Absorption coefficient	5.896 mm^{-1}	
F(000)	3772	
Crystal size	0.20 x 0.12 x 0.03 mm^3	
Theta range for data collection	1.033 to 27.349°.	
Index ranges	-20<=h<=26,-12<=k<=13,-47<=l<=40	
Reflections collected	53754	
Independent reflections	17186[R(int) = 0.0812]	
Completeness to theta =27.349°	98.299995%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.843 and 0.385	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17186/ 120/ 893	
Goodness-of-fit on F^2	0.941	
Final R indices [I>2sigma(I)]	R1 = 0.0598, wR2 = 0.1542	
R indices (all data)	R1 = 0.0883, wR2 = 0.1702	
Largest diff. peak and hole	5.522 and -2.700 $e.Å^{-3}$	

5. DFT calculations

All density functional calculations were performed using the Gaussian09 suit.[6] The functional B3LYP was used in conjunction with Grimme's D3 dispersion correction using a 6-31G(p,d) + SDD(f,g) for Au basis set. Additionally, the Polarizable Continuum Model (PCM) was used to simulate toluene as solvent throughout all calculations. All structures were fully optimized prior frequency analysis. No imaginary frequencies for minima and a single imaginary frequency corresponding to the reaction coordinate in the case of the transition states were found.

5.1. Fully dissociative mechanism

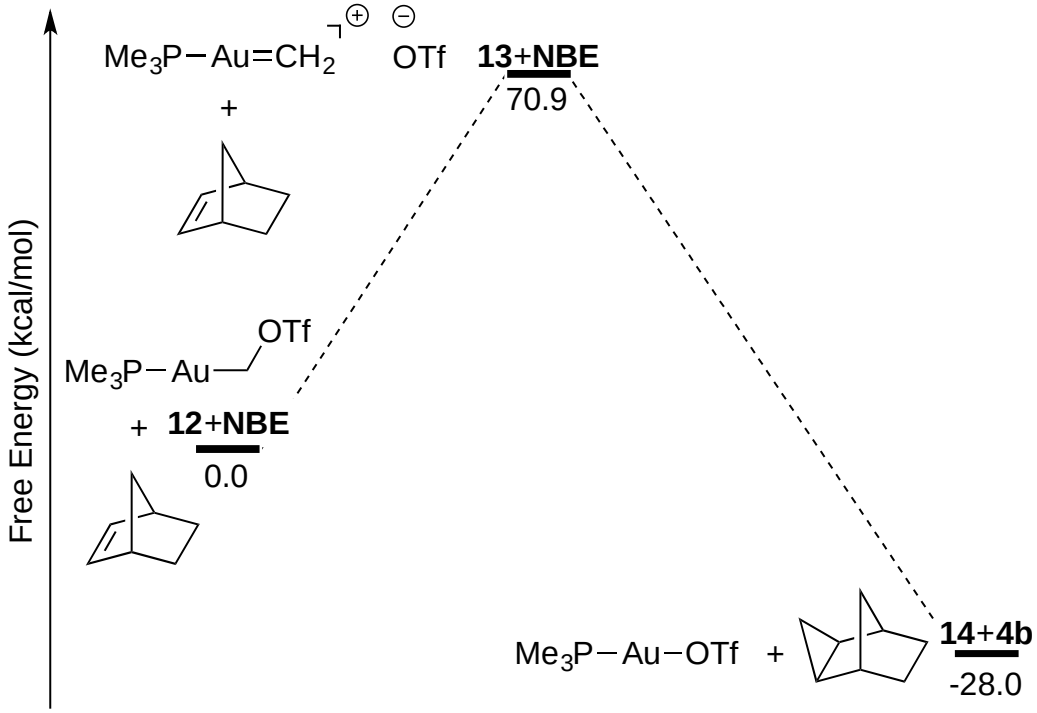
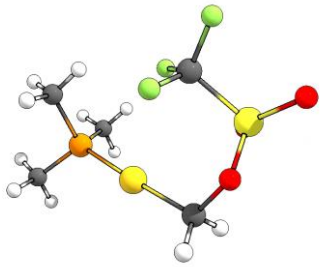


Figure S31. Fully dissociative mechanism for the cyclopropanation of norbornene.

12

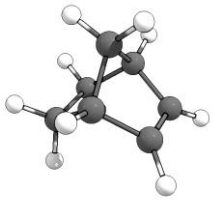
G_{298K} = -1597.560721 Ha



P	2.539235000	0.631858000	0.143403000
C	4.165844000	0.063351000	-0.496817000
H	4.452748000	-0.860303000	0.011875000
H	4.082269000	-0.141405000	-1.567041000
H	4.935134000	0.823679000	-0.330777000
C	2.272070000	2.250771000	-0.686319000
H	2.191184000	2.092388000	-1.764691000
H	1.332564000	2.679126000	-0.330270000
H	3.096311000	2.939538000	-0.478789000
C	2.881695000	1.083071000	1.892001000
H	1.979100000	1.512304000	2.333830000
H	3.145736000	0.183187000	2.453054000
H	3.700420000	1.806261000	1.955371000
Au	0.720979000	-0.814220000	-0.123211000
C	-0.962303000	-2.030384000	-0.331049000
H	-0.933198000	-2.655755000	-1.225887000
H	-1.135817000	-2.675583000	0.534923000
O	-2.268736000	-1.304856000	-0.555383000
S	-2.724038000	-0.162895000	0.449669000
C	-1.965522000	1.401727000	-0.322176000
F	-0.971726000	1.862193000	0.451257000
F	-1.486535000	1.148858000	-1.543354000
F	-2.909983000	2.335618000	-0.406762000
O	-4.161925000	-0.006624000	0.282926000
O	-2.112372000	-0.311373000	1.766485000

NBE (Norbornene)

G_{298K} = -272.624595 Ha

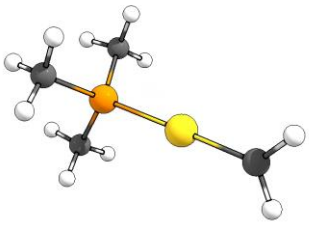


C	1.279703000	0.670622000	-0.506109000
C	0.087338000	1.128372000	0.323826000

C	0.087819000	-1.128290000	0.324015000
C	1.280193000	-0.670254000	-0.505730000
H	1.919352000	1.328980000	-1.084701000
H	1.919226000	-1.328390000	-1.085253000
C	0.037184000	0.000113000	1.381419000
H	-0.884190000	-0.000037000	1.975943000
H	0.904543000	0.000348000	2.048100000
C	-1.189701000	0.780848000	-0.518893000
H	-2.086811000	1.176791000	-0.031203000
H	-1.141814000	1.207261000	-1.524461000
C	-1.189254000	-0.781347000	-0.518934000
H	-2.086230000	-1.177785000	-0.031403000
H	-1.141001000	-1.207692000	-1.524513000
H	0.118227000	2.156855000	0.689794000
H	0.119014000	-2.156709000	0.690136000

13 (PMe_3AuCH_2)

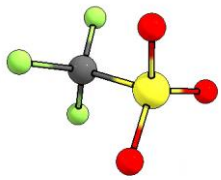
G_{298K} = -635.899159 Ha



P	1.580538000	0.003347000	0.002855000
C	2.314033000	-0.996481000	-1.346168000
H	1.979713000	-2.032560000	-1.257326000
H	1.997217000	-0.601924000	-2.314196000
H	3.405082000	-0.958584000	-1.277579000
C	2.312704000	1.673861000	-0.161017000
H	1.999277000	2.120503000	-1.107507000
H	1.968559000	2.306392000	0.660812000
H	3.403915000	1.605315000	-0.135174000
C	2.270782000	-0.687758000	1.553621000
H	1.940279000	-0.085135000	2.402602000
H	1.920093000	-1.713632000	1.687392000
H	3.363411000	-0.678915000	1.504847000
Au	-0.806141000	0.000180000	-0.010961000
C	-2.767685000	0.003961000	0.041115000
H	-3.387210000	0.908212000	0.046865000
H	-3.392303000	-0.895602000	0.087069000

13 (OTf)

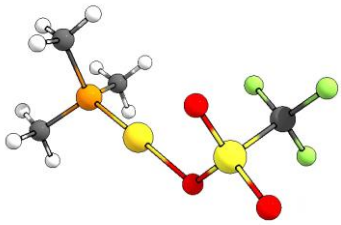
G_{298K} = -961.548587 Ha



O	1.242651000	1.296023000	-0.639995000
S	0.916521000	0.000114000	0.000117000
C	-0.944517000	0.000551000	0.000453000
F	-1.438711000	1.074203000	0.650698000
F	-1.435651000	0.026545000	-1.255498000
F	-1.436099000	-1.100633000	0.604879000
O	1.238902000	-1.202490000	-0.802977000
O	1.243061000	-0.094305000	1.442309000

14

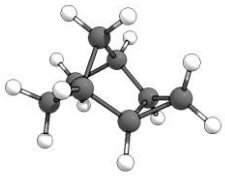
G_{298K} = -1558.321249 Ha



P	-2.772206000	0.318137000	0.179152000
C	-3.083326000	0.596984000	1.963664000
H	-2.903710000	-0.331322000	2.510650000
H	-2.394959000	1.359090000	2.336015000
H	-4.115298000	0.923818000	2.121898000
C	-3.227174000	1.895581000	-0.636393000
H	-2.539740000	2.680882000	-0.313767000
H	-3.142950000	1.780204000	-1.719432000
H	-4.252448000	2.174790000	-0.376047000
C	-4.060029000	-0.874941000	-0.348064000
H	-3.984831000	-1.036956000	-1.425754000
H	-3.900594000	-1.827940000	0.161514000
H	-5.054589000	-0.489884000	-0.103947000
Au	-0.667928000	-0.352044000	-0.252034000
O	1.279194000	-0.997315000	-0.705400000
S	2.412621000	-0.746837000	0.312991000
C	2.823471000	1.032614000	-0.064549000
F	3.176135000	1.170772000	-1.346159000
F	1.748598000	1.811686000	0.167765000
F	3.825897000	1.446033000	0.715221000
O	1.933355000	-0.738580000	1.701854000
O	3.607864000	-1.514318000	-0.033330000

4b

G_{298K} = -311.908741 Ha



C	2.120119000	0.000072000	0.015055000
H	2.331188000	-0.001037000	1.080337000
H	3.016114000	-0.000411000	-0.599445000
C	0.945609000	0.762156000	-0.551365000
C	-0.244419000	1.135453000	0.339681000
C	-0.244119000	-1.135653000	0.339188000
C	0.945588000	-0.761477000	-0.551979000
H	1.081472000	1.323274000	-1.472542000
H	1.081761000	-1.322258000	-1.473303000
C	-0.275372000	-0.000303000	1.385620000
H	-1.201519000	-0.000641000	1.969561000
H	0.562769000	-0.000090000	2.085451000
C	-1.511270000	0.784942000	-0.491157000
H	-2.412935000	1.180568000	-0.011413000
H	-1.465704000	1.204681000	-1.501196000
C	-1.511206000	-0.784916000	-0.491183000
H	-2.412724000	-1.180683000	-0.011286000
H	-1.465846000	-1.204598000	-1.501246000
H	-0.232318000	2.154513000	0.736504000
H	-0.231834000	-2.154978000	0.735423000

5.2. Concerted cyclopropanation (Simmons-Smith's type TS)

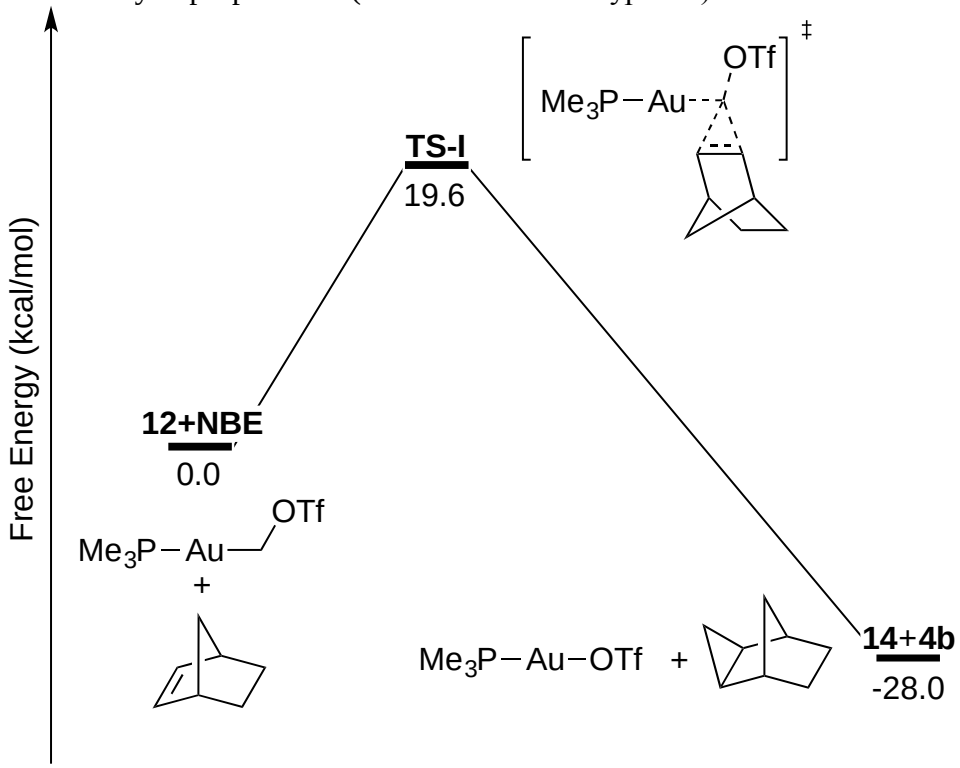
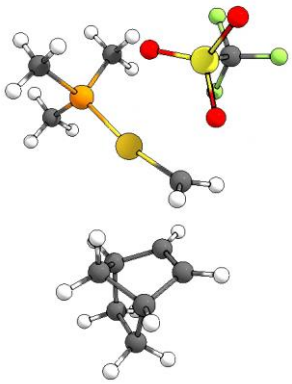


Figure S32. Concerted Simmons-Smith type TS for the cyclopropanation of norbornene.

TS-I

G_{298K} = -1870.154079 Ha



C	-0.795882000	-1.432025000	0.090397000
H	-0.671164000	-2.143990000	-0.719769000
H	-1.195881000	-1.888841000	0.990973000
Au	-0.232271000	0.524986000	-0.011542000
P	0.855121000	2.579968000	0.046505000
C	1.373721000	3.005433000	1.753469000
H	1.944270000	2.159047000	2.142397000
H	0.492262000	3.158562000	2.380840000
H	1.989745000	3.909738000	1.757889000
C	2.435105000	2.505931000	-0.884255000
H	2.999241000	3.435303000	-0.761387000
H	3.013952000	1.663544000	-0.499303000
H	2.230620000	2.338524000	-1.944498000
C	0.002119000	4.080903000	-0.583020000
H	-0.920069000	4.239090000	-0.018019000
H	0.644368000	4.960993000	-0.481694000
H	-0.254066000	3.939288000	-1.636083000
S	2.423154000	-1.601118000	0.883556000
O	1.071359000	-2.264203000	0.781106000
O	2.391200000	-0.186711000	1.321394000
O	3.437375000	-2.461521000	1.506299000
C	2.956825000	-1.484034000	-0.901492000
F	1.987951000	-0.936417000	-1.670534000
F	4.046904000	-0.706360000	-1.007509000
F	3.239654000	-2.693666000	-1.395589000
C	-3.000375000	-0.868963000	-1.037314000
C	-3.783137000	0.258496000	-0.383976000
C	-4.241759000	-1.633680000	0.766986000
C	-3.284831000	-2.004931000	-0.352051000
H	-2.509287000	-0.800021000	-2.000847000
H	-3.045028000	-3.019656000	-0.648703000
C	-3.772465000	-0.196431000	1.092846000
H	-4.484517000	0.353489000	1.716773000
H	-2.780396000	-0.150406000	1.548031000
C	-5.282951000	-0.019877000	-0.753553000
H	-5.909186000	0.813354000	-0.420333000
H	-5.426705000	-0.132978000	-1.831416000
C	-5.602003000	-1.324891000	0.043932000
H	-6.386723000	-1.156237000	0.787823000
H	-5.923028000	-2.149958000	-0.597341000
H	-3.434845000	1.268924000	-0.601105000
H	-4.317675000	-2.341391000	1.593612000

5.3. Cyclopropanation via a reductive elimination from metallacyclobutane structures.

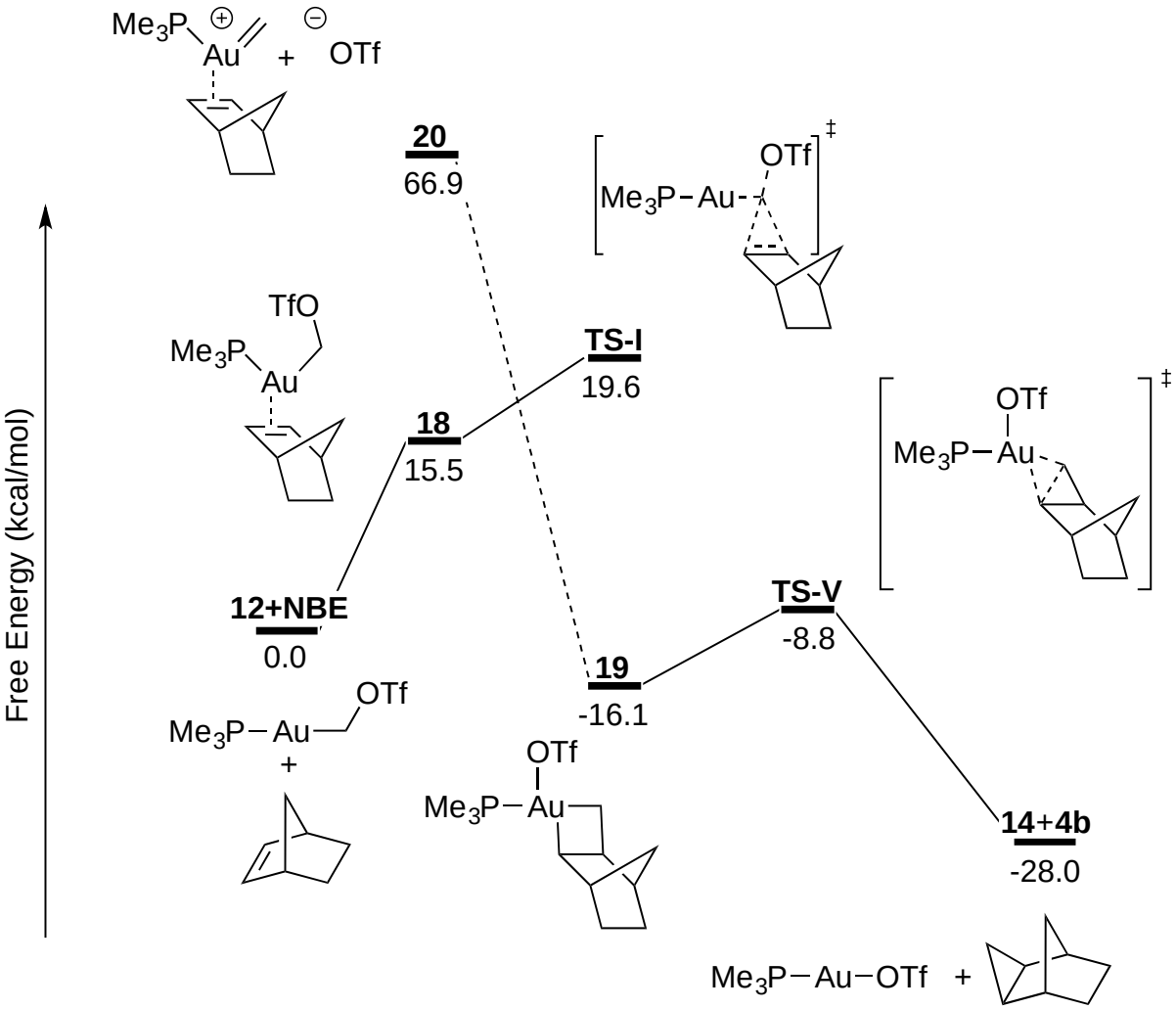
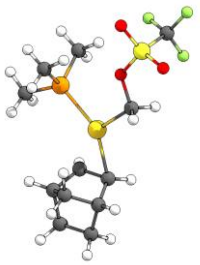


Figure S33. Cyclopropanation via a reductive elimination from metallacyclobutane structures.

It was found that cyclopropane **4b** could easily be formed from a stable auracyclobutane **19** over **TS-V**, however attempts at forming this intermediate from norbornene-coordinated carbenoid complex **18** led to the concerted Simmons-Smith-type transition state **TS-I**, from which the products can directly be formed. Conceivably, **19** could arise from the [2+2] cycloaddition between a gold methylidene with norbornene as a ligand in a process reminiscent of olefin metathesis, however intermediate **20** lies far above **TS-I**, presumably due to the charge separation.

18

G_{298K}: -1870.160691 Ha

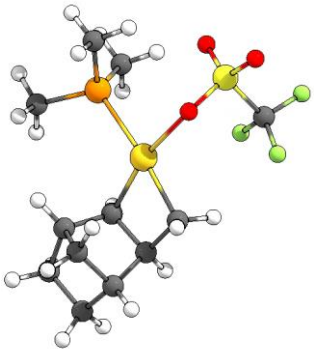


P	-0.119209000	2.193261000	0.051842000
C	-1.349023000	3.546629000	-0.177004000
H	-1.779150000	3.478164000	-1.179635000
H	-2.155804000	3.424543000	0.550678000
H	-0.888569000	4.531423000	-0.045762000
C	0.617232000	2.569113000	1.695578000
H	-0.125111000	2.389677000	2.477880000
H	1.467894000	1.904348000	1.856235000
H	0.947266000	3.611766000	1.743031000
C	1.223893000	2.637333000	-1.124664000
H	2.050068000	1.937060000	-0.993125000
H	0.852886000	2.555087000	-2.149825000
H	1.576287000	3.658684000	-0.949034000
Au	-0.944558000	-0.085954000	-0.189375000
C	0.831256000	-1.196279000	0.277616000
H	0.745750000	-1.833273000	1.161209000
H	1.194572000	-1.805235000	-0.554136000
O	1.925001000	-0.198328000	0.589258000
S	3.409121000	-0.685711000	0.922628000
C	4.128111000	-0.685550000	-0.800377000
F	3.431050000	-1.515650000	-1.584707000

F	4.065930000	0.550193000	-1.311044000
F	5.400179000	-1.080232000	-0.756311000
O	4.070336000	0.399762000	1.637768000
O	3.450756000	-2.064763000	1.396250000
C	-3.045499000	0.033026000	-0.806951000
C	-4.112464000	0.257707000	0.267402000
C	-3.498649000	-1.917260000	0.448984000
C	-2.664820000	-1.341531000	-0.696078000
H	-3.135925000	0.541631000	-1.765045000
H	-2.430773000	-1.968157000	-1.553811000
C	-3.651087000	-0.700434000	1.388537000
H	-4.417330000	-0.853155000	2.155784000
H	-2.716186000	-0.399643000	1.872199000
C	-5.375723000	-0.505260000	-0.245811000
H	-6.239244000	-0.285457000	0.390881000
H	-5.638616000	-0.219695000	-1.268734000
C	-4.950959000	-2.007061000	-0.123856000
H	-5.599696000	-2.546959000	0.573670000
H	-4.982024000	-2.537209000	-1.080325000
H	-4.294306000	1.297323000	0.548978000
H	-3.126472000	-2.842845000	0.891938000

19

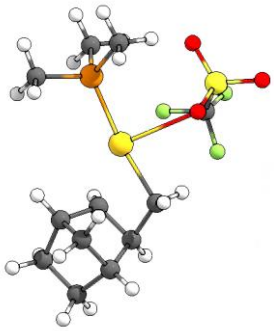
G_{298K}: -1870.210985 Ha



P	-0.122508000	2.403609000	0.195684000
C	1.389638000	3.447315000	0.275743000
H	2.062934000	3.058241000	1.043837000
H	1.906299000	3.421832000	-0.687045000
H	1.129781000	4.482547000	0.516105000
C	-1.178160000	3.218516000	-1.061334000
H	-0.720905000	3.110028000	-2.047918000
H	-2.148737000	2.720479000	-1.059001000
H	-1.302130000	4.280565000	-0.829174000
C	-0.961021000	2.712629000	1.797720000
H	-1.917322000	2.187109000	1.782640000
H	-0.344230000	2.321671000	2.611424000
H	-1.124626000	3.784041000	1.948205000
Au	0.330128000	0.030601000	-0.174224000
C	0.962200000	-1.959219000	-0.269872000
H	1.013484000	-2.270869000	-1.315858000
H	0.235752000	-2.554707000	0.283913000
O	-1.622442000	-0.247100000	-1.267018000
S	-2.983995000	-0.235114000	-0.587658000
C	-2.806398000	-1.595992000	0.678654000
F	-2.359714000	-2.722096000	0.105324000
F	-1.922512000	-1.235572000	1.635196000
F	-3.981818000	-1.839824000	1.262780000
O	-3.215400000	0.974327000	0.226063000
O	-4.054941000	-0.679446000	-1.482517000
C	2.215688000	-0.240568000	0.671164000
C	3.380516000	0.350123000	-0.134433000
C	3.573483000	-1.890245000	-0.457105000
C	2.316678000	-1.770045000	0.429770000
H	2.138967000	0.095923000	1.707378000
H	2.407423000	-2.365020000	1.344137000
C	3.491153000	-0.618344000	-1.332924000
H	4.397111000	-0.453030000	-1.924815000
H	2.626390000	-0.588474000	-2.001910000
C	4.663396000	-0.019061000	0.665061000
H	5.523043000	0.527452000	0.263698000
H	4.579197000	0.239943000	1.725415000
C	4.800899000	-1.560906000	0.426277000
H	5.730346000	-1.794752000	-0.102016000
H	4.801659000	-2.132482000	1.359807000
H	3.296336000	1.411552000	-0.370789000
H	3.640865000	-2.841910000	-0.991323000

TS-V

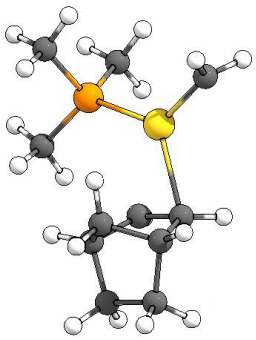
G298K: -1870.199314 Ha



P	-0.627877000	2.491353000	0.033559000
C	0.528297000	3.917634000	0.140961000
H	1.190376000	3.787763000	1.000871000
H	1.137335000	3.961340000	-0.765519000
H	-0.026776000	4.854408000	0.249824000
C	-1.748449000	2.899046000	-1.356320000
H	-1.186543000	2.893872000	-2.293383000
H	-2.523090000	2.130997000	-1.390692000
H	-2.200349000	3.883617000	-1.201798000
C	-1.670196000	2.621746000	1.534785000
H	-2.453198000	1.864748000	1.461350000
H	-1.060389000	2.435905000	2.422392000
H	-2.117953000	3.618189000	1.599078000
Au	0.464868000	0.403088000	-0.208956000
C	1.273681000	-1.559876000	-0.747207000
H	1.323199000	-1.378027000	-1.820863000
H	0.413839000	-2.139308000	-0.421687000
O	-1.728040000	-0.609890000	-1.352716000
S	-2.981539000	-0.792582000	-0.556878000
C	-2.365806000	-1.602914000	1.011217000
F	-1.577020000	-2.662018000	0.733829000
F	-1.628522000	-0.739917000	1.754904000
F	-3.384493000	-2.023023000	1.767050000
O	-3.567068000	0.474431000	-0.057723000
O	-3.919913000	-1.781492000	-1.108888000
C	2.321514000	-0.557205000	0.642472000
C	3.512787000	0.321459000	0.263202000
C	3.893777000	-1.651840000	-0.797771000
C	2.567671000	-1.877617000	-0.047750000
H	1.952996000	-0.575244000	1.666252000
H	2.546214000	-2.777208000	0.567981000
C	3.828484000	-0.152447000	-1.170407000
H	4.786623000	0.228677000	-1.535331000
H	3.052662000	0.108697000	-1.894679000
C	4.708632000	-0.295253000	1.053853000
H	5.563231000	0.387069000	1.012665000
H	4.468949000	-0.453016000	2.109939000
C	4.996037000	-1.632193000	0.289719000
H	5.989063000	-1.618074000	-0.168922000
H	4.947642000	-2.508511000	0.943211000
H	3.373539000	1.392279000	0.413531000
H	4.069406000	-2.350585000	-1.618869000

20 (cation)

G_{298K}: -908.530086 Ha



P	1.901968000	1.080296000	0.028835000
C	1.306773000	2.802611000	-0.170868000
H	0.782339000	2.916055000	-1.121947000
H	0.627205000	3.055679000	0.644708000
H	2.160659000	3.486222000	-0.147831000

C	2.779384000	1.089866000	1.638902000
H	2.055406000	1.228802000	2.445824000
H	3.284842000	0.132240000	1.780511000
H	3.512588000	1.901475000	1.666015000
C	3.205443000	0.895717000	-1.247936000
H	3.691782000	-0.075612000	-1.133832000
H	2.752319000	0.948902000	-2.241144000
H	3.947852000	1.692762000	-1.146397000
Au	0.417206000	-0.811896000	-0.067727000
C	0.901270000	-2.644759000	0.319148000
H	0.871953000	-3.095117000	1.316124000
H	1.318517000	-3.343555000	-0.412467000
C	-1.306636000	0.693316000	-0.805210000
C	-2.018241000	1.501911000	0.274342000
C	-2.865565000	-0.599385000	0.373043000
C	-1.850818000	-0.586533000	-0.755163000
H	-0.901690000	1.140952000	-1.707730000
H	-1.884622000	-1.282986000	-1.587074000
C	-2.268816000	0.430645000	1.357493000
H	-2.987504000	0.754606000	2.114813000
H	-1.358291000	0.084019000	1.858312000
C	-3.472185000	1.683300000	-0.284273000
H	-4.027803000	2.369854000	0.360224000
H	-3.477091000	2.099504000	-1.294898000
C	-4.057569000	0.238026000	-0.216372000
H	-4.908247000	0.180595000	0.467952000
H	-4.387917000	-0.138194000	-1.187812000
H	-1.538092000	2.429144000	0.582672000
H	-3.141244000	-1.578298000	0.763268000

5.4. Ethylene formation involving a neutral, three-coordinated carbene species.

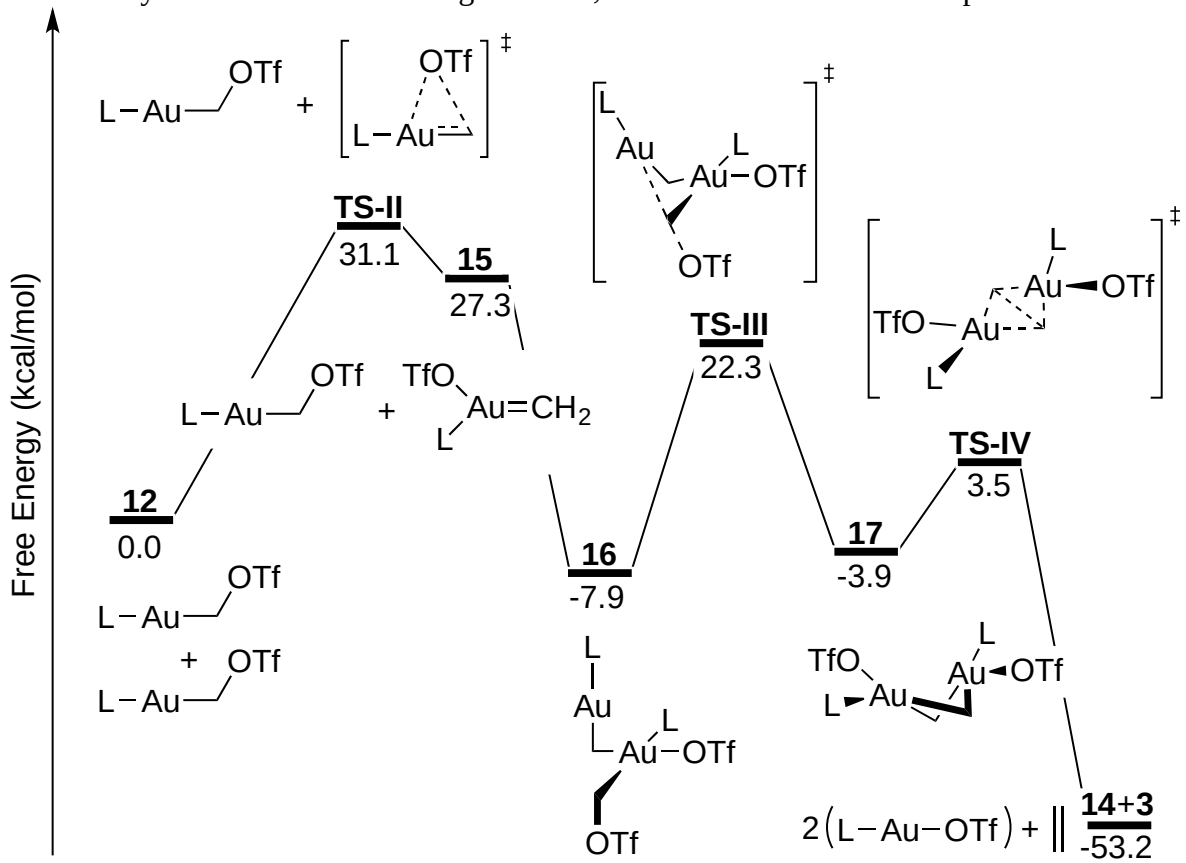
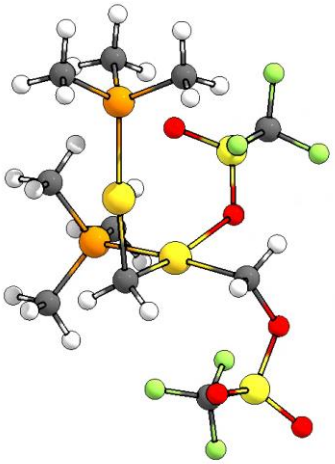


Figure S34. Ethylene formation via a neutral, three-coordinated carbene species.

16

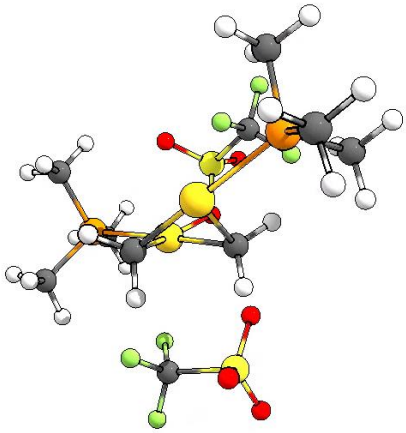
G_{298K}: -3195.133997 Ha



P	-0.455392000	0.089431000	2.646474000
C	-0.993029000	1.656393000	3.429203000
H	-0.320067000	2.451385000	3.107414000
H	-2.007935000	1.898430000	3.106171000
H	-0.963997000	1.562052000	4.518771000
C	-1.419773000	-1.208920000	3.516337000
H	-2.474450000	-1.114818000	3.248022000
H	-1.071807000	-2.197606000	3.208307000
H	-1.305178000	-1.109803000	4.599645000
C	1.273198000	-0.154292000	3.198007000
H	1.631603000	-1.120255000	2.833688000
H	1.875811000	0.641556000	2.758252000
H	1.339180000	-0.120295000	4.289633000
Au	-0.797394000	0.047107000	0.255519000
C	-1.284250000	0.031249000	-1.778758000
H	-0.815614000	0.894422000	-2.247383000
H	-1.011001000	-0.887526000	-2.298408000
O	-2.719285000	0.296459000	-2.018228000
S	-3.793998000	-0.851730000	-1.717164000
C	-4.251500000	-0.528637000	0.095236000
F	-3.589120000	-1.369923000	0.899024000
F	-3.957878000	0.728265000	0.439488000
F	-5.557623000	-0.733425000	0.234960000
O	-4.984718000	-0.509250000	-2.477067000
O	-3.185276000	-2.175949000	-1.767409000
P	3.949428000	-0.858689000	-0.468167000
C	5.321563000	-2.030261000	-0.115619000
H	5.258125000	-2.881130000	-0.798698000
H	5.229646000	-2.399949000	0.908819000
H	6.290958000	-1.537655000	-0.238216000
C	4.283176000	0.576972000	0.630471000
H	4.229743000	0.251349000	1.672514000
H	3.515213000	1.338253000	0.472921000
H	5.274193000	0.996522000	0.432176000
C	4.332841000	-0.218558000	-2.147985000
H	3.636312000	0.588480000	-2.382429000
H	4.208559000	-1.016717000	-2.883787000
H	5.358697000	0.159919000	-2.188974000
Au	1.755503000	-1.618602000	-0.195956000
C	-0.277299000	-1.974021000	0.101205000
H	-0.574099000	-2.465259000	1.031411000
H	-0.848287000	-2.408997000	-0.720334000
O	1.373364000	2.447890000	1.235367000
S	0.433262000	3.078602000	0.283196000
C	1.234710000	2.761405000	-1.373569000
F	1.536222000	1.447518000	-1.512811000
F	2.374064000	3.452885000	-1.474175000
F	0.417392000	3.102865000	-2.375433000
O	0.264754000	4.531624000	0.346822000
O	-0.887630000	2.335861000	0.168921000

TS-III

G_{298K}: -3195.085890 Ha



Au	-0.777944000	0.297108000	0.332249000
C	0.488932000	-0.886369000	-0.768455000
H	1.085884000	-0.455919000	-1.569624000
H	0.207083000	-1.930401000	-0.885484000
C	-0.042955000	-1.111479000	1.686632000
H	-0.133715000	-0.745308000	2.711707000
H	-0.608210000	-2.027539000	1.508834000
Au	1.892937000	-1.162603000	0.909695000
P	4.031068000	-0.996061000	-0.160236000
C	3.908309000	-0.882241000	-1.985969000
H	4.908196000	-0.837061000	-2.426929000
H	3.378390000	-1.754782000	-2.375633000
H	3.353714000	0.017751000	-2.259638000
C	4.947664000	0.514157000	0.337538000
H	4.329373000	1.387241000	0.116787000
H	5.147203000	0.487320000	1.411784000
H	5.894454000	0.585475000	-0.205625000
C	5.176160000	-2.393802000	0.155729000
H	4.720187000	-3.320901000	-0.200461000
H	6.126423000	-2.233734000	-0.361812000
H	5.358941000	-2.483403000	1.229570000
P	-2.205823000	1.488142000	1.823523000
C	-1.271488000	2.539773000	2.994809000
H	-0.693045000	3.259857000	2.414503000
H	-1.955933000	3.061327000	3.670022000
H	-0.592713000	1.913589000	3.580099000
C	-3.217499000	0.382814000	2.876562000
H	-2.558869000	-0.279635000	3.444025000
H	-3.824912000	0.973499000	3.568061000
H	-3.859485000	-0.231296000	2.244706000
C	-3.391716000	2.586997000	0.972549000
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H	-3.939944000	2.007985000	0.226272000
O	-1.044555000	1.794880000	-1.290790000
S	-0.298789000	3.120075000	-1.212412000
O	-0.346055000	3.730406000	0.129739000
O	-0.550383000	3.969534000	-2.375398000
C	1.493243000	2.596672000	-1.391823000
F	1.926912000	1.970112000	-0.268414000
F	2.272959000	3.656617000	-1.598210000
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O	-1.669842000	-1.148595000	-2.194808000
S	-2.347691000	-2.414881000	-1.785667000
O	-1.480951000	-3.327570000	-0.998051000
O	-3.183947000	-3.035331000	-2.824130000
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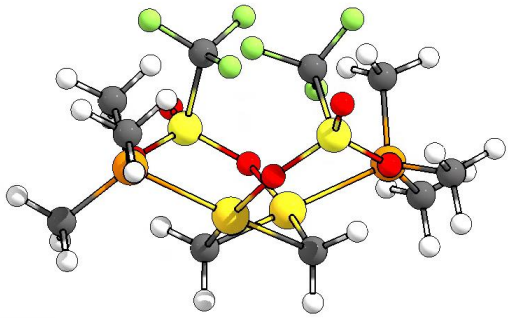
17

G_{298K}: -3195.127713 Ha



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Au	-1.531190000	0.358365000	-1.063559000
C	-0.436134000	-1.253835000	-1.807459000
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H	0.233516000	-3.678167000	0.284475000
H	1.017825000	-4.174430000	-1.225467000
H	1.664924000	-4.749991000	0.334316000
C	3.874388000	-2.931703000	-0.850959000
H	3.722926000	-3.160554000	-1.908811000
H	4.576479000	-2.098192000	-0.768591000
H	4.284514000	-3.809264000	-0.342732000
C	2.638278000	-2.204142000	1.681268000
H	3.319070000	-1.361003000	1.803310000
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H	3.087441000	-3.110356000	2.097947000
Au	1.338383000	-0.454811000	-1.101795000
C	0.206986000	1.120121000	-1.884084000
H	0.123708000	1.086539000	-2.971266000
H	0.474189000	2.098322000	-1.491329000
O	-3.194714000	-0.743564000	-0.090944000
S	-3.000273000	-1.966877000	0.802456000
O	-2.245784000	-3.060257000	0.168915000
O	-4.224356000	-2.289471000	1.536881000
C	-1.815510000	-1.316695000	2.097145000
F	-2.168293000	-0.080217000	2.497824000
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F	-1.787228000	-2.122300000	3.157226000
O	3.095608000	0.634419000	-0.274896000
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O	2.070726000	2.932648000	-0.176768000
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C	2.264210000	1.554608000	2.058297000
F	3.106844000	0.826741000	2.802695000
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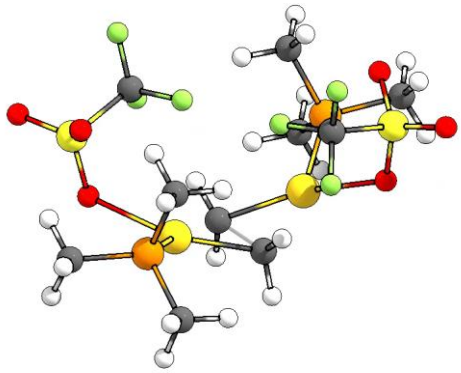
TS-IV

G_{298K}: -3195.115855 Ha



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H	-2.231544000	-3.734389000	-1.440648000
H	-3.881104000	-4.155687000	-0.909103000
C	-2.737808000	-2.483024000	1.374447000
H	-1.699715000	-2.819475000	1.315940000
H	-2.806809000	-1.650951000	2.077699000
H	-3.373767000	-3.309453000	1.705044000
C	-5.032865000	-1.426069000	-0.095017000
H	-5.102596000	-0.603912000	0.618992000
H	-5.423827000	-1.098138000	-1.061475000
H	-5.610242000	-2.284186000	0.261790000
Au	-1.754539000	-0.166462000	-1.034168000
C	-0.085918000	0.982056000	-1.599314000
H	-0.175407000	1.840202000	-0.934217000
H	-0.093105000	1.236563000	-2.657390000
P	3.266614000	1.874303000	-0.272210000
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H	3.634266000	3.112303000	-2.334805000
H	2.231389000	3.734447000	-1.440597000
H	3.880968000	4.155766000	-0.909129000
C	2.737862000	2.482973000	1.374415000
H	1.699765000	2.819422000	1.315984000
H	2.806909000	1.650868000	2.077622000
H	3.373836000	3.309390000	1.705014000
C	5.032847000	1.426128000	-0.095243000
H	5.102641000	0.603946000	0.618730000
H	5.423753000	1.098239000	-1.061739000
H	5.610233000	2.284242000	0.261557000
Au	1.754480000	0.166512000	-1.034257000
C	0.085832000	-0.981981000	-1.599369000
H	0.175350000	-1.840162000	-0.934322000
H	0.092960000	-1.236433000	-2.657458000
O	-3.025301000	1.622614000	-0.372383000
S	-3.188879000	1.898901000	1.115029000
O	-3.517180000	0.689568000	1.893557000
O	-3.945119000	3.124743000	1.378203000
C	-1.437388000	2.293609000	1.654560000
F	-0.874316000	3.215684000	0.845571000
F	-0.662719000	1.189165000	1.603019000
F	-1.429348000	2.758501000	2.902487000
O	3.025302000	-1.622569000	-0.372653000
S	3.188953000	-1.898925000	1.114739000
O	3.517232000	-0.689615000	1.893312000
O	3.945263000	-3.124744000	1.377818000
C	1.437503000	-2.293748000	1.654325000
F	0.874433000	-3.215790000	0.845298000
F	0.662779000	-1.189337000	1.602902000
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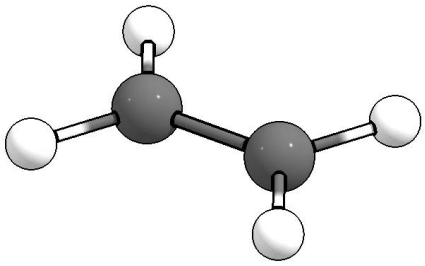
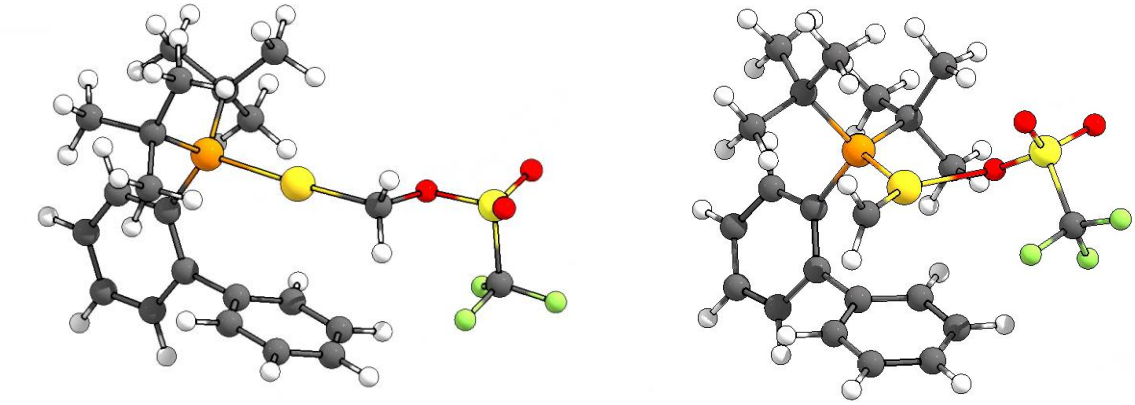
3

G_{298K}: -78.563798 Ha



C	0.000000000	0.000000000	-0.665692000
H	0.000000000	0.923666000	-1.239156000
H	0.000000000	-0.923666000	-1.239156000
C	0.000000000	0.000000000	0.665692000
H	0.000000000	-0.923666000	1.239156000
H	0.000000000	0.923666000	1.239156000

5.5. Optimized structures of **7a** and **15a**



7a **15a**

Figure S35. Optimized structures of **7a** and **15a.**

7a

G_{298K}: -2255.989805 Ha

P	-2.233245000	-0.660727000	0.061530000
C	-2.996429000	0.973143000	0.498137000
C	-2.308423000	2.203648000	0.365906000
C	-4.314882000	1.001478000	0.995341000
C	-2.962101000	3.393368000	0.732209000
C	-4.945793000	2.188285000	1.356806000
H	-4.868782000	0.079688000	1.101587000
C	-4.263665000	3.396876000	1.224271000
H	-2.421894000	4.329081000	0.624456000
H	-5.962231000	2.164397000	1.737767000
H	-4.738869000	4.333312000	1.500747000
Au	0.066607000	-0.667629000	-0.488968000
C	-0.910442000	2.364826000	-0.141307000
C	-0.671181000	2.592438000	-1.503456000
C	0.169420000	2.396412000	0.754144000
C	0.625640000	2.828046000	-1.964287000
H	-1.503570000	2.584163000	-2.200376000
C	1.465571000	2.630843000	0.292422000
H	-0.010656000	2.224249000	1.811187000
C	1.695631000	2.848171000	-1.067621000
H	0.798032000	2.999023000	-3.022995000
H	2.295939000	2.625981000	0.989850000
H	2.704907000	3.023864000	-1.424502000
C	-3.225049000	-1.270771000	-1.451473000
C	-2.445741000	-1.778438000	1.609409000
C	-2.778020000	-2.709435000	-1.778207000
H	-3.196391000	-3.000691000	-2.748722000
H	-1.688573000	-2.792218000	-1.841620000
H	-3.139066000	-3.429094000	-1.038364000
C	-4.757865000	-1.223171000	-1.316416000
H	-5.123279000	-0.200785000	-1.197974000
H	-5.199080000	-1.623386000	-2.236897000
H	-5.133130000	-1.825622000	-0.487294000
C	-2.815568000	-0.336220000	-2.612046000
H	-1.740426000	-0.376203000	-2.808790000
H	-3.342840000	-0.645364000	-3.522122000
H	-3.089248000	0.702977000	-2.404576000
C	-3.852690000	-2.353703000	1.853782000
H	-3.828274000	-2.951184000	2.772695000
H	-4.614987000	-1.586502000	1.996677000
H	-4.170467000	-3.017280000	1.045895000
C	-1.462521000	-2.966882000	1.488131000
H	-1.566690000	-3.597292000	2.379137000
H	-1.663238000	-3.590879000	0.614864000
H	-0.423689000	-2.632090000	1.431418000
C	-2.012511000	-0.916763000	2.815021000
H	-2.720317000	-0.110202000	3.021562000
H	-1.953355000	-1.553831000	3.704854000
H	-1.022671000	-0.475430000	2.654550000
C	2.090581000	-0.781183000	-0.959975000
H	2.369190000	-1.603528000	-1.623103000
H	2.459358000	0.157577000	-1.381333000
O	2.835522000	-1.005777000	0.331889000
S	4.431957000	-1.070101000	0.311488000
O	4.863017000	-1.730207000	1.536450000
O	4.954515000	-1.449937000	-0.997191000
C	4.845768000	0.737547000	0.536957000
F	4.225199000	1.217366000	1.619722000
F	6.163654000	0.872604000	0.688147000
F	4.453029000	1.436561000	-0.537042000

15a

G_{298K}: -2255.943839 Ha

Au	0.450324000	0.022848000	-0.943581000
C	0.609949000	0.977352000	-2.588873000
H	0.590786000	0.510879000	-3.579440000
H	0.473693000	2.061020000	-2.655861000
O	1.690433000	-0.837884000	0.720070000
S	3.115785000	-1.303975000	0.426474000
C	4.057661000	0.292855000	0.618323000
F	3.657797000	1.191230000	-0.297808000
F	3.844394000	0.815174000	1.838691000
F	5.368897000	0.081001000	0.465772000
O	3.622684000	-2.178339000	1.489232000
O	3.320183000	-1.701393000	-0.974255000
P	-1.568793000	-0.894895000	0.095567000
C	-2.779115000	0.430956000	0.568718000
C	-2.471519000	1.813940000	0.670742000
C	-4.113913000	0.032747000	0.787250000
C	-3.512216000	2.714026000	0.972211000
C	-5.125273000	0.938928000	1.089856000
H	-4.378601000	-1.011819000	0.714300000
C	-4.821507000	2.295867000	1.180958000
H	-3.266015000	3.768066000	1.054754000
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C	-0.031658000	2.138816000	1.287885000
C	0.240984000	4.067141000	-0.709058000
H	-1.830024000	3.670215000	-1.154713000
C	1.194260000	2.780637000	1.097978000
H	-0.132486000	1.404735000	2.075908000
C	1.335470000	3.741287000	0.095440000
H	0.339515000	4.820530000	-1.485451000
H	2.040703000	2.508698000	1.718203000
H	2.291861000	4.231843000	-0.057237000
C	-2.353541000	-1.860215000	-1.382839000
C	-1.380919000	-1.988894000	1.657159000
C	-1.223395000	-2.625957000	-2.113133000
H	-1.668398000	-3.199418000	-2.934353000
H	-0.480693000	-1.951001000	-2.544104000
H	-0.700187000	-3.329254000	-1.462583000
C	-3.445315000	-2.887841000	-1.024088000
H	-4.307093000	-2.450913000	-0.518048000
H	-3.816672000	-3.328969000	-1.956221000
H	-3.055697000	-3.705449000	-0.414412000
C	-2.938306000	-0.808384000	-2.347575000
H	-2.198222000	-0.044284000	-2.606897000
H	-3.240532000	-1.309486000	-3.274101000
H	-3.815971000	-0.309446000	-1.929849000
C	-2.706909000	-2.484915000	2.269268000
H	-2.459372000	-3.115351000	3.131307000
H	-3.319954000	-1.659644000	2.637894000
H	-3.304923000	-3.090403000	1.588338000
C	-0.491595000	-3.195879000	1.298203000
H	-0.245261000	-3.734430000	2.220273000
H	-1.004744000	-3.900666000	0.638461000
H	0.447331000	-2.885546000	0.837586000
C	-0.678650000	-1.123599000	2.725431000
H	-1.293873000	-0.261482000	3.003599000
H	-0.543732000	-1.732164000	3.627111000
H	0.305045000	-0.789760000	2.397594000

7. References

[1] W. L. F. Armarego, C. L. L. Chai, in *Purification of Laboratory Chemicals (Fifth Edition)*, Butterworth-Heinemann, Burlington, **2003**, pp. 80-388.

[2] D. S. Wulfman, S. Yousefian, J. M. White, *Synth. Commun.* **1988**, *18*, 2349-2352.

[3] a) E. C. Friedrich, J. M. Domek, R. Y. Pong, *J. Org. Chem.* **1985**, *50*, 4640-4642; b) T. d. Hartog, J. M. S. Toro, P. Chen, *Org. Lett.* **2014**, *16*, 1100-1103.

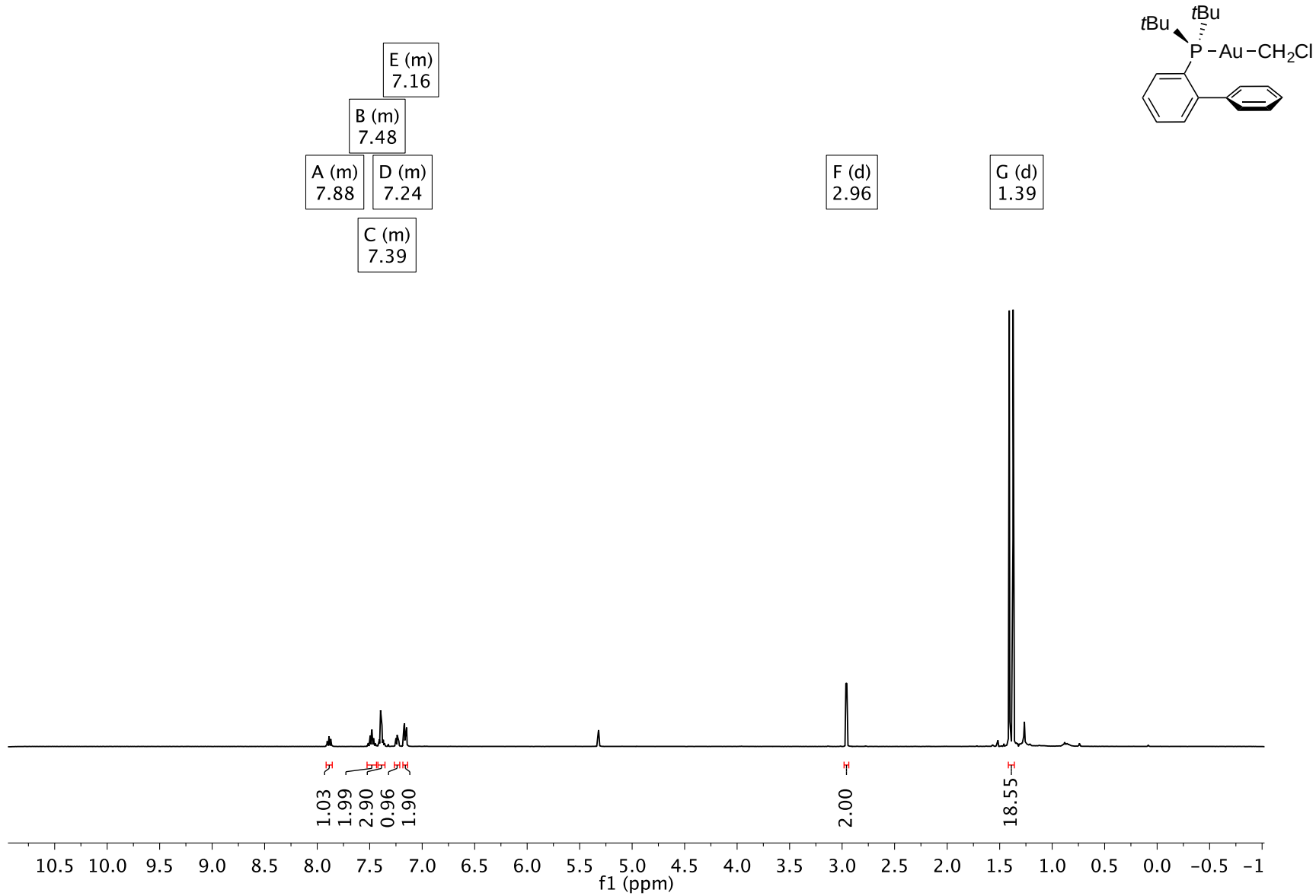
[4] U. M. Dzhemilev, V. A. Dokichev, S. Z. Sultanov, R. A. Sadykov, G. A. Tolstikov, O. M. Nefedov, *Russ. Chem. Bull.* **1991**, *40*, 945-950.

[5] H. Eyring, *J. Chem. Phys.* **1935**, *3*, 107-115.

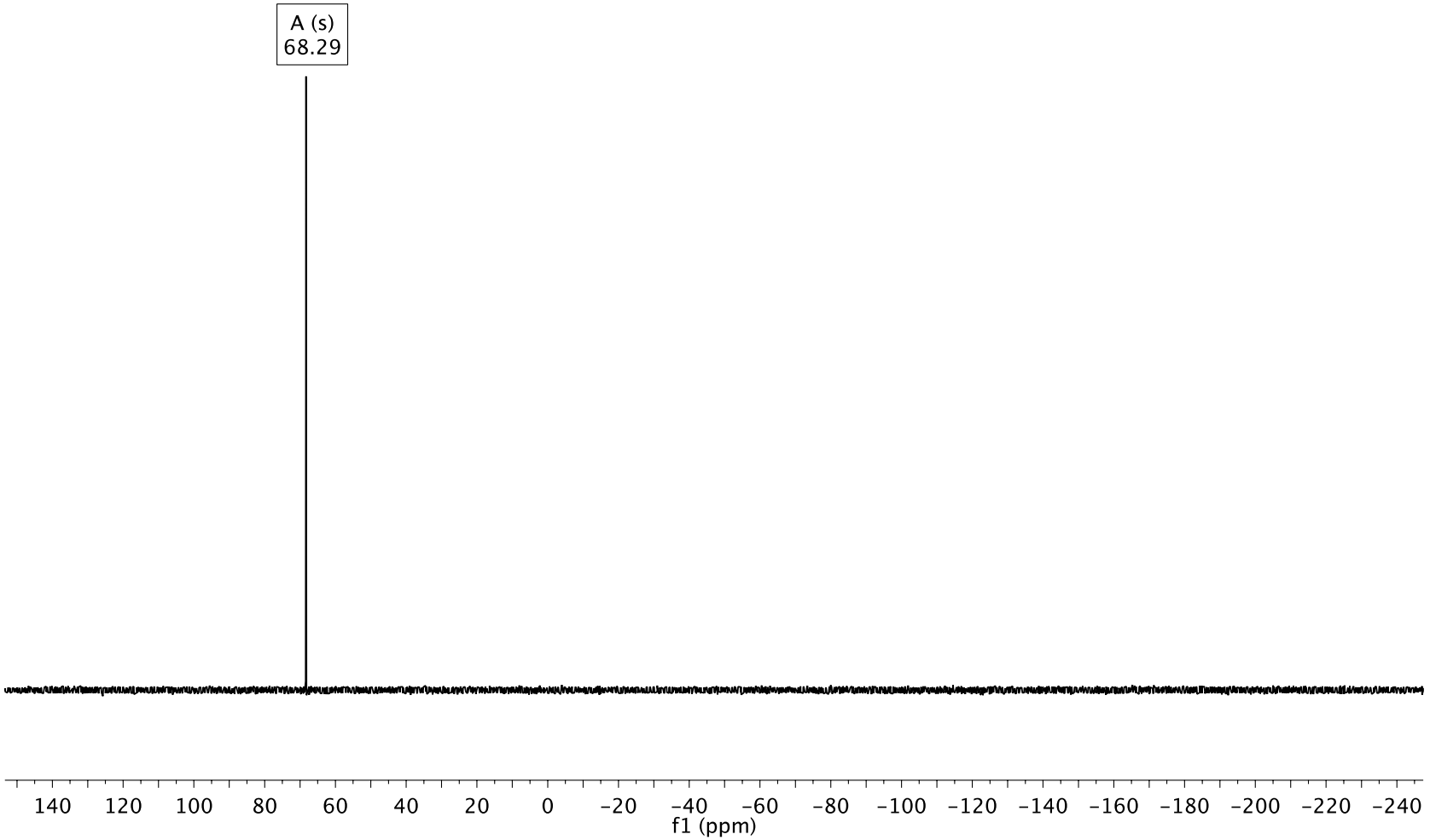
[6] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford, CT, USA, **2009**.

8. NMR spectra

8.1. (Chloromethyl)(2-(di-*tert*-butylphosphino)biphenyl)gold (**1a**)



^{1}H NMR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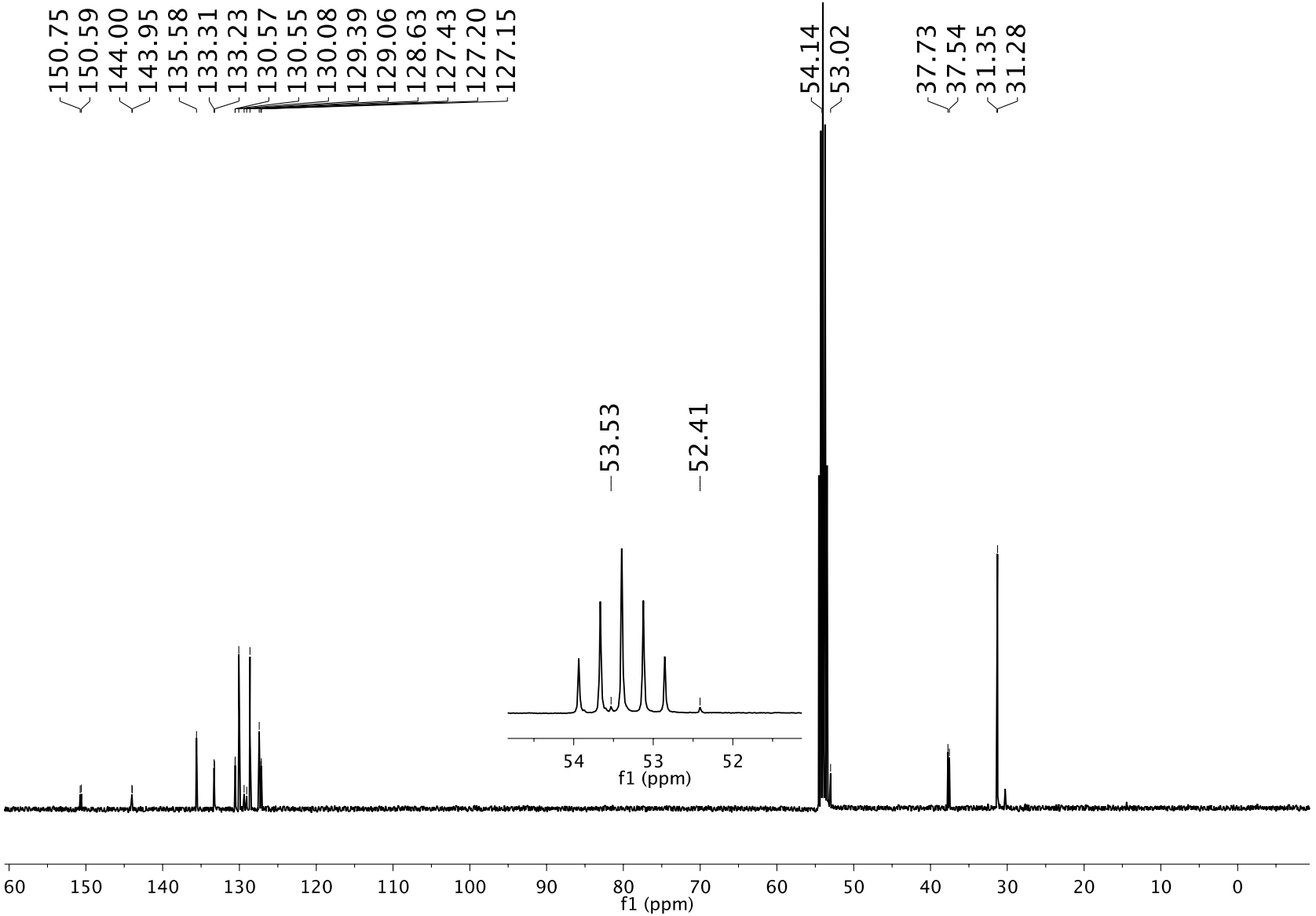
^{31}P NMR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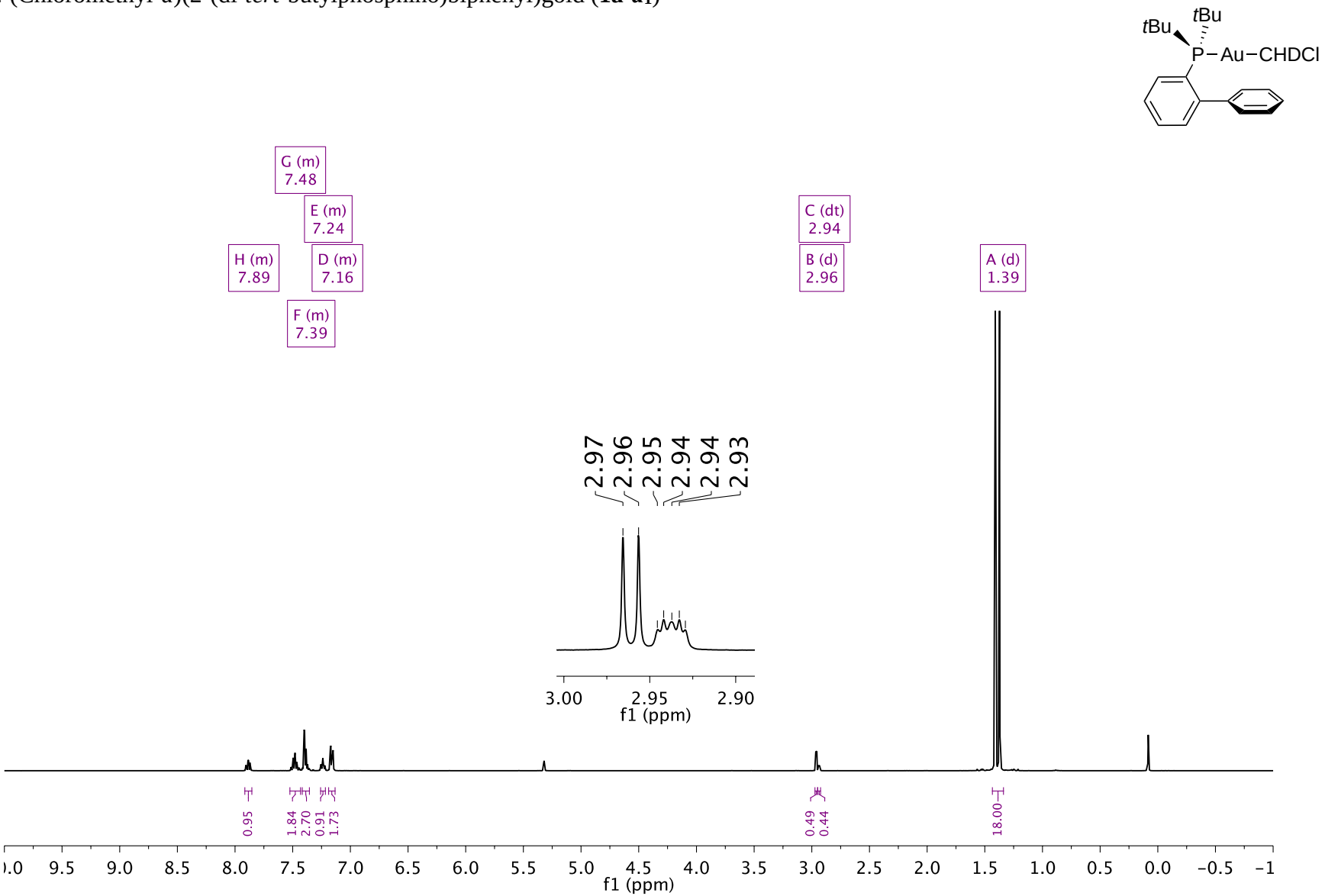
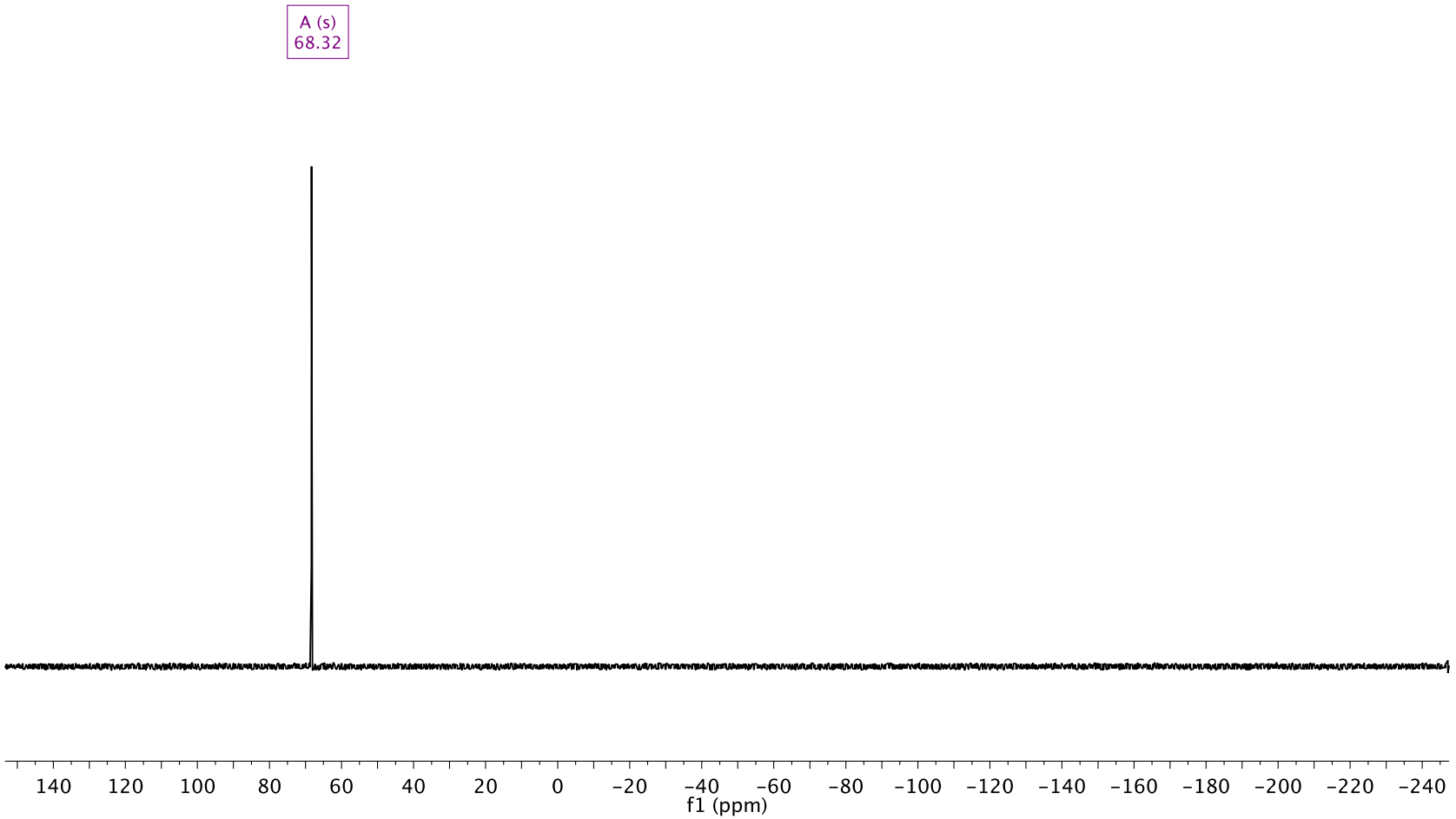
37.54
31.35
31.28
53.53
52.41
54
53
52
f1 (ppm)
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{31}C NMR

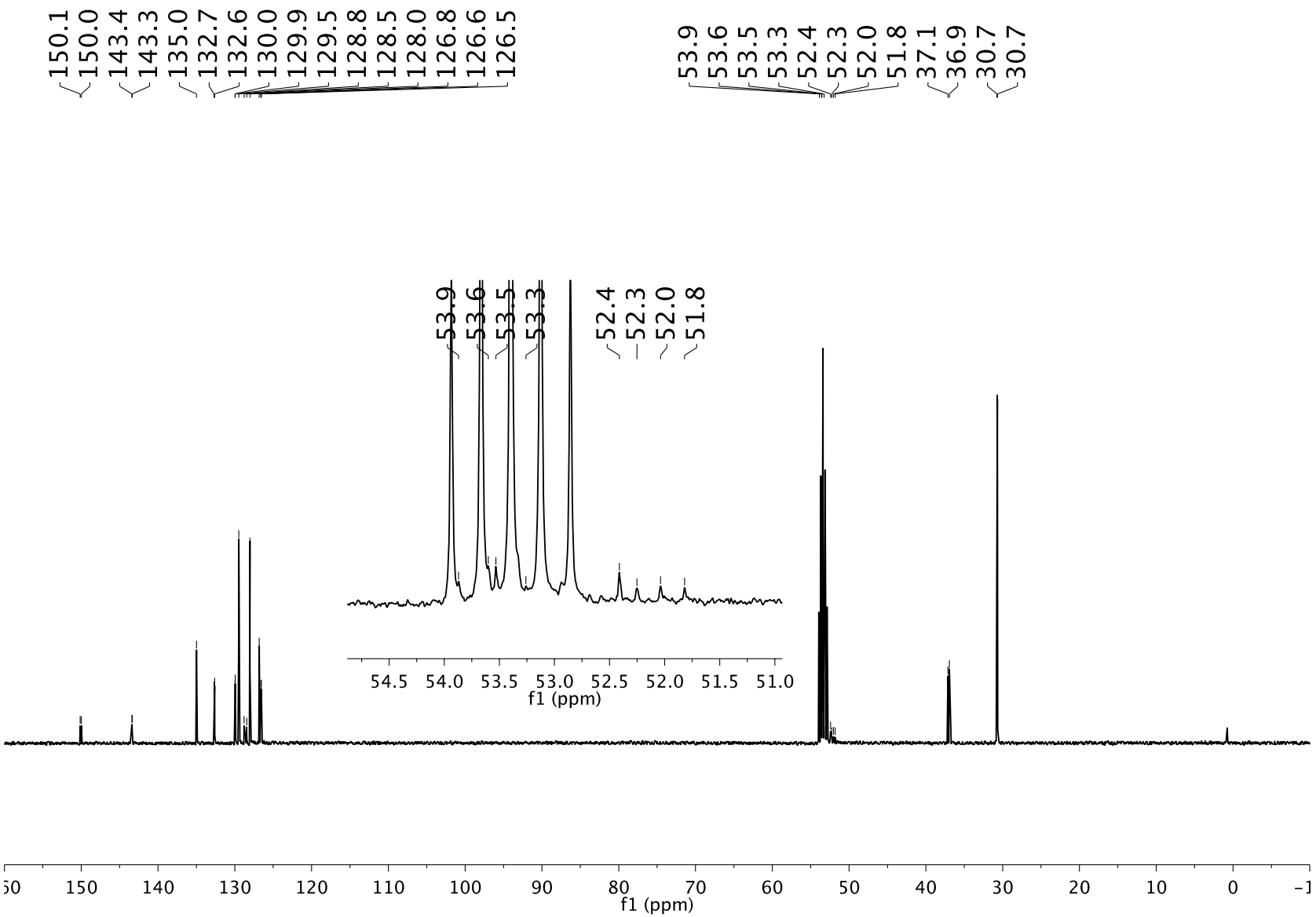
8.2. (Chloromethyl-*d*)(2-(di-*tert*-butylphosphino)biphenyl)gold (**1a-*d*$_1$**)



^{1}H NMR

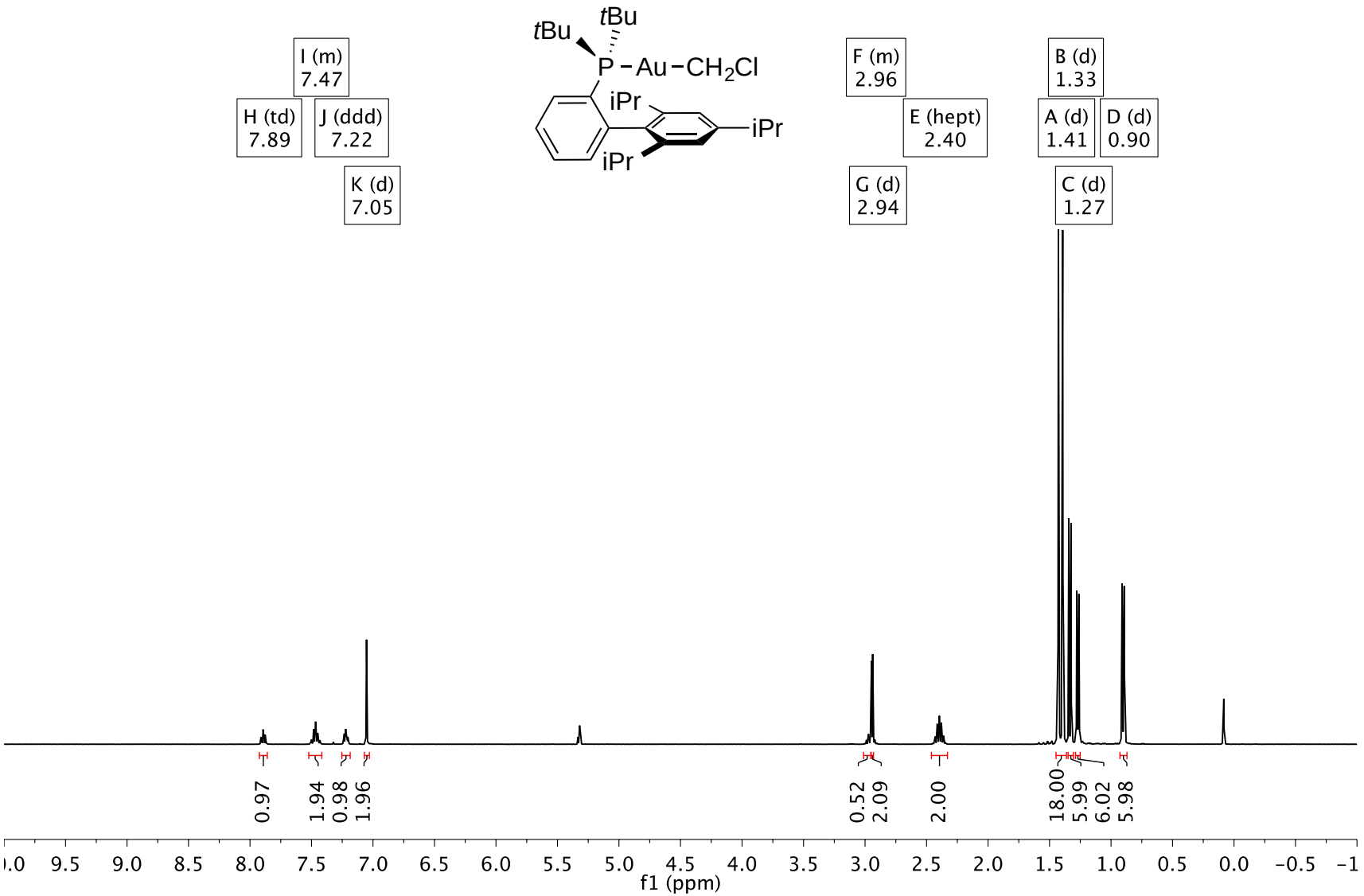

A (s)
68.32
140
120
100
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
−220
−240
f1 (ppm)

^{31}P NMR

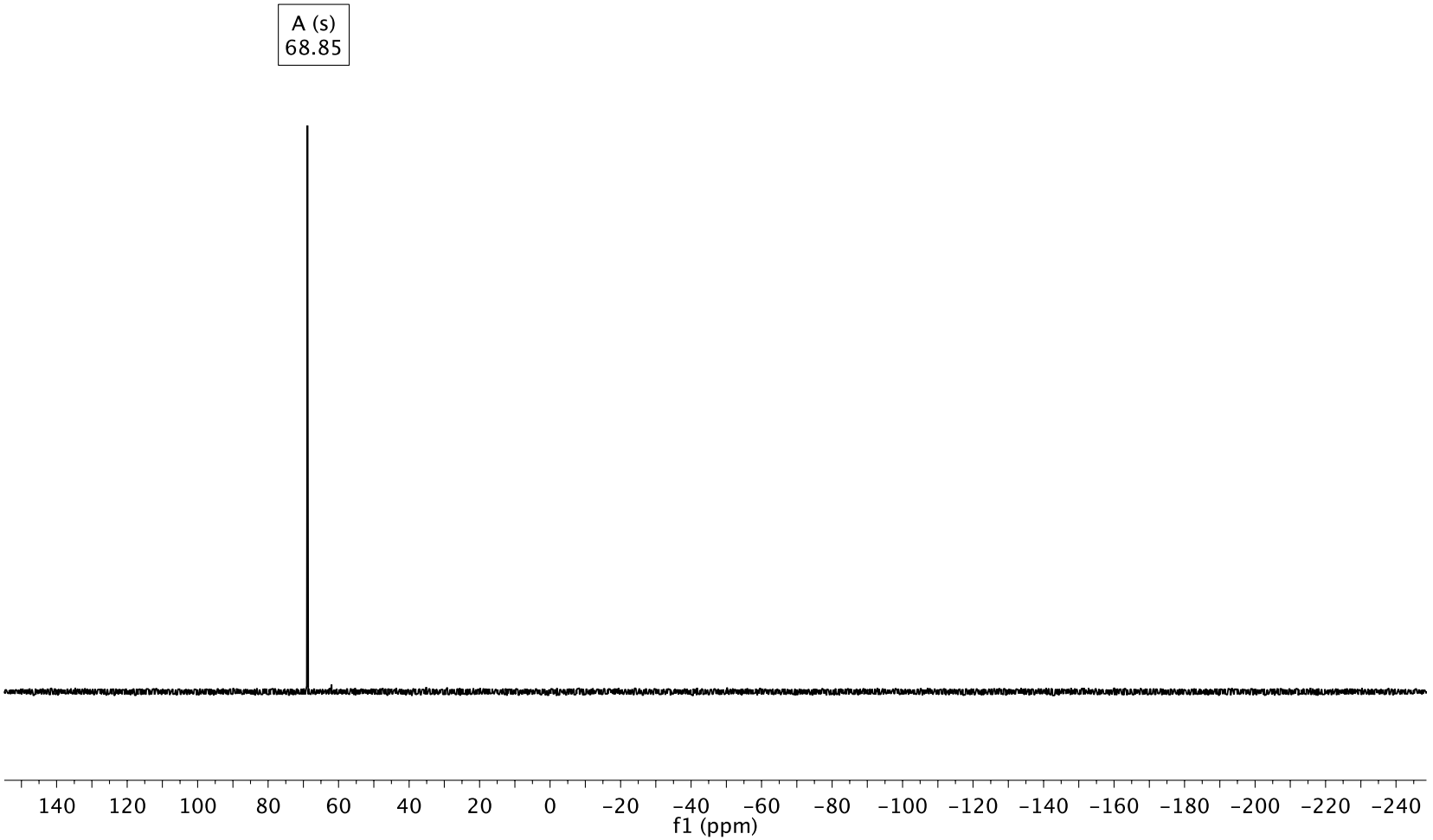

150.1
150.0
143.4
143.3
135.0
132.7
132.6
130.0
129.9
129.5
128.8
128.5
128.0
126.8
126.6
126.5
53.9
53.6
53.5
53.3
52.4
52.3
52.0
51.8
37.1
36.9
30.7
30.7
54.5 54.0 53.5 53.0 52.5 52.0 51.5 51.0
f1 (ppm)
f1 (ppm)

^{13}C NMR

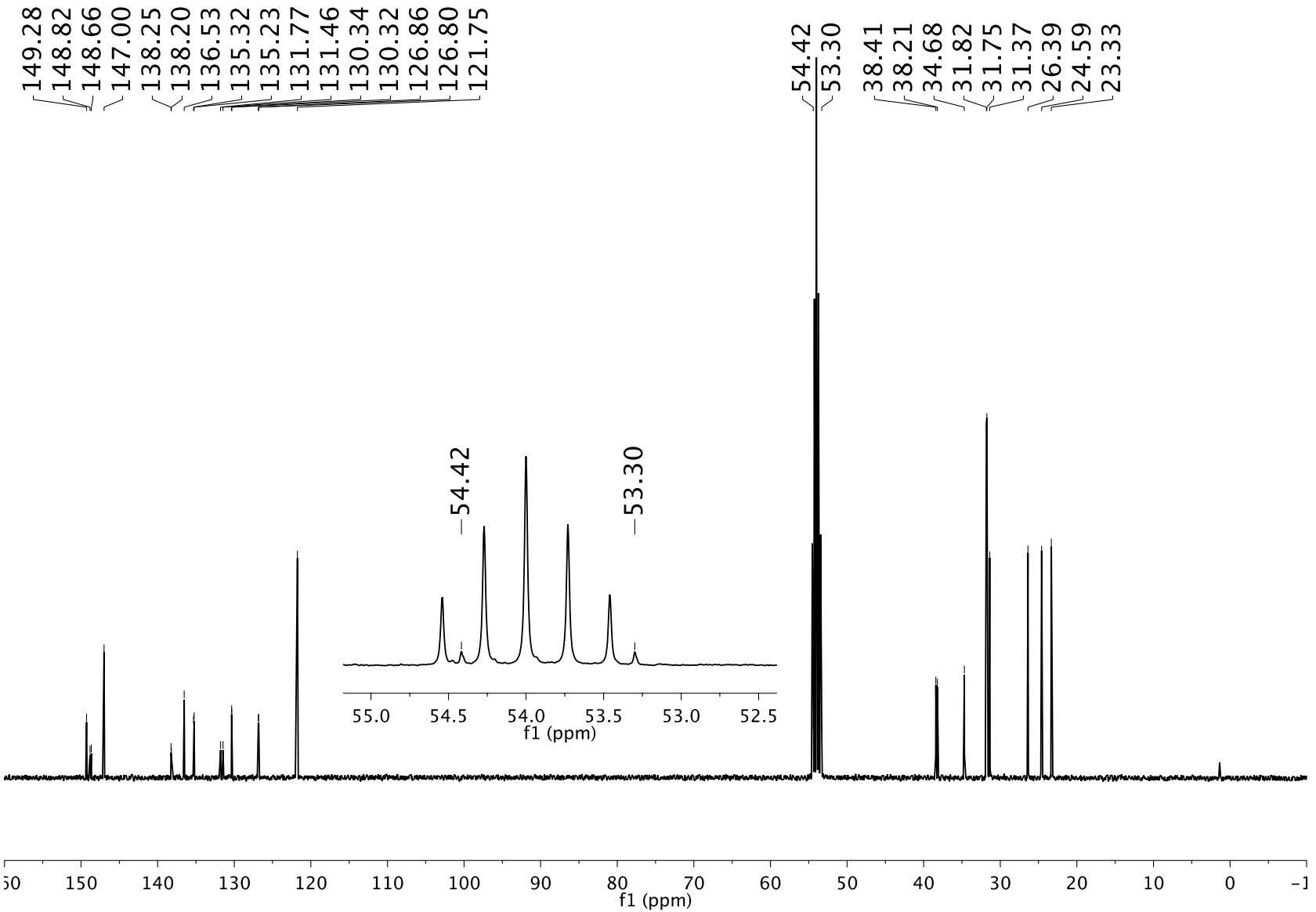
8.3. (Chloromethyl)(2-(di-*tert*-butylphosphino)-2′,4′,6′-triisopropylbiphenyl)gold (**1b**)



^{1}H NMR

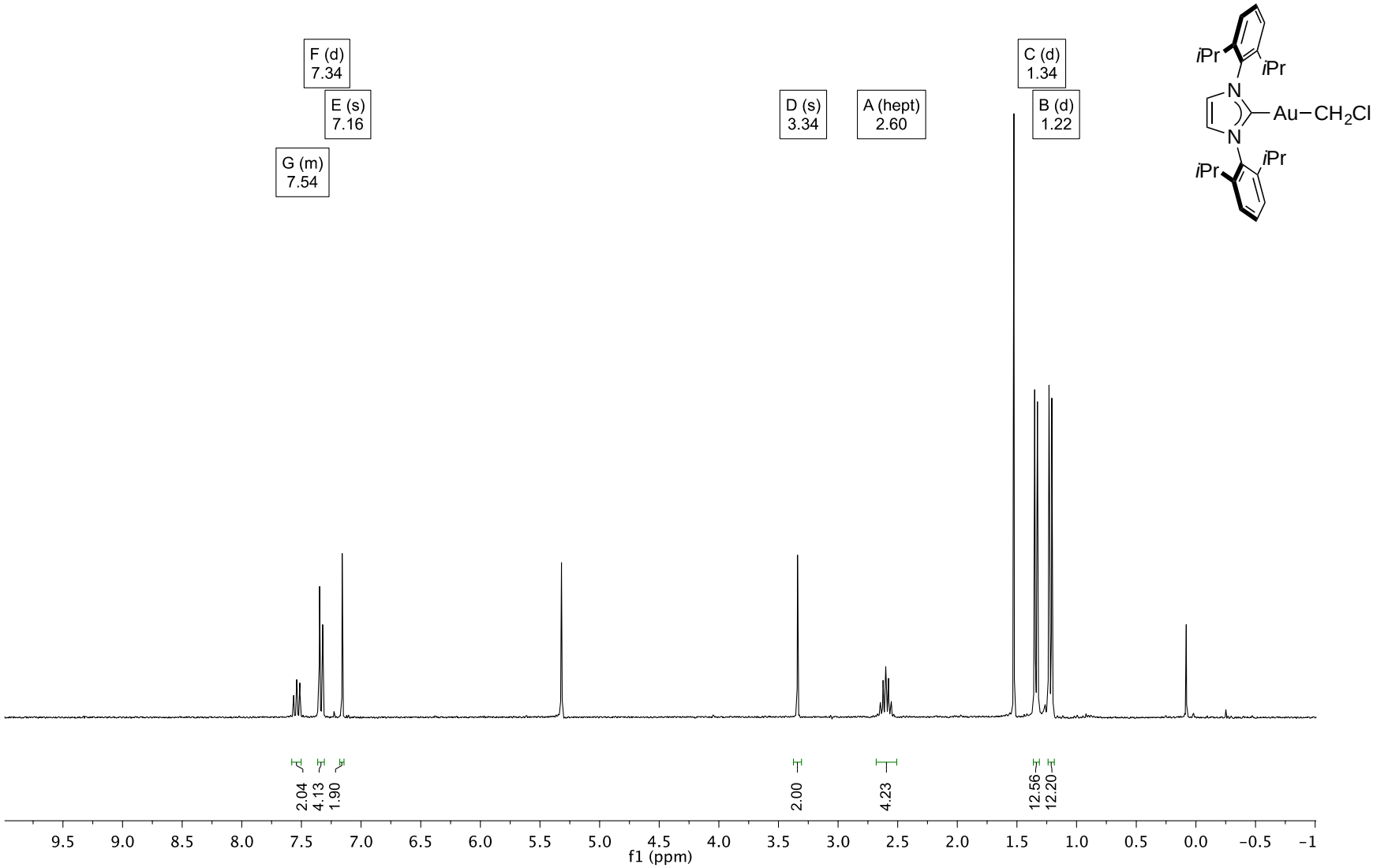

A (s)
68.85
140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240
f1 (ppm)

^{31}P NMR

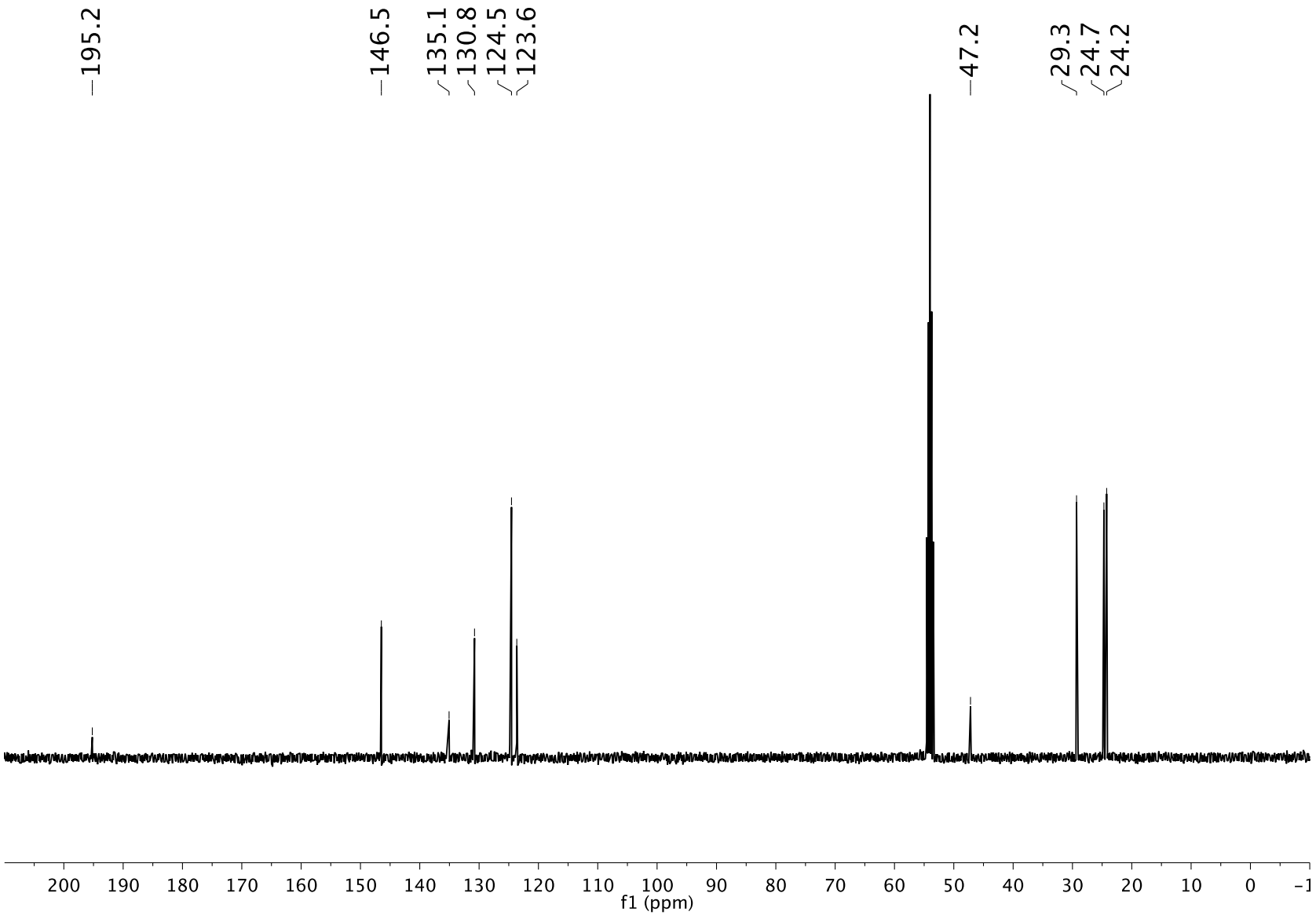

149.28
148.82
148.66
147.00
138.25
138.20
136.53
135.32
135.23
131.77
131.46
130.34
130.32
126.86
126.80
121.75
54.42
53.30
38.41
38.21
34.68
31.82
31.75
31.37
26.39
24.59
23.33
54.42
53.30
55.0
54.5
54.0
53.5
53.0
52.5
f1 (ppm)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{13}C NMR

8.4. (Chloromethyl)(1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene)gold (**1c**)

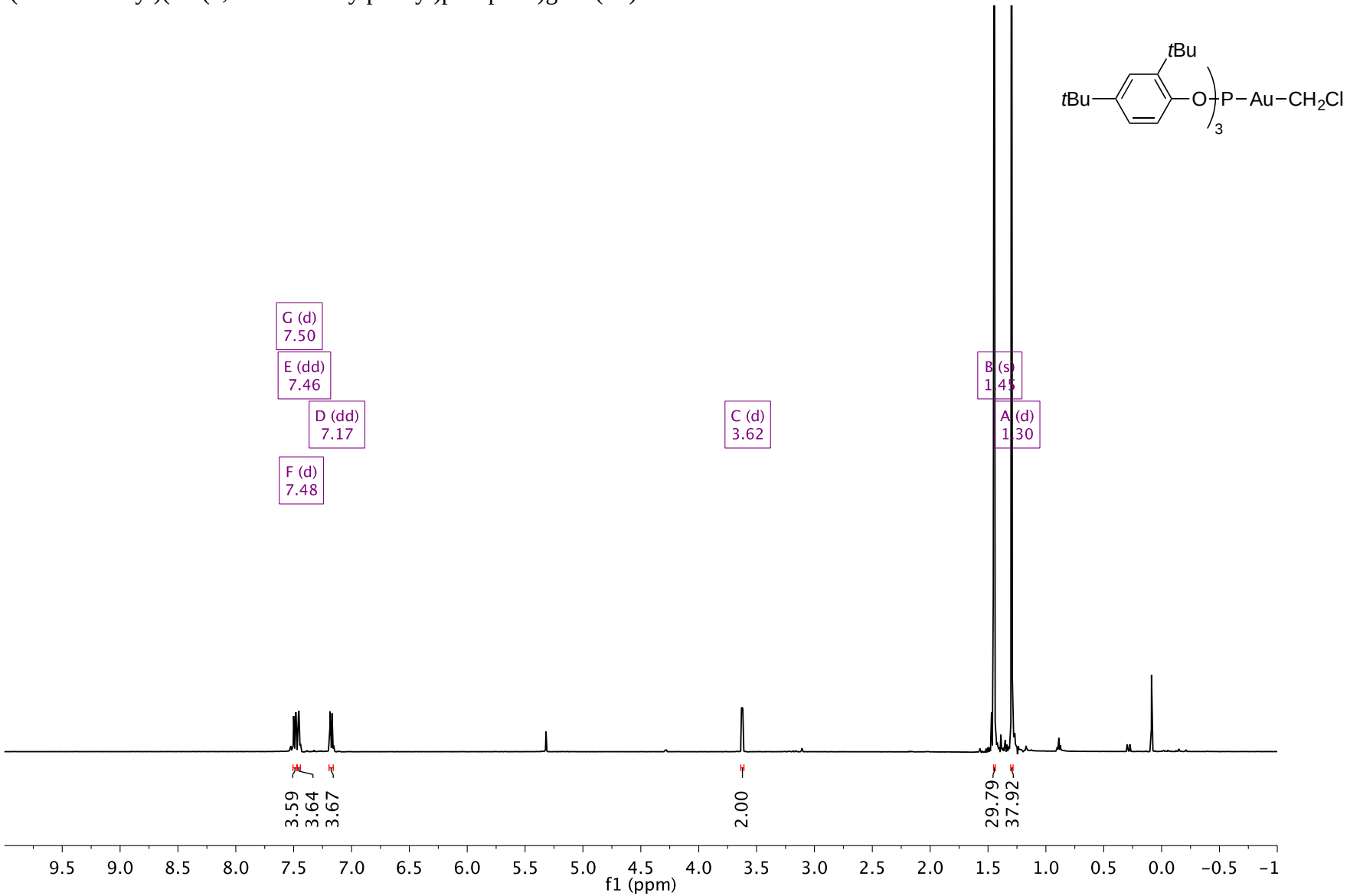


^{1}H NMR

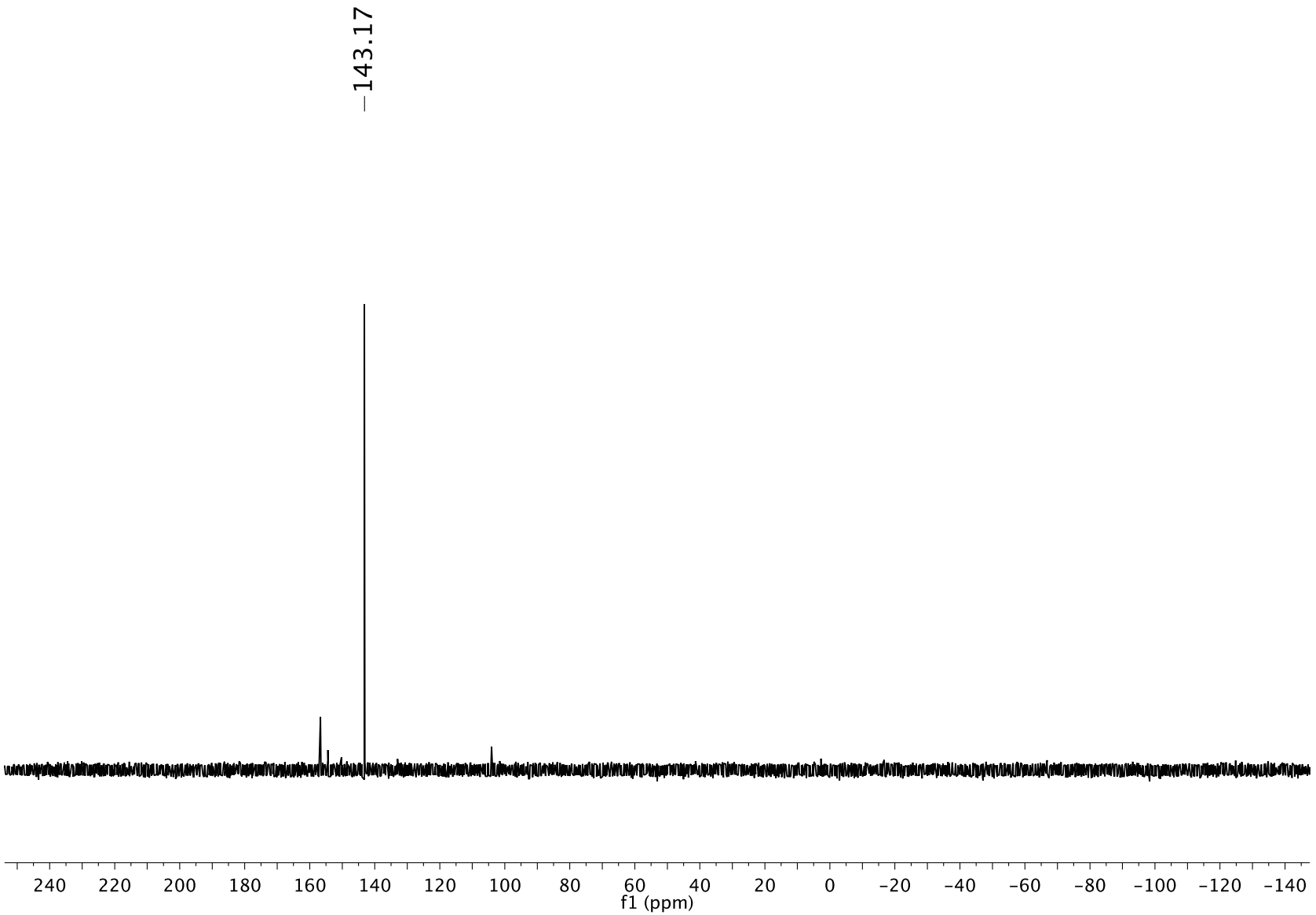

195.2
146.5
135.1
130.8
124.5
123.6
47.2
29.3
24.7
24.2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{13}C NMR

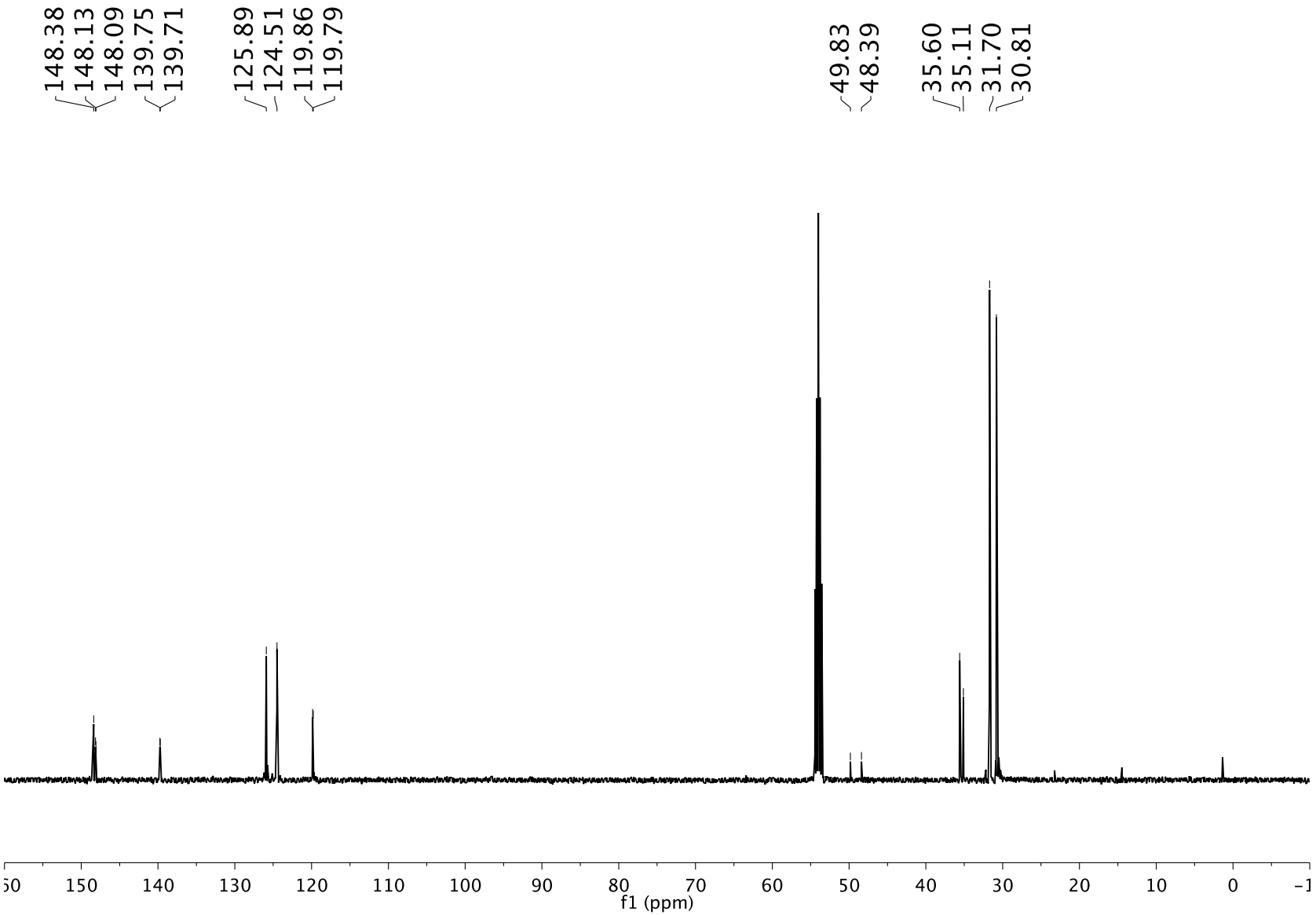
8.5. (Chloromethyl)(tris(2,4-di-tert-butylphenyl)phosphite)gold (**1d**)



^{1}H NMR

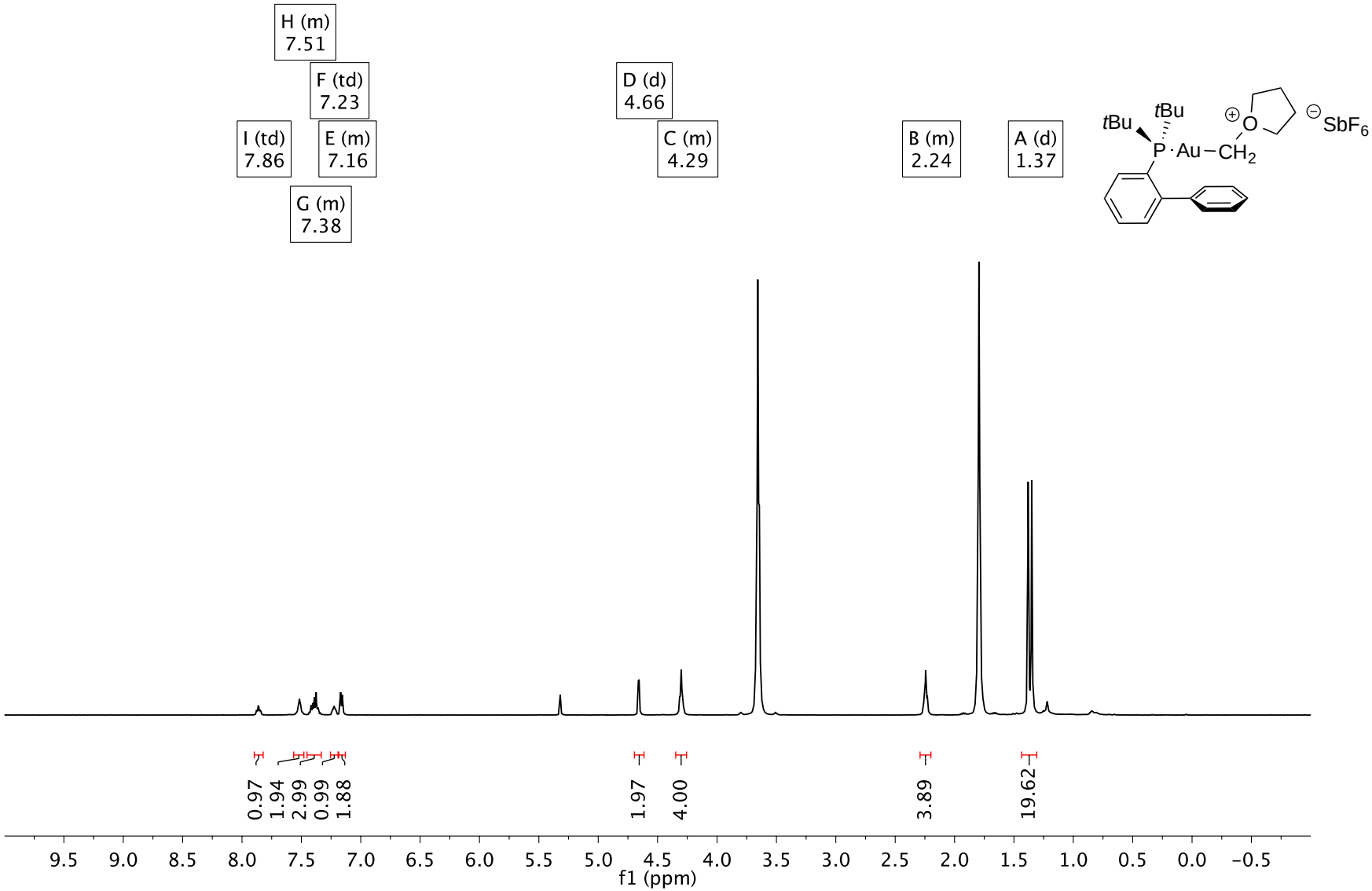

−143.17
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
f1 (ppm)

^{31}P NMR

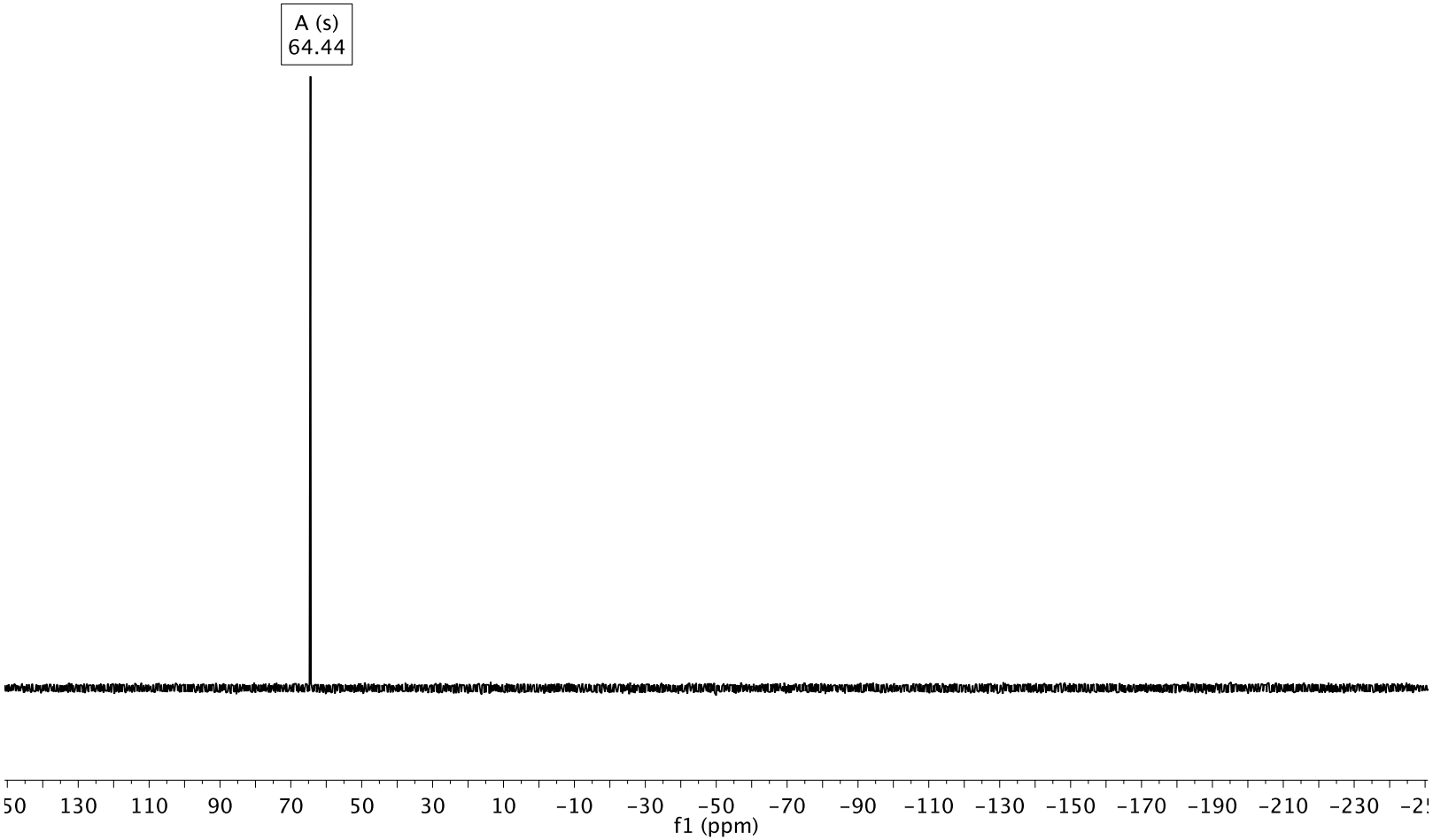

148.38
148.13
148.09
139.75
139.71
125.89
124.51
119.86
119.79
49.83
48.39
35.60
35.11
31.70
30.81
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{13}C NMR

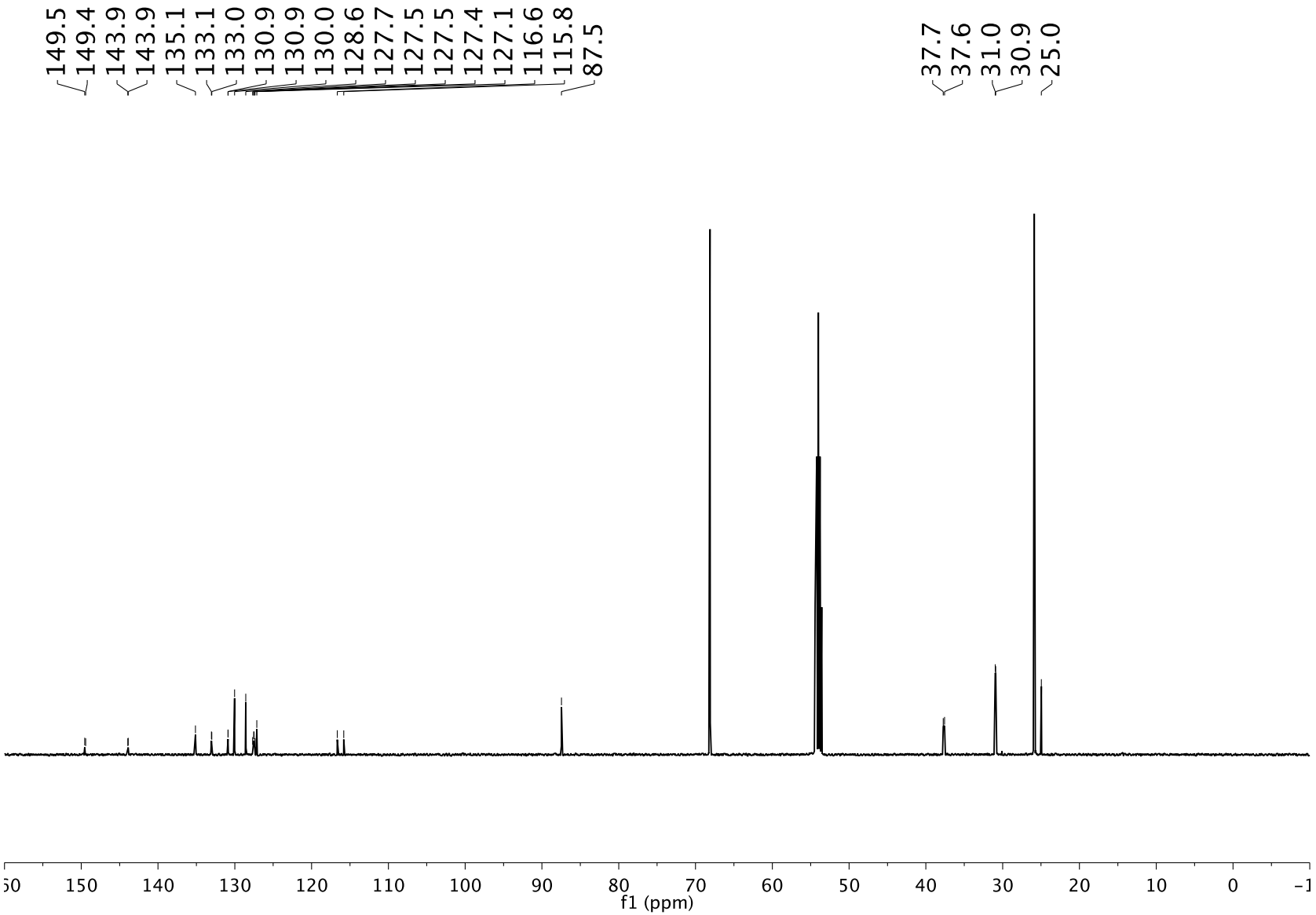
8.6. ((Tetrahydro-1*H*-furan-1-ium-1-yl)methyl)(2-(di-*tert*-butylphosphino)biphenyl)gold hexafluoroantimonate (**8**)



^{1}H NMR


A (s)
64.44
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230
f1 (ppm)

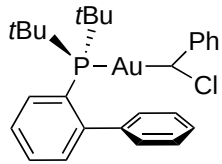
^{31}P NMR

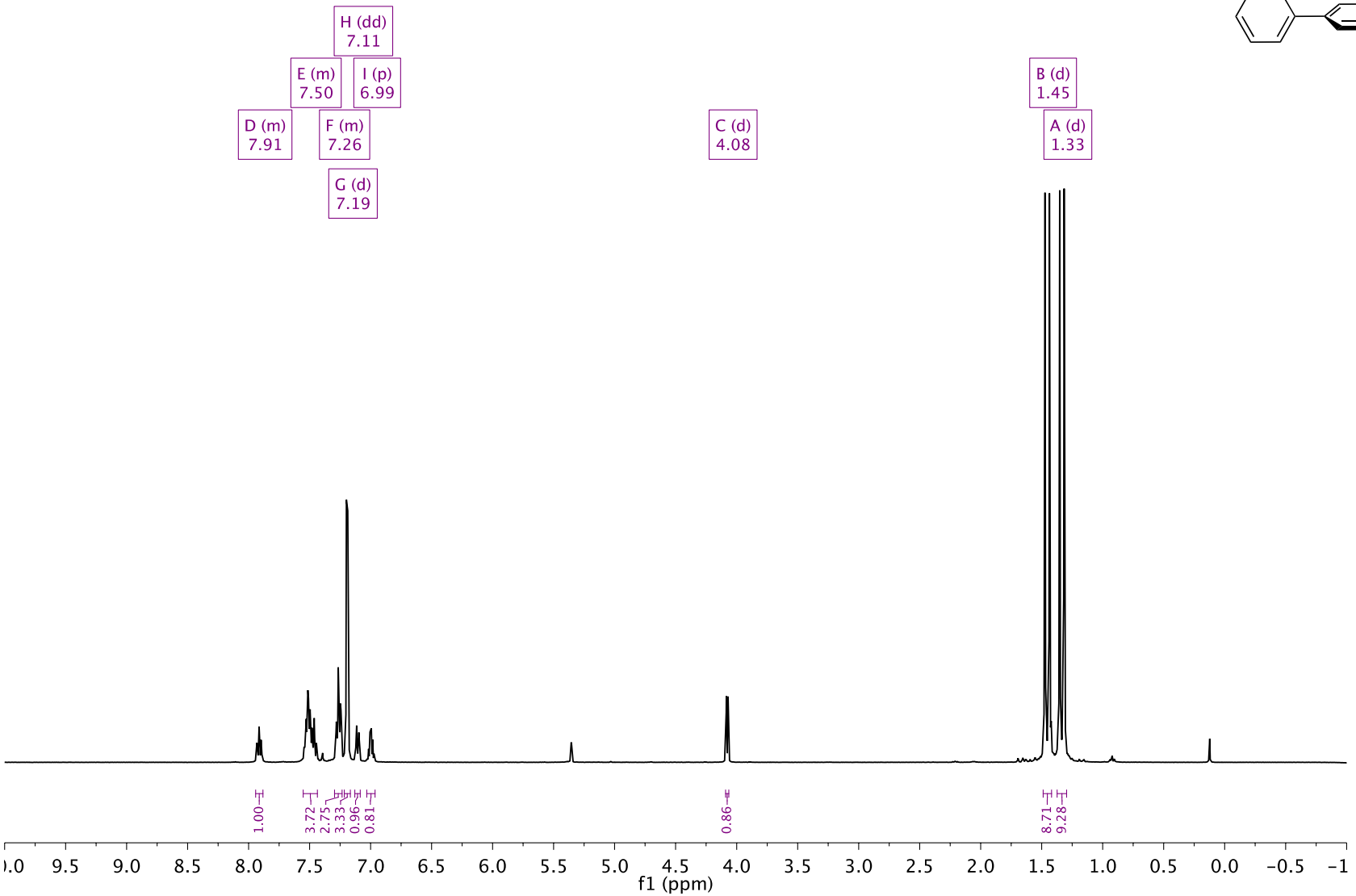

149.5
149.4
143.9
143.9
135.1
133.1
133.0
130.9
130.9
130.0
128.6
127.7
127.5
127.5
127.4
127.1
116.6
115.8
87.5
37.7
37.6
31.0
30.9
25.0
f1 (ppm)

^{13}C NMR

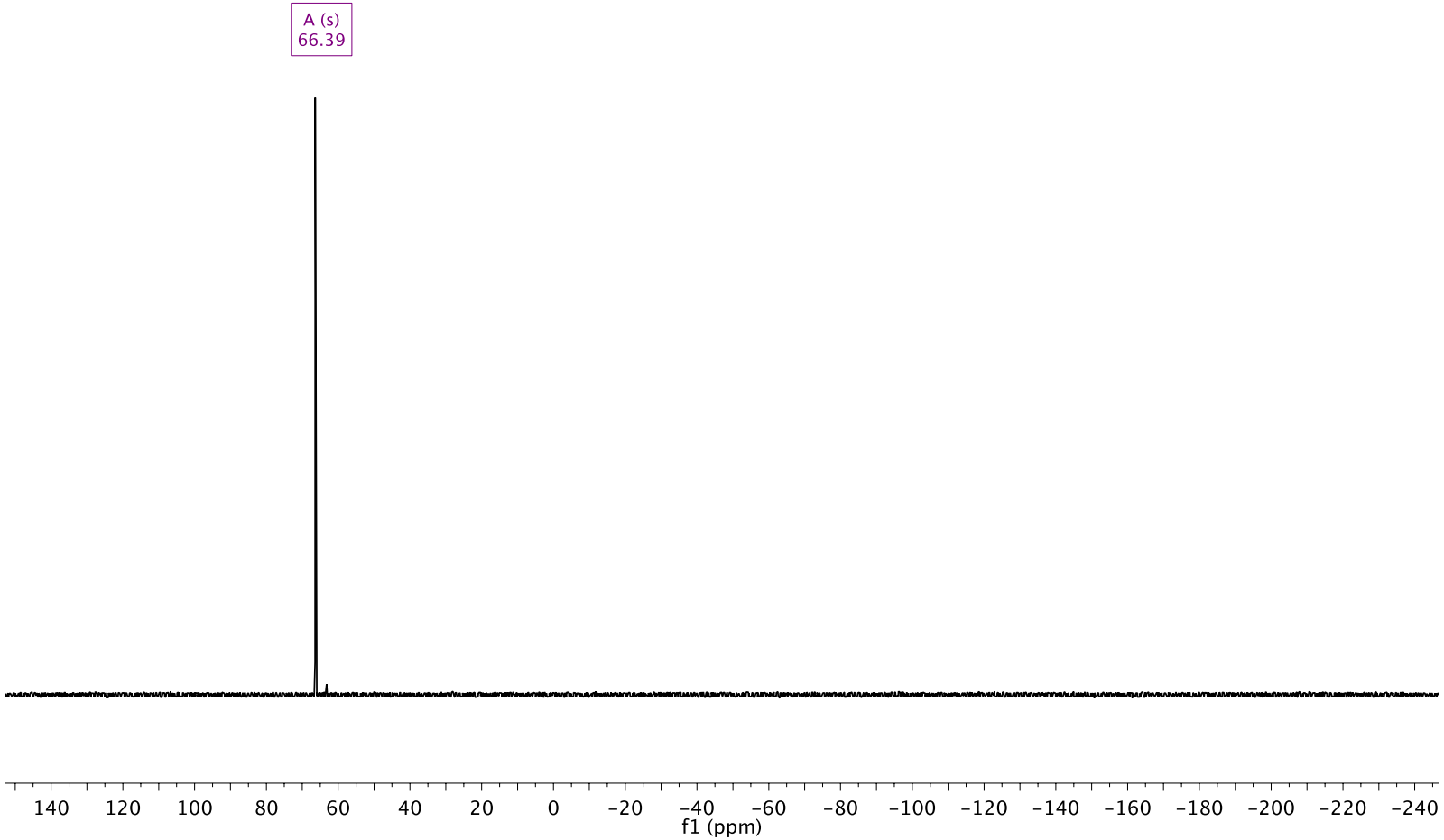
8.7. (Chloro(phenyl)methyl)(2-(di-*tert*-butylphosphino)biphenyl)gold (**9**)

^{1}H NMR

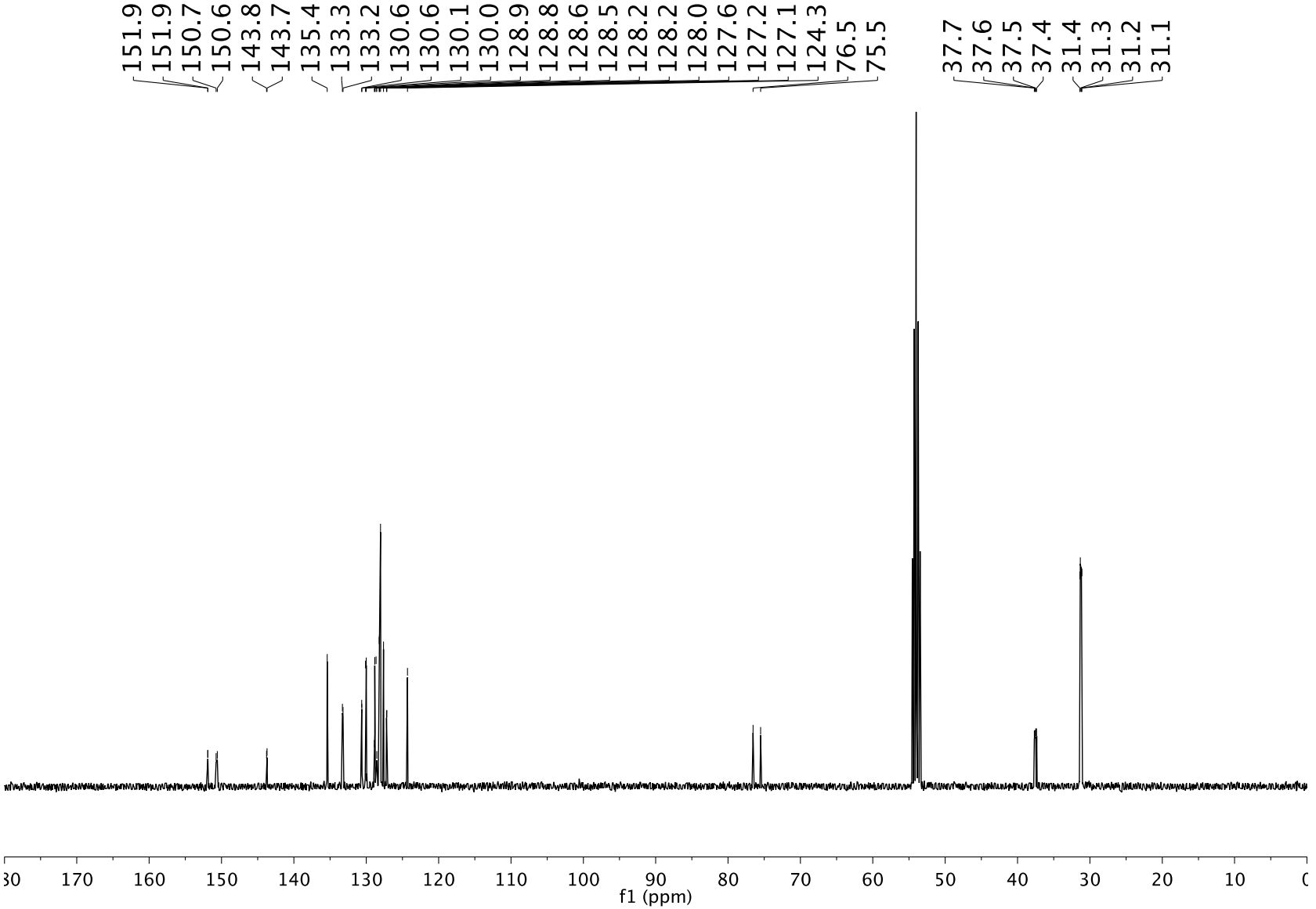




^{31}P NMR


A (s)
66.39
140
120
100
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
−220
−240
f1 (ppm)

^{13}C NMR


151.9
151.9
150.7
150.6
143.8
143.7
135.4
133.3
133.2
130.6
130.6
130.1
130.0
128.9
128.8
128.6
128.5
128.2
128.2
128.0
127.6
127.2
127.1
124.3
76.5
75.5
37.7
37.6
37.5
37.4
31.4
31.3
31.2
31.1
f1 (ppm)

9. Mass spectrometry

9.1. ESI-MS spectra of **1a**

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	W:\Data\160610\160610_CGJS190-1_RE3_01_10680.d	Acquisition Date	10/06/2016 14:29:32
Method	tune_low_hplc-exactas3min-noe.m	Operator	ICIQ
Sample Name	160610_CGJS190-1	Instrument / Ser#	micrOTOF 213750.10394
Comment	0.5 uL starting sol, MeOH injection, END PLATE. -700V		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	8.0 l/min
Scan End	2000 m/z	Set End Plate Offset	-700 V	Set Divert Valve	Source