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Supporting Information

Supporting Information

Dissecting Anion Effects in Gold(I)-Catalyzed Intermolecular Cycloadditions

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Supporting Information

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6. Mechanistic Study

1. General Information

Unless otherwise stated, reactions were carried out under argon atmosphere in solvents dried by passing through an activated alumina column on a PureSolv^{TM} solvent purification system (Innovative Technologies, Inc., MA). Analytical thin layer chromatography was carried out using TLC-aluminium sheets with 0.2 mm of silica gel (Merck GF$_{234}$) using UV light as the visualizing agent and an acidic solution of vanillin in ethanol as the developing agent. Chromatograpy purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40-60 mm) or automated flash chromatographer CombiFlash Companion. Preparative TLC was performed on 20 cm × 20 cm silica gel plates (2.0 mm thick, catalogue number 02015, Analtech). If indicated, preparative TLC was performed on 20 cm x 20 cm aluminum oxide plates (0.25 mm thick, 90066, Fluka). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator.

NMR spectra was recorded at 298 K on a Bruker Avance 400 Ultrashield and Bruker Avance 500 Ultrashield apparatus. Mass spectra was recorded on a Waters Micromass LCT Premier (ESI), Waters Micromass GCT (EI, CI) and Bruker Daltonics Autoflex (MALDI) spectrometers. Elemental analyses were performed on a LECO CHNS 932 micro-analyzer at the Universidad Complutense de Madrid. Melting points were determined using a Büchi melting point apparatus and are uncorrected.

Crystal structure determinations were carried out using a Bruker-Nonius diffractomer equipped with an APPEX 2 4K CCD area detector, a FR591 rotating anode with MoK$_a$ radiation, Montel mirrors as monochromator and a Kryoflex low temperature device (T = -173 ºC). Full-sphere data collection was used with w and j scans. *Programs used*: Data collection APEX-2, data reduction Bruker Saint V/.60A and absorption correction SADABS. Structure Solution and Refinement: Crystal structure solution was achieved using direct methods as implement in SHELXTL and visualized using the program XP. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F2 using all measured intensities was carried out using the program SHELXTL. All non-hydrogen atoms were refined including anisotropic displacement parameters.

Alkynes, alkenes, 5-methylhex-5-en-2-one as well as the silver salts, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate and catalyst **A1** were used as received from Alfa Aesar or Aldrich. Alkene **2f**[1] and 1,4-enyne **10**[2] were prepared according the described procedure. Catalysts **B1**[3], **B2**[4] and {phenylethynyl [(2′,4′,6′-triisopropyl-1,1′-biphenyl-2-yl) di-*tert*-butylphosphine] gold(I)} [(2′,4′,6′-triisopropyl-1,1′-biphenyl-2-yl) di-*tert*-butylphosphine] gold(I) hexafuloroantimonate[5] were prepared according to the literature too.

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[1] T.B. Durham, N. Blanchard, B.M. Savall, N.A. Powell, W.R. Roush, *J. Am. Chem. Soc.* **2004**, *126*, 9307-9317.

[2] C. Obradors, D. Lebœuf, J. Aydin, A. M. Echavarren, *Org. Lett.* **2013**, DOI: 10.1021/ol400358f.

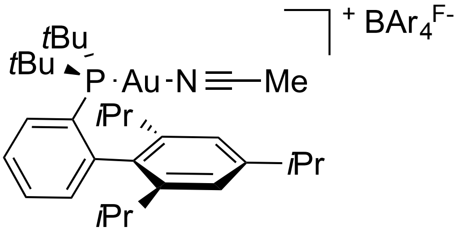
[3] C. H. M. Amijs, V. López-Carrillo, M. Raducan, P. Pérez-Galán, C. Ferrer, A. M. Echavarren, *J. Org. Chem.* **2008**, *73*, 7721-7730.

[4] N. Huguet, D. Lebœuf, A. M. Echavarren, *Chem. Eur. J.* **2013**, DOI: 10.1002/chem.201300646.

[5] C. Obradors, A. M. Echavarren, *Chem. Eur. J.* **2013**, *19*, 3547–3551.

2. Synthesis of Gold(I) Complexes

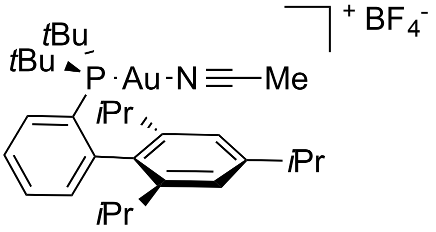
(Acetonitrile)[(2′,4′,6′-triisopropyl-1,1′-biphenyl-2-yl)di-*tert*-butylphosphine]gold(I) tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (A2)



Chloro[(2’,4’,6’-triisopropyl-1,1’-biphenyl-2-yl)di-*tert*-butylphosphine]gold(I) (100.0 mg, 0.152 mmol) and acetonitrile (9.5 μl, 0.183 mmol) were dissolved in CH_2Cl_2 (6.6 ml). Then, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (135.0 mg, 0.152 mmol) was added and the reaction mixture was stirred at room temperature for 30 min. The crude was filtered through Celite and concentrated. Finally, it was filtered through Teflon 0.22 and washed with CH_2Cl_2. The solvent was removed to afford a white powder (224.3 mg, 0.147 mmol, 97%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 7.92 – 7.85 (m, 1H), 7.75 – 7.70 (m, 8H), 7.66 – 7.58 (m, 2H), 7.56 (s, 4H), 7.32 (m, 1H), 7.16 (s, 2H), 2.94 (p, *J* = 6.9 Hz, 1H), 2.33 (dt, *J* = 13.4, 6.7 Hz, 2H), 2.25 (broad s, 3H), 1.41 (d, *J* = 16.3 Hz, 18H), 1.32 (d, *J* = 6.9 Hz, 6H), 1.25 (d, *J* = 6.8 Hz, 6H), 0.93 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ (ppm) 162.3 (q, *J* (^{13}C-^{11}B) = 50.1 Hz), 150.4, 148.0, 147.6 (d, *J* (^{13}C-^{31}P) = 12.8 Hz), 136.7 (d, *J* (^{13}C-^{31}P) = 6.1 Hz), 135.5, 135.4, 134.7 (d, *J* (^{13}C-^{31}P) = 4.6 Hz), 132.1 (d, *J* (^{13}C-^{31}P) = 2.6 Hz), 129.5 (q, *J* (^{13}C-^{19}F) = 28.6 Hz), 128.1 (d, *J* (^{13}C-^{31}P) = 8.1 Hz), 126.0 (d, *J* (^{13}C-^{31}P) = 50.2 Hz), 125.2 (q, *J* (^{13}C-^{19}F) = 272.3 Hz), 122.5, 118.1 (p, *J* (^{13}C-^{19}F) = 4.0 Hz), 39.2 (d, *J* (^{13}C-^{31}P) = 29.3 Hz), 34.6, 31.5 (d, *J* (^{13}C-^{31}P) = 4.3 Hz), 31.5, 26.3, 24.5, 23.4, 3.3 and one carbon is missing probably because of overlapping. ^{31}P {^{1}H} NMR (162 MHz, CD_2Cl_2): δ (ppm) 58.68. ^{19}F {^{1}H} NMR (376 MHz, CD_2Cl_2): δ (ppm) -62.97. ^{11}B {^{1}H} NMR (128 MHz, CD_2Cl_2): δ (ppm) -6.68. MALDI$^+$: *m/z* calcd for $C_{31}H_{48}AuNP^+$ $[M-C_{32}H_{12}BF_{24}]^+$: 662.3175, found: 662.3184. Anal. calcd for $C_{63}H_{60}AuBF_{24}NP$: C, 49.59; H, 3.97; N, 0.92; found: C, 49.56; H, 3.94; N, 0.97.

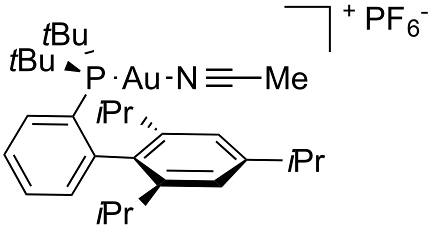
(Acetonitrile)[(2′,4′,6′-triisopropyl-1,1′-biphenyl-2-yl)di-*tert*-butylphosphine]gold(I) tetrafluoroborate (A3)



Chloro[(2’,4’,6’-triisopropyl-1,1’-biphenyl-2-yl)di-*tert*-butylphosphine]gold(I) (100.0 mg, 0.152 mmol) and acetonitrile (9.5 μl, 0.183 mmol) were dissolved in CH_2Cl_2 (6.6 ml). Then, silver tetrafluoroborate (29.6 mg, 0.152 mmol) was added and the reaction mixture was stirred at room temperature for 20 min. The crude was filtered through and concentrated. Finally, it was filtered through Teflon 0.22 and washed with CH_2Cl_2. The solvent was removed to afford a white powder (113.9 mg, 0.152 mmol, 100%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 7.90 (td, *J* = 8.9, 8.1, 2.3 Hz, 1H), 7.69 – 7.54 (m, 2H), 7.32 (ddd, *J* = 6.9, 4.9, 2.5 Hz, 1H), 7.17 (s, 2H), 2.97 (hept, *J* = 6.8 Hz, 1H), 2.39 (s, 3H), 2.33 (hept, *J* = 6.7 Hz, 2H), 1.43 (d, *J* = 16.3 Hz, 18H), 1.33 (d, *J* = 6.9 Hz, 6H), 1.27 (d, *J* = 6.8 Hz, 6H), 0.93 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ (ppm) 150.5, 147.8, 147.7 (d, *J* (^{13}C-^{31}P) = 12.7 Hz), 136.6 (d, *J* (^{13}C-^{31}P) = 6.0 Hz), 135.4 (d, *J* (^{13}C-^{31}P) = 8.1 Hz), 134.8 (d, *J* (^{13}C-^{31}P) = 4.3 Hz), 132.0, 128.0 (d, *J* (^{13}C-^{31}P) = 7.8 Hz), 126.3 (d, *J* (^{13}C-^{31}P) = 47.8 Hz), 122.5, 120.0 (d, *J* (^{13}C-^{31}P) = 4.4 Hz), 39.2 (d, *J* (^{13}C-^{31}P) = 28.2 Hz), 34.5, 31.6 (d, *J* (^{13}C-^{31}P) = 5.8 Hz), 31.5, 26.4, 24.5, 23.4, 3.3. ^{31}P {^{1}H} NMR (162 MHz, CD_2Cl_2): δ (ppm) 58.58. ^{19}F {^{1}H} NMR (376 MHz, CD_2Cl_2): δ (ppm) -153.10. ^{11}B {^{1}H} NMR (128 MHz, CD_2Cl_2): δ (ppm) -1.23. MALDI$^+$: *m/z* calcd for $C_{31}H_{48}AuNP^+$ $[M-BF_4]^+$: 662.3184, found: 662.3180. Anal. calcd for $C_{63}H_{60}AuBF_{24}NP$: C, 49.68; H, 6.46; N, 1.87; found: C, 48.89; H, 6.20; N, 1.64.

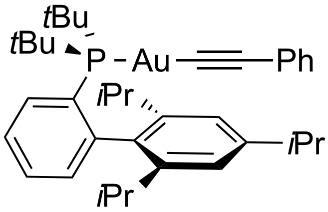
(Acetonitrile)[(2´,4´,6´-triisopropyl-1,1´-biphenyl-2-yl)di-*tert*-butylphosphine]gold(I) hexafluorophosphate (A4)



Chloro[(2’,4’,6’-triisopropyl-1,1’-biphenyl-2-yl)di-*tert*-butylphosphine]gold(I) (350.0 mg, 0.533 mmol) and acetonitrile (33.0 µl, 0.639 mmol) were dissolved in CH_2Cl_2 (23 ml). Then, silver hexafluorophosphate (135.0 mg, 0.533 mmol) was added and the reaction mixture was stirred at room temperature for 20 min. The crude was filtered through Celite and concentrated. Finally, it was filtered through Teflon 0.22 and washed with CH_2Cl_2. The solvent was removed to afford a white powder (221.0 mg, 0.274 mmol, 51%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 7.90 (ddd, J = 9.0, 7.1, 2.2 Hz, 1H), 7.60 (dq, J = 7.1, 2.0 Hz, 2H), 7.33 (td, J = 6.6, 5.7, 3.2 Hz, 1H), 7.17 (s, 1H), 2.95 (hept, J = 6.9 Hz, 1H), 2.38 – 2.27 (m, 4H), 1.43 (d, J = 16.3 Hz, 18H), 1.33 (d, J = 6.9 Hz, 6H), 1.27 (d, J = 6.7 Hz, 6H), 0.93 (d, J = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ (ppm) 149.9, 147.8, 136.6 (d, J (^{13}C-^{31}P) = 7.1 Hz), 135.3 (d, J (^{13}C-^{31}P) = 9.3 Hz), 134.8 (d, J (^{13}C-^{31}P) = 4.2 Hz), 132.0, 128.0 (d, J (^{13}C-^{31}P) = 7.2 Hz), 122.4, 117.9, 39.2 (d, J (^{13}C-^{31}P) = 29.2 Hz), 34.55, 31.56 (d, J = 5.6 Hz), 26.35, 24.47, 23.39, 3.23. Two signals are missing due to overlapping. ^{31}P {^{1}H} NMR (162 MHz, CD_2Cl_2): δ (ppm) 58.53, -139.23 (hept, J (^{31}P-^{19}F) = 715.0 Hz). ^{19}F {^{1}H} NMR (376 MHz, CD_2Cl_2): δ (ppm) -73.46 (d, J (^{19}F-^{31}P)= 710.3 Hz). ESI$^+$: *m/z* calcd for $C_{31}H_{48}AuNP^+$ $[M-PF_6]^+$: 662.3184, found: 662.3176.

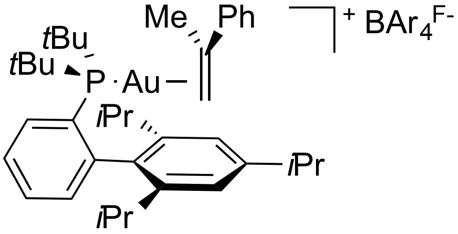
[(2´,4´,6´-Triisopropyl-1,1´-biphenyl-2-yl)di-*tert*-butylphosphine](2-phenylethynyl)gold(I) (16)



Lithium bis(trimethylsilyl)amide (53.5 mg, 0.320 mmol) was dissolved in THF (4.0 ml) and cooled to 0 ºC. Ethynylbenzene (35.1 μl, 0.320 mmol) was added and the solution was stirred for 30 min. Afterwards, chloro[(2',4',6'-triisopropyl-1,1'-biphenyl-2-yl)di-*tert*-butylphosphine]gold(I) (200.0 mg, 0.304 mmol) dissolved in THF (3.0 ml) was added and the solution was stirred overnight at room temperature. The crude was concentrated, dissolved in CH_2Cl_2 and filtered through Teflon 0.22. The solvent was removed to afford a white powder (219.0 mg, 0.303 mmol, 99%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ (ppm) 7.92 (td, *J* = 7.4, 1.8 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.30 – 7.28 (m, 3H), 7.21 – 7.18 (m, 2H), 7.15 – 7.12 (m, 3H), 2.93 (p, *J* = 6.9 Hz, 1H), 2.40 (p, *J* = 6.7 Hz, 2H), 1.43 (d, *J* = 14.8 Hz, 18H), 1.36 (d, *J* = 6.8 Hz, 6H), 1.27 (d, *J* = 6.9 Hz, 6H), 0.92 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ (ppm) 150.0, 148.7 (d, *J* (^{13}C-^{31}P) = 15.6 Hz), 146.4, 137.3 (d, *J* (^{13}C-^{31}P) = 133.1 Hz), 136.6 (d, *J* (^{13}C-^{31}P) = 5.1 Hz), 136.1 (d, *J* (^{13}C-^{31}P) = 1.6 Hz), 135.2 (d, *J* (^{13}C-^{31}P) = 7.9 Hz), 132.2, 130.4 (d, *J* (^{13}C-^{31}P) = 2.2 Hz), 129.9 (d, *J* (^{13}C-^{31}P) = 37.0 Hz), 128.3, 127.4 (d, *J* (^{13}C-^{31}P) = 2.7 Hz), 126.9 (d, *J* (^{13}C-^{31}P) = 6.0 Hz), 126.0, 122.3, 101.5 (d, *J* (^{13}C-^{31}P) = 23.9 Hz), 38.5 (d, *J* (^{13}C-^{31}P) = 23.2 Hz), 34.5, 31.7 (d, *J* (^{13}C-^{31}P) = 6.8 Hz), 31.4, 26.5, 24.4, 23.2. ^{31}P {^{1}H} NMR (202 MHz, CD_2Cl_2): δ (ppm) 66.89. MALDI$^+$: *m/z* calcd for $C_{37}H_{50}AuPNa^+$ [M+Na]$^+$: 745.3208, found: 745.3216. Structure confirmed by X-ray crystallography: CCDC 953709.

(α-Methylstyrene)[(2′,4′,6′-triisopropyl-1,1′-biphenyl-2-yl)di-*tert*-butylphosphine]gold(I) tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (15b)

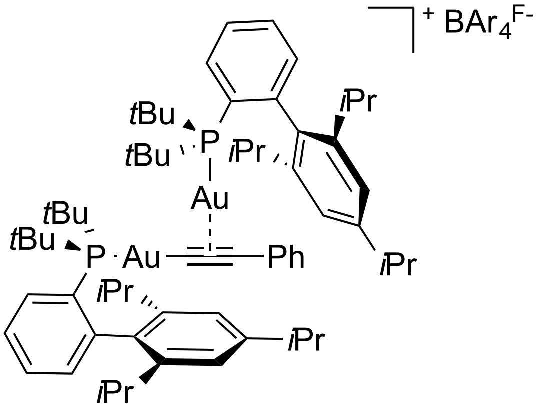


Chloro[(2',4',6'-triisopropyl-1,1'-biphenyl-2-yl)di-*tert*-butylphosphine]gold(I) (100.0 mg, 0.152 mmol) and α-methylstyrene (30.0 µl, 0.228 mmol) were dissolved in CH_2Cl_2 (10.0 ml). Then, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (135.0 mg, 0.152 mmol) was added and the reaction mixture was stirred at room temperature for 30 min. The crude was filtered through Celite and concentrated. Finally, it was filtered through Teflon 0.22 and washed with CH_2Cl_2. The solvent was removed to afford a white powder (210.4 mg, 0.131 mmol, 86%).

^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ (ppm) 7.82 (td, *J* = 7.8, 1.6 Hz, 1H), 7.76 – 7.70 (m, 8H), 7.63 – 7.53 (m, 6H), 7.50 – 7.39 (m, 5H), 7.29 (s, 2H), 7.21 (ddd, *J* = 7.3, 3.7, 1.7 Hz, 1H), 4.27 (dd, *J* = 4.5, 0.8 Hz, 1H), 3.95 (d, *J* = 4.5 Hz, 1H), 3.12 (p, *J* = 6.9 Hz, 1H), 2.50 (s, 3H), 2.42 – 2.19 (m, 2H), 1.43 (d, *J* = 6.9 Hz, 6H), 1.39 – 1.03 (m, 24H), 0.92 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2, 213 K): it was not possible to properly assign all the signals due to the broadening of some peaks because of the weak coordination of the metal to the alkene combined with the complexity of the heterocouplings with ^{31}P, ^{19}F and ^{11}B δ (ppm) 162.95, 162.55, 162.16, 161.76, 155.99, 151.76, 149.09, 147.08, 146.97, 135.95, 135.75, 135.47, 135.32, 135.04, 133.40, 132.93, 132.61, 132.26, 130.29, 129.79, 129.61, 129.36, 129.07, 128.44, 127.14, 126.67, 126.27, 124.11, 123.63, 123.12, 121.94, 118.55, 118.21, 117.88, 117.55, 89.01, 88.68, 38.61, 38.41, 34.76, 31.64, 31.42, 31.11, 26.27, 26.04, 25.90, 25.02, 24.82, 24.64, 24.45, 23.82. ^{31}P {^1H} NMR (162 MHz, CD_2Cl_2, 298 K): δ (ppm) 69.34. ^{19}F {^1H} NMR (376 MHz, CD_2Cl_2, 298 K): δ (ppm) -62.83. ^{11}B {^1H} NMR (128 MHz, CD_2Cl_2, 298 K): δ (ppm) -6.67. ESI$^+$: *m/z* calcd for $C_{29}H_{45}AuP^+$ $[M-C_{31}H_{22}BF_{24}]^+$: 621.2919, found: 621.2916. Structure confirmed by X-ray crystallography: CCDC 953708.

{Phenylethynyl[(2′,4′,6′-triisopropyl-1,1′-biphenyl-2-yl)di-tert-butylphosphine]gold(I)}

[(2′,4′,6′-triisopropyl-1,1′-biphenyl-2-yl)di-tert-butylphosphine]gold(I) tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (9b)



Chloro[(2’,4’,6’-triisopropyl-1,1’-biphenyl-2-yl)di-*tert*-butylphosphine]gold(I) (68.2 mg, 0.104 mmol) and [(2′,4′,6′-triisopropyl-1,1′-biphenyl-2-yl)di-*tert*-butylphosphine](2-phenylethynyl)gold(I) (75 mg, 0.104 mmol) were dissolved in CH_2Cl_2 (9.4 ml). Then, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (92 mg, 0.104 mmol)was added and the reaction mixture was stirred at room temperature for 30 min. The crude was filtered through Celite and concentrated. Finally, it was filtered through Teflon 0.22 and washed with CH_2Cl_2. The solvent was removed to afford a white powder (223.0 mg, 0.101 mmol, 97%).

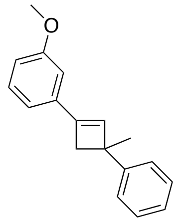
^1H NMR (400 MHz, CD_2Cl_2): δ (ppm) 7.95 – 7.87 (m, 2H), 7.73 (dd, *J* = 4.2, 2.0 Hz, 8H), 7.57 (broad s, 4H), 7.56 – 7.49 (m, 4H), 7.48 – 7.42 (m, 1H), 7.42 – 7.37 (m, 2H), 7.34 – 7.30 (m, 2H), 7.26 – 7.22 (m, 2H), 6.84 (s, 4H), 2.39 – 2.29 (m, 6H), 1.42 (d, *J* = 15.6 Hz, 36H), 1.14 (d, *J* = 6.8 Hz, 12H), 1.09 (d, *J* = 6.9 Hz, 12H), 0.85 (d, *J* = 6.6 Hz, 12H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ (ppm) 162.3 (q, *J* (^{13}C-^{11}B) = 50.0 Hz), 150.0, 148.1 (d, *J* (^{13}C-^{31}P) = 14.3 Hz), 147.1, 136.2 (d, *J* (^{13}C-^{31}P) = 5.6 Hz), 135.5, 135.4, 135.0 (d, *J* (^{13}C-^{31}P) = 1.2 Hz), 133.1, 131.4, 130.6, 130.0 – 129.0 (m), 129.0, 127.7 (d, *J* (^{13}C-^{31}P) = 42.5 Hz), 127.6, 127.5, 125.2 (q, *J* (^{13}C-^{19}F) = 272.6 Hz), 122.2, 121.3, 118.2 – 118.0 (m), 39.3 (d, *J* (^{13}C-^{31}P) = 24.6 Hz), 34.0, 31.9 (d, *J* (^{13}C-^{31}P) = 6.8 Hz), 31.4, 26.4, 24.3, 23.6 and one signal missing because of overlapping. ^{31}P {^1H} NMR (162 MHz, CD_2Cl_2): δ (ppm) 65.09. ^{19}F {^1H} NMR (376 MHz, CD_2Cl_2): δ (ppm) -62.95. ^{11}B {^1H} NMR (128 MHz, CD_2Cl_2): δ (ppm) -6.67.

MALDI$^+$: *m/z* calcd for $C_{66}H_{95}Au_2P_2^+$ [M-$C_{32}H_{12}BF_{24}$]$^+$: 1343.6235, found: 1343.5751. Structure confirmed by X-ray crystallography: CCDC 953710.

3. General Procedure for the Preparation of Cyclobutenes

Alkyne and alkene (2 equiv) were dissolved in dichloromethane (0.48 M) and the cationic gold (I) catalyst (3 mol%) was added. The reaction mixture was stirred at room temperature until no alkyne was observed by TLC. The reaction was quenched by adding a drop of a solution of Et_3N in cyclohexane (1M) and the solvent was removed. Preparative TLC was used to purify the resulting cyclobutenes.

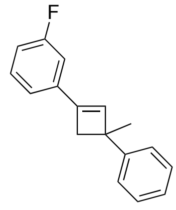
1-Methoxy-3-(3-methyl-3-phenylcyclobut-1-en-1-yl)benzene (3g)



Cyclobutene **3g** was synthetized following the general procedure starting from 1-ethynyl-3-methoxybenzene (**1g**) (21 μl, 0.169 mmol) and α-methylstyrene (**2a**) (44 μl, 0.338 mmol) with catalyst **A2** (7.7 mg, 0.05 mmol). The reaction time was 8 h and a mixture of pentane and diethyl ether (9:1) was used as eluent in the separation to obtain 33 mg (0.132 mmol) of **3g** as a colorless oil in 78% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.40 – 7.35 (m, 2H), 7.33 – 7.28 (m, 1H), 7.25 (td, *J* = 7.2, 1.4 Hz, 1H), 7.05 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.00 – 6.95 (m, 1H), 6.87 (dd, *J* = 7.8, 3.2 Hz, 1H), 6.78 (s, 1H), 3.87 (s, 3H), 3.02 (d, *J* = 12.7 Hz, 1H), 2.95 (d, *J* = 12.5 Hz, 1H), 1.68 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.83, 147.74, 143.86, 136.25, 134.28, 129.51, 128.26, 125.98, 125.83, 117.37, 113.77, 109.98, 55.37, 46.08, 44.46, 27.68. HRMS-APCI m/z calculated for $C_{18}H_{18}O$ $[M+H]^+$ 251.1430, found 251.1434.

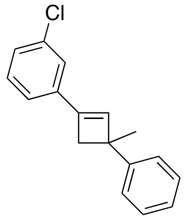
1-Fluoro-3-(3-methyl-3-phenylcyclobut-1-en-1-yl)benzene (3j)



Cyclobutene **3j** was synthetized following the general procedure starting from 1-ethynyl-3-fluorobenzene (**1j**) (21 μl, 0.169 mmol) and α-methylstyrene (**2a**) (44 μl, 0.338 mmol) with catalyst **A2** (7.7 mg, 0.05 mmol). The reaction time was 24 h and a mixture of pentane and diethyl ether (90:1) was used as eluent in the separation to obtain 31 mg (0.130 mmol) of **3j** as a yellowish oil in 77% yield.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.40 – 7.35 (m, 2H), 7.34 – 7.29 (m, 2H), 7.29 – 7.24 (m, 1H), 7.21 – 7.17 (m, 1H), 7.14 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.05 (ddd, *J* = 9.8, 2.6, 1.5 Hz, 1H), 6.94 (tdd, *J* = 8.3, 2.6, 1.0 Hz, 1H), 6.75 (s, 1H), 2.95 (d, *J* = 12.6 Hz, 1H), 2.88 (d, *J* = 12.5 Hz, 1H), 1.62 (s, 1H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 163.17 (d, *J* = 245.8 Hz), 147.45, 142.97 (d, *J* = 2.5 Hz), 137.09 (d, *J* = 7.6 Hz), 135.39, 129.99 (d, *J* = 8.3 Hz), 128.32, 125.96, 125.94, 120.48 (d, *J* = 2.8 Hz), 114.77 (d, *J* = 21.4 Hz), 111.51 (d, *J* = 21.4 Hz), 46.29, 44.34, 27.68. HRMS-APCI m/z calculated for $C_{17}H_{15}F$ $[M+H]^+$ 239.1234, found 239.1231.

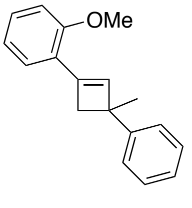
1-Chloro-3-(3-methyl-3-phenylcyclobut-1-en-1-yl)benzene (3k)



Cyclobutene **3k** was synthetized following the general procedure starting from 1-ethynyl-3-chlorobenzene (**1k**) (21 μl, 0.169 mmol) and α-methylstyrene (**2a**) (44 μl, 0.338 mmol) with catalyst **A2** (7.7 mg, 0.05 mmol). The reaction time was 24 h and a mixture of pentane and diethyl ether (90:1) was used as eluent in the separation to obtain 36 mg (0.141 mmol) of **3k** as a yellowish oil in 83% yield.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.40 – 7.35 (m, 3H), 7.35 – 7.30 (m, 2H), 7.27 – 7.17 (m, 4H), 6.77 (s, 1H), 2.96 (d, *J* = 12.5 Hz, 1H), 2.89 (d, *J* = 12.5 Hz, 1H), 1.63 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 147.39 , 142.74 , 136.61 , 135.57 , 134.55 , 129.74 , 128.32 , 127.87 , 125.94 , 124.90 , 122.86 , 46.35 , 44.31 , 27.66. HRMS-APCI m/z calculated for $C_{17}H_{15}Cl$ $[M+H]^+$ 255.0935, found 255.0935.

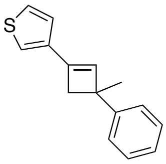
1-Methoxy-3-(3-methyl-3-phenylcyclobut-1-en-1-yl)benzene (3l)



Cyclobutene **3l** was synthetized following the general procedure starting from 1-ethynyl-2-methoxybenzene (**1l**) (22 μl, 0.169 mmol) and α-methylstyrene (**2a**) (44 μl, 0.338 mmol) with catalyst **A2** (7.7 mg, 0.05 mmol). The reaction time was 48 h and a mixture of pentane and diethyl ether (9:1) was used as eluent in the separation to obtain 11 mg (0.044 mmol) of **3l** as a colorless oil in 24% yield.

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.47 – 7.39 (m, 2H), 7.36 – 7.28 (m, 2H), 7.25 – 7.14 (m, 3H), 6.98 – 6.86 (m, 2H), 6.80 (s, 1H), 3.92 (s, 3H), 3.03 (d, *J* = 12.4 Hz, 1H), 2.95 (d, *J* = 12.3 Hz, 1H), 1.65 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 158.63, 148.22, 140.29, 138.70, 128.91, 128.19, 127.15, 126.04, 125.65, 123.58, 120.34, 110.50, 55.29, 46.88, 45.40, 27.86. HRMS-APCI m/z calculated for $C_{18}H_{18}O$ [M+H]$^+$ 251.1430, found 251.1433.

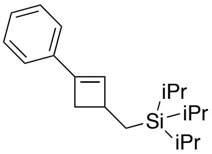
3-(3-Methyl-3-phenylcyclobut-1-en-1-yl)thiophene (3m)



Cyclobutene **3m** was synthetized following the general procedure starting from 3-ethynylthiophene (**1m**) (17 μl, 0.169 mmol) and α-methylstyrene (**2a**) (44 μl, 0.338 mmol) with catalyst **A2** (7.7 mg, 0.05 mmol). The reaction time was 24 h and a mixture of pentane and diethyl ether (90:1) was used as eluent in the separation to obtain 33 mg (0.146 mmol) of **3m** as a brownish oil in 86% yield.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.43 – 7.39 (m, 2H), 7.36 – 7.31 (m, 2H), 7.30 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.23 – 7.19 (m, 2H), 7.17 (dd, *J* = 3.0, 1.2 Hz, 1H), 6.51 (s, 1H), 2.97 (d, *J* = 12.5 Hz, 1H), 2.91 (d, *J* = 12.4 Hz, 1H), 1.65 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 147.83, 139.38, 137.87, 132.74, 128.25, 126.04, 125.95, 125.82, 125.13, 121.14, 47.17, 45.20, 27.75z. HRMS-APCI m/z calculated for $C_{15}H_{14}S$ [M+H]$^+$ 239.0889, found 239.0896.

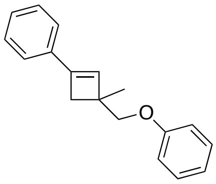
Triisopropyl((1-methyl-3-phenylcyclobut-2-en-1-yl)methyl)silane (3q)



Cyclobutene **3q** was synthetized following the general procedure starting from phenylacetylene (**1a**) (19 µl, 0.169 mmol) and allyltriisopropylsilane (**2d**) (81 µl, 0.338 mmol) with catalyst **A2** (7.7 mg, 0.05 mmol). The reaction time was 72 h and a mixture of pentane 100% was used as eluent in the separation. **3q** was isolated as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.28 (m, 4H), 7.25 – 7.20 (m, 1H), 6.39 (d, *J* = 1.1 Hz, 1H), 3.07 – 2.94 (m, 2H), 2.31 (dd, *J* = 12.4, 1.4 Hz, 1H), 1.08 (s, 23H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.85, 135.24, 133.78, 128.41, 127.54, 124.48, 38.60, 35.50, 19.04, 15.31, 11.41. HRMS-APCI m/z calculated for $C_{20}H_{32}Si$ $[M+H]^+$ 301.2346, found 301.2352.

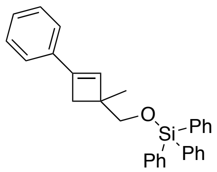
(3-Methyl-3-(phenoxymethyl)cyclobut-1-en-1-yl)benzene (3r)



Cyclobutene **3r** was synthetized following the general procedure starting from phenylacetylene (**1a**) (19 µl, 0.169 mmol) and ((2-methylallyl)oxy)benzene (**2e**) (52 µl, 0.338 mmol) with catalyst **A2** (7.7 mg, 0.05 mmol). The reaction time was 72 h and a mixture of pentane and diethyl ether (20:1) was used as eluent in the separation in a preparative TLC in Alumina oxide. **3r** was isolated as a colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.36 (m, 2H), 7.36 – 7.31 (m, 2H), 7.30 – 7.26 (m, 2H), 6.96 – 6.91 (m, 3H), 6.47 (s, 1H), 3.98 (d, *J* = 8.7 Hz, 1H), 3.95 (d, *J* = 8.7 Hz, 1H), 2.74 (d, *J* = 12.8 Hz, 1H), 2.56 (d, *J* = 12.8 Hz, 1H), 1.42 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.62, 144.31, 134.84, 132.96, 129.52, 128.47, 128.00, 124.70, 120.66, 114.79, 75.46, 42.91, 38.91, 21.79. HRMS-APCI m/z calculated for $C_{18}H_{18}O$ $[M+H]^+$ 251.1426, found 251.1430.

((1-methyl-3-phenylcyclobut-2-en-1-yl)methoxy)triphenylsilane (3s)



Cyclobutene **3s** was synthetized following the general procedure starting from phenylacetylene (**1a**) (19 μl, 0.169 mmol) and ((2-methylallyl)oxy)triphenylsilane (**2f**) (112 mg, 0.338 mmol) with catalyst **A2** (7.7 mg, 0.05 mmol). The reaction time was 72 h and a mixture of pentane and diethyl ether (20:1) was used as eluent in the separation in a preparative TLC in Alumina oxide. **3s** was isolated as a colorless oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.68 – 7.57 (m, 7H), 7.46 – 7.28 (m, 14H), 6.29 (s, 1H), 3.80 (s, 2H), 2.61 (d, *J* = 12.7 Hz, 1H), 2.40 (d, *J* = 12.7 Hz, 1H), 1.30 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 143.92, 135.60, 135.07, 134.60, 133.51, 130.07, 128.39, 127.94, 127.73, 124.62, 71.07, 44.64, 38.30, 21.51. HRMS-APCI m/z calculated for $C_{30}H_{28}OSi$ $[M+H]^+$ 433.1982, found 433.1984.

4. Procedure for the Macrocyclization Reaction

To a solution of the 1,n-enyne (0.263 mmol) in CH_2Cl_2 (0.007 M) gold(I) complex (0.00789 mmol) was added. The reaction mixture was stirred at room temperature for 12 h. The reaction was quenched with 0.05 ml of triethylamine and the solvent was removed under reduced pressure. The crude product was purified by preparative TLC.

5. General Procedure for the Preparation of [3.2.1]Oxabicycles

Alkyne (3.5 equiv) and oxoalkene were dissolved in 1,2-dichloroethane (0.50 M) and the cationic gold (I) catalyst (5 mol%) was added. The reaction mixture was stirred at 50 ºC untill no oxoalkene was observed by TLC. Then, the mixture was quenched by adding a drop of of Et_3N and the solvent was removed. Preparative TLC was used to purify the [3.2.1]oxabicycle product.

6. Mechanistic Study

Order of reagents

Figure S1. ^{1}H NMR monitoring of the intermolecular gold(I)-catalyzed [2+2] cycloaddition of α-methylstyrene (0.50 mmol) and changing quantities of phenylacetylene with catalyst **A2** (7.2 μmol) in CD_2Cl_2 (0.56 ml) at room temperature and using diphenylmethane as internal standard.

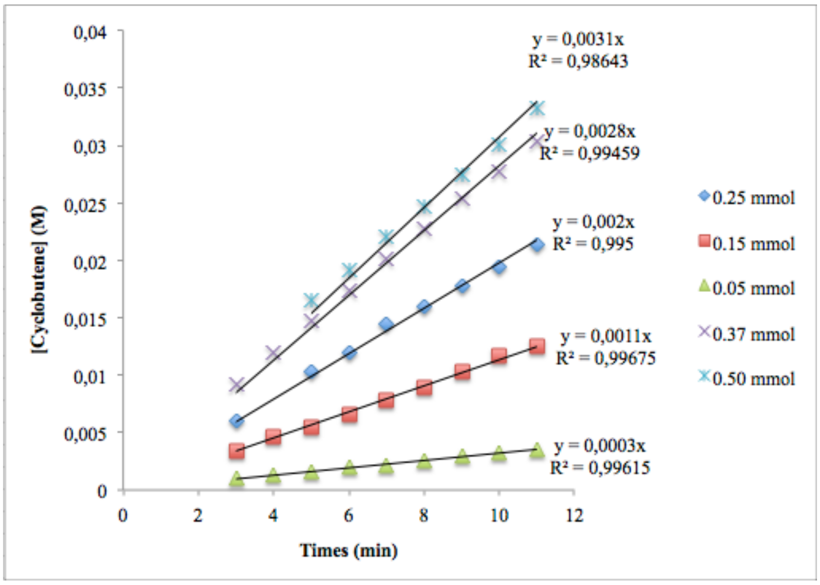


Figure S2. ^{1}H NMR monitoring of the intermolecular gold(I)-catalyzed [2+2] cycloaddition of phenylacetylene (0.25 mmol) and changing quantities of α-methylstyrene with catalyst **A2** (7.2 μmol) in CD_2Cl_2 (0.56 mL) at room temperature and using diphenylmethane as internal standard.

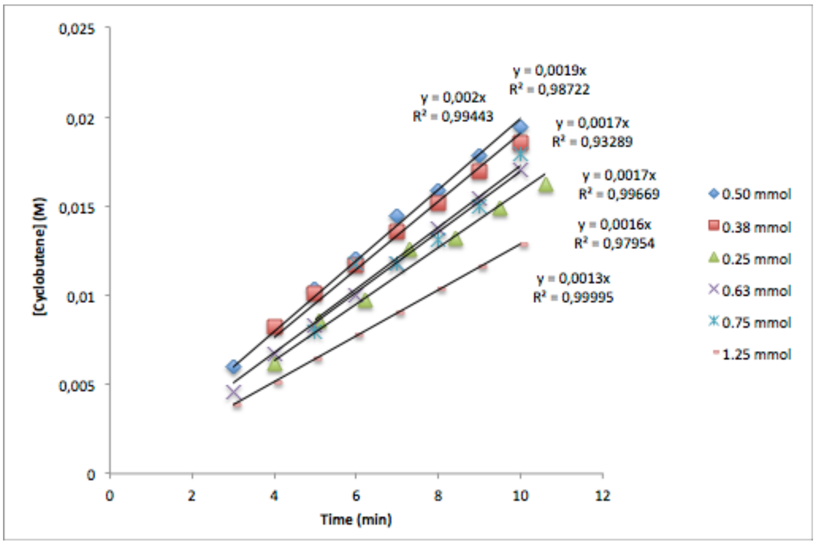


Figure S3. ^{1}H NMR monitoring of the intermolecular gold(I)-catalyzed [2+2] cycloaddition of phenylacetylene (0.25 mmol) and α-methylstyrene (0.50 mmol) with changing quantities of catalyst **A2** in CD_2Cl_2 (0.56 ml) at room temperature and using diphenylmethane as internal standard.

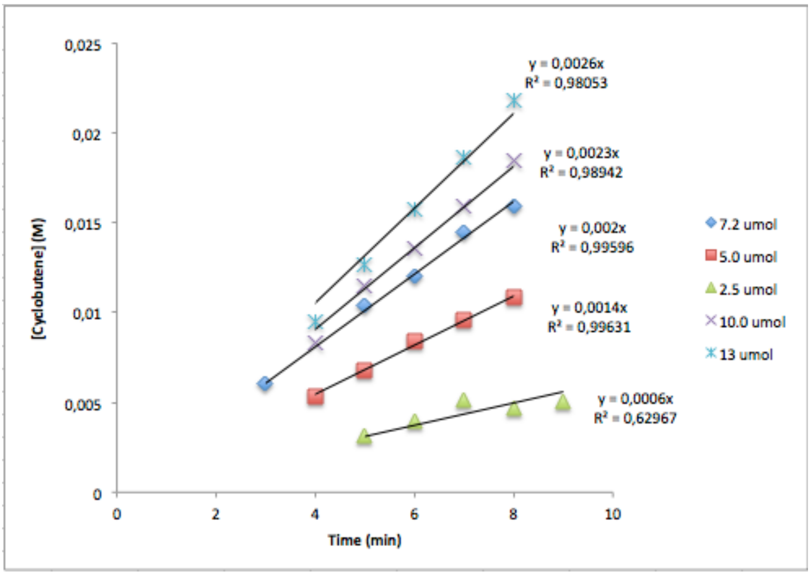
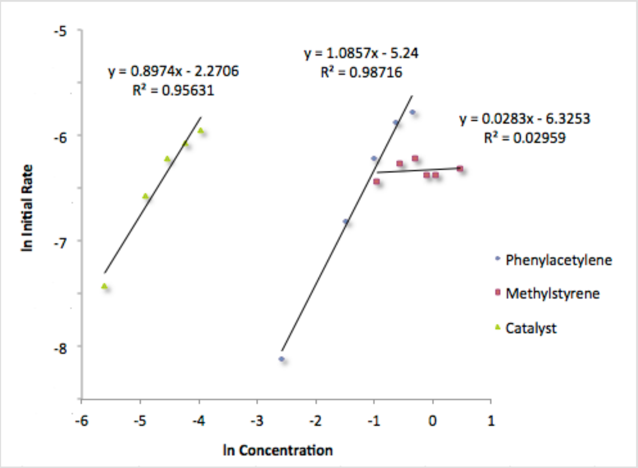


Figure S4. According to the method of the initial rates, it is possible to determine the order of the reagents by the logarithmic graph of the initial formation of the product and the concentration of the varying reagent.



Kinetics

Figure S5. ^{1}H NMR monitoring of the intermolecular gold(I)-catalyzed [2+2] cycloaddition of phenylacetylene (0.25 mmol) and α-methylstyrene (2 equivalents) with [LAuNCMe]X (3 mol%, L = *t*BuXPhos) in CD_2Cl_2 (0.55 ml) at room temperature and using diphenylmethane as internal standard (0.5 equivalents). Spectra recorded every 10 min during 10 h and then at 15 h.

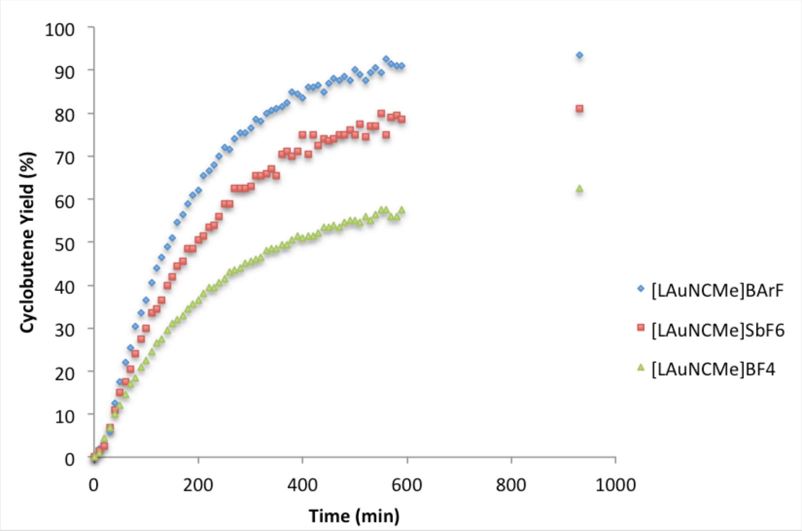
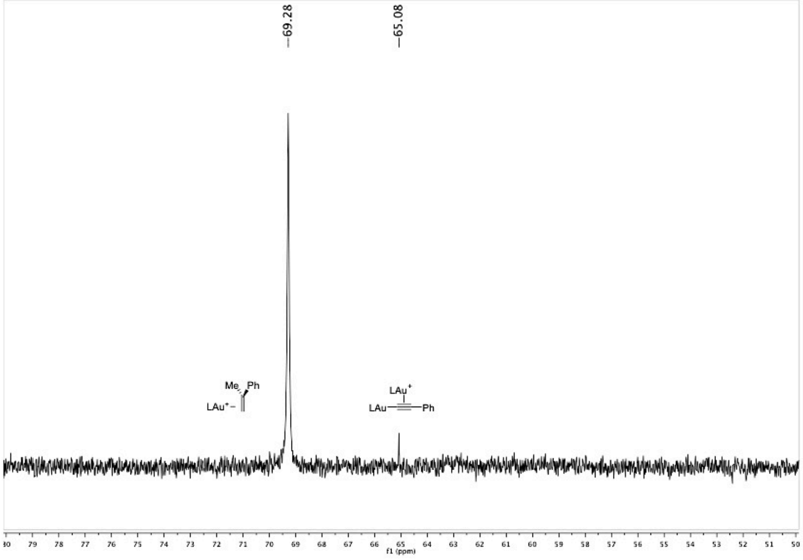


Figure S6. Initial ^{31}P NMR spectrum of the intermolecular gold(I)-catalyzed [2+2] cycloaddition of phenylacetylene and α-methylstyrene with **A2** (3 mol%) in CD_2Cl_2 and at room temperature shown in *Figure S5*.



Equilibrium Constants

The equilibrium constants between catalysts **A1** and **A2** and their related digold and alkene complexes were determined using the van't Hoff equation. Therefore, several samples (substrate:sample 0.5 M = 1:2, 1:1, 2:1, 3.5:1 and 5:1) in CD_2Cl_2 (0.5 ml) were analysed immediately from 263 to 278, to 293 and to 308K by ^{1}H and ^{31}P NMR.

Figure S7. Correlation between the equilibrium constant of **A1** and the digold complex with the temperature was already reported ($\Delta H^{\neq}>0$).[5]

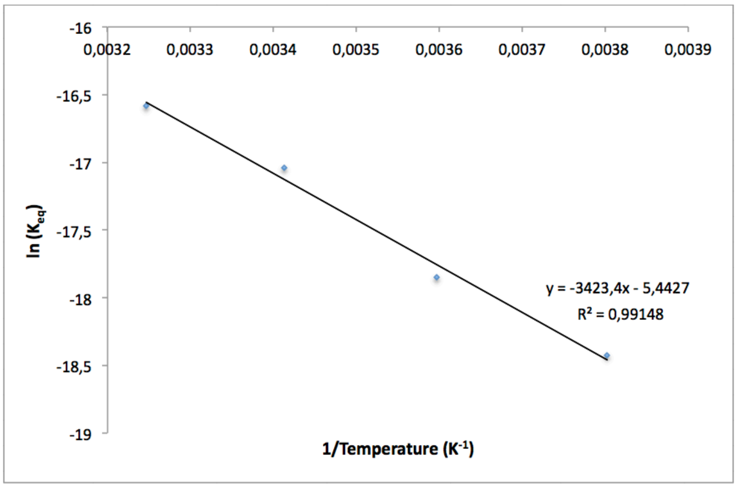
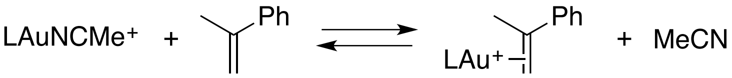


Figure S8. Correlation between the equilibrium constant of **A1** and the alkene complex with the temperature ($\Delta H^{\neq}<0$).



$$Keq = \frac{[\mathbf{15}]\cdot[MeCN]}{[A]\cdot[Alkene]} = \frac{[\mathbf{15}]^2}{([A]_0 - [\mathbf{15}])\cdot([Alkene]_0 - [\mathbf{15}])}$$

$$Integrals\ ratio = \frac{[\mathbf{15}]}{([A]_0 - [\mathbf{15}])}$$

Substrate:sample	263 K	278 K	293 K	308 K
1:2	5.93	5.96	6.41	6.90
1:1	4.01	-	4.77	5.91
2:1	2.76	2.78	2.77	3.63

3.5:1	1.78	1.96	2.00	1.97
5:1	1.49	1.57	1.70	1.75

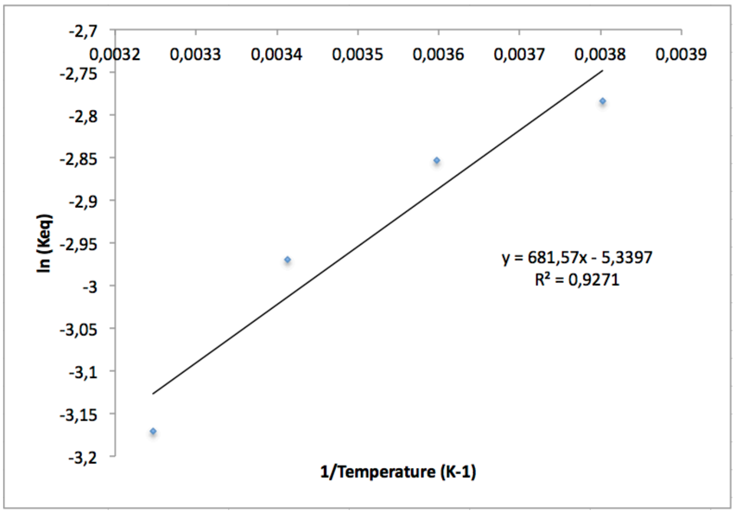
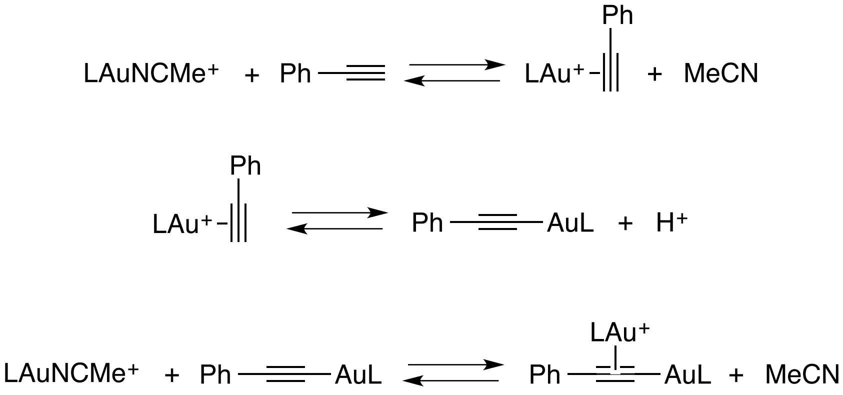


Figure S9. Correlation between the equilbrium constant of **A2** and the digold complex with the temperature ($\Delta H^{\neq}>0$).



$$Keq = \frac{[\mathbf{9}]\cdot[H^{+}]\cdot[MeCN]^{2}}{[\boldsymbol{A}]^{2}\cdot[Alkyne]} = \frac{4\cdot[\mathbf{9}]^{4}}{([\boldsymbol{A}]_{0}-2\cdot[\mathbf{9}])^{2}\cdot([Alkyne]-[\mathbf{9}])}$$

$$Integrals\ ratio = \frac{[\mathbf{9}]}{([\boldsymbol{A}]_{0}-2\cdot[\mathbf{9}])}$$

Substrate:sample	263 K	278 K	293 K	308 K
1:2	160.29	103.04	86.90	56.60

1:1	155.16	97.66	78.90	59.71
2:1	113.30	79.36	49.29	46.04
3.5:1	107.32	65.03	46.26	39.33
5:1	82.45	52.90	42.26	35.38

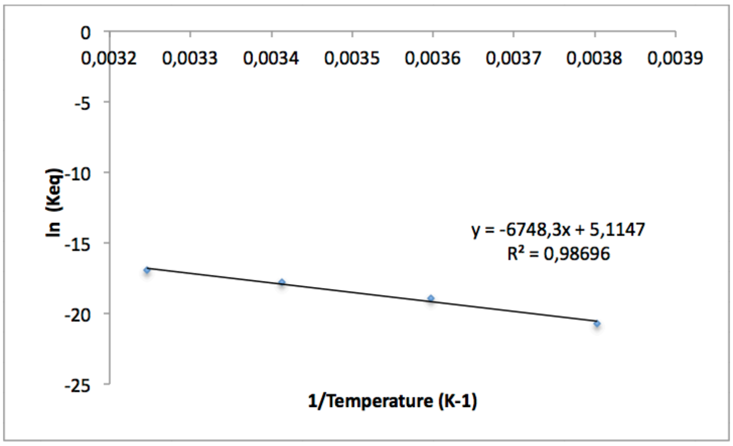
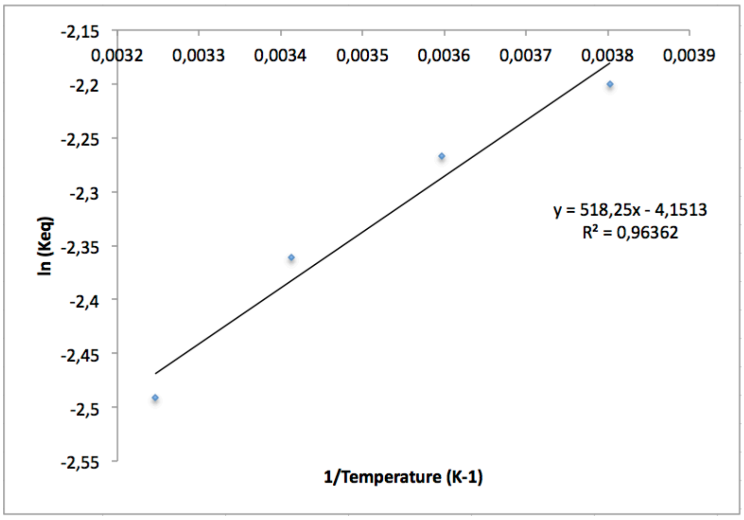


Figure S10. Correlation between the equilbrium constant of **A1** and the alkene complex with the temperature ($\Delta H^{\neq}<0$).

Substrate:sample	263 K	278 K	293 K	308 K
1:2	4.84	4.90	4.97	5.05
1:1	3.01	3.03	3.32	3.53
2:1	1.85	1.98	2.04	2.19
3.5:1	1.32	1.36	1.46	1.57
5:1	0.98	1.06	1.12	1.32


-2,15
-2,2
-2,25
-2,3
-2,35
-2,4
-2,45
-2,5
-2,55
0,0032
0,0033
0,0034
0,0035
0,0036
0,0037
0,0038
0,0039
ln (Keq)
1/Temperature (K-1)
y = 518,25x - 4,1513
R² = 0,96362

Low temperature NMR experiments

Figure S11. ^{31}P NMR spectrum of a mixture of phenylacetylene and complex **A1** (10:1) in CD_2Cl_2 from 213 – 298 K already reported.[5]

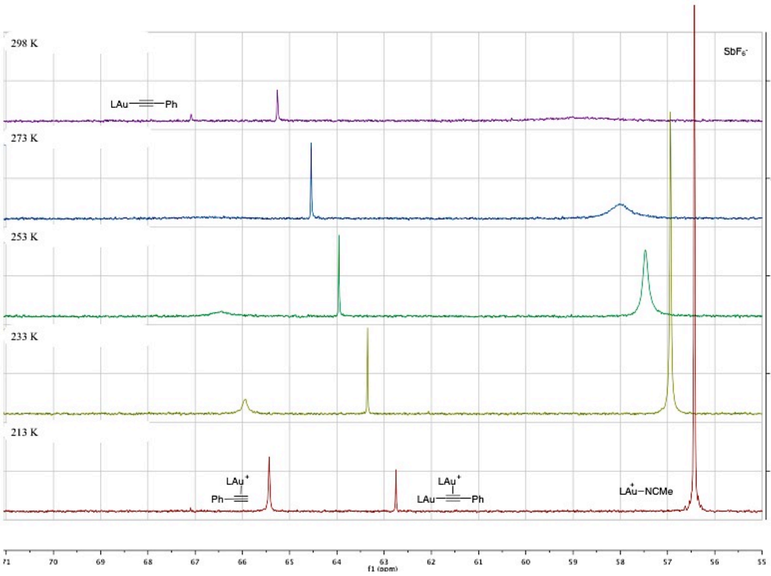
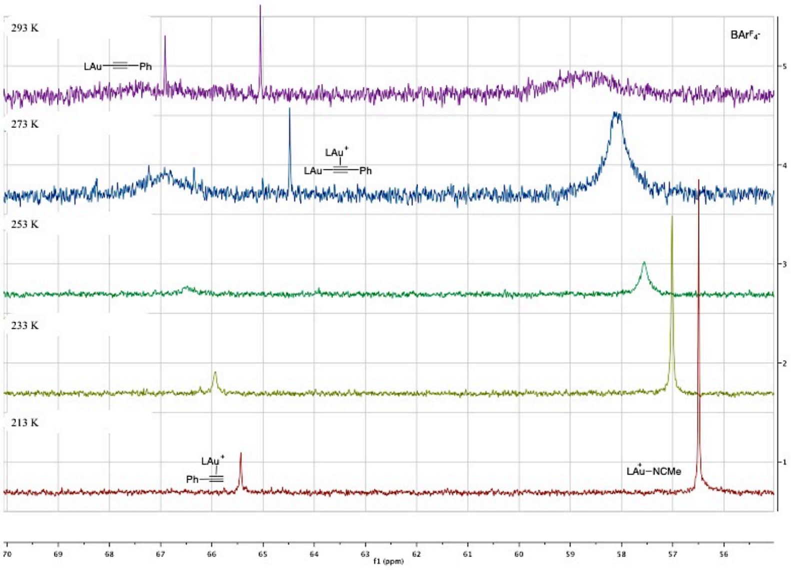


Figure S12. ^{31}P NMR spectrum of a mixture of phenylacetylene and 25 mg of complex **A2** (10:1) in CD_2Cl_2 (0.5 ml) from 213 – 298 K.



Electrondensity Surfaces

Total SCF density mapped with ESP (r = 0.03 e/Å^3). Structures calculated with Gaussian 09 using M06 with 6-31G(d) (C, H, P, B, F) and SDD (Au, Sb) in CH_2Cl_2.

Figure S13. (*t*BuXPhosAu(η^2-phenylacetylene)SbF_6 (**8a**).

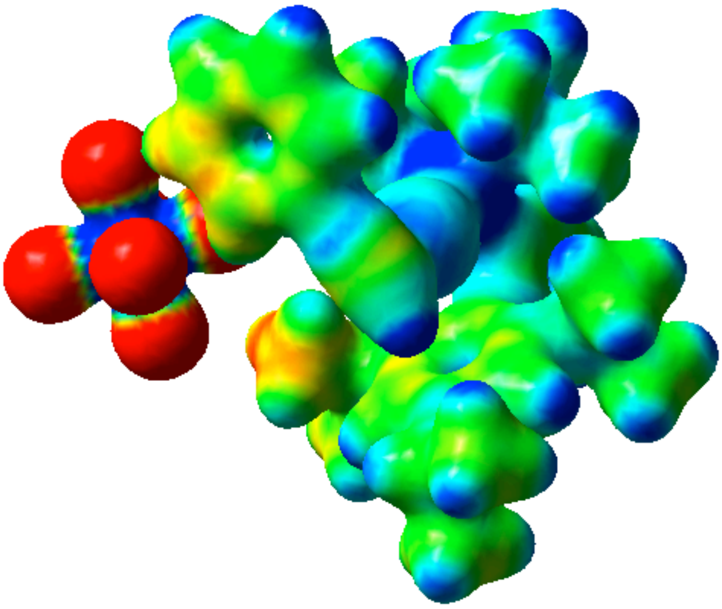


Figure S14. (*t*BuXPhosAu(η^2-phenylacetylene)BAr_4^{F-} (**8b**).

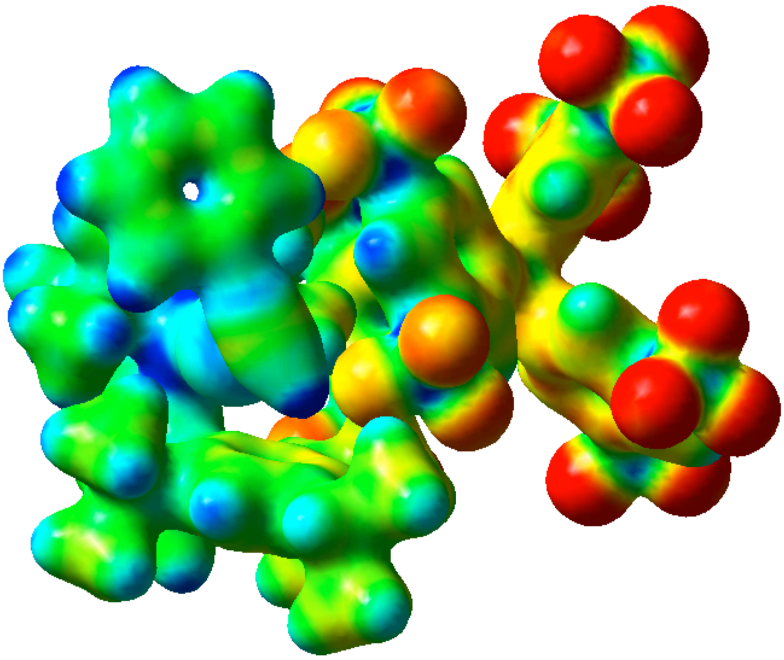
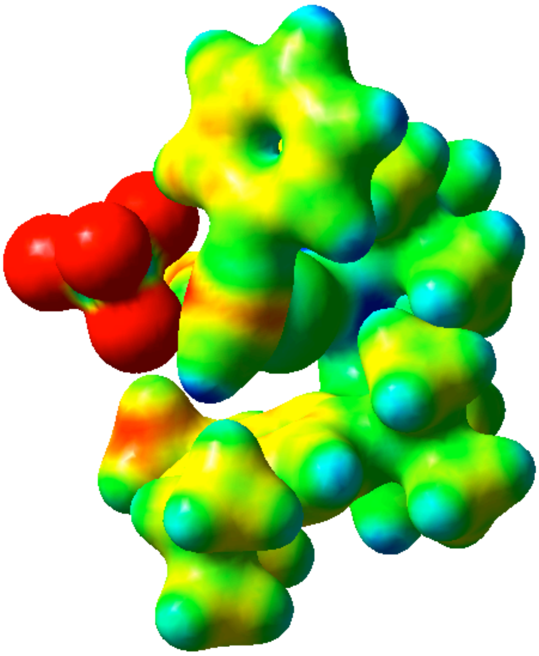


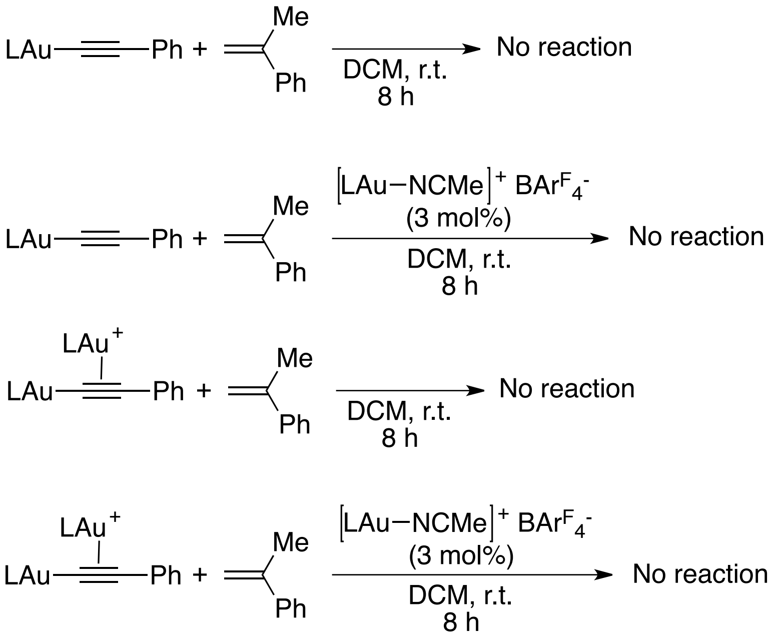
Figure S15. (*t*BuXPhosAu(η^2-phenylacetylene)SbF$_6$ (**8c**).



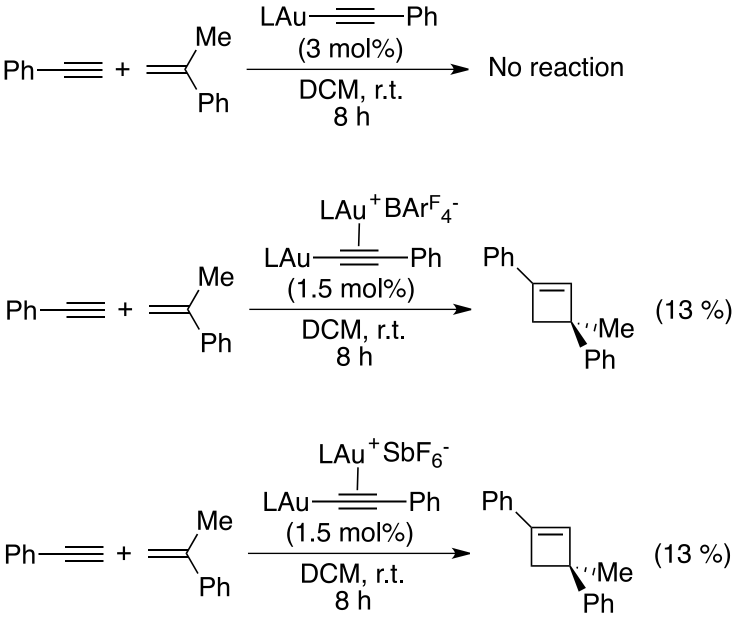
Additional Experiments

We also performed some additional catalytic tests to exclude any other mechanistic pathways. We started reacting the isolable intermediates stoichiometrically with α-methylstyrene and none of them reacted at all.

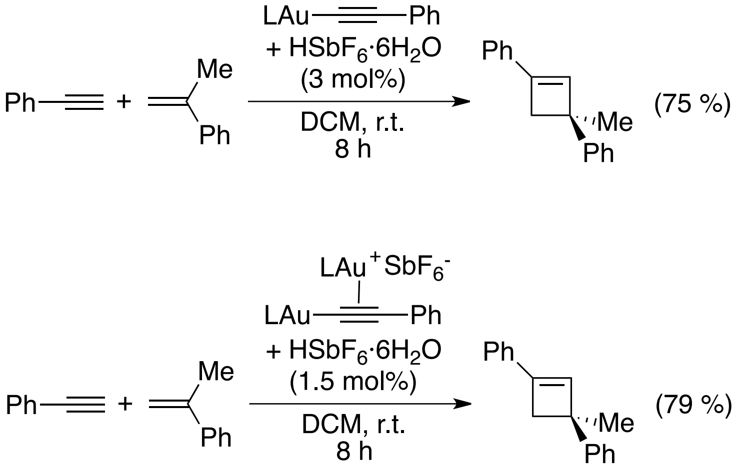
Scheme S1. Stoichiometric reaction between **16** or **9b** and α-methylstyrene under the optimized conditions (L = *t*BuXPhos).



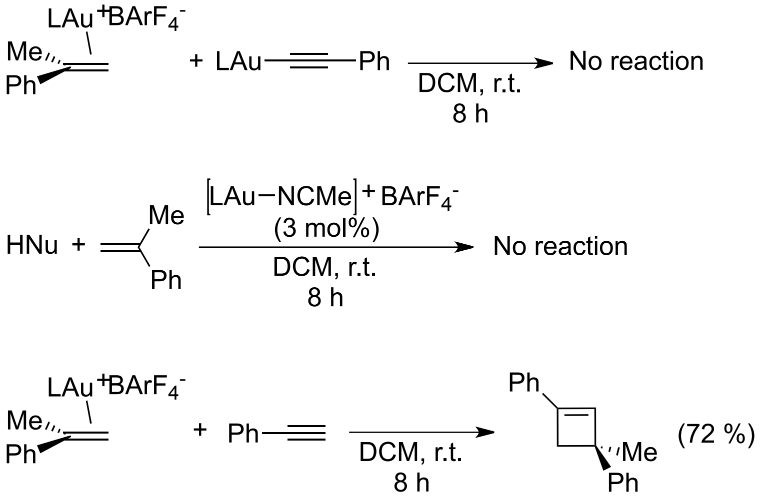
Scheme S2. Intermolecular gold(I)-catalyzed reaction between phenylacetylene and α-methylstyrene with **16** or **9b** under the optimized conditions (L = *t*BuXPhos).



Scheme S3. Intermolecular gold(I)-catalyzed reaction between phenylacetylene and α-methylstyrene with **16** or **9a** and substoichiometric amounts of $HSbF_6 \cdot 6H_2O$ under the optimized conditions (L = *t*BuXPhos). The activity increases as a result of the reestablishment of the equilibrium to the monogold complex **8a**.



Scheme S4. Intermolecular gold(I)-catalyzed reaction between **15b** and **16** or phenylacetylene under the optimized conditions (L = tBuXPhos). We also tried to add other carbonucleophiles, for example, allyltrimethylsilane, indole, 1,3,5-trimethoxybenzene or 1,3-diphenylpropane-1,3-dione to the alkene using **A2**.



7. X-Ray Crystallographic Data

[(2´,4´,6´-triisopropyl-1,1´-biphenyl-2-yl)di-*tert*-butylphosphine](2-phenylethynyl)gold(I) (16)

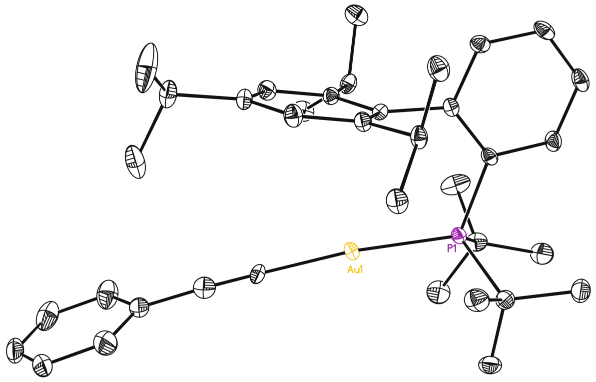


Table S1. Crystal data and structure refinement for CCDC 953709.

Empirical formula	C36 H50 Au N P	
Formula weight	724.71	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.8245(8) Å	a= 101.506(2) °.
	b = 12.6401(9) Å	b = 95.285(2) °.
	c = 13.3697(10) Å	g = 112.126(2) °.
Volume	1632.1(2) Å^3	
Z	2	
Density (calculated)	1.475 Mg/m^3	
Absorption coefficient	4.580 mm^{-1}	
F(000)	734	
Crystal size	0.25 x 0.12 x 0.10 mm^3	
Theta range for data collection	1.80 to 30.39 °.	
Index ranges	-14 <=h<=13 ,-14 <=k<=17 ,-17 <=l<=17	
Reflections collected	26200	
Independent reflections	8605 [R(int) = 0.0279]	
Completeness to theta =30.39 °	87.1%	
Absorption correction	Empirical	
Max. and min. transmission	0.6573 and 0.3939	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8605 / 0 / 364	

Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0196 , wR2 = 0.0483
R indices (all data)	R1 = 0.0213 , wR2 = 0.0490
Largest diff. peak and hole	1.618 and -1.437 e.Å^{-3}

(α-Methylstyrene)[(2′,4′,6′-triisopropyl-1,1′-biphenyl-2-yl)di-*tert*-butylphosphine]gold(I) tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (15b)

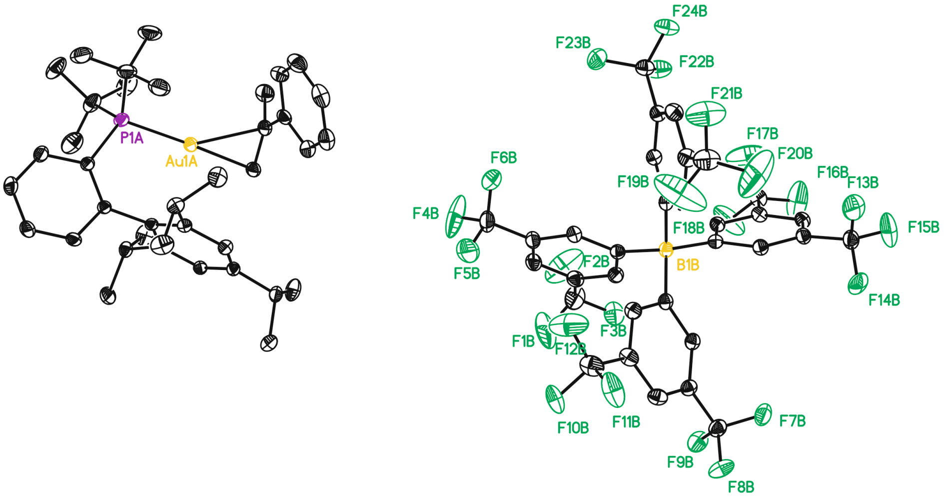


Table 2. Crystal data and structure refinement for CCDC 953708.

Empirical formula	C70 H67 Au B F24 P	
Formula weight	1602.98	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.876(11) Å	a= 90.00 °.
	b = 14.771(3) Å	b = 90.39(2) °.
	c = 36.339(8) Å	g = 90.00 °.
Volume	6911(6) Å^3	
Z	4	
Density (calculated)	1.541 Mg/m^3	
Absorption coefficient	2.257 mm^{-1}	
F(000)	3208	
Crystal size	0.20 x 0.20 x 0.20 mm^3	
Theta range for data collection	2.37 to 36.40 °.	
Index ranges	-20 <=h<=21 ,0 <=k<=24 ,0 <=l<=59	

Reflections collected	31125
Independent reflections	31125 [R(int) = 0.0000]
Completeness to theta =36.40 °	92.299995%
Absorption correction	Empirical
Max. and min. transmission	0.6610 and 0.6610
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	31125 / 790 / 1353
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0347 , wR2 = 0.0866
R indices (all data)	R1 = 0.0506 , wR2 = 0.0902
Largest diff. peak and hole	2.035 and -0.829 e.Å^{-3}

{Phenylethynyl[(2´,4´,6´-triisopropyl-1,1´-biphenyl-2-yl)di-tert-butylphosphine]gold(I)}

[(2´,4´,6´-triisopropyl-1,1´-biphenyl-2-yl)di-tert-butylphosphine]gold(I) tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (9b)

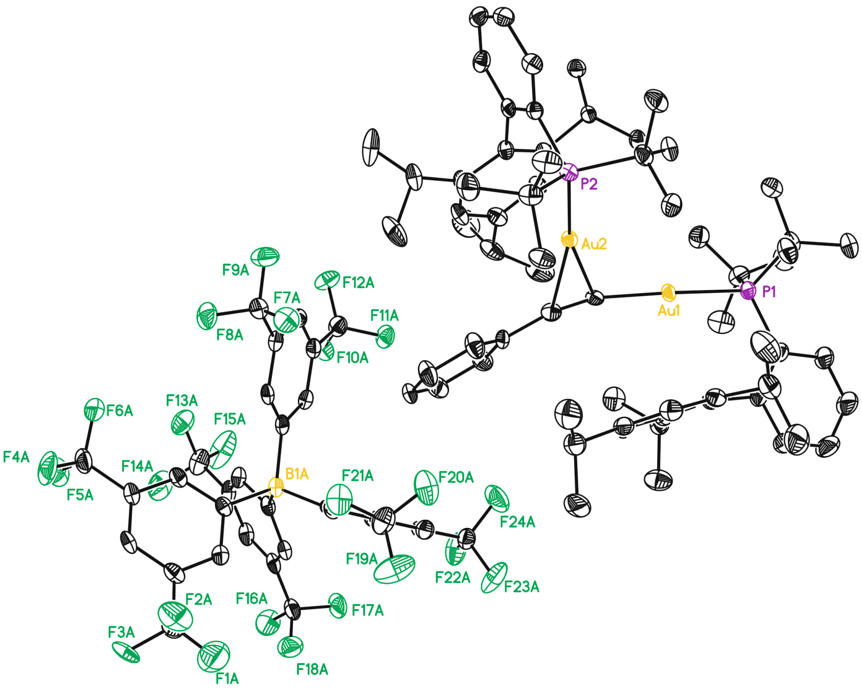


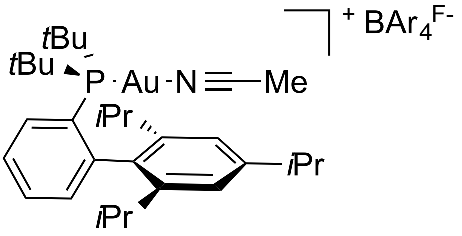
Table S3. Crystal data and structure refinement for CCDC 953710.

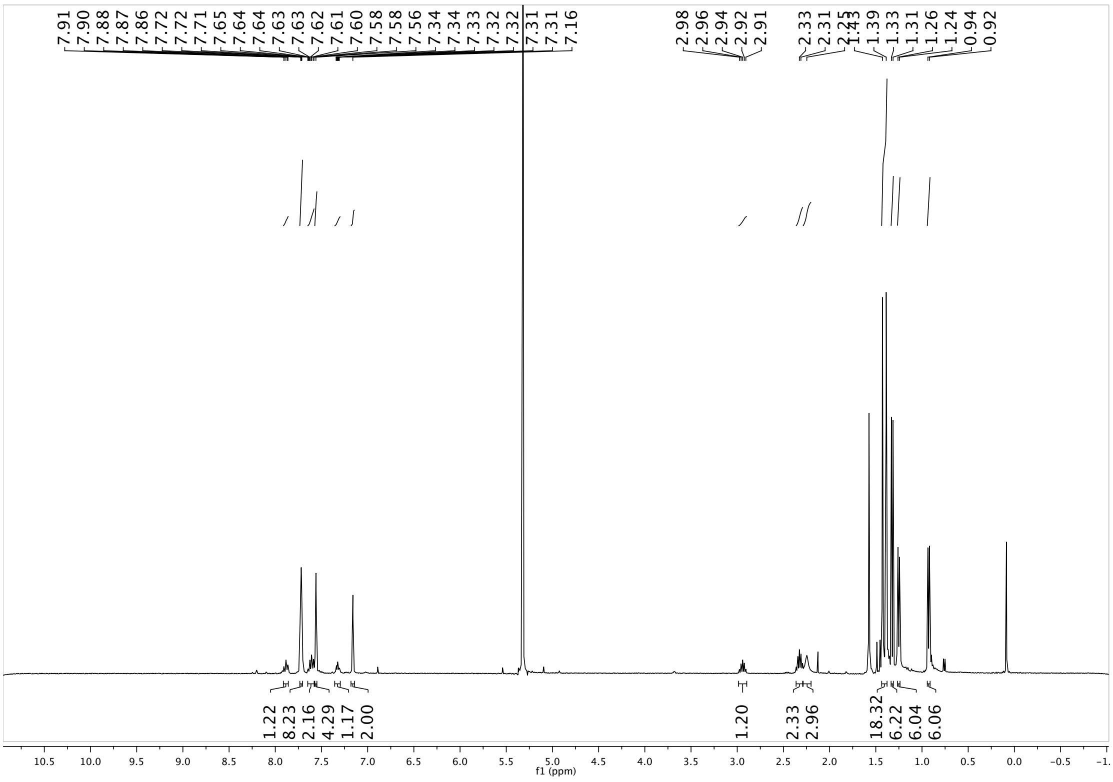
Empirical formula	C98.25 H108.50 Au2 B Cl0.50 F24 P2
Formula weight	2229.76
Temperature	100(2) K
Wavelength	0.71073 Å

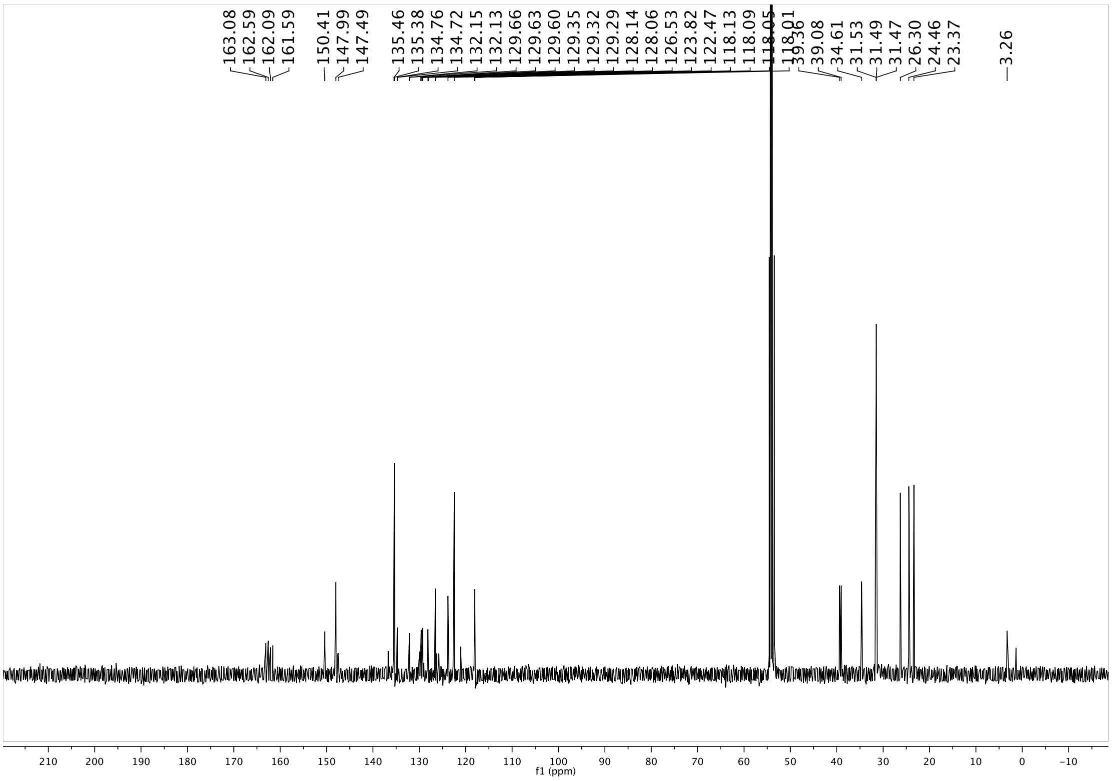
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.7748(13) Å	a= 107.801(3) °.
	b = 17.3827(17) Å	b = 95.994(4) °.
	c = 22.973(2) Å	g = 93.979(3) °.
Volume	4802.8(8) Å^3	
Z	2	
Density (calculated)	1.542 Mg/m^3	
Absorption coefficient	3.190 mm^{-1}	
F(000)	2231	
Crystal size	0.20 x 0.12 x 0.02 mm^3	
Theta range for data collection	0.94 to 26.48 °.	
Index ranges	-15 <=h<=16 ,-21 <=k<=21 ,-28 <=l<=28	
Reflections collected	138270	
Independent reflections	19731 [R(int) = 0.0485]	
Completeness to theta =26.48 °	99.4%	
Absorption correction	Empirical	
Max. and min. transmission	0.9390 and 0.5679	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	19731 / 108 / 1263	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0275 , wR2 = 0.0615	
R indices (all data)	R1 = 0.0397 , wR2 = 0.0670	
Largest diff. peak and hole	1.871 and -0.734 e.Å^{-3}	

8. NMR Spectra

(Acetonitrile)[(2´,4´,6´-triisopropyl-1,1´-biphenyl-2-yl)di-*tert*-butylphosphine]gold(I) tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (A2)



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162.09
161.59
150.41
147.99
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135.46
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134.76
134.72
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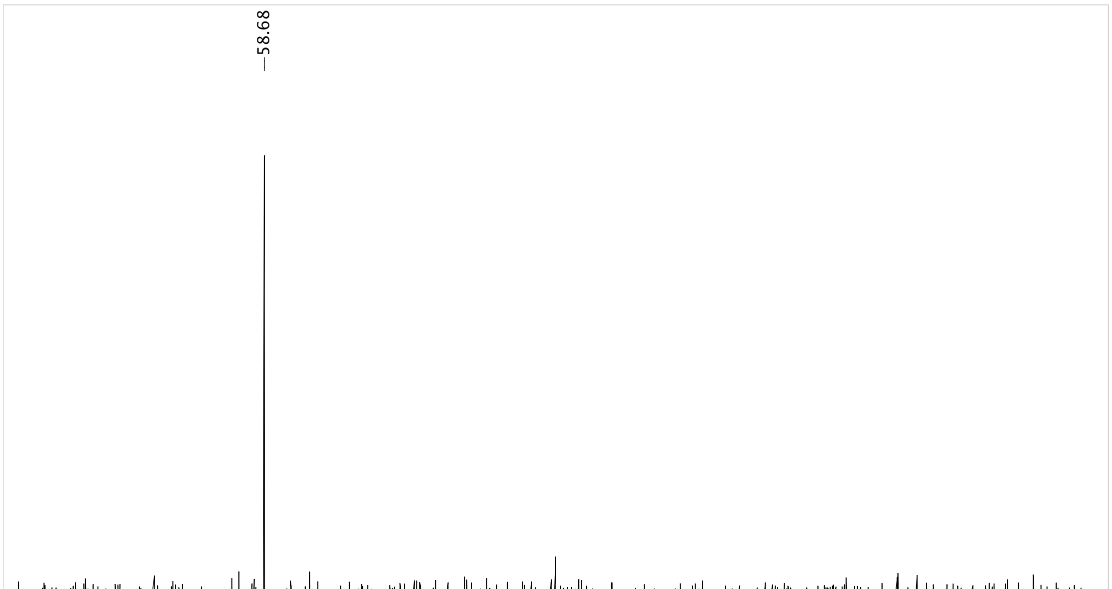
132.13
129.66
129.63
129.60
129.35
129.32
129.29
128.14
128.06
126.53
123.82
122.47
118.13
118.09
118.05
118.01
39.36
39.08
34.61
31.53
31.49
31.47
26.30
24.46
23.37
3.26
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


58.68
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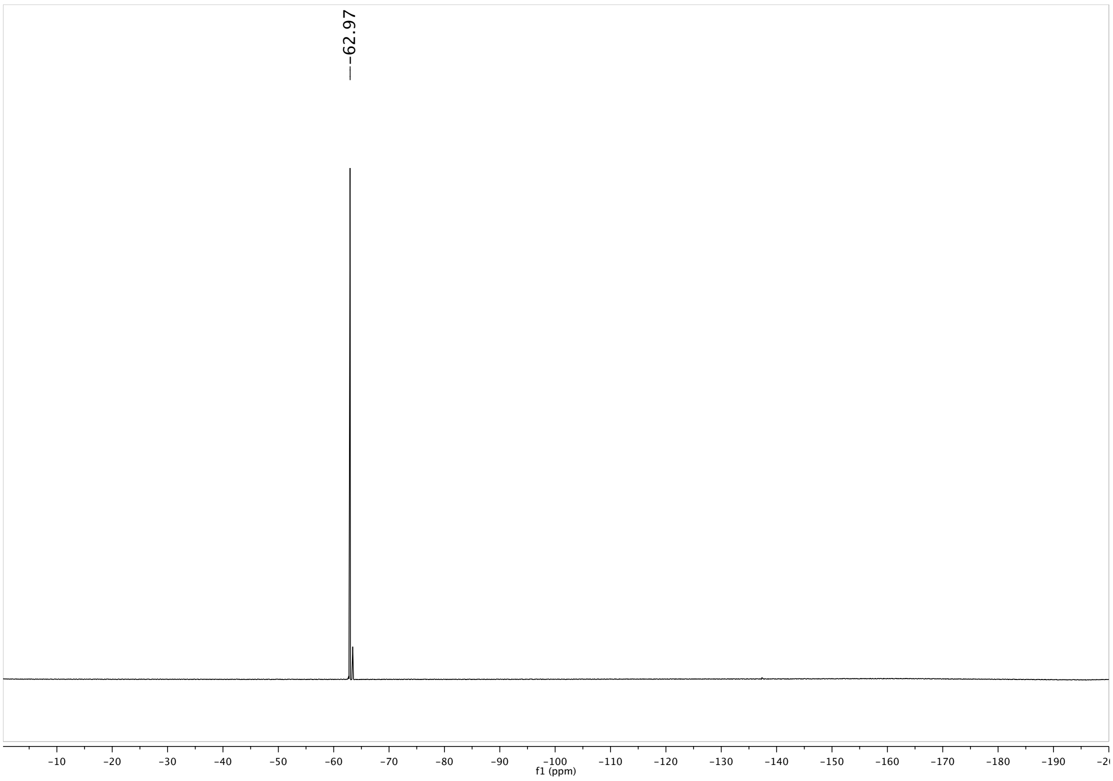
f1 (ppm)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−30
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−50
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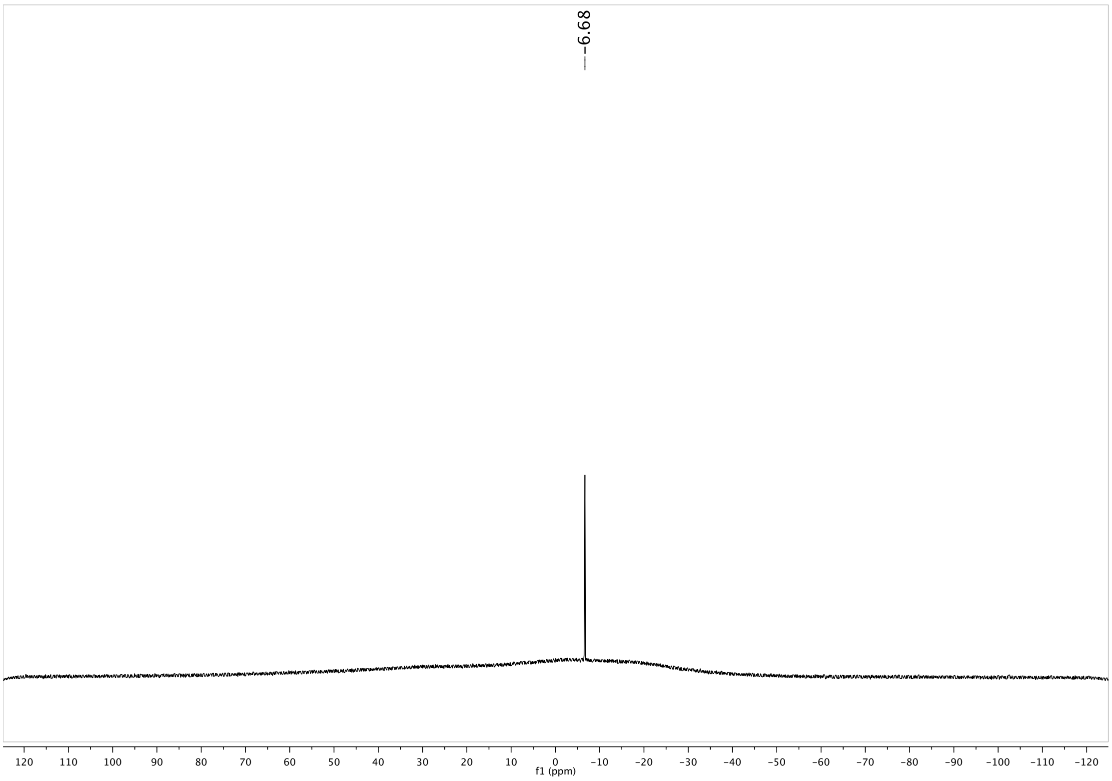
−170
−180
−190
f1 (ppm)


−6.68
120
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−10
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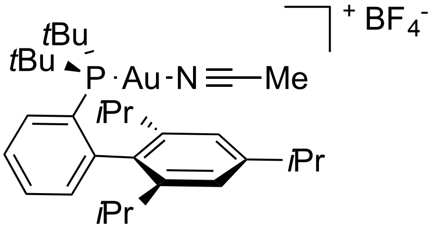
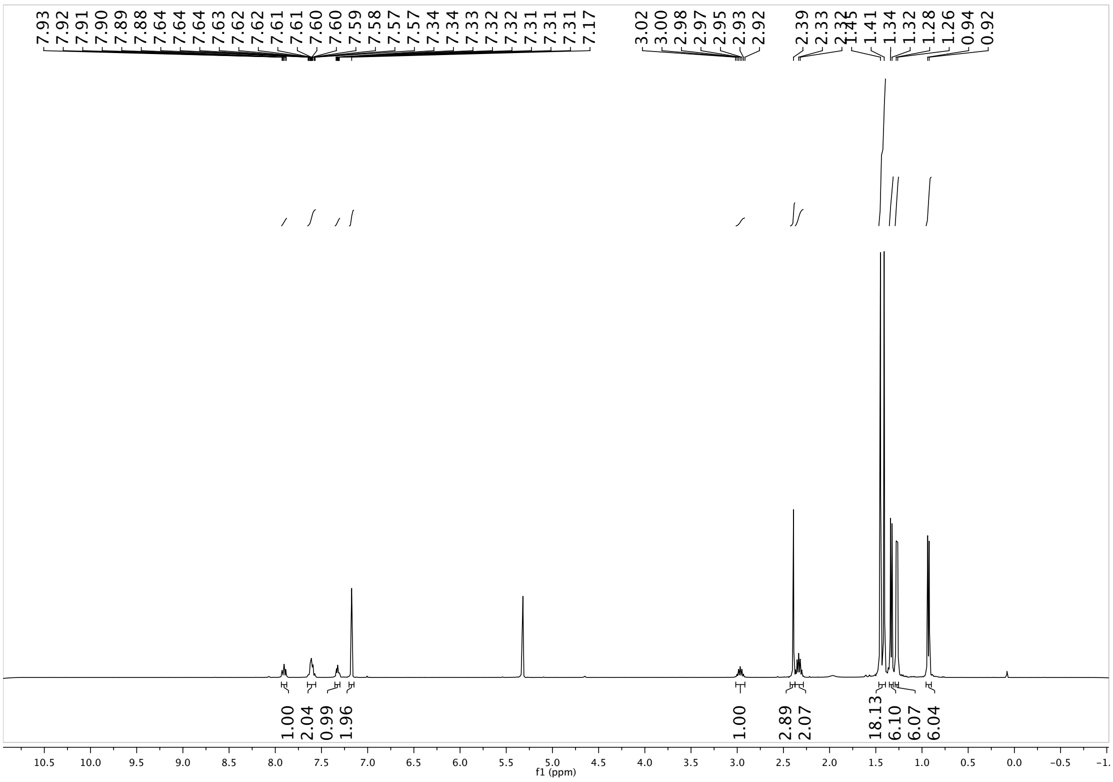
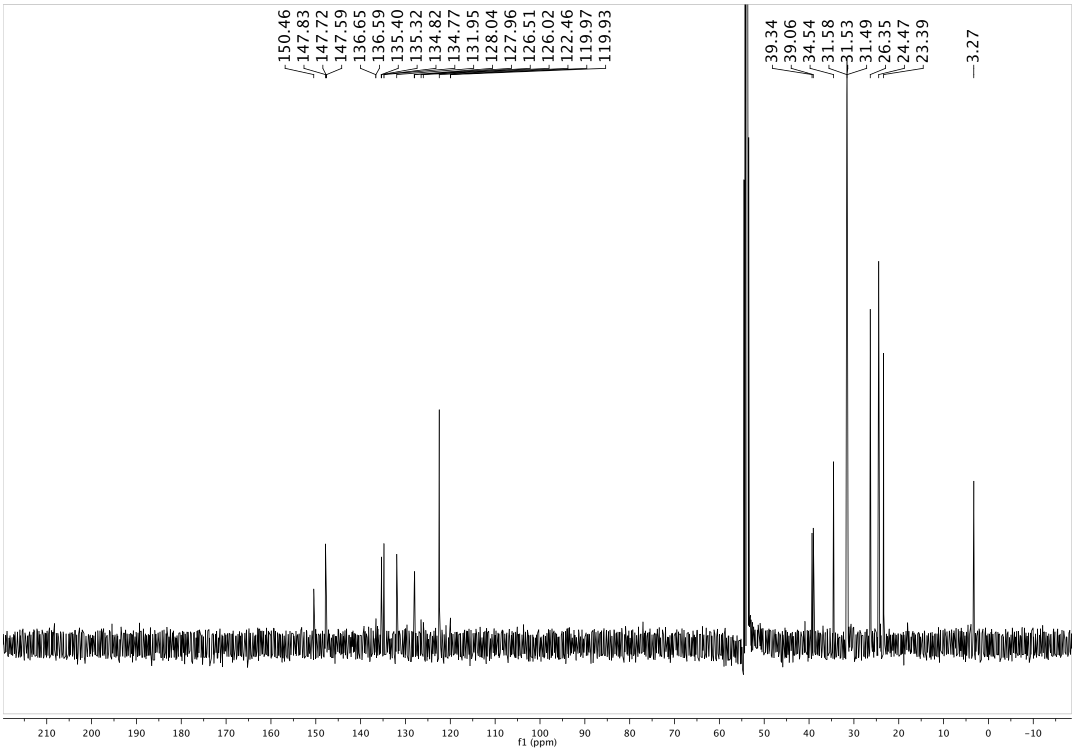
−40
−50
−60
−70
−80
−90
−100
−110
−120
f1 (ppm)

(Acetonitrile)[(2´,4´,6´-triisopropyl-1,1´-biphenyl-2-yl)di-*tert*-butylphosphine]gold(I) tetrafluoroborate (A3)



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136.59
135.40
135.32
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134.77
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127.96
126.51
126.02
122.46
119.97
119.93
39.34
39.06
34.54
31.58
31.53
31.49
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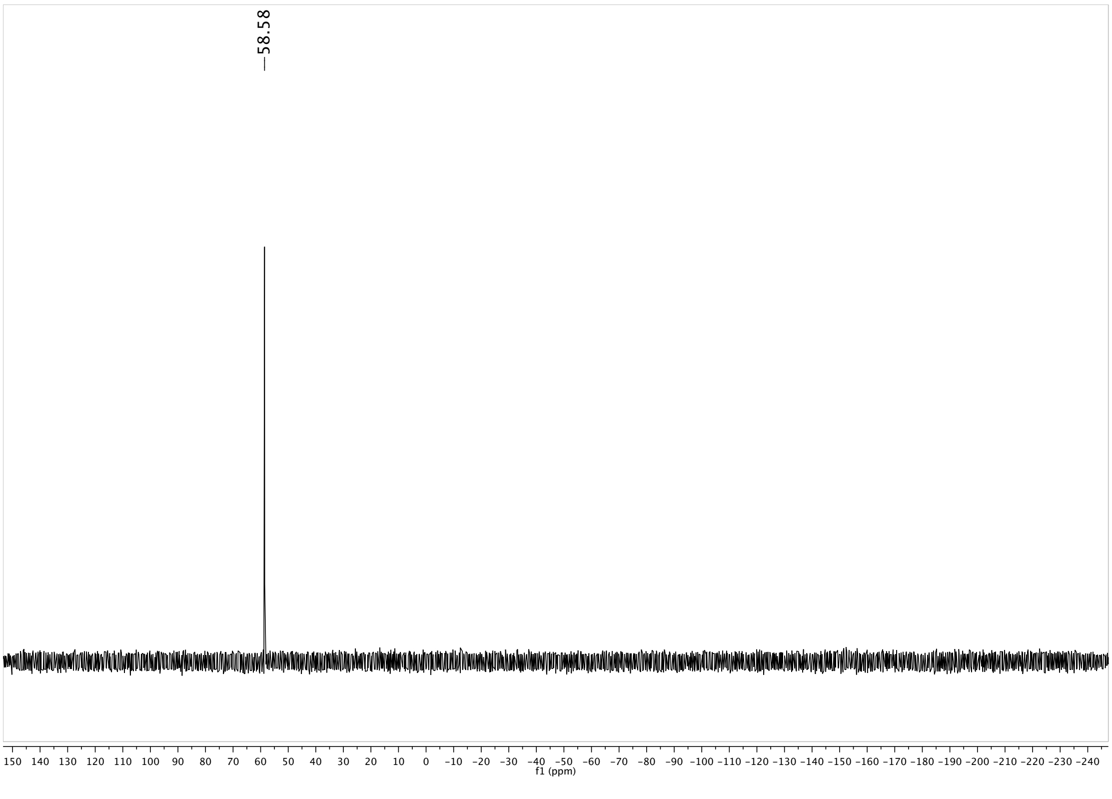
24.47
23.39
3.27
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


58.58
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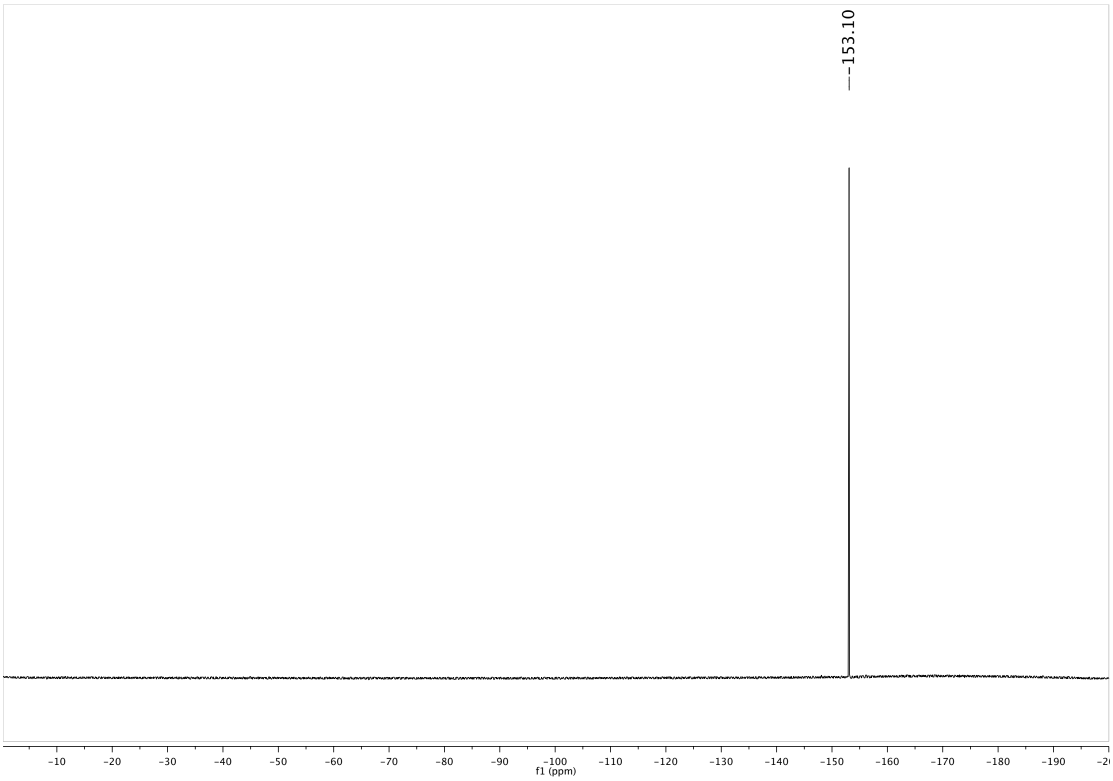
f1 (ppm)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-10
-20
-30
-40
-50
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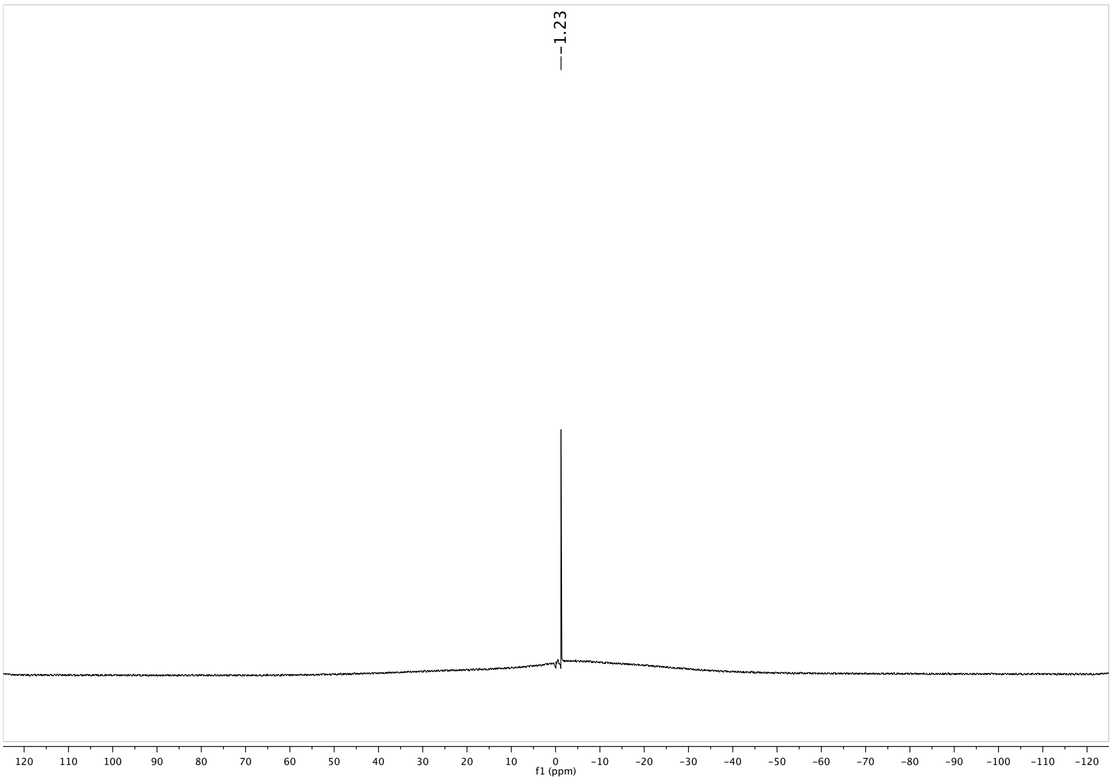
-140
-150
-160
-170
-180
-190
f1 (ppm)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100
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80
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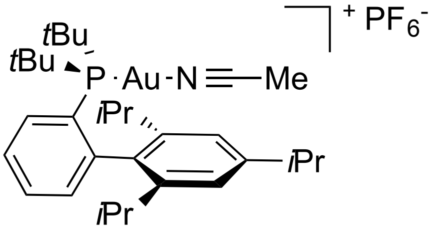
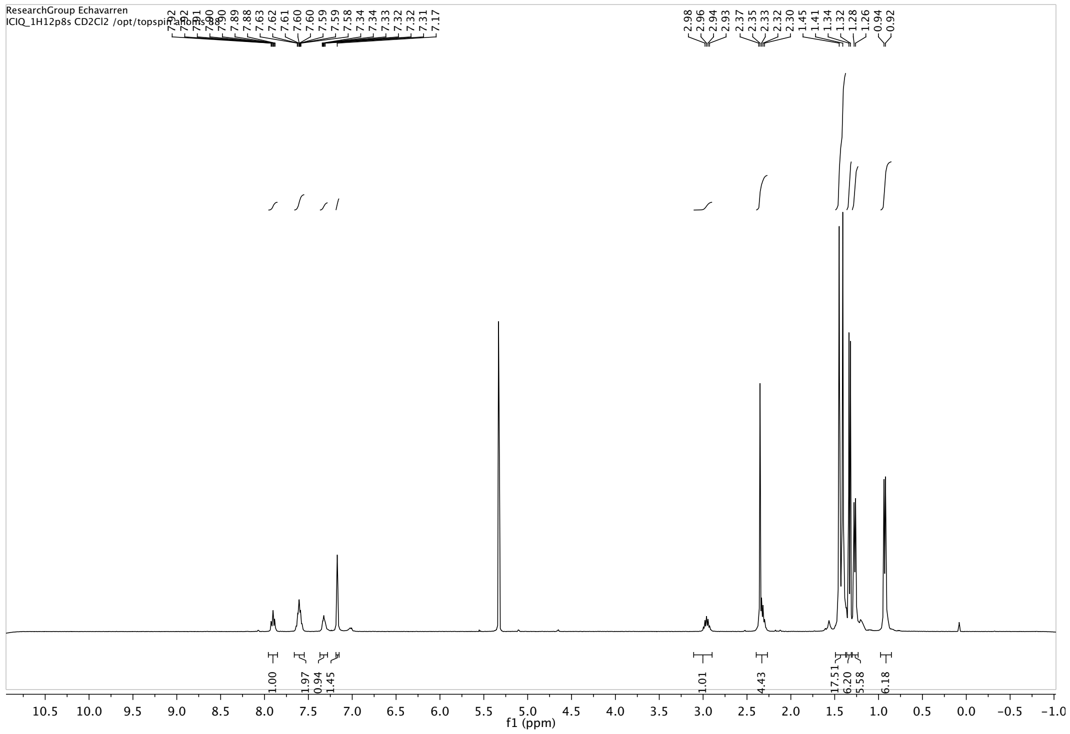
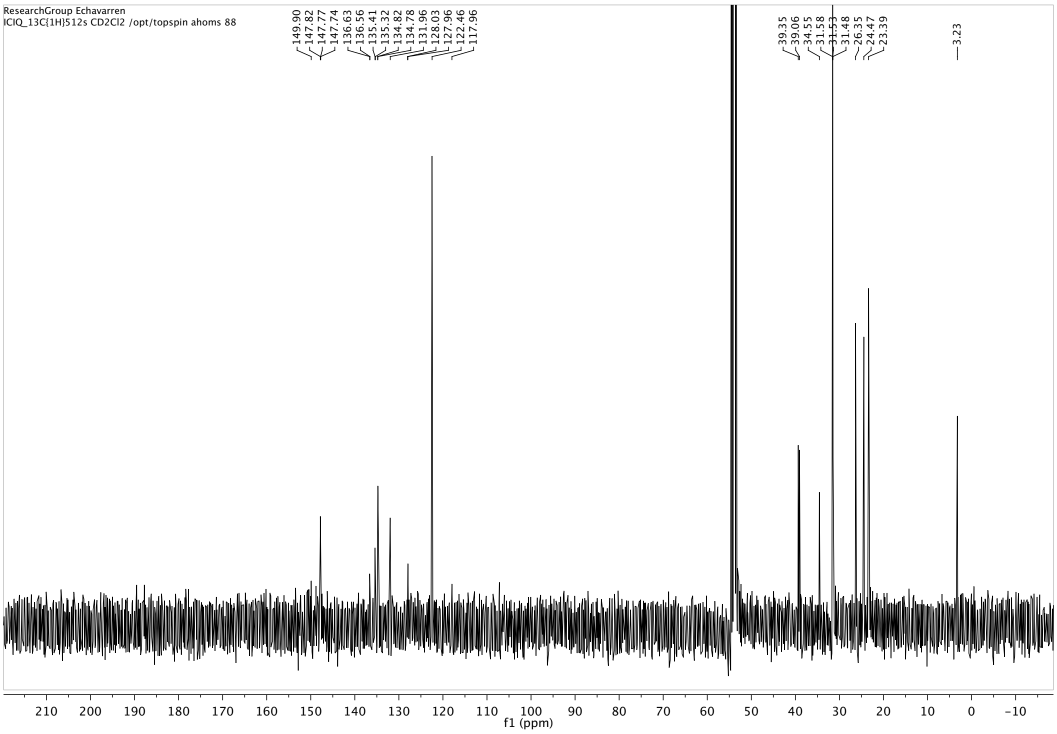
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
f1 (ppm)

(Acetonitrile)[(2´,4´,6´-triisopropyl-1,1´-biphenyl-2-yl)di-*tert*-butylphosphine]gold(I) hexafluorophosphate (A4)






ResearchGroup Echavarren
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147.77
147.74
136.63
136.56
135.41
135.32
134.82
134.78
131.96
128.03
127.96
122.46
117.96
39.35
39.06
34.55
31.58
31.53
31.48
26.35
24.47
23.39
3.23
210
200
190
180
170
160
150
140
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120
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100
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60
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40
30
20
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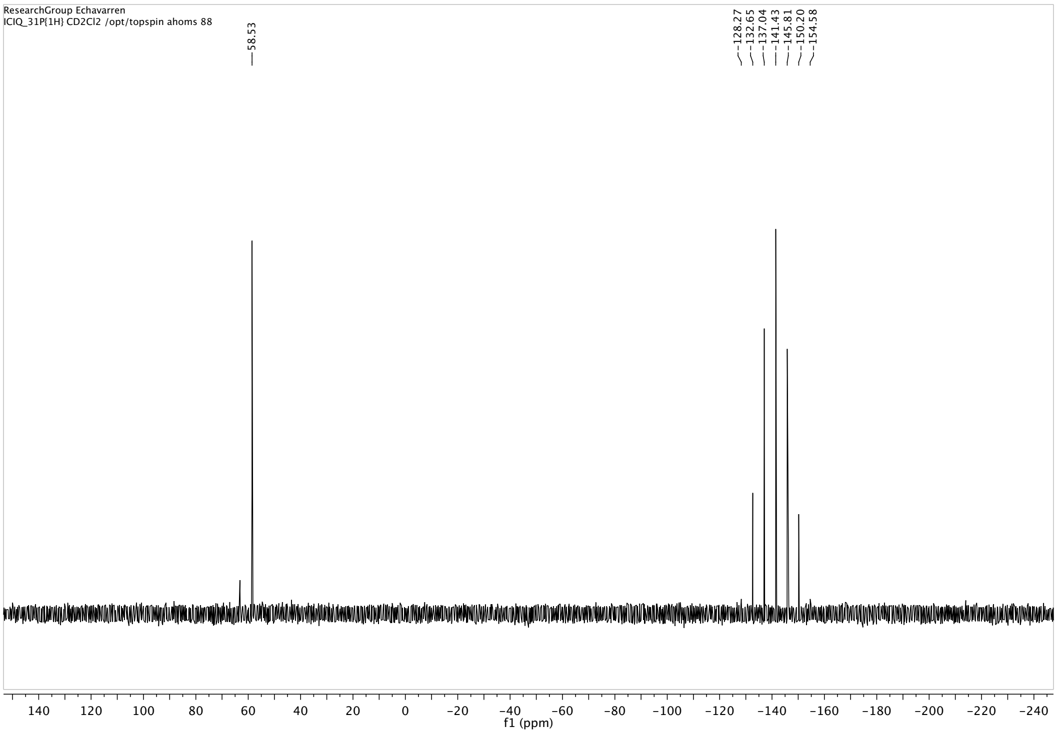
0
−10
f1 (ppm)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−145.81
−150.20
−154.58
140
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80
60
40
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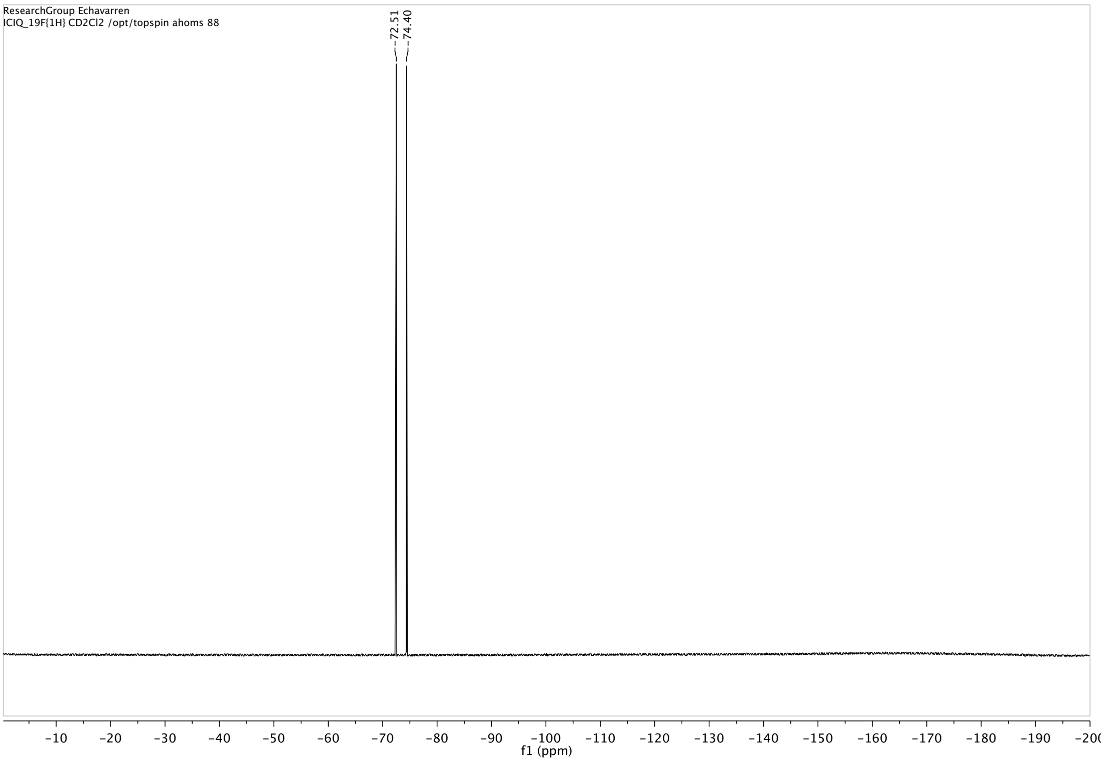
−60
−80
−100
−120
−140
−160
−180
−200
−220
−240
f1 (ppm)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-10
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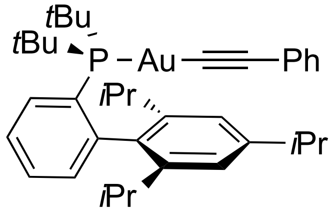
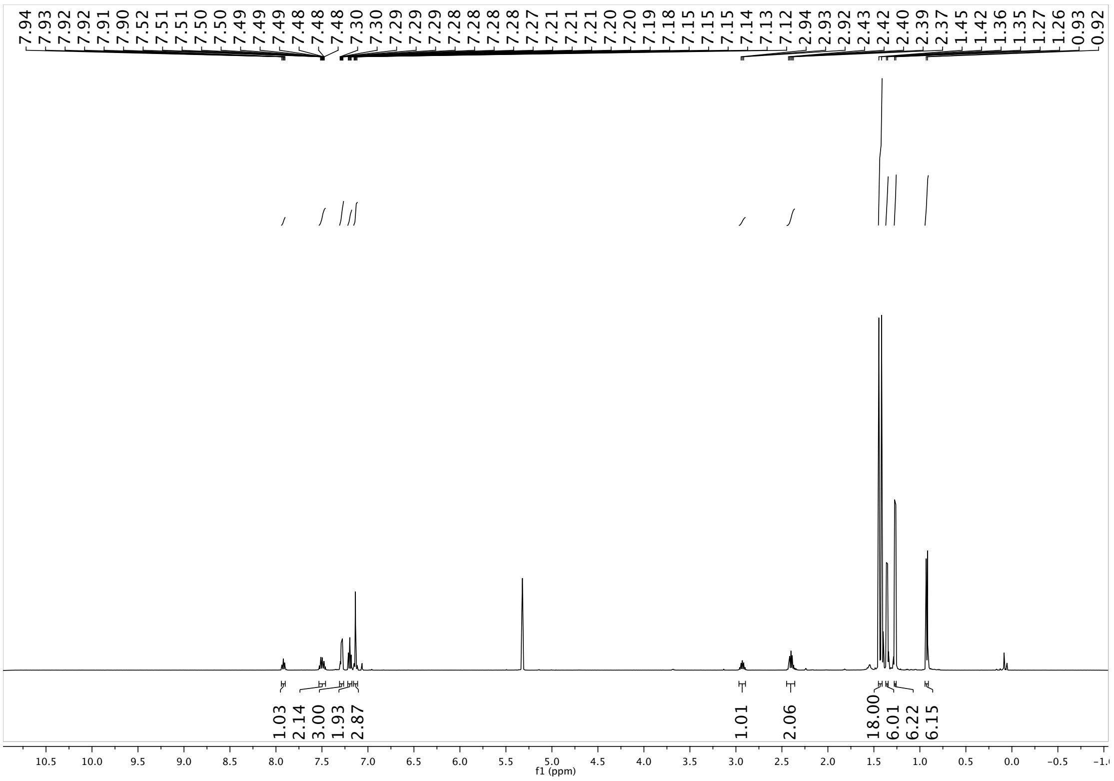
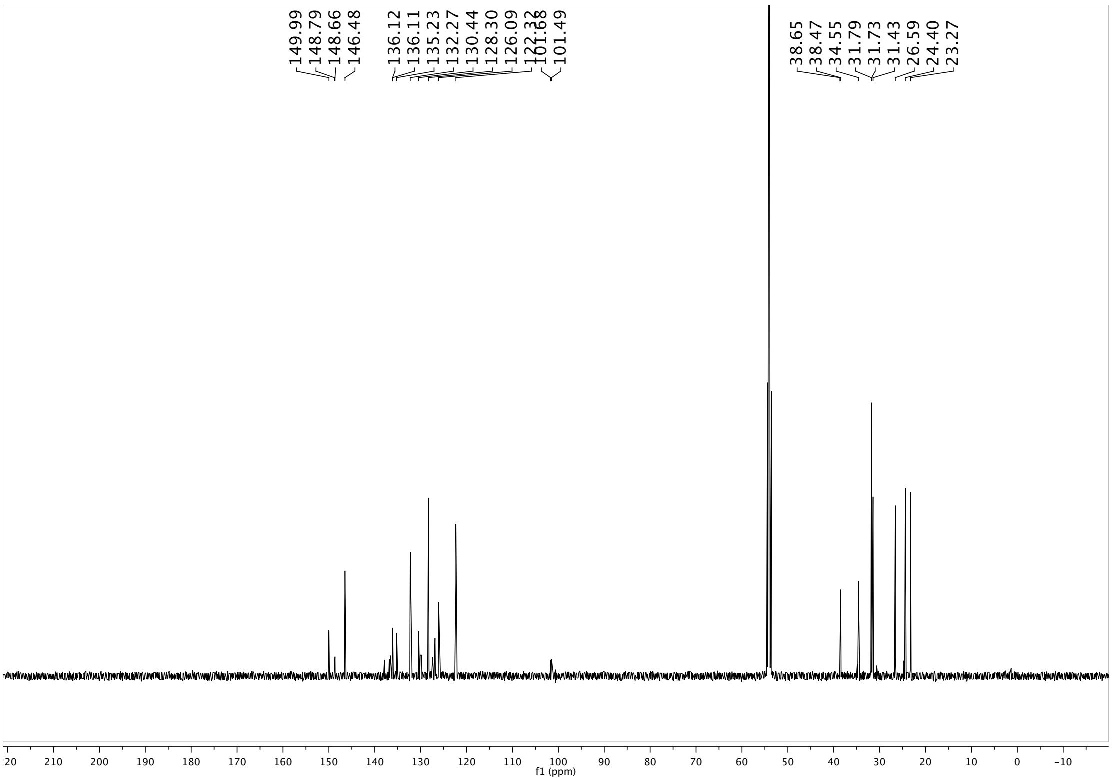
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

[(2´,4´,6´-triisopropyl-1,1´-biphenyl-2-yl)di-*tert*-butylphosphine](2-phenylethynyl)gold(I) (16)



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136.11
135.23
132.27
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101.68
101.49
38.65
38.47
34.55
31.79
31.73
31.43
26.59
24.40
23.27
220
210
200
190
180
170
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100
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40
30
20
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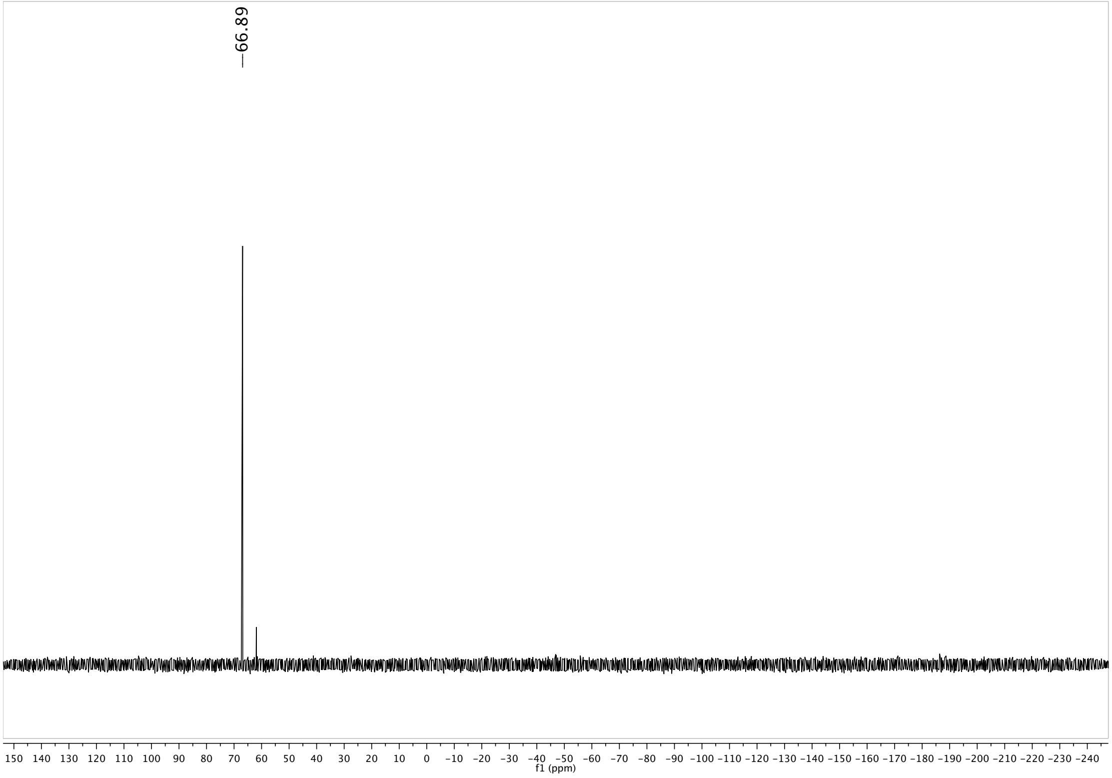
0
−10
f1 (ppm)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−60
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−90
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−150
−160
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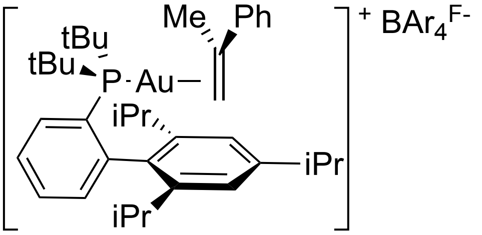
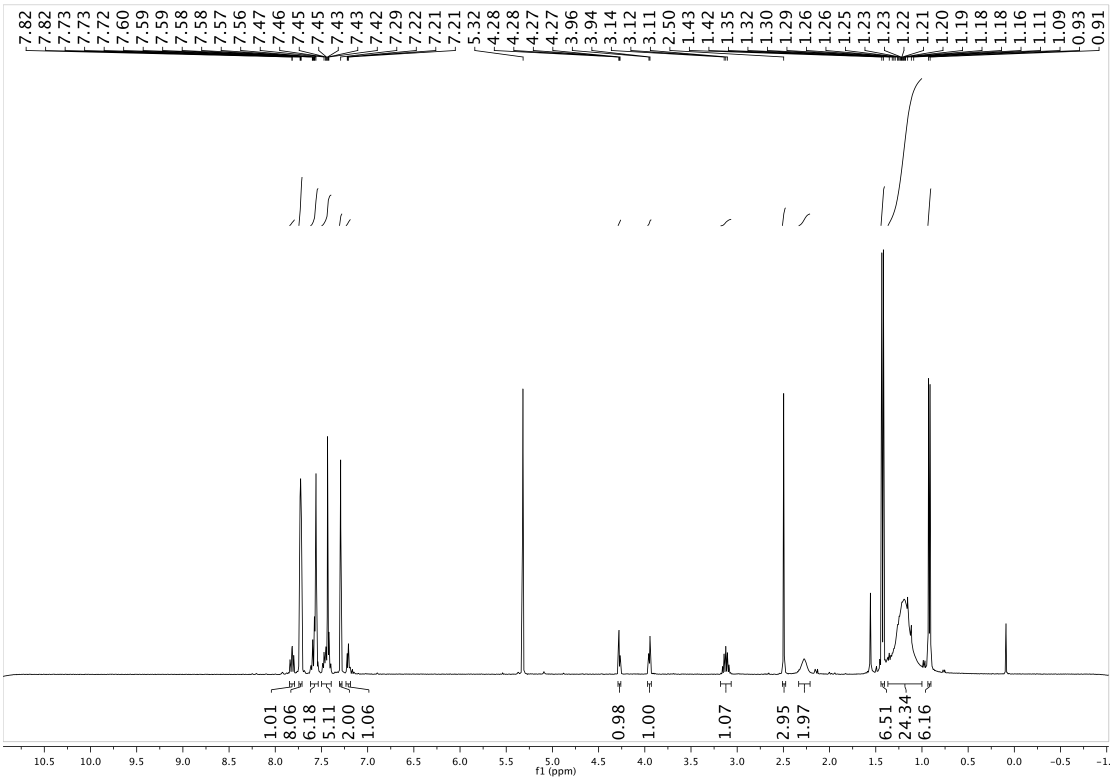
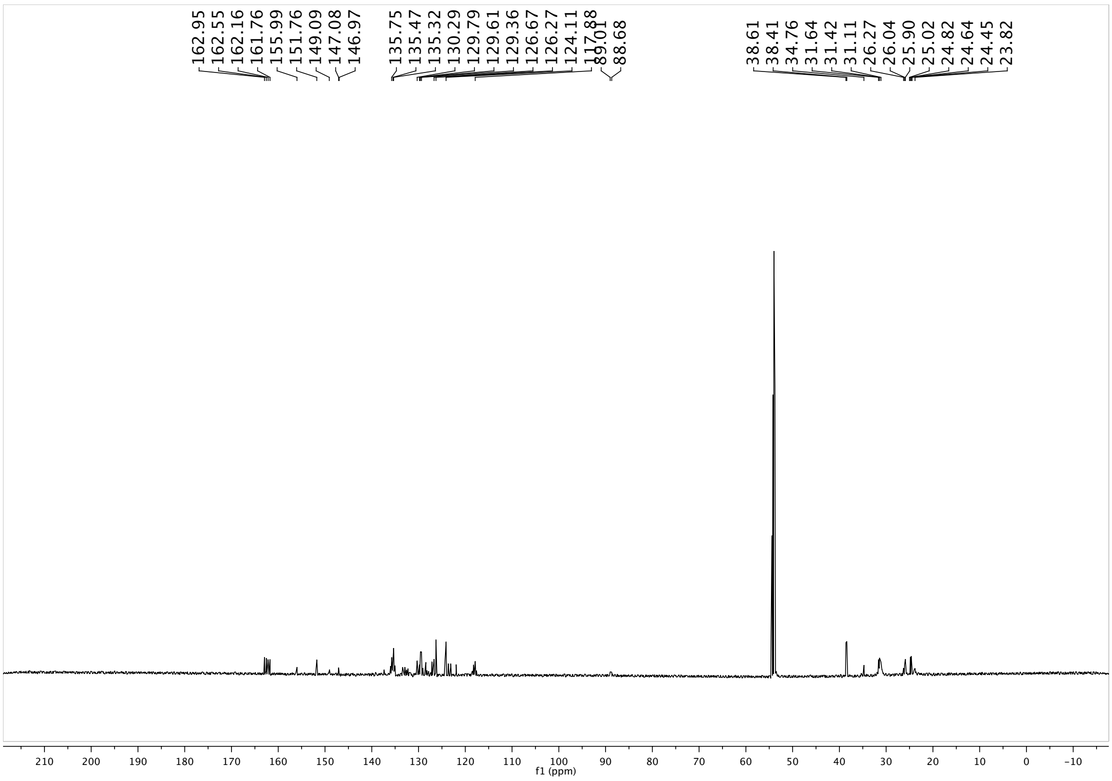
−180
−190
−200
−210
−220
−230
−240
f1 (ppm)

(α-Methylstyrene)[(2′,4′,6′-triisopropyl-1,1′-biphenyl-2-yl)di-*tert*-butylphosphine]gold(I) tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (15b)



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129.61
129.36
126.67
126.27
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117.88
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88.68
38.61
38.41
34.76
31.64
31.42
31.11
26.27
26.04
25.90
25.02
24.82
24.64
24.45
23.82
210
200
190
180
170
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120
110
100
90
80
70
60
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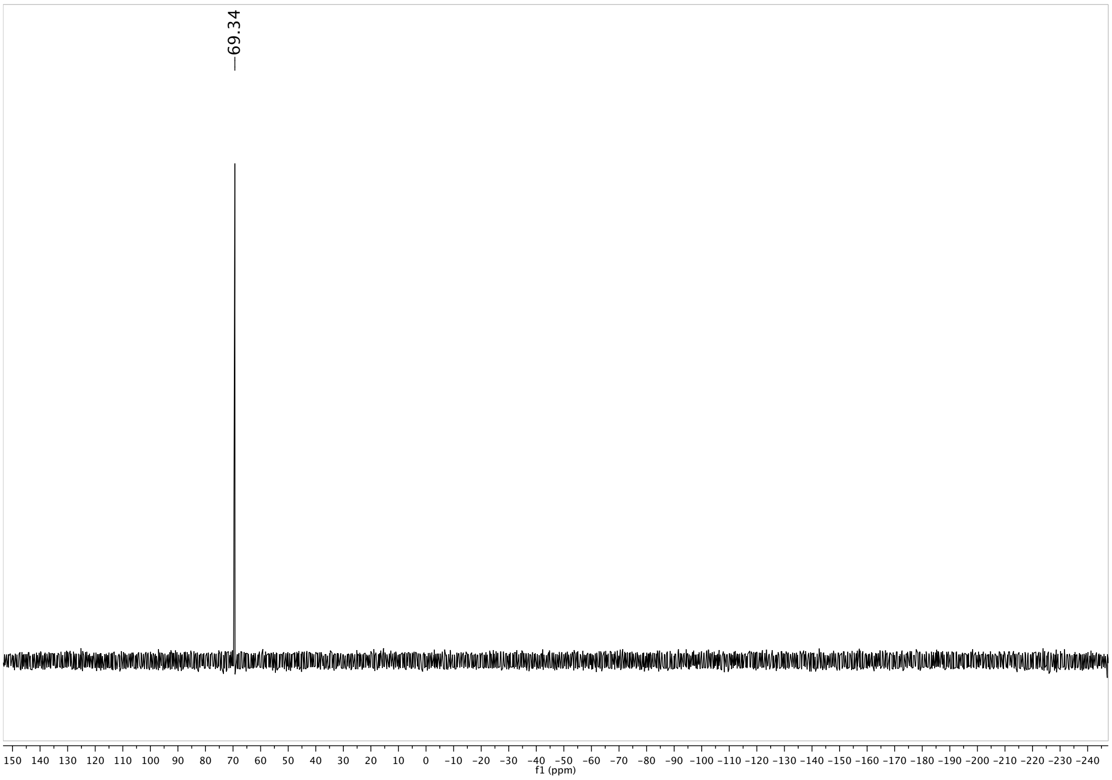
40
30
20
10
0
-10
f1 (ppm)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60
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-30
-40
-50
-60
-70
-80
-90
-100
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-160
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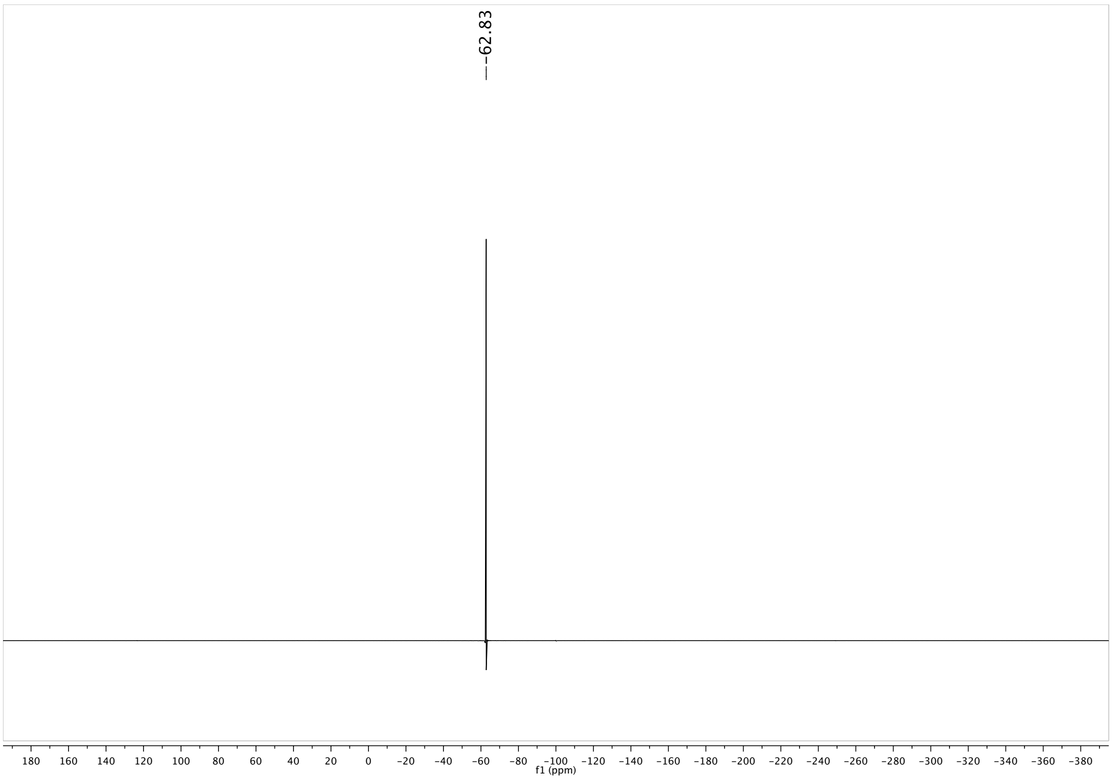
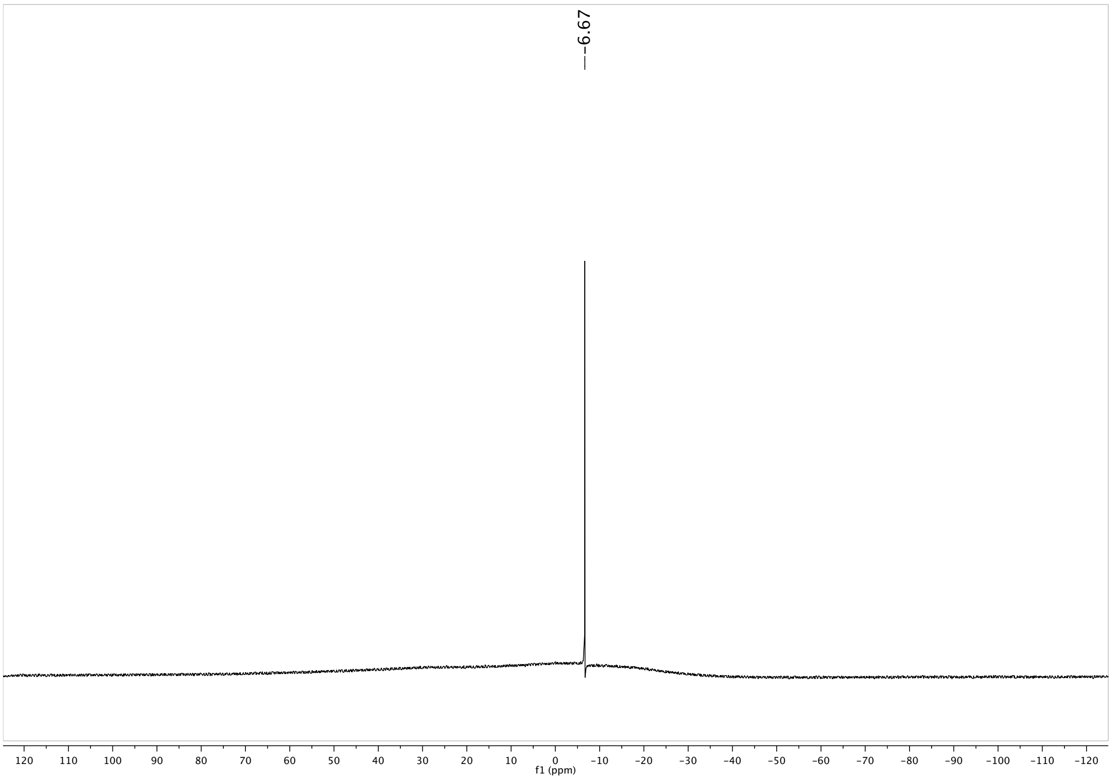
-220
-230
-240
f1 (ppm)



−62.83
180 160 140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240 −260 −280 −300 −320 −340 −360 −380
f1 (ppm)

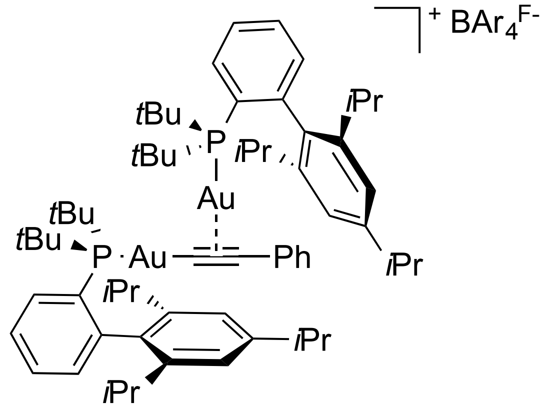


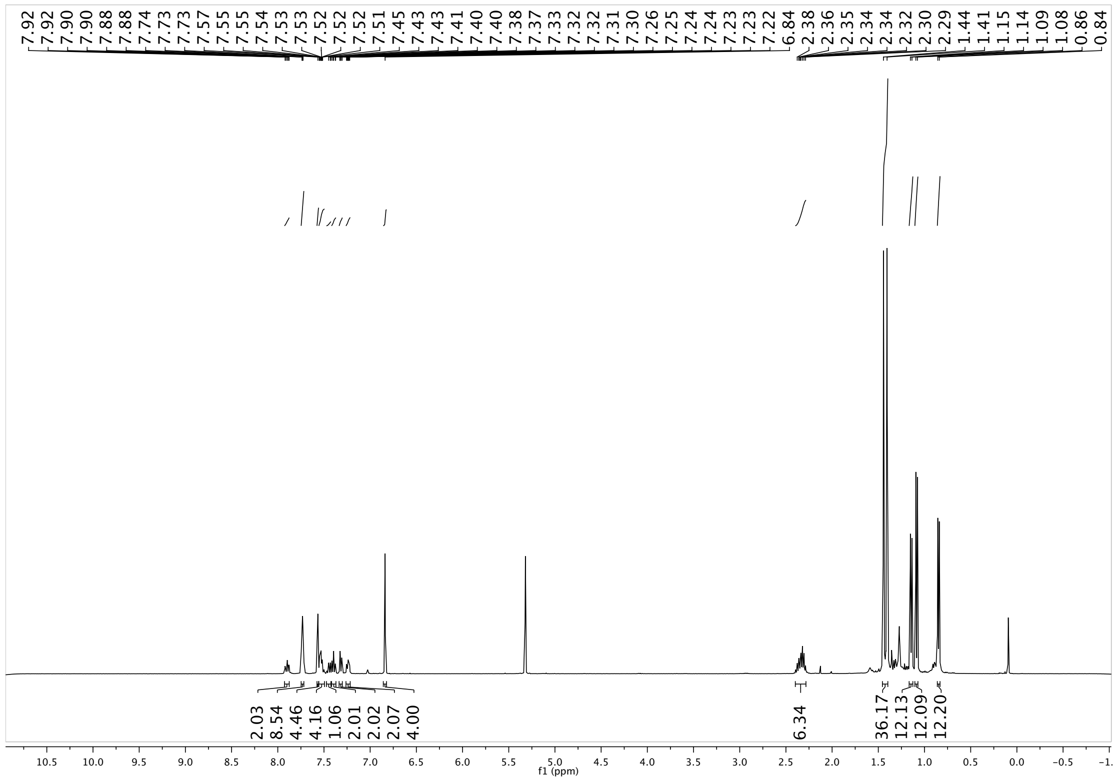
−6.67
120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120
f1 (ppm)

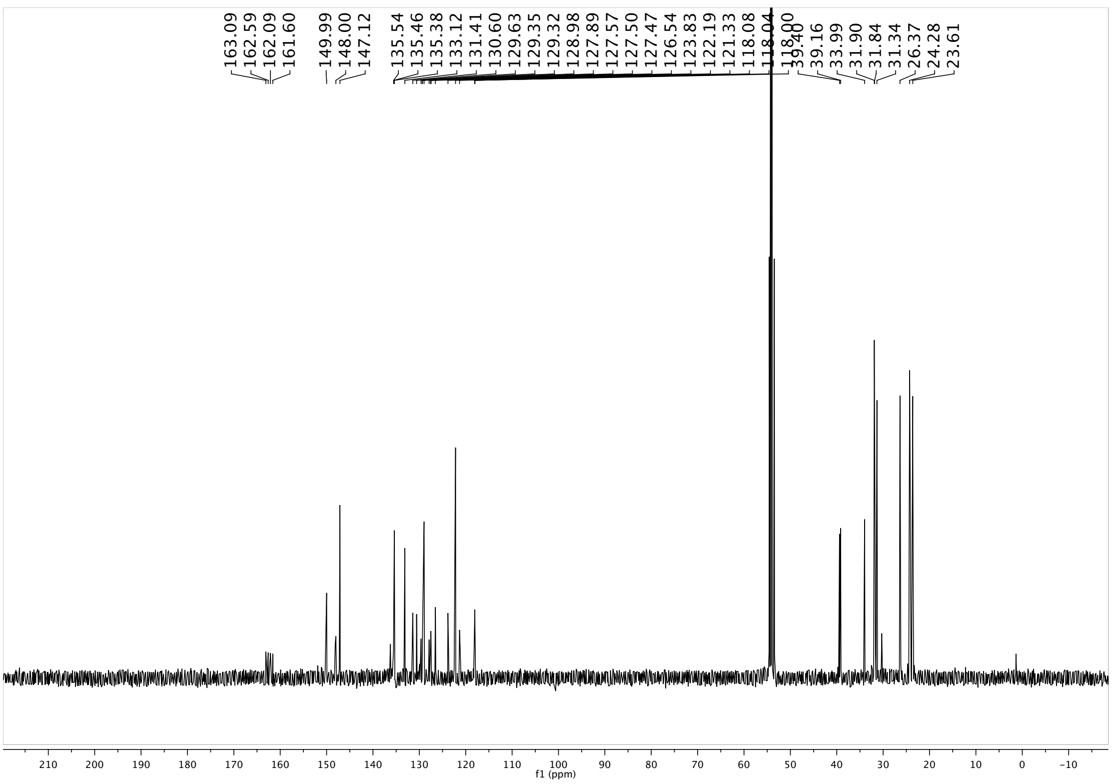
{Phenylethynyl[(2´,4´,6´-triisopropyl-1,1´-biphenyl-2-yl)di-tert-butylphosphine]gold(I)}

[(2´,4´,6´-triisopropyl-1,1´-biphenyl-2-yl)di-tert-butylphosphine]gold(I)

tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (9b)






163.09
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162.09
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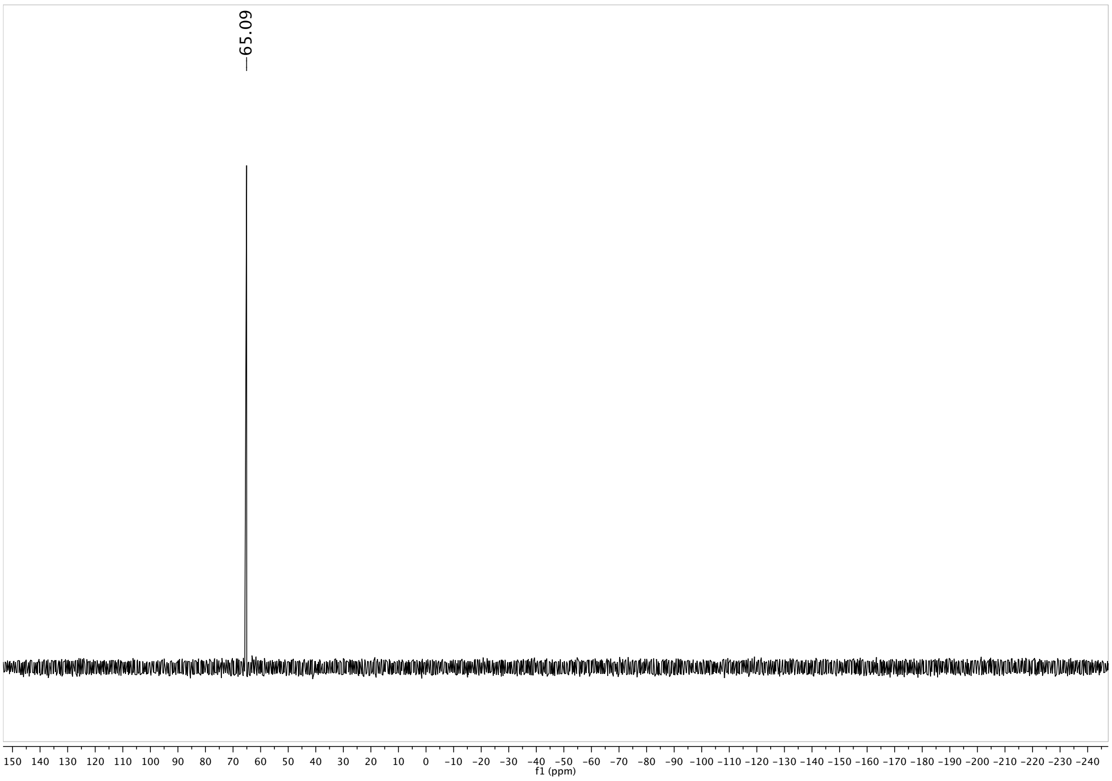
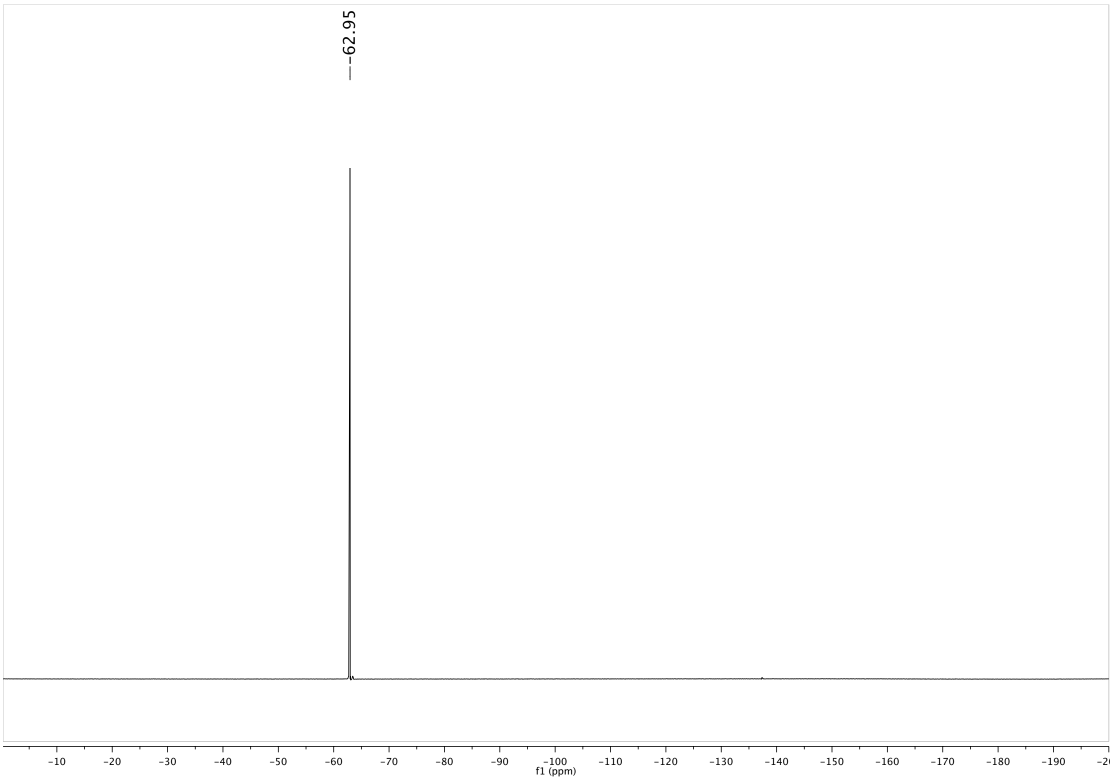
129.63
129.35
129.32
128.98
127.89
127.57
127.50
127.47
126.54
123.83
122.19
121.33
118.08
118.04
118.00
39.40
39.16
33.99
31.90
31.84
31.34
26.37
24.28
23.61
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


−65.09
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220 −230 −240
f1 (ppm)



−62.95
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
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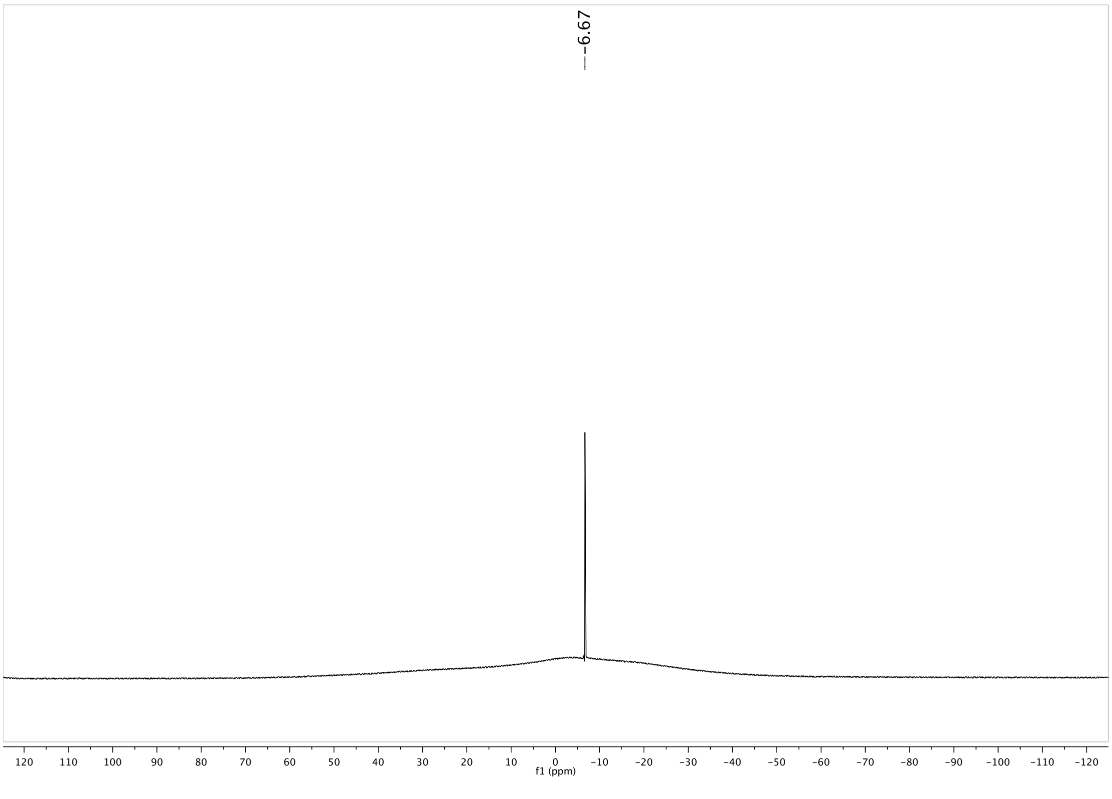
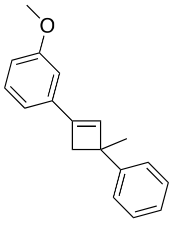
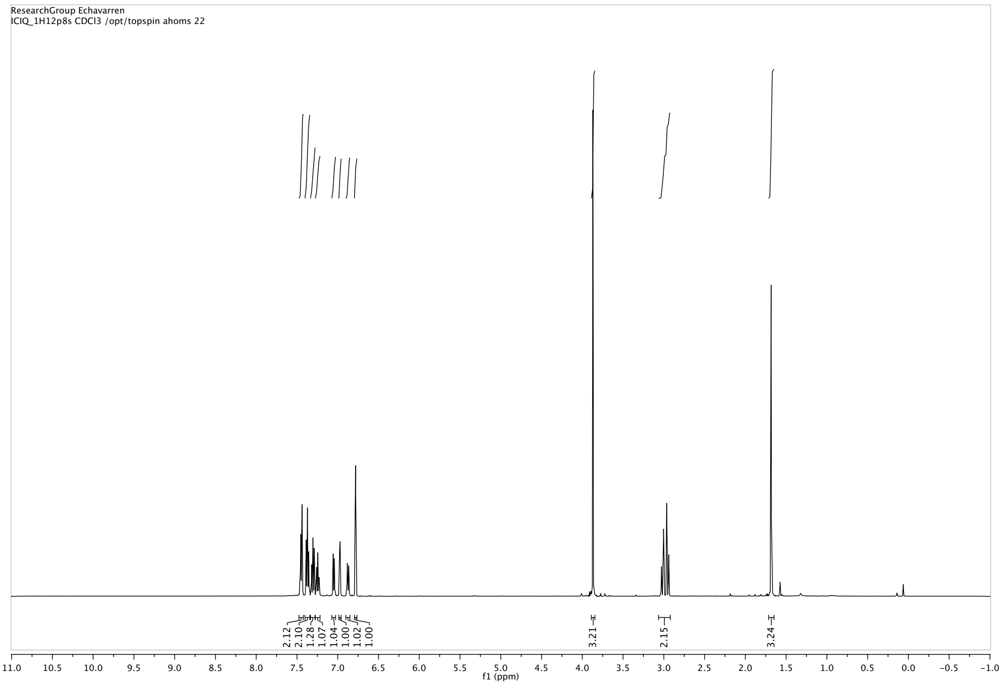
−170
−180
−190
f1 (ppm)

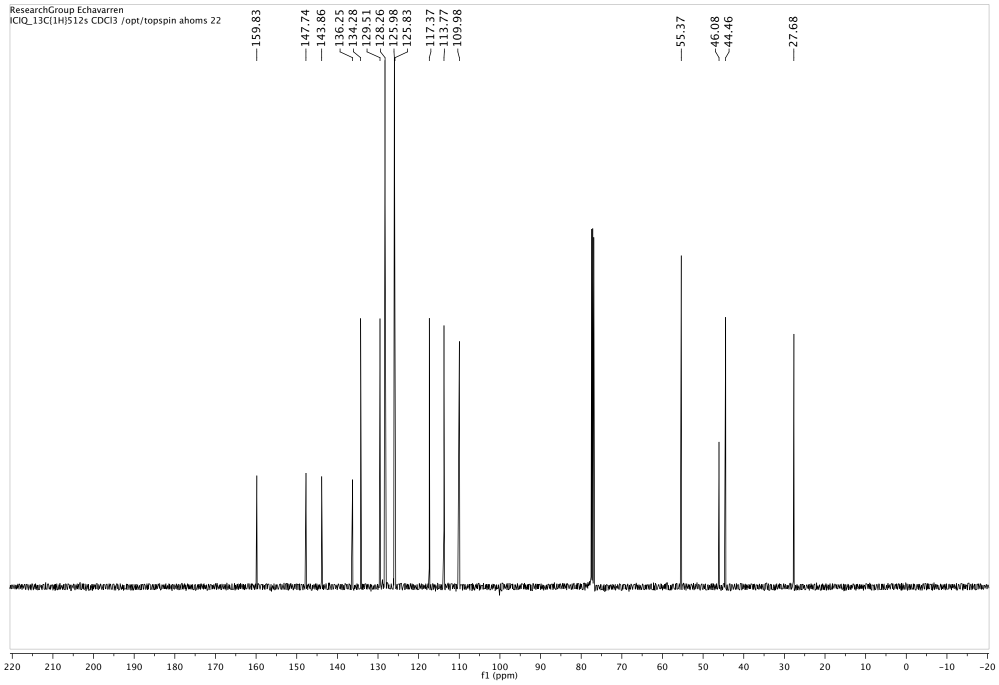


−6.67
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
f1 (ppm)

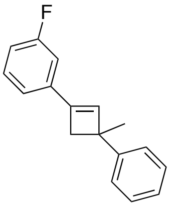
Methoxy-3-(3-methyl-3-phenylcyclobut-1-en-1-yl)benzene (3g)

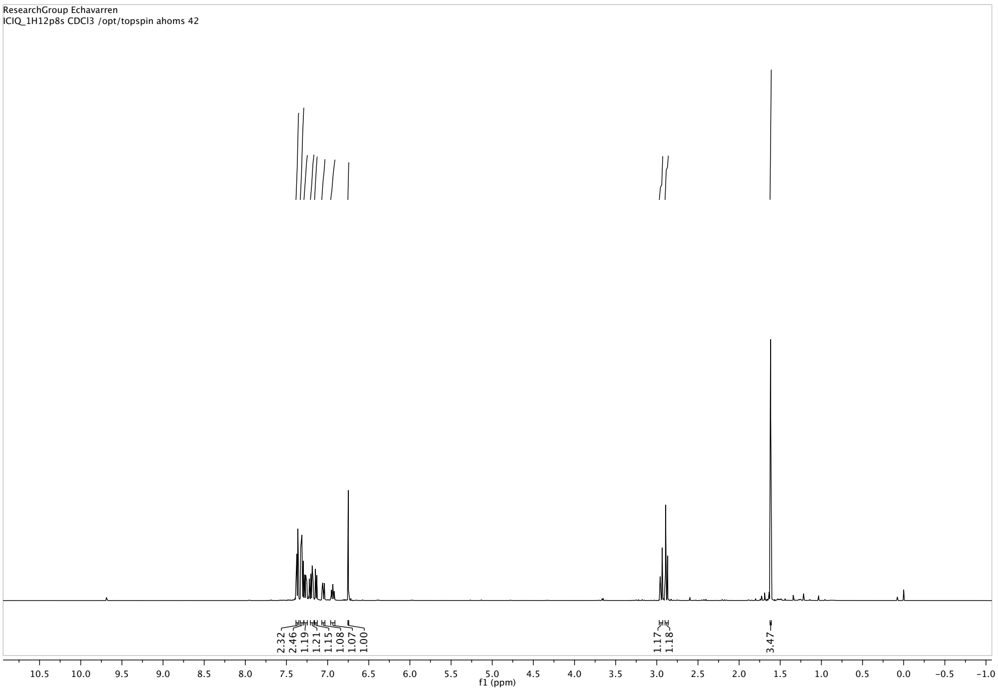


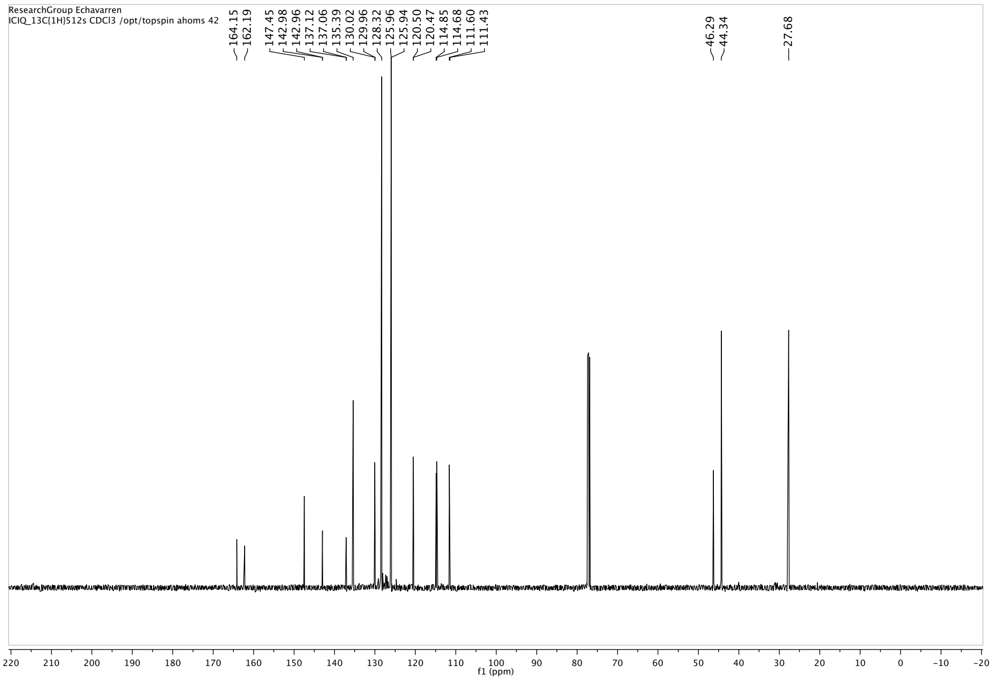




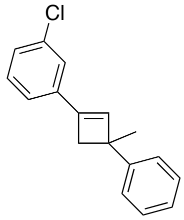
1-Fluoro-3-(3-methyl-3-phenylcyclobut-1-en-1-yl)benzene (3j)

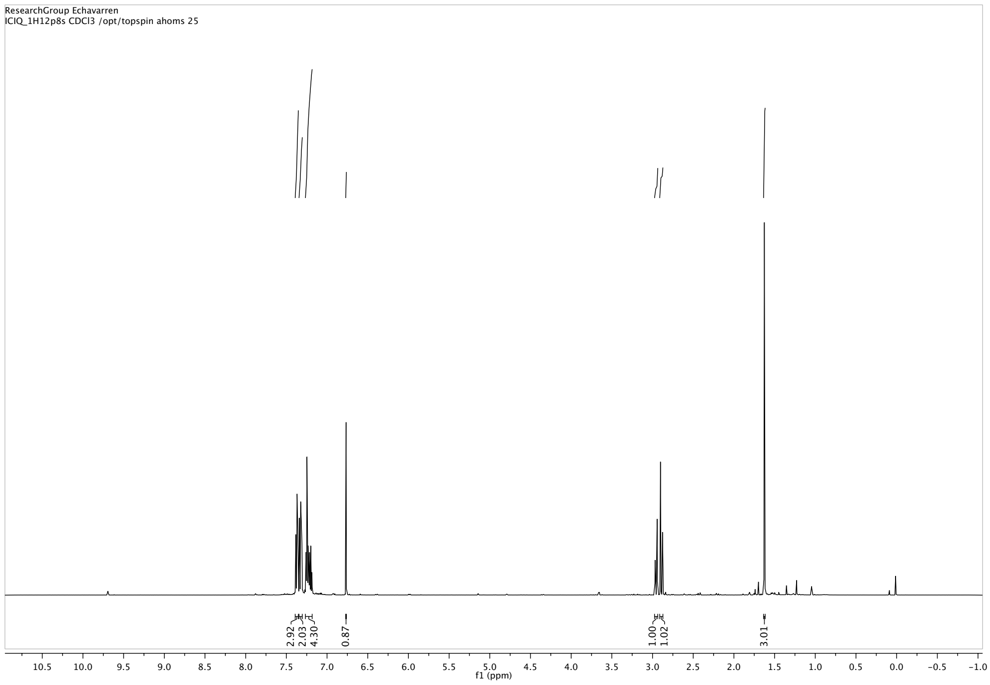


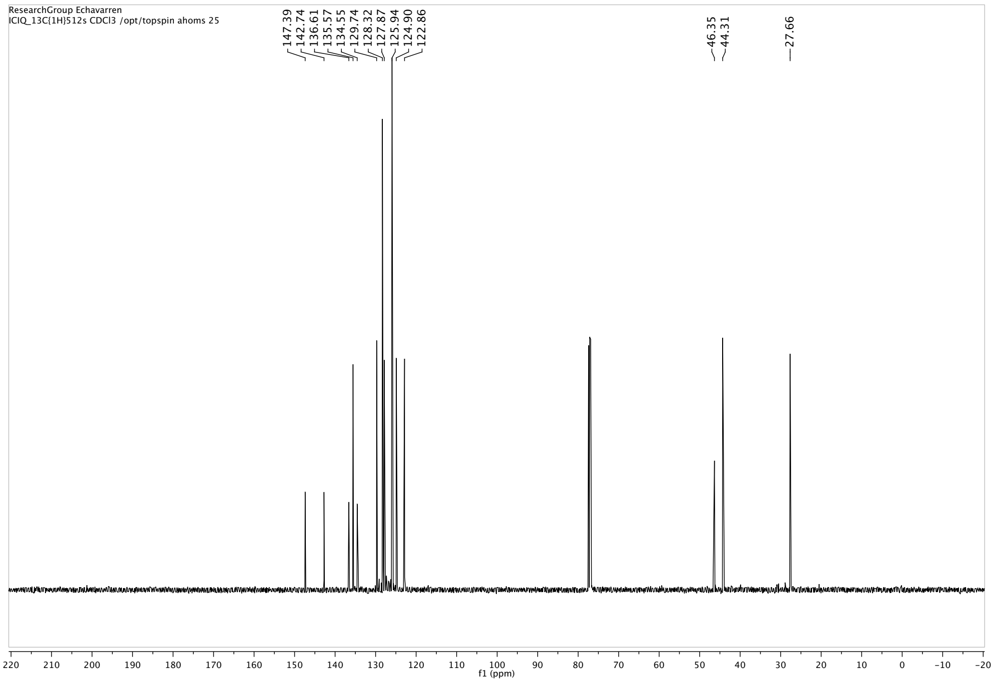




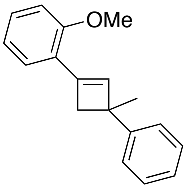
1-Chloro-3-(3-methyl-3-phenylcyclobut-1-en-1-yl)benzene (3k)

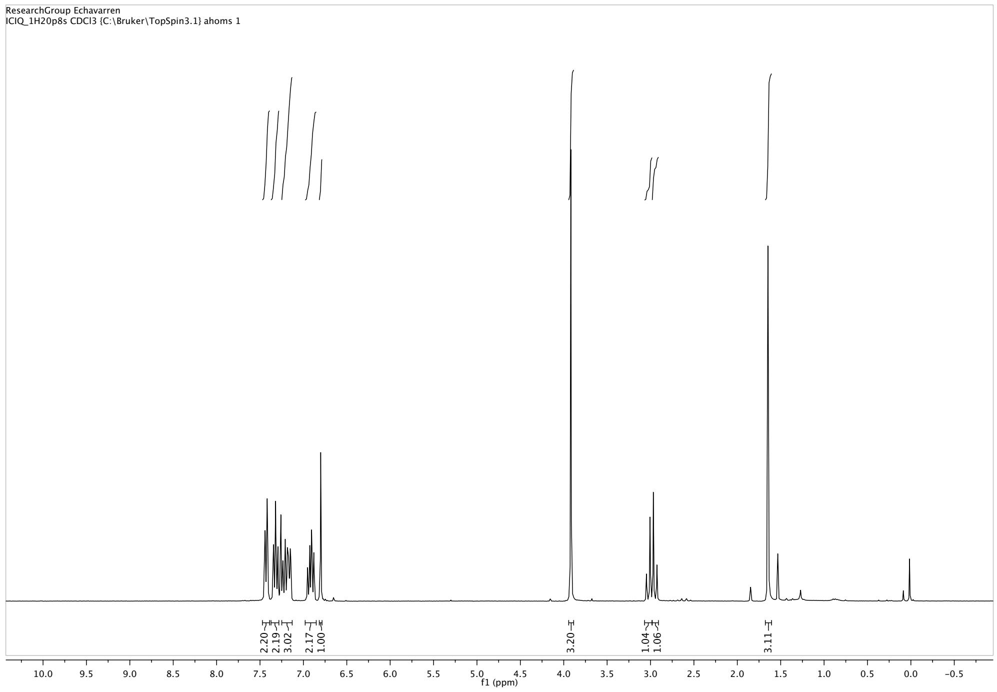


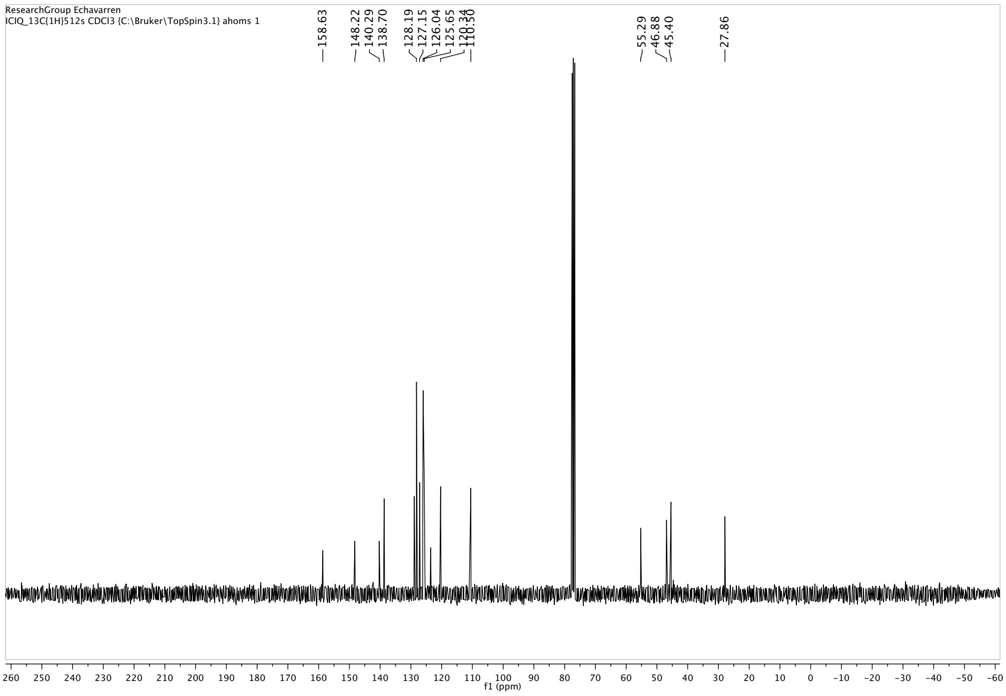




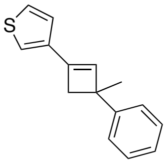
1-Methoxy-3-(3-methyl-3-phenylcyclobut-1-en-1-yl)benzene (3l)

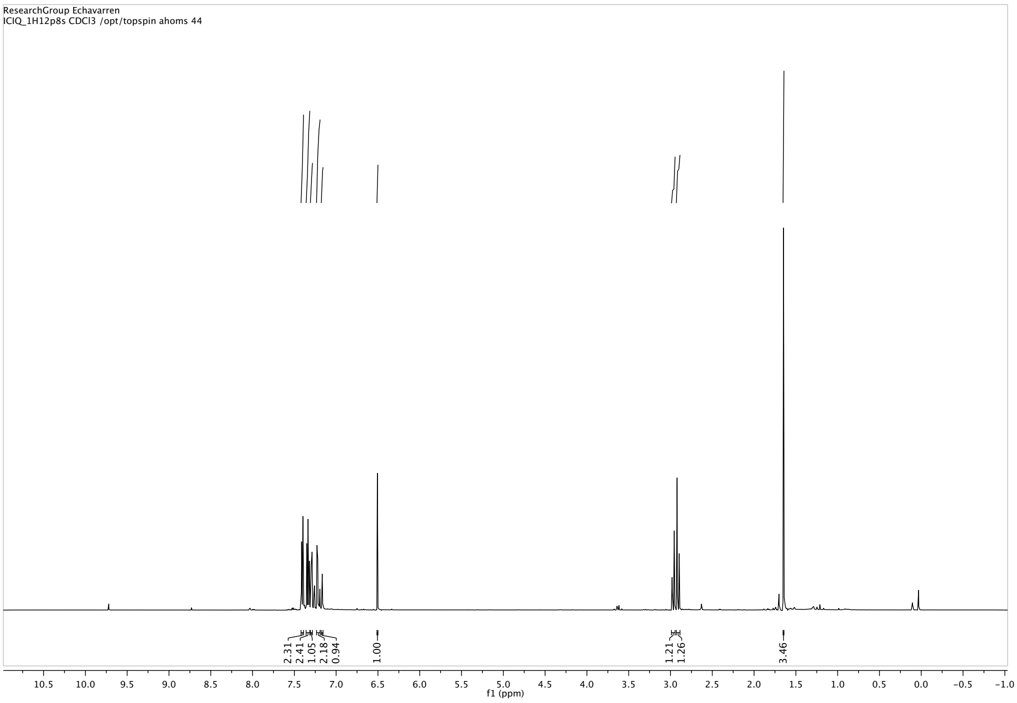


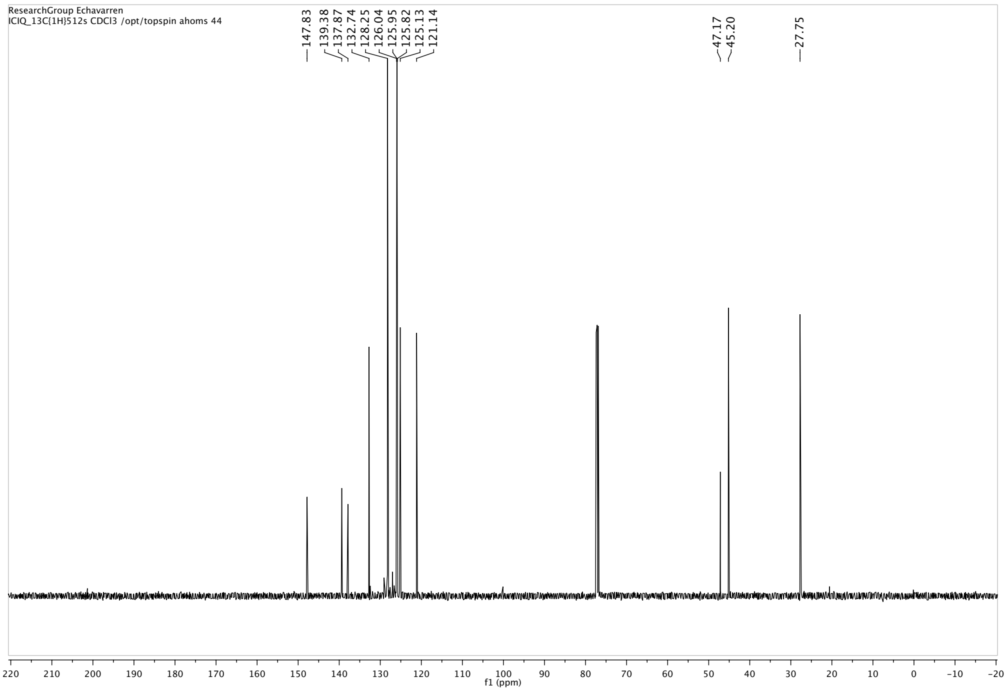




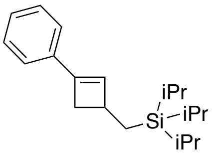
3-(3-Methyl-3-phenylcyclobut-1-en-1-yl)thiophene (3m)

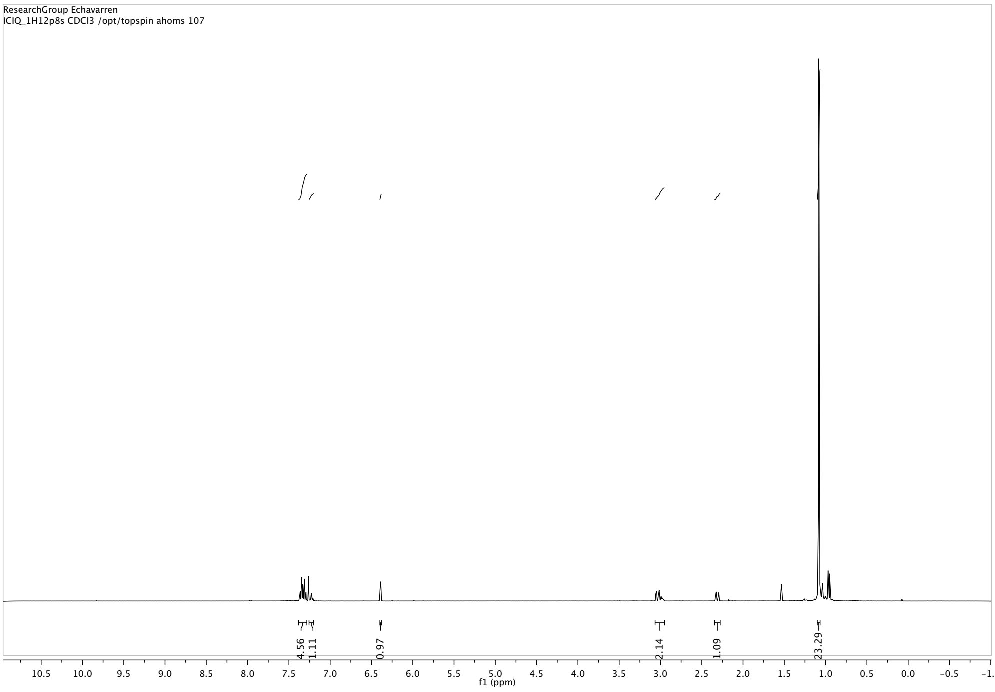


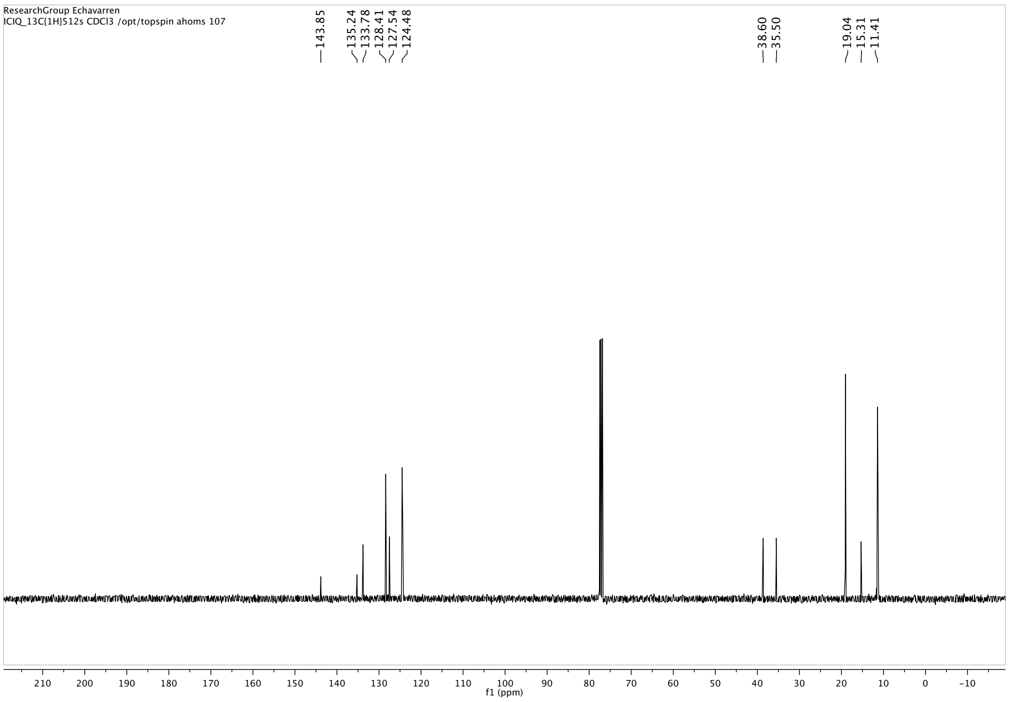




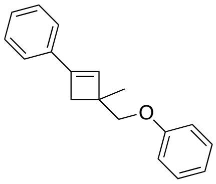
Triisopropyl((1-methyl-3-phenylcyclobut-2-en-1-yl)methyl)silane (3q)

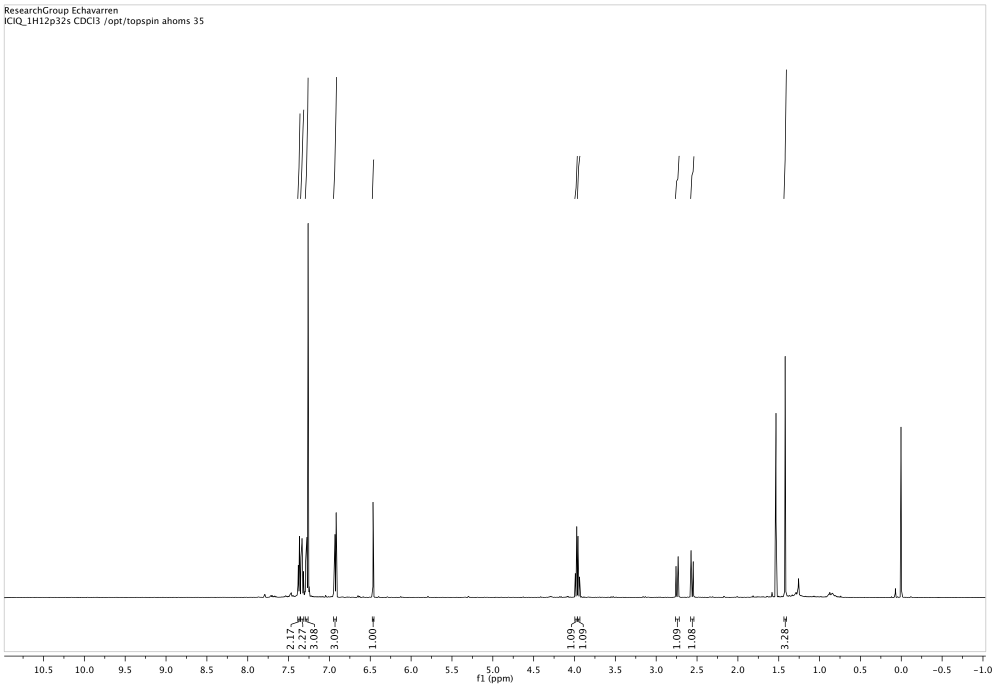


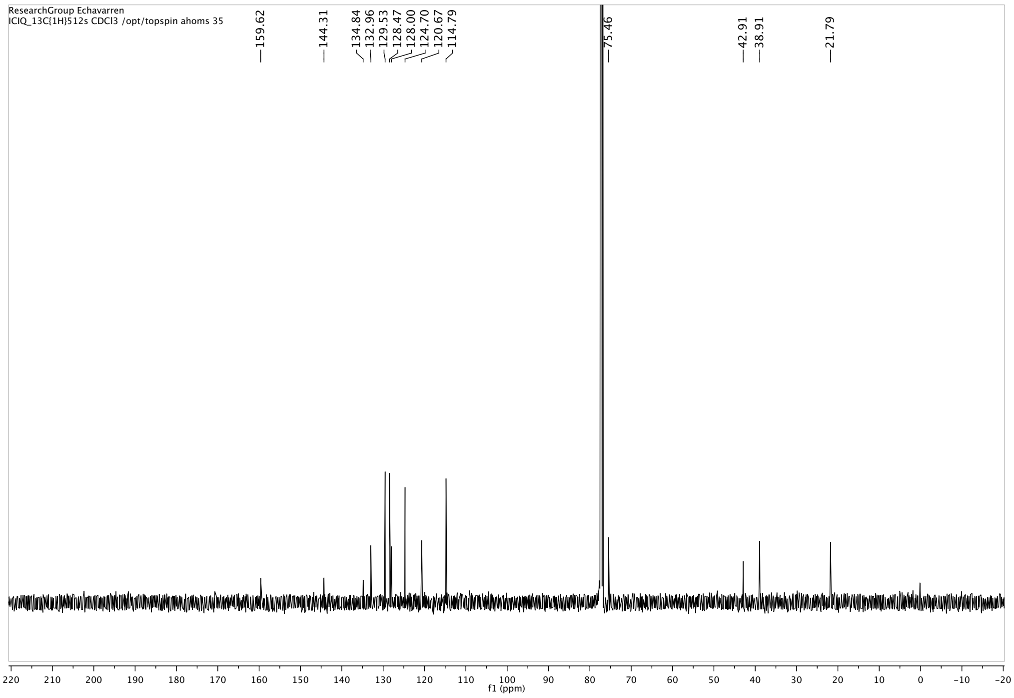




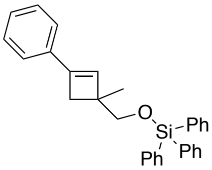
(3-Methyl-3-(phenoxymethyl)cyclobut-1-en-1-yl)benzene (3r)

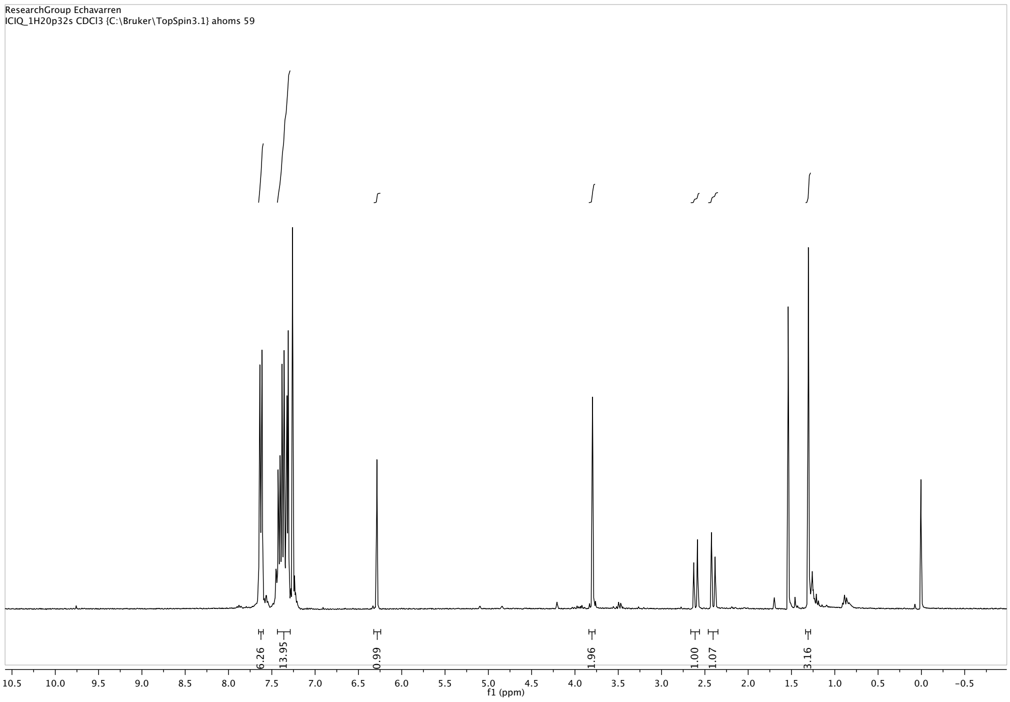


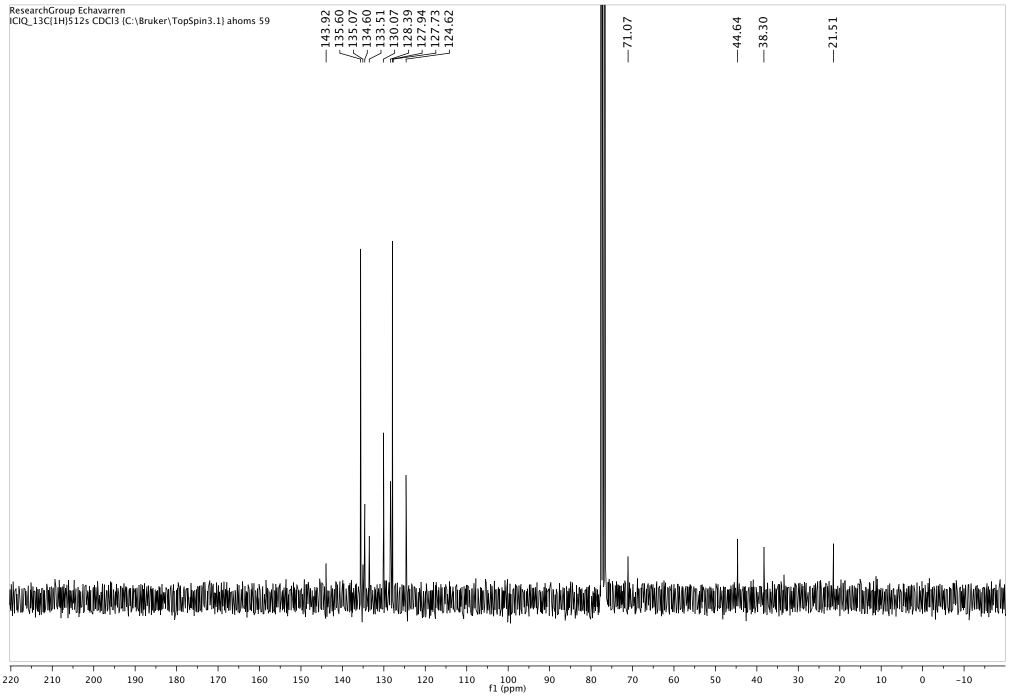




((1-methyl-3-phenylcyclobut-2-en-1-yl)methoxy)triphenylsilane (3s)







9. DFT's Data

Calculations were carried out with DFT using the M06 functional[6] as implemented in Gaussian 09.[7] The 6-31G(d) basis set[8] was used for all atoms except gold and antimony, which were treated with SDD and the associated effective core potential.[9] Frequency calculations were performed to characterize the stationary points as minima. The solvent effect was taken into account by single-point calculations using the polarizable continuum model (PCM),[10], [11], [12], [13] in particular IEF-PCM as implemented in Gaussian 09. Default options were used, except that individual spheres were placed on all hydrogen atoms to get a more accurate cavity. The calculations were performed using CH_2Cl_2 ($\varepsilon = 8.93$) as solvent. The standard Gibbs energies in dichloromethane (ΔG_{DCM}) were obtained by adding the solvation energies to the gas phase Gibbs energies computed at 298 K. The same procedure was employed to calculate zero-point corrected energies in CH2Cl2.

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[6] (a) A. D. J. Becke, *Chem. Phys.* **1993**, *98*, 5648–5652; (b) C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789; (c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623–1627.

[7] 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. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, K. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. 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, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, revision 02; Gaussian, Inc.: Wallingford, CT, **2009**.

[8] (a) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. Defrees, J. A. Pople, *J. Chem. Phys.* **1982**, *77*, 3654–3665. (b) W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257–2261.

[9] D. Andrae, U. Haussermann, M. Dolg, H. Stoll and H.Preuss, *Theor. Chim. Acta* **1990**, *77*, 123–141.

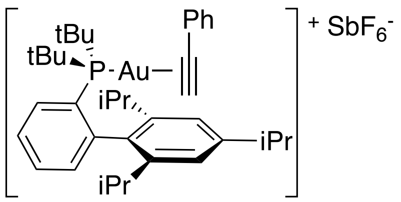
[10] E. Cances, B. Mennucci and J. J. Tomasi, *Chem. Phys.* **1997**, *107*, 3032–3041.

[11] M. Cossi, V. Barone, B. Mennucci and J. Tomasi, *Chem. Phys. Lett.* **1998**, *286*, 253-260.

[12] B. Mennucci and J. J. Tomasi, *Chem. Phys.* **1997**, *106*, 5151–5158.

[13] S. Miertus and J. Tomasi, *J. Chem. Phys.* **1982**, *65*, 239–245.

Table S4. *t*BuXPhosAu(η^2-phenylacetylene)SbF$_6$ complex **8a**.



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Number	Number	X	Y	Z
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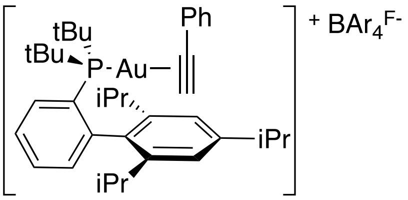
3	6	-2.315312	-3.445661	0.587625
4	79	-0.943476	-0.292388	1.039915
5	6	1.395771	-1.236041	4.094960
6	6	2.476061	-2.083819	4.289297
7	6	3.632799	-1.930782	3.521641
8	6	3.722800	-0.923044	2.564055
9	6	2.653997	-0.059505	2.371179
10	6	1.487414	-0.218565	3.131894
11	1	0.478428	-1.352080	4.670298
12	1	2.415871	-2.873741	5.034892
13	1	4.468896	-2.611566	3.670334
14	1	4.606758	-0.815782	1.938790
15	1	2.713905	0.719084	1.614445
16	6	0.372543	0.619682	2.843818
17	6	-0.578118	1.336872	2.511143
18	1	-1.250210	2.179512	2.482791
19	6	-2.521079	-1.508618	-1.757237
20	6	-2.942910	-2.458642	-2.701747
21	6	-2.929185	-0.160041	-1.913783
22	6	-3.710865	-2.111878	-3.804066
23	1	-2.670454	-3.504659	-2.572889
24	6	-3.686360	0.165755	-3.048736
25	6	-4.069048	-0.782332	-3.987926
26	1	-4.021493	-2.876278	-4.512846
27	1	-3.995633	1.203495	-3.177013
28	1	-4.659754	-0.483181	-4.851463
29	6	-2.207064	-4.857154	0.012100
30	1	-2.837262	-5.519614	0.623347
31	1	-2.569657	-4.934737	-1.020190
32	1	-1.186320	-5.255319	0.060004
33	6	-1.731936	-3.455204	2.006044
34	1	-0.648582	-3.630968	2.021887
35	1	-1.929286	-2.511627	2.534066
36	1	-2.209893	-4.265366	2.576326
37	6	-3.790507	-3.061358	0.676080

38	1	-4.296538	-3.764915	1.352881
39	1	-3.924961	-2.053866	1.089104
40	1	-4.294554	-3.109209	-0.298016
41	6	0.012396	-3.843504	-2.231236
42	1	1.013628	-4.103974	-2.603638
43	1	-0.427729	-4.756061	-1.819504
44	1	-0.577633	-3.525609	-3.099561
45	6	1.121940	-3.164539	-0.091453
46	1	2.108412	-3.373523	-0.529670
47	1	1.263171	-2.384428	0.671898
48	1	0.782432	-4.084595	0.402380
49	6	0.800560	-1.530728	-1.941707
50	1	0.996365	-0.682804	-1.276899
51	1	1.772654	-1.841260	-2.350582
52	1	0.175829	-1.200321	-2.782974
53	6	-2.732826	0.990198	-0.961387
54	6	-3.752055	1.274863	-0.022731
55	6	-1.683198	1.922320	-1.142118
56	6	-3.688261	2.454369	0.722956
57	6	-1.667842	3.084627	-0.371356
58	6	-2.657280	3.376182	0.565478
59	1	-4.484595	2.661317	1.438467
60	1	-0.855194	3.801743	-0.509693
61	6	-0.590425	1.722098	-2.169257
62	1	-0.655685	0.687509	-2.532601
63	6	-2.613568	4.688707	1.318162
64	1	-1.550090	4.927528	1.490957
65	6	-3.315862	4.651396	2.669455
66	1	-2.957929	3.829624	3.305337
67	1	-3.147305	5.592218	3.208310
68	1	-4.402896	4.535367	2.553696
69	6	-3.205963	5.798210	0.447231
70	1	-3.150128	6.769435	0.956727
71	1	-2.679217	5.882823	-0.512046
72	1	-4.263941	5.586244	0.232854
73	6	0.804760	1.930955	-1.582795
74	1	0.929571	1.414150	-0.617706
75	1	1.583386	1.552963	-2.256434
76	1	1.016572	2.996283	-1.413388
77	6	-0.806861	2.636186	-3.375870
78	1	-0.777328	3.694160	-3.078118
79	1	-0.019419	2.477086	-4.124778
80	1	-1.776795	2.450164	-3.856526
81	6	-4.958583	0.375415	0.157931
82	1	-4.740195	-0.591425	-0.318854
83	6	-5.279072	0.112976	1.628509
84	1	-5.690201	1.005410	2.119980
85	1	-6.032370	-0.681361	1.719203
86	1	-4.386530	-0.192047	2.195156
87	6	-6.178952	0.965784	-0.550559

88	1	-7.050506	0.308002	-0.431735
89	1	-6.437181	1.947537	-0.128395
90	1	-5.996509	1.098818	-1.625022
91	51	4.878765	0.695626	-0.895334
92	9	4.675845	1.588450	0.756587
93	9	3.962476	2.095020	-1.756329
94	9	3.242205	-0.191430	-0.576019
95	9	6.513745	1.572119	-1.181054
96	9	5.785981	-0.701720	-0.005614
97	9	5.041606	-0.223877	-2.525713

Table S5. *t*BuXPhosAu(η^2-phenylacetylene)BAr$_4^F$ complex **8b**.



Center Number	Atomic Number	Cartesian Coordinates (Angstroms)		
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3	6	1.848076	1.268603	2.087464
4	79	3.950976	0.645668	-0.591248
5	6	3.784318	4.113133	-2.484423
6	6	4.011281	5.445271	-2.172235
7	6	5.279575	5.857811	-1.766556
8	6	6.326712	4.940908	-1.675916
9	6	6.109219	3.604323	-1.978139
10	6	4.831427	3.185986	-2.379969
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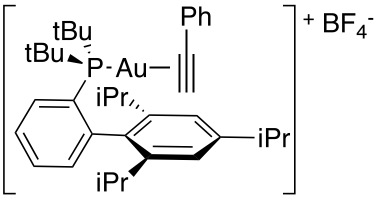
12	1	3.196793	6.162855	-2.245709
13	1	5.455620	6.903334	-1.521771
14	1	7.315097	5.270962	-1.364086
15	1	6.914328	2.875095	-1.900986
16	6	4.570481	1.805394	-2.627195
17	6	4.329609	0.607196	-2.800594
18	1	4.207555	-0.353705	-3.272789
19	6	3.963634	-0.862643	2.556692
20	6	3.875641	-0.903891	3.958845
21	6	4.331589	-2.045996	1.866870
22	6	4.172136	-2.047551	4.686718
23	1	3.575813	-0.015903	4.508344
24	6	4.659037	-3.176066	2.629729

25	6	4.586886	-3.190029	4.015366
26	1	4.086564	-2.036865	5.770980
27	1	4.959224	-4.079522	2.098446
28	1	4.842821	-4.093881	4.564575
29	6	1.540690	1.609276	3.543081
30	1	0.480108	1.886354	3.613879
31	1	1.696768	0.762253	4.222365
32	1	2.114988	2.471529	3.903443
33	6	1.472820	2.465486	1.211921
34	1	1.987563	3.391321	1.490173
35	1	1.661735	2.270074	0.145619
36	1	0.391991	2.641005	1.333667
37	6	0.988368	0.088642	1.641858
38	1	-0.072745	0.366362	1.733996
39	1	1.167293	-0.162903	0.586082
40	1	1.152440	-0.807351	2.253944
41	6	5.017016	2.069411	3.948653
42	1	5.700223	2.893347	4.200951
43	1	4.062303	2.278136	4.444497
44	1	5.443771	1.154961	4.375964
45	6	4.591415	3.387814	1.876945
46	1	5.459744	4.040123	2.051462
47	1	4.392970	3.388598	0.794322
48	1	3.737271	3.844304	2.391530
49	6	6.284199	1.569365	1.893030
50	1	6.332535	1.599401	0.796438
51	1	7.041504	2.266175	2.281029
52	1	6.561979	0.561233	2.229074
53	6	4.340109	-2.281352	0.383114
54	6	3.200022	-2.869277	-0.216575
55	6	5.522384	-2.131121	-0.373623
56	6	3.251533	-3.222967	-1.563628
57	6	5.518501	-2.504175	-1.720642
58	6	4.392733	-3.036589	-2.341410
59	1	2.361391	-3.657442	-2.021349
60	1	6.432936	-2.387410	-2.306339
61	6	6.823333	-1.671882	0.252355
62	1	6.590306	-1.224151	1.229455
63	6	4.439518	-3.458420	-3.793625
64	1	5.371727	-3.050717	-4.220084
65	6	3.272116	-2.916484	-4.614685
66	1	3.186939	-1.822486	-4.554566
67	1	3.393996	-3.185136	-5.672046
68	1	2.313977	-3.335310	-4.278397
69	6	4.502854	-4.981672	-3.903353
70	1	4.592358	-5.294923	-4.952162
71	1	5.358981	-5.387052	-3.348719
72	1	3.589630	-5.437625	-3.494104
73	6	7.558163	-0.623382	-0.579589
74	1	6.895822	0.207924	-0.865150

75	1	8.399949	-0.208037	-0.008796
76	1	7.970824	-1.051907	-1.503560
77	6	7.734952	-2.872179	0.513150
78	1	7.984612	-3.383008	-0.427800
79	1	8.674674	-2.550042	0.981983
80	1	7.257626	-3.605545	1.176469
81	6	1.954025	-3.215464	0.577893
82	1	1.969605	-2.644236	1.516442
83	6	0.654621	-2.876481	-0.146845
84	1	0.470886	-3.547154	-0.998095
85	1	-0.191968	-2.993370	0.543031
86	1	0.648428	-1.848483	-0.528168
87	6	1.948775	-4.700265	0.948795
88	1	1.050037	-4.942079	1.531990
89	1	1.941811	-5.324211	0.043144
90	1	2.826871	-4.981884	1.543404
91	5	-3.570401	0.020412	-0.032033
92	6	-4.243384	-1.312157	-0.701972
93	6	-4.341034	-1.477500	-2.089673
94	6	-4.903964	-2.277345	0.068836
95	6	-5.028682	-2.541744	-2.669380
96	1	-3.872576	-0.747601	-2.753700
97	6	-5.590141	-3.348094	-0.501147
98	1	-4.893747	-2.196225	1.158019
99	6	-5.656470	-3.497658	-1.880479
100	1	-6.187636	-4.331936	-2.329514
101	6	-4.806890	1.094873	-0.003444
102	6	-5.730068	1.143888	1.048543
103	6	-5.095530	1.914822	-1.102033
104	6	-6.854588	1.967366	1.016560
105	1	-5.574022	0.515550	1.928842
106	6	-6.217727	2.738565	-1.144214
107	1	-4.426770	1.914017	-1.965906
108	6	-7.110707	2.780068	-0.080604
109	1	-7.984201	3.425254	-0.110626
110	6	-2.941562	-0.259075	1.453357
111	6	-2.829911	0.758855	2.405072
112	6	-2.338674	-1.482401	1.791186
113	6	-2.177539	0.573327	3.625262
114	1	-3.261099	1.740418	2.196325
115	6	-1.693805	-1.678274	3.008430
116	1	-2.382347	-2.308092	1.079658
117	6	-1.608390	-0.649843	3.944530
118	1	-1.101413	-0.803519	4.895283
119	6	-2.287863	0.590156	-0.877530
120	6	-1.430420	-0.239197	-1.614398
121	6	-1.917153	1.938595	-0.797562
122	6	-0.296743	0.256252	-2.255239
123	1	-1.659149	-1.302133	-1.703598
124	6	-0.775248	2.440005	-1.418935

125	1	-2.540625	2.628672	-0.226981
126	6	0.046490	1.602493	-2.163136
127	1	0.936707	1.982596	-2.665728
128	6	-5.045265	-2.640231	-4.161014
129	6	-6.215547	-4.348490	0.416754
130	6	-7.768812	1.956275	2.199474
131	6	-6.410794	3.609177	-2.343936
132	6	-1.024309	-2.972262	3.346951
133	6	-2.124187	1.727903	4.572409
134	6	-0.488844	3.906864	-1.348454
135	6	0.596572	-0.633771	-3.057949
136	9	-8.235921	0.724035	2.451865
137	9	-7.135073	2.354167	3.313907
138	9	-8.829783	2.755891	2.042150
139	9	-7.606139	4.210702	-2.360216
140	9	-5.481058	4.577233	-2.399473
141	9	-6.298567	2.913868	-3.485245
142	9	-5.464721	-1.498918	-4.727280
143	9	-5.837959	-3.620986	-4.607845
144	9	-3.816290	-2.872822	-4.650486
145	9	-6.946286	-5.262664	-0.231004
146	9	-5.284013	-5.013578	1.119608
147	9	-7.017766	-3.761659	1.317497
148	9	0.318315	-2.837345	3.375112
149	9	-1.293084	-3.948074	2.471697
150	9	-1.377665	-3.412972	4.560835
151	9	-1.327007	1.500609	5.622374
152	9	-1.662402	2.834488	3.958483
153	9	-3.335313	2.040484	5.049565
154	9	-1.122202	4.583832	-2.315306
155	9	0.822176	4.174173	-1.487148
156	9	-0.873829	4.442459	-0.183048
157	9	0.076851	-1.843585	-3.275060
158	9	0.892543	-0.098360	-4.251907
159	9	1.783494	-0.826227	-2.439653

Table S6. *t*BuXPhosAu(η^2-phenylacetylene)BF_4 complex **8c**.



Center	Atomic	Cartesian Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	15	0.297605	2.070894	0.125488
2	6	0.853979	2.670720	1.835029
3	6	1.266091	2.935933	-1.274485
4	79	0.612061	-0.252583	-0.048170
5	6	3.493681	-1.483878	-2.613470
6	6	4.728711	-1.006541	-3.029487
7	6	5.720635	-0.729273	-2.089589
8	6	5.485089	-0.935205	-0.730636
9	6	4.256105	-1.414639	-0.299131
10	6	3.255849	-1.686020	-1.246031
11	1	2.703118	-1.694202	-3.332861
12	1	4.919279	-0.845973	-4.088539
13	1	6.686123	-0.350859	-2.420434
14	1	6.265233	-0.720415	-0.003258
15	1	4.035062	-1.576178	0.755003
16	6	1.970935	-2.116730	-0.797532
17	6	0.858839	-2.456490	-0.391649
18	1	0.007146	-3.031930	-0.070778
19	6	-1.477548	2.514134	-0.096578
20	6	-1.799524	3.881285	-0.131296
21	6	-2.513056	1.570198	-0.299033
22	6	-3.089747	4.334925	-0.362088
23	1	-1.018605	4.620891	0.023414
24	6	-3.808927	2.054937	-0.536258
25	6	-4.104965	3.409904	-0.570307
26	1	-3.294764	5.403087	-0.382066
27	1	-4.604351	1.327121	-0.699160
28	1	-5.124850	3.738791	-0.759736
29	6	1.585628	4.412577	-1.032297
30	1	2.129164	4.788617	-1.911459
31	1	0.689986	5.036232	-0.927487
32	1	2.232577	4.578194	-0.163281
33	6	2.582849	2.177015	-1.483906
34	1	3.211055	2.148173	-0.585981
35	1	2.409193	1.140576	-1.807853
36	1	3.155220	2.682752	-2.275789
37	6	0.449967	2.819334	-2.561195

38	1	1.054074	3.209837	-3.393197
39	1	0.205833	1.775663	-2.795180
40	1	-0.482925	3.396405	-2.526963
41	6	0.427422	4.094528	2.185138
42	1	0.823621	4.330665	3.183518
43	1	0.819903	4.849409	1.493600
44	1	-0.663841	4.195391	2.236352
45	6	2.375208	2.542887	1.932558
46	1	2.663236	2.705885	2.981782
47	1	2.724284	1.540173	1.656804
48	1	2.903936	3.293902	1.333024
49	6	0.218622	1.714701	2.844422
50	1	0.563391	0.681128	2.712676
51	1	0.501643	2.036582	3.857993
52	1	-0.877662	1.738006	2.788040
53	6	-2.412925	0.071017	-0.289020
54	6	-2.272682	-0.634910	-1.504103
55	6	-2.690626	-0.641832	0.900900
56	6	-2.393595	-2.026590	-1.504663
57	6	-2.770651	-2.033125	0.850161
58	6	-2.635103	-2.748324	-0.339839
59	1	-2.294445	-2.559116	-2.451664
60	1	-2.982030	-2.586965	1.767616
61	6	-3.015586	0.063724	2.203110
62	1	-2.673269	1.106233	2.120013
63	6	-2.835628	-4.248729	-0.334158
64	1	-2.436603	-4.624836	0.623308
65	6	-2.122869	-4.980744	-1.464334
66	1	-1.052113	-4.739551	-1.513075
67	1	-2.216381	-6.065586	-1.328187
68	1	-2.565339	-4.739537	-2.441387
69	6	-4.332846	-4.562766	-0.372049
70	1	-4.508523	-5.645838	-0.324513
71	1	-4.866611	-4.091122	0.463225
72	1	-4.772735	-4.187293	-1.308012
73	6	-2.338606	-0.561105	3.420752
74	1	-1.265819	-0.728248	3.261510
75	1	-2.463993	0.094983	4.293221
76	1	-2.794678	-1.526954	3.680238
77	6	-4.531399	0.106381	2.410091
78	1	-4.941353	-0.911553	2.481503
79	1	-4.777905	0.633992	3.341631
80	1	-5.042967	0.617956	1.584115
81	6	-2.050059	0.069316	-2.827597
82	1	-1.861130	1.133211	-2.621254
83	6	-0.838562	-0.480896	-3.579446
84	1	-0.993443	-1.523122	-3.891718
85	1	-0.649057	0.108670	-4.487368
86	1	0.068573	-0.454264	-2.955267
87	6	-3.301715	-0.007466	-3.701619

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   88          1                -3.147874    0.532025   -4.645987
   89          1                -3.547276   -1.050248   -3.947802
   90          1                -4.172599    0.430706   -3.196619
   91          5                 2.089686   -1.750394    2.933176
   92          9                 2.189244   -1.958502    4.299429
   93          9                 0.723024   -1.681238    2.567884
   94          9                 2.705076   -0.538250    2.584078
   95          9                 2.704682   -2.789610    2.232308
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