Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Supporting Information

A silver-free system for the direct C–H auration of arenes and heteroarenes from gold chloride complexes

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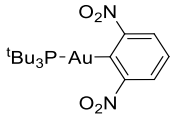
General Information

All reactions were carried out in disposable vials using reagents obtained from commercial sources and used without further purification. NaOH pellets were ground in an agate mortar immediately before use. Column chromatography was carried out on silica gel, particle size 40-63 μm, using flash techniques. Analytical thin layer chromatography was performed on pre-coated silica gel F254 plates with visualisation under UV light. Melting points were obtained using a Gallenkamp hot stage apparatus and are uncorrected. IR spectra were recorded using a Bruker Tensor 37 FTIR machine, relevant bands are quoted in cm^{-1}. ^{1}H NMR spectra, recorded at 400 or 600 MHz, are referenced to the residual solvent peak at 7.26 ppm ($CDCl_3$), 3.31 ppm (CD_3OD) or 7.16 ppm (C_6D_6), and quoted in ppm to 2 decimal places with coupling constants (*J*) to the nearest 0.1 Hz. ^{13}C NMR spectra, recorded at 100 MHz or 151 MHz, are referenced to the solvent peak at 77.16 ppm ($CDCl_3$) or 128.06 ppm (C_6D_6) and quoted in ppm to 1 decimal place with coupling constants (*J*) to the nearest 0.1 Hz. ^{19}F $\{^{1}H\}$ NMR spectra were recorded at 376 or 565 MHz in $CDCl_3$ or C_6D_6 and quoted in ppm to 2 decimal places and with coupling constants (*J*) to the nearest 0.1 Hz. ^{31}P $\{^{1}H\}$ NMR spectra were recorded at 162 MHz in $CDCl_3$ and quoted in ppm to 1 decimal place and with coupling constants (*J*) to the nearest 0.1 Hz.

General procedure for the preparation of (hetero)aryl-gold compounds

A mixture of $[Au(PR_3)Cl]$ (R = ^{t}Bu, Et, Ph; 0.060 mmol), (hetero)arene (0.24 mmol) and base (NaOH or NaO^{t}Bu; 0.24 mmol) was dissolved in DMF or 1,4-dioxane (0.30 mL). The reaction mixture was stirred at the temperature and for the time indicated. The mixture was allowed to cool down to room temperature, CH_2Cl_2 (5 mL) was added, and the suspension was filtered through a plug of celite. Evaporation of the solvent under vacuum and purification by silica gel column chromatography afforded the corresponding (hetero)aryl-Au(I) complexes.

Characterisation data of (hetero)aryl-gold compounds

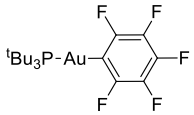


2,6-Dinitrophenyl(tri-tert-butylphosphine)gold(I) ***3aa***

The general procedure was applied with $[Au(P^{t}Bu_3)Cl]$ (26 mg, 0.060 mmol), 1,3-dinitrobenzene (40 mg, 0.24 mmol) and NaO^{t}Bu (23 mg, 0.24 mmol) in DMF at 75 °C for 5 h. Column chromatography (hexane/EtOAc 100:0 - 95:5) afforded the title product as a yellow solid (28 mg, 82%).

Spectroscopic data matched those previously reported.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.0, 1.1 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 1.56 (d, *J* = 13.3 Hz, 27H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, *J* = 93.4 Hz), 159.0 (d, *J* = 1.8 Hz), 127.6 (d, *J* = 2.9 Hz), 126.2, 39.1 (d, *J* = 17.0 Hz), 32.5 (d, *J* = 4.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 91.4. Anal. Calcd for $C_{18}H_{30}AuN_2O_4P$: C, 38.27; H, 5.34; N, 4.95. Found: C, 38.24; H, 5.06; N, 4.94.

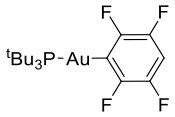


Pentafluorophenyl(tri-tert-butylphosphine)gold(I) ***3ab***

The general procedure was applied with [Au(P^{t}Bu$_3$)Cl] (30 mg, 0.070 mmol), pentafluorobenzene (31 µL, 0.28 mmol) and NaO^{t}Bu (27 mg, 0.28 mmol) in DMF at 50°C for 15 h. Column chromatography (hexane/DCM 100:0 - 90:10) afforded the title product as a white solid (36 mg, 79%).

Spectroscopic data matched those previously reported.[1]

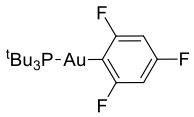
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.56 (d, *J* = 13.3 Hz, 27H). ^{31}C NMR (151 MHz, $CDCl_3$) δ (C *ipso* to Au not observed), 148.7 (dm, *J* = 226.7 Hz), 138.9 (dm, *J* = 236.3 Hz), 137.4 (dm, *J* = 251.5 Hz), 39.5 (d, *J* = 16.7 Hz), 32.6 (d, *J* = 3.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 92.1 (app. quint., *J* = 6.8 Hz). ^{19}F NMR (367 MHz, $CDCl_3$) δ –116.65 - –116.82 (m), –159.56 (t, *J* = 19.7 Hz), –162.60 - –162.80 (m). Anal. Calcd for $C_{18}H_{27}AuF_5P$: C, 38.17; H, 4.81. Found: C, 38.60; H, 4.57. Accurate elemental analysis was not obtained due to product decomposition.



2,3,5,6-Tetrafluorophenyl(tri-tert-butylphosphine)gold(I) ***3ac***

The general procedure was applied with [Au(P^{t}Bu$_3$)Cl] (26 mg, 0.060 mmol), 1,2,4,5-tetrafluorobenzene (27 µL, 0.24 mmol) and NaOH (10 mg, 0.24 mmol) in 1,4-dioxane at 50 °C for 15 h. Column chromatography (hexane/EtOAc 100:0 - 95:5) afforded the title product as a white solid (32 mg, 96%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.68 (tt, *J* = 9.3, 6.8 Hz, 1H), 1.57 (d, *J* = 13.2 Hz, 27H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (C *ipso* to Au not observed), 149.0 (dm, *J* = 225.6 Hz), 146.1 (dm, *J* = 249.6 Hz), 103.0 (t, *J* = 23.5 Hz), 39.5 (d, *J* = 16.7 Hz), 32.6 (d, *J* = 4.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 92.1 (app. quint, *J* = 6.8 Hz). ^{19}F NMR (367 MHz, $CDCl_3$) δ –118.72 - –118.88 (m), –140.68 - –140.80 (m). IR (ATR) 2953, 1452, 1189, 1173, 888, 705. m.p. 120-122 °C. HRMS (EI) *m/z* calcd. $C_{18}H_{28}AuF_4P$: $[M]^+$ 548.1525; found: $[M]^+$ 548.1515. Anal. Calcd for $C_{18}H_{28}AuF_4P$: C, 39.43; H, 5.15. Found: C, 39.60; H, 4.91.

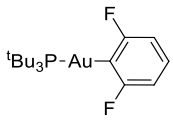


2,4,6-Trifluorophenyl(tri-tert-butylphosphine)gold(I) ***3ad***

The general procedure was applied with [Au(P^{t}Bu$_3$)Cl] (30 mg, 0.070 mmol), 1,3,5-trifluorobenzene (29 µL, 0.28 mmol) and NaO^{t}Bu (27 mg, 0.28 mmol) in DMF at 50 °C for 3 h. Removal of starting material *in vacuo* afforded the title product as a white solid (36 mg, 98%).

Spectroscopic data matched those previously reported.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 - 6.55 (m, 2H), 1.56 (d, *J* = 13.1 Hz, 27H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (C *ipso* to Au not observed), 168.4 (dddd, *J* = 230.7, 29.1, 14.8, 3.6 Hz), 161.8 (dt, *J* = 242.3, 14.1 Hz), 98.6 (app. ddt, J = 36.1, 24.2, 3.7 Hz), 39.4 (d, *J* = 16.4 Hz), 32.6 (d, *J* = 4.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 92.3 (t, *J* = 6.3 Hz). ^{19}F NMR (367 MHz, $CDCl_3$) δ –86.14 (t, *J* = 6.6 Hz), –114.97 - –115.02 (m). Anal. Calcd for $C_{18}H_{29}AuF_3P$: C, 40.76; H, 5.51. Found: C, 41.18; H, 5.01. Accurate elemental analysis was not obtained due to product decomposition.

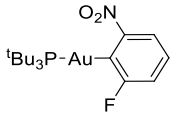


2,6-Difluorophenyl(tri-tert-butylphosphine)gold(I) ***3ae***

The general procedure was applied with [Au(P^{t}Bu$_3$)Cl] (30 mg, 0.070 mmol), 1,3-difluorobenzene (27 µL, 0.28 mmol) and NaO^{t}Bu (27 mg, 0.28 mmol) in DMF at 50 °C for 24 h. Removal of starting material *in vacuo* afforded the title product as a white solid (33 mg, 94%).

Spectroscopic data matched those previously reported.[1]

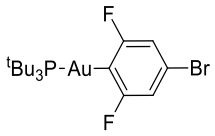
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05-6.98 (m, 1H), 6.85-6.81 (m, 2H), 1.57 (d, *J* = 13.0 Hz, 27H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (C *ipso* to Au not observed), 168.9 (ddd, *J* = 230.8, 24.5, 3.8 Hz), 127.5 (t, *J* = 8.4 Hz), 109.9 (app. dt, *J* = 30.8, 2.9 Hz), 39.4 (d, *J* = 16.0 Hz), 32.5 (d, *J* = 4.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 92.5 (t, *J* = 6.5 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ –88.30 (d, *J* = 6.5 Hz). Anal. Calcd for $C_{18}H_{30}AuF_2P$: C, 42.19; H, 5.90. Found: C, 41.44; H, 5.56. Accurate elemental analysis was not obtained due to product decomposition.



2-Fluoro-6-nitrophenyl(tri-tert-butylphosphine)gold(I) ***3af***

The general procedure was applied with [Au(P^{t}Bu$_3$)Cl] (26 mg, 0.060 mmol), 1-fluoro-3-nitrobenzene (26 µL, 0.24 mmol) and NaOH (10 mg, 0.24 mmol) in DMF at 50 °C for 15 h. Column chromatography (hexane/EtOAc 100:0 - 95:5) afforded the title product as a pale yellow solid (28 mg, 90%).

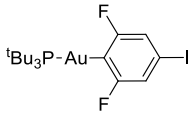
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.9 Hz, 1H), 7.25-7.21 (m, 1H), 7.17 (app. td, *J* = 7.9, 6.1 Hz, 1H), 1.58 (d, *J* = 13.1 Hz, 27 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2 (dd, *J* = 230.6 Hz, 3.9 Hz), 158.2 (d, *J* = 21.7 Hz), 153.9 (dd, *J* = 93.7, 68.6 Hz), 126.9 (d, *J* = 7.0 Hz), 119.8 (app t, *J* = 3.0 Hz), 118.8 (dd, *J* = 32.3, 2.3 Hz), 39.3 (d, *J* = 16.7 Hz), 32.6 (d, *J* = 4.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 91.9 (d, *J* = 3.7 Hz). ^{19}F NMR (367 MHz, $CDCl_3$) δ –83.63 (d, *J* = 3.7 Hz). IR (ATR) 2954, 1510, 1338, 1213, 798. m.p. 160-162 °C. HRMS (EI) *m/z* calcd. $C_{18}H_{30}AuFNO_2P$: $[M]^+$ 539.1656; found: $[M]^+$ 539.1645. Anal. Calcd for $C_{18}H_{30}AuFNO_2P$: C, 40.08; H, 5.61; N, 2.60. Found: C, 37.88; H, 4.09; N, 2.27. Accurate elemental analysis was not obtained due to product decomposition.



4-Bromo-2,6-difluorophenyl(tri-tert-butylphosphine)gold(I) ***3ag***

The general procedure was applied with [Au(P^{t}Bu$_3$)Cl] (26 mg, 0.060 mmol), 1-bromo-3,5-difluorobenzene (28 µL, 0.24 mmol) and NaO^{t}Bu (23 mg, 0.24 mmol) in DMF at 35 °C for 15 h. Column chromatography (hexane/EtOAc 100:0 - 95:5) afforded the title product as a white solid (29 mg, 82%) in a 99:1 mixture with its C3 regioisomer.

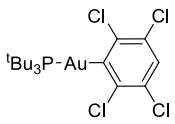
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (dd, *J* = 4.1, 1.6 Hz, 2H), 1.56 (d, *J* = 13.1 Hz, 27H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7 (ddd, *J* = 234.0, 26.5, 3.7 Hz), 142.2 (dt, *J* = 93.8, 62.1 Hz), 118.3 (t, *J* = 11.2 Hz), 113.7 (app. dt, *J* = 35.3, 3.3 Hz), 39.4 (d, *J* = 16.4 Hz), 32.6 (d, *J* = 4.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 92.3 (t, *J* = 6.3 Hz). ^{19}F NMR (367 MHz, $CDCl_3$) δ –86.64 (d, *J* = 6.3 Hz). IR (ATR) 2997, 1579, 1392, 1171, 983, 834. m.p. 120-122 °C. HRMS (EI) *m/z* calcd. $C_{18}H_{29}AuBrF_2P$: $[M]^+$ 590.0817; found: $[M]^+$ 590.0808. Anal. Calcd for $C_{18}H_{29}AuBrF_2P$: C, 36.56; H, 4.94. Found: C, 36.31; H, 4.30. Accurate elemental analysis was not obtained due to product decomposition.



2,6-Difluoro-4-iodoophenyl(tri-tert-butylphosphine)gold(I) ***3ah***

The general procedure was applied with [Au(P^{t}Bu$_3$)Cl] (26 mg, 0.060 mmol), 3,5-difluoroiodobenzene (58 mg, 0.24 mmol) and NaO^{t}Bu (23 mg, 0.24 mmol) in DMF at 35 °C for 15 h. Column chromatography (hexane/EtOAc 100:0 - 95:5) afforded the title product as a white solid (28 mg, 73%) in a 99:1 mixture with its C3 regioisomer.

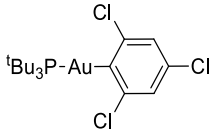
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 4.0, 1.5 Hz, 2H), 1.56 (d, *J* = 13.1 Hz, 27H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5 (ddd, *J* = 235.2, 25.6, 3.6 Hz), 143.3 (dt, *J* = 93.9, 61.9 Hz), 119.4 (app. dt, *J* = 34.5, 3.3 Hz), 88.2 (t, *J* = 9.4 Hz), 39.4 (d, *J* = 16.2 Hz), 32.6 (d, *J* = 4.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 92.4 (t, *J* = 6.3 Hz). ^{19}F NMR (367 MHz, $CDCl_3$) δ –86.70 (d, *J* = 6.3 Hz). IR (ATR) 2997, 1572, 1391, 1175, 977, 810. m.p. 158-160 °C. HRMS (EI) *m/z* calcd. $C_{18}H_{29}AuF_2IP$: $[M]^+$ 638.0680; found: $[M]^+$ 638.0675. Anal. Calcd for $C_{18}H_{29}AuF_2IP$: C, 33.87; H, 4.58. Found: C, 33.79; H, 4.35.



2,3,5,6-Tetrachlorophenyl(tri-tert-butylphosphine)gold(I) ***3ai***

The general procedure was applied with [Au(P^{t}Bu$_3$)Cl] (26 mg, 0.060 mmol), 1,2,4,5-tetrachlorobenzene (52 mg, 0.24 mmol) and NaO^{t}Bu (23 mg, 0.24 mmol) in DMF at 50 °C for 15 h. Column chromatography (hexane/EtOAc 100:0 - 95:5) afforded the title product as a white solid (36 mg, 96%).

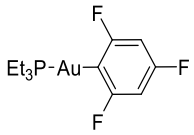
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 1.57 (d, *J* = 13.1 Hz, 27H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9 (d, *J* = 97.7 Hz), 138.4 (d, *J* = 4.1 Hz), 130.9 (d, *J* = 7.1 Hz), 128.4, 39.5 (d, *J* = 16.3 Hz), 32.5 (d *J* = 4.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 90.4. IR (ATR) 2955, 1355, 1149, 1055, 854. m.p. 202-204 °C. HRMS (EI) *m/z* calcd. $C_{18}H_{28}AuCl_4P$: $[M]^+$ 614.0315; found: $[M]^+$ 614.0296. Anal. Calcd for $C_{18}H_{28}AuCl_4P$: C, 35.20; H, 4.60. Found: C, 35.40; H, 4.32.



2,4,6-Trichlorophenyl(tri-tert-butylphosphine)gold(I) ***3aj***

The general procedure was applied with [Au(P^{t}Bu$_3$)Cl] (26 mg, 0.060 mmol), 1,3,5-trichlorobenzene (44 mg, 0.24 mmol) and NaO^{t}Bu (23 mg, 0.24 mmol) in DMF at 75 °C for 6 h. Column chromatography (hexane/EtOAc 100:0 - 95:5) afforded the title product as a white solid (29 mg, 83%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 1.2 Hz, 2H), 1.56 (d, *J* = 13.1 Hz, 27H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0 (d, *J* = 99.5 Hz), 143.7 (d, *J* = 3.6 Hz), 131.4, 125.9 (d, *J* = 3.8 Hz), 39.4 (d, *J* = 15.9 Hz), 32.6 (d, *J* = 4.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 90.9 (s). IR (ATR) 2954, 1172, 903, 726. m.p. 204-208 °C. HRMS (EI) *m/z* calcd. $C_{18}H_{29}AuCl_3P$: $[M]^+$ 578.0731; found: $[M]^+$ 578.0717. Anal. Calcd for $C_{18}H_{29}AuCl_3P$: C, 37.29; H, 5.04. Found: C, 37.16; H, 5.05.

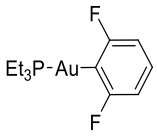


2,4,6-Trifluorophenyl(triethylphosphine)gold(I) ***3bd***

The general procedure was applied with [Au(PEt$_3$)Cl] (21 mg, 0.060 mmol), 1,3,5-trifluorobenzene (25 µL, 0.24 mmol) and NaO^{t}Bu (23 mg, 0.24 mmol) in DMF at 50 °C for 15 h. Column chromatography (hexane/EtOAc 100:0 - 95:5) afforded the title product as a colourless oil (25 mg, 93%).

Spectroscopic data matched those previously reported.[1]

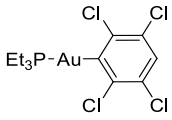
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 – 6.55 (m, 2H), 1.87 (dq, *J* = 9.3, 7.7 Hz, 6H), 1.26 (dt, *J* = 17.9, 7.7 Hz, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (C *ipso* to Au not observed), 168.5 (ddd, 231.3, 28.7, 15.0 Hz) 161.9 (app. dt, 242.7, 14.3 Hz), 98.7 (ddd, 36.2, 24.1, 4.5 Hz), 18.2 (d, *J* = 31.6 Hz), 9.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 40.4 (t, *J* = 7.9 Hz). ^{19}F NMR (367 MHz, $CDCl_3$) δ –86.05 (t, *J* = 7.4 Hz), –114.31 - –114.34 (m).



2,6-Difluorophenyl(triethylphosphine)gold(I) ***3be***

The general procedure was applied with [Au(PEt$_3$)Cl] (21 mg, 0.060 mmol), 1,3-difluorobenzene (24 µL, 0.24 mmol) and NaO^{t}Bu (23 mg, 0.24 mmol) in DMF at 50 °C 15 h. Column chromatography (hexane/EtOAc 100:0 - 95:5) afforded the title product as a colourless oil (24 mg, 90%).

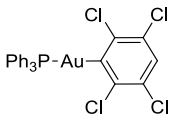
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06-6.99 (m, 1H), 6.86-6.82 (m, 2H), 1.88 (dq, *J* = 9.2, 7.7 Hz, 6H), 1.27 (dt, *J* = 17.8, 7.7 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8 (ddd, *J* = 231.1, 24.4, 3.9 Hz), 142.5 (dt, *J* = 102.6, 60.24 Hz), 127.8 (t, *J* = 8.5 Hz), 109.9 (app dt, *J* = 30.9, 3.1 Hz), 18.2 (d, *J* = 31.0 Hz), 9.2. ^{31}P NMR (162 MHz, $CDCl_3$) 40.6 (t, *J* = 8.1 Hz). ^{19}F NMR δ (376 MHz, $CDCl_3$) –88.28 (d, *J* = 8.1 Hz). IR (ATR) 2967, 1433, 1200, 952, 770. HRMS (EI) *m/z* calcd. $C_{12}H_{18}AuF_2P$: $[M]^+$ 428.0772; found: $[M]^+$ 428.0771.



2,3,5,6-Tetrachlorophenyl(triethylphosphine)gold(I) ***3bi***

The general procedure was applied with [Au(PEt$_3$)Cl] (21 mg, 0.060 mmol), 1,2,4,5-tetrachlorobenzene (52 mg, 0.24 mmol) and NaO^{t}Bu (23 mg, 0.24 mmol) in DMF at 50 °C for 15 h. Column chromatography (hexane/EtOAc 100:0 - 95:5) afforded the title product as a white solid (29 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 1.87 (dq, *J* = 9.4, 7.7 Hz, 6H), 1.28 (dt, J = 17.9, 7.7 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6 (d, *J* = 107.1 Hz), 138.4 (d, *J* = 3.7 Hz), 130.9 (d, *J* = 7.3 Hz), 128.6, 18.3 (d, *J* = 31.5 Hz), 9.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 37.9. IR (ATR) 2970, 1455, 1354, 1149, 1050, 765. m.p. 84-86 °C. HRMS (EI) *m/z* calcd. $C_{12}H_{16}AuCl_4P$: $[M]^+$ 529.9374; found: $[M]^+$ 529.9359. Anal. Calcd for $C_{12}H_{16}AuCl_4P$: C, 27.19; H, 3.04. Found: C, 27.11; H, 2.91.

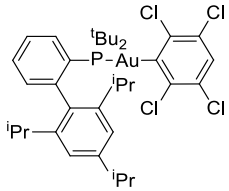


2,3,5,6-Tetrachlorophenyl(triphenylphosphine)gold(I) ***3ci***

The general procedure was applied with [Au(PPh$_3$)Cl] (30 mg, 0.060 mmol), 1,2,4,5 - tetrachlorobenzene (52 mg, 0.24 mmol) and NaO^{t}Bu (23 mg, 0.24 mmol) in DMF at 50 °C for 15 h. Column chromatography (hexane/EtOAc 100:0 - 95:5) afforded the title product as a white solid (36 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.59 (m, 6H), 7.55-7.46 (m, 9H), 7.27 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7 (d, *J* = 109.2 Hz), 138.4 (d, *J* = 4.3 Hz), 134.5 (d, *J* = 13.7 Hz), 131.7 (d, *J* = 2.3 Hz), 130.9 (d, *J* = 8.0 Hz), 130.0, 129.7 (d, *J* = 169.1 Hz), 129.3 (d, *J* = 11.3 Hz). ^{31}P NMR (162 MHz,

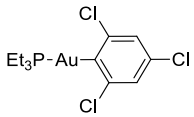
$CDCl_3$) δ 39.7. IR (ATR) 3056, 1436, 1100, 905, 730. m.p. 119-122 °C. HRMS (EI) *m/z* calcd. $C_{24}H_{16}AuCl_4P$: $[M]^+$ 671.9404. found: $[M]^+$ 671.9398. Anal. Calcd for $C_{24}H_{16}AuCl_4P$: C, 42.76; H, 2.39. Found: C, 42.41; H, 2.05.



2,3,5,6-Tetrachlorophenyl(ᵗBuXPhos)gold(I) ***3di***

The general procedure was applied with [Au(ᵗBuXPhos)Cl] (39 mg, 0.060 mmol), 1,2,4,5-tetrachlorobenzene (52 mg, 0.24 mmol) and NaOᵗBu (23 mg, 0.24 mmol) in DMF at 50 °C for 15 h. Column chromatography (hexane/EtOAc 100:0 - 95:5) afforded the title product as a white solid (22 mg, 42%).

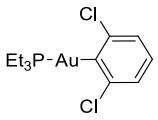
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (app. td, *J* = 7.3, 1.5 Hz, 1H), 7.50-7.43 (m, 2H), 7.34-7.30 (m, 1H), 7.14 (s, 1H), 6.98 (s, 2H), 2.55-2.48 (m, 1H), 2.46-2.37 (m, 2H), 1.48 (d, *J* = 14.7 Hz, 18H), 1.35 (d, *J* = 6.8 Hz, 6H), 0.93 (d, *J* = 6.9 Hz, 6H), 0.90 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0 (d, *J* = 101.7 Hz), 148.6 (d, *J* = 16.1 Hz), 148.4, 145.7, 137.9 (d, *J* = 4.4 Hz), 135.6 (d, *J* = 5.1 Hz), 135.4, 134.6 (d, *J* = 8.1 Hz), 130.3 (d, *J* = 7.3 Hz), 129.7 (d, *J* = 33.9 Hz), 129.7 (d, *J* = 2.2 Hz), 127.5, 126.1 (d, *J* = 5.9 Hz), 121.7, 38.4 (d, *J* = 21.2 Hz), 33.3, 31.3 (d, *J* = 6.6 Hz), 30.9, 26.6, 23.2, 22.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.5. IR (ATR) 2960, 1461, 1370, 1150, 1051, 911, 735. m.p. (decomposition above 240 °C). HRMS (EI) *m/z* calcd. $C_{35}H_{46}AuCl_4P$: $[M]^+$ 834.1751; found: $[M]^+$ 834.1744. Anal. Calcd for $C_{35}H_{46}AuCl_4P$: C, 50.25; H, 5.54. Found: C, 48.27; H, 4.49. Accurate elemental analysis was not obtained due to product decomposition.



2,4,6-Trichlorophenyl(triethylphosphine)gold(I) ***3bj***

The general procedure was applied with [Au(PEt_3)Cl] (21 mg, 0.060 mmol), 1,3,5-trichlorobenzene (44 mg, 0.24 mmol) and NaOᵗBu (23 mg, 0.24 mmol) in DMF at 50 °C 15 h. Column chromatography (hexane/EtOAc 100:0 - 95:5) afforded a colourless oil (25 mg, 84%).

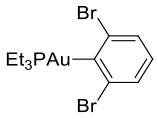
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 2H), 1.86 (dq, *J* = 9.4 7.6 Hz, 6H), 1.28 (dt, *J* = 17.8, 7.6 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8 (d, *J* = 108.9 Hz), 143.7 (d, *J* = 3.7 Hz), 131.7, 126.0 (d, *J* = 4.4. Hz), 18.3 (d, *J* = 31.3 Hz), 9.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.9. IR (ATR) 2966, 1524, 1348, 1038, 770. HRMS (EI) *m/z* calcd. $C_{12}H_{17}AuCl_3P$: $[M]^+$ 493.9793; found: $[M]^+$ 493.9782.



2,6-Dichlorophenyl(triethylphosphine)gold(I) ***3bk***

The general procedure was applied with [Au(PEt_3)Cl] (21 mg, 0.060 mmol), 1,3-dichlorobenzene (27 µL, 0.24 mmol) and NaO^tBu (23 mg, 0.24 mmol) in DMF at 50 °C for 15 h. Column chromatography (hexane/EtOAc 100:0 - 95:5) afforded the title product as a colourless oil (26 mg, 94%).

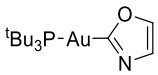
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.9 Hz, 2H), 6.91 (t, *J* = 7.9 Hz, 1H), 1.85 (dq, *J* = 9.3, 7.7 Hz, 6H), 1.28 (dt, J = 17.9, 7.7 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3 (d, *J* = 108.5 Hz), 143.7 (d, *J* = 3.7 Hz), 127.6, 126.0 (d, *J* = 3.9 Hz), 18.5 (d, *J* = 30.9 Hz), 9.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.0. IR (ATR) 2968, 1408, 1132, 1049, 756. HRMS (EI) *m/z* calcd. $C_{12}H_{18}AuCl_2P$: $[M]^+$ 460.0189; found: $[M]^+$ 460.0177. Anal. Calcd for $C_{12}H_{18}AuCl_2P$: C, 31.26; H, 3.93. Found: C, 30.10; H, 3.44. Accurate elemental analysis was not obtained due to product decomposition.



2,6-Dibromophenyl(triethylphosphine)gold(I) ***3bo***

The general procedure was applied with [Au(PEt_3)Cl] (35 mg, 0.10 mmol), 1,3-dibromobenzene (48 µL, 0.40 mmol) and NaOH (16 mg, 0.40 mmol) in 1,4-dioxane at 50 °C for 15 h. Column chromatography (hexane/DCM 100:0 - 60:40) afforded the title product as a white solid (36 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 7.8, 1.5 Hz, 2H), 6.69 (t, *J* = 7.8 Hz, 1H), 1.77 (dq, *J* = 9.4, 7.7 Hz, 6H), 1.21 (dt, *J* = 17.9, 7.7 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.6 (d, *J* = 109.4 Hz), 134.7 (d, *J* = 4.6 Hz), 129.4 (d, *J* = 4.4 Hz), 128.0, 18.4 (d, *J* = 31.1 Hz), 9.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.9. IR (ATR) 2961, 1528, 1400, 907, 733. m.p. 89-92 °C. HRMS (EI) *m/z* calcd. $C_{12}H_{18}AuBr_2P$: $[M]^+$ 547.9172; found: $[M]^+$ 547.9167. Anal. Calcd for $C_{12}H_{18}AuBr_2P$: C, 26.20; H, 3.30. Found: C, 26.62; H, 2.82. Accurate elemental analysis was not obtained due to product decomposition.

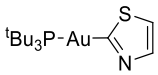


Oxazol-2-yl(tri-tert-butylphosphine)gold(I) ***5aa***

The general procedure was applied with [Au(P^tBu_3)Cl] (26 mg, 0.060 mmol), oxazole (16 µL, 0.24 mmol) and NaOH (10 mg, 0.24 mmol) in 1,4-dioxane at 35 °C for 15 h. Column chromatography (hexane/EtOAc 5:1 - 1:1 with 1% Et_3N) afforded the title product as a white solid (27 mg, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.12 (s, 1H), 1.55 (d, *J* = 13.2 Hz, 27H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8 (d, *J* = 137.4 Hz), 138.4 (d, *J* = 2.1 Hz), 124.8 (d, *J* = 5.1 Hz) 39.2 (d, *J* = 16.7 Hz), 32.6 (d, *J* = 4.5 Hz). ^{31}P NMR δ (162 MHz, $CDCl_3$) δ 90.7. IR (ATR) 2964, 1435, 1172, 1058, 732. m.p. 204-206 °C (decomposition). HRMS (EI) *m/z* calcd. $C_{15}H_{29}AuNOP$: $[M]^+$ 467.1645; found:

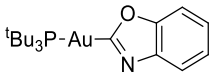
$[M]^+$ 467.1645. Anal. Calcd for $C_{15}H_{29}AuNOP$: C, 38.55; H, 6.25; N, 3.00. Found: C, 36.85; H, 5.67; N, 2.58. Accurate elemental analysis was not obtained due to product decomposition.



Thiazol-2-yl(tri-tert-butylphosphine)gold(I) ***5ab***

The general procedure was applied with [Au(P^{t}Bu$_3$)Cl] (11 mg, 0.025 mmol), thiazole (28 µL, 0.10 mmol) and NaOH (4 mg mg, 0.10 mmol) in 1,4-dioxane at 35 °C for 15 h. Column chromatography (hexane/EtOAc 5:1 - 1:1 with 1% Et_3N) afforded the title product as a white solid (12 mg, 95%).

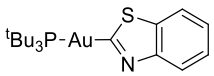
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 3.1 Hz, 1H), 7.51 (dd, *J* = 3.1, 1.1 Hz, 1H), 1.57 (d, *J* = 13.1 Hz, 27H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.4 (d, *J* = 132.8 Hz), 143.7 (d, *J* = 9.7 Hz), 117.6, 39.2 (d, *J* = 16.1 Hz), 32.6 (d, *J* = 4.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 90.8. IR (ATR) 2951, 1393, 1170, 918. m.p. 178-183 °C (decomposition). HRMS (EI) *m/z* calcd. $C_{15}H_{29}AuNPS$: $[M]^+$ 483.1424; found: $[M]^+$ 483.1404. Anal. Calcd for $C_{15}H_{29}AuNPS$: C, 37.27; H, 6.05; N, 2.90. Found: C, 37.23; H, 5.82; N, 2.62.



Benzoxazol-2-yl(tri-tert-butylphosphine)gold(I) ***5ac***

The general procedure was applied with [Au(P^{t}Bu$_3$)Cl] (30 mg, 0.070 mmol), benzoxazole (33 mg, 0.28 mmol) and NaOH (11 mg, 0.28 mmol) in 1,4-dioxane at 35 °C for 15 h. Removal of starting material *in vacuo* afforded the title product as a brown solid (33 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.65 (m, 1H), 7.48-7.45 (m, 1H), 7.21-7.19 (m, 2H), 1.59 (d, *J* = 13.3 Hz, 27H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.5 (d, *J* = 136.4 Hz), 151.4 (d, *J* = 2.2 Hz), 141.3 (d, *J* = 5.0 Hz), 123.2, 122.9, 119.0, 110.0, 39.3 (d, *J* = 16.9 Hz), 32.6 (d, *J* = 4.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 90.7. IR (ATR) 2954, 1441, 1171, 904, 727. m.p. 180-183 °C. HRMS (EI) *m/z* calcd. $C_{19}H_{31}AuNOP$: $[M]^+$ 517.1802; found: $[M]^+$ 517.1791. Anal. Calcd for $C_{19}H_{31}AuNOP$: C, 44.11; H, 6.04; N, 2.71. Found: C, 44.06; H, 5.56; N, 2.67. Accurate elemental analysis was not obtained due to product decomposition.

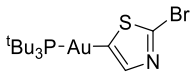


Benzothiazol-2-yl(tri-tert-butylphosphine)gold(I) ***5ad***

The general procedure was applied with [Au(P^{t}Bu$_3$)Cl] (26 mg, 0.060 mmol), benzothiazole (26 µL, 0.24 mmol) and NaOH (10 mg, 0.24 mmol) in 1,4-dioxane at 35 °C for 15 h. Column chromatography (hexane/EtOAc 5:1 - 1:1) afforded the title product as a white solid (18 mg, 55%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.42-7.38 (m, 1H), 7.32-7.28 (m, 1H), 1.61 (d, *J* = 13.1 Hz, 27H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.6 (d, *J* = 132.5 Hz),

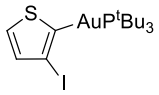
155.7 (d, *J* = 9.5 Hz), 135.3, 124.6, 123.2, 122.3, 121.3, 39.2, (d, *J* = 16.1 Hz), 32.6 (d, *J* = 4.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 90.7. IR (ATR) 2971, 1400, 1172, 900, 761. m.p. 190-193 °C (decomposition). HRMS (EI) *m/z* calcd. $C_{19}H_{31}AuNPS$: $[M]^+$ 533.1573; found: $[M]^+$ 533.1569. Anal. Calcd for $C_{19}H_{31}AuNPS$: C, 42.78; H, 5.86; N, 2.63. Found: C, 42.60; H, 5.64; N, 2.56.



5-Bromothiazol-2-yl(tri-tert-butylphosphine)gold(I) ***5ae***

The general procedure was applied with [Au(P^{t}Bu$_3$)Cl] (26 mg, 0.060 mmol), 2-bromothiazole (22 µL, 0.24 mmol) and NaOH (10 mg, 0.24 mmol) in 1,4-dioxane at 50 °C for 15 h. Column chromatography (hexane/EtOAc 5:1 - 1:1 with 1% Et_3N) afforded the title product as a white solid (27 mg, 80%).

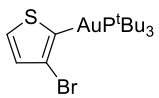
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 1.6 Hz, 1H), 1.55 (d, *J* = 13.2 Hz, 27H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9 (d, *J* = 111.2 Hz), 146.7 (d, *J* = 2.2 Hz), 136.7 (d, *J* = 5.9 Hz), 39.3 (d, *J* = 16.8 Hz), 32.6 (d, *J* = 4.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 92.2. IR (ATR) 3014, 1468, 1173, 994. m.p. 130-134 °C (decomposition). HRMS (EI) *m/z* calcd. $C_{15}H_{28}AuBrNPS$: $[M]^+$ 561.0522; found: $[M]^+$ 561.0522. Anal. Calcd for $C_{15}H_{28}AuBrNPS$: C, 32.04; H, 5.02; N, 2.49. Found: C, 31.86; H, 4.68; N, 2.46.



3-Iodothiophen-2-yl(tri-tert-butylphosphine)gold(I) ***5ag***

The general procedure was applied with [Au(P^{t}Bu$_3$)Cl] (43 mg, 0.10 mmol), 3-iodothiophene (41 µL, 0.40 mmol) and NaOH (16 mg, 0.40 mmol) in 1,4-dioxane at 50 °C for 15 h. Removal of starting material *in vacuo* afforded the title product as a white solid (58 mg, 95%) in a 97:3 mixture with its C5 regioisomer.

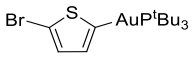
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 4.7, 0.9 Hz, 1H), 7.31 (dd, *J* = 4.7, 2.0 Hz, 1H), 1.58 (d, *J* = 13.1 Hz, 27H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1 (d, *J* = 112.7 Hz), 135.0 (d, *J* = 5.5 Hz), 128.8 (d, *J* = 3.1 Hz), 85.4, 39.3 (d, *J* = 16.2 Hz), 32.6 (d, *J* = 4.5). ^{31}P NMR (162 MHz, $CDCl_3$) δ 91.5. IR (ATR) 2949, 1457, 1391, 1170, 841, 696. m.p. 164-168 °C. HRMS (EI) *m/z* calcd. $C_{16}H_{29}AuIPS$: $[M]^+$ 608.0432; found: $[M]^+$ 608.0422. Anal. Calcd for $C_{16}H_{29}AuIPS$: C, 31.59; H, 4.81. Found: C, 31.62; H, 4.55.



3-Bromothiophen-2-yl(tri-tert-butylphosphine)gold(I) ***5ah***

The general procedure was applied with [Au(P^{t}Bu$_3$)Cl] (43 mg, 0.10 mmol), 3-bromothiophene (37 µL, 0.40 mmol) and NaOH (16 mg, 0.40 mmol) in 1,4-dioxane at 50 °C for 15 h. Removal of starting material *in vacuo* afforded the title product as a white solid (53 mg, 94%) in a 97:3 mixture with its C5 regioisomer.

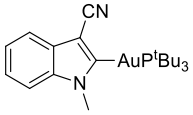
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 4.8, 2.1 Hz 1H), 7.24 (dd, *J* = 4.8, 1.0 Hz, 1H), 1.57 (d, *J* = 13.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6 (d, *J* = 111.5 Hz), 130.2 (d, *J* = 5.2 Hz), 128.7 (d, *J* = 3.2 Hz), 115.9, 39.3 (d, *J* = 16.3 Hz, 27H), 32.6 (d, *J* = 4.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 91.8. IR (ATR) 2951, 1469, 1171, 844, 700. m.p. 182-184 °C. HRMS (EI) *m/z* calcd. $C_{16}H_{29}AuBrPS$: $[M]^+$ 560.0571; found: $[M]^+$ 560.0563. Anal. Calcd for $C_{16}H_{29}AuBrPS$: C, 34.24; H, 5.21. Found: C, 34.28; H, 4.99.



5-Bromothiophen-2-yl(tri-tert-butylphosphine)gold(I) ***5ai***

The general procedure was applied with [Au(P^{t}Bu$_3$)Cl] (43 mg, 0.10 mmol), 2-bromothiophene (39 µL, 0.40 mmol) and NaOH (16 mg, 0.40 mmol) in 1,4-dioxane at 50 °C for 24 h. Removal of starting material *in vacuo* afforded the title product as a white solid (52 mg, 92%) in a 99:1 mixture with its C4 regioisomer.

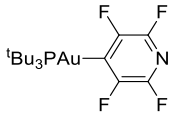
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 3.2, 1.3 Hz, 1H), 6.81 (app t, *J* = 3.2 Hz, 1H), 1.55 (d, *J* = 13.0 Hz, 27H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6 (d, *J* = 114.1Hz), 133.3, 130.2 (d, *J* = 5.3 Hz). 112.8 (d, *J* = 5.0 Hz), 39.1 (d, *J* = 16.0 Hz), 32.6 (d, *J* = 4.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 92.0. IR (ATR) 2948, 1481, 1170 1391, 1170, 784. m.p. 72-75 °C. HRMS (EI) *m/z* calcd. $C_{16}H_{29}AuBrPS$: $[M]^+$ 560.0571; found: $[M]^+$ 560.0569. Anal. Calcd for $C_{16}H_{29}AuBrPS$: C, 34.24; H, 5.21. Found: C, 34.01; H, 4.84.



3-Cyano-1-methylindol-2-yl(tri-tert-butylphosphine)gold(I) ***5aj***

The general procedure was applied with [Au(P^{t}Bu$_3$)Cl] (43 mg, 0.10 mmol), 1-methylindole-3-carbonitrile (62 mg, 0.40 mmol) and NaOH (16 mg, 0.40 mmol) in 1,4-dioxane at 50 °C for 15 h. Column chromatography (hexane/EtOAc 50:50 - 30:70) afforded the title product as a white solid (49 mg, 88%).

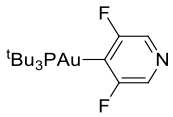
^{1}H NMR (400 MHz, CD_3OD) δ 7.47-7.44 (m, 1H), 7.35-7.32 (m, 1H), 7.17-7.10 (m, 2H), 3.91 (s, 3H), 1.63 (d, *J* = 13.3 Hz, 27H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6 (d, *J* = 110.0 Hz), 138.7 (d, *J* = 4.9 Hz), 129.7 (d, *J* = 3.8 Hz), 121.3, 121.0, 120.4, 118.5, 109.6, 92.8 (d, *J* = 2.8 Hz), 39.5 (d, *J* = 16.5 Hz), 36.3, 32.7 (d, *J* = 4.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 91.7. IR (ATR) 2947, 2200, 1470, 1173, 744. m.p. 198-199 °C. HRMS (EI) *m/z* calcd. $C_{22}H_{34}AuN_2P$: $[M]^+$ 554.2118; found: $[M]^+$ 554.2108. Anal. Calcd for $C_{22}H_{34}AuN_2P$: C, 47.66; H, 6.18; N, 5.05. Found: C, 46.88; H, 5.47; N, 4.95. Accurate elemental analysis was not obtained due to product decomposition.



2,3,5,6-Tetrafluoropyridin-4-yl(tri-tert-butylphosphine)gold(I) ***5ak***

The general procedure was applied with [Au(P^{t}Bu$_3$)Cl] (43 mg, 0.10 mmol), 2,3,5,6-tetrafluoropyridine (40 µL, 0.40 mmol) and NaOH (16 mg, 0.40 mmol) in 1,4-dioxane at 50 °C for 15 h. Column chromatography (hexane/EtOAc 100:0 - 95:5) afforded the title product as a white solid (42 mg, 77%).

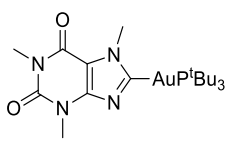
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.57 (d, *J* = 13.4 Hz, 27H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.7 (dt, *J* = 90.1, 56.3 Hz), 145.4 (dm, *J* = 237.0 Hz), 143.7 (dm, *J* = 246.51 Hz), 39.6 (d, *J* = 17.3 Hz), 32.6 (d, *J* = 4.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 91.6 (app. quint, *J* = 5.6 Hz). ^{19}F NMR (367 MHz, $CDCl_3$) δ –96.97 (m),–122.57 (app t, *J* = 25.1 Hz). IR (ATR) 2955, 1621, 1421, 1202, 918. m.p. 147-150 °C. HRMS (EI) *m/z* calcd. $C_{17}H_{27}AuF_4NP$: $[M]^+$ 549.1476; found: $[M]^+$ 549.1473. Anal. Calcd for $C_{17}H_{27}AuF_4NP$: C, 37.17; H, 4.95; N, 2.55. Found: C, 37.10; H, 4.53; N, 2.37. Accurate elemental analysis was not obtained due to product decomposition.



3,5-Difluoropyridin-4-yl(tri-tert-butylphosphine)gold(I) ***5al***

The general procedure was applied with [Au(P^{t}Bu$_3$)Cl] (43 mg, 0.10 mmol), 3,5-difluoropyridine (37 µL, 0.40 mmol) and NaOH (16 mg, 0.40 mmol) in 1,4-dioxane at 50 °C for 15 h. Column chromatography (hexane/EtOAc 100:0 - 60:40) afforded the title product as a white solid (46 mg, 90%).

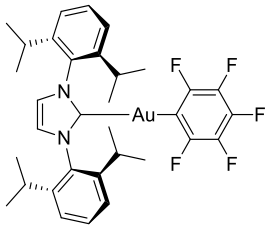
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 1.8 Hz, 2H), 1.58 (d, *J* = 13.2 Hz, 27H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.6 (dd, *J* = 240.8, 17.9 Hz), 152.0 (dt, *J* = 92.2, 56.1 Hz) 132.0 (app. dt, *J* = 33.3, 2.4 Hz), 39.5 (d, *J* = 16.4 Hz), 32.6 (d, *J* = 4.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 92.0 (t, *J* = 6.6 Hz). ^{19}F NMR (367 MHz, $CDCl_3$) δ –104.33 (br. s). IR (ATR) 2951, 1528, 1402, 1222, 983, 872. m.p. 160-165 °C. HRMS (EI) *m/z* calcd. $C_{17}H_{29}AuF_2NP$: $[M]^+$ 513.1664; found: $[M]^+$ 513.1656. Anal. Calcd for $C_{17}H_{29}AuF_2NP$: C, 39.77; H, 5.69; N, 2.73. Found: C, 39.53; H, 5.28; N, 2.65. Accurate elemental analysis was not obtained due to product decomposition.



1,3,7-trimethyl-2,6-dioxo-2,3,6,7-tetrahydropurin-8-yl(tri-tert-butylphosphine)gold(I) ***5am***

The general procedure was applied with [Au(P^{t}Bu$_3$)Cl] (43 mg, 0.10 mmol), caffeine (78 mg, 0.11 mmol) and NaOH (16 mg, 0.40 mmol) in 1,4-dioxane at 50 °C for 65 h. Washing with ice cold acetone (5 cm^3) afforded the title product as a white solid (46 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.08 (s, 3H), 3.63 (s, 3H), 3.40 (s, 3H), 1.58 (d, *J* = 13.2 Hz, 27H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7 (d, *J* = 125.0 Hz), 155.6, 152.3, 150.4 (d, *J* = 7.4 Hz), 108.1 (d, *J* = 3.0 Hz), 39.4 (d, *J* = 16.7 Hz), 34.9, 32.6 (d, *J* = 4.3), 30.0, 27.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 91.4. IR (ATR) 2928, 1693, 1646, 1312, 748. m.p. 254-258 °C. HRMS (EI) *m/z* calcd. $C_{20}H_{36}AuN_4O_2P$: $[M]^+$ 592.2241; found: $[M]^+$ 592.2218. Anal. Calcd for $C_{20}H_{36}AuN_4O_2P$: C, 40.54; H, 6.12; N, 9.46. Found: C, 39.18; H, 5.81; N, 9.05. Accurate elemental analysis was not obtained due to product decomposition.



Pentafluorophenyl(IPr)gold(I) ***7b***

The general procedure was applied with [Au(IPr)Cl] (37 mg, 0.060 mmol), pentafluorobenzene (27 µL, 0.24 mmol) and NaOH (10 mg, 0.24 mmol) or NaO^{t}Bu (23 mg, 0.24 mmmol) in DMF at 50 °C for 16 h. Washing with pentane (3 cm^3) afforded the title product as a white solid (with NaOH 43 mg, 95%; with NaO^{t}Bu 42 mg, 93%).

Spectroscopic data matched those previously reported.[2]

^{1}H NMR (400 MHz, C_6D_6): δ 7.19 (t, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 4H), 6.30 (s, 2H), 2.60 (sept, *J* = 6.9 Hz, 4H), 1.50 (d, *J* = 6.9 Hz, 12H), 1.09 (d, *J* = 6.9 Hz, 12H). ^{13}C NMR (151 MHz, C_6D_6): δ (3x C pentafluorobenzyl not observed), 192.8, 149.7 (dm, *J* = 219.3 Hz), 145.9, 134.5, 130.9, 124.3, 122.8, 29.1, 24.7, 23.9. ^{19}F (376 MHz, C_6D_6): δ –116.2 - –116.3 (m), –161.1 (t, *J* = 20.0 Hz), –163.7 - –163.9 (m). Anal. Calcd for $C_{33}H_{36}AuF_5N_2$: C, 52.66; H, 4.82; N, 3.72. Found: C, 48.92; H, 3.67; N, 3.19. Accurate elemental analysis was not obtained due to product decomposition.

Mechanistic Studies

Procedure for the titration of [Au(P^{t}Bu$_3$)Cl] with NaOH

A mixture of [Au(P^{t}Bu$_3$)Cl] (43.5 mg, 0.1 mmol) and NaOH (0.5 equiv., 0.67 equiv., 1.0 equiv. or 1.5 equiv.) was dissolved in DMF (0.5 mL). The reaction mixture was sonicated for 10 mins then stirred at 50 ^{o}C for 30 mins. The mixture was allowed to cool down to room temperature and analysed by ^{31}P NMR using a $CDCl_3$ insert. When using 1.5 equiv. NaOH, only one peak was seen by ^{31}P NMR

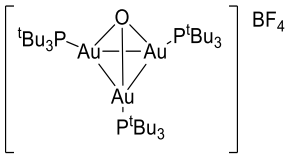
^{31}P NMR (162 MHz, $CDCl_3$) δ 83.5.

Procedure for the titration of [Au(P^{t}Bu$_3$)Cl] with NaO^{t}Bu

A mixture of [Au(P^{t}Bu$_3$)Cl] (43.5 mg, 0.1 mmol) and a solution of NaO^{t}Bu (2 M in THF, 0.5 equiv., 0.67 equiv. or 1.0 equiv.) was dissolved in DMF (0.45 mL). The reaction mixture was then stirred at 50 ^{o}C for 30 mins. The mixture was allowed to cool down to room temperature and analysed by ^{31}P NMR using a $CDCl_3$ insert. When using 1.0 equiv. NaO^{t}Bu (2M in THF), only one peak was seen by ^{31}P NMR

^{31}P NMR (162 MHz, $CDCl_3$) δ 83.2.

Preparation of [Au(P^{t}Bu$_3$)$_3$O]BF$_4$ 9'



In a vial, [Au(P^{t}Bu$_3$)Cl] (30 mg, 0.07 mmol) and finely powdered NaOH (11 mg, 0.28 mmol) were suspended in DMF (0.3 mL) and stirred for 30 min. Thereafter $NaBF_4$ (35 mg, 0.32 mmol) was added and the mixture was stirred for a further 30 min. The suspension was diluted with CH_2Cl_2 (5 mL), filtered through a plug of cotton wool, and the solvent was removed under vacuum. To remove residual salts, the resulting solid was re-dissolved in CH_2Cl_2 (5 mL) and filtered through a plug of cotton. Evaporation of the solvent afforded the product as a white solid (26 mg, 92%).

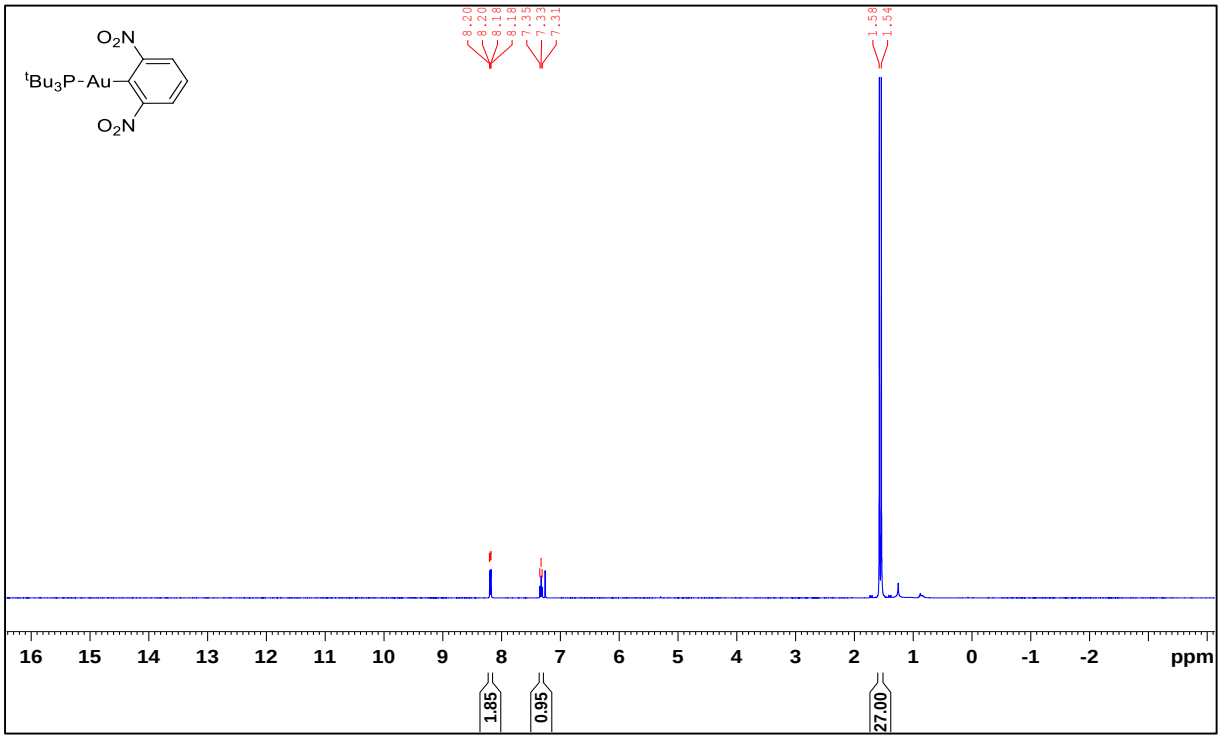
Spectroscopic data matched those previously reported.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52 (d, *J* = 13.7 Hz, 81H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.1 (d, *J* = 22.0 Hz); 32.1 (d, *J* = 3.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 83.5.

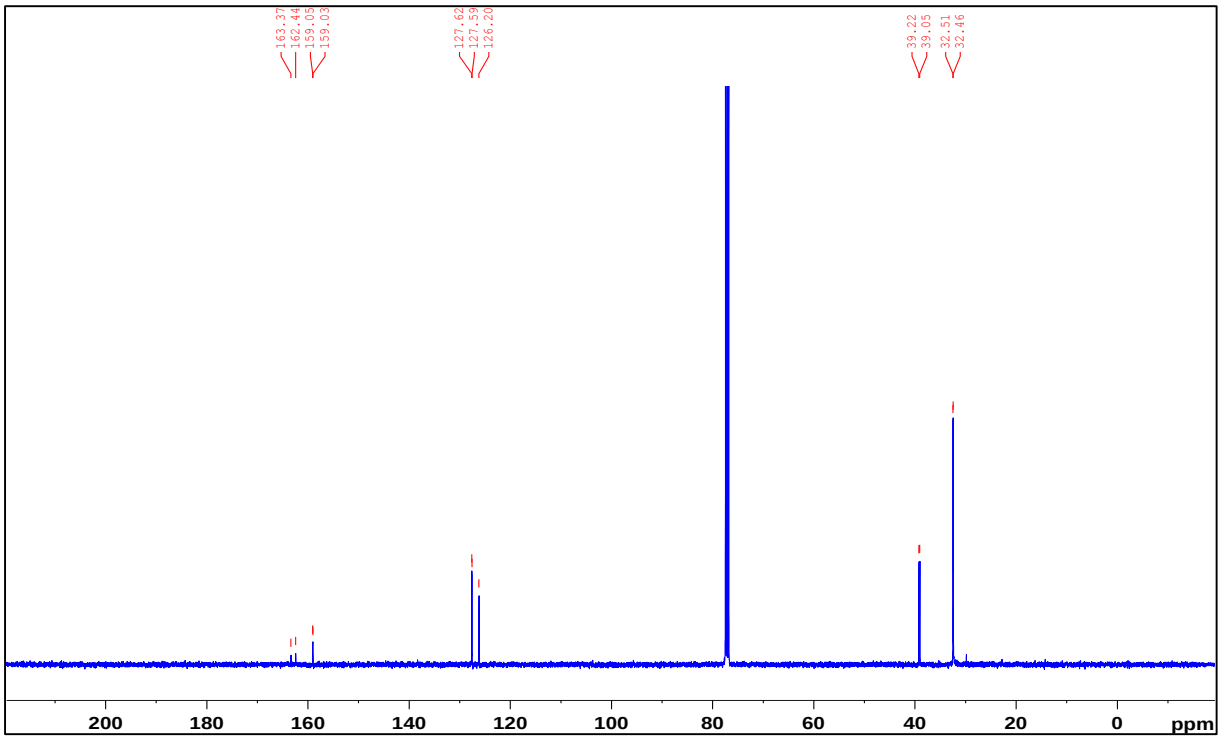
NMR Spectra

2,6-Dinitrophenyl(tri-tert-butylphosphine)gold(I) ***3aa***

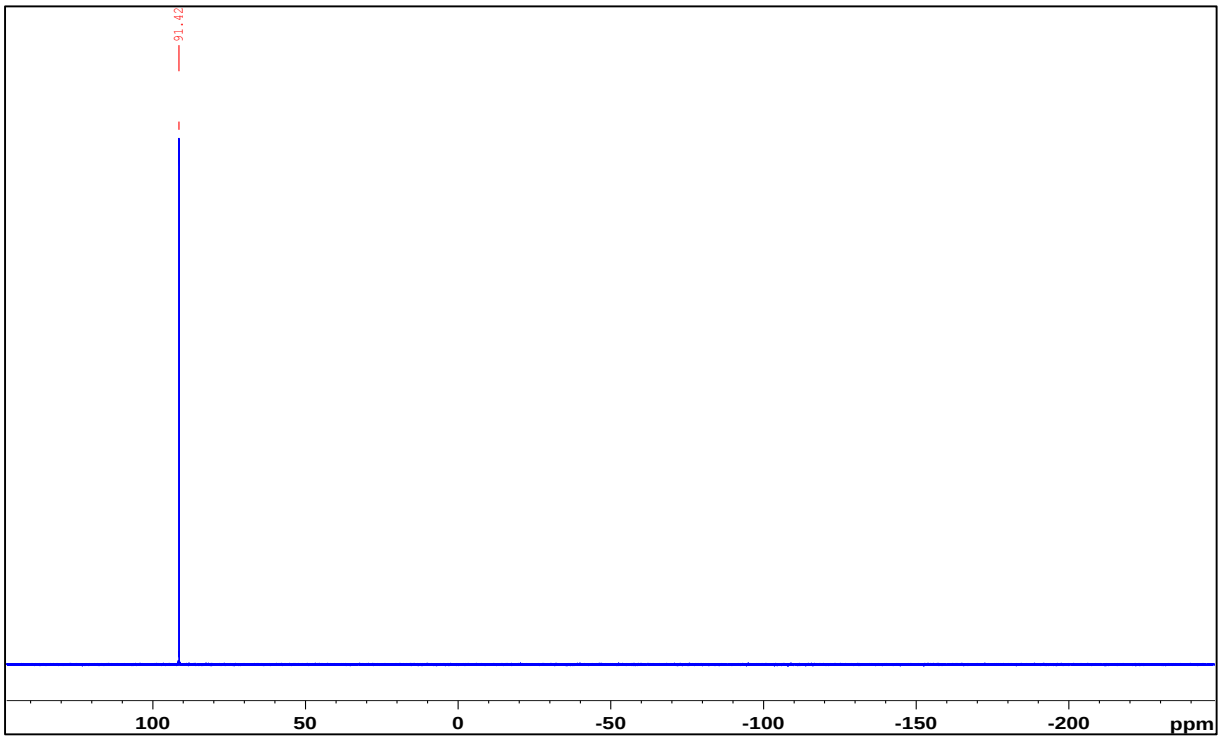
^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)

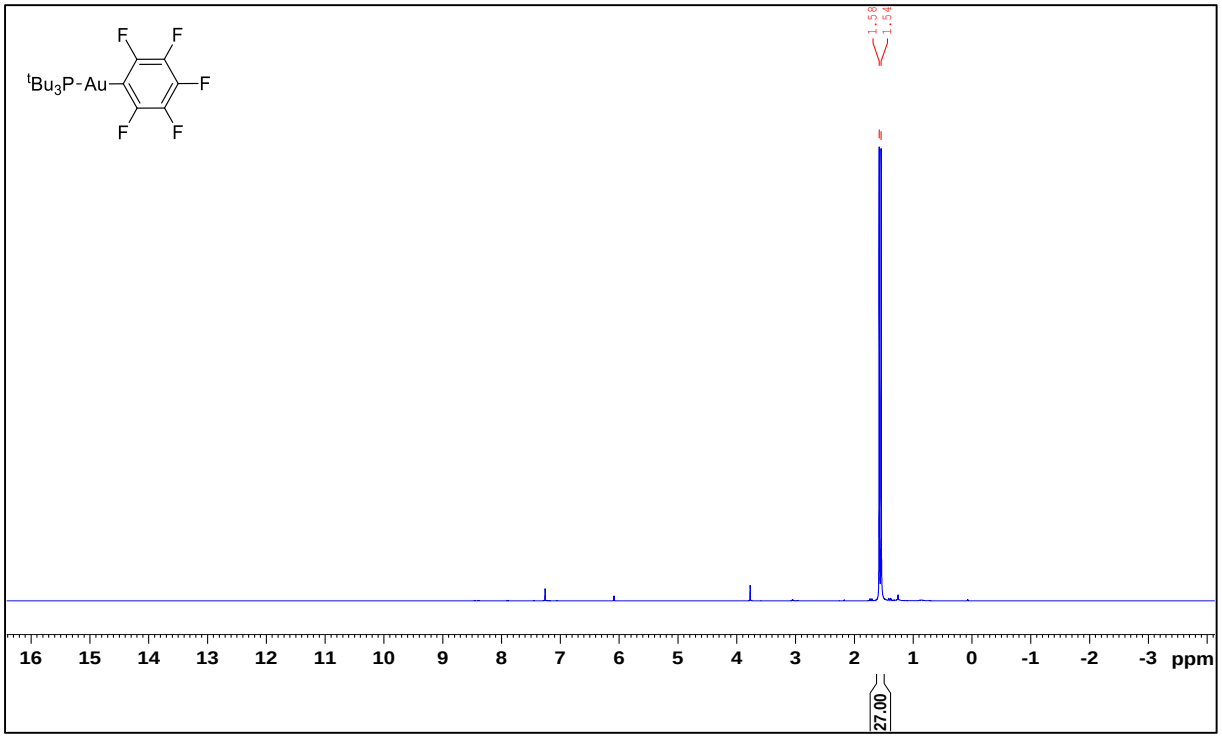


^{31}P NMR ($CDCl_3$)

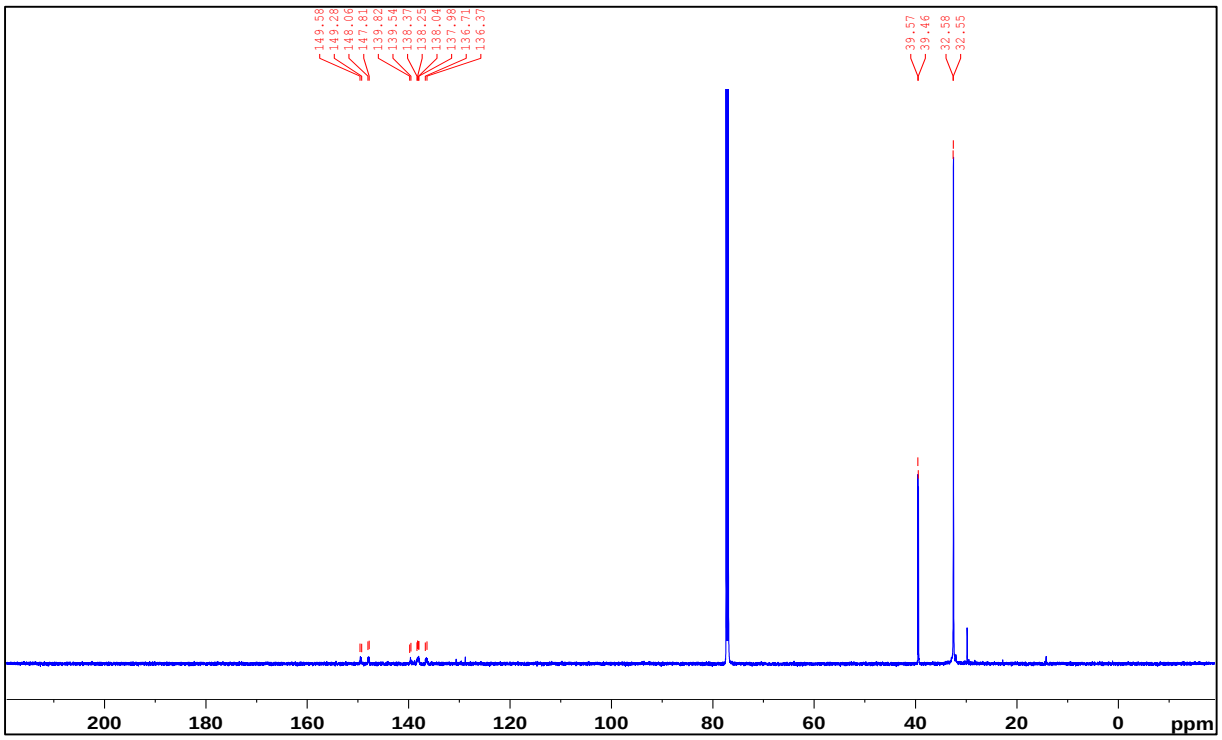


Pentafluorophenyl(tri-tert-butylphosphine)gold(I) ***3ab***

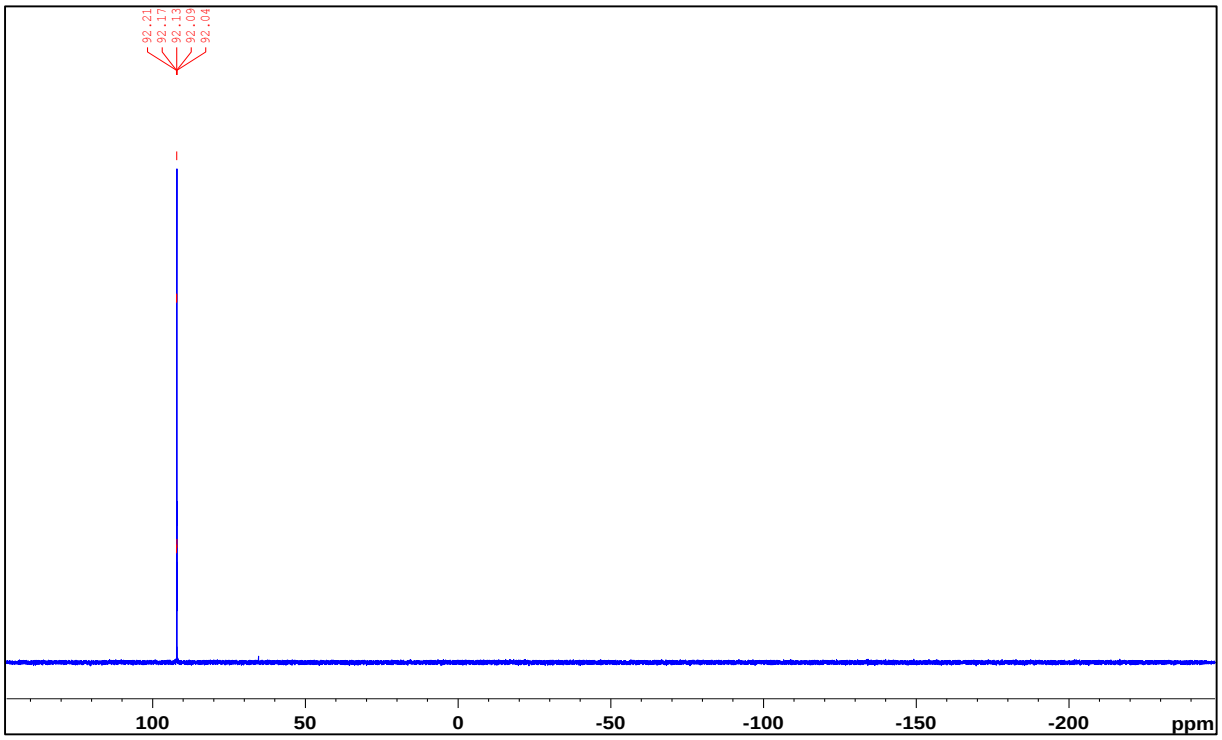
^{1}H NMR ($CDCl_3$)



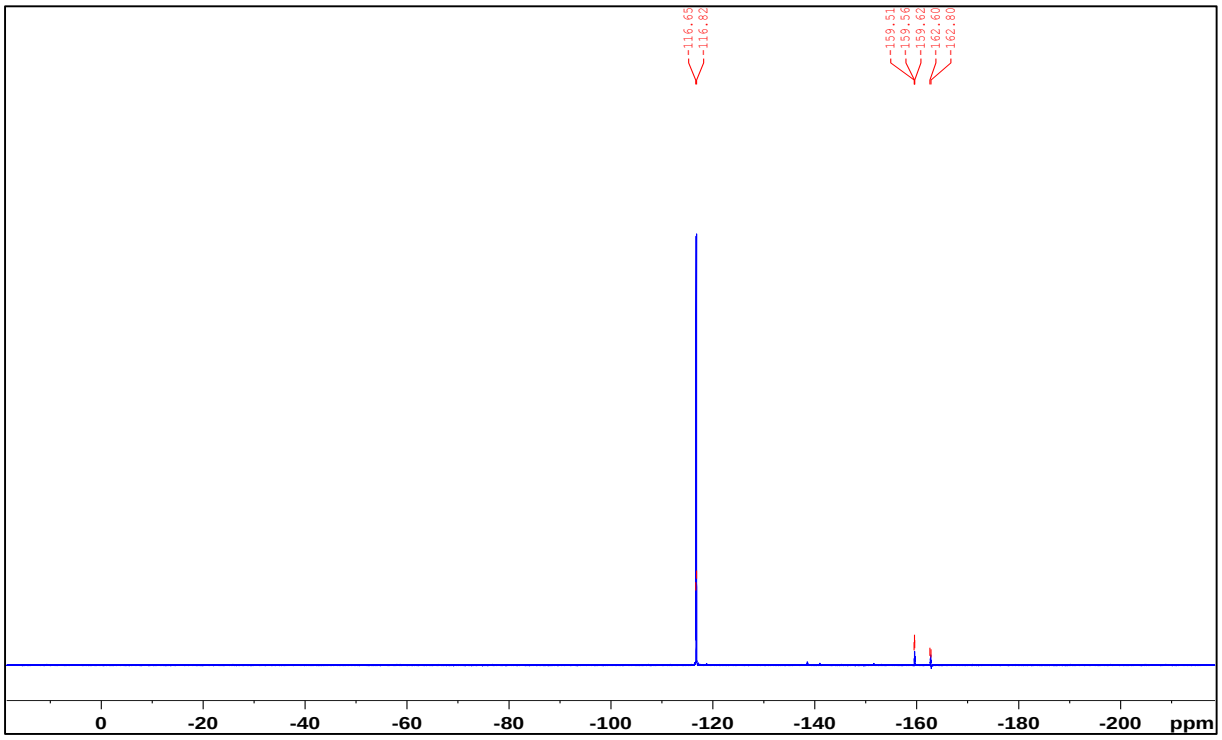
^{13}C NMR ($CDCl_3$)



^{31}P NMR ($CDCl_3$)

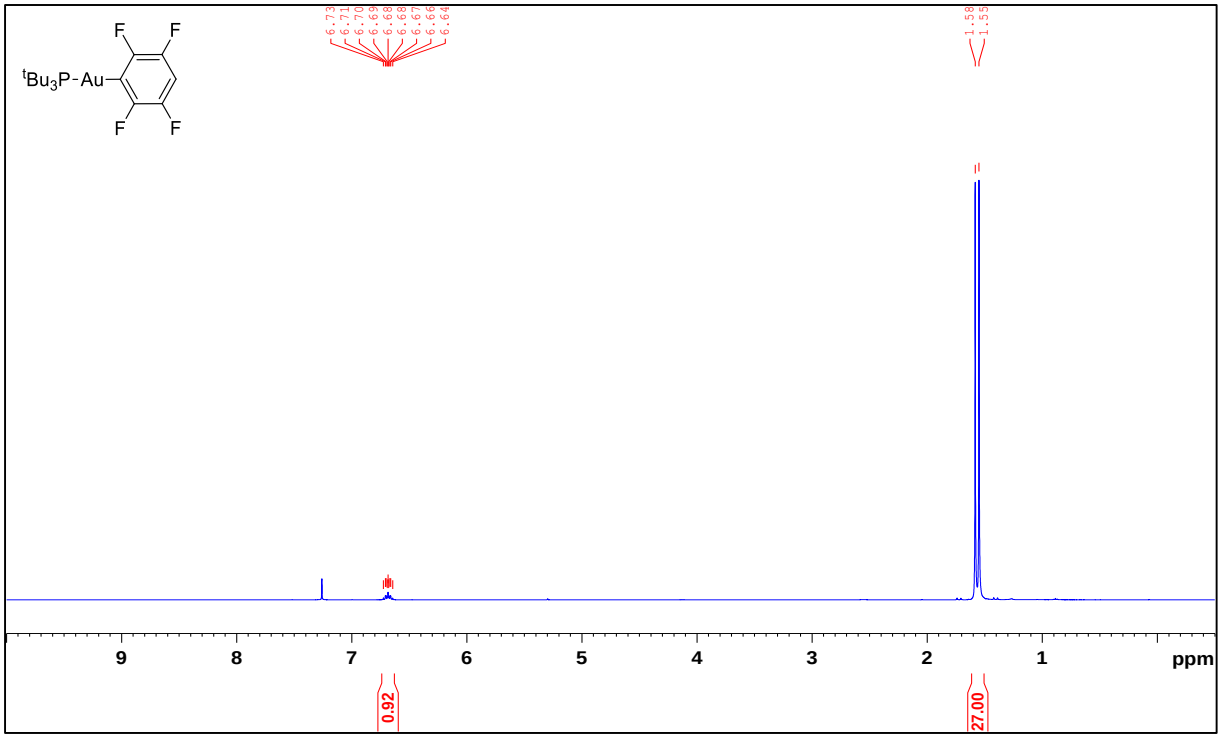


^{19}F NMR ($CDCl_3$)

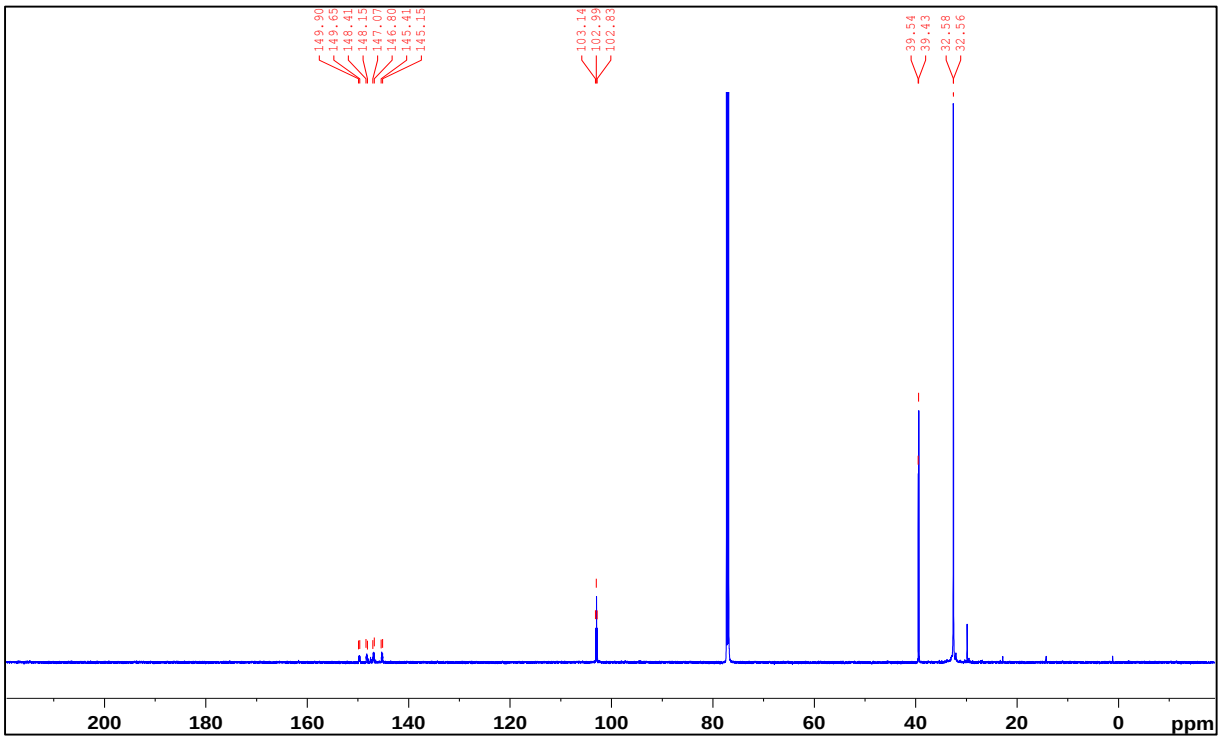


2,3,5,6-Tetrafluorophenyl(tri-tert-butylphosphine)gold(I) ***3ac***

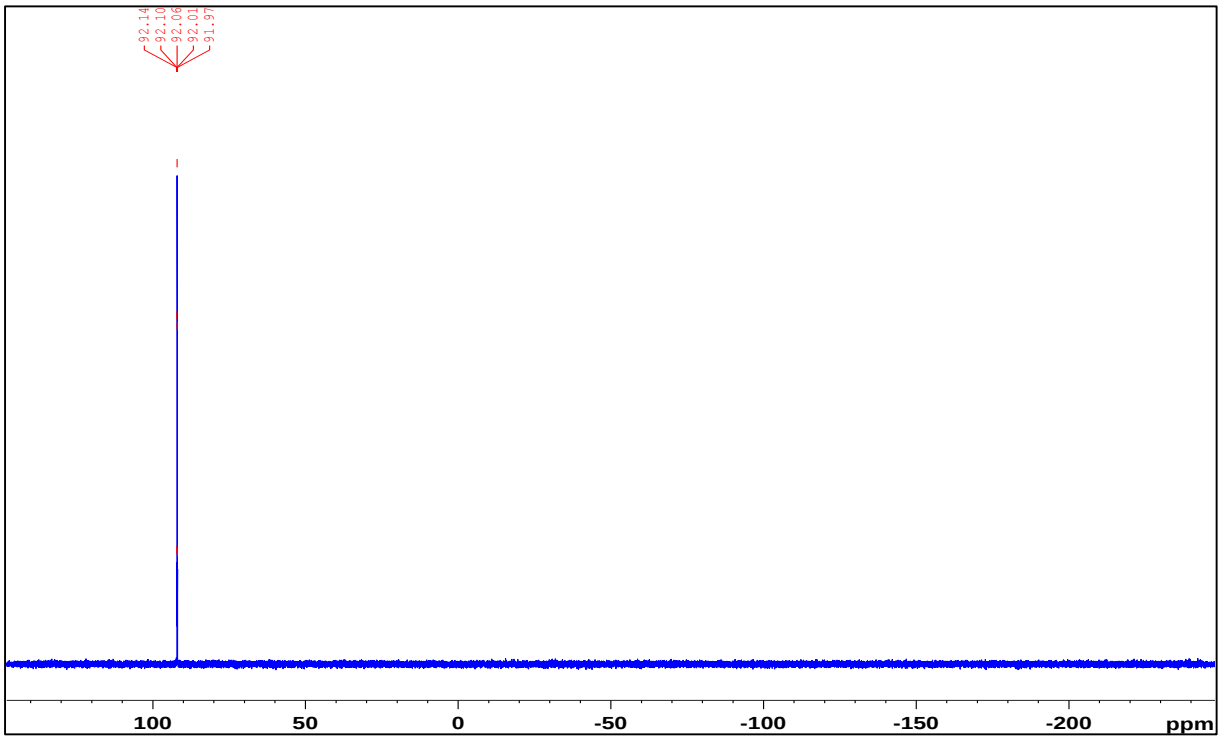
^{1}H NMR ($CDCl_3$)



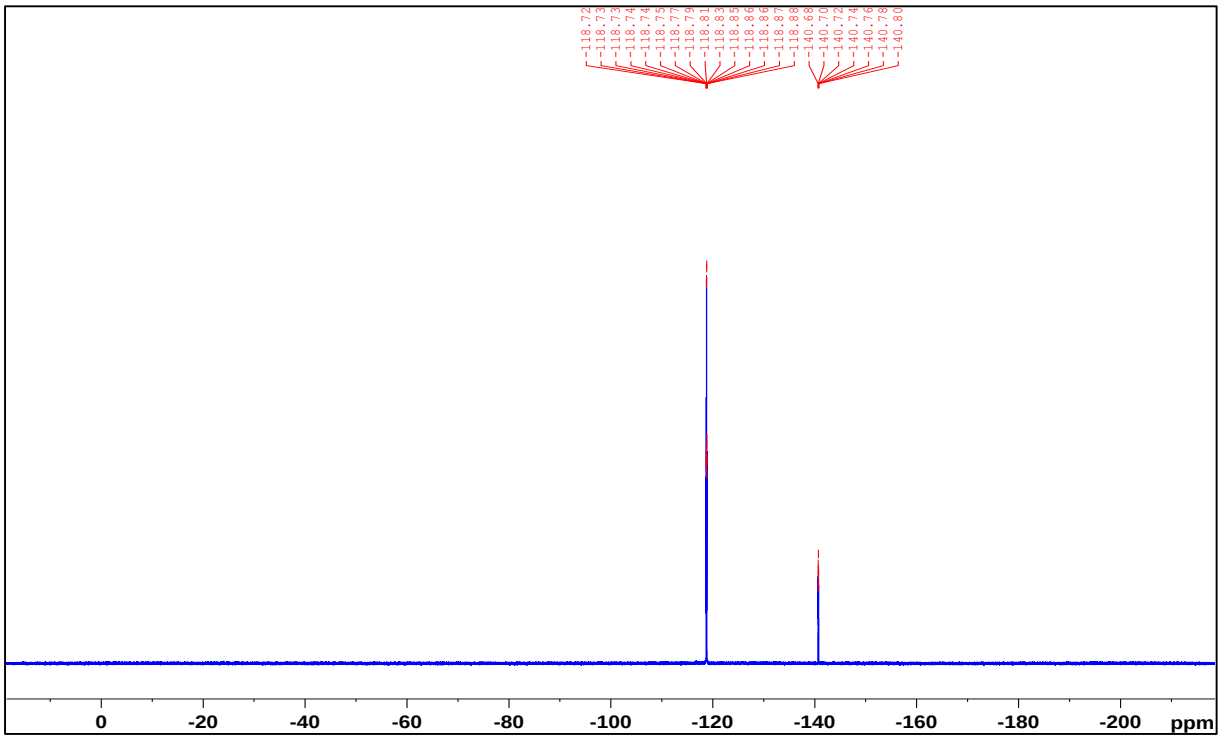
^{13}C NMR ($CDCl_3$)



^{31}P NMR ($CDCl_3$)

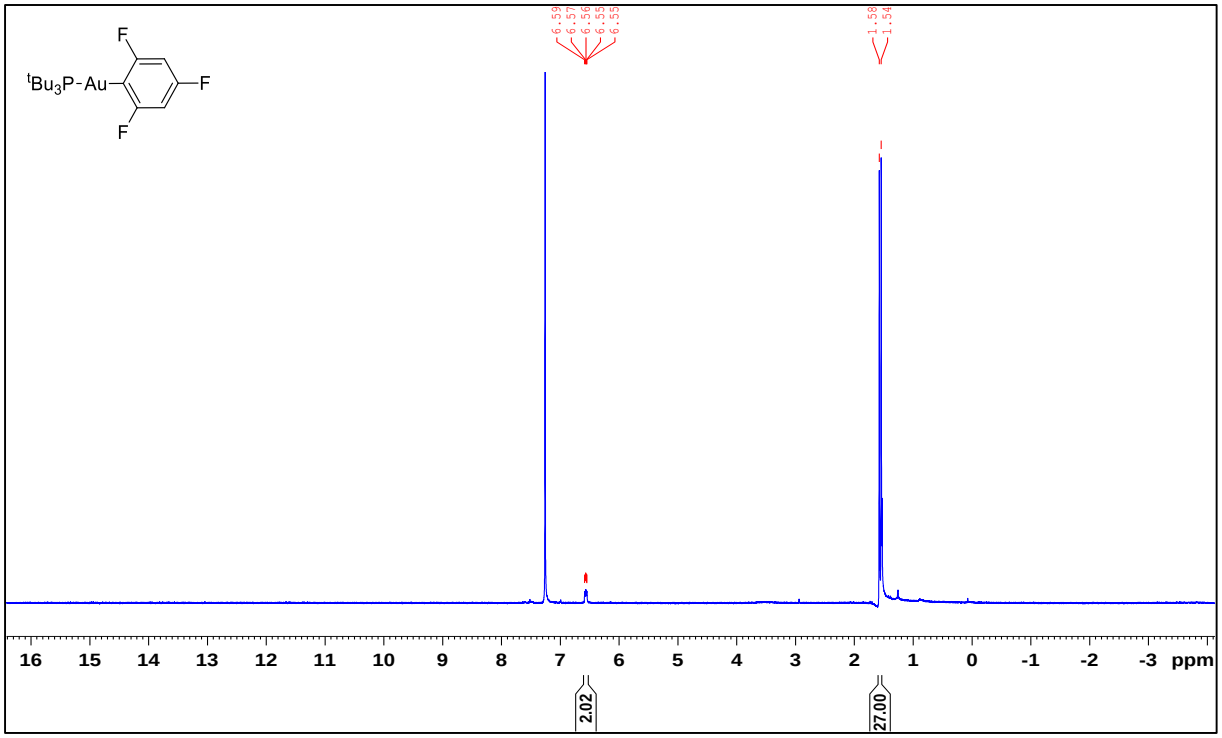


^{19}F NMR ($CDCl_3$)

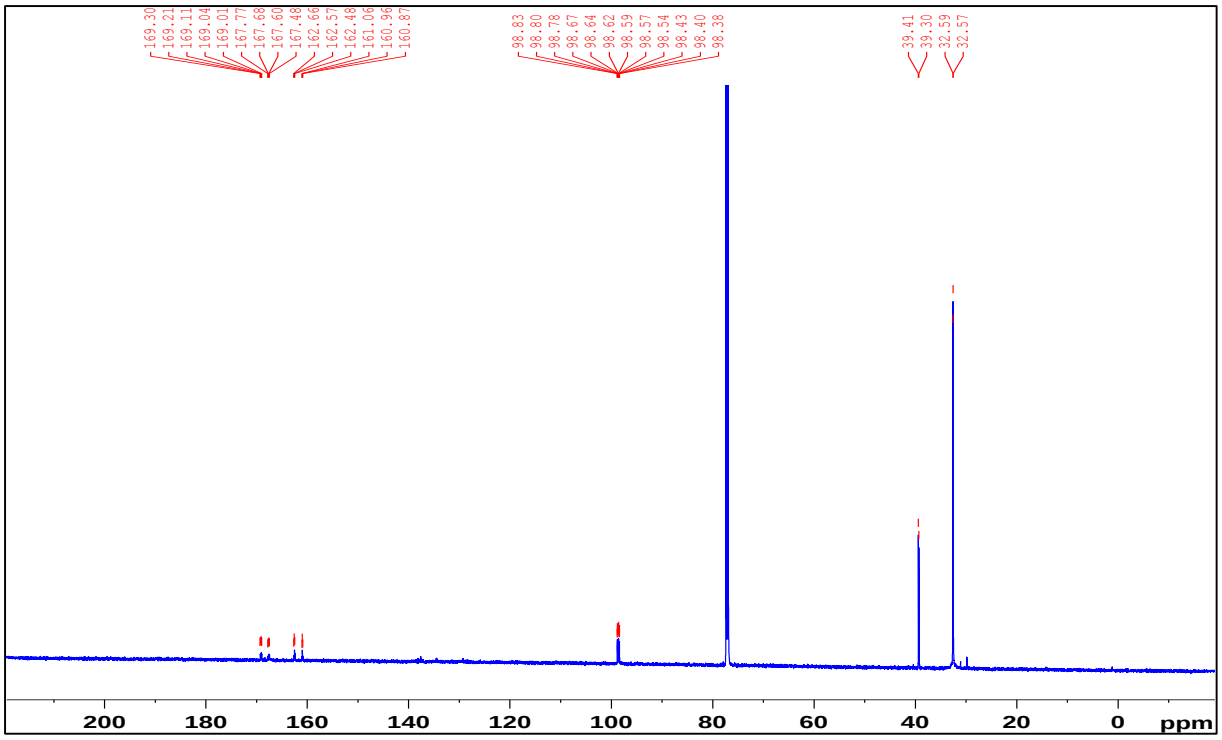


2,4,6-Trifluorophenyl(tri-tert-butylphosphine)gold(I) ***3ad***

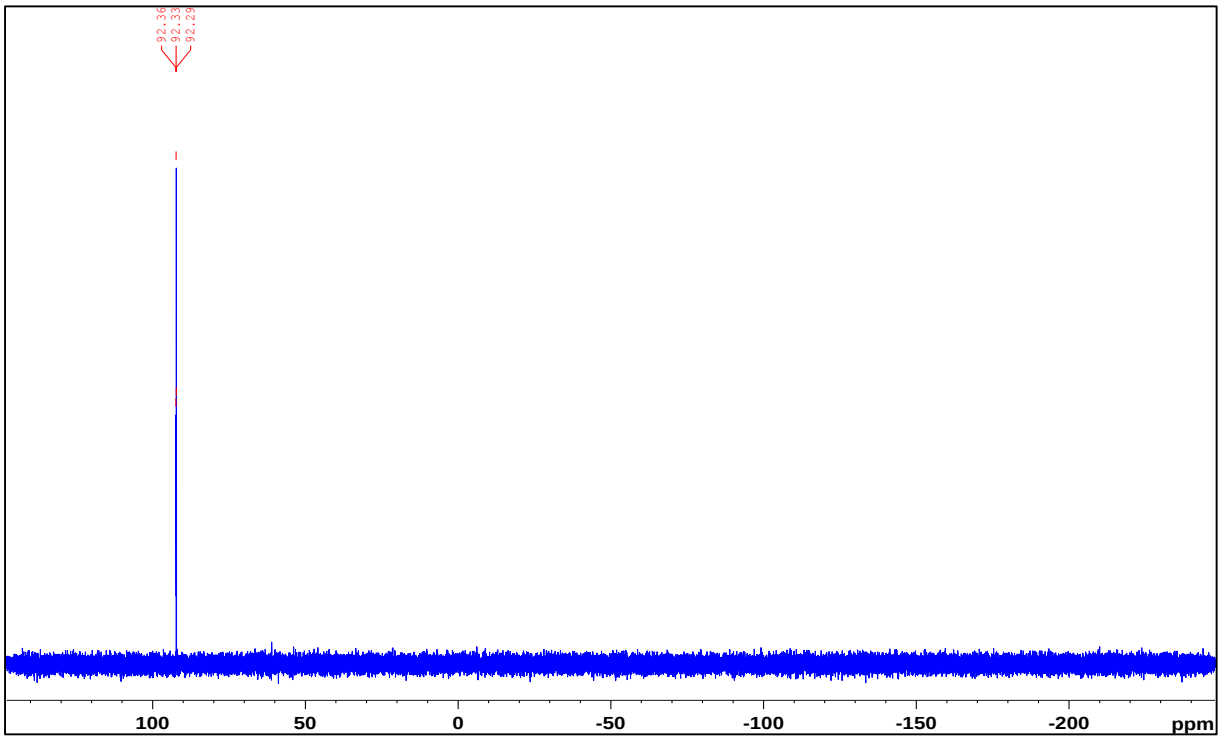
^{1}H NMR ($CDCl_3$)



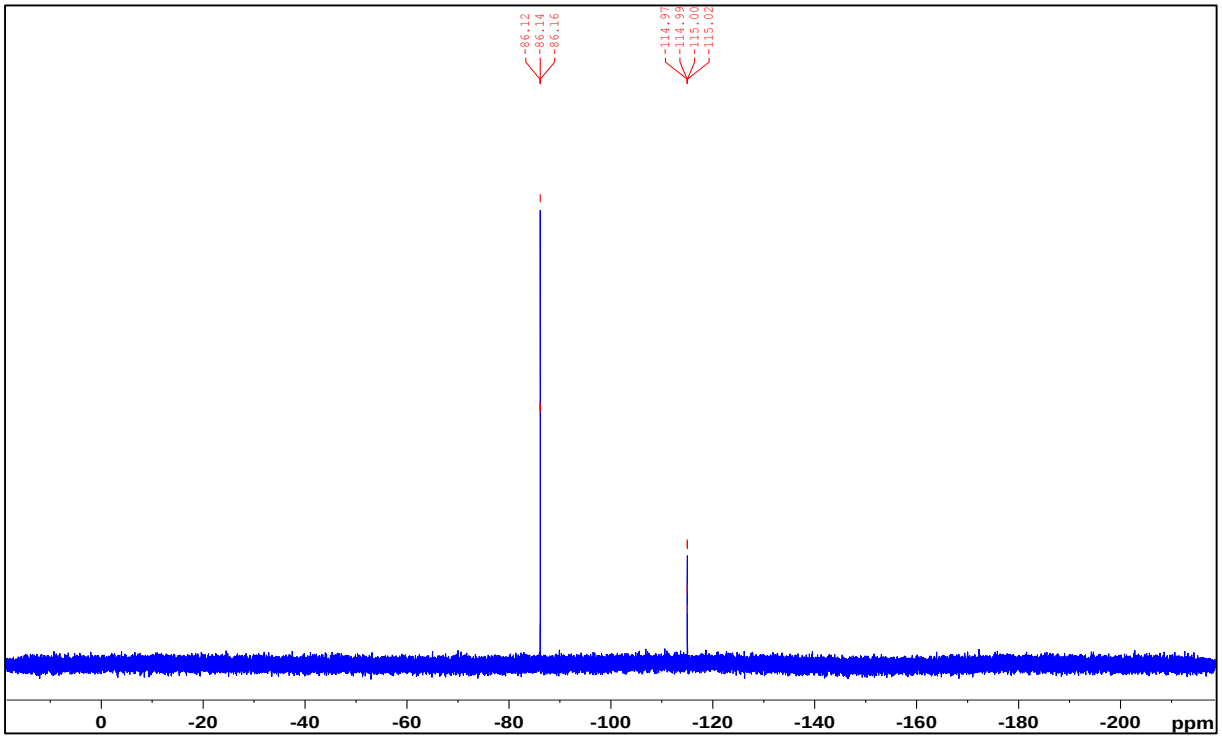
^{13}C NMR ($CDCl_3$)



^{31}P NMR ($CDCl_3$)

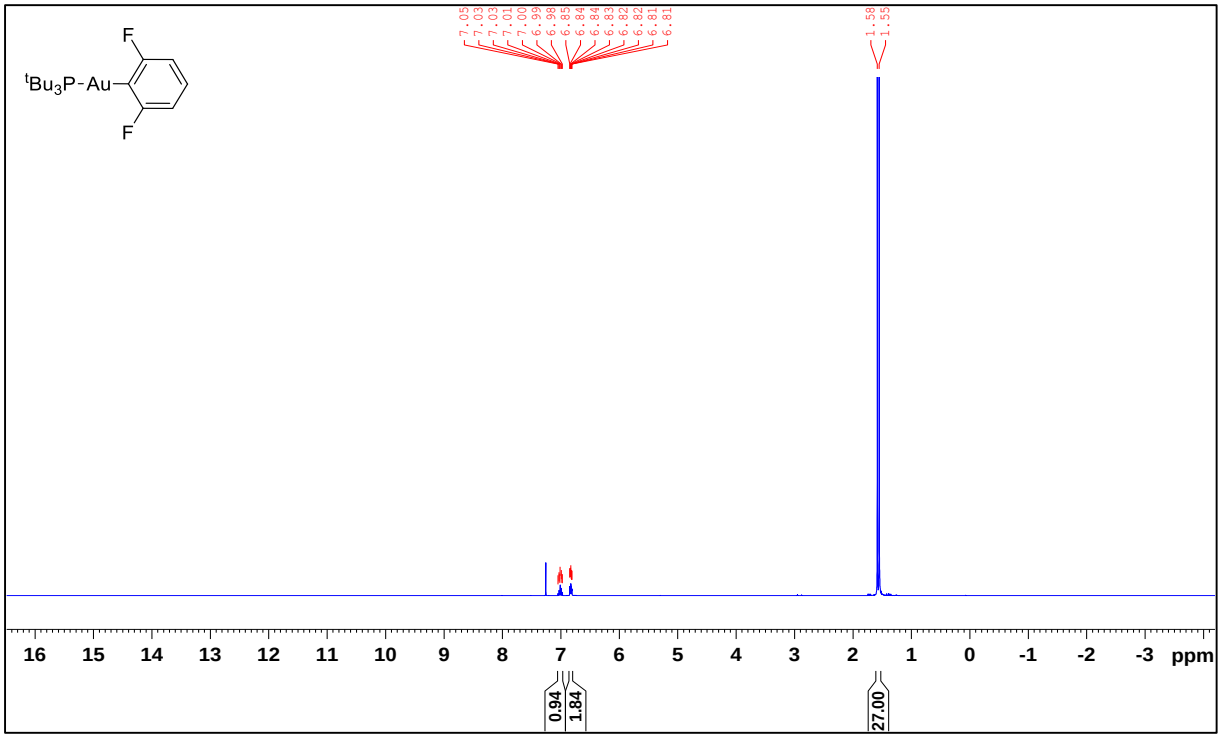


^{19}F NMR ($CDCl_3$)

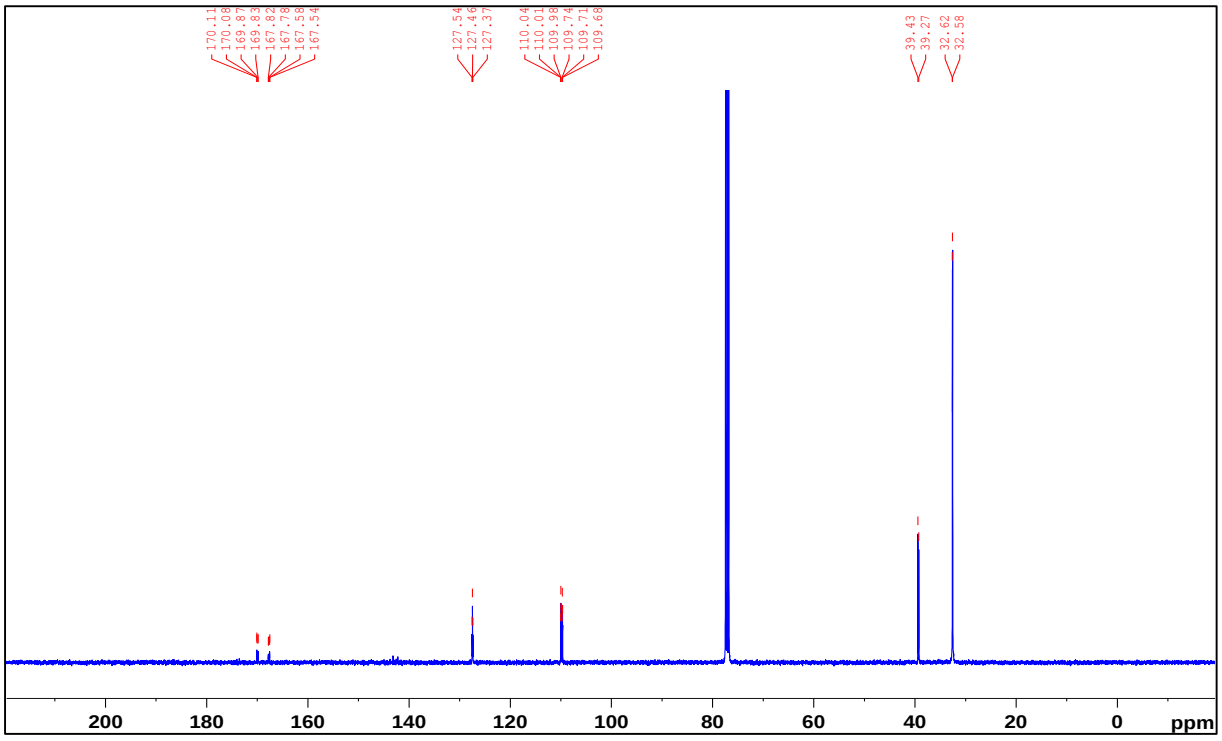


2,6-Difluorophenyl(tri-tert-butylphosphine)gold(I) ***3ae***

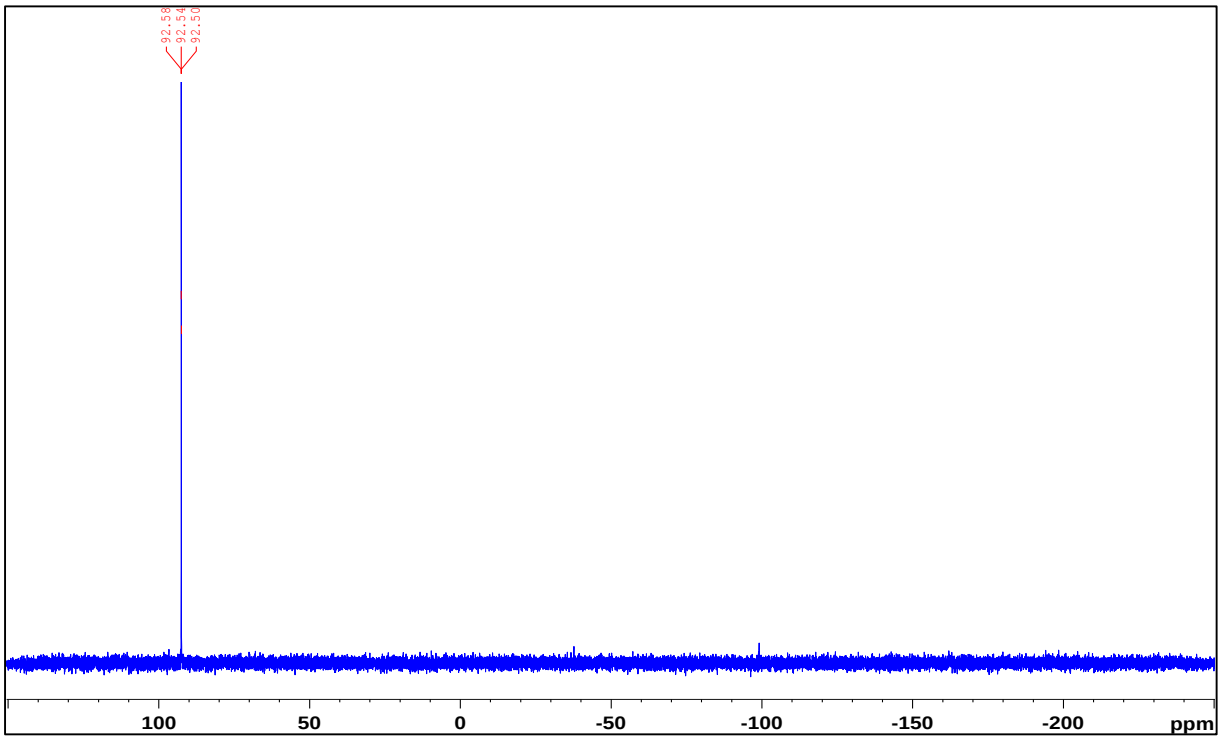
^{1}H NMR ($CDCl_3$)



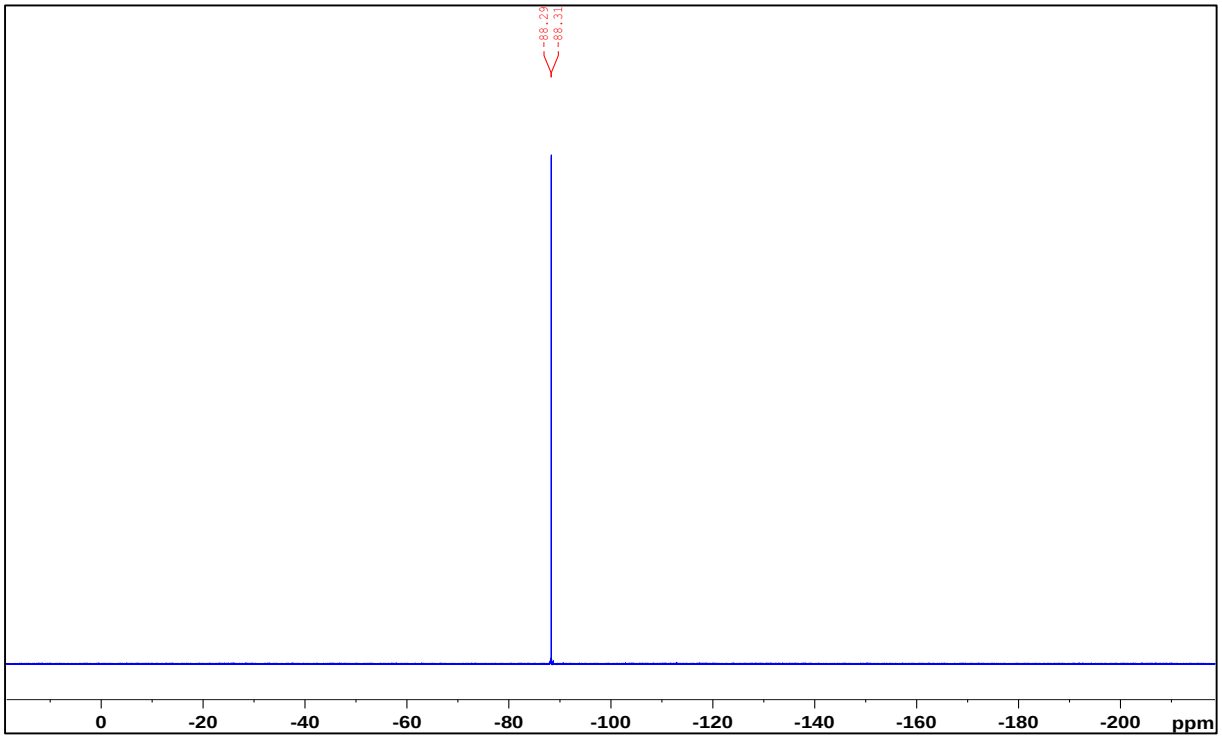
^{13}C NMR ($CDCl_3$)



^{1}P NMR ($CDCl_3$)

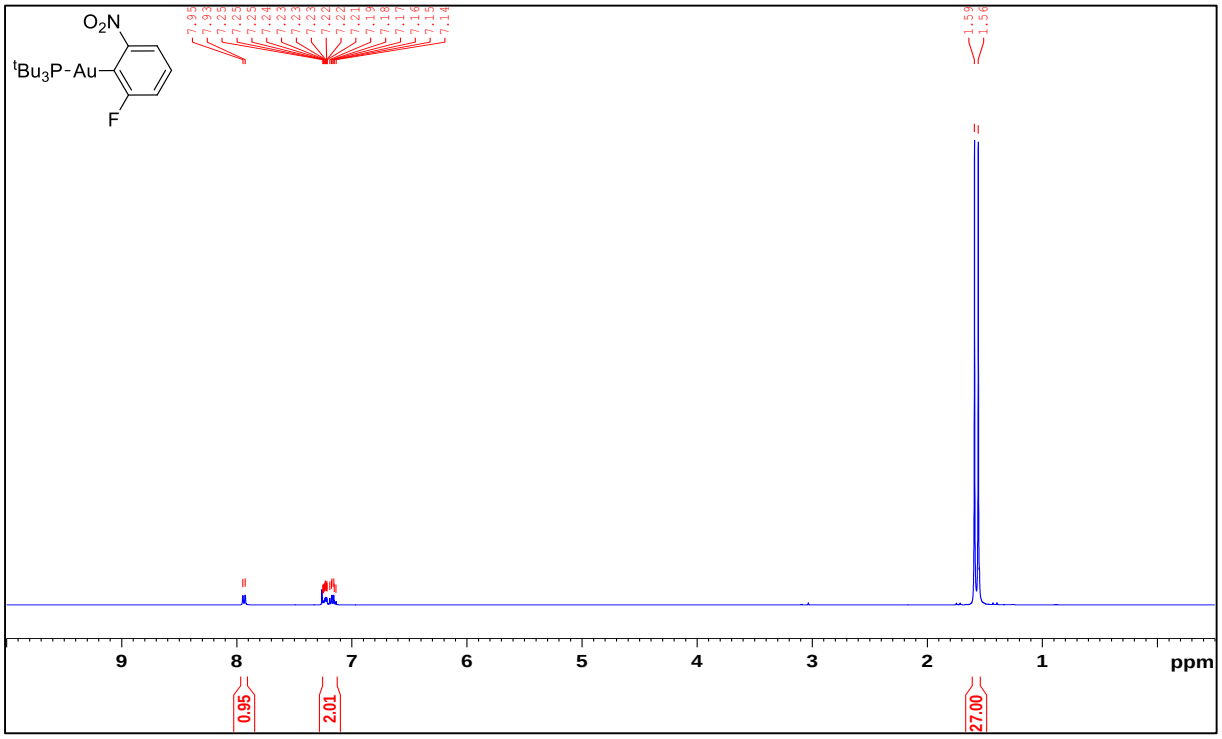


^{19}F NMR ($CDCl_3$)

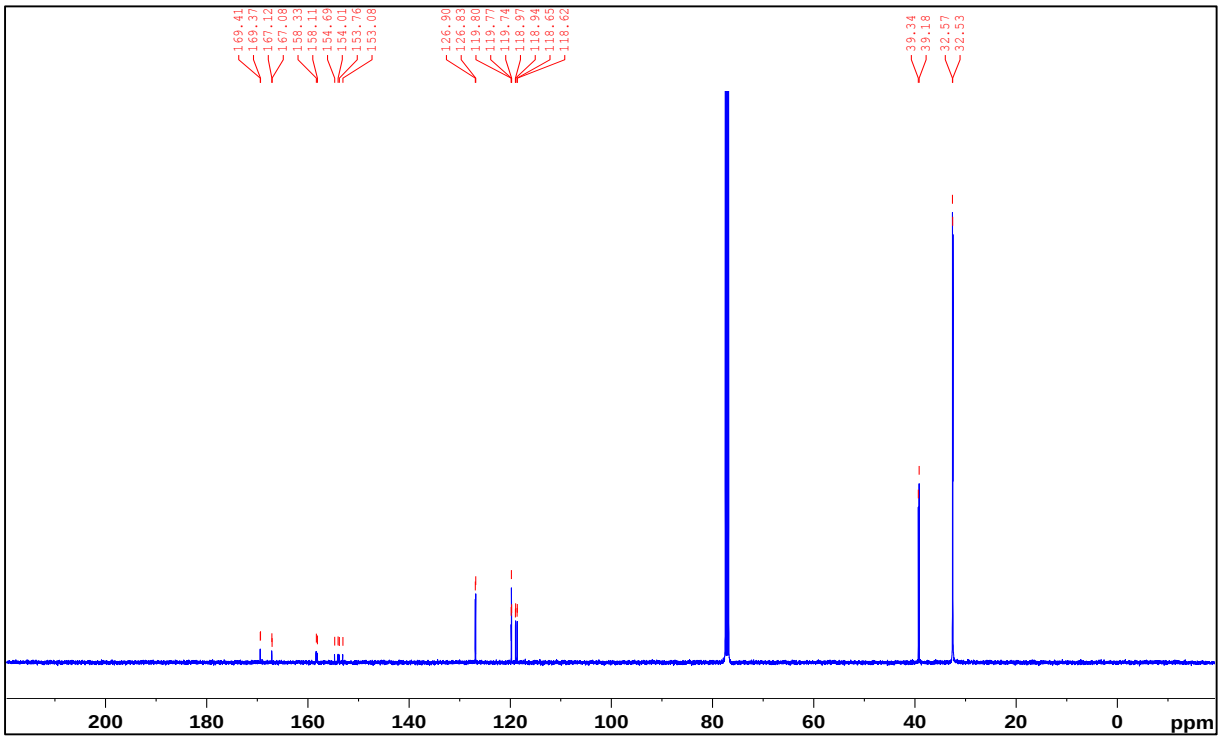


2-Fluoro-6-nitrophenyl(tri-tert-butylphosphine)gold(I) ***3af***

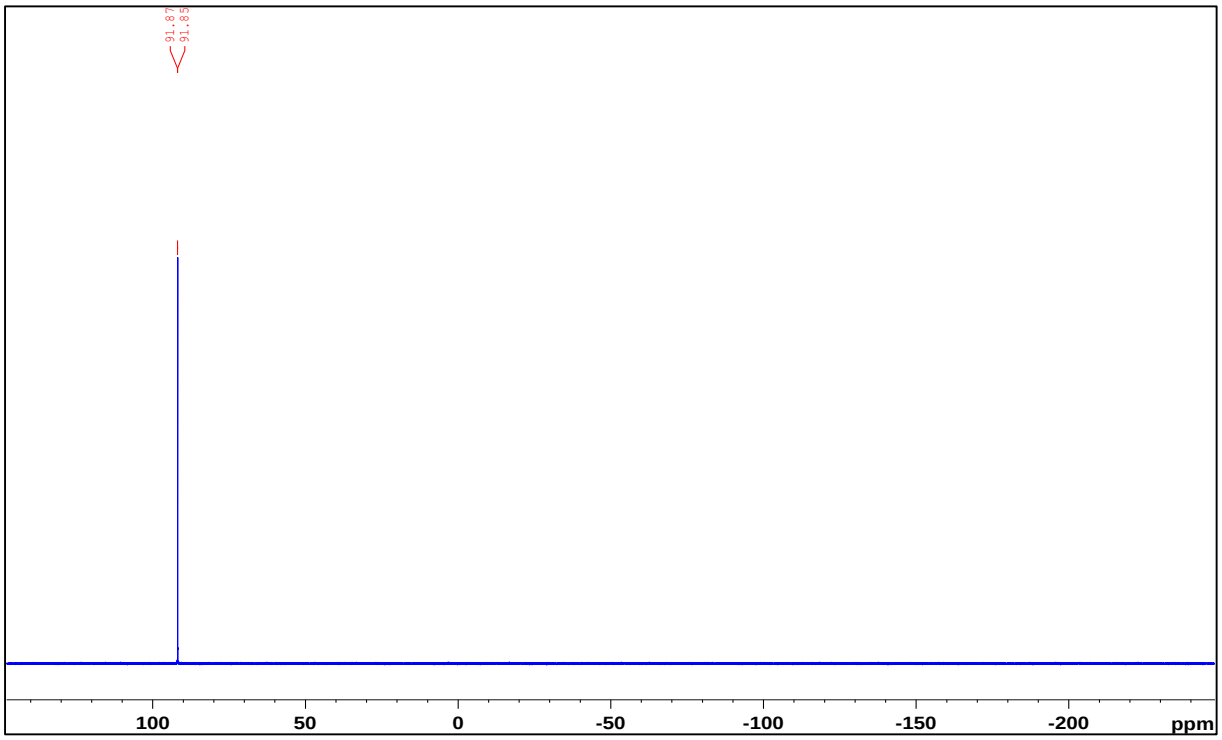
^{1}H NMR ($CDCl_3$)



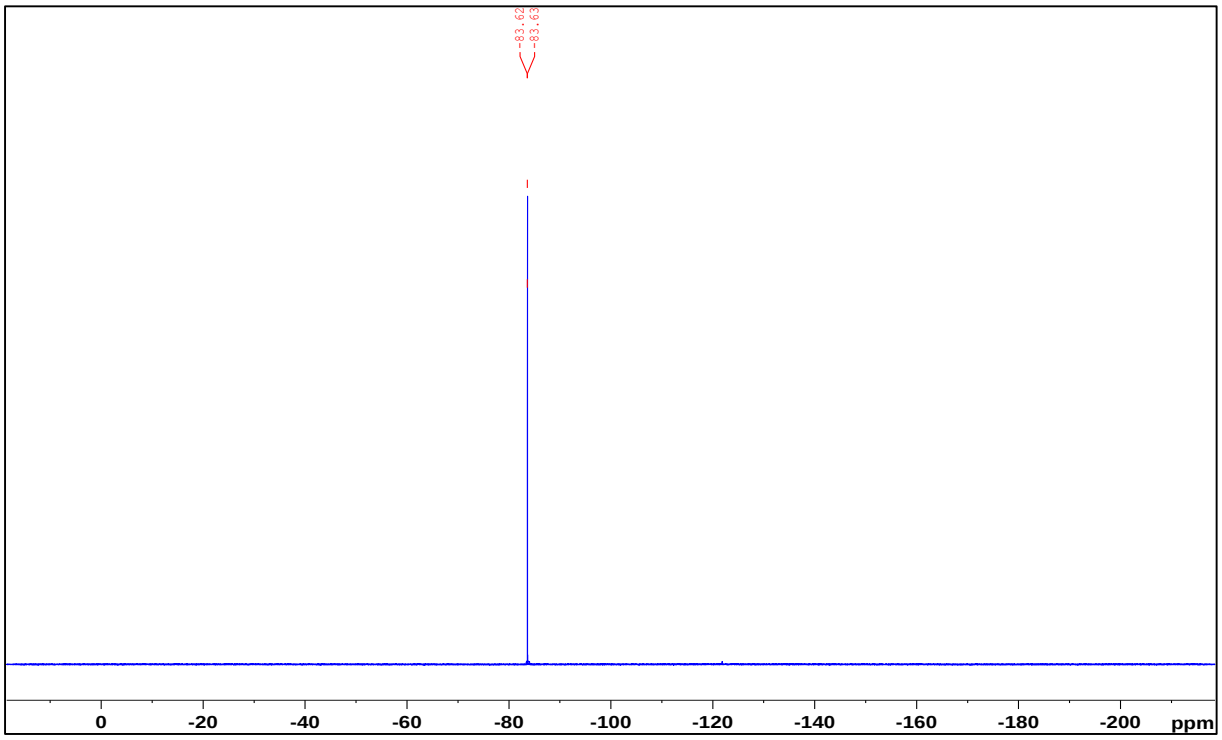
^{13}C NMR ($CDCl_3$)



^{1}P NMR ($CDCl_3$)

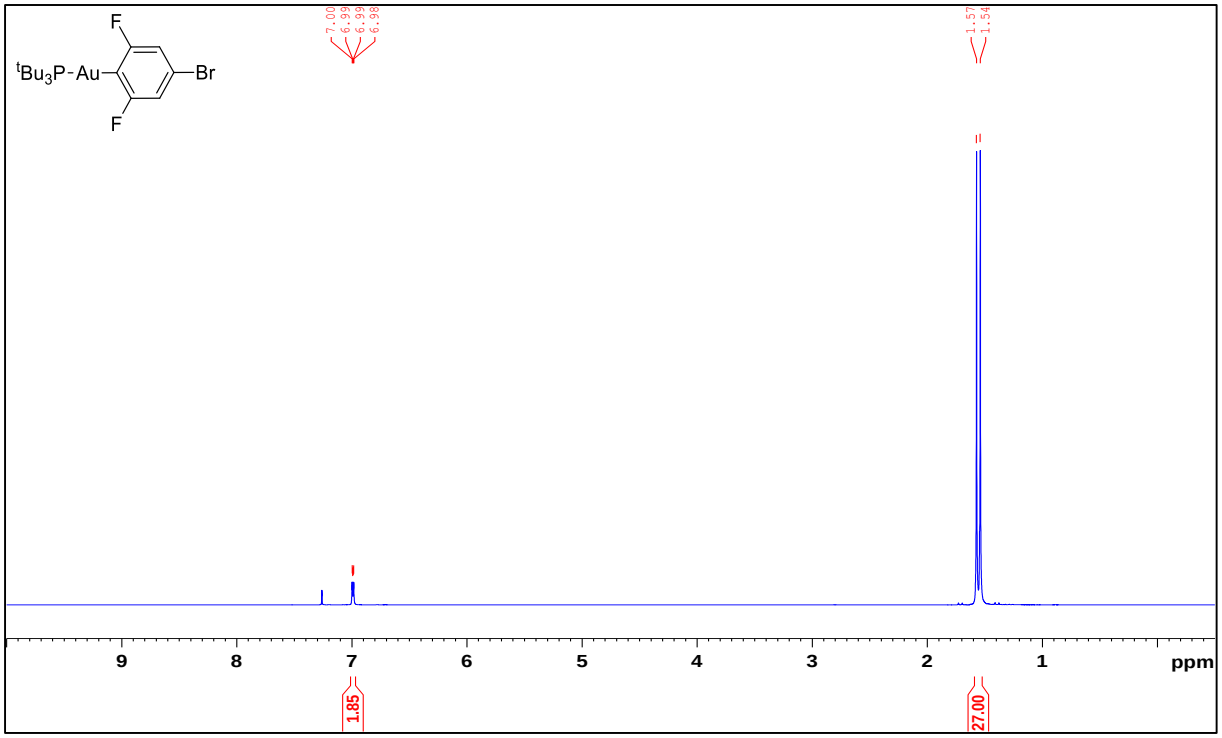


^{19}F NMR ($CDCl_3$)

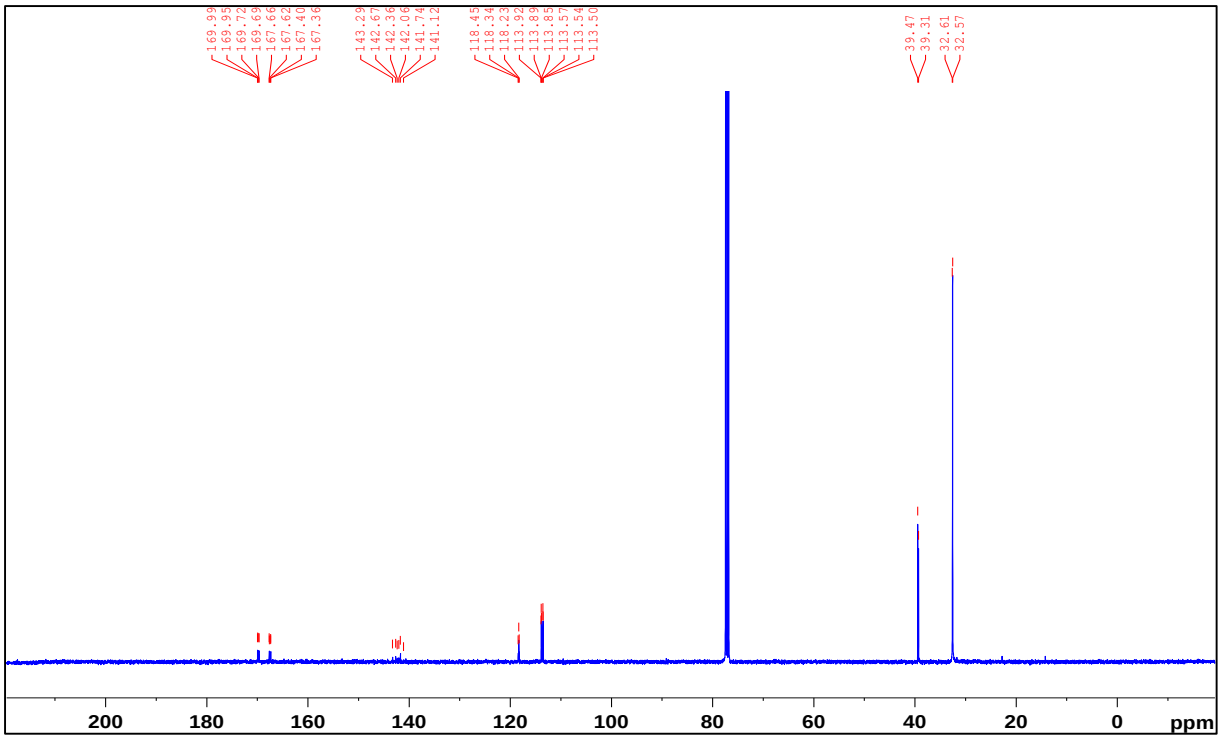


4-Bromo-2,6-difluorophenyl(tri-tert-butylphosphine)gold(I) ***3ag***

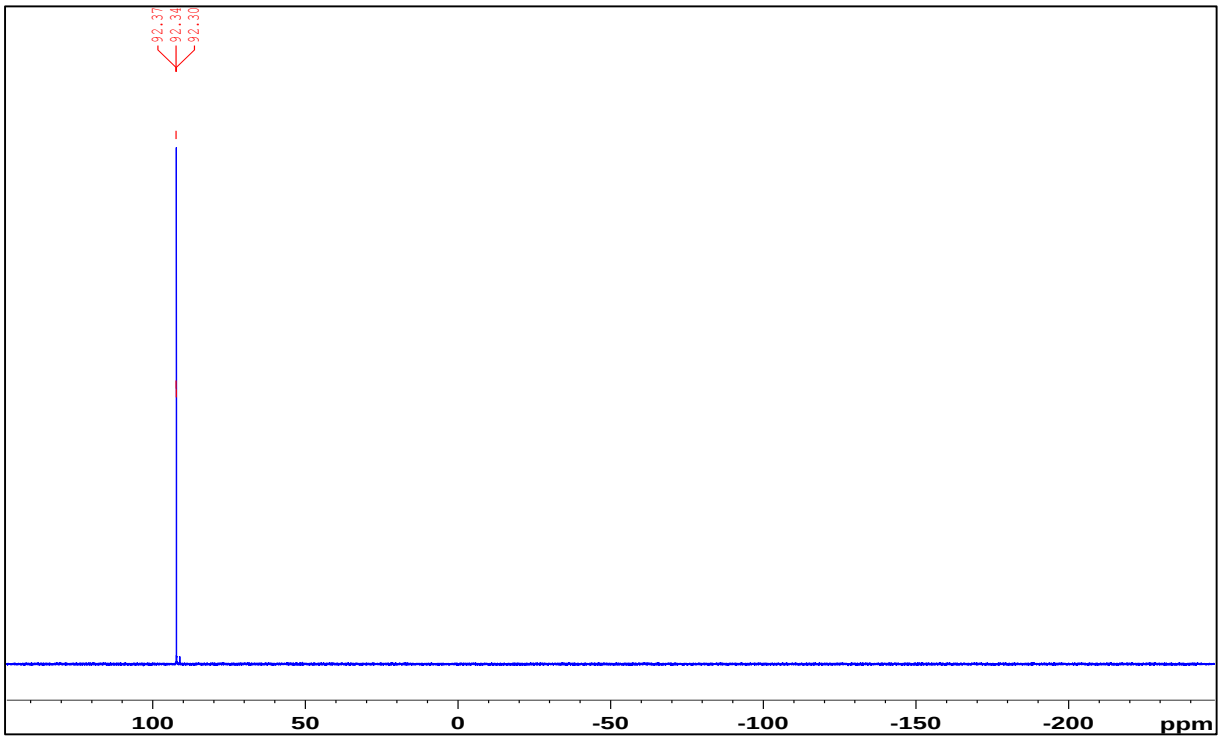
^{1}H NMR ($CDCl_3$)



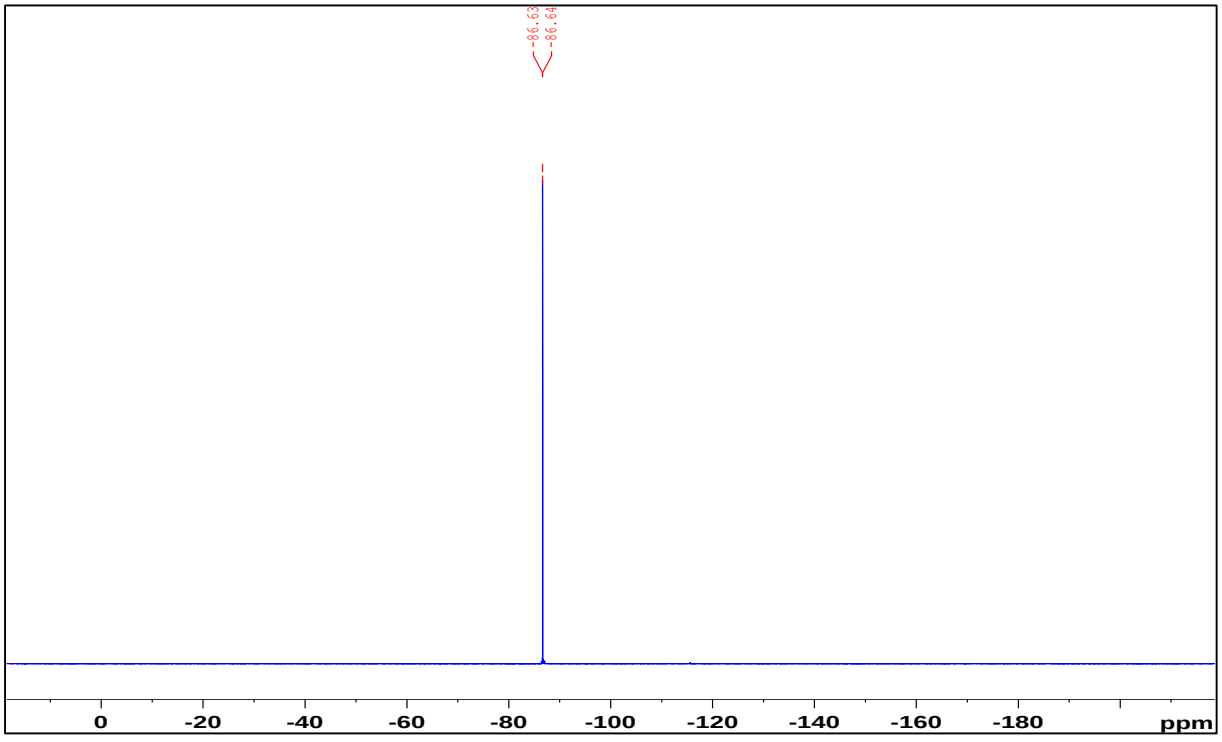
^{13}C NMR ($CDCl_3$)



^{31}P NMR ($CDCl_3$)

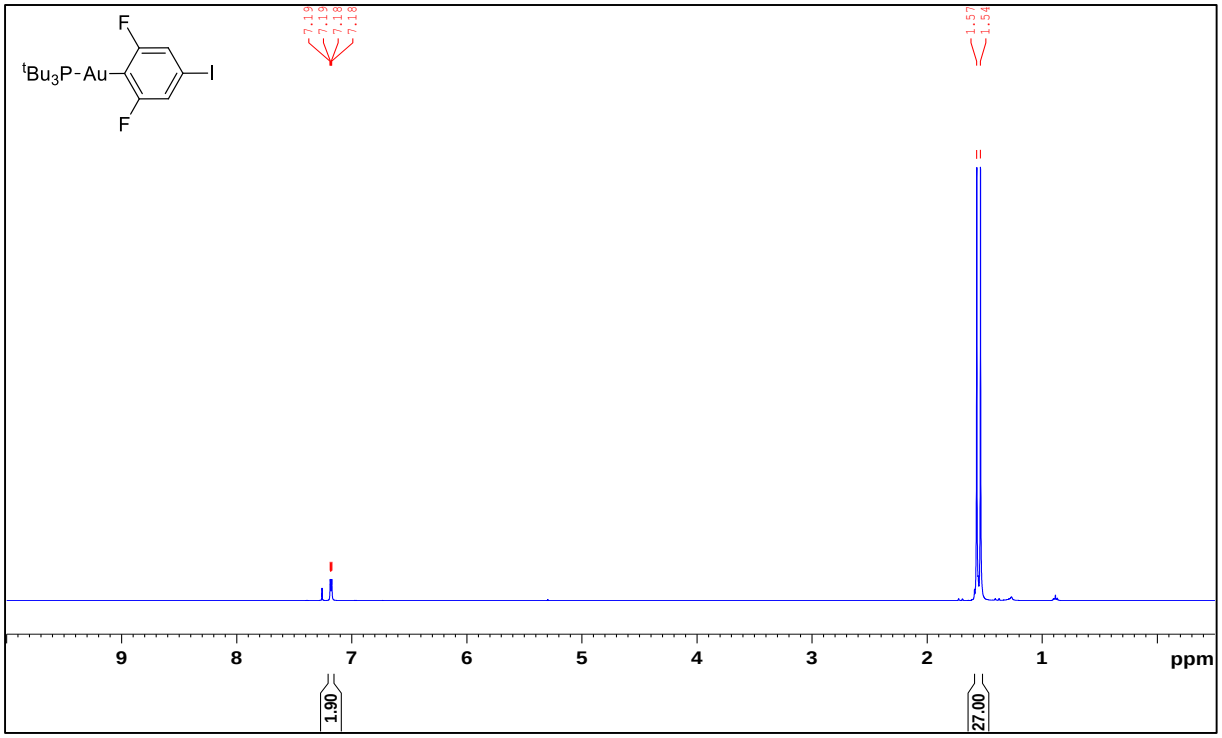


^{19}F NMR ($CDCl_3$)

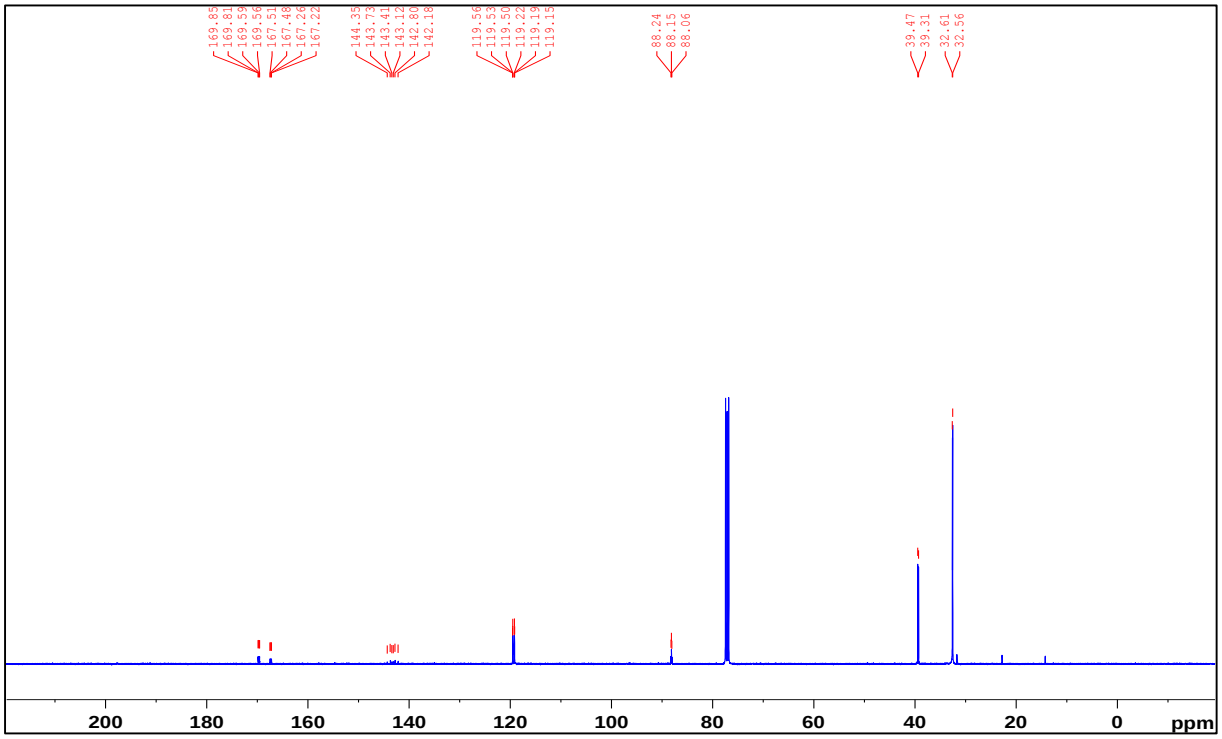


2,6-Difluoro-4-iodoophenyl(tri-tert-butylphosphine)gold(I) ***3ah***

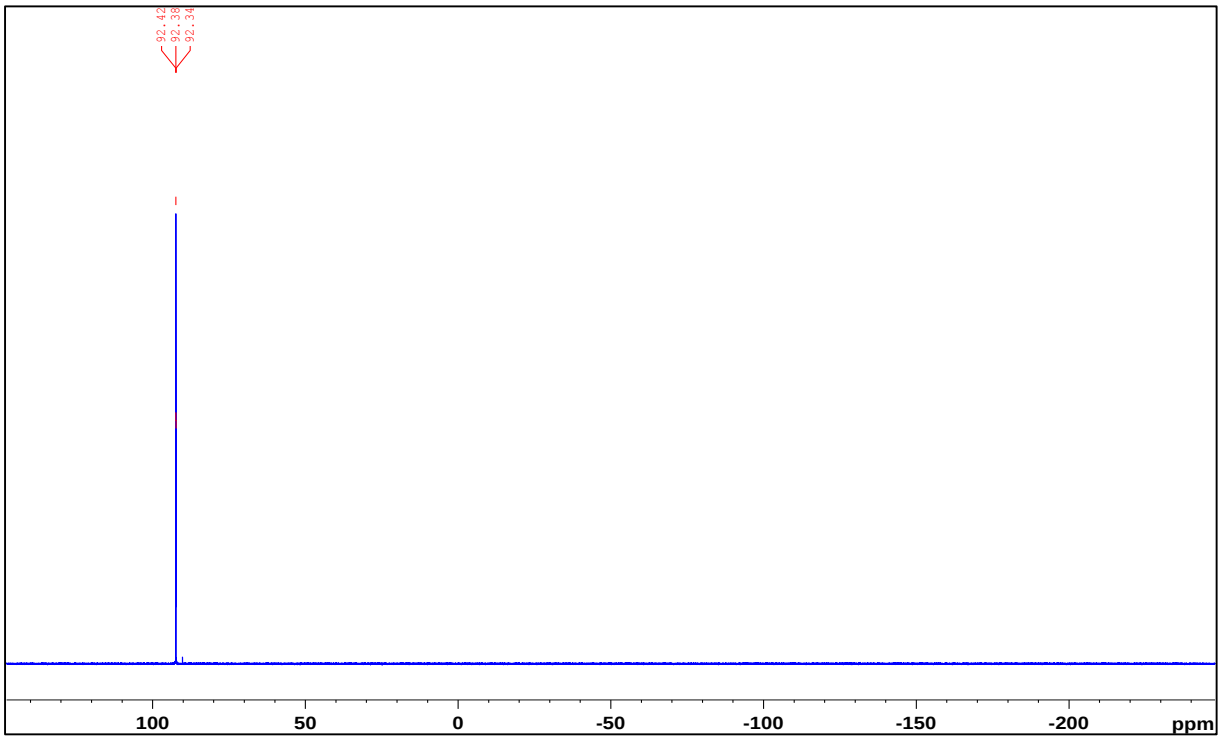
^{1}H NMR ($CDCl_3$)



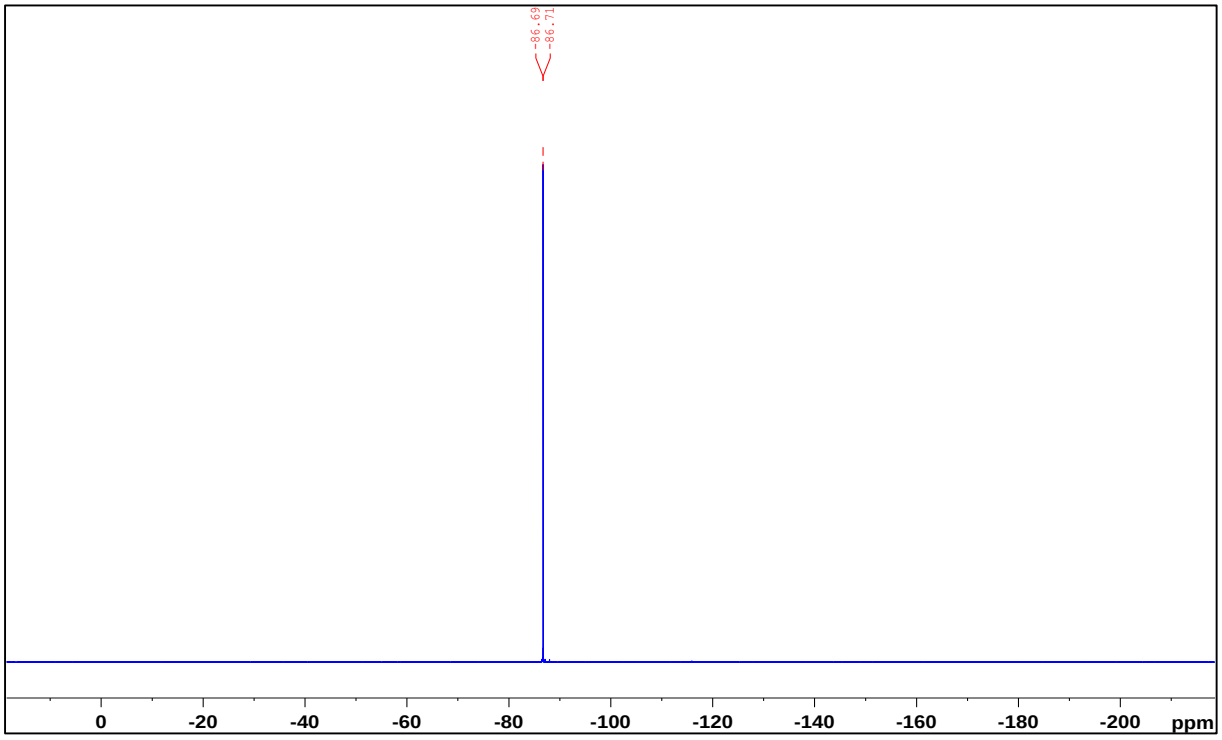
^{13}C NMR ($CDCl_3$)



^{31}P NMR ($CDCl_3$)

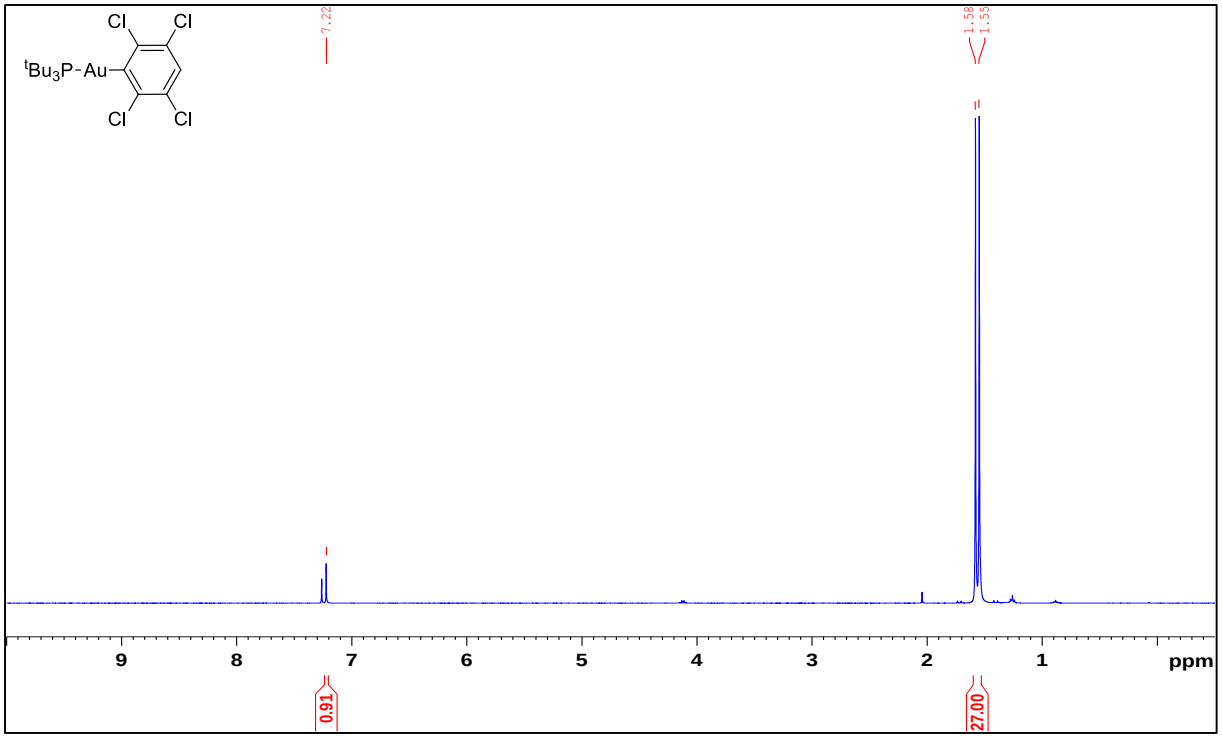


^{19}F NMR ($CDCl_3$)

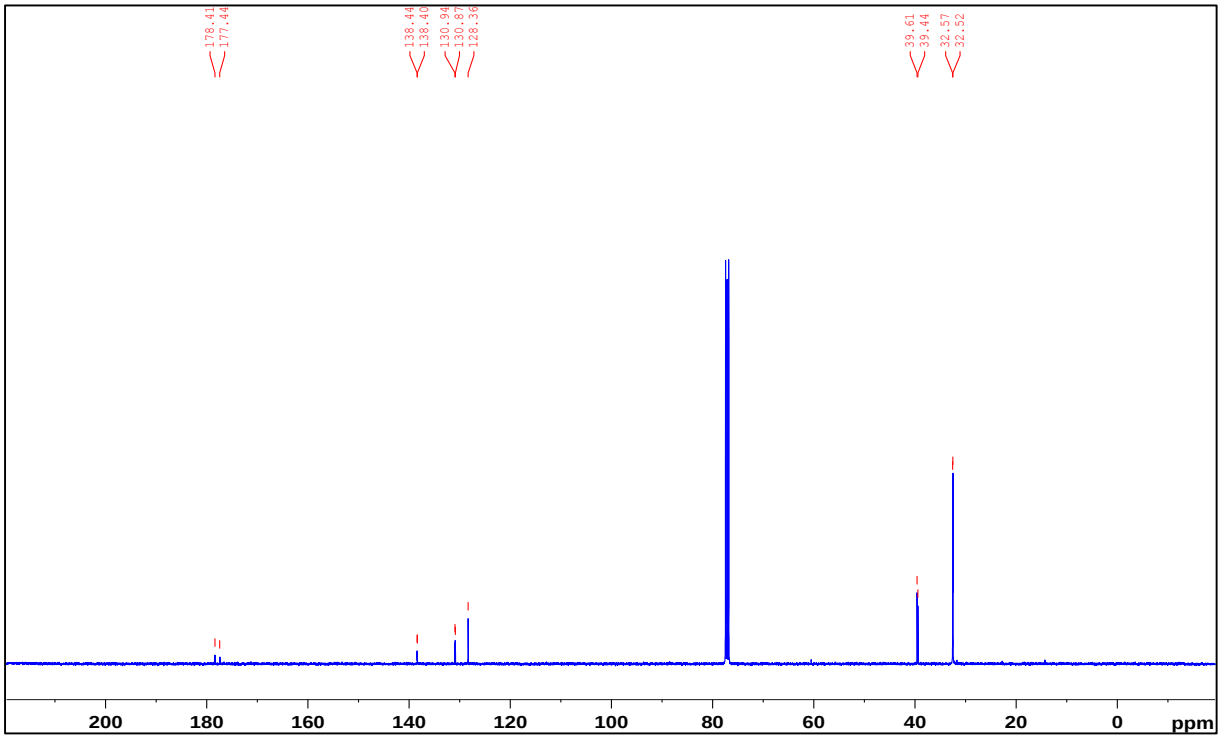


2,3,5,6-Tetrachlorophenyl(tri-tert-butylphosphine)gold(I) ***3ai***

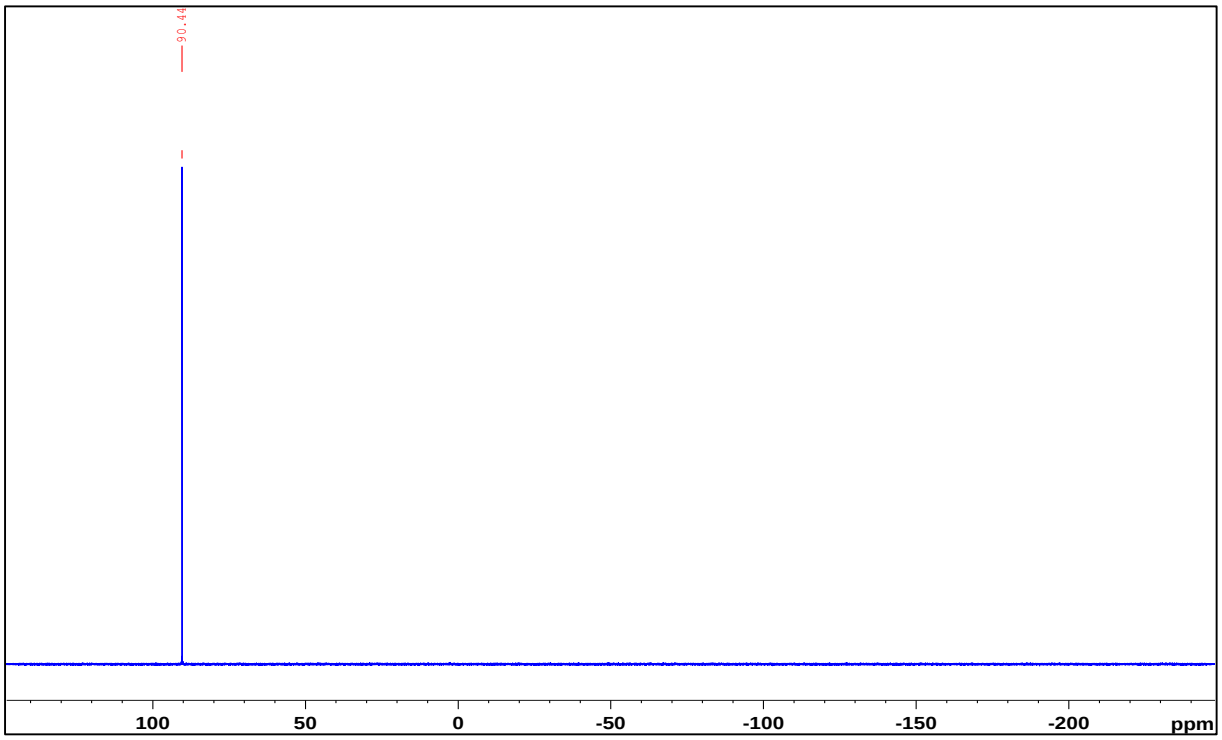
^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)

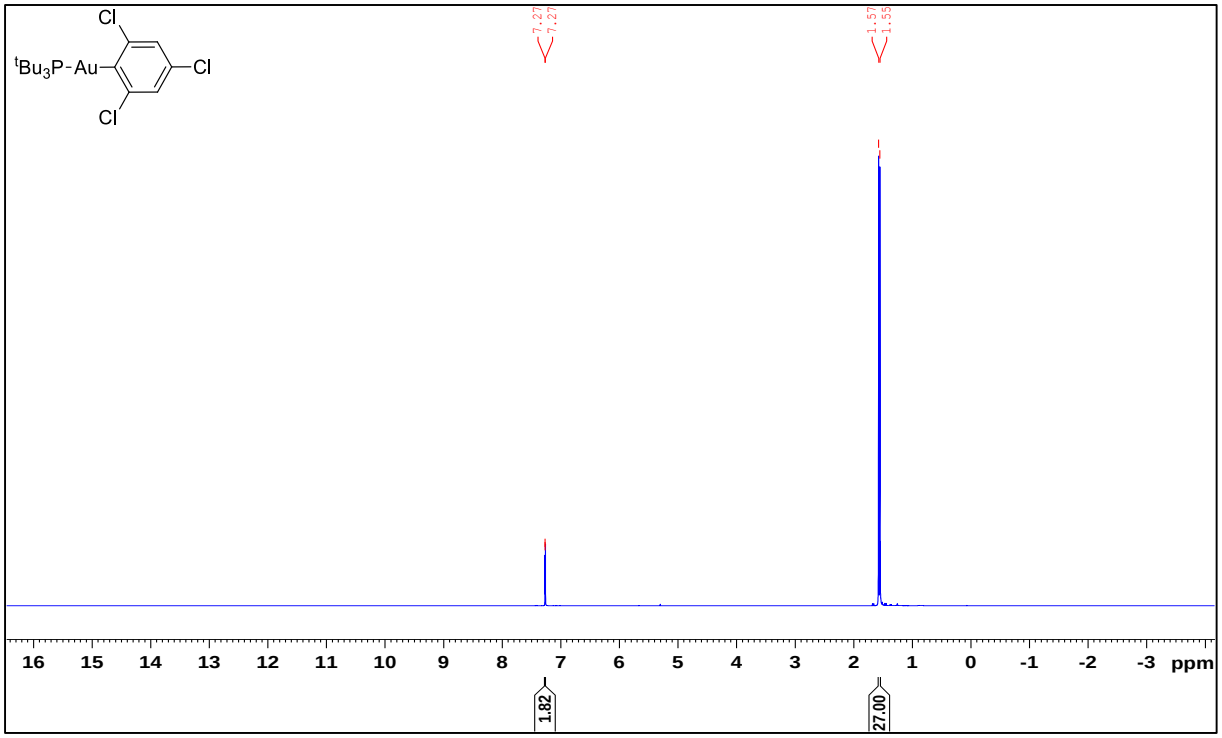


^{31}P NMR ($CDCl_3$)

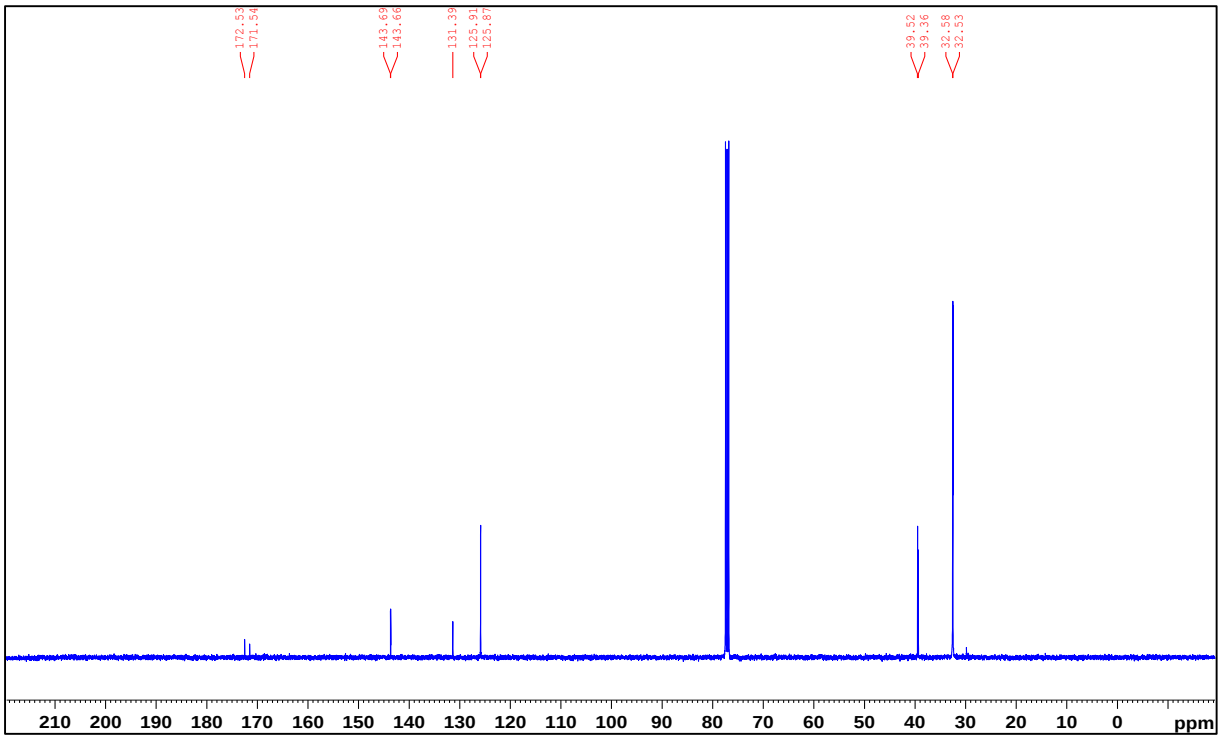


2,4,6-Trichlorophenyl(tri-tert-butylphosphine)gold(I) ***3aj***

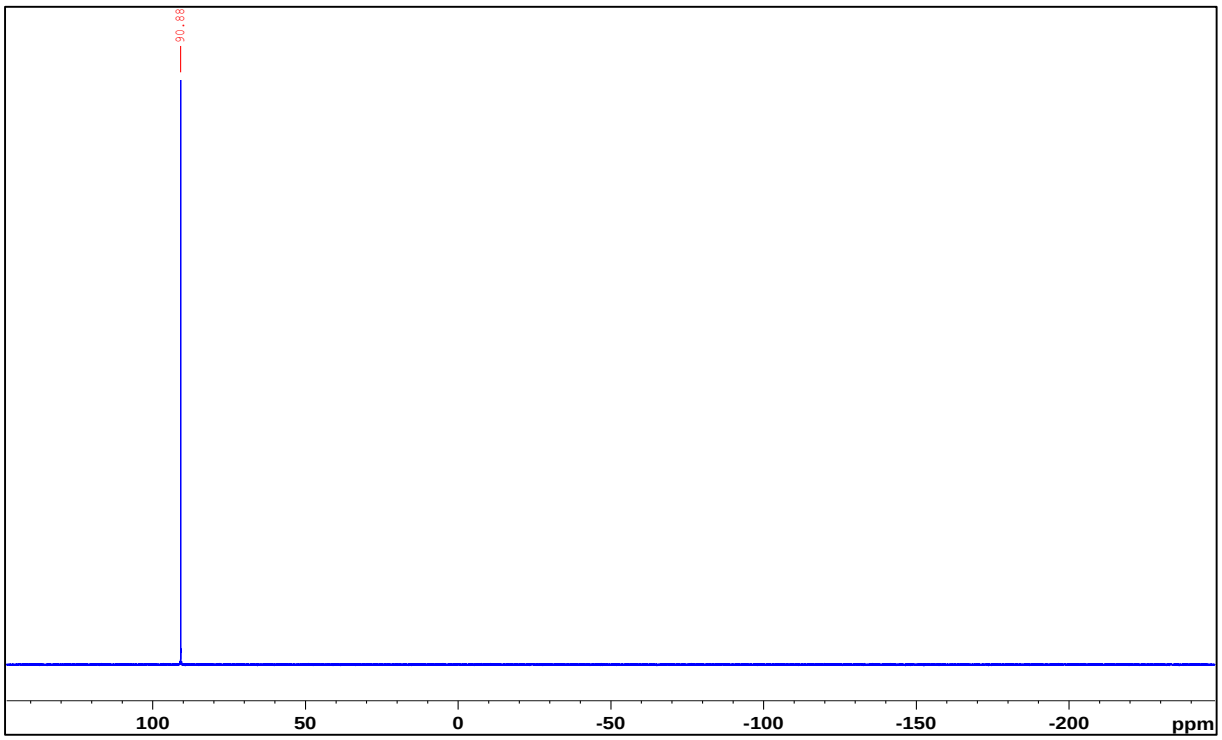
^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)

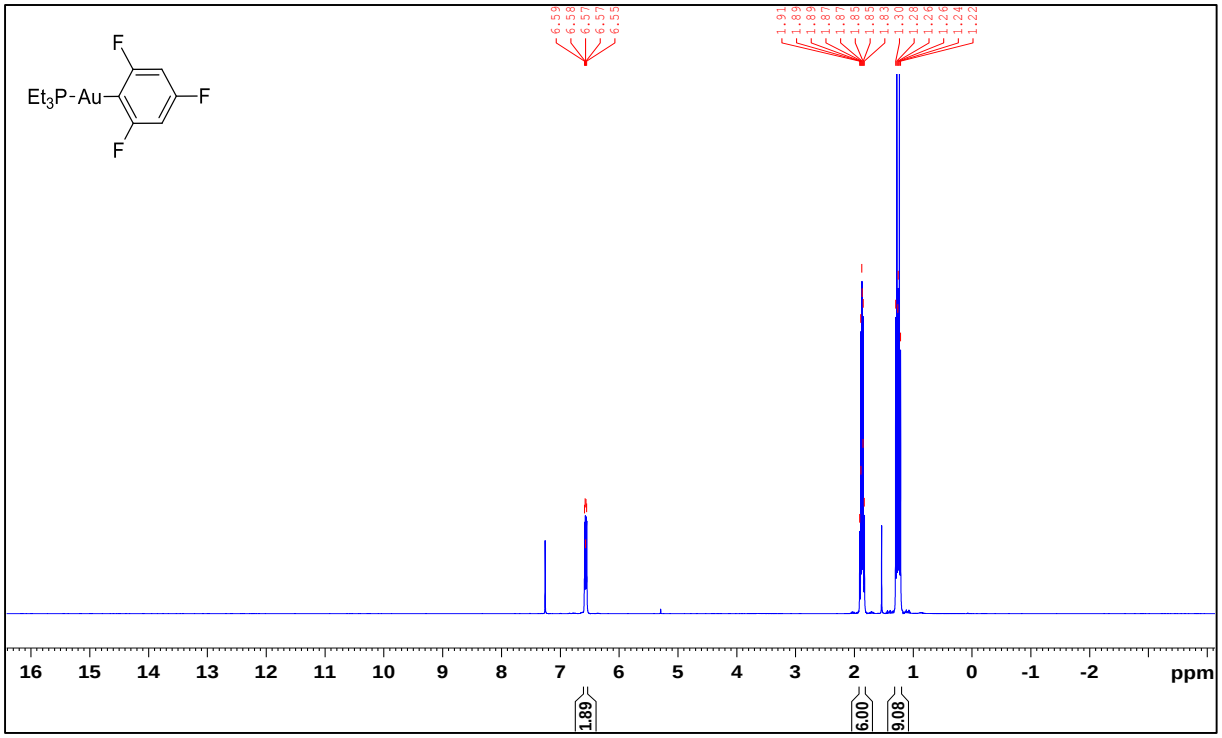


^{31}P NMR ($CDCl_3$)

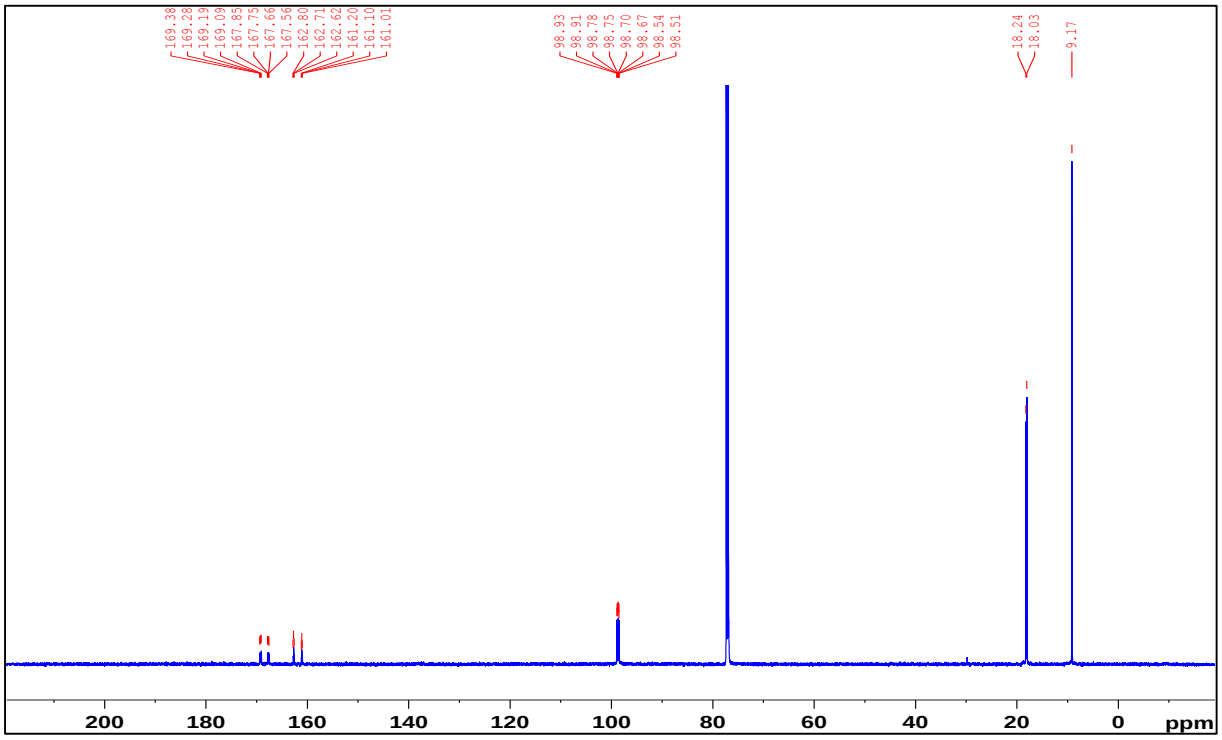


2,4,6-Trifluorophenyl(triethylphosphine)gold(I) ***3bd***

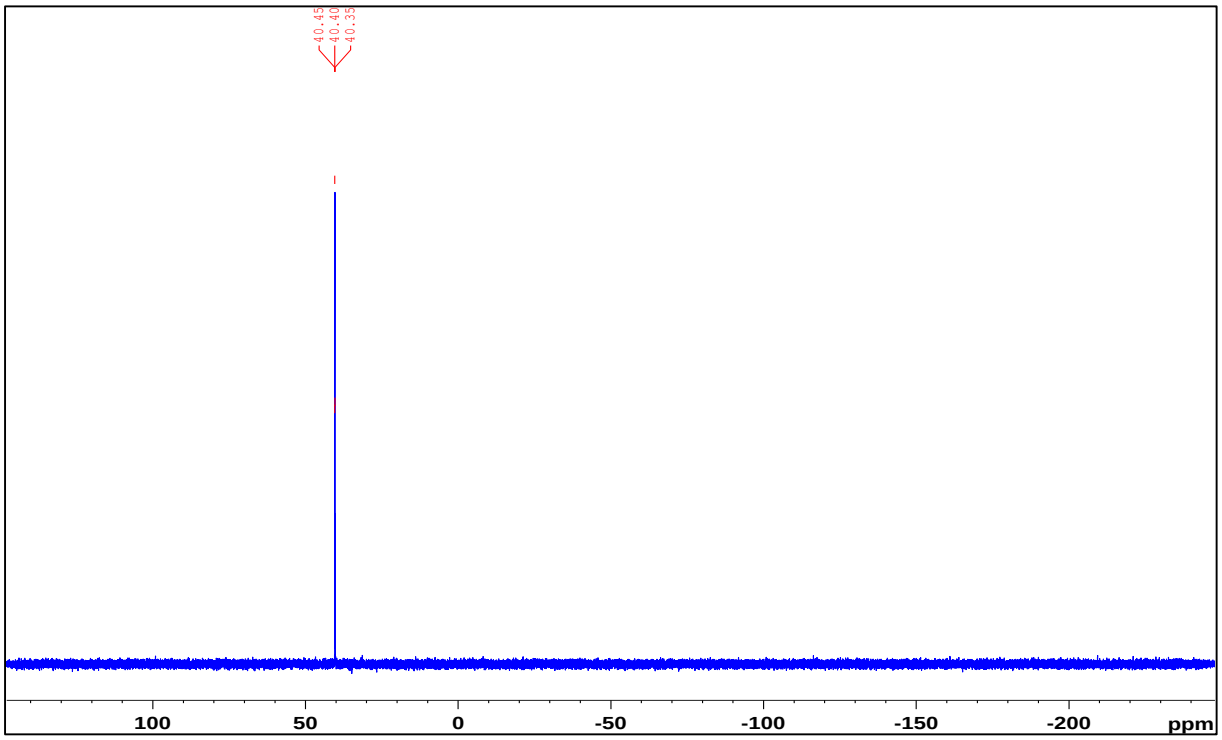
^{1}H NMR ($CDCl_3$)



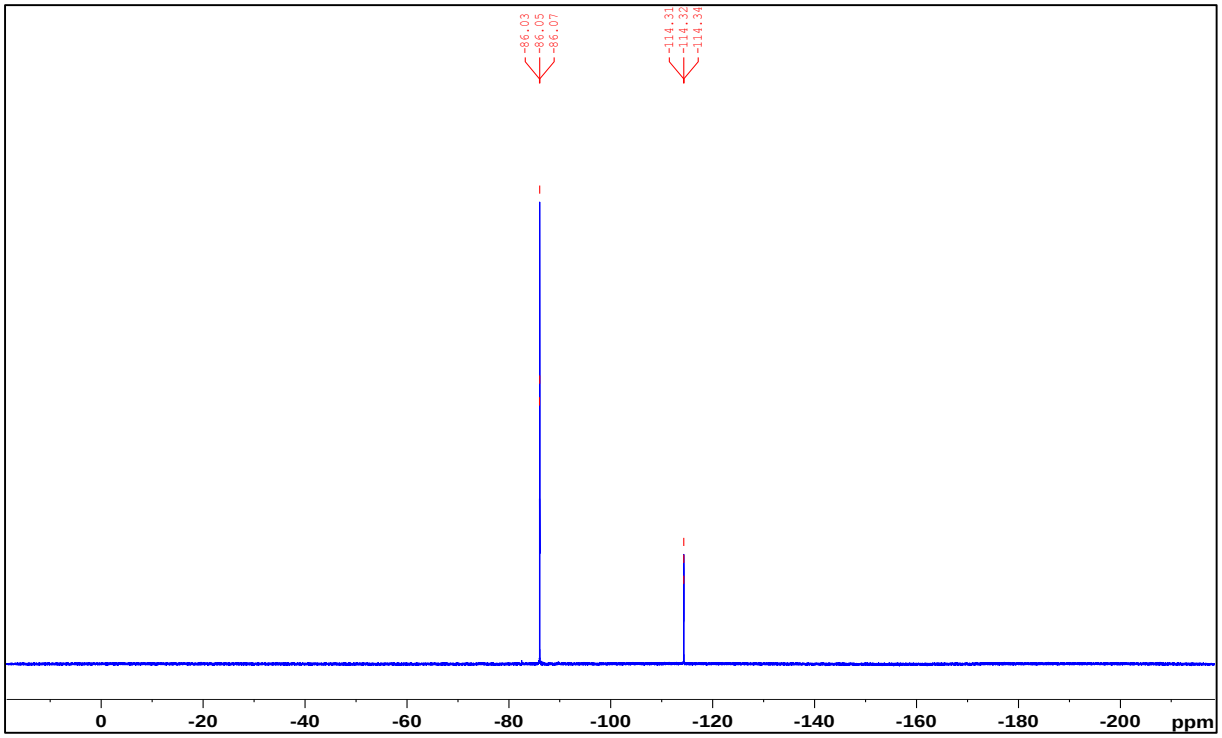
^{13}C NMR ($CDCl_3$)



^{31}P NMR ($CDCl_3$)

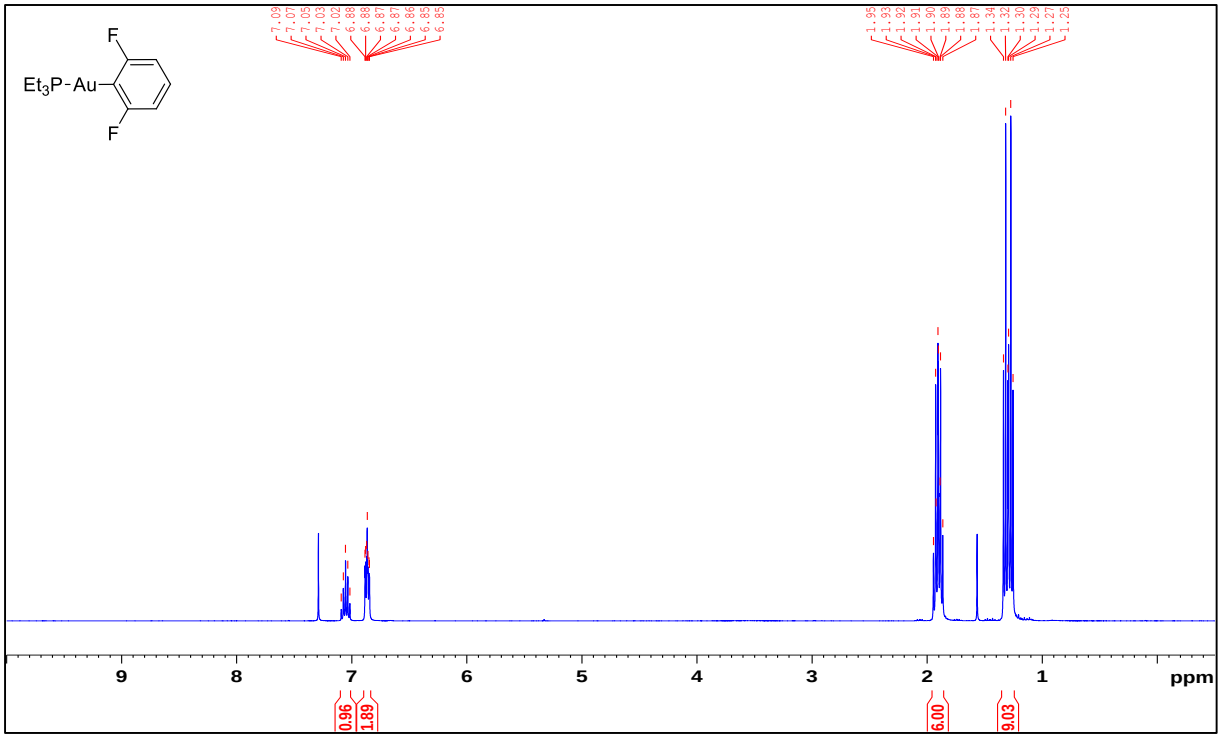


^{19}F NMR ($CDCl_3$)

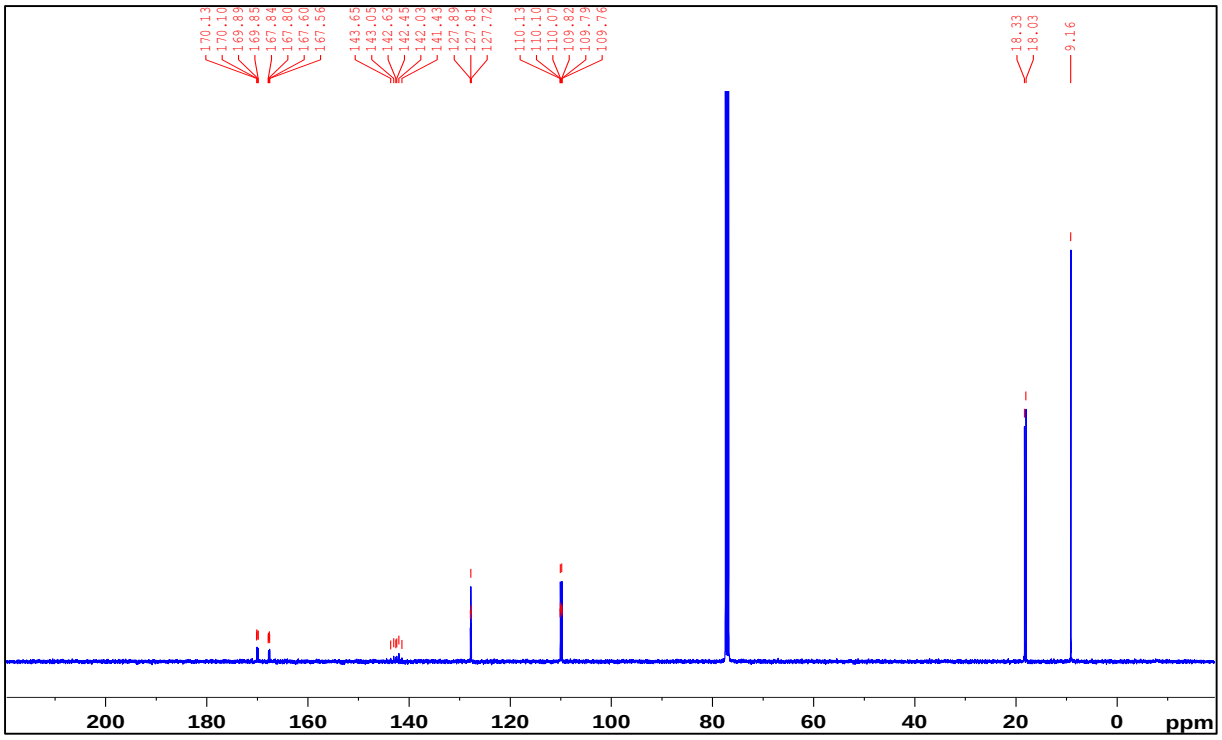


2,6-Difluorophenyl(triethylphosphine)gold(I) ***3be***

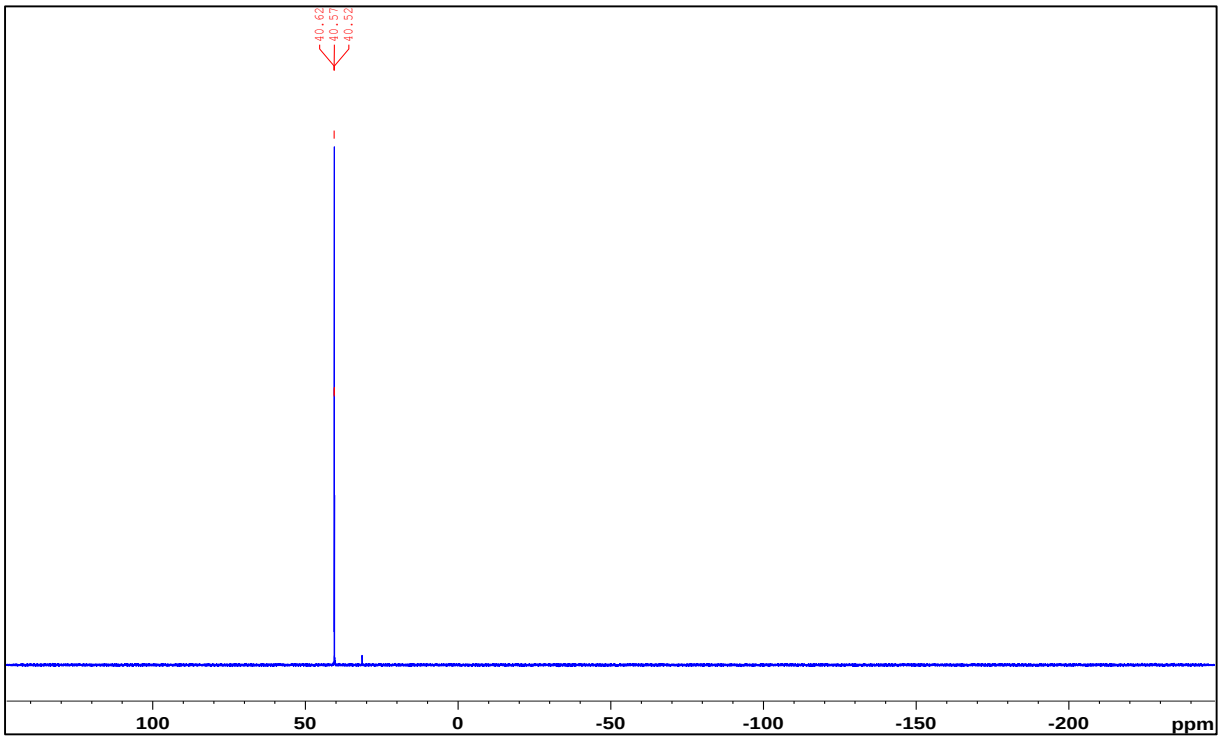
^{1}H NMR ($CDCl_3$)



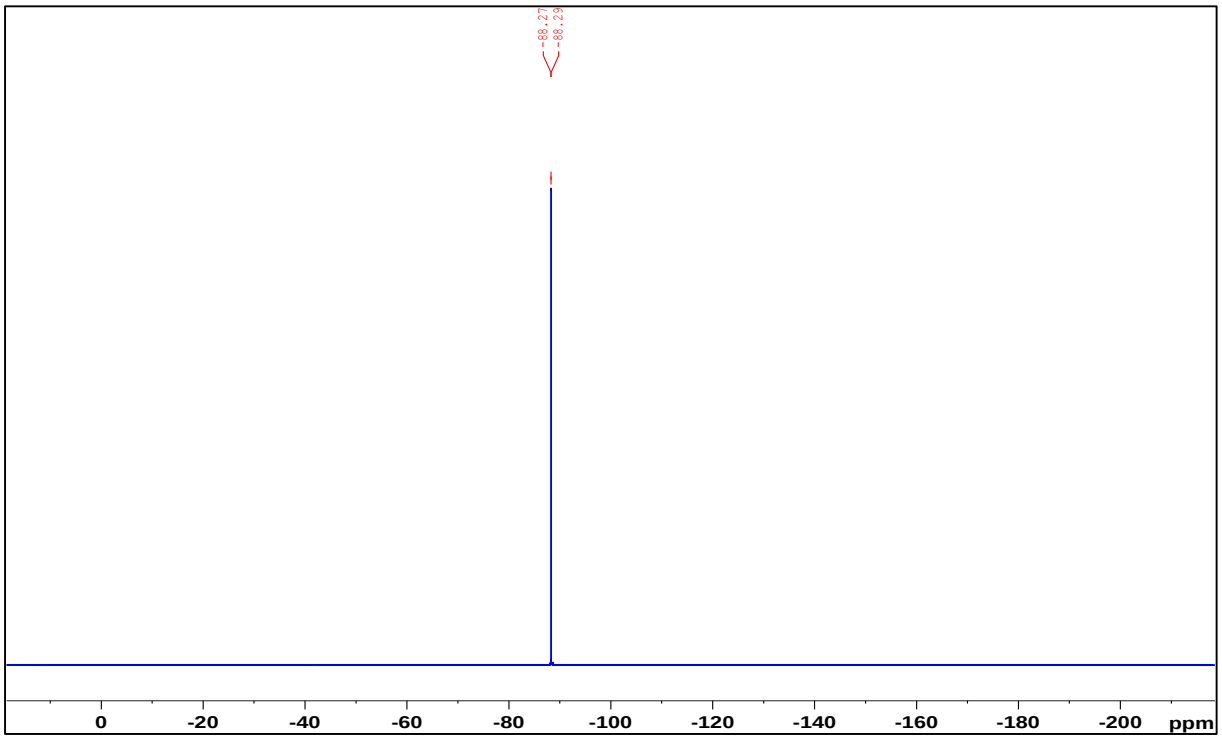
^{13}C NMR ($CDCl_3$)



^{31}P NMR ($CDCl_3$)

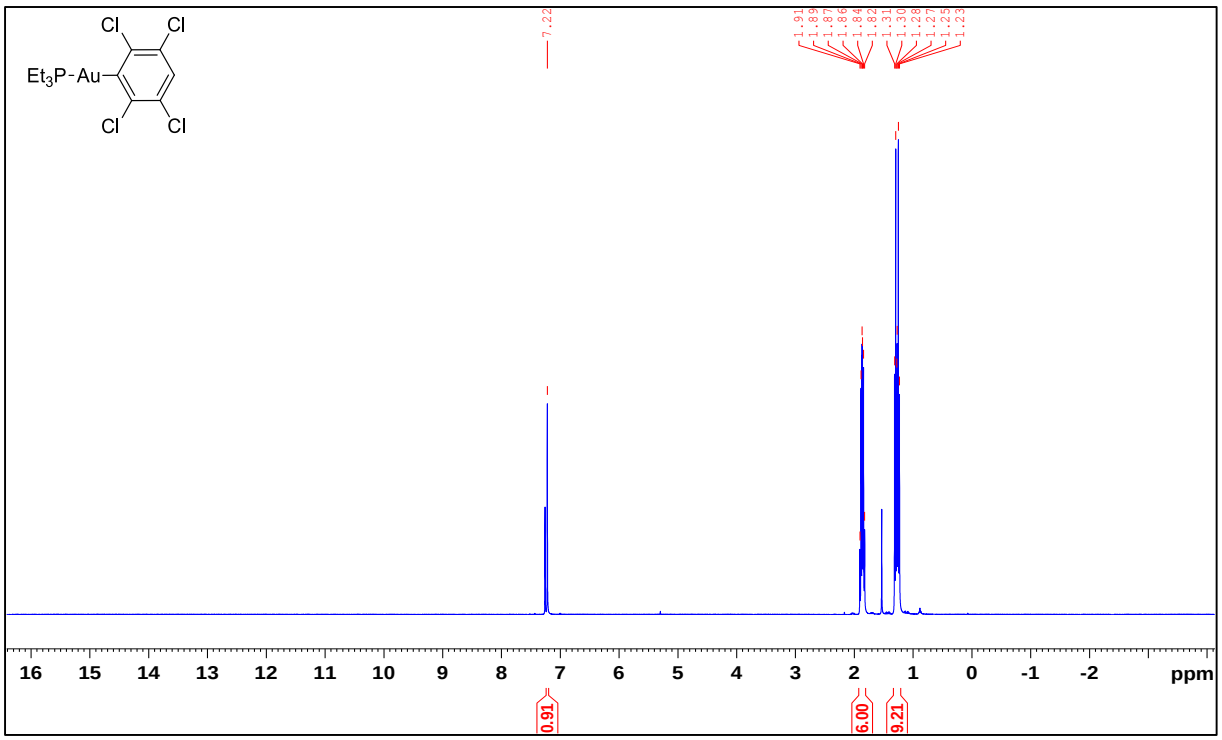


^{19}F NMR ($CDCl_3$)

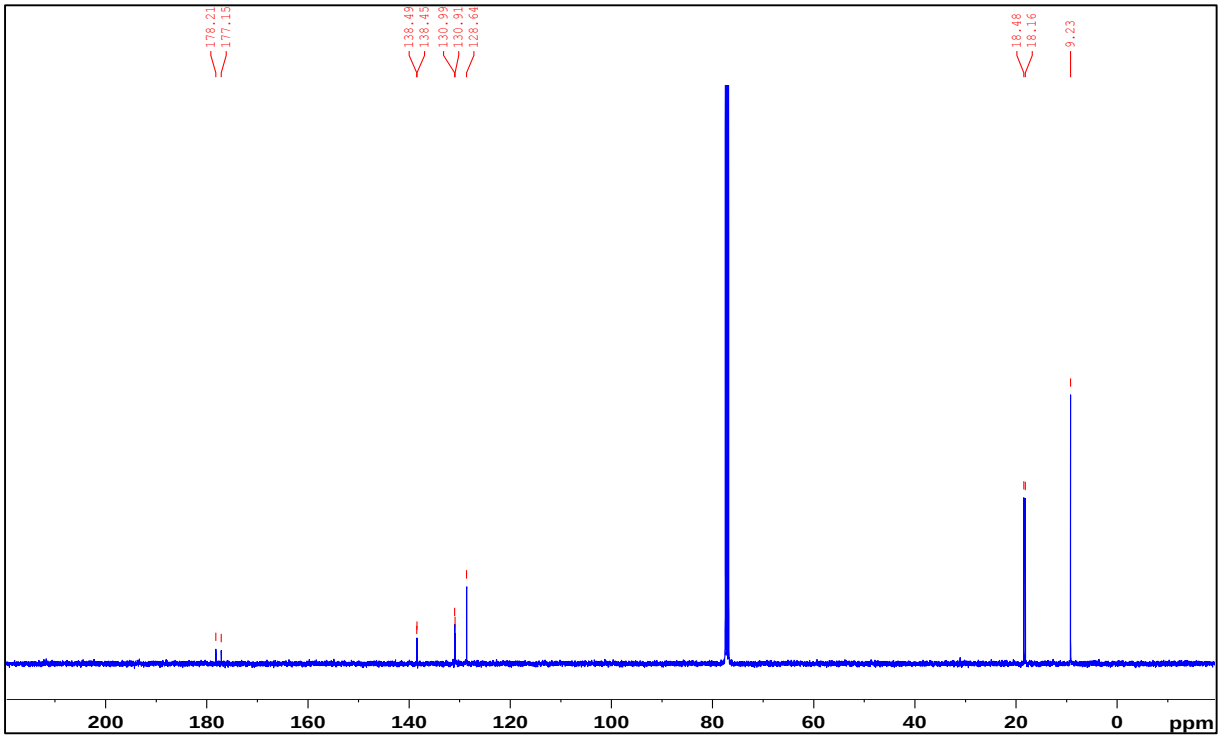


2,3,5,6-Tetrachlorophenyl(triethylphosphine)gold(I) ***3bi***

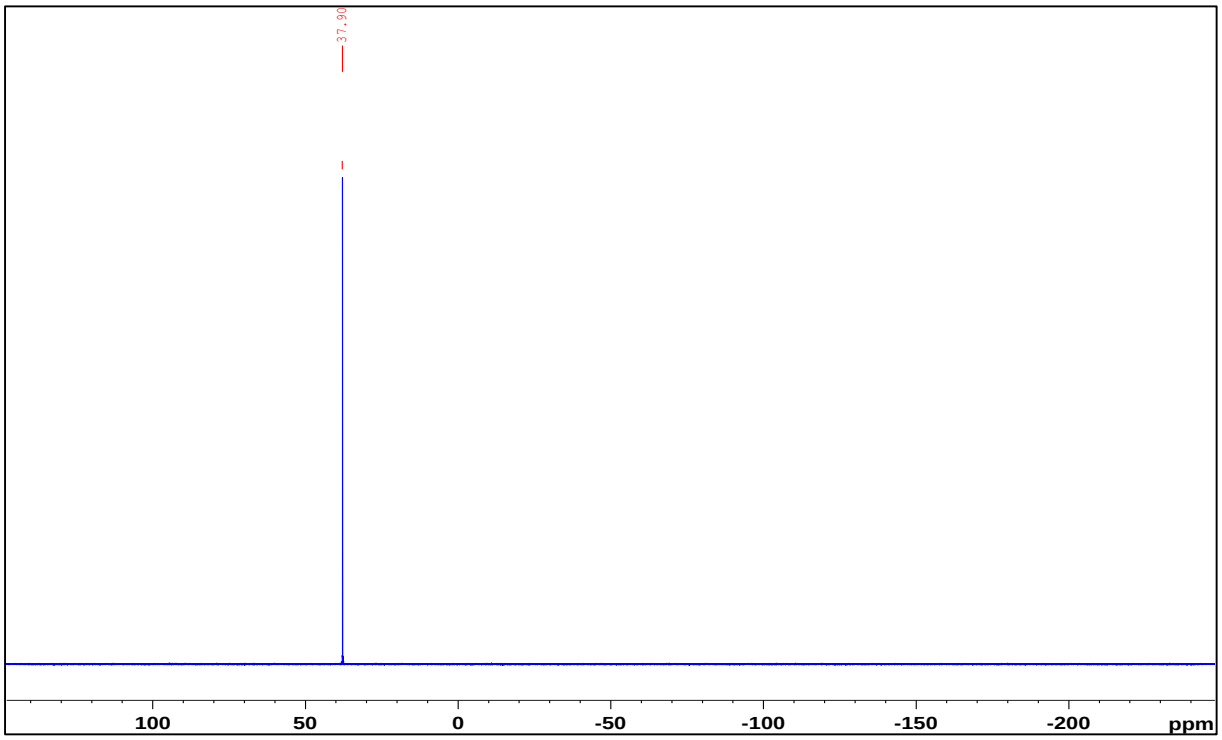
^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)

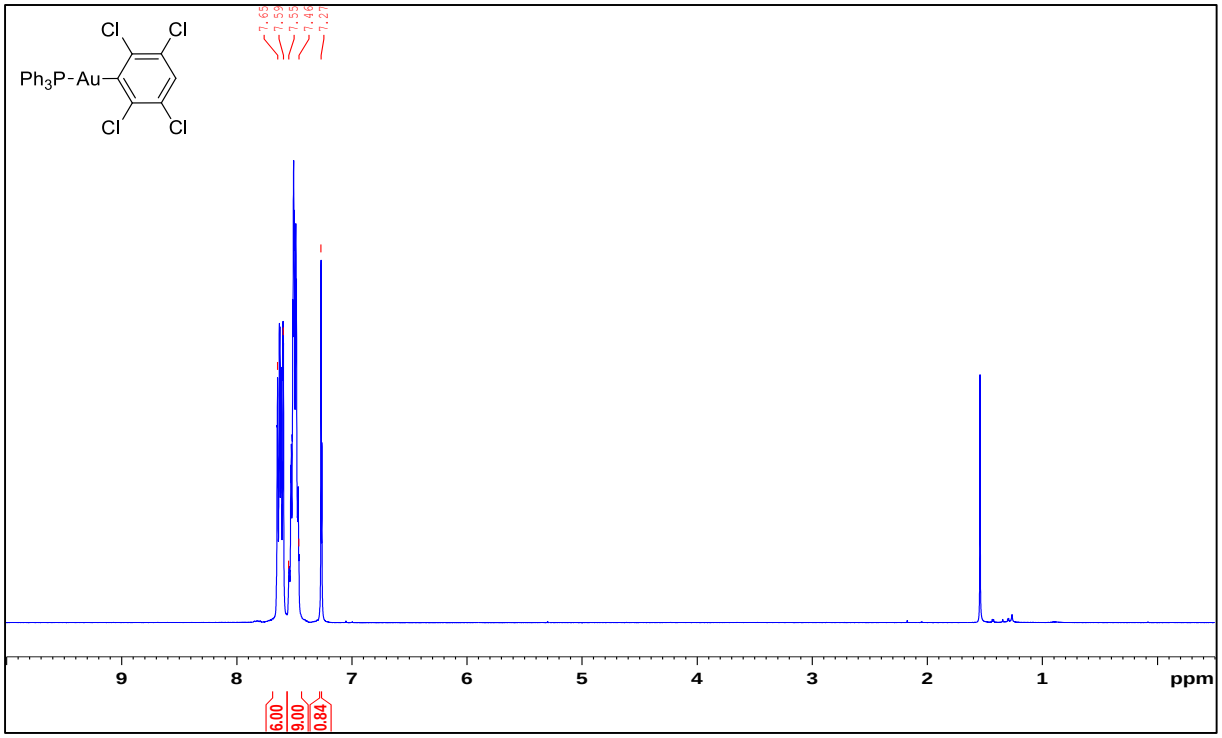


^{31}P NMR ($CDCl_3$)

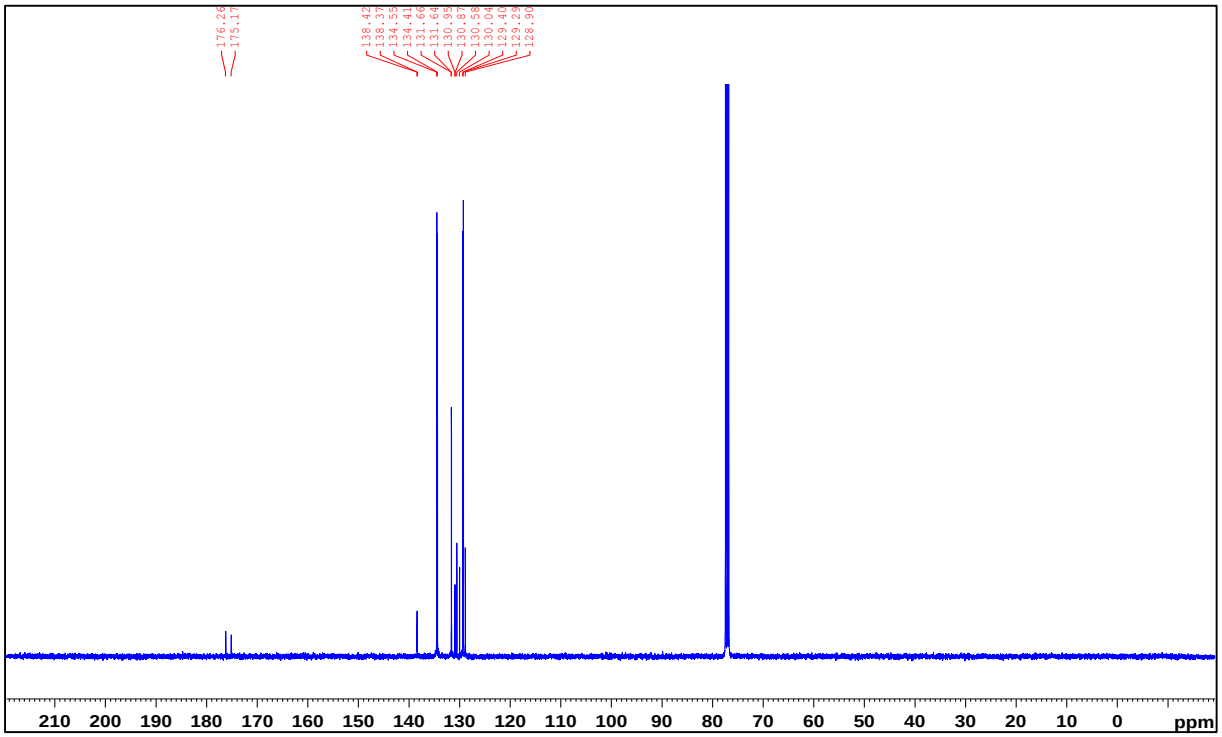


2,3,5,6-Tetrachlorophenyl(triphenylphosphine)gold(I) ***3ci***

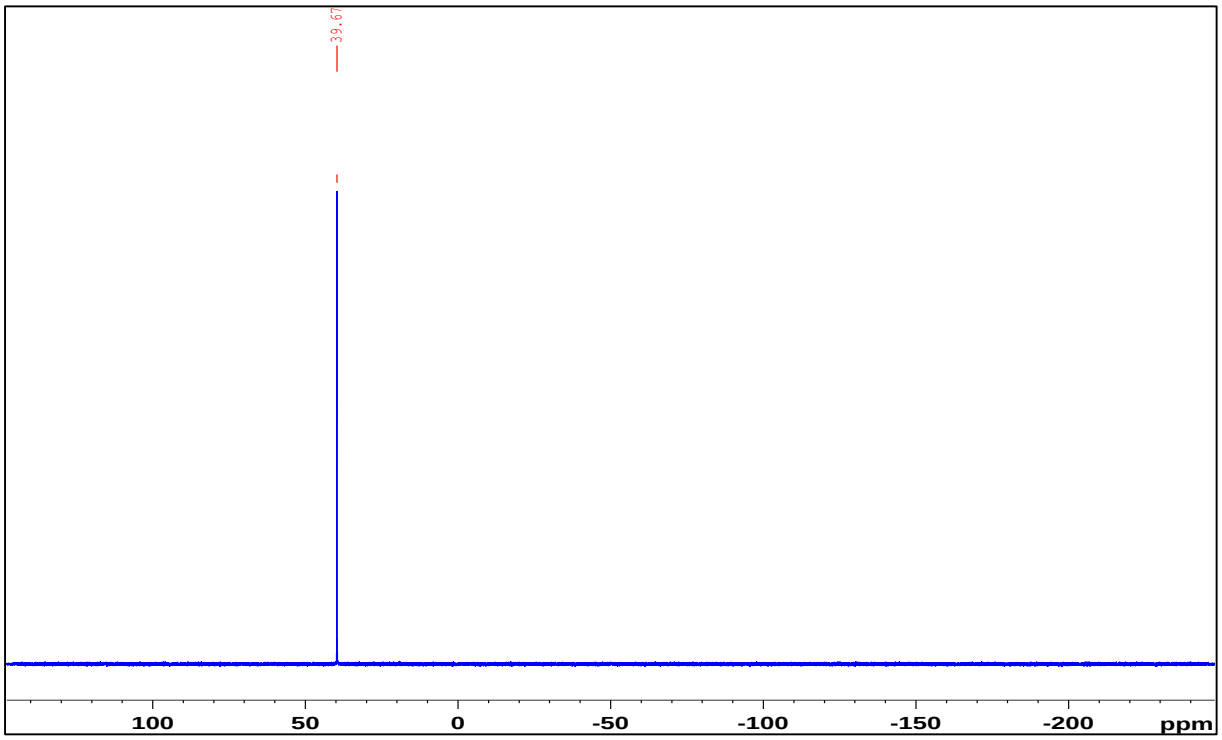
^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)

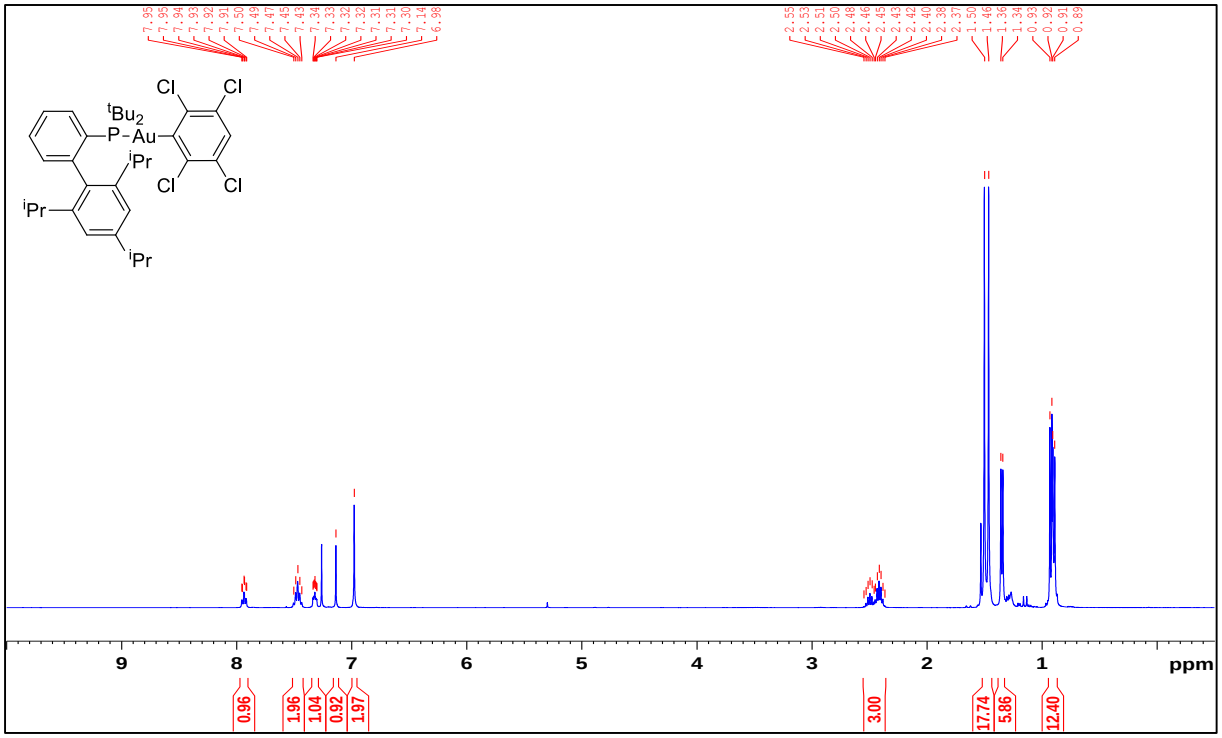


^{31}P NMR ($CDCl_3$)

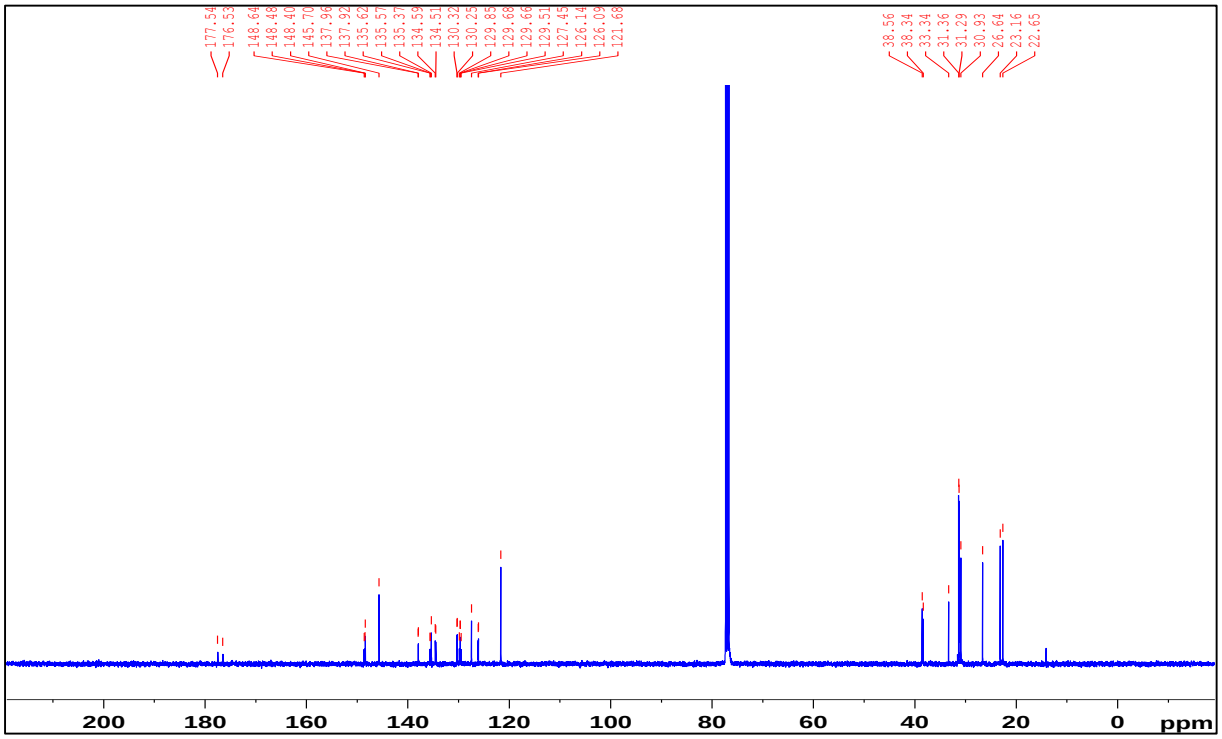


2,3,5,6-Tetrachlorophenyl(^{t}*BuXPhos)gold(I)* ***3di***

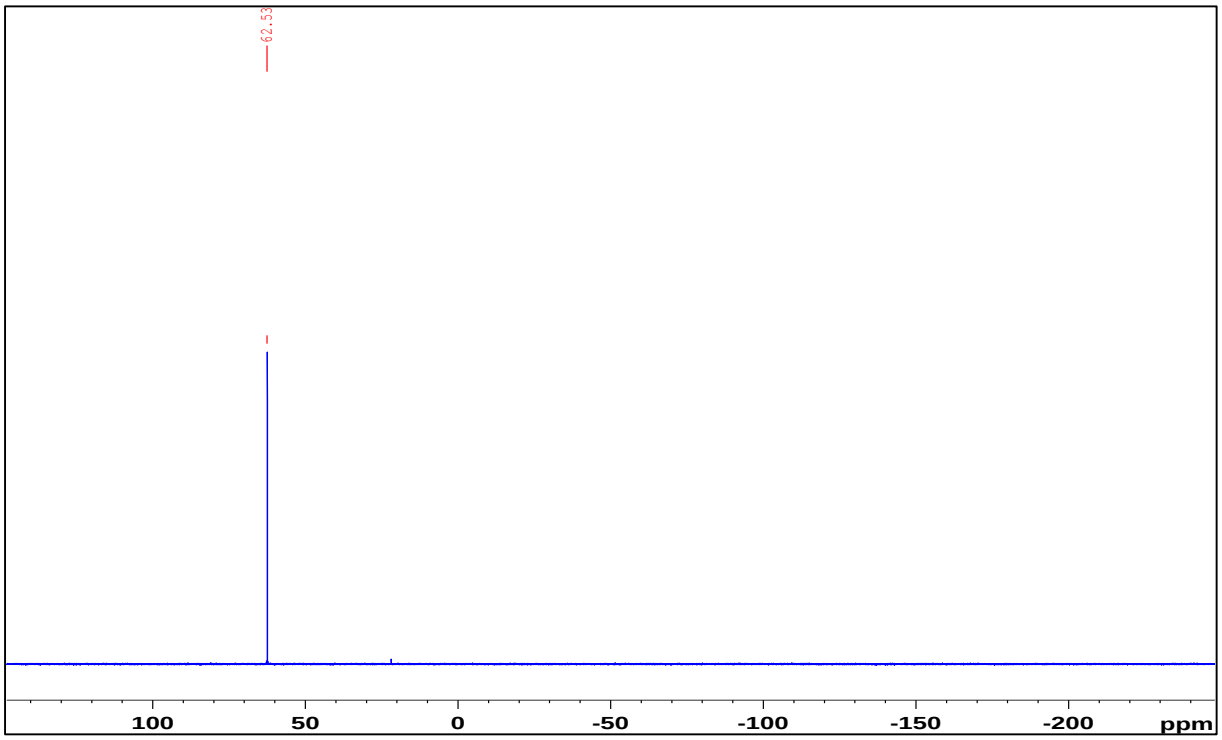
^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)

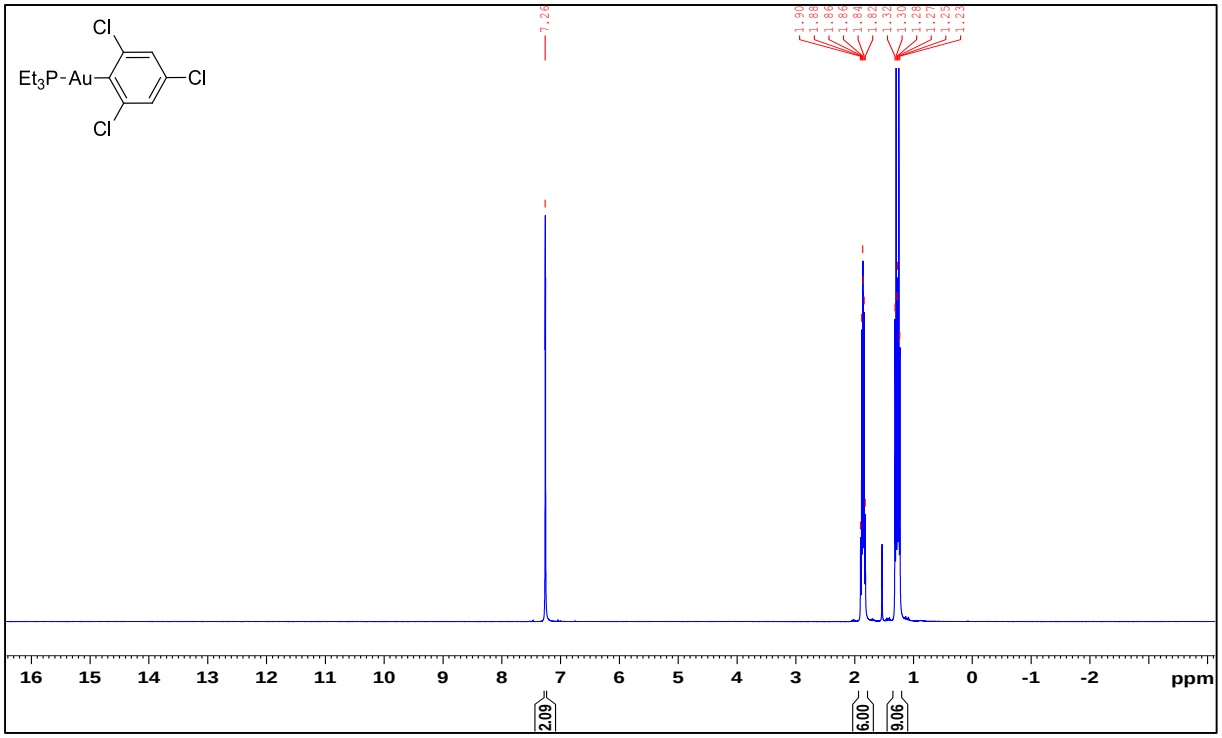


^{31}P NMR ($CDCl_3$)

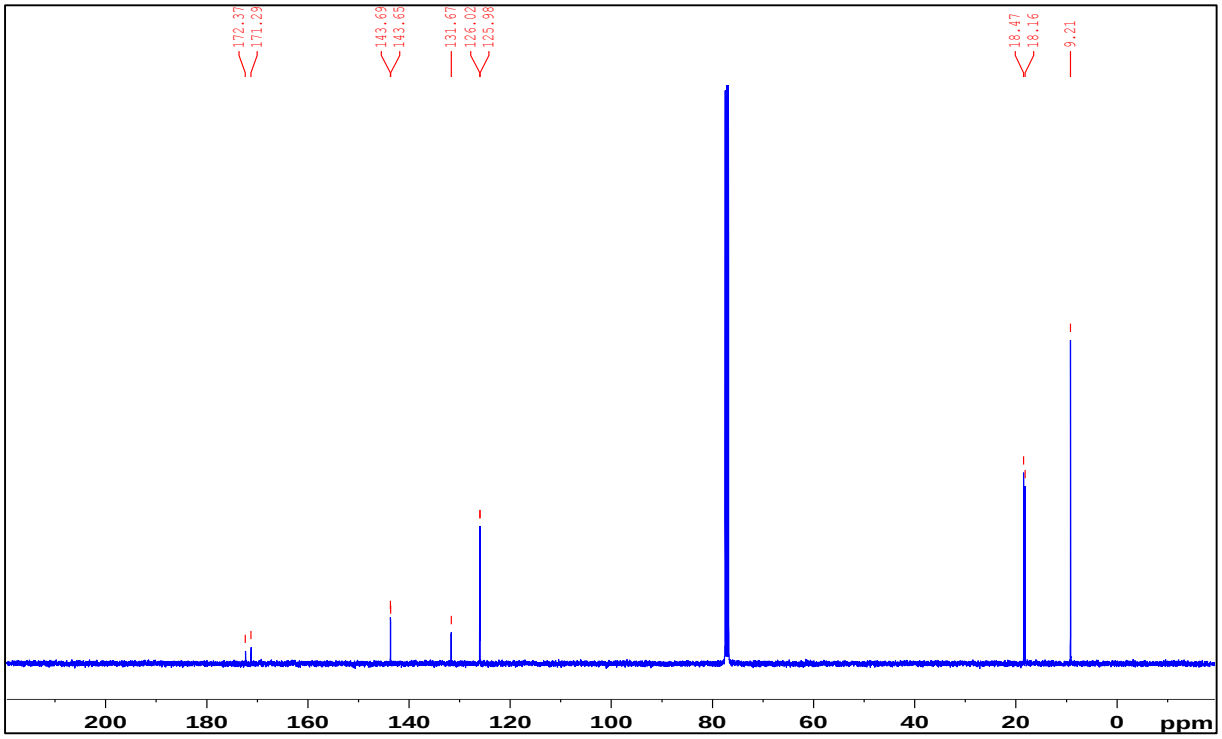


2,4,6-Trichlorophenyl(triethylphosphine)gold(I) ***3bj***

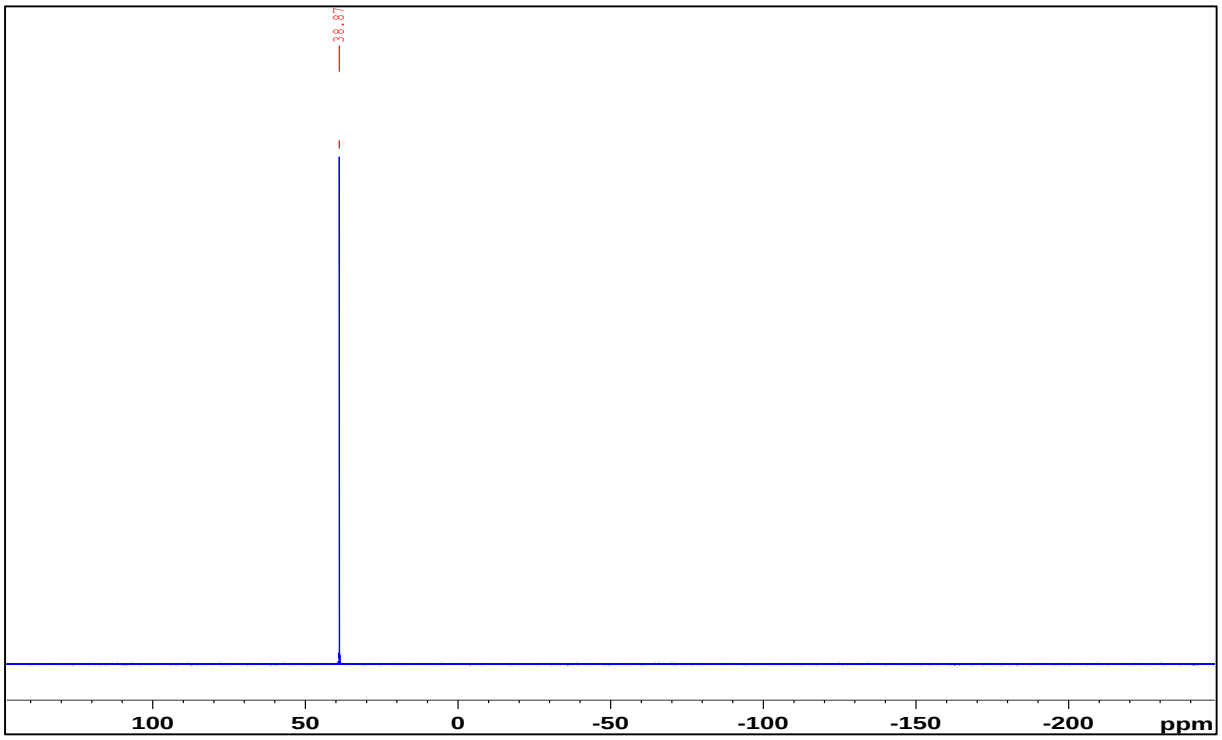
^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)

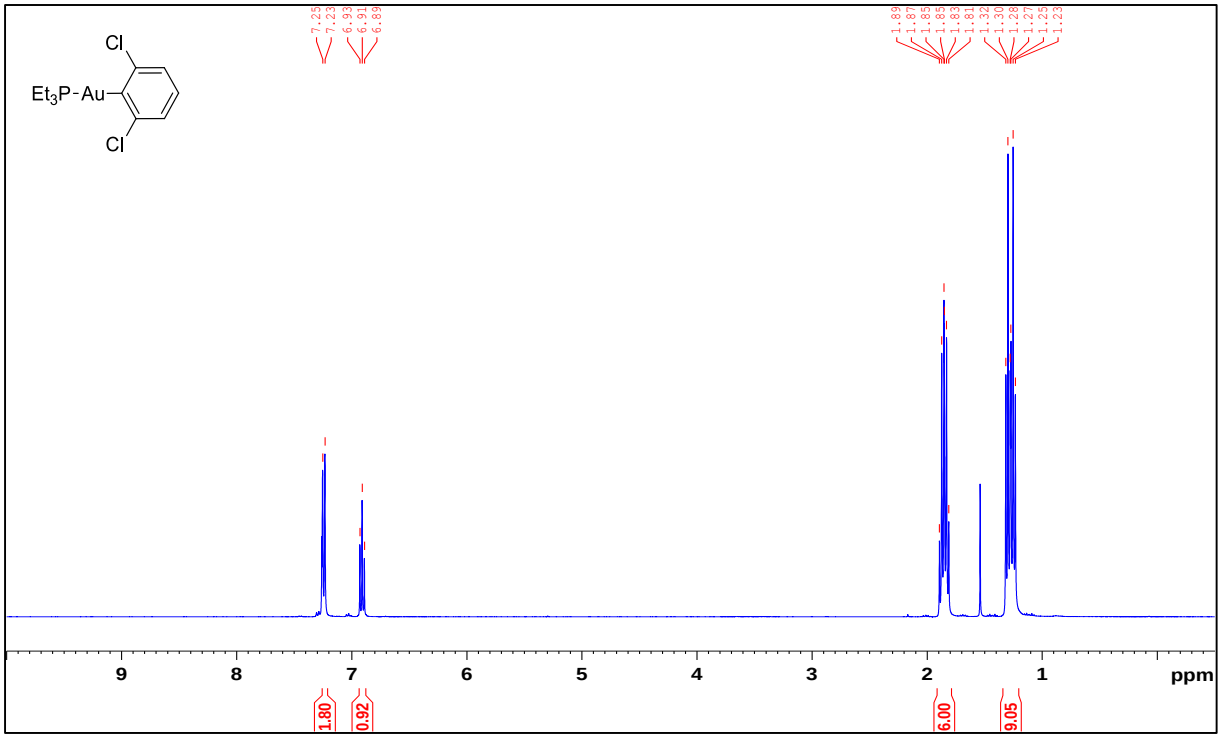


^{31}P NMR ($CDCl_3$)

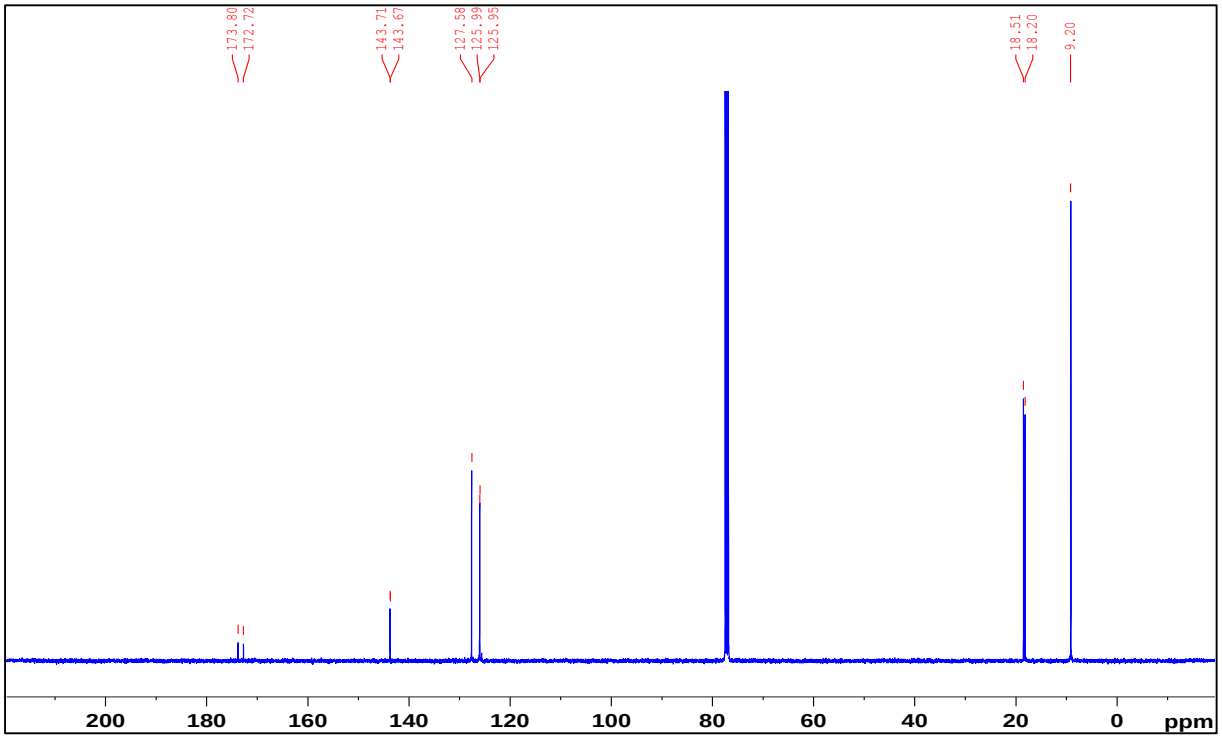


2,6-Dichlorophenyl(triethylphosphine)gold(I) ***3bk***

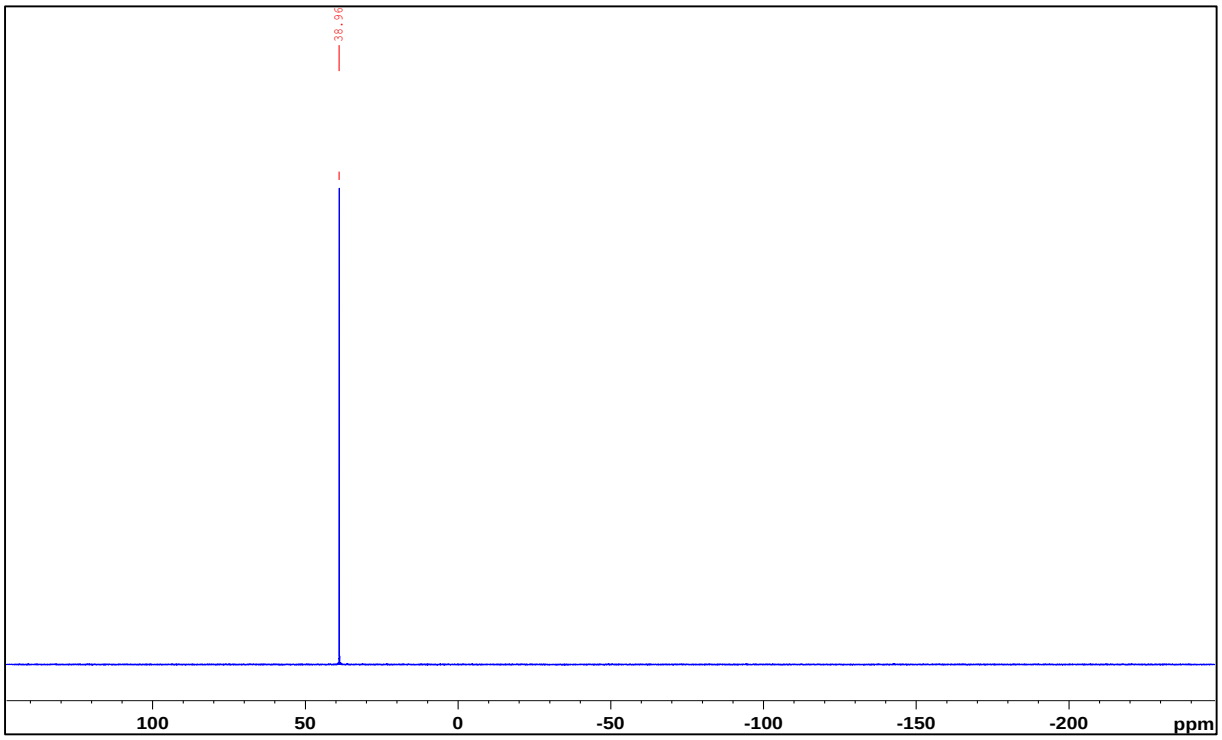
^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)

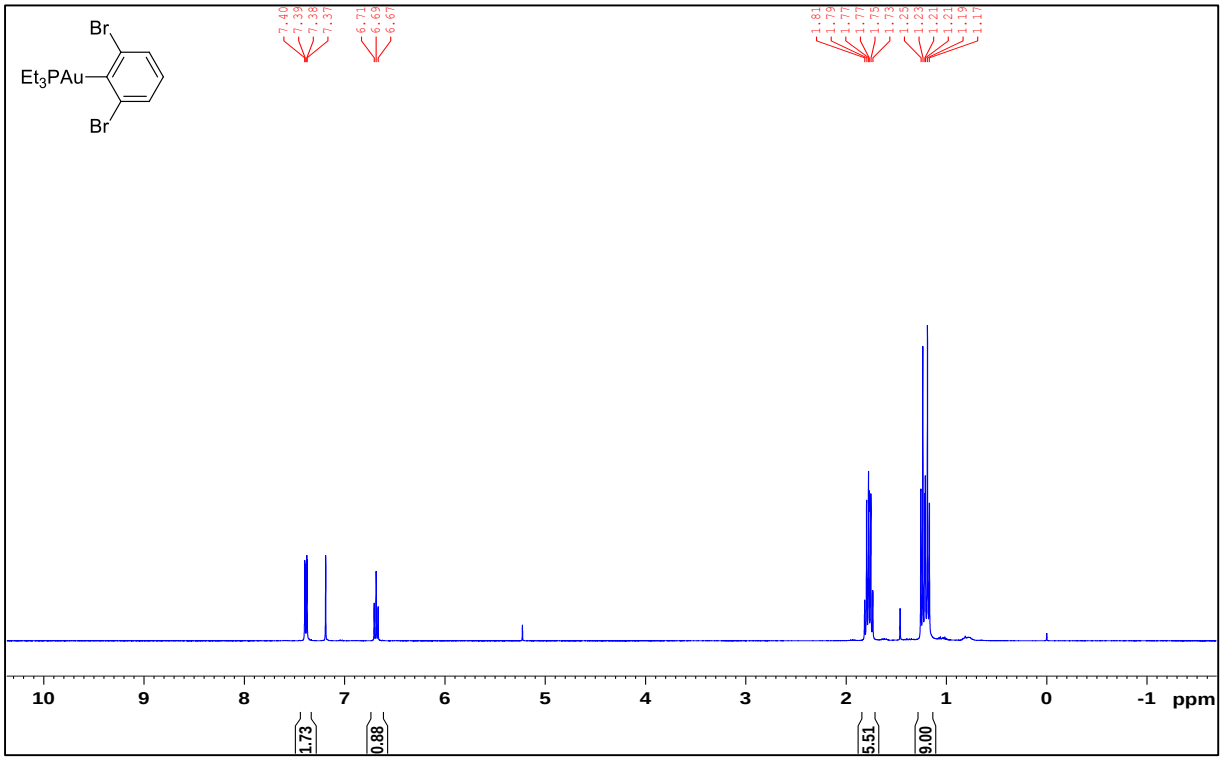


^{31}P NMR ($CDCl_3$)

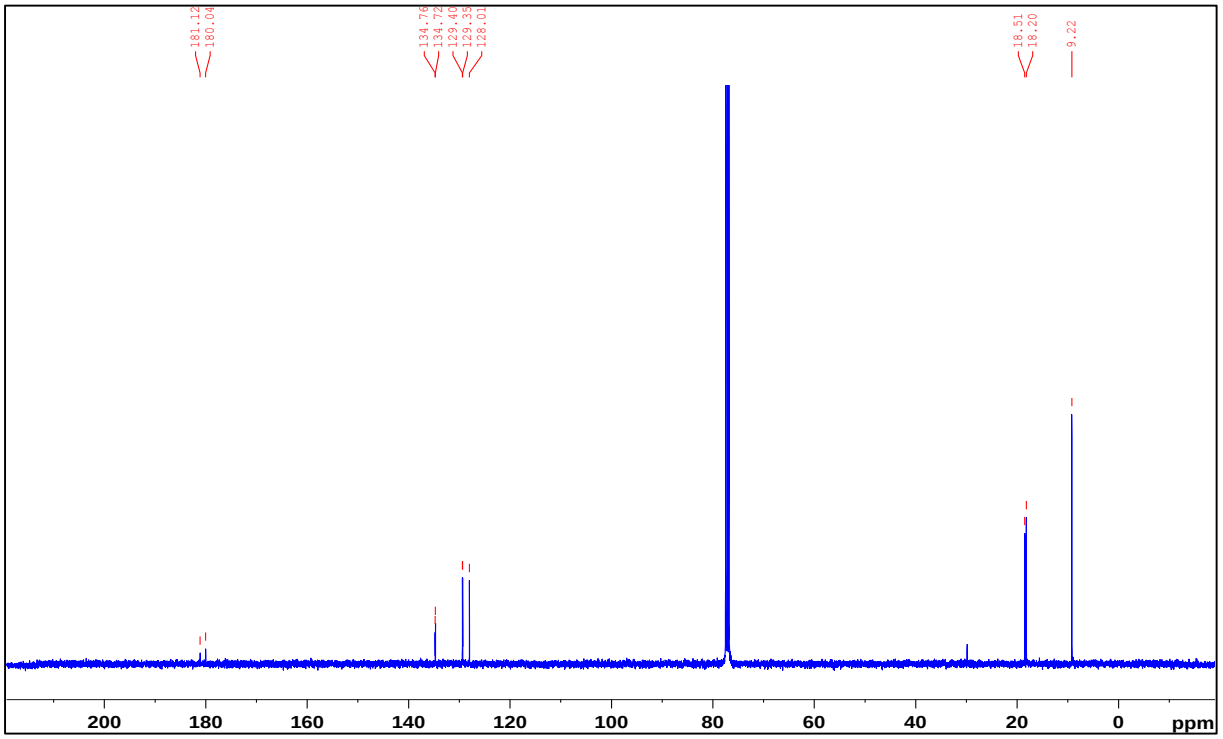


2,6-Dibromophenyl(triethylphosphine)gold(I) ***3bo***

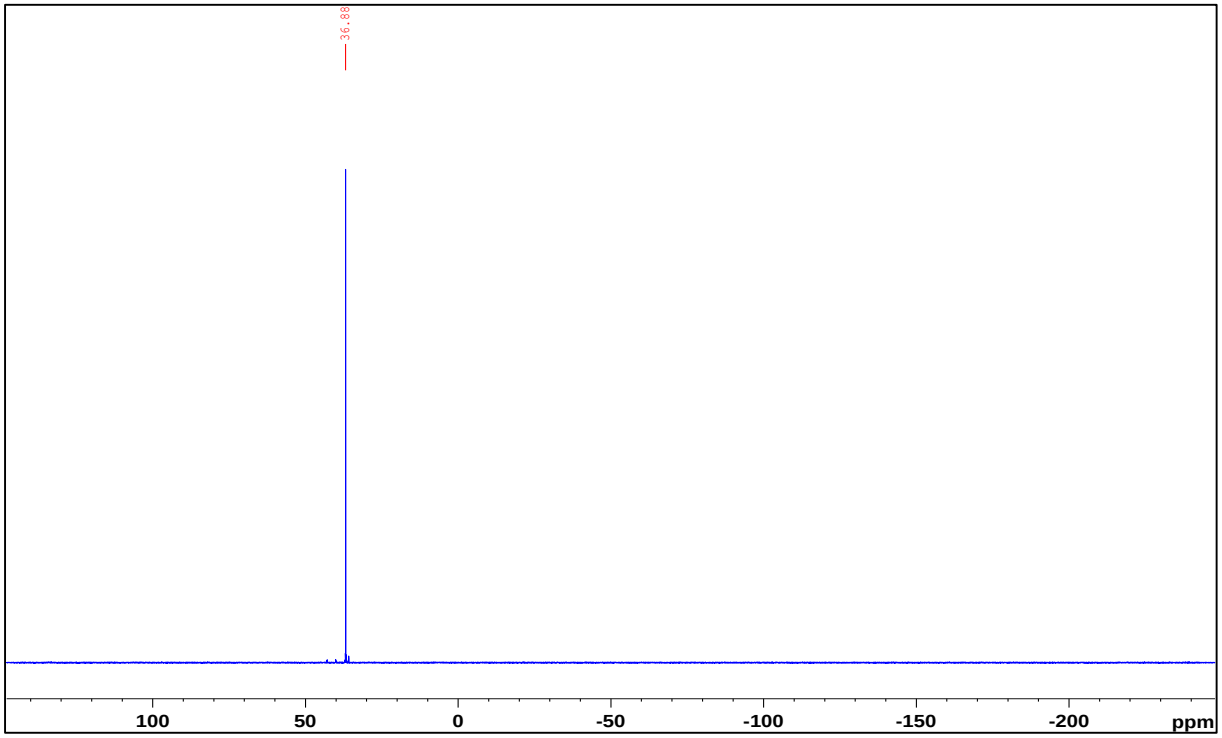
^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)

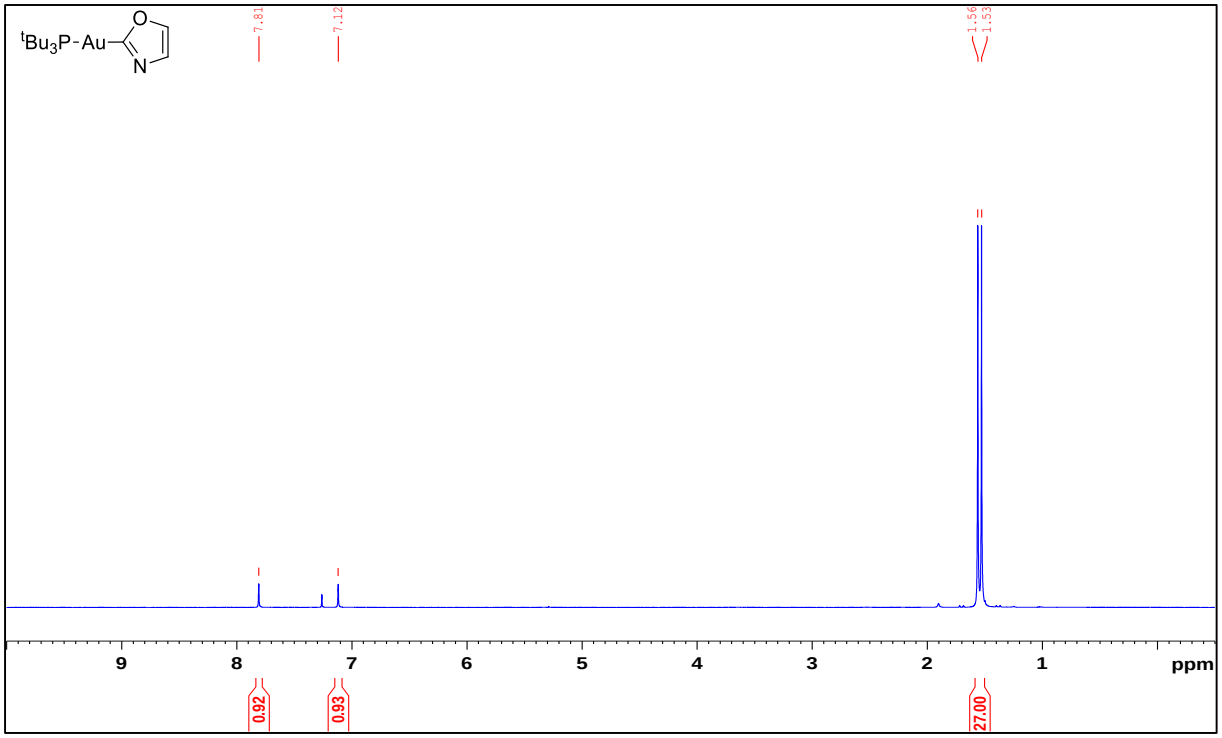


^{31} P NMR ($CDCl_3$)

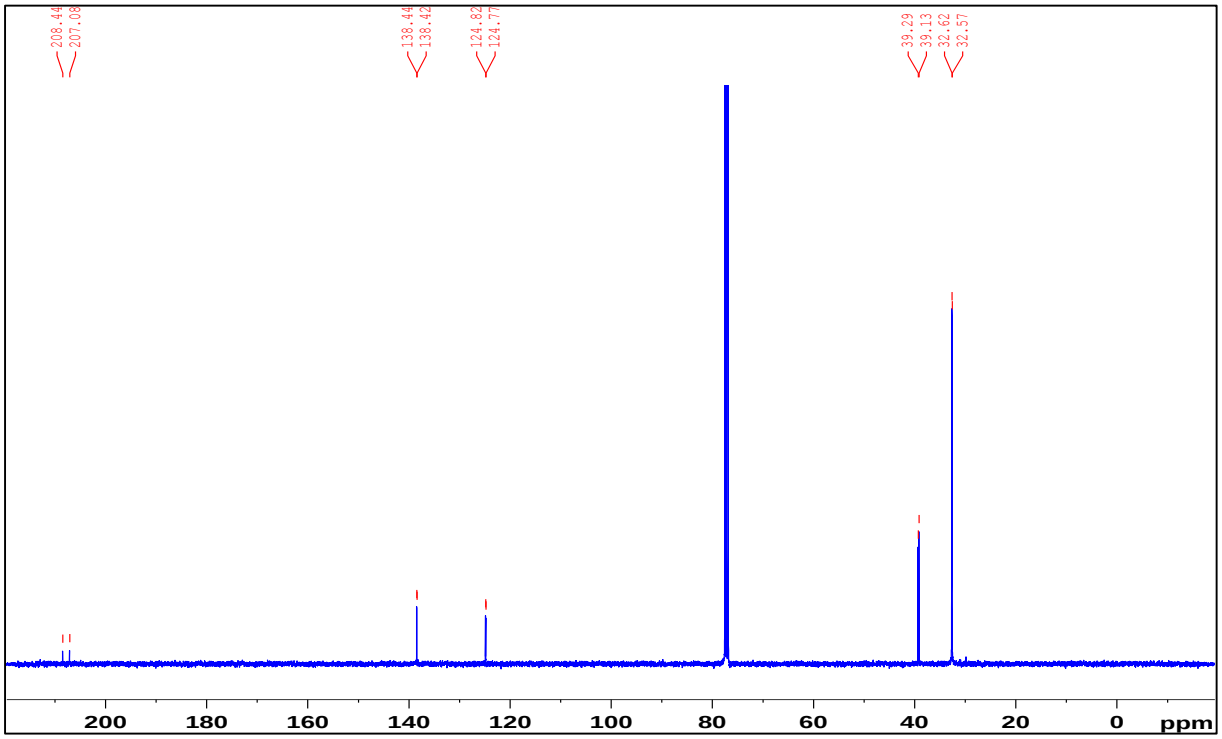


Oxazol-2-yl(tri-tert-butylphosphine)gold(I) ***5aa***

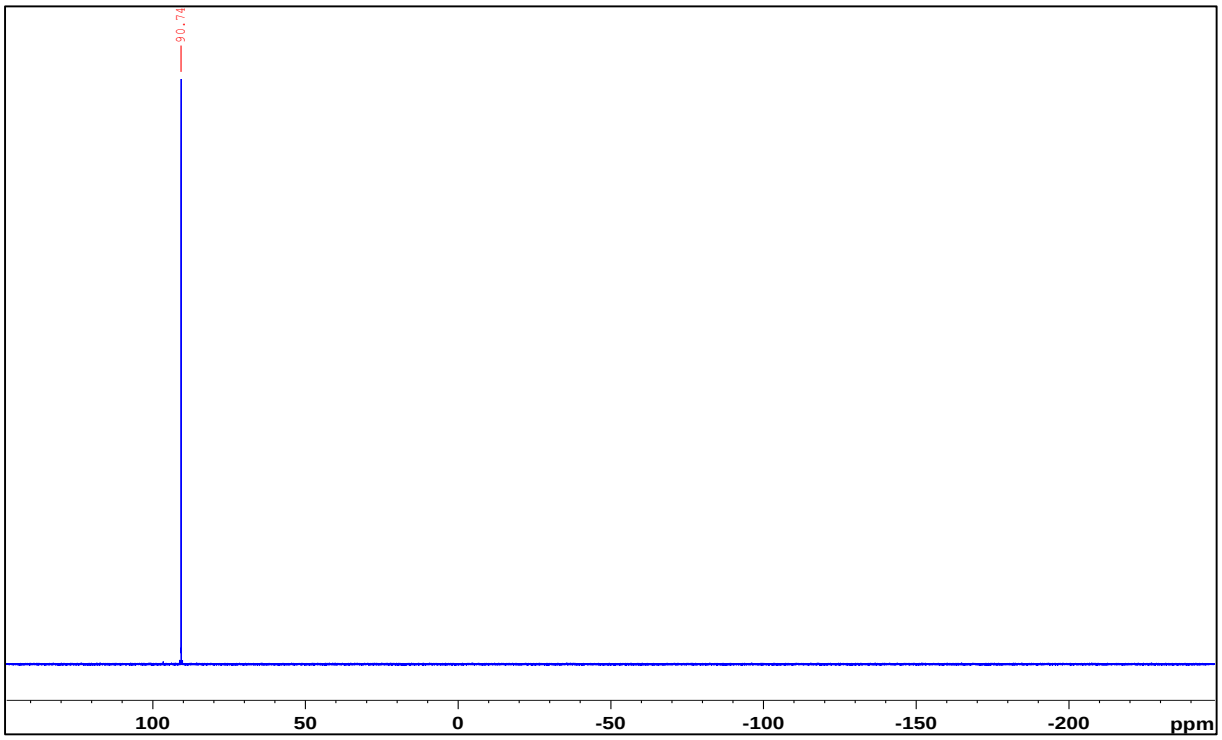
^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)

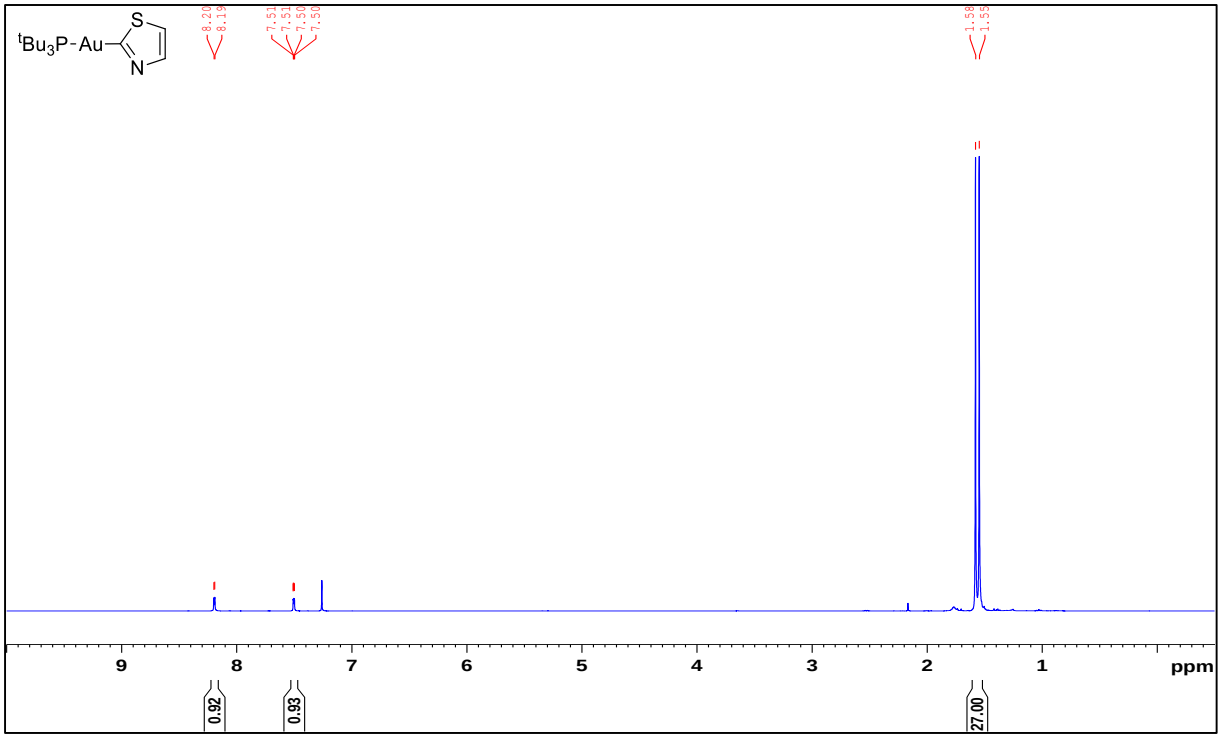


^{31}P NMR ($CDCl_3$)

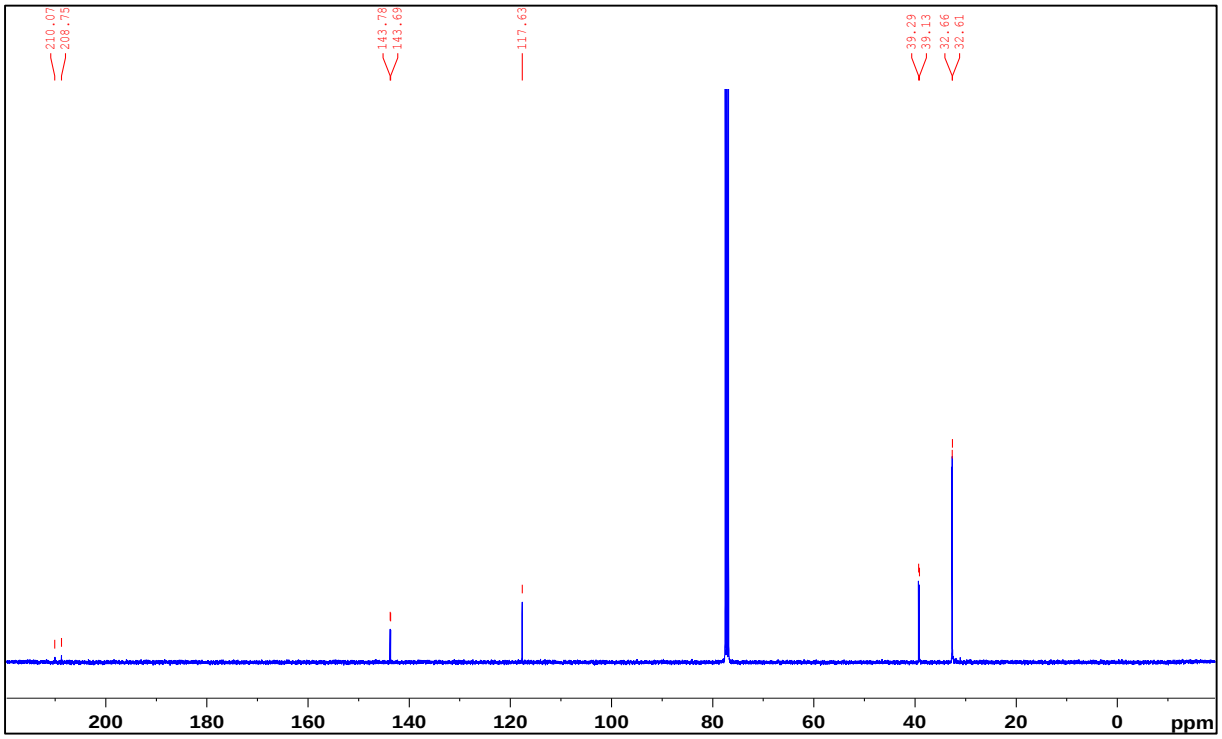


Thiazol-2-yl(tri-tert-butylphosphine)gold(I) ***5ab***

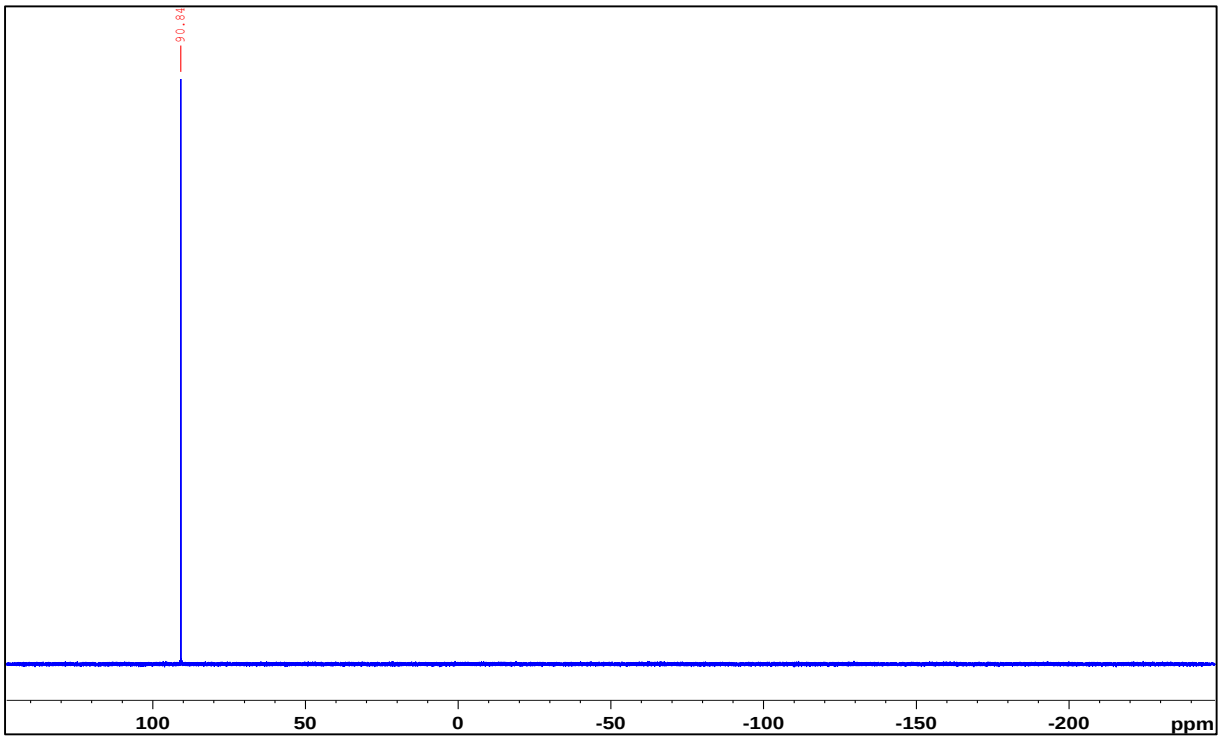
^{1}H NMR ($CDCl_3$)



^{13}C NMR

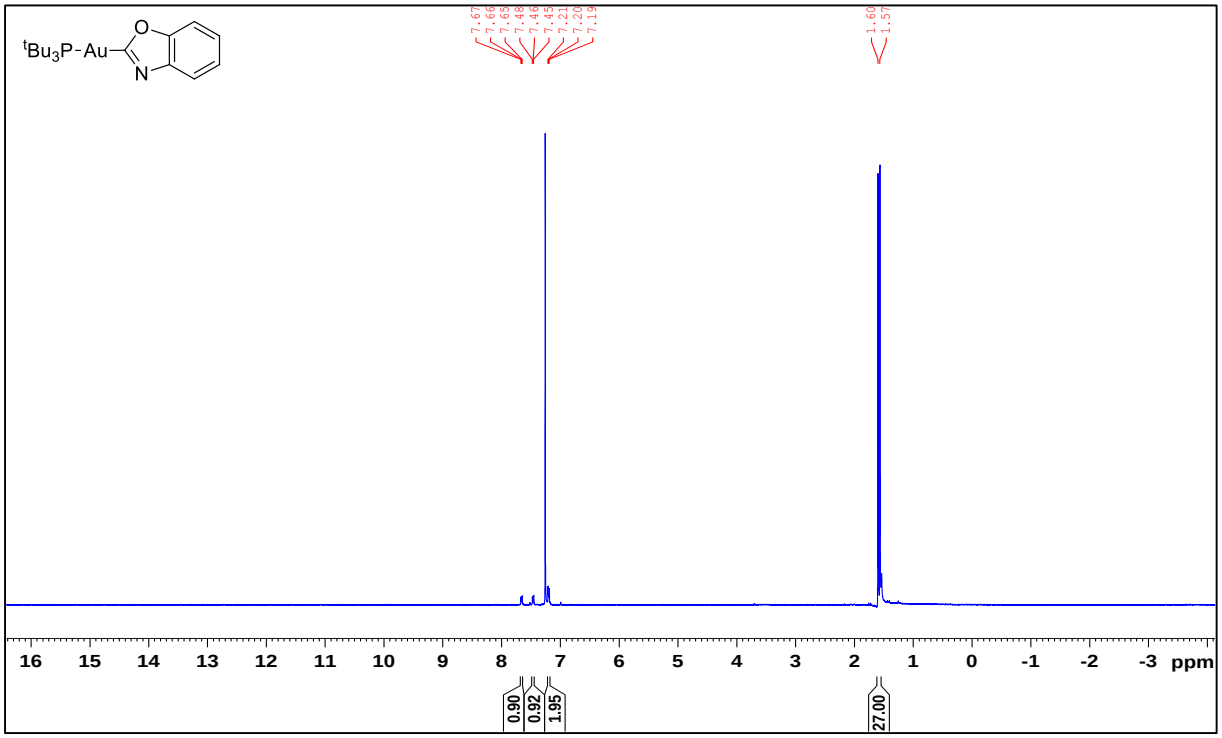


^{31}P NMR ($CDCl_3$)

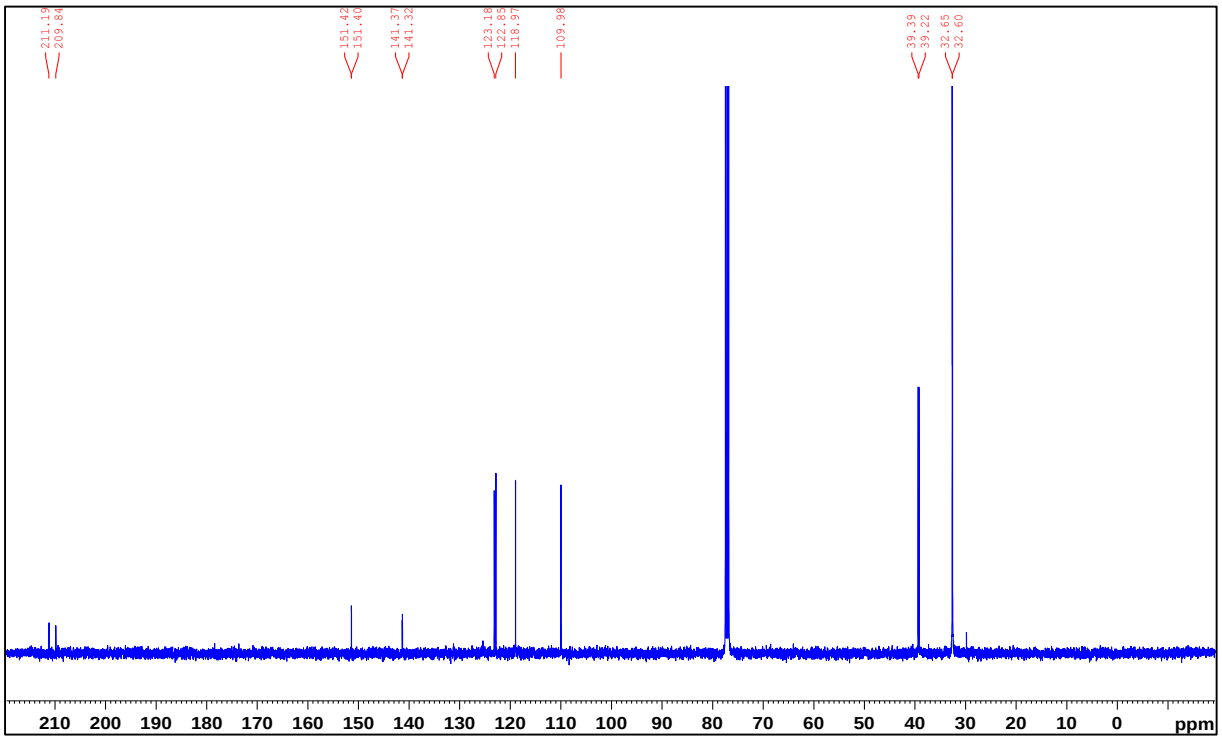


Benzoxazol-2-yl(tri-tert-butylphosphine)gold(I) ***5ac***

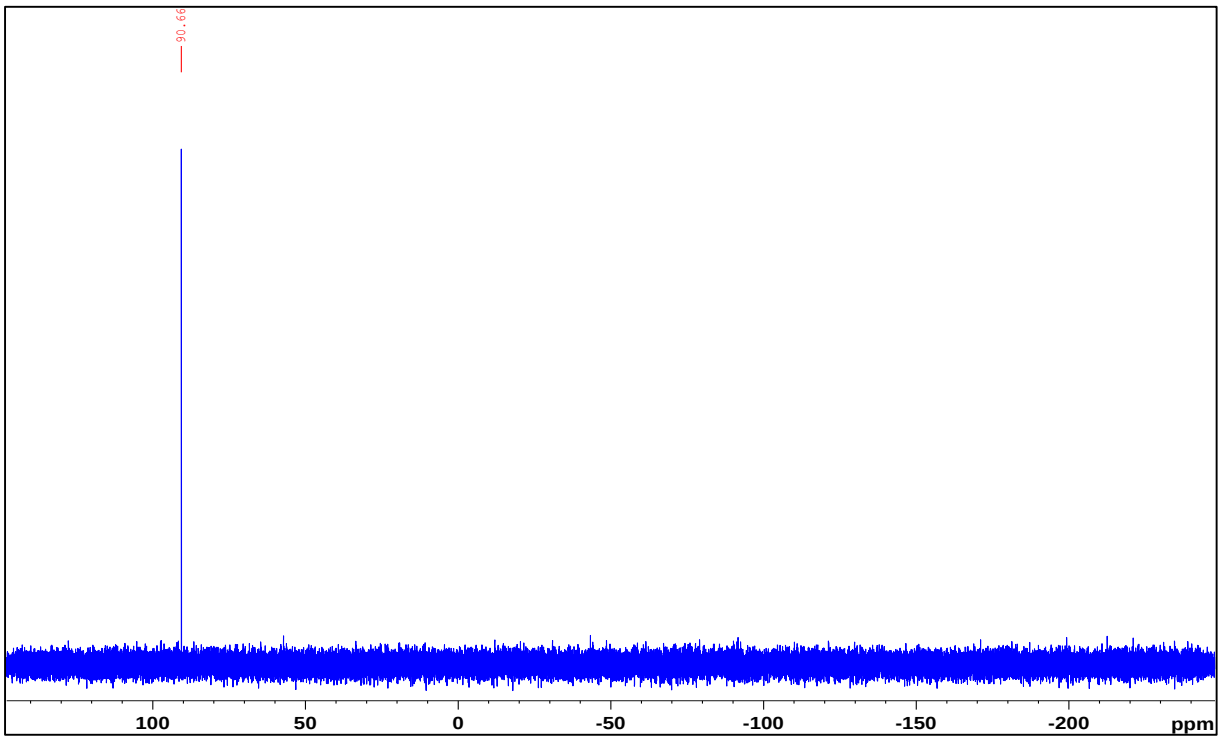
^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)

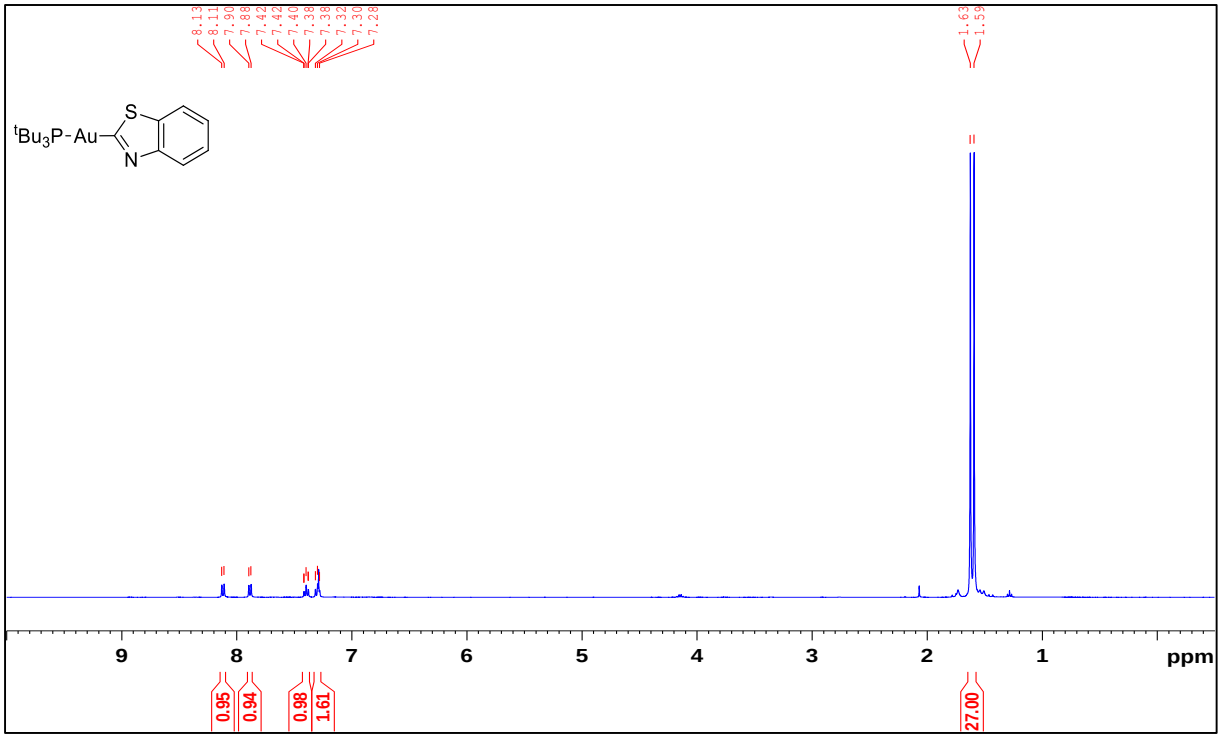


^{31}P NMR ($CDCl_3$)

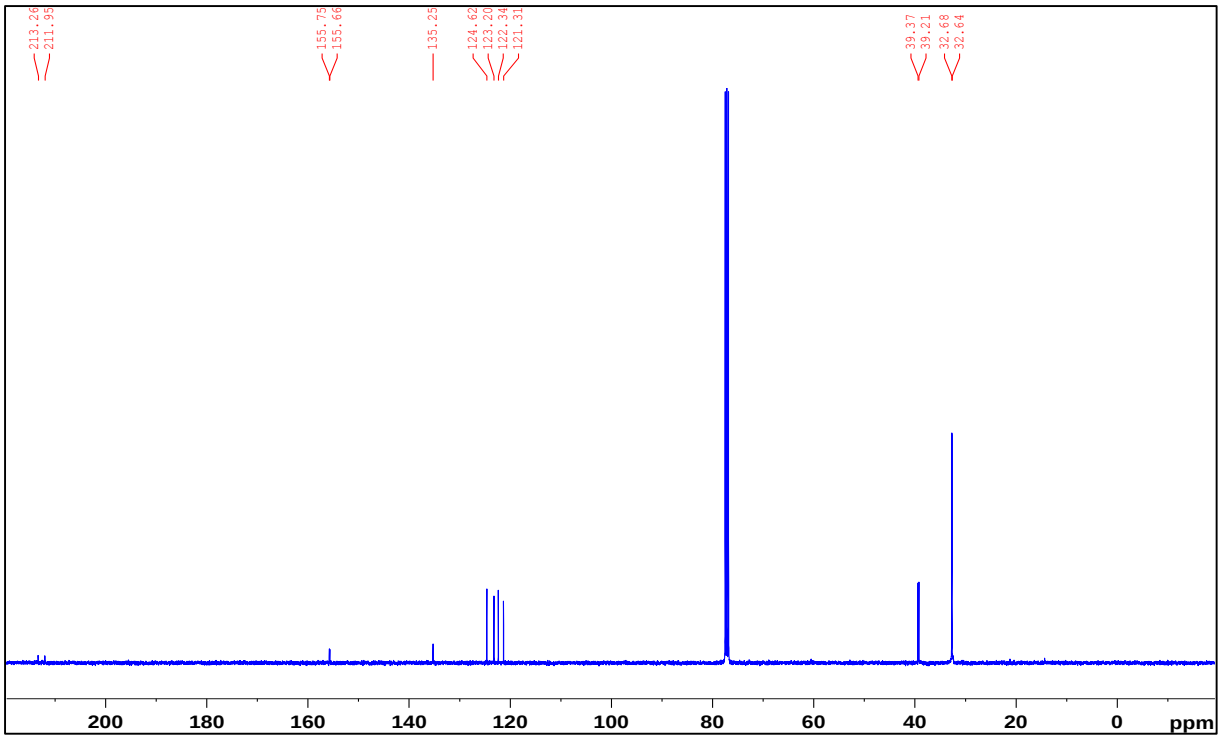


Benzothiazol-2-yl(tri-tert-butylphosphine)gold(I) ***5ad***

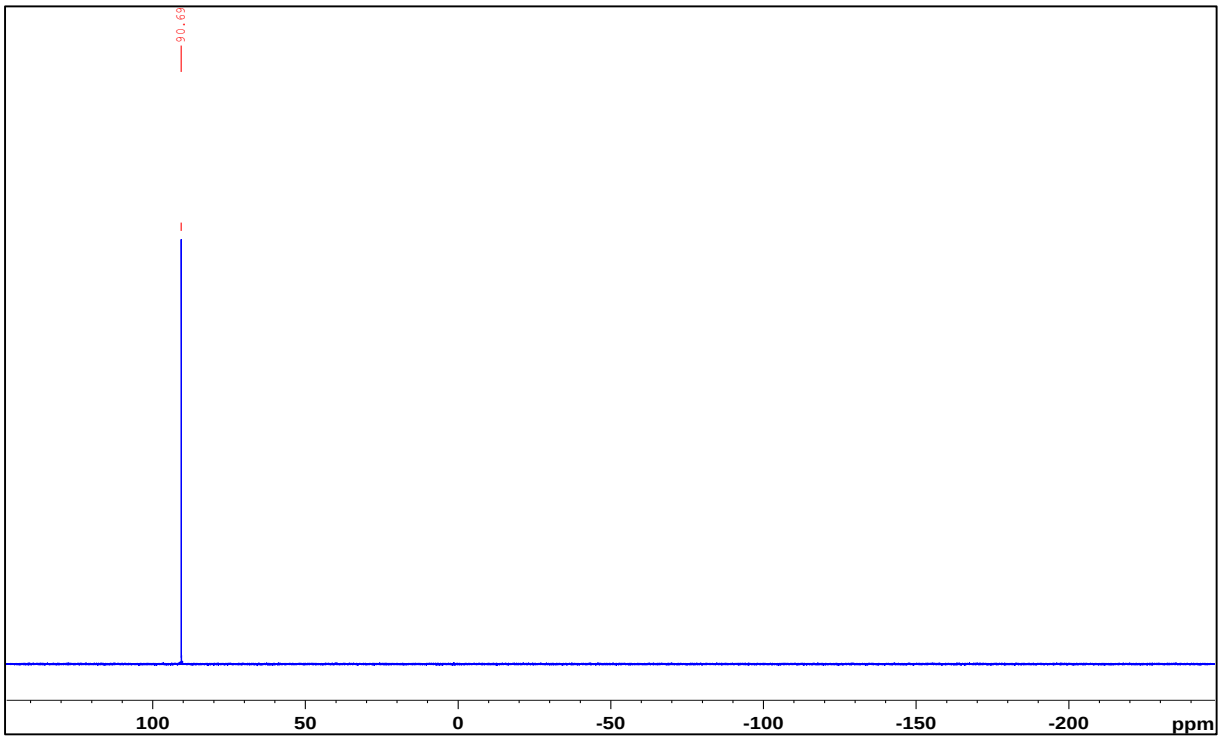
^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)

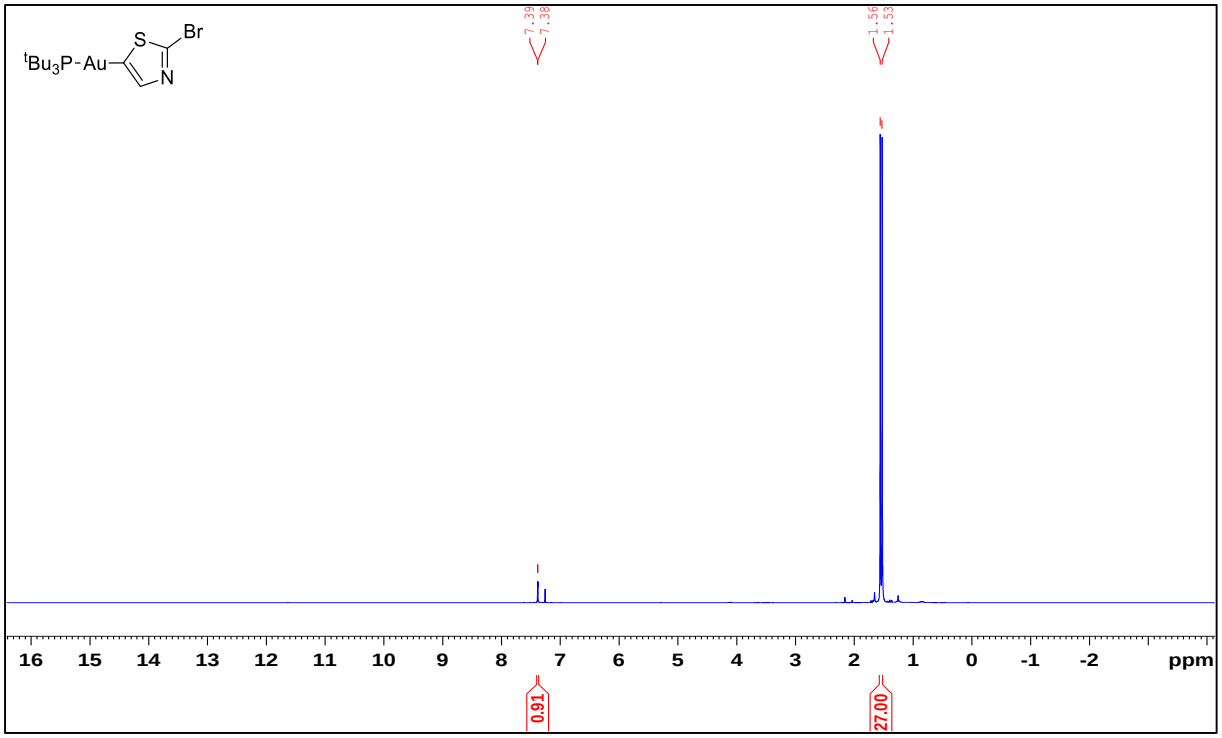


^{31}P NMR ($CDCl_3$)

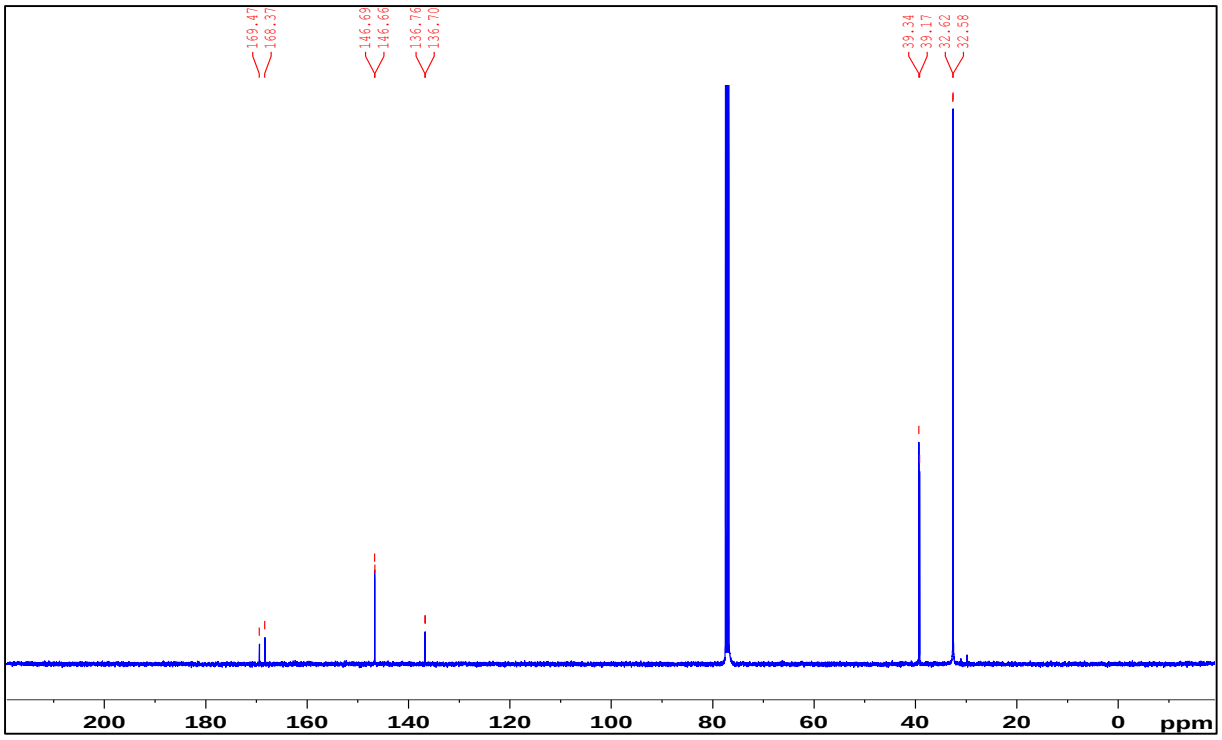


5-Bromothiazol-2-yl(tri-tert-butylphosphine)gold(I) ***5ae***

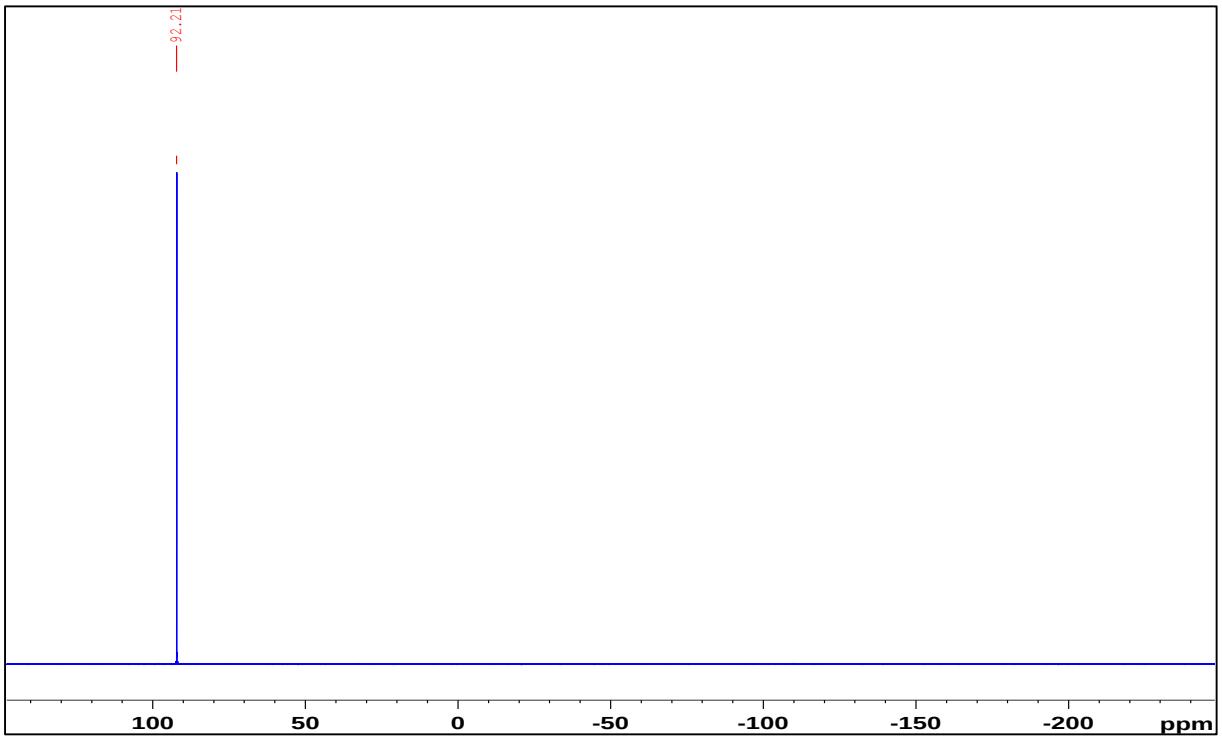
^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)

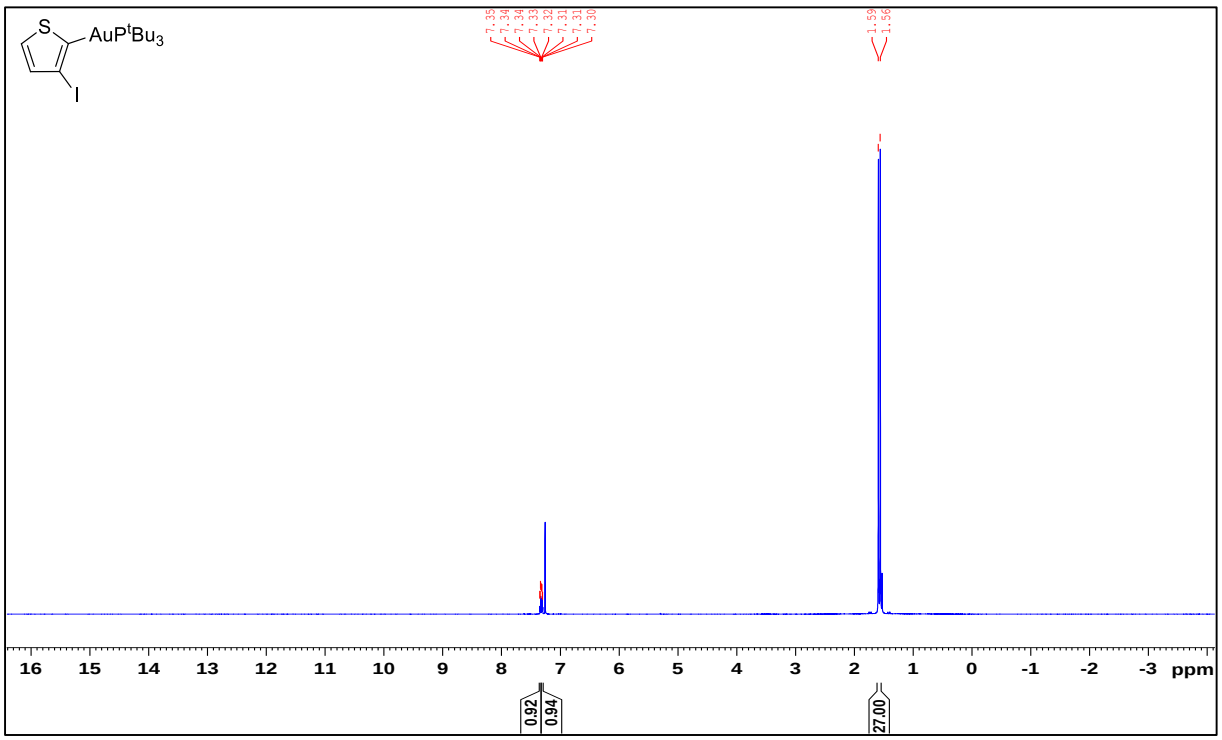


^{31}P NMR ($CDCl_3$)

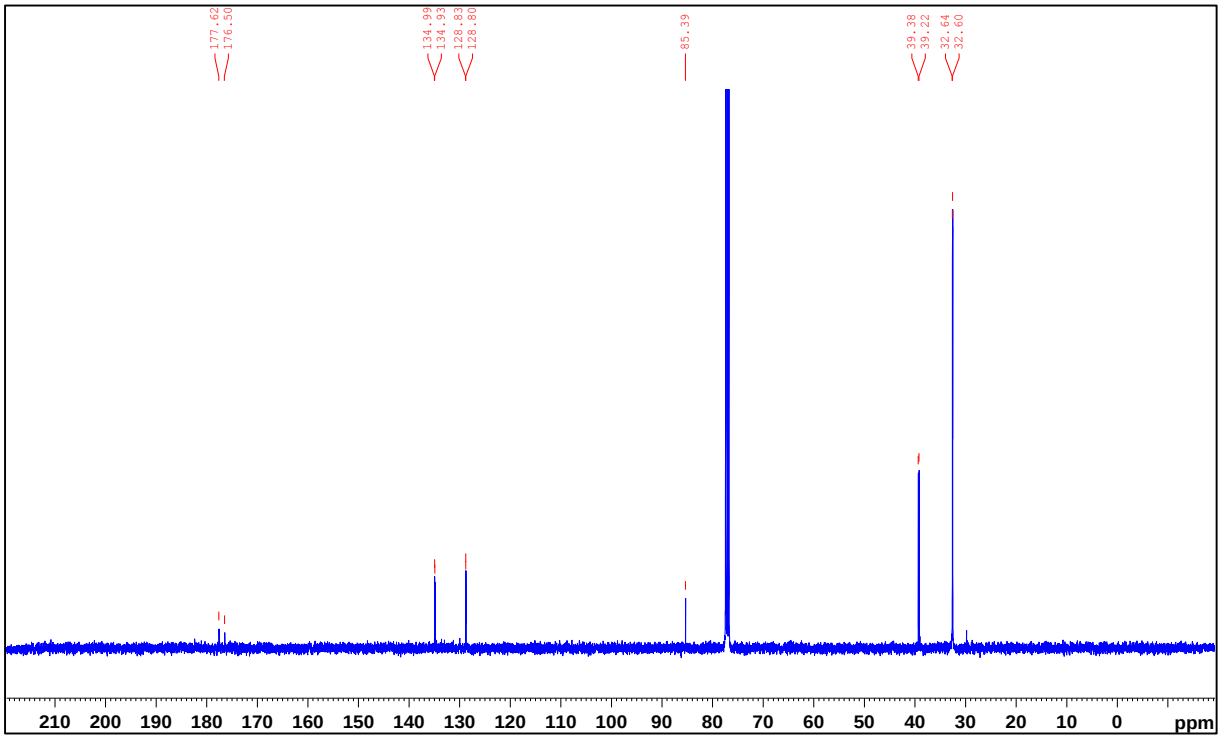


3-Iodothiophen-2-yl(tri-tert-butylphosphine)gold(I) ***5ag***

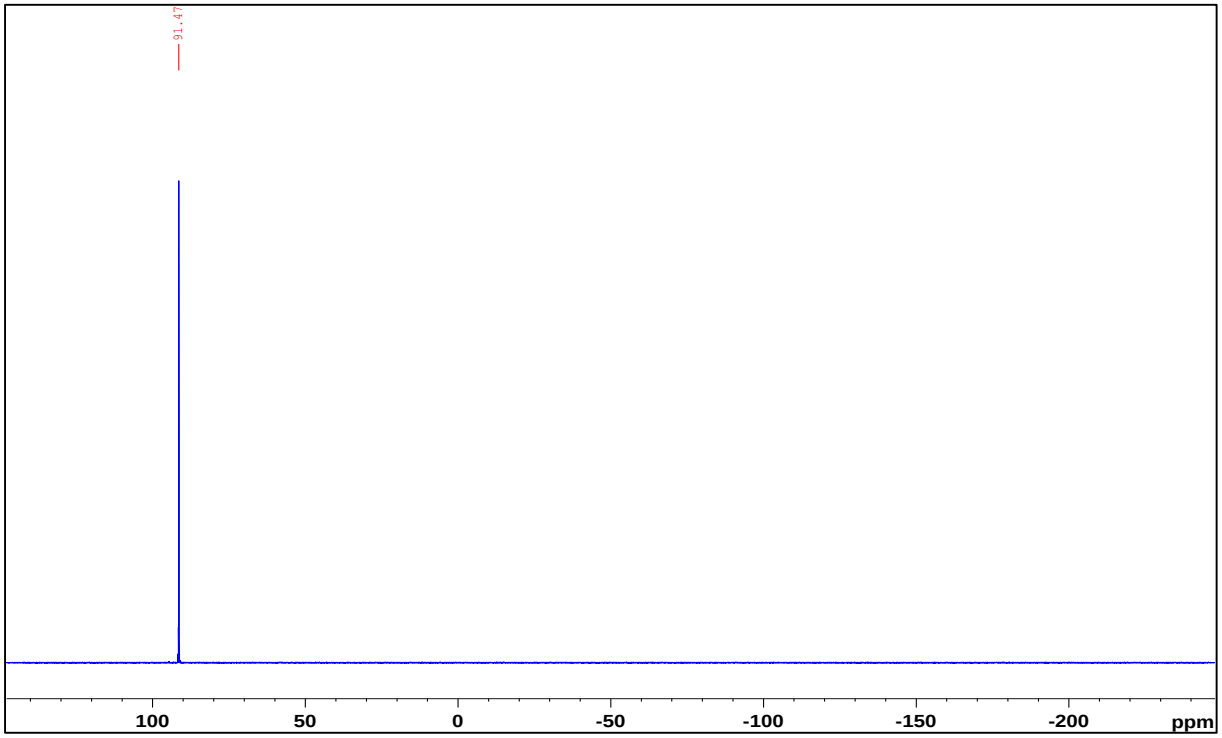
^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)

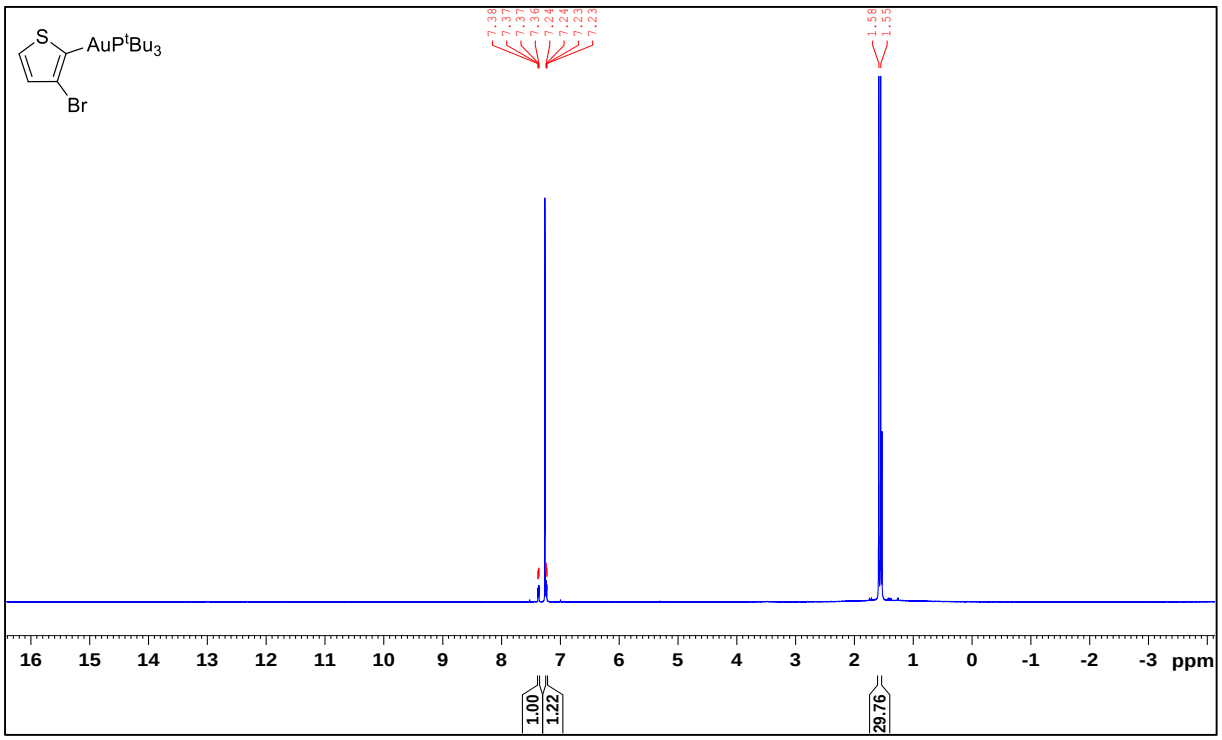


^{31}P NMR ($CDCl_3$)

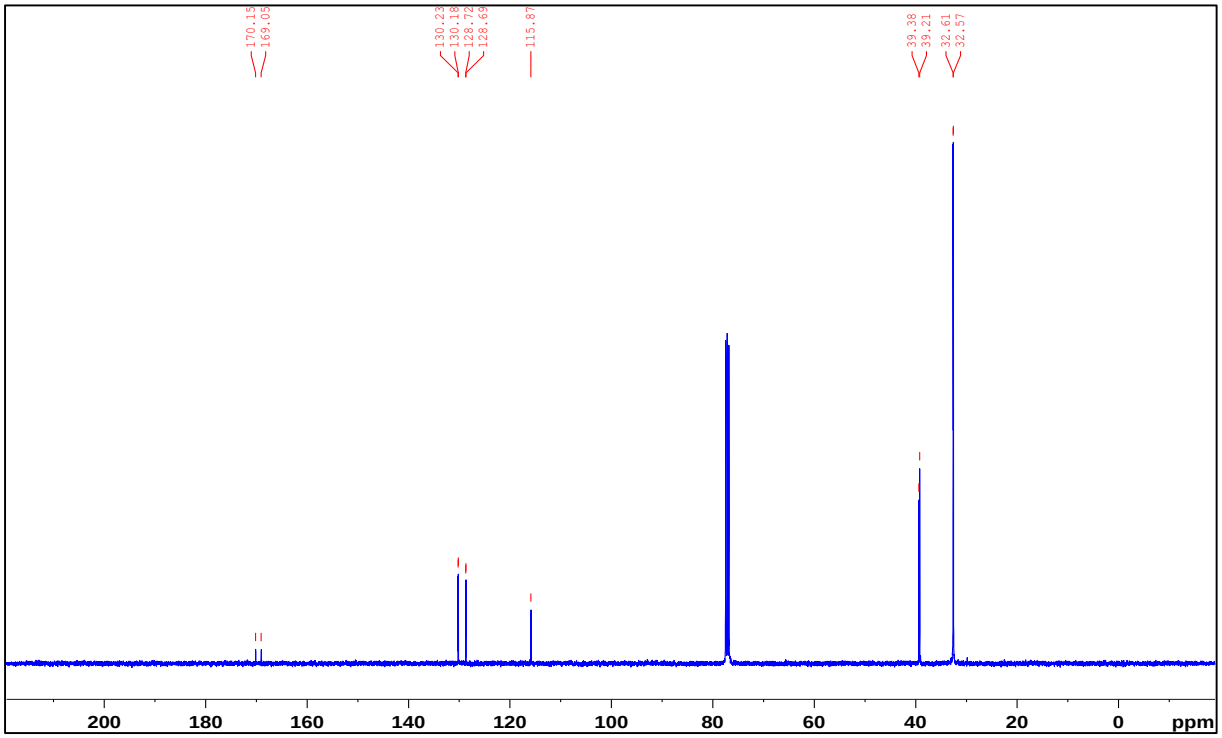


3-Bromothiophen-2-yl(tri-tert-butylphosphine)gold(I) ***5ah***

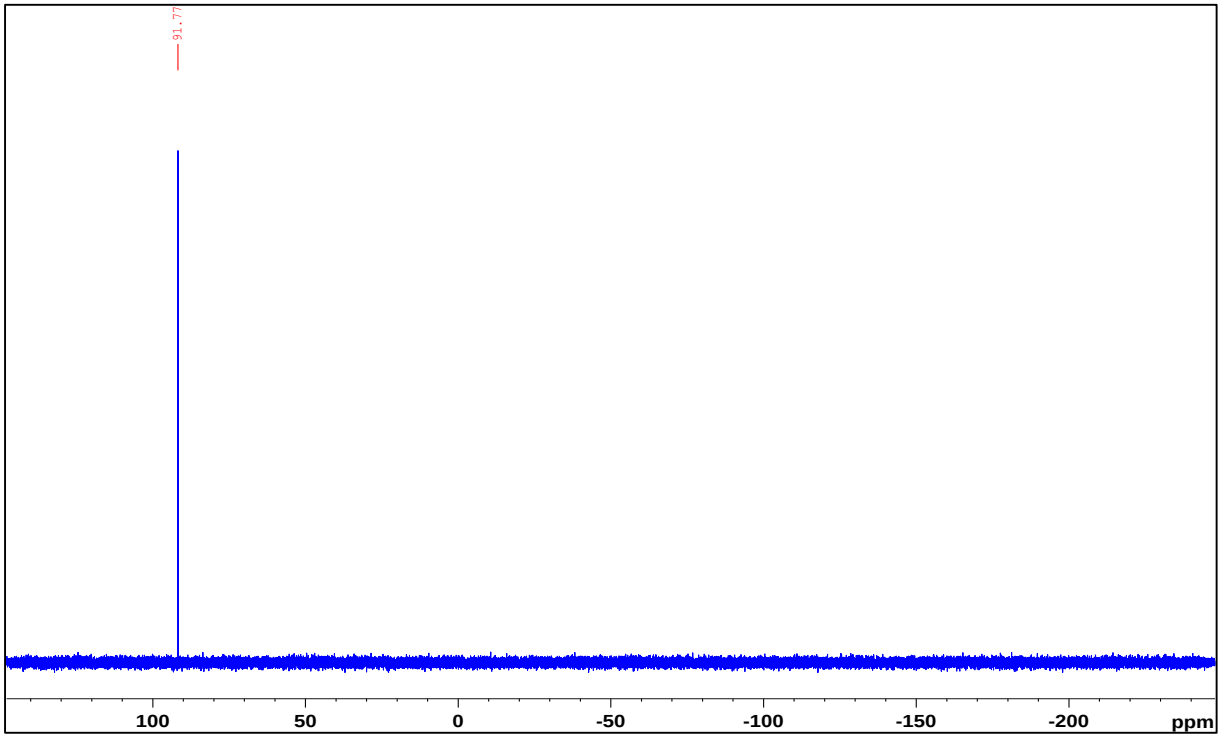
^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)

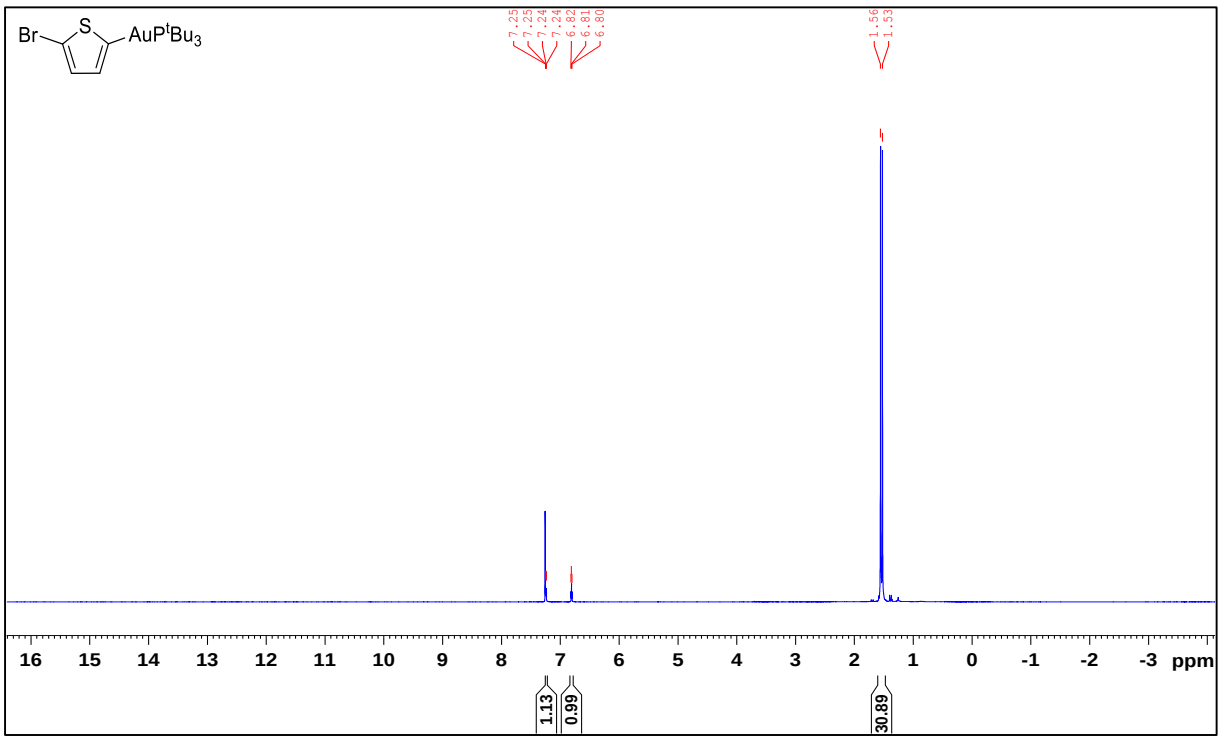


^{31}P NMR ($CDCl_3$)

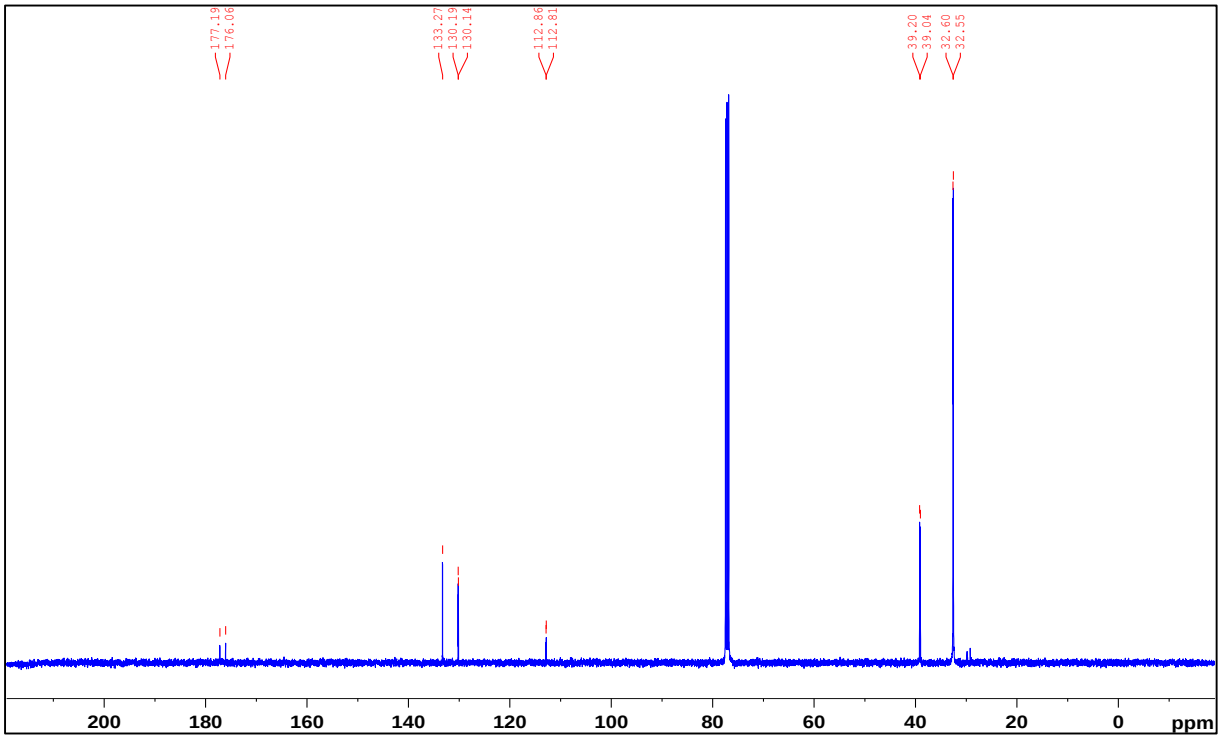


5-Bromothiophen-2-yl(tri-tert-butylphosphine)gold(I) ***5ai***

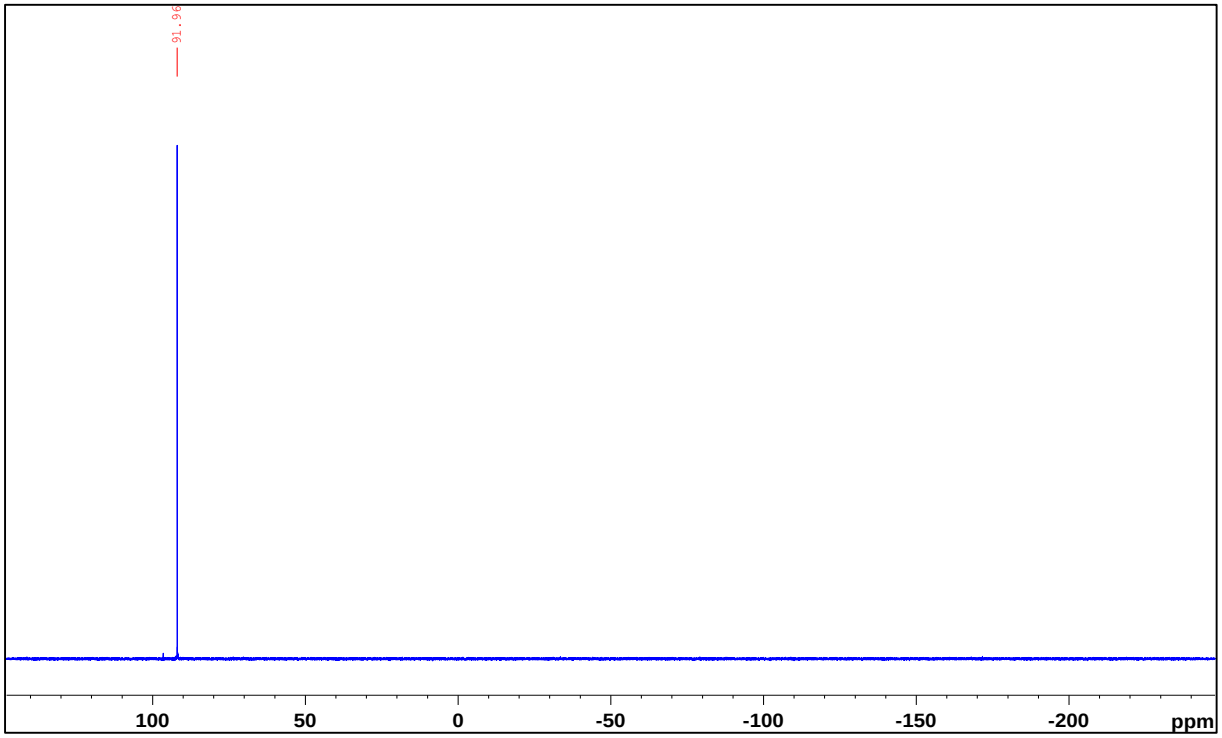
^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)

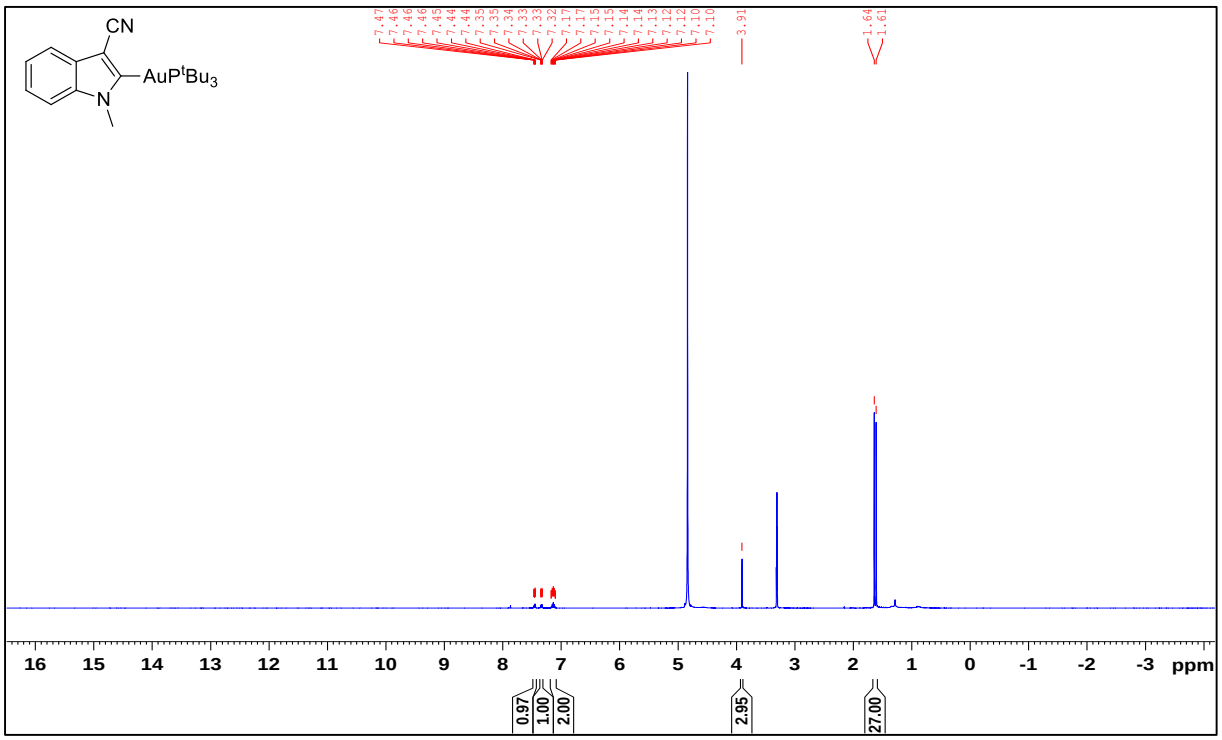


^{31}P NMR ($CDCl_3$)

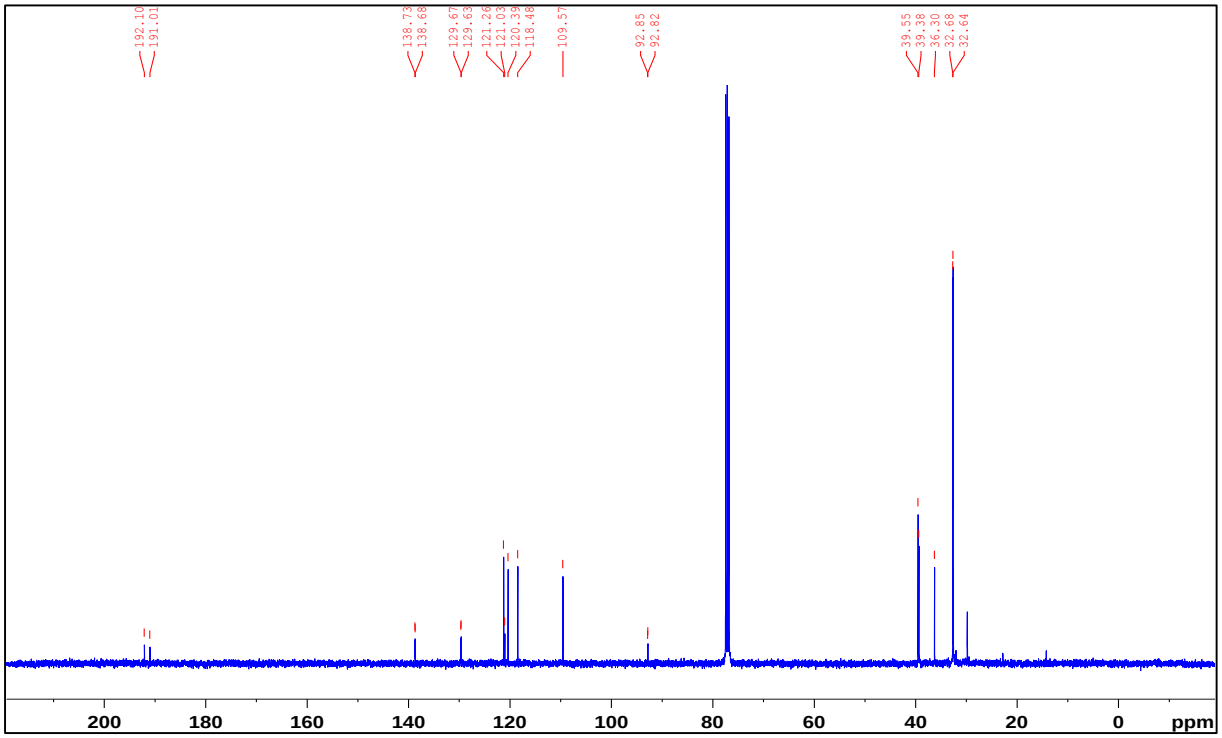


3-Cyano-1-methylindol-2-yl(tri-tert-butylphosphine)gold(I) ***5aj***

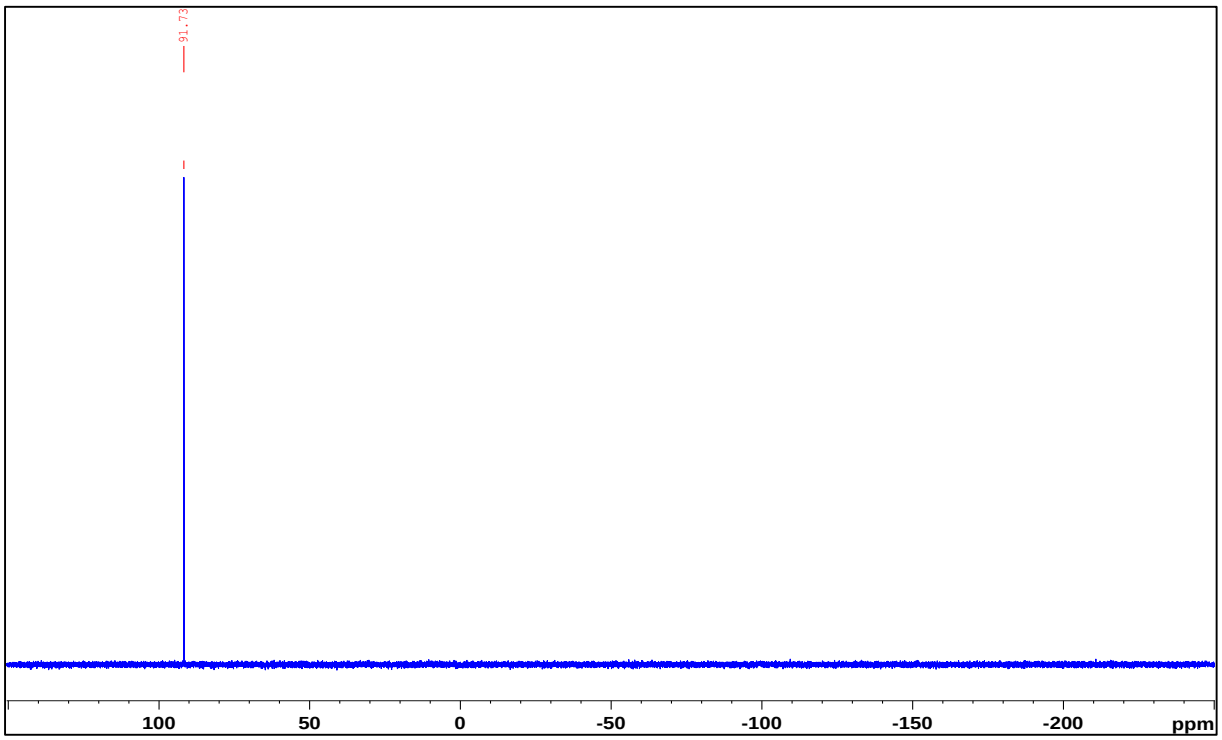
^{1}H NMR (CD_3OD)



^{13}C NMR ($CDCl_3$)

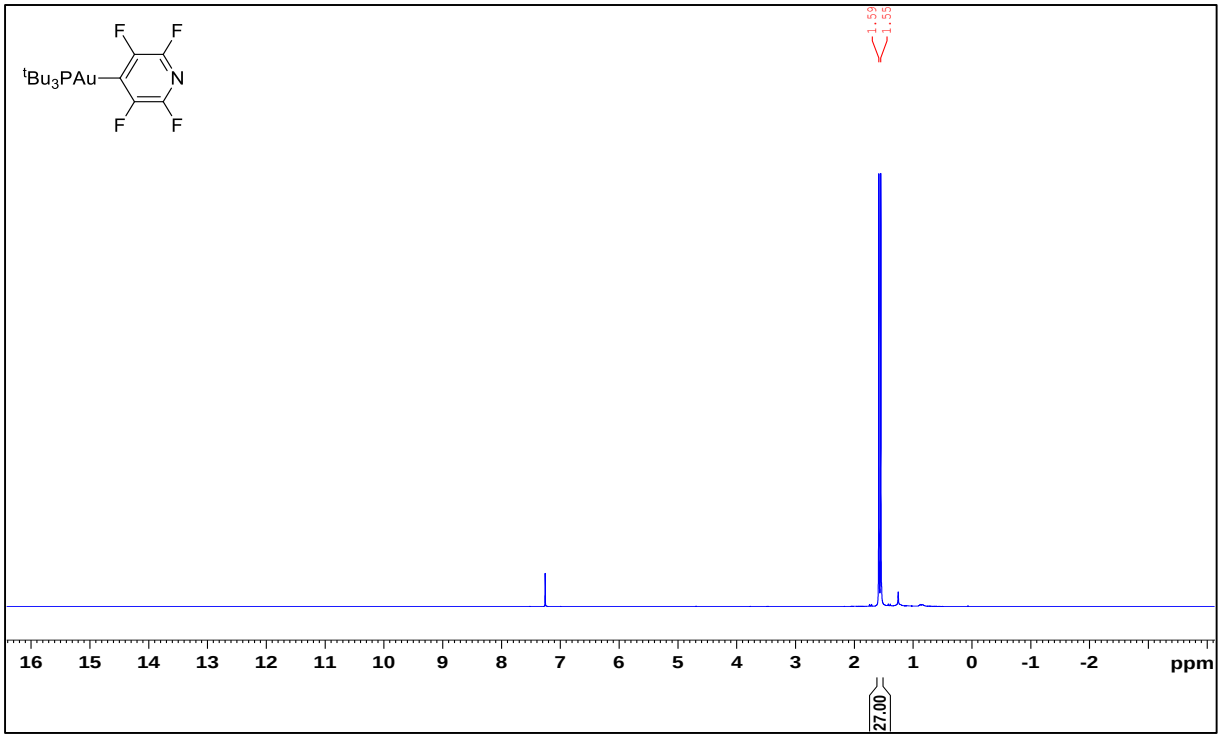


^{31}P NMR ($CDCl_3$)

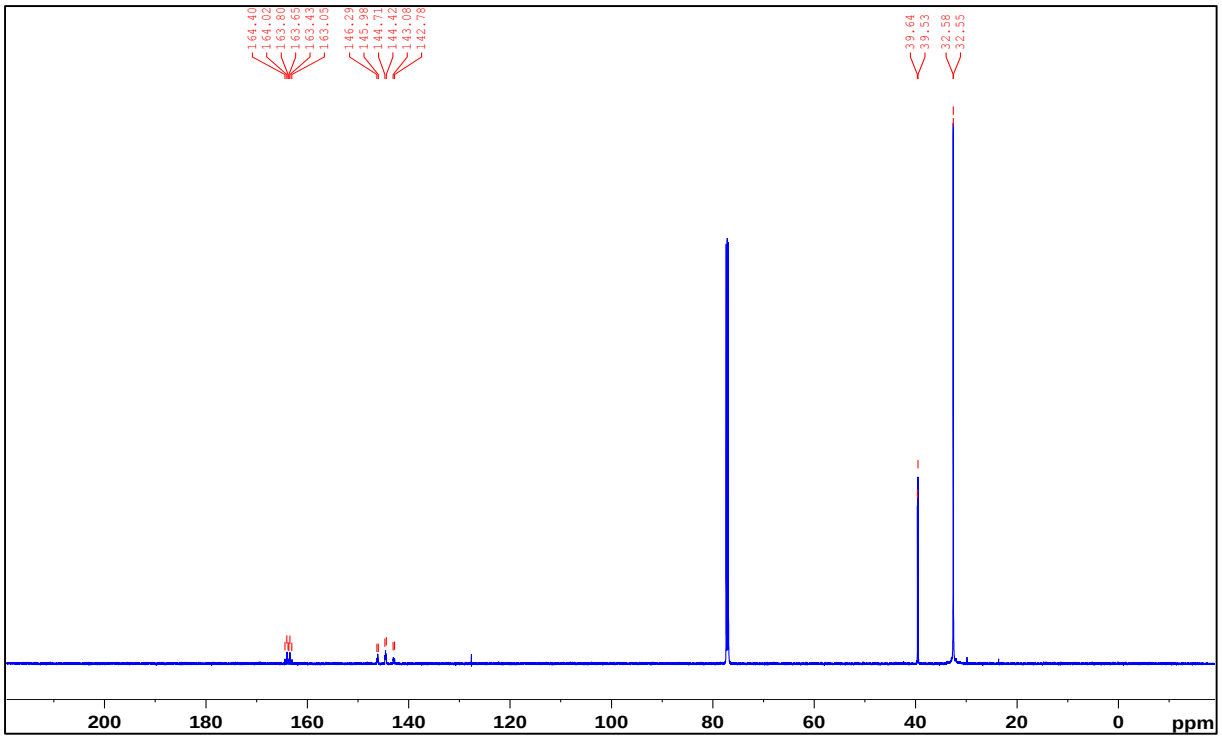


2,3,5,6-Tetrafluoropyridin-4-yl(tri-tert-butylphosphine)gold(I) ***5ak***

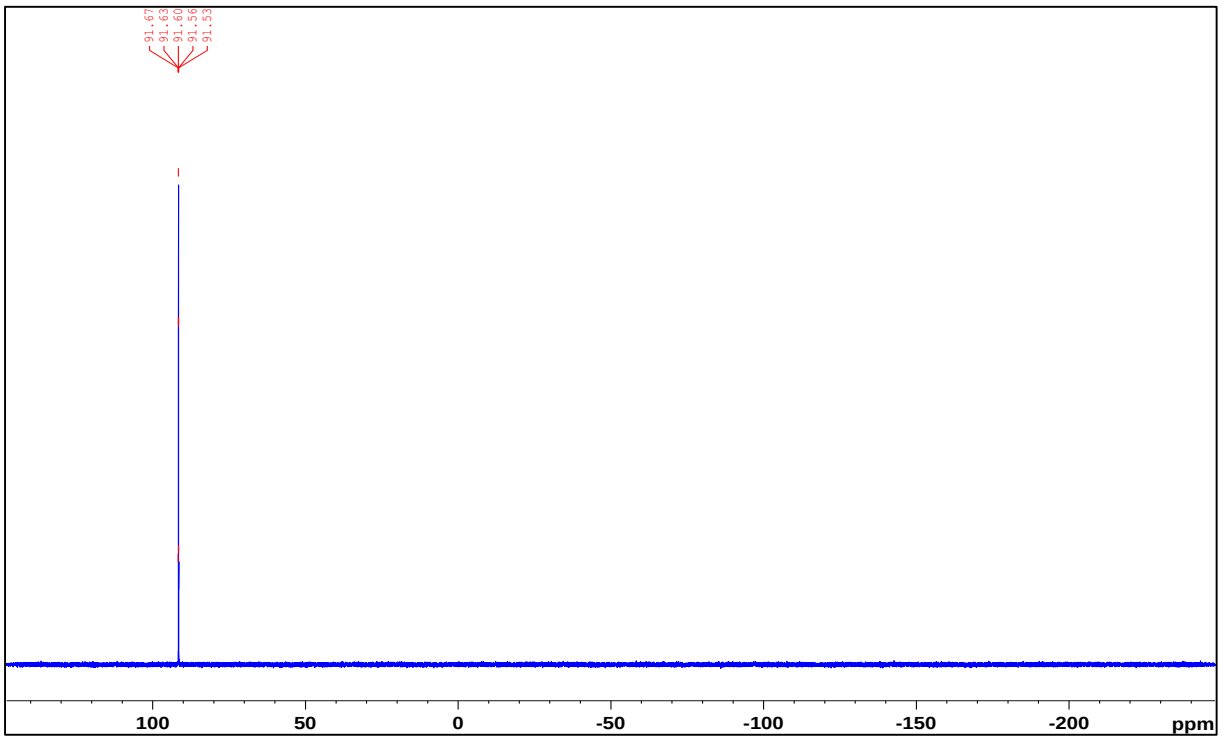
^{1}H NMR ($CDCl_3$)



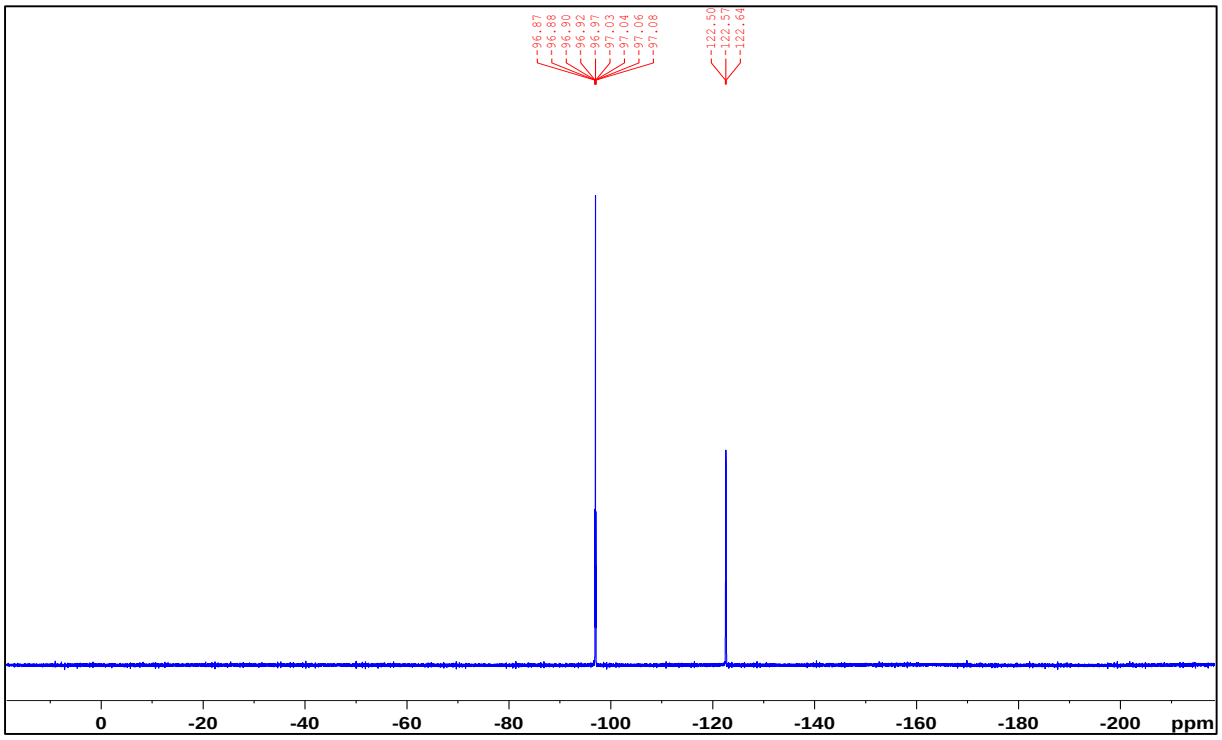
^{13}C NMR ($CDCl_3$)



^{31}P NMR ($CDCl_3$)

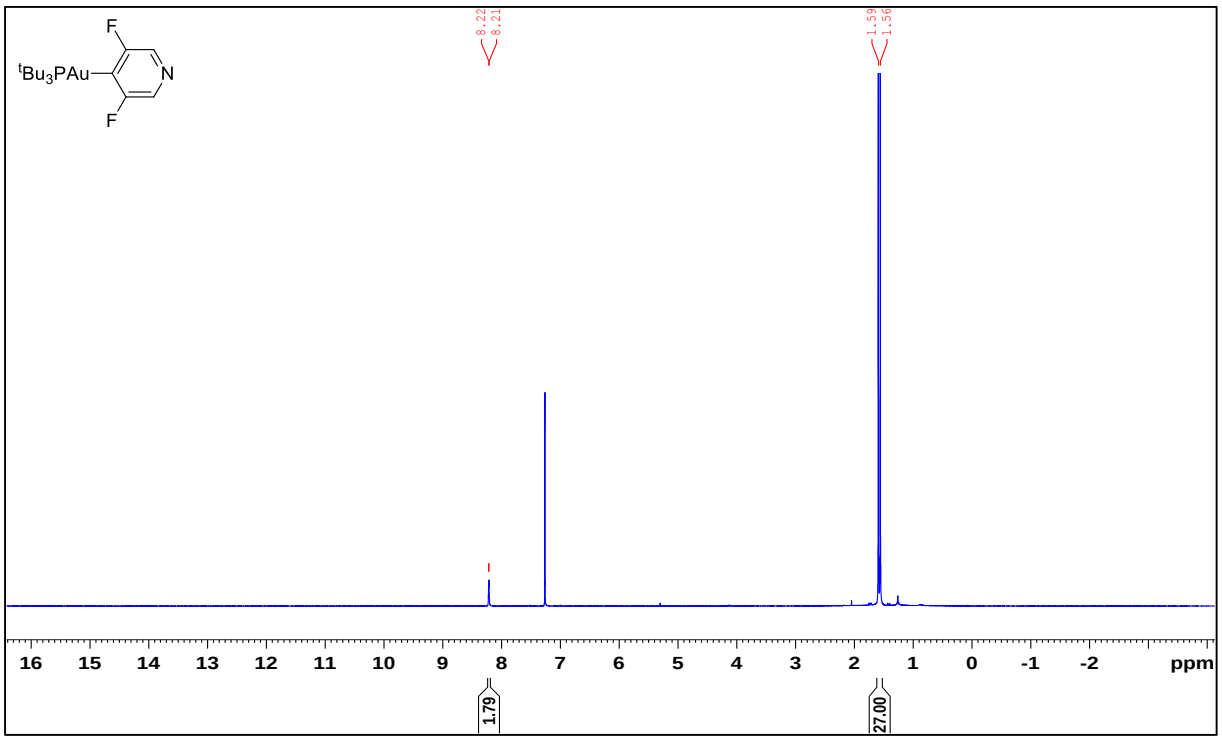


^{19}F NMR ($CDCl_3$)

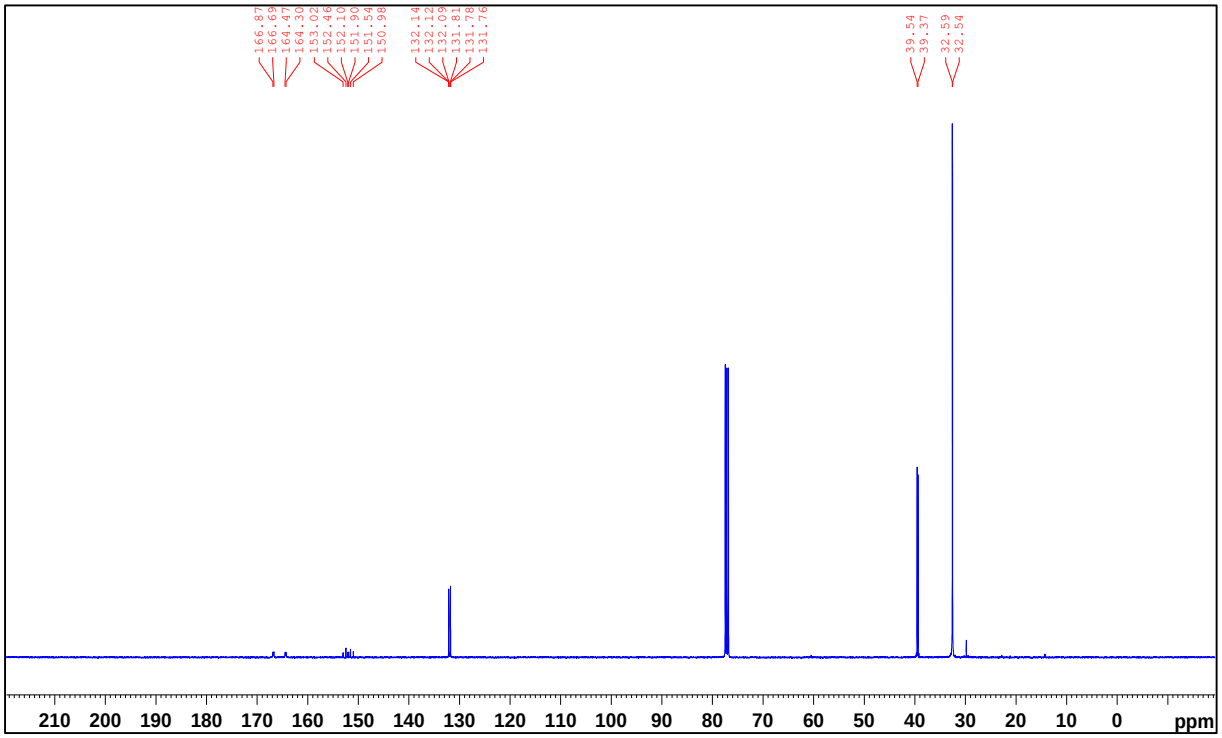


3,5-Difluoropyridin-4-yl(tri-tert-butylphosphine)gold(I) ***5al***

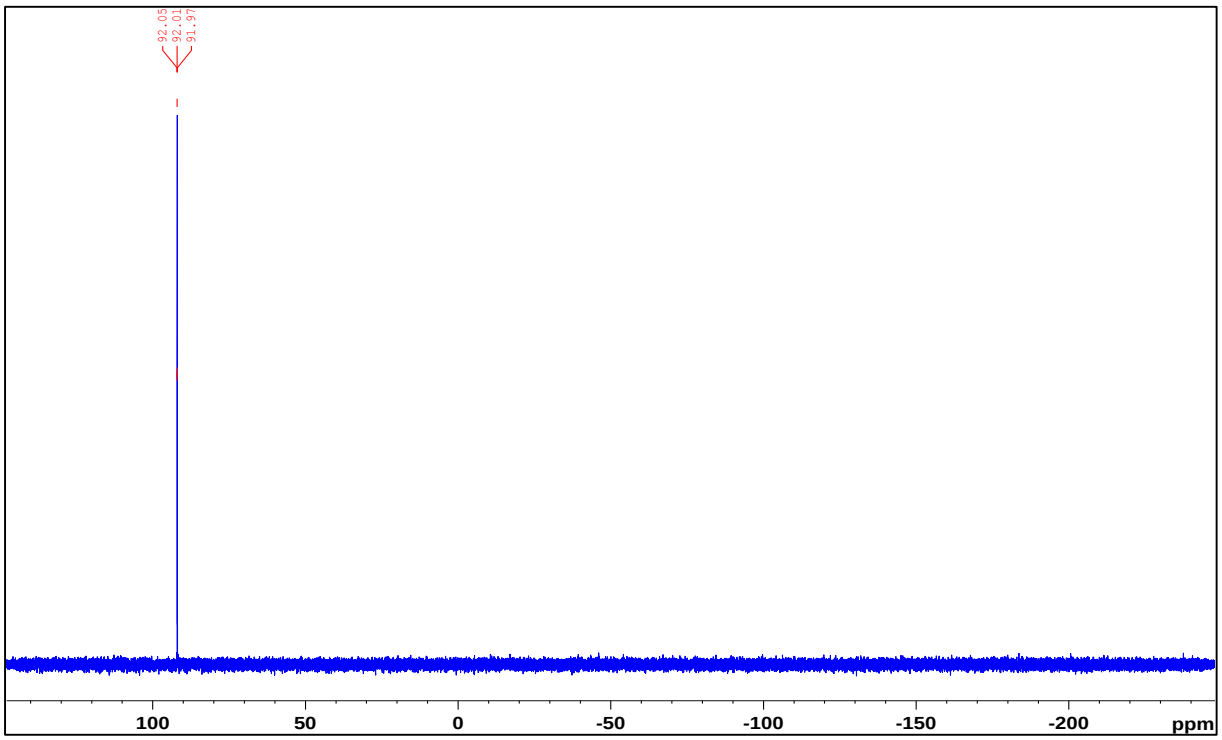
^{1}H NMR ($CDCl_3$)



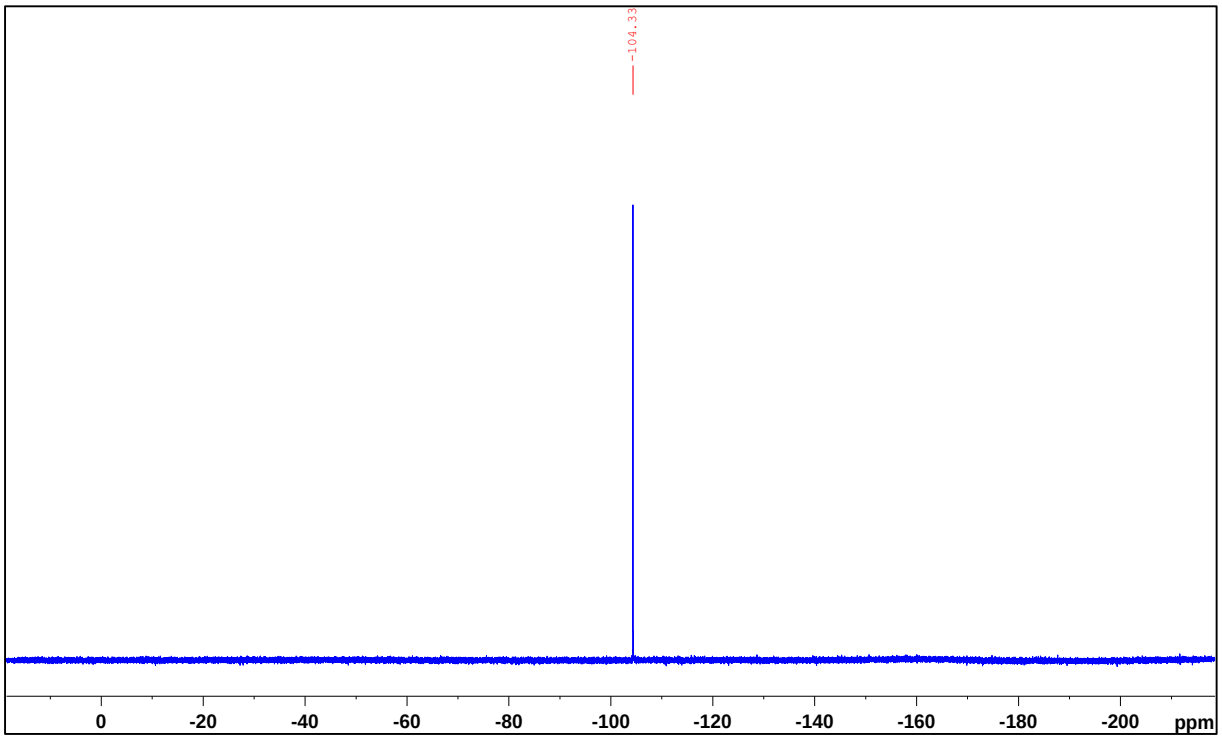
^{13}C NMR ($CDCl_3$)



^{31}P NMR ($CDCl_3$)

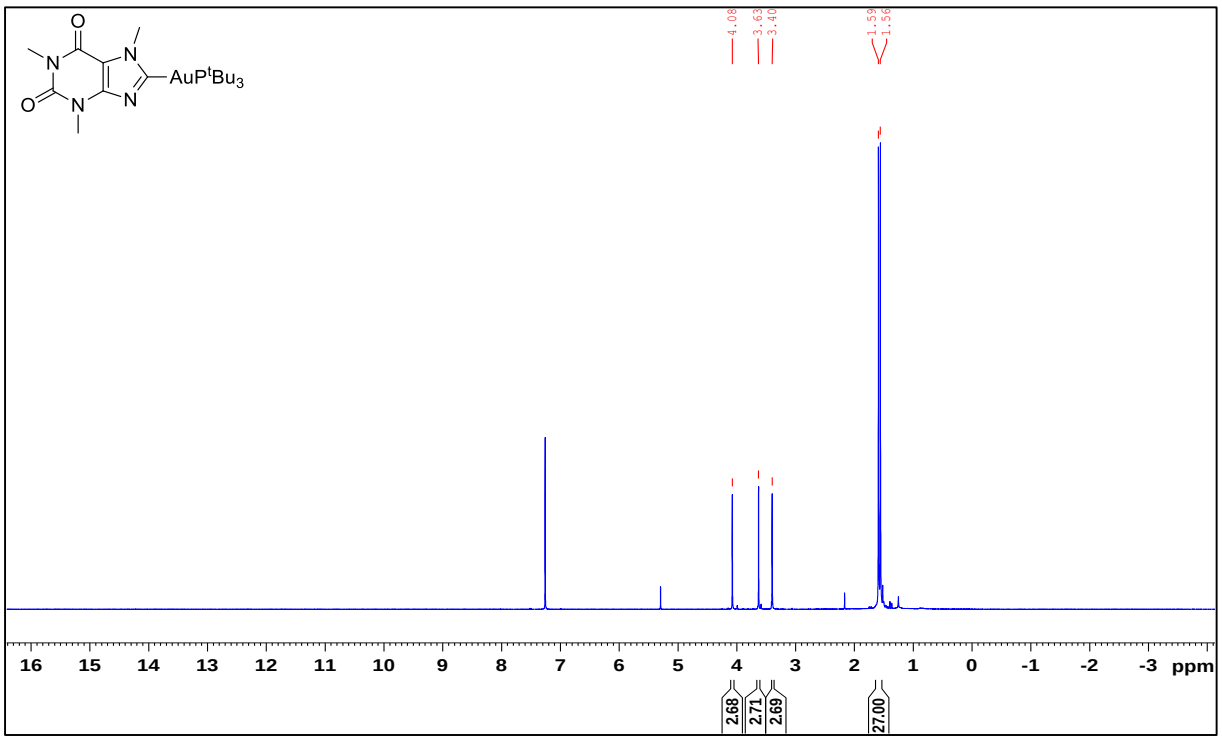


^{19}F NMR ($CDCl_3$)

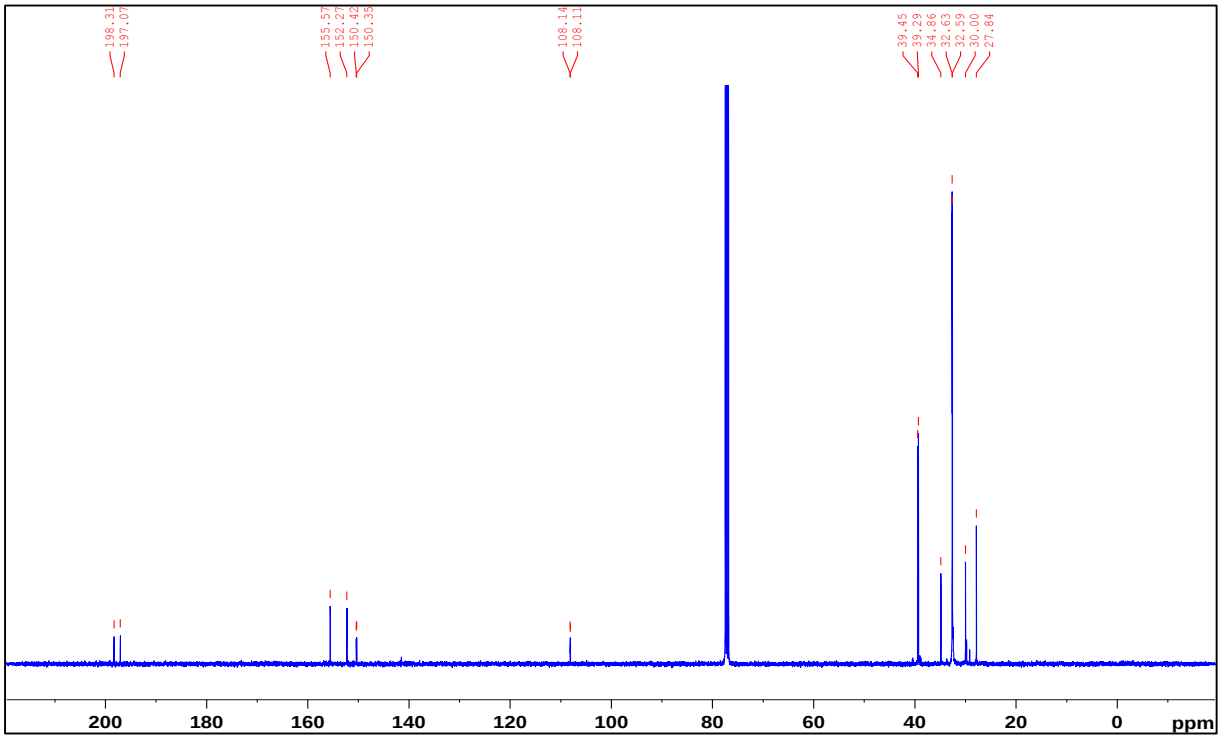


(1,3,7-trimethyl-2,6-dioxo-2,3,6,7-tetrahydropurin-8-yl)gold (tri-tert-butylphosphine)gold(I) ***5am***

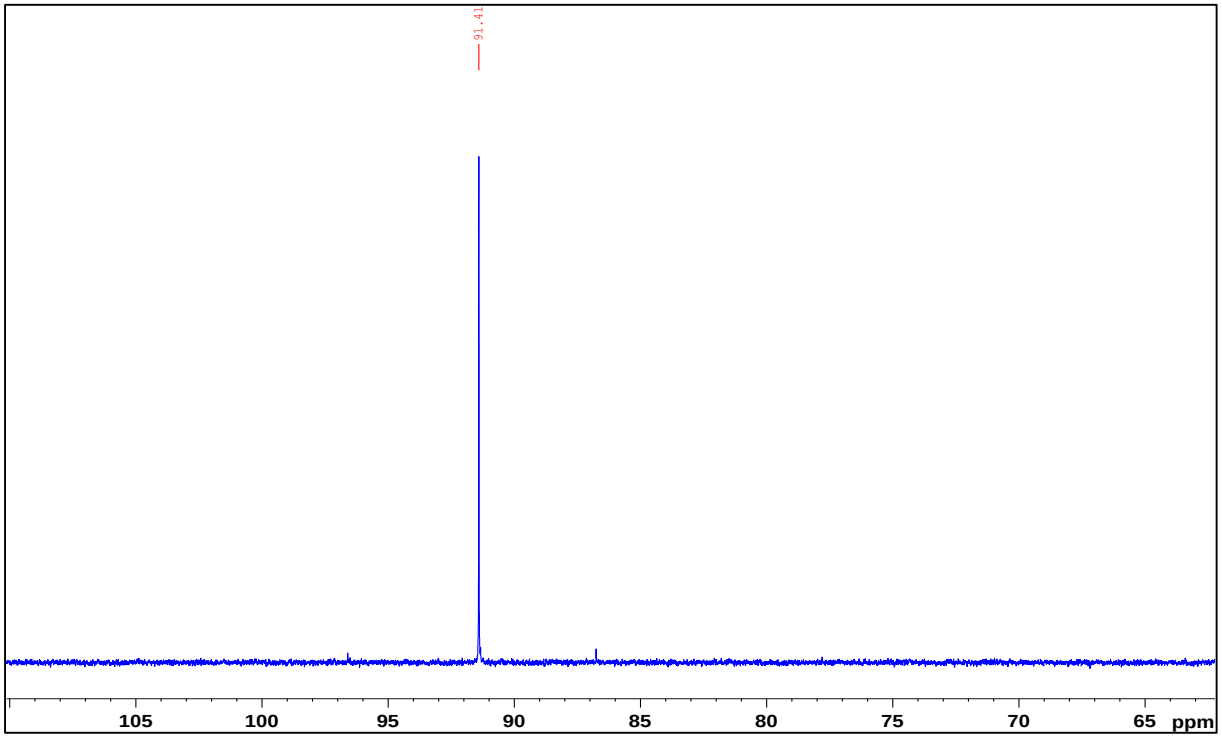
^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)

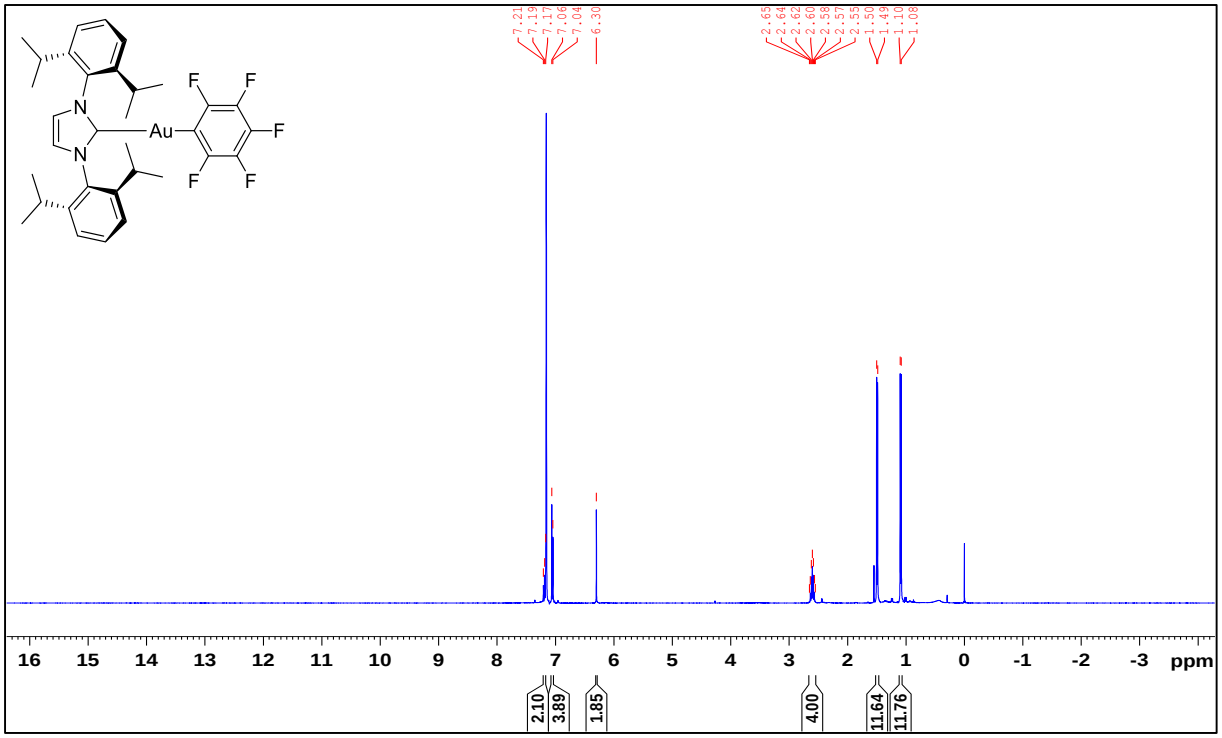


^{31}P NMR ($CDCl_3$)

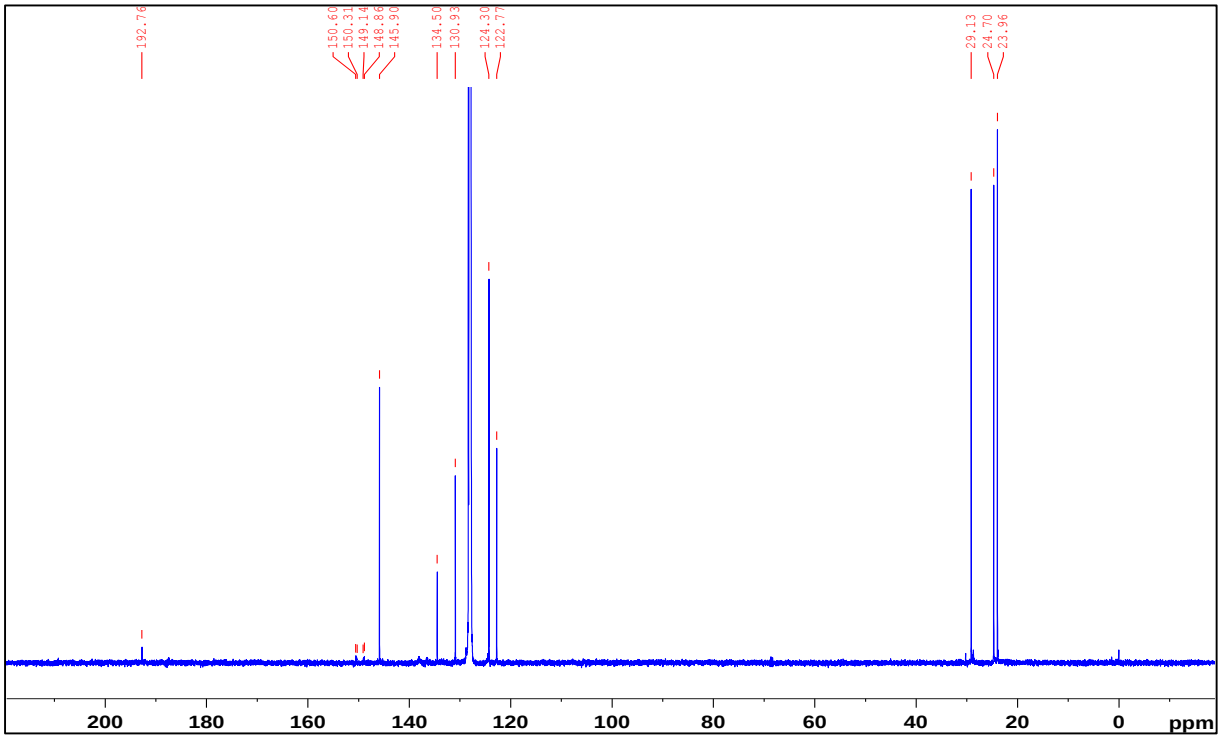


Pentafluorophenyl(IPr)gold(I) ***7b***

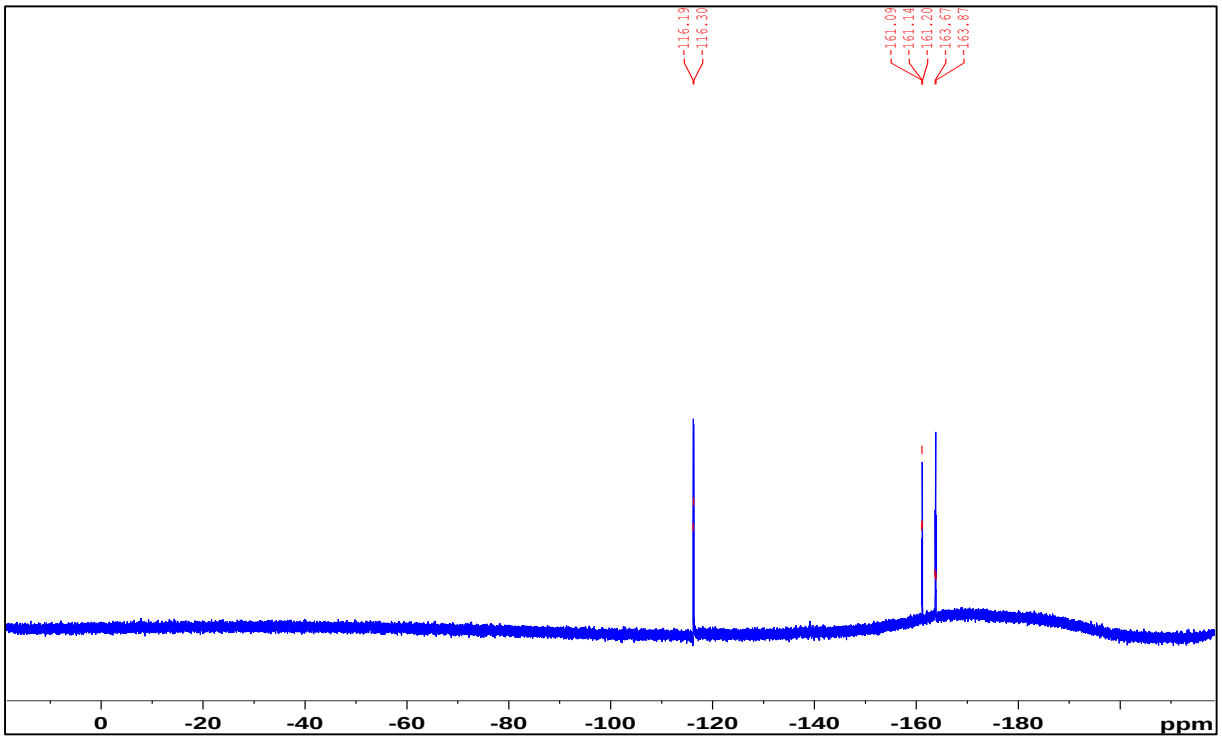
^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)



^{19}F NMR ($CDCl_3$)



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[1] P. Lu, T. C. Boorman, A. M. Z. Slawin and I. Larrosa, *J. Am. Chem. Soc.*, 2010, **132**, 5580-5581.

[2] S. Gaillard, A. M. Z. Slawin and S. P. Nolan, *Chem. Commun.*, 2010, **46**, 2742-2744.

[3] H. Schmidbaur, A. Kolb, E. Zeller, A. Schier and H. Beruda, *Anorg. Allg. Chem.*, 1993, **619**, 1575-1579.