Electronic Supporting Information

Chemo-Selective Stille-type Coupling of Acyl-Chlorides Upon Phosphine-Borane Au(I) Catalysis

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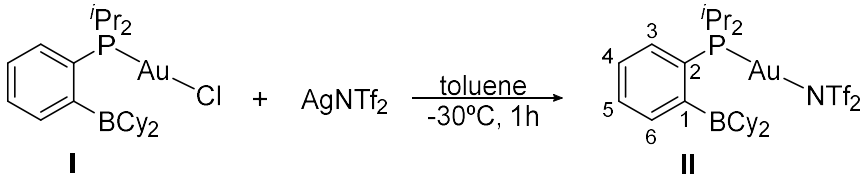
1. General considerations

All preparations and manipulations were performed by using standard Schlenk and glovebox techniques, under an atmosphere of argon. All solvents were dried using a MBRAUN Solvent Purification System (SPS) and degassed using freeze-pump-thaw method. Internal standards, C_6F_6 and 1,2-dichloroethane, were dried with 3 Å molecular sieves and degassed prior to use. $PBCy_2$,[1] $PBCy_2AuCl$ (**I**),[1] $PBMes_2$[2] and PBpin[3] and were prepared as previously described. All other reagents were used as received from commercial suppliers. Mass spectra were recorded on a Waters LCT mass spectrometer. ^1H, ^{13}C, ^{31}P, ^{11}B and ^{19}F NMR spectra were recorded on a Bruker Avance III HD 500, Avance III HD 400, Avance II 300 and Avance I 300 spectrometers. NMR experiments were performed in deuterated solvents and recorded at ambient temperature (298 K). Chemical shifts (δ) are reported in parts per million (ppm) relative to residual ^1H and ^{13}C solvent signals. External $BF_3{\cdot}OEt_2$, 85% H_3PO_4 in water and $CFCl_3$ were used as reference for ^{11}B, ^{31}P and ^{19}F NMR, respectively. The following abbreviations and their combinations are used: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

2. Procedures, spectroscopic data and NMR spectra

Synthesis of the Au complex II



I II

To a solution of $PBCy_2AuCl$ (**I**) (100 mg, 0.166 mmol, 1 Equiv.) in toluene (5 mL) was added $AgNTf_2$ (64.4 mg, 0.166 mmol, 1 Equiv.) in toluene (5 mL) under Ar atmosphere. The mixture covered with aluminium foil was stirred at -30 ºC for 1 hour. The solution was filtered to remove white precipitate of AgCl, and the volatiles were removed under vacuum to yield complex **II** as white powder (71 mg, 50%). M.p.= 100.5 ºC (decomposition).

^{1}H NMR (500 MHz, 298 K, C_6D_6) δ 7.09 (pseudo-tdd, $^3J_{H-H}$ = 7.6, $^4J_{H-H}$ = 1.2, $^5J_{H-P}$ = 2.4 Hz, 1H, H_5), 6.89 (pseudo-tdd, $^3J_{H-H}$ = 7.6, $^4J_{H-H}$ = 1.2, $^4J_{H-P}$ = 2.4 Hz, 1H, H_4), 6.77 (dbr, $^3J_{H-H}$ = 7.6 Hz, 1H, H_6), 6.72 (pseudo-tbr, $^3J_{H-H}$ = $^3J_{H-P}$ = 7.6 Hz, 1H, H_3), 2.20 – 2.09 (m, 4H, CH_{Cy}, CH_{2Cy}), 1.98 – 1.92 (m, 2H, CH_{2Cy}), 1.88 – 1.82 (m, 2H, CH_{2Cy}), 1.76 – 1.64 (m, 6H, CH_{iPr}, CH_{2Cy}), 1.55 – 1.39 (m, 4H, CH_{2Cy}), 1.34 – 1.14 (m, 4H, CH_{2Cy}), 1.04 – 0.96 (m, 2H, CH_{2Cy}), 0.86 (dd, $^3J_{H-H}$ = 7.0, $^3J_{H-P}$ = 18.7 Hz, 6H, CH_{3iPr}), 0.69 (dd, $^3J_{H-H}$ = 7.0, $^3J_{H-P}$ = 17.1 Hz, 6H, CH_{3iPr}).

^{13}C{^{1}H} NMR (126 MHz, 298 K, C_6D_6) δ 157.6 (d, $^2J_{C-P}$ = 25 Hz, C_1), 131.0 (d, $^2J_{C-P}$ = 6 Hz, C_3), 130.4 (d, $^4J_{C-P}$ = 3 Hz, C_5), 126.6 (d, $^3J_{C-P}$ = 17 Hz, C_6), 126.2 (d, $^3J_{C-P}$ = 9 Hz, C_4), 125.1 (d, $^1J_{C-P}$ = 58 Hz, C_2), 120.7 (q, $^1J_{C-F}$ = 323 Hz, CF_3), 39.2 (sbr, B–CH_{Cy}), 31.2 (s, CH_{2Cy}), 29.0 (s, CH_{2Cy}), 28.4 (s, CH_{2Cy}), 27.9 (d, $^1J_{C-P}$ = 36 Hz, CH_{iPr}), 27.8 (s, CH_{2Cy}), 27.2 (s, CH_{2Cy}), 19.5 (s, CH_{3iPr}).

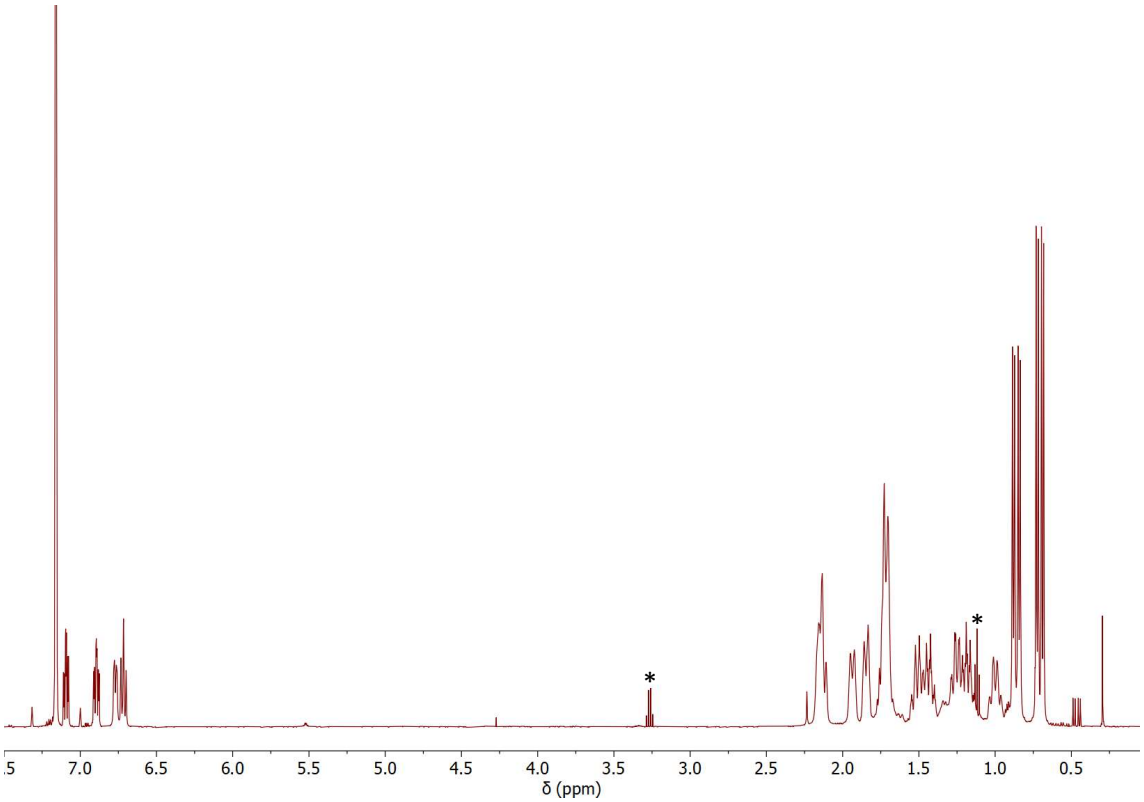
^{31}P{^{1}H} NMR (203 MHz, 298 K, C_6D_6) δ 53.0.

^{19}F{^{1}H} NMR (282 MHz, 298 K, C_6D_6) δ -73.7.

^{11}B{^{1}H} NMR (160 MHz, 298 K, C_6D_6) δ Not detected.

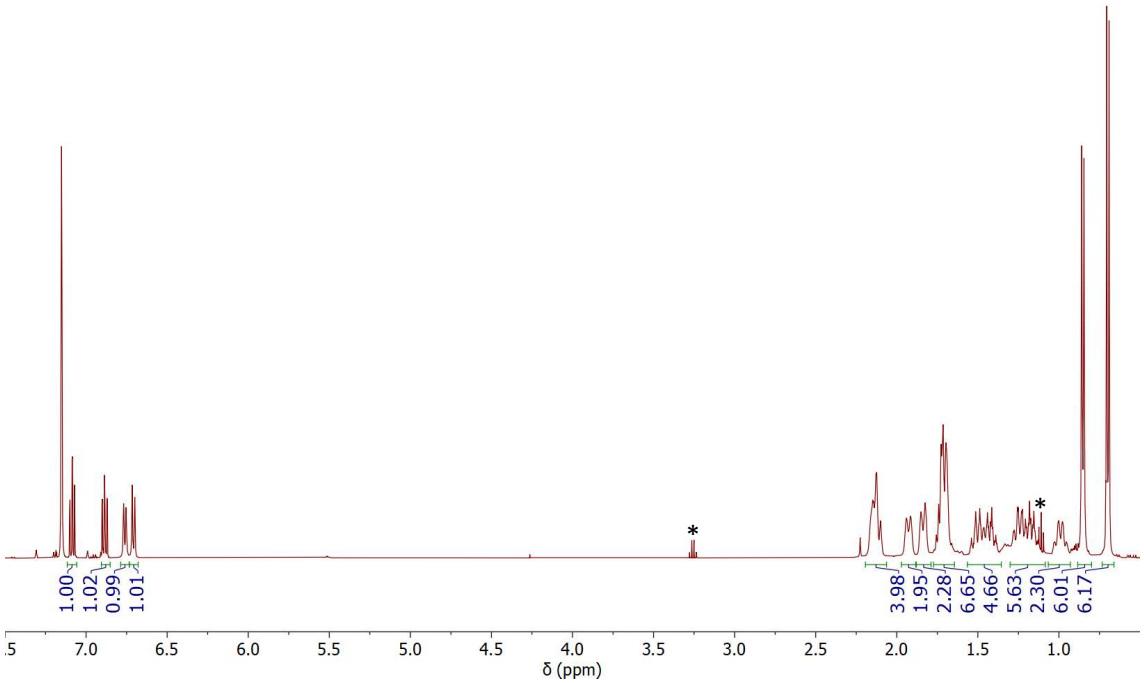
HRMS-DCI(CH_4) (*m/z*): found $[M]^+$ 846.1721, calcd. $C_{29}H_{39}Au^{11}BF_6NO_4PS_2$ requires 846.1721.

^{1}H NMR spectrum (500 MHz, 298 K) in C_6D_6



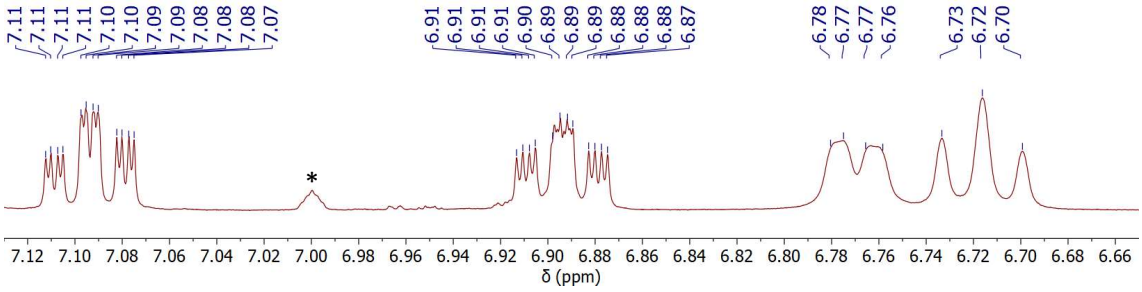
* Et_2O

$^{1}H\{^{31}P\}$ NMR spectrum (500 MHz, 298 K) in C_6D_6



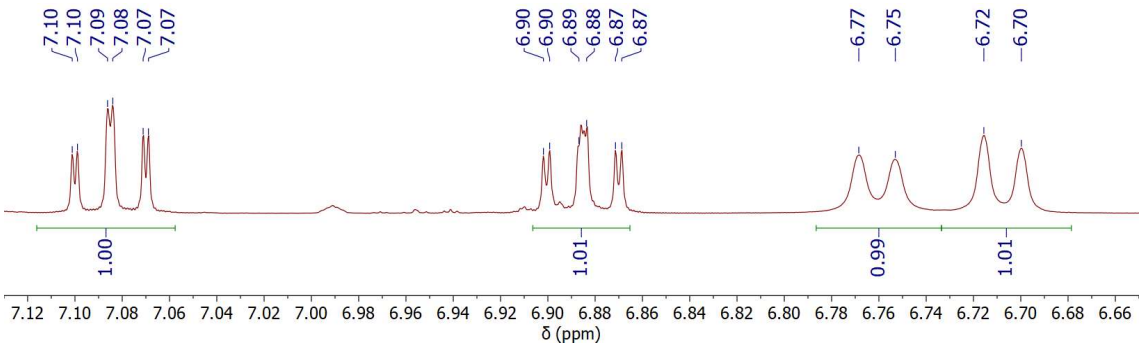
* Et_2O

^{1}H NMR spectrum (500 MHz, 298 K) in C_6D_6; aromatic region

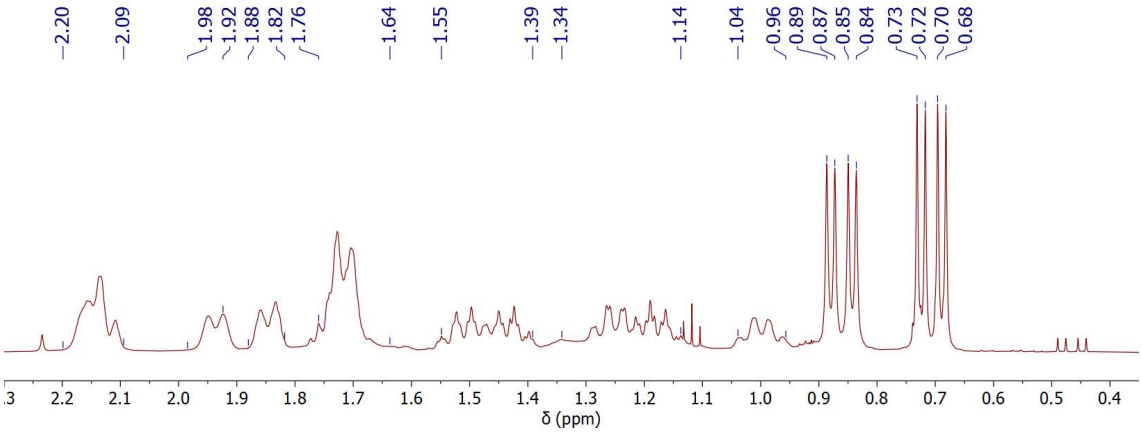


* Unidentified minor impurity

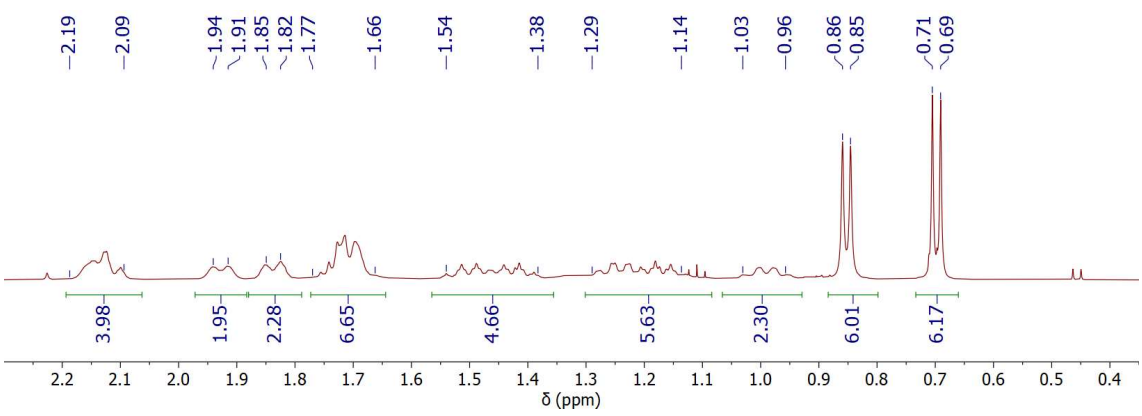
^{1}H{^{31}P} NMR spectrum (500 MHz, 298 K) in C_6D_6; aromatic region



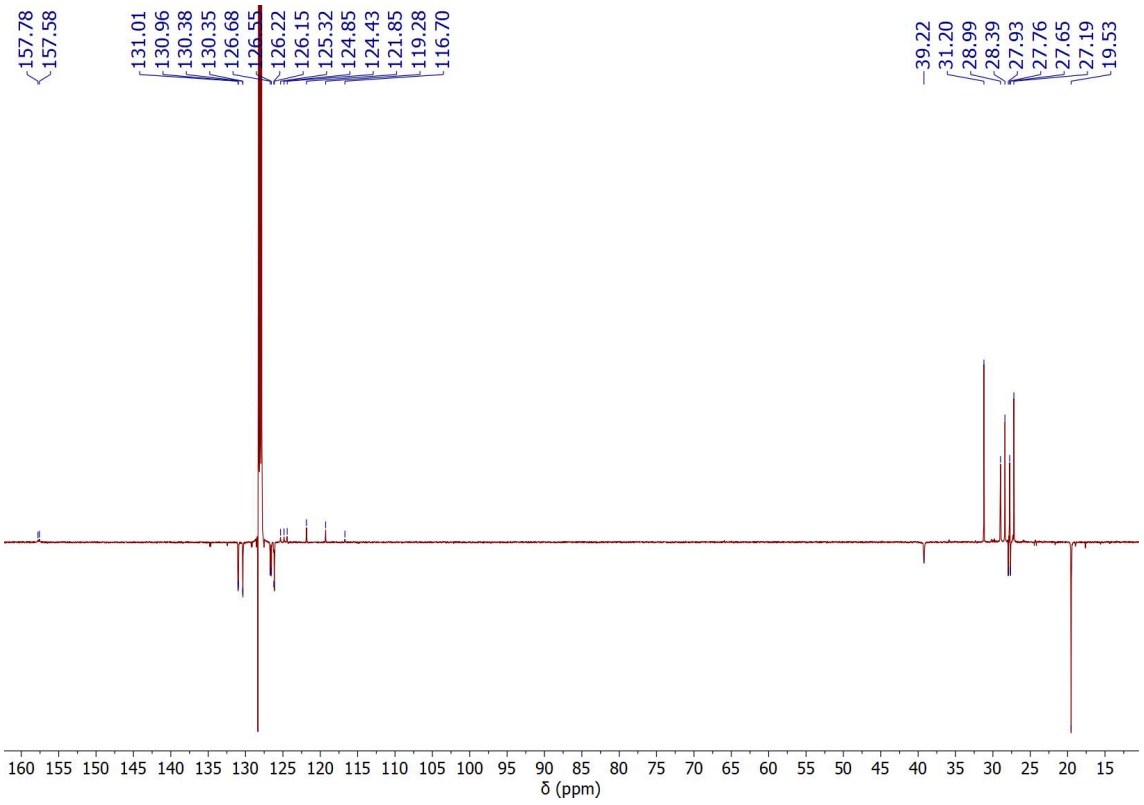
^{1}H NMR spectrum (500 MHz, 298 K) in C_6D_6; aliphatic region



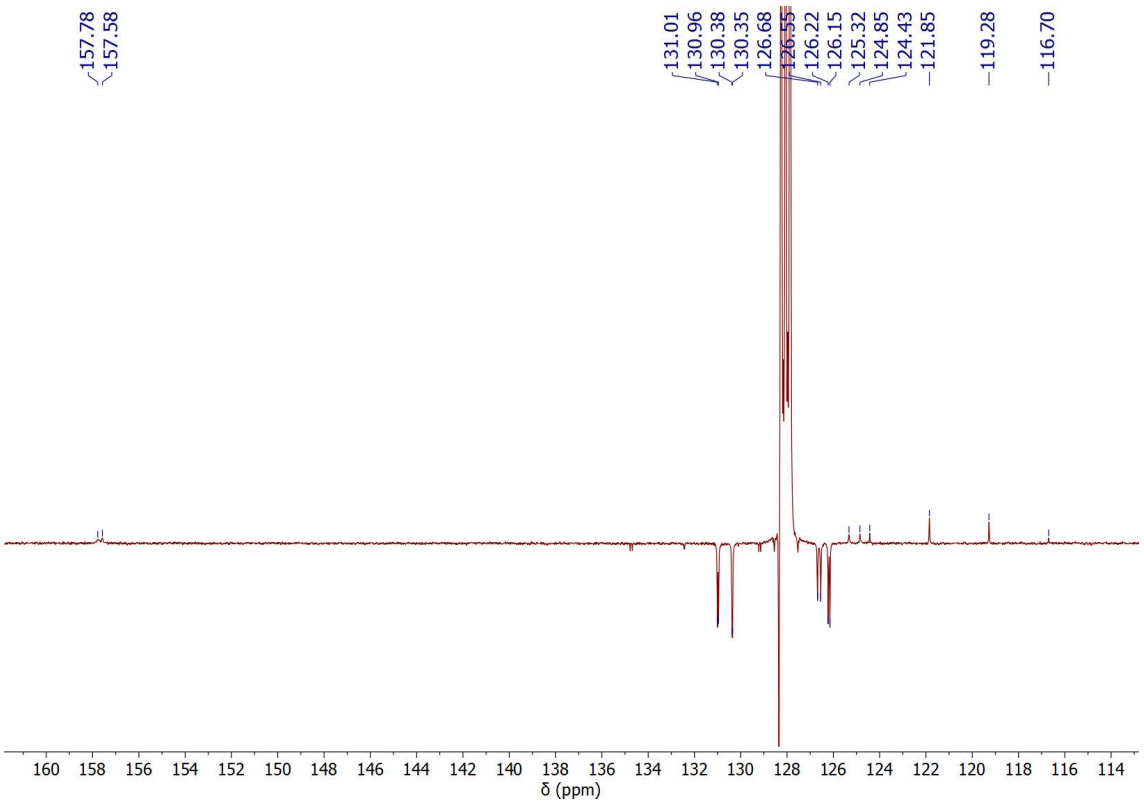
^{1}H{^{31}P} NMR spectrum (500 MHz, 298 K) in C_6D_6; aliphatic region



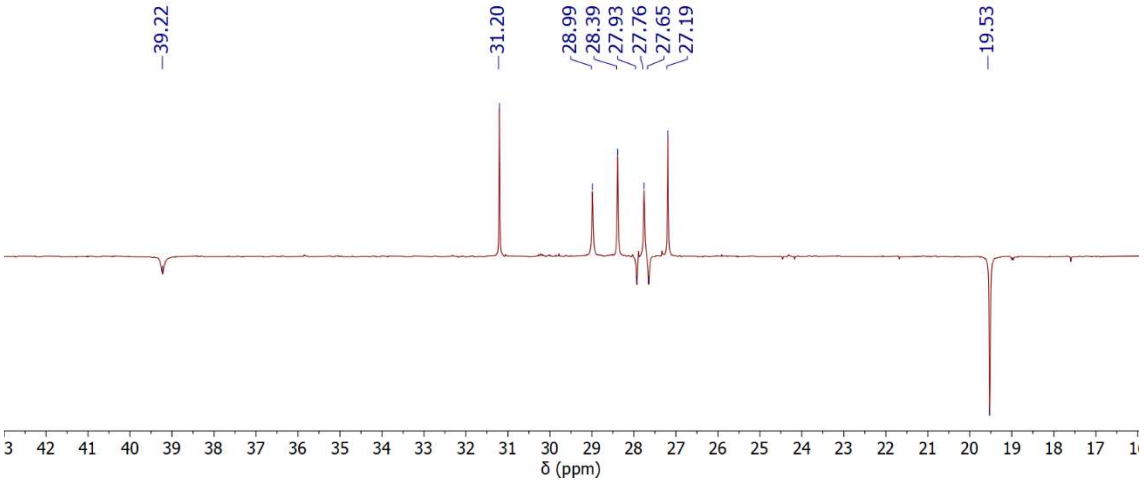
$^{13}C\{^{1}H\}$ NMR (JMOD) spectrum (126 MHz, 298 K) in C_6D_6



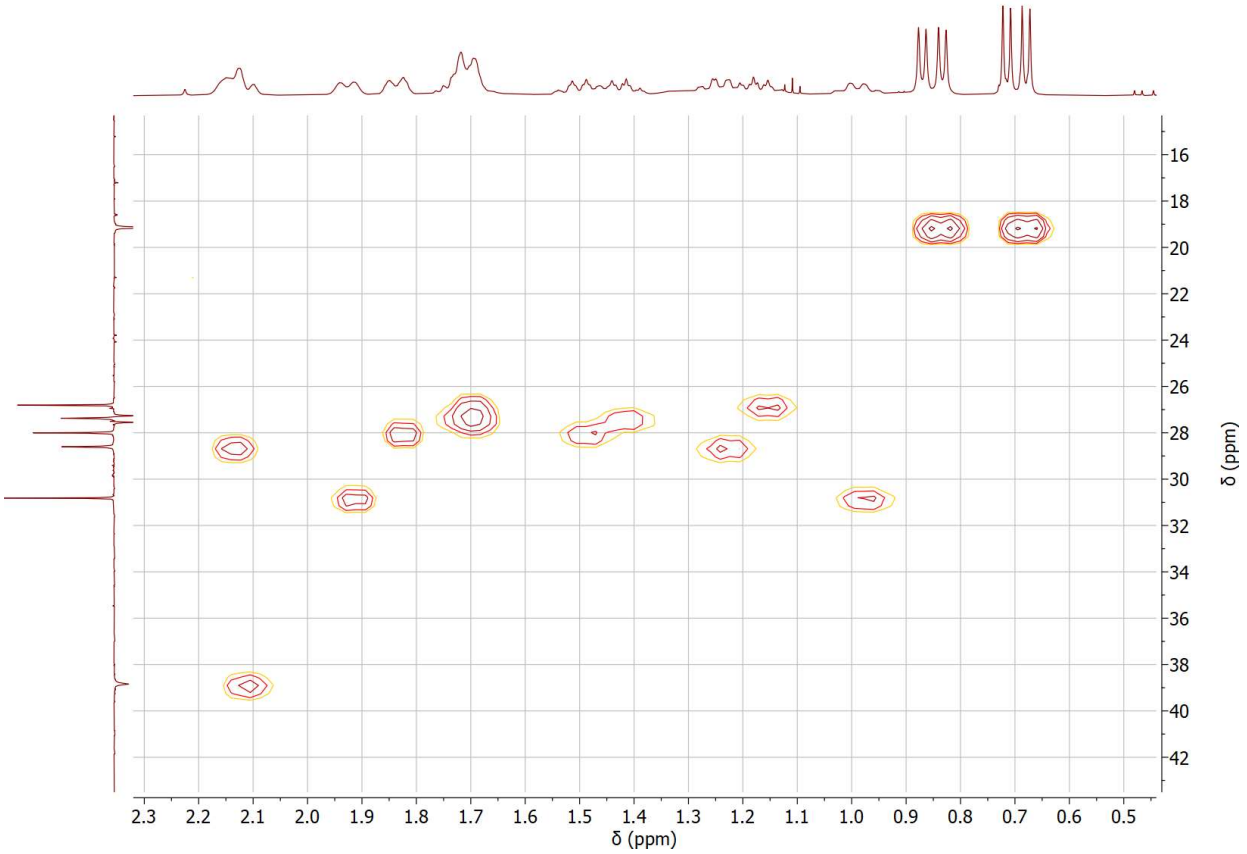
$^{13}C\{^{1}H\}$ NMR (JMOD) spectrum (126 MHz, 298 K) in C_6D_6; aromatic region



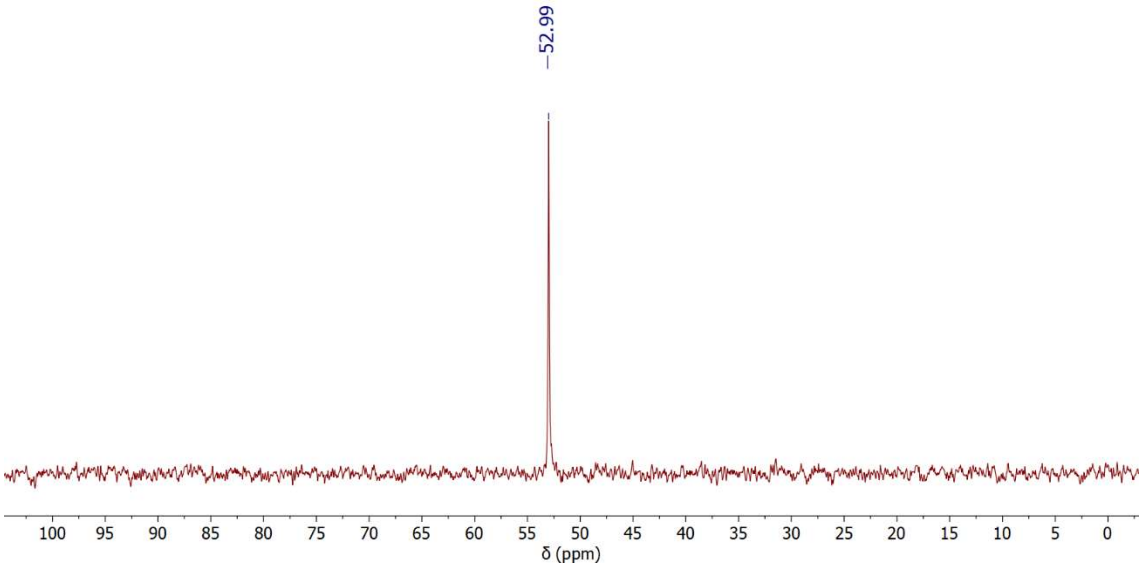
$^{13}C\{^{1}H\}$ NMR (JMOD) spectrum (126 MHz, 298 K) in C_6D_6; aliphatic region



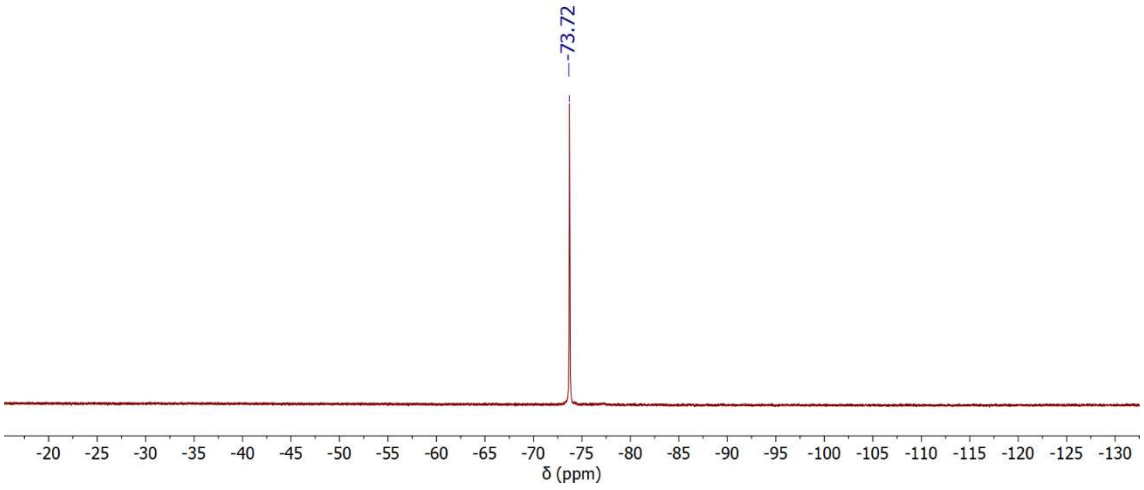
HSQC NMR (100 MHz, 298 K) in C_6D_6; aliphatic region



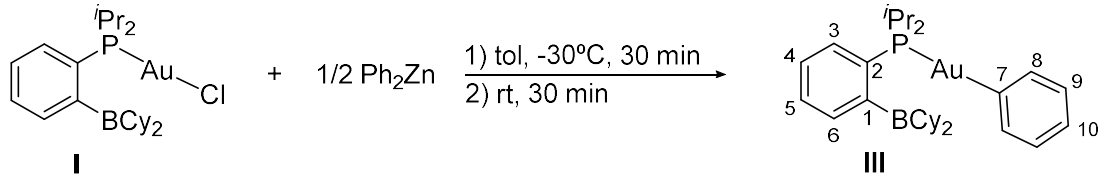
$^{31}P\{^{1}H\}$ NMR spectrum (203 MHz, 298 K) in C_6D_6



$^{19}F\{^{1}H\}$ NMR spectrum (282 MHz, 298 K) in C_6D_6



Synthesis of the Au complex III



A solution of Ph_2Zn (12.8 mg, 0.058 mmol, 1 Equiv.) in 5 mL of toluene was added to a solution of gold complex **I** (70 mg, 0.120 mmol, 2 Equiv.) in toluene (3 mL) at -30 ºC. The reaction was stirred at that temperature for 30 min and 30 min at room temperature and then, it was filtered to remove $ZnCl_2$ and the supernatant was evaporated. The crude was dissolved in Et_2O (10 mL), filtered, and concentrated (2 mL approx.). **III** was isolated as colourless solid by crystallization of saturated solution of Et_2O after 1 day at -30 ºC (41 mg, 55%). M.p.= 79.8 ºC (decomposition).

^{1}H NMR (400 MHz, 298 K, C_6D_6) δ 7.98 (pseudo-ddbr, $^3J_{H\text{-}H}$ = $^3J_{H\text{-}P}$ =7.6, $^4J_{H\text{-}P}$ = 1.7 Hz, 2H, H_8), 7.52 (td, $^3J_{H\text{-}H}$ = 7.6, $^5J_{H\text{-}P}$ = 1.6 Hz, 2H, H_9), 7.22 (pseudo-ttd, $^3J_{H\text{-}H}$ = 7.6, $^4J_{H\text{-}H}$ = 1.5, $^6J_{H\text{-}P}$ = 0.5 Hz, 1H, H_{10}), 7.18 – 7.14 (m, 1H, H_5), 7.01 (pseudo-tdd, $^3J_{H\text{-}H}$ = 7.6, $^4J_{H\text{-}H}$ = 1.5, $^4J_{H\text{-}P}$ = 1.7 Hz, 1H, H_4), 6.98 – 6.91 (m, 2H, H_3, H_6), 2.25 – 2.22 (m, 2H, CH_{2Cy}), 2.13 – 1.96 (m, 6H, CH_{2Cy}, CH_{Cy}, CH_{iPr}), 1.82–1.70 (m, 6H, CH_{2Cy}), 1.48 – 1.30 (m, 6H, CH_{2Cy}), 1.26 – 1.11 (m, 4H, CH_{2Cy}), 1.02 (dd, $^3J_{H\text{-}H}$ = 6.9, $^3J_{H\text{-}P}$ = 15.8 Hz, 6H, CH_{3iPr}), 0.92 (dd, $^3J_{H\text{-}H}$ = 6.9, $^3J_{H\text{-}P}$ = 15.8 Hz, 6H, CH_{3iPr}).

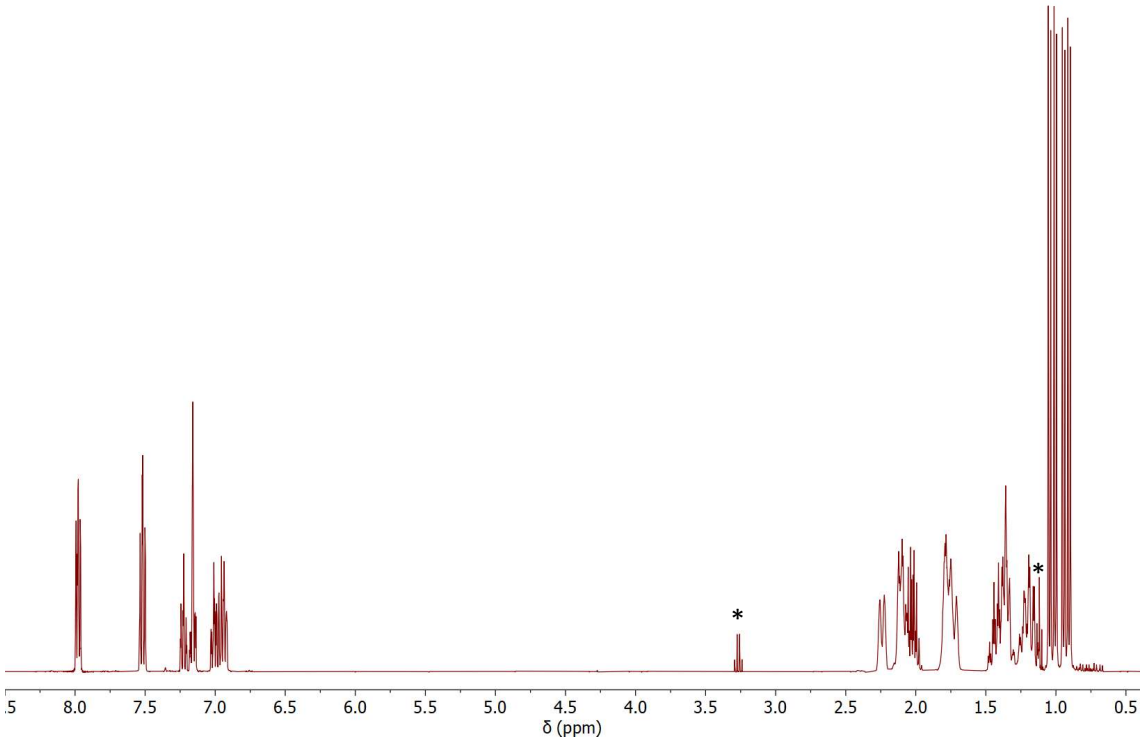
^{13}C{^{1}H} NMR (100 MHz, 298 K, C_6D_6) δ 178.9 (d, $^2J_{C\text{-}P}$ = 113 Hz, C_7), 159.3 (sbr, C_1), 139.8 (sbr, C_8), 131.5 (d, $^2J_{C\text{-}P}$ = 3 Hz, C_3), 129.7 (d, $^1J_{C\text{-}P}$ = 45 Hz, C_2), 129.4 (d, $^4J_{C\text{-}P}$ = 3 Hz, C_5), 128.0 (s, C_9), 127.1 (d, $^3J_{C\text{-}P}$ = 18 Hz, C_6), 126.2 (s, C_{10}), 125.9 (d, $^3J_{C\text{-}P}$ = 7 Hz, C_4), 39.6 (s, B–CH_{Cy}), 31.4 (s, CH_{2Cy}), 29.7 (s, CH_{2Cy}), 28.8 (s, CH_{2Cy}), 28.5 (s, CH_{2Cy}), 27.5 (s, CH_{2Cy}), 27.1 (d, $^1J_{C\text{-}P}$ = 27 Hz, CH_{iPr}), 19.9 (d, $^2J_{C\text{-}P}$ = 2 Hz, CH_{3iPr}), 19.7 (d, $^2J_{C\text{-}P}$ = 5 Hz, CH_{3iPr}).

^{31}P{^{1}H} NMR (162 MHz, 298 K, C_6D_6) δ 61.4.

^{11}B{^{1}H} NMR (128 MHz, 298 K, C_6D_6) δ Not detected.

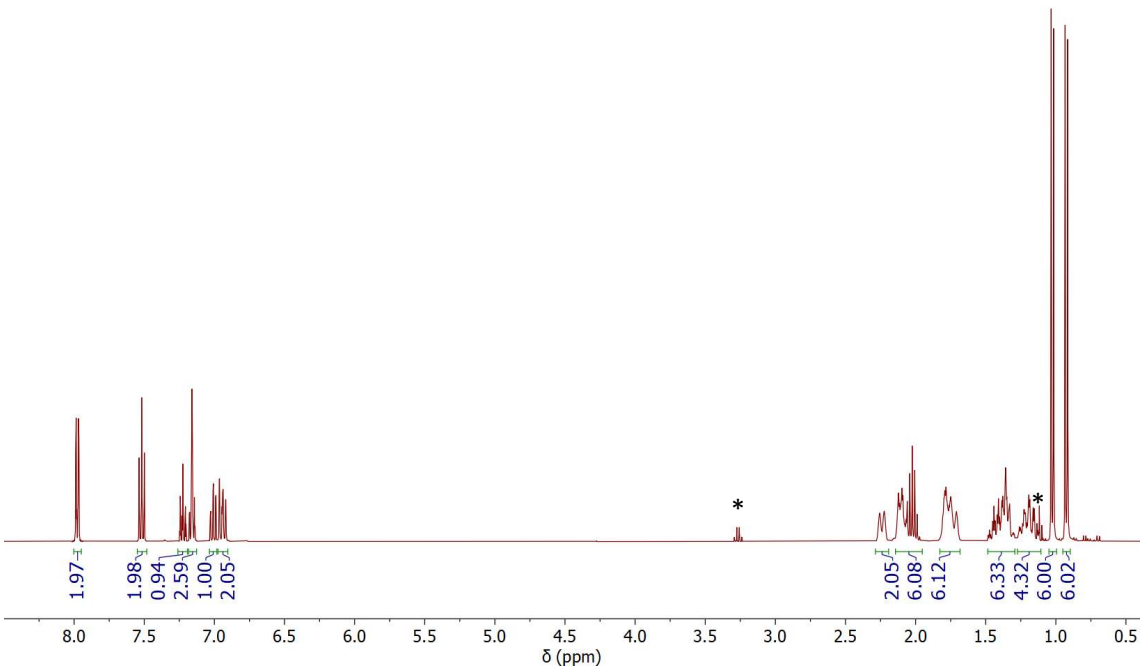
HRMS-DCI(CH_4) (*m/z*): found $[MH]^+-C_6H_6$ 567.2625, calcd. $C_{24}H_{40}Au^{11}BP$ requires 567.2626.

^{1}H NMR spectrum (400 MHz, 298 K) in C_6D_6



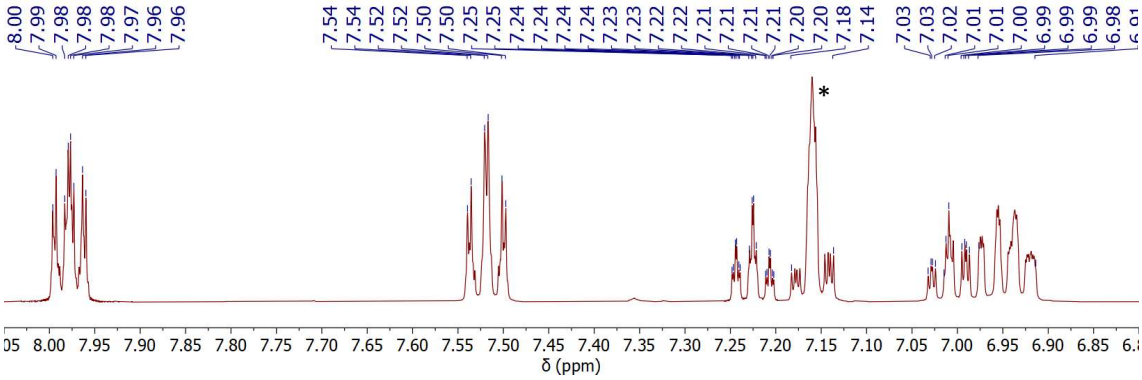
* Et_2O

$^{1}H\{^{31}P\}$ NMR spectrum (400 MHz, 298 K) in C_6D_6



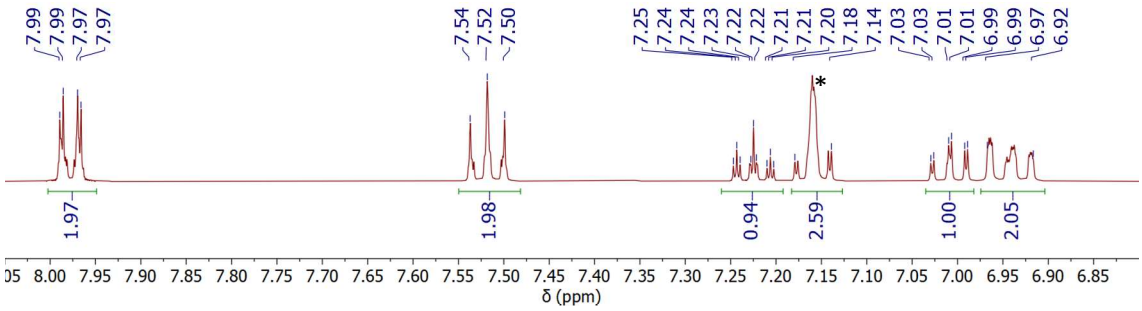
* Et_2O

^{1}H NMR spectrum (400 MHz, 298 K) in C_6D_6; aromatic region



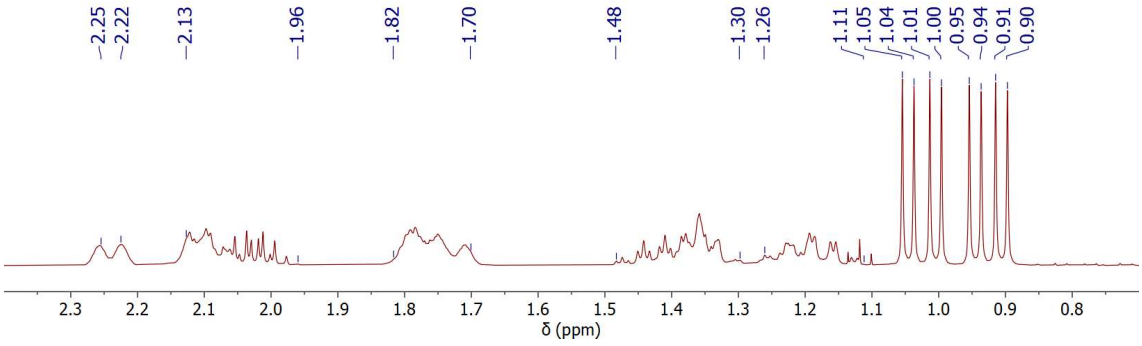
* C_6H_6 residual

$^{1}H\{^{31}P\}$ NMR spectrum (400 MHz, 298 K) in C_6D_6; aromatic region

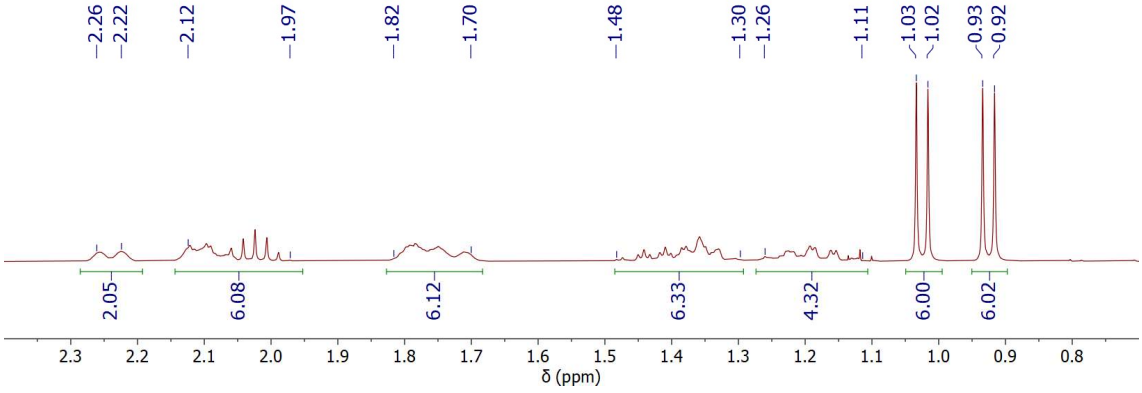


* C_6H_6 residual

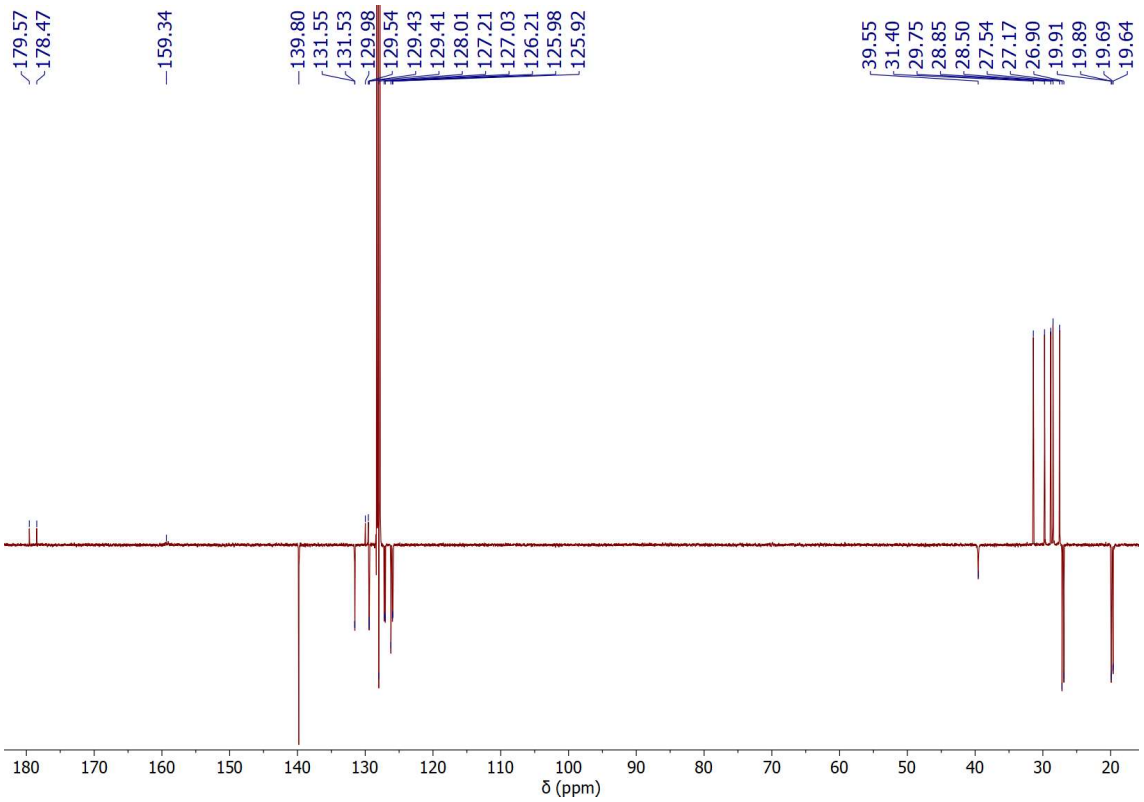
^{1}H NMR spectrum (400 MHz, 298 K) in C_6D_6; aliphatic region



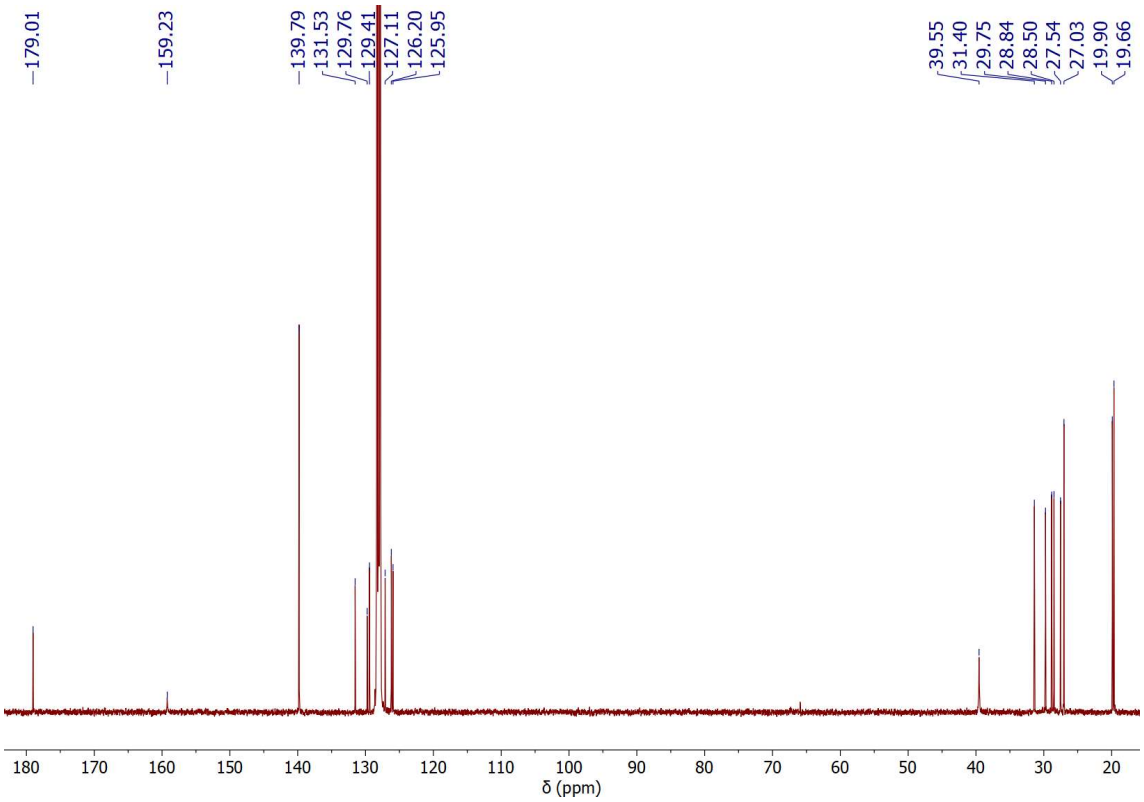
$^{1}H\{^{31}P\}$ NMR spectrum (400 MHz, 298 K) in C_6D_6; aliphatic region



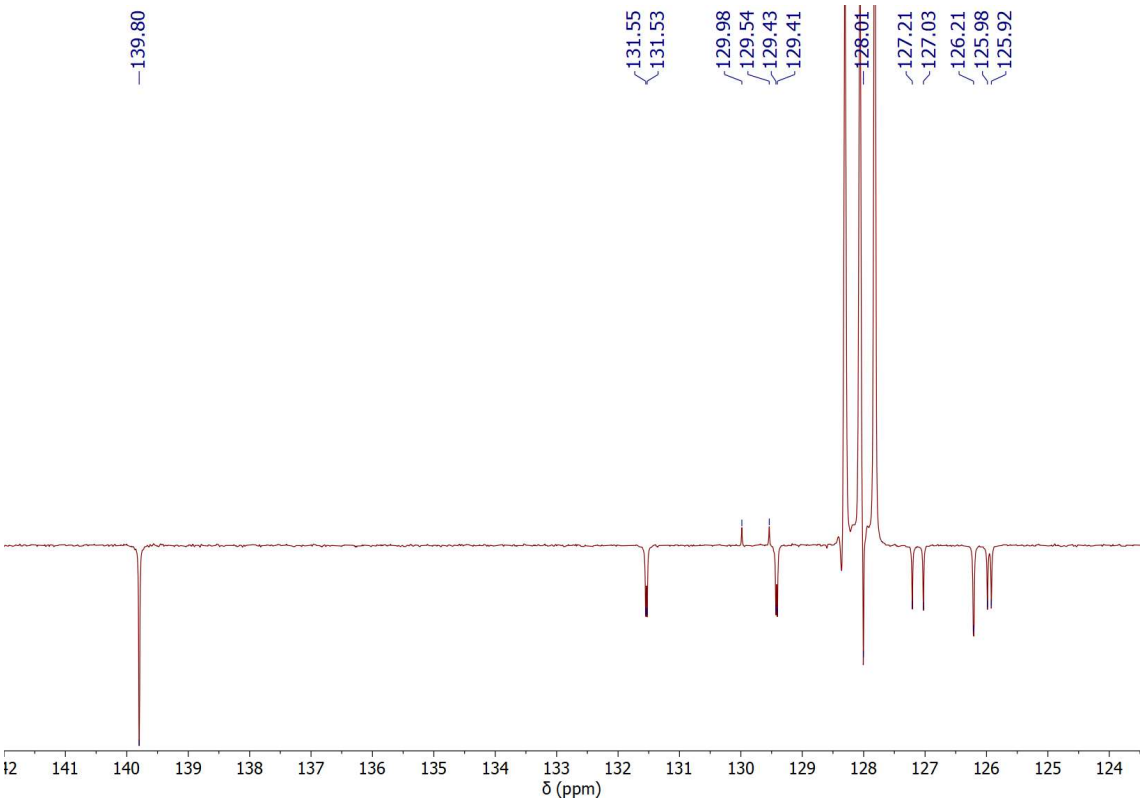
$^{13}C\{^{1}H\}$ NMR (JMOD) spectrum (100 MHz, 298 K) in C_6D_6



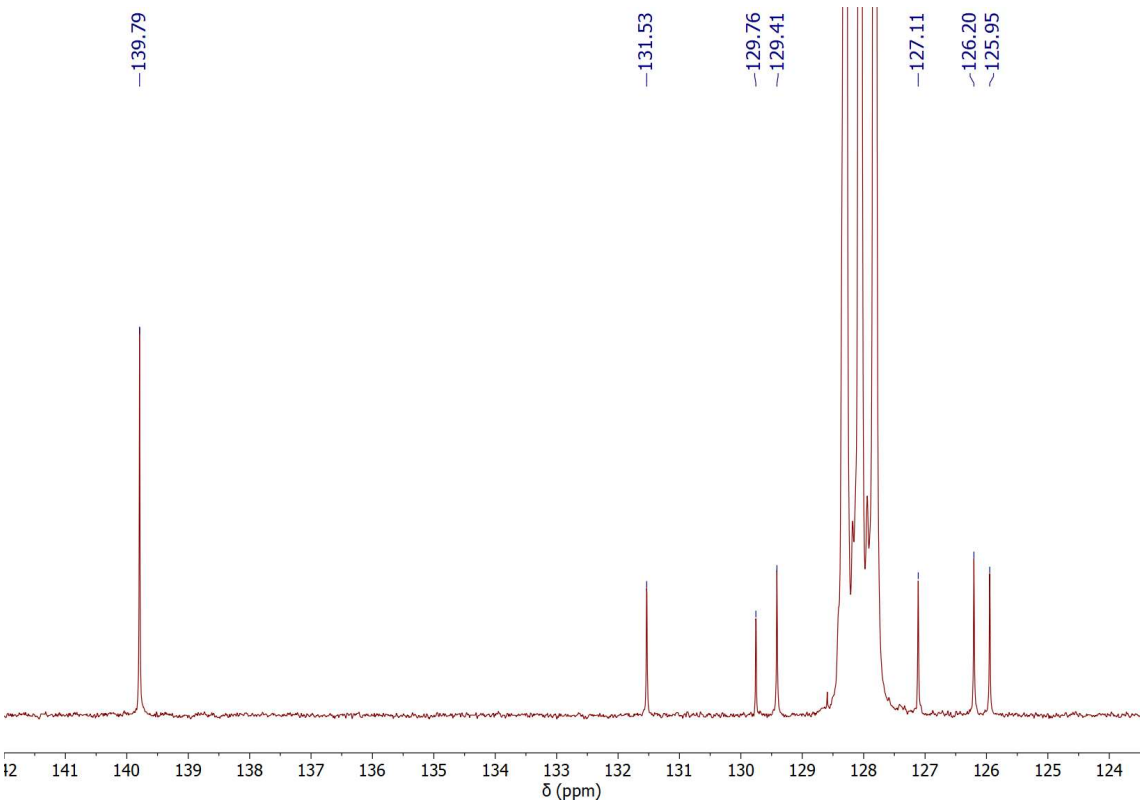
$^{13}C\{^{1}H;^{31}P\}$ NMR spectrum (100 MHz, 298 K) in C_6D_6



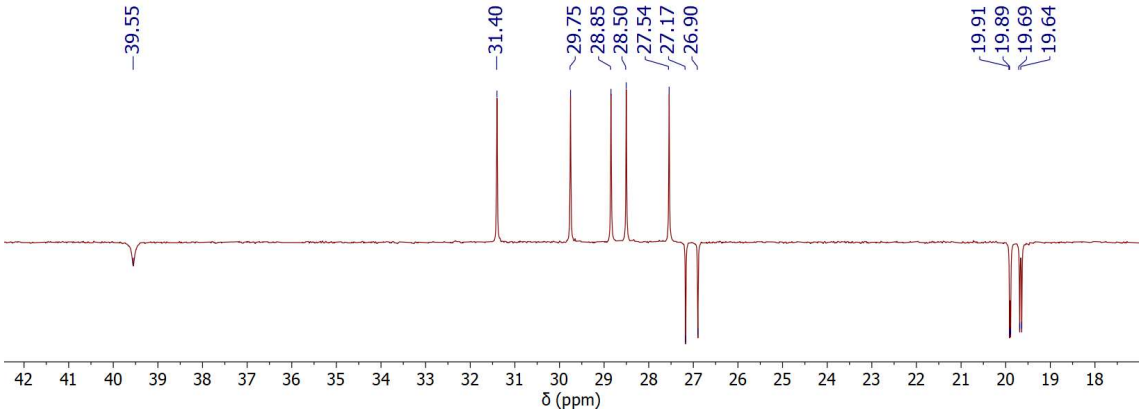
$^{13}C\{^{1}H\}$ NMR (JMOD) spectrum (100 MHz, 298 K) in C_6D_6; aromatic region



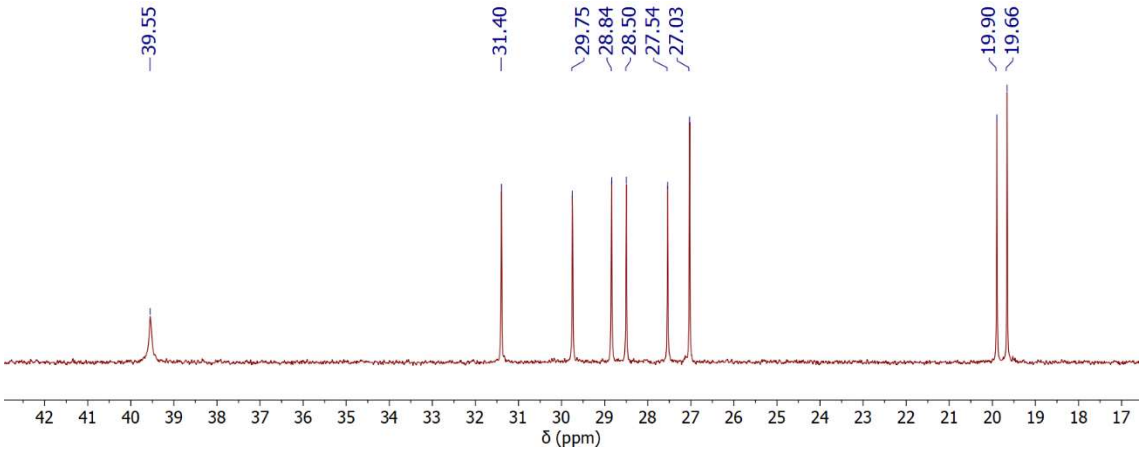
$^{13}C\{^{1}H;^{31}P\}$ NMR spectrum (100 MHz, 298 K) in C_6D_6; aromatic region



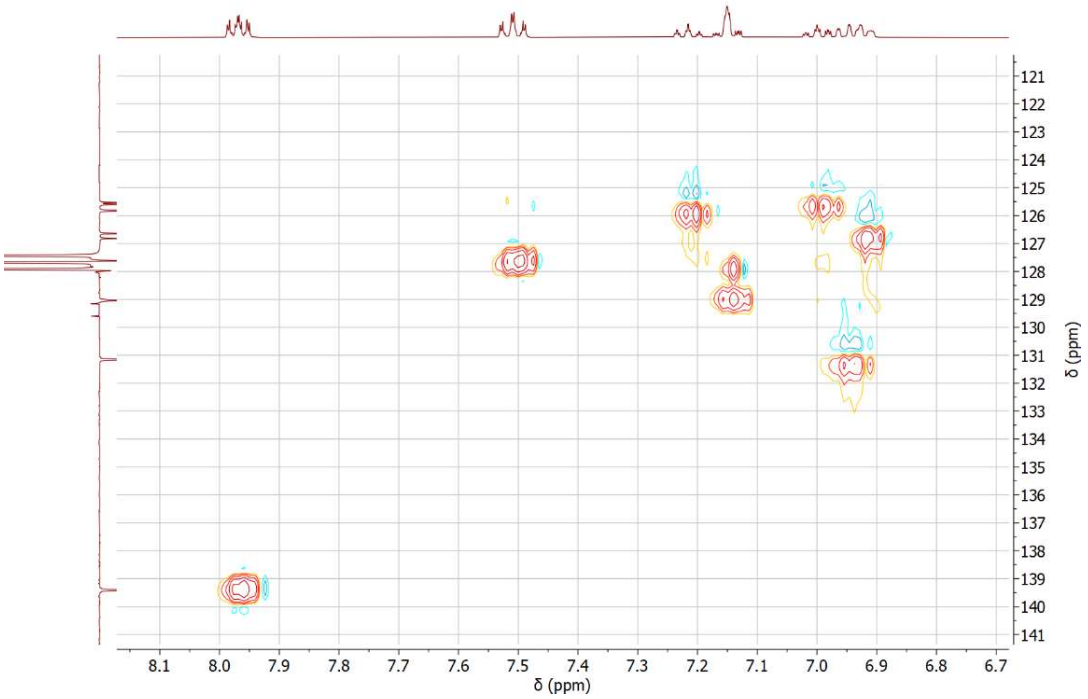
$^{13}C\{^{1}H\}$ NMR (JMOD) spectrum (100 MHz, 298 K) in C_6D_6; aliphatic region



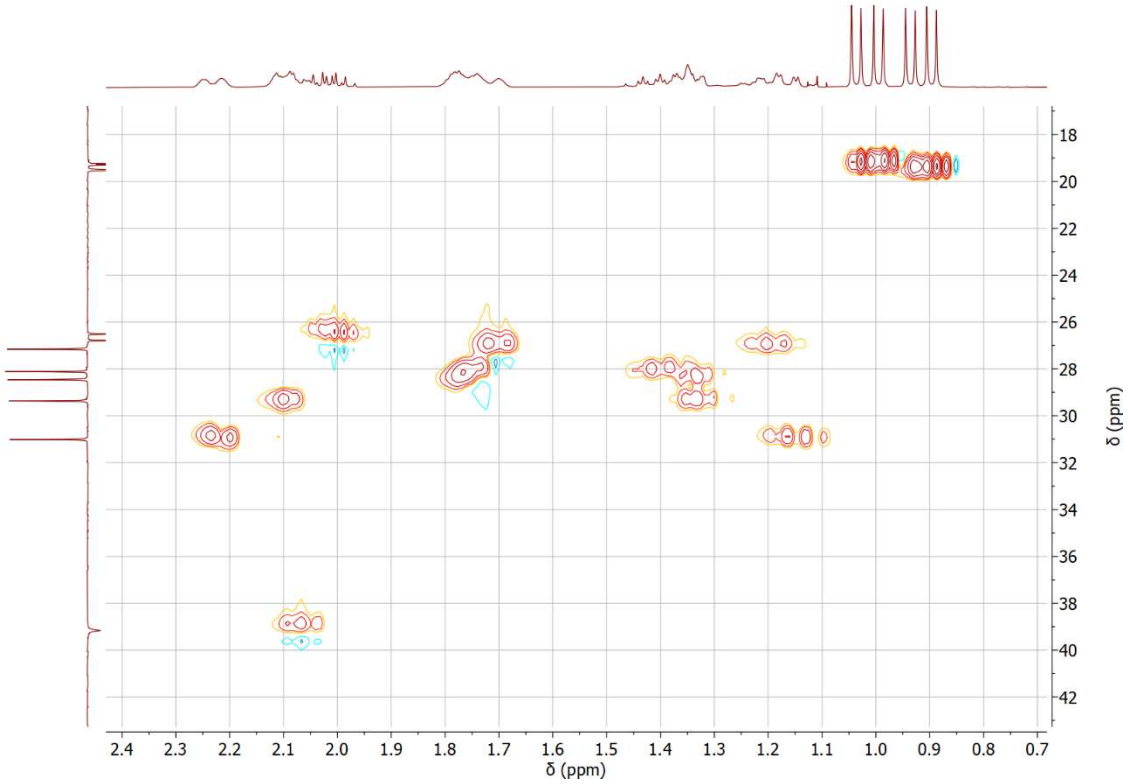
$^{13}C\{^{1}H;^{31}P\}$ NMR (JMOD) spectrum (100 MHz, 298 K) in C_6D_6; aliphatic region



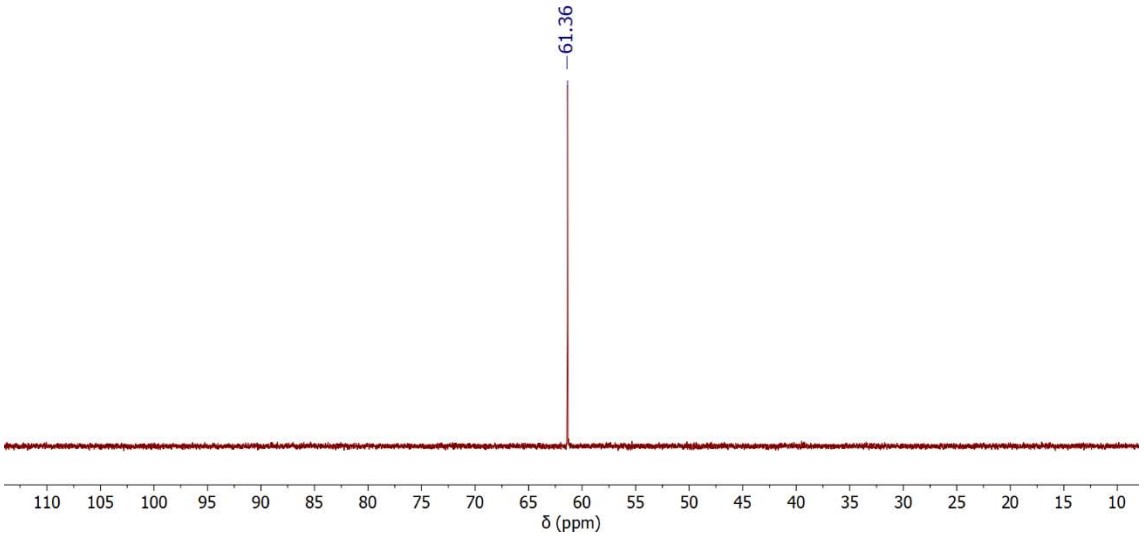
HSQC NMR (100 MHz, 298 K) in C_6D_6; aromatic region



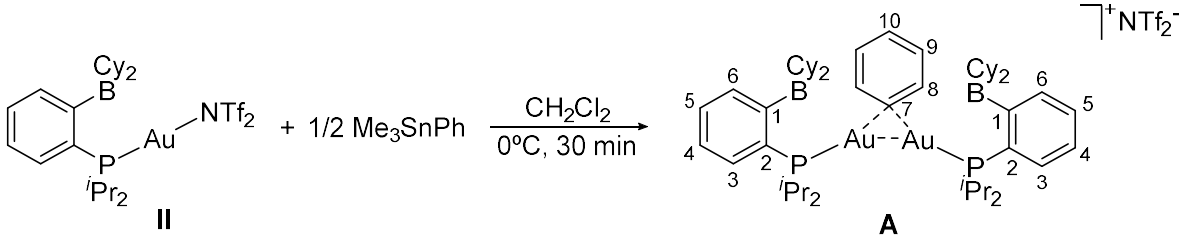
HSQC NMR (100 MHz, 298 K) in C_6D_6; aliphatic region



$^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 298 K) in C_6D_6



Synthesis of digold complex A



From Me_3SnPh:

A solution of Me_3SnPh (6 µL, 0.030 mmol, 0.5 Equiv.) in 5 mL of CH_2Cl_2 was added at 0 ºC to a solution of compound **II** (50 mg, 0.059 mmol, 1 Equiv.) in 5 mL of CH_2Cl_2. The reaction mixture was stirred for 30 min at that temperature and after 30 min at room temperature, it was filtered to remove solid impurities. The volatiles were removed under vacuum to yield complex A (57 mg, 61%). X-Ray quality crystals of A were obtained by crystallization of saturated solution of Et_2O overnight at -30 ºC. M.p.= 73.6 ºC (decomposition).

^{1}H NMR (400 MHz, 298 K, CD_2Cl_2) δ 8.02-7.99 (m, 2H, H_8), 7.79 (m, 3H, H_9, H_{10}), 7.55 – 7.47 (m, 4H, H_4, H_5), 7.44 – 7.39 (m, 2H, H_3), 6.90 (dm, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H, H_6), 2.68 (septd, $^3J_{H\text{-}H}$ = 7.0, $^2J_{H\text{-}P}$ = 8 Hz, 4H, CH_{iPr}), 1.80 – 1.75 (m, 8H, CH_{2Cy}), 1.70 – 1.66 (m, 4H, CH_{2Cy}), 1.59 – 1.56 (m, 8H, CH_{2Cy}), 1.41 (dd, $^3J_{H\text{-}H}$ = 7, $^3J_{H\text{-}P}$ = 18.9 Hz, 12H, CH_{3iPr}), 1.38 – 1.30 (m, 6H, CH_{Cy}, CH_{2Cy}), 1.22 (dd, $^3J_{H\text{-}H}$ = 7, $^3J_{H\text{-}P}$ = 18.9 Hz, 12H, CH_{3iPr}), 1.22 – 0.96 (m, 14H, CH_{2Cy}), 0.87 – 0.77 (m, 4H, CH_{2Cy}).

^{13}C{^{1}H} NMR (100 MHz, 298 K, CD_2Cl_2) δ 156.3 (d, $^2J_{C\text{-}P}$ = 21 Hz, C_1), 150.3 (s, C_8), 145.7 (t, $^2J_{C\text{-}P}$ = 49 Hz, C_7), 138.3 (s, C_{10}), 131.9 (s, C_4), 130.3 (s, C_5), 129.4 (s, C_9), 126.6 (d, $^2J_{C\text{-}P}$ = 9 Hz, C_3),125.6 (d, $^3J_{C\text{-}P}$ = 18 Hz, C_6), 124.4 (d, $^1J_{C\text{-}P}$ = 52 Hz, C_2), 120.0 (q, $^1J_{C\text{-}F}$ = 323 Hz, CF_3), 39.8 (sbr, B–CH_{Cy}), 30.8 (s, CH_{2Cy}), 28.3 (s, CH_{2Cy}), 27.8 (s, CH_{2Cy}), 27.7 (d, $^1J_{C\text{-}P}$ = 32 Hz, CH_{iPr}), 27.4 (s, CH_{2Cy}), 26.6 (s, CH_{2Cy}), 20.2 (s, CH_{3iPr}), 19.3 (s, CH_{3iPr}).

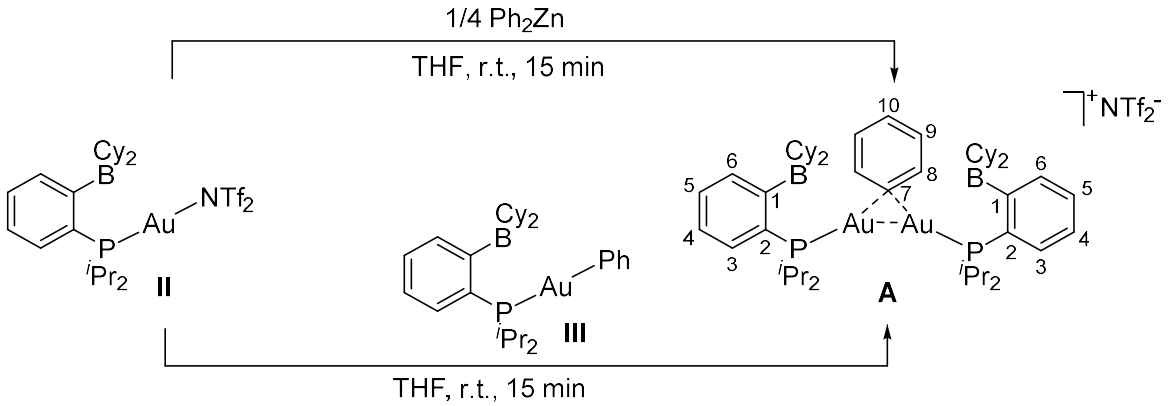
^{31}P{^{1}H} NMR (162 MHz, 298 K, CD_2Cl_2) δ 57.4.

^{19}F{^{1}H} NMR (282 MHz, 298 K, CD_2Cl_2) δ -79.5.

^{11}B{^{1}H} NMR (128 MHz, 298 K, CD_2Cl_2) δ Not detected.

HRMS-DCI(CH_4) (*m/z*): found $[M]^+$ 1211.5659, calcd. $C_{54}H_{85}Au_2{}^{11}BP_2$ requires 1211.5644.

Alternative procedures from Ph_2Zn or complex III



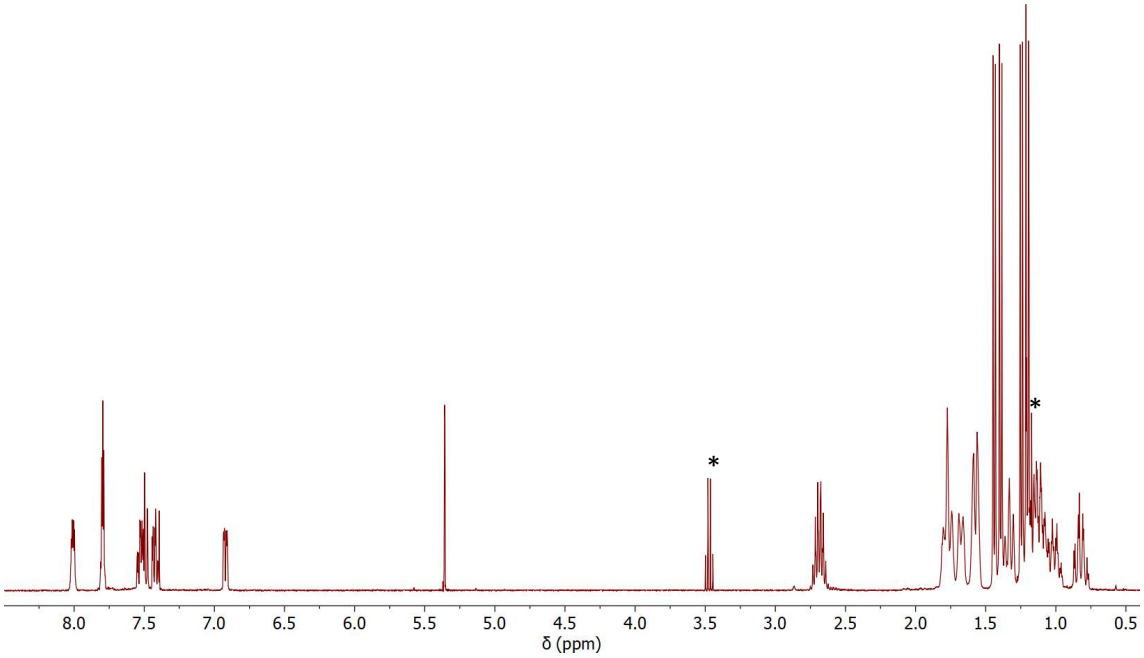
From Ph_2Zn:

To a solution of **II** (8.5 mg, 0.010 mmol, 1 Equiv.) in 0.4 mL of THF in NMR tube was added 0.1 mL of a solution of $ZnPh_2$ in THF (25 mM, 0.25 Equiv.). ^{31}P NMR indicates the major formation of complex **A** (88%) alone with complex **III** (12 %).

From complex III:

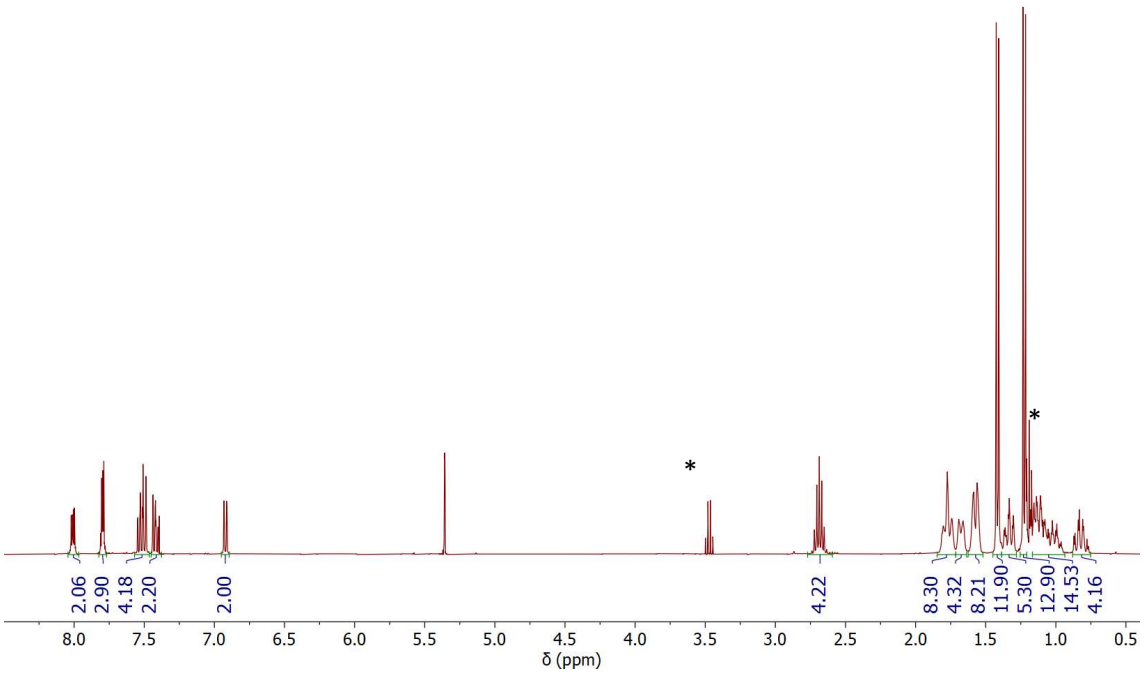
To a solution of complex **II** (20 mg, 0.024 mmol, 1 Equiv.) in THF (0.6 mL) in NMR tube was added complex **III** (14 mg, 0.024 mmol, 1 Equiv.) at room temperature. After 15 minutes, ^{31}P NMR indicates full conversion of **II** and **III** into **A**.

^{1}H NMR spectrum (400 MHz, 298 K) in CD_2Cl_2



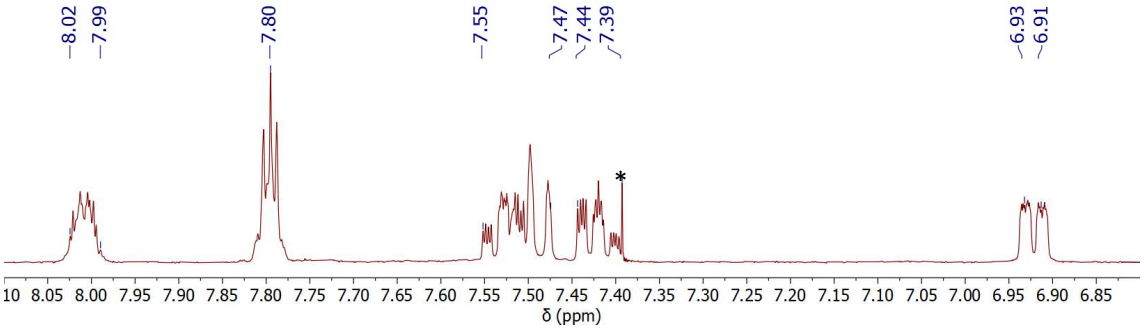
* Et_2O

$^{1}H\{^{31}P\}$ NMR spectrum (400 MHz, 298 K) in CD_2Cl_2



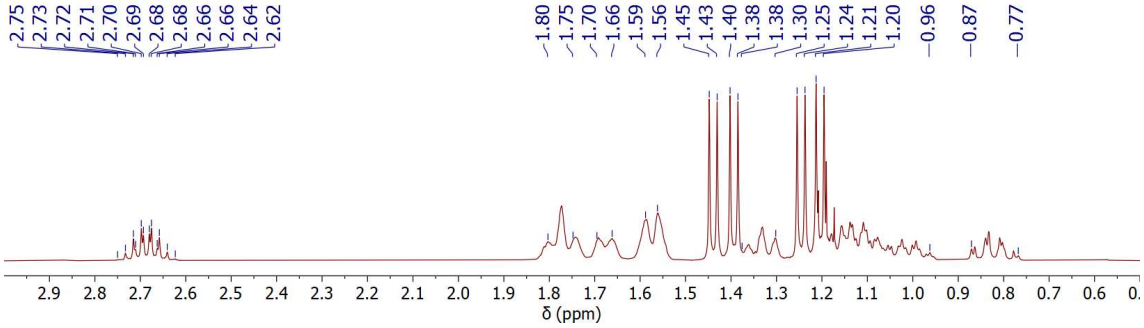
* Et_2O

^{1}H NMR spectrum (400 MHz, 298 K) in CD_2Cl_2; aromatic region

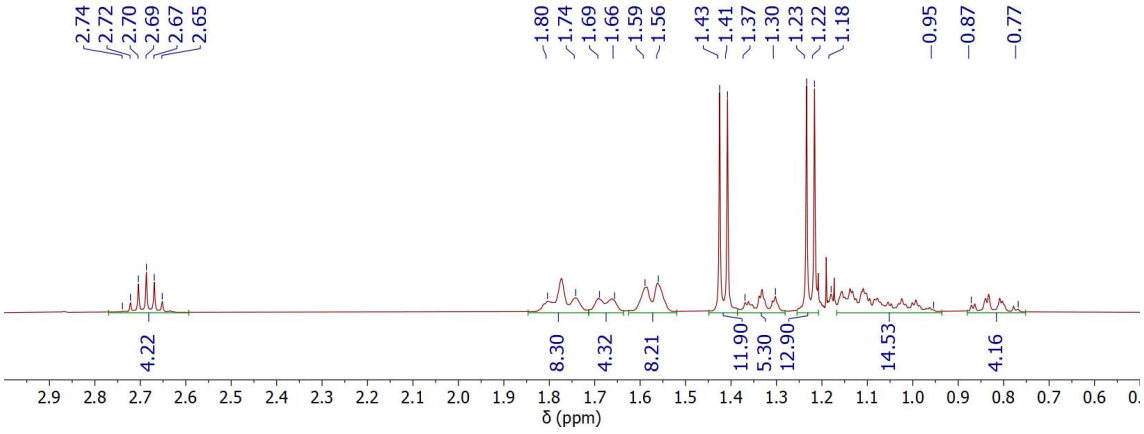


* Unidentified minor impurity.

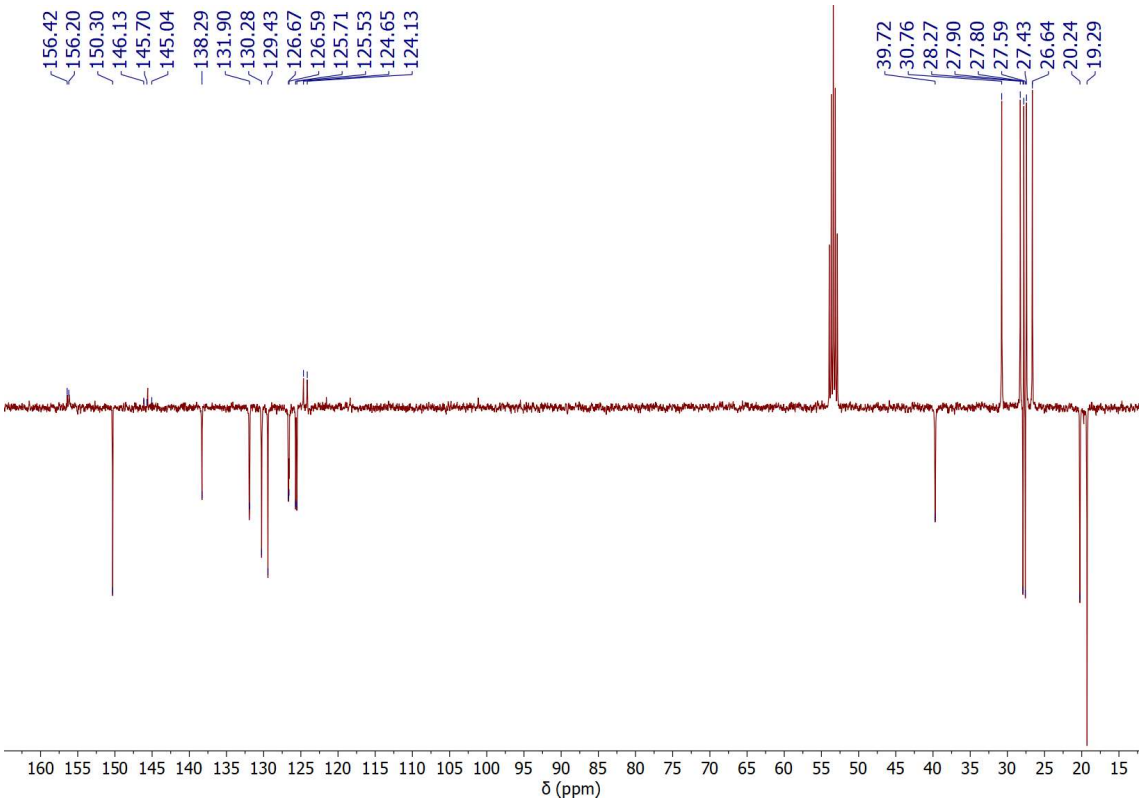
^{1}H NMR spectrum (400 MHz, 298 K) in CD_2Cl_2; aliphatic region



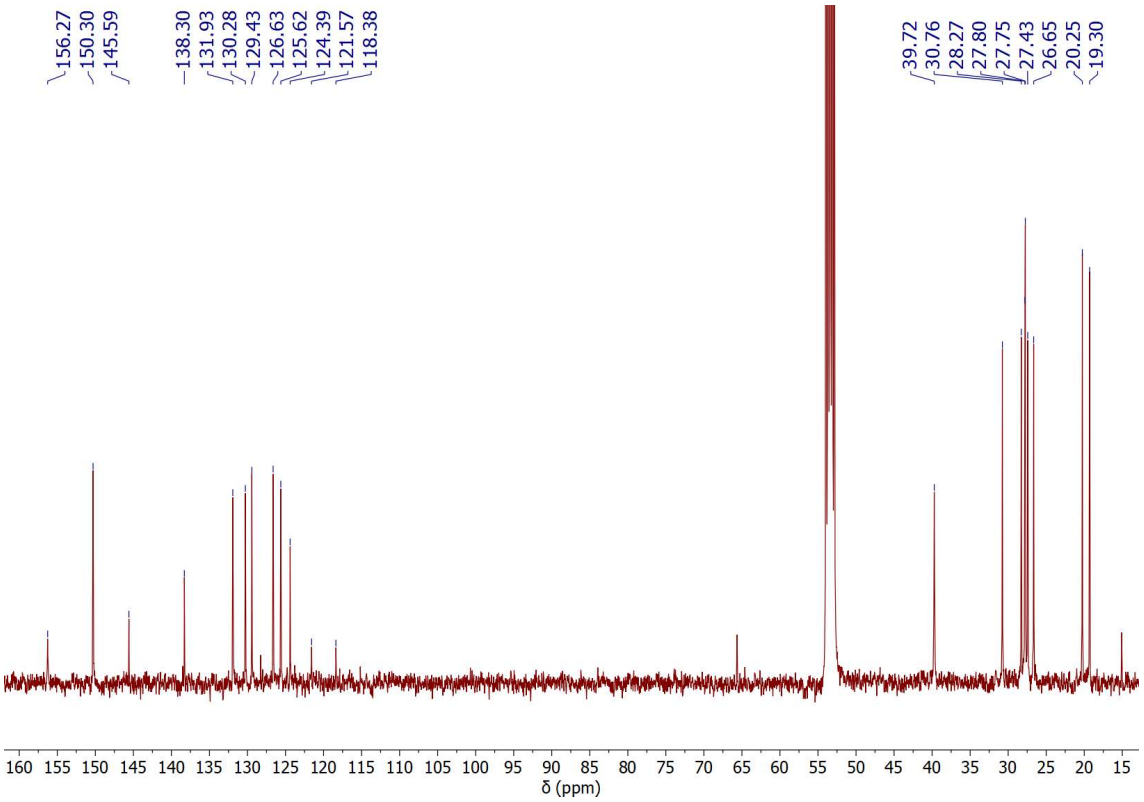
^{1}H{^{31}P} NMR spectrum (400 MHz, 298 K) in CD_2Cl_2; aliphatic region



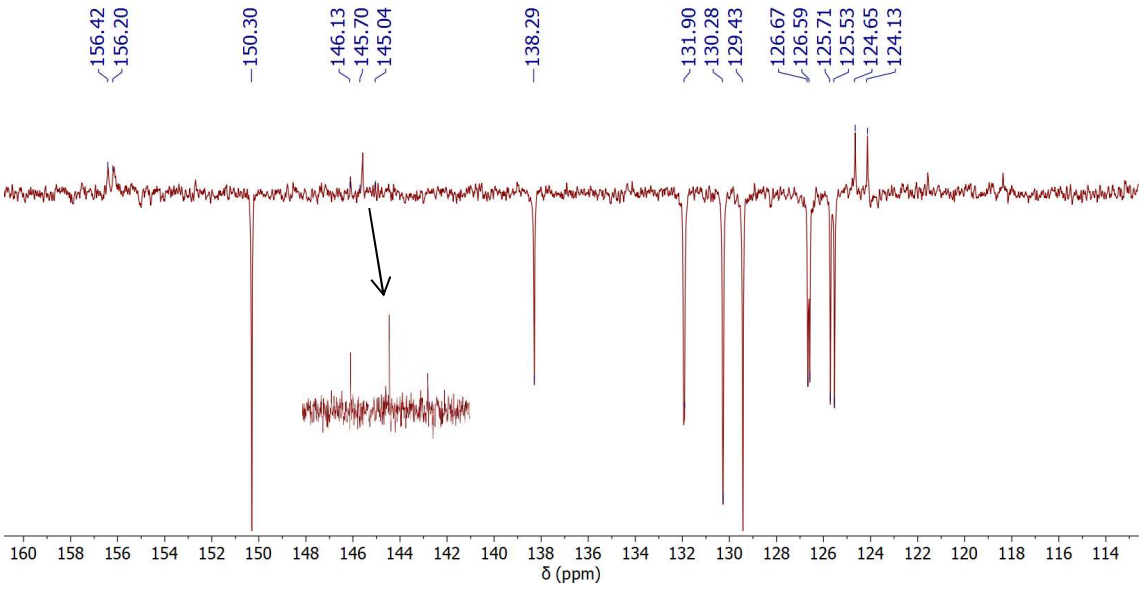
$^{13}C\{^{1}H\}$ NMR (JMOD) spectrum (100 MHz, 298 K) in CD_2Cl_2



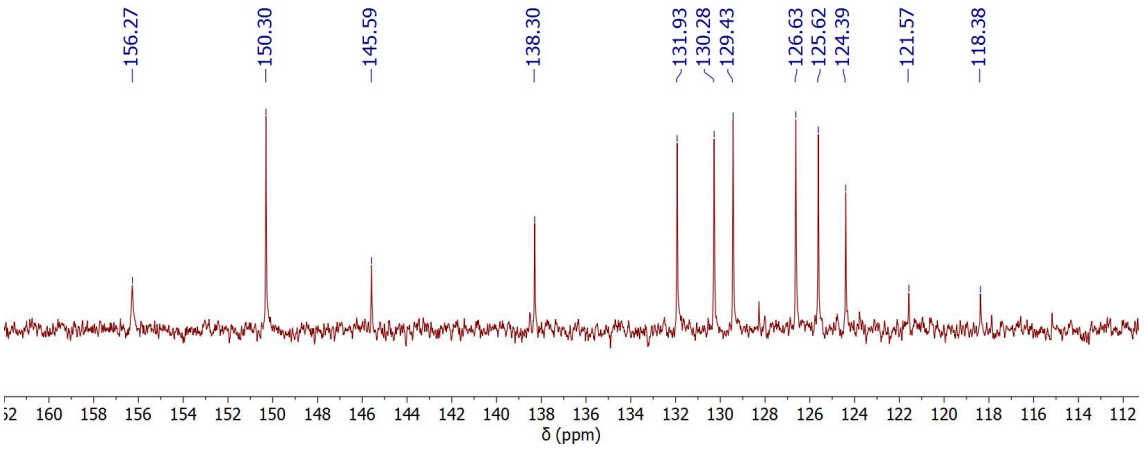
$^{13}C\{^{1}H;^{31}P\}$ NMR spectrum (100 MHz, 298 K) in CD_2Cl_2



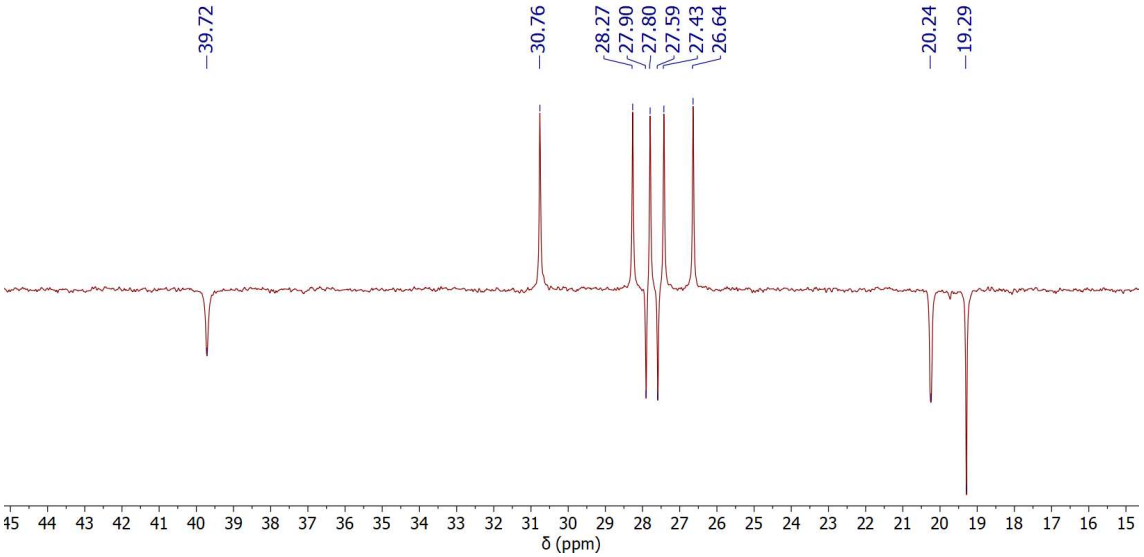
$^{13}C\{^{1}H\}$ NMR (JMOD) spectrum (100 MHz, 298 K) in CD_2Cl_2; aromatic region



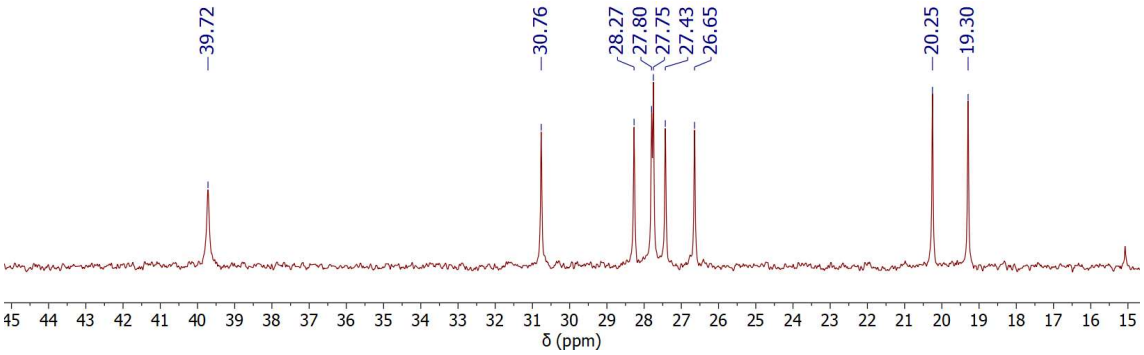
$^{13}C\{^{1}H;^{31}P\}$ NMR spectrum (100 MHz, 298 K) in CD_2Cl_2; aromatic region



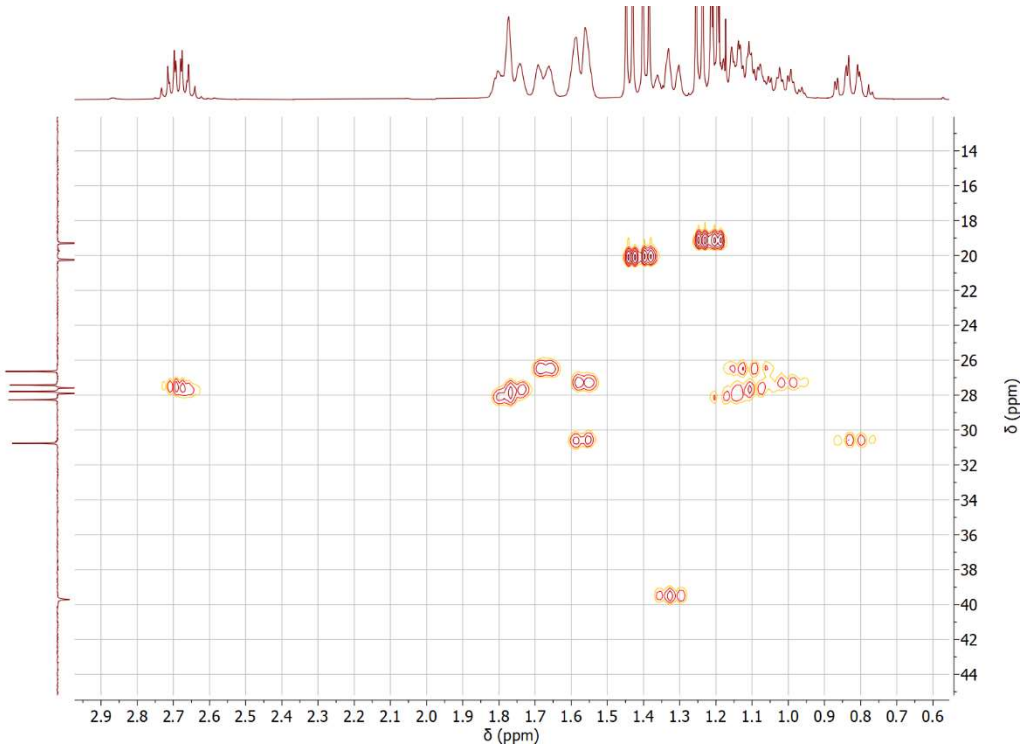
$^{13}C\{^{1}H\}$ NMR (JMOD) spectrum (100 MHz, 298 K) in CD_2Cl_2; aliphatic region



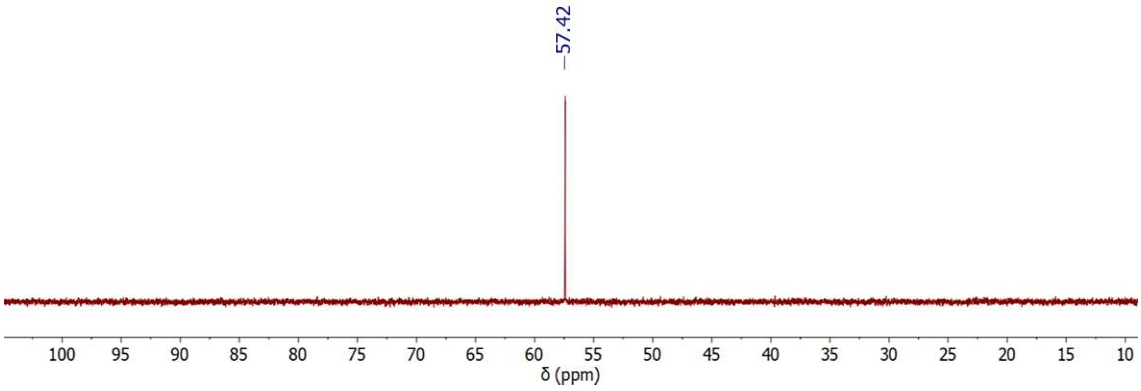
$^{13}C\{^{1}H;^{31}P\}$ NMR spectrum (100 MHz, 298 K) in CD_2Cl_2; aliphatic region



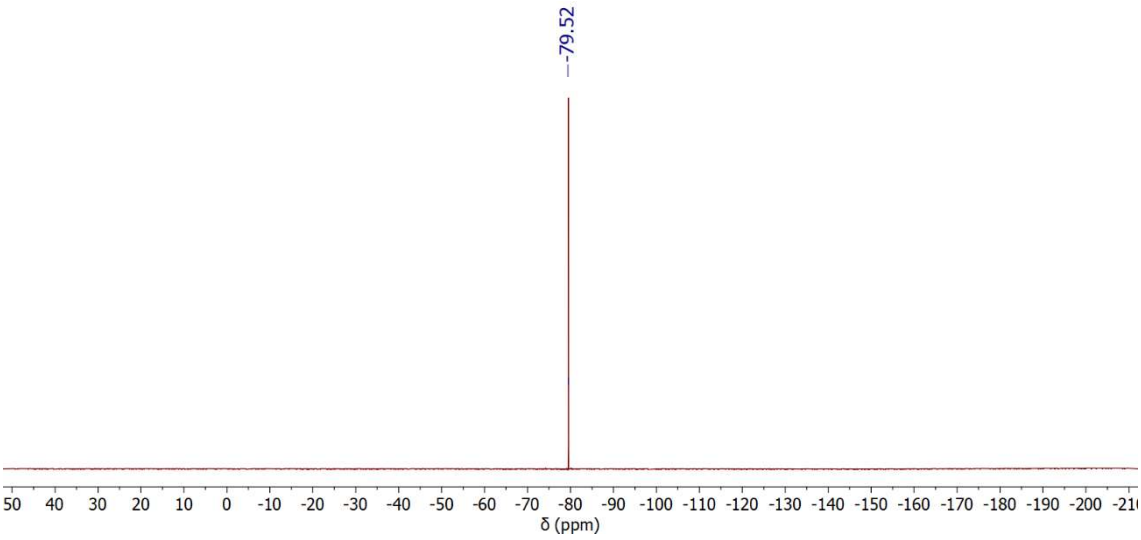
HSQC NMR (100 MHz, 298 K) in CD_2Cl_2; aliphatic region



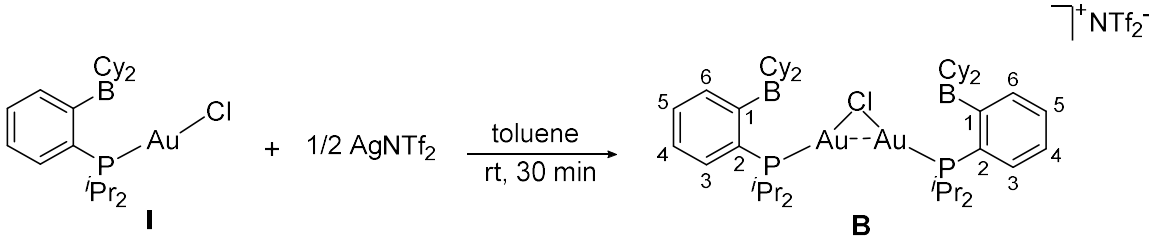
$^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 298 K) in CD_2Cl_2



$^{19}F\{^{1}H\}$ NMR spectrum (282 MHz, 298 K) in CD_2Cl_2



Synthesis of digold complex B



0.5 equivalent of $AgNTf_2$ (16 mg, 0.041 mmol, 0.5 Equiv.) was added to a solution of $PBCy_2AuCl$ **I** (50 mg, 0.083 mmol, 1 Equiv.) in toluene (5 ml) at room temperature. After 30 min, the reaction was filtered over celite to remove AgCl. The solvent was removed under vacuum to obtain a white powder (70 mg, 58%). X-Ray quality crystals were grown by diffusion of pentane into Et_2O solution of **B** (1:2 by vol.) at -30 ºC. M.p. = 74.8 ºC (decomposition).

^{1}H NMR (500 MHz, 298 K, C_6D_6) δ 7.09 (pseudo-tdd, $^3J_{H-H}$ = 7.6, $^4J_{H-H}$ = 1.2, $^5J_{H-P}$ = 2.4 Hz, 2H, H_5), 6.90 (pseudo-tdd, $^3J_{H-H}$ = 7.6, $^4J_{H-H}$ = 1.2, $^4J_{H-P}$ = 2.4 Hz, 2H, H_4), 6.80 (dbr, $^3J_{H-H}$ = 7.6 Hz, 2H, H_6), 6.75 (pseudo-tbr, $^3J_{H-H}$ = $^3J_{H-P}$ = 7.6 Hz, 2H, H_3), 2.38 –2.22 (m, 4H, CH_{2Cy}), 2.19 – 2.14 (m, 4H, B–CH_{Cy}), 2.10 – 1.98 (m, 4H, CH_{2Cy}), 1.87 – 1.81 (m, 4H, CH_{2Cy}), 1.80 – 1.66 (m, 12H, CH_{iPr}, CH_{2Cy}), 1.51 – 1.38 (m, 8H, CH_{2Cy}), 1.38 – 1.25 (m, 4H, CH_{2Cy}), 1.25 – 1.04 (m, 8H, CH_{2Cy}), 0.83 (dd, $^3J_{H-H}$ = 7.0, $^3J_{H-P}$ = 18.6 Hz, 12H, CH_{3iPr}), 0.70 (dd, $^3J_{H-H}$ = 7.0, $^3J_{H-P}$ = 17.5 Hz, 6H, CH_{3iPr}).

^{13}C{^{1}H} NMR (100 MHz, 298 K, C_6D_6) δ 157.9 (s, C_1 or C_2),* 130.7 (d, $^2J_{C-P}$ = 6 Hz, s, C_3), 129.8 (d, $^4J_{C-P}$ = 2 Hz, C_5), 126.5 (d, $^3J_{C-P}$ = 18 Hz, C_6), 125.7 (d, $^3J_{C-P}$ = 8 Hz, C_4), 120.2 (q, $^1J_{C-F}$ = 323 Hz, CF_3), 39.3 (s, CH_{Cy}), 30.9 (s, CH_{2Cy}), 28.9 (s, CH_{2Cy}), 28.2 (s, CH_{2Cy}), 27.6 (s, CH_{2Cy}), 27.1 (d, $^1J_{C-P}$ = 35 Hz, CH_{iPr}), 26.9 (s, CH_{2Cy}), 19.1 (d, $^2J_{C-P}$ = 3 Hz, CH_{3iPr}), 19.1 (s, CH_{3iPr}). *The quaternary carbon C_1 and C_2 are not visible, one of them was deduced from the HMBC spectrum.

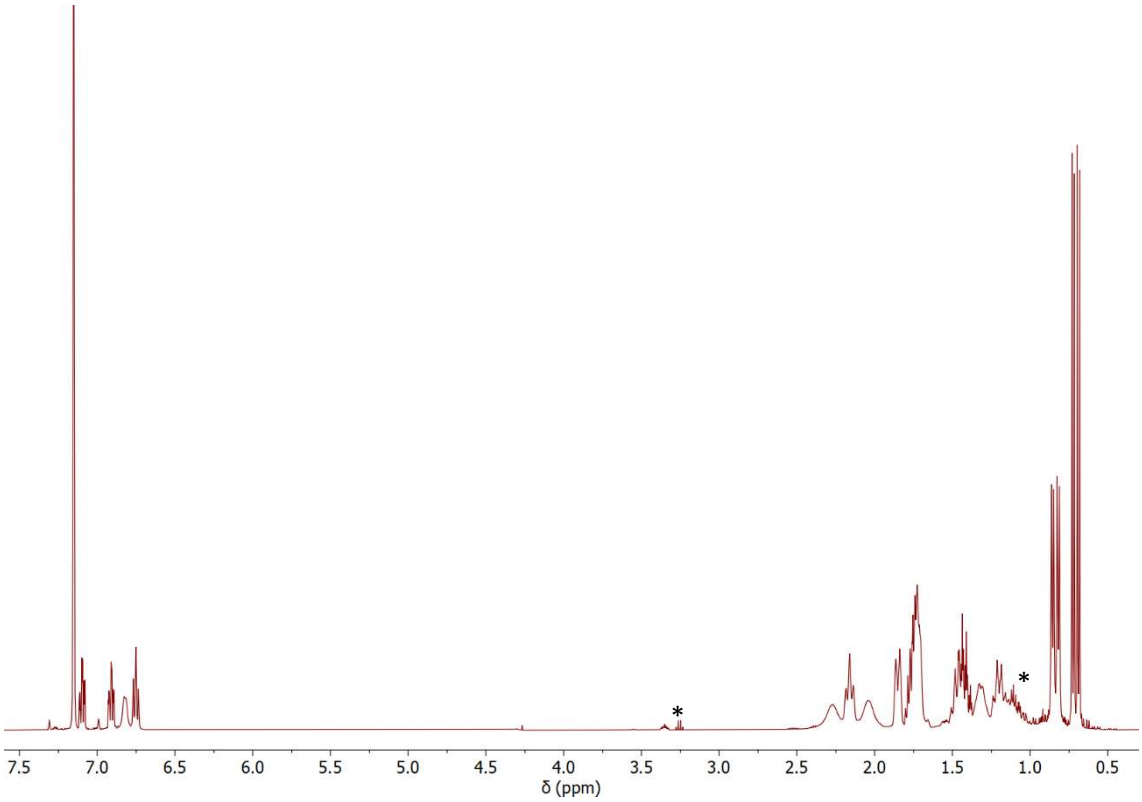
^{31}P{^{1}H} NMR (121 MHz, 298 K, C_6D_6) δ 54.6 (br).

^{19}F{^{1}H} NMR (282 MHz, 298 K, C_6D_6) δ -73.8.

^{11}B{^{1}H} NMR (160 MHz, 298 K, C_6D_6) δ Not detected.

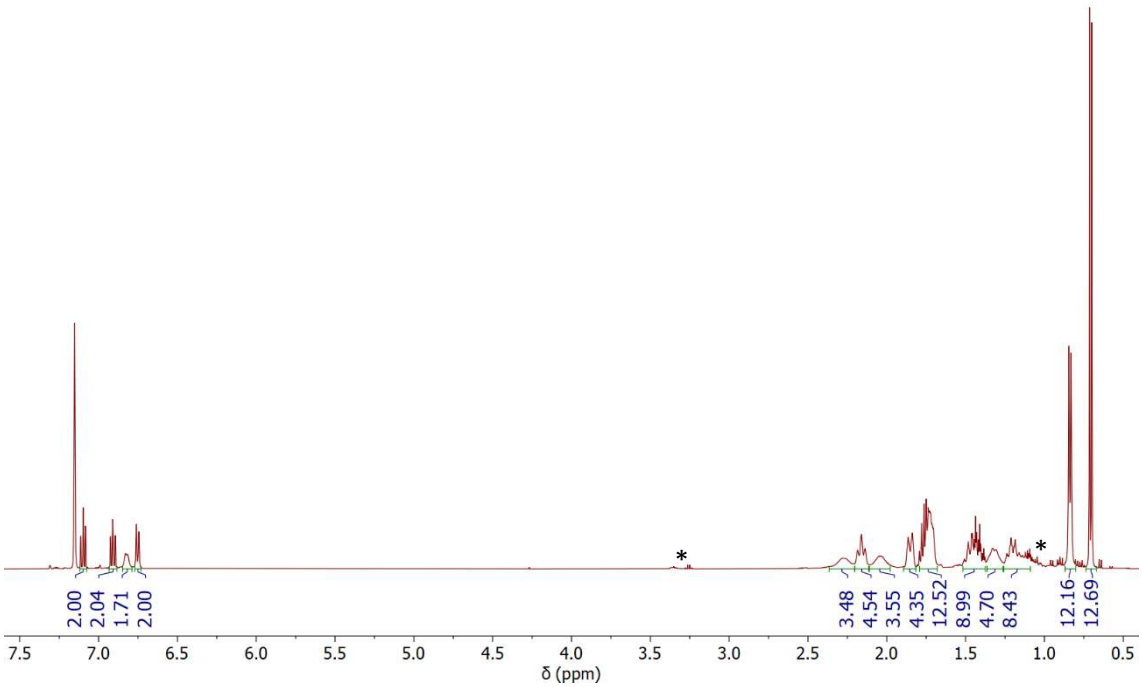
HRMS-DCI(CH_4) (*m/z*): found $[M]^+$ 1169.5007, calcd. $C_{48}H_{80}Au_2{}^{11}B_2ClP_2$ requires 1169.4941.

^{1}H NMR spectrum (500 MHz, 298 K) in C_6D_6



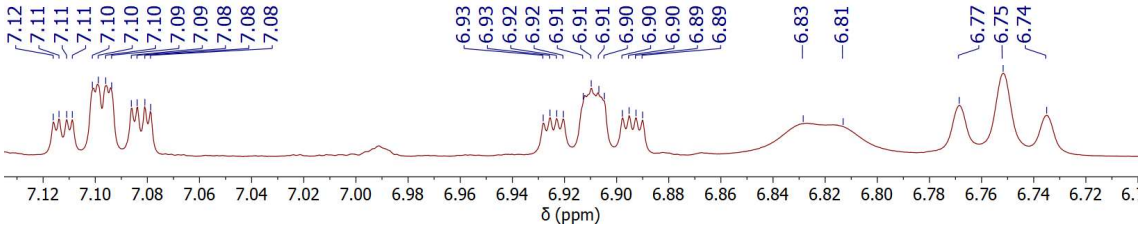
*Et_2O

$^{1}H\{^{31}P\}$ NMR spectrum (500 MHz, 298 K) in C_6D_6

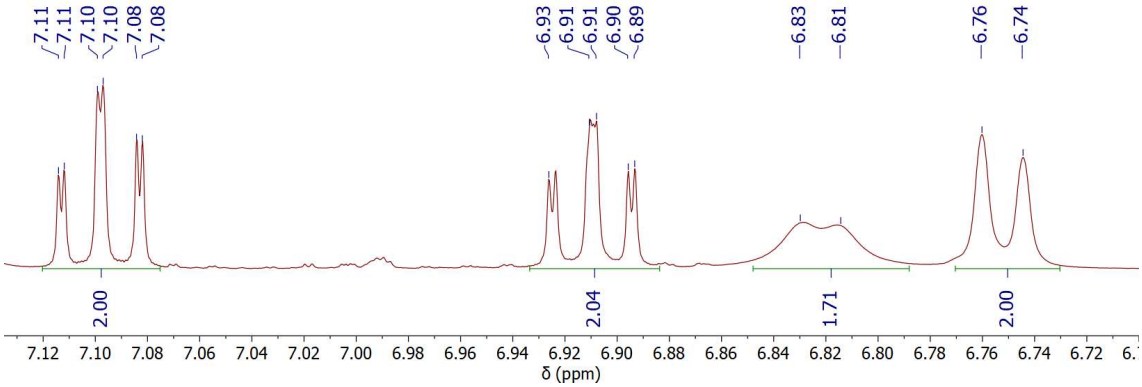


*Et_2O

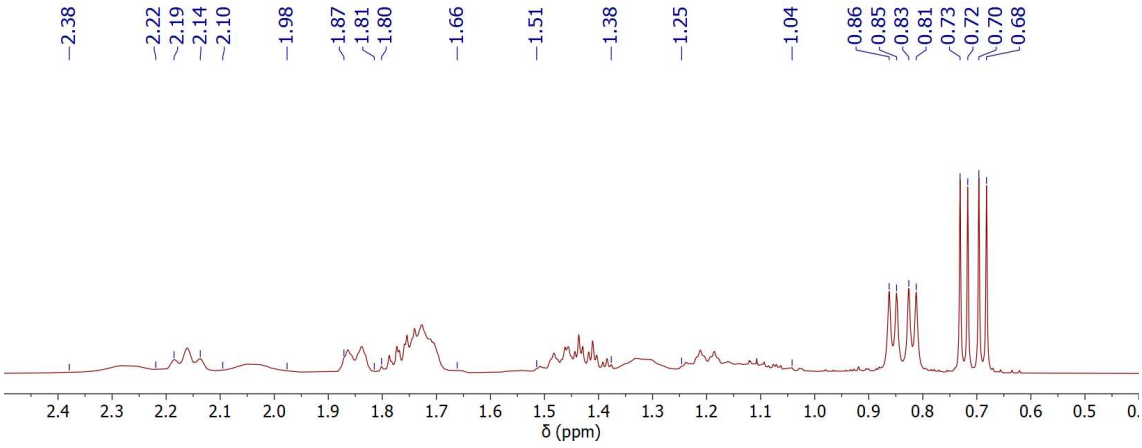
^{1}H NMR spectrum (500 MHz, 298 K) in C_6D_6; aromatic region



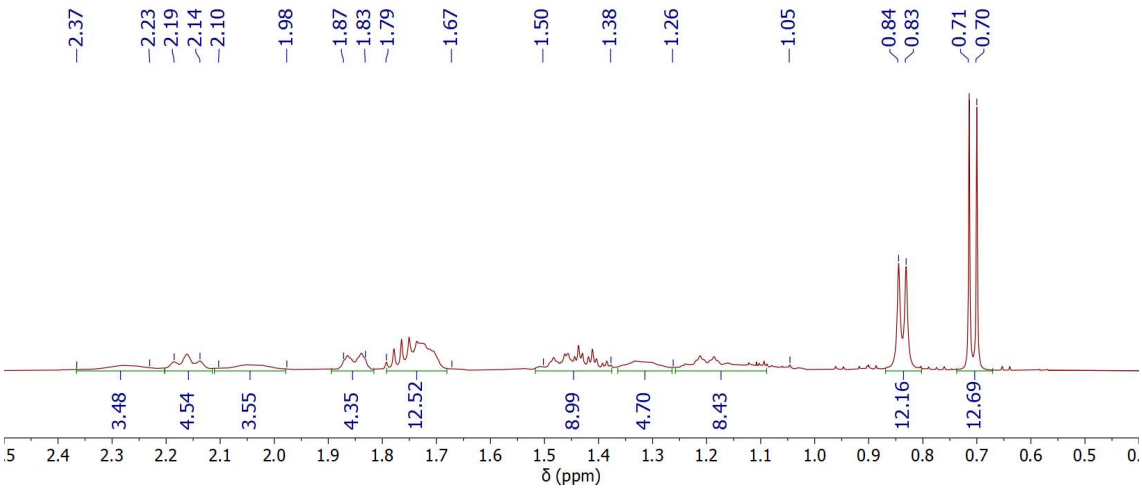
^{1}H{^{31}P} NMR spectrum (500 MHz, 298 K) in C_6D_6; aromatic region



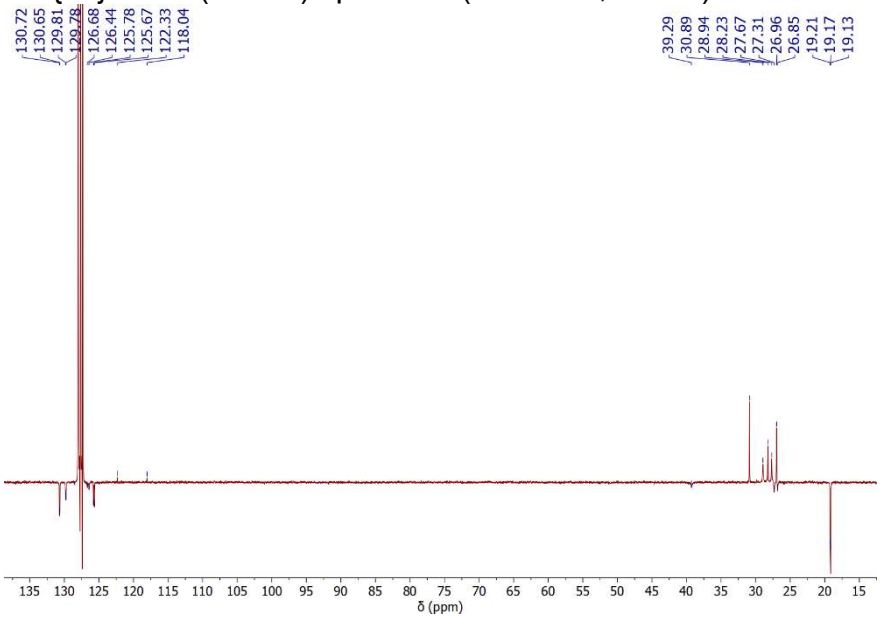
^{1}H NMR spectrum (500 MHz, 298 K) in C_6D_6; aliphatic region



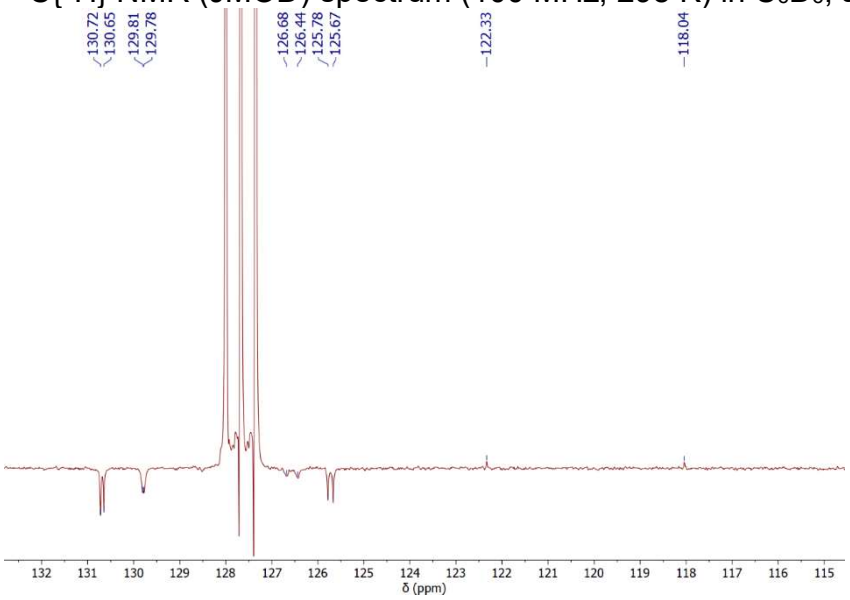
^{1}H{^{31}P} NMR spectrum (500 MHz, 298 K) in C_6D_6; aliphatic region



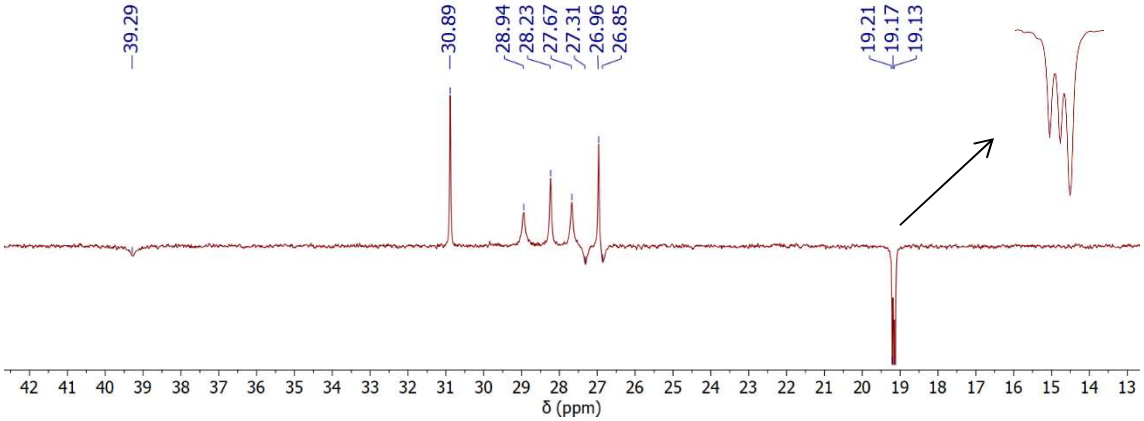
$^{13}C\{^{1}H\}$ NMR (JMOD) spectrum (100 MHz, 298 K) in C_6D_6



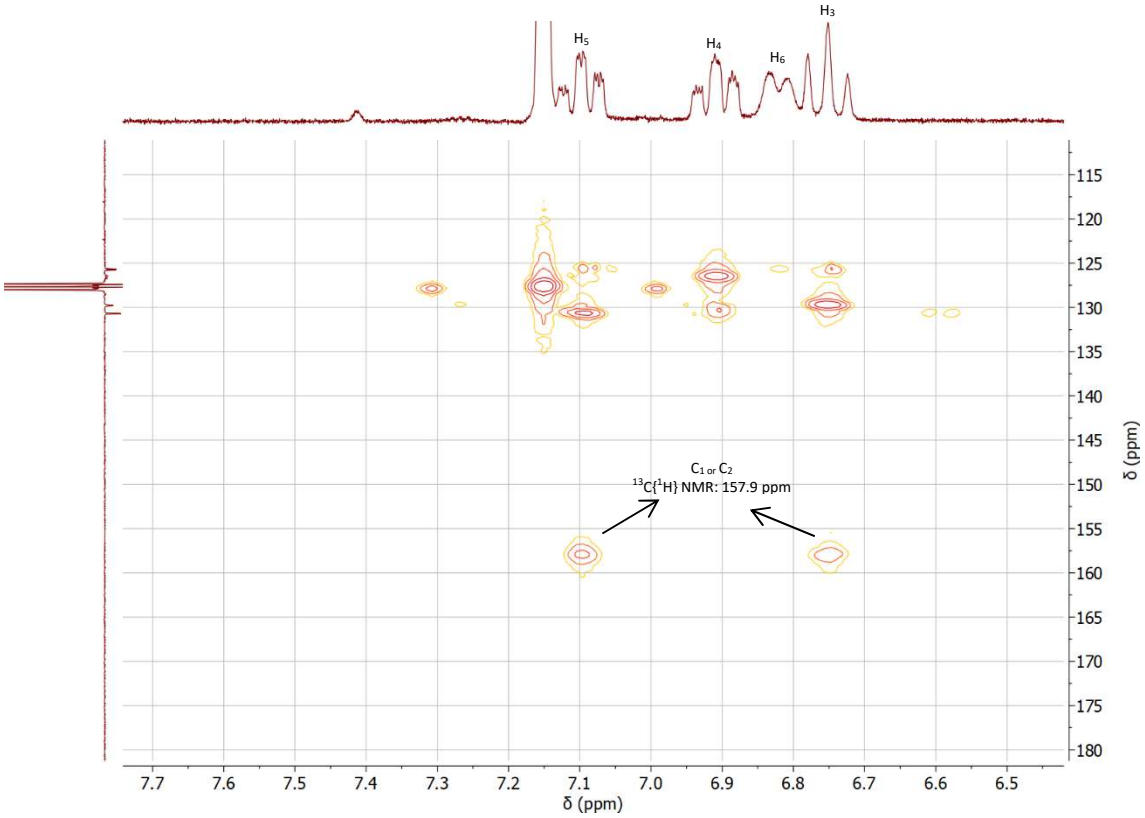
$^{13}C\{^{1}H\}$ NMR (JMOD) spectrum (100 MHz, 298 K) in C_6D_6; aromatic region



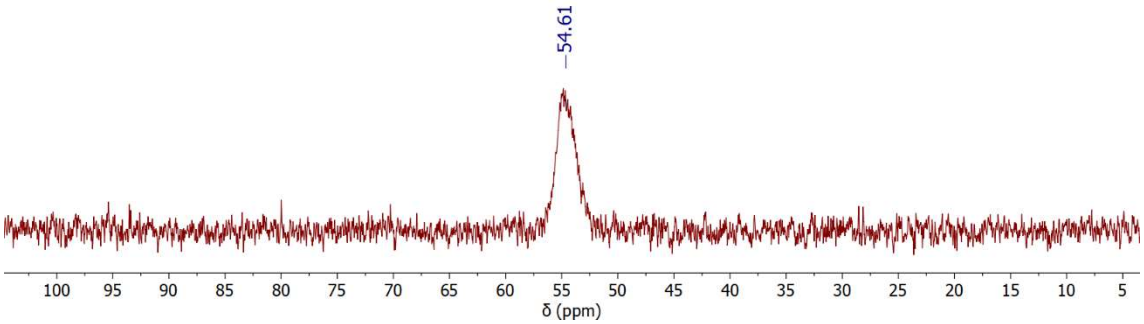
$^{13}C\{^{1}H\}$ NMR (JMOD) spectrum (100 MHz, 298 K) in C_6D_6; aliphatic region



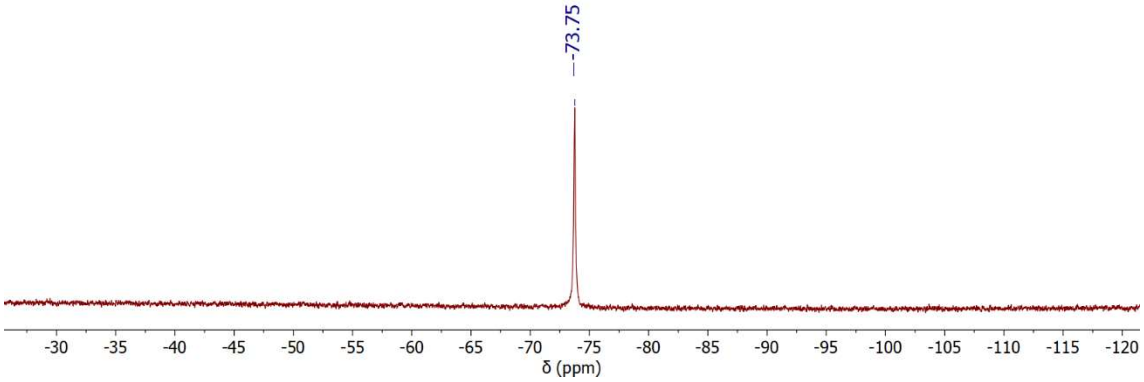
HMBC NMR spectrum (298 K) in C_6D_6



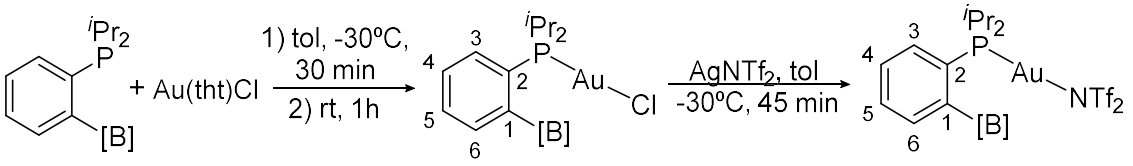
$^{31}P\{^1H\}$ NMR spectrum (121 MHz, 298 K) in C_6D_6



$^{19}F\{^1H\}$ NMR spectrum (282 MHz, 298 K) in C_6D_6



General procedure for the synthesis of (PBMes$_2$)AuNTf$_2$ and (PBpin)AuNTf$_2$



[B] = BMes$_2$, Bpin

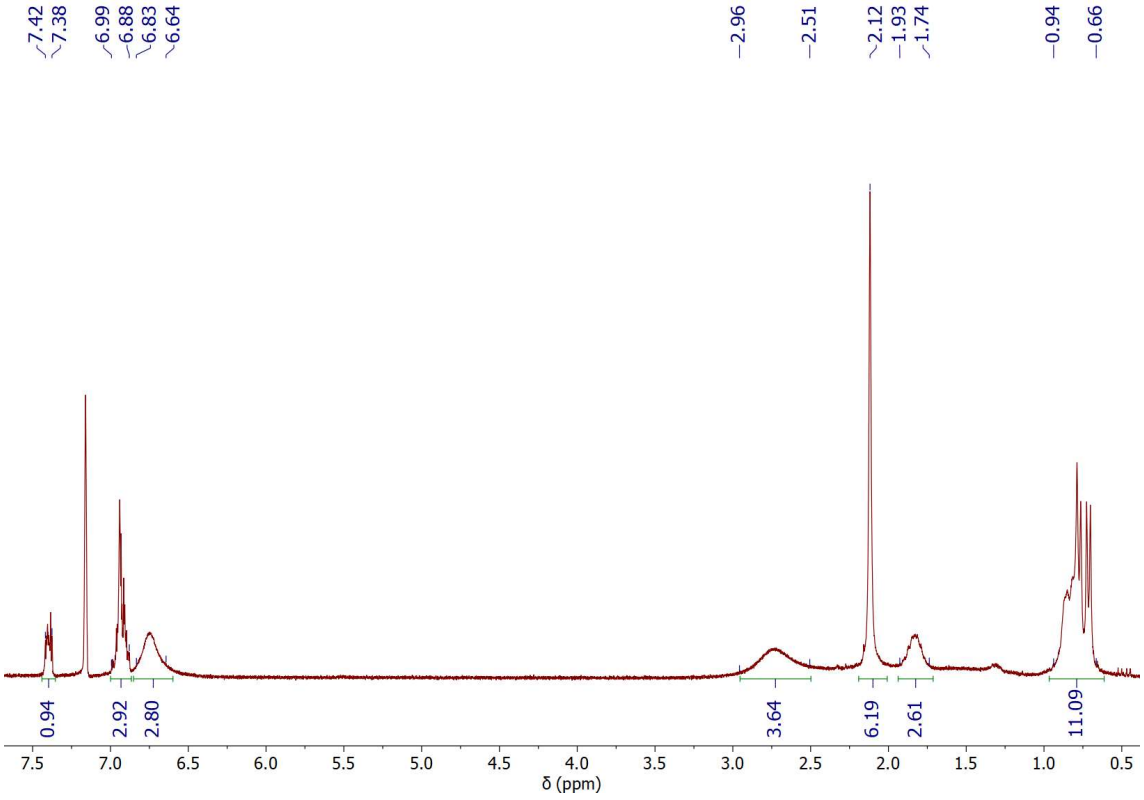
A solution of PB ligand (0.226 mmol, 1 Equiv.) in 5 mL of toluene was added to a solution of Au(tht)Cl (0.226 mmol, 1 Equiv.) in toluene (3 mL) at -30 ºC. The reaction was stirred at that temperature for 30 min and 1 hour at room temperature and then, it was filtered to remove solid impurities and the supernatant was evaporated. To a solution of obtained PBAuCl (0.074 mmol, 1 Equiv.) in toluene (5 mL) was added AgNTf$_2$ (0.074 mmol, 1 Equiv.) in toluene (5 mL). The mixture covered with aluminium foil was stirred at -30 ºC for 45 minutes. The solution was filtered to remove white precipitate of AgCl, and the volatiles were removed under vacuum to yield complex as white powder (~ 50%).

PBMes$_2$AuCl

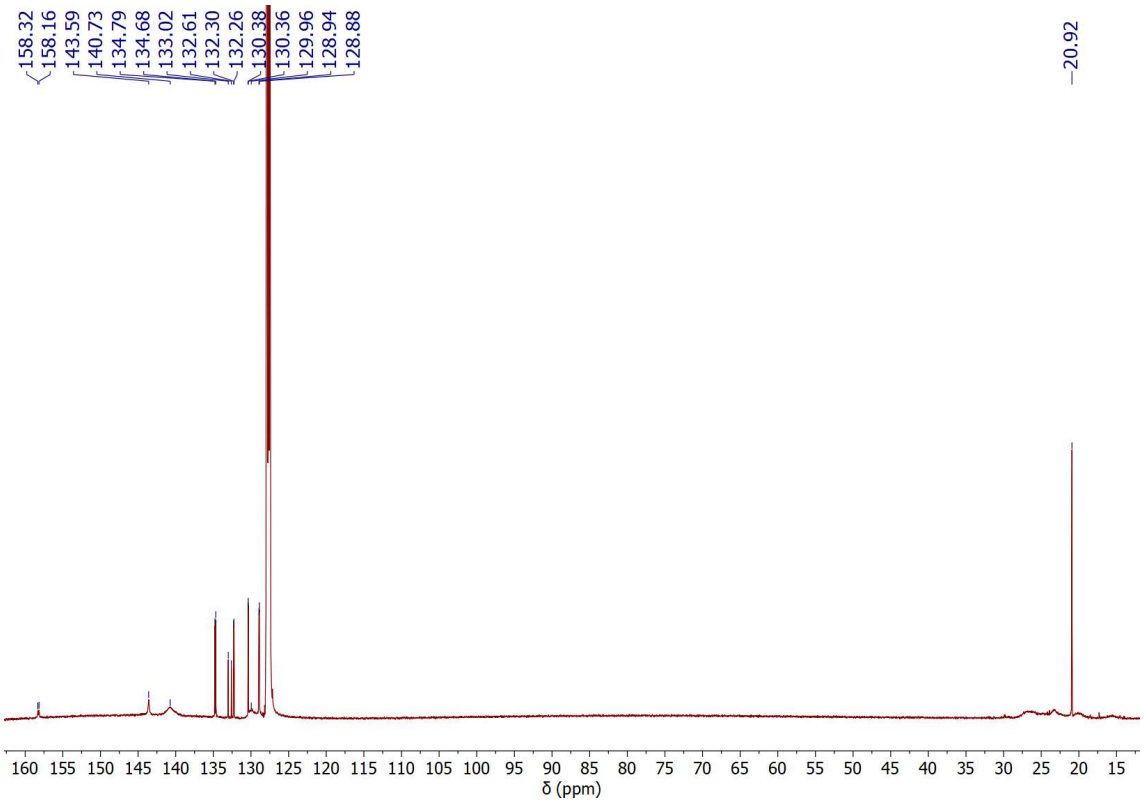
^{1}H NMR (500 MHz, 298 K, C_6D_6) δ 7.42 – 7.38 (m, 1H, CH_{Ar}), 6.99 – 6.88 (m, 3H, CH_{Ar}), 6.83 – 6.64 (brs, 2H, CH_{Mes}), 2.96 – 2.51 (brs, 3H, CH_{3Mes}), 2.12 (s, 6H, CH_{3Mes}), 1.93 – 1.74 (brs, 2H, CH_{i}Pr,), 0.94 – 0.66 (m, 12H CH_{3i}Pr).
^{13}C{^{1}H} NMR (100 MHz, 298 K, C_6D_6) δ 158.2 (d, $^1J_{C\text{-}P}$ = 21 Hz, $C_{ipso\text{-}P}$), 143.6 (br, $C_{ipso\text{-}B}$), 140.7 (br, C_{Mes}), 134.7 (d, $J_{C\text{-}P}$ = 14 Hz, C_{Ar}), 133.0 (C_{Mes}), 132.6 (C_{Mes}), 132.3 (d, $J_{C\text{-}P}$ = 5 Hz, C_{Ar}), 130.4 (d, $J_{C\text{-}P}$ = 3 Hz, C_{Ar}), 129.9 (br, C_{Mes}), 128.9 (d, $J_{C\text{-}P}$ = 8 Hz, C_{Ar}), 20.9 (CH_{3Mes}). CH_{3Mes}, CH_{3i}Pr and CH_{i}Pr described the δ as broad signal and precise by *confirmed by HSQC and not HMBC.
^{31}P{^{1}H} NMR (203 MHz, 298 K, C_6D_6) δ 53.1.
^{11}B{^{1}H} NMR (160 MHz, 298 K, C_6D_6) δ Not detected.

HRMS-DCI(CH_4) (*m/z*): found $[M]^+$ 555.1470, calcd. $C_{31}H_{29}Au^{11}BClP$ requires 555.1454.

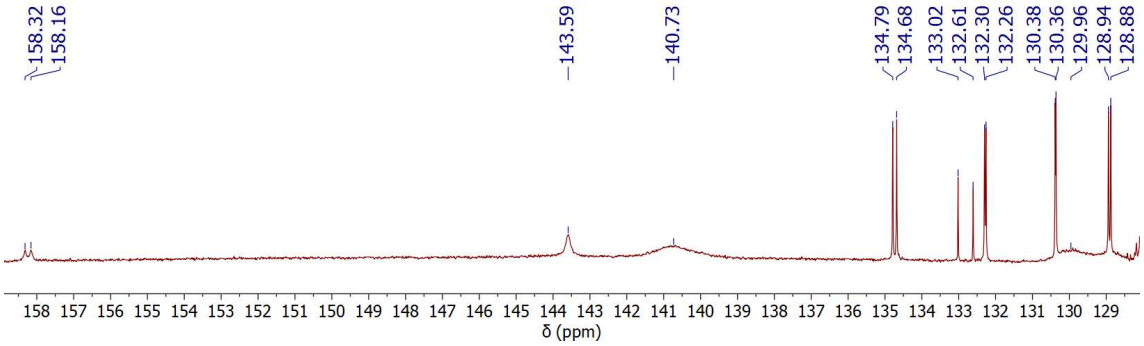
^{1}H NMR spectrum (500 MHz, 298 K) in C_6D_6



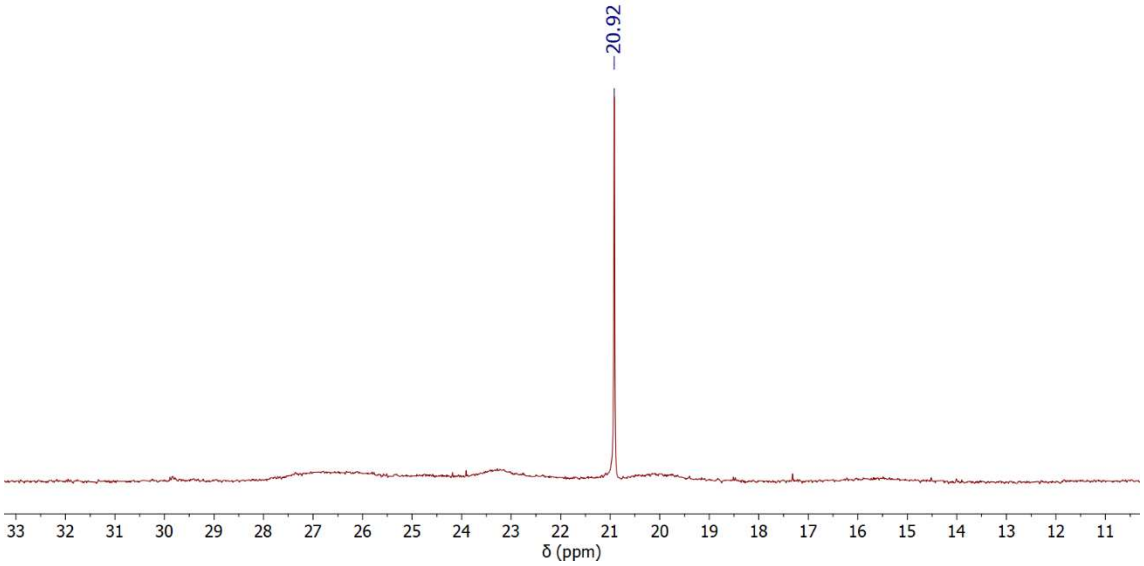
^{13}C{^{1}H} NMR spectrum (150 MHz, 298 K) in C_6D_6



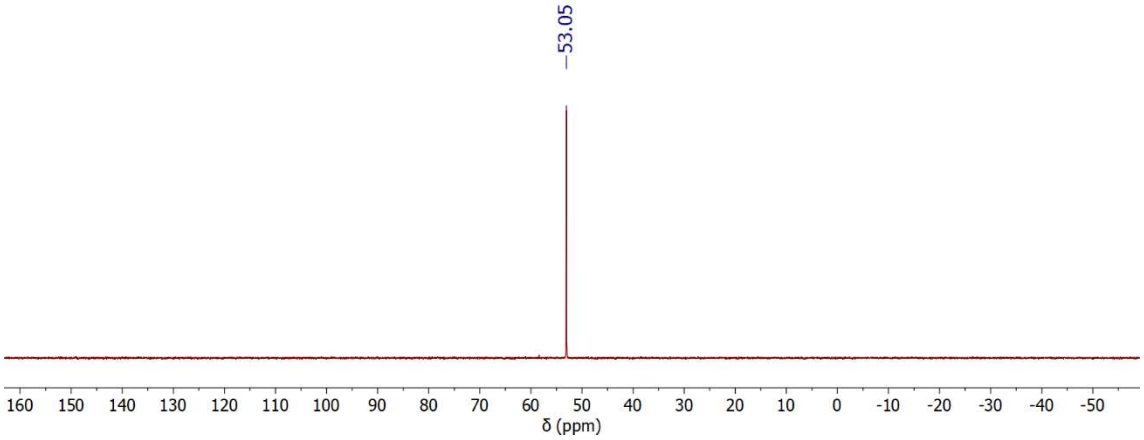
$^{13}C\{^{1}H\}$ NMR spectrum (150 MHz, 298 K) in C_6D_6; aromatic region



$^{13}C\{^{1}H\}$ NMR spectrum (150 MHz, 298 K) in C_6D_6; aliphatic region



$^{31}P\{^{1}H\}$ NMR spectrum (121 MHz, 298 K) in C_6D_6



PBMes$_2$AuNTf$_2$

^{1}H NMR (300 MHz, 298 K, C_6D_6) δ 7.37 – 7.33 (m, 1H, CH_{Ar}), 7.02 – 6.88 (m, 3H, CH_{Ar}), 6.81 – 6.65 (brs, 2H, CH_{Mes}), 2.29 – 1.09 (brs, 3H, CH_{3Mes}), 2.09 (s, 6H, CH_{3Mes}), 1.80 – 1.67 (brs, 2H, CH_{iPr},), 0.8 – 0.69 (m, 12H, CH_{3iPr}).

^{13}C{^{1}H} NMR (150 MHz, 298 K, C_6D_6) δ 157.7 (d, $^1J_{C\text{-}P}$ = 18 Hz, $C_{ipso\text{-}P}$), 142.7 (br, $C_{ipso\text{-}B}$), 141.0 (br, C_{Mes}), 135.1 (d, $J_{C\text{-}P}$ = 13 Hz, CH_{Ar}), 133.0 (d, $J_{C\text{-}P}$ = 8 Hz, CH_{Ar}), 130.9 (d, $J_{C\text{-}P}$ = 3 Hz, CH_{Ar}), 130.4 (C_{Mes}), 130.1 (C_{Mes}), 129.5 (br, C_{Mes}), 129.1 (d, $J_{C\text{-}P}$ = 9 Hz, CH_{Ar}), 120.1 (q, $J_{C\text{-}F}$ = 323 Hz, CF_3), 20.8 (CH_{3Mes}). CH_{3Mes}, CH_{3iPr} and CH_{iPr} are not visible. HSQC spectrum indicated coupling with the corresponding signals of ^{1}H NMR

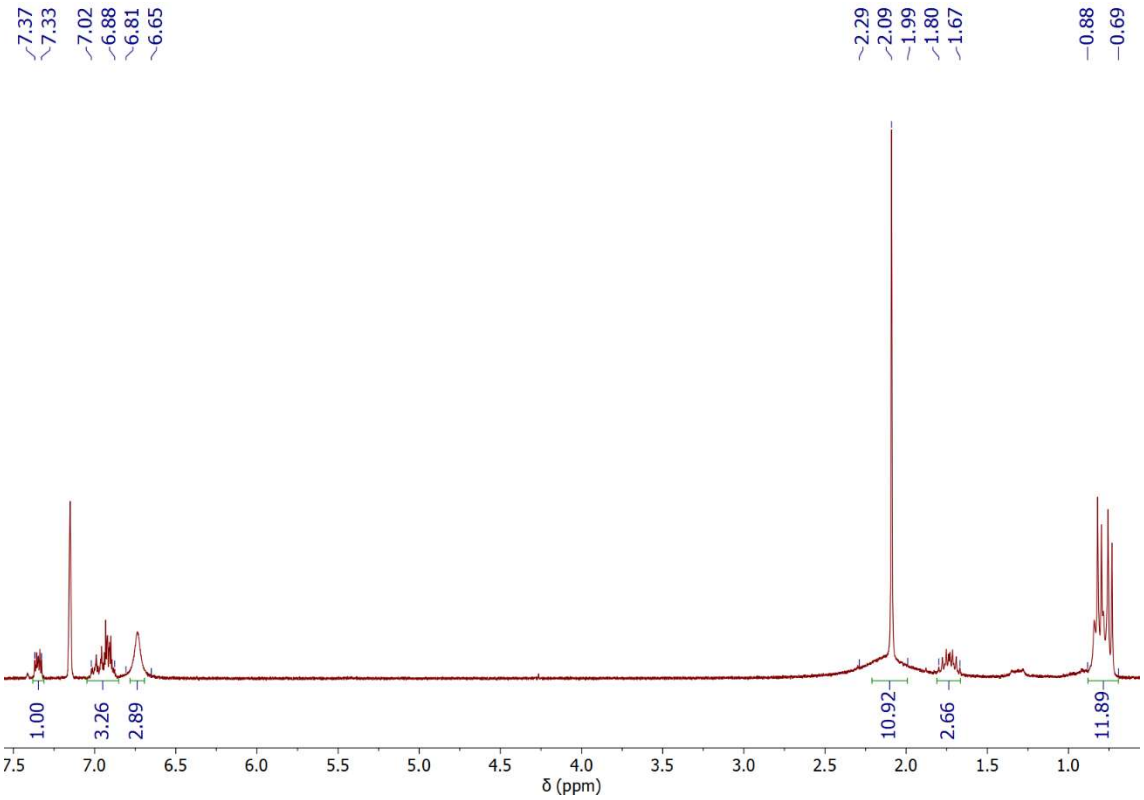
^{31}P{^{1}H} NMR (203 MHz, 298 K, C_6D_6) δ 54.2.

^{19}F{^{1}H} NMR (282 MHz, 298 K, C_6D_6) δ -74.3.

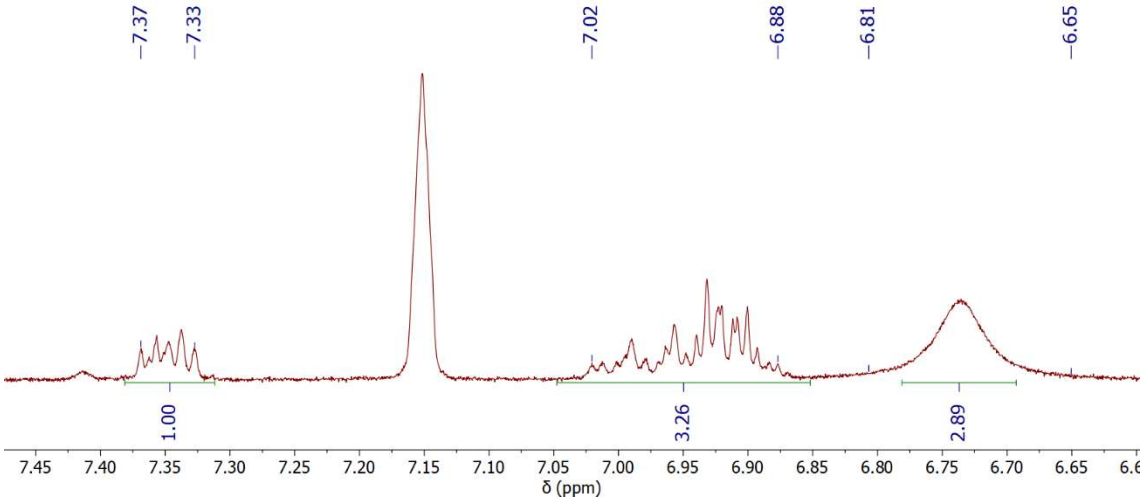
^{11}B{^{1}H} NMR (160 MHz, 298 K, C_6D_6) δ Not detected.

HRMS-DCI(CH_4) (*m/z*): found $[M]^+$ 800.1014, calcd. $C_{23}H_{29}Au^{11}BF_6NO_4PS_2$ requires 800.0939.

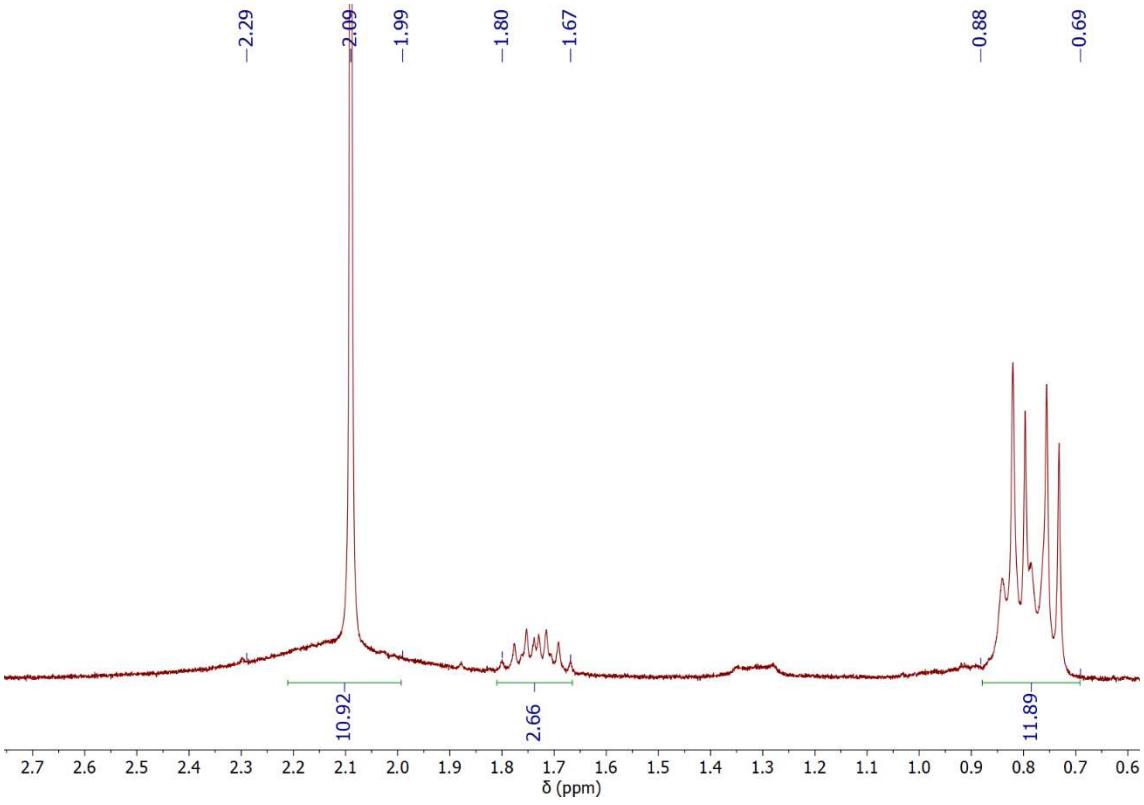
^{1}H NMR spectrum (300 MHz, 298 K) in C_6D_6



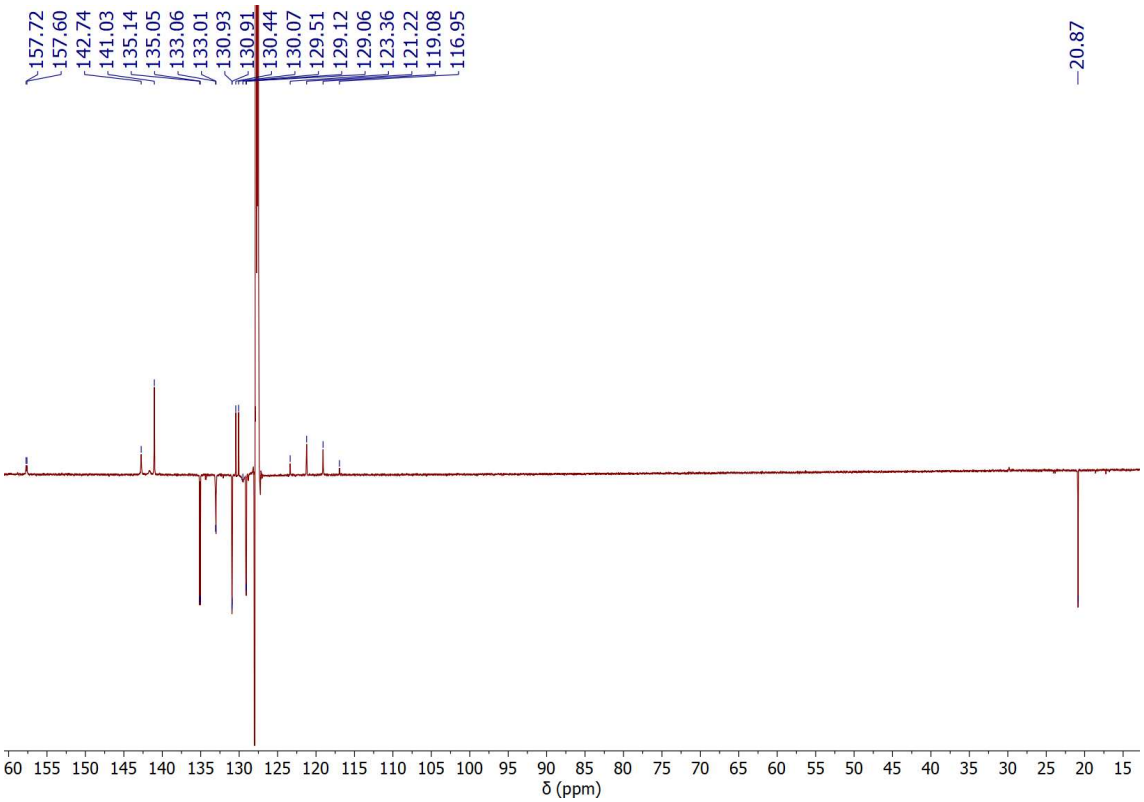
^{1}H NMR spectrum (300 MHz, 298 K) in C_6D_6; aromatic region



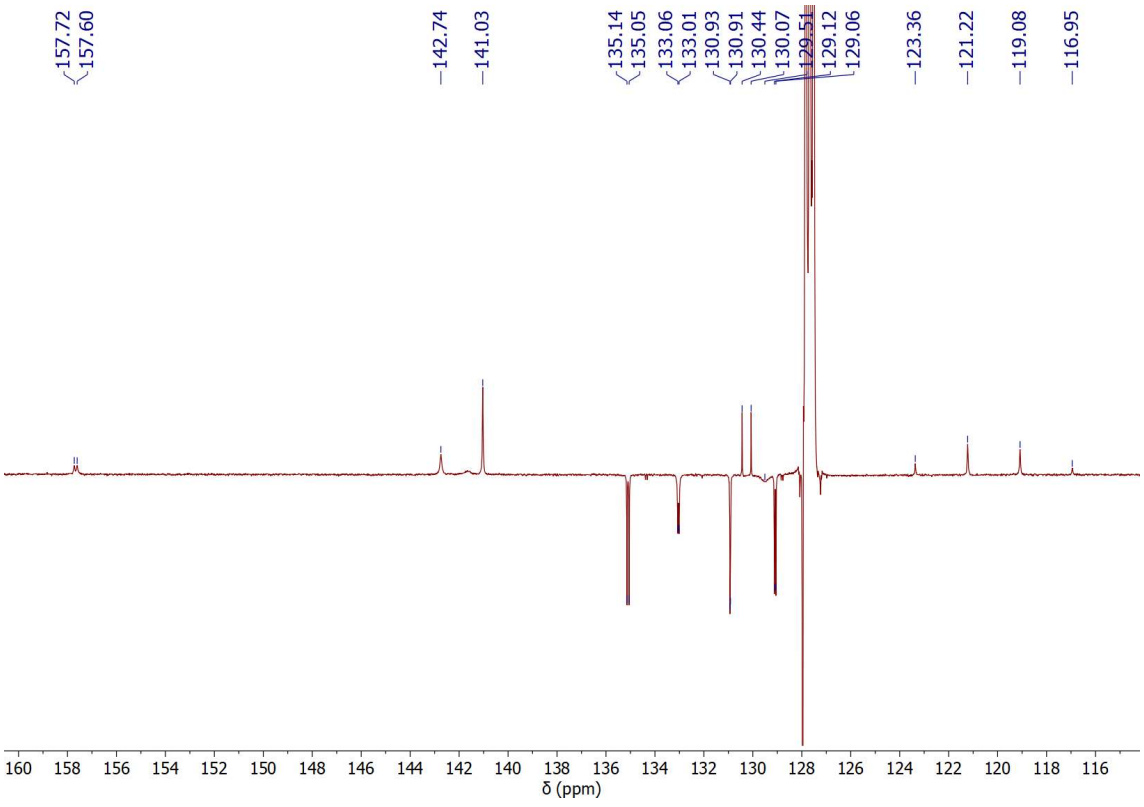
^{1}H NMR spectrum (300 MHz, 298 K) in C_6D_6; aliphatic region



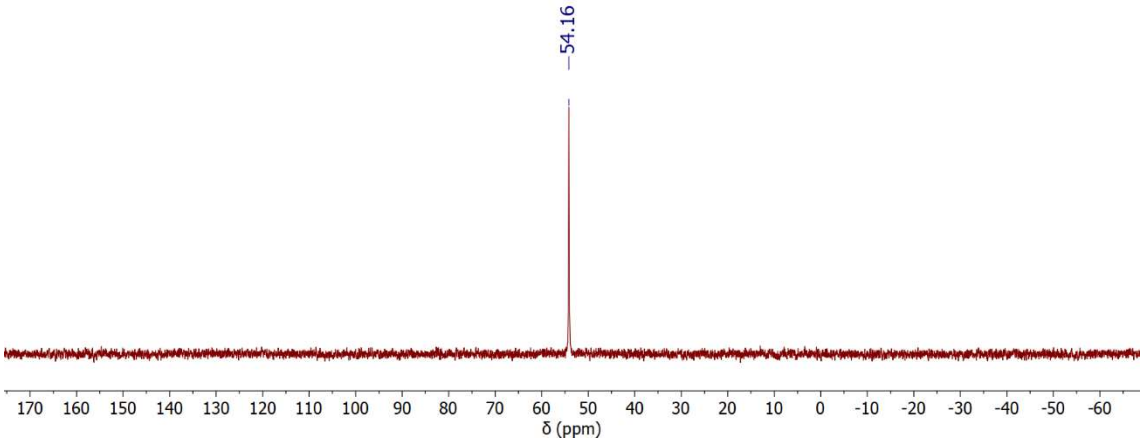
$^{13}C\{^{1}H\}$ NMR spectrum (150 MHz, 298 K) in C_6D_6



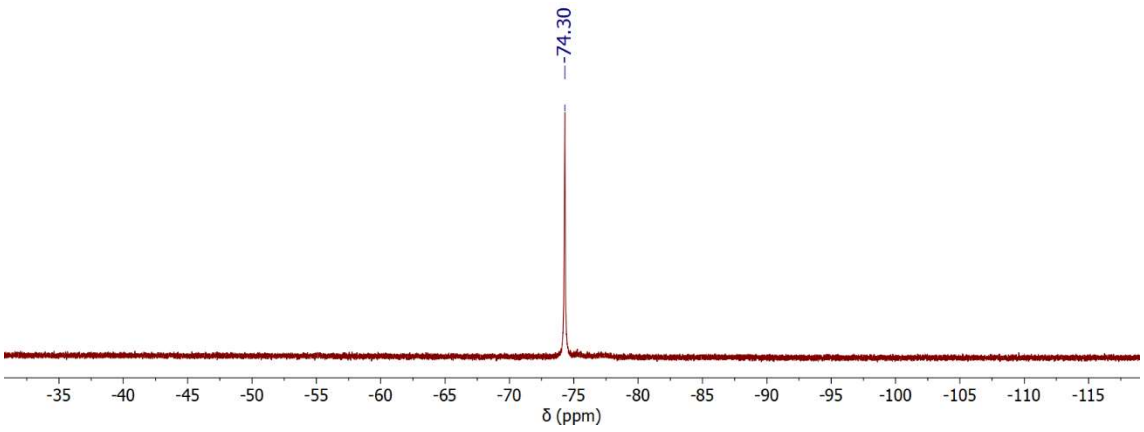
$^{13}C\{^{1}H\}$ NMR spectrum (150 MHz, 298 K) in C_6D_6; aromatic region



$^{31}P\{^{1}H\}$ NMR spectrum (203 MHz, 298 K) in C_6D_6



$^{19}F\{^{1}H\}$ NMR spectrum (282 MHz, 298 K) in C_6D_6



PBpinAuCl

^{1}H NMR (600 MHz, 298 K, C_6D_6) δ 7.93 (pseudo-ddd, $^{3}J_{H\text{-}H}$ = 7.6, $^{4}J_{H\text{-}H}$ = 1.5, $^{3}J_{H\text{-}P}$ = 2.9 Hz, 1H, H_3), 7.39 (brs, 1H, H_6), 7.05 (pseudo-tdd, $^{3}J_{H\text{-}H}$ = 7.6, $^{4}J_{H\text{-}H}$ = 1.5, $^{4}J_{H\text{-}P}$ = 2.3 Hz, 1H, H_4), 6.98 (pseudo-ttt, $^{3}J_{H\text{-}H}$ = 7.6, $^{4}J_{H\text{-}H}$ = 1.5, $^{5}J_{H\text{-}P}$ = 2.4 Hz, 1H, H_5), 2.34 (brs, 2H, $CH_{i\text{Pr}}$), 1.25 (s, 12H, $CH_{3\text{pin}}$), 0.93 (dd, $^{3}J_{H\text{-}H}$ = 7.0, $^{3}J_{H\text{-}P}$ = 17.1 Hz, 6H, $CH_{3i\text{Pr}}$), 0.77 (dd, $^{3}J_{H\text{-}H}$ = 7.0, $^{3}J_{H\text{-}P}$ = 17.1 Hz, 6H, $CH_{3i\text{Pr}}$).

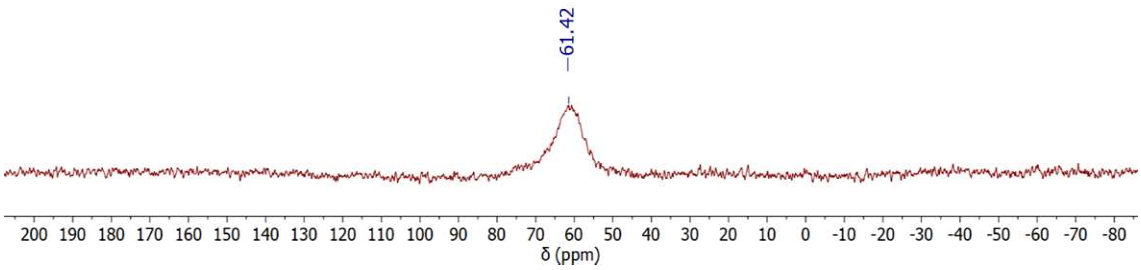
^{13}C{^{31}P}{^{1}H} NMR (150 MHz, 298 K, C_6D_6) δ 136.9 (C_3), 133.4 (C_1), 129.9 (C_4), 129.7 (C_5), 84.8 (C_{pin}), 25.8 ($CH_{i\text{Pr}}$), 25.0 ($CH_{3\text{pin}}$), 24.3 ($CH_{3\text{pin}}$), 19.9 ($CH_{3i\text{Pr}}$), 19.1 ($CH_{3i\text{Pr}}$). *The quaternary carbon C_2 is not visible in 1D or 2D experiments.

^{31}P{^{1}H} NMR (203 MHz, 298 K, C_6D_6) δ 61.4.

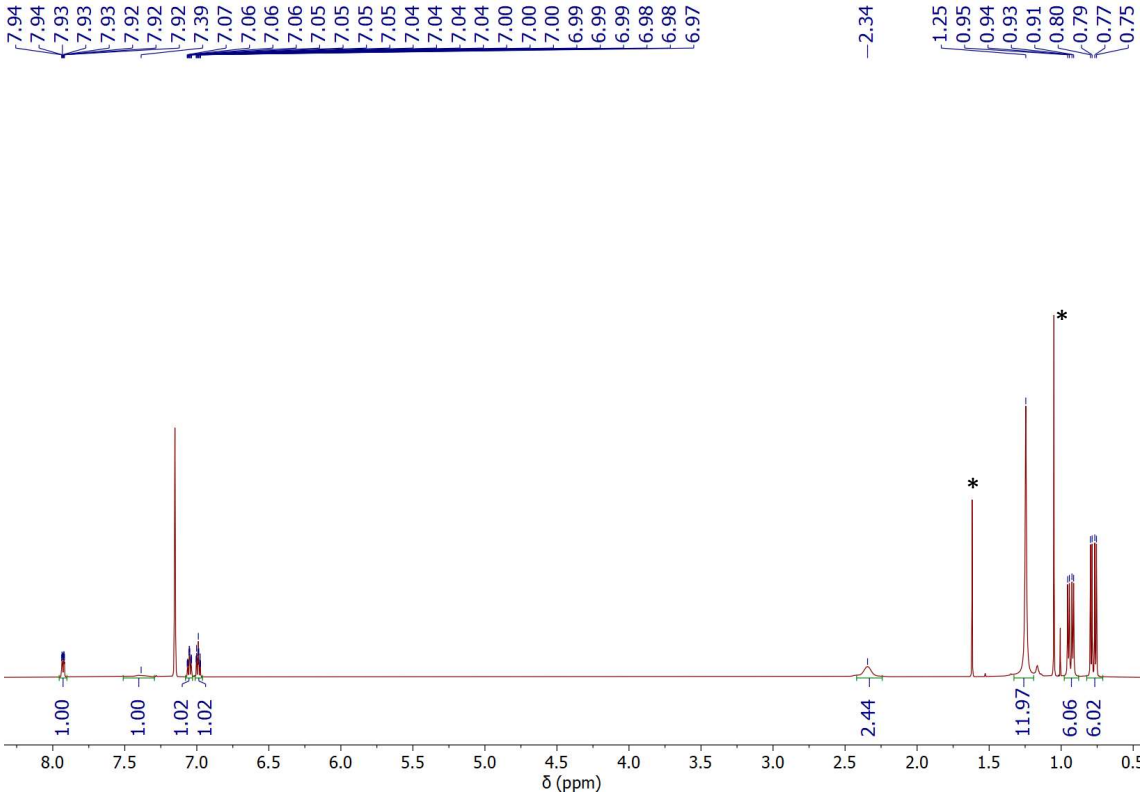
^{11}B{^{1}H} NMR (160 MHz, 298 K, C_6D_6) δ Not detected.

HRMS-DCI(CH_4) (*m/z*): found $[M]^+$ 552.1431, calcd. $C_{18}H_{30}Au^{11}BClO_2P$ requires 552.1431.

^{31}P{^{1}H} NMR spectrum (203 MHz, 298 K) in C_6D_6

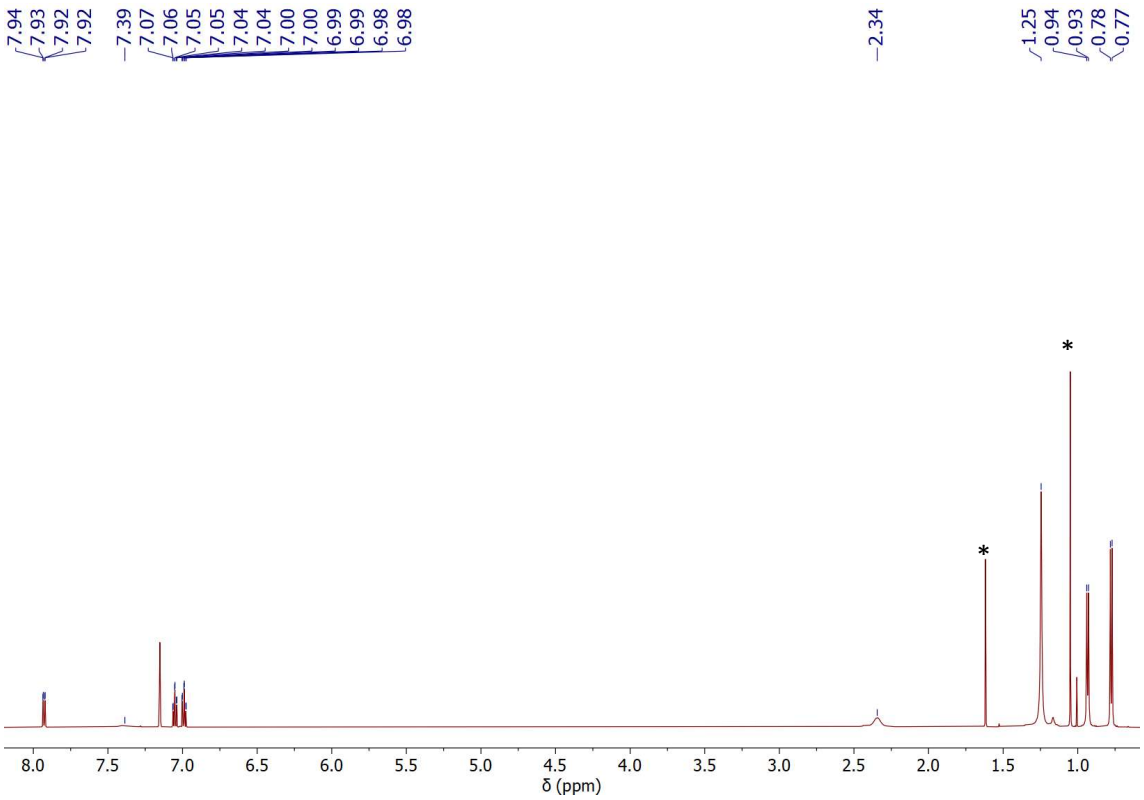


^{1}H NMR spectrum (600 MHz, 298 K) in C_6D_6



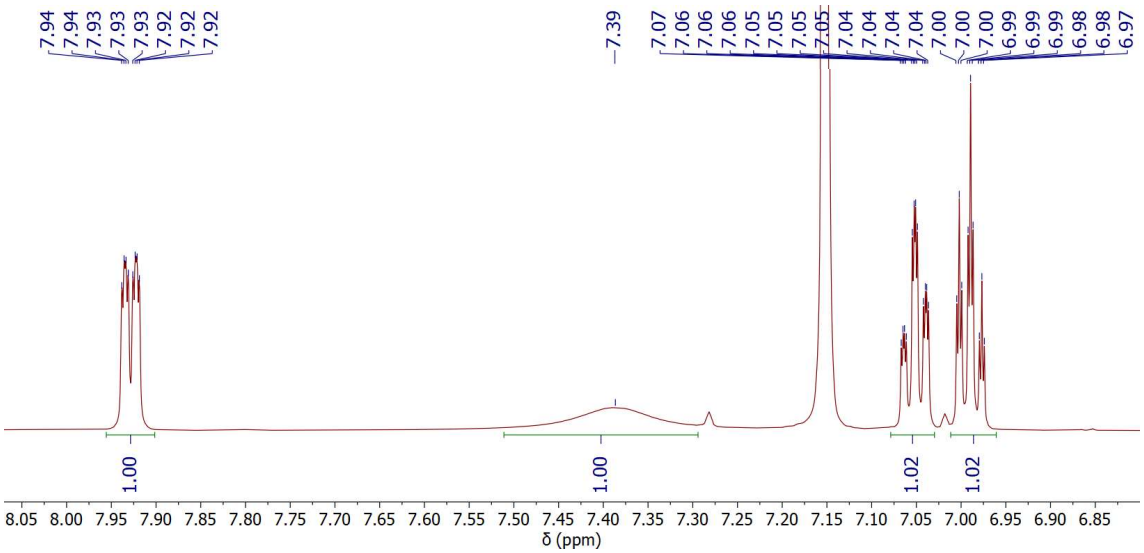
*Acetone and pinacol

$^{1}H\{^{31}P\}$ NMR spectrum (600 MHz, 298 K) in C_6D_6

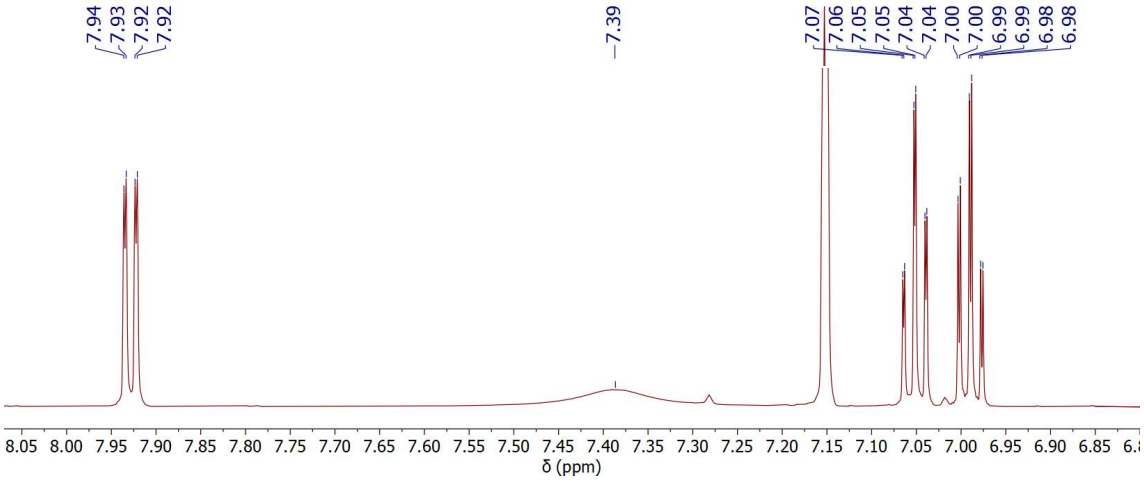


*Acetone and pinacol

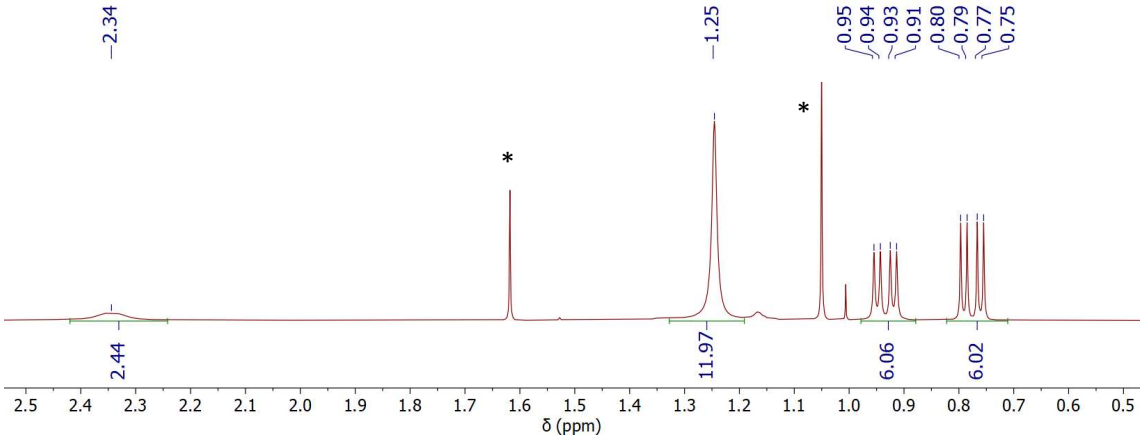
^{1}H NMR spectrum (600 MHz, 298 K) in C_6D_6; aromatic region



$^{1}H\{^{31}P\}$ NMR spectrum (600 MHz, 298 K) in C_6D_6; aromatic region

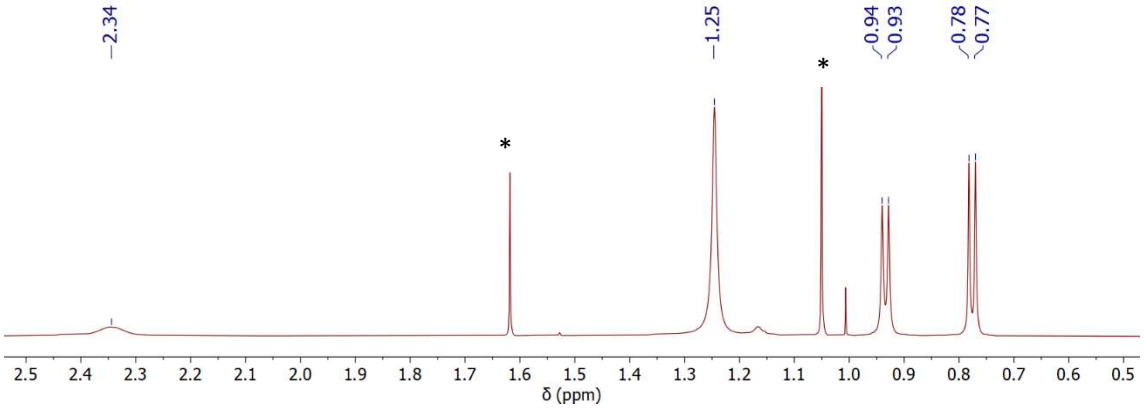


^{1}H NMR spectrum (600 MHz, 298 K) in C_6D_6; aliphatic region



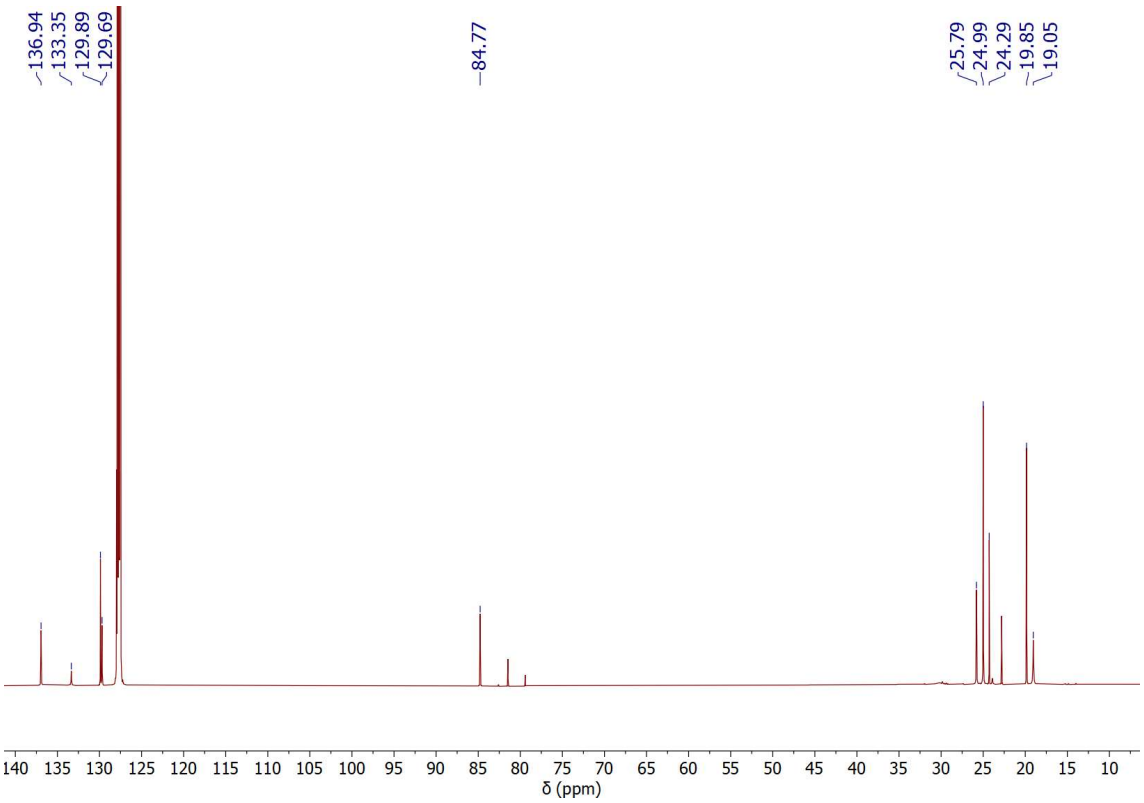
*Acetone and pinacol

$^{1}H\{^{31}P\}$ NMR spectrum (600 MHz, 298 K) in C_6D_6; aliphatic region

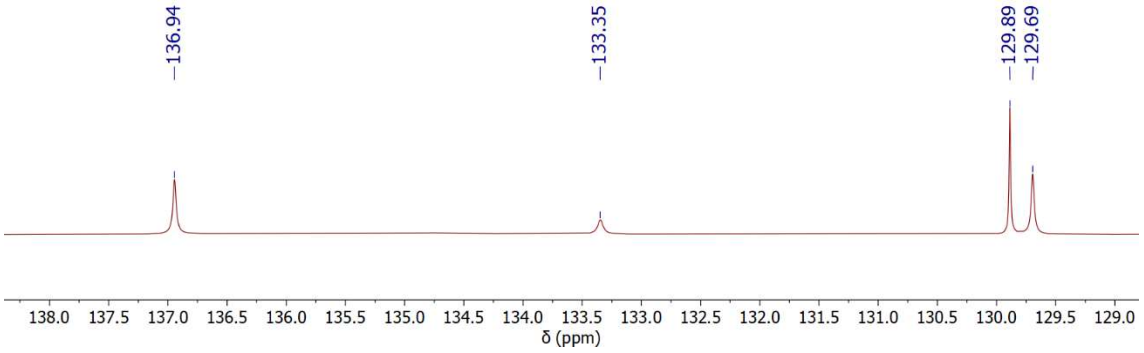


*Acetone and pinacol

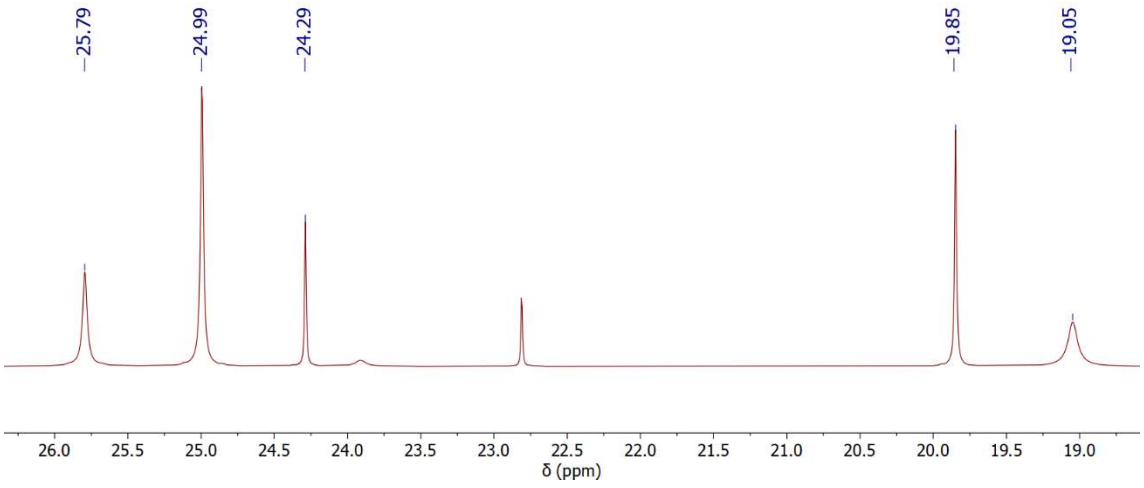
$^{13}C\{^{31}P\}\{^{1}H\}$ NMR spectrum (150 MHz, 298 K) in C_6D_6



$^{13}C\{^{31}P\}\{^{1}H\}$ NMR spectrum (150 MHz, 298 K) in C_6D_6; aromatic region



$^{13}C\{^{31}P\}\{^{1}H\}$ NMR spectrum (150 MHz, 298 K) in C_6D_6; aliphatic region



PBpinAuNTf$_2$

^{1}H NMR (600 MHz, 298 K, C_6D_6) δ 8.21 (brs, 1H, H_6), 8.12 – 8.09 (m, 1H, H_3), 7.17 – 7.07 (m, 2H, H_4, H_5), 2.91 – 2.82 (m, 2H, $CH_{i\mathrm{Pr}}$), 1.20 (dd, $^{3}J_{H\text{-}H}$ = 7.0, $^{3}J_{H\text{-}P}$ = 18 Hz, 6H, $CH_{3i\mathrm{Pr}}$), 1.11 (s, 12H, $CH_{3\mathrm{pin}}$), 0.88 (dd, $^{3}J_{H\text{-}H}$ = 7.0, $^{3}J_{H\text{-}P}$ = 18 Hz, 6H, $CH_{3i\mathrm{Pr}}$).

^{13}C{^{1}H} NMR (150 MHz, 298 K, C_6D_6) δ 138.6 (d, $^{2}J_{C\text{-}P}$ = 10 Hz, C_3), 132.3 (d, $^{1}J_{C\text{-}P}$ = 55 Hz, C_2), 131.2 (d, $^{3}J_{C\text{-}P}$ = 14 Hz, C_4), 130.9 (d, $^{4}J_{C\text{-}P}$ = 3 Hz, C_5), 120.2 (q, $^{1}J_{C\text{-}F}$ = 323 Hz, CF_3), 84.5 (C_{pin}), 26.6 (d, $^{1}J_{C\text{-}P}$ = 33 Hz, $CH_{i\mathrm{Pr}}$), 24.4 ($CH_{3\mathrm{pin}}$), 20.5 (d, $^{2}J_{H\text{-}P}$ = 3 Hz, $CH_{3i\mathrm{Pr}}$). C_1 is not observed. One C_{Ar} is under the signal of C_6D_6.

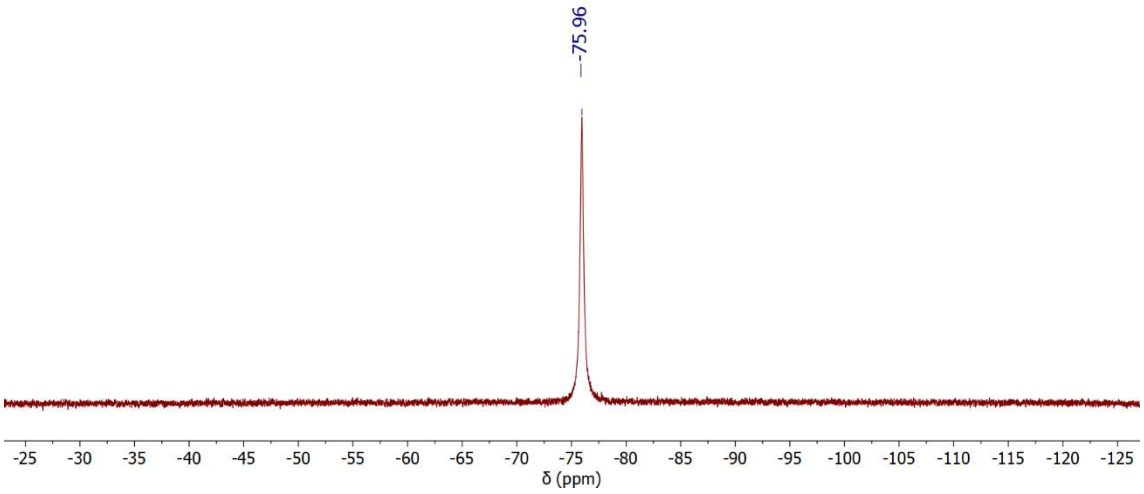
^{31}P{^{1}H} NMR (203 MHz, 298 K, C_6D_6) δ 76.4.

^{19}F{^{1}H} NMR (282 MHz, 298 K, C_6D_6) δ -75.9.

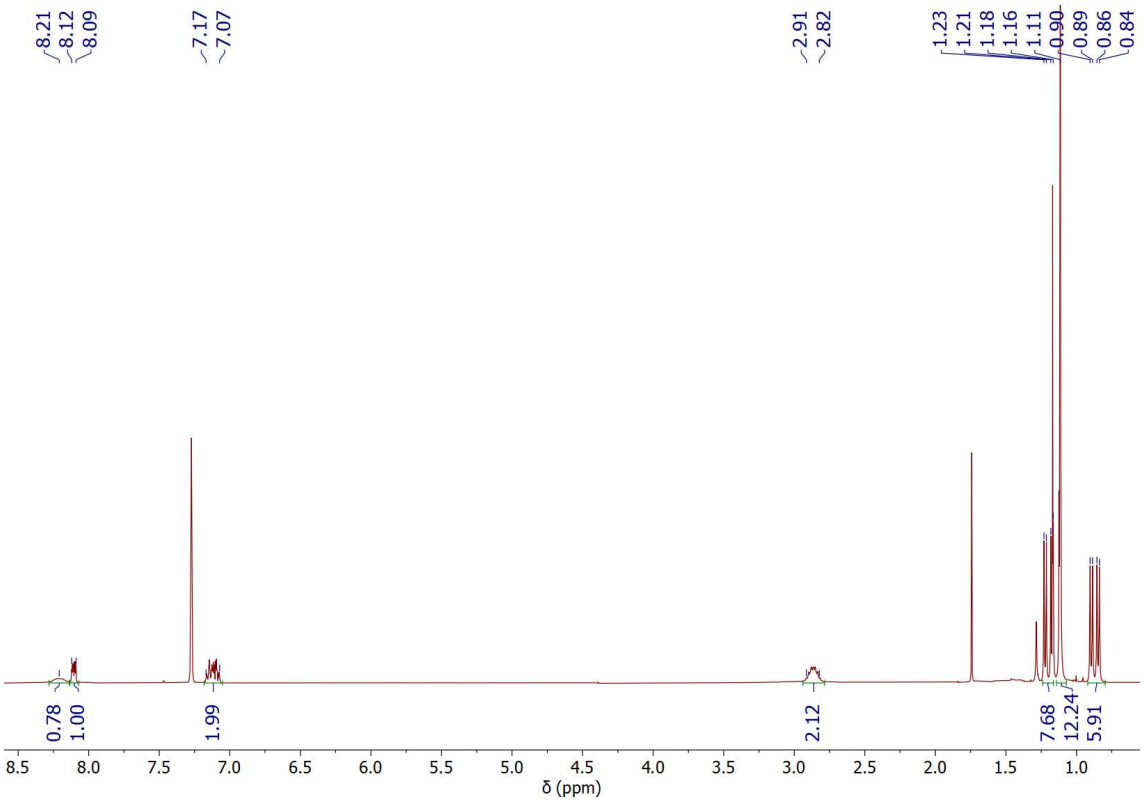
^{11}B{^{1}H} NMR (160 MHz, 298 K, C_6D_6) δ Not detected.

HRMS-DCI(CH_4) (*m/z*): found $[M]^+$ 797.0933, calcd. $C_{20}H_{30}Au^{11}BF_6NO_6PS_2$ requires 797.0915.

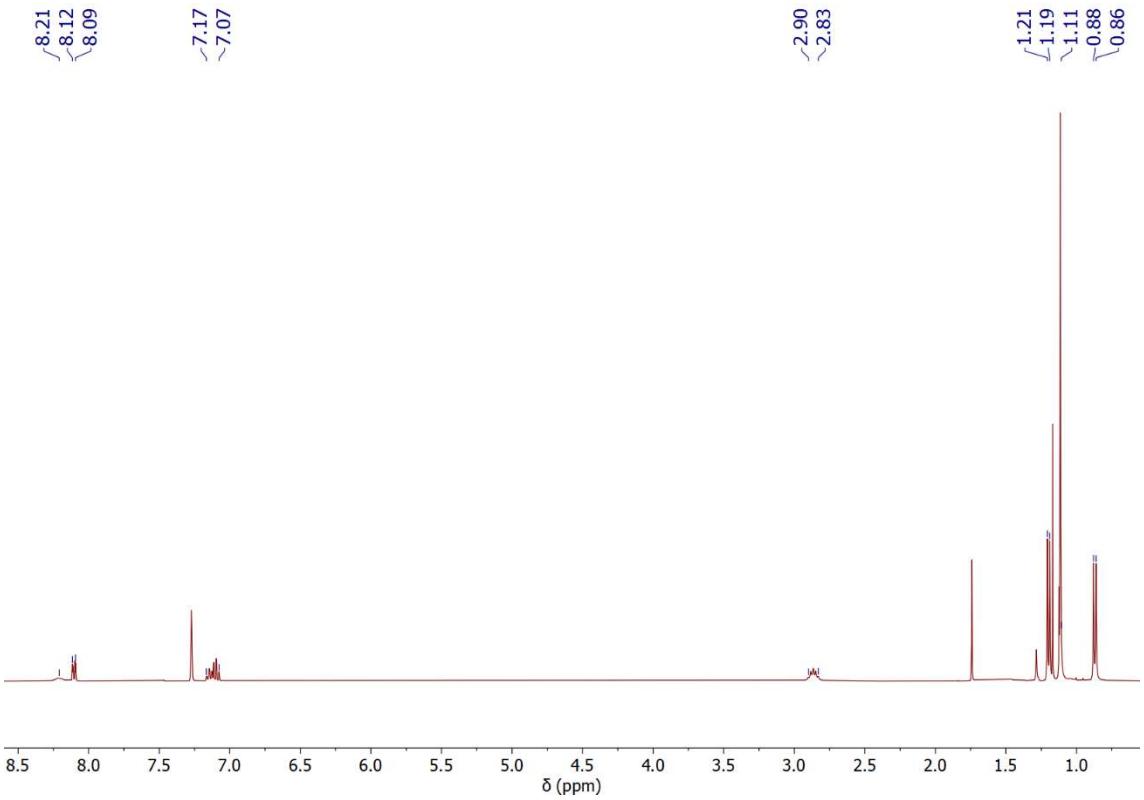
^{19}F{^{1}H} NMR spectrum (282 MHz, 298 K) in C_6D_6



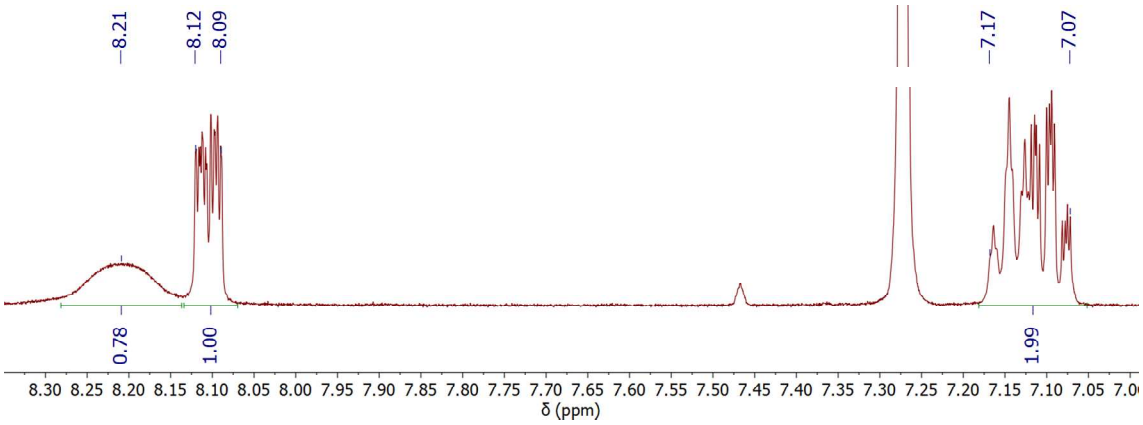
^{1}H NMR spectrum (600 MHz, 298 K) in C_6D_6



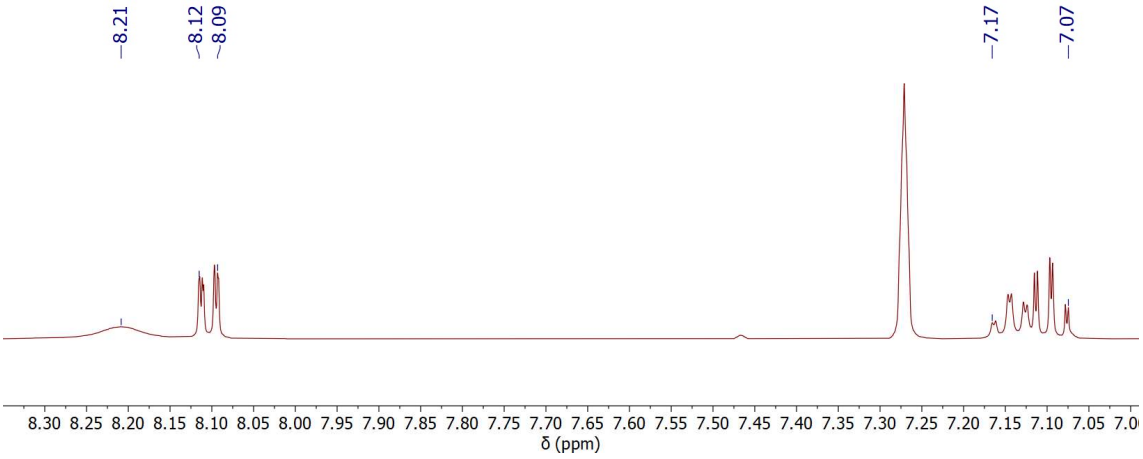
$^{1}H\{^{31}P\}$ NMR spectrum (600 MHz, 298 K) in C_6D_6



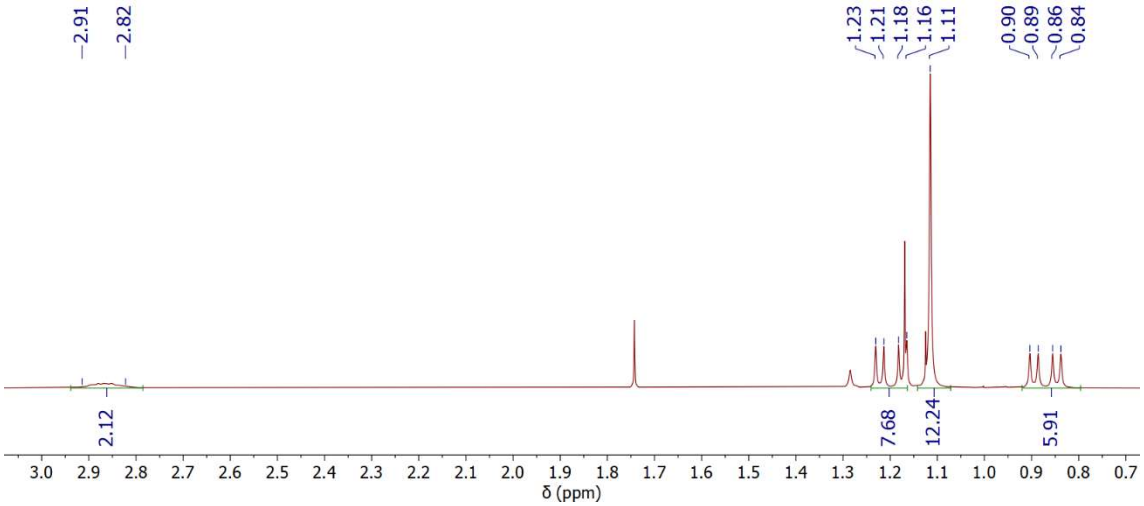
^{1}H NMR spectrum (600 MHz, 298 K) in C_6D_6; aromatic region



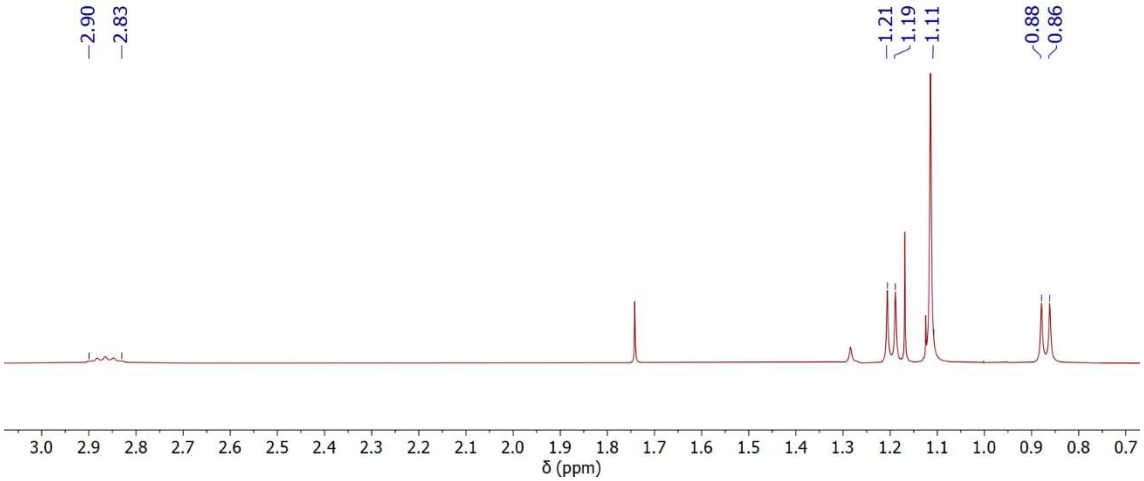
$^{1}H\{^{31}P\}$ NMR spectrum (600 MHz, 298 K) in C_6D_6; aromatic region



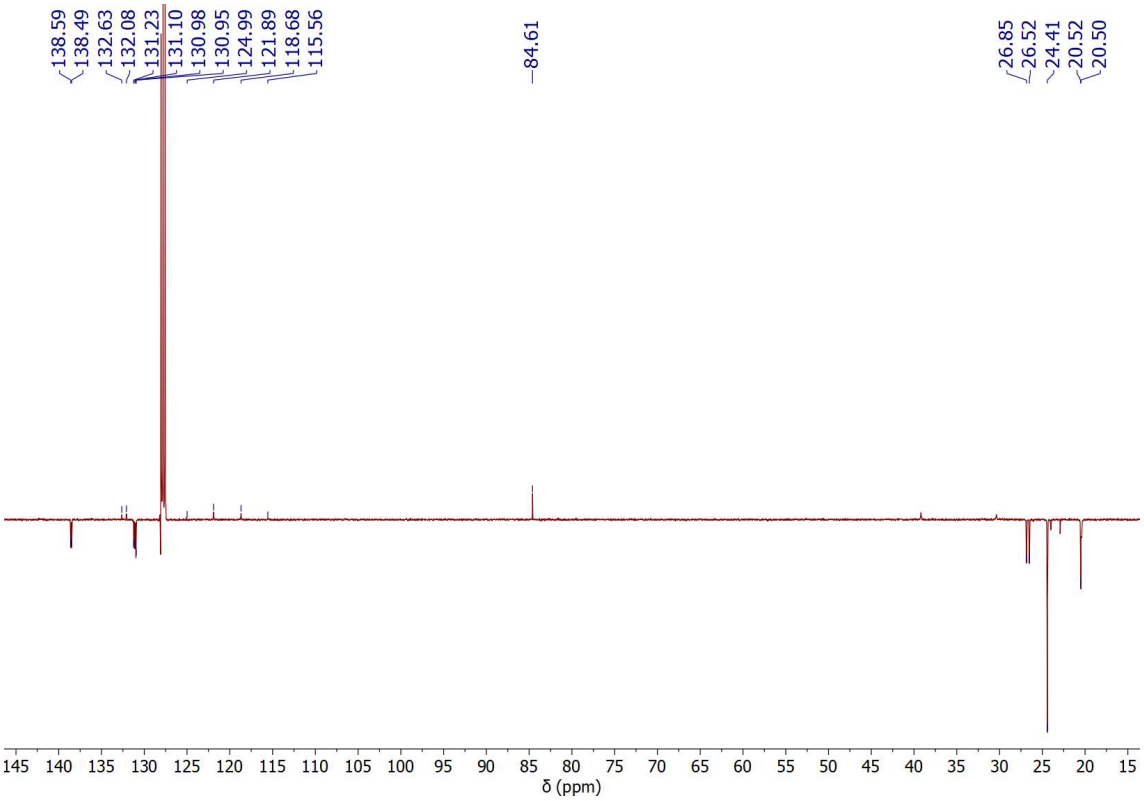
^{1}H NMR spectrum (600 MHz, 298 K) in C_6D_6; aliphatic region



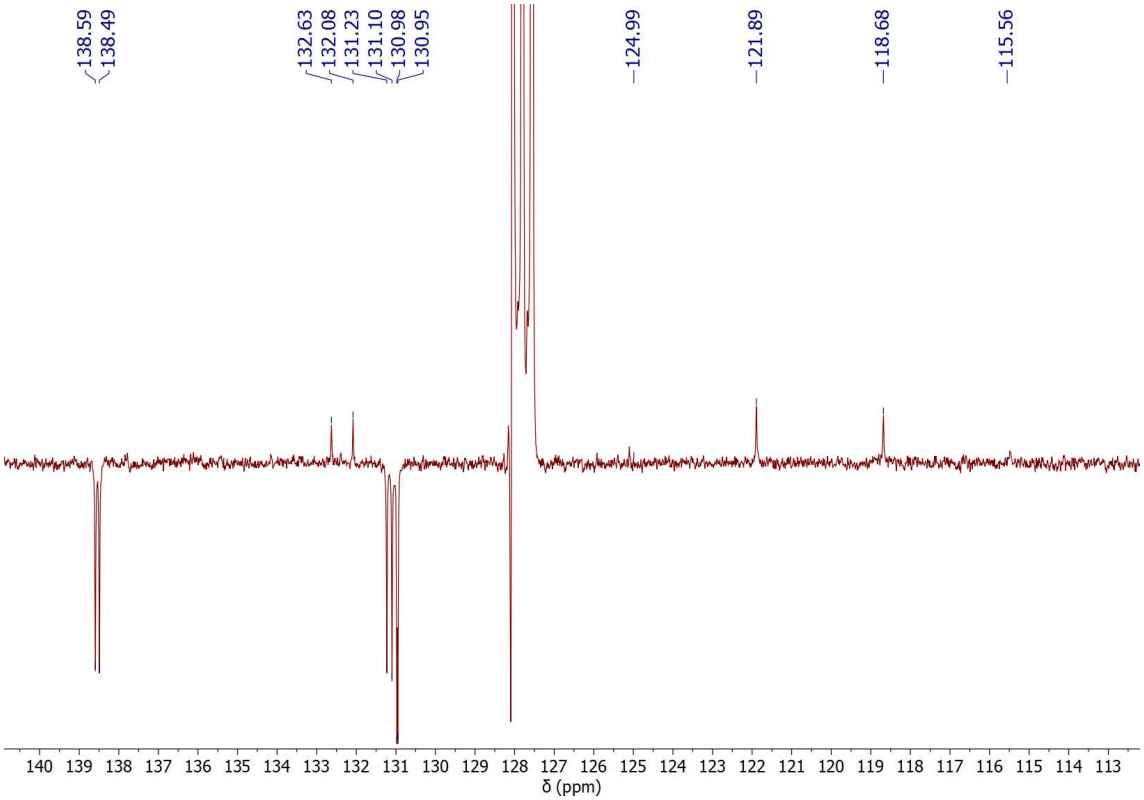
$^{1}H\{^{31}P\}$ NMR spectrum (600 MHz, 298 K) in C_6D_6; aliphatic region



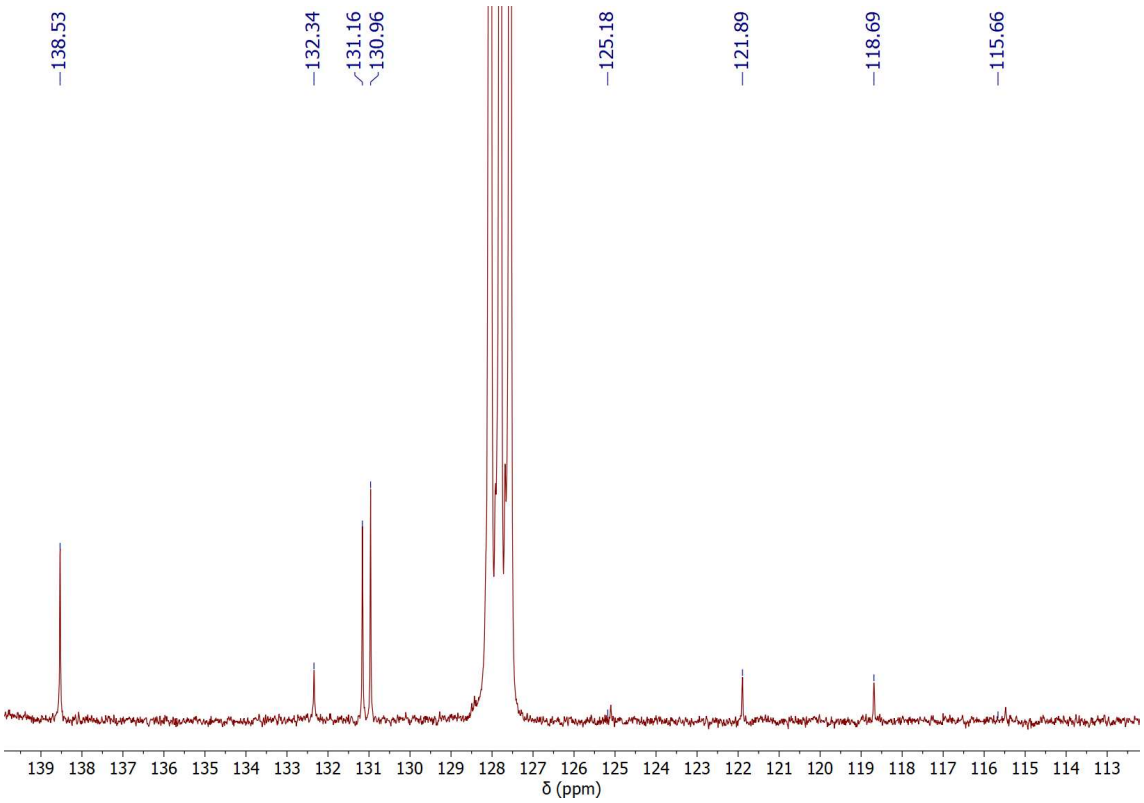
$^{13}C\{^{1}H\}$ NMR spectrum (150 MHz, 298 K) in C_6D_6



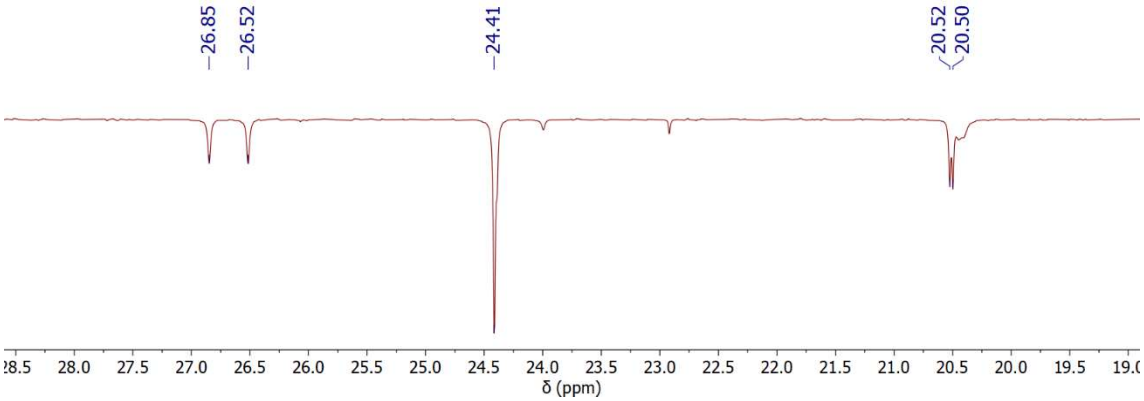
$^{13}C\{^{1}H\}$ NMR spectrum (150 MHz, 298 K) in C_6D_6; aromatic region



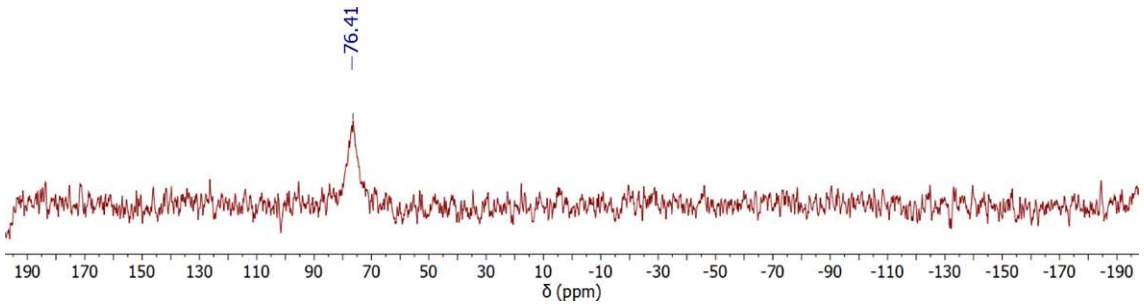
$^{13}C\{^{31}P\}\{^{1}H\}$ NMR spectrum (150 MHz, 298 K) in C_6D_6; aromatic region



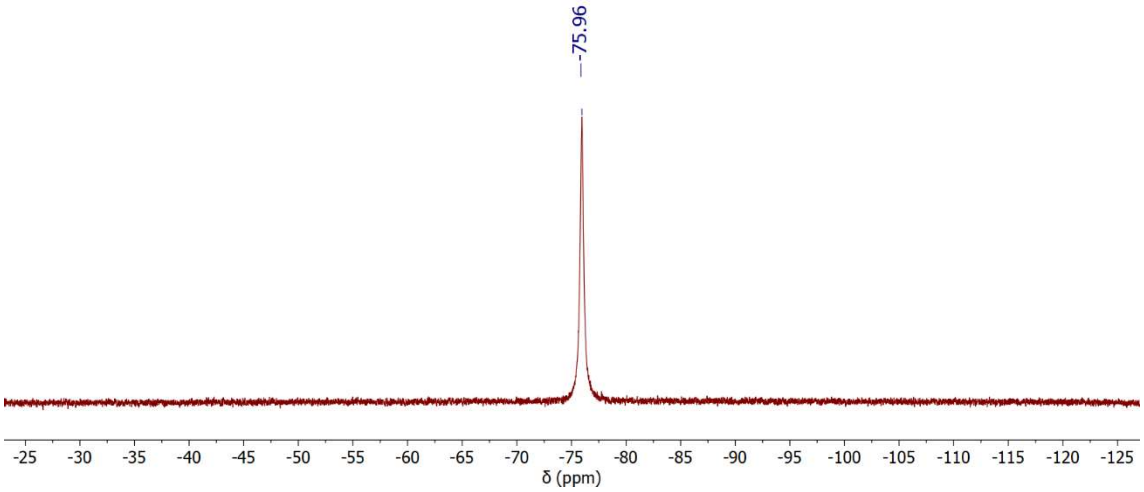
$^{13}C\{^{1}H\}$ NMR spectrum (150 MHz, 298 K) in C_6D_6; aliphatic region



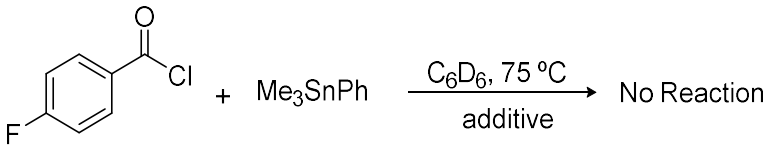
$^{31}P\{^{1}H\}$ NMR spectrum (203 MHz, 298 K) in C_6D_6



$^{19}F\{^{1}H\}$ NMR spectrum (282 MHz, 298 K) in C_6D_6

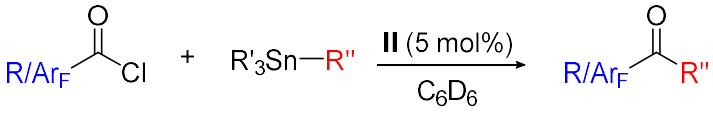


3. General procedure for control experiments



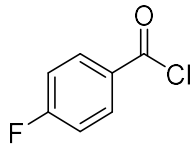
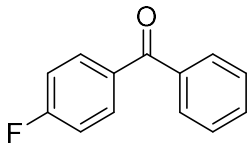
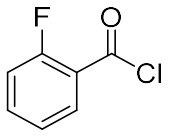
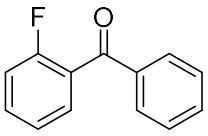
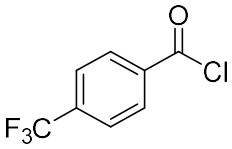
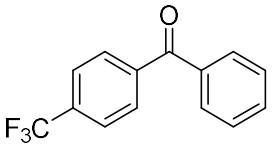
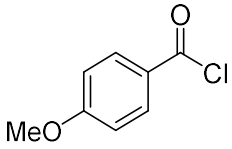
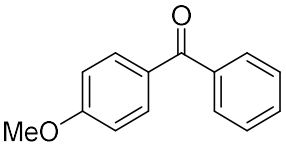
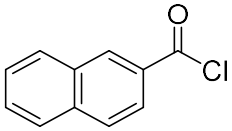
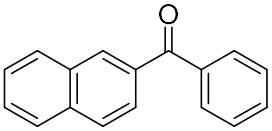
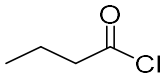
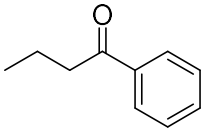
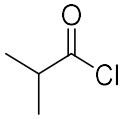
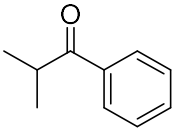
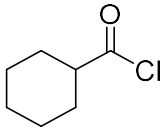
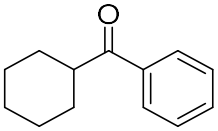
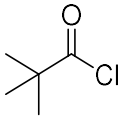
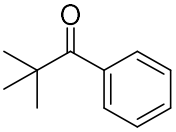
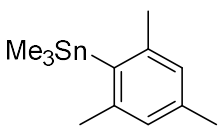
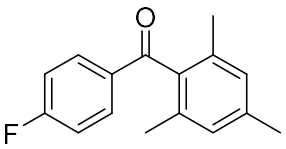
A mixture of acyl chloride (0.33 mmol, 1 Equiv.) and trimethyl(phenyl)tin (60 µL, 0.33 mmol, 1 Equiv.) was dissolved in 0.6 ml C_6D_6. The solution was added to NMR tube containing C_6F_6 (0.017 mmol) or/and 1,2-dichloroethane (0.025 mmol) as internal standard. The reaction was heated at 75 ºC and monitored by ^{1}H and ^{19}F NMR spectroscopy and GC-MS. After 48 hours at 75 ºC, no sign of conversion was detected. In the same conditions, no reaction was observed in the presence of additive: 5 mol% of BPh_3, 5 mol% of $BMes_3$ or 5 mol % of ligand $PBCy_2$.

4. General procedure for Stille coupling with $(PBCy_2)AuNTf_2$ complex II as catalyst and associated competitive experiments



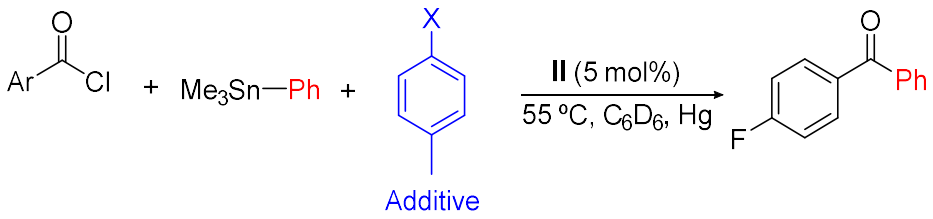
A mixture of acyl chloride (0.33 mmol) and tin compound (0.33 mmol) was dissolved in 0.6 mL of C_6D_6. The solution was added to NMR tube containing catalyst **II** (14 mg, 0.017 mmol, 5 mol%), Hg drops and C_6F_6 (0.017 mmol) or/and 1,2-dichloroethane (0.025 mmol) as internal standard. The reaction was monitored by ^{1}H, ^{19}F and $^{31}P\{^{1}H\}$ NMR spectroscopy and GC-MS. NMR data for coupling products were in accordance with those reported in the literature.

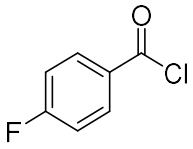
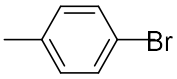
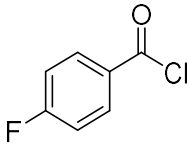
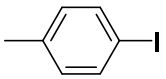
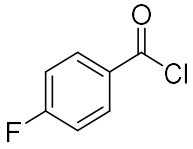
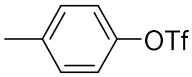
Scope

Acyl Chloride	Conditions	Product	Yield (%)[a]	Ref
	55 ºC / 12h C_6F_6 (IS)		89	4
	55 ºC / 20h C_6F_6 (IS)		80	5
	55 °C / 20h C_6F_6 (IS)		50	6
	rt / 1h 1,2-dichloroethane (IS)		85	4
	rt / 1h 1,2-dichloroethane (IS)		80	7
	rt / 1h 1,2-dichloroethane (IS)		62	8
	rt / 1h 1,2-dichloroethane (IS)		60	9
	rt / 1h 1,2-dichloroethane (IS)		85	10
	55 ºC / 2h 1,2-dichloroethane (IS)		88	11
	55 ºC / 8h C_6F_6 (IS)		85	12

[a]Determined by relative integration with 1,2-dichloroethane or/and C_6F_6 as internal standards.

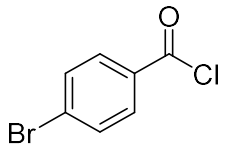
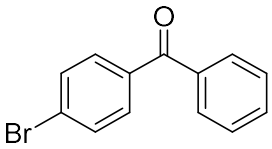
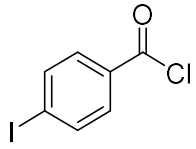
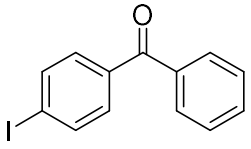
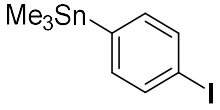
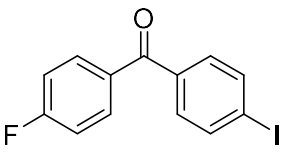
Competitive Stille experiments with complex II as catalyst



Acyl Chloride	Additive	Conditions	% of unreacted additive[a]	Yield of the product (%)[b]
		55 °C / 20h	98	76
		55 °C / 20h	98	83
		55 °C / 20h	98	80

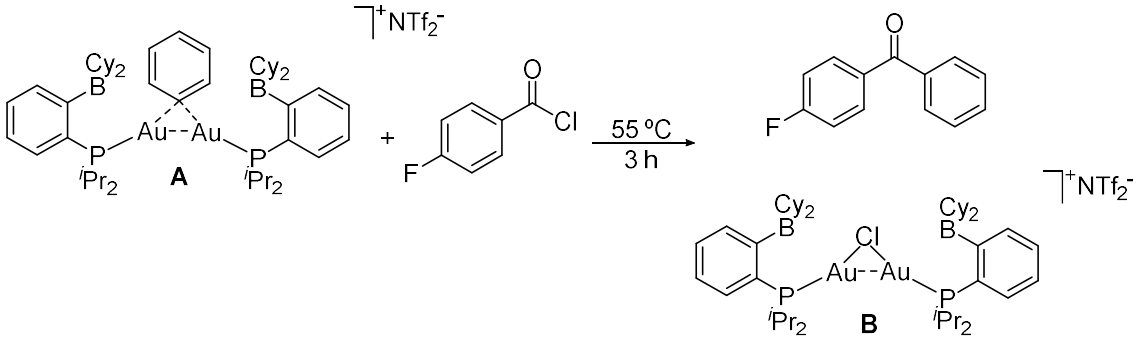
[a]Determined by relative integration with 1,2-dichloroethane as an internal standard. [b]Determined by relative integration with 1,2-dichloroethane and C_6F_6 as internal standards.

Selective Stille coupling of bifunctional substrates

Acyl Chloride	Conditions	Product	Yield (%)[a]	Ref
	55 °C / 4h 1,2-dichloroethane (IS) *$CDCl_3$		75	13
	55 °C / 3h 1,2-dichloroethane (IS) *$CDCl_3$		85	14
	55 °C / 6.5h C_6F_6 (IS)		80	15

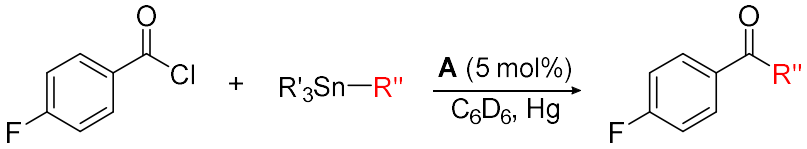
5. Stoichiometric and catalytic reactions of (μ-Ph)[Au(PBCy$_2$)]$_2$NTf$_2$ complex A

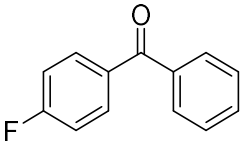
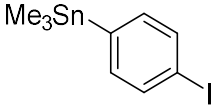
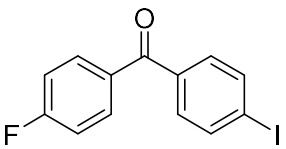
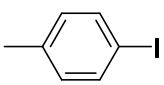
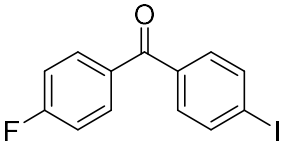
Stoichiometric reactions of complex A with 4-fluorobenzoyl chloride



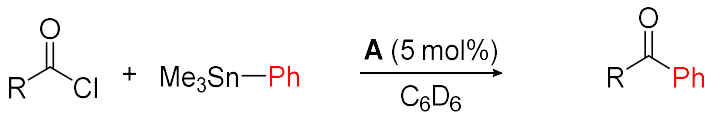
In NMR tube, a mixture of 4-fluorobenzoyl chloride (0.2 M in C_6D_6, 10 μL, 0.002 mmol, 1 Equiv.) and complex **A** (3 mg, 0.002 mmol, 1 Equiv.) was added and dissolved in 0.6 ml C_6D_6. The reaction was monitored by ^{1}H, ^{19}F and $^{31}P\{^{1}H\}$ NMR spectroscopy at 55 ºC. After 3 hours, 4-fluorobenzophenone (90%), and **A** were observed (1:1 ratio).

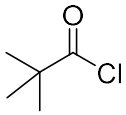
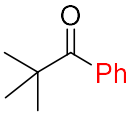
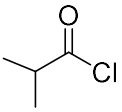
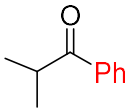
Stille coupling with A as catalyst



Organostannane	Conditions	Additive	Product	Yield (%)[a]	Ref
Me_3SnPh	55 ºC / 20h C_6F_6 (IS)	None		87	4
	55 ºC / 6.5h C_6F_6 (IS)	None		93	15
Me_3SnPh	55 ºC / 6.5h C_6F_6 and 1,2-dichloroethane (IS)			82	4

[a]Determined by relative integration with 1,2-dichloroethane or/and C_6F_6 as internal standards.

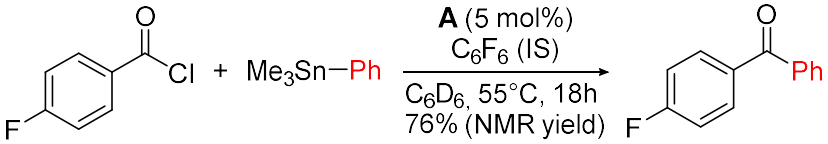


Acid chloride	Conditions	Product	Yield (%)[a]	Ref
	55°C / 1h30 C_6Me_6 (IS)		70	12
	r.t. / 1h C_6Me_6 (IS)		78	10

[a]Determined by relative integration with hexamethylbenzene as internal standard

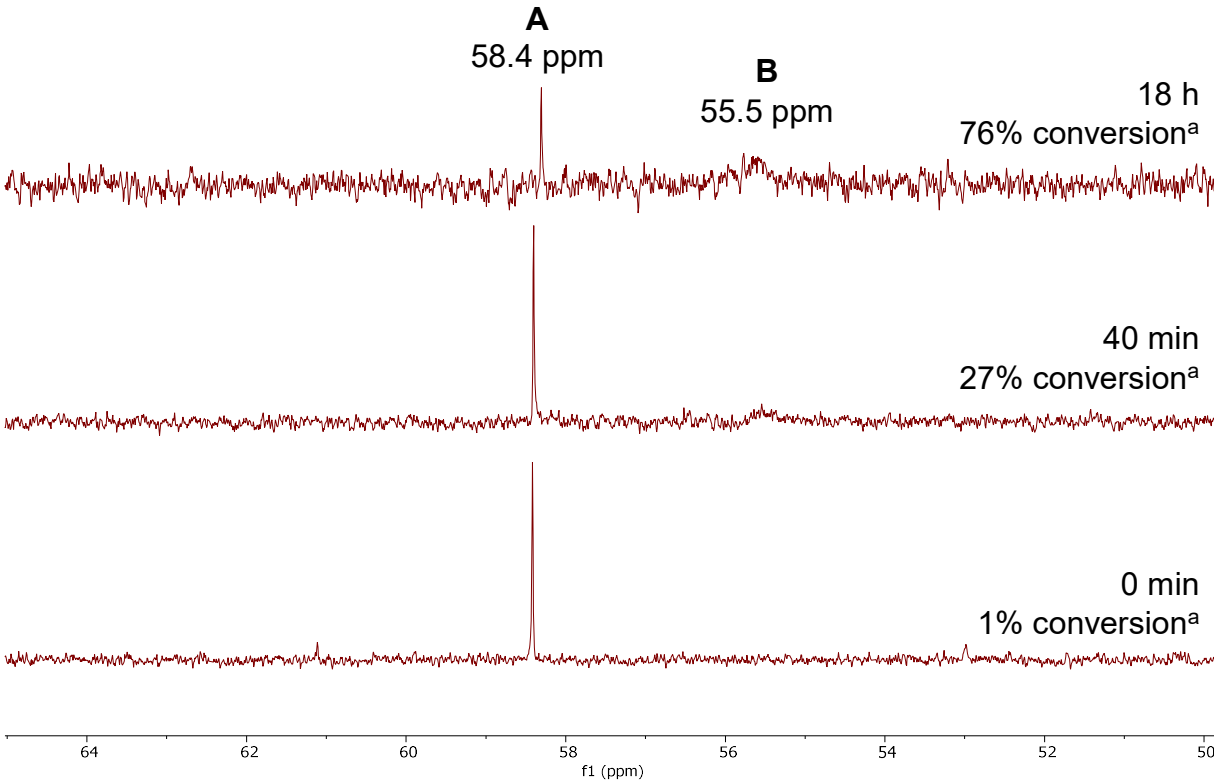
6. ^{31}P NMR monitoring of catalytic Stille coupling with II as catalyst

Catalytic Stille coupling of 4-fluorobenzoyl chloride or tertbutyl acid chloride and Me_3SnPh with **II** as catalyst were monitored by ^{31}P NMR spectroscopy. Only complex **A** (δ ~ 58 ppm) and **B** (δ ~ 55 ppm) were observed.

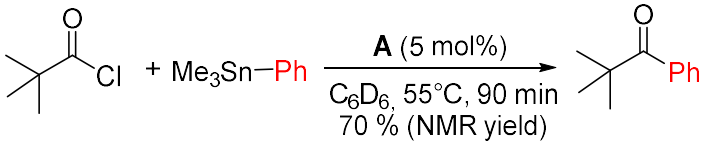


A solution of 4-fluorobenzoyl chloride (4.8 µL, 0.040 mmol, 1 equiv.), Me_3SnPh (7.3 µL, 0.040 mmol, 1 equiv.) and C_6F_6 (2 µL, 0.017 mmol, 0.43 1 equiv.) in 0.6 mL of C_6D_6 was added to the catalyst **A** (3 mg, 0.002 mmol, 5 mol%) in an NMR tube. The tube was sealed and the reaction monitored by ^{19}F{^{1}H} NMR and ^{31}P{^{1}H} NMR spectroscopy at 55°C.

^{31}P{^{1}H} NMR spectrum (121 MHz, 298 K) in C_6D_6

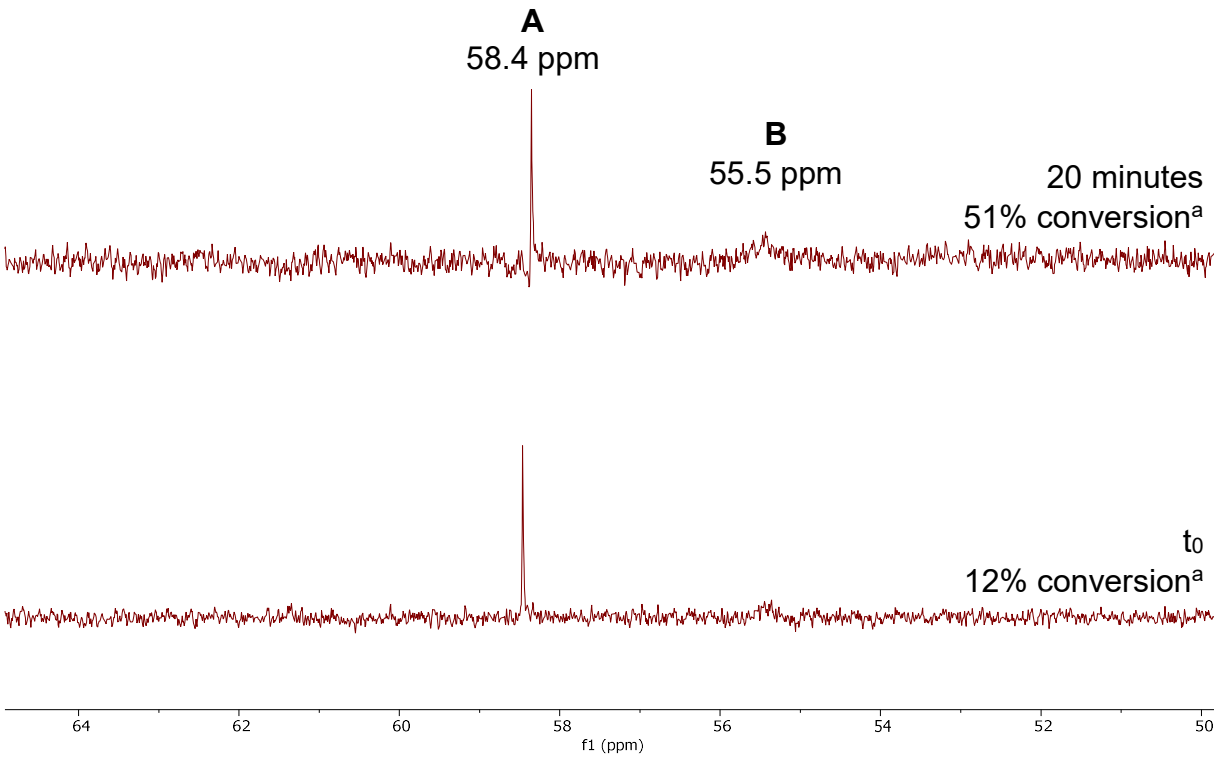


[a]Conversion of *p*-FPhCOCl determined by relative integration with C_6F_6 as internal standard.



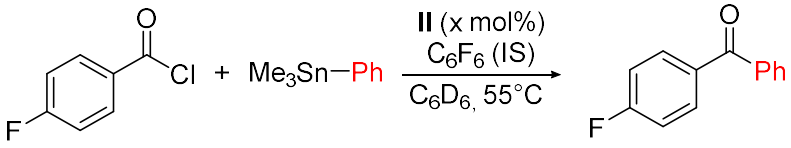
A solution of pivaloyl chloride (4.8 µL, 0.039 mmol, 1 equiv.) and Me_3SnPh (7.3 µL, 0.040 mmol, 1 equiv.) in 0.6 mL of C_6D_6 was added to the catalyst **A** (3 mg, 0.002 mmol, 5 mol%) and hexamethylbenzene (7 mg, 0.043 mmol, 1.1 Equiv.) as internal standard inside an NMR tube. The tube was sealed and monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy at 55°C.

$^{31}P\{^1H\}$ NMR spectrum (121 MHz, 298 K)



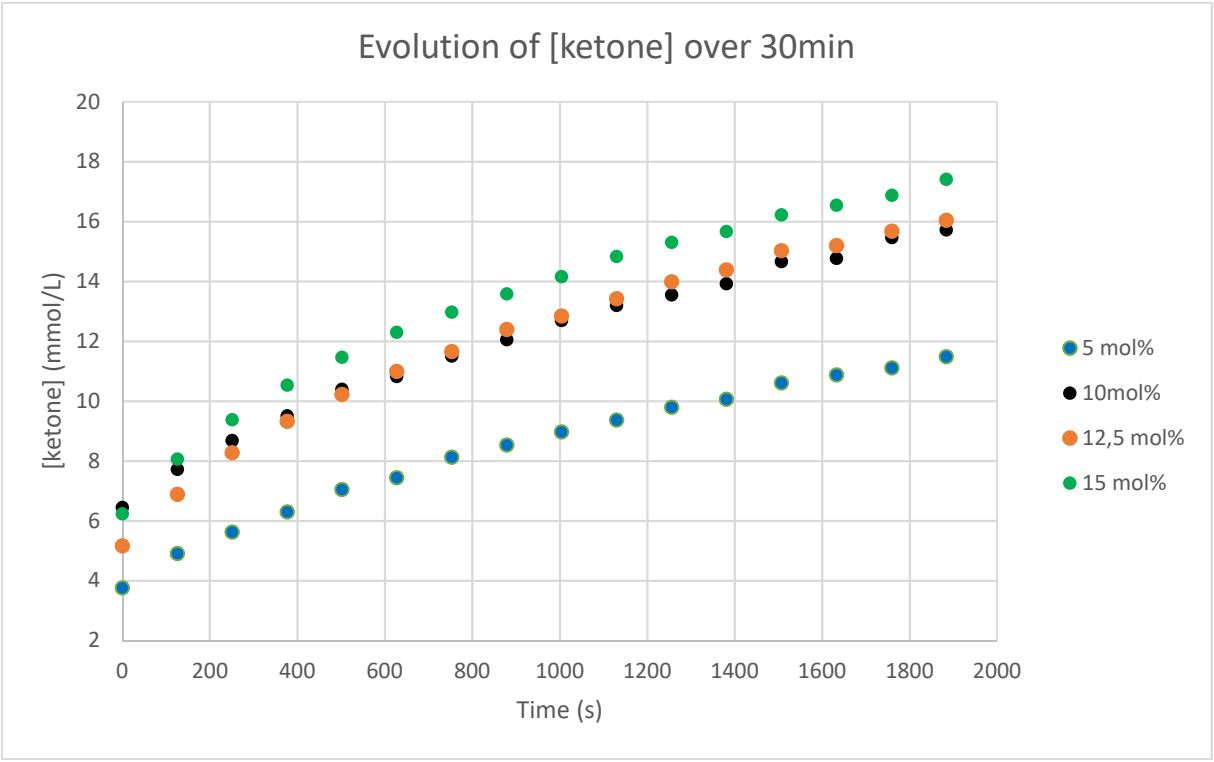
[a]Conversion of *t*BuCOCl determined by relative integration with hexamethylbenzene as internal standard.

7. Determination of kinetic dependence on II in catalytic Stille coupling

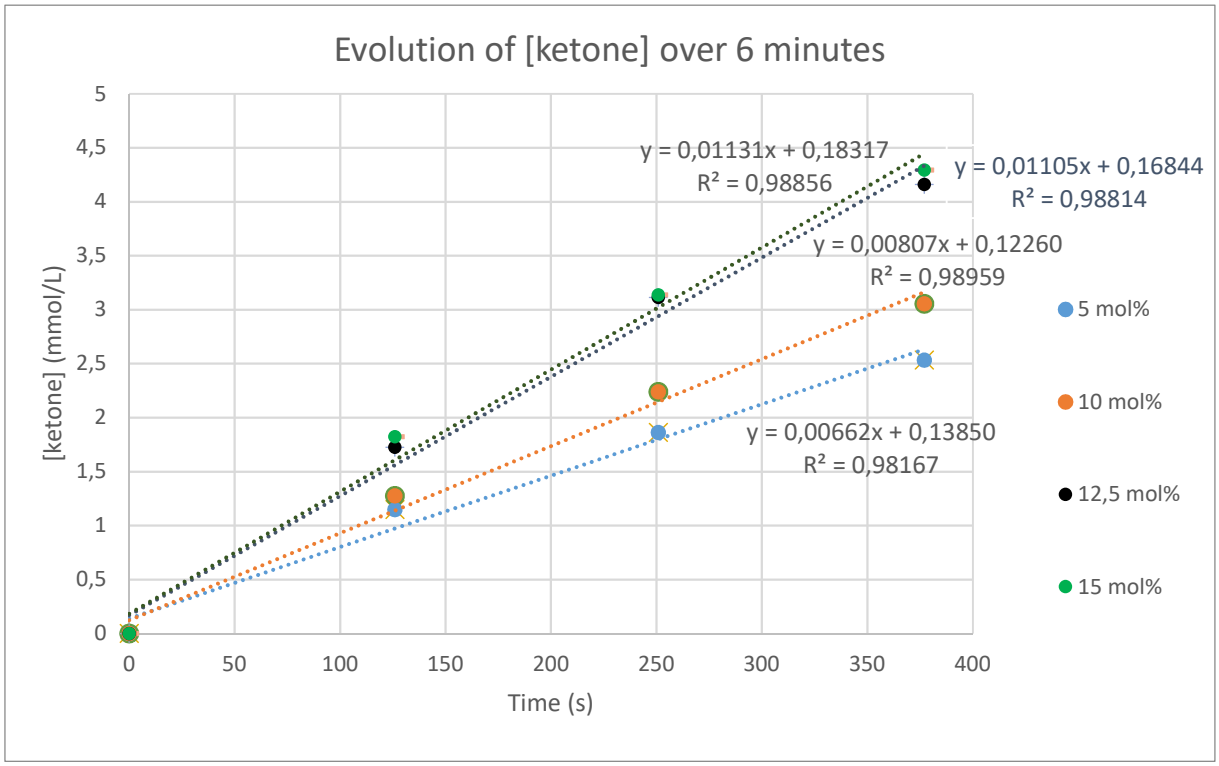


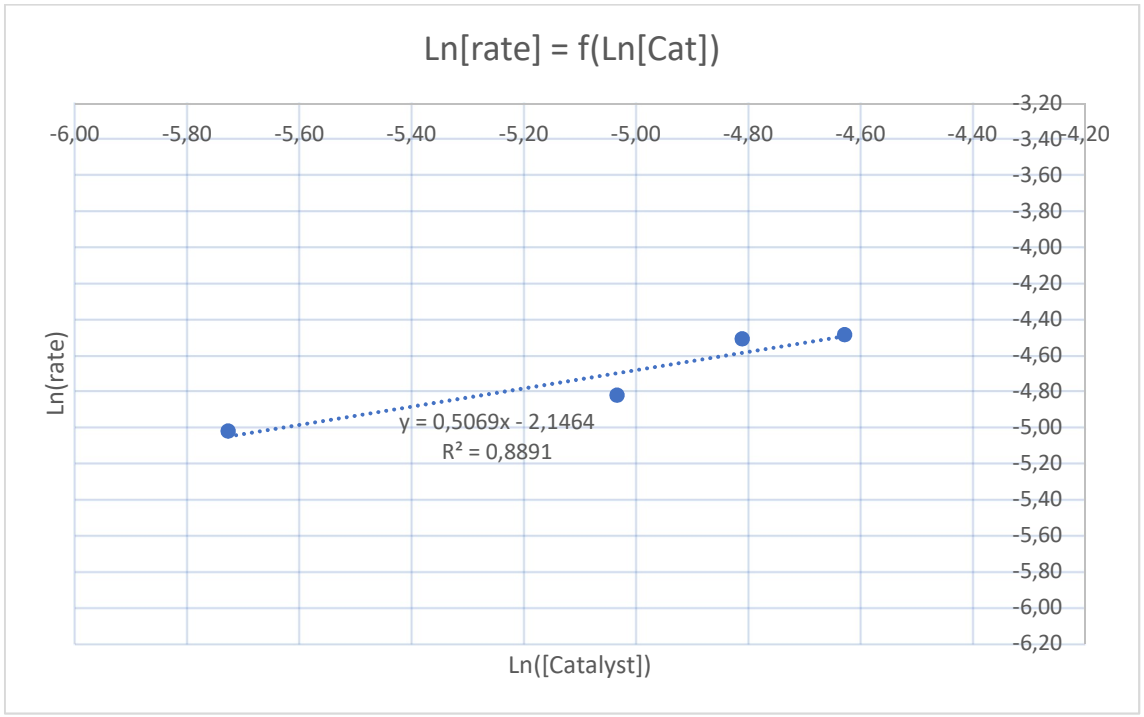
A solution of 4-fluorobenzoyl chloride (4.8 µL, 0.040 mmol, 1 Equiv.), trimethyl(phenyl)tin (7.3 µL, 0.040 mmol, 1 Equiv.) and C_6F_6 (0.017 mmol) in 600 µL of C_6D_6, for a total volume of 614.1 µL was prepared. The solution was added to different amount of catalyst **II** in an NMR tube. The tube was sealed and the reaction was monitored by $^{19}F\{^1H\}$ NMR spectroscopy at 55°C every 2 minutes for 30 minutes.

m of **II** (mg)	n of **II** (mmol)	x mol %
1.7	0.002	5.0%
3.4	0.004	10.0%
4.2	0.005	12.5%
5.1	0.006	15.0%

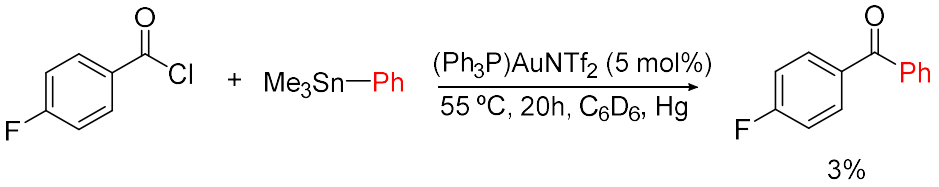


Initial rates were determined through linear regression over the first 6 minutes. The initial conversions were corrected to take into account the set up of the reaction and NMR monitoring.


Evolution of [ketone] over 6 minutes
[ketone] (mmol/L)
Time (s)
y = 0,01131x + 0,18317
R² = 0,98856
y = 0,01105x + 0,16844
R² = 0,98814
y = 0,00807x + 0,12260
R² = 0,98959
y = 0,00662x + 0,13850
R² = 0,98167
5 mol%
10 mol%
12,5 mol%
15 mol%

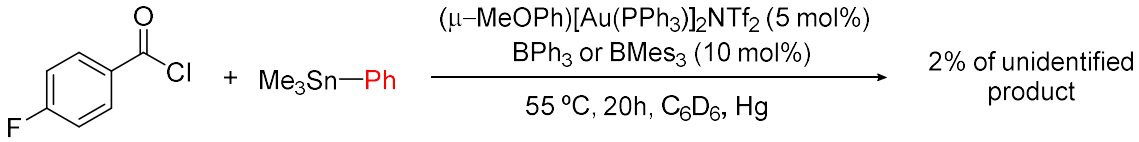

Ln[rate] = f(Ln[Cat])
Ln(rate)
Ln([Catalyst])
y = 0,5069x - 2,1464
R² = 0,8891

8. Stille coupling with $(Ph_3P)AuNTf_2$ as catalyst



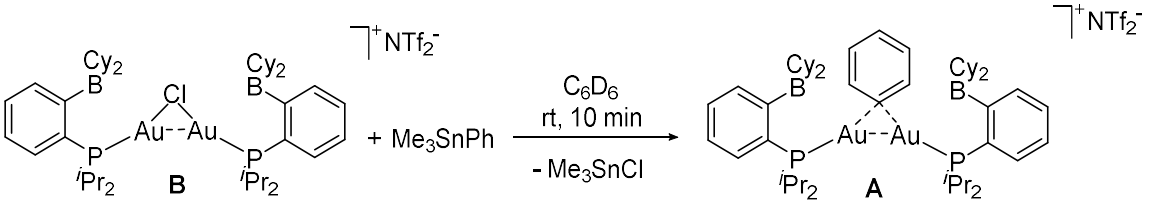
A mixture of acyl chloride (40 µL, 0.34 mmol, 1 Equiv.) and Me_3SnPh (61 µL, 0.34 mmol, 1 Equiv.) was dissolved in 0.6 mL of C_6D_6. The solution was added to NMR tube containing catalyst $(Ph_3P)AuNTf_2$ (13 mg, 0.017 mmol, 5 mol%), Hg drops and C_6F_6 (0.017 mmol) as internal standard. The reaction was monitored by multinuclear NMR spectroscopy. At 55 °C, after 20h, only a 3% of 4-fluorobenzophenone was formed.

9. Stille coupling with $(\mu\text{-MeOPh})[Au(PPh_3)]_2NTf_2$ in the presence of BPh_3 or $BMes_3$



A mixture of acyl chloride (10 µL, 0.08 mmol, 1 Equiv.) and Me_3SnPh (14 µL, 0.08 mmol, 1 Equiv.) was dissolved in 0.6 mL of C_6D_6. The solution was added to NMR tube containing catalyst $(\mu\text{-MeOPh})[Au(PPh_3)]_2NTf_2$ (5 mg, 0.004 mmol, 5 mol%) and BPh_3 or $BMes_3$ (10 mol%), Hg drops and C_6F_6 (0.017 mmol) as internal standard. The reaction was monitored by multinuclear NMR spectroscopy. At 55 °C after 20h, no traces of ketone were detected and only 2% of unidentified product was observed.

10. Stoichiometric reaction of complex B with Me_3SnPh



A solution of Me_3SnPh (0.007 mmol, 1 Equiv.) in 0.3 ml of C_6D_6 was added at room temperature to a solution of complex **B** (10 mg, 0.007 mmol) in 0.3 ml of C_6D_6. The reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. A mixture of complex **A** and Me_3SnCl was observed (1:1 ratio).

11. Crystallographic Data

Crystallographic data were collected at low temperature (193(2) K) on a Bruker APEX II Quazar diffractometer equipped with a 30 W air-cooled microfocus source using MoK_α radiation (λ = 0.71073 Å) for **A**, and on a Bruker D8 VENTURE diffractometer equipped with a PHOTON III detector, using MoK_α radiation (λ = 0.71073 Å) for **I** and a microfocus source with CuK_α radiation (λ = 1.54184 Å) for **B**. Phi and Omega scans were performed for data collection. An empirical absorption correction was applied[16] and the structures were solved by intrinsic phasing method (ShelXT).[17] All non-hydrogen atoms were refined anisotropically by means of least-squares procedures on F^2 with ShelXL [3].[18] All the hydrogen atoms were refined isotropically at calculated positions using a riding model.

Crystal Data, Data Collection, and Structure Refinement for III, A and B.

ID	**III**	**A**	B
formula	$C_{30}H_{45}AuBP$	$C_{54}H_{85}Au_2B_2P_2$, $C_2F_6NO_4S_2$	$C_{48}H_{80}Au_2B_2ClP_2$, $C_2F_6NO_4S_2$
M_r	644.41	1491.88	1450.23
crystal system	orthorhombic	triclinic	monoclinic
space group	*Pbca*	$P\bar{1}$	$P2_1/n$
a (Å)	8.4826(8)	10.8707(11)	9.5720(4)
b (Å)	17.7973(16)	11.6793(12)	39.2345(15)
c (Å)	37.589(5)	48.430(5)	15.7352(6)
α (°)	90	89.013(2)	90
β (°)	90	86.081(2)	95.739(2)
γ (°)	90	85.987(2)	90
V (Å^3)	5674.7(11)	6118.9(11)	5879.8(4)
Z	8	4	4
ρ_{calc} (g cm^{-3})	1.509	1.619	1.638
μ (mm^{-1})	5.257	4.972	11.344
F(000)	2592	2976	2880
crystal size (mm^3)	0.28 x 0.12 x 0.10	0.08 x 0.06 x 0.04	0.20 x 0.18 x 0.16
T/K	193(2)	193(2)	193(2)
measd reflns	131410	89767	135298
Unique reflns (Rint)	11338 (0.0710)	24972 (0.1017)	10790 (0.0568)
Data/restraints/parameters	11338 / 0/ 302	24972 / 1144 / 1628	10790 / 0 / 639
GOF on F^2	1.038	1.020	1.087
R_1[a] [I>2σ(I)]	0.0224	0.0566	0.0271
wR_2[b] [all data]	0.0528	0.1203	0.0678

[a]$R_1 = \Sigma||F_o| - |F_c||/ \Sigma |F_o|$. [b]$wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$.

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