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# Electronic Supplementary Information

*for*

## Post-metallation functionalization of the $[(C\text{^}C)Au(P\text{^}P)]^+$ scaffold through a hydrothiolation reaction

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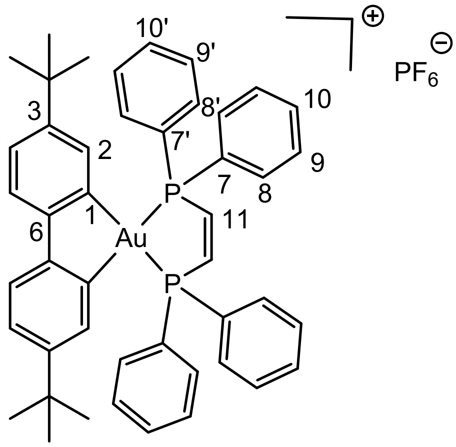
# Experimental part

### General remarks

Anhydrous solvents were obtained by standard procedures. Chemicals were purchased from various manufacturers and used as received. $^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra were acquired Bruker 300 or 400 MHz spectrometers. Chemical shifts (δ) are expressed as ppm referenced to the solvent residual signal. Splitting patterns are expressed as follows: s, singlet; d, doublet; t, triplet; m, multiplet. Mass spectrometry was carried out at the Mass Spectrometry Sciences Sorbonne University (MS3U) platform of Sorbonne Université (Paris). Elemental analysis were performed at the Service Chromato-Masse Microanalyse of the Université Paris-Saclay (Châtenay-Malabry, France). Dimeric gold precursor has been synthesized according to a reported procedure.[1]

### Synthesis of complex 1



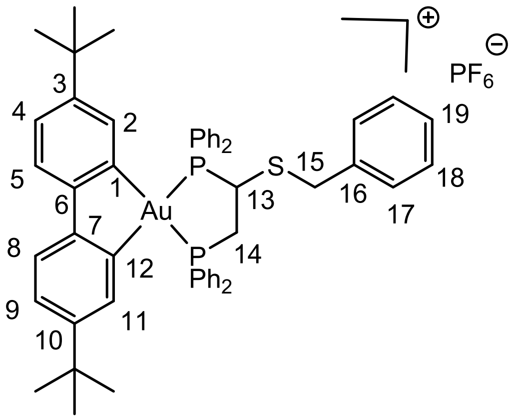

In a Schlenk tube under $N_2$ atmosphere, the **gold dimer** (200 mg, 0.2 mmol) is supended into degassed dichloromethane (20 mL). ***Cis*-1,2-bis(diphenylphosphino)ethylene** (159 mg, 0.4 mmol) is added and the reaction is kept under $N_2$ atmosphere at room temperature for 2 h. **Potassium hexafluorophosphate** (184 mg, 1.0 mmol) is dissolved into degassed acetonitrile (5 mL) and added onto the mixture. The reaction is kept under $N_2$ atmosphere at room temperature for 2 h. Some dichloromethane (15 mL) is added into the mixture before filtration. The reaction mixture was filtered through a glass frit with Celite and the obtained solution was concentrated under reduced pressure. Upon addition of a large amount of $Et_2O$, a pale yellow precipitate was formed which was recovered and gave after drying the pure product (350 mg, 0.35 mmol, 87 % yield). $^{1}H$ NMR ($CDCl_3$, 300 MHz, 300 K): δ 7.97 (d, $^{2}J_{P\text{-}H}$ = 20.8 Hz, 2 H, $H^{11}$), 7.86-7.77 (m, 8 H, $H^{9}$ + $H^{9'}$), 7.69-7.56 (m, 12 H, $H^{8}$ + $H^{8'}$ + $H^{10}$ + $H^{10'}$), 7.48 (m, 2 H, $H^{5}$), 7.40 (dd, $^{3}J_{H\text{-}H}$ = 8 Hz, $^{4}J_{H\text{-}H}$ = 2 Hz, 2 H, $H^{4}$), 7.19 (dm, $^{3}J_{P\text{-}H}$ = 8 Hz, 2 H, $H^{2}$), 0.87 (s, 18 H, $^{t}$Bu). $^{13}C\{^{1}H\}$ Jmod NMR ($CDCl_3$, 75.5 MHz, 300 K): δ 163.2 (dd, $^{2}J_{P\text{-}C}$ = 118 Hz, $^{2}J_{P\text{-}C}$ = 13 Hz, $C^{1}$), 152.0 (s, $C^{6}$), 151.1 (t, $^{4}J_{P\text{-}C}$ = 6 Hz, $C^{3}$), 144.9 (m, $C^{11}$), 136.1 (t, $^{3}J_{P\text{-}C}$= 8 Hz, $C^{2}$), 134.1 (s, $C^{10}$ + $C^{10'}$), 134.0 (m, $C^{8}$ + $C^{8'}$), 130.6 (m, $C^{9}$ + $C^{9'}$), 125.7 (s, $C^{4}$), 125.6 (s, $C^{4}$), 123.3 (d, $^{1}J_{P\text{-}C}$ = 65 Hz, $C^{7/7'}$), 123.2 (d, $^{1}J_{P\text{-}C}$ = 65 Hz, $C^{7/7'}$), 122.1 (m, $C^{5}$), 34.9 (s, $C_{quat.tBu}$), 31.0 (s, $CH_{3\text{-}tBu}$). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz, 300 K): δ 63.4 (s, 2 P, P-Au), -144.3 (h, $^{1}J_{P\text{-}F}$ = 716 Hz, 1 P, $PF_6$). ESI-MS (MeCN) *positive mode exact mass for* $[C_{46}H_{46}P_2Au]^+$ (857.2735): measured *m/z* 857.2738 $[M\text{-}PF_6]^+$. Calcd for $C_{46}H_{46}P_2AuPF_6.H_2O$ (1020.77): C, 54.13; H, 4.74. Found: C, 53.76; H 4.70.

**Reaction conditions optimization**

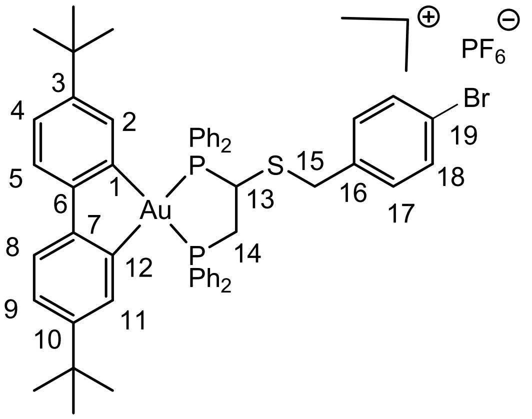
In a sealed tube, **1** (10 mg, 0.01 mmol) or *cis*-1,2-diphenylphosphinoethylene (4.0 mg, 0.01 mmol) is dissolved into deuterated chloroform (1 mL). **Nucleophile** (1-5 eq, 0.01-0.05 mmol) and when mentioned **$NEt_3$** (1 eq., 0.01 mmol, 1.4 µL) are added and the mixture is reacted at room temperature or 50 °C for 1 or 6 h. At the end of the reaction **$PPh_3$** (1 eq., 0.01 mmol, 2.6 mg) is added into the reaction mixture as internal standard and the reaction mixture is analyzed directly by $^{31}P\{^1H\}$ NMR spectroscopy. Intensity of the picks are normalized according the internal standard prior to NMR yield calculation.

**Addition of thiols on complex 1**

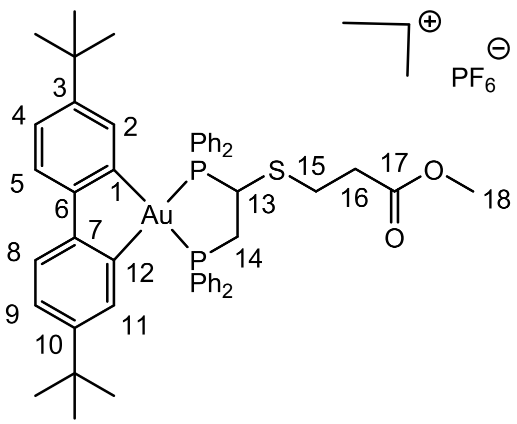
In a sealed tube, **1** (40 mg, 0.04 mmol) is dissolved into chloroform (4 mL). **Thiol** (0.2 mmol) and **$NEt_3$** (5.6 µL, 0.04 mmol) are added and the mixture is heated at 50 °C for 6 h. The products are purified by silica column (pure DCM, $R_f \approx 0.15$) to give, after drying, the pure products as pale yellow powders.




**2a**: **benzylmercaptan** (23 µL, 25 mg, 0.2 mmol), product (31 mg, 0.028 mmol, 69 % yield). $^1H$ NMR ($CDCl_3$, 300 MHz, 300 K): δ 7.93-8.01 (m, 6 H, 6x$H_{ortho\text{-}PPh2}$), 7.57-7.69 (m, 12 H, 8x$H_{meta\text{-}PPh2}$ + 4x$H_{para\text{-}PPh2}$), 7.38-7.45 (m, 6 H, $H^5 + H^8 + H^{18}$ + 2x$H_{ortho\text{-}PPh2}$), 7.04-7.16 (m, 6 H, $H^2 + H^{11} + H^4 + H^9 + H^{19}$), , 6.73 (d, $^3J_{H\text{-}H}$ = 7 Hz, 2 H, $H^{17}$), 4.33-4.42 (dm, $^2J_{P\text{-}H}$ = 30 Hz, 1 H, $H^{13}$), 3.42-3.52 (m, 2 H, $H^{14} + H^{15}$), 3.18-3.30 (m, 2 H, $H^{14} + H^{15}$), 0.75 (s, 9 H, $^t$Bu), 0.73 (s, 9 H, $^t$Bu). $^{13}C\{^1H\}$ Jmod NMR ($CDCl_3$, 75.5 MHz, 300 K): δ 163.4 (dd, $^2J_{P\text{-}C}$ = 110 Hz, $^2J_{P\text{-}C}$ = 6 Hz, $C^{1/12}$), 162.9 (dd, $^2J_{P\text{-}C}$ = 112 Hz, $^2J_{P\text{-}C}$ = 7 Hz, $C^{1/12}$), 152.0 (m, $C^6 + C^7$), 151.0 (m, $C^3 + C^{10}$), 136.1-136.4 (m, $C^2 + C^{11}$), 135.7 (d, $^2J_{P\text{-}C}$ = 11 Hz, $C_{ortho\text{-}PPh2}$), 135.3 (d, $^2J_{P\text{-}C}$ = 12 Hz, $C_{ortho\text{-}PPh2}$), 135.0 (s, $C^{16}$), 134.3 (d, $^2J_{P\text{-}C}$ = 12 Hz, $C_{ortho\text{-}PPh2}$), 134.1 (d, $^4J_{P\text{-}C}$ = 3 Hz, $C_{para\text{-}PPh2}$), 134.0 (d, $^4J_{P\text{-}C}$ = 3 Hz, $C_{para\text{-}PPh2}$), 133.7 (d+d, $^3J_{P\text{-}C}$ = 12 Hz + $^4J_{P\text{-}C}$ = 2 Hz, $C_{meta\text{-}PPh2} + C_{para\text{-}PPh2}$ ), 133.3 (d, $^4J_{P\text{-}C}$ = 3 Hz, $C_{para\text{-}PPh2}$), 130.7 (d, $^3J_{P\text{-}C}$ = 12 Hz, $C_{meta\text{-}PPh2}$), 130.3 (d, $^2J_{P\text{-}C}$ = 12 Hz, $C_{ortho\text{-}PPh2}$), 130.1 (d, $^3J_{P\text{-}C}$ = 12 Hz, $C_{meta\text{-}PPh2}$), 129.8 (d, $^3J_{P\text{-}C}$ = 11 Hz, $C_{meta\text{-}PPh2}$), 129.2 (s, $C^{17}$), 128.7 (s, $C^{18}$), 127.6 (s, $C^{19}$), 126.4 (s, $C^4 + C^9$), 124.4 (d, $^1J_{P\text{-}C}$ = 52 Hz, $C_{ipso\text{-}PPh2}$), 123.5 (d, $^1J_{P\text{-}C}$ = 51 Hz, $C_{ipso\text{-}PPh2}$), 122.5 (d, $^1J_{P\text{-}C}$ = 48 Hz, $C_{ipso\text{-}PPh2}$), 122.3 (d, $^1J_{P\text{-}C}$ = 50 Hz, $C_{ipso\text{-}PPh2}$), 121.8 (d, $^4J_{P\text{-}C}$ = 2 Hz, $C^{5/8}$), 121.7 (d, $^4J_{P\text{-}C}$ = 2 Hz, $C^{5/8}$), 45.3 (dd, $^1J_{P\text{-}C}$ = 32 Hz, $^2J_{P\text{-}C}$ = 8 Hz, $C^{13}$), 37.9 (d, $^3J_{P\text{-}C}$ = 3 Hz, $C^{15}$), 37.3 (dd, $^1J_{P\text{-}C}$ = 35 Hz, $^2J_{P\text{-}C}$ = 14 Hz, $C^{14}$), 34.9 (s, $C_{quat.tBu}$), 34.7 (s, $C_{quat.tBu}$), 30.9 (s, $CH_{3.tBu}$), 30.8 (s, $CH_{3.tBu}$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz, 300 K): δ 68.2 (d, $^2J_{P\text{-}P}$ = 2 Hz, 1 P, P-Au), 50.8 (d, $^2J_{P\text{-}P}$ = 2 Hz, 1 P, P-Au), -144.2 (h, $^1J_{P\text{-}F}$ = 714 Hz, 1 P, $PF_6$). ESI-MS (MeCN) *positive mode exact mass* for $[C_{53}H_{54}SP_2Au]^+$ (981.3081): measured *m/z* 981.3078 $[M\text{-}PF_6]^+$. Calcd for $C_{53}H_{54}P_2SAuPF_6.H_2O$ (1136.0): C, 56.04; H, 4.88; S, 2.82. Found: C, 55.92; H 4.87; S, 3.07.

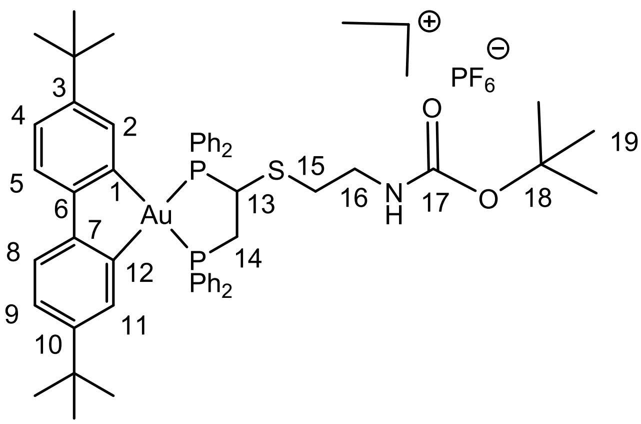



**2b: 4-bromobenzylmercaptan** (41 mg, 0.2 mmol), product (39 mg, 0.032 mmol, 81 % yield). $^1$H NMR ($CDCl_3$, 300 MHz, 300 K): 7.97 (m, 6 H, 6x$H_{ortho\text{-}PPh2}$), 7.48-7.69 (m, 14 H, 2x$H_{ortho\text{-}PPh2}$ + 8x$H_{meta\text{-}PPh2}$ + 4x$H_{para\text{-}PPh2}$), 7.38 (broad s, 2 H, $H^5$ + $H^8$), 7.23 (broad s, 2 H, $H^2$ + $H^{11}$), 7.10-7.15 (m, 4 H, $H^4$ + $H^9$ + $H^{17}$), 6.58 (d, $^3J_{H\text{-}H}$ = 7 Hz, 2 H, $H^{18}$), 4.29 (dm, $^2J_{P\text{-}H}$ = 30 Hz, 1 H, $H^{13}$), 3.15-3.45 (m, 4 H, $H^{14}$ + $H^{15}$), 0.75 (s, 9 H, $^t$Bu), 0.72 (s, 9 H, $^t$Bu). $^{13}$C{$^1$H} Jmod NMR ($CDCl_3$, 75.5 MHz, 300 K): δ 163.5 (dd, $^2J_{P\text{-}C}$ = 110 Hz, $^2J_{P\text{-}C}$ = 7 Hz, $C^{1/12}$), 163.0 (dd, $^2J_{P\text{-}C}$ = 111 Hz, $^2J_{P\text{-}C}$ = 7 Hz, $C^{1/12}$), 151.9 (m, $C^6$ + $C^7$), 151.0 (m, $C^3$ + $C^{10}$), 136.2 (m, $C^2$ + $C^{11}$), 135.8 (d, $^2J_{P\text{-}C}$ = 11 Hz, $C_{ortho\text{-}PPh2}$), 135.2 (d, $^2J_{P\text{-}C}$ = 12 Hz, $C_{ortho\text{-}PPh2}$), 134.4 (s, $C^{16}$), 134.2-134.4 (d + shoulder, $^2J_{P\text{-}C}$ = 11 Hz, $C_{ortho\text{-}PPh2}$ + $C_{para\text{-}PPh2}$), 134.0 (d, $^4J_{P\text{-}C}$ = 2 Hz, $C_{para\text{-}PPh2}$), 133.7-133.9 (d + shoulder, $^2J_{P\text{-}C}$ = 12 Hz, $C_{ortho\text{-}PPh2}$ + $C_{para\text{-}PPh2}$), 133.4 (d, $^4J_{P\text{-}C}$ = 2 Hz, $C_{para\text{-}Ph2}$), 131.7 (s, $C^{17}$), 130.9 (s, $C^{18}$), 130.7 (d, $J_{P\text{-}C}$ = 11 Hz, $C_{meta\text{-}PPh2}$), 130.4 (d, $J_{P\text{-}C}$ = 11 Hz, $C_{meta\text{-}PPh2}$), 130.1 (d, $J_{P\text{-}C}$ = 12 Hz, $C_{meta\text{-}PPh2}$), 129.8 (d, $J_{P\text{-}C}$ = 12 Hz, $C_{meta\text{-}PPh2}$), 125.4 (s, $C^4$ + $C^9$), 124.3 (d, $^1J_{P\text{-}C}$ = 52 Hz, $C_{ipso\text{-}PPh2}$), 123.5 (d, $^1J_{P\text{-}C}$ = 52 Hz, $C_{ipso\text{-}PPh2}$), 122.5 (d, $^1J_{P\text{-}C}$ = 47 Hz, $C_{ipso\text{-}PPh2}$), 121.9 (d, $^1J_{P\text{-}C}$ = 53 Hz, $C_{ipso\text{-}PPh2}$), 121.8 (d, $^4J_{P\text{-}C}$ = 6 Hz, $C^5$ + $C^8$), 121.4 (s, $C^{19}$), 45.6 (dd, $^1J_{P\text{-}C}$ = 32 Hz, $^2J_{P\text{-}C}$ = 9 Hz, $C^{13}$), 37.3 (dd, $^1J_{P\text{-}C}$ = 34 Hz, $^2J_{P\text{-}C}$ = 14 Hz, $C^{14}$), 37.2 (d, $^3J_{P\text{-}C}$ = 3 Hz, $C^{15}$), 34.9 (s, $C_{quat\text{-}tBu}$), 34.7 (s, $C_{quat\text{-}tBu}$), 30.9 (s, $CH_{3\text{-}tBu}$), 30.8 (s, $CH_{3\text{-}tBu}$). $^{31}$P{$^1$H} NMR ($CDCl_3$, 121.5 MHz, 300 K): δ 68.1 (s, 1 P, P-Au), 50.5 (s, 1 P, P-Au), -144.2 (h, $^1J_{P\text{-}F}$ = 718 Hz, 1 P, $PF_6$). ESI-MS (MeCN) *positive mode exact mass* for $[C_{53}H_{53}SBrP_2Au]^+$ (1059.2187): measured *m/z* 1059.2193 $[M\text{-}PF_6]^+$. Calcd for $C_{53}H_{53}P_2SBrAuPF_6$ (1205.8): C, 52.79; H, 4.43; S, 2.66. Found: C, 52.87; H 5.01; S, 2.54.



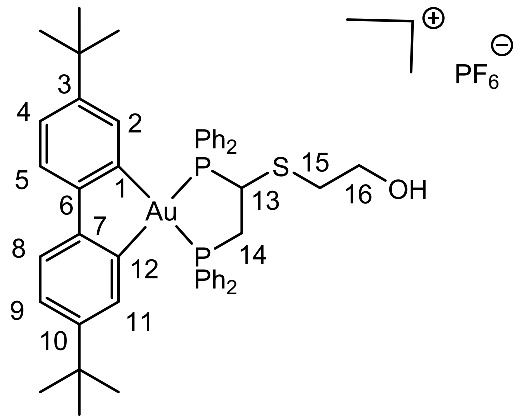

**2c**: **methyl 3-mercaptopropionate** (22 µL, 24 mg, 0.2 mmol), product (42 mg, 0.038 mmol, 94 % yield). $^1$H NMR ($CDCl_3$, 300 MHz, 300 K): δ 8.24 (m, 2 H, 2x$H_{ortho\text{-}PPh2}$), 8.03 (dd, $^3J_{P\text{-}H}$ = 12.6 Hz, $^3J_{H\text{-}H}$ = 8 Hz, 2 H, 2x$H_{ortho\text{-}PPh2}$), 7.90 (dd, $^3J_{P\text{-}H}$ = 12 Hz, $^3J_{H\text{-}H}$ = 7.9 Hz, 2 H, 2x$H_{ortho\text{-}PPh2}$), 7.61-7.72 (m, 8 H, 2x$H_{meta\text{-}PPh2}$ + 4x$H_{para\text{-}PPh2}$), 7.32-7.53 (m, 9 H, $H^5$ + $H^8$ + $H^{11}$ + 2x$H_{ortho\text{-}PPh2}$ + 4x$H_{meta\text{-}PPh2}$), 7.17 (d, $^3J_{H\text{-}H}$ = 8 Hz, 1 H, $H^{4/9}$), 7.15 (d, $^3J_{H\text{-}H}$ = 7.9 Hz, 1 H, $H^{4/9}$), 4.85 (dm, $^2J_{P\text{-}H}$ = 38 Hz, 1 H, $H^{13}$), 3.55-3.81 (m, 1 H, $H^{14}$), 3.51 (s, 3 H,

$H^{18}$), 2.96 (m, 1 H, $H^{14}$), 2.25 (m, 2 H, $H^{16}$), 2.00-2.14 (m, 2 H, $H^{15}$), 0.78 (s, 9 H, $^{t}$Bu), 0.72 (s, 9 H, $^{t}$Bu). $^{13}C\{^{1}H\}$ Jmod NMR ($CDCl_3$, 75.5 MHz, 300 K): δ 171.9 (s, $C^{17}$), 163.3 (dd, $^{2}J_{P\text{-}C}$ = 110 Hz, $^{2}J_{P\text{-}C}$ = 8 Hz, $C^{1/12}$), 163.0 (dd, $^{2}J_{P\text{-}C}$ = 112 Hz, $^{2}J_{P\text{-}C}$ = 7 Hz, $C^{1/12}$), 152.1 (d, $^{3}J_{P\text{-}C}$ = 3 Hz, $C^{6/7}$), 151.9 (d, $^{3}J_{P\text{-}C}$ = 3 Hz, $C^{6/7}$), 151.0 (m, $C^{3}$ + $C^{10}$), 136.7 (m, $C^{2/11}$), 136.3 (m, $C^{2/11}$), 135.9 (d, $^{2}J_{P\text{-}C}$= 13 Hz, $C_{ortho\text{-}PPh2}$), 135.5 (d, $^{2}J_{P\text{-}C}$= 10 Hz, $C_{ortho\text{-}PPh2}$), 134.9 (d, $^{2}J_{P\text{-}C}$= 12 Hz, $C_{ortho\text{-}PPh2}$), 134.3 (d, $^{4}J_{P\text{-}C}$= 2 Hz, $C_{para\text{-}PPh2}$), 133.8 (s, 2x$C_{para\text{-}PPh2}$), 133.0 (d+d, $^{2}J_{P\text{-}C}$= 12 Hz + $^{4}J_{P\text{-}C}$= 2 Hz, $C_{ortho\text{-}PPh2}$ + $C_{para\text{-}PPh2}$), 130.9 (d, $^{3}J_{P\text{-}C}$= 11 Hz, $C_{meta\text{-}PPh2}$), 130.2 (d, $^{3}J_{P\text{-}C}$= 11 Hz, $C_{meta\text{-}PPh2}$), 130.0 (d, $^{3}J_{P\text{-}C}$= 12 Hz, $C_{meta\text{-}PPh2}$), 129.6 (d, $^{3}J_{P\text{-}C}$= 11 Hz, $C_{meta\text{-}PPh2}$), 125.5 (s, $C^{4/9}$), 125.4 (s, $C^{4/9}$), 125.3 (d, $^{1}J_{P\text{-}C}$= 52 Hz, $C_{ipso\text{-}PPh2}$), 123.2 (d, $^{1}J_{P\text{-}C}$= 52 Hz, $C_{ipso\text{-}PPh2}$), 123.0 (d, $^{1}J_{P\text{-}C}$= 51 Hz, $C_{ipso\text{-}PPh2}$), 122.5 (d, $^{1}J_{P\text{-}C}$= 49 Hz, $C_{ipso\text{-}PPh2}$), 121.8 (m, $^{4}J_{P\text{-}C}$= 7 Hz, $C^{5}$ + $C^{8}$), 51.8 (s, $C^{18}$), 46.4 (dd, $^{1}J_{P\text{-}C}$= 34 Hz, $^{2}J_{P\text{-}C}$= 8 Hz, $C^{13}$), 38.0 (dd, $^{1}J_{P\text{-}C}$= 35 Hz, $^{2}J_{P\text{-}C}$= 14 Hz, $C^{14}$), 34.9 (s, $C_{quat.tBu}$), 34.6 (s, $C_{quat.tBu}$), 33.9 (s, $C^{16}$), 31.0 (s, $CH_{3.tBu}$), 30.7 (s, $CH_{3.tBu}$), 28.6 (d, $^{3}J_{P\text{-}C}$ = 3 Hz, $C^{15}$). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162.0 MHz, 300 K): δ 70.3 (d, $^{2}J_{P\text{-}P}$ = 6 Hz, 1 P, P-Au), 54.2 (d, $^{2}J_{P\text{-}P}$ = 6 Hz, 1 P, P-Au), -144.2 (h, $^{1}J_{P\text{-}F}$ = 715 Hz, 1 P, $PF_6$). ESI-MS (MeCN) *positive mode exact mass* for $[C_{50}H_{54}SP_2O_2Au]^+$ (977.2980): measured *m/z* 977.2972 $[M\text{-}PF_6]^+$. Calcd for $C_{50}H_{54}P_2SO_2AuPF_6.0.5H_2O$ (1131.9): C, 53.06; H, 4.90; S, 2.83. Found: C, 52.91; H 4.94; S, 2.70.

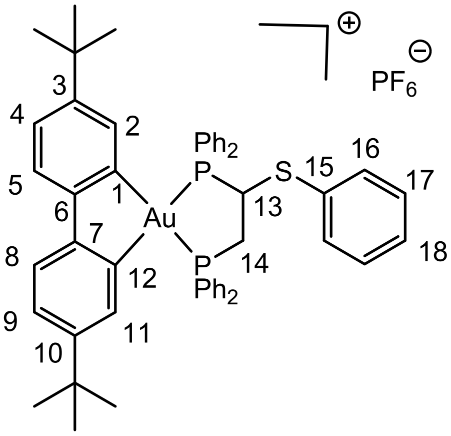



**2d: 2-N-Boc-cysteamine** (34 µL, 35 mg, 0.2 mmol), product: (30 mg, 0.025 mmol, 64 % yield). $^{1}H$ NMR ($CDCl_3$, 300 MHz, 300 K): δ 8.29 (broad s, 2 H, 2x$H_{ortho\text{-}PPh2}$), 8.04 (m, 2 H, 2x$H_{ortho\text{-}PPh2}$), 7.88 (m, 2 H, 2x$H_{ortho\text{-}PPh2}$), 7.60-7.73 (m, 7 H, 4x$H_{meta\text{-}PPh2}$ + 3x$H_{para\text{-}PPh2}$), 7.35-7.50 (m, 11 H, $H^{2}$ + $H^{5}$ + $H^{8}$ + $H^{11}$ + 2x$H_{ortho\text{-}PPh2}$ + 4x$H_{meta\text{-}PPh2}$ + $H_{para\text{-}PPh2}$), 4.81 (s+ broad d, $^{2}J_{P\text{-}H}$ = 42 Hz, 2 H, NH + $H^{13}$), 3.68 (dm, $^{2}J_{P\text{-}H}$ = 42 Hz, 1 H, $H^{14}$), 2.91 (broad s, 3 H, $H^{14}$ + $H^{16}$), 2.03 (broad s, 1 H, $H^{15}$), 1.70 (broad s, 1 H, $H^{15}$), 1.35 (s, 9 H, $H^{19}$), 0.77 (s, 9 H, $^{t}$Bu), 0.71 (s, 9 H, $^{t}$Bu). ). $^{13}C\{^{1}H\}$ Jmod NMR ($CDCl_3$, 75.5 MHz, 300 K): δ 163.3 (dd, $^{2}J_{P\text{-}C}$ = 111 Hz, $^{2}J_{P\text{-}C}$ = 7 Hz, $C^{1/12}$), 163.0 (dd, $^{2}J_{P\text{-}C}$ = 112 Hz, $^{2}J_{P\text{-}C}$ = 7 Hz, $C^{1/12}$), 156.1 (s, $C^{17}$), 152.1 (d, $^{3}J_{P\text{-}C}$ = 4 Hz, $C^{6/7}$), 152.0 (d, $^{3}J_{P\text{-}C}$ = 4 Hz, $C^{6/7}$), 151.0 (m, $C^{3}$ + $C^{10}$), 136.7 (m, $C^{2/11}$), 136.3 (m, $C^{2/11}$), 136.0 (d, $^{2}J_{P\text{-}C}$ = 12 Hz, $C_{ortho\text{-}PPh2}$), 135.5 (d, $^{2}J_{P\text{-}C}$ = 10 Hz, $C_{ortho\text{-}PPh2}$), 134.9 (d, $^{2}J_{P\text{-}C}$ = 12 Hz, $C_{ortho\text{-}PPh2}$), 134.3 (d, $^{4}J_{P\text{-}C}$ = 2 Hz, $C_{para\text{-}PPh2}$), 133.9 (d, $^{4}J_{P\text{-}C}$ = 3 Hz, $C_{para\text{-}PPh2}$), 133.8 (d, $^{4}J_{P\text{-}C}$ = 3 Hz, $C_{para\text{-}PPh2}$), 132.9 (m, $C_{ortho\text{-}PPh2}$ + $C_{para\text{-}PPh2}$), 131.0 (d, $^{3}J_{P\text{-}C}$ = 11 Hz, $C_{meta\text{-}PPh2}$), 130.1 (d, $^{3}J_{P\text{-}C}$ = 11 Hz, $C_{meta\text{-}PPh2}$), 130.0 (d, $^{3}J_{P\text{-}C}$ = 11 Hz, $C_{meta\text{-}PPh2}$), 129.5 (d, $^{3}J_{P\text{-}C}$ = 12 Hz, $C_{meta\text{-}PPh2}$), 125.7 (d, $^{1}J_{P\text{-}C}$ = 52 Hz, $C_{ipso\text{-}PPh2}$), 125.5 (s, $C^{4/9}$), 125.4 (s, $C^{4/9}$), 123.1 (d, $^{1}J_{P\text{-}C}$ = 51 Hz, $C_{ipso\text{-}PPh2}$), 122.9 (d, $^{1}J_{P\text{-}C}$ = 51 Hz, $C_{ipso\text{-}PPh2}$), 122.1 (d, $^{1}J_{P\text{-}C}$ = 50 Hz, $C_{ipso\text{-}PPh2}$), 121.8 (m, $C^{5}$ + $C^{8}$), 79.2 (s, $C^{18}$), 45.6 (dd, $^{1}J_{P\text{-}C}$ = 38 Hz, $^{2}J_{P\text{-}C}$ = 7.7 Hz, $C^{13}$), 39.7 (s, $C^{16}$), 38.3 (dd, $^{1}J_{P\text{-}C}$ = 36 Hz, $^{2}J_{P\text{-}C}$ = 15 Hz, $C^{14}$), 34.9 (s, $C_{quat.tBu}$), 34.6 (s, $C_{quat.tBu}$), 32.7 (s, $C^{15}$), 31.0 (s, $CH_{3.tBu}$), 30.7 (s, $CH_{3.tBu}$), 28.5 (s, $C^{19}$). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.0 MHz, 300 K): δ 70.7 (d, $^{2}J_{P\text{-}P}$ = 5 Hz, 1 P, P-Au), 54.7 (d, $^{2}J_{P\text{-}P}$ = 5 Hz, 1 P, P-Au), -144.2 (h, $^{1}J_{F\text{-}P}$ = 719 Hz, 1 P, $PF_6^-$). ESI-MS (MeCN) *positive mode exact mass* for $[C_{53}H_{61}SNP_2O_2Au]^+$ (1034.3558):

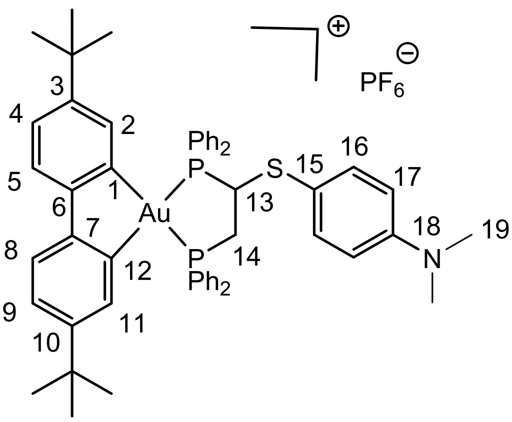
measured *m/z* 1034.3562 $[M-PF_6]^+$. Calcd for $C_{53}H_{61}P_2SNO_2AuPF_6$ (1180.0): C, 53.95; H, 5.21; N, 1.19; S, 2.72. Found: C, 54.23; H 6.24; N, 1.09; S, 2.72.




**2e**: **2-mercaptoethanol** (22 µL, 24 mg, 0.2 mmol), product (35 mg, 0.032 mmol, 80 % yield). $^1$H NMR ($CDCl_3$, 400 MHz, 300 K): δ 8.22 (dd, $^3J_{P-H}$ = 11 Hz, $^3J_{H-H}$ = 7 Hz, 2 H, 2x$H_{ortho-PPh2}$), 8.03 (dd, $^3J_{P-H}$ = 12 Hz, $^3J_{H-H}$ = 7 Hz, 2 H, 2x$H_{ortho-PPh2}$), 7.93 (dd, $^3J_{P-H}$ = 12 Hz, $^3J_{H-H}$ = 7 Hz, 2 H, 2x$H_{ortho-PPh2}$), 7.59-7.71 (m, 7 H, 4x$H_{meta-PPh2}$ + 3x$H_{para-PPh2}$), 7.47-7.54 (m, 5 H, 2x$H_{ortho-PPh2}$ + 2x$H_{meta-PPh2}$ + $H_{para-PPh2}$), 7.40-7.43 (m, 4 H, $H^5$ + $H^8$ + 2x$H_{meta-PPh2}$), 7.32 (d, $^4J_{P-H}$ = 13 Hz, 2 H, $H^2$ + $H^{11}$), 7.16 (m, 2 H, $H^4$ + $H^9$), 4.95 (dm, $^2J_{P-H}$ = 36 Hz, 1 H, $H^{13}$), 3.59-3.74 (m, 1 H, $H^{14}$), 3.52 (q, $^3J_{H-H}$ = 5 Hz, $H^{16}$), 3.07 (m, 1 H, $H^{14}$), 2.31 (t, $^3J_{H-H}$ = 5 Hz, 1 H, OH), 2.17 (m, 1 H, $H^{15}$), 1.85 (m, 1 H, $H^{15}$), 0.77 (s, 9 H, $^t$Bu), 0.72 (s, 9 H, $^t$Bu). $^{13}$C{$^1$H} Jmod NMR ($CDCl_3$, 75.5 MHz, 300 K): δ 163.4 (dd, $^2J_{P-C}$ = 110 Hz, $^2J_{P-C}$ = 7 Hz, $C^{1/12}$), 163.1 (dd, $^2J_{P-C}$ = 111 Hz, $^2J_{P-C}$ = 7 Hz, $C^{1/12}$), 152.1 (d, $^3J_{P-C}$ = 3.8 Hz, $C^{6/7}$), 152.0 (d, $^3J_{P-C}$ = 3 Hz, $C^{6/7}$), 151.0 (m, $C^3$ + $C^{10}$), 136.5 (dd, $^3J_{P-C}$ = 10 Hz, $^3J_{P-C}$ = 5 Hz, $C^{2/11}$), 136.3 (dd, $^3J_{P-C}$ = 10 Hz, $^3J_{P-C}$ = 5 Hz, $C^{2/11}$), 135.7 (d, $^2J_{P-C}$ = 13 Hz, $C_{ortho-PPh2}$), 135.6 (d, $^2J_{P-C}$ = 11 Hz, $C_{ortho-PPh2}$), 134.8 (d, $^2J_{P-C}$ = 11 Hz, $C_{ortho-PPh2}$), 134.3 (d, $^4J_{P-C}$ = 2 Hz, $C_{para-PPh2}$), 133.9 (d, $^4J_{P-C}$ = 3 Hz, $C_{para-PPh2}$), 133.7 (d, $^4J_{P-C}$ = 3 Hz, $C_{para-PPh2}$), 133.3 (d, $^2J_{P-C}$ = 12 Hz, $C_{ortho-PPh2}$), 133.2 (d, $^4J_{P-C}$ = 3 Hz, $C_{para-PPh2}$), 130.8 (d, $^3J_{P-C}$ = 11 Hz, $C_{meta-PPh2}$), 130.2 (d, $^3J_{P-C}$ = 12 Hz, $C_{meta-PPh2}$), 130.0 (d, $^3J_{P-C}$ = 12 Hz, $C_{meta-PPh2}$), 129.5 (d, $^3J_{P-C}$ = 12 Hz, $C_{meta-PPh2}$), 125.4 (s, $C^{5/8}$), 125.3 (s, $C^{5/8}$), 124.8 (d, $^1J_{P-C}$ = 52 Hz, $C_{ipso-PPh2}$), 123.4 (d, $^1J_{P-C}$ = 52 Hz, $C_{ipso-PPh2}$), 122.8(d, $^1J_{P-C}$ = 52 Hz, $C_{ipso-PPh2}$), 122.4 (d, $^1J_{P-C}$ = 45 Hz, $C_{ipso-PPh2}$), 121.8 (d, $^4J_{P-C}$ = 3 Hz, $C^{4/9}$), 121.7 (d, $^4J_{P-C}$ = 4 Hz, $C^{4/9}$), 62.7 (s, $C^{16}$), 46.1 (dd, $^1J_{P-C}$ = 33 Hz, $^2J_{P-C}$ = 8 Hz, $C^{13}$), 38.0 (dd, $^1J_{P-C}$ = 36 Hz, $^2J_{P-C}$ = 16 Hz, $C^{14}$), 65.6 (d, $^3J_{P-C}$ = 3 Hz, $C^{13}$), 34.9 (s, $C_{quat.tBu}$), 34.6 (s, $C_{quat.tBu}$), 30.9 (s, $CH_{3.tBu}$), 30.7 (s, $CH_{3.tBu}$). $^{31}$P{$^1$H} NMR ($CDCl_3$, 162.0 MHz, 300 K): δ 69.6 (d, $^2J_{P-P}$ = 4 Hz, 1 P, P-Au), 53.4 (d, $^2J_{P-P}$ = 4 Hz, 1 P, P-Au), -144.2 (h, $^1J_{P-F}$ = 716 Hz, 1 P, $PF_6$). ESI-MS (MeCN) *positive mode exact mass* for $[C_{48}H_{52}SP_2OAu]^+$ (935.2874): measured *m/z* 935.2880 $[M-PF_6]^+$. Calcd for $C_{48}H_{52}P_2SOAuPF_6 \cdot 0.5H_2O$ (1089.9): C, 52.90; H, 4.90; S, 2.94. Found: C, 52.70; H 4.99; S, 2.95.

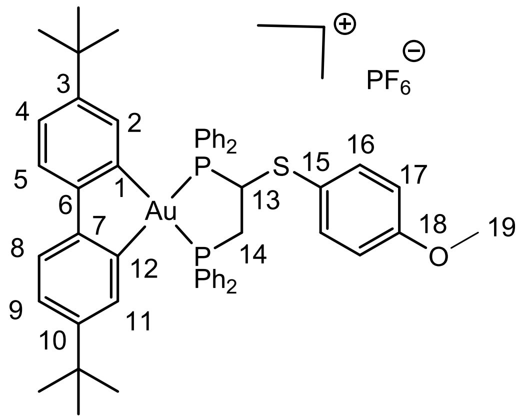



**2f**: **thiophenol** (20 µL, 22 mg, 0.2 mmol), product (43 mg, 0.039 mmol, 97 % yield). $^1$H NMR (CDCl$_3$, 300 MHz, 300 K): δ 8.25-830 (m, 2 H, 2x$H_{ortho\text{-}PPh2}$), 7.85-7.92 (m, 4 H, 4x$H_{ortho\text{-}PPh2}$), 7.75 (m, 3 H, 2x$H_{meta\text{-}PPh2}$ + $H_{para\text{-}PPh2}$), 7.67 (t, $^3J_{H\text{-}H}$ = 8 Hz, 1 H, $H_{para\text{-}PPh2}$), 7.51-7.59 (m, 3 H, 2x$H_{meta\text{-}PPh2}$ + $H_{para\text{-}PPh2}$), 7.40-7.48 (m, 5 H, $H^5$ + $H^8$ + 2x$H_{meta\text{-}PPh2}$ + $H_{para\text{-}PPh2}$), 5.28-5.34 (m, 6 H, $H^2$ + $H^{11}$ + 2x$H_{ortho\text{-}PPh2}$ + 2x$H_{meta\text{-}PPh2}$), 7.19 (d, $^3J_{H\text{-}H}$ = 8 Hz, 1 H, $H^{4/9}$), 7.17 (d, $^3J_{H\text{-}H}$ = 8 Hz, 1 H, $H^{4/9}$), 7.06 (m, 3 H, $H^{17}$ + $H^{18}$), 6.77 (m, 2 H, $H^{16}$), 5.21 (dm, $^2J_{P\text{-}H}$ = 36.1 Hz, 1 H, $H^{13}$), 3.61 (dm, $^2J_{P\text{-}H}$ = 38 Hz, 1 H, $H^{14}$), 2.99 (m, 1 H, $H^{14}$), 0.78 (s, 9 H, $^t$Bu), 0.72 (s, 9 H, $^t$Bu). $^{13}$C{$^1$H} Jmod NMR (CDCl$_3$, 75.5 MHz, 300 K): δ 163.4 (dd, $^2J_{P\text{-}C}$ = 111 Hz, $^2J_{P\text{-}C}$ = 7 Hz, $C^{1/12}$), 163.2 (dd, $^3J_{P\text{-}C}$ = 112 Hz, $^2J_{P\text{-}C}$ = 7 Hz, $C^{1/12}$), 152.0 (m, $C^6$ + $C^7$), 151.0 (m, $C^3$ + $C^{10}$), 136.7 (m, $C^{2/11}$), 136.2 (m, $C^{2/11}$), 135.9 (d, $^2J_{P\text{-}C}$ = 12 Hz, $C_{ortho\text{-}PPh2}$), 135.4 (d, $^2J_{P\text{-}C}$ = 11 Hz, $C_{ortho\text{-}PPh2}$), 134.9 (d, $^2J_{P\text{-}C}$ = 13 Hz, $C_{ortho\text{-}PPh2}$), 134.5 (d, $^4J_{P\text{-}C}$ = 3 Hz, $C_{para\text{-}PPh2}$), 134.0 (d, $^4J_{P\text{-}C}$ = 2 Hz, $C_{para\text{-}PPh2}$), 133.6 (d, $^4J_{P\text{-}C}$ = 2 Hz, $C_{para\text{-}PPh2}$), 132.9 (m, $C_{para\text{-}PPh2}$ + $C_{ortho\text{-}PPh2}$), 131.1 (d, $^3J_{P\text{-}C}$ = 11 Hz, $C_{meta\text{-}PPh2}$), 130.7 (s, $C^{16}$), 130.3 (s, $C^{15}$), 130.2 (d, $^3J_{P\text{-}C}$ = 12 Hz, $C_{meta\text{-}PPh2}$), 130.0 (d, $^3J_{P\text{-}C}$ = 11 Hz, $C_{meta\text{-}PPh2}$), 129.7 (m, $C_{meta\text{-}PPh2}$ + $C^{17}$), 128.0 (s, $C^{18}$), 125.5 (s, $C^{4/9}$), 125.4 (s, $C^{4/9}$), 125.1 (d, $^1J_{P\text{-}C}$ = 52 Hz, $C_{ipso\text{-}PPh2}$), 123.3 (d, $^1J_{P\text{-}C}$ = 52 Hz, $C_{ipso\text{-}PPh2}$), 122.0 (d, $^1J_{P\text{-}C}$ = 51 Hz, $C_{ipso\text{-}PPh2}$), 121.9 (d, $^4J_{P\text{-}C}$ = 4 Hz, $C^{5/8}$), 121.8 (d, $^4J_{P\text{-}C}$ = 4 Hz, $C^{5/8}$), 121.5 (d, $^1J_{P\text{-}C}$ = 48 Hz, $C_{ipso\text{-}PPh2}$), 48.4 (dd, $^1J_{P\text{-}C}$ = 33 Hz, $^2J_{P\text{-}C}$ = 10 Hz, $C^{13}$), 36.7 (dd, $^1J_{P\text{-}C}$ = 36 Hz, $^2J_{P\text{-}C}$ = 14 Hz, $C^{14}$), 35.0 (s, $C_{quat\text{-}tBu}$), 34.7 (s, $C_{quat\text{-}tBu}$), 31.0 (s, $CH_{3\text{-}tBu}$), 30.7 (s, $CH_{3\text{-}tBu}$). $^{31}$P{$^1$H} NMR (CDCl$_3$, 121.5 MHz, 300 K): δ 68.6 (d, $^2J_{P\text{-}P}$ = 4 Hz, 1 P, P-Au), 52.8 (d, $^2J_{P\text{-}P}$ = 4 Hz, 1 P, P-Au), -144.2 (h, $^1J_{P\text{-}F}$ = 716 Hz, 1 P, PF$_6$). ESI-MS (MeCN) *positive mode exact mass* for [$C_{52}H_{52}SP_2Au$]$^+$ (967.2925): measured *m/z* 967.2922 [M-PF$_6$]$^+$. Calcd for $C_{52}H_{52}P_2SAuPF_6$ (1112.9): C, 56.12; H, 4.71; S, 2.88. Found: C, 56.35; H 4.85; S, 2.95.



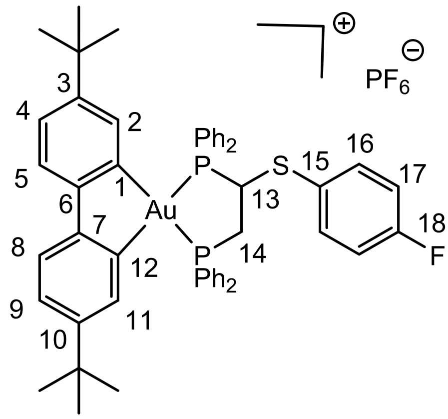

**2g: 4-N,N-dimethylaminothiophenol** (31 mg, 0.2 mmol), product (31 mg, 0.026 mmol, 66 % yield). $^1$H NMR (CDCl$_3$, 300 MHz, 300 K): δ 8.14-8.20 (m, 2 H, 2x$H_{ortho\text{-}PPh2}$), 7.87-7.98 (m, 4 H, 4x$H_{ortho\text{-}PPh2}$), 7.63-7.70 (m, 5 H, 2x$H_{meta\text{-}PPh2}$ + 3x$H_{para\text{-}PPh2}$), 7.46-7.60 (m, 5 H, 4x$H_{meta\text{-}PPh2}$ + $H_{para\text{-}PPh2}$),7.30-7.43 (m, 8 H, $H^2$

+ $H^5$ + $H^8$ + $H^{11}$ + 2x$H_{ortho\text{-}PPh2}$ + 2x$H_{meta\text{-}PPh2}$), 7.17 (m, 2 H, $H^4$ + $H^9$), 6.59 (d, $^3J_{H\text{-}H}$ = 9 Hz, 2 H, $H^{17}$), 6.41 (d, $^3J_{H\text{-}H}$ = 8.9 Hz, 2 H, $H^{16}$), 4.65 (dm, $^1J_{P\text{-}H}$ = 32 Hz, 1 H, $H^{13}$), 3.07-3.42 (m, 2 H, $H^{14}$), 2.90 (s, 6 H, $H^{19}$), 0.78 (s, 9 H, $^t$Bu), 0.73 (s, 9 H, $^t$Bu). $^{13}$C{$^1$H} Jmod NMR ($CDCl_3$, 75.5 MHz, 300 K): δ 163.3 (dd, $^2J_{P\text{-}C}$ = 111 Hz, $^2J_{P\text{-}C}$ = 7 Hz, $C^{1/12}$), 163.2 (dd, $^2J_{P\text{-}C}$ = 112 Hz, $^2J_{P\text{-}C}$ = 7 Hz, $C^{1/12}$), 152.0 (m, $C^6$ + $C^7$), 151.0 (m, $C^3$ + $C^{10}$), 150.9 (s, $C^{18}$), 136.4 (m, $C^{2/11}$), 136.2 (m, $C^{2/11}$), 135.6 (d, $^2J_{P\text{-}C}$ = 12 Hz, $C_{ortho\text{-}PPh2}$), 135.3 (d, $^2J_{P\text{-}C}$ = 12 Hz, $C_{ortho\text{-}PPh2}$), 134.6 (d, $^2J_{P\text{-}C}$ = 12 Hz, $C_{ortho\text{-}PPh2}$), 134.4 (s, $C^{17}$), 134.2 (d, $^4J_{P\text{-}C}$ = 3 Hz, $C_{para\text{-}PPh2}$), 134.1 (d, $^4J_{P\text{-}C}$ = 3 Hz, $C_{para\text{-}PPh2}$), 133.6 (d, $^4J_{P\text{-}C}$ = 3 Hz, $C_{para\text{-}PPh2}$), 133.4 (d+d, $^2J_{P\text{-}C}$ = 12 Hz, $^4J_{P\text{-}C}$ = 3 Hz, $C_{ortho\text{-}PPh2}$ + $C_{para\text{-}PPh2}$), 130.8 (d, $^3J_{P\text{-}C}$ = 11 Hz, $C_{meta\text{-}PPh2}$), 130.3 (d, $^3J_{P\text{-}C}$ = 11 Hz, $C_{meta\text{-}PPh2}$), 130.1 (d, $^3J_{P\text{-}C}$ = 12 Hz, $C_{meta\text{-}PPh2}$), 129.8 (d, $^3J_{P\text{-}C}$ = 12 Hz, $C_{meta\text{-}PPh2}$), 125.5 (s, $C^4$ + $C^9$), 124.1 (d, $^1J_{P\text{-}C}$ = 51 Hz, $C_{ipso\text{-}PPh2}$), 123.7 (d, $^1J_{P\text{-}C}$ = 51 Hz, $C_{ipso\text{-}PPh2}$), 122.4 (d, $^1J_{P\text{-}C}$ = 48 Hz, $C_{ipso\text{-}PPh2}$), 121.8 (d, $^4J_{P\text{-}C}$ = 7 Hz, $C^5$ + $C^8$), 121.7 (d, $^1J_{P\text{-}C}$ = 50 Hz, $C_{ipso\text{-}PPh2}$), 114.5 (d, $^3J_{P\text{-}C}$ = 7 Hz, $C^{15}$), 113.2 (s, $C^{17}$), 50.7 (dd, $^1J_{P\text{-}C}$ = 30 Hz, $^2J_{P\text{-}C}$ = 8 Hz, $C^{13}$), 40.3 (s, $C^{19}$), 36.7 (dd, $^1J_{P\text{-}C}$ = 34 Hz, $^2J_{P\text{-}C}$ = 13 Hz, $C^{14}$), 34.9 (s, $C_{quat.tBu}$), 34.7 (s, $C_{quat.tBu}$), 31.0 (s, $CH_{3.tBu}$), 30.8 (s, $CH_{3.tBu}$). $^{31}$P{$^1$H} NMR ($CDCl_3$, 121.5 MHz, 300 K): δ 64.9 (s, 1 P, P-Au), 50.5 (s, 1 P, P-Au), -144.2 (h, $^1J_{P\text{-}F}$ = 718 Hz, 1 P, $PF_6$). ESI-MS (MeCN) *positive mode exact mass* for $[C_{54}H_{57}SNP_2Au]^+$ (1010.3347): measured *m/z* 1010.3345 $[M\text{-}PF_6]^+$. Calcd for $C_{54}H_{57}P_2SNAuPF_6$ (1156.0): C, 56.11; H, 4.97; N, 1.21; S, 2.77. Found: C, 55.90; H 5.28; N, 1.21; S, 2.94.

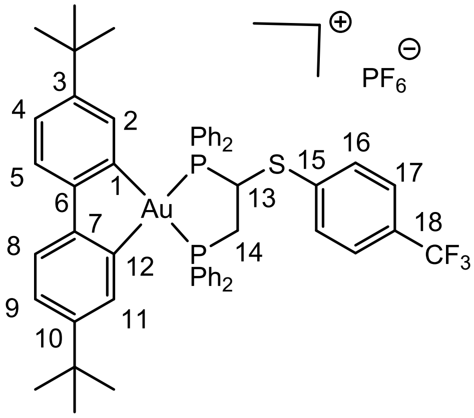



**2h: 4-methoxythiophenol** (25 µL, 28 mg, 0.2 mmol), product (41 mg, 0.036 mmol, 90 % yield). $^1$H NMR ($CDCl_3$, 300 MHz, 300 K): δ 8.21-8.27 (m, 2 H, 2x$H_{ortho\text{-}PPh2}$), 7.86-7.97 (m, 4 H, 4x$H_{ortho\text{-}PPh2}$), 7.74 (m, 3 H, 2x$H_{meta\text{-}PPh2}$ + $H_{para\text{-}PPh2}$), 7.67 (m, 1 H, $H_{para\text{-}PPh2}$), 7.46-7.62 (m, 5 H, 4x$H_{meta\text{-}PPh2}$ + $H_{para\text{-}PPh2}$), 7.39-7.44 (m, 3 H, $H^5$ + $H^8$ + $H_{para\text{-}PPh2}$), 7.30-7.36 (m, 6 H, $H^2$ + $H^{11}$ + 2x$H_{ortho\text{-}PPh2}$, 2x$H_{meta\text{-}PPh2}$), 7.19 (d, $^3J_{H\text{-}H}$ = 7 Hz, 1 H, $H^{4/9}$), 7.16 (d, $^3J_{H\text{-}H}$ = 8 Hz, 1 H, $H^{4/9}$), 6.68 (d, $^3J_{H\text{-}H}$ = 9 Hz, 2 H, $H^{17}$), 6.63 (d, $^3J_{H\text{-}H}$ = 9 Hz, 2 H, $H^{16}$), 5.02 (dm, $^2J_{P\text{-}H}$ = 36 Hz, 1 H, $H^{13}$), 3.73 (s, 3 H, $H^{19}$), 3.54 (dm, $^2J_{P\text{-}H}$ = 37 Hz, 1 H, $H^{14}$), 2.95-3.08 (m, 1 H, $H^{14}$), 0.78 (s, 9 H, $^t$Bu), 0.73 (s, 9 H, $^t$Bu). $^{13}$C{$^1$H} Jmod NMR ($CDCl_3$, 75.5 MHz, 300 K): δ 163.6 (dd, $^2J_{P\text{-}C}$ = 111 Hz, $^3J_{P\text{-}C}$ = 7 Hz, $C^{1/12}$), 163.1 (dd, $^2J_{P\text{-}C}$ = 111 Hz, $^2J_{P\text{-}C}$ = 7 Hz, $C^{1/12}$), 160.1 (s, $C^{18}$), 152.0 (d, $^3J_{P\text{-}C}$ = 4 Hz, $C^6$ + $C^7$), 151.0 (m, $C^3$ + $C^{10}$), 136.6 (dd, $^3J_{P\text{-}C}$ = 10 Hz, $^3J_{P\text{-}C}$ = 5 Hz, $C^{2/11}$), 136.2 (dd, $^3J_{P\text{-}C}$ = 10 Hz, $^3J_{P\text{-}C}$ = 5 Hz, $C^{2/11}$), 135.8 (d, $^2J_{P\text{-}C}$ = 12 Hz, $C_{ortho\text{-}PPh2}$), 135.5 (d, $^2J_{P\text{-}C}$ = 11 Hz, $C_{ortho\text{-}PPh2}$), 134.8 (d, $^2J_{P\text{-}C}$ = 12 Hz, $C_{ortho\text{-}PPh2}$), 134.4 (d, $^4J_{P\text{-}C}$ = 3 Hz, $C_{para\text{-}PPh2}$), 134.0 (d, $^4J_{P\text{-}C}$ = 3 Hz, $C_{para\text{-}PPh2}$), 133.7 (s, $C^{17}$), 133.6 (d, $^4J_{P\text{-}C}$ = 3 Hz, $C_{para\text{-}PPh2}$), 133.1 (m, $C_{ortho\text{-}PPh2}$ + $C_{para\text{-}PPh2}$), 131.0 (d, $^3J_{P\text{-}C}$ = 11 Hz, $C_{meta\text{-}PPh2}$), 130.2 (d, $^3J_{P\text{-}C}$ = 10 Hz, $C_{meta\text{-}PPh2}$), 130.0 (d, $^3J_{P\text{-}C}$ = 10 Hz, $C_{meta\text{-}PPh2}$), 129.7 (d, $^3J_{P\text{-}C}$ = 12 Hz, $C_{meta\text{-}PPh2}$), 125.5 (s, $C^{4/9}$), 125.4 (s, $C^{4/9}$), 124.7 (d, $^1J_{P\text{-}C}$ = 53 Hz, $C_{ipso\text{-}PPh2}$), 123.6 (d, $^1J_{P\text{-}C}$ = 51 Hz, $C_{ipso\text{-}PPh2}$), 122.0 (d, $^1J_{P\text{-}C}$ = 51 Hz, $C_{ipso\text{-}PPh2}$), 121.9 (d, $^1J_{P\text{-}C}$ = 47 Hz, $C_{ipso\text{-}PPh2}$), 121.8 (d, $^4J_{P\text{-}C}$ = 3 Hz, $C^{5/8}$), 121.7 (d, $^4J_{P\text{-}C}$ = 3 Hz, $C^{5/8}$), 120.6 (d, $^3J_{P\text{-}C}$ = 7 Hz, $C^{15}$), 115.3 (s, $C^{16}$), 55.6 (s, $C^{19}$), 49.8 (dd, $^1J_{P\text{-}C}$ = 32 Hz, $^2J_{P\text{-}C}$ = 9 Hz, $C^{13}$), 36.8 (dd, $^1J_{P\text{-}C}$ = 36 Hz, $^2J_{P\text{-}C}$ = 13 Hz, $C^{14}$), 34.9 (s, $C_{quat.tBu}$), 34.7 (s, $C_{quat.tBu}$), 31.0 (s, $CH_{3.tBu}$), 30.7 (s, $CH_{3.tBu}$). $^{31}$P{$^1$H} NMR ($CDCl_3$, 121.5

MHz, 300 K): δ 67.9 (d, $^2J_{P-P}$ = 3.9 Hz, 1 P, P-Au), 53.1 (d, $^2J_{P-P}$ = 3.9 Hz, 1 P, P-Au), -144.2 (h, $^1J_{P-F}$ = 709 Hz, 1 P, $PF_6$). ESI-MS (MeCN) *positive mode exact mass* for $[C_{53}H_{54}SOP_2Au]^+$ (997.3031): measured *m/z* 997.3031 $[M-PF_6]^+$. Calcd for $C_{53}H_{54}P_2SOAuPF_6.0.3C_5H_{12}$ (1167.0): C, 56.26; H, 5.01; S, 2.75. Found: C, 56.21; H 4.89; S, 3.01.

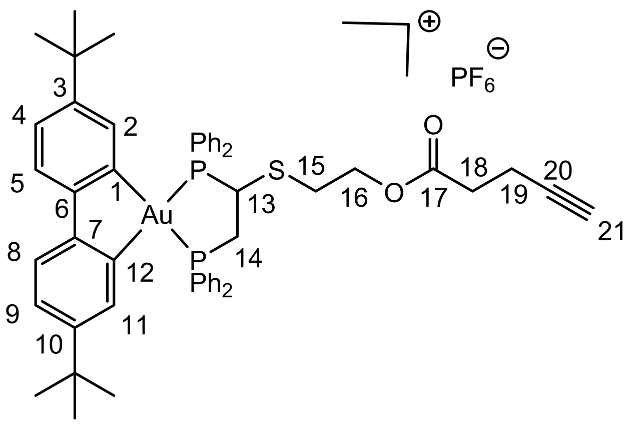



**2i**: **4-fluorothiophenol** (21 µL, 26 mg, 0.2 mmol), product (27 mg, 0.023 mmol, 59 % yield). $^1$H NMR ($CDCl_3$, 300 MHz, 300 K): δ 8.26 (m, 2 H, 2x$H_{ortho-PPh2}$), 7.84-7.98 (m, 4 H, 4x$H_{ortho-PPh2}$), 7.76 (m, 3 H, 2x$H_{meta-PPh2}$ + $H_{para-PPh2}$), 7.69 (dd, $^3J_{H-H}$ = 6.9 Hz, $^5J_{P-H}$ = 1.8 Hz, 1 H, $H_{para-PPh2}$), 7.55-7.61 (m, 3 H, 2x$H_{meta-PPh2}$ + $H_{para-PPh2}$), 7.40-7.50 (m, 6 H, $H^2$ + $H^{11}$ + $H^5$ + $H^8$ + 2x$H_{meta-PPh2}$), 7.28-7.36 (m, 5 H, 2x$H_{orthoPPh2}$ + 2x$H_{meta-PPh2}$ + $H_{para-PPh2}$), 7.19 (d, $^3J_{H-H}$ = 8 Hz, 1 H, $H^{4/9}$), 7.17 (d, $^3J_{H-H}$ = 8 Hz, 1 H, $H^{4/9}$), 6.77 (d, $^3J_{F-H}$ = 4 Hz, 2 H, $H^{17}$), 6.75 (s, 2 H, $H^{16}$), 5.28 (dm, $^2J_{P-H}$ = 38 Hz, 1 H, $H^{13}$), 3.66 (dm, $^2J_{P-H}$ = 40 Hz, 1 H, $H^{14}$), 2.96 (m, 1 H, $H^{14}$), 0.79 (s, 9 H, $^t$Bu), 0.73 (s, 9 H, $^t$Bu). Jmod NMR ($CDCl_3$, 75.5 MHz, 300 K): δ 164.0 (dd, $^2J_{P-C}$ = 112 Hz, $^2J_{P-C}$ = 8 Hz, $C^{1/12}$), 162.8 (d, $^1J_{F-C}$ = 249 Hz, $C^{18}$), 162.5 (dd, $^2J_{P-C}$ = 112 Hz, $^2J_{P-C}$ = 7 Hz, $C^{1/12}$), 152.0 (m, $C^6$ + $C^7$), 151.0 (m, $C^3$ + $C^{10}$), 136.7 (dd, $^3J_{P-C}$ = 10 Hz, $^3J_{P-C}$ = 6 Hz, $C^{2/11}$), 136.2 (d+m, $^3J_{P-C}$ = 12 Hz, $C^{2/11}$ + $C_{ortho-PPh2}$), 135.3 (d, $^3J_{P-C}$ = 11 Hz $C_{ortho-PPh2}$), 135.0 (d, $^3J_{P-C}$ = 12 Hz $C_{ortho-PPh2}$), 134.5 (d, $^4J_{P-C}$ = 3 Hz $C_{para-PPh2}$), 133.9 (d, $^4J_{P-C}$ = 3 Hz $C_{para-PPh2}$), 133.7 (d, $^4J_{P-C}$ = 3 Hz $C_{para-PPh2}$), 133.3 (d, $^3J_{F-C}$ = 9 Hz, $C^{16}$), 132.9 (d, $^4J_{P-C}$ = 3 Hz $C_{para-PPh2}$), 132.8 (d, $^2J_{P-C}$ = 12 Hz $C_{ortho-PPh2}$), 131.0 (d, $^3J_{P-C}$ = 11 Hz $C_{meta-PPh2}$), 130.0 (d, $^3J_{P-C}$ = 11 Hz $C_{meta-PPh2}$), 129.9 (d, $^3J_{P-C}$ = 12 Hz $C_{meta-PPh2}$), 129.6 (d, $^3J_{P-C}$ = 12 Hz $C_{meta-PPh2}$), 125.6 (s, $C^{4/9}$) , 125.5 (s, $C^{4/9}$), 125.3 (m, $C^{15}$), 125.0 (d, $^1J_{P-C}$ = 52 Hz, $C_{ipso-PPh2}$), 123.2 (d, $^1J_{P-C}$ = 51 Hz, $C_{ipso-PPh2}$), 122.1 (d, $^1J_{P-C}$ = 43 Hz, $C_{ipso-PPh2}$), 121.8 (m, $C^5$ + $C^8$), 121.4 (d, $^1J_{P-C}$ = 46 Hz, $C_{ipso-PPh2}$), 116.7 (d, $^2J_{F-C}$ = 21 Hz, $C^{17}$), 49.1 (dd, $^1J_{P-C}$ = 34 Hz, $^2J_{P-C}$ = 10 Hz, $C^{13}$), 36.7 (dd, $^1J_{P-C}$ = 35 Hz, $^2J_{P-C}$ = 13 Hz, $C^{14}$), 34.9 (s, $C_{quat.tBu}$), 34.6 (s, $C_{quat.tBu}$), 30.9 (s, $CH_{3.tBu}$), 30.6 (s, $CH_{3.tBu}$). $^{19}$F{$^1$H} NMR ($CDCl_3$, 282.4 MHz, 300 K): δ -72.4 (d, $^1J_{P-F}$ = 712 Hz, 6 F, $PF_6$), -112.4 (s, $^7J_{P-F}$ = 4 Hz, 1 F, $F^{18}$). $^{31}$P{$^1$H} NMR ($CDCl_3$, 121.5 MHz, 300 K): δ 69.5 (m, 1 P, P-Au), 54.1 (m, 1 P, P-Au), -144.1 (h, $^1J_{P-F}$ = 712 Hz, 1 P, $PF_6$). ESI-MS (MeCN) *positive mode exact mass* for $[C_{52}H_{51}SFP_2Au]^+$ (985.2831): measured *m/z* 985.2839 $[M-PF_6]^+$. Calcd for $C_{52}H_{51}P_2SFAuPF_6.H_2O$ (1148.9): C, 54.36; H, 4.65; S, 2.79. Found: C, 54.23; H 4.46; S, 2.89.




**2j: 4-trifluoromethylthiophenol** (27 µL, 36 mg, 0.2 mmol), product (32 mg, 0.027 mmol, 68 % yield). $^{1}$H NMR (CDCl$_3$, 300 MHz, 300 K): δ 8.38 (m, 2 H, 2xH$_{ortho\text{-}PPh2}$), 7.94 (dd, $^{3}J_{P\text{-}H}$ = 12.3 Hz, $^{3}J_{H\text{-}H}$ = 8.6 Hz, 2 H, 2xH$_{ortho\text{-}PPh2}$), 7.79 (m, 5 H, 2xH$_{ortho\text{-}PPh2}$ + 3xH$_{para\text{-}PPh2}$), 7.67 (t, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 1 H, H$_{para\text{-}PPh2}$), 7.51 (m, 4 H, 2xH$_{ortho\text{-}PPh2}$ + 2xH$_{meta\text{-}PPh2}$), 7.36-7.44 (m, 8 H, H$^{5}$ + H$^{8}$ +6xH$_{meta\text{-}PPh2}$), 7.29 (m, 2 H, H$^{16}$), 7.16-7.23 (m, 4 H, H$^{2}$ + H$^{4}$ + H$^{9}$ + H$^{11}$), 6.93 (d, $^{3}J_{H\text{-}H}$ =8 Hz, H$^{17}$), 5.68 (dd, $^{2}J_{P\text{-}H}$ = 41 Hz, $^{3}J_{H\text{-}H}$ = 10 Hz, 1 H, H$^{13}$), 3.81 (dm, $^{2}J_{P\text{-}H}$ = 41 Hz, 1 H, H$^{14}$), 2.93 (m, 1 H, H$^{14}$), 0.79 (s, 9 H, $^{t}$Bu), 0.71 (s, 9 H, $^{t}$Bu). ). Jmod NMR (CDCl$_3$, 75.5 MHz, 300 K): δ 163.3 (dd, $^{2}J_{P\text{-}C}$ = 110 Hz, $^{2}J_{P\text{-}C}$ = 6.8 Hz, $C^{1/12}$), 162.9 (dd, $^{2}J_{P\text{-}C}$ = 112 Hz, $^{2}J_{P\text{-}C}$ = 7 Hz, $C^{1/12}$), 151.9 (m, $C^{6}$ + $C^{7}$), 151.1 (dd, $^{4}J_{P\text{-}C}$ = 9 Hz, $^{4}J_{P\text{-}C}$ = 2.8 Hz, $C^{3/10}$), 150.8 (dd, $^{4}J_{P\text{-}C}$ = 9 Hz, $^{4}J_{P\text{-}C}$ = 3 Hz, $C^{3/10}$), 136.9 (dd, $^{3}J_{P\text{-}C}$ = 10 Hz, $^{4}J_{P\text{-}C}$ = 6 Hz, $C^{2/11}$), 136.1 (m, $C^{2/11}$ + $C_{ortho\text{-}PPh2}$), 135.1 (d, $^{2}J_{P\text{-}C}$ = 11 Hz, $C_{ortho\text{-}PPh2}$), 135.0 (d, $^{2}J_{P\text{-}C}$ = 12 Hz, $C_{ortho\text{-}PPh2}$), 134.6 (d, $^{4}J_{P\text{-}C}$ = 3 Hz, $C_{para\text{-}PPh2}$), 133.8 (d, $^{4}J_{P\text{-}C}$ = 3 Hz, $C_{para\text{-}PPh2}$), 133.6 (d, $^{4}J_{P\text{-}C}$ = 3 Hz, $C_{para\text{-}PPh2}$), 132.7 (d, $^{4}J_{P\text{-}C}$ = 3 Hz, $C_{para\text{-}PPh2}$), 132.4 (d, $^{2}J_{P\text{-}C}$ = 11 Hz, $C_{ortho\text{-}PPh2}$), 131.2 (d, $^{3}J_{P\text{-}C}$ = 11 Hz, $C_{meta\text{-}PPh2}$), 129.9 (d, $^{3}J_{P\text{-}C}$ = 11 Hz, $C_{meta\text{-}PPh2}$), 129.7 (d, $^{3}J_{P\text{-}C}$ = 10 Hz, $C_{meta\text{-}PPh2}$), 129.6 (s, $C^{16}$), 129.5 (d, $^{3}J_{P\text{-}C}$ = 12 Hz, $C_{meta\text{-}PPh2}$), 128.9 (s, $C^{15}$), 126.1 (m, $C^{17}$), 125.5 (s, $C^{4/9}$), 125.4 (s, $C^{4/9}$), 123.9 (q, $^{1}J_{F\text{-}C}$ = 215 Hz, $CF_3$), 122.9 (d, $^{1}J_{P\text{-}C}$ = 52 Hz, $C_{ipso\text{-}PPh2}$), 121.8 (m, $C^{5}$ + $C^{8}$), 120.8 (d, $^{1}J_{P\text{-}C}$ = 45 Hz, $C_{ipso\text{-}PPh2}$), 47.0 (dd, $^{1}J_{P\text{-}C}$ = 33 Hz, $^{2}J_{P\text{-}C}$ = 8 Hz, $C^{13}$), 36.3 (dd, $^{1}J_{P\text{-}C}$ = 36 Hz, $^{2}J_{P\text{-}C}$ = 12 Hz, $C^{14}$), 34.9 (s, $C_{quat.tBu}$), 34.5 (s, $C_{quat.tBu}$), 30.9 (s, $CH_{3.tBu}$), 30.6 (s, $CH_{3.tBu}$), $C^{18}$ not visible. $^{19}$F{$^{1}$H} NMR (CDCl$_3$, 282.4 MHz, 300 K): δ -62.8 (s, 3 F, CF$_3$), -72.5 (d, $^{1}J_{P\text{-}F}$ = 713 Hz, 6 F, PF$_6$). $^{31}$P{$^{1}$H} NMR (CDCl$_3$, 121.5 MHz, 300 K): δ 70.8 (d, $^{2}J_{P\text{-}P}$ = 5 Hz, 1 P, P-Au), 54.0 (d, $^{2}J_{P\text{-}P}$ = 5 Hz, 1 P, P-Au), -144.1 (h, $^{1}J_{P\text{-}F}$ = 713 Hz, 1 P, PF$_6$). ESI-MS (MeCN) *positive mode exact mass* for [$C_{53}H_{51}SF_3P_2Au$]$^{+}$ (1035.2799): measured *m/z* 1035.2790 [M-PF$_6$]$^{+}$. Calcd for $C_{53}H_{51}P_2SF_3AuPF_6$ (1180.9): C, 53.91; H, 4.35; S, 2.71. Found: C, 54.29; H 4.53; S, 2.85.

**Synthesis of complex 3**



In a sealed tube is added **2e** (60 mg, 0.056 mmol), **pentynoic acid** (8 mg, 0.083 mmol), **N-Me-2-chloropyridinium iodide** (21 mg, 0.083 mmol), **N,N-dimethylaminopyridine** (10 mg, 0.083 mmol) dissolved into dry dichloromethane (5 mL). The reaction mixture is heated at 60 °C for 24 h. After cooling down to room temperature, the crude material is purified by column chromatography with silica gel and pure dichloromethane as eluent ($R_f$ = 0.1). The pure product is obtained as a beige powder after evaporation and drying from a dichloromehane/petroleum ether solution (34 mg, 0.029 mmol, 52 % yield). $^1$H NMR ($CDCl_3$, 300 MHz, 300 K): δ 8.28 (m, 2 H, 2x$H_{ortho\text{-}PPh2}$), 8.06 (dd, $^3J_{P\text{-}H}$ = 13 Hz, $^3J_{H\text{-}H}$ = 7 Hz, 2 H, 2x$H_{ortho\text{-}PPh2}$), 7.89 (dd, $^3J_{P\text{-}H}$ = 12 Hz, $^3J_{H\text{-}H}$ = 8 Hz, 2 H, 2x$H_{ortho\text{-}PPh2}$), 7.74 (m, 4 H, 2x$H_{meta\text{-}PPh2}$ + 2x$H_{para\text{-}PPh2}$), 7.63 (m, 2 H, 2x$H_{meta\text{-}PPh2}$), 7.39-7.53 (m, 10 H, $H^5$ + $H^8$ + 2x$H_{ortho\text{-}PPh2}$ + 4x$H_{meta\text{-}PPh2}$ + 2x$H_{para\text{-}PPh2}$), 7.33 (d, $^4J_{P\text{-}H}$ = 11 Hz, 2 H, $H^2$ + $H^{11}$), 7.17 (m, 2 H, $H^4$ + $H^9$), 4.86 (dm, $^2J_{P\text{-}H}$ = 40 Hz, $H^{13}$), 3.63-3.92 (m, 3 H, $H^{14}$ + $H^{16}$), 2.95 (m, 1 H, $H^{14}$), 2.29 (s, 4 H, $H^{18}$ + $H^{19}$), 2.14 (m, 2 H, $H^{15}$), 1.94 (s, 1 H, $H^{21}$), 0.78 (s, 9 H, $^t$Bu), 0.71 (s, 9 H, $^t$Bu). ). Jmod NMR ($CDCl_3$, 75.5 MHz, 300 K): δ 171.2 (s, $C^{17}$), 163.4 (dd, $^2J_{P\text{-}C}$ = 111 Hz, $^2J_{P\text{-}C}$ = 8 Hz, $C^{1/12}$), 163.0 (dd, $^2J_{P\text{-}C}$ = 113 Hz, $^2J_{P\text{-}C}$ = 7 Hz, $C^{1/12}$), 152.1 (m, $C^6$ + $C^7$), 151.1 (m, $C^3$ + $C^{10}$), 136.7 (m, $C^{2/11}$), 136.3 (m, $C^{2/11}$), 136.0 (d, $^2J_{P\text{-}C}$ = 13 Hz, $C_{ortho\text{-}PPh2}$), 135.5 (d, $^2J_{P\text{-}C}$ = 11 Hz, $C_{ortho\text{-}PPh2}$), 135.0 (d, $^2J_{P\text{-}C}$ = 12 Hz, $C_{ortho\text{-}PPh2}$), 134.4 (d, $^4J_{P\text{-}C}$ = 2 Hz, $C_{para\text{-}PPh2}$), 133.9 (s, 2x$C_{para\text{-}PPh2}$), 133.0 (d+d, $^2J_{P\text{-}C}$ = 11 Hz, $^4J_{P\text{-}C}$ = 2 Hz, $C_{ortho\text{-}PPh2}$ + $C_{para\text{-}PPh2}$), 131.0 (d, $^3J_{P\text{-}C}$ = 11 Hz, $C_{meta\text{-}PPH2}$), 130.2 (d, $^3J_{P\text{-}C}$ = 11 Hz, $C_{meta\text{-}PPH2}$), 130.0 (d, $^3J_{P\text{-}C}$ = 12 Hz, $C_{meta\text{-}PPH2}$), 129.6 (d, $^3J_{P\text{-}C}$ = 12 Hz, $C_{meta\text{-}PPH2}$), 125.5 (s, $C^{4/9}$), 125.4 (s, $C^{4/9}$), 125.3 (d, $^1J_{P\text{-}C}$ = 53 Hz, $C_{ipso\text{-}PPh2}$), 123.3 (d, $^1J_{P\text{-}C}$ = 51 Hz, $C_{ipso\text{-}PPh2}$), 122.9 (d, $^1J_{P\text{-}C}$ = 50 Hz, $C_{ipso\text{-}PPh2}$), 121.9 (d, $^1J_{P\text{-}C}$ = 45 Hz, $C_{ipso\text{-}PPh2}$), 121.8 (m, $C^5$ + $C^8$), 82.6 (s, $C^{20}$), 69.2 (s, $C^{21}$), 61.9 (s, $C^{16}$), 45.9 (dd, $^1J_{P\text{-}C}$ = 34 Hz, $^2J_{P\text{-}C}$ = 9 Hz, $C^{13}$), 37.7 (dd, $^1J_{P\text{-}C}$ = 35 Hz, $^2J_{P\text{-}C}$ = 14 Hz, $C^{14}$), 34.9 (s, $C_{quat\text{-}tBu}$), 34.6 (s, $C_{quat.tBu}$), 33.1 (s, $C^{18}$), 32.2 (d, $^3J_{P\text{-}C}$ = 2 Hz, $C^{15}$), 31.0 (s, $CH_{3.tBu}$), 30.7 (s, $CH_{3.tBu}$), 14.3 (s, $C^{19}$). $^{31}$P{$^1$H} NMR ($CDCl_3$, 121.5 MHz, 300 K): δ 70.6 (d, $^2J_{P\text{-}P}$ = 6 Hz, 1 P, P-Au), 54.4 (d, $^2J_{P\text{-}P}$ = 6 Hz, 1 P, P-Au), -144.2 (h, $^1J_{P\text{-}F}$ = 712 Hz, 1 P, $PF_6$). ESI-MS (MeCN) *positive mode exact mass* for $[C_{53}H_{56}SP_2O_2Au]^+$ (1015.3136): measured *m/z* 1015.3130 $[M\text{-}PF_6]^+$. Calcd for $C_{53}H_{56}P_2SO_2AuPF_6.H_2O$ (1179.0): C, 53.99; H, 4.96; S, 2.72. Found: C, 53.96; H 4.96; S, 2.74. FT-IR (ATR): 3287 (-C≡**C-H**), 2349 (-C≡C-), 1738 (C=O).

**X-Ray crystal structure determination**

Single crystals of **1**, **2a**, **2e** and **2f** were selected, mounted onto a cryoloop and transferred into a cold nitrogen gas stream. Intensity data were collected with a Bruker Kappa-APEX2 CCD diffractometer using a graphite-monochromated MoKα radiation (**1** and **2e**) or a micro-focused CuKα radiation (**2a** and **2f**). Data collections, unit-cell parameters determinations, integration and data reductions were performed with the Bruker APEX/SAINT[2] suite at 200K. The structures were solved with SHELXT[3] or SHELXS[4] by direct method (for **2a**) and refined anisotropically by full-matrix least-squares methods with SHELXL[5], using Olex2[6] software. All non-hydrogen atoms are refined anistropically and H atoms are located geometrically.
The structures were deposited at the Cambridge Crystallographic Data Centre with numbers CCDC 2340607 - 2340610 and can be obtained free of charge via www.ccdc.cam.ac.uk.

**Computational work**

DFT calculations were performed using the Gaussian 16 software.[7] Geometry optimization, frequency and energy calculations were obtained using the hybrid PBE0 functional[8,9] coupled to the triple-ζ Ahlrichs type basis set def2-TZVP.[10] The effect of solvation (in chloroform) was modeled using the Polarizable Continuum Model (PCM) model.[11] Vibrational analysis served to locate minima (no imaginary frequency) or transition structures (one imaginary frequency).

**Table S1.** Crystallographic and refinement data for **1**, **2a**, **2e** and **2f**.

| | **1** | **2a (85%) + 1 (15%)** | **2e (75%) + 1 (25%)** | **2f** |
|---|---|---|---|---|
| ***CCDC deposit number*** | *2340607* | *2340608* | *2340609* | *2340610* |
| **Empirical formula[a]** | $C_{46}H_{46}AuF_6P_3$ | $C_{52.45}H_{53.8}AuClF_6P_3S_{0.85}$ | $C_{47.5}H_{50.}5AuF_6O_{0.75}P_3S_{0.75}$ | $C_{54.25}H_{56.5}AuCl_{4.5}F_6P_3S$ |
| **Moiety Formula** | $C_{46}H_{46}AuP_2^+$, $F_6P^-$ | $C_{51.95}H_{52.8}AuP_2S_{0.85}^+$, $F_6P^-$, 0.5($CH_2Cl_2$) | $C_{47.5}H_{50.5}AuO_{0.75}P_2S_{0.75}^+$, $F_6P^-$ | $C_{52}H_{52}AuP_2S^+$, F6P$^-$, 2.25($CH_2Cl_2$) |
| **Formula weight (g/mol)** | 1002.70 | 1150.73 | 1061.30 | 1303.95 |
| **Temperature (K)** | 200 | 200 | 200 | 200 |
| **Crystal system** | Triclinic | Orthorhombic | Triclinic | Monoclinic |
| **Space group** | P-1 | Pna2$_1$ | P-1 | C2/c |
| **a (Å)** | 9.167(3) | 20.5099(7) | 9.9276(9) | 42.5037(14) |
| **b (Å)** | 13.791(5) | 18.1939(7) | 10.8859(10) | 10.6374(3) |
| **c (Å)** | 18.034(6) | 14.1942(6) | 22.748(2) | 30.6654(10) |
| **α (°)** | 107.196(6) | 90 | 100.7210(10) | 90 |
| **β (°)** | 103.478(6) | 90 | 92.650(2) | 124.544(2) |
| **γ (°)** | 94.662(7) | 90 | 91.870(2) | 90 |
| **Volume (Å$^3$)** | 2090.1(13) | 5296.6(4) | 2410.7(4) | 11420.2(7) |
| **Z** | 2 | 4 | 2 | 8 |
| **$\rho_{calc}$ (g/cm$^3$)** | 1.593 | 1.443 | 1.462 | 1.517 |
| **Final R indexes[b c] [all data]** | R1 = 0.0710, wR2 = 0.0726 | R1 = 0.0367, wR2 = 0.0939 | R1 = 0.0936, wR2 = 0.1727 | R1 = 0.0731, wR2 = 0.1560 |
| **Final R indexes[b c] [I ≥ 2σ(I)]** | R1 = 0.0493, wR2 = 0.0664 | R1 = 0.0345, wR2 = 0.0925 | R1 = 0.0699, wR2 = 0.1643 | R1 = 0.0628, wR2 = 0.1495 |

[a] Including solvent molecules (if presence)

[b] $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ [c] $wR2 = \sqrt{\sum \left(w\left(F_o^2 - F_c^2\right)\right) / \sum \left(w\left(F_o^2\right)^2\right)}$

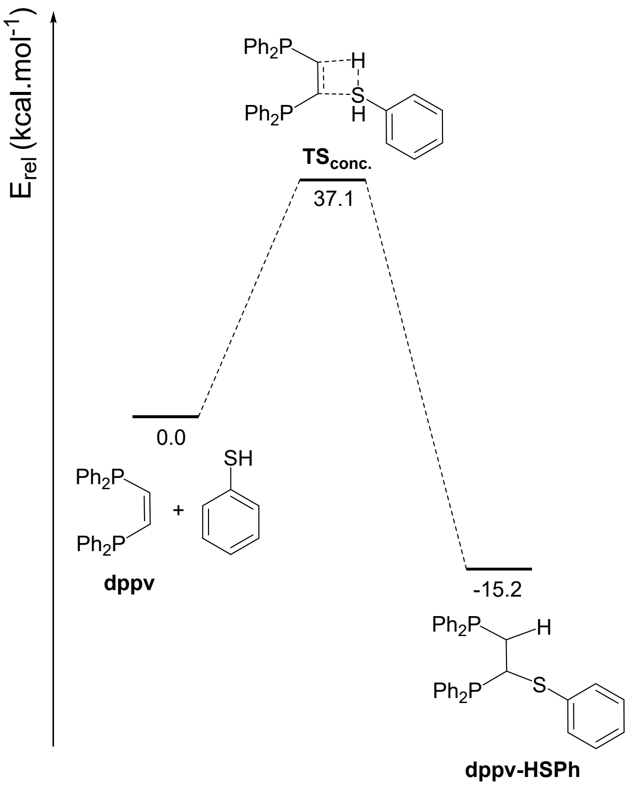
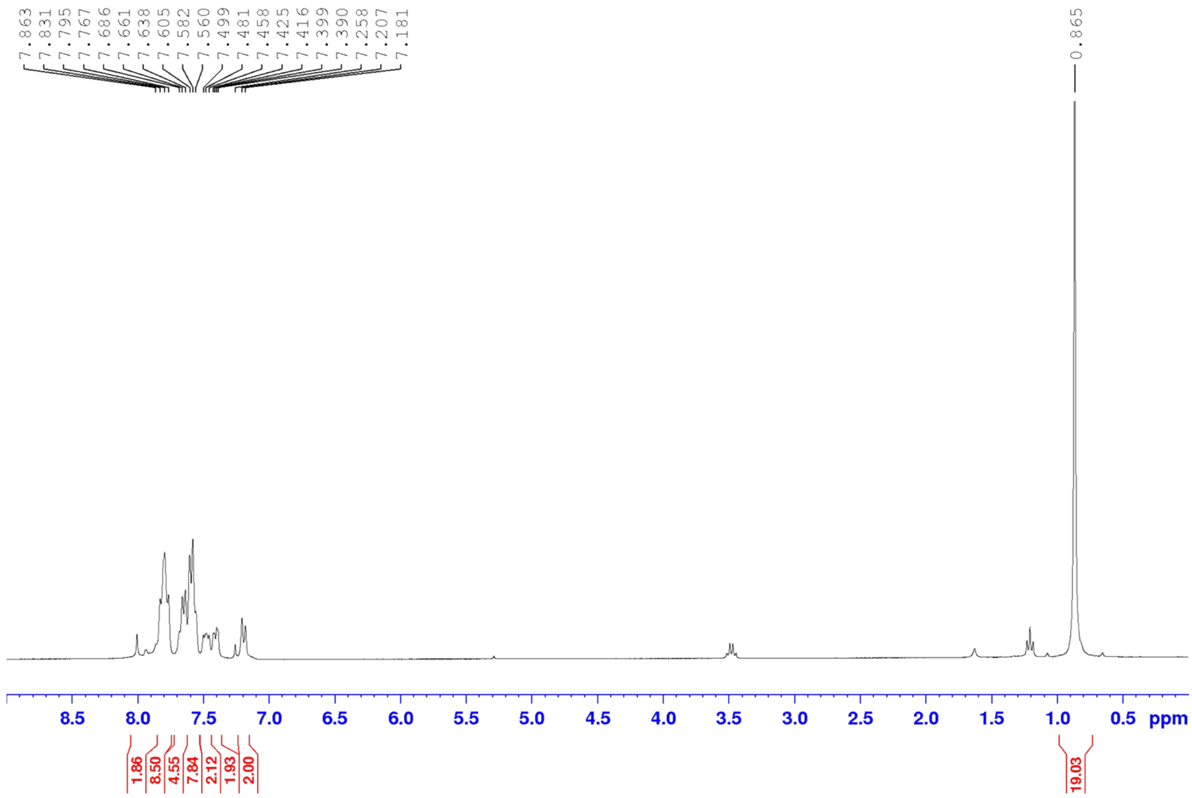



**Figure S1.** Potential energy diagram of the reaction of dppv with PhSH. Relative electronic energies are in kcal/mol and given relatively to the reactants.

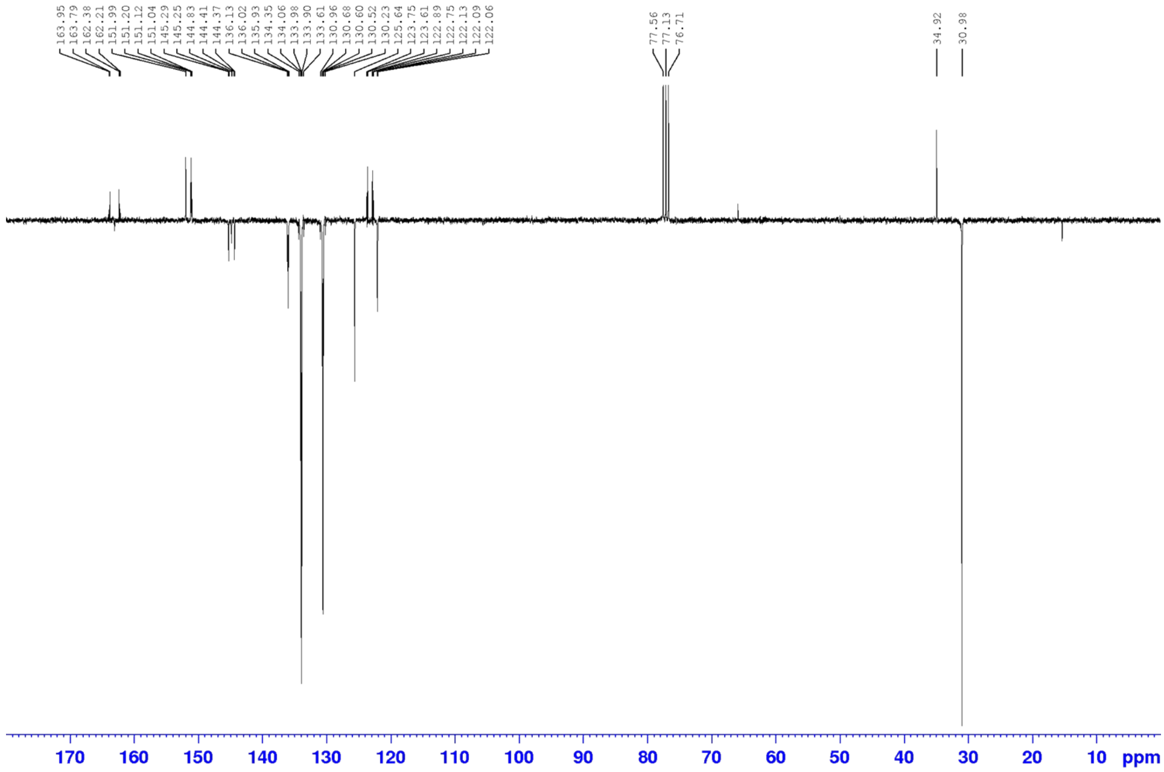
**Table S2.** Calculated electronic and zero-point energies (in hartrees, H) of all compounds studied in this work.

| | **Electronic energy** | **Zero-point energy** |
|---|---|---|
| **1** | -2597.168907 | 0.790978 |
| **$^{-}$S-Ph** | -629.6307799 | 0.0906984 |
| **HS-Ph** | -630.116209 | 0.100243 |
| **1-SPh** | -3226.819 | 0.881863 |
| **2f** | -3856.969474 | 0.9879373 |
| **dppv** | -1685.607522 | 0.401487 |
| **dppv-HSPh** | -2315.7539 | 0.507628 |
| **TS1** | -3226.813097 | 0.881143 |
| **TS2** | -3856.933371 | 0.9824737 |
| **$TS_{conc.}$** | -2315.664697 | 0.5018514 |

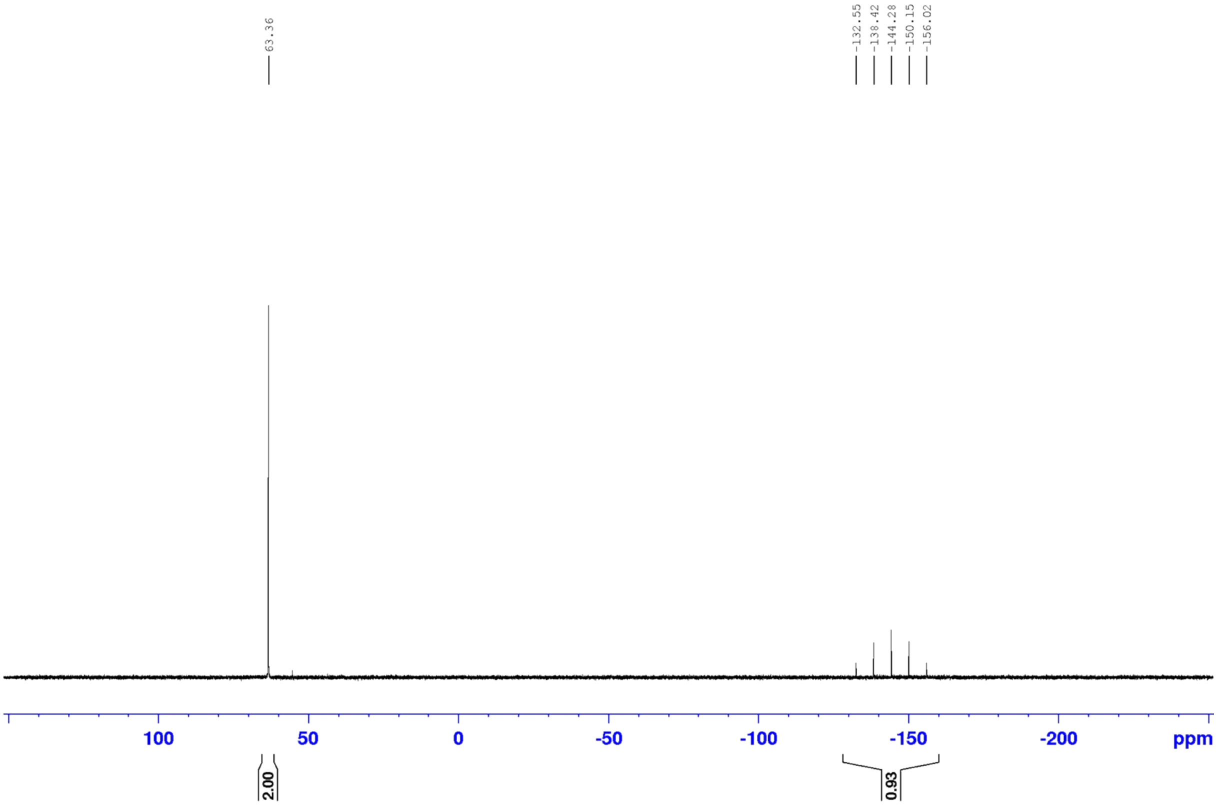
# NMR spectra



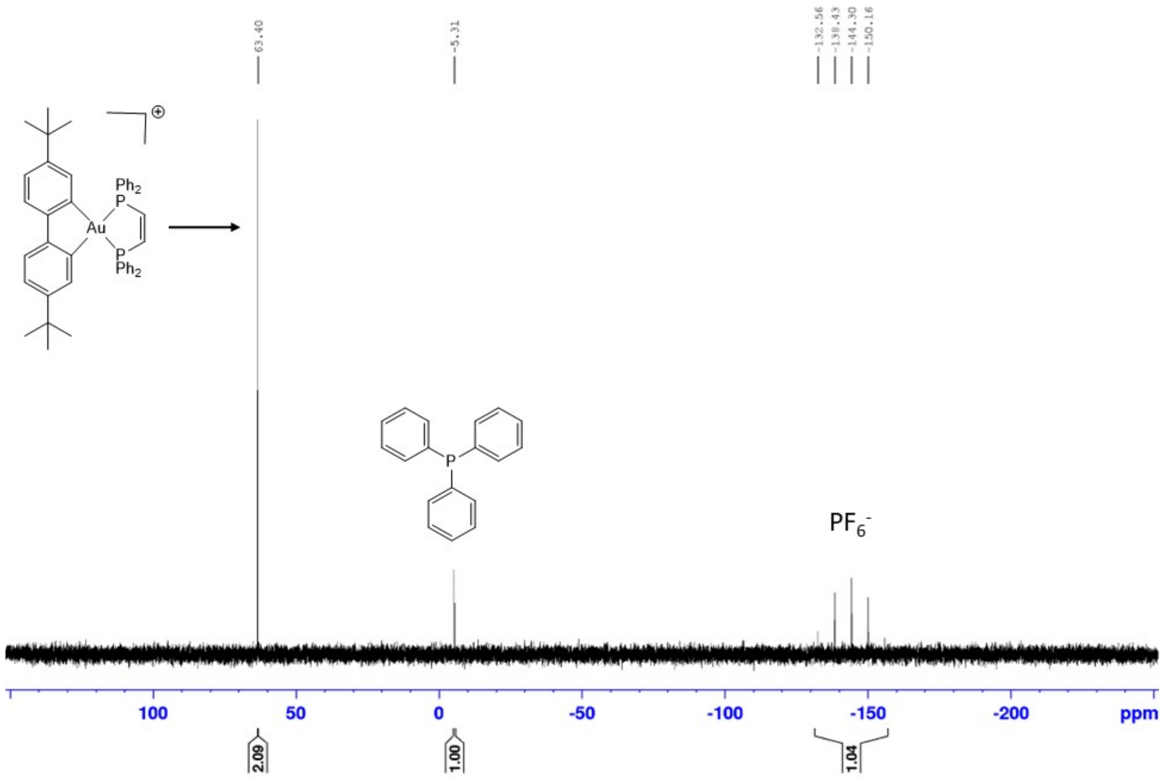

$^{1}H$ NMR spectrum of complex **1** in $CDCl_3$



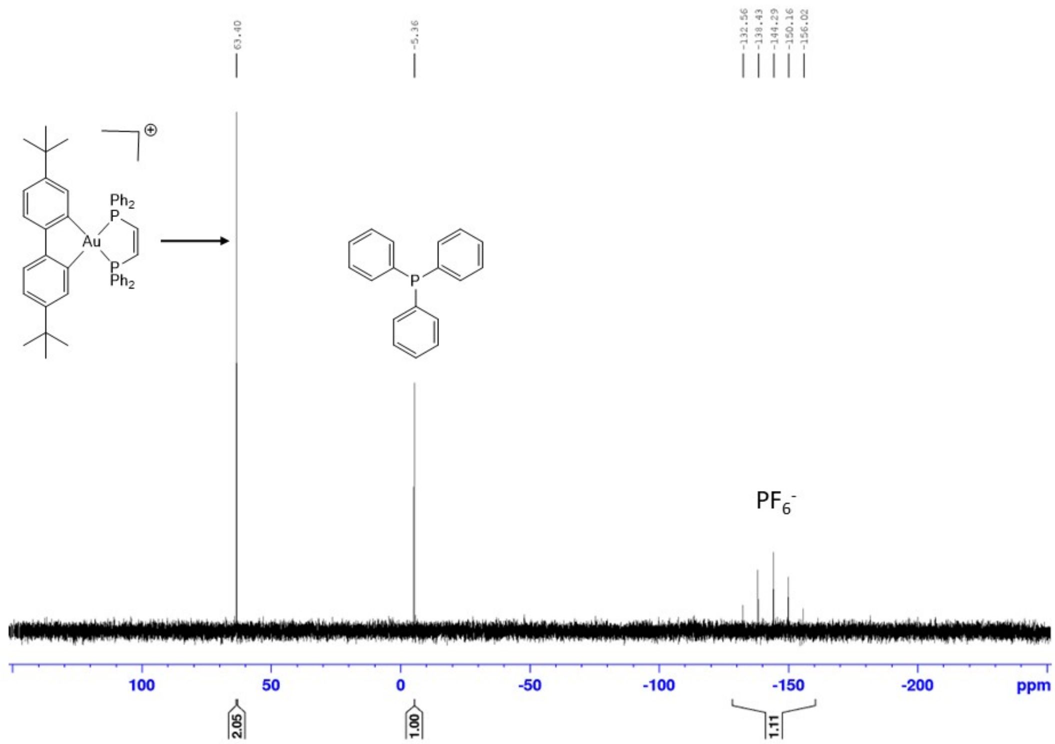

$^{13}C\{^{1}H\}$ Jmod NMR spectrum of complex **1** in $CDCl_3$



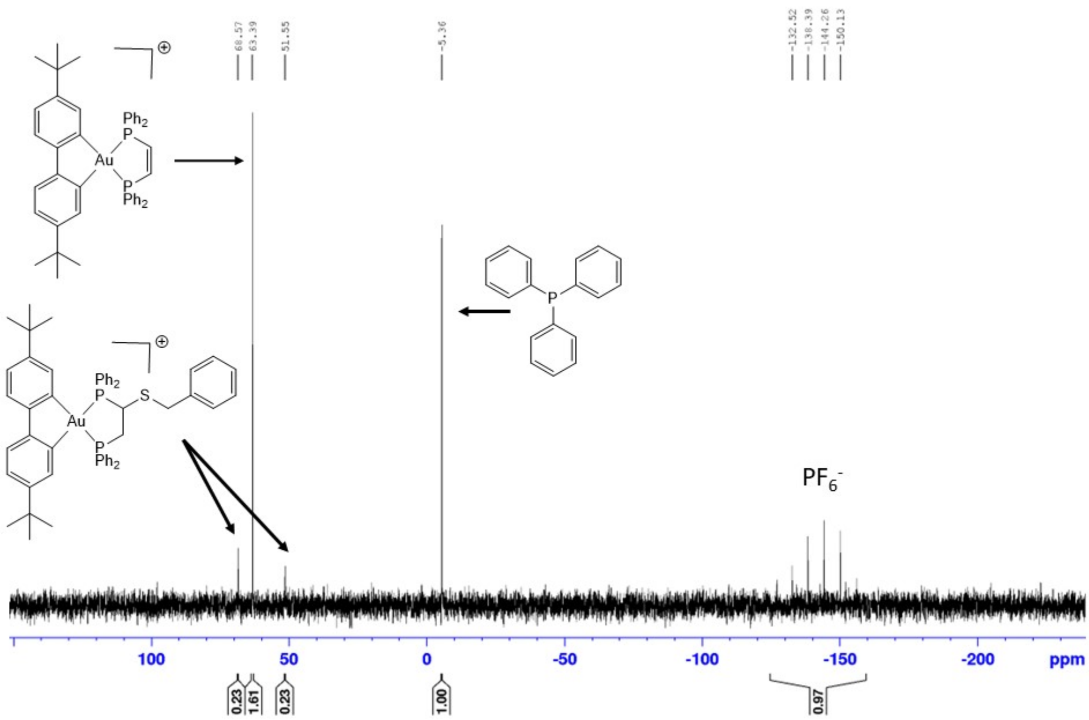

$^{31}P\{^{1}H\}$ NMR spectrum of complex **1** in $CDCl_3$



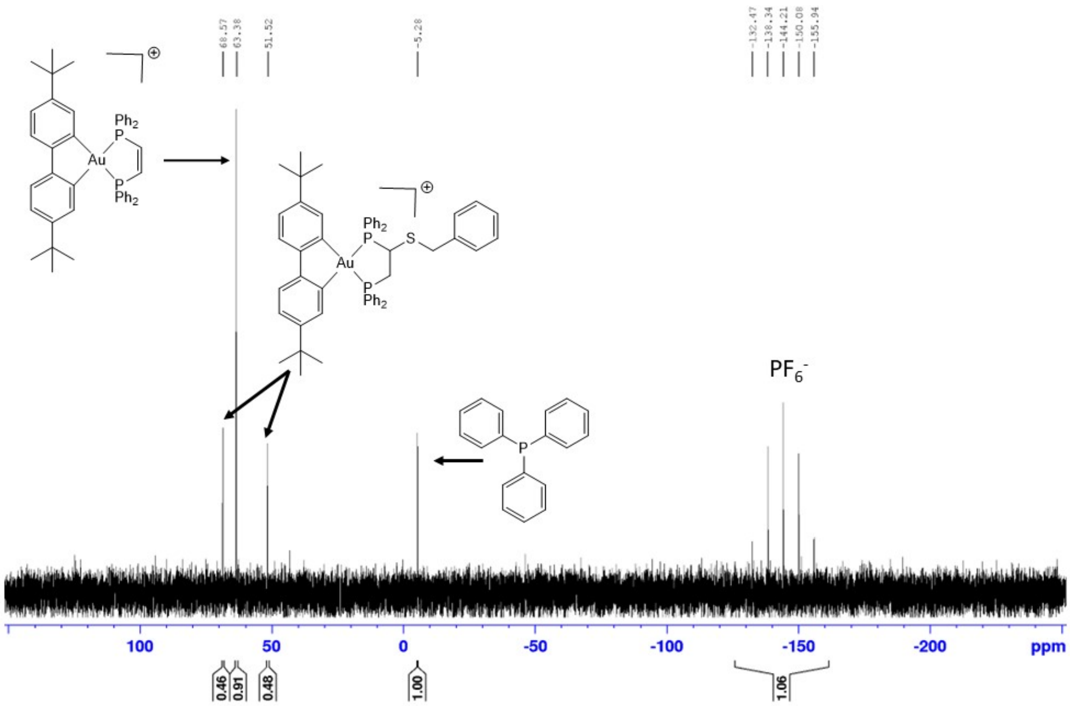

$^{31}P\{^{1}H\}$ NMR spectrum of complex **1** reacted 6 h at 298 K with 1 eq. of BzSH (table 1, entry 1).



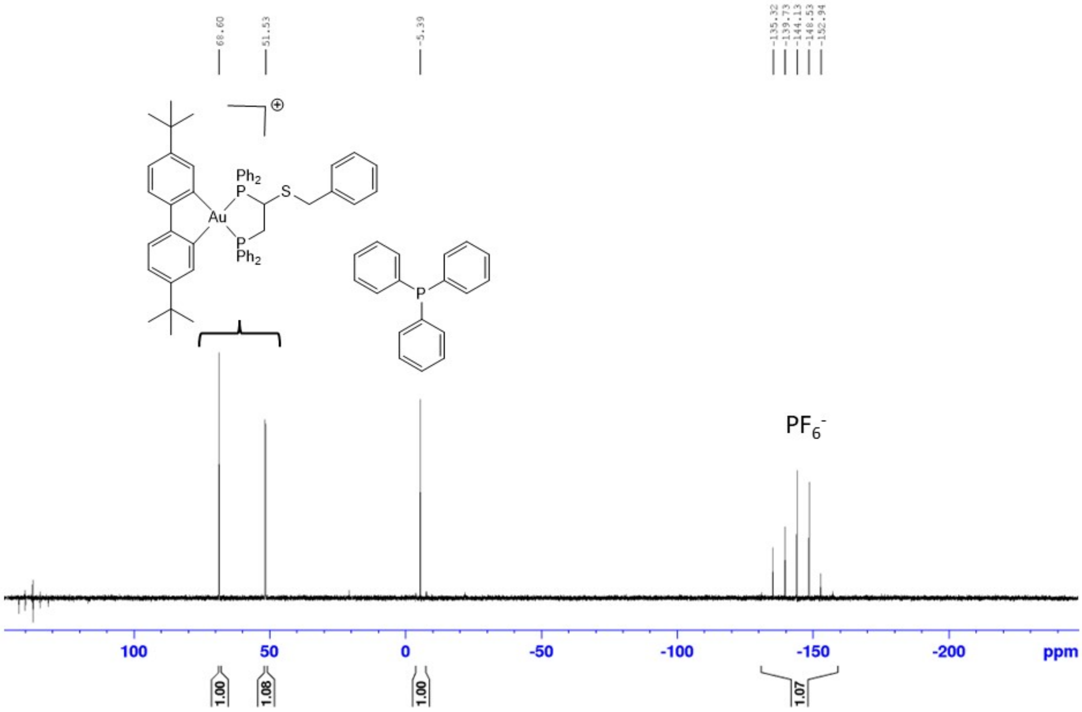

$^{31}P\{^{1}H\}$ NMR spectrum of complex **1** reacted 6 h at 323 K with 1 eq. of BzSH (table 1, entry 2).



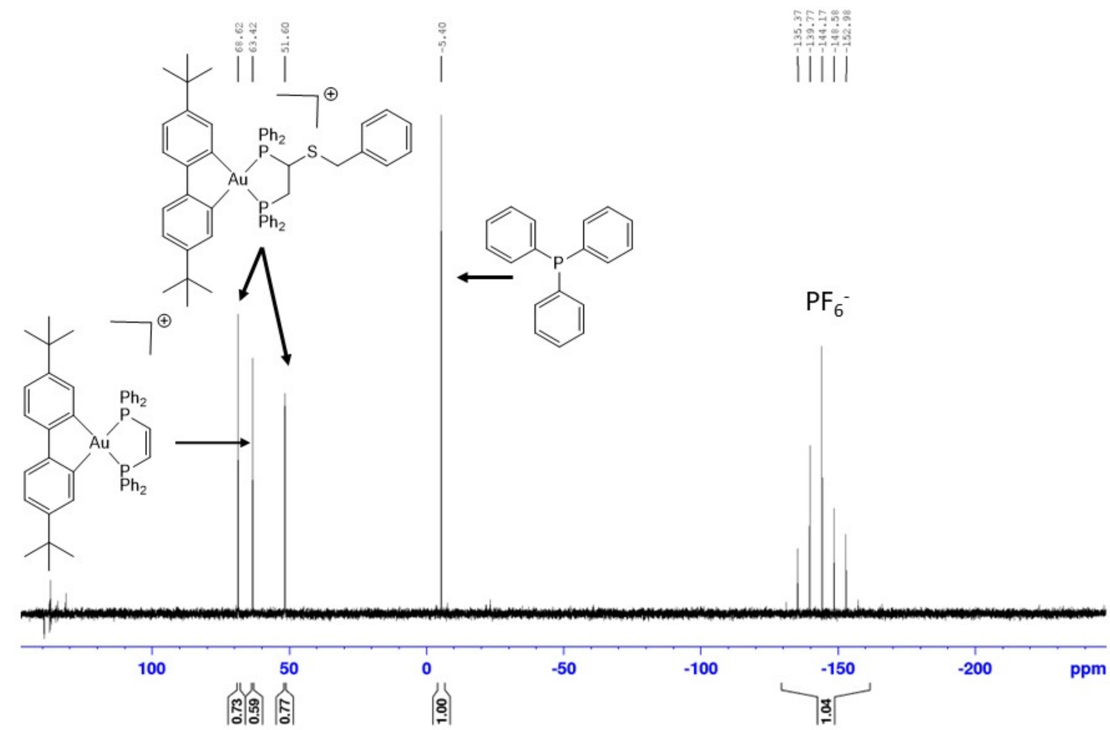

$^{31}P\{^{1}H\}$ NMR spectrum of complex **1** reacted 6 h at 323 K with 1 eq. of BzSH and 1 eq. of $NEt_3$ (table 1, entry 3).



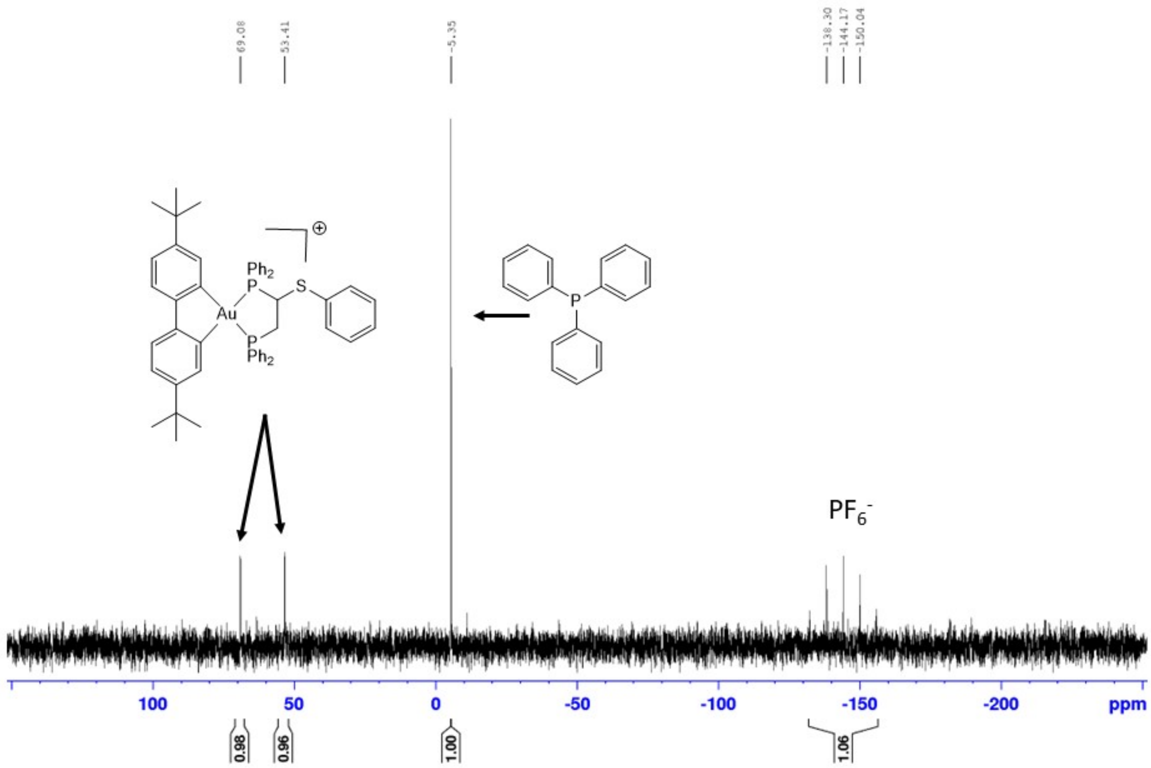

$^{31}P\{^{1}H\}$ NMR spectrum of complex **1** reacted 6 h at 323 K with 3 eq. of BzSH and 1 eq. of $NEt_3$ (table 1, entry 4).



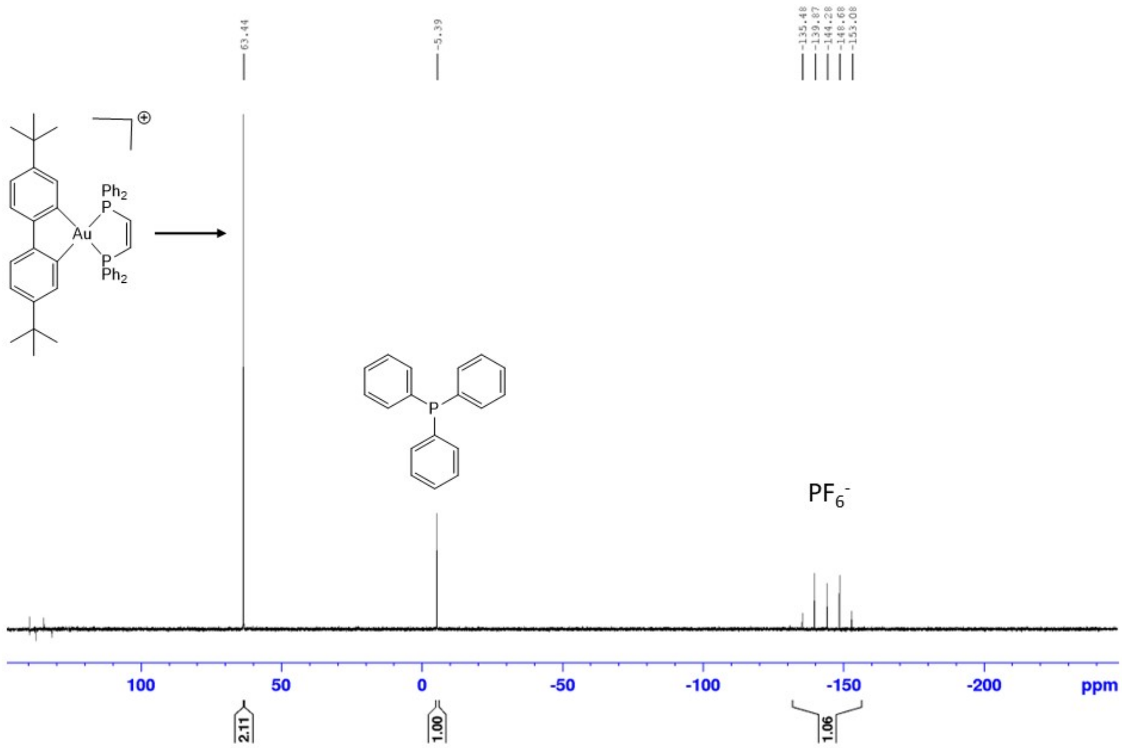

$^{31}P\{^{1}H\}$ NMR spectrum of complex **1** reacted 6 h at 323 K with 5 eq. of BzSH and 1eq. of $NEt_3$ (table 1, entry 5).



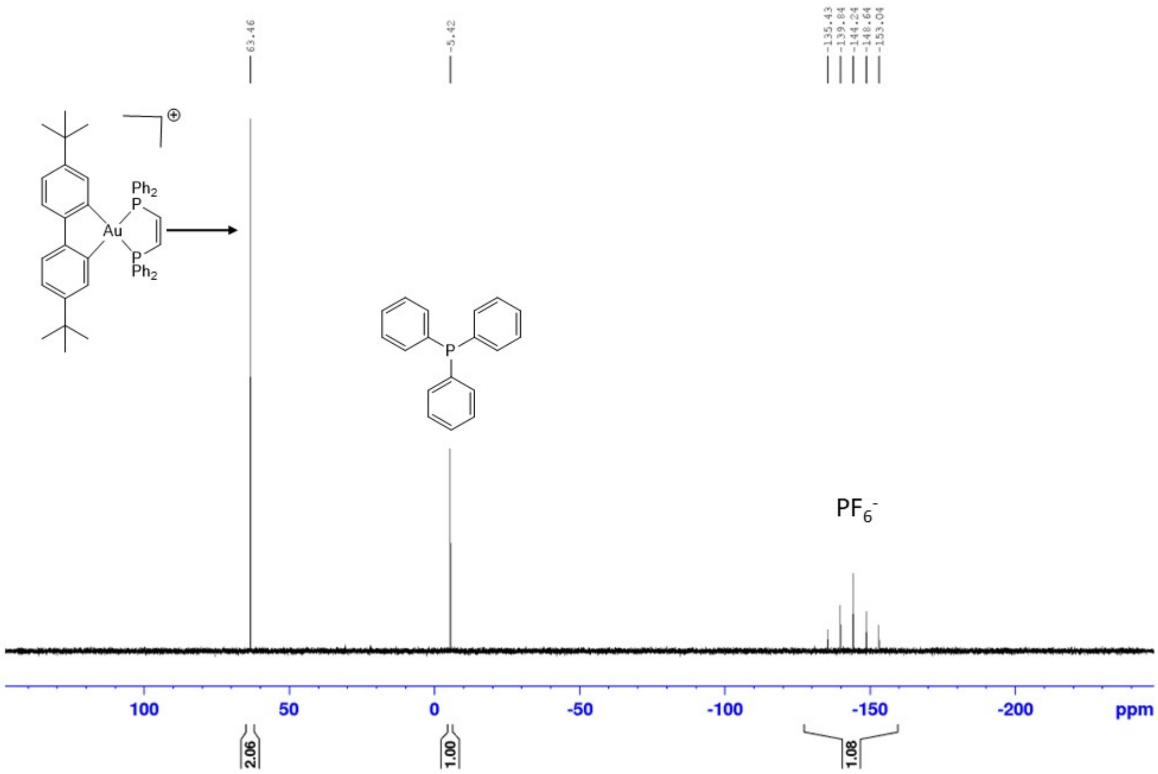

$^{31}P\{^{1}H\}$ NMR spectrum of complex **1** reacted 3 h at 323 K with 5 eq. of BzSH and 1eq. of $NEt_3$ (table 1, entry 6).



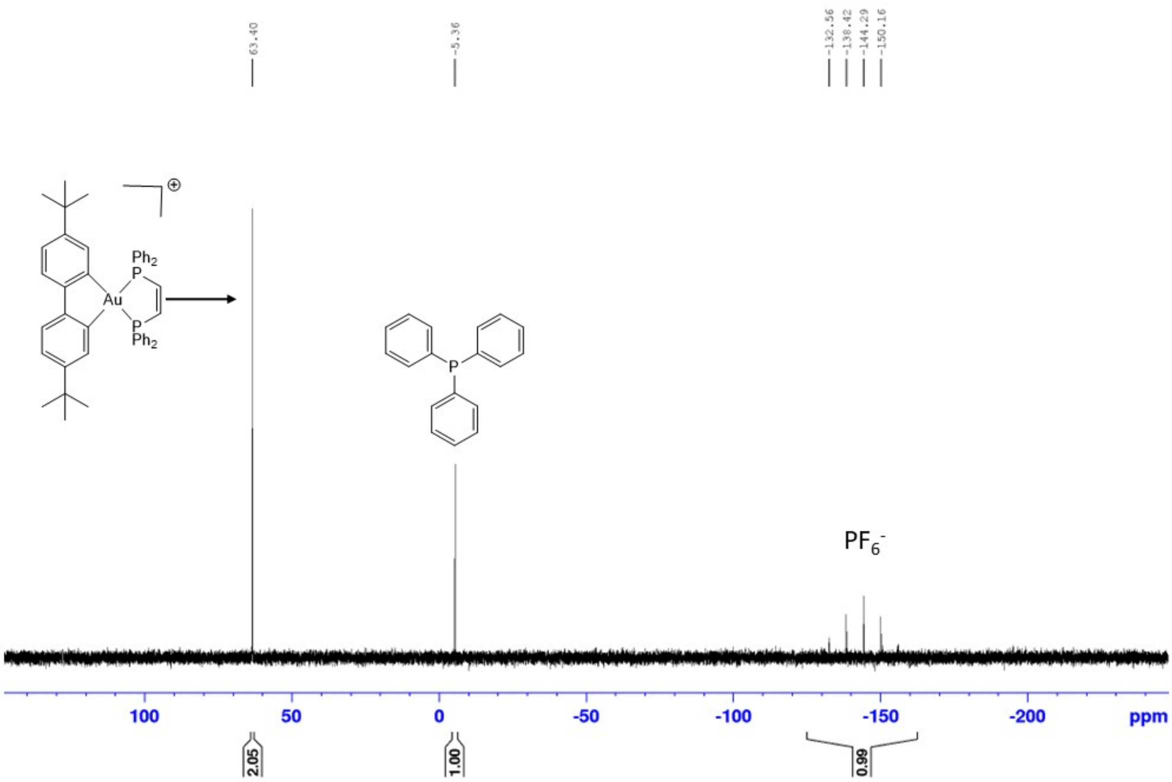

$^{31}P\{^{1}H\}$ NMR spectrum of complex **1** reacted 6 h at 323 K with 5 eq. of PhSH and 1eq. of $NEt_3$ (table 1, entry 7).



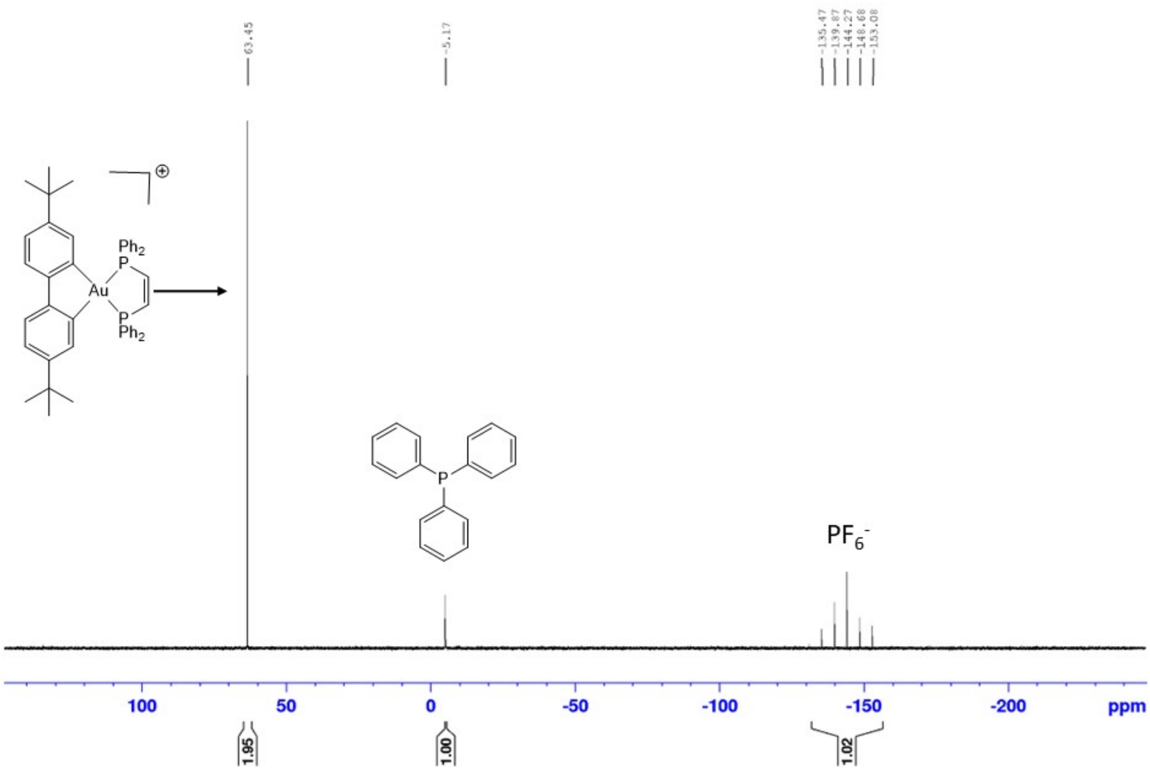

$^{31}P\{^{1}H\}$ NMR spectrum of complex **1** reacted 6 h at 323 K with 5 eq. of BzOH and 1eq. of $NEt_3$ (entry 8).



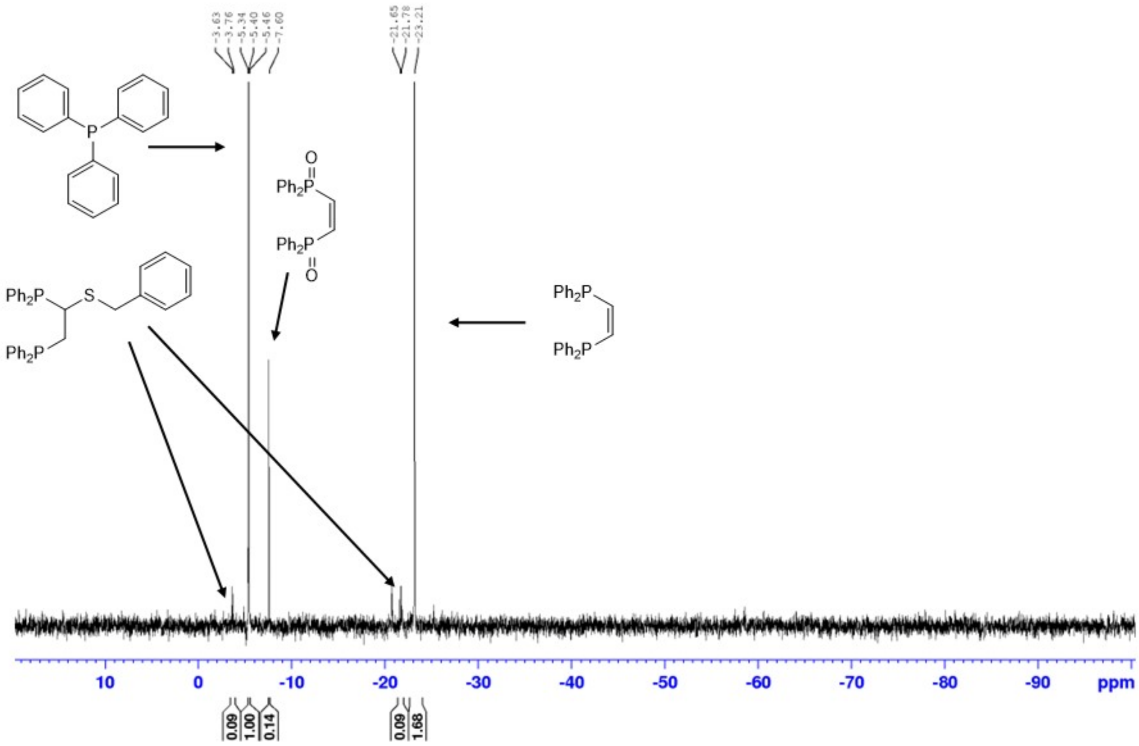

$^{31}P\{^{1}H\}$ NMR spectrum of complex **1** reacted 6 h at 323 K with 5 eq. of PhOH and 1eq. of $NEt_3$ (entry 9).



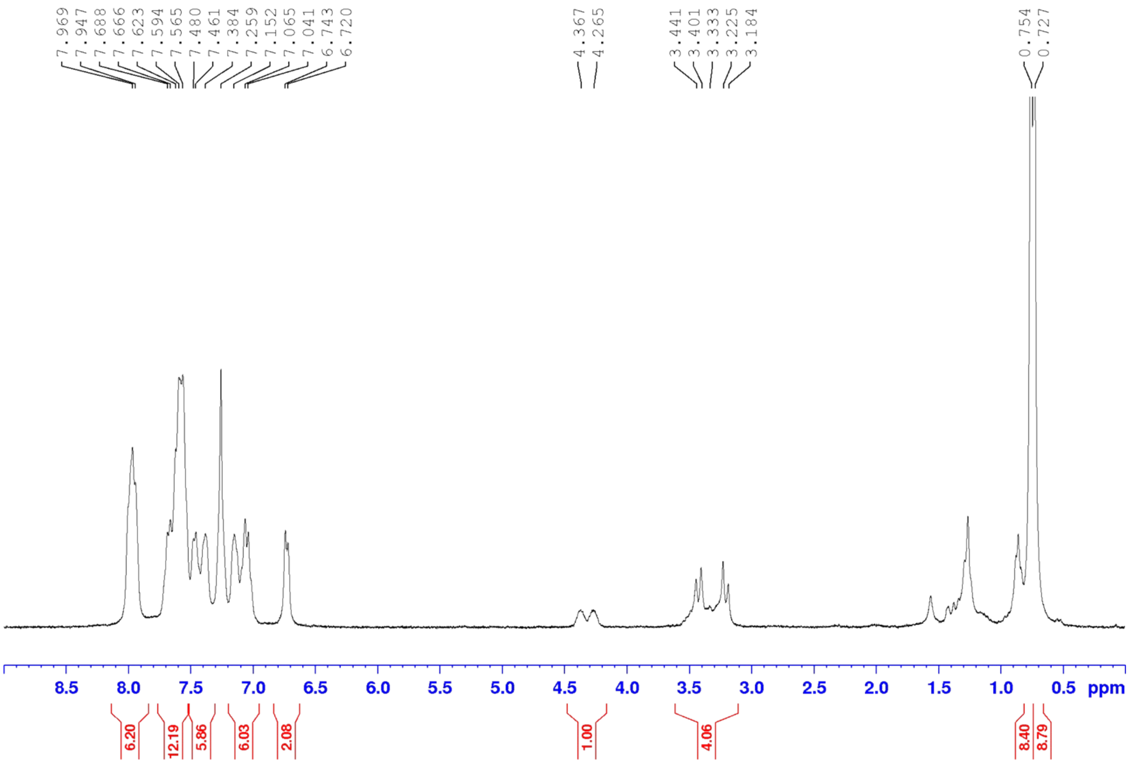

$^{31}P\{^1H\}$ NMR spectrum of complex **1** reacted 6 h at 323 K with 5 eq. of $BzNH_2$ and 1eq. of $NEt_3$ (entry 10).



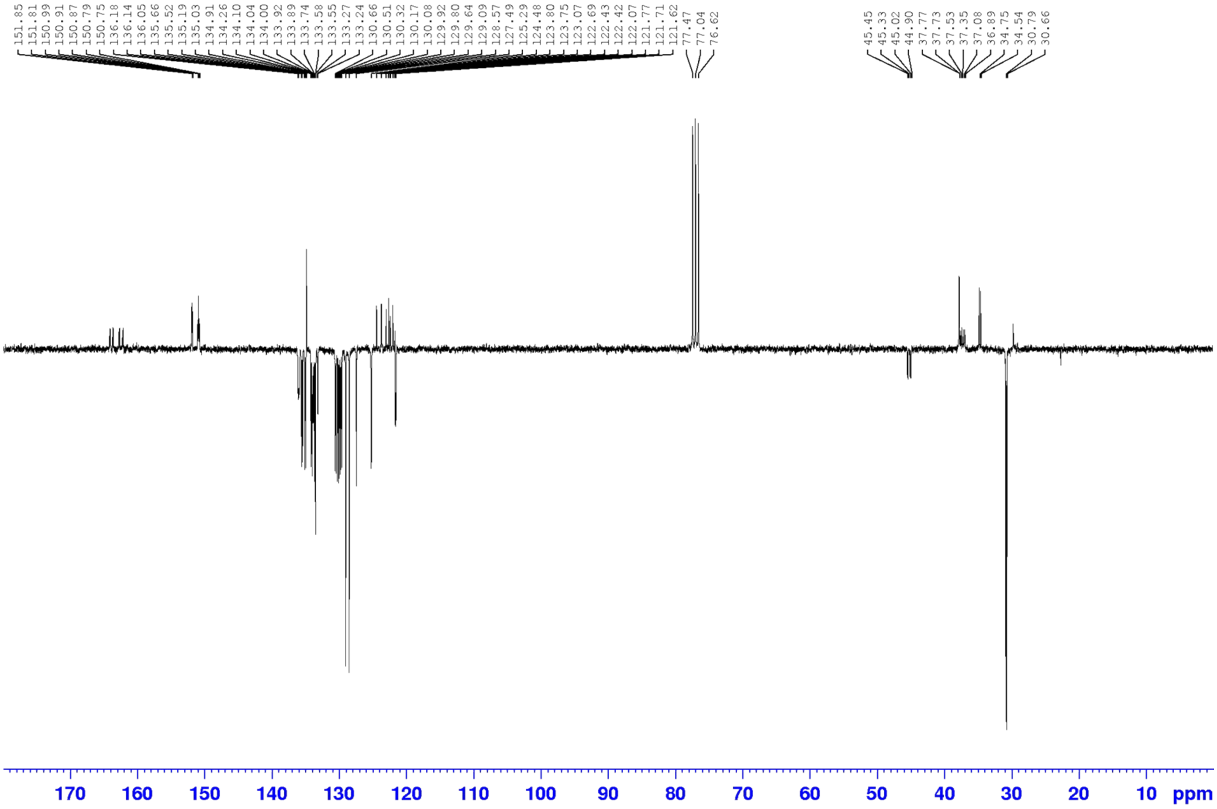

$^{31}P\{^1H\}$ NMR spectrum of complex **1** reacted 6 h at 323 K with 5 eq. of $PhNH_2$ and 1eq. of $NEt_3$ (entry 11).



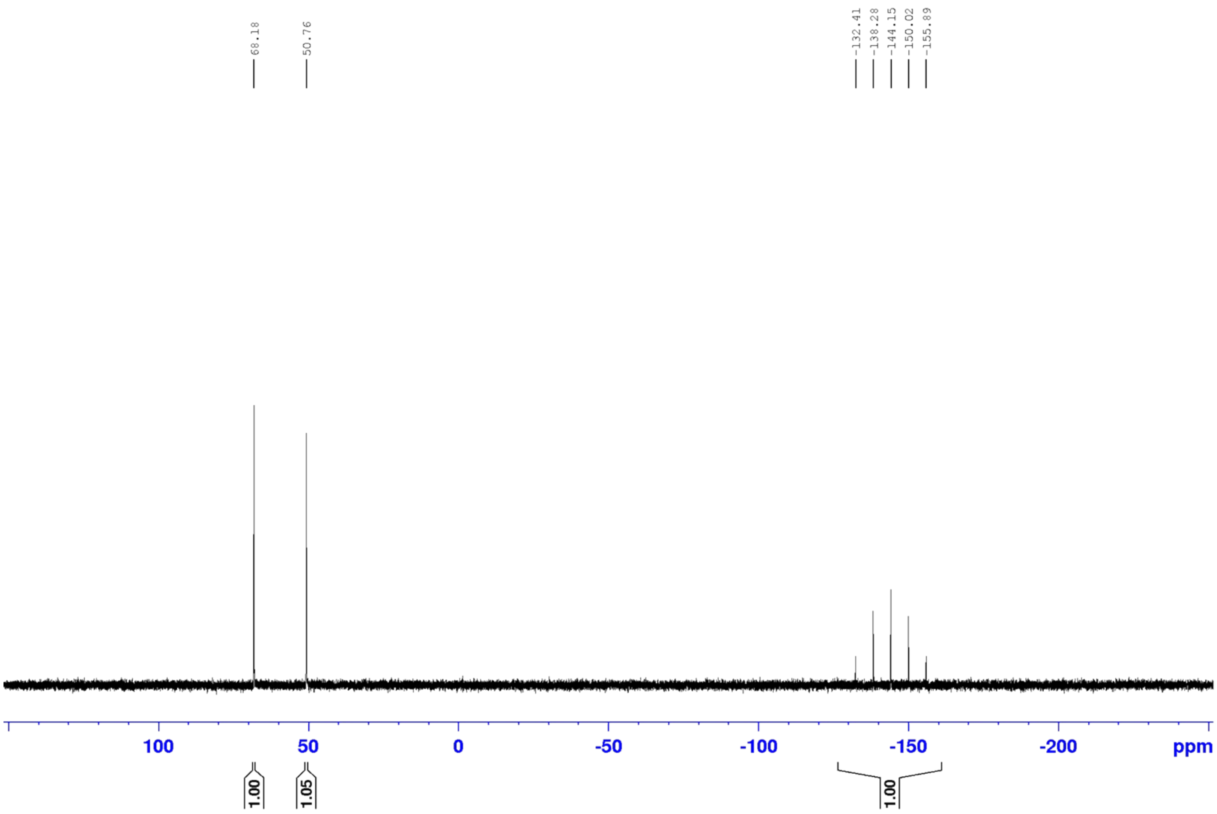

$^{31}P\{^{1}H\}$ NMR spectrum of free *cis*-1,2-diphenylphosphinoethylene reacted 6 h at 323 K with 5 eq. of BzSH and 1eq. of $NEt_3$.



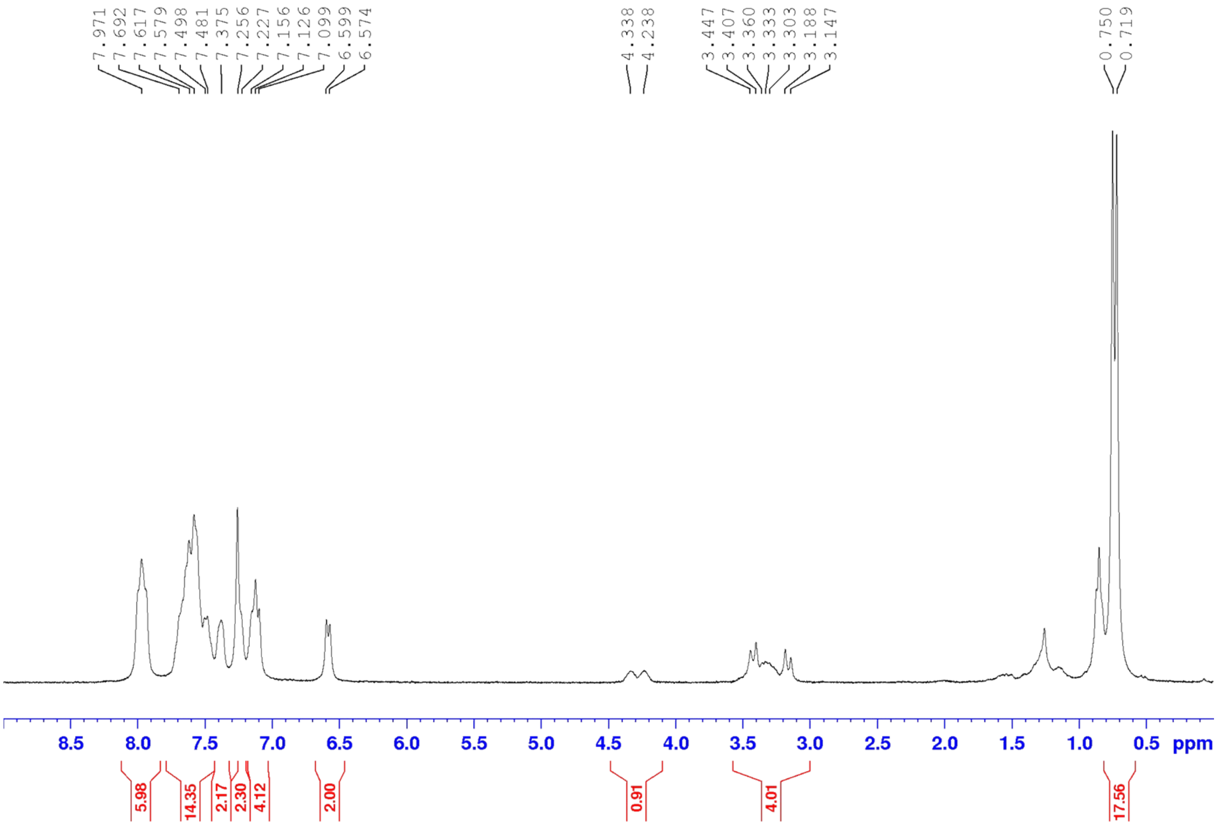

$^{1}H$ NMR spectrum of complex **2a** in $CDCl_3$



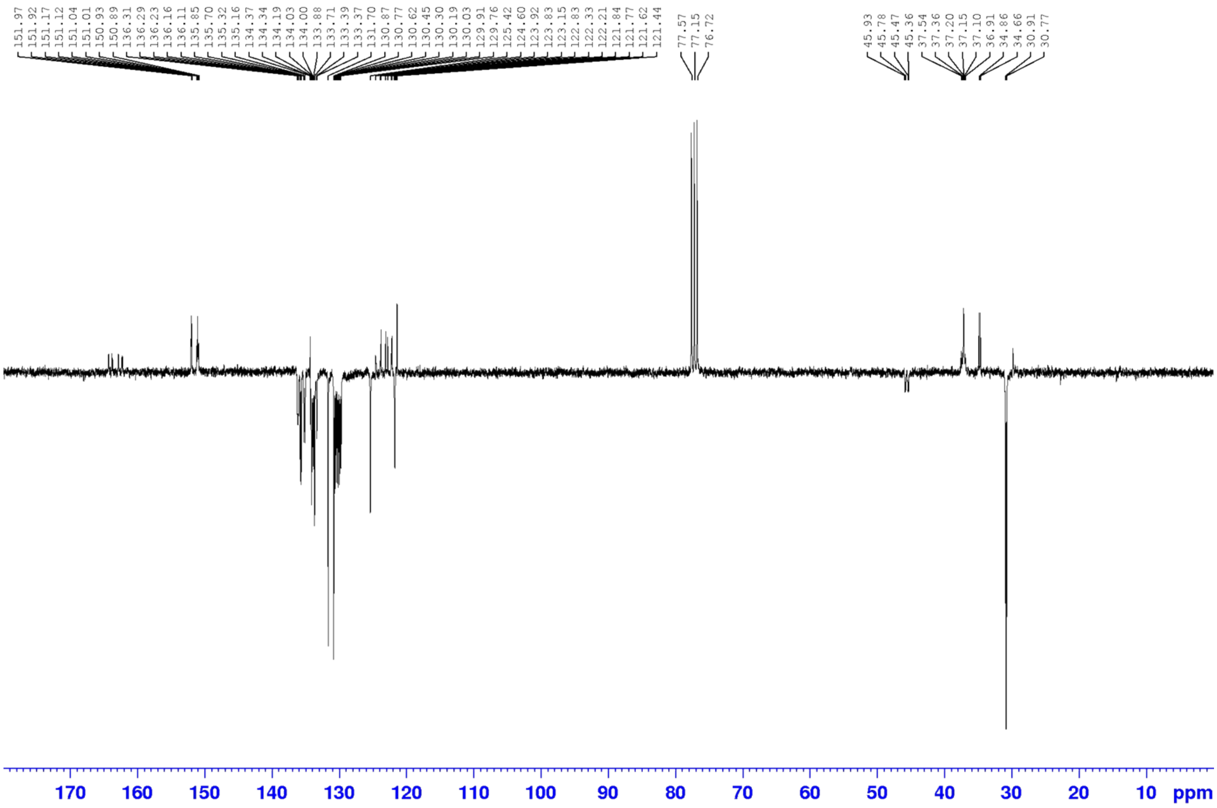

$^{13}C\{^{1}H\}$ Jmod NMR spectrum of complex **2a** in $CDCl_3$



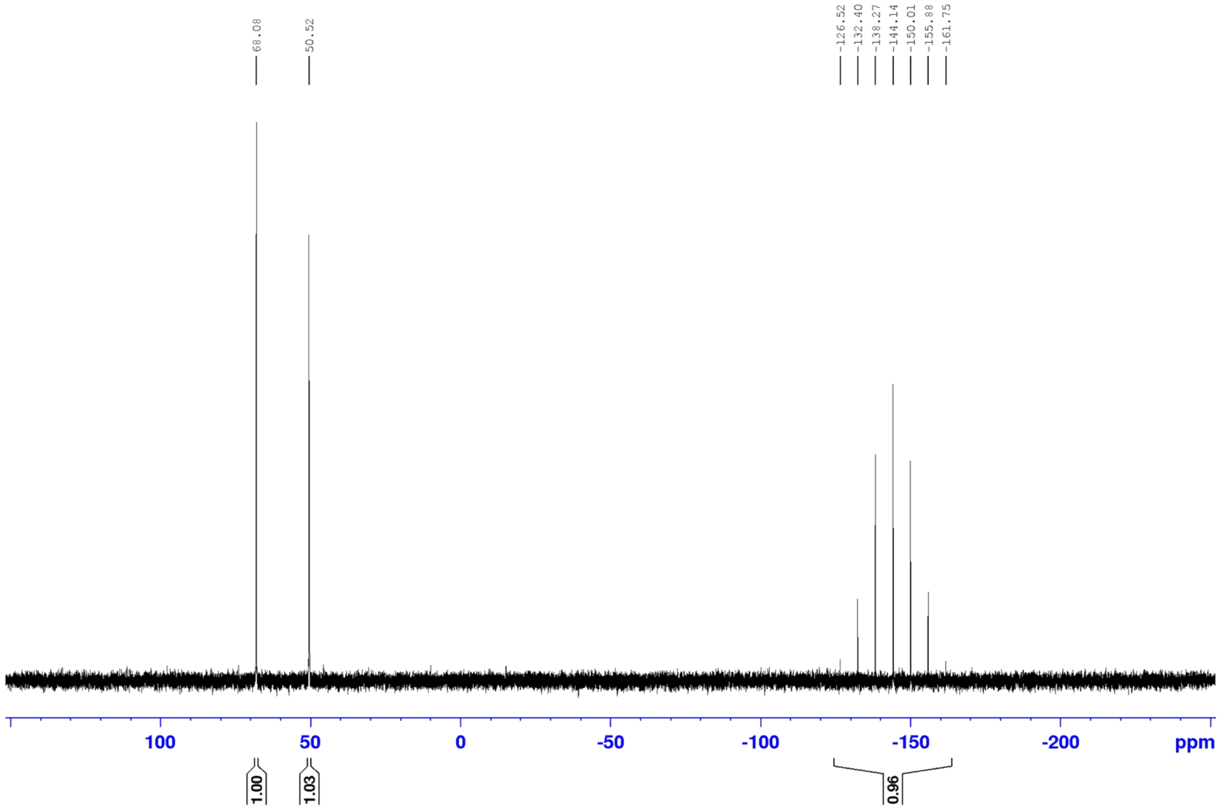

$^{31}P\{^{1}H\}$ NMR spectrum of complex **2a** in $CDCl_3$



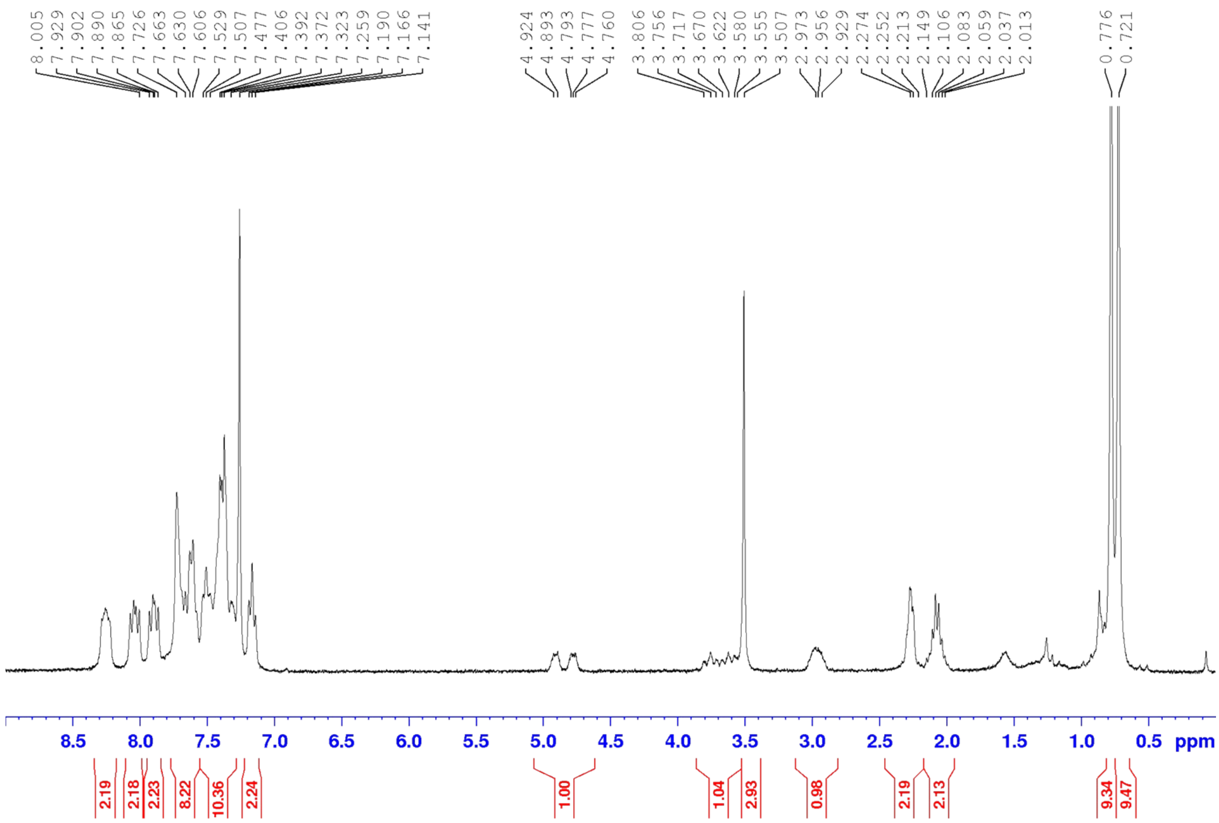
$^{1}H$ NMR spectrum of complex **2b** in $CDCl_3$



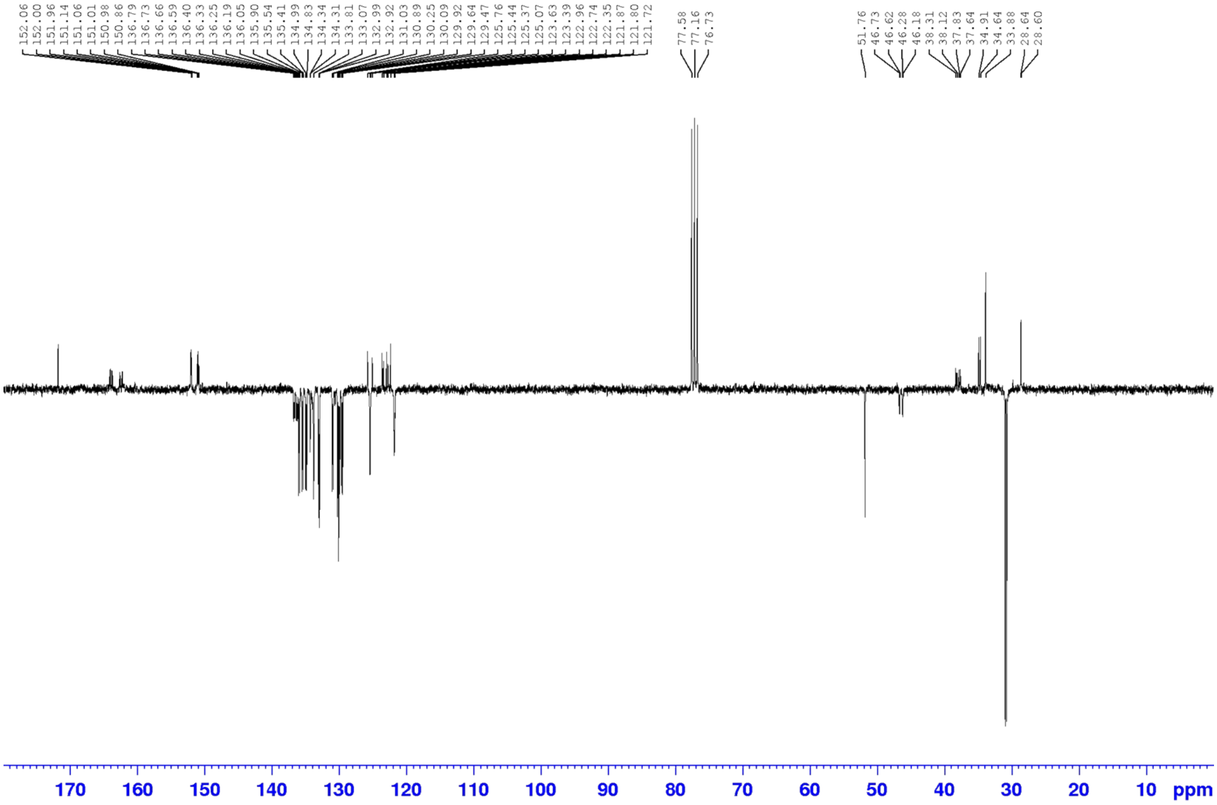
$^{13}C\{^{1}H\}$ Jmod NMR spectrum of complex **2b** in $CDCl_3$



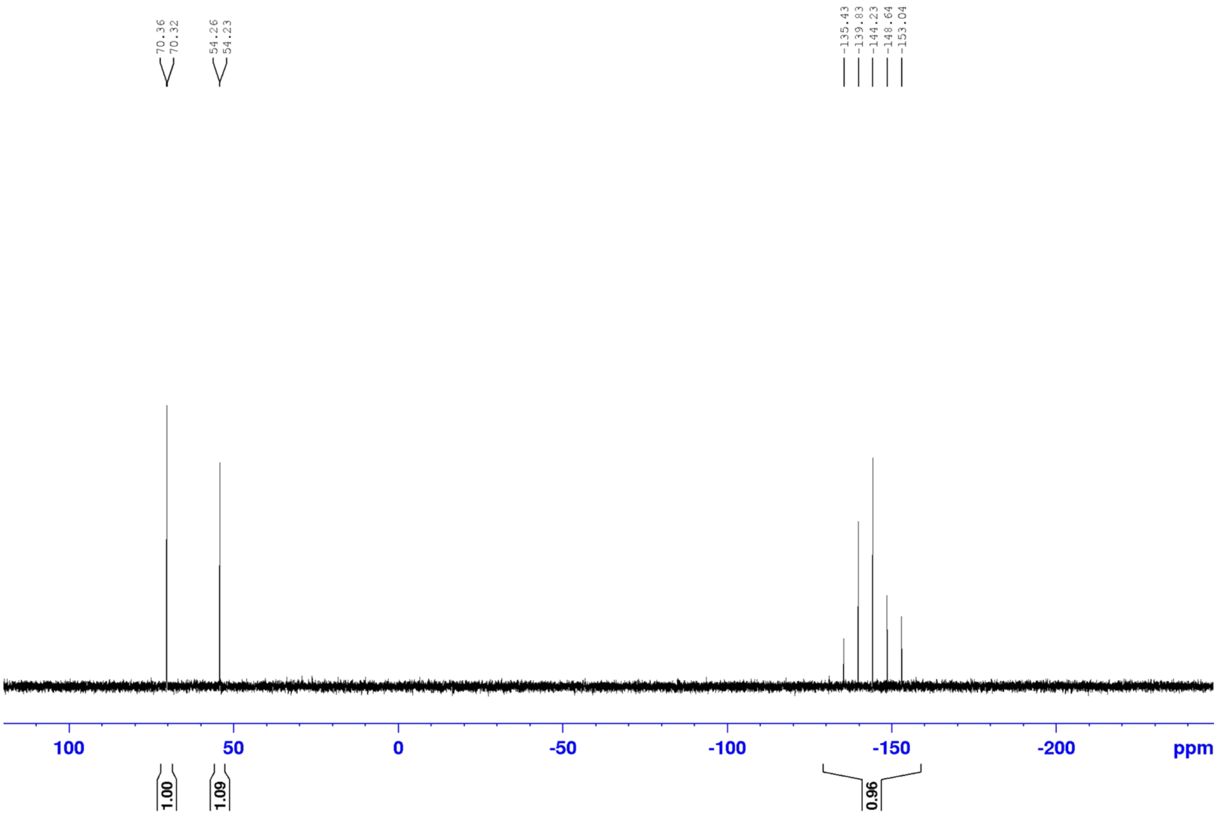

$^{31}P\{^{1}H\}$ NMR spectrum of complex **2b** in $CDCl_3$



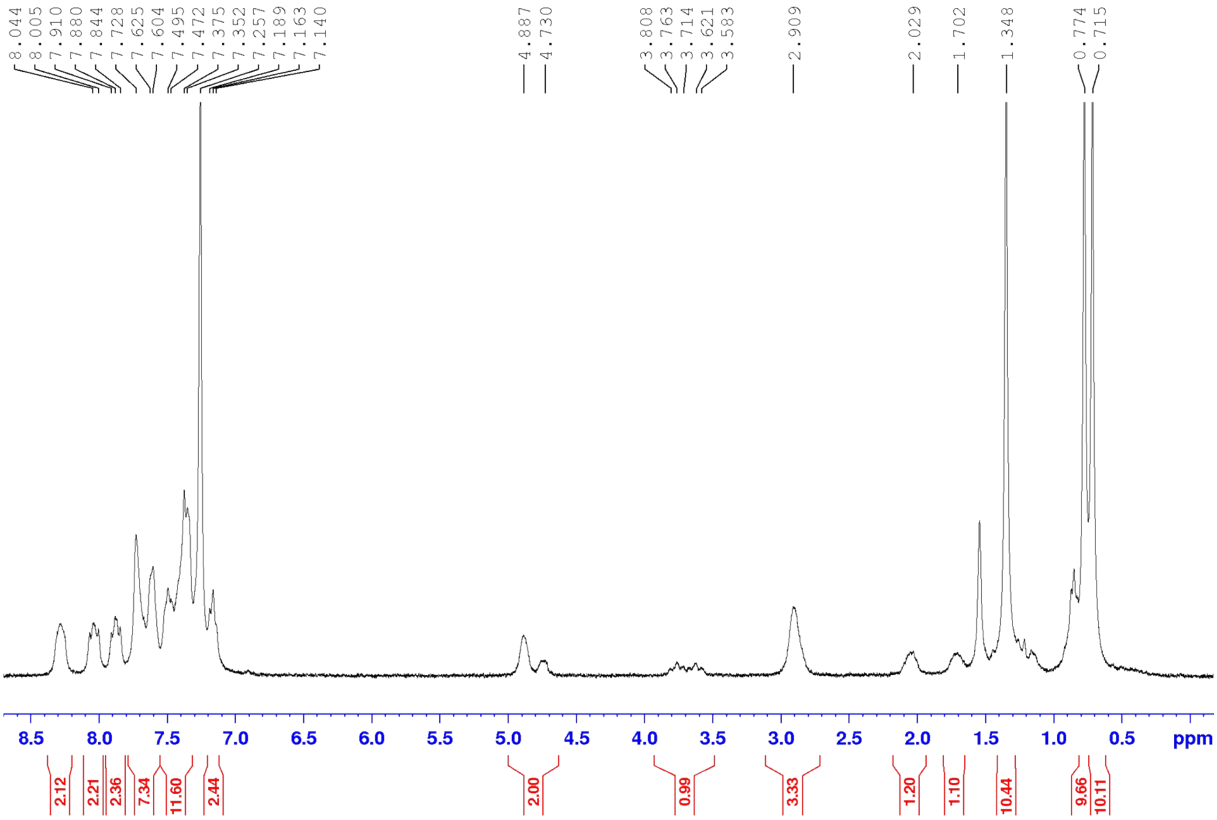

$^{1}H$ NMR spectrum of complex **2c** in $CDCl_3$



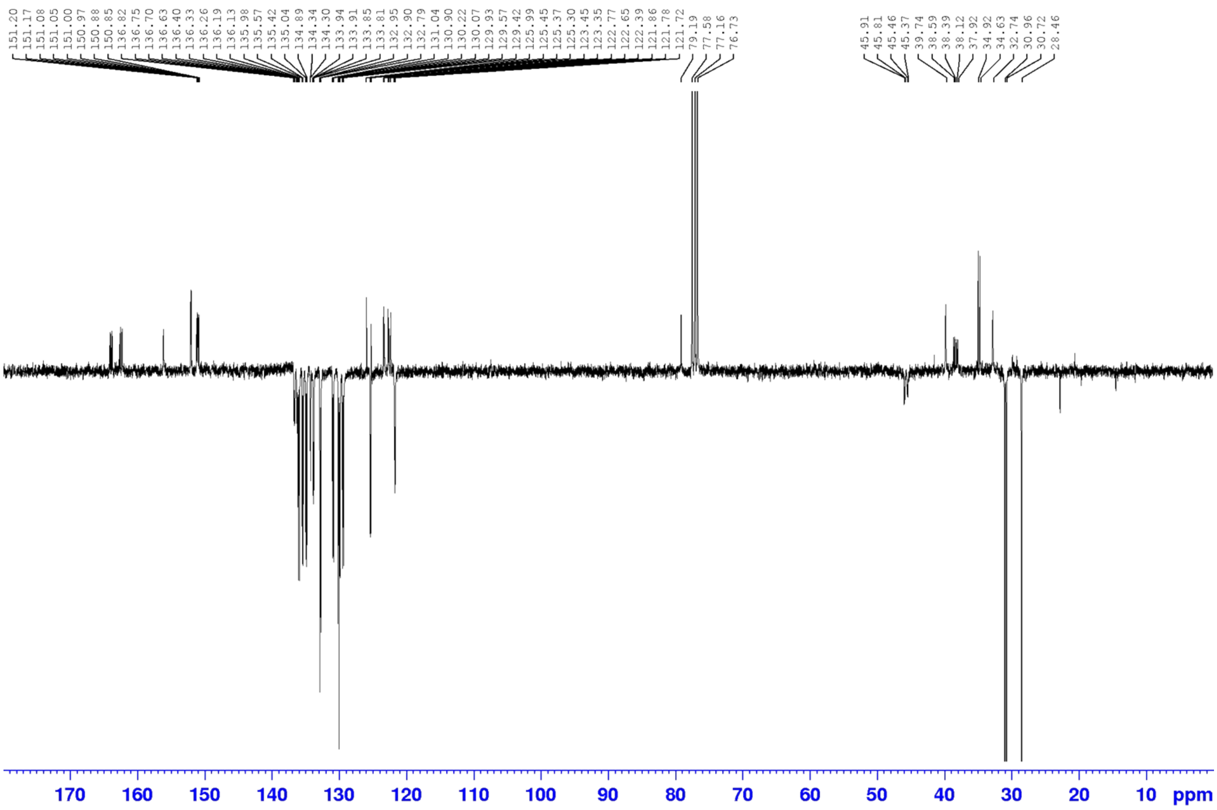

$^{13}C\{^1H\}$ Jmod NMR spectrum of complex **2c** in $CDCl_3$



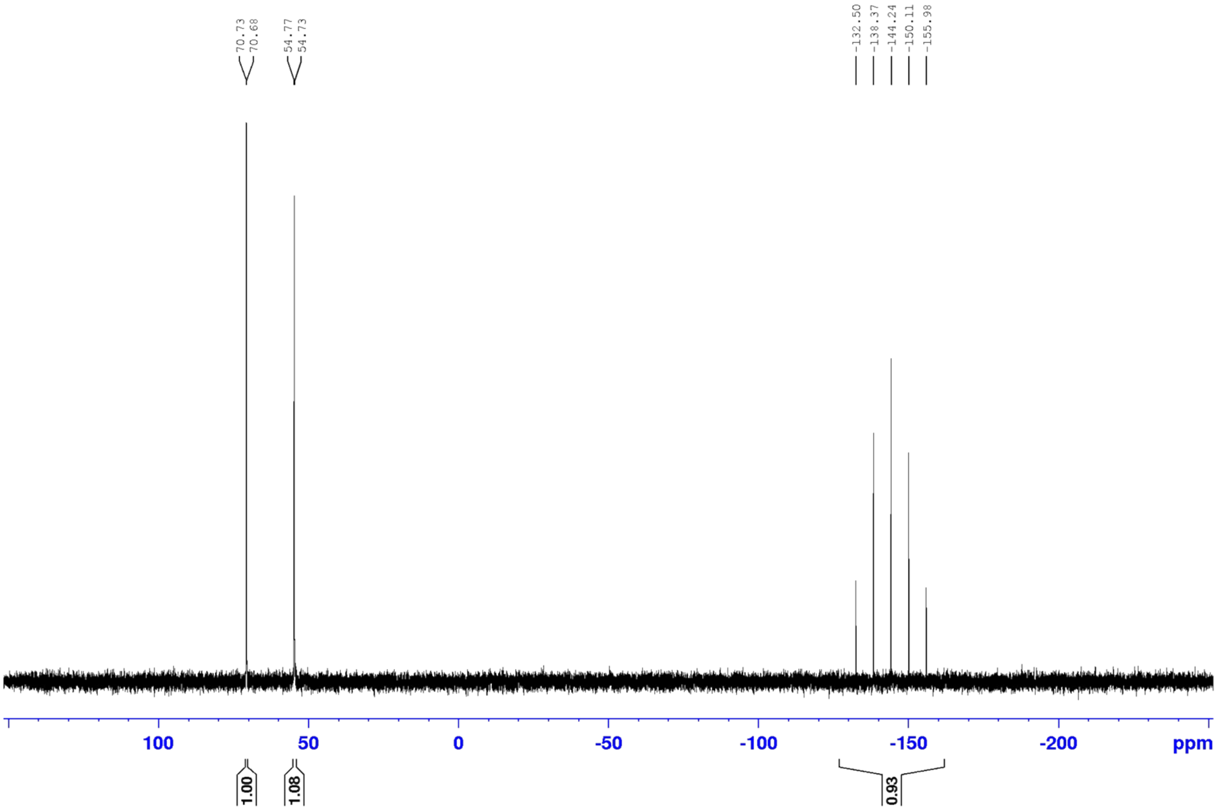

$^{31}P\{^1H\}$ NMR spectrum of complex **2c** in $CDCl_3$



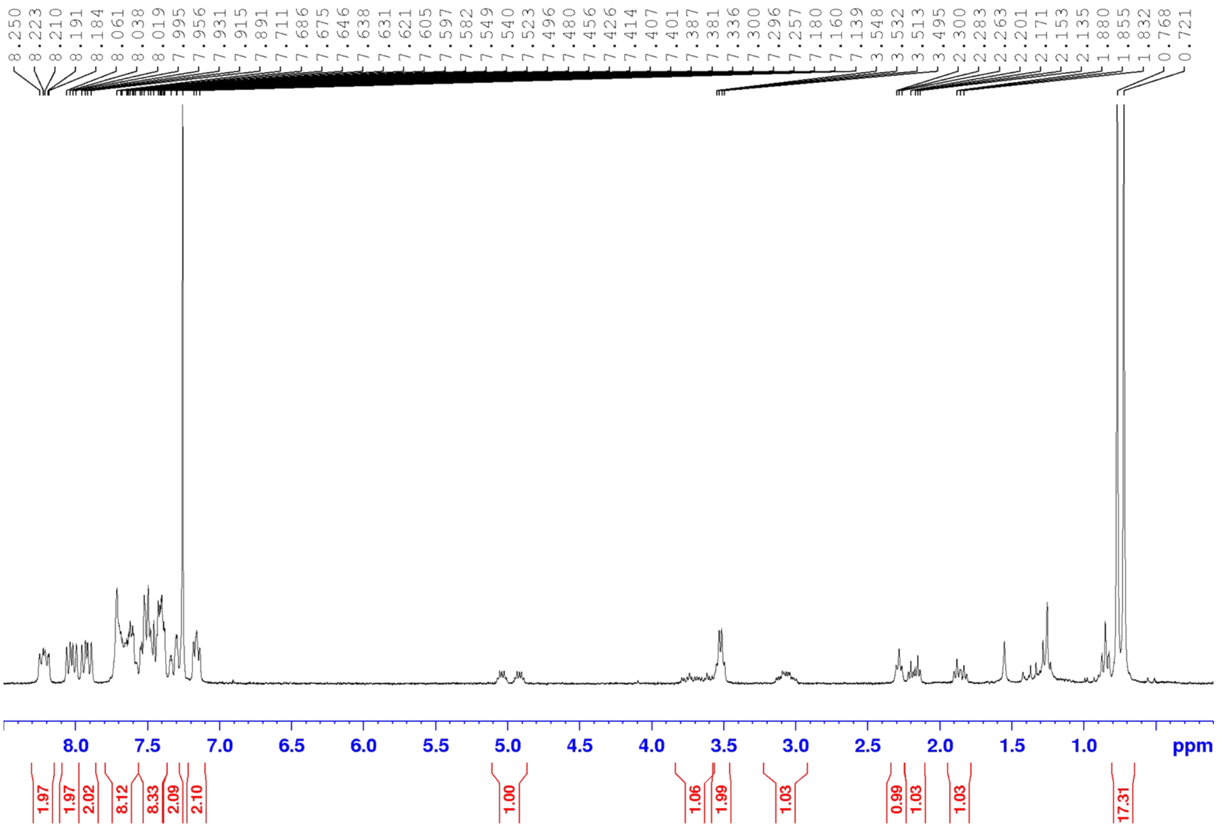

[1]H NMR spectrum of complex **2d** in $CDCl_3$



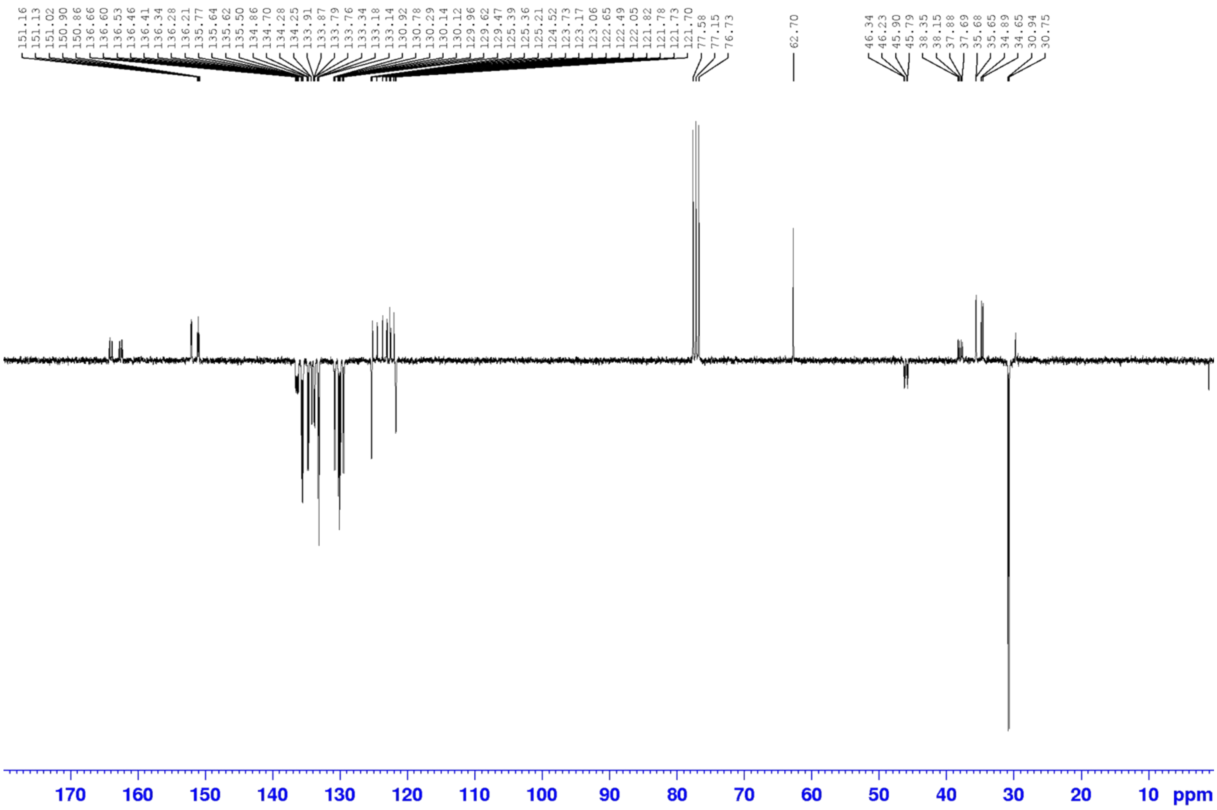

[13]C{[1]H} Jmod NMR spectrum of complex **2d** in $CDCl_3$



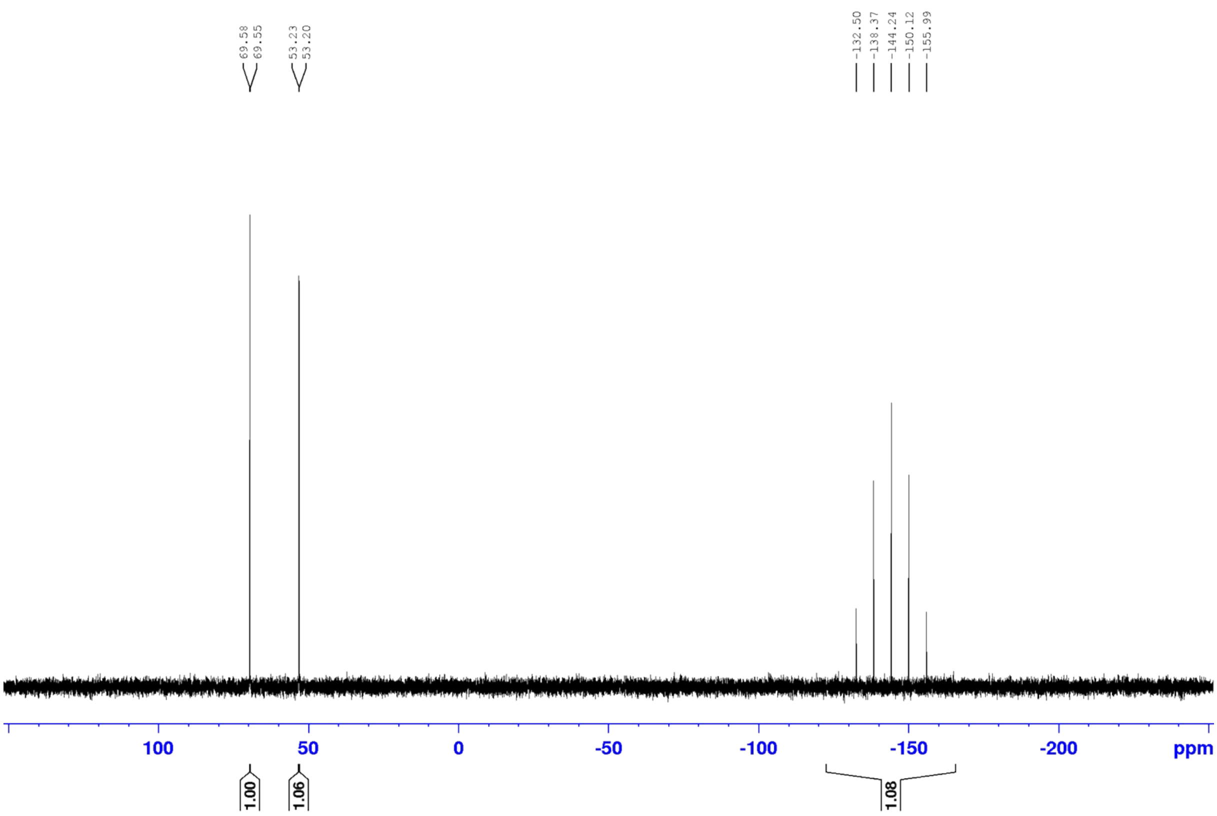
$^{31}P\{^{1}H\}$ NMR spectrum of complex **2d** in $CDCl_3$



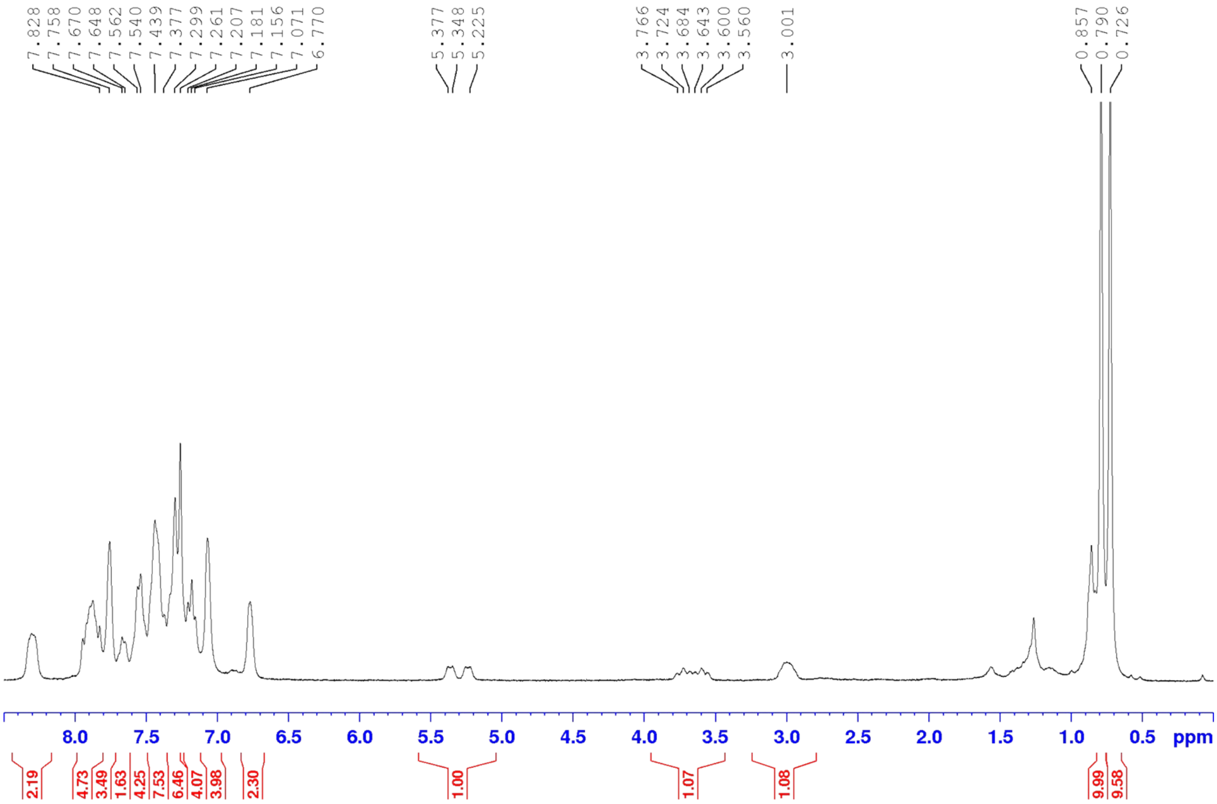
$^{1}H$ NMR spectrum of complex **2e** in $CDCl_3$



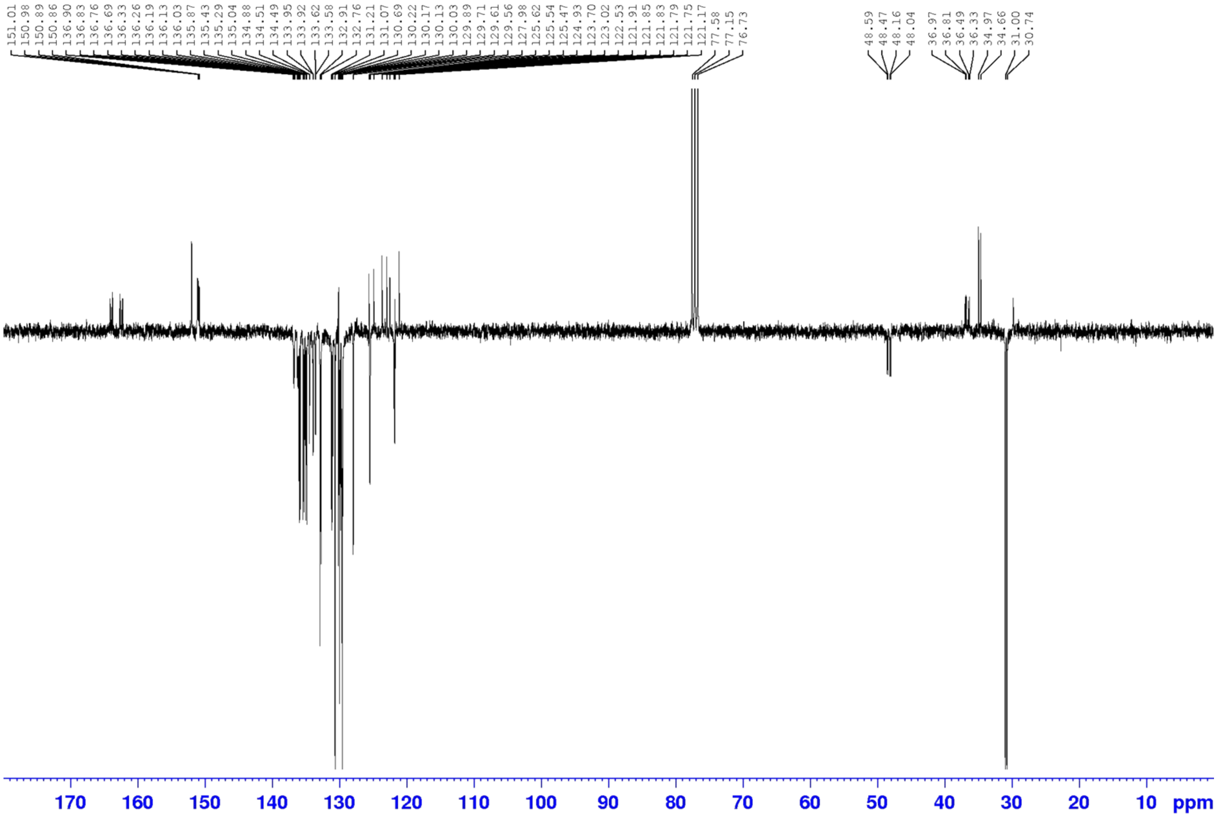
$^{13}C\{^{1}H\}$ Jmod NMR spectrum of complex **2e** in $CDCl_3$



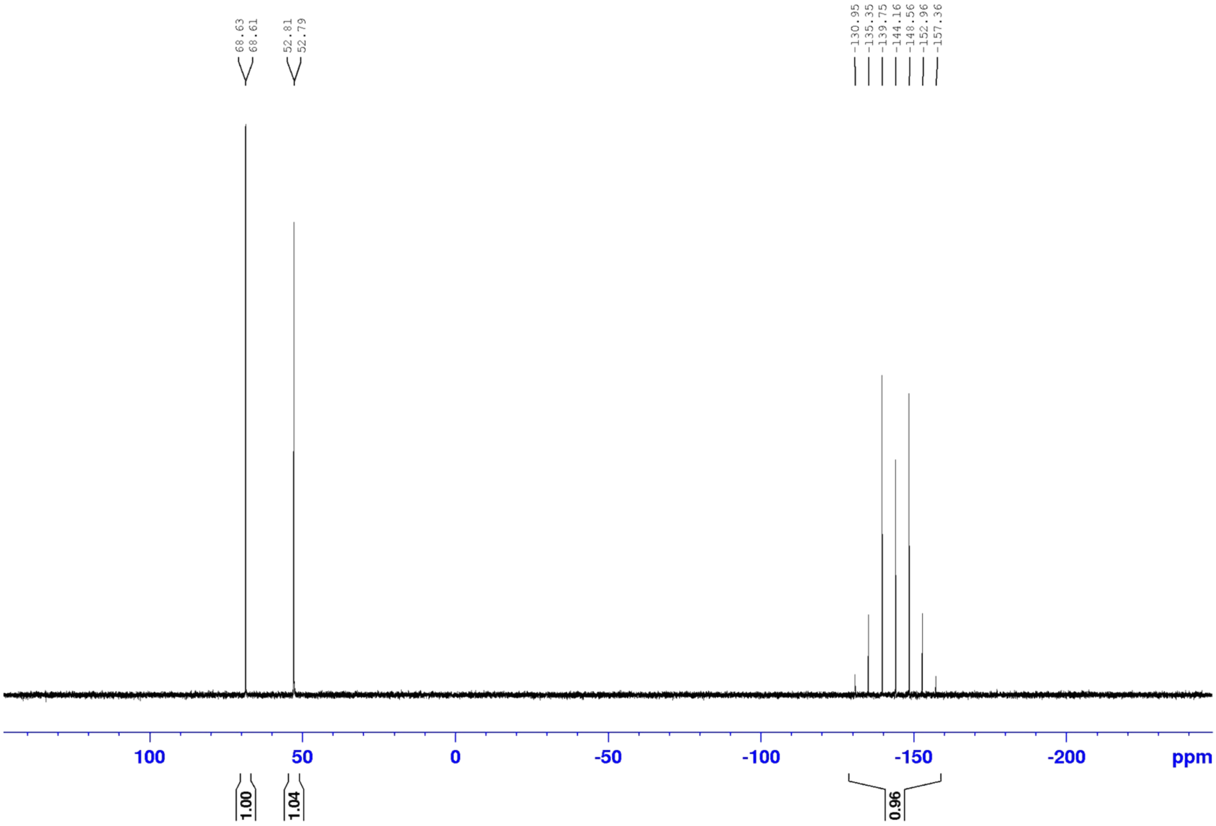
$^{31}P\{^{1}H\}$ NMR spectrum of complex **2e** in $CDCl_3$



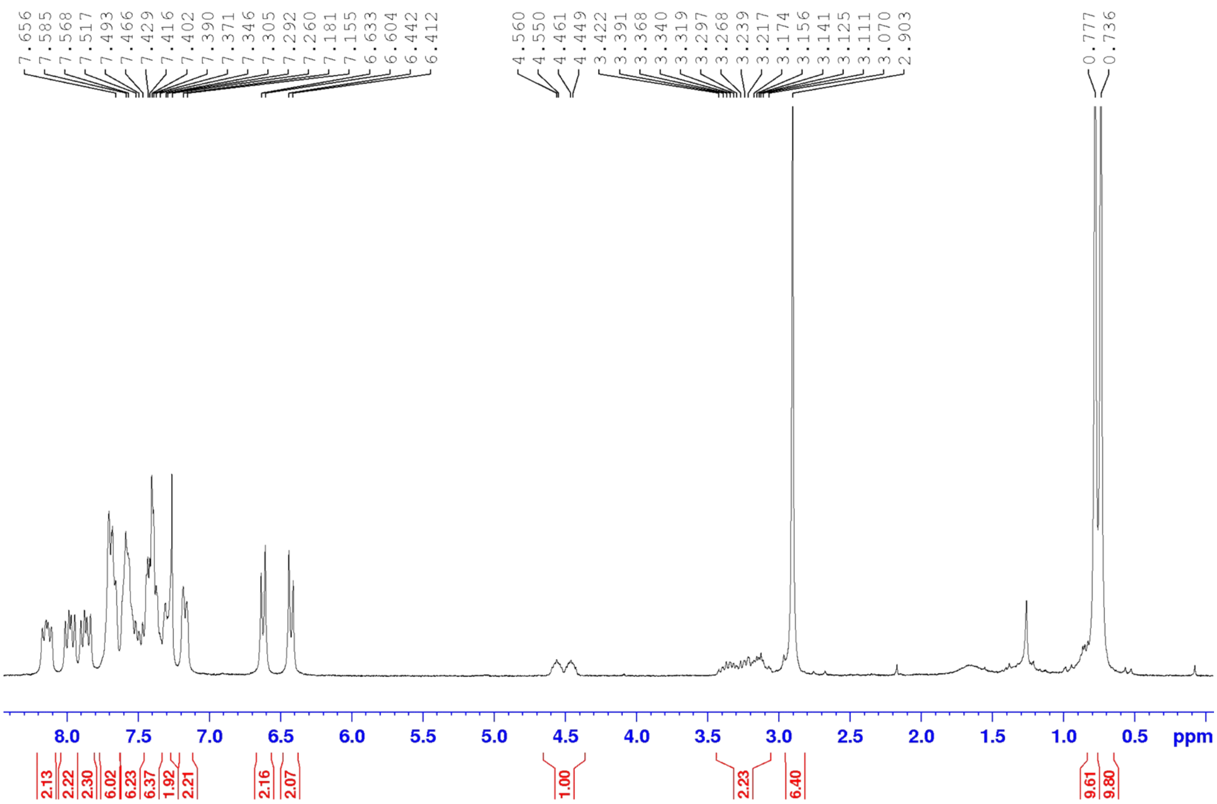
$^1$H NMR spectrum of complex **2f** in $CDCl_3$



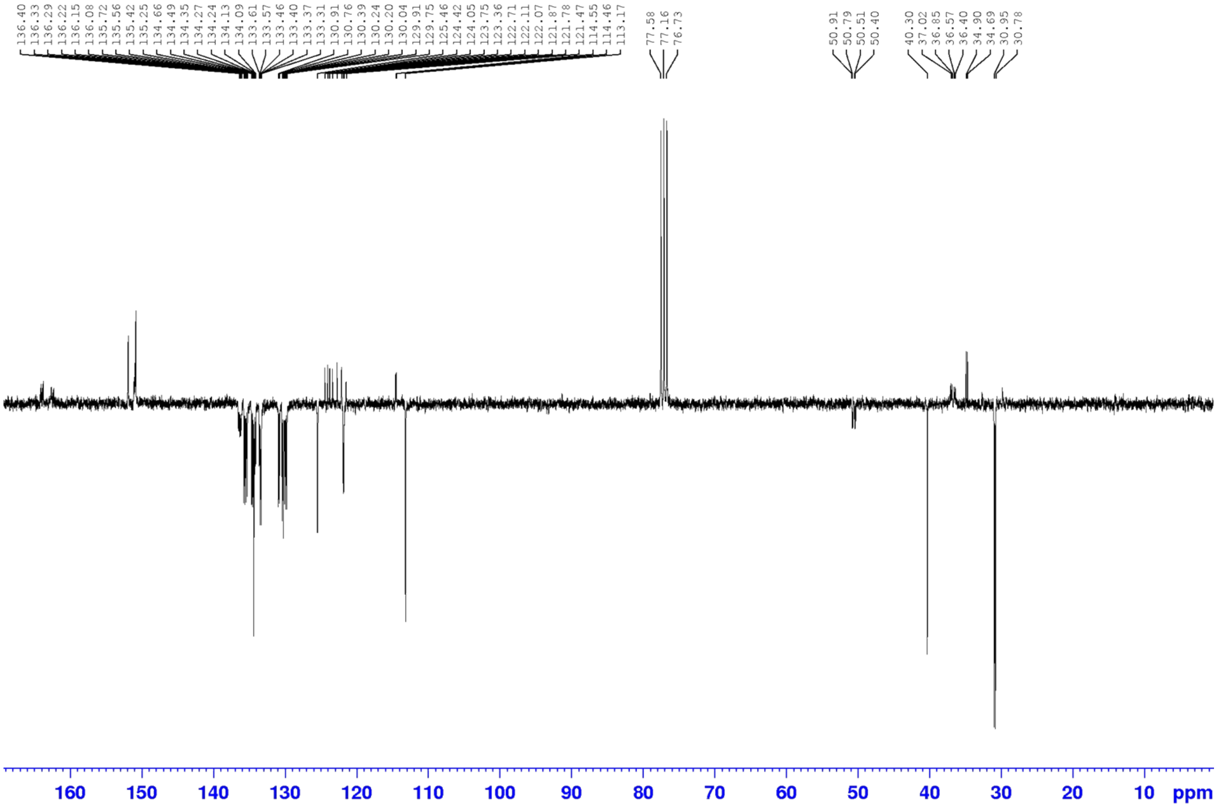
$^{13}C\{^1H\}$ Jmod NMR spectrum of complex **2f** in $CDCl_3$



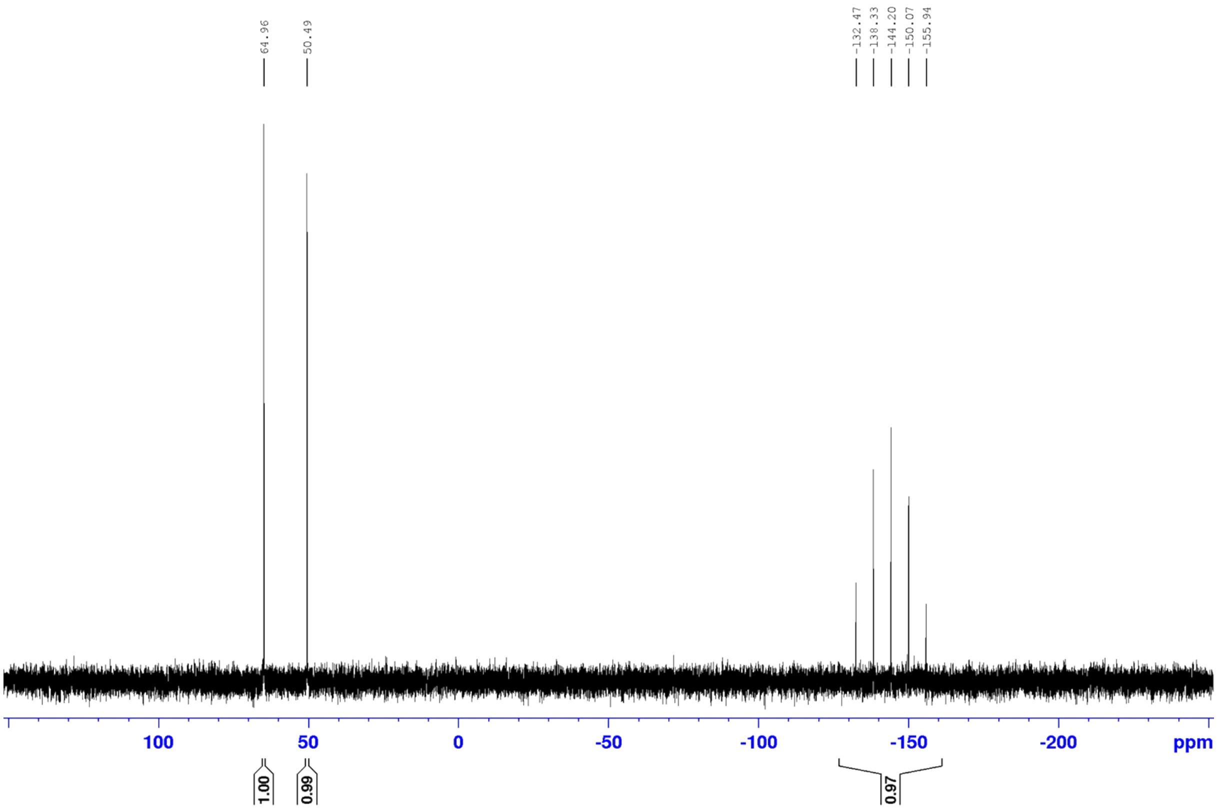
$^{31}P\{^1H\}$ NMR spectrum of complex **2f** in $CDCl_3$



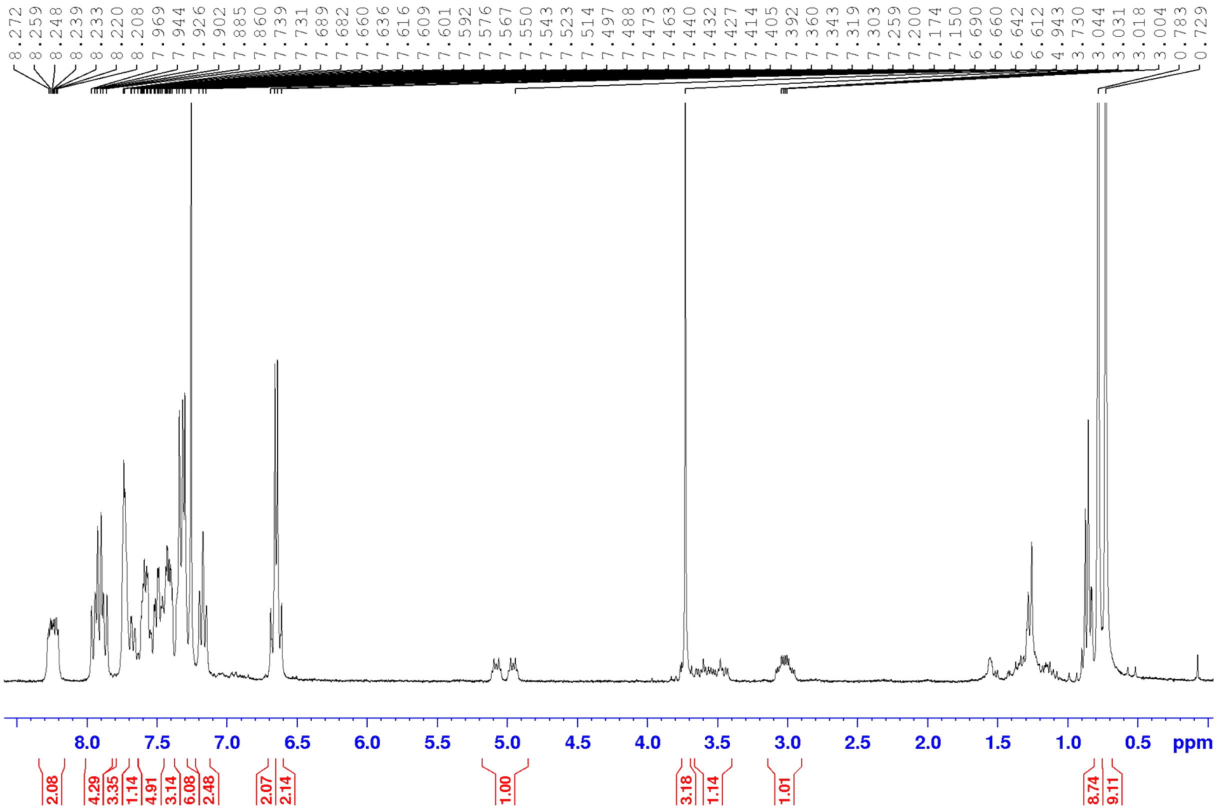
$^1H$ NMR spectrum of complex **2g** in $CDCl_3$



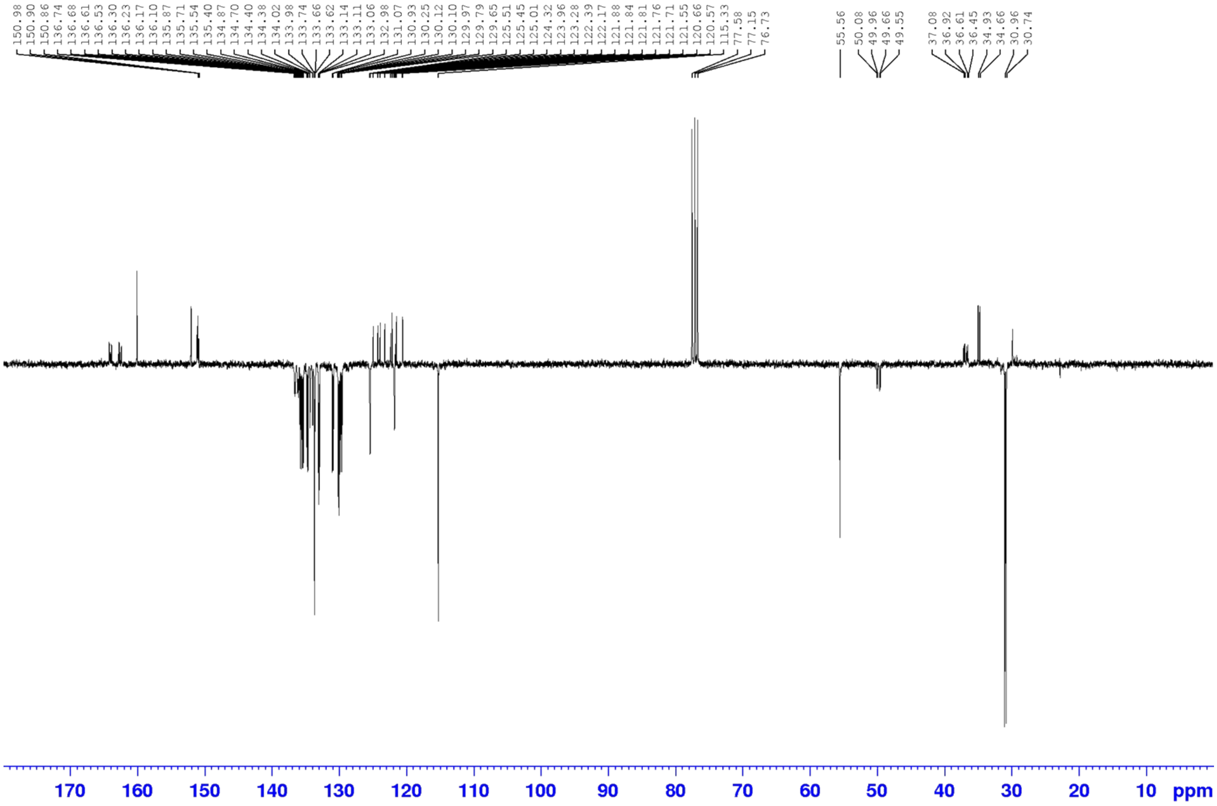

$^{13}C\{^{1}H\}$ Jmod NMR spectrum of complex **2g** in $CDCl_3$



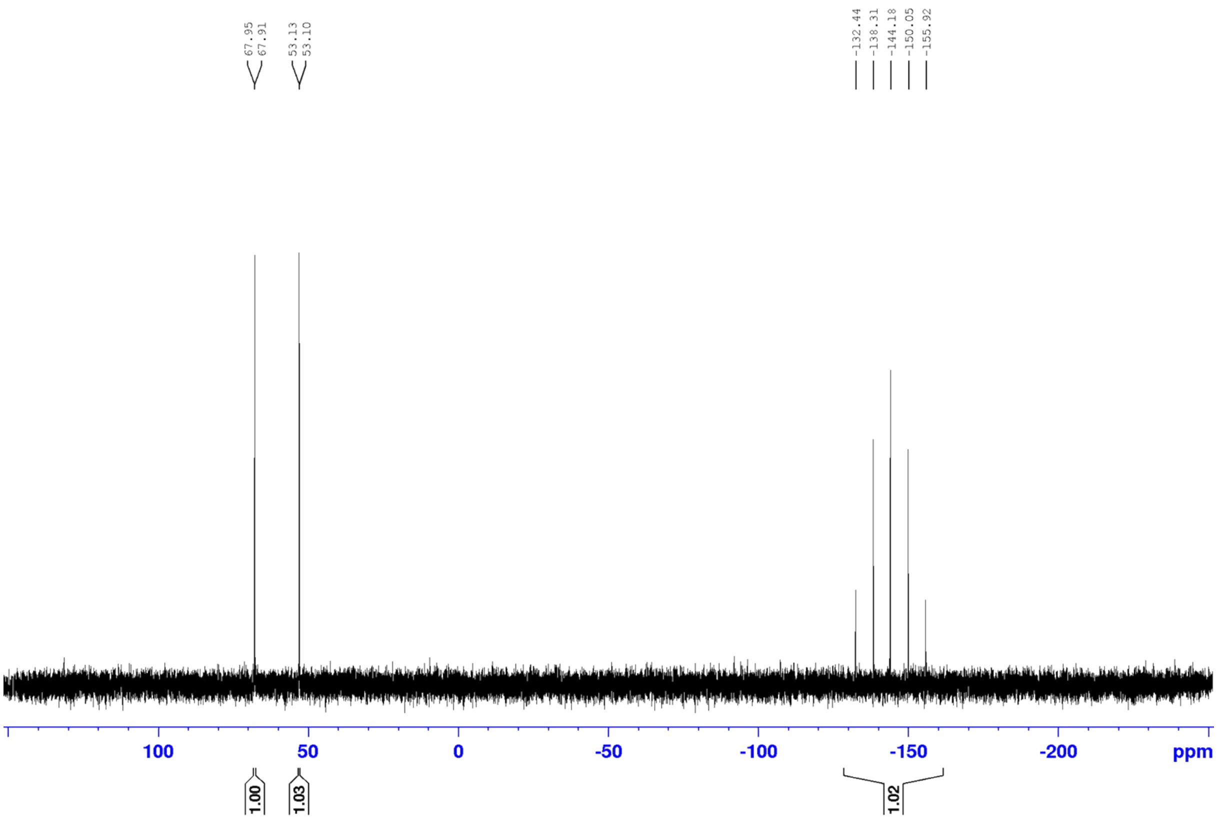

$^{31}P\{^{1}H\}$ NMR spectrum of complex **2g** in $CDCl_3$



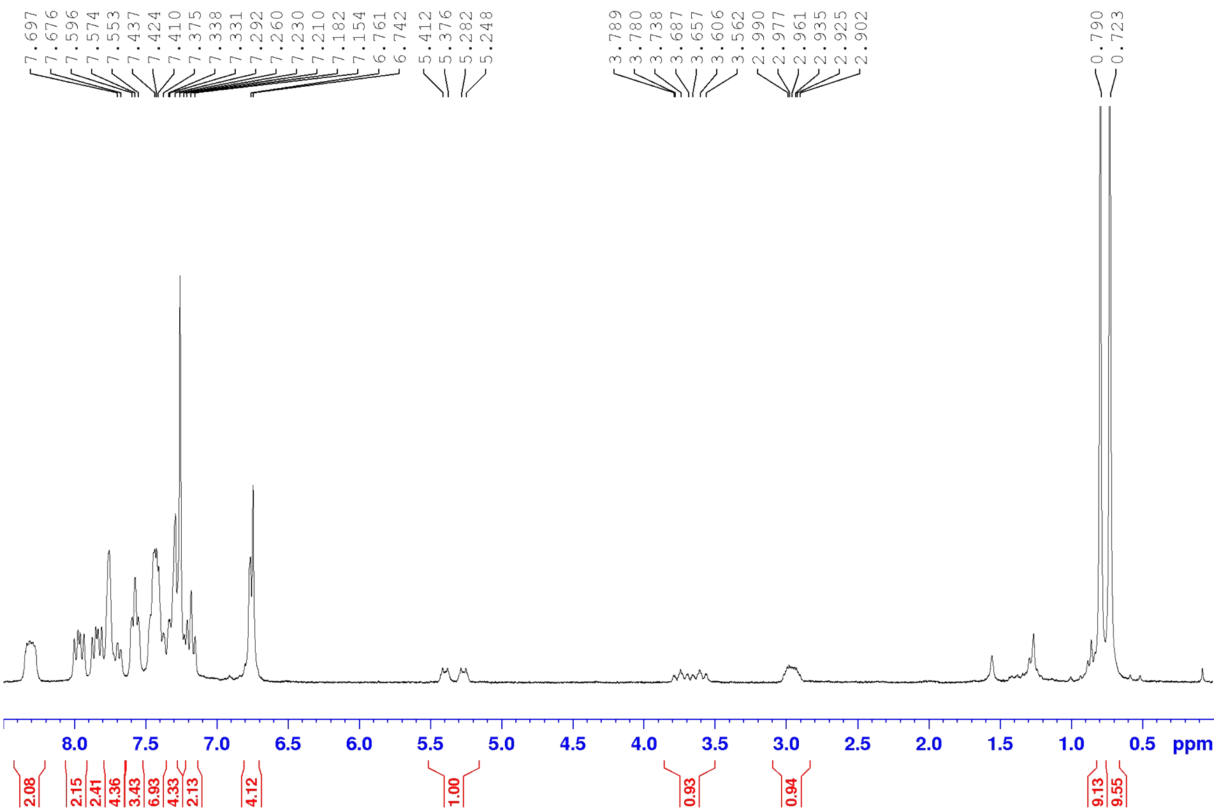
[1]H NMR spectrum of complex **2h** in $CDCl_3$



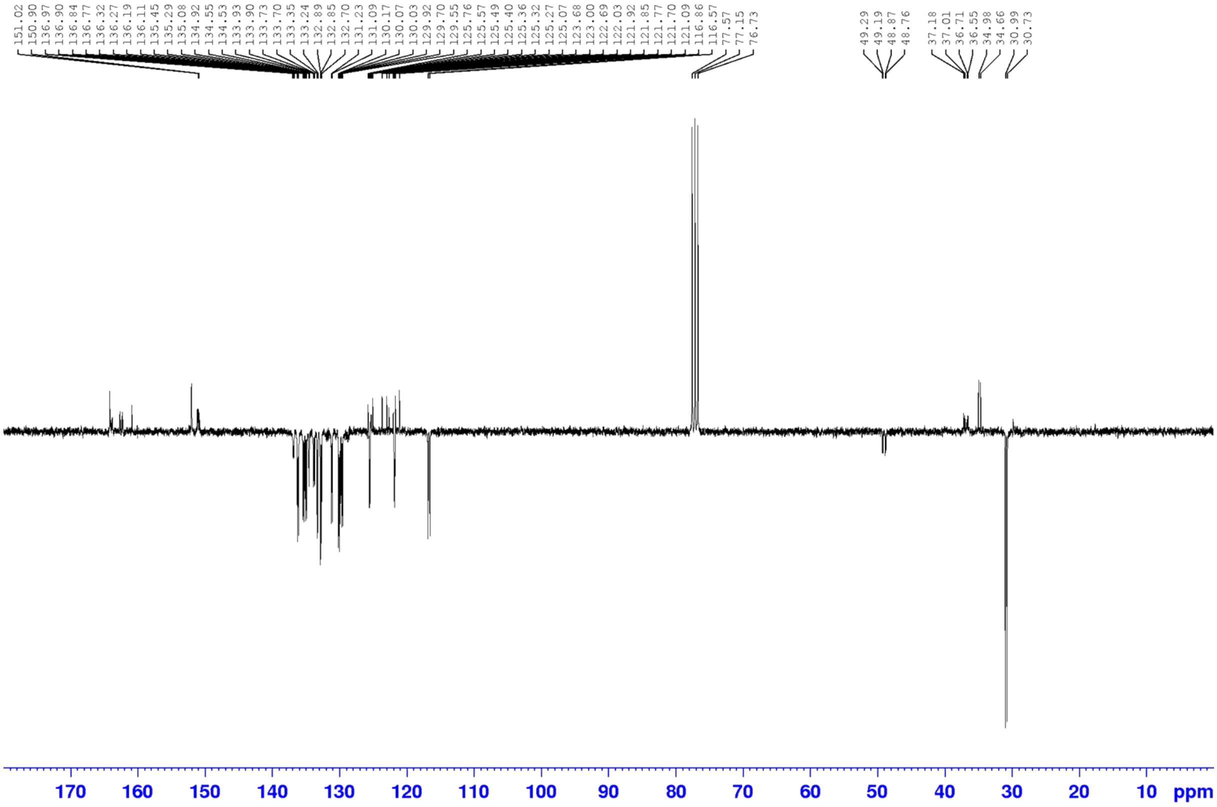
[13]C{[1]H} Jmod NMR spectrum of complex **2h** in $CDCl_3$



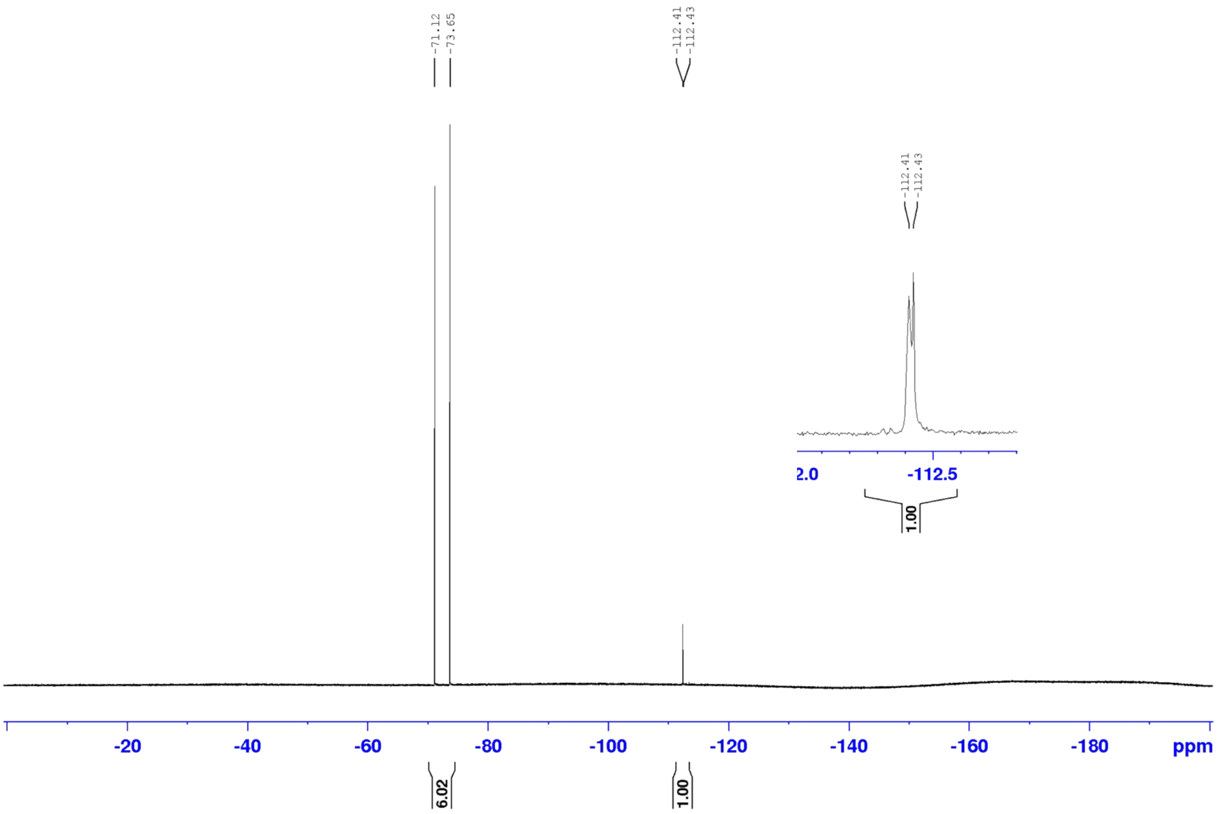

$^{31}P\{^{1}H\}$ NMR spectrum of complex **2h** in $CDCl_3$



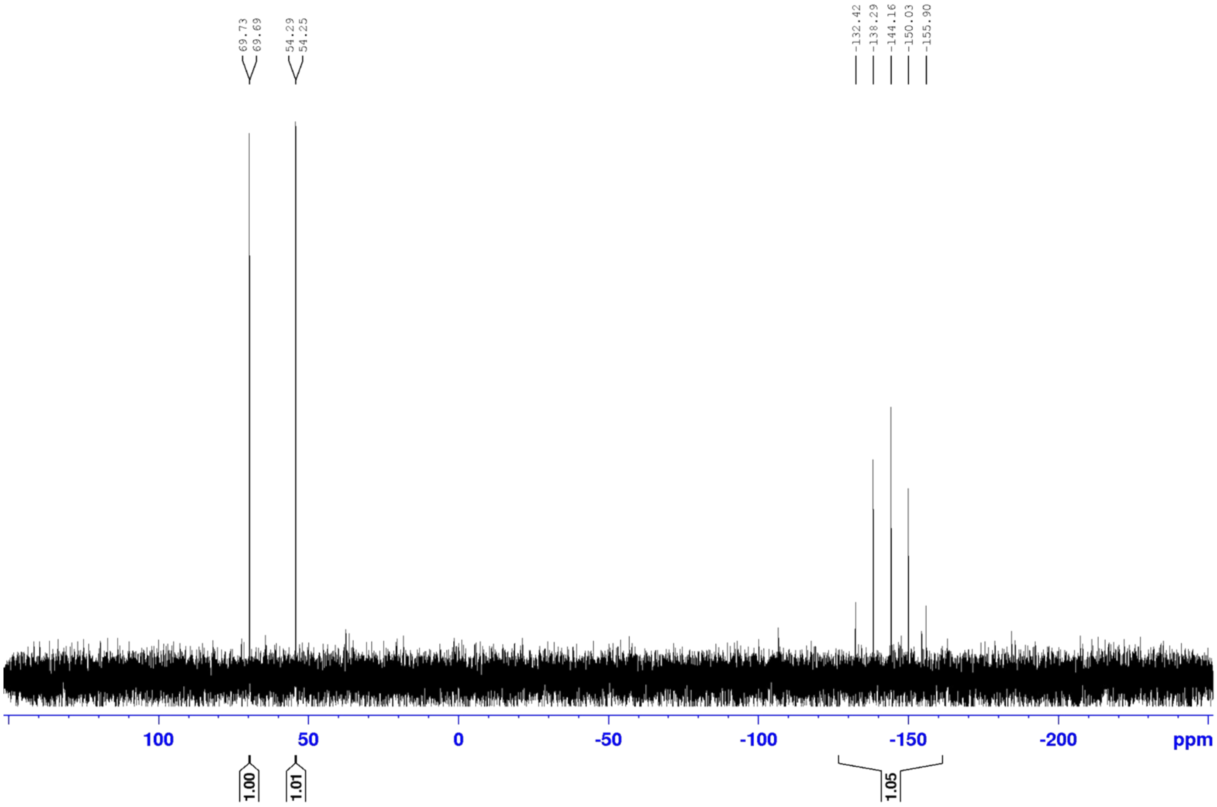

$^{1}H$ NMR spectrum of complex **2i** in $CDCl_3$



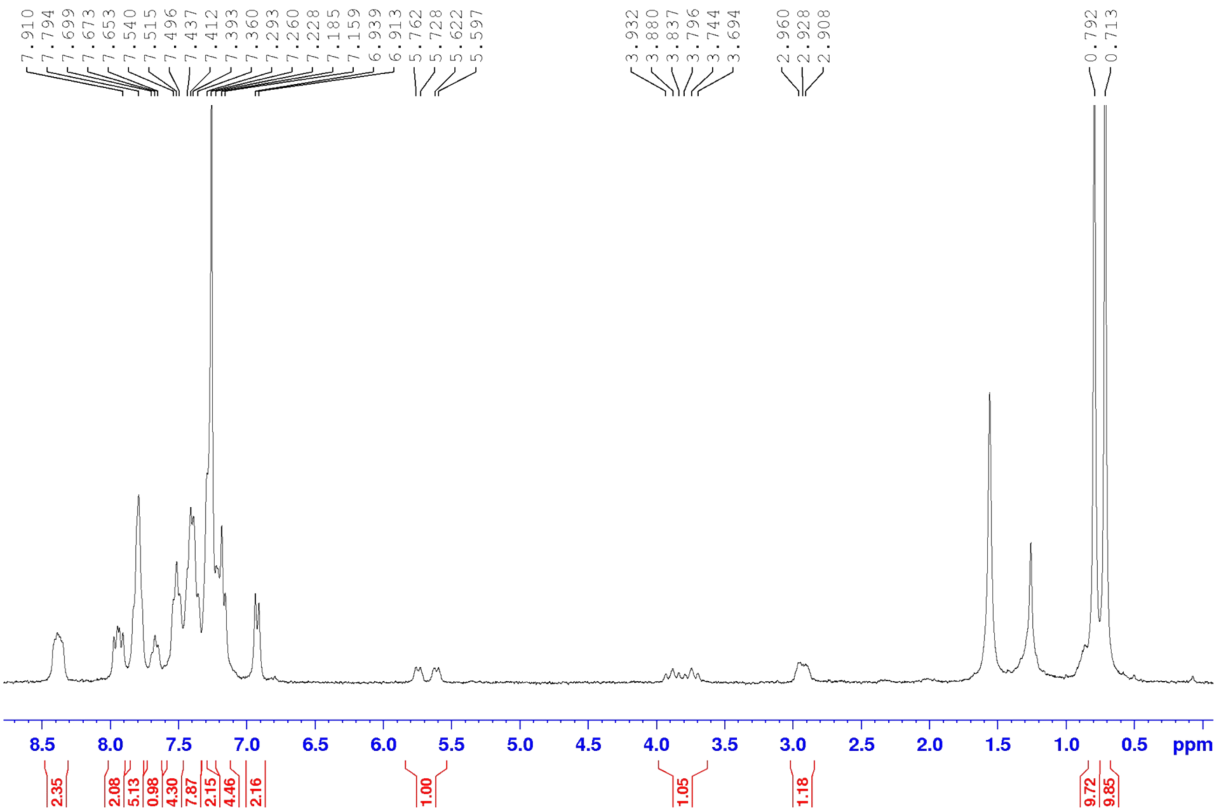

$^{13}C\{^{1}H\}$ Jmod NMR spectrum of complex **2i** in $CDCl_3$



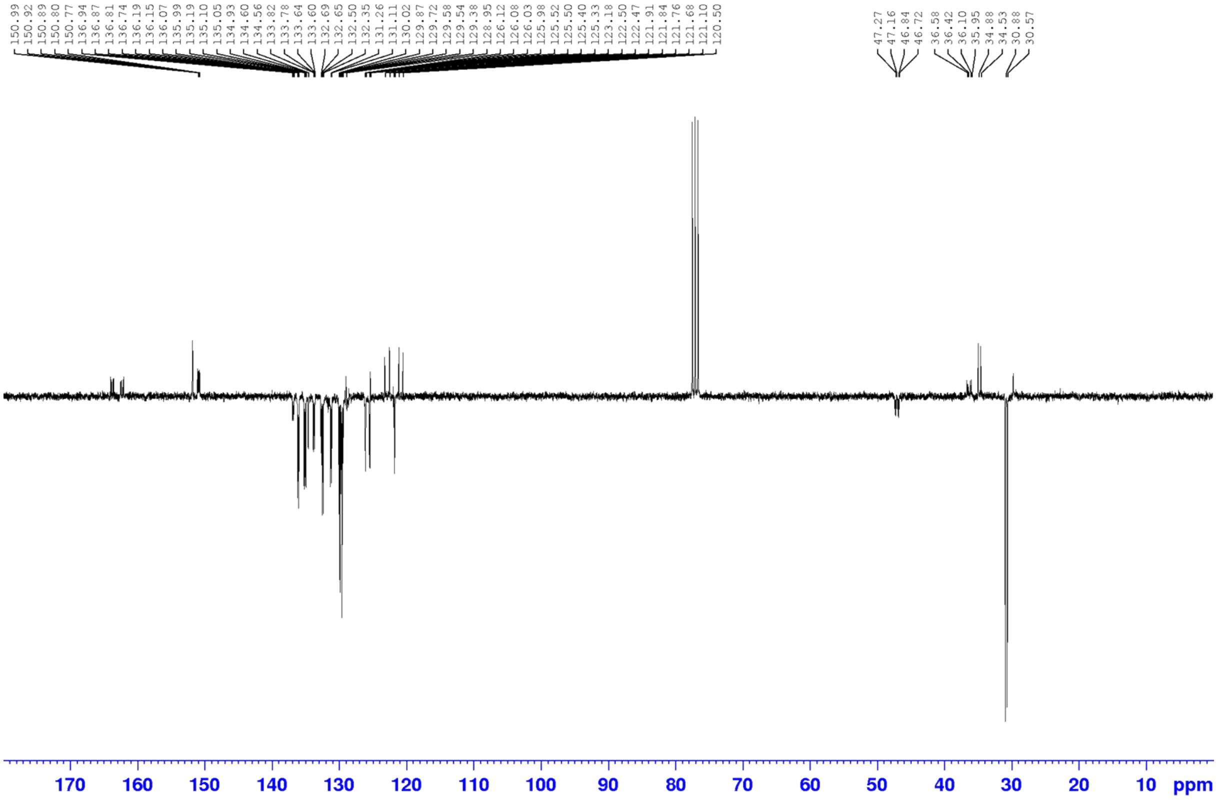

$^{19}F\{^{1}H\}$ NMR spectrum of complex **2i** in $CDCl_3$



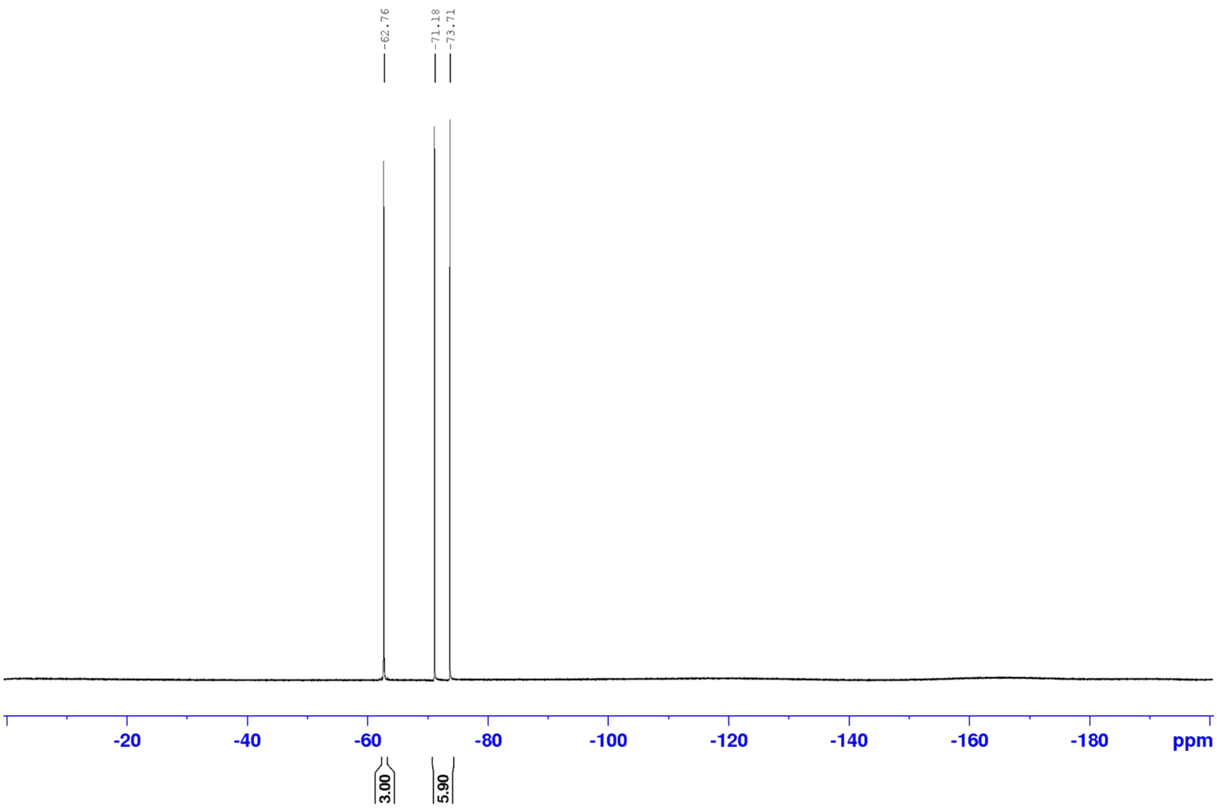

$^{31}P\{^1H\}$ NMR spectrum of complex **2i** in $CDCl_3$



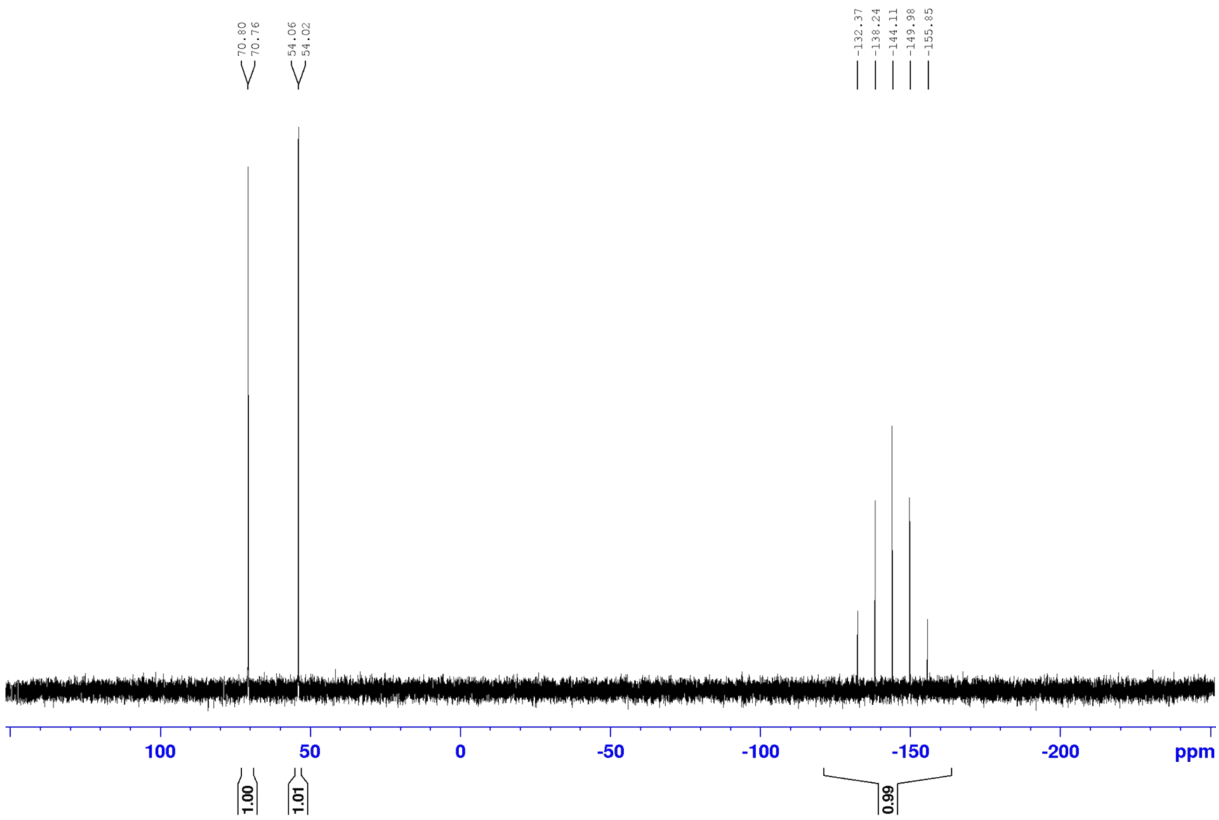

$^1H$ NMR spectrum of complex **2j** in $CDCl_3$



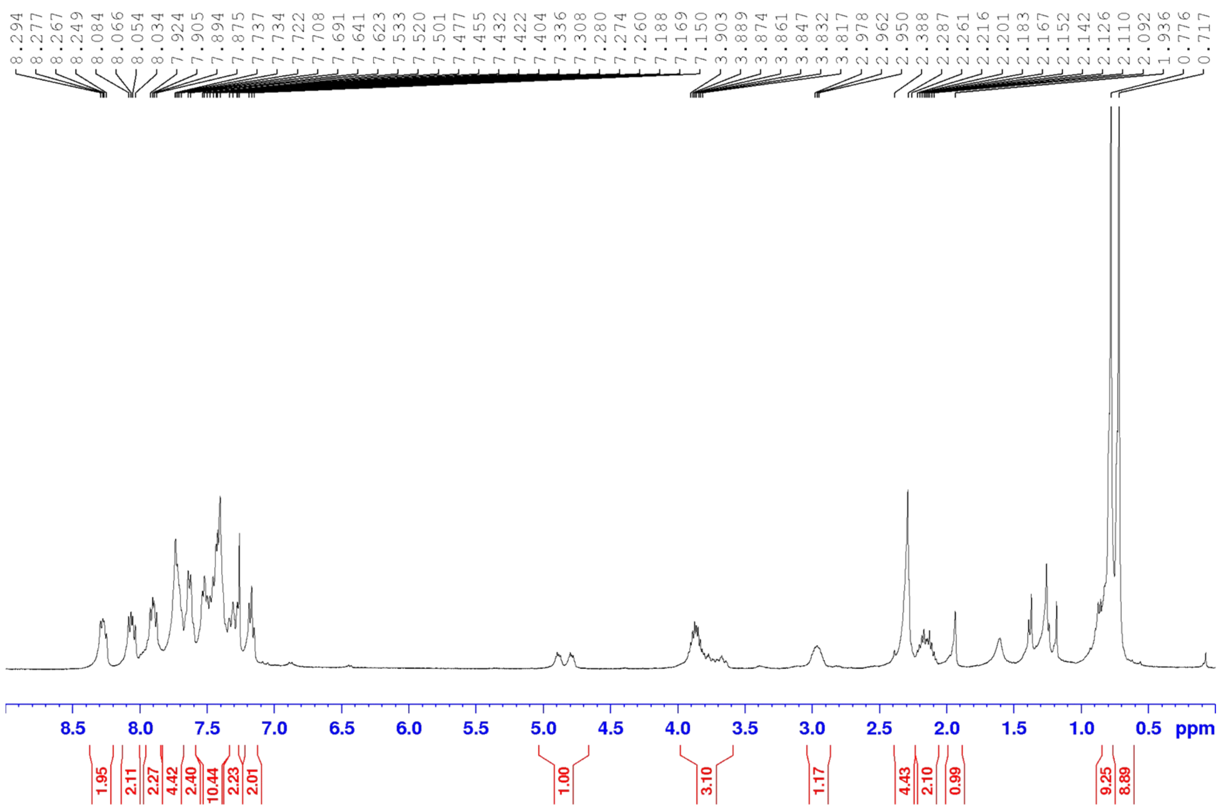

$^{13}C\{^{1}H\}$ Jmod NMR spectrum of complex **2j** in $CDCl_3$



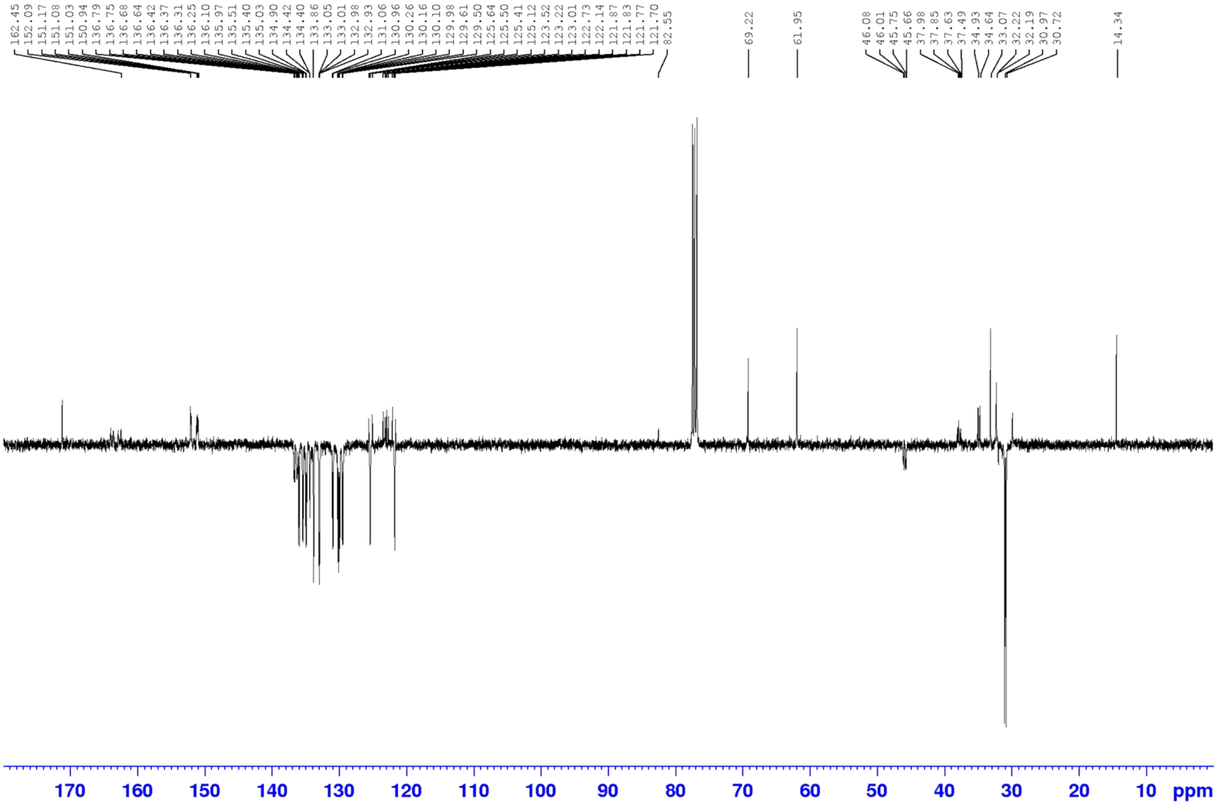

$^{19}F\{^{1}H\}$ NMR spectrum of complex **2j** in $CDCl_3$



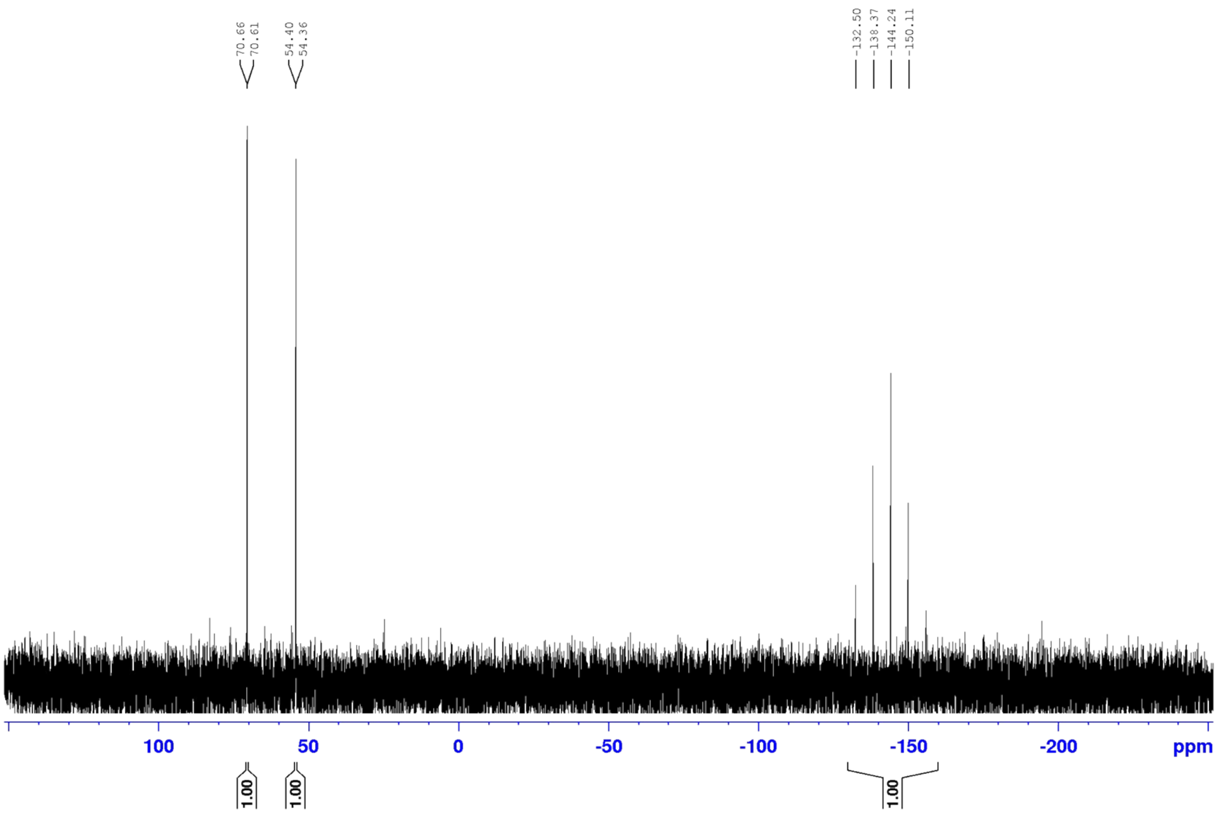
$^{31}P\{^1H\}$ NMR spectrum of complex **2j** in $CDCl_3$



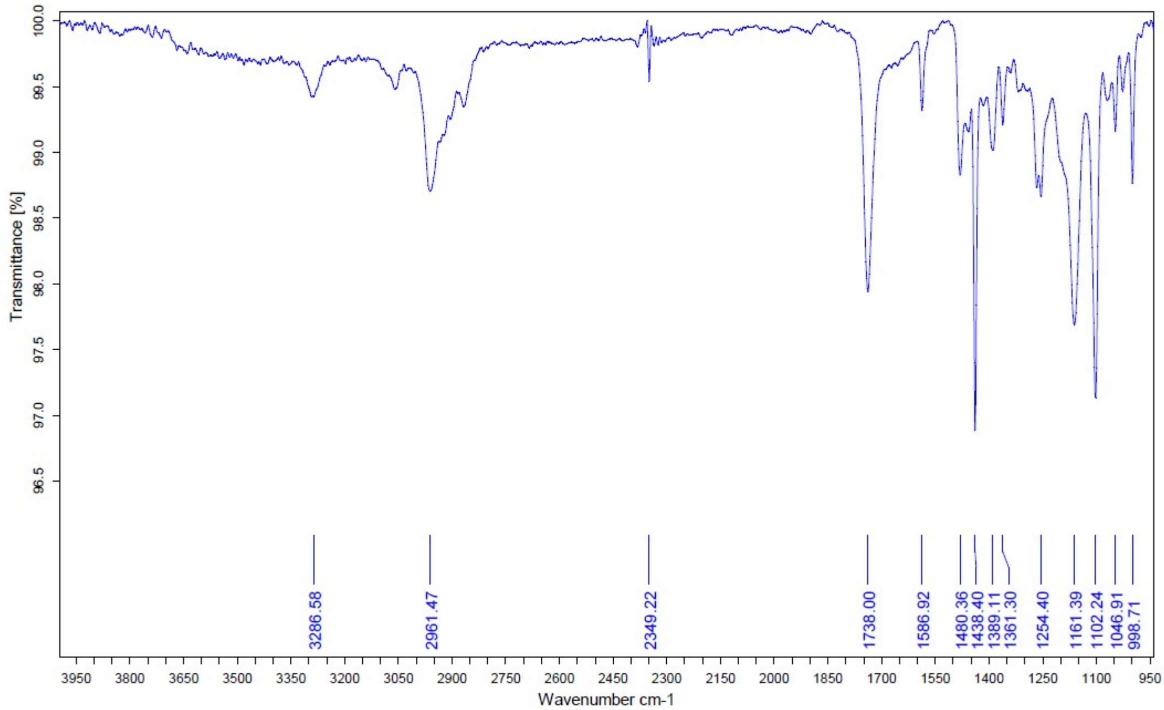
$^1H$ NMR spectrum of complex **3** in $CDCl_3$




$^{13}C\{^{1}H\}$ Jmod NMR spectrum of complex **3** in $CDCl_3$




$^{31}P\{^{1}H\}$ NMR spectrum of complex **3** in $CDCl_3$




FT-IR (ATR mode) of complex **3**.

**Table S3.** Cartesian coordinates (x,y,z) of optimized geometries of compounds studied in this work.

| | | | |
|---|---|---|---|
| **1** | | | |
| AuC46P2H46 | | | |
| Au | 0.000415 | 0.184688 | 0.067514 |
| C | 1.34158 | 1.720648 | -0.295424 |
| C | 0.727687 | 2.934975 | -0.672304 |
| C | 2.726159 | 1.640648 | -0.211202 |
| C | 1.540045 | 4.026532 | -0.977245 |
| C | -0.735715 | 2.931584 | -0.675817 |
| C | 3.555234 | 2.741325 | -0.512661 |
| H | 3.204476 | 0.713056 | 0.107286 |
| C | 2.929908 | 3.928264 | -0.902854 |
| H | 1.089728 | 4.977305 | -1.273544 |
| C | -1.345187 | 1.716243 | -0.296068 |
| C | -1.552685 | 4.016626 | -0.992147 |
| H | 3.524718 | 4.807983 | -1.150656 |
| C | -2.729763 | 1.628561 | -0.221257 |
| C | -2.942558 | 3.910709 | -0.92677 |
| H | -1.105942 | 4.967697 | -1.292844 |
| C | -3.563496 | 2.721926 | -0.535099 |
| H | -3.205739 | 0.700233 | 0.098242 |
| H | -3.540822 | 4.785342 | -1.184192 |
| C | -5.083577 | 2.567695 | -0.424713 |
| C | -5.549691 | 1.409348 | -1.321388 |
| C | -5.452001 | 2.265551 | 1.037013 |
| C | -5.820927 | 3.836957 | -0.857522 |
| H | -5.294539 | 1.598523 | -2.375815 |
| H | -5.094005 | 0.450659 | -1.030365 |
| H | -6.642722 | 1.29106 | -1.251718 |
| H | -5.135598 | 3.085884 | 1.699791 |
| H | -6.54273 | 2.146735 | 1.138424 |
| H | -4.980636 | 1.33909 | 1.398025 |
| H | -6.906995 | 3.680672 | -0.771198 |
| H | -5.560731 | 4.699437 | -0.225025 |
| H | -5.605413 | 4.099724 | -1.904695 |
| C | 5.075317 | 2.599933 | -0.386669 |
| C | 5.430138 | 2.314738 | 1.08186 |
| C | 5.560376 | 1.437192 | -1.267062 |
| C | 5.807255 | 3.870836 | -0.823958 |
| H | 5.100588 | 3.139226 | 1.732947 |
| H | 4.961009 | 1.388404 | 1.446017 |
| H | 6.520523 | 2.204691 | 1.196435 |
| H | 5.312708 | 1.612634 | -2.325618 |
| H | 6.653791 | 1.330166 | -1.186468 |
| H | 5.111479 | 0.477575 | -0.969246 |
| H | 6.893668 | 3.722429 | -0.728579 |
| H | 5.597326 | 4.124051 | -1.874631 |
| H | 5.537252 | 4.736513 | -0.200051 |
| P | 1.612583 | -1.61211 | 0.428099 |
| P | -1.612049 | -1.601492 | 0.454106 |
| C | -0.667647 | -2.998288 | 1.141026 |
| C | 0.669152 | -3.005841 | 1.123365 |
| C | -2.407882 | -2.254002 | -1.045176 |
| C | -2.873581 | -3.577201 | -1.10233 |
| C | -2.541952 | -1.421546 | -2.165044 |
| C | -3.473949 | -4.052712 | -2.265359 |
| H | -2.771422 | -4.247279 | -0.245761 |
| C | -3.146317 | -1.905488 | -3.324269 |
| H | -2.173784 | -0.393118 | -2.135413 |
| C | -3.61239 | -3.218086 | -3.375112 |
| H | -3.83391 | -5.083187 | -2.304511 |
| H | -3.247789 | -1.251176 | -4.192834 |
| H | -4.082628 | -3.595861 | -4.285968 |
| C | -2.895313 | -1.291779 | 1.707324 |
| C | -4.208818 | -1.755538 | 1.567706 |
| C | -2.520792 | -0.582007 | 2.857117 |
| C | -5.135695 | -1.520346 | 2.582959 |
| H | -4.514521 | -2.294625 | 0.668193 |
| C | -3.451192 | -0.354237 | 3.867139 |
| H | -1.502202 | -0.196349 | 2.957741 |
| C | -4.758127 | -0.825568 | 3.731342 |
| H | -6.160556 | -1.881314 | 2.471644 |
| H | -3.156439 | 0.200172 | 4.760783 |
| H | -5.488525 | -0.64204 | 4.522696 |
| C | 2.390908 | -2.252766 | -1.084521 |
| C | 2.870904 | -3.570409 | -1.148757 |
| C | 2.501946 | -1.416886 | -2.204114 |
| C | 3.458608 | -4.038834 | -2.320901 |
| H | 2.792307 | -4.239374 | -0.288816 |
| C | 3.094289 | -1.89359 | -3.372639 |
| H | 2.127165 | -0.39107 | -2.166328 |
| C | 3.571464 | -3.201784 | -3.431952 |
| H | 3.829689 | -5.065105 | -2.366174 |
| H | 3.178119 | -1.237 | -4.24136 |
| H | 4.031958 | -3.573945 | -4.350077 |
| C | 2.915473 | -1.331792 | 1.668669 |
| C | 4.24699 | -1.706597 | 1.454193 |
| C | 2.542622 | -0.733779 | 2.881364 |
| C | 5.194877 | -1.493629 | 2.455136 |
| H | 4.549958 | -2.160274 | 0.507894 |
| C | 3.494365 | -0.527414 | 3.875824 |
| H | 1.507524 | -0.423099 | 3.049533 |
| C | 4.820432 | -0.909098 | 3.663963 |
| H | 6.233456 | -1.785808 | 2.284866 |
| H | 3.200343 | -0.061302 | 4.818777 |
| H | 5.566841 | -0.742741 | 4.444079 |
| H | -1.224206 | -3.836742 | 1.5752 |
| H | 1.227616 | -3.850615 | 1.542665 |

| | | | |
|---|---|---|---|
| **$^{-}$S-Ph** | | | |
| C6H5S | | | |
| C | 0.599725 | 0 | 0.000034 |
| C | -0.15947 | -1.200513 | 0.00001 |
| C | -1.551359 | -1.199685 | 0.000002 |
| C | -2.270739 | 0 | 0.000001 |
| C | -1.55136 | 1.199684 | 0.000001 |
| C | -0.15947 | 1.200513 | 0.000009 |
| H | 0.388422 | -2.147652 | -0.000001 |
| H | -2.086621 | -2.155484 | -0.000009 |
| H | -3.363831 | 0 | -0.00001 |
| H | -2.08662 | 2.155484 | -0.000011 |
| H | 0.38842 | 2.147653 | -0.000003 |
| S | 2.332267 | 0 | -0.000019 |

| | | | |
|---|---|---|---|
| **HS-Ph** | | | |
| C6H6S | | | |
| C | -0.513469 | 0.000733 | 0.000882 |
| C | 0.191698 | 1.211088 | 0.00024 |
| C | 1.585265 | 1.206378 | -0.000041 |
| C | 2.292121 | 0.004061 | -0.000256 |
| C | 1.589123 | -1.200734 | -0.000261 |
| C | 0.19618 | -1.207939 | 0.000433 |
| H | -0.347771 | 2.161608 | 0.000107 |

| | | | |
|---|---|---|---|
| H | 2.122081 | 2.158507 | -0.000275 |
| H | 3.384373 | 0.006101 | -0.000629 |
| H | 2.128749 | -2.151228 | -0.000492 |
| H | -0.343924 | -2.158398 | 0.000764 |
| S | -2.279933 | -0.083967 | -0.000355 |
| H | -2.510087 | 1.245361 | 0.000227 |

**1-SPh**

AuC52P2H51 S

| | | | |
|---|---|---|---|
| Au | -0.477818 | 0.499254 | -0.089703 |
| C | -2.236698 | 1.378093 | -0.764237 |
| C | -2.100664 | 2.747487 | -1.087784 |
| C | -3.460786 | 0.749434 | -0.970805 |
| C | -3.212521 | 3.442271 | -1.565162 |
| C | -0.761462 | 3.317105 | -0.916288 |
| C | -4.58911 | 1.44024 | -1.46197 |
| H | -3.558511 | -0.317012 | -0.760808 |
| C | -4.438023 | 2.800641 | -1.742723 |
| H | -3.128637 | 4.502497 | -1.817969 |
| C | 0.245019 | 2.410044 | -0.515433 |
| C | -0.425504 | 4.657019 | -1.114642 |
| H | -5.279028 | 3.383807 | -2.11978 |
| C | 1.540725 | 2.878459 | -0.319401 |
| C | 0.879003 | 5.107061 | -0.910303 |
| H | -1.190424 | 5.374317 | -1.423712 |
| C | 1.890257 | 4.232176 | -0.504799 |
| H | 2.327079 | 2.185563 | -0.014861 |
| H | 1.094351 | 6.164347 | -1.070025 |
| C | 3.334552 | 4.683427 | -0.262027 |
| C | 3.74291 | 4.341082 | 1.179834 |
| C | 4.264276 | 3.953061 | -1.243538 |
| C | 3.507752 | 6.190732 | -0.463556 |
| H | 3.091185 | 4.851864 | 1.905997 |
| H | 3.686449 | 3.260364 | 1.37872 |
| H | 4.780427 | 4.660635 | 1.369174 |
| H | 4.000802 | 4.192087 | -2.285798 |
| H | 5.310948 | 4.256508 | -1.0781 |
| H | 4.209345 | 2.860772 | -1.126407 |
| H | 4.554874 | 6.471845 | -0.272111 |
| H | 3.266239 | 6.497998 | -1.492749 |
| H | 2.876176 | 6.772291 | 0.22581 |
| C | -5.908267 | 0.690574 | -1.67896 |
| C | -5.696399 | -0.404755 | -2.736235 |
| C | -6.359937 | 0.045501 | -0.359242 |
| C | -7.0242 | 1.619603 | -2.163373 |
| H | -5.380749 | 0.032438 | -3.696484 |
| H | -4.930025 | -1.13032 | -2.425617 |
| H | -6.633307 | -0.960046 | -2.90569 |
| H | -6.500918 | 0.806303 | 0.424635 |
| H | -7.318086 | -0.480352 | -0.499587 |
| H | -5.631499 | -0.693321 | 0.006649 |
| H | -7.952007 | 1.04286 | -2.299674 |
| H | -7.23468 | 2.42134 | -1.438573 |
| H | -6.780399 | 2.085875 | -3.130338 |
| P | -1.348737 | -1.561382 | 0.870678 |
| C | 1.280994 | -2.401061 | 0.505007 |
| C | 0.007553 | -2.582958 | 1.193495 |
| C | 2.163459 | -0.190143 | 2.208463 |
| C | 3.028299 | -1.041307 | 2.913389 |
| C | 1.705585 | 0.981092 | 2.826903 |
| C | 3.42865 | -0.720828 | 4.208578 |
| H | 3.394603 | -1.96494 | 2.458696 |
| C | 2.111732 | 1.299721 | 4.122495 |
| H | 1.022248 | 1.648251 | 2.295534 |
| C | 2.973059 | 0.450704 | 4.814852 |
| H | 4.100648 | -1.392776 | 4.747759 |
| H | 1.744918 | 2.21507 | 4.592619 |
| H | 3.287878 | 0.698627 | 5.831426 |
| C | 3.013355 | -0.214217 | -0.599731 |
| C | 4.340511 | -0.20358 | -0.151415 |
| C | 2.744123 | 0.036097 | -1.952852 |
| C | 5.381925 | 0.037271 | -1.047112 |
| H | 4.569353 | -0.376557 | 0.902185 |
| C | 3.786748 | 0.279056 | -2.843398 |
| H | 1.711661 | 0.051312 | -2.309788 |
| C | 5.107322 | 0.275428 | -2.393048 |
| H | 6.413445 | 0.042201 | -0.687138 |
| H | 3.565062 | 0.478032 | -3.894579 |
| H | 5.924555 | 0.4692 | -3.092143 |
| C | -2.153859 | -1.088324 | 2.459079 |
| C | -1.55309 | -1.474013 | 3.66211 |
| C | -3.311871 | -0.297353 | 2.498839 |
| C | -2.110564 | -1.097945 | 4.884559 |
| H | -0.634001 | -2.06564 | 3.620845 |
| C | -3.86475 | 0.081256 | 3.720458 |
| H | -3.784661 | 0.035355 | 1.572074 |
| C | -3.267532 | -0.320919 | 4.91671 |
| H | -1.633419 | -1.410582 | 5.816984 |
| H | -4.765745 | 0.699674 | 3.737572 |
| H | -3.702028 | -0.021256 | 5.873803 |
| C | -2.663077 | -2.4785 | -0.040661 |
| C | -3.799655 | -3.010721 | 0.580618 |
| C | -2.428147 | -2.77083 | -1.393081 |
| C | -4.684183 | -3.818253 | -0.138094 |
| H | -3.99626 | -2.80163 | 1.634811 |
| C | -3.314135 | -3.57025 | -2.109213 |
| H | -1.534663 | -2.37494 | -1.885816 |
| C | -4.44548 | -4.098404 | -1.481866 |
| H | -5.56462 | -4.231798 | 0.360406 |
| H | -3.120188 | -3.785603 | -3.162907 |
| H | -5.139198 | -4.72942 | -2.042895 |
| H | 2.118449 | -2.89974 | 1.017828 |
| H | -0.202273 | -3.573248 | 1.614601 |
| S | 1.360905 | -3.118298 | -1.262759 |
| C | 3.039473 | -3.661618 | -1.462031 |
| C | 3.644404 | -4.504042 | -0.516299 |
| C | 3.754544 | -3.309326 | -2.614419 |
| C | 4.949024 | -4.955333 | -0.707365 |
| H | 3.082831 | -4.826235 | 0.36449 |
| C | 5.049665 | -3.785782 | -2.813298 |
| H | 3.289542 | -2.653894 | -3.353382 |
| C | 5.655992 | -4.600727 | -1.857312 |
| H | 5.409031 | -5.606828 | 0.040251 |
| H | 5.592867 | -3.506846 | -3.719971 |
| H | 6.674658 | -4.965137 | -2.010666 |
| P | 1.608927 | -0.577439 | 0.51286 |

**2f**

AuC52P2H52S

| | | | |
|---|---|---|---|
| Au | 0.240409 | -0.890448 | -0.029409 |
| C | 1.838149 | -2.201999 | 0.100835 |
| C | 1.454044 | -3.552325 | 0.258563 |
| C | 3.18535 | -1.859115 | 0.110817 |
| C | 2.450106 | -4.513443 | 0.42852 |
| C | 0.014091 | -3.813036 | 0.218303 |
| C | 4.198787 | -2.825449 | 0.284716 |
| H | 3.488525 | -0.82061 | -0.031717 |

| | | | |
|---|---|---|---|
| C | 3.79831 | -4.154371 | 0.443396 |
| H | 2.17969 | -5.564798 | 0.55519 |
| C | -0.808169 | -2.676413 | 0.065609 |
| C | -0.589179 | -5.068148 | 0.290355 |
| H | 4.541811 | -4.940156 | 0.581717 |
| C | -2.185263 | -2.826733 | -0.037224 |
| C | -1.975049 | -5.202636 | 0.201408 |
| H | 0.024328 | -5.964784 | 0.409967 |
| C | -2.804064 | -4.091329 | 0.027842 |
| H | -2.824024 | -1.952771 | -0.179239 |
| H | -2.402733 | -6.204011 | 0.261364 |
| C | -4.327375 | -4.194599 | -0.095976 |
| C | -4.990492 | -3.37799 | 1.02508 |
| C | -4.762684 | -3.639 | -1.461532 |
| C | -4.813087 | -5.641632 | 0.011449 |
| H | -4.698064 | -3.758466 | 2.01626 |
| H | -4.717966 | -2.312307 | 0.978663 |
| H | -6.087331 | -3.444083 | 0.944931 |
| H | -4.301124 | -4.209033 | -2.282847 |
| H | -5.856928 | -3.710839 | -1.569765 |
| H | -4.484702 | -2.581693 | -1.586028 |
| H | -5.909258 | -5.670644 | -0.084048 |
| H | -4.394622 | -6.275515 | -0.785452 |
| H | -4.553175 | -6.091031 | 0.982328 |
| C | 5.668057 | -2.392643 | 0.281707 |
| C | 6.007408 | -1.776701 | -1.084751 |
| C | 5.900075 | -1.350265 | 1.386972 |
| C | 6.611986 | -3.571368 | 0.529392 |
| H | 5.859648 | -2.50932 | -1.893446 |
| H | 5.382973 | -0.898523 | -1.306866 |
| H | 7.060418 | -1.452571 | -1.10619 |
| H | 5.657846 | -1.765308 | 2.377905 |
| H | 6.956216 | -1.037078 | 1.397902 |
| H | 5.28908 | -0.447043 | 1.239225 |
| H | 7.653861 | -3.216315 | 0.527654 |
| H | 6.425019 | -4.048569 | 1.503855 |
| H | 6.523987 | -4.340116 | -0.253595 |
| P | 1.472789 | 1.199173 | -0.255963 |
| C | -1.061132 | 2.347985 | -0.193181 |
| C | 0.240334 | 2.363489 | -0.979257 |
| C | -2.638122 | 0.59567 | 1.553693 |
| C | -3.545323 | 1.622944 | 1.865454 |
| C | -2.411739 | -0.431114 | 2.48166 |
| C | -4.218697 | 1.609536 | 3.084427 |
| H | -3.719972 | 2.438578 | 1.158683 |
| C | -3.091931 | -0.436265 | 3.698314 |
| H | -1.704421 | -1.232586 | 2.257094 |
| C | -3.99579 | 0.58049 | 3.999928 |
| H | -4.923375 | 2.410672 | 3.318835 |
| H | -2.908974 | -1.241012 | 4.4137 |
| H | -4.527365 | 0.574134 | 4.954459 |
| C | -2.842796 | 0.341077 | -1.411208 |
| C | -4.23175 | 0.463987 | -1.282311 |
| C | -2.284857 | 0.022886 | -2.659146 |
| C | -5.05022 | 0.2858 | -2.396527 |
| H | -4.682159 | 0.688386 | -0.313308 |
| C | -3.108615 | -0.146154 | -3.76845 |
| H | -1.204403 | -0.110495 | -2.767379 |
| C | -4.491442 | -0.012972 | -3.638241 |
| H | -6.133177 | 0.379211 | -2.289613 |
| H | -2.668603 | -0.39391 | -4.736873 |
| H | -5.137198 | -0.152827 | -4.508237 |
| C | 1.997992 | 1.917899 | 1.328077 |
| C | 2.053813 | 3.307639 | 1.517355 |
| C | 2.354595 | 1.061653 | 2.380377 |
| C | 2.46624 | 3.828298 | 2.741754 |
| H | 1.77743 | 3.996402 | 0.715518 |
| C | 2.772456 | 1.590421 | 3.600347 |
| H | 2.310177 | -0.02274 | 2.249256 |
| C | 2.827609 | 2.971599 | 3.781999 |
| H | 2.50444 | 4.910876 | 2.882166 |
| H | 3.050897 | 0.916722 | 4.413633 |
| H | 3.15013 | 3.384131 | 4.740846 |
| C | 2.864123 | 1.271247 | -1.425266 |
| C | 4.02275 | 2.009762 | -1.155917 |
| C | 2.731262 | 0.59785 | -2.648429 |
| C | 5.03382 | 2.083814 | -2.113774 |
| H | 4.140285 | 2.527236 | -0.200887 |
| C | 3.743334 | 0.680811 | -3.600538 |
| H | 1.840158 | -0.0025 | -2.855294 |
| C | 4.893636 | 1.42588 | -3.334759 |
| H | 5.937046 | 2.660038 | -1.90087 |
| H | 3.636761 | 0.154571 | -4.551667 |
| H | 5.688649 | 1.486222 | -4.081602 |
| H | -0.882707 | 2.685075 | 0.842189 |
| H | 0.657201 | 3.381848 | -1.030793 |
| S | -2.321739 | 3.44866 | -0.936365 |
| C | -1.621457 | 5.034975 | -0.518583 |
| C | -1.133607 | 5.850479 | -1.545286 |
| C | -1.607218 | 5.490904 | 0.805506 |
| C | -0.631033 | 7.117012 | -1.245827 |
| H | -1.152446 | 5.490213 | -2.576459 |
| C | -1.087446 | 6.749579 | 1.098646 |
| H | -2.007738 | 4.862222 | 1.605032 |
| C | -0.602562 | 7.564947 | 0.074043 |
| H | -0.256079 | 7.753873 | -2.05056 |
| H | -1.074668 | 7.101843 | 2.132881 |
| H | -0.205048 | 8.555655 | 0.306705 |
| H | 0.076236 | 2.036786 | -2.019456 |
| P | -1.70895 | 0.597238 | -0.009554 |

**dppv**

$C_{26}P_2H_{22}$

| | | | |
|---|---|---|---|
| P | 1.601528 | -0.462015 | 0.547104 |
| P | -1.769389 | -0.660028 | 0.656371 |
| C | -0.768919 | -1.056353 | -0.831731 |
| C | 0.570436 | -0.970294 | -0.878777 |
| C | -1.985898 | 1.160453 | 0.455741 |
| C | -2.477865 | 1.75011 | -0.719217 |
| C | -1.596294 | 1.984587 | 1.517801 |
| C | -2.575599 | 3.135192 | -0.825089 |
| H | -2.790384 | 1.119799 | -1.556319 |
| C | -1.694319 | 3.373493 | 1.411483 |
| H | -1.205674 | 1.533033 | 2.43389 |
| C | -2.182677 | 3.949266 | 0.240704 |
| H | -2.960152 | 3.584577 | -1.744343 |
| H | -1.385017 | 4.005864 | 2.247307 |
| H | -2.25888 | 5.03619 | 0.155152 |
| C | -3.404369 | -1.320279 | 0.133854 |
| C | -4.595732 | -0.63143 | 0.404538 |
| C | -3.486252 | -2.606354 | -0.422218 |
| C | -5.83164 | -1.204298 | 0.106927 |
| H | -4.559387 | 0.367891 | 0.846019 |
| C | -4.722769 | -3.17556 | -0.724057 |
| H | -2.574632 | -3.177821 | -0.621276 |
| C | -5.900707 | -2.476133 | -0.461779 |
| H | -6.748699 | -0.648617 | 0.319407 |

| | | | |
|---|---|---|---|
| H | -4.764301 | -4.175239 | -1.164206 |
| H | -6.870035 | -2.922407 | -0.69697 |
| C | 2.22231 | 1.179639 | -0.016861 |
| C | 1.475058 | 2.006627 | -0.865822 |
| C | 3.422611 | 1.673415 | 0.518738 |
| C | 1.923323 | 3.290171 | -1.18135 |
| H | 0.530438 | 1.648761 | -1.28324 |
| C | 3.870858 | 2.952598 | 0.197621 |
| H | 4.018248 | 1.04859 | 1.190678 |
| C | 3.122567 | 3.766747 | -0.654676 |
| H | 1.327256 | 3.91984 | -1.847 |
| H | 4.81146 | 3.317216 | 0.618664 |
| H | 3.47411 | 4.770749 | -0.904984 |
| C | 3.073561 | -1.537819 | 0.260441 |
| C | 3.919534 | -1.410379 | -0.851482 |
| C | 3.326979 | -2.553033 | 1.191427 |
| C | 4.991309 | -2.282796 | -1.02719 |
| H | 3.742832 | -0.616296 | -1.582483 |
| C | 4.399999 | -3.42838 | 1.014966 |
| H | 2.676626 | -2.656965 | 2.064731 |
| C | 5.232952 | -3.293886 | -0.094275 |
| H | 5.644114 | -2.173376 | -1.897075 |
| H | 4.586636 | -4.215381 | 1.749994 |
| H | 6.075595 | -3.976019 | -0.232931 |
| H | 1.085207 | -1.22384 | -1.815809 |
| H | -1.308208 | -1.387714 | -1.729621 |

**dppv-HSPh**

C32P2H28S

| | | | |
|---|---|---|---|
| P | 1.747462 | 1.200269 | -0.992636 |
| P | -1.610344 | 0.894899 | -0.996651 |
| C | -0.516975 | -0.146371 | 0.12322 |
| C | 0.772944 | 0.58848 | 0.483962 |
| C | -3.102993 | -0.140324 | -1.250688 |
| C | -3.072333 | -1.542105 | -1.223169 |
| C | -4.288739 | 0.493929 | -1.657061 |
| C | -4.198955 | -2.28512 | -1.575717 |
| H | -2.168993 | -2.07321 | -0.91664 |
| C | -5.415119 | -0.249861 | -2.001421 |
| H | -4.334907 | 1.585784 | -1.702514 |
| C | -5.374969 | -1.644052 | -1.961795 |
| H | -4.154902 | -3.376631 | -1.541428 |
| H | -6.329614 | 0.265198 | -2.306419 |
| H | -6.257387 | -2.228586 | -2.233268 |
| C | -2.181022 | 2.221316 | 0.144375 |
| C | -3.225653 | 2.078165 | 1.070128 |
| C | -1.501888 | 3.446632 | 0.072293 |
| C | -3.573755 | 3.135396 | 1.908366 |
| H | -3.773734 | 1.134911 | 1.131964 |
| C | -1.844616 | 4.500524 | 0.919997 |
| H | -0.697907 | 3.57397 | -0.658928 |
| C | -2.882289 | 4.346231 | 1.837917 |
| H | -4.389911 | 3.012033 | 2.624784 |
| H | -1.304782 | 5.448437 | 0.854261 |
| H | -3.158111 | 5.172942 | 2.497454 |
| C | 2.059262 | -0.403227 | -1.853237 |
| C | 2.87935 | -1.411705 | -1.32435 |
| C | 1.416021 | -0.626675 | -3.078109 |
| C | 3.04439 | -2.617542 | -2.003453 |
| H | 3.400111 | -1.24875 | -0.37645 |
| C | 1.577487 | -1.836684 | -3.755728 |
| H | 0.78084 | 0.156153 | -3.502164 |
| C | 2.391501 | -2.832908 | -3.219404 |
| H | 3.689113 | -3.393947 | -1.583281 |
| H | 1.068606 | -1.997527 | -4.709441 |
| H | 2.523156 | -3.778665 | -3.751094 |
| C | 3.386947 | 1.528204 | -0.222017 |
| C | 4.496148 | 1.657125 | -1.075285 |
| C | 3.568704 | 1.767428 | 1.146981 |
| C | 5.750223 | 1.991304 | -0.572366 |
| H | 4.376421 | 1.487648 | -2.149707 |
| C | 4.825556 | 2.112415 | 1.649137 |
| H | 2.730318 | 1.688051 | 1.842149 |
| C | 5.92006 | 2.221796 | 0.794628 |
| H | 6.60114 | 2.077037 | -1.253089 |
| H | 4.945901 | 2.29267 | 2.720511 |
| H | 6.903269 | 2.488421 | 1.190005 |
| H | 1.406228 | -0.076142 | 1.094929 |
| H | 0.527216 | 1.46707 | 1.103471 |
| H | -0.282142 | -1.02869 | -0.495678 |
| S | -1.387289 | -0.707488 | 1.623441 |
| C | -0.410626 | -2.055892 | 2.230289 |
| C | -0.66665 | -2.452017 | 3.553173 |
| C | 0.542085 | -2.759198 | 1.482017 |
| C | 0.009436 | -3.534554 | 4.107771 |
| H | -1.400755 | -1.902676 | 4.148902 |
| C | 1.223678 | -3.835041 | 2.052479 |
| H | 0.766666 | -2.481075 | 0.450632 |
| C | 0.961913 | -4.231859 | 3.362222 |
| H | -0.205585 | -3.82968 | 5.137978 |
| H | 1.967204 | -4.368957 | 1.454909 |
| H | 1.497653 | -5.076367 | 3.801468 |

**TS1**

AuC52P2H51S

| | | | |
|---|---|---|---|
| Au | 0.356494 | 0.590417 | -0.129438 |
| C | -0.530038 | 2.363925 | -0.754911 |
| C | 0.366154 | 3.264664 | -1.361981 |
| C | -1.853374 | 2.748814 | -0.537807 |
| C | -0.108351 | 4.514816 | -1.772383 |
| C | 1.749913 | 2.802773 | -1.484732 |
| C | -2.335293 | 4.011418 | -0.925961 |
| H | -2.547122 | 2.058184 | -0.061627 |
| C | -1.434305 | 4.876638 | -1.561063 |
| H | 0.567653 | 5.225911 | -2.25416 |
| C | 2.024202 | 1.52912 | -0.936737 |
| C | 2.786029 | 3.514189 | -2.088725 |
| H | -1.765708 | 5.863478 | -1.893632 |
| C | 3.309967 | 1.007745 | -1.028789 |
| C | 4.073899 | 2.982897 | -2.159371 |
| H | 2.595102 | 4.500305 | -2.52001 |
| C | 4.366037 | 1.721102 | -1.636768 |
| H | 3.520094 | 0.012237 | -0.634223 |
| H | 4.853229 | 3.574947 | -2.640468 |
| C | 5.764424 | 1.098993 | -1.705416 |
| C | 6.266846 | 0.816562 | -0.280459 |
| C | 5.694852 | -0.215946 | -2.497698 |
| C | 6.772291 | 2.022729 | -2.393689 |
| H | 6.32836 | 1.74628 | 0.306831 |
| H | 5.606567 | 0.118761 | 0.255382 |
| H | 7.271964 | 0.365766 | -0.311477 |
| H | 5.34291 | -0.036259 | -3.525561 |
| H | 6.692371 | -0.681017 | -2.554937 |
| H | 5.015426 | -0.943501 | -2.030311 |
| H | 7.759922 | 1.537042 | -2.419648 |
| H | 6.484442 | 2.242653 | -3.433276 |
| H | 6.886901 | 2.978247 | -1.858786 |
| C | -3.786073 | 4.448539 | -0.693904 |

| | | | |
|---|---|---|---|
| C | -4.476309 | 4.62785 | -2.056041 |
| C | -4.577446 | 3.422275 | 0.120384 |
| C | -3.806127 | 5.782583 | 0.069218 |
| H | -3.966706 | 5.382491 | -2.674213 |
| H | -4.486026 | 3.681397 | -2.618705 |
| H | -5.519898 | 4.954406 | -1.918234 |
| H | -4.129309 | 3.254197 | 1.112221 |
| H | -5.603678 | 3.788476 | 0.27798 |
| H | -4.649861 | 2.451364 | -0.392133 |
| H | -4.845111 | 6.105545 | 0.243036 |
| H | -3.312061 | 5.684187 | 1.048509 |
| H | -3.298329 | 6.585485 | -0.485449 |
| P | -1.61088 | -0.594289 | 0.671449 |
| P | 1.417387 | -1.34209 | 0.955524 |
| C | 0.161644 | -2.575476 | 1.164424 |
| C | -1.102927 | -2.342156 | 0.66664 |
| C | 2.041555 | -0.78556 | 2.582699 |
| C | 1.692743 | -1.481354 | 3.745983 |
| C | 2.852483 | 0.354644 | 2.676275 |
| C | 2.163124 | -1.051993 | 4.986327 |
| H | 1.039666 | -2.355089 | 3.676843 |
| C | 3.322591 | 0.778272 | 3.91808 |
| H | 3.11357 | 0.919821 | 1.777209 |
| C | 2.97991 | 0.07514 | 5.073724 |
| H | 1.885511 | -1.599931 | 5.890068 |
| H | 3.953497 | 1.667977 | 3.982976 |
| H | 3.345014 | 0.412174 | 6.047039 |
| C | 2.811752 | -2.23832 | 0.179927 |
| C | 4.061804 | -2.374154 | 0.795384 |
| C | 2.566789 | -2.873421 | -1.047608 |
| C | 5.058771 | -3.139145 | 0.18782 |
| H | 4.257682 | -1.893175 | 1.756508 |
| C | 3.568804 | -3.631348 | -1.648334 |
| H | 1.577662 | -2.800733 | -1.514709 |
| C | 4.814938 | -3.766824 | -1.032382 |
| H | 6.030215 | -3.246051 | 0.676539 |
| H | 3.371447 | -4.126072 | -2.602422 |
| H | 5.597044 | -4.365744 | -1.505373 |
| C | -1.880794 | -0.173323 | 2.435421 |
| C | -2.231644 | -1.150153 | 3.377416 |
| C | -1.735484 | 1.15732 | 2.850255 |
| C | -2.44704 | -0.796537 | 4.70819 |
| H | -2.328977 | -2.196071 | 3.077957 |
| C | -1.951986 | 1.506806 | 4.182644 |
| H | -1.442105 | 1.92769 | 2.132249 |
| C | -2.309516 | 0.53164 | 5.112593 |
| H | -2.720206 | -1.565939 | 5.434381 |
| H | -1.831597 | 2.546899 | 4.494531 |
| H | -2.47448 | 0.805355 | 6.157517 |
| C | -3.253179 | -0.413209 | -0.105611 |
| C | -4.413684 | -0.580702 | 0.660908 |
| C | -3.363106 | -0.132242 | -1.47501 |
| C | -5.669704 | -0.497686 | 0.058445 |
| H | -4.344408 | -0.779 | 1.732702 |
| C | -4.619271 | -0.039429 | -2.068141 |
| H | -2.464009 | 0.000862 | -2.077465 |
| C | -5.773239 | -0.229823 | -1.305372 |
| H | -6.568879 | -0.639572 | 0.662468 |
| H | -4.696173 | 0.177303 | -3.136013 |
| H | -6.756981 | -0.162022 | -1.776378 |
| H | 0.480997 | -3.595091 | 1.401134 |
| H | -1.895751 | -3.088426 | 0.790077 |
| S | -1.206728 | -2.643964 | -1.757426 |
| C | -2.327463 | -3.985169 | -1.888866 |
| C | -3.668152 | -3.886111 | -1.462081 |
| C | -1.902515 | -5.218377 | -2.426011 |
| C | -4.53606 | -4.972064 | -1.565073 |
| H | -4.029178 | -2.938132 | -1.056492 |
| C | -2.778452 | -6.294822 | -2.539313 |
| H | -0.864875 | -5.316741 | -2.755124 |
| C | -4.101973 | -6.183236 | -2.106289 |
| H | -5.570168 | -4.864874 | -1.224709 |
| H | -2.420037 | -7.236384 | -2.965439 |
| H | -4.786657 | -7.030731 | -2.190783 |

**TS2**

C38P2H33S2

| | | | |
|---|---|---|---|
| P | 1.420396 | 1.371346 | -1.26891 |
| C | -0.594189 | 0.071207 | 0.045018 |
| C | 0.894414 | 0.141117 | -0.142976 |
| C | -1.339602 | -2.052356 | -1.908996 |
| C | -1.674641 | -2.952033 | -0.871142 |
| C | -0.9221 | -2.57865 | -3.167448 |
| C | -1.576475 | -4.331461 | -1.085455 |
| H | -2.00857 | -2.569413 | 0.091443 |
| C | -0.856917 | -3.949173 | -3.360007 |
| H | -0.693536 | -1.900223 | -3.989531 |
| C | -1.174348 | -4.852853 | -2.321247 |
| H | -1.822406 | -5.033005 | -0.256379 |
| H | -0.538514 | -4.337687 | -4.34784 |
| H | -1.101103 | -5.916841 | -2.471444 |
| C | -3.183351 | 0.232153 | -1.736661 |
| C | -4.22388 | -0.730739 | -1.794923 |
| C | -3.513057 | 1.612267 | -1.702579 |
| C | -5.555191 | -0.326102 | -1.804938 |
| H | -3.990235 | -1.809766 | -1.825187 |
| C | -4.863746 | 2.022384 | -1.716609 |
| H | -2.701335 | 2.374459 | -1.65386 |
| C | -5.883606 | 1.03845 | -1.772372 |
| H | -6.350187 | -1.091457 | -1.865326 |
| H | -5.088768 | 3.095316 | -1.727139 |
| H | -6.923359 | 1.352385 | -1.77199 |
| C | 3.033103 | 0.645064 | -1.89324 |
| C | 4.271473 | 1.174138 | -1.454177 |
| C | 3.025316 | -0.464635 | -2.778908 |
| C | 5.464129 | 0.544322 | -1.856202 |
| H | 4.292727 | 2.009785 | -0.760119 |
| C | 4.219597 | -1.059152 | -3.207957 |
| H | 2.064873 | -0.895865 | -3.114341 |
| C | 5.448842 | -0.522025 | -2.738972 |
| H | 6.41472 | 0.945631 | -1.488292 |
| H | 4.185629 | -1.903606 | -3.905649 |
| H | 6.38028 | -1.021822 | -3.087617 |
| C | 1.848049 | 2.957052 | -0.466376 |
| C | 2.410577 | 3.007658 | 0.847473 |
| C | 1.568542 | 4.178168 | -1.12404 |
| C | 2.648978 | 4.228517 | 1.46578 |
| H | 2.582037 | 2.074799 | 1.391481 |
| C | 1.833979 | 5.405135 | -0.506699 |
| H | 1.115178 | 4.158505 | -2.10388 |
| C | 2.377771 | 5.431947 | 0.792074 |
| H | 3.074085 | 4.252987 | 2.472389 |
| H | 1.615713 | 6.333349 | -1.032663 |
| H | 2.591176 | 6.406617 | 1.281639 |
| H | -0.846589 | -0.810104 | 0.649977 |
| H | 1.380352 | -0.848687 | -0.282374 |
| S | -1.216302 | 1.558826 | 1.000952 |

| | | | |
|---|---|---|---|
| C | -2.653711 | 0.807479 | 1.857852 |
| C | -2.504081 | -0.344635 | 2.738472 |
| C | -3.887762 | 1.470601 | 1.809924 |
| C | -3.545983 | -0.681783 | 3.597532 |
| H | -1.505703 | -0.788171 | 2.930146 |
| C | -4.941461 | 1.065257 | 2.627495 |
| H | -4.01864 | 2.336607 | 1.119061 |
| C | -4.775493 | 0.008357 | 3.546859 |
| H | -3.373399 | -1.483765 | 4.326213 |
| H | -5.916469 | 1.58473 | 2.568876 |
| H | -5.587275 | -0.269758 | 4.225253 |
| P | -1.405759 | -0.211081 | -1.681903 |
| H | 1.306157 | 0.168771 | 1.472537 |
| C | 3.795807 | -3.954131 | 2.699963 |
| C | 4.029674 | -2.881453 | 1.816255 |
| C | 3.302233 | -1.696408 | 1.901958 |
| C | 2.285234 | -1.555585 | 2.867575 |
| C | 2.073654 | -2.612244 | 3.791335 |
| C | 2.828345 | -3.787783 | 3.710519 |
| H | 4.3787 | -4.88962 | 2.627809 |
| H | 4.804782 | -2.967593 | 1.028791 |
| H | 3.51187 | -0.867467 | 1.200179 |
| H | 1.299781 | -2.511364 | 4.569765 |
| H | 2.614894 | -4.610845 | 4.399815 |
| S | 1.247104 | -0.072531 | 2.95939 |

**TS$_{conc.}$**

C32P2H28S

| | | | |
|---|---|---|---|
| P | 1.704228 | -0.714484 | -1.474665 |
| P | -1.748494 | -0.459008 | -1.105994 |
| C | -0.50415 | 0.810524 | -0.4881 |
| C | 0.874944 | 0.685216 | -0.866974 |
| C | -2.245766 | -1.392175 | 0.402297 |
| C | -2.247429 | -0.874556 | 1.704397 |
| C | -2.698463 | -2.699903 | 0.193032 |
| C | -2.680924 | -1.657269 | 2.771165 |
| H | -1.900356 | 0.145773 | 1.900764 |
| C | -3.146906 | -3.478132 | 1.258984 |
| H | -2.693665 | -3.114381 | -0.822177 |
| C | -3.133048 | -2.958441 | 2.550891 |
| H | -2.668565 | -1.243161 | 3.783578 |
| H | -3.501377 | -4.49764 | 1.079041 |
| H | -3.478088 | -3.567972 | 3.391469 |
| C | -3.188367 | 0.677766 | -1.315656 |
| C | -4.395034 | 0.545514 | -0.619792 |
| C | -3.087749 | 1.667548 | -2.305149 |
| C | -5.465507 | 1.39556 | -0.895171 |
| H | -4.503691 | -0.225599 | 0.149796 |
| C | -4.152152 | 2.522323 | -2.570572 |
| H | -2.1587 | 1.769557 | -2.879871 |
| C | -5.347262 | 2.387512 | -1.864681 |
| H | -6.400911 | 1.282111 | -0.339099 |
| H | -4.051313 | 3.294225 | -3.339219 |
| H | -6.187762 | 3.055356 | -2.074171 |
| C | 1.102949 | -2.217072 | -0.624091 |
| C | 1.030495 | -2.282476 | 0.772982 |
| C | 0.770635 | -3.334713 | -1.398204 |
| C | 0.621451 | -3.464519 | 1.384361 |
| H | 1.277277 | -1.40241 | 1.380098 |
| C | 0.370507 | -4.514886 | -0.778303 |
| H | 0.818404 | -3.273834 | -2.490674 |
| C | 0.295409 | -4.577752 | 0.612339 |
| H | 0.547817 | -3.510257 | 2.474633 |
| H | 0.113381 | -5.388611 | -1.383906 |
| H | -0.026419 | -5.502922 | 1.099778 |
| C | 3.472775 | -0.50236 | -1.057551 |
| C | 4.417341 | -0.903879 | -2.009577 |
| C | 3.895421 | 0.006939 | 0.175406 |
| C | 5.77737 | -0.796762 | -1.731923 |
| H | 4.083705 | -1.298773 | -2.975744 |
| C | 5.257731 | 0.118684 | 0.442341 |
| H | 3.15736 | 0.320652 | 0.928632 |
| C | 6.196817 | -0.282224 | -0.506545 |
| H | 6.512599 | -1.110919 | -2.478103 |
| H | 5.585774 | 0.521462 | 1.405267 |
| H | 7.265322 | -0.19256 | -0.289853 |
| H | 1.474301 | 1.610925 | -0.903513 |
| H | -0.870866 | 1.843214 | -0.624443 |
| H | -0.369894 | 0.75403 | 0.672984 |
| S | 0.95105 | 1.123187 | 2.267917 |
| C | 1.010535 | 2.767583 | 1.65595 |
| C | 2.206954 | 3.340284 | 1.178487 |
| C | -0.154181 | 3.55992 | 1.597898 |
| C | 2.231043 | 4.633039 | 0.661196 |
| H | 3.132417 | 2.755564 | 1.225878 |
| C | -0.124478 | 4.849006 | 1.074564 |
| H | -1.094344 | 3.141689 | 1.975506 |
| C | 1.066911 | 5.398125 | 0.600018 |
| H | 3.178049 | 5.047984 | 0.300312 |
| H | -1.048889 | 5.434985 | 1.040724 |
| H | 1.088391 | 6.412373 | 0.191408 |

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