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Supporting Information

Coordination of azol(in)ium dithiocarboxylate ligands to Au(III): unexpected formation of a novel family of cyclometallated Au(III) complexes, DFT calculations and catalytic studies

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Contents

I.- General Methods and Materials

All reagents were obtained from commercial suppliers and used without further purification. NMR spectra were recorded on Bruker Avance III HD 300 (^{1}H 300 MHz; ^{13}C 75 MHz; ^{31}P 121 MHz) and Bruker Avance III HD 400 (^{1}H 400 MHz; ^{13}C 100 MHz; ^{31}P 161 MHz). All chemical shifts (δ) are given in parts per million (ppm) and referenced to the residual solvent signal as internal standard. The following abbreviations are used to indicate the multiplicity of signal: s – singlet, d – doublet, t – triplet, q – quartet, hept – heptet. High Resolution Mass Spectra (HRMS) were recorded on an Agilent Technologies LC/MSD-TOF and HP 1100 MSD spectrometer using electrospray ionization. IR spectra were recorded in neat form on a Jasco FT/IR-4700 spectrophotometer and, and ν_{max} values are given in cm^{-1} for the main absorption bands. Thin-layer chromatography (TLC) was conducted with Silica Gel 60 F254 precoated plates and visualized with a UV lamp. Column chromatography was performed using silica gel 60 (230-240 mesh).

II.- Experimental Procedures and Characterisation

II.1.- Synthesis of azol(in)ium-2-thiocarboxylate ligands 14-20.

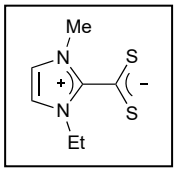
Method A

A mixture of the appropriate azolium salt (1 mmol) and Cs_2CO_3 (1.5 mmol) in acetonitrile (5 mL) was vigorously stirred at r.t. After 30 minutes, the mixture was cooled down to 0ºC and CS_2 (8 mmol) was added dropwise. The resulting mixture was stirred at r.t. for 4 hours and then evaporated under reduced pressure. The solid residue was taken up with a saturated aqueous NH_4Cl solution (10 mL). The suspension was stirred for 15 min at r.t. and then was filtered and the solid was washed with water (3 x 5 mL) and dried under high vacuum to afford ligands **14**, **15** and **20**. The characterization date were consistent with those reported in the literature [1]

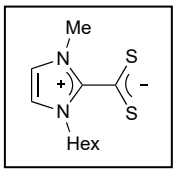
Method B

A mixture of the appropriate azolium salt (1 mmol) and KO^{t}Bu (1.1 mmol) in THF (20 mL) was added with a vigorous stirring. vigorously stirred at r.t. After 30 minutes, the mixture was cooled down to 0ºC and CS_2 (2 mmol) was added dropwise. After stirring at room temperature for 1 hour, the reaction was dried under vacuum. The resulting mixture

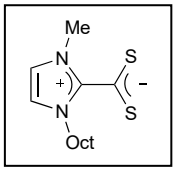
was stirred at r.t. for 1 hour and then evaporated under reduced pressure. The residue was purified by flash column chromatography (SiO_2) eluting with CH_2Cl_2/EtOAc 1:1 to afford ligands **16-19**. The spectroscopic data obtained for the known complex **18** agree with those described in the literature [2]. The complete characterization of the new complexes **16**, **18** and **19** is shown below.



1-Ethyl-3-methylimidazolium-2-dithiocarboxylate (16): Method A. 145.3 mg (78% yield). Orange solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.51 (t, 3H, *J* = 7.4 Hz), 3.79 (s, 3H), 4.20 (q, 2H, *J* = 7.4 Hz), 6.90 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 15.3, 35.0, 43.8, 112.2, 119.5, 149.3, 224.6 ppm. HRMS (ESI^+) $[M+H]^+$ calcd. for $C_7H_{11}N_2S_2^+$, 187.0350; found, 187.0351.



1-Hexyl-3-methylimidazolium-2-dithiocarboxylate (18): Method A. 181.8 g (75% yield). Orange solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.83 (m, 3H), 1.27 (m, 6H), 1.84 (m, 2H), 3.77 (s, 3H), 4.09 (m, 2H), 6.90 (s, 2H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 14.0, 22.5, 26.2, 29.7, 31.2, 34.9, 48.7, 117.8, 119.4, 150.0, 224.7 ppm. HRMS (ESI^+) $[M]^+$ calcd. for $C_{11}H_{19}N_2S_2^+$, 243.0984; found, 243.0974.



1-Octyl-3-methylimidazolium-2-dithiocarboxylate (19): Method A. 186.6 mg (69% yield). Orange solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85 (m, 3H), 1.23 (m,10H), 1.85 (m, 2H), 3.77 (s, 3H), 4.08 (m, 2H), 6.89 (s, 2H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 14.2, 22.7, 26.6, 29.0, 29.1, 29.8, 31.8, 35.0, 117.7, 119.3, 150.0, 224.6 ppm. HRMS (ESI^+) $[M]^+$ calcd. for $C_{13}H_{23}N_2S_2^+$, 271.1297; found, 271.1297.

II.2.- Synthesis of dithiocarboxylate azol(in)ium complexes 21-27

To a mixture of Au(dppta)Cl_2 precursor (0.1 mmol) in acetonitrile (10 mL), the corresponding azol(in)ium-2-thiocarboxylate ligand **14-20** (0.1 mmol) was added and the resulting mixture was vigorously stirred at r.t. After 12 h, a solution of KPF_6 (1.5 mmol) in water (0.5 mL) was added and the resulting mixture was stirred for further 15 minutes. After removal of the acetonitrile under reduced pressure, the solid was washed with water (3 x 5 mL) and diethyl ether (3 x 5 mL) and purified by flash column chromatography (SiO_2) eluting with CH_2Cl_2/EtOAc (1:2).

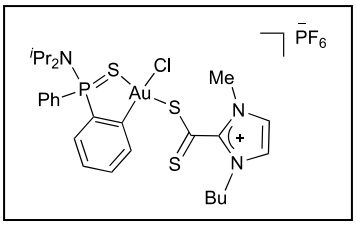
***trans*-[2-((Diisopropylamino)(phenyl)phosphorothioyl)phenyl] [1,3-dimethylbenzimidazolium-2-dithiocarboxylate-κ^{1}S] gold(III) chloride hexafluorophosphate (21):** 71 mg (78% yield). *d.e.* 73%. Dark red solid. ^{1}H NMR (300 MHz, acetone-d$_6$) δ 1.31 (d, $^3J_{HH}$ 6.8 Hz, 6H, CH(C<u>H</u>$_3$)$_2$), 1.39 (d, $^3J_{HH}$ 6.8 Hz, 6H, CH(C<u>H</u>$_3$)$_2$), 3.77-3.99 (m, 2H, C<u>H</u>(CH$_3$)$_2$), 4.12 (s, 6H, NCH$_3$), 7.51-7.69 (m, 2H), 7.74-8.09 (m, 8H), 8.25-8.41 (m, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, acetone-d$_6$) δ 23.4 (d, $^3J_{PC}$ 2.7 Hz), 23.5 (d, $^3J_{PC}$ 3.3 Hz), 33.0, 33.9, 51.4, 114.1, 114.2, 127.7, 128.4, 128.5 (d, $^1J_{PC}$ 101.0 Hz), 128.8 (d, $^3J_{PC}$ 12.3 Hz), 130.5 (d, $^2J_{PC}$ 13.7 Hz), 132.3, 133.5 (d, $^3J_{PC}$ 11.7 Hz), 134.5 (d, $^3J_{PC}$ 12.3 Hz), 135.5 (d, $^4J_{PC}$ 3.3 Hz), 136.0 (d, $^4J_{PC}$ 3.2 Hz), 136.6 (d, $^2J_{PC}$ 16.5 Hz), 139.5 (d, $^1J_{PC}$ 120.0 Hz), 145.7 (d, $^2J_{PC}$ 23.7 Hz), 149.0, 206.1 ppm. ^{31}P{^{1}H} NMR (121 MHz, DMSO-d$_6$) δ -144.1 (hept, $^1J_{PF}$ 708.1 Hz), 68.0 ppm. HRMS (ESI$^+$) [M]$^+$ calcd. for $C_{28}H_{33}AuClN_3PS_3$, 770.0923; found, 770.0914.

***trans*-[2-((Diisopropylamino)(phenyl)phosphorothioyl)phenyl] [1,3-mesitylimidazolinium-2-dithiocarboxylate-κ^{1}S] gold(III) chloride hexafluorophosphate (22):** 62 mg (58% yield). *d.e.* 85%. Dark red solid. ^{1}H NMR (400 MHz, acetone-d$_6$) δ 1.20 (d, $^3J_{HH}$ 6.8 Hz, 6H, CH(C<u>H</u>$_3$)$_2$), 1.26 (d, $^3J_{HH}$ 6.8 Hz, 6H, CH(C<u>H</u>$_3$)$_2$), 2.34 (s, 6H, 2 x CH$_3$), 2.45 (s, 6H, 2 x CH$_3$), 2.51 (s, 6H, 2 x CH$_3$), 3.66-3.82 (m, 2H, C<u>H</u>(CH$_3$)$_2$), 4.69 (s, 4H, 2 x CH$_2$), 6.81 (dd, $^3J_{HH}$ 8.0 Hz, $^4J_{PH}$ 3.9 Hz, 1H), 7.05 (s, 1H), 7.10 (s, 1H), 7.45-7.51 (m, 1H), 7.69-7.73 (m, 5H), 8.15 (dd, $^3J_{PH}$ 14.5 Hz, $^3J_{HH}$ 7.4 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, acetone-d$_6$) δ 18.6, 18.7, 21.1, 23.1 (d, $^3J_{PC}$ 3.0 Hz), 23.4 (d, $^3J_{PC}$ 2.7 Hz), 51.3 (d, $^2J_{PC}$ 3.5 Hz), 51.7, 128.3 (d, $^1J_{PC}$ 101.0 Hz), 130.2 (d, $^3J_{PC}$ 13.7 Hz), 130.9, 131.0 (d, $^2J_{PC}$ 10.0 Hz), 134.8 (d, $^3J_{PC}$ 12.0 Hz), 135.3 (d, $^4J_{PC}$ 3.0 Hz), 135.5 (d, $^2J_{PC}$ 17.5 Hz), 136.0 (d, $^4J_{PC}$ 3.6 Hz), 137.0 (d, $^3J_{PC}$ 4.3 Hz), 139.7 (d, $^1J_{PC}$ 121.2 Hz), 141.3, 143.44 (d, $^2J_{PC}$ 24.6 Hz), 165.5, 207.6 ppm.^{31}P{^{1}H} NMR (121 MHz, acetone-d$_6$) δ = -144.1 (sep, $^1J_{PF}$ 708.0 Hz), 68.9, 70.0 ppm. HRMS (ESI$^+$) [M]$^+$ calcd. for $C_{40}H_{49}AuClN_3PS_3$, 930.2175; found, 930.2170.

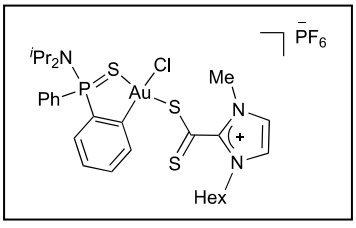
***trans*-[2-((Diisopropylamino)(phenyl)phosphorothioyl)phenyl] [1-ethyl-3-methylimidazolium-2-dithiocarboxylate-κ^{1}S] gold(III)**

chloride hexafluorophosphate (23): 69 g (78% yield). *d.e.* 90%. Dark red solid. ^{1}H NMR (300 MHz, acetone-d_6) δ 1.28 (d, $^{3}J_{HH}$ 6.8 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.36 (d, $^{3}J_{HH}$ 6.8 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.47 (d, $^{3}J_{HH}$ 7.3 Hz, 3H, NCH$_2$C$\underline{H}_3$), 3.74-3.95 (m, 2H, C$\underline{H}$(CH$_3$)$_2$), 3.88 (s, 3H, NCH$_3$), 4.27 (q, $^{3}J_{HH}$ 7.3 Hz, 2H, NC$\underline{H}_2$CH$_3$), 7.55-8.04 (m, 8H), 8.33 (dd, $^{3}J_{PH}$ 14.6 Hz, $^{3}J_{HH}$ 7.3 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6) δ 15.9, 23.47 (d, $^{3}J_{PC}$ 3.1 Hz), 23.52 (d, $^{3}J_{PC}$ 2.8 Hz), 36.1, 51.3 (d, $^{2}J_{PC}$ 3.5 Hz), 51.7, 122.2, 124.4, 128.1 (d, $^{1}J_{PC}$ 100.6 Hz), 129.0 (d, $^{3}J_{PC}$ 12.3 Hz), 130.2 (d, $^{2}J_{PC}$ 13.9 Hz), 133.9 (d, $^{3}J_{PC}$ 10.9 Hz), 135.2 (d, $^{3}J_{PC}$ 12.2 Hz), 135.5 (d, $^{4}J_{PC}$ 2.9 Hz), 135.9 (d, $^{4}J_{PC}$ 3.4 Hz), 136.1 (d, $^{2}J_{PC}$ 17.0 Hz), 139.7 (d, $^{1}J_{PC}$ 122.1 Hz), 144.0 (d, $^{2}J_{PC}$ 23.9 Hz), 141.3, 210.4 ppm. ^{31}P{^{1}H} NMR (121 MHz, acetone-d_6) δ -144.1 (hept, $^{1}J_{PF}$ 707.4 Hz), 68.2, 70.1 ppm. HRMS (ESI^{+}) [M]$^{+}$ calcd. for $C_{25}H_{33}AuClN_3PS_3$, 734.0923; found, 734.0903.

***trans*-[2-((Diisopropylamino)(phenyl)phosphorothioyl)phenyl] [1-butyl-3-methylimidazolium-2-dithiocarboxylate-κ^{1}S] gold(III) chloride hexafluorophosphate (24):** 74 mg (82% yield). *d.e.* 88%. Dark red solid. ^{1}H NMR (300 MHz, acetone-d_6) δ 0.87 (t, $^{3}J_{HH}$, 7.4 Hz, N(CH$_2$)$_3$C$\underline{H}_3$, 3H), 1.28 (d, $^{3}J_{HH}$ 6.8 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.32-1.39 (m, 2H, N(CH$_2$)$_2$C$\underline{H}_2$CH$_3$), 1.36 (d, $^{3}J_{HH}$ 6.8 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.85 (p, $^{3}J_{HH}$ 7.6 Hz, NCH$_2$C$\underline{H}_2$CH$_2$CH$_3$, 1H), 3.77-3.93 (m, 2H, C$\underline{H}$(CH$_3$)$_2$), 3.89 (s, 3H, NCH$_3$), 4.20-4.25 (m, 2H, NC$\underline{H}_2$(CH$_2$)$_2$CH$_3$), 7.57-7.81 (m, 2H), 7.85-7.97 (m, 6H), 8.15-8.19 (m, 1H), 8.33 (dd, $^{3}J_{PH}$ 14.4 Hz, $^{3}J_{HH}$ 7.4 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6) δ 13.7, 20.1, 23.46 (d, $^{3}J_{PC}$ 2.6 Hz), 23.52 (d, $^{3}J_{PC}$ 3.1 Hz), 32.6, 36.1, 49.7, 51.4 (d, $^{2}J_{PC}$ 3.3 Hz), 51.7, 122.6, 124.4, 128.2 (d, $^{1}J_{PC}$ 100.8 Hz), 129.0 (d, $^{3}J_{PC}$ 12.2 Hz), 130.2 (d, $^{2}J_{PC}$ 13.9 Hz), 130.5 (d, $^{3}J_{PC}$ 13.9 Hz), 133.9 (d, $^{3}J_{PC}$ 10.9 Hz), 135.2 (d, $^{3}J_{PC}$ 12.2 Hz), 135.5 (d, $^{4}J_{PC}$ 3.1 Hz), 135.9 (d, $^{4}J_{PC}$ 3.4 Hz), 136.2 (d, $^{2}J_{PC}$ 16.7 Hz), 139.7 (d, $^{1}J_{PC}$ 122.0 Hz), 144.0 (d, $^{2}J_{PC}$ 24.5 Hz), 145.0, 210.4 ppm. ^{31}P{^{1}H} NMR (121 MHz, acetone-d_6) δ -144.1 (hept, $^{1}J_{PF}$ 707.7 Hz), 68.2, 70.1 ppm. HRMS (ESI^{+}) [M]$^{+}$ calcd. for $C_{27}H_{37}AuClN_3PS_3$, 762.1236; found, 762.1217.

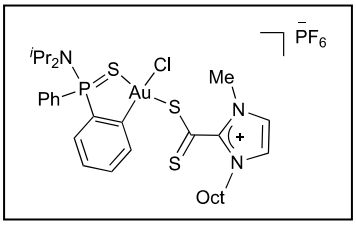


***trans*-[2-((Diisopropylamino)(phenyl)phosphorothioyl)phenyl] [1-hexyl-3-methylimidazolium-2-dithiocarboxylate-κ^{1}S] gold(III) chloride hexafluorophosphate (25):** 75 mg (79% yield). *d.e.* 87%. Dark red solid. ^{1}H NMR (300 MHz, acetone-d_6)

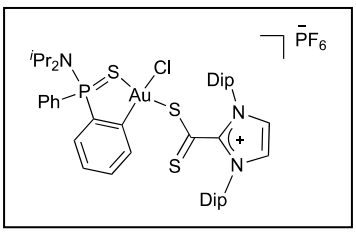


δ 0.86 (t, $^{3}J_{HH}$, 6.0 Hz, $N(CH_2)_5C\underline{H}_3$, 3H), 1.28-1.38 (m, 18H, $CH(C\underline{H}_3)_2$, $N(CH_2)_2(C\underline{H}_2)_3CH_3$), 1.83-1.91 (m, 2H, $NCH_2C\underline{H}_2(CH_2)_3CH_3$), 3.79-3.94 (m, 2H, $C\underline{H}(CH_3)_2$), 3.90 (s, 3H, NCH_3), 4.21-4.26 (m, 2H, $NC\underline{H}_2(CH_2)_4CH_3$), 7.50-7.66 (m, 2H), 7.74-7.98 (m, 6H), 8.16-8.20 (m, 1H), 8.34 (dd, $^{3}J_{PH}$ 14.7 Hz, $^{3}J_{HH}$ 7.6 Hz, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, acetone-d_6) δ 14.2, 15.6, 23.0, 23.5 (d, $^{3}J_{PC}$ 2.7 Hz), 23.6 (d, $^{3}J_{PC}$ 3.3 Hz), 30.6, 31.7, 36.1, 49.9, 51.4 (d, $^{2}J_{PC}$ 3.3 Hz), 66.1, 122.6, 124.4, 128.2 (d, $^{1}J_{PC}$ 100.8 Hz), 129.0 (d, $^{3}J_{PC}$ 12.3 Hz), 130.2 (d, $^{2}J_{PC}$ 13.8 Hz), 133.9 (d, $^{3}J_{PC}$ 10.8 Hz), 135.2 (d, $^{3}J_{PC}$ 12.3 Hz), 135.5 (d, $^{4}J_{PC}$ 3.3 Hz), 135.9 (d, $^{4}J_{PC}$ 3.4 Hz), 136.2 (d, $^{2}J_{PC}$ 17.0 Hz), 139.8 (d, $^{1}J_{PC}$ 121.0 Hz), 144.1 (d, $^{2}J_{PC}$ 24.6 Hz), 145.0, 210.4 ppm. $^{31}P\{^{1}H\}$ NMR (121 MHz, acetone-d_6) δ -144.1 (hept, $^{1}J_{PF}$ 707.7 Hz), 68.2, 70.1 ppm. HRMS (ESI^+) $[M]^+$ calcd. for $C_{29}H_{41}AuClN_3PS_3$, 790.1549; found, 790.1575.

***trans*-[2-((Diisopropylamino)(phenyl)phosphorothioyl)phenyl] [1-octyl-3-methylimidazolium-2-dithiocarboxylate-κ^{1}S] gold(III) chloride hexafluorophosphate (26):** 69 mg (72% yield). *d.e.* 88%. Dark red solid. ^{1}H NMR (300 MHz, acetone-d_6) δ 0.87 (t, $^{3}J_{HH}$, 6.3 Hz, $N(CH_2)_5C\underline{H}_3$, 3H), 1.28-1.38 (m, 18H, $CH(C\underline{H}_3)_2$, $N(CH_2)_2(C\underline{H}_2)_3CH_3$), 1.83-1.91 (m, 2H, $NCH_2C\underline{H}_2(CH_2)_3CH_3$), 3.79-3.94 (m, 2H, $C\underline{H}(CH_3)_2$), 3.90 (s, 3H, NCH_3), 4.21-4.26 (m, 2H, $NC\underline{H}_2(CH_2)_4CH_3$), 7.50-7.66 (m, 2H), 7.74-7.98 (m, 6H), 8.16-8.20 (m, 1H), 8.34 (dd, $^{3}J_{PH}$ 14.6 Hz, $^{3}J_{HH}$ 7.3 Hz, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, acetone-d_6) δ 14.1, 22.6, 23.0, 23.4, 23.5, 26.2, 28.9, 29.0, 30.1, 31.6, 35.8, 49.5, 50.6, 121.4, 123.4, 127.0 (d, $^{1}J_{PC}$ 100.0 Hz), 128.3 (d, $^{3}J_{PC}$ 11.8 Hz), 129.5 (d, $^{2}J_{PC}$ 13.4 Hz), 132.3 (d, $^{3}J_{PC}$ 9.7 Hz), 134.3 (d, $^{3}J_{PC}$ 11.8 Hz), 134.6, 135.1, 135.4 (d, $^{2}J_{PC}$ 16.7 Hz), 138.7 (d, $^{1}J_{PC}$ 123.0 Hz), 143.1 (d, $^{2}J_{PC}$ 24.2 Hz), 144.2, 208.3 ppm. $^{31}P\{^{1}H\}$ NMR (121 MHz, acetone-d_6) δ -144.1 (hept, $^{1}J_{PF}$ 707.6 Hz), 68.3, 70.1 ppm. HRMS (ESI^+) $[M]^+$ calcd. for $C_{31}H_{45}AuClN_3PS_3$, 818.1873; found, 818.1862.



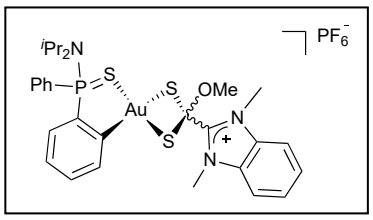
***trans*-[2-((Diisopropylamino)(phenyl)phosphorothioyl)phenyl] [1,3-bis(diisopropylphenyl)imidazolium-2-dithiocarboxylate-κ^{1}S] gold(III) chloride hexafluorophosphate (25):** 63 g (54% yield). *d.e.* 94%. Dark red solid. 1.06 (d, $^{3}J_{HH}$ 6.7 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.12 (d, $^{3}J_{HH}$ 6.8 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.19 (d, $^{3}J_{HH}$ 6.8 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.23 (d, $^{3}J_{HH}$ 6.8 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.27 (d,



$^{3}J_{HH}$ 6.8 Hz, 6H, CH(C<u>H</u>$_3$)$_2$), 1.37 (d, $^{3}J_{HH}$ 6.7 Hz, 6H, CH(C<u>H</u>$_3$)$_2$), 2.47 (sept, $^{3}J_{HH}$ 6.4 Hz, 1H, C<u>H</u>(CH$_3$)$_2$), 2.60 (sept, $^{3}J_{HH}$ 6.1 Hz, 1H, C<u>H</u>(CH$_3$)$_2$), 3.74 (dsept, $^{3}J_{HP}$ 20.5 Hz, $^{3}J_{HH}$ 6.9 Hz, 1H, C<u>H</u>(CH$_3$)$_2$), 6.77-6.81 (m, 1H), 6.97-7.02 (m, 1H), 7.43 (d, $^{3}J_{HH}$ 7.7 Hz, 2H), 7.43 (d, $^{3}J_{HH}$ 7.5 Hz, 2H), 7.44–7.48 (m, 1H), 7.63-7.81 (m, 6H), 8.11 (dd, $^{3}J_{PH}$ 14.7 Hz, $^{3}J_{HH}$ 7.7 Hz, 2H), 8.35 (s, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, acetone-d$_6$) δ 22.66, 22.72, 23.47 (d, $^{3}J_{PC}$ 2.7 Hz), 23.50 (d, $^{3}J_{PC}$ 3.6 Hz), 25.7, 25.9, 30.1, 30.2, 30.3, 30.6, 49.7, 51.2 (d, $^{2}J_{PC}$ 3.3 Hz), 125.7, 126.1, 126.3, 127.9 (d, $^{1}J_{PC}$ 100.6 Hz), 128.1 (d, $^{3}J_{PC}$ 11.9 Hz), 130.04 (d, $^{2}J_{PC}$ 14.0 Hz), 130.9, 133.1, 133.4 (d, $^{3}J_{PC}$ 10.8 Hz), 135.05 (d, $^{2}J_{PC}$ 17.2 Hz), 135.3 (d, $^{4}J_{PC}$ 3.0 Hz), 135.4 (d, $^{3}J_{PC}$ 12.7 Hz), 136.5 (d, $^{4}J_{PC}$ 1.9 Hz), 138.9 (d, $^{1}J_{PC}$ 121.6 Hz), 143.9 (d, $^{2}J_{PC}$ 24.9 Hz), 146.3, 146.5, 146.7, 210.0 ppm. ^{31}P{^{1}H} NMR (121 MHz, acetone-d$_6$) δ -144.1 (hept, $^{1}J_{PF}$ 707.5 Hz), 67.0, 68.0 ppm. HRMS (ESI$^+$) [M]$^+$ calcd. for $C_{46}H_{59}AuClN_3PS_3$, 1012.2957; found, 1012.3000.

II.3.- Synthesis of dithiolate azol(in)ium complexes 28-34.

To a mixture of Au(dppta)Cl$_2$ precursor (0.1 mmol) in methanol (10 mL), the corresponding azol(in)ium-2-thiocarboxilate ligand **14-20** (0.1 mmol) was added and the resulting mixture was vigorously stirred at r.t. After 12 h, a solution of KPF_6 (1.5 mmol) in water (0.5 mL) was added and the resulting mixture was stirred for further 15 minutes. After removal of the acetonitrile under reduced pressure, the solid was washed with water (3 x 5 mL) and diethyl ether (3 x 5 mL) and purified by flash column chromatography (SiO_2) eluting with CH_2Cl_2/EtOAc (1:2).

***trans*-[2-((Diisopropylamino)(phenyl)phosphorothioyl)phenyl] [1,3-dimethylbenzimidazolium-2-(methoxy)methanedithiol-κ^{2}S,S] gold(III) chloride hexafluorophosphate (28):** 

83 mg (64% yield). Orange solid. ^{1}H NMR (300 MHz, acetone-d$_6$) δ 1.30-1.39 (m, 12H, 2 x CH(C<u>H</u>$_3$)$_2$), 3.69, 3.83 (2 x s, 6H, OCH$_3$), 3.86-3.97 (m, 4H, C<u>H</u>(CH$_3$)$_2$), 4.43, 4.57 (2 x s, 12H, NCH$_3$), 7.49-7.80 (m, 3H), 7.73-7.80 (m, 5H), 7.99-8.09 (m, 3H), 8.26-8.37 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, acetone-d$_6$) δ 22.2 (d, $^{3}J_{PC}$ 3.2 Hz), 22.6 (d, $^{3}J_{PC}$ 3.2 Hz), 22.7 (d, $^{3}J_{PC}$ 3.3 Hz), 35.6, 35.7, 48.6, 48.7, 50.3, 92.9, 113.16, 113.21, 127.1 (d, $^{3}J_{PC}$ 12.1 Hz), 127.2 (d, $^{3}J_{PC}$ 12.6 Hz), 127.28, 127.33, 129.2 (d, $^{1}J_{PC}$ 102.5 Hz), 129.3 (d, $^{1}J_{PC}$ 101.0 Hz), 129.39 (d, $^{3}J_{PC}$ 13.5 Hz), 129.42 (d, $^{3}J_{PC}$ 12.6 Hz), 130.6 (d, $^{2}J_{PC}$ 18.0 Hz), 130.7 (d, $^{2}J_{PC}$ 18.0 Hz), 132.2, 132.3, 132.7 (d, $^{2}J_{PC}$ 13.3 Hz),

133.0 (d, $^{2}J_{PC}$ 13.7 Hz), 133.4 (d, $^{3}J_{PC}$ 11.6 Hz), 133.5 (d, $^{3}J_{PC}$ 11.7 Hz), 134.3-134.4 (m), 139.7 (d, $^{1}J_{PC}$ 124.8 Hz), 140.0 (d, $^{1}J_{PC}$ 124.1 Hz), 148.7 (d, $^{2}J_{PC}$ 30.8 Hz), 148.8, 149.0 (d, $^{2}J_{PC}$ 29.9 Hz) ppm. $^{31}P\{^{1}H\}$ NMR (121 MHz, acetone-d_6) δ -144.1 (h, $^{1}J_{PF}$ 712.3 Hz), 76.5, 78.2 ppm. HRMS (ESI^{+}) $[M]^{+}$ calcd. for $C_{29}H_{36}AuN_3OPS_3$, 766.1418; found, 766.1430.

***trans*-[2-((Diisopropylamino)(phenyl)phosphorothioyl)phenyl] [1,3-mesitylimidazolinium-2-(methoxy)methanedithiol-κ^{2}S,S] gold(III) chloride hexafluorophosphate (29):** 63 mg (57% yield). Dark red solid. ^{1}H NMR (400 MHz, acetone-d_6) δ 1.19 (d, $^{3}J_{HH}$ 6.7 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.24 (d, $^{3}J_{HH}$ 6.7 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.31 (d, $^{3}J_{HH}$ 6.7 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.39 (d, $^{3}J_{HH}$ 6.7 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 2.36 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 2.78 (s, 3H, CH_3), 2.91 (s, 3H, CH_3), 3.01 (s, 3H, CH_3), 3.70-3.88 (m, 2H, C$\underline{H}$(CH$_3$)$_2$), 3.75 (s, 3H, OCH_3), 4.43, 4.49 (2 x s, 4H, 2 x CH_2), 6.39 (s, 1H), 6.79-7.05 (m, 4H), 7.47-7.54 (m, 2H), 7.56-7.96 (m, 4H), 8.19, 8.40 (2 x dd, $^{3}J_{PH}$ 13.9 Hz, $^{3}J_{HH}$ 7.5 Hz, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, acetone-d_6) δ 18.8, 18.9, 19.4, 20.9, 23.3 (d, $^{3}J_{PC}$ 3.0 Hz), 23.5 (d, $^{3}J_{PC}$ 2.7 Hz), 49.1, 51.07 (d, $^{2}J_{PC}$ 2.8 Hz), 51.9, 52.0, 92.5, 127.5 (d, $^{3}J_{PC}$ 13.1 Hz), 127.6 (d, $^{3}J_{PC}$ 13.2 Hz), 129.7 (d, $^{1}J_{PC}$ 101.0 Hz), 130.0 (d, $^{2}J_{PC}$ 13.6 Hz), 130.27, 130.29, 130.4 (d, $^{2}J_{PC}$ 13.4 Hz), 130.6, 130.7, 133.3 (d, $^{3}J_{PC}$ 13.6 Hz), 134.5 (d, $^{3}J_{PC}$ 11.4 Hz), 134.7-135.0 (m), 135.7, 135.8, 135.9, 136.0, 140.2, 140.3, 140.6 (d, $^{1}J_{PC}$ 126.4 Hz), 148.3 (d, $^{2}J_{PC}$ 32.0 Hz), 168.9 ppm. $^{31}P\{^{1}H\}$ NMR (161 MHz, acetone-d_6) δ = -144.1 (h, $^{1}J_{PF}$ 712.3 Hz), 78.5, 79.6 ppm. HRMS (ESI^{+}) $[M]^{+}$ calcd. for $C_{41}H_{52}AuN_3OPS_3$, 926.2670; found, 926.2670.

***trans*-[2-((Diisopropylamino)(phenyl)phosphorothioyl)phenyl] [1-ethyl-3-methylimidazolium-2-(methoxy)methanedithiol-κ^{2}S,S] gold(III) chloride hexafluorophosphate (30):** 60 mg (69% yield). Dark red solid. ^{1}H NMR (300 MHz, acetone-d_6) δ 1.22–1.38 (m, 15H), 1.43, 1.56 (2 x t, $^{3}J_{HH}$ 7.3 Hz, 3H, NCH$_2$C$\underline{H}_3$), 3.60, 3.73 (2 x s, 3H, OCH_3), 3.73-4.00 (m, 2H, C$\underline{H}$(CH$_3$)$_2$), 4.15, 4.32 (2 x s, 3H, NCH_3), 4.74, 4.83 (q, $^{3}J_{HH}$ 7.1 Hz, 2H, NC$\underline{H}_2$CH$_3$), 7.43-7.48 (m, 1H), 7.51-7.83 (m, 7H), 7.96-7.99 (m, 1H), 8.30 (dd, $^{3}J_{PH}$ 14.2 Hz, $^{3}J_{HH}$ 7.0 Hz, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, acetone-d_6) δ 16.8, 17.0, 23.5 (d, $^{3}J_{PC}$ 3.1 Hz),

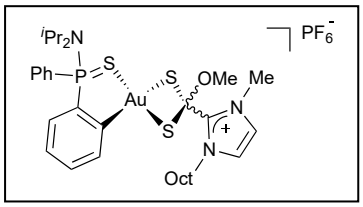
23.6 (d, $^{3}J_{PC}$ 2.8 Hz), 40.5, 40.6, 50.7 (d, $^{2}J_{PC}$ 2.8 Hz), 50.8, 51.2, 93.27, 93.32, 123.5, 123.6, 125.8, 125.9, 127.8 (d, $^{1}J_{PC}$ 100.3 Hz), 128.0 (d, $^{3}J_{PC}$ 12.2 Hz), 128.1 (d, $^{3}J_{PC}$ 11.9 Hz), 130.3 (d, $^{3}J_{PC}$ 13.6 Hz), 130.4 (d, $^{3}J_{PC}$ 13.6 Hz), 131.6 (d, $^{2}J_{PC}$ 18.0 Hz), 131.8 (d, $^{2}J_{PC}$ 18.0 Hz), 133.6 (d, $^{2}J_{PC}$ 13.4 Hz), 134.0 (d, $^{2}J_{PC}$ 13.9 Hz), 134.4 (d, $^{3}J_{PC}$ 12.5 Hz), 134.5 (d, $^{3}J_{PC}$ 12.2 Hz), 135.1 (d, $^{4}J_{PC}$ 2.9 Hz), 135.9 (d, $^{4}J_{PC}$ 3.1 Hz), 136.1 (d, $^{2}J_{PC}$ 17.0 Hz), 140.5 (d, $^{1}J_{PC}$ 124.7 Hz), 141.0 (d, $^{1}J_{PC}$ 123.9 Hz), 148.4, 148.5, 149.7 (d, $^{2}J_{PC}$ 32.3 Hz), 149.8 (d, $^{2}J_{PC}$ 38.9 Hz) ppm. $^{31}P\{^{1}H\}$ NMR (121 MHz, acetone-d_6) δ = -144.1 (sep, $^{1}J_{PF}$ 708.3 Hz), 73.4, 78.3 ppm. HRMS (ESI^{+}) $[M]^{+}$ calcd. for $C_{26}H_{36}AuN_3OPS_3$, 730.1418; found, 730.1434.

***trans*-[2-((Diisopropylamino)(phenyl)phosphorothioyl)phenyl] [1-butyl-3-methylimidazolium-2-(methoxy)methanedithiol-κ²S,S] gold(III) chloride hexafluorophosphate (31):** 93 mg (60% yield). Dark red solid. ^{1}H NMR (400 MHz, acetone-d_6) δ 0.77, 0.95 (2 x t, $^{3}J_{HH}$ 7.3 Hz, 3H, 2 x $N(CH_2)_3C\underline{H}_3$), 1.21-1.46 (m, 14H, 2 x $CH(C\underline{H}_3)_2$, 2 x $N(CH_2)_2C\underline{H}_2CH_3$), 1.83-2.00 (m, 2H, 2 x $NCH_2C\underline{H}_2CH_2CH_3$), 3.61, 3.74 (2 x s, 2 x OCH_3), 3.78-3.92 (m, 2H $C\underline{H}(CH_3)_2$), 4.14, 4.31 (2 x s, 2 x NMe), 4.68, 4.79 (2 x t, $^{3}J_{HH}$ 7.7 Hz, 3H, $NC\underline{H}_2(CH_2)_2CH_3$), 7.45-7.47 (m, 1H), 7.56-7.79 (m, 7H), 7.96-7.99 (m, 1H), 8.25-8.35 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, acetone-d_6) δ 13.9, 13.8, 20.1, 20.3, 23.06, 23.10, 23.4 (d, $^{3}J_{PC}$ 3.4 Hz), 23.5 (d, $^{3}J_{PC}$ 3.6 Hz), 33.9, 34.1, 40.46, 40.50, 49.4, 51.2 (d, $^{2}J_{PC}$ 2.6 Hz), 52.7, 52.8, 93.16, 93.19, 123.9, 124.0, 125.5, 125.6, 127.9 (d, $^{3}J_{PC}$ 11.7 Hz), 128.0 (d, $^{3}J_{PC}$ 11.8 Hz), 130.0 (d, $^{1}J_{PC}$ 100.4 Hz), 130.1 (d, $^{2}J_{PC}$ 13.6 Hz), 130.2 (d, $^{2}J_{PC}$ 13.8 Hz), 131.48 (d, $^{2}J_{PC}$ 17.6 Hz), 131.53 (d, $^{2}J_{PC}$ 18.4 Hz), 133.5 (d, $^{3}J_{PC}$ 13.2 Hz), 133.9 (d, $^{3}J_{PC}$ 13.6 Hz), 134.2 (d, $^{3}J_{PC}$ 11.3 Hz), 134.3 (d, $^{3}J_{PC}$ 11.4 Hz), 135.0-135.1 (m), 140.4 (d, $^{1}J_{PC}$ 124.2 Hz), 140.9 (d, $^{1}J_{PC}$ 122.3 Hz), 148.4, 149.3 (d, $^{2}J_{PC}$ 22.5 Hz), 149.7 (d, $^{2}J_{PC}$ 22.5 Hz) ppm. $^{31}P\{^{1}H\}$ NMR (161 MHz, acetone-d_6) δ = -144.1 (hept, $^{1}J_{PF}$ 708.3 Hz), 76.8, 78.6 ppm. HRMS (ESI^{+}) $[M]^{+}$ calcd. for $C_{28}H_{40}AuN_3OPS_3$, 758.1731; found, 758.1755.

***trans*-[2-((Diisopropylamino)(phenyl)phosphorothioyl)phenyl] [1-hexyl-3-methylimidazolium-2-(methoxy)methanedithiol-κ²S,S] gold(III) chloride hexafluorophosphate (32):** 63 mg (66% yield). Dark red solid. ^{1}H NMR (300 MHz, acetone-d_6) δ 0.80-0.93 (m, 3H, $N(CH_2)_5C\underline{H}_3$), 1.20-1.46 (m, 18H,

$CH(C\underline{H}_3)_2$, $N(CH_2)_2(C\underline{H}_2)_3CH_3$), 1.78-1.95 (m, 2H, $NCH_2C\underline{H}_2(CH_2)_3CH_3$), 3.60 (s, 3H, NCH_3), 3.86 (s, 3H, OCH_3), 3.77-3.94 (m, 2H, $C\underline{H}(CH_3)_2$), 4.15 (s, 3H, OCH_3), 4.29 (s, 3H, NCH_3), 4.67-4.85 (m, 2H, $NC\underline{H}_2(CH_2)_4CH_3$), 7.44-7.48 (m, 1H), 7.54-7.58 (m, 2H), 7.63-7.67 (m, 1H), 7.69-7.82 (m, 4H), 7.96-8.00 (m, 1H), 8.25-8.36 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, acetone-d_6) δ 14.1, 14.2, 23.07 (d, $^3J_{PC}$ 3.4 Hz), 23.13 (d, $^3J_{PC}$ 3.7 Hz), 23.49 (d, $^3J_{PC}$ 3.6 Hz), 23.54 (d, $^3J_{PC}$ 3.7 Hz), 31.8, 31.97, 32.03, 32.1, 40.5, 40.6, 49.40, 49.44, 51.1, 52.94, 52.98, 66.1, 93.2, 123.9, 124.00, 125.59, 130.0 (d, $^1J_{PC}$ 102.0 Hz), 130.1 (d, $^1J_{PC}$ 101.0 Hz), 123.6, 124.0, 125.6, 125.7, 127.9 (d, $^3J_{PC}$ 12.0 Hz), 128.0 (d, $^3J_{PC}$ 12.0 Hz), 130.2 (d, $^2J_{PC}$ 13.3 Hz), 130.3 (d, $^2J_{PC}$ 13.4 Hz), 131.60 (d, $^2J_{PC}$ 17.9 Hz), 131.65 (d, $^2J_{PC}$ 18.0 Hz), 133.6 (d, $^3J_{PC}$ 13.3 Hz), 133.99 (d, $^3J_{PC}$ 13.8 Hz), 134.3 (d, $^3J_{PC}$ 11.4 Hz), 134.4 (d, $^3J_{PC}$ 11.9 Hz), 140.6 (d, $^1J_{PC}$ 124.6 Hz), 140.8 (d, $^1J_{PC}$ 123.4 Hz), 148.1, 149.5 (d, $^2J_{PC}$ 31.7 Hz), 149.6 (d, $^2J_{PC}$ 31.9 Hz) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, acetone-d_6) δ = -144.1 (h, $^1J_{PF}$ 706.9 Hz), 77.1, 78.4 ppm. HRMS (ESI^+) $[M]^+$ calcd. for $C_{30}H_{44}AuN_3OPS_3$, 786.2044; found, 786.2045.

***trans*-[2-((Diisopropylamino)(phenyl)phosphorothioyl)phenyl] [1-octyl-3-methylimidazolium-2-(methoxy)methanedithiol-κ²S,S] gold(III) chloride hexafluorophosphate (33):** 62 mg (64% yield). Dark red solid. ^1H NMR (400 MHz, acetone-d_6) δ 0.84-0.89 (m, 3H, $N(CH_2)_5C\underline{H}_3$), 1.27-1.37 (m, 18H, $CH(C\underline{H}_3)_2$, $N(CH_2)_2(C\underline{H}_2)_3CH_3$), 1.86-1.97 (m, 2H, $NCH_2C\underline{H}_2(CH_2)_3CH_3$), 3.59, 3.73 (2 x s, 3H, OCH_3), 3.59-3.93 (m, 2H, $C\underline{H}(CH_3)_2$), 4.14, 4.29 (2 x s, 3H, NCH_3), 4.62-4.83 (m, 2H, $NC\underline{H}_2(CH_2)_4CH_3$), 7.46-7.47 (m, 1H), 7.55-7.64 (m, 3H), 7.77-7.80 (m, 4H), 7.95-7.98 (m, 1H), 8.25-8.33 (m, 2H) ppm.$^{13}C\{^1H\}$ NMR (101 MHz, acetone-d_6) δ 14.2, 14.4, 23.0, 23.1, 23.3 (d, $^3J_{PH}$ 3.8 Hz), 23.6 (d, $^3J_{PH}$ 3.8 Hz), 26.6, 26.8, 31.8, 31.98, 32.04, 32.1, 49.42, 49.46, 51.2, 52.99, 53.01, 93.2, 123.9, 124.0, 125.6, 125.7, 127.9 (d, $^3J_{PC}$ 11.9 Hz), 128.0 (d, $^3J_{PC}$ 12.2 Hz), 130.10 (d, $^1J_{PC}$ 101.8 Hz), 130.15 (d, $^1J_{PC}$ 100.8 Hz), 130.2 (d, $^2J_{PC}$ 13.6 Hz), 130.3 (d, $^2J_{PC}$ 13.3 Hz), 131.60 (d, $^2J_{PC}$ 18.0 Hz), 131.64 (d, $^2J_{PC}$ 18.0 Hz), 133.6 (d, $^3J_{PC}$ 13.6 Hz), 133.9 (d, $^3J_{PC}$ 13.6 Hz), 135.12-135.15 (m), 140.6 (d, $^1J_{PC}$ 96.0 Hz), 148.6, 149.6 (d, $^2J_{PC}$ 31.8 Hz), 149.7 (d, $^2J_{PC}$ 31.7 Hz) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, acetone-d_6) δ = -144.7 (sep, $^1J_{PF}$ 707.3 Hz), 76.9 78.3 ppm. HRMS (ESI^+) $[M]^+$ calcd. for $C_{32}H_{48}AuN_3OPS_3$, 814.2357; found, 814.2341.



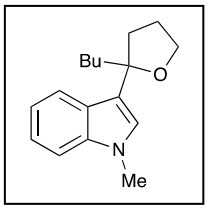
***trans*-[2-((Diisopropylamino)(phenyl)phosphorothioyl)phenyl] [1,3-bis(diisopropylphenyl)imidazolium-2-(methoxy)methanedithiol-κ²S,S] gold(III) chloride hexafluorophosphate (34):** 65 mg (55% yield). Orange solid. ^{1}H NMR (400 MHz, acetone-d_6) δ 1.13-1.45 (m, 36H), 2.57-2.72 (m, 4H, 4 x C<u>H</u>$(CH_3)_2$), 3.1, 3.2 (2 x s, 2 x OMe), 3.67-3.82 (m, 2H, 2 x C<u>H</u>$(CH_3)_2$), 6.94-7.05 (m, 1H), 7.22-7.35 (m, 3H), 7.41–7.95 (m, 9H), 8.16-8.24 (m, 4H) ppm. ^{13}C{^{1}H} NMR (101 MHz, acetone-d_6) δ 21.8, 21.9, 22.2 (d, $^{3}J_{PC}$ 3.4 Hz), 22.3 (d, $^{3}J_{PC}$ 2.8 Hz), 22.5 (d, $^{3}J_{PC}$ 2.6 Hz), 22.6 (d, $^{3}J_{PC}$ 3.0 Hz), 24.6, 24.7, 24.8, 48.2, 48.3, 50.07, 50.12, 50.2, 91.39, 91.44, 124.0, 124.2, 124.3, 124.4, 126.0, 126.7 (d, $^{3}J_{PC}$ 12.0 Hz), 126.8 (d, $^{3}J_{PC}$ 11.9 Hz), 129.2, (d, $^{1}J_{PC}$ 101.9 Hz), 129.2 (d, $^{2}J_{PC}$ 12.9 Hz), 130.1 (d, $^{2}J_{PC}$ 18.3 Hz), 130.4 (d, $^{2}J_{PC}$ 18.3 Hz), 131.2, 131.5, 132.7, 132.7, 133.1 (d, $^{3}J_{PC}$ 10.7 Hz), 133.3 (d, $^{3}J_{PC}$ 11.8 Hz), 133.7 (d, $^{2}J_{PC}$ 11.8 Hz), 133.8 (d, $^{2}J_{PC}$ 11.8 Hz), 134.0 (d, $^{4}J_{PC}$ 2.7 Hz), 134.2 (d, $^{4}J_{PC}$ 2.7 Hz), 136.5 (d, $^{4}J_{PC}$ 1.9 Hz), 139.4 (d, $^{1}J_{PC}$ 124.7 Hz), 140.1 (d, $^{1}J_{PC}$ 124.1 Hz), 145.95, 145.04, 145.24, 147.73 (d, $^{2}J_{PC}$ 32.8 Hz), 148.48 (d, $^{2}J_{PC}$ 32.2 Hz), 148.9, 149.3 ppm. ^{31}P{^{1}H} NMR (121 MHz, acetone-d_6) δ -144.6 (hept, $^{1}J_{PF}$ 707.5 Hz), 68.9, 79.2 ppm. HRMS (ESI^{+}) $[M]^{+}$ calcd. for $C_{47}H_{62}AuN_3OPS_3$, 1008.4453; found, 1008.4451.

II.4.- Synthesis of Alkylated Indoles A mixture of alkynyl alcohol **35** (0.24 mmol), indole **36** (0.2 mmol), the corresponding gold complex **4** (2.5 mol %) and $AgBF_4$ (5 mol %) in CH_2Cl_2 (2 mL) was stirred at room temperature for 2 h. The reaction mixture was diluted with CH_2Cl_2 (5 mL), washed with water (2 x 5 mL) and brine (5 mL), dried, filtered and evaporated to dryness. The residue was purified by flash column chromatography over silica gel eluting with mixtures of EtOAc/Hex. Data for indoles **37** are in accordance with those reported in the literature. [3]

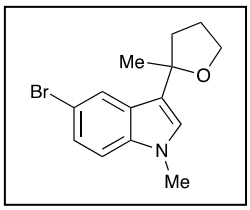
1-Methyl-3-(2-methyltetrahydrofuran-2-yl)-1*H*-indole 37a: Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.71 (s, 3H, CH_3), 1.95–2.09 (m, 3H), 2.39–2.44 (m, 1H), 3.77 (s, 3H, CH_3), 3.99–4.04 (m, 2H), 6.97 (s, 1H), 7.11 (ddd, $^{3}J_{HH}$ 8.0, 6.8, 1.3 Hz, 1H), 7.19–7.25 (m, 1H), 7.30 (ddd, $^{3}J_{HH}$ 8.2, 1.3, 0.8 Hz, 1H), 7.71 (ddd, $^{3}J_{HH}$ 8.0, 1.2, 0.8 Hz, 1H) ppm.

3-(2-Ethyltetrahydrofuran-2-yl)-1-methyl-1*H*-indole 37b: Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.82 (t, 3H, $^{3}J_{HH}$ 7.3 Hz, CH_3), 1.90–

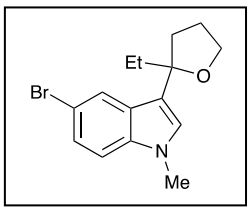
2.11 (m, 5H), 2.33–2.37 (m, 1H), 3.77 (s, 3H, CH_3), 3.91–3.99 (m, 2H), 6.96 (s, 1H), 7.10 (t, $^3J_{HH}$ 8.0 Hz, 1H), 7.23 (t, $^3J_{HH}$ 7.2 Hz, 1H), 7.28–7.32 (m, 1H), 7.71 (d, $^3J_{HH}$ 8.0 Hz, 1H) ppm.



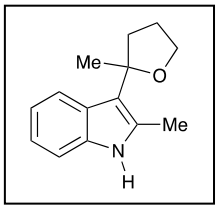
3-(2-Butyltetrahydrofuran-2-yl)-1-methyl-1*H*-indole 37c: Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.82 (t, 3H, $^3J_{HH}$ 7.0 Hz, CH_3), 1.09-1.36 (m, 4H), 1.84–2.11 (m, 5H), 2.32–2.40 (m, 1H), 3.76 (s, 3H, CH_3), 3.89–4.01 (m, 2H), 6.95 (s, 1H), 7.10 (dd, 1H, $^3J_{HH}$ 8.0, 6.9 Hz), 7.20–7.25 (m, 1H), 7.30 (t, 1H, $^3J_{HH}$ 8.2 Hz), 7.71 (t, 1H, $^3J_{HH}$ 8.0 Hz) ppm.



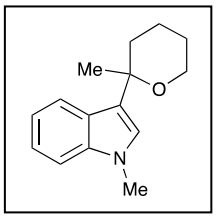
5-Bromo-1-methyl-3-(2-methyltetrahydrofuran-2-yl)-1*H*-indole 37d: Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.64 (s, 3H, CH_3), 1.81–2.15 (m, 3H), 2.32 (ddd, 1H, $^3J_{HH}$ 9.3, 6.5, 3.0 Hz), 3.72 (s, 3H, CH_3), 3.87–4.20 (m, 2H), 6.95 (s, 1H), 7.14 (t, 1H, $^3J_{HH}$ 8.7 Hz), 7.24 (t, 1H, $^3J_{HH}$ 7.0 Hz), 7.82 (d, 1H, $^3J_{HH}$ 1.9 Hz) ppm.



5-Bromo-3-(2-ethyltetrahydrofuran-2-yl)-1-methyl-1*H*-indole 37e: Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.82 (t, 3H, $^3J_{HH}$ 7.4 Hz), 1.90–2.01 (m, 3H, CH_3), 1.98 (q, 2H, $^3J_{HH}$ 7.4 Hz, CH_2), 2.18–2.47 (m, 1H), 3.75 (s, 3H, CH_3), 3.85–4.06 (m, 2H), 6.96 (s, 1H), 7.16 (d, 1H, $^3J_{HH}$ 8.7 Hz), 7.30 (dd, 1H, $^3J_{HH}$ 8.7, 1.8 Hz), 7.85 (d, $^3J_{HH}$ 1.8 Hz, 1H) ppm.



2-Methyl-3-(2-Methyltetrahydro-2*H*-pyran-2-yl)-1*H*-indole 37f: Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.64 (s, 3H, CH_3), 1.90-2.11 (m, 2H), 2.13-2.19 (m, 1H), 2.19-2.51 (m, 1H), 2.53 (s, 3H, CH_3), 3.85-4.05 (m, 2H), 7.02-7.12 (m, 2H), 7.23-7.26 (m, 1H), 7.62-7.65 (m, 2H) ppm.



2-Methyl-3-(2-propyltetrahydro-2*H*-pyran-2-yl)-1*H*-indole 37g: Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.59 (s, 3H, CH_3), 1.62–1.90 (m, 5H), 2.20–2.32 (m, 2H), 3.72 (s, 3H, CH_3), 3.50 (td, 1H, J_{HH} 11.3, 2.7 Hz), 3.51–3.82 (m, 1H), 6.95 (s, 1H), 7.13 (ddd, 1H, $^3J_{HH}$ 8.0, 6.8, 1.3 Hz), 7.20–7.39 (m, 1H), 7.96 (dd, 1H, $^3J_{HH}$ 8.0, 1.0 Hz) ppm.

III.- NMR spectra

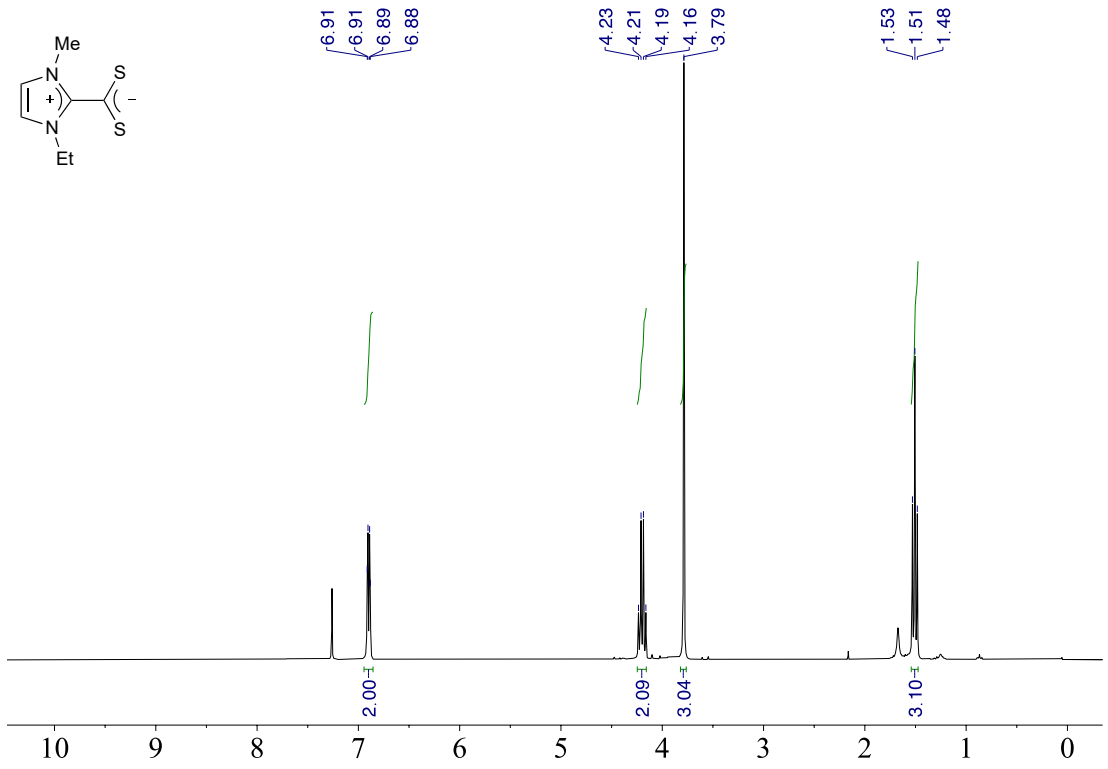


Figure S1. ^{1}H-NMR of **16** in $CDCl_3$.

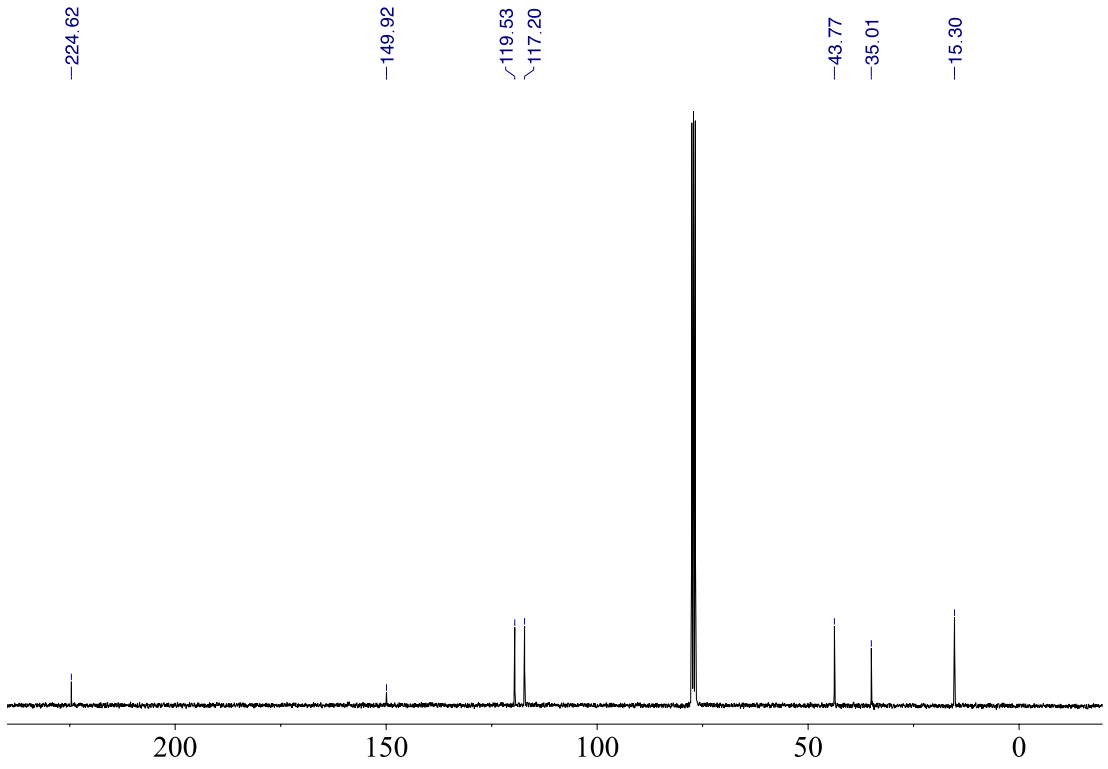


Figure S2. ^{13}C-NMR of **16** in $CDCl_3$.

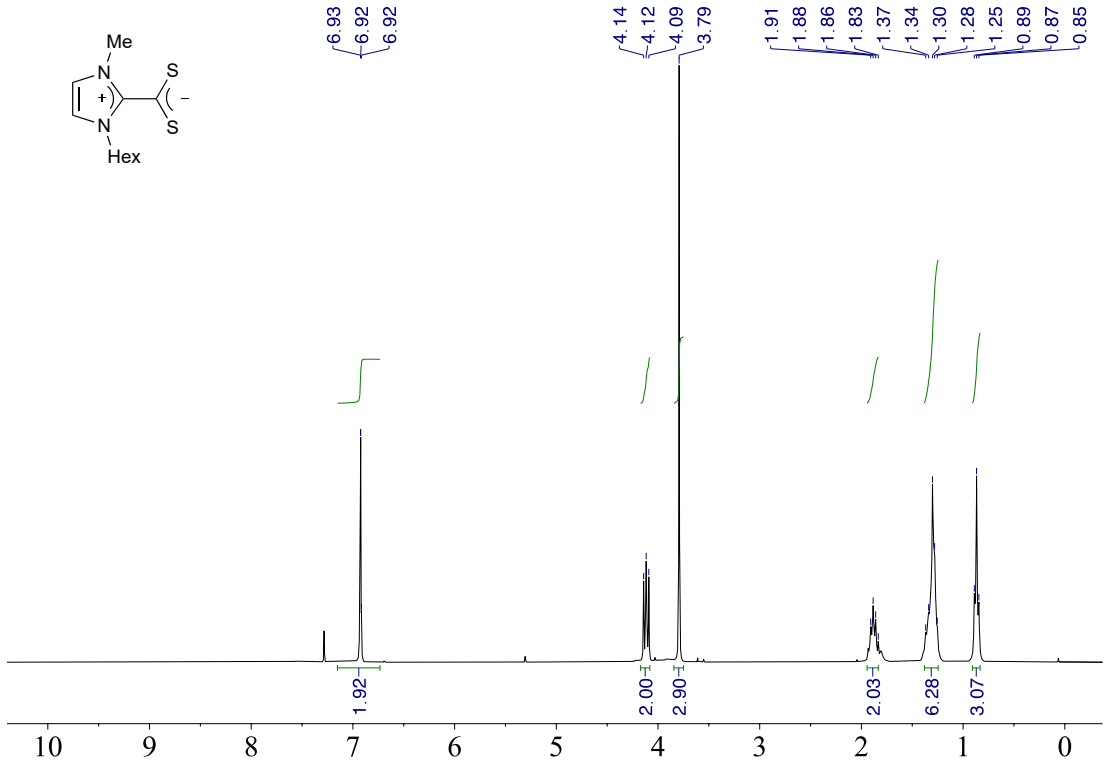


Figure S3. ^{1}H-NMR of **18** in $CDCl_3$.

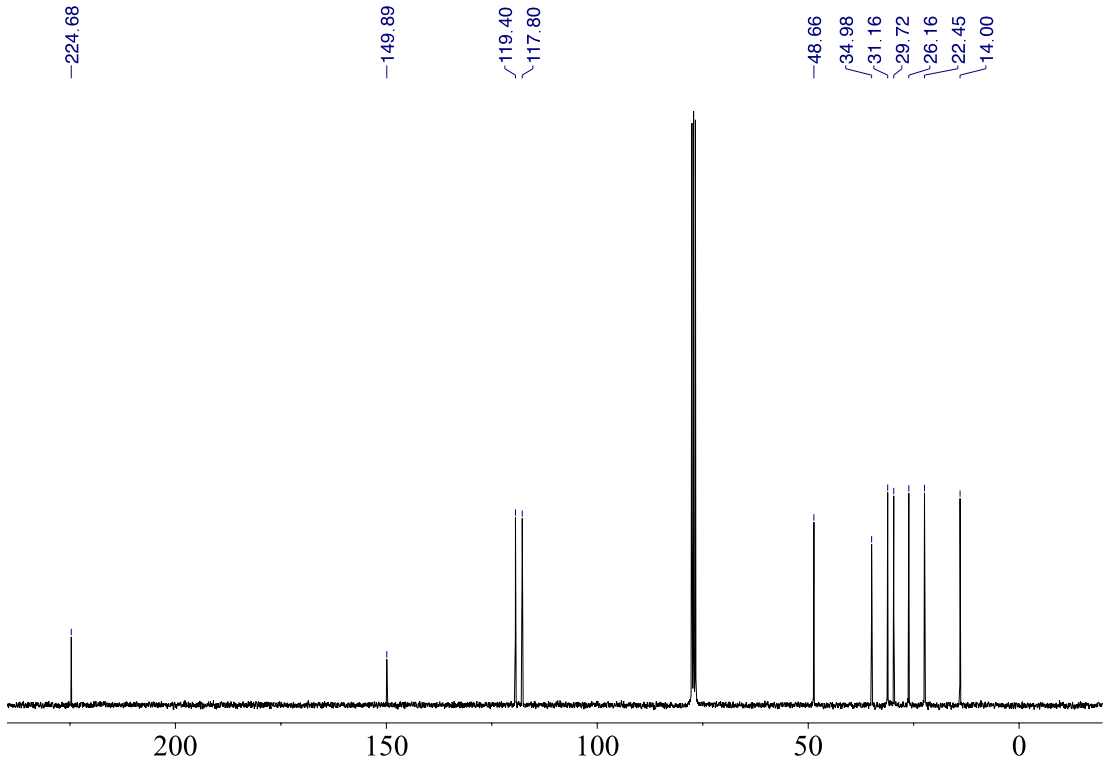


Figure S4. ^{13}C-NMR of **18** in $CDCl_3$.

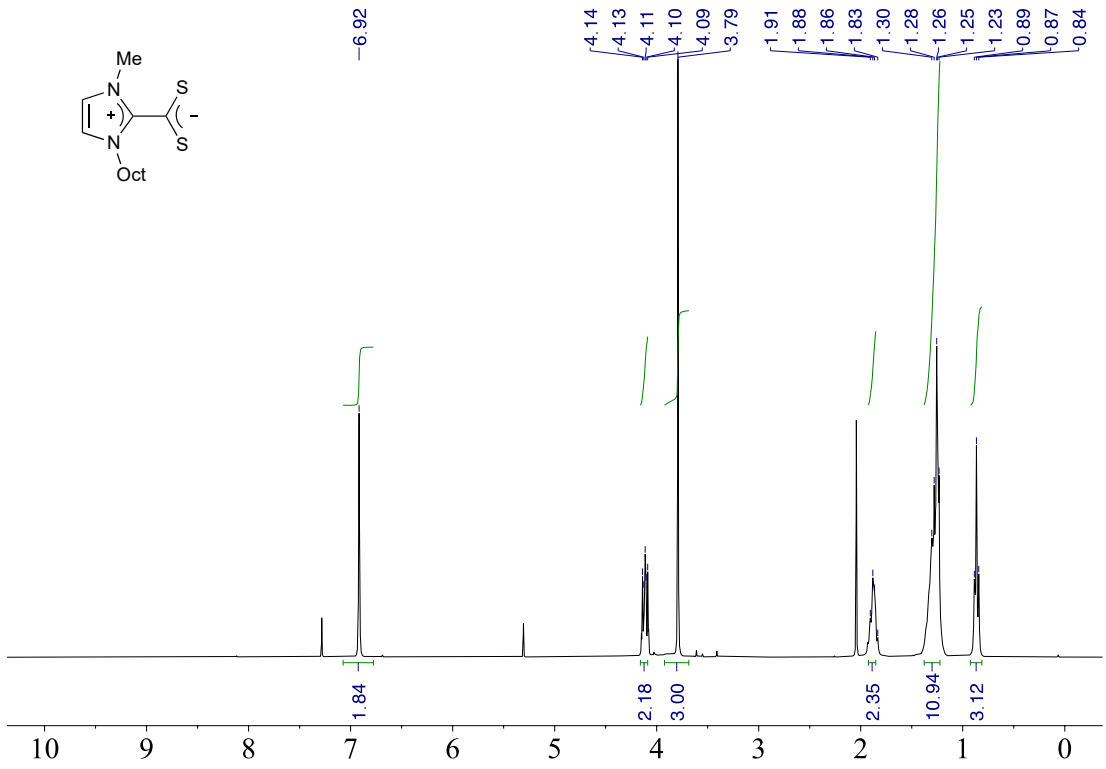


Figure S5. ^{1}H-NMR of **19** in $CDCl_3$.

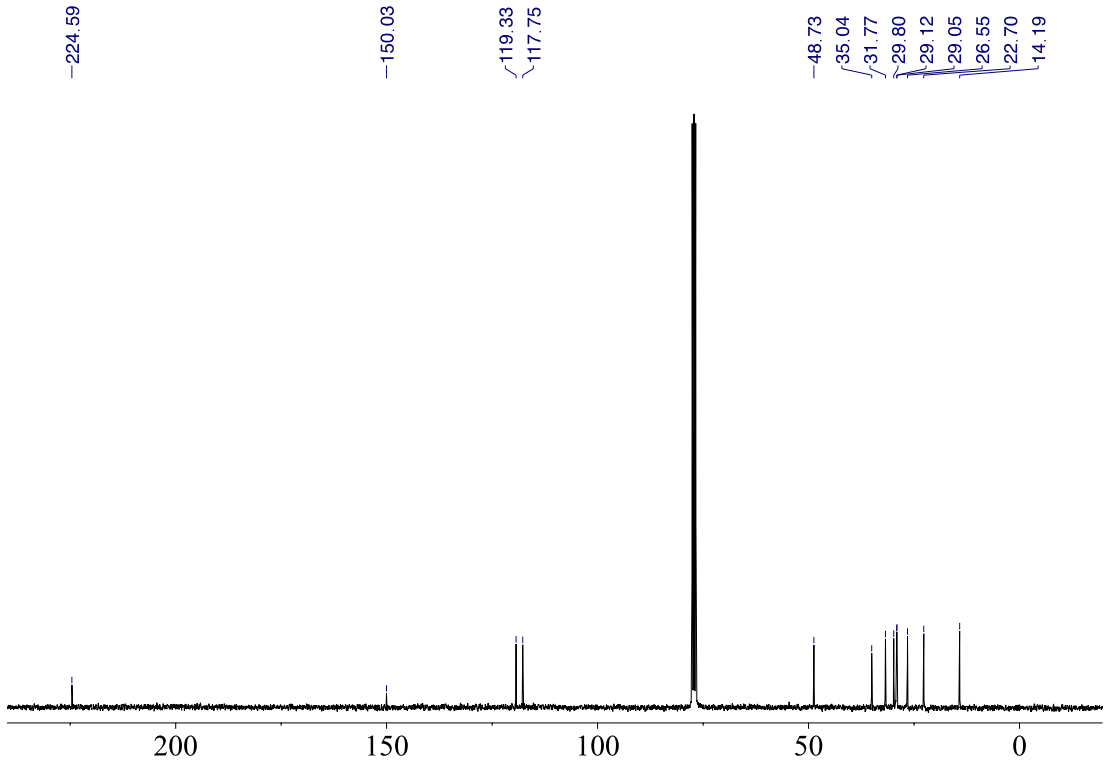


Figure S6. ^{13}C-NMR of **19** in $CDCl_3$.

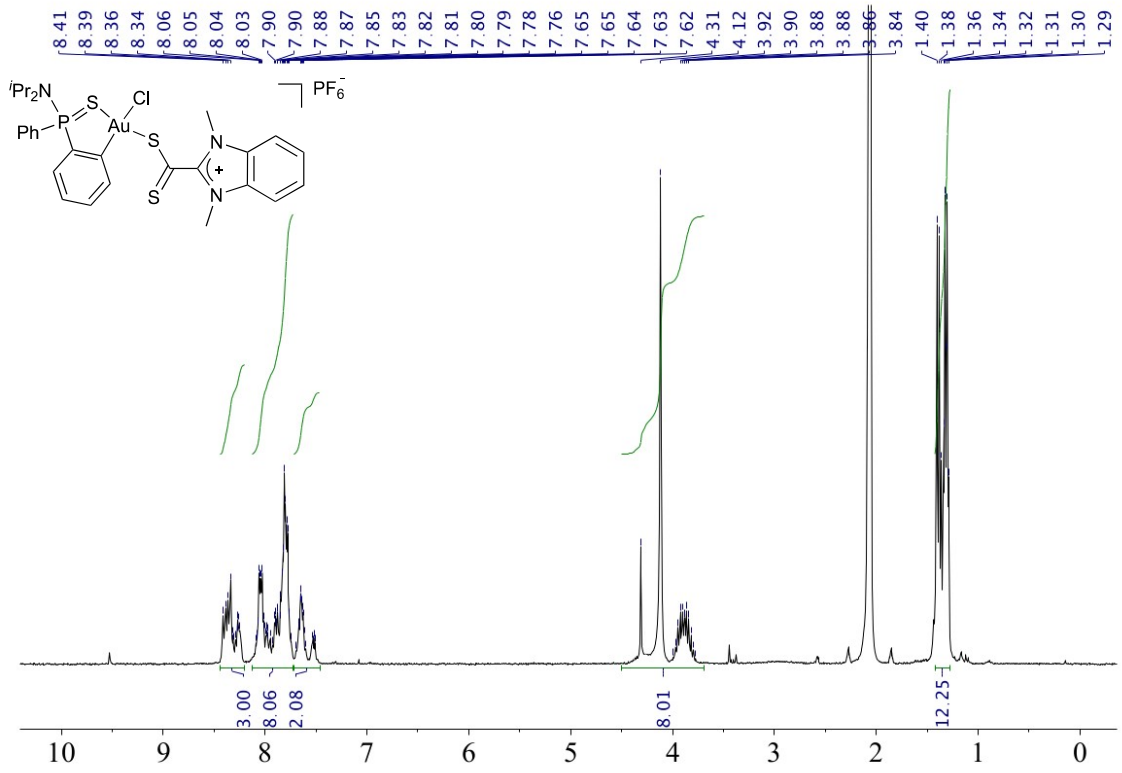


Figure S7. ^{1}H-NMR of **21** in acetone-d_6.

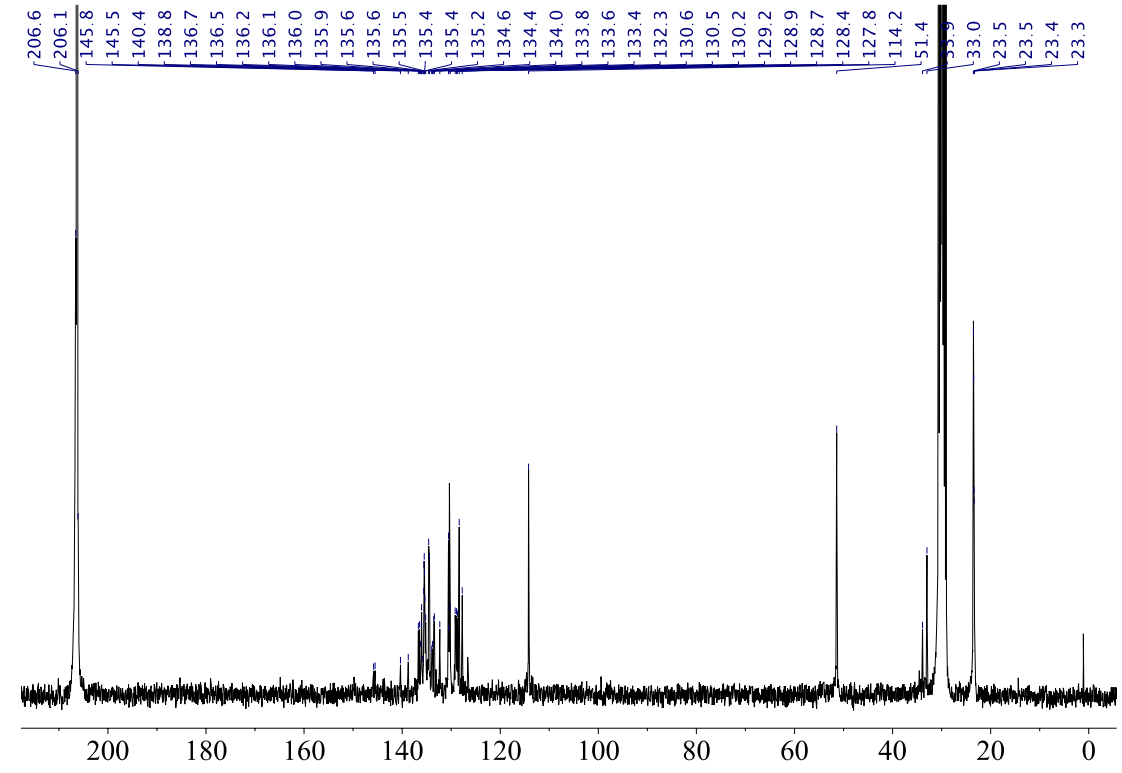


Figure S8. ^{13}C-NMR of **21** in acetone-d_6.

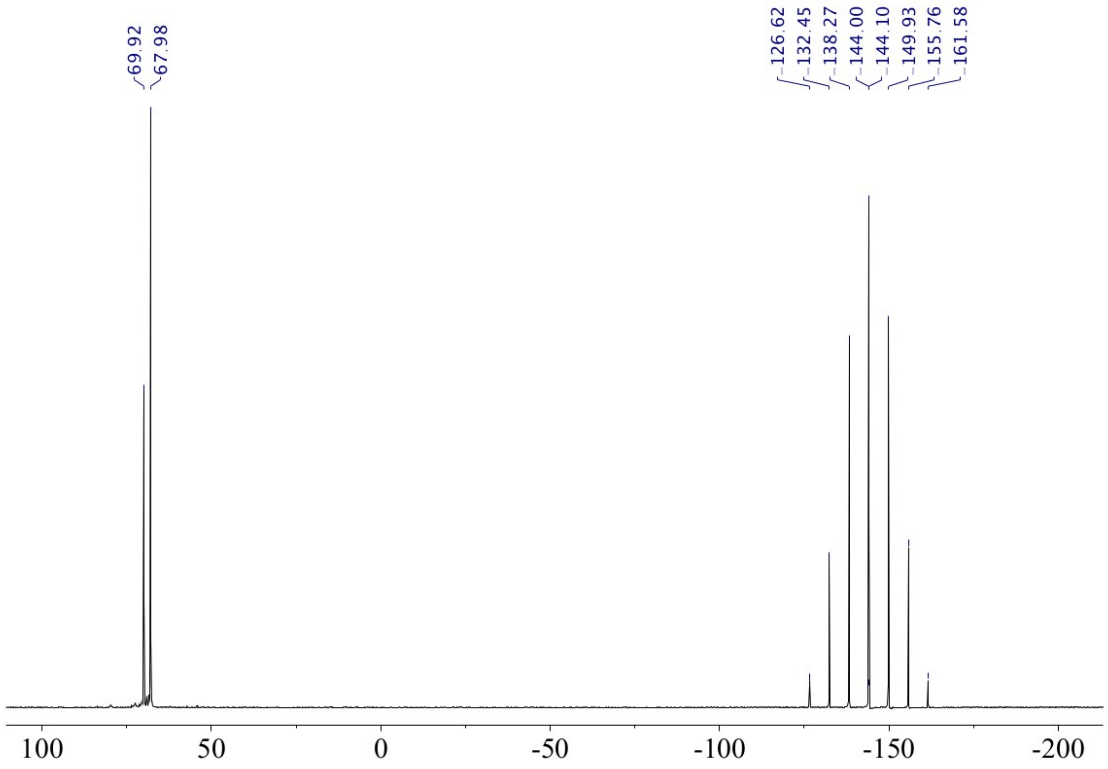


Figure S9. ^{31}P-NMR of **21** in acetone-d_6.

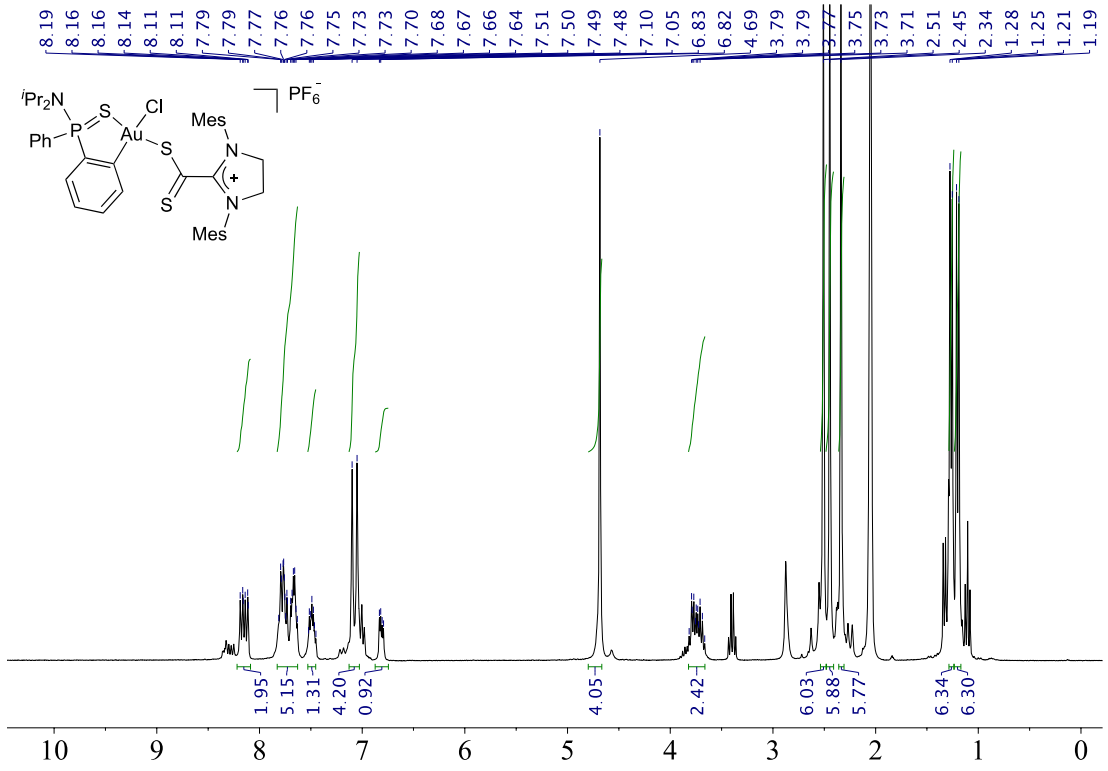


Figure S10. ^{1}H-NMR of **22** in acetone-d_6.

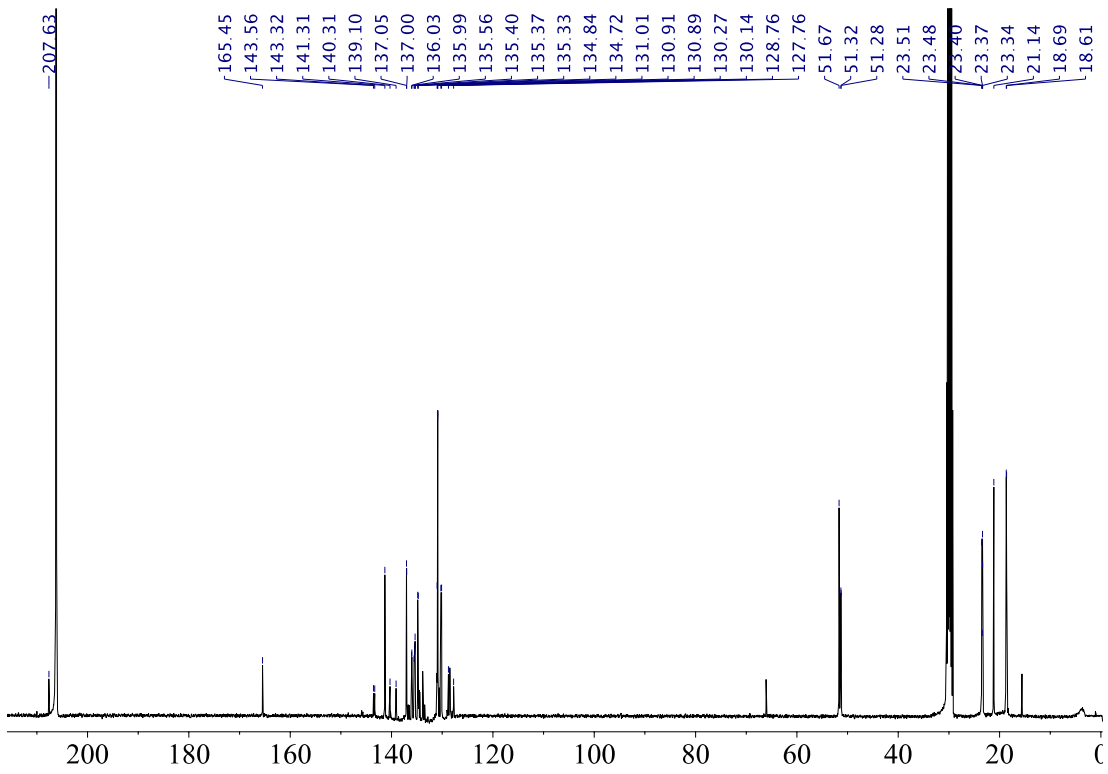


Figure S11. ^{13}C-NMR of **22** in acetone-d_6.

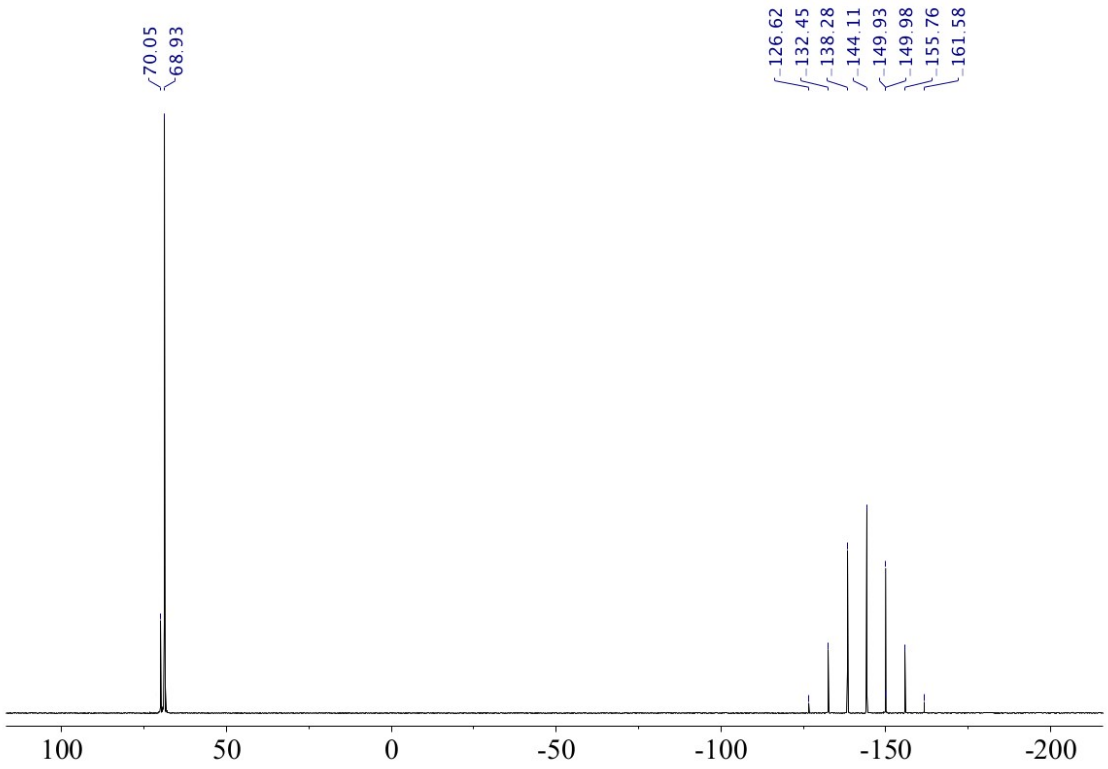


Figure S12. ^{31}P-NMR of **22** in acetone-d_6.

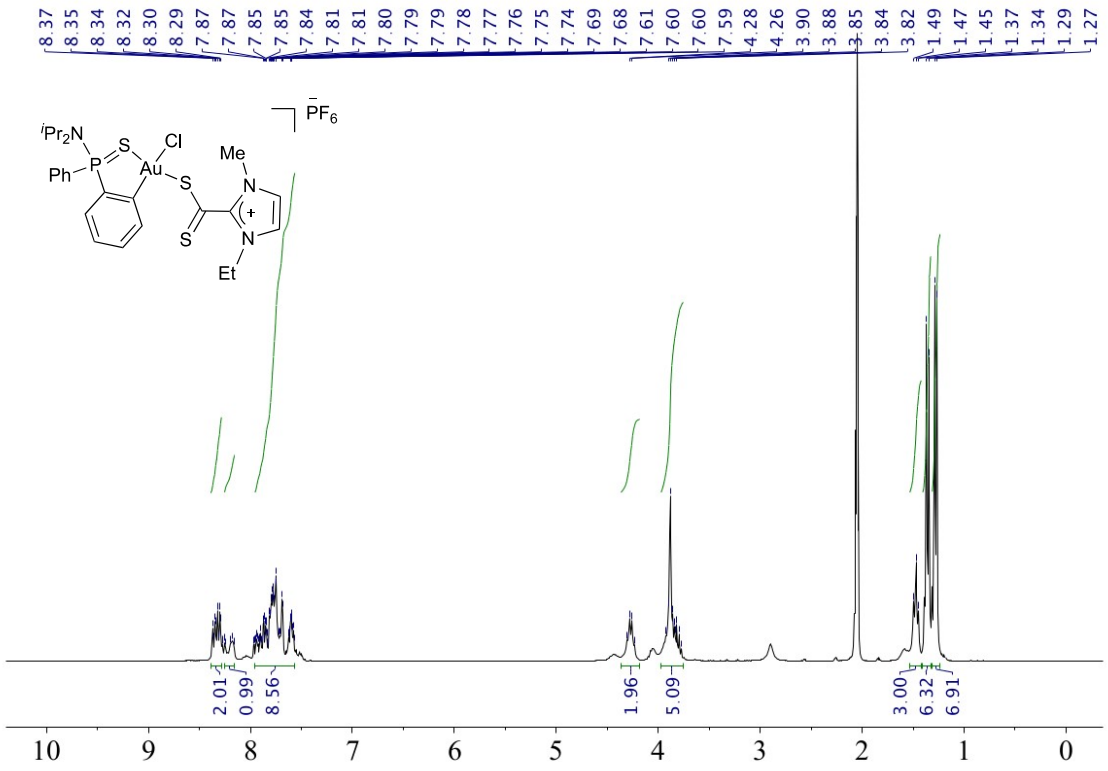


Figure S13. ^{1}H-NMR of **23** in acetone-d_6.

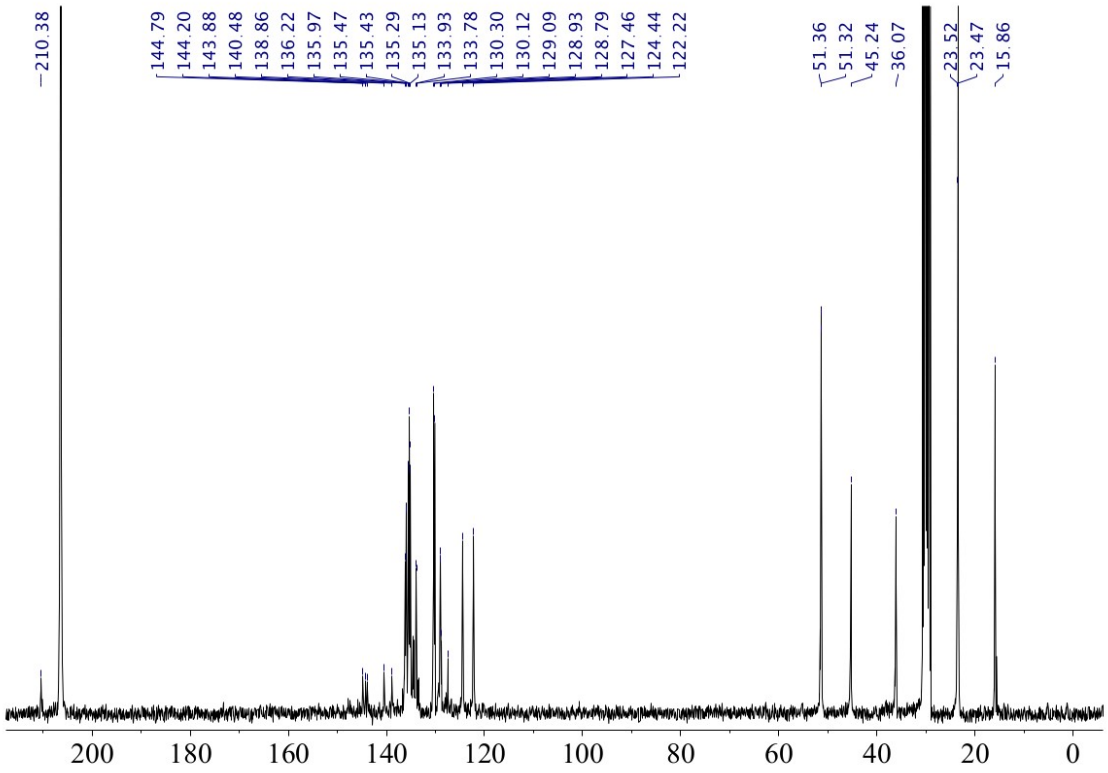


Figure S14. ^{13}C-NMR of **23** in acetone-d_6.

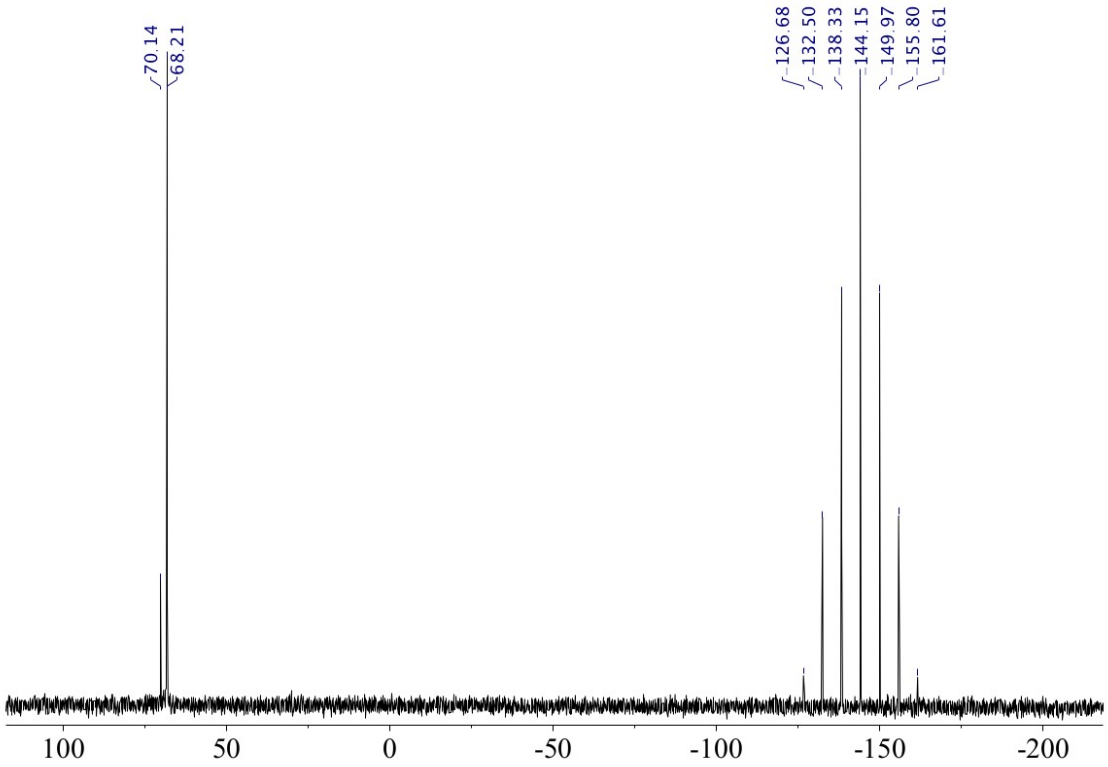


Figure S15. ^{31}P-NMR of **23** in acetone-d_6.

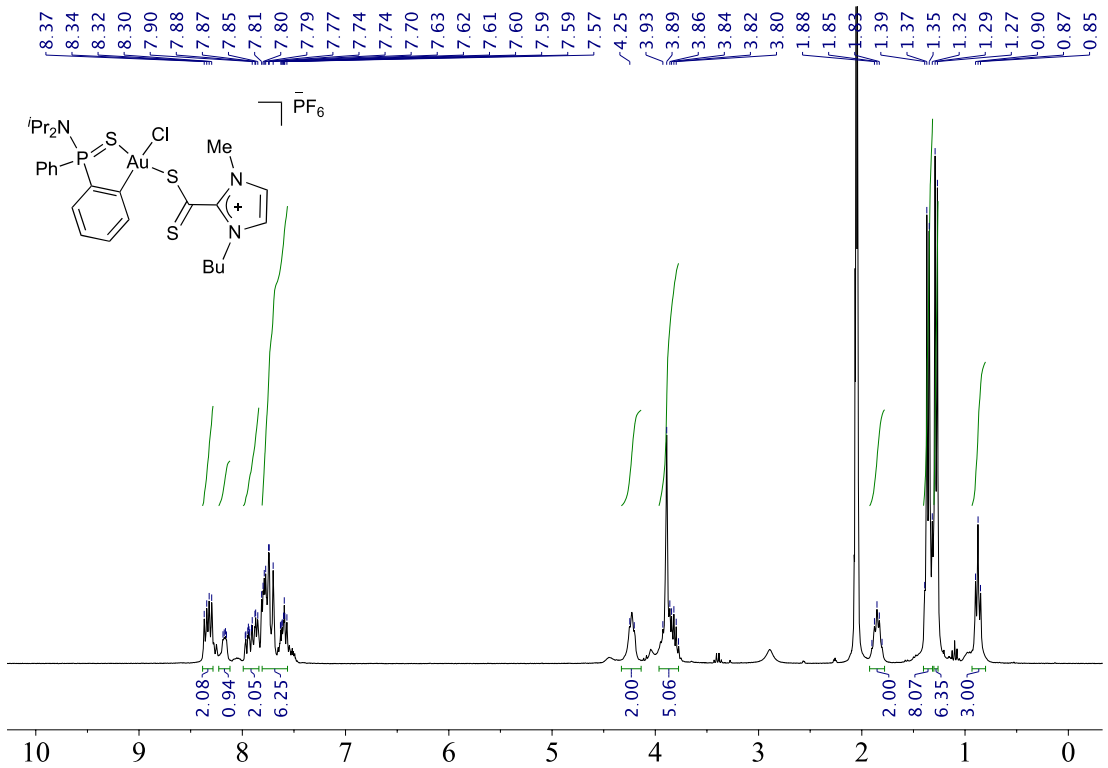


Figure S16. ^{1}H-NMR of **24** in acetone-d_6.

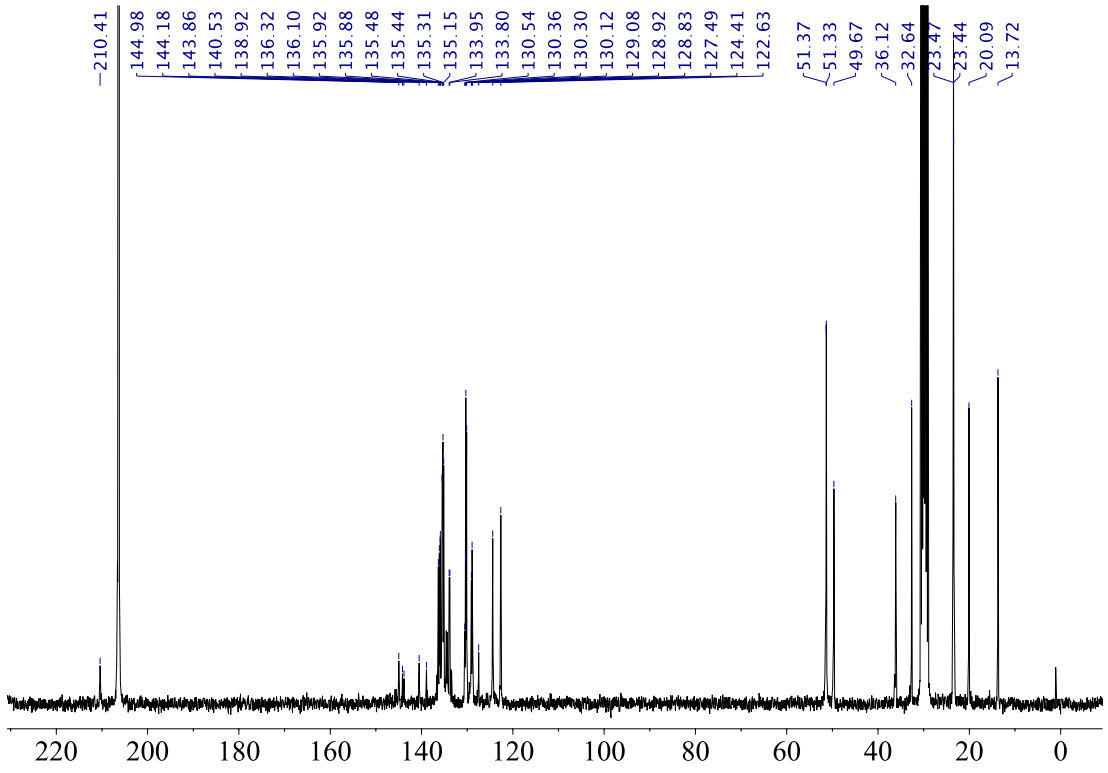


Figure S17. ^{13}C-NMR of **24** in acetone-d_6.

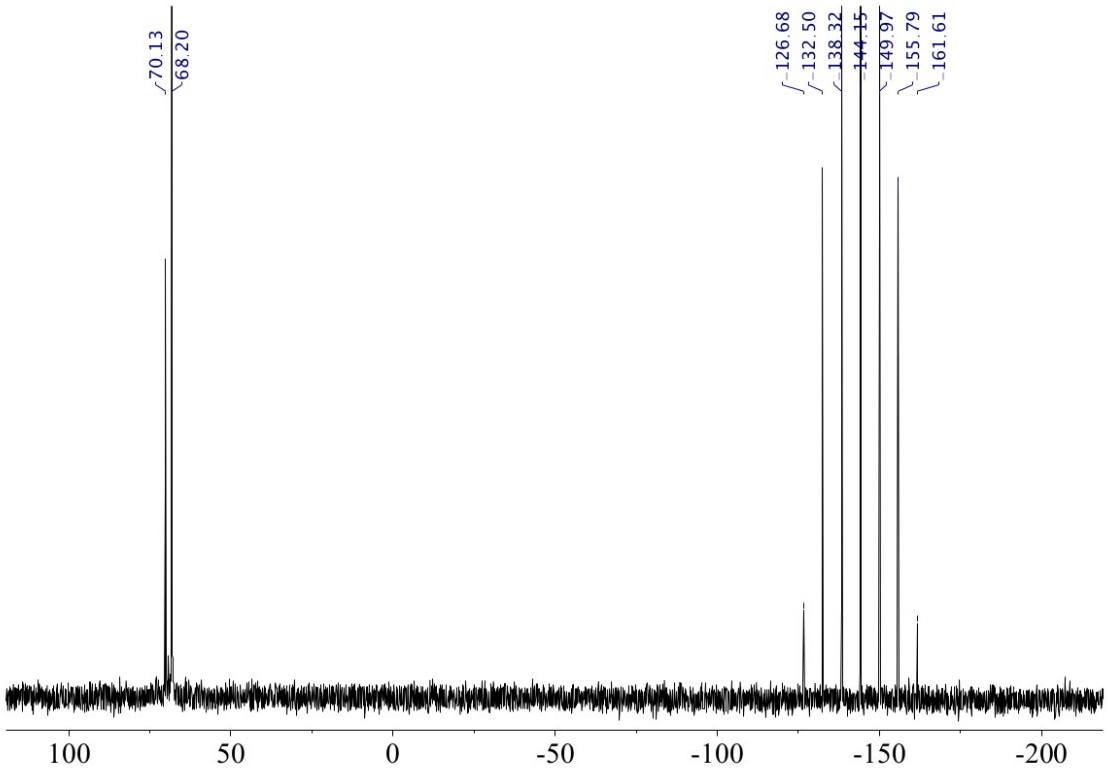


Figure S18. ^{31}P-NMR of **24** in acetone-d_6.

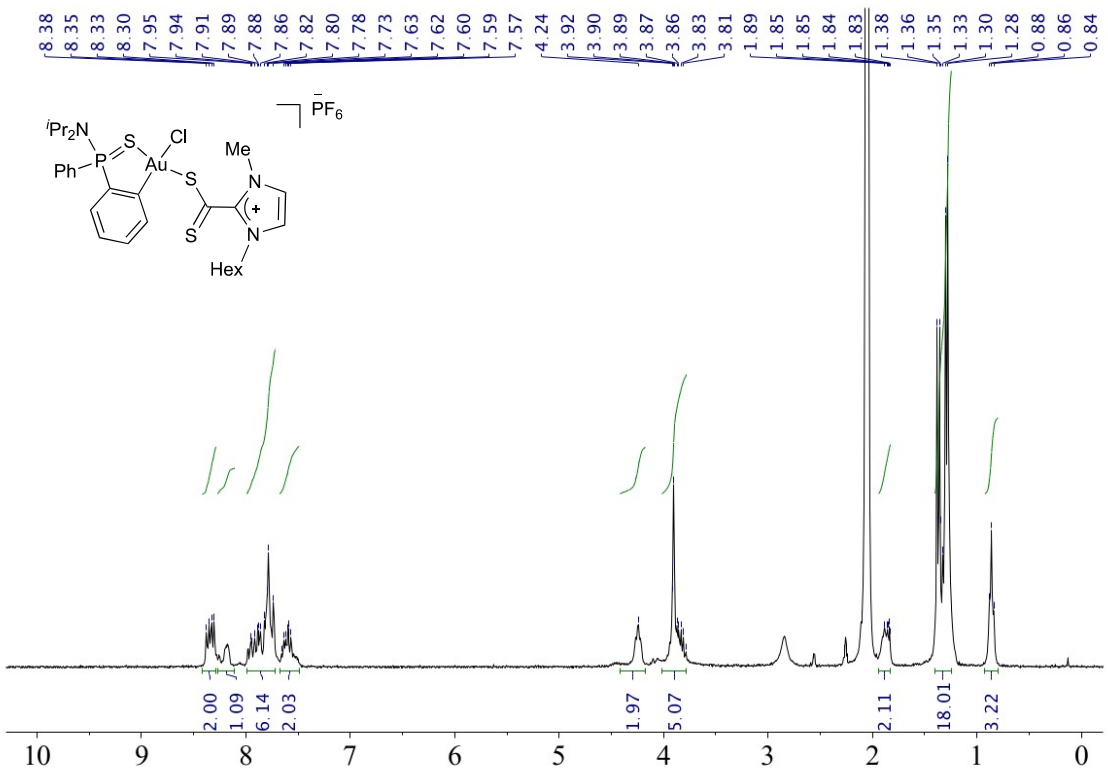


Figure S19. ^{1}H-NMR of **25** in acetone-d_6.

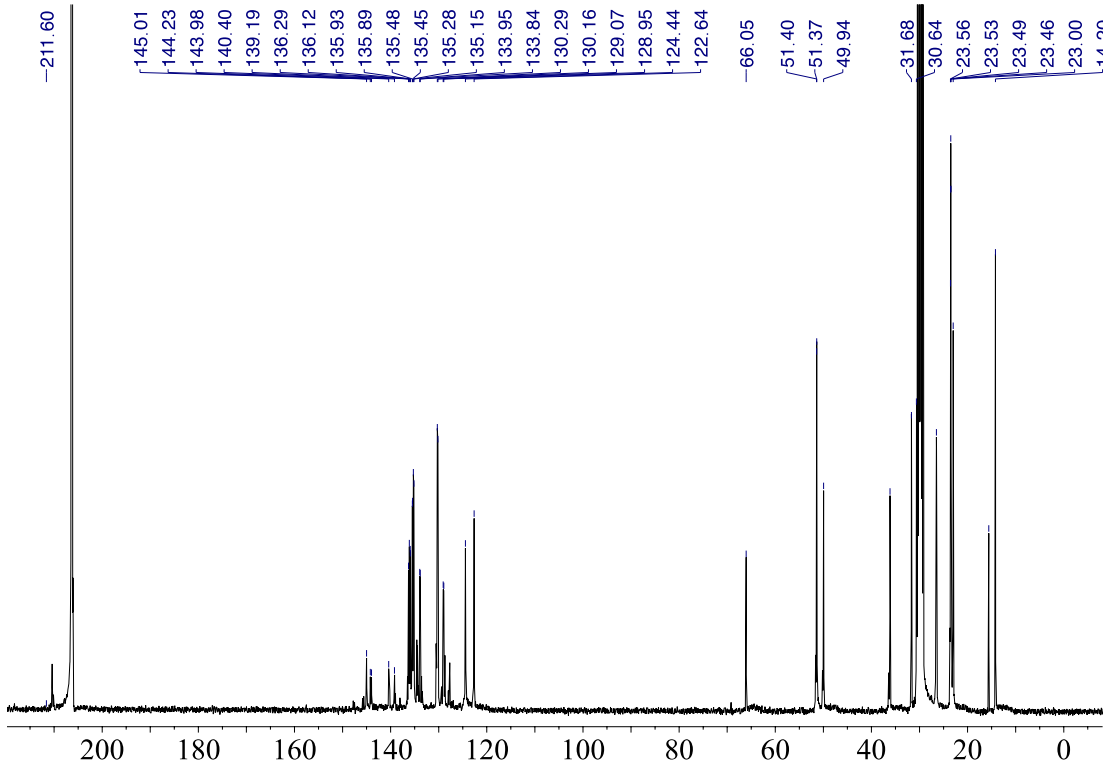


Figure S20. ^{13}C-NMR of **25** in acetone-d_6.

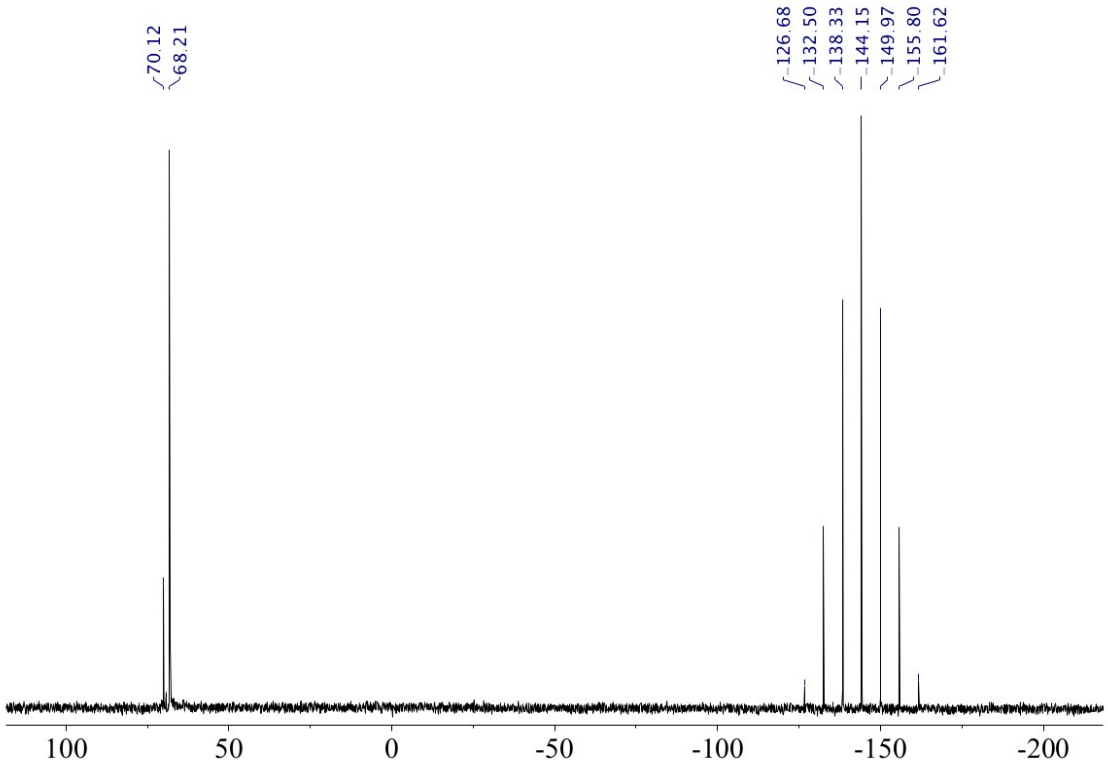


Figure S21. ^{31}P-NMR of **25** in acetone-d_6.

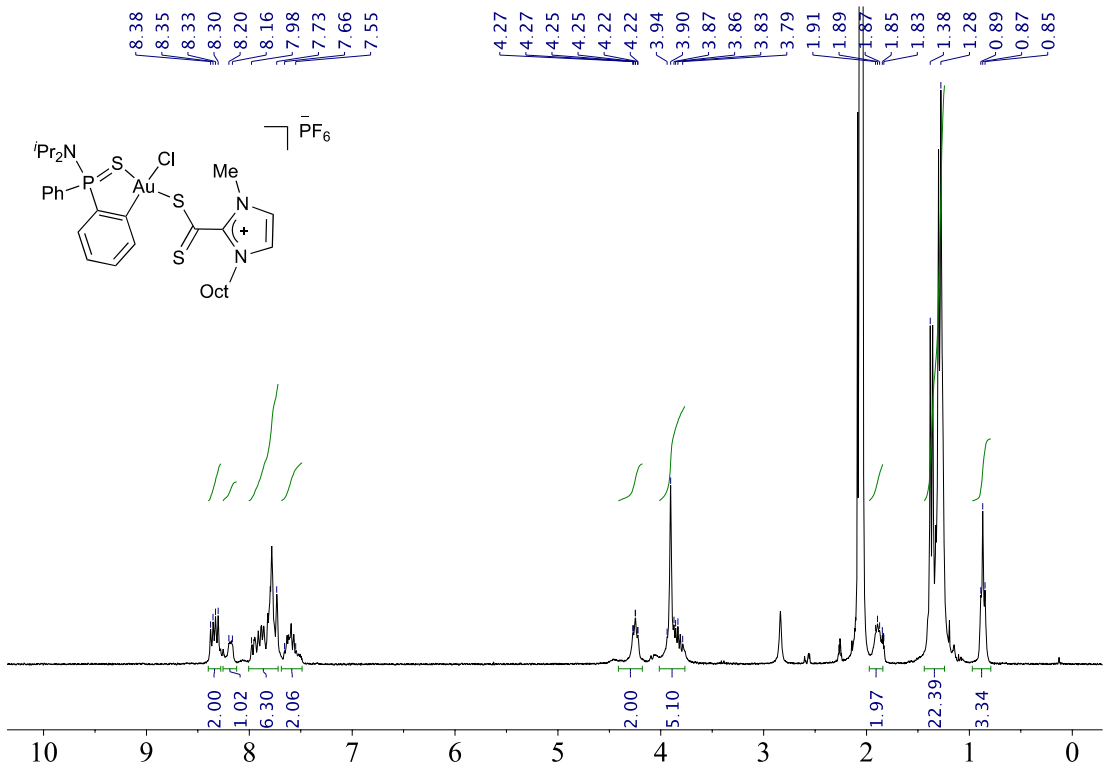


Figure S22. ^{1}H-NMR of **26** in acetone-d_6.

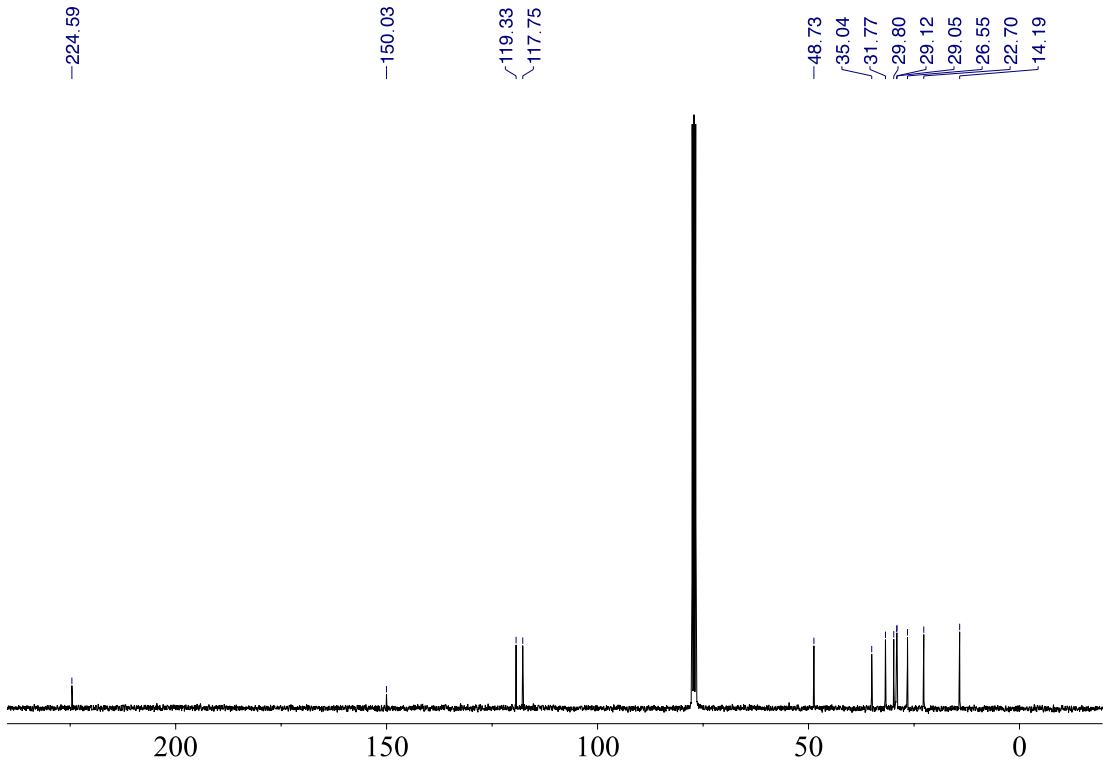


Figure S23. ^{13}C-NMR of **26** in acetone-d_6.

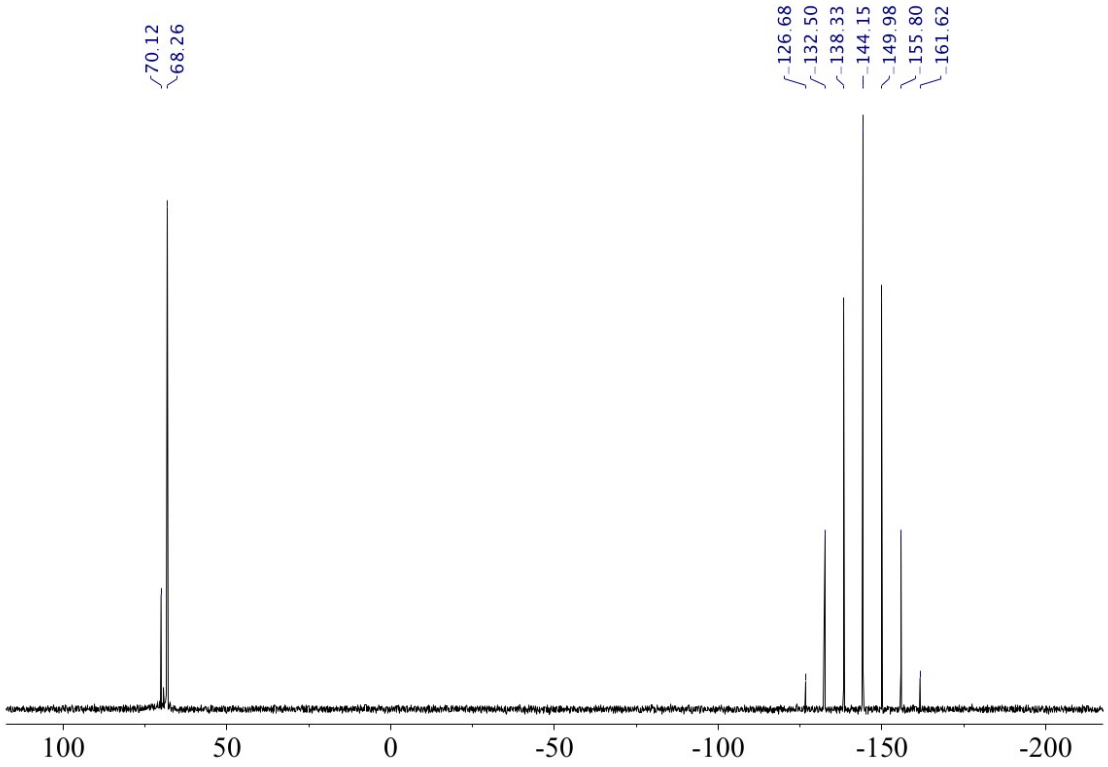


Figure S24. ^{31}P-NMR of **26** in acetone-d_6.

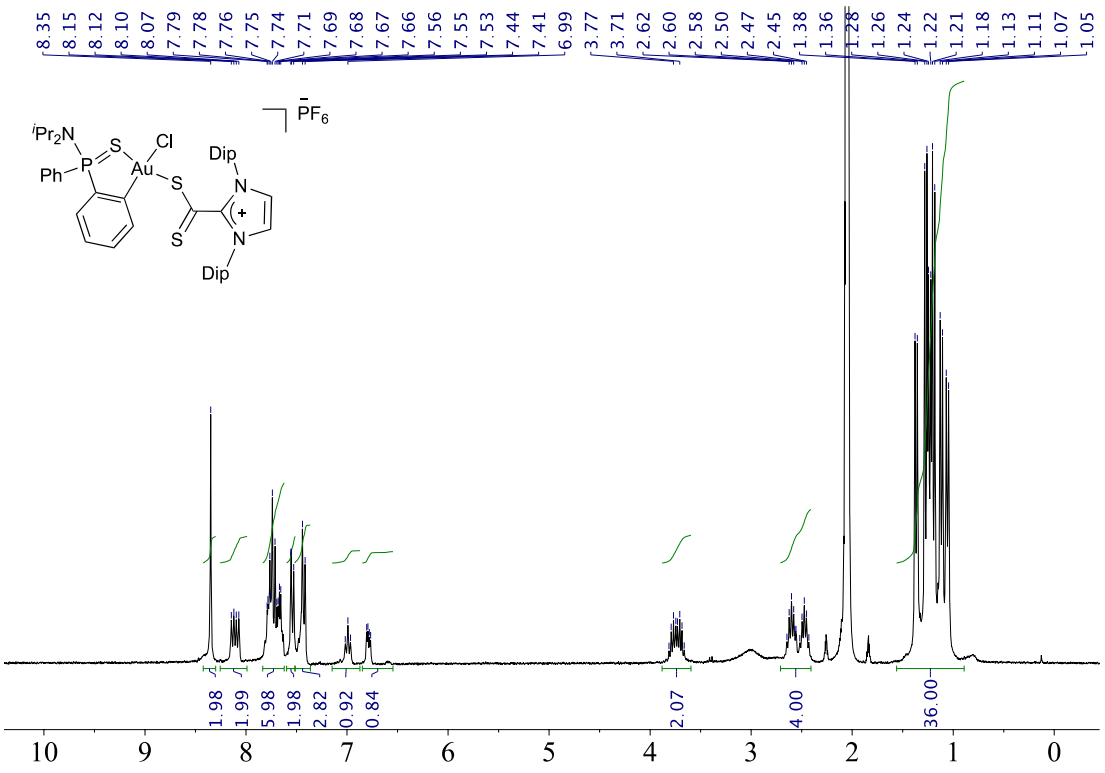


Figure S25. ^{1}H-NMR of **27** in acetone-d_6.

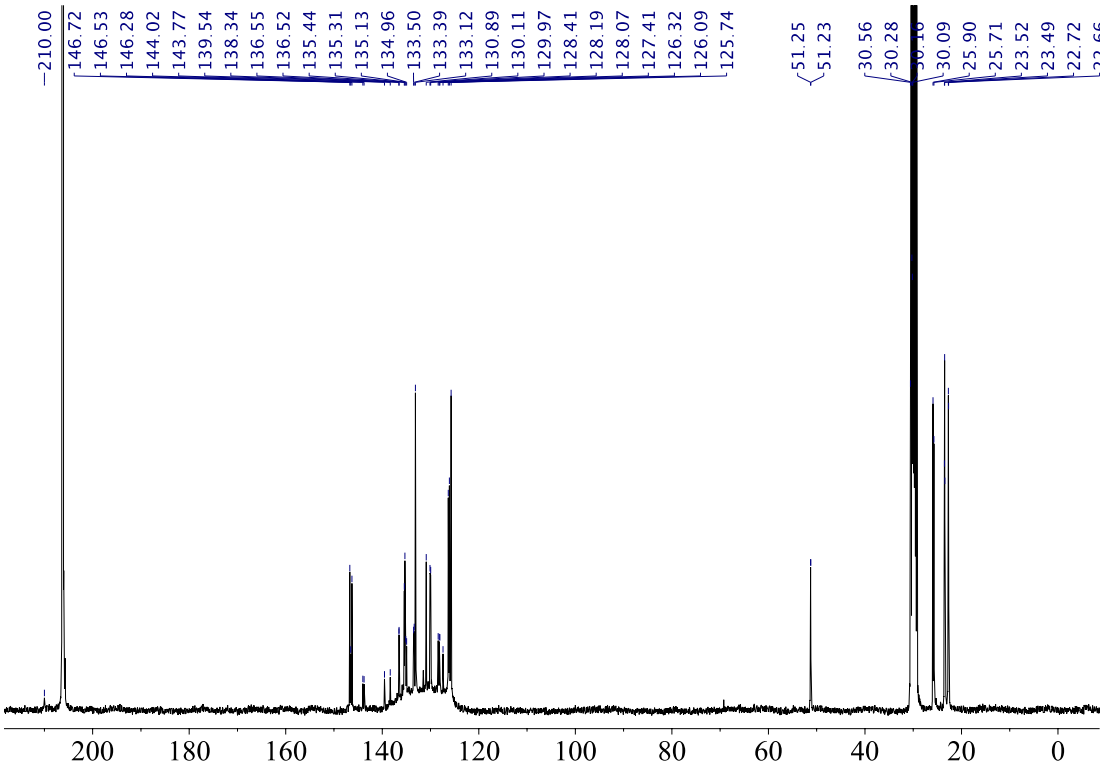


Figure S26. ^{13}C-NMR of **27** in acetone-d_6.

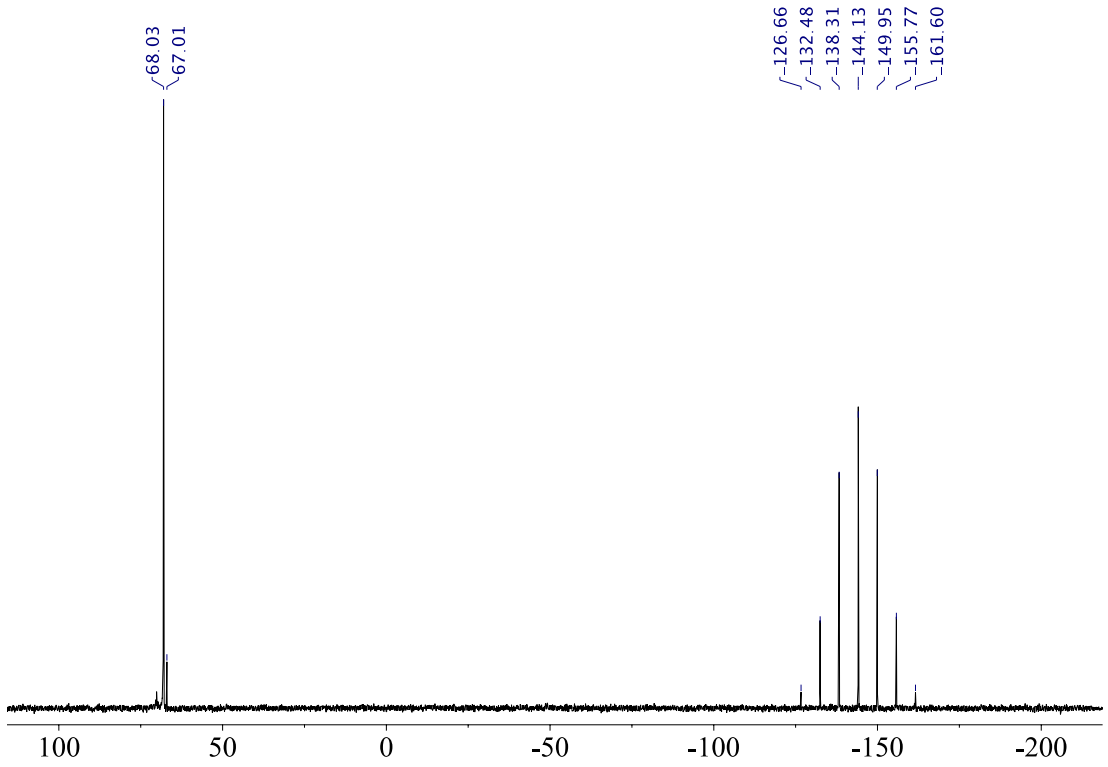


Figure S27. ^{31}P-NMR of **27** in acetone-d_6.

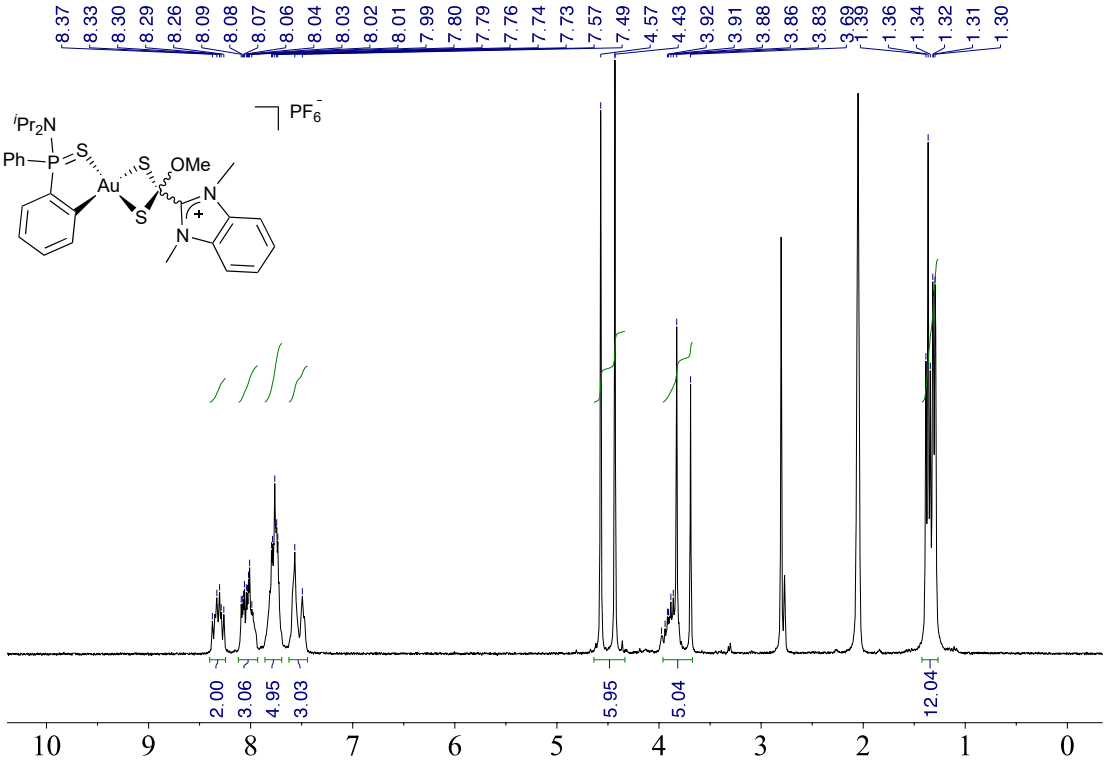


Figure S28. ^{1}H-NMR of **28** in acetone-d_6.

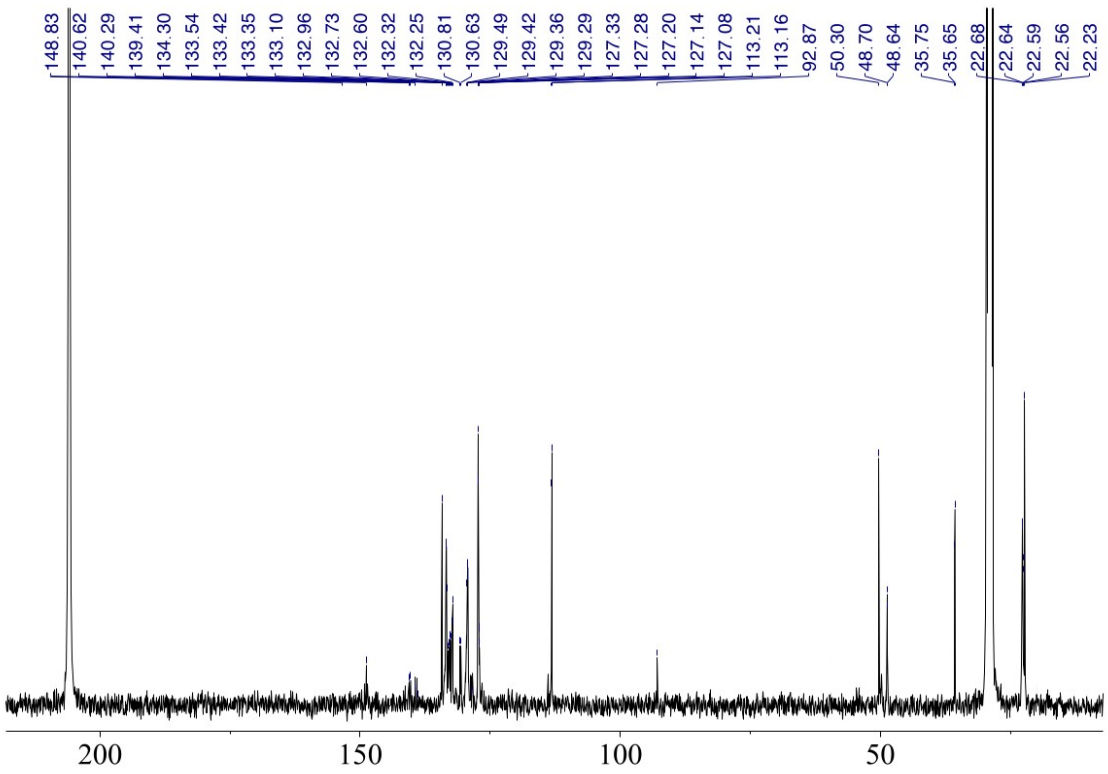


Figure S29. ^{13}C-NMR of **28** in acetone-d_6.

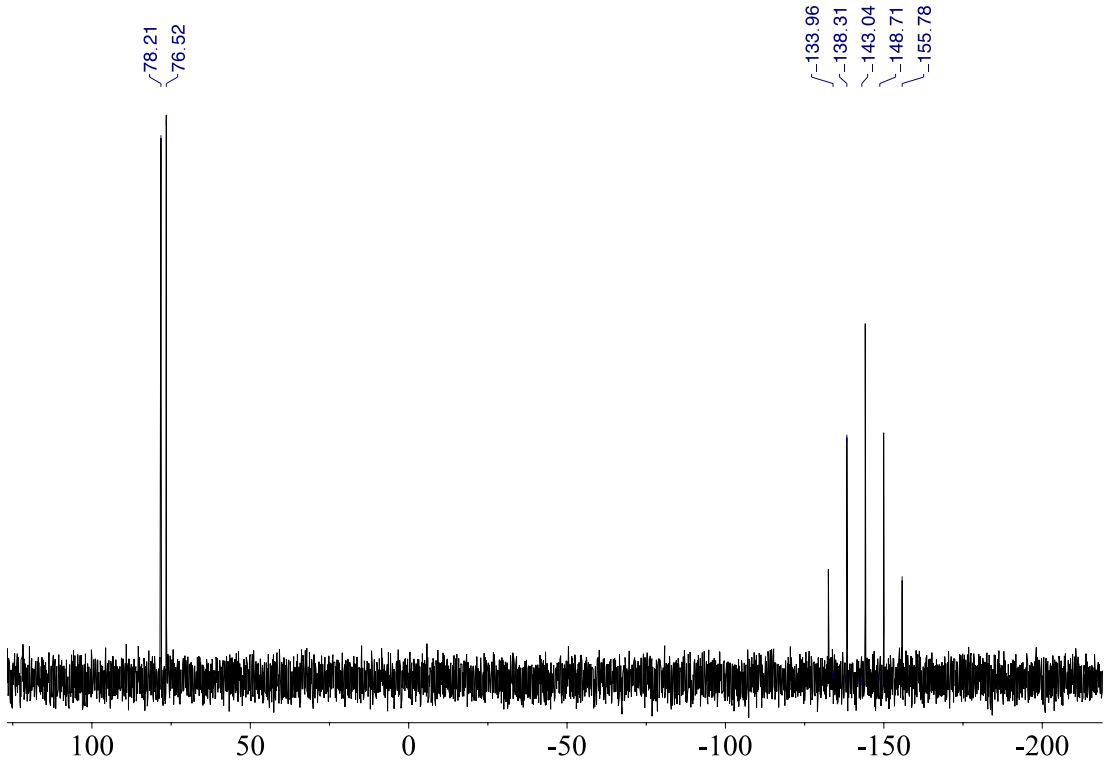


Figure S30. ^{31}P-NMR of **28** in acetone-d_6.

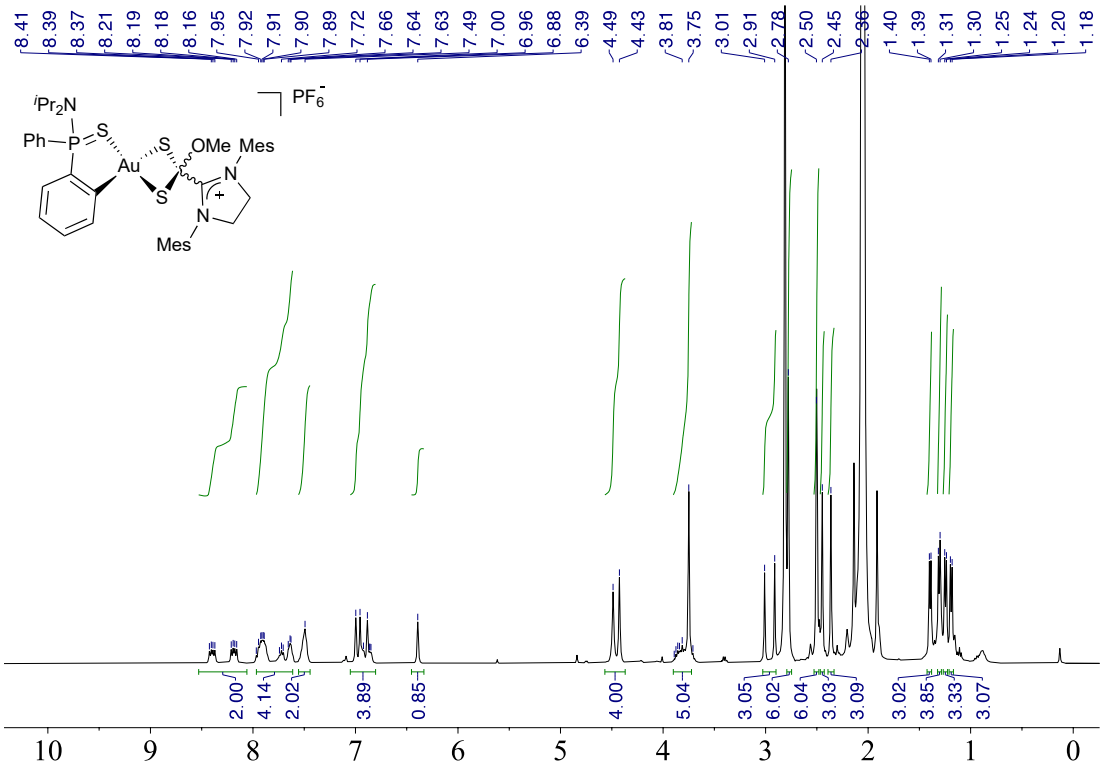


Figure S31. ^{1}H-NMR of **29** in acetone-d_6.

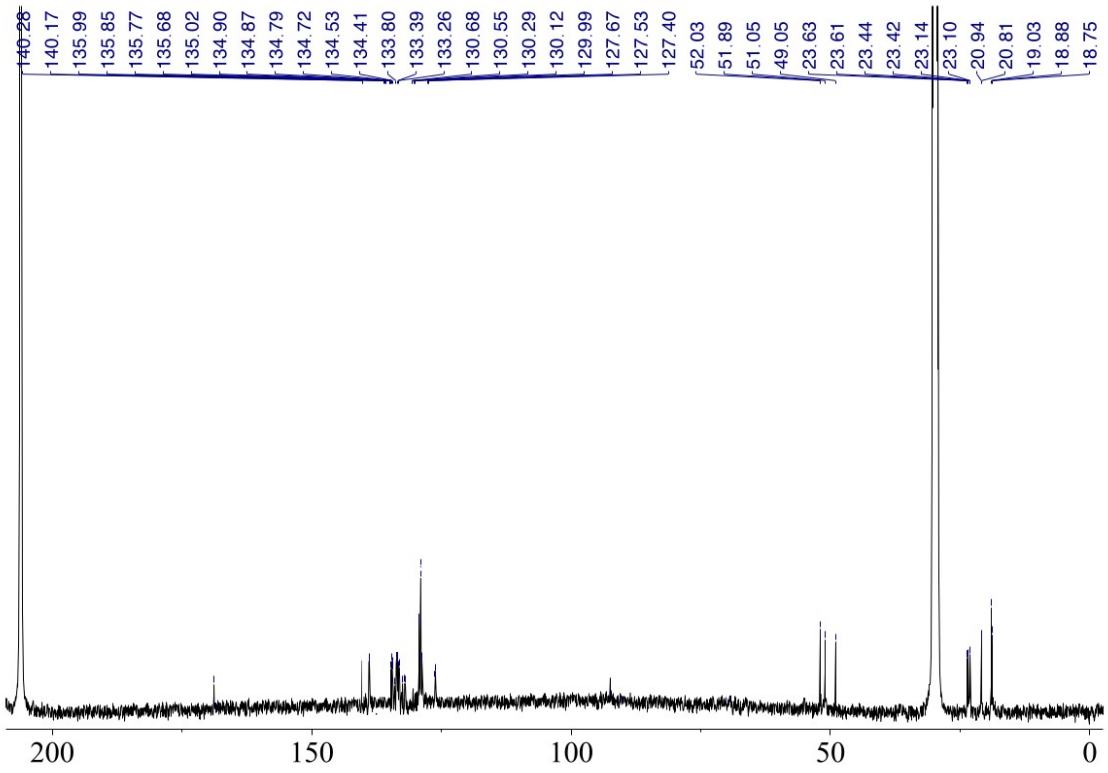


Figure S32. ^{13}C-NMR of **29** in acetone-d_6.

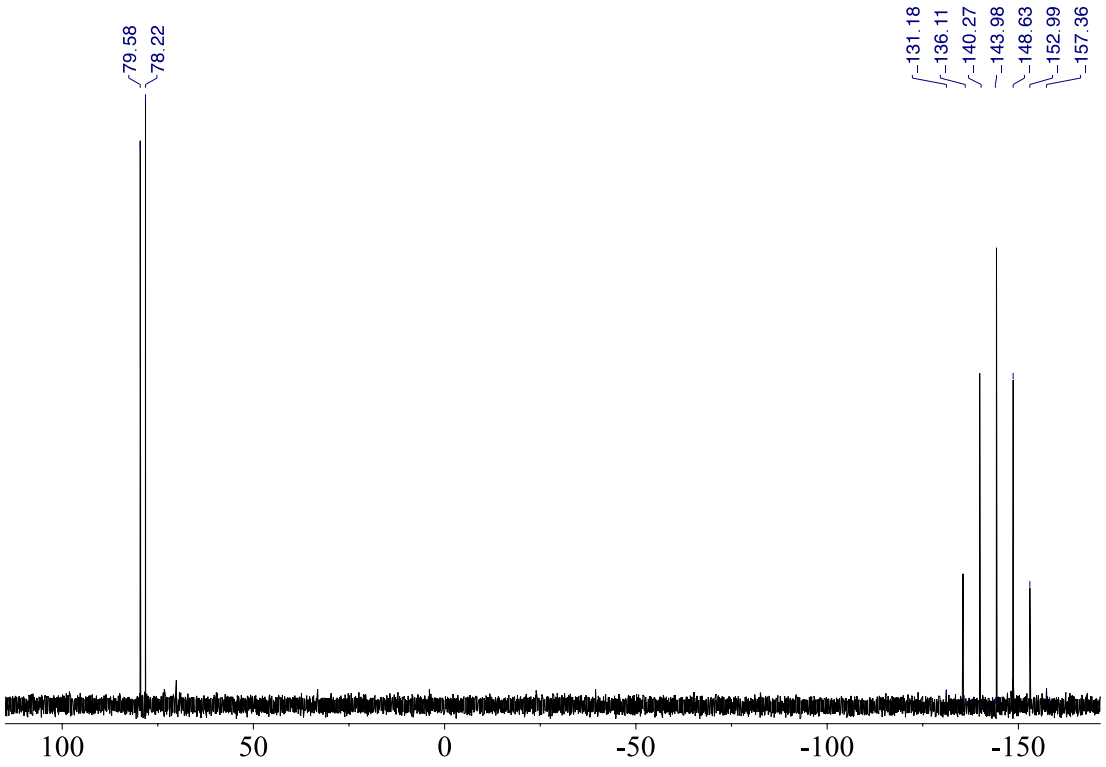


Figure S33. ^{31}P-NMR of **29** in acetone-d_6.

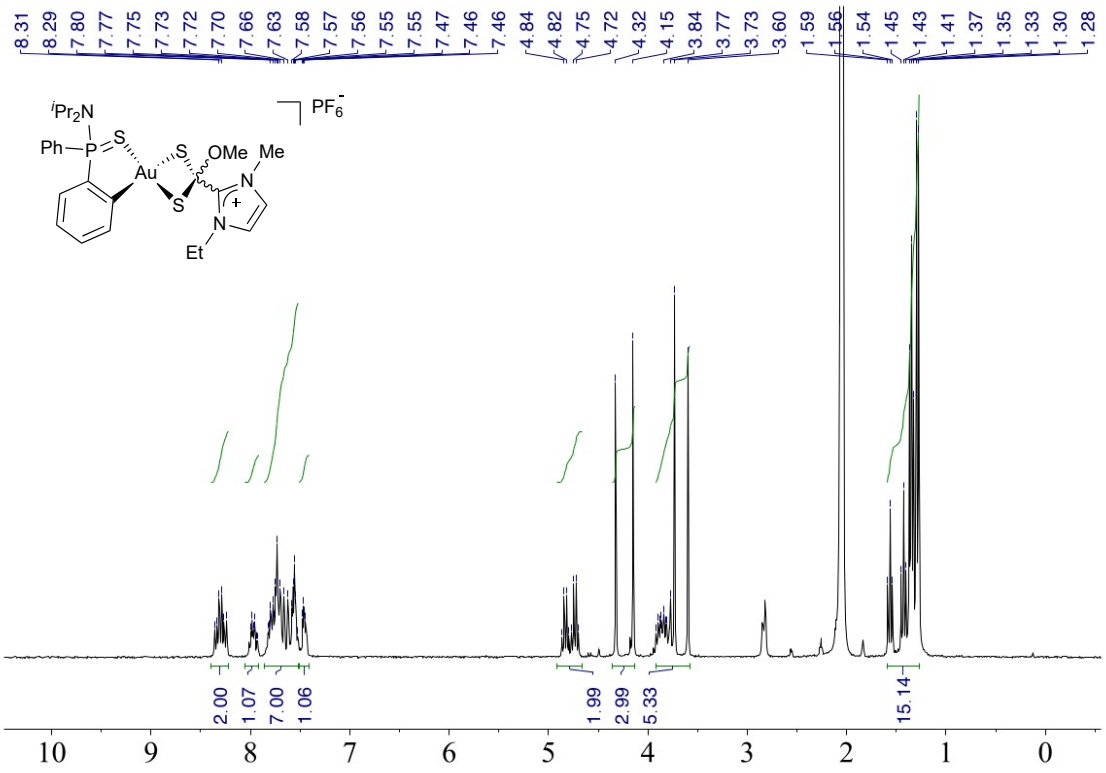


Figure S34. ^{1}H-NMR of **30** in acetone-d_6.

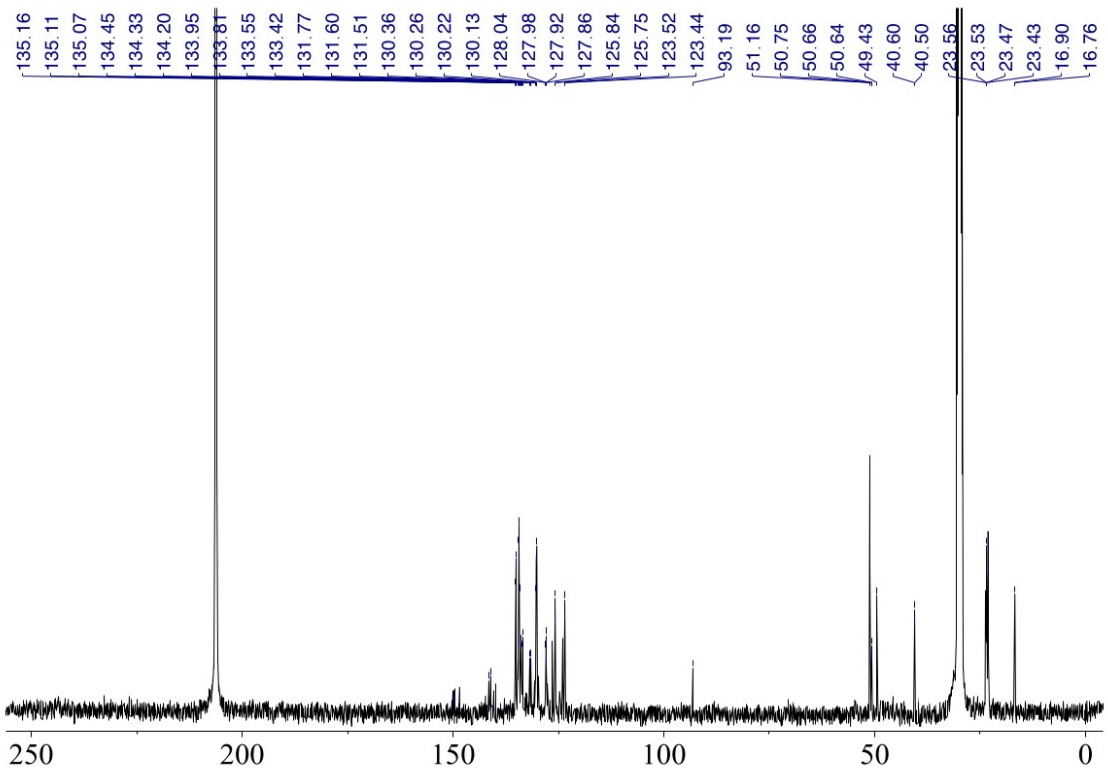


Figure S35. ^{13}C-NMR of **30** in acetone-d_6.

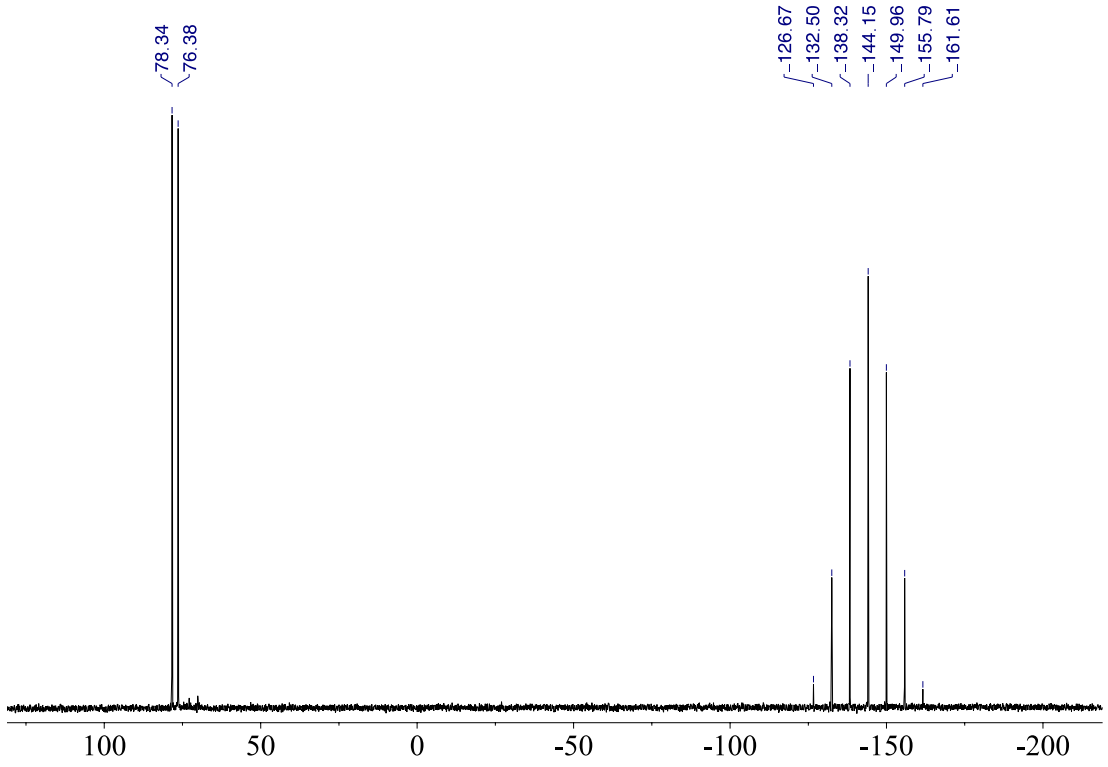


Figure S36. ^{31}P-NMR of **30** in acetone-d_6.

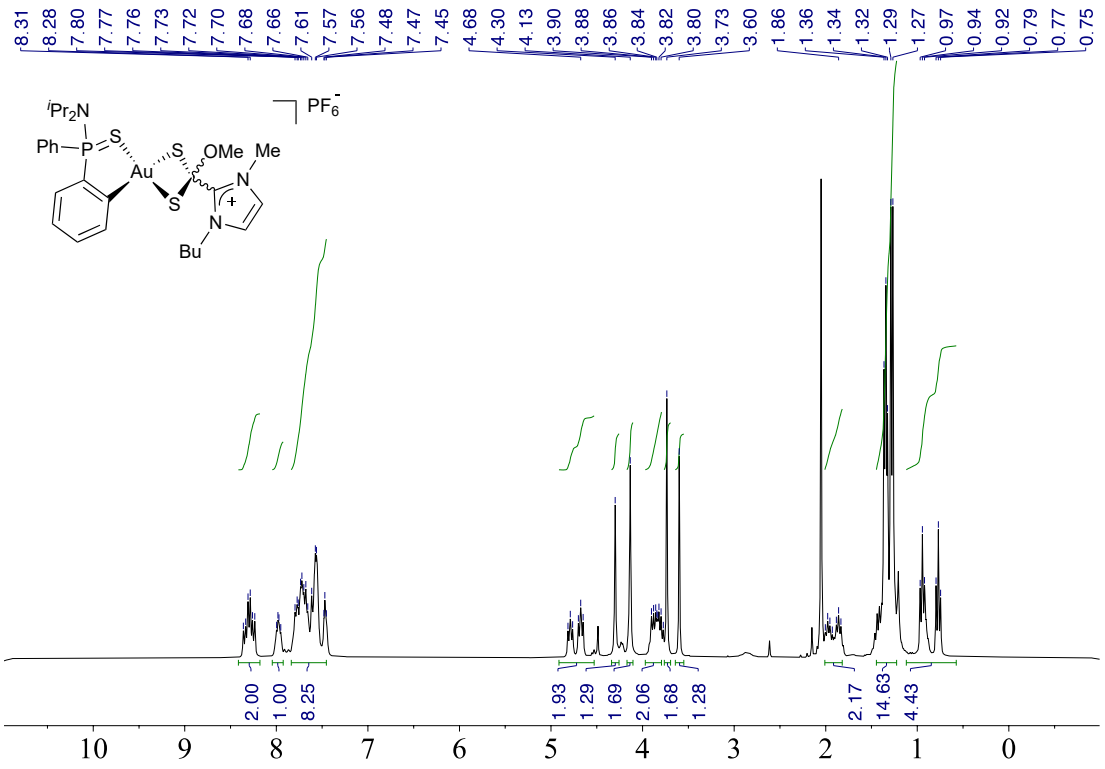


Figure S37. ^{1}H-NMR of **31** in acetone-d_6.

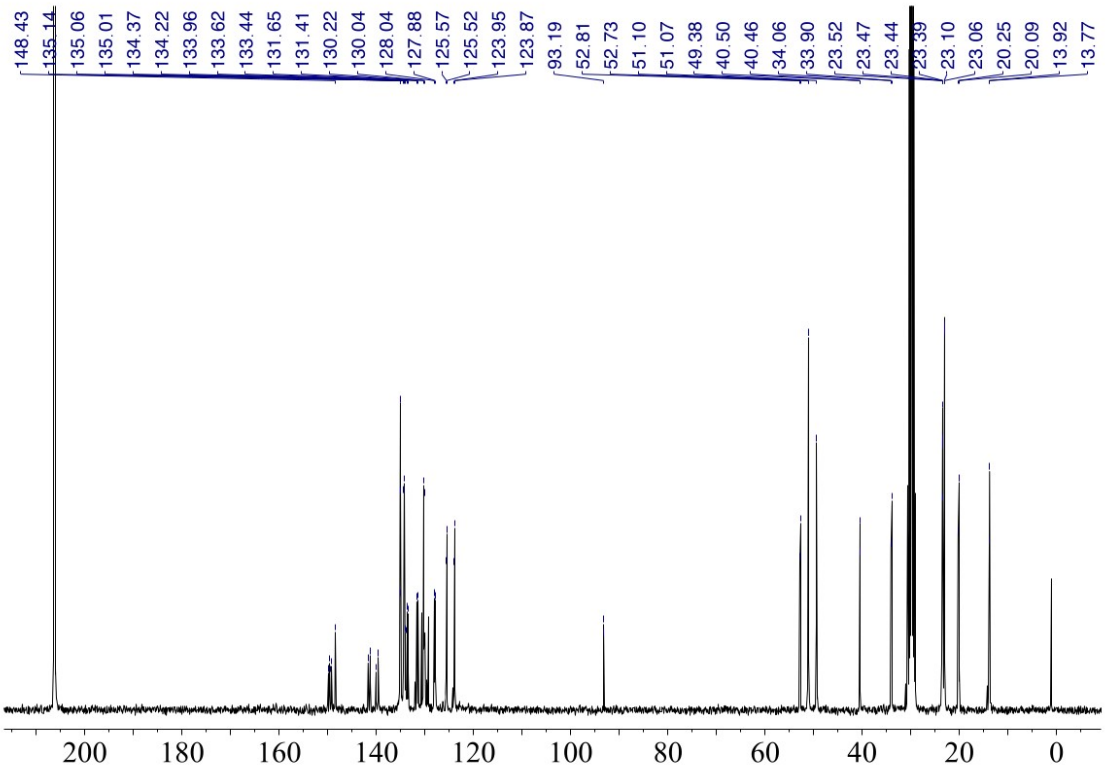


Figure S38. ^{13}C-NMR of **31** in acetone-d_6.

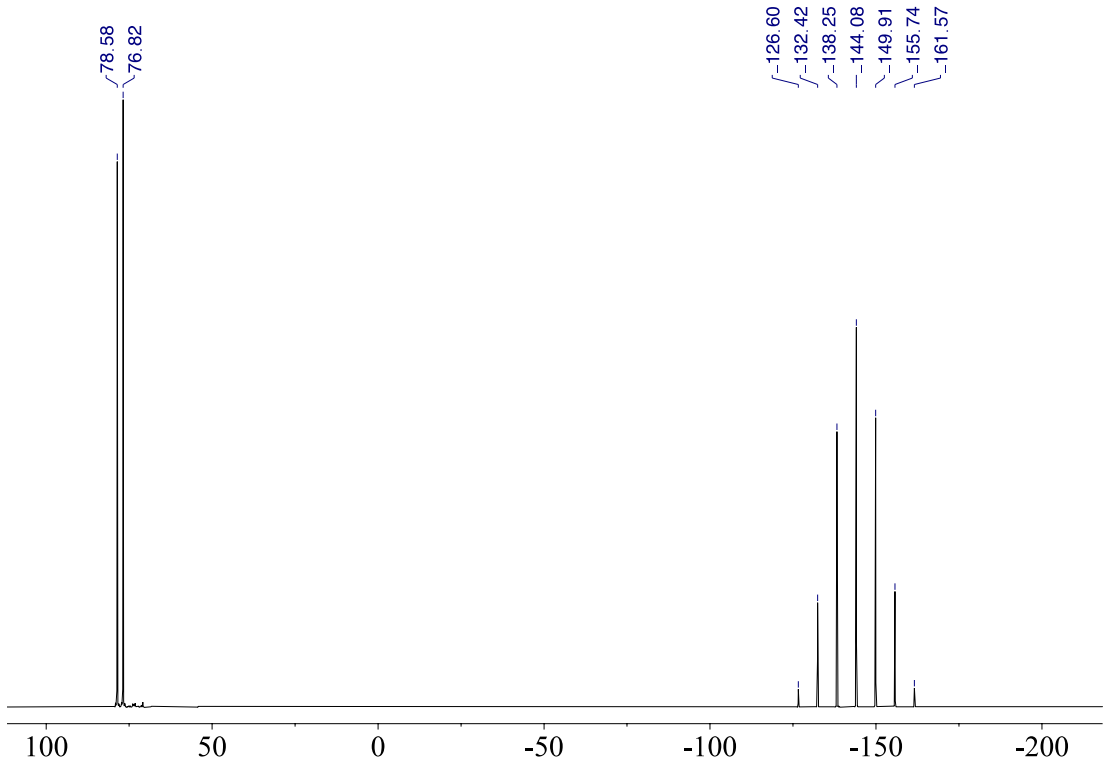


Figure S39. ^{31}P-NMR of **31** in acetone-d_6.

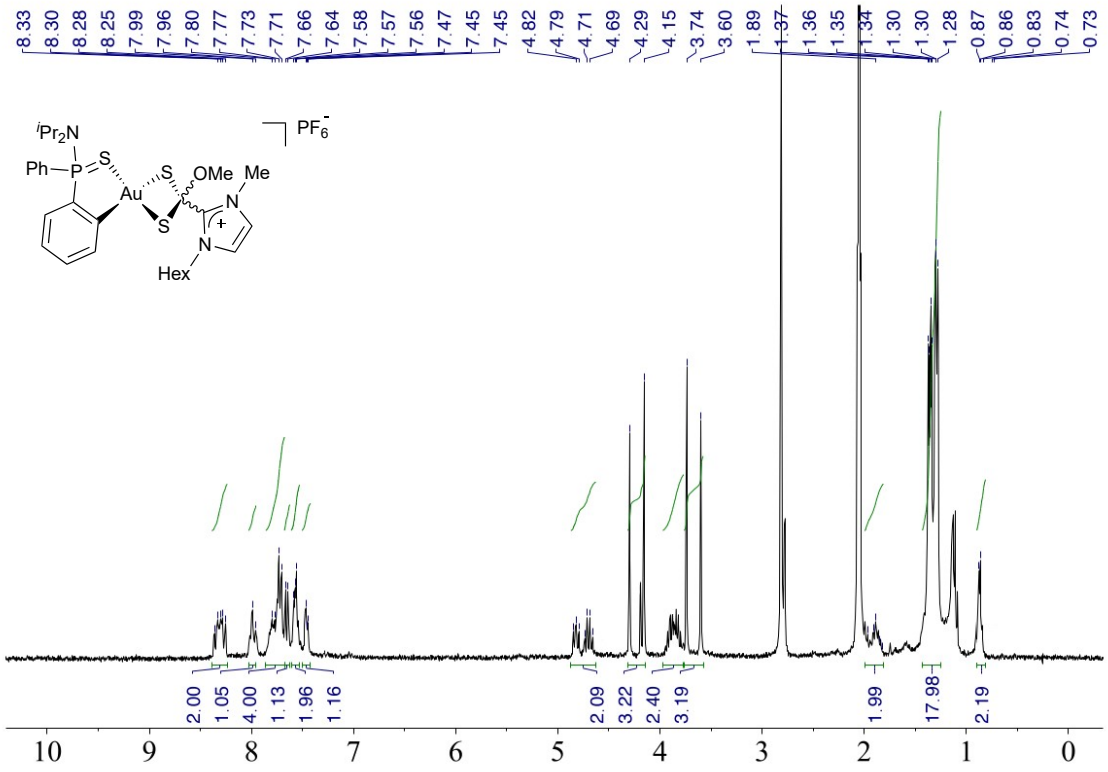


Figure S40. ^{1}H-NMR of **32** in acetone-d_6.

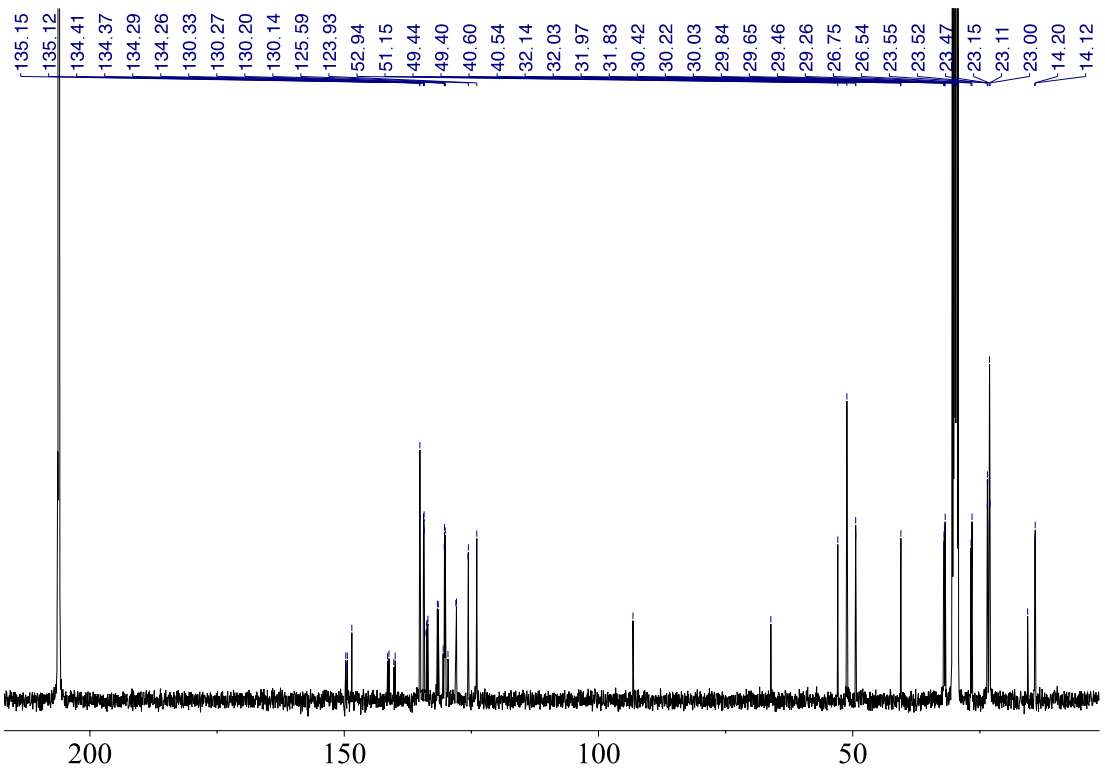


Figure S41. ^{13}C-NMR of **32** in acetone-d_6.

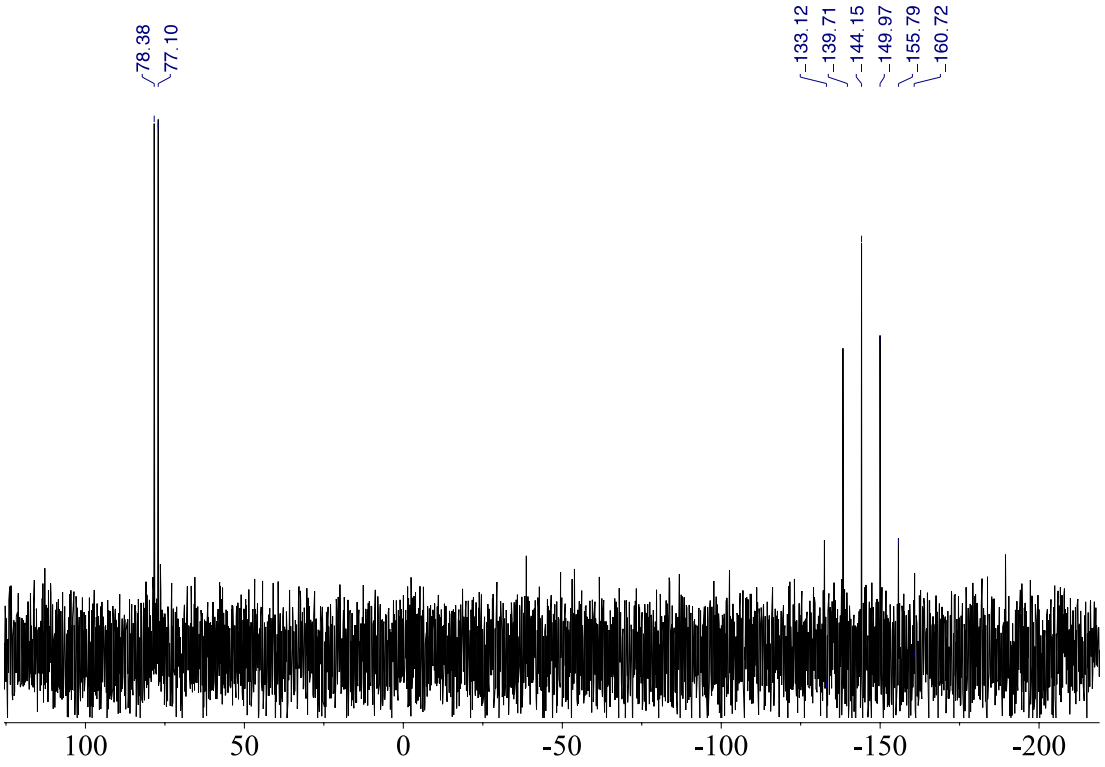


Figure S42. ^{31}P-NMR of **32** in acetone-d_6.

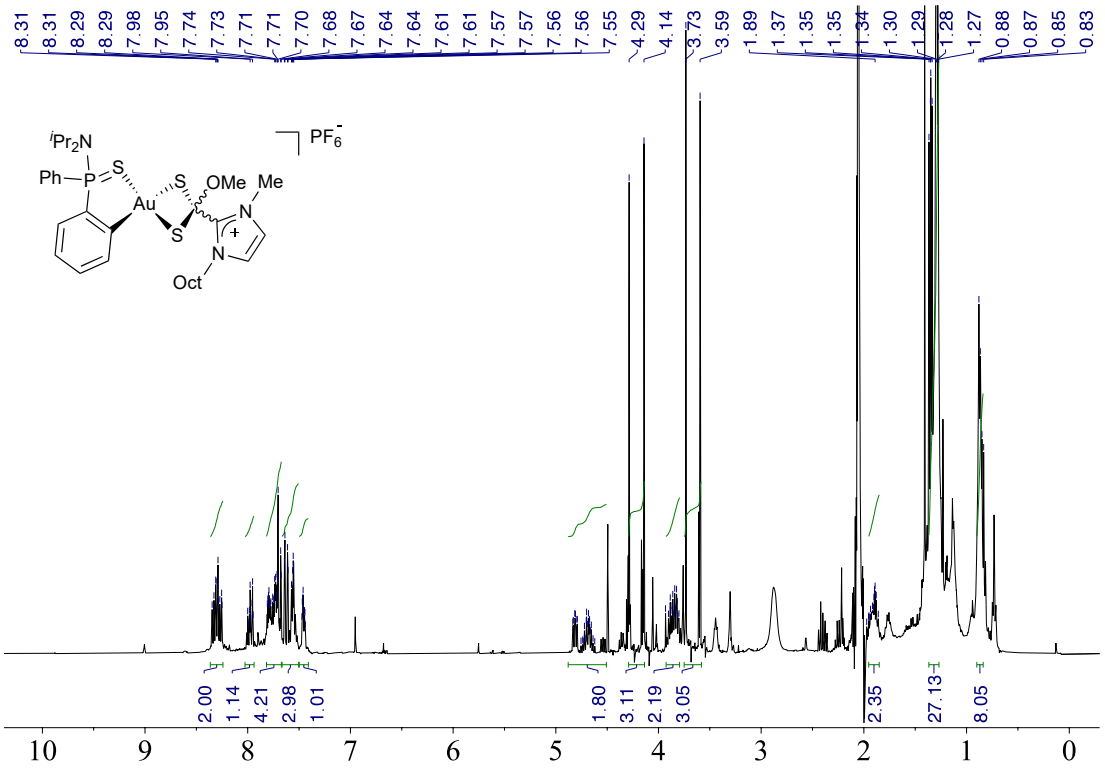


Figure S43. ^{1}H-NMR of **33** in acetone-d_6.

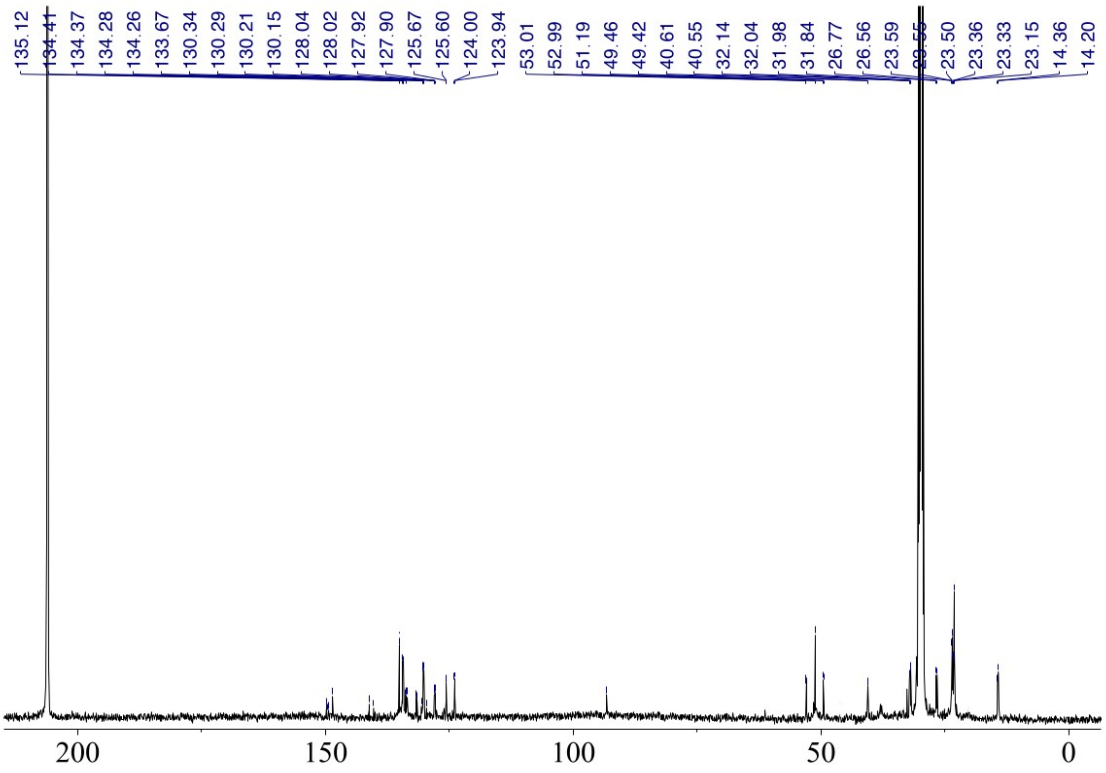


Figure S44. ^{13}C-NMR of **33** in acetone-d_6.

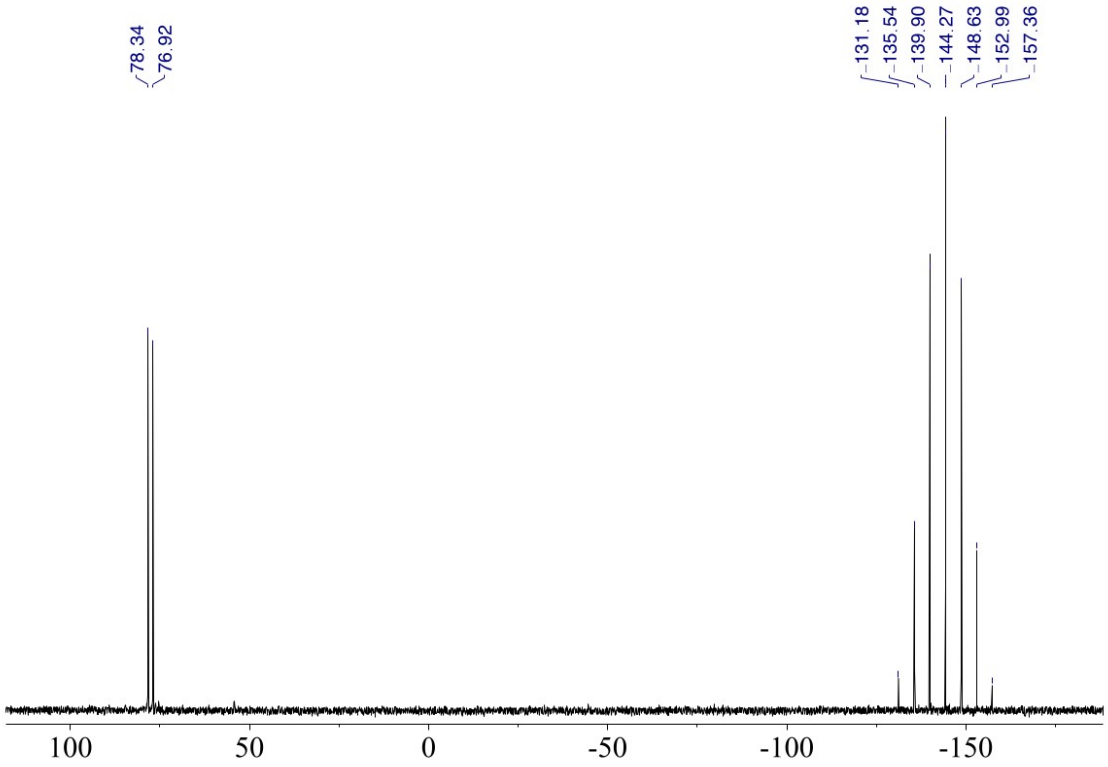


Figure S45. ^{31}P-NMR of **33** in acetone-d_6.

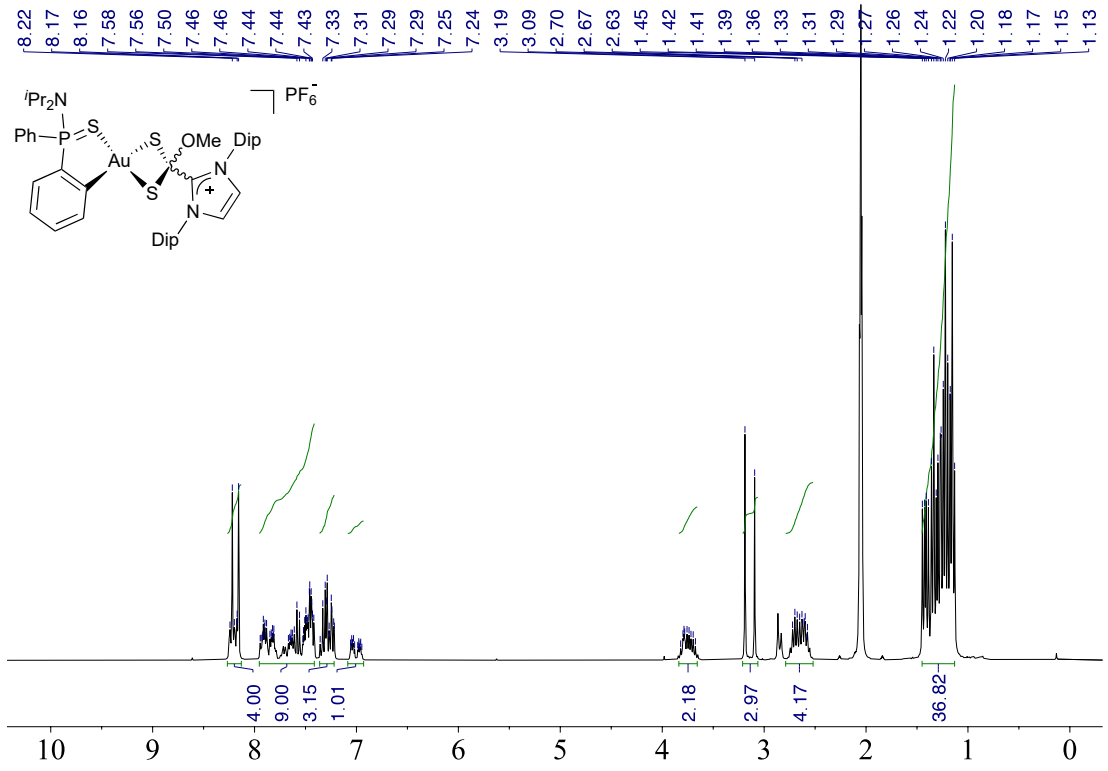


Figure S46. ^{1}H-NMR of **34** in acetone-d_6.

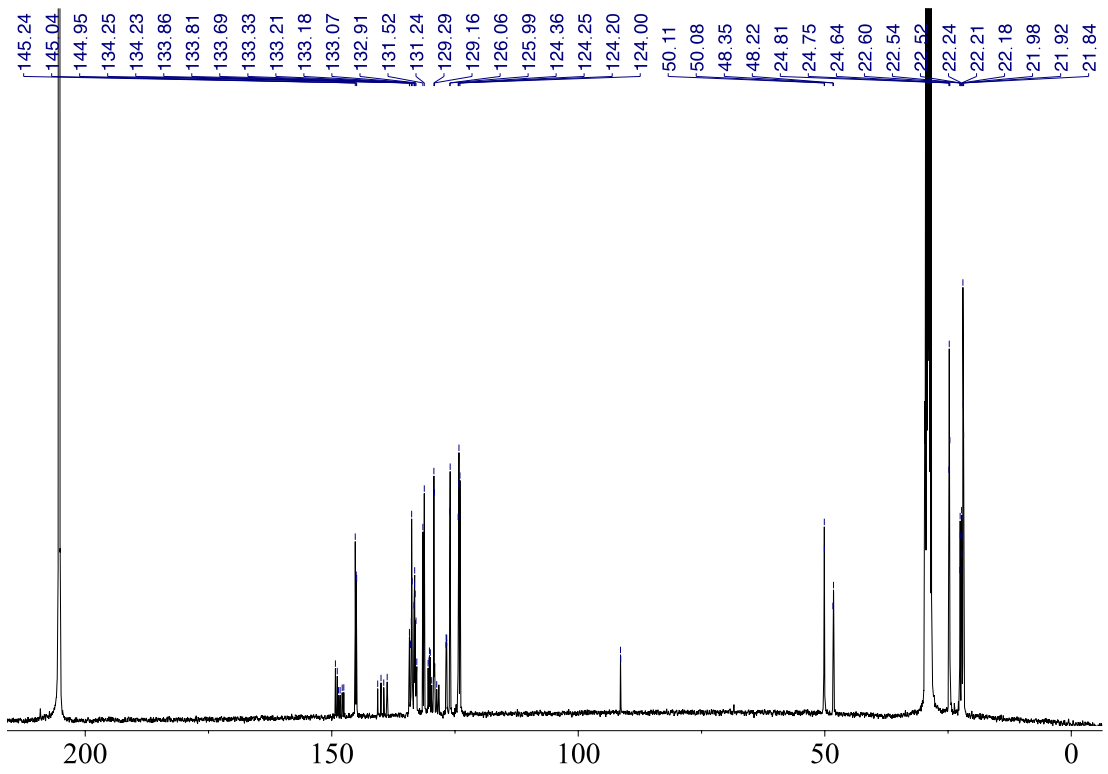


Figure S47. ^{13}C-NMR of **34** in acetone-d_6.

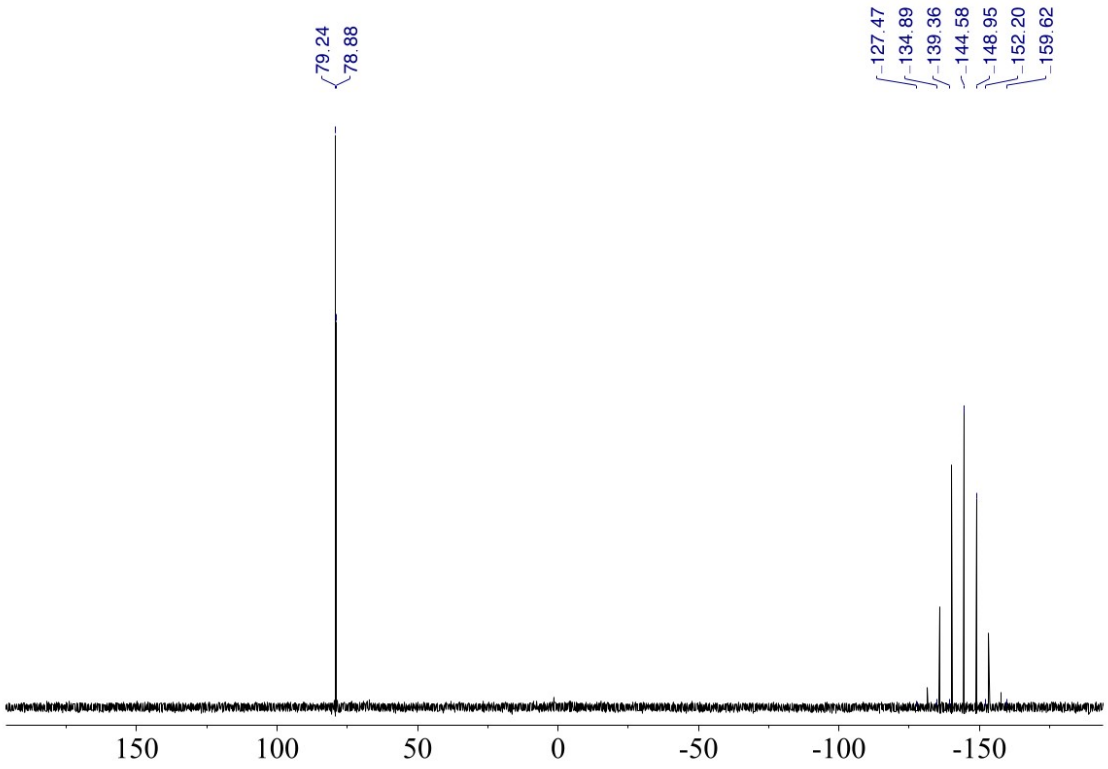


Figure S48. ^{31}P-NMR of **34** in acetone-d_6.

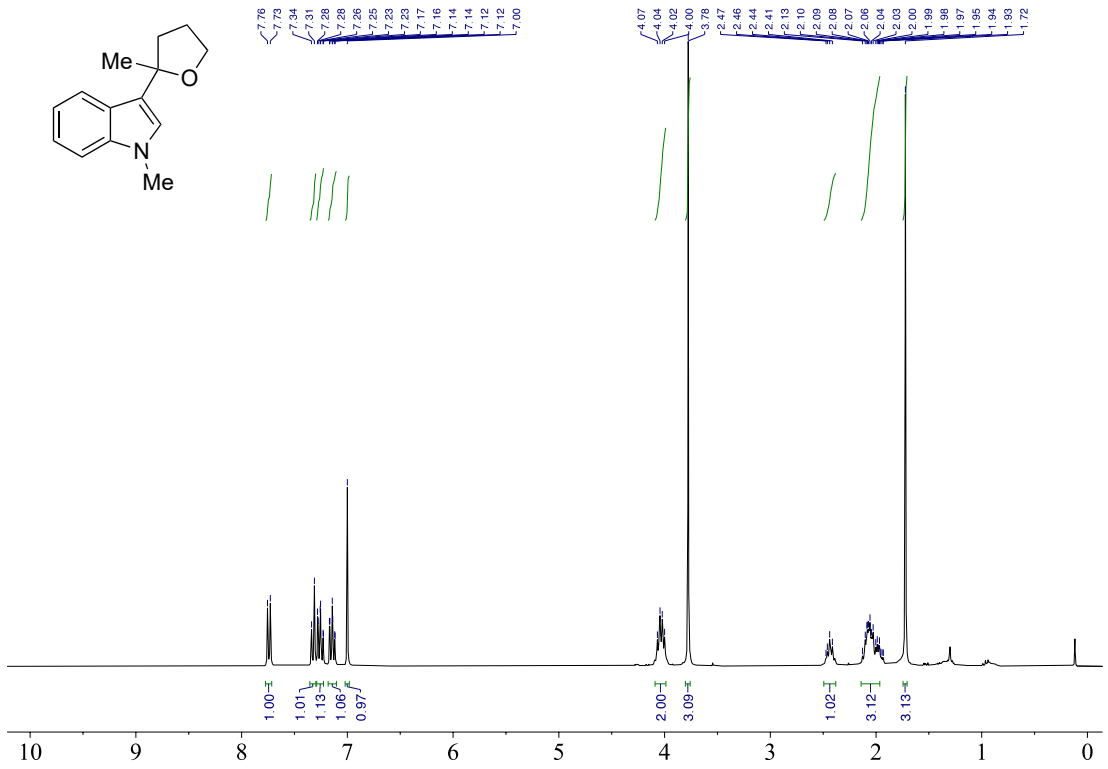


Figure S49. ^{1}H-NMR of **37a** in $CDCl_3$.

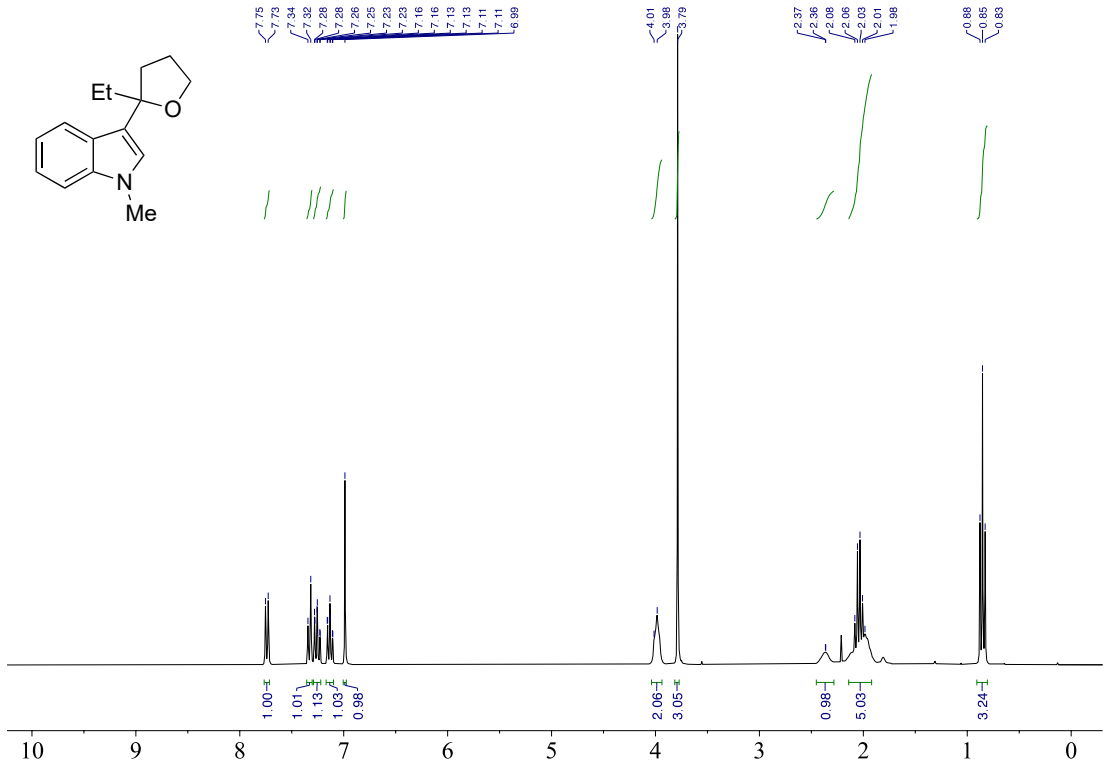


Figure S50. ^{1}H-NMR of **37b** in $CDCl_3$.

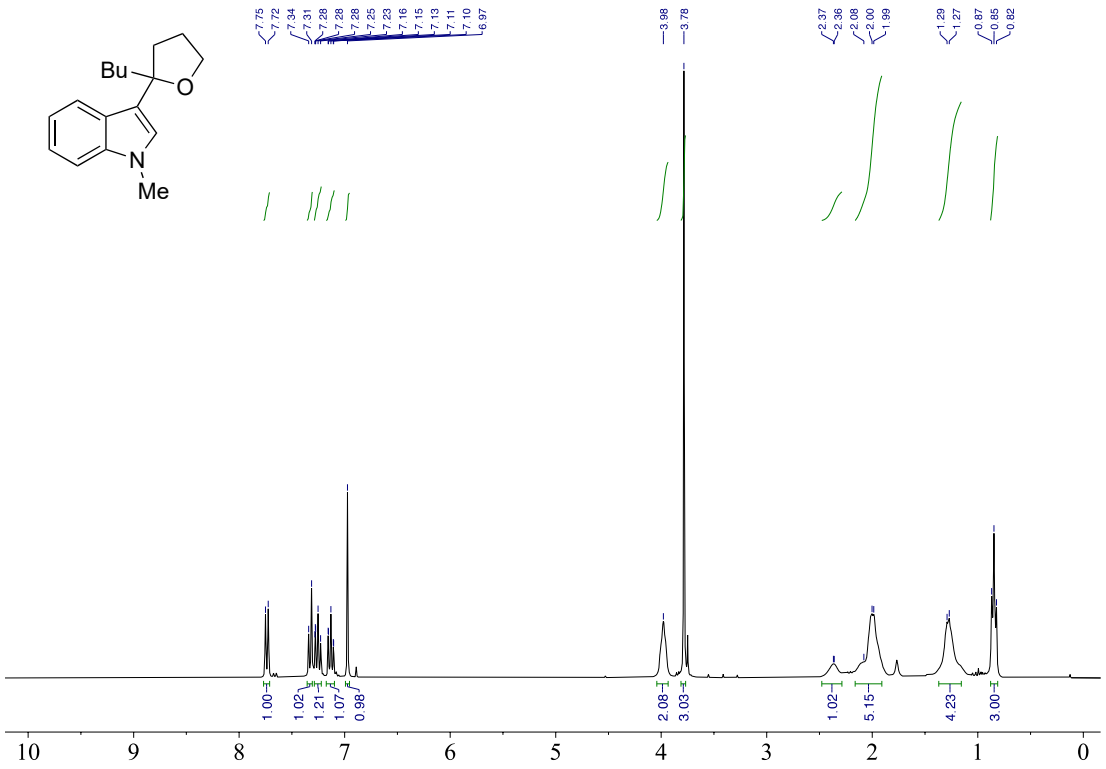


Figure S51. ^{1}H-NMR of **37c** in $CDCl_3$.

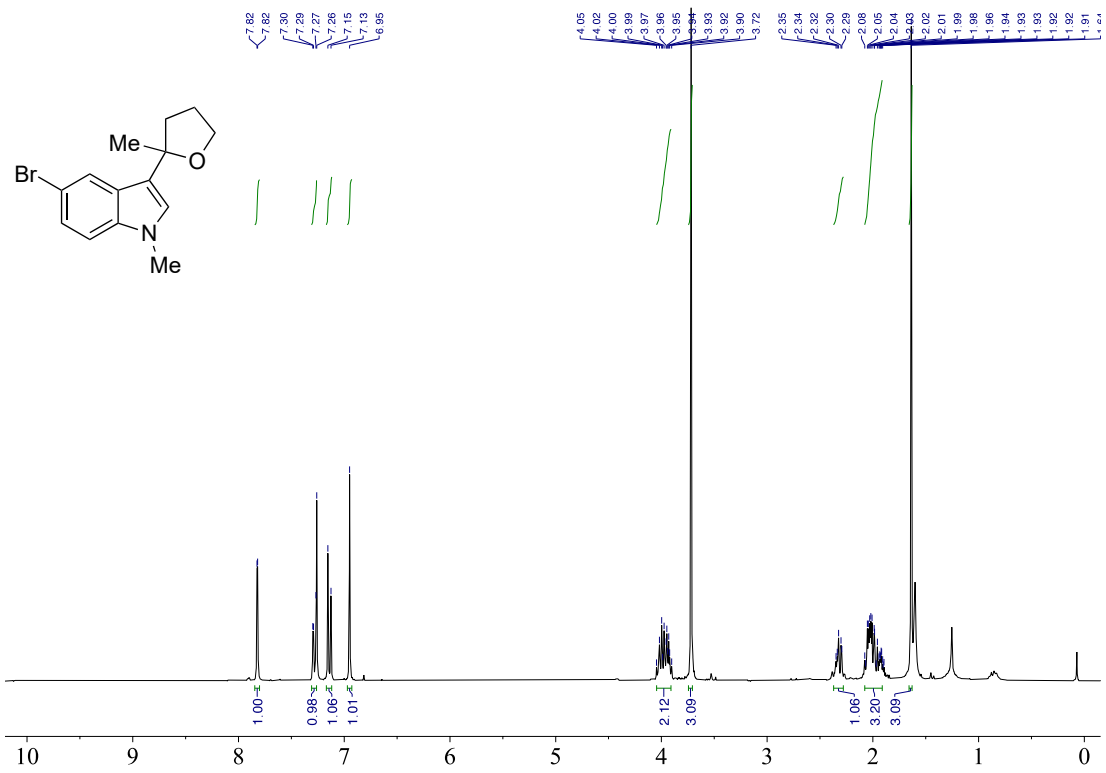


Figure S52. ^{1}H-NMR of **37d** in $CDCl_3$.

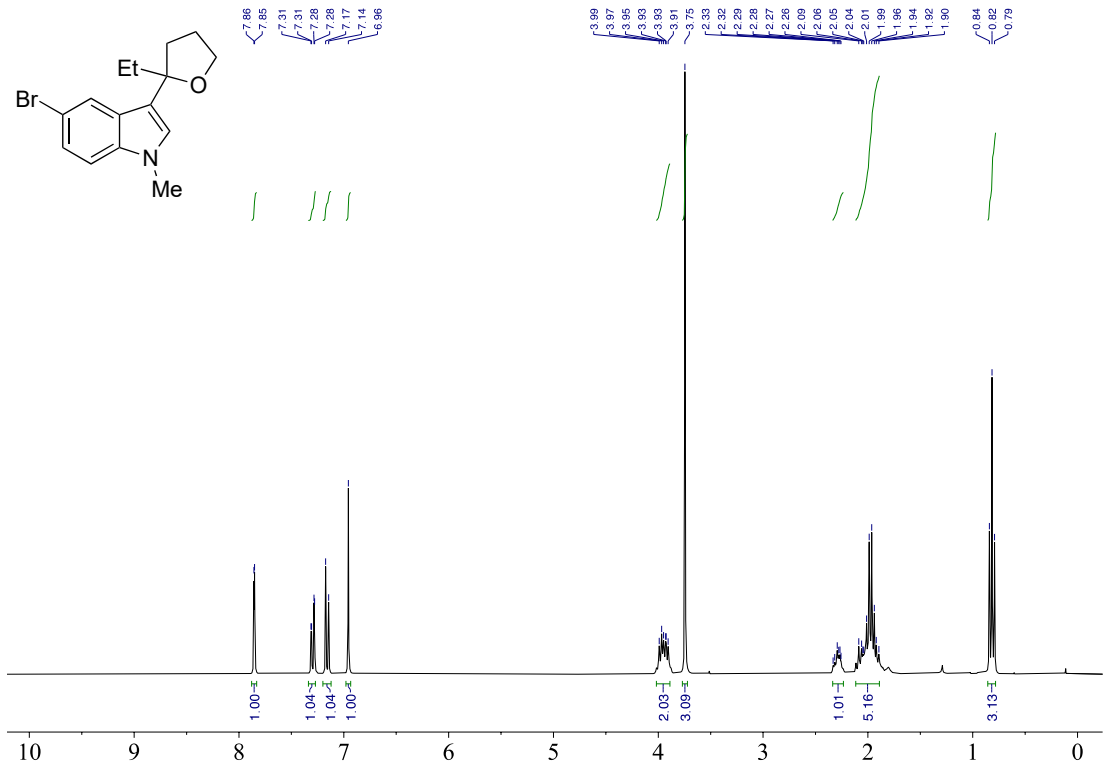


Figure S53. ^{1}H-NMR of **37e** in $CDCl_3$.

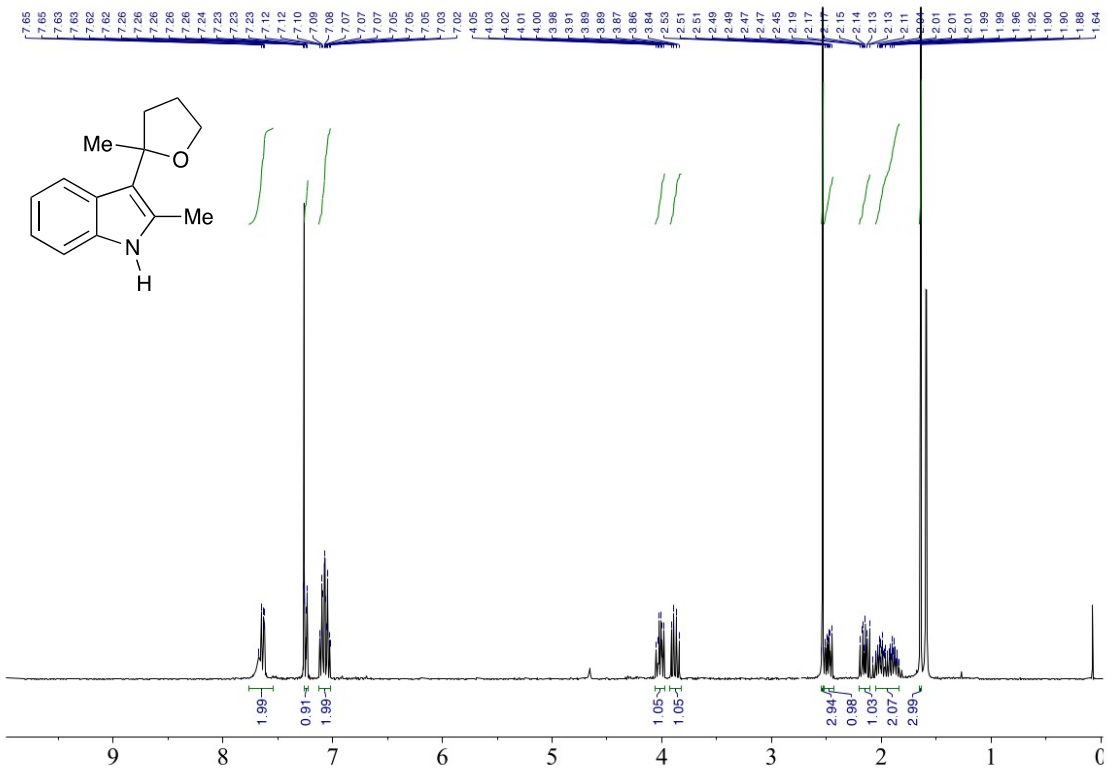


Figure S54. ^{1}H-NMR of **37f** in $CDCl_3$.

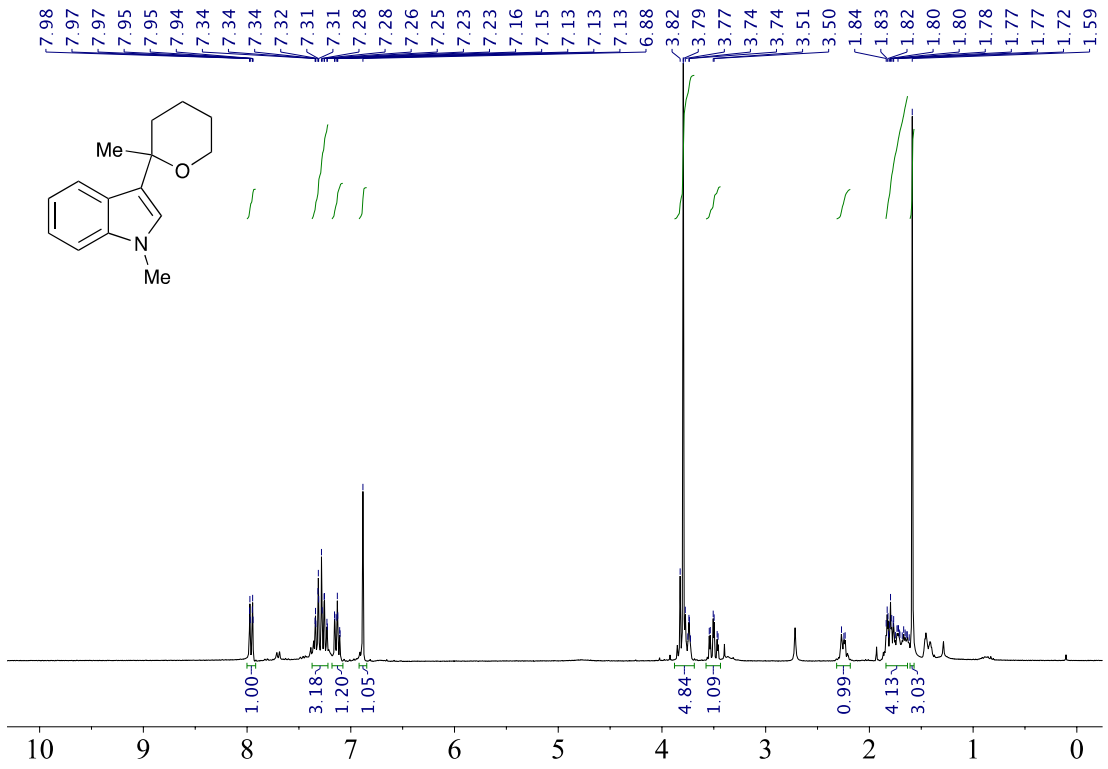


Figure S55. ^{1}H-NMR of **37g** in $CDCl_3$.

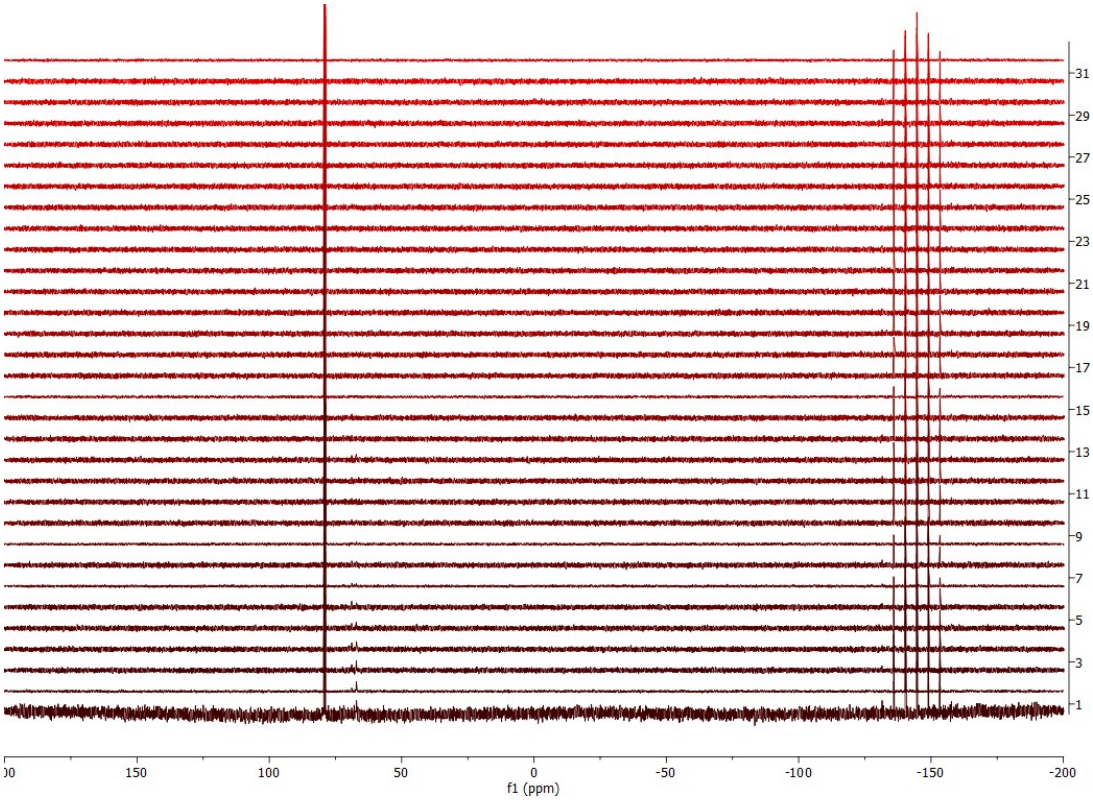


Figure S56. ^{31}P-NMR of **27** in CD_3OD recorded at 10 min. intervals (-200 to 200 ppm).

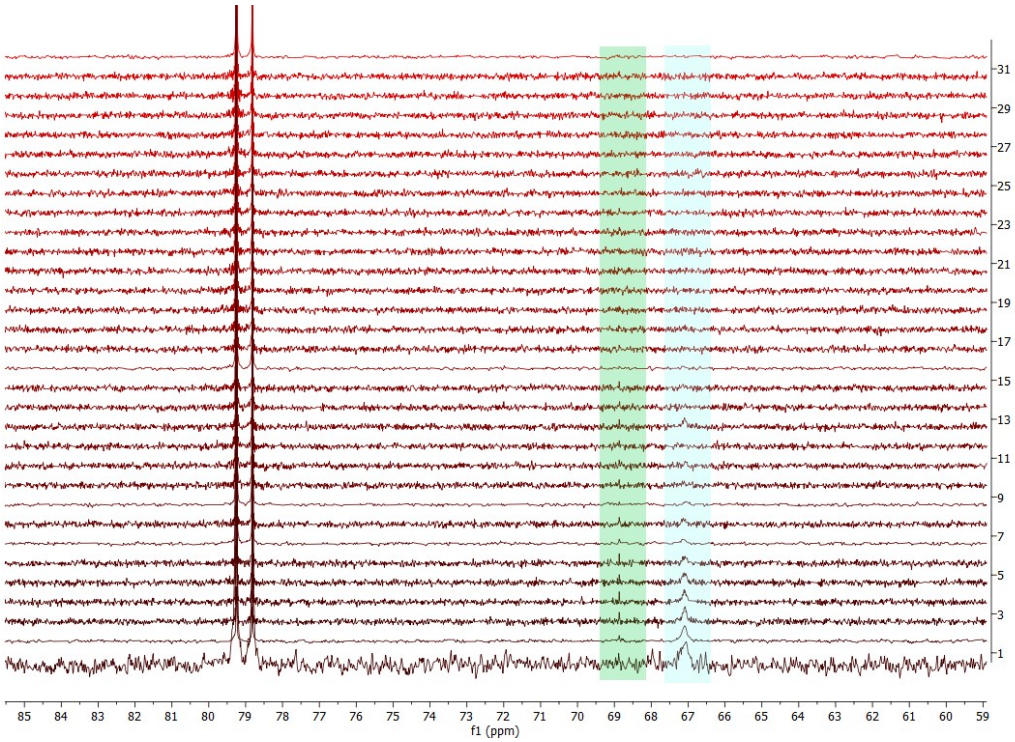


Figure S57. ^{31}P-NMR of **27** in CD_3OD recorded at 10 min. intervals (59 to 85 ppm).

IV.- X-Ray data

Crystals were mounted on a glass fibre and cooled to the 100 K for compounds **22** and **34**, and room temperature for compound **27**. Data for compounds **22** and **34** were collected on a Bruker APEX II CCD-based diffractometer equipped with a graphite monochromated MoKα radiation source (λ=0.71073 Å). Intensities were integrated in SAINT [4] and absorption corrections based on equivalent reflections were applied using SADABS. [5] For compound **27** data were collected on an Oxford Diffraction Xcalibur Nova single crystal diffractometer, using CuKα radiation. Images were collected at a 62 mm fixed crystal-detector distance using the oscillation method, with 1.0-1.2º oscillation and variable exposure time per image. Data collection strategy was calculated with the program CrysAlis Pro CCD, [6] and data reduction and cell refinement were performed with the program CrysAlis Pro RED. [6] An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED. Structures were solved using ShelXT, [7] all of the structures were refined by full matrix least squares against F^2 in ShelXL [8, 9] using Olex2. [10] All of the non-hydrogen atoms were refined anisotropically, while all of the hydrogen atoms were located geometrically and refined using a riding model. Compounds **22** and **27** show some disordered fragments/solvent molecule and the occupancies of the disordered group were refined with their sum set to equal 1 and subsequently fixed at the refined values.

Restraints were applied to maintain sensible thermal and geometric parameters. The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers 2346965, 2346966 and 2346967 for **22**, **27** and **34** respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif

Identification code	**22**	**27**	**34**
Empirical formula	$C_{92}H_{122}Au_2Cl_2F_{12}N_6O_3P_4S_6$	$C_{54}H_{74}AuClF_6N_3O_2P_2S_3$	$C_{59}H_{77}AuF_6N_3OP_2S_3$
Formula weight	2369.02	1301.69	1313.32
Temperature/K	100.0	297(2)	100.0
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	$P2_1/c$	$P2_1/n$
a/Å	12.6165(5)	16.1777(2)	9.3336(14)
b/Å	13.2076(5)	31.2292(3)	30.361(4)
c/Å	17.0154(6)	11.99430(10)	21.123(3)
α/°	73.469(2)	90	90
β/°	71.9980(10)	97.6750(10)	98.283(5)
γ/°	74.327(2)	90	90
Volume/Å^3	2532.93(17)	6005.43(11)	5923.4(15)
Z	1	4	4
ρ_{calc}g/cm^3	1.553	1.440	1.473
μ/mm^{-1}	3.204	6.982	2.704
F(000)	1196.0	2652.0	2684.0
Crystal size/mm^3	0.13 × 0.104 × 0.087	0.555 × 0.497 × 0.295	0.18 × 0.04 × 0.04
Radiation	MoKα (λ = 0.71073)	Cu Kα (λ = 1.54184)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.27 to 61.016	5.66 to 139.198	4.122 to 56.564
Index ranges	-18 ≤ h ≤ 18, -18 ≤ k ≤ 18, -24 ≤ l ≤ 24	-19 ≤ h ≤ 19, -25 ≤ k ≤ 37, -14 ≤ l ≤ 14	-12 ≤ h ≤ 12, -40 ≤ k ≤ 40, -28 ≤ l ≤ 28
Reflections collected	143889	31746	220506
Independent reflections	15458 [R_{int} = 0.0586, R_{sigma} = 0.0257]	11165 [R_{int} = 0.0480, R_{sigma} = 0.0450]	14700 [R_{int} = 0.0589, R_{sigma} = 0.0226]
Data/restraints/parameters	15458/566/749	11165/655/837	14700/0/692
Goodness-of-fit on F^2	1.048	1.045	1.148
Final R indexes [I>=2σ (I)]	R_1 = 0.0220, wR_2 = 0.0546	R_1 = 0.0504, wR_2 = 0.1305	R_1 = 0.0330, wR_2 = 0.0733
Final R indexes [all data]	R_1 = 0.0243, wR_2 = 0.0558	R_1 = 0.0539, wR_2 = 0.1362	R_1 = 0.0372, wR_2 = 0.0749
Largest diff. peak/hole / e Å^{-3}	1.26/-1.21	1.61/-2.40	2.01/-1.47

V.- Computational calculations

All DFT calculations were carried out using the GAUSSIAN16 package [11], and the M06L functional [12]. A pruned numerical integration grid (99,590) was used for all the calculations via keyword Int=Ultrafine, together with the empirical dispersion correction from Grimme and co-workers via keyword GD3 [13]. Effective core potentials and their associated double-ζ LANL2DZ basis set were used for Au [14]. The light elements (C, H, N, O, P and S) were described using the 6-31G* basis [15]. Geometry optimizations were performed under no symmetry restrictions, using analytical gradient techniques, and starting from initial coordinates derived from X-ray data when available. Transition States were searched for, either by using Synchronous Transit-Guided Quasi-Newton (STQN) methodologies (keywords QST2 or QST3), or by the "distinguished reaction coordination procedure" by choosing an internal coordinate (typically a distance) as reaction coordinate and running an energy scan calculation along it, with the maxima of this plot being then used as starting point for a conventional transition state optimization. Frequency analysis was performed for all the stationary points to ensure that either, a minimum structure with no imaginary frequencies, or a saddle point with only one negative frequency along the reaction coordinate, were achieved. This calculation also provides thermochemical information about the reaction pathways at 298.15 K and 1 atm using the harmonic approximation. The connectivity of the optimized transition states was fully corroborated in the forward and backward direction via IRC calculations, or by manual displacement of the geometrical parameters along the negative frequency and further optimization of the resulting geometries.

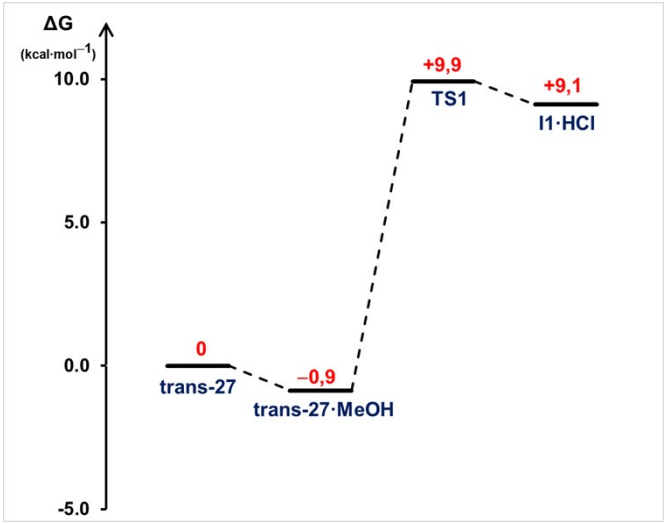


Figure S58. DFT computed reaction profile for the chloride to methoxyde ligand substitution (***trans*-27 → I1**).

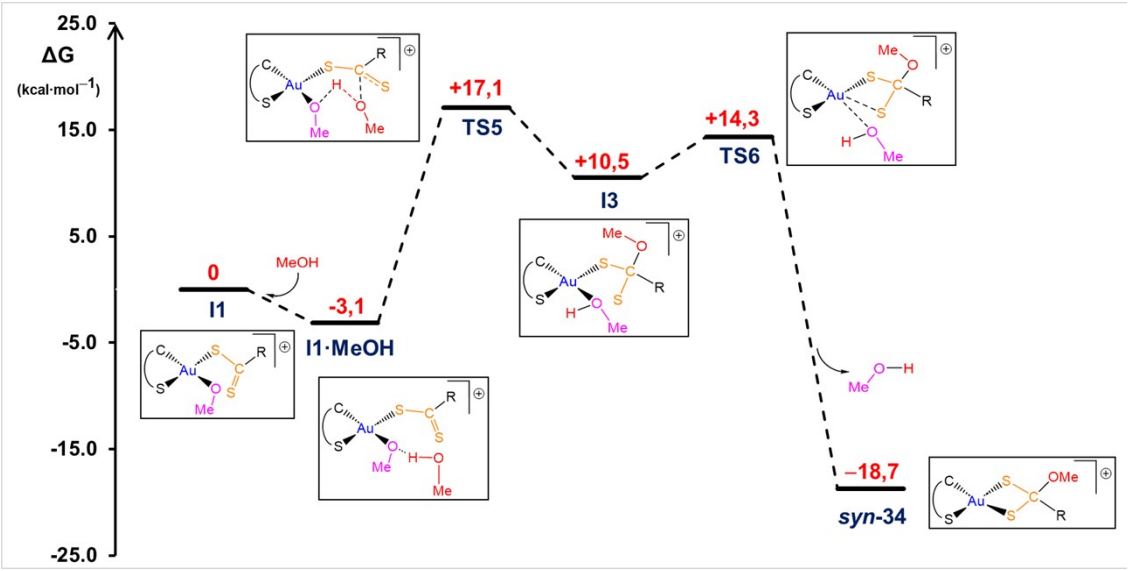


Figure S59. DFT computed reaction profile for the **I1** → ***syn*-34** transformation (C^S = *N*,*N*-diisopropyl-*P*,*P*-diphenylphosphinothioic amide-κ²C,S).

VI.- Reference section

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