Electronic Supplementary Material (ESI) for ChemComm.

Synthesis of Substituted Phosphathiahelicenes *via* Regioselective Bromination of a Preformed Helical Scaffold: a New Approach to Modular Ligands for Enantioselective Gold-Catalysis

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I. General information.

All non-aqueous reactions were run under an inert atmosphere (argon), by using standard techniques for manipulating air-sensitive compounds. Anhydrous solvents were obtained by filtration through drying columns (THF, Et_2O and CH_2Cl_2). All reagents and solvents were of commercial quality and were used without further purification. Analytical thin-layer chromatography (TLC) was performed on plates precoated with silica gel (Merck 60 F_{254}). The developed chromatogram was visualized by UV absorbance. Flash column chromatography was performed using 40-63 mesh silica gel. Purifications have been performed on a CombiFlash Companion TS Chromatography system, unless otherwise stated. Nuclear magnetic resonance spectra (^1H, ^{13}C, ^{31}P) were recorded on either Brucker AV 500 or AV 300 spectrometers. Chemical shifts are reported in parts per million relative to an internal standard of residual chloroform (δ = 7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR). IR spectra were recorded on a Perkin-Elmer FT-IR spectrophotometer and are reported in reciprocal centimeters (cm^{-1}). High resolution mass spectra (HRMS-ESI) were obtained on a LCT Waters equipment. Optical rotations were determined on a JASCO P-1010 polarimeter. Data are reported as follows: $[\alpha]_D^{temp}$ (c in g/100 mL, solvent). HPLC was performed at a column temperature of 20°C on a Waters 2695 Separations Module equipped with a diode array UV detector.

Phospha-thiahelicene (*P*)-**4** was synthesized according to our previous work.[1]

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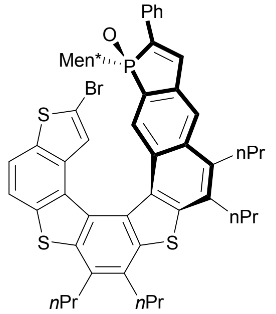
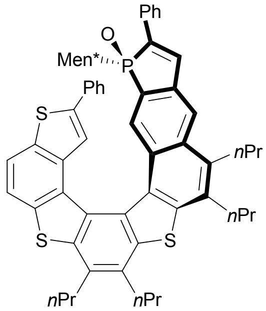
[1] P. Aillard, A. Voituriez, D. Dova, S. Cauteruccio, E. Licandro, A. Marinetti, *Chem. Eur. J.,* 2014, **20**, 12373.

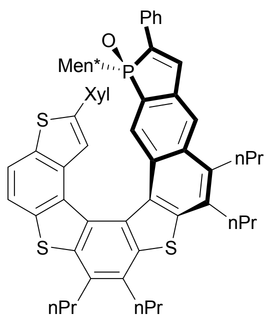
II. Experimental Procedures.



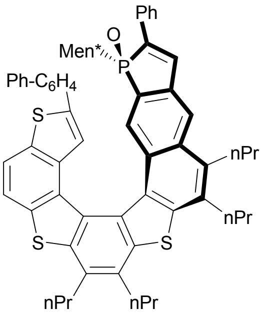
II.1. (*P*)-**5**. To a solution of phospha-thiahelicene (*P*)-**4** (0.058 mmol, 50 mg) in 4 mL of $CHCl_3$ was added NBS (0.12 mmol, 21 mg). The reaction mixture was stirred for 3 h at r.t.. The reaction mixture was then concentrated and the residue was purified by flash chromatography on silica gel (10% EtOAc/ heptane) to afford the desired compound (*P*)-**5** as a pale yellowish powder (45 mg, 83%). Mp 172-174°C; R_f = 0.4 (10% EtOAc/heptane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, J = 9.5 Hz, 1H), 7.97 (brs, 1H), 7.95 (d, J = 8.5 Hz, 1H), 7.73 (d, J = 7.5 Hz, 3H), 7.42-7.28 (m, 4H), 6.62 (brs, 1H), 3.36-3.06 (m, 8H), 2.00-1.80 (m, 8H), 1.60-1.54 (m, 2H), 1.37-1.15 (m, 16H), 0.89-0.46 (m, 13H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.5 (d, J_{C-P} = 21.8 Hz, C), 139.1 (C), 138.5 (brs, CH), 137.2 (d, J_{C-P} = 60.0 Hz, C), 135.9 (C), 135.0 (C), 134.4 (C), 132.6 (C), 132.5 (C), 131.5 (C), 131.0 (C), 128.83 (CH), 128.76 (C), 128.6 (CH), 128.3 (C), 128.1 (C), 127.1 (brs, CH), 126.9 (d, J_{C-P} = 4.9 Hz, C), 126.7 (CH), 126.6 (CH), 120.9 (brs, CH), 119.6 (CH), 119.1 (brs, CH), 113.2 (C), 42.6 (CH), 38.0 (d, J_{C-P} = 64.4 Hz, CH), 35.7 (CH_2), 34.4 (CH_2), 34.2 (CH_2), 34.0 (CH_2), 32.6 (brs, CH), 30.8 (CH_2), 27.2 (CH), 25.1 (d, J_{C-P} = 13.1 Hz, CH_2), 25.0 (CH_2), 23.61 (CH_2), 26.58 (CH_2), 23.3 (CH_2), 23.0 (CH_3), 21.5 (CH_3), 15.8 (CH_3), 14.9 (CH_3), 14.81 (CH_3), 14.77 (CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 58.9 ppm; IR: ν_{max} = 3057, 2955, 2962, 2867, 1453, 1200, 1155, 1090, 900, 760, 728, 694 cm^{-1}; HRMS (ESI) calcd. for $C_{54}H_{59}BrOPS_3$ $[M+H]^+$: 929.2649, found: 929.2659; $[\alpha]_D^{25}$ = + 1753 (c = 1, $CHCl_3$).



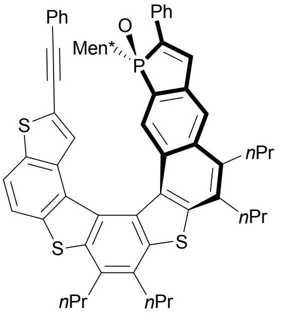
II.2. (*P*)-**6**. To a solution of phenylboronic acid (0.096 mmol, 12 mg) in 3 mL of THF were added (*P*)-**5** (0.096 mmol, 45 mg), tetrakis(triphenylphosphine)palladium (0.0024 mmol, 3 mg), 3 mL of a solution of Na_2CO_3 (0.45 M in water) and 1.5 mL of EtOH. The reaction mixture was stirred for 2h at 85°C. The crude mixture was extracted with EtOAc, washed with water and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel 0% to 10% EtOAc/heptane) to afford the desired compound (*P*)-**6** as a pale yellow solid (45 mg, 99%). R_f = 0.4 (10% EtOAc/heptane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, J = 10.0 Hz, 1H), 7.93 (d, J = 8.5 Hz, 1H), 7.86 (brs, 1H), 7.80 (d, J = 8.5 Hz, 1H), 7.69 (d, J = 7.5 Hz, 2H), 7.36-7.25 (m, 4H), 7.20-7.12 (m, 3H), 6.92 (brs, 1H), 6.86 (d, J = 7.0 Hz, 2H), 3.30-3.10 (m, 8H), 2.05-1.84 (m, 8H), 1.59-1.52 (m, 2H), 1.40-1.16 (m, 16H), 0.91-0.38 (m, 13H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.9 (C), 140.5 (C), 139.1 (C), 138.2 (brs, CH), 137.9 (C), 136.23 (d, J_{C-P} = 40.9 Hz, C), 136.16 (C), 135.6 (C), 135.3 (C), 134.5 (C), 134.0 (C), 132.60 (C), 132.55 (C), 132.3 (C), 131.9 (C), 130.1 (brs, C), 129.6 (C), 128.8 (CH), 128.7 (CH), 128.5 (CH), 127.8 (CH), 127.5 (brs, CH), 126.62 (CH), 126.57 (CH), 126.0 (CH), 121.6 (CH), 120.3 (brs, CH), 119.5 (CH), 42.6 (CH), 37.9 (d, J_{C-P} = 62.2 Hz, CH), 35.5 (CH_2), 34.4 (CH_2), 34.2 (CH_2), 33.8 (CH_2), 32.2 (d, J_{C-P} = 19.7 Hz, CH), 31.4 (CH_2), 27.3 (CH), 25.4 (CH_2), 25.1 (d, J_{C-P} = 13.1 Hz, CH_2), 23.7 (CH_2), 23.6 (CH_2), 23.3 (CH_2), 22.8 (CH_3), 21.5 (CH_3), 15.8 (CH_3), 15.2 (CH_3), 14.8 (CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 58.9 ppm; HRMS (ESI) calcd. for $C_{60}H_{64}OPS_3$ $[M+H]^+$: 927.3857, found: 927.3903; $[\alpha]_D^{25}$= +1716 (c = 1, $CHCl_3$).



II.3. (*P*)-**7** was synthesized following the same procedure as for the synthesis of compound (*P*)-**6**, using 3,5-dimethylphenylboronic acid. (*P*)-**7** was obtained in 78% yield. $R_f = 0.37$ (10% EtOAc/heptane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, $J = 9.5$ Hz, 1H), 7.94 (d, $J = 8.5$ Hz, 1H), 7.90-7.82 (m, 2H), 7.69 (d, $J = 7.0$ Hz, 2H), 7.35-7.22 (m, 4H), 6.98 (brs, 1H), 6.82 (brs, 1H), 6.54 (s, 2H), 3.34-3.08 (m, 8H), 2.23 (s, 6H), 2.10-1.73 (m, 8H), 1.61-1.52 (m, 2H), 1.32-1.14 (m, 16H), 0.82-0.59 (m, 12H), 0.52-0.36 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.3 (C), 140.5 (C), 139.1 (C), 138.3 (brs, CH), 138.1 (C), 137.9 (d, $J_{C\text{-}P} = 26.2$ Hz, C), 136.3 (C), 136.1 (d, $J_{C\text{-}P} = 45.8$ Hz, C), 135.0 (C), 134.8 (C), 133.8 (C), 132.7 (C), 132.6 (C), 132.4 (C), 132.2 (C), 131.9 (C), 130.1 (brs, C), 129.7 (CH), 128.8 (CH), 128.6 (CH), 127.6 (brs, CH), 126.6 (d, $J_{C\text{-}P} = 4.9$ Hz, CH), 123.7 (CH), 121.3 (CH), 120.3 (brs, CH), 119.3 (CH), 42.7 (CH), 37.9 (d, $J_{C\text{-}P} = 62.2$ Hz, CH), 35.3 (CH_2), 34.4 (CH_2), 34.2 (CH_2), 33.9 (CH_2), 32.3 (brs, CH), 32.0 (CH_2), 27.3 (CH), 25.1 (d, $J_{C\text{-}P} = 13.7$ Hz, CH_2), 24.9 (CH_2), 23.9 (CH_2), 23.6 (CH_2), 23.3 (CH_2), 22.9 (CH_3), 21.5 (CH_3), 21.4 (CH_3), 15.9 (CH_3), 15.1 (CH_3), 15.0 (CH_3), 14.8 (CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 59.1 ppm; HRMS (ESI) calcd. for $C_{62}H_{68}OPS_3$ $[M+H]^+$: 955.4170, found: 955.4216; $[\alpha]_D^{25} = +1562$ (c = 1, $CHCl_3$).

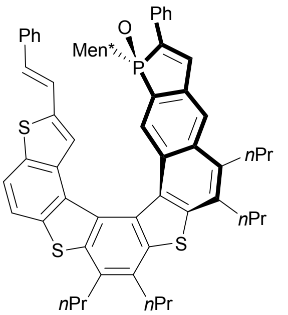


II.4. (*P*)-**8** was synthesized following the same procedure as for the synthesis of compound (*P*)-**6**, using 4-biphenylboronic acid. (*P*)-**8** was obtained in 89% yield. $R_f = 0.3$ (10% EtOAc/heptane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, $J = 10.0$ Hz, 1H), 7.99 (d, $J = 7.5$ Hz, 1H), 7.93 (d, $J = 8.5$ Hz, 1H), 7.90-7.85 (m, 1H), 7.80 (d, $J = 8.5$ Hz, 1H), 7.72-7.66 (m, 2H), 7.60-7.50 (m, 2H), 7.45 (dd, $J = 8.0$, 7.5 Hz, 2H), 7.40-7.35 (m, 3H), 7.34-7.25 (m, 3H), 6.98-6.94 (m, 1H), 6.92 (d, $J = 8.0$ Hz, 2H), 3.35-3.05 (m, 8H), 2.05-1.84 (m, 8H), 1.60-1.50 (m, 2H), 1.35-1.10 (m, 16H), 0.92-0.55 (m, 11H), 0.47-0.38 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.3 (C), 140.5 (C), 140.4 (C), 139.0 (C), 138.3 (d, $J_{C\text{-}P} = 10.9$ Hz, CH), 137.9 (C), 136.4 (C), 136.1 (C), 135.9 (C), 135.6 (d, $J_{C\text{-}P} = 8.7$ Hz, C), 135.4 (C), 134.5 (C), 133. 0 (C), 132.6 (C), 132.5 (C), 132.2 (C), 131.8 (C), 130.1 (d, $J_{C\text{-}P} = 11.0$ Hz, C), 129.0 (CH), 128.8 (CH), 128.6 (CH), 128.5 (C), 127.6 (CH), 127.2 (CH), 126.8 (CH), 126.6 (CH), 126.2 (CH), 121.5 (CH), 120.5 (CH), 120.0 (CH), 119.4 (CH), 42.6 (CH), 37.8 (d, $J_{C\text{-}P} = 63.6$ Hz, CH), 35.6 (CH_2), 34.4 (CH_2), 34.2 (CH_2), 33.8 (CH_2), 32.2 (d, $J_{C\text{-}P} = 13.9$ Hz, CH), 31.3 (CH_2), 27.2 (CH), 25.6 (CH_2), 25.0 (d, $J_{C\text{-}P} = 13.1$ Hz, CH_2), 23.7 (CH_2), 23.4 (CH_2), 22.9 (CH_3), 21.5 (CH_3), 15.8 (CH_3), 15.3 (CH_3), 14.8 (CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 58.9 ppm; HRMS (ESI) calcd. for $C_{66}H_{68}OPS_3$ $[M+H]^+$: 1003.4170, found: 1003.4191; $[\alpha]_D^{25} = +1607$ (c = 1, $CHCl_3$).



II.5. (*P*)-**9**. To a solution of phenyl acetylene (0.118 mmol, 13 μL) in 3 mL of triethylamine were added (*P*)-**5** (0.059 mmol, 55 mg), copper iodide (0.0012 mmol, 0.2 mg) and *bis*(triphenylphosphine)palladium dichloride (0.0024 mmol, 3 mg). The reaction mixture was stirred for 6h at 80°C. The crude mixture was concentrated and purified by flash chromatography on silica gel (0% to 10% EtOAc/heptane) to afford the desired compound (*P*)-**9** as a yellow solid (38 mg, 68%). $R_f = 0.32$ (10% EtOAc/heptane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, $J = 10.5$ Hz, 1H), 8.01 (d, $J = 8.4$ Hz, 1H), 7.93 (brs, 1H), 7.80 (d, $J = 9.0$ Hz, 1H), 7.73 (d, $J = 6.9$ Hz, 2H), 7.43-7.28 (m, 9H), 6.82 (brs,

1H), 3.35-3.05 (m, 8H), 2.04-1.81 (m, 8H), 1.74-1.52 (m, 2H), 1.34-1.04 (m, 16H), 0.94-0.59 (m, 13H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.6 (C), 139.0 (C), 138.4 (brs, CH), 137.2 (C), 136.7 (C), 135.9 (C), 134.7 (C), 134.1 (C), 132.5 (C), 131.7 (C), 131.6 (C), 131.4 (CH), 130.5 (CH), 128.8 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 127.3 (brs, CH), 126.6 (brs ,CH), 122.8 (C), 120.8 (brs, CH), 120.6 (CH), 119.6 (brs, CH), 94.4 (C), 82.9 (C), 42.6 (CH), 38.0 (d, $J_{C\text{-}P}$ = 65.4 Hz, CH), 35.7 (CH_2), 34.4 (CH_2), 34.2 (CH_2), 33.9 (CH_2), 32.5 (d, $J_{C\text{-}P}$ = 18.0 Hz, CH), 30.9 (CH_2), 27.3 (CH), 25.3 (CH_2), 25.1 (d, $J_{C\text{-}P}$ = 13.6 Hz, CH_2), 23.63 (CH_2), 23.60 (CH_2), 23.4 (CH_2), 23.0 (brs, CH_3), 21.5 (CH_3), 15.8 (CH_3), 14.9 (CH_3), 14.84 (CH_3), 14.79 (CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 58.6 ppm; HRMS (ESI) calcd. for $C_{62}H_{64}OPS_3$ $[M+H]^+$: 951.3857, found: 951.3898; $[\alpha]_D^{25}$= +2141 (c = 1, $CHCl_3$).



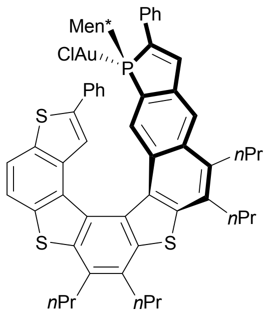
II.6. (*P*)-**10**. To a solution of styrene (0.07 mmol, 8 µL) in 1 mL of DMF were added (*P*)-**5** (0.032 mmol, 30 mg), *trans-bis*(acetato)*bis*[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II), Herrmann-Beller catalyst) (1.5 mg) and sodium acetate (0.064 mmol, 5.3 mg). The reaction mixture was stirred for 16h at 130°C. The crude mixture was concentrated and purified by flash chromatography on silica gel (0% to 20% EtOAc/heptane) to afford the desired compound (*P*)-**10** as a yellow solid (25 mg, 80%). R_f = 0.28 (15% EtOAc/heptane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 10.5 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.89 (brs, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.40-7.24 (m, 10H), 6.57 (d, *J* = 16.0 Hz, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 3.38-3.05 (m, 8H), 2.04-1.83 (m, 8H), 1.65-1.10 (m, 18H), 0.94-0.50 (m, 13H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.6 (C), 140.5 (C), 139.0 (C), 138.1 (brs, CH), 136.7 (C), 136.2 (d, $J_{C\text{-}P}$ = 97.4 Hz, C), 135.6 (C), 135.5 (C), 134.2 (C), 132.6 (C), 132.4 (C), 132.2 (C), 131.9 (C), 131.7 (C), 130.3 (C), 129.9 (CH), 128.9 (CH), 128.8 (CH), 128.6 (CH), 128.0 (CH), 126.7 (brs, CH), 126.4 (CH), 125.7 (brs, CH), 122.0 (CH), 120.7 (CH), 120.0 (brs, CH), 119.8 (CH), 42.7 (CH), 37.9 (d, $J_{C\text{-}P}$ = 63.8 Hz, CH), 35.7 (CH_2), 34.4 (CH_2), 34.2 (CH_2), 33.9 (CH_2), 32.4 (d, $J_{C\text{-}P}$ = 14.5 Hz, CH), 30.9 (CH_2), 27.3 (CH), 25.3 (CH_2), 25.1 (d, $J_{C\text{-}P}$ = 13.6 Hz, CH_2), 23.7 (CH_2), 23.6 (CH_2), 23.4 (CH_2), 23.0 (brs, CH_3), 21.6 (CH_3), 15.8 (CH_3), 14.94 (CH_3), 14.90 (CH_3), 14.84 (CH_3), 14.79 (CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 58.6 ppm; HRMS (ESI) calcd. for $C_{62}H_{66}OPS_3$ $[M+H]^+$: 953.4013, found: 953.4045; $[\alpha]_D^{25}$= +2168 (c = 1, $CHCl_3$).

Reduction of the phosphine oxide and formation of the gold complexes

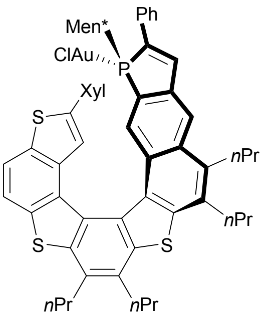
To the enantiopure phosphahelicenes **6-10** (1.0 equiv) in degassed anhydrous toluene (0.1 M), in a Schlenk tube under argon, was added $PhSiH_3$ (3.0 equiv) and *bis*(4-nitrophenyl)phosphate (15 mol%). Then the reaction mixture was stirred 2h at 100°C under argon before being quenched by a degassed solution of sodium hydroxide in water (1 M) and extracted twice with degassed dichloromethane. The combined organic layers were then evaporated under inert atmosphere.

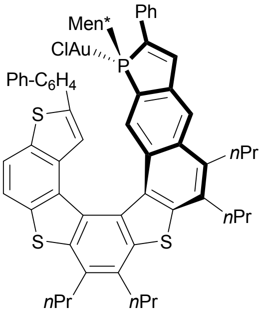
To a solution of Me_2SAuCl (1.0 equiv) in degassed dichloromethane (0.1 M) was added a solution of the phosphine in degassed dichloromethane (0.1 M). The reaction was stirred at room temperature for 1 h. Then the solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (10% to 20% EtOAc/Petroleum Ether) to obtain the complexes as yellow powders.

II.7. (*P*)-**11**. Starting from (*P*)-**6**, the two steps procedure (reduction /complexation) give the desired complex in 76% yield. Mp 185-187°C; R_f= 0.5 (10% EtOAc / heptane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, J = 8.5 Hz, 1H), 8.07 (s, 1H), 7.98 (d, J = 9.0 Hz, 1H), 7.89 (d, J = 9.5 Hz, 1H), 7.81 (d, J = 7.5 Hz, 2H), 7.57 (d, J_{H-P} = 26.0 Hz, 1H), 7.39 (t, J = 8.0 Hz, 2H), 7.35-7.28 (m, 1H), 7.18-7.09 (m, 3H), 6.83 (d, J = 7.0 Hz, 2H), 6.46 (s, 1H), 3.35-3.11 (m, 8H), 2.07-1.80 (m, 8H), 1.69-1.55 (m, 2H), 1.38-1.08 (m, 14H), 0.96-0.66 (m, 7H), 0.40-0.30 (m, 6H), 0.23-0.16 (m, 1H), (-)0.25-(-)0.35 (m, 1H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 142.7 (C), 141.8 (d, J_{C-P} = 15.3 Hz, C), 140.8 (C), 140.2 (C), 138.8 (C), 138.1 (d, J_{C-P} = 53.4 Hz, C), 137.7 (C), 137.2 (d, J_{C-P} = 8.8 Hz, CH), 136.2 (C), 135.9 (C), 135.2 (C), 134.6 (C), 134.2 (C), 133.8 (d, J_{C-P} = 12.5 Hz, C), 132.8 (C), 132.1 (C), 131.8 (C), 131.0 (C), 130.4 (C), 130.0 (d, J_{C-P} = 12.5 Hz, CH), 129.3 (CH), 129.0 (CH), 128.5 (C), 128.41 (C), 128.36 (CH), 128.2 (C), 127.5 (CH), 126.9 (d, J_{C-P} = 7.7 Hz, CH), 126.3 (CH), 124.6 (CH), 123.5 (d, J_{C-P} = 62.2 Hz, C), 121.5 (CH), 120.8 (d, J_{C-P} = 6.5 Hz, CH), 117.6 (CH), 43.5 (CH), 39.6 (d, J_{C-P} = 28.9 Hz, CH), 35.7 (CH_2), 34.6 (CH_2), 34.0 (d, J_{C-P} = 6.5 Hz, CH_2), 33.6 (CH_2), 33.0 (d, J_{C-P} = 11.4 Hz, CH), 31.3 (CH_2), 29.8 (d, J_{C-P} = 8.7 Hz, CH), 25.2 (CH_2), 24.7 (d, J_{C-P} = 11.4 Hz, CH_2), 23.63 (CH_2), 23.57 (CH_2), 23.51 (CH_2), 22.0 (CH_3), 20.5 (CH_3), 16.7 (CH_3), 15.2 (CH_3), 15.0 (CH_3), 14.8 (CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 25.5 ppm; IR: v_{max} = 3058, 2955, 2925, 2867, 1454, 1156, 1132, 1090, 757, 687 cm^{-1}; $[\alpha]_D^{25}$= +1764 (c = 1, $CHCl_3$).

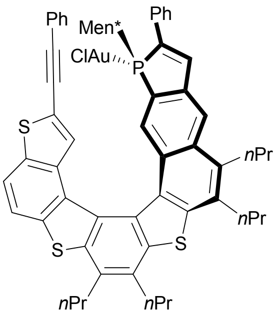


II.8. (*P*)-**12**. Starting from (*P*)-**7**, the two steps procedure (reduction /complexation) give the desired complex in 78% yield. Mp 191-193°C; R_f= 0.5 (10% EtOAc / heptane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, J = 8.5 Hz, 1H), 8.04 (d, J = 2.0 Hz, 1H), 7.98 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 9.0 Hz, 1H), 7.82 (d, J = 7.5 Hz, 2H), 7.57 (d, J_{H-P} = 26.5 Hz, 1H), 7.39 (t, J = 7.5 Hz, 2H), 7.32 (t, J = 7.5 Hz, 1H), 6.78 (brs, 1H), 6.49 (s, 2H), 6.45 (s, 1H), 3.37-3.09 (m, 8H), 2.20 (s, 6H), 2.13-1.78 (m, 9H), 1.75-1.67 (m, 1H), 1.35-1.05 (m, 16H), 0.90 (d, J = 6.5 Hz, 3H), 0.82-0.70 (m, 2H), 0.36-0.34 (m, 6H), 0.26-0.17 (m, 1H), (-)0.27-(-)0.38 (m, 1H); ^{13}C NMR (125 Hz, $CDCl_3$) δ 143.1 (C), 141.8 (d, J_{C-P} = 15.5 Hz, C), 140.6 (C), 140.1 (C), 138.8 (C), 138.1 (d, J_{C-P} = 53.8 Hz, C), 137.7 (C), 137.6 (C), 137.1 (d, J_{C-P} = 8.6 Hz, CH), 136.1 (C), 135.9 (C), 135.0 (C), 134.6 (C), 133.9 (C), 133.8 (d, J_{C-P} = 12.8 Hz, C), 132.7 (C), 132.0 (C), 131.8 (C), 131.2 (C), 130.4 (C), 130.0 (d, J_{C-P} = 12.8 Hz, CH), 129.3 (CH), 129.0 (CH), 128.55 (C), 128.49 (C), 128.3 (d, J_{C-P} = 11.4 Hz, C), 126.8 (d, J_{C-P} = 7.3 Hz, CH), 124.7 (CH), 124.0 (CH), 123.5 (d, J_{C-P} = 61.4 Hz, C), 121.3 (CH), 120.6 (d, J_{C-P} = 6.4 Hz, CH), 117.5 (CH), 43.6 (CH), 39.7 (d, J_{C-P} = 29.1 Hz, CH), 35.5 (CH_2), 34.6 (CH_2), 34.0 (d, J_{C-P} = 5.9 Hz, CH_2), 33.6 (CH_2), 33.0 (d, J_{C-P} = 11.4 Hz, CH), 31.8 (CH_2), 29.8 (d, J_{C-P} = 9.6 Hz, CH), 25.0 (CH_2), 24.8 (d, J_{C-P} = 11.4 Hz, CH_2), 23.8 (CH_2), 23.6 (CH_2), 23.5 (CH_2), 22.1 (CH_3), 21.4 (CH_3), 20.5 (CH_3), 16.7 (CH_3), 15.2 (CH_3), 15.0 (CH_3), 14.9 (CH_3), 14.8 (CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 25.3 ppm; IR: v_{max} = 3057, 2955, 2925, 2867, 1599, 1455, 1316, 1156, 1090, 898, 840, 758 cm^{-1}; $[\alpha]_D^{25}$= +1779 (c = 1, $CHCl_3$).





II.9. (*P*)-**13**. Starting from (*P*)-**8**, the two steps procedure (reduction /complexation) give the desired complex in 51% yield. Mp 188-190°C; R_f= 0.5 (10% EtOAc / heptane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.5 Hz, 1H), 8.07 (bs, 1H), 7.99 (d, *J* = 9.0 Hz, 1H), 7.89 (d, *J* = 9.5 Hz, 1H), 7.81 (d, *J* = 7.5 Hz, 2H), 7.62-7.53 (m, 3H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.46-7.28 (m, 6H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.51 (s, 1H), 3.35-3.10 (m, 8H), 2.10-1.83 (m, 8H), 1.69-1.60 (m, 2H), 1.38-1.05 (m, 14H), 0.96-0.70 (m, 7H), 0.40-0.30 (m, 6H), 0.24-0.16 (m, 1H), (-)0.25-(-)0.40 (m, 1H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 142. 2 (C), 141.8 (d, $J_{C\text{-}P}$ = 15.5 Hz, C), 140.8 (C), 140.6 (C), 140.2 (C), 140.1 (C), 138.7 (d, $J_{C\text{-}P}$ = 29.7 Hz, C), 137.7 (C), 137.2 (d, $J_{C\text{-}P}$ = 8.5 Hz, CH), 136.2 (C), 136.0 (C), 135.2 (C), 134.6 (C), 133.7 (d, $J_{C\text{-}P}$ = 12.5 Hz, C), 133.2 (C), 132.8 (C), 132.1 (C), 131.8 (C), 131.0 (C), 130.4 (C), 130.0 (d, $J_{C\text{-}P}$ = 12.8 Hz, CH), 129.3 (CH), 129.0 (CH), 128.39 (C), 128.33 (d, $J_{C\text{-}P}$ = 17.0 Hz, C), 127.54 (CH), 127.53 (d, $J_{C\text{-}P}$ = 29.5 Hz, CH), 127.0 (CH), 126.9 (CH), 126.8 (CH), 126.6 (CH), 124.6 (CH), 123.5 (d, $J_{C\text{-}P}$ = 61.4 Hz, C), 121.5 (CH), 120.8 (d, $J_{C\text{-}P}$ = 5.8 Hz, CH), 117.7 (CH), 43.5 (CH), 39.6 (d, $J_{C\text{-}P}$ = 29.0 Hz, CH), 35.7 (CH_2), 34.6 (CH_2), 33.9 (d, $J_{C\text{-}P}$ = 5.7 Hz, CH_2), 33.6 (CH_2), 32.9 (d, $J_{C\text{-}P}$ = 10.7 Hz, CH), 29.9 (CH_2), 29.8 (CH), 25.3 (CH_2), 24.7 (d, $J_{C\text{-}P}$ = 11.2 Hz, CH_2), 23.7 (CH_2), 23.6 (CH_2), 23.5 (CH_2), 22.1 (CH_3), 20.5 (CH_3), 16.7 (CH_3), 15.2 (CH_3), 15.0 (CH_3), 14.8 (CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 25.2 ppm; IR: v_{max} = 3058, 2955, 2932, 2866, 1599, 1455, 1156, 1090, 832, 757, 692 cm^{-1}; $[\alpha]_D^{25}$= +1679 (c = 1, $CHCl_3$).

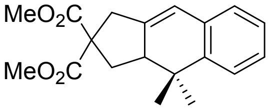


II.10. (*P*)-**14**. Starting from (*P*)-**9**, the two steps procedure (reduction /complexation) give the desired complex in 37% yield. R_f = 0.3 (5% EtOAc / heptane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.5 Hz, 1H), 8.22 (brs, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.75 (s, 1H), 7.73 (d, $J_{H\text{-}P}$ = 36.0 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.37-7.29 (m, 6H), 6.36 (s, 1H), 3.34-3.10 (m, 8H), 2.10-1.86 (m, 8H), 1.70-1.65 (m, 2H), 1.30-1.07 (m, 14H), 0.96-0.66 (m, 7H), 0.35 (d, *J* = 6.0 Hz, 3H), 0.32 (d, *J* = 6.5 Hz, 3H), 0.26-0.17 (m, 1H), (-)0.26-(-)0.35 (m, 1H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 141.8 (d, $J_{C\text{-}P}$ = 15.8 Hz, C), 140.8 (C), 140.2 (C), 138.84 (C), 138.76 (C), 138.0 (d, $J_{C\text{-}P}$ = 54.0 Hz, C), 137.3 (d, $J_{C\text{-}P}$ = 9.0 Hz, CH), 136.4 (C), 135.7 (C), 134.4 (C), 134.1 (C), 133.8 (d, $J_{C\text{-}P}$ = 12.5 Hz, C), 132.6 (C), 132.3 (C), 131.7 (C), 131.4 (CH), 130.5 (C), 130.4 (CH), 130.2 (C), 129.8 (d, $J_{C\text{-}P}$ = 13.1 Hz, CH), 129.3 (CH), 129.0 (CH), 128.32 (CH), 128.30 (C), 128.2 (C), 126.88 (d, $J_{C\text{-}P}$ = 7.6 Hz, CH), 124.1 (CH), 123.4 (d, $J_{C\text{-}P}$ = 61.1 Hz, C), 123.1 (C), 121.5 (C), 121.2 (d, $J_{C\text{-}P}$ = 6.0 Hz, CH), 118.7 (CH), 94.2 (C), 83.2 (C), 43.5 (CH), 39.5 (d, $J_{C\text{-}P}$ = 29.0 Hz, CH), 35.8 (CH_2), 34.6 (CH_2), 33.9 (d, $J_{C\text{-}P}$ = 6.0 Hz, CH_2), 33.6 (CH_2), 32.9 (d, $J_{C\text{-}P}$ = 11.0 Hz, CH), 31.1 (CH_2), 29.8 (d, $J_{C\text{-}P}$ = 8.2 Hz, CH), 25.2 (CH_2), 24.7 (d, $J_{C\text{-}P}$ = 11.0 Hz, CH_2), 23.7 (CH_2), 23.6 (CH_2), 23.5 (CH_2), 22.1 (CH_3), 20.4 (CH_3), 16.7 (CH_3), 15.0 (CH_3), 14.9 (CH_3), 14.8 (CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.7 ppm; $[\alpha]_D^{25}$= +1902 (c = 1, $CHCl_3$).

General procedure for the gold-catalyzed cycloisomerization reactions

Silver salt (8 mol %) was added to a solution (0.1 M) of gold catalyst (4 mol %) and substrate **15** (1 equiv.) in toluene. The reaction was stirred under the desired condition and monitored by ^{1}H NMR.

The solvent was removed under reduced pressure and the final product **16** was purified by flash chromatography. Enantiomeric excesses have been measured by chiral HPLC.



II.11. Dimethyl 4,4-dimethyl-3a,4-dihydro-1*H*-cyclopenta[b]naphthalene-2,2(3*H*)-dicarboxylate (**16**).[2] ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.30-7.25 (m, 1H), 7.20-7.12 (m, 2H), 7.02-7.00 (d, *J* = 6.5 Hz, 1H), 6.35 (brs, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 3.30 (d, *J* = 18.0 Hz, 1H), 2.98 (d, *J* = 18.0 Hz, 1H), 2.75-2.64 (m, 1H), 2.59 (dd, *J* = 12.0, 8.0 Hz, 1H), 2.14 (t, *J* = 12.0 Hz, 1H), 1.42 (s, 3H), 0.92 (s, 3H); HPLC Analysis: [CHIRALPAK ® IA , 25°C, 2% iPrOH/ *n*-heptane, 1mL/min, 274 nm, retention times: 6.3 min (major) and 7.2 min (minor)].

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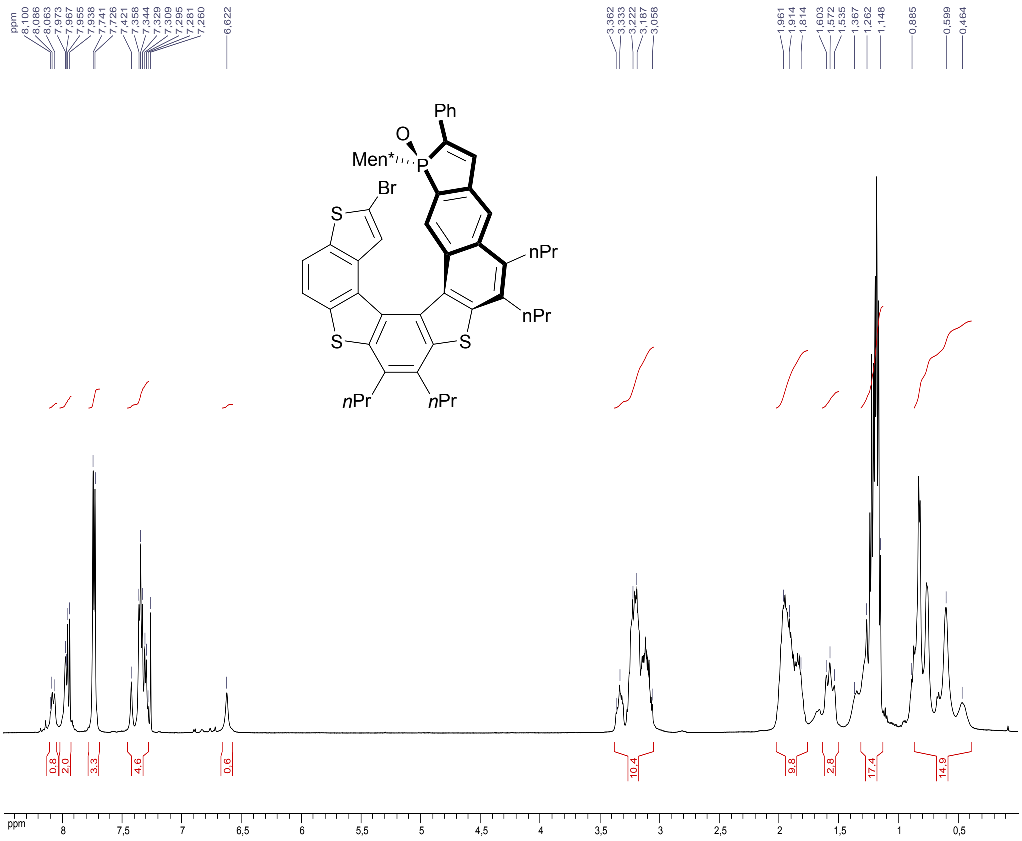
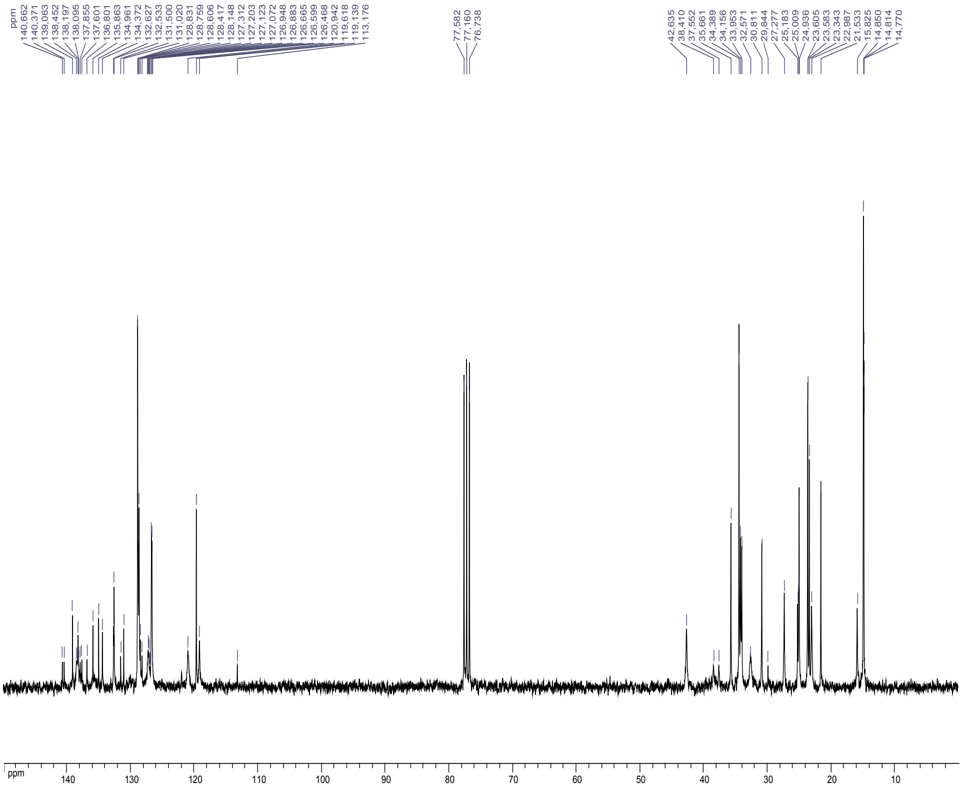
[2] N. Delpont, I. Escofet, P. Perez-Galan, D. Spiegl, M. Raducan, C. Bour, R. Sinisi, A. M. Echavarren, *Catalysis Science & Technology* 2013, **3**, 3007.

III. NMR Spectra (^{1}H, ^{13}C and ^{31}P NMR).

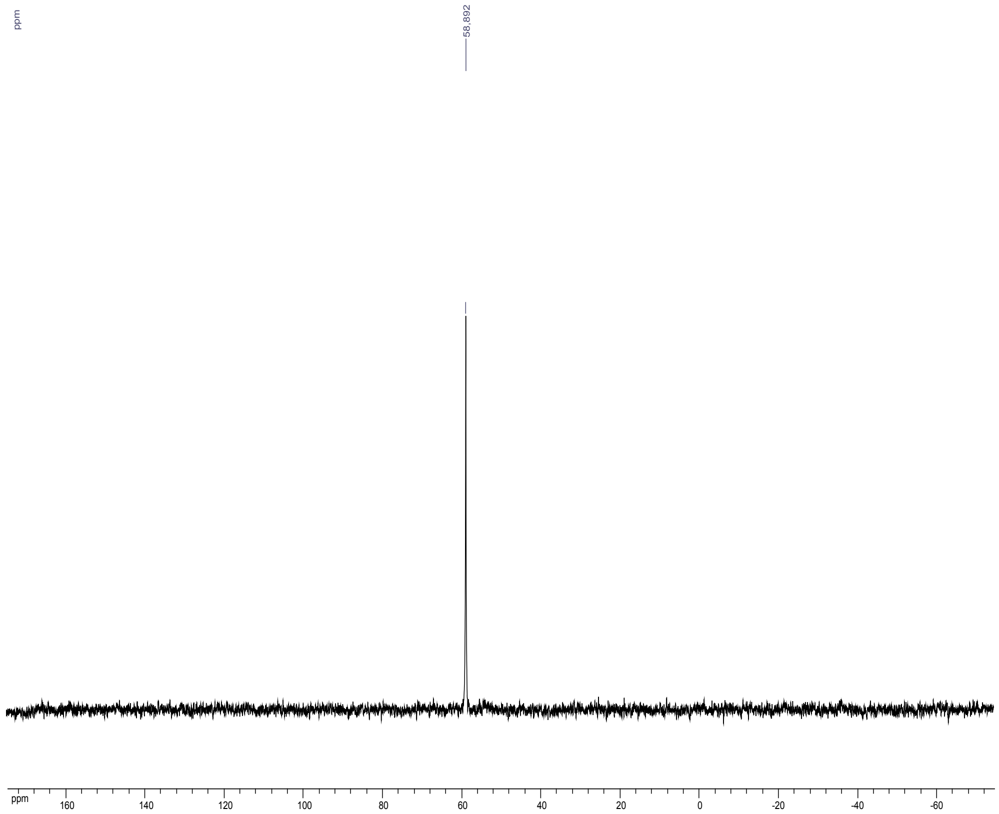
III.1. ^{1}H NMR (300 MHz, $CDCl_3$) (*P*)-5:



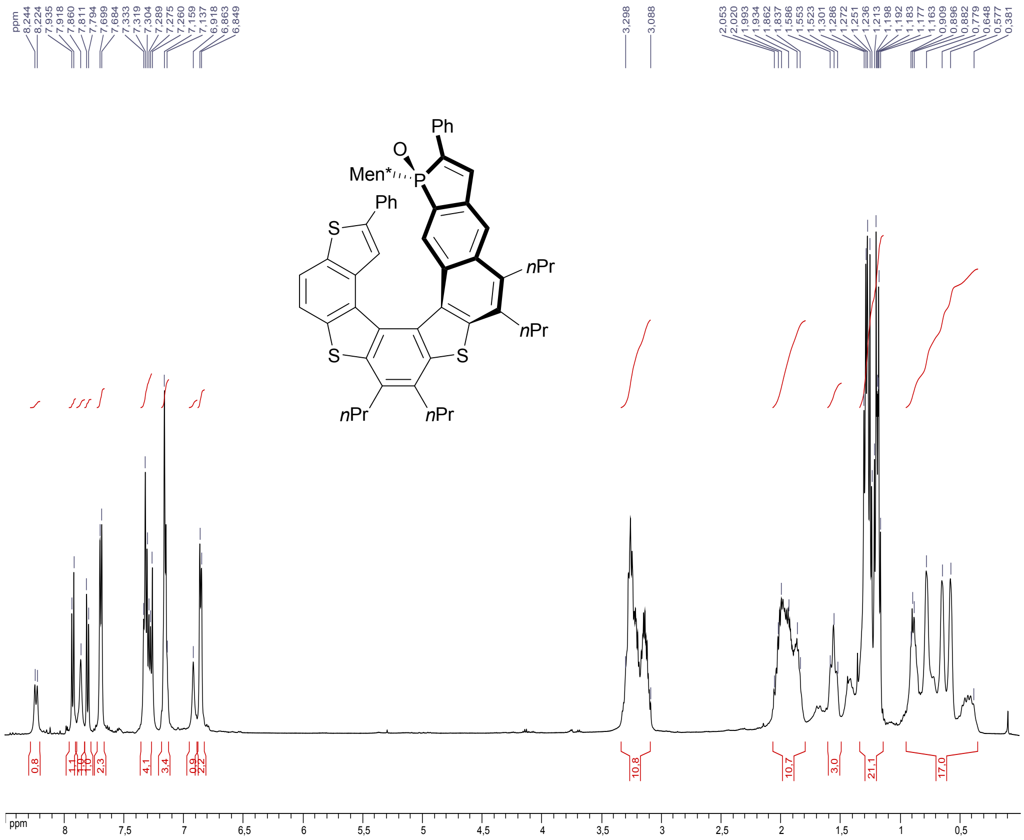
^{13}C NMR (75 MHz, $CDCl_3$):



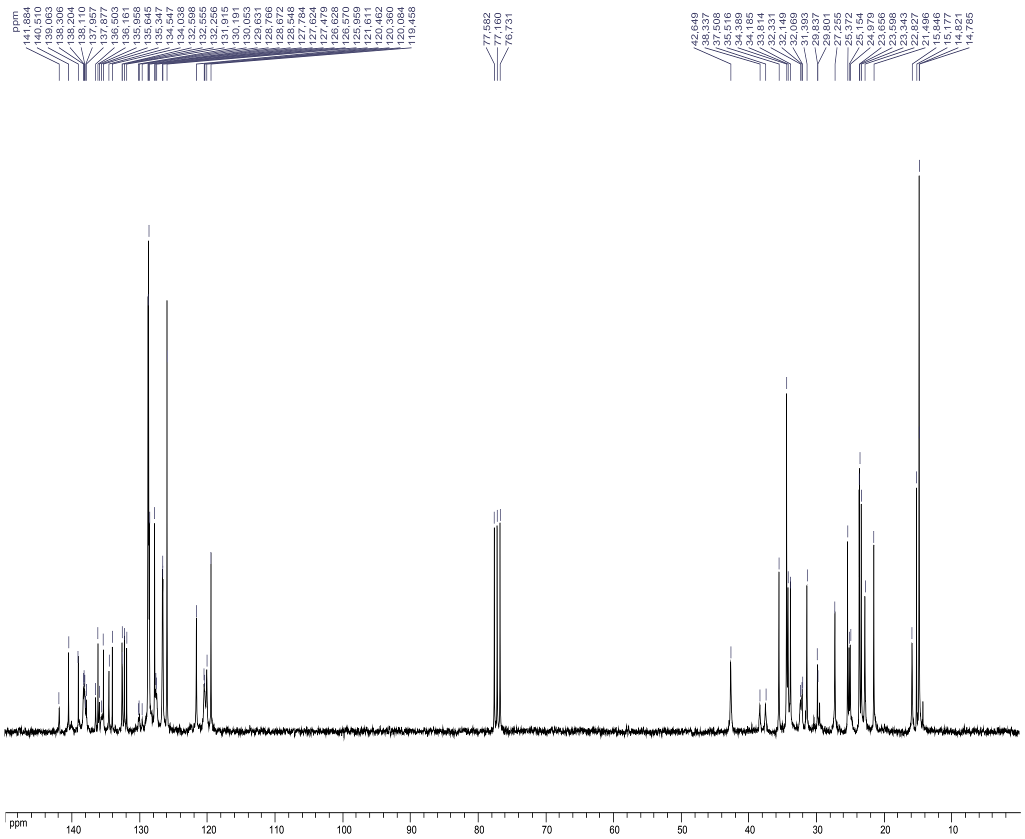
^{31}P NMR (202.5 MHz, $CDCl_3$):



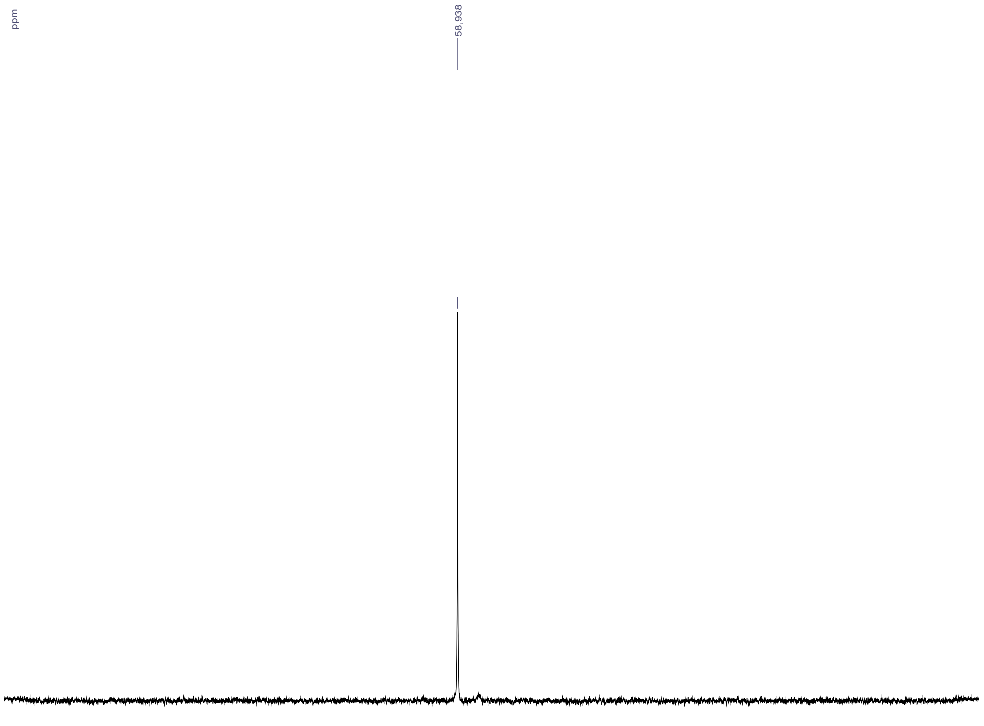
III.2. ^{1}H NMR (300 MHz, $CDCl_3$) (*P*)-6:



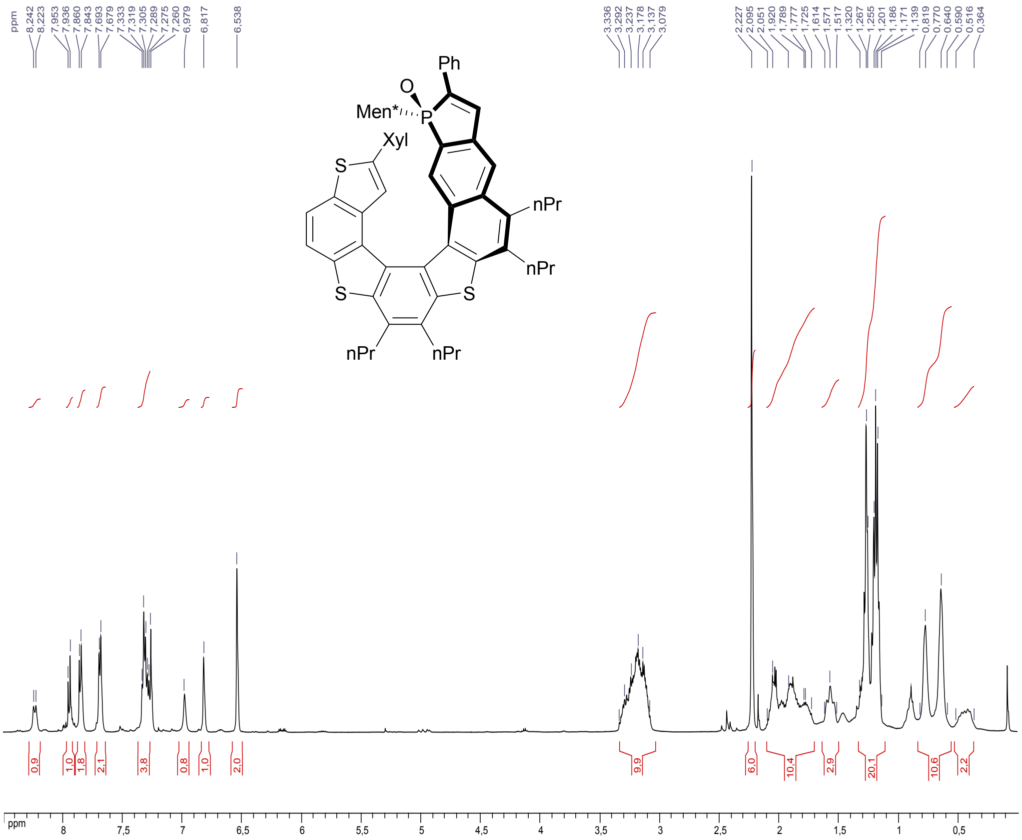
^{13}C NMR (75 MHz, CDCl$_3$):



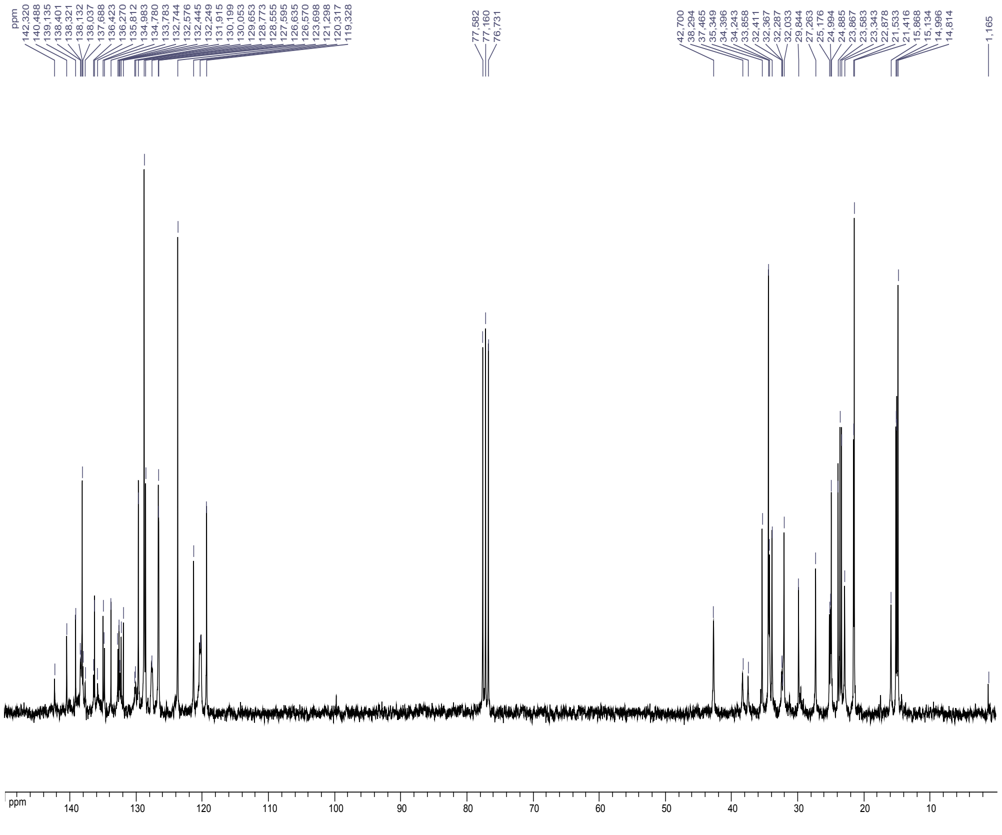
^{31}P NMR (202.5 MHz, CDCl$_3$):



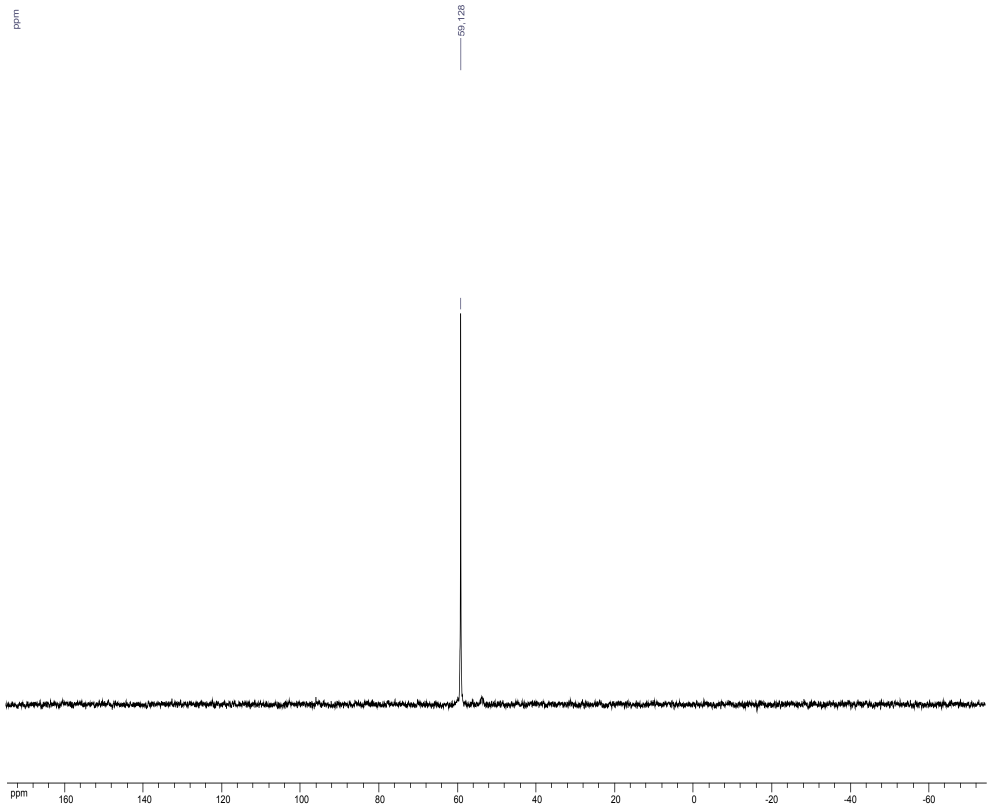
III.3. ^{1}H NMR (300 MHz, CDCl$_3$) (*P*)-7:



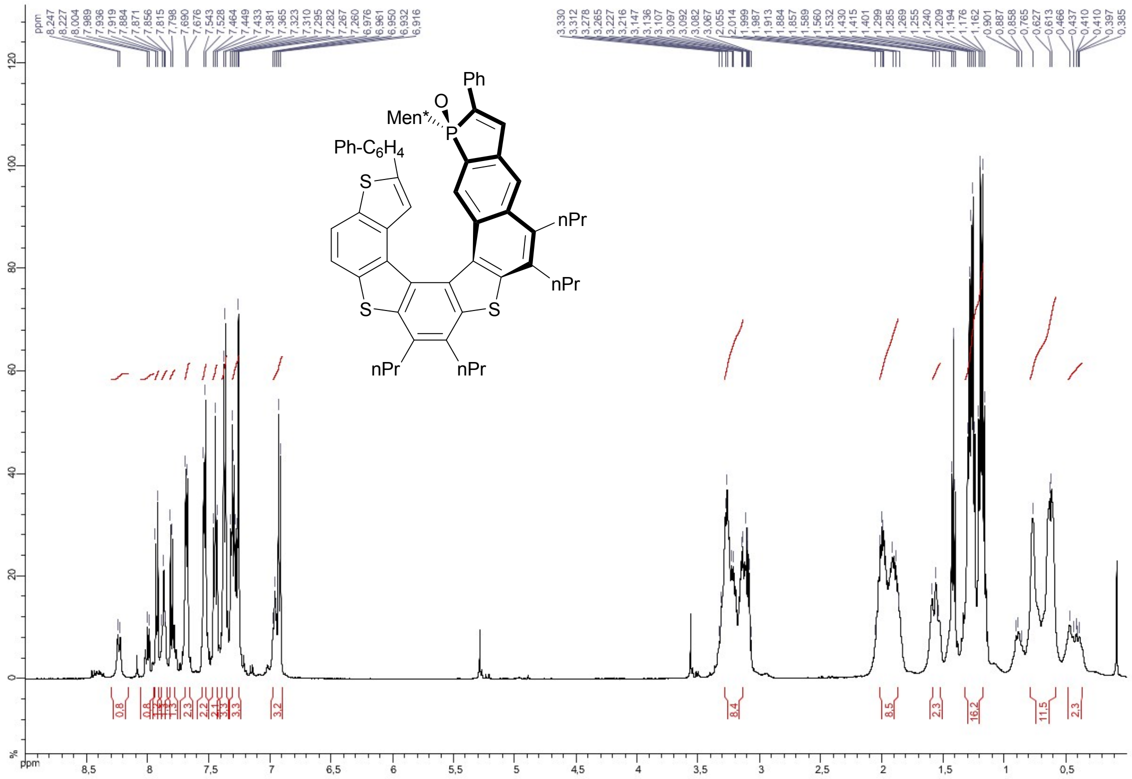
^{13}C NMR (75 MHz, CDCl$_3$):



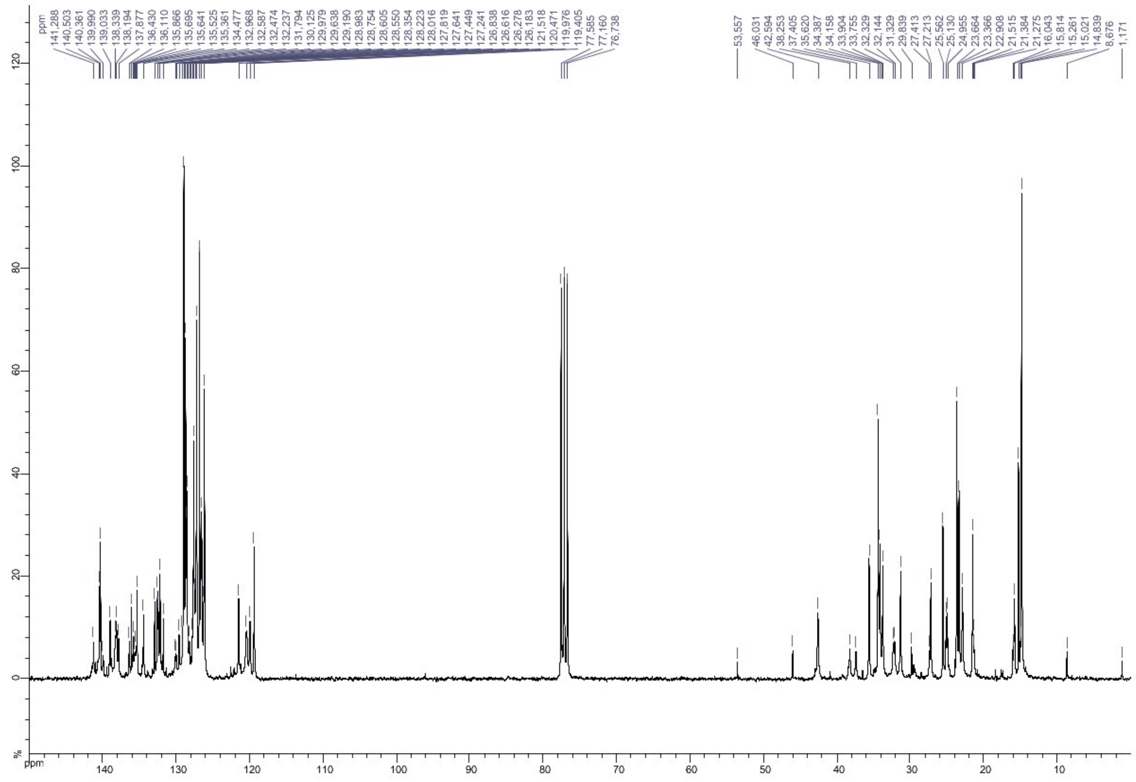
^{31}P NMR (202.5 MHz, CDCl$_3$):



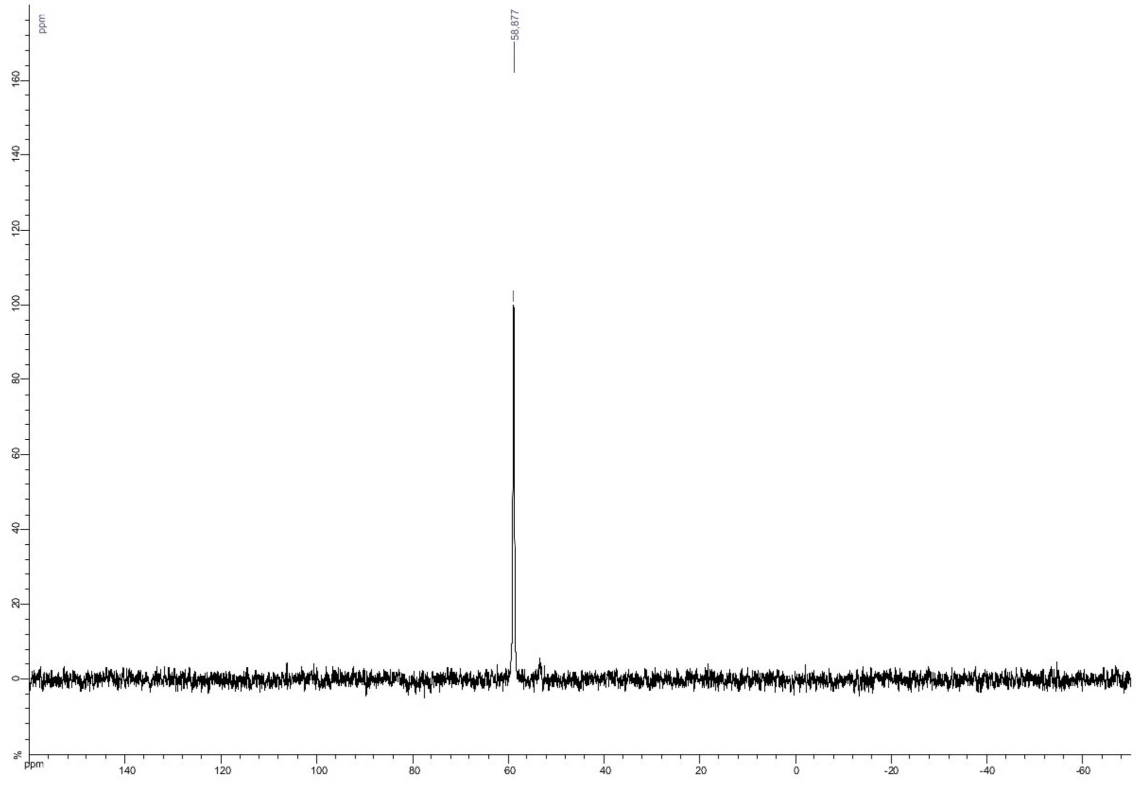
III.4. ^{1}H NMR (300 MHz, CDCl$_3$) (*P*)-8:



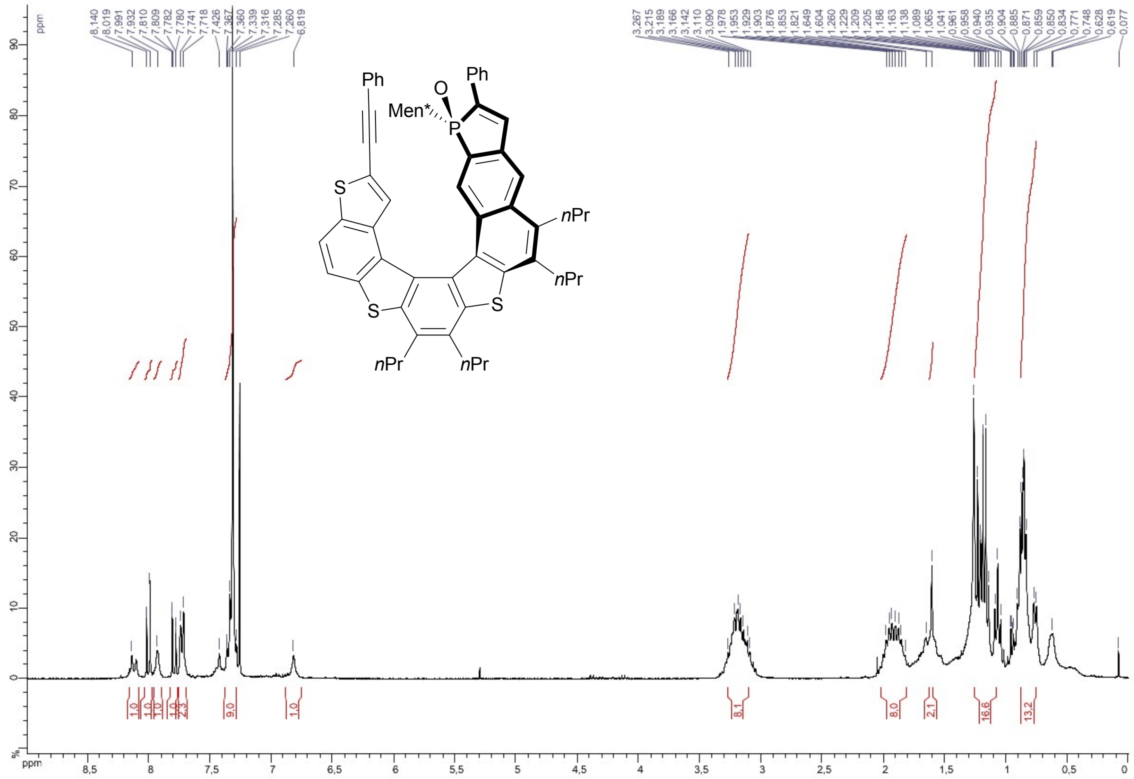
^{13}C NMR (75 MHz, CDCl$_3$):



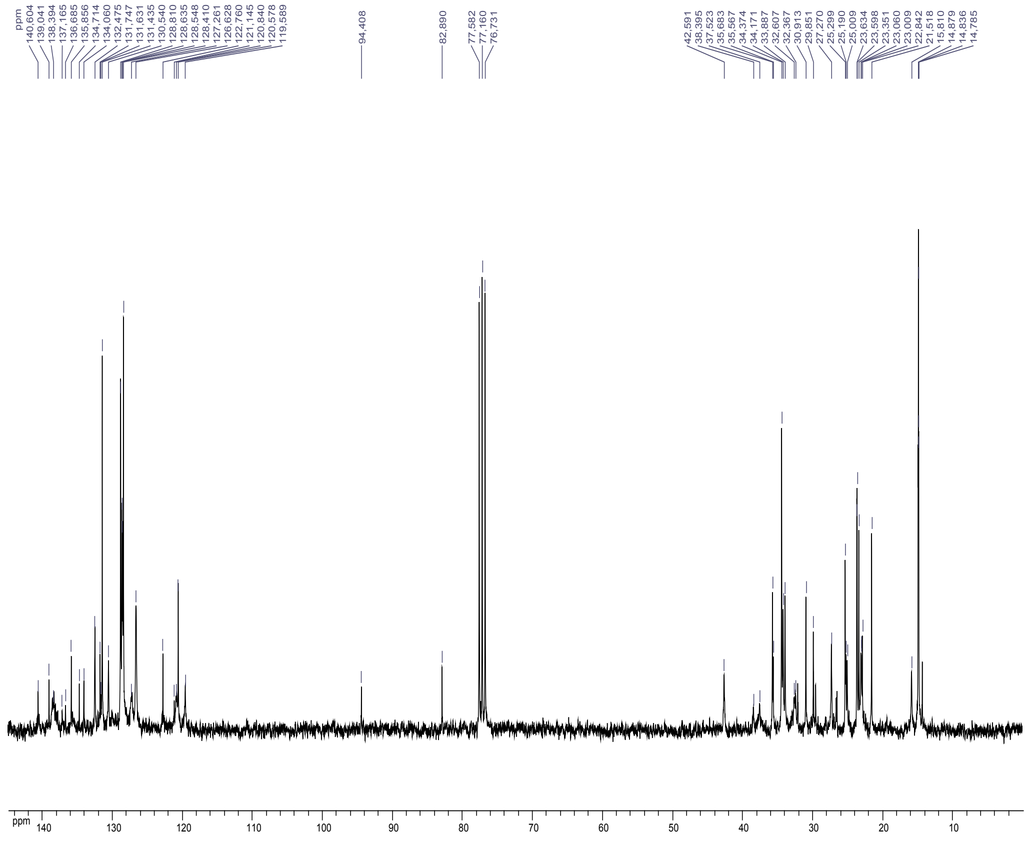
^{31}P NMR (202.5 MHz, CDCl$_3$):



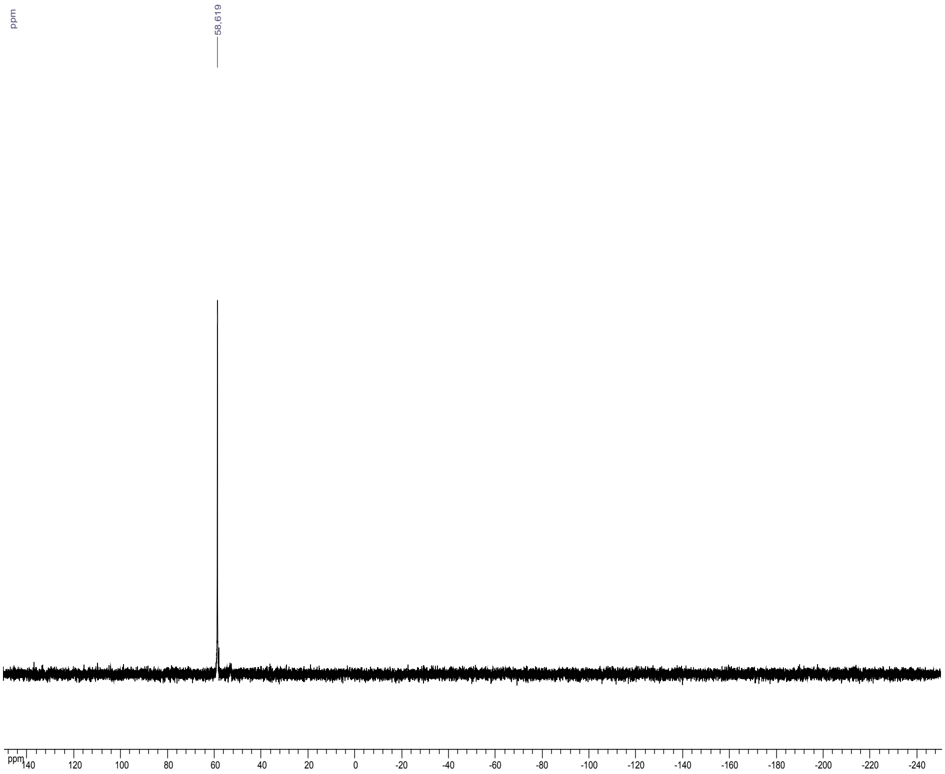
III.4. ^{1}H NMR (300 MHz, CDCl$_3$) (*P*)-9:



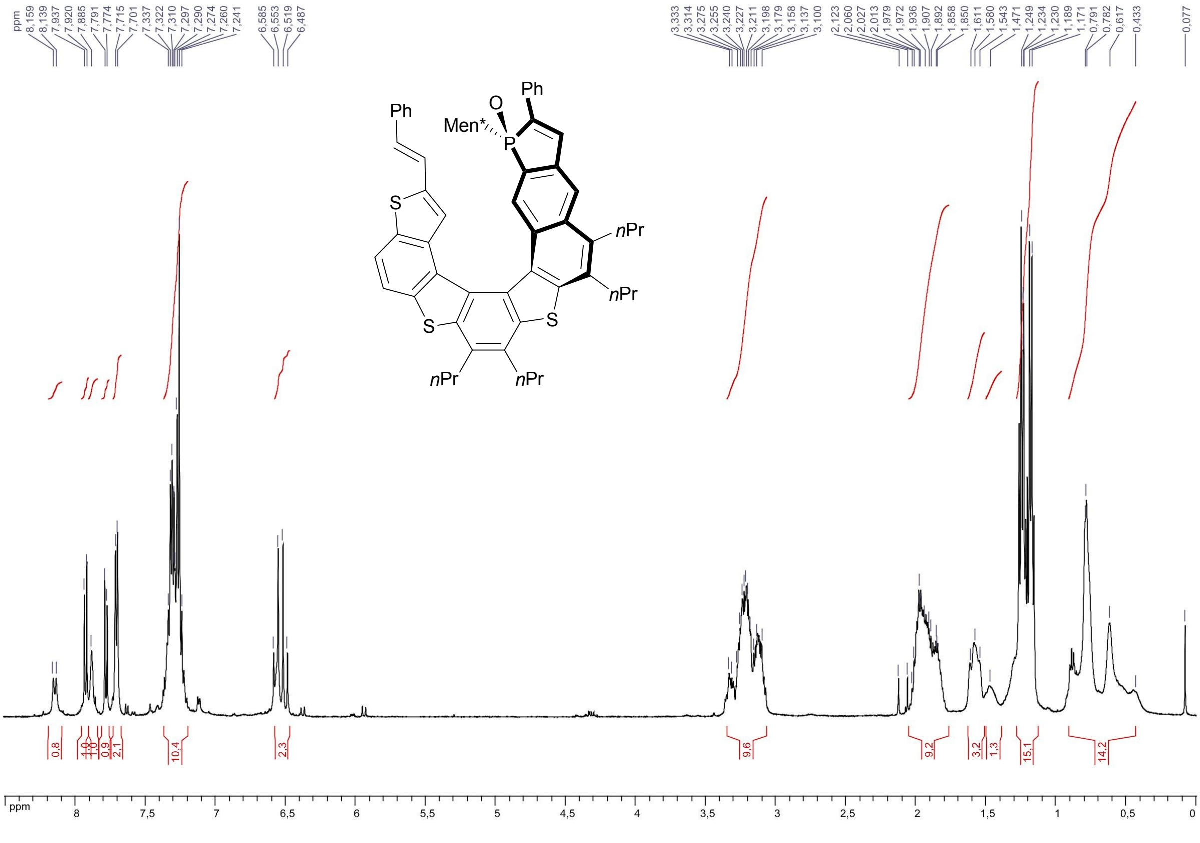
^{13}C NMR (75 MHz, CDCl$_3$):



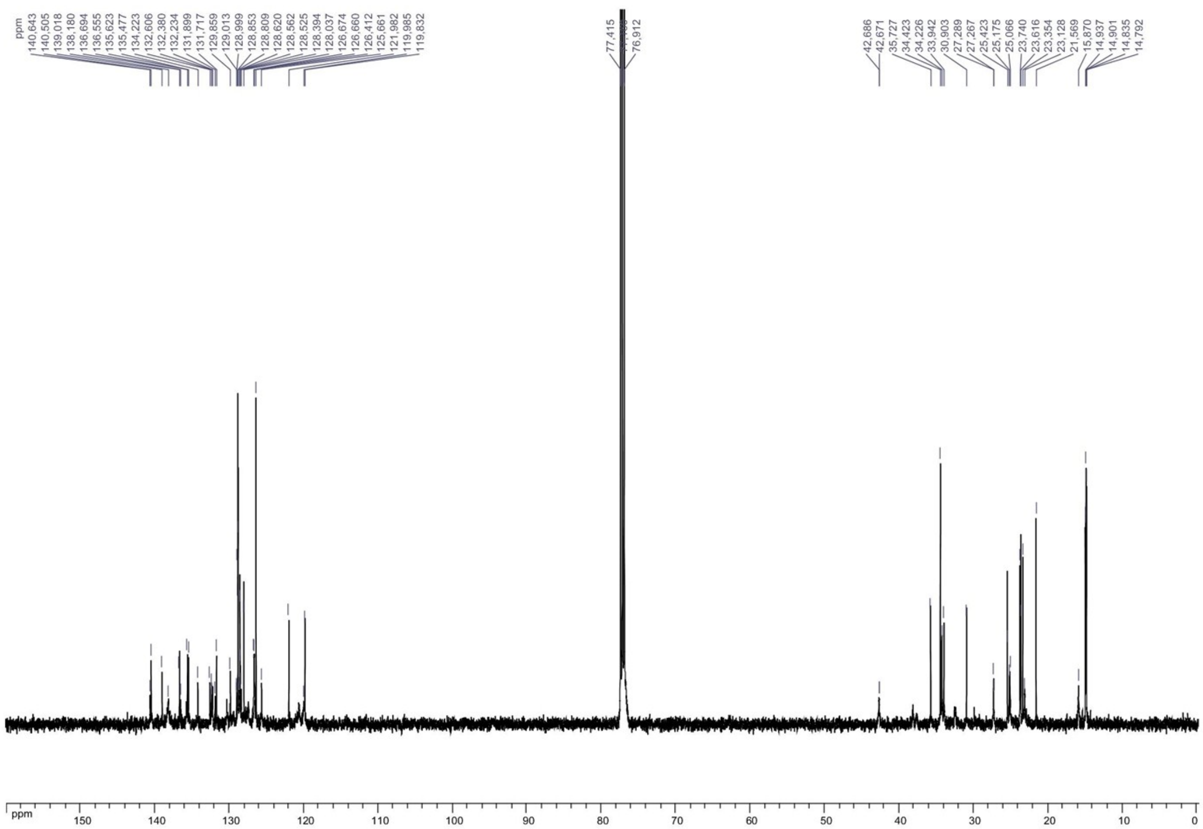
^{31}P NMR (202.5 MHz, $CDCl_3$):



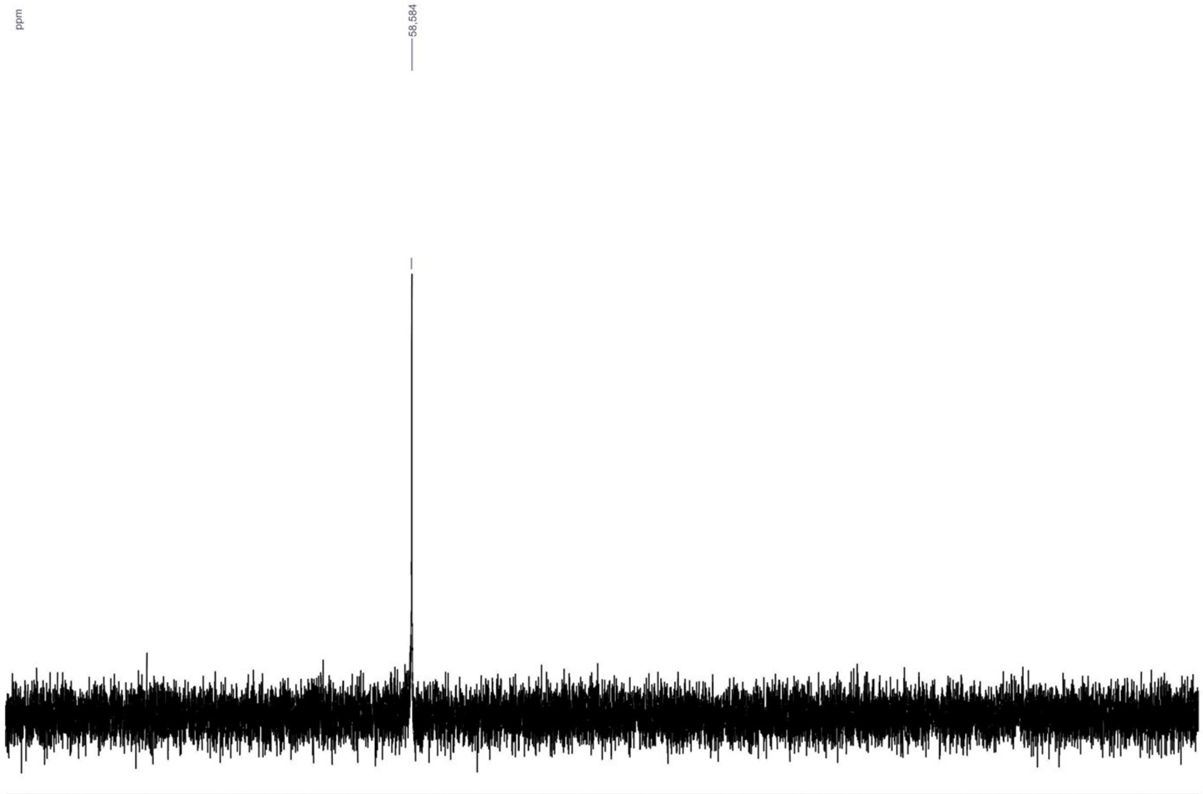
III.5. ^1H NMR (300 MHz, $CDCl_3$) (*P*)-10:



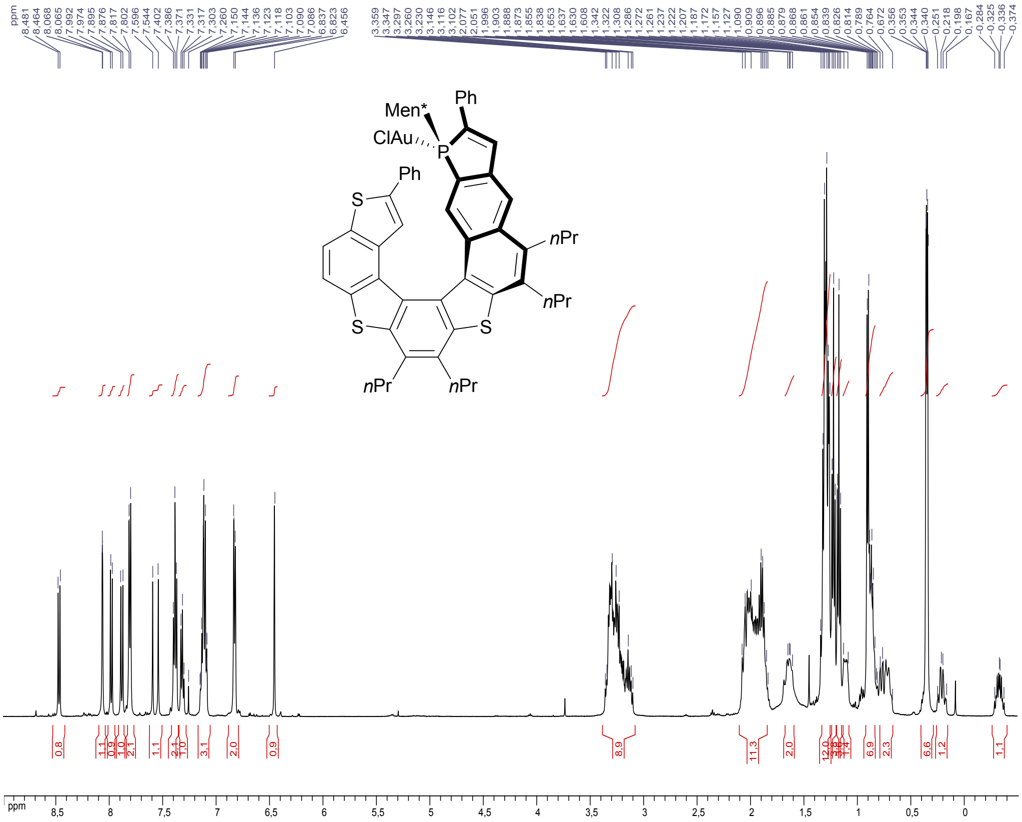
^{13}C NMR (75 MHz, CDCl$_3$):

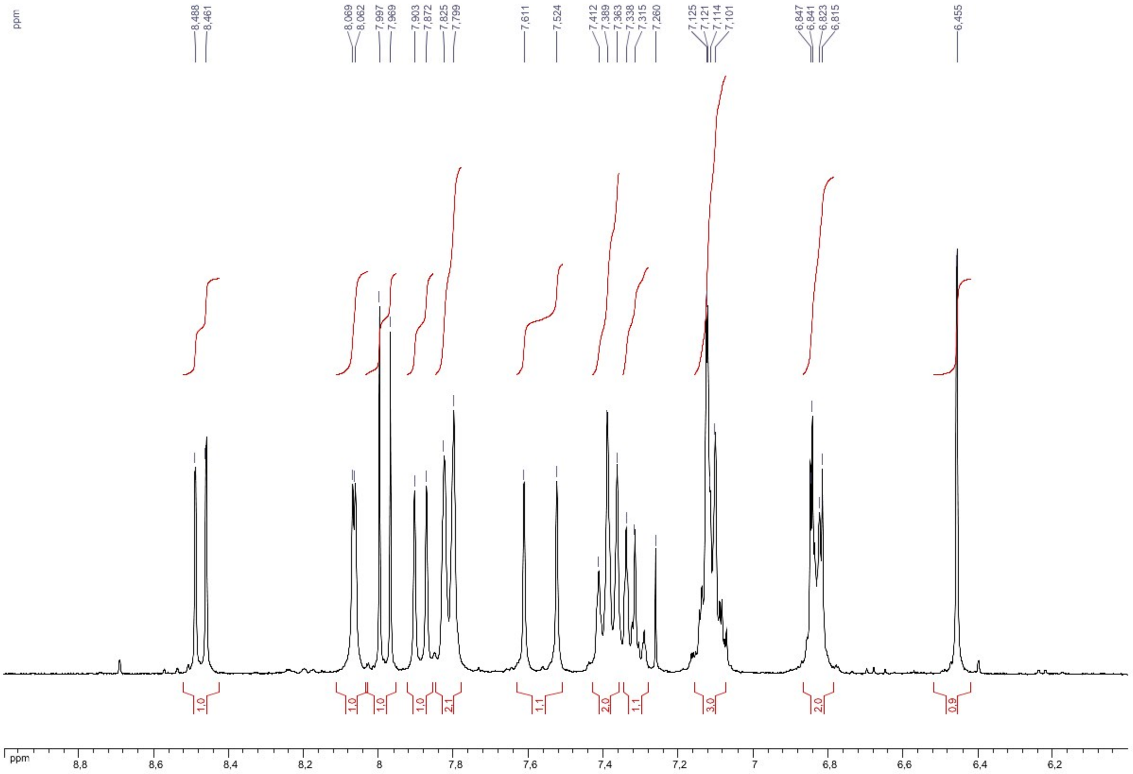


^{31}P NMR (202.5 MHz, CDCl$_3$):

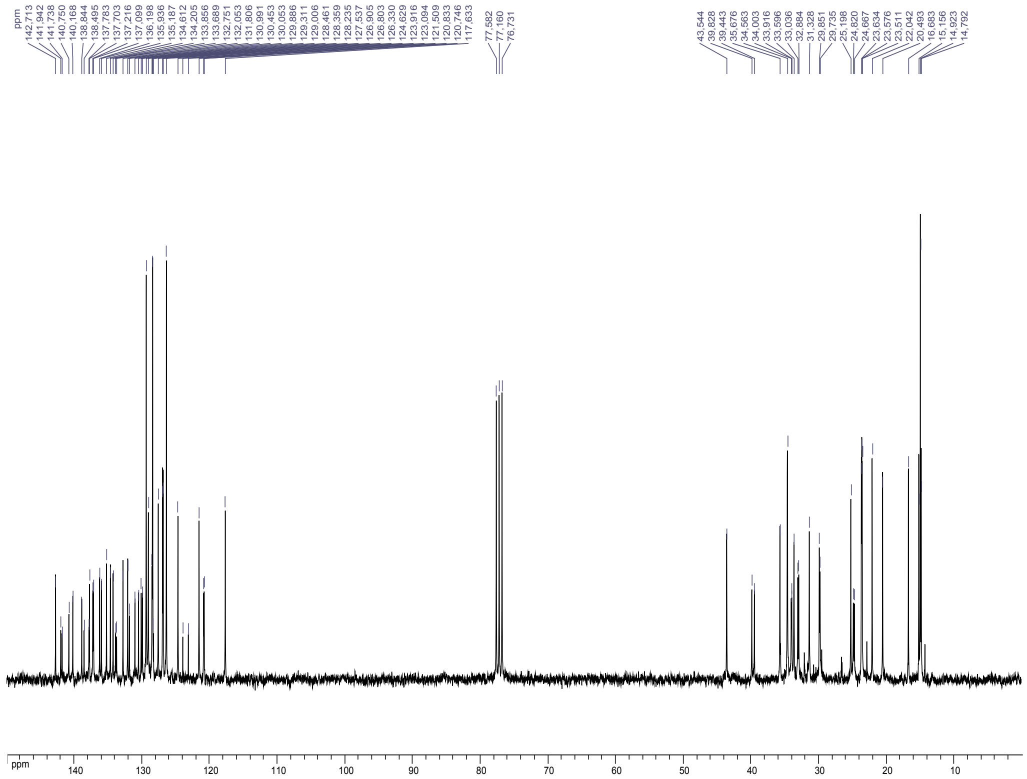


III.6. ¹H NMR (300 MHz, CDCl$_3$) (*P*)-11:





^{13}C NMR (75 MHz, CDCl$_3$):



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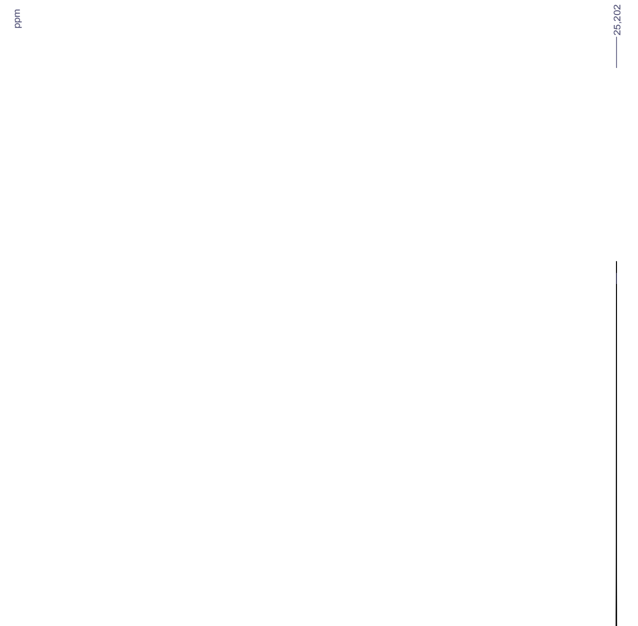
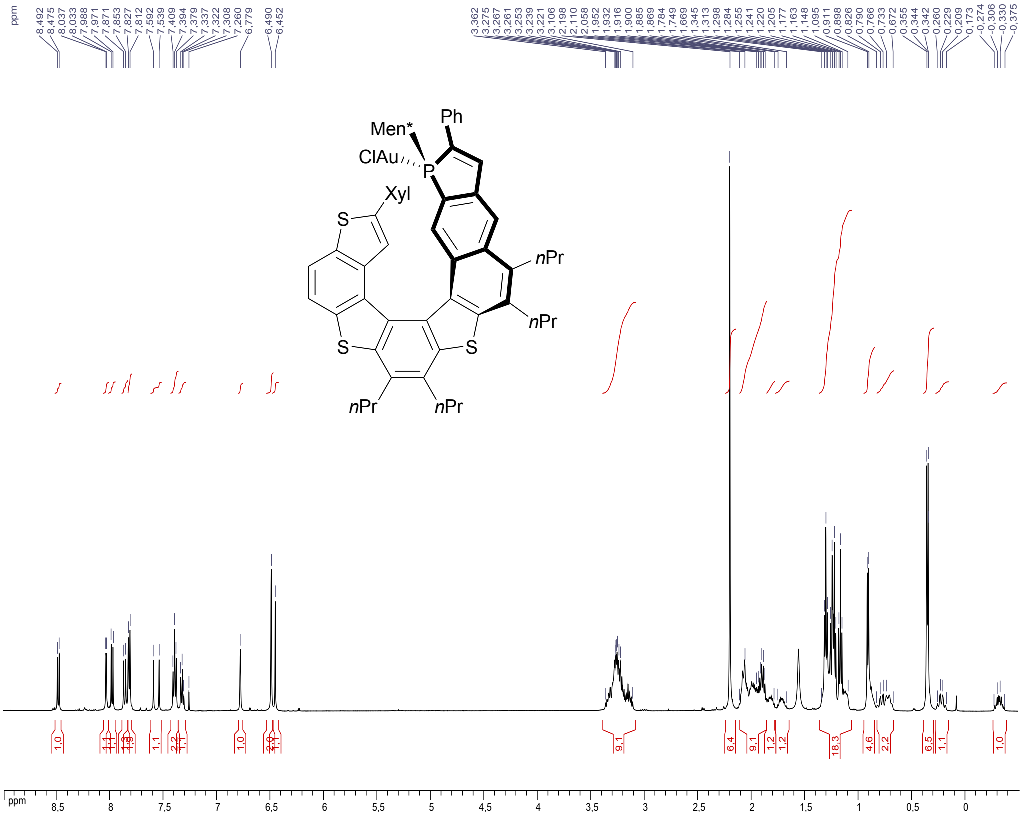
^{31}P NMR (202.5 MHz, CDCl$_3$):



III.7. ^{1}H NMR (300 MHz, CDCl$_3$) (*P*)-12:



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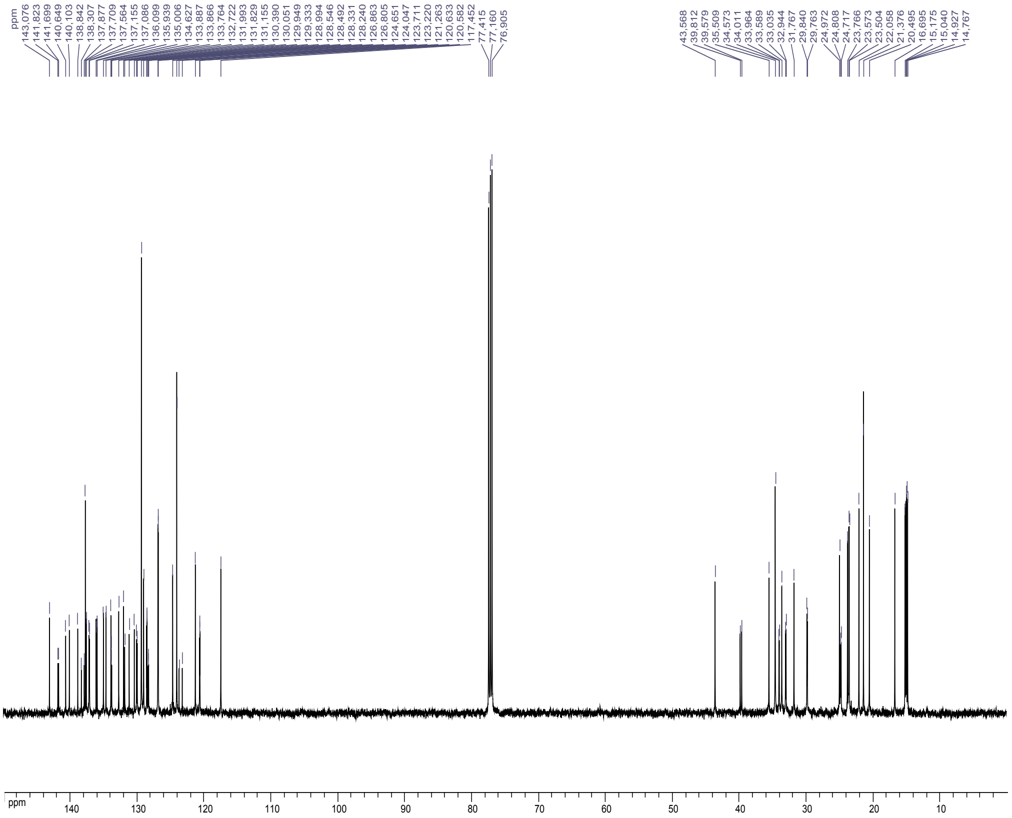
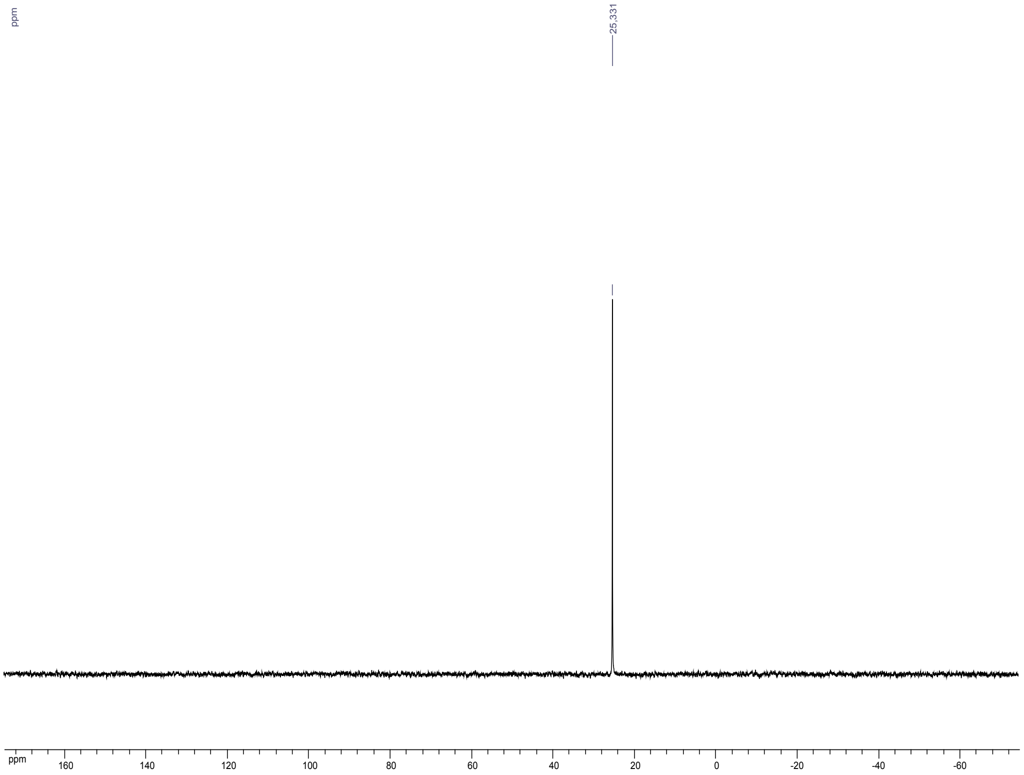
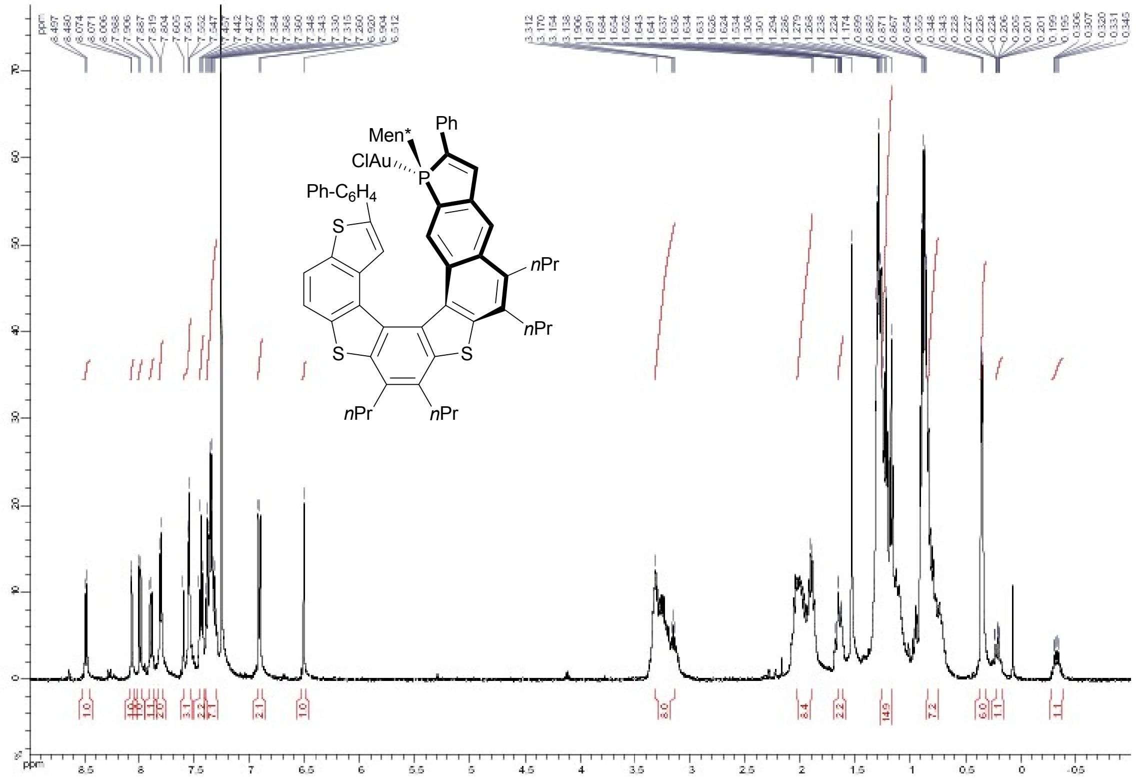
^{13}C NMR (75 MHz, CDCl$_3$):



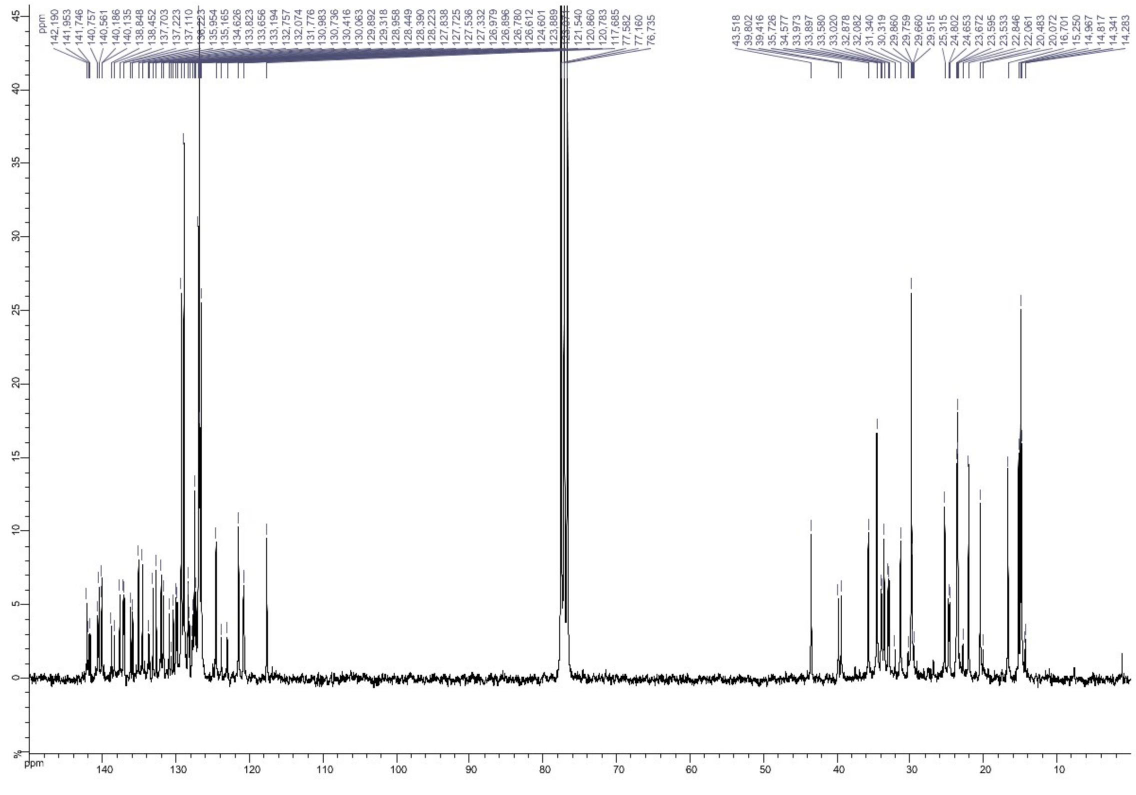
^{31}P NMR (202.5 MHz, $CDCl_3$):



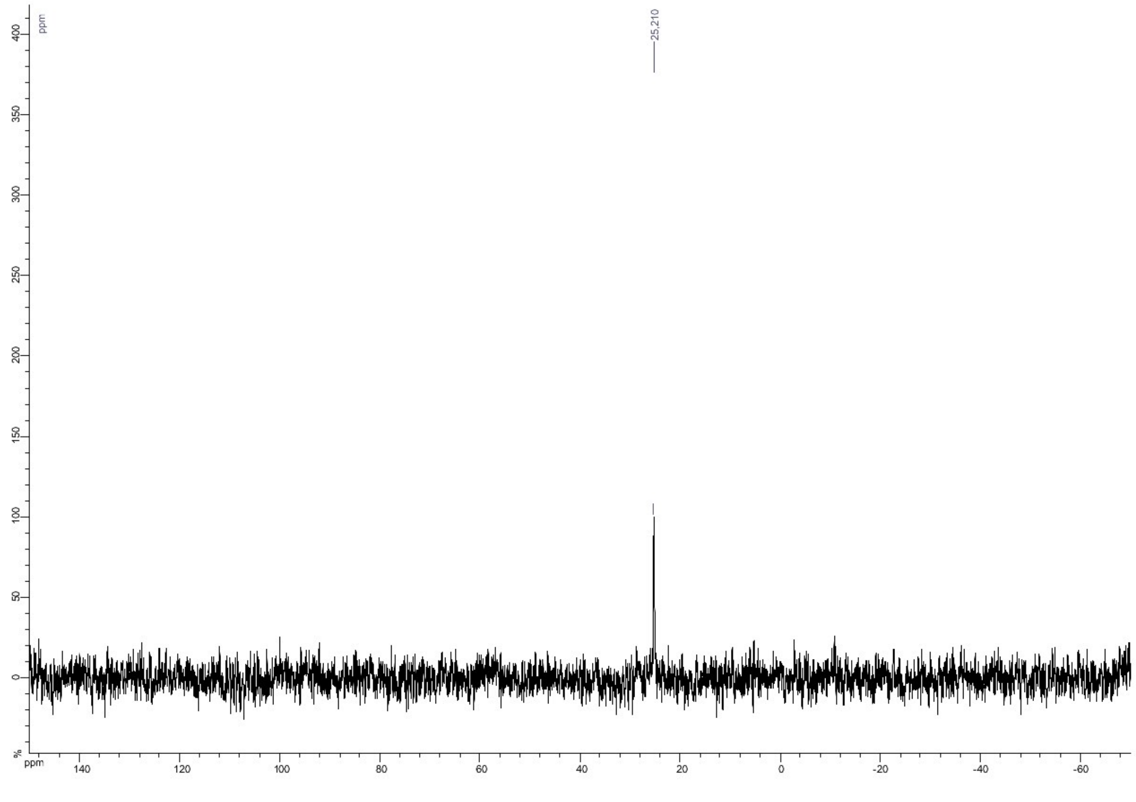
III.8. ^{1}H NMR (500 MHz, $CDCl_3$) (*P*)-13:



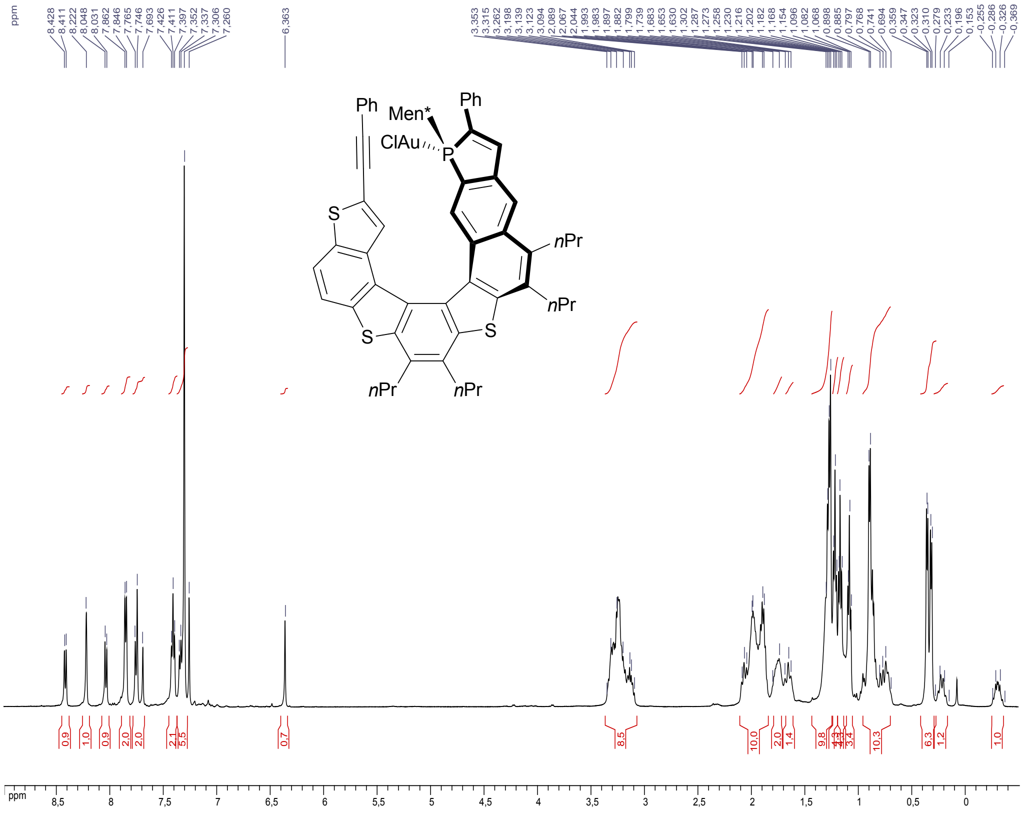
^{13}C NMR (75 MHz, CDCl$_3$):

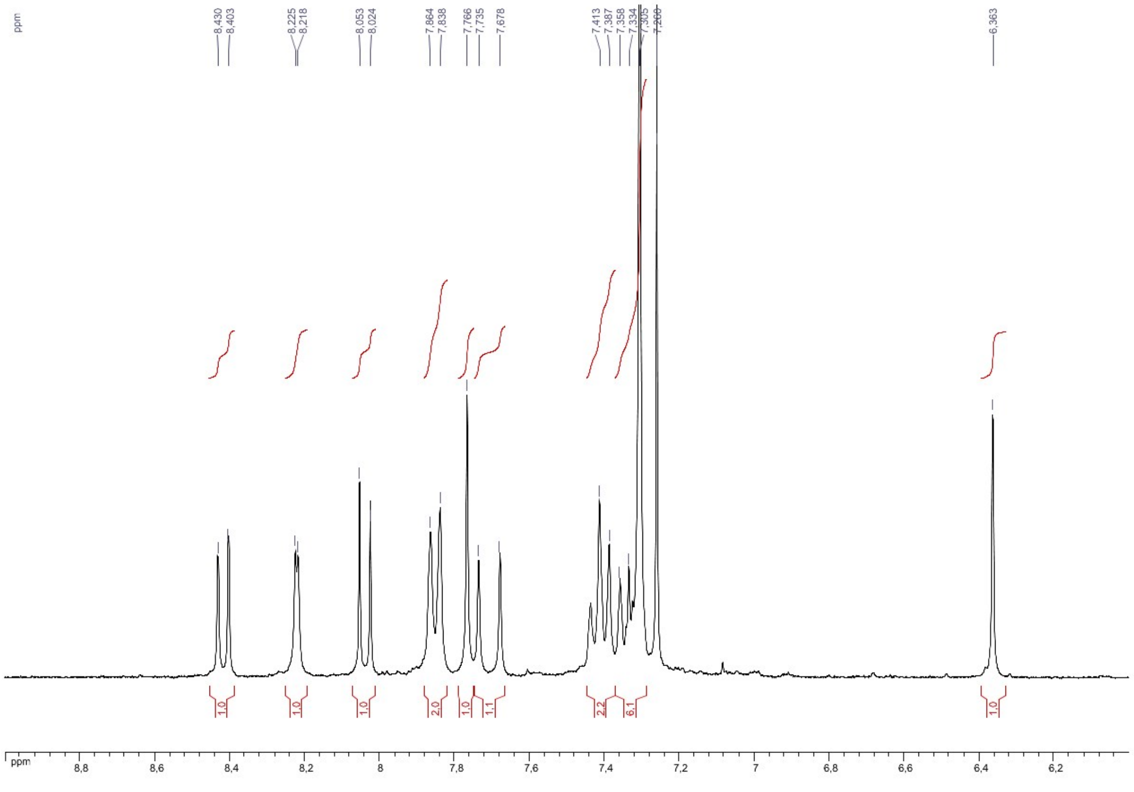


^{31}P NMR (202.5 MHz, CDCl$_3$):

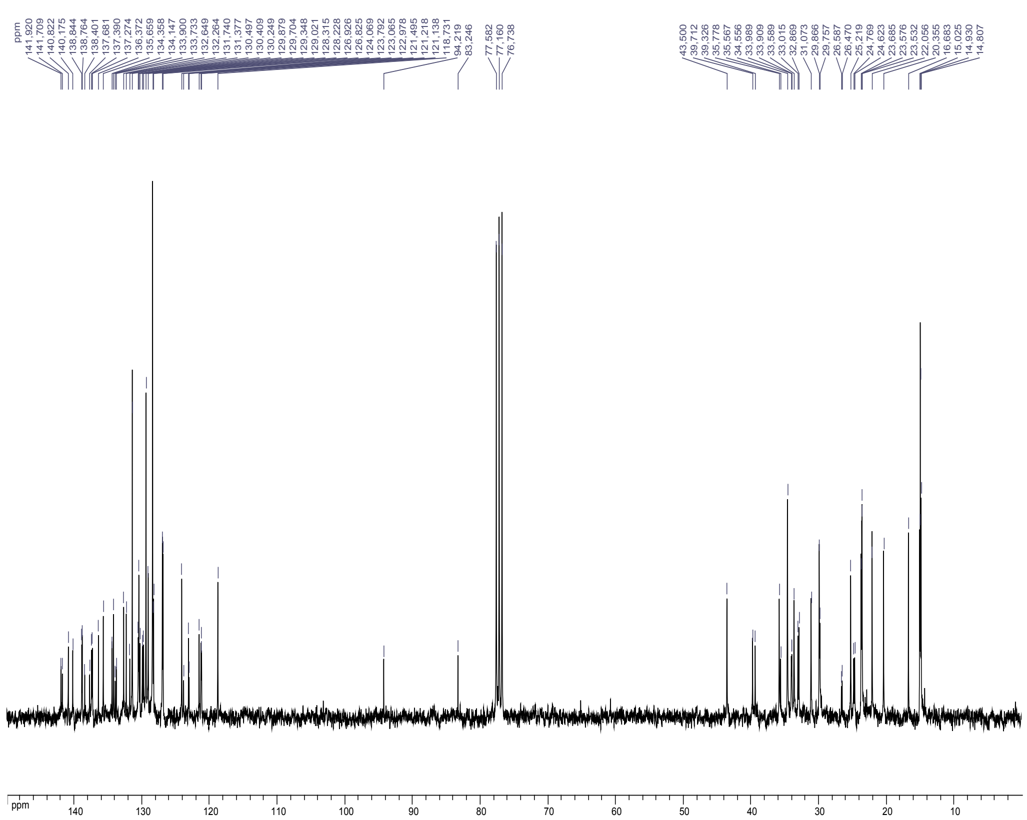


III.8. ^{1}H NMR (300 MHz, CDCl$_3$) (*P*)-14:

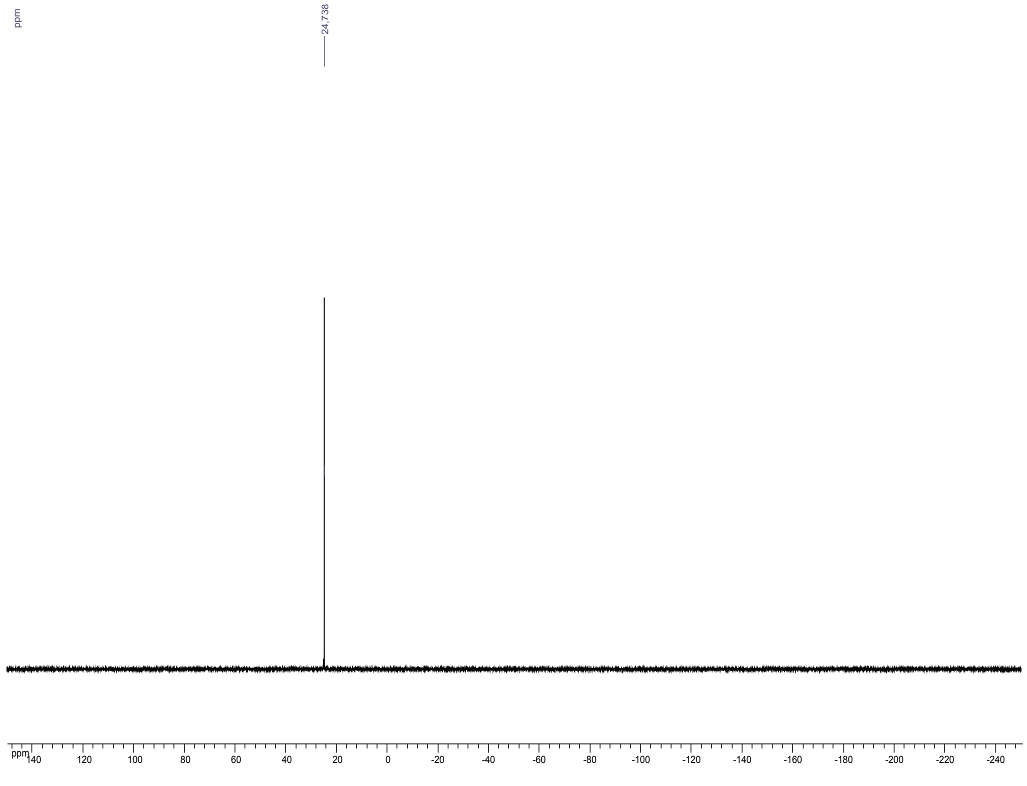




^{13}C NMR (75 MHz, CDCl$_3$):

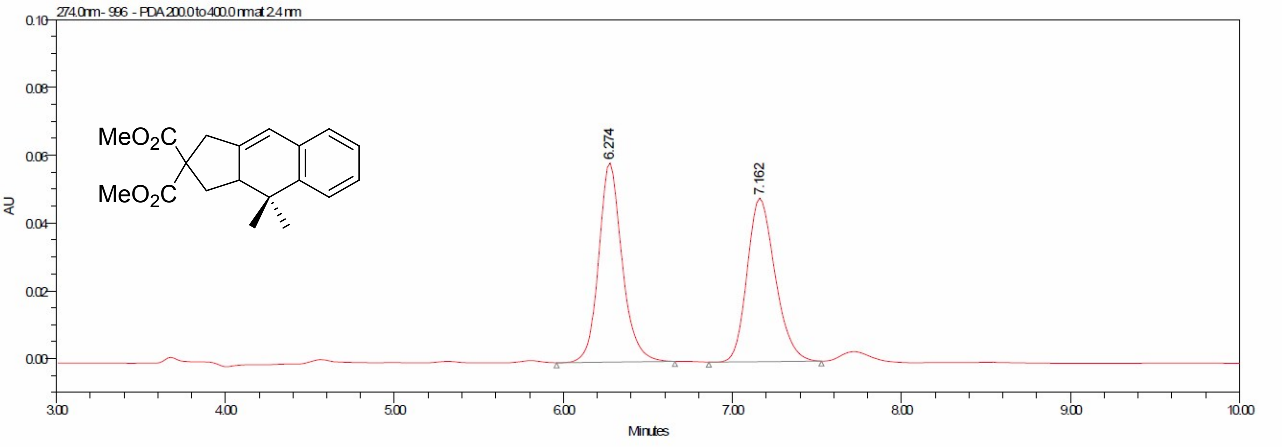


^{31}P NMR (202.5 MHz, CDCl$_3$):

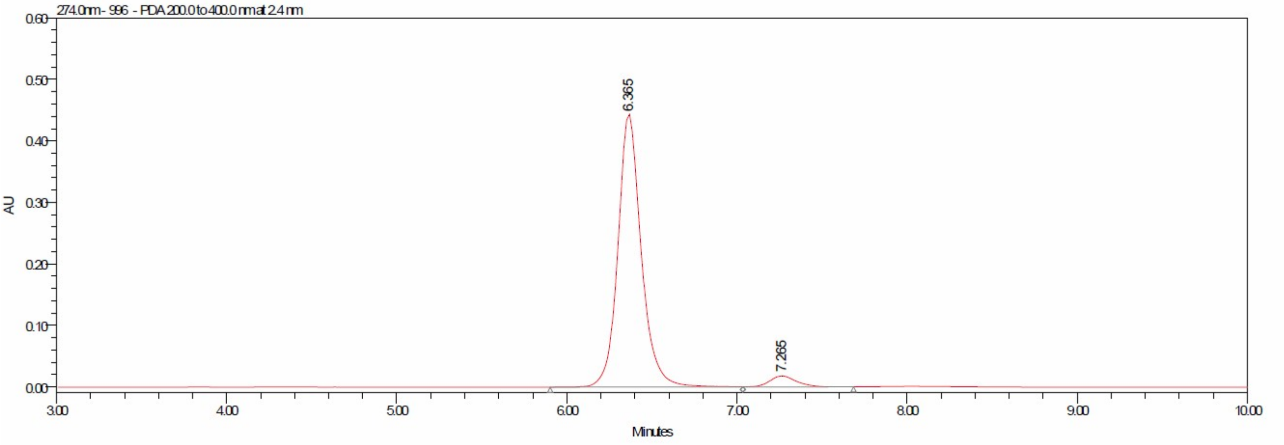


IV. HPLC Data for compound 16.

HPLC Analysis: 91% ee [CHIRALPAK ® IA, 25°C, 2% iPrOH/ *n*-heptane, 1mL/min, 274 nm].



	Channel Description	RT	Area	%Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	6.274	566331	50.46
2	PDA 200.0 to 400.0 nm at 2.4 nm	7.162	556025	49.54



	Channel Description	RT	Area	%Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	6.365	4239465	95.64
2	PDA 200.0 to 400.0 nm at 2.4 nm	7.265	193363	4.36

V. X-Ray crystal structure determination

The crystal structure of compound (*P*)-**11** was solved from an elongated platelet obtained by slow evaporation of a saturated compound solution in chloroform. X-ray crystallographic data were collected[1] at ambient temperature (293(2) K) on a Rigaku MM007 HF copper (λ = 1.54187 Å) rotating-anode diffractometer, equipped with Osmic CMF optics and a Rapid II curved Image Plate. A total of 77 ω–oscillation images were recorded in four sweeps for a 385° angular range in 5.0° steps. The exposure rate was 180.0 sec./°. The crystal-to-detector distance was 127.40 mm and the configuration set-up allowed the measurement of data to a maximum 2θ value of 136.5° even if very little data was obtainable beyond 1.0Å of resolution limits. Out of the 13030 reflections that were collected, 7065 were unique (R_{int} = 0.124). The linear absorption coefficient, μ, for Cu-Kα radiation is 7.334 cm^{-1}. An empirical absorption correction was applied[1] which resulted in transmission factors ranging from 0.20 to 0.60. The data were corrected[1] for Lorentz and polarization effects. The structure was solved using direct methods *(SHELXD-2013)*[2] and all non-hydrogen atoms were refined with anisotropic displacement parameters using *SHELX-L2014* [3] by full-matrix least squares on F^2 values. Most of the hydrogen sp2 atoms were located on difference-Fourier syntheses but all were refined with a riding model and with U_{iso} set to 1.2 times that of the attached C-atom (1.5 times those attached to the methyl C). Probably due to weak (ratio observed /unique reflections < 50%) and poor (large Rint and Rsigma) data quality, rigid-bond restraint (RIGU) were applied with default standard deviation value throughout the entire helical molecule to give idealized anisotropic displacement parameters.

The relative configuration of the helical chirality is given by the l-menthyl fragment and the molecule displays an (*R*)-configured phosphorus and a *P*–configured helical scaffold. Cross-validation was performed by exploiting the anomalous scattering contribution from 2365 Friedel opposites (52% of coverage) kept unmerged during the structure refinement. Flack (1983) parameter,[4] (0.00(2)) using 661 quotients [(I+)-(I-)]/[(I+)+(I-)],[5] and the following indicators provided by the Bayesian analyses as implemented within *PLATON* [6] (*e.g.* Hooft parameter[7] , y = 0.02 (2); 112 out of 123 $\Delta F \geq 1\sigma$ show sign agreement between calculated and observed differences, All of the 32 $\Delta F \geq 2\sigma$; P2(true) and P3(true) = 1.00 (Bayesian statistics)) fully agreed with the configuration of the compound).

CCDC- 1063854 (compound **11**) contains the supplementary crystallographic data for this paper**.** These data can be obtained free of charge on application to the Director, CCDC 12 Union Road, Cambridge CB2 1EZ, UK (fax (+44) 1223-336033; or e-mail deposit@ccdc.cam.ac.uk) or via www.ccdc.cam.ac.uk/data_request/cif

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Figure An ORTEP-3 [8] plot of the compound **11**. Ellipsoids are drawn at the 30% probability level and H atoms are not shown for clarity.

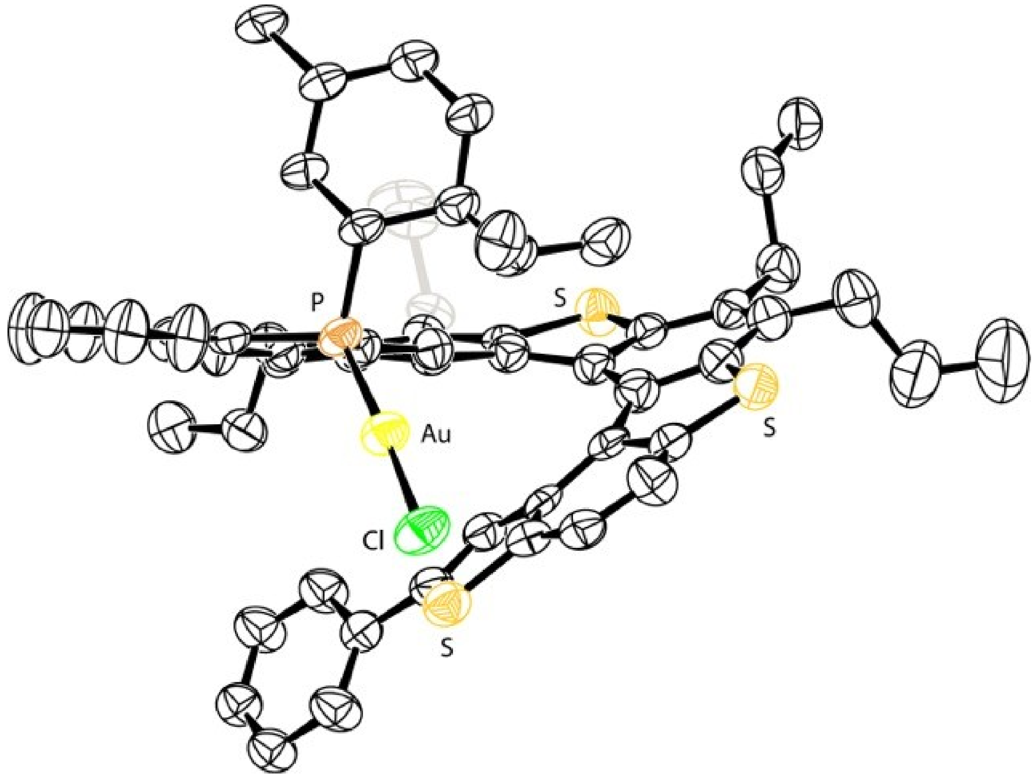

Table 1. Crystal data and structure refinement for **11**.

Identification code	**11**	
Empirical formula	$C_{60} H_{62} Au Cl P S_3$	
Formula weight	1142.66	
Temperature	293(2) K	
Wavelength	1.54187 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 9.8334(14) Å	α= 90°.
	b = 21.319(3) Å	β= 95.590(7)°.
	c = 12.7266(18) Å	γ = 90°.
Volume	2655.3(7) $Å^3$	
Z	2	
Density (calculated)	1.429 Mg/m^3	
Absorption coefficient	7.334 mm^{-1}	
F(000)	1162	
Crystal size	0.370 x 0.140 x 0.07 mm^3	
Theta range for data collection	3.490 to 66.574°.	
Index ranges	$-6 \leq h \leq 11$, $-25 \leq k \leq 24$, $-14 \leq l \leq 15$	
Reflections collected	13030	
Independent reflections	7065 [R(int) = 0.1240]	
Completeness to theta = 66.574°	97.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.60 and 0.20	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7062 / 578 / 601	
Goodness-of-fit on F^2	0.958	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0837, wR2 = 0.1848	
R indices (all data)	R1 = 0.2175, wR2 = 0.2576	
Absolute structure parameter	0.00(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.137 and -1.244 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **11**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	7766(1)	5917(1)	3629(1)	92(1)
Cl(1)	9953(9)	5639(5)	4140(7)	113(4)
S(1)	3715(9)	7063(4)	-2764(7)	91(3)
P(1)	5595(8)	6169(4)	3268(6)	74(3)
C(1)	4340(30)	5602(13)	3670(20)	73(7)
S(2)	9185(10)	7776(4)	-273(7)	93(3)
C(2)	3630(30)	5389(16)	2880(20)	89(10)
S(3)	8779(10)	5083(5)	1399(8)	97(3)
C(3)	3780(30)	5629(13)	1890(20)	68(7)
C(4)	4830(30)	6078(14)	1890(20)	70(7)
C(5)	5070(30)	6360(14)	980(20)	77(8)
C(6)	4310(30)	6207(13)	10(20)	69(7)
C(7)	3130(30)	5810(16)	0(20)	73(7)
C(8)	2970(30)	5499(15)	960(20)	76(8)
C(9)	2220(30)	5746(13)	-940(20)	68(7)
C(10)	2290(30)	6095(15)	-1820(20)	82(8)
C(11)	3500(30)	6497(13)	-1800(20)	61(6)
C(12)	4510(30)	6546(14)	-970(20)	74(7)
C(13)	5670(30)	6920(15)	-1230(20)	77(7)
C(14)	7070(40)	7060(17)	-730(30)	88(8)
C(15)	7610(30)	7639(17)	-1110(30)	90(9)
C(16)	7130(40)	8057(18)	-1860(30)	91(8)
C(17)	5990(30)	7849(16)	-2400(20)	77(7)
C(18)	5310(30)	7300(15)	-2050(20)	71(7)
C(19)	7950(30)	6700(17)	10(20)	70(7)
C(20)	9130(30)	7066(15)	320(20)	81(7)
C(21)	10110(40)	6852(18)	1190(30)	107(11)
C(22)	10040(30)	6249(15)	1600(30)	89(8)
C(23)	8940(30)	5860(20)	1130(20)	82(7)
C(24)	7960(30)	6044(17)	310(20)	73(6)
C(25)	7210(30)	5537(17)	10(30)	82(8)
C(26)	7430(30)	4988(18)	380(30)	82(8)
C(27)	6840(30)	4350(16)	270(20)	74(7)
C(28)	7560(40)	3804(17)	440(30)	106(11)

C(29)	6930(30)	3208(17)	220(30)	91(9)
C(30)	5550(30)	3242(18)	-150(20)	84(9)
C(31)	4820(40)	3753(19)	-290(30)	109(12)
C(32)	5410(30)	4324(17)	-150(30)	93(10)
C(33)	4470(30)	5390(16)	4790(20)	82(9)
C(34)	5440(40)	5579(18)	5600(20)	121(14)
C(35)	5400(40)	5390(20)	6660(30)	117(14)
C(36)	4540(40)	5021(19)	7030(30)	110(13)
C(37)	3610(40)	4850(20)	6260(30)	141(16)
C(38)	3440(40)	4998(17)	5170(30)	110(12)
C(39)	950(30)	5313(14)	-890(20)	81(8)
C(40)	1250(40)	4653(16)	-1300(30)	101(11)
C(41)	0(40)	4261(17)	-1470(30)	125(13)
C(42)	1260(30)	6156(14)	-2770(20)	83(8)
C(43)	60(30)	6582(16)	-2500(30)	97(10)
C(44)	-1080(30)	6543(18)	-3380(30)	122(14)
C(45)	5300(30)	8221(15)	-3370(20)	99(9)
C(46)	4240(30)	8711(15)	-2980(20)	101(11)
C(47)	3460(30)	9086(16)	-3820(30)	111(12)
C(48)	7950(40)	8610(17)	-2100(30)	114(10)
C(49)	8990(50)	8430(20)	-2960(40)	178(19)
C(50)	9580(70)	8910(30)	-3550(50)	300(40)
C(51)	4960(30)	6928(14)	3690(20)	75(6)
C(52)	3390(30)	6923(16)	3660(30)	93(8)
C(53)	2900(30)	7547(17)	4010(30)	107(9)
C(54)	3320(30)	8078(17)	3280(30)	102(9)
C(55)	4870(30)	8095(16)	3360(30)	98(9)
C(56)	5530(30)	7497(16)	3060(30)	87(7)
C(57)	7060(40)	7544(19)	3170(30)	100(8)
C(58)	7690(40)	7670(20)	4290(30)	125(13)
C(59)	7520(30)	8027(17)	2350(30)	112(11)
C(60)	1280(30)	7534(17)	4010(30)	115(12)

Table 3. Bond lengths [Å] and angles [°] for **11**.

Au(1)-P(1)	2.206(8)
Au(1)-Cl(1)	2.264(9)
S(1)-C(11)	1.74(3)
S(1)-C(18)	1.80(3)
P(1)-C(1)	1.83(3)
P(1)-C(51)	1.83(3)
P(1)-C(4)	1.85(3)
C(1)-C(2)	1.25(4)
C(1)-C(33)	1.50(4)
S(2)-C(20)	1.70(3)
S(2)-C(15)	1.82(3)
C(2)-C(3)	1.38(4)
S(3)-C(23)	1.70(4)
S(3)-C(26)	1.78(3)
C(3)-C(8)	1.39(4)
C(3)-C(4)	1.40(3)
C(4)-C(5)	1.35(3)
C(5)-C(6)	1.41(4)
C(6)-C(7)	1.44(4)
C(6)-C(12)	1.46(4)
C(7)-C(8)	1.41(4)
C(7)-C(9)	1.43(3)
C(9)-C(10)	1.35(4)
C(9)-C(39)	1.56(4)
C(10)-C(11)	1.46(4)
C(10)-C(42)	1.51(4)
C(11)-C(12)	1.39(4)
C(12)-C(13)	1.46(4)
C(13)-C(18)	1.34(4)
C(13)-C(14)	1.49(4)
C(14)-C(19)	1.44(4)
C(14)-C(15)	1.45(4)
C(15)-C(16)	1.36(4)
C(16)-C(17)	1.34(4)
C(16)-C(48)	1.47(4)
C(17)-C(18)	1.44(4)
C(17)-C(45)	1.57(4)

C(19)-C(20)	1.42(4)
C(19)-C(24)	1.45(4)
C(20)-C(21)	1.47(4)
C(21)-C(22)	1.39(4)
C(22)-C(23)	1.45(4)
C(23)-C(24)	1.41(4)
C(24)-C(25)	1.34(4)
C(25)-C(26)	1.27(4)
C(26)-C(27)	1.48(4)
C(27)-C(28)	1.36(4)
C(27)-C(32)	1.46(4)
C(28)-C(29)	1.42(4)
C(29)-C(30)	1.40(4)
C(30)-C(31)	1.31(4)
C(31)-C(32)	1.35(4)
C(33)-C(34)	1.39(4)
C(33)-C(38)	1.43(4)
C(34)-C(35)	1.41(4)
C(35)-C(36)	1.28(4)
C(36)-C(37)	1.33(5)
C(37)-C(38)	1.41(4)
C(39)-C(40)	1.54(4)
C(40)-C(41)	1.49(4)
C(42)-C(43)	1.55(4)
C(43)-C(44)	1.50(4)
C(45)-C(46)	1.59(3)
C(46)-C(47)	1.486(12)
C(48)-C(49)	1.61(4)
C(49)-C(50)	1.44(3)
C(51)-C(52)	1.54(4)
C(51)-C(56)	1.59(4)
C(52)-C(53)	1.50(4)
C(53)-C(54)	1.55(4)
C(53)-C(60)	1.60(4)
C(54)-C(55)	1.51(4)
C(55)-C(56)	1.50(4)
C(56)-C(57)	1.51(4)
C(57)-C(58)	1.52(5)
C(57)-C(59)	1.56(4)

P(1)-Au(1)-Cl(1)	175.2(3)
C(11)-S(1)-C(18)	90.0(15)
C(1)-P(1)-C(51)	104.0(12)
C(1)-P(1)-C(4)	88.2(14)
C(51)-P(1)-C(4)	104.4(13)
C(1)-P(1)-Au(1)	116.4(10)
C(51)-P(1)-Au(1)	120.4(10)
C(4)-P(1)-Au(1)	118.0(9)
C(2)-C(1)-C(33)	130(3)
C(2)-C(1)-P(1)	111(3)
C(33)-C(1)-P(1)	118(3)
C(20)-S(2)-C(15)	93.0(17)
C(1)-C(2)-C(3)	120(4)
C(23)-S(3)-C(26)	92.4(17)
C(2)-C(3)-C(8)	127(3)
C(2)-C(3)-C(4)	113(3)
C(8)-C(3)-C(4)	120(3)
C(5)-C(4)-C(3)	120(3)
C(5)-C(4)-P(1)	133(3)
C(3)-C(4)-P(1)	108(2)
C(4)-C(5)-C(6)	122(3)
C(5)-C(6)-C(7)	120(3)
C(5)-C(6)-C(12)	122(3)
C(7)-C(6)-C(12)	117(3)
C(8)-C(7)-C(9)	125(3)
C(8)-C(7)-C(6)	115(3)
C(9)-C(7)-C(6)	120(3)
C(3)-C(8)-C(7)	123(3)
C(10)-C(9)-C(7)	124(3)
C(10)-C(9)-C(39)	117(3)
C(7)-C(9)-C(39)	118(3)
C(9)-C(10)-C(11)	115(3)
C(9)-C(10)-C(42)	129(3)
C(11)-C(10)-C(42)	116(3)
C(12)-C(11)-C(10)	125(3)
C(12)-C(11)-S(1)	111(2)
C(10)-C(11)-S(1)	123(2)
C(11)-C(12)-C(13)	112(3)

C(11)-C(12)-C(6)	118(3)
C(13)-C(12)-C(6)	130(3)
C(18)-C(13)-C(12)	111(3)
C(18)-C(13)-C(14)	112(3)
C(12)-C(13)-C(14)	136(3)
C(19)-C(14)-C(15)	117(3)
C(19)-C(14)-C(13)	131(3)
C(15)-C(14)-C(13)	112(3)
C(16)-C(15)-C(14)	133(4)
C(16)-C(15)-S(2)	121(3)
C(14)-C(15)-S(2)	105(2)
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C(17)-C(16)-C(48)	127(3)
C(15)-C(16)-C(48)	121(3)
C(16)-C(17)-C(18)	120(3)
C(16)-C(17)-C(45)	121(3)
C(18)-C(17)-C(45)	119(3)
C(13)-C(18)-C(17)	130(3)
C(13)-C(18)-S(1)	112(3)
C(17)-C(18)-S(1)	119(2)
C(20)-C(19)-C(14)	108(3)
C(20)-C(19)-C(24)	118(3)
C(14)-C(19)-C(24)	132(3)
C(19)-C(20)-C(21)	120(3)
C(19)-C(20)-S(2)	115(3)
C(21)-C(20)-S(2)	124(3)
C(22)-C(21)-C(20)	121(3)
C(21)-C(22)-C(23)	116(3)
C(24)-C(23)-C(22)	125(4)
C(24)-C(23)-S(3)	111(3)
C(22)-C(23)-S(3)	124(3)
C(25)-C(24)-C(23)	108(3)
C(25)-C(24)-C(19)	136(3)
C(23)-C(24)-C(19)	117(3)
C(26)-C(25)-C(24)	125(4)
C(25)-C(26)-C(27)	140(4)
C(25)-C(26)-S(3)	105(3)
C(27)-C(26)-S(3)	115(2)
C(28)-C(27)-C(32)	119(3)

C(28)-C(27)-C(26)	126(3)
C(32)-C(27)-C(26)	115(3)
C(27)-C(28)-C(29)	122(3)
C(30)-C(29)-C(28)	114(3)
C(31)-C(30)-C(29)	127(4)
C(30)-C(31)-C(32)	120(4)
C(31)-C(32)-C(27)	118(3)
C(34)-C(33)-C(38)	112(3)
C(34)-C(33)-C(1)	128(3)
C(38)-C(33)-C(1)	120(3)
C(33)-C(34)-C(35)	123(3)
C(36)-C(35)-C(34)	128(4)
C(35)-C(36)-C(37)	109(4)
C(36)-C(37)-C(38)	132(4)
C(37)-C(38)-C(33)	116(3)
C(40)-C(39)-C(9)	110(2)
C(41)-C(40)-C(39)	112(3)
C(10)-C(42)-C(43)	110(2)
C(44)-C(43)-C(42)	109(3)
C(17)-C(45)-C(46)	109(2)
C(47)-C(46)-C(45)	115(3)
C(16)-C(48)-C(49)	110(3)
C(50)-C(49)-C(48)	120(4)
C(52)-C(51)-C(56)	113(3)
C(52)-C(51)-P(1)	111(2)
C(56)-C(51)-P(1)	112(2)
C(53)-C(52)-C(51)	110(3)
C(52)-C(53)-C(54)	111(3)
C(52)-C(53)-C(60)	110(3)
C(54)-C(53)-C(60)	110(3)
C(55)-C(54)-C(53)	108(3)
C(56)-C(55)-C(54)	115(3)
C(55)-C(56)-C(57)	112(3)
C(55)-C(56)-C(51)	110(3)
C(57)-C(56)-C(51)	114(3)
C(56)-C(57)-C(58)	114(3)
C(56)-C(57)-C(59)	109(3)
C(58)-C(57)-C(59)	113(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **11**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Au(1)	80(1)	105(1)	91(1)	2(1)	9(1)	13(1)
Cl(1)	72(6)	154(11)	113(6)	3(6)	2(5)	25(6)
S(1)	92(6)	94(7)	84(5)	17(5)	-2(5)	1(5)
P(1)	52(5)	91(7)	78(4)	4(4)	8(4)	13(4)
C(1)	69(13)	74(13)	79(8)	-4(8)	18(7)	21(10)
S(2)	90(6)	96(7)	94(6)	3(5)	13(5)	-2(5)
C(2)	96(17)	99(18)	74(9)	5(9)	18(9)	-18(15)
S(3)	80(7)	107(7)	105(6)	5(5)	12(5)	10(6)
C(3)	56(14)	76(15)	74(8)	5(8)	17(8)	15(11)
C(4)	58(12)	79(15)	75(7)	9(7)	12(7)	11(10)
C(5)	81(15)	77(16)	74(8)	8(8)	12(8)	3(13)
C(6)	71(12)	71(15)	65(8)	1(8)	16(7)	16(11)
C(7)	66(11)	76(16)	78(8)	2(9)	14(8)	16(11)
C(8)	59(14)	89(16)	80(9)	4(9)	15(8)	12(12)
C(9)	63(11)	59(14)	84(9)	-2(8)	12(8)	22(10)
C(10)	79(11)	79(16)	88(10)	9(10)	5(8)	8(10)
C(11)	67(10)	59(12)	59(9)	-4(8)	13(7)	22(9)
C(12)	77(11)	79(15)	67(9)	4(9)	11(8)	11(10)
C(13)	80(9)	86(14)	67(11)	5(10)	15(8)	8(9)
C(14)	82(10)	93(12)	90(15)	4(11)	8(9)	7(8)
C(15)	89(12)	92(13)	90(14)	2(11)	11(11)	2(9)
C(16)	93(12)	93(13)	88(13)	3(10)	9(10)	3(10)
C(17)	88(12)	83(12)	61(12)	0(9)	21(9)	7(9)
C(18)	71(11)	79(12)	64(11)	-1(9)	16(8)	13(9)
C(19)	65(12)	87(10)	63(13)	-10(8)	28(9)	15(8)
C(20)	72(12)	92(11)	81(13)	-4(9)	20(10)	10(9)
C(21)	98(16)	101(14)	117(18)	9(12)	-15(15)	0(12)
C(22)	72(14)	98(13)	97(16)	-1(10)	10(12)	17(10)
C(23)	68(13)	91(10)	91(13)	-8(9)	20(10)	18(9)
C(24)	57(13)	91(10)	76(12)	-6(8)	37(9)	12(8)
C(25)	67(15)	88(11)	91(15)	0(9)	17(12)	12(9)
C(26)	73(14)	87(11)	86(15)	2(9)	11(12)	12(9)
C(27)	71(13)	90(11)	60(15)	11(9)	3(11)	11(9)

C(28)	84(16)	87(13)	140(30)	6(12)	-17(15)	11(11)
C(29)	84(17)	86(14)	100(20)	7(12)	-11(15)	11(12)
C(30)	80(17)	91(16)	80(20)	9(14)	-3(15)	11(12)
C(31)	79(15)	89(16)	150(30)	10(15)	-18(15)	9(11)
C(32)	76(14)	90(16)	110(20)	10(13)	-15(13)	11(11)
C(33)	70(17)	96(19)	78(9)	5(9)	4(9)	1(14)
C(34)	106(19)	180(30)	74(11)	24(13)	-4(11)	-50(20)
C(35)	110(20)	170(30)	75(12)	25(13)	-8(13)	-30(20)
C(36)	110(30)	130(30)	82(14)	18(14)	7(13)	-20(20)
C(37)	140(20)	190(30)	89(13)	31(16)	-3(13)	-50(30)
C(38)	90(19)	150(30)	87(13)	19(14)	-1(12)	-29(19)
C(39)	68(13)	81(14)	91(17)	16(12)	-3(11)	6(11)
C(40)	90(20)	76(16)	130(30)	0(14)	13(18)	2(13)
C(41)	120(20)	100(20)	150(30)	-10(20)	20(20)	-20(17)
C(42)	85(13)	70(20)	90(12)	1(11)	-3(10)	13(11)
C(43)	96(16)	90(20)	100(19)	-12(16)	-10(13)	32(16)
C(44)	97(18)	150(30)	110(20)	-20(20)	-20(16)	54(19)
C(45)	106(18)	103(18)	87(13)	23(12)	10(12)	0(14)
C(46)	90(20)	90(20)	120(20)	15(15)	11(16)	-10(16)
C(47)	90(20)	110(20)	130(20)	30(20)	8(19)	-7(19)
C(48)	120(20)	112(16)	110(20)	26(13)	-11(15)	-18(14)
C(49)	180(30)	190(30)	180(40)	0(30)	70(30)	-40(30)
C(50)	390(90)	240(50)	300(70)	20(40)	190(80)	-80(40)
C(51)	59(11)	96(10)	71(13)	3(8)	5(9)	24(8)
C(52)	61(11)	97(14)	120(20)	10(12)	15(11)	27(10)
C(53)	70(13)	104(15)	150(20)	7(13)	34(14)	24(11)
C(54)	77(13)	101(16)	130(20)	0(14)	18(13)	18(11)
C(55)	74(13)	106(13)	120(20)	11(12)	22(13)	21(11)
C(56)	71(11)	100(12)	91(16)	8(10)	12(11)	19(9)
C(57)	68(12)	119(19)	114(17)	3(14)	11(11)	19(11)
C(58)	80(20)	170(30)	118(17)	11(16)	-5(14)	-20(20)
C(59)	80(20)	140(20)	120(20)	12(17)	15(15)	16(18)
C(60)	68(13)	110(20)	180(30)	0(20)	33(15)	31(13)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **11**.

	x	y	z	U(eq)
H(2)	3005	5070	2961	107
H(5)	5757	6661	986	92
H(8)	2302	5193	972	91
H(21)	10795	7124	1474	128
H(22)	10669	6103	2141	107
H(25)	6477	5591	-503	98
H(28)	8471	3821	696	127
H(29)	7406	2831	316	109
H(30)	5113	2864	-322	101
H(31)	3880	3723	-476	131
H(32)	4921	4689	-330	111
H(34)	6142	5843	5438	145
H(35)	6080	5548	7139	140
H(36)	4560	4897	7733	132
H(37)	2958	4571	6469	169
H(38)	2699	4852	4729	132
H(39A)	715	5284	-172	97
H(39B)	175	5492	-1321	97
H(40A)	1654	4690	-1968	121
H(40B)	1910	4447	-803	121
H(41A)	-571	4411	-2071	187
H(41B)	-497	4287	-853	187
H(41C)	246	3833	-1580	187
H(42A)	911	5745	-2987	99
H(42B)	1691	6337	-3355	99
H(43A)	-272	6446	-1846	117
H(43B)	367	7012	-2417	117
H(44A)	-1181	6942	-3731	183
H(44B)	-1915	6435	-3095	183
H(44C)	-864	6228	-3878	183
H(45A)	4829	7933	-3876	118
H(45B)	5991	8441	-3726	118
H(46A)	3590	8484	-2591	122

H(46B)	4732	8997	-2483	122
H(47A)	3684	8944	-4495	167
H(47B)	3704	9521	-3729	167
H(47C)	2501	9036	-3768	167
H(48A)	8465	8758	-1457	137
H(48B)	7350	8945	-2372	137
H(49A)	9732	8191	-2593	214
H(49B)	8505	8144	-3462	214
H(50A)	9365	9331	-3435	356
H(50B)	10176	8809	-4045	356
H(51)	5312	6982	4428	91
H(52A)	2992	6836	2948	112
H(52B)	3108	6596	4121	112
H(53)	3312	7629	4733	128
H(54A)	2960	7998	2560	122
H(54B)	2971	8477	3501	122
H(55A)	5146	8430	2916	117
H(55B)	5204	8196	4085	117
H(56)	5241	7427	2307	105
H(57)	7408	7135	2967	120
H(58A)	7679	8112	4425	187
H(58B)	8615	7520	4366	187
H(58C)	7170	7455	4778	187
H(59A)	8489	7990	2315	168
H(59B)	7313	8443	2575	168
H(59C)	7048	7944	1674	168
H(60A)	862	7689	3349	173
H(60B)	1012	7794	4574	173
H(60C)	981	7111	4114	173