Supporting information for:

A catalytic approach towards chiral P,N-chelate complexes utilizing the asymmetric hydrophosphination protocol

Dávid Katona, Yunpeng Lu, Yongxin Li, Sumod A. Pullarkat*, and Pak-Hing Leung*

Division of Chemistry & Biological Chemistry, School of Physical & Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

Email: sumod@ntu.edu.sg;
pakhing@ntu.edu.sg

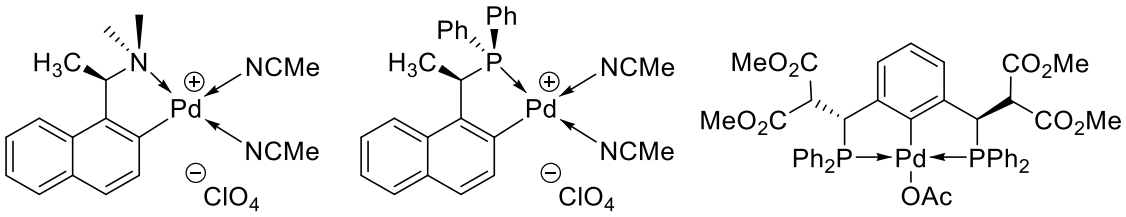
Table of Contents

1. General Information

For preparing and handling air-sensitive phosphines and complexes, positive nitrogen and argon flow was used (standard Schlenk-techniques). Solvents were degassed previously for all reactions and measurements when it was necessary. Reagents for carrying out synthetic steps were purchased for Sigma Aldrich, TCI, Strem, Alfa Aesar, Acros Organics. Purifications by flash column chromatography were carried out on Merck Silica Gel 60.

For the NMR data Bruker AV500 (^{1}H 500.1 MHz, ^{13}C 125.7 MHz, ^{19}F 470.6 MHz, ^{31}P 202.4 MHz), Bruker AV400 and BBFO 400 (^{1}H 400.1 MHz, ^{13}C 100.6 MHz, ^{19}F 376.5 MHz, ^{31}P 162.0 MHz) instruments were used for the characterization of new compounds and the coordination study. Chemical shifts were reported in ppm by using internal standard TMS for ^{1}H NMR measurements, $CDCl_3$ for ^{13}C NMR measurements, external standard H_3PO_4 for ^{31}P NMR-measurements and $CFCl_3$ for ^{19}F NMR-measurements. HRMS data was recorded on Waters Q-TOF Premier spectrometer by using ESI positive mode. Elemental Analysis was carried out on PerkinElmer CHNS/O Series II 2400 EA instrument. The determination of ee was performed on Agilent 1200 Series chromatograph with Daicel Chiralpack ID and IF columns in *n*-hexane-isopropanol solvent system. Optical rotation measurements were performed on Jasco P-1030 polarimeter using the D-lines of sodium (589 nm) as light source.

(*R*)-**1**, (*S*)-**2** and (*R*,*R*)-**7** complexes were prepared as described in literature[1].

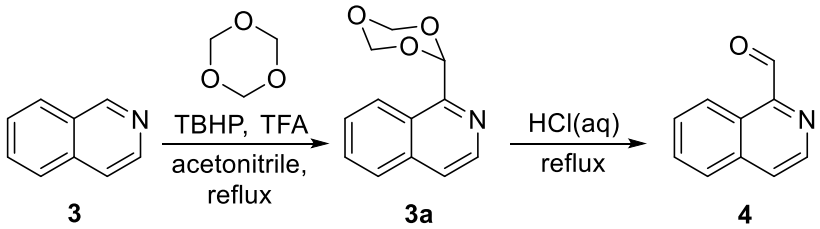


(*R*)-**1** (*R*)-**2** (*R*,*R*)-**7**

Caution! *Perchlorate salts of metal complexes are dangerous as being potentially explosive compounds. Those chemicals must be handled with care.*

2. Experimental section

Preparation of isoquinoline-1-carbaldehyde (4)[2]



3 **3a** **4**

Isoquinoline (5.4 mmol, 0.70 g, 1.0 equiv.) was dissolved in 35 ml acetonitrile, then trioxane (488.6 mmol, 44.01 g, 90.0 equiv.), *tert*-butyl hydroperoxide (11.13 mmol, 1.02 g, 2.1 equiv.), trifluoroacetic acid (5.4 mmol, 0.62 g, 1.0 equiv.) and iron(II)sulfate (0.27 mmol, 0.04 g, 0.05 equiv.) were added and the solution was refluxed overnight. After the reaction was complete (monitored by TLC), volatiles were removed by evaporation, saturated sodium bicarbonate solution was poured on the residue and extracted with diethyl ether. The organic layer was then washed with brine, dried and evaporated.

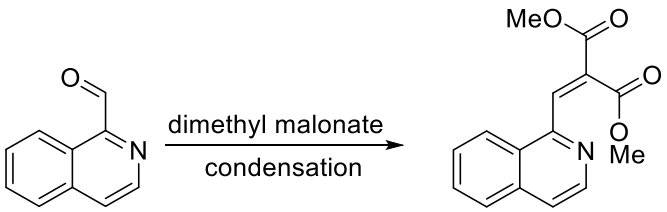
The isolated crude acetal was refluxed at 110 °C in 20 m/m% HCl solution for one hour and neutralized at 0 °C with sodium carbonate. The aqueous solution was extracted with dichloromethane, the organic layer was washed with brine, dried and evaporated. The obtained

crude material was purified with flash column chromatography on silica gel (*n*-hexane/ethyl acetate 2:1 to 1:1) to collect the pure product.

4 red-brown solid. Yield: 49%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.40 (s, 1H, C*H*O), 9.32 (dd, $^3J_{HH}$ = 8.4, 4.3 Hz, 1H, Ar*H*), 8.76 (d, $^3J_{HH}$ = 5.5 Hz, 1H, Ar*H*), 7.97 – 7.84 (m, 2H, Ar*H*), 7.83 – 7.75 (m, 2H, Ar*H*); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.68 (s, 1C, *C*HO), 149.85 (s), 142.47 (s), 136.91 (s), 130.79 (s), 130.06 (s), 126.96 (s), 126.36 (s), 125.75 (s), 125.52 (s). **HRMS** (+ESI) m/z: $(M + H)^+$ calc'd for $C_{10}H_8NO$, 158.0606; found, 158.0608. **Anal**. Calc'd for $C_{10}H_7NO$: C, 76.42; H, 4.49; N, 8.91. Found: C, 75.76; H, 4.77; N, 8.73%.

Preparation of dimethyl 2-(isoquinolin-1-ylmethylene)malonate (5a)[3]



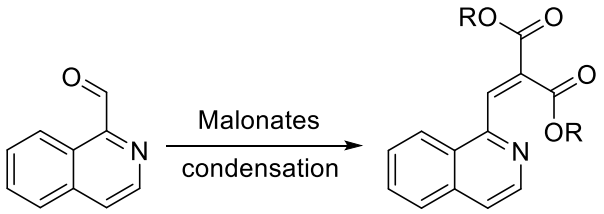
4 **5a**

4 carbadehyde (5.60 mmol, 0.89 g, 1.0 equiv.) and dimethyl malonate (6.52 mmol, 0.86 g, 1.15 equiv.) were dissolved in 40.0 ml benzene and heated to reflux temperature. *N*-methyl piperidine (0.85 mmol, 0.08 g, 0.15 equiv.) and benzoic acid (0.42 mmol, 0.05 g, 0.075 equiv.) were dissolved in 10.0 ml benzene and added to the boiling solution of the starting material and the malonate. The solution was refluxed overnight with the use of Dean-Stark apparatus and 4 Å molecular sieve. After the reaction was complete, saturated aqueous sodium bicarbonate was added to the solution and extracted with DCM. The combined organic layer was washed with brine, dried and evaporated. The residue was purified with column chromatography on silica gel (*n*-hexane/ethyl acetate 4:1 to 2:1) to afford the pure diester.

5a yellow-brown solid. Yield: 52%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (s, 1H, Ar*H*), 8.55 (d, $^3J_{H\text{-}H}$ = 5.5 Hz, 1H, Ar*H*), 8.31 (d, $^3J_{H\text{-}H}$ = 8.4 Hz, 1H, Ar*H*), 7.87 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 1H, C=C*H*Ar), 7.78 – 7.60 (m, 3H, Ar*H*), 3.92 (s, 3H, COOCH_3), 3.90 (s, 3H, COOCH_3); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.22 (s, 1C, *C*=O), 164.43 (s, 1C, *C*=O), 150.11 (s, 1C, N=*C*-CH), 142.40 (s), 136.54 (s), 136.11 (s), 130.39 (s), 130.30 (s), 128.23 (s), 127.78 (s), 127.53 (s), 123.89 (s), 122.49 (s), 52.92 (s, 1C, COO*C*H_3), 52.45 (s, 1C, COO*C*H_3). **HRMS** (+ESI) m/z: $(M + H)^+$ calc'd for $C_{15}H_{14}NO_4$, 272.0923; found, 272.0923. **Anal.** Calc'd for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.16. Found: C, 66.15; H, 4.15; N, 5.16%.

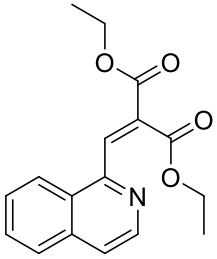
General procedure for the preparation of diethyl, diisopropyl and dibenzyl 2-(isoquinolin-1-ylmethylene)malonates (5b, 5c, 5d)[4]



4 **5b** R=Et
5c R=^{i}Pr
5d R=Bn

$TiCl_4$ (2.0 mmol, 2.1 equiv.) was dissolved in 1.5 ml CCl_4 and this solution was added dropwise to 12 ml THF at 0 °C. Upon the yellow adduct appeared, **4** carbaldehyde (0.95 mmol, 1.0 equiv.) and the corresponding malonate (0.95 mmol, 1.0 equiv.) were dissolved in 2.0 ml THF and added to the $TiCl_4$ solution dropwise. THF solution of pyridine (16.0 mmol, 16.6 equiv.) was also added to the reaction mixture, which then was stirred under nitrogen at 0 °C for 1 hour and further at rt until the reaction was complete. Upon completion the reaction mixture was quenched with 10.0 ml H_2O, then 20.0 ml ethyl acetate and Na_2CO_3(aq.) were added (to adjust the pH to neutral), and the solution was extracted with ethyl acetate. The organic layer was further washed with $NaHCO_3$ and brine, then dried and evaporated. The resulting diester was the purified with column chromatography on silica gel (*n*-hexane/ethyl acetate 5:1 to 1:1) to obtain the pure product.

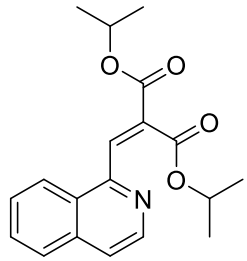
Diethyl 2-(isoquinolin-1-ylmethylene)malonate (5b)



5b is a brown oil. Yield: 29%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, $^{3}J_{H\text{-}H}$ = 5.6 Hz, 1H, Ar*H*), 8.52 (s, 1H, Ar*H*), 8.28 (d, $^{3}J_{H\text{-}H}$ = 8.5 Hz, 1H, Ar*H*), 7.85 (d, $^{3}J_{H\text{-}H}$ = 8.0 Hz, 1H, C=C*H*Ar), 7.74 – 7.62 (m, 3H, Ar*H*), 4.39 (q, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 2H, OC*H*$_2$CH$_3$), 4.37 (q, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 2H, OC*H*$_2$CH$_3$), 4.22 (q, $^{3}J_{H\text{-}H}$ = 7.15 Hz, 1H), 1.38 (t, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 3H, OCH$_2$C*H*$_3$), 1.31 (t, $^{3}J_{H\text{-}H}$ = 7.15 Hz, 3H, OCH$_2$C*H*$_3$), 1.24 (t, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.57 (1C, *C*=O), 164.05 (1C, *C*=O), 150.44 (1C, N=*C*-CH), 142.21 (s), 136.47 (s), 135.52 (s), 131.17 (s), 130.32 (s), 128.12 (s), 127.68 (s), 127.48 (s), 123.99 (s), 122.29 (s), 61.90 (1C, COO*C*H$_2$CH$_3$), 61.34 (1C, COO*C*H$_2$CH$_3$), 14.16 (1C, COOCH$_2$*C*H$_3$), 14.03 (1C, COOCH$_2$*C*H$_3$). **HRMS** (+ESI) m/z: (M + H)$^{+}$ calc'd for $C_{17}H_{18}NO_4$, 300.1236; found, 300.1236.

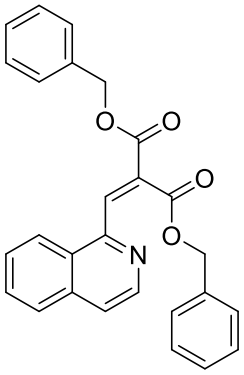
Diisopropyl 2-(isoquinolin-1-ylmethylene)malonate (5c)



5c is a brown oil. Yield: 38%

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, $^{3}J_{H\text{-}H}$ = 5.6 Hz, 1H, Ar*H*), 8.47 (s, 1H, Ar*H*), 8.29 (d, $^{3}J_{H\text{-}H}$ = 8.5 Hz, 1H, Ar*H*), 7.85 (d, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 1H, Ar*H*), 7.76 – 7.63 (m, 3H, Ar*H*), 5.32 (hept, $^{3}J_{H\text{-}H}$ = 6.3 Hz, 1H, COOC*H*$(CH_3)_2$), 5.22 (hept, $^{3}J_{H\text{-}H}$ = 6.2 Hz, 1H, COOC*H*$(CH_3)_2$), 1.36 (d, $^{3}J_{H\text{-}H}$ = 6.3 Hz, 6H, COOCH(C*H*$_3)_2$), 1.32 (d, $^{3}J_{H\text{-}H}$ = 6.2 Hz, 6H, COOCH(C*H*$_3)_2$), 1.28 – 1.20 (m, 1H), 1.16 (d, $^{3}J_{H\text{-}H}$ = 6.3 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.00 (s, 1C, *C*=O), 163.60 (s, 1C, *C*=O), 150.66 (s, 1C, N=*C*-CH), 142.05 (s), 136.44 (s), 134.92 (s), 131.97 (s), 130.27 (s), 128.04 (s), 127.63 (s), 127.45 (s), 124.09 (s), 122.16 (s), 69.59 (s), 69.54 (s, 1C, COO*C*H$(CH_3)_2$), 68.77 (s), 68.69 (s, 1C, COO*C*H$(CH_3)_2$), 21.78 (s, 2C, COOCH(*C*H$_3)_2$), 21.61 (s, 2C, COOCH(*C*H$_3)_2$). **HRMS** (+ESI) m/z: $(M + H)^+$ calc'd for $C_{19}H_{22}NO_4$, 328.1549; found, 328.1548.

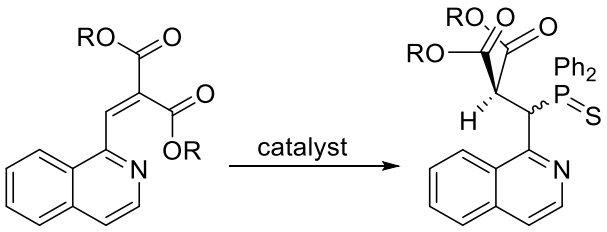
Dibenzyl 2-(isoquinolin-1-ylmethylene)malonate (5d)



5d is a brown solid. Yield: 22%

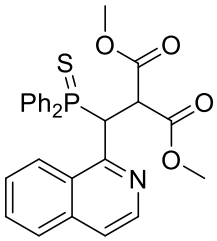
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (s, 1H, Ar*H*), 8.33 (d, $^{3}J_{H\text{-}H}$ = 5.5 Hz, 1H, Ar*H*), 8.26 (d, $^{3}J_{H\text{-}H}$ = 8.4 Hz, 1H, Ar*H*), 7.84 (d, $^{3}J_{H\text{-}H}$ = 8.1 Hz, 1H, C=C*H*Ar), 7.74 – 7.58 (m, 3H, Ar*H*), 7.42 – 7.33 (m, 5H, Ar*H*), 7.33 – 7.26 (m, 6H, Ar*H*), 5.35 (s, 2H, benzyl CH_2), 5.34 (s, 2H, benzyl CH_2). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.44 (s, 1C, *C*=O), 163.82 (s, 1C, *C*=O), 150.07 (s, 1C, N=*C*-CH), 142.29 (s), 136.48 (s), 136.35 (s), 135.59 (s), 135.49 (s), 130.43 (s), 130.35 (s), 128.66 (s), 128.63 (s), 128.50 (s), 128.44 (s), 128.31 (s), 128.20 (s), 128.17 (s), 128.14 (s), 128.05 (s), 128.00 (s), 127.71 (s), 127.51 (s), 127.25 (s), 123.90 (s), 122.42 (s), 67.38 (s, 1C, benzyl *C*H_2), 67.22 (s, 1C, benzyl *C*H_2). **HRMS** (+ESI) m/z: $(M + H)^+$ calc'd for $C_{27}H_{22}NO_4$, 424.1549; found, 424.1549.

General procedure for catalytic hydrophosphination on dialkyl and diaralkyl 2-((diphenylphosphorothioyl)(isoquinolin-1-ylmethylene)malonates (optimization of conditions; 6a, 6b and 6c)[5]



Diphenylphosphine (0.05 mmol, 9.31 mg, 1.0 equiv.) was weighed into a Schlenk flask under positive N_2 flow and 2.0 ml previously degassed solvent was added. Malonate substrate (0.05 mmol, 1.0 equiv.) and the catalyst (0.0025 mmol, 0.05 equiv.) were added to the solution and then the required temperature was adjusted. Upon the required temperature was reached, base (0.05 mmol, 1.0 equiv.) was added dropwise to the reaction mixture. The reaction was monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy. Upon completion of the reaction excess sulfur was added and the mixture was allowed to warm up and the volatiles were evaporated. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate 5:1 to 2:1) to obtain the pure sulfurized phosphine product.

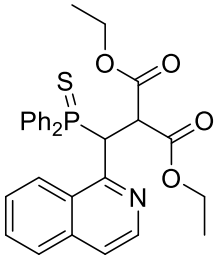
Dimethyl 2-((diphenylphosphorothioyl)(isoquinolin-1-yl)methyl)malonate (6a)



6a is a pale yellow solid. Yield: 86%

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, $^{3}J_{H\text{-}H}$ = 5.6 Hz, 1H, Ar*H*), 8.11 (dd, $^{3}J_{H\text{-}H}$ = 11.6, 7.0 Hz, 2H, Ar*H*), 8.02 (d, $^{3}J_{H\text{-}H}$ = 8.3 Hz, 1H, Ar*H*), 7.57 (d, $^{3}J_{H\text{-}H}$ = 8.1 Hz, 1H, Ar*H*), 7.51 – 7.37 (m, 7H, Ar*H*), 7.35 (d, $^{3}J_{H\text{-}H}$ = 5.0 Hz, 1H, Ar*H*), 7.04 (t, $^{3}J_{H\text{-}H}$ = 6.7 Hz, 1H, Ar*H*), 6.91 (m, 2H, Ar*H*), 5.83 (t, $^{3}J_{H\text{-}H}$, $^{3}J_{H\text{-}P}$ = 10.2 Hz, 1H, C*H*CH(PPh_2)Ar), 5.28 (t, $^{3}J_{H\text{-}H}$, $^{2}J_{H\text{-}P}$ = 10.7 Hz, 1H, CHC*H*(PPh_2)Ar), 3.37 (s, 3H, COOCH_3), 3.36 (s, 3H, COOCH_3). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.46 – 168.11 (m, 2C, *C*=O), 155.43 (d, $^{2}J_{P\text{-}C}$ = 6.6 Hz, 1C, Ar, N=*C*-C(H)P), 141.29 (d, $J_{P\text{-}C}$ = 3.0 Hz, 1C), 135.90, 132.46 (d, $^{1}J_{P\text{-}C}$ = 9.7 Hz, 1C, Ar, P-C_6H_5), 131.93 (d, $^{1}J_{P\text{-}C}$ = 10.1 Hz, 1C, Ar, P-C_6H_5), 131.61 (s), 131.10 (s), 130.96 (s), 130.86 (s), 130.48 (s), 130.31 (s), 129.53 (s), 128.21 (d, $J_{P\text{-}C}$ = 12.0 Hz), 128.00 (s), 127.40 (s), 127.31 (s), 127.17 (s), 127.14 (s), 124.50 (s), 120.13 (s), 54.40 (d, $^{2}J_{P\text{-}C}$ = 3.0 Hz, 1C, *C*HCH(PPh_2)Ar), 52.63 (s, 2C, COO*C*H_3), 44.84 (d, $^{1}J_{P\text{-}C}$ = 47.3 Hz, 1C, CH*C*H(PPh_2)Ar). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$) δ 48.73 (s). **HRMS** (+ESI) m/z: $(M + H)^+$ calc'd for $C_{27}H_{25}NO_4PS$, 490.1242; found, 490.1240. Anal. Calc'd for $C_{27}H_{24}NO_4PS$: C, 66.25; H, 4.94; N, 2.86. Found: 65.73; H, 4.80; N, 2.99%.

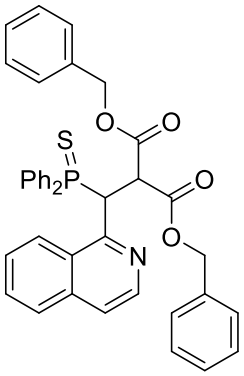
Diethyl 2-((diphenylphosphorothioyl)(isoquinolin-1-yl)methyl)malonate (6b)



6b is a yellow solid. Yield: 58%

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, $^{3}J_{H\text{-}H}$ = 5.6 Hz, 1H, Ar*H*), 8.10 (dd, $^{3}J_{H\text{-}H}$ = 12.1, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 2H, Ar*H*), 8.05 (d, $^{3}J_{H\text{-}H}$ = 8.4 Hz, 1H, Ar*H*), 7.57 (d, $^{3}J_{H\text{-}H}$ = 8.0 Hz, 1H, Ar*H*), 7.53 – 7.36 (m, 7H, Ar*H*), 7.34 (d, $^{3}J_{H\text{-}H}$ = 5.2 Hz, 1H, Ar*H*), 7.05 (t, $^{3}J_{H\text{-}H}$ = 7.0 Hz, 1H, Ar*H*), 6.94 (d, $^{3}J_{H\text{-}H}$ = 5.2 Hz, 2H, Ar*H*), 5.85 (t, $^{3}J_{H\text{-}H}$, $^{3}J_{H\text{-}P}$ = 10.3 Hz, 1H C*H*CH(PPh_2)Ar), 5.22 (t, $^{3}J_{H\text{-}H}$, $^{2}J_{H\text{-}P}$ = 10.8 Hz, 1H, CHC*H*(PPh_2)Ar), 3.95 – 3.63 (m, 4H, COOC$H_2$$CH_3$), 1.10 (t, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 3H, $COOCH_2CH_3$), 0.76 (t, $^{3}J_{H\text{-}H}$ = 7.0 Hz, 3H, $COOCH_2CH_3$). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.79 – 167.08 (m, 2C, *C*=O), 155.79 (d, $^{2}J_{P\text{-}C}$ = 6.0 Hz, 1C, Ar, N=*C*-C(H)P), 141.31 (d, $J_{P\text{-}C}$ = 2.9 Hz), 135.86 (s), 132.45 (d, $^{1}J_{P\text{-}C}$ = 9.7 Hz, 1C, Ar, P-C_6H_5,), 132.03 (d, $^{1}J_{P\text{-}C}$ = 10.0 Hz, 1C, Ar, P-C_6H_5,), 131.50 (s), 130.78 (s), 129.49 (s), 128.11 (d, $J_{P\text{-}C}$ = 12.1 Hz), 127.34 (d, $J_{P\text{-}C}$ = 12.2 Hz), 124.63 (s), 119.96 (s), 61.82 (s, 1C, COO*C*$H_2$$CH_3$), 61.41 (s, 1C, COO*C*$H_2$$CH_3$), 54.93 (d, $^{2}J_{P\text{-}C}$ = 2.8 Hz, 1C, *C*HCH(PPh_2)Ar), 44.80 (d, $^{1}J_{P\text{-}C}$ = 47.3 Hz, 1C, CH*C*H(PPh_2)Ar), 13.71 (s, 1C, $COOCH_2CH_3$), 13.65 (s, 1C, $COOCH_2CH_3$). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$) δ 48.81 (s). **HRMS** (+ESI) m/z: $(M + H)^+$ calc'd for $C_{29}H_{29}NO_4PS$, 518.1555; found, 518.1555.

Dibenzyl 2-((diphenylphosphorothioyl)(isoquinolin-1-yl)methyl)malonate (6c)



6c is a yellow solid. Yield: 64%

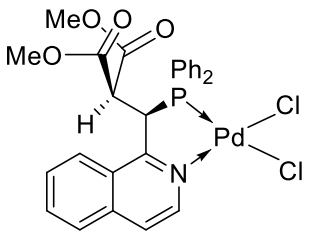
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, $^{3}J_{H\text{-}H}$ = 5.6 Hz, 1H, Ar*H*), 8.05 (dd, $^{3}J_{H\text{-}H}$ = 12.2, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 2H, Ar*H*), 7.97 (d, $^{3}J_{H\text{-}H}$ = 8.3 Hz, 1H, Ar*H*), 7.58 – 7.27 (m, 14H, Ar*H*), 7.25 – 7.19 (m, 2H, Ar*H*), 7.15 (t, $^{3}J_{H\text{-}H}$ = 7.4 Hz, 1H, Ar*H*), 7.07 (t, $^{3}J_{H\text{-}H}$ = 7.5 Hz, 2H, Ar*H*), 7.05 (s, 1H, Ar*H*), 6.92 (m, 2H, Ar*H*), 6.83 (d, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 2H, Ar*H*), 5.87 (t, $^{3}J_{H\text{-}H}$, $^{3}J_{H\text{-}P}$ = 10.4 Hz, 1H, C*H*CH(PPh_2)Ar), 5.39 (t, $^{3}J_{H\text{-}H}$, $^{2}J_{H\text{-}P}$ = 10.7 Hz, 1H, CHC*H*(PPh_2)Ar), 4.85 – 4.77 (m, 2H, benzyl CH_2), 4.72 (s, 2H, benzyl CH_2). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.79 – 167.08 (m, 2C, *C*=O), 155.46 (d, $^{2}J_{P\text{-}C}$ = 6.2 Hz, 1C, Ar, N=*C*-C(H)P), 141.27 (d, $J_{P\text{-}C}$ = 3.0 Hz), 135.87 (s), 135.29 (s), 134.86 (s), 132.42 (d, $^{1}J_{P\text{-}C}$ = 9.4 Hz 1C, Ar, P-C_6H_5), 132.08 (d, $^{1}J_{P\text{-}C}$ = 9.9 Hz, 1C, Ar, P-C_6H_5,), 131.48 (d, $J_{P\text{-}C}$ = 2.8 Hz), 130.80 (s), 130.32 (s), 129.46 (s), 128.35 (s), 128.19 (s), 128.07 (s), 127.99 (s), 127.94 (s), 127.90 (s), 127.87 (s), 127.36 (d, $J_{P\text{-}C}$ = 12.4 Hz), 127.09 (s), 124.58 (s), 120.03 (s), 67.30 (s, 1C, benzyl *C*H_2), 67.12 (s, 1C, benzyl *C*H_2), 54.89 (d, $^{2}J_{P\text{-}C}$ = 3.0 Hz, 1C, *C*HCH(PPh_2)Ar), 45.15 (d, $^{1}J_{P\text{-}C}$

= 45.7 Hz, 1C, CH*C*H(PPh$_2$)Ar). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$) δ 48.66 (s). **HRMS** (+ESI) m/z: $(M + H)^+$ calc'd for $C_{39}H_{33}NO_4PS$, 642.1868; found, 642.1865.

General procedure for generating dichloro P,N palladium and platinum complexes ((*R*)-9 and (*R*)-10)

Diphenylphosphine (0.17 mmol, 0.032 g, 1.0 equiv.) was weighed into a Schlenk flask under positive N_2 flow and 7.0 ml previously degassed DCM was added. Substrate **5a** (0.17 mmol, 0.046 g, 1.0 equiv.) and (*S*)-**2** catalyst (0.0085 mmol, 0.005 g, 0.05 equiv.) were added to the solution and then the mixture was cooled down to -80 °C. Upon the required temperature was reached, triethylamine (0.17 mmol, 0.017 g, 1.0 equiv.) was added dropwise to the reaction mixture. After the reaction reached the desired conversion, TEA and the solvent was removed by using nitrogen flow and vacuum while the low temperature was permanently maintained. The residue was then triturated four times with degassed hexane to remove excess diphenylphosphine. The crude material was redissolved in DCM and filtered through a short celite plug under Schlenk conditions. $MCl_2(MeCN)_2$ (0.17 mmol, 1.0 equiv.) was then added to the free P,N ligand **8** at -80 °C, stirred for an hour and allowed to rt. Each of the resulting air-stable complex was filtered through short celite plug and recrystallized from DCM with diethyl ether to afford enantiopure crystals.

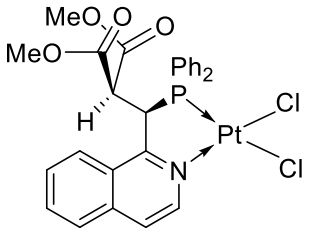
(*R*)-(κ^2-P,N)-(dimethyl 2-((diphenylphosphaneyl)(isoquinolin-1-yl)methyl)malonate)-dichloropalladium(II) ((*R*)-9)



9 is a yellow solid. Yield: 85%. $[\alpha]^{25}_D$ = -479 (*c* 1.0 , CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.79 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 1H, Ar*H*, HC=C*H*-N), 8.29 (d, $^3J_{H\text{-}H}$ = 8.6 Hz, 1H, Ar*H*), 8.02 – 7.86 (m, 7H, Ar*H*), 7.81 – 7.70 (m, 2H, Ar*H*), 7.59 (t, $^3J_{H\text{-}H}$ = 6.9 Hz, 2H, Ar*H*), 7.53 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H, Ar*H*), 7.48 (td, $^3J_{H\text{-}P}$ = 7.7 Hz, $^3J_{H\text{-}H}$ = 2.7 Hz, 2H, P-C$_6$*H*$_5$), 7.43 (td, $^3J_{H\text{-}P}$ = 7.7 Hz, $^3J_{H\text{-}H}$ = 2.5 Hz, 2H, P-C$_6$*H*$_5$), 5.89 (dd, $^3J_{P\text{-}H}$ = 14.8 Hz, $^3J_{H\text{-}H}$ = 9.4 Hz, 1H, C*H*CH(PPh$_2$)Ar), 4.49 (dd, $^2J_{P\text{-}H}$ = 15.6 Hz, $^3J_{H\text{-}H}$ = 9.4 Hz, 1H, CHC*H*(PPh$_2$)Ar), 3.30 (s, 3H, COOC*H*$_3$), 3.25 (s), 2.76 (s), 2.73 (s, 3H, COOC*H*$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.89 (s, 1C, Ar, HC=*C*H-N), 166.17 (d, $^3J_{P\text{-}C}$ = 12.0 Hz, 1C, *C*=O), 161.97 (d, $^3J_{P\text{-}C}$ = 8.1 Hz, 1C, *C*=O), 145.40 (s), 136.54 (s), 136.29 (d, $^2J_{P\text{-}C}$ = 11.3 Hz, 1C, Ar, N=*C*-C(H)P), 133.44 (s), 133.10 (d, $J_{P\text{-}C}$ = 2.8 Hz), 132.74 (d, $J_{P\text{-}C}$ = 2.9 Hz), 132.61 (d, $^1J_{P\text{-}C}$ = 10.5 Hz, 1C, Ar, P-*C*$_6$H$_5$), 129.93 (s), 129.71 (d, $^1J_{P\text{-}C}$ = 11.4 Hz, 1C, Ar, P-*C*$_6$H$_5$), 128.62 (d, $J_{P\text{-}C}$ = 12.1 Hz), 126.71 (d, $J_{P\text{-}C}$ = 10.6 Hz), 125.04 (d, $J_{P\text{-}C}$ = 53.6 Hz), 123.27 (s), 122.60 (d, $J_{P\text{-}C}$ = 56.0 Hz), 53.22 (s, 1C, COO*C*H$_3$), 53.17 (d, $^2J_{P\text{-}C}$ = 5.3 Hz, 1C, *C*HCH(PPh$_2$)Ar), 52.71 (s, 1C, COO*C*H$_3$), 47.08 (d, $^1J_{P\text{-}C}$ = 30.4 Hz, 1C, CH*C*H(PPh$_2$)Ar), 30.93 (s), 29.69 (s). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$) δ 52.13 (s). **HRMS** (+ESI) m/z: $(M + H)^+$ calc'd for

$C_{27}H_{25}Cl_2NO_4PPd$, 635.9937; found, 635.9931. **Anal**. Calc'd for $C_{27}H_{24}Cl_2NO_4PPd$: C, 51.09; H, 3.81; N, 2.21. Found: C, 48.51; H, 3.61; N, 2.03%.

(*R*)-(κ^2-P,N)-(dimethyl 2-((diphenylphosphaneyl)(isoquinolin-1-yl)methyl)malonate)-dichloroplatinum(II) ((*R*)-10)

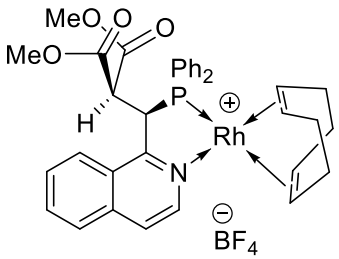


10 is a light brown solid. Yield: 67%. $[\alpha]^{25}_D$ = -43 (*c* 0.5, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.03 (d, $^3J_{H\text{-}H}$ = 6.7 Hz, 1H, Ar*H*, HC=C*H*-N), 8.30 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 1H, Ar*H*), 8.08 – 7.94 (m, 5H, Ar*H*), 7.93 (s, Ar*H*), 7.91 (s, 1H, Ar*H*), 7.90 (s, 1H, Ar*H*), 7.73 (m, 1H, Ar*H*), 7.69 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 1H, Ar*H*), 7.57 (m, 2H, Ar*H*), 7.53 – 7.41 (m, 6H, Ar*H*), 5.83 (dd, $^3J_{P\text{-}H}$ = 12.3, $^3J_{H\text{-}H}$ = 9.9 Hz, 1H, C*H*CH(PPh$_2$)Ar), 4.52 (dd, $^2J_{P\text{-}H}$ = 14.7, $^3J_{H\text{-}H}$ = 9.9 Hz, 1H, CHC*H*(PPh$_2$)Ar), 3.30 (s), 3.27 (s, 3H, COOC*H*$_3$), 2.74 (s), 2.69 (s, 3H, COOC*H*$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.98 (s, 1C, Ar, HC=*C*H-N), 166.34 (d, $^3J_{P\text{-}C}$ = 12.2 Hz, 1C, *C*=O), 162.84 (d, $^3J_{P\text{-}C}$ = 5.7 Hz, 1C, *C*=O), 144.38 (s), 141.96 (s), 139.29 (s), 136.26 (d, $^2J_{P\text{-}C}$ = 11.7 Hz, 1C, Ar, N=*C*-C(H)P), 135.95 (s), 133.18 (s), 132.94 (s), 132.66 (d, $^1J_{P\text{-}C}$ = 10.9 Hz, 1C, Ar, P-*C*$_6$H$_5$), 132.45 (s), 130.16 (s), 129.50 (d, $^1J_{P\text{-}C}$ = 11.5 Hz, 1C, Ar, P-*C*$_6$H$_5$), 128.51 (d, $J_{P\text{-}C}$ = 12.4 Hz), 127.56 (d, $J_{P\text{-}C}$ = 48.2 Hz), 126.99 (d, $J_{P\text{-}C}$ = 8.7 Hz), 124.60 (d, $J_{P\text{-}C}$ = 62.1 Hz), 123.34 (s), 120.84 (d, $J_{P\text{-}C}$ = 63.8 Hz), 53.14 (s, 1C, COO*C*H$_3$), 52.56 (s, 1C, COO*C*H$_3$), 52.12 (d, $^2J_{P\text{-}C}$ = 4.3 Hz, 1C, *C*HCH(PPh$_2$)Ar), 46.23 (d, $^1J_{P\text{-}C}$ = 37.1 Hz, 1C, CH*C*H(PPh$_2$)Ar), 33.82 (s), 31.93 (s), 29.70 (s), 29.36 (s), 22.69 (s), 14.12 (s). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$) δ 28.71 (s), 28.72 (d, $^1J_{Pt\text{-}P}$ = 3826.9 Hz). **HRMS** (+ESI) m/z: $(M + H)^+$ calc'd for $C_{27}H_{25}Cl_2NO_4PPt$, 723.0546; found, 723.0544. **Anal**. Calc'd for $C_{27}H_{24}Cl_2NO_4PPt$: C, 44.83; H, 3.34; N, 1.94. Found: C, 44.67; H, 3.45; N, 2.10%.

General procedure for synthesizing P,N rhodium and iridium COD tetrafluoroborate complexes (13 and 14)[6]

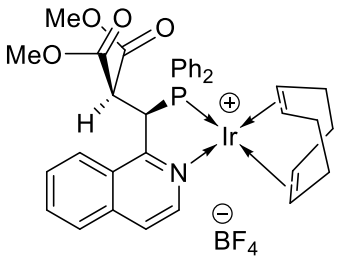
[M(COD)Cl]$_2$ (0.04 mmol, 0.5 equiv.) was dissolved in 5.0 ml degassed DCM and stirred under nitrogen. $AgBF_4$ (0.08 mmol, 1.0 equiv.) was dissolved in degassed methanol and this was added to the DCM solution. This mixture was stirred at rt in the dark for 3 hrs.
The resulting $M^+(COD)\ ^-BF_4$ complex was filtered through a short celite plug under nitrogen and immediately added to the DCM solution of **8** P,N ligand (0.08 mmol, 1.0 equiv) (obtained in the aforementioned way) at -80 °C, stirred for an hour under nitrogen and allowed to rt. The forming $(P,N)M^+(COD)\ ^-BF_4$ complex was filtered through a short celite plug under Schlenk conditions and the solvent was removed by vacuum.

[(κ^2-P,N)-(dimethyl 2-((diphenylphosphaneyl)(isoquinolin-1-yl)methyl)malonate)][(1,2,5,6- η)(1Z,5Z)-cycloocta-1,5-diene]-rhodium(I) tetrafluoroborate (13)



13 is a brown solid. Yield: 99.6 % (crude). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (d, $^3J_{H\text{-}H}$ = 8.7 Hz, 1H, Ar*H*), 8.07 (d, $^3J_{H\text{-}H}$ = 6.5 Hz, 1H, Ar*H*), 7.96 (t, $^3J_{H\text{-}H}$ = 9.1 Hz, 1H, Ar*H*), 7.89 (d, $^3J_{H\text{-}H}$ = 6.4 Hz, 1H, Ar*H*), 7.86 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 1H, Ar*H*), 7.77 (d, $^3J_{H\text{-}H}$ = 7.3 Hz, 1H, Ar*H*), 7.74-7.69 (m, 3H, Ar*H*), 7.68 – 7.63 (m, 1H, Ar*H*), 7.55 – 7.49 (m, 1H, Ar*H*), 7.48 – 7.38 (m, 5H, Ar*H*), 7.33 – 7.27 (m, 3H, Ar*H*), 5.88 (dd, $^3J_{P\text{-}H}$ = 13.2 Hz, $^3J_{H\text{-}H}$ = 8.1 Hz, 1H, C*H*CH(PPh$_2$)Ar), 5.67 (dd, $^3J_{H\text{-}H}$ = 15.1 Hz, $^2J_{Rh\text{-}H}$ = 1.4 Hz, 2H, COD *H*C=CH), 4.65 (dd, $^2J_{P\text{-}H}$ = 15.0 Hz, $^3J_{H\text{-}H}$ = 8.1 Hz, 1H, CHC*H*(PPh$_2$)Ar), 4.38 (d, $^3J_{H\text{-}H}$ = 55.1 Hz, $^2J_{Rh\text{-}H}$ = 5.5 Hz, 2H, COD *H*C=CH), 3.70 – 3.60 (m), 3.46 (s, 3H, COOC*H*$_3$), 3.24 – 3.14 (m, 1H), 2.81 (s, 3H, COOC*H*$_3$), 2.74 – 2.53 (m, 2H, COD C*H*$_2$), 2.37 (m, 3H, COD C*H*$_2$), 2.10 – 1.99 (m, 2H, COD C*H*$_2$). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.26 (s, 1C, Ar, HC=*C*H-N), 166.16 (d, $^3J_{P\text{-}C}$ = 9.4 Hz, 1C, *C*=O), 162.56 (d, $^3J_{P\text{-}C}$ = 9.3 Hz, 1C, *C*=O), 142.02 (s), 136.68 (s), 133.84 – 133.40 (m), 133.55 (d, $^2J_{P\text{-}C}$ = 10.8 Hz, 1C, Ar, N=*C*-C(H)P), 133.16 (d, $^1J_{P\text{-}C}$ = 10.8 Hz, 1C, Ar, P-*C*$_6$H$_5$) 132.51 (d, $J_{P\text{-}C}$ = 2.4 Hz), 132.33 (d, $J_{P\text{-}C}$ = 2.1 Hz), 130.07 (s), 129.63 (dd, $^2J_{Rh\text{-}C}$ = 20.9 Hz, $^1J_{P\text{-}C}$ = 10.3 Hz, 1C, Ar, P-*C*$_6$H$_5$), 128.01 (s), 128.00 (s), 127.68 (s), 127.09 (s), 127.02 (s), 126.97 (s), 124.62 (d, $J_{P\text{-}C}$ = 2.2 Hz), 124.45 (s), 124.32 (d, $J_{P\text{-}C}$ = 2.7 Hz), 114.05 (s), 109.30 – 108.82 (m, 1C, COD, H*C*=CH), 107.50 (d, *J* = 7.8 Hz), 106.60 – 106.16 (m, 1C, COD, H*C*=CH), 79.44 (dd, $^2J_{P\text{-}C}$ = 10.8 Hz, $^1J_{Rh\text{-}C}$ = 4.9 Hz, 1C, COD, H*C*=CH), 78.07 (s), 76.47 – 76.24 (m, 1C, COD, H*C*=CH), 55.89 (d, $^2J_{P\text{-}C}$ = 8.4 Hz, 1C, *C*HCH(PPh$_2$)Ar), 53.46 (s, 1C, COO*C*H$_3$), 52.85 (s, 1C, COO*C*H$_3$), 47.75 (s), 47.59 (d, $^1J_{P\text{-}C}$ = 25.2 Hz, 1C, CH*C*H(PPh$_2$)Ar), 35.55 (s), 33.81 (s), 31.91 (s), 30.88 (s), 29.34 (s), 29.14 (s), 28.97 (s), 26.03 (s), 22.67 (s), 18.36 (s), 14.10 (s), 9.13 (s), 1.00 (s). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -153.06 (s). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$) δ 49.69 (d, $^1J_{Rh\text{-}P}$ = 156.2 Hz). **HRMS** (+ESI) m/z: (M + H – BF_4^-)$^+$ calc'd for $C_{35}H_{37}NO_4PRh$, 669.1515; found, 669.1519.

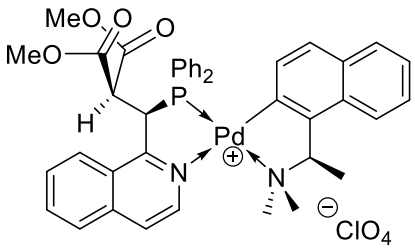
[(κ^2-P,N)-(dimethyl 2-((diphenylphosphaneyl)(isoquinolin-1-yl)methyl)malonate)][(1,2,5,6- η)(1Z,5Z)-cycloocta-1,5-diene]-iridium(I) tetrafluoroborate (14)



14 is a dark-red solid. Yield: >99.9% (crude). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.49 (d, $^3J_{H\text{-}H}$ = 6.5 Hz, 1H, Ar*H*), 8.20 (d, $^3J_{H\text{-}H}$ = 8.7 Hz, 1H, Ar*H*), 8.08 (d, $^3J_{H\text{-}H}$ = 6.4 Hz, 1H, Ar*H*), 7.93 (d, $^3J_{H\text{-}H}$ = 8.1 Hz, 1H, Ar*H*), 7.83 – 7.79 (m, 2H, Ar*H*), 7.72 – 7.61 (m, 4H, Ar*H*), 7.53 (d, $^3J_{H\text{-}H}$ = 3.9 Hz, 2H, Ar*H*), 7.50 – 7.43 (m, 4H, Ar*H*), 7.36 (d, $^3J_{H\text{-}H}$ = 5.2 Hz, 3H, Ar*H*), 7.16 (s, Ar*H*), 6.97 (d, $^3J_{H\text{-}H}$ = 9.2 Hz, 1H, Ar*H*), 6.09 (dd, $^3J_{P\text{-}H}$ = 12.2 Hz, $^3J_{H\text{-}H}$ = 9.05 Hz, 1H, C*H*CH(PPh_2)Ar), 5.62 (s, 1H, COD *H*C=CH), 5.36 (s, 1H, COD *H*C=CH), 4.56 (dd, $^2J_{P\text{-}H}$ = 14.1 Hz, $^3J_{H\text{-}H}$ = 9.05 Hz, 1H, CHC*H*(PPh_2)Ar), 4.20 (s, 1H, COD *H*C=CH), 3.82 (s, 1H, COD *H*C=CH), 3.42 (s), 3.40 (s, 3H, COOCH_3), 3.19 – 3.10 (m), 2.73 (s, 3H, COOCH_3), 2.58 (s, 4H, COD CH_2), 2.32 – 2.16 (m, 2H, COD CH_2), 1.82 – 1.65 (m, 2H, COD CH_2). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.03 (s, 1C, Ar, HC=*C*H-N), 166.09 (d, $^3J_{P\text{-}C}$ = 10.3 Hz, 1C, *C*=O), 165.17 (d, $^3J_{P\text{-}C}$ = 7.4 Hz, 1C, *C*=O), 164.54 (s), 142.34 (s), 136.85 (s), 134.22 – 133.81 (m), 133.62 (d, $^2J_{P\text{-}C}$ = 10.6 Hz, 1C, Ar, N=*C*-C(H)P), 132.72 (d, $^2J_{P\text{-}C}$ = 19.0 Hz, 1C, Ar, P-*C*$_6$H$_5$), 131.12 (d, $J_{P\text{-}C}$ = 9.0 Hz), 130.54 (s), 129.86 (d, $^2J_{P\text{-}C}$ = 10.7 Hz, 1C, Ar, P-*C*$_6$H$_5$), 129.50 (d, $J_{P\text{-}C}$ = 10.5 Hz), 129.01 (d, $J_{P\text{-}C}$ = 9.9 Hz), 128.15 (s), 127.62 (s), 127.49 (s), 127.18 – 126.79 (m), 125.19 (s), 122.49 (d, $J_{P\text{-}C}$ = 46.8 Hz), 99.76 (s), 97.35 (d, $^2J_{P\text{-}C}$ = 7.7 Hz, 1C, COD, H*C*=CH), 96.87 (d, $^2J_{P\text{-}C}$ = 8.9 Hz, 1C, COD, H*C*=CH) 65.79 (d, $^2J_{P\text{-}C}$ = 10.4 Hz, 1C, COD, H*C*=CH), 63.06 (d, $^2J_{P\text{-}C}$ = 13.8 Hz 1C, COD, H*C*=CH), 55.28 (d, $^2J_{P\text{-}C}$ = 6.8 Hz, 1C, *C*HCH(PPh_2)Ar), 53.43 (s, 1C, COO*C*H$_3$), 52.86 (s, 1C, COO*C*H$_3$), 49.59 (s), 48.22 (d, $^1J_{P\text{-}C}$ = 30.3 Hz, 1C, CH*C*H(PPh_2)Ar), 47.73 (s), 43.77 (d, *J* = 8.6 Hz), 36.80 (s), 32.60 (s), 31.91 (s), 29.68 (s), 29.34 (s), 28.94 (s), 25.75 (s), 25.14 (s), 23.24 (d, *J* = 4.3 Hz), 23.04 (s), 22.68 (s), 14.10 (s), 9.13 (s). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -153.26 (s). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$) δ 41.49 (s). **HRMS** (+ESI) m/z: $(M + H - BF_4^-)^+$ calc'd for $C_{35}H_{37}NO_4PIr$, 759.2090; found, 759.2097.

Preparation of {(*R*)-(κ^2-C^2,N)-1-[1-(dimethylamino)ethyl]naphthyl}-{(*R*)-(κ^2-P,N)-(dimethyl 2-((diphenylphosphaneyl)(isoquinolin-1-yl)methyl)malonate)}-palladium(II) perchlorate ((*R*,*R*)-22).

Diphenylphosphine (0.08 mmol, 0.015 g, 1.0 equiv.) was weighed into a Schlenk flask under positive N_2 flow and 3.0 ml previously degassed DCM was added. Malonate substrate **5a** (0.08 mmol, 0.022 g, 1.0 equiv.) and (*S*)-**2** catalyst (0.004 mmol, 0.0025 g, 0.05 equiv.) were added to the solution and then the mixture was cooled down to -80 °C. Upon the required temperature was reached, triethylamine (0.08 mmol, 0.009 g, 1.0 equiv) was added dropwise to the reaction mixture. After the completion of the reaction, (*R*)-**1** complex (0.08 mmol, 0.042 g, 1.0 equiv.) was added and the mixture was allowed to warm up to rt. The solution was washed with water and brine, dried, filtered through short celite plug, then the solvent was evaporated. The crude complex was recrystallized from DCM with diethyl ether to afford diastereomerically pure crystals.



(*R*,*R*)-**22** is a bright-yellow solid. Yield: 33%. $[\alpha]^{25}_D$ = -247 (*c* 2.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, $^3J_{H\text{-}H}$ = 6.1 Hz, 1H, Ar*H*, HC=C*H*-N), 8.32 (d, $^3J_{H\text{-}H}$ = 8.6 Hz, 1H, Ar*H*), 8.25 (d, $^3J_{H\text{-}H}$ = 6.1 Hz, 1H, Ar*H*), 7.99 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 1H, Ar*H*), 7.89 – 7.76 (m, 5H, Ar*H*), 7.74 (d, $^3J_{H\text{-}H}$ = 8.1 Hz, 1H, Ar*H*), 7.58 – 7.47 (m, 5H, Ar*H*), 7.47 – 7.40 (m, 3H, Ar*H*), 7.30 (t, $^3J_{H\text{-}H}$ = 6.9 Hz, 2H, Ar*H*), 7.20 (d, $^3J_{H\text{-}H}$ = 8.4 Hz, 1H, Ar*H*), 6.97 – 6.91 (m, 1H, Ar*H*), 5.91 (dd, $^3J_{H\text{-}P}$ = 13.7, $^3J_{H\text{-}H}$ = 8.6 Hz, 1H, C*H*CH(PPh$_2$)Ar), 4.74 – 4.60 (m, 2H, NC*H*CH$_3$, CHC*H*(PPh$_2$)Ar), 3.31 (s, 3H, COOC*H*$_3$), 3.28 (s), 3.19 (s), 3.13 (d, $^4J_{P\text{-}H}$ = 3.0 Hz, 3H, NC*H*$_3$), 3.09 (s, 3H, NC*H*$_3$), 2.85 (s, 3H, COOC*H*$_3$), 2.22 (d, $^3J_{H\text{-}H}$ = 6.2 Hz, 3H, NCHC*H*$_3$), 1.29 (s), 1.26 (s). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.60 (s, 1C, Ar, HC=*C*H-N), 165.95 (d, $^3J_{P\text{-}C}$ = 11.3 Hz, 1C, *C*=O), 158.91 (d, $^3J_{P\text{-}C}$ = 5.4 Hz, 1C, *C*=O), 150.18 (s), 146.55 (s), 142.29 (s), 137.27 (d, $^2J_{P\text{-}C}$ = 12.6 Hz, Ar, N=*C*-C(H)P), 137.02 (s), 135.44 (d, $^1J_{P\text{-}C}$ = 12.0 Hz, Ar, P-*C*$_6$H$_5$), 133.17 (s), 133.07 (s), 132.96 (t, 1C, $J_{P\text{-}C}$ = 2.8 Hz, Ar), 131.81 (s), 130.06 (s), 129.96 (d, $J_{P\text{-}C}$ = 4.5 Hz, 1C, Ar), 129.01 (d, $^1J_{P\text{-}C}$ = 11.2 Hz, Ar, P-*C*$_6$H$_5$), 128.91 (d, $J_{P\text{-}C}$ = 3.9 Hz), 128.37 (s), 127.11 (d, $J_{P\text{-}C}$ = 6.0 Hz), 126.66 (d, $J_{P\text{-}C}$ = 7.2 Hz), 126.30 (s), 125.39 (s), 125.18 (s), 124.80 (s), 123.27 (s), 123.17 (s), 122.82 (s), 74.33 (d, $^3J_{P\text{-}C}$ = 2.8 Hz, 1C, N*C*H$_3$), 55.02 (d, $^2J_{P\text{-}C}$ = 9.4 Hz, 1C, *C*HCH(PPh$_2$)Ar), 53.23 (s, 1C, COO*C*H$_3$), 52.89 (s, 1C, COO*C*H$_3$), 52.09 (d, $^3J_{P\text{-}C}$ = 2.4 Hz, 1C, N*C*H$_3$), 47.29 (s, 1C, N*C*HCH$_3$), 46.08 (d, $^1J_{P\text{-}C}$ = 32.3 Hz, 1C, CH*C*H(PPh$_2$)Ar), 29.69 (s), 24.51 (s, 1C, NCH*C*H$_3$). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$) δ 57.75 (s), 54.85 (s). **HRMS** (+ESI) m/z: $(M + H)^+$ calc'd for $C_{41}H_{41}ClN_2O_8PPd$, 861.1324; found, 861.1301.

3. References

1. (a) Allen, D. G.; McLaughlin, G. M.; Robertson, G. B.; Steffen, W. L.; Salem, G.; Wild, S. B., Resolutions with metal complexes. Preparation and resolution of (R,S)-methylphenyl(8-quinolyl)phosphine and its arsenic analog. Crystal and molecular structure of (+)589-[(R)-dimethyl(1-ethyl-.alpha.-naphthyl)aminato-C2,N][(S)-methylphenyl(8-quinolyl)phosphine]palladium(II) hexafluorophosphate. *Inorg. Chem.* **1982,** *21* (3), 1007-1014; (b) Ng, J. K.-P.; Tan, G.-K.; Vittal, J. J.; Leung, P.-H., Optical Resolution and the Study of Ligand Effects on the Ortho-Metalation Reaction of Resolved (±)-Diphenyl[1-(1-naphthyl)ethyl]phosphine and Its Arsenic Analogue. *Inorg. Chem.* **2003,** *42* (23), 7674-7682; (c) Huang, Y.; Chew, R. J.; Li, Y.; Pullarkat, S. A.; Leung, P.-H., Direct Synthesis of Chiral Tertiary Diphosphines via Pd(II)-Catalyzed Asymmetric Hydrophosphination of Dienones. *Org. Lett.* **2011,** *13* (21), 5862-5865; (d) Yang, X.-Y.; Tay, W. S.; Li, Y.; Pullarkat, S. A.; Leung, P.-H., Versatile Syntheses of Optically Pure PCE Pincer Ligands: Facile Modifications of the Pendant Arms and Ligand Backbones. *Organometallics* **2015,** *34* (8), 1582-1588.
2. (a) Giordano, C.; Minisci, F.; Vismara, E.; Levi, S., A general, selective, and convenient procedure of homolytic formylation of heteroaromatic bases. *J. Org. Chem.* **1986,** *51* (4), 536-537; (b) Landa, A.; Minkkilä, A.; Blay, G.; Jørgensen, K. A., Bis(oxazoline) Lewis Acid Catalyzed Aldol Reactions of Pyridine N-Oxide Aldehydes—Synthesis of Optically Active 2-(1-Hydroxyalkyl)pyridine Derivatives: Development, Scope, and Total Synthesis of an Indolizine Alkaloid. *Chem. Eur. J.* **2006,** *12* (13), 3472-3483.
3. Allinson, G.; J. Bushby, R.; V. Jesudason, M.; Paillaud, J.-L.; Taylor, N., The synthesis of singlet ground state derivatives of non-Kekulé polynuclear aromatics. *J. Chem. Soc., Perkin Trans. 2* **1997,** (2), 147-156.
4. Chen, H.; Luzy, J.-P.; Gresh, N.; Garbay, C., An Efficient and Enantioselective Synthesis of Suitably Protected β-[1-(4-Malonyl)naphthyl]-L-alanine and β-[1-(4-Malonylmethyl)naphthyl]-L-alanine: Novel Fluorescent and Non-Hydrolysable Phosphotyrosine Mimetics. *Eur. J. Org. Chem.* **2006,** *2006* (10), 2329-2335.
5. Xu, C.; Jun Hao Kennard, G.; Hennersdorf, F.; Li, Y.; Pullarkat, S. A.; Leung, P.-H., Chiral Phosphapalladacycles as Efficient Catalysts for the Asymmetric Hydrophosphination of Substituted Methylidenemalonate Esters: Direct Access to Functionalized Tertiary Chiral Phosphines. *Organometallics* **2012,** *31* (8), 3022-3026.
6. Aydemir, M.; Meric, N.; Kayan, C.; Ok, F.; Baysal, A., Rhodium-catalyzed transfer hydrogenation with functionalized bis(phosphino)amine ligands. *Inorg. Chim. Acta* **2013,** *398*, 1-10.

4. NMR spectra

NMR spectroscopic data of isoquinoline-1-carbaldehyde (4)

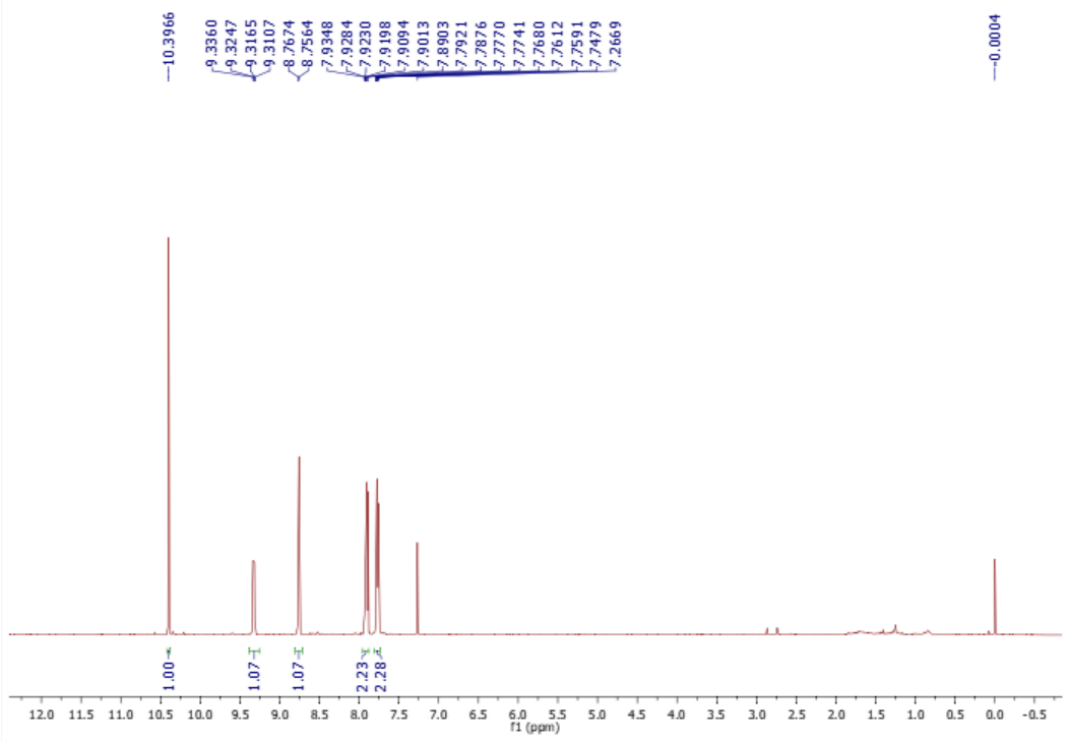


Figure S1. ^{1}H-NMR spectrum of **4** carbaldehyde (500 MHz, $CDCl_3$, 295 K).

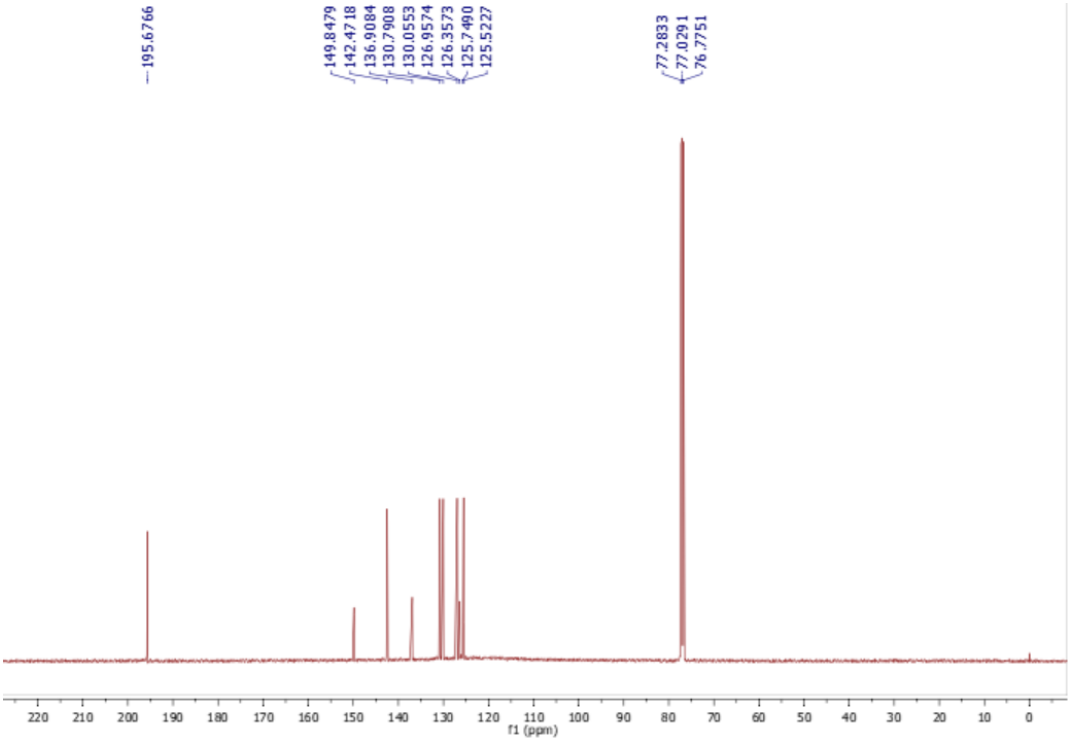


Figure S2. ^{13}C-NMR spectrum of **4** carbaldehyde (126 MHz, $CDCl_3$, 295 K).

NMR spectroscopic data of dimethyl 2-(isoquinolin-1-ylmethylene)malonate (5a)

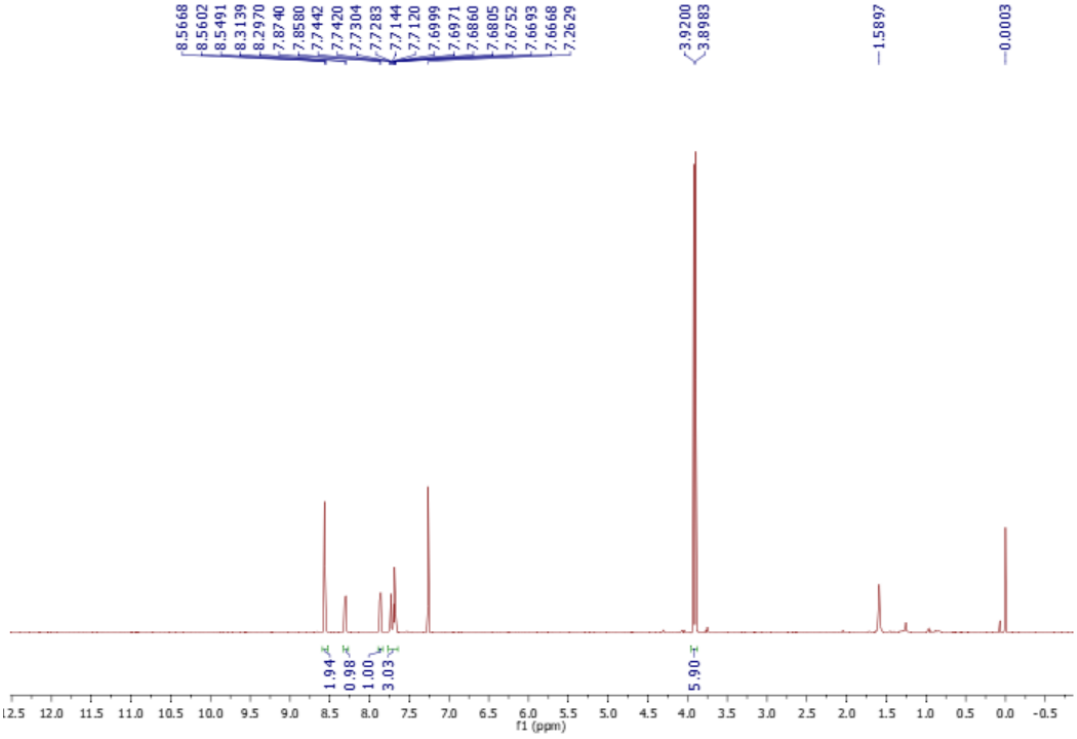


Figure S3. ^{1}H-NMR spectrum of **5a** diester (500 MHz, $CDCl_3$, 295 K).

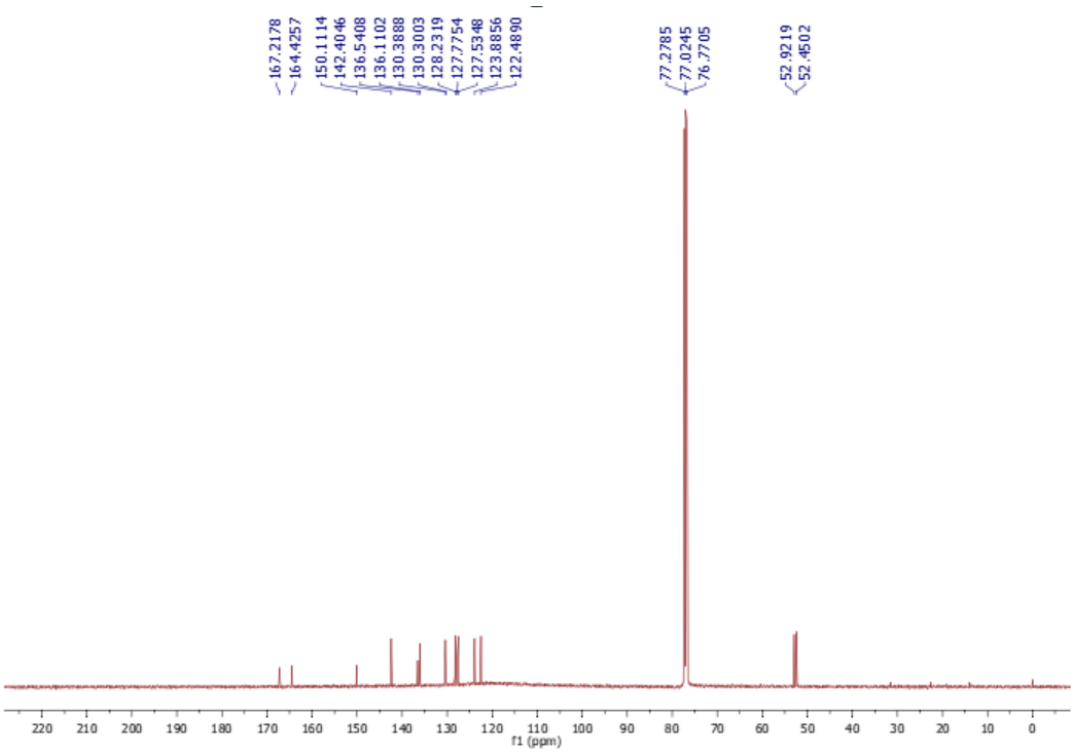


Figure S4. ^{13}C-NMR spectrum of **5a** diester (*126* MHz, $CDCl_3$, 295 K).

NMR spectroscopic data of diethyl 2-(isoquinolin-1-ylmethylene)malonate (5b)

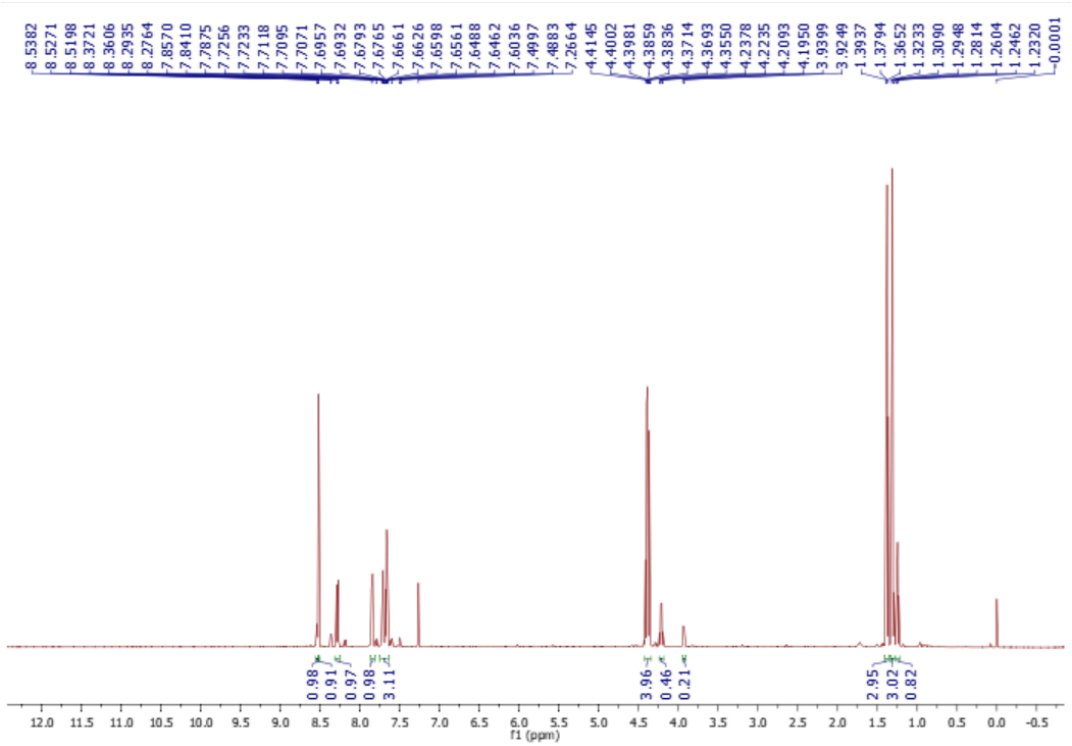


Figure S5. ^{1}H-NMR spectrum of **5b** diester (500 MHz, $CDCl_3$, 295 K).

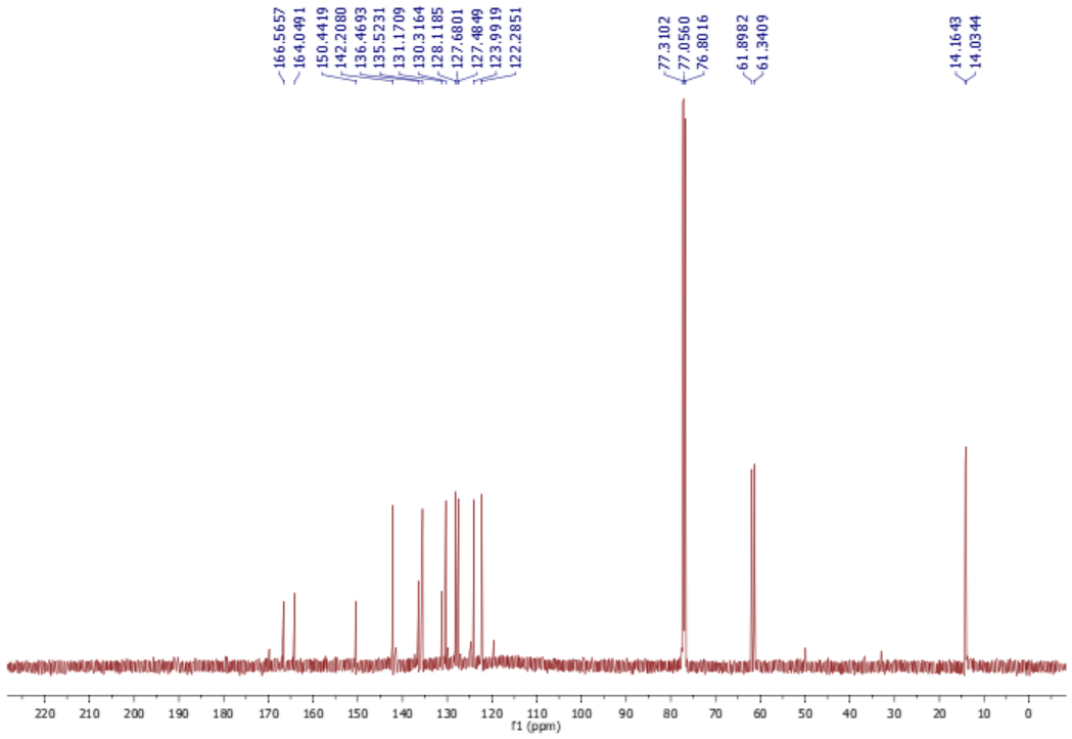


Figure S6. ^{13}C-NMR spectrum of ***5b*** diester (126 MHz, $CDCl_3$, 295 K).

NMR spectroscopic data of diisopropyl 2-(isoquinolin-1-ylmethylene)malonate (5c)

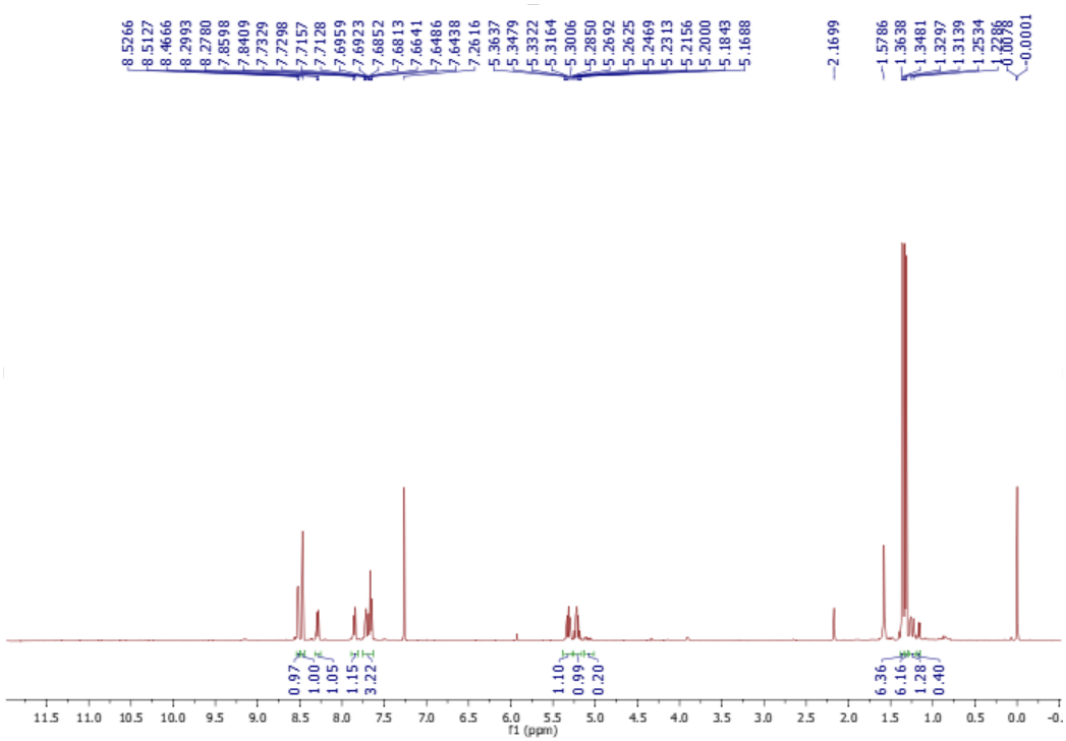


Figure S7. ^{1}H-NMR spectrum of **5c** diester (500 MHz, $CDCl_3$, 295 K).

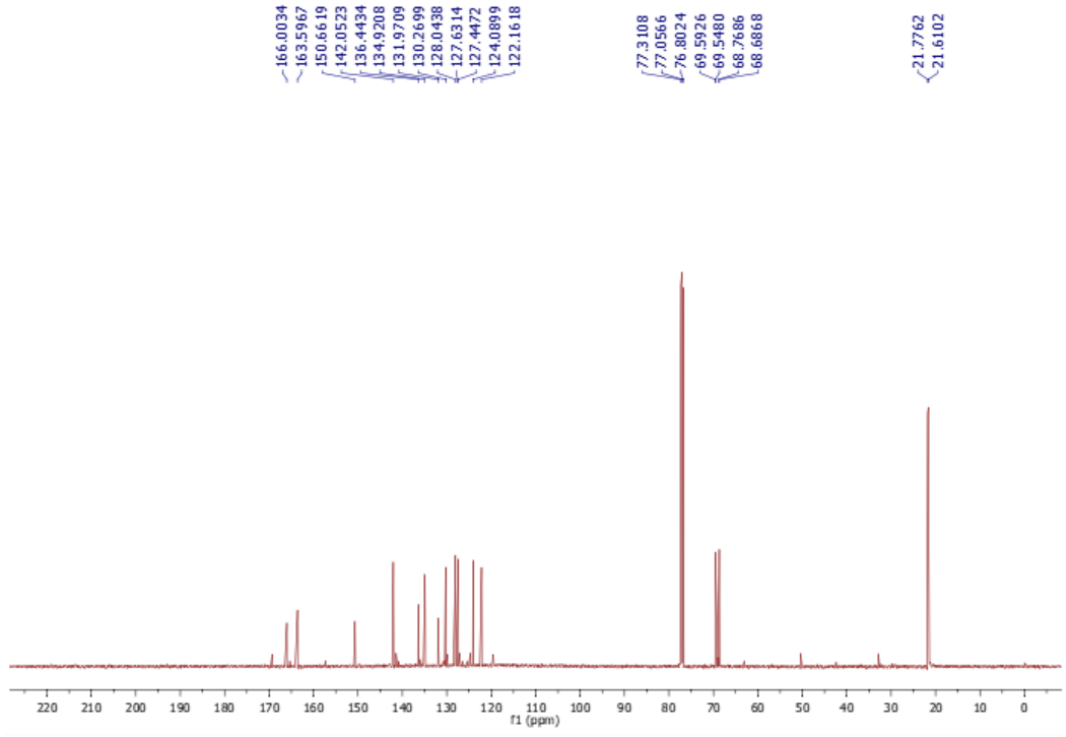


Figure S8. ^{13}C-NMR spectrum of **5c** diester (126 MHz, $CDCl_3$, 295 K).

NMR spectroscopic data of dibenzyl 2-(isoquinolin-1-ylmethylene)malonate (5d)

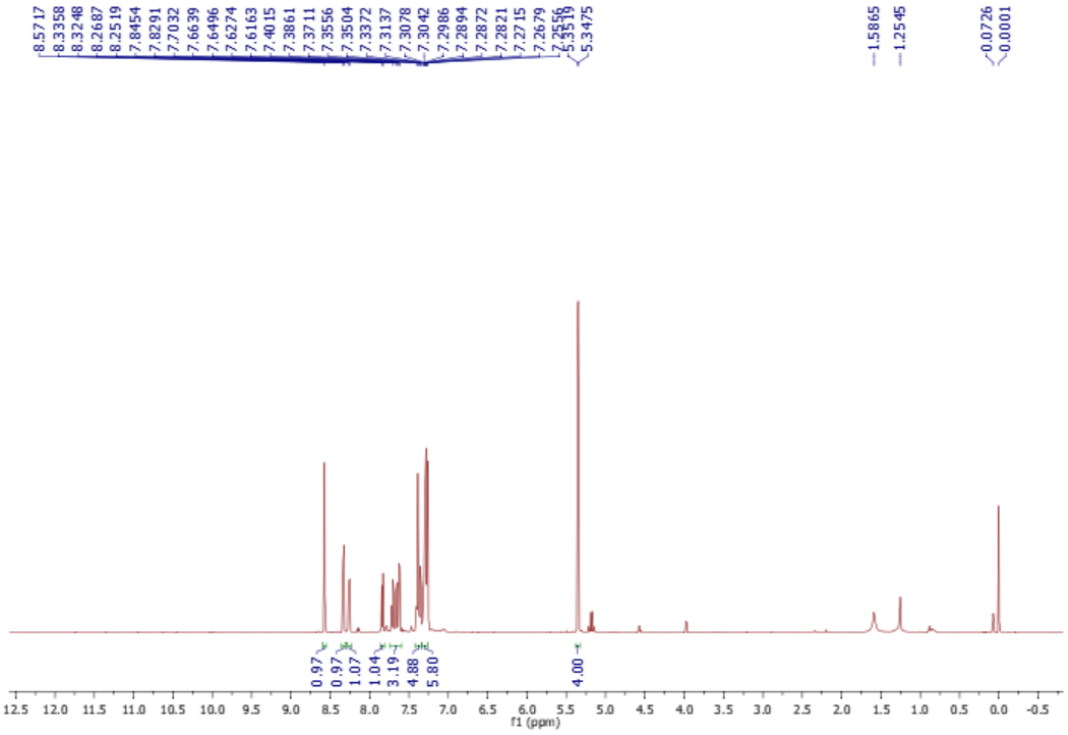


Figure S9. ^{1}H-NMR spectrum of **5d** diester (500 MHz, $CDCl_3$, 295 K).

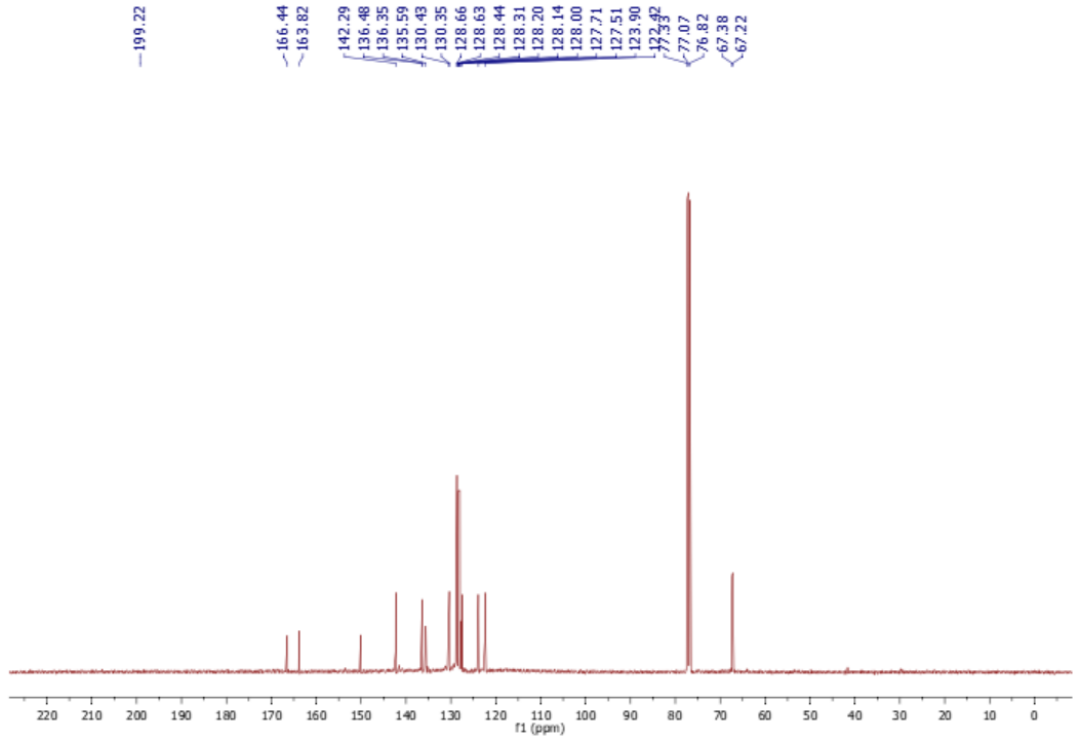


Figure S10. ^{13}C-NMR spectrum of **5d** diester (126 MHz, $CDCl_3$, 295 K).

NMR spectroscopic data of dimethyl 2-((diphenylphosphorothioyl)(isoquinolin-1-yl)methyl)malonate (6a)

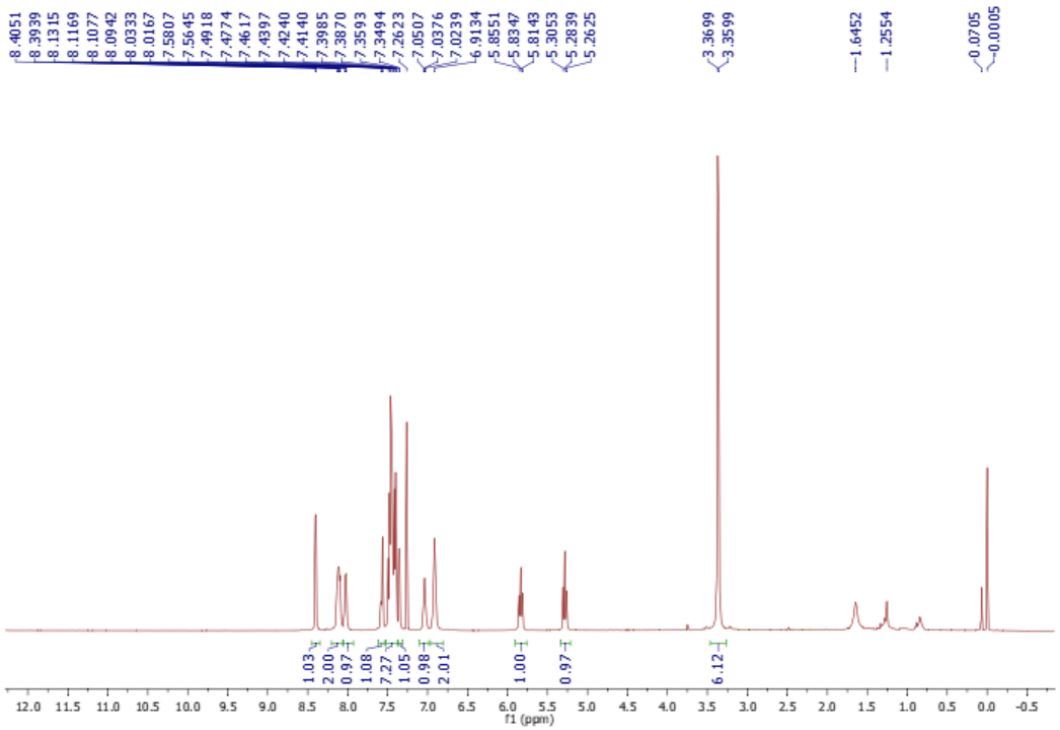


Figure S11. ^{1}H-NMR spectrum of **6a** phosphine sulfide (500 MHz, $CDCl_3$, 295 K).

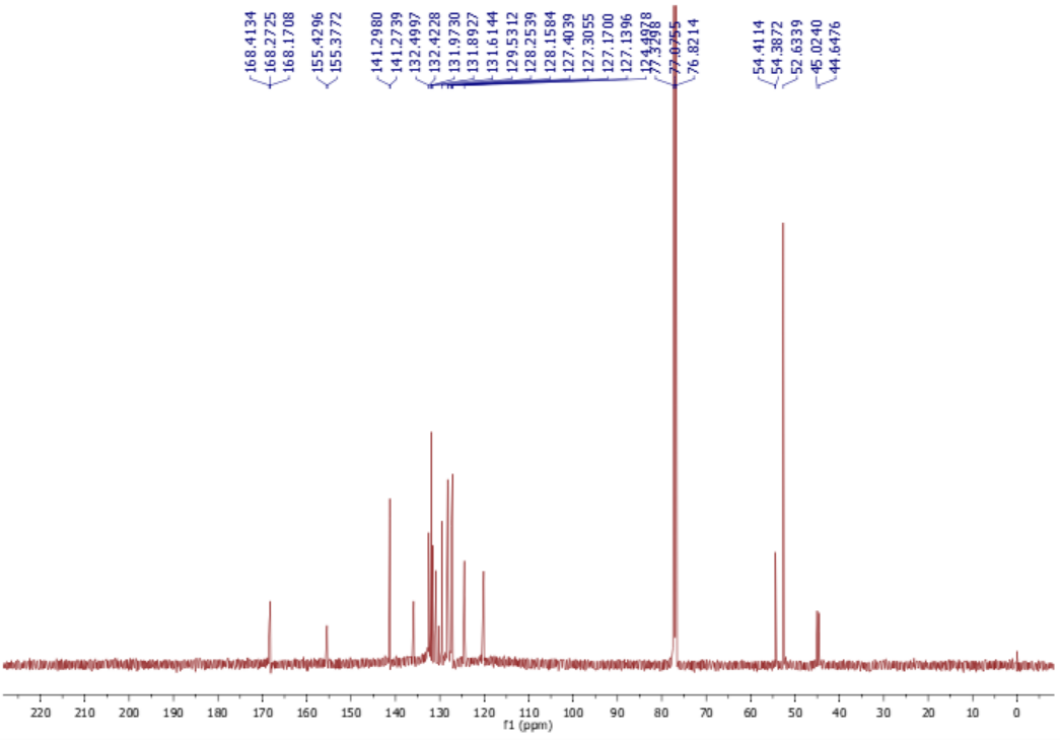


Figure S12. ^{13}C-NMR spectrum of **6a** phosphine sulfide (126 MHz, $CDCl_3$, 295 K).

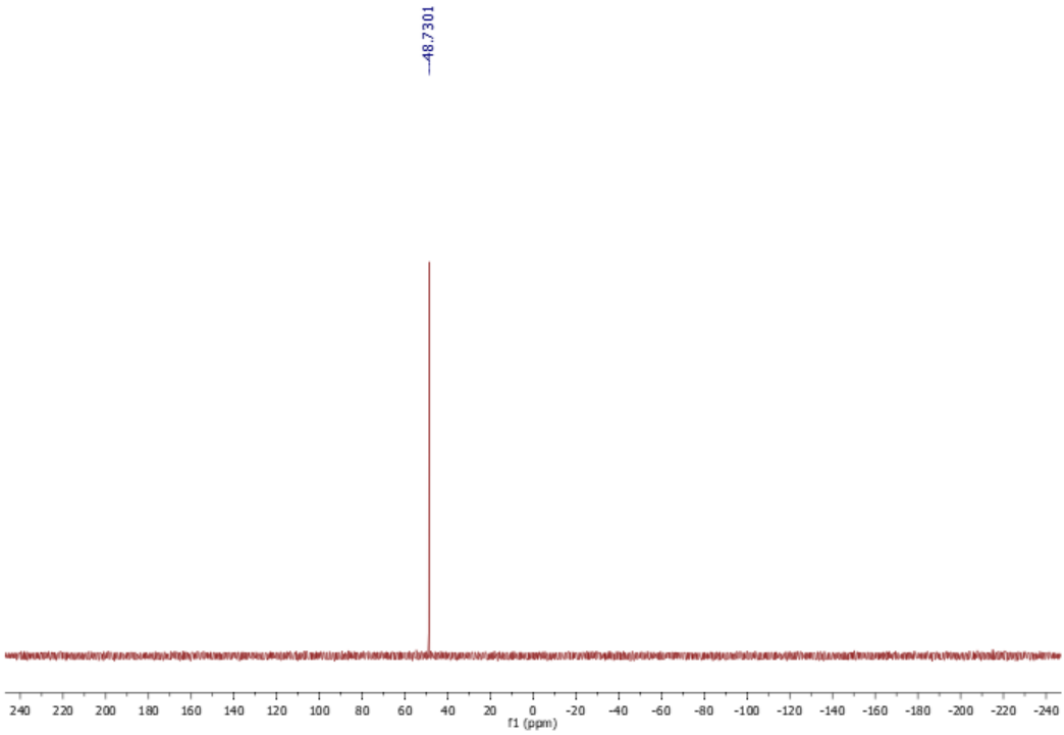


Figure S13. ^{31}P-NMR spectrum of **6a** phosphine sulfide (202 MHz, $CDCl_3$, 295 K).

NMR spectroscopic data of diethyl 2-((diphenylphosphorothioyl)(isoquinolin-1-yl)methyl)malonate (6b)

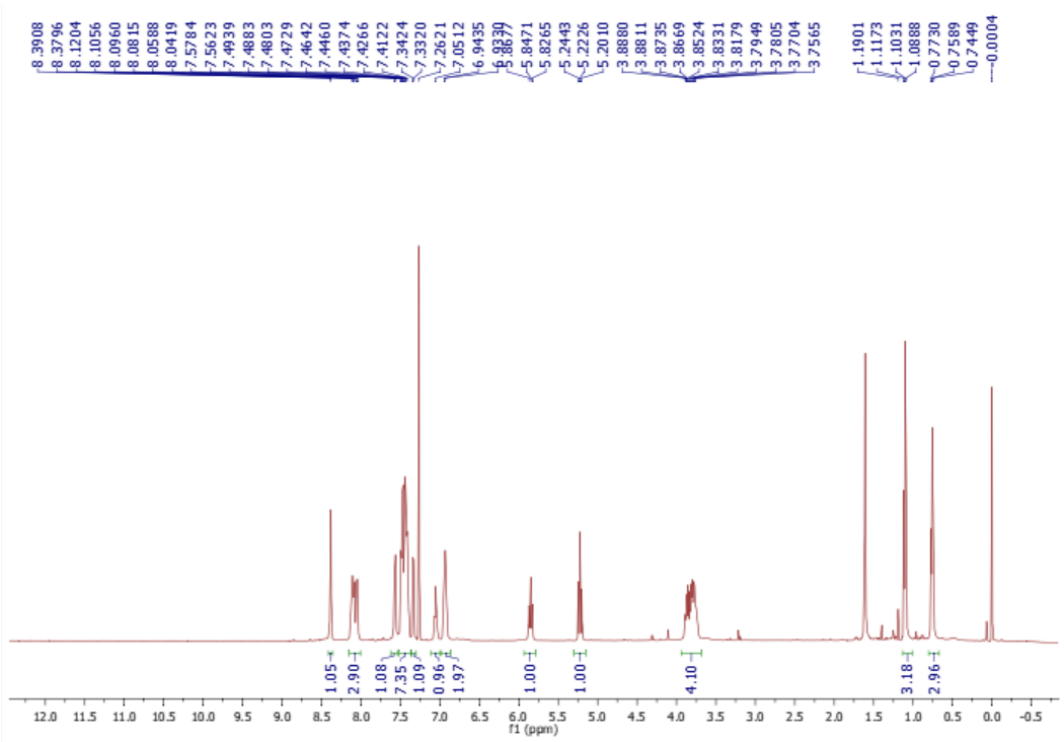


Figure S14. ^{1}H-NMR spectrum of **6b** phosphine sulfide (500 MHz, $CDCl_3$, 295 K).

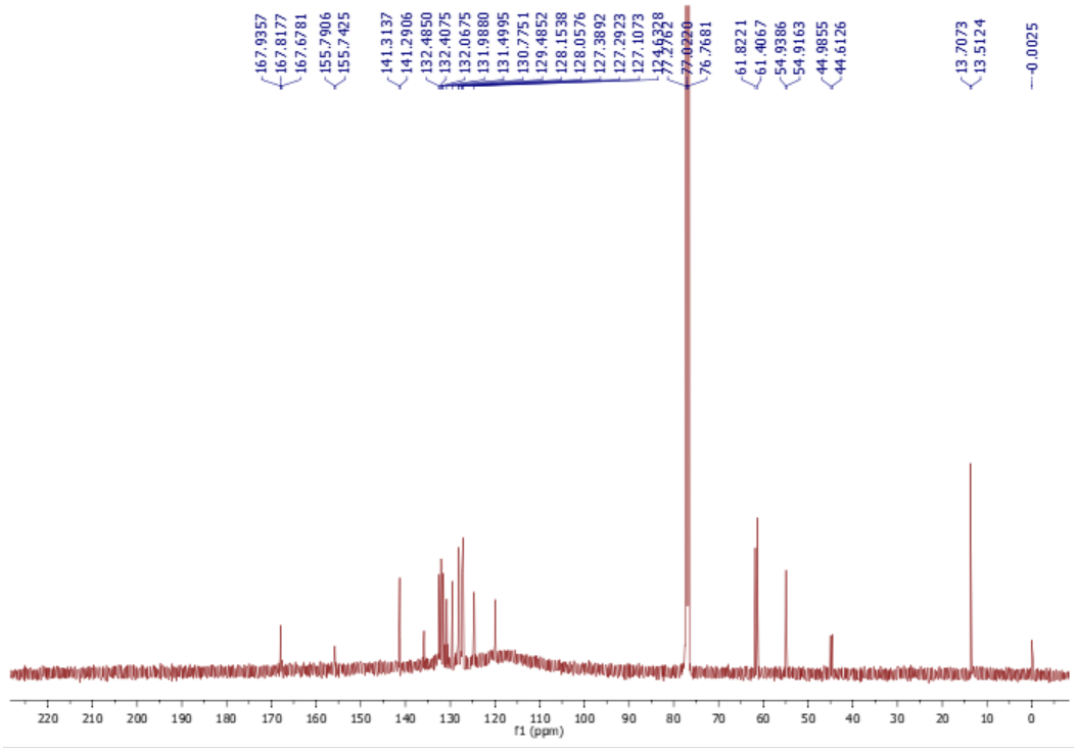


Figure S15. ^{13}C-NMR spectrum of **6b** phosphine sulfide (126 MHz, $CDCl_3$, 295 K).

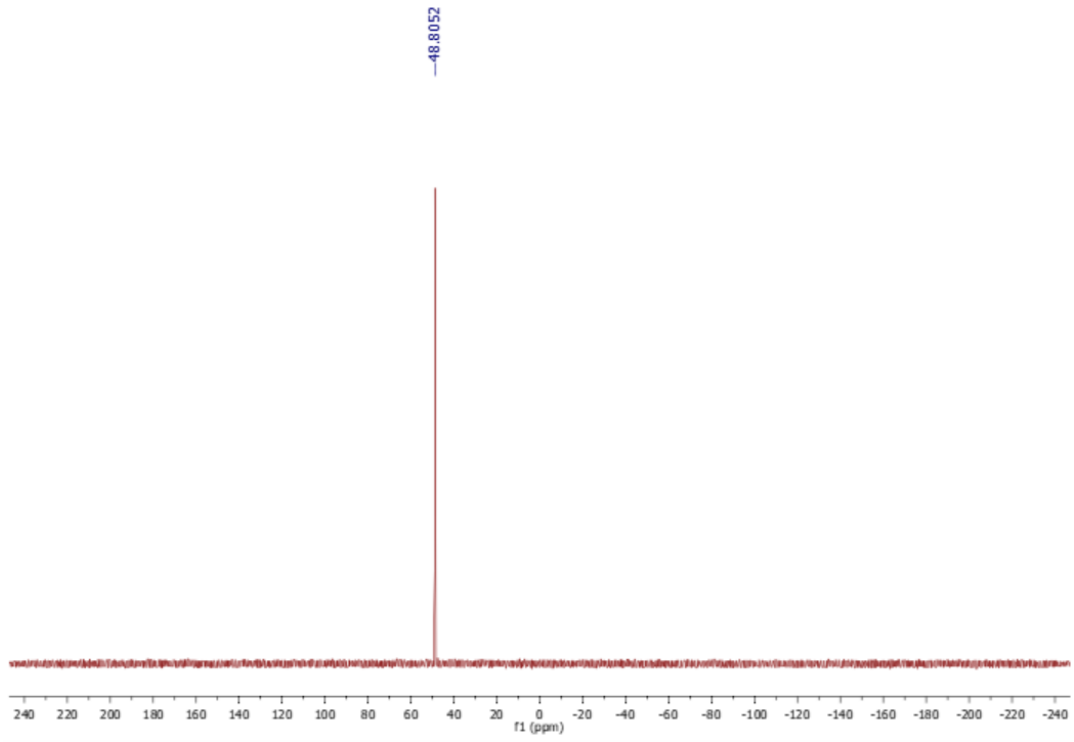


Figure S16. ^{31}P-NMR spectrum of **6b** phosphine sulfide (202 MHz, $CDCl_3$, 295 K).

NMR spectroscopic data of dibenzyl 2-((diphenylphosphorothioyl)(isoquinolin-1-yl)methyl)malonate (6c)

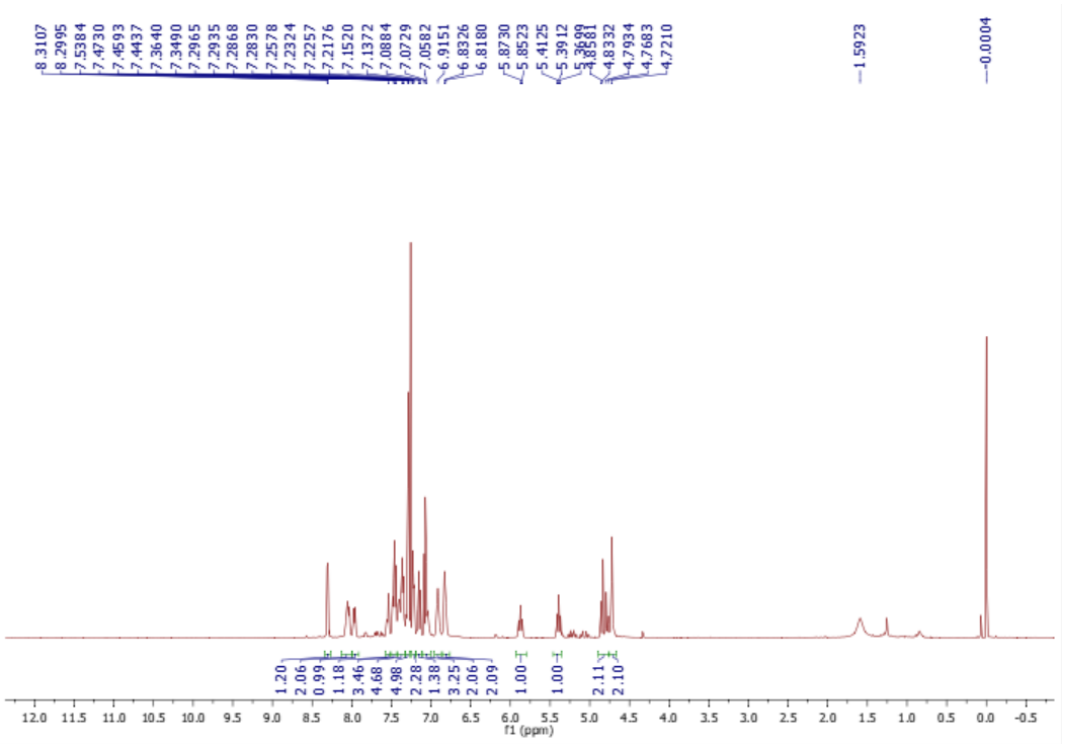


Figure S17. ^{1}H-NMR spectrum of **6c** phosphine sulfide (500 MHz, $CDCl_3$, 295 K).

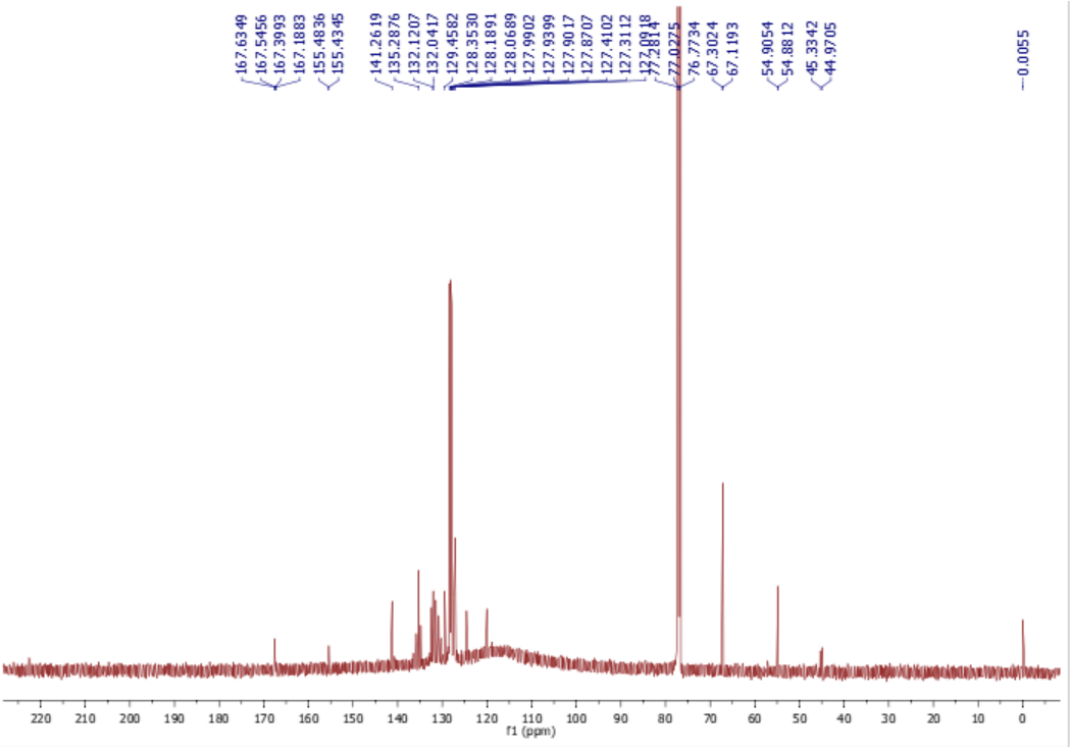


Figure S18. ^{13}C-NMR spectrum of **6c** phosphine sulfide (126 MHz, $CDCl_3$, 295 K).

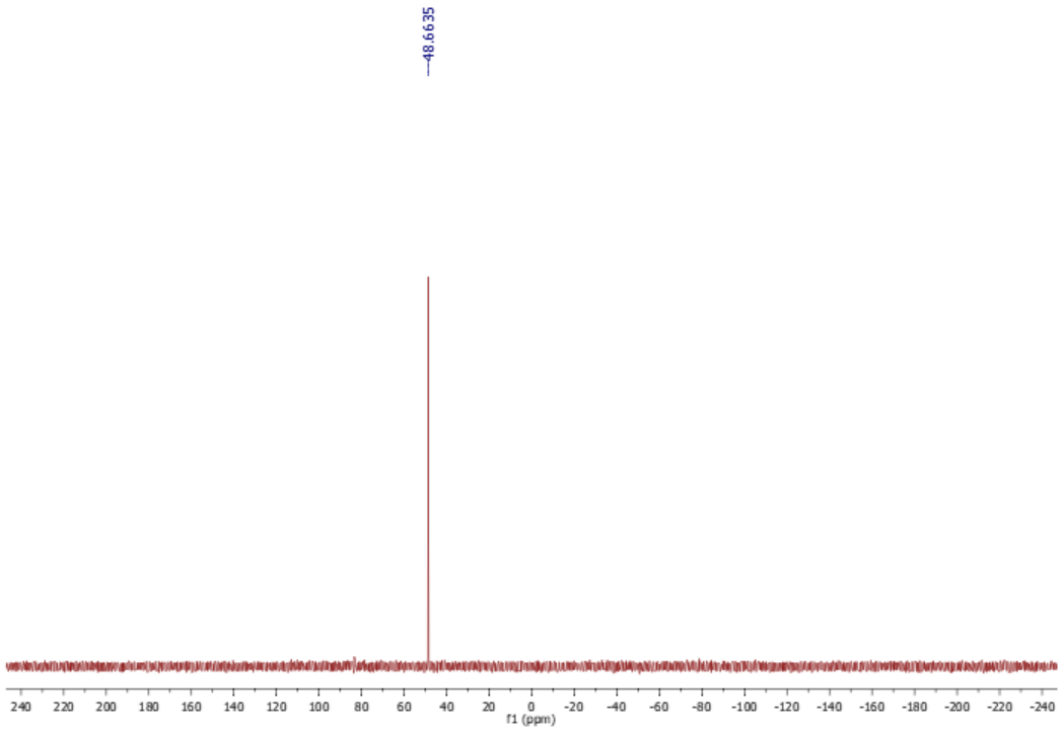


Figure S19. ^{31}P-NMR spectrum of **6c** phosphine sulfide (202 MHz, $CDCl_3$, 295 K).

NMR spectroscopic data of (*R*)-(κ^2-P,N)-(dimethyl 2-((diphenylphosphaneyl)(isoquinolin-1-yl)methyl)malonate)-dichloropalladium(II) ((*R*)-9)

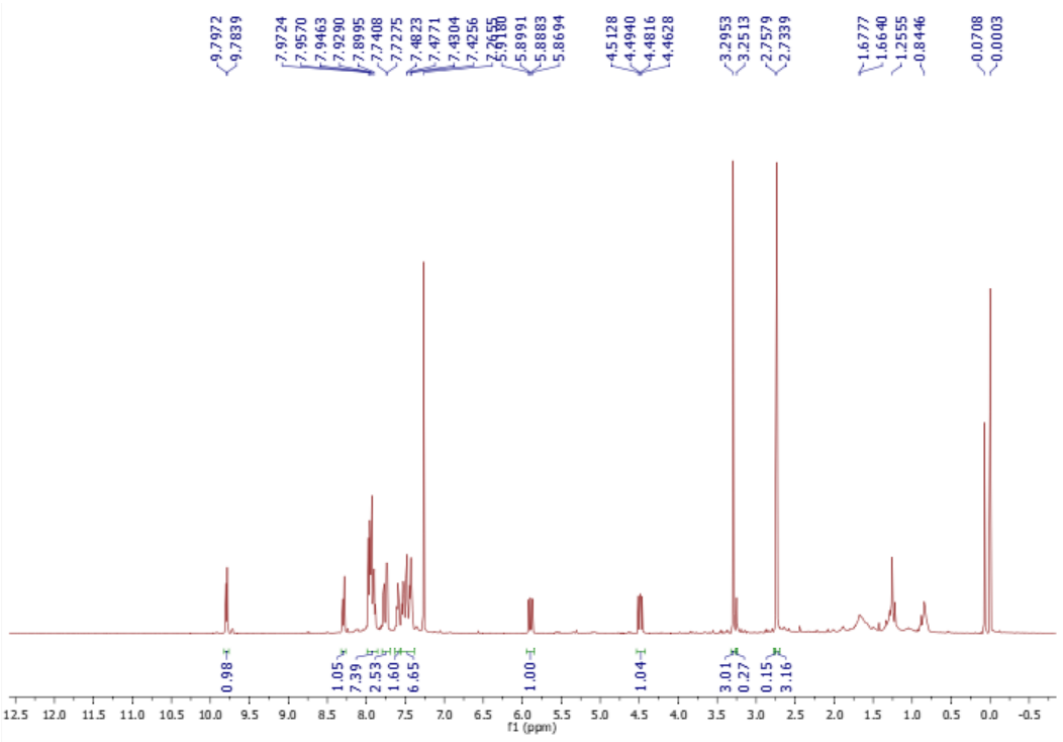


Figure S20. ^{1}H-NMR spectrum of palladium complex (*R*)-**9** (500 MHz, $CDCl_3$, 295 K).

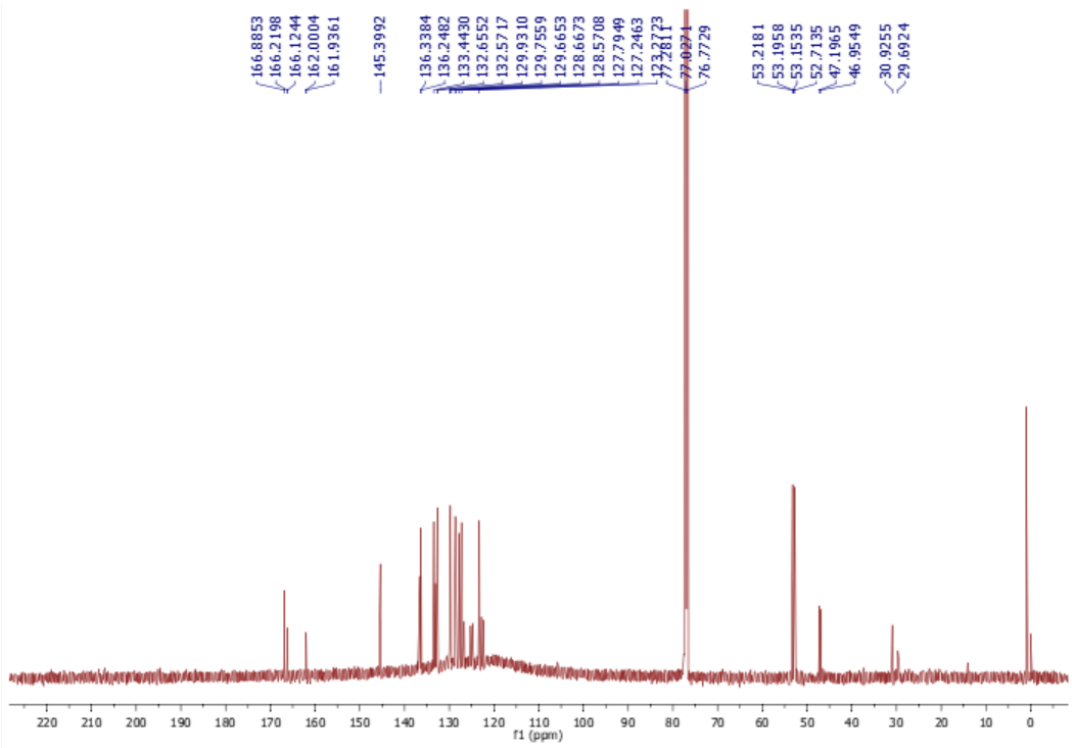


Figure S21. ^{13}C-NMR spectrum of palladium complex (*R*)-**9** (126 MHz, $CDCl_3$, 295 K).

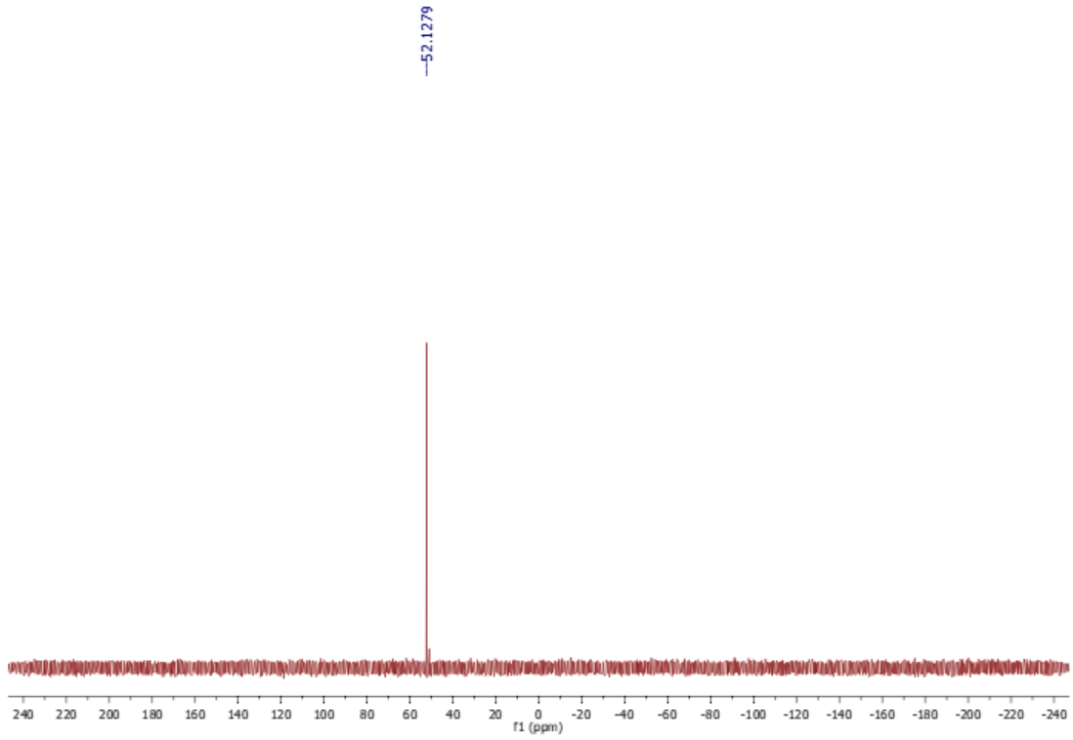


Figure S22. ^{31}P-NMR spectrum of palladium complex (*R*)-**9** (202 MHz, $CDCl_3$, 295 K).

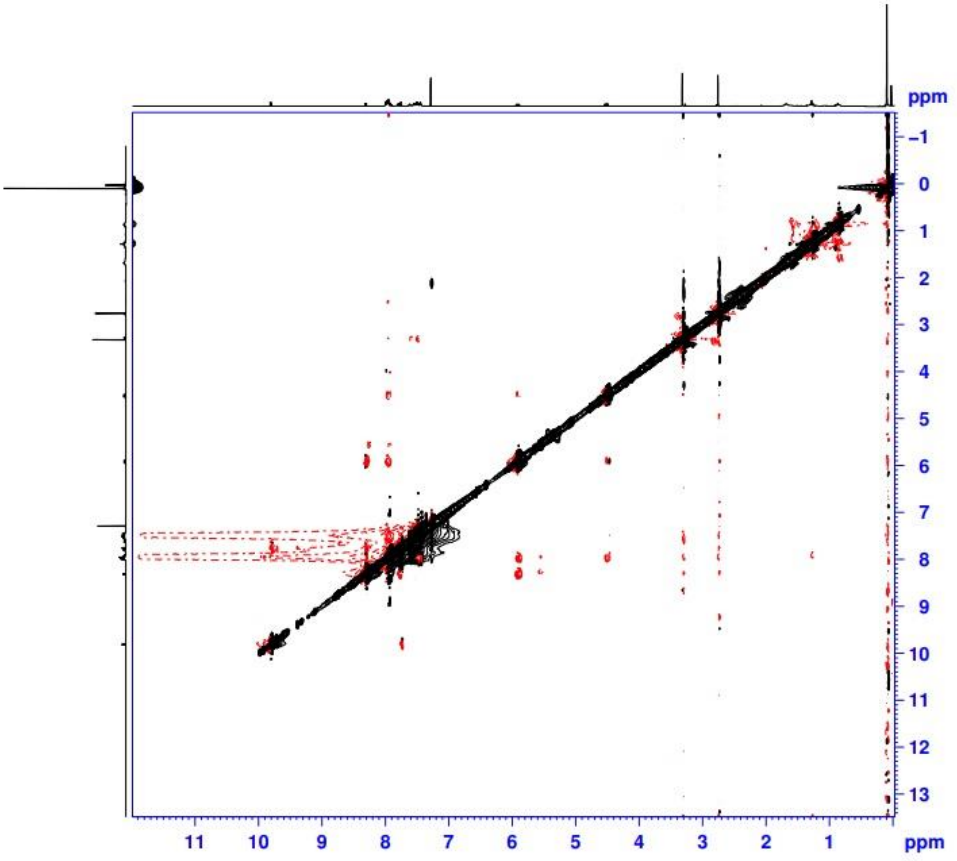


Figure S23. ^{1}H-^{1}H ROESY correlation spectrum of palladium complex (*R*)-**9**.

NMR spectroscopic data of (*R*)-(κ^2-P,N)-(dimethyl 2-((diphenylphosphaneyl)(isoquinolin-1-yl)methyl)malonate)-dichloroplatinum(II) ((*R*)-10)

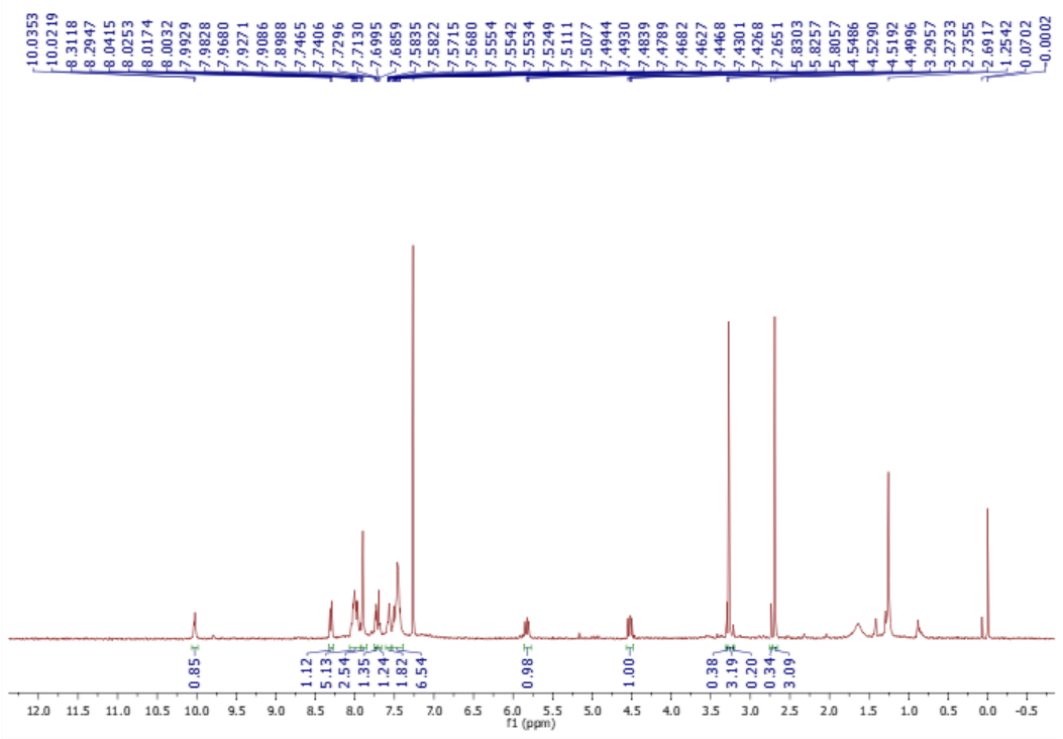


Figure S24. ^{1}H-NMR spectrum of platinum complex (*R*)-**10** (500 MHz, $CDCl_3$, 295 K).

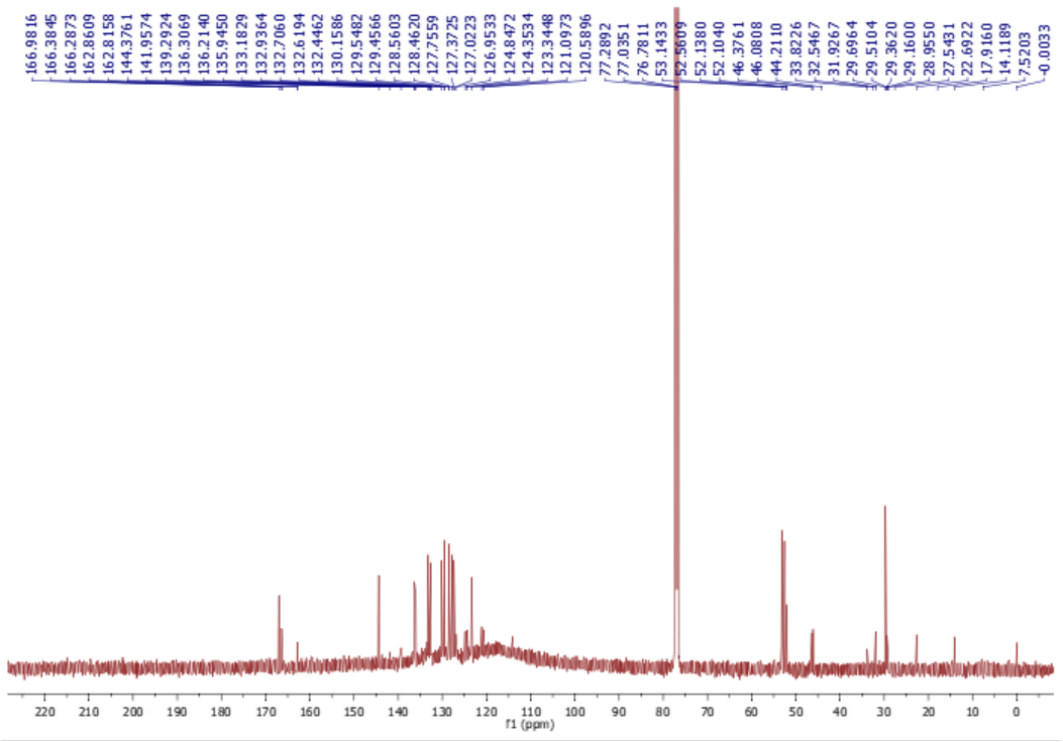


Figure S25. ^{13}C-NMR spectrum of platinum complex (*R*)-**10** (126 MHz, $CDCl_3$, 295 K).

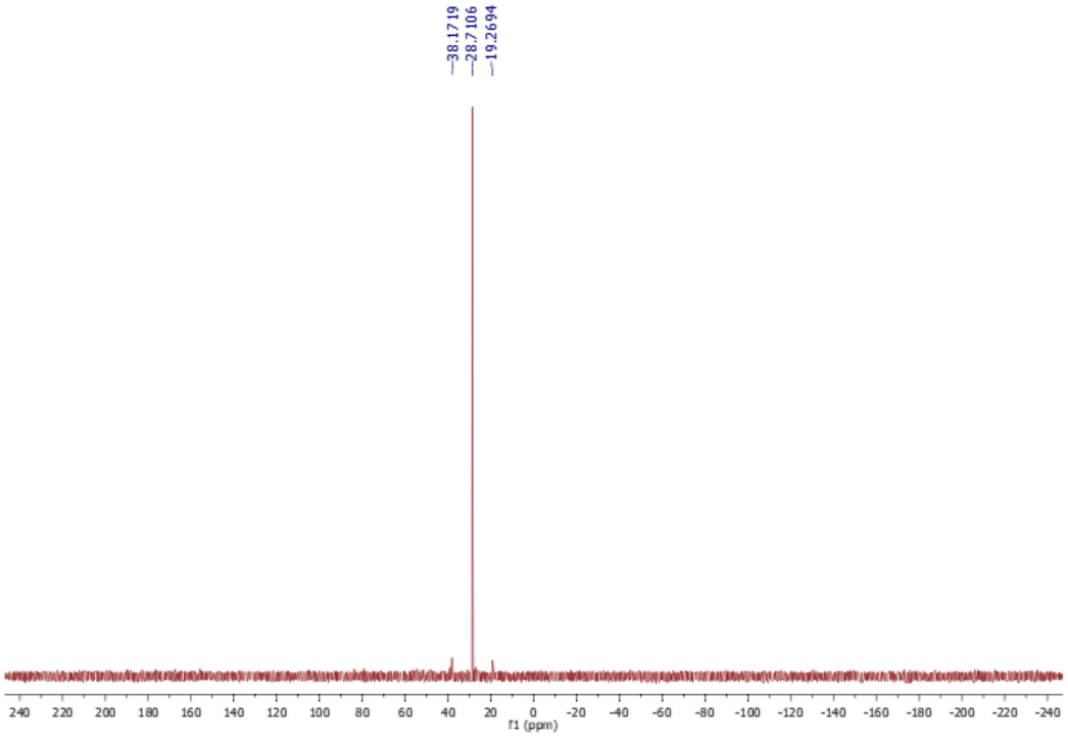


Figure S26. ^{31}P-NMR spectrum of platinum complex (*R*)-**10** (202 MHz, $CDCl_3$, 295 K).

NMR spectroscopic data of [(κ^2-P,N)-(dimethyl 2-((diphenylphosphaneyl)(isoquinolin-1-yl)methyl)malonate)][(1,2,5,6- η)(1Z,5Z)-cycloocta-1,5-diene]-rhodium(I) tetrafluoroborate (13)

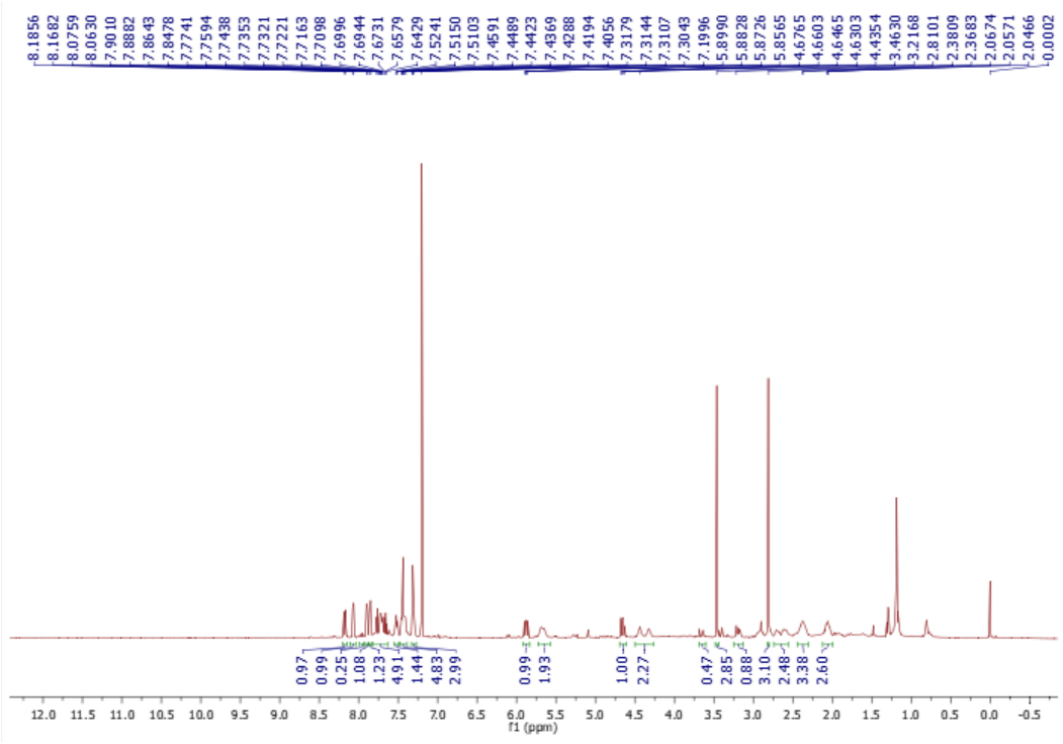


Figure S27. ^{1}H-NMR spectrum of rhodium complex **13** (500 MHz, $CDCl_3$, 295 K).

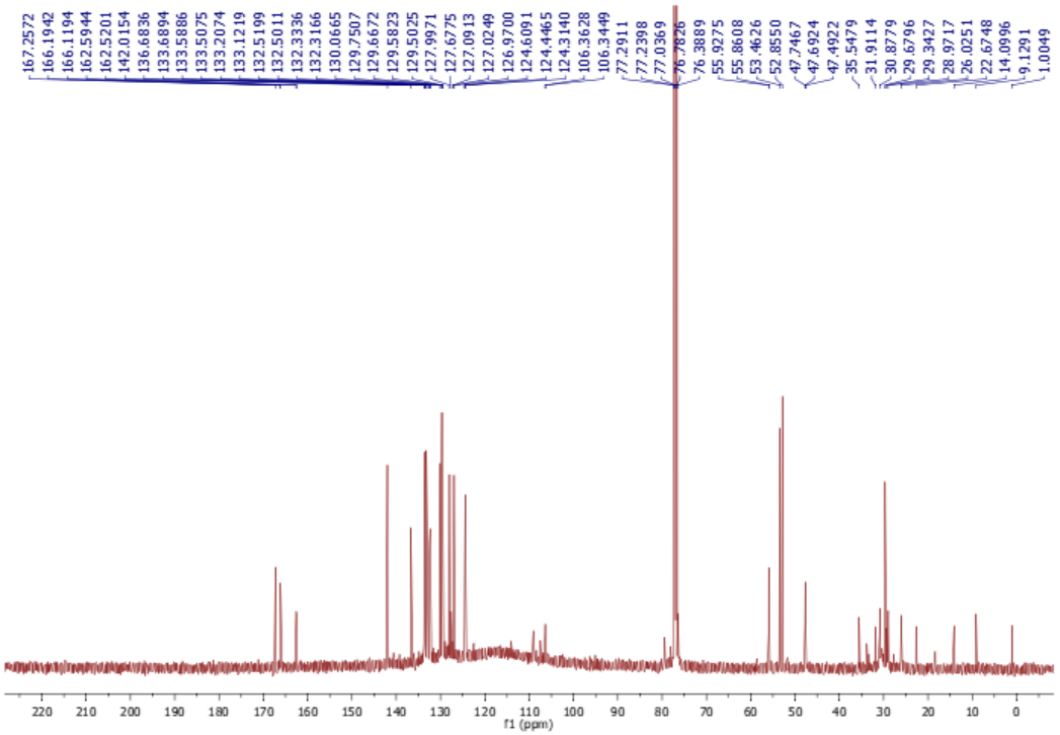


Figure S28. ^{13}C-NMR spectrum of rhodium complex **13** (126 MHz, $CDCl_3$, 295 K).

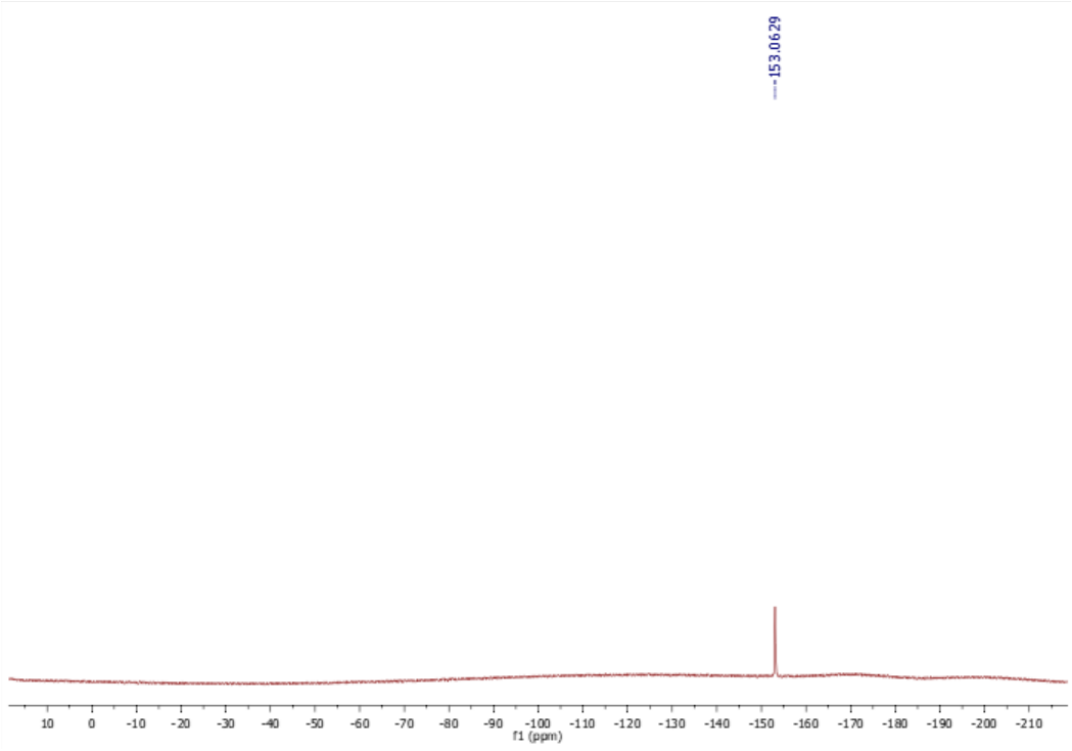


Figure S29. ^{19}F-NMR spectrum of rhodium complex **13** (376 MHz, $CDCl_3$, 295 K).

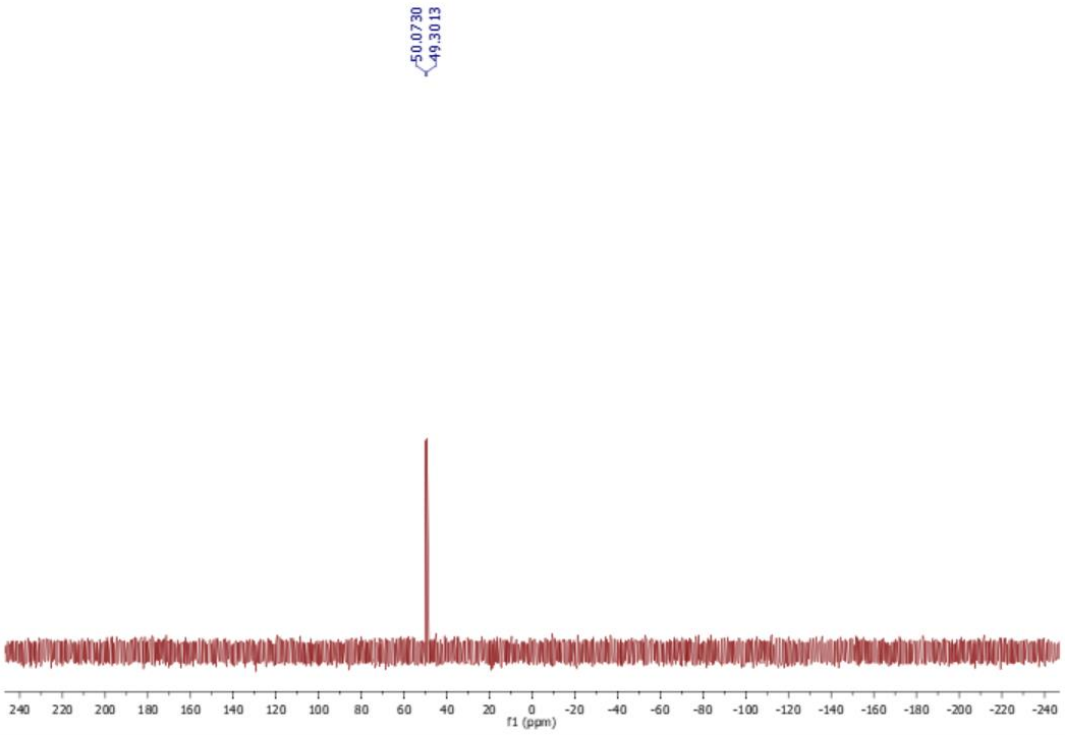


Figure S30. ^{31}P-NMR spectrum of rhodium complex **13** (202 MHz, $CDCl_3$, 295 K).

NMR spectroscopic data of [(κ^2-P,N)-(dimethyl 2-((diphenylphosphaneyl)(isoquinolin-1-yl)methyl)malonate)][(1,2,5,6-η)(1Z,5Z)-cycloocta-1,5-diene]-iridium(I) tetrafluoroborate (14)

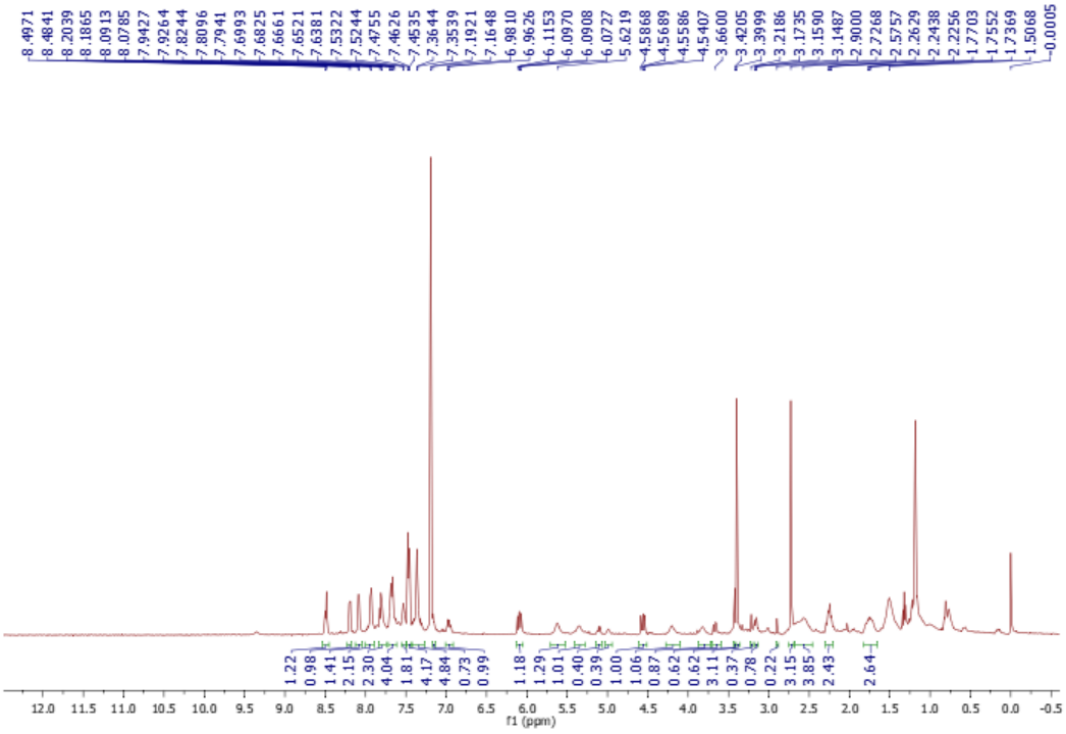


Figure S31. ^{1}H-NMR spectrum iridium complex **14** (500 MHz, $CDCl_3$, 295 K).

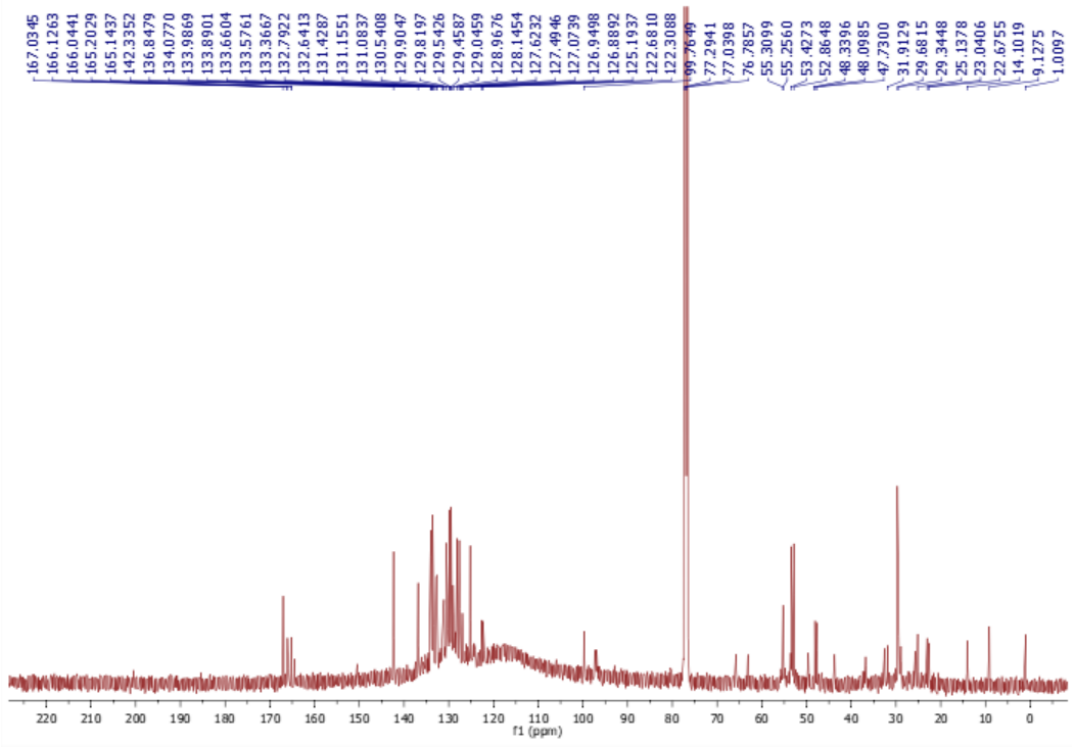


Figure S32. ^{13}C-NMR spectrum of iridium complex **14** (126 MHz, $CDCl_3$, 295 K).

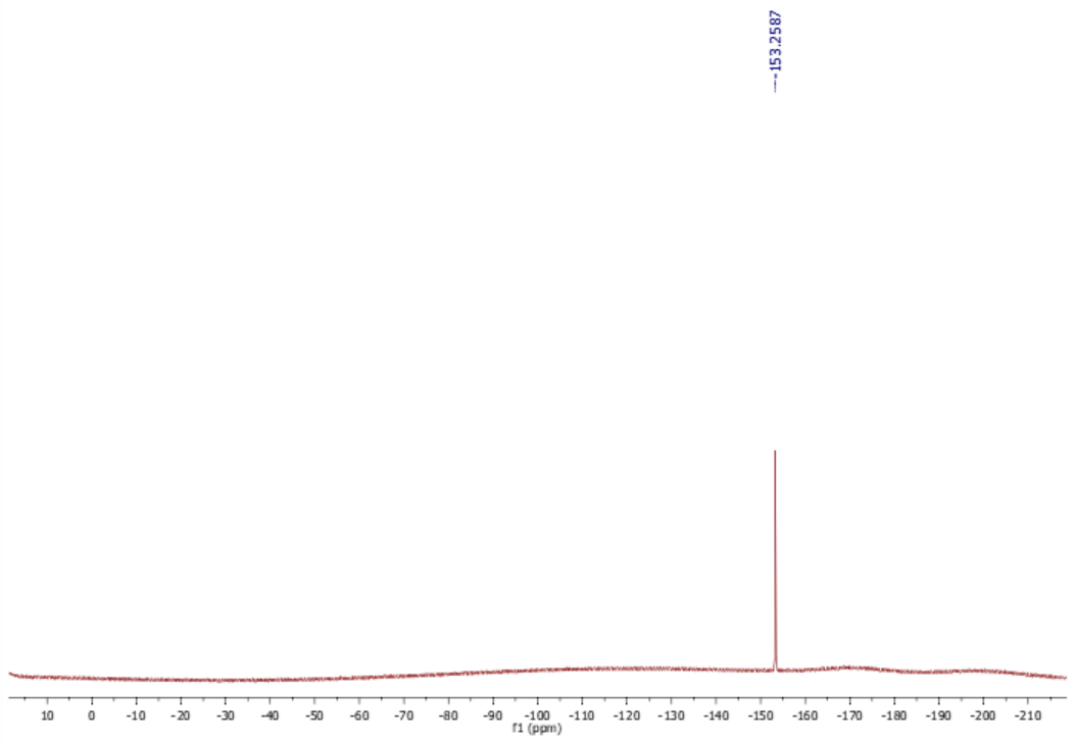


Figure S33. ^{19}F-NMR spectrum of iridium complex **14** (376 MHz, $CDCl_3$, 295 K).

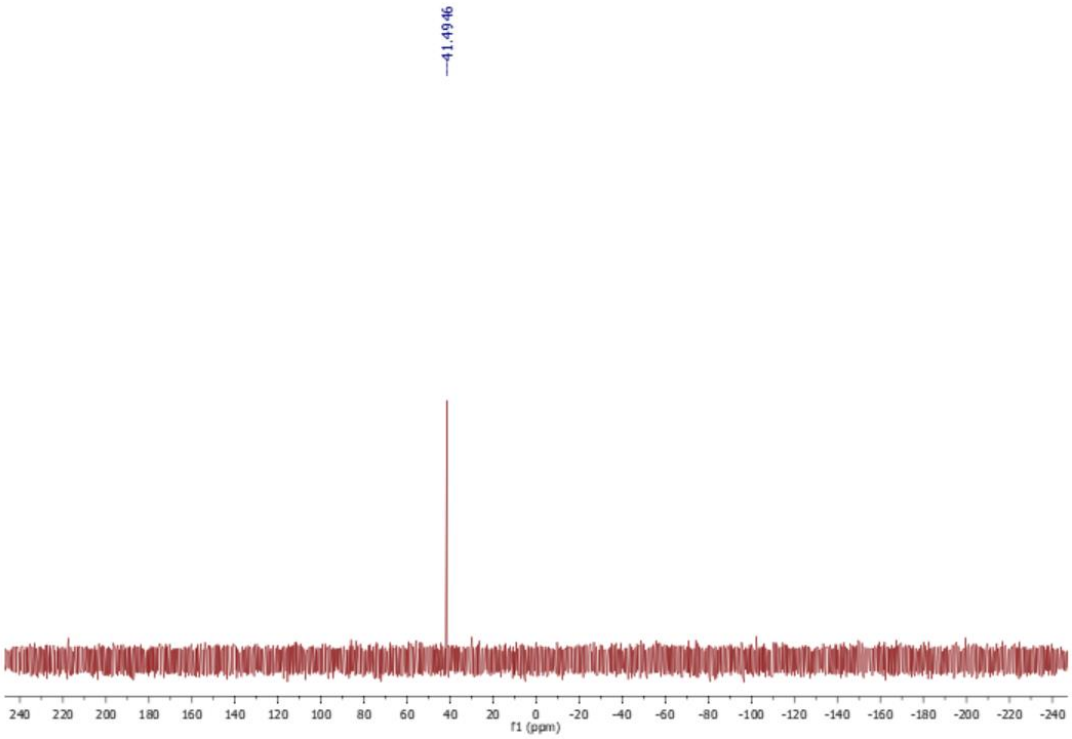


Figure S34. ^{31}P-NMR spectrum of iridium complex **14** (202 MHz, $CDCl_3$, 295 K).

NMR spectroscopic data of {(R)-(κ^2-C^2,N)-1-[1-(dimethylamino)ethyl]naphthyl}-{(R)-(κ^2-P,N)-(dimethyl 2-((diphenylphosphaneyl)(isoquinolin-1-yl)methyl)malonate)}-palladium(II) perchlorate ((*R*,*R*)-22)

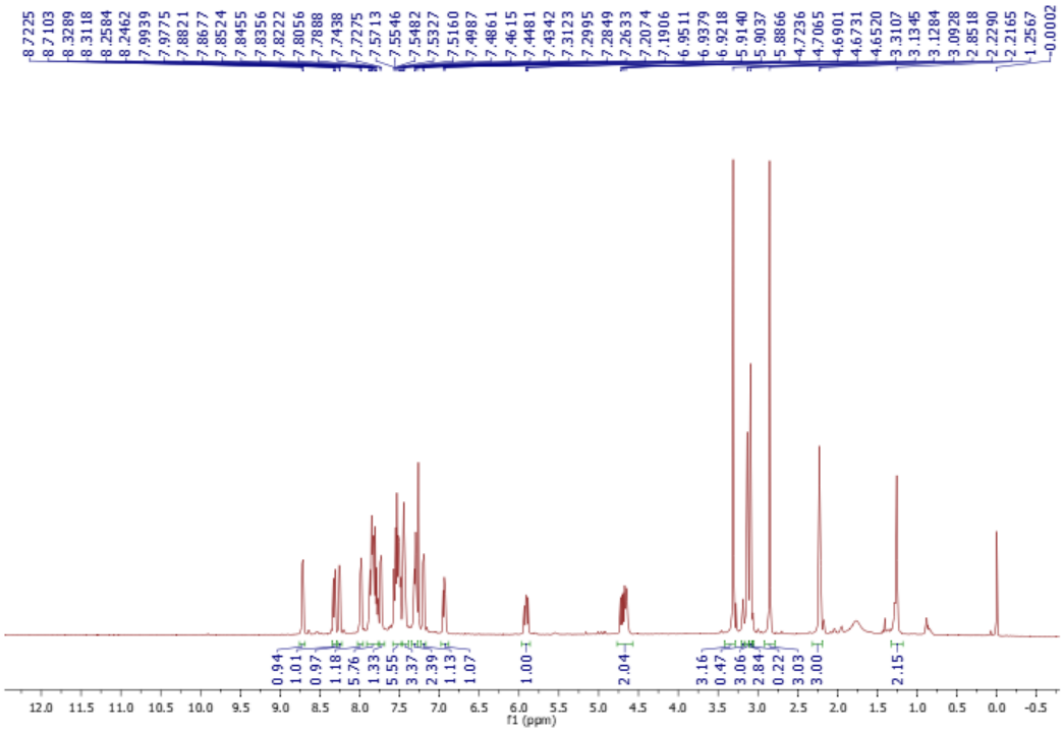


Figure S35. ^{1}H-NMR spectrum of palladium complex (*R*,*R*)-**22** (500 MHz, $CDCl_3$, 295 K).

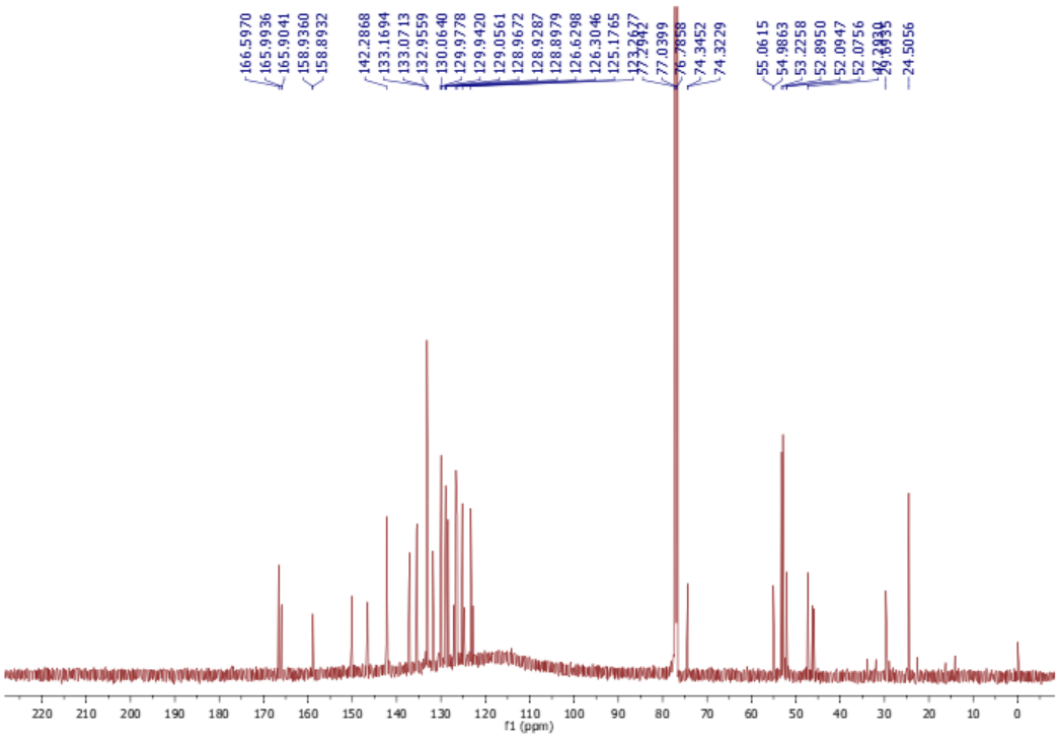


Figure S36. ^{13}C-NMR spectrum of palladium complex (*R*,*R*)-**22** (126 MHz, $CDCl_3$, 295 K).

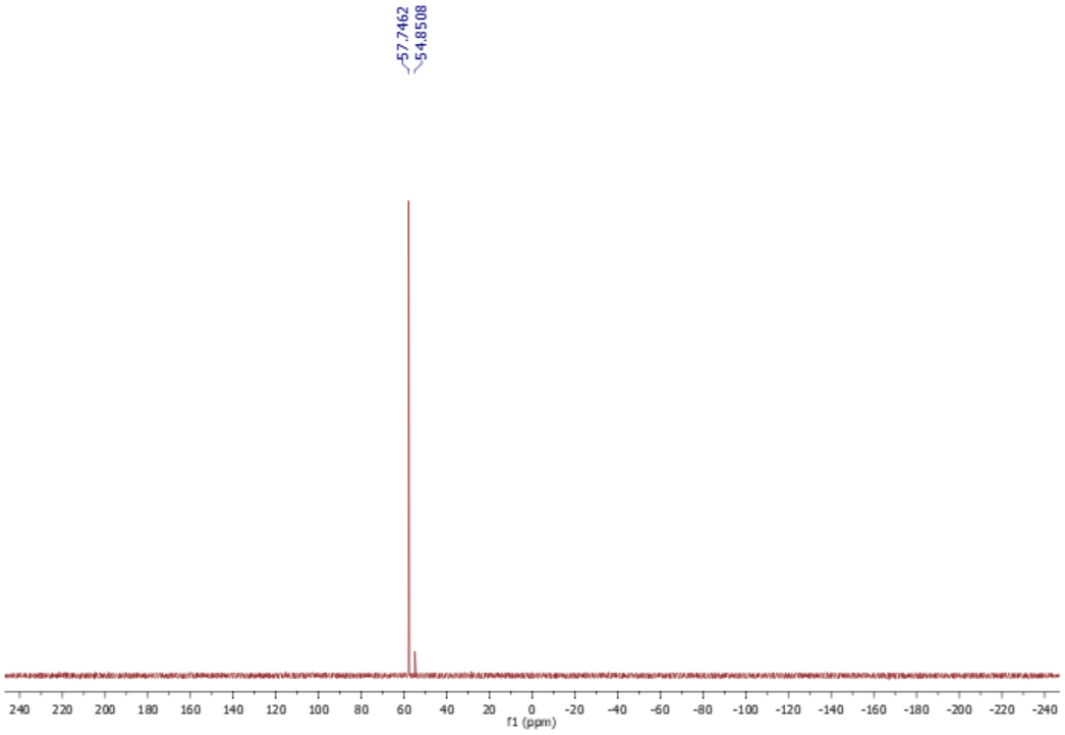
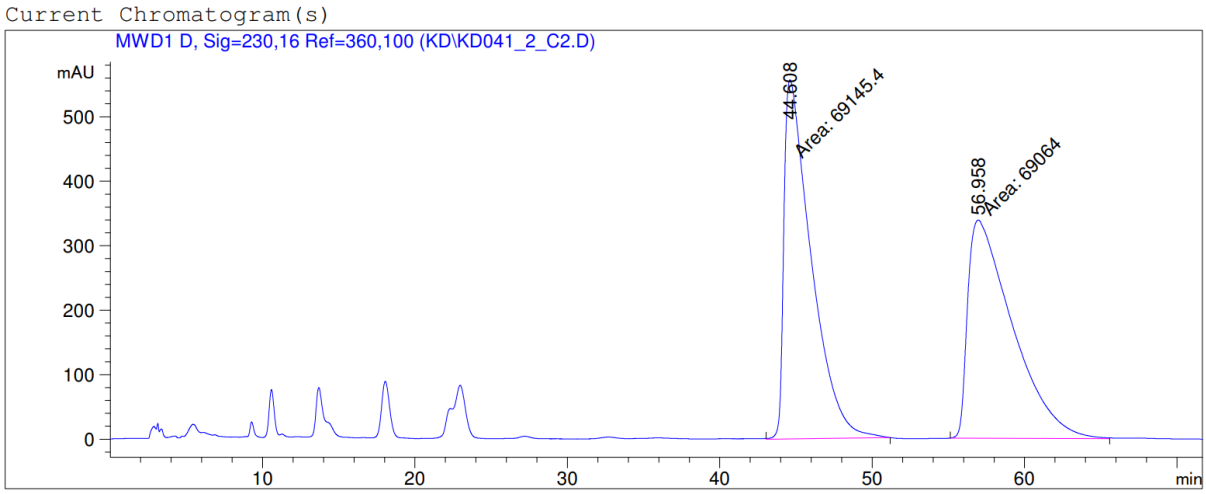


Figure S37. ^{31}P-NMR spectrum of palladium complex (*R*,*R*)-**22** (202 MHz, $CDCl_3$, 295 K).

5. HPLC chromatograms

The determination of ee for **6a** and **6c** (for Entries 1-16 and 19) was performed on Agilent 1200 Series chromatograph with Daicel Chiralpack ID column in *n*-hexane/isopropanol 85:15 solvent system at 25 °C with 1.2 ml/min flow rate. Injected volume: 20 µL in MeOH/DCM.

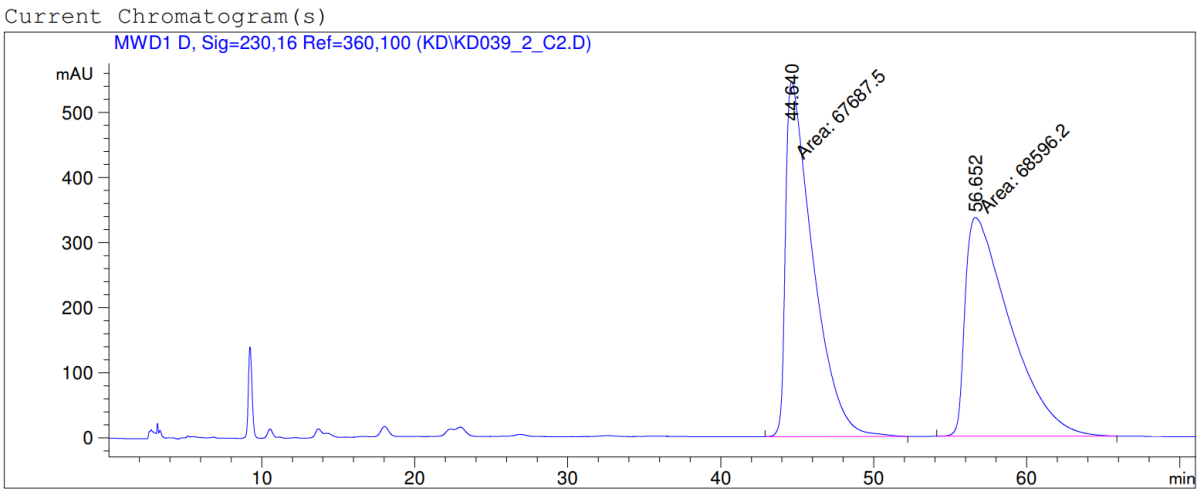
Table 1 Entry 1



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.608	MM	2.0689	6.91454e4	557.02429	50.0294
2	56.958	MM	3.4005	6.90640e4	338.50012	49.9706
Totals :				1.38209e5	895.52441	

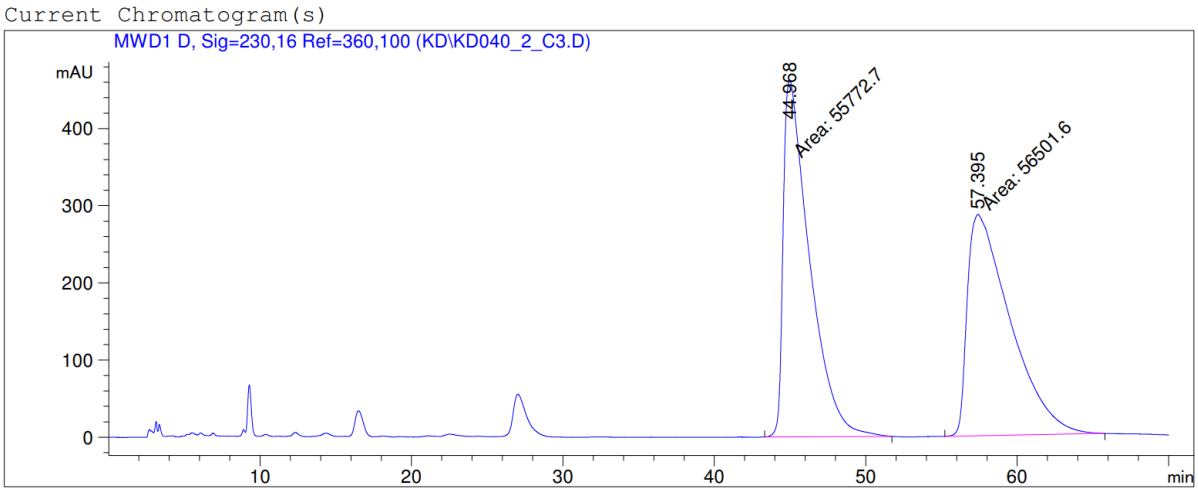
Table 1 Entry 2



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.640	MM	2.0675	6.76875e4	545.64996	49.6666
2	56.652	MM	3.4043	6.85962e4	335.82751	50.3334
Totals :				1.36284e5	881.47748	

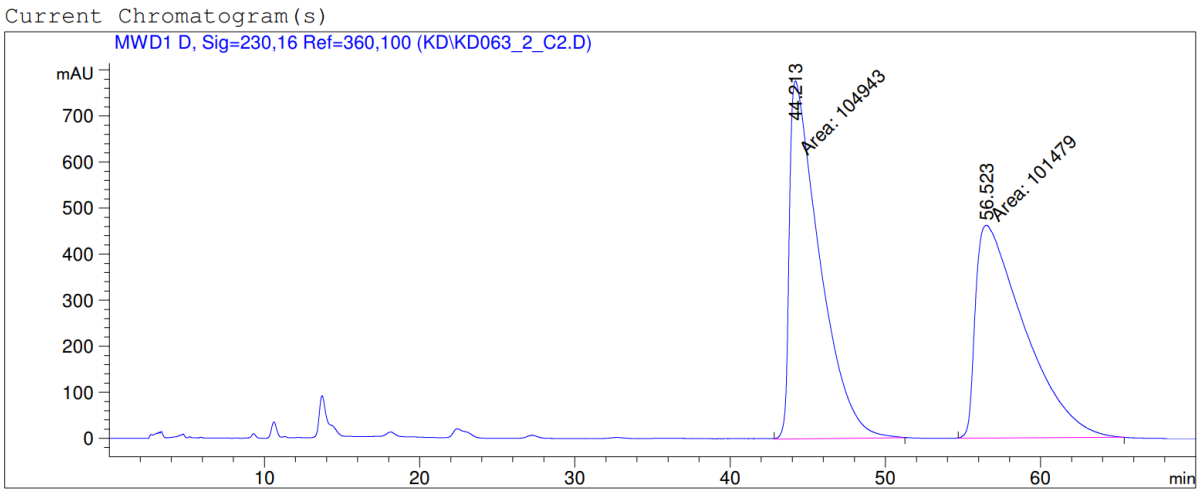
Table 1 Entry 3



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.968	MM	2.0089	5.57727e4	462.70401	49.6754
2	57.395	MM	3.2828	5.65016e4	286.85309	50.3246
Totals :				1.12274e5	749.55710	

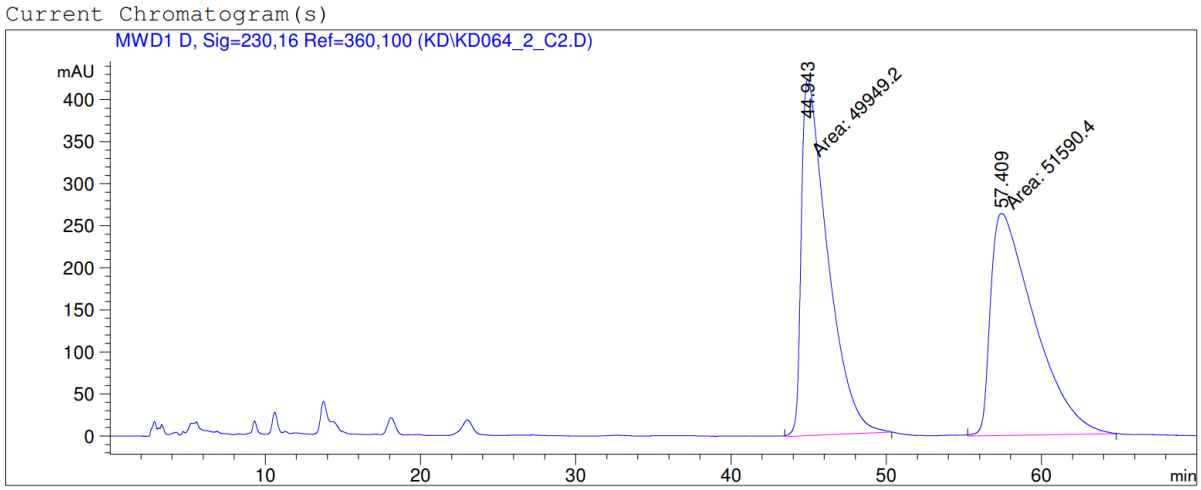
Table 1 Entry 4



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.213	MM	2.2502	1.04943e5	777.27722	50.8391
2	56.523	MM	3.6595	1.01479e5	462.17377	49.1609
Totals :				2.06423e5	1239.45099	

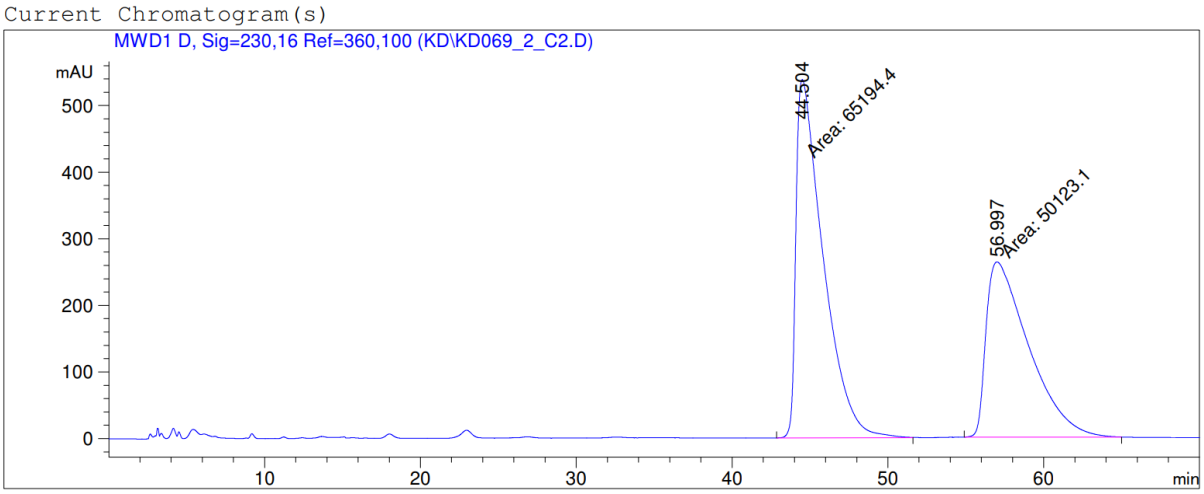
Table 1 Entry 5



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.943	MM	1.9624	4.99492e4	424.21576	49.1918
2	57.409	MM	3.2557	5.15904e4	264.10367	50.8082
Totals :				1.01540e5	688.31943	

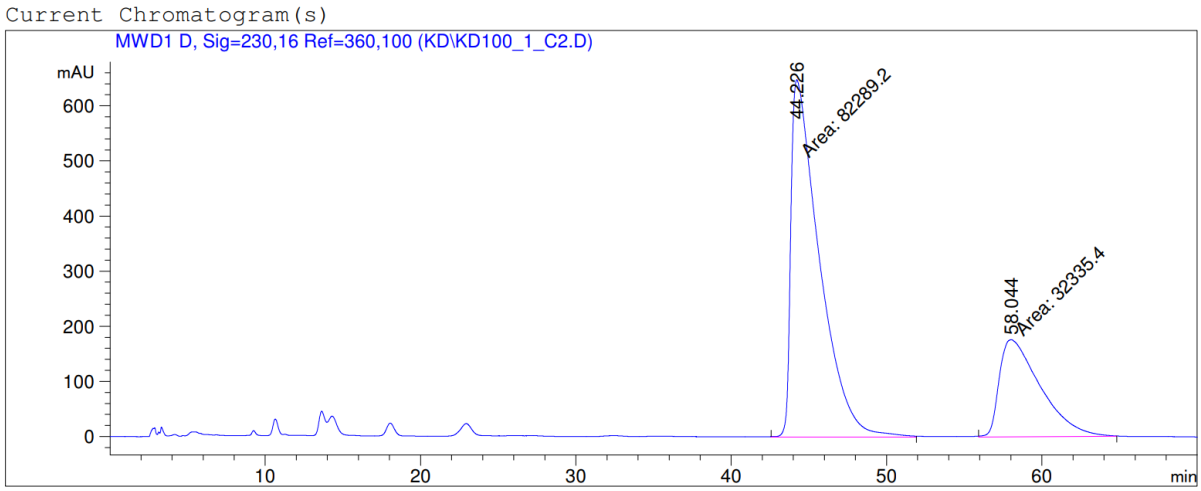
Table 1 Entry 6



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.504	MM	2.0188	6.51944e4	538.23322	56.5347
2	56.997	MM	3.1748	5.01231e4	263.13232	43.4653
Totals :				1.15318e5	801.36554	

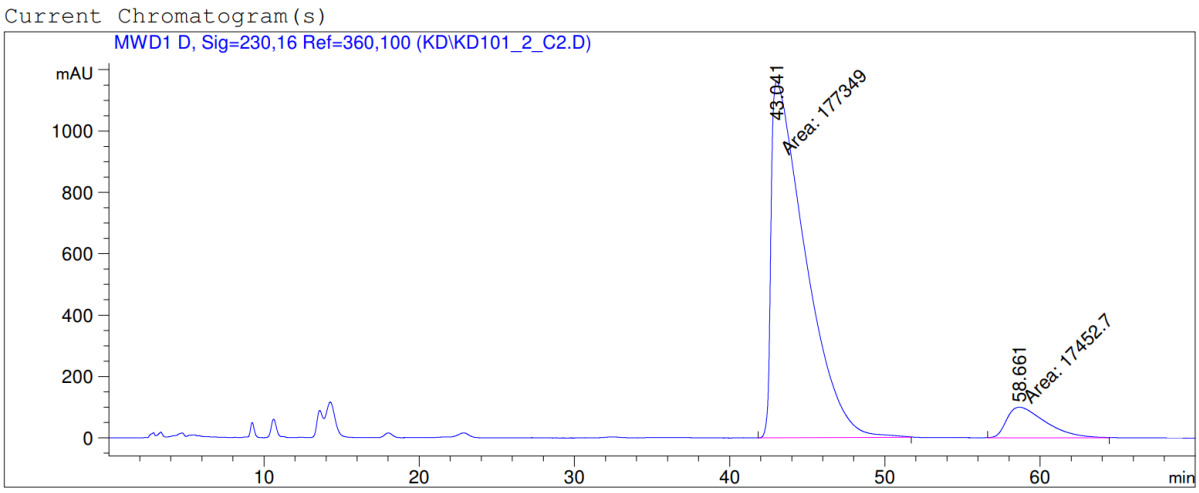
Table 1 Entry 7



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.226	MM	2.1163	8.22892e4	648.06805	71.7901
2	58.044	MM	3.0584	3.23354e4	176.20940	28.2099
Totals :				1.14625e5	824.27745	

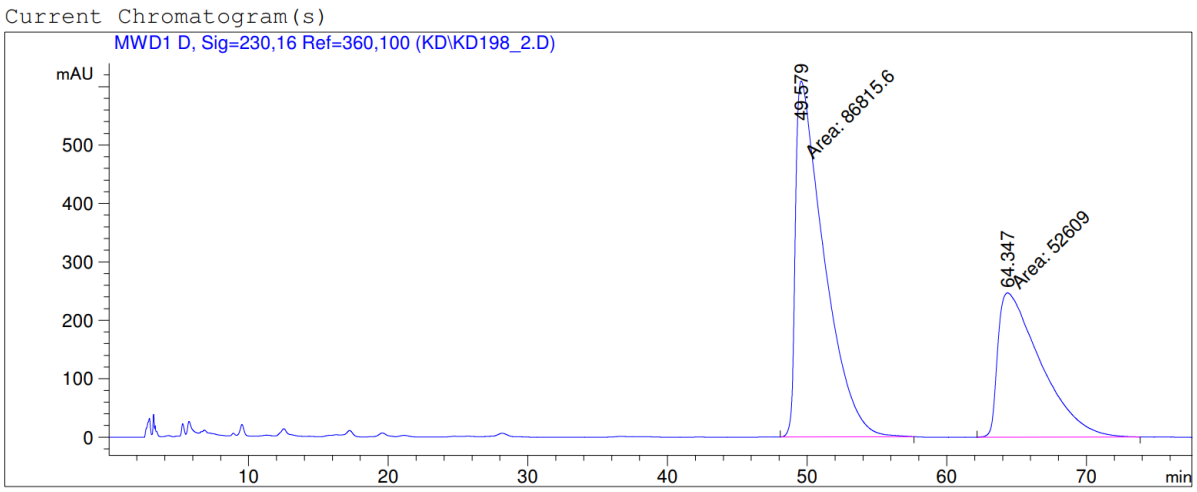
Table 1 Entry 8



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.041	MM	2.5417	1.77349e5	1162.92957	91.0408
2	58.661	MM	2.9068	1.74527e4	100.06971	8.9592
Totals :				1.94802e5	1262.99928	

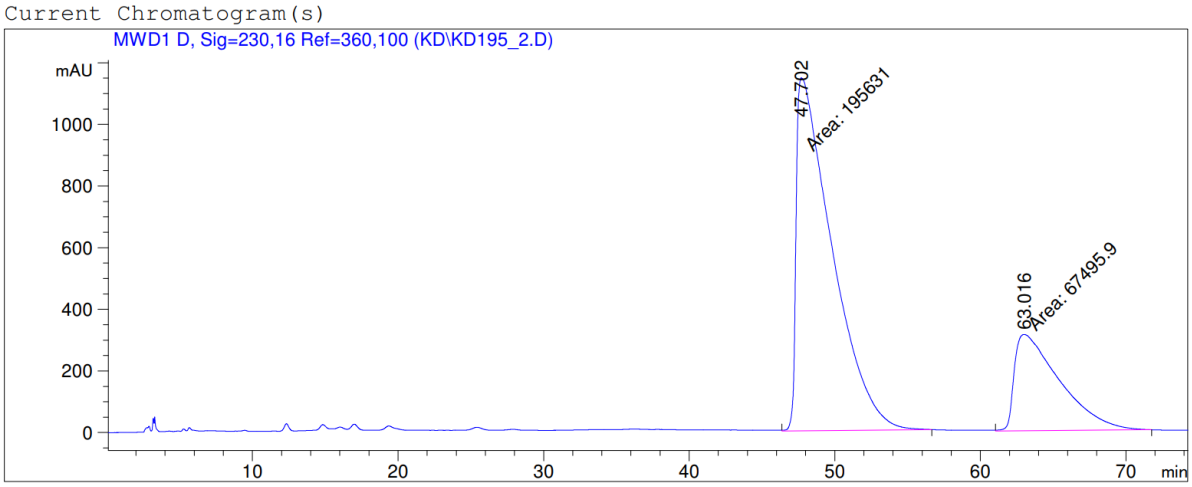
Table 1 Entry 9



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	49.579	MM	2.3757	8.68156e4	609.04187	62.2671
2	64.347	MM	3.5499	5.26090e4	246.99883	37.7329
Totals :				1.39425e5	856.04070	

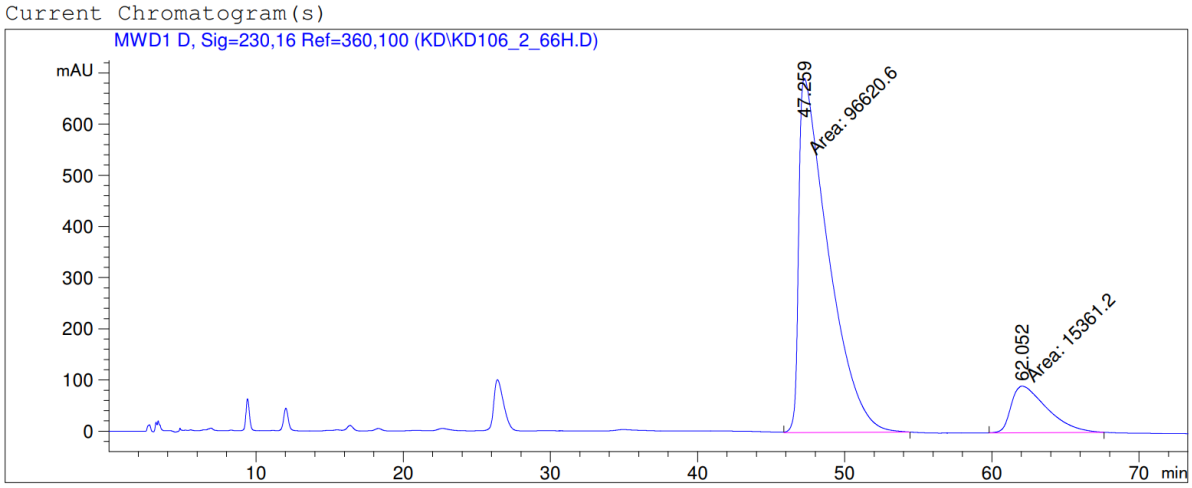
Table 1 Entry 10



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.702	MM	2.8475	1.95631e5	1145.06335	74.3486
2	63.016	MM	3.6049	6.74959e4	312.05606	25.6514
Totals :				2.63127e5	1457.11942	

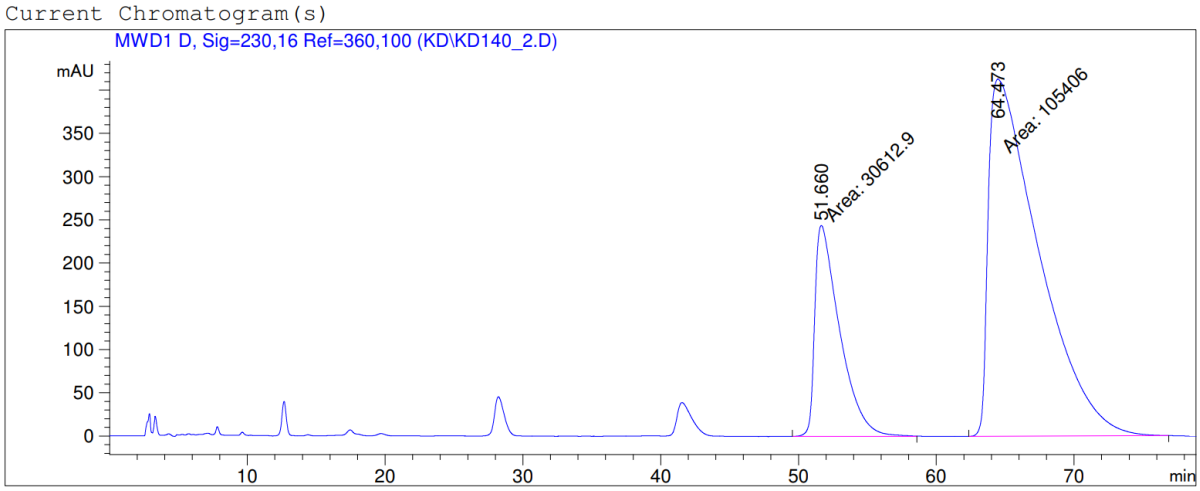
Table 1 Entry 11



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.259	MM	2.3254	9.66206e4	692.50116	86.2824
2	62.052	MM	2.8058	1.53612e4	91.24812	13.7176
Totals :				1.11982e5	783.74928	

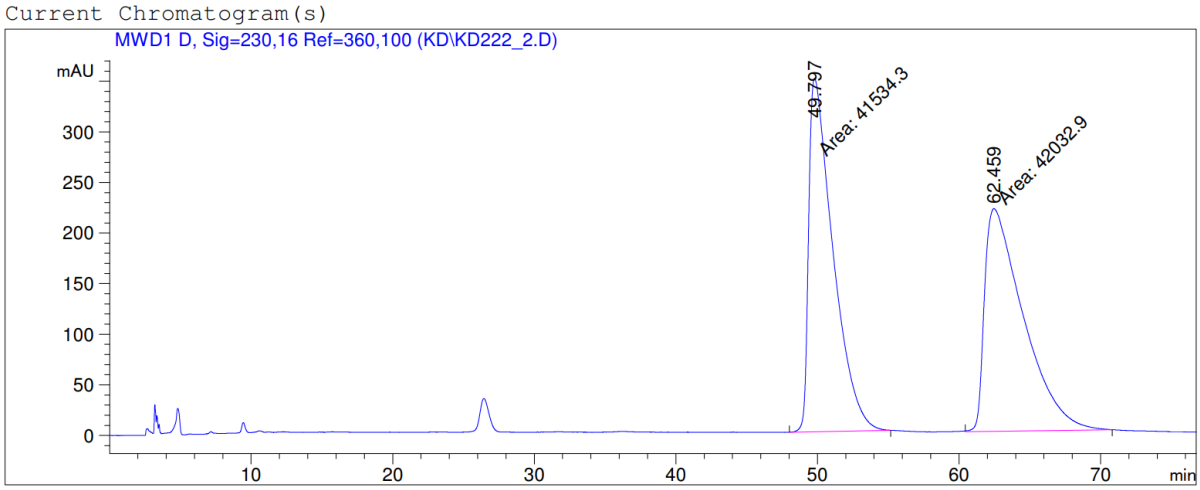
Table 1 Entry 12



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	51.660	MM	2.0915	3.06129e4	243.94930	22.5064
2	64.473	MM	4.2491	1.05406e5	413.44702	77.4936
Totals :				1.36019e5	657.39632	

Table 1 Entry 16

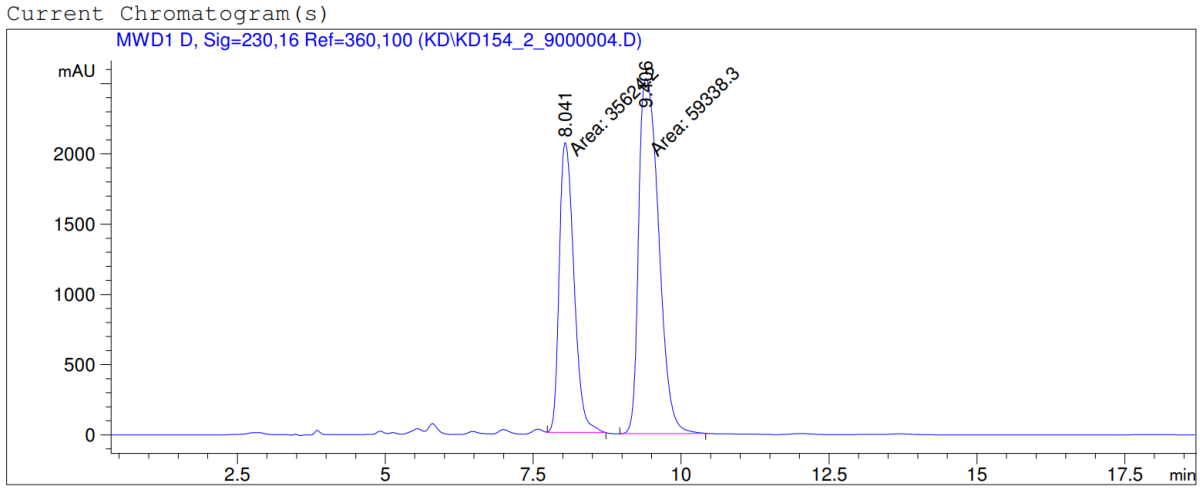


Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	49.797	MM	1.9819	4.15343e4	349.28497	49.7016
2	62.459	MM	3.1835	4.20329e4	220.05296	50.2984
Totals :				8.35672e4	569.33794	

Table 1 Entry 17

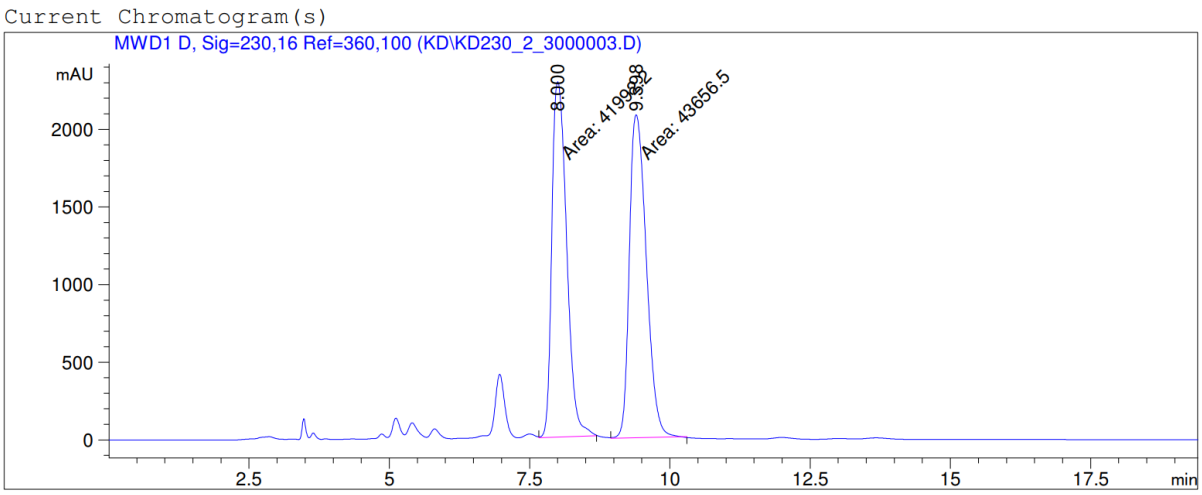
Only for Entry 17: the determination of ee for **6b** was performed on Agilent 1200 Series chromatograph with Daicel Chiralpack IF column in *n*-hexane/isopropanol 70:30 solvent system, at 25 °C with 1.2 ml/min flow rate. Injected volume: 20 µL in MeOH/DCM.



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.041	MM	0.2878	3.56242e4	2063.13428	37.5140
2	9.406	MM	0.3912	5.93383e4	2527.85889	62.4860
Totals :				9.49626e4	4590.99316	

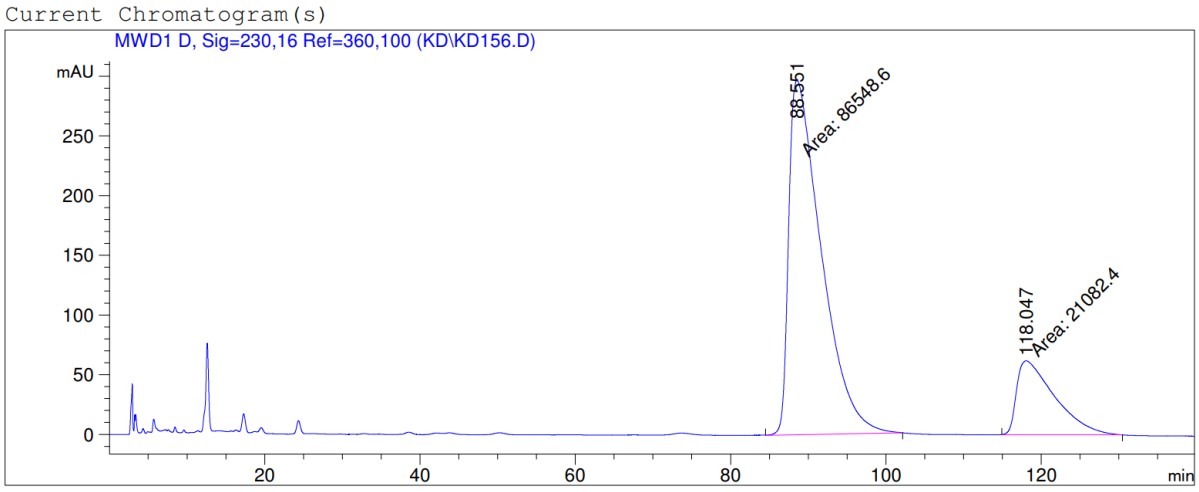
Racemic data for Entry 17



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.000	MM	0.3057	4.19922e4	2289.10327	49.0284
2	9.398	MM	0.3498	4.36565e4	2080.32104	50.9716
Totals :				8.56487e4	4369.42432	

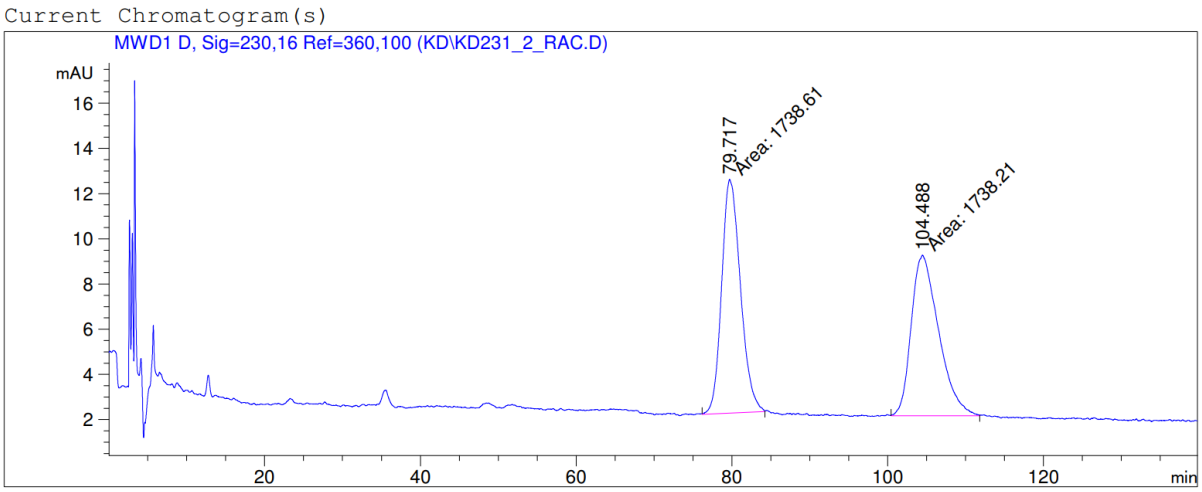
Table 1 Entry 19



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	88.551	MM	4.8427	8.65486e4	297.86652	80.4124
2	118.047	MM	5.6625	2.10824e4	62.05291	19.5876
Totals :				1.07631e5	359.91943	

Racemic data for Entry 19



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	79.717	MM	2.8004	1738.60901	10.34738	50.0057
2	104.488	MM	4.0757	1738.21021	7.10796	49.9943
Totals :				3476.81921	17.45534	

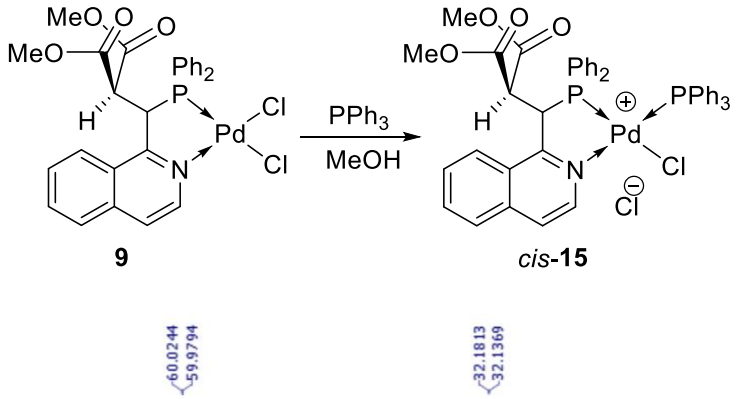
6. Coordination study

To investigate the coordination behavior of PN and PC metal complexes we added 1.0 equiv. PPh_3 to their solution (with respect to the metal centre of each complex) and stirred for 1 hour. The resulting products were scrutinized by $^{31}P\{^1H\}$ NMR spectroscopy. P_1 is the phosphorus atom in the PN ligand (**8**), P_2 is the phosphorus atom in PPh_3 in the figures.

$PNPd^+(PPh_3)Cl\ Cl^-$ (15)

To a recrystallized batch of $PNPdCl_2$ (**9**) 1.0 equiv. PPh_3 was added and stirred in methanol. The coupling constants occurred in the following way:

^{31}P NMR (162 MHz, MeOH) δ 60.00 (d, $^2J_{P1\text{-}P2}$ = 7.25 Hz), 32.16 (d, $^2J_{P1\text{-}P2}$ = 7.25 Hz).



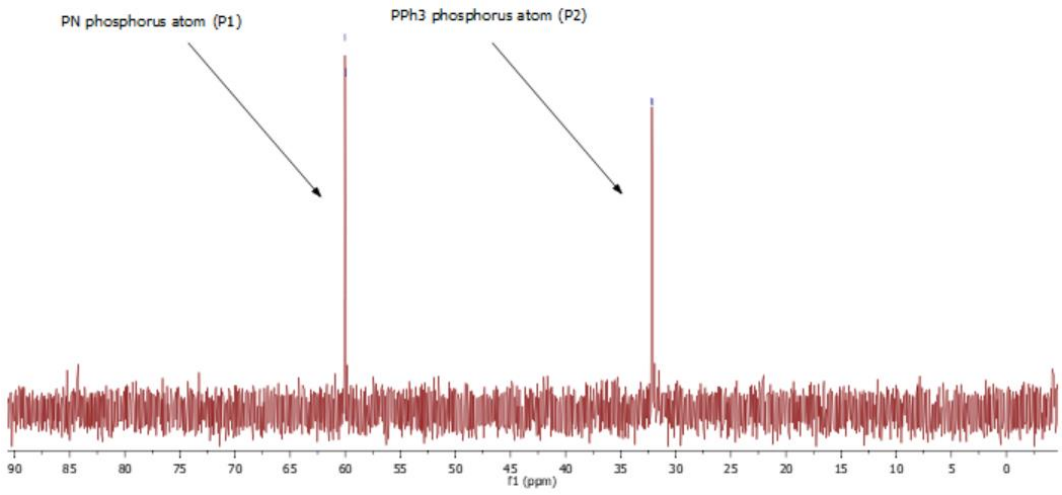


Figure S38. $^{31}P\{^1H\}$ spectrum of the coordination product of complex **9** and triphenylphosphine.

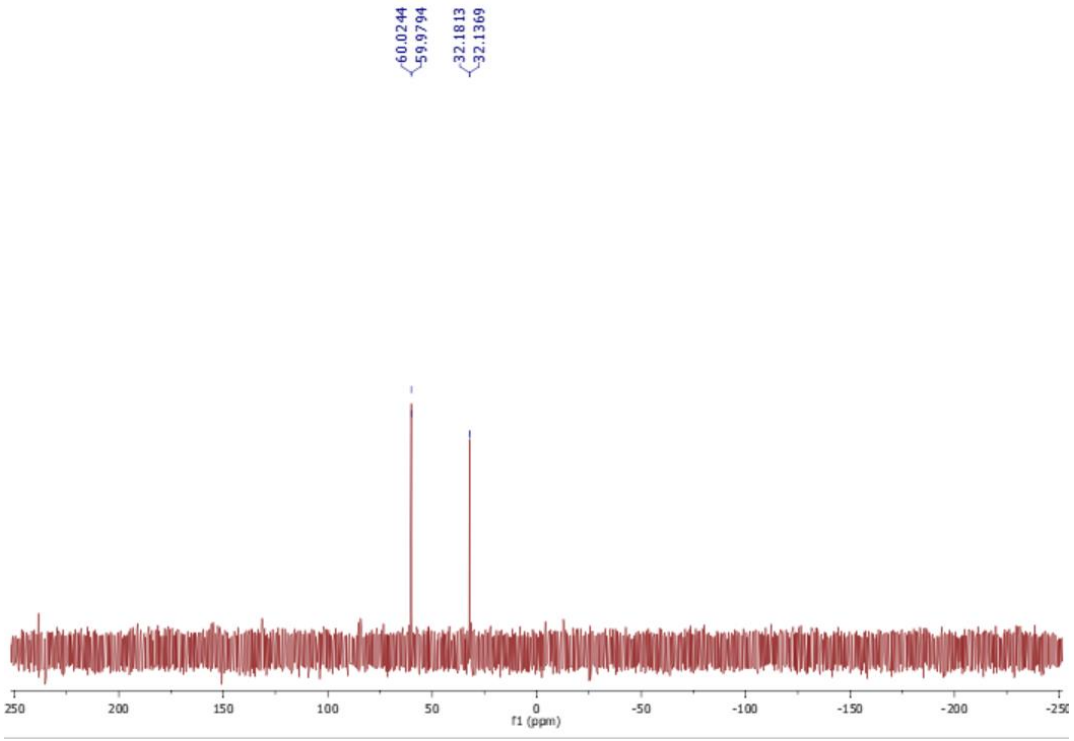
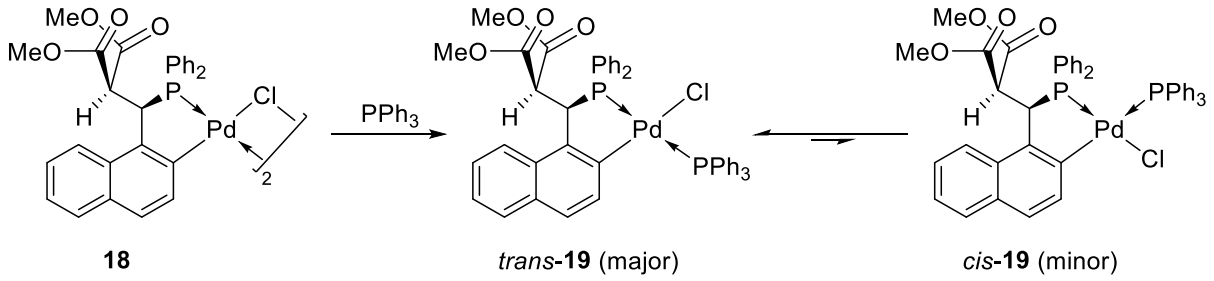


Figure S39. The full $^{31}P\{^{1}H\}$ spectrum of the coordination product of complex **9** and triphenylphosphine.

PCPd(PPh$_3$)Cl (19)

To a recrystallized batch of $[PCPdCl]_2$ dimer (**18**) 0.5 equiv. PPh_3 was added and stirred in dichloromethane. The coupling constants occurred in the following way:

^{31}P NMR (162 MHz, DCM) δ 63.65 (d, $^{2}J_{P1\text{-}P2}$ = 26.45 Hz), 54.69 (d, $^{2}J_{P1\text{-}P2}$ = 427.2 Hz), 26.36 (d, $^{2}J_{P1\text{-}P2}$ = 427.2 Hz), 17.72 (d, $^{2}J_{P1\text{-}P2}$ = 26.45 Hz).



18 *trans*-**19** (major) *cis*-**19** (minor)

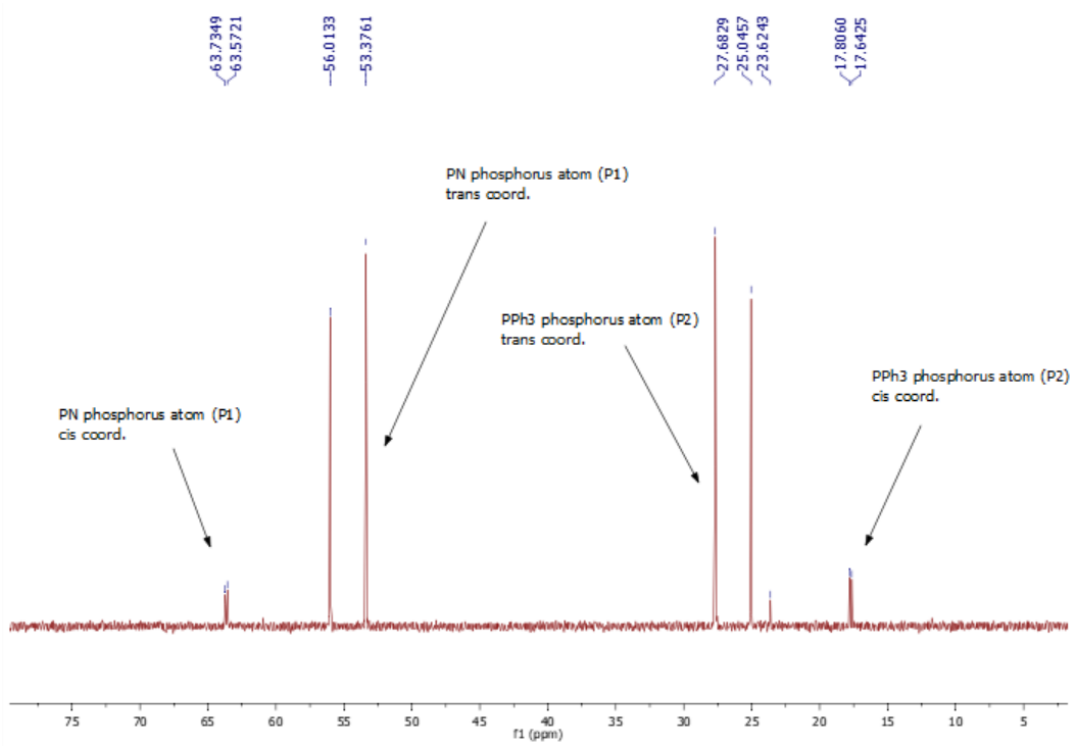


Figure S40. $^{31}P\{^{1}H\}$ spectrum of the coordination products of complex **18** and triphenylphosphine.

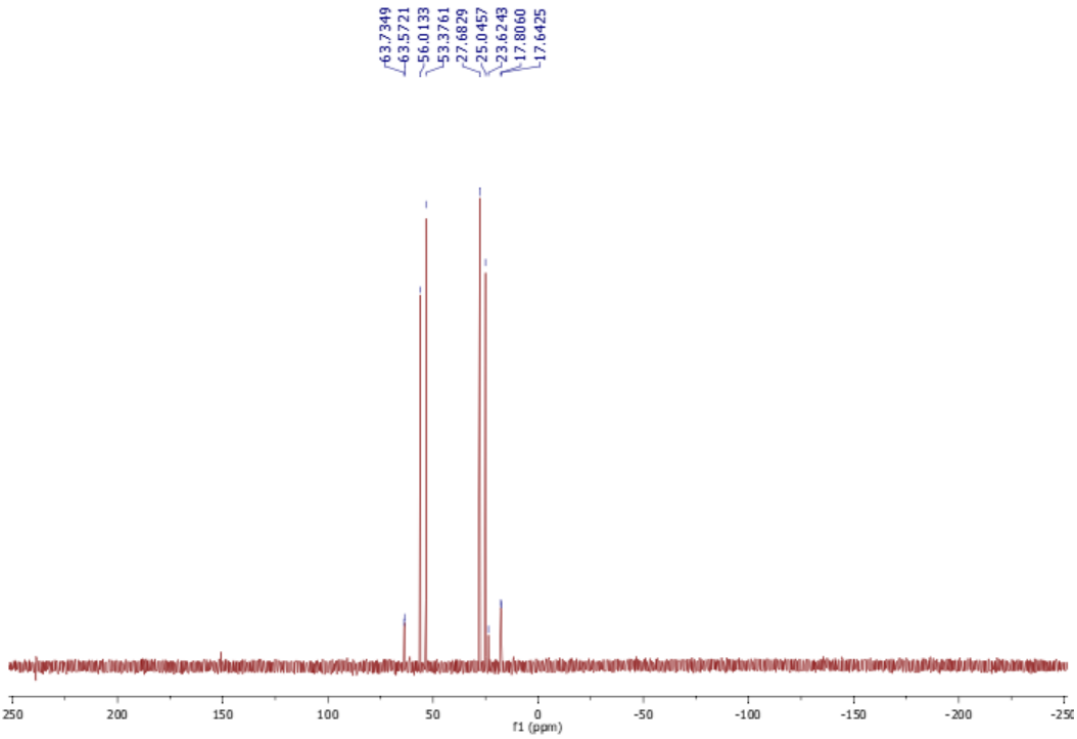
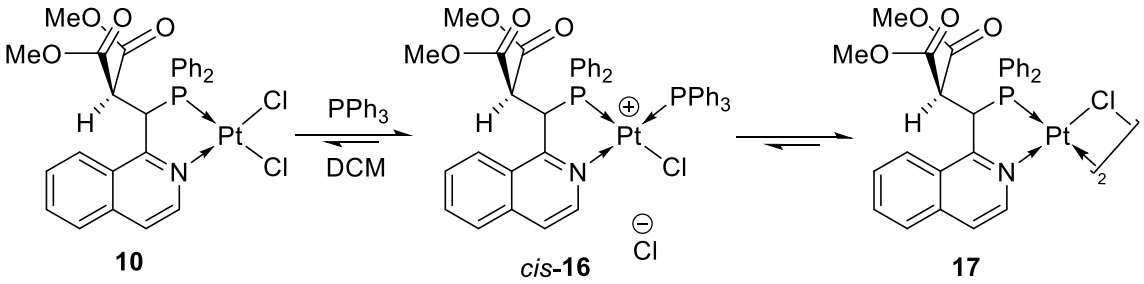


Figure S41. The full $^{31}P\{^{1}H\}$ spectrum of the coordination products of complex **18** and triphenylphosphine.

PNPt^{+}(PPh$_3$)Cl Cl^{-} (16)

To a recrystallized batch of PNPtCl$_2$ (**10**) 1.0 equiv. PPh$_3$ was added and stirred in dichloromethane. The coupling constants occurred in the following way:

^{31}P NMR (162 MHz, DCM) δ 39.76 (d, $^{2}J_{P1\text{-}P2}$ = 13.25 Hz), 39.74 (d, $^{1}J_{Pt\text{-}P1}$ = 3693.6 Hz, 13.2 Hz); 28.72 (s), 28.72 (d, $^{1}J_{Pt\text{-}P}$ = 3798.0 Hz); 14.00 (s), 14.00 (d, $^{1}J_{Pt\text{-}P}$ = 3680.0 Hz); 6.35 (d, $^{1}J_{Pt\text{-}P2}$ = 3445.6 Hz), 6.31 (d, $^{2}J_{P1\text{-}P2}$ = 13.25 Hz).



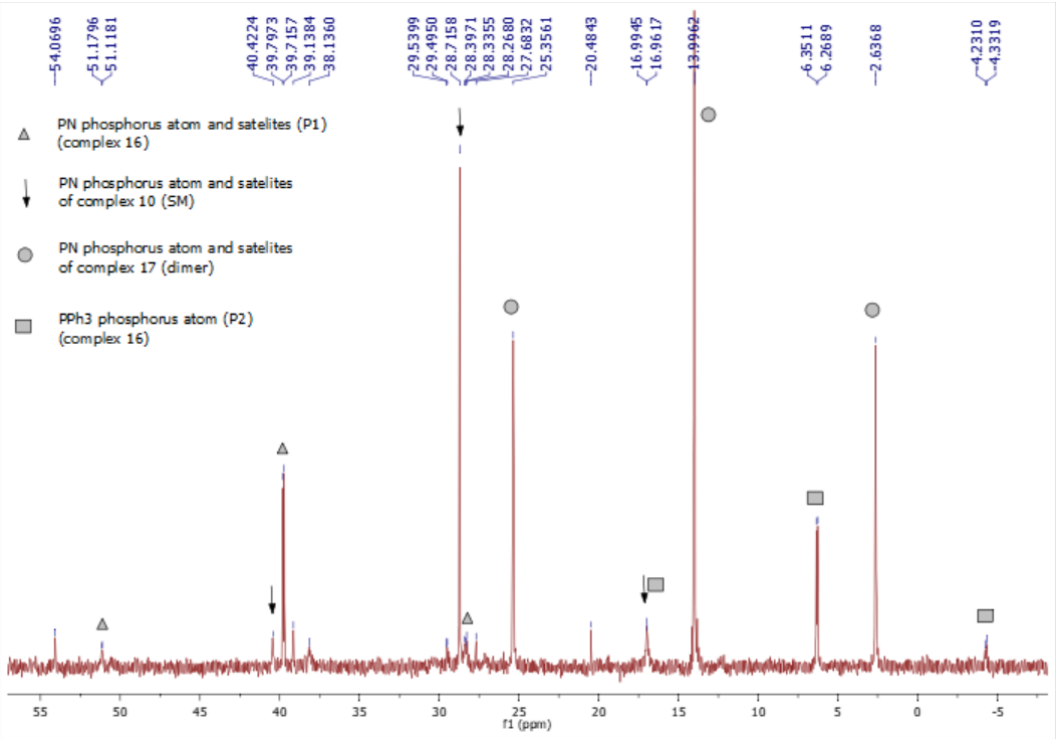


Figure S42. ^{31}P{^{1}H} spectrum of the coordination products of complex **10** and triphenylphosphine.

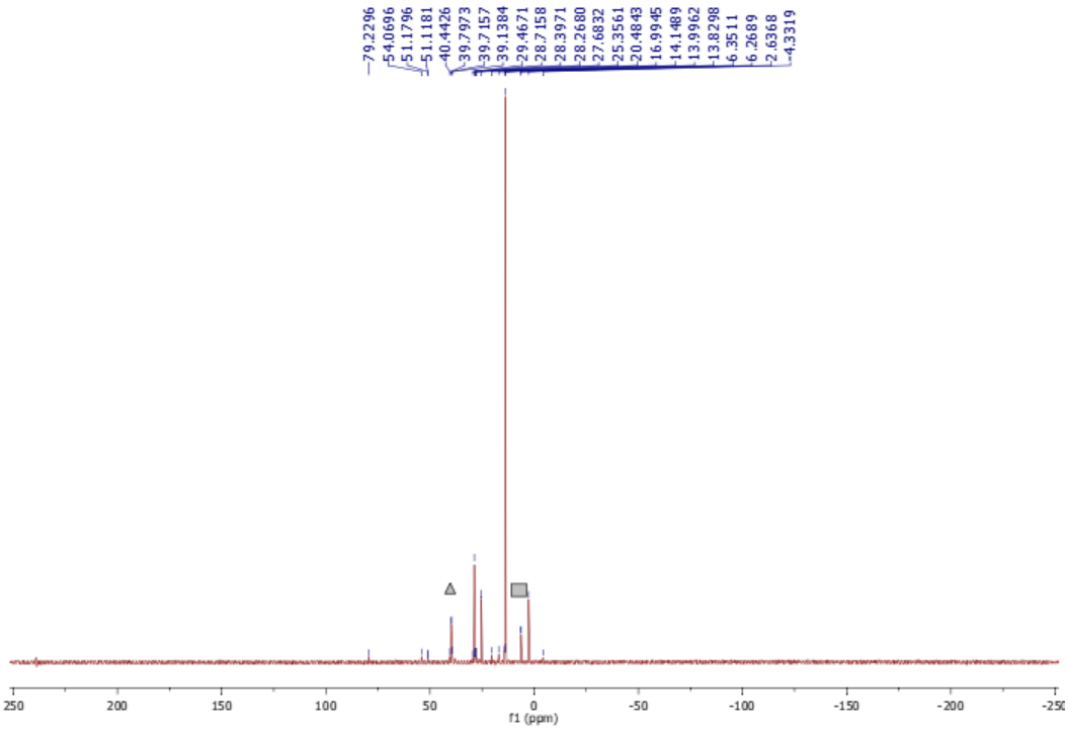


Figure S43. The full $^{31}P\{^{1}H\}$ spectrum of the coordination products of complex **10** and triphenylphosphine.

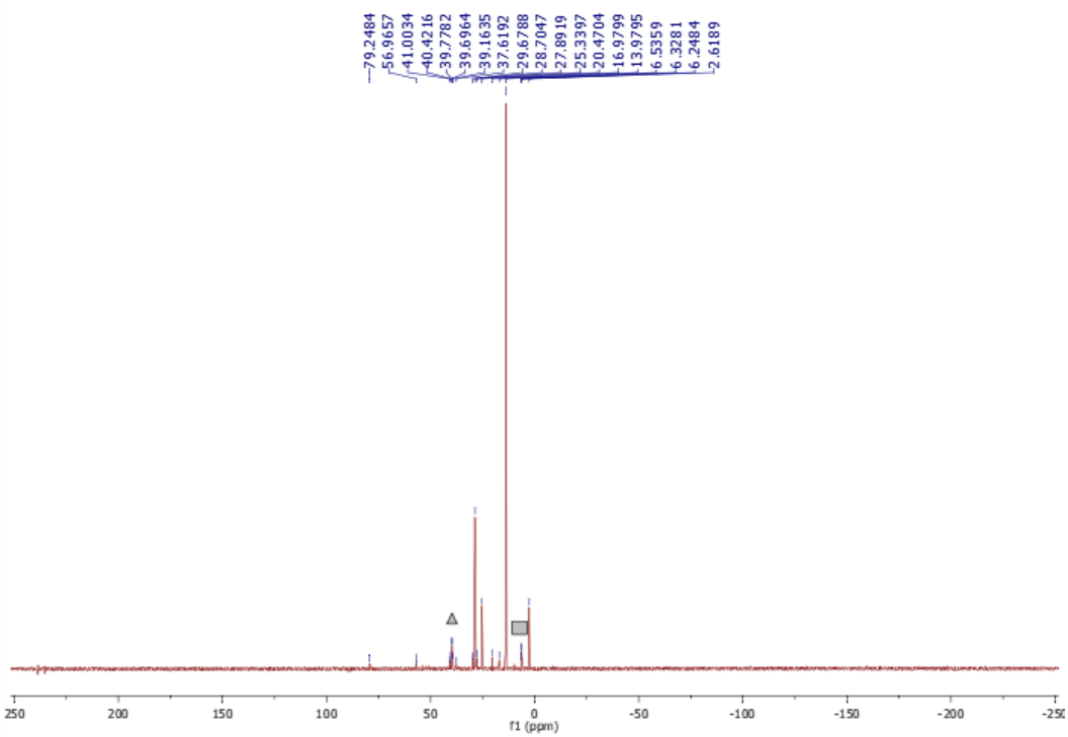


Figure S44. The full $^{31}P\{^{1}H\}$ spectrum of the coordination products of complex **10** and triphenylphosphine after 2 weeks.

PNRh(PPh$_3$)Cl (20)

To a newly synthesized batch of (**8**) PN ligand 0.5 equiv. [Rh(ethylene)Cl]$_2$ and 1.0 equiv. PPh$_3$ were added. The coupling constants occurred in the following way:

^{31}P NMR (162 MHz, DCM) δ 75.16 (dd, $^{1}J_{Rh\text{-}P1}$ = 200.3 Hz, $^{2}J_{P1\text{-}P2}$ = 41.55 Hz), 46.20 (dd, $^{1}J_{Rh\text{-}P2}$ = 171.9 Hz, $^{2}J_{P1\text{-}P2}$ = 41.55 Hz).

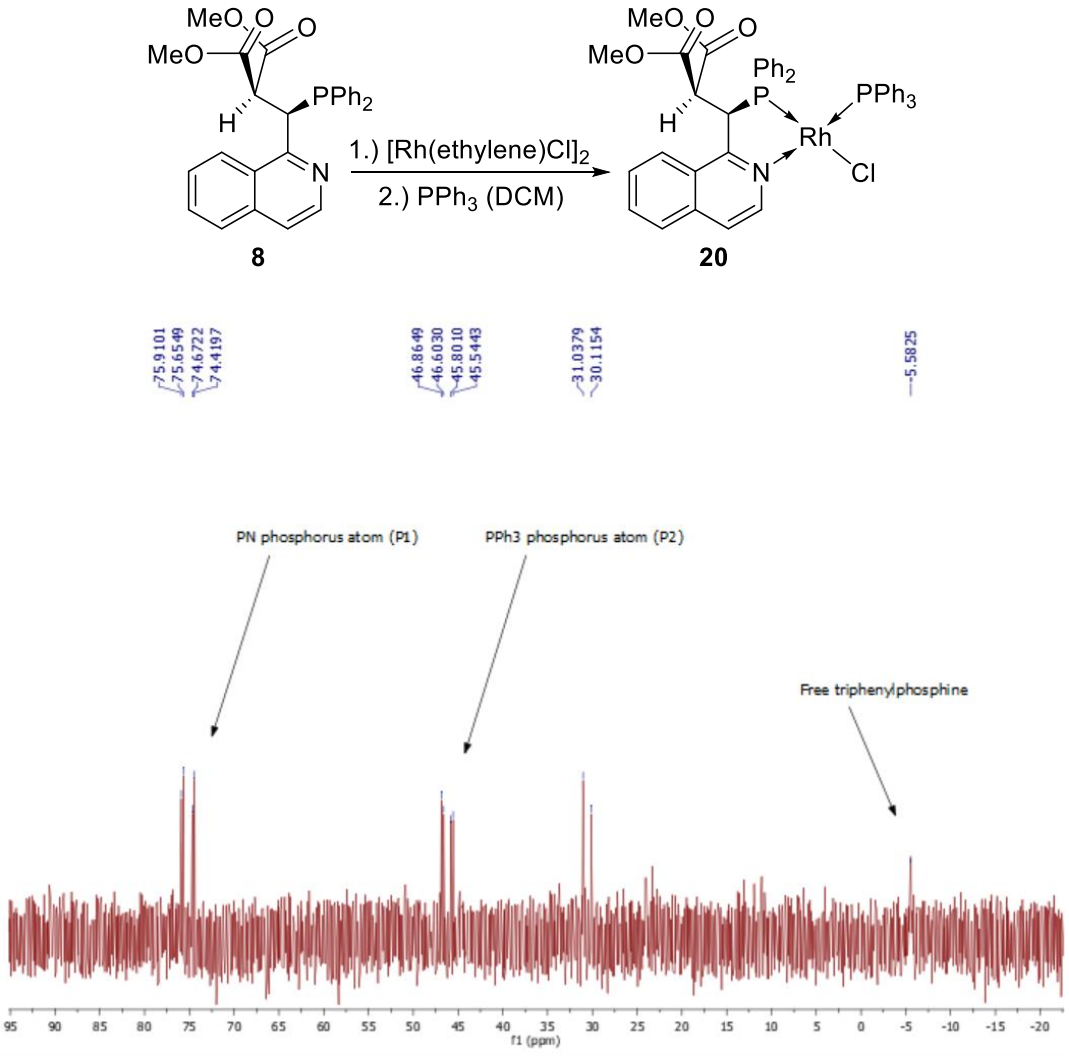


Figure S45. ^{31}P{^{1}H} spectrum of coordination product **20**.

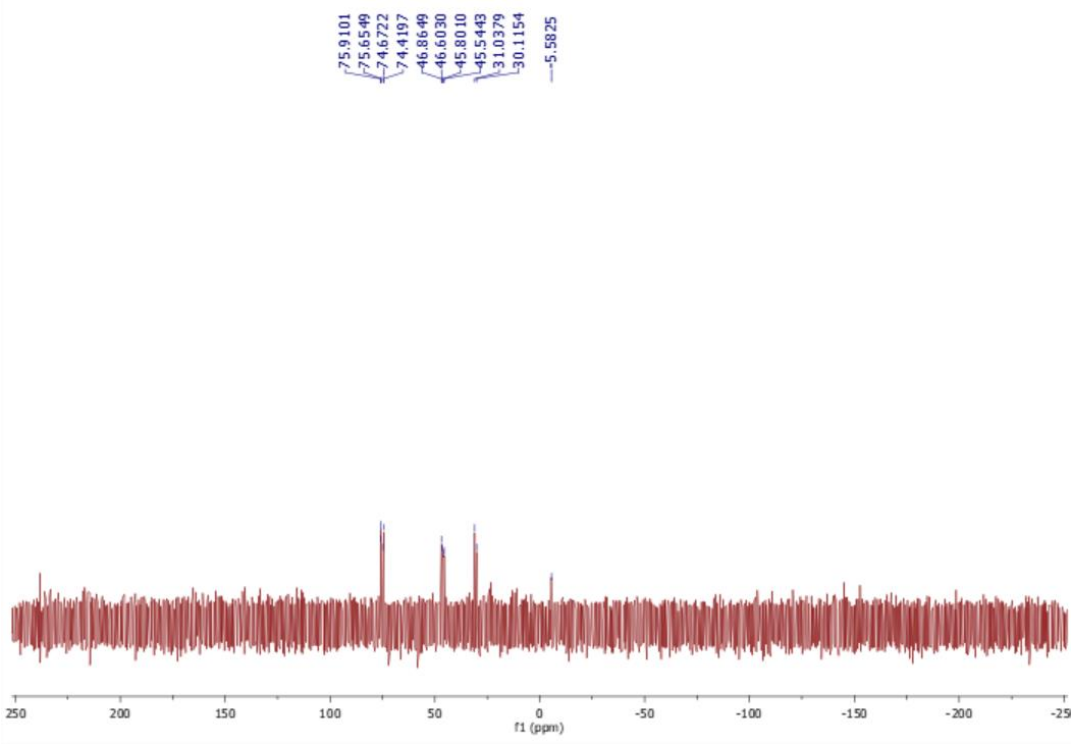
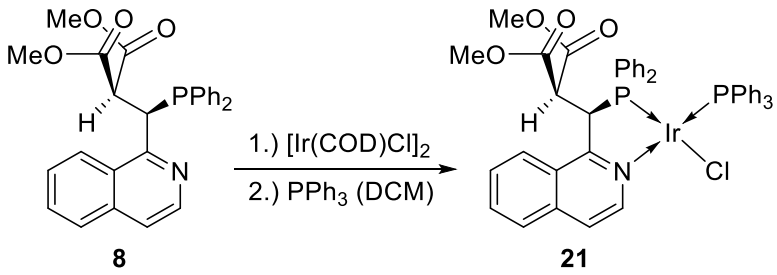


Figure S46. The full $^{31}P\{^{1}H\}$ spectrum of coordination product **20**.

PNIr(PPh$_3$)Cl (21)

To a newly synthesized batch of (**8**) PN ligand 0.5 equiv. $[Ir(COD)Cl]_2$ and 1.0 equiv. PPh_3 were added. The coupling constants occurred in the following way:

^{31}P NMR (162 MHz, DCM) δ 32.14 (d, $^{2}J_{P1\text{-}P2}$ = 32.8 Hz), -30.31 (d, $^{2}J_{P1\text{-}P2}$ = 32.8 Hz).



8 **21**

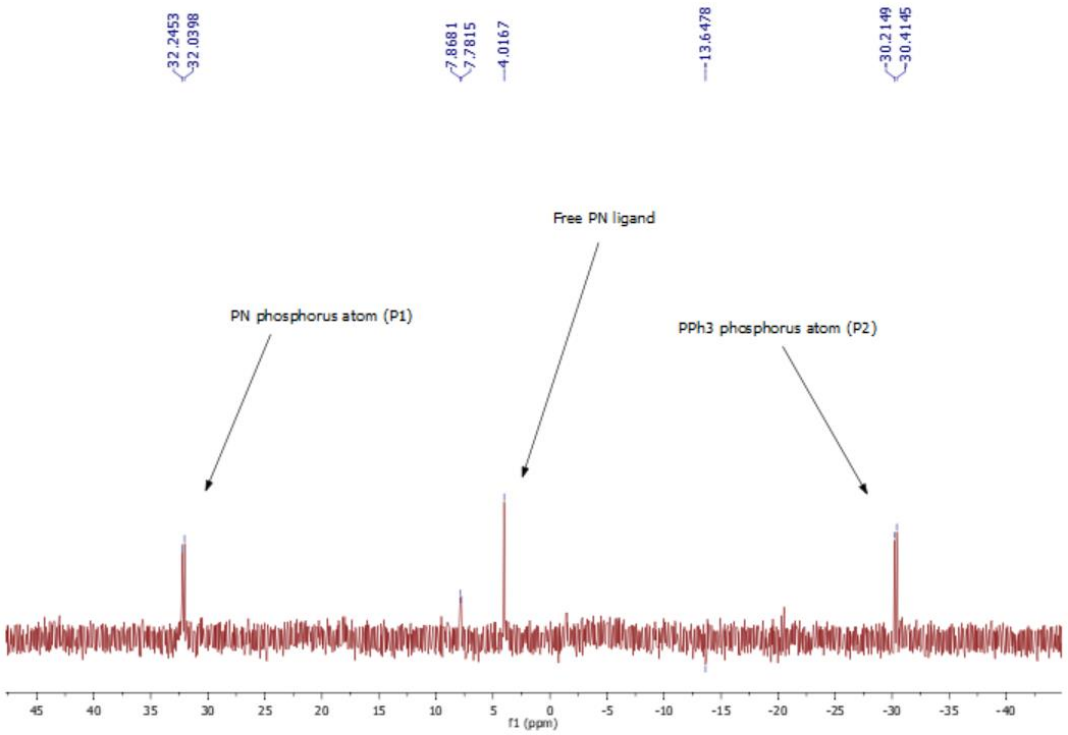


Figure S47. $^{31}P\{^{1}H\}$ spectrum of coordination product **21**.

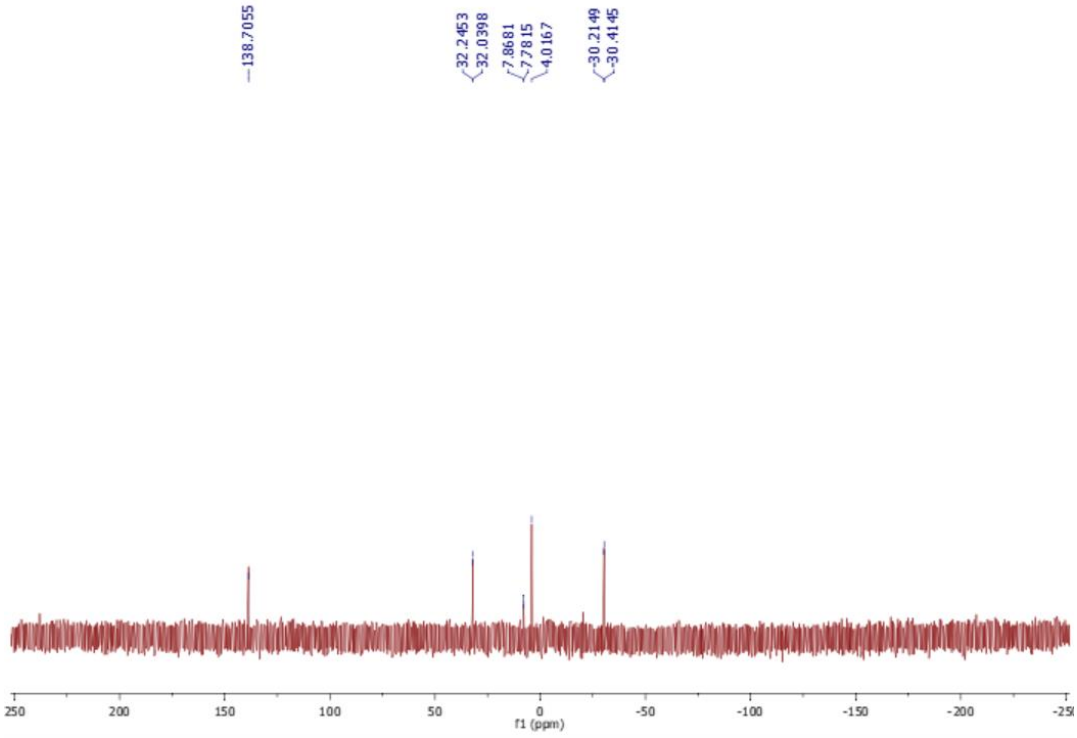


Figure S48. The full $^{31}P\{^{1}H\}$ spectrum of coordination product **21**.

7. NBO analysis and the XYZ coordinates for the optimized geometries

List of authors of Gaussian 09

Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

Computational Methods

Geometries were optimized with Gaussian 09.E01 by the DFT method B3LYP with general basis set. SDD effective core potential basis set was used for Pd and Pt atoms, and 6-31G* basis set was used for the remaining atoms. NBO analyses were performed to evalulate π-electron delocalization energies. In our NBO analysis, *d*(Pt) to π^*(C=N) interaction was split into two pairs, thus, we defined the sum of energies for these pairs as π-electron delocalization energy.

Results and Discussion

Complex **9** contains palladium metal center and ligand with coordinating N atom, and complex **18** contains the same metal center and ligand with coordinating C atom. The π-electron delocalization energy of complex **9** is 1.94 kcal/mol and that of complex **18** is 4.72 kcal/mol, which means there is a stronger *d*(Pd) to π^*(aromatic) interaction in complex **18**.

The only difference between complex **9** and **10** is the metal center. In complex **9**, the metal is Pd as there is Pt in complex **10**. The π-electron delocalization energy of complex **9** is 1.94 kcal/mol and that of complex **10** is 4.45 kcal/mol, which means there is a stronger *d*(metal) to π^*(C=N) interaction in complex **10**. The difference may arise from the fact that 5*d* atomic orbitals in Pt (compared to 4*d* orbitals in Pd) are more diffuse and easier to donate to the ligand's π^* orbital when the symmetry of orbitals matches up.

Table S1. Second-order interaction energy (E^2, kcal/mol) between donor and acceptor orbitals in complex **9**.

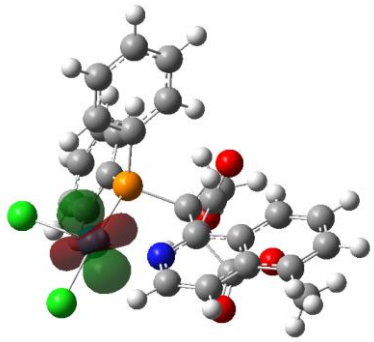
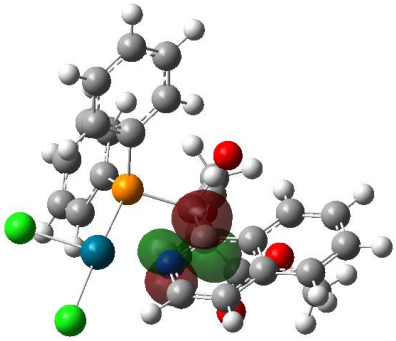
NBO Donor	NBO Acceptor	Type of NBO	E^2 / kcal/mol
 NBO132	 NBO147	NBO132: LP of Pd NBO147: BD* of C-N	1.94

Table S2. Second-order interaction energy (E^2, kcal/mol) between donor and acceptor orbitals in complex **10**.

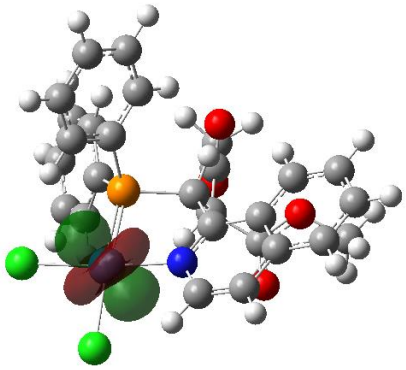
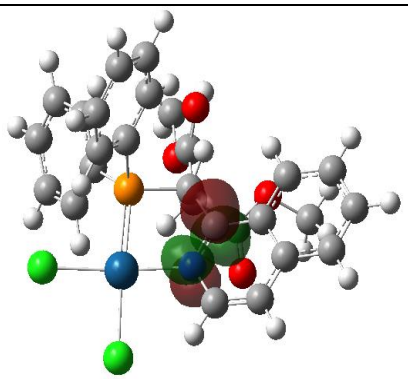
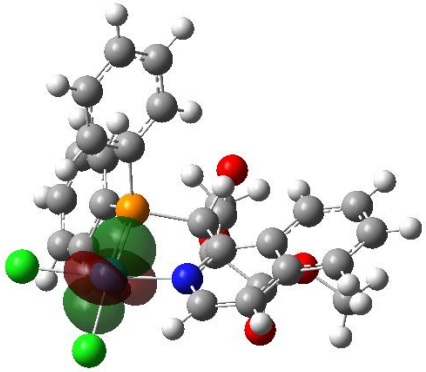
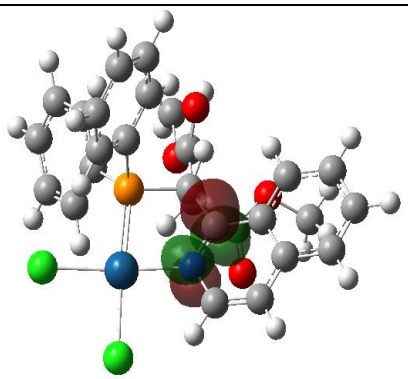
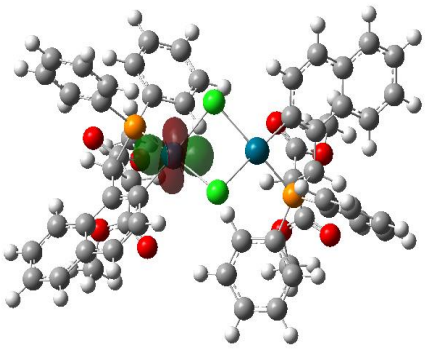
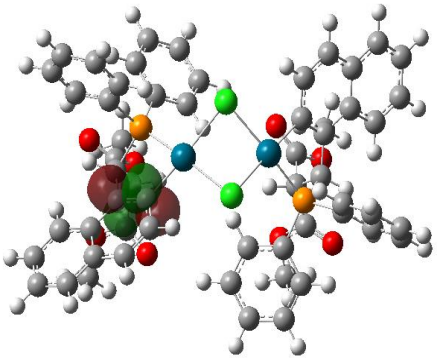
NBO Donor	NBO Acceptor	Type of NBO	E^2 / kcal/mol
 NBO134	 NBO147	NBO134: LP of Pt NBO147: BD* of C-N	3.10
 NBO138	 NBO147	NBO134: LP of Pt NBO147: BD* of C-N	1.35

Table S3. Second-order interaction energy (E^2, kcal/mol) between donor and acceptor orbitals in complex **18**.

NBO Donor	NBO Acceptor	Type of NBO	E^2 / kcal/mol
 NBO242	 NBO298	NBO242: LP of Pd NBO298: BD* of C-C	4.72

XYZ coordinates of the optimized geometries (Å)

Complex **9**

C	1.845310	-2.821550	-0.751908
H	1.370247	-3.621901	-1.307161
C	3.140243	-2.881026	-0.313429
H	3.735879	-3.765362	-0.518359
C	3.692987	-1.801303	0.413588
C	5.018907	-1.823925	0.919946
H	5.629907	-2.704780	0.742650
C	5.516392	-0.750943	1.622327
H	6.530821	-0.775129	2.010229
C	4.707845	0.390392	1.844105
H	5.108513	1.231969	2.401727
C	3.417975	0.444226	1.363983
H	2.830521	1.338549	1.535340
C	2.868821	-0.652298	0.636676
C	1.531652	-0.667873	0.122824
C	0.630098	0.539159	0.298198
H	0.862170	1.021990	1.246731
C	0.792302	1.646058	-0.795362
H	0.096510	1.470192	-1.620017
C	0.482079	3.012144	-0.177287
C	-0.118483	5.234375	-0.665161
H	-0.982107	5.226329	0.003578
H	-0.333168	5.810759	-1.564655
H	0.748101	5.642844	-0.139531
C	2.171523	1.652120	-1.470961
C	4.273717	2.712849	-1.593848
H	4.842994	1.809325	-1.363157

H	4.742269	3.589111	-1.146161
H	4.193737	2.824934	-2.677411
C	-2.254163	1.300175	-0.137971
C	-2.733164	2.263511	0.764229
H	-2.471759	2.208789	1.815338
C	-3.561508	3.292934	0.315552
H	-3.935926	4.027318	1.023636
C	-3.918881	3.370088	-1.032870
H	-4.570421	4.168703	-1.377415
C	-3.455427	2.408806	-1.932726
H	-3.748679	2.449618	-2.977683
C	-2.635596	1.371422	-1.488699
H	-2.320882	0.596029	-2.180172
C	-1.473716	-0.378092	2.159300
C	-2.253581	-1.493628	2.507152
H	-2.647848	-2.138250	1.726730
C	-2.527637	-1.761966	3.849144
H	-3.130575	-2.627231	4.109336
C	-2.026857	-0.927304	4.849734
H	-2.237652	-1.142142	5.893863
C	-1.254247	0.185597	4.509257
H	-0.866252	0.839670	5.285313
C	-0.977170	0.463695	3.170140
H	-0.387831	1.342273	2.921574
Cl	-0.776612	-3.778129	-2.368879
Cl	-3.347759	-2.043278	-1.097531
N	1.044935	-1.735222	-0.520584
O	0.160609	3.898263	-1.125556
O	0.534791	3.263989	1.010083
O	2.961747	2.636053	-1.001657
O	2.500194	0.863477	-2.325140
P	-1.161554	-0.077451	0.380717
Pd	-1.032408	-1.908945	-0.942597

Complex **10**

Pt	-1.194929	-1.605089	-0.711959
C	0.836635	0.625626	0.318597
C	1.543005	-0.709921	0.195058
C	2.886350	-0.865475	0.664344
C	3.618802	0.178784	1.301822
C	4.904829	-0.037317	1.745380
C	5.528568	-1.297102	1.574579
C	4.851769	-2.324206	0.958389
C	3.525144	-2.134594	0.492199
C	2.791132	-3.160545	-0.146690
C	1.502639	-2.938771	-0.546198
C	1.101628	1.615503	-0.863237
C	2.452991	1.393744	-1.558098
C	4.676274	2.149356	-1.775558

C	0.981446	3.053331	-0.351961
C	0.649450	5.288462	-1.008827
C	-1.944658	1.752080	-0.053981
C	-2.367520	1.804900	-1.393249
C	-3.071546	2.913524	-1.863681
C	-3.375755	3.968557	-1.001880
C	-2.975842	3.913674	0.335650
C	-2.264345	2.811408	0.810546
C	-1.279460	0.122507	2.310560
C	-0.645140	0.964938	3.240524
C	-0.888633	0.807587	4.605587
C	-1.765053	-0.184321	5.052122
C	-2.401156	-1.019682	4.132100
C	-2.160321	-0.872442	2.765181
Cl	-1.252105	-3.576622	-2.066671
Cl	-3.526907	-1.448329	-0.875145
N	0.875502	-1.732965	-0.360125
O	2.657091	0.511478	-2.357982
O	3.376865	2.292924	-1.168656
O	1.087973	3.387427	0.811066
O	0.758042	3.896862	-1.365158
P	-1.015956	0.273659	0.504805
H	1.181271	1.130543	1.219970
H	3.176510	1.159300	1.432655
H	5.445658	0.767327	2.235066
H	6.542951	-1.448461	1.932540
H	5.319415	-3.295153	0.819910
H	3.241438	-4.134078	-0.314195
H	0.896552	-3.692530	-1.033210
H	0.366315	1.461253	-1.657280
H	5.132906	1.207738	-1.461329
H	5.258272	2.998427	-1.417467
H	4.590365	2.166738	-2.864173
H	-0.202342	5.436519	-0.341228
H	0.497775	5.816520	-1.949877
H	1.564420	5.626856	-0.516556
H	-2.175842	0.963883	-2.051883
H	-3.399432	2.939189	-2.898795
H	-3.937264	4.824644	-1.366431
H	-3.226830	4.723310	1.015585
H	-1.970672	2.777321	1.853856
H	0.028808	1.750361	2.907915
H	-0.393230	1.460593	5.318891
H	-1.950108	-0.305643	6.115995
H	-3.083223	-1.792359	4.475197
H	-2.652357	-1.522462	2.047479

Complex **18**

C	-3.129586	1.312792	-1.234563
C	-3.218977	2.512869	-1.994133
H	-2.450040	2.742057	-2.722546
C	-4.265209	3.385820	-1.815064
H	-4.320358	4.299037	-2.404305
C	-5.296796	3.113625	-0.879816
C	-6.396959	3.996404	-0.718073
H	-6.425456	4.901620	-1.320487
C	-7.410392	3.717376	0.170804
H	-8.249281	4.399230	0.281330
C	-7.357951	2.530307	0.937031
H	-8.162681	2.300721	1.630995
C	-6.298490	1.655739	0.809711
H	-6.285000	0.761632	1.422505
C	-5.228046	1.913607	-0.095645
C	-4.108556	1.029070	-0.280774
C	-3.991097	-0.253406	0.519962
H	-4.968607	-0.680486	0.746965
C	-3.222972	-0.150481	1.875179
H	-2.144756	-0.200152	1.703709
C	-3.425552	1.188958	2.590410
C	-4.815423	2.406185	4.057579
H	-3.954508	2.745408	4.638345
H	-5.659282	2.181598	4.710027
H	-5.089213	3.168705	3.324691
C	-3.622891	-1.305601	2.796506
C	-3.001797	-2.502966	4.726118
H	-3.976508	-2.364797	5.201015
H	-2.201382	-2.450040	5.464129
H	-2.983118	-3.463382	4.205509
C	-2.287140	-2.777271	0.261791
C	-0.990513	-2.572888	0.763297
H	-0.468762	-1.644449	0.553535
C	-0.342256	-3.568553	1.495098
H	0.660246	-3.383612	1.868754
C	-0.980860	-4.790682	1.715311
H	-0.474607	-5.575588	2.271422
C	-2.263035	-5.012417	1.205374
H	-2.757405	-5.967102	1.364637
C	-2.916020	-4.013125	0.483405
H	-3.910219	-4.201100	0.093408
C	-4.403208	-2.156653	-1.690521
C	-4.194037	-2.287612	-3.072056
H	-3.267750	-1.928652	-3.511911
C	-5.173781	-2.868514	-3.878753
H	-5.003206	-2.962051	-4.947572
C	-6.369352	-3.318243	-3.315705
H	-7.133670	-3.764991	-3.945851

C	-6.584936	-3.190180	-1.941571
H	-7.514820	-3.537656	-1.499735
C	-5.608128	-2.613087	-1.129117
H	-5.784226	-2.528524	-0.060224
C	3.129866	-1.312483	-1.234676
C	3.219398	-2.512318	-1.994594
H	2.450584	-2.741303	-2.723199
C	4.265628	-3.385298	-1.815635
H	4.320878	-4.298339	-2.405139
C	5.297076	-3.113349	-0.880171
C	6.397238	-3.996155	-0.718543
H	6.425826	-4.901197	-1.321214
C	7.410556	-3.717362	0.170533
H	8.249444	-4.399232	0.280970
C	7.358000	-2.530512	0.937092
H	8.162644	-2.301110	1.631216
C	6.298535	-1.655932	0.809898
H	6.284955	-0.762006	1.422953
C	5.228197	-1.913555	-0.095659
C	4.108696	-1.029003	-0.280663
C	3.991035	0.253243	0.520433
H	4.968472	0.680244	0.747895
C	3.222439	0.149837	1.875341
H	2.144278	0.199209	1.703444
C	3.425163	-1.189685	2.590398
O	4.511426	-1.170463	3.385957
C	3.621675	1.304821	2.797140
C	2.999518	2.501463	4.726864
H	3.973760	2.363082	5.202671
H	2.198415	2.448582	5.464131
H	2.981491	3.461926	4.206335
C	4.403744	2.156994	-1.689563
C	4.194849	2.288134	-3.071130
H	3.268668	1.929194	-3.511220
C	5.174737	2.869173	-3.877550
H	5.004379	2.962850	-4.946391
C	6.370185	3.318853	-3.314197
H	7.134618	3.765717	-3.944121
C	6.585496	3.190596	-1.940040
H	7.515286	3.538026	-1.497970
C	5.608541	2.613367	-1.127860
H	5.784447	2.528636	-0.058949
C	2.287214	2.777333	0.262356
C	0.990495	2.572870	0.763573
H	0.468796	1.644451	0.553618
C	0.342068	3.568460	1.495335
H	-0.660503	3.383455	1.868777
C	0.980594	4.790585	1.715779
H	0.474204	5.575431	2.271852
C	2.262864	5.012401	1.206110

H	2.757181	5.967082	1.365555
C	2.916017	4.013185	0.484189
H	3.910285	4.201225	0.094402
Cl	-0.024050	1.655254	-2.519373
Cl	0.024442	-1.654719	-2.519666
O	-4.511774	1.169764	3.386025
O	-2.697577	2.147203	2.463925
O	-2.738211	-1.434725	3.798546
O	-4.601621	-2.008265	2.657743
O	2.736644	1.433331	3.798955
O	4.600186	2.007885	2.658893
P	-3.083382	-1.406493	-0.667180
P	3.083677	1.406681	-0.666669
Pd	-1.670651	0.003408	-1.715137
Pd	1.670988	-0.002976	-1.715071
O	2.697269	-2.147994	2.463837
C	4.815239	-2.406919	4.057385
H	5.659093	-2.182294	4.709827
H	3.954378	-2.746285	4.638144
H	5.089090	-3.169326	3.324408

8. Crystallographic data

Crystallographic data of complex (*R*)-9

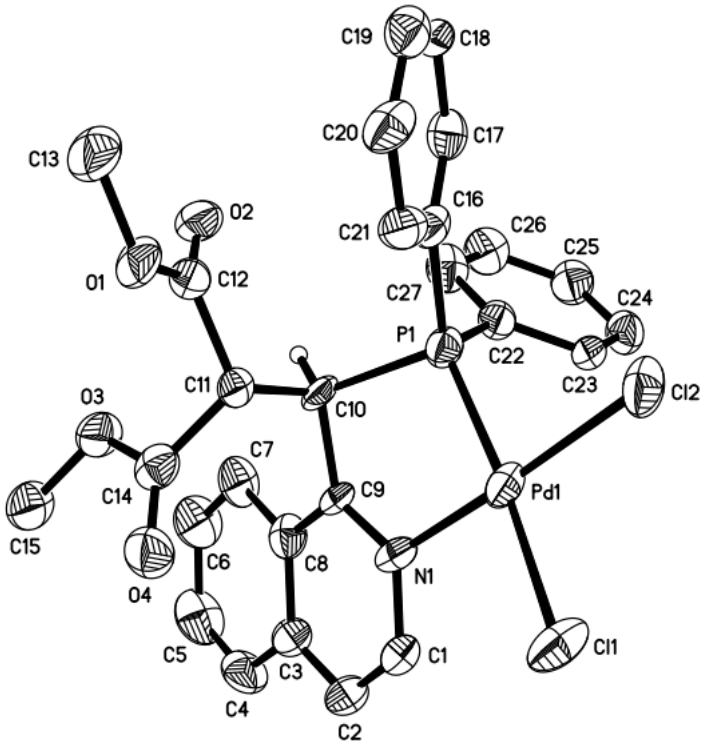


Figure 5 Structure of complex (*R*)-**9** with the thermal ellipsoids

Table S4. Crystal Data of (*R*)-**9** palladium complex

Crystal data		
Identification code	CCDC 1968108	
Chemical formula	$C_{27}H_{24}Cl_2NO_4PPd$	
Formula weight	634.74 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.060 x 0.100 x 0.220 mm	
Crystal habit	yellow block	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 10.1645(14) Å	α = 90°
	b = 14.880(2) Å	β = 90°
	c = 17.932(3) Å	γ = 90°
Volume	2712.2(7) $Å^3$	

Z	4
Density (calculated)	1.555 g/cm^3
Absorption coefficient	0.974 mm^{-1}
F(000)	1280

Data collection	
Theta range for data collection	2.27 to 26.42°
Index ranges	-12<=h<=9, -18<=k<=18, -22<=l<=22
Reflections collected	16735
Independent reflections	5536 [R(int) = 0.0933]
Coverage of independent reflections	99.7%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9440 and 0.8140
Structure solution technique	direct methods
Structure solution program	XT, VERSION 2014/5

Refinement		
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5536 / 0 / 327	
Goodness-of-fit on F^2	1.020	
Final R indices	3717 data; I>2σ(I)	R1 = 0.0566, wR2 = 0.1094
	all data	R1 = 0.1028, wR2 = 0.1307
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0484P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.03(4)	
Largest diff. peak and hole	0.864 and -0.582 eÅ^{-3}	
R.M.S. deviation from mean	0.119 eÅ^{-3}	

Crystallographic data of complex 10

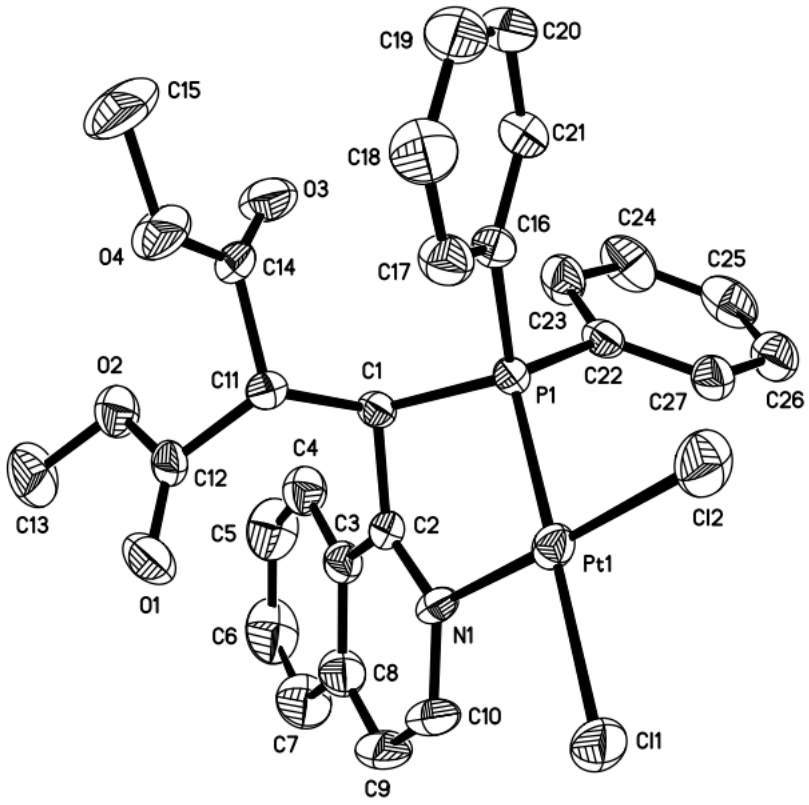


Figure 6 Structure of complex **10** with the thermal ellipsoids

Table S5. Crystal Data of **10** platinum complex

Crystal data		
Identification code	CCDC 1968110	
Chemical formula	$C_{27}H_{24}Cl_2NO_4PPt$	
Formula weight	723.43 g/mol	
Temperature	250(2) K	
Wavelength	0.71073 Å	
Crystal size	0.040 x 0.060 x 0.100 mm	
Crystal habit	yellow plate	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.0515(12) Å	α = 116.404(3)°
	b = 11.2817(12) Å	β = 96.725(3)°
	c = 11.9017(12) Å	γ = 93.542(3)°
Volume	1309.1(2) $Å^3$	
Z	2	
Density (calculated)	1.835 g/cm^3	
Absorption coefficient	5.659 mm^{-1}	

F(000)	704

Data collection	
Theta range for data collection	2.76 to 30.55°
Index ranges	-15<=h<=15, -16<=k<=16, -16<=l<=17
Reflections collected	19663
Independent reflections	7915 [R(int) = 0.0489]
Coverage of independent reflections	98.7%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8050 and 0.6010
Structure solution technique	direct methods
Structure solution program	XT, VERSION 2014/5

Refinement		
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	7915 / 0 / 327	
Goodness-of-fit on F^2	1.040	
Δ/σ_{max}	0.001	
Final R indices	6611 data; I>2σ(I)	R1 = 0.0369, wR2 = 0.0875
	all data	R1 = 0.0505, wR2 = 0.0953
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0470P)^2+0.2195P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.747 and -1.975 eÅ^{-3}	
R.M.S. deviation from mean	0.161 eÅ^{-3}	

Crystallographic data of complex (*R*,*R*)-22

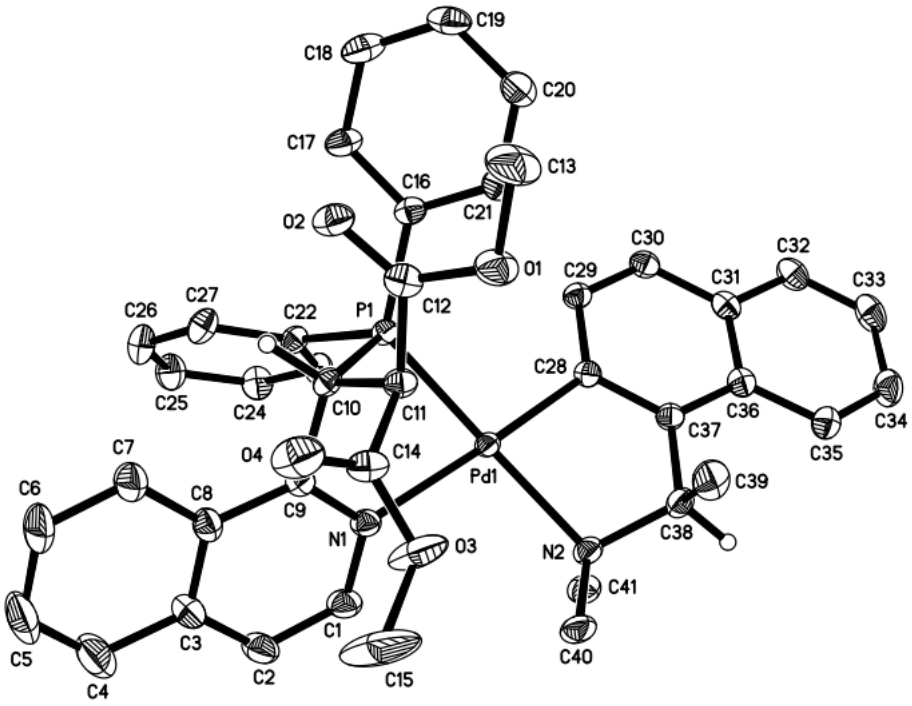


Figure 7 Structure of complex (*R*,*R*)-**22** with the thermal ellipsoids

Table S6. Crystal Data of (*R*,*R*)-**22** platinum complex

Crystal data		
Identification code	CCDC 1968111	
Chemical formula	$C_{44.40}H_{48.40}Cl_{1.40}N_2O_{8.80}PPd$	
Formula weight	937.85 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.100 x 0.220 x 0.240 mm	
Crystal habit	yellow block	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 10.0501(2) Å	α = 90°
	b = 11.1476(3) Å	β = 90°
	c = 38.2901(11) Å	γ = 90°
Volume	4289.81(19) $Å^3$	
Z	4	
Density (calculated)	1.452 g/cm^3	
Absorption coefficient	0.614 mm^{-1}	

F(000)	1936

Data collection		
Theta range for data collection	2.43 to 34.97°	
Index ranges	-16<=h<=9, -17<=k<=17, -61<=l<=40	
Reflections collected	55340	
Independent reflections	18695 [R(int) = 0.0557]	
Coverage of independent reflections	99.6%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9410 and 0.8670	
Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2014/5	
Refinement		
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	18695 / 317 / 613	
Goodness-of-fit on F^2	1.029	
Δ/σ_{max}	0.003	
Final R indices	15734 data; $I>2\sigma(I)$	R1 = 0.0419, wR2 = 0.0749
	all data	R1 = 0.0581, wR2 = 0.0825
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0239P)^2+0.6303P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.007(9)	
Largest diff. peak and hole	0.691 and -0.888 eÅ^{-3}	
R.M.S. deviation from mean	0.090 eÅ^{-3}	