Electronic Supplementary Material (ESI) for Dalton Transactions.

A comparison of MOP-phosphonite ligands and their applications in Rh(I)- and Pd(II)-catalysed asymmetric transformations

Supporting Information

James T. Fleming, Corinne Wills, Paul G. Waddell, Ross W. Harrington and Lee J. Higham*

School of Chemistry, Bedson Building, Newcastle University,

Newcastle upon Tyne, NE1 7RU, UK

E-mail: lee.higham@ncl.ac.uk

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1. General Considerations and Chemical Analyses

General Procedures. All air- and/or water-sensitive reactions were performed under a nitrogen atmosphere using standard Schlenk line techniques in oven dried glassware. Solvents were freshly distilled prior to use; toluene was dried over sodium, tetrahydrofuran and diethyl ether were dried over sodium/benzophenone and dichloromethane was dried over calcium hydride. Hexane was dried over sodium/benzophenone and *d*-chloroform was dried over phosphorus pentoxide, prior to distillation and storage over molecular sieves. (*S*)-[1,1'-binaphthalen]-2-yldiphenylphosphine ((*S*)-H-MOP),[1] (*R*)-(2'-methoxy-[1,1'-binaphthalen]-2-yl)diphenylphosphine ((*R*)-MeO-MOP),[2] platinum(II) dichloride triethylphosphine dimer,[3] chloro(1,5-cyclooctadiene)rhodium(I) dimer,[4] bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate,[5] methyl (Z)-2-acetamidocinnamate (MAC),[6] chlorobis(ethylene)rhodium(I) dimer,[7] 1-(*p*-methoxybenzyl)-5-chloroisatin,[8] bis(acetonitrile) dichloropalladium(II)[9] and 1-bromo-2-methoxynaphthalene[10] were prepared according to literature procedures. All other chemicals were used as received without further purification. Flash chromatography was performed on silica gel (Fluorochem, 60A, 40-63 μm). Thin-layer-chromatography was performed on Merck silica gel coated aluminium sheets with fluorescent indicator (UV_{254}), UV light was used for indicating. Melting points were determined in open glass capillary tubes on a Stuart SMP3 melting point apparatus. Optical rotation values were determined on an Optical Activity Polaar 2001 device. Infrared spectra were measured on a Varian 800 FT-IR Scimitar Series spectrometer. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Bruker 700 (^{1}H 700.13 MHz), Bruker 500 (^{1}H 500.15 MHz), JEOL 400 (^{1}H 399.78 MHz) or Bruker 300 (^{1}H 300.13 MHz) spectrometer at room temperature (21-25 °C) if not otherwise stated, using the indicated solvent as internal reference. Two-dimensional NMR experiments (^{1}H-^{1}H COSY, ^{1}H-^{1}H ROESY, HSQC, HMBC) were used for the assignment of proton and carbon resonances, the numbering schemes are given in Figure 1. High resolution mass spectrometry was carried out by the EPSRC National Mass Spectrometry Facility, Swansea. Analytical gas chromatography was performed on a Shimadzu GC2014 instrument with a flame ionisation detector, using a Supelco β-dex™ 225 capillary column (L = 30 m, I.D. = 0.25 mm, d_f = 0.25 μm) and helium (purge flow 3 ml/min) as the carrier gas. High-performance liquid chromatography was performed on a Shimadzu Prominence UFLC instrument with a UV-Vis absorbance detector, using a Lux® 5μ Cellulose-1 or Lux® 5μ Cellulose-3 column (250 × 4.6 mm).

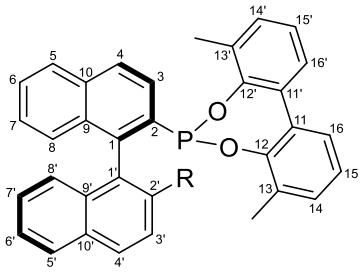


Fig. 1 Numbering scheme used to assign proton and carbon resonances in the NMR spectra.

2. Experimental Procedures

2.1 Ligand properties

2.1.1 General procedure for the synthesis of L^P(Se).

The ligand (50.0 µmol, 1.0 eq.) and potassium selenocyanate (14.4 mg, 100 µmol, 2.0 eq.) were dissolved in THF (1.0 mL) and stirred at 50 °C for 2 h, after which the volatiles were removed *in vacuo*. The residue was dissolved in $CDCl_3$, filtered through Celite® and the solution was analysed by $^{31}P\{^1H\}$ NMR spectroscopy.

2.1.2 General procedure for the synthesis of *trans*-[Rh(L^P)$_2$(CO)Cl] complexes.

The ligand (12.4 µmol, 1.0 eq.) and rhodium(I) dicarbonyl chloride dimer (1.2 mg, 3.1 µmol, 0.25 eq.) were dissolved in DCM (0.5 mL) and stirred at room temperature for 15 min, after which the solution was concentrated and analysed by IR spectroscopy.

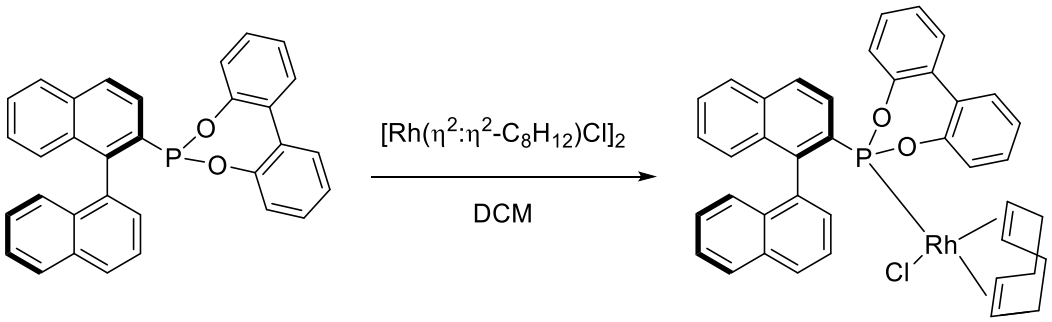
2.1.3 General procedure for the synthesis of [Pt(L^P)(PEt_3)Cl_2] complexes.

The ligand (50.0 µmol, 1.0 eq.) and platinum(II) dichloride triethylphosphine dimer (19.2 mg, 25.0 µmol, 0.5 eq.) were dissolved in CD_2Cl_2 (0.6 mL) and stirred at room temperature for 30 min, after which the solution was analysed by $^{31}P\{^1H\}$ NMR spectroscopy.

2.2 General procedure for the synthesis of [Rh(L^P)(η^2:η^2-cod)Cl] complexes.

Phosphonite ligand (40.0 µmol, 1.0 eq.) and chloro(1,5-cyclooctadiene)rhodium(I) dimer (9.9 mg, 20 µmol, 1.0 eq.) were dissolved in DCM (0.5 mL) and stirred at room temperature for 10 min, after which the $^{31}P\{^1H\}$ NMR spectrum showed no free ligand resonance. To remove small quantities of a phosphorus(V) impurity, the solution with diluted with diethyl ether/hexane and cooled in a salt/ice bath until the pure title compound precipitated as a yellow solid.

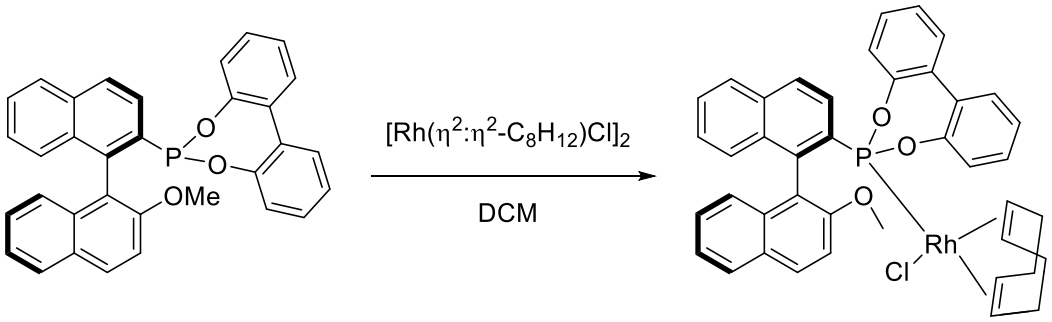
2.2.1 [Rh((*S*)-**2a**)(η^2:η^2-cod)Cl] (*S*)-**8a**



Single crystals were grown by slow diffusion of diethyl ether into a DCM solution.

MP: 206-208 °C (decomp.). **IR** (neat): ν = 3064.4 (w), 2918.2 (m), 1495.1 (m), 1472.2 (m), 1434.7 (s), 1368.4 (w), 1244.9 (m), 1197.8 (s), 1094.6 (s), 1015.9 (m), 953.0 (w), 895.2 (s), 869.4 (s), 820.2 (w), 781.8 (s), 748.0 (s), 674.4 (m), 633.8 (m) cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 50 °C): δ (ppm) = 8.14 (d, $^3J_{HH}$ = 8.3 Hz, 1H, *H*4), 8.05 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*5), 8.02-7.98 (m, 2H, *H*6'), 7.88 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.83 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *H*5'), 7.79 (*apparent*-t (dd), *J* = 7.6 Hz, 1H, *H*3), 7.56 (ddd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, *H*6), 7.54-7.48 (m, 4H, *H*4'), 7.41 (ddd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, *H*7), 7.39-7.29 (m, 6H, *H*7/*H*8), 6.76 (ddd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 6.8 Hz, *J* = 1.2 Hz, 1H, *H*3'), 7.00 (d, $^3J_{HH}$ = 8.6 Hz, 1H, *H*2'), 5.35 (br s, 1H, cod-C*H*), 5.01 (br s, 1H, cod-C*H*), 2.61 (br s, 2H, cod-C*H*), 2.09-1.99 (m, 1H, cod-CH_2), 1.73-1.56 (m, 5H, cod-CH_2), 1.43-1.37 (m, 2H, cod-CH_2). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 50 °C): δ (ppm) = 151.1 (*overlapping*-d, *C*12/*C*12'), 143.1 (d, $^2J_{CP}$ = 24.6 Hz, *C*1), 135.5 (d, $^1J_{CP}$ = 8.0 Hz, *C*2), 133.4 (d, $^4J_{CP}$ = 1.5 Hz, *C*9'), 133.9 (*C*9), 133.6 (*C*10), 133.6 (d, $^3J_{CP}$ = 11.0 Hz, *C*1'), 131.2 (*C*6'), 130.9, 129.8, 129.5, 129.2 (m, *C*8), 129.0 (*C*4), 128.0 (*C*10'), 127.7 (*C*5), 127.5 (*C*4'), 127.2 (m, *C*2'/*C*5'), 126.4 (*C*3'), 126.2 (*C*6), 126.0 (*C*7), 125.6 (d, J_{CP} = 3.1 Hz), 125.4, 125.1 (*C*3), 123.4, 122.5, 111.4 (dd, *J* = 14.3 Hz, *J* = 5.8 Hz, cod-*C*H), 109.8 (m, cod-*C*H), 70.8 (m, cod-*C*H), 70.1 (m, cod-*C*H), 32.9 (cod-*C*H_2), 31.7 (cod-*C*H_2), 27.6 (cod-*C*H_2), 27.1 (cod-*C*H_2). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$, 50 °C): δ (ppm) = 162.9 (d, $^1J_{PRh}$ = 224 Hz). **HRMS** (NSI$^+$, DCM/MeOH + NH_4OAc): Found: *m*/*z* = 571.0319. Calculated for [M – (Cl + cod)]$^+$: *m*/*z* = 571.0329.

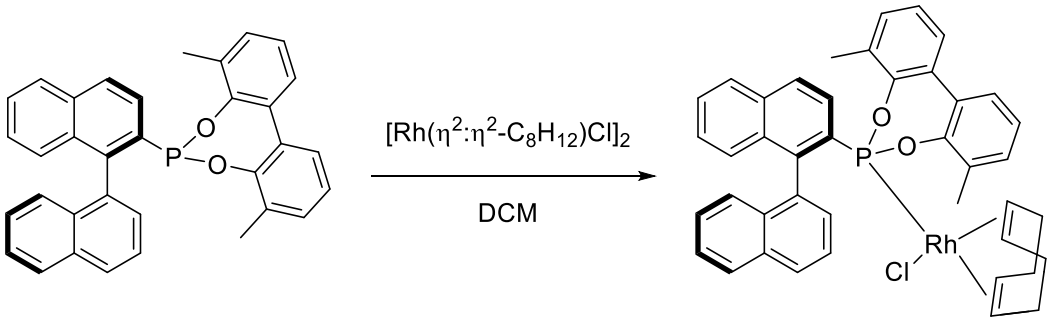
2.2.2 [Rh((*R*)-**2b**)(η^2:η^2-cod)Cl] (*R*)-**8b**



Single crystals were grown by slow diffusion of diethyl ether into a DCM solution.

MP: 236-238 °C (decomp.). **IR** (neat): ν = 3054.8 (w), 1593.1 (w), 1495.7 (m), 1471.0 (m), 1434.5 (s), 1195.5 (s), 1124.6 (w), 1092.5 (m), 1050.3 (m), 961.9 (w), 894.0 (s), 873.9 (s), 817.9 (m), 779.2 (s), 747.5 (m), 743.2 (s), 673.8 (s), 637.0 (s) cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C): δ (ppm) = 8.21 (d, $^3J_{HH}$ = 9.1 Hz, 1H, *H*4'), 7.98 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*5'), 7.95 (dd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HP}$ = 6.2 Hz, 1H, *H*3), 7.89 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*5), 7.86-7.77 (br s, 1H), 7.80 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *H*4), 7.56 (d, $^3J_{HH}$ = 9.1 Hz, 1H, *H*3'), 7.55-7.45 (m, 4H, *H*6), 7.42 (ddd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 6.2 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, *H*6'), 7.39-7.32 (m, 3H, *H*7'/*H*8'), 7.27-7.21 (m, 2H, *H*7), 7.20-7.08 (m, 2H), 7.01 (d, $^3J_{HH}$ = 8.6 Hz, 1H, *H*8), 5.30 (br s, 1H, cod-C*H*), 4.59 (br s, 1H, cod-C*H*), 3.88 (s, 3H, OCH_3), 2.85 (br s, 1H, cod-C*H*), 2.55 (br s, 1H, cod-C*H*), 1.95-1.86 (m, 1H, cod-CH_2), 1.63-1.57 (m, 3H, cod-CH_2), 1.51-1.45 (m, 3H, cod-CH_2), 1.45-1.38 (m, 1H, cod-CH_2). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 25 °C): δ (ppm) = 155.7 (*C*2'), 151.3 (*overlapping*-d, *C*12/*C*12'), 140.1 (d, $^2J_{CP}$ = 24.9 Hz, *C*1), 135.1 (*C*10), 134.7 (*C*9'), 133.2 (d, $^1J_{CP}$ = 11.1 Hz, *C*2), 131.4, 131.1 (*C*4'), 130.8, 129.8, 129.2, 129.0 (m, *C*6/*C*10'), 128.1 (*C*5), 127.6, 127.2 (*C*5'), 127.0 (d, $^3J_{CP}$ = 5.9 Hz, *C*4), 126.7 (*C*7'), 126.6 (*C*8), 126.4 (*C*7), 125.7 (d, $^2J_{CP}$ = 2.1 Hz, *C*3), 125.6 (*C*8'), 125.1, 124.4, 124.2 (*C*6'), 122.7, 120.1 (d, $^3J_{CP}$ = 7.9 Hz, *C*1'), 112.8 (*C*3'), 110.9 (m, cod-*C*H), 110.0 (m, cod-*C*H), 56.1 (O*C*H_3), 33.1 (cod-*C*H_2), 31.8 (cod-*C*H_2), 27.2 (cod-*C*H_2), 27.2 (cod-*C*H_2); resonances for *C*9 and two cod-*C*H were obscured. **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$, 25 °C): δ (ppm) = 163.3 (d, $^1J_{PRh}$ = 221 Hz). **HRMS** (NSI^+, DCM/MeOH + NH_4OAc): Found: *m*/*z* = 601.0427. Calculated for $[M - (Cl + cod)]^+$: *m*/*z* = 601.0434.

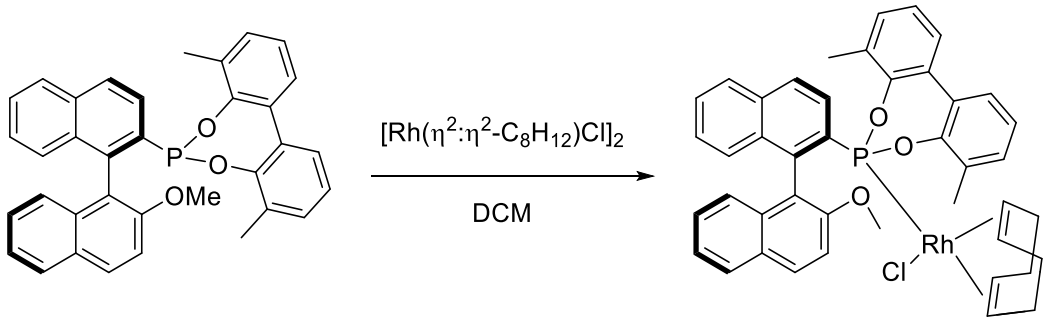
2.2.3 [Rh((*S*)-**3a**)(η^2:η^2-cod)Cl] (*S*)-**9a**



Single crystals were grown by slow diffusion of diethyl ether into a DCM solution. Three isomers were observed in the solution NMR spectra at −55 °C (approximate ratios: isomer A 76%; isomer B 14%; isomer C 10%), the ^{1}H and ^{13}C assignments correspond to the major isomer.

MP: 218-220 °C (decomp.). **IR** (neat): ν = 3048.6 (w), 2922.6 (m), 2875.2 (w), 1557.7 (w), 1453.3 (m), 1418.4 (m), 1367.6 (w), 1308.3 (w), 1260.1 (m), 1188.6 (s), 1085.4 (s), 1018.1 (m), 886.5 (s), 800.3 (s), 769.7 (s), 690.3 (s), 634.9 (s), 614.5 (s) cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, −55 °C): *δ* (ppm) = 8.77 (dd, $^{3}J_{HP}$ = 17.1 Hz, $^{3}J_{HH}$ = 8.6 Hz, 1H, *H*3), 8.21 (d, $^{3}J_{HH}$ = 8.6 Hz, 1H, *H*4), 7.98 (d, $^{3}J_{HH}$ = 8.4 Hz, 1H, *H*5), 7.70-7.66 (m, 2H, *H*5'/*H*6'), 7.55 (*apparent*-t (dd), $^{3}J_{HH}$ = 7.5 Hz, 1H, *H*6), 7.48 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H, *H*4'), 7.40-7.33 (m, 2H, *H*7'/*H*8'), 7.25-7.21 (m, 2H, *H*7/H16), 7.11-7.03 (m, 6H, *H*8/*H*14/*H*14'/*H*15/*H*15'/*H*16'), 6.76 (dd, $^{3}J_{HH}$ = 8.2 Hz, $^{3}J_{HH}$ = 7.0 Hz, 1H, *H*3'), 5.68 (br s, 1H, cod-C*H*), 5.64 (br s, 1H, cod-C*H*), 5.58 (d, $^{3}J_{HH}$ = 7.0 Hz, 1H, *H*2'), 4.15 (br s, 1H, cod-C*H*), 2.89 (br s, 1H, cod-C*H*), 2.59-2.55 (m, 1H, cod-CH_2), 2.51-2.44 (m, 1H, cod-CH_2), 2.18-1.98 (m, 4H, cod-CH_2), 1.88 (s, 3H, CH_3'), 1.84-1.78 (m, 1H, cod-CH_2), 1.69-1.64 (m, 1H, cod-CH_2), 1.63 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, −55 °C): *δ* (ppm) = 148.9 (d, $^{2}J_{CP}$ = 13.8 Hz, *C*12), 147.2 (d, $^{2}J_{CP}$ = 6.8 Hz, *C*12'), 141.3 (*C*1), 136.6 (*C*1'), 134.5 (*C*10), 133.4 (*C*9'), 133.0 (d, $^{3}J_{CP}$ = 6.7 Hz, *C*9), 132.0 (*C*10'), 131.3 (*C*13'), 131.1 (*C*11 or *C*11'), 130.7 (*C*14), 130.5 (*obscured*-d, *C*2), 130.4 (m, *C*3/*C*14'), 130.4 (*C*13), 129.6 (*C*11 or *C*11'), 128.8 (*C*16'), 128.3 (*C*8), 128.2 (*C*5/*C*6'), 128.1 (*C*6), 127.5 (d, $^{3}J_{CP}$ = 19.0 Hz, *C*4), 127.4 (*C*15 or *C*15'), 127.2 (*C*5'), 126.9 (*C*7), 126.8 (*C*4'), 126.0 (*C*2'), 125.9 (*C*7' or *C*8'), 125.6 (*C*7' or *C*8'), 125.2 (*C*15 or *C*15'), 125.2 (*C*16), 124.4 (*C*3'), 113.0 (br d, *J* = 13.5 Hz, cod-*C*H), 112.3 (br d, *J* = 14.3 Hz, cod-*C*H), 71.3 (d, *J* = 12.6 Hz, cod-*C*H), 70.4 (d, *J* = 11.8 Hz, cod-*C*H), 33.4 (cod-*C*H_2), 32.9 (cod-*C*H_2), 28.5 (cod-*C*H_2), 28.2 (cod-*C*H_2), 17.9 (*C*H_3'), 17.0 (*C*H_3). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$, −55 °C): *δ* (ppm) = 170.2 (d, $^{1}J_{PRh}$ = 225 Hz, P^{A}), 169.4 (d, $^{1}J_{PRh}$ = 224 Hz, P^{B}), 162.0 (d, $^{1}J_{PRh}$ = 223 Hz, P^{C}). **HRMS** (ASAP^{+}, solid): Found: *m*/*z* = 707.1570. Calculated for [M − Cl]$^{+}$: *m*/*z* = 707.1581.

2.2.4 [Rh((*R*)-**3b**)(η^2:η^2-cod)Cl] (*R*)-**9b**



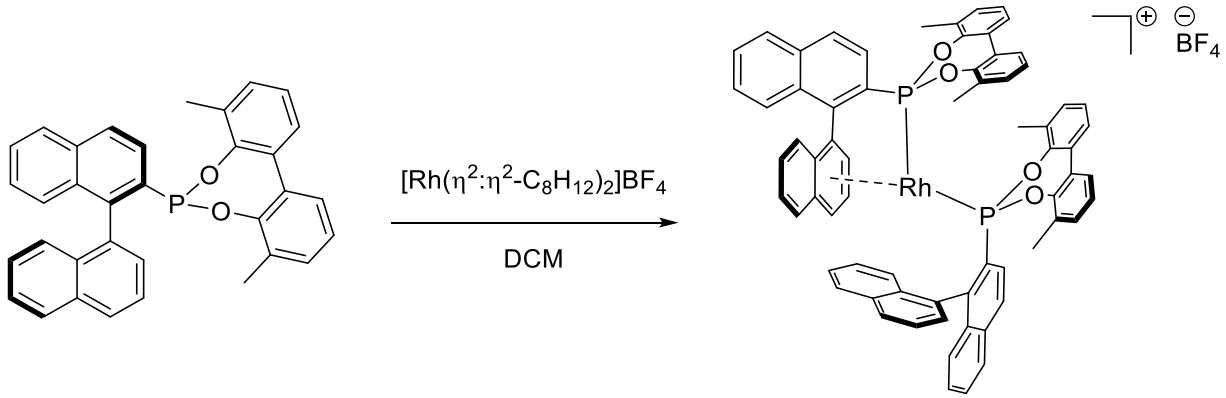
Single crystals were grown by slow diffusion of diethyl ether into a DCM solution. Five isomers were observed in the solution NMR spectra at −55 °C (approximate ratios: isomer A 13%; isomer B 80%; isomer C 1%; isomer D 3%; isomer E 3%), the ^{1}H and ^{13}C assignments correspond to the major isomer.

MP: 230-232 °C (decomp.). **IR** (neat): ν = 2925.4 (w), 2832.5 (w), 1622.4 (w), 1593.6 (w), 1557.8 (w), 1510.6 (m), 1453.6 (m), 1418.0 (m), 1334.8 (w), 1251.2 (s), 1189.5 (s), 1081.6 (s), 1021.0 (m), 965.5 (w), 896.7 (s), 806.6 (s), 771.3 (s), 744.6 (s), 687.7 (s), 637.4 (s) cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, −55 °C): *δ* (ppm) = 8.68 (dd, $^{3}J_{HP}$ = 16.9 Hz, $^{3}J_{HH}$ = 8.6 Hz, 1H, *H*3), 8.21 (d, $^{3}J_{HH}$ = 8.6 Hz, 1H, *H*4), 7.98 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H, *H*5), 7.76 (d, $^{3}J_{HH}$ = 8.4 Hz, 1H, *H*8'), 7.70 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H, *H*5'), 7.66 (d, $^{3}J_{HH}$ = 9.1 Hz, 1H, *H*4'), 7.55 (*apparent*-t (dd), $^{3}J_{HH}$ = 7.5 Hz, 1H, *H*6), 7.35-7.31 (m, 1H, *H*7'), 7.30-7.26 (m, 1H, *H*6'), 7.25-7.20 (m, 1H, *H*7), 7.15 (d, $^{3}J_{HH}$ = 8.6 Hz, 1H, *H*8), 7.13-7.05 (m, 6H, *H*14/*H*14'/*H*15/*H*15'/*H*16/*H*16'), 6.79 (d, $^{3}J_{HH}$ = 9.1 Hz, 1H, *H*3'), 5.69 (br s, 1H, cod-C*H*), 5.50 (br s, 1H, cod-C*H*), 4.19 (br s, 1H, cod-C*H*), 2.92 (s, 3H, OCH_3), 2.64-2.54 (m, 2H, cod-C*H*/cod-CH_2), 2.38-2.29 (m, 1H, cod-CH_2), 2.13-1.96 (m, 4H, cod-CH_2), 1.81 (s, 3H, CH_3'), 1.72 (s, 3H, CH_3), 1.70-1.65 (m, 1H, cod-CH_2), 1.50-1.40 (m, 1H, cod-CH_2). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, −55 °C): *δ* (ppm) = 153.3 (*C*2'), 149.4 (d, $^{2}J_{CP}$ = 14.8 Hz, *C*12'), 148.0 (d, $^{2}J_{CP}$ = 6.3 Hz, *C*12), 137.8 (*C*1), 134.5 (*C*10), 134.3 (*C*9'), 132.4 (d, $^{3}J_{CP}$ = 7.3 Hz, *C*9), 132.1 (d, $^{1}J_{CP}$ = 41.7 Hz, *C*2), 132.0 (*C*13 or *C*13'), 131.0 (*C*13 or *C*13'), 130.7 (*C*14 or *C*14'), 130.5 (*C*14 or *C*14'), 130.1 (*obscured*-d, *C*3), 130.0 (*C*11 or *C*11'), 129.4 (*C*11 or *C*11'), 129.3 (*C*4'), 128.2 (*C*5), 128.0 (*C*6), 127.9 (*C*8'), 127.8 (*C*16 or *C*16'), 127.7 (*C*16 or *C*16'), 127.6 (*C*10'), 127.5 (*C*8), 127.3 (d, $^{3}J_{CP}$ = 18.1 Hz, *C*4), 126.9 (*C*7), 126.8 (*C*5'), 126.3 (*C*7'), 125.4 (*C*15 or *C*15'), 124.7 (*C*15 or *C*15'), 123.3 (*C*6'), 120.2 (*C*1'), 113.0 (br d, *J* = 14.0 Hz, cod-*C*H), 111.5 (br d, *J* = 15.0 Hz, cod-*C*H), 110.9 (*C*3'), 72.8 (d, *J* = 11.7 Hz, cod-*C*H), 70.0 (d, *J* = 11.5 Hz, cod-*C*H), 56.1 (O*C*H_3), 34.0 (cod-*C*H_2), 32.2 (cod-*C*H_2), 29.0 (cod-*C*H_2), 27.5 (cod-*C*H_2), 17.6 (*C*H_3'), 17.5 (*C*H_3). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$, −55 °C): *δ* (ppm) = 168.1 (d, $^{1}J_{PRh}$ = 227 Hz, P^{A}), 167.5 (d, $^{1}J_{PRh}$ = 226 Hz, P^{B}), 165.1 (d, $^{1}J_{PRh}$ = 227 Hz, P^{C}), 163.4 (d, $^{1}J_{PRh}$ = 224 Hz, P^{D}), 162.8 (d, $^{1}J_{PRh}$ = 223 Hz, P^{E}). **HRMS** (ASAP^{+}, solid): Found: *m*/*z* = 737.1686. Calculated for [M − Cl]$^{+}$: *m*/*z* = 737.1686.

2.3 General procedure for the synthesis of $[Rh(L^P)_2]BF_4$ complexes.

Phosphonite ligand (40.0 µmol, 1.0 eq.) and bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate (8.1 mg, 20 µmol, 1.0 eq.) were dissolved in DCM (1.0 mL) and stirred at room temperature for 10 min, after which the $^{31}P\{^1H\}$ NMR spectrum showed no free ligand resonance. To remove small quantities of a phosphorus(V) impurity, the solution with diluted with diethyl ether and cooled in a salt/ice bath until the pure title compound precipitated as an orange solid.

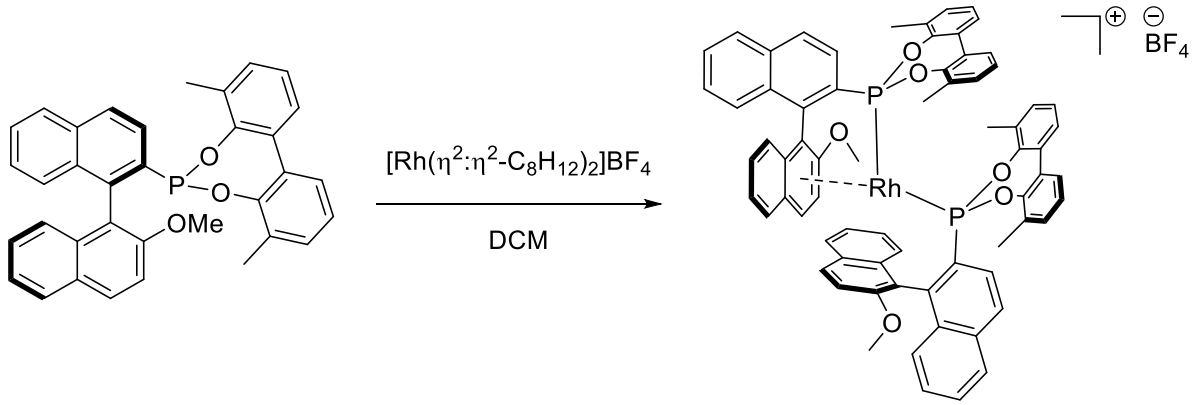
2.3.1 $[Rh((S)\text{-}\mathbf{3a})_2]BF_4$ (*S*)-**10a**



MP: 260-262 °C (decomp.). **IR** (neat): ν = 1485.1 (w), 1436.2 (m), 1418.7 (m), 1365.0 (w), 1249.9 (m), 1188.7 (s), 1052.4 (s), 910.3 (s), 761.7 (s), 726.8 (m), 688.8 (s), 632.5 (s) cm^{-1}. **^{1}H NMR** (700 MHz, $CDCl_3$, 5 °C): *δ* (ppm) = 8.78 (dd, $^3J_{HP}$ = 16.6 Hz, $^3J_{HH}$ = 8.6 Hz, 1H, *H*3^A), 8.67 (d, $^3J_{HH}$ = 8.6 Hz, 1H, *H*4^A), 8.24 (*apparent*-t (dd), $^3J_{HH}$ = 6.3 Hz, 1H, *H*3'^{B}), 8.16 (d, $^3J_{HH}$ = 8.4 Hz, 1H, *H*5^A), 7.99 (d, $^3J_{HH}$ = 8.3 Hz, 1H, *H*5^B), 7.82 (d, $^3J_{HH}$ = 8.6 Hz, 1H, *H*8^B), 7.70-7.76 (m, 3H, *H*4^B/*H*5'^{B}/*H*6^B), 7.67 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*5'^{A}), 7.63 (*apparent*-t (dd), $^3J_{HH}$ = 7.6 Hz, 1H, *H*6^A), 7.59 (*apparent*-t (dd), $^3J_{HH}$ = 7.8 Hz, 1H, *H*7^B), 7.57-7.52 (m, 3H, *H*2'^{B}/*H*6'^{B}/*H*7'^{A}), 7.48 (*apparent*-t (dd), $^3J_{HH}$ = 7.6 Hz, 1H, *H*7'^{B}), 7.45 (*apparent*-t (dd), $^3J_{HH}$ = 7.5 Hz, 1H, *H*6'^{A}), 7.30-7.26 (m, 3H, *H*4'^{A}/*H*7^A/*H*8'^{A}), 7.11-7.01 (m, 5H, *H*8^A/*H*8'^{B}/*H*15^A/*H*15^B/*H*16^B), 6.98 (d, $^3J_{HH}$ = 7.4 Hz, 1H, *H*14^B), 6.88 (d, $^3J_{HH}$ = 7.4 Hz, 1H, *H*14^A), 6.80-6.77 (m, 2H, *H*14'^{B}/*H*16^A), 6.75 (d, $^3J_{HH}$ = 7.6 Hz, 1H, *H*16'^{B}), 6.72 (*apparent*-t (dd), *J* = 7.8 Hz, 1H, *H*3^B), 6.58 (*apparent*-t (dd), $^3J_{HH}$ = 7.6 Hz, 1H, *H*3'^{A}), 6.46 (d, $^3J_{HH}$ = 7.5 Hz, 1H, *H*16'^{A}), 6.37 (*apparent*-t (dd), $^3J_{HH}$ = 7.5 Hz, 1H, *H*15'^{B}), 6.27-6.24 (m, 2H, *H*4'^{B}/*H*14'^{A}), 6.09 (*apparent*-t (dd), $^3J_{HH}$ = 7.5 Hz, 1H, *H*15'^{A}), 5.27 (d, $^3J_{HH}$ = 6.9 Hz, 1H, *H*2'^{A}), 2.57 (s, 3H, CH_3'^{B}), 1.66 (s, 3H, CH_3^{A}), 1.37 (s, 3H, CH_3^{B}), 0.09 (s, 3H, CH_3'^{A}). **^{13}C{^{1}H} NMR** (176 MHz, $CDCl_3$, 5 °C): *δ* (ppm) = 149.5 (d, $^1J_{CP}$ = 58.9 Hz, *C*2^B), 148.7 (d, $^2J_{CP}$ = 15.5 Hz, *C*12^B), 148.2 (d, $^2J_{CP}$ = 14.5 Hz, *C*12^A), 147.7 (d, $^2J_{CP}$ = 7.9 Hz, *C*12'^{B}), 146.6 (d, $^2J_{CP}$ = 7.5 Hz, *C*12'^{A}), 140.1 (*C*1^A), 140.0 (d, $^2J_{CP}$ = 32.1 Hz, *C*1^B), 136.2 (*C*1'^{A}), 135.1 (*C*10^B), 134.9 (*C*10^A), 133.5 (d, $^1J_{CP}$ = 45.8 Hz, *C*2^A), 132.9 (*C*9'^{A}), 132.4 (*C*9^A/*C*10'^{A}), 131.4 (*C*11'^{B}), 131.2 (*C*11^A), 131.1 (*C*7'^{B}), 130.9 (*C*6'^{B}), 130.9 (d, $^2J_{CP}$ = 36.6 Hz, *C*3^A), 130.5 (*obscured*-d, *C*9^B), 130.4 (*C*14^A/*C*14^B/*C*14'^{B}), 130.3 (*C*4^B), 130.1 (*C*13^A), 129.7 (*C*6^B), 129.2 (d, $^3J_{CP}$ = 17.1 Hz, *C*4^A), 129.0

(*C*11'^{A}/*C*13^{B}/*C*14'^{A}), 128.9 (*C*7^{B}/*C*16^{A}/*C*16^{B}), 128.8 (*C*11^{B}), 128.7 (*C*5^{A}), 128.7 (*C*6^{A}), 128.6 (*C*5^{B}), 128.3 (*C*8^{A}), 128.2 (*C*5'^{A}), 127.7 (*C*13'^{A}), 127.6 (*C*13'^{B}), 127.4 (*C*7^{A}), 127.0 (*C*2'^{A}), 126.8 (*C*4'^{A}/*C*5'^{B}/*C*16'^{B}), 126.5 (*C*16'^{A}), 126.4 (*C*8^{B}), 125.8 (*C*7'^{A}), 125.8 (*C*8'^{A}), 125.5 (*C*15^{B}), 125.2 (*C*6'^{A}), 125.0 (*C*15^{A}), 124.6 (*C*3'^{A}), 124.5 (*C*15'^{B}), 124.0 (*C*9'^{B}), 123.9 (*C*15'^{A}), 123.6 (*C*3^{B}), 123.4 (*C*8'^{B}), 118.6 (*C*10'^{B}), 110.5 (d, *J* = 11.3 Hz, *C*1'^{B}), 107.9 (*C*3'^{B}), 103.2 (*C*2'^{B}), 100.3 (d, *J* = 12.8 Hz, *C*4'^{B}), 18.4 (*C*H$_3$'^{B}), 16.7 (*C*H$_3$^{A}), 15.9 (*C*H$_3$^{B}), 14.1 (*C*H$_3$'^{A}). **^{31}P{^{1}H} NMR** (202 MHz, CDCl$_3$, 5 °C): *δ* (ppm) = 176.8 (dd, $^{1}J_{PRh}$ = 288 Hz, $^{2}J_{PP}$ = 27 Hz, *P*^{A}), 171.7 (dd, $^{1}J_{PRh}$ = 294 Hz, $^{2}J_{PP}$ = 27 Hz, *P*^{B}). **HRMS** (NSI$^+$, DCM/MeOH): Found: *m*/*z* = 1095.2221. Calculated for [M − BF$_4$]$^+$: *m*/*z* = 1095.2234.

2.3.2 [Rh((*R*)-**3b**)$_2$]BF$_4$ (*R*)-**10b**



MP: 280-282 °C (decomp.). **IR** (neat): ν = 1623.3 (w), 1595.9 (w), 1452.7 (m), 1416.5 (m), 1278.8 (w), 1249.1 (s), 1193.3 (s), 1047.9 (s), 925.3 (s), 869.1 (m), 804.1 (m), 759.8 (s), 709.7 (m), 682.8 (m), 633.0 (s) cm^{-1}. **^{1}H NMR** (500 MHz, CDCl$_3$, −20 °C): *δ* (ppm) = 8.06 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H, *H*5^{B}), 7.91 (d, $^{3}J_{HH}$ = 8.4 Hz, 1H, *H*8^{B}), 7.84 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H, *H*4^{B}), 7.83 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H, *H*5^{A}), 7.80-7.75 (m, 2H, *H*3'^{B}/*H*6^{B}), 7.71 (d, $^{3}J_{HH}$ = 9.0 Hz, 1H, *H*4'^{A}), 7.66 (*apparent*-t (dd), $^{3}J_{HH}$ = 7.7 Hz, 1H, *H*7^{B}), 7.60 (dd, $^{3}J_{HP}$ = 16.5 Hz, $^{3}J_{HH}$ = 8.8 Hz, 1H, *H*3^{A}), 7.57-7.49 (m, 4H, *H*3'^{A}/*H*4^{A}/*H*6^{A}/*H*7'^{B}), 7.44 (d, $^{3}J_{HH}$ = 8.1 Hz, 1H, *H*5'^{A}), 7.32-7.28 (m, 4H, *H*4'^{B}/*H*14^{B}/*H*15^{B}/*H*16^{B}), 7.24 (*apparent*-t (dd), $^{3}J_{HH}$ = 7.7 Hz, 1H, *H*7^{A}), 7.21 (d, $^{3}J_{HH}$ = 7.5 Hz, 1H, *H*14^{A}), 7.11 (*apparent*-t (dd), $^{3}J_{HH}$ = 7.7 Hz, 1H, *H*15^{A}), 7.07 (*overlapping*-d, $^{3}J_{HH}$ = 8.5 Hz, 2H, *H*8^{A}/*H*8'^{B}), 6.94 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, *H*16^{A}), 6.91 (*apparent*-t (dd), *J* = 8.0 Hz, 1H, *H*3^{B}), 6.87 (*apparent*-t (dd), $^{3}J_{HH}$ = 7.5 Hz, 1H, *H*6'^{A}), 7.83-7.76 (m, 4H, *H*5'^{B}/*H*6'^{B}/H15'^{B}/H16'^{A}), 6.60 (d, $^{3}J_{HH}$ = 7.2 Hz, 1H, H14'^{B}), 6.46 (d, $^{3}J_{HH}$ = 7.2 Hz, 1H, H14'^{A}), 6.31 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, H16'^{B}), 6.26 (*apparent*-t (dd), $^{3}J_{HH}$ = 7.6 Hz, 1H, H15'^{A}), 6.21 (*apparent*-t (dd), $^{3}J_{HH}$ = 7.7 Hz, 1H, *H*7'^{A}), 5.53 (d, $^{3}J_{HH}$ = 8.6 Hz, 1H, *H*8'^{A}), 4.28 (s, 3H, OC*H*$_3$^{A}), 3.84 (s, 3H, OC*H*$_3$^{B}), 2.46 (s, 3H, C*H*$_3$^{A}), 1.93 (s, 3H, C*H*$_3$^{B}), 1.37 (s, 3H, C*H*$_3$'^{B}), 1.25 (s, 3H, C*H*$_3$'^{A}). **^{13}C{^{1}H} NMR** (126 MHz, CDCl$_3$, −20 °C): *δ* (ppm) = 153.3 (*C*2'^{A}), 149.5 (d, $^{1}J_{CP}$ = 57.0 Hz, *C*2^{B}), 148.4 (*overlapping*-d, *C*12^{B}/*C*12'^{B}), 147.7 (d, $^{2}J_{CP}$ = 8.3 Hz, *C*12'^{A}), 146.8 (*C*2'^{B}), 146.2 (d, $^{2}J_{CP}$ = 8.2 Hz, *C*12^{A}), 138.0 (d, $^{2}J_{CP}$ = 32.4 Hz, *C*1^{B}), 135.9 (d, $^{1}J_{CP}$ = 47.2 Hz, *C*2^{A}), 135.3 (*C*10^{B}), 134.9 (*C*10^{A}), 133.9 (*C*9'^{A}), 133.6 (*C*1^{A}), 131.9

(d, $^{3}J_{CP}$ = 8.4 Hz, *C*9^{A}), 131.2 (*C*14'^{A}), 131.1 (*obscured*-d, *C*9^{B}), 131.0 (*C*14^{B}), 130.8 (*C*14^{A}), 130.7 (*C*7'^{B}), 130.5 (*C*6'^{B}), 130.2 (*C*4^{B}/*C*13^{B}), 130.1 (*C*13^{A}), 130.1 (*C*13'^{A}), 129.9 (*C*14'^{B}), 129.7 (*C*6^{B}/*C*11'^{B}), 129.4 (*C*4'^{A}), 129.2 (*C*11^{A}/*C*11^{B}), 129.2 (*C*16^{B}), 129.0 (*C*13'^{B}), 128.8 (*C*7^{B}), 128.7 (*C*5^{B}), 128.5 (*C*6^{A}/*C*16^{A}), 128.0 (*C*11'^{A}), 127.8 (*C*16'^{B}), 127.8 (*obscured*-d, *C*3^{A}), 127.8 (*C*8^{A}), 127.6 (*C*10'^{A}), 127.5 (*C*5^{A}), 127.3 (*C*7^{A}), 127.2 (*C*5'^{A}), 127.0 (*C*16'^{A}), 126.6 (*obscured*-d, *C*4^{A}), 126.6 (*C*8^{B}), 126.3 (*C*7'^{A}), 126.2 (*C*15^{B}), 125.4 (*C*15'^{B}), 125.0 (*C*15^{A}), 124.9 (*C*5'^{B}), 124.3 (*C*3^{B}), 124.1 (*C*15'^{A}), 122.6 (*C*8'^{A}), 122.5 (*C*9'^{B}), 122.3 (*C*8'^{B}), 122.1 (*C*6'^{A}), 120.8 (*C*1'^{A}), 113.4 (*C*10'^{B}), 112.7 (*C*3'^{A}), 101.3 (d, *J* = 15.2 Hz, *C*1'^{B}), 93.7 (d, *J* = 10.4 Hz, *C*4'^{B}), 93.4 (*C*3'^{B}), 57.9 (O*C*H$_3$^{B}), 57.1 (O*C*H$_3$^{A}), 16.9 (*C*H$_3$^{B}), 16.6 (*C*H$_3$^{A}/ *C*H$_3$'^{B}), 14.9 (*C*H$_3$'^{A}). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$, −20 °C): *δ* (ppm) = 182.0 (dd, $^{1}J_{PRh}$ = 283 Hz, $^{2}J_{PP}$ = 32 Hz, *P*^{A}), 173.2 (dd, $^{1}J_{PRh}$ = 310 Hz, $^{2}J_{PP}$ = 32 Hz, *P*^{B}). **HRMS** (NSI^{+}, DCM/MeOH): Found: *m*/*z* = 1155.2423. Calculated for $[M - BF_4]^{+}$: *m*/*z* = 1155.2445.

2.4 General procedure for the asymmetric hydrogenation of alkenes

The alkene substrate (3.70 mmol, 1.0 eq.) was dissolved in DCM (6 mL) in an autoclave vessel at room temperature. The MOP-ligand (15 µmol, 0.004 eq.) and bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate (3.0 mg, 7.4 µmol, 0.002 eq.) were dissolved in DCM (2 mL) and stirred at room temperature for 30 min, after which the solution was transferred to the autoclave vessel and pressurised to 2 bar with hydrogen gas. The reaction mixture was stirred for 48h, after which the conversion was obtained by ^{1}H NMR spectroscopy. The reaction mixture was filtered through silica with rinsing by DCM, the volatiles were removed *in vacuo* and the enantiomeric excess determined.

2.4.1 Dimethyl methylsuccinate

The ^{1}H NMR matched that of a commercial sample. The *ee* was determined by chiral GC (Fig. 6.1); the absolute configuration was assigned by comparison to an enantiopure, commercially acquired sample.

2.4.2 Methyl *N*-acetylalaninate

The ^{1}H spectroscopic data matched that of an authentic sample, which was prepared via a literature procedure from N-acetyl-L-alanine.[11] The ^{1}H and ^{13}C NMR spectroscopic data matched that of data reported in the literature,[12] and the HRMS data was in accordance with the calculated values. The *ee* was determined by chiral GC analysis; the absolute configuration was assigned by comparison to the enantiopure, authentically prepared sample.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.12 (br s, 1H), 4.53 (apparent quintet (dq), $^{3}J_{HH}$ = 7.2 Hz, 1H), 3.69 (s, 3H), 1.95 (s, 3H), 1.34 (d, $^{3}J_{HH}$ = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ (ppm) = 173.7, 169.7, 52.5, 48.0, 23.1, 18.5. **HRMS** (NSI^+, DCM/MeOH + NH_4OAc): Found: *m*/*z* = 146.0808. Calculated for $[M + H]^+$: *m*/*z* = 146.0812.

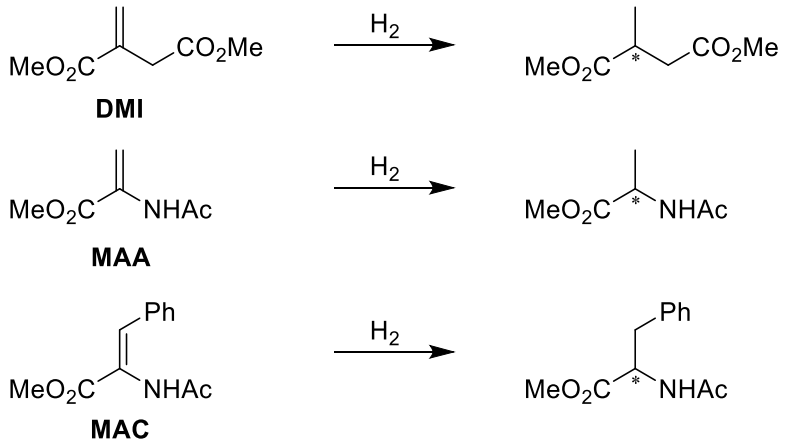
2.4.3 Methyl *N*-acetylphenylalaninate

The ^{1}H spectroscopic data matched that of an authentic sample, which was prepared via a literature procedure from N-acetyl-L-phenylalanine.[11] The ^{1}H and ^{13}C NMR spectroscopic data matched that of data reported in the literature,[12] and the HRMS data was in accordance with the calculated values. The *ee* was determined by chiral HPLC analysis; the absolute configuration was assigned by comparison to the enantiopure, authentically prepared sample.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.25-7.16 (m, 3H), 7.04-7.00 (m, 2H), 5.94 (br d, 1H), 4.81 (dt, $^{3}J_{HH}$ = 7.9 Hz, $^{3}J_{HH}$ = 5.8 Hz, 1H), 3.65 (s, 3H), 3.12-2.97 (m, 2H), 1.91 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ (ppm) = 172.1, 169.7, 135.9, 129.2, 128.6, 127.1, 53.1, 52.3, 37.9, 23.1. **HRMS** (NSI^+, DCM/MeOH + NH_4OAc): Found: *m*/*z* = 222.1122. Calculated for $[M + H]^+$: *m*/*z* = 222.1125.

2.4.4 Catalysis results: Table 1

Table 1 Rhodium-catalysed asymmetric hydrogenation of prochiral alkenes.[a]



	Catalyst	Substrate	Conversion[b]	*ee*[c]
1	(*S*)-**10a**	DMI	47	0[d]
2	(*R*)-**10b**	DMI	70	0[d]
3	(*S*)-**10a**	MAA	26	1 (*R*)[d]
4	(*R*)-**10b**	MAA	8	3 (*S*)[d]
5	(*S*)-**10a**	MAC	<1	–
6	(*R*)-**10b**	MAC	3	34 (*S*)[e]

[a] 0.1 mol% $[Rh(L^P)_2]BF_4$ catalyst in DCM at room temperature and 2 bar pressure for 48 h. [b] % Conversion determined by ^{1}H NMR spectroscopy. [c] Absolute configuration was assigned by comparison to authentic samples. [d] % *ee* determined by chiral GC (Supelco β-dex). [e] % *ee* determined by chiral HPLC (Lux Cellulose) with hexane/2-propanol (90:10).

2.5 General procedure for the asymmetric hydroformylation of styrene

MOP-ligand (38 µmol, 0.004 eq.) and (acetylacetonato)dicarbonylrhodium(I) (5.0 mg, 19 µmol, 0.002 eq.) were dissolved in C_6D_6 (1 mL) and stirred at room temperature for 10 min, after which the solution was transferred to an autoclave vessel at 36 °C and pressurised to 40 bar with syngas and stirred for 1h. The vessel was depressurised before styrene (1.1 mL, 1.0 g, 9.6 mmol, 1.0 eq.) was added, the vessel was subsequently re-pressurised to 40 bar with syngas and left to stir for 16 h, after which the conversion was obtained by ^{1}H NMR spectroscopy; the ^{1}H spectroscopic data matched that of commercially acquired samples of 2-phenylpropionaldehyde and 3-phenylpropionaldehyde. The reaction mixture was filtered through silica with rinsing by DCM, the volatiles were removed *in vacuo* and the enantiomeric excess determined immediately by chiral GC analysis; the absolute configuration was assigned by comparison to literature data.[13]

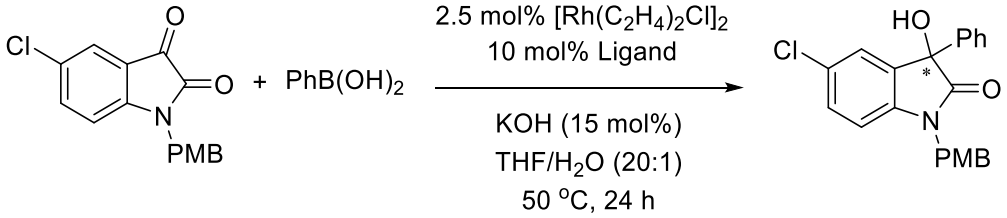
2.6 General procedure for the asymmetric addition of phenyl boronic acid to 1-(*p*-methoxybenzyl)-5-chloroisatin

MOP-ligand (20.0 µmol, 0.1 eq.) and chlorobis(ethylene)rhodium(I) dimer (1.9 mg, 5.0 µmol, 0.025 eq.) were dissolved in THF (1.0 mL) and stirred at room temperature for 10 min, after which 1-(*p*-methoxybenzyl)-5-chloroisatin (60.3 mg, 200 µmol, 1.0 eq.), phenyl boronic acid (48.8 mg, 400 µmol, 2.0 eq.), THF (1.0 mL) and potassium hydroxide (0.1 mL, 0.3 M (aq), 0.3 mmol) were added sequentially. The reaction mixture was heated to 50 °C and left to stir for 24 h, after which the conversion was obtained by ^{1}H NMR spectroscopy. Filtration through silica with rinsing by ethyl acetate, removal of the volatiles *in vacuo* and silica gel column chromatography (ethyl acetate/chloroform, 95:5) yielded the pure product as a white solid. The ^{1}H and ^{13}C NMR spectroscopic data matched that of data reported in the literature,[8] and the HRMS data was in accordance with the calculated values. The enantiomeric excess was determined by chiral HPLC analysis; the absolute configuration was assigned by comparison to literature data.[8]

R_f = 0.21 (silica gel; ethyl acetate/chloroform, 95:5). **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.30-7.22 (m, 5H), 7.16-7.07 (m, 4H), 6.79-6.73 (m, 2H), 6.62 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 4.85 (d, $^{2}J_{HH}$ = 15.4 Hz, 1H), 4.65 (d, $^{2}J_{HH}$ = 15.4 Hz, 1H), 4.04 (br s, 1H), 3.69 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ (ppm) = 177.4, 159.3, 141.1, 139.7, 133.5, 129.6, 129.0, 128.8, 128.7, 128.6, 127.0, 125.5, 125.2, 114.4, 110.8, 78.0, 55.3, 43.7. **HRMS** (NSI^{+}, DCM/MeOH + NH_4OAc): Found: *m*/*z* = 380.1047. Calculated for $[M + H]^{+}$: *m*/*z* = 380.1048.

2.6.1 Catalysis results: Table 2

Table 2 Rhodium-catalysed asymmetric addition of phenylboronic acid to 1-(*p*-methoxybenzyl)-5-chloroisatin.



	Ligand	Conversion[a]	*ee*[b]
1	(*S*)-H-MOP	>99	70 (*S*)
2	(*R*)-MeO-MOP	83 (92)[c]	88 (*S*) (90)[c]
3	(*S*)-**1a**	0	–
4	(*R*)-**1b**	0	–
5	(*S*)-**2a**	20	32 (*S*)
6	(*R*)-**2b**	43	39 (*S*)
7	(*S*)-**3a**	41	32 (*S*)
8	(*R*)-**3b**	40	11 (*S*)

[a] % Conversion determined by ^{1}H NMR spectroscopy. [b] % *ee* determined by chiral HPLC (Lux Cellulose) with hexane/2-propanol (80:20); absolute configuration was assigned according to literature data. [c] Isolated yield and *ee* reported by Hayashi *et al*. in parenthesis.

2.7 General procedure for the asymmetric Suzuki-Miyaura cross-coupling reactions

MOP-ligand (20.0 µmol, 0.04 eq.) and bis(acetonitrile)dichloropalladium(II) (2.6 mg, 10 µmol, 0.02 eq.) were dissolved in DCM (2.0 mL) and stirred at room temperature for 2 h, after which the volatiles were removed *in vacuo*. Subsequently, the 1-bromo-naphthalene derivative (500 µmol, 1.0 eq.), naphthalene-1-boronic acid (112 mg, 650 µmol, 1.3 eq.), caesium carbonate (277 mg, 850 µmol, 1.7 eq.) and toluene (2.0 mL) were added. The reaction mixture was heated to 80 °C with stirring, and the conversion was monitored by ^{1}H NMR spectroscopy.

2.7.1 2-Methoxy-1,1'-binaphthyl

Silica gel column chromatography (petrol) yielded the pure product as a white solid. The ^{1}H and ^{13}C NMR spectroscopic data matched that of data reported in the literature,[14] and the HRMS data was in accordance with the calculated values. The enantiomeric excess was determined by chiral HPLC analysis; the absolute configuration was assigned by comparison to literature data.[15]

R_f = 0.07 (silica gel; petrol). **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.93-7.84 (m, 3H), 7.80 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.54 (dd, $^{3}J_{HH}$ = 8.2 Hz, $^{3}J_{HH}$ = 7.0 Hz, 1H), 7.42-7.34 (m, 3H), 7.28-7.05 (m, 5H), 3.69 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ (ppm) = 154.6, 134.6, 134.3, 133.7, 133.0, 129.5, 129.0, 128.4, 128.2, 127.8, 127.7, 126.4, 126.2, 125.9, 125.7, 125.6, 125.5, 123.6, 123.3, 113.9, 56.8. **HRMS** (ASAP^{+}, solid): Found: *m*/*z* = 285.1276. Calculated for $[M + H]^{+}$: *m*/*z* = 285.1274.

2.7.2 2-Methyl-1,1'-binaphthyl

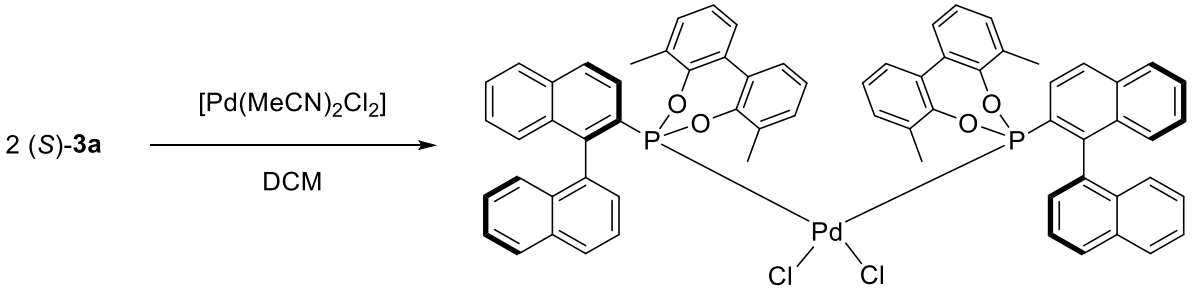
Silica gel column chromatography (petrol) yielded the product as a white solid, which contained a small amount of the inseparable homocoupling side product 1,1'-binaphthyl.[16] The ^{1}H and ^{13}C NMR spectroscopic data matched that of data reported in the literature,[14] and the HRMS data was in accordance with the calculated values. The enantiomeric excess was determined by chiral HPLC analysis; the absolute configuration was assigned by comparison to literature data.[15]

R_f = 0.28 (silica gel; petrol). **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.88 (*overlapping*-d, $^{3}J_{HH}$ = 8.3 Hz, 2H), 7.83-7.78 (m, 2H), 7.54 (dd, $^{3}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 7.0 Hz, 1H), 7.44-7.36 (m, 2H), 7.34-7.28 (m, 2H), 7.23-7.04 (m, 4H), 2.04 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ (ppm) = 137.5, 136.1, 134.4, 133.8, 133.5, 132.6, 132.0, 128.6, 128.3, 127.8, 127.8, 127.6, 127.6, 126.3, 126.1, 126.0, 125.9, 125.9, 125.7, 124.8, 20.5. **HRMS** (ASAP^{+}, solid): Found: *m*/*z* = 269.1326. Calculated for $[M + H]^{+}$: *m*/*z* = 269.1325.

2.8 General procedure for the synthesis of $[Pd(L^P)_2Cl_2]$ complexes.

Phosphonite ligand (40.0 µmol, 1.0 eq.) and bis(acetonitrile)dichloropalladium(II) (5.2 mg, 20 µmol, 1.0 eq.) were dissolved in DCM (2.0 mL) and stirred at room temperature for 2 h, after which the volatiles were removed *in vacuo*. The residue was washed with diethyl ether and dried *in vacuo*, to yield the pure title compound quantitatively as an off-white solid.

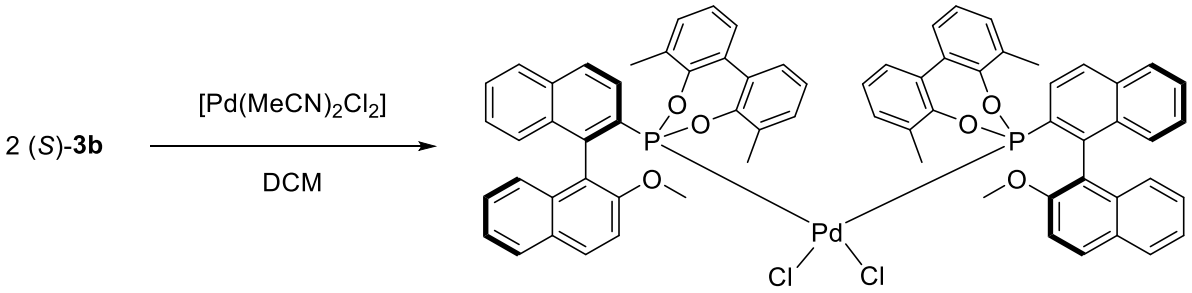
2.8.1 $[Pd((S)\text{-}\mathbf{3a})_2Cl_2]$ (*S*)-**11a**



Single crystals were grown by slow diffusion of hexane into a $CDCl_3$ solution.

MP: 255-257 °C (decomp.). **IR** (neat): ν = 3046.2 (w), 2360.3 (m), 1557.7 (w), 1452.7 (m), 1416.3 (m), 1249.8 (m), 1185.6 (s), 1087.4 (m), 912.0 (s), 873.0 (w), 800.6 (m), 771.3 (s), 745.1 (m), 690.1 (s), 634.8 (s), 613.0 (m) cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, −40 °C): δ (ppm) = 7.96 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *H*4), 7.89 (d, $^3J_{HH}$ = 8.3 Hz, 1H, *H*5), 7.85 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*5'), 7.70-7.66 (m, 2H, *H*3/*H*8'), 7.53 (*apparent*-t (dd), $^3J_{HH}$ = 7.6 Hz, 1H, *H*6), 7.46 (d, $^3J_{HH}$ = 8.3 Hz, 1H, *H*4'), 7.40 (*apparent*-t (dd), $^3J_{HH}$ = 7.4 Hz, 1H, *H*6'), 7.38-7.32 (m, 2H, *H*7'/*H*14'), 7.22-7.16 (m, 2H, *H*7/H15'), 7.15 (*apparent*-t (dd), $^3J_{HH}$ = 7.5 Hz, 1H, *H*15), 7.04-6.98 (m, 3H, *H*8/*H*16/*H*16'), 6.88 (d, $^3J_{HH}$ = 7.2 Hz, 1H, *H*14), 6.66 (*apparent*-t (dd), $^3J_{HH}$ = 7.5 Hz, 1H, *H*3'), 5.34 (d, $^3J_{HH}$ = 6.9 Hz, 1H, *H*2'), 2.09 (s, 3H, CH_3'), 0.84 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, −40 °C): δ (ppm) = 148.4 (*apparent*-t, J_{CP} = 6.6 Hz, *C*12), 146.5 (*apparent*-t, J_{CP} = 3.6 Hz, *C*12'), 141.5 (*C*1), 135.7 (*C*1'), 134.4 (*C*10), 133.1 (*C*9'), 132.7 (*apparent*-t, J_{CP} = 4.8 Hz, *C*9), 132.0 (*C*10'), 131.0 (*C*11'/*C*14/*C*14'), 130.3 (*C*13), 130.2 (*obscured*-m, *C*2), 130.2 (*C*11), 130.0 (*C*13'), 129.1 (*C*16), 128.9 (*C*5'), 128.5 (*C*6), 128.3 (*C*8), 128.0 (m, *C*3/*C*5), 127.7 (*C*4/*C*16'), 127.2 (*C*7), 127.1 (*C*4'), 127.0 (*C*8'), 126.4 (*C*15'), 126.1 (*C*7'), 126.0 (*C*2'), 125.8 (*C*6'), 125.4 (*C*15), 124.1 (*C*3'), 17.8 (*C*H_3'), 16.0 (*C*H_3). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$, −40 °C): δ (ppm) = 144.3 (s). **LRMS** (MALDI$^+$): Found: *m*/*z* = 1131.1. Calculated for $[M - Cl]^+$: *m*/*z* = 1131.2.

2.8.2 [Pd((*R*)-**3b**)$_2$Cl$_2$] (*R*)-**11b**



Single crystals were grown by slow diffusion of diethyl ether into a DCM solution.

MP: 247-249 °C (decomp.). **IR** (neat): ν = 2968.9 (w), 2361.2 (m), 1591.3 (w), 1486.3 (m), 1456.0 (m), 1250.7 (m), 1184.6 (m), 1081.1 (m), 963.3 (m), 915.5 (s), 806.1 (s), 773.2 (s), 745.9 (s), 685.4 (m), 638.2 (s), 617.4 (m) cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, −40 °C): δ (ppm) = 7.88 (d, $^3J_{HH}$ = 8.4 Hz, 1H, *H*5), 7.75 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *H*4), 7.70-7.65 (m, 2H, *H*4'/*H*5'), 7.57 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*8'), 7.53-7.46 (m, 2H, *H*6/H15'), 7.42 (d, $^3J_{HH}$ = 7.3 Hz, 1H, *H*14'), 7.31-7.25 (m, 3H, *H*6'/*H*7'/*H*16'), 7.21-7.17 (m, 1H, *H*7), 7.10 (d, $^3J_{HH}$ = 8.5 Hz, 1H, *H*8), 7.05 (d, $^3J_{HH}$ = 7.8 Hz, 1H, *H*16), 6.92 (*apparent*-t (dd), $^3J_{HH}$ = 7.5 Hz, 1H, *H*15), 6.75 (d, $^3J_{HH}$ = 7.2 Hz, 1H, *H*14), 6.68 (d, $^3J_{HH}$ = 9.1 Hz, 1H, *H*3'), 6.60-6.52 (m, 1H, *H*3), 2.73 (s, 3H, OCH_3), 1.69 (s, 3H, CH_3'), 1.13 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, −40 °C): δ (ppm) = 153.4 (*C*2'), 149.1 (*apparent*-t, J_{CP} = 7.2 Hz, *C*12), 148.3 (*apparent*-t, J_{CP} = 3.0 Hz, *C*12'), 136.8 (*C*1), 134.4 (*C*10), 134.0 (*C*9'), 132.8 (*C*13'), 132.4 (*apparent*-t, J_{CP} = 4.8 Hz, *C*9), 132.2 (*apparent*-t, J_{CP} = 34.8 Hz, *C*2), 131.5 (*C*14'), 130.8 (*C*11'), 130.4 (*C*13/*C*14), 129.7 (*C*4'), 128.6 (*C*16'), 128.4 (*C*16), 128.2 (*C*6), 128.0 (m, *C*4/*C*5/*C*8'), 127.7 (*C*10'), 127.5 (*C*8), 127.0 (m, *C*3/*C*7), 126.9 (*C*11), 126.7 (*C*5'), 126.5 (*C*7'), 126.4 (*C*15'), 124.1 (*C*15), 123.6 (*C*6'), 119.3 (*C*1'), 110.8 (*C*3'), 55.2 (O*C*H$_3$), 17.4 (*C*H$_3$'), 16.3 (*C*H$_3$). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$, −40 °C): δ (ppm) = 139.4 (s). **LRMS** (MALDI$^+$): Found: *m*/*z* = 1191.3. Calculated for [M − Cl]$^+$: *m*/*z* = 1191.2.

3. Density Functional Theory Calculations

Performed with the B3LYP functional and 6-31G* basis set, using the *Spartan* program. In each case the calculations were considered to be complete and converged to a minimum on the potential energy surface after vibrational frequency analysis did not report any negative frequencies.

3.1 DFT Calculations: Table 3

Table 3 Calculated conformational energy differences versus dihedral angle for the ligands (*S*)-**3a** and (*R*)-**3b**, relative to the energy at the optimised dihedral angle.

Dihedral angle[a]	Relative energy[b]	
	(*S*)-**3a**	(*R*)-**3b**
−90.00	14.26	14.34
−75.00	5.93	5.87
−60.00	1.31	1.29
−46.11	0.00	–
−46.00	–	0.00
−45.00	0.01	0.02
−30.00	1.46	1.15
−15.00	5.44	5.71
0.00	7.34	7.39
15.00	5.70	5.91
30.00	2.07	2.28
45.00	0.71	0.76
45.56	0.71	–
45.60	–	0.75
60.00	2.11	2.19
75.00	6.73	6.93
90.00	15.11	15.45

[a] C12−C11−C11'−C12' (°). [b] Optimised ligand geometry (kcal/mol).

4. **X-ray Diffraction**

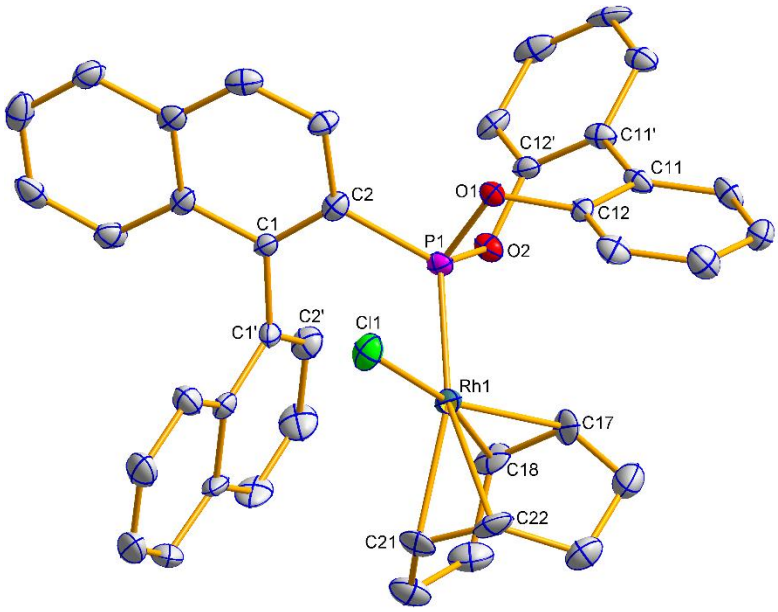


Fig. 2 Molecular structure of (*S*)-**8a**. Hydrogen atoms have been omitted for clarity. Selected average bond distances (Å) and angles (°): Rh1–P1 2.211(2), Rh1–Cl1 2.364(2), Rh1–C17 2.123(8), Rh1–C18 2.116(8), Rh1–C21 2.233(8), Rh1–C22 2.265(8), P1–C2 1.812(8), P1–O1 1.621(6), P1–O2 1.619(5), C17–C18 1.426(13), C21–C22 1.358(13); P1–Rh1–Cl1 86.00(8), P1–Rh1–C17 93.0(3), P1–Rh1–C18 97.0(3), P1–Rh1–C21 162.7(2), P1–Rh1–C22 162.0(3), C2–C1–C1'–C2' –82.6(10), C12–C11–C11'–C12' –46.6(11).

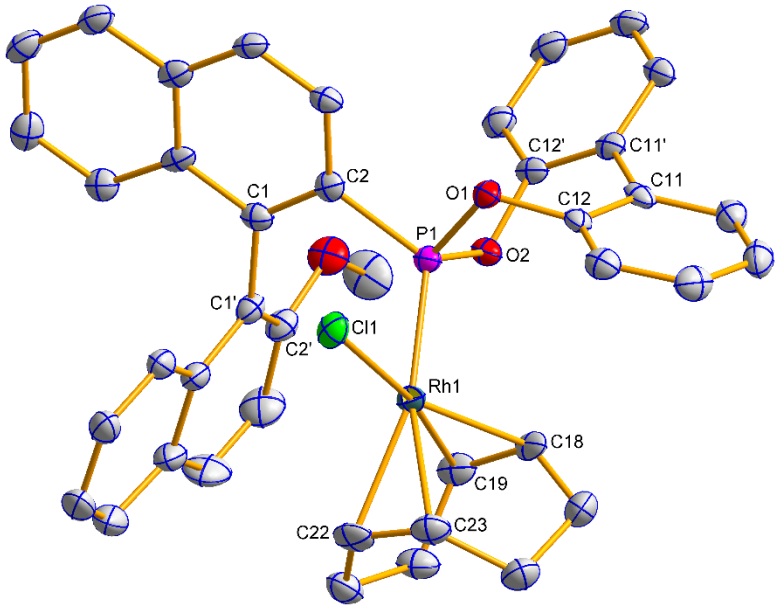


Fig. 3 Molecular structure of (*R*)-**8b**. Hydrogen atoms have been omitted for clarity. Selected average bond distances (Å) and angles (°): Rh1–P1 2.2104(13), Rh1–Cl1 2.3757(12), Rh1–C18 2.106(4), Rh1–C19 2.129(4), Rh1–C22 2.243(5), Rh1–C23 2.273(5), P1–C2 1.810(5), P1–O1 1.628(3), P1–O2 1.628(3), C18–C19 1.404(8), C22–C23 1.353(7); P1–Rh1–Cl1 86.00(4), P1–Rh1–C18 93.15(14), P1–Rh1–C19 96.99(14), P1–Rh1–C22 162.30(15), P1–Rh1–C23 162.61(14), C2–C1–C1'–C2' –90.9(6), C12–C11–C11'–C12' –43.3(6).

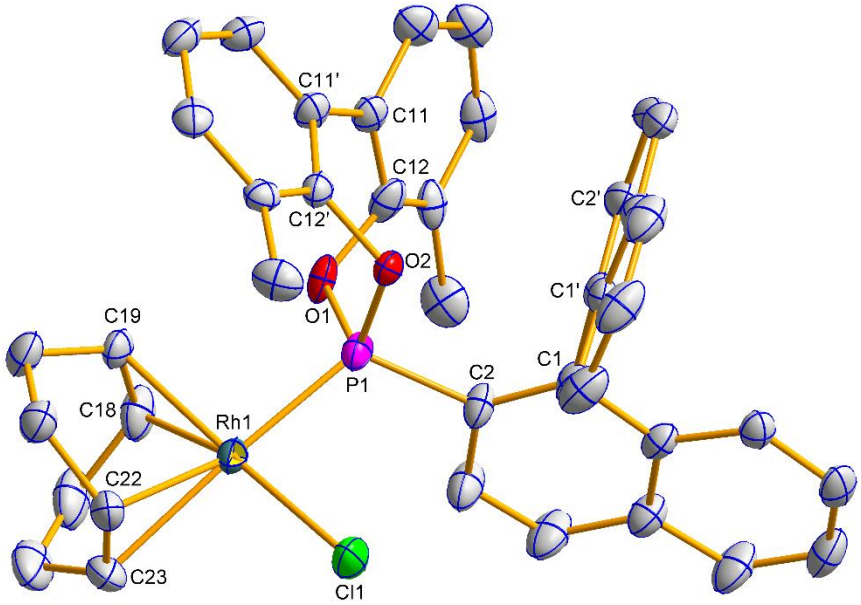


Fig. 4 Molecular structure of one of the two independent molecules of (*S*)-**9a** (the asymmetric unit comprises two molecules in different conformations). Hydrogen atoms have been omitted for clarity. Selected average bond distances (Å) and angles (°): Rh1–P1 2.2139(12), Rh1–Cl1 2.3686(17), Rh1–C18 2.110(5), Rh1–C19 2.131(6), Rh1–C22 2.240(5), Rh1–C23 2.287(5), P1–C2 1.804(5), P1–O1 1.621(14), P1–O2 1.612(3), C18–C19 1.408(8), C22–C23 1.366(7); P1–Rh1–Cl1 87.72(6), P1–Rh1–C18 94.71(16), P1–Rh1–C19 93.08(15), P1–Rh1–C22 153.63(13), P1–Rh1–C23 171.16(13), C2–C1–C1'–C2' –89.0(6), C12–C11–C11'–C12' 35.2.

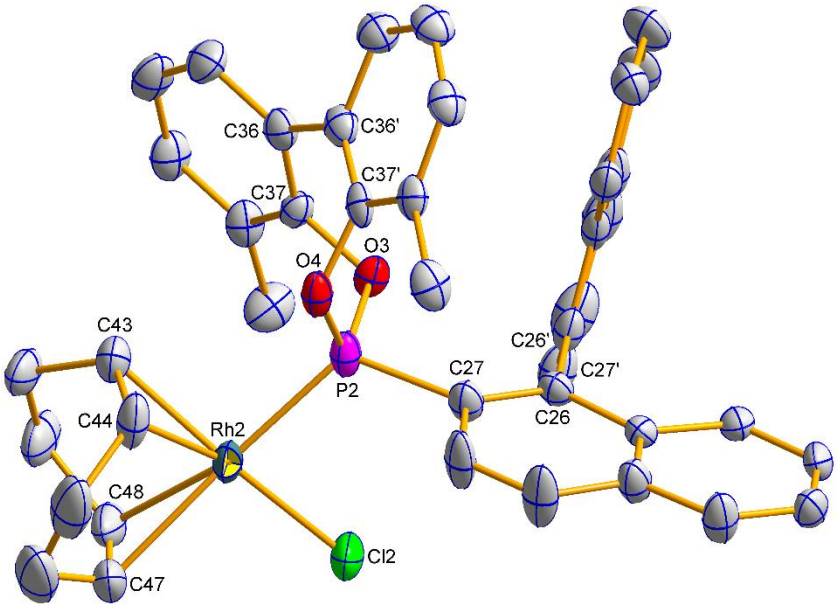


Fig. 5 Molecular structure of the second of the two independent molecules of (*S*)-**9a**. Hydrogen atoms have been omitted for clarity. Selected average bond distances (Å) and angles (°): Rh2–P2 2.2173(13), Rh2–Cl2 2.353(2), Rh2–C43 2.141(7), Rh2–C44 2.122(6), Rh2–C47 2.291(6), Rh2–C48 2.248(6), P2–C27 1.816(5), P2–O3 1.611(3), P2–O4 1.550(10), C43–C44 1.408(8), C47–C48 1.322(9); P2–Rh2–Cl2 87.72(6), P2–Rh2–C43 92.83(16), P2–Rh2–C44 96.29(17), P2–Rh2–C47 173.18(18), P2–Rh2–C48 152.96(17), C27–C26–C26'–C27' –87.0(7), C37–C36–C36'–C37' –43(3).

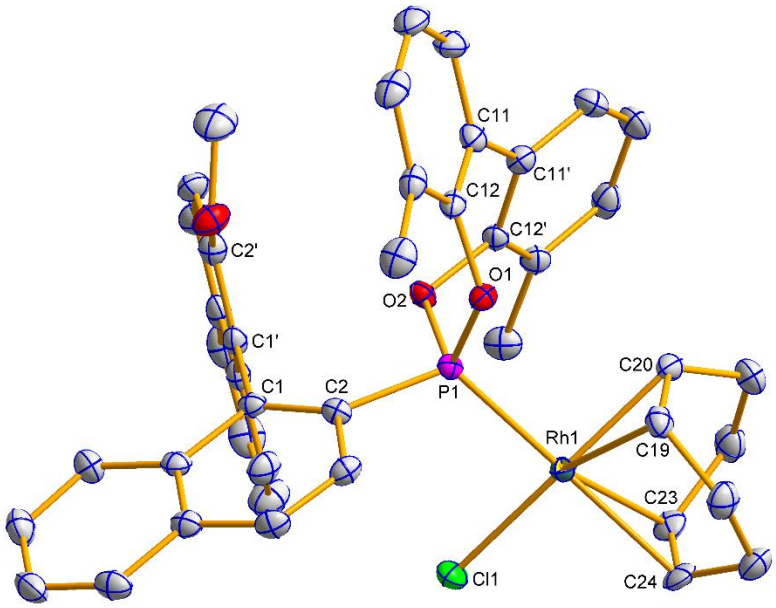


Fig. 6 Molecular structure of one of the two independent molecules of (*R*)-**9b** (the asymmetric unit comprises two molecules in different conformations). Hydrogen atoms have been omitted for clarity. Selected average bond distances (Å) and angles (°): Rh1–P1 2.2365(11), Rh1–Cl1 2.3529(12), Rh1–C19 2.124(5), Rh1–C20 2.139(5), Rh1–C23 2.249(5), Rh1–C24 2.287(5), P1–C2 1.812(4), P1–O1 1.619(3), P1–O2 1.611(3), C19–C20 1.414(7), C23–C24 1.358(7); P1–Rh1–Cl1 91.14(4), P1–Rh1–C19 95.88(14), P1–Rh1–C20 92.01(13), P1–Rh1–C23 150.26(14), P1–Rh1–C24 174.67(14), C2–C1–C1'–C2' –82.8(6), C12–C11–C11'–C12' 44.4(7).

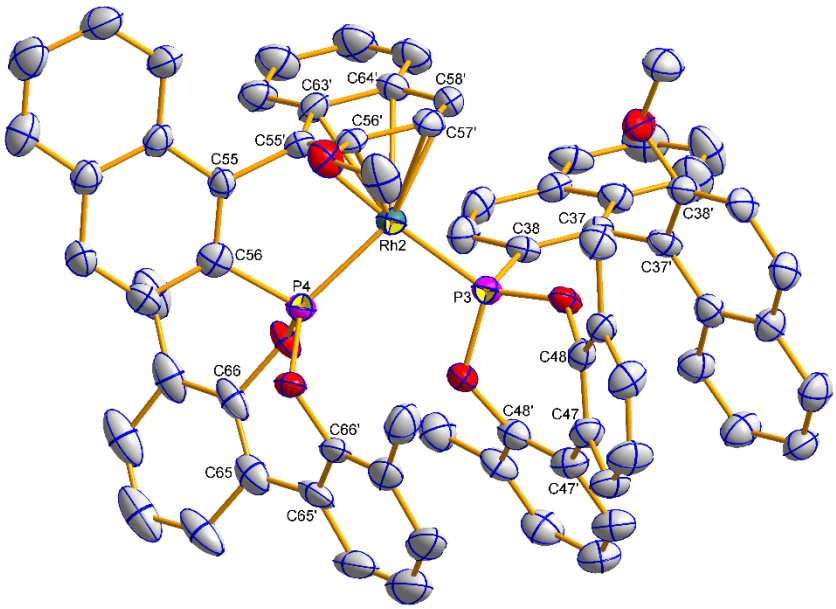


Fig. 7 Molecular structure of one of the cations of (*R*)-**10b** (the asymmetric unit comprises two cations and two anions in different conformations). Hydrogen atoms have been omitted for clarity. Selected average bond distances (Å) and angles (°): Rh2–P3 2.2148(18), Rh2–P4 2.1743(18), Rh2–C55' 2.174(7), Rh2–C56' 2.314(6), Rh2–C57' 2.321(6), Rh2–C58' 2.305(7), Rh2–C63' 2.474(7), Rh2–C64' 2.500(6), P3–C38 1.823(7), P4–C56 1.822(7); P3–Rh2–P4 98.97(7), Rh2–P3–C38 111.7(2), Rh2–P4–C56 105.7(2), C38–C37–C37'–C38' –84.4(8), C48–C47–C47'–C48' –34.7(12), C56–C55–C55'–C56' –92.5(8), C66–C65–C65'–C66' 38(3).

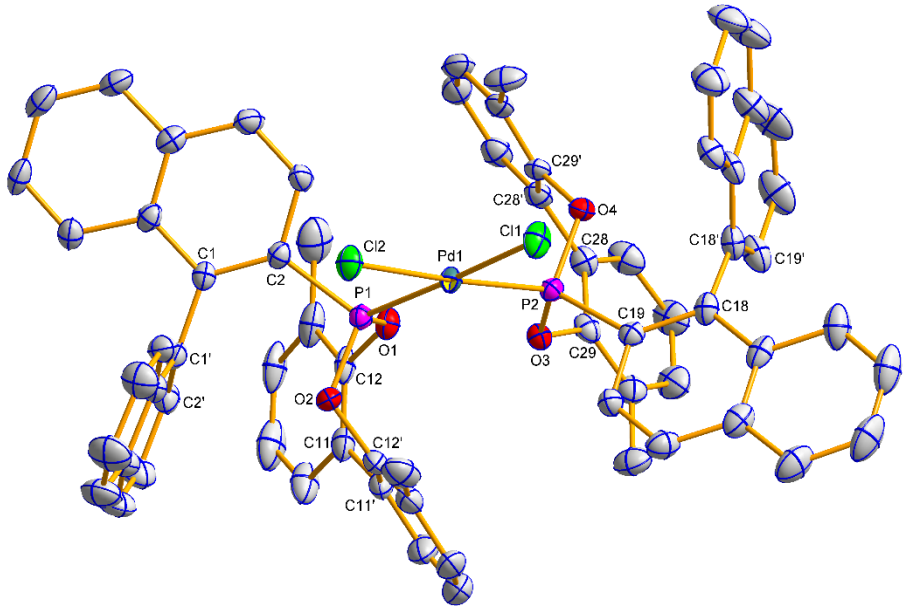


Fig. 8 Molecular structure of (*S*)-**11a**, pseudo-polymorph 1. Hydrogen atoms have been omitted for clarity. Selected average bond distances (Å) and angles (°): Pd1–P1 2.2246(14), Pd1–P2 2.2331(15), Pd1–Cl1 2.3372(15), Pd1–Cl2 2.3485(15), P1–C2 1.811(6), P1–O1 1.596(4), P1–O2 1.597(4), P2–C19 1.807(6), P2–O3 1.594(4), P2–O4 1.598(4); P1–Pd1–P2 99.79(5), P1–Pd1–Cl1 175.23(6), P1–Pd1–Cl2 84.30(5), C2–C1–C1'–C2' –94.3(7), C12–C11–C11'–C12' 45.6(9), C19–C18–C18'–C19' –87.6(7), C29–C28–C28'–C29' –44.1(8).

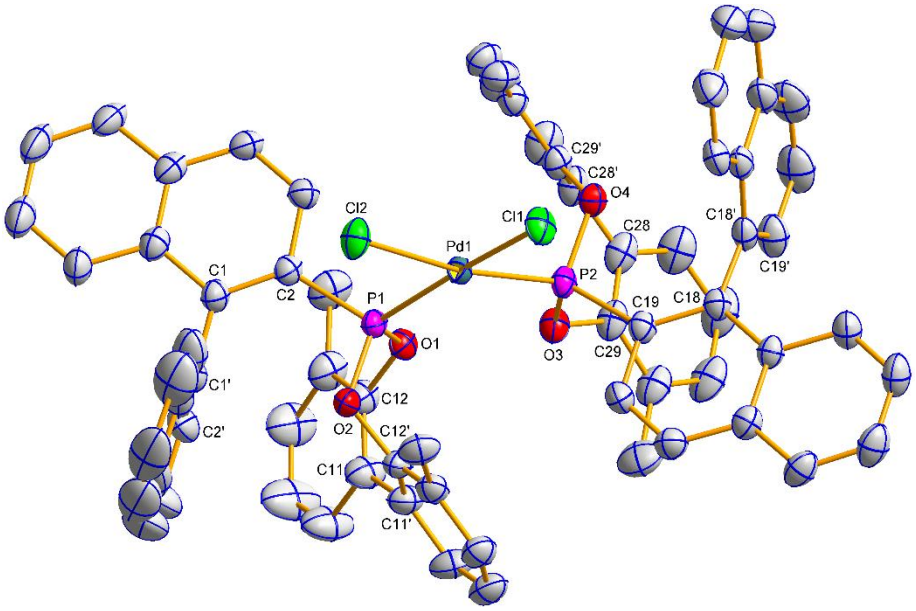


Fig. 9 Molecular structure of (*S*)-**11a**, pseudo-polymorph 2. Hydrogen atoms have been omitted for clarity. Selected average bond distances (Å) and angles (°): Pd1–P1 2.2234(9), Pd1–P2 2.2302(10), Pd1–Cl1 2.3411(9), Pd1–Cl2 2.3302(9), P1–C2 1.807(4), P1–O1 1.598(3), P1–O2 1.596(3), P2–C19 1.803(4), P2–O3 1.599(3), P2–O4 1.597(3); P1–Pd1–P2 101.16(3), P1–Pd1–Cl1 170.96(4), P1–Pd1–Cl2 84.57(4), C2–C1–C1'–C2' –89.9(5), C12–C11–C11'–C12' 47.1(7), C19–C18–C18'–C19' –93.0(5), C29–C28–C28'–C29' 45.4(6).

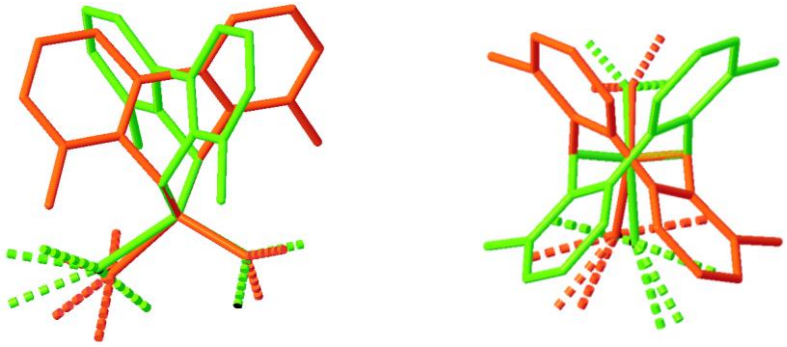


Fig. 10 Two views of an overlay image of the biphenyl moiety in the two independent molecules of (*R*)-**9b**.

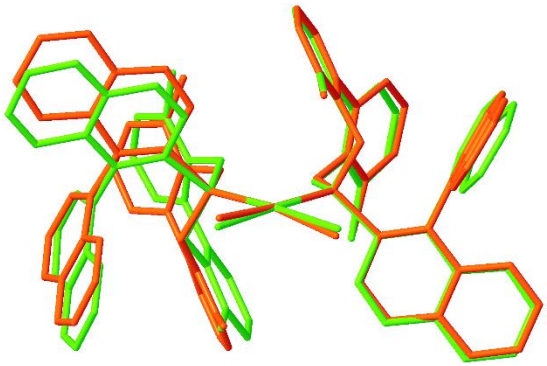


Fig. 11 An overlay image of the two pseudo-polymorphs of (*S*)-**11a**.

Measurements were made at 150 K on an Oxford Diffraction (Agilent Technologies) Gemini A Ultra diffractometer, using CuKα radiation (λ =1.54184 Å) for (*R*)-**10b**, (*S*)-**11a** (pseudo-polymorph 2) and (*R*)-**11b** and MoKα radiation (λ = 0.71073 Å) for (*R*)-**6b**, (*S*)-**8a**, (*R*)-**8b**, (*S*)-**9a**, (*R*)-**9b** and (*S*)-**11a** (pseudo-polymorph 1). Cell parameters were refined from the observed positions of all strong reflections. Intensities were corrected for absorption, using a semi-empirical method based on symmetry-equivalent and repeated reflections for (*S*)-**8a** and (*R*)-**8b** and analytically using a multi-faceted crystal model for (*R*)-**6b**, (*S*)-**9a**, (*R*)-**9b**, (*R*)-**10b**, (*S*)-**11a** (pseudo-polymorphs 1 and 2) and (*R*)-**11b**.[17] The structures were solved by direct methods and refined on F^2 values for all unique data. All non-hydrogen atoms were refined anisotropically, and H atoms were positioned with idealised geometry and their thermal parameters constrained using the riding model; $U_{(H)}$ was set at 1.2 times U_{eq} for the parent C atom. Oxford Diffraction CrysAlisPro was used for data collection and processing,[18] and Olex2[19] using SHELX[20] for structure solution, refinement, and to generate the molecular overlap figures. Crystal Impact Diamond was used to generate all other molecular graphics with displacement ellipsoids drawn at the 50% probability level.[21]

4.1 Crystal data and structure refinement for [Pt((*R*)-**2b**)(PEt_3)Cl_2] (*R*)-**6b**

Molecular formula	$C_{39}H_{38}O_3P_2Cl_2Pt$
Formula weight	882.62
Temperature/K	150.00(10)
Crystal system	trigonal
Space group	$P3_2$
a/Å	11.52064(15)
b/Å	11.52064(15)
c/Å	22.9152(3)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	2633.95(8)
Z	3
ρ_{calc}g/cm^3	1.669
μ/mm^{-1}	4.276
F(000)	1314.0
Crystal size/mm^3	0.21 × 0.17 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.414 to 56.796
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -30 ≤ l ≤ 30
Reflections collected	83576
Independent reflections	8250 [R_{int} = 0.0495, R_{sigma} = 0.0282]
Data/restraints/parameters	8250/400/428
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0200, wR_2 = 0.0353
Final R indexes [all data]	R_1 = 0.0227, wR_2 = 0.0363
Largest diff. peak/hole / e Å^{-3}	0.99/-0.44
Flack parameter	-0.0247(18)

4.2 Crystal data and structure refinement for [Rh((*S*)-**2a**)(η^2:η^2-cod)Cl] (*S*)-**8a**

Molecular formula	$C_{40}H_{33}O_2PClRh$
Formula weight	714.99
Temperature/K	150.0(2)
Crystal system	hexagonal
Space group	$P6_5$
a/Å	10.4774(2)
b/Å	10.4774(2)
c/Å	49.1495(16)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	4672.6(2)
Z	6
ρ_{calc}g/cm^3	1.525
μ/mm^{-1}	0.722
F(000)	2196.0
Crystal size/mm^3	0.3 × 0.3 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.582 to 56.418
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 12, -64 ≤ l ≤ 59
Reflections collected	31490
Independent reflections	6807 [R_{int} = 0.0613, R_{sigma} = 0.0456]
Data/restraints/parameters	6807/1/406
Goodness-of-fit on F^2	1.220
Final R indexes [I>=2σ (I)]	R_1 = 0.0574, wR_2 = 0.1080
Final R indexes [all data]	R_1 = 0.0591, wR_2 = 0.1090
Largest diff. peak/hole / e Å^{-3}	0.66/-1.67
Flack parameter	0.065(15)

4.3 Crystal data and structure refinement for [Rh((*R*)-**2b**)(η^2:η^2-cod)Cl] (*R*)-**8b**

Molecular formula	$C_{41}H_{35}O_3PClRh$
Formula weight	745.02
Temperature/K	150.0(2)
Crystal system	trigonal
Space group	$P3_2$
a/Å	10.6324(3)
b/Å	10.6324(3)
c/Å	24.9502(8)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	2442.68(16)
Z	3
ρ_{calc}g/cm^3	1.519
μ/mm^{-1}	0.696
F(000)	1146.0
Crystal size/mm^3	0.24 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.602 to 56.85
Index ranges	-14 ≤ h ≤ 10, -11 ≤ k ≤ 12, -31 ≤ l ≤ 32
Reflections collected	15538
Independent reflections	6762 [R_{int} = 0.0369, R_{sigma} = 0.0556]
Data/restraints/parameters	6762/1/425
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0351, wR_2 = 0.0638
Final R indexes [all data]	R_1 = 0.0413, wR_2 = 0.0680
Largest diff. peak/hole / e Å^{-3}	0.55/-0.45
Flack parameter	-0.059(15)

4.4 Crystal data and structure refinement for [Rh((*S*)-**3a**)(η^2:η^2-cod)Cl] (*S*)-**9a**

Molecular formula	$C_{42}H_{37}O_2PClRh$
Formula weight	743.04
Temperature/K	150.0(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.46454(10)
b/Å	18.62602(18)
c/Å	18.5228(2)
α/°	90
β/°	92.0930(9)
γ/°	90
Volume/Å^3	3607.92(6)
Z	4
ρ_{calc}g/cm^3	1.368
μ/mm^{-1}	0.626
F(000)	1528.0
Crystal size/mm^3	0.22 × 0.19 × 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.604 to 56.462
Index ranges	-13 ≤ h ≤ 13, -24 ≤ k ≤ 24, -24 ≤ l ≤ 24
Reflections collected	115490
Independent reflections	16266 [R_{int} = 0.0501, R_{sigma} = 0.0350]
Data/restraints/parameters	16266/1097/889
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0340, wR_2 = 0.0763
Final R indexes [all data]	R_1 = 0.0439, wR_2 = 0.0802
Largest diff. peak/hole / e Å^{-3}	0.44/-0.89
Flack parameter	-0.013(12)

4.5 Crystal data and structure refinement for [Rh((*R*)-**3b**)(η^2:η^2-cod)Cl] (*R*)-**9b**

Molecular formula	$C_{43}H_{39}O_3PClRh$
Formula weight	773.07
Temperature/K	150.0(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.69170(6)
b/Å	17.44304(12)
c/Å	20.04701(13)
α/°	90
β/°	90.6504(6)
γ/°	90
Volume/Å^3	3388.78(4)
Z	4
ρ_{calc}g/cm^3	1.515
μ/mm^{-1}	0.672
F(000)	1592.0
Crystal size/mm^3	0.32 × 0.17 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.59 to 55.754
Index ranges	-12 ≤ h ≤ 12, -22 ≤ k ≤ 22, -26 ≤ l ≤ 26
Reflections collected	107785
Independent reflections	15240 [R_{int} = 0.0451, R_{sigma} = 0.0327]
Data/restraints/parameters	15240/1/889
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0344, wR_2 = 0.0845
Final R indexes [all data]	R_1 = 0.0401, wR_2 = 0.0877
Largest diff. peak/hole / e Å^{-3}	0.62/-1.14
Flack parameter	-0.028(6)

4.6 Crystal data and structure refinement for [Rh((*R*)-**3b**)$_2$]BF$_4$ (*R*)-**10b**

Molecular formula	$C_{70}H_{54}O_6P_2Rh^+ \cdot BF_4^-$
Formula weight	1242.79
Temperature/K	150.0(2)
Crystal system	triclinic
Space group	P1
a/Å	11.7059(2)
b/Å	16.9283(3)
c/Å	17.9950(4)
α/°	73.4211(18)
β/°	73.7906(17)
γ/°	89.1816(15)
Volume/Å^3	3273.51(11)
Z	2
ρ_{calc}g/cm^3	1.261
μ/mm^{-1}	3.070
F(000)	1276.0
Crystal size/mm^3	0.19 × 0.11 × 0.08
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.35 to 133.952
Index ranges	-13 ≤ h ≤ 13, -20 ≤ k ≤ 20, -20 ≤ l ≤ 21
Reflections collected	89533
Independent reflections	22461 [R_{int} = 0.0631, R_{sigma} = 0.0517]
Data/restraints/parameters	22461/292/1574
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0455, wR_2 = 0.1105
Final R indexes [all data]	R_1 = 0.0539, wR_2 = 0.1155
Largest diff. peak/hole / e Å^{-3}	1.81/-0.84
Flack parameter	-0.026(3)

4.7 Crystal data and structure refinement for [Pd((*S*)-**3a**)$_2$Cl$_2$] (*S*)-**11a**, pseudo-polymorph 1

Molecular formula	$C_{68}H_{50}O_4P_2Cl_2Pd \cdot 3CHCl_3$
Formula weight	1528.42
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	11.5925(9)
b/Å	21.8177(11)
c/Å	14.4054(11)
α/°	90
β/°	111.477(8)
γ/°	90
Volume/Å^3	3390.4(4)
Z	2
ρ_{calc}g/cm^3	1.497
μ/mm^{-1}	0.803
F(000)	1548.0
Crystal size/mm^3	0.27 × 0.17 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.864 to 57.792
Index ranges	-14 ≤ h ≤ 14, -28 ≤ k ≤ 29, -19 ≤ l ≤ 19
Reflections collected	22655
Independent reflections	13225 [R_{int} = 0.0402, R_{sigma} = 0.0727]
Data/restraints/parameters	13225/787/831
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0455, wR_2 = 0.0810
Final R indexes [all data]	R_1 = 0.0608, wR_2 = 0.0892
Largest diff. peak/hole / e Å^{-3}	0.66/-0.64
Flack parameter	-0.052(15)

4.8 Crystal data and structure refinement for [Pd((*S*)-**3a**)$_2$Cl$_2$] (*S*)-**11a**, pseudo-polymorph 2

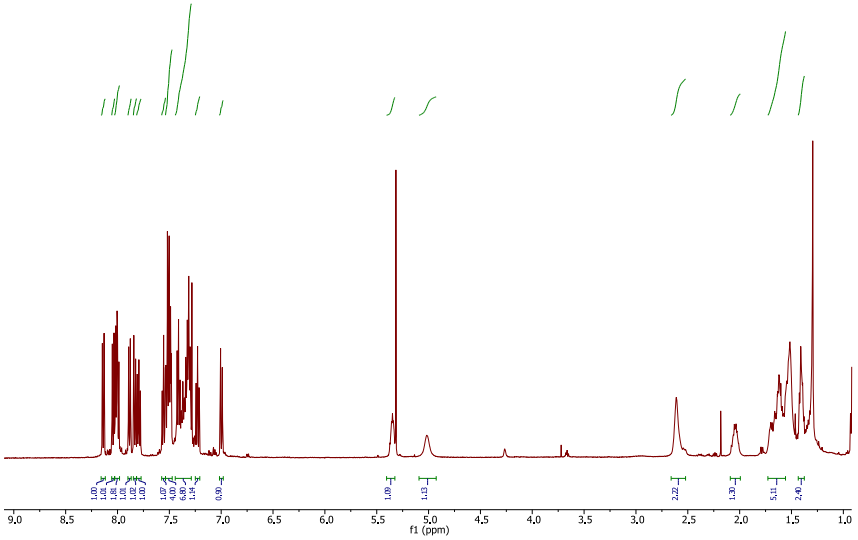
Molecular formula	$C_{68}H_{50}O_4P_2Cl_2Pd \cdot CHCl_3$
Formula weight	1289.69
Temperature/K	150.01(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	11.54920(12)
b/Å	17.81230(17)
c/Å	29.1165(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	5989.78(11)
Z	4
ρ_{calc}g/cm^3	1.430
μ/mm^{-1}	5.450
F(000)	2632.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.816 to 132.694
Index ranges	-13 ≤ h ≤ 13, -16 ≤ k ≤ 21, -34 ≤ l ≤ 33
Reflections collected	52298
Independent reflections	10465 [R_{int} = 0.0385, R_{sigma} = 0.0294]
Data/restraints/parameters	10465/702/734
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0266, wR_2 = 0.0627
Final R indexes [all data]	R_1 = 0.0289, wR_2 = 0.0643
Largest diff. peak/hole / e Å^{-3}	0.59/-0.47
Flack parameter	-0.024(2)

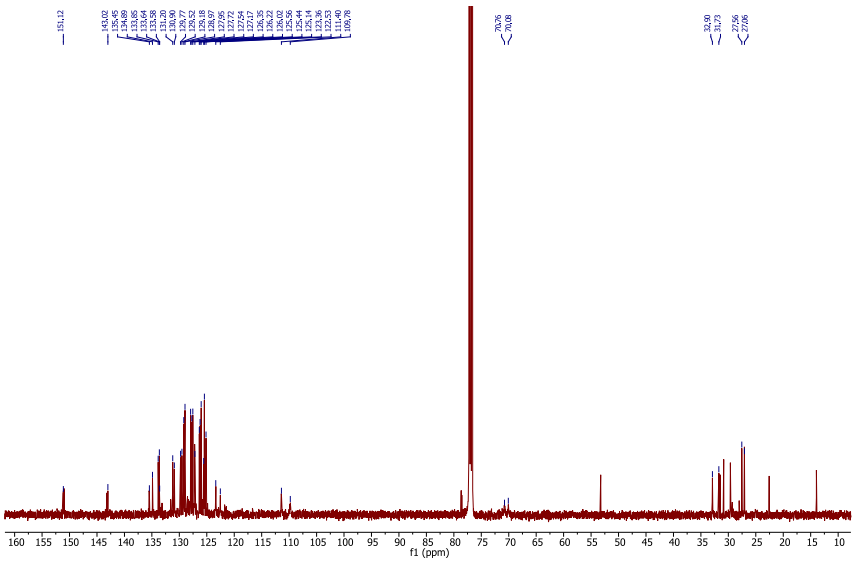
4.9 Crystal data and structure refinement for [Pd((*R*)-**3b**)$_2$Cl$_2$] (*R*)-**11b**

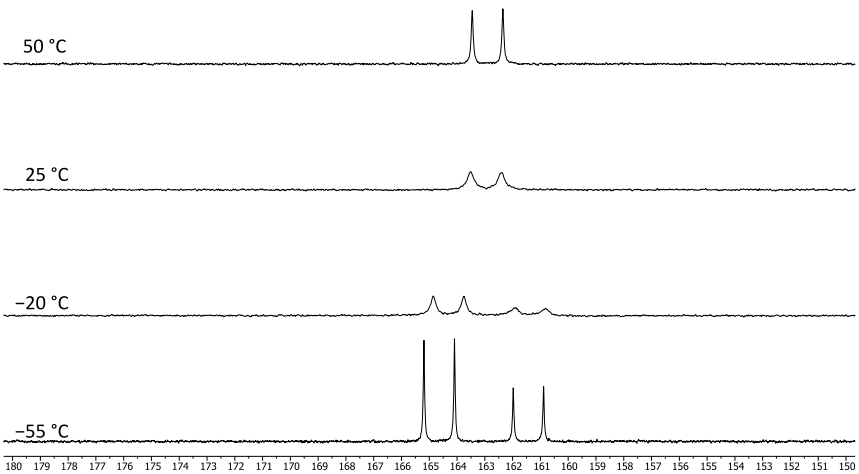
Molecular formula	$C_{70}H_{54}O_6P_2Cl_2Pd$
Formula weight	1230.37
Temperature/K	150.0(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	11.28960(10)
b/Å	20.94262(17)
c/Å	14.09792(13)
α/°	90
β/°	101.7126(8)
γ/°	90
Volume/Å^3	3263.82(5)
Z	2
ρ_{calc}g/cm^3	1.252
μ/mm^{-1}	3.897
F(000)	1264.0
Crystal size/mm^3	0.19 × 0.16 × 0.11
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.402 to 133.838
Index ranges	-13 ≤ h ≤ 13, -25 ≤ k ≤ 24, -16 ≤ l ≤ 16
Reflections collected	43167
Independent reflections	11588 [R_{int} = 0.0448, R_{sigma} = 0.0382]
Data/restraints/parameters	11588/1/736
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0293, wR_2 = 0.0690
Final R indexes [all data]	R_1 = 0.0329, wR_2 = 0.0710
Largest diff. peak/hole / e Å^{-3}	0.26/-0.27
Flack parameter	-0.016(4)

5. **NMR Spectra**

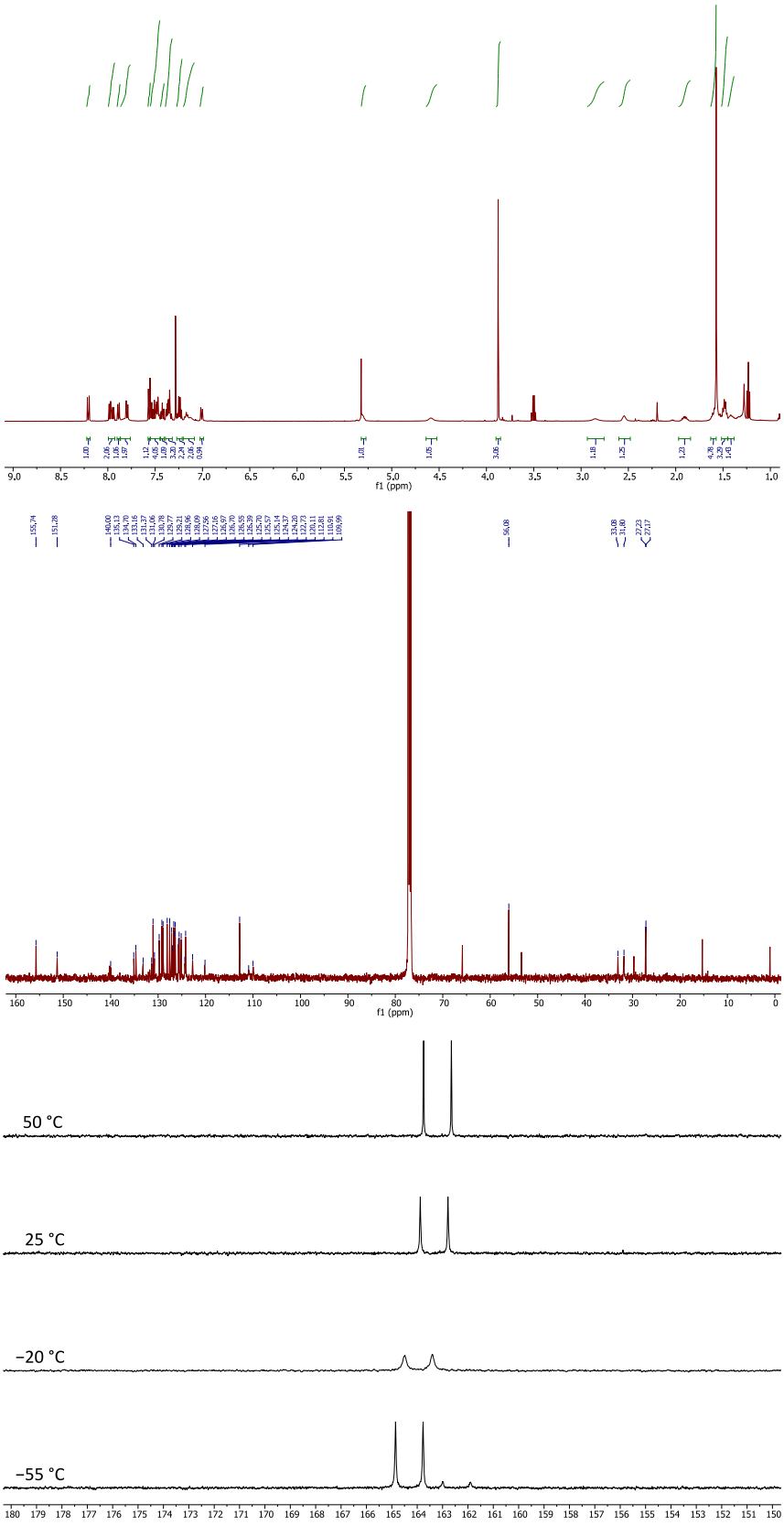
5.1 ^{1}H, ^{13}C and ^{31}P NMR spectra for [Rh((*S*)-**2a**)(η^2:η^2-cod)Cl] (*S*)-**8a**



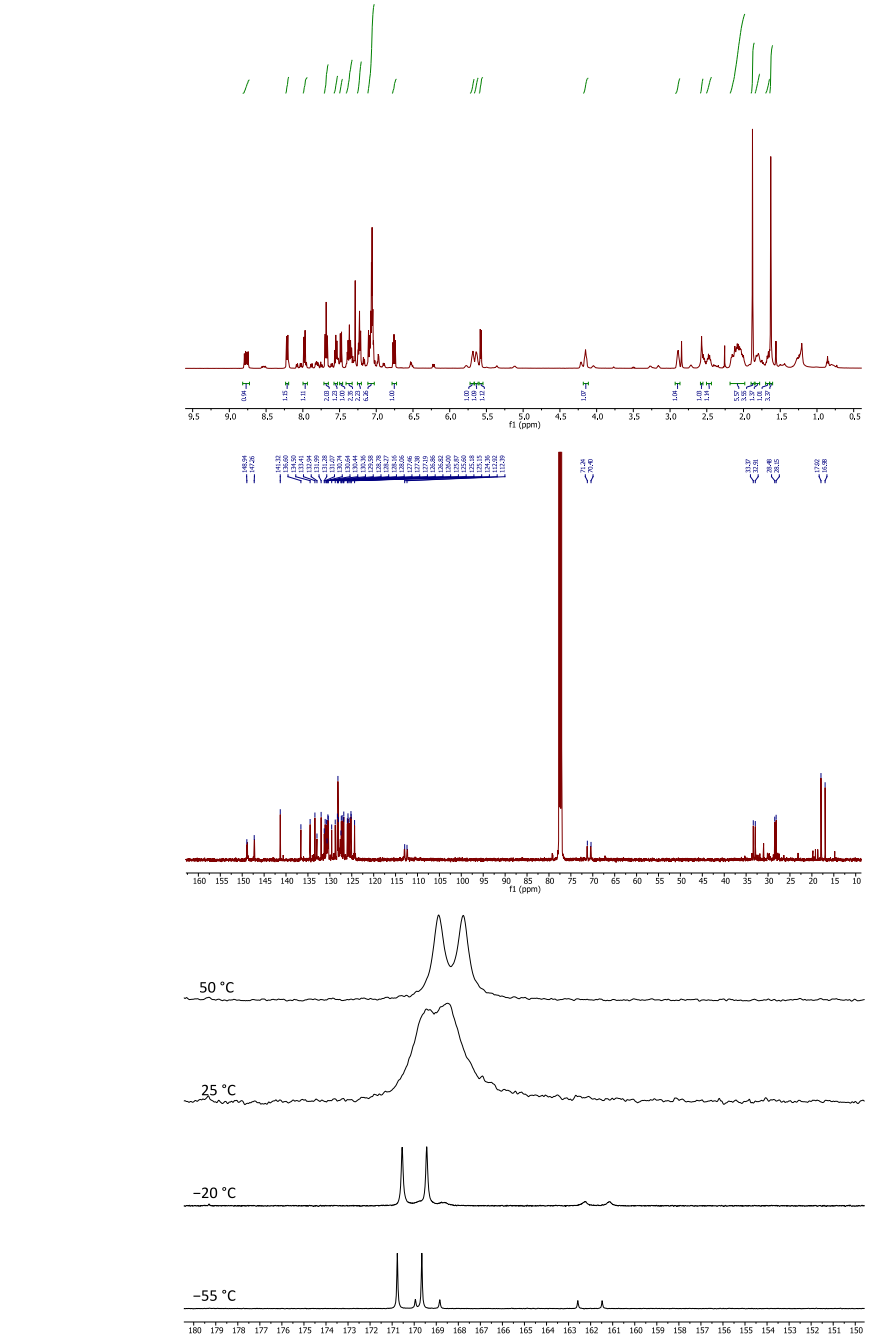




5.2 ^{1}H, ^{13}C and ^{31}P NMR spectra for [Rh((*R*)-**2b**)(η^2:η^2-cod)Cl] (*R*)-**8b**

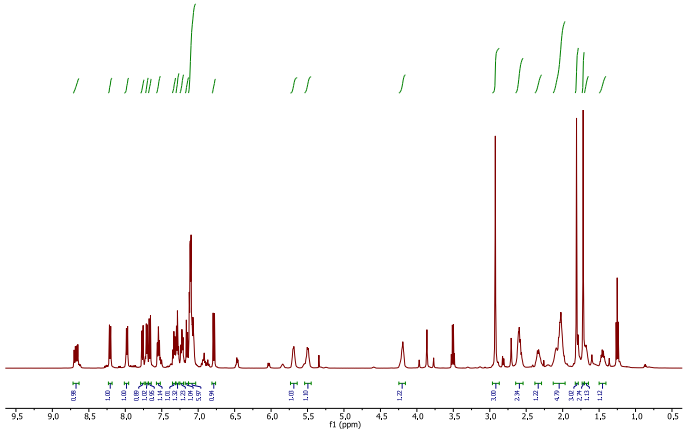


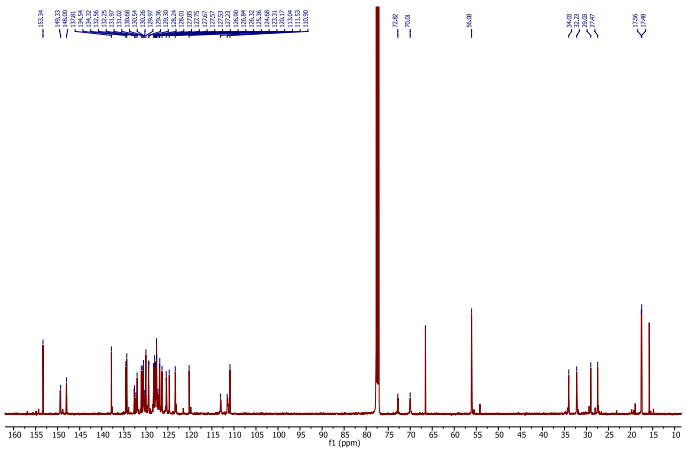
5.3 ^{1}H, ^{13}C and ^{31}P NMR spectra for [Rh((*S*)-**3a**)(η^2:η^2-cod)Cl] (*S*)-**9a**

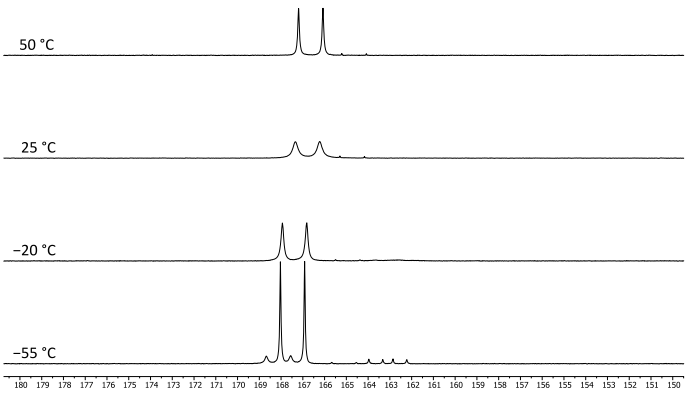


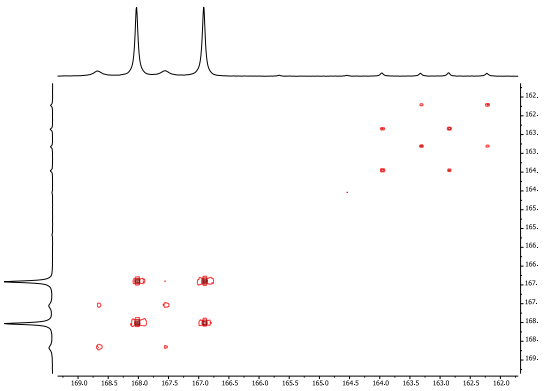
2D phase-sensitive $^{31}P\{^{1}H\}$ EXSY NMR spectra in $CDCl_3$ at −55 °C, with a mixing time of 100 ms. The diagonal and exchange cross-peaks are phased positive (red).

5.4 ^{1}H, ^{13}C and ^{31}P NMR spectra for [Rh((*R*)-**3b**)(η^2:η^2-cod)Cl] (*R*)-**9b**



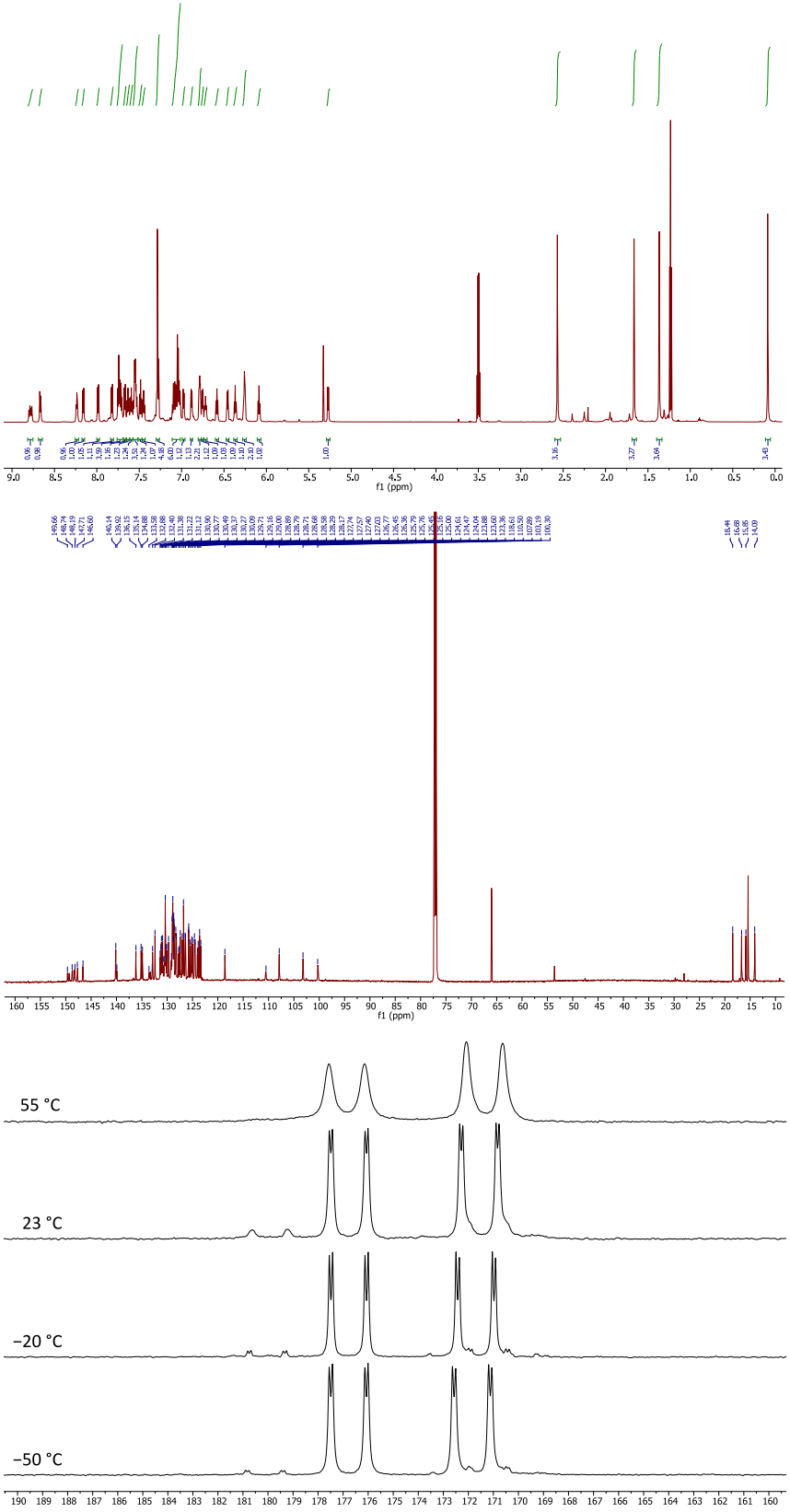




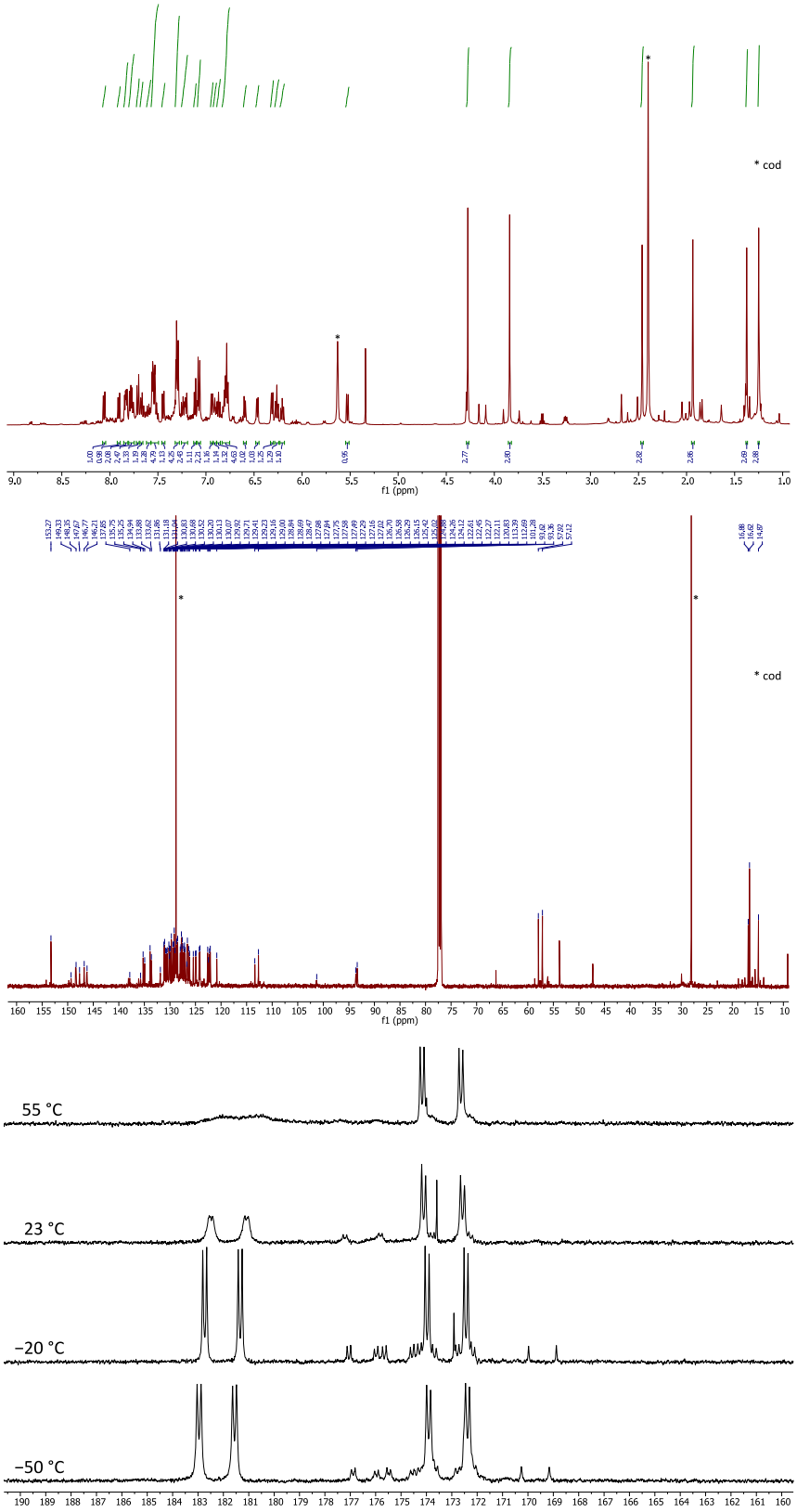


2D phase-sensitive $^{31}P\{^{1}H\}$ EXSY NMR spectra in $CDCl_3$ at −55 °C, with a mixing time of 100 ms. The diagonal and exchange cross-peaks are phased positive (red).

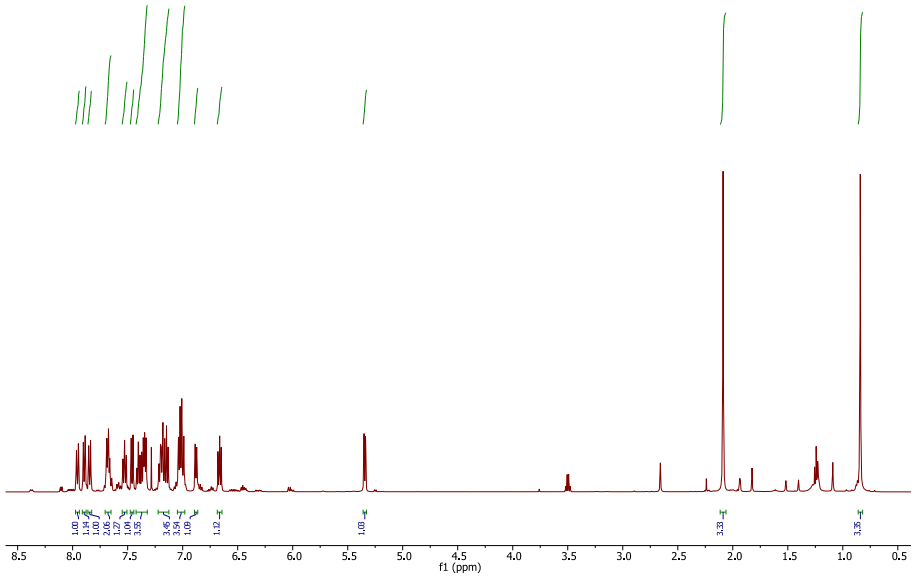
5.5 ^{1}H, ^{13}C and ^{31}P NMR spectra for $[Rh((S)\text{-}\mathbf{3a})_2]BF_4$ (*S*)-**10a**

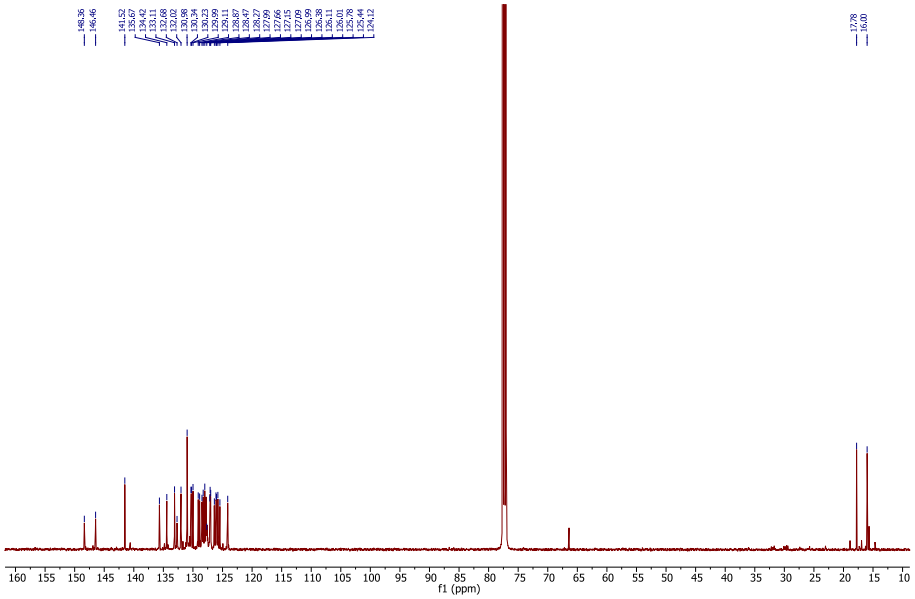


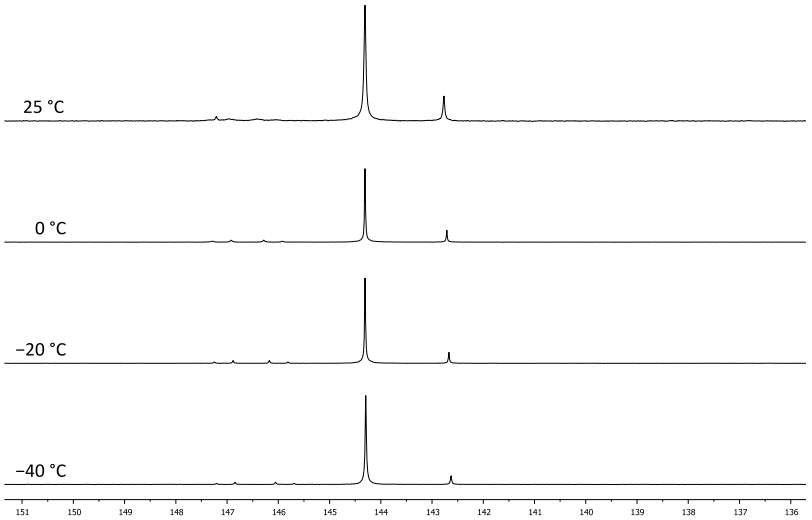
5.6 ^{1}H, ^{13}C and ^{31}P NMR spectra for $[Rh((R)\text{-}\mathbf{3b})_2]BF_4$ (*R*)-**10b**



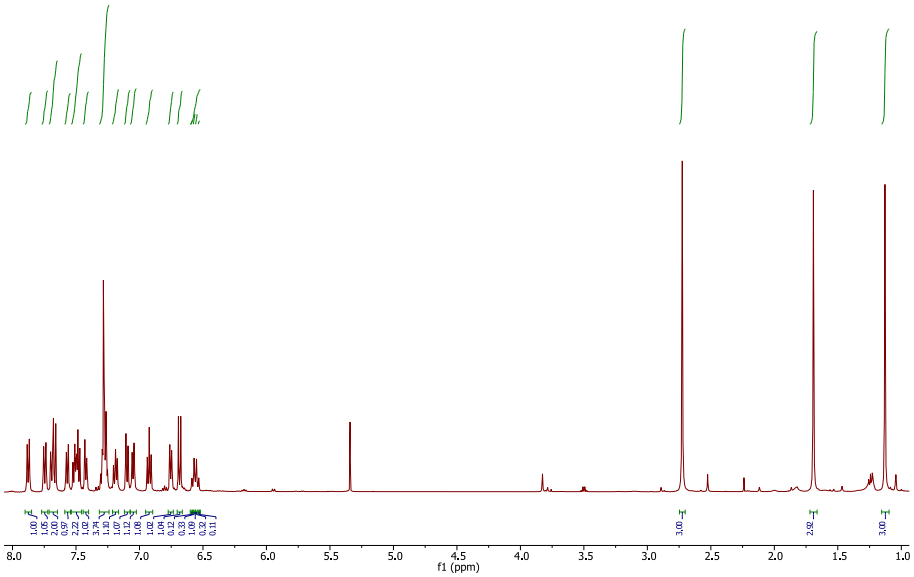
5.7 ^{1}H, ^{13}C and ^{31}P NMR spectra for [Pd((*S*)-**3a**)$_2$Cl$_2$] (*S*)-**11a**

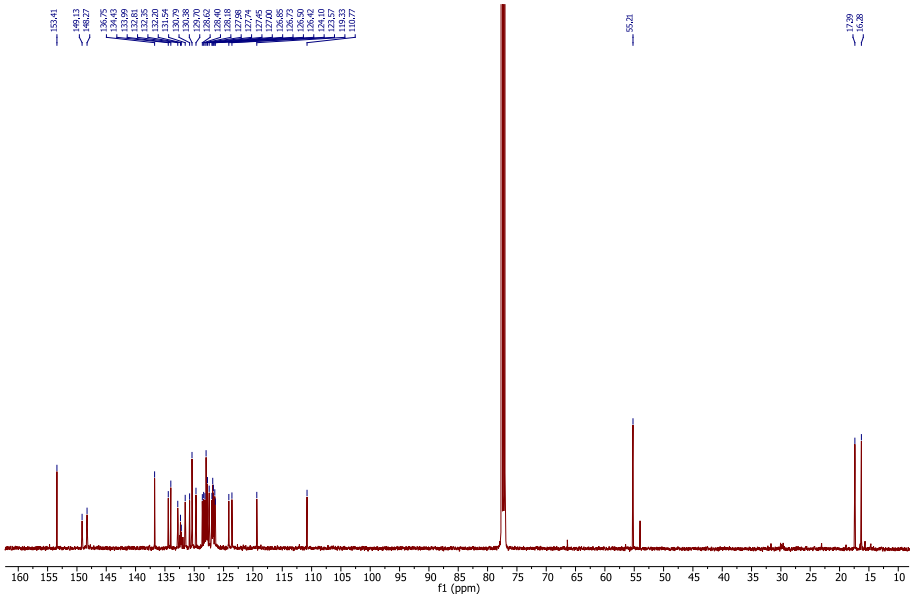


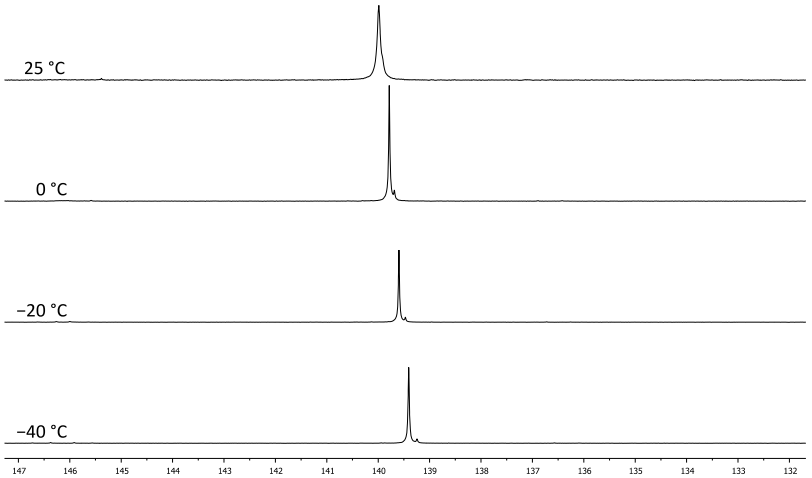




5.8 ^{1}H, ^{13}C and ^{31}P NMR spectra for [Pd((*R*)-**3b**)$_2$Cl$_2$] (*R*)-**11b**





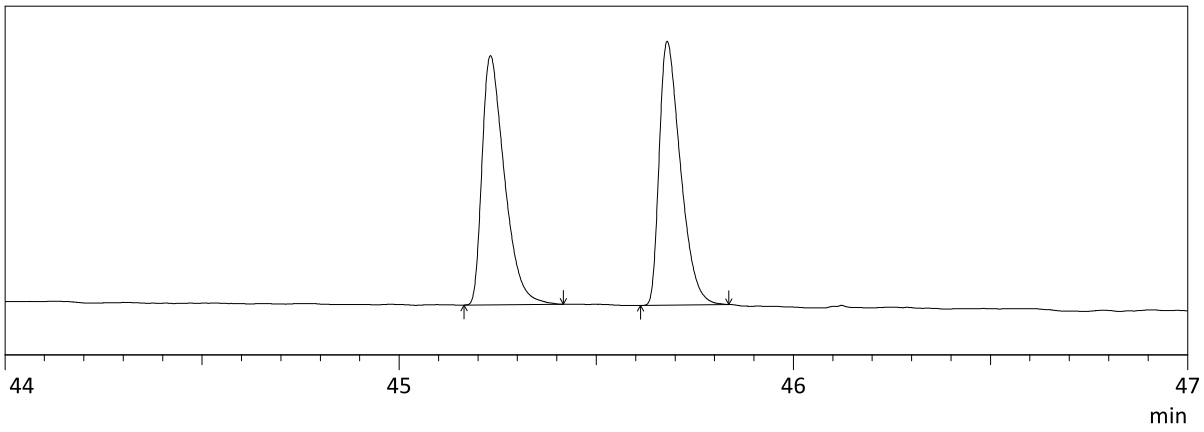


6. Chiral GC and HPLC

6.1 Dimethyl methylsuccinate

GC conditions (Supelco β-dex 225) – injection temperature: 220 °C, detection temperature 200 °C, oven temperature: 70 °C for 40 min, then ramp to 180 °C at 10 °C/min, retention times: 45.2 min (*S*) and 45.7 min (*R*).

Chromatogram for racemic sample.

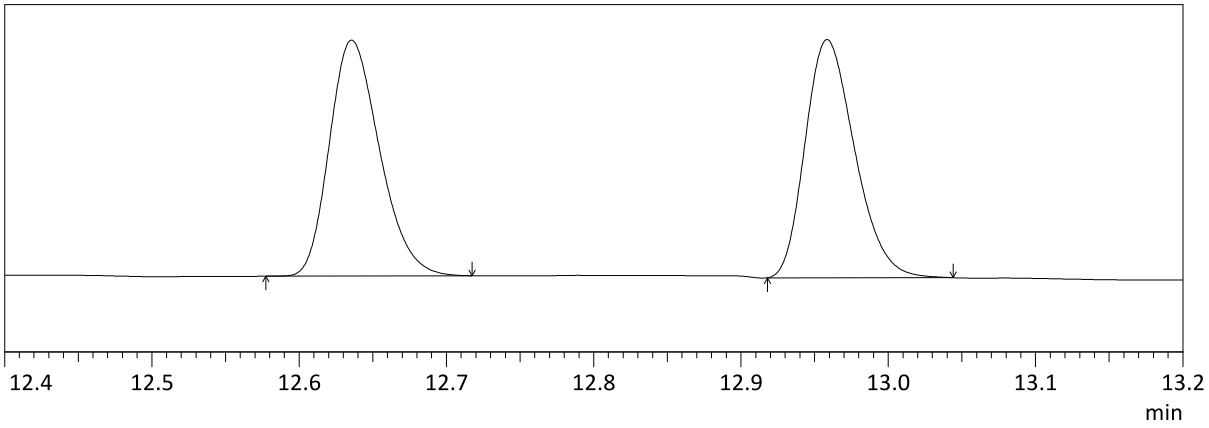


Peak Start	Peak End	Ret.Time	Area%
45.16	45.42	45.23	50.00
45.61	45.84	45.68	50.00

6.2 Methyl N-acetylalaninate

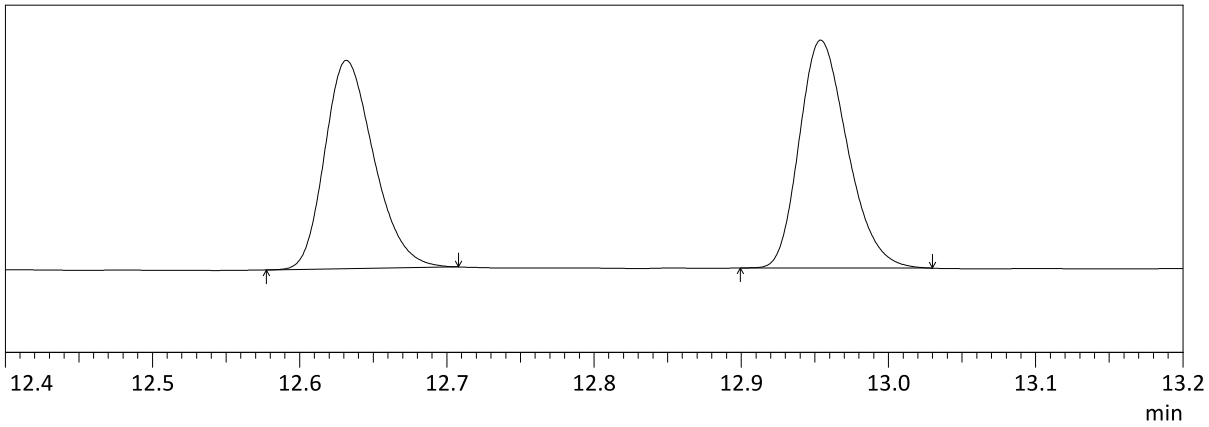
GC conditions (Supelco β-dex 225) – injection temperature: 220 °C, detection temperature 200 °C, oven temperature: 100 °C for 5 min, then ramp to 180 °C at 10 °C/min, retention times: 12.6 min (*R*) and 13.0 min (*S*).

Chromatogram for racemic sample.



Peak Start	Peak End	Ret.Time	Area%
12.58	12.72	12.64	50.02
12.92	13.04	12.96	49.98

Chromatogram for ESI Table 1: Entry 4.

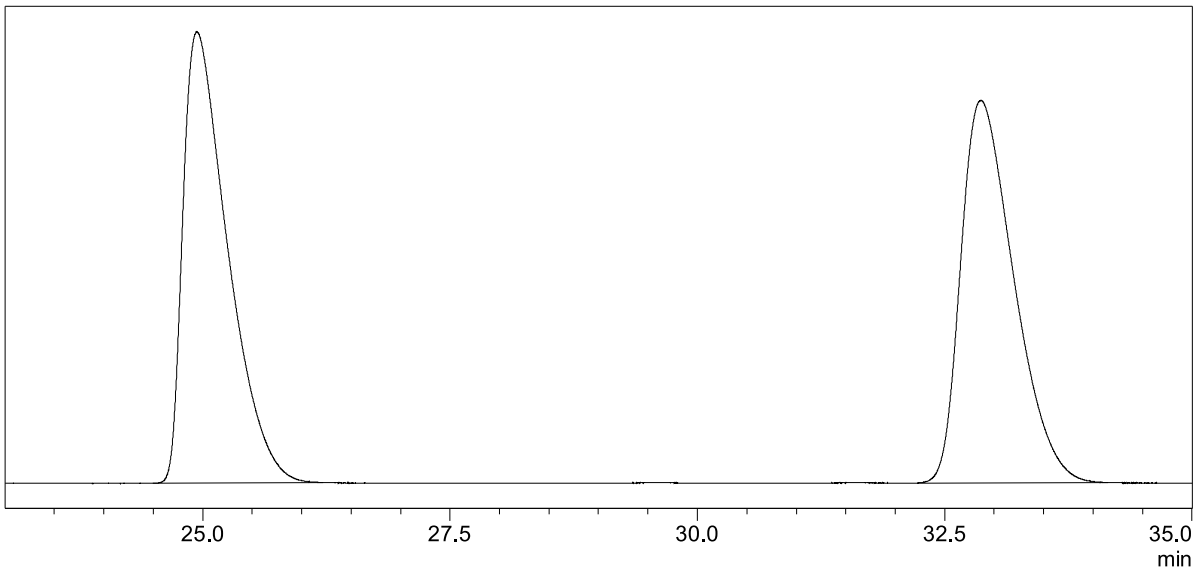


Peak Start	Peak End	Ret.Time	Area%
12.58	12.71	12.63	48.27
12.90	13.03	12.95	51.73

6.3 Methyl N-acetylphenylalaninate

HPLC conditions (Lux Cellulose-1) – oven temperature: 40 °C, mobile phase: hexane/2-propanol (90:10), flow rate: 0.5 mL/min, detection: 216 nm, retention times: 24.9 min (*R*) and 32.9 min (*S*).

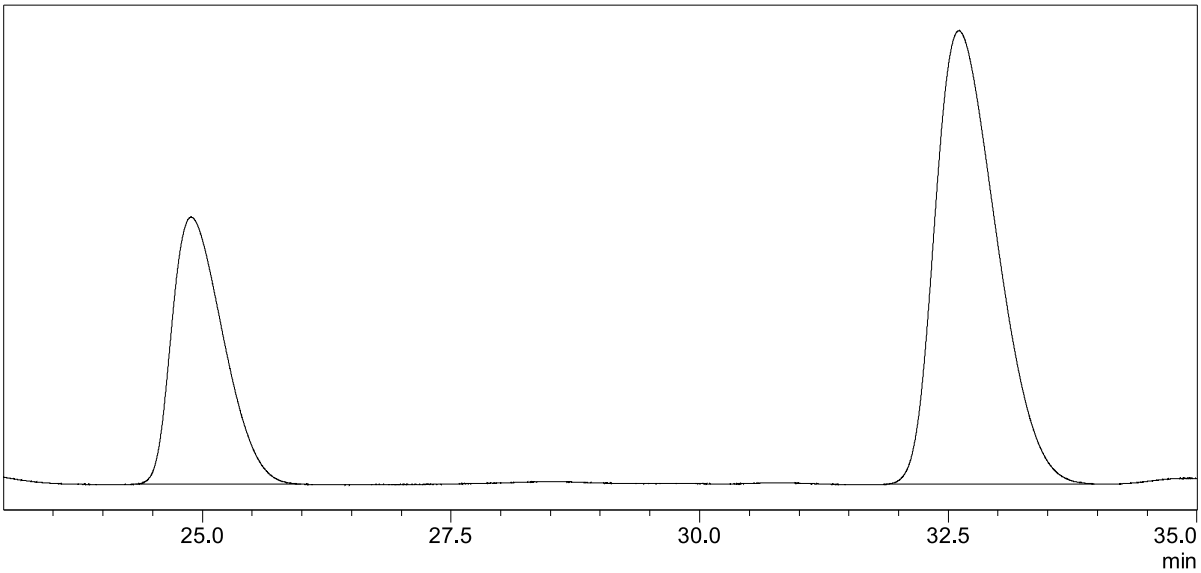
Chromatogram for racemic sample.



PDA Ch1 216nm

Peak Start	Peak End	Ret. Time	Area%
24.50	26.22	24.94	49.85
32.22	34.15	32.87	50.15

Chromatogram for ESI Table 1: Entry 6.



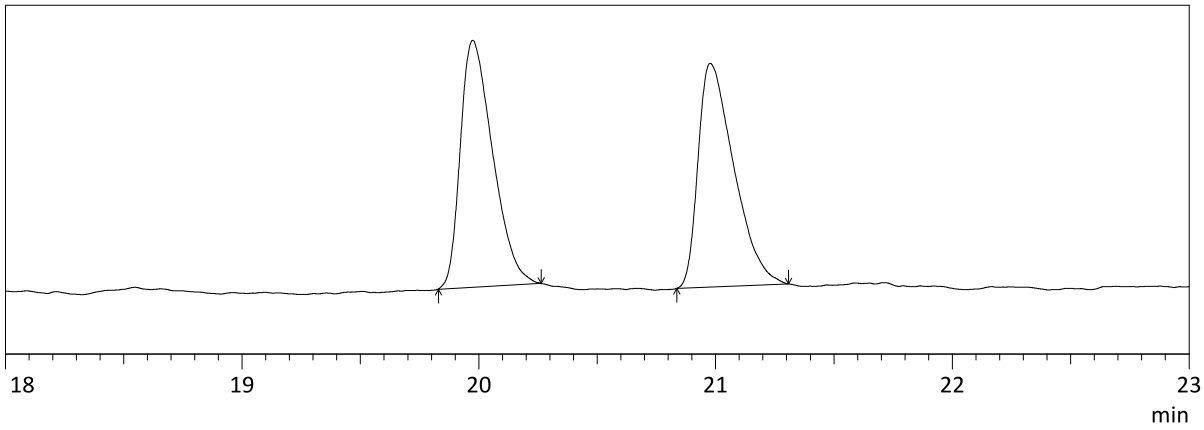
PDA Ch1 216nm

Peak Start	Peak End	Ret. Time	Area%
24.33	25.99	24.89	32.91
31.88	33.97	32.61	67.09

6.4 2-Phenylpropionaldehyde

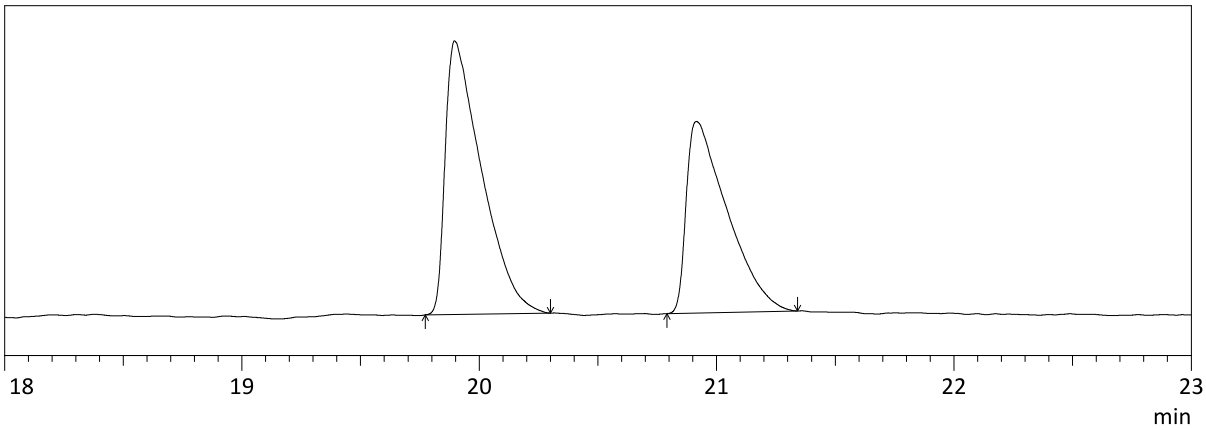
GC conditions (Supelco β-dex 225) – injection temperature: 200 °C, detection temperature 200 °C, oven temperature: 100 °C, retention times: 20.0 min (*S*) and 21.0 min (*R*).

Chromatogram for racemic sample.



Peak Start	Peak End	Ret.Time	Area%
19.83	20.26	19.97	50.02
20.84	21.31	20.98	49.98

Chromatogram for Table 4: Entry 8.

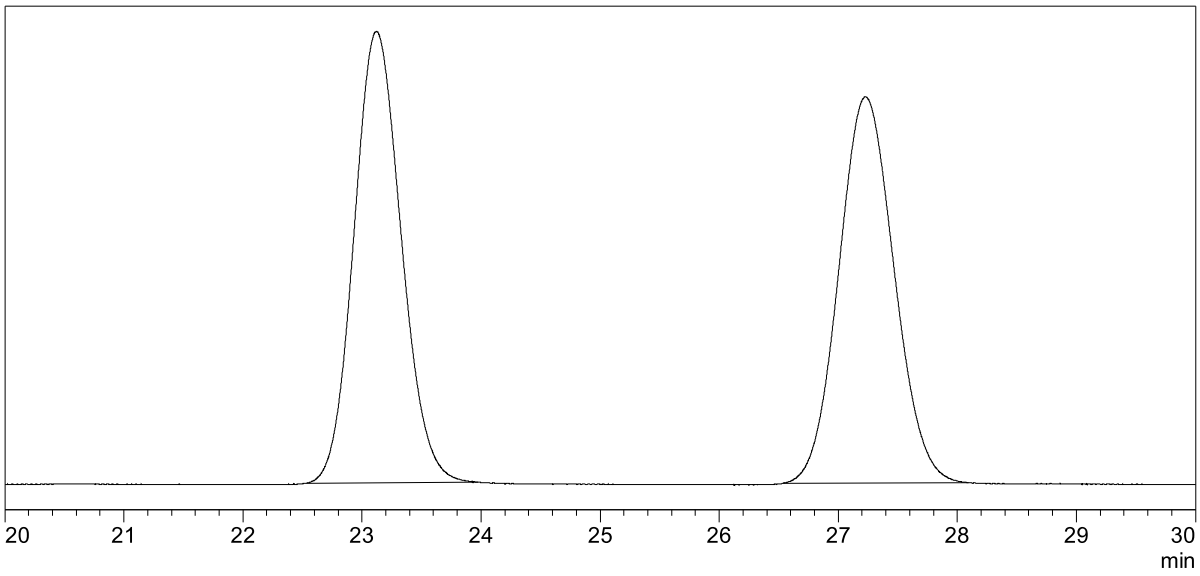


Peak Start	Peak End	Ret.Time	Area%
19.77	20.30	19.90	55.89
20.79	21.34	20.92	44.11

6.5 5-Chloro-3-hydroxy-1-(4-methoxybenzyl)-3-phenylindolin-2-one

HPLC conditions (Lux Cellulose-1) – oven temperature: 40 °C, mobile phase: hexane/2-propanol (80:20), flow rate: 0.5 mL/min, detection: 264 nm, retention times: 23.1 min (*S*) and 27.2 min (*R*).

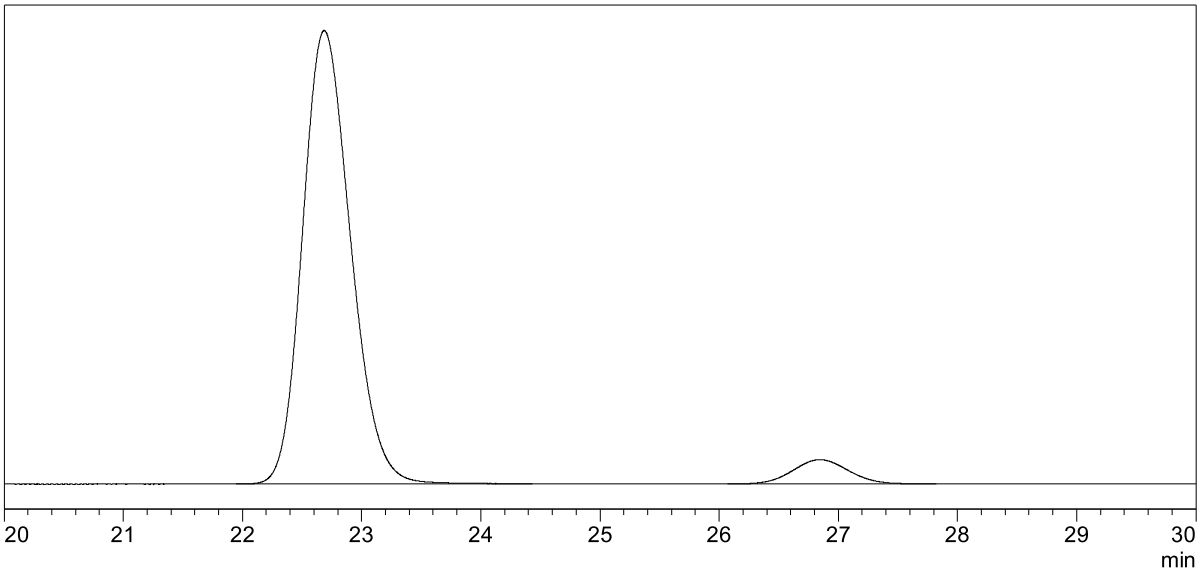
Chromatogram for racemic sample.



PDA Ch1 264nm

Peak Start	Peak End	Ret. Time	Area%
22.54	23.98	23.12	50.00
26.54	28.10	27.23	50.00

Chromatogram for ESI Table 2: Entry 2.



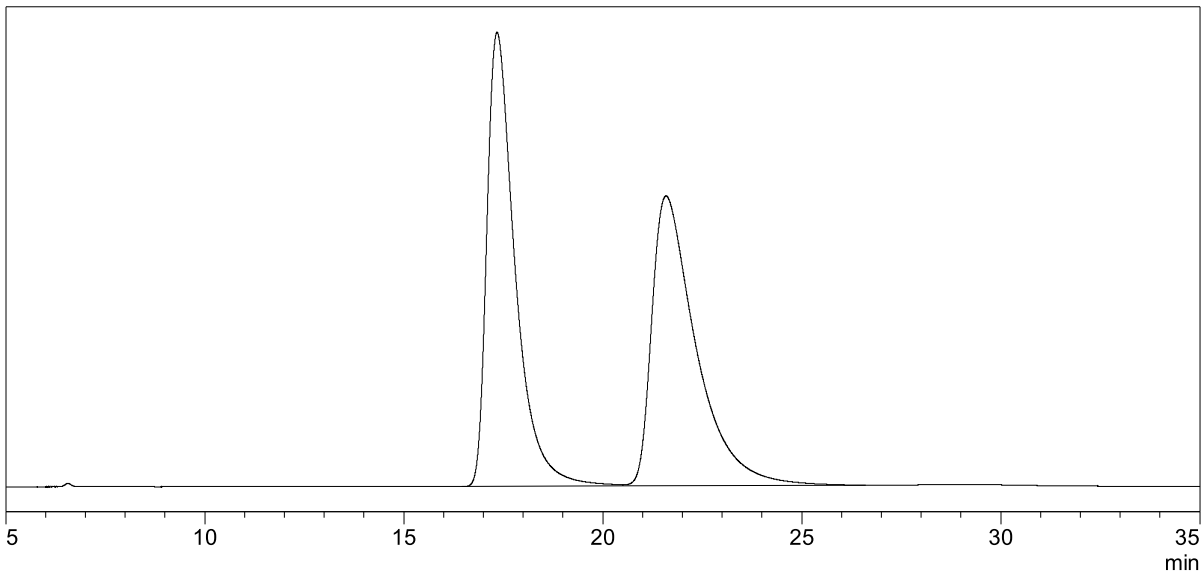
PDA Ch1 264nm

Peak Start	Peak End	Ret. Time	Area%
21.94	24.43	22.69	94.14
26.07	27.82	26.85	5.86

6.6 2-Methoxy-1,1'-binaphthyl

HPLC conditions (Lux Cellulose-3) – oven temperature: 40 °C, mobile phase: hexane/2-propanol (99:1), flow rate: 0.5 mL/min, detection: 221 nm, retention times: 17.3 min (*S*) and 21.6 min (*R*).

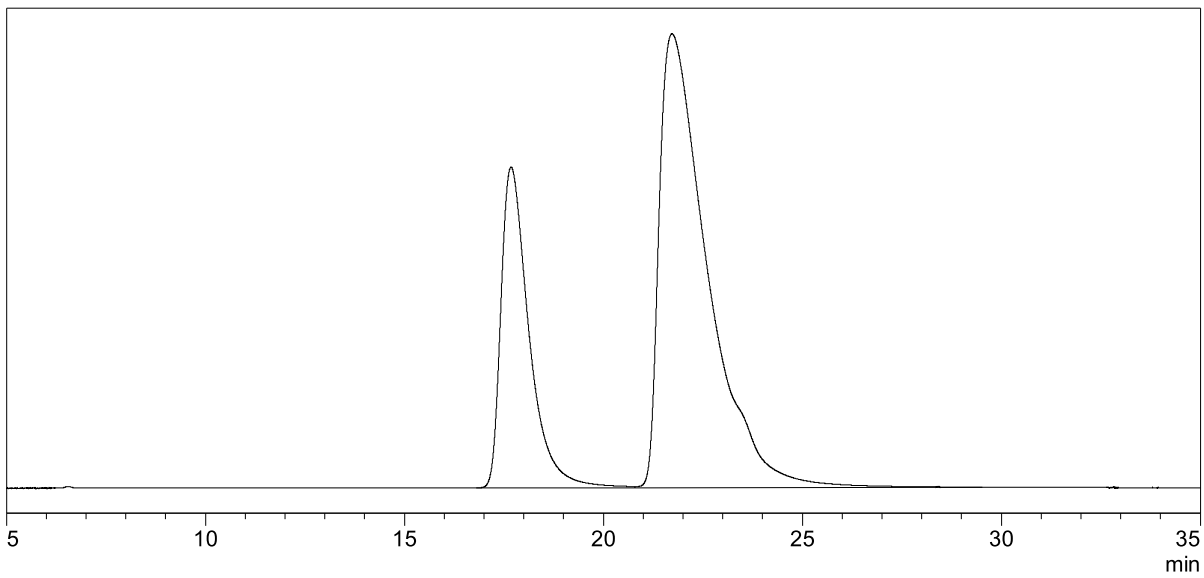
Chromatogram for racemic sample.



PDA Ch1 221nm

Peak Start	Peak End	Ret. Time	Area%
16.46	20.50	17.34	50.02
20.50	26.61	21.59	49.98

Chromatogram for Table 5: Entry 8.



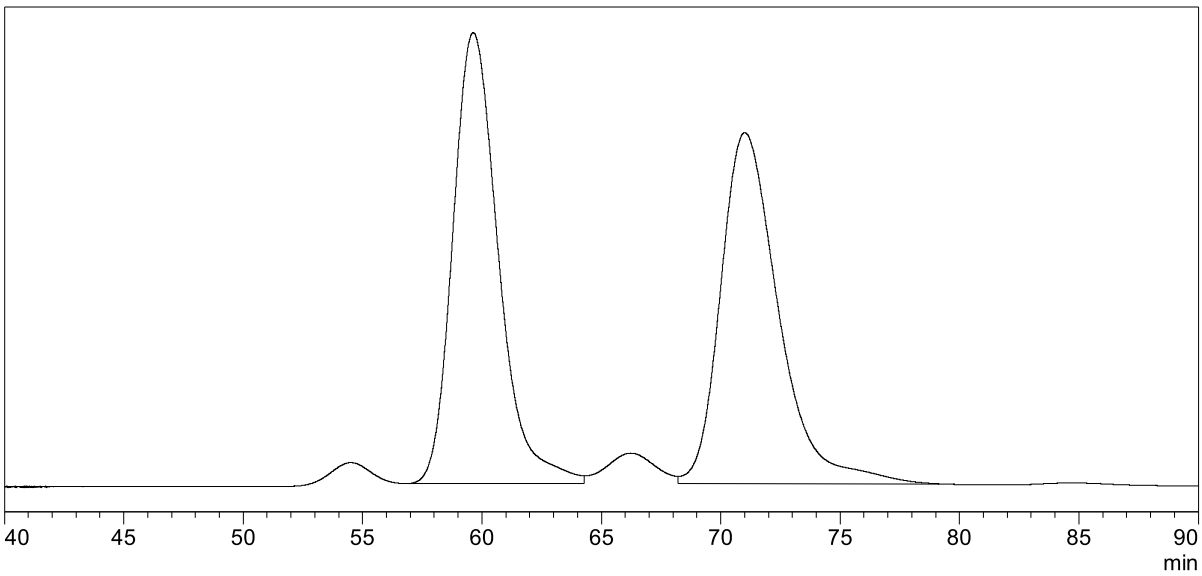
PDA Ch1 221nm

Peak Start	Peak End	Ret. Time	Area%
16.80	20.80	17.68	29.24
20.80	29.53	21.72	70.76

6.7 2-Methyl-1,1'-binaphthyl

HPLC conditions (Lux Cellulose-3) – oven temperature: 40 °C, mobile phase: hexane/2-propanol (99:1), flow rate: 0.1 mL/min, detection: 217 nm, retention times: 59.6 min (*R*) and 71.0 min (*S*).

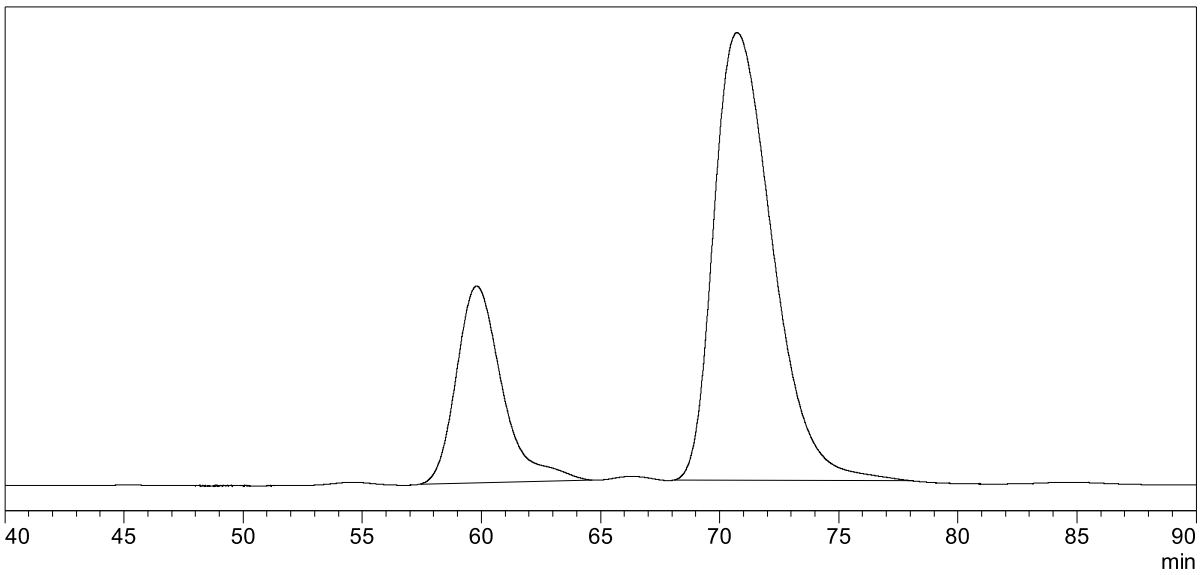
Chromatogram for racemic sample.



PDA Ch1 217nm

Peak Start	Peak End	Ret. Time	Area%
56.93	64.28	59.63	50.20
68.21	79.15	71.00	49.80

Chromatogram for Table 6: Entry 8.



PDA Ch1 217nm

Peak Start	Peak End	Ret. Time	Area%
57.45	64.65	59.80	25.46
68.10	78.14	70.73	74.54

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