Supplementary Information

Enantiomerically pure bicyclo[3.3.1] nona-2,6-diene as the sole source of enantioselectivity in BIPHEP-Rh asymmetric hydrogenation

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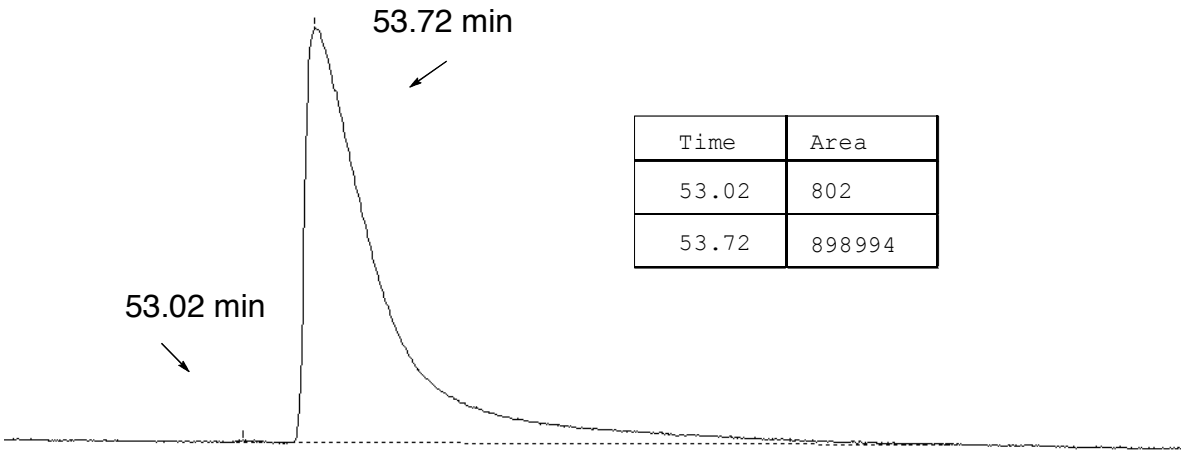
1. Materials and Methods

All reactions used in anhydrous reactions was dried overnight in a 120 ^{o}C oven and was subsequently cooled under an atmosphere of nitrogen gas. Moisture or oxygen sensitive reactions were performed under an argon atmosphere using Schlenk techniques. All solvents were purified via standard methods when required. Iodomethane (99%) and copper (99%, 45 μm powder) were obtained from Acros. diphenylphosphinic chloride (98%), iodopropane (99%), benzyl bromide (98%) and 3-bromophenol (98%) were purchased from Aldrich.

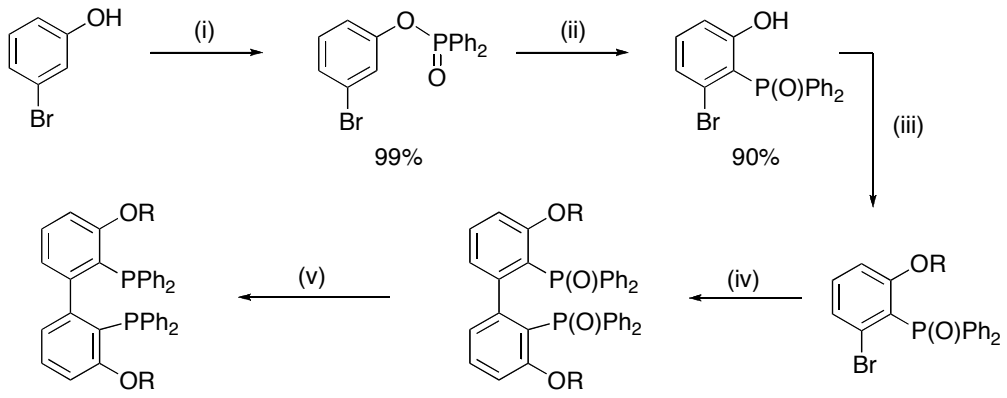
Column chromatography was performed using silica gel (40-60 micron). NMR spectra (^{1}H, ^{13}C and ^{31}P) were recorded on Bruker spectrometers. Chemical shifts for ^{1}H and ^{13}C NMR are reported in ppm downfield from tetramethylsilane as the external standard. For ^{31}P NMR, the chemical shifts are reported in ppm in relation to H_3PO_4 as the external standard. HRMS spectra were recorded on a Bruker Daltonics micrOTOF. Mass ratios (*m/z*) of bromine containing compounds are quoted for ^{79}Br. IR spectra were obtained using a Bruker Tensor 27. Melting points were recorded using Reichert apparatus and are uncorrected.

2. GC analysis of (S,S)-bicyclo[3.3.1]nona-2,6-diene employed in this work (Cydex B)



Time	Area
53.02	802
53.72	898994

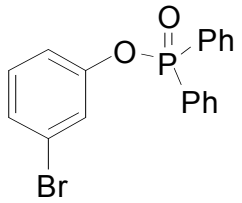
3. Synthesis of Alkoxybiphenyldiphosphines



R	Yield (%)
Me	82
i-Pr	77
Bn	80

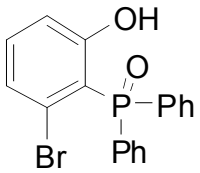
R	Yield (%)
Me	63
i-Pr	80
Bn	85

R	Yield (%)
Me	95
i-Pr	89
Bn	82

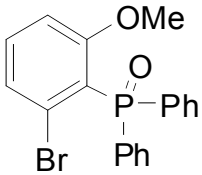


3-Bromophenyl diphenylphosphinate. To a stirred solution of 3-bromophenol (10 mmol, 1.73 g) at 0° C in CH_2Cl_2 (50 ml) was added DMAP (5 mol%) and triethyl amine (12.5 mmol, 1.75 ml). Diphenylphosphinc chloride (12.5 mmol, 2.38 g) was then added dropwise and the reaction was allowed to stir at room temperature for 18 h. The reaction was then quenched with hexane (10 ml), filtered and evaporated. The product was purified on silica gel column chromatography using ethyl acetate and pentane (1:9) as eluent to afford **2** as a colorless solid (3.71g, 99%). M.p. 89-90 °C; δ_H (400 MHz, $CDCl_3$) 7.94 (d, *J* 12.6, 2H), 7.92 (dd, *J* 1.5,12.9, 2H), 7.52-7.59 (m, 2H), 7.52-7.44 (m, 4H), 7.36-7.43 (m, 1H), 7.25 (d, *J* 12.9, 1H), 7.20 (d, *J* 12.8, 1H), 7.09 (t, *J* 8.1, 1H); δ_C (100 MHz, $CDCl_3$) 151.40 (d, *J* 8.3), 132.69 (d, *J* 2.9), 131.74 (d, *J* 10.4), 130.68, 130.47 (d, *J* 138.1), 128.71 (d, *J* 13.5), 127.86, 124.10 (d, *J* 5.5), 122.58, 119.54 (d, *J* 5.0); δ_P ($CDCl_3$, 162 MHz) 31.57; *v* (thin film) 2999, 1586, 1471,

1439, 1204, 929 cm^{-1}. ESI-MS $[M+NH_4+CH_3CN]^+$ 431.0503 (calculated for $C_{20}H_{21}PO_2BrN_2^+$ 431.0524).

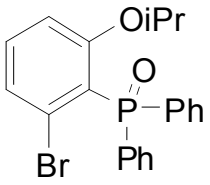


3-Bromo-2-(diphenylphosphoryl)phenol. To a stirred solution of diisopropyl amine (1.25 ml, 8.16 mmol) in THF (15 ml) at 0 ^oC was added n-BuLi (2.5 M in hexane, 4.5 ml) dropwise and this solution was stirred for 20 minutes. In a separate flask, 3-bromophenyl diphenylphosphinate (2.5 g, 6.8 mmol) in THF (25 ml) was cooled to -78 ^oC. The LDA solution was then added dropwise to the solution of the substrate and the reaction was allowed to warm up to room temperature and stirred for 18 h. The reaction was then quenched with saturated NH_4Cl, evaporated and the residue was extracted with CH_2Cl_2 (2 x 50 ml). Drying (Mg_2SO_4) and evaporation of the solvent provided a solid which was purified on silica gel column chromatography using ethyl acetate and hexane (1:4) as eluent to afford the product as a colorless solid (2.25 g, 90%). M. p. 140-141; δ_H ($CDCl_3$, 400 MHz) 13.02 (bs, 1H), 7.94-7.82 (m, 4H), 7.66-7.58 (m, 2H), 7.57-7.47 (m, 4H), 7.33-7.23 (m, 1H), 7.09-6.97 (m, 2H); δ_C ($CDCl_3$, 100 MHz) 167.53 (d, *J* 3.3), 135.18, 132.65, 132.61 (d, *J* 10.7), 130.6 (d, *J* 109.5), 128.58 (d, *J* 13.0), 125.04 (d, *J* 5.3), 124.92 (d, *J* 7.4), 118.69 (d, *J* 6.7), 110.19 (d, *J* 105.7); δ_P ($CDCl_3$, 162 MHz) 45.44; *v* (thin film): 3400, 3010, 1588, 1437, 1303, 1216, 1119, 755 cm^{-1}. ESI-MS $[M^++H]^+$ 372.9988 (calculated for $C_{18}H_{15}PO_2Br^+$ 372.9993).

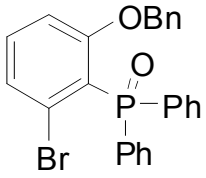


1-Bromo-2-(diphenylphosphoryl)-3-methoxybenzene. To a stirred solution of 3-bromo-2-diphenylphosphinophenol (363 mg, 1 mmol) at 0 ^oC in acetone (5 ml) was added Cs_2CO_3 (700 mg, 2 mmol). Methyl iodide (1.41 g, 10 mmol) was then added

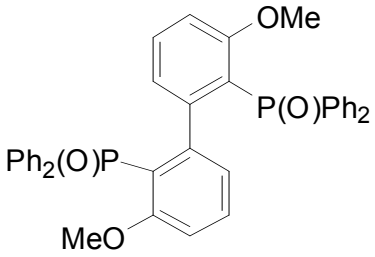
dropwise and the reaction mixture was allowed to stir at room temperature for 12 h. The solvent was then evaporated and the residue was treated with water (5 ml) and extracted with CH_2Cl_2 (2 x 10 ml). The combined organic solution was washed with water (1 x 5 ml), dried (Na_2SO_4) and evaporated to afford a solid which was passed through a short pad of silica gel using ethyl acetate and pentane (1:1) to provide the product as a colourless solid (360 mg, 95%). M. p.104 ^oC. δ_H ($CDCl_3$, 400 MHz) 7.69-7.57 (m, 4H), 7.49-7.42 (m, 2H), 7.42-7.33 (m, 4H), 7.30-7.23 (m, 2H), 6.85-6.77 (m, 1H), 3.15 (s, 3H); δ_C ($CDCl_3$, 100 MHz) 163.33 (d, *J* 4.4), 134.36, 134.35 (d, *J* 110.8), 131.36 (d, *J* 2.8), 131.06 (d, *J* 10.3), 128.35 (d, *J* 7.7), 128.34, 128.21 (d, *J* 12.9), 119.97 (d, *J* 103.5), 111.27 (d, *J* 5.4), 55.41; δ_P ($CDCl_3$, 162 MHz) δ 29.29. ESI-MS $[M+Na]^+$ 408.9963 (calculated for $C_{19}H_{16}NaPO_2Br$+ 408.9969).



1-Bromo-2-(diphenylphosphoryl)-3-isopropyloxybenzene. To a stirred solution of 3-bromo-2-diphenylphosphinophenol (4.5 g, 12.4 mmol) at 0 ^oC in acetone (50 ml) was added Cs_2CO_3 (8.7 g, 24.7 mmol). 2-Iodopropane (10.5 g, 62 mmol) was then added dropwise and the reaction mixture was allowed to stir at room temperature for 12 h. The solvent was then evaporated and the residue was treated with water (5 ml) and extracted with CH_2Cl_2 (3 x 40 ml). The combined organic solution was washed with water (3 x 20 ml), dried (Na_2SO_4) and evaporated to afford a solid which was crystallized in acetone to provide the product as a colourless solid (4.5 g, 89%). M. p.112 ^oC; δ_H ($CDCl_3$, 400 MHz) 7.75-7.61 (m, 4H), 7.53-7.31 (m, 6H), 7.30-7.17 (m, 2H), 6.83-6.68 (m, 1H), 4.35 (s, *J* 5.3, 1H,), 0.71 (d *J* 4.8, 3H), 0.69 (d, *J* 5.0, 3H); δ_C ($CDCl_3$, 100 MHz) 160.38 (d, *J* 2.7), 135.37 (d, *J* 110.1), 133.80, 131.22 (d, *J* 10.2), 131.03 (d, *J* 2.7), 128.98, 128.15 (d, *J* 12.8), 127.50 (d, *J* 7.7), 120.10 (d, J 101.4), 111.13 (d, *J* 5.5), 69.92, 20.51; δ_P ($CDCl_3$, 162 MHz) δ 27.13; *v* (thin film) 3020, 1575, 1436, 1216 cm^{-1}. ESI-MS $[M+Na]^+$ 437.0265 (calculated for $C_{21}H_{20}NaPO_2Br^+$ 437.0282).

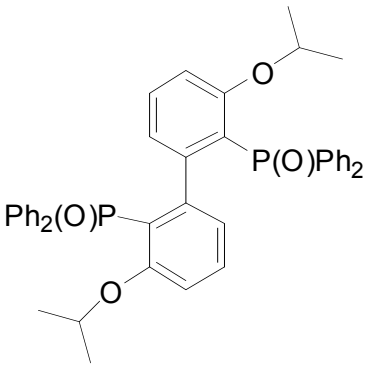


1-Bromo-2-(diphenylphosphoryl)-3-benzyloxybenzene. To a stirred solution of 3-bromo-2-diphenylphosphinophenol (4.5 g, 12.4 mmol) at 0 ^{o}C in acetone (50 mL) was added Cs_2CO_3 (8.7 g, 24.7 mmol). Benzyl bromide (6.36 g, 37.19 mmol) was then added dropwise and the reaction mixture was allowed to stir at room temperature for 12 h. The solvent was then evaporated and the residue was treated with water (15 ml) and extracted with CH_2Cl_2 (3 x 50 ml). The combined organic solution was washed with water (10 mL), dried (Na_2SO_4) and evaporated to afford a solid which was passed through a short pad of silica gel using ethyl acetate and pentane (4:1) as eluent to afford the product as a colourless solid (4.7 g, 82%). M. p. 204 ^{o}C; δ_H ($CDCl_3$, 400 MHz) 7.69-7.57 (m, 4H), 7.46-7.36 (m, 2H), 7.35-7.26 (m, 5H), 7.27-7.13 (m, 4H), 6.85-6.74 (m, 3H), 4.54 (s, 2H); δ_C ($CDCl_3$, 100 MHz) 161.45 (d, *J* 3.5), 134.57 (d, *J* 110.3), 134.51 (d, *J* 108.6), 131.24 (d, *J* 10.3), 131.15 (d, *J* 2.9), 128.66, 128.59, 128.39, 128.39, 128.11 (d, *J* 12.8), 128.09, 127.51, 120.07 (d, *J* 101.6), 111.66 (d, *J* 5.4), 70.77; δ_P ($CDCl_3$, 162 MHz) 27.67; *v* (thin film) 3019, 2981, 1577, 1562, 1436, 1261, 1216, 1118, 1004 cm^{-1}. ESI-MS $[M+1]^+$ 463.0457 (calculated for $C_{25}H_{21}BrO_2P^+$ 463.0463).

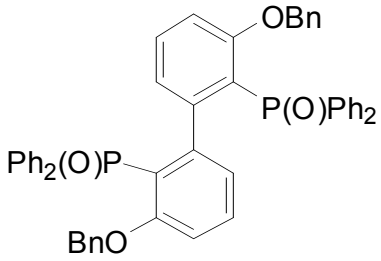


3,3'-Dimethoxy-2,2'-diphenylphosphinyl-1,1'-biphenyl. To a stirred solution of 1-bromo-2-(diphenylphosphoryl)-3-methoxybenzene (2.0 g, 5.3 mmol) in pyridine (20 ml), copper (2.69 g, 44 mmol) was added. The reaction was then heated to reflux and stirred for 12 h. The solvent was then evaporated and the residue was passed through a short pad of silica gel using dichloromethane and methanol (4:1) as eluent. Evaporation of the solvent provided a solid which was crystallized in acetone

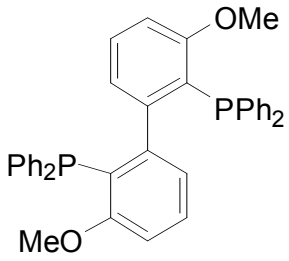
to provide the product as a colourless solid (1.0 g, 63%). δ_H (400 MHz, $CDCl_3$) 7.92-7.82 (m, 4H), 7.80-7.70 (m, 4H), 7.56-7.42 (m, 6H), 7.34 (t, *J* 8.5, 2H), 7.31-7.24 (m, 2H), 7.24-7.15 (m, 4H), 6.86-6.75 (m, 4H), 3.27 (s, 6H); δ_C ($CDCl_3$, 100 MHz) 160.08 (d, *J* 3.8), 149.88 (t, *J* 3.9), 136.51 (d, *J* 110.8), 134.86 (d, *J* 104.4), 132.23 (d, *J* 10.1), 131.61 (d, J 10.8), 131.46, 130.87 (d, *J* 2.3), 129.97 (d, *J* 2.6), 127.78 (d, *J* 12.2), 127.38 (d, *J* 13.1), 124.96 (d, *J* 10.1), 118.19 (d, *J* 103.0), 110.42 (d, *J* 5.9), 54.81; δ_P ($CDCl_3$, 162 MHz) 28.29; *v* (thin film) 3020, 1565, 1458, 1436, 1263, 1216, 1186, 1118, 1026 cm^{-1}. ESI-MS $[M+1]^+$ 615.1846 (calculated for $C_{38}H_{33}O_4P_2^+$ 615.1854).



3,3'-Diisopropyloxy-2,2'-diphenylphosphinyl-1,1'-biphenyl. To a solution of 1-bromo-2-(diphenylphosphoryl)-3-isopropyloxybenzene (3.5 g, 8.29 mmol) in pyridine (50 ml), copper (5.2 g, 82.9 mmol) was added. The reaction was then heated to reflux and stirred for 12 h. Evaporation of the solvent provided a residue which was passed through a short pad of silica gel using dichloromethane and methane (4:1) as eluent. Removal of solvent provided solid which was crystallized in acetone to give the product as a colourless solid (2.0 g, 80%). δ_H (400 MHz, $CDCl_3$) 7.99-7.89 (m, 4H), 7.85-7.69 (m, 4H), 7.57-7.39 (m, 6H), 7.32-7.23 (m, 4H), 7.23-7.33 (m, 4H), 6.75-6.66 (m, 4H), 4.40 (H, *J* 6.4, 2H), 0.97 (d, *J* 6.0, 6H), 0.56 (s, *J* 6.2, 6H); δ_C ($CDCl_3$, 100 MHz) 158.10 (d, *J* 4.0), 150.84 (d, *J* 4.1), 136.96 (d, *J* 111.1), 134.60 (d, *J* 104.4), 132.47 (d, *J* 9.9), 131.7 (d, *J* 10.9), 131.19, 130.82 (d, *J* 2.5), 129.87 (d, *J* 2.7), 127.60 (d, *J* 19.6), 127.48 (d, *J* 20.3), 123.94 (d, *J* 10.3), 117.36 (d, *J* 103.1), 109.71 (d, *J* 6.2), 69.11, 21.35, 20.46; δ_P ($CDCl_3$, 162 MHz) 28.45; *v* (thin film) 3020, 1564, 1439, 1216 cm^{-1}. ESI-MS $[M+H]^+$ 671.2471 (calculated for $C_{42}H_{41}O_4P_2^+$ 671.2480).

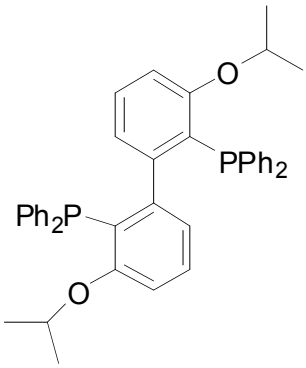


3,3'-Dibenzyloxy-2,2'-diphenylphosphinyl-1,1'-biphenyl. To a solution of 1-bromo-2-(diphenylphosphoryl)-3-benzyloxybenzene (750 mg, 1.6 mmol) in pyridine (5 ml), copper powder (1.02g, 16 mmol) was added. The reaction mixture was heated to reflux and stirred for 12 h. The solvent was then evaporated and the residue was passed through a short pad of silica gel using 1:5 dichloromethane and methanol as eluent. The solvent was evaporated and the resultant solid was crystallized in acetone to afford the product as a colourless solid (520 mg, 85%). δ_H (CDCl3, 400 MHz) 7.79-7.60 (m, 8H), 7.50-7.03 (m, 20H), 6.99-6.90 (m, 2H), 6.89-6.80 (m, 2H), 6.78-6.68 (m, 4H); δ_C ($CDCl_3$, 100 MHz) 159.26 (d, *J* 4.1), 150.39 (d, *J* 4.0), 135.83, 135.39 (d, *J* 110.7), 134.47 (d, *J* 104.8), 132.63 (d, *J* 9.9), 131.80 (d, J 11.1), 131.32, 130.71 (d, *J* 2.3), 130.04 (d, *J* 2.5), 128.06 (d, *J* 31.1), 127.86, 127.60, 127.48, 127.37, 124.87 (d, *J* 10.0), 117.73 (d, *J* 102.5), 110.36 (d, *J* 6.1), 70.29; δ_P ($CDCl_3$, 162 MHz) 28.40; *v* (thin film) 3020, 2401, 1563, 1439, 1216 cm^{-1}. ESI-MS $[M+H]^+$ 767.2457 (calculated for $C_{50}H_{41}O_4P_2^+$ 767.2480).

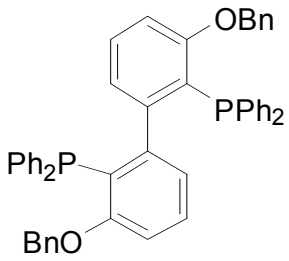


3,3'-Dimethoxy-2,2'-bis(diphenylphosphino)-1,1'-biphenyl. To a solution of 3,3'-dimethoxy-2,2'-bis(diphenylphosphinyl)-1,1'-biphenyl (1.1 g, 1.79 mmol) in *m*-xylene (20 ml) was added Bu_3N (5.12 ml, 21.5 mmol) followed by $HSiCl_3$ (1.8 ml, 17.9 mmol). The reaction was then heated to 120 ^oC and stirred for 12 h. Upon cooling to 0 ^oC, 30% NaOH (10 ml) was added and the reaction was stirred for 1 h at room temperature. The reaction mixture was then diluted with a 1:19 mixture of ethyl

acetate and pentane (100 ml) and the organic solution was dried (Na_2SO_4) and passed through a short pad of silica gel. Evaporation of the solvent provided the product as a colourless solid (850 mg, 82%). δ_H ($CDCl_3$, 500 MHz) 7.61-7.47 (m, 4H), 7.44-7.20 (m, 12H), 7.19-7.06 (m, 6H), 6.95-6.79 (m, 4H), 3.33 (s, 6H); δ_C ($CDCl_3$, 125 MHz) 161.98, 152.68 (d, *J* 9.4), 152.38 (d, *J* 9.2), 137.62 (d, *J* 164.7), 137.52 (d, *J* 165.2), 133.20 (d, *J* 19.6), 131.63 (d, *J* 19.5), 130.40, 127.74 (d, *J* 6.6), 127.27 (d, *J* 5.7), 127.06 (d, *J* 126.9), 123.57 (d, *J* 6.1), 122.61 (d, *J* 16.2), 110.88, 54.75; δ_P ($CDCl_3$, 203 MHz) -14.77; ESI-MS $[M+H]^+$ 583.1849 (calculated for $C_{38}H_{33}O_2P_2^+$ 582.1856).



3,3'-Diisopropyloxy-2,2'-bis(diphenylphosphosphino)-1,1'-biphenyl. To a solution of 3,3'-isopropyloxy-2,2'-bis(diphenylphosphinyl)-1,1'-biphenyl (300 mg, 0.47 mmol) in *m*-xylene (10 ml) was added Bu_3N (1.34 ml, 3.6 mmol) followed by $HSiCl_3$ (0.47 ml, 4.7 mmol). The reaction was then heated to 120 ^oC and stirred for 13 h. Upon cooling to 0 ^oC, 30% NaOH (2.5 ml) was added and the reaction was stirred for 1 h at room temperature. The reaction mixture was then diluted with a 1:4 mixture of ethyl acetate and pentane (50 ml) and the organic solution was dried (Na_2SO_4) and passed through a short pad of silica gel. Evaporation of the solvent provided the product as a colourless solid (220 mg, 77%). δ_H (400 MHz, $CDCl_3$) 7.63-7.51 (m, 4H), 7.40-7.19 (m, 12H), 7.12-7.00 (m, 6H), 6.86-6.74 (m, 4H), 4.39 (s, *J* 6.6, 2H), 0.90 (d, *J* 6.2, 6H), 0.69 (d, *J* 6.1, 6H); δ_C ($CDCl_3$, 100 MHz) 159.73, 153.68 (d, *J* 9.8), 153.30 (d, *J* 9.8), 137.87 (d, *J* 136.3), 137.74 (d, *J* 137.1), 133.23 (d, *J* 19.5), 131.48 (d, *J* 19.5), 130.18, 127.63 (d, J 6.7), 127.30 (d, *J* 2.8), 126.86 (d, *J* 113.7), 122.68 (d, *J* 6.2), 122.61 (d, *J* 6.0), 121.97 (d, *J* 16.9), 68.50, 21.09, 20.81; δ_p ($CDCl_3$, 162 MHz) -16.35; ESI-MS $[M+H]^+$ 639.2576 (calculated for $C_{42}H_{41}O_2P_2^+$ 639.2582).



3,3'-Dibenzyloxy-2,2'-bis(diphenylphosphino)-1,1'-biphenyl. To a solution of 3,3'-dibenzyloxy-2,2'-bis(diphenylphosphoryl)-1,1'-biphenyl (400 mg, 0.55 mmol) in *m*-xylene (40 ml) was added Bu_3N (1.6 ml, 6.5 mmol) followed by $HSiCl_3$ (0.55 ml, 5.5 mmol). The reaction was then heated to 120 ^oC and stirred for 16 h. Upon cooling to 0 ^oC, 30% NaOH (3ml) was added and the reaction was stirred for 1 h at room temperature. The reaction mixture was then diluted with a 1:1 mixture of dichloromethane and pentane (100 ml) and the organic solution was dried (Na_2SO_4) and passed through a short pad of silica gel. Evaporation of the solvent provided the product as a colourless solid (310 mg, 80%). δ_H (400 MHz, $CDCl_3$) 7.47-7.40 (m, 4H), 7.39-7.31 (m, 2H), 7.30-7.09 (m, 16H), 7.07-6.99 (m, 2H),6.99-6.90 (m, 6H), 6.89-6.84 (m, 2H), 6.78-6.70 (m, 4H), 4.72 (d, *J* 12.9, 2H), 4.62 (d, *J* 12.4, 2H); δ_C ($CDCl_3$, 100 MHz) 160.98, 153.18 (d, *J* 9.5), 152.88 (d, *J* 9.5), 137.20 (d, *J* 64.4), 137.10 (d, *J* 66.7), 136.41, 133.39 (d, *J* 19.9), 131.61 (d, *J* 19.5), 130.38, 127.78 (d, *J* 69.4), 127.67, 127.61 (d, J 6.9), 127.25 (d, *J* 5.7), 126.41, 123.76 (d, *J* 6.1), 123.71 (d, *J* 5.9), 122.64 (d, *J* 18.4), 111.02, 69.92; δ_p ($CDCl_3$, 162 MHz) δ -16.60. ESI-MS $[M+H]^+$ 735.2577 (calculated for $C_{50}H_{41}O_2P_2^+$ 735.2582).

4. Crystal structure

Single-crystal X-ray diffraction report for $[Rh(C_9H_{12})(Ph_2PC_6H_4C_6H_4PPh_2)][O_3SCF_3]\cdot CH_2Cl_2$ (**4**)

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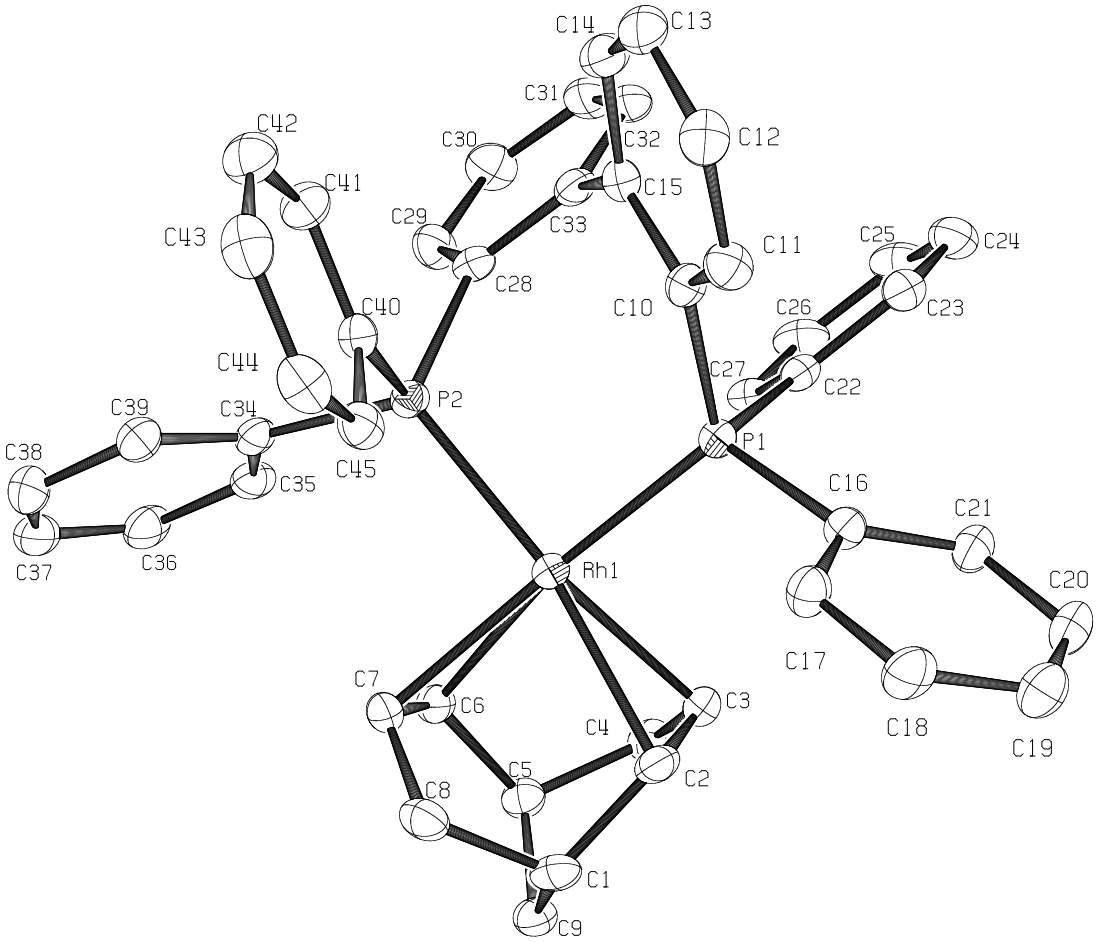


The solvent, counterion and hydrogen atoms are not shown.

Crystals of **ARC1270** were grown by solvent diffusion ($CDCl_3$; $CH2Cl_2$; pentane). A single crystal having dimensions approximately 0.14 x 0.16 x 0.22 mm was mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150K in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated MoK_α radiation, λ = 0.71073 Å). Intensity data were processed using the DENZO-SMN package[1].

Examination of the systematic absences of the intensity data showed the space group to be *P* $2_1/n$. The structure was solved using the direct-methods

program SIR92[2], which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite[3]. Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. The hydrogen atoms bonded to the cxoordinated carbon atoms were located in a difference Fourier map and their coordinates and isotropic thermal parameters subsequently refined. Other hydrogen atoms were positioned geometrically after each cycle of refinement. A 3-term Chebychev polynomial weighting scheme was applied. Refinement converged satisfactorily to give R = 0.0360, wR = 0.0403.

Attached is a thermal ellipsoid plot (ORTEP-3[4]) at 40% probability. A summary of crystallographic data is given below, as are full lists of atomic coordinates, anisotropic thermal parameters and those bond lengths and angles not concerning H atoms.

Comment:

The coordinated diene approximates to local twofold rotational symmetry. The Rh and P atoms and the centroids of the two coordinated C=C bonds are approximately coplanar. The C=C bond axes are not perpendicular to this plane but are instead inclined at angles of *ca*. 76°.

The diphosphine does not closely approximate to any local symmetry. In addition to differences in the orientations of the phenyl substituents, the 7-membered chelate ring is also unsymmetrical, as illustrated by the Rh-P-C angles (see Table 6 below).

There are significant deviations of the angles around C(15) and C(33) from 120° and the substituents of one of the aryl rings of the biphenyl link are not coplanar, resulting in the torsion angle P(2)-C(28)-C(33)-C(15) being -15.9°. These suggest that formation of the chelate ring may subject the biphenyl to significant steric strain.

References:

1 Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods Enzymol.*, 1997, **276**, Eds C. W. Carter and R. M. Sweet, Academic Press.

2 A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi ,M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst*. 1994, **27**, 435.

3 CRYSTALS Issue 12, P. W. Betteridge, J. R. Cooper, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Cryst.*, 2003, **36**, 1487

4 ORTEP-3 v. 1.0.2, C. K. Johnson and M. K. Burnett, 1998.

Table 1: Crystal data and refinement details

Crystal identification	ARC1270
Chemical formula	$C_{47}H_{42}Cl_2F_3O_3P_2RhS$
Formula weight	979.67
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P\,2_1/n$
a (Å)	14.1068(2)
b (Å)	14.0628(2)
c (Å)	21.3831(3)
α (°)	90
β (°)	96.1711(9)
γ (°)	90
Cell volume (Å^3)	4217.42(10)
Z	4
Calculated density (Mg/m^3)	1.543
Absorption coefficient (mm^{-1})	0.713
F_{000}	2000
Crystal size (mm)	0.14 x 0.16 x 0.22
Description of crystal	Orange block
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.85, 0.91
θ range for data collection (°)	$5.0 \le \theta \le 27.5$
Index ranges	$-18 \le h \le 18$, $0 \le k \le 18$, $0 \le l \le 27$
Reflections measured	44152
Unique reflections	9963
R_{int}	0.066
Observed reflections ($I > 3\sigma(I)$)	6023
Refinement method	Full-matrix least-squares on *F*
Parameters refined	548
Weighting scheme	Chebychev 3-term polynomial
Goodness of fit	1.1079
R	0.0360
wR	0.0403
Residual electron density (min,max) (eÅ^{-3})	-0.64, 0.68

Table 2: Atomic coordinates and equivalent isotropic thermal parameters (Å^2) of non-hydrogen atoms

Atom	x	y	z	U_{equiv}
Rh(1)	0.232158(17)	0.321314(18)	0.335042(11)	0.0210
C(1)	0.1426(2)	0.3502(3)	0.19683(15)	0.0284
C(2)	0.1188(2)	0.2908(3)	0.25225(15)	0.0280
C(3)	0.1646(3)	0.2067(3)	0.27054(16)	0.0286
C(4)	0.2471(3)	0.1704(2)	0.23831(15)	0.0295
C(5)	0.2884(2)	0.2538(2)	0.20516(15)	0.0270
C(6)	0.3245(2)	0.3278(3)	0.25362(15)	0.0259
C(7)	0.2830(3)	0.4147(2)	0.25966(15)	0.0269
C(8)	0.1916(3)	0.4420(3)	0.22143(16)	0.0309
C(9)	0.2099(3)	0.2963(2)	0.15815(15)	0.0285
P(1)	0.14486(6)	0.26289(6)	0.41081(4)	0.0215
C(10)	0.1427(2)	0.3254(2)	0.48611(14)	0.0234
C(11)	0.0610(2)	0.3709(3)	0.50224(16)	0.0292
C(12)	0.0599(3)	0.4167(3)	0.55996(17)	0.0316
C(13)	0.1390(3)	0.4139(3)	0.60367(17)	0.0332
C(14)	0.2204(3)	0.3679(3)	0.58844(16)	0.0328
C(15)	0.2257(2)	0.3255(3)	0.52956(15)	0.0256
C(16)	0.0186(2)	0.2504(2)	0.38175(15)	0.0259
C(17)	-0.0321(2)	0.3318(3)	0.36049(16)	0.0290
C(18)	-0.1280(2)	0.3249(3)	0.33556(17)	0.0344
C(19)	-0.1722(3)	0.2370(3)	0.33011(19)	0.0385
C(20)	-0.1220(3)	0.1562(3)	0.34909(19)	0.0386
C(21)	-0.0267(2)	0.1622(3)	0.37509(17)	0.0315
C(22)	0.1856(2)	0.1453(2)	0.43831(15)	0.0247
C(23)	0.1407(3)	0.0983(3)	0.48474(16)	0.0303
C(24)	0.1774(3)	0.0120(3)	0.50877(17)	0.0381
C(25)	0.2591(3)	-0.0253(3)	0.48880(17)	0.0408
C(26)	0.3052(3)	0.0215(3)	0.44335(17)	0.0352
C(27)	0.2682(2)	0.1067(2)	0.41785(15)	0.0266
P(2)	0.33373(6)	0.39618(6)	0.41138(4)	0.0217
C(28)	0.3787(2)	0.3148(2)	0.47524(14)	0.0242
C(29)	0.4699(2)	0.2764(3)	0.47650(17)	0.0320
C(30)	0.5009(3)	0.2034(3)	0.51737(18)	0.0370
C(31)	0.4411(3)	0.1679(3)	0.55877(17)	0.0352
C(32)	0.3523(3)	0.2088(3)	0.56098(16)	0.0310
C(33)	0.3187(2)	0.2819(2)	0.51962(15)	0.0249
C(34)	0.4389(2)	0.4496(2)	0.38136(15)	0.0250
C(35)	0.5016(2)	0.3940(3)	0.35050(15)	0.0295
C(36)	0.5708(3)	0.4359(3)	0.31801(17)	0.0363
C(37)	0.5784(3)	0.5338(3)	0.31531(17)	0.0417
C(38)	0.5186(3)	0.5903(3)	0.34714(18)	0.0384
C(39)	0.4493(2)	0.5492(3)	0.38009(16)	0.0308
C(40)	0.2826(2)	0.4989(2)	0.44796(15)	0.0252
C(41)	0.3205(2)	0.5339(3)	0.50645(16)	0.0302
C(42)	0.2848(3)	0.6169(3)	0.52993(18)	0.0368
C(43)	0.2117(3)	0.6663(3)	0.49546(19)	0.0358
C(44)	0.1739(3)	0.6312(3)	0.43752(18)	0.0340
C(45)	0.2080(2)	0.5473(3)	0.41392(16)	0.0278
S(1)	0.52481(7)	0.11922(8)	0.28099(5)	0.0421
O(1)	0.5768(3)	0.2070(2)	0.2822(2)	0.0690
O(2)	0.4627(2)	0.1079(3)	0.32996(16)	0.0632

O(3)	0.4865(2)	0.0883(3)	0.21930(14)	0.0559
C(46)	0.6180(3)	0.0322(3)	0.30245(18)	0.0370
F(1)	0.5842(2)	-0.05602(19)	0.30024(15)	0.0668
F(2)	0.68674(16)	0.0371(2)	0.26448(11)	0.0494
F(3)	0.6595(2)	0.0460(2)	0.36092(12)	0.0654
C(47)	0.5523(4)	0.3159(4)	0.1511(3)	0.0759
Cl(1)	0.65980(9)	0.37591(10)	0.16766(6)	0.0593
Cl(2)	0.46298(9)	0.38261(10)	0.10886(7)	0.0661

Table 3: Atomic coordinates and isotropic thermal parameters (Å^2) of hydrogen atoms

Atom	x	y	z	U_{iso}
H(11)	0.0822	0.3648	0.1696	0.0333
H(21)	0.062(3)	0.306(2)	0.2681(16)	0.020(8)
H(31)	0.136(3)	0.166(3)	0.2970(18)	0.028(10)
H(41)	0.2968	0.1429	0.2701	0.0352
H(42)	0.2246	0.1204	0.2069	0.0352
H(51)	0.3426	0.2324	0.1821	0.0324
H(61)	0.385(2)	0.316(2)	0.2721(15)	0.017(8)
H(71)	0.319(3)	0.465(3)	0.2810(18)	0.033(10)
H(81)	0.1495	0.4772	0.2483	0.0370
H(82)	0.2054	0.4831	0.1854	0.0370
H(91)	0.2384	0.3407	0.1288	0.0339
H(92)	0.1747	0.2445	0.1334	0.0339
H(111)	0.0020	0.3707	0.4718	0.0352
H(121)	0.0015	0.4516	0.5697	0.0383
H(131)	0.1377	0.4446	0.6458	0.0403
H(141)	0.2773	0.3648	0.6206	0.0394
H(171)	0.0002	0.3952	0.3631	0.0346
H(181)	-0.1645	0.3836	0.3217	0.0407
H(191)	-0.2405	0.2322	0.3124	0.0456
H(201)	-0.1539	0.0927	0.3443	0.0457
H(211)	0.0091	0.1031	0.3889	0.0372
H(231)	0.0827	0.1264	0.5006	0.0361
H(241)	0.1440	-0.0231	0.5407	0.0454
H(251)	0.2856	-0.0864	0.5071	0.0482
H(261)	0.3647	-0.0058	0.4291	0.0418
H(271)	0.3008	0.1402	0.3849	0.0315
H(291)	0.5142	0.3020	0.4471	0.0385
H(301)	0.5665	0.1766	0.5168	0.0441
H(311)	0.4617	0.1132	0.5869	0.0415
H(321)	0.3108	0.1857	0.5929	0.0366
H(351)	0.4965	0.3231	0.3518	0.0351
H(361)	0.6153	0.3951	0.2964	0.0436
H(371)	0.6268	0.5637	0.2906	0.0499
H(381)	0.5254	0.6611	0.3463	0.0455
H(391)	0.4067	0.5905	0.4030	0.0364
H(411)	0.3735	0.4990	0.5315	0.0359
H(421)	0.3120	0.6414	0.5720	0.0442
H(431)	0.1866	0.7266	0.5123	0.0438
H(441)	0.1215	0.6667	0.4124	0.0412
H(451)	0.1790	0.5218	0.3726	0.0335
H(471)	0.5292	0.2965	0.1918	0.0875

H(472)	0.5641	0.2579	0.1260	0.0875

Table 4: Anisotropic thermal parameters (Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh(1)	0.02042(11)	0.02270(12)	0.01940(11)	0.00003(11)	-0.00018(8)	-0.00168(11)
C(1)	0.0298(17)	0.0308(18)	0.0226(15)	0.0015(13)	-0.0064(13)	0.0056(14)
C(2)	0.0230(16)	0.0384(19)	0.0215(15)	-0.0040(14)	-0.0021(13)	-0.0045(14)
C(3)	0.0313(17)	0.0303(18)	0.0236(16)	-0.0013(13)	0.0001(14)	-0.0102(14)
C(4)	0.0374(18)	0.0227(17)	0.0279(16)	-0.0063(14)	0.0006(14)	-0.0015(15)
C(5)	0.0295(17)	0.0267(17)	0.0247(16)	-0.0035(13)	0.0025(13)	0.0010(14)
C(6)	0.0200(15)	0.0355(18)	0.0224(14)	0.0004(14)	0.0027(12)	-0.0050(15)
C(7)	0.0350(18)	0.0230(17)	0.0227(16)	0.0020(13)	0.0028(13)	-0.0075(14)
C(8)	0.042(2)	0.0259(18)	0.0246(16)	0.0052(14)	0.0024(14)	0.0031(15)
C(9)	0.0365(19)	0.0267(18)	0.0215(15)	-0.0023(12)	-0.0001(14)	-0.0027(14)
P(1)	0.0198(4)	0.0229(4)	0.0214(4)	0.0001(3)	0.0007(3)	-0.0016(3)
C(10)	0.0236(14)	0.0205(15)	0.0260(15)	-0.0018(14)	0.0021(12)	-0.0003(14)
C(11)	0.0279(16)	0.0311(19)	0.0289(17)	0.0013(14)	0.0042(14)	0.0016(15)
C(12)	0.0297(17)	0.0285(18)	0.0376(19)	-0.0040(15)	0.0087(15)	0.0009(15)
C(13)	0.0373(19)	0.0345(19)	0.0290(17)	-0.0101(15)	0.0092(15)	-0.0066(16)
C(14)	0.0308(18)	0.041(2)	0.0266(17)	-0.0067(15)	0.0027(14)	-0.0048(16)
C(15)	0.0248(15)	0.0273(16)	0.0250(15)	0.0004(14)	0.0045(12)	-0.0049(14)
C(16)	0.0244(15)	0.0292(17)	0.0240(15)	-0.0012(13)	0.0019(12)	-0.0032(14)
C(17)	0.0226(15)	0.0293(18)	0.0346(17)	0.0004(15)	0.0008(13)	-0.0013(14)
C(18)	0.0222(15)	0.043(2)	0.0367(18)	0.0015(18)	-0.0034(13)	0.0031(17)
C(19)	0.0222(17)	0.050(2)	0.041(2)	0.0017(18)	-0.0035(15)	-0.0038(17)
C(20)	0.0289(18)	0.044(2)	0.041(2)	0.0010(17)	-0.0044(15)	-0.0135(16)
C(21)	0.0267(16)	0.033(2)	0.0334(18)	0.0018(15)	-0.0030(14)	-0.0072(15)
C(22)	0.0250(16)	0.0265(16)	0.0215(15)	-0.0038(13)	-0.0023(12)	-0.0030(13)
C(23)	0.0335(18)	0.0300(18)	0.0267(17)	0.0002(14)	-0.0002(14)	-0.0042(15)
C(24)	0.053(2)	0.033(2)	0.0272(18)	0.0043(15)	0.0010(16)	-0.0049(18)
C(25)	0.060(3)	0.032(2)	0.0291(18)	0.0010(15)	-0.0042(17)	0.0127(19)
C(26)	0.044(2)	0.0328(19)	0.0278(17)	-0.0064(15)	-0.0019(15)	0.0121(17)
C(27)	0.0317(17)	0.0287(17)	0.0184(14)	-0.0025(13)	-0.0019(13)	0.0024(14)
P(2)	0.0190(4)	0.0246(4)	0.0211(4)	0.0000(3)	0.0002(3)	-0.0003(3)
C(28)	0.0245(15)	0.0263(16)	0.0206(14)	-0.0022(13)	-0.0031(12)	0.0009(14)
C(29)	0.0241(16)	0.039(2)	0.0327(18)	0.0058(16)	0.0045(14)	-0.0002(15)
C(30)	0.0293(18)	0.043(2)	0.038(2)	0.0055(16)	-0.0009(15)	0.0087(16)
C(31)	0.0328(18)	0.043(2)	0.0284(17)	0.0086(16)	-0.0057(14)	0.0025(17)
C(32)	0.0300(17)	0.039(2)	0.0224(15)	0.0041(14)	-0.0043(13)	-0.0033(15)
C(33)	0.0217(15)	0.0296(17)	0.0225(15)	-0.0034(13)	-0.0023(12)	-0.0027(13)
C(34)	0.0187(14)	0.0325(18)	0.0228(15)	-0.0006(13)	-0.0022(12)	-0.0039(13)
C(35)	0.0234(16)	0.041(2)	0.0235(16)	-0.0009(14)	-0.0008(13)	-0.0020(15)
C(36)	0.0248(17)	0.054(2)	0.0303(18)	-0.0070(17)	0.0035(14)	-0.0096(17)
C(37)	0.035(2)	0.063(3)	0.0268(18)	0.0028(18)	0.0011(15)	-0.021(2)
C(38)	0.0334(19)	0.043(2)	0.037(2)	0.0051(17)	-0.0021(16)	-0.0155(17)
C(39)	0.0248(16)	0.035(2)	0.0310(18)	0.0009(15)	-0.0028(14)	-0.0038(15)
C(40)	0.0226(15)	0.0264(16)	0.0270(16)	0.0008(13)	0.0044(13)	-0.0039(13)
C(41)	0.0272(17)	0.0315(18)	0.0312(17)	-0.0029(14)	-0.0001(14)	0.0014(15)
C(42)	0.041(2)	0.037(2)	0.0333(19)	-0.0068(16)	0.0051(16)	-0.0023(17)
C(43)	0.0368(19)	0.0268(19)	0.046(2)	-0.0019(16)	0.0144(16)	0.0026(16)
C(44)	0.0302(18)	0.033(2)	0.040(2)	0.0081(16)	0.0094(15)	0.0055(15)
C(45)	0.0222(15)	0.0331(19)	0.0285(16)	0.0042(14)	0.0040(13)	0.0000(14)
S(1)	0.0303(5)	0.0466(6)	0.0492(6)	-0.0011(5)	0.0038(4)	0.0008(4)
O(1)	0.060(2)	0.0375(18)	0.109(3)	0.0018(18)	0.008(2)	0.0012(16)
O(2)	0.0342(16)	0.100(3)	0.058(2)	-0.0218(19)	0.0146(14)	-0.0059(17)
O(3)	0.0337(15)	0.093(3)	0.0395(16)	0.0086(16)	-0.0027(12)	-0.0012(16)

C(46)	0.0357(19)	0.040(2)	0.0356(19)	0.0069(17)	0.0028(16)	-0.0029(17)
F(1)	0.0725(19)	0.0386(15)	0.090(2)	0.0091(14)	0.0115(16)	-0.0076(13)
F(2)	0.0343(12)	0.0661(17)	0.0488(14)	0.0005(12)	0.0094(10)	0.0065(12)
F(3)	0.0556(16)	0.101(2)	0.0364(13)	0.0065(14)	-0.0106(12)	0.0006(16)
C(47)	0.082(4)	0.042(3)	0.095(4)	0.011(3)	-0.032(3)	-0.016(3)
Cl(1)	0.0576(7)	0.0696(8)	0.0542(6)	-0.0117(6)	0.0230(5)	-0.0112(6)
Cl(2)	0.0571(7)	0.0570(7)	0.0871(9)	0.0169(7)	0.0209(7)	0.0049(6)

Table 5: Bond lengths (Å)

Rh(1) - C(2)	2.295(3)	Rh(1) - C(6)	2.286(3)
Rh(1) - C(3)	2.264(3)	Rh(1) - C(7)	2.255(3)
Rh(1) - P(1)	2.2903(8)	Rh(1) - P(2)	2.3072(8)
C(1) - C(2)	1.517(5)	C(5) - C(6)	1.517(5)
C(1) - C(9)	1.527(5)	C(5) - C(9)	1.534(5)
C(2) - C(3)	1.383(5)	C(6) - C(7)	1.368(5)
C(3) - C(4)	1.504(5)	C(7) - C(8)	1.500(5)
C(4) - C(5)	1.518(5)	C(8) - C(1)	1.530(5)
P(1) - C(10)	1.838(3)	P(2) - C(28)	1.841(3)
P(1) - C(16)	1.831(3)	P(2) - C(34)	1.839(3)
P(1) - C(22)	1.827(3)	P(2) - C(40)	1.828(3)
C(10) - C(11)	1.393(5)	C(28) - C(29)	1.393(5)
C(10) - C(15)	1.415(4)	C(28) - C(33)	1.416(5)
C(11) - C(12)	1.394(5)	C(29) - C(30)	1.387(5)
C(12) - C(13)	1.376(5)	C(30) - C(31)	1.380(5)
C(13) - C(14)	1.388(5)	C(31) - C(32)	1.384(5)
C(14) - C(15)	1.402(5)	C(32) - C(33)	1.404(5)
C(15) - C(33)	1.485(5)		
C(16) - C(17)	1.398(5)	C(34) - C(35)	1.398(5)
C(16) - C(21)	1.395(5)	C(34) - C(39)	1.409(5)
C(17) - C(18)	1.403(4)	C(35) - C(36)	1.389(5)
C(18) - C(19)	1.383(6)	C(36) - C(37)	1.382(6)
C(19) - C(20)	1.377(6)	C(37) - C(38)	1.390(6)
C(20) - C(21)	1.402(5)	C(38) - C(39)	1.391(5)
C(22) - C(23)	1.399(5)	C(40) - C(41)	1.396(5)
C(22) - C(27)	1.399(5)	C(40) - C(45)	1.391(5)
C(23) - C(24)	1.396(5)	C(41) - C(42)	1.387(5)
C(24) - C(25)	1.375(6)	C(42) - C(43)	1.388(6)
C(25) - C(26)	1.392(6)	C(43) - C(44)	1.386(6)
C(26) - C(27)	1.394(5)	C(44) - C(45)	1.389(5)
S(1) - O(1)	1.435(4)	C(46) - F(1)	1.328(5)
S(1) - O(2)	1.445(3)	C(46) - F(2)	1.332(4)
S(1) - O(3)	1.438(3)	C(46) - F(3)	1.337(5)
S(1) - C(46)	1.818(4)		
C(47) - Cl(1)	1.738(6)	C(47) - Cl(2)	1.743(6)

Note – H atoms have been excluded

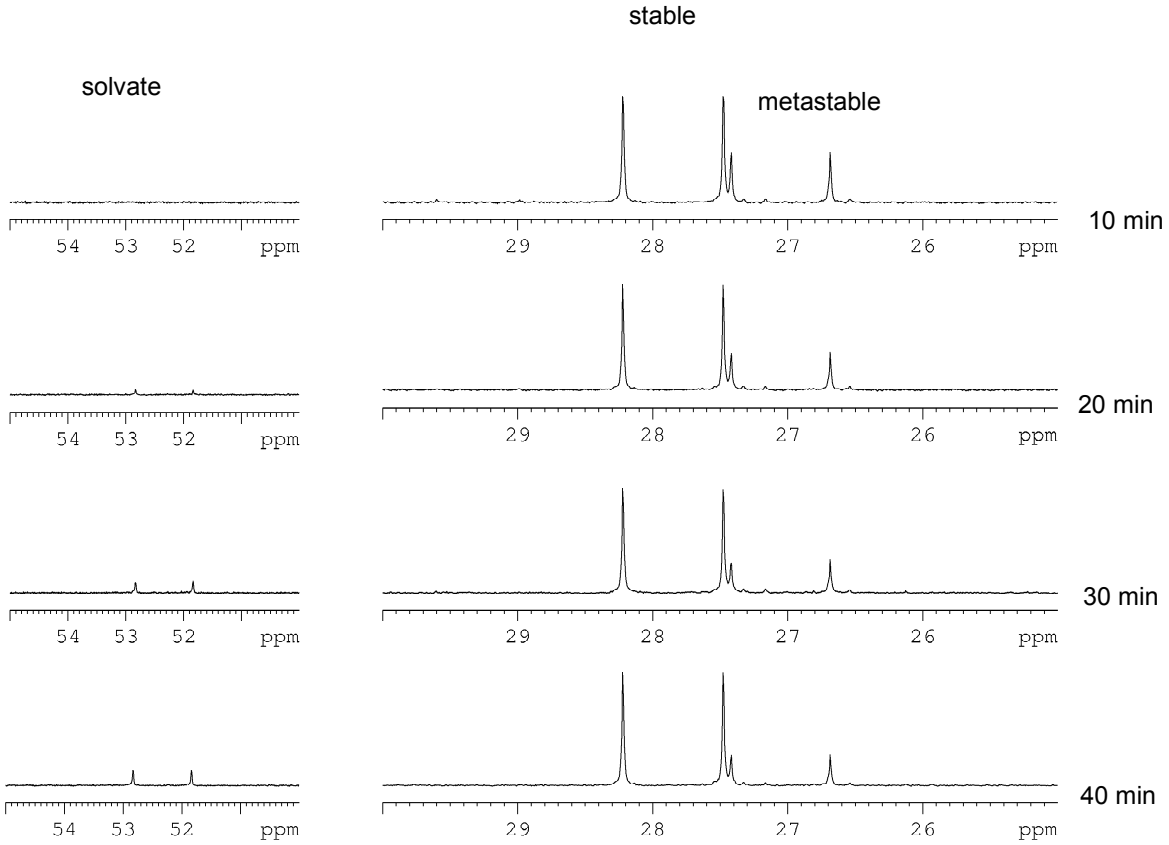
Table 6: Bond angles (°)

C(2) - Rh(1) - C(3)	35.32(13)	C(6) - Rh(1) - C(7)	35.05(13)
C(2) - Rh(1) - C(6)	80.03(12)		
C(2) - Rh(1) - C(7)	78.83(13)	C(6 - Rh(1) - C(3)	78.54(12)
C(3) - Rh(1) - C(7)	97.15(13)		
C(2) - Rh(1) - P(1)	95.48(9)	C(6) - Rh(1) - P(2)	99.16(8)
C(3) - Rh(1) - P(1)	87.28(9)	C(7) - Rh(1) - P(2)	91.10(9)
C(6) - Rh(1) - P(1)	161.25(10)	C(2) - Rh(1) - P(2)	163.62(10)
C(7) - Rh(1) - P(1)	161.98(10)	C(3) - Rh(1) - P(2)	160.83(10)
P(1) - Rh(1) - P(2)	90.20(3)		
C(2) - C(1) - C(8)	109.0(3)	C(6) - C(5) - C(4)	109.2(3)
C(2) - C(1) - C(9)	110.6(3)	C(6) - C(5) - C(9)	110.3(3)
C(8) - C(1) - C(9)	108.7(3)	C(4) - C(5) - C(9)	108.7(3)
Rh(1) - C(2) - C(1)	107.8(2)	Rh(1) - C(6) - C(5)	108.4(2)
Rh(1) - C(2) - C(3)	71.12(19)	Rh(1) - C(6) - C(7)	71.23(19)
C(1) - C(2) - C(3)	123.8(3)	C(5) - C(6) - C(7)	124.1(3)
Rh(1) - C(3) - C(2)	73.6(2)	Rh(1) - C(7) - C(6)	73.72(19)
Rh(1) - C(3) - C(4)	103.0(2)	Rh(1) - C(7) - C(8)	102.6(2)
C(2) - C(3) - C(4)	121.4(3)	C(6) - C(7) - C(8)	121.9(3)
C(3) - C(4) - C(5)	107.8(3)	C(7) - C(8) - C(1)	107.6(3)
C(1) - C(9) - C(5)	106.6(3)		
Rh(1) - P(1) - C(10)	120.60(11)	Rh(1) - P(2) - C(28)	112.30(11)
Rh(1) - P(1) - C(16)	111.83(11)	Rh(1) - P(2) - C(34)	113.73(10)
C(10) - P(1) - C(16)	103.63(15)	C(28) - P(2) - C(34)	106.62(15)
Rh(1) - P(1) - C(22)	112.22(11)	Rh(1) - P(2) - C(40)	114.82(11)
C(10) - P(1) - C(22)	100.69(15)	C(28) - P(2) - C(40)	107.12(15)
C(16) - P(1) - C(22)	106.46(15)	C(34) - P(2) - C(40)	101.35(15)
P(1) - C(10) - C(11)	121.9(2)	P(2) - C(28) - C(29)	120.0(3)
P(1) - C(10) - C(15)	119.0(2)	P(2) - C(28) - C(33)	121.1(2)
C(11) - C(10) - C(15)	119.1(3)	C(29) - C(28) - C(33)	118.5(3)
C(10) - C(11) - C(12)	121.3(3)	C(28) - C(29) - C(30)	121.8(3)
C(11) - C(12) - C(13)	120.2(3)	C(29) - C(30) - C(31)	119.9(3)
C(12) - C(13) - C(14)	119.0(3)	C(30) - C(31) - C(32)	119.3(3)
C(13) - C(14) - C(15)	122.3(3)	C(31) - C(32) - C(33)	121.8(3)
C(10) - C(15) - C(14)	118.0(3)	C(28) - C(33) - C(32)	118.4(3)
C(10) - C(15) - C(33)	126.0(3)	C(28) - C(33) - C(15)	124.2(3)
C(14) - C(15) - C(33)	115.9(3)	C(32) - C(33) - C(15)	117.1(3)
P(1) - C(16) - C(17)	118.4(2)	P(2) - C(34) - C(35)	120.7(3)
P(1) - C(16) - C(21)	122.5(3)	P(2) - C(34) - C(39)	120.2(3)
C(17) - C(16) - C(21)	118.8(3)	C(35) - C(34) - C(39)	118.3(3)
C(16) - C(17) - C(18)	120.3(3)	C(34) - C(35) - C(36)	120.9(3)
C(17) - C(18) - C(19)	120.1(3)	C(35) - C(36) - C(37)	120.4(4)
C(18) - C(19) - C(20)	120.0(3)	C(36) - C(37) - C(38)	119.7(3)
C(19) - C(20) - C(21)	120.5(3)	C(37) - C(38) - C(39)	120.5(4)
C(16) - C(21) - C(20)	120.2(3)	C(34) - C(39) - C(38)	120.2(3)
P(1) - C(22) - C(23)	120.4(3)	P(2) - C(40) - C(41)	122.1(3)
P(1) - C(22) - C(27)	119.7(3)	P(2) - C(40) - C(45)	118.3(3)
C(23) - C(22) - C(27)	119.6(3)	C(41) - C(40) - C(45)	119.5(3)
C(22) - C(23) - C(24)	119.6(3)	C(40) - C(41) - C(42)	120.1(3)
C(23) - C(24) - C(25)	120.4(4)	C(41) - C(42) - C(43)	120.5(3)
C(24) - C(25) - C(26)	120.5(3)	C(42) - C(43) - C(44)	119.3(3)
C(25) - C(26) - C(27)	119.7(3)	C(43) - C(44) - C(45)	120.8(3)
C(22) - C(27) - C(26)	120.1(3)	C(40) - C(45) - C(44)	119.8(3)
O(1) - S(1) - O(2)	115.6(2)	S(1) - C(46) - F(1)	111.9(3)
O(1) - S(1) - O(3)	114.6(2)	S(1) - C(46) - F(2)	111.5(3)

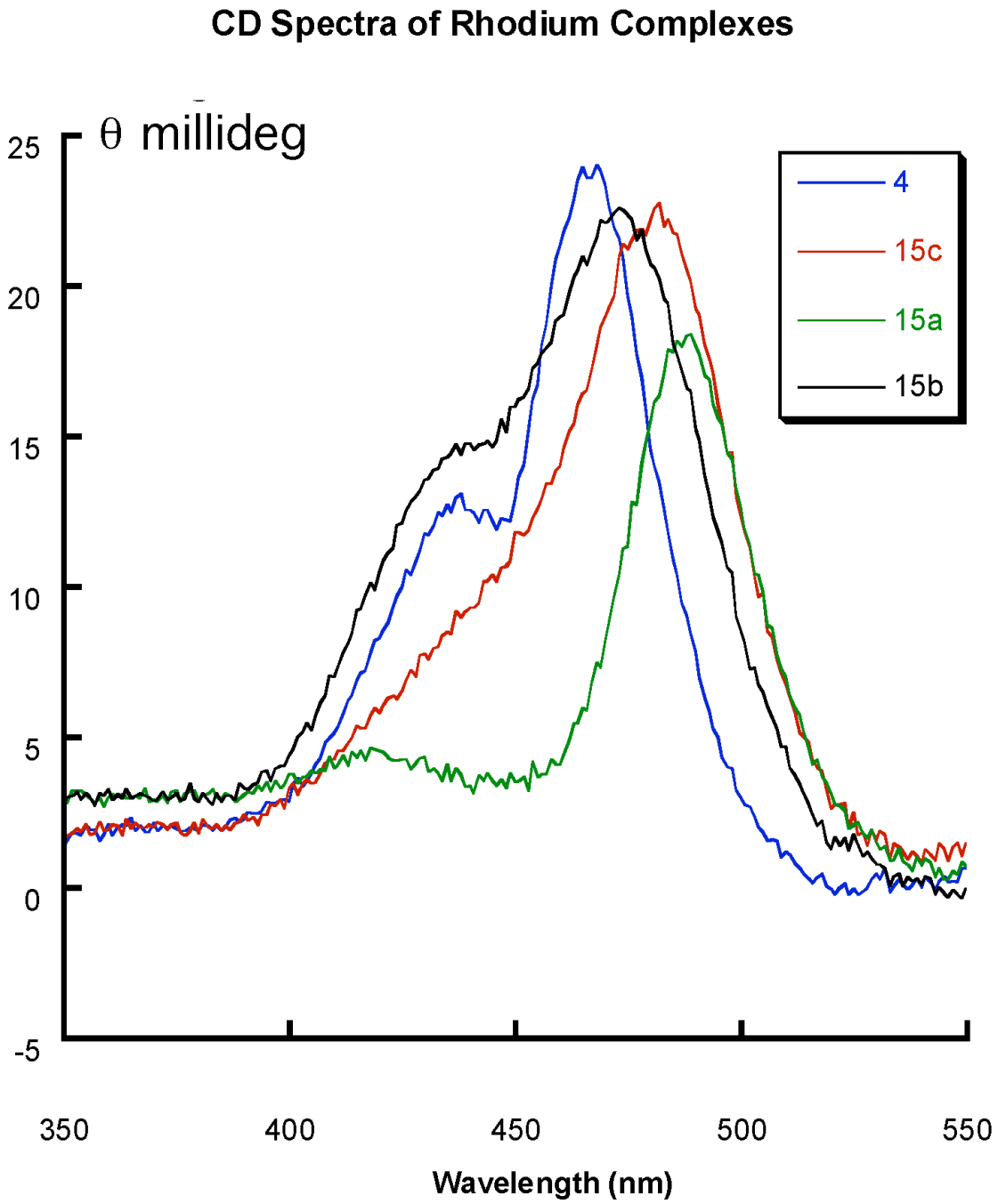
O(2) - S(1) - O(3)	115.72(19)	F(1) - C(46) - F(2)	107.9(3)
O(1) - S(1) - C(46)	102.7(2)	S(1) - C(46) - F(3)	111.8(3)
O(2) - S(1) - C(46)	102.8(2)	F(1) - C(46) - F(3)	106.7(3)
O(3) - S(1) - C(46)	102.6(2)	F(2) - C(46) - F(3)	106.7(3)
Cl(1) - C(47) - Cl(2)	114.2(3)		

Note – H atoms have been excluded

5. ^{31}P NMR spectra for Fig 2.



6. CD Spectra of Rhodium Complexes

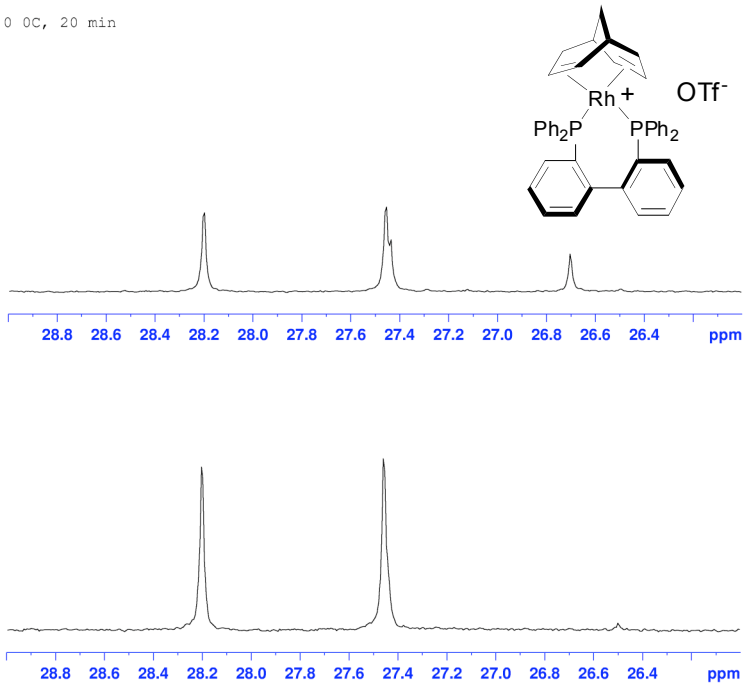


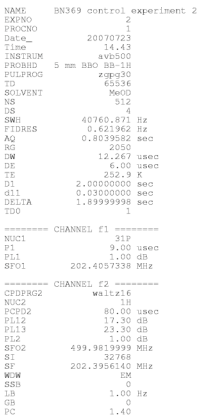
All CD were collected on a ChiraScan machine, using 1 mg/ml solution of the complex, with path-length 1.0 cm .

7. ^{31}P NMR Spectra of Rhodium Catalyst Precursors ; above before, and below after thermal equilibration in each pair of spectra.

Preparation of Rhodium diphosphine complexes:

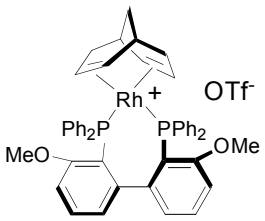
Preparation of [Rh(diene)BIPHEP]OTf: To a solution of [Rh(diene)(acac)] (14.1 mg, 0.048 mmol) in degassed methanol (0.5 mL) at 0 °C was added trimethylsilyl trifluoro-methanesulfonate (9.5 mL, 0.053 mmol). The reaction mixture was stirred for five minutes before BIPHEP (25 mg, 0.048 mmol) was added with vigorous stirring. The resulting solution was stirred at RT for 24 h. before hydrogenation. ^{31}P NMR (δ_P 27.8 (δ, $J_{Rh,P}$ 150.5) d_P 27.1 (d, $J_{Rh,P}$ 148.4)). Upper NMR trace shows initial mixture; final NMR trace after equilibration. ESI-MS [Rh(diene)dppb]$^+$ 745.1666 (calculated for $C_{45}H_{40}P_2Rh^+$ 745.1655).

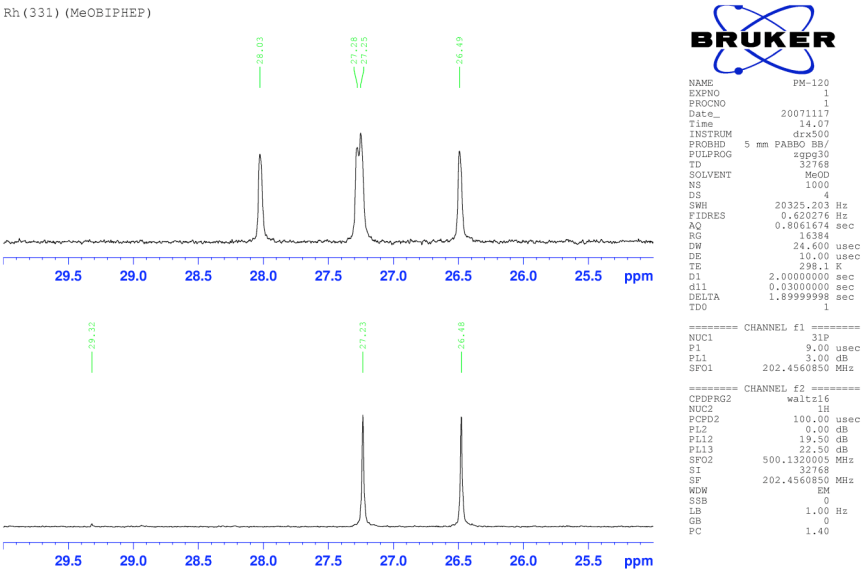




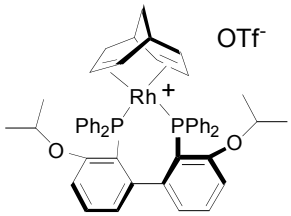
Preparation of [Rh(diene)[3,3'-diOMeBIPHEP]OTf: To a degassed anhydrous MeOH (2 ml), chiral rhodium(I) diene complex (14.7 mg, 0.047 mmol), phosphine (25 mg, 0.044 mmol) and TMSOTf (7.5 μl, 0.044 mmol) were added at ambient temperature and stirred for 1 h. ^{31}P NMR (203 MHz, MeOH-d_4) δ 27.66 (d, J = 151.8 Hz), 26.87 (d, J =154.1 Hz).

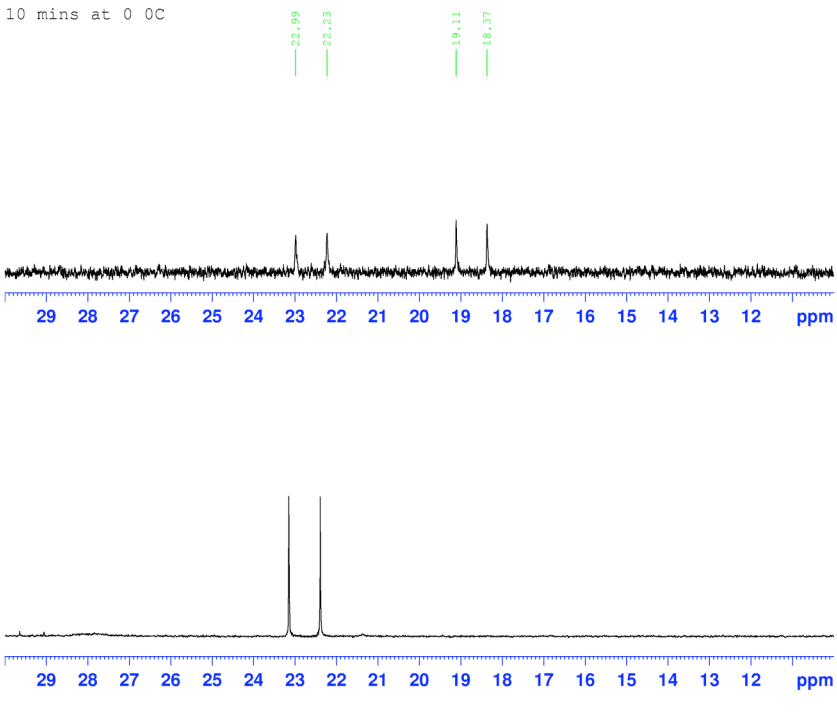
The reaction mixture was then stirred at 50 °C for 5 h to equilibrate to a single diastereoisomer. ^{31}P NMR (203 MHz, MeOH-d_4) δ 26.87 (d, J =154.07 Hz); HR-Mass (ESI) Caculated for $C_{47}H_{44}O_2P_2Rh$ 805.1872. Found: 805.1870.





Preparation of [Rh(diene)[3,3'-di-OP^{i}BIPHEP]OTf: To a degassed anhydrous MeOH (2 ml), chiral rhodium(I) complex **7** (14.7 mg, 0.047 mmol), phosphine (27.8 mg, 0.044 mmol) and TMSOTf (7.5 μl, 0.044 mmol) were added at ambient temperature and stirred for 1 h. ^{31}P NMR (203 MHz, MeOH-d_4) δ 22.61 (d, J = 153.3 Hz), 18.74 (d, J =150.8 Hz). The reaction mixture was then stirred at 50 ^{o}C for 5 h to equilibrate to a single diastereoisomer **8b**. ^{31}P NMR (203 MHz, MeOH-d_4) δ 22.61 (d, J =153.3 Hz). HRMS (ES-MS)$^{+}$ Calc. for $C_{51}H_{52}O_2P_2Rh$: 861.2498. Found: 861.2255





BRUKER

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PROCNO                   1

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TD0                    1

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PL1                  3.00 dB
SFO1        202.4601341 MHz

======== CHANNEL f2 ========
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PCPD2             100.00 usec
PL2                  0.00 dB
PL12                19.50 dB
PL13                22.50 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
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WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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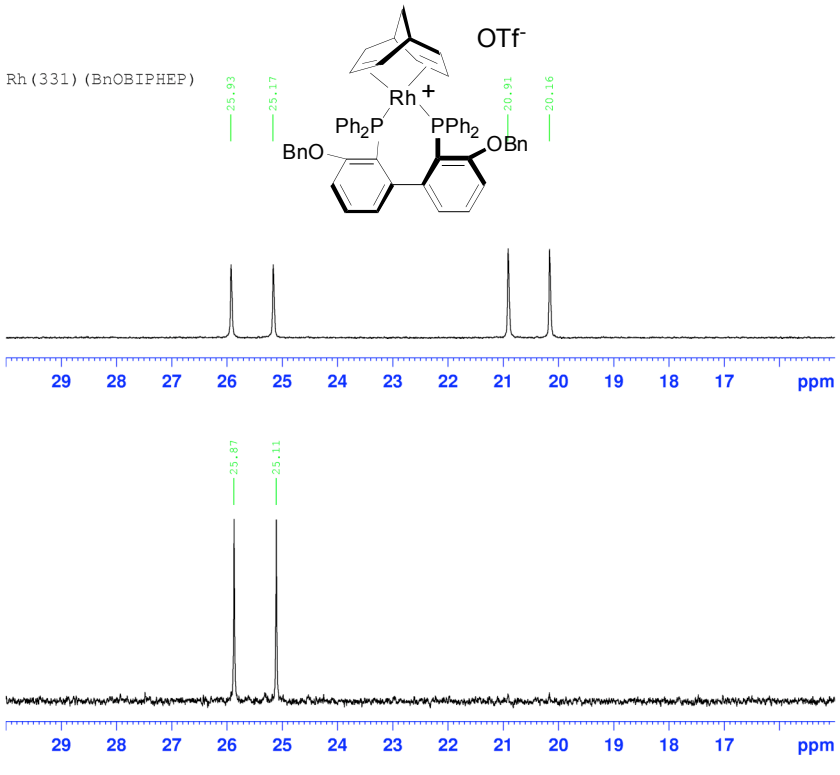
*Preparation of [Rh(*diene*)[3,3'-di-OBnBIPHEP]OTf*:

To a degassed anhydrous MeOH (2 ml), chiral rhodium(I) complex **7** (14.7 mg, 0.047 mmol), phosphine **6c** (31.29 mg, 0.044 mmol) and TMSOTf (7.5 ml, 0.044 mmol) were added at ambient temperature and stirred for 1 h. ^{31}P NMR (203 MHz, MeOH-d_4) δ 25.55 (d, J = 154.87 Hz), 20.54 (d, J =152.17 Hz).

The reaction mixture was then stirred at 50 ^{o}C for 12 h to equilibrate to a diastereoisomeric mixture; 97:3 preferred diastereomer: ^{31}P NMR (203 MHz, MeOH-d_4) δ 25.55 (d, J =154.87 Hz). HRMS calculated for $C_{59}H_{52}O_2P_2Rh$: 957.2498. Found: 957.2519.

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PL1                     3.00 dB
SFO1           202.4560850 MHz

======== CHANNEL f2 ========
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PL12                   19.50 dB
PL13                   22.50 dB
SFO2           500.1320005 MHz

F2 - Processing parameters
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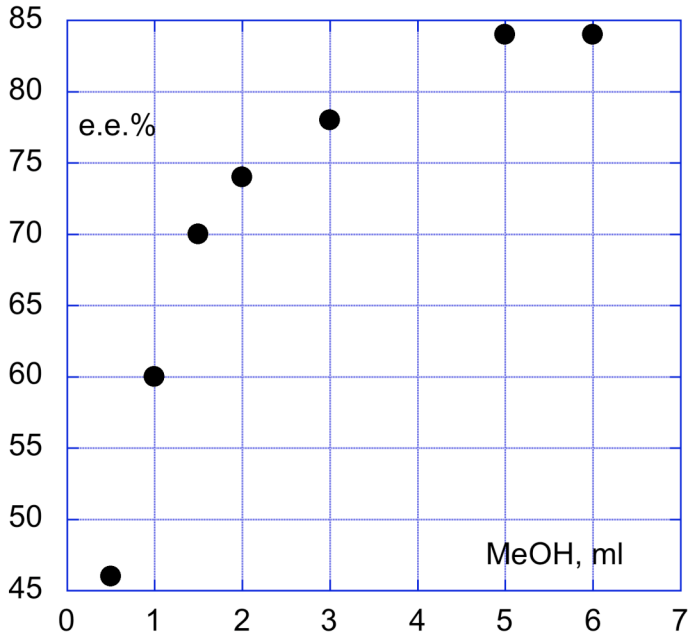
8. General Hydrogenation Procedure

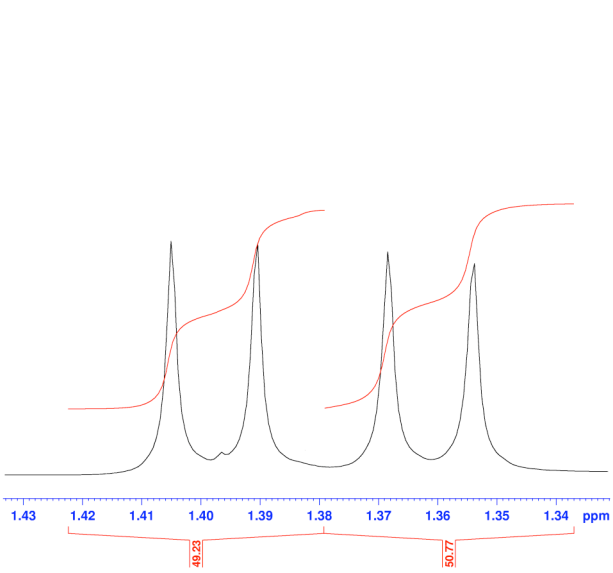
Degassed methanol (5 ml), chiral rhodium complex (0.0046 mmole) and substrate (0.23 mmole) were placed in a closed hydrogenation Schlenk vessel fitted with a pressure sensor. The Schlenk was evacuated and purged with hydrogen (6 times) at -78 °C. The reaction vessel was then pressurized to 1.8 atm and allowed to warm up to room temperature before stirring was started. The pressure was monitored until no more hydrogen consumption was detected and the reaction stopped. The resulted solution was passed through a short pad of silica gel using 1:1 ethyl acetate and pentane. After solvent removal, the crude product was used directly for GC and HPLC analysis for enantiomeric excess. ^{1}H NMR of the crude product indicated 100% conversion to hydrogenation product unless otherwise stated.

Hydrogenation of compound **8a** by catalyst **15b**; effect of solvent volume with conditions as Table 1 of manuscript:



9. Ee determination in asymmetric hydrogenation to dehydroamino ester 9, using the Ema-Sakai shift reagent (^{1}H NMR, $CDCl_3$, $CHCH_3$ region)

Run 1 Table 1 (<1% ee)



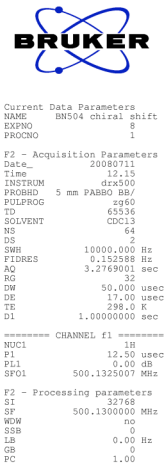


Figure 5 (95% ee)