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Electronic Supplementary Information

A one-step, modular route to optically-active diphos ligands

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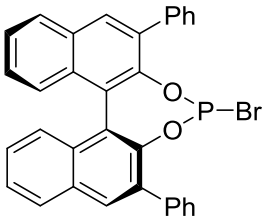
General Considerations

Unless otherwise stated, all of the following manipulations were carried out using Schlenk-line or glove-box techniques under a dry atmosphere of argon or N_2. Toluene and dichloromethane were dried using a Grubbs type solvent system and degassed by three sequential freeze-pump-thaw cycles. Deuterated benzene (C_6D_6) and dichloromethane (CD_2Cl_2) were dried over CaH_2, distilled and degassed by three sequential freeze-pump-thaw cycles and stored over 4 Å molecular sieves. (*S*)-(1,1'-binaphthalene-2,2'-dioxy)chlorophosphine **(1a)**,[1] the (*S*)-3,3'-diphenyl-1,1'-binaphthalene-2,2'-diol (**1b**)[2] and (*S*)-3,3'-dimesityl-1,1'-binaphthalene-2,2'diol (**1c**),[3] (2*R*,5*R*)-1-chloro-2,5-diphenylphospholane (**1d**),[4] $Me_3Si(CH_2)PPh_2$ **(2a)**,[5] $Me_3Si(CH_2)P^iPr_2$ **(2b)**,[5] $Me_3Si(CH_2)PCy_2$ **(2c)**,[6] and $Me_3Si(CH_2)P^tBu_2$ **(2d)**[7] were synthesised following literature methods or modifications thereof. All other reagents were used as received from Sigma-Aldrich, Acros or Strem Chemicals.

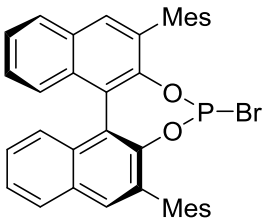
All NMR spectra were recorded on a Jeol ECS 400, Varian 400-MR, Varian VNMRS500 or a Bruker Avance IIIHD 500 equipped with a ^{13}C-observe (DCH) cryogenic probe at ambient temperature. Mass spectra were recorded by the Mass Spectrometry service, School of Chemistry, University of Bristol on a VG Analytical Autospec, VG Analytical Quattro or Brüker Daltonics Apex IV spectrometer. Chemical shifts are referenced relative to high frequency of residual solvent (^{1}H and ^{13}C), 85% H_3PO_4 (^{31}P) and $BF_3{\cdot}OEt_2$ (^{11}B). Elemental analysis was carried out by the Microanalytical Laboratory of the School of chemistry at the University of Bristol.

Synthesis of (*S*)-3,3'-diphenyl-1,1'-binaphthalene-2,2'-dioxy)bromophosphine (1b)



Prepared by modification of a literature procedure for (*S*)-(1,1'-binaphthalene-2,2'-dioxy)bromophosphine.[8] To a suspension of the (*S*)-3,3'-diphenyl-1,1'-binaphthalene-2,2'-diol (0.51 g, 1.2 mmol) in toluene (10 mL) cooled to 0 °C, was added NEt_3 (0.32 mL, 2.3 mmol) and PBr_3 (0.12 mL, 1.3 mmol)). The reaction mixture was warmed to ambient temperature and stirred for 5 h. The reaction mixture was then filtered and the solvent and excess PBr_3 removed under reduced pressure (with further addition/evaporation of toluene to remove any traces of PBr_3) to give the product as a light orange solid (0.37 g, 0.68 mmol, 57%). **$^{31}P\{^1H\}$ NMR** (162 MHz, C_6D_6): δ 192.74. **^1H NMR** (400 MHz, C_6D_6) : δ 6.94-7.32 (ar. C*H*), 7.45-7.91 (ar. C*H*). **$^{13}C\{^1H\}$ NMR** (101 MHz, C_6D_6): δ 125.10 (d, *J* = 2.5 Hz, quat. *C*), 126.10 (ar. *C*H), 126.27 (ar. *C*H), 126.30 (ar. *C*H), 126.32 (ar. *C*H), 126.86 (ar. *C*H), 127.01 (ar. *C*H), 127.34 (ar. *C*H), 127.39 (ar. *C*H), 127.97 (ar. *C*H), 128.17 (ar. *C*H), 128.35 (ar. *C*H), 128.48 (ar. *C*H), 128.57 (quat. *C*), 128.67 (ar. *C*H), 128.91 (ar. *C*H), 128.97 (ar. *C*H), 130.10 (ar. *C*H), 130.15 (ar. *C*H), 130.68 (ar. *C*H), 131.54 (ar. *C*H), 131.68 (ar. *C*H), 132.05 (quat. *C*), 132.42 (quat. *C*), 132.60 (quat. *C*), 132.99 (quat. *C*), 134.89 (d, *J* = 1.8 Hz, quat. *C*), 135.00 (d, *J* = 1.6 Hz, quat. *C*), 136.98 (quat. *C*), 138.21 (quat. *C*), 146.54 (d, *J* = 4.5 Hz, quat. *C*), 146.80 (d, *J* = 3.6 Hz, quat. *C*). **HR-MS** (EI) *m/z* calculated for $C_{32}H_{20}BrO_2P_2$ $[M]^{\bullet+}$: 546.0384, found 546.0378. Satisfactory elemental analyses were not obtained but the NMR spectra indicated that it was >90% pure (see Appendix Figure S1 and S2 for annotated spectra).

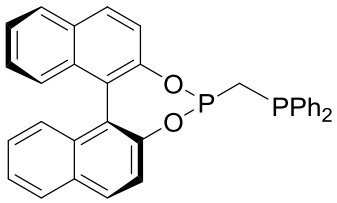
Synthesis of (*S*)-3,3'-diphenyl-1,1'-binaphthalene-2,2'-dioxy)bromophosphine (1c)



Prepared by modification of a literature procedure for (*S*)-(1,1'-Binaphthalene-2,2'-dioxy)bromophosphine.[8] To a suspension of the (*S*)-3,3'-dimesityl-1,1'-binaphthalene-2,2'diol (0.51 g, 0.97 mmol) in toluene (10 mL) cooled to 0 °C, was added NEt_3 (0.27 mL, 1.9 mmol) and PBr_3 (0.10 mL, 1.0 mmol). The reaction mixture was warmed to ambient temperature and stirred for 5 h. The reaction mixture was then filtered and the solvent and excess PBr_3 removed under reduced pressure (with further addition/evaporation of toluene to remove any traces of PBr_3) to give the product as a light orange solid (0.43 g, 0.68 mmol, 70%). **$^{31}P\{^1H\}$ NMR** (162 MHz, C_6D_6): δ 187.86. **^1H NMR** (400 MHz, C_6D_6): δ

2.00 (3H, s, mes-CH_3), 2.12 (6H, s, mes-CH_3), 2.17 (6H, s, mes-CH_3), 2.33 (3H, s, mes-CH_3), 6.79-7.12 (7H, ar. C*H*), 7.42-7.65 (7H, ar. C*H*). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ 20.62 (s, mes-*C*H_3), 20.65 (s, mes-*C*H_3), 21.12 (d, *J* = 9.1 Hz, mes-*C*H_3), 21.19 (s, mes-*C*H_3), 21.44 (s, mes-*C*H_3), 22.41 (s, mes-*C*H_3), 124.40 (d, *J* = 2.9 Hz, quat. *C*), 125.70 (quat. *C*), 125.90 (ar. *C*H), 126.11 (ar. *C*H), 126.28 (d, *J* = 6.4 Hz, quat. *C*), 126.69 (ar. *C*H), 126.85 (ar. *C*H), 127.47 (ar. *C*H), 127.67 (ar. *C*H), 128.50 (ar. *C*H), 128.57 (quat. *C*), 128.69 (ar. *C*H), 128.80 (ar. *C*H), 128.94 (ar. *C*H), 129.16 (ar. *C*H), 129.34 (ar. *C*H), 131.71 (d, *J* = 0.8 Hz, quat. *C*), 132.05 (ar. *C*H), 132.45 (ar. *C*H), 132.65 (d, *J* = 1.4 Hz, quat. *C*), 132.92 (d, *J* = 1.8 Hz, quat. *C*), 133.09 (d, *J* = 1.6 Hz, quat. *C*), 133.40 (quat. *C*), 133.92 (quat. *C*), 134.16 (d, *J* = 2.0 Hz, quat. *C*), 136.05 (quat. C), 137.20 (quat. *C*), 137.21 (d, *J* = 0.7 Hz, quat. *C*), 137.35 (quat. *C*), 137.63 (quat. *C*), 147.57 (d, *J* = 6.6 Hz, quat. *C*), 147.67 (d, *J* = 2.8 Hz, quat. *C*). **HR-MS** (EI) *m/z* calculated for $C_{38}H_{32}BrO_2P_2$ $[M]^{\bullet+}$: 630.1323, found 630.1313. Satisfactory elemental analyses were not obtained but the NMR spectra indicated that it was >90% pure (see Appendix Figure S3 and S4 for annotated spectra).

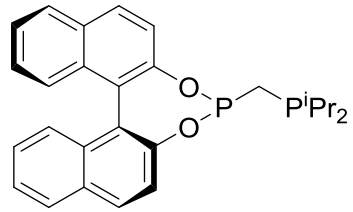
Synthesis of L_a



A mixture of **1a** (0.30 g, 0.76 mmol) and **2a** (0.21 g, 0.76 mmol) in toluene (5 mL) was heated to reflux for 3 d with stirring. The solvent was then removed under reduced pressure to give the product as an off-white solid which was suitable for use without further purification (0.36 g, 0.69 mmol, 90%). **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6) : δ -28.9 (d, J_{PP} = 113.9 Hz, *P*Ph_2), 207.7 (d, J_{PP} = 113.8 Hz, *P*$(OR)_2$). **^{1}H NMR** (400 MHz, C_6D_6) : δ 2.52 (2H, dd, J_{HP} = 2.3 Hz, J_{HP} = 2.3 Hz, CH_2), 6.80-7.57 (22 H, m, ar. C*H*). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ 34.97 (dd, J_{CP} = 26.6 Hz, J_{CP} = 49.1 Hz, *C*H_2), 121.09 (quat. *C*), 121.32 (d, *J* = 1.3 Hz, ar. *C*H), 122.49 (d, *J* = 1.9 Hz, ar. *C*H), 124.21 (d, *J* = 2.9 Hz, quat. *C*), 124.76 (ar. *C*H), 124.78 (ar. *C*H), 124.84 (d, *J* = 5.5 Hz, quat. *C*), 126.27 (d, *J* = 3.3 Hz, ar. *C*H), 126.92 (ar. *C*H), 127.03 (ar. *C*H), 127.95 (ar. *C*H), 128.28 (ar. *C*H), 128.35 (ar. *C*H), 128.36 (ar. *C*H), 128.41 (ar. *C*H), 128.44 (ar. *C*H), 128.49 (ar. *C*H), 128.57 (ar. *C*H), 128.66 (ar. *C*H), 129.69 (ar. *C*H), 130.70 (ar. *C*H), 131.26 (quat. *C*), 131.67 (quat. *C*), 132.70 (ar. *C*H), 132.85 (ar. *C*H), 132.93 (ar. *C*H), 133.08 (ar. *C*H), 133.20 (d, *J* = 1.2 Hz, quat. *C*), 138.11 (dd, *J* = 6.6 Hz, *J* = 14.9 Hz,

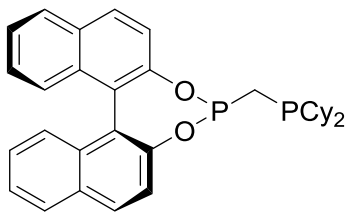
quat. *C*), 138.76 (dd, *J* = 4.4 Hz, *J* = 13.9 Hz, quat. *C*), 148.54 (d, *J* = 6.5 Hz, quat. *C*), 150.70 (d, *J* = 2.7 Hz, quat. *C*). **Anal.** Found: C, 76.90; H, 4.97. Calc. for $C_{33}H_{24}O_2P_2$: C, 77.04; H, 4.70. **HR-MS** (EI) *m/z* calculated for $C_{33}H_{24}O_2P_2$ $[M]^{\bullet+}$: 514.1252, found 514.1250.

Synthesis of L_b



A solution of **1a** (0.30 g, 0.86 mmol) and **2b** (0.18 g, 0.86 mmol) in toluene (5 mL) was stirred at ambient temperature for 3 h. The solvent was then removed under reduced pressure to give the product as a white solid which was suitable for use without further purification (0.24 g, 0.54 mmol, 64%). **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -10.0 (d, J_{PP} = 103.1 Hz, *P*^{i}Pr$_2$), 210.9 (d, J_{PP} = 103.4 Hz, *P*(OR)$_2$). **^{1}H NMR** (400 MHz, C_6D_6): δ 0.88 (12H, m, C*H*$_3$), 1.54 (2H, m, C*H*$_2$), 1.80 (2H, m, C*H*(CH$_3$)$_2$), 7.47 (12H, m, ar. C*H*). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ 18.3 (d, J_{CP} = 8.6 Hz, *C*H$_3$), 19.0 (m, *C*H$_3$), 19.6 (m, *C*H$_3$), 19.9 (d, J_{CP} = 17.1 Hz, *C*H$_3$), 24.1 (m, *C*(CH$_3$)$_2$), 28.6 (dd, J_{CP} = 33.5 Hz, J_{CP} = 47.5 Hz, *C*H$_2$), 121.51 (ar. *C*H), 122.96 (ar. *C*H), 122.98 (ar. *C*H), 124.37 (d, *J* = 2.9 Hz, ar. *C*H), 124.83 (d, *J* = 2.6 Hz, ar. *C*H), 125.00 (d, *J* = 5.6 Hz, ar. *C*H), 125.38 (quat. *C*), 126.35 (d, *J* = 2.2 Hz, ar. *C*H), 127.07 (d, *J* = 9.2 Hz, ar. *C*H), 128.25 (quat. *C*), 128.40 (d, *J* = 16.0 Hz, ar. *C*H), 129.02 (ar. *C*H), 129.49 (ar. *C*H), 130.8 (ar. *C*H), 131.30 (quat. *C*), 131.76 (quat. *C*), 133.24 (quat. *C*), 137.57 (quat. *C*), 148.66 (d, *J* = 6.8 Hz, quat. *C*), 151.08 (d, *J* = 2.9 Hz, quat. *C*). **Anal.** Found: C, 72.61; H, 6.44. Calc. for $C_{27}H_{28}O_2P_2$: C, 72.64, H 6.32. **HR-MS** (EI) *m/z* calculated for $C_{27}H_{28}O_2P_2$ $[M]^{\bullet+}$: 446.1565, found 446.1567.

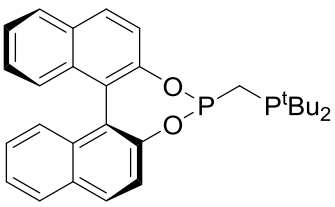
Synthesis of L_c



A solution of **1a** (0.30 g, 0.86 mmol) and **2c** (0.25 g, 0.86 mmol) in toluene (5 mL) was stirred at ambient temperature for 6 h. The solvent was then removed under reduced pressure to give the product as a white solid which was suitable for use without further purification (0.23 g, 0.44 mmol, 51%). **^{31}P{^{1}H} NMR** (122 MHz, C_6D_6): δ -18.7 (d, J_{PP} = 103.3 Hz, *P*Cy$_2$), 211.64 (d, J_{PP} = 103.4 Hz, *P*(OR)$_2$). **^{1}H NMR** (400 MHz, C_6D_6): δ 1.11 (10H, m, PC*y*$_2$), 1.60 (10H, m, PC*y*$_2$), 1.75 (2H, m, P(C*H*)), 1.93 (2H, m, C*H*$_2$), 6.92 (4H, m, ar. C*H*), 7.50 (8H, m, ar. C*H*). **^{13}C{^{1}H} NMR**

(101 MHz, C_6D_6): δ 26.30 (d, *J* = 1.3 Hz, *C*H_2), 27.02 (d, *J* = 7.1 Hz, *C*H_2), 27.04 (d, *J* = 7.7 Hz, *C*H_2), 27.16 (d, *J* = 11.4 Hz, *C*H_2), 27.17 (d, *J* = 12.0 Hz, *C*H_2), 28.38 (dd, *J* = 33.8 Hz, *J* = 47.5 Hz, P*C*H_2P), 28.70 (d, *J* = 8.1 Hz, *C*H_2), 29.30 (d, *J* = 8.6 Hz, *C*H_2), 29.35 (d, *J* = 8.3 Hz, *C*H_2), 30.16 (dd, *J* = 2.6 Hz, *J* = 15.0 Hz, *C*H_2), 30.32 (d, *J* = 15.4 Hz, *C*H_2), 33.93 (dd, *J* = 3.6 Hz, *J* = 15.6 Hz, *C*H), 34.07 (dd, *J* = 6.8 Hz, *J* = 16.0 Hz, *C*H), 121.43 (d, *J* = 1.4 Hz, ar. *C*H), 122.97 (d, *J* = 2.5 Hz, ar. *C*H), 124.32 (d, *J* = 3.0 Hz, quat. *C*), 124.71 (ar. *C*H), 124.73 (ar. *C*H), 124.94 (d, *J* = 5.5 Hz, quat. *C*), 126.26 (d, *J* = 1.1 Hz, ar. *C*H), 126.95 (ar. *C*H), 127.03 (ar. *C*H), 127.92 (ar. *C*H), 128.21 (ar. *C*H), 128.37 (ar. *C*H), 129.37 (ar. *C*H), 130.70 (ar. *C*H), 131.23 (quat. *C*), 131.66 (quat. *C*), 133.16 (d, *J* = 1.5 Hz, quat. *C*), 133.21 (d, *J* = 1.0 Hz, quat. *C*), 148.67 (d, *J* = 6.8 Hz, quat. *C*), 151.04 (d, *J* = 3.0 Hz, quat. *C*). **Anal.** Found: C, 74.92; H, 6.99. Calc. for $C_{33}H_{36}O_2P_2$: C, 75.27; H, 6.89. **HR-MS** (EI) *m/z* calculated for $C_{33}H_{36}O_2P_2$ $[M]^{\bullet+}$: 526.2191, found 526.2201.

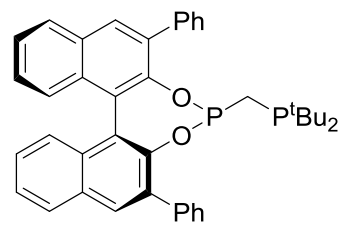
Synthesis of L_d



A solution of **1a** (0.23 g, 0.65 mmol) in toluene (5 mL) was added to a solution of **2d** (0.15 g, 0.65 mmol) in toluene (5 mL). The resulting mixture was heated to 50 °C and left to stir overnight. The solvent was removed under reduced pressure to give the product as a white solid which was suitable for use without further purification (0.27 g, 0.57 mmol, 88%). **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ 10.7 (d, J_{PP} = 117.8 Hz, *P*^{t}Bu$_2$), 210.5 (d, J_{PP} = 117.3 Hz, *P*(OR)$_2$). **^{1}H NMR** (400 MHz, C_6D_6): δ 1.01 (9H, d, J_{HP} = 11.3 Hz, C(C*H*$_3$)$_3$), 1.08 (9H, d, J_{HP} = 11.1 Hz, C(C*H*$_3$)$_3$), 2.00 (2H, m, C*H*$_2$), 6.89-6.95 (2H, m, ar. C*H*), 7.09-7.15 (2H, m, ar. C*H*), 7.44-7.68 (8H, m, ar. C*H*). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ 28.4 (dd, J_{CP} = 38.6 Hz, J_{CP} = 48.1 Hz, *C*H_2), 29.1 (dd, J_{PP} = 1.7 Hz, J_{PP} = 14.2 Hz, C(*C*H$_3$)$_3$), 29.4 (dd, J_{PP} = 3.4 Hz, J_{PP} = 14.3 Hz, C(*C*H$_3$)$_3$), 31.0 (dd, J_{PP} = 5.0 Hz, J_{PP} = 19.5 Hz, quat. *C*, *C*(CH$_3$)$_3$), 31.3 (dd, J_{PP} = 5.9 Hz, J_{PP} = 20.3 Hz, quat. *C*, *C*(CH$_3$)$_3$), 121.4 (d, *J* = 1.6 Hz, ar. *C*H), 122.85 (d, *J* = 1.9 Hz, ar. *C*H), 124.23 (d, *J* = 3.0 Hz, quat. *C*), 124.71 (d, *J* = 4.1 Hz, ar. *C*H), 126.2 (d, *J* = 4.1 Hz, ar. *C*H), 124.98 (d, *J* = 5.6 Hz, quat. *C*), 126.15 (d, *J* = 4.1 Hz, ar. *C*H), 126.86 (ar. *C*H), 126.98 (ar. *C*H), 127.86 (ar. *C*H), 128.11 (ar. *C*H), 128.30 (ar. *C*H), 128.84 (quat. *C*), 129.25 (ar. *C*H), 130.62 (ar. *C*H), 131.07 (quat. *C*), 131.58 (quat. *C*), 133.06 (dd, *J* = 1.6 Hz, *J* = 2.7 Hz, quat. *C*), 148.61

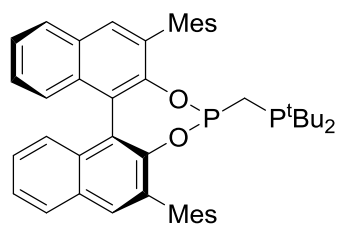
(d, J = 6.4 Hz, quat. *C*), 151.01 (d, J = 2.6 Hz, quat. *C*). **Anal.** Found: C, 73.20; H, 6.82. Calc. for $C_{29}H_{32}O_2P_2$: C, 73.40; H 6.80. **HR-MS** (EI) *m/z* calculated for $C_{29}H_{32}O_2P_2$ $[M]^{\bullet+}$: 474.1878, found 474.1880.

Synthesis of L_e



A solution of **1b** (0.093 g, 0.17 mmol) in toluene (0.5 mL) was added to a solution of **2d** (0.040 g, 0.17 mmol) in toluene (0.5 mL) and stirred for 16 h. The solvent was then removed under reduced pressure to give the product as an off-white solid (0.052 g, 0.08 mmol, 47%). **^{31}P{^{1}H} NMR** (202 MHz, C_6D_6): δ 10.5 (d, J_{PP} = 152.6 Hz, P^tBu_2), 209.7 (d, J_{PP} = 152.5 Hz, $P(OR)_2$). **^{1}H NMR** (400 MHz, C_6D_6): δ 0.79 (9H, d, J_{HP} = 2.5 Hz, C(CH_3)$_3$), 0.82 (9H, d, J_{HP} = 2.3 Hz, C(CH_3)$_3$), 1.15 (1H, m, CH_2), 1.78 (1H, app. d, J_{HP} = 14.1 Hz, CH_2), 6.91-7.99 (ar. C*H*). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ 27.80 (dd, J_{CP} = 38.3 Hz, J_{CP} = 46.4 Hz, *C*H$_2$), 29.00 (app. d, J = 14.5 Hz, C(*C*H$_3$)$_3$), 29.08 (dd, J_{PP} = 3.8 Hz, J_{PP} = 14.6 Hz, C(*C*H$_3$)$_3$), 31.00 (dd, J_{PP} = 12.3 Hz, J_{PP} = 25.1 Hz, quat. *C*, *C*(CH$_3$)$_3$), 31.01 (app d, J = 24.4 Hz, quat. *C*, *C*(CH$_3$)$_3$), 125.10 (ar. *C*H), 125.29 (ar. *C*H), 125.65 (d, J = 2.8 Hz, quat. *C*), 126.13 (ar. *C*H), 126.26 (ar. *C*H), 126.34 (d, J = 5.8 Hz, quat. *C*), 126.90 (ar. *C*H), 127.07 (ar. *C*H), 127.33 (ar. *C*H), 127.34 (ar. *C*H), 127.95 (m, ar. *C*H), 128.05 (ar. *C*H), 128.16 (ar. *C*H), 128.26 (ar. *C*H), 128.35 (ar. *C*H), 128.54 (ar. *C*H), 128.93 (ar. *C*H), 129.84 (ar. *C*H), 130.17 (ar. *C*H), 130.28 (ar. *C*H), 130.42 (ar. *C*H), 130.92 (ar. *C*H), 131.25 (quat. *C*), 131.64 (quat. *C*), 132.78 (quat. *C*), 134.89 (quat. *C*), 135.16 (quat. *C*), 137.42 (quat. *C*), 137.47 (quat. *C*), 138.59 (quat. *C*), 146.72 (d, J = 5.1 Hz, quat. *C*), 148.66 (d, J = 2.9 Hz, quat. *C*). **HR-MS** (EI) *m/z* calculated for $C_{41}H_{40}O_2P_2$ $[M]^{\bullet+}$: 626.2504, found 626.2497. Satisfactory elemental analyses were not obtained but the NMR spectra indicated that it was >90% pure (see Appendix Figure S5 and S6 for annotated spectra).

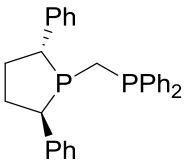
Synthesis of L_f



A solution of **1c** (0.087 g, 0.14 mmol) in toluene (0.5 mL) was added to a solution of **2d** (0.032 g , 0.14 mmol) in toluene (0.5 mL) and stirred for 8 h at ambient temperature. The solvent was removed under reduced pressure to give the product as an off-white solid (0.086 g, 0.12 mmol,

85%). **$^{31}P\{^{1}H\}$ NMR** (162 MHz, C_6D_6): δ 12.8 (d, J_{PP} = 219.6 Hz, P^tBu_2), 208.9 (d, J_{PP} = 220.9 Hz, $P(OR)_2$). **^{1}H NMR** (400 MHz, C_6D_6): δ 0.80 (9H, d, J_{HP} = 3.5 Hz, $C(CH_3)_3$), 0.82 (9H, d, J_{HP} = 3.9 Hz, $C(CH_3)_3$), 1.15 (1H, m, CH_2), 1.83 (1H, app. d, J = 14.5 Hz, CH_2), 2.18 (3H, s, Mes-CH_3), 2.21 (3H, s, Mes-CH_3), 2.25 (6H, s, Mes-CH_3), 2.26 (6H, s, Mes-CH_3), 6.81-7.18 (ar. C*H*), 7.49-7.66 (ar. C*H*) **$^{13}C\{^{1}H\}$ NMR** (126 MHz, C_6D_6): δ 20.39 (s, Mes-CH_3), 20.49 (s, Mes-CH_3), 20.69 (s, Mes-CH_3), 20.82 (s, Mes-CH_3), 21.18 (d, J = 9.1 Hz, Mes-CH_3), 21.84 (s, Mes-CH_3), 28.29 (dd, J = 36.0 Hz, J = 47.4 Hz, CH_2), 28.98 (dd, J = 1.5 Hz, J = 14.5 Hz, $C(CH_3)_3$), 29.27 (d, J = 15.0 Hz, $C(CH_3)_3$), 30.78 (dd, J = 10.3 Hz, J = 25.5 Hz, quat. $C(CH_3)_3$), 31.38 (dd, J = 10.3 Hz, J = 25.5 Hz, quat. $C(CH_3)_3$), 124.30 (d, J = 2.6, quat. *C*), 124.76 (ar. *C*H), 124.86 (ar. *C*H), 125.89 (ar. *C*H), 125.99 (ar. *C*H), 126.07 (d, J = 6.1 Hz, quat. *C*), 127.19 (d, J = 9.1 Hz, ar. *C*H), 127.79 (ar. *C*H), 127.94 (ar. *C*H), 128.05 (ar. *C*H), 128.16 (ar. *C*H), 128.49 (ar. *C*H), 128.56 (ar. *C*H), 128.59 (ar. *C*H), 130.80 (quat. *C*), 130.92 (ar. *C*H), 131.12 (ar. *C*H), 131.02 (quat. *C*), 132.05 (d, J = 9.5 Hz, quat. *C*), 132.78 (quat. *C*), 132.86 (quat. *C*), 133.09 (quat. *C*), 133.8 (d, J = 20.0 Hz, quat. *C*), 134.17 (quat. *C*), 134.23 (quat. *C*), 134.64 (quat. *C*), 135.30 (quat. *C*), 136.42 (quat. *C*), 136.56 (quat. *C*), 138.29 (quat. *C*), 148.30 (d, J = 6.1 Hz, quat. *C*), 149.74 (d, J = 2.0 Hz, quat. *C*). **HR-MS** (EI) *m/z* calculated for $C_{47}H_{52}O_2P_2$ $[M]^{\bullet+}$: 710.3443, found 710.3446. Satisfactory elemental analyses were not obtained but the NMR spectra indicated that it was >95% pure (see Appendix Figure S7 and S8 for annotated spectra).

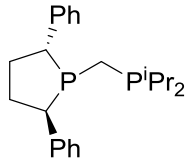
Synthesis of L_g



A solution of **1d** (0.051 g, 0.19 mmol) in toluene (0.5 mL) was added to a solution of **2a** (0.051 g, 0.19 mmol) in toluene (0.5 mL) and heated to reflux for 5 d. The solvent was removed under reduced pressure to give the product as a viscous oil (0.075 g, 0.17 mmol, 90%). **$^{31}P\{^{1}H\}$ NMR** (162 MHz, C_6D_6): δ -23.14 (d, J_{PP} = 110.5 Hz, PPh_2), 6.26 (d, J_{PP} = 110.5 Hz, $P(CH)_2$). **^{1}H NMR** (400 MHz, C_6D_6): δ 1.68 (1H, m, phospholane-CH_2), 1.87 (1H, dd, J = 6.1 Hz, J = 13.1 Hz, CH_2), 1.95 (1H, dd, J = 3.8 Hz, J = 13.1 Hz, CH_2), 2.02 (2H, m, phospholane-CH_2), 2.30 (1H, m, phospholane-CH_2), 3.48 (2H, m, phospholane-C*H*), 6.91 -7.48 (20H, m, ar-C*H*). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, C_6D_6): δ 24.36 (dd, J = 23.1 Hz, J = 37.0 Hz, CH_2), 31.53 (d, J = 4.1 Hz, phospholane-CH_2), 37.28 (s, phospholane-CH_2), 46.97 (dd, J = 9.7 Hz, J = 18.5 Hz, phospholane-*C*H),

50.64 (dd, *J* = 5.9 Hz, *J* = 18.0 Hz, phospholane-*C*H), 125.30 (ar. *C*H), 125.70 (d, *J* = 2.2 Hz, ar. *C*H), 125.78 (d, *J* = 1.8 Hz, ar. *C*H), 127.74 (d, *J* = 3.8 Hz, ar. *C*H), 127.95 (br. s, ar. *C*H), 128.09 (d, *J* = 6.8 Hz, ar. *C*H), 128.17 (ar. *C*H), 128.21 (ar. *C*H), 128.22 (ar. *C*H), 128.26 (ar. *C*H), 128.29 (ar. *C*H), 128.31 (ar. *C*H), 128.94 (ar. *C*H), 132.07 (ar. *C*H), 132.21 (ar. *C*H), 132.54 (ar. *C*H), 132.69 (ar. *C*H), 132.83 (d, *J* = 2.3 Hz, ar. *C*H), 132.98 (d, *J* = 2.2 Hz, ar. *C*H), 137.49 (ar. *C*H), 138.81 (dd, *J* = 4.0 Hz, *J* = 14.4 Hz, quat. *C*), 139.07 (s, quat. *C*), 140.03 (dd, *J* = 7.2 Hz, *J* = 16.3 Hz, quat. *C*), 144.93 (d, *J* = 17.6 Hz, quat. *C*). **HR-MS** (EI) *m/z* calculated for $C_{29}H_{28}P_2$ $[M]^{\bullet+}$: 438.1666, found 438.1674. Satisfactory elemental analyses were not obtained but the NMR spectra indicated that it was >90% pure (see Appendix Figure S9 and S10 for annotated spectra).

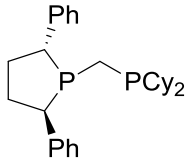
Synthesis of L_h



A solution of **1d** (0.038 g, 0.14 mmol) in toluene (0.5 mL) was added to a solution of **2b** (0.028 g, 0.14 mmol) in toluene (0.5 mL) and heated to 70 °C for 4 h. The solvent was removed under reduced pressure to give the product as a viscous oil which was suitable for use without further purification (0.048 g, 0.13 mmol, 93%). **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -5.90 (d, *J* = 88.90 Hz, *P*^{i}Pr$_2$), 7.95 (d, *J* = 88.9 Hz, *P*(CH)$_2$). **^{1}H NMR** (400 MHz, C_6D_6): δ 0.85 (12H, m, C*H*$_3$), 0.95 (1H, m, C*H*$_2$), 1.30 (1H, dd, *J* = 2.7 Hz, *J* = 13.3 Hz, C*H*$_2$), 1.36 (1H, m, C*H*(CH$_3$)$_2$), 1.45 (1H, m, C*H*(CH$_3$)$_2$), 1.69 (1H, m, phospholane-C*H*$_2$), 1.99 (2H, m, phospholane-C*H*$_2$), 2.28 (1H, m, phospholane-C*H*$_2$), 3.46 (1H, m, phospholane-C*H*), 3.55 (1H, m, phospholane-C*H*), 6.93-7.03 (2H, m, ar. C*H*), 7.08-7.20 (6H, m, ar. C*H*), 7.43-7.47 (2H, m, ar. C*H*). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ 17.49 (dd, *J* = 30.3 Hz, *J* = 35.7 Hz, *C*H$_2$), 18.68 (d, *J* = 10.1 Hz, *C*H$_3$), 19.18 (dd, *J* = 4.6 Hz, *J* = 11.1 Hz, *C*H$_3$), 19.36 (dd, *J* = 3.7 Hz, *J* = 13.4 Hz, *C*H$_3$), 20.14 (d, *J* = 17.7 Hz, *C*H$_3$), 23.84 (dd, *J* = 7.5 Hz, *J* = 15.8 Hz, *C*H), 23.91 (dd, *J* = 3.9 Hz, *J* = 15.3 Hz, *C*H), 31.15 (d, *J* = 4.1 Hz, phospholane-C*H*$_2$), 37.25 (s, phospholane-C*H*$_2$), 47.13 (dd, *J* = 8.0 Hz, *J* = 18.5 Hz, phospholane-*C*H), 50.44 (dd, *J* = 6.3 Hz, *J* = 17.8 Hz, phospholane-*C*H), 125.70 (ar. *C*H), 125.72 (ar. *C*H), 127.66 (ar. *C*H), 127.70 (ar. *C*H), 128.30 (ar. *C*H), 128.31 (ar. *C*H), 128.33 (ar. *C*H), 128.50 (ar. *C*H), 128.36 (ar. *C*H), 128.42 (d, *J* = 1.7 Hz, ar. *C*H), 139.50 (quat. *C*), 145.28 (d, *J* = 17.3 Hz, quat. *C*). **Anal.** Found: C, 74.51; H,

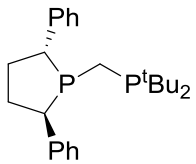
8.77. Calc. for $C_{23}H_{32}P_2$: C, 74.57; H 8.71. **HR-MS** (EI) *m/z* calculated for $C_{23}H_{32}P_2$ $[M]^{\bullet+}$: 370.1979, found 370.1971.

Synthesis of L_i



A solution of **1d** (0.016 g, 0.060 mmol) in toluene (0.5 mL) was added to a solution of **2c** (0.016 g, 0.060 mmol) in toluene (0.5 mL) and heated to 60 °C for 16 h. The solvent was removed under reduced pressure to give the product as a viscous oil which was suitable for use without further purification (0.020 g, 0.044 mmol, 74%). **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ -13.08 (d, J_{PP} = 91.4 Hz, *P*Cy_2), 8.31 (d, J_{PP} = 91.8 Hz, *P*$(CH)_2$) **^{1}H NMR** (400 MHz, C_6D_6): δ 0.82-1.68 (22H, m, Cy-C*H*$_2$, Cy-C*H* and C*H*$_2$), 1.72 (1H, m, phospholane-C*H*$_2$), 2.01 (2H, m, phospholane-C*H*$_2$), 2.31 (1H, m, phospholane-C*H*$_2$), 6.93-7.21 (8H, m, ar. C*H*), 7.43-7.50 (2H, m, ar. C*H*). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ 16.67 (dd, *J* = 28.6 Hz, *J* = 35.9 Hz, *C*H$_2$), 26.44 (s, Cy-*C*H$_2$), 26.50 (s, Cy-*C*H$_2$), 27.00 (d, *J* = 10.5 Hz, Cy-*C*H$_2$), 27.08 (d, *J* = 14.6 Hz, Cy-*C*H$_2$), 27.21 (d, *J* = 12.6 Hz, Cy-*C*H$_2$), 27.28 (d, *J* = 14.2 Hz, Cy-*C*H$_2$), 28.95 (d, *J* = 8.7 Hz, Cy-*C*H$_2$), 29.54 (dd, , *J* = 4.1 Hz, *J* = 9.6 Hz, Cy-*C*H$_2$), 29.73 (dd, , *J* = 3.4 Hz, *J* = 11.9 Hz, Cy-*C*H$_2$), 30.51 (d, *J* = 15.7 Hz, Cy-*C*H$_2$), 31.29 (d, *J* = 4.0 Hz, phospholane-*C*H$_2$), 33.81 (d, *J* = 15.2 Hz, Cy-*C*H), 33.86 (dd, *J* = 3.4 Hz, *J* = 15.2 Hz, Cy-*C*H), 37.23 (s, phospholane-*C*H$_2$), 47.23 (dd, *J* = 8.3 Hz, *J* = 18.7 Hz, phospholane-*C*H), 50.54 (dd, *J* = 6.5 Hz, *J* = 17.9 Hz, phospholane-*C*H), 125.31 (ar. *C*H), 125.65 (ar. *C*H), 125.66 (ar. *C*H), 127.58 (ar. *C*H), 128.72 (ar. *C*H), 127.96 (ar. *C*H), 128.27 (ar. *C*H), 128.30 (ar. *C*H), 128.35 (d, *J* = 1.7 Hz, ar. *C*H), 128.42 (d, *J* = 1.6 Hz, ar. *C*H), 139.50 (quat. *C*), 145.33 (d, *J* = 17.3 Hz, quat. *C*). **Anal.** Found: C, 76.89; H, 8.91. Calc. for $C_{29}H_{40}P_2$: C, 77.30; H, 8.95. **HR-MS** (EI) *m/z* calculated for $C_{29}H_{40}P_2$ $[M]^{\bullet+}$: 450.2605, found 450.2608.

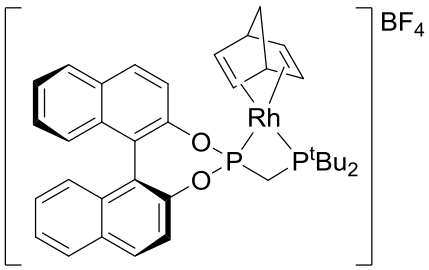
Synthesis of L_j



A solution of **1d** (0.059 g, 0.22 mmol) in toluene (0.5 mL) was added to a solution of **2d** (0.050 g, 0.22 mmol) in toluene (0.5 mL) and heated to 70 °C for 16 h. The solvent was removed under reduced pressure to give the product as a viscous oil which was suitable for use without further purification (0.080 g, 0.20 mmol, 91%). **^{31}P{^{1}H} NMR** (162

MHz, C_6D_6): δ 11.99 (d, J_{PP} = 100.0 Hz, *P*(CH)$_2$), 14.78 (d, J_{PP} = 100.3 Hz, *P*^{t}Bu$_2$). **^{1}H NMR** (400 MHz, C_6D_6): δ 0.88 (9H, d, J_{HP} = 11.2 Hz, C(C*H*$_3$)$_3$), 0.96 (9H, d, J_{HP} = 11.0 Hz, C(C*H*$_3$)$_3$), 1.02 (1H, app. d, *J* = 11.0 Hz, C*H*$_2$), 1.31 (1H, app. d, *J* = 13.8 Hz, C*H*$_2$), 1.73 (1H, m, phospholane-C*H*$_2$), 2.04 (2H, m, phospholane-C*H*$_2$), 2.33 (1H, m, phospholane-C*H*$_2$), 3.47 (1H, m, C*H*), 3.67 (1H, m, C*H*), 6.93-7.02 (2H, m, ar. C*H*), 7.08-7.19 (2H, m, ar. C*H*), 7.45-7.50 (2H, m, ar. C*H*). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ 16.31 (app t., *J* = 34.7 Hz, *C*H$_2$), 29.33 (d, *J* = 13.8 Hz, C(*C*H$_3$)), 29.73 (d, *J* = 5.1 Hz, *J* = 13.4 Hz, C(*C*H$_3$)), 31.01 (d, *J* = 4.04, phospholane-*C*H$_2$), 31.32 (dd, *J* = 7.0 Hz, *J* = 24.4 Hz, quat. *C*, *C*(CH$_3$)$_3$), 31.63 (dd, *J* = 2.0 Hz, *J* = 23.3 Hz, quat. *C*, *C*(CH$_3$)$_3$), 37.08 (s, phospholane-*C*H$_2$), 47.48 (dd, *J* = 9.0 Hz, *J* = 18.4 Hz, phospholane-*C*H), 49.77 (dd, *J* = 6.2 Hz, *J* = 18.7 Hz, phospholane-*C*H), 125.59 (dd, *J* = 2.0 Hz, *J* = 3.7 Hz, ar. *C*H), 127.53 (d, *J* = 3.6 Hz, ar. *C*H), 128.21 (d, *J* = 0.8 Hz, ar. *C*H), 128.27 (s, ar. *C*H), 128.36 (dd, *J* = 2.0 Hz, *J* = 8.2 Hz, ar. *C*H), 139.55 (quat. *C*), 145.37 (d, *J* = 17.5 Hz, quat. *C*). **Anal.** Found: C, 75.25; H, 9.17. Calc. for $C_{25}H_{36}P_2$: C, 75.35; H 9.11. **HR-MS** (EI) *m/z* calculated for $C_{25}H_{36}P_2$ [M]$^{\bullet+}$: 398.2292, found 398.2297.

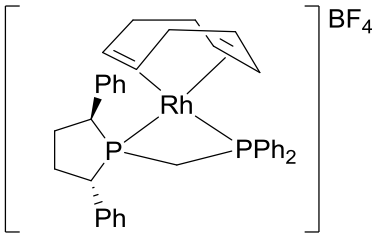
Synthesis of [Rh(nbd)(L$_d$)]BF$_4$ (3d)



A solution of **L$_d$** (0.037 g, 0.078 mmol) in dichloromethane (0.25 mL) was added dropwise to a stirred solution of [Rh(nbd)$_2$]BF$_4$ (0.029 g, 0.078 mmol) in dichloromethane (0.25 mL). The solution was then poured into rapidly stirred diethyl ether, the supernatant filtered and the solid dried under reduced pressure to give the product as a dark orange solid (0.05g, 0.066 mmol, 85%). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2): δ 11.28 (dd, J_{PP} = 71.9 Hz, J_{PRh} = 140.0 Hz, *P*^{t}Bu$_2$), 114.38 (dd, J_{PP} = 72.1 Hz, J_{PRh} = 220.4 Hz, *P*(OR)$_2$). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 1.42 (9H, d, J_{HP} = 15.5 Hz, C(C*H*$_3$)$_3$), 1.50 (9H, d, J_{HP} = 15.5 Hz, C(C*H*$_3$)$_3$), 1.65 (1H, m, C*H*$_2$), 1.76 (1H, m, C*H*$_2$), 3.35 (1H, m, C*H*$_2$), 3.71 (1H, m, C*H*$_2$), 4.16 (1H, br. s, nbd alkyl C*H*), 4.28 (1H, br. s, nbd alkyl C*H*), 5.27 (1H, br, s, alkene C*H*), 5.65 (1H, br, s, alkene C*H*), 6.39 (1H, br, s, alkene C*H*), 6.56 (1H, br, s, alkene C*H*), 6.89-6.95 (m, 2H, BINOL), 7.24-7.54 (m, 8H, ar. C*H*), 7.97-8.20 (m, 4H, ar. C*H*). **Anal.** Calc. for $C_{36}H_{40}BF_4O_2P_2Rh.0.2CH_2Cl_2$: C 56.22,

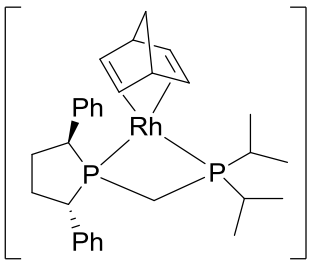
H 5.27. Found: C 56.24, H 5.46. **HR-MS** (ESI) *m/z* calculated for $C_{36}H_{40}O_2P_2Rh$ $[M]^+$: 669.1559, found 669.1555.

Synthesis of [Rh(cod)(L_g)]BF_4 (3g)



A solution of $\mathbf{L_g}$ (0.048 g, 0.11 mmol) in dichloromethane (1 mL) was added dropwise to a solution of $[Rh(cod)_2]BF_4$ (0.042 g, 0.10 mmol) in dichloromethane (1 mL). The dichloromethane solution was then poured into rapidly stirred diethyl ether, the supernatant removed and the solid dried under reduced pressure to give the product as an orange powder (0.052 g, 0.071 mmol, 65%). **$^{31}P\{^1H\}$ NMR** (162 MHz, CD_2Cl_2): δ (ppm) -36.18 (dd, J_{PP} = 76.33 Hz, J_{PRh} = 129.19 Hz, PPh_2), -5.73 (dd, J_{PP} = 76.51 Hz, J_{PRh} = 135.72 Hz, $P(CH_2)_2$). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 1.71-2.69 (10H, br. m, C*H*$_2$), 2.91 (1H, m, C*H*$_2$), 3.07 (1H, m, C*H*$_2$), 3.24-4.06 (4H, br. m, C*H*$_2$ and 2 x C*H*), 4.56 (1H, br. s, alkene-C*H*), 4.84 (1H, br. s, alkene-C*H*), 5.02 (1H, br. s, alkene-C*H*), 5.62 (1H, br. s, alkene-C*H*), 6.14-7.19 (20H, ar. *H*). **Anal.** Calc. for $C_{37}H_{40}BF_4P_2Rh$: C 60.35, H 5.48. Found: C 60.37, H 5.45. **HR-MS** (ESI) *m/z* calculated for $C_{37}H_{40}P_2Rh$ $[M]^+$: 649.1655, found 649.1654.

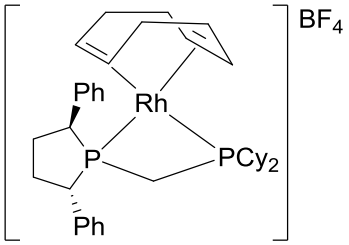
Synthesis of [Rh(nbd)(L_h)]BF_4 (3h)



A solution of $\mathbf{L_h}$ (0.029 g, 0.079 mmol) in dichloromethane (1 mL) was added dropwise to a solution of $[Rh(nbd)_2]BF_4$ (0.029 g, 0.078 mmol) in dichloromethane (1 mL) with rapid stirring. The dichloromethane solution was then poured into rapidly stirred diethyl ether, sonicated, filtered and dried under reduced pressure to give the product as an orange powder (0.036 g, 0.055 mmol, 70%). **$^{31}P\{^1H\}$ NMR** (162 MHz, CD_2Cl_2): δ -9.10 (dd, J_{PP} = 68.1 Hz, J_{PRh} = 133.2 Hz), -6.79 (dd, J_{PP} = 68.1 Hz, J_{PRh} = 144.0 Hz). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 0.51 (6H, m, $CH(CH_3)_2$), 1.17 (6H, m, $CH(CH_3)_2$), 1.40 (1H, m, phospholane-C*H*), 1.61 (2H, m, phospholane-CH_2), 2.01 (1H, m, phospholane-C*H*), 2.07 (1H, m, C*H*$_2$), 2.23 (1H, m, C*H*$_2$), 2.44 (1H, m, C*H*$_2$), 2.71 (1H, m, C*H*$_2$), 3.04 (2H, m, C*H*$_2$), 3.86 (1H, br. s, nbd alkyl C*H*), 4.19 (1H, br. s, nbd alkyl C*H*), 4.43 (1H, br. s, alkene C*H*), 5.43 (1H, br. s, alkene C*H*), 5.69 (1H, br. s, alkene C*H*), 5.82 (1H, br. s, alkene C*H*),

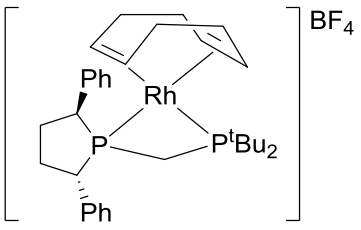
7.25-7.57 (10H, m, ar. C*H*). **Anal.** Calc. for $C_{30}H_{40}BF_4P_2Rh$: C 55.25, H 6.18. Found: C 55.44, H 6.26. **HR-MS** (ESI) *m/z* calculated for $C_{30}H_{40}P_2Rh$ $[M]^+$: 565.1655, found 565.1649.

Synthesis of [Rh(cod)(L_i)]BF_4 (3i)



A solution of $\mathbf{L_i}$ (0.042 g, 0.093 mmol) in dichloromethane (1 mL) was added dropwise to a solution of $[Rh(cod)_2]BF_4$ (0.038 g, 0.093 mmol) in dichloromethane (1 mL) with rapid stirring. The dichloromethane solution was then poured into rapidly stirred diethyl ether, the supernatant removed and the solid dried under reduced pressure to give the product as an orange powder (0.054 g, 0.072 mmol, 78%). **$^{31}P\{^1H\}$ NMR** (162 MHz, CD_2Cl_2): δ -23.57 (dd, J_{PP} = 67.5 Hz, J_{PRh} = 124.6 Hz, *P*Cy_2), -9.94 (J_{PP} = 67.6 Hz, J_{PRh} = 138.4 Hz, *P*$(CH_2)_2$). **^{1}H NMR** (400 MHz, CD_2Cl_2) : δ 0.93 (4H, m, C*H*$_2$), 1.21-1.55 (9H, br. m, C*H*, 4 x C*H*$_2$), 1.63 (1H, m, C*H*$_2$), 1.72-1.99 (8H, br. m, C*H*, C*H*$_2$), 2.04 (2H, m, C*H*$_2$), 2.14 (2H, m, C*H*$_2$), 2.29 (4H, br. m, C*H*$_2$), 2.39-2.82 (4H, br. m, C*H*$_2$), 3.05 (2H, m, C*H*$_2$), 3.82 (3H, br. m, alkene-C*H*, 2 x C*H*), 5.17 (1H, br. s, alkene-C*H*), 5.28 (1H, br. s, alkene-C*H*), 5.43 (1H, br. s, alkene-C*H*), 7.32-7.51 (10H, m, ar. C*H*). **Anal.** Calc. for $C_{37}H_{52}BF_4P_2Rh.0.2CH_2Cl_2$: C 58.37, H 6.90. Found: C 58.39, H 7.08. **HR-MS** (ESI) *m/z* calculated for $C_{37}H_{52}P_2Rh$ $[M]^+$: 661.2594, found 661.2590.

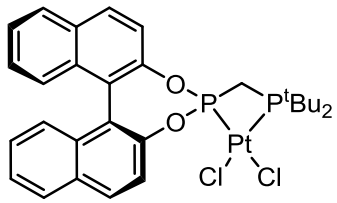
Synthesis of [Rh(cod)(L_j)]BF_4 (3j)



A solution of $\mathbf{L_j}$ (0.11 g, 0.28 mmol) in dichloromethane (1 mL) was added dropwise to a solution of $[Rh(cod)_2]BF_4$ (0.11 g, 0.28 mmol) in dichloromethane (1 mL) with rapid stirring. The dichloromethane solution was then poured into rapidly stirred diethyl ether, sonicated, filtered and dried under reduced pressure to give the product as an orange powder (0.11 g, 0.16 mmol, 56%). Crystals suitable for X-ray diffraction were grown by vapour diffusion of Et_2O into a solution of **3j** in dichloromethane. **$^{31}P\{^1H\}$ NMR** (162 MHz, CD_2Cl_2): δ -8.91 (dd, J_{PP} = 54.6 Hz, J_{PRh} = 138.7 Hz, *P*^{t}Bu_2), -2.11 (dd, J_{PP} = 54.7 Hz, J_{PRh} = 124.4 Hz, *P*$(CH)_2$). **^{1}H NMR** (400 MHz, CD_2Cl_2) : δ 0.70 (9H, d, J_{HP} = 14.7 Hz, C(C*H*$_3$)$_3$), 1.39 (9H, d, J_{HP} = 14.7 Hz, C(C*H*$_3$)$_3$), 3.71 (1H, br. s, alkene-C*H*), 5.18 (1H, br. s, alkene-C*H*), 5.38 (1H, br. s, alkene-C*H*), 5.47 (1H, br. s, alkene-C*H*), 7.26-7.53 (10H, m, ar. C*H*).

Anal. Calc. for $C_{33}H_{48}BF_4P_2Rh$: C 56.92, H 6.95. Found: C 57.05, H 6.71. **HR-MS** (ESI) *m/z* calculated for $C_{33}H_{48}P_2Rh$ $[M]^+$: 609.2281, found 609.2279.

Synthesis of $[PtCl_2(L_d)]$ (4d)

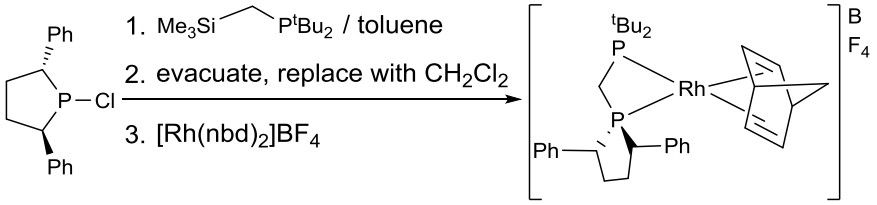


A solution of $\mathbf{L_d}$ (0.030 g, 0.063 mmol) in dichloromethane (0.5 mL) was added to a solution of $[PtCl_2(cod)]$ (0.023g, 0.063 mmol) in dichloromethane (0.5 mL). The solvent was removed under reduced pressure to give a solid which was washed with hexane and dried under reduced pressure to give the product as a white solid (0.031 g, 0.042 mmol, 67%). Crystals suitable for X-ray Crystallography were grown by layering hexane on a solution of the product in dichloromethane. **$^{31}P\{^1H\}$ NMR** (122 MHz): δ (ppm) -3.7 (d, $^2J_{PP}$ = 58.2 Hz, $^1J_{PPt}$ = 3106.7 Hz), 53.6 (d, $^2J_{PP}$ = 58.6 Hz, $^1J_{PPt}$ = 4510.8 Hz). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 1.59 (d, *J* = 16.67 Hz, C(C*H*$_3$)$_3$), 1.65 (d, *J* = 16.63 Hz, C(C*H*$_3$)$_3$), 2.25 (br. m, C*H*$_2$), 2.68 (br. m, C*H*$_2$), 7.27-8.10 (ar. C*H*). **Anal.** Calc. for $C_{29}H_{32}Cl_2O_2P_2Pt.0.5CH_2Cl_2$: C 45.67, H 4.22. Found: C 45.49, H 4.41. **HR-MS** (ESI) *m/z* calculated for $C_{29}H_{32}ClO_2P_2Pt$ $[M]^+$: 704.1214, found 704.1231.

General procedure for asymmetric hydrogenation

Substrate and catalyst (1 mol%) were weighed into autoclave cells which were then placed in to a stainless steel 10 cell Baskerville autoclave, which was purged with N_2 3 times. Dichloromethane (5 mL) was added via syringe to each cell, and then the mixture was stirred for 5 min to ensure the solutions were homogenized. The autoclave was then purged 3 times with H_2 and then pressurised with 5 bar H_2. After stirring the mixture for 1 h at ambient temperature, the autoclave was depressurised and samples for G.C. analysis were prepared by dissolving 0.1 mL of the reaction mixture with dichloromethane in a G.C. vial.

One-pot procedure



Into a Youngs tube with a stirrer bar was placed a stock solution of the chlorophospholane in toluene (2.5 mL, 8.0 μM, 0.020 mmol) and a stock solution of the phosphinosilane in toluene (2.6 mL, 7.7 μM, 0.020 mmol). The resulting solution was heated to 70 °C for 48 h. The solvent was removed under reduced pressure to give the crude oil, to which a stock solution of $[Rh(nbd)_2]BF_4$ in dichloromethane (2.8 mL, 7.3 x 10^{-3} mM, 0.020 mmol) was added. The resulting solution was left to stir at ambient temperature for 2 h. The solvent was removed under reduced pressure to give an orange solid, which was redissolved in 2 mL of dichloromethane and added to an autoclave cell in a stainless steel 10 cell Baskerville autoclave charged with the substrate (0.20 mmol) under a N_2 atmosphere. A further portion of dichloromethane (3 mL) was added via syringe to the autoclave cell and the mixture was stirred for 5 min to ensure the solution was homogenized. The autoclave was then purged 3 times with H_2 and then pressurised with 5 bar H_2. After stirring the mixture for 1 h at ambient temperature, the autoclave was depressurised and samples for G.C. analysis were prepared by dissolving 0.1 mL of the reaction mixture with dichloromethane in a G.C. vial.

G.C. conditions for enantiomer resolution

MAC : Varian CP-chirasil-DEX CD (25 m) column, 120 °C for 1 min then 3 °C / min to 175 °C for 11 min. Retention times : 18.64 min (*R*), 18.78 min (*S*).

MAA : Varian CP-chirasil-DEX CD (25 m) column, 90 °C for 1 min then 5 °C / min to 140 °C for 10 min. Retention times : 7.81 min (*S*), 7.97 min (*R*).

DMI : SUPELCO γ-DEX225 (30 m) column, 85 °C for 20 min then 2 °C / min to 95 °C for 10 min. Retention times: 26.00 min (*S*), 26.99 min (*R*).

Crystal Structure determination

X-ray diffraction on **3j** and **4d** were carried out at 100K on a Bruker APEX II diffractometer using graphite monochromised Mo-K_α radiation (λ = 0.71073 Å). Data collections were performed using a CCD area detector from a single crystal mounted on a glass fibre. Absorption corrections were based on equivalent reflections using SADABS.[9] Structure **3j** was solved using SHELXS while **4d** was solved using SIR2004. The structures were refined by full matrix least squares on F^2 data, with all of the non-hydrogen atoms refined anisotropically. The hydrogen atoms were located geometrically and refined using a riding model in SHELXL[10] within Olex2.[11] Crystal structure and refinement data are given in Table S1.

Table S1. Crystal data and structure refinement details.

Crystal	**3j**	**4d**
Empirical formula	$C_{33}H_{48}BF_4P_2Rh$	$C_{30}H_{34}O_2P_2Cl_4Pt$
Formula weight	696.37	825.40
Temperature/K	100(2)	100(2)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1$	$P2_12_12_1$
a/Å	10.6347(3)	9.8749(6)
b/Å	29.6678(7)	10.7553(6)
c/Å	10.7567(3)	29.0217(18)
α/°	90	90
β/°	105.968(1)	90
γ/°	90	90
Volume/Å^3	3262.9(2)	3082.3(3)
Z	4	4
ρ_{calc}g/cm^3	1.418	1.779
μ/mm^{-1}	0.666	5.030
F(000)	1448.0	1624.0
Crystal size/mm^3	0.278 × 0.276 × 0.224	0.3 × 0.22 × 0.21
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.746 to 55.216	4.038 to 55.308
Index ranges	-13 ≤ h ≤ 13, -38 ≤ k ≤ 38, -14 ≤ l ≤ 14	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -37 ≤ l ≤ 37
Reflections collected	114262	108079
Independent reflections	15088 [R_{int} = 0.0382, R_{sigma} = 0.0242]	7145 [R_{int} = 0.0488, R_{sigma} = 0.0240]
Data/restraints/parameters	15088/1/752	7145/0/358
Goodness-of-fit on F^2	1.041	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0218, wR_2 = 0.0494	R_1 = 0.0159, wR_2 = 0.0367
Final R indexes [all data]	R_1 = 0.0234, wR_2 = 0.0501	R_1 = 0.0173, wR_2 = 0.0371
Largest diff. peak/hole / e Å^{-3}	0.71/-0.32	0.97/-0.73
Flack parameter	-0.018(13)	0.007(2)

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Appendix

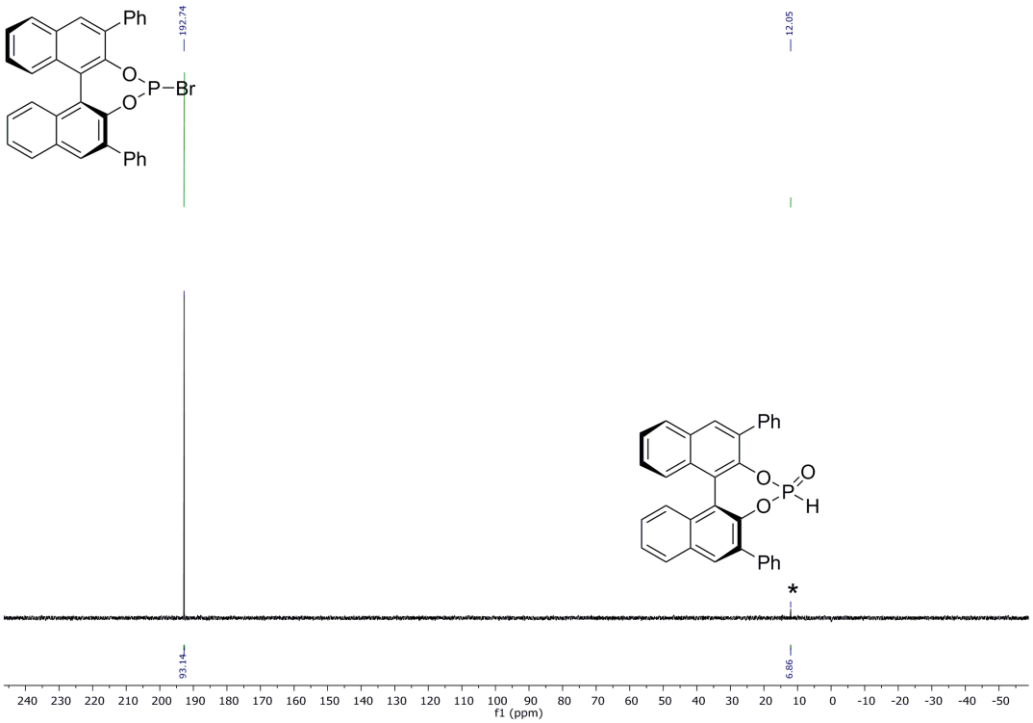

Figure S1. $^{31}P\{^{1}H\}$ NMR spectrum of **1b** in C_6D_6. Impurity *: 3,3'-disubstitutedBINOLP(O)H.

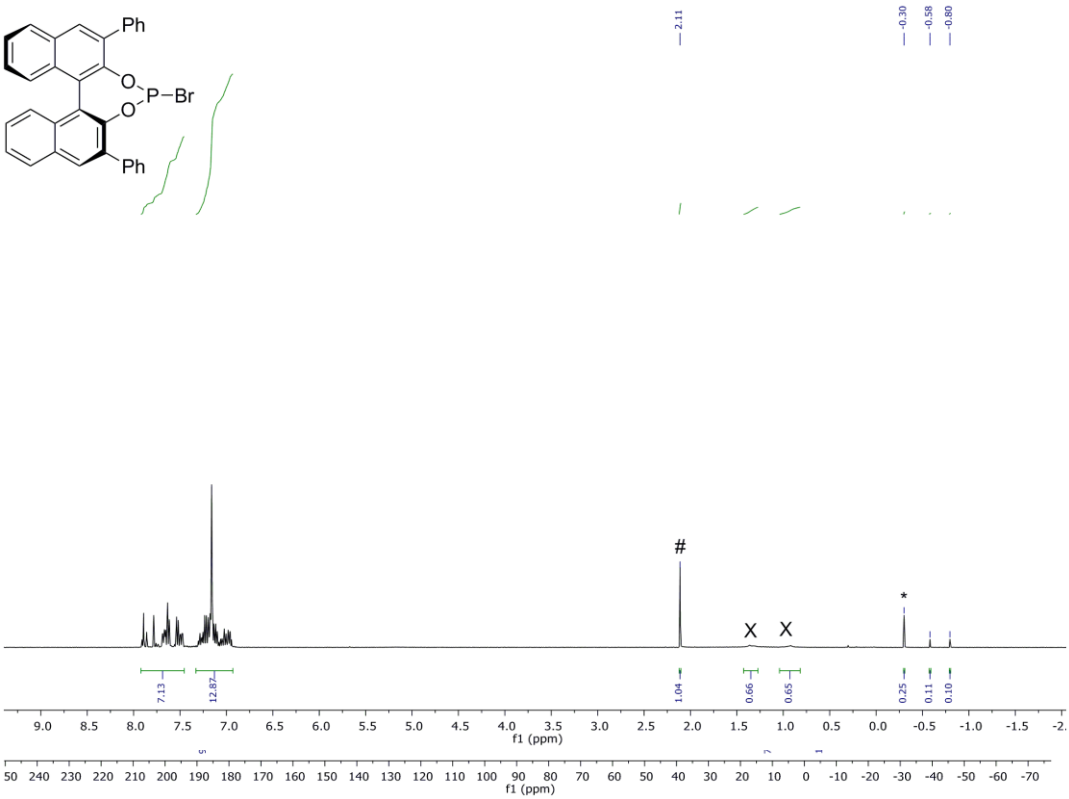

Figure S2. ^{1}H NMR spectrum of **1b** in C_6D_6. Impurity #: solvent, impurity *: grease, impurity X: unknown impurity.

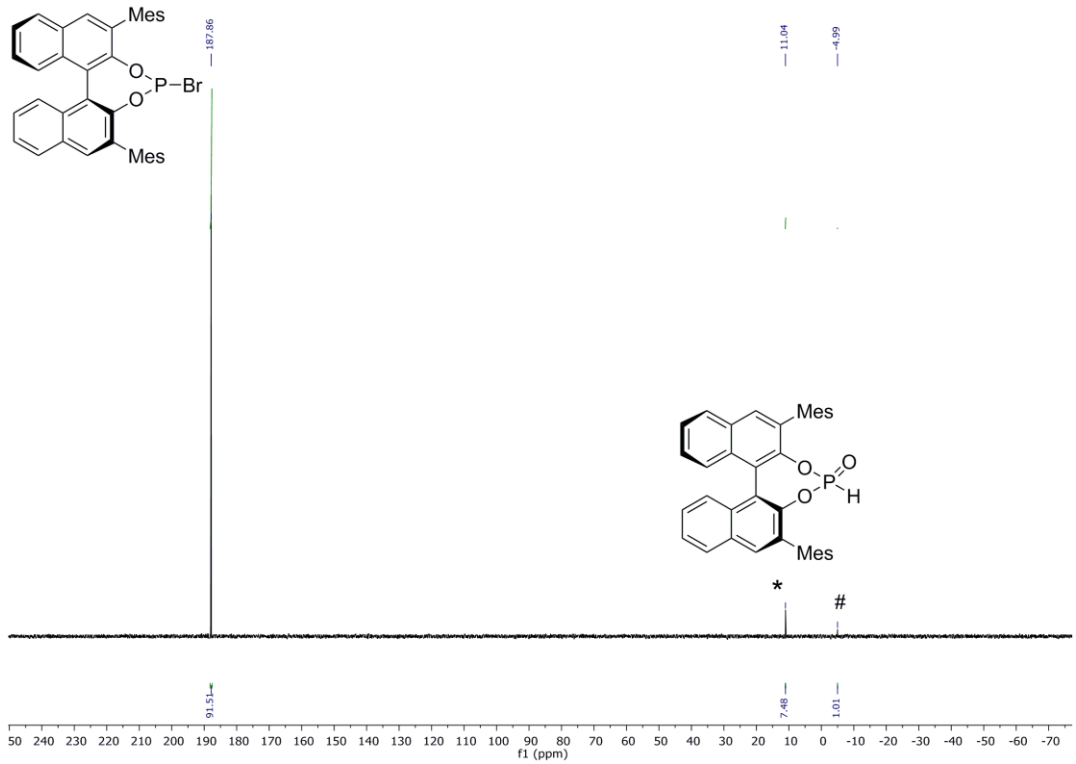

Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of **1c** in C_6D_6. Impurity *: 3,3'-disubstitutedBINOLP(O)H; impurity #: unknown impurity.

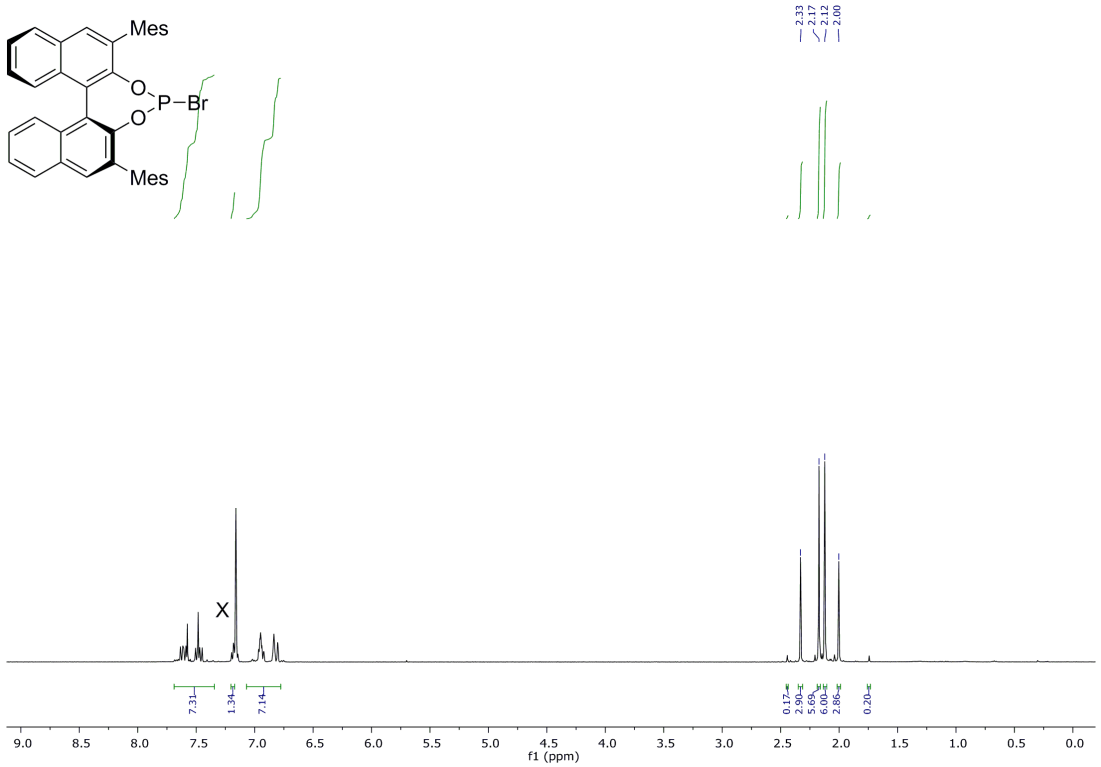

Figure S4. ^{1}H NMR spectrum of **1c** in C_6D_6. Impurity X: ar. C*H* proton integrations deviate from expected value due to 3,3'-disubstitutedBINOLP(O)H impurity.

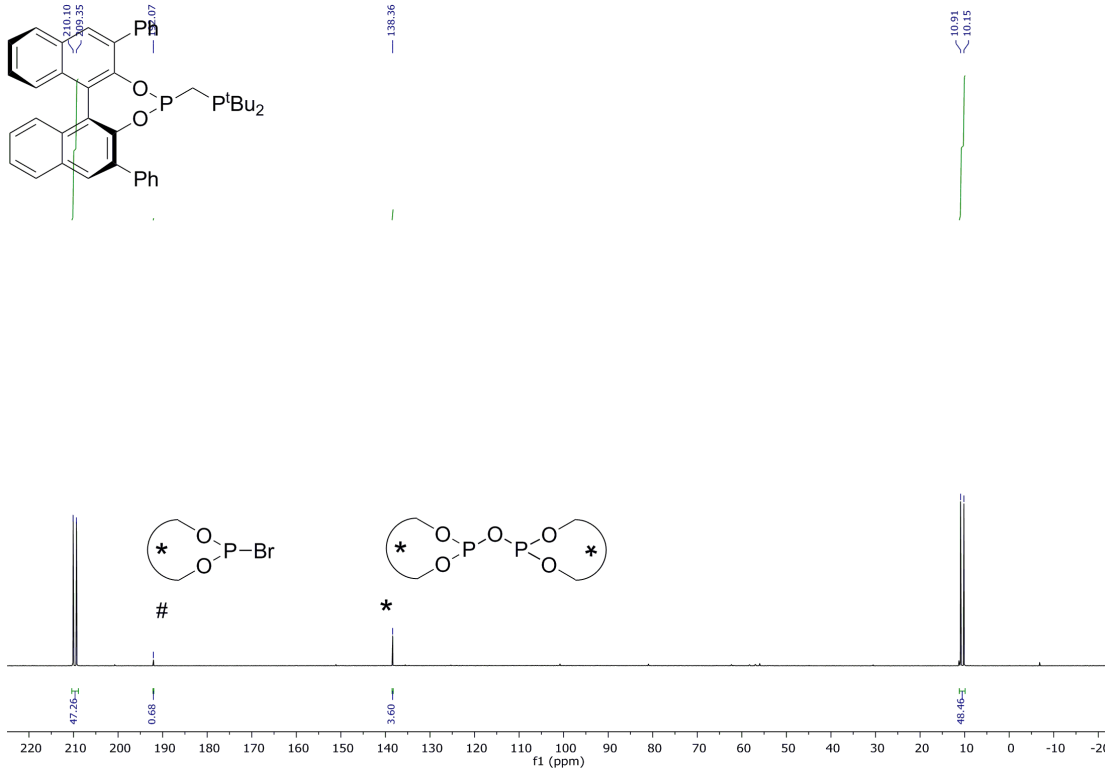

Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum of $\mathbf{L_e}$ in C_6D_6. Impurity #: BINOLPBr starting material, impurity *: (BINOL)POP(BINOL)

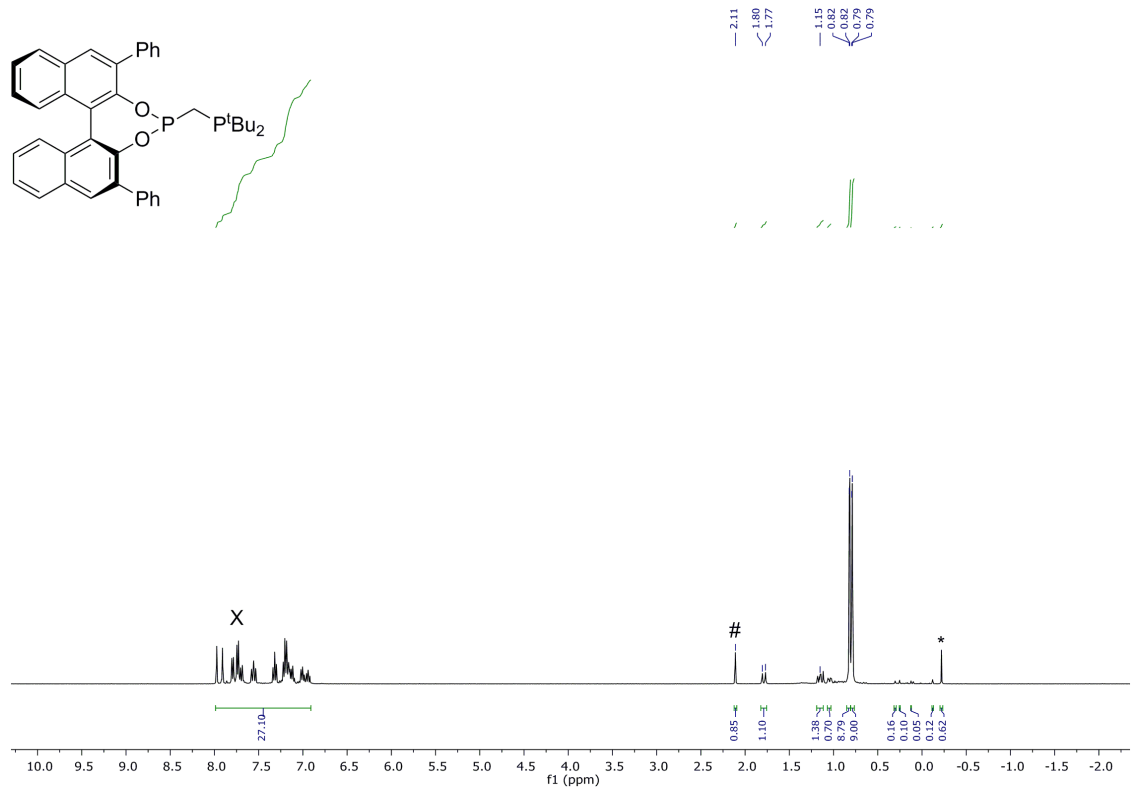

Figure S6. ^{1}H NMR spectrum of $\mathbf{L_e}$ in C_6D_6. Impurity #: solvent, impurity *: grease, impurity X: ar. C*H* proton integrations deviates from expected value due to BINOLPBr starting material and (BINOL)POP(BINOL) impurity.

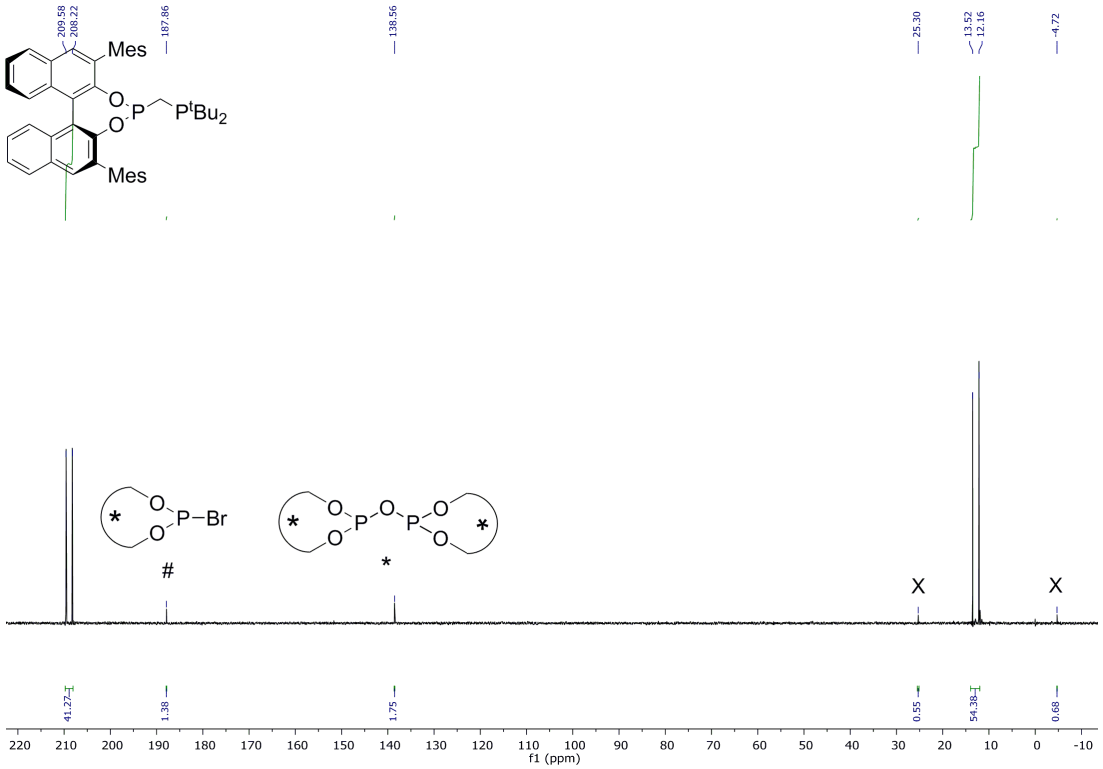

Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of $\mathbf{L_f}$ in C_6D_6. Impurity #: BINOLPBr starting material, impurity *: (BINOL)POP(BINOL), impurity X: unknown impurity.

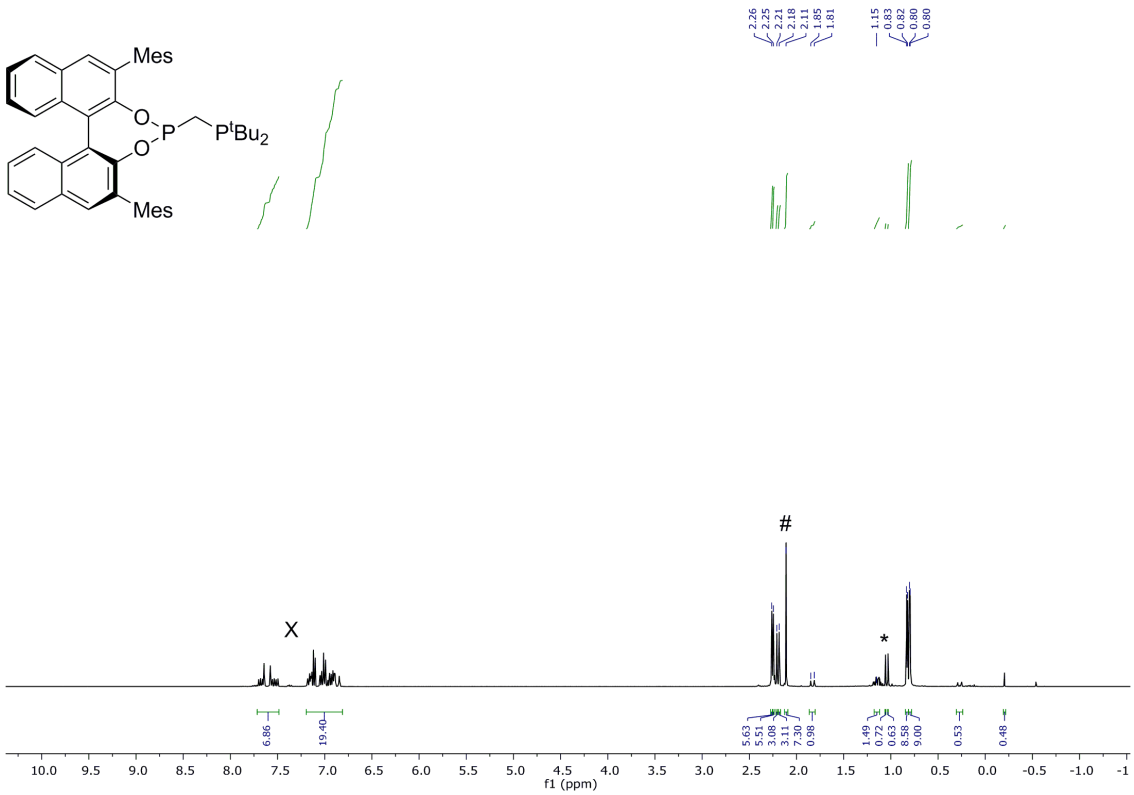

Figure S8. ^{1}H NMR spectrum of $\mathbf{L_f}$ in C_6D_6. Impurity #: solvent, impurity *: unknown impurity, impurity X: ar. C*H* proton integrations deviates from expected value due to BINOLPBr starting material and (BINOL)POP(BINOL) impurity.

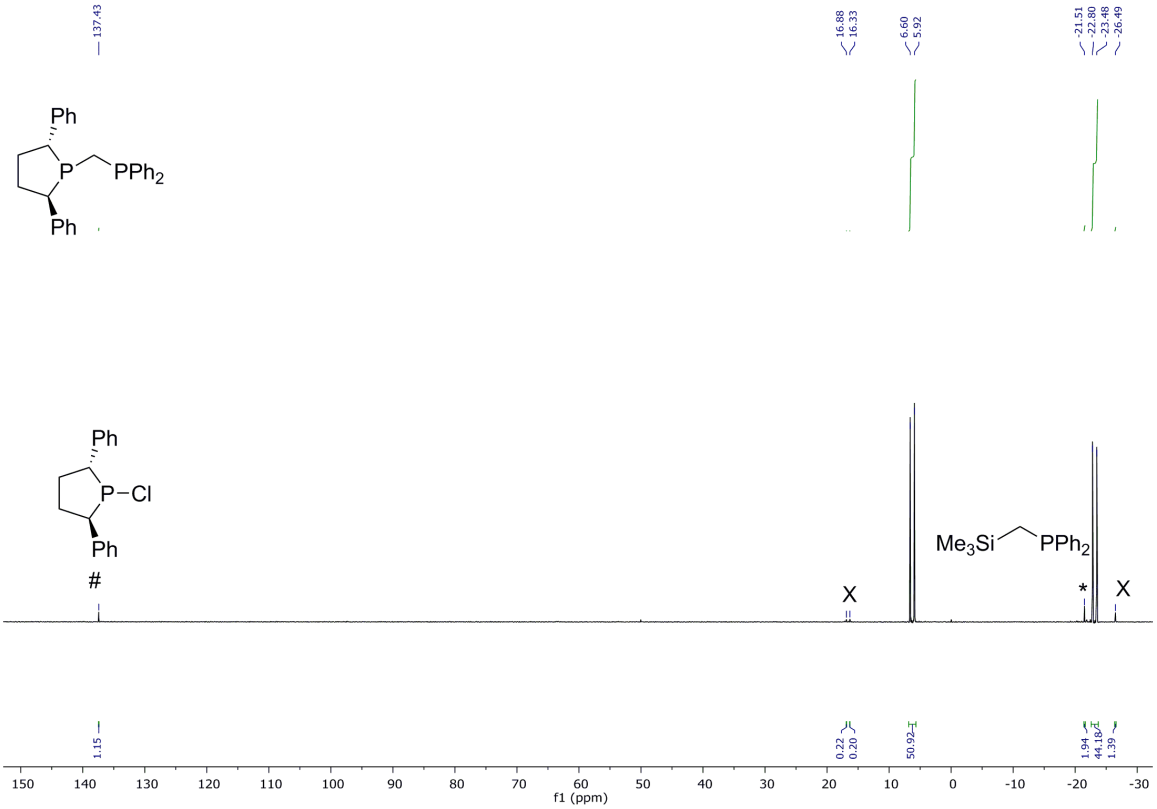

Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of $\mathbf{L_g}$ in C_6D_6. Impurity #: Phospholane-PCl starting material, impurity *: $Me_3SiCH_2PPh_2$ starting material, impurity X: unknown impurity.

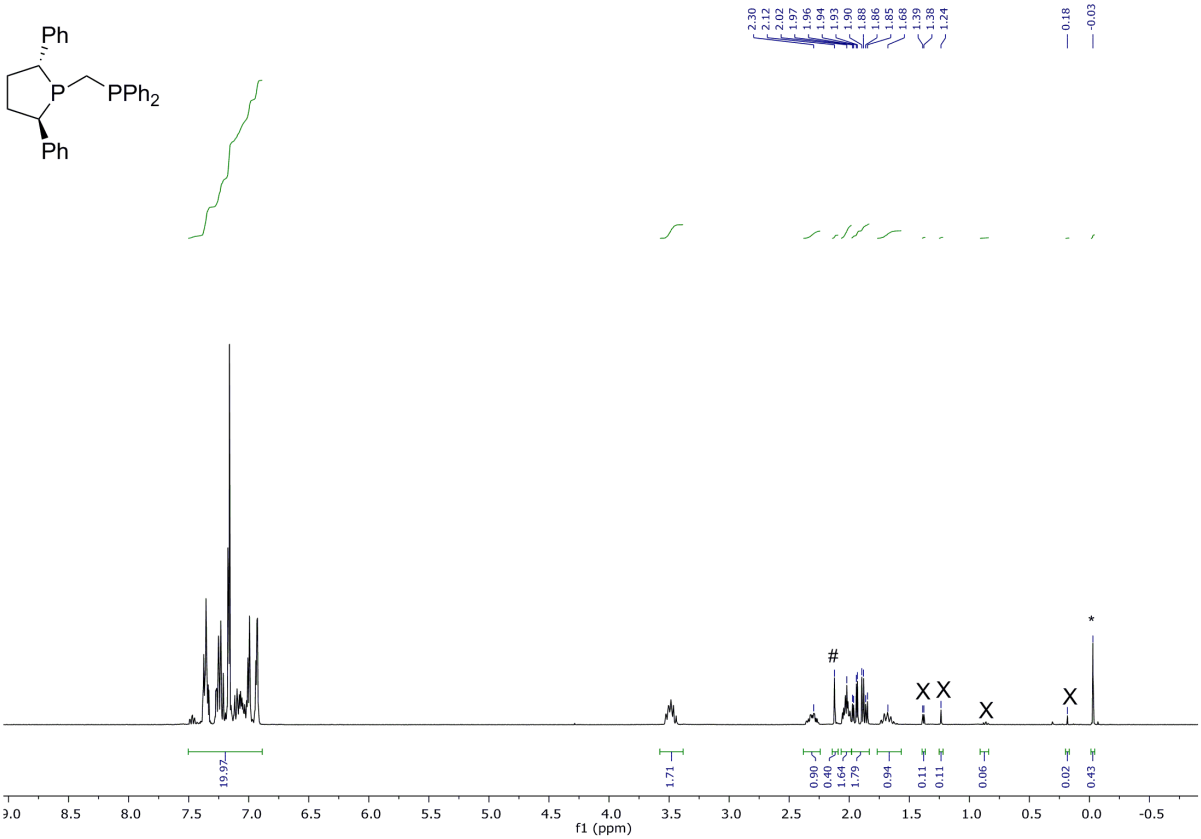

Figure S10. ^{1}H NMR spectrum of $\mathbf{L_g}$ in C_6D_6. Impurity #: solvent, impurity *: grease, impurity X: unknown impurity.