

Supporting Information For

3,3'-Disubstituted BINAP Derivatives: Synthesis, Resolution and Applications in Asymmetric Hydrogenation

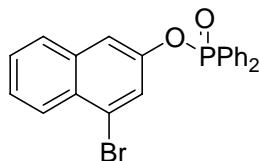
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*Department of Chemistry, University of Calgary, 2500 University Dr. NW, Calgary, Alberta, Canada T2N 1N4***A. Experimental Conditions**

All glassware used in anhydrous reactions was dried overnight in a 120 °C oven and was subsequently cooled in a desiccator containing Drierite® or under an atmosphere of nitrogen gas. Moisture or oxygen sensitive reactions were performed under an atmosphere of nitrogen gas or through the use of Schlenk techniques. All solvents and reagents were purified via standard methods when required. Tetrahydrofuran was distilled immediately prior to use from sodium benzophenone ketyl. Dichloromethane was freshly distilled from calcium hydride. *N,N*-Dimethylformamide was purchased as an anhydrous solvent in a Sure/Seal bottle from the Aldrich Chemical Company. Other reagents including triethylamine, diisopropylamine, and xylenes were dried by distillation from calcium hydride and were stored in Sure/Seal bottles. Iodomethane and 2-bromopropane were passed through a plug of basic alumina immediately before use. *n*-Butyllithium was titrated prior to use with *N*-benzylbenzamide as the indicator. Rh(COD)₂OTf was used as received from Aldrich. Rh(NBD)₂BF₄ was used as received from Alfa Aesar. Column chromatography was performed using silica gel 60 (E. Merck, 0.04-0.063 mm, 230-400 mesh). ¹H and ¹³C NMR spectra were recorded on a Bruker AC-300 spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane as the external standard. ³¹P NMR spectra were recorded on a Varian XL-200 spectrometer. Chemical shifts are reported in ppm in relation to H₃PO₄ as the external standard. Optical rotations were obtained on a Rudolph Research Autopole IV polarimeter. MS spectra were recorded on a Micromass VG7070F for LR-EI, a Kratos MS80 RFA for HRMS, and a Bruker Esquire 3000 for ESI. GC analyses were carried out on a Shimadzu GC-9A gas chromatograph using a chiral column (Cyclodex B).

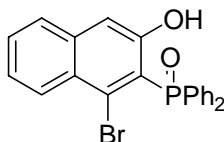
B. Synthesis of Ligands 2-4

1. Synthesis of Diphenyl-phosphinic acid 4-bromo-naphthalen-2-yl ester **17**.



To a solution of 4-bromo-2-naphthol¹ (**16**) (2.995 g, 13.43 mmol) in CH₂Cl₂ (30 ml) was added DMAP (5 mol%) and triethylamine (2.35 ml, 16.9 mmol). Diphenylphosphinic chloride (3.20 ml, 16.8 mmol) was then added dropwise and the reaction was allowed to stir at r.t. for 18 h. The reaction was then quenched with hexane, filtered and evaporated. The product was purified by SiO₂ chromatography (10% EtOAc/Hexanes) to afford an orange solid (4.996 g, 11.80 mmol, 88%). Mp 125-128 °C; IR (KBr) 3050, 1596, 1434, 1337, 1221, 1124 cm⁻¹; ¹H-NMR (300 MHz) δ 7.40-7.94 (m, 9H), 7.65-7.70 (m, 3H), 7.88-7.95 (m, 3H), 8.08-8.11 (m, 1H) ppm; ¹³C-NMR (75 MHz) δ 117.28 (d, J=4.88 Hz), 122.98, 123.61, 124.85 (d, J=5.49 Hz), 126.90 (d, J=15.87 Hz), 127.53, 128.17, 128.88 (d, J=13.43 Hz), 129.67 (d, J=20.14 Hz), 131.63, 131.94 (d, J=10.38 Hz), 132.84 (d, J=3.05 Hz), 134.506, 148.10 (d, J=7.94 Hz) ppm; ³¹P-NMR (81 MHz) δ 29.84 ppm; LRMS 424.2 (M⁺ ⁸¹Br), 422.1 (M⁺ ⁷⁹Br), 201.0, 152.1, 114.1, 77.1; HRMS Anal. Calculated For: 422.00713 Found: 422.01018 C₂₂H₁₆PO₂⁷⁹Br, Anal. Calculated For: 424.00508 Found: 424.00820 C₂₂H₁₆PO₂⁸¹Br; Elemental Analysis Calcd: C: 62.43, H: 3.81 Found: C: 62.38, H: 4.00.

2. Synthesis of 4-Bromo-3-(diphenylphosphinoyl)-naphthalen-2-ol **18**.

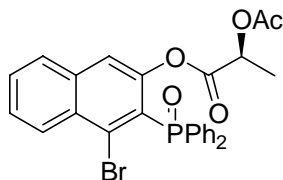


To a solution of diisopropylamine (1.90 ml, 13.6 mmol) in THF (20 ml) at 0 °C was added *n*BuLi (11.00 ml, 1.17M, 12.87 mmol) dropwise and this solution was stirred for 20 min. In a separate flask, **17** (4.996 g, 11.80 mmol) in THF (50 ml) was cooled to -78 °C. The LDA solution was then added dropwise to the solution of **17** and the

¹ Newman, M.S.; Sankaran, V.; Olson, D.R. *J. Am. Chem. Soc.* **1976**, 98, 3237.

reaction was allowed to warm to r.t. and stir for 16 h. The reaction was then quenched with saturated NH_4Cl (50 ml) and the layers were separated. The aqueous layer was extracted with EtOAc (3×20 ml) and the combined organics were dried (MgSO_4), filtered and evaporated. The product was purified by SiO_2 chromatography (20% EtOAc/Hexanes) to afford a pale orange solid (4.19 g, 9.92 mmol, 84%). Mp 172-173 °C; IR (KBr) 3457, 3049, 1621, 1544, 1434, 1317, 1117 cm^{-1} ; ^1H -NMR (300 MHz) δ 7.324 (t, $J=7.69$ Hz, 1H), 7.411 (d, $J=4.10$ Hz, 1H), 7.430-7.612 (m, 7H), 7.672 (d, $J=8.20$ Hz, 1H), 7.826-7.922 (m, 4H), 8.078 (d, $J=8.72$ Hz, 1H) ppm; ^{13}C -NMR (75 MHz) δ 113.45 (d, $J=6.71$ Hz), 122.81, 125.06, 126.72, 126.91 (d, $J=8.54$ Hz), 127.56, 128.57 (d, $J=12.82$ Hz), 129.12, 129.98, 131.44, 132.54 (d, $J=3.05$ Hz), 132.54 (d, $J=10.38$ Hz), 137.45 (d, $J=1.22$ Hz), 161.22 (d, $J=3.66$ Hz) ppm; ^{31}P -NMR (81 MHz) δ 44.32 ppm; LRMS 424.0 ($\text{M}^+ ^{81}\text{Br}$), 422.0 ($\text{M}^+ ^{79}\text{Br}$), 345.0 ($\text{M}^+ ^{81}\text{Br}$), 343.0 ($\text{M}^+ ^{79}\text{Br}$), 265.1, 237.1, 189.1, 165.1, 77.1, 52.0; HRMS Anal. Calculated For: 422.00713 Found: 422.00762 $\text{C}_{22}\text{H}_{16}\text{PO}_2 ^{79}\text{Br}$, Anal. Calculated For: 424.00508 Found: 424.00716 $\text{C}_{22}\text{H}_{16}\text{PO}_2 ^{81}\text{Br}$.

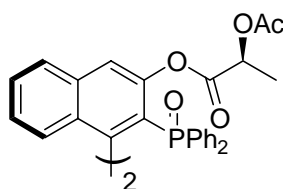
3. Synthesis of 2-Acetoxy-propionic acid 4-bromo-3-(diphenyl-phosphinoyl)-naphthalen-2-yl ester **19**.



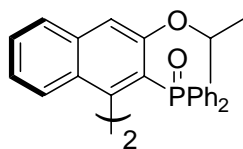
To a solution of **18** (1.001 g, 2.365 mmol) in CH_2Cl_2 (10 ml) was added DMAP (5 mol%) and triethylamine (0.41 ml, 2.94 mmol). (*S*)-2-Acetoxypropanoyl chloride (0.445 g, 2.96 mmol) was then added dropwise and the reaction was allowed to stir at r.t. for 7 h. The reaction was quenched with hexane, filtered and evaporated. The product was purified by SiO_2 chromatography (30% EtOAc/Hexanes) to afford a pale orange solid (1.078 g, 2.010 mmol, 85%). Mp 60-62 °C; IR (KBr) 3057, 2921, 1770, 1737, 1428, 1240, 1085 cm^{-1} ; ^1H -NMR (300 MHz) δ 1.454 (d, $J=7.18$ Hz, 3H), 2.202 (s, 3H), 4.776 (q, $J=7.18$ Hz, 1H), 7.397-7.619 (m, 9H), 7.689-7.797 (m, 5H), 8.340 (d, $J=8.72$ Hz, 1H) ppm; ^{13}C -NMR (75 MHz) δ 16.378, 20.65, 68.87, 121.61 (d, $J=5.49$ Hz), 127.81, 128.02, 128.42, 128.59, 129.34, 130.36 (d, $J=3.05$ Hz), 131.23 (d, $J=7.94$ Hz), 131.72 (d, $J=3.05$ Hz),

131.72 (d, $J=17.09$ Hz), 133.15 (d, $J=22.58$ Hz), 134.61 (d, $J=23.19$ Hz), 135.19 (d, $J=1.83$ Hz), 149.44 (d, $J=2.44$ Hz), 169.40, 170.10 ppm; ^{31}P -NMR (81 MHz) δ 27.94 ppm; LRMS 422.1 ($\text{M}^+-\text{C}_5\text{H}_7\text{O}_3$), 342.3, 231.2, 201.2, 119; ESI-MS 576.83 ($\text{M}+\text{K}$) $^+$, 560.86 ($\text{M}+\text{Na}$) $^+$, 538.87 ($\text{M}^+ ^{81}\text{Br}$), 536.87 ($\text{M}^+ ^{79}\text{Br}$); HRMS Anal. Calculated For: 536.03882 Found: 536.03933 $\text{C}_{27}\text{H}_{22}\text{PO}_5 ^{79}\text{Br}$, Anal. Calculated For: 538.03678 Found: 538.03749 $\text{C}_{27}\text{H}_{22}\text{PO}_5 ^{81}\text{Br}$.

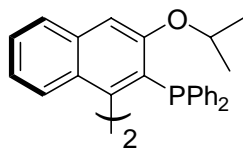
4. Synthesis of **20**



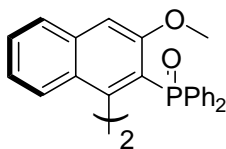
To a solution of **19** (5.668 g, 10.57 mmol) in DMF (50 ml) was added Cu(0) powder (2.413 g, 37.97 mmol). The reaction was then heated to 140 °C and stirred for 3 h before being cooled and filtered. The solution was diluted with w EtOAc (100 ml) and washed with brine. The aqueous layer was then extracted with EtOAc (50 ml) and the combined organic were washed with brine (5×50 ml), dried (MgSO_4), filtered and evaporated. The product was purified by SiO_2 chromatography (2:1 EtOAc:Hexanes) to afford a pale orange solid. This solid was triturated with TBME and filtered to afford an off white solid, diastereomerically pure (1.054 g, 1.152 mmol, 44%). Mp 169-171 °C (decomposed); IR (KBr) 3051, 2927, 1775, 17427, 1434, 1229, 1062 cm^{-1} ; ^1H -NMR (300MHz) δ 0.93 (d, $J=7.18$ Hz, 6H), 2.00 (s, 6H), 4.40 (q, $J=7.18$ Hz, 2H), 6.81-6.86 (m, 2H), 6.94-6.97 (m, 2H), 7.12-7.18 (m, 4H), 7.21-7.29 (m, 6H), 7.33-7.48 (m, 8H), 7.66-7.82 (m, 8H) ppm; ^{13}C -NMR (75 MHz) δ 16.10, 20.73, 68.46, 119.71, 125.93, 127.54 (d, $J=34.79$ Hz), 128.09 (d, $J=4.27$ Hz), 128.26 (d, $J=3.05$ Hz), 130.87 (d, $J=2.44$ Hz), 131.38 (d, $J=11.60$ Hz), 131.98 (d, $J=9.76$ Hz), 132.05 (d, $J=10.98$ Hz), 132.45 (d, $J=6.10$ Hz), 134.70 (d, $J=1.22$ Hz), 135.03, 136.49, 146.96 (d, $J=3.66$ Hz), 168.39, 169.96 ppm; ^{31}P -NMR (81 MHz) δ 24.34 ppm; ESI-MS 953.37 ($\text{M}+\text{K}$) $^+$, 937.42 ($\text{M}+\text{Na}$) $^+$, 915.12 ($\text{M}+\text{H}$) $^+$, 818.68, 770.54.

5. Synthesis of (*S*)-3,3'-di-isopropoxy-2,2'-diphenylphosphinyl-1,1'-binaphthalene **23**

To a solution of **20** (0.488 g, 1.15 mmol) in THF:MeOH (5:1, 12 ml) was added LiOH (1.0M, 3.50 ml, 3.50 mmol). The reaction was stirred for 30 min before being diluted with CHCl₃ (20 ml) and washed with H₂O. The aqueous layer was extracted with CHCl₃ (2×10 ml) and the combined organics were dried (MgSO₄), filtered and evaporated to afford a white solid. To a solution of this crude product in DMF (10 ml) was added K₂CO₃ (0.442 g, 3.20 mmol). The mixture was stirred for 10 min before the addition of 2-bromopropane (1.00 ml, 10.7 mmol). The reaction was allowed to stir for 24 h before being diluted with EtOAc (50 ml) and washed with brine. The aqueous layer was extracted with EtOAc (1×50 ml) and the combined organics were washed with brine (5×50 ml), dried (MgSO₄), filtered and evaporated to afford a pale yellow solid. The product was purified by SiO₂ chromatography (2:1 EtOAc:Hexanes) to afford a white solid (0.323 g, 0.419 mmol, 79% 2 steps). $[\alpha]_D^{20}$ -176.64 (c=0.018, CHCl₃) Mp >275 °C (decomposed); IR (KBr) 3056, 2925, 1657, 1564, 1450 cm⁻¹; ¹H-NMR (300 MHz) δ 0.76 (d, J=6.15 Hz, 6H), 1.05 (d, J=6.15 Hz, 6H), 4.61 (m, 2H), 6.89 (t, J=7.69 Hz, 2H), 6.97-7.06 (m, 4H), 7.09-7.27 (m, 10H), 7.30-7.41 (m, 4H), 7.50-7.61 (m, 4H), 7.64-7.77 (m, 6H) ppm; ¹³C-NMR (75 MHz) δ 20.78, 20.95, 69.27, 105.86 (d, J=6.1 Hz), 119.80, 121.14, 122.97, 126.30, 126.76 (d, J=12.21 Hz), 127.01 (d, J=13.43 Hz), 127.30 (d, J=13.42 Hz), 129.99, 130.10 (d, J=44.55 Hz), 131.40 (d, J=10.99 Hz), 132.76 (d, J=9.77 Hz), 132.96, 134.35, 135.57, 135.80, 147.99 (t, J=4.27 Hz), 154.47 (d, J=4.27 Hz) ppm; ³¹P-NMR (81 MHz) 26.90 ppm; ESI-MS 771.44 (M+H)⁺.

6. Synthesis of (*S*)-3,3'-di-isopropoxy-2,2'-diphenylphosphino-1,1'-binaphthalene **2**

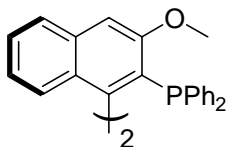
To a solution of **23** (0.323 g, 0.419 mmol) in xylenes (10 ml) was added Bu₃N (2.50 ml, 10.5 mmol) followed by HSiCl₃ (0.85 ml, 8.4 mmol). The reaction was then heated at 140 °C for 16 h. Upon cooling to 60°C, 30% NaOH was added (10 ml) and the reaction was stirred for 1 h. The cooled reaction was then diluted with CHCl₃ (50 ml) and the layers were separated. The organic layer was dried (Na₂SO₄), filtered and evaporated to afford a yellow solid. The product was purified by SiO₂ chromatography (25:1 Hexanes:EtOAc) to afford a white solid (0.266 g, 0.360 mmol, 86%). [α]_D²⁰ -152.49 (c=0.016, CHCl₃); Mp 190-192 °C; IR (KBr) 3056, 2972, 1589, 1434, 1311, 1188 cm⁻¹; ¹H-NMR (300 MHz) δ 0.85 (d, J=6.15 Hz, 6H), 0.93 (d, J=6.15 Hz, 6H), 4.58 (p, J=6.15 Hz, 2H), 6.85-6.99 (m, 8H), 7.01-7.21 (m, 14H), 7.23-7.31 (m, 4H), 7.38 (t, J=7.69 Hz, 2H), 7.75 (d, J=8.20 Hz, 2H) ppm; ¹³C-NMR (75 MHz) δ 20.88, 20.93, 68.72, 106.23, 123.20, 126.24 (d, J=10.99 Hz), 127.02 (d, J=5.5 Hz), 127.22 (d, J=7.33 Hz), 127.60, 128.44 (d, 2.44 Hz), 131.32 (dd, J=17.7, 2.44 Hz), 133.79 (d, J=20.76 Hz), 135.55, 136.73 (d, J=8.54 Hz), 137.14 (d, J=14.041 Hz), 150.75 (d, J=11.6 Hz), 156.44 ppm; ³¹P-NMR (81 MHz) δ -16.17 ppm; ESI-MS 739.14 (M+H)⁺, 553.16.

7. Synthesis of (*S*)-3,3'-di-methoxy-2,2'-diphenylphosphinyl-1,1'-binaphthalene **24**

To a solution of **20** (0.702 g, 0.767 mmol) in THF:MeOH (5:1, 12 ml) was added LiOH (1.0M, 4.60 ml, 4.60 mmol). The reaction was stirred for 30 min before being diluted with CHCl₃ (30 ml) and washed with H₂O. The aqueous layer was extracted with CHCl₃ (2×20 ml) and the combined organics were dried (MgSO₄), filtered and evaporated to afford a white solid. To a solution of this crude product in DMF (10 ml) was added K₂CO₃ (0.629 g, 4.551 mmol). The mixture was stirred for 10 min before the addition of

iodomethane (1.00 ml, 16.1 mmol). The reaction was allowed to stir for 24 h before being diluted with EtOAc (50 ml) and washed with brine. The aqueous layer was extracted with EtOAc (1×50 ml) and the combined organics were washed with brine (5×50 ml), dried (MgSO₄), filtered and evaporated to afford a pale yellow solid. The product was purified by SiO₂ chromatography (1:1 EtOAc:Hexanes) to afford a white solid (0.439 g, 0.614 mmol, 85% 2 steps). $[\alpha]_D^{20}$ -163.46 (c=0.014, CHCl₃); Mp >275 °C (decomposed); IR (KBr) 3054, 2918, 1656, 1558, 1454 cm⁻¹; ¹H-NMR (400 MHz) δ 3.51 (s, 6H), 6.93-7.01 (m, 6H), 7.07-7.24 (m, 10H), 7.33-7.44 (m, 8H), 7.52-7.57 (m, 4H), 7.76 (d, J=8.1 Hz, 2H) ppm; ¹³C-NMR (100 MHz) δ 54.4, 106.00 (d, J=5.90 Hz), 123.6, 126.7, 127.1, 127.1 (d, J=23.5 Hz), 127.6 (d, J=10.3 Hz), 130.1, 130.6, 131.5 (d, J=11.3 Hz), 132.8 (d, J=9.8 Hz), 134.0 (d, J=24.2 Hz), 135.1 (d, J=39.5 Hz), 135.7, 156.6 (d, J=4.7 Hz) ppm; ³¹P-NMR (81 MHz) δ 26.94 ppm; ESI-MS 753 (M+K)⁺, 737 (M+Na)⁺, 715 (M+H)⁺, 413, 365; HRMS Anal. Calculated For: 513.16196 Found: 513.16373 C₃₄H₂₆PO₃ (M⁺-POPh₂).

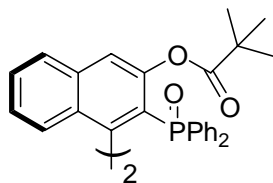
8. Synthesis of (S)-3,3'-di-methoxy-2,2'-diphenylphosphino-1,1'-binaphthalene **3**



To a solution of **24** (0.439 g, 0.614 mmol) in xylenes (10 ml) was added Bu₃N (3.66 ml, 15.4 mmol) followed by HSiCl₃ (1.24 ml, 12.3 mmol). The reaction was then heated at 140 °C for 16 h. Upon cooling to 60 °C, 30% NaOH was added (10 ml) and the reaction was stirred for 1 h. The cooled reaction was then diluted with CHCl₃ (50 ml) and the layers were separated. The organic layer was dried (Na₂SO₄), filtered and evaporated to afford a yellow solid. The product was purified by SiO₂ chromatography (25:1 Hexanes:EtOAc) to afford a white solid (0.317 g, 0.464 mmol, 76%). $[\alpha]_D^{20}$ -213.16 (c=0.0145, CHCl₃); Mp >275 °C (decomposed); IR (KBr) 3050, 2972, 1699, 1654, 1557, 1427, 1311, 1195 cm⁻¹; ¹H-NMR (300 MHz) δ 3.52 (s, 6H), 6.88-6.97 (m, 5H), 7.00-7.32 (m, 21H), 7.43 (t, J=7.44 Hz, 2H), 7.81 (d, J=7.69 Hz, 2H) ppm; ¹³C-NMR (75 MHz) δ 54.47, 106.35, 123.54, 126.33 (d, J=21.97 Hz), 126.97 (d, J=4.89 Hz), 127.19 (d, J=7.94

Hz), 127.31, 127.77, 128.40, 129.52 (dd, $J=9.16, 3.05$ Hz), 131.16 (d, $J=17.09$ Hz), 134.04, 134.33, 135.48, 136.82 (d, $J=9.16$ Hz), 137.19 (d, $J=14.65$ Hz), 149.64 (d, $J=10.37$ Hz), 150.14 (d, $J=10.37$ Hz), 158.82 ppm; ^{31}P -NMR (81 MHz) δ -15.696 ppm; ESI-MS 683.01 ($\text{M}+\text{H}$) $^{+}$, 497.20.

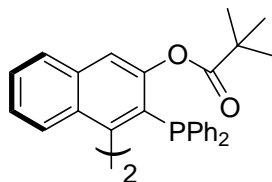
9. Synthesis of (*S*)-3,3'-di-trimethylacetoxy-2,2'-diphenylphosphinyl-1,1'-binaphthalene 25



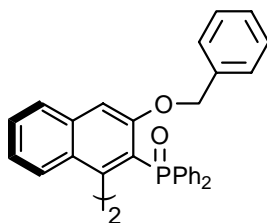
To a solution of **20** (0.501 g, 0.548 mmol) in THF:MeOH (5:1, 12 ml) was added LiOH (1.0M, 3.50 ml, 3.50 mmol). The reaction was stirred for 30 min before being diluted with CHCl_3 (30 ml) and washed with H_2O . The aqueous layer was extracted with CHCl_3 (2 \times 20 ml) and the combined organics were dried (MgSO_4), filtered and evaporated to afford a white solid. To a solution of this crude product in CH_2Cl_2 (10 ml) was added DMAP (5 mol %), triethylamine (0.610 ml, 4.38 mmol), and trimethylacetyl chloride (0.540 ml, 4.38 mmol). The reaction was allowed to stir for 24 h before being quenched with hexane, filtered and evaporated to afford a yellow solid. The product was purified by SiO_2 chromatography (2:1 EtOAc:Hexanes) to afford a pale yellow solid (0.351 g, 0.411 mmol, 75% 2 steps). $[\alpha]_{\text{D}}^{20}$ -80.658 ($c=0.0155$, CHCl_3); Mp >275 $^{\circ}\text{C}$ (decomposed); IR (KBr) 3056, 2966, 1686, 1653, 1557, 1428, 1085 cm^{-1} ; ^1H -NMR (300 MHz) δ 0.79 (s, 18H), 6.88-7.07 (m, 6H), 7.08-7.22 (m, 8H), 7.26-7.41 (m, 4H), 7.42-7.60 (m, 8H), 7.71 (d, $J=8.71$ Hz, 2H) ppm; ^{13}C -NMR (75 MHz) δ 26.50, 39.05, 120.38 (d, $J=6.10$ Hz), 122.43, 125.70, 127.38, 127.49, 127.75 (d, $J=12.82$ Hz), 127.87, 130.59, 130.95 (d, $J=2.44$ Hz), 131.59 (d, $J=10.38$ Hz), 132.32 (d, $J=10.99$ Hz), 133.09, 134.62, 148.73, 176.40 ppm; ^{31}P -NMR (81 MHz) δ 25.65 ppm; ESI-MS 877.49 ($\text{M}+\text{Na}$) $^{+}$.

10. Synthesis of (*S*)-3,3'-di-trimethylacetoxo-2,2'-diphenylphosphino-1,1'-binaphthalene

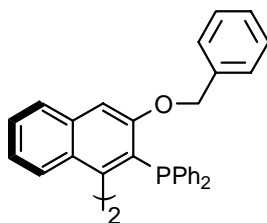
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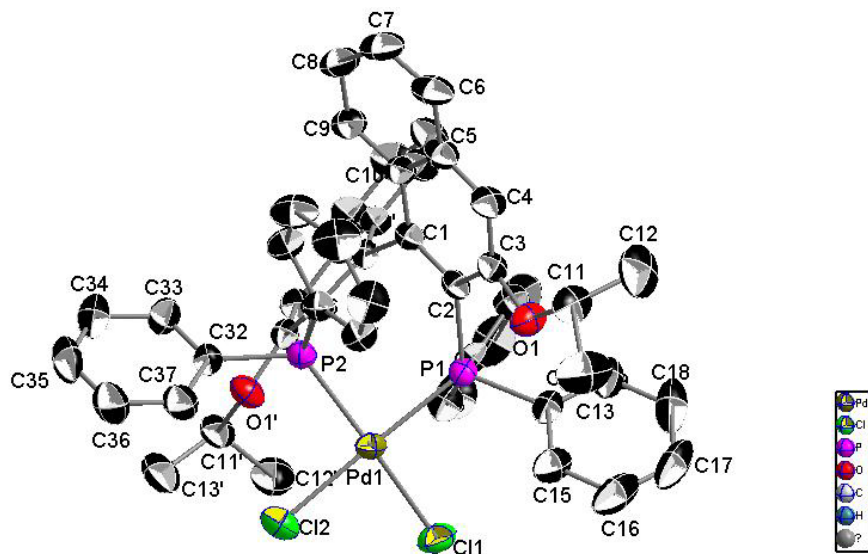
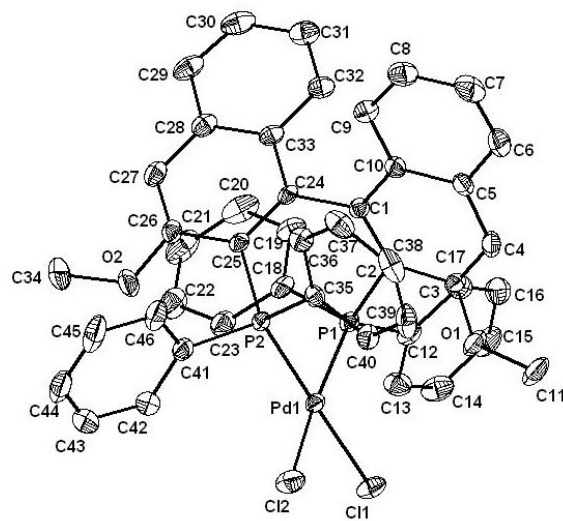
To a solution of **25** (0.332 g, 0.388 mmol) in xylenes (5 ml) was added Bu₃N (2.31 ml, 9.71 mmol) followed by HSiCl₃ (0.78 ml, 7.77 mmol). The reaction was then heated to 140 °C and stirred for 22 h. Upon cooling to 60 °C, 30% NaOH was added (10 ml) and the reaction was stirred for 1 h. The cooled reaction was then diluted with CHCl₃ (50 ml) and the layers were separated. The aqueous layer was extracted with CHCl₃ (3×20 ml) and the combined organics were dried (Na₂SO₄), filtered and evaporated to afford a yellow solid. ³¹P-NMR analysis of the crude indicated the presence of two species, one of which was believed to be the desired product, and the other was thought to be the mono-ester derivative. Therefore, the crude product was reacted with an excess of trimethylacetyl chloride in CH₂Cl₂ to afford the desired diester. The product was purified by SiO₂ chromatography (25:1 Hexanes:EtOAc) to afford a pale yellow solid (0.230 g, 0.280 mmol, 72%). [α]_D²⁰ -96.99 (c=0.0135, CHCl₃); Mp >275 °C (decomposed); IR (KBr) 3043, 2952, 1744, 1647, 1427, 1121 cm⁻¹; ¹H-NMR (300 MHz) δ 0.74 (s, 18H), 6.84-7.04 (m, 8H), 7.06-7.20 (m, 12H), 7.22-7.33 (m, 4H), 7.39 (t, J=7.18 Hz, 2H), 7.68 (s, 2H), 7.83 (d, J=8.21 Hz, 2H) ppm; ¹³C-NMR (75 MHz) δ 26.46, 38.92, 120.66, 125.61, 126.57, 127.06 (d, J=4.27 Hz), 127.42 (d, J=4.89 Hz), 127.54 (d, J=3.05 Hz), 127.81 (d, J=6.10 Hz), 130.65 (d, J=17.09 Hz), 131.78 (d, J=19.53 Hz), 134.40, 135.86 (d, J=14.03 Hz), 136.40 (d, J=17.09 Hz), 150.27 (d, J=10.38 Hz), 150.72, 176.48 ppm; ³¹P-NMR (81 MHz) δ -16.48 ppm; ESI-MS 861 (M+K)⁺, 845 (M+Na)⁺, 823 (M+H)⁺, 637 (M⁺-PPh₂), 551, 390, 288, 105.

11. Synthesis of (*S*)-3,3'-di-benzyloxy-2,2'-diphenylphosphinyl-1,1'-binaphthalene **26**

To a solution of **20** (0.867 g, 0.948 mmol) in THF:MeOH (5:1, 12 ml) was added LiOH (1.0M, 5.70 ml, 5.70 mmol). The reaction was stirred for 30 min before being diluted with CHCl₃ (30 ml) and washed with H₂O. The aqueous layer was extracted with CHCl₃ (2×20 ml) and the combined organics were dried (MgSO₄), filtered and evaporated to afford a white solid. To a solution of this crude product in DMF (10 ml) was added K₂CO₃ (0.831 g, 6.013 mmol). The mixture was stirred for 10 min before the addition of benzyl bromide (0.70 ml, 5.89 mmol). The reaction was allowed to stir for 24 h before being diluted with EtOAc (50 ml) and washed with brine. The aqueous layer was extracted with EtOAc (1×50 ml) and the combined organics were washed with brine (5×50 ml), dried (MgSO₄), filtered and evaporated to afford a pale yellow solid. The product was purified by SiO₂ chromatography (1:1 EtOAc:Hexanes) to afford a white solid (0.666 g, 0.768 mmol, 81% 2 steps). [α]_D²⁰ -179.47 (c=0.017, CHCl₃); Mp 157-159 °C; IR (KBr) 3050, 2953, 1654, 1557, 1434, 1319, 1117 cm⁻¹; ¹H-NMR (300 MHz) δ 4.88 (s, 4H), 6.71 (d, J=7.69 Hz, 4H), 6.90-7.05 (m, 8H), 7.06-7.38 (m, 20H), 7.49 (t, J=7.18 Hz, 2H), 7.56-7.70 (m, 4H), 7.83 (d, J=8.20 Hz, 2H) ppm; ¹³C-NMR (75 MHz) δ 70.39, 106.30 (d, J=5.50 Hz), 119.58, 120.92, 123.60, 126.64, 126.79, 127.19 (d, J=13.43 Hz), 127.61 (d, J=14.04 Hz), 127.94, 128.34 (d, J=32.34 Hz), 130.24 (dd, J=26.24, 2.44 Hz), 131.02 (d, J=11.59 Hz), 131.61 (d, J=11.60 Hz), 132.72, 133.33 (d, J=9.15 Hz), 133.54, 134.13, 135.01, 135.40, 135.56 (d, J=1.22 Hz), 148.12 (t, J=8.55 Hz), 156.03 (d, J=4.88 Hz) ppm; ³¹P-NMR (81 MHz) δ 27.02 ppm; ESI-MS 905.65 (M+K)⁺, 867.15 (M+H)⁺, 550.56, 413.19, 324.18.

12. Synthesis of (*S*)-3,3'-di-benzoyloxy-2,2'-diphenylphosphino-1,1'-binaphthalene **5**

To a solution of **26** (0.666 g, 0.768 mmol) in xylenes (10 ml) was added Bu_3N (4.60 ml, 19.31 mmol) followed by HSiCl_3 (1.60 ml, 15.85 mmol). The reaction was then heated to 140 °C and stirred for 22 h. Upon cooling to 60 °C, 30% NaOH was added (10 ml) and the reaction was stirred for 1 h. The cooled reaction was then diluted with CHCl_3 (50 ml) and the layers were separated. The aqueous layer was extracted with CHCl_3 (3×20 ml) and the combined organics were dried (Na_2SO_4), filtered and evaporated to afford a yellow solid. The product was purified by SiO_2 chromatography (25:1 Hexanes:EtOAc) to afford a pale yellow solid (0.412 g, 0.493 mmol, 64%). $[\alpha]_{\text{D}}^{20}$ -233.57 ($c=0.0145$, CHCl_3); Mp 107-109 °C; IR (KBr) 3050, 2992, 1654, 1576, 1434, 1311, 1182, 1066 cm^{-1} ; ^1H -NMR (300 MHz) δ 4.82 (ABq, $J=11.28$ Hz, 2H), 4.87 (ABq, $J=11.28$ Hz, 2H), 6.74 (d, $J=7.18$ Hz, 4H), 6.77-6.94 (m, 8H), 6.97-7.17 (m, 20H), 7.20 (d, $J=6.67$ Hz, 2H), 7.30 (s, 2H), 7.43 (t, $J=6.67$ Hz, 2H), 7.78 (d, $J=8.20$ Hz, 2H) ppm; ^{13}C -NMR (75 MHz) δ 70.16, 106.79, 123.76, 126.03, 126.65, 127.00 (t, $J=2.44$ Hz), 127.09, 127.64 (t, $J=14.65$ Hz), 128.07, 128.28, 128.71 (d, $J=2.44$ Hz), 129.66 (dd, $J=9.15$, 3.66 Hz), 131.12 (dd, $J=15.87$, 3.05 Hz), 134.77 (d, $J=21.97$ Hz), 135.49, 136.09, 136.34 (d, $J=14.65$ Hz), 136.69 (d, $J=7.94$ Hz), 150.46 (dd, $J=38.46$, 10.99 Hz) ppm; ^{31}P -NMR (81 MHz) δ -15.77 ppm; ESI-MS 835.19 ($\text{M}+\text{H}$) $^+$, 649.01, 558.99, 186.09.

C. ORTEP Diagrams for (S)-27 and (S)-28**(S)-27****(±)-28**

D. General Procedure for Asymmetric Hydrogenations

A MeOH (1 ml) solution of the Rh catalyst precursor (0.1 mmol) and the appropriate ligand (0.011 mmol) are stirred for 15 min under an inert atmosphere. The olefin is then added, followed by additional MeOH (1 ml). The reaction is placed in a Parr hydrogenation apparatus and is evacuated and purged with H₂ (3×). The reaction vessel is then pressurized to 2 atm and is shaken for 24 h. Upon release of H₂ pressure, the reaction mixture is passed through a short column of SiO₂ which is eluted with 1:1 EtOAc:Hexanes. After solvent removal, the crude product is used directly for GC analysis.

2-Acetylamino-propionic acid methyl ester: GC Column: Cyclodex B, Isothermal 90°C, t₁=31.8 min, t₂=32.8 min.

N-(1-Phenyl-ethyl)-acetamide: GC Column: Cyclodex B, Isothermal 130°C, t₁=28.3 min, t₂=29.4 min.

