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Supporting Information

The phosphoric acids used in the study were prepared according to the reaction scheme depicted in Figure 1.

Figure 1 General reaction scheme (Ar = aromatic group)

Preparation of (S)-2,2'-dimethoxy-1,1'-binaphthyl.

(S)-BINOL (50 g, 0.18 mol) was dissolved in acetone (1 L). K_2CO_3 (823 g, 0.6 mol) was added and the suspension was stirred for 15 min. Me_2SO_4 (50 g, 67.6 mL, 0.40 mol) was added dropwise. The reaction mixture was stirred overnight and filtered. The solvent was evaporated *in vacuo*, giving (S)-2,2'-dimethoxy-1,1'-binaphthyl (52 g, 92 %) as a white powder. $[\alpha]_D^{20} = -564.0$ (c 1.00, $CHCl_3$). M.p. 195-199 °C. 1H NMR (400 MHz, $CDCl_3$) δ ppm 7.96 (d, $J = 9.00$ Hz, 2H), 7.85 (d, $J = 8.12$ Hz, 2H), 7.45 (d, $J = 9.03$ Hz, 2H), 7.30 (m, 2H), 7.19 (m, 2H), 7.09 (dd, $J = 8.52, 0.59$ Hz, 2H), 3.75 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ ppm 155.2, 134.2, 129.6, 129.4, 128.1, 126.5, 125.5, 123.7, 119.8, 114.5, 57.1; MS(EI+): 314 $[M^+]$.

Preparation of (S)-3,3'-dibromo-2,2'-dimethoxy-1,1'-binaphthyl.

(S)-2,2'-Dimethoxy-1,1'-binaphthyl (25.0 g, 79.5 mmol) was suspended in Et₂O dried over sodium (0.7 L) and the mixture was mechanically stirred under a nitrogen atmosphere at rt. TMEDA (38 mL), dried over Na₂SO₄, was added followed by dropwise addition of n-BuLi (2.5 M in hexanes, 140 mL, 0.35 mol, 4.4 eq.). The reaction mixture was stirred overnight and turned from a white suspension into a light brown suspension. The conversion was examined by quenching a sample with Br₂ showing full conversion. The reaction mixture was cooled to -80 °C and Br₂ (35 mL, 0.69 mol) was added dropwise over a period of 1h. The reaction mixture was stirred for one more hour at -80 °C and allowed to warm to -10 °C. A saturated aqueous solution of Na₂SO₃ (400 mL) was added dropwise and the reaction mixture was stirred overnight at rt. The layers were separated and the aqueous phase was subsequently extracted with EtOAc and DCM. The combined organic layers were dried with brine and Na₂SO₄, filtered and the solvent was removed *in vacuo*. The crude product was filtered over silica (eluent: EtOAc:Pentane 1:1) and triturated in ether. The obtained solid was dried for 16h in a vacuum oven at T = 40 °C giving (S)-3,3'-dibromo-2,2'-dimethoxy-1,1'-binaphthyl (22.6 g, 60 %) as an off-white powder. $[\alpha]_D^{20} = -121.0$ (c 1.00, CHCl₃). M.p. 157-159 °C. ¹H NMR (400 MHz, CDCl₃) δ ppm 8.27 (s, 2H), 7.82 (d, *J* = 8.15 Hz, 2H), 7.42 (m, 2H), 7.27 (m, 2H), 7.08 (d, *J* = 8.50 Hz, 2H), 3.51 (s, 6H), . ¹³C NMR (50 MHz, CDCl₃): δ ppm 133.3, 133.2, 131.7, 127.3, 127.1, 126.1, 126.0, 117.7, 61.3; MS(EI+): 472 [M⁺].

General procedure for the preparation of (S)-3,3'-diaryl-2,2'-dimethoxy-1,1'-binaphthyls.

A literature procedure of Chong *et al.*¹ was followed for the Suzuki coupling used for this synthesis. (S)-3,3'-Dibromo-2,2'-dimethoxy-1,1'-binaphthyl (typically 500 mg) and Pd(PPh₃)₄ (0.1 eq.) were dissolved in DME (2.5 mL). The reaction mixture was flushed three times with Ar. The aryl boronic acid (3.5 eq.) was added, followed by an aqueous 2 M Na₂CO₃ (0.56 mL) solution. The reaction mixture was flushed three more times with Ar and stirred for 16h at 95 °C. TLC revealed full conversion. The reaction mixture was filtered over Celite and the solvent of the filtrate was evaporated *in vacuo*. The crude product was dissolved in DCM, washed with sat. NH₄Cl (aq), water and brine and dried over Na₂SO₄. The solvent was evaporated *in vacuo*. The crude product was dissolved in DCM (100 mL) and the solution was cooled in an ice-bath. A solution of BBr₃ (10 eq.) in DCM (10 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 16h. ¹H-NMR analysis revealed complete conversion. The resulting mixture was cooled in an ice bath and ice water was added dropwise. The reaction mixture was stirred for 1h and sat. aqueous NaHCO₃ solution was added dropwise. The layers were separated, the organic layer was washed with water and brine and dried over Na₂SO₄. The solvent was evaporated *in vacuo*. The crude product was purified using silica gel chromatography (eluent: pentane, 5 v-% EtOAc) yielding the (S)-3,3'-diaryl-2,2'-hydroxy-1,1'-binaphthyl.

(S)-3,3'-Bis(3,5-ditrifluoromethyl)phenyl)-2,2'- dihydroxy -1,1'-binaphthyl

The product was obtained as a white powder (23.4 g, 85 %). $[\alpha]_D^{20} = -35.4$ (c 1.00, CHCl_3). M.p. 97-99 °C. ^1H NMR (400 MHz, CHCl_3): δ 8.24-8.20 (m, 4H), 8.12-8.09 (m, 2H), 7.99 (d, $J = 7.75$ Hz, 2H), 7.92-7.89 (m, 2H), 7.47 (m, 2H), 7.41 (m, 2H), 7.22 (d, $J = 7.94$ Hz, 2H), 5.35 (d, $J = 0.52$ Hz, 2H). ^{13}C NMR (50 MHz, CDCl_3): δ 144.1, 144.0, 139.0, 132.6, 132.1, 131.9, 131.5, 131.3, 130.2, 128.8, 127.68, 127.3, 126.8, 126.1, 122.9, 120.7. MS(EI+): 710 $[\text{M}^+]$. Anal. Calcd for $\text{C}_{36}\text{H}_{18}\text{F}_{12}\text{O}_2$: C, 60.86; H, 2.55; Found: C, 60.74 H, 2.57.

(S)-3,3'-Bis-2-phenyl-2,2'- dihydroxy -1,1'-binaphthyl

The product was obtained as a white powder (0.20 g, 45 %)). $[\alpha]_D^{20} = -71.8$ (c 1.00, CHCl_3); M.p. 203-205 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.03 (d, $J = 0.60$ Hz, 2H), 7.93 (d, $J = 8.09$ Hz, 2H), 7.74 (dd, $J = 7.22, 1.10$ Hz, 4H), 7.50 (m, 4H), 7.41 (m, 4H), 7.32 (m, 2H), 7.29-7.21 (m, 2H), 5.47-5.26 (s, 2H). ^{13}C NMR (50 MHz, CDCl_3): δ 112.6, 124.5, 124.6, 127.6, 128.0, 128.7, 128.8, 129.7, 129.8, 130.9, 131.6, 133.2, 137.7, 150.4. MS: 438.2 $[\text{M}^+]$; Anal. Calcd for $\text{C}_{32}\text{H}_{22}\text{O}_2$: C, 87.65; H, 5.06 Found: C, 87.18 H, 5.14.

(S)-3,3'-Bis-2-(4-phenyl)-phenyl-2,2'- dihydroxy -1,1'-binaphthyl

The product was obtained as a white powder (1.38 g, 43 %). $[\alpha]_D^{20} = +65.4$ (c 1.00, CHCl_3). M.p. 219-222 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.12-8.09 (s, 2H), 7.96 (d, $J = 7.95$ Hz, 2H), 7.85 (d, $J = 8.08$ Hz, 4H), 7.74 (d, $J = 8.11$ Hz, 4H), 7.68 (d, $J = 8.23$ Hz, 4H), 7.48 (t, $J = 7.64$ Hz, 4H), 7.45-7.32 (m, 2H), 7.29-7.24 (m, 6H), 5.44-5.41 (s, 2H). ^{13}C NMR (50 MHz, CDCl_3): δ ppm 112.6, 124.5, 124.7, 127.4, 127.5, 127.7, 128.8, 129.1, 129.8, 130.3, 130.5, 131.7, 133.2, 136.7, 140.9, 141.0, 150.5. MS: 590 $[\text{M}^+]$; Anal. Calcd for $\text{C}_{44}\text{H}_{30}\text{O}_2$: C, 89.46; H, 5.12; Found: C, 89.38; H, 5.12.

General procedure for the preparation of (S)-3,3'-Diaryl-2,2'-diyl hydrogenphosphate-1,1'-binaphthyls.

A modified literature procedure of Akiyama *et al.*² was followed for the phosphoric acid synthesis. The (S)-3,3'-diaryl-2,2'-hydroxy-1,1'-binaphthyl (typically 50 mg) was dissolved in pyridine (1 mL) and POCl_3 (2.0 eq.) was added at rt. The reaction mixture was stirred overnight. TLC revealed full conversion. The reaction mixture was cooled in an ice-bath and water (1 mL) was added carefully. The reaction mixture was stirred for 30 min at rt. and DCM (30 mL) was added. Subsequently, 1 M HCl (aq., 30 mL) was added and the layers were separated. The solvent of the organic phase was evaporated *in*

vacuo and the product was purified by chromatography using C18RP-silica and a water/MeOH gradient. The fractions containing pure product were collected and the solvent was evaporated *in vacuo*. The product was stripped with toluene and dried 16 h in a vacuum oven at 40 °C.

(S)-3,3'-bis(3,5-Ditrifluoromethyl)phenyl)-2,2'-diyl hydrogenphosphate-1,1'-binaphthyl (PAI)

The product was obtained as a white powder² (1.2 g, 37 %). $[\alpha]_D^{20} = +238$ (c 1.00, CHCl₃). M.p. 174-180 °C (dec). ¹H NMR (400 MHz, CDCl₃): δ 8.91 (s, 1H), 8.12 – 7.85 (m, 8H), 7.57 (m, 4H), 7.45 – 7.29 (m, 4H). ¹³C NMR (50 MHz, CDCl₃): δ 143.5, 138.6, 132.3, 132.0, 131.4, 131.4, 131.1, 129.9, 128.7, 127.6, 127.1, 126.8, 123.1, 122.5, 121.5. ³¹P NMR (189 MHz, CDCl₃): δ 6.0 ppm (s). ¹⁹F NMR (376 MHz, CDCl₃): δ -62.6 (s). HRMS (EI⁺) calcd for C₃₆H₁₈F₁₂O₄P: *m/z* 773.0751; found 773.0750. IR(DCM) 3522, 1622, 1597, 1502, 1474, 1462, 1427, 1377, 1358, 1335, 1281, 1236, 1182, 1140, 1036, 989 cm⁻¹.

(S)-2,2'-Diyl hydrogen phosphate-1,1'-binaphthyl (PA2)

The product was obtained as a white powder² (0.40 g, 90 %). $[\alpha]_D^{20} = +457$ (c 1.00, CHCl₃). M.p. 232-235 °C (dec). ¹H NMR (200 MHz, CDCl₃): δ 8.69 (d, $J = 5.45$ Hz, 1H), 8.04 (t, $J = 8.13$ Hz, 1H), 7.87 (d, $J = 8.47$ Hz, 4H), 7.55 (d, $J = 8.84$ Hz, 2H), 7.41 (dd, $J = 13.43, 7.14$ Hz, 4H), 7.32-7.20 (m, 1H); ¹³C NMR (50 MHz, CDCl₃): δ 142.4, 132.6, 131.6, 130.9, 128.6, 127.3, 126.5, 125.4, 122.1, 121.6; MS(EI⁺): 348 [M⁺], HRMS (EI⁺) calcd for C₂₀H₁₄O₄P: m/z 349.0630; found 349.0624.

(S)-3,3'-Diphenyl-2,2'-diyl hydrogen phosphate-1,1'-binaphthyl (PA3)

The product was obtained as a white powder³ (0.12 g, 48 %). $[\alpha]_D^{20} = +337$ (c 1.00, CHCl₃). M.p. 194-197 °C (dec). ¹H NMR (400 MHz, CDCl₃): δ 8.56 – 8.32 (m, 1H), 7.99 (s, 2H), 7.95 (d, $J = 8.2$ Hz, 2H), 7.58 (d, $J = 7.2$ Hz, 4H), 7.53 – 7.45 (m, 2H), 7.38 (d, $J = 8.3$ Hz, 2H), 7.34 – 7.27 (m, 2H), 7.27 – 7.20 (m, 4H), 7.17 (d, $J = 7.3$ Hz, 2H). ¹³C NMR (50 MHz, CDCl₃): δ 144.9, 144.7, 137.0, 134.3, 132.2, 131.8, 131.5, 128.6, 128.4, 127.8, 127.3, 126.7, 126.2, 122.6 ppm. ³¹P NMR (189 MHz, CDCl₃): δ 4.2 ppm (s). MS: 500 [M⁺], HRMS (EI⁺) calcd for C₂₁H₁₄O₄PNa: m/z 523.1075 found: 523.1048.

(S)-3,3'-Bis-2-(4-Phenyl)-phenyl-2,2'-diyl hydrogen phosphate-1,1'-binaphthyl (PA4)

The product was obtained as a white powder (0.13 g, 59 %). $[\alpha]_D^{20} = +357$ (c 1.00, CHCl₃). M.p. 220-223 °C (dec). ¹H NMR (400 MHz, CDCl₃): δ 8.02 (s, 2H), 7.96 (d, J = 8.1 Hz, 2H), 7.61 (d, J = 8.1 Hz, 4H), 7.51 (t, J = 7.0 Hz, 2H), 7.46 – 7.28 (m, 12H), 7.17 (d, J = 3.6 Hz, 6H). ¹³C NMR (50 MHz, CDCl₃): δ 144.8, 144.6, 141.0, 140.7, 135.8, 133.9, 133.8, 132.1, 131.8, 131.6, 130.3, 128.7, 127.4, 127.2, 126.8, 126.7, 126.3, 122.6. ³¹P NMR (162 MHz, CDCl₃): δ ppm 5.02 (s). MS: 652 [M⁺]; HRMS (EI⁺) calcd for C₄₄H₃₀O₄PNa: *m/z* 653.1882 found: 653.1876.

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