Supplementary information

Catechol-based Phosphoramidites: A New Class of Chiral Ligands for Rhodium-Catalyzed Asymmetric Hydrogenations.

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General remarks:

All reactions were performed in a dry argon atmosphere using standard Schlenk techniques. Et$_2$O (Na), CH$_2$Cl$_2$ (CaH) and EtOAc (boiling chips) were distilled before use. The chiral amines for L1 – L9 were commercially available or made by literature procedures$^1$. $^1$H-NMR, $^{13}$C-NMR and $^{31}$P-NMR spectra were recorded on a Varian Gemini-200 (50.32 Hz) or an Varian 300 (75.48 MHz) in CDCl$_3$. Mass spectra (HRMS) were recorded on an AEI MS-902.

General procedure ligand synthesis:

To a solution of 1.5 g. (8.60 mmol) of o-phenylene phosphorochloridite and 0.87 g. (8.60 mmol) of Et$_3$N in 5 ml of Et$_2$O was added a solution of 8.60 mmol of the appropriate amine in 5 ml Et$_2$O at 0°C. This suspension was warmed to RT and stirred for 1.5 hrs. The reaction mixture was filtered over celite. The filtrate was concentrated. The ligand was purified by filtration over a short plug of silica gel (eluent pentane:EtOAc 10:1), yielding the ligands in 25-45% yield.

$^1$H NMR (200 MHz) δ = 7.26-7.14 (m, 12H), 7.01-6.98 (m, 2H), 4.45 (m, 2H), 1.79 (dd, J = 1.8, 7.1, 6H); $^{13}$C NMR (50.32 MHz) δ = 146.8, 142.0, 129.1, 127.9, 127.7, 127.6, 126.9, 121.7, 53.3, 53.0, 22.4, 22.2; $^{31}$P NMR (81 MHz) δ = 151.9; HRMS calculated for C$_{22}$H$_{22}$NO$_2$P 363.138 found 363.138; [α]$_D$ = -264° (c= 0.79, CHCl$_3$).

$^1$H NMR (200 MHz) δ = 7.35-7.13 (m, 10H), 6.96-6.78 (m, 4H), 4.34-4.29 (m, 1H), 3.69 (ddd, J = 6.8, 15.7, 33.8, 2H), 1.43 (dd, J = 1.8, 7.1, 3H); $^{13}$C NMR (50.32 MHz) δ = 146.7, 146.6, 146.5, 146.3, 141.9, 138.4, 128.5, 128.3, 128.1, 127.3, 127.2, 121.7, 111.4, 56.2, 55.9, 47.2, 47.1, 22.3, 22.1; $^{31}$P NMR (81 MHz) δ = 146.1; HRMS calculated for C$_{22}$H$_{22}$NO$_2$P 349.123 found 349.122; [α]$_D$ = -21° (c= 1.17, CHCl$_3$).

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$^1$H NMR (200 MHz) δ = 7.42-7.22 (m, 5H), 7.04-6.95 (m, 2H), 6.90-6.81 (m, 2H), 4.43-4.37 (m, 1H), 3.18-3.05 (m, 1H), 1.54 (dd, J = 0.5, 7.1, 3H), 1.35 (d, J = 6.8, 3H), 0.96 (d, J = 6.8, 3H);

$^{13}$C NMR (50.32 MHz) δ = 146.7, 128.2, 127.6, 127.0, 121.6, 111.4, 52.5, 52.4, 46.5, 46.1, 26.3, 26.1, 25.1, 24.9, 20.7, 20.6;

$^{31}$P NMR (81 MHz) δ = 152.5; HRMS calculated for C$_{17}$H$_{20}$NO$_2$P 301.123 found 301.123; [α]$_D$ = +214° (c= 1.02, CHCl$_3$).

$^1$H NMR (200 MHz) δ = 7.45-7.28 (m, 5H), 7.06-6.89 (m, 4H), 4.73-4.65 (m, 1H), 2.79-2.64 (m, 2H), 1.69 (dd, J = 1.6, 7.2, 3H), 0.89 (t, J = 7.1, 3H);

$^{13}$C NMR (50.32 MHz) δ = 146.7, 146.6, 146.4, 142.3, 142.3, 128.4, 127.1, 121.6, 111.2, 55.7, 55.1, 37.2, 37.1, 21.5, 21.2, 17.0, 16.9; $^{31}$P NMR (81 MHz) δ = 149.5; HRMS calculated for C$_{16}$H$_{18}$NO$_2$P 287.108 found 287.108; [α]$_D$ = -65° (c= 1.36, CHCl$_3$).

$^1$H NMR (200 MHz) δ = 7.42-7.26 (m, 5H), 7.05-6.97 (m, 2H), 6.94-6.87 (m, 2H), 4.79-4.71 (m, 1H), 2.20 (d, J = 6.1, 3H), 1.59 (dd, J = 0.6, 7.0, 3H);

$^{13}$C NMR (50.32 MHz) δ = 146.7, 141.0, 128.4, 127.1, 121.6, 111.1, 55.0, 54.4, 26.2, 26.1, 18.8, 18.6; $^{31}$P NMR (81 MHz) δ = 147.0; HRMS calculated for C$_{15}$H$_{16}$NO$_2$P 273.092 found 273.091; [α]$_D$ = -28° (c= 1.09, CHCl$_3$).

$^1$H NMR (200 MHz) δ = 7.36-6.78 (m, 9H), 4.21-4.06 (m, 1H), 3.84 (m, 1H), 1.86 (d, J = 6.8, 3H);

$^{13}$C NMR (50.32 MHz) δ = 146.0, 144.5, 128.3, 126.9, 125.6, 121.8, 121.7, 111.6, 11.3, 50.0, 25.2; $^{31}$P NMR (81 MHz) δ = 137.6; HRMS calculated for C$_{14}$H$_{14}$NO$_2$P 259.076 found 259.077; [α]$_D$ = -205° (c= 1.27, CHCl$_3$).

$^1$H NMR (200 MHz) δ = 7.26-7.11 (m, 10H), 6.97 (d, J = 7.7, 1H), 6.75 (dt, J = 1.1, 7.7, 1H), 6.51 (dt, J = 1.1, 7.7, 1H), 5.95 (d, J = 7.7, 2H), 2.36-2.25 (m, 2H), 1.67-1.57 (m, 2H);

$^{13}$C NMR (50.32 MHz) δ = 145.0, 128.1, 126.8, 126.1, 121.6, 121.2, 111.5, 110.3, 63.2, 63.1, 33.7; $^{31}$P NMR (81 MHz) δ = 143.9; HRMS calculated for C$_{22}$H$_{20}$NO$_2$P 361.122 found 361.123; Anal. Calc. for C$_{22}$H$_{20}$NO$_2$P: C, 73.12 %; H, 5.58 %; N, 3.88 %, found : C, 73.09 %; H, 5.58 %; N, 3.89 %; [α]$_D$ = -104° (c= 0.79, CHCl$_3$).

$^1$H NMR (200 MHz) δ = 7.40-7.15 (m, 10H), 6.97 (d, J = 7.7, 1H), 6.75 (dt, J = 1.1, 7.7, 1H), 6.51 (dt, J = 1.1, 7.7, 1H), 5.95 (d, J = 7.7, 2H), 2.36-2.25 (m, 2H), 1.67-1.57 (m, 2H);

$^{13}$C NMR (50.32 MHz) δ = 146.0, 144.5, 128.3, 126.9, 125.6, 121.8, 121.7, 111.6, 11.3, 50.0, 25.2, 25.2; $^{31}$P NMR (81 MHz) δ = 149.5; HRMS calculated for C$_{17}$H$_{20}$NO$_2$P 301.123 found 301.123; [α]$_D$ = +214° (c= 1.02, CHCl$_3$).
$^1$H NMR (200 MHz) $\delta = 7.43-7.25$ (m, 10H), 7.00-6.82 (m, 8H), 4.32-4.29 (m, 4H), 1.49 (dd, $J = 1.71, 7.0, 6H$), 1.53-1.21 (m, 4H); $^{13}$C NMR (50.32 MHz) $\delta = 146.0, 141.8, 128.4, 127.2, 127.1, 121.7, 111.2, 55.5, 55.0, 40.3, 40.2, 31.8, 21.5, 21.2; ^{31}$P NMR (81 MHz) $\delta = 148.5$; HRMS calculated for $\text{C}_{31}\text{H}_{32}\text{N}_2\text{O}_4\text{P}_2$ 558.184 found 558.184; $[\alpha]_D = +79^\circ$ (c= 1.41, CHCl$_3$).

**General procedure hydrogenations:**

In a glass tube, 0.81 mg (2 $\mu$mol) of Rh(COD)$_2$BF$_4$, 4 $\mu$mol of ligand (2 $\mu$mol in case of the bidentate ligands L8 and L9), 200 $\mu$mol of the substrate and 4 ml of solvent, was added. This small glass tube was placed in a semi-automated autoclave with eight reactors (Endeavor) that was purged 4 times with nitrogen and once with hydrogen. Then, the autoclave was pressurized with 5 or 25 bar of hydrogen. The reaction was stirred for 16 hours. A sample of the resulting mixture was filtered over a silica plug and subjected to conversion ($^1$H NMR) and e.e. determination (capillary GC). Full conversion was observed in most cases. As typical examples the isolated yields for 13, 15, 16 and 26 were determined. The complete reaction mixtures were filtered over a short silica plug (EtOAc) to yield the corresponding products in 99% yield. The $^1$H NMR's of the products are added at the end of the SI. Absolute configurations were determined by comparison with reference compounds (26, 27, 31), literature values (GC or HPLC injections; 6, 12, 13, 14, 15, 16, 29),$^{2a,b,c}$ optical rotation (28)$^{2d}$ or assigned by analogy through chiral GC elution order (30, 32).

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$^*$Methods A, C-I are GC methods and method B is HPLC method.

Method A: CP Chiralsil-L-Val from Chrompack (30m x 0.25mm x 0.12µm), 160°C
Method B: Chiralcel-OD (0.46 cm x 25 cm), i-PrOH: heptane 1:9
Method C: CP Chiralsil-L-Val from Chrompack (30m x 0.25mm x 0.12µm), 110°C
Method D: CP Chiralsil-Dex CB from Chrompack (25m x 0.25mm x 0.25µm), 160°C
Method E: CP Chiralsil-Dex CB from Chrompack (25m x 0.25mm x 0.25µm), 170°C
Method F: CP Chiralsil-Dex CB from Chrompack (25m x 0.25mm x 0.25µm), 130°C
Method G: CP Chiralsil-Dex CB from Chrompack (25m x 0.25mm x 0.25µm), 100°C
Method H: CP Chiralsil-Dex CB from Chrompack (25m x 0.25mm x 0.25µm), 140°C
Method I: CP Chiralsil-Dex CB from Chrompack (25m x 0.25mm x 0.25µm), 150°C