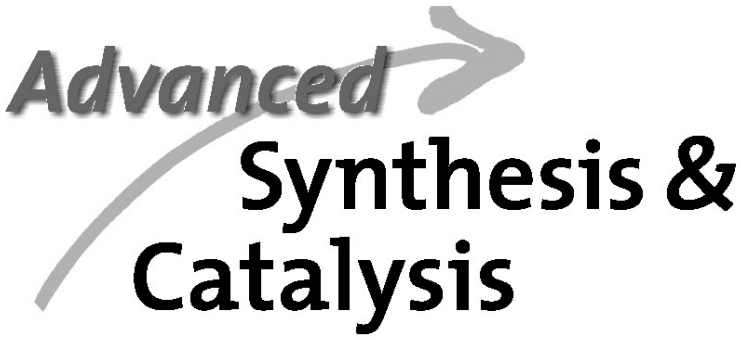

Supporting Information

Supporting Information

Binaphthol-Based Diphosphite Ligands in Asymmetric Nickel-Catalyzed Hydrocyanation of Styrene and 1,3-Cyclohexadiene: Influence of Steric Properties

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Chemicals were purchased from Aldrich, Acros or Merck and used as received. Styrene and 4-methylstyrene were distilled over CaH_2 prior to use. All preparations were carried out under an argon atmosphere using standard Schlenk techniques. $Ni(cod)_2$ [24], $PtCl_2(cod)$ [25] and HCN [26] were synthesized according to literature procedures. NMR spectra were recorded on a Varian Unity Inova 500 (VT NMR), Mercury 400 and Mercury 200 spectrometer (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$). Maldi-TOF mass spectroscopy was performed on a PerSeptive Biosystems Voyager-DE PRO spectrometer. Elemental analysis was performed on a Perkin Elmer 2400 apparatus. IR spectra were recorded on an Avatar 360 FT-IR instrument in ATR mode.

Caution! HCN is a highly toxic, volatile liquid (bp 27 °C) that is also susceptible to explosive polymerization in the presence of base catalysts. It should be handled only in a well-ventilated fume hood and by teams of at least two technically qualified persons who have received appropriate medical training for treating HCN poisoning. Sensible precautions include having available proper first aid equipment as well as HCN monitors. Uninhibited HCN should be stored at a temperature lower than its melting point (-13 °C). Excess of HCN may be disposed by addition to aqueous sodium hypochlorite, which converts the cyanide to cyanate.

General procedure for ligands L1-L9

The appropriate phenol (14.0 mmol) and Et_3N (6 mL, 43.00 mmol) were added drop wise at –10 °C to a solution of PCl_3 (0.95 g, 6.99 mmol) in 200 mL of toluene and the mixture was stirred for 30 minutes. The (*R*)-binaphthol derivative (1.00 g, 3.50 mmol) dissolved in 10 mL of THF was added drop wise to the mixture at –10 °C. The mixture was stirred for 1h at room temperature. Salts were filtered off over a short path of basic alumina (4 cm) and all volatiles were evaporated.

(*R*)-[1,1']-Binaphthalenyl-2,2'-bis(diphenylphosphite) (L1)

PCl_3 (0.95 g, 6.99 mmol), phenol (1.31 g, 13.93 mmol), Et_3N (6 mL, 43.00 mmol), (*R*)-2,2'-binaphthol (1.00 g, 3.50 mmol)

A white paste was obtained after purification by column chromatography (silica 60, hexanes/EtOAc (10:1)) Yield: 1.04 g (1.45 mmol, 41%)

^1H NMR: (200 MHz, $CDCl_3$) δ (ppm): 7.89 (dd, ^3J=8.98Hz, ^4J=3.12Hz, 4H), 7.50 (d, ^3J=8.98Hz, 2H), 7.44-7.35 (m, 2H), 7.22 (d, ^3J=4.68Hz, 4H), 7.12-6.95 (m, 12H), 6.69 (d, ^3J=7.42Hz, 4H), 6.32 (d, ^3J=7.03Hz, 4H) ^{13}C NMR: (100 MHz, $CDCl_3$) δ (ppm): 151.30, 151.10, 147.96, 133.85, 130.70, 129.83, 129.62, 129.27, 129.17, 127.91, 126.76, 125.94, 124.91, 123.74, 123.72, 120.60 (m), 120.40 (m) ^{31}P NMR: (162 MHz, C_6D_6) δ (ppm): 127.5 (s) Maldi-TOF: 717.45 (M^+-1), 741.45 (M^++Na) Elemental Analysis: Calculated (Found): %C 73.53 (73.55), %H 4.49 (4.65)

(*R*)-[1,1']-Binaphthalenyl-2,2'-bis(di(*o*-tolyl)lphosphite) (L2)

PCl_3 (0.95 g, 6.99 mmol), *o*-cresol (1.51 g, 13.97 mmol), Et_3N (6 mL, 43.00 mmol), (*R*)- 2,2'-binaphthol (1.00 g, 3.50 mmol)

A white paste was obtained after purification by column chromatography (silica 60, hexanes/EtOAc (9:1). Yield: 1.12 g (1.43 mmol, 40 %)

^1H NMR: (400 MHz, $CDCl_3$) δ (ppm): 7.82 (d, ^3J=8.79Hz, 4H), 7.47 (d, ^3J=9.16Hz, 2H), 7.35 (m, 2H), 7.19 (m, 4H), 7.00 (d, ^3J=7.33Hz, 4H), 6.87 (t, ^3J=7.33Hz, 4H), 6.68 (q, ^3J=8.06Hz, 4H), 6.62 (d, ^3J=7.69Hz, 2H), 6.57 (d, ^3J=7.69Hz, 2H), 1.93 (s, $12H^{CH3}$)

^{13}C NMR: (100 MHz, $CDCl_3$) δ (ppm): 149.97, 149.92, 147.93, 133.85, 130.87, 130.84, 130.67, 129.72, 129.42, 126.60, 126.49, 126.46, 125.96, 124.85, 123.58, 122.94, 120.9 (m), 120.0 (m), 16.39, 16.37 ^{31}P NMR: (162 MHz, $CDCl_3$) δ (ppm): 130.0 (s) Maldi-TOF: 773.54 (M^+-1) Elemental Analysis: Calculated (Found): %C 74.4 (73.9), %H 5.2 (5.4)

(*R*)-[1,1']-Binaphthalenyl-2,2'-bis(di(*o*-isopropylphenyl)phosphite) (L3)

PCl_3 (0.98 g, 7.21 mmol), 2-(isopropyl)phenol (1.96 g, 14.40 mmol), Et_3N (6 mL, 43.00 mmol), (*R*)- 2,2'-binaphthol (1.03 g, 3.60 mmol)

The product crystallized from 5 mL *n*-heptane at –30 ℃ as a white crystalline solid. Yield: 2.2 g (2.48 mmol, 69 %)

^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm): 7.93 (d, ^3J=8.8 Hz, 2H), 7.91 (d, ^3J=6.2 Hz, 2H), 7.62 (d, ^3J=8.8 Hz, 2H), 7.43 (t, ^3J=6.6 Hz, 2H), 7.32-7.26 (m, 4H), 7.19 (d, ^3J=7.7 Hz, 4H), 7.02 (t, ^3J=7.3 Hz, 4H), 6.84 (dt, ^3J=8.1 Hz, 4H), 6.70 (d, ^3J=8.1 Hz, 2H), 6.67 (d, ^3J=8.1 Hz, 2H), 3.30 (sept, ^3J=6.2Hz, **H**C$(CH_3)_2$, 4H), 0.97 (m, HC(C**H**$_3)_2$, 24H) ^{13}C NMR: (100 MHz, $CDCl_3$) δ (ppm): 148.9, 148.0, 139.41,139.37, 134.0, 130.8, 129.7, 127.9, 126.6, 126.29, 126.25, 126.21, 126.16, 126.10, 124.9, 123.8, 121.24, 121.20, 121.15, 120.07, 120.01, 119.95, 119.91, 119.86, 119.80, 26.64, 26.59, 22.82, 22.78, 22.69 ^{31}P NMR: (162 MHz, $CDCl_3$) δ (ppm): 131.4 (s) Maldi-TOF: 885.57 (M^+-1), 919.60 (M^++O_2) Elemental Analysis: Calculated (Found): %C 75.8 (75.0), %H 6.4 (6.5)

(*R*)-[1,1']-Binaphthalenyl-2,2'-bis(di(*o*-[1,3]-Dioxan-2-yl-phenyl)phosphite) (L4)

PCl_3 (0.60 g, 4.42 mmol), 2-(1,3-dioxan-2-yl)phenol (1.30 g, 7.22 mmol), Et_3N (3mL, 21.50 mmol), (*R*)-2,2'-binaphthol (0.60 g, 3.33 mmol)

A white solid was obtained after recrystallization from cyclohexane. Yield: 180 mg (0.17 mmol, 5 %)

^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm): 7.89 (d, ^3J=8.79Hz, 2H), 7.86 (d, ^3J=8.06Hz, 2H), 7.65 (d, ^3J=9.15Hz, 2H), 7.55 (dd, ^3J=7.69 Hz, ^4J=1.83 Hz, 2H), 7.52 (dd, ^3J=7.69 Hz, ^4J=1.83 Hz, 2H), 7.36 (dt, ^3J=7.51 Hz, ^4J=1.47 Hz, 2H), 7.29-7.16 (m, 4H), 7.05-6.94 (m, 6H), 6.89 (dt, ^3J=7.69 Hz, ^4J=1.83 Hz, 2H), 6.66 (d, ^3J=8.06Hz, 2H), 6.52 (d, ^3J=8.05 Hz, 2H), 5.55 (s, 2H), 5.51 (s, 2H) 4.04-.92 (m, 8H), 3.69-3.51 (m, 8H), 2.13-1.99 (m, 4H), 1.19 (d, ^3J=12.45 Hz, 4H) ^{13}C NMR: (100 MHz, $CDCl_3$) δ (ppm): 148.81, 147.96, 133.91, 130.82, 129.86, 129.81, 129.71, 127.88, 127.26, 127.19, 126.80, 126.13, 125.06, 123.88, 123.82, 121.20 (m), 119.70 (m), 96.7, 67.2, 26.9, 25.7 ^{31}P NMR: (162 MHz, $CDCl_3$) δ (ppm): 130.3 Maldi-TOF: 1061.71 (M^+-1, 100%), 1085.73 (M^++Na, 50%), 1101.73 (M^++K, 60%)

(*R*)-[1,1']Binaphthalenyl-2,2'-bis(di(*o*-^{t}butylphenyl)phosphite) (L5)

PCl_3 (1.03 g, 7.58 mmol), 2-(^{t}Bu)phenol (2.24 g, 14.92 mmol), Et_3N (6 mL, 43.00 mmol), (*R*)-2,2'-binaphthol (1.07 g, 3.74 mmol)

A white solid was obtained after purification by column chromatography (silica 60, *n*-hexanes/EtOAc (9:1)) Yield: 1.51g (1.60 mmol, 43 %)

^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm): 7.82 (d, ^3J=8.42Hz, 2H), 7.80 (d, ^3J=8.79Hz, 2H), 7.45 (d, ^3J=9.15Hz, 2H), 7.37-7.32 (m, 2H), 7.23-7.17 (m, 8H), 6.91-6.84 (m, 6H), 6.77-6.67 (m, 6H), 1.20 (s, 18H^{CH3}), 1.18 (s, 18H^{CH3}) ^{13}C NMR: (100 MHz, $CDCl_3$) δ (ppm): 151.1 (d, J=4.57Hz), 139.6, 134.0, 130.8, 129.8, 127.9, 126.9 (d, J=3.05Hz), 126.7 (d, J=3.82Hz), 126.7, 126.1, 124.9, 122.9 (d, J=6.86Hz), 120.8 (d, J=5.22Hz), 120.0 (d, J=8.36Hz), 119.8 (d, J=3.91Hz), 119.6 (d, J=9.15Hz), 34.5 (d, J=3.82Hz, *C*CH_3), 29.9 (s,

CH_3) ^{31}P NMR: (162 MHz, $CDCl_3$) δ (ppm): 129.4 (s) Maldi-TOF: 941.37 (M^+-1), 965.40 (M^++Na), 981.39 (M^++K) Elemental Analysis: Calculated (Found): %C 76.4 (76.2), %H 6.8 (6.9)

(*R*)-2,2'-Bis(1-ethoxyethoxy))-1,1'-binaphthyl

Azeotropically dried pyridinium *p*-toluenesulfonate (880 mg, 3.49 mmol) was dissolved in 300 mL CH_2Cl_2. Azeotropically dried (*R*)-2,2'-binaphthol (10.0 g, 34.9 mmol) was added to the mixture, followed by drop wise addition of distilled ethyl vinyl ether (10 mL, 104.7 mmol). The mixture was stirred at room temperature for 3 days. All volatiles were evaporated and the residue was purified with column chromatography (Silica 60, EtOAc/hexanes, 1:7). Yield: 10.03 g (23.0 mmol, 66.7 %)

^{1}H NMR: (200 MHz, $CDCl_3$) d (ppm): 7.85-7 (m, 12H), 5.2 (m, 1H), 5.1 (m, 1H), 3.5 (m, 2H), 3.25 (m, 2H), 1.1 (m, 3H), 1.01 (m, 3H), 0.85 (m, 6H)

(*R*)-3-Methyl-2,2'-bis(1-ethoxyethoxy)-1,1'-binaphthyl

To a solution of (*R*)-2,2'-Bis(1-ethoxyethoxy))-1,1'-binaphthyl (5.015 g, 11.65 mmol) in 50 mL of THF 12 mL ^{n}BuLi (2.5 M in hexanes) was added at –78 ℃. The mixture was stirred at -78 ℃ for 3h. Methyl iodide (6.4 g, 45.0 mmol) was added drop wise at –78 ℃, then the cooling was removed and the mixture was stirred overnight at room temperature. The mixture was concentrated, and the residue was redissolved in CH_2Cl_2 and washed with water. The organic layer was dried over $MgSO_4$ and concentrated. Yield: 4.77 g (10.74 mmol, 92%)

^{1}H NMR: (200 MHz, $CDCl_3$) d (ppm): 7.92-7.13 (m, 11H), 5.29 (m, 1H), 5.18 (m, 1H), 3.4 (m, 2H), 3.05 (m, 2H), 2.6 (s, 3H), 0.99 (m, 3H), 0.88 (m, 3H), 0.72 (t, 6H)

(*R*)-3-Methyl-2,2'-binaphthol

To a solution of (*R*)-3-Methyl-2,2'-bis(1-ethoxyethoxy)-1,1'-binaphthyl (1.0 g, 2.25 mmol) in a 20 mL benzene and 4 mL methanol, 4 mL of an HCl solution (2.0 M in Et_2O) was added drop wise. The mixture was stirred overnight at room temperature. All volatiles were evaporated and no further purification was necessary. Yield: 676 mg (2.25 mmol, 100%)

^{1}H NMR: (200 MHz, $CDCl_3$) d (ppm): 8.0-7.1 (m, 11H), 5.1 (s, 1H), 5.06 (s, 1H), 2.5 (s, 3H)

(*R*)-3-Methyl-[1,1']-binaphthalenyl-2,2'-bis(di(*o*-isopropylphenyl)phosphite) (L6)

PCl_3 (240 mg, 1.73 mmol), 2-isopropylphenol (413 mg, 3.03 mmol), Et_3N (700 mg, 6.93 mmol) and (*R*)-3-Methyl-2,2'-binaphthol (260 mg, 0.87 mmol)

The residue was purified with column chromatography over silica 60 eluting with EtOAc/hexanes, 1:16. Yield: 0.26 g (0.29 mmol, 33 %)

^{1}H NMR: (400 MHz, $CDCl_3$) d (ppm):7.80-6.70 (m, 27H), 3.0 (sept, 4H), 2.45 (s, 3H), 1.0 (m, 24H) ^{13}C NMR: (100 MHz, $CDCl_3$) d (ppm): 149.1, 139.3-119.7 (aromatic signals), 26.6, 22.9, 22.7, 22.6, 22.5, 18.3 ^{31}P NMR: (162 MHz, $CDCl_3$) d (ppm): 134.3 (d, J_{PP}=24Hz), 129.8 (d, J_{pp}=24Hz) Maldi-TOF: 899.20 (M^+-1, 100%), 923.21 (M^++Na, 10%)

(*R*)-3-Methyl-[1,1']-binaphthalenyl-2,2'-bis(di(*o*-[1,3]-Dioxan-2-yl-phenyl)phosphite) (L8)

PCl_3 (915 mg, 6.66 mmol), 2-(1,3-dioxan-2-yl)phenol (2.10 g, 11.66 mmol), Et_3N (2.7 g, 26.64 mmol), (*R*)-3-Methyl-2,2'-binaphthol (1 g, 3.33 mmol)

The product was recrystallized from isopropanol/acetone. Yield: 1.31 g (1.22 mmol, 37 %)
^{1}H NMR: (400 MHz, $CDCl_3$) d (ppm): 7.79-6.94 (m, 27H), 5.57 (s, 1H), 5.45 (s, 1H), 5.43 (s, 1H), 5.22 (s, 1H), 4.0 (m, 8H), 3.56 (m, 8H), 2.49 (s, 3H), 1.22 (m, 8H)
^{13}C NMR: (100 MHz, $CDCl_3$) d (ppm): 145.0, 144.0, 130.2-120.0 (aromatic signals), 96.7, 67.2, 25.7, 19.1 ^{31}P NMR: (162 MHz, $CDCl_3$) d (ppm): 132.4 (d, J_{PP}=17Hz), 129.73 (d, J_{PP}=17Hz) Maldi-TOF: 1075.52 (M^+-1, 100%), 1099.53 (M^++Na, 25%), 1115.52 (M^++K, 20%) Elemental Analysis: Calculated (Found): %C 67.9 (67.8), %H 5.2 (5.6)

(*R*)-3,3'-Dimethyl-2,2'-bis(1-ethoxyethoxy)-1,1'-binaphthyl

To a solution of (*R*)-2,2'-bis(1-ethoxyethoxy))-1,1'-binaphthyl (2.0 g, 4.65 mmol) in 24 mL of THF 4.64 mL ^{n}BuLi (2.5 M in hexanes) was added at –78 ℃. The mixture was stirred at 0 ℃ for 3h. Methyl iodide (2.51 g, 17.65 mmol) was added drop wise at –78 ℃, then the cooling was removed and the mixture was stirred overnight at room temperature. The mixture was concentrated, and the residue was redissolved in CH_2Cl_2 and washed with water. The organic layer was dried over $MgSO_4$ and concentrated. Yield: 1.90 g (4.14 mmol, 89 %)
^{1}H NMR: (200MHz, $CDCl_3$) d (ppm): 7.80-7.15 (m, 10H), 4.34 (m, 2H), 3.45 –3.04 (m, 4H), 2.56 (s, 6H), 1.07 (m, 3H), 0.94 (m, 3H), 0.74 (m, 6H)

(*R*)-3,3'-Dimethyl-2,2'-binaphthol

To a solution of (*R*)-3,3'-dimethyl-2,2'-bis(1-ethoxyethoxy)-1,1'-binaphthyl (1.90 g, 4.14 mmol) in a 30 mL benzene and 6 mL methanol, 6 mL of an HCl solution (2.0 M in Et_2O) was added drop wise. The mixture was stirred overnight at room temperature. All volatiles were evaporated and no further purification was necessary. Yield: 1.30 g (4.14 mmol, 100 %)
^{1}H NMR: (200MHz, $CDCl_3$) d (ppm): 7.83-7.1 (m, 10H), 5.1 (s, 2H), 2.5 (s, 6H)

(*R*)-3,3'-Dimethyl-[1,1']-binaphthalenyl-2,2'-bis(di(*o*-isopropylphenyl)phosphite) (L7)

PCl_3 (871 mg, 6.36 mmol), 2-isopropylphenol (1.52 g, 11.13 mmol), Et_3N (2.57 g, 25.44 mmol) and (*R*)-3,3'-dimethyl-2,2'-binaphthol (1 g, 3.18 mmol)
The residue was purified with column chromatography over silica 60 eluting with EtOAc/hexanes, 1:20. Yield: 0.43 g (0.47 mmol, 15 %)
^{1}H NMR: (400 MHz, $CDCl_3$) d (ppm): 7.72-6.56 (m, 26H), 2.94 (sept, 4H), 2.47 (s, 6H), 0.92 (d, 24H, *J*=1.6Hz) ^{13}C NMR: (100 MHz, $CDCl_3$) d (ppm): 149.2, 148.5, 139.2, 139.1, 133.3, 131.4, 131.0, 130.2, 127.1, 126.5, 126.1, 126.0, 125.5, 124.8, 123.5, 119.9(m), 119.3(m), 26.4, 22.8, 22.7, 22.6, 22.5, 18.2 ^{31}P NMR: (162 MHz, $CDCl_3$) d (ppm): 133 (s) Maldi-TOF: 913.66 (M^+-1, 20%), 937.66 (M^++Na, 50%)
Elemental Analysis: Calculated (Found): %C 76.1 (76.3), %H 6.6 (6.5)

(*R*)-3,3'-Dimethyl-[1,1']-binaphthalenyl-2,2'-bis(di(*o*-[1,3]-Dioxan-2-yl-phenyl)phosphite) (L9)

PCl_3 (871 mg, 6.36 mmol), 2-(1,3-dioxan-2-yl)phenol (2.01 g, 11.13 mmol), Et_3N (2.57 g, 25.44 mmol) and (*R*)-3,3'-dimethyl-2,2'-binaphthol (1 g, 3.18 mmol)
The product was crystallized from isopropanol/acetone. Yield: 1.63 g (1.50 mmol, 47 %)
^{1}H NMR: (400 MHz, $CDCl_3$) d (ppm): 7.90-6.90 (m, 26H), 5.37 (s, 2H), 5.16 (s, 2H), 4.0 (m, 8H), 3.62 (m, 8H), 2.36 (s, 6H), 1.49 (m, 8H) ^{13}C NMR: (100 MHz, $CDCl_3$) d (ppm): 148.8, 148,4, 133.3, 131.3, 131.0, 130.3, 129.7, 129.5, 129.4, 127.3, 127.2, 127.0, 126.5, 125.7, 125.0, 123.7, 123.5, 119.7(m), 118.8(m), 96.6, 96.3, 67.5, 67.2, 67.1, 66.9, 25.7,

18.2 ^{31}P NMR: (162 MHz, $CDCl_3$) d (ppm): 131.3 (s) Maldi-TOF (M/z, rel. int.): 1089.11 (M^+-1, 100%), 1113.12 (M^++Na, 50%)

L3Ni(cod): 5 mg (0.018 mmol) $Ni(cod)_2$ and 16 mg (0.018 mmol) **L3** were dissolved in 1 ml toluene and stirred for 30 minutes. All volatiles were evaporated and the solids were dissolved in 0.75 mL of benzene-d_6.
^{1}H NMR: (400 MHz, C_6D_6) δ (ppm): 7.83 (d, ^3J=8.06 Hz, 2H), 7.63 (d, ^3J=8.79 Hz, 2H), 7.54 (d, ^3J=8.05 Hz, 2H), 7.46 (d, ^3J=8.78 Hz, 2H), 7.31 (d, ^3J=8.42 Hz, 2H), 7.83 (dd, ^3J=7.69 Hz, ^4J=1.84 Hz, 2H), 7.83 (dt, ^3J=7.51 Hz, ^4J=0.74 Hz, 2H), 6.94-6.83 (m, 6H), 6.80 (dt, ^3J=7.88 Hz, ^4J=1.83 Hz, 2H), 6.74 (dt, ^3J=7.32 Hz, ^4J=1.10 Hz, 2H), 6.47 (dt, ^3J=7.51 Hz, ^4J=1.47 Hz, 2H), 6.41 (d, ^3J=7.33 Hz, 2H), 5.15 (br s, 2H), 4.67 (br s, 2H), 3.79 (sept, ^3J=6.96 Hz, 2H), 2.91 (sept, ^3J=6.96 Hz, 2H), 2.80 (br s, 2H), 2.32 (br s, 2H), 2.20 (br s, 2H), 1.99 (br s, 2H), 1.35 (d, ^3J=6.59 Hz, 6H), 1.21 (d, ^3J=6.59 Hz, 6H), 0.91 (d, ^3J=6.96 Hz, 6H), 0.70 (d, ^3J=7.81 Hz, 6H). ^{31}P NMR: (162 MHz, C_6D_6) δ (ppm): 147.8 (s)

L3$PtCl_2$: A solution of 119 mg (13.40 mmol) **L3** in 3 mL CH_2Cl_2 and 2 mL CH_3CN was added to 50 mg (13.40 mmol) $Pt(cod)Cl_2$ and was stirred for 1 hour at 25 ℃. After 7 days at –30 ℃ crystals were formed suitable for X-ray analysis. Filtration and evaporation of all volatiles gave 123 mg (10.64 mmol, 79%) of white crystalline product.

^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm): 7.92 (d, ^3J=8.79 Hz, 2H^{napht}), 7.85 (d, ^3J=8.06 Hz, 2H^{arA}), 7.78 (d, ^3J=8.06 Hz, 2H^{napht}), 7.71 (d, ^3J=9.16 Hz, 2H^{napht}), 7.50 (t, ^3J=7.32 Hz, 2H^{arA}), 7.34 (t, ^3J=7.69 Hz, 2H^{arA}), 7.26-7.19 (m, 4H), 7.12-7.03 (m, 4H), 6.92 (d, ^3J=6.59 Hz, 2H^{arB}), 6.78 (t, ^3J=7.32 Hz, 2H^{arB}), 6.14 (t, ^3J=7.69 Hz, 2H^{arB}), 6.04 (d, ^3J=8.05 Hz, 2H^{arB}), 3.26 (sept, ^3J=6.95 Hz, 2H^{arA}), 2.79 (sept, ^3J=6.96 Hz, 2H^{arB}), 1.10 (d, ^3J=6.96 Hz, 6H^{arA}), 1.03 (d, ^3J=6.59 Hz, 6H^{arA}), 0.78 (d, ^3J=6.95 Hz, 6H^{arB}), 0.68 (d, ^3J=6.96 Hz, 6H^{arB}). ^{13}C NMR: (100 MHz, $CDCl_3$) d (ppm): 148.5 (m), 147.9 (m), 139.4, 138.2, 133.5, 131.7, 131.3, 128.5, 127.7, 127.0, 126.4, 126.3, 126.2, 125.9, 125.6, 125.5, 124.7, 123.1, 121.5, 119.4, 118.3, 26.6, 25.6, 23.2, 22.9, 22.6, 22.5 ^{31}P NMR: (162 MHz, $CDCl_3$) δ (ppm): 57.2 (s), 57.2 (d, $^1J_{PtP}$=5782 Hz) Elemental Analysis: calculated for **L3**$PtCl_2$.0.5CH_2Cl_2 (found): %C 58.4 (58.2), %H 4.9 (4.7)

Table S1 *Selected bond lengths [Å], angles and torsion angles [°] in the crystal structure of* ***L3****$PtCl_2$*

Selected bond lengths [Å]			
Pt1-Cl1	2.3350(19)	Pt1-Cl2	2.3356(17)
Pt1-P1	2.1976(16)	Pt1-P2	2.2097(16)
P1-O11	1.596(3)	P2-O21	1.599(3)
P1-O12	1.584(3)	P2-O22	1.568(3)
P1-O13	1.579(3)	P2-O23	1.585(3)
O11-C12	1.422(5)	O21-C22	1.402(5)
O12-C31	1.411(5)	O22-C51	1.401(5)
O13-C41	1.427(5)	O23-C61	1.411(5)
Selected angles [°]			
Cl1-Pt1-Cl2	88.12(7)	P1-Pt1-P2	95.73(6)
Cl1-Pt1-P1	86.63(7)	Cl2-Pt1-P2	89.51(6)
Cl1-Pt1-P2	177.59(9)	Cl2-Pt1-P1	174.63(8)

O11-P1-O12	96.24(18)	O21-P2-O22	99.65(17)
O11-P1-O13	110.01(19)	O21-P2-O23	106.70(17)
O12-P1-O13	104.38(19)	O22-P2-O23	101.41(17)
P1-O11-C12	119.5(2)	P2-O21-C22	128.2(2)
P1-O12-C31	123.8(3)	P2-O22-C51	131.4(3)
P1-O13-C41	128.9(3)	P2-O23-C61	125.2(2)
Selected torsion angles [°]			
C12-C11-C21-C22	-102.5(2)	C19-C11-C21-C29	-100.7(4)

General procedure for the hydrocyanation experiments

A solution of 1.1 eq. (0.020 mmol) of ligand in 500 µL of toluene was added to 5 mg (0.018 mmol) $Ni(cod)_2$ in a glovebox (N_2 atmosphere). From this stock solution 200 µL were added with an Eppendorf pipette to a 15 mL reaction Schlenk tube equipped with a Teflon coated stirring bar followed by 500 eq. (350 µL, 3.65 mmol) of 1,3-cyclo-hexadiene. A round bottom Schlenk flask was filled with 1 mL toluene and 100 µL hydrogen cyanide, which was taken up in a 5 mL syringe and added to the reaction mixture by syringe pump in 2 hours (closed system). The reaction was stirred for another 2 hours, after which the reaction mixture was cooled to 0 °C and was flushed with a gentle stream of argon for 1 minute to remove traces of HCN. The reaction product was then analysed by GC. The second enantiomer on the chiral GC trace, for all products, is the enantiomer in excess.

Yield is defined as (area of product) / (area of substrate + area of product) and was performed on a Shimadzu GC17A with FID and Ultra 2 column (25 m with inner diameter of 0.20 mm) with a variable temperature program which consists of an initial isothermic temperature followed by an increase with 20 °C/min to 280 °C with a constant velocity pressure program using He as carrier gas. For styrene the area was corrected for the response factor with n-decane as internal standard. The yields for the other products were not corrected by the response factor and therefore have an error of ±5%.

Table S2 *Selected retention times for the substrates and products*

Substrate	Initial Temp	Time	RT substrate	RT product
Styrene	90 °C	3 min	2.80 min	6.25 min
4-MeStyrene	110 °C	4 min	2.98 min	6.94 min
Trans-ß-MeStyrene	110 °C	4 min	3.42 min	6.62 min
Piperylene	90 °C	3 min	1.22 min	2.18 min
1,3-cyclohexadiene	90 °C	3 min	1.49 min	4.65 min

Enantiomeric excess is defined as (area of enantiomer 1 – area of enantiomer 2) / (area of enantiomer 1 + area of enantiomer 2) and was determined on a Carlo Erba 6000 Vega series 2 GC with FID and Lipodex E column (25 m with inner diameter of 0.25 mm), using an isothermic temperature program with 50 kPa H_2 pressure.

Table S3 *Retention times for the enantiomers of the chiral products*

Substrate	Isothermic Temp	RT enantiomer 1	RT enantiomer 2
Styrene	150 °C	3.24 min	3.50 min
4-MeStyrene	120 °C	6.12 min	6.37 min

Trans-ß-MeStyrene	130 °C	3.38 min	3.67 min
Piperylene	100 °C	2.47 min	3.16 min
1,3-cyclohexadiene	130 °C	3.30 min	3.46 min

Isomerization of 2M3BN to 3PN

A solution of 1 eq. (0.018 mmol) or 3 eq. (0.054 mmol) respectively of **L** in 2.0 mL of toluene was added to 5 mg (0.018 mmol) $Ni(cod)_2$ in a Schlenk tube and was stirred for 5 minutes. To this solution 0.5 mL (5.20 mmol) 2M3BN was added and the Schlenk tube was placed in an oil bath at 100 °C. Samples for GC analysis were taken over time to determine the TOF (h^{-1}).

TOF is defined as formation of 3PN in mole per mole nickel per hour. Yield is defined as (area of product) / (area of substrate + area of product) and was performed on a Shimadzu GC17A with FID and Ultra 2 column (25 m with inner diameter of 0.20 mm) with a variable temperature program which consists of an initial isothermic temperature, 40 °C for 5 min followed by an increase of 5 °C/min to 60 °C followed by an increase of 25 °C/min to 280 °C with a constant velocity pressure program using He as carrier gas. This resulted in the following retention times: 2M3BN (3.28 min), toluene (5.15 min) and 3PN (5.86 min).

Table S4 *Results of the isomerization of 2M3BN to 3PN*

L	TOF (1 eq.) {h^{-1}}	TOF (3 eq.) {h^{-1}}
L2	78	36
L3	74	85
L5	3	nd