Supporting Information

for

Angew. Chem. Int. Ed. Z54146

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69451 Weinheim, Germany

**A Staudinger Approach towards BINOL-derived MAP-type Bidentate
P,N-Ligands**

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General information: Unless noted otherwise, materials were purchased from commercial suppliers and used without purification. Toluene, DMSO, dichloromethane and acetonitrile were freshly distilled from calcium hydride. Tetrahydrofuran and diethyl ether were freshly distilled from sodium with benzophenone as indicator. Triethylamine and DIPEA were stored over potassium hydroxide pellets and used as such. All air and moisture sensitive reactions were carried out under an inert atmosphere of dry argon. Column chromatography was performed using Aldrich silica gel (70-230 mesh, 60 Å). Infrared spectra were recorded on a Bruker IFS 28 spectrophotometer. All NMR spectra were recorded in CDCl₃, unless states otherwise. ¹H NMR and ¹³C NMR (APT) spectra were measured on a Bruker ARX 400 (400 and 100.6 MHz, respectively) or a Varian Inova-500 (500 and 125 MHz, respectively). Spectra are reported in units of ppm on the δ scale, relative to chloroform (7.26 ppm for ¹H NMR and 77.0 ppm for ¹³C NMR). ³¹P NMR spectra were recorded on a Bruker 300 AMX (121.5 MHz) or a Varian Inova-500 (202.4 MHz). Chemical shifts are given in ppm downfield from 85% H₃PO₄. ¹⁹F NMR spectra were recorded on a Varian Inova-500 (470.4 MHz). Chemical shifts are given in ppm downfield from CFCl₃. Mass spectra were measured using a JEOL JMS SX/SX102A four-sector mass spectrometer, coupled to a JEOL MS-MP7000 data system.

4-Azido-butyric acid *tert*-butyl ester (5f).

To a solution of 4-azido-butyric acid^[1] (0.30 g, 2.33 mmol) in 3.5 mL THF at -40 °C was added TFAA (0.70 mL, 5.0 mmol) dropwise. After 30 min. a solution of *tert*-butanol (3.0 mL, 32 mmol) in THF (0.6 mL) was added and the reaction mixture was stirred for 17 h at room temperature. The reaction was quenched by pouring the solution into an aqueous saturated NaHCO₃ solution (50 mL). The mixture was extracted with Et₂O (2 x 50 mL) and the combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Purification by column chromatography (pentane:Et₂O = 20:1→10:1) afforded **5f** as a colourless oil (0.42 g, 2.28 mmol, 98%). ¹H NMR (400 MHz): δ = 3.33 (t, *J* = 6.7, 2H, N₃CH₂), 2.31 (t, *J* = 7.2, 2H, C(O)CH₂), 1.86 (m, 2H, N₃CH₂CH₂), 1.45 (s, 9H, OC(CH₃)₃). ¹³C NMR (125 MHz): δ = 171.9, 80.5, 50.6, 32.3, 28.0, 24.3. IR: ν 2981, 2101, 1731.

(5-Azido-pentyloxy)-*tert*-butyldimethylsilane (5e).

To a solution of NaN₃ (83 mg, 1.28 mmol) in DMSO (2 mL) was added 5-bromo-pentyloxy-*tert*-butyldimethylsilane (0.30 g, 1.07 mmol). The solution was stirred for 65 h at room temperature. The mixture was diluted by adding Et₂O (40 mL) and washed with H₂O (4 x 30 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Purification by column chromatography (pentane:Et₂O = 10:0→10:1) afforded **5e** as a colourless oil (0.25 g, 1.03 mmol, 96%). ¹H NMR (400 MHz): δ = 3.61 (t, *J* = 6.4, 2H, OCH₂), 3.27 (t, *J* = 6.9, 2H, N₃CH₂), 1.51-1.66 (m, 4H), 1.40-1.46 (m, 2H), 0.89 (s, 9H), 0.05 (s, 6H). ¹³C NMR (125 MHz): δ = 62.9, 51.4, 32.3, 28.7, 25.9, 23.1, 18.3, -5.3. IR: ν 2930, 2858, 2095. HRMS (EI): calcd for C₇H₁₆N₃Osi (*M*-^tBu): 186.1063, found: 186.1060.

2-Azido-3-phenyl-propionic acid ethyl ester (5g).^[2]

To a solution of 2-azido-3-phenyl-propionic acid (710 mg, 3.71 mmol) in CH₂Cl₂ (90 mL) was added DMAP (48 mg, 0.39 mmol) and ethanol (1 mL). After stirring for 5 minutes at room temperature EDC (1.42 g, 7.42 mmol) was added and the orange suspension was stirred for another 19 h. The mixture was diluted by adding EtOAc (100 mL) and washed with H₂O (2 x 20 mL). The organic layer was dried (Na₂SO₄) and concentrated *in vacuo* to afford **5g** as a yellow oil (0.781 g, 3.56 mmol, 96%), which was spectroscopically identically as described in the literature.

The 3rd-generation azido-carbosilane dendritic wedge **5i** was prepared by reaction of the iodine functionalized precursor^[3] with NaN₃. Experimental detail will be reported elsewhere (manuscript in preparation).

(R)-1,1,2,2,3,3,4,4,4-nonafluoro-butane-1-sulfonic acid 2'-(diphenylphosphinoyl)-[1,1']binaphthalenyl-2-yl ester (3).

To a solution of (R)-BINOL (4.61 g, 16.1 mmol) in acetonitrile (160 mL) was added Et₃N (9.0 mL, 64.4 mmol) and perfluorobutanesulfonyl fluoride (7.2 mL, 40.3 mmol). After stirring the mixture for 1 h, EtOAc (200 mL) was added and the resulting mixture was washed twice with H₂O (100 mL) and an aqueous saturated NaHSO₄ solution (100 mL). The organic layer was dried (Na₂SO₄) and concentrated *in vacuo*. The crude product was dissolved in DMSO (47 mL) and Pd(OAc)₂ (0.36 g, 1.61 mmol), dppb (0.69 g, 1.61 mmol), diphenylphosphine oxide (4.88 g, 24.2 mmol) and diisopropylethylamine (11.2 mL, 64.4 mmol) were added. The resulting reaction mixture was stirred for 4 h at 115 °C. After cooling the mixture to room temperature, EtOAc (400 mL) was added and the mixture was washed four times with a mixture of H₂O, aqueous saturated NaHCO₃, and brine (1:1.5:1, 200 mL). The organic layer was dried (Na₂SO₄) and concentrated

in vacuo. Purification by column chromatography (PE:EtOAc = 1:1→1:2) afforded **3** as an off-white foam (11.5 g, 15.3 mmol, 95%). ¹H NMR (400 MHz): δ = 8.00 (dd, *J* = 8.6, 2.1, 1H), 7.93 (d, *J* = 8.2, 1H), 7.90 (d, *J* = 9.1, 1H), 7.83 (d, *J* = 8.2, 1H), 7.65 (d, *J* = 8.6, 1H), 7.62 (d, *J* = 8.6, 1H), 7.57 (t, *J* = 7.1, 1H), 7.35-7.50 (m, 9H), 7.35 (dt, *J* = 8.4, 1.0, 1H), 7.23-7.27 (m, 4H), 7.17 (d, *J* = 8.6, 1H), 7.13 (dt, *J* = 8.3, 1.0, 1H), 6.97 (d, *J* = 8.4, 1H). ³¹P NMR (121.5 MHz): δ = 29.1. IR: ν 3059, 1420, 1239, 1204. HRMS (FAB+): calcd for C₃₆H₂₃F₉O₄PS (*M*+H⁺): 753.0911, found: 753.0903. [α]_D²¹ = +36 (*c* = 1.05, CHCl₃).

(*R*)-1,1,2,2,3,3,4,4,4-Nonafluoro-butane-1-sulfonic acid 2'-diphenylphosphanyl-[1,1'-binaphthalenyl-2-yl ester (2).

The phosphine **3** (4.00 g, 5.32 mmol) was dissolved in neat phenylsilane (32 mL) and was stirred at 114 °C for 17 h. After addition of EtOAc the mixture was concentrated *in vacuo*. Purification by column chromatography (PE:EtOAc = 25:1→10:1) afforded **2** as an off-white foam (3.68 g, 5.00 mmol, 94%). ¹H NMR (400 MHz): δ = 8.09 (d, *J* = 9.0, 1H), 7.91-7.96 (m, 3H), 7.58 (d, *J* = 9.0, 1H), 7.52 (t, *J* = 7.0, 1H), 7.44-7.48 (m, 2H), 7.25-7.32 (m, 6H), 7.18-7.21 (m, 2H), 7.07-7.13 (m, 3H), 7.00-7.03 (m, 2H), 6.92 (d, *J* = 8.5, 1H). δ = ³¹P NMR (121.5 MHz): δ = -12.2. ¹⁹F NMR: δ = -80.9, -110.5, -121.3, -126.2. IR: ν 3054, 1421, 1239, 1204. HRMS (FAB+): calcd for C₃₆H₂₃F₉O₃PS (*M*+H⁺): 737.0962, found: 737.0954. [α]_D²¹ = -5.6 (*c* = 1.00, CHCl₃).

General procedure for the Staudinger reaction.

The phosphine was added to a solution of an azide (1.2 equiv.) in toluene/THF 1:1 (0.1 M). The reaction was stirred at 115 °C until all the phosphine was consumed (the reaction was

monitored by ^{31}P NMR of an aliquot in C_6D_6). The mixture was cooled to room temperature and concentrated *in vacuo*. The remaining phosphonium salt was stirred for 2 h at 65 °C in a mixture of THF (2 mL), EtOH (2 mL) and aqueous 0.1 M NaOH (2 mL). After cooling the mixture, Et_2O was added and the organic phase was washed with H_2O (25 mL) and brine (25 mL). The organic layer was dried (Na_2SO_4) and concentrated *in vacuo*. Purification was performed by column chromatography.

(R)-Benzyl-[2'-(diphenyl-phosphinoyl)-[1,1']binaphthalenyl-2-yl-amine (4b).

Phosphine **2** (150 mg, 0.20 mmol) was reacted with azidomethylbenzene **5b** (33 mg, 0.24 mmol) according to the general procedure. After 17 h the reaction mixture was concentrated *in vacuo* yielding the phosphonium salt **7b** as a yellow oil in a quantitative yield: ^1H NMR (500 MHz): δ = 8.25 (m, 1H), 8.15 (d, J = 8.5, 1H), 7.89–7.96 (m, 5H), 7.77–7.80 (m, 2H), 7.66–7.70 (m, 2H), 7.51–7.62 (m, 7H), 7.45 (t, J = 7.5, 1H), 7.39 (t, J = 7.5, 1H), 7.26 (m, 1H), 7.19 (t, J = 7.0, 1H), 7.07–7.12 (m, 5H), 5.79 (dd, J = 17.5, 5.0, 1H), 4.74 (dd, J = 17.5, 11.0, 1H). ^{31}P NMR (202.4 MHz): δ = 38.5. ^{19}F NMR: δ = -80.9, -114.5, -121.4, -125.8. HRMS (FAB+): calcd for $\text{C}_{39}\text{H}_{29}\text{NP}$ ($M-\text{ONf}^-$): 542.2038, found: 542.2050. $[\alpha]_{\text{D}}$ = -219 (c = 1.07, CHCl_3). After hydrolysis of the intermediate and purification by column chromatography (Et_2O :pentane = 4:1→15:1) afforded **4b** (0.11 g, 0.20 mmol, 99%) as a yellow foam. ^1H NMR (500 MHz): δ = 8.02 (d, J = 8.5, 1H), 7.96 (d, J = 8.0, 1H), 7.90 (dd, J = 11.5, 9.0, 1H), 7.73 (d, J = 11.0, 1H), 7.72 (d, J = 11.5, 1H), 7.58 (t, J = 6.5, 1H), 7.42–7.50 (m, 3H), 7.25–7.36 (m, 10H), 7.22 (m, 1H), 7.03–7.08 (m, 2H), 6.97 (t, J = 6.5, 1H), 6.78–6.88 (m, 2H), 6.86 (d, J = 9.0, 1H), 6.60 (d, J = 8.5, 1H), 4.42 (s, 2H), 4.19 (br. s, 1H). ^{13}C NMR (125 MHz, non-aromatic only): δ = 48.2. ^{31}P NMR (202.4 MHz): δ = 28.4. IR: 3342, 1624, 1526, 1468 ν . HRMS (FAB+): calcd for $\text{C}_{39}\text{H}_{31}\text{NOP}$

($M+H^+$): 560.2143, found: 560.2139. $[\alpha]_D^{21} = -144$ ($c = 0.21$, $CHCl_3$).

(R)-2'-(Diphenyl-phosphinoyl)-[1,1']binaphthalenyl-2-ylamine (4c).

Phosphine **2** (120 mg, 0.16 mmol) was reacted with TMS-azide **5c** (75 mg, 0.65 mmol) according to the general procedure. After 12 h the reaction mixture was recharged with 75 mg of TMS-azide, and this operation was repeated once more after an additional 12 h. The reaction mixture was concentrated *in vacuo* yielding the phosphonium salt **7c** as a yellow oil in a quantitative yield: ^{31}P -NMR (202.4 MHz, C_6D_6): $\delta = 37.3$. After hydrolysis of the intermediate and purification by column chromatography (EtOAc:PE = 2:1→3:1) afforded **4c** (74 mg, 0.158 mmol, 97%) as a yellow foam. ^1H NMR: $\delta = 8.00$ (dd, $J = 8.5, 1.5$, 1H), 7.94 (d, $J = 8.5$, 1H), 7.86 (dd, $J = 11.5, 8.5$, 1H), 7.66 (d, $J = 11.5$, 1H), 7.65 (d, $J = 11.5$, 1H), 7.56 (t, $J = 7.0$, 1H), 7.51 (d, $J = 9.0$, 1H), 7.46 (d, $J = 8.0$, 1H), 7.40 (t, $J = 7.0$, 1H), 7.21–7.33 (m, 6H), 7.00–7.05 (m, 2H), 6.86–6.96 (m, 4H), 6.54 (d, $J = 8.5$, 1H), 3.90 (br. s, 2H). ^{31}P NMR (202.4 MHz): $\delta = 27.6$. IR: 1625, 1175, 1118 ν . HRMS (FAB+): calcd for $C_{32}H_{25}NOP$: 470.1674, found: 470.1651. $[\alpha]_D^{21} = -205$ ($c = 0.12$, $CHCl_3$), lit.⁴ $[\alpha]_D^{24} = -199$ ($c = 1.0$, $CHCl_3$).

(R)-[2'-(Diphenyl-phosphinoyl)-[1,1']binaphthalenyl-2-yl]-octyl-amine (4d).

Phosphine **2** (150 mg, 0.20 mmol) was reacted with 1-azido-octane **5d** (38 mg, 0.24 mmol) according to the general procedure. After 17 h the reaction mixture was concentrated *in vacuo* yielding the phosphonium salt **7d** as a yellow oil in a quantitative yield: ^{31}P NMR (202.4 MHz, C_6D_6): $\delta = 37.3$. Hydrolysis of the intermediate and purification by column

chromatography (Et₂O:pentane = 1:1→4:1) afforded **4d** (0.11 g, 0.19 mmol, 96%) as an off-white foam. ¹H NMR (500 MHz): δ = 8.02 (dd, *J* = 8.5, 2.0, 1H), 7.90–7.94 (m, 2H), 7.61–7.64 (m, 2H), 7.56 (t, *J* = 7.3, 1H), 7.40–7.52 (m, 2H), 7.39 (t, *J* = 7.0, 1H), 7.24–7.31 (m, 6H), 7.08 (t, *J* = 7.0, 1H), 7.02 (t, *J* = 7.5, 1H), 6.96 (t, *J* = 7.0, 1H), 6.89–6.93 (m, 2H), 6.85 (d, *J* = 8.5, 1H), 6.58 (d, *J* = 8.5, 1H), 3.55 (br. s, 1H), 3.04–3.14 (m, 2H), 1.42–1.49 (m, 2H), 1.20–1.33 (m, 10H), 0.90 (t, *J* = 7.0, 3H). ¹³C NMR (125 MHz, non-aromatic only): δ = 44.2, 31.7, 29.7, 29.2, 29.1, 26.9, 22.6, 14.0. ³¹P NMR (202.4 MHz): δ = 28.8. IR: ν 3400, 3054, 2924, 2853, 1619, 1598. HRMS (FAB+): calcd for C₄₀H₄₁NOP (*M*+H⁺): 582.2926, found: 582.2915. [α]_D²¹ = -139 (*c* = 0.45, CHCl₃).

(*R*)-[5-(*tert*-Butyldimethylsilanyloxy)-pentyl]-[2'-(diphenylphosphinoyl)-[1,1']binaphthalenyl-2-yl]-amine (4e**).**

Phosphine **2** (150 mg, 0.20 mmol) was reacted with (5-azido-pentyloxy)-*tert*-butyldimethylsilane **5e** (60 mg, 0.24 mmol) according to the general procedure. After 17 h the reaction mixture was concentrated *in vacuo* yielding the phosphonium salt **7e** as a yellow oil in a quantitative yield: ³¹P NMR (202.4 MHz, C₆D₆): δ = 37.4. After hydrolysis of the intermediate and purification by column chromatography (Et₂O:pentane = 2:1→8:1) afforded **4e** (0.13 g, 0.19 mmol, 93%) as an off-white foam. ¹H NMR (500 MHz): δ = 8.02 (dd, *J* = 8.5, 2.0, 1H), 7.89–7.97 (m, 2H), 7.62–7.66 (m, 2H), 7.58 (t, *J* = 7.5, 1H), 7.47–7.52 (m, 2H), 7.41 (t, *J* = 7.5, 1H), 7.22–7.33 (m, 6H), 7.01–7.08 (m, 2H), 6.96 (t, *J* = 7.0, 1H), 6.85–6.91 (m, 3H), 6.56 (d, *J* = 8.5, 1H), 3.57 (br. s, 1H), 3.54 (t, *J* = 6.5, 2H), 3.12 (m, 2H), 1.43–1.50 (m, 4H), 1.23–1.30 (m, 4H), 0.89 (s, 9H), 0.04 (s, 6H). ¹³C NMR (125 MHz, non-aromatic only): δ = 63.0, 44.2, 32.5, 29.6, 26.9, 23.2, 18.2 –5.3. ³¹P NMR (202.4 MHz): δ = 28.5. IR: 3325, 2946, 1631, 1489 ν. HRMS (FAB+): calcd for

C₄₃H₄₉NO₂PSi: 670.3270, found: 670.3267. $[\alpha]_D^{21} = -69$ (c = 0.53, CHCl₃).

(R)-4-[2'-(Diphenyl-phosphinoyl)-[1,1']binaphthalenyl-2-ylamino]-butyric acid tert-butyl ester (4f).

Phosphine **2** (100 mg, 0.14 mmol) was reacted with 4-azido-butyric acid tert-butyl ester **5f** (33 mg, 0.18 mmol) according to the general procedure. After 17 h the reaction mixture was concentrated *in vacuo* yielding the phosphonium salt **7f** as a yellow oil in a quantitative yield: ³¹P-NMR (202.4 MHz, C₆D₆): δ = 37.8. After hydrolysis of the intermediate (using aqueous 0.1N NaHCO₃ instead of aqueous 0.1 N NaOH) and purification by column chromatography (EtOAc:PE = 2:1→3:1) afforded **4f** (82 mg, 0.13 mmol, 99%) as a yellow foam. ¹H NMR (500 MHz): δ = 8.00 (dd, *J* = 8.5, 1.5, 1H), 7.94 (d, *J* = 8.5, 1H), 7.86 (dd, *J* = 11.5, 8.5, 1H), 7.66 (d, *J* = 11.5, 1H), 7.65 (d, *J* = 11.5, 1H), 7.56 (t, *J* = 7.0, 1H), 7.51 (d, *J* = 9.0, 1H), 7.46 (d, *J* = 8.0, 1H), 7.40 (t, *J* = 7.0, 1H), 7.21-7.33 (m, 6H), 7.00-7.05 (m, 2H), 6.86-6.96 (m, 4H), 6.54 (d, *J* = 8.5, 1H), 3.70 (br. s, 1H), 3.17 (m, 2H), 2.19 (t, *J* = 7.0, 2H), 1.77 (m, 2H), 1.43 (s, 9H). ¹³C NMR (125 MHz, non-aromatic only): δ = 172.6, 80.1, 43.5, 32.8, 28.0, 25.2. ³¹P NMR (202.4 MHz): δ = 28.5. IR: ν 3400, 3055, 2925, 2854, 1724, 1619, 1598. HRMS (FAB+): calcd for C₄₀H₃₉NO₃P: 612.2668, found: 612.2671. $[\alpha]_D^{21} = -58$ (c = 0.52, CHCl₃).

(R)-2-[2'-(Diphenyl-phosphinoyl)-[1,1']binaphthalenyl-2-ylamino]-3-phenyl-propionic acid ethyl ester (4g).

Phosphine **2** (188 mg, 0.25 mmol) was reacted with 2-azido-3-phenyl-propionic acid ethyl ester **5g** (84 mg, 0.38 mmol) according to the general procedure. After 17 h the reaction mixture was concentrated *in vacuo* yielding the phosphonium

salt **7g** as a yellow oil: ^{31}P NMR: $\delta = 38.4$. After hydrolysis of the intermediate (using water instead of aqueous 0.1 N NaOH) and purification by column chromatography (EtOAc:PE = 3:2) afforded **4g** (64 mg, 0.09 mmol, 39%) as an off white foam. ^1H NMR: $\delta = 8.00$ (dd, $J = 8.6, 1.7$, 1H), 7.98-7.93 (m, 2H), 7.56-7.54 (m, 1H), 7.59 (d, $J = 7.9$, 1H), 7.41 (d, $J = 8.9$, 1H), 7.34-7.27 (m, 5H), 7.21-7.19 (m, 3H), 7.13-7.09 (m, 5H), 7.08-6.99 (m, 4H), 6.92-6.90 (m, 2H), 6.68 (d, $J = 8.3$, 1H), 6.47 (d, $J = 8.9$, 1H), 5.4 (br. s, 1H), 4.15-4.12 (m, 1H), 3.93-3.80 (m, 2H), 2.99-2.89 (m, 2H), 0.94 (t, $J = 7.1$, 3H). ^{13}C NMR (non-aromatic only): $\delta = 173.1, 60.7, 58.1, 39.2, 13.9$. ^{31}P NMR: $\delta = 27.7$. IR: 3410, 3140, 2930, 1729, 1620, 1598, 1496, 1437 cm^{-1} . HRMS (FAB+): calcd for $\text{C}_{45}\text{H}_{40}\text{NO}_3\text{P}$ ($M+\text{H}^+$): 645.2433, found: 645.2437. $[\alpha]_{\text{D}}^{21} = -30.5$ ($c = 1.07$).

(R)-[2'-(diphenyl-phosphinoyl)-[1,1']binaphthalenyl-2-yl]-phenyl-amine (4h).

Phosphine **2** (105 mg, 0.14 mmol) was reacted with azido-benzene **5h** (54 mg, 0.19 mmol) according to the general procedure. After 72 h the reaction mixture was concentrated *in vacuo* yielding the phosphonium salt **7h** as a yellow oil: ^{31}P NMR (202.4 MHz, C_6D_6): $\delta = 35.6$. Hydrolysis of the intermediate and purification by column chromatography (EtOAc:PE = 3:7) afforded **4h** (48 mg, 0.09 mmol, 62%) as an off-white foam. ^1H NMR (400 MHz): $\delta = 7.95$ -7.91 (m, 3H), 7.88 (d, $J = 8.2$, 1H), 7.65 (d, $J = 8.6$, 1H), 7.62 (d, $J = 8.6$, 1H), 7.56-7.46 (m, 7H), 7.30-7.23 (m, 3H), 7.15-7.10 (m, 3H), 6.97-6.94 (m, 3H), 6.92-6.80 (m, 1H), 6.76-6.71 (m, 3H), 6.53 (d, $J = 8.4$, 1H). ^{31}P NMR (202.4 MHz): $\delta = 29.3$. IR: ν 3395, 3049, 2936, 2852. HRMS (FAB+): calcd for $\text{C}_{38}\text{H}_{29}\text{NOP}$ ($M+\text{H}^+$): 546.1987, found: 546.1984. $[\alpha]_{\text{D}}^{21} = -48$ ($c = 0.53$, CHCl_3).

3rd-Generation carbosilane dendrimer attached to the (R)-bisnaphthyl skeleton (4i).

Phosphine **2** (27 mg, 36 μ mol) was reacted with azido-3rd-generation carbosilane wedge **5i** (89 mg, 42 μ mol) according to the general procedure. After 48 h the reaction mixture was concentrated *in vacuo* yielding the phosphonium salt **7i** as a yellow oil in a quantitative yield: ³¹P NMR (202.4 MHz, C₆D₆): δ = 37.4. After hydrolysis of the intermediate (using 10 mL of THF instead of 2 mL) and purification by column chromatography (with hexane to elute the starting azido-G3-carbosilane and then with CH₂Cl₂) afforded **4i** (56 mg, 22 μ mol, 52%) as a yellow oil. ¹H NMR: δ = 8.00 (dd, J = 8.7, 1.9, 1H), 7.95-7.93 (m, 2H), 7.57-7.52 (m, 3H), 7.26-7.20 (m, 6H), 7.10-7.08 (m, 1H), 7.00-6.96 (m, 1H), 6.94-6.92 (m, 3H), 6.77 (d, J = 8.4, 1H), 6.55 (d, J = 8.3, 1H), 3.54 (br. s, 1H), 3.05 (m, 1H), 2.99 (m, 1H), 1.65 (m, 2H), 1.34-1.29 (m, 78H), 0.96-0.92 (m, 81H), 0.56-0.07 (m, 104H). ¹³C NMR (non-aromatic only): δ = 32.0, 18.8, 17.6, 15.5. ³¹P NMR (202.4 MHz): δ = 28.0. MALDI-TOF calcd for C₁₅₂H₂₉₀NOPSi₁₃: 2541.944, 2542.948, 2543.947, found: 2541.949, 2542.949, 2543.949. $[\alpha]_D^{21}$ = -14.4 (c = 2.21, CHCl₃).

(R)-Benzyl-[2'-(diphenyl-phosphino)-[1,1']binaphthalenyl-2-yl-amine (1b).

Phosphine **2** (108 mg, 0.15 mmol) was reacted with azidomethylbenzene **5b** (25 mg, 0.18 mmol) according to the general procedure. After 17 h the reaction mixture was concentrated *in vacuo* yielding the phosphonium salt **7b** as a yellow oil. ³¹P NMR (202.4 MHz): δ = 38.5. The salt was redissolved in THF and DIBAL-H (1.5M in toluene, 416 μ L, 0.62 mmol) was added at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 24h. The reaction was stopped by adding 0.5 mL of degassed water. The volatiles were evaporated and the residue purified by column chromatography (CH₂Cl₂) to afford **1b** (52 mg, 0.095 mmol, 66%) as a yellow foam. ¹H NMR (500 MHz): δ

= 7.90-7.88 (m, 2H), 7.82 (d, J = 8.9, 1H), 7.71 (d, J = 8.9, 1H), 7.65-7.53 (m, 2H), 7.51-7.49 (m, 2H), 7.47-7.03 (m, 17H), 7.00-6.97 (m, 1H), 6.62 (d, J = 8.4, 1H), 4.18 (dd, J = 15.7, 6.1, 1H), 4.01 (dd, J = 15.3, 5.8, 1H), 3.70 (br. s, 1H). ^{13}C NMR (125 MHz, non-aromatic only): δ = 47.7. ^{31}P NMR (202.4 MHz): δ = -13.9. IR: ν 1603, 1499, 1345. HRMS (FAB+): calcd for $\text{C}_{39}\text{H}_{31}\text{NP}$ ($M+\text{H}^+$): 543.2116, found: 543.2119. $[\alpha]_{\text{D}}^{21}$ = -33 (c = 0.79, CHCl_3), lit.^[4] $[\alpha]_{\text{D}}^{24}$ = -34 (c = 1.0, CHCl_3).

The phosphine oxide **4b** (11 mg, 14 μmol) was reduced according to the procedure used to prepare **2** (see above) to offer phosphine **1b** (9 mg, 12 μmol , 84%), which was spectroscopically and optically identical with **1b** obtained after DIBAL-H reduction of the phosphonium salt as described above.

Benzyl-[3`-(diphenyl-phosphinoyl)-9,9`-bis-(toluene-4-sulfonyl)-9H,9`H-[4,4`]bicarbazolyl-3-yl]-amine (9).

Phosphine **8**^[5] (150 mg, 0.13 mmol) was reacted with azidomethyl-benzene (23 mg, 0.17 mmol) according to the general procedure. After 17 h the reaction mixture was concentrated *in vacuo* yielding the intermediate phosphonium salt as a yellow oil in a quantitative yield: ^{31}P NMR (202.4 MHz, C_6D_6): δ = 38.8. Hydrolysis of the phosphonium salt and purification by column chromatography (Et_2O :pentane = 2:1 $\rightarrow$ 6:1) afforded **9** (0.12 g, 0.125 mmol, 98%) as an off-white powder of which crystals were obtained by slow evaporation of CH_2Cl_2 . M.p. 227-228 $^\circ\text{C}$. ^1H NMR (500 MHz): δ = 8.53 (d, J = 7.5, 1H), 8.21 (d, J = 8.5, 1H), 8.04 (d, J = 8.5, 1H), 8.03 (d, J = 9.0, 1H), 7.86 (dd, J = 12.5, 8.5, 1H), 7.74-7.78 (m, 2H), 7.71 (d, J = 8.0, 2H), 7.62 (d, J = 8.0, 1H), 7.48 (t, J = 7.5, 1H), 7.36-7.39 (m, 2H), 7.24-7.28 (m, 1H), 7.12-7.18 (m, 12H), 6.79-6.82 (m, 2H), 6.53-6.60 (m, 4H), 5.89 (d, J = 8.0, 1H), 5.57 (d, J = 8.0, 1H), 4.48 (br. s, 1H), 4.36 (m, 2H),

2.33 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, non-aromatic only): δ = 48.8, 21.5, 21.5. ^{31}P NMR (202.4 MHz): δ = 27.4. IR: ν 3400, 2922, 1599, 1517. HRMS (FAB+): calcd for $\text{C}_{57}\text{H}_{45}\text{N}_3\text{O}_5\text{PS}_2$: 946.2538, found: 946.2556.

X-ray data for **9**:

Abstract. (T31BOT) $\text{C}_{57}\text{H}_{44}\text{N}_3\text{O}_5\text{PS}_2$, Mr=946.1, monoclinic, $\text{P}2_1/\text{a}$, $a=12.159(2)$, $b=20.352(5)$, $c=20.815(12)\text{\AA}$, $\beta=102.34(2)^\circ$, $V=5032(3)\text{\AA}^3$, $Z=4$, $D_x=1.25\text{ gcm}^{-3}$, $\lambda(\text{CuK}\alpha)=1.5418\text{\AA}$, $\mu(\text{CuK}\alpha)=1.670\text{ mm}^{-1}$, $F(000)=1976$, room temperature, Final $R=0.082$ for 5106 observed reflections.

Experimental.

A crystal with dimensions 0.20 x 0.20 x 0.50 mm approximately was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated $\text{CuK}\alpha$ radiation and ω - 2θ scan. A total of 5472 unique reflections was measured within the range $-15\leq h\leq 13$, $0\leq k\leq 25$, $0\leq l\leq 26$. Of these, 5106 were above the significance level of $4\sigma(F_{\text{obs}})$ and were treated as observed. The range of $(\sin \theta)/\lambda$ was $0.035\text{--}0.626\text{\AA}^{-1}$ ($3.1\leq\theta\leq 74.8^\circ$). Two reference reflections ($[0\ 2\ 0]$, $[1\ 1\ 3]$) were measured hourly and showed no decrease during the 137 h collecting time. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with $39.84\leq 2\theta\leq 40.87$. Corrections for Lorentz and polarisation effects were applied. Absorption correction was performed with the program PLATON^[6], following the method of North et al.^[7] using Ψ -scans of five reflections, with coefficients in the range $0.851\text{--}0.981$. The structure was solved by the PATTY option of the DIRDIF-99 program system.^[8] After isotropic refinement a ΔF synthesis revealed some residual electron density, probably due to a solvent molecule, but they could not be interpreted as such. This electron density was corrected for with the SQUEEZE option of PLATON, based on the BYPASS-procedure.^[9] The volume of the solvent area was $220\text{ \AA}^3$, positioned around $0.0;0.5;0.5$ and the

electron-count corrected for was 89. The hydrogen atoms were calculated. Full-matrix least-squares refinement on F , anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, restraining the latter in such a way that the distance to their carrier remained constant at approximately 1.0 Å and keeping their atomic displacement parameters fixed at $U=0.1 \text{ Å}^2$, converged to $R=0.082$, $R_w=0.081$, $(\Delta/\sigma)_{\text{max}}=0.06$, $S=1.08$. A weighting scheme $w=[8. + 0.01*(\sigma(\text{Fobs}))^2 + 0.01/(\sigma(\text{Fobs}))]^{-1}$ was used. During refinement atom C20 turned out to behave extremely anisotropic, so it was decided to refine C20 isotropically and fix the three H-atoms connected to C20 at their calculated positions. A final difference Fourier map revealed a residual electron density between -0.92 and 0.91 eÅ^{-3} . Scattering factors were taken from Cromer and Mann and the International Tables for X-ray Crystallography (1974).^[10] The anomalous scattering of P and S was taken into account.^[11] All calculations were performed with XTAL3.7^[12], unless stated otherwise.

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