Electronic Supplementary Information (ESI) for:


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1. General information.

Unless otherwise noted, materials were obtained from commercial sources and used without further purification.
All syntheses of dendritic ligands and [2+2+2] cycloaddition reactions were carried out with standard high-vacuum and dry-nitrogen techniques. Toluene and THF were distilled under a nitrogen atmosphere over sodium as drying agent. When necessary, reaction mixtures were chromatographed in a silica gel column (230–400 mesh) or alumina gel column (particle size 0.05–0.15 mm) using a gradient solvent system as the eluent. NMR and mass spectroscopic data obtained for [2+2+2] cycloadducts were identical to previously reported data. $^1$H, $^{13}$C, and $^{31}$P NMR spectra were recorded with Bruker ARX250, DPX300, AV300 or AV400 spectrometers. References for NMR chemical shifts are 85% H$_3$PO$_4$ for $^{31}$P NMR, SiMe$_4$ for $^1$H and $^{13}$C NMR. NMR signal attribution was carried out using Jmod, two dimensional HBMC and HMQC, or CW $^{31}$P decoupling experiments when necessary.


The corresponding aldehyde-capped dendrimer (0.35 mmol – n = 1, 0.15 mmol – n = 2, 0.21 mmol – n = 3) was added to an ice-cooled solution of n-butylamine (7.08 mmol – n = 1, 6.07 mmol – n = 2, 15.58 mmol – n = 3, respectively) in THF (25 mL, 11 mL, 15 mL, respectively) and in the presence of molecular sieves. The reaction mixture was kept at room temperature for 24 hours before filtering through cannula and evaporated under reduced pressure. After this, the residue was then dissolved in THF:MeOH 1.5:1 (166 mL, 70 mL, 100 mL, respectively) and ice-cooled. NaBH$_4$ (11.20 mmol, 9.80 mmol, 26.44 mmol, respectively) was then slowly added and the reaction mixture was left to reach room temperature. After 18 hours, the reaction was quenched by the addition of water and concentrated under reduced pressure. The mixture was then diluted in 50 mL of dichloromethane and was washed with saturated NaHCO$_3$ solution, water and brine (20 mL each), dried over MgSO$_4$ and filtered. The removal of the solvent under reduced pressure yielded the corresponding product as a colorless foam.

A-G1 was obtained in an 89 % yield (2 steps).
$^{31}$P $^1$H NMR (121 MHz, CDCl$_3$) δ 62.78 (s, P$_1$), 8.51 (s, P$_0$). $^1$H NMR (250 MHz, CDCl$_3$) δ 7.62 (d, $^1$J$_{HH}$ = 8.6 Hz, 12H, H-C$_1$), 7.59 (s, 6H, CH=NH-P$_1$), 7.24 (d, $^1$J$_{HH}$ = 8.6 Hz, 24H, H-C$_4$), 7.14 (d, $^1$J$_{HH}$ = 7.5 Hz, 24H, H-C$_3$), 7.01 (d, $^1$J$_{HH}$ = 8.6 Hz, 12H, H-C$_2$), 3.71 (s, 24H, C$_6$H$_2$-N), 3.24 (d, $^1$J$_{HP}$ = 10.2 Hz, 18H, CH$_3$-N-P$_1$), 2.60 (t, $^1$J$_{HH}$ = 7.1 Hz, 24H, N-C$_7$H$_2$), 1.69 – 1.41 (m, 36H, C$_8$H$_2$, NH), 1.24 – 1.40 (sx, $^1$J$_{HH}$ = 7.1 Hz, 24H, C$_9$H$_2$), 0.90 (t, $^1$J$_{HH}$ = 7.2 Hz, 36H, C$_{10}$H$_3$). $^{13}$C $^1$H NMR (75 MHz, CDCl$_3$) δ 151.2 (d, $^2$J$_{CP}$ = 7.2 Hz, C$_9$), 149.5 (d, $^2$J$_{CP}$ = 7.2 Hz, C$_8$), 138.4 (d, $^2$J$_{CP}$ = 14.2 Hz, CH=NH-N-P$_1$), 137.7 (d, $^2$J$_{CP}$ = 1.4 Hz, C$_5$), 132.2 (s, C$_4$), 129.2 (s, C$_4$), 128.2 (s, C$_3$), 121.4 (bs, C$_4$), 121.2 (d, $^3$J$_{CP}$ = 4.6 Hz, C$_1$), 133.3 (s, C$_5$), 49.2 (s, C$_9$), 33.0 (d, $^2$J$_{CP}$ = 12.1 Hz, CH$_3$-N-P$_1$), 32.1 (s, C$_8$), 20.4 (s, C$_7$), 14.0 (s, C$_{10}$). Anal. Calcd for C$_{180}$H$_{240}$N$_{27}$O$_{18}$P$_9$S$_6$ (3541.16): C, 61.05; H, 6.83; N, 10.68. Found: C, 61.18; H, 6.88; N, 10.72.

**A-G2** was obtained in a 78% yield (2 steps).

$^3$P $^1$H NMR (161 MHz, CDCl$_3$) δ 62.89 (s, P$_2$), 62.41 (s, P$_1$), 8.54 (s, P$_0$). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.64 (d, $^1$J$_{HH}$ = 8.4 Hz, 36H, H-C$_1$), 7.56 (s, 18H, CH=NH-N-P$_1$, CH=NH-N-P$_2$), 7.27 – 7.21 (m, 48H, H-C$_4$), 7.19 (d, $^1$J$_{HH}$ = 8.0 Hz, 24H, H-C$_3$), 7.14 (d, $^1$J$_{HH}$ = 8.0 Hz, 48H, H-C$_5$), 6.93 (d, $^1$J$_{HH}$ = 8.3 Hz, 12H, H-C$_2$), 3.71 (s, 48H, C$_6$H$_2$-N), 3.28 (d, $^1$J$_{HP}$ = 10.2 Hz, 36H, CH$_3$-N-P$_2$), 3.22 (d, $^1$J$_{HP}$ = 10.2 Hz, 18H, CH$_3$-N-P$_1$), 2.58 (t, $^1$J$_{HH}$ = 6.8 Hz, 48H, N-C$_7$H$_2$), 1.52 – 1.40 (m, 72H, C$_8$H$_2$, NH), 1.25 – 1.39 (sx, $^1$J$_{HH}$ = 6.8 Hz, 48H, C$_9$H$_2$), 0.89 (t, $^1$J$_{HH}$ = 7.2 Hz, 72H, C$_{10}$H$_3$). $^{13}$C $^1$H NMR (100 MHz, CDCl$_3$) δ 151.2 (d, $^2$J$_{CP}$ = 7.1 Hz, C$_9$), 149.4 (d, $^2$J$_{CP}$ = 7.0 Hz, C$_8$), 139.0 (d, $^2$J$_{CP}$ = 13.6 Hz, CH=NH-N-P$_1$), 138.4 (d, $^2$J$_{CP}$ = 13.7 Hz, CH=NH-N-P$_2$), 137.8 (s, C$_5$), 132.4 (s, C$_4$), 132.1 (s, C$_3$), 129.1 (s, C$_4$), 128.2 (s, C$_3$), 128.3 (s, C$_3$), 121.7 (d, $^3$J$_{CP}$ = 3.9 Hz, C$_1$), 121.4 (bs, C$_4$), 121.2 (d, $^3$J$_{CP}$ = 4.3 Hz, C$_3$), 53.4 (s, C$_8$), 49.2 (s, C$_9$), 33.3 – 32.8 (m, CH$_3$-N-P$_1$), 32.2 (s, C$_8$), 20.4 (s, C$_7$), 14.0 (s, C$_{10}$). Anal. Calcd for C$_{408}$H$_{528}$N$_{63}$O$_{42}$P$_9$S$_{18}$ (8214.57): C, 59.65; H, 6.48; N, 10.74. Found: C, 59.66; H, 6.48; N, 10.79.

S3
A-G3 was obtained in a 65 % yield (2 steps).

$^{31}$P {$^1$H} NMR (121 MHz, CDCl$_3$) $\delta$ 62.71 (s, P$_3$), 62.45 (bs, P$_{1,2}$), 8.20 (bs, P$_0$). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.80 – 7.45 (m, 126H, H-C$_0^3$, H-C$_1^3$, H-C$_2^3$, CH=N-N-P$_{1,2,3}$), 7.40 – 6.99 (m, 276H, H-C$_0^2$, H-C$_1^2$, H-C$_2^2$, H-C$_3^2$, H-C$_4^2$), 3.70 (bs, 96H, C$_6$H$_2$-N), 3.50 – 3.10 (m, 126H, CH$_3$-N-P$_{1,2,3}$), 2.57 (bs, 96H, N-C$_7$H$_2$), 1.70 – 1.10 (m, 240H, C$_8$H$_2$, NH, C$_9$H$_2$), 0.86 (bs, 144H, C$_{10}$H$_3$). $^{13}$C {$^1$H} NMR (75 MHz, CDCl$_3$) $\delta$ 151.2 (m, C$_0^1$, C$_1^1$, C$_2^1$), 149.4 (m, C$_2$), 139.0 (d, $^3$J$_{CP}$ = 12.5 Hz, CH=N-N-P$_1$), 138.4 (d, $^3$J$_{CP}$ = 13.1 Hz, CH=N-N-P$_{2,3}$), 137.8 (s, C$_5$), 132.4 (bs, C$_0^4$, C$_1^4$, C$_2^4$), 129.1 (bs, C$_4$), 128.2 (bs, C$_0^3$, C$_1^3$, C$_2^3$), 121.8 (bs, C$_0^2$, C$_2^2$), 121.3 (s, C$_5$), 120.9 (s, C$_6^5$), 53.4 (bs, C$_6$), 49.2 (bs, C$_7$), 33.0 (d, $^2$J$_{CP}$ = 12.6 Hz, CH$_3$-N-P$_{1,2,3}$), 32.2 (s, C$_6^5$), 20.4 (s, C$_9$), 14.0 (s, C$_{10}$). Anal. Calcd for C$_{865}$H$_{1108}$N$_{135}$O$_{90}$P$_{45}$S$_{42}$ (17577.45): C, 59.11; H, 6.35; N, 10.76. Found: C, 59.15; H, 6.34; N, 10.37.

3. General procedure for the synthesis of the dendritic phosphoramidite ligands Gn.

A solution of (S)-BINOL-derived chlorophosphite$^1$ (10 mL, 0.1M) was added dropwise to a solution of the amine-capped dendrimer A-G1 (0.24 g, 0.07 mmol) and N-methylmorpholine (NMM) (0.18 mL, 1.64 mmol) in 5 mL of dry THF at 0 ºC. The reaction mixture was allowed to warm to room temperature and was stirred for 24 hours. The precipitate of NMM.HCl was filtered through cannula. After the solvent was removed under reduced pressure, the residue was redissolved in dichloromethane and precipitated in pentane. The resulting solid was then filtered and washed first with pentane:Et$_2$O 1:1, then with Et$_2$O and finally with MeOH, affording a colorless powder.

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**G1** was obtained in a 78 % yield.

$^{31}$P $^{1}H$ NMR (121 MHz, CDCl$_3$) $\delta$ 146.74 (s, P$'$), 62.85 (s, P$_1$), 8.25 (s, P$_0$). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.99 – 7.72 (m, 48H, H-C$_{\text{Binaph}}$), 7.62 – 6.29 (m, 174H, H-C$_{0}^{3}$, CH=N-N-P$_1$, H-C$_1^{3}$, H-C$_0^{2}$, H-C$_{\text{Binaph}}$), 4.20 – 3.96 (m, 12H, C$_6^{6}$$H_2$-N), 3.56 (b abs, 12H, C$_6^{6}$$H_2$-N), 3.05 – 3.30 (m, 18H, CH$_2$-N-P$_1$), 2.89 (b abs, 12H, N-C$_7^{7}$$H_2$), 2.56 (b abs, 12H, N-C$_7^{7}$$H_2$), 1.40 (b abs, 24H, C$_6^{6}$$H_2$), 1.28 – 1.05 (m, 24H, C$_6^{6}$$H_2$), 0.87 – 0.67 (m, 36H, C$_3^{3}$). $^{13}$C $^{1}H$ NMR (62.5 MHz, CDCl$_3$) $\delta$ 149.7 (m, C$_0^{1}$, C$_2^{2}$, C$_{\text{q Binaph}}$), 149.3 (s, C$_{\text{q Binaph}}$), 135.4 (bs, CH=N-N-P$_1$, C$_5^{5}$), 132.7 (s, C$_{\text{q Binaph}}$), 132.5 (s, C$_{\text{q Binaph}}$), 132.1 (s, C$_0^{4}$), 131.3 (s, C$_{\text{q Binaph}}$), 130.6 (s, C$_{\text{q Binaph}}$), 130.2 (s, CH$_{\text{Binaph}}$), 130.0 (s, CH$_{\text{Binaph}}$), 129.5 (s, C$_3^{3}$), 128.3 (s, CH$_{\text{Binaph}}$), 128.2 (s, C$_0^{2}$, C$_3^{3}$), 126.9 (s, CH$_{\text{Binaph}}$), 126.8 (bs, CH$_{\text{Binaph}}$), 126.1 (s, CH$_{\text{Binaph}}$), 124.8 (s, CH$_{\text{Binaph}}$), 124.6 (s, CH$_{\text{Binaph}}$), 123.9 (d, $^{3}J_{CP}$ = 4.4 Hz, C$_{\text{q Binaph}}$), 122.5 (s, C$_{\text{q Binaph}}$), 122.1 (s, CH$_{\text{Binaph}}$), 121.6 (s, CH$_{\text{Binaph}}$), 121.1 (bs, C$_0^{2}$, C$_3^{3}$), 47.6 – 46.8 (m, C$_6^{6}$), 44.9 – 43.9 (m, C$_7^{7}$), 33.3 – 32.5 (m, CH$_3$-N-P$_1$), 30.3 (s, C$_8^{8}$), 19.8 (s, C$_9^{9}$), 13.7 (s, C$_{10}^{10}$). Anal. Calcd for C$_{420}$H$_{372}$N$_2$O$_{42}$P$_{2}$S$_6$ (7312.44): C, 68.99; H, 5.13; N, 5.17. Found: C, 69.01; H, 5.17; N, 5.20. $[\alpha]_{D}^{20}$ +222.69 (c 0.52, THF).

**G2** was obtained in a 60 % yield.

$^{31}$P $^{1}H$ NMR (121 MHz, CDCl$_3$) $\delta$ 146.74 (s, P$'$), 62.94 (s, P$_2$), 62.43 (s, P$_1$), 8.31 (s, P$_0$). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.99 – 7.71 (m, 102H, H-C$_{\text{Binaph}}$), 7.70 – 6.78 (m, 372H, H-C$_{0}^{3}$, H-C$_1^{3}$, CH=N-N-P$_{1,2}$, H-C$^4$, H-C$^3$, H-C$_0^{2}$, H-C$_1^{2}$, H-C$_{\text{Binaph}}$), 4.06 (b abs, 24H, C$_6^{6}$$H_2$-N), 3.58 (b abs, 24H, C$_6^{6}$$H_2$-N), 3.16 (b abs, 54H, CH$_3$-N-P$_{1,2}$), 2.88 (b abs, 24H, N-C$_7^{7}$$H_2$), 2.55 (b abs, 24H, N-C$_7^{7}$$H_2$), 1.40 (b abs, 48H, C$_6^{6}$$H_2$), 1.15 (b abs, 48H, C$_6^{6}$$H_2$), 0.76 (b abs, 72H, C$_{10}^{10}$). $^{13}$C $^{1}H$ NMR (75 MHz, CDCl$_3$) $\delta$ 151.2 (d, $^{2}J_{CP} = \ldots$)
7.2 Hz, C₀¹, C₁¹), 149.6 (m, C², C₉ Binapht), 149.3 (s, C₄ Binapht), 138.5 – 138.3 (m, CH=N-N-P₁₂), 135.4 (s, C⁵), 132.7 (s, C₅ Binapht), 132.6 – 131.8 (m, C₀⁴, C₁⁴), 131.3 (s, C₆ Binapht), 130.6 (s, C₇ Binapht), 130.3 (s, CH Binapht), 130.1 (s, CH Binapht), 129.5 (s, C⁴), 128.3 (s, CH Binapht), 128.2 (s, C₀³, C₁³, CH Binapht), 126.9 (s, CH Binapht), 126.8 (s, CH Binapht), 126.1 (s, CH Binapht), 124.8 (s, CH Binapht), 124.6 (s, CH Binapht), 123.9 (d, JʃCP = 4.8 Hz, C₄ Binapht), 122.6 (s, C₅ Binapht), 122.1 (s, CH Binapht), 121.9 – 121.4 (m, CH Binapht • C₀², C₁², C⁵), 47.2 (d, JʃCP = 12.6 Hz, C⁶), 44.4 (d, JʃCP = 28.1 Hz, C⁷), 32.9 (d, JʃCP = 12.6 Hz, CH₃-N-P₁₂), 30.3 (s, C⁸), 19.8 (s, C⁹), 13.7 (s, C¹⁰). Anal. Calcd for C₄₈₈H₇₉₂N₆₃O₉₆P₂₅S₁₈ (15757.15): C, 67.69; H, 5.07; N, 5.60. Found: C, 67.71; H, 5.05; N, 5.64. [α]²⁰D +230.57 (c 0.53, THF).

G₃ was obtained in an 88 % yield.

³¹P {¹H} NMR (121 MHz, CDCl₃) δ 146.76 (s, P'), 62.84 (s, P₃), 62.43 (bs, P₁₂), 8.10 (bs, P₀). ¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.44 (m, 396H, H-CBinapht, H-C⁰³, H-C₁³, H-C₂³, CH=N-N-P₁₂). 7.40 – 7.07 (m, 582H, H-CBinapht • H-C⁰², H-C₁², H-C₂², H-C³, H-C⁴), 4.10 (b abs, 48H, C⁶H₂-N), 3.19 (b abs, 126H, CH₃-N-P₁₂), 2.89 (b abs, 48H, N-C¹⁰H₂), 2.56 (b abs, 48H, N-C⁷H₂), 1.40 (b abs, 96H, C⁸H₂), 1.26 – 1.02 (m, 96H, C⁰⁰H₂), 0.77 (b abs, 144H, C¹⁰H₃). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 151.3 (d, JʃCP = 7.0 Hz, C₀¹, C₁¹, C₂¹), 149.8 – 149.5 (m, C², C₄ Binapht), 149.3 (s, C₆ Binapht), 139.3 – 138.2 (m, CH=N-N-P₁₂), 135.3 (s, C⁵), 132.7 (s, C₇ Binapht), 132.5 (s, C₈), 132.4 – 131.9 (m, C₉, C₄), 131.3 (s, C₉ Binapht), 130.6 (s, C₈ Binapht), 130.3 (s, CH Binapht), 130.1 (s, CH Binapht), 129.5 (s, C⁸), 128.3 (s, CH Binapht), 128.2 (s, CH Binapht), 126.0 (s, CH Binapht), 126.8 (s, CH Binapht), 125.8 (s, CH Binapht), 124.8 (s, CH Binapht), 124.6 (s, CH Binapht), 123.9 (d, JʃCP = 4.5 Hz, C₆ Binapht), 122.6 (s, C₇ Binapht), 122.1 (s, CH Binapht), 121.9 – 121.4 (m, CH Binapht • C₀², C₁², C⁵), 121.2 (s, C⁶), 47.3 (d, JʃCP = 10.9 Hz, C⁷), 44.4 (d, JʃCP = 27.4 Hz, C⁸), 32.9 (d, JʃCP = 12.3 Hz, CH₃-N-P₁₂), 30.3 (s, C⁸), 19.8 (s, C⁹), 13.8 (s, C¹⁰). Anal. Calcd for C₁₈₂₄H₂₆₃₂N₁₃₅O₁₈₅P₂₅S₄₂ (32646.56): C, 67.11; H, 5.04; N, 5.79. Found: C, 67.14; H, 5.07; N, 5.75. [α]²⁰D +242.77 (c 0.51, THF).
5. Synthesis of the monomeric phosphoramidite ligand M and characterization data.

A solution of (S)-BINOL-derived chlorophosphate (11 mL, 0.1M) was added dropwise to a solution of N-(4-methoxybenzyl)-1-butanamine (0.20 g, 1.03 mmol) and N-methylmorpholine (NMM) (0.56 mL, 5.17 mmol) in 5 mL of dry THF at 0 ºC. The reaction mixture was allowed to warm to room temperature and was stirred for 24 hours. The precipitate of NMM.HCl was filtered through cannula. After the solvent was removed under reduced pressure, the residue was purified by flash chromatography to give M (0.47 g, 89 % yield) as a colorless foam.

\[ \text{CH}_{3}\text{O}\text{C}_{2}\text{C}_{5}\text{C}_{4}\text{C}_{3}\text{N}_{6}\text{7} \]

\[ \text{1}^3\text{P}\{\text{H}\}\text{NMR (121 MHz, CDCl}_3\text{) }\delta 147.16 \text{ (s, P').} \]

\[ \text{1}^1\text{H NMR (300 MHz, CDCl}_3\text{) }\delta 8.05 – 7.84 \text{ (m, 4H, H-C}_{\text{Binapht.}}, 7.59 \text{ (d, }^3\text{J}_{\text{HH}} = 8.7 \text{ Hz, 1H, H-C}_{\text{Binapht.}})\text{, }7.48 – 7.32 \text{ (m, 5H, H-C}_{\text{Binapht.}}\text{, }7.31 – 7.23 \text{ (m, 2H, H-C}_{\text{Binapht.}}\text{, }7.22 \text{ (d, }^3\text{J}_{\text{HH}} = 8.7 \text{ Hz, 2H, H-C}^3\text{)}, 6.88 \text{ (d, }^3\text{J}_{\text{HH}} = 8.7 \text{ Hz, 2H, H-C}^3\text{)}, 4.17 \text{ (dd, }^2\text{J}_{\text{HH}} = 14.9 \text{ Hz, }^3\text{J}_{\text{HP}} = 9.1 \text{ Hz, 1H, C}^6\text{H}_2\text{-N), 3.01 – 2.85 (m, 1H, N-C}_{\text{7}}\text{H}_{2}\text{), 2.74 – 2.53 (m, 1H, N-C}^7\text{H}_2\text{), 1.55 – 1.42 (m, 2H, C}^8\text{H}_2\text{), 1.38 – 1.10 (m, 2H, C}_{\text{9}}\text{H}_2\text{), 0.86 (t, }^3\text{J}_{\text{HH}} = 7.3 \text{ Hz, 3H, C}^{10}\text{H}_3\text{).} \]

\[ \text{13}^1\text{C NMR (75 MHz, CDCl}_3\text{) }\delta 158.7 \text{ (s, C}_{\text{2}}\text{), 149.9 (d, }^2\text{J}_{\text{CP}} = 5.2 \text{ Hz, C}_{\text{q Binapht.}}\text{), 149.5 (s, C}_{\text{q Binapht.}}\text{), 132.8 (s, C}_{\text{q Binapht.}}\text{), 132.6 (s, C}_{\text{q Binapht.}}\text{), 131.4 (s, C}_{\text{q Binapht.}}\text{), 130.6 (s, C}_{\text{q Binapht.}}\text{), 130.2 (s, C}^5\text{), 130.1 (s, CH}_{\text{Binapht.}}\text{), 129.9 (s, CH}_{\text{Binapht.}}\text{), 129.6 (s, C}^6\text{), 128.3 (s, CH}_{\text{Binapht.}}\text{), 128.2 (s, CH}_{\text{Binapht.}}\text{), 127.0 (s, CH}_{\text{Binapht.}}\text{), 126.9 (s, CH}_{\text{Binapht.}}\text{), 126.0 (s, CH}_{\text{Binapht.}}\text{), 125.9 (s, CH}_{\text{Binapht.}}\text{), 124.7 (s, CH}_{\text{Binapht.}}\text{), 124.5 (s, CH}_{\text{Binapht.}}\text{), 124.0 (d, }^3\text{J}_{\text{CP}} = 4.9 \text{ Hz, C}_{\text{q Binapht.}}\text{), 122.6 (d, }^3\text{J}_{\text{CP}} = 2.1 \text{ Hz, C}_{\text{q Binapht.}}\text{), 122.2 (d, }^3\text{J}_{\text{CP}} = 1.7 \text{ Hz, CH}_{\text{Binapht.}}\text{), 121.8 (s, CH}_{\text{Binapht.}}\text{), 113.6 (s, C}^3\text{), 55.3 (s, CH}_{3}\text{O}, 47.3 (d, }^2\text{J}_{\text{CP}} = 14.3 \text{ Hz, C}^6\text{), 44.1 (d, }^2\text{J}_{\text{CP}} = 26.9 \text{ Hz, C}^7\text{), 30.3 (d, }^3\text{J}_{\text{CP}} = 2.2 \text{ Hz, C}^8\text{), 19.8 (s, C}^9\text{), 13.8 (s, C}^{10}\text{).} \]

Anal. Calcd for C_{32}H_{30}NO_3P (507.56): C, 75.72; H, 5.96; N, 2.76. Found: C, 75.69; H, 6.00; N, 2.79. [\alpha]^{20}_D +322.26 (c 0.53, THF).
6. Synthesis of the dimeric phosphoramidite branch B and characterization data.

Synthesis of B-(CHO)$_2$

B-(P(S)Cl)$_2$ [MeOC$_6$H$_4$CH=N-N(Me)-P(S)Cl]$_2$ (2.00g, 6.73 mmol) was dissolved in THF, and then 4-hydroxybenzaldehyde (13.6 mmol) and cesium carbonate (13.6 mmol) were added. Reaction mixture was stirred overnight at room temperature, and then centrifuged. The solution was concentrated and the solid obtained was washed few times in pentane/Et$_2$O (9:1) mixture. The resulting powder was filtered and dried under vacuum to yield the desired product (2.68g, 85% yield) as a colorless solid.

$^{31}$P {$_1$H} NMR (121.5 MHz, CDCl$_3$) δ 60.60 (s, P). $^1$H NMR (300 MHz, CDCl$_3$) δ 9.98 (s, 2H, CHO), 7.89 (d, $^3$J$_{HH}$ = 8.6 Hz, 4H, H-C$^4$), 7.63 (m, 3H, H-C$^0$, and CH=N-N-P), 7.43 (d, $^3$J$_{HH}$ = 8.6 Hz, 4H, H-C$^5$), 6.94 (d, $^3$J$_{HH}$ = 8.8 Hz, 2H, H-C$^0$), 3.85 (s, 3H, CH$_3$O), 3.41 (d, $^3$J$_{HP}$ = 11.1 Hz, 3H, CH$_3$-N-P), 2.57 (bs, 4H, N-C$_7$H$_2$), 1.87 (bs, 2H, NH), 1.45 (bs, 4H, C$_6$H$_2$), 1.32 (bs, 4H, C$_6$H$_2$), 0.89 (bs, 6H, C$_{10}$H$_3$). $^{13}$C ($^1$H) NMR (75 MHz, CDCl$_3$) δ 190.77 (s, CHO), 161.03 (s, C$_0$), 155.28 (d, $^2$J$_{CP}$ = 7.3 Hz, C$^2$), 140.67 (d, $^3$J$_{CP}$ = 13.8 Hz, CH=N-N-P), 133.64 (s, C$^5$), 131.42 (s, C$^4$), 128.52 (s, C$_0$), 127.17 (s, C$_0$), 121.05 (s, C$^3$), 114.28 (s, C$_0$), 57.40 (s, CH$_3$O), 32.85 (d, $^2$J$_{CP}$ = 13.7 Hz, CH$_3$-N-P). Anal. Calcd for C$_{23}$H$_{21}$N$_2$O$_5$PS (468.46): C, 58.97; H, 4.52; N, 5.98. Found: C, 59.01; H, 4.50; N, 5.96.

Synthesis of B-(NH)$_2$

To an ice-cooled solution of n-butylamine (10.5 mmol) in THF (30 mL) and in the presence of molecular sieves was added B-(CHO)$_2$ (1.52 g, 3.25 mmol). After the addition, the reaction mixture was kept at room temperature for 24 hours and was then filtered through cannula and evaporated...

---

under reduced pressure. After that, the residue was then dissolved in THF:MeOH 1.5:1 (166 mL, 70 mL, 100 mL, respectively) and ice-cooled. Then, NaBH₄ (17.3 mmol) was slowly added and the reaction mixture was led to reach room temperature. After 18 hours, the reaction was quenched by addition of water and concentrated under reduced pressure. The mixture was then diluted in 50 mL of dichloromethane and was washed with sat. NaHCO₃ solution, water and brine (20 mL each), dried over MgSO₄ and filtered. Removal of the solvent under reduced pressure yielded the corresponding product (1.42 g, 75 % yield over two steps) as a colorless oil.

![Chemical Structure]

³¹P {¹H} NMR (121.5 MHz, CDCl₃) δ 62.86 (s, P). ¹H NMR (300 MHz, CDCl₃) δ 7.63 (m, 3H, H-C₀ and CH=N-N-P), 7.21 (m, 8H, H-C³ and H-C⁴), 6.90 (bs, 2H, H-C₀), 3.77 (s, 3H, CH₃), 3.70 (bs, 4H, C₆H₂-N), 3.29 (d, ³J_HP = 9.0 Hz, 3H, CH₃-N-P), 2.57 (bs, 4H, N-C⁴H₂), 1.87 (bs, 2H, NH), 1.45 (bs, 4H, C₈H₂), 1.32 (bs, 4H, C₈H₂), 0.89 (bs, 6H, C¹⁰H₂). ¹³C {¹H} NMR (75 MHz, CDCl₃) δ 160.68 (s, C₁), 149.62 (d, ²J_CP = 7.2 Hz, C²), 139.45 (d, ³J_CP = 13.7 Hz, CH=N-N-P), 137.50 (s, C⁵), 129.15 (s, C⁴), 128.45 (s, C₀), 127.73 (s, C₀), 121.34 (d, ³J_CP = 4.45 Hz, C³), 114.14 (s, C₀), 55.31 (s, CH₃O), 53.34 (s, C⁶), 49.14 (s, C⁵), 33.0 (d, ²J_CP = 13.0 Hz, CH₃-N-P), 32.12 (s, C⁶), 20.46 (s, C⁹), 14.05 (s, C¹⁰). Anal. Calcd for C₃₁H₄₃N₄O₃PS (582.74): C, 63.89; H, 7.44; N, 9.61. Found: C, 63.62; H, 7.89; N, 9.73.

Synthesis of B

A solution of (S)-BINOL-derived chlorophosphite (23 mL, 0.1M) was added dropwise to a solution of B-(NH)₂(1.23 g, 2.11 mmol) and N-methylmorpholine (NMM) (0.56 mL, 5.17 mmol) in 15 mL of dry THF at 0 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 24 hours. The precipitate of NMM.HCl was filtered through cannula. After the solvent was removed under reduced pressure, the residue was purified by flash chromatography to give B (0.80 g, 31 % yield) as a colorless solid.
$^{31}$P $^1$H NMR (160 MHz, CDCl$_3$) $\delta$ 146.90 (s, P’), 146.86 (s, P’), 63.03 (s, P$_1$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (d, $^3$J$_{HH} = 8.8$ Hz, 2H, H-C$_{Binapht.}$), 7.90 (d, $^3$J$_{HH} = 8.0$ Hz, 2H, H-C$_{Binapht.}$), 7.86 – 7.81 (m, 4H, H-C$_{Binapht.}$), 7.64 (d, $^3$J$_{HH} = 8.8$ Hz, 2H, H-C$_{0}^3$), 7.57 (m, 1H, CH=N-N-P$_1$), 7.53 (d, $^3$J$_{HH} = 8.8$ Hz, 2H, H-C$_{0}^3$), 7.12 – 7.42 (m, 22H, H-C$_4$, H-C$_3$, H-C$_{Binapht.}$), 6.90 (d, $^3$J$_{HH} = 8.8$ Hz, 2H, H-C$_{0}^3$), 4.07 – 4.14 (m, 2H, C$_6$H$_2$-N), 3.81 (s, 3H, CH$_3$O), 3.56 – 3.64 (m, 2H, C$_6'$H$_2$-N), 3.32 (d, $^3$J$_{CP} = 10.8$ Hz, 3H, CH$_3$-N-P$_1$), 2.97 – 2.85 (m, 2H, N-C$_7$H$_2$), 2.65 – 2.51 (m, 2H, N-C$_7$H$_2$), 1.52 – 1.39 (m, 4H, C$_8$H$_2$), 1.23 – 1.08 (m, 2H, C$_9$H$_2$), 0.82 (t, $^3$J$_{HH} = 7.4$ Hz, 6H, C$_{10}^3$H$_3$)$_2$. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.7 (s, C$_0^1$), 149.7 (d, $^2$J$_{CP} = 5.6$ Hz, C$_5$), 149.3 (s, C$_q$ Binaph.), 139.4 (d, $^3$J$_{CP} = 13.6$ Hz, CH=N-N-P), 135.2 (s, C$_5$), 132.8 (s, C$_q$ Binaph.), 132.5 (s, C$_q$ Binaph.), 131.3 (s, C$_q$ Binaph.), 130.6 (s, C$_q$ Binaph.), 130.2 (s, CH$_{Binapht.}$), 130.0 (s, CH$_{Binapht.}$), 129.4 (s, C$_4$), 128.4 (s, C$_0^3$), 128.3 (s, CH$_{Binapht.}$), 128.2 (s, CH$_{Binapht.}$), 127.7 (s, C$_0^4$), 127.0 (s, CH$_{Binapht.}$), 126.9 (s, CH$_{Binapht.}$), 126.0 (s, CH$_{Binapht.}$), 124.7 (s, CH$_{Binapht.}$), 124.5 (s, CH$_{Binapht.}$), 124.0 (m, C$_q$ Binaph.), 122.5 (m, C$_q$ Binaph.), 122.1 (s, CH$_{Binapht.}$), 121.6 (s, CH$_{Binapht.}$), 121.3 (d, $^3$J$_{CP} = 4.7$ Hz, C$_3$), 114.1 (s, C$_0^2$), 55.3 (s, CH$_3$O), 47.2 (d, $^2$J$_{CP} = 11.7$ Hz, C$_8$), 44.4 (d, $^2$J$_{CP} = 29.1$ Hz, C$_7$), 33.0 (d, $^2$J$_{CP} = 13.1$ Hz, CH$_3$-N-P), 30.3 (d, $^3$J$_{CP} = 1.9$ Hz, C$_8$), 19.8 (s, C$_9$), 13.7 (s, C$_{10}$).
7. Rhodium-catalyzed \( [2 + 2 + 2] \) cycloaddition of \( \text{N,N-bis(2-butynyl)-(4-methylphenyl)sulfonamide} \) 1 with phenylacetylene 2. General Procedure.

Dendrimer bearing phosphoramidite end groups \( \text{Gn} \) (generation 1: 4.6 mg, \( 6.2 \times 10^{-4} \) mmol, generation 2: 4.9 mg, \( 3.1 \times 10^{-4} \) mmol, generation 3: 5.1 mg, \( 1.6 \times 10^{-4} \) mmol; each case corresponds to 5 mol% end groups) and \([\text{Rh(C}_2\text{H}_4\text{Cl}_2]\) 2 (1.2 mg, \( 3.7 \times 10^{-3} \) mmol) were dissolved in dry toluene (1.0 mL) and the mixture was stirred at room temperature for 30 min. To this solution a toluene (1.0 mL) solution of \( \text{N,N-bis(2-butynyl)-(4-methylphenyl)sulfonamide} \) (41.3 mg, 0.15 mmol) and phenylacetylene (84 \( \mu \)L, 0.75 mmol) was added dropwise over 10 min at RT. The mixture was stirred at reflux for 2 h. Hexanes (10 mL) was then added to precipitate the dendritic catalyst, which was recovered by filtration and washed twice with hexanes. The precipitated catalyst was dried and kept for a future use following the same procedure without reloading with rhodium. The filtrate and the washing solutions were concentrated together and purified by column chromatography (hexane:AcOEt = 20:1) to afford the corresponding product.

8. Rhodium-Catalyzed Enantioselective \( [2 + 2 + 2] \) Cycloaddition of \( \text{N,N-bis(2-butynyl)-(4-methylphenyl)sulfonamide} \) 1 with alkynyl substrate 4. General Procedure.

Dendrimer bearing phosphoramidite end groups \( \text{Gn} \) (generation 1: 3.0 mg, \( 4.2 \times 10^{-4} \) mmol, generation 2: 3.3 mg, \( 2.1 \times 10^{-4} \) mmol, generation 3: 3.4 mg, \( 1.0 \times 10^{-4} \) mmol; each case corresponding to 5 mol% end groups) and \([\text{Rh(C}_2\text{H}_4\text{Cl}_2]\) 2 (1.0 mg, \( 2.5 \times 10^{-3} \) mmol) were dissolved in dry toluene (0.2 mL) and the mixture was stirred at RT for 30 min. A toluene (0.2 mL) solution of the alkynyl phosphonate or carbonate 4 (31.8 mg, 0.10 mmol) was then added to this and then a toluene (0.6 mL) solution of \( \text{N,N-bis(2-butynyl)-(4-methylphenyl)sulfonamide} \) 1 (41.3 mg, 0.15 mmol) was added dropwise over 20 min at RT. After stirring at RT for 48 h, 10 mL of hexanes were added to precipitate the dendritic catalyst, which was recovered by filtration and washed twice with hexanes. The precipitated catalyst was dried and kept for a future use following the same procedure without reloading with rhodium. The filtrate and the washing solutions were concentrated together and purified by column chromatography (hexane:AcOEt = 1:1) to afford the corresponding product 5.
9. $^{31}$P \textsuperscript{1}H NMR, $^{1}$H NMR and $^{13}$C \textsuperscript{1}H NMR spectra of dendrimers A-Gn

A-G1, $^{31}$P \textsuperscript{1}H NMR (121 MHz, CDCl\textsubscript{3})

A-G1, $^{1}$H NMR (250 MHz, CDCl\textsubscript{3})
A-G1, $^{13}$C ($^1$H) NMR (75 MHz, CDCl$_3$)

A-G2, $^{31}$P ($^1$H) NMR (161 MHz, CDCl$_3$)
A-G2, $^1$H NMR (400 MHz, CDCl$_3$)

A-G2, $^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$)
A-G3, $^3$P $^1$H NMR (121 MHz, CDCl$_3$)

A-G3, $^1$H NMR (300 MHz, CDCl$_3$)
A-G3, $^{13}$C ($^1$H) NMR (75 MHz, CDCl$_3$)

10. $^{31}$P ($^1$H) NMR, $^1$H NMR and $^{13}$C ($^1$H) NMR spectra of dendrimers Gn

G1, $^{31}$P ($^1$H) NMR (121 MHz, CDCl$_3$)
SI, ¹H NMR (300 MHz, CDCl₃)

G1, ¹³C [¹H] NMR (62 MHz, CDCl₃)
Electronic Supplementary Material (ESI) for Chemical Communications
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G2, $^{31}$P ($^1$H) NMR (121 MHz, CDCl$_3$)

G2, $^1$H NMR (300 MHz, CDCl$_3$)
G2, $^{13}$C($^1$H)-RMN (75 MHz, CDCl$_3$) δ (ppm):

![NMR Spectrum](image1)

G3, $^{31}$P($^1$H)-RMN (121 MHz, CDCl$_3$) δ (ppm):

![NMR Spectrum](image2)
G3, $^1$H NMR (400 MHz, CDCl$_3$)

G3, $^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$)
11. $^{31}$P ($^1$H) NMR, $^1$H NMR and $^{13}$C ($^1$H) NMR spectra of M and B

M, $^{31}$P ($^1$H) NMR (121 MHz, CDCl$_3$)

M, $^1$H NMR (300 MHz, CDCl$_3$)
M, $^{13}\text{C} \left( ^1\text{H} \right)$ NMR (75 MHz, CDCl$_3$)

B, $^{31}\text{P} \left( ^1\text{H} \right)$ NMR (162 MHz, CDCl$_3$)
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012
12. HPLC chromatograms of compounds 5

Racemic mixture:

![HPLC chromatogram of a racemic mixture](image)

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Totals: 55437292 964185 100.00

- Entry 1, Table 2:

![HPLC chromatogram for Entry 1, Table 2](image)

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### Entry 2, Table 2:

![Retention Time Graph](image)

**UV-254nm Results**

**Reprocessed**

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**Totals**

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### Entry 3, Table 2:

![Retention Time Graph](image)

**UV-254nm Results**

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- **Racemic mixture:**

![Racemic mixture graph](image)

**Table 2: UV-254 nm Results (Reprocessed)**

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- **Entry 6, Table 2:**

![Entry 6 graph](image)

**Table 2: UV-254 nm Results (Reprocessed)**

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**Entry 9, Table 2:**

![Graph showing retention time vs. peak area]

**UV-254nm Results**
**(Reprocessed)**

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**Totals**

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