Electronic Supplementary Information (ESI) for:

Dendritic Phosphoramidite Ligands for Rh-catalyzed [2+2+2] Cycloaddition Reactions: Unprecedented Enhancement of Enantiodiscrimination

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Contents

1. General information.

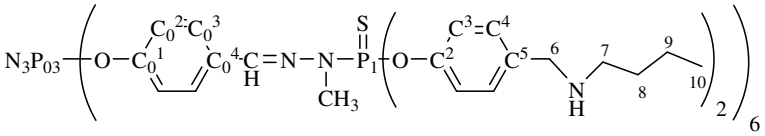
Unless otherwise noted, materials were obtained from commercial sources and used without further purification.

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_3PO_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.

2. Synthesis of dendrimers A-Gn.

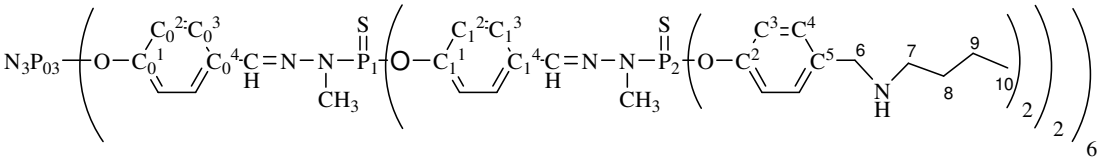
The corresponding aldehyde-capped dendrimer (0.35 mmol – n = 1, 0.15 mmol – n = 2, 0.21 mmol – n = 3) was added to an ice-cooled solution of *n*-butylamine (7.08 mmol – n = 1, 6.07 mmol – n = 2, 15.58 mmol – n = 3, respectively) in THF (25 mL, 11 mL, 15 mL, respectively) and in the presence of molecular 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).



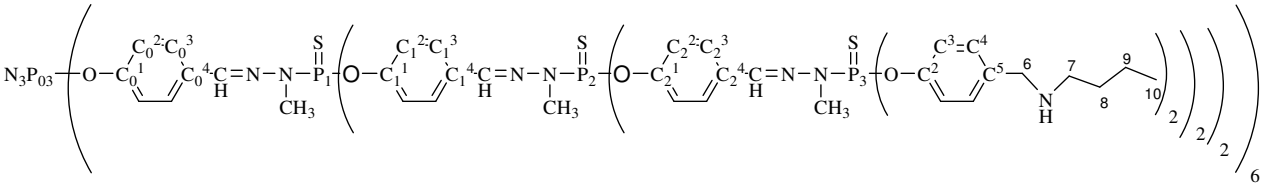
^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$) δ 62.78 (s, P_1), 8.51 (s, P_0). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.62 (d, $^{3}J_{HH}$ = 8.6 Hz, 12H, H-C_0^3), 7.59 (s, 6H, CH=N-N-P_1), 7.24 (d, $^{3}J_{HH}$ = 8.6 Hz, 24H, H-C^4), 7.14 (d, $^{3}J_{HH}$ = 7.5 Hz, 24H, H-C^3), 7.01 (d, $^{3}J_{HH}$ = 8.6 Hz, 12H, H-C_0^2), 3.71 (s, 24H, C^6H_2-N), 3.24 (d, $^{3}J_{HP}$ = 10.2 Hz, 18H, CH_3-N-P_1), 2.60 (t, $^{3}J_{HH}$ = 7.1 Hz, 24H, N-C^7H_2), 1.69 – 1.41 (m, 36H, C^8H_2, NH), 1.24 – 1.40 (sx, $^{3}J_{HH}$ = 7.1 Hz, 24H, C^9H_2), 0.90 (t, $^{3}J_{HH}$ = 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_0^1), 149.5 (d, $^{2}J_{CP}$ = 7.2 Hz, C^2), 138.4 (d, $^{3}J_{CP}$ = 14.2 Hz, CH=N-N-P_1), 137.7 (d, $^{5}J_{CP}$ = 1.4 Hz, C^5), 132.2 (s, C_0^4), 129.2 (s, C^4), 128.2 (s, C_0^3), 121.4 (bs, C_0^2), 121.2 (d, $^{3}J_{CP}$ = 4.6 Hz, C^3), 53.3 (s, C^6), 49.2 (s, C^7), 33.0 (d, $^{2}J_{CP}$ = 12.1 Hz, CH_3-N-P_1), 32.1 (s, C^8), 20.4 (s, C^9), 14.0 (s, C^{10}). Anal. Calcd for $C_{180}H_{240}N_{27}O_{18}P_9S_6$ (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).



^{31}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, $^{3}J_{HH}$ = 8.4 Hz, 36H, H-C_0^3, H-C_1^3), 7.56 (s, 18H, CH=N-N-P_1, CH=N-N-P_2), 7.27 – 7.21 (m, 48H, H-C^4), 7.19 (d, $^{3}J_{HH}$ = 8.0 Hz, 24H, H-C_1^2), 7.14 (d, $^{3}J_{HH}$ = 8.0 Hz, 48H, H-C^3), 6.93 (d, $^{3}J_{HH}$ = 8.3 Hz, 12H, H-C_0^2), 3.71 (s, 48H, C^6H_2-N), 3.28 (d, $^{3}J_{HP}$ = 10.2 Hz, 36H, CH_3-N-P_2), 3.22 (d, $^{3}J_{HP}$ = 10.2 Hz, 18H, CH_3-N-P_1), 2.58 (t, $^{3}J_{HH}$ = 6.8 Hz, 48H, N-C^7H_2), 1.52 – 1.40 (m, 72H, C^8H_2, NH), 1.25 – 1.39 (sx, $^{3}J_{HH}$ = 6.8 Hz, 48H, C^9H_2), 0.89 (t, $^{3}J_{HH}$ = 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_0^1, C_1^1), 149.4 (d, $^{2}J_{CP}$ = 7.0 Hz, C^2), 139.0 (d, $^{3}J_{CP}$ = 13.6 Hz, CH=N-N-P_1), 138.4 (d, $^{3}J_{CP}$ = 13.7 Hz, CH=N-N-P_2), 137.8 (s, C^5), 132.4 (s, C_1^4), 132.1 (s, C_0^4), 129.1 (s, C^4), 128.2 (s, C_1^3), 128.3 (s, C_0^3), 121.7 (d, $^{3}J_{CP}$ = 3.9 Hz, C_1^2), 121.4 (bs, C_0^2), 121.2 (d, $^{3}J_{CP}$ = 4.3 Hz, C^3), 53.4 (s, C^6), 49.2 (s, C^7), 33.3 – 32.8 (m, CH_3-N-$P_{1,2}$), 32.2 (s, C^8), 20.4 (s, C^9), 14.0 (s, C^{10}). Anal. Calcd for $C_{408}H_{528}N_{63}O_{42}P_{21}S_{18}$ (8214.57): C, 59.65; H, 6.48; N, 10.74. Found: C, 59.66; H, 6.48; N, 10.79.

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



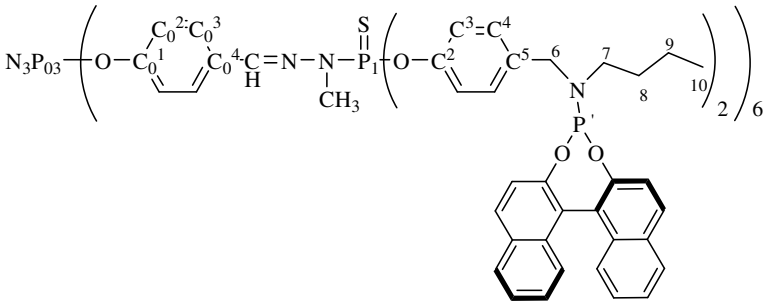
^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$) δ 62.71 (s, P_3), 62.45 (bs, $P_{1,2}$), 8.20 (bs, P_0). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 – 7.45 (m, 126H, H-C_0^3, H-C_1^3, H-C_2^3, CH=N-N-$P_{1,2,3}$), 7.40 – 6.99 (m, 276H, H-C_0^2, H-C_1^2, H-C_2^2, H-C^3, H-C^4), 3.70 (bs, 96H, C^6H_2-N), 3.50 – 3.10 (m, 126H, CH_3-N- $P_{1,2,3}$), 2.57 (bs, 96H, N-C^7H_2), 1.70 – 1.10 (m, 240H, C^8H_2, NH, C^9H_2), 0.86 (bs, 144H, $C^{10}H_3$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 151.2 (m, C_0^1, C_1^1, C_2^1), 149.4 (m, C^2), 139.0 (d, $^3J_{CP}$ = 12.5 Hz, CH=N-N-P_1), 138.4 (d, $^3J_{CP}$ = 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_1^2, C_2^2), 121.3 (s, C^3), 120.9 (s, C_0^2), 53.4 (bs, C^6), 49.2 (bs, C^7), 33.0 (d, $^2J_{CP}$ = 12.6 Hz, CH_3-N-$P_{1,2,3}$), 32.2 (s, C^8), 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_2O 1:1, then with Et_2O and finally with MeOH, affording a colorless powder.

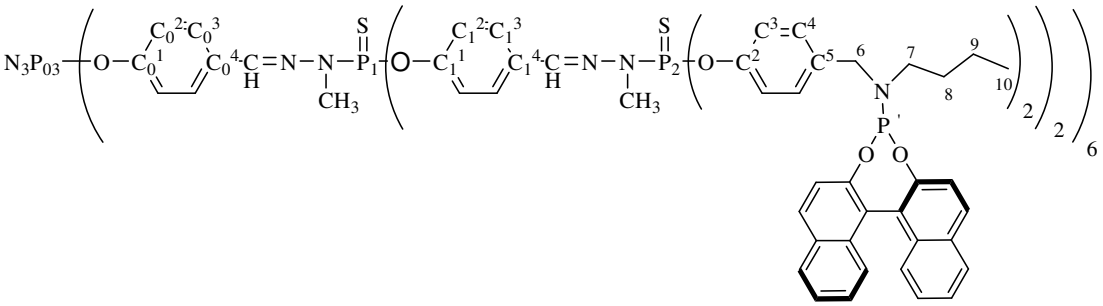
[1] H. Bernsmann, M. van den Berg, R. Hoen, A. J. Minnaard, G. Mehler, M. T. Reetz, J. G. De Vries and B. L. Feringa, *J. Org. Chem.*, **2005**, *70*, 943.

G1 was obtained in a 78 % yield.



^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$) δ 146.74 (s, P'), 62.85 (s, P_1), 8.25 (s, P_0). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 – 7.72 (m, 48H, H-$C_{Binapht.}$), 7.62 – 6.29 (m, 174H, H-C_0^3, CH=N-N-P_1, H-C^4, H-C^3, H-C_0^2, H-$C_{Binapht}$), 4.20 – 3.96 (m, 12H, C^6H_2-N), 3.56 (b abs, 12H, $C^{6'}H_2$-N), 3.05 – 3.30 (m, 18H, CH_3-N-P_1), 2.89 (b abs, 12H, N-C^7H_2), 2.56 (b abs, 12H, N-$C^{7'}H_2$), 1.40 (b abs, 24H, C^8H_2), 1.28 – 1.05 (m, 24H, C^9H_2), 0.87 – 0.67 (m, 36H, $C^{10}H_3$). ^{13}C {^{1}H} NMR (62.5 MHz, $CDCl_3$) δ 149.7 (m, C_0^1, C^2, $C_{q\ Binapht.}$), 149.3 (s, $C_{q\ Binapht.}$), 135.4 (bs, CH=N-N-P_1, C^5), 132.7 (s, $C_{q\ Binapht.}$), 132.5 (s, $C_{q\ Binapht.}$), 132.1 (s, C_0^4), 131.3 (s, $C_{q\ Binapht.}$), 130.6 (s, $C_{q\ Binapht.}$), 130.2 (s, $CH_{\ Binapht.}$), 130.0 (s, $CH_{\ Binapht.}$), 129.5 (s, C^4), 128.3 (s, $CH_{\ Binapht.}$), 128.2 (s, C_0^3, $CH_{\ Binapht.}$), 126.9 (s, $CH_{\ Binapht.}$), 126.8 (bs, $CH_{\ Binapht.}$), 126.1 (s, $CH_{\ Binapht.}$), 124.8 (s, $CH_{\ Binapht.}$), 124.6 (s, $CH_{\ Binapht.}$), 123.9 (d, $^{3}J_{CP}$ = 4.4 Hz, $C_{q\ Binapht.}$), 122.5 (s, $C_{q\ Binapht.}$), 122.1 (s, $CH_{\ Binapht.}$), 121.6 (s, $CH_{\ Binapht.}$), 121.1 (bs, C_0^2, C^3), 47.6 – 46.8 (m, C^6), 44.9 – 43.9 (m, C^7), 33.3 – 32.5 (m, CH_3-N-P_1), 30.3 (s, C^8), 19.8 (s, C^9), 13.7 (s, C^{10}). Anal. Calcd for $C_{420}H_{372}N_{27}O_{42}P_{21}S_6$ (7312.44): C, 68.99; H, 5.13; N, 5.17. Found: C, 69.01; H, 5.17; N, 5.20. $[\alpha]^{20}_D$ +222.69 (*c* 0.52, THF).

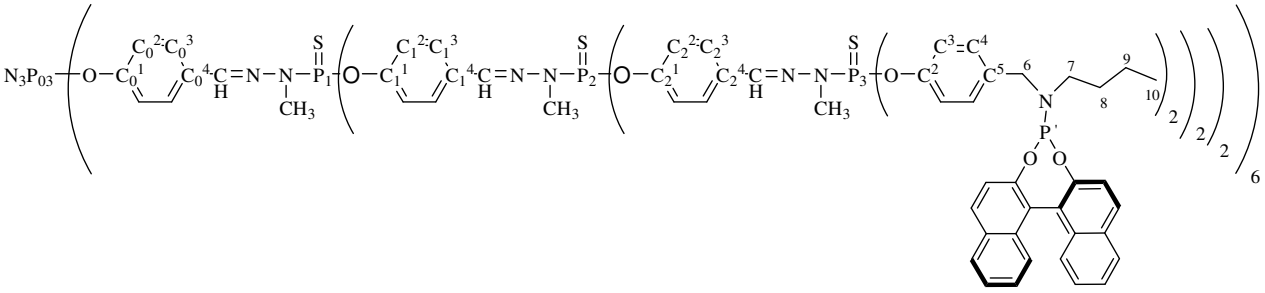
G2 was obtained in a 60 % yield.



^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$) δ 146.74 (s, P'), 62.94 (s, P_2), 62.43 (s, P_1), 8.31 (s, P_0). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 – 7.71 (m, 102H, H-$C_{Binapht.}$), 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-$C_{Binapht}$), 4.06 (b abs, 24H, C^6H_2-N), 3.58 (b abs, 24H, $C^{6'}H_2$-N), 3.16 (b abs, 54H, CH_3-N-$P_{1,2}$), 2.88 (b abs, 24H, N-C^7H_2), 2.55 (b abs, 24H, N-$C^{7'}H_2$), 1.40 (b abs, 48H, C^8H_2), 1.15 (b abs, 48H, C^9H_2), 0.76 (b abs, 72H, $C^{10}H_3$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 151.2 (d, $^{2}J_{CP}$ =

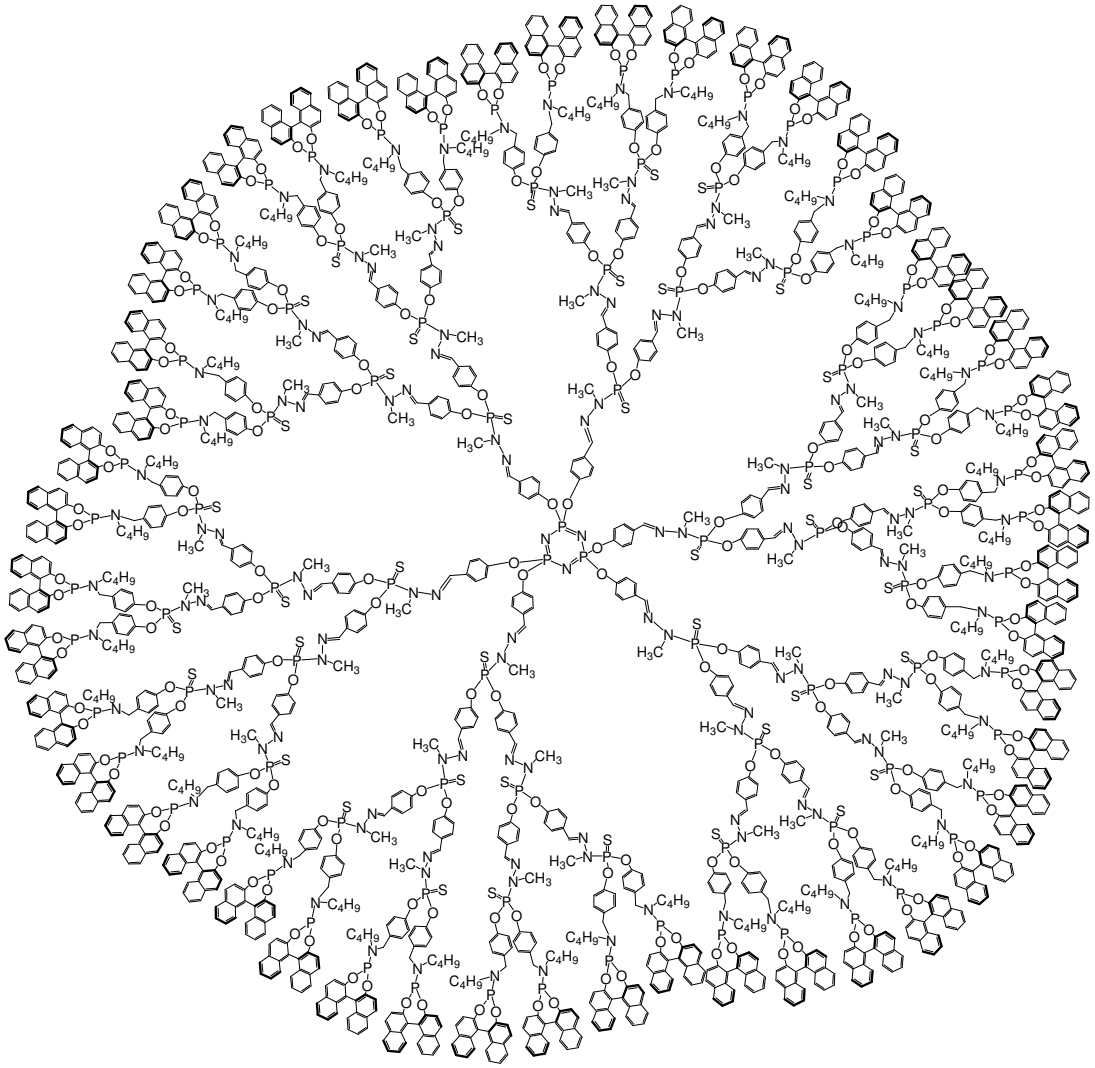
7.2 Hz, C_0^1, C_1^1), 149.6 (m, C^2, $C_{q\ Binapht}$), 149.3 (s, $C_{q\ Binapht.}$), 138.5 – 138.3 (m, CH=N-N-$P_{1,2}$), 135.4 (s, C^5), 132.7 (s, $C_{q\ Binapht.}$), 132.6 – 131.8 (m, C_0^4, C_1^4), 131.3 (s, $C_{q\ Binapht.}$), 130.6 (s, $C_{q\ Binapht.}$), 130.3 (s, CH $_{Binapht.}$), 130.1 (s, CH $_{Binapht.}$), 129.5 (s, C^4), 128.3 (s, CH $_{Binapht.}$), 128.2 (s, C_0^3, C_1^3, 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, $^3J_{CP}$ = 4.8 Hz, $C_{q\ Binapht.}$), 122.6 (s, $C_{q\ Binapht.}$), 122.1 (s, CH $_{Binapht.}$), 121.9 – 121.4 (m, CH $_{Binapht.}$, C_0^2, C_1^2, C^3), 47.2 (d, $^2J_{CP}$ = 12.6 Hz, C^6), 44.4 (d, $^2J_{CP}$ = 28.1 Hz, C^7), 32.9 (d, $^2J_{CP}$ = 12.6 Hz, CH_3-N-$P_{1,2}$), 30.3 (s, C^8), 19.8 (s, C^9), 13.7 (s, C^{10}). Anal. Calcd for $C_{888}H_{792}N_{63}O_{90}P_{45}S_{18}$ (15757.15): C, 67.69; H, 5.07; N, 5.60. Found: C, 67.71; H, 5.05; N, 5.64. $[\alpha]^{20}_D$ +230.57 (*c* 0.53, THF).

G3 was obtained in an 88 % yield.



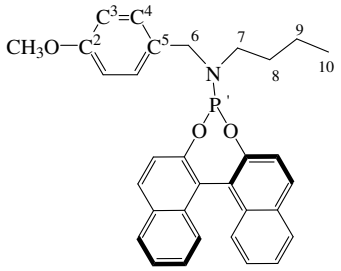
^{31}P {^1H} NMR (121 MHz, $CDCl_3$) δ 146.76 (s, P'), 62.84 (s, P_3), 62.43 (bs, $P_{1,2}$), 8.10 (bs, P_0). ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.44 (m, 396H, H-$C_{Binapht.}$, H-C_0^3, H-C_1^3, H-C_2^3, CH=N-N-$P_{1,2,3}$), 7.40 – 7.07 (m, 582H, H-$C_{Binapht.}$, H-C_0^2, H-C_1^2, H-C_2^2, H-C^3, H-C^4), 4.10 (b abs, 48H, C^6H_2-N), 3.59 (b abs, 48H, $C^{6'}H_2$-N), 3.19 (b abs, 126H, CH_3-N-$P_{1,2,3}$), 2.89 (b abs, 48H, N-C^7H_2), 2.56 (b abs, 48H, N-$C^{7'}H_2$), 1.40 (b abs, 96H, C^8H_2), 1.26 – 1.02 (m, 96H, C^9H_2), 0.77 (b abs, 144H, $C^{10}H_3$). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 151.3 (d, $^2J_{CP}$ = 7.0 Hz, C_0^1, C_1^1, C_2^1), 149.8 – 149.5 (m, C^2, $C_{q\ Binapht}$), 149.3 (s, $C_{q\ Binapht.}$), 139.3 – 138.2 (m, CH=N-N-$P_{1,2,3}$), 135.3 (s, C^5), 132.7 (s, $C_{q\ Binapht.}$), 132.5 (s, C_2^4), 132.4 – 131.9 (m, C_0^4, C_1^4), 131.3 (s, $C_{q\ Binapht.}$), 130.6 (s, $C_{q\ Binapht.}$), 130.3 (s, CH $_{Binapht.}$), 130.1 (s, CH $_{Binapht.}$), 129.5 (s, C^4), 128.3 (s, CH $_{Binapht.}$), 128.2 (s, 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, $^3J_{CP}$ = 4.5 Hz, $C_{q\ Binapht.}$), 122.6 (s, $C_{q\ Binapht.}$), 122.1 (s, CH $_{Binapht.}$), 121.9 – 121.4 (m, CH $_{Binapht.}$, C_0^2, C_1^2, C_2^2), 121.2 (s, C^3), 47.3 (d, $^2J_{CP}$ = 10.9 Hz, C^6), 44.4 (d, $^2J_{CP}$ = 27.4 Hz, C^7), 32.9 (d, $^2J_{CP}$ = 12.3 Hz, CH_3-N-$P_{1,2,3}$), 30.3 (s, C^8), 19.8 (s, C^9), 13.8 (s, C^{10}). Anal. Calcd for $C_{1824}H_{1632}N_{135}O_{186}P_{93}S_{42}$ (32646.56): C, 67.11; H, 5.04; N, 5.79. Found: C, 67.14; H, 5.07; N, 5.75. $[\alpha]^{20}_D$ +242.77 (*c* 0.51, THF).

4. Full representation of dendrimer G3.



5. Synthesis of the monomeric phosphoramidite ligand M and characterization data.

A solution of (*S*)-BINOL-derived chlorophosphite (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.

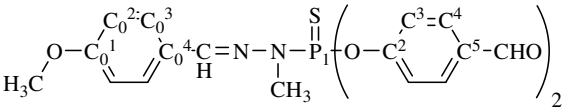


^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$) δ 147.16 (s, P'). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 – 7.84 (m, 4H, H-$C_{Binapht.}$), 7.59 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H, H-$C_{Binapht.}$), 7.48 – 7.32 (m, 5H, H-$C_{Binapht.}$), 7.31 – 7.23 (m, 2H, H-$C_{Binapht.}$), 7.22 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H, H-C^4), 6.88 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H, H-C^3), 4.17 (dd, $^{2}J_{HH}$ = 14.9 Hz, $^{3}J_{HP}$ = 6.6 Hz, 1H, C^6H_2-N), 3.81 (s, 3H, CH_3O), 3.66 (dd, $^{2}J_{HH}$ = 14.9 Hz, $^{3}J_{HP}$ = 9.1 Hz, 1H, $C^{6'}H_2$-N), 3.01 – 2.85 (m, 1H, N-C^7H_2), 2.74 – 2.53 (m, 1H, N-$C^{7'}H_2$), 1.55 – 1.42 (m, 2H, C^8H_2), 1.38 – 1.10 (m, 2H, C^9H_2), 0.86 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H, $C^{10}H_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7 (s, C^2), 149.9 (d, $^{2}J_{CP}$ = 5.2 Hz, $C_{q\ Binapht.}$), 149.5 (s, $C_{q\ Binapht.}$), 132.8 (s, $C_{q\ Binapht.}$), 132.6 (s, $C_{q\ Binapht.}$), 131.4 (s, $C_{q\ Binapht.}$), 130.6 (s, $C_{q\ Binapht.}$), 130.2 (s, C^5), 130.1 (s, $CH_{\ Binapht.}$), 129.9 (s, $CH_{\ Binapht.}$), 129.6 (s, C^4), 128.3 (s, $CH_{\ Binapht.}$), 128.2 (s, $CH_{\ Binapht.}$), 127.0 (s, $CH_{\ Binapht.}$), 126.9 (s, $CH_{\ Binapht.}$), 126.0 (s, $CH_{\ Binapht.}$), 125.9 (s, $CH_{\ Binapht.}$), 124.7 (s, $CH_{\ Binapht.}$), 124.5 (s, $CH_{\ Binapht.}$), 124.0 (d, $^{3}J_{CP}$ = 4.9 Hz, $C_{q\ Binapht.}$), 122.6 (d, $^{3}J_{CP}$ = 2.1 Hz, $C_{q\ Binapht.}$), 122.2 (d, $^{3}J_{CP}$ = 1.7 Hz, $CH_{\ Binapht.}$), 121.8 (s, $CH_{\ Binapht.}$), 113.6 (s, C^3), 55.3 (s, CH_3O), 47.3 (d, $^{2}J_{CP}$ = 14.3 Hz, C^6), 44.1 (d, $^{2}J_{CP}$ = 26.9 Hz, C^7), 30.3 (d, $^{3}J_{CP}$ = 2.2 Hz, C^8), 19.8 (s, C^9), 13.8 (s, C^{10}). 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] (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.



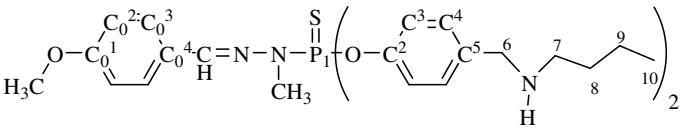
^{31}P {^{1}H} NMR (121.5 MHz, CDCl$_3$) δ 60.60 (s, P). ^{1}H NMR (300 MHz, CDCl$_3$) δ 9.98 (s, 2H, CHO), 7.89 (d, $^3J_{HH}$ = 8.6 Hz, 4H, H-C^4), 7.63 (m, 3H, H-C$_0^3$ and CH=N-N-P), 7.43 (d, $^3J_{HH}$ = 8.6 Hz, 4H, H-C^3), 6.94 (d, $^3J_{HH}$ = 8.8 Hz, 2H, H-C$_0^2$), 3.85 (s, 3H, CH$_3$O), 3.41 (d, $^3J_{HP}$ = 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^{8}H$_2$), 1.32 (bs, 4H, C^{9}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$_0^1$),155.28 (d, $^2J_{CP}$ = 7.3 Hz, C^2), 140.67 (d, $^3J_{CP}$ = 13.8 Hz, CH=N-N-P), 133.64 (s, C^5), 131.42 (s, C^4), 128.52 (s, C$_0^3$), 127.17 (s, C$_0^4$), 121.05 (s, C^3), 114.28 (s, C$_0^2$), 57.40 (s, CH$_3$O), 32.85 (d, $^2J_{CP}$ = 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

[2] M. Keller, M. Ianchuk, S. Ladeira, M. Taillefer, A.-M. Caminade, J.-P. Majoral, A. Ouali, *Eur. J. Org. Chem.*, **2012**, 1056.

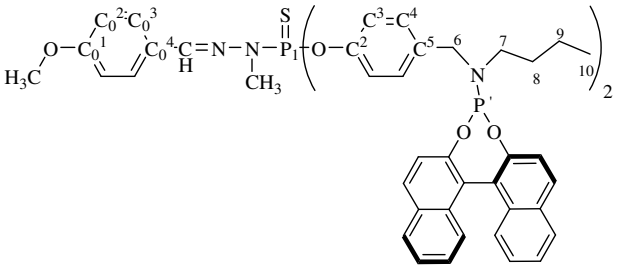
under reduced pressure. After that, the residue was then dissolved in THF:MeOH 1.5:1 (166 mL, 70 mL, 100 mL, respectively) and ice-cooled. Then, $NaBH_4$ (17.3 mmol) was slowly added and the reaction mixture was led to reach room temperature. After 18 hours, the reaction was quenched by addition of water and concentrated under reduced pressure. The mixture was then diluted in 50 mL of dichloromethane and was washed with sat. $NaHCO_3$ solution, water and brine (20 mL each), dried over $MgSO_4$ 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.



^{31}P {^1H} NMR (121.5 MHz, $CDCl_3$) δ 62.86 (s, P). ^1H NMR (300 MHz, $CDCl_3$) δ 7.63 (m, 3H, H-C_0^3 and CH=N-N-P), 7.21 (m, 8H, H-C^3 and H-C^4), 6.90 (bs, 2H, H-C_0^2), 3.77 (s, 3H, CH_3O), 3.70 (bs, 4H, C^6H_2-N), 3.29 (d, $^3J_{HP}$ = 9.0 Hz, 3H, CH_3-N-P), 2.57 (bs, 4H, N-C^7H_2), 1.87 (bs, 2H, NH), 1.45 (bs, 4H, C^8H_2), 1.32 (bs, 4H, C^9H_2), 0.89 (bs, 6H, $C^{10}H_3$). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$) δ 160.68 (s, C_0^1), 149.62 (d, $^2J_{CP}$ = 7.2 Hz, C^2), 139.45 (d, $^3J_{CP}$ = 13.7 Hz, CH=N-N-P), 137.50 (s, C^5), 129.15 (s, C^4), 128.45 (s, C_0^3), 127.73 (s, C_0^4), 121.34 (d, $^3J_{CP}$ = 4.45 Hz, C^3), 114.14 (s, C_0^2), 55.31 (s, CH_3O), 53.34 (s, C^6), 49.14 (s, C^7), 33.0 (d, $^2J_{CP}$ = 13.0 Hz, CH_3-N-P), 32.12 (s, C^8), 20.46 (s, C^9), 14.05 (s, C^{10}). Anal. Calcd for $C_{31}H_{43}N_4O_3PS$ (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 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 **B** (0.80 g, 31 % yield) as a colorless solid.



^{31}P {^{1}H} NMR (160 MHz, $CDCl_3$) δ 146.90 (s, P'), 146.86 (s, P'), 63.03 (s, P_1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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-$C_{Binapht.}$), 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-$C_0{}^2$), 4.07 – 4.14 (m, 2H, C^6H_2-N), 3.81 (s, 3H, CH_3O), 3.56 – 3.64 (m, 2H, $C^{6'}H_2$-N), 3.32 (d, $^{3}J_{HP}$ = 10.8 Hz, 3H, CH_3-N-P_1), 2.97 – 2.85 (m, 2H, N-C^7H_2), 2.65 – 2.51 (m, 2H, N-$C^{7'}H_2$), 1.52 – 1.39 (m, 4H, C^8H_2), 1.23 – 1.08 (m, 2H, C^9H_2), 0.82 (t, $^{3}J_{HH}$ = 7.4 Hz, 6H, $C^{10}H_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7 (s, $C_0{}^1$), 149.7 (d, $^{2}J_{CP}$ = 5.6 Hz, C^2), 149.3 (s, $C_{q\ Binapht.}$), 139.4 (d, $^{3}J_{CP}$ = 13.6 Hz, CH=N-N-P), 135.2 (s, C^5), 132.8 (s, $C_{q\ Binapht.}$), 132.5 (s, $C_{q\ Binapht.}$), 131.3 (s, $C_{q\ Binapht.}$), 130.6 (s, $C_{q\ Binapht.}$), 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, $C_{q\ Binapht.}$), 122.5 (m, $C_{q\ Binapht.}$), 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_3O), 47.2 (d, $^{2}J_{CP}$ = 11.7 Hz, C^6), 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 *N*,*N*-bis(2-butynyl)-(4-methylphenyl)sulfonamide 1 with phenylacetylene 2. General Procedure.

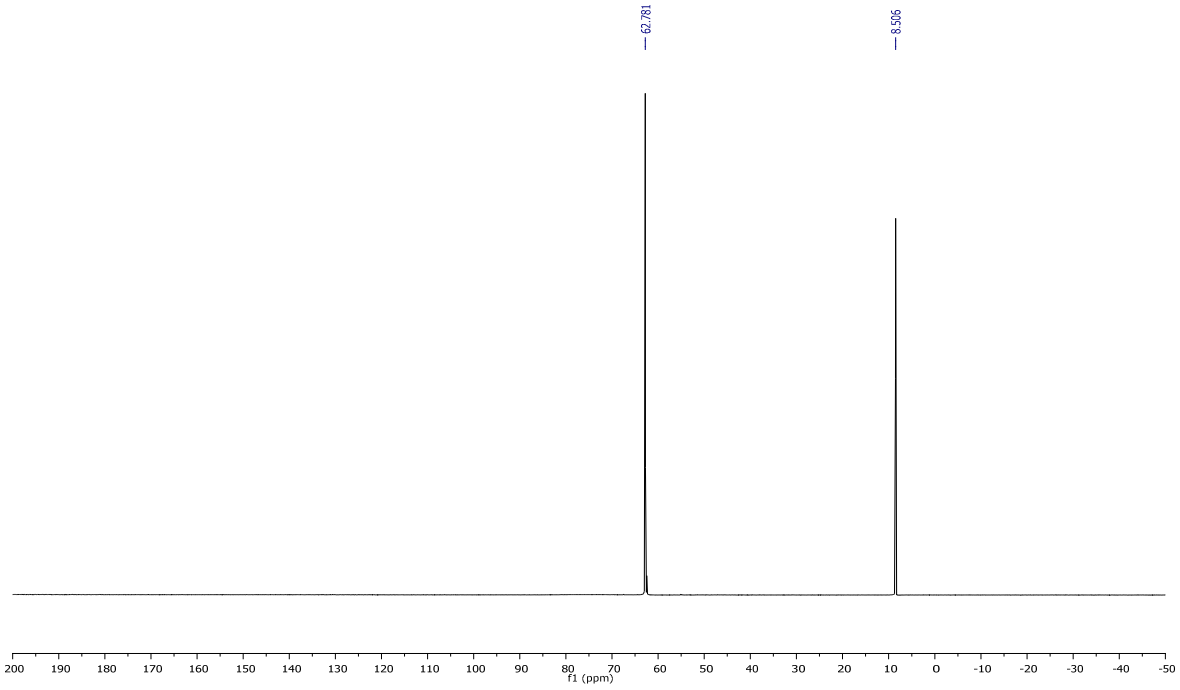
Dendrimer bearing phosphoramidite end groups **Gn** (generation 1: 4.6 mg, $6.2.10^{-4}$ mmol, generation 2: 4.9 mg, $3.1.10^{-4}$ mmol, generation 3: 5.1 mg, $1.6.10^{-4}$ mmol; each case corresponds to 5 mol% end groups) and $[Rh(C_2H_4)_2Cl]_2$ (1.2 mg, $3.7.10^{-3}$ mmol) were dissolved in dry toluene (1.0 mL) and the mixture was stirred at room temperature for 30 min. To this solution a toluene (1.0 mL) solution of *N*,*N*-bis(2-butynyl)-(4-methylphenyl)sulfonamide (41.3 mg, 0.15 mmol) and phenylacetylene (84 µL, 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 *N*,*N*-bis(2-butynyl)-(4-methylphenyl)sulfonamide 1 with alkynyl substrate 4. General Procedure.

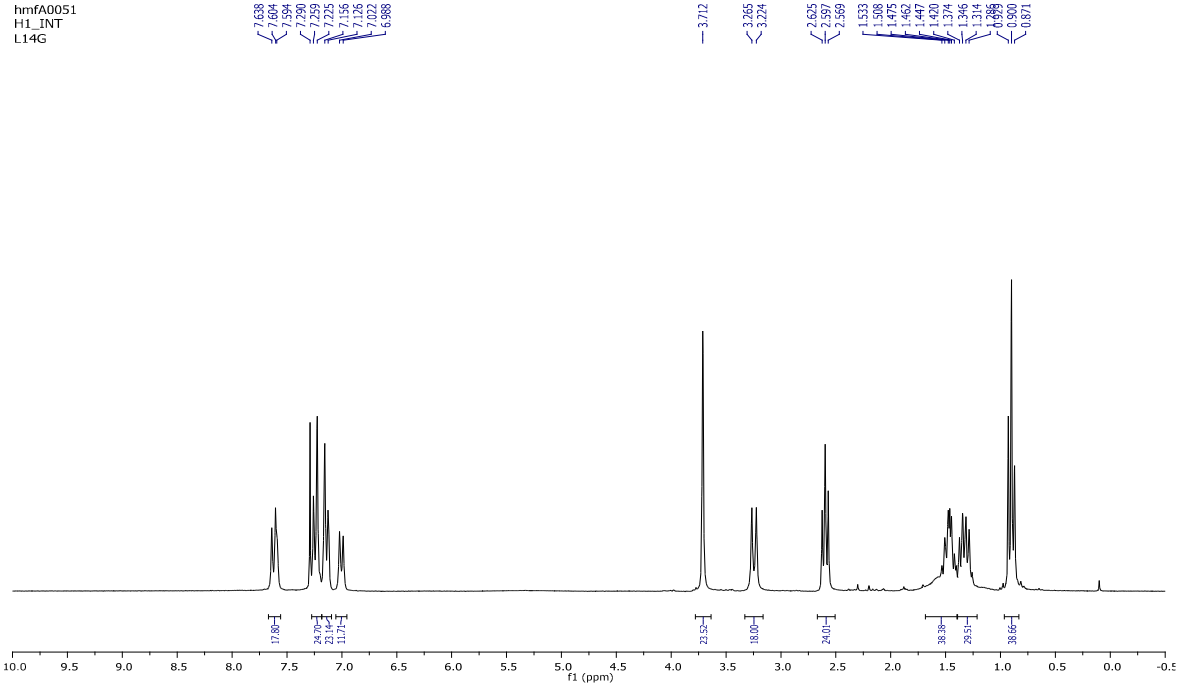
Dendrimer bearing phosphoramidite end groups **Gn** (generation 1: 3.0 mg, $4.2.10^{-4}$ mmol, generation 2: 3.3 mg, $2.1.10^{-4}$ mmol, generation 3: 3.4 mg, $1.0.10^{-4}$ mmol; each case corresponding to 5 mol% end groups) and $[Rh(C_2H_4)_2Cl]_2$ (1.0 mg, $2.5.10^{-3}$ mmol) were dissolved in dry 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 *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 {^{1}H} NMR, ^{1}H NMR and ^{13}C {^{1}H} NMR spectra of dendrimers A-Gn

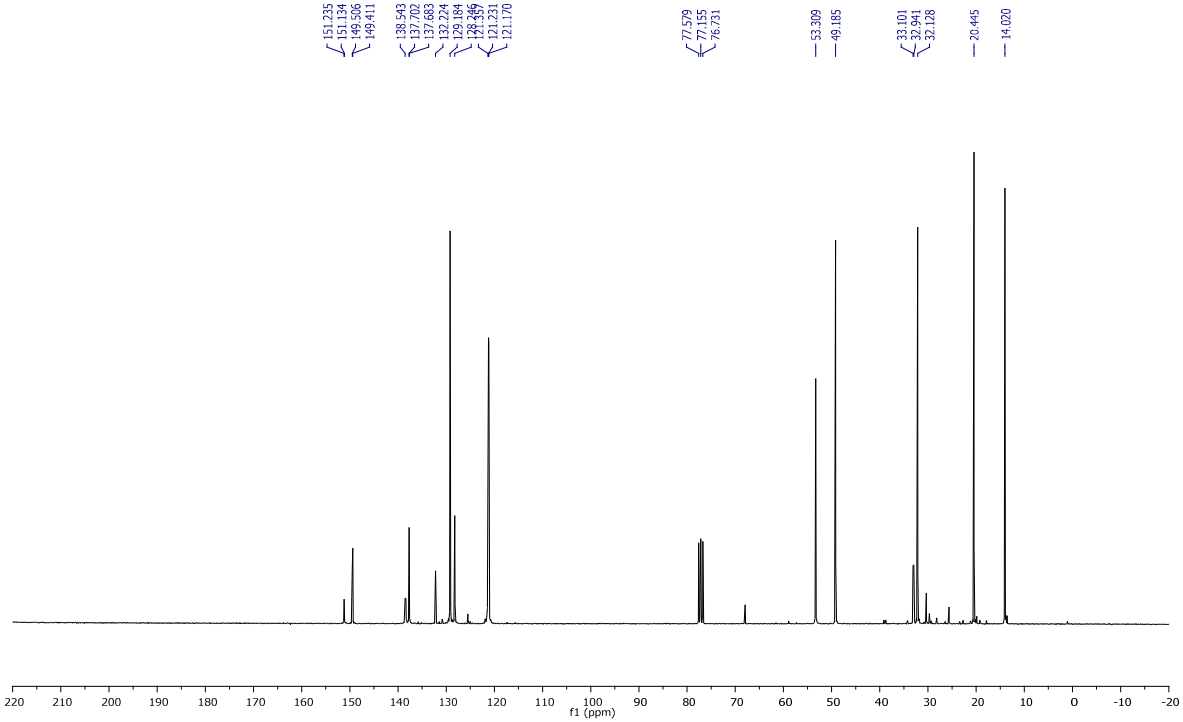
A-G1, ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$)



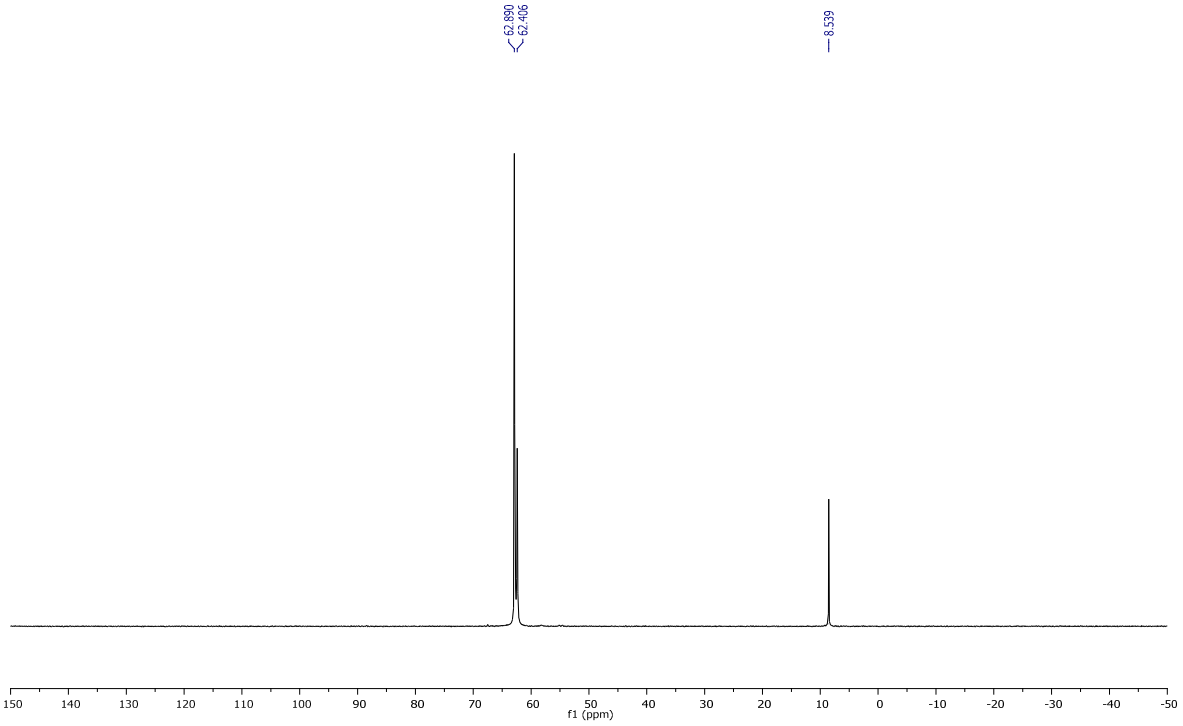
A-G1, ^{1}H NMR (250 MHz, $CDCl_3$)



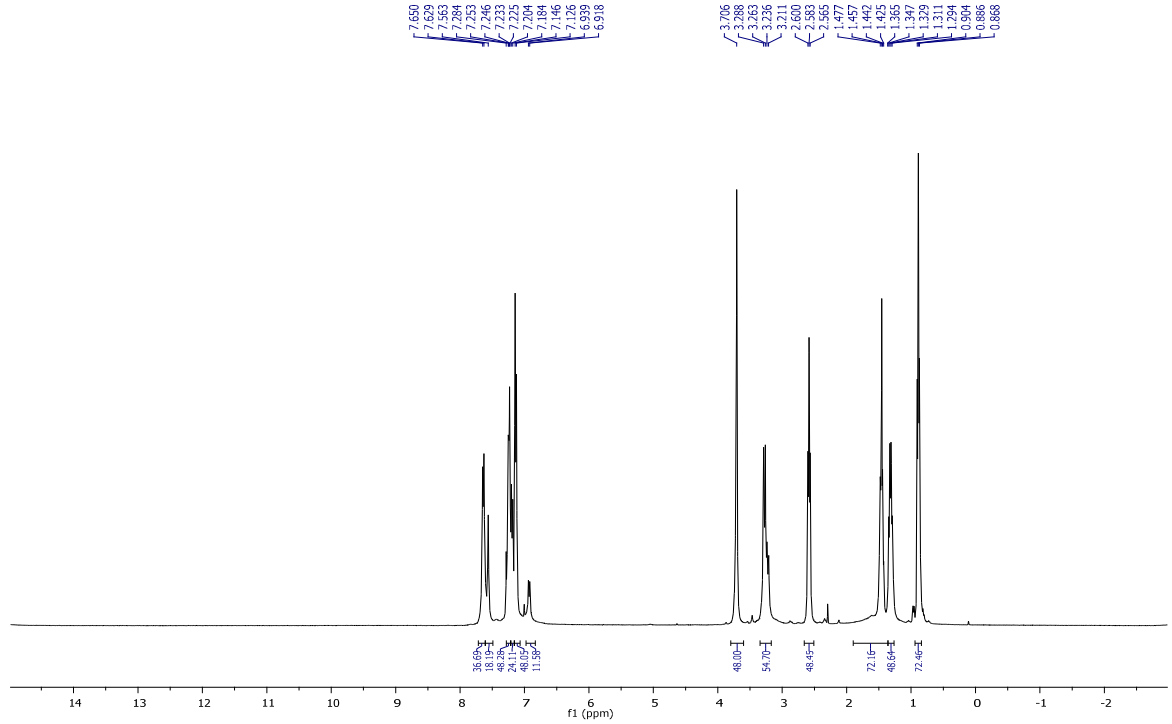
A-G1, ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$)



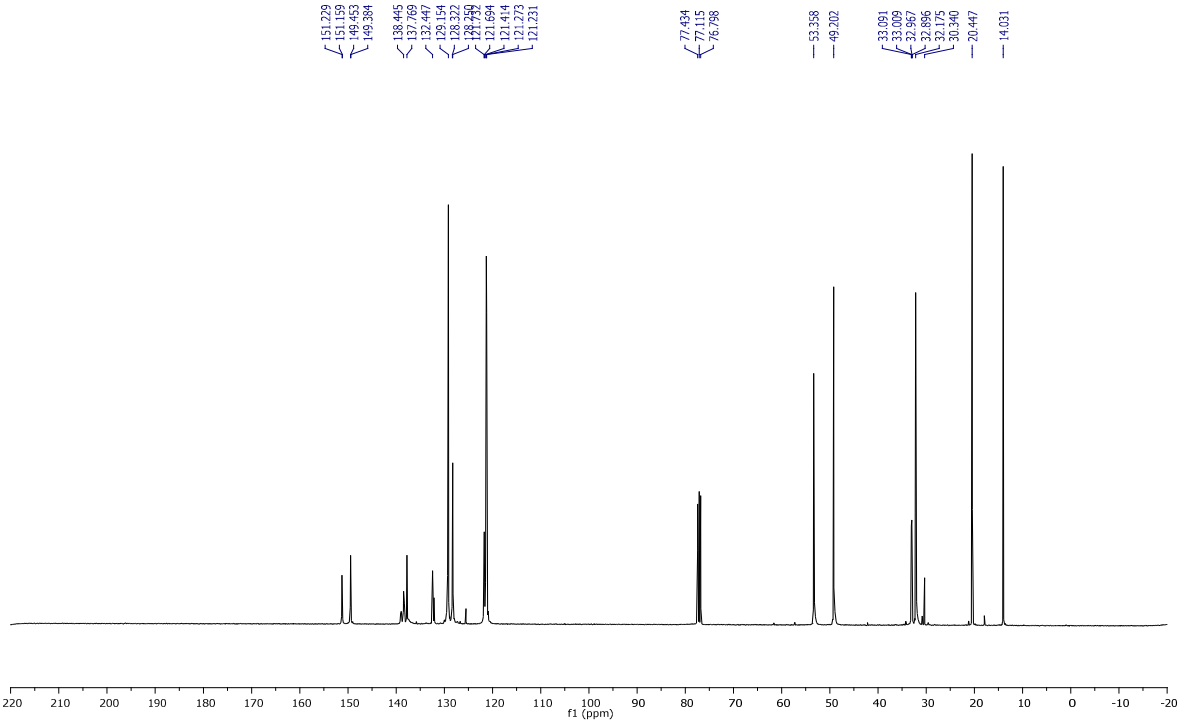
A-G2, ^{31}P {^{1}H} NMR (161 MHz, $CDCl_3$)



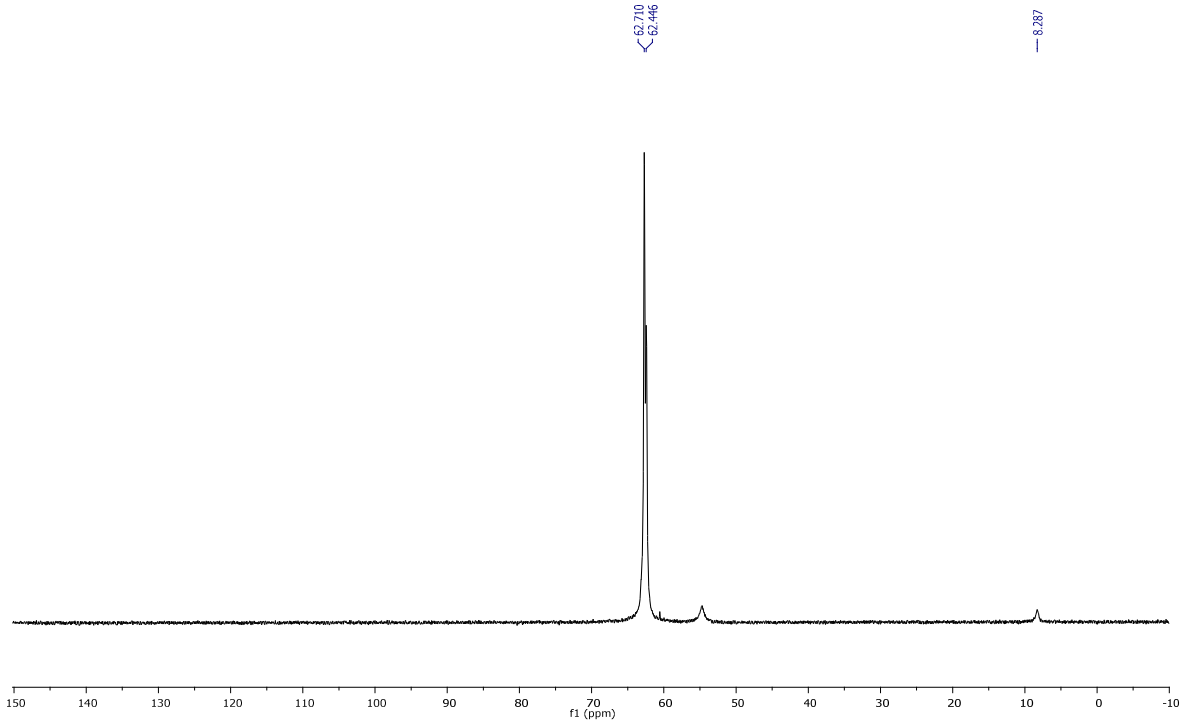
A-G2, ^{1}H NMR (400 MHz, $CDCl_3$)



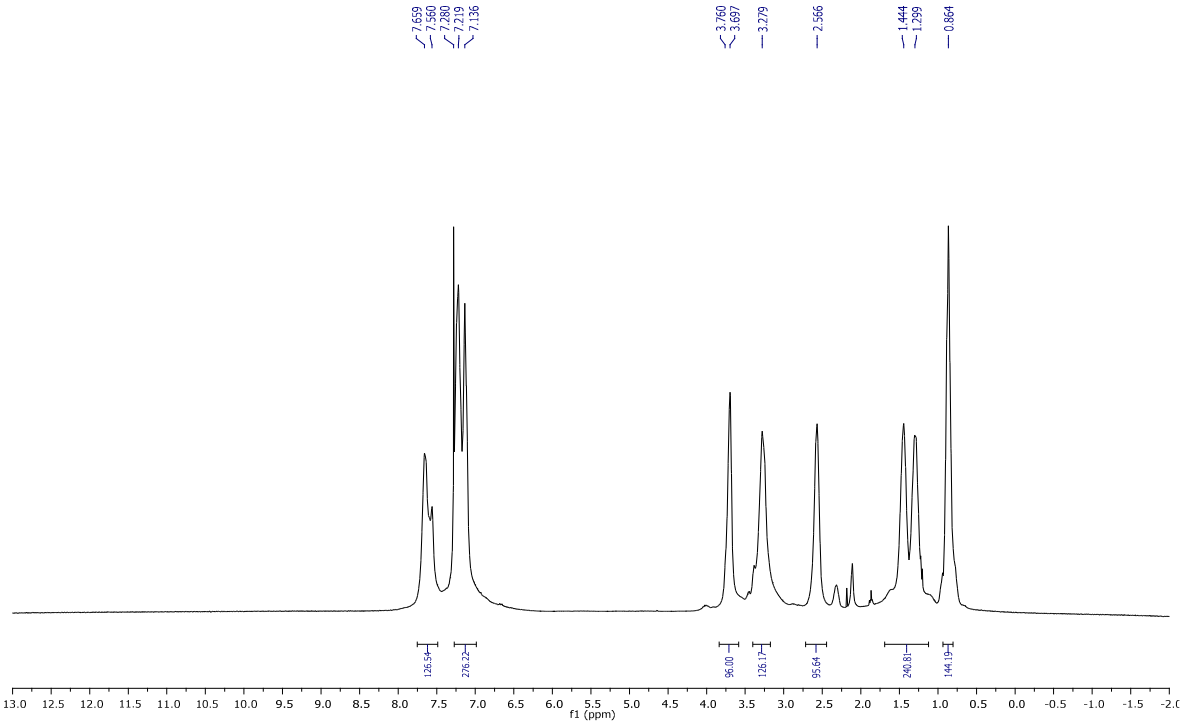
A-G2, ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



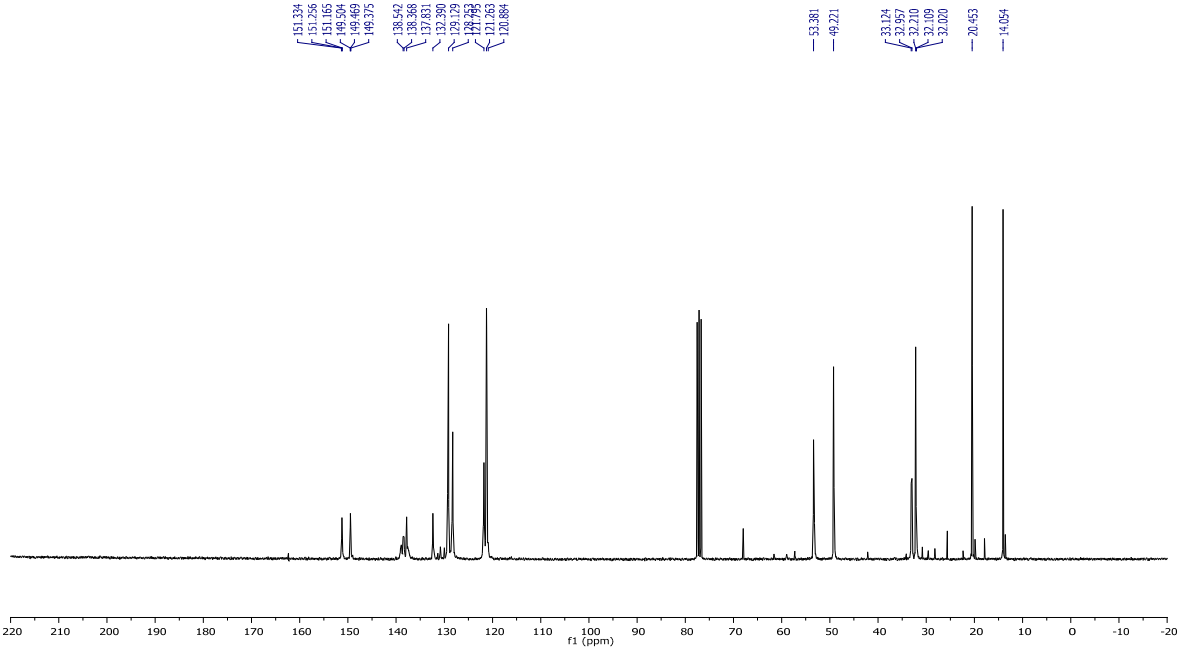
A-G3, $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)



A-G3, ^{1}H NMR (300 MHz, $CDCl_3$)

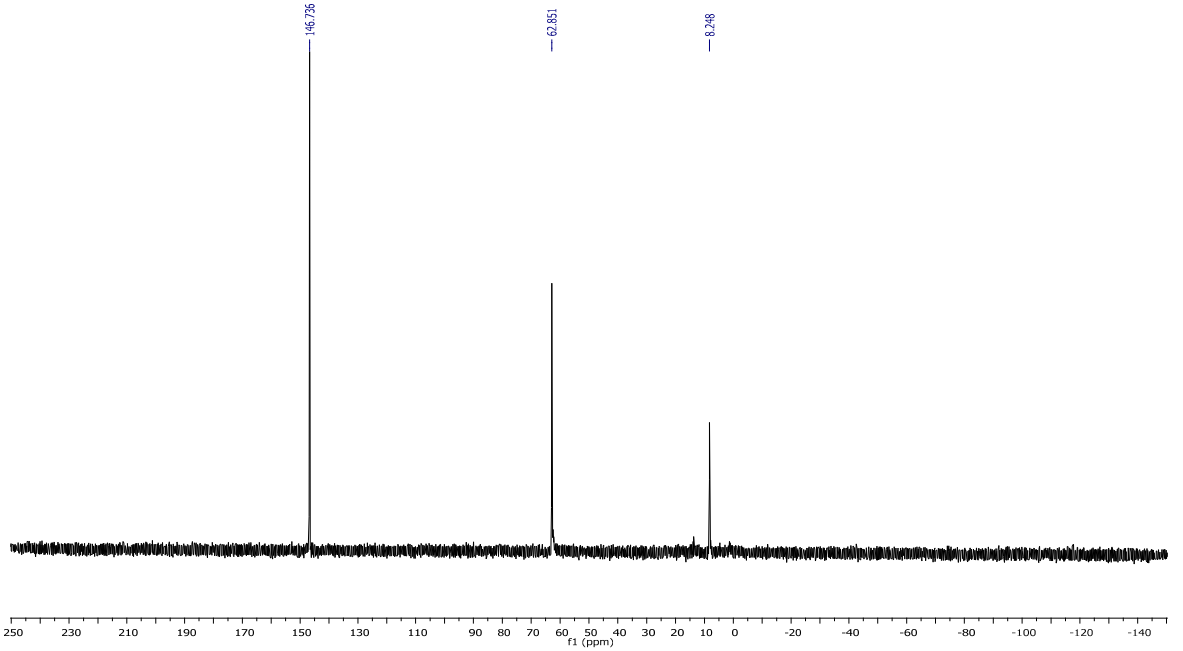


A-G3, ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$)

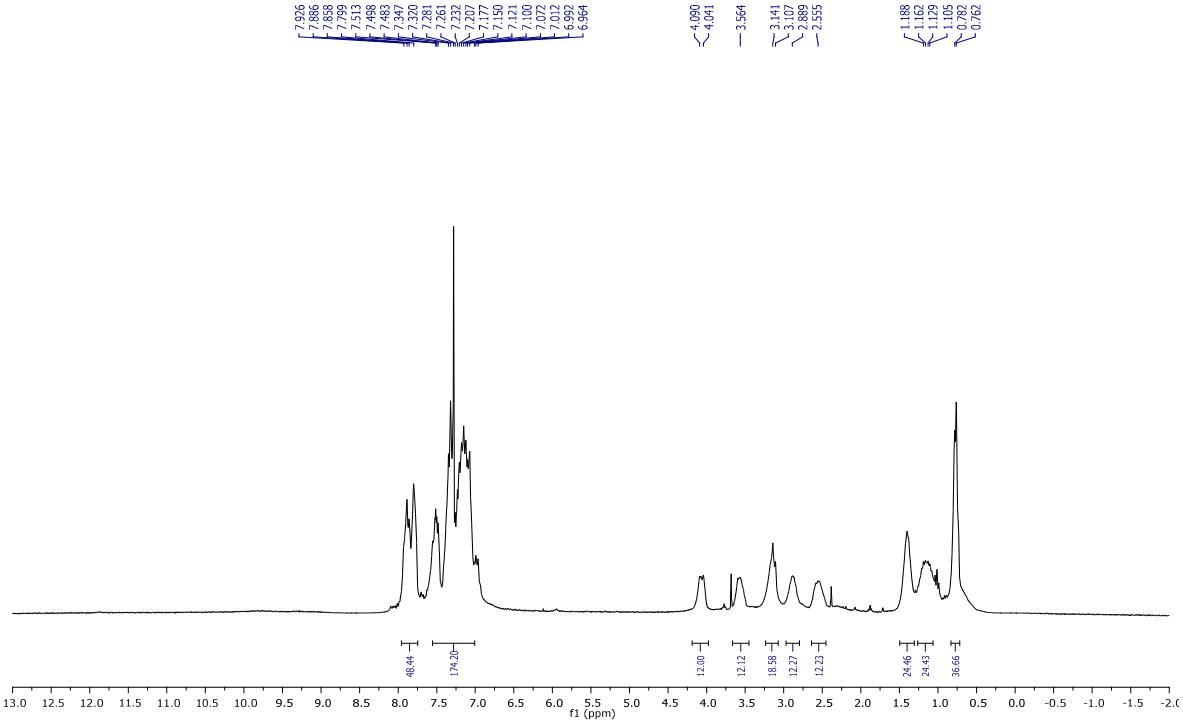


10. ^{31}P {^{1}H} NMR, ^{1}H NMR and ^{13}C {^{1}H} NMR spectra of dendrimers Gn

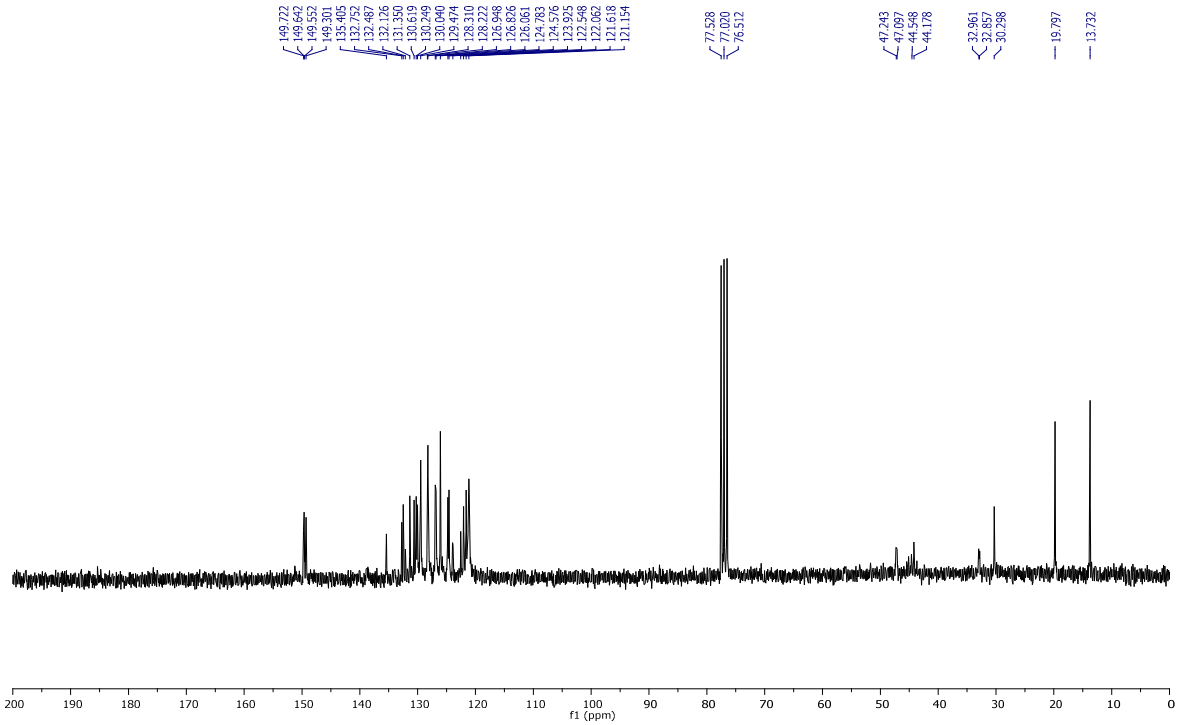
G1, ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$)



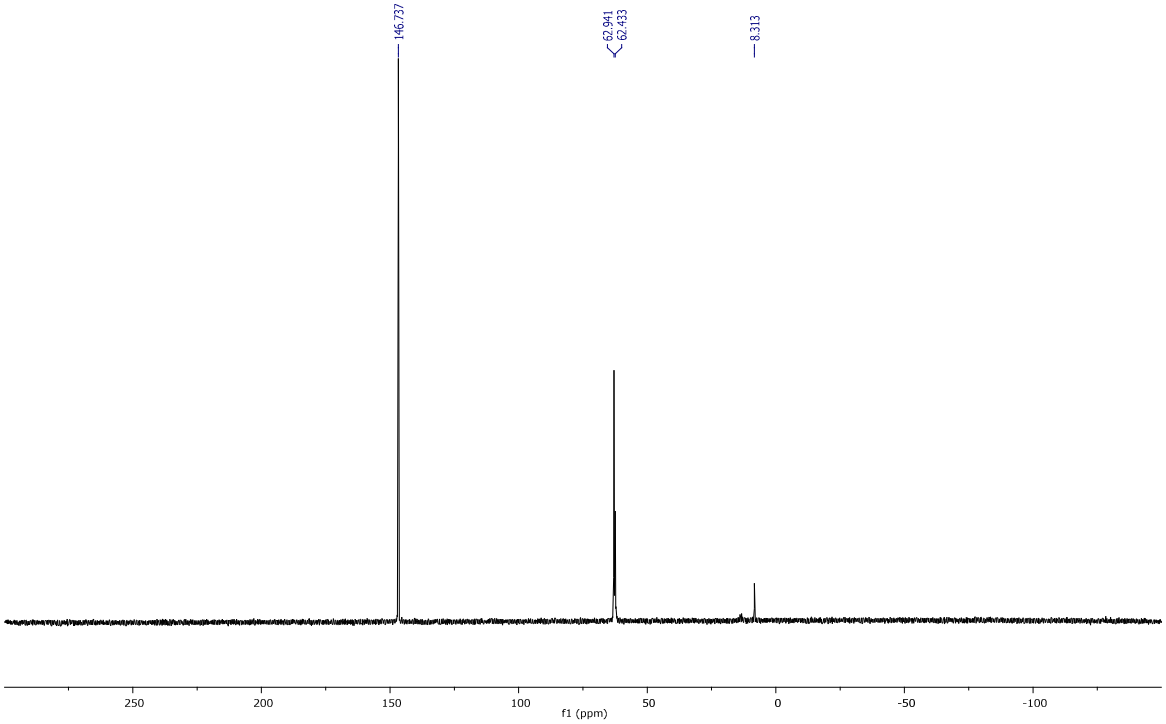
G1, ^{1}H NMR (300 MHz, $CDCl_3$)



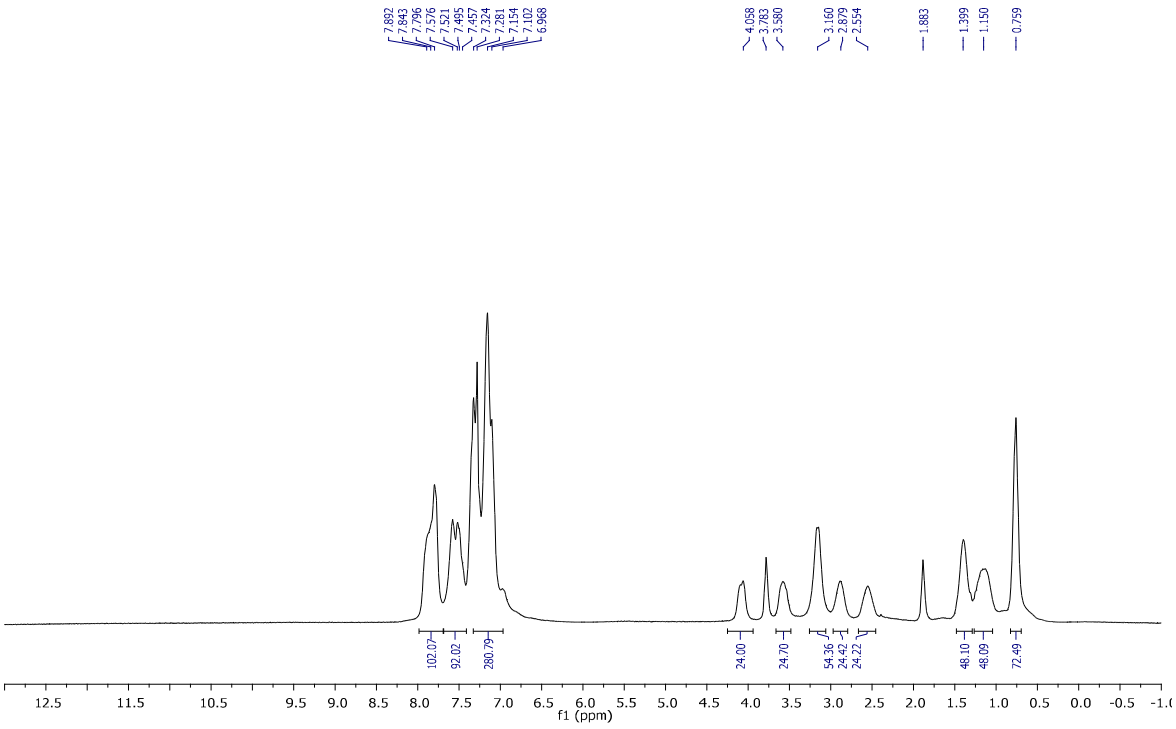
G1, ^{13}C {^{1}H} NMR (62 MHz, $CDCl_3$)



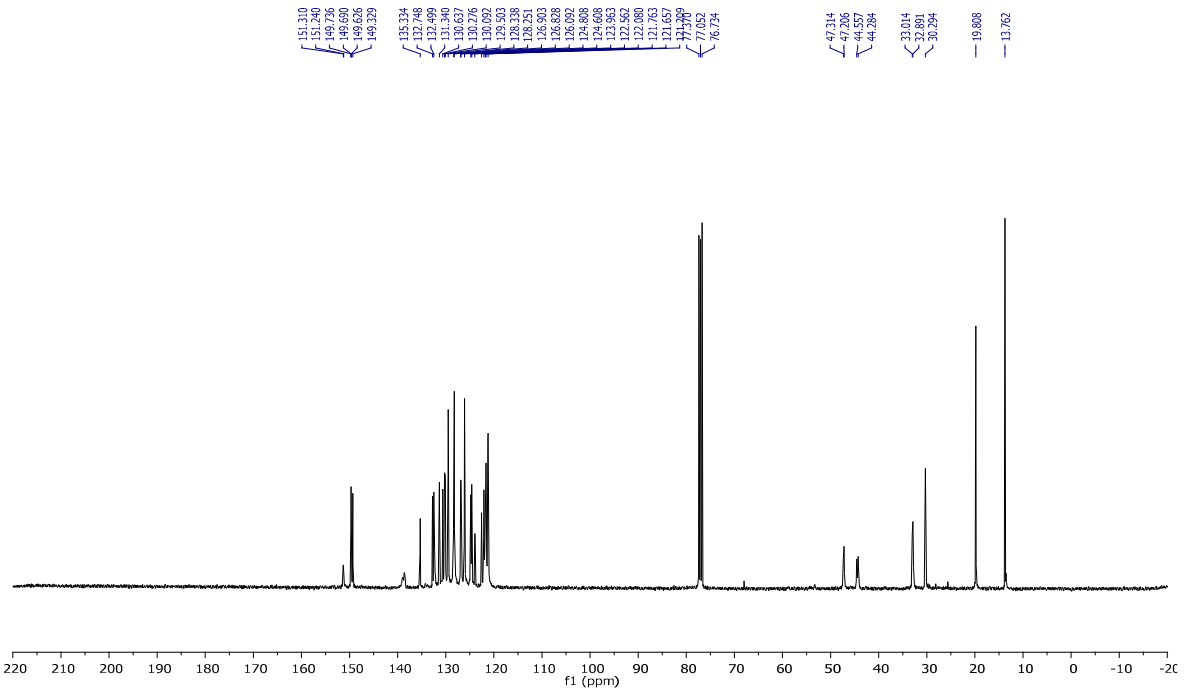
G2, ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$)



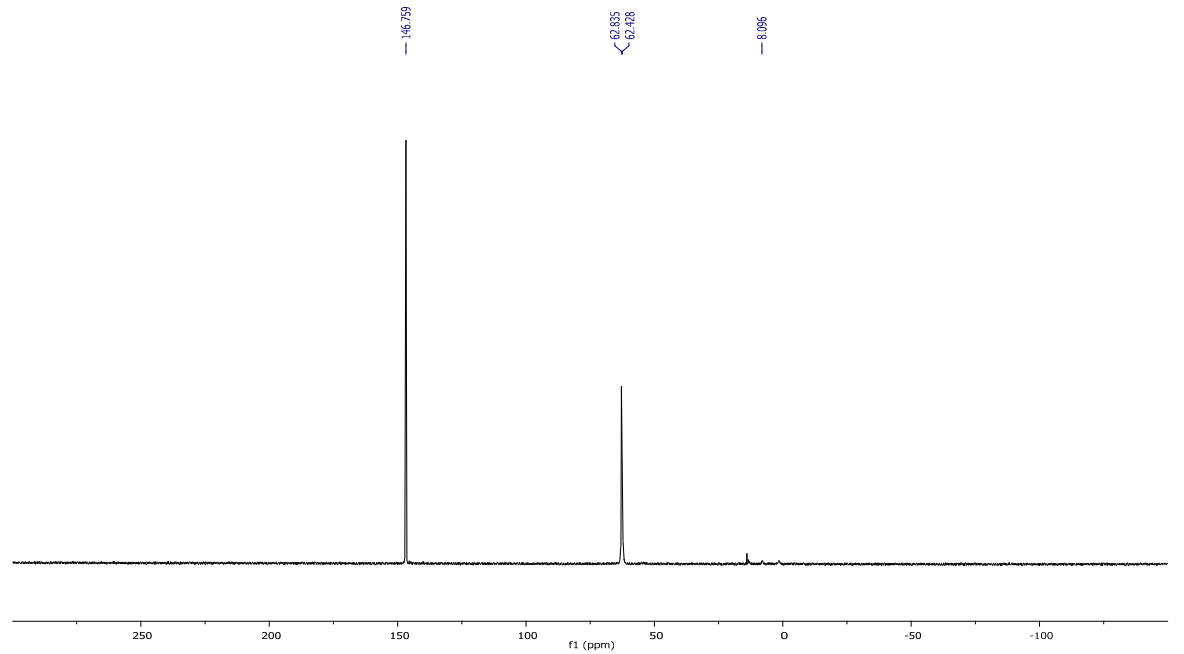
G2, ^{1}H NMR (300 MHz, $CDCl_3$)



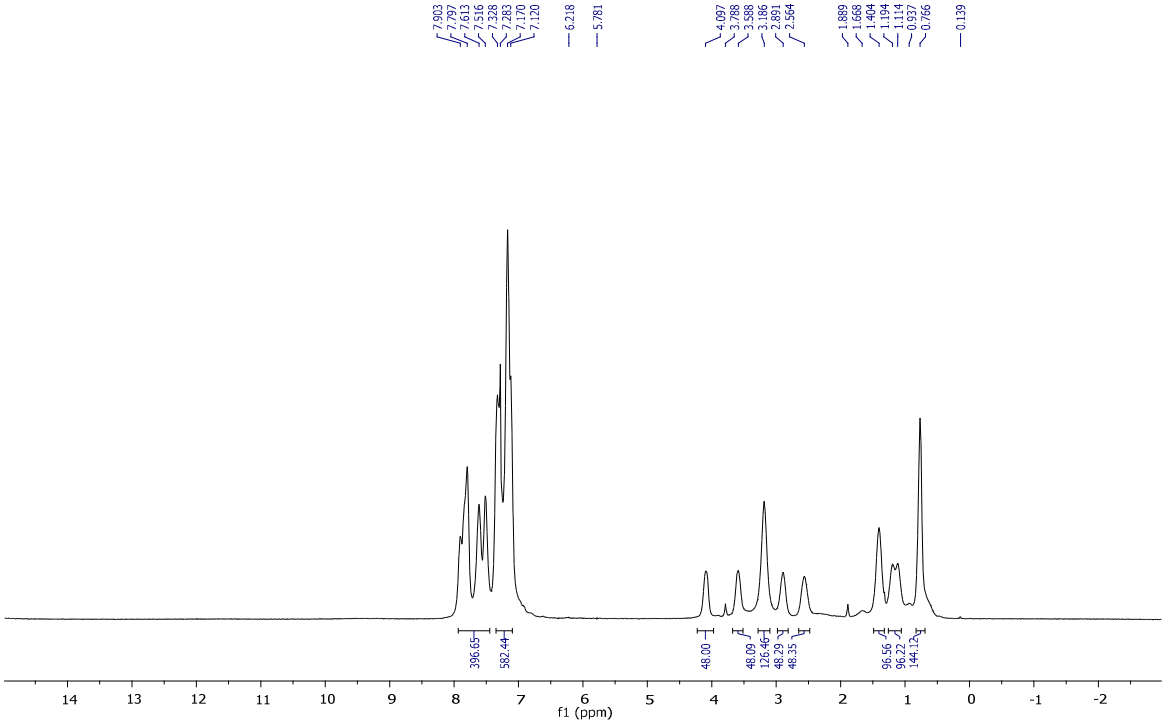
G2, $^{13}C\{^{1}H\}$-RMN (75 MHz, $CDCl_3$) δ (ppm):



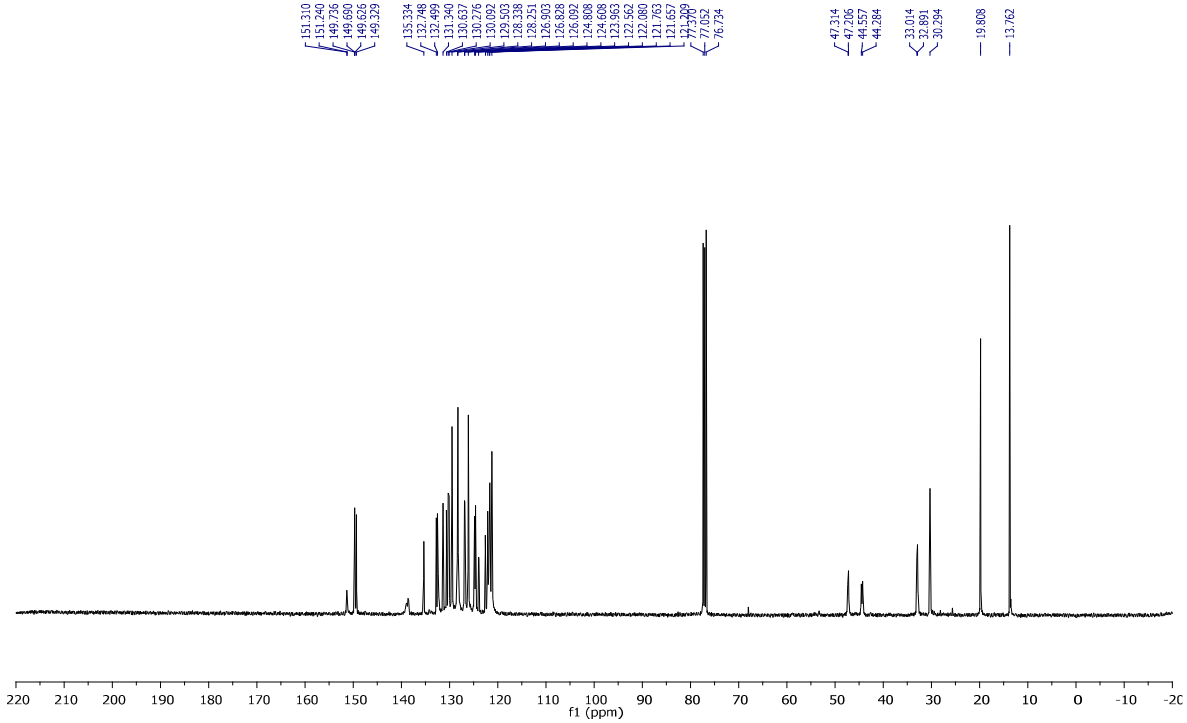
G3, $^{31}P\{^{1}H\}$-RMN (121 MHz, $CDCl_3$) δ (ppm):



G3, ^{1}H NMR (400 MHz, $CDCl_3$)

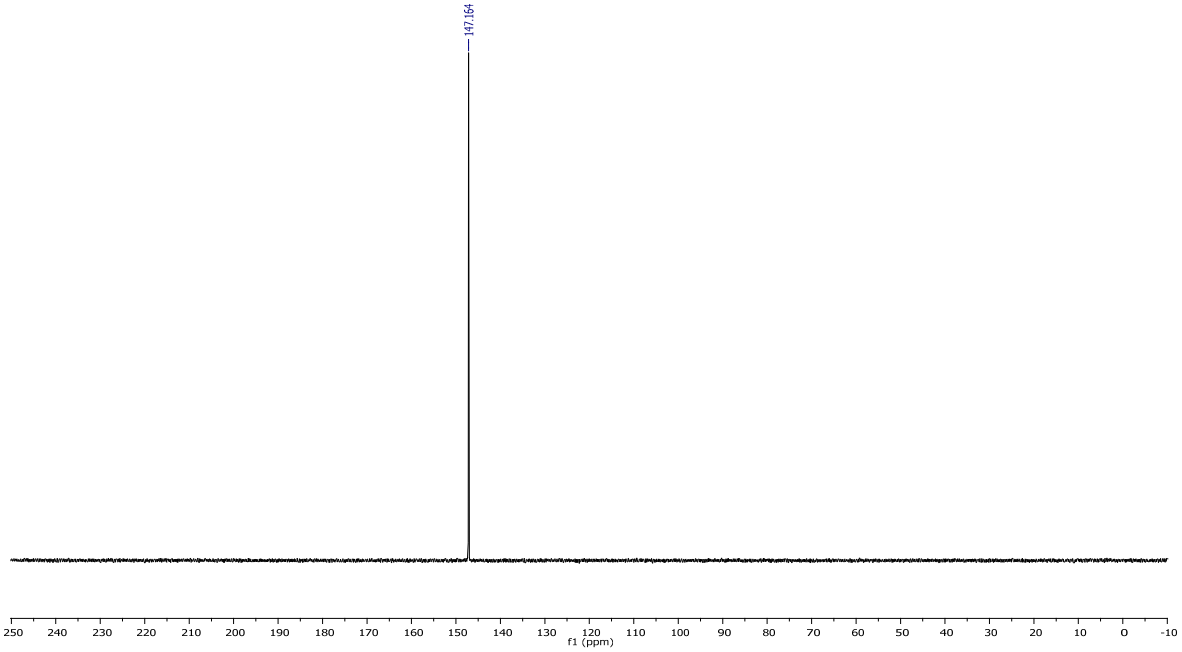


G3, ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)

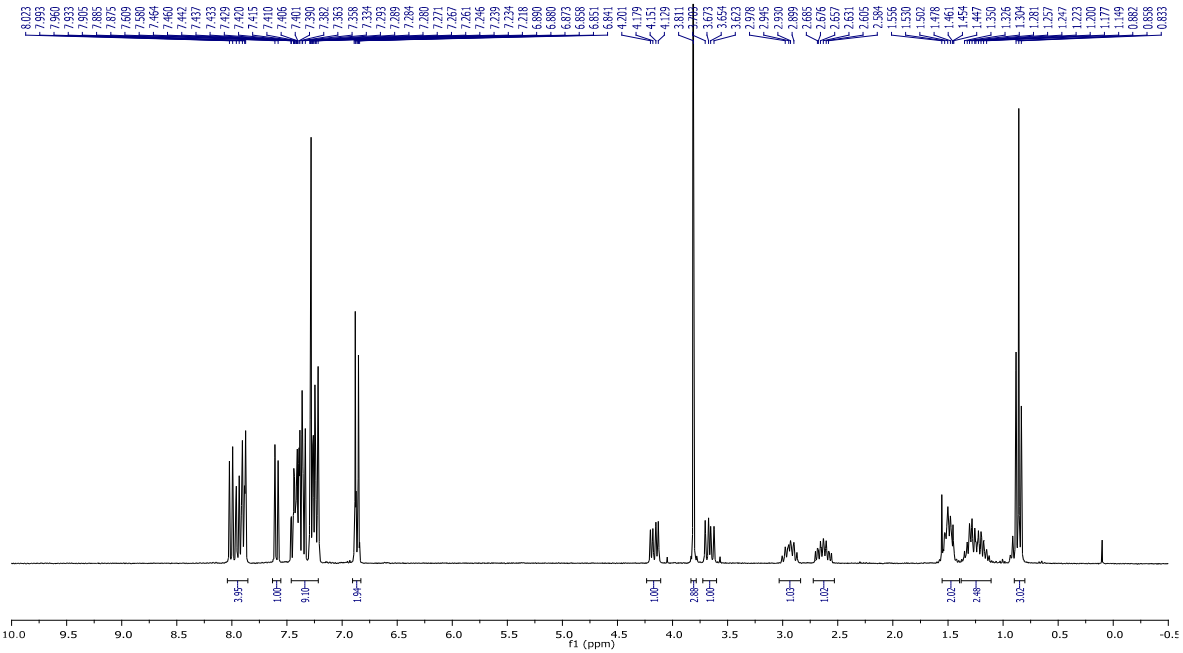


11. ^{31}P {^{1}H} NMR, ^{1}H NMR and ^{13}C {^{1}H} NMR spectra of M and B

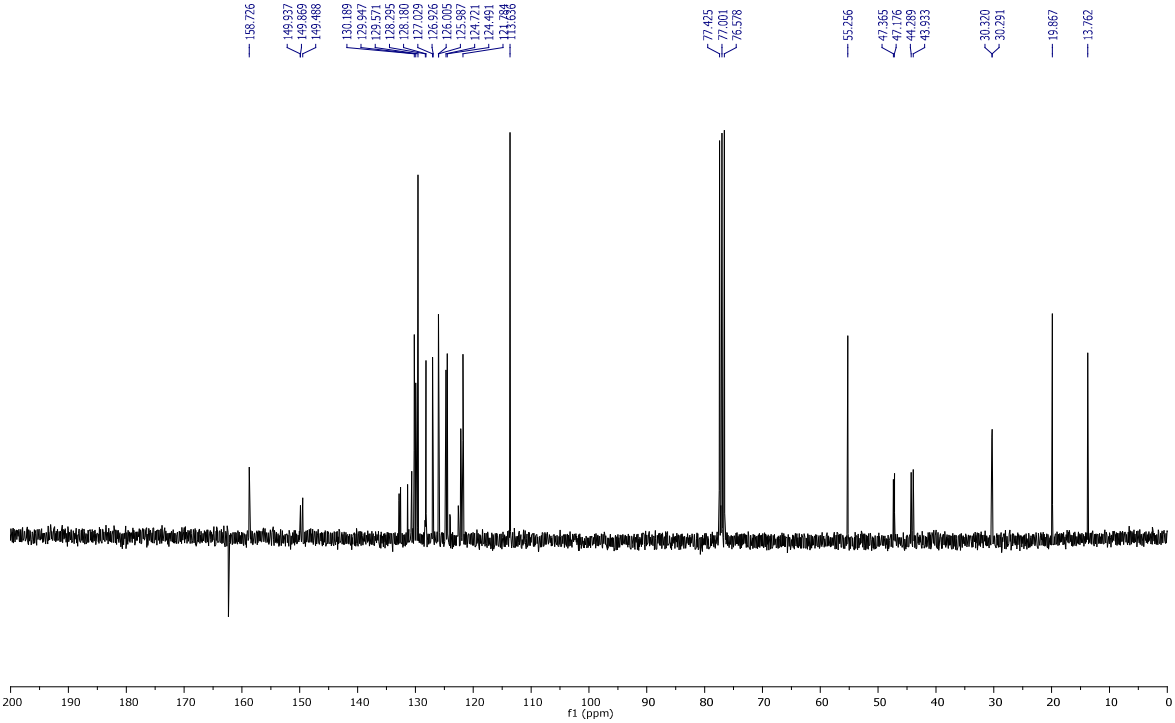
M, ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$)



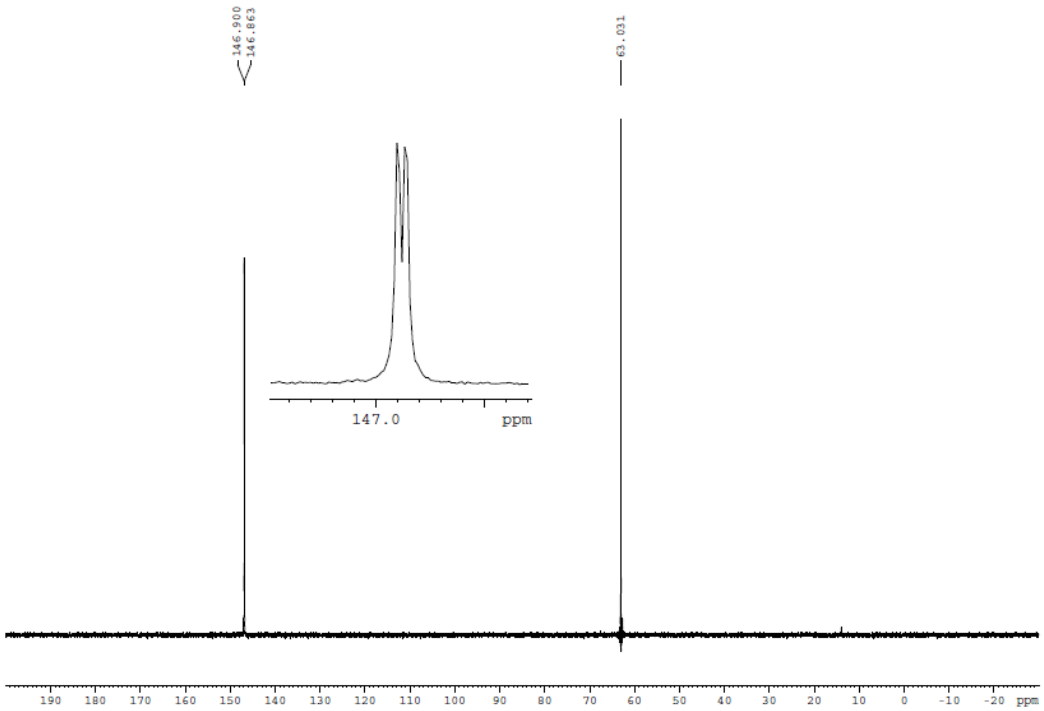
M, ^{1}H NMR (300 MHz, $CDCl_3$)



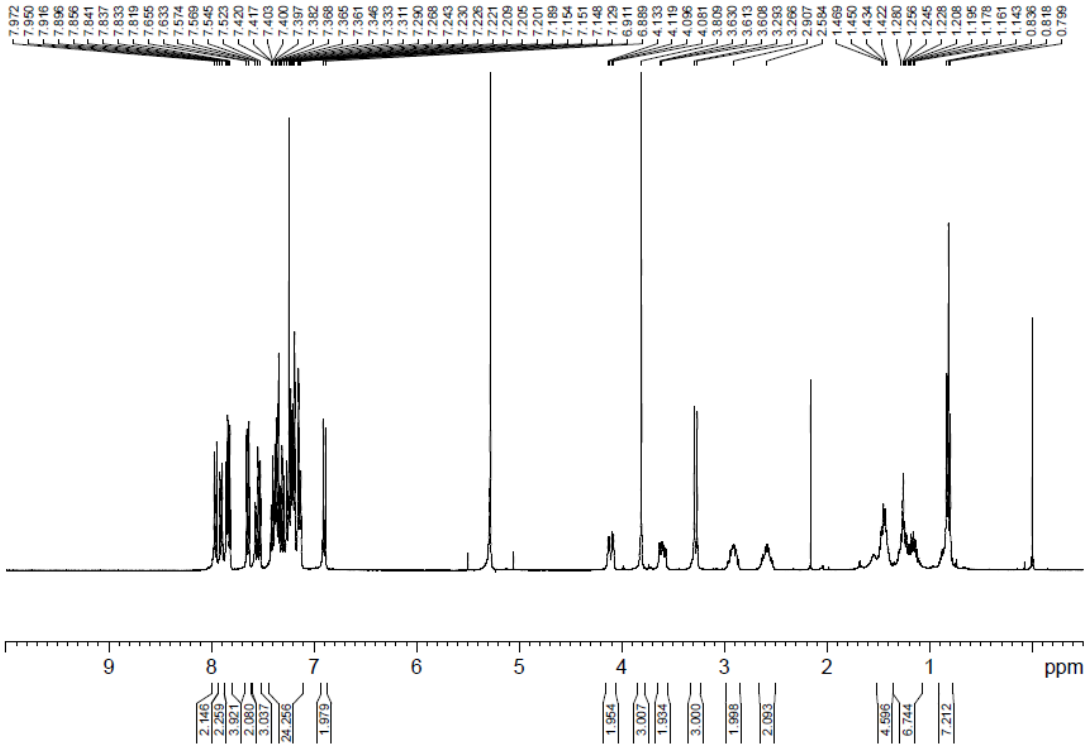
M, ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$)



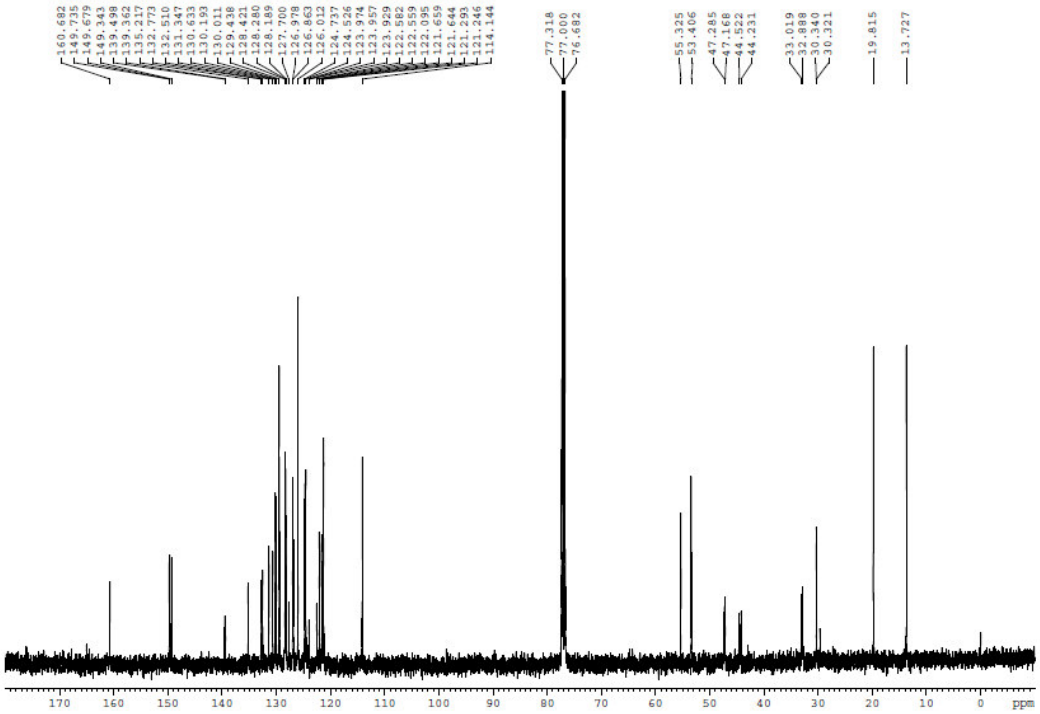
B, ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$)



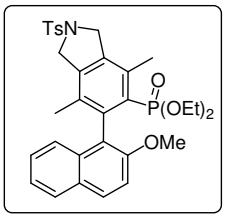
B, ^{1}H NMR (400 MHz, $CDCl_3$)



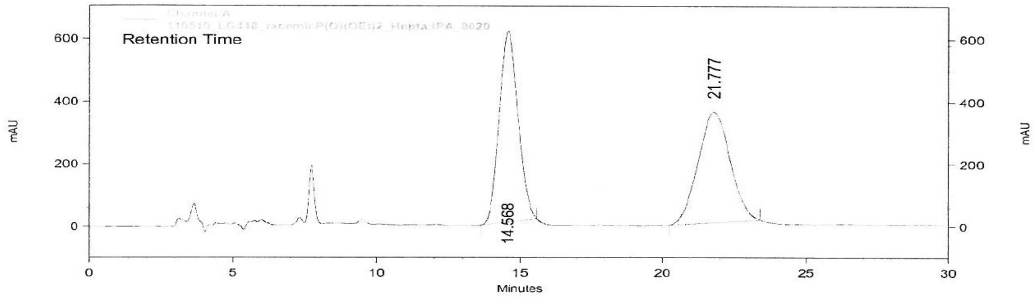
B, ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



12. HPLC chromatograms of compounds 5



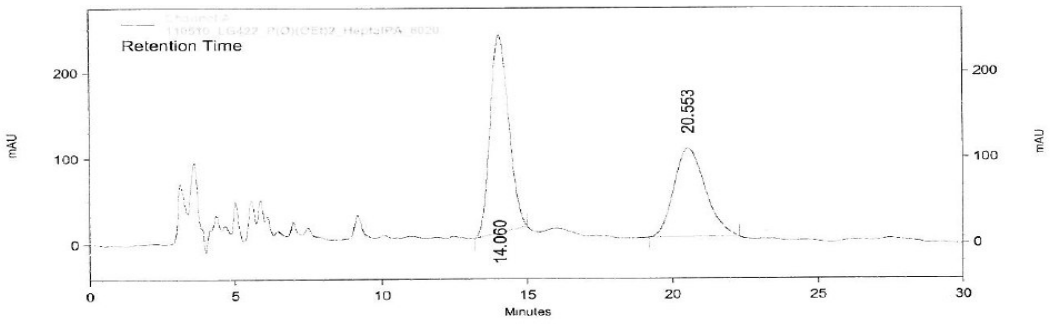
Racemic mixture:



UV-254nm Results (Reprocessed)

Name	Retention Time	Area	Height	Area Percent	Integration Codes
	14.568	28112744	609910	50.71	MM
	21.777	27324548	354275	49.29	MM
Totals		55437292	964185	100.00	

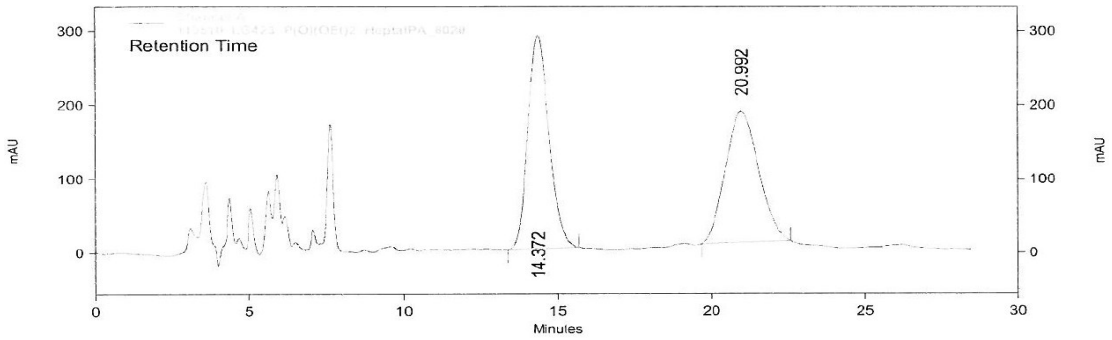
- **Entry 1, Table 2:**



UV-254nm Results (Reprocessed)

Name	Retention Time	Area	Height	Area Percent	Integration Codes
	14.060	10242685	230446	56.83	MM
	20.553	7781231	103330	43.17	MM
Totals		18023916	333776	100.00	

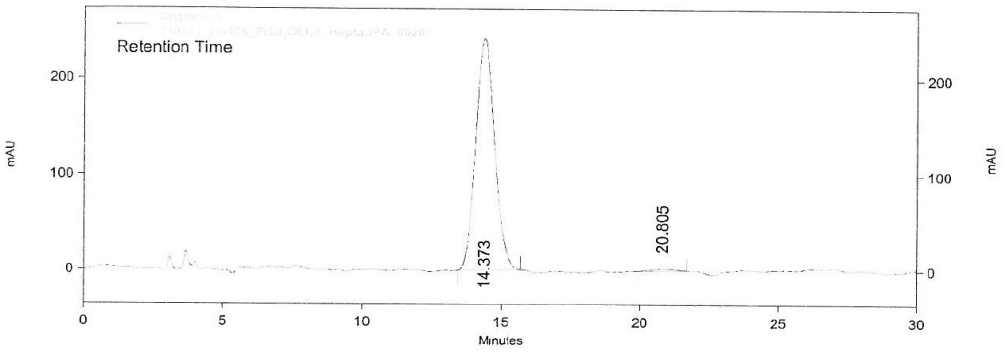
- **Entry 2, Table 2:**



UV-254nm Results (Reprocessed)

Name	Retention Time	Area	Height	Area Percent	Integration Codes
	14.372	13840413	288432	50.81	MM
	20.992	13400347	177400	49.19	MM
Totals		27240760	465832	100.00	

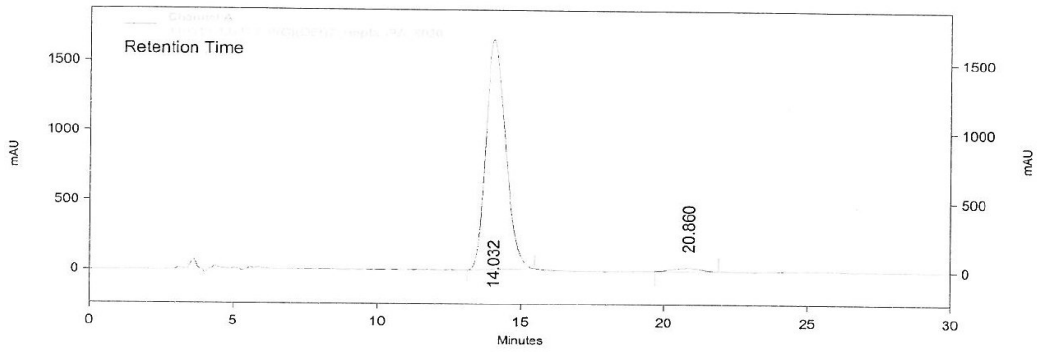
- **Entry 3, Table 2:**



UV-254nm Results (Original)

Name	Retention Time	Area	Height	Area Percent	Integration Codes
	14.373	11678498	242637	98.87	MM
	20.805	133310	2308	1.13	MM
Totals		11811808	244945	100.00	

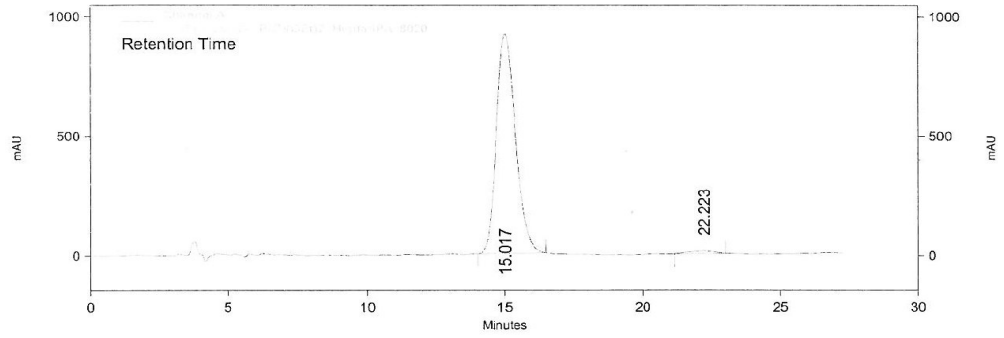
- **Entry 4, Table 2:**



UV-254nm
Results (Original)

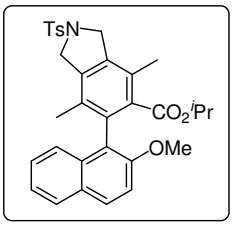
Name	Retention Time	Area	Height	Area Percent	Integration Codes
	14.032	79987670	1658301	98.08	MM
	20.860	1562039	22825	1.92	MM
Totals		81549709	1681126	100.00	

- **Entry 5, Table 2:**

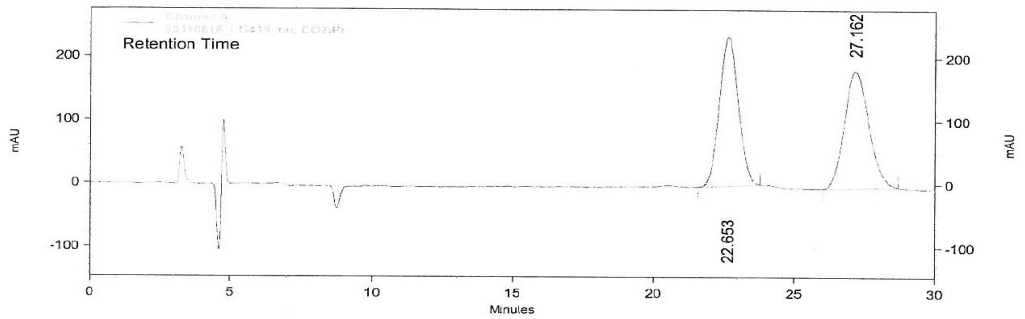


UV-254nm
Results
(Reprocessed)

Name	Retention Time	Area	Height	Area Percent	Integration Codes
	15.017	44140118	918656	98.43	MM
	22.223	705265	10872	1.57	MM
Totals		44845383	929528	100.00	



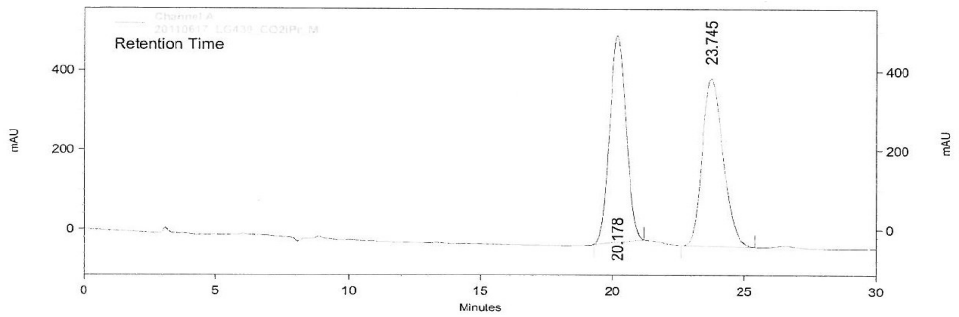
- **Racemic mixture:**



UV-254nm Results (Reprocessed)

Name	Retention Time	Area	Height	Area Percent	Integration Codes
	22.653	11158325	235426	49.94	MM
	27.162	11186485	185219	50.06	MM
Totals		22344810	420645	100.00	

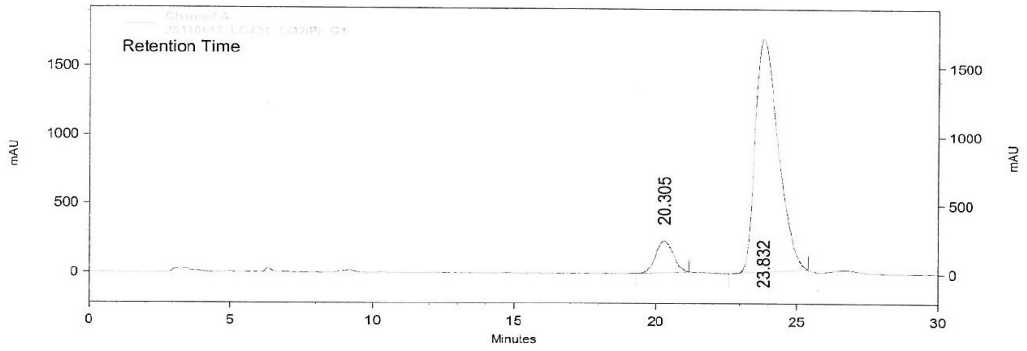
- **Entry 6, Table 2:**



UV-254nm Results (Reprocessed)

Name	Retention Time	Area	Height	Area Percent	Integration Codes
	20.178	22606332	521334	48.93	MM
	23.745	23594847	423859	51.07	MM
Totals		46201179	945193	100.00	

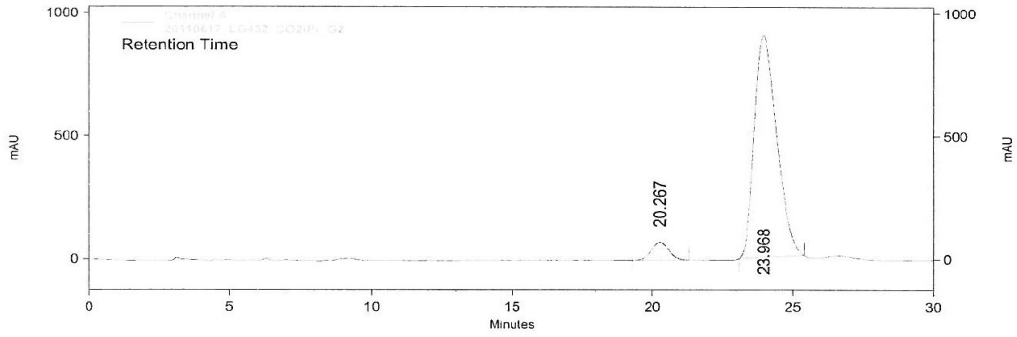
- **Entry 7, Table 2:**



UV-254nm
Results (Original)

Name	Retention Time	Area	Height	Area Percent	Integration Codes
	20.305	10006971	230849	9.47	MM
	23.832	95659636	1696217	90.53	MM
Totals		105666607	1927066	100.00	

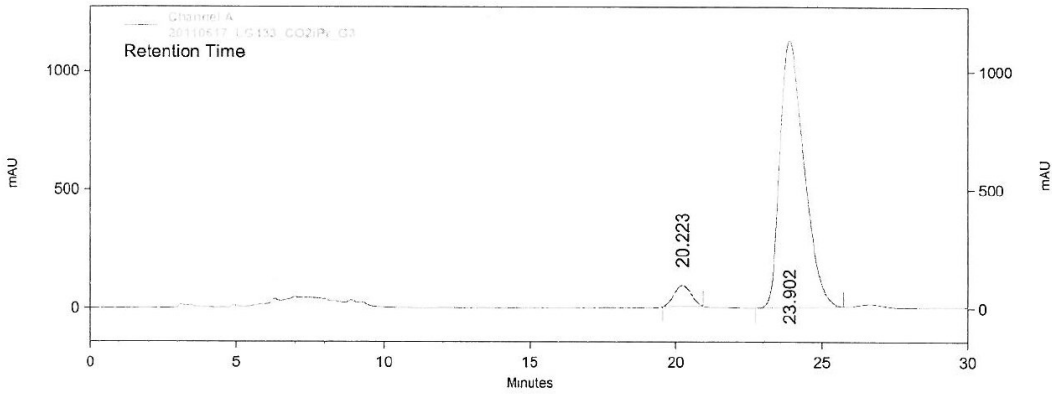
- **Entry 8, Table 2:**



UV-254nm
Results
(Reprocessed)

Name	Retention Time	Area	Height	Area Percent	Integration Codes
	20.267	3106192	71885	5.85	MM
	23.968	49994658	903543	94.15	MM
Totals		53100850	975428	100.00	

- **Entry 9, Table 2:**



UV-254nm Results (Reprocessed)

Name	Retention Time	Area	Height	Area Percent	Integration Codes
	20.223	3517959	87472	5.20	MM
	23.902	64136963	1126726	94.80	MM
Totals		67654922	1214198	100.00	