Supplementary Material (ESI) for Chemical Communications

Supporting Information:

to

Directing the Pathway of Orthogonal 'Click' Reactions by Modulating Copper-Catalytic Activity

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Materials

2-Bromoethanol (98%), imidazole (99%), *t*-butylchlorodiphenylsilane (98%), dimethyl 5-hydroxyisophthalate (98%), lithium aluminium hydride (LAH, 98%), diphenyl phosphoryl azide (DPPA, 97%), 1,8-diazabicylco[5,4,0]undec-7-ene (DBU, 98%), tetrabutylammonium fluoride hydrate (TBAF, 98%), 18-crown-6 ether (18-C-6, 99%), 2-bromopropionyl bromide (BPB, 95%), *t*-butyldimethyl(2-propynyloxy)silane (**1**, 97%), methyl 2-bromopropionate (MBP, 97%), N,N,N',N',N''- pentamethyldiethylenetriamine (PMDETA, 99 %), propargyl bromide (80 wt % in toluene), diethanolamine (99%) and dimethyl sulfoxide (DMSO, >99.9%) were used as received from Sigma-Aldrich. Acryloyl chloride (>96%, Merck) and benzyl mercaptan (99%, Fluka) were used as received. Methanol (MeOH), dichloromethane (DCM), chloroform ($CHCl_3$), tetrahydrofuran (THF) and toluene (TOL) were purchased from Merck and used as received. Ethyl acetate (repacked) and petroleum spirit (repacked, b.p 40-60 ^oC) were obtained from The University of Queensland Chemical Store and used as received. Tris-(2-dimethylaminoethyl)amine (Me_6TREN) was synthesized using a previously published literature procedure.[1]

Measurement

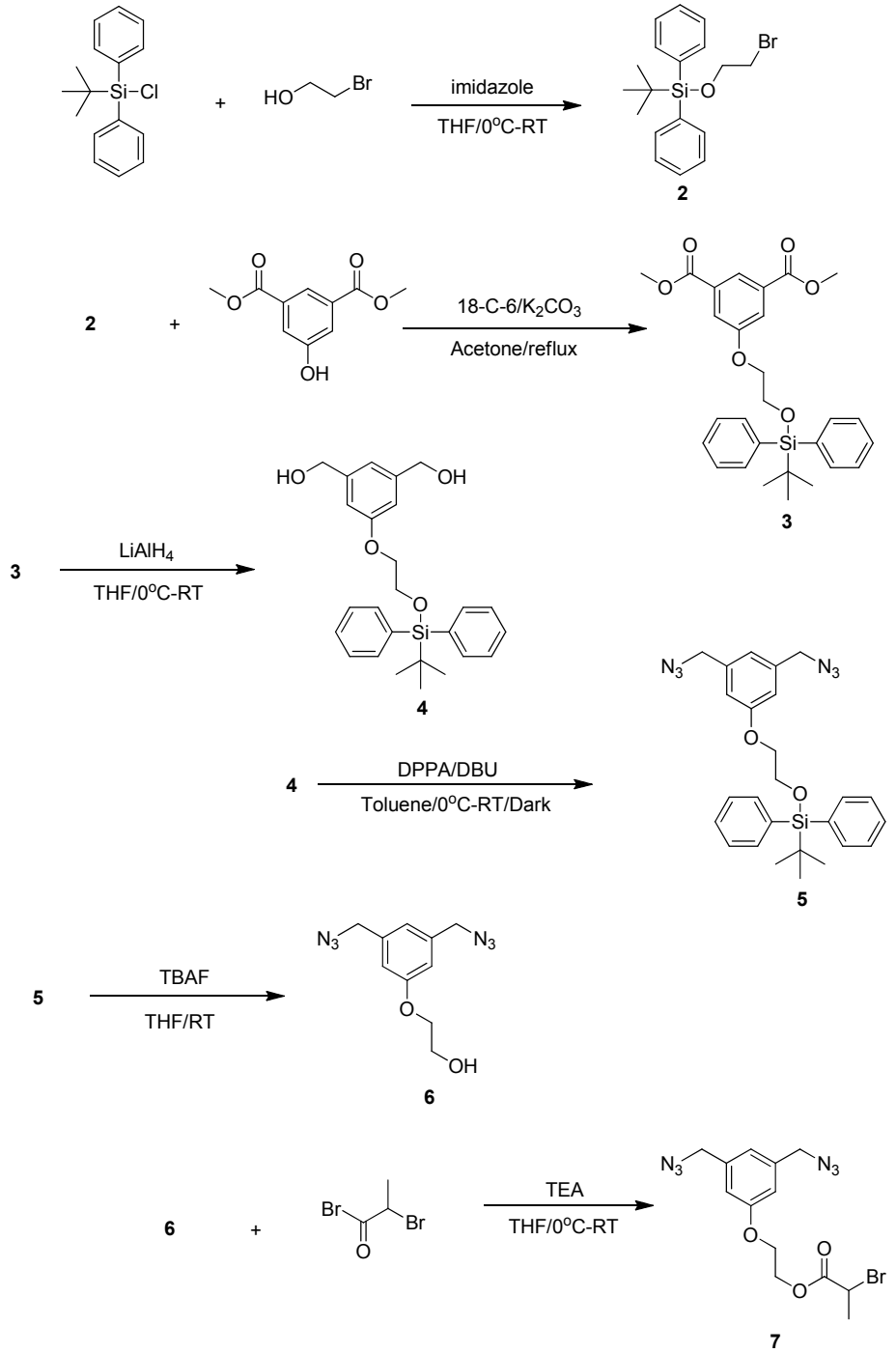
^1H and ^{13}C Nuclear Magnetic Resonance (NMR). All NMR spectra were recorded on a Bruker DRX 300 and Bruker DRX 500 MHz spectrometer, unless otherwise specified.

Low Resolution-Electrospray Ionization-Mass Spectrometry (LR-ESI-MS). All mass spectra were recorded on a Bruker Esquire HCT (High Capacity 3D ion trap) instrument with a Bruker ESI source and positive ion model.

Size Exclusion Chromatography (SEC). The molecular weight distributions of the polymers was determined using a Waters 2695 separations module, fitted with a Waters 410 refractive index detector maintained at 35 ^oC, a Waters 996 photodiode array detector, and two Ultrastyragel linear columns (7.8 x 300 mm) arranged in series. These columns were maintained at 40 ^oC for all analyses and were capable of separating polymers in the molecular weight range of 500-4 million g/mol with high resolution. All samples were eluted at a flow rate of 1.0 mL/min. Calibration was performed using narrow molecular weight PSTY standards (PDI $\leq$ 1.1) ranging from 500 to 2 million g/mol. Data acquisition was performed using Empower software, and molecular weights were calculated relative to polystyrene standards.

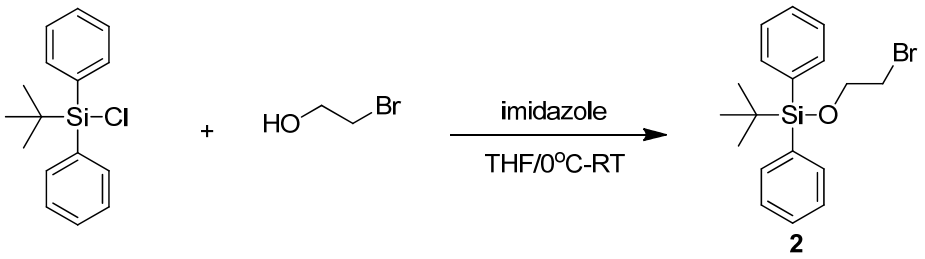
Absolute Molecular Weight Determination by Triple Detection-SEC. Absolute molecular weights of polymers were determined using a Polymer Laboratories GPC50 Plus equipped with dual angle laser light scattering detector, viscometer, and differential refractive index detector. HPLC grade tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL/min. Separations were achieved using two PLGel Mixed C (7.8 x 300 mm) SEC columns connected in series and held at a constant temperature of 40 ^oC. The triple detection system was calibrated using a 2 mg/mL PSTY standard (Polymer Laboratories: M_{wt}=110 K, d*n*/d*c*=0.185 mL/g, and IV=0.4872 mL/g). Samples of known

concentration were freshly prepared in THF and passed through a 0.45 μm PTFE syringe filter prior to injection. The absolute molecular weights and d*n*/d*c* values were determined using Polymer Laboratories Multi-Cirrus software based on the quantitative mass recovery technique.



Scheme S1: Synthetic Path to obtain compound **7**.

Synthesis of (2-bromoethoxy)(tert-butyl)diphenylsilane (2)



2-bromoethanol (7.50 g, 0.06 mol) and imidazole (3.71 g, 0.055 mol) were dissolved in 100 mL THF at 0 °C, and then tert-butylchlorodiphenylsilane (15.00 g, 0.055 mol) dissolved in 20 mL THF was added dropwise into the reaction. The reaction mixture was stirred at room temperature overnight, after which the formation of a precipitate was observed. The precipitate was filtered, and the filtrate concentrated, redissolved in n-hexane and then washed with Milli-Q water. The organic phase was dried over anhydrous magnesium sulphate, filtered and concentrated by rotary evaporation to dryness. The crude product was purified by column chromatography with ethyl acetate/petroleum spirit (1/8, v/v) as the eluent. The product, **2**, was obtained as colorless oil (15.60 g, 78.3 %). R_f (1:8 EtOAc/petroleum spirit) 0.56; ^{1}H NMR ($CDCl_3$, 298K, 500 MHz), δ, ppm: 7.67 (m, 4H; *m*-phenyl protons), 7.38-7.45 (m, 6H; Ar), 3.93 (t, *J*= 6.41 Hz, 2H; -OC*H*$_2$CH$_2$Br), 3.42 (t, *J*= 6.41 Hz, 2H; -OCH$_2$C*H*$_2$Br), 1.07 (s, 9H; -C*H*$_3$). ^{13}C NMR ($CDCl_3$, 298K, 500 MHz) δ, ppm: 135.58, 133.35, 129.99, 127.92, 64.20, 33.22, 26.83, 19.16.

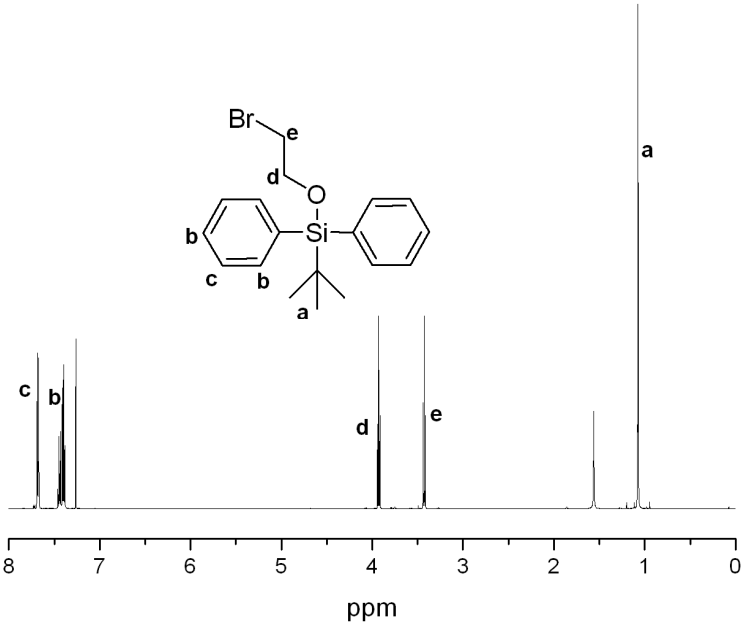


Figure S1: ^{1}H NMR spectrum of 2-(*t*-butyldiphenylsilyloxy)bromoethane, **2**.

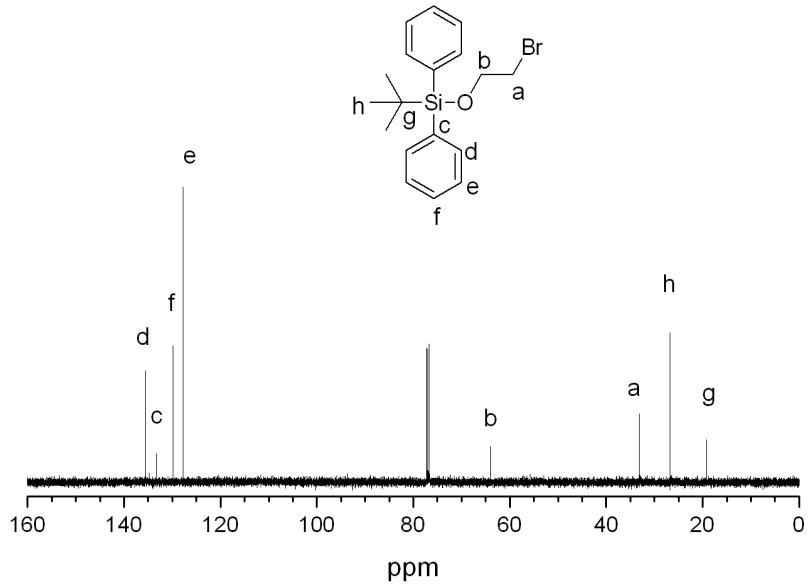
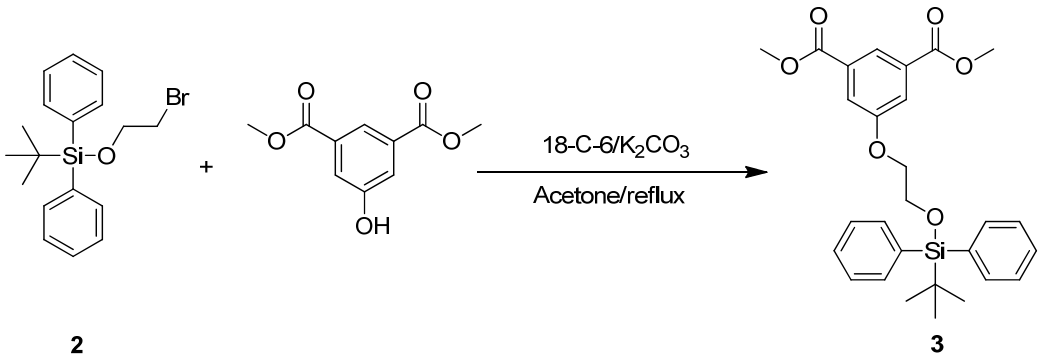


Figure S2: ^{13}C NMR spectrum of 2-(*t*-butyldiphenylsilyloxy)bromoethane, **2**.

Synthesis of dimethyl 5-(2-((tert-butyldiphenylsilyl)oxy)ethoxy)isophthalate (3)



2 **3**

Dimethyl 5-hydroxyisophthalate (4.92 g, 0.023 mol), **2** (10.2 g, 0.028 mol) and 18-crown-6 ether (0.74 g, 2.8 x 10^{-3} mol) were dissolved in 200 mL of acetone. Anhydrous potassium carbonate (3.84 g, 0.028 mol) was added and the reaction was refluxed at 80 ^{o}C for 48 h. The reaction was then cooled to room temperature, filtered, and the filtrate was concentrated by rotary evaporation. The crude product was purified by column chromatography using ethyl acetate/petroleum spirit (1/5, v/v) as the eluent. Upon drying the product, **3**, was obtained as white crystals (7.50 g, 66.3 %). R_f (1/5 EtOAc/petroleum spirit) 0.46; ^{1}H NMR ($CDCl_3$, 298K, 300 MHz) δ, ppm: δ 8.27 (d, *J*=1.45 Hz, 1H; aromatic proton), 7.69-7.74 (m, 6H; aromatic protons), 7.38-7.42 (m, 6H; aromatic protons), 4.18 (t, *J*=4.90 Hz, 2H; -SiOC*H*$_2$CH$_2$O-), 4.02 (t, *J*=4.86 Hz, 2H; -SiOCH$_2$C*H*$_2$O-), 3.95 (s, 6H; C*H*$_3$O-), 1.06 (s, 9H; methyl protons). ^{13}C NMR ($CDCl_3$, 298K, 500 MHz) δ, ppm: 166.27, 159.21, 135.74, 133.50, 131.82, 129.84, 127.81, 123.11, 120.09, 69.86, 62.70, 52.51, 26.87, 19.32.

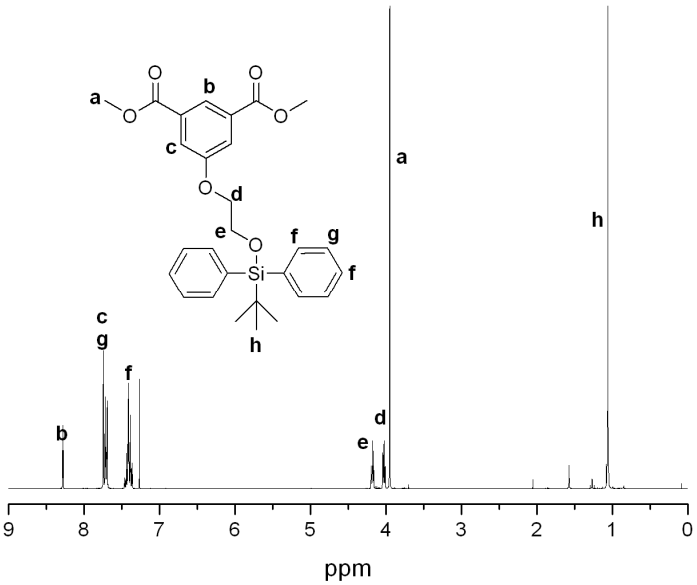


Figure S3: ^{1}H NMR spectrum of dimethyl 5-(2-((tert-butyldiphenylsilyl)oxy)ethoxy)isophthalate, **3**.

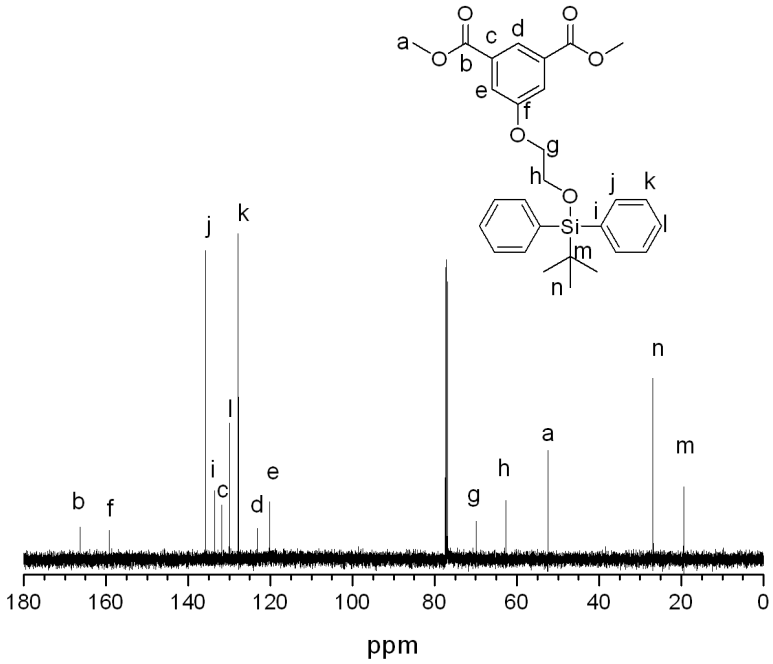
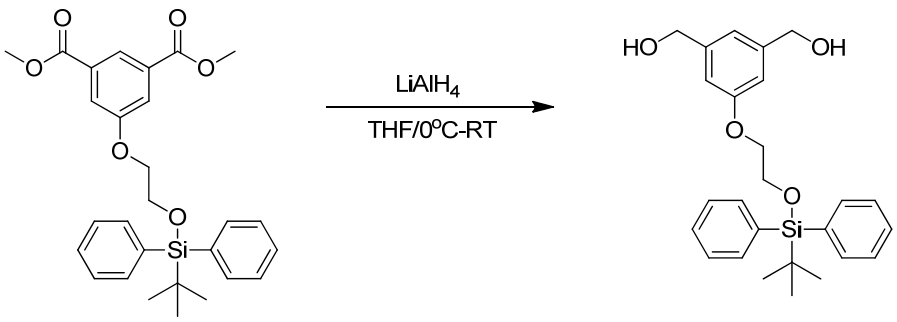


Figure S4: ^{13}C NMR spectrum of dimethyl 5-(2-((tert-butyldiphenylsilyl)oxy)ethoxy)isophthalate, **3**.

Synthesis of (2-(3,5-bis(hydroxymethyl)phenoxy)ethoxy)(tert-butyl)diphenylsilane (4)



3 **4**

3 (7.20 g, 0.015 mol) was dissolved in 150 mL of dry THF at 0 °C under argon. Lithium aluminium hydride (1.33 g, 0.035 mol) was added to the solution portion-wise over 30 min. After stirring for 16 h, the reaction was quenched by slowly adding crushed $Na_2SO_4.10H_2O$. *Caution! Hydrogen is produced.* The mixture was filtered and the filtrate concentrated by rotary evaporation. The product was purified by column chromatography using methanol/dichloromethane (1/4, v/v) as the eluent, and the product, **4**, was obtained as a colorless oil (3.30 g, 51.7 %). R_f (1/4 MeOH/DCM) 0.53; ^{1}H NMR ($CDCl_3$, 298K, 400 MHz); δ 7.67-7.75 (m, 4H; aromatic protons), 7.40-7.45 (m, 6H; aromatic protons), 6.96 (bd, 1H; aromatic proton), 6.84 (bd, 2H; aromatic proton), 4.68 (s, 4H; HOC*H*$_2$-), 4.13 (t, *J*=5.13 Hz, 2H; -SiOC*H*$_2$CH$_2$O-), 4.02 (t, *J*=5.14 Hz, 2H; -SiOCH$_2$C*H*$_2$O-), 1.63 (bd, 2H; *H*OCH$_2$-), 1.08 (s, 9H; methyl protons); ^{13}C NMR ($CDCl_3$, 298K, 400 MHz); δ 159.39, 142.78, 135.70, 133.51, 129.67, 127.67, 117.50, 112.18, 69.14, 64.99, 62.67, 26.78, 19.22.

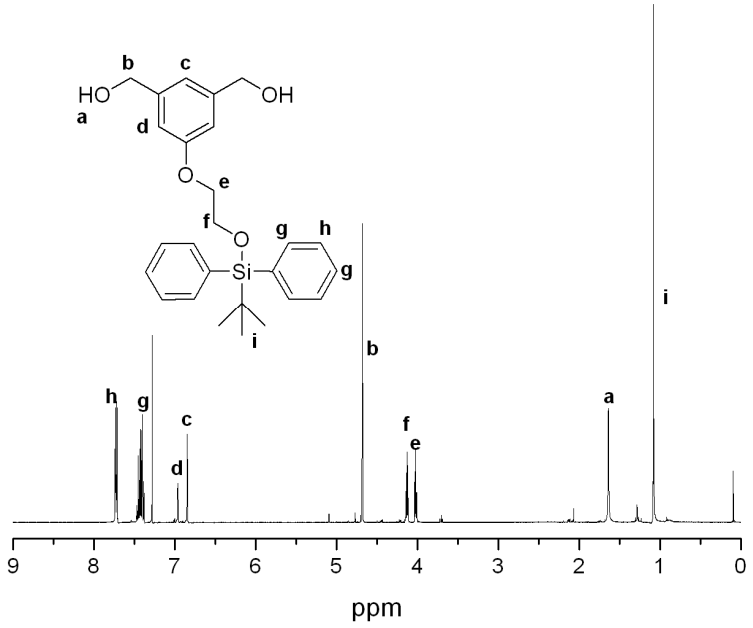


Figure S5: ^{1}H NMR spectrum of (2-(3,5-bis(hydroxymethyl)phenoxy)ethoxy)(tert-butyl)diphenylsilane, **4**.

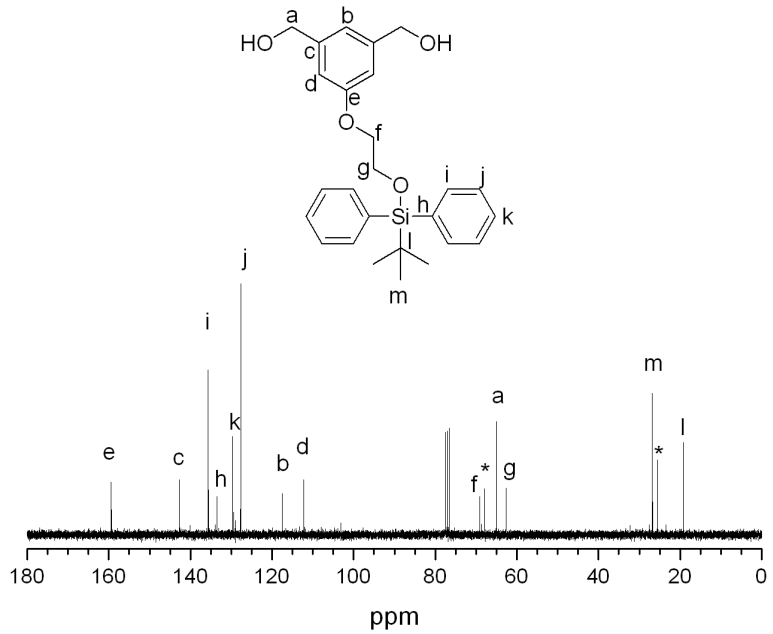
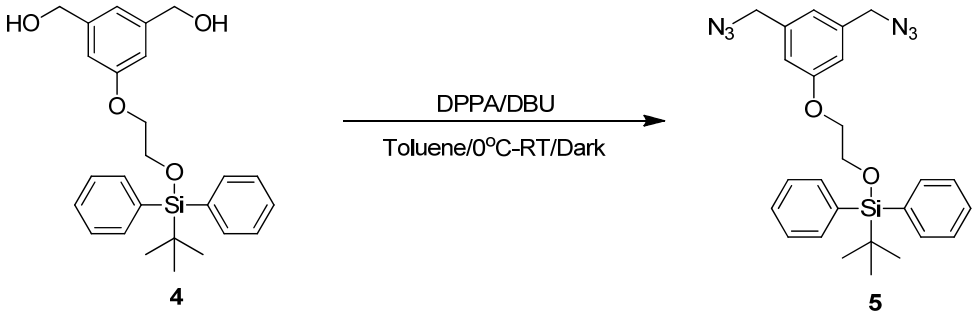


Figure S6: ^{13}C NMR spectrum of (2-(3,5-bis(hydroxymethyl)phenoxy)ethoxy)(tert-butyl)diphenylsilane, **4**. **(*** represents THF peaks)

Synthesis of (2-(3,5-bis(azidomethyl)phenoxy)ethoxy)(tert-butyl)diphenylsilane 5



4 (3.20 g, 7.34 x 10^{-3} mol), DPPA (4.85 g, 17.6 x 10^{-3} mol) and DBU (2.68 g, 17.6 x 10^{-3} mol) were added to 60 mL of dry toluene at 0 ^{o}C. The flask was wrapped in aluminium foil to avoid light. The solution was stirred for 16 h, and then poured into a separation funnel. The colorless toluene phase was then collected and concentrated by rotary evaporation. The product was purified by column chromatography using ethyl acetate/petroleum spirit (1/4, v/v) as the eluent and the product, **5**, was obtained as a colorless oil (2.90 g, 81.3 %). R_f (1/4 EtOAc/petroleum spirit) 0.59; ^{1}H NMR ($CDCl_3$, 298K, 300 MHz); δ 7.70-7.73 (m, 4H; aromatic protons), 7.39-7.42 (m, 6H; aromatic protons), 6.85 (bd, 1H; aromatic proton), 6.80 (bd, 2H; aromatic proton), 4.32 (s, 4H; N_3CH_2-), 4.11 (t, *J*=4.8 Hz, 2H; -SiOCH_2CH$_2$O-), 4.00 (t, *J*=4.8 Hz, 2H; -SiOCH$_2$CH_2O-), 1.07 (s, 9H; methyl protons); ^{13}C NMR ($CDCl_3$, 298K, 500 MHz); δ 159.83, 137.61, 135.76, 133.59, 129.85, 127.82, 120.03, 114.27, 69.43, 62.72, 54.64, 26.91, 19.36.

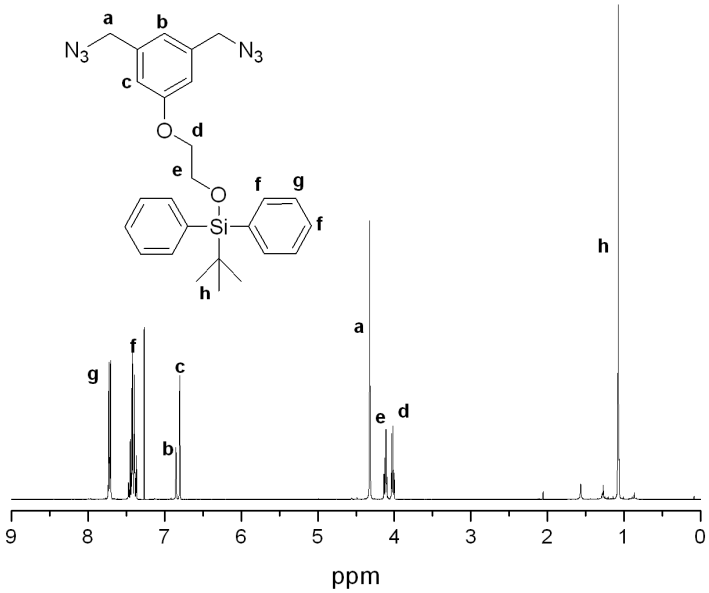


Figure S7: ^{1}H NMR spectrum of (2-(3,5-bis(azidomethyl)phenoxy)ethoxy)(tert-butyl)diphenylsilane, **5**.

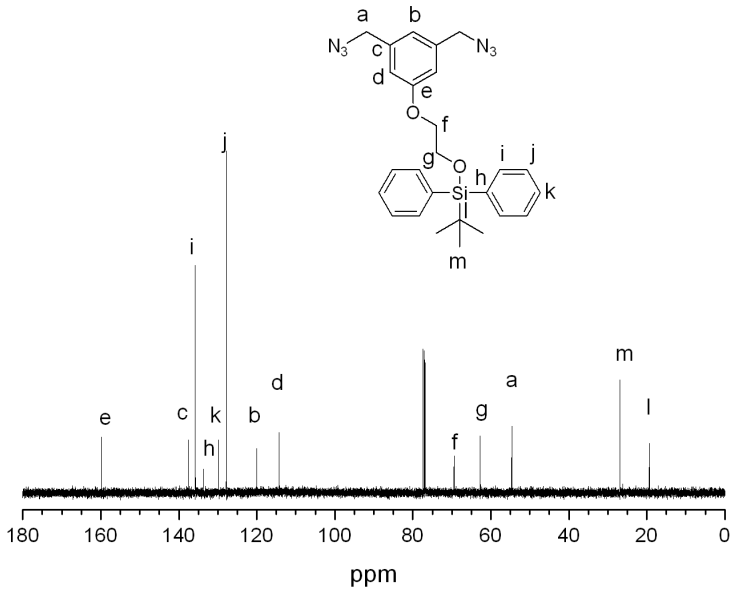
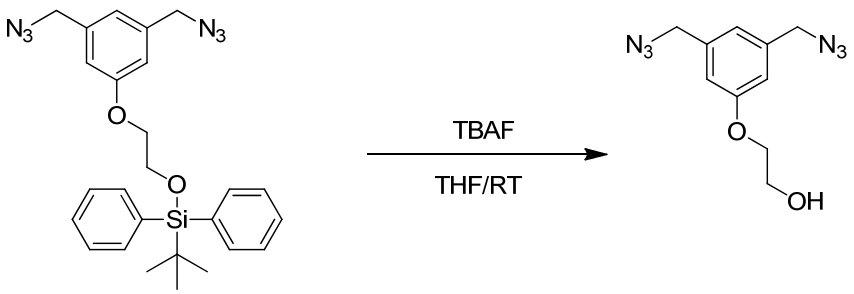


Figure S8: ^{13}C NMR spectrum of (2-(3,5-bis(azidomethyl)phenoxy)ethoxy)(tert-butyl)diphenylsilane, **5**.

Synthesis of 2-(3,5-bis(azidomethyl)phenoxy)ethanol (6)



5 **6**

5 (2.80 g, 5.76 x 10^{-3} mol) was dissolved in 50 mL of dry THF, and then TBAF (2.26 g, 8.64 x 10^{-3} mol) was added to the solution. The solution was stirred for 15 h at room temperature and then concentrated by rotary evaporation. The crude product was purified by column chromatography using methanol/dichloromethane (1/19, v/v) as the eluent and the product, **6**, was obtained as a pale yellow oil (1.25 g, 87.5 %). R_f (1/19 MeOH/DCM) 0.50; ^{1}H NMR ($CDCl_3$, 298K, 300 MHz); δ 6.87 (m, 3H; aromatic proton), 4.34 (s, 4H; N_3CH_2-), 4.12 (t, *J*=4.5 Hz, 2H; -$HOCH_2$-CH_2O-), 3.98 (t, *J*=4.5 Hz, 2H; $HOCH_2CH_2O$-), 1.92 (bd, 1H; $HOCH_2CH_2O$-); ^{13}C NMR ($CDCl_3$, 298K, 300 MHz); δ 159.37, 137.68, 135.26, 120.30, 114.27, 69.38, 61.35, 54.44.

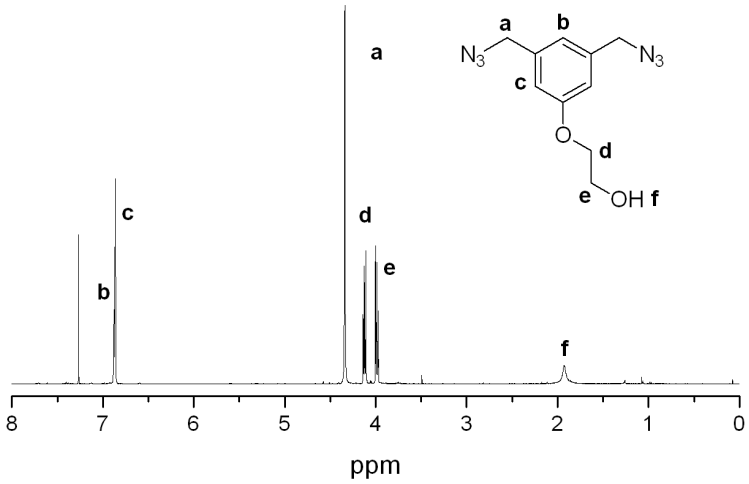


Figure S9: ^{1}H NMR spectrum of 2-(3,5-bis(azidomethyl)phenoxy)ethanol, **6**.

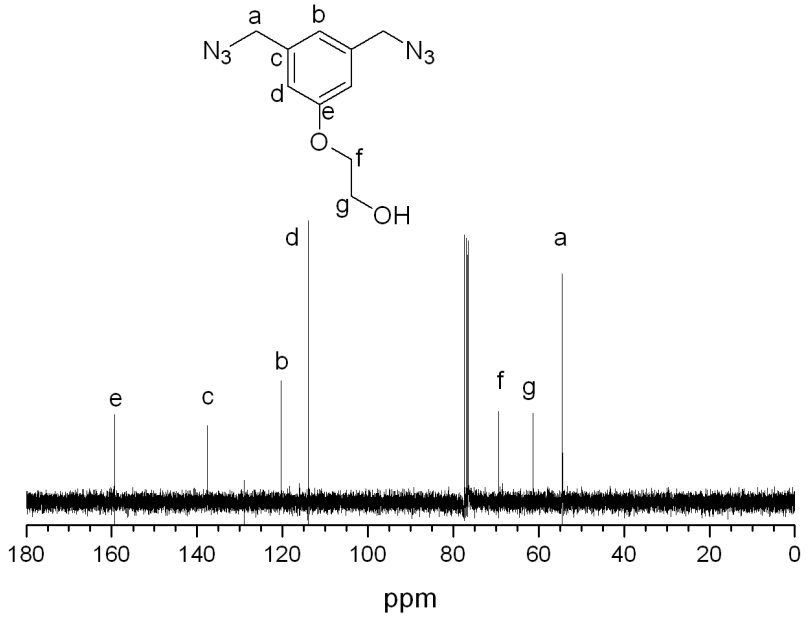
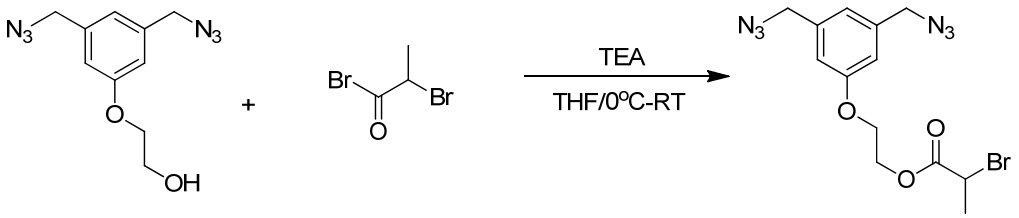


Figure S10: ^{13}C NMR spectrum of 2-(3,5-bis(azidomethyl)phenoxy)ethanol, **6**.

Synthesis of 2-(3,5-bis(azidomethyl)phenoxy)ethyl 2-bromopropanoate (7)



6 **7**

A solution containing 2-bromopropionyl bromide (2.15 g, 0.01 mol) dissolved in 5 mL of dry THF was added dropwise to another solution containing **6** (1.20 g, 4.8 x 10^{-3} mol) and triethylamine (1.01 g, 0.01 mol) dissolved in 20 mL of dry THF at 0 ^{o}C. The reaction was allowed to stir for 4 h, filtered to remove the salts and the filtrate concentrated by rotary evaporation. The crude product was purified by column chromatography using ethyl acetate/petroleum spirit (1/4, v/v) as the eluent. The product, **7**, was obtained as pale yellow oil (1.22 g, 65.8 %). R_f (1/2 EtOAc/petroleum spirit) 0.50; ^{1}H NMR ($CDCl_3$, 298K, 500 MHz); δ 6.85 (bd, 1H; aromatic proton), 6.80 (bd, 2H; aromatic proton), 4.55 (t, *J*=4.71 Hz, 2H; -OCH_2CH_2OCO-), 4.41 (q, *J*=6.93 Hz, 1H; -BrC*H*(CH_3)COO-), 4.30 (s, 4H; N_3CH_2-), 4.25 (dd, *J*=7.66, 4.44 Hz, 2H; -OCH_2CH_2OCO-), 1.85 (d, *J*=6.93, 3H; BrCH(CH_3)COO-); ^{13}C NMR ($CDCl_3$, 298K, 500 MHz); δ 170.35, 159.24, 137.85, 120.58, 114.23, 65.89, 64.08, 54.55, 39.75, 21.69; Microanalysis: Calculated for $C_{13}H_{15}BrN_6O_3$: C, 40.75; H, 3.95; N, 21.93; Found: C, 41.26; H, 4.02; N, 21.60%.

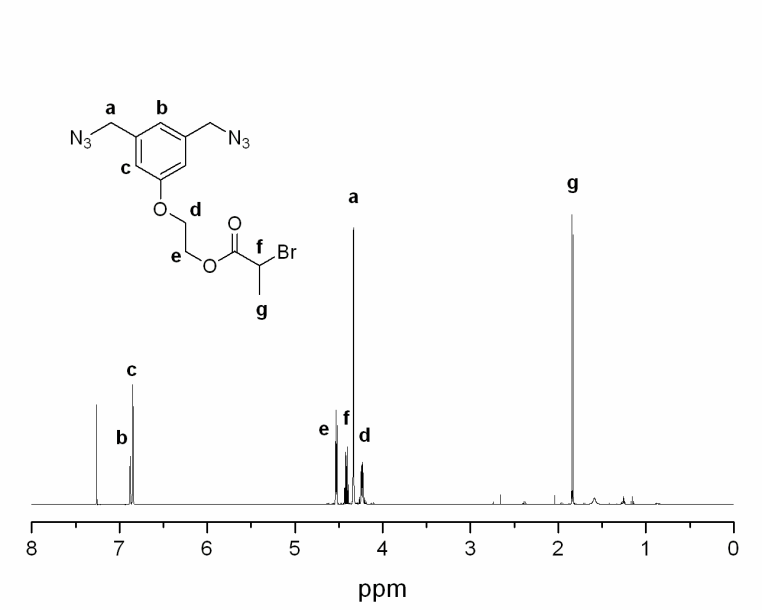


Figure S11: ^{1}H NMR spectrum of 2-(3,5-bis(azidomethyl)phenoxy)ethyl 2-bromopropanoate, **7**.

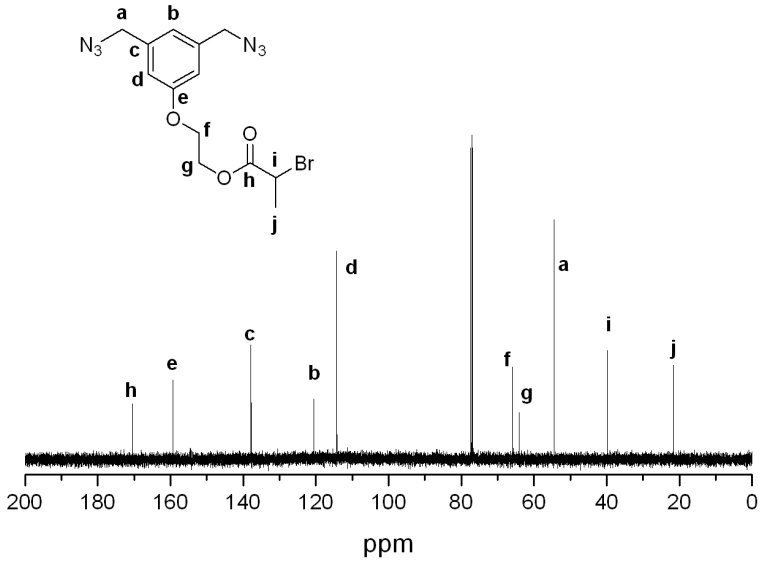
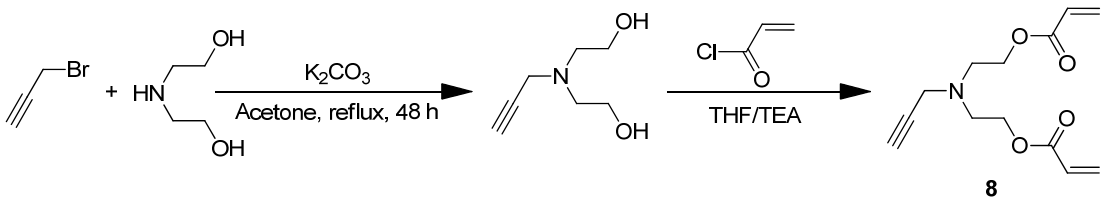


Figure S12: ^{13}C NMR spectrum of 2-(3,5-bis(azidomethyl)phenoxy)ethyl 2-bromopropanoate, **7**.

Synthesis of (prop-2-yn-1-ylazanediyl)bis(ethane-2,1-diyl) diacrylate (8)



8

Propargyl bromide (80% in toluene; 20.00 g, 0.134 mol) and diethanol amine (14.07 g, 0.134 mol) were dissolved in 200 ml of acetone. Anhydrous potassium carbonate (20.00 g 0.145 mol) was added, and the mixture was refluxed for 48 h. The reaction mixture was then filtered to remove the salt, and concentrated by rotary evaporation. The crude product was purified by column chromatography using MeOH/DCM (1/9 v/v) as the eluent. The product, 2,2'-(prop-2-yn-1-ylazanediyl)diethanol, was obtained as pale pink oil (10.52 g, 54.9 %). R_f (1/9 MeOH/DCM) 0.55; ^{1}H NMR ($CDCl_3$, 298K, 300 MHz); δ 3.97 (b, 2H; *H*OCH_2CH_2-), 3.55 (t, *J*=5.25 Hz, 4H; HO*H*$_2$CH_2-), 3.40 (d, *J*=2.37 Hz, 2H; HC≡C-C*H*$_2$-), 2.64 (t, *J*=5.25 Hz, 4H; HOCH$_2$C*H*$_2$-), 2.17 (t, *J*=2.35 Hz, 1H; *H*C≡C-CH$_2$-). ^{13}C NMR ($CDCl_3$, 298K, 500 MHz); δ 78.35, 77.07, 59.10, 55.16, 42.15.

Compound **8** was synthesized using the following procedure: 2,2'-(prop-2-yn-1-ylazanediyl)diethanol (4.30 g, 0.03 mol) and TEA (7.88 g, 0.078 mol) were dissolved in 100 ml of dry THF. The mixture was cooled down to 0 ^{o}C, and acryloyl chloride (7.00 g, 0.078 mol) added dropwise. The reaction was allowed to stir for 3 h. The TEA.HCl salt was filtered, and the filtrate was concentrated. The crude product was purified by column chromatography using MeOH/DCM (2.5/97.5 v/v) as the eluent. The product, **8**, was obtained as a pale yellow oil (4.00 g, 53.1 %). R_f (2.5/97.5 MeOH/DCM) 0.42; ^{1}H NMR ($CDCl_3$, 298K, 300 MHz); δ 6.41 (dd, *J*=17.32, 1.52 Hz, 2H; C*H*$_2$=CH-), 6.12 (dd, *J*=17.31, 10.38 Hz, 1H; CH$_2$=C*H*-), 5.82 (dd, *J*=10.40, 1.52 Hz, 2H; C*H*$_2$=CH-), 4.22 (t, *J*=5.78 Hz, 4H; -C(=O)OC*H*$_2$CH$_2$-), 3.49 (d, *J*=2.35 Hz, 2H; HC≡C-C*H*$_2$-), 2.86 (t, *J*=5.78 Hz, 4H; -C(=O)OCH$_2$C*H*$_2$-), 2.20 (t, *J*=2.35 Hz, 1H; *H*C≡C-CH$_2$-).^{13}C NMR ($CDCl_3$, 298K, 500 MHz); δ 165.97, 130.82, 128.25, 78.17, 73.32, 62.37, 52.25, 43.08.

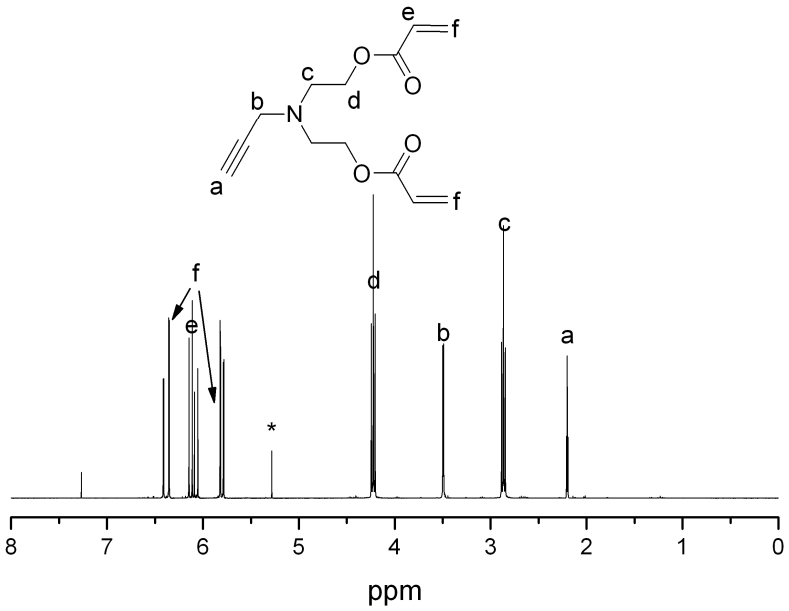


Figure S13: ^{1}H NMR spectrum of (prop-2-yn-1-ylazanediyl)bis(ethane-2,1-diyl) diacrylate, **8**. (***** represents a peak from dichloromethane)

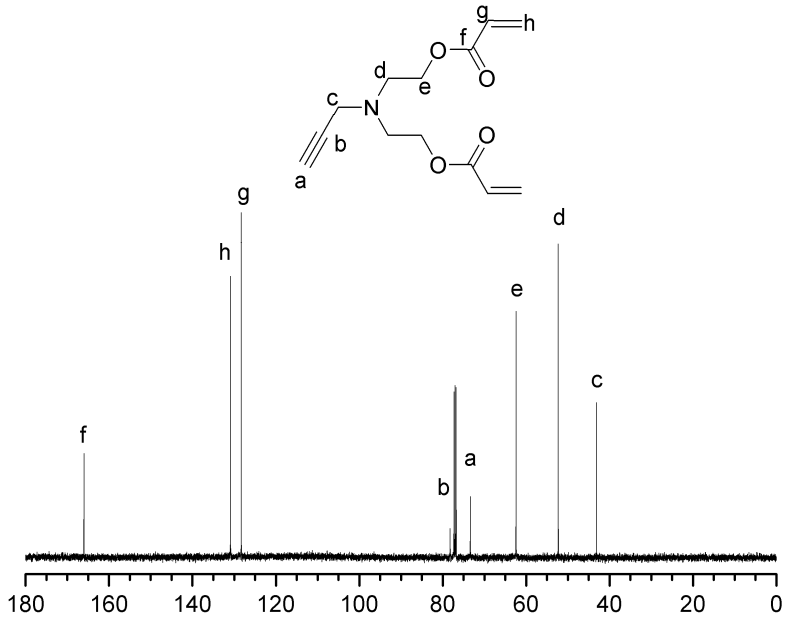
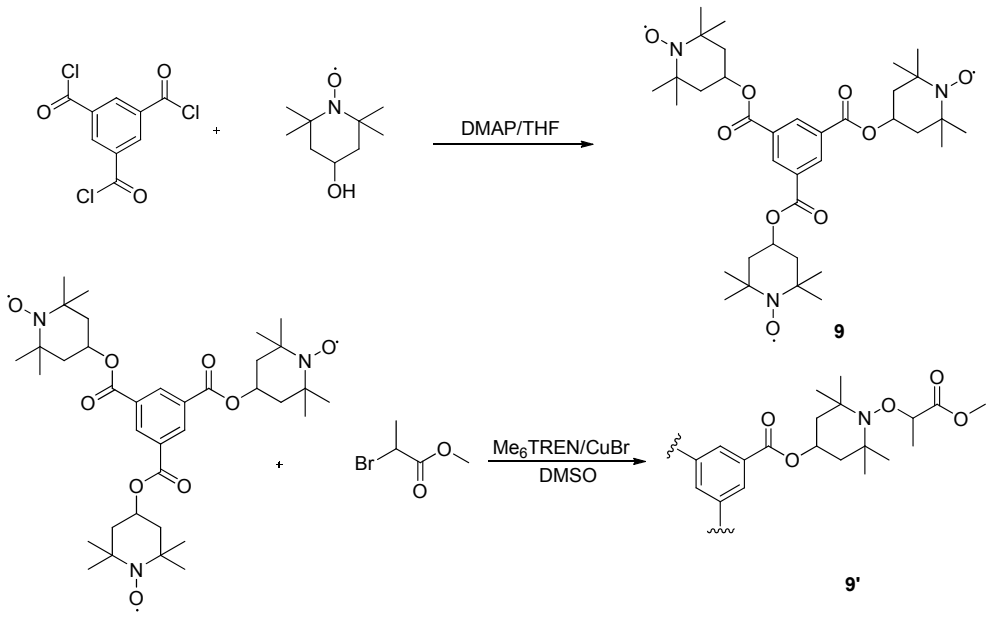


Figure S14: ^{13}C NMR spectrum of (prop-2-yn-1-ylazanediyl)bis(ethane-2,1-diyl) diacrylate, **8**.

Synthesis of tri-nitroxide, tris(4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxyl)-benzene-1,3,5-tricarboxylate (9)



Tri-nitroxide **9** was synthesized according to our previous procedure.[2]

Synthesis of model alkoxyamine, tris(1-((1-methoxy-1-oxopropan-2-yl)oxy)-2,2,6,6-tetramethylpiperidin-4-yl) benzene-1,3,5-tricarboxylate (9')

9 (0.2 g, 2.98 x 10^{-4} mol), Me_6TREN (0.226 g, 9.81 x 10^{-4} mol) and MBP (0.109 mL, 9.77 x 10^{-4} mol) were dissolved in 4 mL of 50 % v/v DMSO/toluene. The solution was purged with argon for 20 min to remove oxygen. Cu(I)Br (0.141 g, 9.83 x 10^{-4} mol) was added to the solution under a positive pressure of argon and the reaction was allowed to stir at room temperature for 1 h. The reaction mixture was then cooled to 0 ^{o}C, diluted with 4 mL of dichloromethane and passed through a basic Al_2O_3 plug to remove the copper. The filtrate was then taken to dryness and the residue was recrystallized from a minimum of hot petroleum spirit to give white needle-like crystals, **9'**, (0.20 g, 72 %). ^{1}H NMR ($CDCl_3$, 298K, 500 MHz): δ 8.73 (s, 3H; Ar*H*), 5.28 (m, COOC*H*CH_2), 4.38 (q, *J*=7 Hz, 3H; OCOC*H*CH_3), 3.73 (s, 9H; COOCH_3), 1.98 (m, *J*=12 Hz, 6H; CHCH_2C), 1.74 (m, *J*=12 Hz, 6H; CHCH_2C), 1.43 (d, *J*=7 Hz, 9H; OCOCHCH_3), 1.28 (s, 27H; CH_3CNO), 1.12 (s, 9H; CH_3CNO); ^{13}C NMR ($CDCl_3$, 298K, 500 MHz): δ 174.13, 164.41, 134.22, 131.39, 81.64, 68.15, 60.42, 59.86, 51.50, 44.38, 44.18, 33.51, 32.75, 20.95, 20.81, 18.03; Microanalysis: Calculated for $C_{48}H_{75}N_3O_{15}$: C, 61.72; H, 8.09; N, 4.50. Found: C, 61.69; H, 8.20; N, 4.50 %.

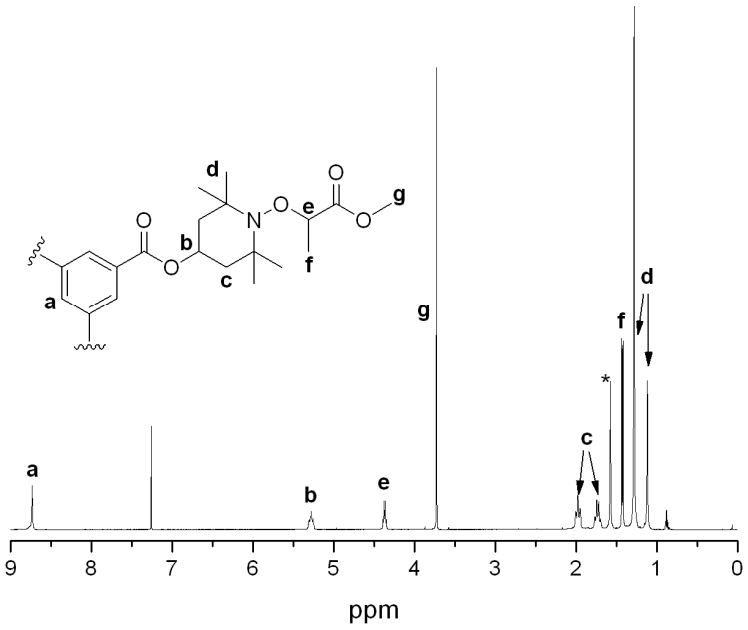


Figure S15: ^{1}H NMR spectrum of model alkoxyamine, **9'**. (***** represents a peak from H_2O)

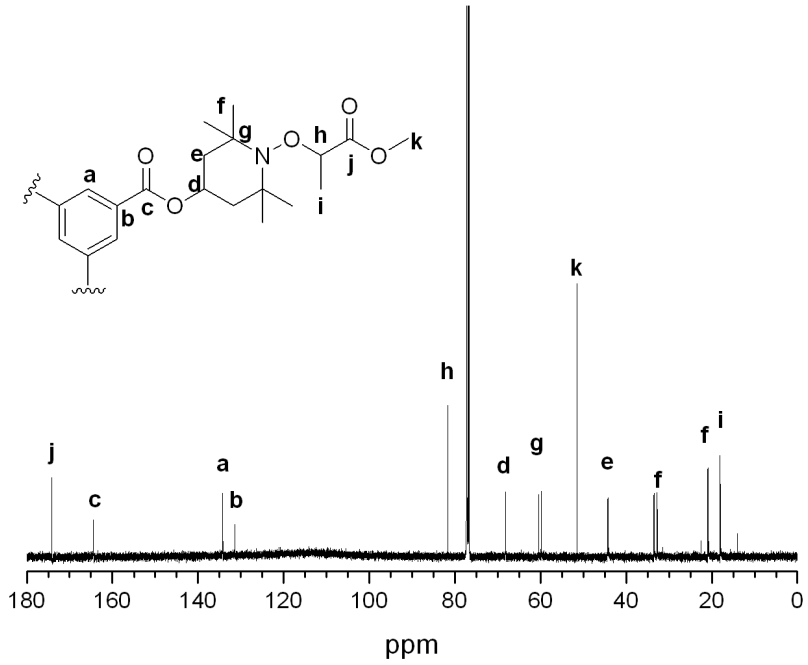


Figure S16: ^{13}C NMR spectrum of model alkoxyamine, **9'**.

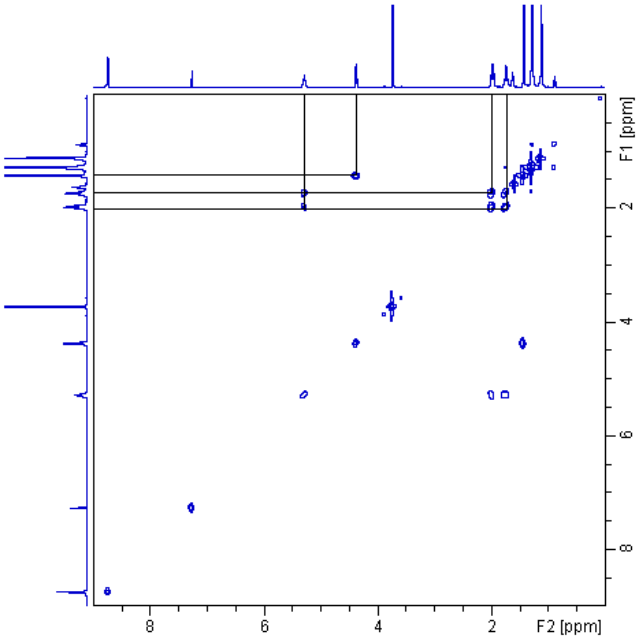


Figure S17: 2D COSY NMR spectrum of model alkoxyamine, **9'**.

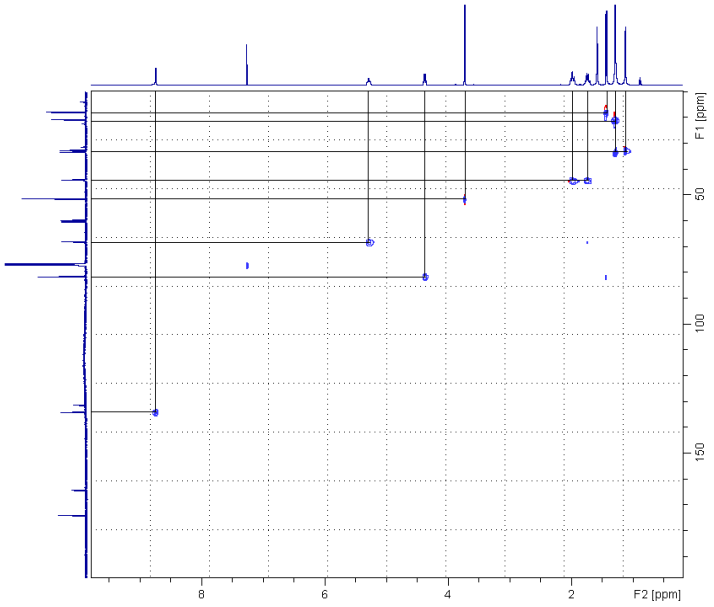
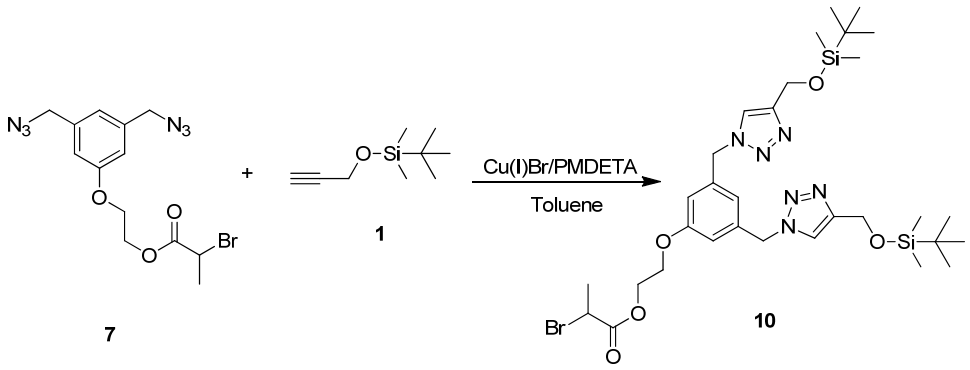


Figure S18: 2D HSQC NMR spectrum of model alkoxyamine, **9'**.

Synthesis of wedge structure (10)



7 (38.3 mg, 1.0 × 10^{-5} mol), **1** (37.4 mg, 2.2 x 10^{-5} mol) and PMDETA (8.7 mg, 5.0 x 10^{-6} mol) were dissolved in 3 mL of toluene. The solution was purged with argon for 30 min, and Cu(I)Br (7.2 mg, 5.0 x 10^{-6} mol) was then added under a positive argon atmosphere. The reaction was carried out at 25 ^{o}C for 3 h. The toluene solution was reduced in volume using an air flow over the top of the reaction mixture; the residue was redissolved in chloroform and washed with Milli-Q water (3 times) to remove the copper complex. The chloroform phase was dried with anhydrous magnesium sulphate, passed through a small Al_2O_3 plug, concentrated and taken to complete dryness on a high vacuum line to give a colorless sticky product, **10**, (57 mg, 78.8 % yield, 99 % purity). ^{1}H NMR ($CDCl_3$, 298K, 500 MHz); δ 7.42 (s, 2H; protons from triazole ring), 6.78 (s, 1H; aromatic proton), 6.73 (s, 2H; aromatic proton), 5.44 (s, 4H; -ArCH_2N-), 4.82 (s, 4H; -SiOCH_2C-), 4.45 (t, *J*=4.75 Hz, 2H; -ArOCH$_2$CH_2O-), 4.38 (q, *J*=6.94 Hz, 1H; -OC(O)C*H*(CH$_3$)Br), 4.10 (m, 2H; -ArOCH_2CH$_2$O-), 1.81 (d, *J*=6.93 Hz, 3H; -OC(O)CH(CH_3)Br), 0.88 (s, 18H; -OSi((CH$_3$)$_2$)C(CH_3)$_3$), 0.07 (s, 12H; -OSi((CH_3)$_2$)C(CH$_3$)$_3$). ^{13}C NMR ($CDCl_3$, 298K, 500 MHz): δ 170.25, 159.54, 149.37, 137.54, 121.77, 119.91, 114.29, 65.90, 63.85, 58.01, 53.66, 39.67, 25.99, 21.66, 18.44, -5.15; Microanalysis: Calculated for $C_{31}H_{51}BrN_6O_5Si_2$: C, 51.44; H, 7.10; N, 11.61; Found: C, 51.67; H, 7.33; N, 11.67 %.

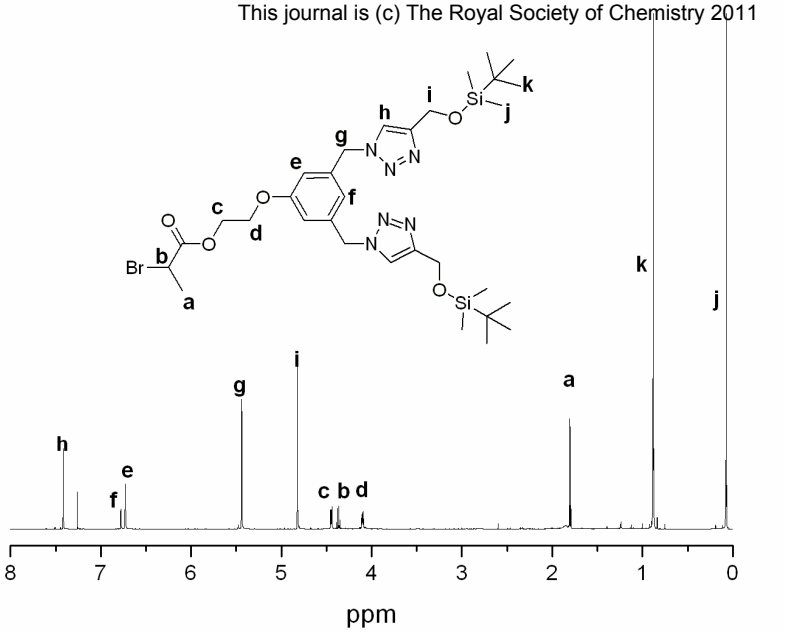


Figure S19: ^{1}H NMR spectrum of wedge structure **10** (formed using toluene as solvent and PMDETA as ligand; **7**:**1**:PMDETA:CuBr =1:2.1:0.5:0.5).

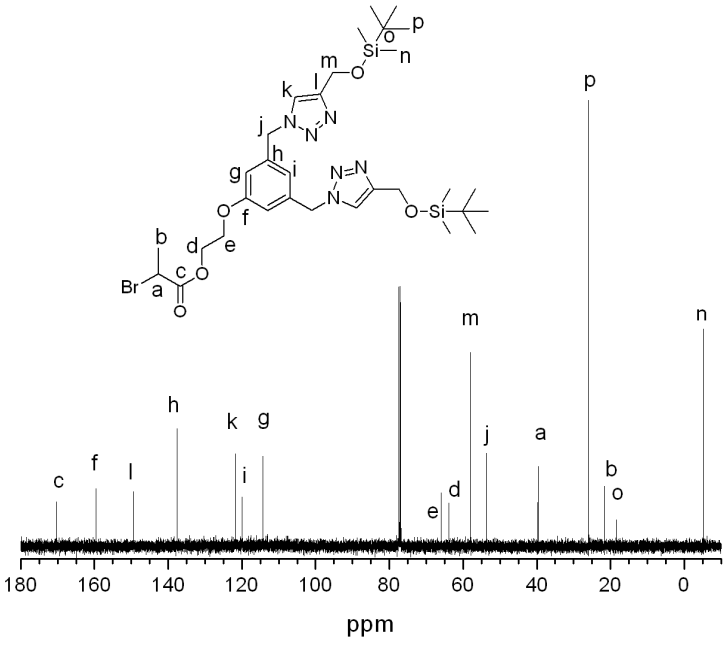


Figure S20: ^{13}C NMR spectrum of wedge structure **10** (formed using toluene as solvent and PMDETA as ligand; **7**:**1**:PMDETA:CuBr =1:2.1:0.5:0.5).

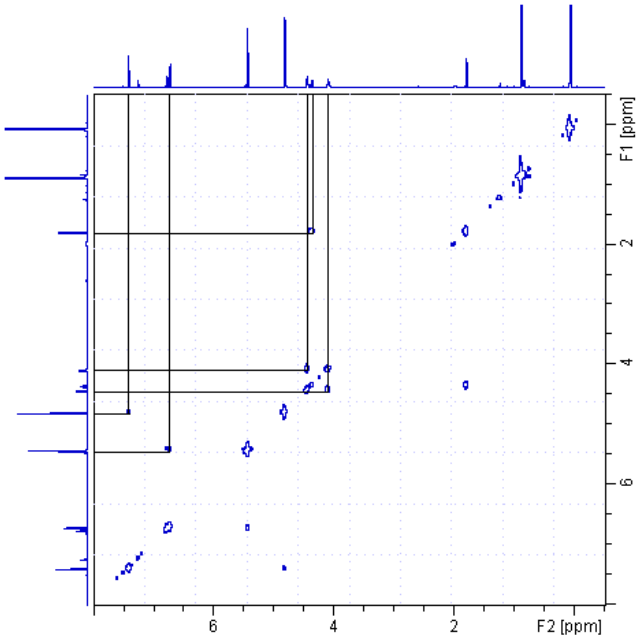


Figure S21: 2D COSY NMR spectrum of wedge structure **10** (formed using toluene as solvent and PMDETA as ligand; **7**:**1**:PMDETA:CuBr =1:2.1:0.5:0.5).

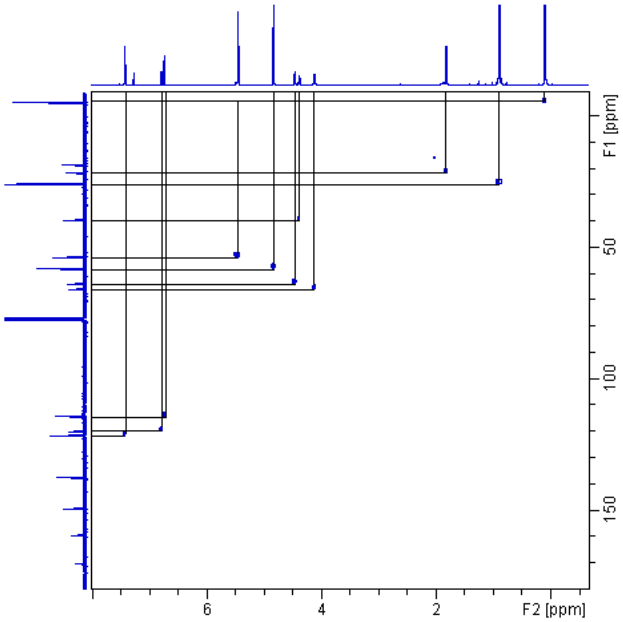
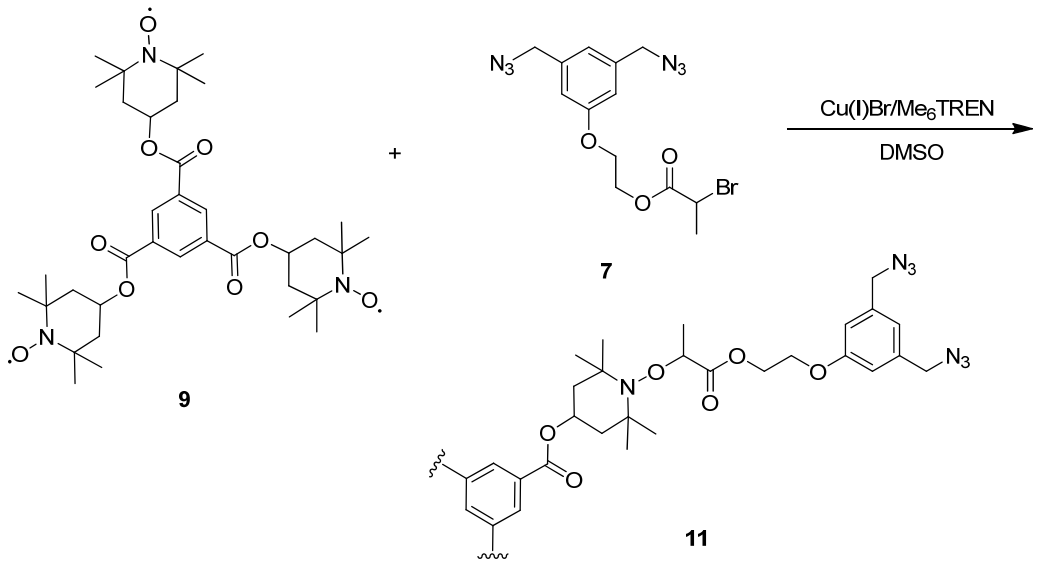


Figure S22: 2D HSQC NMR spectrum of wedge structure **10** (formed using toluene as solvent and PMDETA as ligand; **7**:**1**:PMDETA:CuBr =1:2.1:0.5:0.5).

Synthesis of 1st generation dendrimer (11)



9 (22.4 mg, 3.33 x 10^{-5} mol), **7** (40.0 mg, 1.05 x 10^{-4} mol) and Me_6TREN (30.0 mg, 1.3 x 10^{-4} mol) were dissolved in 2 mL of DMSO. The solution was purged with argon for 30 min, and Cu(I)Br (18.6 mg, 1.3 x 10^{-4} mol) was then added under an argon atmosphere. The reaction was carried out at 25 ^{o}C for 40 min. The solution was diluted by the addition of 4 mL chloroform, and then washed with Milli-Q water (3 times) to remove DMSO and the copper complex. The chloroform phase was dried over anhydrous magnesium sulphate, passed through a small Al_2O_3 plug, concentrated and taken to complete dryness on a high vacuum line to give a pale yellow sticky product, **11**, (45.0 mg, 85.3 % yield, 96 % purity). ^{1}H NMR ($CDCl_3$, 298K, 500 MHz); δ 8.72 (s, 3H; core aromatic protons), 6.87 (s, 3H; aromatic protons), 6.83 (s, 6H; aromatic protons), 5.27 (m, 3H; -(O)COC*H*$_2$CH$_2$-), 4.49 (m, 6H; -(O)COC*H*$_2$CH$_2$OAr-), 4.42 (q, *J*=6.88 Hz, 3H; -NOC*H*(CH$_3$)C(O)O-), 4.30 (s, 12H; -ArC*H*$_2$N$_3$), 4.23 (t, *J*=4.12 Hz, 6H; -(O)COCH$_2$C*H*$_2$OAr-), 1.96 (m, 6H; -OCHC*H*$_2$C), 1.70 (m, 6H; -OCHC*H*$_2$C), 1.46 (d, *J*=6.91 Hz, 9H; -NOCH(C*H*$_3$)C(O)O-)), 1.27 (s, 27H; -ONCC*H*$_3$), 1.13 (s, 9H; -ONCC*H*$_3$); ^{13}C NMR ($CDCl_3$, 298K, 500 MHz): δ 173.89, 170.25, 159.29, 137.74, 134.44, 131.60, 120.45, 114.10, 81.95, 68.31, 65.96, 62.92, 60.05, 54.58, 44.50, 33.81, 33.02, 21.03, 18.60; Microanalysis: Calculated for $C_{75}H_{99}N_{21}O_{18}$: C, 56.91; H, 6.30; N, 18.58; Found: C, 56.84; H, 6.65; N, 17.49 %.

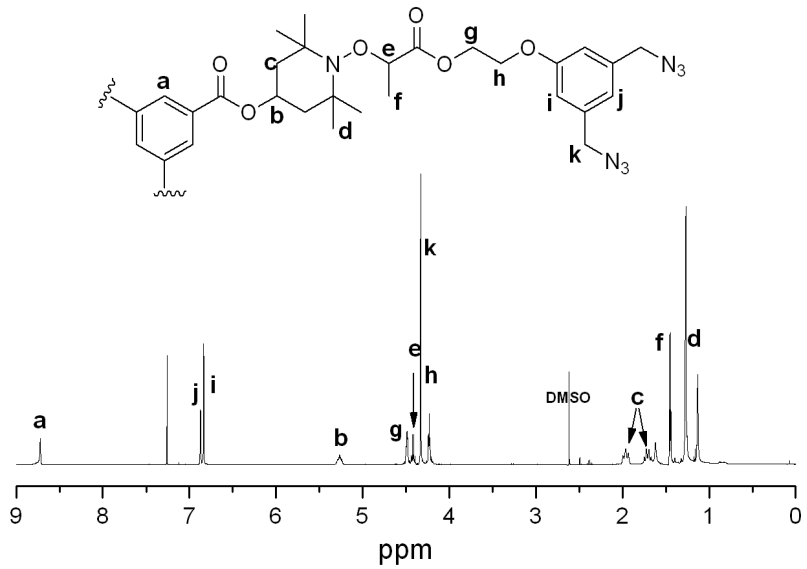


Figure S23: ^{1}H NMR spectrum of G1 dendrimer, **11** (formed using DMSO as solvent and Me_6TREN as ligand, **9**:**7**:Me_6TREN:CuBr=1:3.15:4:4).

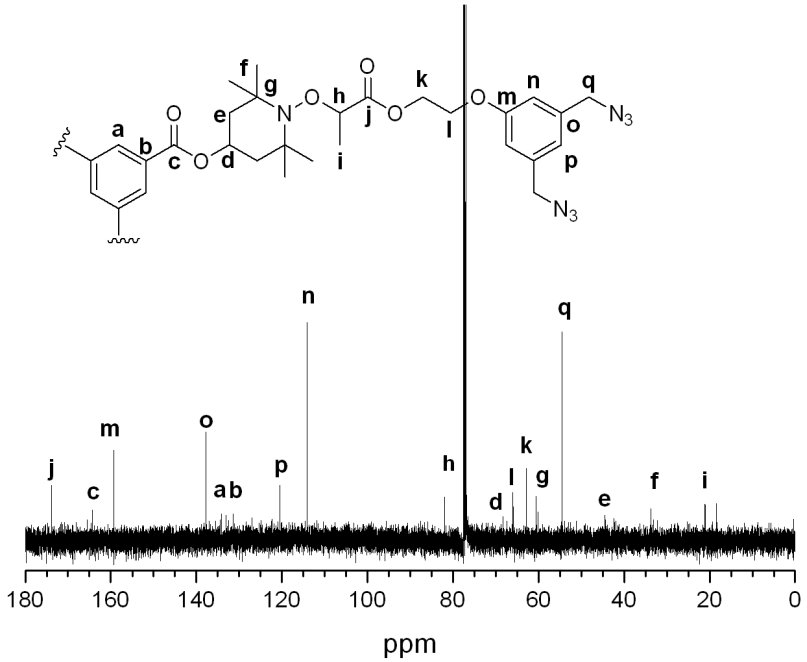


Figure S24: ^{13}C NMR spectrum of G1 dendrimer, **11** (formed using DMSO as solvent and Me_6TREN as ligand, **9**:**7**:Me_6TREN:CuBr=1:3.15:4:4).

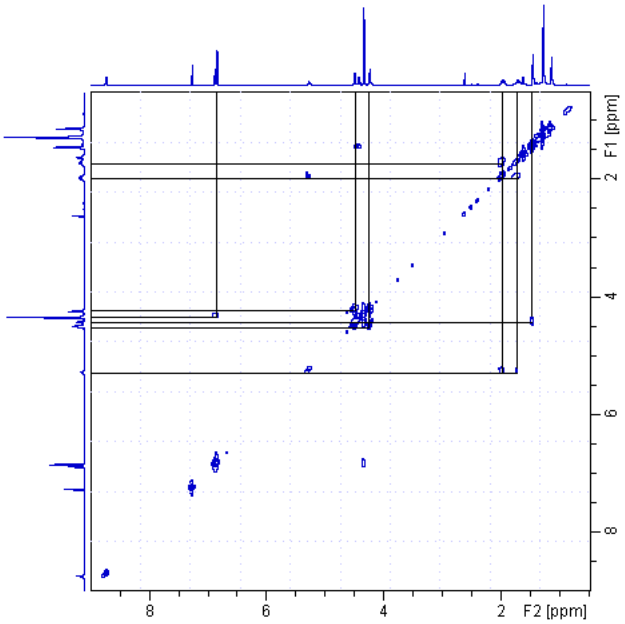


Figure S25: 2D COSY NMR spectrum of G1 dendrimer, **11** (formed using DMSO as solvent and Me_6TREN as ligand, **9**:**7**:Me_6TREN:CuBr=1:3.15:4:4).

Synthesis of 2nd generation dendrimer (12)

(i) Convergent synthesis

9 (44.8 mg, 6.67 x 10^{-5} mol), **7** (80.0 mg, 2.0 x 10^{-4} mol), **1** t-butyldimethyl(2-propynyloxy)silane (78.0 mg, 4.4 x 10^{-4} mol) and PMDETA (46.2 mg, 2.67 x 10^{-4} mol) were dissolved in 4 mL of toluene. The solution was purged by argon flow for 30 min, and Cu(I)Br (38.3 mg, 2.67 x 10^{-4} mol) was then added under an argon atmosphere. The reaction was carried out at 25 ^{o}C. Samples (0.3 mL of solution) were taken at the predetermined intervals for SEC analysis. The samples for ^{1}H NMR determinations were processed as following: the sample solution was blown to remove the toluene, the residue was dissolved in $CDCl_3$, and washed with Milli-Q water (3 times). The chloroform phase was dried over anhydrous $MgSO_4$, passed through a small Al_2O_3 plug, and then another 0.1 mL of $CDCl_3$ containing 3 µl phenylhydrazine was added under Ar flow. The mixture was then immediately checked by ^{1}H NMR. The final 2 mL of solution was dried by air flow and the residue was redissolved in 4 mL chloroform. This solution was then washed by Milli-Q water (3 times) to remove the copper complex. The chloroform phase was dried over anhydrous $MgSO_4$, passed through a small Al_2O_3 plug, concentrated and taken to complete dryness on a high vacuum line to give a pale yellow sticky product, **12** (79.0 mg, 91.0 % yield, 94 % purity).

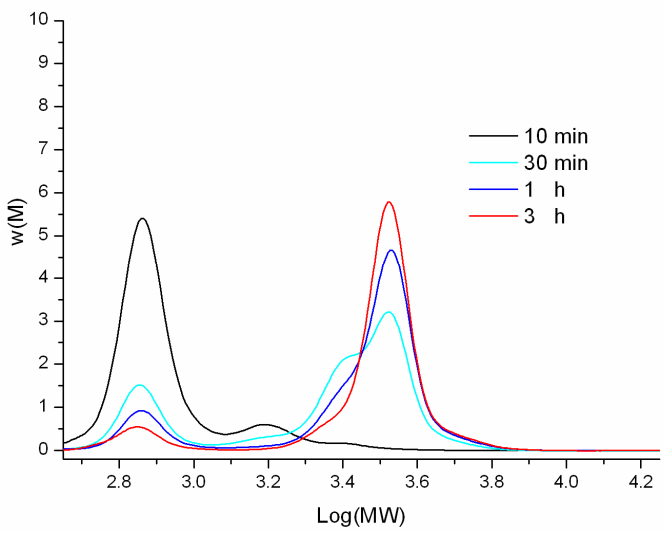


Figure S26: Size Exclusion Chromatography (SEC) traces of the synthesis of the G2 dendrimer, **12,** by convergent procedure at 25 ^{o}C using toluene as solvent and PMDETA as ligand, **9**:**7**:**1**:PMDETA:Cu(I)Br =1:3.15:6.6:4:4

(ii) Divergent synthesis

9 (44.8 mg, 6.7 x 10^{-5} mol), **7** (80.0 mg, 2.0 x 10^{-4} mol), **1** t-butyldimethyl(2-propynyloxy)silane (78.0 mg, 4.4 x 10^{-4} mol) and Me_6TREN (61.3 mg, 2.7 x 10^{-4} mol) were dissolved in 4 mL of DMSO. The solution was purged with argon for 30 min, and Cu(I)Br (38.3 mg, 2.67 x 10^{-4} mol) was then added under a positive argon atmosphere. The reaction was carried out at 25 ^{o}C. Samples (0.3 mL of solution) were taken at the predetermined intervals and diluted with chloroform. The solution was then washed by Milli-Q water, dried over $MgSO_4$ and taken to dryness. The residue was analyzed by ^{1}H NMR and SEC. The final 2 mL of solution was diluted with 6 mL of chloroform and washed with Milli-Q water (3 times) to remove DMSO and the copper complex. The chloroform phase was dried over anhydrous magnesium sulphate, passed through a small Al_2O_3 plug, concentrated and taken to complete dryness on a high vacuum line to give a pale yellow sticky product, **12**, (81.0 mg, 93.3 % yield, 97 % purity).

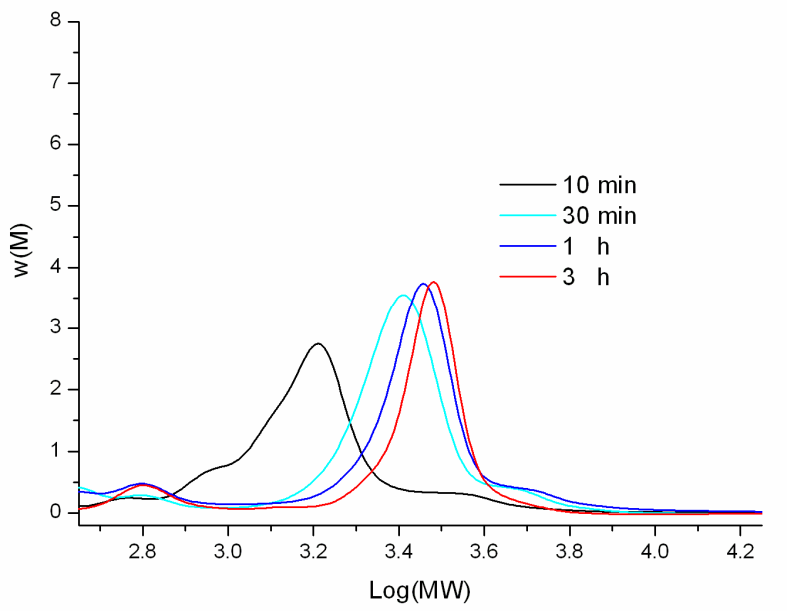


Figure S27: Size Exclusion Chromatography (SEC) traces of the synthesis of the G2 dendrimer, **12,** by the divergent procedure at 25 ^{o}C with DMSO as solvent and Me_6TREN as ligand, **9**:**7**:**1**:Me_6TREN:Cu(I)Br =1:3.15:6.6:4:4.

(iii) Parallel synthesis

9 (44.8 mg, 6.7 x 10^{-5} mol), **7** (80.0 mg, 2.0 x 10^{-4} mol), **1** t-butyldimethyl(2-propynyloxy)silane (78.0 mg, 4.4 x 10^{-4} mol) and PMDETA (46.2 mg, 2.7 x 10^{-4} mol) were dissolved in 4 mL of DMSO. The solution was purged with argon for 30 min, and Cu(I)Br (38.3 mg, 2.7 x 10^{-4} mol) was then added under a positive argon atmosphere. The reaction was carried out at 25 ^{o}C. Samples (0.3 mL of solution) were taken at the predetermined intervals and diluted with chloroform. The solution was then washed with Milli-Q water, dried over $MgSO_4$ and taken to dryness. The residue was analysed by ^{1}H NMR and SEC. The final 2 mL of solution was diluted with 6 mL of chloroform and washed with Milli-Q water (3 times) to remove DMSO and the copper complex. The chloroform phase was dried over anhydrous magnesium sulphate, passed through a small Al_2O_3 plug, concentrated and taken to complete dryness on a high vacuum line to give a pale yellow sticky product, **12**, (82 mg, 94.5 % yield, 94 % purity). ^{1}H NMR ($CDCl_3$, 298K, 500 MHz); δ 8.72 (s, 3H; core aromatic protons), 7.42 (s, 6H; triazole protons), 6.77 (s, 3H; aromatic protons), 6.71 (s, 6H; aromatic protons), 5.44 (s, 12H; -SiOC*H*$_2$-), 5.27 (m, 3H; -(O)COC*H*$(CH_2)CH_2$-), 4.81 (s, 12H; -ArC*H*$_2$triazole-), 4.35-4.5 (bd, 9H; -NOC*H*(CH_3)C(O)O-, -(O)COC*H*$_2CH_2$OAr-), 4.10 (t, 6H; -(O)COCH$_2$C*H*$_2$OAr-), 1.96 (m, 6H; -OCHC*H*$_2$C), 1.70 (m, 6H; -OCHC*H*$_2$C), 1.41 (d, *J*=6.9 Hz, 9H; -NOCH(C*H*$_3$)C(O)O-)), 1.25 (s, 27H; -ONC(C*H*$_3$)$_2$), 1.10 (s, 9H; -ONC(C*H*$_3$)$_2$), 0.87 (s, 54H; -Si(CH$_3$)$_2$C(C*H*$_3$)$_3$), 0.06 (s, 36H; -Si(C*H*$_3$)$_2$C(CH$_3$)$_3$); ^{13}C NMR ($CDCl_3$, 298K, 500 MHz): δ 173.76, 164.62, 159.58, 149.41, 137.54, 134.44, 131.60, 121.78, 119.78, 114.12, 81.85, 68.34, 65.97, 62.51, 60.58, 60.14, 58.01, 53.70, 44.56, 33.75, 33.09, 25.88, 21.16, 18.47, -5.10; Microanalysis: Calculated for $C_{129}H_{207}N_{21}O_{24}Si_6$ C, 59.48; H, 8.01; N, 11.29; Found: C, 60.12; H, 8.08; N, 11.24 %.

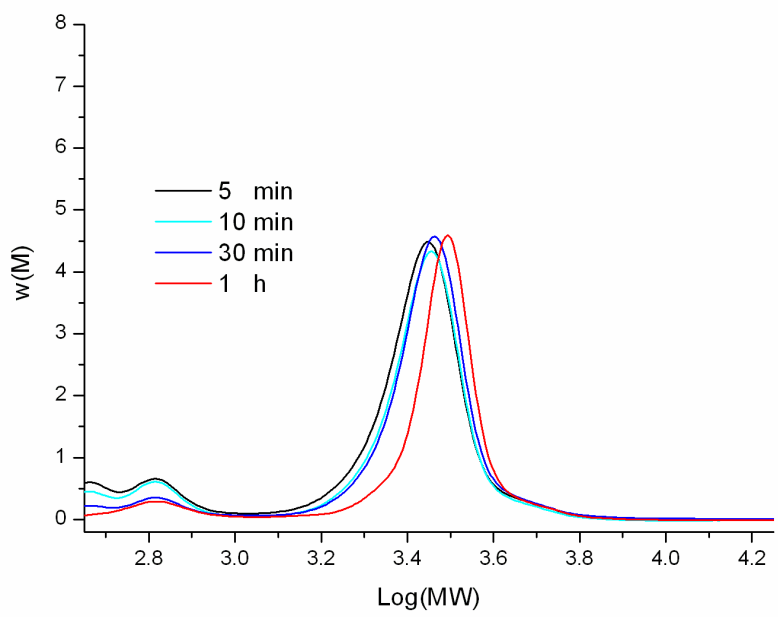


Figure S28: Size Exclusion Chromatography (SEC) traces of the synthesis of the G2 dendrimer, **12,** by parallel procedure at 25 ^{o}C with DMSO as solvent and PMDETA as ligand, **9**:**7**:**1**:PMDETA:Cu(I)Br =1:3.15:6.6:4:4.

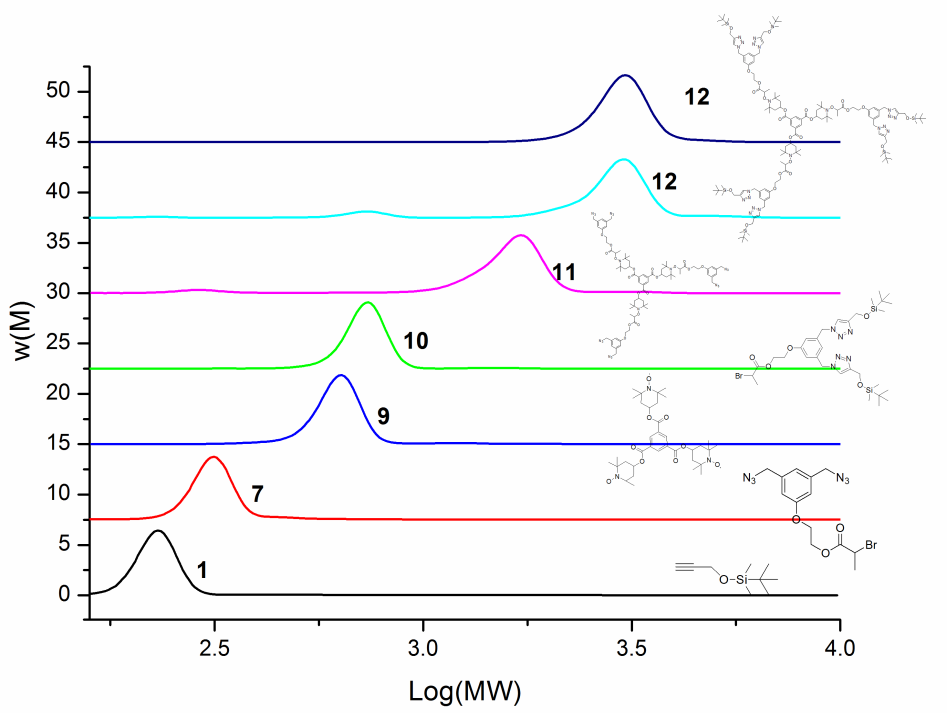


Figure S29. Overall SEC traces of G2 dendrimer, intermediate and starting compounds: **1** TBDPS-Alkyne, **7** bromine-diazide and **9** tri-nitroxide; **10** wedge structure (synthesized from **1** and **7**)**; 11** G1 dendrimer (synthesized from **7** and **9**) and **12** G2 dendrimer before and after purification (synthesized from **1**, **7** and **9** by convergent procedure).

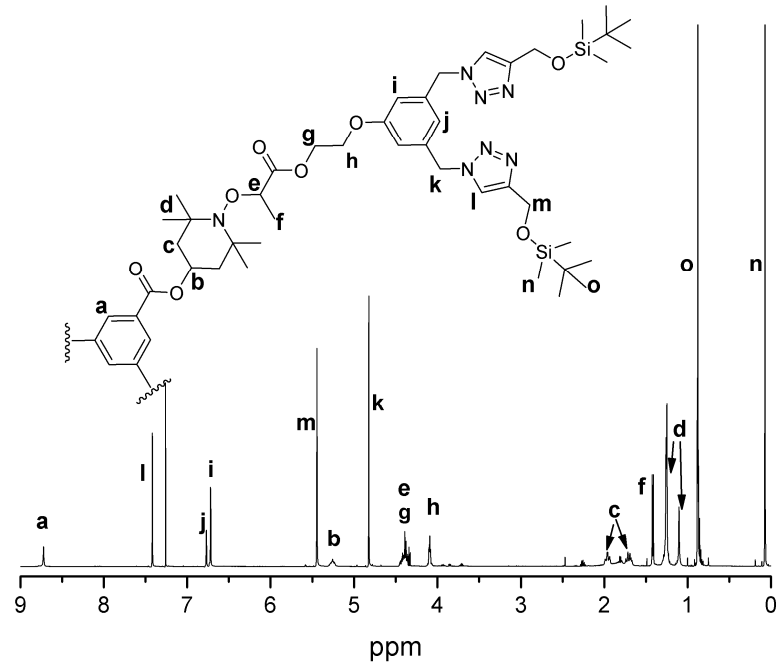


Figure S30: ^{1}H NMR spectrum of G2 dendrimer, **12,** by the parallel procedure at 25 ^{o}C using DMSO as solvent and PMDETA as ligand, **9**:**7**:**1**:PMDETA:Cu(I)Br =1:3.15:6.6:4:4.

(Note: **g** & **h** are tentative assignments)

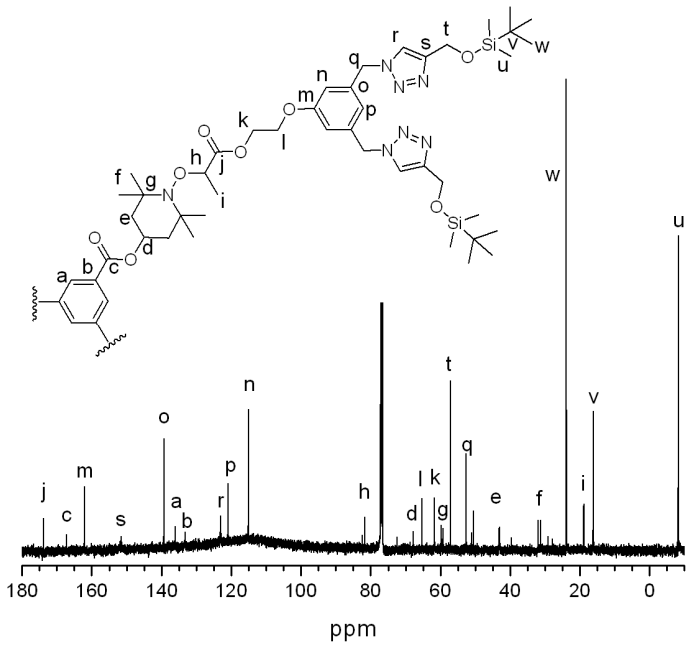


Figure S31: ^{13}C NMR spectrum of G2 dendrimer, **12,** by the parallel procedure at 25 ^{o}C using DMSO as solvent and PMDETA as ligand, **9**:**7**:**1**:PMDETA:Cu(I)Br =1:3.15:6.6:4:4.

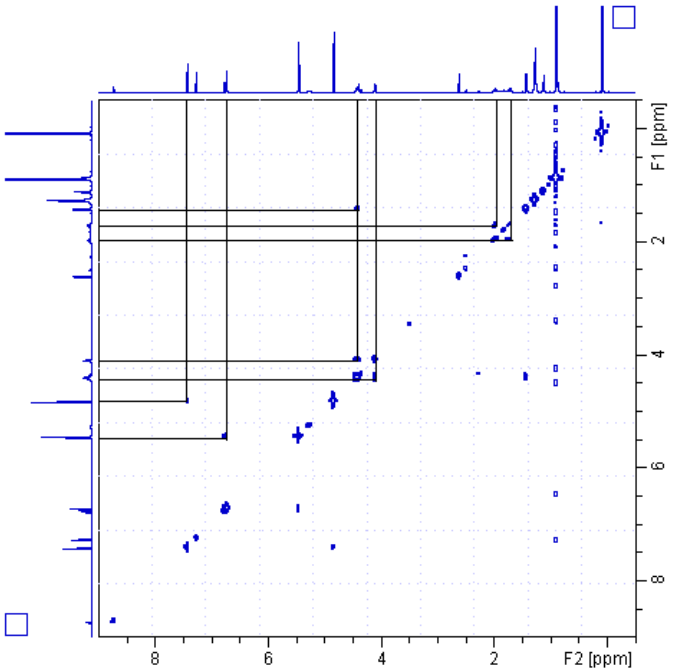


Figure S32: 2D COSY NMR spectrum of G2 dendrimer, **12,** by the parallel procedure at 25 ^{o}C using DMSO as solvent and PMDETA as ligand, **9**:**7**:**1**:PMDETA:Cu(I)Br =1:3.15:6.6:4:4.

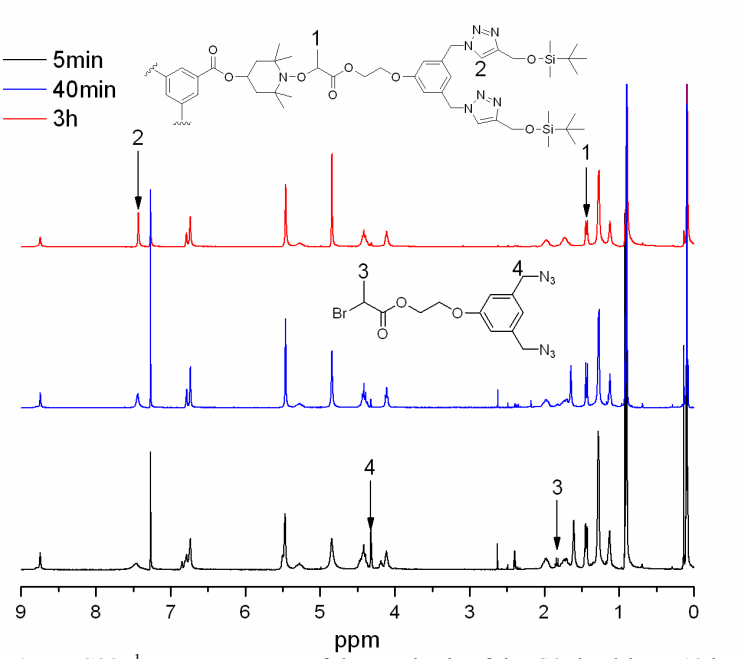


Figure S33: ^{1}H NMR spectra of the synthesis of the G2 dendrimer **12** by the divergent procedure at 25 ^{o}C using DMSO as solvent and Me_6TREN as ligand, **9**:**7**:**1**:Me_6TREN:Cu(I)Br =1:3.15:6.6:4:4.

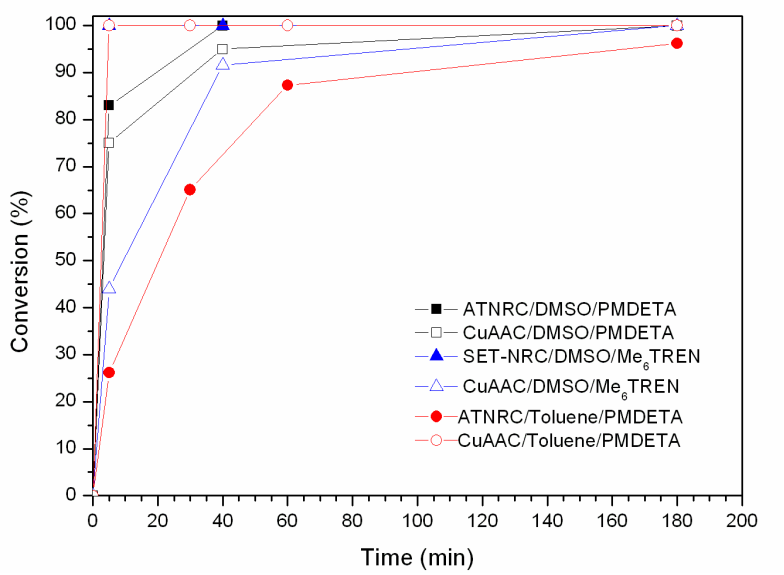


Figure S34: Kinetics of the synthesis of the G2 dendrimer **12** by the divergent approach (blue, using DMSO as solvent and Me_6TREN as ligand, **9**:**7**:**1**:Me_6TREN:Cu(I)Br =1:3.15:6.6:4:4), convergent (red, using toluene as solvent and PMDETA as ligand, **9**:**7**:**1**:Me_6TREN:Cu(I)Br =1:3.15:6.6:4:4) and parallel procedure (black, using DMSO as solvent and PMDETA as ligand, **9**:**7**:**1**:Me_6TREN:Cu(I)Br =1:3.15:6.6:4:4).

Synthesis of wedge structure (13)

In a vial, **8** (251.0 mg, 1.0 x 10^{-3} mol) and Me_6TREN (46.0 mg, 2.0 x 10^{-4} mol) were dissolved in 2 mL of DMSO. The solution was purged with argon for 30 min, and benzyl mercaptan (0.273 g, 2.2 x 10^{-3} mol) was then added. After 3 min, the solution was diluted by chloroform and washed by Milli-Q water three times to remove the Me_6TREN and DMSO. The chloroform phase was dried over $MgSO_4$ and concentrated. The residue was further purified by column chromatography using ethyl acetate/petroleum spirit (1/2, v/v) as the eluent and the product, **13**, was obtained as a colorless oil (211 mg, 42.2 %). R_f (1/2 EtOAc/petroleum spirit) 0.36; ^{1}H NMR (DMSO-d_6, 298K, 300 MHz); δ 7.22-7.30 (m, 10H; aromatic protons), 4.06 (t, *J*=5.84 Hz, 4H; -(O)COCH_2CH$_2$-), 3.73 (s, 4H; -CH_2-Ph), 3.40 (d, *J*=2.34 Hz, 2H; CH≡C-CH_2-), 3.12 (t, *J*=2.32 Hz, 1H; C*H*≡C-CH$_2$-), 2.70 (t, *J*=5.85 Hz, 4H; C*H*≡C-CH$_2$-), 2.56 (m, 8H; -ArCH$_2$N$_3$); ^{13}C NMR (DMSO-d_6, 298K, 500 MHz): δ 171.34, 138.45, 128.80, 128.34, 126.79, 79.14, 75.64, 62.22, 51.70, 42.65, 34.87, 33.97, 25.72. Microanalysis: Calculated for $C_{27}H_{33}NO_4S_2$ C, 64.90; H, 6.66; N, 2.80 Found C, 64.73; H, 6.73; N, 2.73; % (S is not measured due to immiscibility of the V_2O_5 catalyst).

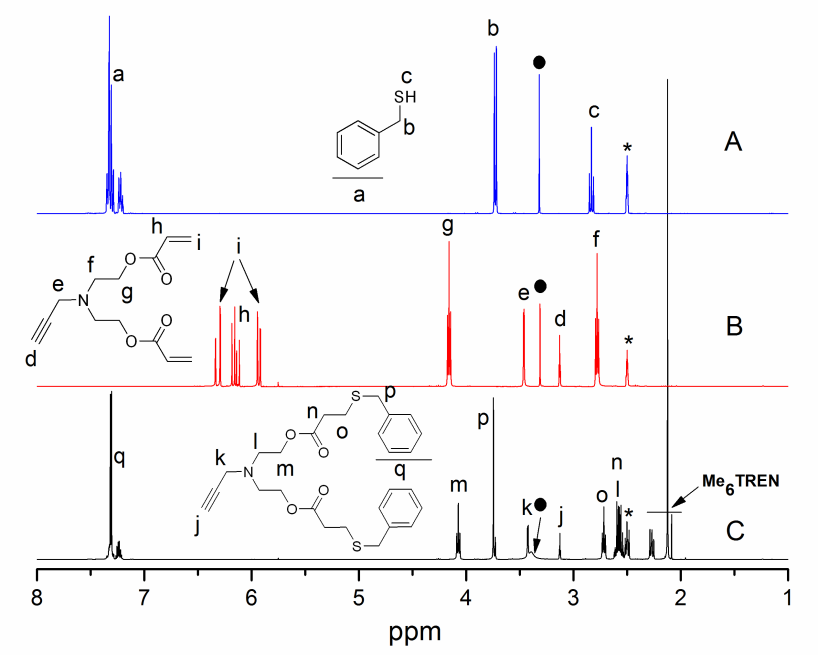


Figure S35: ^{1}H NMR spectra of (A) benzyl mercaptan; (B) (prop-2-yn-1-ylazanediyl)bis(ethane-2,1-diyl) diacrylate, **8**, and (C) **13** with Me_6TREN as base and DMSO-d_6 as solvent (**8**:benzyl mercaptan:Me_6TREN=1:2.1:1). (* represents a peak from DMSO and ● represents a peak from H_2O.)

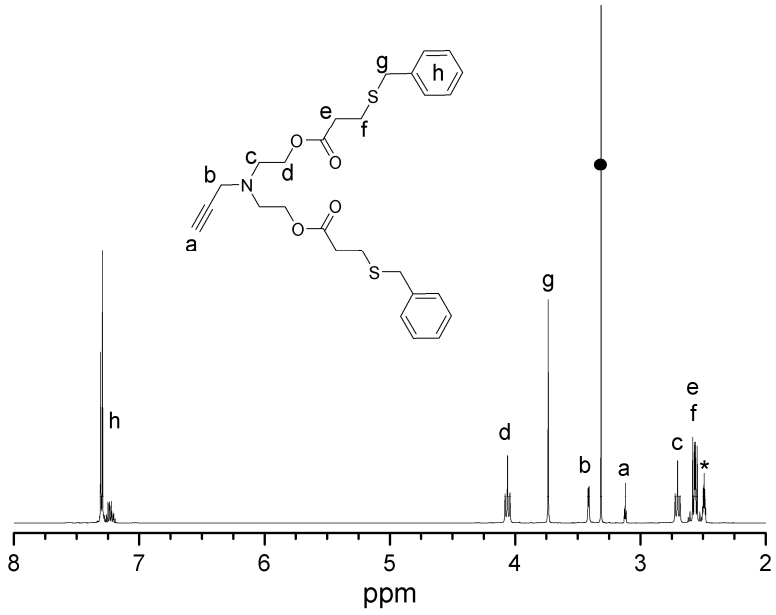


Figure S36: ^{1}H NMR spectra of **13** in DMSO-d_6 synthesized with Me_6TREN as base and DMSO as solvent (**8**:benzyl mercaptan:Me_6TREN=1:2.2:0.2). (* represents a peak from DMSO and ● represents a peak from H_2O.)

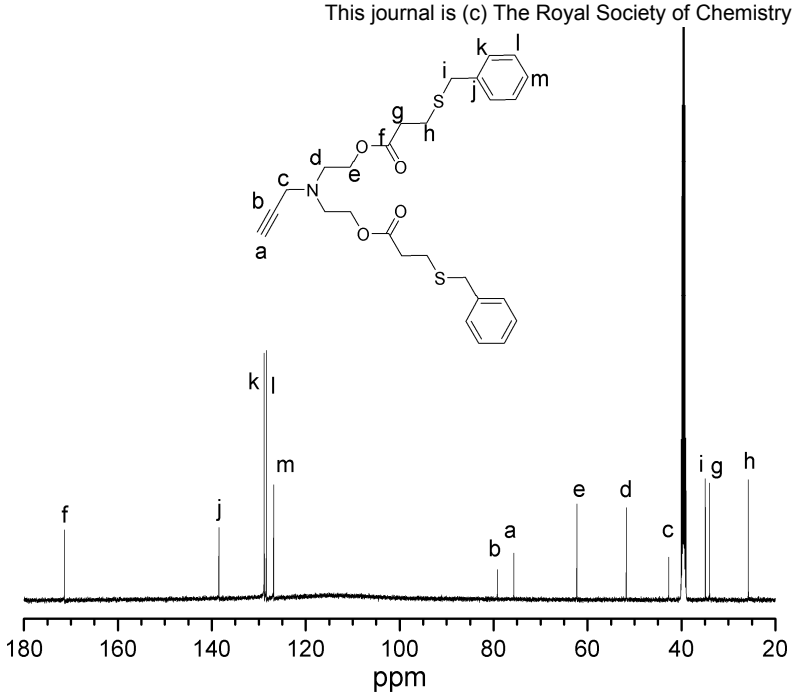


Figure S37: ^{13}C NMR spectra of **13** in DMSO-d_6 synthesized with Me_6TREN as base and DMSO as solvent (**8**:benzyl mercaptan:Me_6TREN=1:2.2:0.2).

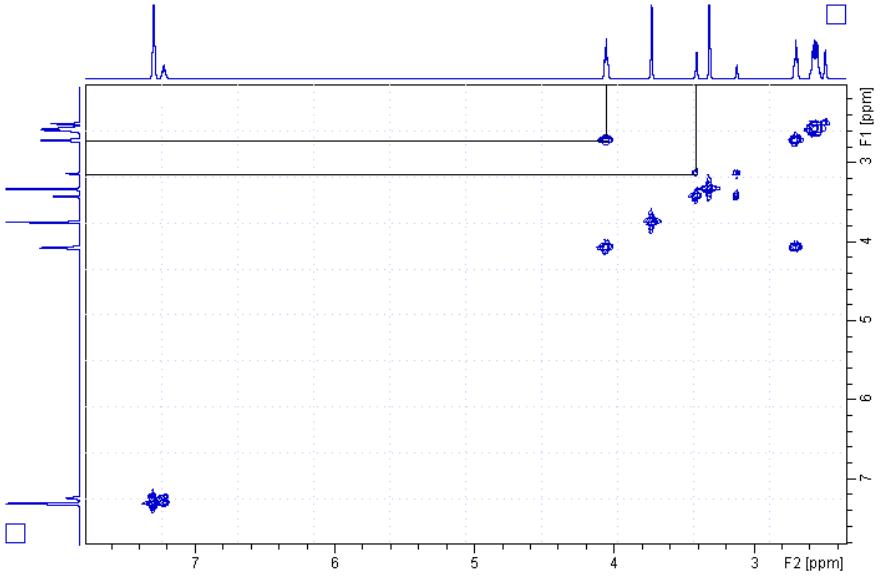


Figure S38: 2D COSY NMR spectra of **13** in DMSO-d_6 synthesized with Me_6TREN as base and DMSO as solvent (**8**:benzyl mercaptan:Me_6TREN=1:2.2:0.2).

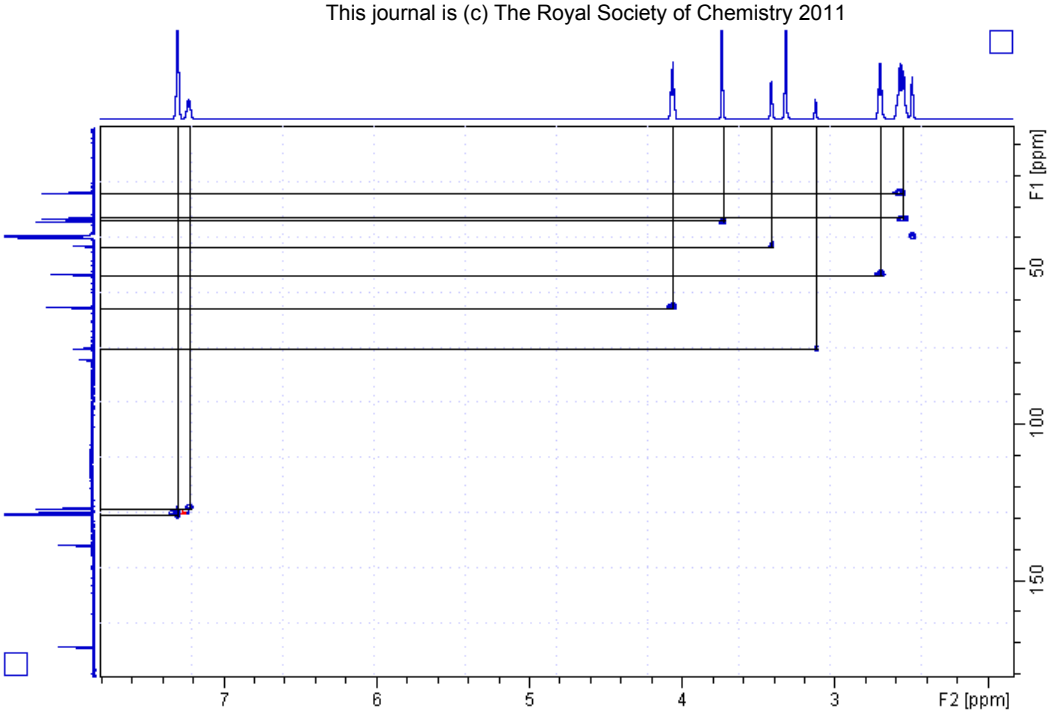


Figure S39: 2D HSQC NMR spectra of **13** in DMSO-d_6 synthesized with Me_6TREN as base and DMSO as solvent (**8**:benzyl mercaptan:Me_6TREN=1:2.2:0.2).

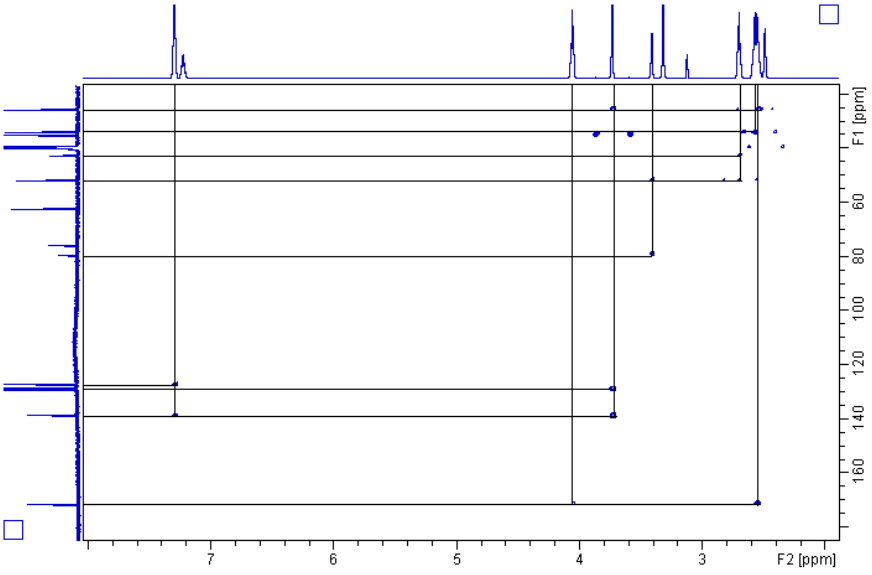
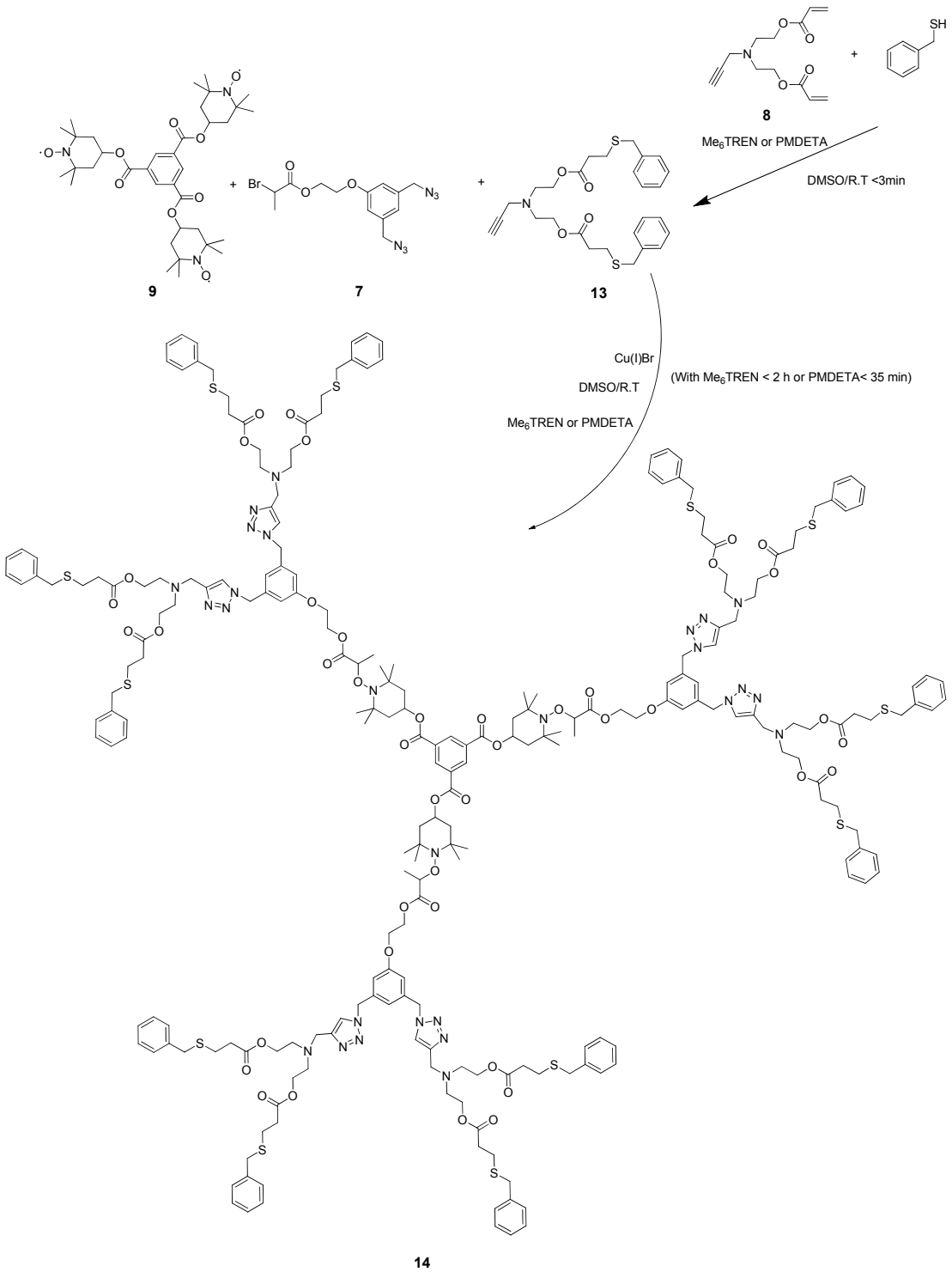


Figure S40: 2D HMBC NMR spectra of **13** in DMSO-d_6 synthesized with Me_6TREN as base and DMSO as solvent (**8**:benzyl mercaptan:Me_6TREN=1:2.2:0.2).

Synthesis of 3rd generation dendrimer (14)



In a vial, **8** (117.1 mg, 4.67 x 10^{-4} mol), PMDETA (11.6 mg, 6.7 x 10^{-5} mol) or Me_6TREN (15.4 mg, 6.7 x 10^{-5} mol) were dissolved in 1 mL of DMSO. The solution was purged with argon for 30 min, and benzyl mercaptan (0.124 g, 1.0 x 10^{-3} mol) was then added. After 3 min, the solution of **13** was transferred to the mixture containing **9** (44.8 mg, 6.7 x 10^{-5} mol), **7** (80.0 mg, 2.0 x 10^{-4} mol) and PMDETA (46.4 mg, 2.68 x 10^{-4} mol) or Me_6TREN (61.6 mg, 2.68 x

10^{-4} mol) in 2 mL of DMSO which had been purged with argon for 30 min. Finally, Cu(I)Br (48 mg, 3.35 x 10^{-4} mol) was added. The reaction was carried out at 25 ^{o}C for 35 min with PMDETA or 2 h with Me_6TREN. The solution was diluted with 6 mL of chloroform and washed with Milli-Q water (3 times) to remove DMSO and the copper complex. The chloroform phase was dried over anhydrous magnesium sulphate, passed through a small Al_2O_3 plug, concentrated and taken to complete dryness on a high vacuum line to give a pale yellow sticky product, **14**, (using Me_6TREN as ligand gave 225 mg, 73.7 % yield, and 92.5 % purity as measured by SEC; using PMDETA as ligand 240 mg, 78.6 % yield, and 91.8 % purity as measured by SEC). The crude product was purified by repeating dissolving in THF and precipitating into diethyl ether (using Me_6TREN the purity increased to 97.8 %, and using PMDETA the purity increased to 98.2 %). ^{1}H NMR ($CDCl_3$, 298K, 500 MHz); δ 8.73 (s, 3H; core aromatic protons), 7.44 (s, 6H; triazole protons), 7.21-7.44 (m, 60H; benzyl ring), 6.76 (s, 3H; aromatic protons), 6.71 (s, 6H; aromatic protons), 5.40 (s, 12H; -ArCH_2triazole-), 5.26 (m, 3H; -(O)COCH(CH_2)CH_2-), 4.35-4.45 (bd, 9H; -NOCH(CH_3)C(O)O-, -(O)COC$H_2$$CH_2$OAr-), 4.08-4.15 (bd, 30H; -NCH_2CH_2OC(O)-, -(O)$COCH_2CH_2$OAr-), 2.64 (t, J=7.18 Hz, 24H;-(O)COC$H_2$$CH_2$$SCH_2$Ar), 2.51 (t, J=7.04 Hz, 24H; -(O)$COCH_2CH_2SCH_2$Ar), 1.96 (m, 6H; -OCHCH_2C), 1.71 (m, 6H; -OCHCH_2C), 1.42 (d, 9H; -NOCH(CH_3)C(O)O-)), 1.25 (s, 27H; -ONC(CH_3)$_2$), 1.10 (s, 9H; -ONC(CH_3)$_2$); ^{13}C NMR ($CDCl_3$, 298K, 500 MHz): δ 173.79, 171.82, 164.62, 159.53, 138.11, 137.50, 134.42, 131.60, 130.18, 129.19, 129.04, 128.94, 128.70, 120.10, 114.28, 83.05, 68.39, 65.98, 62.48, 60.60, 60.17, 54.37, 53.66, 52.54, 49.67, 44.56, 36.39, 34.50, 33.78, 33.12, 26.31, 25.88, 21.15, 18.50; Microanalysis: Calculated for $C_{237}H_{297}N_{27}O_{42}S_{12}$: C, 62.14; H, 6.54; N, 8.26; S, 8.40; Found: C, 61.18; H, 6.57; N, 8.60; S, 8.54 %.

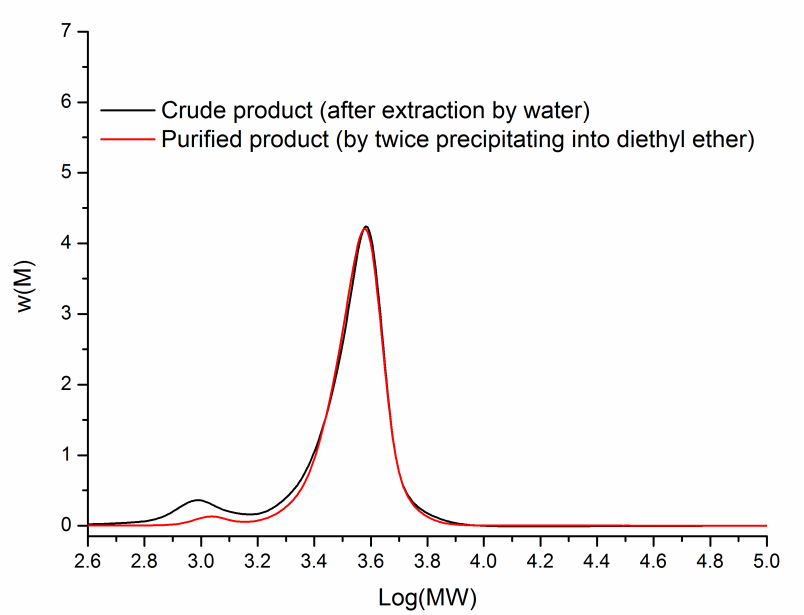


Figure S41: Size Exclusion Chromatography (SEC) traces for the synthesis of the G3 dendrimer, **14,** at 25 ^{o}C using DMSO as solvent and Me_6TREN as ligand, **9**:**7**:**8**:benzyl mercaptan:Me_6TREN:Cu(I)Br =1:3.15:7:15:5:5. Before and after purification by repeated dissolving in THF and precipitating in diethyl ether.

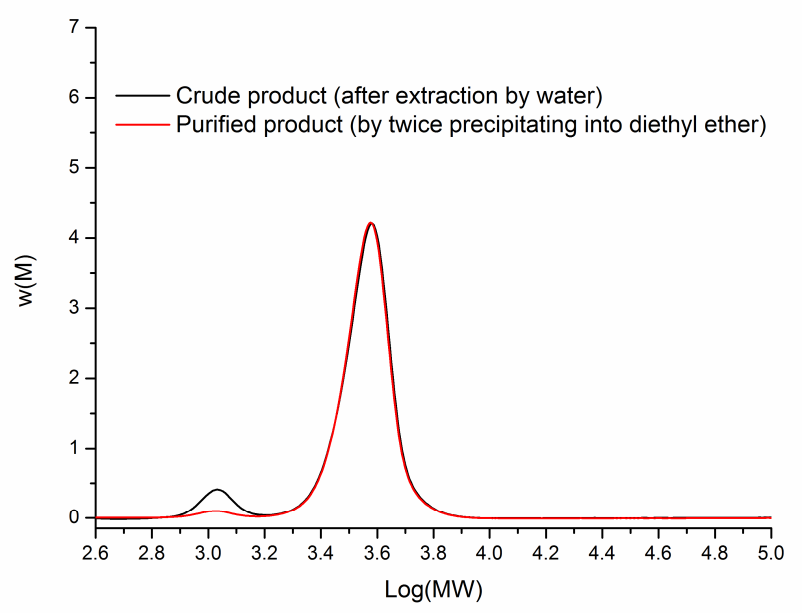


Figure S42: Size Exclusion Chromatography (SEC) traces for the synthesis of the G3 dendrimer, **14,** at 25 ^{o}C using DMSO as solvent and PMDETA as ligand, **9**:**7**:**8**:benzyl mercaptan:PMDETA:Cu(I)Br =1:3.15:7:15:5:5. Before and after purification by repeated dissolving in THF and precipitating in diethyl ether.

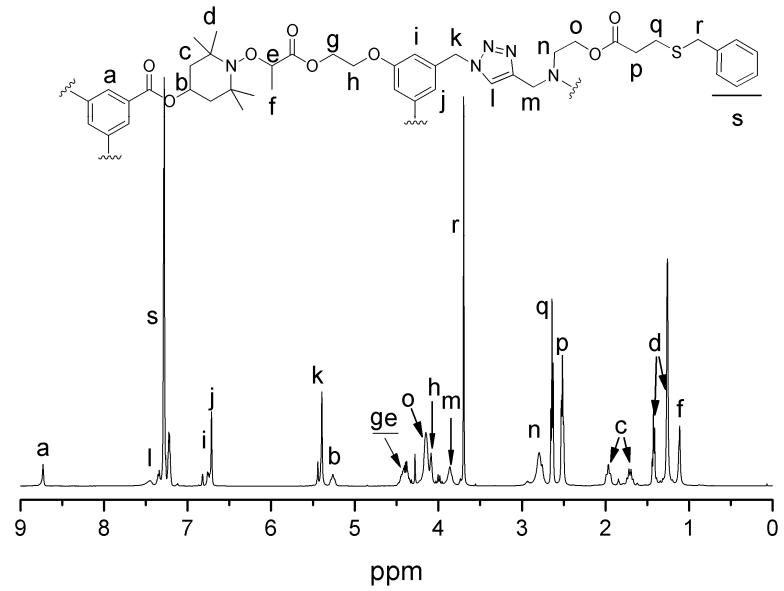


Figure S43: ^{1}H NMR spectrum of G3 dendrimer, **14**, at 25 ^{o}C using DMSO as solvent and PMDETA as ligand; **9**:**7**:**8**:benzyl mercaptan:PMDETA:Cu(I)Br =1:3.15:7:15:5:5.

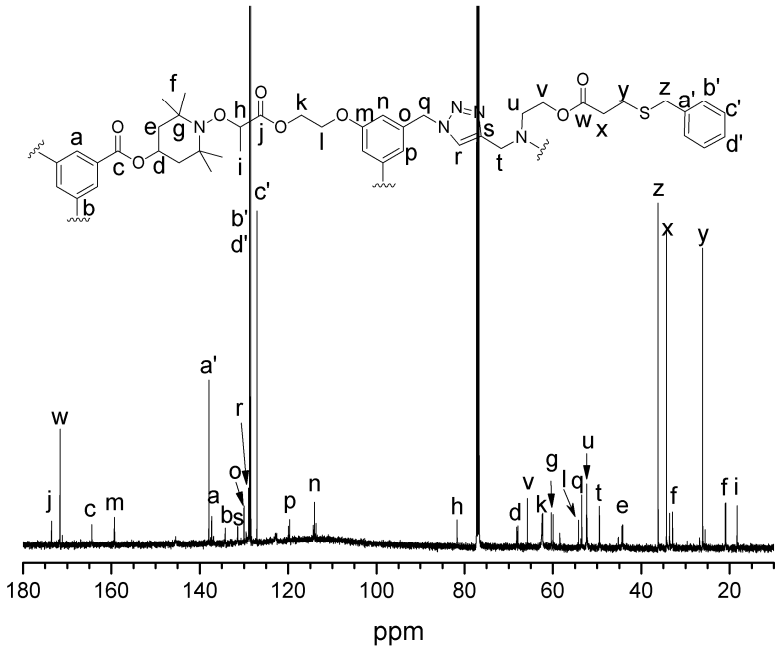


Figure S44: ^{13}C NMR spectrum of G3 dendrimer **14** at 25 ^{o}C with DMSO as solvent and PMDETA as ligand, **9**/**7**/**8**/benzyl mercaptan/PMDETA/Cu(I)Br =1/3.15/7/15/5/5

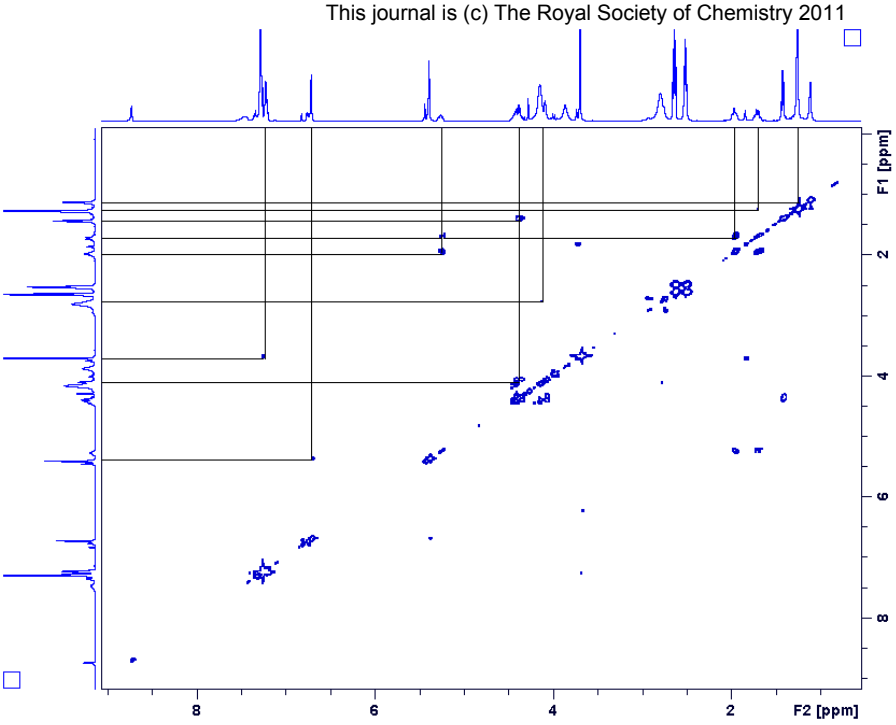


Figure S45: 2D COSY NMR spectrum of G3 dendrimer, **14,** at 25 ^{o}C formed in the presence of DMSO as solvent and PMDETA as ligand; **9**:**7**:**8**:benzyl mercaptan:PMDETA:Cu(I)Br =1:3.15:7:15:5:5.

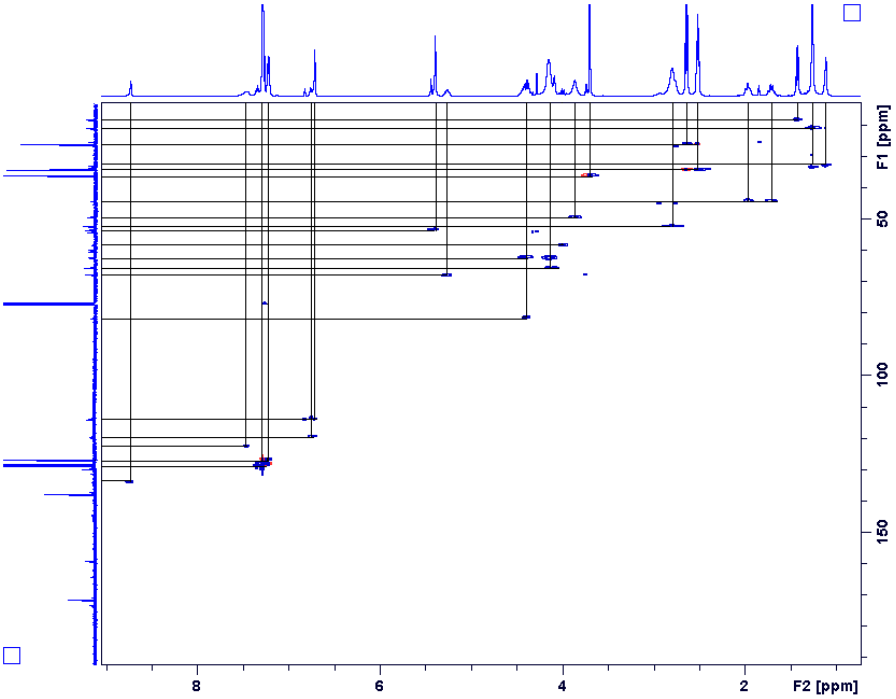


Figure S46: 2D HSQC NMR spectrum of G3 dendrimer, **14,** at 25 ^{o}C formed in the presence of DMSO as solvent and PMDETA as ligand, **9**:**7**:**8**:benzyl mercaptan:PMDETA:Cu(I)Br =1:3.15:7:15:5:5.

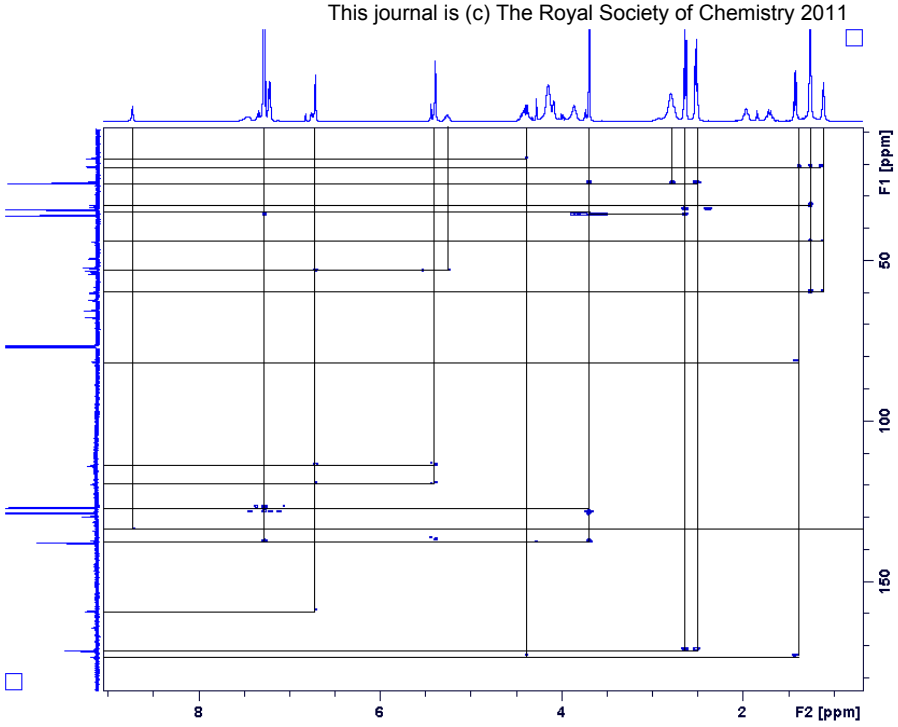


Figure S47: 2D HMBC NMR spectrum of G3 dendrimer, **14,** at 25 ^{o}C formed in the presence of DMSO as solvent and PMDETA as ligand, **9**:**7**:**8**:benzyl mercaptan:PMDETA:Cu(I)Br =1:3.15:7:15:5:5.

Table 1: SEC data of G2 and G3 dendrimers and their precursors (all the reactions were carried out at 25 °C).

	$M_{n(th)}$	SEC (THF, RI detection)				SEC (THF, Triple detection)			
		M_n	M_w	M_p	PDI	M_n	M_w	M_p	PDI
1	170.2	227	230	231	1.01	—	—	—	—
7	383.2	312	318	315	1.02	—	—	—	—
9	672.8	610	621	638	1.02	—	—	—	—
10[a]	723.8	715	725	739	1.01	—	—	—	—
11[b]	1582.7	1593	1661	1711	1.04	—	—	—	—
12 Divergent[c]	2604.6	2974	3071	3087	1.03	2616	2646	2696	1.01
12 Convergent[d]	2604.6	3010	3112	3087	1.03	2675	2802	2835	1.04
12 Parallel[e]	2604.6	3026	3142	3140	1.04	2631	2649	2680	1.01
13[f]	499.7	469	475	484	1.01	—	—	—	—
14[g]	4580.8	3460	3630	3810	1.05	4280	4530	4900	1.05
14[h]	4580.8	3560	3710	3750	1.04	4312	4670	5060	1.08

[a] Toluene as solvent and PMDETA as ligand, **7**/**1**/PMDETA/Cu(I)Br =1/2.1/0.5/0.5; [b] DMSO as solvent and Me_6TREN as ligand, **9**/**7**/Me_6TREN/Cu(I)Br=1/3.15/4/4; [c] DMSO as solvent and Me_6TREN as ligand, **9**/**7**/**1**/Me_6TREN/Cu(I)Br =1/3.15/6.6/4/4; [d] Toluene as solvent and PMDETA as ligand, **9**/**7**/**1**/PMDETA /Cu(I)Br =1/3.15/6.6/4/4; [e] DMSO as solvent and PMDETA as ligand, **9**/**7**/**1**/PMDETA/Cu(I)Br =1/3.15/6.6/4/4; G2 dendrimer d*n*/d*c* was measured and calculated as 0.082 mL/g. [f] DMSO as solvent and Me_6TREN as base, **8**/benzyl mercaptan/ Me_6TREN =1/2.2/0.2; [g] DMSO as solvent and Me_6TREN as ligand, **9**/**7**/**8**/benzyl mercaptan/ Me_6TREN /Cu(I)Br =1/3.15/7/15/5/5; [h] DMSO as solvent and PMDETA as ligand, **9**/**7**/**8**/benzyl mercaptan/PMDETA/Cu(I)Br =1/3.15/7/15/5/5; G3 dendrimer d*n*/d*c* was measured and calculated as 0.134 mL/g.

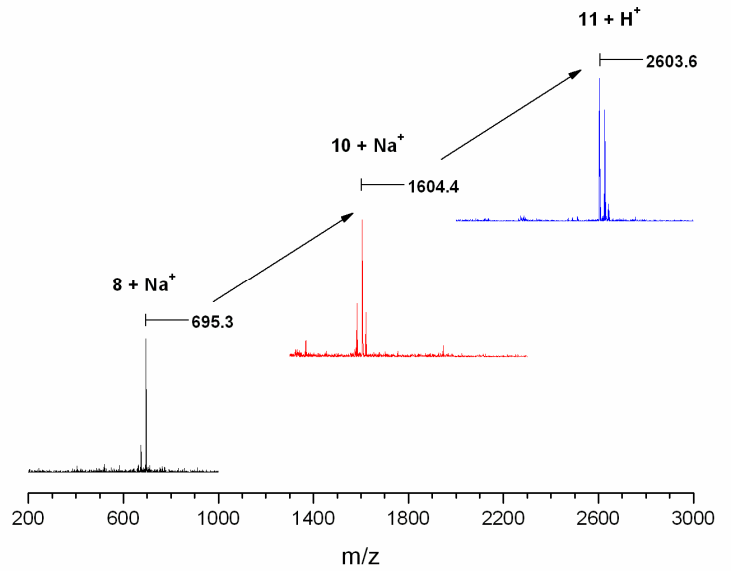


Figure S48: ESI-MS of tri-nitroxide **9**, G1 dendrimer **11** and G2 dendrimer **12** (using DMSO as solvent and PMDETA as ligand at 25 °C).

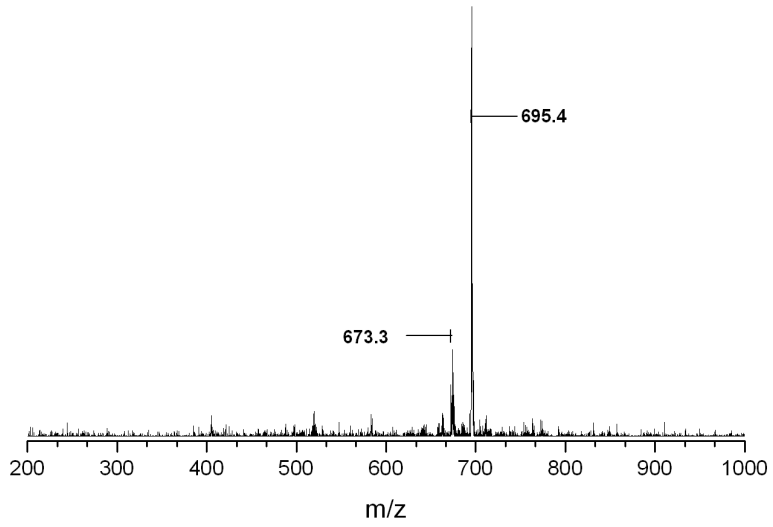


Figure S49: ESI-MS of tri-nitroxide, **9**.

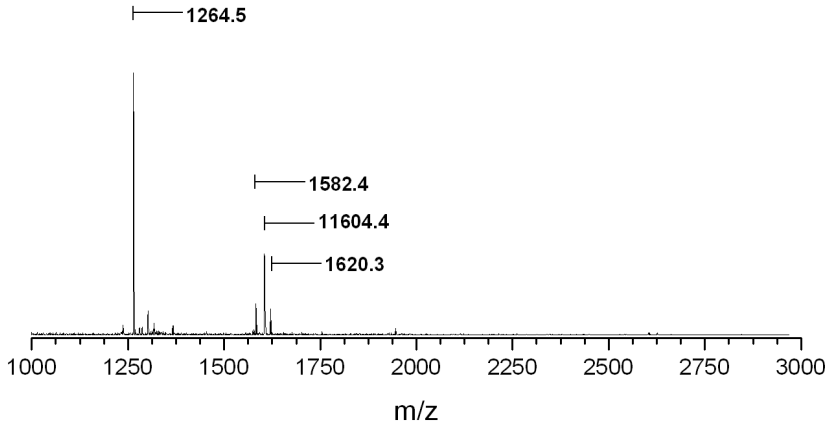


Figure S50: ESI-MS of G1 dendrimer, **11**.

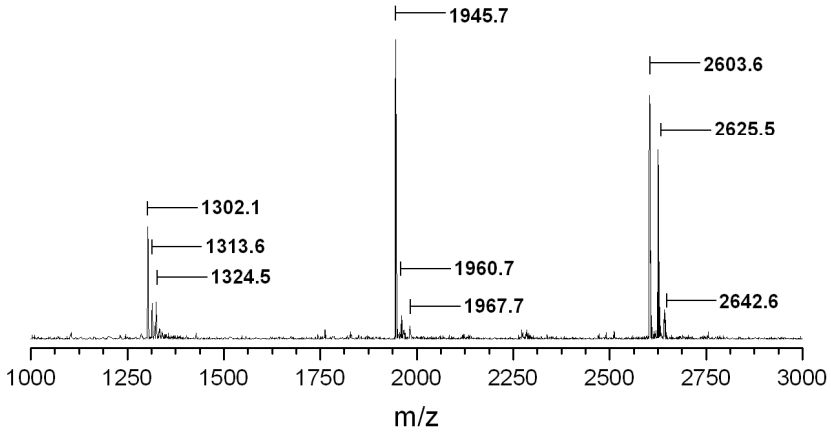


Figure S51: ESI-MS of G2 dendrimer **12** (synthesized with DMSO as solvent and PMDETA as ligand at 25 ^{o}C).

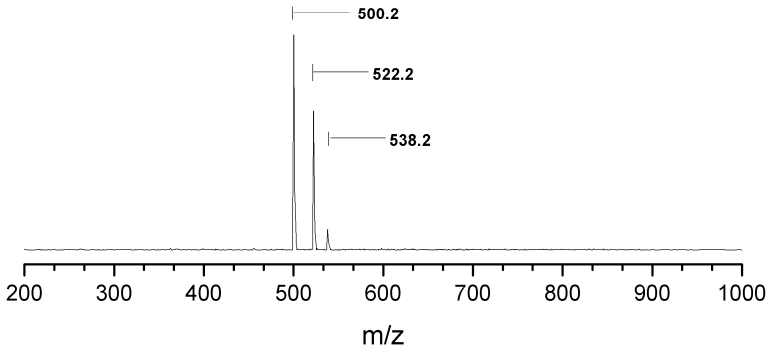


Figure S52: ESI-MS of wedge structure **13** (synthesized with DMSO as solvent and Me_6TREN as base at 25 ^{o}C).

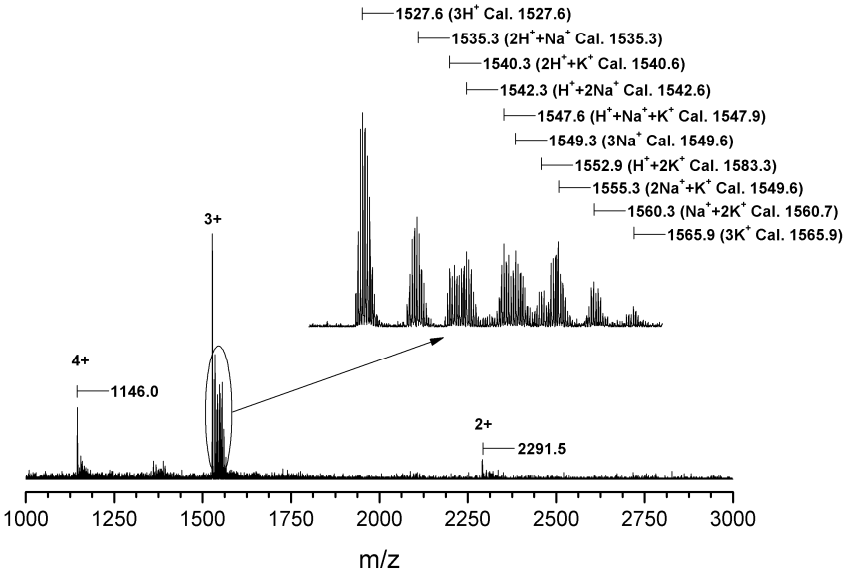


Figure S53: ESI-MS of G3 dendrimer, **14** (synthesized with DMSO as solvent and Me_6TREN as ligand at 25 ^{o}C).

References:
1. Ciampolini, M.; Nardi, N. *Inorganic Chemistry* **1966,** 5, 41-44.
2. Kulis, J.; Bell, C. A.; Micallef, A. S.; Jia, Z. F.; Monteiro, M. J. *Macromolecules* **2009,** 42, (21), 8218-8227.