Supporting Information

for

A divergent synthesis of modular dendrimers *via* sequential C-C bond fragmentation thio-Michael addition

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I. General Procedures

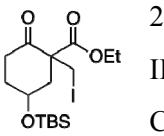
Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on a Bruker DRX400 spectrometer operating at 400 MHz for proton and 100 MHz for carbon nuclei or a Varian DRX 500 spectrometer operating at 500 MHz for proton and 125 MHz for carbon. Infrared spectra (ν_{max}) were recorded on a Perkin-Elmer RXI FTIR Spectrometer. Low resolution mass spectrometry (ESI) was performed on a Micromass Platform QMS spectrometer. High resolution mass spectra (HRMS) were recorded on a Bruker BioApex 47e FTMS fitted with an Analytical electrospray source using NaI for accurate mass calibration. MALDI-TOF was recorded on a Voyager DESTR with ABSciex workstation using a THF/α-Cyano/NaCl matrix, 25 kV accelerator voltage, a 200 ns delay and 89% grid voltage. Gel permeation chromatography was performed on a Tosoh EcosHLC-8320 GPC equipped with both refractive index (RI) and ultraviolet (UV) detectors (UV detection, λ = 280 nm) using Tosoh α 4000 and 2500 columns. Chloroform was used as the solvent. Calibration curves were obtained using polystyrene standards. As these standards are linear, while dendrimers are spherical, the PDIs have to be regarded as approximations only. Flash column chromatography was performed on silica gel (Davisil LC60A, 40-63 μm silica media) using compressed air or nitrogen. Thin layer chromatography (TLC) was performed using aluminum-backed plates coated with 0.2 mm silica (Merck, DC-Platten, Kieselgel; 60 F_{254} plates). Eluted plates were visualized using a 254 nm UV lamp and/or by treatment with a suitable stain followed by heating.

Starting materials and reagents were purchased from Sigma-Aldrich and were used as supplied or, in case of some liquids, distilled. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl,

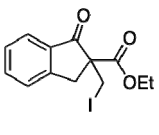
while ethanol and acetonitrile were distilled from calcium hydride. Unless stated otherwise all reactions were conducted in flame dried glassware in an inert atmosphere (N_2).

II. Preparation of fragmentation precursors 3b and e and thiol 9

Ethyl 5-(*tert*-butyldimethylsilyloxy)-1-(iodomethyl)-2-oxocyclohexanecarboxylate (**3b**) (854 mg, 27%, colourless oil) was prepared following the procedure of Beckwith.[i] R_f 0.7 (CH_2Cl_2); IR ν_{max} 2954, 2930, 2857, 1737, 1721, 1472, 1464, 1257, 1099; ^{1}H-NMR (400 MHz, $CDCl_3$) δ *diastereomer 1*: 0.11 (s, 3H), 0.13 (s, 3H), 0.91 (s, 9H), 1.29 (t, *J* = 7.0 Hz, 3H), 1.66-2.72 (m, 6H), 3.40 (d, *J* = 10.0 Hz, 1H), 3.64 (d, *J* = 10.0 Hz, 1H), 4.18-4.25 (m, 2H) *diastereomer 2*: 0.08 (s, 3H), 0.09 (s, 3H), 0.89 (s, 9H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.66-2.72 (m, 6H), 3.12 (td, *J* = 14.0 Hz, 6.0 Hz, 1H), 3.29 (d, *J* = 10.0 Hz, 1H), 3.49 (d, *J* = 10.0 Hz, 1H), 4.18-4.25 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ *diastereomer 1*: -4.76, -4.52, 8.93, 14.25, 18.22, 25.97, 35.16, 37.30, 44.02, 59.85, 62.40, 66.69, 168.98, 203.94 *diastereomer 2*: -4.98, 7.83, 14.09, 18.42, 25.97, 34.46, 35.52, 44.65, 57.34, 62.04, 65.78, 169.73, 205.56; HRMS Found $(M+H)^+$ 441.0950, $C_{16}H_{29}IO_4Si$ requires $(M+H)^+$ 441.0958; found $(M+Na)^+$ 463.0769, requires $(M+Na)^+$ 463.0777.

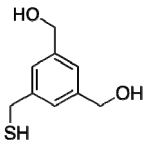


Ethyl 2-(iodomethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**3e**) (600 mg, 44%, yellow oil) was synthesised starting from ethyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate[ii] following the procedure of Beckwith.[1] R_f 0.7 (CH_2Cl_2); IR ν_{max} 3036, 2980, 2936, 1714, 1607, 1589, 1465, 1417, 1251, 1209; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.22 (t, *J* = 7.0 Hz, 3H), 3.25 (d, *J* = 17.5 Hz, 1H), 3.53 (d, *J* = 10.0 Hz, 1H), 3.80 (d, *J* = 17.5 Hz, 1H), 3.82 (d, *J* = 10.0 Hz, 1H), 4.14-4.22 (m, 2H), 7.40 (td, *J* = 7.5 Hz, 1.0 Hz, 1H), 7.51 (dt, *J* = 7.5 Hz, 1.0 Hz, 1H), 7.65 (td, *J* = 7.5 Hz, 1.0 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 7.70, 14.11, 39.11, 61.34, 62.48, 125.32, 126.53, 128.11, 134.70, 135.96, 152.90, 168.34, 198.94; HRMS Found $(M+H)^+$ 344.9982, $C_{13}H_{13}IO_3$ requires $(M+H)^+$ 344.9988.



(5-(Mercaptomethyl)-1,3-phenylene)dimethanol (**9**)

A solution of benzene-1,3,5-triyltrimethanol[iii] (3.8 g, 22.7 mmol) and CBr_4 (8.28 g, 25 mmol) in dry acetonitrile (200 mL) was maintained at 0°C. PPh_3 (6.53 g, 25 mmol) was added in small portions over a period of 60 min. The ice bath was then removed and the mixture stirred for 5 h at room temperature. Concentration *in vacuo* followed by column chromatography (1:49 → 1:24, v/v MeOH:CH_2Cl_2) yielded (5-(bromomethyl)-1,3-phenylene)-dimethanol as a white solid (2.08 g, 40%). R_f 0.1 (1:49, v/v MeOH: CH_2Cl_2); IR ν_{max} 3193, 2852, 1607, 1007; ^{1}H-NMR (400 MHz, MeOD) δ 4.52 (s, 2H), 4.56 (s, 4H), 7.24 (s, 1H), 7.27 (s, 2H); ^{13}C-NMR (100 MHz, MeOD) δ 34.02, 64.79, 126.38, 127.48, 139.78, 143.55. The previously prepared bromide (721 mg, 3.1 mmol), thioacetic acid (312 μL, 4.4 mmol) and K_2CO_3 (517 mg, 3.7 mmol) in

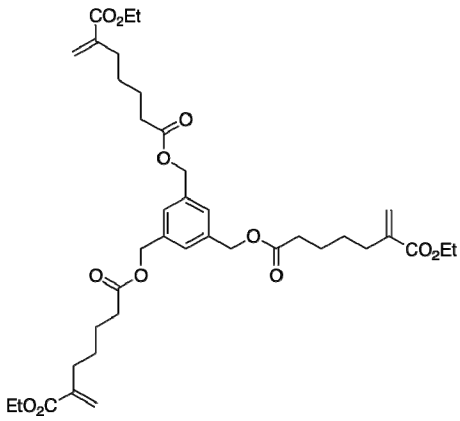


THF (15 mL) were stirred for 90 minutes at room temperature, then H_2O (2 mL) was added and the pH was checked (~ pH 6, adjust with HCl if required). The product was extracted with CH_2Cl_2 (2 x 7.5 mL), the combined organic layers washed with brine (10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Column chromatography (1:19, v/v MeOH:CH_2Cl_2) afforded S-3,5-bis(hydroxymethyl)benzyl ethanethioate as a slightly yellow oil (602 mg, 85%). R_f 0.2 (1:19, v/v MeOH:CH_2Cl_2); IR ν_{max} 3348, 2923, 2873, 1686, 1696, 1454, 1422, 1355, 1134, 1060, 962; ^{1}H-NMR (400 MHz, MeOD) δ 2.32 (s, 3H), 4.12 (s, 2H), 4.57 (s, 4H), 7.19 (s, 2H), 7.22 (s, 1H); ^{13}C-NMR (100 MHz, MeOD) δ 30.16, 34.03, 64.92, 125.38, 127.23, 139.38, 143.30, 196.68; HRMS Found $(M+Na)^+$ 249.0554, $C_{11}H_{14}O_3S$ requires $(M+Na)^+$ 249.0561. A solution of the previously prepared thioacetate (565 mg, 2.5 mmol) and K_2CO_3 (414 mg, 3.0 mmol) in methanol (20 mL) was stirred at room temperature for 90 minutes. 2 M HCl (2 mL) was added and the suspension filtered through a small plug of silica with methanol and concentrated. Column chromatography (1:19, v/v MeOH:CH_2Cl_2) yielded the target compound as a white solid (254 mg, 55%). R_f 0.2 (1:19, v/v MeOH:CH_2Cl_2); IR ν_{max} 3205, 2849, 1711, 1602, 1068, 1007; ^{1}H-NMR (400 MHz, MeOD) δ 3.73 (s, 2H), 4.59 (s, 4H), 7.21 (s, 1H), 7.24 (s, 2H); ^{13}C-NMR (100 MHz, MeOD) δ 29.10, 65.03, 125.09, 126.62, 143.24 (1xC overlapping); HRMS Found $(M+Na)^+$ 207.0447, $C_9H_{12}O_2S$ requires $(M+Na)^+$ 207.0456.

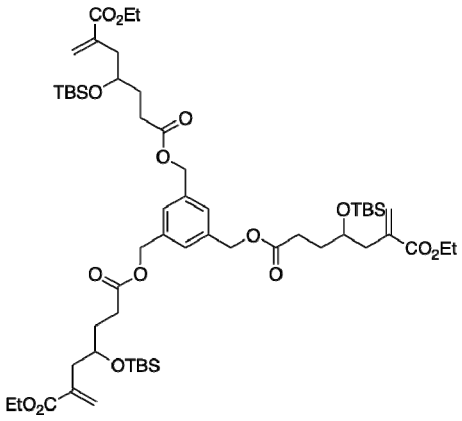
III Synthesis of [G1]-ene$_{3/4}$ dendrimers 7a-e and 8a

General procedure: In a dry test-tube, maintained under nitrogen, benzene-1,3,5-triyltrimethanol (16.8 mg, 0.1 mmol), fragmentation precursor (0.6 mmol) and K_2CO_3 (83 mg, 0.6 mmol) were stirred at 70^{o}C for 72 h. The resulting milky-white suspension was filtered through a plug of silica with EtOAc; NMR of the crude residue confirmed complete conversion. Purification *via* column chromatography (1:4, v/v EtOAc:hexane) afforded the products as colourless viscous oils.

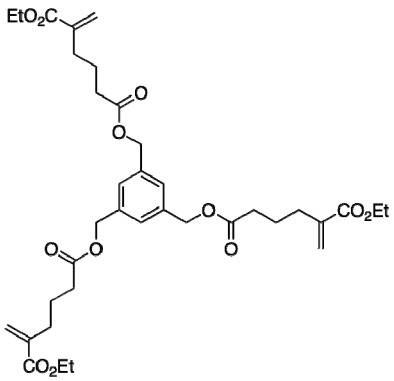
[G1]-ene$_3$ 7a (99 mg, 93%). R_f 0.1 (1:4, v/v EtOAc:hexane); IR ν_{max} 2949, 1733, 1714, 1632, 1184, 1027; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.0 Hz, 9H), 1.48-1.54 (m, 6H), 1.63-1.71 (m, 6H), 2.30 (t, *J* = 7.0 Hz, 6H), 2.38 (t, *J* = 7.0 Hz, 6H), 4.18 (q, *J* = 7.0 Hz, 6H), 5.10 (s, 6H), 5.50 (q, *J* = 1.0 Hz, 3H), 6.12 (t, *J* = 1.0 Hz, 3H), 7.27 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.31, 24.53, 27.97, 31.59, 34.09, 60.69, 65.69, 124.68, 127.69, 137.05, 140.58, 167.24, 173.35; HRMS Found $(M+NH_4)^+$ 732.3954, $C_{39}H_{54}O_{12}$ requires $(M+NH_4)^+$ 732.3959; found $(M+Na)^+$ 737.3499, requires $(M+Na)^+$ 737.3513; PDI: 1.003.



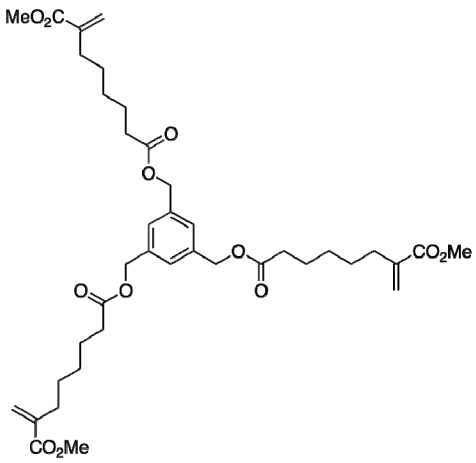
[G1]-ene$_3$ 7b (96 mg, 87%). R_f 0.3 (1:4, v/v EtOAc:hexane); IR ν_{max} 2931, 2857, 1740, 1718, 1631, 1464, 1256, 1161, 1085; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.01 (s, 18H), 0.86 (s, 27H), 1.30 (t, *J* = 7.0 Hz, 9H), 1.66-1.75 (m, 3H), 1.80-1.89 (m, 3H), 2.37-2.51 (m, 12H), 3.89-3.95 (m, 3H), 4.19 (qd, *J* = 7.0 Hz, 1.0 Hz, 6H), 5.10 (s, 6H), 5.59 (d, *J* = 1.0 Hz, 3H), 6.21 (d, *J* = 1.0 Hz, 3H), 7.27 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ -4.56, -4.32, 14.37, 18.14, 25.99, 29.79, 31.66, 40.37, 60.81, 65.81, 69.73, 127.92, 128.12, 136.98, 137.36, 167.07, 173.62; HRMS Found $(M+H)^+$ 1105.6129, $C_{57}H_{96}O_{15}Si_3$ requires $(M+H)^+$ 1105.6135; found $(M+Na)^+$ 1127.5953, requires $(M+Na)^+$ 1127.5955.



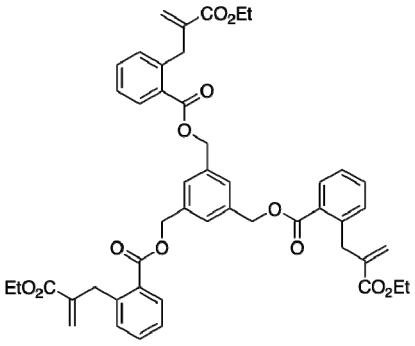
[G1]-ene$_3$ 7c (167 mg, 98%). R_f 0.2 (1:4, v/v EtOAc:hexane); IR ν_{max} 2960, 2935, 2874, 1736, 1719, 1630, 1274, 1161, 1136; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.29 (t, *J* = 7.0 Hz, 9H), 1.80-1.88 (m, 6H), 2.33-2.41 (m, 12H), 4.19 (q, *J* = 7.0 Hz, 6H), 5.11 (s, 6H), 5.52 (q, *J* = 1.0 Hz, 3H), 6.16 (t, *J* = 1.0 Hz, 3H), 7.29 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.32, 23.71, 31.33, 33.64, 60.80, 65.76, 125.28, 127.78, 137.06, 140.05, 167.08, 173.17; HRMS Found $(M+NH_4)^+$ 690.3483, $C_{36}H_{48}O_{12}$ requires $(M+NH_4)^+$ 690.3490; found $(M+Na)^+$ 695.3039, requires $(M+Na)^+$ 695.3043.



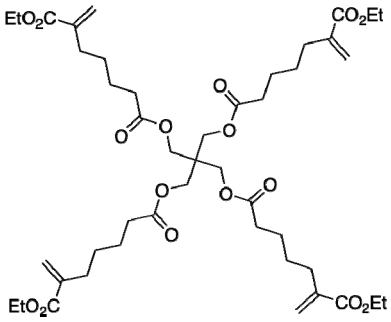
[G1]-ene$_3$ 7d (84 mg, 91%). R_f 0.2 (1:4, v/v EtOAc:hexane); IR ν_{max} 2948, 1728, 1722, 1631, 1439, 1163; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.31-1.38 (m, 6H), 1.44-1.51 (m, 6H), 1.62-1.70 (m, 6H), 2.28 (t, *J* = 7.0 Hz, 6H), 2.36 (t, *J* = 7.5 Hz, 6H), 3.74 (s, 9H), 5.10 (s, 6H), 6.09 (q, *J* = 1.0 Hz, 3H), 6.12 (t, *J* = 1.0 Hz, 3H), 7.28 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 24.78, 28.13, 28.78, 31.81, 34.26, 51.92, 65.70, 124.85, 127.70, 137.06, 140.59, 167.84, 173.55; HRMS Found $(M+NH_4)^+$ 732.3957, $C_{39}H_{54}O_{12}$ requires $(M+NH_4)^+$ 732.3959; found $(M+Na)^+$ 737.3508, requires $(M+Na)^+$ 737.3513.



[G1]-ene$_3$ 7e (91 mg, 88%). R_f 0.3 (1:4, v/v EtOAc:hexane); IR ν_{max} 2928, 1732, 1715, 1634, 1604, 1577, 1455, 1368, 1257; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.25 (t, *J* = 7.0 Hz, 9H), 4.06 (s, 6H), 4.18 (q, *J* = 7.0 Hz, 6H), 5.21 (q, *J* = 1.0 Hz, 3H), 5.35 (s, 6H), 6.19 (d, *J* = 1.0 Hz, 3H), 7.26-7.30 (m, 6H), 7.45-7.49 (m, 6H), 7.97 (dd, *J* = 8.0 Hz, 1.5 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.23, 35.94, 60.82, 66.19, 125.62, 126.68, 127.58, 129.79, 130.95, 131.69, 132.30, 137.02, 140.38, 140.55, 166.93, 166.95; HRMS Found $(M+NH_4)^+$ 834.3484, $C_{48}H_{48}O_{12}$ requires $(M+NH_4)^+$ 834.3490; found $(M+Na)^+$ 839.3040, requires $(M+Na)^+$ 839.3043.



[G1]-ene$_4$ 8a (155 mg, 89%) was synthesised from 2,2-bis(hydroxymethyl)propane-1,3-diol (27 mg, 0.2 mmol), ethyl 1-(iodomethyl)-2-oxocyclohexanecarboxylate (496 mg, 1.6 mmol) and K_2CO_3 (221 mg, 1.6 mmol) following the general procedure. R_f 0.4 (3:7, v/v EtOAc:hexane); IR ν_{max} 2938, 2868, 1736, 1716, 1633, 1464, 1180; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.29 (t, *J* = 7.0 Hz, 12H), 1.45-1.52 (m, 8H), 1.59-1.67 (m, 8H), 2.28-2.34 (m, 16H), 4.10 (s, 8H), 4.19 (q, *J* = 7.0 Hz, 8H), 5.52 (d, *J* = 1.0 Hz, 4H), 6.14 (d, *J* = 1.0 Hz, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.34, 24.46, 27.97, 31.59, 33.91, 42.04, 60.75, 62.17, 124.82, 140.51, 167.26, 173.08; HRMS Found $(M+NH_4)^+$ 882.4840, $C_{45}H_{68}O_{16}$ requires $(M+NH_4)^+$ 882.4851; found $(M+Na)^+$ 887.4399, requires $(M+Na)^+$ 887.4405.



IV Synthesis of [G4]-ene$_{24}$ 11a

General procedure for [G(X)]-ene$_n$: In a dry test-tube, maintained under nitrogen, [G(X)]-ol$_n$ (0.1 mmol), fragmentation precursor **3a-e** (2n · 0.1 mmol) and K_2CO_3 (2n · 0.1 mmol) were stirred at 70°C for 72 h. Gradient column chromatography (1:4, v/v EtOAc:hexane → EtOAc) was applied to obtain pure [G(X)]-ene$_n$ as colourless oil.

General procedure for [G(X+1)]-ol$_{2n}$: A solution of [G(X)]-ene$_n$ (0.1 mmol), thiol **9** (n · 0.1 mmol) and dimethylphenylphosphine (n · 0.01 mmol) in acetonitrile (2.5 mL) was stirred under nitrogen for 60 minutes at room temperature. Evaporation of the volatiles followed by column chromatography (1:19, v/v MeOH:CH_2Cl_2 → 1:14, v/v MeOH:EtOAc) yielded [G(X+1)]-ol$_{2n}$ as colourless oil.

[G1]-ol$_6$ 10a (292 mg, 68%). R_f 0.3 (1:9, v/v MeOH:DCM); IR ν_{max} 3418, 2935, 2867, 1738, 1732, 1715, 1607, 1455, 1162; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.23 (t, *J* = 7.0 Hz, 9H), 1.21-1.34 (m, 6H), 1.46-1.61 (m, 12H), 2.28-2.86 (m, 21H), 3.66 (s, 6H), 4.12 (q, *J* = 7.0 Hz, 6H), 4.60 (s, 12H), 5.08 (s,

6H), 7.19-7.23 (m, 9H), 7.27 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.40, 24.58, 26.58, 31.41, 33.25, 34.02, 36.62, 45.61, 60.82, 64.89, 65.84, 124.36, 126.65, 127.85, 137.01, 138.83, 141.94, 173.62, 174.82; HRMS Found $(M+H)^+$ 1267.5371, $C_{66}H_{90}O_{18}S_3$ requires $(M+H)^+$ 1267.5368; found $(M+Na)^+$ 1289.5166, requires $(M+Na)^+$ 1289.5187.

[G2]-ene$_6$ (426 mg, 97%). R_f 0.5 (1:1, v/v EtOAc: hexane); IR ν_{max} 2939, 2867, 1743, 1730, 1714, 1631, 1609, 1462, 1415, 1371, 1174, 1028, 733; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.25 (t, *J* = 7.0 Hz, 9H), 1.29 (t, *J* = 7.0 Hz, 18H), 1.26-1.34 (m, 3H), 1.47-1.71 (m, 39H), 2.29-2.40 (m, 30H), 2.49-2.58 (m, 6H), 2.65-2.73 (m, 3H), 3.70 (s, 6H), 4.14 (q, *J* = 7.0 Hz, 6H), 4.19 (q, *J* = 7.0 Hz, 12H), 5.08 (s, 12H), 5.09 (s, 6H), 5.06 (d, *J* = 1.0 Hz, 6H), 6.13 (t, *J* = 1.0 Hz, 6H), 7.20 (s, 3H), 7.26 (s, 3H), 7.27 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.35, 14.45, 24.58, 24.78, 26.82, 28.02, 31.63, 31.72, 33.68, 34.05, 34.14, 36.54, 45.74, 60.72, 65.80, 124.70, 126.68, 127.79, 128.51, 136.99, 137.07, 139.11, 140.65, 167.29, 173.23, 173.40, 174.51 (2 overlapping); HRMS Found $(M+NH_4)^+$ 2377.1248, $C_{126}H_{174}O_{36}S_3$ requires $(M+NH_4)^+$ 2377.1291; found $(M+Na)^+$ 2382.0855, requires $(M+Na)^+$ 2382.0845; PDI: 1.097.

[G2]-ol$_{12}$ (353 mg, 57%). UV/Vis (0.75 mM in $CHCl_3$) λ_{max} (log ε) 266.0 (3.13); IR ν_{max} 3441, 2981, 2939, 2866, 1731, 1607, 1456, 1377, 1267, 1165, 1029, 911, 734; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.18-1.22 (m, 45H), 1.44-1.58 (m, 36H), 2.25-2.61 (m, 45H), 3.43 (br s, 12H), 3.61 (s, 12H), 3.65 (s, 6H); 4.03-4.12 (m, 18H), 4.53 (s, 24H), 5.02 (s, 12H), 5.04 (s, 6H), 7.12-7.22 (m, 30H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.15, 14.24, 24.48, 24.58, 26.48, 26.60, 31.35, 31.50, 33.14, 33.44, 33.87 (x2), 36.29, 36.43, 45.49, 45.55, 60.65 (x2), 64.53, 65.62, 65.74, 124.14, 126.37, 126.56, 127.61, 128.41, 136.71, 136.86, 138.47, 138.99, 141.82, 173.22, 173.42, 174.52, 174.70.

[G3]-ene$_{12}$ (328 mg, 65%). UV/Vis (0.75 mM in $CHCl_3$) λ_{max} (log ε) 253.0 (3.40); IR ν_{max} 2939, 2866, 1736, 1631,1609, 1462, 1372, 1158, 1028, 916, 734; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.20-1.31 (m, 81H), 1.44-1.68 (m, 84H), 2.26-2.37 (m, 66H), 2.45-2.54 (m, 18H), 2.60-2.68 (m, 9H), 3.67 (s, 18H), 4.09-4.18 (m, 42H), 5.04 (s, 12H), 5.05 (s, 24H), 5.06 (s, 6H), 5.47 (d, *J* = 1.0 Hz, 12H), 6.09 (t, *J* = 1.0 H, 12H), 7.17-7.24 (m, 30H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.21, 14.31, 24.42, 24.45, 24.57, 24.63, 26.86, 26.87, 31.47, 31.49, 31.55, 33.46, 33.89, 33.90, 33.98, 34.01, 36.35, 36.40, 45.50, 45.57, 45.59, 60.56, 64.68, 65.59, 65.63, 65.67, 65.80, 124.56, 124.59, 125.27, 126.51, 126.57, 127.14, 127.62, 128.35, 128.39, 136.69, 136.77, 136.79, 136.84, 136.92, 138.79, 138.98, 138.99, 140.49, 142.03, 167.10, 167.14, 173.05, 173.07, 173.09, 173.18, 173.22, 173.24, 174.34, 174.35, 174.43; PDI: 1.194.

[G3]-ol$_{24}$ (166 mg, 38%). IR ν_{max} 3447, 2926, 2860, 1732, 1607, 1456, 1377, 1162, 1030, 911, 736; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.21-1.33 (m, 105H), 1.47-1.67 (m, 84H), 2.28-2.67 (m, 105H), 2.86 (br s, 24H), 3.66 (s, 12H), 3.67 (s, 6H), 3.68 (s, 24H), 4.09-4.16 (m, 42H), 4.59 (s, 48H), 5.06 (s, 36H), 5.07 (s, 6H), 7.18-7.25 (m, 66H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.29, 14.39, 14.42, 21.12, 24.58, 24.68, 24.73, 26.49, 26.59, 26.69, 26.75, 29.78, 31.43, 31.56, 31.66, 33.26, 33.61, 33.72, 34.00, 36.46, 36.49, 36.59, 45.42, 45.59, 45.64, 45.70, 60.49, 60.78, 64.64, 64.82, 65.74, 65.83, 65.88, 66.07, 124.31, 124.46, 125.44, 126.58, 126.71, 126.74, 127.33, 127.75, 128.52, 128.56, 136.68, 136.84, 136.99, 138.74, 138.87, 138.97, 139.09, 139.13, 141.72, 141.93, 142.18, 171.25, 173.29, 173.34, 173.42, 173.56, 173.60, 174.58, 174.63, 174.70, 174.78, 174.84; MALDI MS Found $(M+Na)^+$ 7893.9, $C_{408}H_{558}O_{108}S_{21}$ requires $(M+Na)^+$ 7887.1.

[G4]-ene$_{24}$ 11a (159 mg, 91%). IR ν_{max} 2939, 1732, 1633, 1608, 1463, 1372, 1161, 1028, 733; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.21-1.30 (m, 177H), 1.45-1.69 (m, 180H), 2.27-2.38 (m, 138H), 2.47-2.55 (m, 42H), 2.64-2.69 (m, 21H), 3.68 (s, 42H), 4.10-4.10 (m, 90H), 5.05-5.08 (m, 90H), 5.48 (d, *J* = 1.0 Hz, 24H), 6.11 (d, *J* = 1.0 Hz, 24H), 7.18-7.25 (m, 66H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 14.24, 14.34, 24.45, 24.67, 26.72, 27.87, 31.52, 31.63, 33.47, 33.61, 33.94, 34.01, 36.27, 36.35, 45.59, 60.63, 65.60, 65.70, 65.82, 124.64, 124.72, 126.63, 127.69, 128.44, 129.54, 136.78, 136.83, 136.91, 138.99, 140.46, 167.16, 173.16, 173.31, 174.44; PDI: 1.156.

V Random branching Theory

Random Branching Theory (RBT) constructs a model solution structure for a branched polymer by randomly assembly from units that may be oligomers or larger clusters. It has been shown to describe accurately the structures of a variety of synthetic[iv,v] and natural,[vi,vii] regular and randomly branched polymers. Remarkably, the assembly of a model structure based on random branching provides a good model of the density distributions of simulated dendrimers,[4] though perhaps this is understandable now that we know that monomers of the outermost generation are often distributed through the dendrimer.

In Figure A we compare the hydrodynamic radii of dendrimers [G1]-ene$_3$ to [G4]-ene$_{24}$ to the predictions of RBT. Two theoretical predictions are shown, one with the Flory-Huggins parameter χ chosen to vanish, one under θ conditions ($\chi = 1/2$). We assume that each simple unit is a random walk that chooses a new direction every two bonds, and that the maximum density of these units is given by the random-close packing of spheres of radius equal to the radius of gyration of the linear simple units. A full description of the theory has been published.[4,5] No parameters were varied to improve the fit.

The radii of the real dendrimers grow faster than the theoretical predictions. This might be because the theory does not explicitly include for the side groups of each simple unit, but accounting for these by reducing the maximum permitted density does not much improve the agreement. Indeed, no choice of parameters allows RBT to predict the sharp increase of size with the

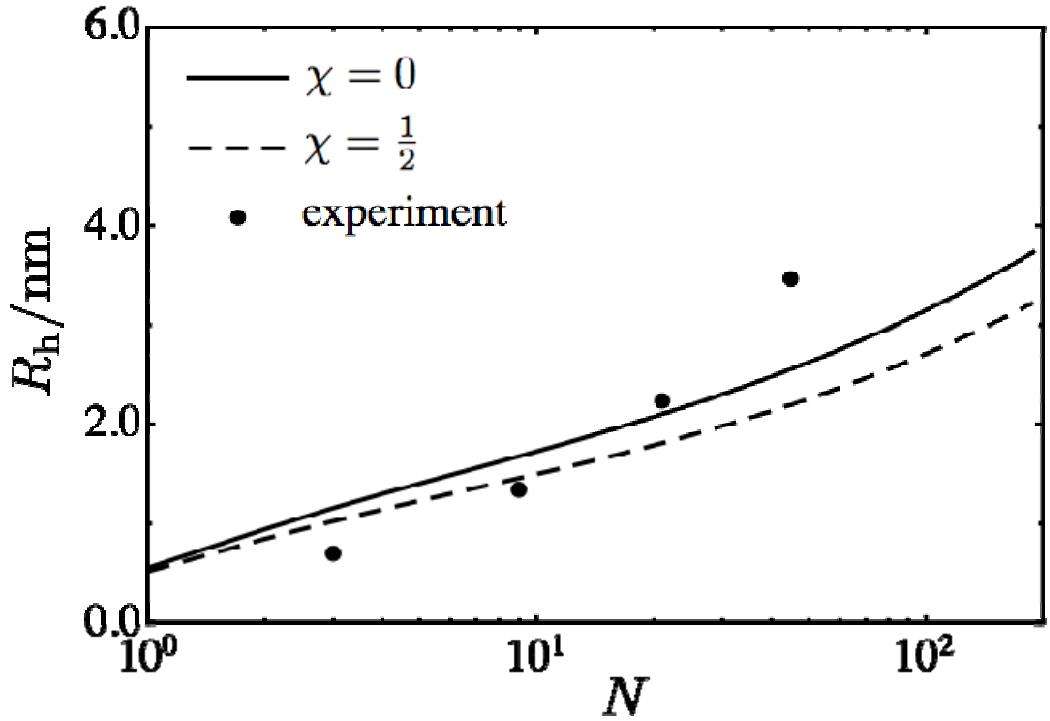
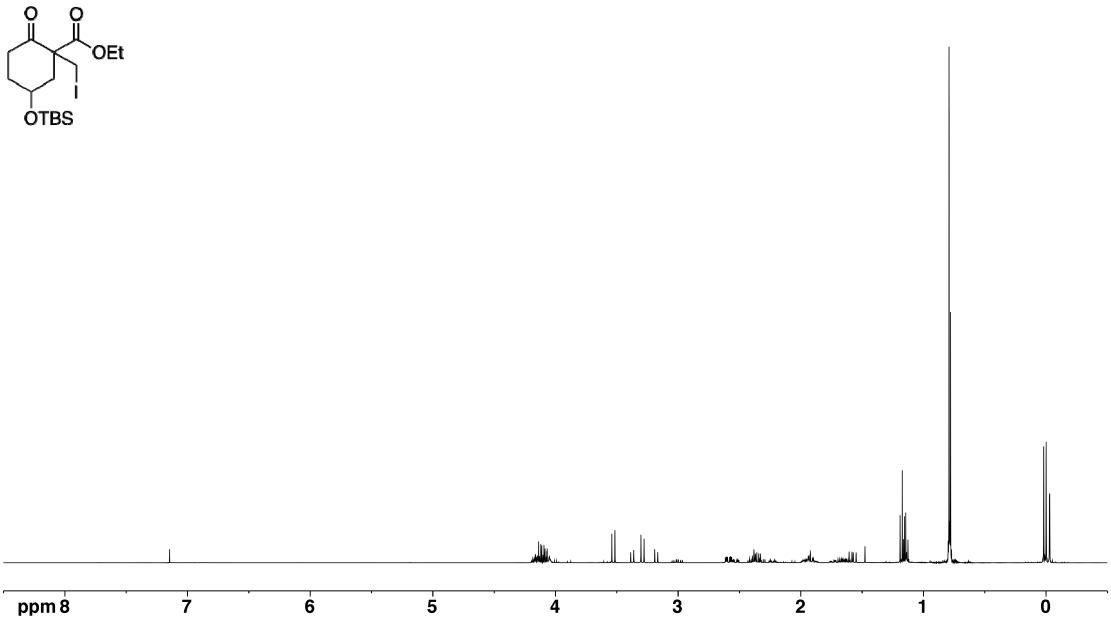


Figure A: The hydrodynamic radii of the [G1]-ene$_3$ **7a** to [G4]-ene$_{24}$ **11a** dendrimers obtained by Gel-Permeation Chromatography, compared to the predictions of Random-Branching Theory (RBT), for two values of the Flory-Huggins parameter χ.

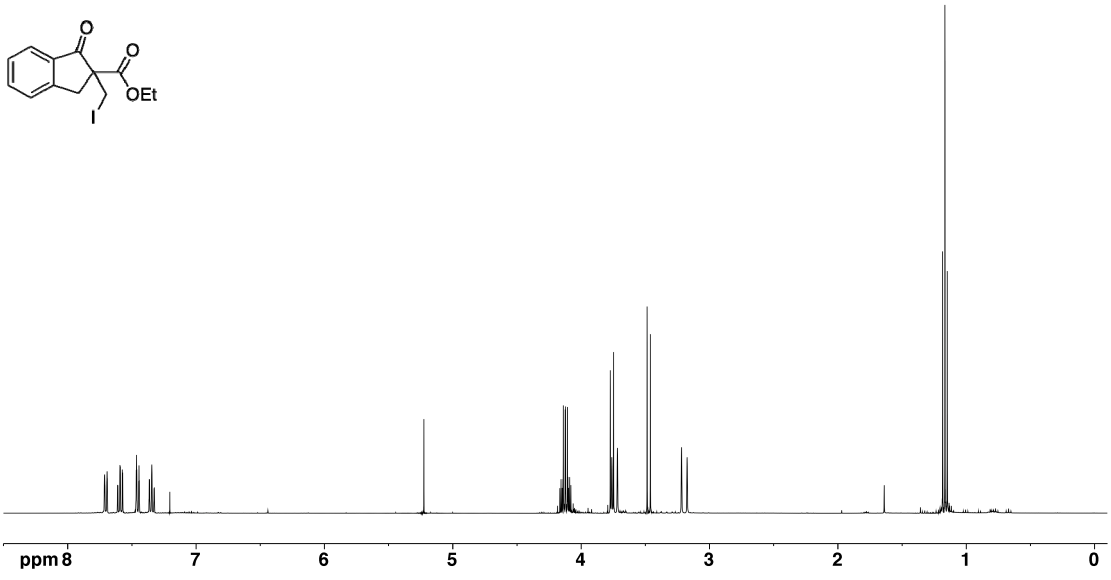
mass of these dendrimers. We conclude that though there is surprisingly good agreement between the theory and simple, simulation models of dendrimers, it does not accurately describe the structure of real dendrimers. The theoretical predictions are qualitatively correct, suggesting that including a better description of the regular branching structure will lead to a useful theory capable of accurate predictions.

VI ^{1}H NMR spectra of new compounds

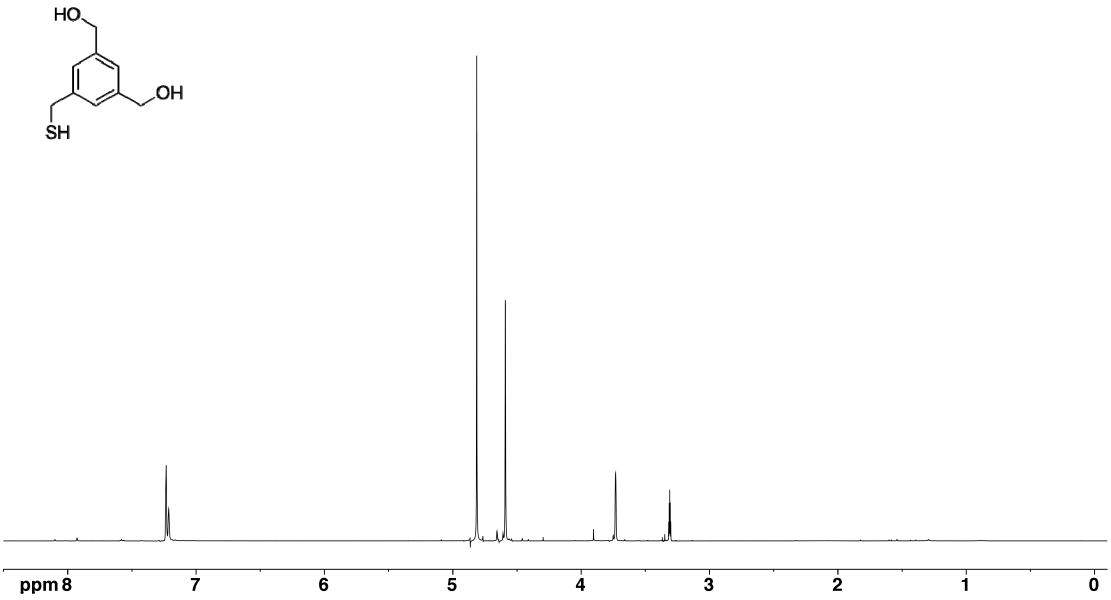
Ethyl 5-(*tert*-butyldimethylsilyloxy)-1-(iodomethyl)-2-oxocyclohexanecarboxylate (3b)



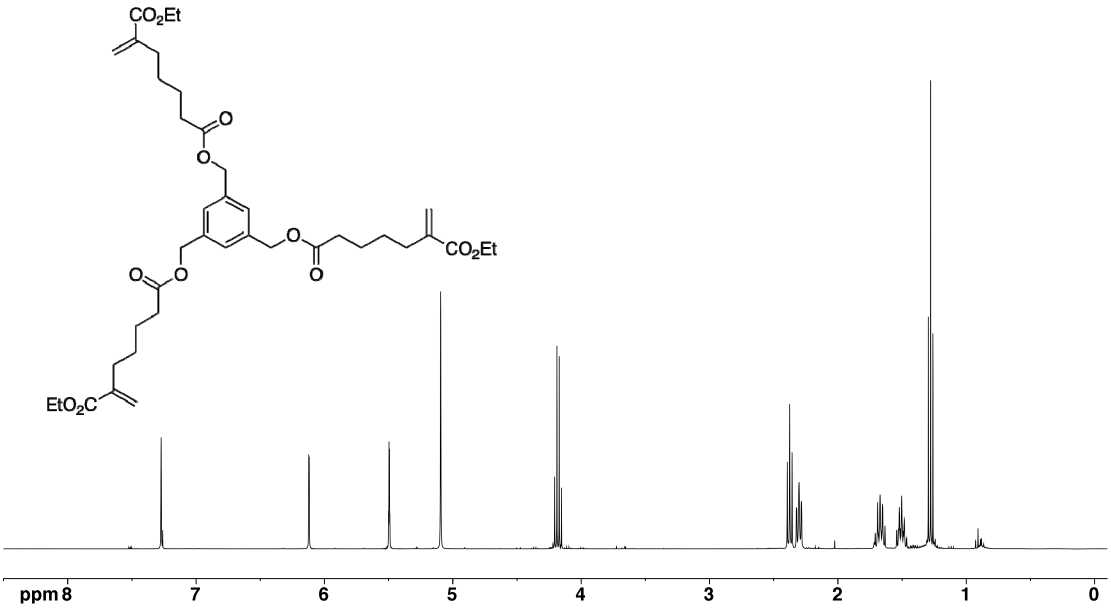
Ethyl 2-(iodomethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3e)



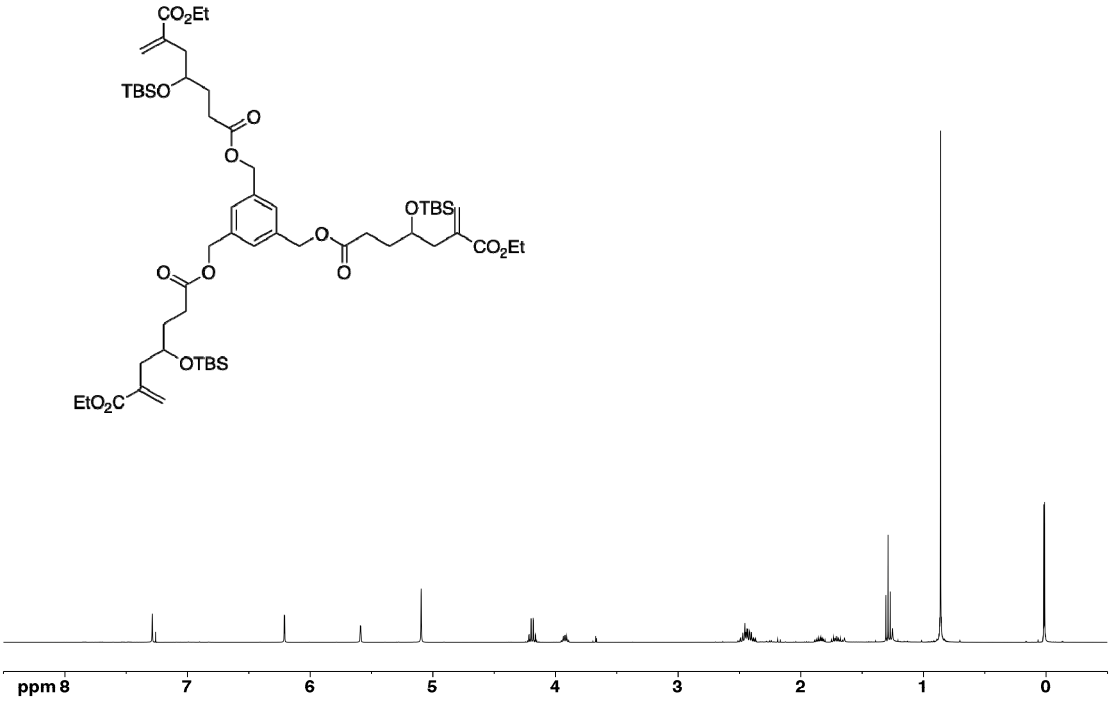
(5-(Mercaptomethyl)-1,3-phenylene)dimethanol (5)



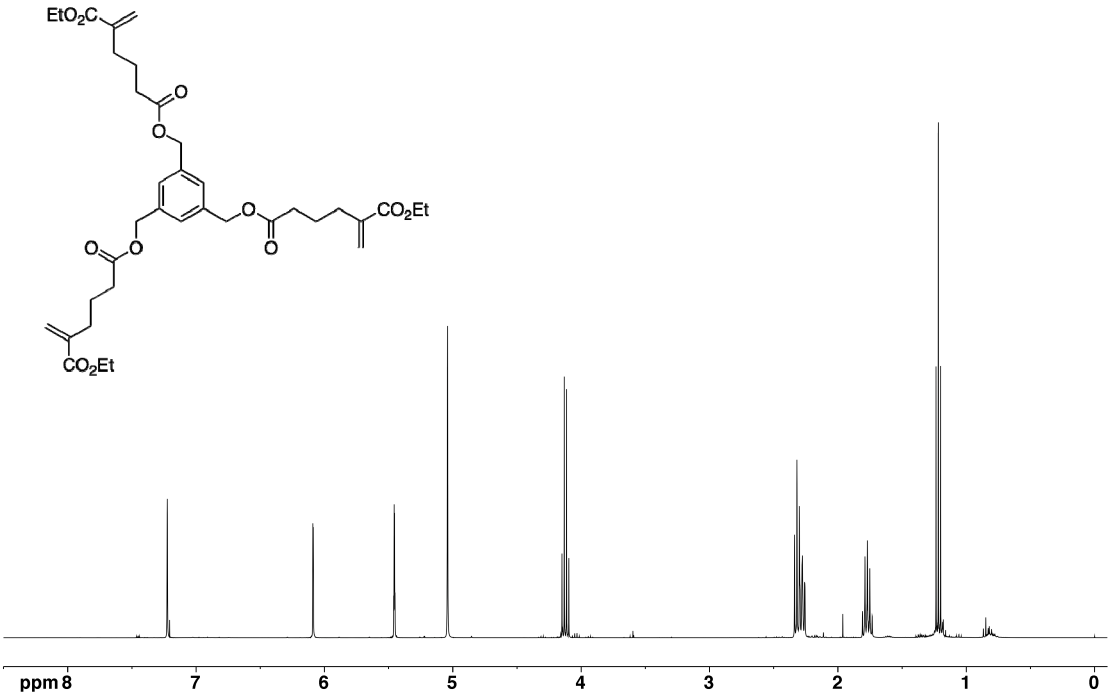
[G1]-ene$_3$ 7a



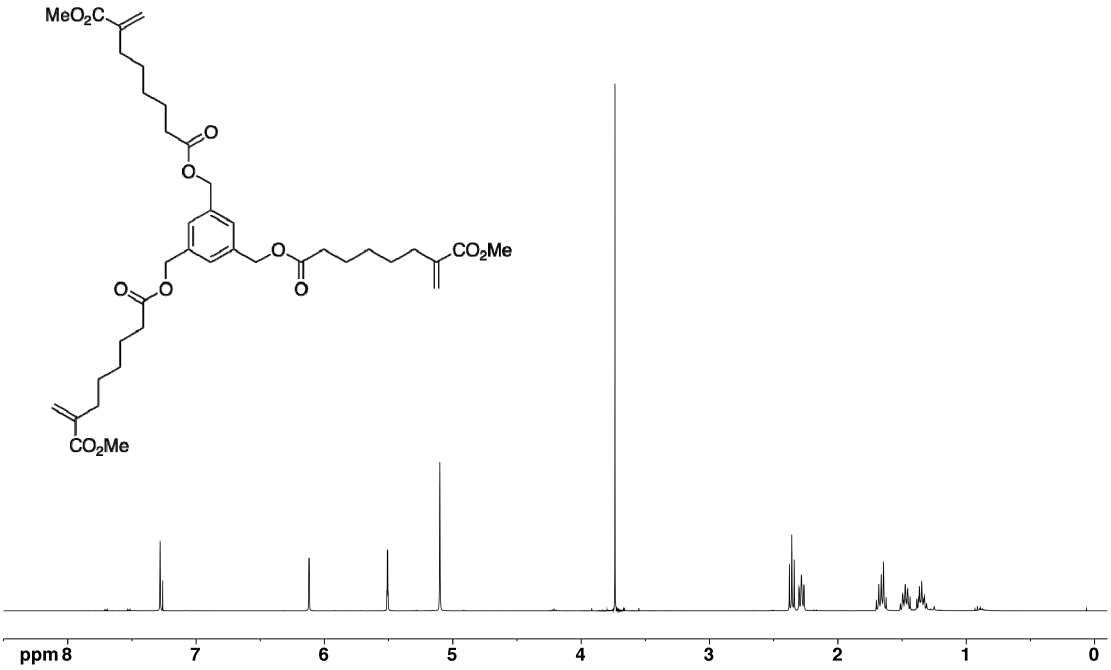
[G1]-ene$_3$ 7b



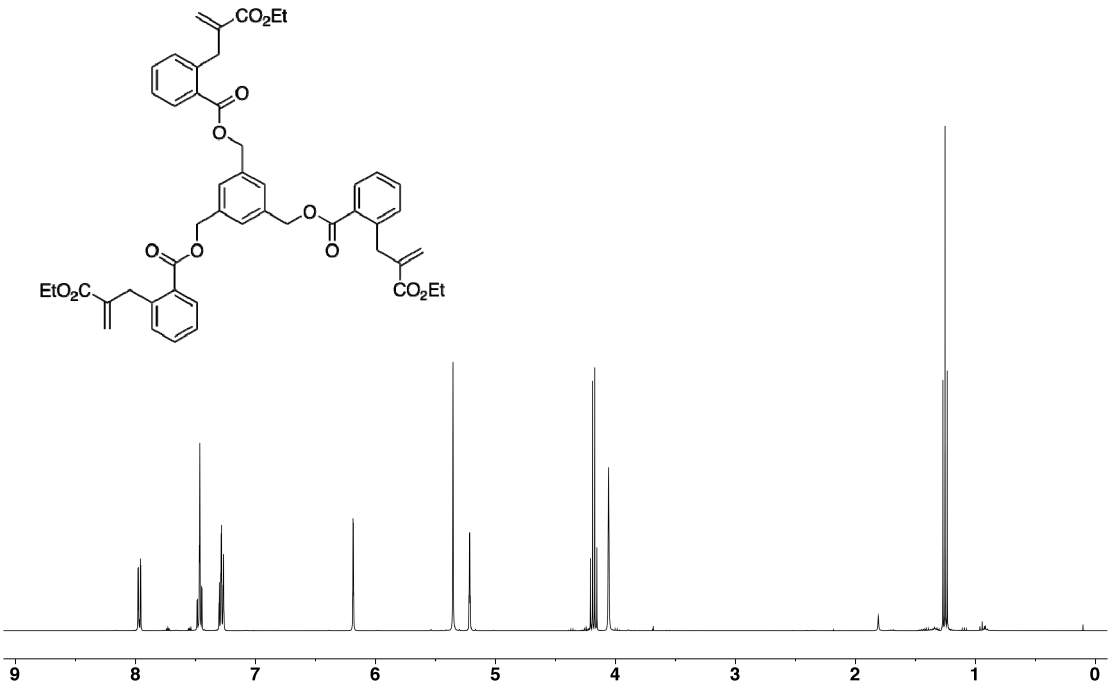
[G1]-ene$_3$ 7c



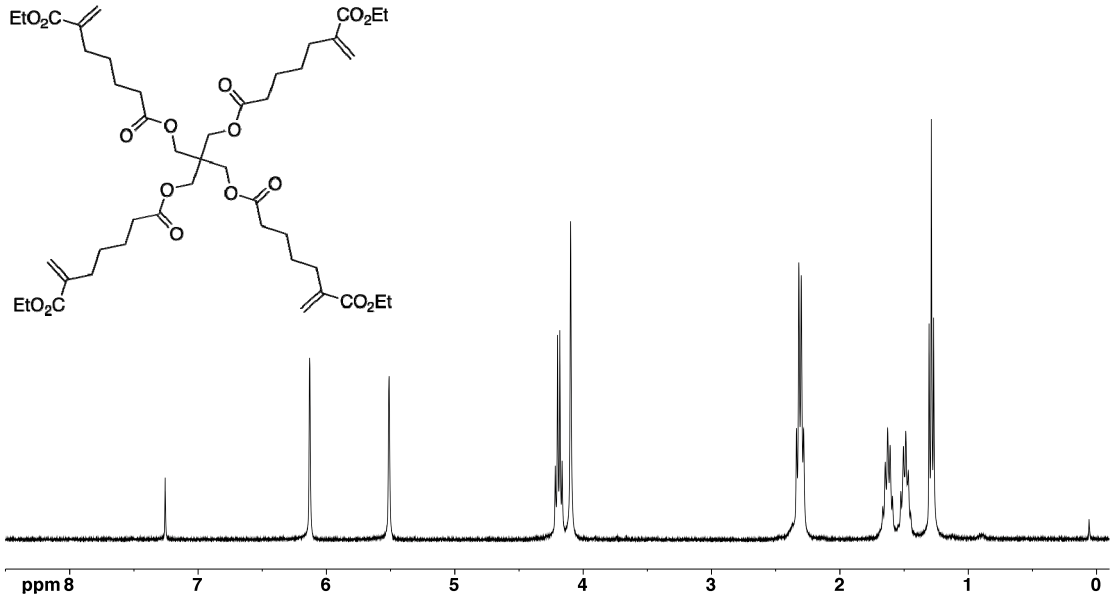
[G1]-ene$_3$ 7d



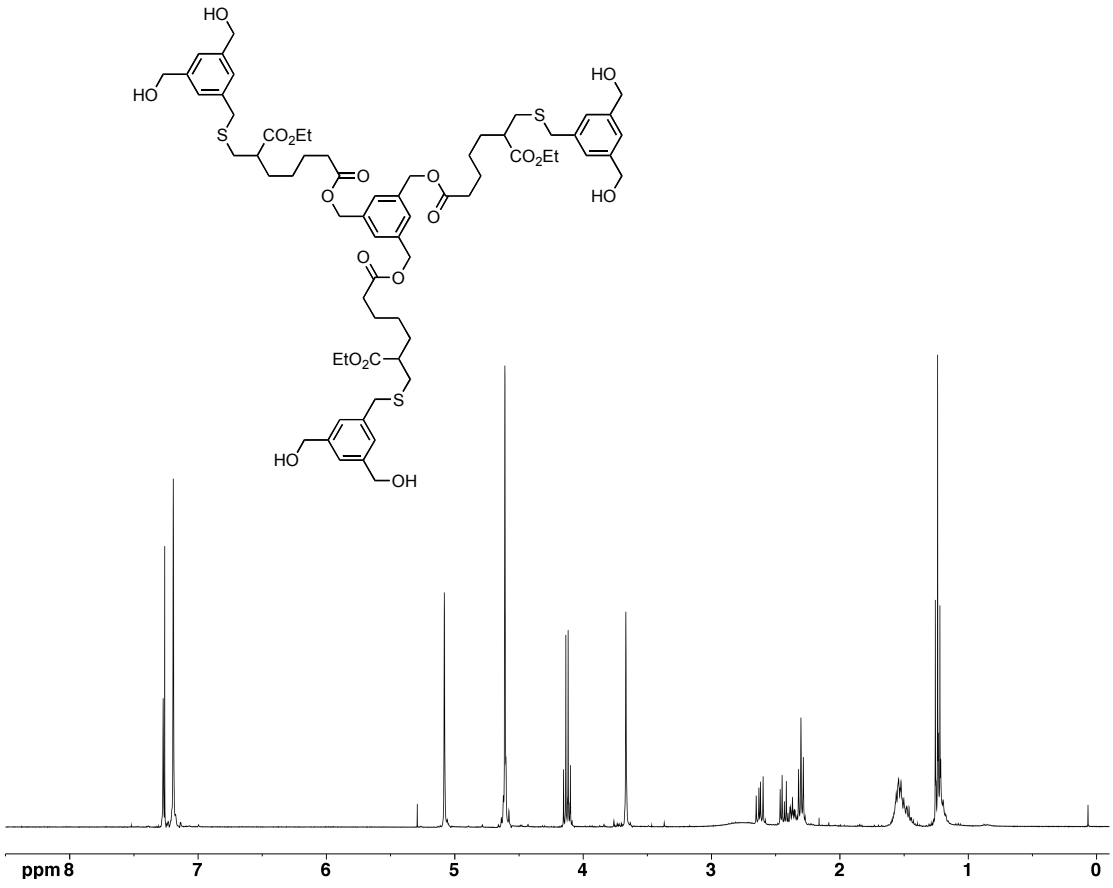
[G1]-ene$_3$ 7e



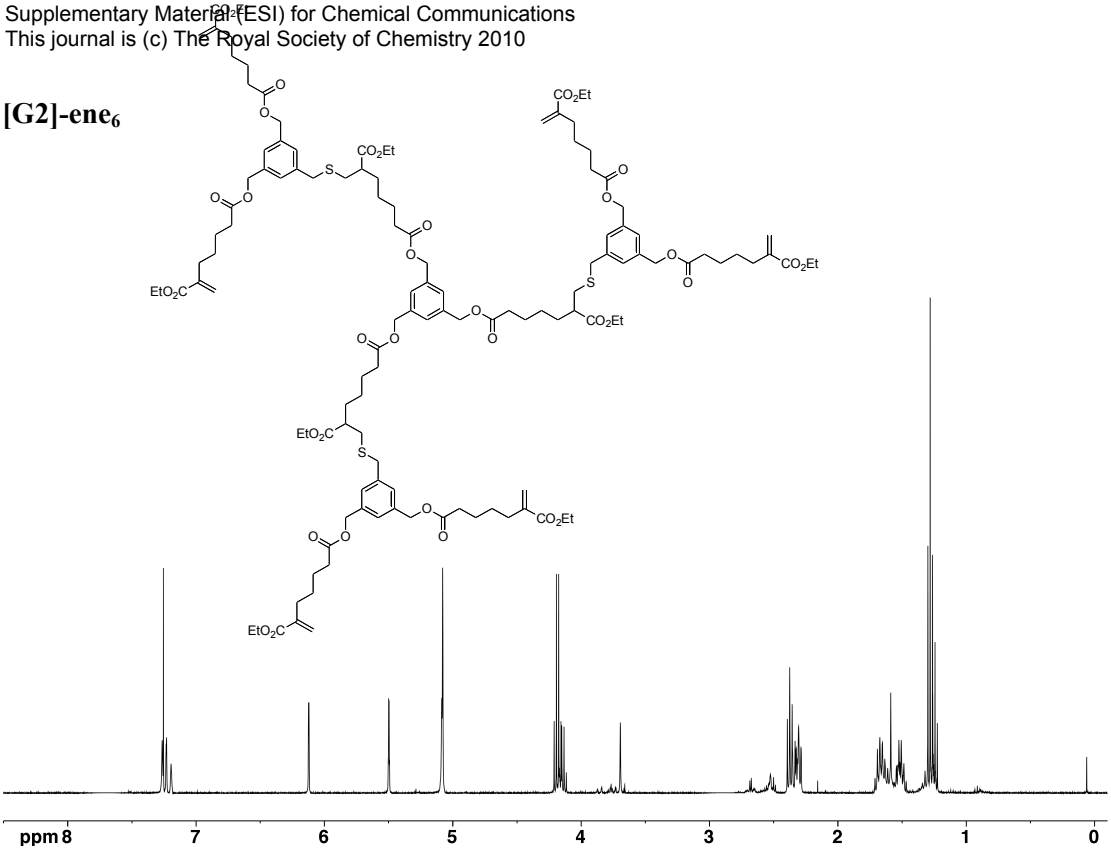
[G1]-ene$_4$ 8a



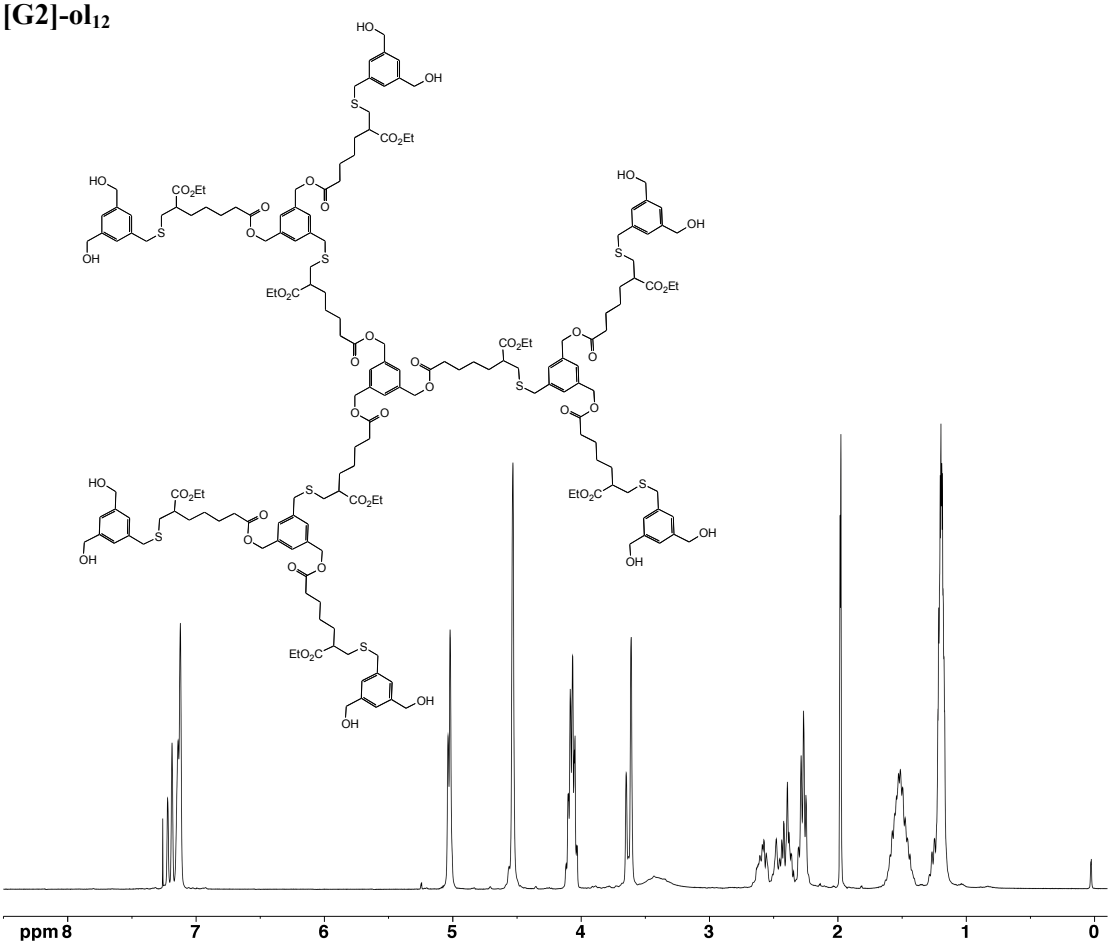
[G1]-ol$_6$ 10a



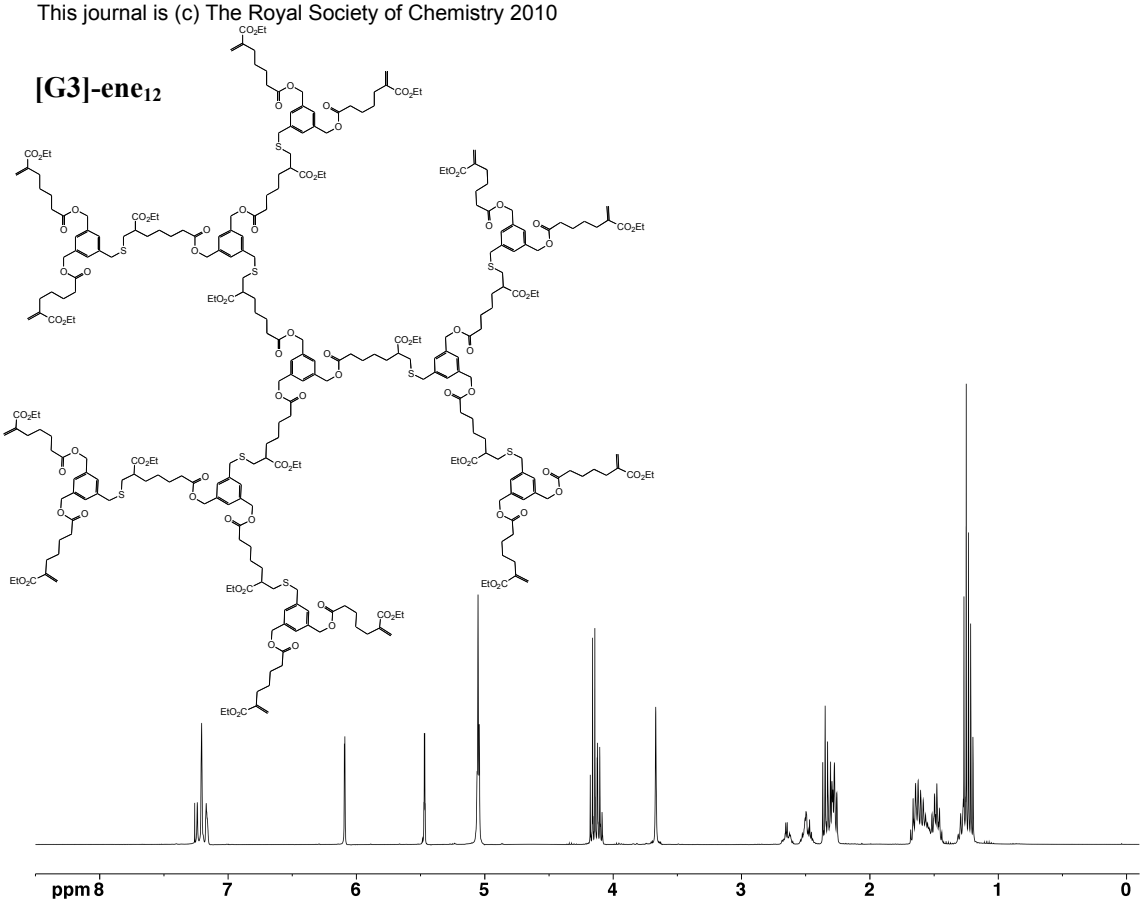
[G2]-ene$_6$



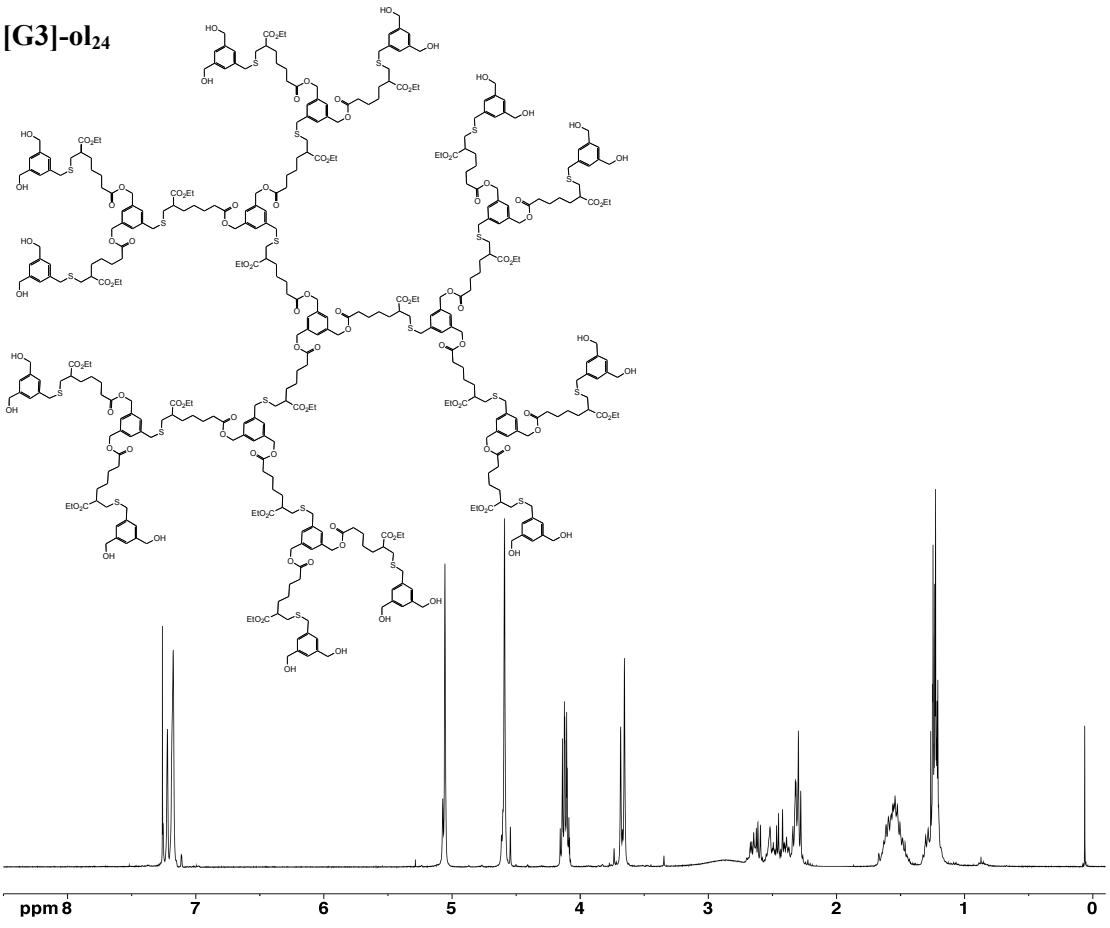
[G2]-ol$_{12}$



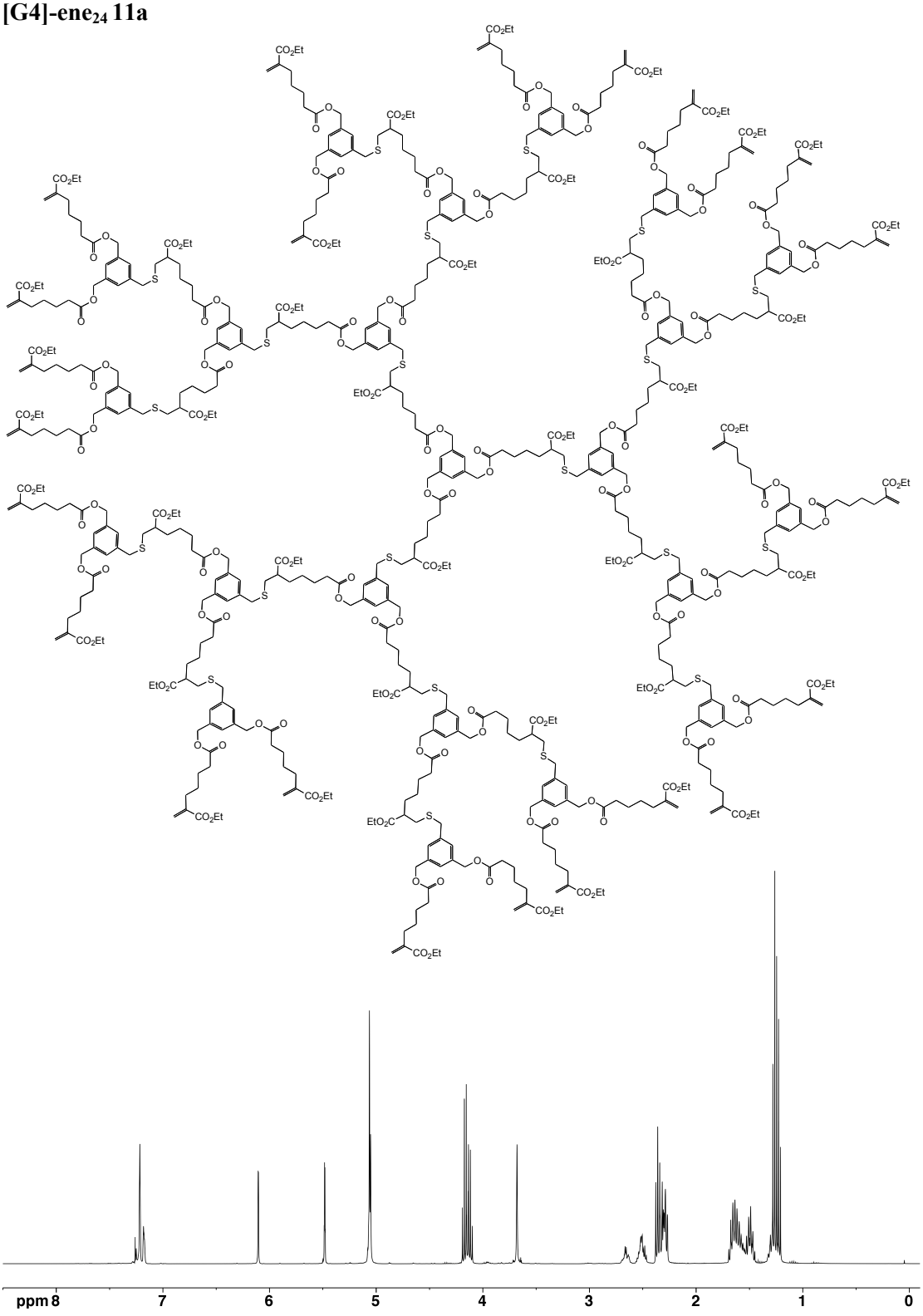
[G3]-ene$_{12}$



[G3]-ol$_{24}$



[G4]-ene$_{24}$ 11a



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