Supporting Information

Monofunctionalization of Dendrimers Using 'Click' Chemistry

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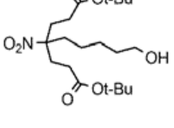
General. All reagents were purchased either from Acros Organics, Aldrich or Alfa Aesar and used without further purification unless otherwise noted. NMR spectra were acquired with a Varian Mercury 400 (^{1}H, 400.0 Hz; ^{13}C, 100.6 MHz) or a Varian Mercury 300 (^{1}H, 300.0 MHz; ^{13}C, 75.5 MHz) spectrometer. Chemical shifts are reported in ppm and referenced to the residual nuclei in the corresponding deuterated solvents. Abbreviations used include singlet (s), broad singlet (bs), doublet (d), triplet (t), quartet (q), and unresolved multiplet (m). Mass spectral analyses were provided by the Georgia Tech Mass Spectrometry Facility on a VG-70se spectrometer using fast atom bombardment (FAB), and on ABI 4700 Proteomics Analyzer for matrix assisted laser desorption ionization (MALDI) tandem time-of-flight (TOF). Elemental analyses were performed using Perkin Elmer Series II CHNS/O Analyzer 2400. All microwave irradiation experiments were carried out in a CEM Focused Monomodal Microwave™ Synthesis System, Model Discover.

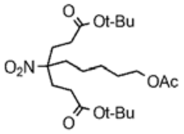
Detailed Experimental

Di-*tert*-butyl 4-(5-hydroxypentyl)-4-nitroheptanedioate (1). To a solution of 6-nitrohexanol[1] (16.31 g, 110 mmol) and *tert*-butyl acrylate (35.38 mL, 244 mmol) in THF (220 mL) was added Triton-B (5.5 mL, 40 wt % solution in MeOH) at room temperature in a portion over 2 hours. After stirring for 15 hours at room temperature, all the volatiles were removed in vacuo to give a dark yellowish residue, which was dissolved in diethyl ether, washed with 5% aqueous HCl, 10% aqueous $NaHCO_3$, and brine, and then dried over $MgSO_4$. After filtration, the organic mixture was concentrated *in vacuo* to give a residue that was purified by silica gel column chromatography eluting with EtOAc/hexanes (1:1) to give 24.42 g of the title compound **1** as a white solid in 55% yield.



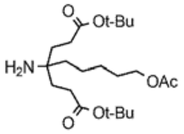
^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.25 (m, 2H), 1.38 (m, 2H), 1.44 (s, 18H), 1.56 (m, 3H), 1.88 (t, *J* = 7.8 Hz, 2H), 2.19 (m, 8H), 3.63 (t, *J* = 6.3 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 23.3, 25.7, 27.9, 29.8, 30.3, 32.1, 35.3, 62.3, 81.0, 92.9, 171.2. HRMS MALDI-TOF: $[M + H]^+$ calcd for $C_{20}H_{38}NO_7$, 404.2648; found, 404.2661. Anal. calcd for $C_{20}H_{37}NO_7$: C, 59.53; H, 9.24; N, 3.47. found C, 59.40; H, 9.32; N, 3.48.

Di-*tert*-butyl 4-(5-acetoxypentyl)-4-nitroheptanedioate (2). To a solution of **1** (21.82 g, 54.1 mmol) and pyridine (5.25 mL, 64.9 mmol) in $CHCl_3$ (180 mL) was added Ac_2O (6.09 mL, 64.9 mmol) at 0 °C. The mixture was warmed up to room temperature slowly and stirred for 15 hours. The mixture was washed with water, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude was purified by silica gel column chromatography eluting with EtOAc/hexanes (1:3) to give 19.95 g of the title compound **2** as a white solid in 83% yield.



^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.25 (m, 2H), 1.37 (m, 2H), 1.43 (s, 18H), 1.63 (m, 2H), 1.88 (t, *J* = 8.1 Hz, 2H), 2.19 (m, 8H), 2.04 (s, 3H), 4.04 (t, *J* = 6.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 20.9, 23.3, 26.0, 28.0, 28.3, 29.8, 30.3, 35.3, 64.2, 81.1, 92.8, 171.1, 171.2. HRMS MALDI-TOF: $[M + H]^+$ calcd for $C_{22}H_{40}NO_8$, 446.2754; found, 446.2776. Anal. calcd for $C_{22}H_{39}NO_8$: C, 59.31; H, 8.82; N, 3.14. Found C, 59.20; H, 8.80; N, 3.36.

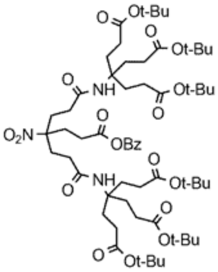
Di-*tert*-butyl 4-(5-acetoxypentyl)-4-aminoheptanedioate (3). To a solution of **2** (7.00 g, 15.7 mmol) in absolute EtOH (160 mL) was added Raney-Ni (6.28 g) and the mixture was stirred under 60 psi of H_2 for 12 hours at room temperature. The catalyst was carefully filtered, and the filtrate was concentrated *in vacuo* to give 6.39 g of amine **3** as a colorless clear oil in 98% yield.



^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.24 (m, 6H), 1.38 (s, 18H), 1.57 (m, 6H), 1.99 (s, 3H), 2.17 (t, *J* = 8.2 Hz, 4H), 3.99 (t, *J* = 6.6 Hz, 2H) ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 20.9, 23.0, 26.5, 28.0, 28.5, 29.9, 34.5, 39.4, 52.5, 64.4, 80.1, 171.0, 173.1. HRMS MALDI-TOF: $[M + H]^+$ calcd for $C_{22}H_{42}NO_6$, 416.3012; found, 416.3017.

Nitro dendron (4).[2] The mixture of di-*tert*-butyl 4-(2-*tert*-benzyloxycarbonylethyl)-4-nitroheptanedioate[2] (33.85 g, 70.6 mmol) dissolved in HCO_2H (266 mL) was stirred for 6 hours at room temperature. The mixture was concentrated *in vacuo* to give 23.83 g of the diacid **4a**[2] as a white solid in 92 % yield. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.26 (m, 6H), 2.36 (m, 6H), 5.11 (s, 2H), 7.34 (m, 5H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 28.4, 28.5, 29.3, 30.6, 67.0, 91.8, 128.3, 128.5, 128.6, 135.2, 171.8, 178.0. HRMS MALDI-TOF: $[M + H]^+$ calcd for $C_{17}H_{22}NO_8$, 368.1345; found, 368.1367. Anal. Calcd for $C_{17}H_{21}NO_8$: C, 55.58; H, 5.76; N, 3.81. Found C, 55.36; H, 5.62; N, 3.81.

To a solution of the above diacid monomer (3.93 g, 10.7 mmol) in DMF (120 mL) were added DCC (4.96 g, 24.1 mmol) and 1-HOBT (3.25 g, 24.1 mmol) at room temperature. After the mixture was stirred for 2 hours, Behera's amine[3] (10.00 g, 24.1 mmol) was added and then the resulting mixture was stirred for 3 days at room temperature. After filtration, the filtrate was concentrated *in vacuo* to give a residue that was dissolved in CH_2Cl_2 and washed with a saturated aqueous solution of $NaHCO_3$ (2×) and then brine. The organic phase was dried over Na_2SO_4, filtered, concentrated *in vacuo*, and purified by silica gel column chromatography eluting with EtOAc/hexanes (2:3) to give 10.94 g of dendron **4** as a white solid in 88% yield.

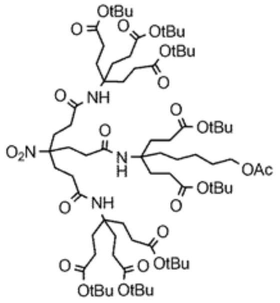


^{1}H NMR ($CDCl_3$, 300MHz): δ 1.39 (s, 54H), 1.91 (m, 12H), 2.06 (m, 4H), 2.17 (m, 18H), 2.35 (m, 2H), 5.08 (s, 2H), 6.16 (s, 2H), 7.31 (m, 5H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 28.0, 28.6, 29.8, 29.9, 31.2, 31.3, 57.6, 66.7, 80.7, 92.3, 128.3, 128.3, 128.5, 135.5, 170.1, 171.8, 172.8. HRMS MALDI-TOF: $[M + Na]^+$ calcd for $C_{61}H_{99}N_3O_{18}Na$, 1184.6821; found, 1184.6507. Anal. calcd for $C_{61}H_{99}N_3O_{18}$: C, 63.03; H, 8.58; N, 3.61. found C, 63.08; H, 9.02; N, 3.73.

Nitro dendron (5). In the presence of 10% Pd on activated carbon (1.20 g), a solution of **4** in absolute EtOH (110 mL) was hydrogenated at 60 psi of H_2 at room temperature for 12 hours. The solution was filtered through Celite, and the solvent was removed *in vacuo* to give 6.11 g of monoacid dendrons **5a**[2] as a white solid in 98% yield. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.42 (s, 54H), 1.92 (m, 12H), 2.10 (m, 4H), 2.20 (m, 16H), 2.31 (m, 4H), 6.14 (s, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 28.0, 28.3, 28.9, 29.8, 30.0, 31.1, 31.3, 57.5, 80.9, 93.1, 170.7, 173.1, 174.7. HRMS MALDI-TOF: $[M + Na]^+$ calcd for $C_{54}H_{93}N_3O_{18}Na$, 1094.6351; found, 1094.6018. Anal. calcd for $C_{54}H_{93}N_3O_{18}$: C, 60.48; H, 8.74; N, 3.92. found C, 60.45; H, 8.97; N, 4.04.

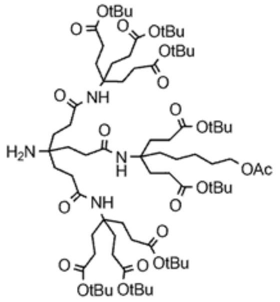
To a solution of the above described monoacid dendron (6.11 g, 5.70 mmol) in DMF (60 mL) were added DCC (1.41 g, 6.84 mmol) and 1-HOBT (0.924 g, 6.84 mmol) at room temperature. After the mixture was stirred for 2 hours, a solution of amine dendron **3** (2.84 g, 6.84 mmol) in DMF (20 mL) was added and then the resulting mixture was stirred for 3 days at room temperature. After filtration, the filtrate was concentrated *in vacuo* to give a residue, which was dissolved in CH_2Cl_2 and washed with a saturated aqueous solution of $NaHCO_3$ (2×) and then brine. The organic phase was dried over

Na_2SO_4, filtered, concentrated *in vacuo*, and purified by silica gel column chromatography eluting with EtOAc/hexanes (1:1) to give 7.76 g of dendron **5** as a white solid in 93% yield.



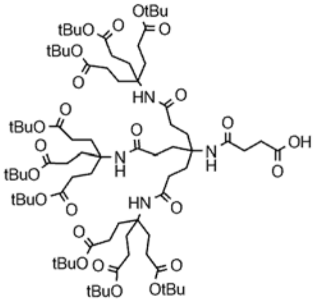
^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.27 (m, 4H), 1.43 (s, 72H), 1.65 (m, 4H), 1.94 (m, 16H), 2.04 (s, 3H), 2.10 (m, 4H), 2.20 (m, 24H), 4.03 (t, *J* = 6.6 Hz, 2H), 5.77 (s, 1H), 6.08 (s, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 21.0, 22.7, 26.0, 28.0, 28.3, 29.7, 29.8, 30.0, 31.2, 34.8, 57.5, 58.0, 64.3, 80.6, 92.5, 170.3, 170.4, 171.3, 172.7, 172.9. HRMS MALDI-TOF: $[M + Na]^+$ calcd for $C_{76}H_{132}N_4O_{23}Na$, 1491.9180; found, 1491.8817. Anal. calcd for $C_{76}H_{132}N_4O_{23}$: C, 62.10; H, 9.05; N, 3.81. found C, 62.09; H, 9.07; N, 4.05.

Amine dendron (6). To a solution of **5** (7.03 g, 4.95 mmol) in absolute EtOH (50 mL) was added Raney-Ni (2.00 g). The mixture was stirred under 60 psi of H_2 for 24 hours at 55 °C. The catalyst was carefully filtered, and the filtrate was concentrated *in vacuo* to give 6.98 g of amine **6** as a white solid in 98% yield.



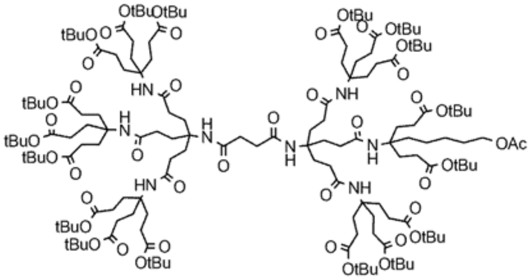
^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.26 (m, 4H), 1.41 (s, 72H), 1.61 (m, 10H), 1.92 (m, 16H), 2.03 (s, 3H), 2.16 (m, 22H), 4.01 (t, *J* = 6.6 Hz, 2H), 5.86 (s, 1H), 6.14 (s, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 21.0, 22.7, 26.1, 28.0, 28.3), 29.8, 29.8, 30.0, 31.5, 31.6, 34.7, 35.2, 52.6, 57.3, 57.7, 64.4, 80.6, 171.3, 172.5, 172.6, 172.7, 172.9. HRMS MALDI-TOF: $[M + H]^+$ calcd for $C_{76}H_{135}N_4O_{21}$, 1439.9613; found, 1439.9455. Anal. calcd for $C_{76}H_{134}N_4O_{21}$: C, 63.39; H, 9.38; N, 3.89. found C, 62.93; H, 9.35; N, 4.06.

Hemisuccinimide (7). A solution of the second generation Behera's amine[4] (1.56 g, 1.08 mmol) and succinic anhydride (0.164 g, 1.63 mmol) in pyridine (22 mL) was stirred at room temperature for 48 hours. The solution was concentrated under reduced pressure and the residue was dissolved in $CHCl_3$ and washed with an aqueous solution of 10% HCl (2×). The organic layer was dried over Na_2SO_4, filtered, and concentrated to dryness. The crude material was purified by silica gel column chromatography eluting with EtOAc/hexanes (2:1) to give 1.39 g of the hemisuccinimide **7** as a white solid in 83% yield.



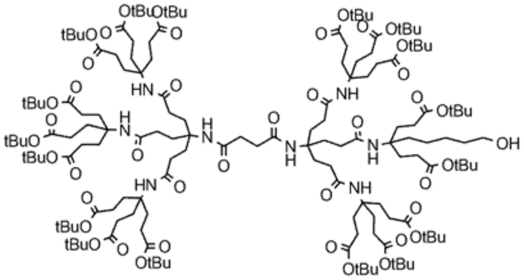
^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.41 (s, 81H), 1.92 (m, 24H), 2.15 (m, 24H), 2.37 (m, 2H), 2.64 (m, 2H), 6.05 (s, 3H), 7.24 (s, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 28.0, 29.8, 30.0, 31.6, 31.7, 57.2, 57.3, 80.7, 171.3, 173.1, 175.3. LRMS-FAB (m/z): $[M + H]^+$ calcd for $C_{80}H_{139}N_4O_{24}$, 1540.0; found, 1539.8. Anal. calcd for $C_{80}H_{138}N_4O_{24}$: C, 62.39; H, 9.03; N, 3.64. found C, 62.34; H, 9.11; N, 3.91.

Dendrimer (8). To a solution of **7** (1.34 g, 0.870 mmol) in DMF (9 mL) were added DCC (0.197 g, 0.957 mmol) and 1-HOBT (0.129 g, 0.957 mmol) at room temperature. After the mixture was stirred for 2 hours, **6** (2.84 g, 0.957 mmol) was added and the resulting mixture was stirred for 3 days at room temperature. After filtration, the filtrate was concentrated *in vacuo* to give a residue, which was dissolved in CH_2Cl_2 and washed with a saturated aqueous solution of $NaHCO_3$ (2×) and then brine. The organic phase was dried over Na_2SO_4, filtered, concentrated *in vacuo*, and purified by silica gel column chromatography eluting with EtOAc/hexanes (3:2) to give 2.17 g of dendrimer **8** as a white solid in 84% yield.



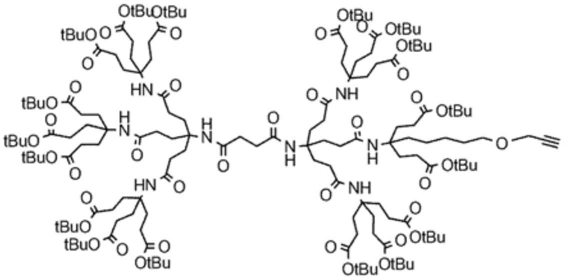
^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.25 (m, 4H), 1.40 (s, 153H), 1.60 (m, 4H), 1.92 (m, 46H), 2.01 (m, 46H), 2.37 (bs, 4H), 4.00 (t, *J* = 6.8 Hz, 2H), 6.23 (s, 1H), 6.38 (s, 5H), 7.24 (s, 1H), 7.30 (s, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 21.0, 26.1, 28.0, 28.1, 29.7, 31.4, 32.8, 52.2, 57.6, 57.7, 64.5, 80.3, 171.2, 171.8, 171.8, 172.7, 172.8, 172.9. LRMS MALDI-TOF: $[M + Na]^+$ calcd for $C_{156}H_{270}N_8O_{44}Na$, 2983.9; found, 2983.2. Anal. calcd for $C_{156}H_{270}N_8O_{44}$: C, 63.26; H, 9.19; N, 3.78. found C, 63.04; H, 9.35; N, 4.13.

Dendrimer (9). To a solution of **8** (1.61 g, 0.544 mmol) in MeOH (20 mL) was added a solution of K_2CO_3 (0.150 g, 1.09 mmol) in H_2O (2 mL) at room temperature. After stirring for 2 hours, the mixture was diluted with CH_2Cl_2 (80 mL) and then quenched with H_2O (20 mL). The resulting solution was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, concentrated *in vacuo*, and purified by silica gel column chromatography eluting with EtOAc/hexanes (2:1) to give 1.46 g of dendrimer **9** as a white solid in 92% yield.



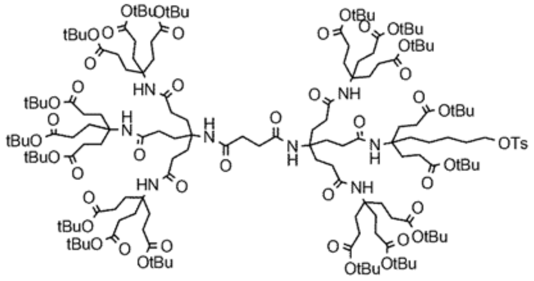
^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.26 (m, 4H), 1.42 (s, 153H), 1.63 (m, 4H), 1.94 (m, 46H), 2.17 (m, 46H), 2.40 (bs, 4H), 3.60 (t, *J* = 6.2 Hz, 2H), 6.34 (s, 2H), 6.41 (s, 1H), 6.44 (s, 3H), 7.44 (bs, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 28.1, 29.8, 31.5, 32.2, 32.8, 52.2, 57.3, 57.3, 57.7, 57.8, 62.3, 80.4, 172.7, 172.8, 172.9, 172.9, 173.0. LRMS MALDI-TOF: $[M + Na]^+$ calcd for $C_{154}H_{268}N_8O_{43}Na$, 2941.9; found, 2942.4. Anal. calcd for $C_{154}H_{268}N_8O_{43}$: C, 63.35; H, 9.25; N, 3.84. found C, 62.82; H, 9.19; N, 4.30.

Dendrimer (10). To a solution of **9** (0.202 g, 0.0691 mmol) in DMF (7 mL) were added Cs_2CO_3 (0.113 g, 0.346 mmol) and propargyl bromide (0.082 g, 0.691 mmol). After heating at 80 °C for 3 days, the mixture was cooled to room temperature, filtered, and concentrated *in vacuo*, and purified by silica gel column chromatography eluting with EtOAc/hexanes (2:1) to give 0.170 g of dendrimer **10** as a white solid in 83% yield.



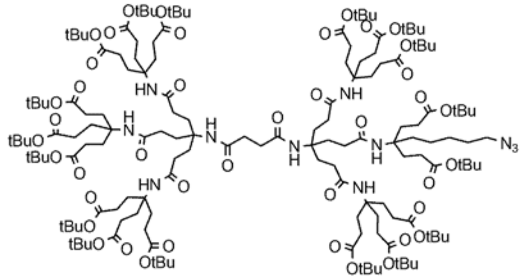
^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.09 (m, 4H), 1.41 (s, 153H), 1.65 (m, 4H), 1.93 (m, 46H), 2.15 (m, 46H), 2.38 (bs, 4H), 2.54 (s, 1H), 4.13 (t, *J* = 4.7 Hz, 2H), 4.70 (s, 2H), 6.32 (s, 1H), 6.46 (s, 5H), 7.17 (bs, 1H), 7.21 (bs, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 25.0, 25.7, 26.0, 28.2, 28.6, 29.9, 31.6, 34.0, 34.6, 55.1, 57.3, 57.7, 57.8, 68.6, 75.7, 77.8, 80.4, 171.7, 172.5, 172.7, 172.8. Anal. calcd for $C_{157}H_{270}N_8O_{43}$: C, 63.75; H, 9.20; N, 3.79. found C, 63.30; H, 9.15; N, 4.20.

Dendrimer (11). To a solution of **9** (0.120 g, 0.041 mmol) in CH_2Cl_2 (2 mL) were added NEt_3 (0.017 mL, 0.123 mmol) and *p*-TsCl (0.031 g, 0.164 mmol) at 0 °C. After stirring for 1 hour at 0 °C, the mixture was warmed to room temperature and stirred for 15 hours. The mixture was quenched with H_2O and then extracted twice with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated *in vacuo*, and purified by silica gel column chromatography eluting with EtOAc/hexanes (2:1) to give 0.086 g of dendrimer **11** as a yellow solid in 68% yield.



^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.19 (m, 4H), 1.39 (s, 153H), 1.60 (m, 4H), 1.92 (m, 46H), 2.16 (m, 46H), 2.37 (br s, 4H), 2.41 (s, 3H), 3.97 (t, *J* = 6.4 Hz, 2H), 6.25 (s, 1H), 6.38 (s, 5H), 7.21 (br s, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.6, 24.6, 25.6, 27.1, 28.0, 28.3, 28.7, 29.7, 31.4, 32.4, 32.9, 36.6, 57.2, 57.6, 57.7, 70.6, 80.3, 127.8, 129.8, 133.0, 144.6, 171.9, 172.7, 172.8, 172.9. LRMS MALDI-TOF: $[M + Na]^+$ calcd for $C_{161}H_{274}N_8O_{45}SNa$, 3095.9; found, 3095.4. Anal. calcd for $C_{161}H_{274}N_8O_{45}S$: C, 62.91; H, 8.98; N, 3.65. found C, 62.65; H, 9.21; N, 3.67.

Dendrimer (12). To a solution of **11** (0.087 g, 0.0283 mmol) in DMF was added NaN_3 (0.00276 g, 0.0424 mmol). The resulting mixture was stirred at 80 °C for 2 days. After the mixture was cooled to room temperature, H_2O was added and the resulting solution was extracted three times with CH_2Cl_2. The combined organic layers were washed with H_2O and then brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give 0.082 g of the title compound as a yellow solid in 99% yield.

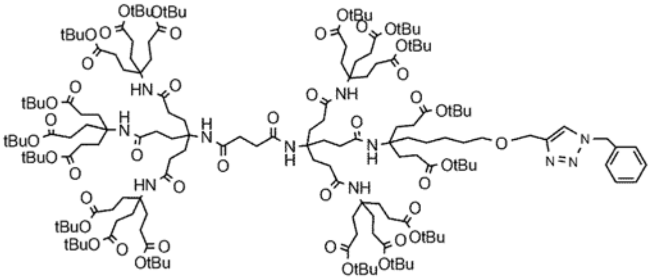


^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.20 (m, 4H), 1.40 (s, 153H), 1.61 (m, 4H), 1.92 (m, 46H), 2.18 (m, 46H), 2.38 (br s, 4H), 3.26 (t, *J* = 6.9 Hz, 2H), 6.25 (s, 1H), 6.36 (s, 5H), 7.30 (s, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 27.0, 28.1, 28.8, 29.2, 29.7, 31.4, 51.4, 57.3, 57.7, 80.4, 172.7, 172.9. LRMS MALDI-TOF: $[M + Na]^+$ calcd for

$C_{154}H_{267}N_{11}O_{42}Na$, 2966.9; found, 2966.2. Anal. calcd for $C_{154}H_{267}N_{11}O_{42}$: C, 62.81; H, 9.14; N, 5.23. found C, 62.50; H, 9.47; N, 4.98.

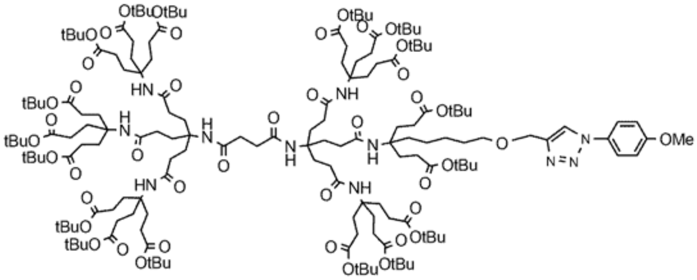
General procedure for the microwave-assisted 'click' chemistry. To a solution of an appropriate azide and acetylene in a 1:1 mixture of water and *tert*-BuOH (0.5 mL each) in a 10 mL glass vial equipped with a small magnetic stir bar were added sodium ascorbate (10 mol%) and $CuSO_4{\cdot}5H_2O$ (5 mol%). After the vial was tightly sealed with an aluminum/Teflon® crimp top, the mixture was irradiated for 10 minutes using the power-time control method at 100 W irradiation power and 100 °C as the shut off temperature. During the reaction, temperature in the glass vial increased but the shut off limit were not reached. After the completion of the reaction, the mixture was cooled down to room temperature and then diluted with CH_2Cl_2 (10 mL). The resulting solution was washed with water twice and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give a target compound.

Compound 13a. Acetylenyl dendrimer **10** (20.0 mg, 0.0067 mmol) was treated with benzyl azide[5] (0.89 mg, 0.0067 mmol) to give 20.2 mg of the compound **13a** as a yellowish solid in 98% yield.



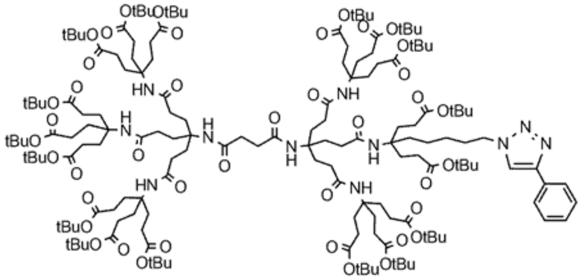
^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.26 (m, 4H), 1.42 (s, 153H), 1.64 (m, 4H), 1.94 (m, 46H), 2.19 (m, 46H), 2.39 (bs, 4H), 4.12 (t, *J* = 6.6 Hz, 2H), 5.54 (s, 2H), 6.25 (s, 1H), 6.40 (s, 5H), 7.20 (s, 1H), 7.24 (s, 1H), 7.32 (m, 2H), 7.36 (m, 3H), 7.62 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 25.0, 25.7, 28.2, 28.7, 29.9, 31.6, 33.0, 34.0, 49.2, 54.3, 57.3, 57.7, 57.8, 80.4, 128.5, 129.1, 129.3, 137.0, 142.8, 157.3, 171.6, 172.5, 172.7, 172.8.

Compound 13b. Acetylenyl dendrimer **10** (25.0 mg, 0.0084 mmol) was treated with 4-methoxy phenyl azide[5] (1.25 mg, 0.0084 mmol) to give 24.7 mg of the compound **13b** as a yellowish solid in 95% yield.



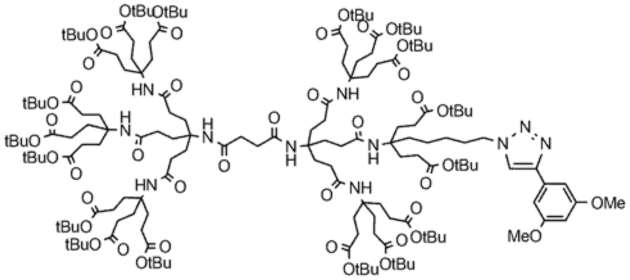
^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.10 (m, 4H), 1.39 (s, 153H), 1.67 (m, 4H), 1.94 (m, 46H), 2.17 (m, 46H), 2.39 (bs, 4H), 3.86 (s, 3H), 4.14 (t, *J* = 6.6 Hz, 2H), 5.34 (s, 2H), 6.39 (s, 5H), 6.47 (s, 1H), 7.01 (d, *J* = 6.9 Hz, 2H), 7.21 (s, 1H), 7.25 (s, 1H), 7.64 (d, *J* = 6.6 Hz, 2H), 8.06 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 25.0, 25.7, 28.2, 28.7, 29.9, 31.3, 31.6, 33.0, 34.0, 34.7, 49.2, 55.7, 57.3, 57.7, 57.8, 60.8, 68.4, 80.4, 114.7, 122.2, 134.5, 142.8, 153.7, 161.5, 171.6, 172.5, 172.7, 172.8.

Compound 13c. Azide dendrimer **12** (30.0 mg, 0.010 mmol) was treated with phenyl acetylene (1.03 mg, 0.010 mmol) to give 30.1 mg of the compound **13c** as a yellowish solid in 98% yield.



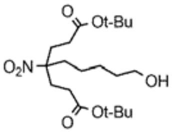
^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.26 (m, 4H), 1.42 (s, 153H), 1.69 (m, 4H), 1.95 (m, 46H), 2.16 (m, 46H), 2.38 (bs, 4H), 4.42 (t, *J* = 7.2 Hz, 2H), 5.30 (s, 2H), 6.37 (s, 3H), 6.41 (s, 3H), 7.20 (s, 1H), 7.25 (s, 1H), 7.33 (d, *J* = 7.1 Hz, 1H), 7.42 (t, *J* = 7.1 Hz, 2H), 7.85 (d, *J* = 7.1 Hz, 2H), 7.95 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 25.4, 25.9, 26.8, 28.2, 29.8, 31.4, 32.2, 47.7, 57.4, 57.7, 57.8, 80.4, 120.0, 125.6, 127.9, 128.4, 133.9, 147.5, 171.6, 172.5, 172.7. HRMS MALDI-TOF: $[M + Na]^+$ calcd for $C_{162}H_{273}N_{11}O_{42}Na$, 3067.9462; found, 3067.9694.

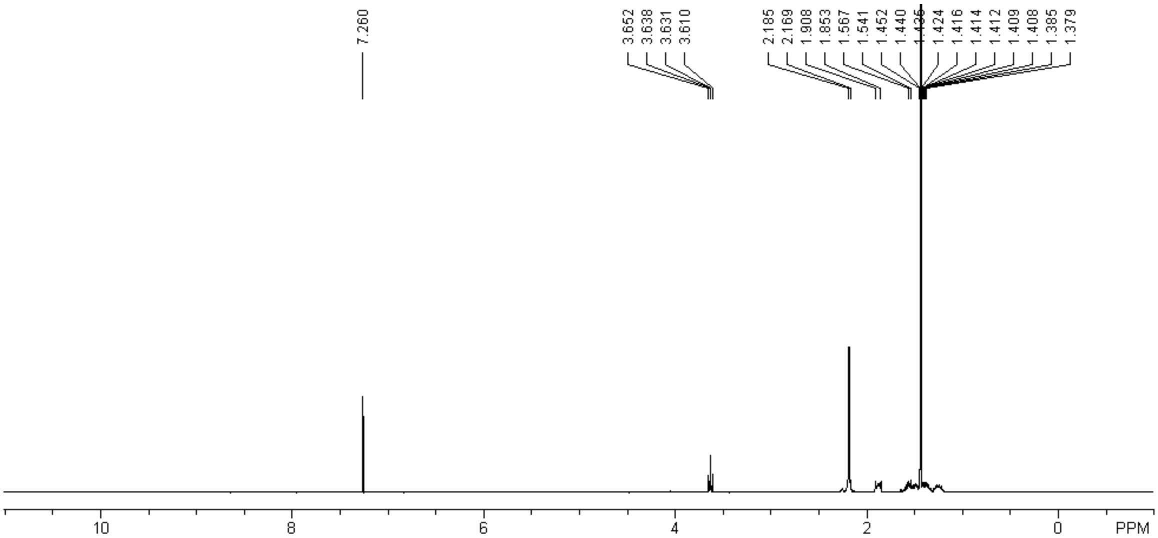
Compound 13d. Azide dendrimer **12** (30.0 mg, 0.010 mmol) was treated with 1-ethynyl-3,5-dimethoxy benzene (1.64 mg, 0.010 mmol) to give 30.5 mg of the compound **13d** as a yellowish solid in 97% yield.

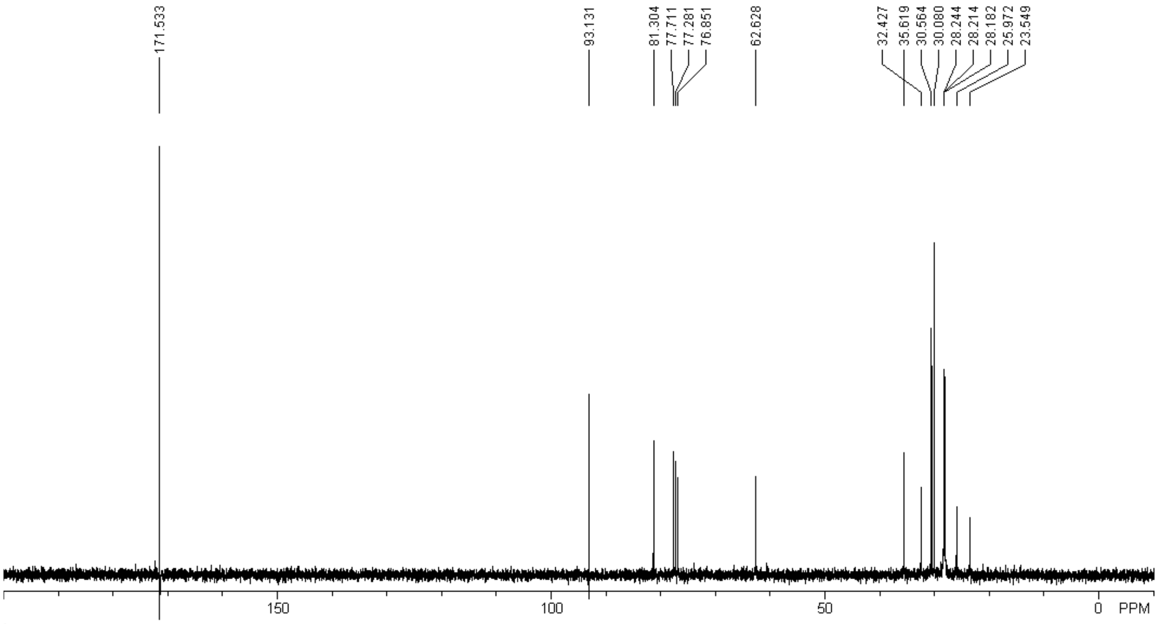


^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.32 (m, 4H), 1.41 (s, 153H), 1.65 (m, 4H), 1.94 (m, 46H), 2.18 (m, 46H), 2.37 (bs, 4H), 3.83 (s, 6H), 4.39 (t, *J* = 7.2 Hz, 2H), 6.36 (s, 3H), 6.39 (s, 3H), 6.43 (t, *J* = 2.2 Hz, 1H), 7.01 (d, *J* = 2.2 Hz, 2H), 7.20 (s, 1H), 7.28 (s, 1H), 7.87 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 25.0, 25.7, 26.8, 28.2, 29.9, 30.3, 31.4, 31.5, 33.0, 50.3, 55.5, 57.3, 57.7, 57.8, 80.4, 100.4, 103.6, 120.1, 132.4, 147.3, 160.9, 171.6, 172.5, 172.7. HRMS MALDI-TOF: $[M + Na]^+$ calcd for $C_{164}H_{277}N_{11}O_{44}Na$, 3127.9674; found, 3127.9781.

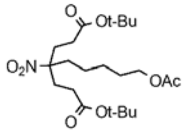
Di-*tert*-butyl 4-(5-hydroxypentyl)-4-nitroheptanedioate(1):

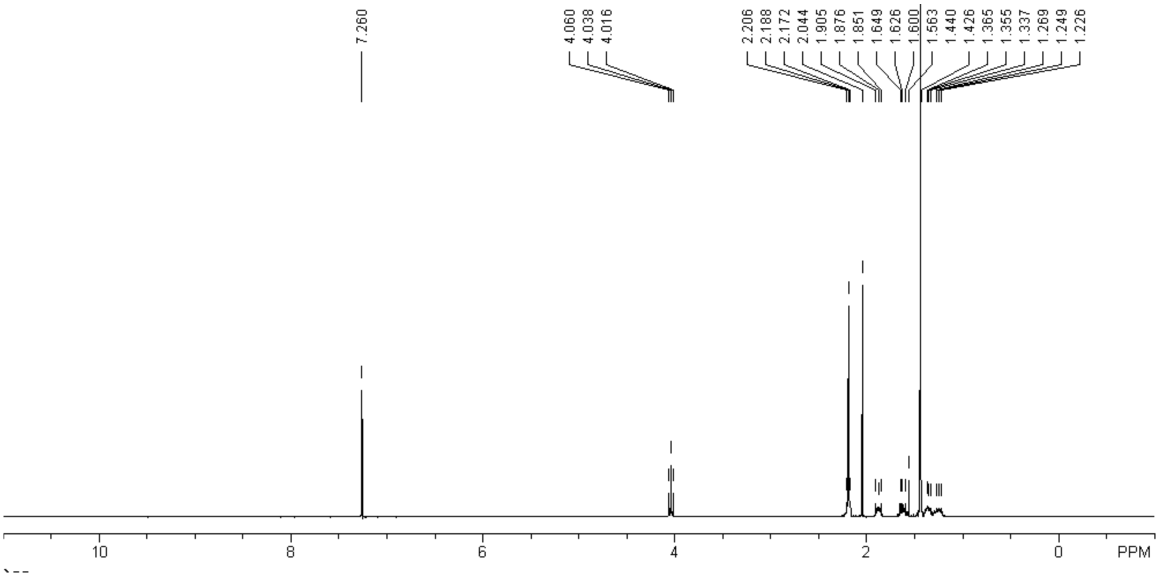


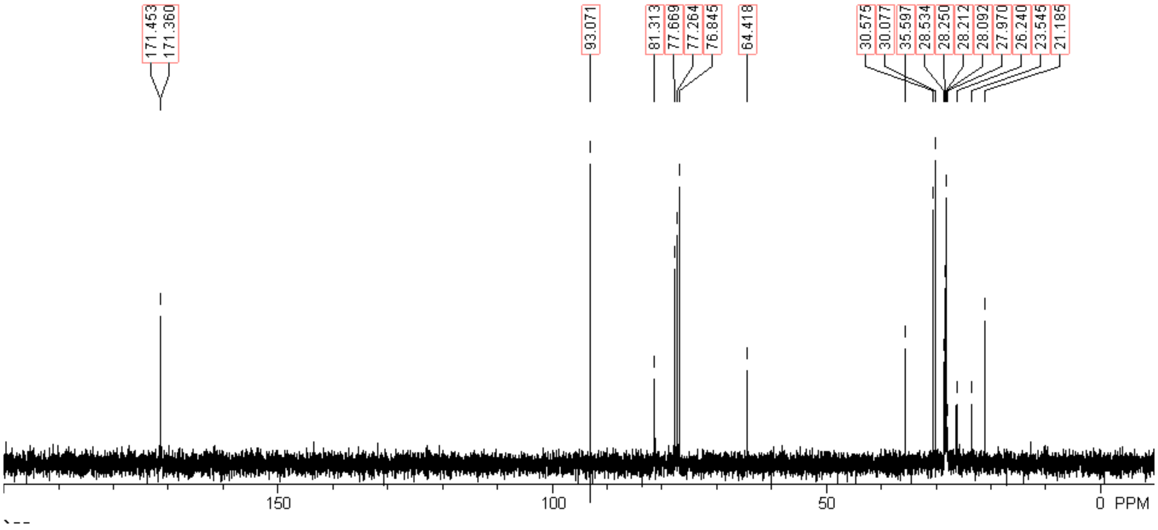




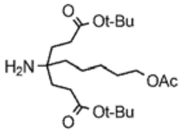
Di-*tert*-butyl 4-(5-acetoxypentyl)-4-nitroheptanedioate (2):

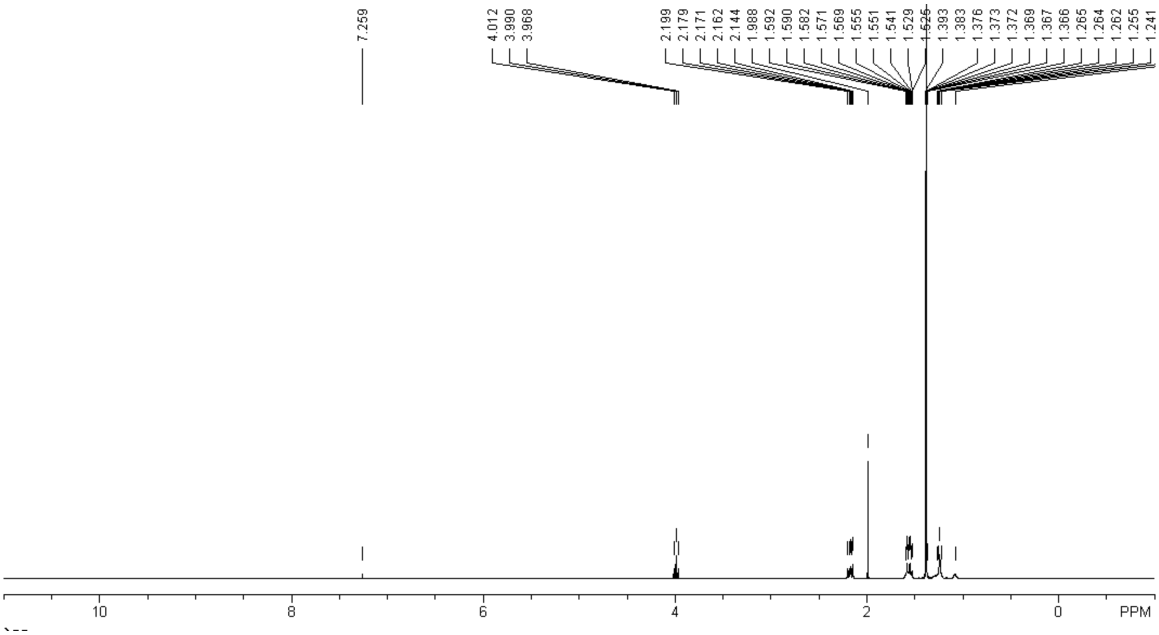


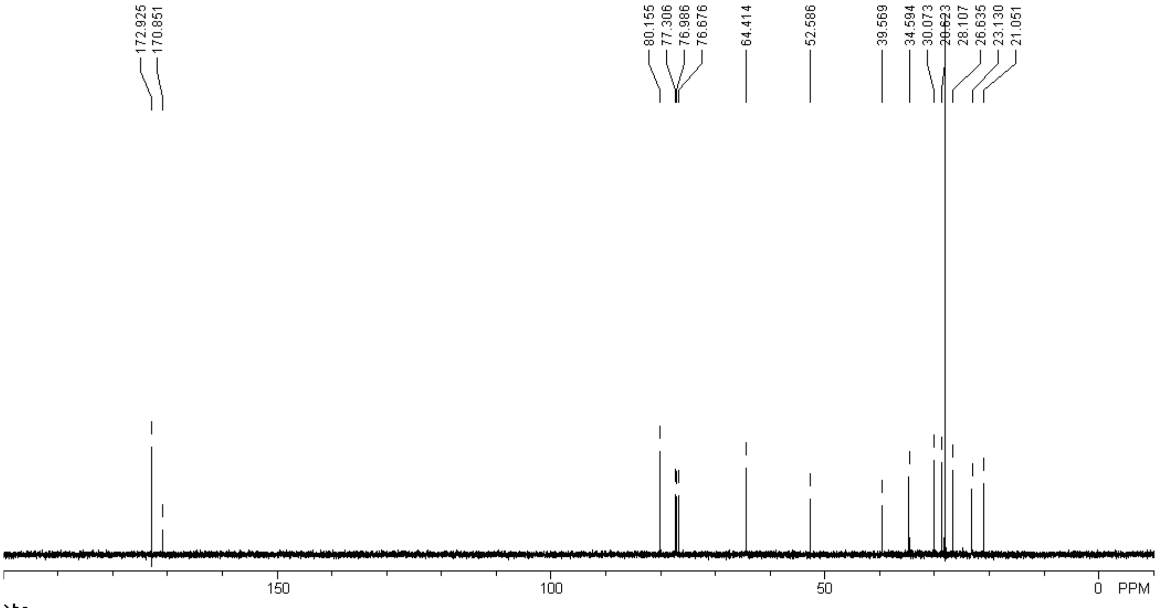




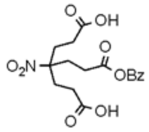
Di-*tert*-butyl 4-(5-acetoxypentyl)-4-aminoheptanedioate (3):

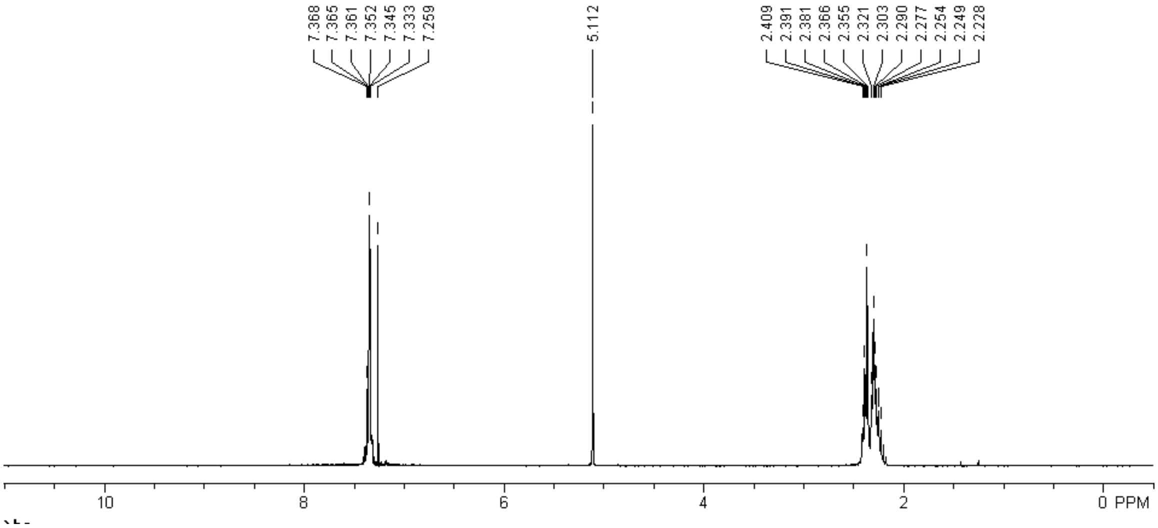


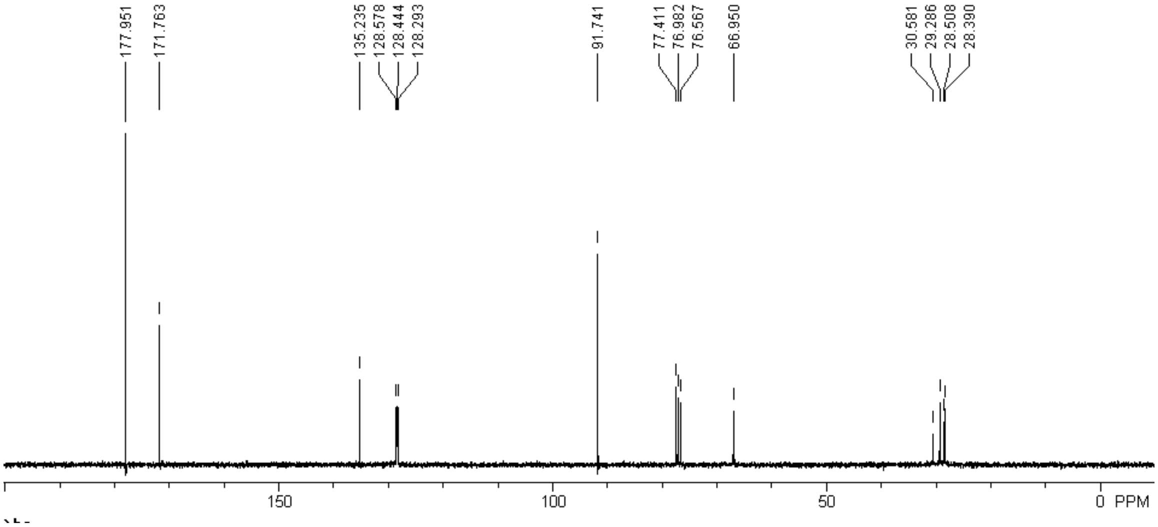




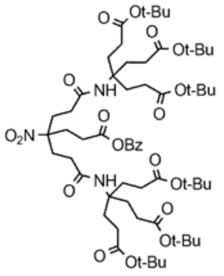
Nitro Dendron (4a):

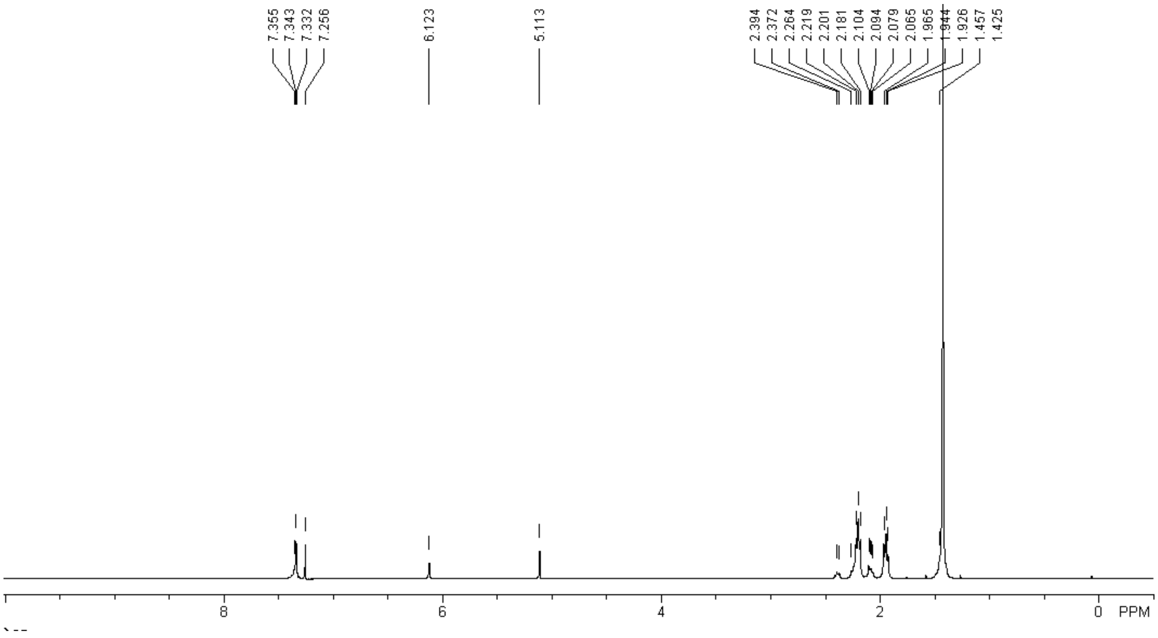


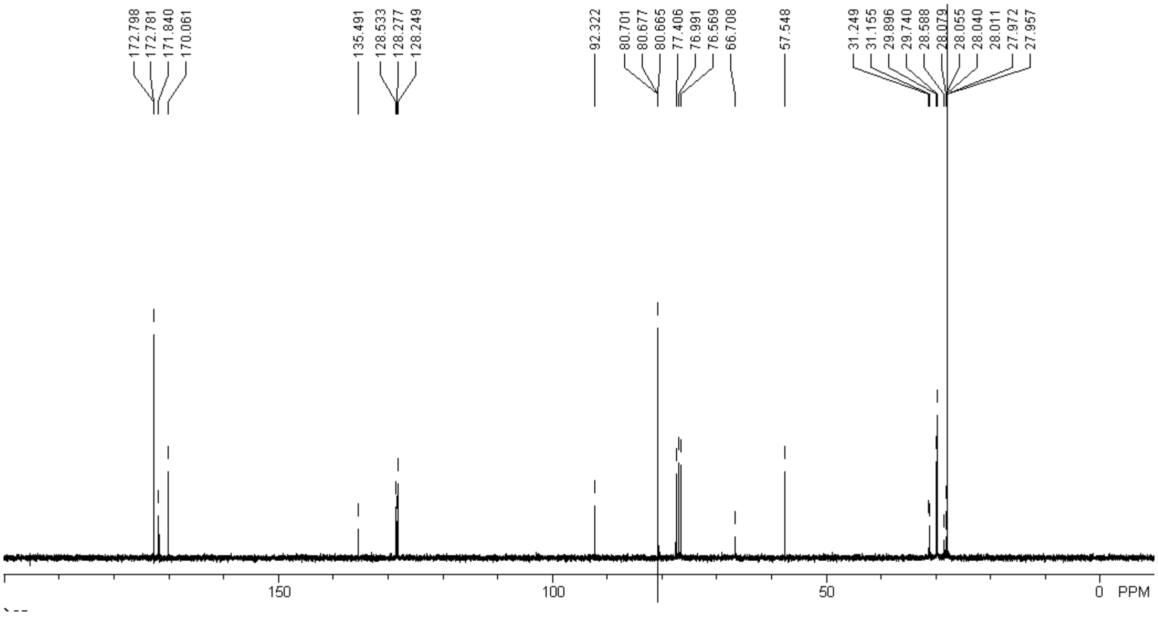




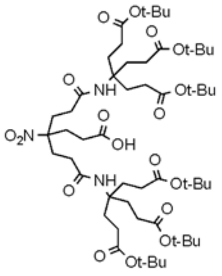
Nitro dendron (4):

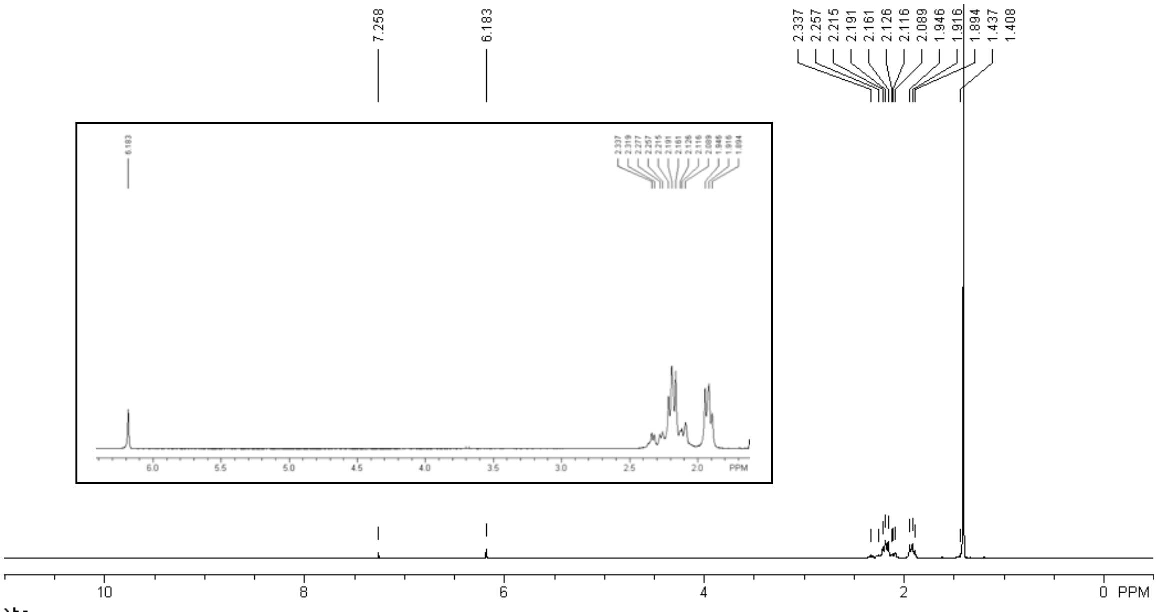


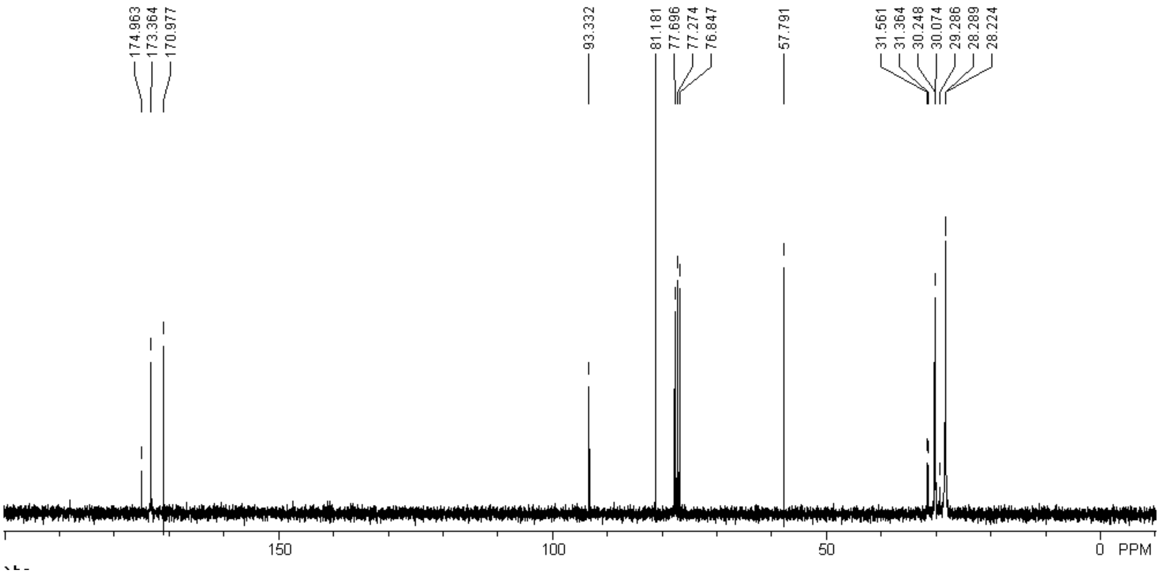




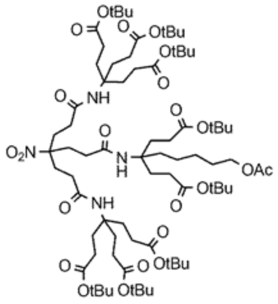
Nitro dendrons (5a):

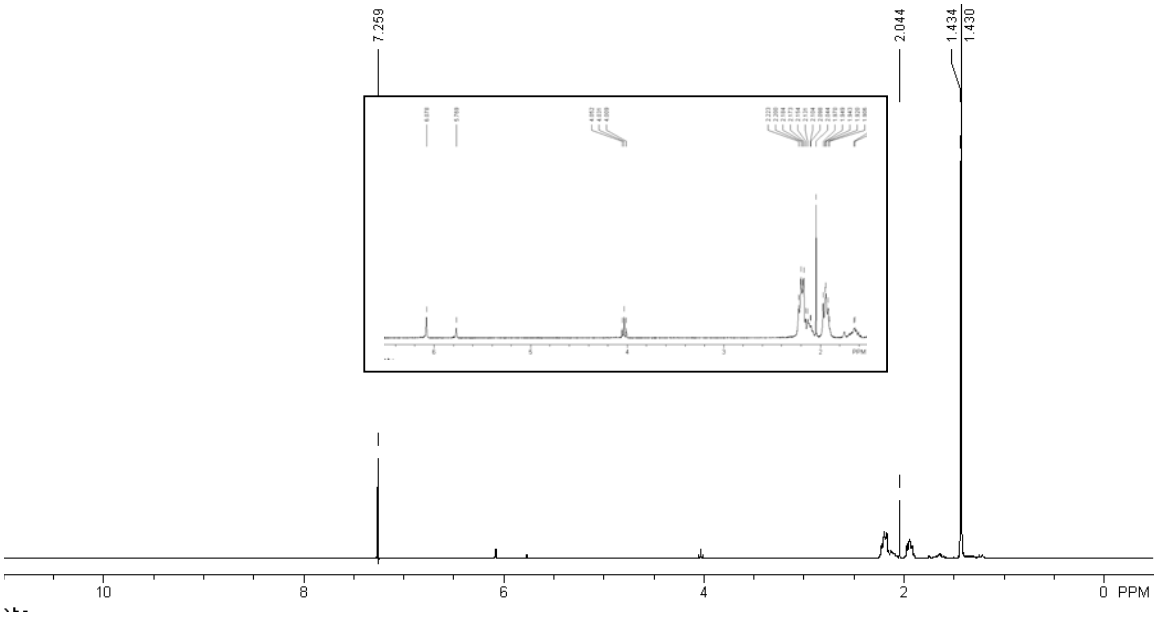


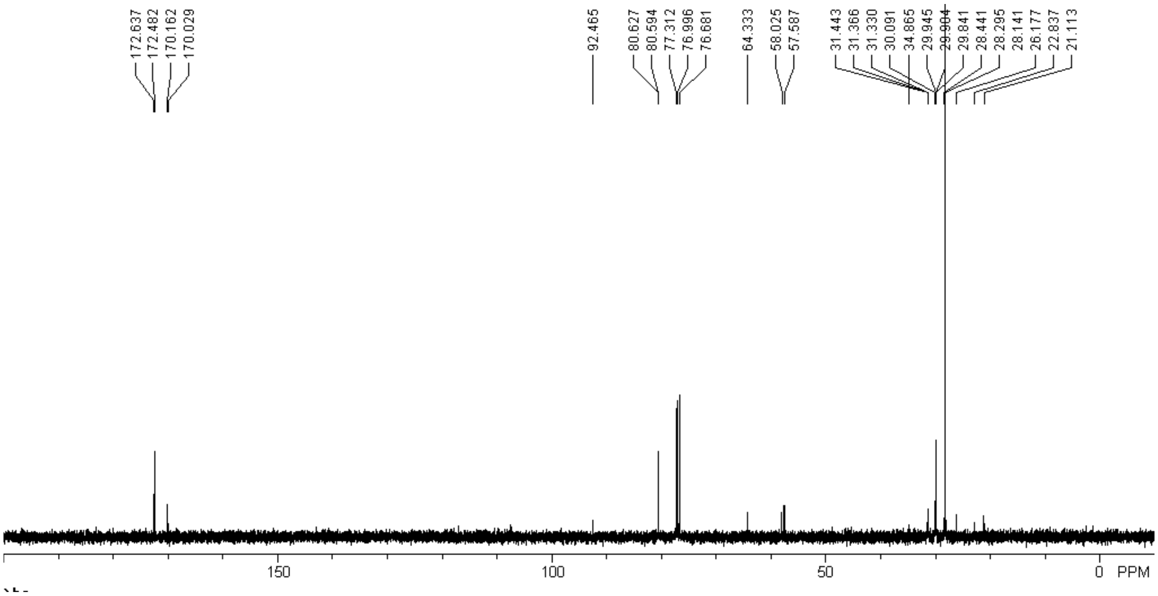




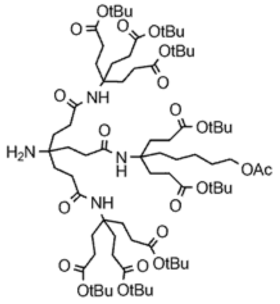
Nitro dendron (5):

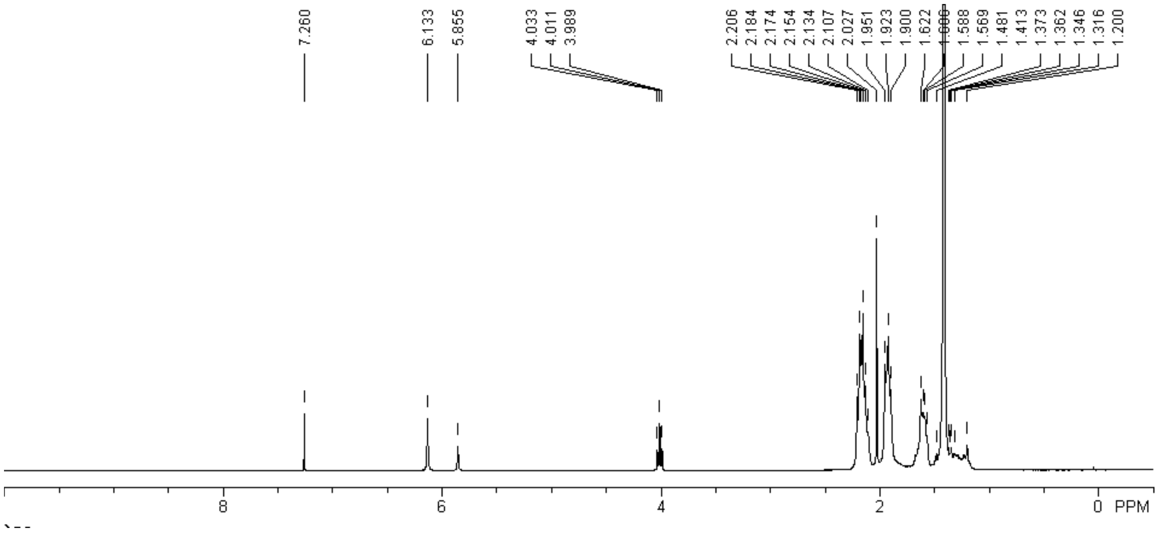


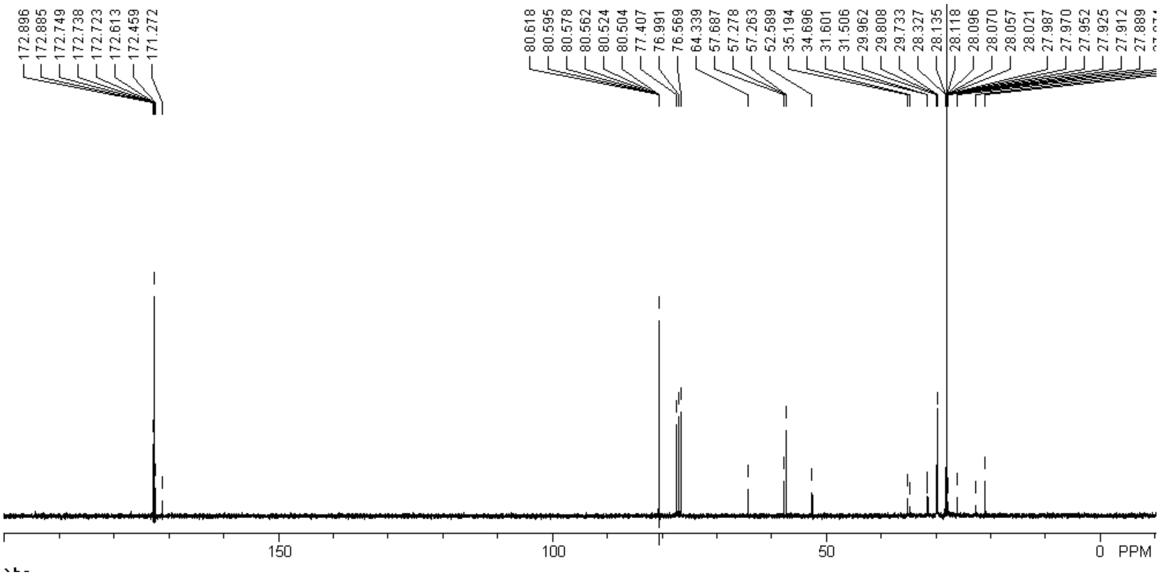




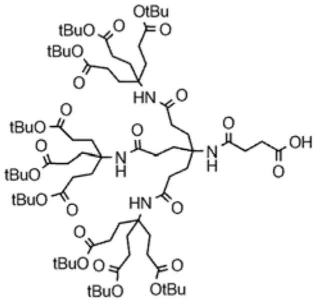
Amine dendron (6):

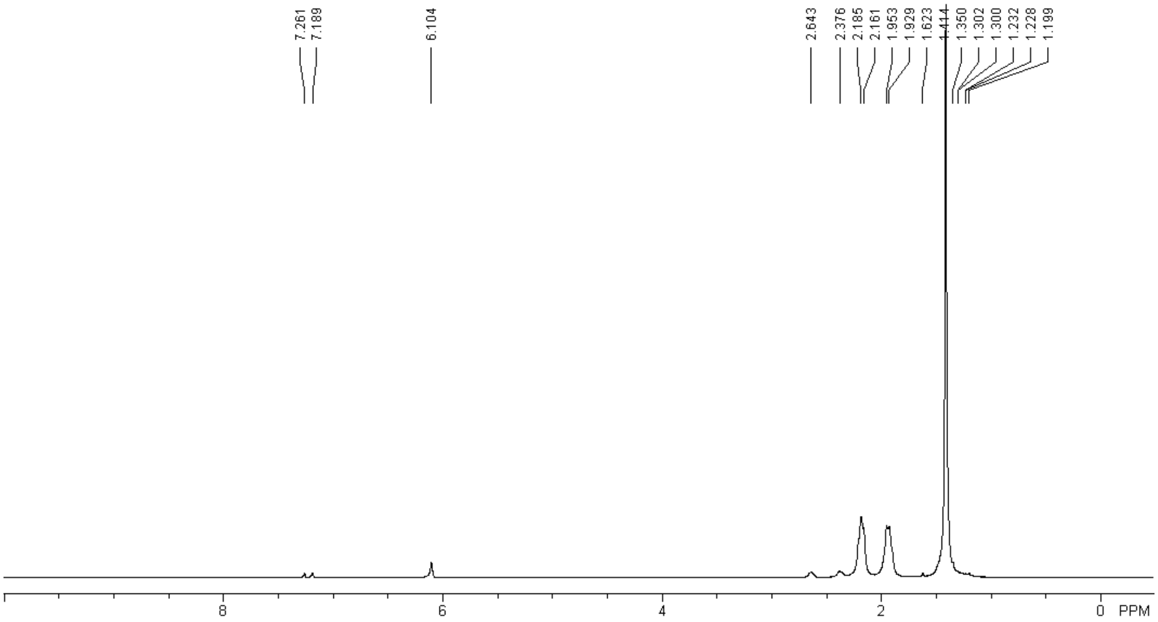


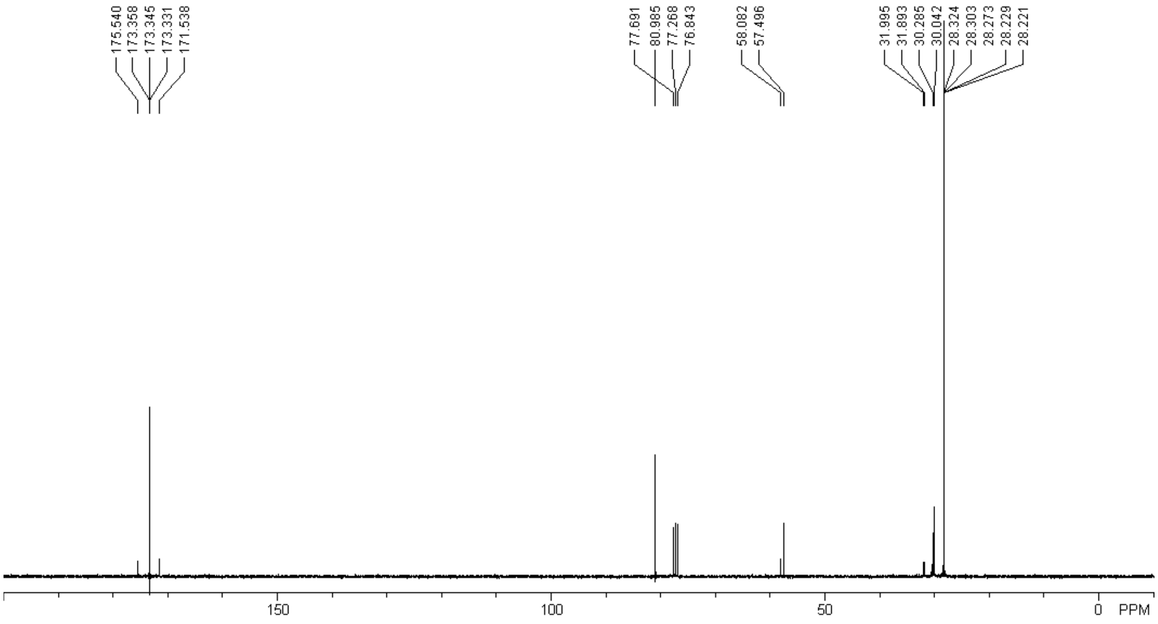




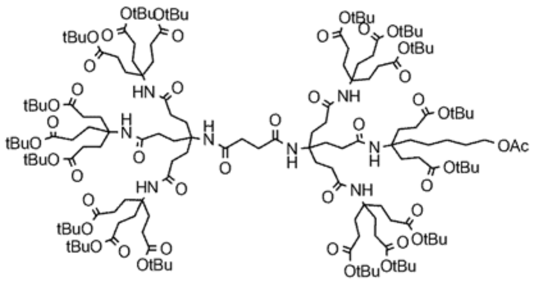
Hemisuccinimide (7):







Dendrimer (8):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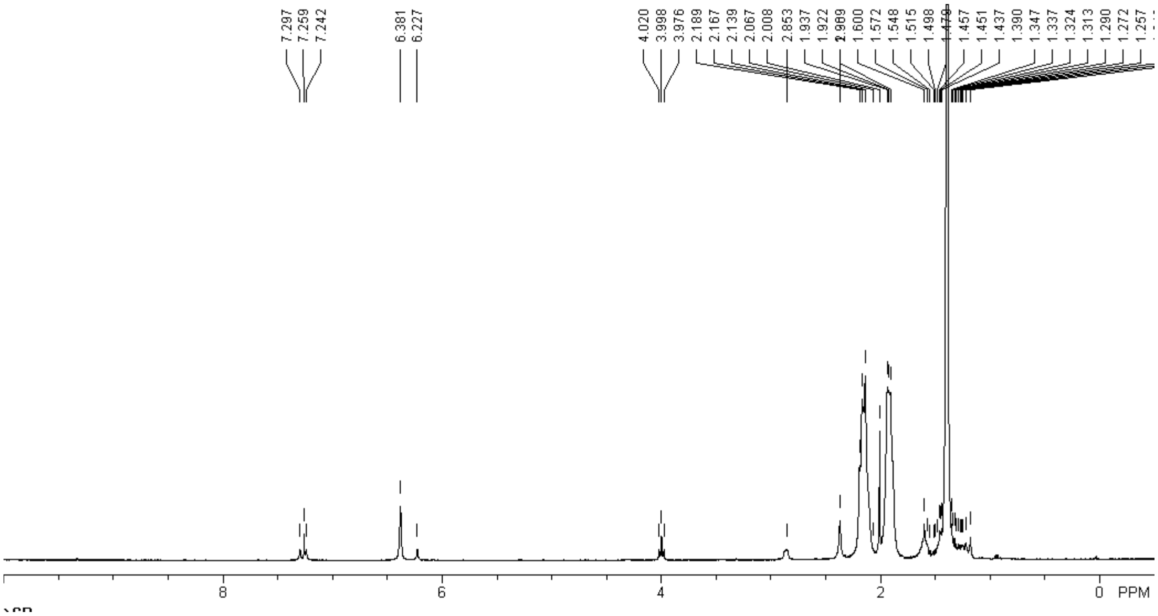
NH
H
N
O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1.548
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1.479
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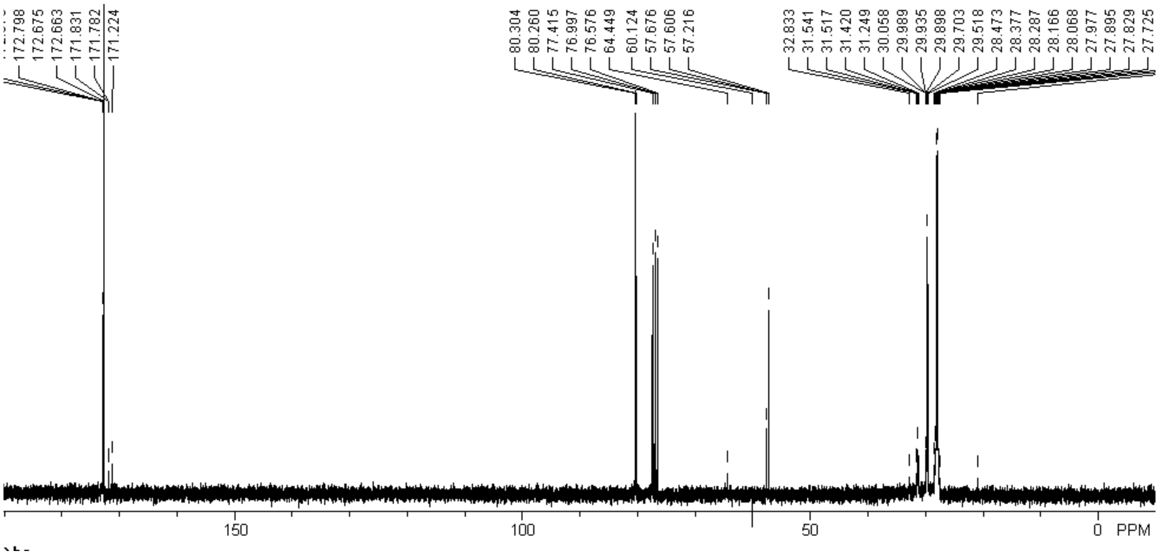
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57.606
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32.833
31.541
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30.058
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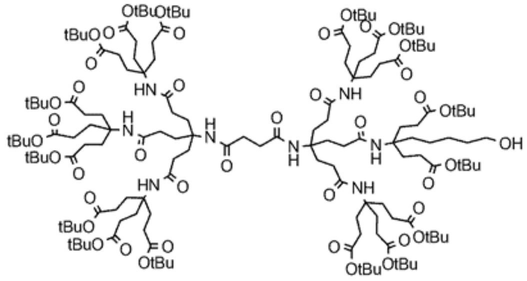
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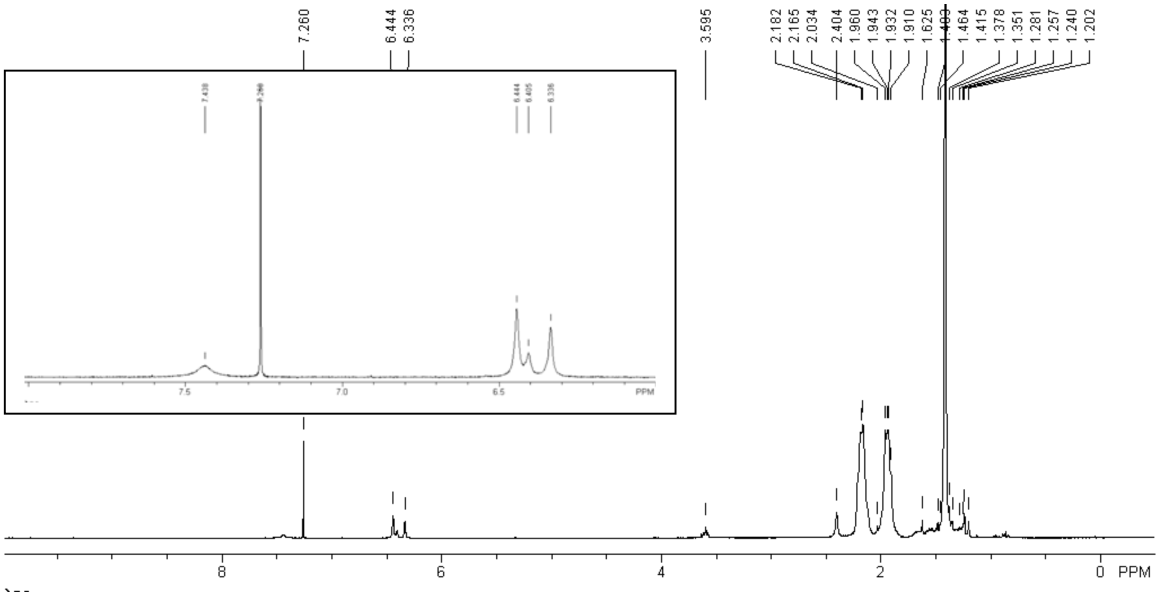
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1.257
1.240
1.202
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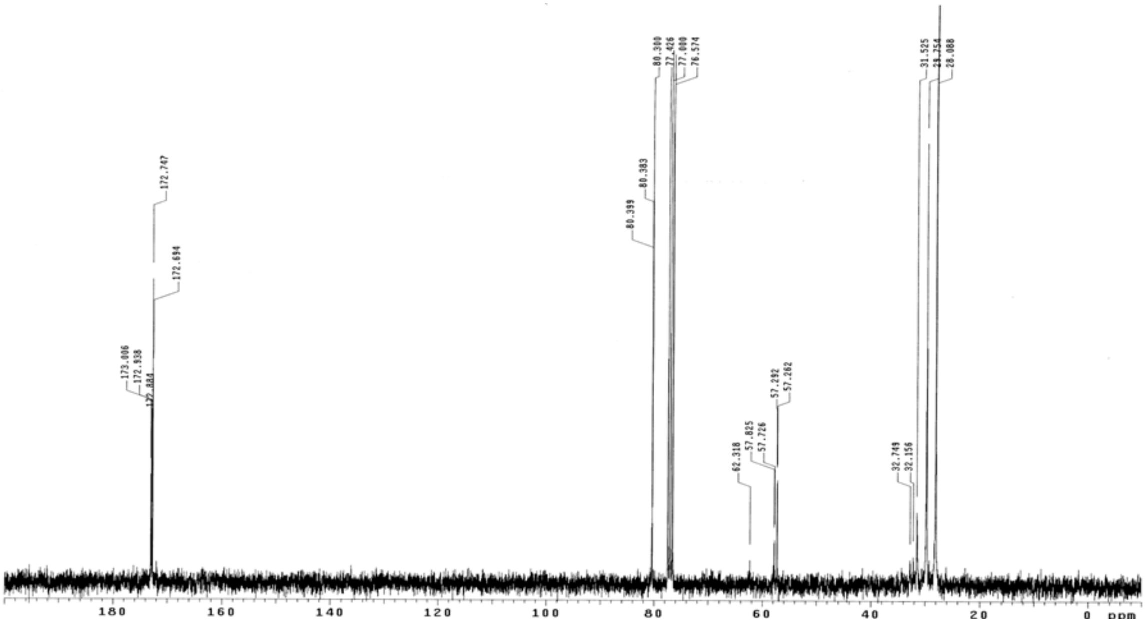
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57.282
57.262
32.749
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80
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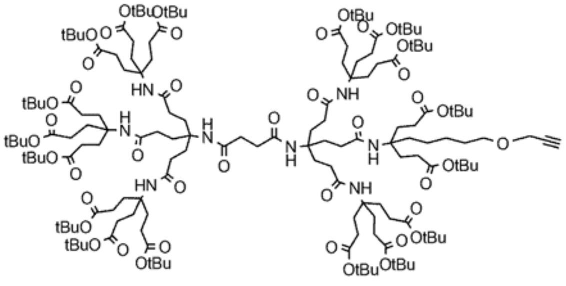

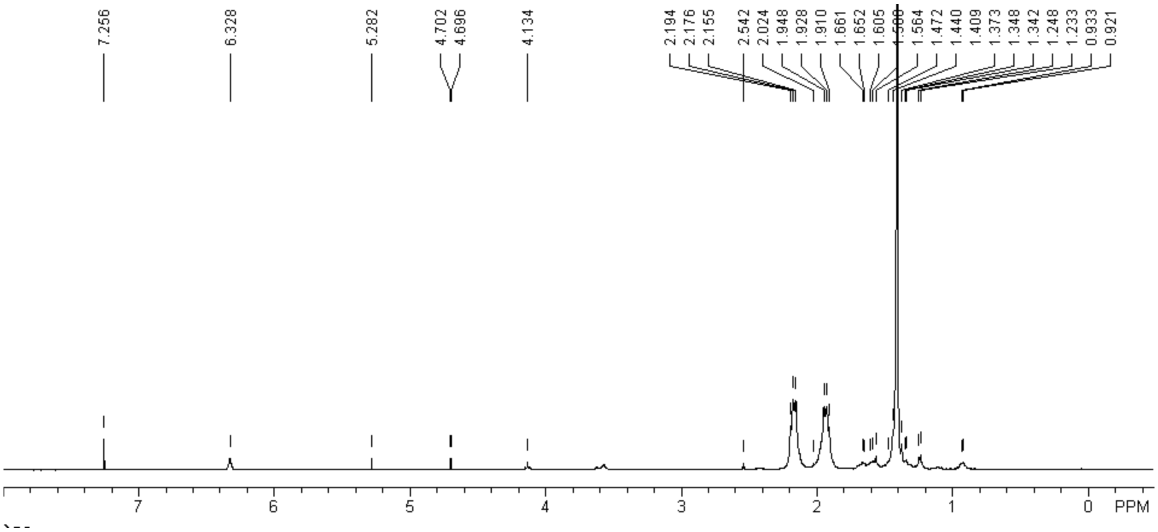

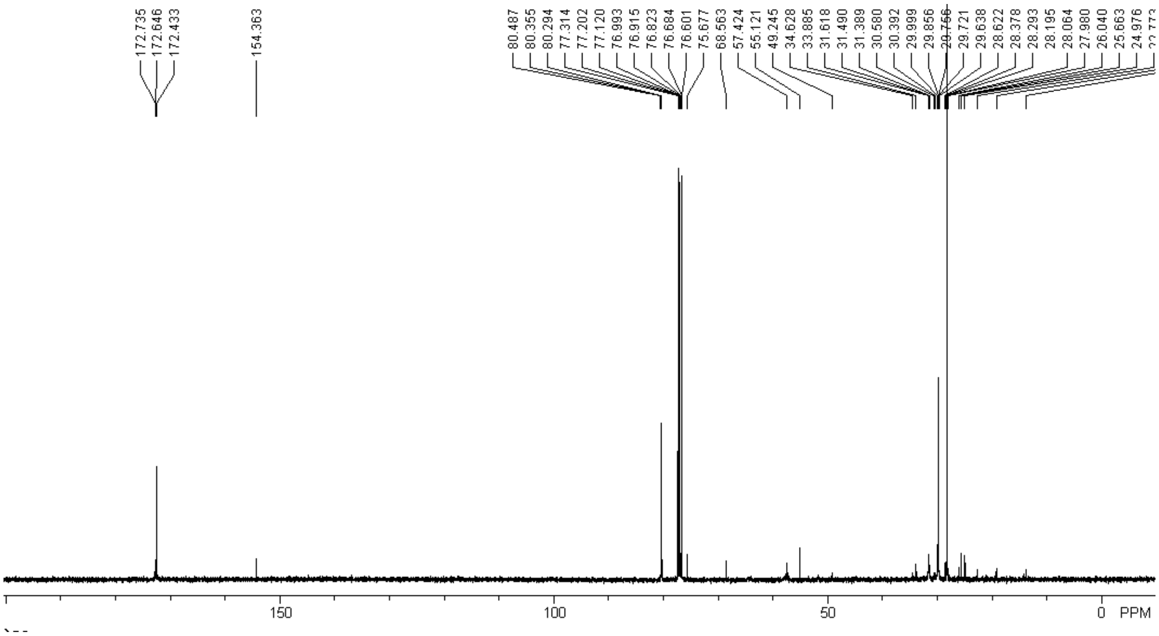

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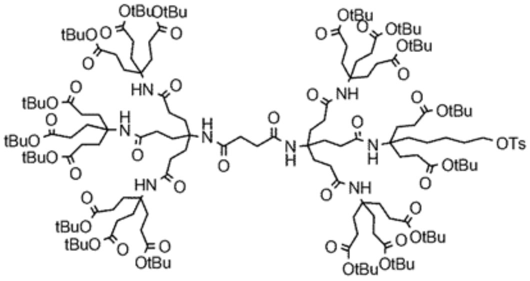

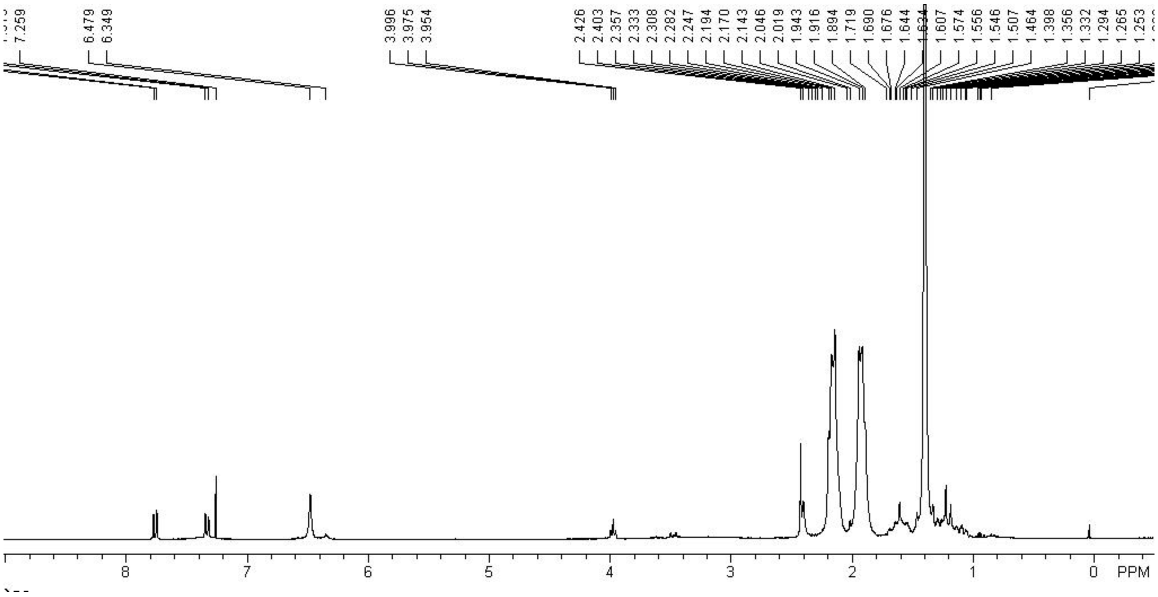

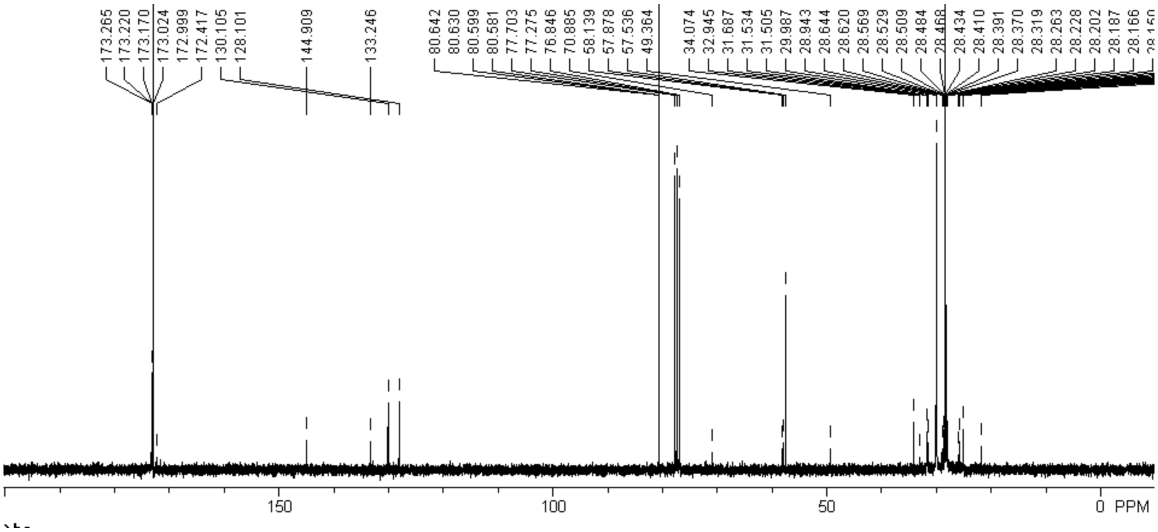

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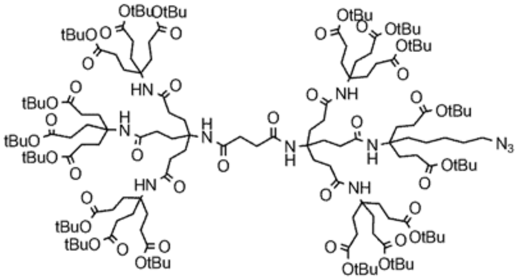
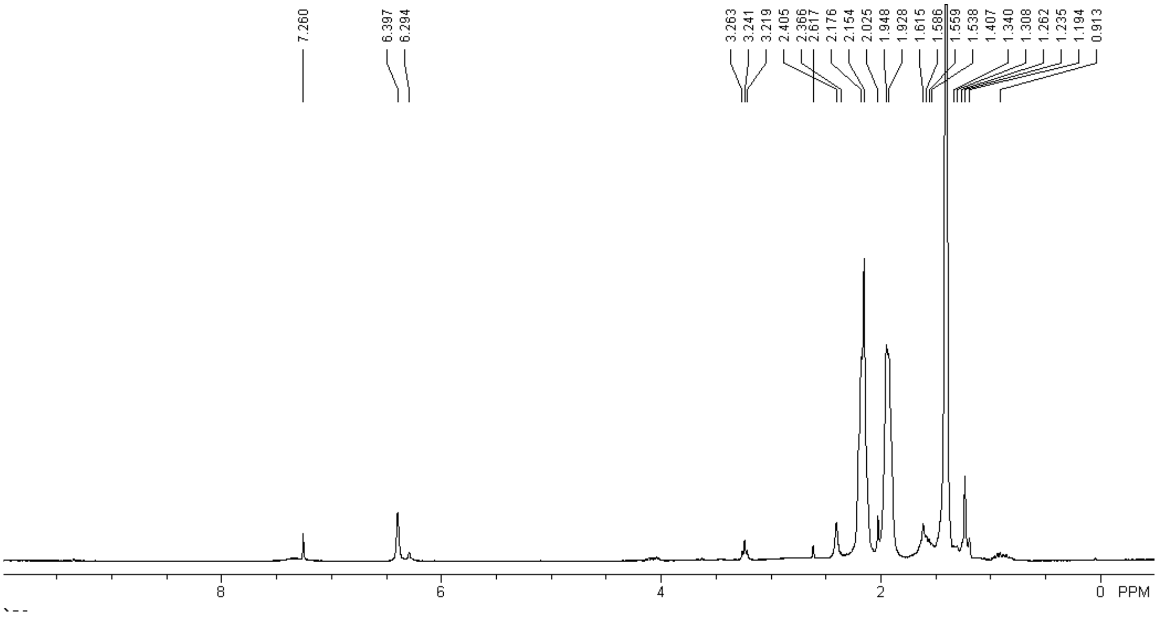
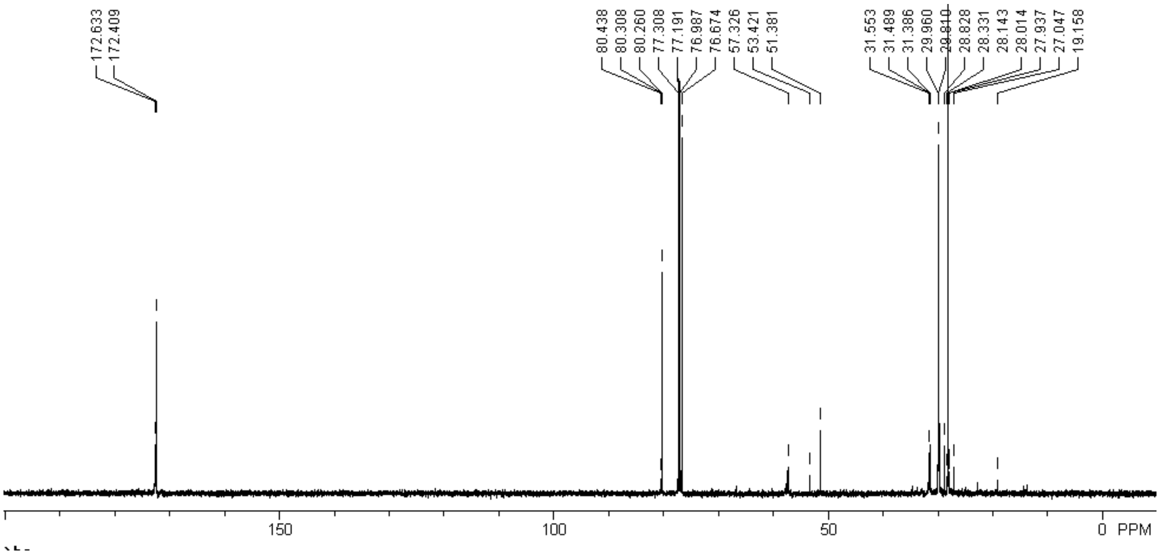
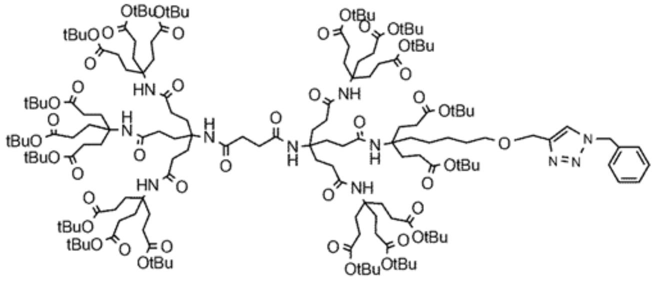
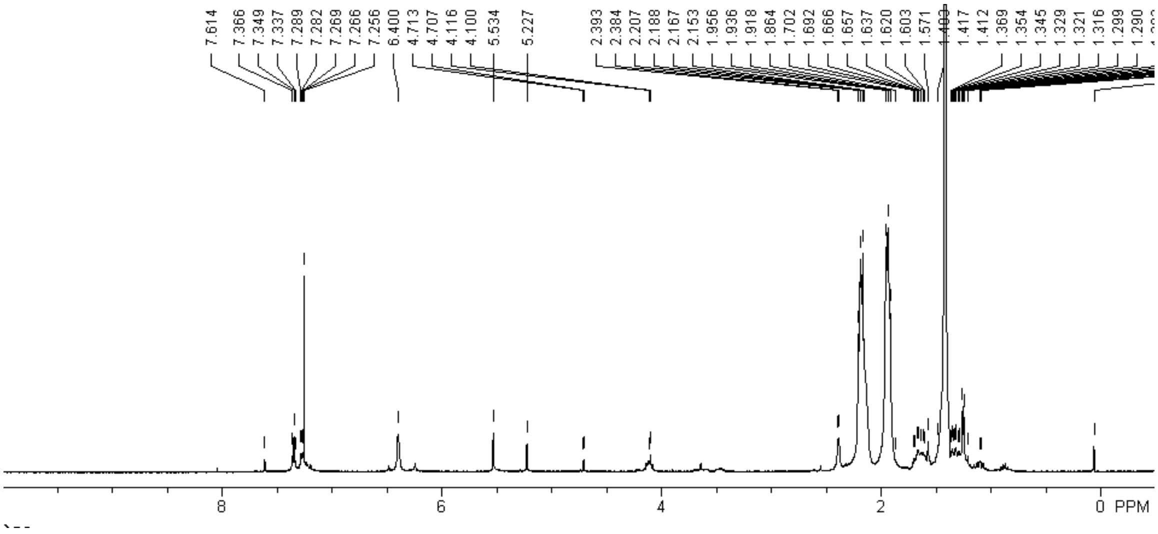


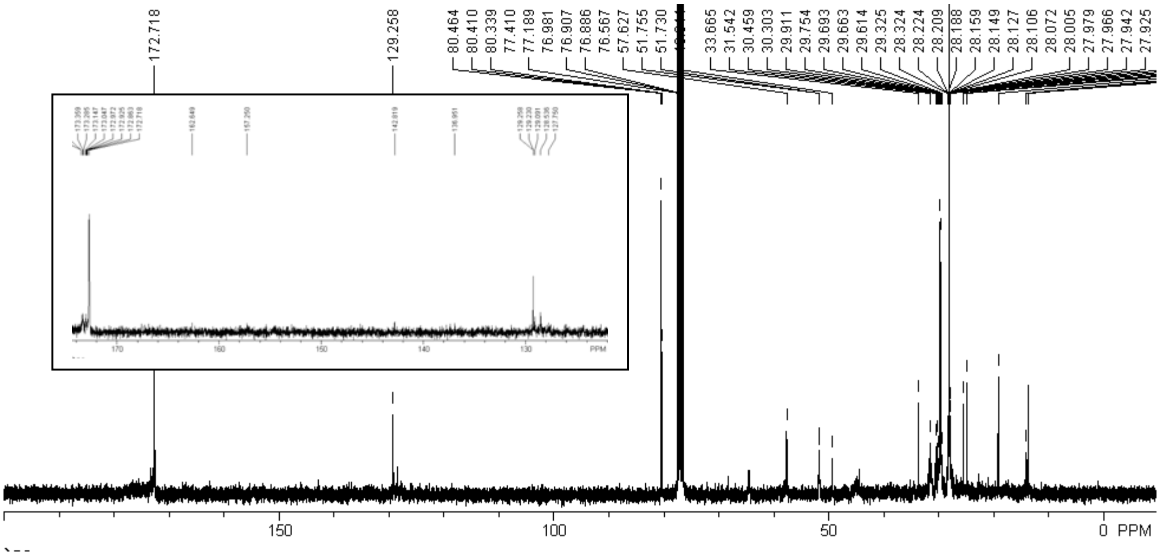




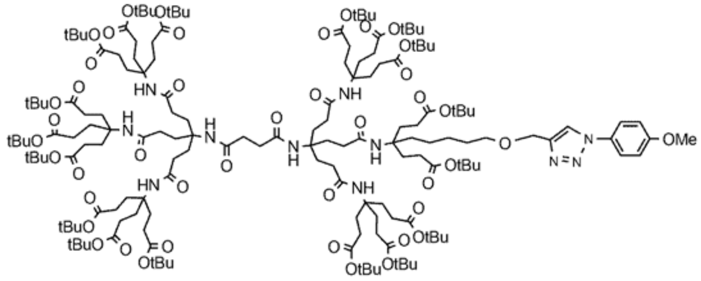
Compound (13a):

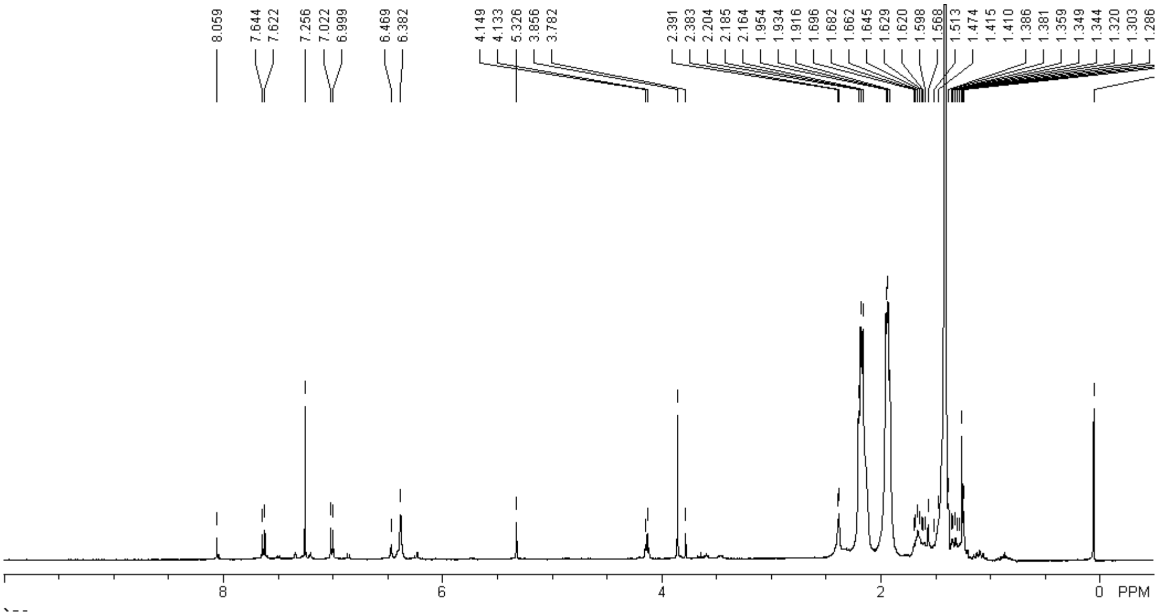


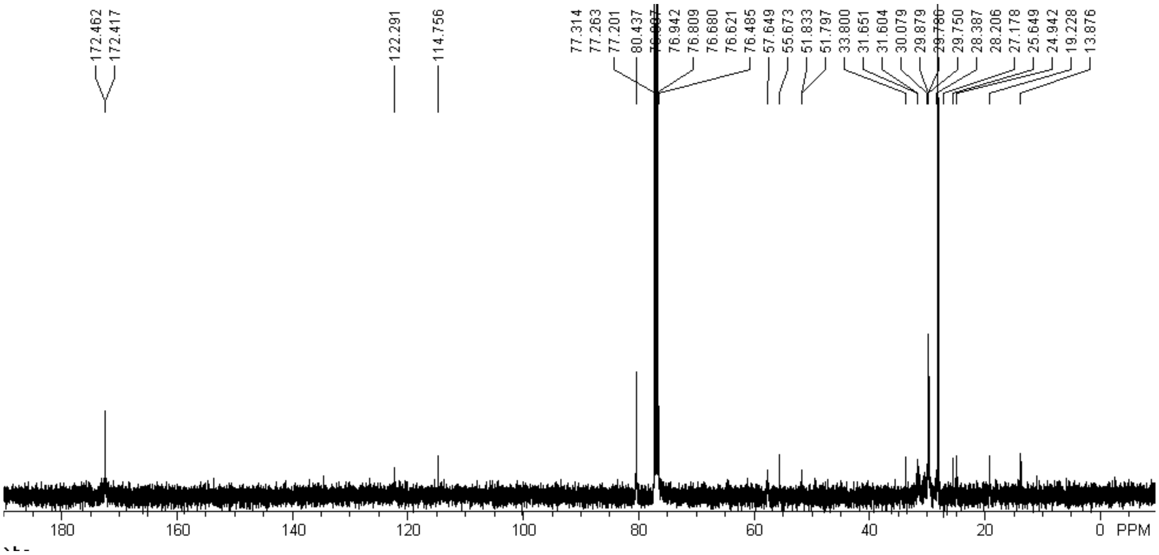




Compound (13b):







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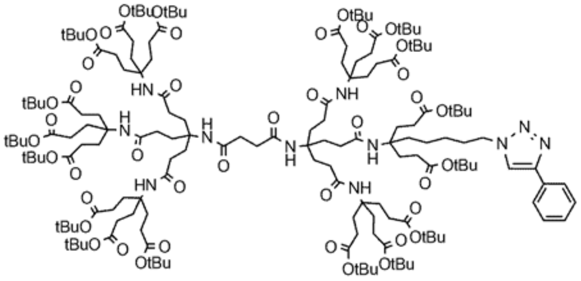

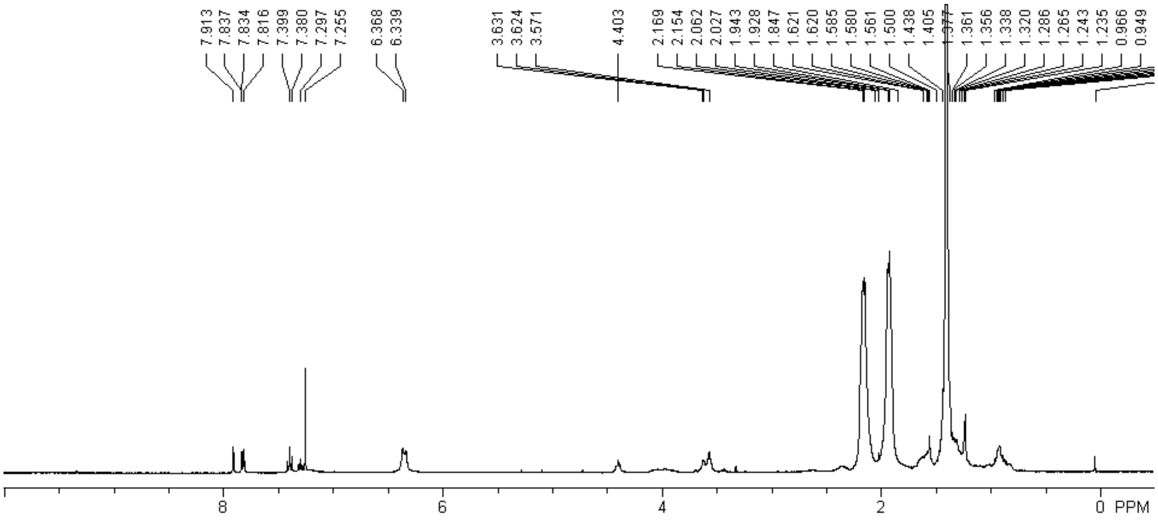

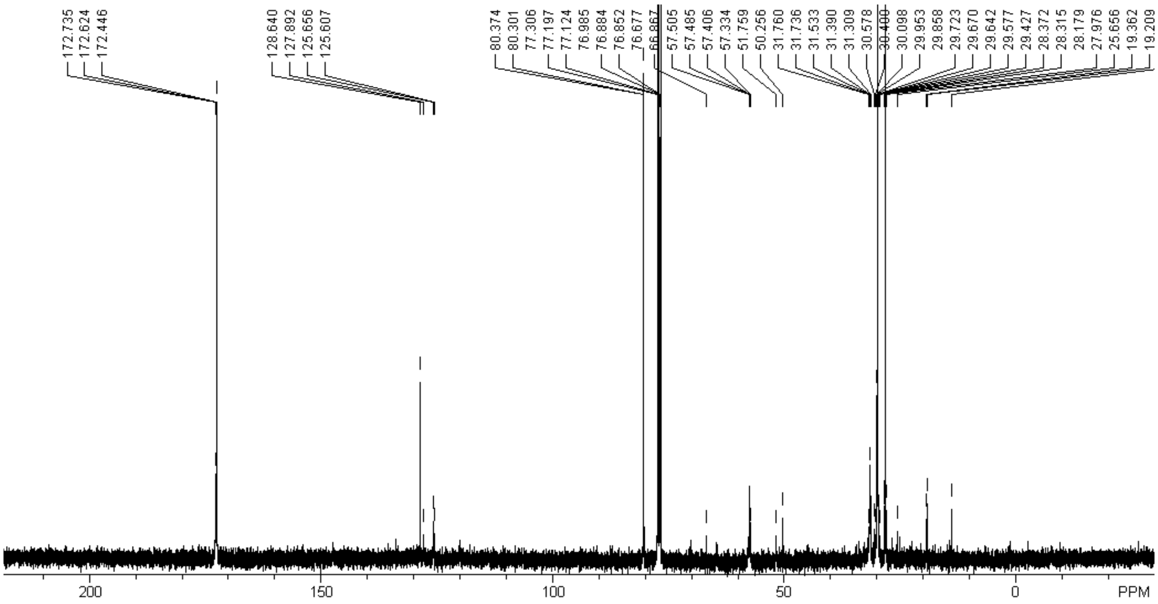

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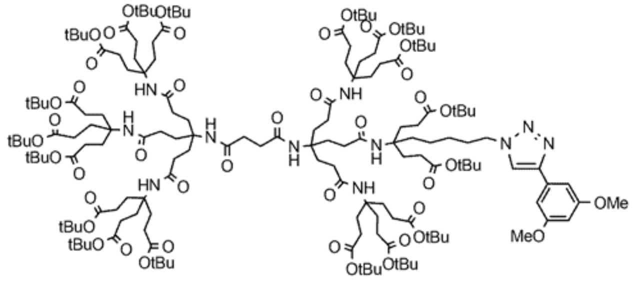

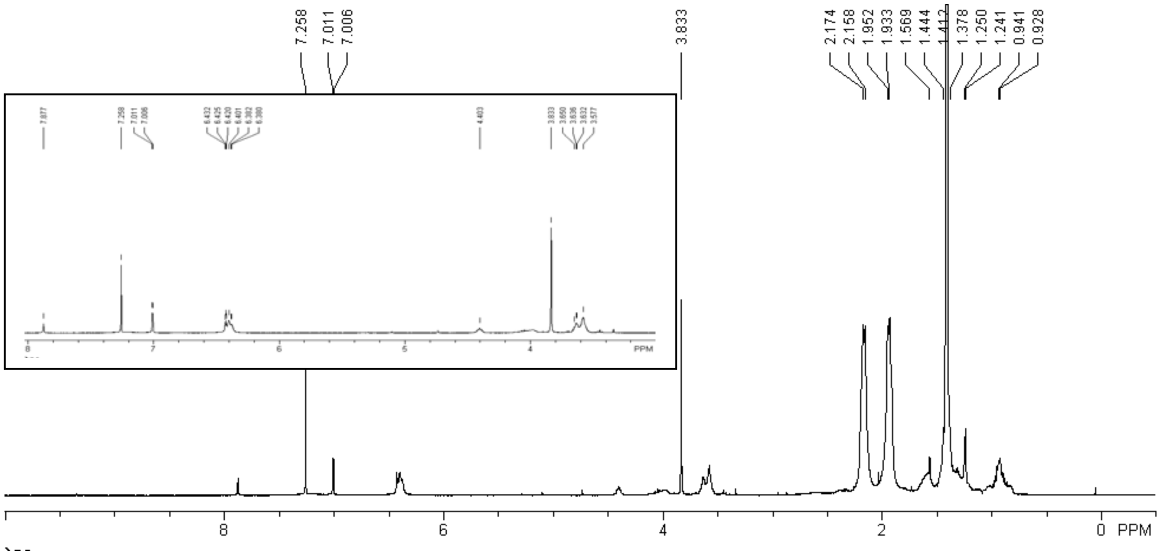

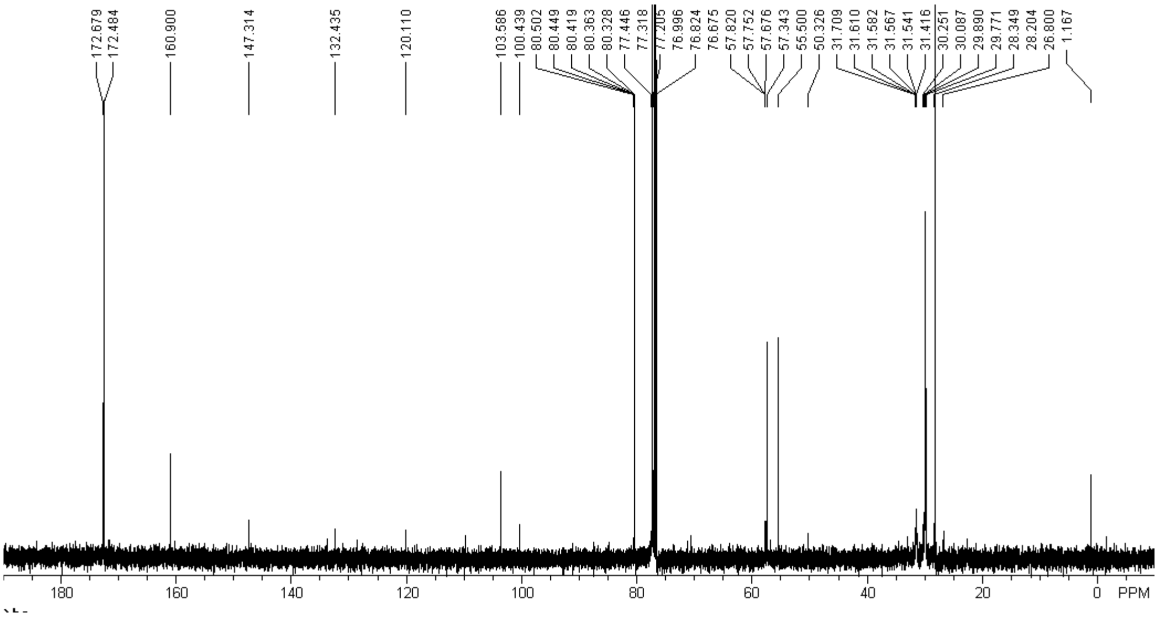

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