Supporting Information

Structural Effects on the Catalytic, Emulsifying and Recycling Properties of Chiral Amphiphilic Dendritic Organocatalysts

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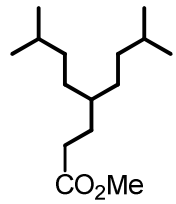
1. General Methods

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. *N*-bromosuccinimide was recrystallized from water. 4 Å molecular sieves were activated by heating at 150 °C in a glass oven under reduced pressure (0.1 mmHg) and stored under nitrogen (N_2). All solvents were analytical reagent grade except ethyl acetate (EtOAc) and hexane (technical grade) which were distilled before use. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl under N_2 prior to use. Toluene was distilled from sodium spheres under N_2. Dichloromethane was distilled from calcium hydride (CaH_2) under N_2. Dimethylformamide (DMF) was distilled from magnesium sulfate ($MgSO_4$) under reduced pressure (0.3 mmHg) and stored over 4 Å molecular sieves. Diisopropylethyl-amine (*i*-Pr_2NEt) and triethylamine (Et_3N) were distilled from potassium hydroxide (KOH) pellets under N_2 and stored over 4 Å molecular sieves. All non-aqueous reactions were conducted under dry N_2 atmosphere. All reactions were monitored by thin layer chromatography (TLC) performed on Merck pre-coated silica gel $60F_{254}$ plates, and compounds were visualized by irradiation with UV light and/or by treatment with a spray of 5% *w*/*v* dodecamolybdo-phosphoric acid in ethanol followed by subsequent heating. Flash chromatography was carried out on columns of Merck Keiselgel 60 (230–400 mesh) or Macherey Nagel Keiselgel 60M (230–400 mesh) silica gel.

Melting points were measured on Electrothermal IA9100 digital melting point apparatus and are uncorrected. Optical rotations $[\alpha]_D$ were measured at 589 nm at 20 °C on a Perkin Elmer 341 Polarimeter. Brüker Avance DPX300 NMR spectrometer was used to obtain ^1H (300 MHz) and ^{13}C (75.5 MHz) NMR spectra. All measurements were carried out at 20 °C in chloroform-*d* ($CDCl_3$) with residual $CHCl_3$ signal(s) as internal standard (δ_H = 7.26; δ_C = 77.16). Chemical shifts are reported in parts per million (ppm) in δ scale and coupling constants (*J*) are reported in hertz (Hz). Mass spectra were obtained on a ThermoFinnigan MAT 95XL double focusing sector mass spectrometer using chemical ionization (CI), electron impact (EI) or electron spray

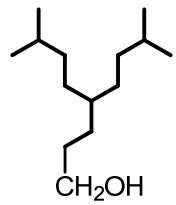
ionization (ESI) technique. The reported molecular mass (m/z) values are monoisotopic mass. Elemental analyses were carried out at MEDAC Ltd., Brunel Science Center, Cooper's Hill Lane, Egham, Surrey TW20 0JZ, United Kingdom.

2. Synthesis of G1–G3 Dendritic HC Intermediates and Dendritic Catalyst Di-S-G1



11

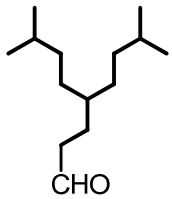
G1-saturated ester 11. A mixture of G1-unsaturated ester **8**[1] (4.75 g, 19.8 mmol) and 10% Pd/C (0.48 g) in EtOH (100 mL) was stirred at 25 °C under H_2 (1 atm) for 24 h. The mixture was filtered through a pad of Celite. After evaporation of solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc = 30/1) to give the product **11** (4.60 g, 96%) as a colorless oil. R_f 0.47 (hexane/EtOAc = 20/1). ^{1}H NMR: 0.87 (12 H, d, J = 6.6), 1.05–1.18 (4 H, m), 1.18–1.30 (5 H, m), 1.47 (2 H, nonet, J = 6.6), 1.53–1.64 (2 H, m), 2.13–2.33 (2 H, m), 3.67 (3 H, s). ^{13}C NMR: 22.7, 28.4, 28.7, 30.9, 31.6, 35.8, 37.4, 51.4, 174.5. MS (CI): 243 [$(M + H)^+$, 100%]. HRMS (CI) Calcd for $C_{15}H_{31}O_2$ $(M + H)^+$: 243.2319; Found: 243.2314. Anal. Calcd for $C_{15}H_{30}O_2$: C, 74.32; H, 12.47; Found: C, 74.38; H, 12.79.



14

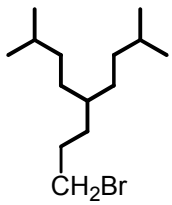
G1-L-OH 14. A solution of G1-saturated ester **11** (4.60 g, 19.0 mmol) in dry THF (50 mL) was added dropwise to a suspension of $LiAlH_4$ (1.53 g, 40.3 mmol) in dry THF (50 mL) at 0 °C over a period of 10 min. The mixture was allowed to warm to 25 °C and stirred for 1.5 h. It was poured into ice water and acidified to pH = 3 with HCl solution (1 M). The mixture was extracted with EtOAc (3 × 50 mL). The combined extracts were washed with saturated NaCl solution, dried ($MgSO_4$) and filtered. After evaporation of solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc = 10/1) to produce the product **14** (4.27 g, 99%) as a colorless oil. R_f 0.17 (hexane/EtOAc = 10/1).

^{1}H NMR: 0.87 (12 H, d, J = 6.6), 1.02–1.18 (4 H, m), 1.18–1.35 (8 H, m), 1.48 (2 H, nonet, J = 6.6), 1.54–1.62 (2 H, m), 3.63 (2 H, t, J = 6.6). ^{13}C NMR: 22.8, 28.5, 29.7, 30.0, 31.2, 35.9, 37.8, 63.3. MS (CI): 213 [$(M - H)^+$, 100%]. HRMS (CI) Calcd for $C_{14}H_{29}O$ $(M - H)^+$: 213.2213; Found: 213.2212. Anal. Calcd for $C_{14}H_{30}O$: C, 78.43; H, 14.10; Found: C, 78.74; H, 14.49.



17

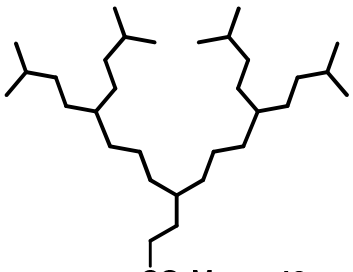
G1-L-CHO 17. A finely powdered mixture of PCC (0.23 g, 1.05 mmol) and silica gel (0.30 g) was added to a solution of G1-L-OH **14** (0.15 g, 0.70 mmol) in dry CH_2Cl_2 (5 mL) at 0 °C. After stirring at 25 °C for 2 h, Et_2O (30 mL) was added and stirred for 30 min. The mixture was filtered through a pad of Celite and silica gel. After evaporation of solvent under reduced pressure, the crude product **17** (0.15 g, 98%) was used immediately in the next step without further purification. R_f 0.66 (hexane/EtOAc = 10/1). ^{1}H NMR: 0.86 (12 H, d, J = 6.6), 1.00–1.17 (4 H, m), 1.17–1.36 (5 H, m), 1.47 (2 H, nonet, J = 6.6), 1.52–1.65 (2 H, m), 2.38 (2 H, dt, J = 1.2 and 7.2), 9.77 (1 H, t, J = 1.8). ^{13}C NMR: 22.8, 25.7, 28.5, 31.0, 35.8, 37.5, 41.5, 203.3.



5

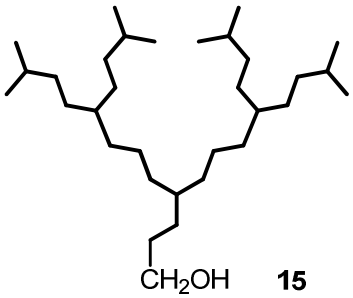
G1-L-Br 5. Powdered PPh_3 (13.1 g, 49.9 mmol) and NBS (8.17 g, 45.9 mmol) were added sequentially to a solution of G1-L-OH **14** (8.94 g, 41.7 mmol) in dry CH_2Cl_2 (80 mL) at −30 °C. The mixture was allowed to warm to 25 °C and stirred for 12 h. The byproduct Ph_3PO was precipitated by addition of hexane (80 mL) and filtered through a pad of Celite and silica gel. After evaporation of filtrate under reduced pressure, the residue was purified by flash column chromatography on silica gel (eluent: hexane) to yield the product **5** (11.2 g, 97%) as a colorless oil. R_f 0.78 (hexane). ^{1}H NMR: 0.88 (12 H, d, J = 6.6), 1.05–1.18 (4 H, m), 1.18–1.32 (5 H, m),

1.32–1.42 (2 H, m), 1.48 (2 H, nonet, J = 6.6), 1.73–1.92 (2 H, m), 3.38 (2 H, t, J = 6.9). ^{13}C NMR: 22.8, 28.5, 30.3, 31.3, 32.3, 34.5, 36.0, 37.4. MS (CI): 275 {[M(^{79}Br) – H]$^+$, 79%}, 277 {[M(^{81}Br) – H]$^+$, 77%}. HRMS (CI) Calcd for $C_{14}H_{28}{}^{79}Br$ (M – H)$^+$: 275.1369; Found: 275.1375. Anal. Calcd for $C_{14}H_{29}Br$: C, 60.64; H, 10.54; Found: C, 60.81; H, 10.67.



12

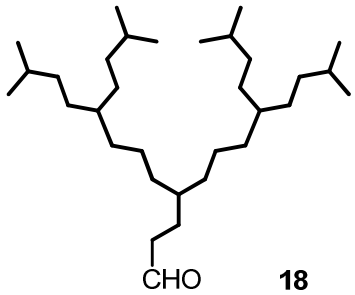
G2-saturated ester 12. A mixture of G2-unsaturated ester **9**[1] (1.92 g, 3.90 mmol) and 10% Pd/C (0.20 g) in EtOH (50 mL) was stirred at 25 °C under H_2 (1 atm) for 24 h. The mixture was filtered through a pad of Celite. After evaporation of solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel (eluent: hexane/$CHCl_3$ = 30/1 gradient to 3/1) to give the product **12** (1.82 g, 94%) as a colorless oil. R_f 0.28 (hexane/$CHCl_3$ = 30/1). ^{1}H NMR: 0.87 (24 H, d, J = 6.6), 1.02–1.38 (31 H, m), 1.47 (4 H, nonet, J = 6.6), 1.54–1.66 (2 H, m), 2.21–2.35 (2 H, m), 3.66 (3 H, s). ^{13}C NMR: 22.9, 23.7, 28.6, 28.9, 31.4, 31.7, 33.8, 34.2, 36.1, 37.1, 37.9, 51.6, 174.8. MS (ESI): 517 [(M + Na)$^+$, 100%]. HRMS (ESI) Calcd for $C_{33}H_{66}O_2Na$ (M + Na)$^+$: 517.4955; Found: 517.4963. Anal. Calcd for $C_{33}H_{66}O_2$: C, 80.09; H, 13.44; Found: C, 79.75; H, 13.26.



15

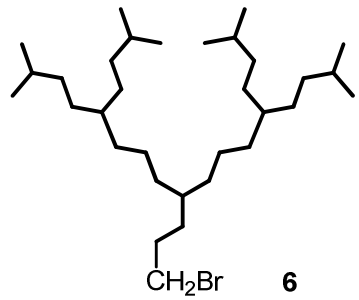
G2-L-OH 15. Powdered $LiAlH_4$ (38.5 mg, 1.01 mmol) was added to a solution of G2-saturated ester **12** (0.25 g, 0.51 mmol) in dry THF (5 mL) at 0 °C. It was allowed to warm to 25 °C and

stirred for 12 h. The mixture was poured into ice water, acidified to pH = 3 with HCl solution (1 M) and extracted with EtOAc (3 × 10 mL). The combined extracts were washed with saturated NaCl solution, dried ($MgSO_4$) and filtered. After evaporation of solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc = 30/1 gradient to 20/1) to produce the product **15** (0.21 g, 90%) as a colorless oil. R_f 0.25 (hexane/EtOAc = 10/1). ^{1}H NMR: 0.87 (24 H, d, J = 6.6), 1.03–1.36 (33 H, m), 1.47 (4 H, nonet, J = 6.6), 1.52–1.65 (3 H, m), 3.63 (2 H, t, J = 6.6). ^{13}C NMR: 22.9, 23.8, 28.6, 29.8, 30.2, 31.4, 34.15, 34.21, 36.1, 37.3, 37.9, 63.7. MS (CI): 465 [$(M - H)^+$, 100%]. HRMS (CI) Calcd for $C_{32}H_{65}O$ $(M - H)^+$: 465.5030; Found: 465.5029. Anal. Calcd for $C_{32}H_{66}O$: C, 82.32; H, 14.25; Found: C, 82.28; H, 14.65.



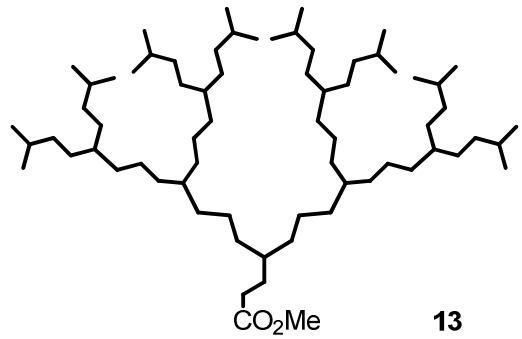
18

G2-L-CHO 18. A finely powdered mixture of PCC (0.24 g, 1.11 mmol) and silica gel (0.30 g) was added to a solution of G2-L-OH **15** (0.35 g, 0.75 mmol) in dry CH_2Cl_2 (10 mL) at 0 °C. After stirring at 25 °C for 4 h, Et_2O (50 mL) was added and stirred for 30 min. The mixture was filtered through a pad of Celite and silica gel. After evaporation of solvent under reduced pressure, the crude product **18** (0.35 g, 99%) was used immediately in the next step without further purification. R_f 0.55 (hexane/EtOAc = 10/1). ^{1}H NMR: 0.86 (24 H, d, J = 6.6), 0.98–1.38 (31 H, m), 1.46 (4 H, nonet, J = 6.6), 1.52–1.65 (2 H, m), 2.38 (2 H, dt, J = 1.5 and 7.2), 9.75 (1 H, t, J = 1.8). ^{13}C NMR: 22.9, 23.7, 25.8, 28.5, 31.4, 33.9, 34.1, 36.1, 37.0, 37.9, 41.5, 202.8.



6

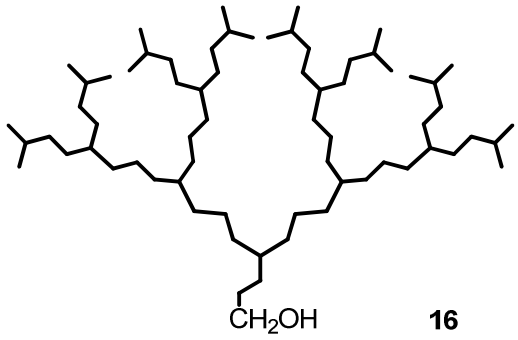
G2-L-Br 6. Powdered PPh_3 (1.12 g, 4.27 mmol) and NBS (0.70 g, 3.93 mmol) were added sequentially to a solution of G2-L-OH **15** (1.67 g, 3.58 mmol) in dry CH_2Cl_2 (20 mL) at −30 °C. The mixture was allowed to warm to 25 °C and stirred for 12 h. The byproduct Ph_3PO was precipitated by the addition of hexane (50 mL) and filtered through a pad of Celite and silica gel. After evaporation of solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel (eluent: hexane) to yield the product **6** (1.76 g, 93%) as a colorless oil. R_f 0.84 (hexane). ^{1}H NMR: 0.88 (24 H, d, J = 6.6), 1.04–1.30 (30 H, m), 1.30–1.43 (3 H, m), 1.48 (4 H, nonet, J = 6.6), 1.76–1.91 (2 H, m), 3.39 (2 H, t, J = 6.9). ^{13}C NMR: 22.9, 23.8, 28.6, 30.3, 31.4, 32.4, 34.1, 34.2, 34.6, 36.1, 36.9, 37.9. MS (CI): 527 {[M(^{79}Br) – H]$^+$, 37%}, 529 {[M(^{81}Br) – H]$^+$, 36%}. HRMS (CI) Calcd for $C_{32}H_{64}{}^{79}Br$ (M – H)$^+$: 527.4186; Found: 527.4180. Anal. Calcd for $C_{32}H_{65}Br$: C, 72.55; H, 12.37; Found: C, 72.33; H, 12.38.



13

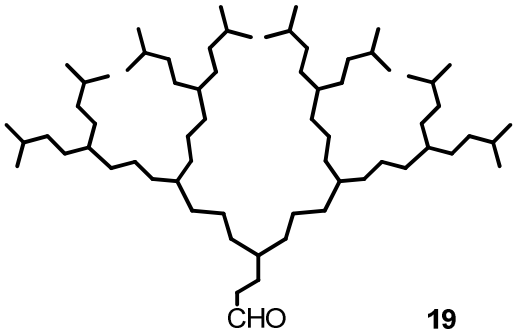
G3-saturated ester 13. A mixture of G3-unsaturated ester **10**[1] (2.62 g, 2.63 mmol) and 10% Pd/C (0.26 g) in EtOH/THF (1/1, 100 mL) was stirred at 25 °C under H_2 (1 atm) for 12 h. The mixture was filtered through a pad of Celite and solvent was evaporated under reduced pressure to give the product **13** (2.60 g, 99%) as a colorless oil. R_f 0.40 (hexane/EtOAc = 50/1). ^{1}H NMR: 0.88 (48 H, d, J = 6.6), 1.00–1.37 (75 H, m), 1.48 (8 H, nonet, J = 6.6), 1.55–1.67 (2 H, m),

2.21–2.36 (2 H, m), 3.66 (3 H, s). ^{13}C NMR: 23.0, 23.8, 28.6, 28.9, 31.4, 31.7, 34.0, 34.3, 34.4, 36.1, 37.3, 37.5, 37.9, 51.5, 174.6. MS (ESI): 1022 [(M + Na)$^+$, 100%]. HRMS (ESI) Calcd for $C_{69}H_{138}O_2Na$ (M + Na)$^+$: 1022.0589; Found: 1022.0592. Anal. Calcd for $C_{69}H_{138}O_2$: C, 82.89; H, 13.91; Found: C, 83.13; H, 14.13.



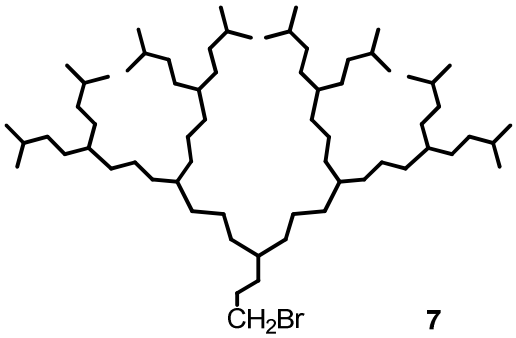
16

G3-L-OH 16. $LiAlH_4$ (0.17 g, 4.48 mmol) was added to a solution of G3-saturated ester **13** (2.22 g, 2.25 mmol) in dry THF (30 mL) at 0 °C. It was allowed to warm to 25 °C and stirred for 4 h. It was poured into ice water and acidified to pH = 3 with HCl solution (1 M). The mixture was extracted with EtOAc (3 × 30 mL). The combined extracts were washed with saturated NaCl solution, dried ($MgSO_4$) and filtered. After evaporation of solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel (eluent: hexane/$CHCl_3$ = 10/1) to produce the product **16** (2.07 g, 94%) as a colorless oil. R_f 0.50 (hexane/EtOAc = 10/1). ^{1}H NMR: 0.88 (48 H, d, J = 6.6), 1.01–1.40 (78 H, m), 1.48 (8 H, nonet, J = 6.6), 1.40–1.62 (2 H, m), 3.63 (2 H, t, J = 6.6). ^{13}C NMR: 22.9, 23.8, 23.9, 28.6, 29.8, 30.2, 31.4, 34.26, 34.35, 34.4, 36.1, 37.5, 37.9, 63.7. MS (ESI): 994 [(M + Na)$^+$, 100%]. HRMS (ESI) Calcd for $C_{68}H_{138}ONa$ (M + Na)$^+$: 994.0640; Found: 994.0635. Anal. Calcd for $C_{68}H_{138}O$: C, 84.04; H, 14.31; Found: C, 84.00; H, 14.22.



19

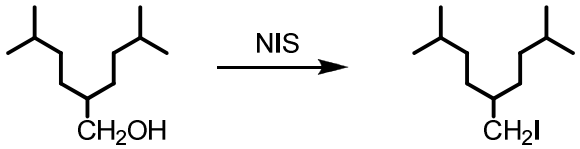
G3-L-CHO 19. A finely powdered mixture of PCC (45 mg, 0.21 mmol) and silica gel (0.10 g) was added to a solution of G3-L-OH **16** (0.13 g, 0.013 mmol) in dry CH_2Cl_2 (5 mL) at 0 °C. After stirring at 25 °C for 6 h, Et_2O (50 mL) was added and stirred for 30 min. The mixture was filtered through a pad of Celite and silica gel. After evaporation of solvent under reduced pressure, the crude product **19** (0.13 g, 98%) was used immediately in the next step without further purification. R_f 0.67 (hexane/EtOAc = 30/1). ^{1}H NMR: 0.88 (48 H, d, J = 6.6), 1.00–1.40 (75 H, m), 1.48 (8 H, nonet, J = 6.6), 1.55–1.70 (2 H, m), 2.40 (2 H, dt, J =1.8 and 6.9), 9.77 (1 H, t, J = 1.5). ^{13}C NMR: 22.9, 23.8, 23.9, 25.8, 28.6, 29.9, 31.4, 34.1, 34.3, 34.4, 36.1, 37.3, 37.5, 37.9, 41.5, 203.0.



7

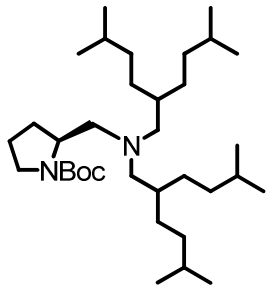
G3-L-Br 7. Powdered PPh_3 (0.33 g, 1.26 mmol) and NBS (0.24 g, 1.35 mmol) were added sequentially to a solution of G3-L-OH **16** (1.01 g, 1.04 mmol) in dry CH_2Cl_2 (10 mL) at 0 °C. The mixture was allowed to warm to 25 °C and stirred for 12 h. The byproduct Ph_3PO was precipitated by the addition of hexane (30 mL) and filtered through a pad of Celite and silica gel. After evaporation of solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel (eluent: hexane) to yield the product **7** (0.99 g, 92%) as a colorless oil. R_f 0.88 (hexane). ^{1}H NMR: 0.89 (48 H, d, J = 6.6), 1.02–1.43 (77 H, m), 1.50 (8 H, nonet, J

= 6.6), 1.76–1.94 (2 H, m), 3.39 (2 H, t, J = 6.6). ^{13}C NMR: 23.0, 23.86, 23.92, 28.6, 30.3, 31.5, 32.3, 34.3, 34.4, 36.2, 37.1, 37.5, 38.0. Anal. Calcd for $C_{68}H_{137}Br$: C, 78.93; H, 13.34; Found: C, 78.89; H, 13.48.



G1-S-OH **G1-S-I**

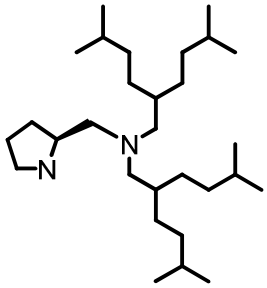
G1-S-I. Powdered PPh_3 (3.85 g, 14.7 mmol) and *N*-iodosuccinimide (NIS) (2.79 g, 12.4 mmol) were added to a solution of **G1-S-OH**[1] (2.10 g, 11.3 mmol) in dry CH_2Cl_2 (20 mL) at −30 °C. The mixture was allowed to warm to 25 °C and stirred for 12 h. The byproduct Ph_3PO was precipitated by the addition of hexane/Et_2O (1/1, 40 mL) and filtered through a pad of Celite and silica gel. After evaporation of solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel (eluent: hexane) to furnish the product **G1-S-I** (3.22 g, 96%) as a colorless oil. R_f 0.82 (hexane). ^{1}H NMR: 0.89 (12 H, d, J = 6.6), 1.11–1.21 (5 H, m), 1.21–1.39 (4 H, m), 1.51 (2 H, nonet, J = 6.6), 3.27 (2 H, d, J = 4.5). ^{13}C NMR: 16.8, 22.7, 22.9, 28.3, 32.3, 35.8, 39.3. MS (EI): 296 (M^+, 1%), 169 [$(M - I)^+$, 20%]. HRMS (EI) Calcd for $C_{12}H_{25}I$ (M^+): 296.0995; Found: 296.0998. Anal. Calcd for $C_{12}H_{25}I$: C, 48.65; H, 8.51; Found: C, 48.84; H, 8.59.



Boc-Di-S-G1

Boc-Di-S-G1. A mixture of *N*-Boc-(*S*)-2-aminomethylpyrrolidine **2** (0.27 g, 1.35 mmol), **G1-S-I** (0.86 g, 2.90 mmol), K_2CO_3 (1.83 g, 13.2 mmol), 18-crown-6 (20 mg) and *i*-Pr_2NEt (2.3 mL, 13.3 mmol) in dry DMF (10 mL) was heated at 70 °C for 6 days. The mixture was cooled to 25 °C, diluted with H_2O (20 mL) and extracted with EtOAc (4 × 20 mL). The combined extracts

were washed with H_2O, saturated NaCl solution, dried ($MgSO_4$) and filtered. After evaporation of solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 15/1 gradient to hexane/EtOAc/Et_3N = 88/11/1) to afford the product **Boc-Di-S-G1** (0.15 g, 21%) as a pale yellow oil. R_f 0.21 (hexane/EtOAc = 10/1). $[\alpha]_D$ −129.4 (*c* = 0.5, $CHCl_3$). ^1H NMR (rotameric mixture): 0.84 + 0.85 (24 H, d, *J* = 6.6), 0.94–1.34 (18 H, m), 1.34–1.68 (4 H, m), 1.45 (9 H, s), 1.68–2.48 (10 H, m), 3.10–3.41 (2 H, m), 3.58–3.95 (1 H, m). ^{13}C NMR (rotameric mixture): 22.7, 22.90, 22.94, 23.4, 28.4, 28.67, 28.73, 28.9, 29.4, 29.9, 30.2, 35.9, 36.3, 36.5, 37.0, 37.1, 46.3 + 46.8, 55.7 + 55.9, 56.9 + 58.5, 60.7 + 61.1, 78.9 + 79.2, 154.7. MS (ESI): 537 [$(M + H)^+$, 100%]. HRMS (ESI) Calcd for $C_{34}H_{69}N_2O_2$ $(M + H)^+$: 537.5354; Found: 537.5355.



Di-S-G1

Di-S-G1. A mixture of TFA (0.11 mL, 1.43 mmol) and **Boc-Di-S-G1** (74 mg, 0.14 mmol) in CH_2Cl_2 (5 mL) was stirred at 25 °C for 12 h. The pH of the solution was adjusted to 10 by the addition of saturated Na_2CO_3 solution at 0 °C. The mixture was then extracted with CH_2Cl_2 (3 × 10 mL) and the combined extracts were washed with saturated NaCl solution, dried ($MgSO_4$) and filtered. The solvent was evaporated under reduced pressure to afford the product **Di-S-G1** (38 mg, 63%) as a pale yellow oil. R_f 0.26 (EtOH). $[\alpha]_D$ −2.3 (*c* = 0.5, $CHCl_3$). ^1H NMR: 0.86 (24 H, d, *J* = 6.6), 0.97–1.58 (23 H, m), 1.64–1.80 (2 H, m), 1.80–1.95 (1 H, m), 1.97–2.35 (6 H, m), 2.70 (1 H, brs), 2.80–3.00 (2 H, m), 3.19 (1 H, quintet, *J* = 6.6). ^{13}C NMR: 22.8, 22.9, 24.6, 28.7, 29.4, 30.0, 36.1, 36.9, 45.5, 56.4, 60.8, 61.0. MS (ESI): 437 (M^+, 100%). HRMS (ESI) Calcd for $C_{29}H_{60}N_2$ (M^+): 437.4829; Found: 437.4833.

3. General Procedure for Asymmetric Aldol Reactions

All aldol reactions were carried out under air in a closed system. TFA (1.4 μL, 18.7 μmol) was added to a mixture of catalyst (18.7 μmol) in H_2O (0.5 mL) at 23 °C with sonication for 15 min. Ketone (375 μmol) and aldehyde (187 μmol) were then sequentially added to form an emulsion. The mixture was stirred in a closed vial for 24 h. The reaction was quenched by the addition of EtOAc/saturated NaCl solution (1/1, 4 mL) to allow phase separation. The organic layer was collected and the aqueous layer was extracted with EtOAc (2 × 1 mL). The combined organic extracts were washed with saturated NaCl solution, dried ($MgSO_4$) and filtered. After evaporation of solvent under reduced pressure, the diastereoselectivity (*anti*/*syn*) of the crude product was determined by ^{1}H NMR analysis. The sample was purified by passing through a short column of silica gel to remove the faster running and baseline materials to obtain the product yield. The ee value of the *anti* adduct was determined by chiral HPLC performed on a Chiralcel OD-H HPLC column (0.5 × 100 mm) obtained from Daicel Chemical Industries, Ltd. Measurements were carried out at 25 °C using either hexane/isopropanol or hexane/ethanol (HPLC grade) as the eluent (flow rate = 0.2, 0.5 or 1.0 mL/min) on a Waters HPLC 515 pump equipped with a Waters 2489 tunable UV-visible absorbance detector at 254 nm.

(2*S*,1'*R*)-2-[Hydroxy-(3-nitrophenyl)methyl]cyclopentanone 25.[2] This compound was synthesized from cyclopentanone (33 μL, 375 μmol) and 3-nitrobenzaldehyde (28.2 mg, 187 μmol). Purification by flash column chromatography on silica gel (eluent: hexane/EtOAc = 5/1) afforded a mixture of *anti* and *syn* aldol adducts as a chrome yellow solid. R_f 0.18 (hexane/EtOAc = 2/1). ^{1}H NMR (*anti* aldol): 1.44–2.58 (7 H, m), 4.80 (1 H, s), 4.83 (1 H, d, J = 9.3), 7.45–7.59 (1 H, m), 7.61–7.75 (1 H, m), 8.04–8.18 (1 H, m), 8.18–8.27 (1 H, m). Chiral HPLC conditions: Eluent: hexane/*i*-PrOH = 90/10; Flow rate: 1.0 mL/min; Retention time: t_R (2*S*,1'*S*) = 14.3 min, t_R (2*R*,1'*R*) = 17.5 min, t_R (2*S*,1'*R*) = 18.9 min, t_R (2*R*,1'*S*) = 22.9 min.

(2*S*,1'*R*)-2-[Hydroxy-(4-nitrophenyl)methyl]cyclohexanone 28 (R = 4-NO_2).[3] This compound was synthesized from cyclohexanone (38 μL, 375 μmol) and 4-nitrobenzaldehyde (28.2 mg, 187

μmol). Purification by flash column chromatography on silica gel (eluent: hexane/EtOAc = 5/1) afforded a mixture of *anti* and *syn* aldol adducts as a yellow solid. R_f 0.30 (hexane/EtOAc = 2/1). ^{1}H NMR (*anti* aldol): 1.15–1.92 (5 H, m), 2.00–2.20 (1 H, m), 2.20–2.53 (2 H, m), 2.53–2.69 (1 H, m), 4.10 (1 H, brs), 4.89 (1 H, d, *J* = 8.4), 7.49 (2 H, d, *J* = 8.7), 8.19 (2 H, d, *J* = 8.4). Chiral HPLC conditions: Eluent: hexane/*i*-PrOH = 97/3; Flow rate: 0.5 mL/min; Retention time: t_R (2*S*,1'*S*) = 82.4 min, t_R (2*R*,1'*R*) = 93.7 min, t_R (2*S*,1'*R*) = 99.1 min, t_R (2*R*,1'*S*) = 148.0 min.

(2*S*,1'*R*)-2-[Hydroxy-(3-nitrophenyl)methyl]cyclohexanone 28 (R = 3-NO$_2$).[4] This compound was synthesized from cyclohexanone (38 μL, 375 μmol) and 3-nitrobenzaldehyde (28.2 mg, 187 μmol). Purification by flash column chromatography on silica gel (eluent: hexane/EtOAc = 5/1) afforded a mixture of *anti* and *syn* aldol adducts as a pale yellow solid. R_f 0.31 (hexane/EtOAc = 2/1). ^{1}H NMR (*anti* aldol): 1.29–1.93 (5 H, m), 2.02–2.20 (1 H, m), 2.26–2.56 (2 H, m), 2.56–2.71 (1 H, m), 4.12 (1 H, d, *J* = 2.4), 4.89 (1 H, dd, *J* = 8.4 and 2.1), 7.46–7.60 (1 H, m), 7.60–7.72 (1 H, m), 8.08–8.27 (2 H, m). Chiral HPLC conditions: Eluent: hexane/*i*-PrOH = 97/3; Flow rate: 0.5 mL/min; Retention time: t_R (2*S*,1'*S*) = 59.3 min, t_R (2*R*,1'*R*) = 62.3 min, t_R (2*S*,1'*R*) = 69.5 min, t_R (2*R*,1'*S*) = 106.5 min.

(2*S*,1'*R*)-2-[Hydroxy-(4-bromophenyl)methyl]cyclohexanone 28 (R = 4-Br).[3] This compound was synthesized from cyclohexanone (38 μL, 375 μmol) and 4-bromobenzaldehyde (34.6 mg, 187 μmol). Purification by flash column chromatography on silica gel (eluent: hexane/EtOAc = 5/1) afforded the mixture of *anti* and *syn* aldol adducts as a white solid. R_f 0.26 (hexane/EtOAc = 4/1). ^{1}H NMR (*anti* aldol): 1.15–1.94 (5 H, m), 1.94–2.15 (1 H, m), 2.25–2.63 (3 H, m), 4.03 (1 H, brs), 4.74 (1 H, d, *J* = 8.7), 7.12–7.24 (2 H, m), 7.38–7.51 (2 H, m). Chiral HPLC conditions: Eluent: hexane/*i*-PrOH = 97/3; Flow rate: 0.5 mL/min; Retention time: t_R (2*S*,1'*S*) = 28.6 min, t_R (2*R*,1'*R*) = 29.8 min, t_R (2*S*,1'*R*) = 39.1 min, t_R (2*R*,1'*S*) = 54.9 min.

(2*S*,1'*R*)-2-[Hydroxy(phenyl)methyl]cyclohexanone 28 (R = H).[4] This compound was

prepared from cyclohexanone (38 μL, 375 μmol) and benzaldehyde (19 μL, 187 μmol). Purification by flash column chromatography on silica gel (eluent: hexane/EtOAc = 5/1) afforded a mixture of *anti* and *syn* aldol adducts as a white solid. R_f 0.42 (hexane/EtOAc = 2/1). ^{1}H NMR (*anti* aldol): 1.18–1.94 (5 H, m), 1.94–2.24 (1 H, m), 2.24–2.55 (2 H, m), 2.55–2.74 (1 H, m), 3.98 (1 H, brs), 4.79 (1 H, d, J = 8.7), 7.22–7.46 (5 H, m). Chiral HPLC conditions: Eluent: hexane/*i*-PrOH = 97/3; Flow rate: 0.5 mL/min; Retention time: t_R (2*S*,1'*S*) = 27.1 min, t_R (2*R*,1'*R*) = 30.8 min, t_R (2*S*,1'*R*) = 36.8 min, t_R (2*R*,1'*S*) = 60.8 min.

(2*S*,1'*R*)-2-[Hydroxy-(4-methoxyphenyl)methyl]cyclohexanone 28 (R = 4-OMe).[5] This compound was synthesized from cyclohexanone (38 μL, 375 μmol) and anisaldehyde (23 μL, 187 μmol). Purification by flash column chromatography on silica gel (eluent: hexane/EtOAc = 5/1) afforded a mixture of *anti* and *syn* aldol adducts as a white solid. R_f 0.38 (hexane/EtOAc = 2/1). ^{1}H NMR (*anti* aldol): 1.15–1.86 (5 H, m), 2.00–2.15 (1 H, m), 2.25–2.53 (2 H, m), 2.53–2.65 (1 H, m), 3.80 (3 H, s), 3.93 (1 H, brs), 4.74 (1 H, d, J = 8.7), 6.88 (2 H, d, J = 8.7), 7.24 (2 H, d, J = 8.7). Chiral HPLC conditions: Eluent: hexane/EtOH = 100/1; Flow rate: 1.0 mL/min; Retention time: t_R (2*S*,1'*S*) = 23.8 min, t_R (2*R*,1'*R*) = 26.8 min, t_R (2*S*,1'*R*) = 31.2 min, t_R (2*R*,1'*S*) = 46.6 min.

4. General Procedure for Asymmetric Michael Additions

All Michael additions were carried out under air in a closed system. TFA (1.4 μL, 18.7 μmol) was added to a mixture of catalyst (18.7 μmol) in H_2O (0.5 mL) at 23 °C with sonication for 15 min. The ketone (375 μmol) and nitrostyrene (187 μmol) were then sequentially added to form an emulsion. The mixture was stirred vigorously in a closed vial for 24 h. The reaction was quenched by adding EtOAc/saturated NaCl solution (1/1, 4 mL) to allow phase separation. The organic layer was collected and the aqueous layer was extracted with EtOAc (2 × 1 mL). The combined organic extracts were washed with saturated NaCl solution, dried ($MgSO_4$) and filtered. After evaporation of solvent under reduced pressure, the diastereoselectivity (*syn*/*anti*) of the crude product was determined by ^{1}H NMR analysis. The sample was purified by passing through a short column of silica gel to remove the faster running and baseline materials to obtain the product yield. The ee value of the *anti* adduct was determined by chiral HPLC performed on a Chiralcel OD-H HPLC column (0.5 × 100 mm) obtained from Daicel Chemical Industries, Ltd. Measurements were carried out at 25 °C using either hexane/isopropanol or hexane/ethanol (HPLC grade) as the eluent (flow rate = 0.2, 0.5 or 1.0 mL/min) on a Waters HPLC 515 pump equipped with a Waters 2489 tunable UV-visible absorbance detector at 254 nm.

(2*S*,1'*R*)-2-(2-nitro-1-phenylethyl)cyclohexanone 30 (R = H).[6] This compound was prepared from cyclohexanone (38 μL, 375 μmol) and *trans*-β-nitrostyrene (27.9 mg, 187 μmol). Purification by flash column chromatography on silica gel (eluent: hexane/EtOAc = 5/1) afforded a mixture of *syn* and *anti* adducts as an ivory white solid. R_f 0.23 (hexane/EtOAc = 4/1). ^{1}H NMR (*syn* adduct): 1.09–1.33 (1 H, m), 1.33–1.90 (4 H, m), 1.90–2.18 (1 H, m), 2.29–2.56 (2 H, m), 2.62–2.81 (1 H, m), 3.78 (1 H, dt, J = 4.2 and 9.9), 4.63 (1 H, dd, J = 12.3 and 10.2), 4.96 (1 H, dd, J = 12.6 and 4.5), 7.15–7.22 (2 H, m), 7.22–7.38 (3 H, m). Chiral HPLC conditions: Eluent: hexane/EtOH = 95/5; Flow rate: 0.5 mL/min; Retention time: t_R (2*R*,1'*S*) = 30.1 min, t_R (2*S*,1'*R*) = 31.8 min.

(2*S*,1'*R*)-2-[1-(4-methoxyphenyl)-2-nitroethyl]cyclohexanone 30 (R = 4-OMe).[6] This

compound was synthesized from cyclohexanone (38 μL, 375 μmol) and *trans*-4-methoxy-β-nitrostyrene (33.5 mg, 187 μmol). Purification by flash column chromatography on silica gel (eluent: hexane/EtOAc = 5/1) afforded a mixture of *syn* and *anti* adducts as a pale yellow solid. R_f 0.21 (hexane/EtOAc = 4/1). ^{1}H NMR (*syn* adduct): 1.09–1.31 (1 H, m), 1.43–1.81 (4 H, m), 1.90–2.22 (1 H, m), 2.22–2.50 (2 H, m), 2.54–2.76 (1 H, m), 3.70 (1 H, dt, *J* = 4.5 and 10.2), 3.75 (3 H, s), 4.56 (1 H, dd, *J* = 12.3 and 9.9), 4.90 (1 H, dd, *J* = 12.3 and 4.5), 6.83 (2 H, d, *J* = 8.7), 7.07 (2 H, d, *J* = 8.7). Chiral HPLC conditions: Eluent: hexane/EtOH = 95/5; Flow rate: 0.5 mL/min; Retention time: t_R (2*R*,1'*S*) = 35.0 min, t_R (2*S*,1'*R*) = 37.6 min.

(2*S*,1'*R*)-2-[1-(4-bromophenyl)-2-nitroethyl]cyclohexanone 30 (R = 4-Br).[6] This compound was synthesized from cyclohexanone (38 μL, 375 μmol) and *trans*-4-bromo-β-nitrostyrene (42.6 mg, 187 μmol). Purification by flash column chromatography on silica gel (eluent: hexane/EtOAc = 5/1) afforded a mixture of *syn* and *anti* adducts as a white solid. R_f 0.22 (hexane/EtOAc = 4/1). ^{1}H NMR (*syn* adduct): 1.10–1.33 (1 H, m), 1.44–1.84 (4 H, m), 1.96–2.18 (1 H, m), 2.26–2.52 (2 H, m), 2.55–2.72 (1 H, m), 3.74 (1 H, dt, *J* = 4.5 and 10.5), 4.58 (1 H, dd, *J* = 12.6 and 10.2), 4.93 (1 H, dd, *J* = 12.9 and 4.5), 7.05 (2 H, d, *J* = 8.4), 7.44 (2 H, d, *J* = 8.4). Chiral HPLC conditions: Eluent: hexane/EtOH = 80/20; Flow rate: 0.5 mL/min; Retention time: t_R (2*R*,1'*S*) = 14.5 min, t_R (2*S*,1'*R*) = 15.4 min.

(2*S*,1'*R*)-2-[2-nitro-1-(2-nitrophenyl)ethyl]cyclohexanone 30 (R = 2-NO$_2$).[7] This compound was synthesized from cyclohexanone (38 μL, 375 μmol) and *trans*-2-nitro-β-nitrostyrene (36.3 mg, 187 μmol). Purification by flash column chromatography on silica gel (eluent: hexane/EtOAc = 5/1) afforded the *syn* and *anti* adducts as a pale yellow solid. R_f 0.24 (hexane/EtOAc = 2/1). ^{1}H NMR (*syn* adduct): 1.36–1.90 (5 H, m), 2.00–2.19 (1 H, m), 2.27–2.54 (2 H, m), 2.85–3.01 (1 H, m), 4.32 (1 H, dt, *J* = 5.7 and 8.1), 4.84–5.00 (2 H, m), 7.34–7.51 (2 H, m), 7.51–7.64 (1 H, m), 7.78–7.91 (1 H, m). Chiral HPLC conditions: Eluent: hexane/*i*-PrOH = 90/10; Flow rate: 0.5 mL/min; Retention time: t_R (2*R*,1'*S*) = 49.5 min, t_R (2*S*,1'*R*) = 55.5 min.

5. General Procedures for Determining the Relative Reaction Reactivities

TFA (2.8 μL, 37.4 μmol) was added to a mixture of the catalyst (37.4 μmol) in H_2O (1.0 mL) at 23 °C with sonication for 15 min. Cyclopentanone (750 μmol) and 3-nitrobenzaldehyde (374 μmol) were then sequentially added and stirred vigorously in a closed vial to form an emulsion. After a specified time interval, 0.1 mL of the reaction mixture was taken out and quenched by the addition of EtOAc/saturated NaCl solution (1/1, 2 mL) to allow phase separation. The organic layer was collected and the solvent was evaporated under reduced pressure. The % conversion of the crude product was determined by ^{1}H NMR analysis from the relative integration of the aldehyde and the aldol product signals assuming no other side reactions. The results were shown in Figure 3 of the manuscript.

6. Determination of Catalyst Partition Ratio after Aldol Reactions

The aldol reaction was carried out as described in *Section 3*. The reaction mixture was then partitioned between HC solvent/MeOH = 1 mL/1 mL. The samples obtained from the HC solvent layer and MeOH layer were then evaporated *in vacuo*. The residues were transferred separately into a 1 mL-volumetric flask and $CDCl_3$ was added up to the mark. 0.60 mL of the sample solution was then taken out for ^1H NMR analysis to obtain the relative amount of the aldol product/organocatalyst/3-nitrobenzaldehyde in the HC solvent and MeOH layers. Addition of an aliquot (0.1 mL) of a standard solution of 3-nitrobenzaldehyde (10 mg in 1.00 mL $CDCl_3$) to the above samples followed by ^1H NMR analysis then allowed us to find out the amount of dendritic catalyst in each layer. The catalyst partition ratios were shown in Table 5 of the manuscript.

7. Catalyst Recovery Studies

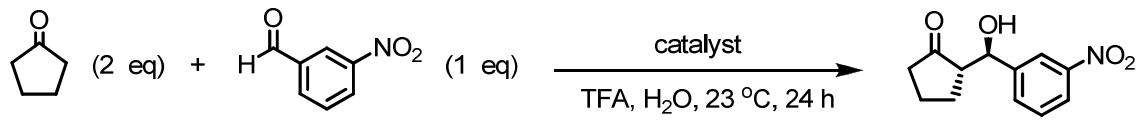
7.1. Asymmetric Michael additions

The procedure of the first run was the same as that described in the general procedure for the asymmetric Michael additions (See *Section 4*). After the reaction, Et_3N (2.6 μL, 18.7 μmol) was added to neutralize the TFA. The work-up procedure was the same as described in *Section 4*. The crude product was subjected to ^1H NMR spectroscopic analysis to obtain the diastereoselectivity (*anti*/*syn*). The contents were then transferred into a vial and the excess solvents were evaporated. Heptane/MeOH (*v*/*v* 3:1) was then added and the vial was shaken. The two layers were separated and the solvent of each layer was evaporated. The sample obtained from the MeOH layer was then subjected to standard analyses to obtain the ee values and isolated yield as described in *Section 4*. The heptane layer was washed with MeOH (*v*/*v* 1:1), NaOH solution (1 M), and saturated NaCl solution, dried ($MgSO_4$) and filtered. The solvent was evaporated under reduced pressure to afford the recovered catalyst. It was reused in the second run and the above procedures were repeated. The results of asymmetric Michael additions using the recovered organocatalysts were shown in Table 6 of the manuscript.

7.2. Asymmetric aldol reactions

The procedure of the first run was the same as described in the general procedure for the asymmetric aldol reactions (see *Section 3*). The recovery procedure was the same as above (see *Section 7.1*) except the heptane/MeOH ratio used in the extraction was 2:1 in Table S1, and 3:1 in Table S2. The results were shown in Tables S1 and S2 below.

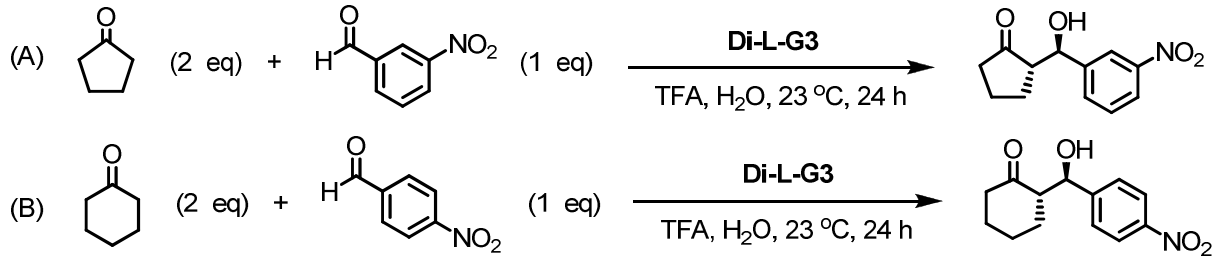
Table S1. Organocatalyst/TFA-catalyzed asymmetric aldol reactions with cyclopentanone and 3-nitrobenzaldehyde in water using recovered catalysts obtained from heptane/MeOH partition.[a]



Run	Catalyst	Yield[b] (%)	*anti* : *syn*[c]	ee[d] (%)
1	**Di-L-G2**	82	35 : 65	57
2	**Di-L-G2**	80	58 : 42	59
3	**Di-L-G2**	79	45 : 55	58
4	**Di-L-G2**	79	33 : 67	64
5	**Di-L-G2**	78	40 : 60	64
1	**Di-L-G3**	79	36 : 64	72
2	**Di-L-G3**	72	50 : 50	70
3	**Di-L-G3**	71	44 : 56	68
4	**Di-L-G3**	76	43 : 57	70
5	**Di-L-G3**	65	51 : 49	69

[a]Conditions of aldol reactions: Cyclopentanone (375 μmol), 3-nitrobenzaldehyde (187 μmol), recovered catalyst and TFA (1 equiv. to the catalyst) in water (0.5 mL) for 24 h. [b]Isolated yield after column chromatography. [c]Determined by ^{1}H NMR analysis of the crude product. [d]Determined by chiral-phase HPLC (Chiralcel OD-H) analysis on the *anti*-product.

Table S2. **Di-L-G3**/TFA-catalyzed asymmetric aldol reactions with different substrates in water using recovered catalysts obtained from heptane/MeOH partition: (A) cyclopentanone and 3-nitrobenzaldehyde; (B) cyclohexanone and 4-nitrobenzaldehyde.[a]



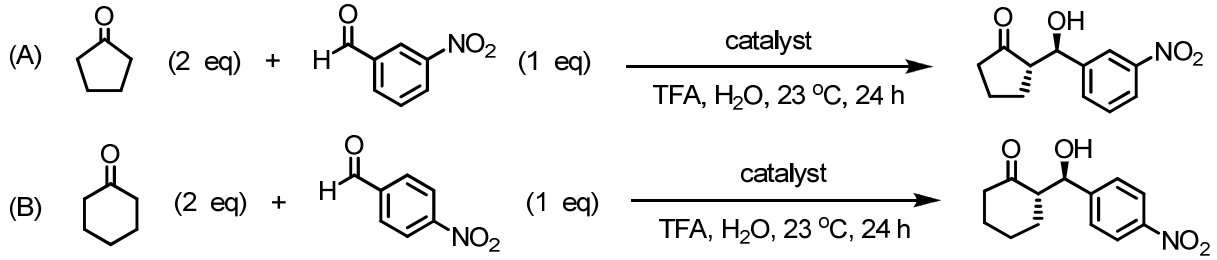
Run	Reaction	Yield[c] (%)	*anti* : *syn*[d]	ee[e] (%)
1	A	78	62 : 38	85
2	B	89	80 : 20	97
3	A	71	62 : 38	83
4	B	82	79 : 21	98
5	A	77	62 : 38	84
6	B	85	78 : 22	98

[a]Conditions of aldol reactions: Ketone (375 μmol), aldehyde (187 μmol), recovered catalyst and TFA (1 equiv. to the catalyst) in water (0.5 mL) for 24 h. [b]Isolated yield after column chromatography. [c]Determined by ^{1}H NMR analysis of the crude product. [d]Determined by chiral-phase HPLC (Chiralcel OD-H) analysis on the *anti*-product.

8. Asymmetric Aldol Reactions at Different Catalyst Loadings

The procedure for carrying out asymmetric aldol reactions at different catalyst loadings was the same as that described in *Section 3*, except the amount of organocatalysts used was different (10, 5 and 1 mol%). The results were summarized in Table S3.

Table S3. Organocatalyst/TFA-catalyzed asymmetric aldol reactions with different substrates in water at different catalyst loading: (A) cyclopentanone and 3-nitrobenzaldehyde; (B) cyclohexanone and 4-nitrobenzaldehyde.[a]

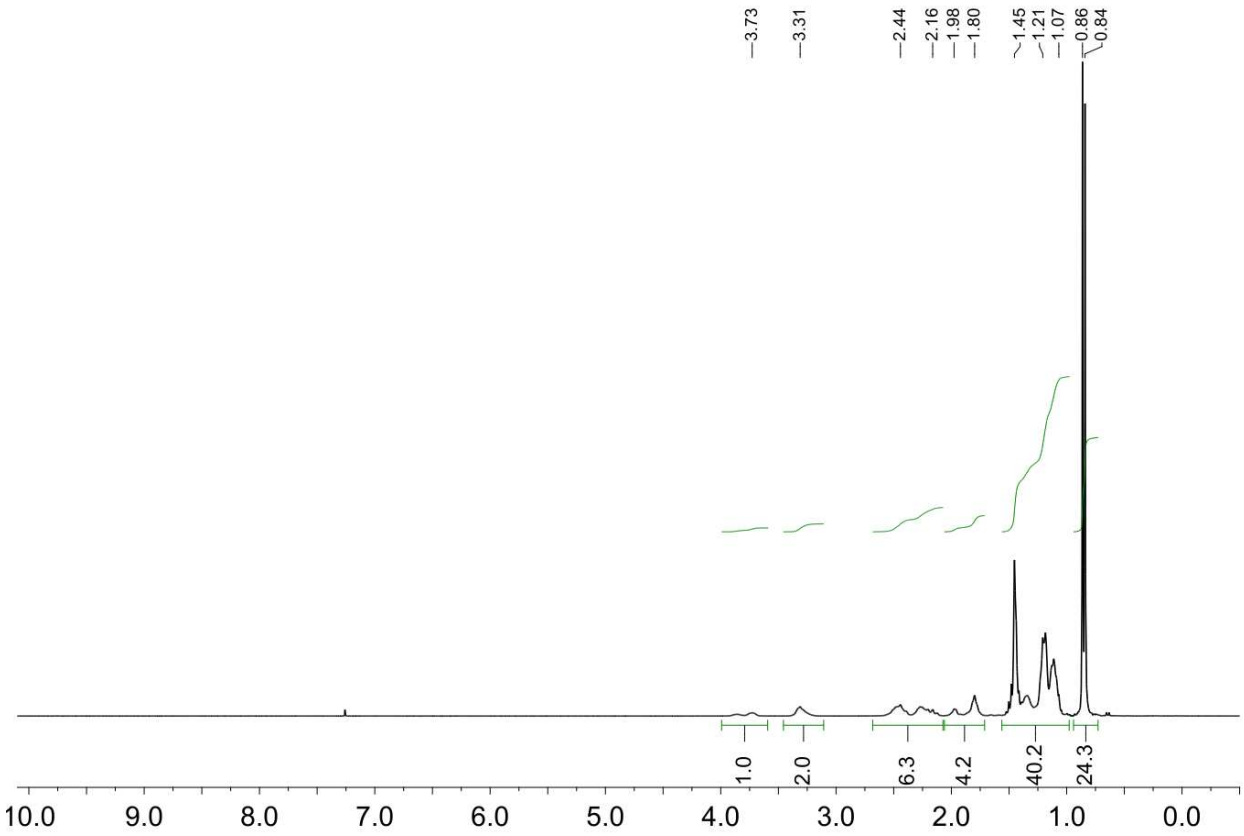


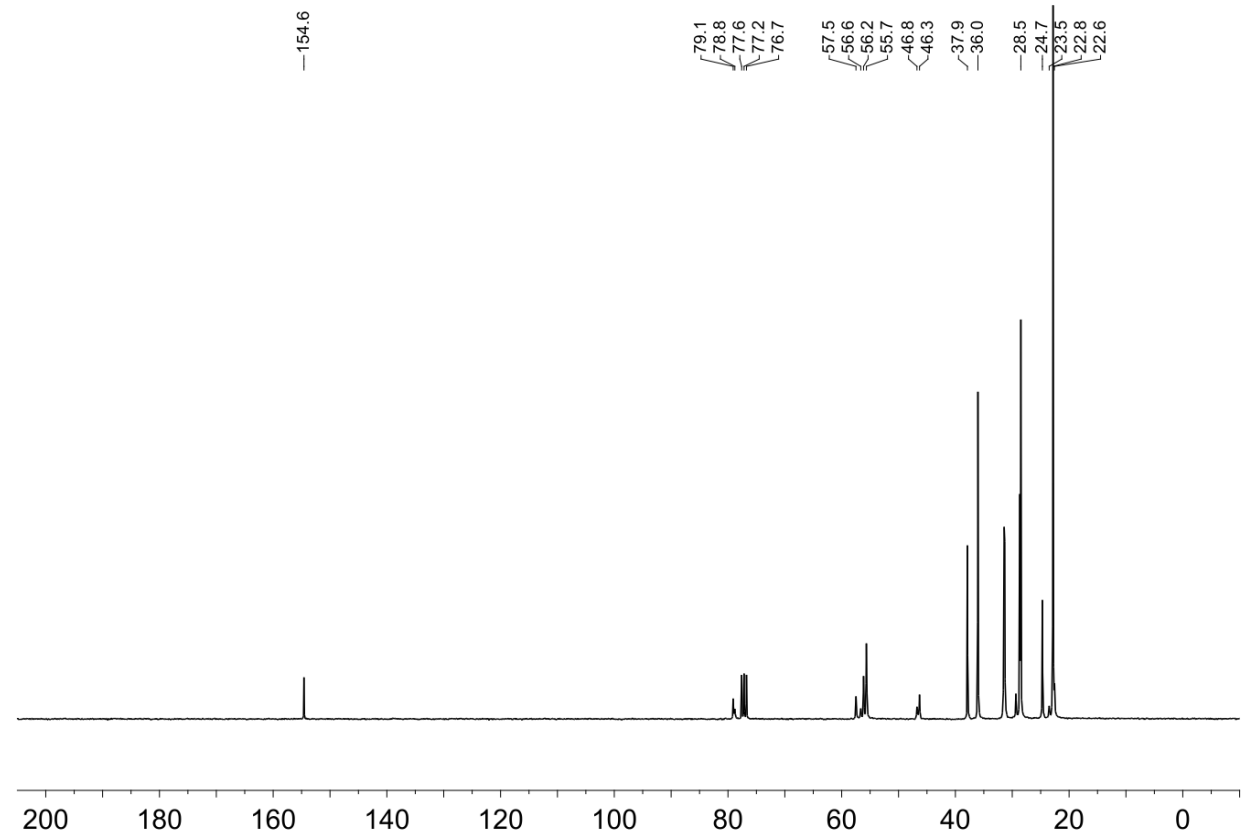
Reaction	Catalyst	Amount of catalyst	Yield[b] (%)	*anti*:*syn*[c]	ee[d] (%)
A	**1**	10 mol%	79	71 : 29	85
A	**1**	5 mol%	71	69 : 31	81
A	**1**	1 mol%	86	74 : 26	63
A	**Di-L-G1**	10 mol%	80	69 : 31	70
A	**Di-L-G1**	5 mol%	75	66 : 34	79
A	**Di-L-G1**	1 mol%	90	71 : 29	82
B	**1**	10 mol%	75	83 : 17	95
B	**1**	5 mol%	63	88 : 12	87
B	**1**	1 mol%	76	87 : 13	99
B	**Di-L-G1**	10 mol%	85	87 : 13	93
B	**Di-L-G1**	5 mol%	86	88 : 12	85
B	**Di-L-G1**	1 mol%	88	87 : 13	99

[a]Conditions: Ketone (375 μmol), aldehyde (187 μmol), organocatalyst and TFA (1 equiv. to the catalyst) in water (0.5 mL) for 24 h. [b]Isolated yield after column chromatography. [c]Determined by ^{1}H NMR analysis of the crude product. [d]Determined by chiral-phase HPLC (Chiralcel OD-H) analysis on the anti-product.

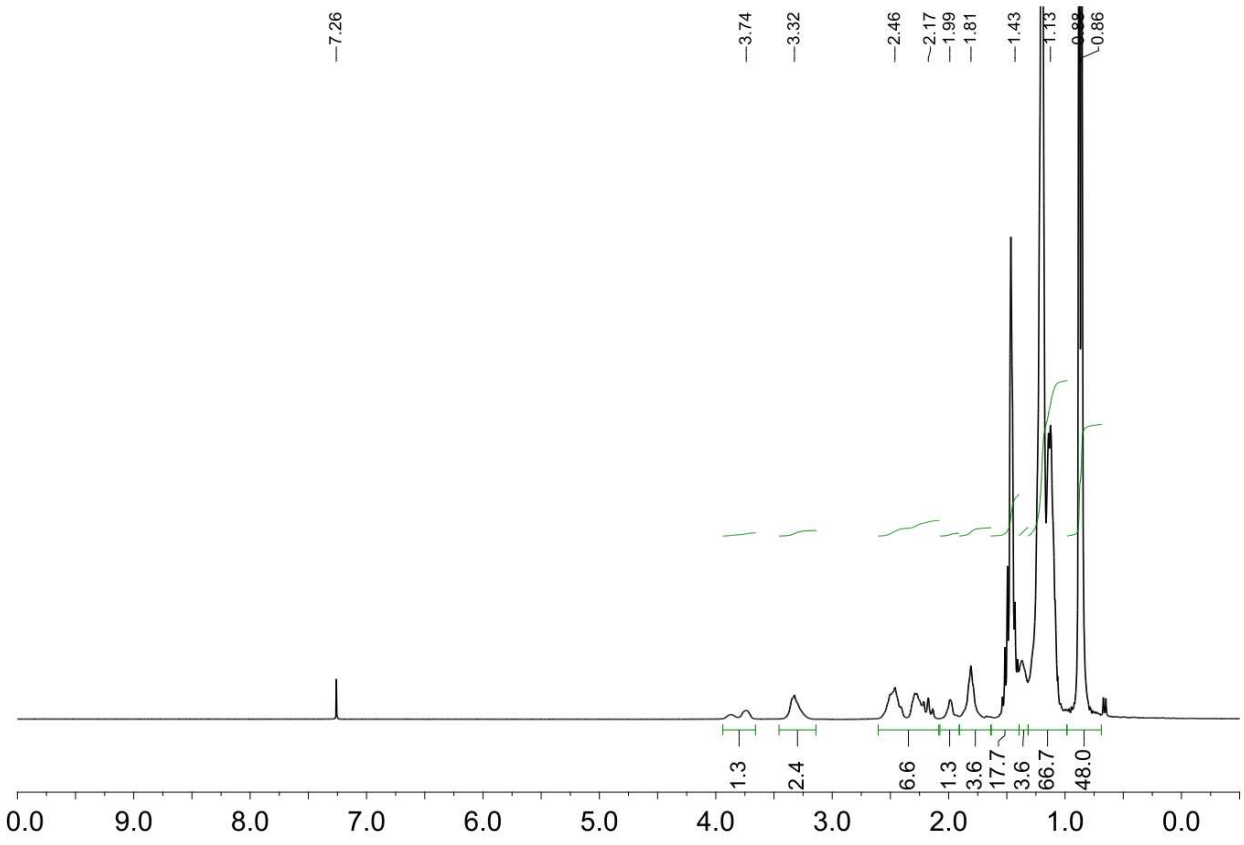
9. ^{1}H and ^{13}C NMR Spectra of New Compounds

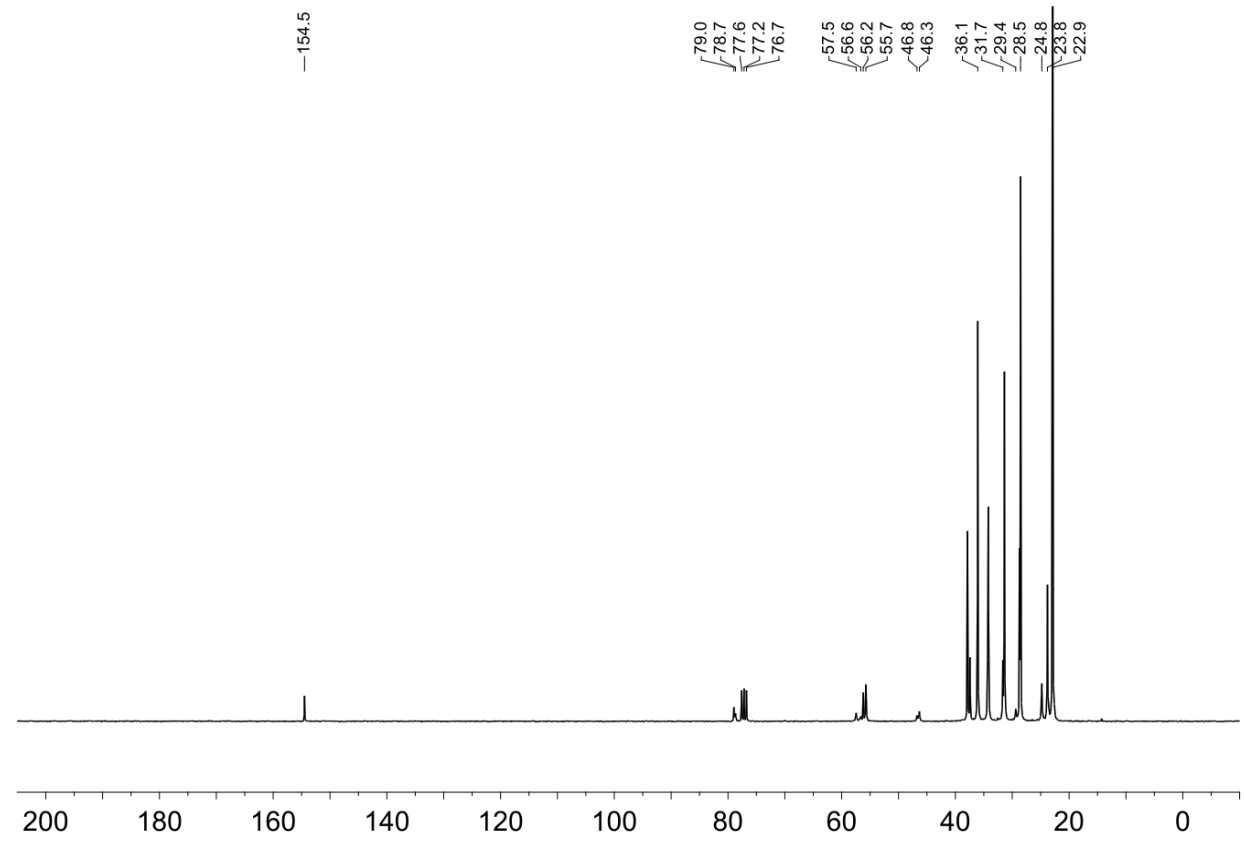
^{1}H and ^{13}C of compound **Boc-Di-L-G1**



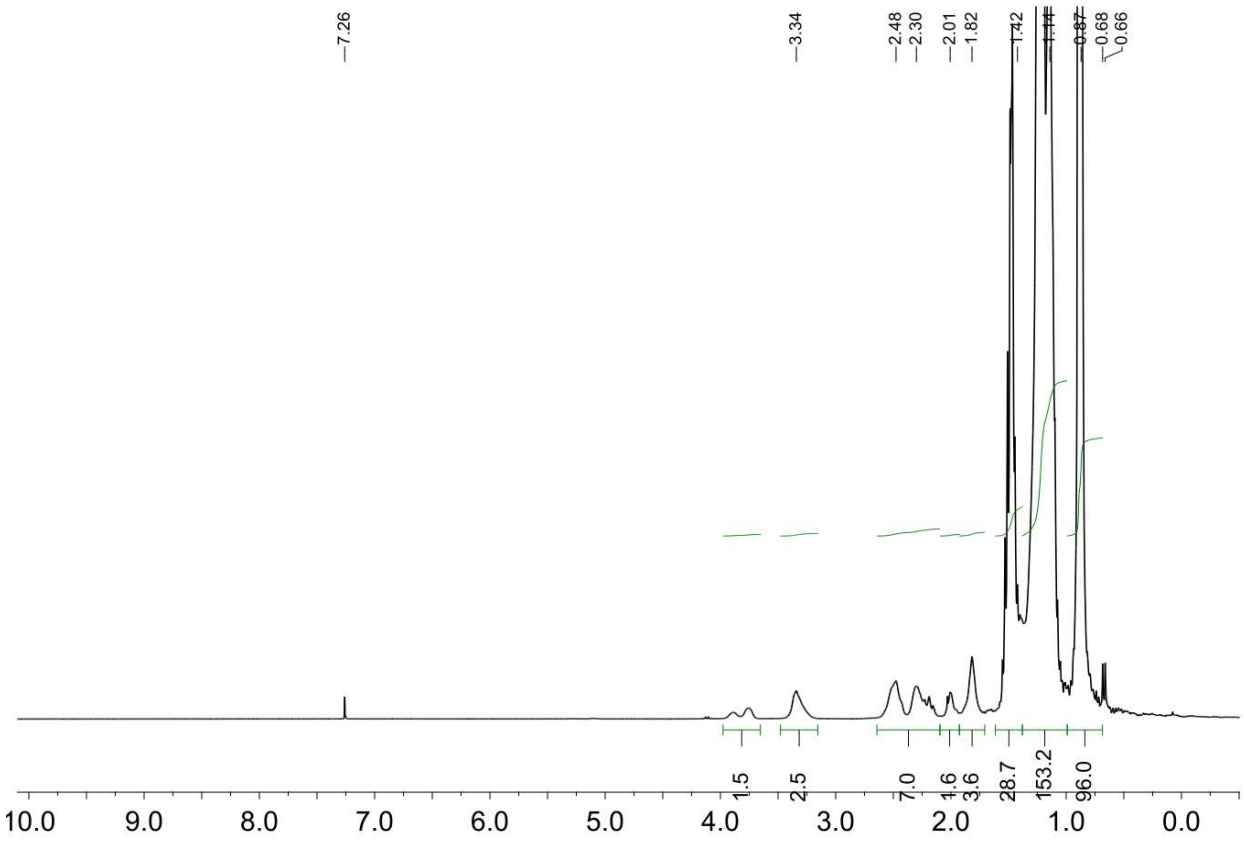


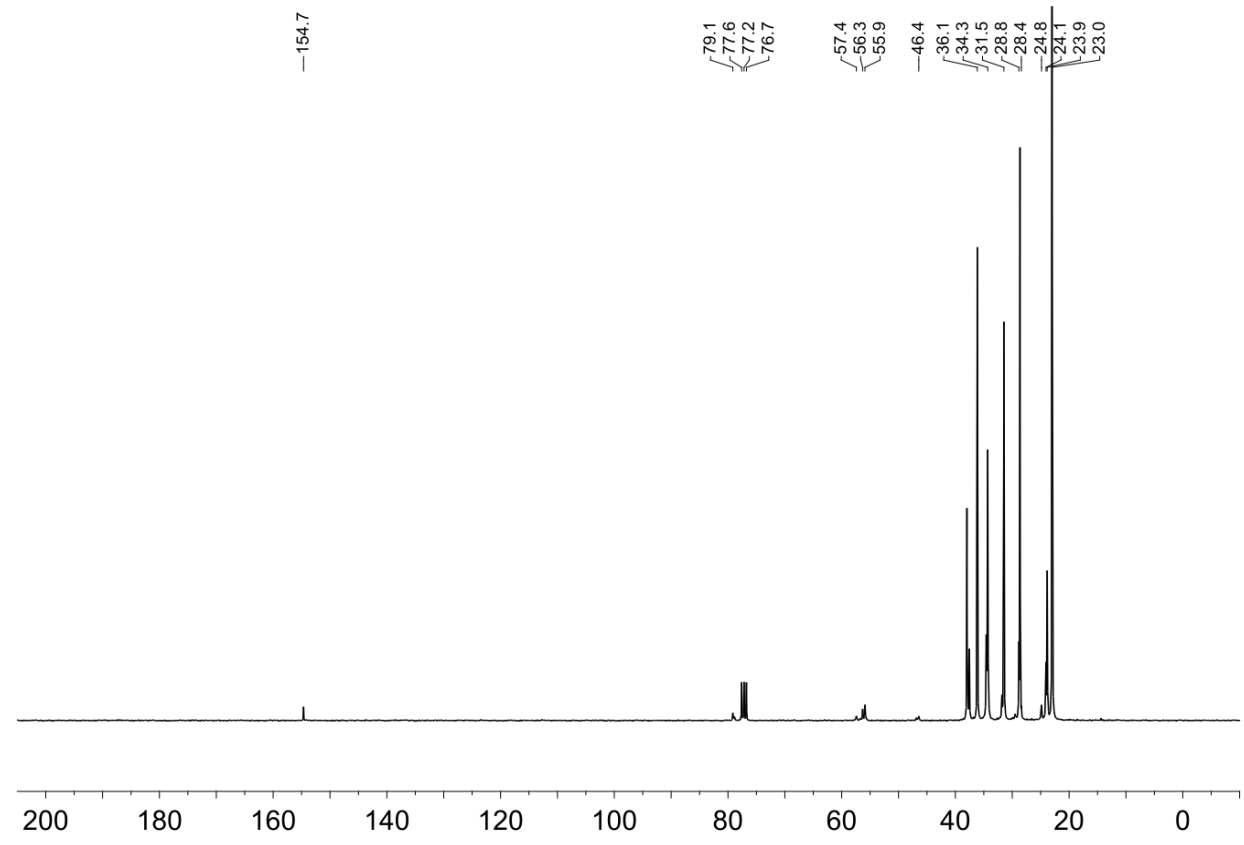
^{1}H and ^{13}C of compound **Boc-Di-L-G2**



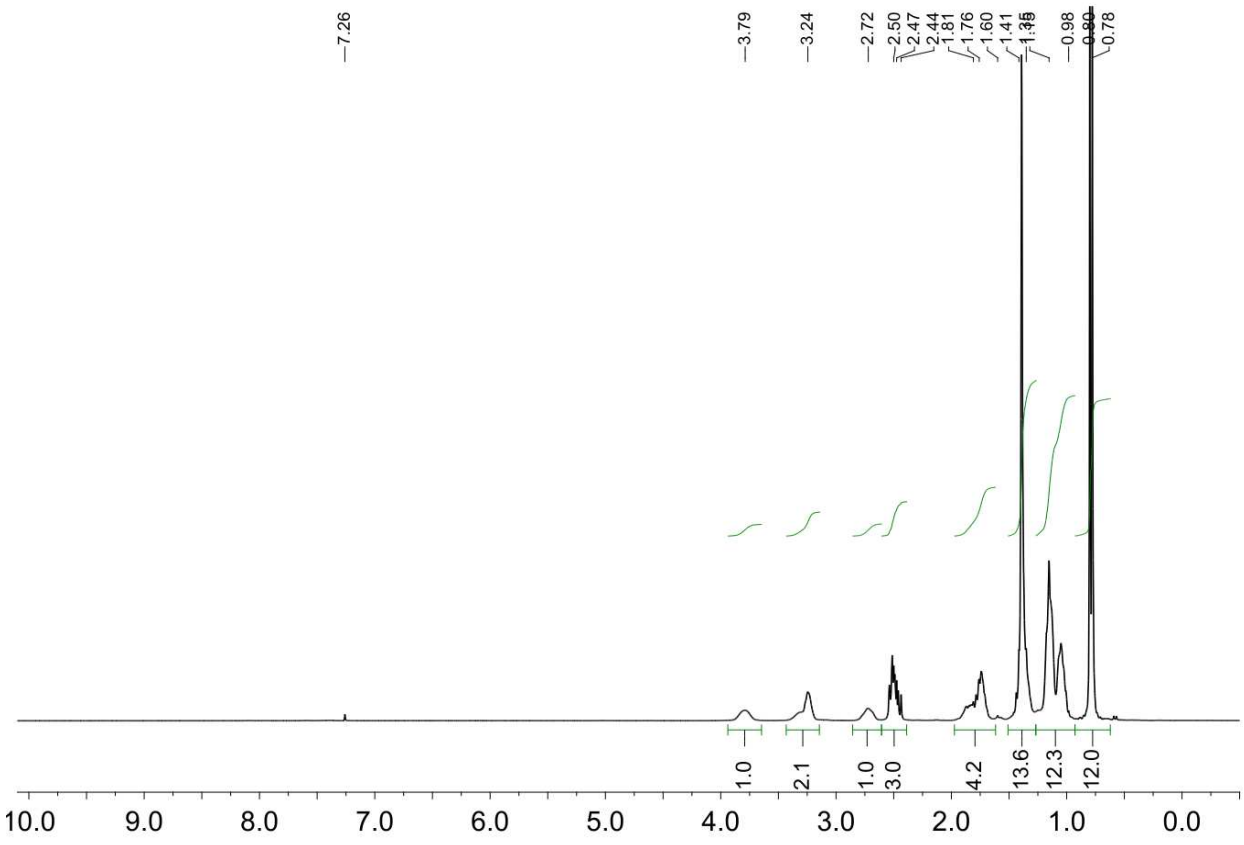


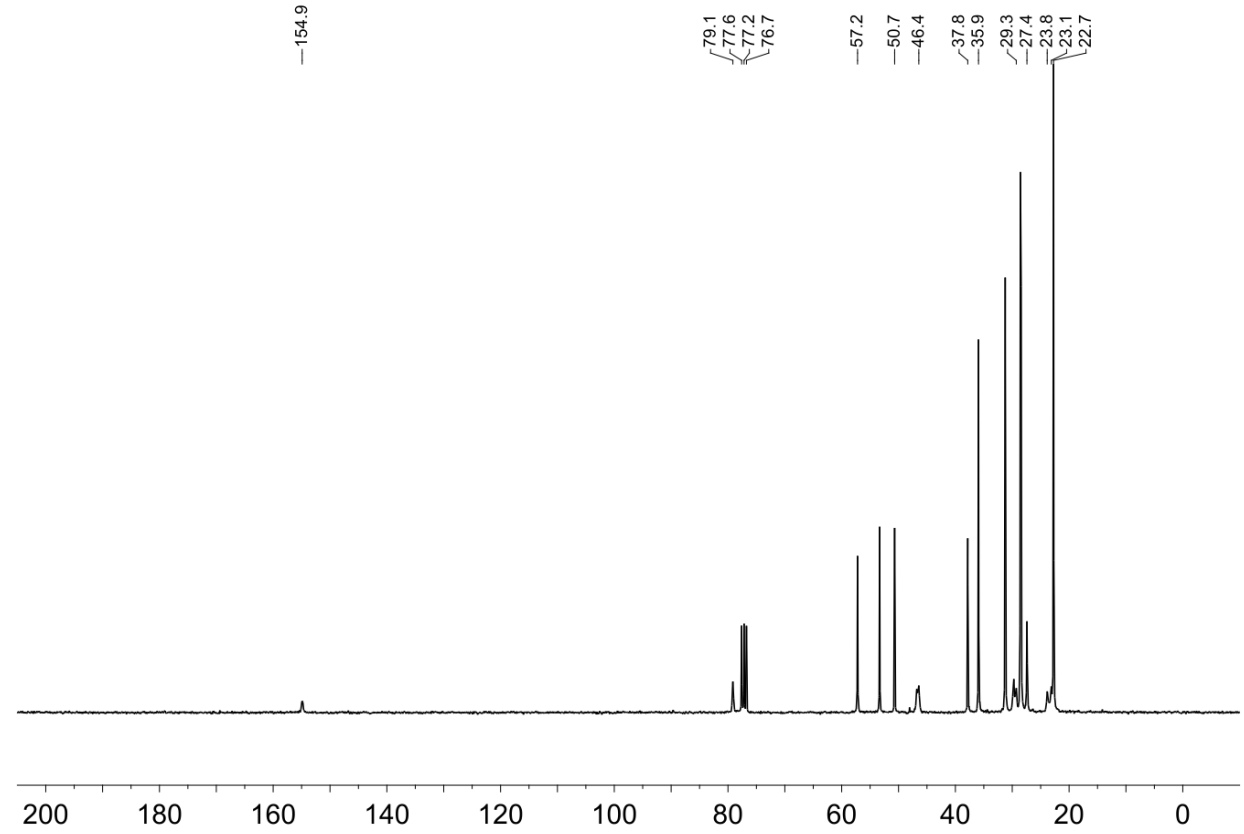
^{1}H and ^{13}C of compound **Boc-Di-L-G3**



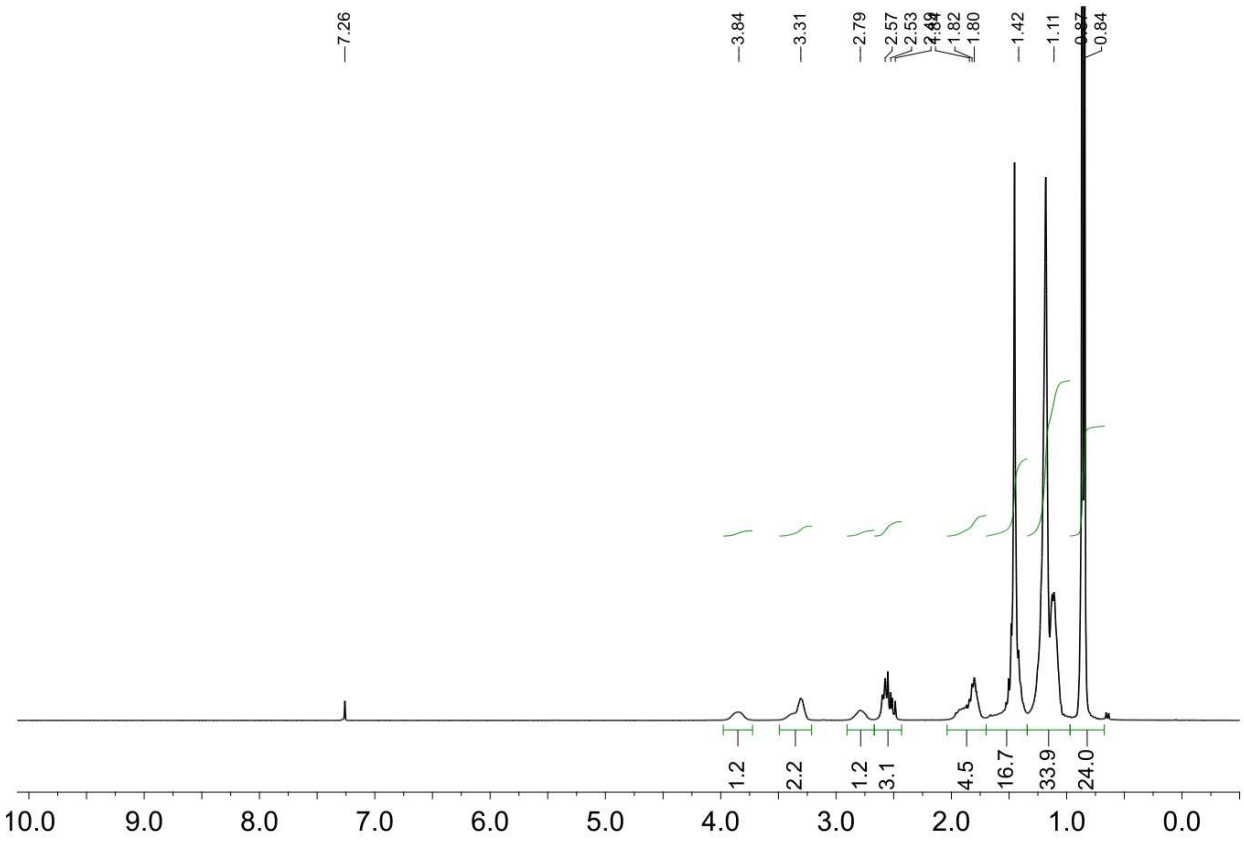


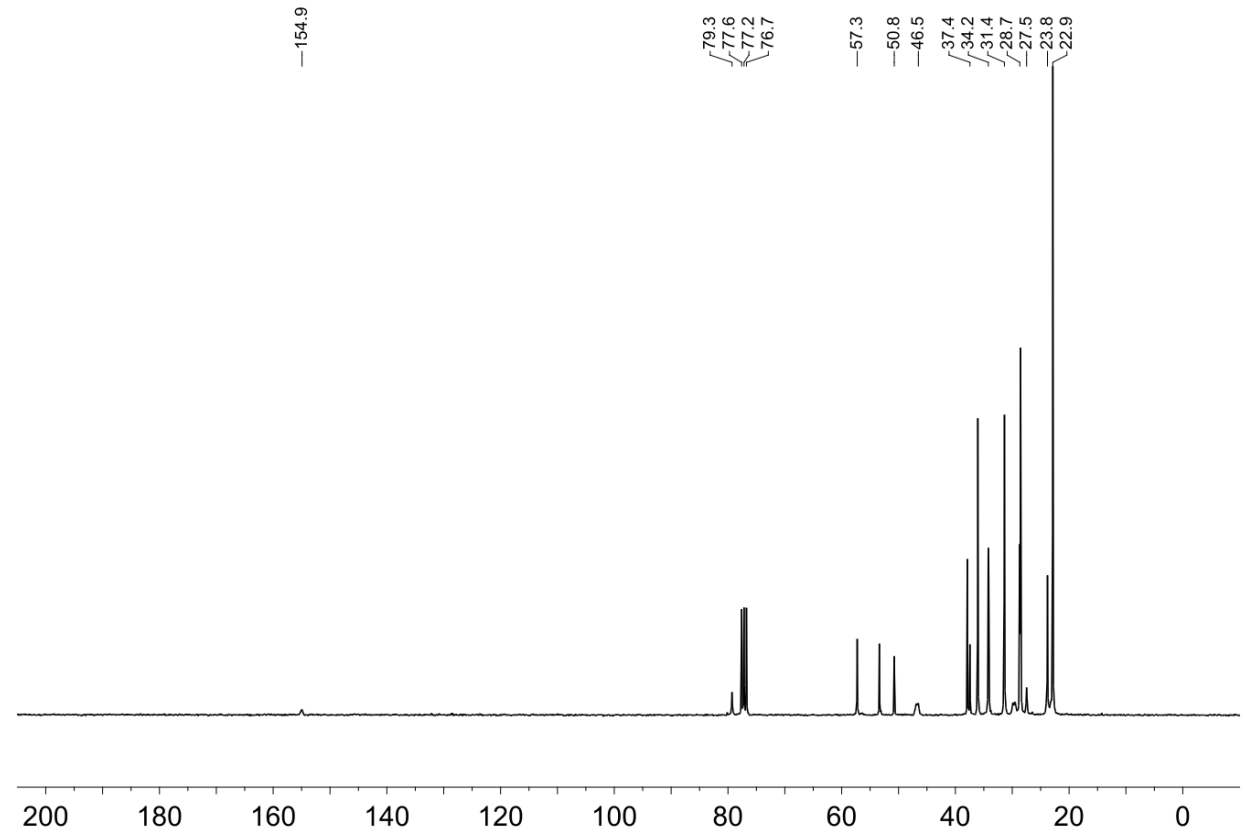
^{1}H and ^{13}C of compound **Boc-Mono-L-G1**



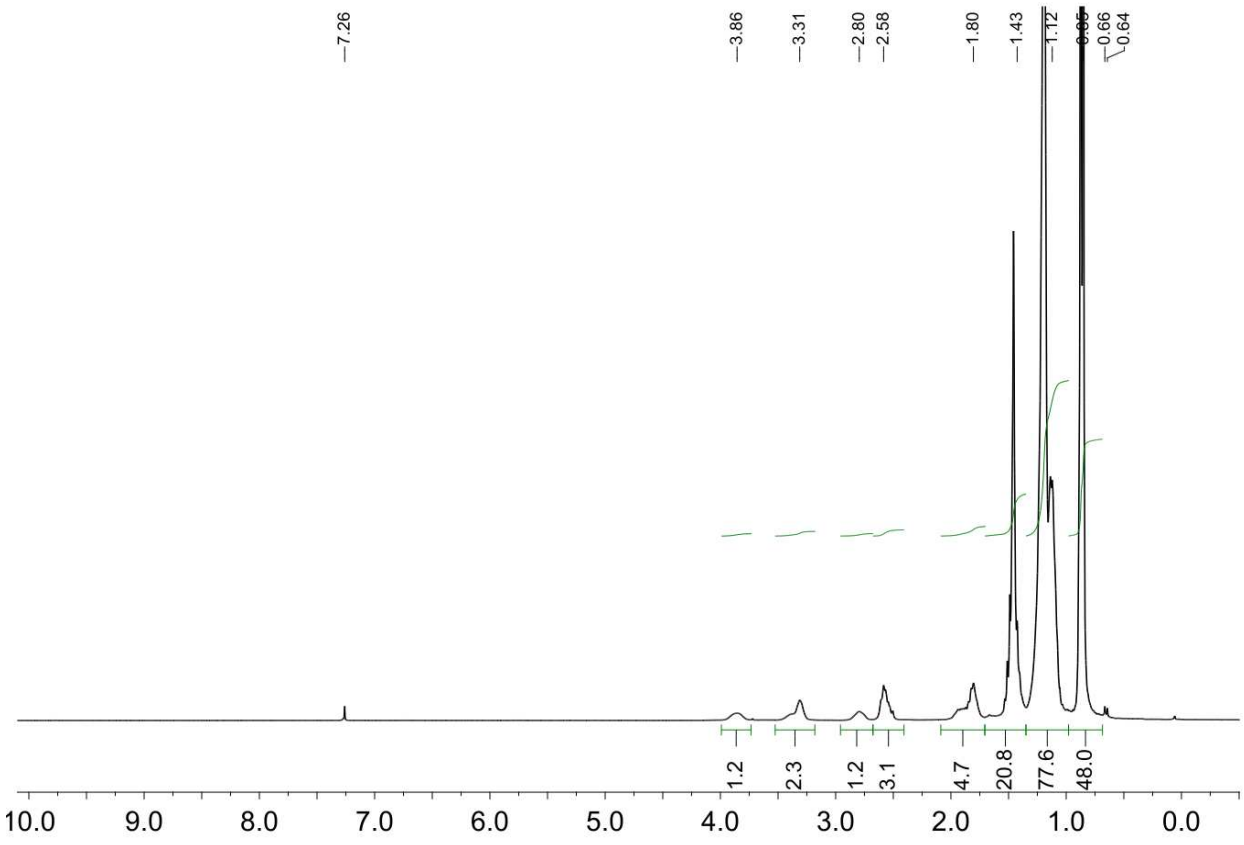


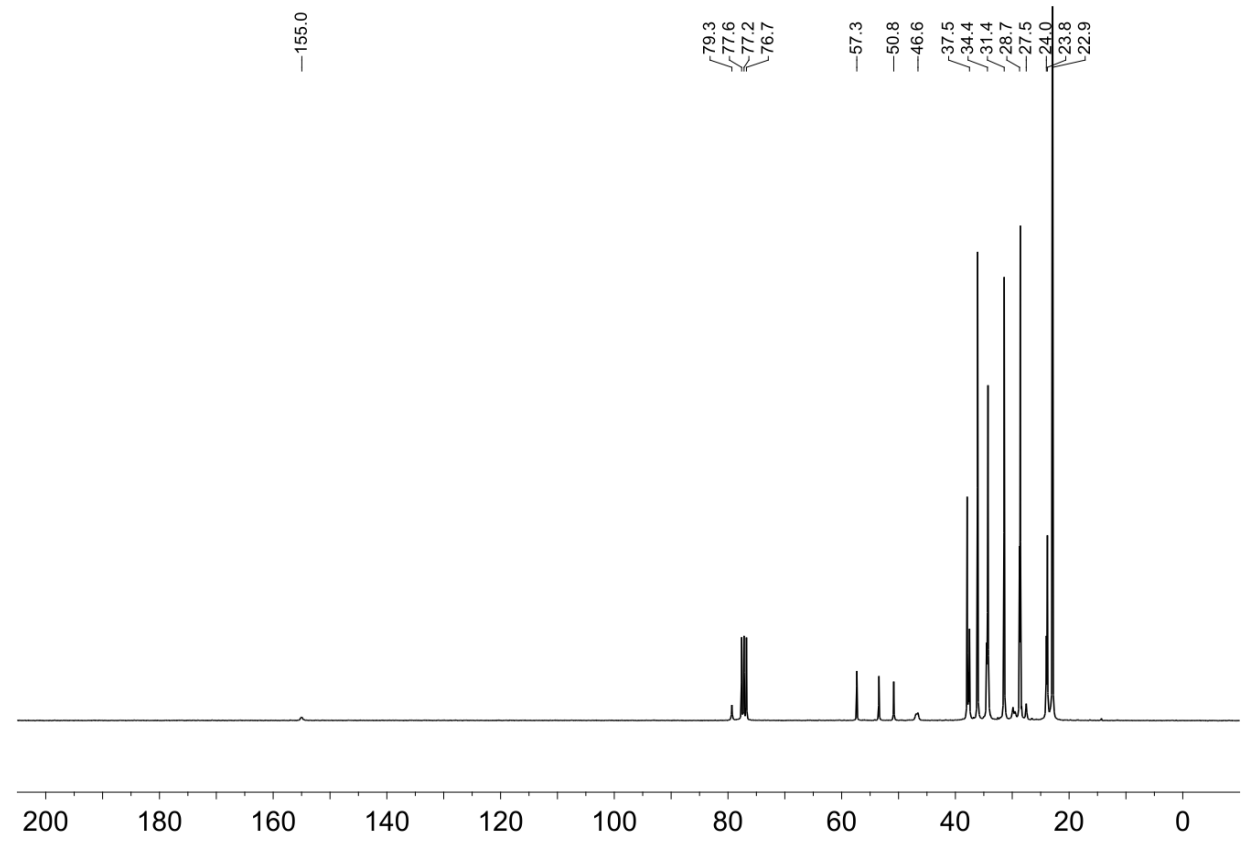
^{1}H and ^{13}C of compound **Boc-Mono-L-G2**



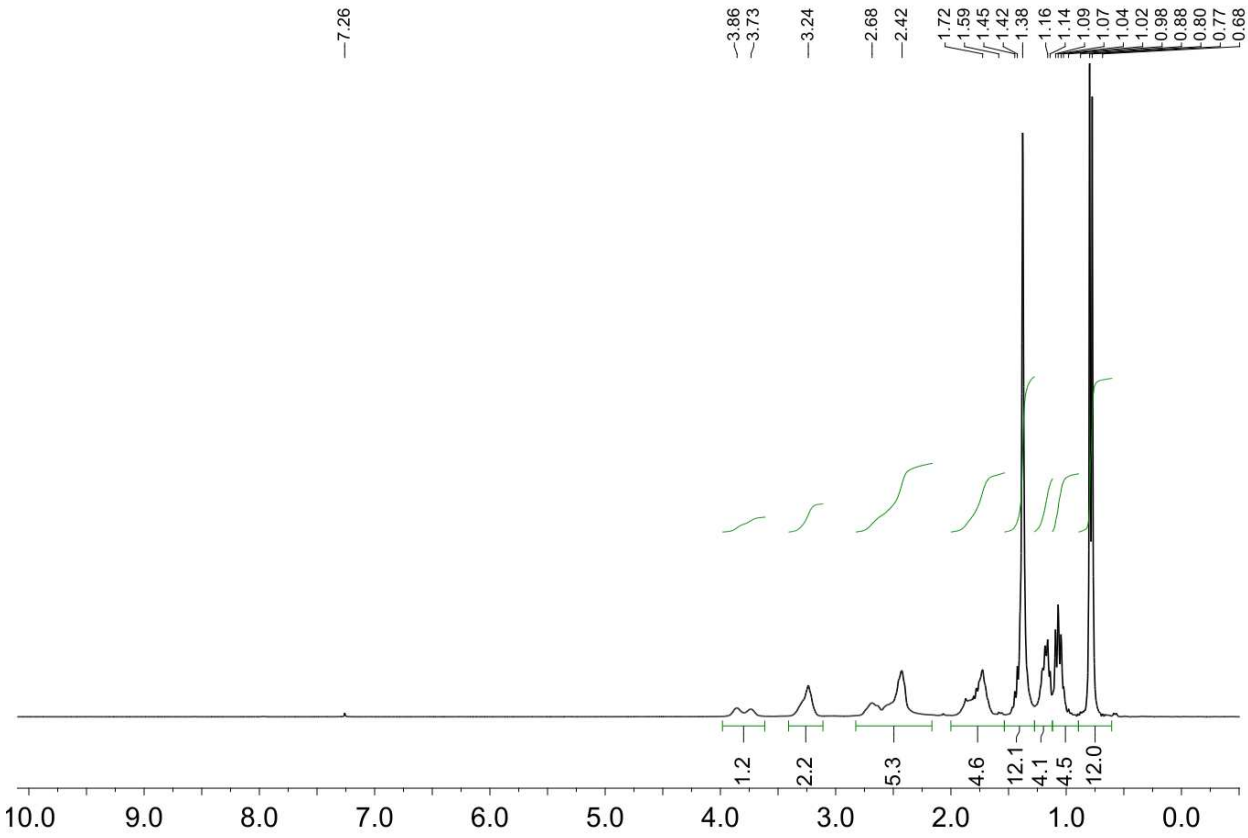


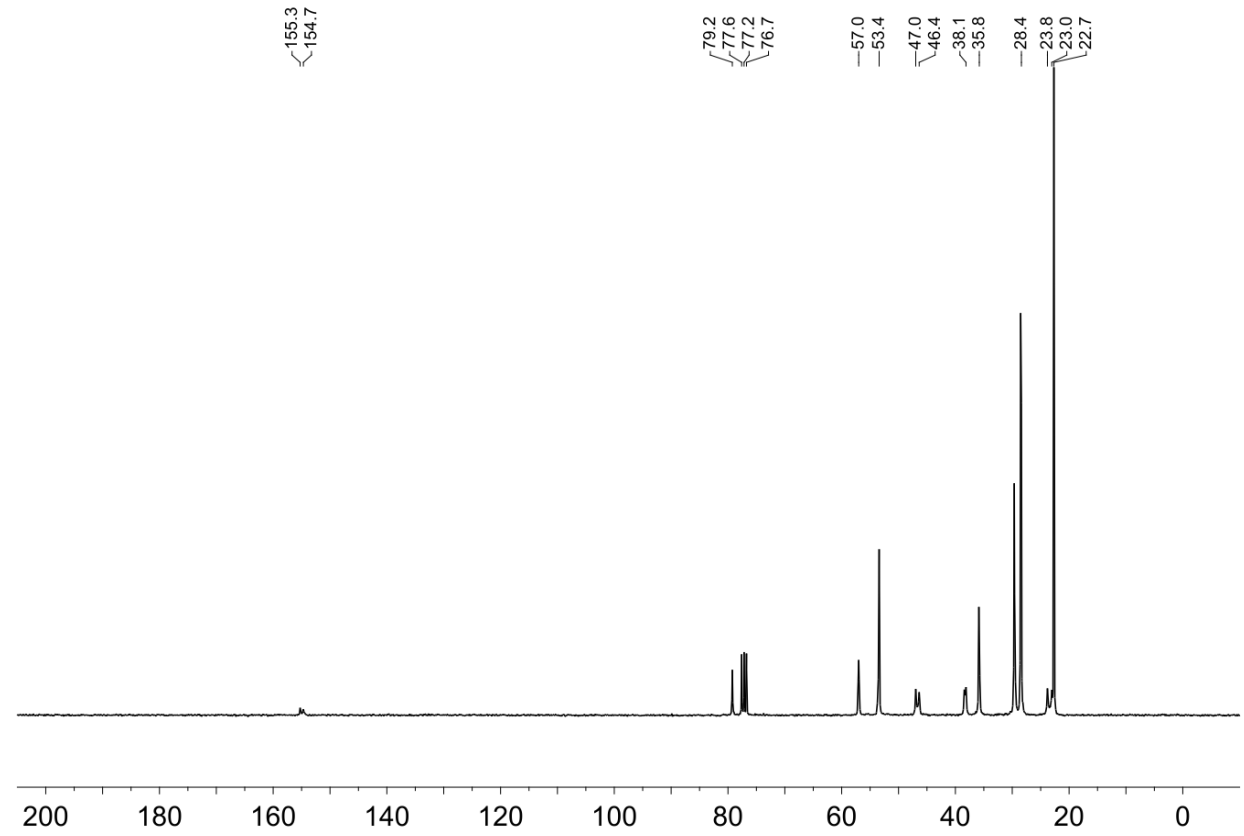
^{1}H and ^{13}C of compound **Boc-Mono-L-G3**



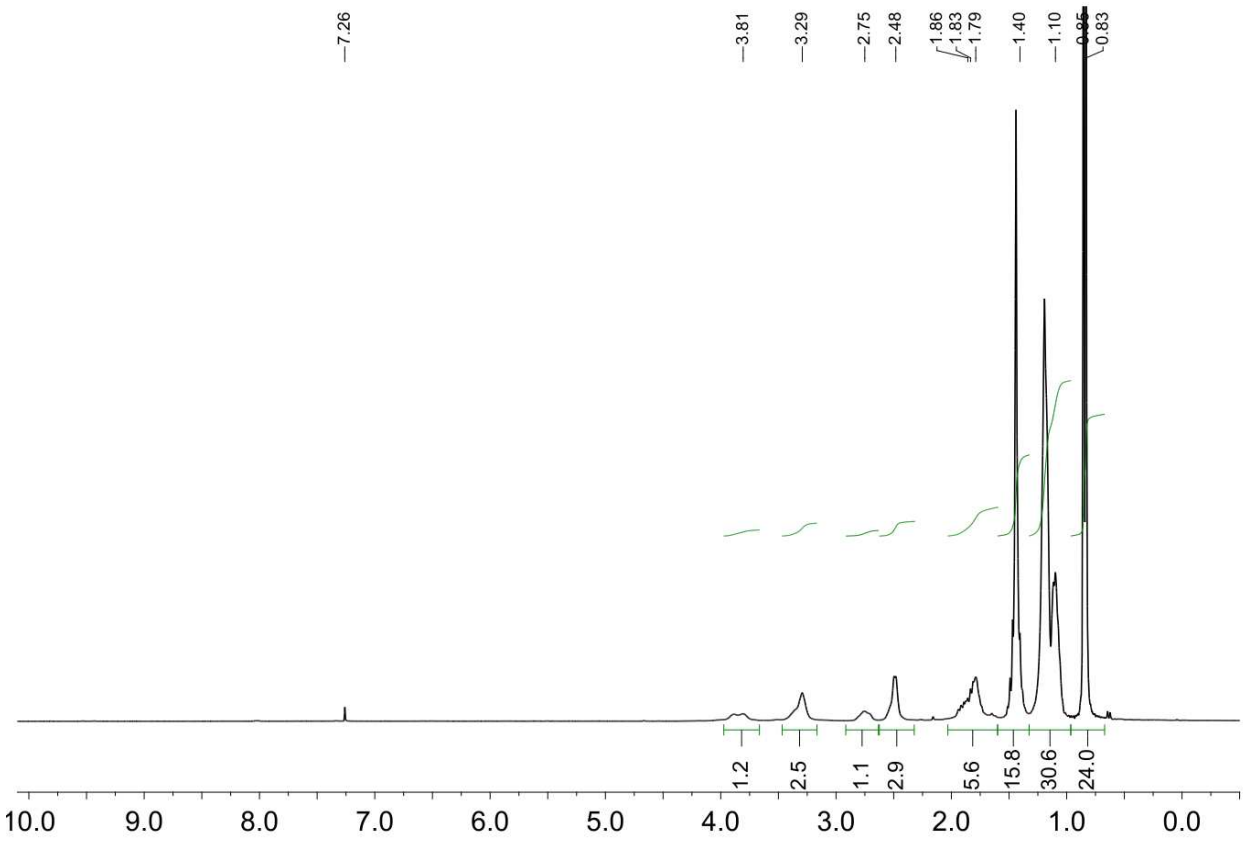


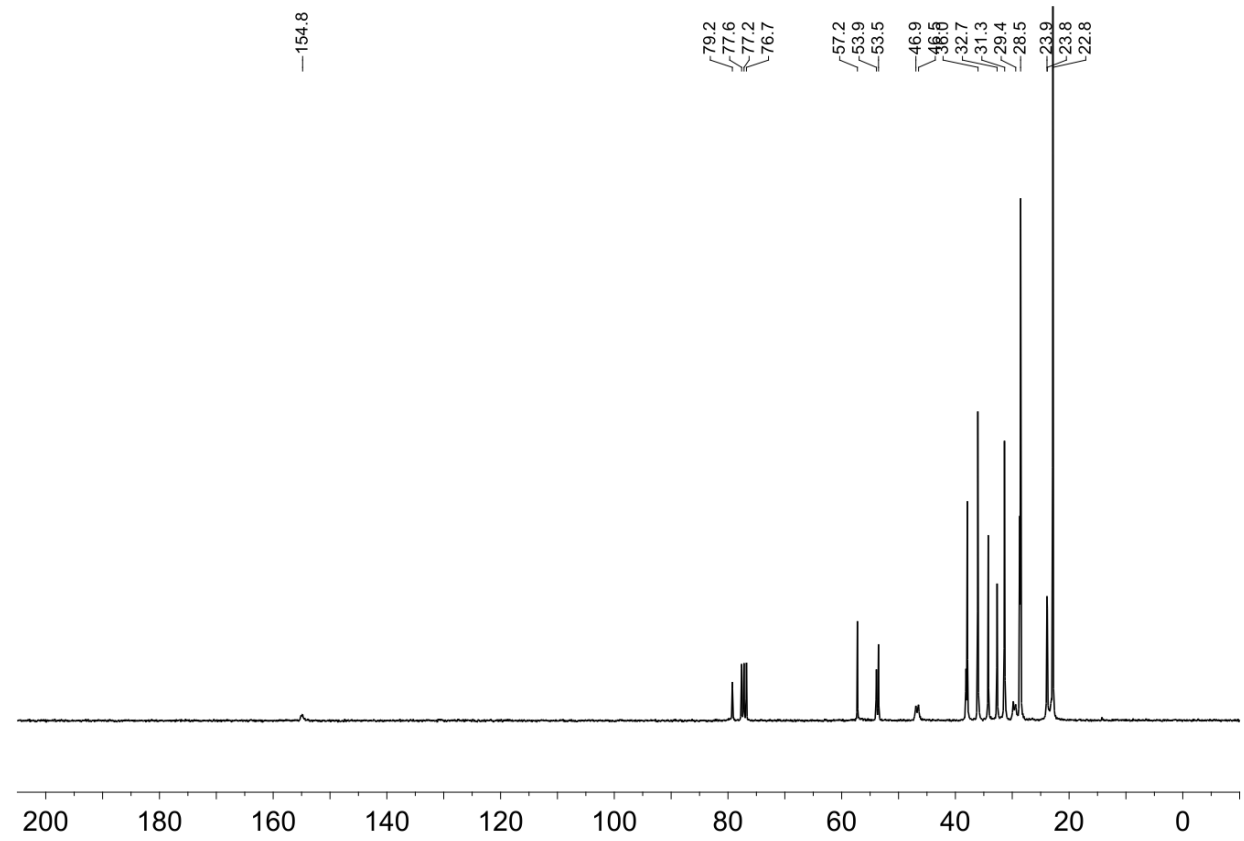
^{1}H and ^{13}C of compound **Boc-Mono-S-G1**



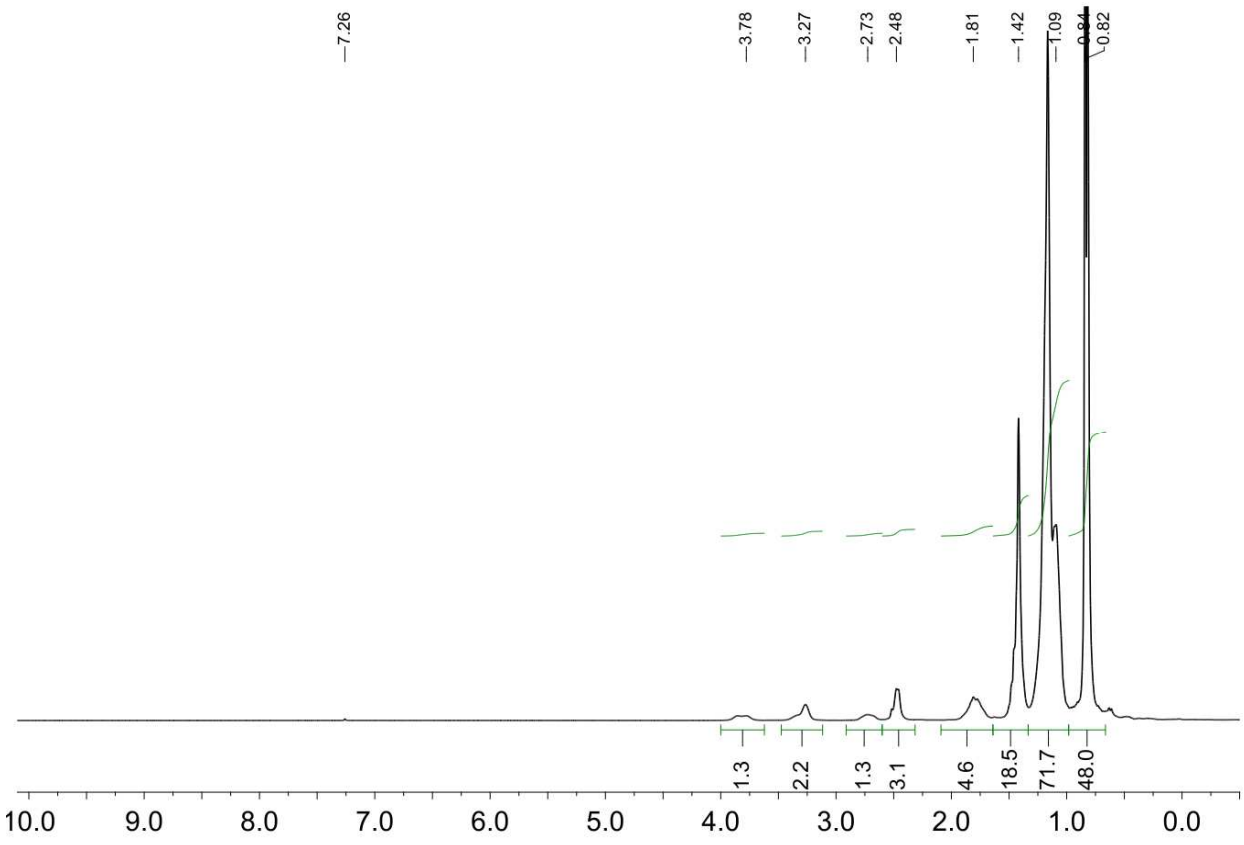


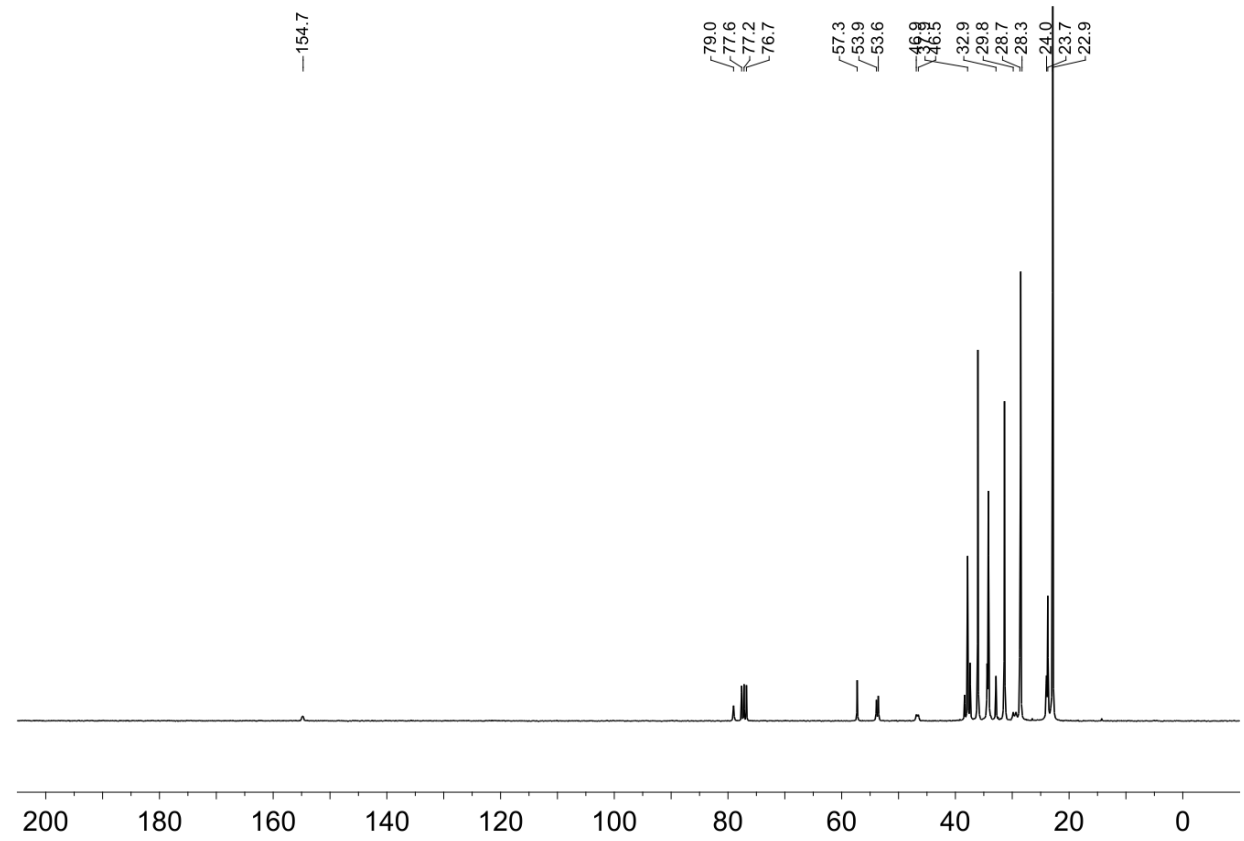
^{1}H and ^{13}C of compound **Boc-Mono-S-G2**



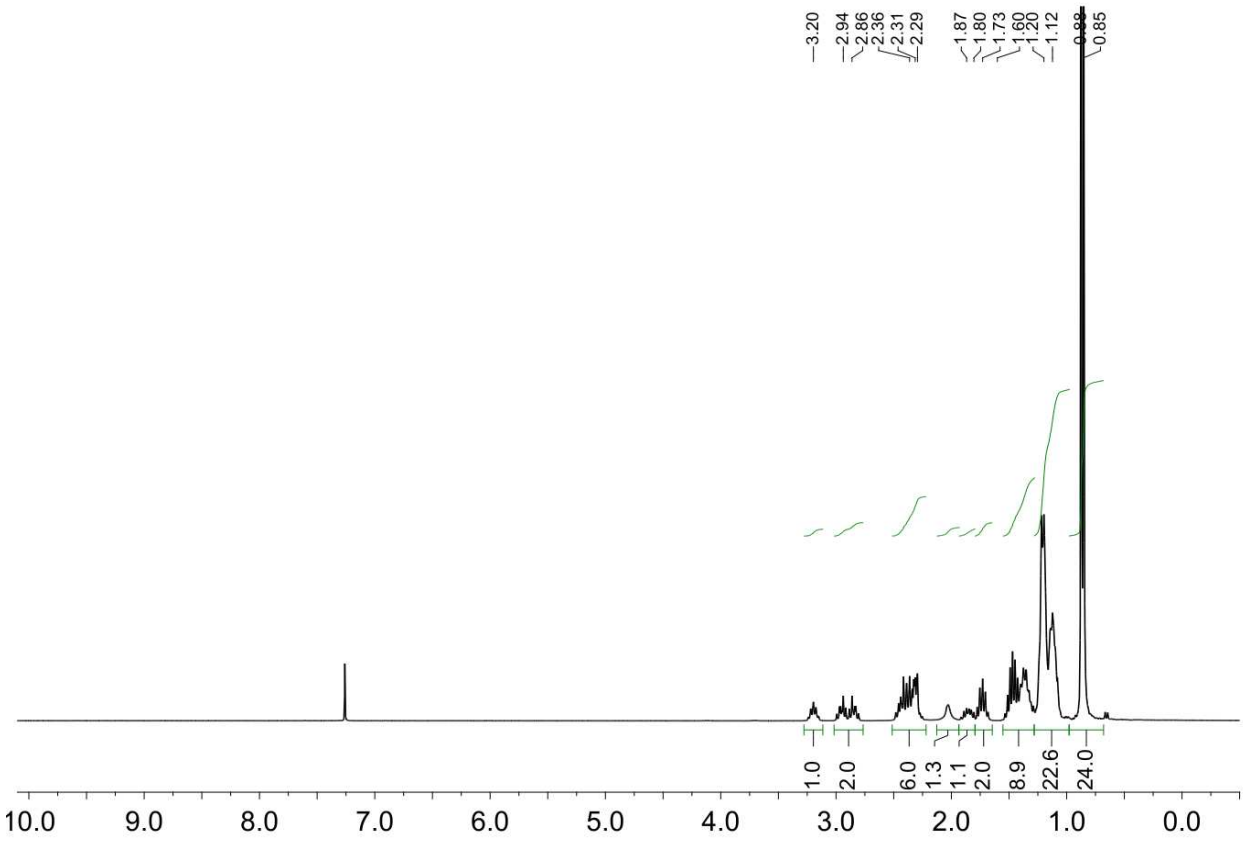


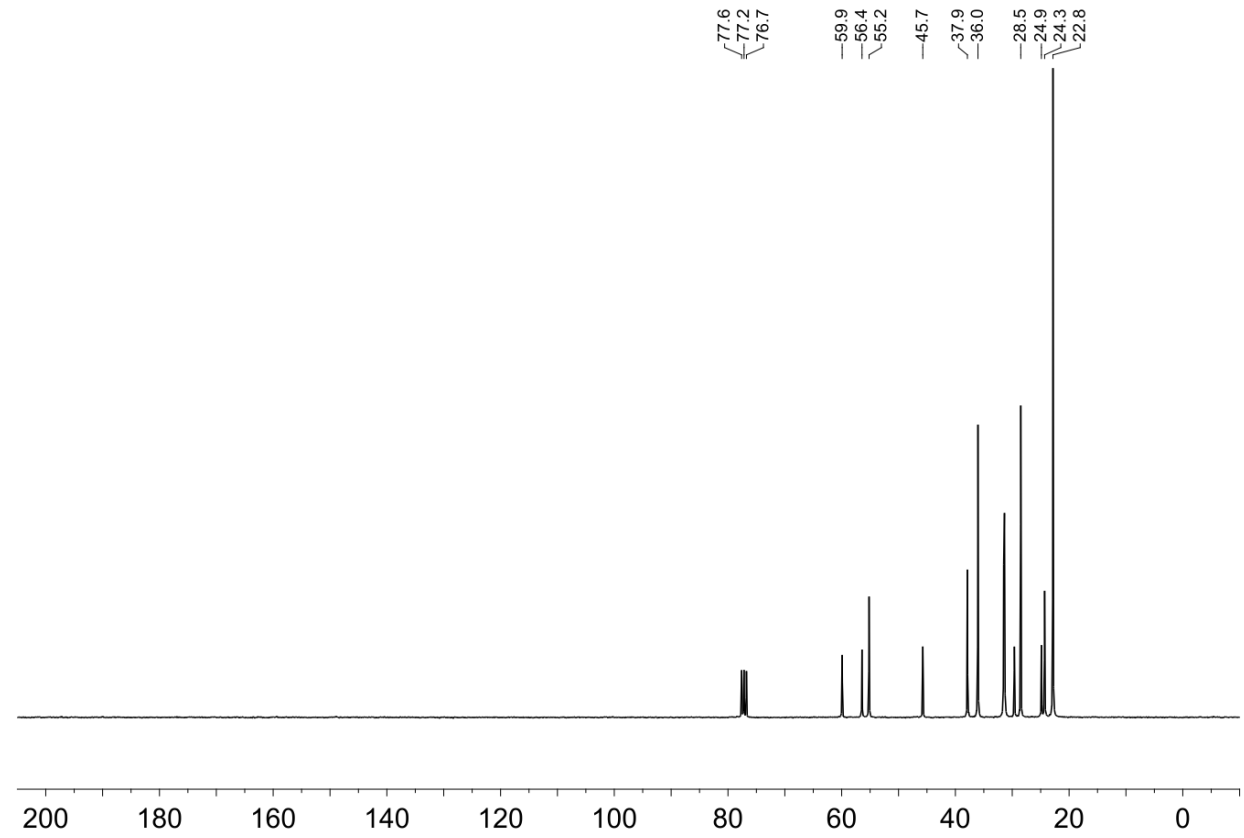
^{1}H and ^{13}C of compound **Boc-Mono-S-G3**



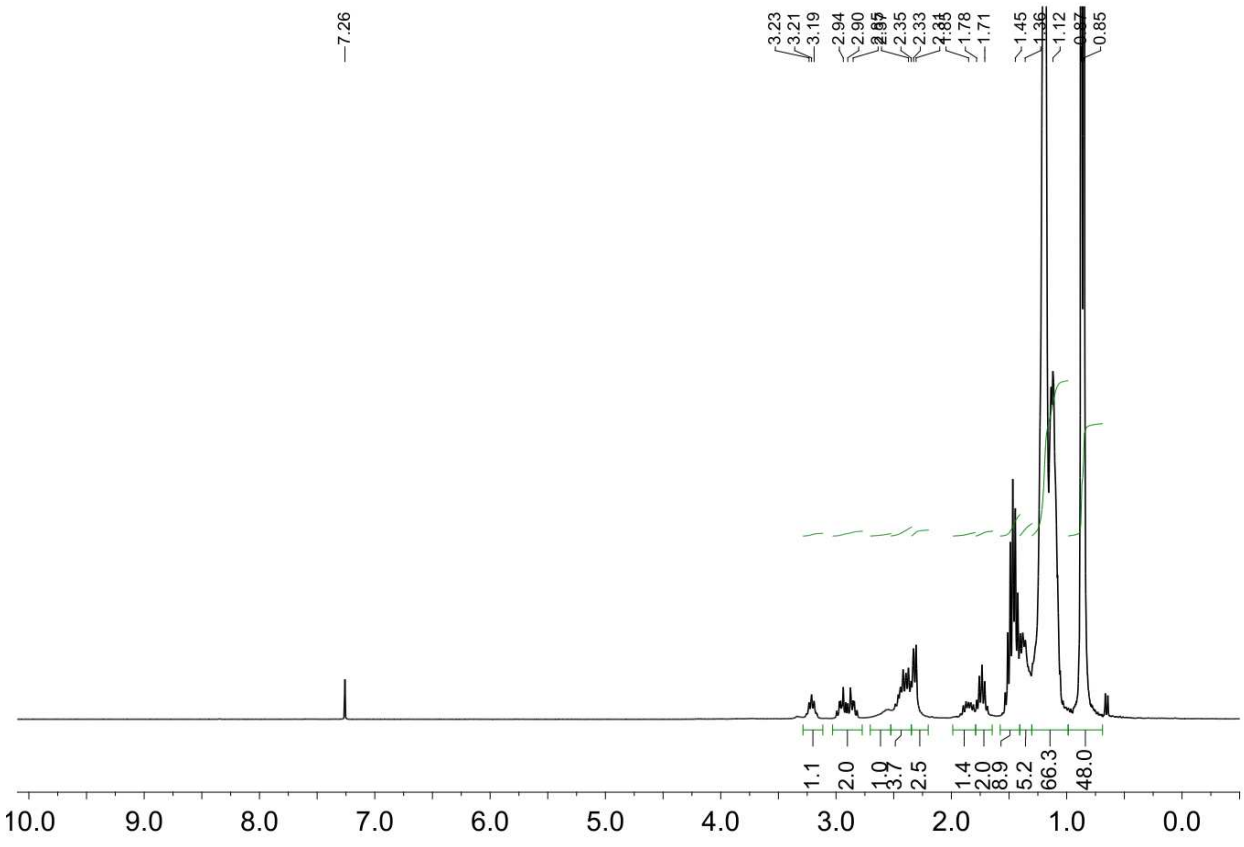


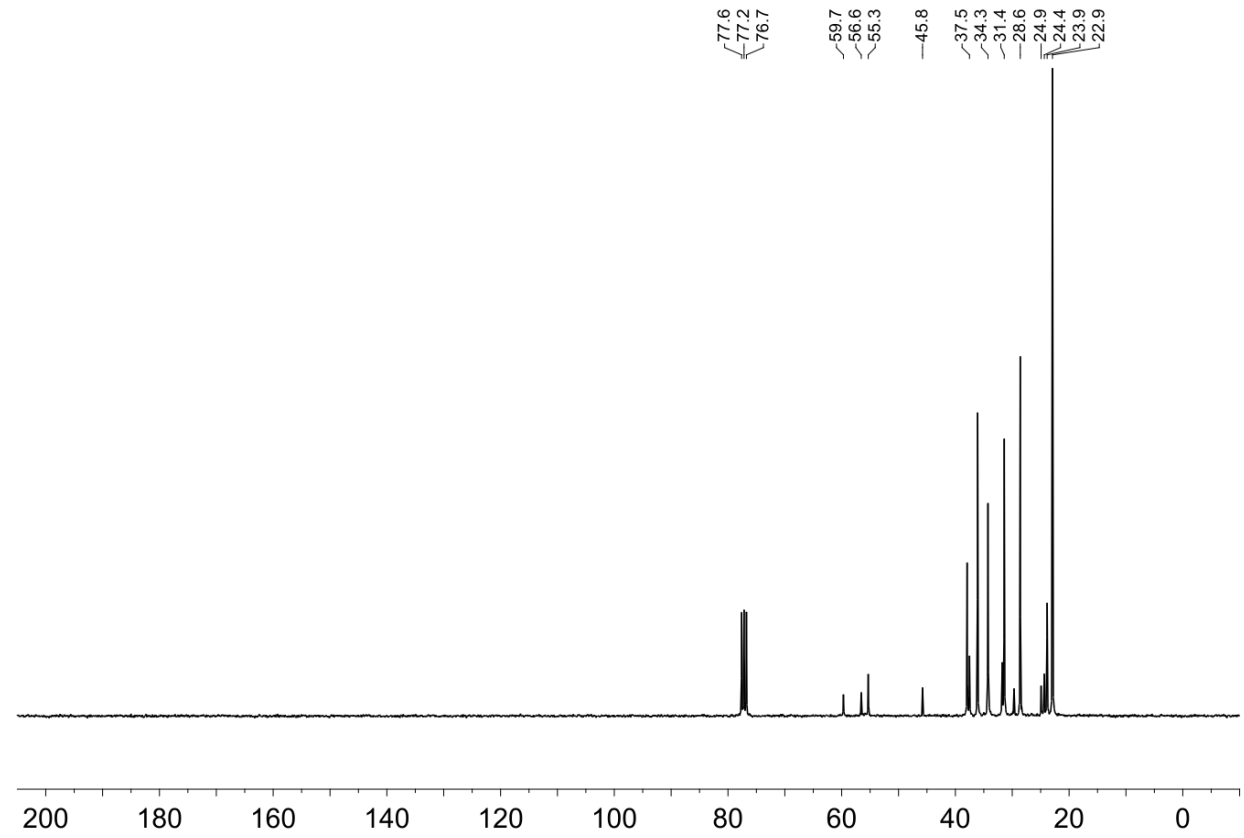
^{1}H and ^{13}C of compound **Di-L-G1**



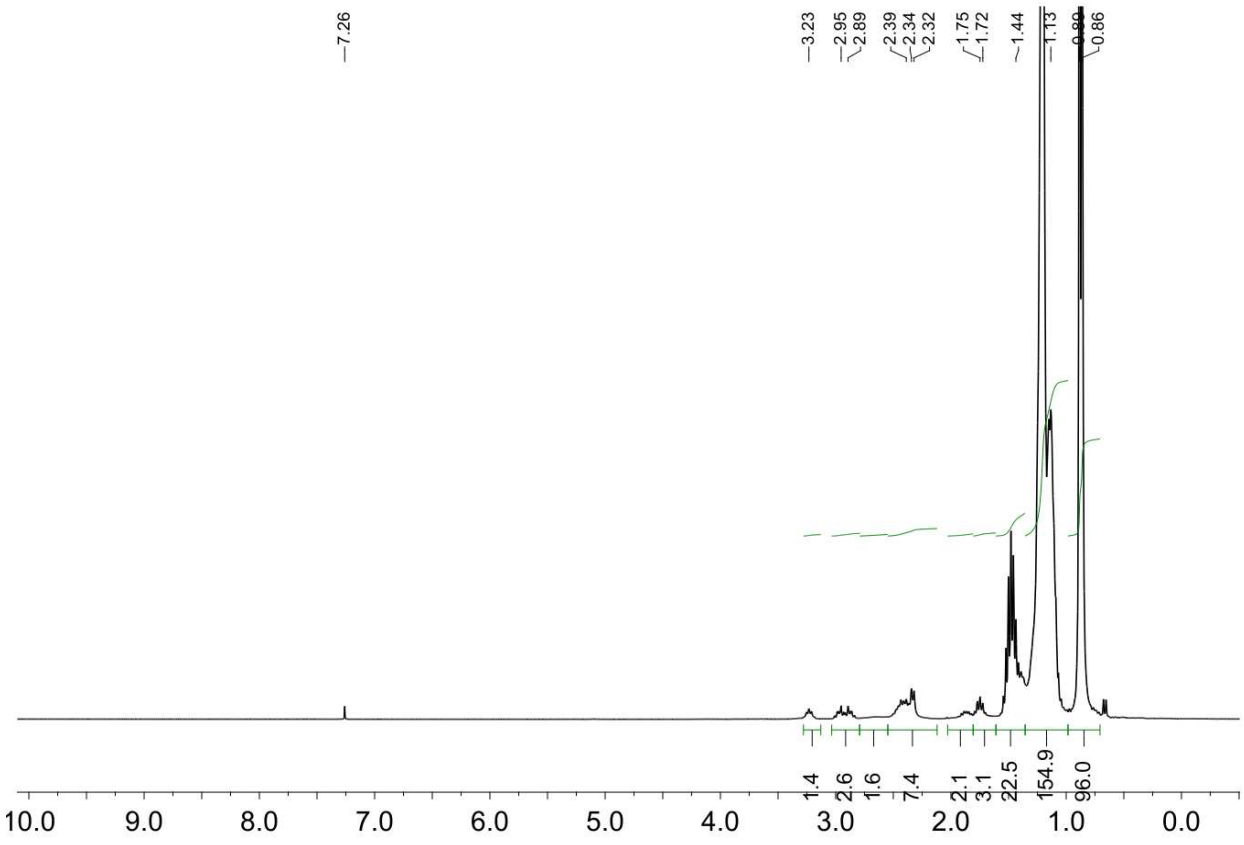


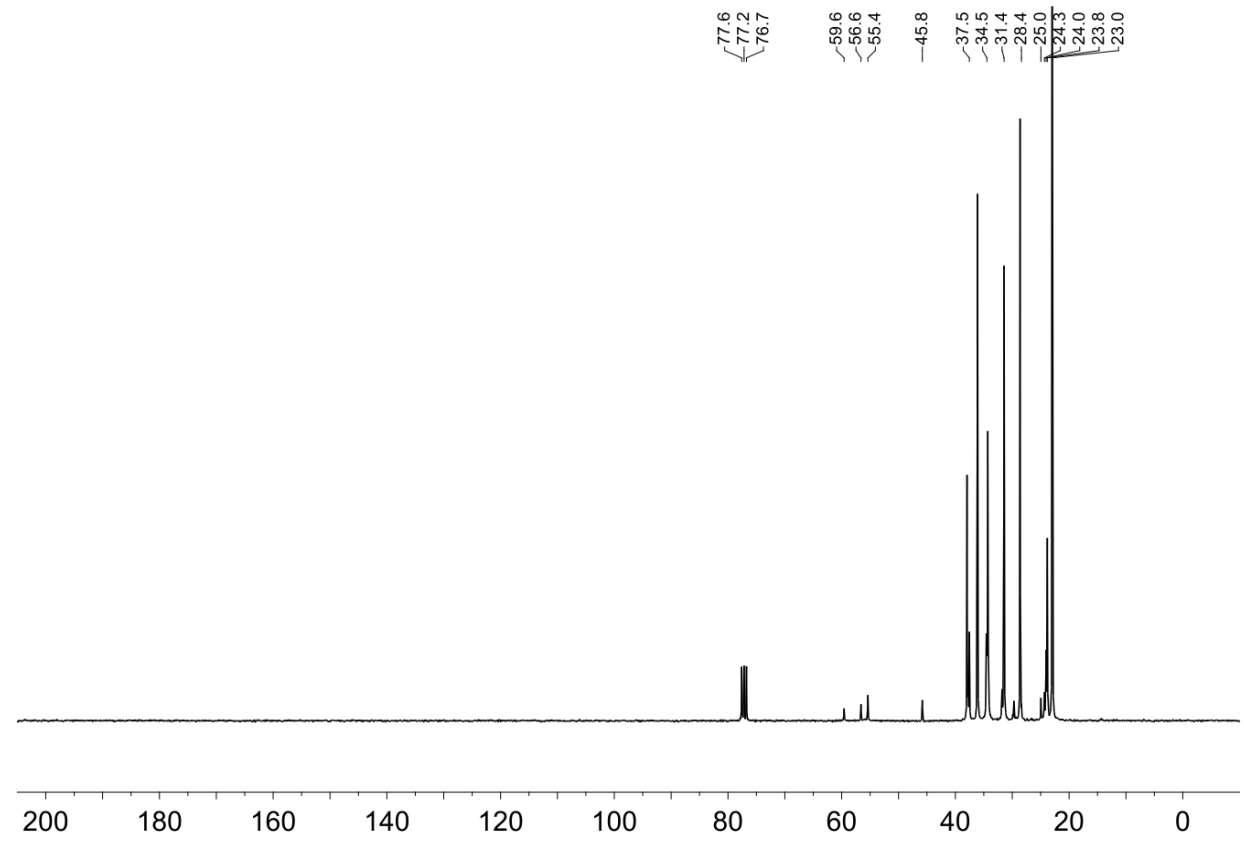
^{1}H and ^{13}C of compound **Di-L-G2**



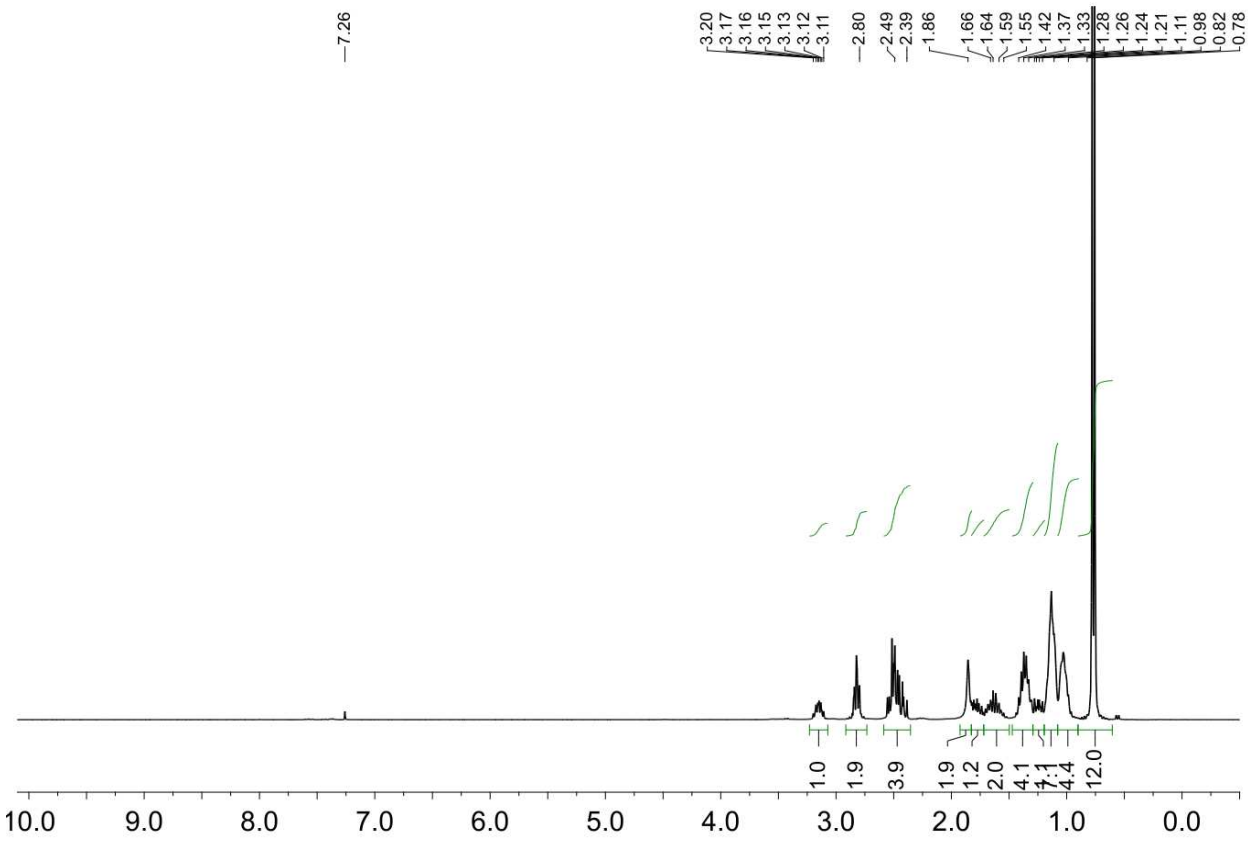


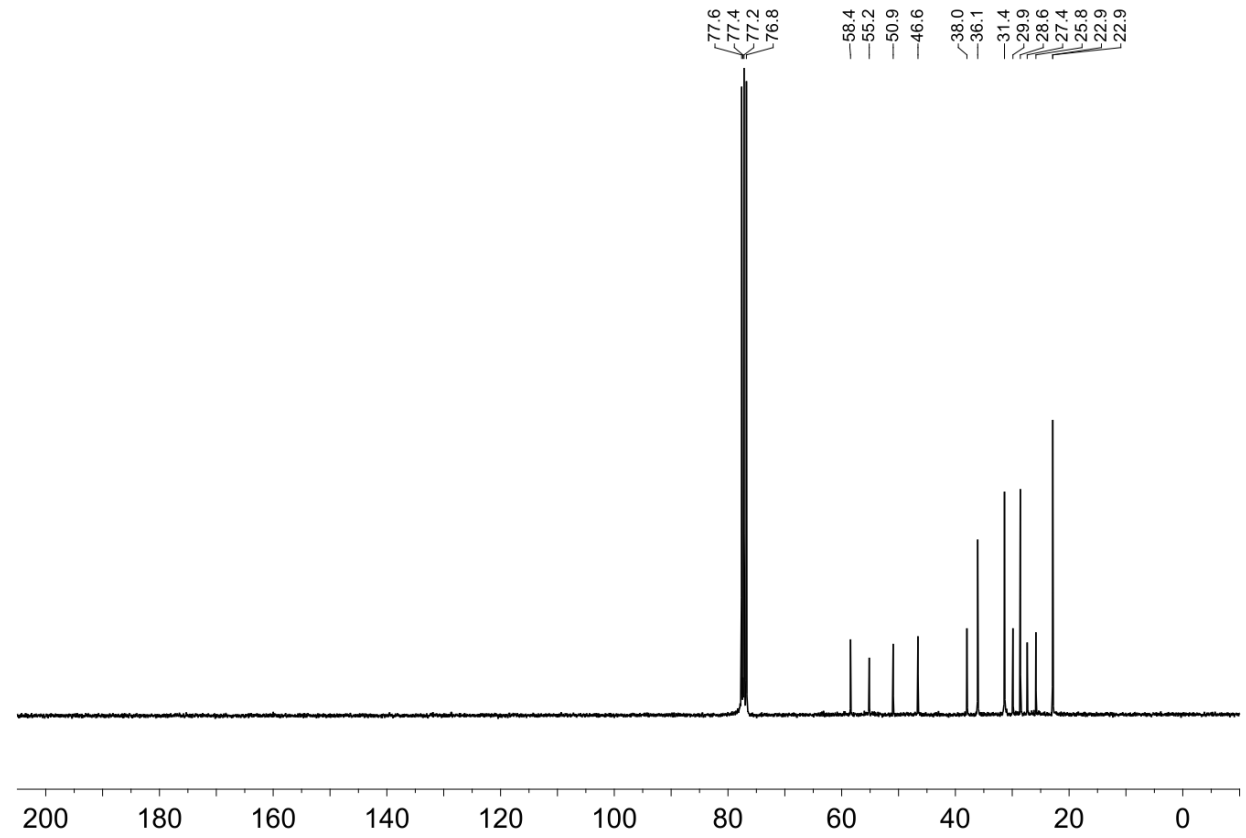
^{1}H and ^{13}C of compound **Di-L-G3**



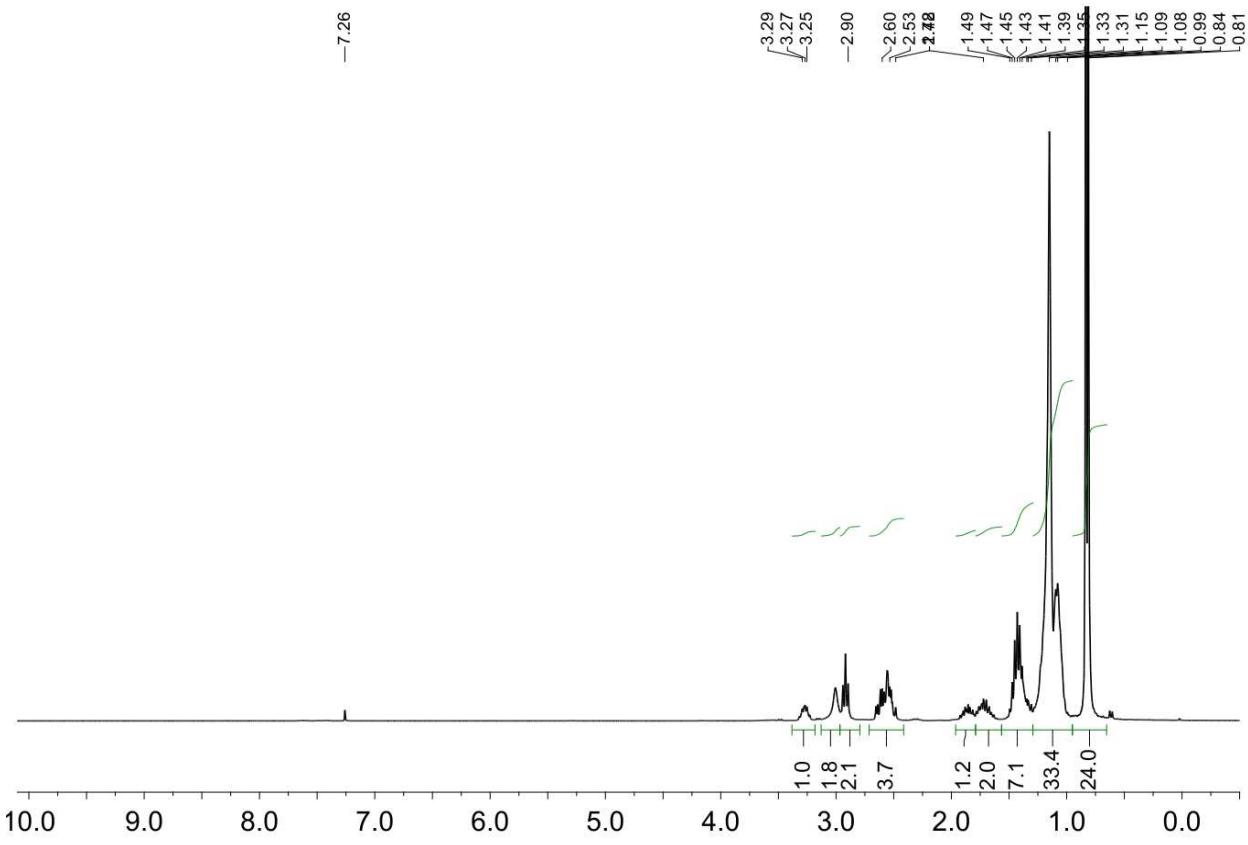


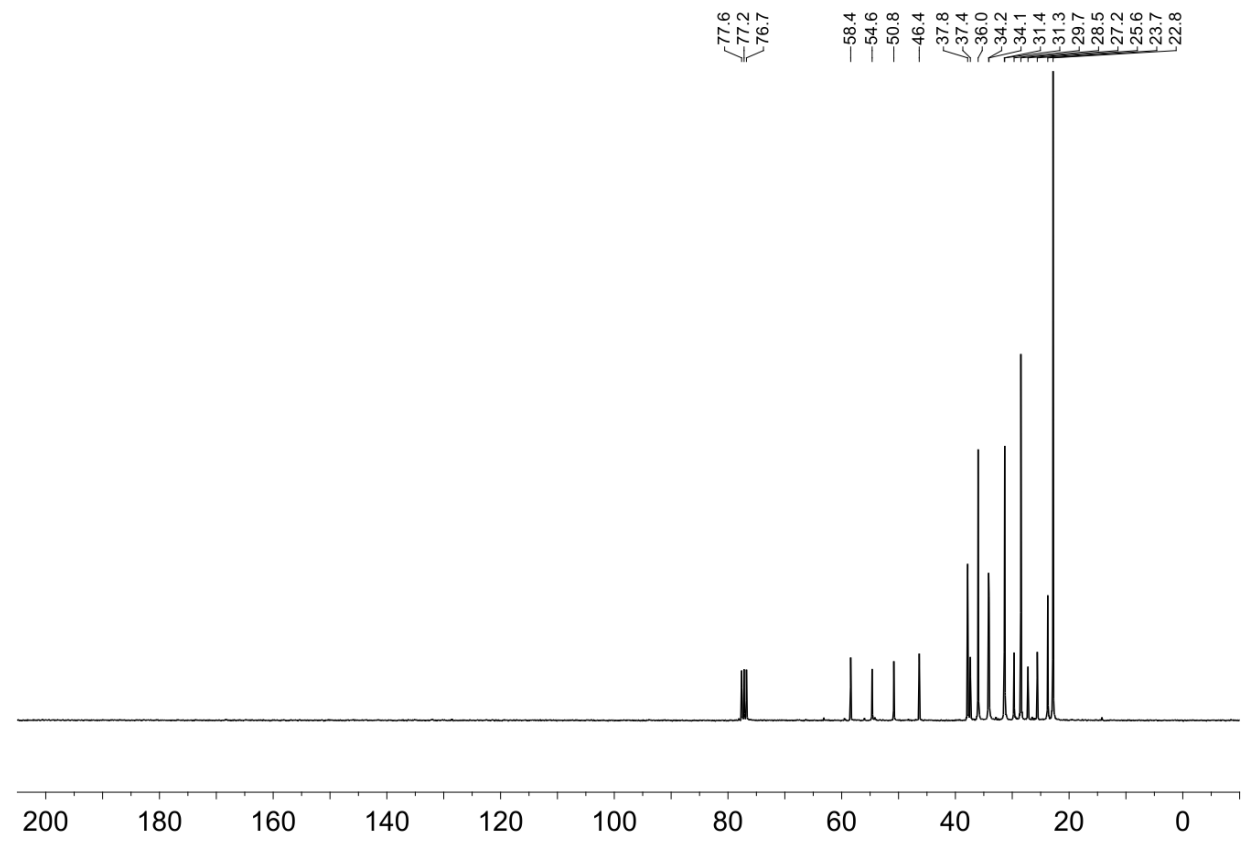
^{1}H and ^{13}C of compound **Mono-L-G1**



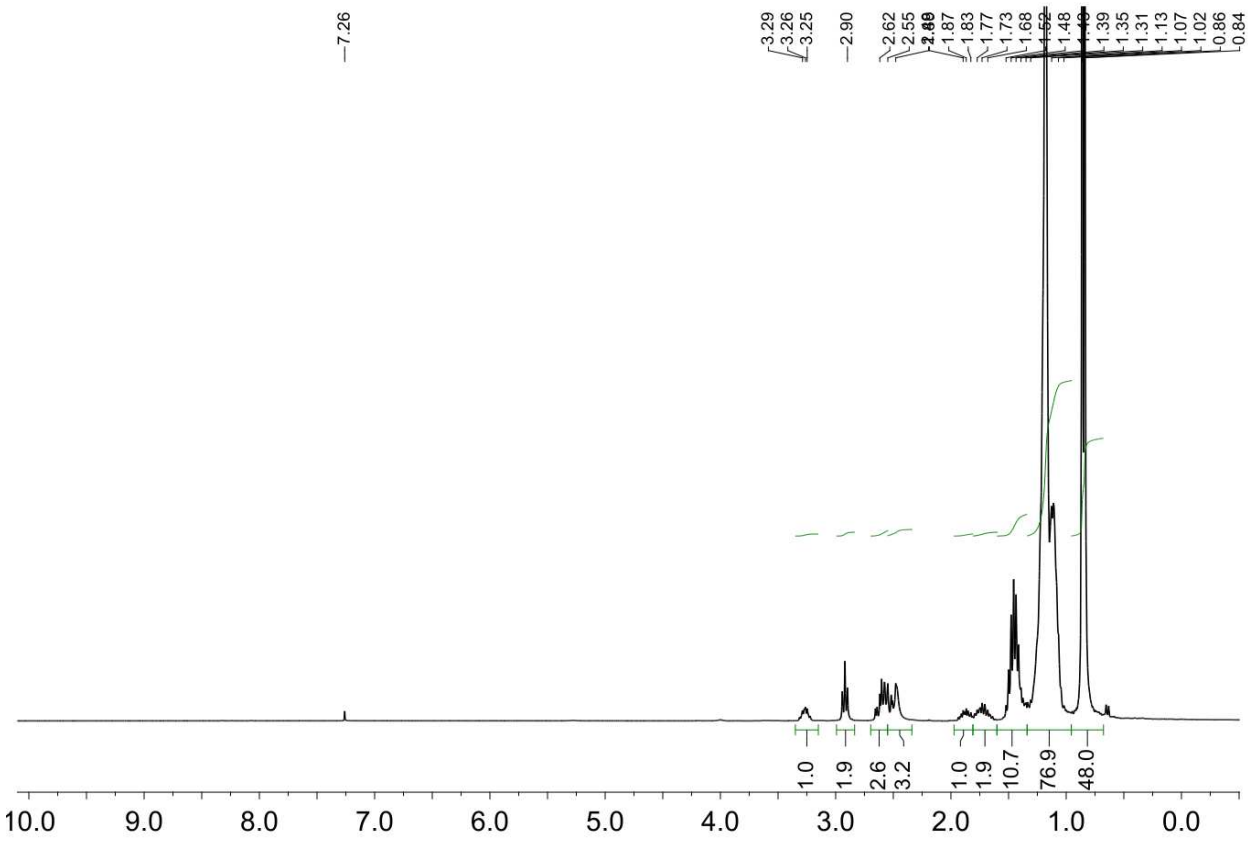


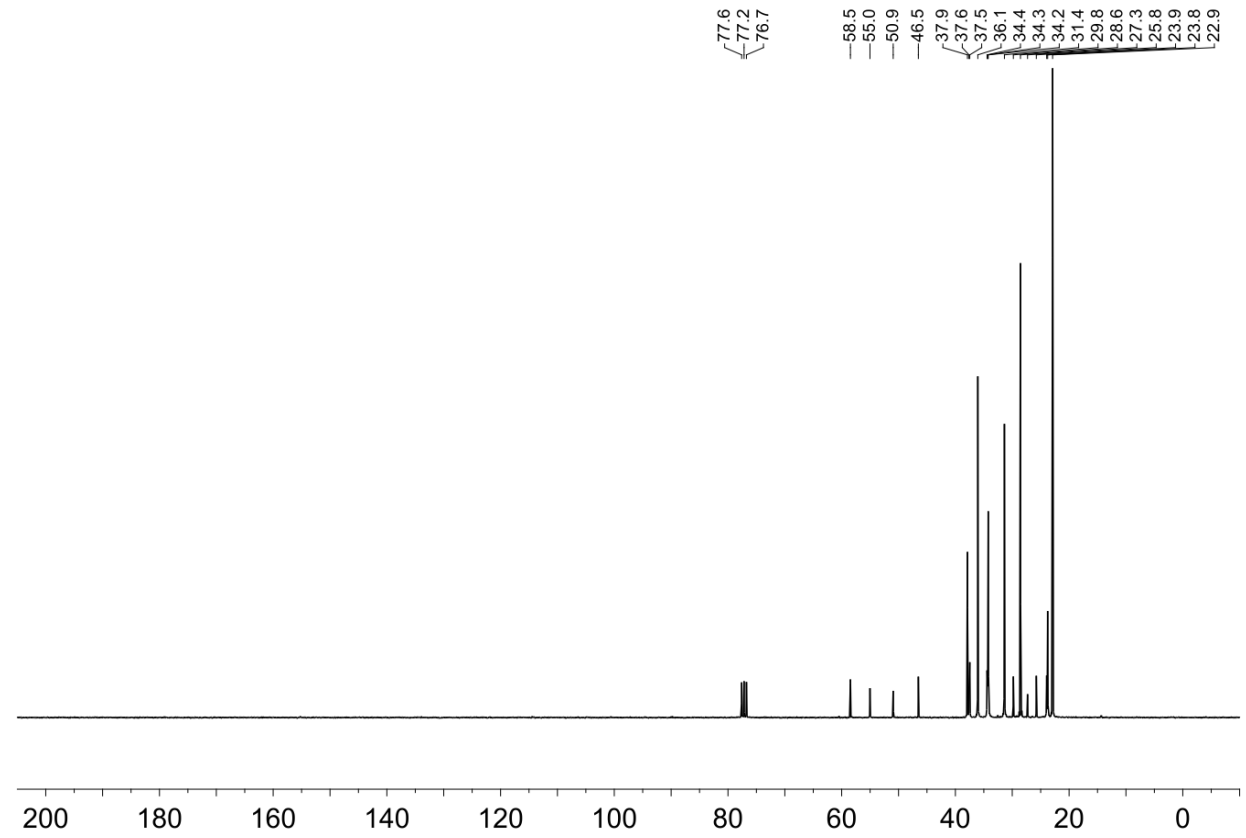
^{1}H and ^{13}C of compound **Mono-L-G2**



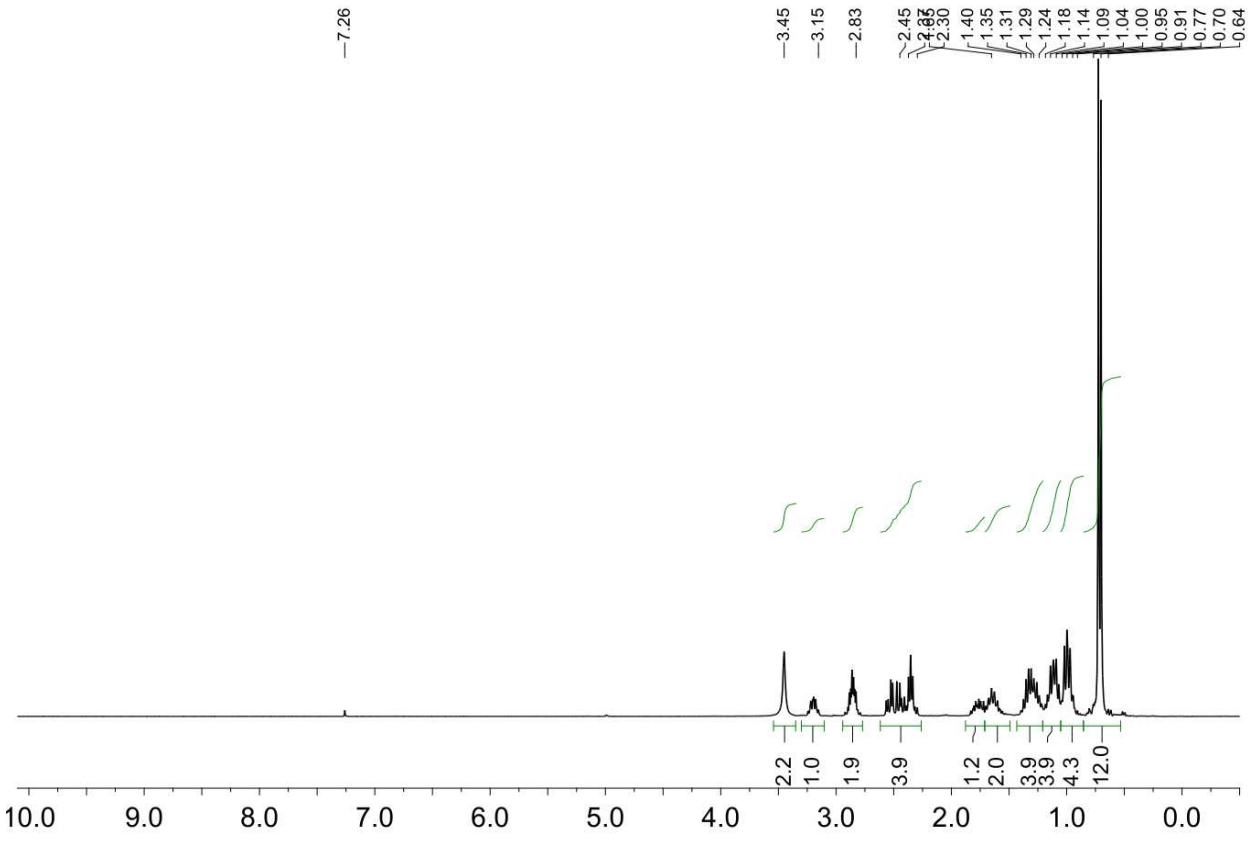


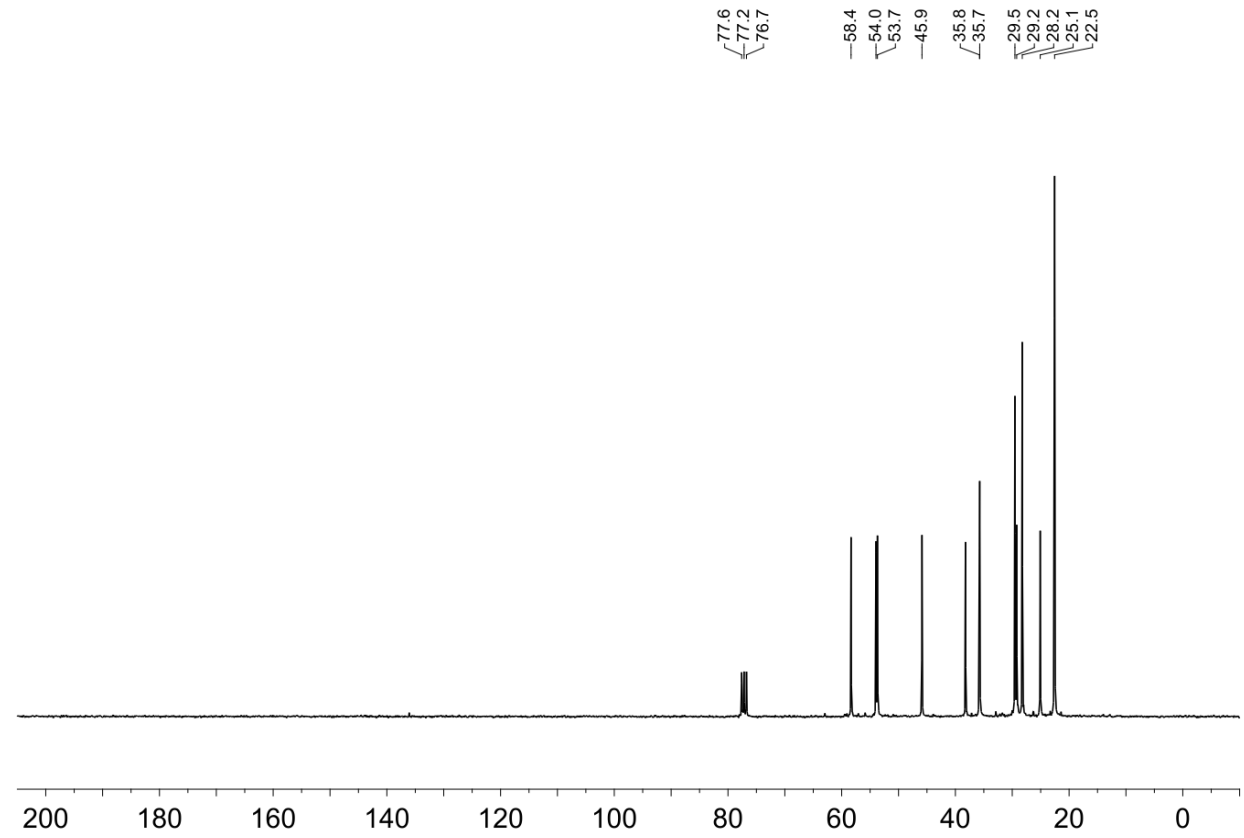
^{1}H and ^{13}C of compound **Mono-L-G3**



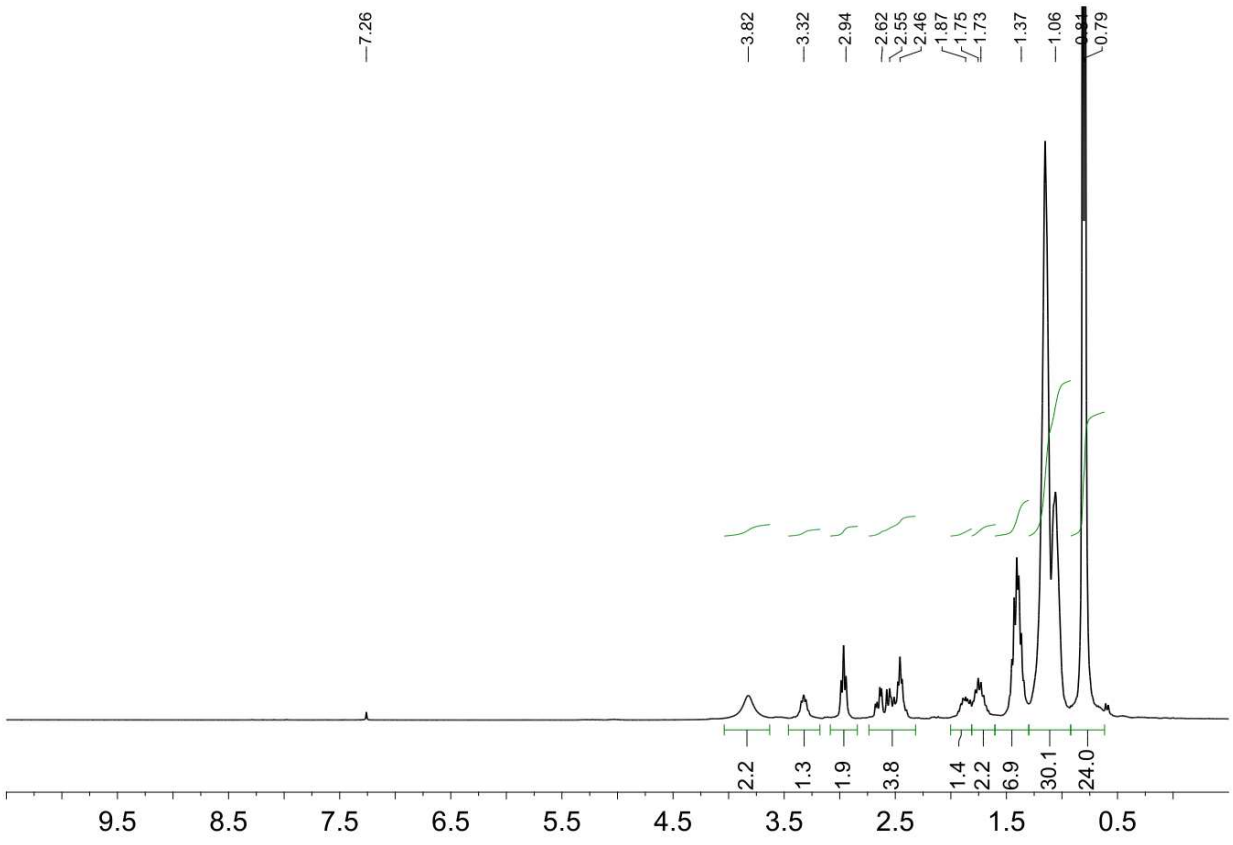


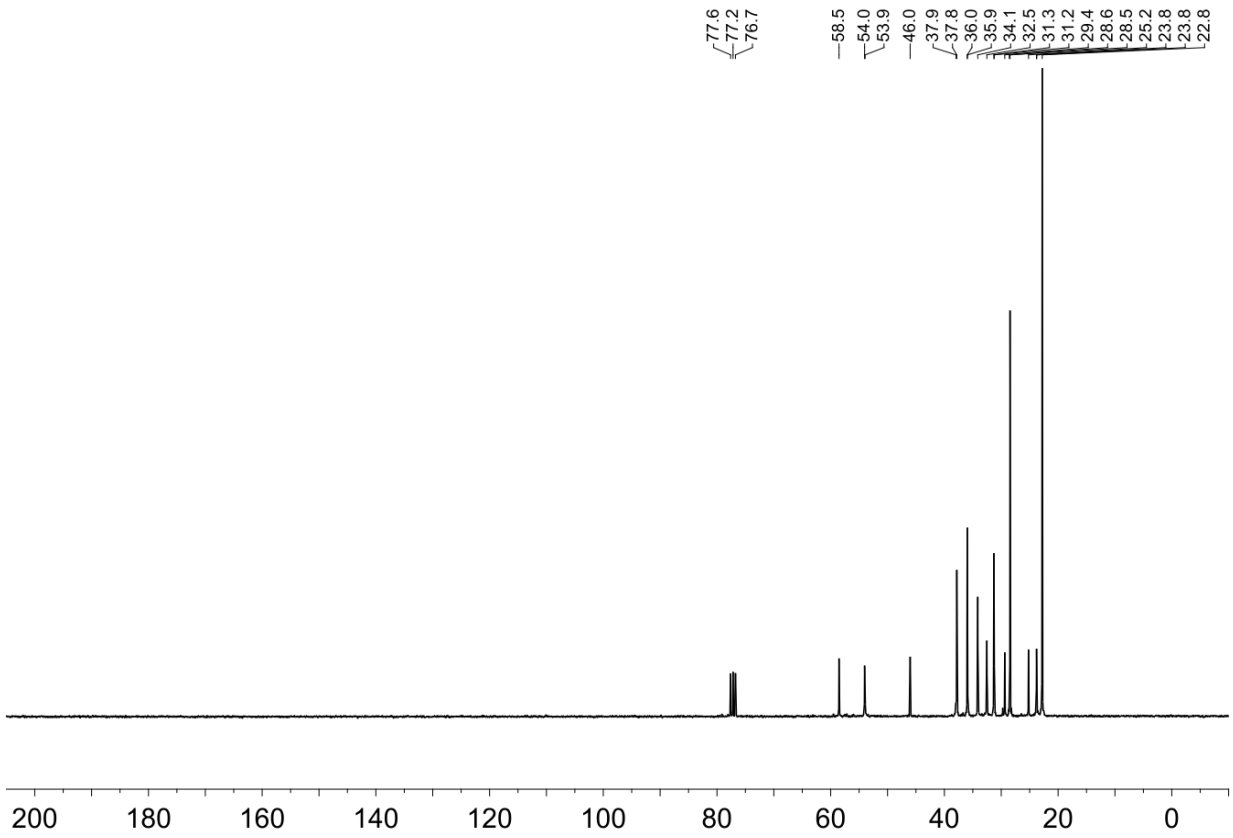
^{1}H and ^{13}C of compound **Mono-S-G1**



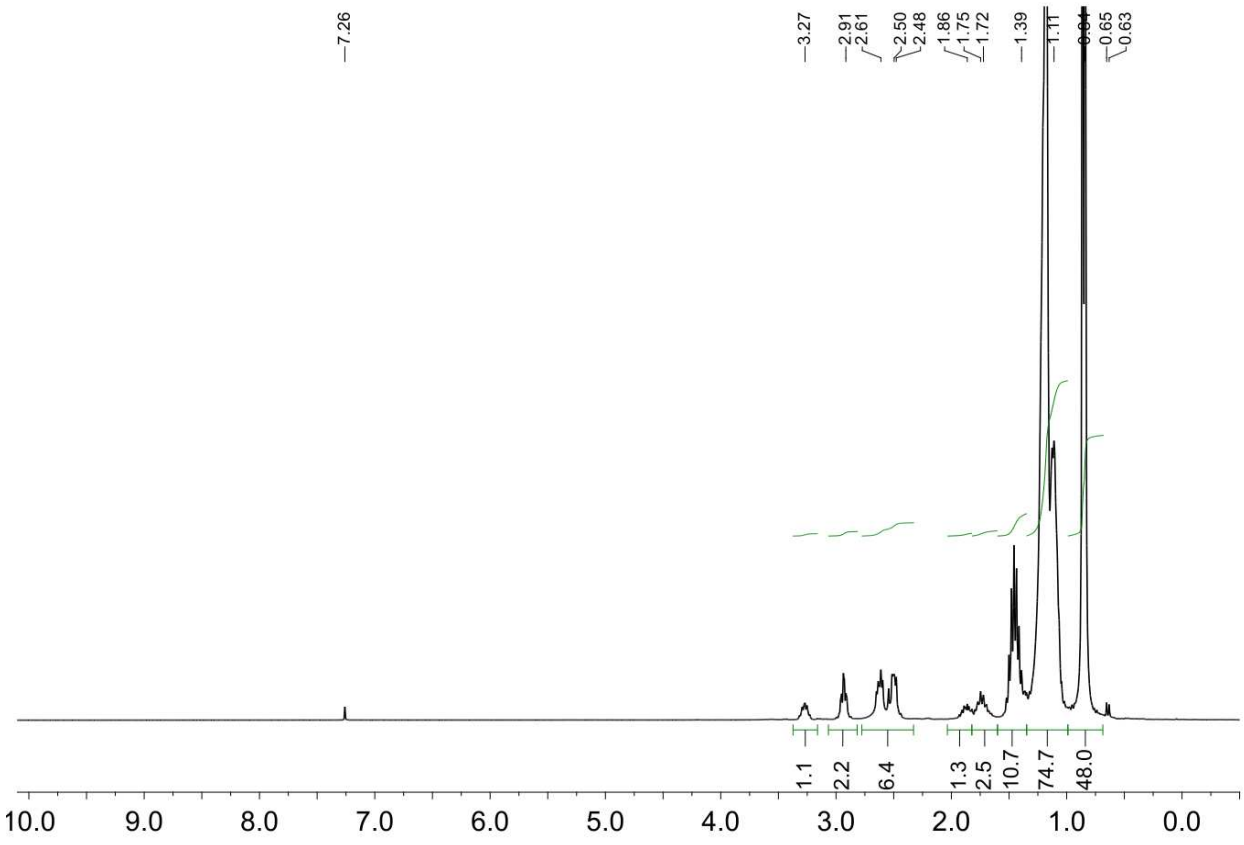


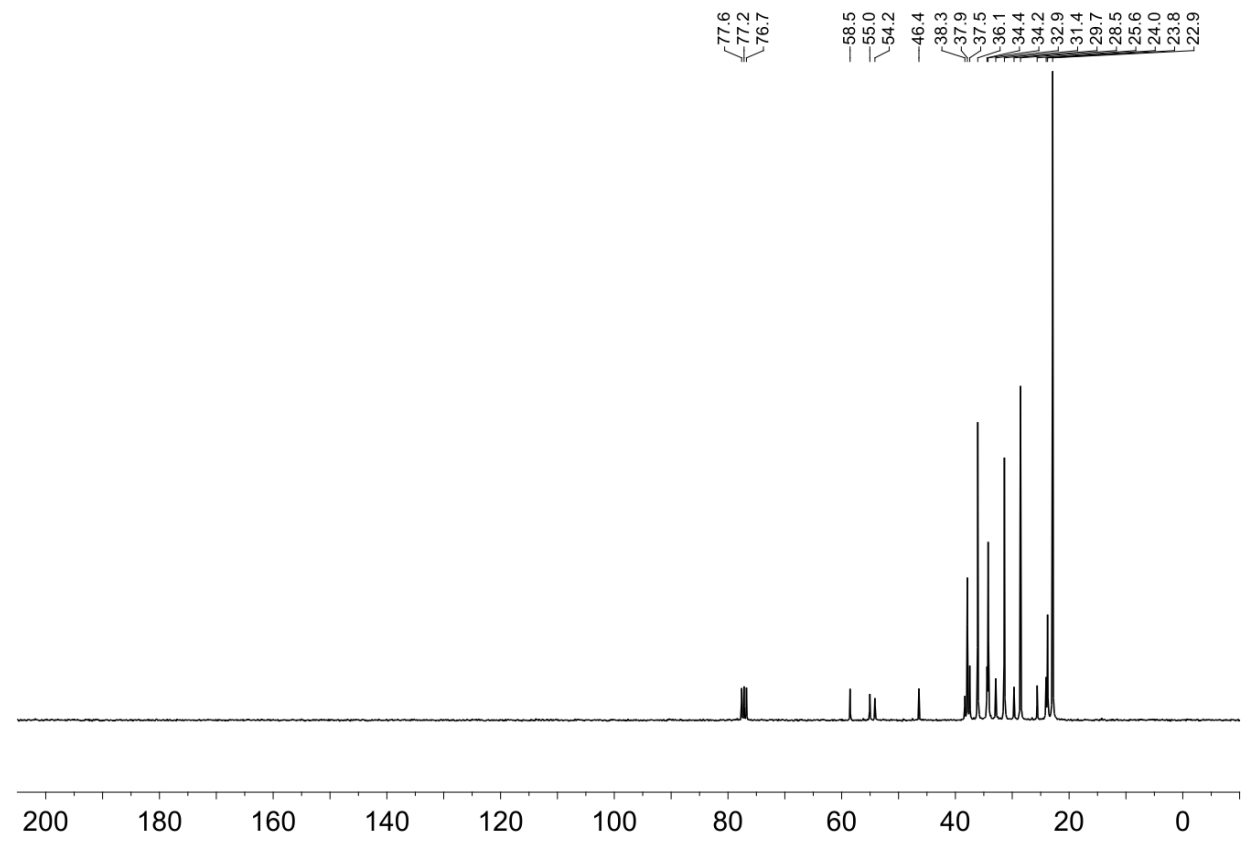
^{1}H and ^{13}C of compound **Mono-S-G2**



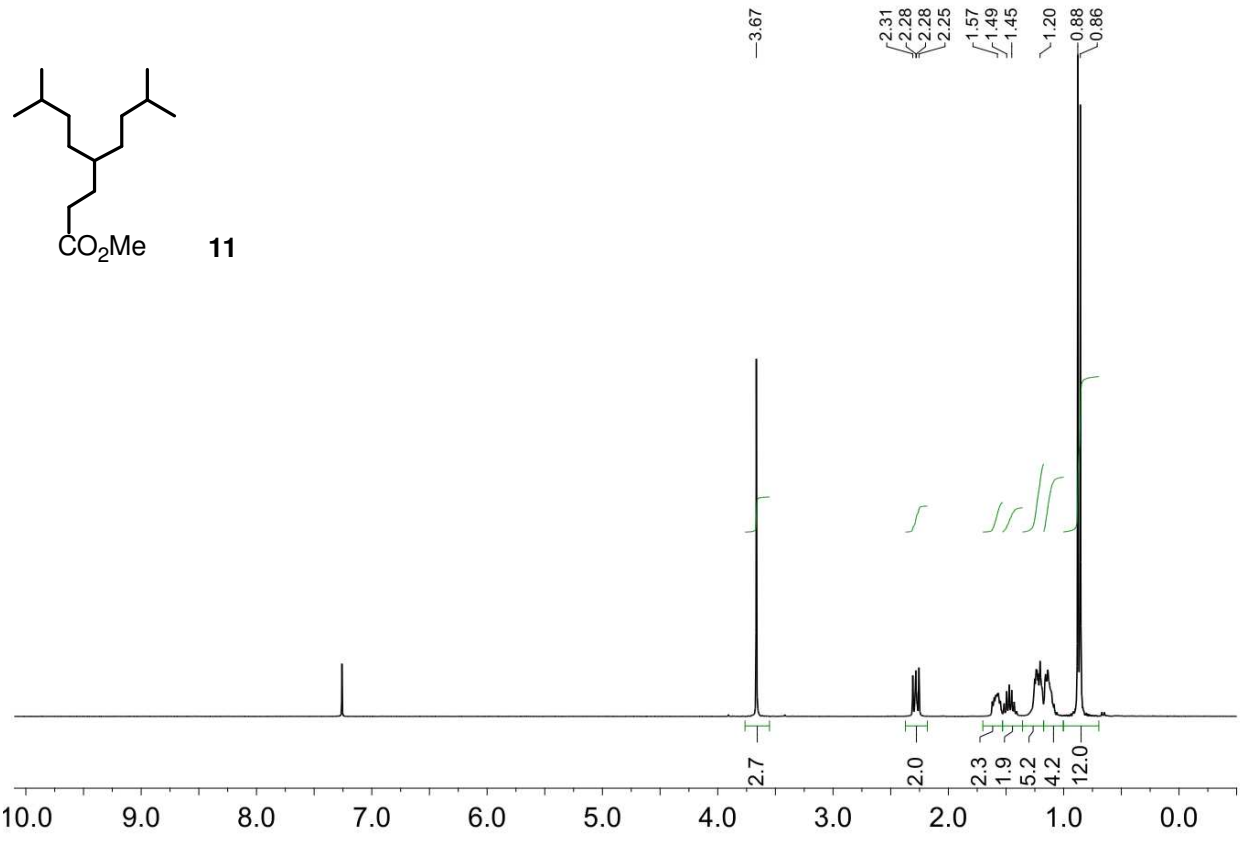


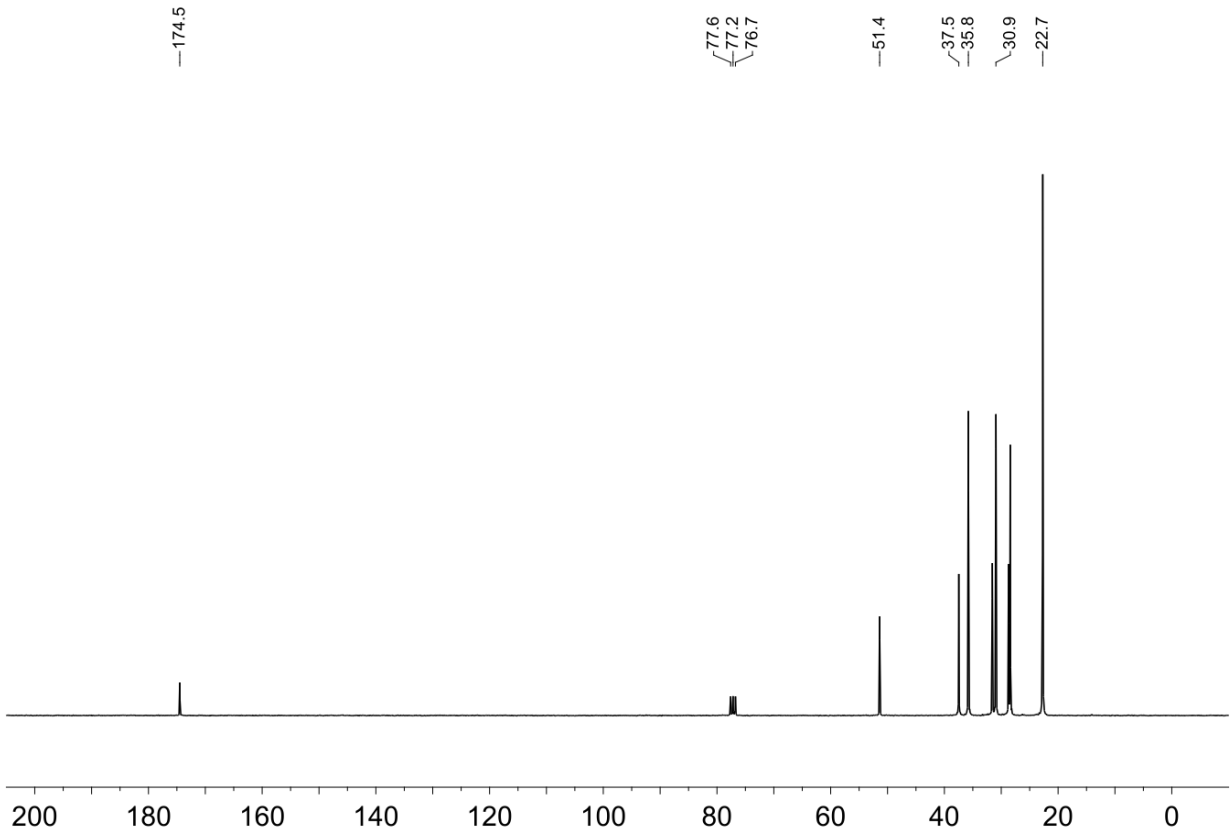
^{1}H and ^{13}C of compound **Mono-S-G3**



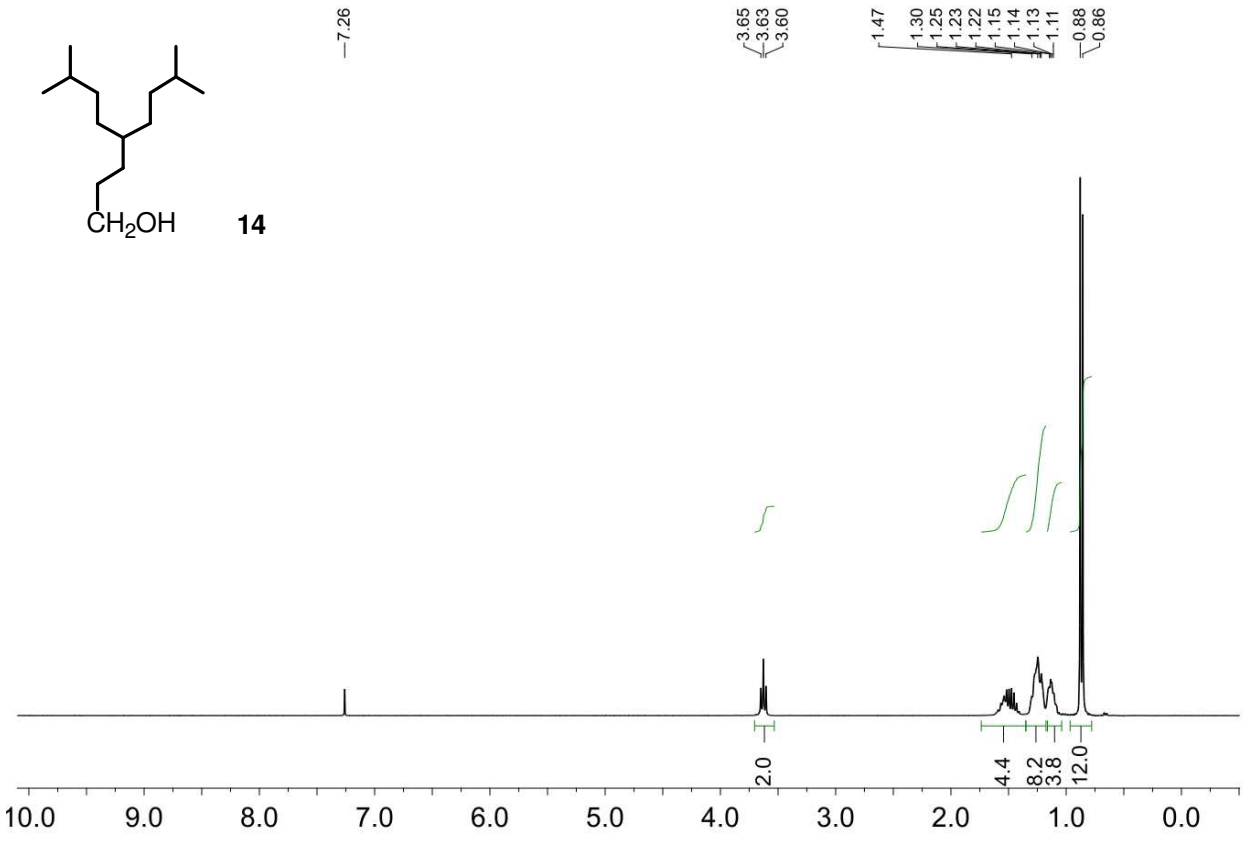


^{1}H and ^{13}C of compound **11**

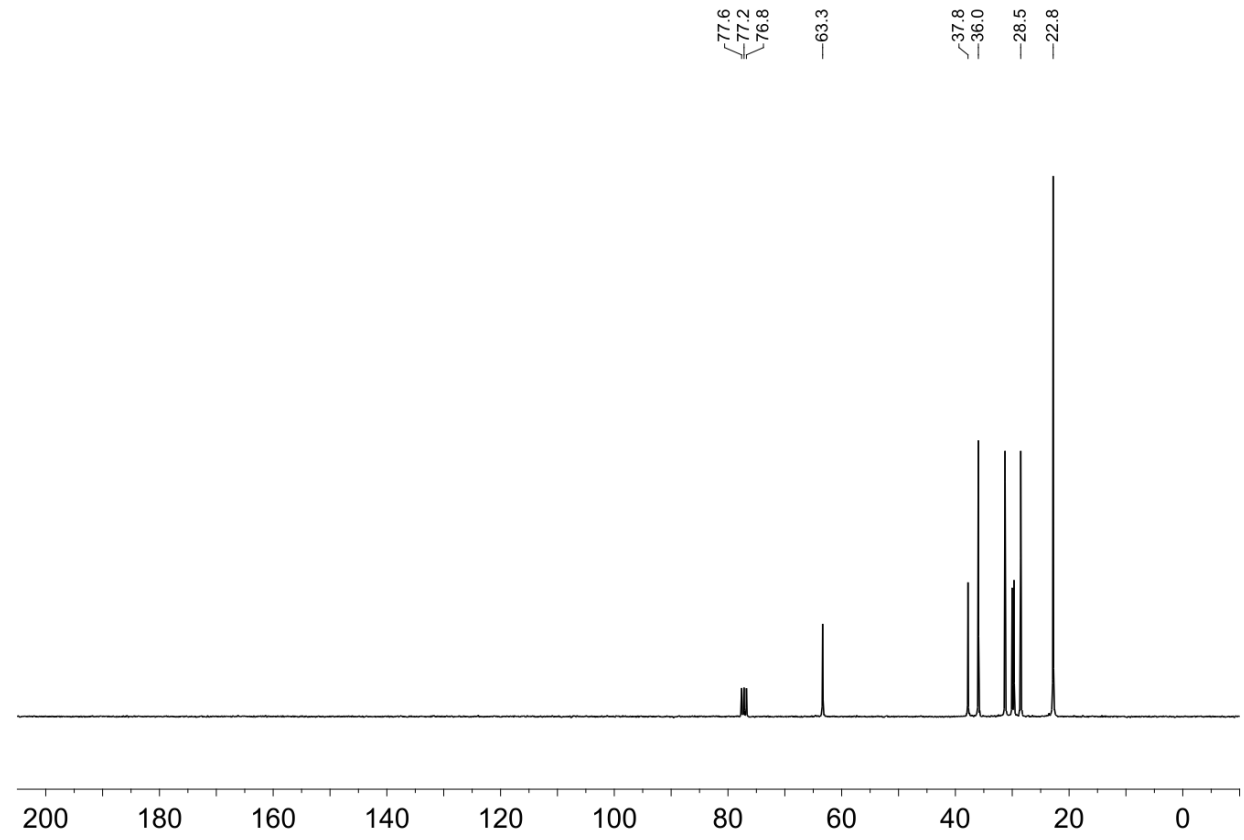




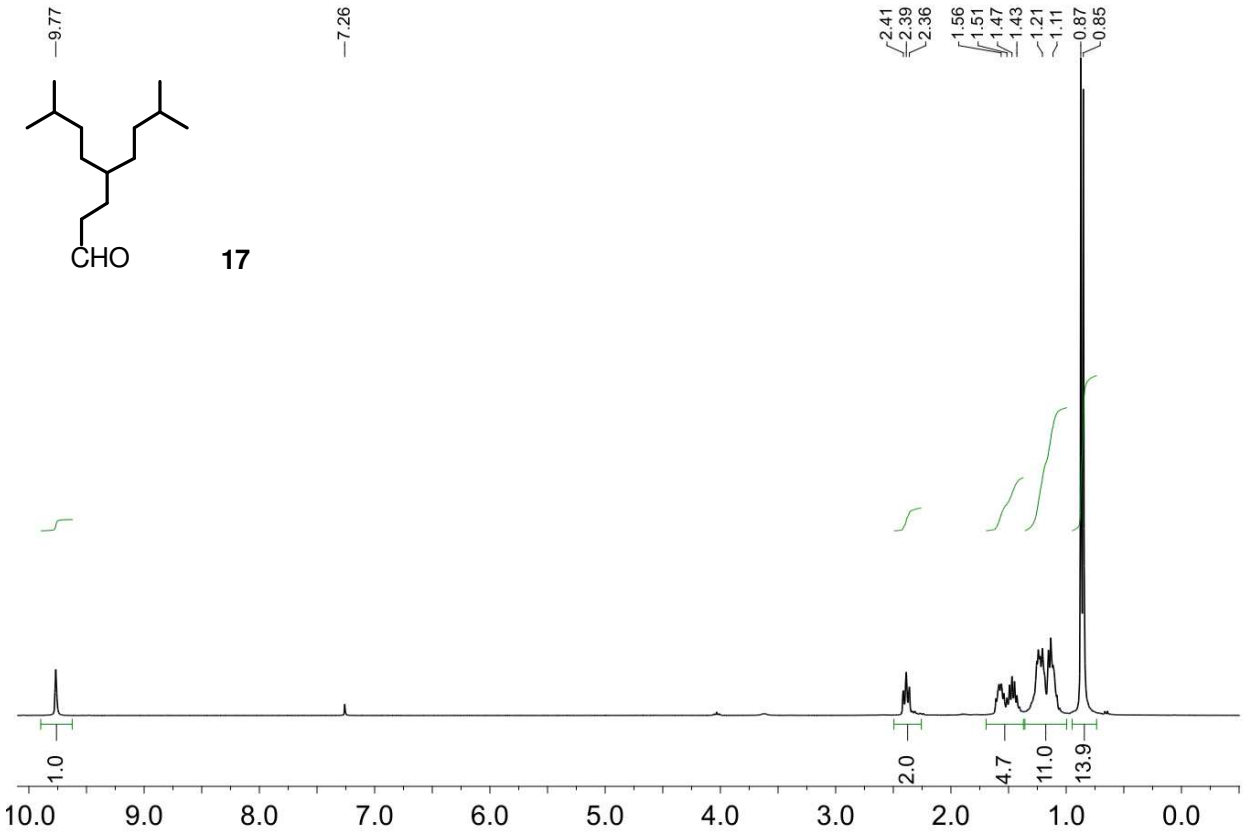
^{1}H and ^{13}C of compound **14**

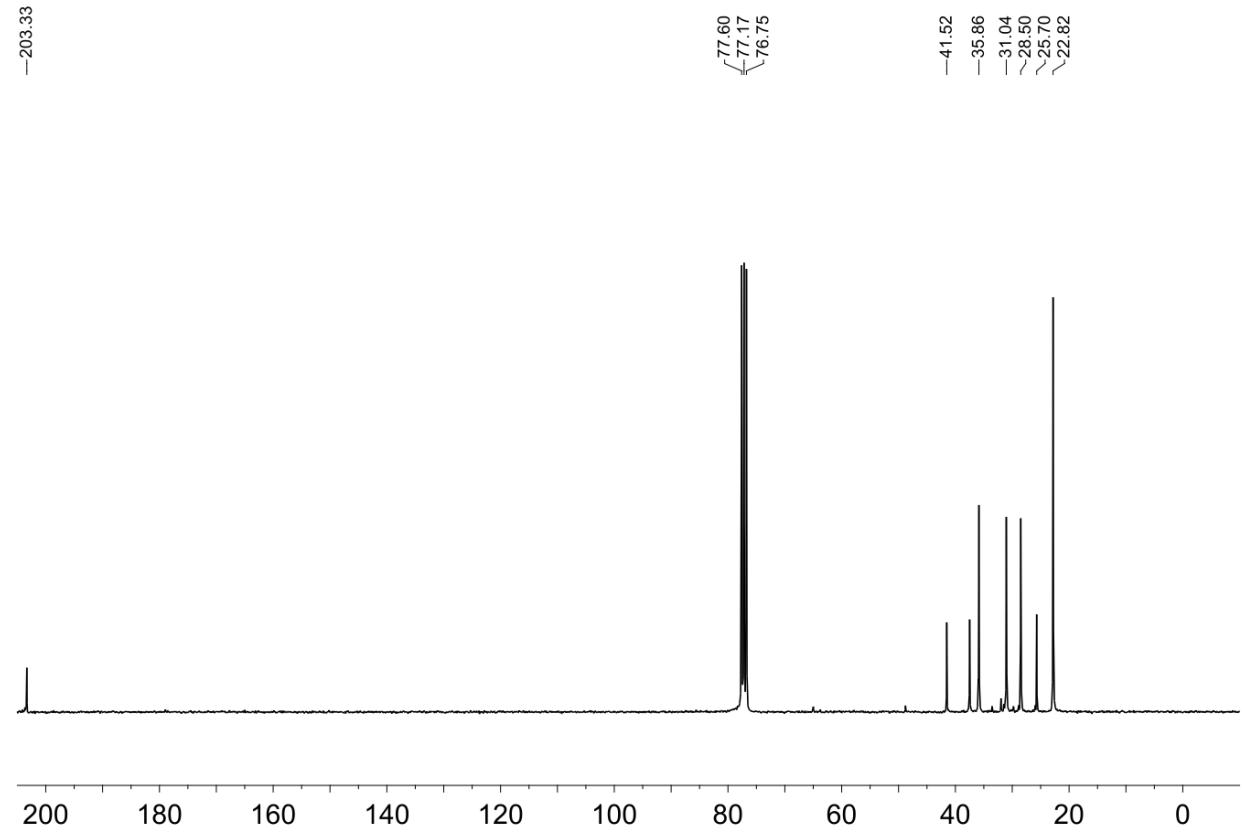


14

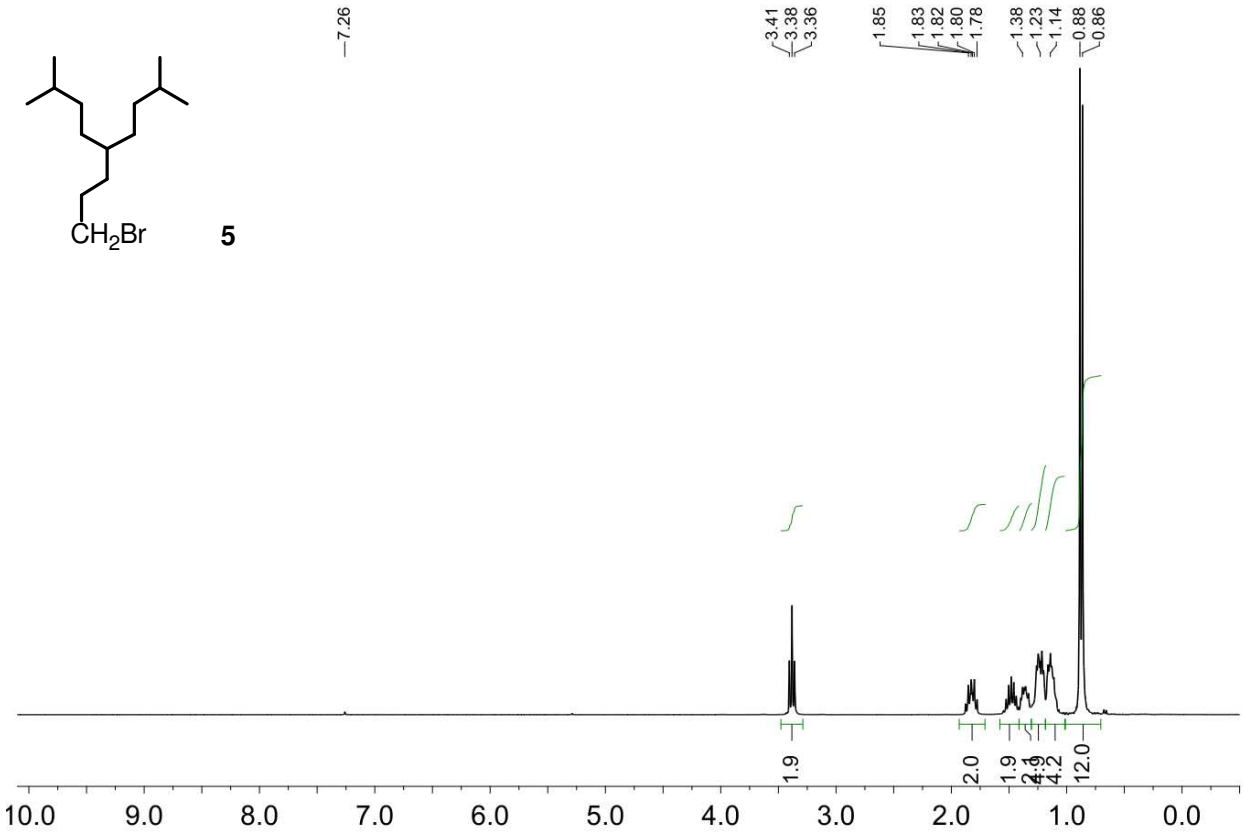


^{1}H and ^{13}C of compound **17**

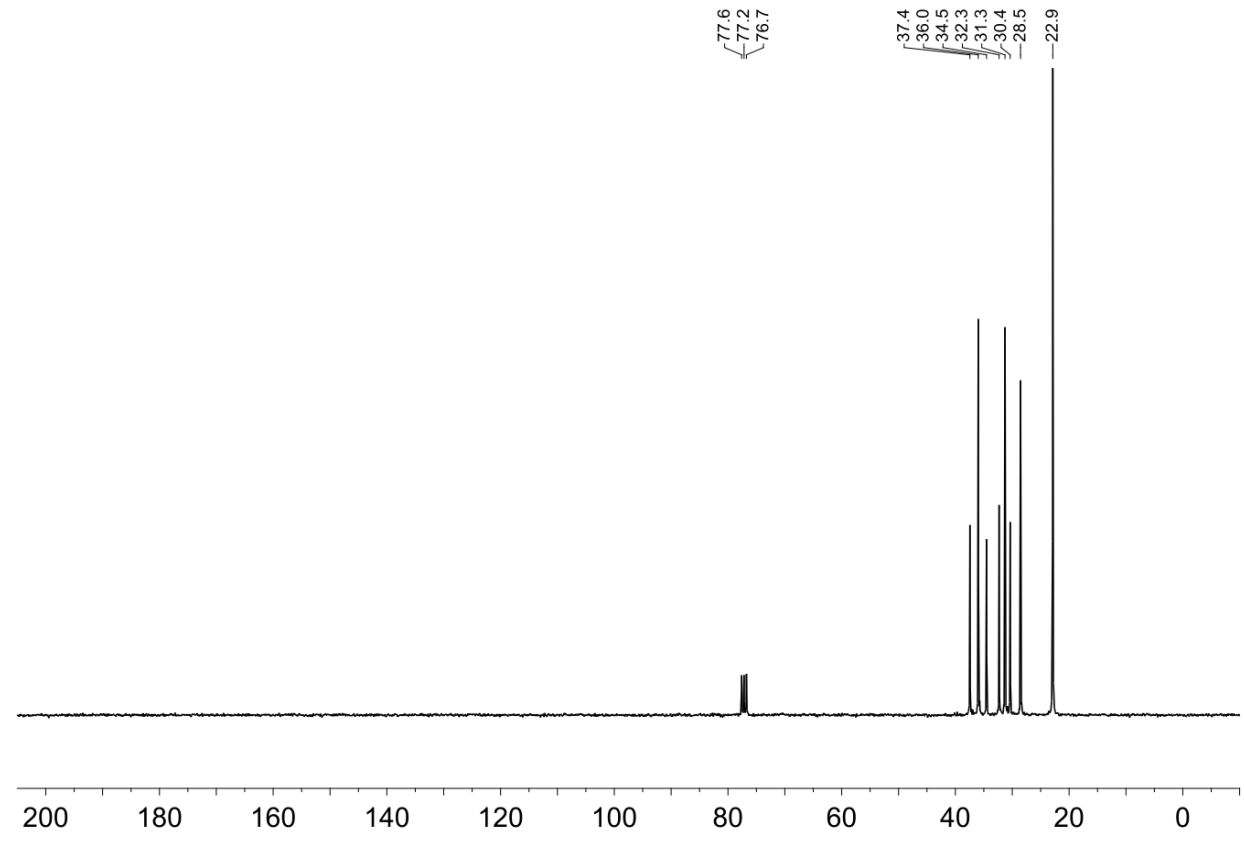




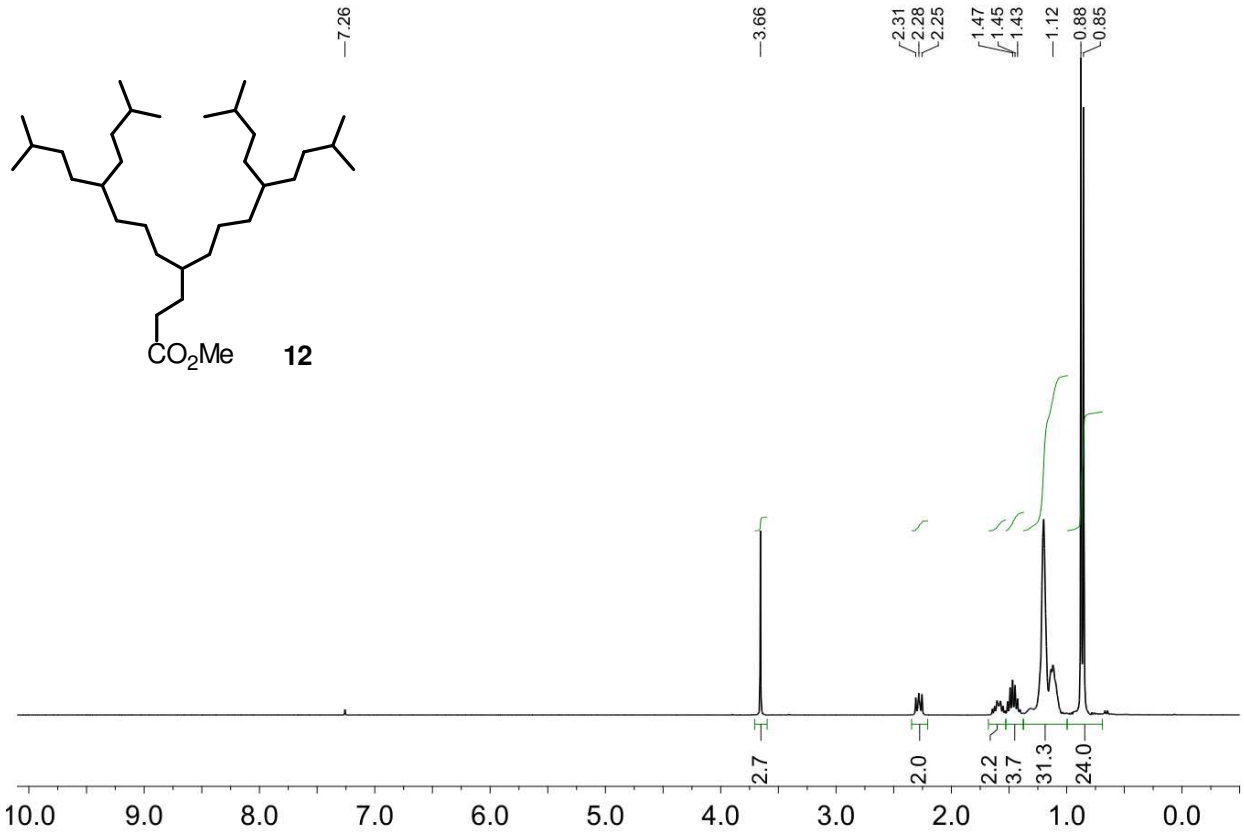
^{1}H and ^{13}C of compound **5**

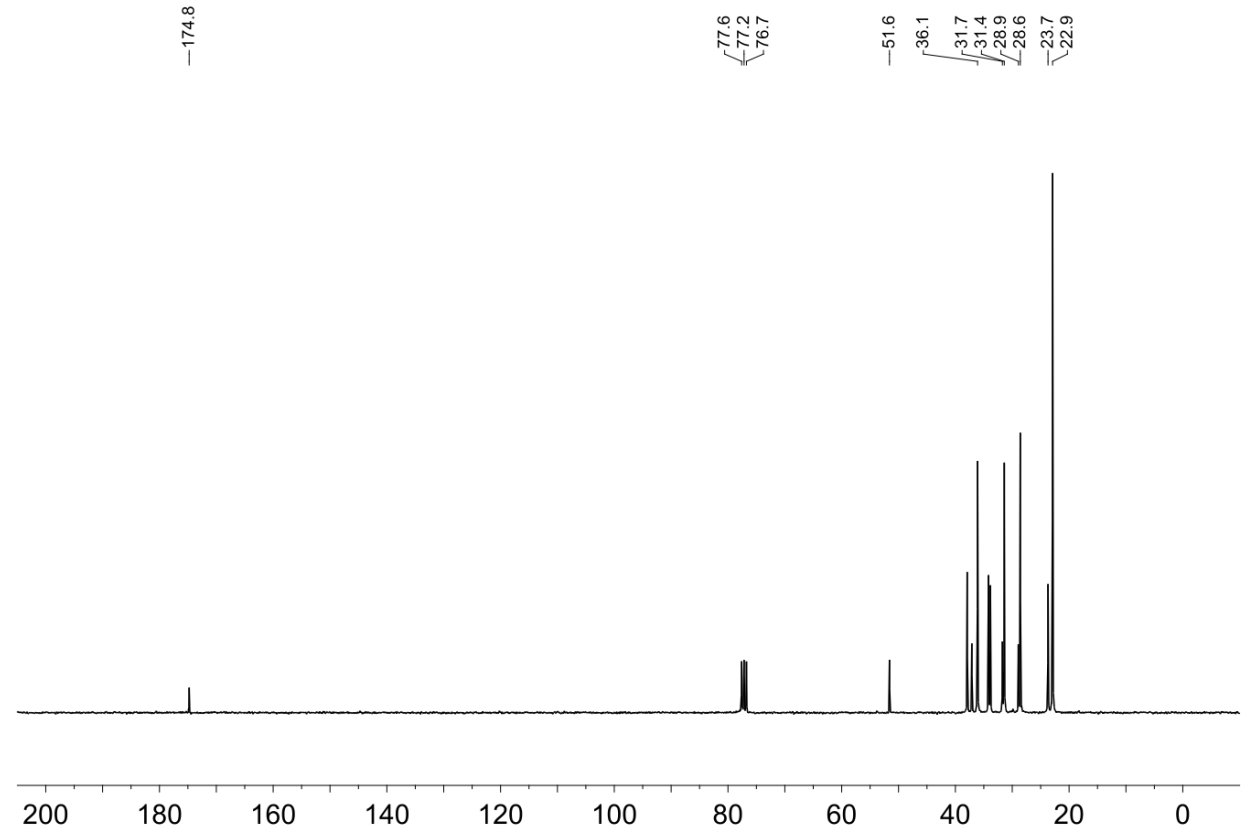


CH_2Br **5**

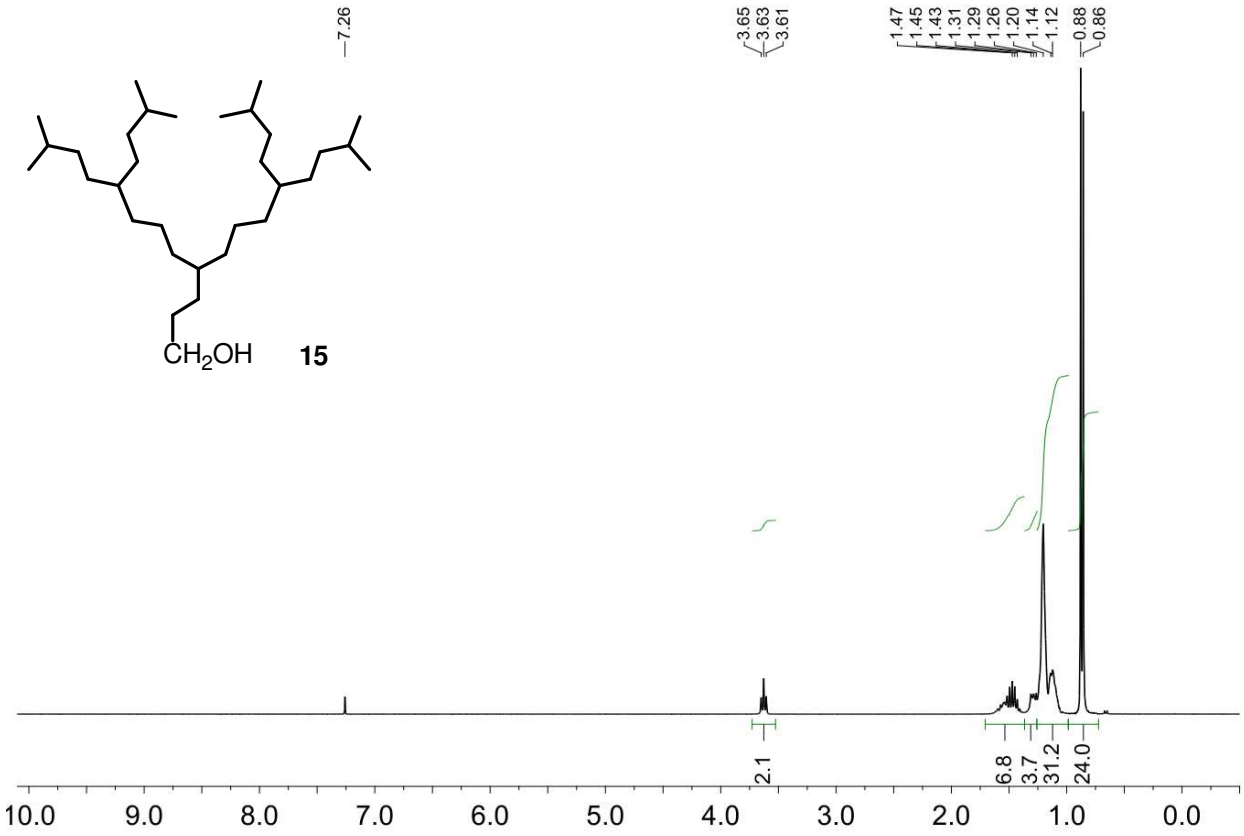


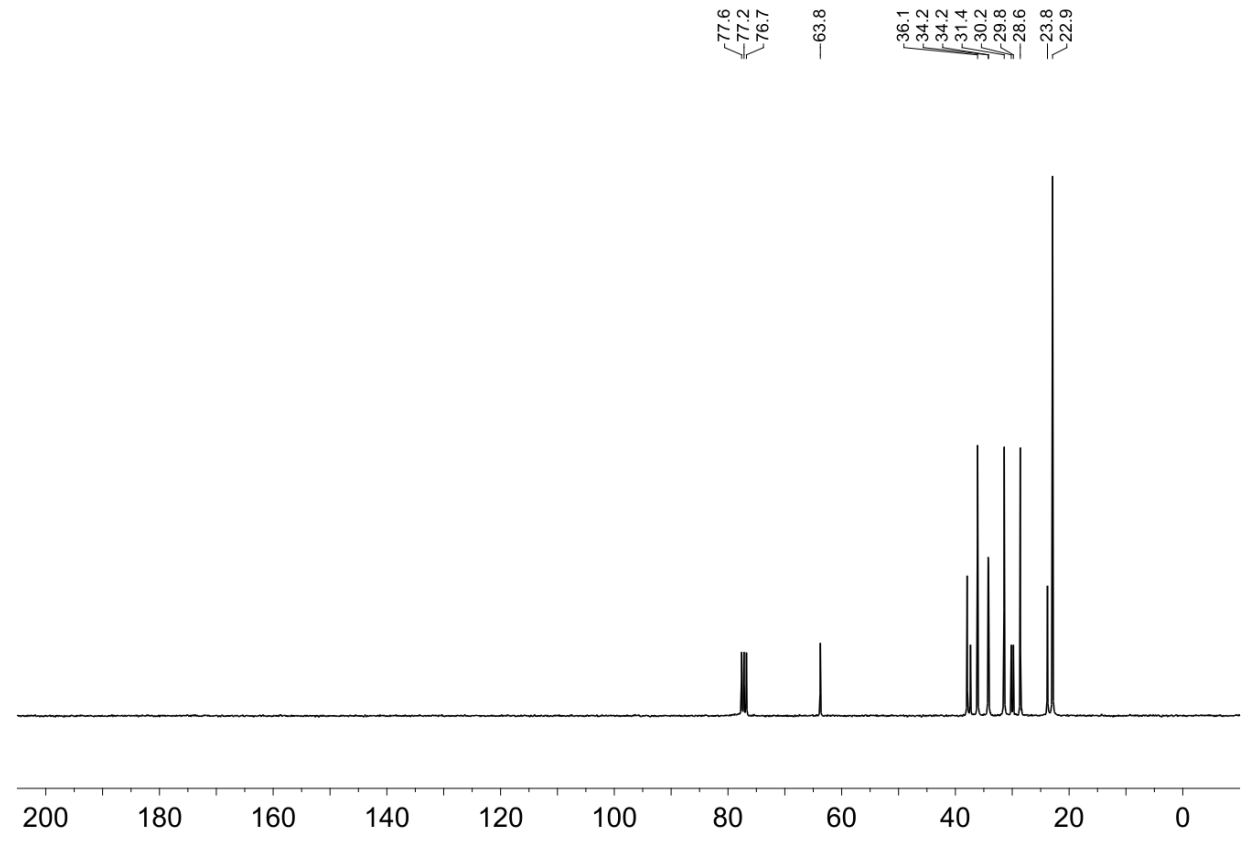
^{1}H and ^{13}C of compound **12**



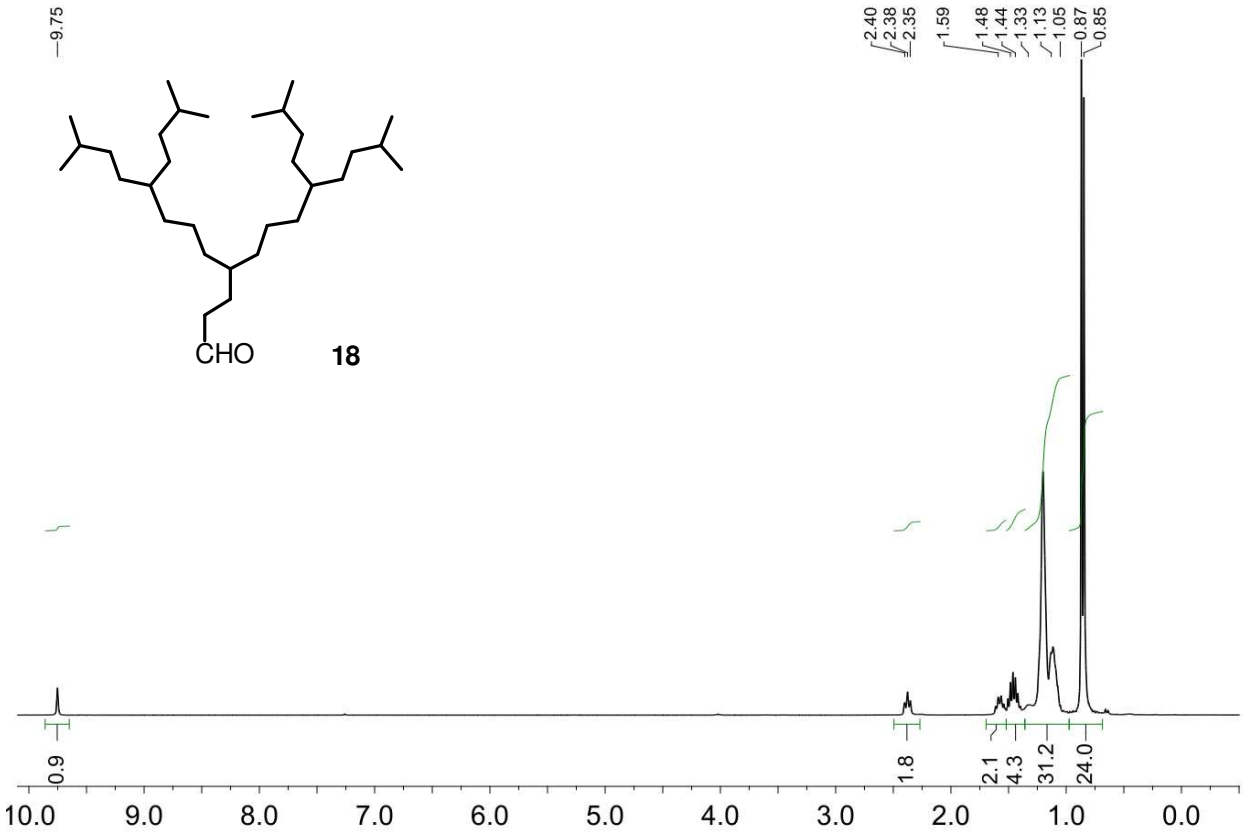


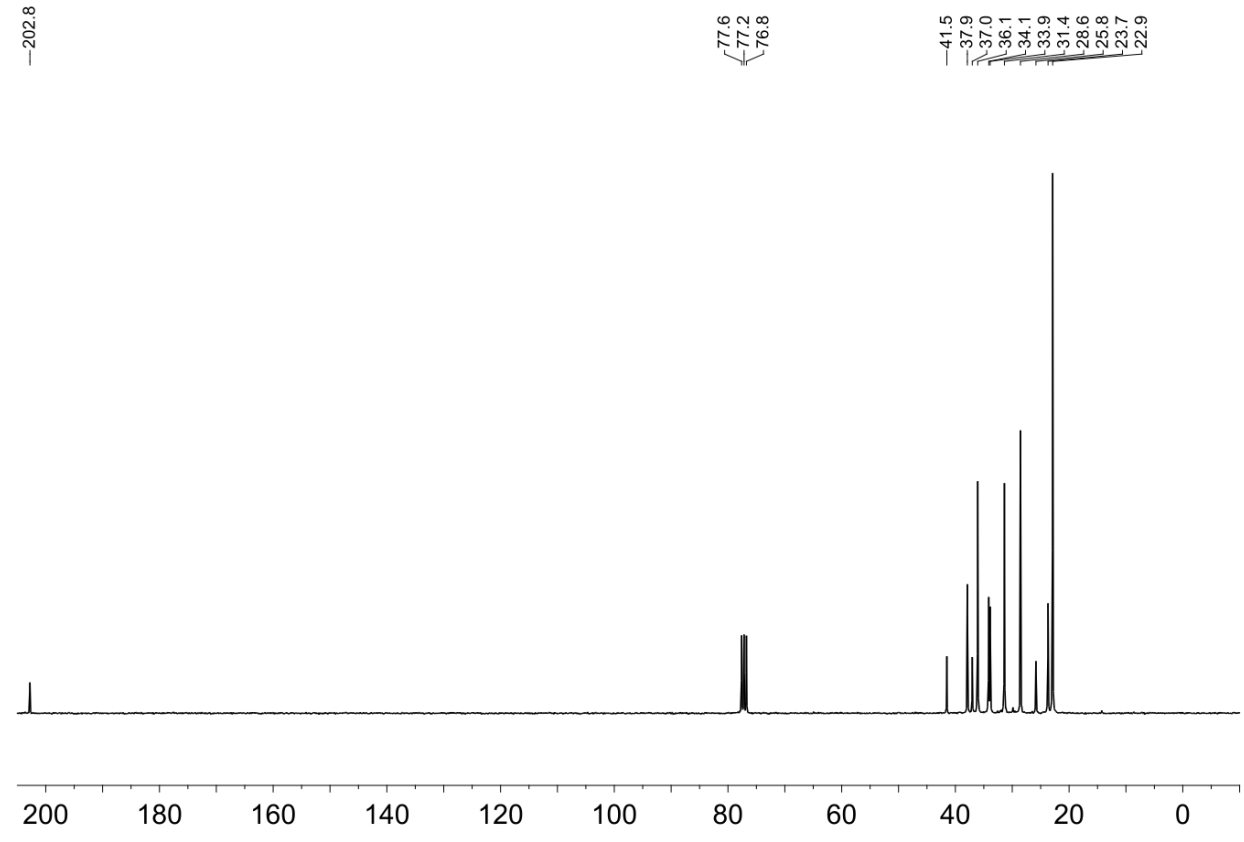
^{1}H and ^{13}C of compound **15**



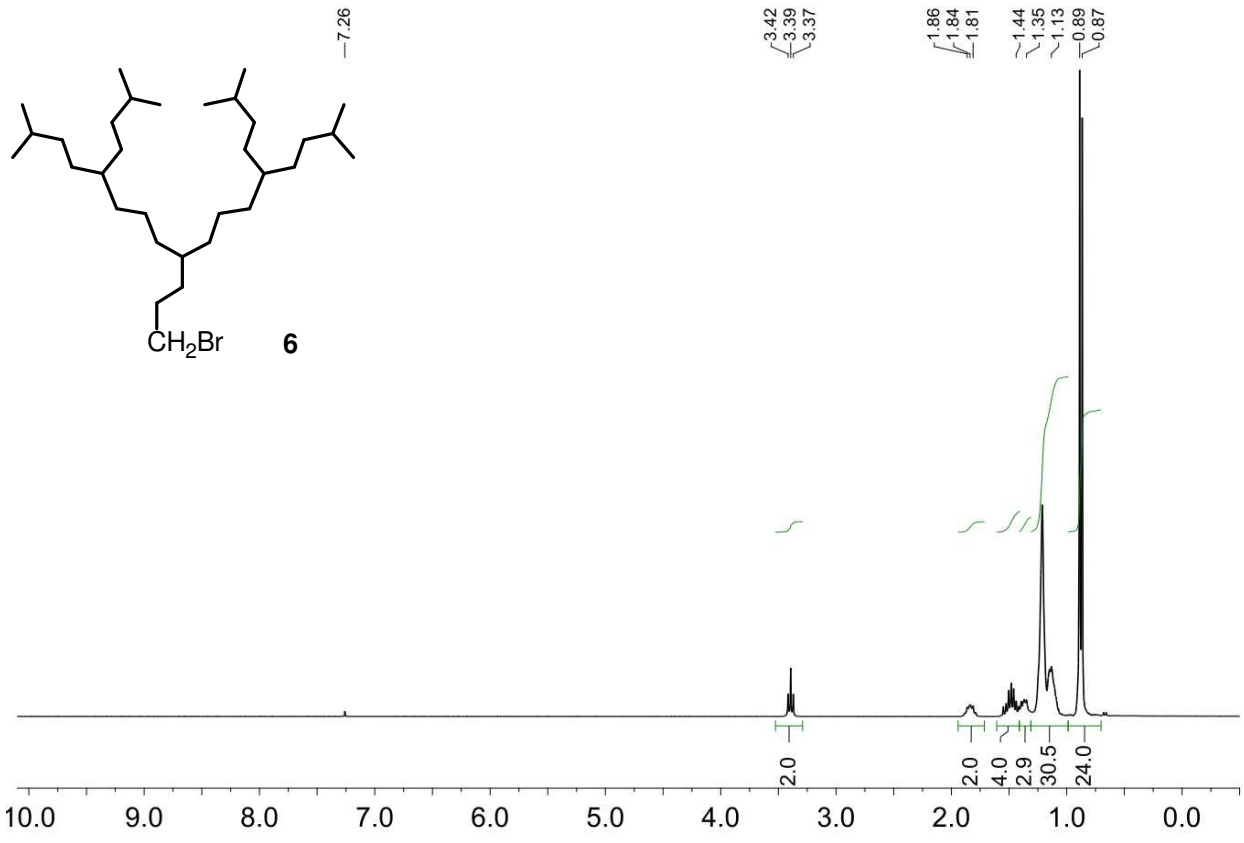


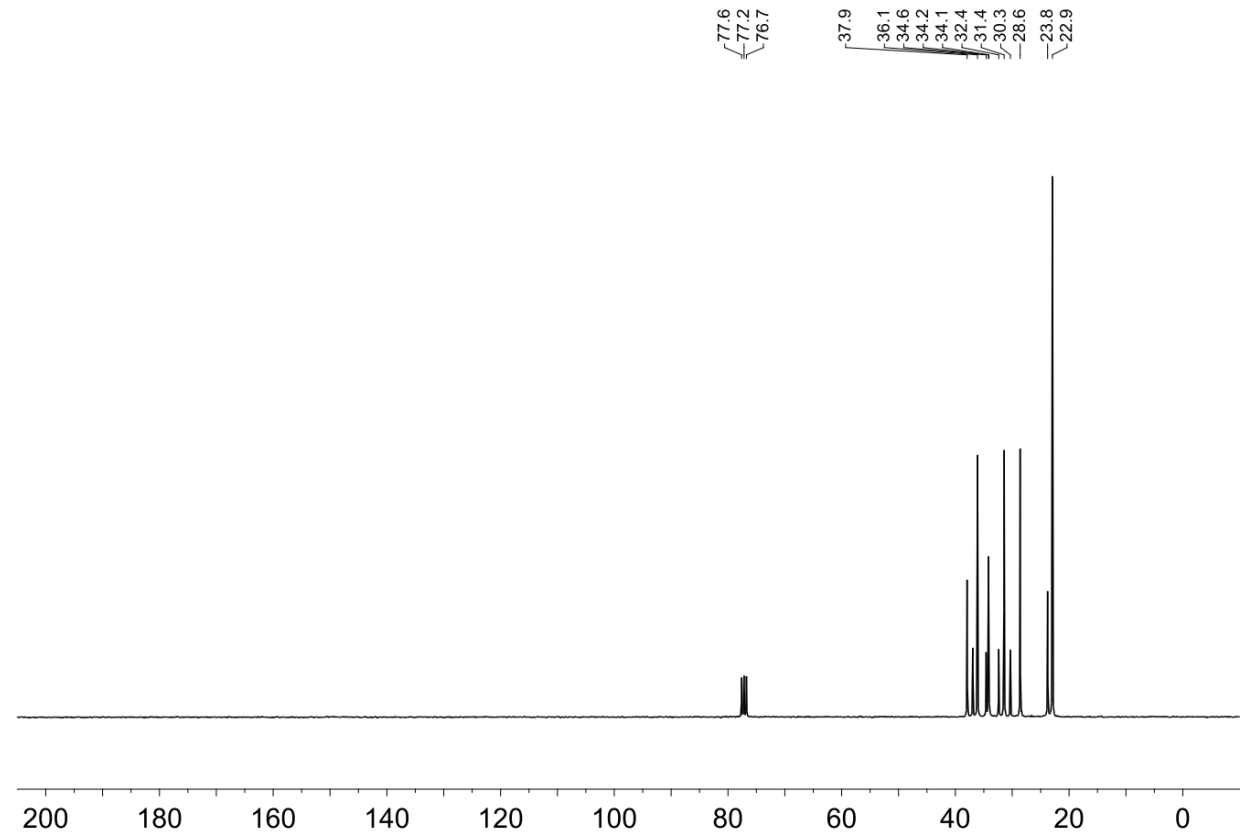
^{1}H and ^{13}C of compound **18**



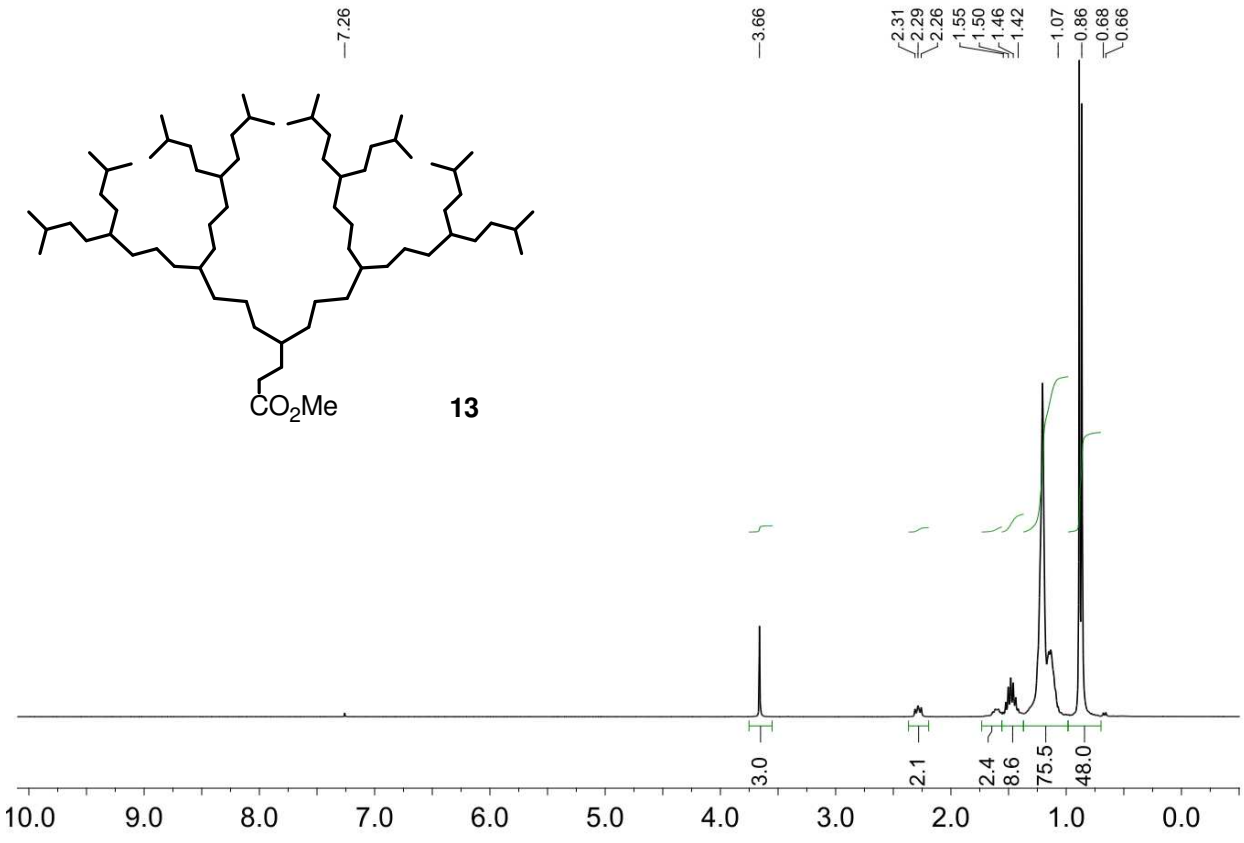


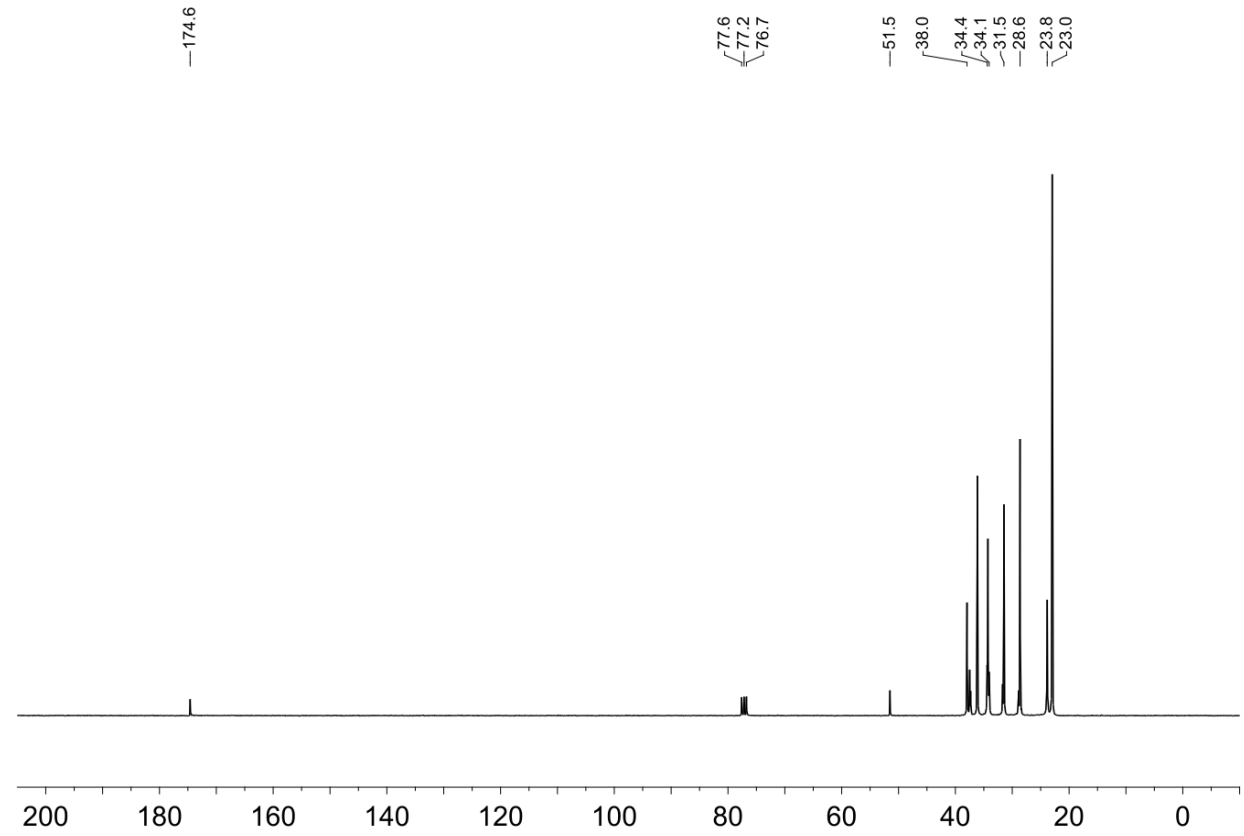
^{1}H and ^{13}C of compound **6**



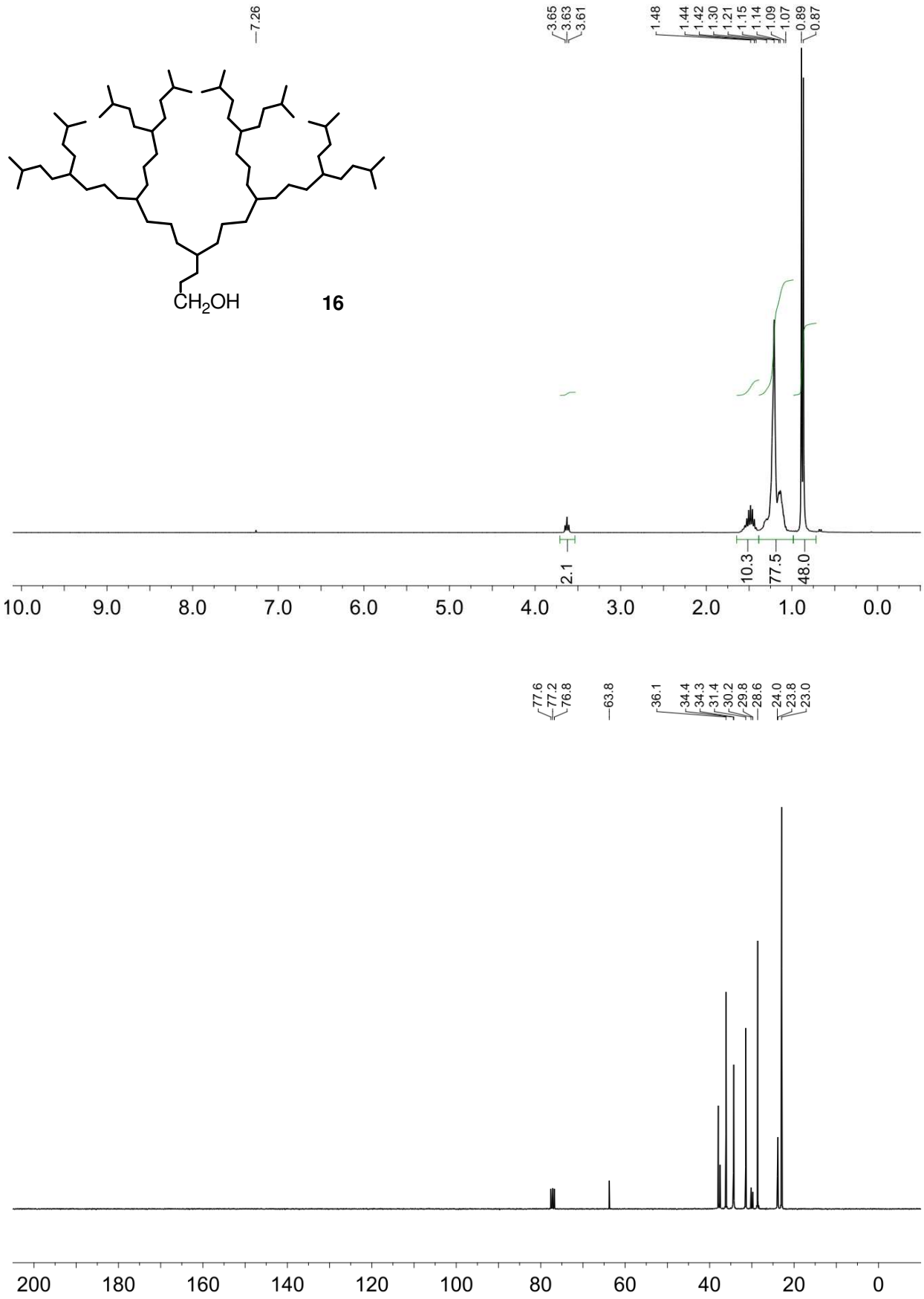


^{1}H and ^{13}C of compound **13**

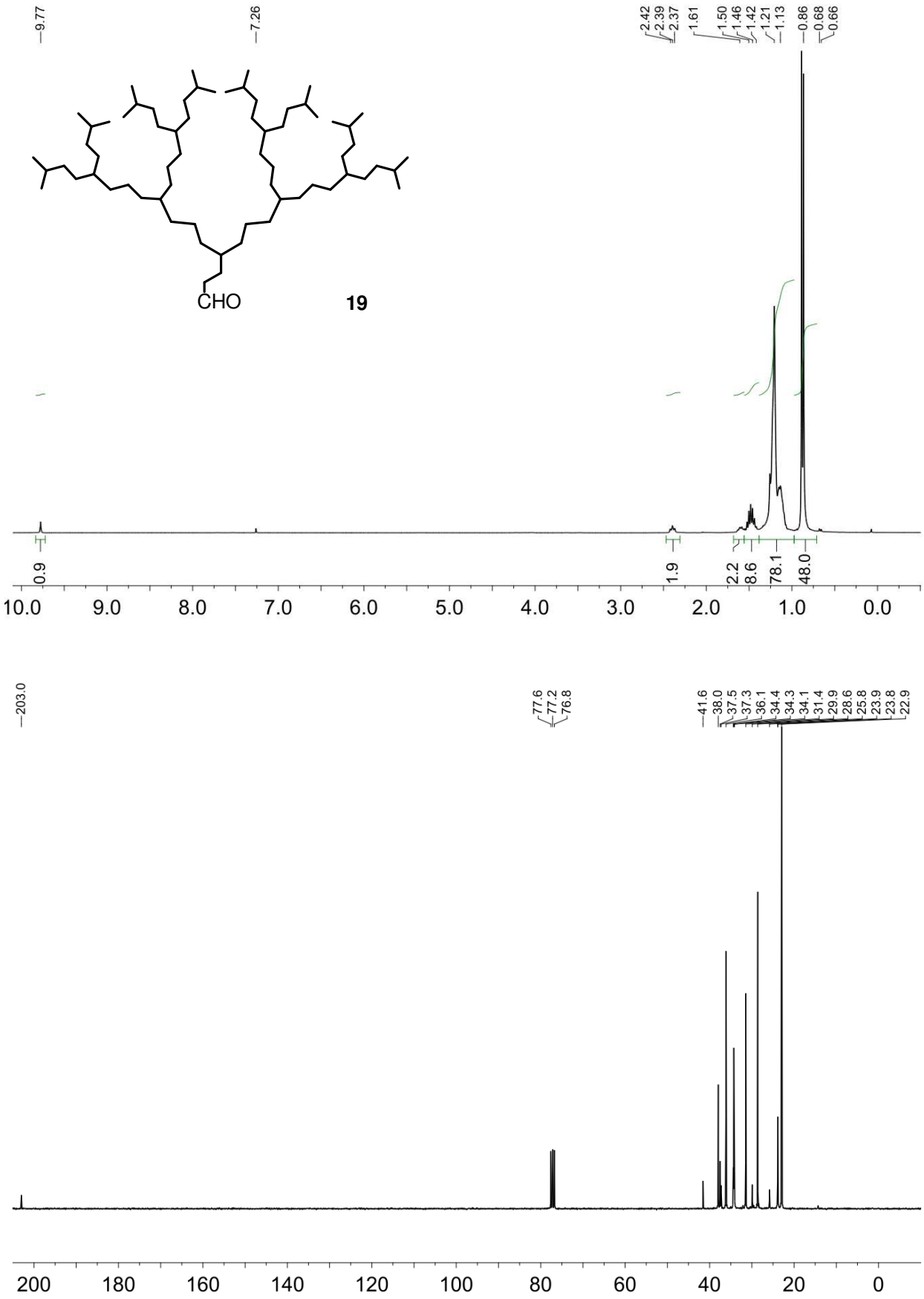




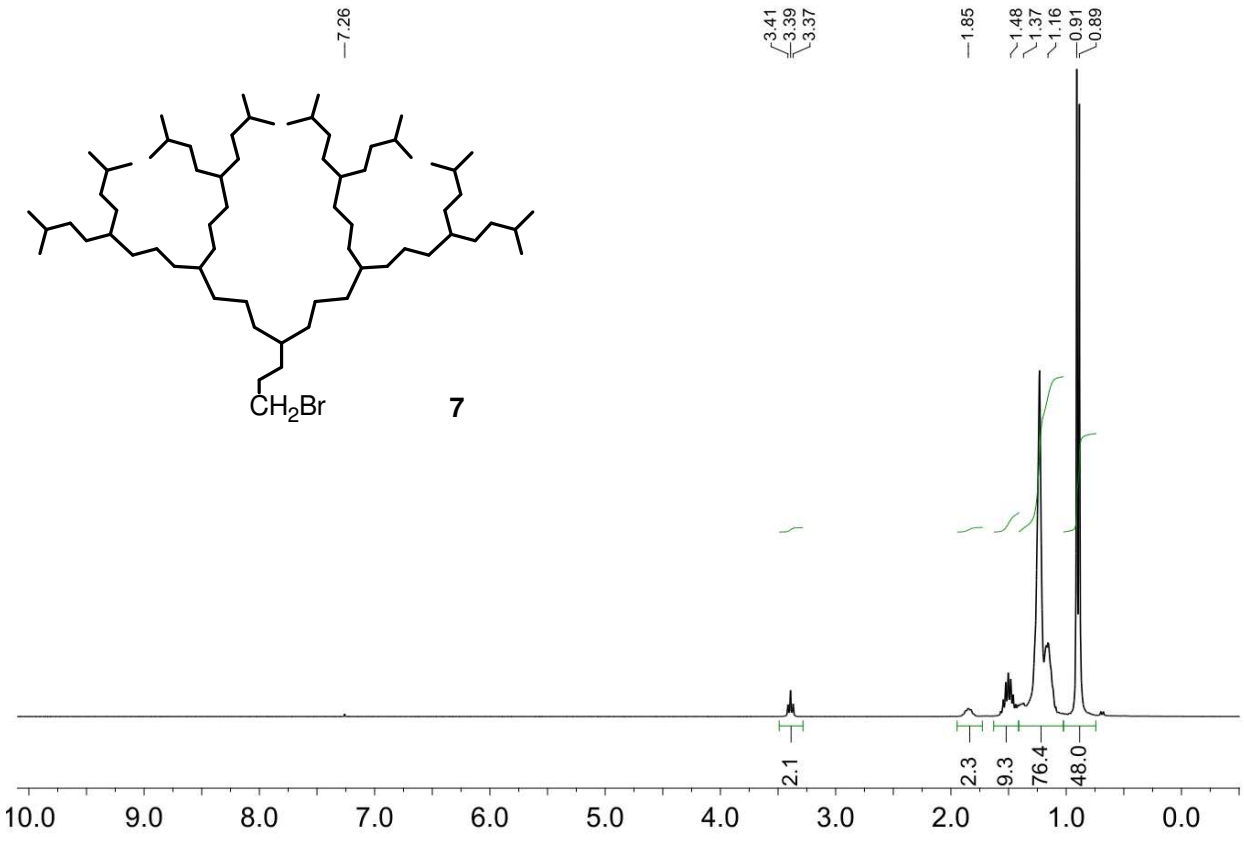
^{1}H and ^{13}C of compound **16**

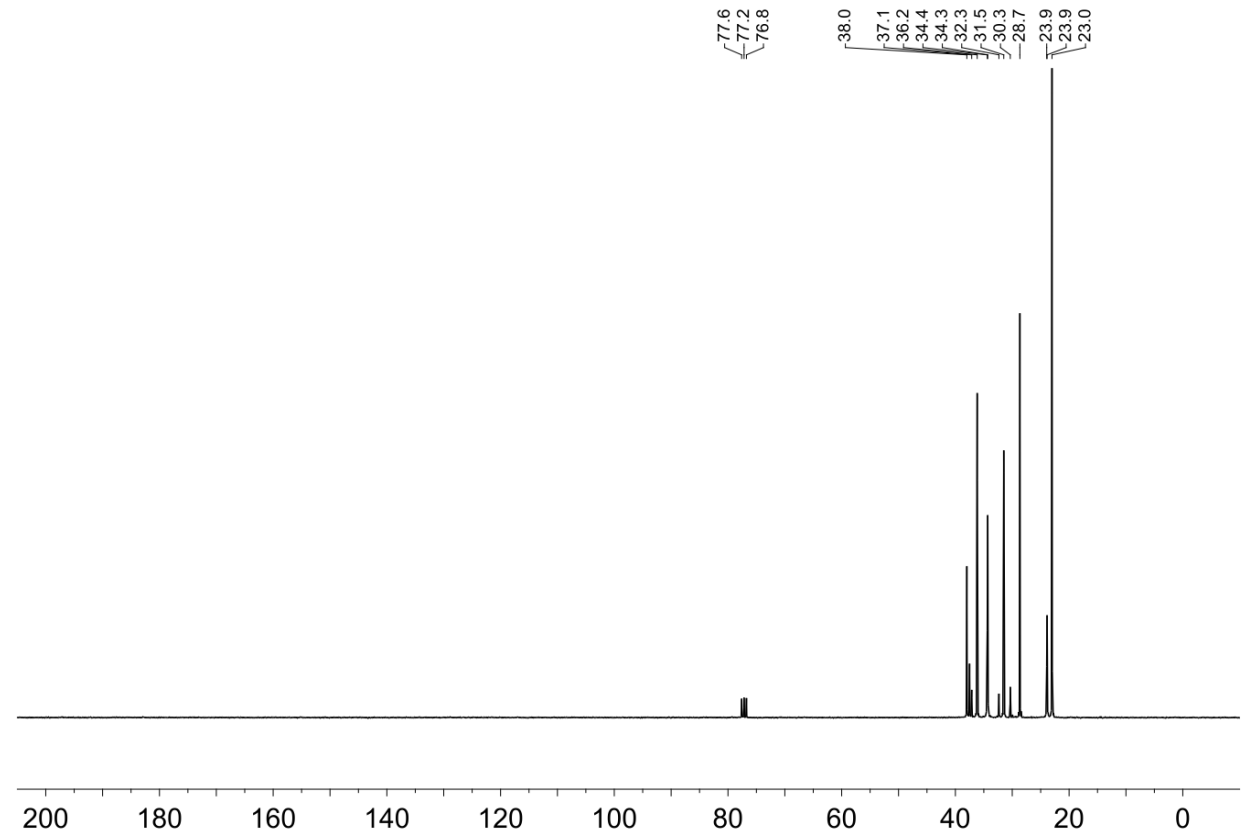


^{1}H and ^{13}C of compound **19**

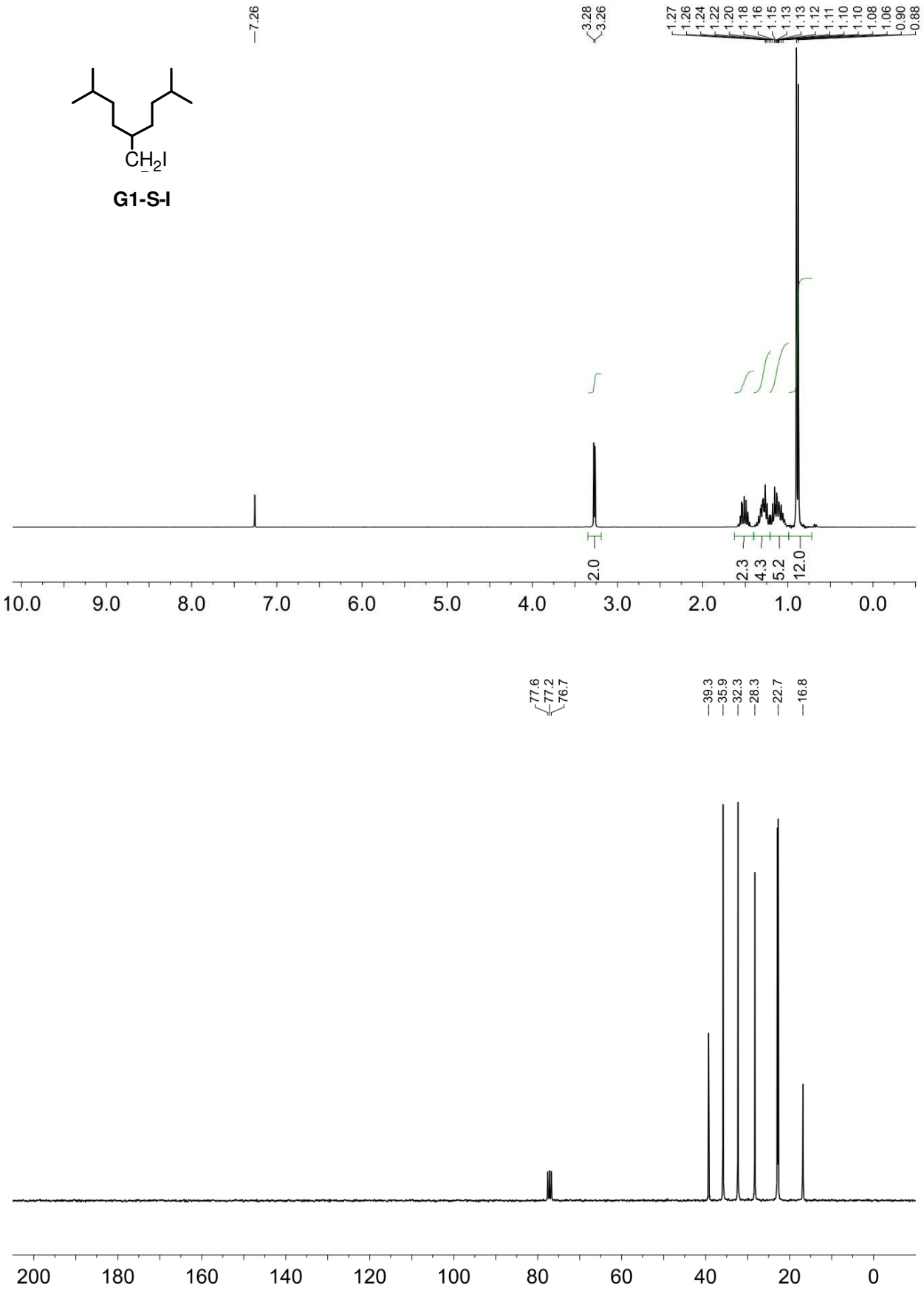


^{1}H and ^{13}C of compound **7**

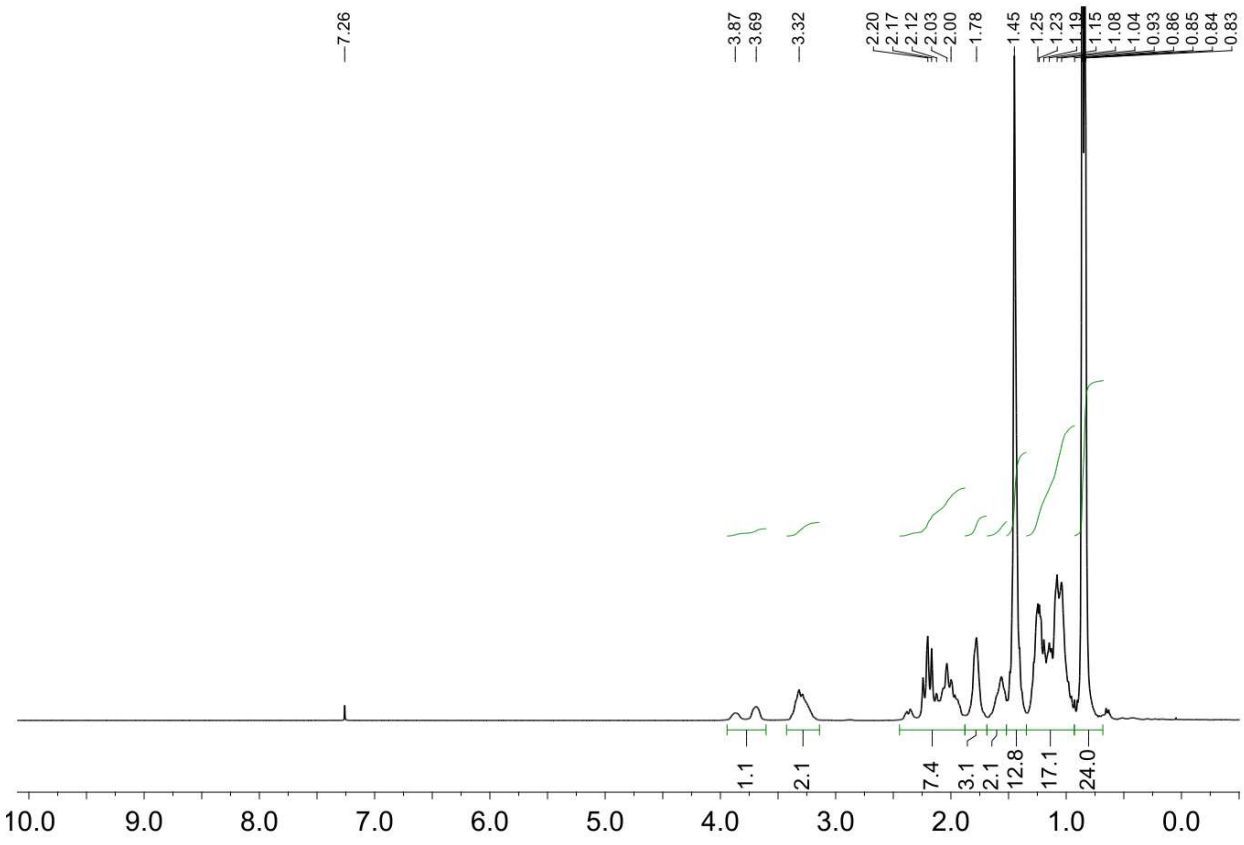


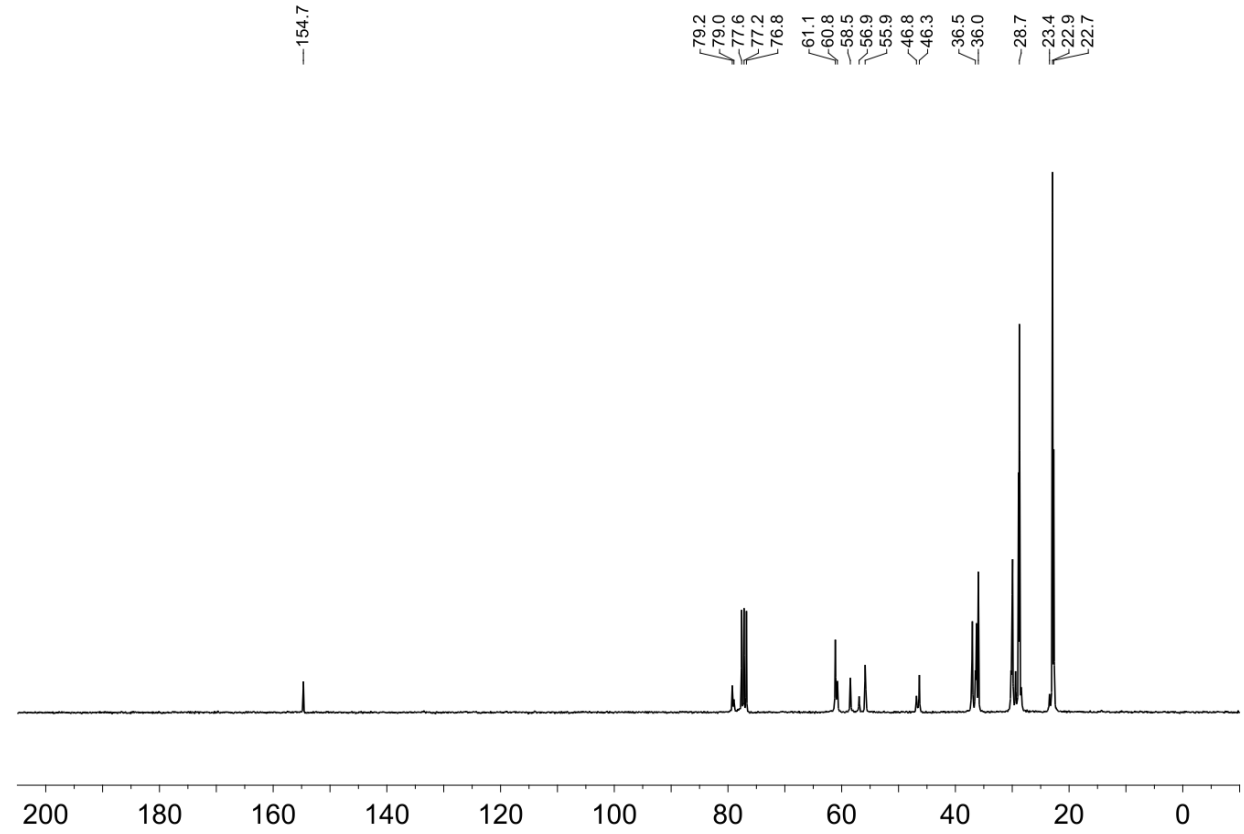


^{1}H and ^{13}C of compound **G1-S-I**

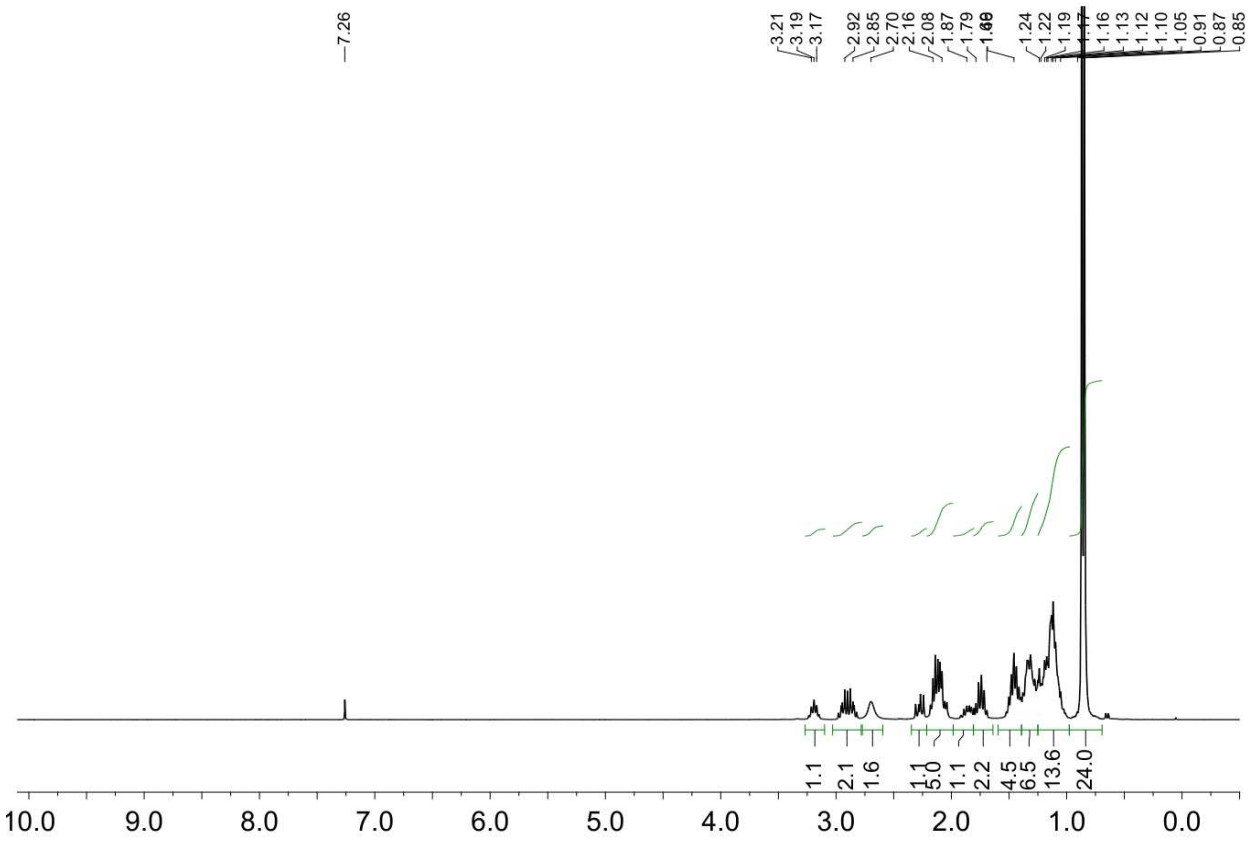


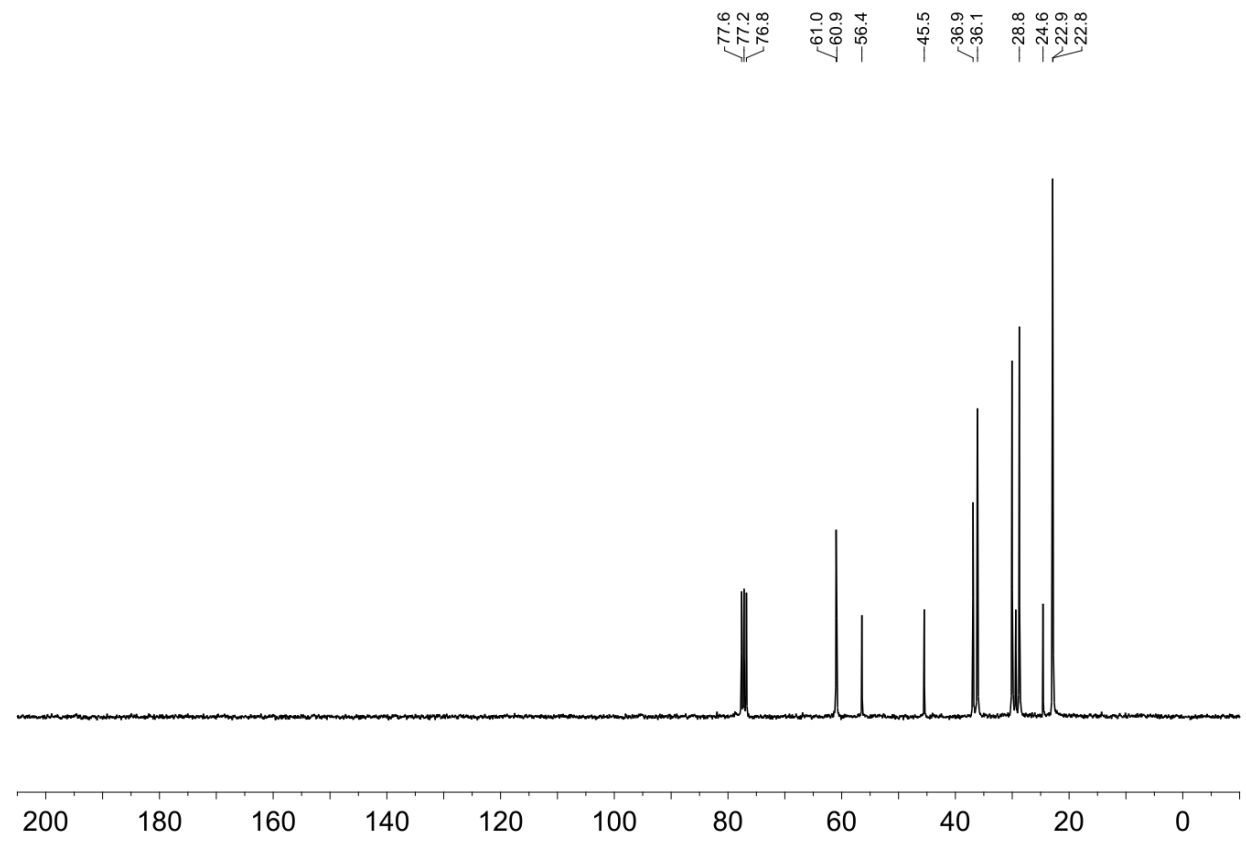
^{1}H and ^{13}C of compound **Boc-Di-S-G1**





^{1}H and ^{13}C of compound **Di-S-G1**



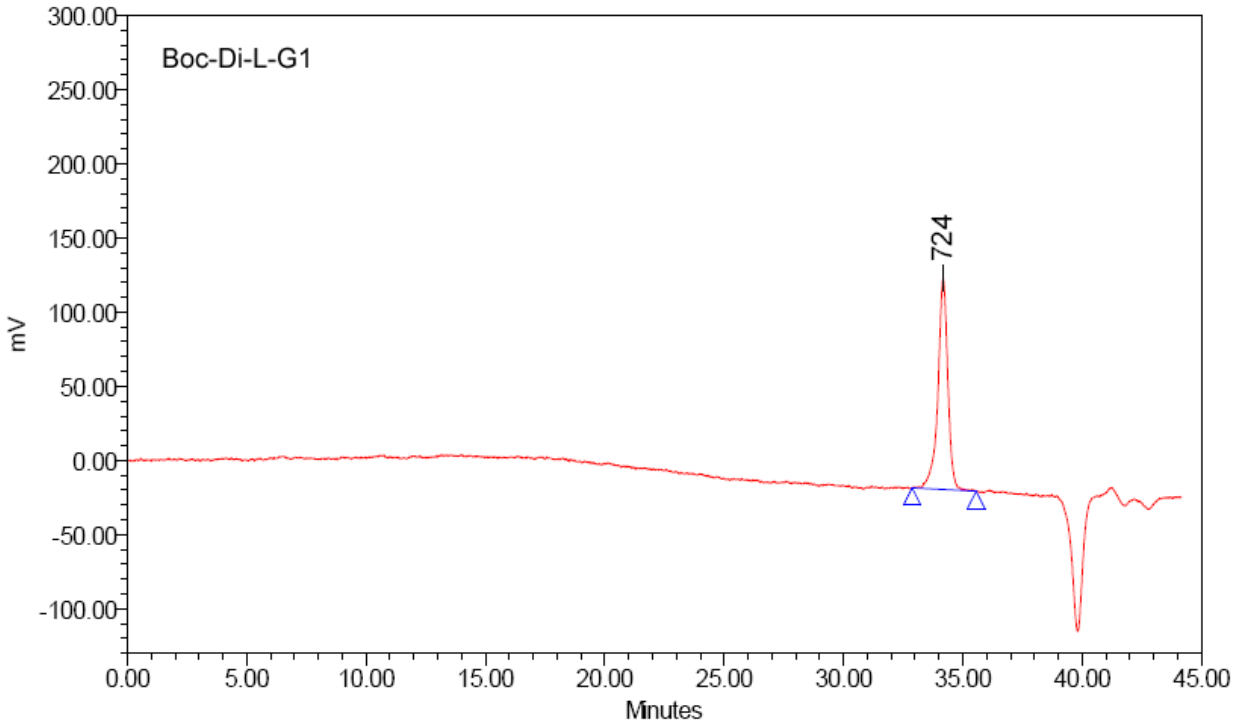


10. SEC Data and Chromatograms of New Compounds

Size exclusion chromatography (SEC) was performed on Waters Styragel GPC columns (HR1–4, 7.8 × 300 mm in serial) at 40 °C using THF as the eluent (flow rate = 1.0 mL/min) on a Water HPLC 515 pump equipped with a Viscotek LR40 laser refractometer. The retention times were reported in minutes. The retention time (t_R), SEC calculated M_w and M_n and PDI values are tabulated in Table S4. The SEC chromatograms of the target organocatalysts are shown in the pages immediately after Table S4.

Table S4.

Compound	Theoretical M_w (g/mol)	SEC calculated results			
		t_R (min)	M_n (g/mol)	M_w (g/mol)	PDI
Boc-Di-L-G1	593	34.18	729	736	1.01
Boc-Di-L-G2	1098	32.37	1515	1528	1.01
Boc-Di-L-G3	2108	30.72	2827	2850	1.01
Boc-Mono-L-G1	397	35.74	531	531	1.00
Boc-Mono-L-G2	649	33.91	807	815	1.01
Boc-Mono-L-G3	1154	32.20	1606	1620	1.01
Boc-Mono-S-G1	369	35.99	521	521	1.00
Boc-Mono-S-G2	621	34.04	768	776	1.01
Boc-Mono-S-G3	1126	32.24	1583	1597	1.01
Di-L-G1	493	35.08	575	580	1.01
Di-L-G2	998	32.74	1291	1313	1.02
Di-L-G3	2008	30.85	2642	2682	1.01
Mono-L-G1	297	35.13	563	583	1.03
Mono-L-G2	549	34.37	661	672	1.02
Mono-L-G3	1054	32.39	1478	1494	1.01
Mono-S-G1	269	36.36	364	378	1.04
Mono-S-G2	521	34.48	636	646	1.02
Mono-S-G3	1026	32.43	1458	1472	1.01
Boc-Di-S-G1	537	34.62	609	614	1.01
Di-S-G1	437	35.45	551	553	1.00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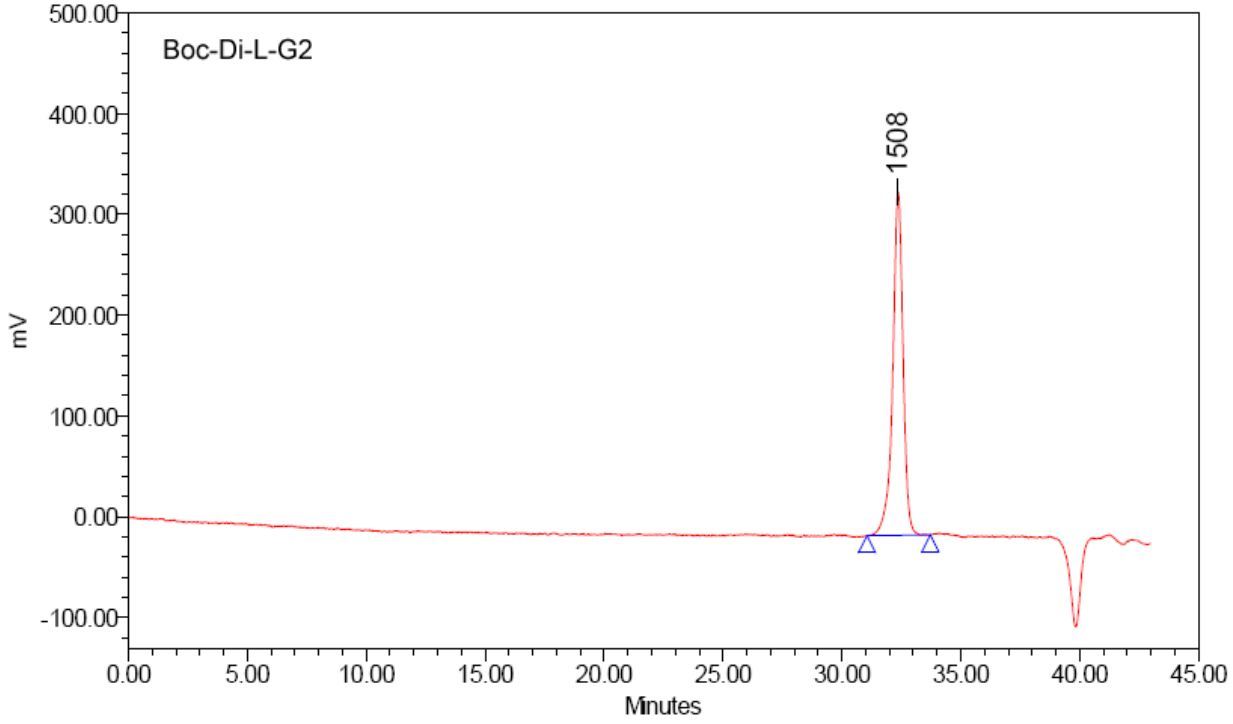
724
mV
300.00
250.00
200.00
150.00
100.00
50.00
0.00
-50.00
-100.00
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
Minutes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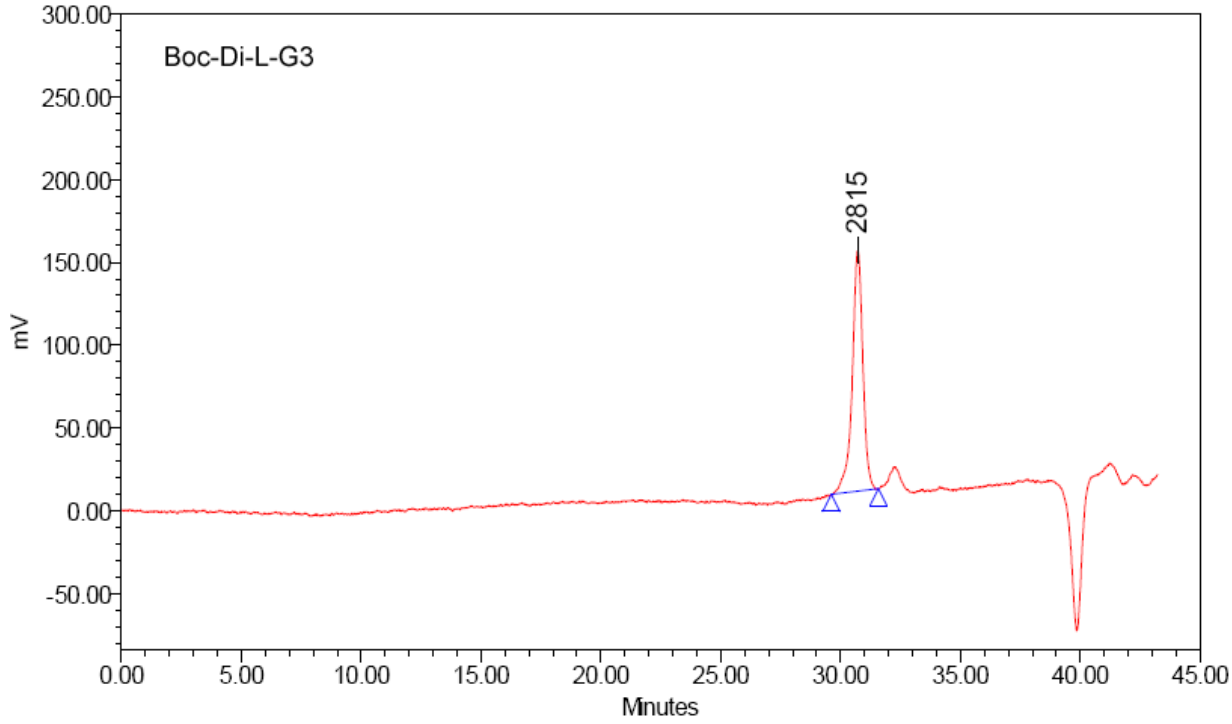
1508
mV
500.00
400.00
300.00
200.00
100.00
0.00
-100.00
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
Minutes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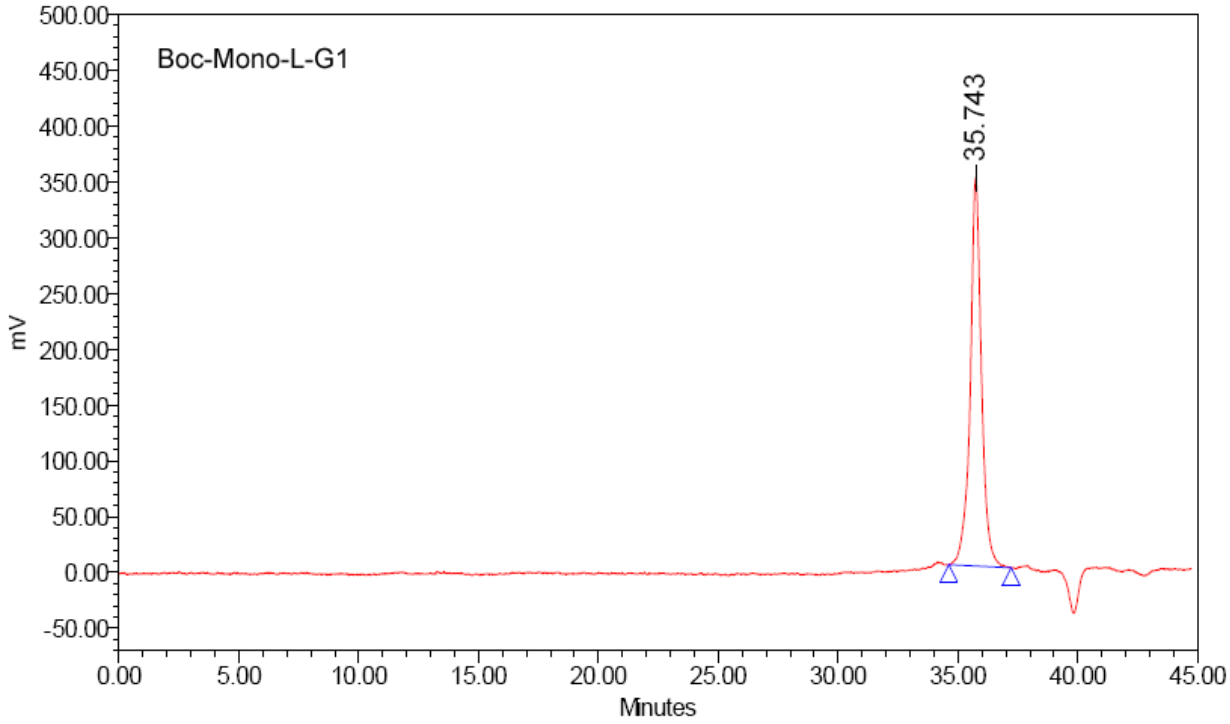
2815
mV
300.00
250.00
200.00
150.00
100.00
50.00
0.00
-50.00
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
Minutes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mV
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450.00
400.00
350.00
300.00
250.00
200.00
150.00
100.00
50.00
0.00
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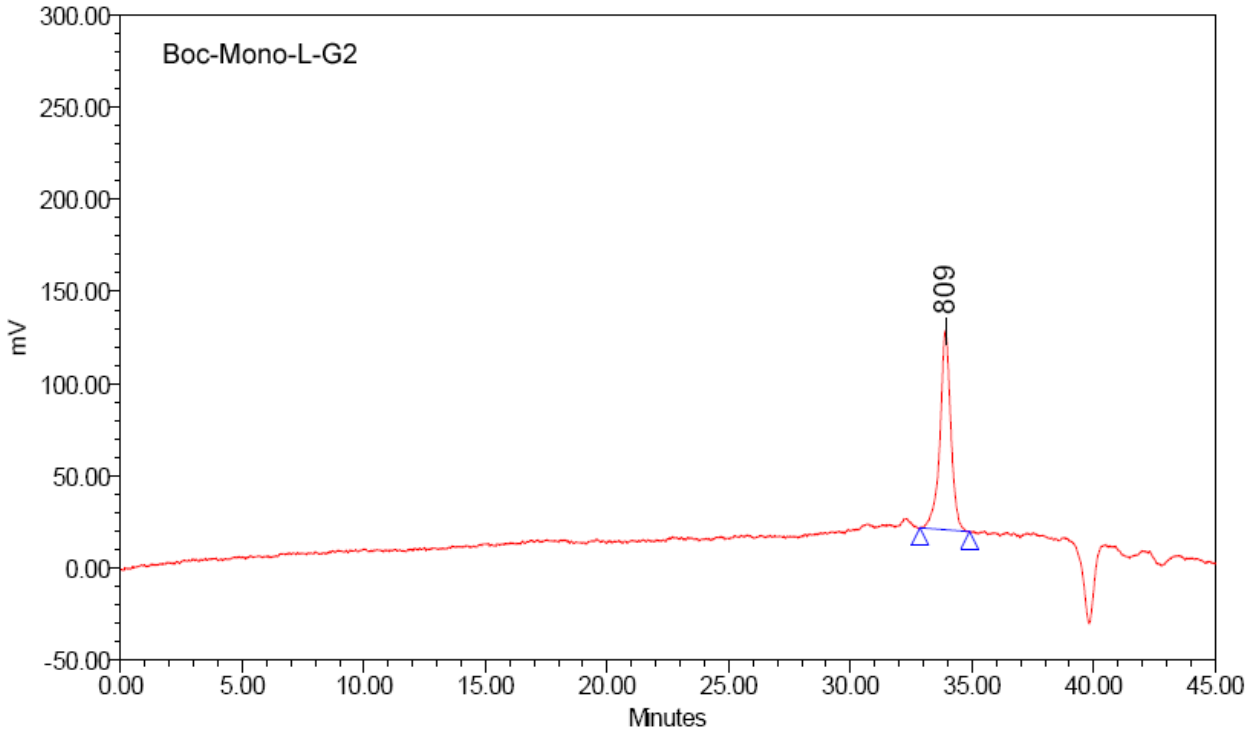
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
Minutes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809
mV
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250.00
200.00
150.00
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50.00
0.00
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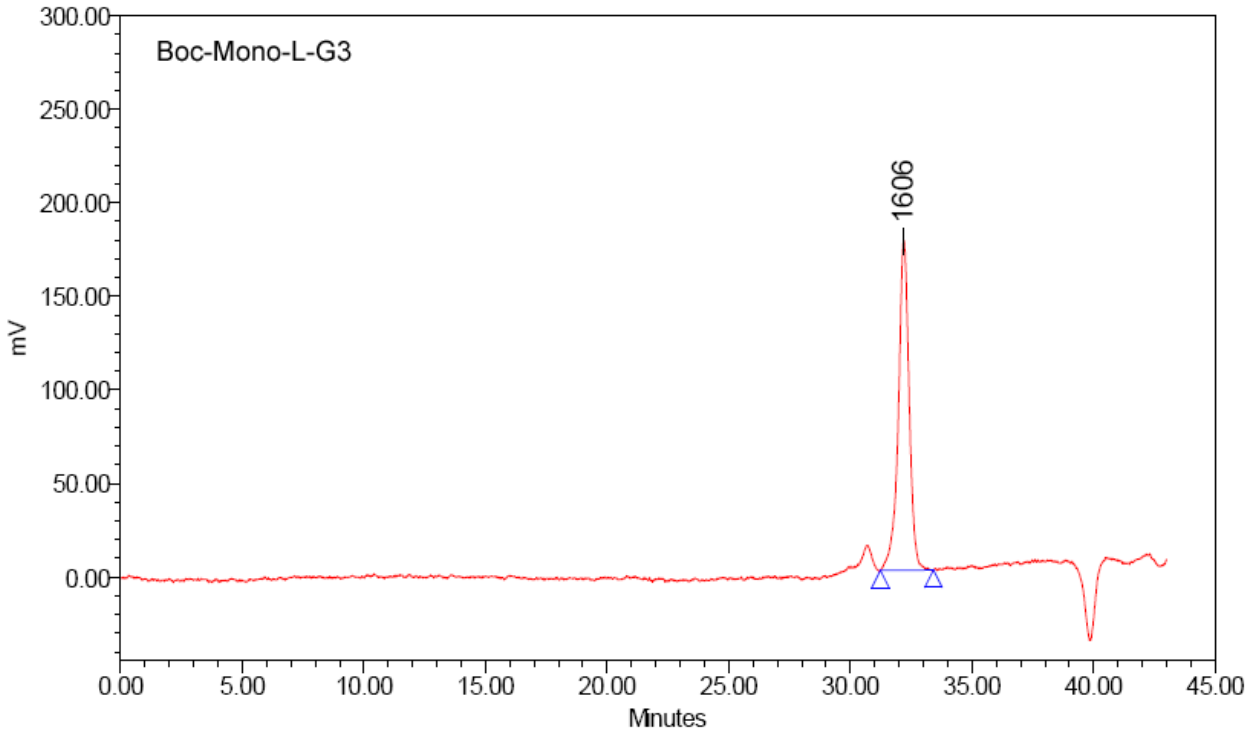
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
Minutes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1606
mV
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100.00
50.00
0.00
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5.00
10.00
15.00
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30.00
35.00
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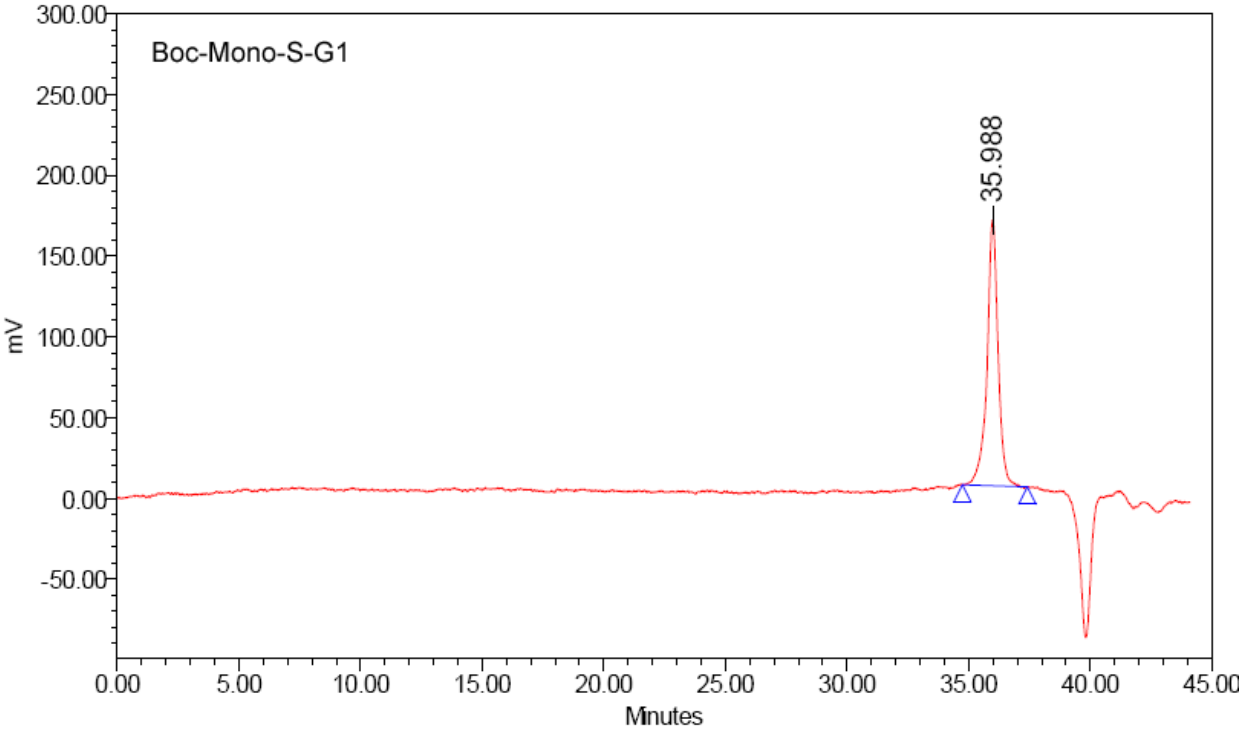
45.00
Minutes


Boc-Mono-S-G1
35.988
mV
300.00
250.00
200.00
150.00
100.00
50.00
0.00
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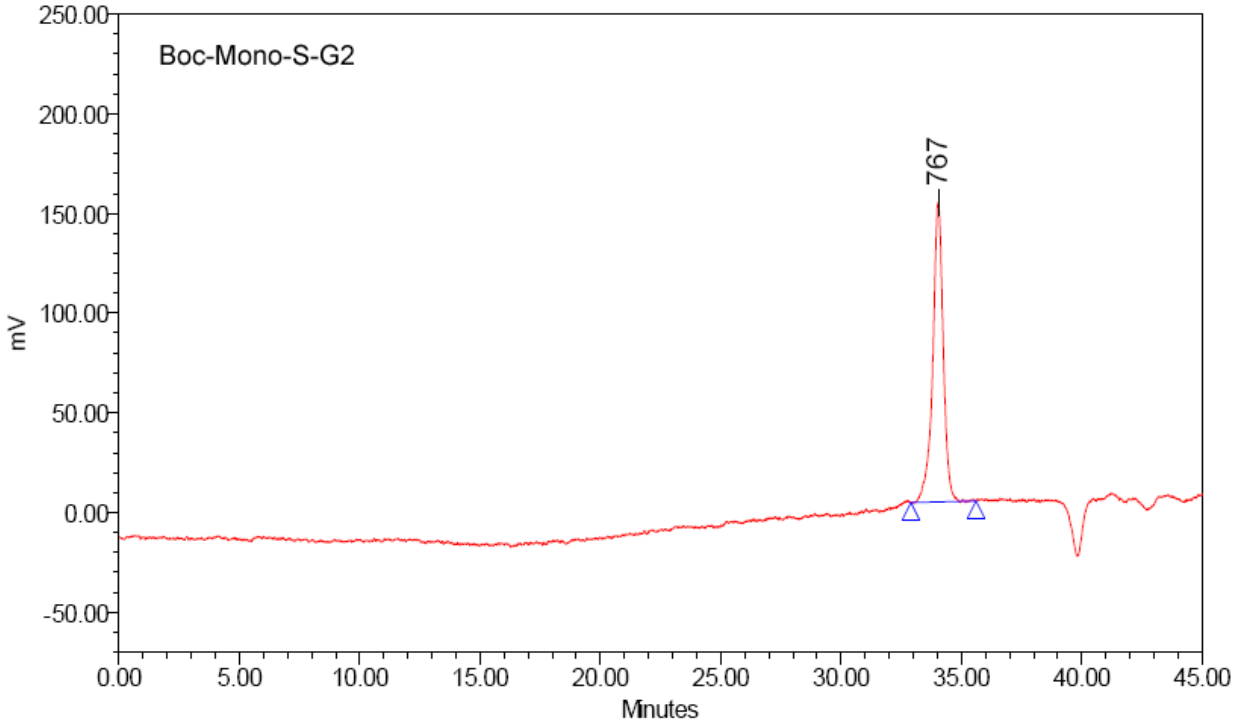
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
Minutes


Boc-Mono-S-G2
767
mV
250.00
200.00
150.00
100.00
50.00
0.00
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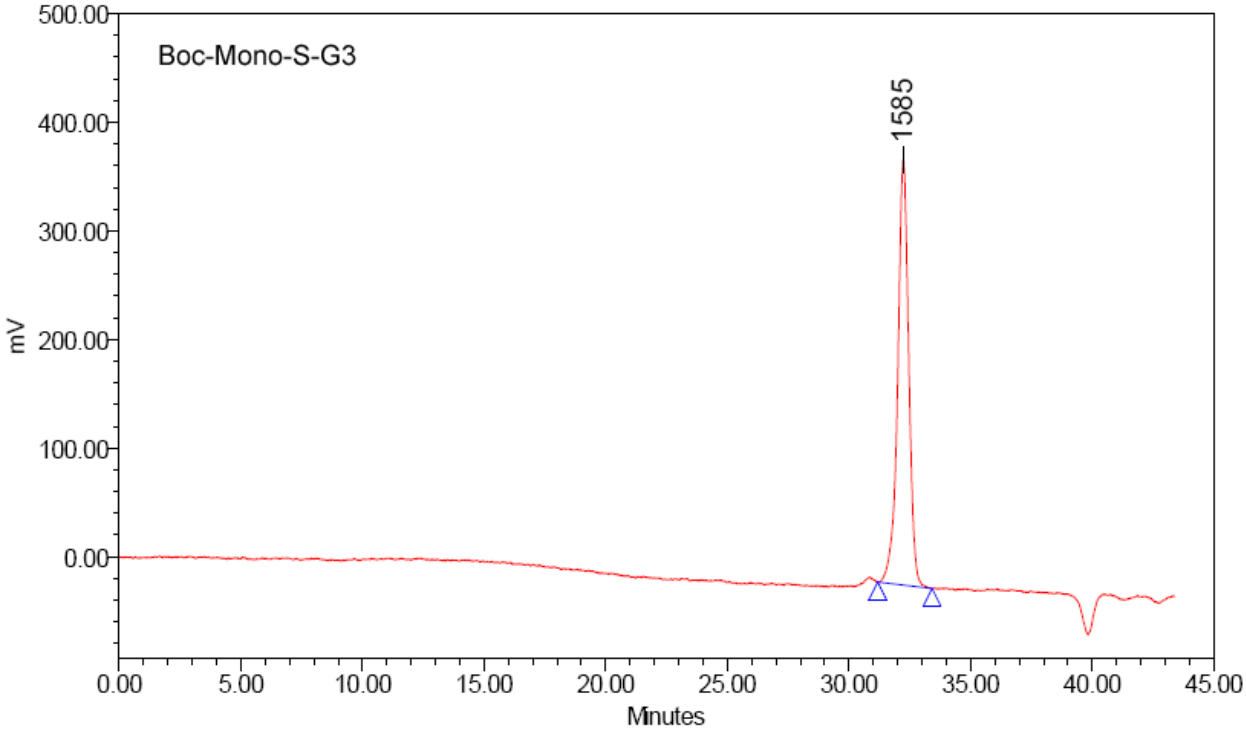
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
Minutes


Boc-Mono-S-G3
1585
mV
500.00
400.00
300.00
200.00
100.00
0.00
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5.00
10.00
15.00
20.00
25.00
30.00
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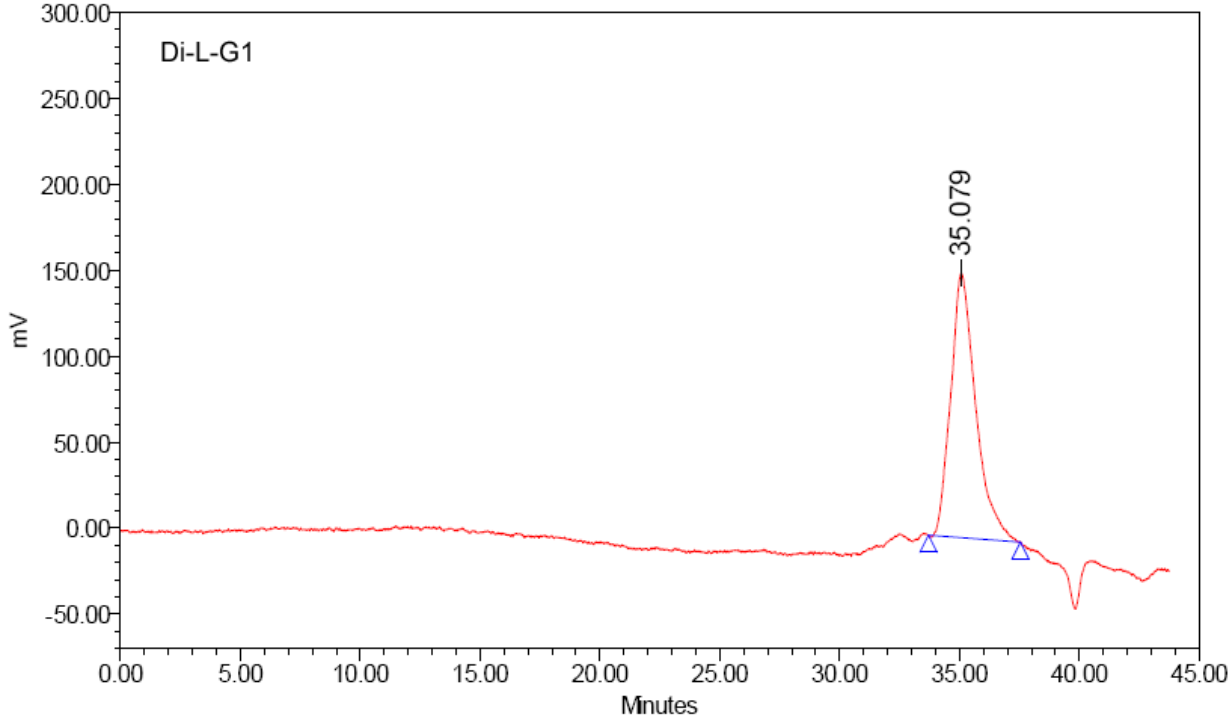
40.00
45.00
Minutes


Di-L-G1
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mV
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250.00
200.00
150.00
100.00
50.00
0.00
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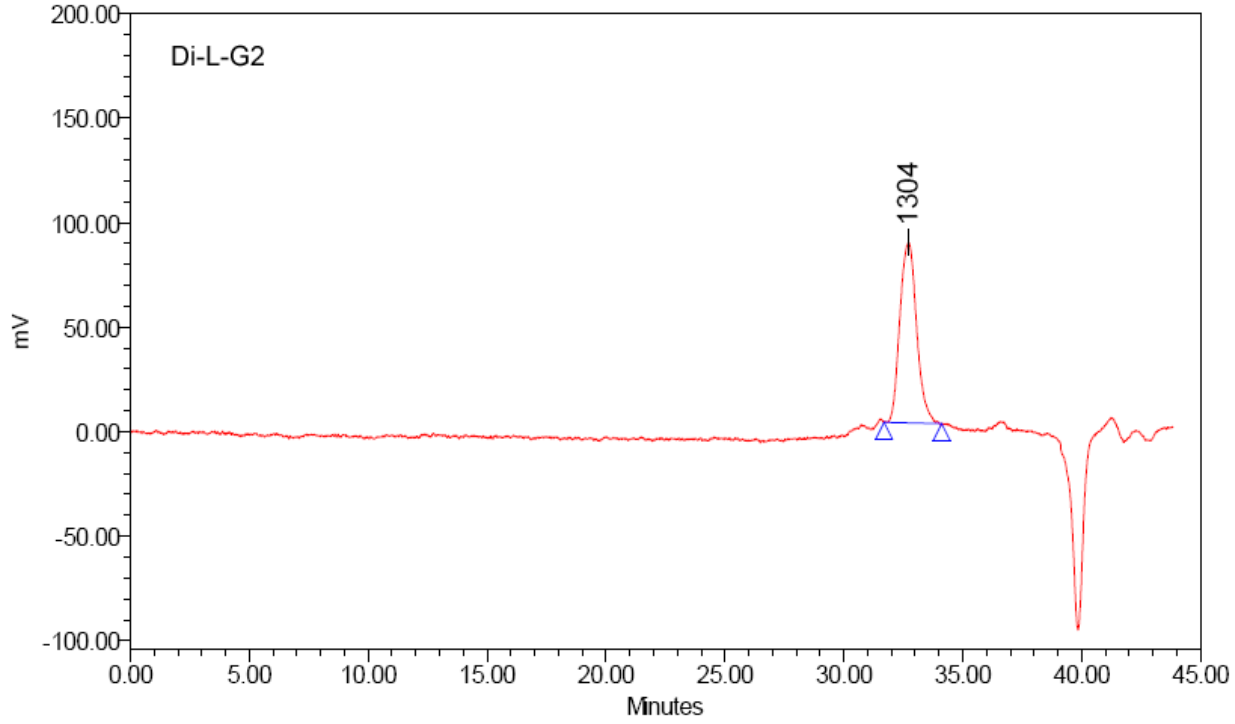
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
Minutes


Di-L-G2
1304
mV
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150.00
100.00
50.00
0.00
-50.00
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5.00
10.00
15.00
20.00
25.00
30.00
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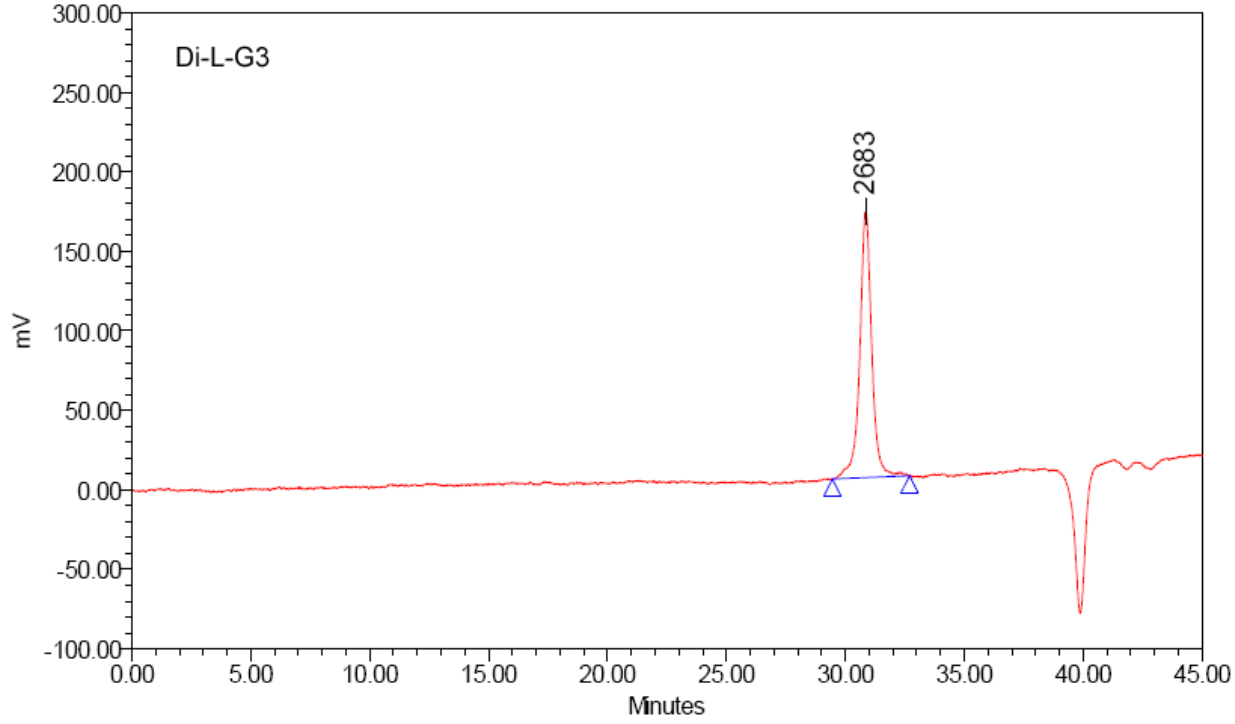
40.00
45.00
Minutes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mV
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200.00
150.00
100.00
50.00
0.00
-50.00
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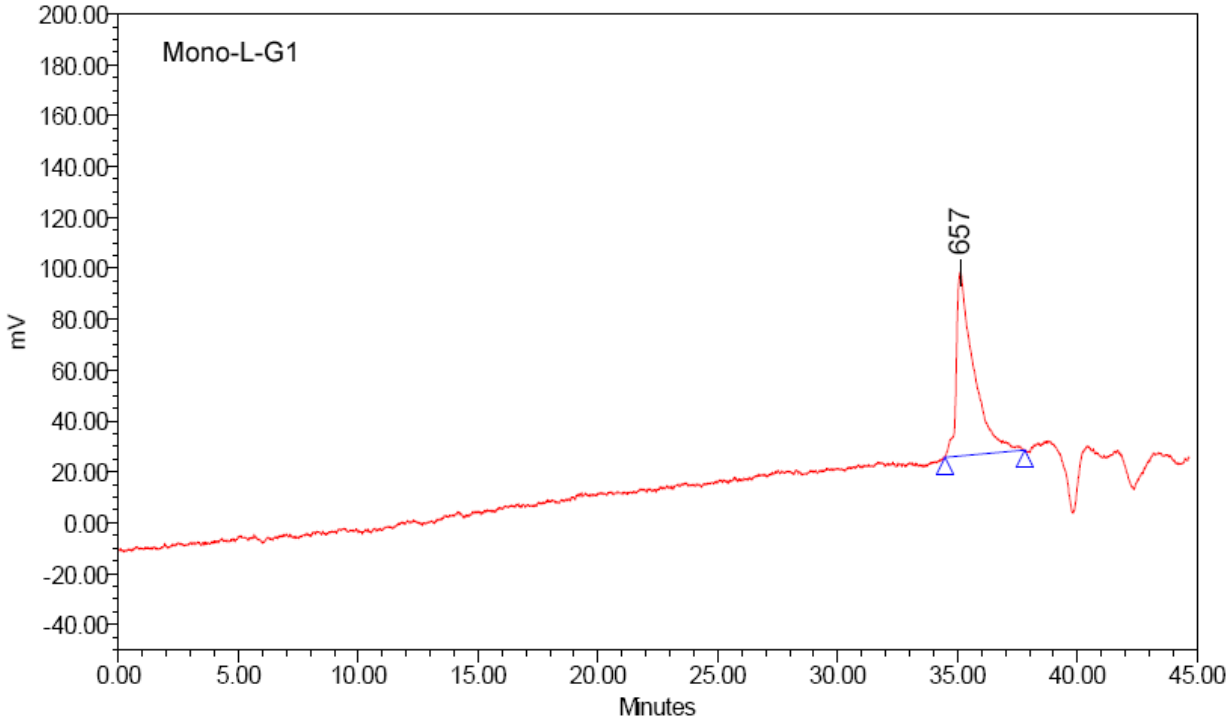
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
Minutes


Mono-L-G1
657
mV
Minutes
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160.00
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
-20.00
-40.00
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5.00
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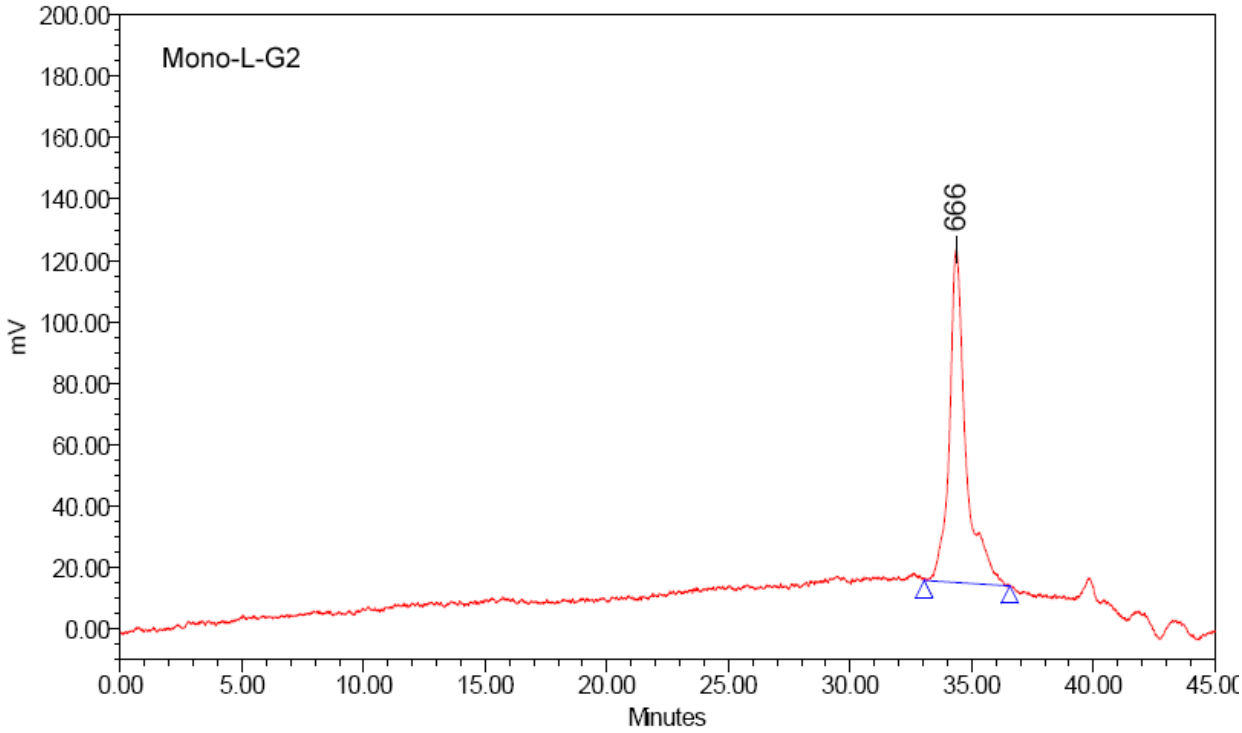
45.00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666
mV
Minutes
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140.00
120.00
100.00
80.00
60.00
40.00
20.00
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0.00
5.00
10.00
15.00
20.00
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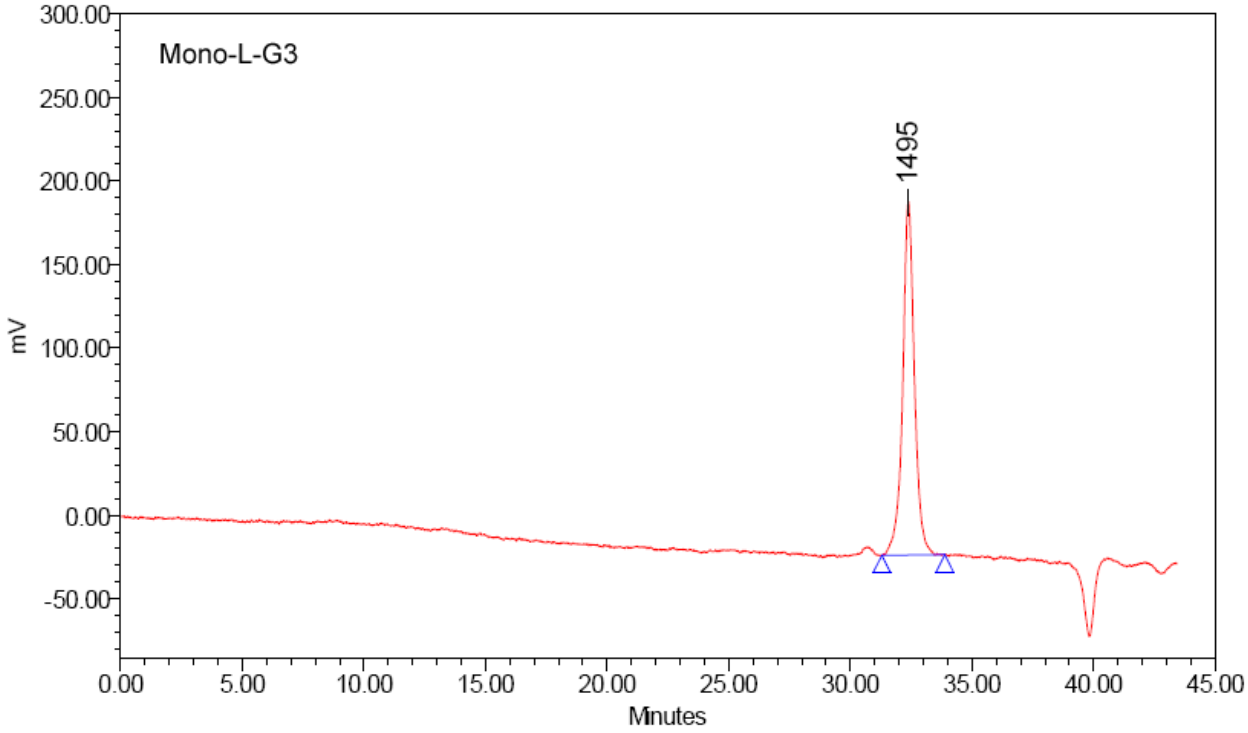
40.00
45.00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mV
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150.00
100.00
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0.00
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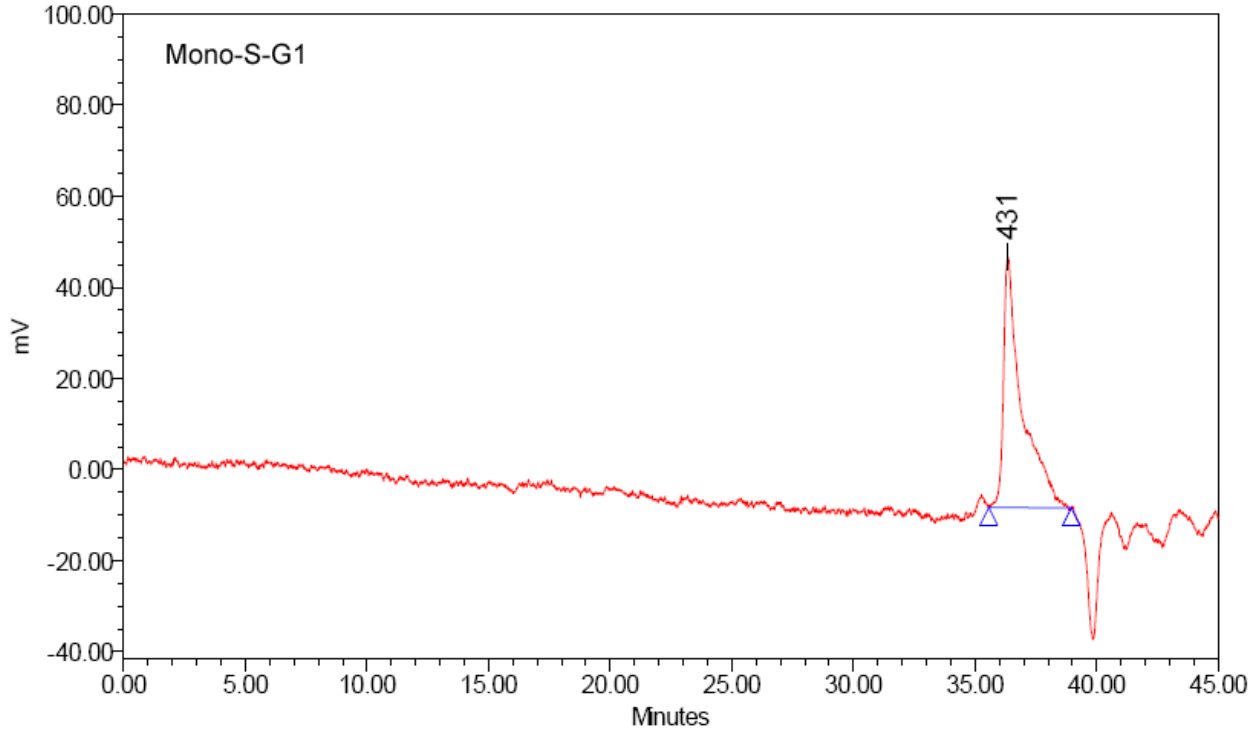
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
Minutes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mV
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80.00
60.00
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20.00
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-20.00
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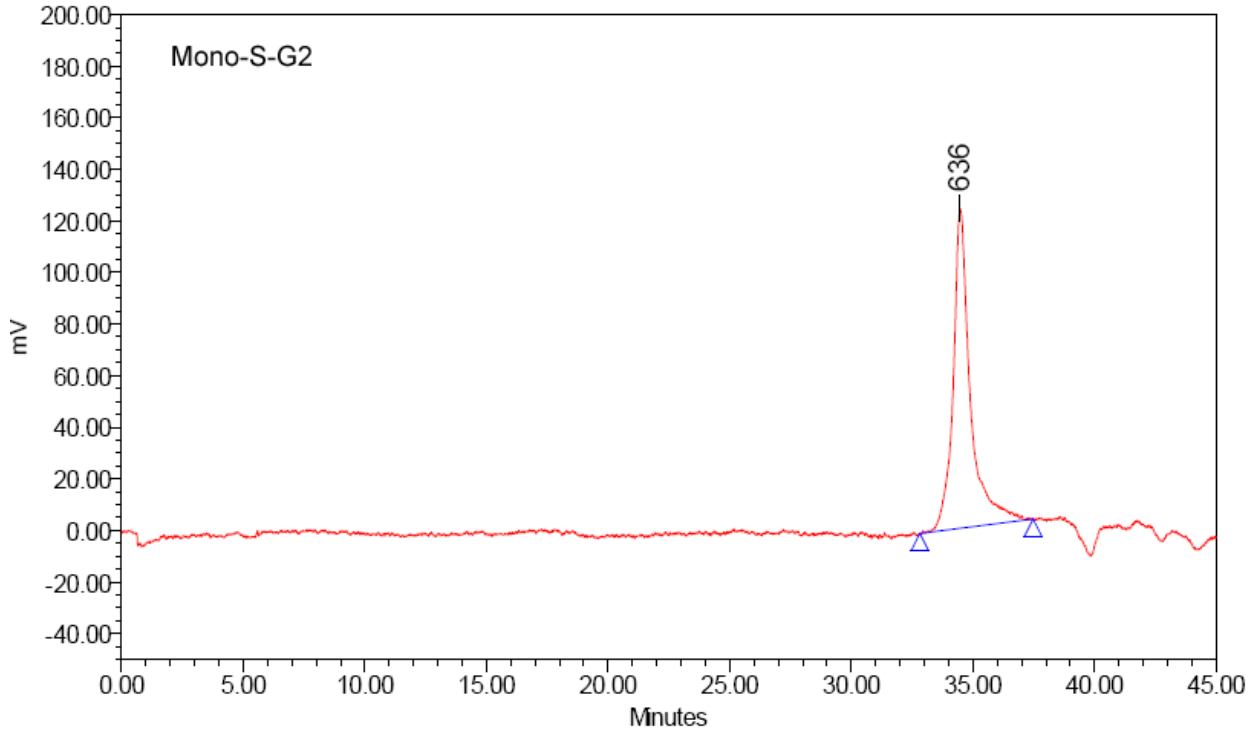
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
Minutes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636
mV
Minutes
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160.00
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
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15.00
20.00
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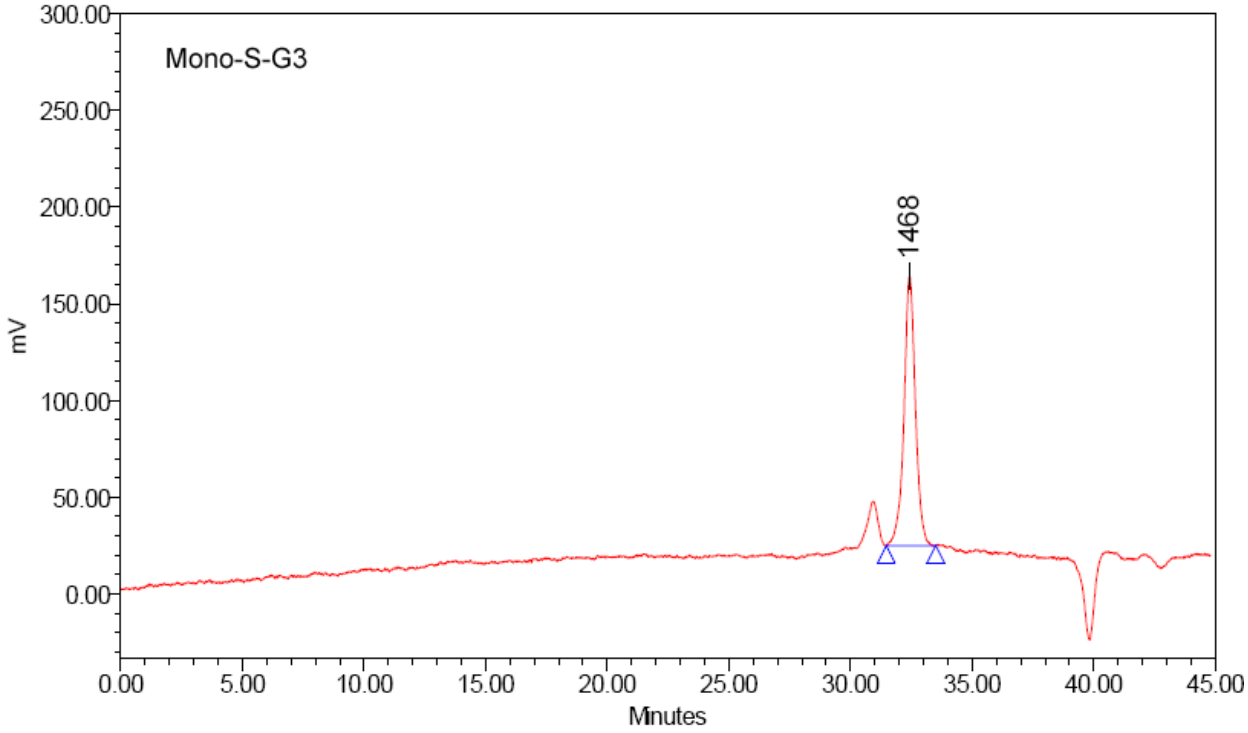
Mono-S-G3
1468
mV
Minutes
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200.00
150.00
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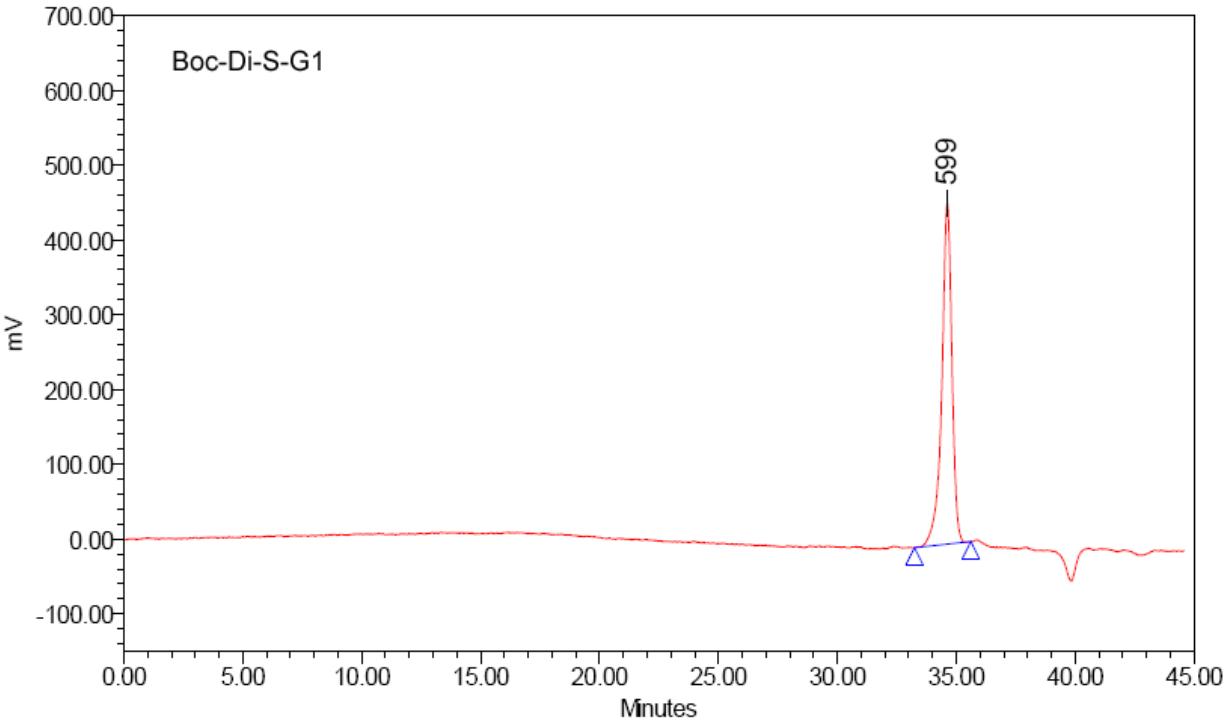
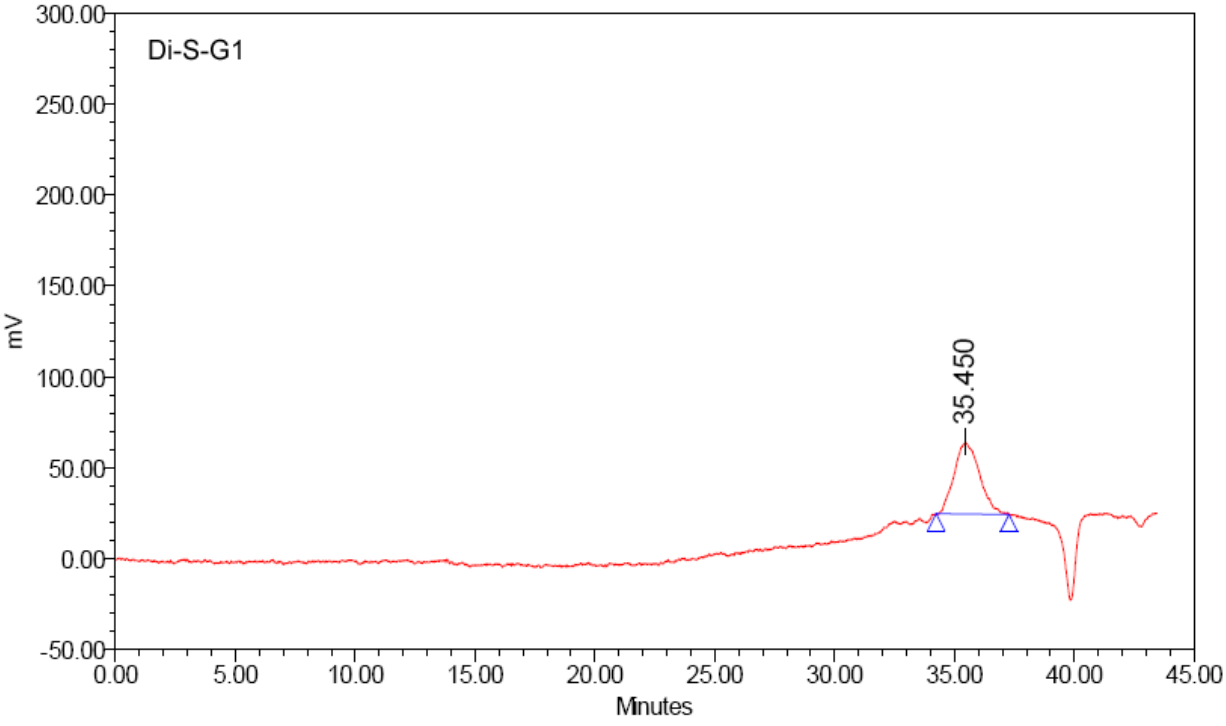
20.00
25.00
30.00
35.00
40.00
45.00


Boc-Di-S-G1
599
mV
700.00
600.00
500.00
400.00
300.00
200.00
100.00
0.00
-100.00
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
Minutes


Di-S-G1
35.450
mV
300.00
250.00
200.00
150.00
100.00
50.00
0.00
-50.00
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
Minutes

11. Comments on NMR and SEC Data

All synthesized compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry (MS) and elemental analysis. As all dendritic compounds contained isopropyl surface groups on the periphery, a distinctive doublet at δ 0.7–0.9 (J = 6.6 Hz) and a nonet at δ 1.4–1.5 (J = 6.6 Hz) that corresponded to the methyl and methine protons of the isopropyl groups, respectively, could be identified in all ^{1}H NMR spectra. The chemical shifts of these signals were not affected by the nature of the focal point functionalities or dendrimer generation. Furthermore, their relative intensities with respective to those of the focal point signals increased with increasing generation due to the exponential increase in the number of the surface groups. After attaching the proline core to the dendrons, the ^{1}H signals due to the pyrrolidine moiety were noticeable. Since the Boc-protected proline derivatives existed as rotameric mixtures, their ^{1}H NMR spectra appeared slightly complicated. Nonetheless, the Boc group appeared as a sharp singlet at δ 1.4–1.5. Besides, the methine proton attaching to the chiral carbon of the pyrrolidine ring appeared as a multiplet at δ 3.6–4.1, while the methylene proton signals due to the β- and γ-positions of the pyrrolidine ring appeared at δ 1.5–2.1. For the methylene protons at the δ-position, the ^{1}H NMR signal existed as a multiplet at δ 3.1–3.6. After removal of the Boc protecting group, the sharp singlet due to the *tert*-butyl group at δ 1.4–1.5 disappeared. Instead, a new signal, due to the N–*H* proton appeared. However, the chemical shift value of this broad singlet was found to vary among the various compounds, and was in the range between δ 1.8–3.8. In addition, the ^{1}H signals of the pyrrolidine ring protons also experienced an upfield shift. Hence, the signal of the α-methine proton shifted to δ 3.0–3.4, while the methylene protons at γ- and δ-position appeared as distinguishable multiplets at δ 1.5–1.8 and δ 2.7–3.1, respectively. On the other hand, those at the β-position were spread out between δ 1.7–2.0, and partly overlapped with the aliphatic hydrocarbon dendron signals.

For ^{13}C NMR spectroscopy, it was interesting to note that the geminal methyl carbons of the isopropyl groups in some compounds (*e.g.* **Di-S-G1** and **Mono-L-G1**) were diastereotopic, and appeared as two carbon signals at about δ 22–23. Similar to ^{1}H NMR, the chemical shifts of ^{13}C signals corresponding to the dendritic part were not affected by the change of focal point functionalities or dendrimer generation. After introduction of the proline core, the Boc-protected compounds showed the signals of the *tert*-butyl group at δ 28–29 and δ 78–80, and the carbonyl carbon at δ 154–160. After deprotection, the carbon signals corresponding to the Boc group disappeared and the target dendritic diamino catalysts showed four characteristic carbon signals in the range of δ 45–61 due to different carbon atoms adjacent to the two nitrogen atoms.

The structural purities of the dendritic compounds were further revealed by the polydispersity index (PDI) as determined by size exclusion chromatography (SEC) using polystyrenes as standards. Since our target compounds do not contain any UV-chromophore, a refractive index (RI) detector was used instead of a conventional UV detector. Most of the synthesized compounds gave a PDI of less than 1.05, and therefore can be regarded as monodisperse compounds. Unlike polystyrenes which are linear polymers, dendrimers are highly branched and therefore possess very different hydrodynamic radius as compared to polystyrene standards of similar molecular weight. Hence the SEC calculated M_w values were very different from the theoretical ones. Nonetheless, their molecular masses could be unambiguously determined by mass spectrometry.

12. References

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