Electronic Supplementary Material (ESI) for Green Chemistry.

Synthesis and polymerisation of α-alkylidene cyclic carbonates obtained from carbon dioxide, epoxides and the primary propargylic alcohol 1,4-butynediol

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1. General Information

1.1. Materials and Methods

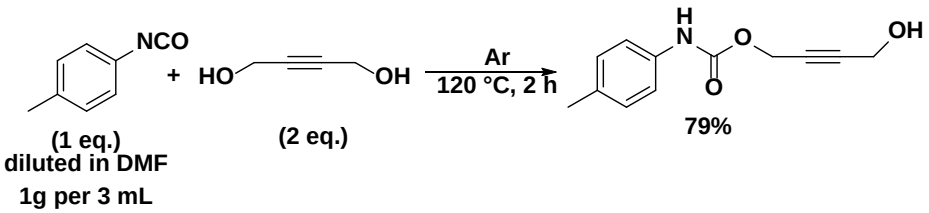
All reagents and solvents were purchased from Sigma-Aldrich or ABCR and used without further purification. Thin-layer chromatography (TLC) analysis was performed on Macherey-Nagel Polygram SIL G/UV254 plates. The reactions were performed in in a 40 mL steel autoclave equipped with a magnetic overhead stirrer purchased from Premex.

1.2. Instruments

NMR spectra were recorded on either Bruker AVANCE III 300 (^{1}H NMR: 300 MHz, ^{13}C NMR: 75 MHz) or on a Bruker AVANCE III 400 (^{1} H NMR: 400 MHz, ^{13}C NMR: 101 MHz) spectrometer at the Institute of Organic Chemistry/Heidelberg University. Chemical shifts (**δ**) are given in ppm relative to the residual solvent peak (CD_3CN: **δ** = 1.94 ppm, $CDCl_3$: **δ** = 7.26 ppm). Spin-spin coupling constants (***J***) are given in Hz. Abbreviations are as follows: s (singlet), d (doublet), t (triplet), m (multiplet), br.s (broad singlet). Mass spectra were recorded on a Vacuum Generators ZAB- 2F, Finnigan MAT TSQ 700 or JEOL JMS-700 spectrometer. IR spectra (in cm^{-1}) were recorded on a Varian 2000, Scimitar Series, FTS2000, as KBr film at room temperature. Gel permeation chromatography was performed on a JASCO PU-2050 GPC unit equipped with a JASCO UV-2075 UV- and a JASCO RI-2031 RI-detector with PSS-SDV columns (8*300 mm, 10 Å, 1000 Å and 10^5 Å pore size) in ethanol stabilized chloroform and calibrated with a polystyrene standard (PSS Ready-Cal-Kit, Mp 370-2520000 Da).

2.0. Synthesis of 1,4-butynediol derivatives as starting materials

4-hydroxybut-2-yn-1-yl *p*-tolylcarbamate

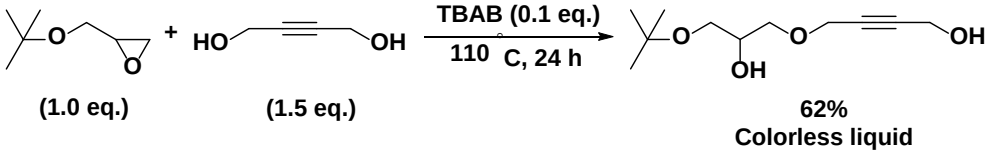


1-methyl-4-isocyanatobenzene (1.0 g, 7.51 mmol, 1.0 eq.) dissolved in DMF (3 mL) was added dropwise (2 drop/sec) into an argon purged 100 mL three-neck round bottom flask containing but-2-yne-1,4-diol (1.30 g, 15.10 mmol, 2.0 eq.), melted at 120 °C. After the addition was complete, the reaction mixture was further stirred at 120 °C for 2 h. Distilled water (30 mL) was then added to the above reaction mixture and the product was extracted with EtOAc (2 X 40 mL). The crude was columned (silica gel, PE/EtOAc = 7:3) to get the product (R_f = 0.62 in PE/EtOAc = 1:1) as a white solid (1.3 g, 79%).

^{1}H NMR (300 MHz, CD_3CN): δ = 7.71 (br.s, 1 H), 7.31 (d, *J* = 8.2 Hz, 2 H), 7.12 (d, *J* = 8.2 Hz, 2 H), 4.78–4.75 (m, 2 H), 4.19–4.18 (m, 2 H), 3.15 (t, *J* = 6.1 Hz, 1 H), 2.28 (s, 3 H). **^{13}C NMR (75 MHz, CD_3CN): δ =** 153.9, 136.8, 133.8, 130.3 (2 C), 119.9 (2 C), 86.4, 80.1, 53.4, 50.6, 20.7. **IR (film): ν =** 3343 (OH), 2927, 2852, 1709 (br.s),

1602, 1546, 1409, 1319, 1225, 1137, 1067, 1027, 854, 813, 761, 720, 675, 505 cm^{-1}. **HRMS (ESI):** *m*/*z* calcd. for $C_{12}H_{13}NO_3$: 461.1683 [2M+Na^+]; found: 461.1683.

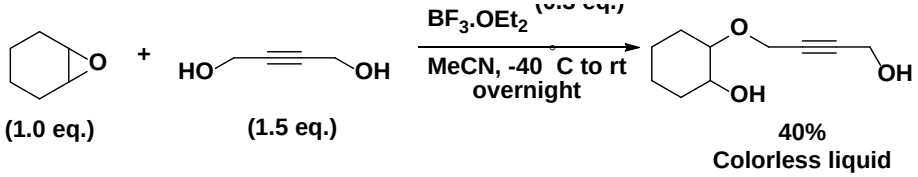
4-(3-(tert-butoxy)-2-hydroxypropoxy)but-2-yn-1-ol



But-2-yne-1,4-diol (3.96 g, 46.09 mmol, 1.5 eq.) and tetrabutylammonium bromide (TBAB, 0.99 g, 3.07 mmol, 0.1 eq.) were taken in an Argon flushed 100 mL three neck round bottom flask. To this, was added 30 mL chlorobenzene and the mixture was heated to 110 °C until the reagents were completely dissolved. A solution of *tert*-butyl glycidyl ether (4 g, 30.7 mmol, 1.0 eq.) in 20 mL chlorobenzene was then added to the above mixture with the help of a syringe and the reaction was heated overnight. Flash chromatography of the crude (silica gel, PE/EtOAc = 3:7) gave the pure product (R_f = 0.22 in PE/EtOAc = 1:1) as a colourless oil (4.1 g, 62%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.19–4.21 (m, 2 H), 4.16–4.15 (m, 2 H), 3.84 (m, 1 H), 3.55–3.45 (m, 2 H), 3.37–3.28 (m, 3 H), 3.00 (br.s, 1 H), 1.13 (s, 9 H). **^{13}C NMR (101 MHz, $CDCl_3$): δ =** 85.4, 81.0, 73.4, 71.2, 69.7, 62.9, 58.8, 50.4, 27.4 (3 C).**IR (film): ν =** 3401 (OH), 2975, 2932, 2871, 1473, 1364, 1236, 1196, 1126, 1086, 1020, 944, 884, 733, 646, 600, 461 cm^{-1}. **HRMS (ESI):** *m*/*z* calcd. for $C_{11}H_{20}O_4$: 239.1254 [M+Na^+]; found: 239.1261.

2-((4-hydroxybut-2-yn-1-yl)oxy)cyclohexan-1-ol

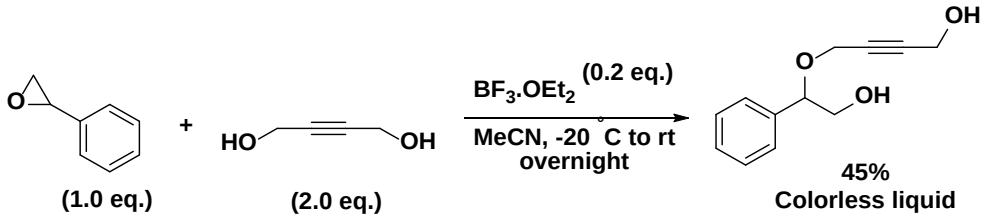


But-2-yne-1,4-diol (2.63 g, 30.5 mmol, 1.5 eq.) in dry MeCN (15 mL) was taken in a 50 mL argon flushed three neck round bottom flask. The mixture was stirred at room temperature till the diol was completely dissolved and this was followed by lowering the reaction temperature to -20 °C. $BF_3.OEt_2$ (0.77 mL, 0.3 eq.) was then added to the above reaction mixture, followed by the dropwise addition of a solution of cyclohexene oxide (2.0 g, 20.3 mmol, 1.0 eq.) in MeCN (10 mL). This reaction mixture was stirred overnight and the temperature was left to gradually increase to room temperature. In the end, the solvent (MeCN) was evaporated and the crude was subjected to flash chromatography (silica gel, MeOH/DCM=1:99) to afford the pure product (R_f = 0.20 in MeOH/DCM = 3:97) as a colourless oil (1.52 g, 40.5%).

^{1}H NMR (300 MHz, CD_3CN): δ = 4.29 (t, *J* = 1.9 Hz, 2 H), 4.20 (t, *J* = 1.8 Hz, 2 H), 3.40–3.31 (m, 1 H), 3,21–3.14 (m, 1 H), 3.04 (br.s, 1 H), 2.23 (br.s, 1 H), 2.08–2.02 (m, 1 H), 1.92–1.85 (m, 1 H), 1.71–1.64 (m, 2 H), 1.29–1.08 (m, 4 H). **^{13}C NMR (75 MHz, CD_3CN): δ =** 85.5, 83.3, 82.4, 74.2, 57.5, 50.7, 33.7, 30.3, 24.8, 24.5. **IR (film): ν =**

3389, 2935, 2862, 1451, 1352, 1268, 1235, 1124, 1081, 1019, 909, 847, 732, 608, 562, 453 cm^{-1}. **HRMS (EI):** *m*/*z* calcd. for $C_{10}H_{16}O_3$: 184.10940 [M^+]; found: 184.11013.

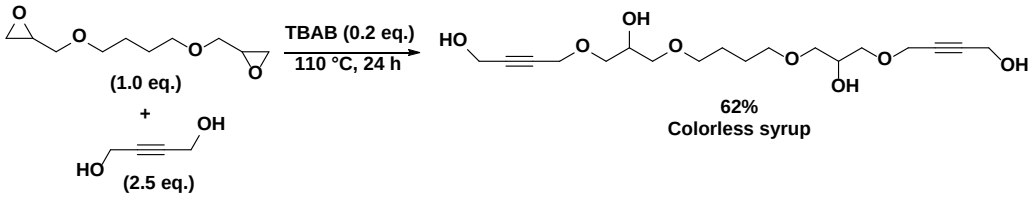
4-(2-hydroxy-1-phenylethoxy)but-2-yn-1-ol



But-2-yne-1,4-diol (4.29 g, 49.8 mmol, 2.0 eq.) in dry MeCN (30 mL) was taken in a 100 mL argon flushed three neck round bottom flask. The mixture was stirred at room temperature till the diol was completely dissolved and this was followed by lowering the reaction temperature to -20 °C. To the above solution was added $BF_3.OEt_2$ (0.60 mL, 0.2 eq.), followed by the dropwise addition of a solution of styrene oxide (2.8 mL, 24.9 mmol, 1.0 eq.) in MeCN (20 mL). The reaction was stirred overnight and the temperature was left to gradually increase to room temperature. The solvent was then evaporated and the crude was subjected to flash chromatography (silica gel, MeOH/DCM=10-20%) to affored the pure product (R_f = 0.25 in MeOH/DCM = 3:97) as a colourless oil (2.3 g, 45%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.22 (m, 5 H), 4.59 (dd, *J* = 8.6 Hz, 3.5 Hz, 1 H), 4.20 (t, *J* = 1.7 Hz, 2 H), 4.15 (dt, *J* = 15.7 Hz, 1.7 Hz, 1 H), 3.91 (dt, *J* = 15.6 Hz, 1.6 Hz, 1 H), 3.66 (dd, *J* = 11.9 Hz, 8.6 Hz, 1 H), 3.56 (dd, *J* = 11.9 Hz, 3.6 Hz, 1 H), 3.21 (br.s, 2 H).**^{13}C NMR (100 MHz, $CDCl_3$): δ =** 137.6, 128.7 (2 C), 128.5, 127.1 (2 C), 85.4, 81.8, 81.2, 67.0, 56.5, 50.7. **IR (film): ν =** 3357, 3031, 2921, 2866, 1493, 1453, 1393, 1346, 1125, 1085, 1026, 865, 759, 702, 638, 539 cm^{-1}. **HRMS (EI):** *m*/*z* calcd. for $C_{12}H_{14}O_3$: 206.09375 [M^+]; found: 206.09250.

5,9,14,18-tetraoxadocosa-2,20-diyne-1,7,16,22-tetraol

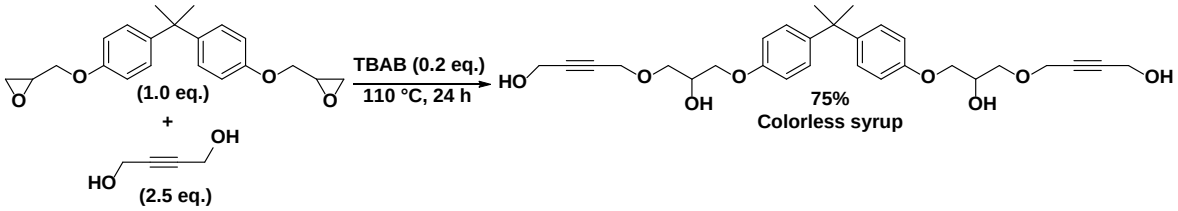


But-2-yne-1,4-diol (1.70 g, 19.75 mmol, 2.5 eq.) and tetrabutylammonium bromide (TBAB, 0.50 g, 1.58 mmol, 0.2 eq.) were taken in an Argon flushed 50 mL three neck round bottom flask. To this, was added 12 mL chlorobenzene and the mixture was heated to 110 °C until the reagents were completely dissolved. A solution of 1,4-butanediol diglycidyl ether (1.60 g, 7.91 mmol, 1.0 eq.) in 10 mL chlorobenzene was then added to the above mixture with the help of a syringe and the reaction was heated overnight. Flash chromatography of the crude (silica gel, EtOAc/MeOH = 96:4) gave the pure product (R_f = 0.22 in EtOAc/MeOH = 96:4) as a colourless oil (1.84 g, 62%).

^{1}H NMR (300 MHz, CD_3CN): δ = 4.18 (s, 8 H), 3.82 (br.s, 2 H), 3.51 (dd, *J* = 9.9 Hz, 4.4 Hz, 2 H), 3.46–3.32 (m, 12 H), 3.17 (br.s, 2 H), 1.61–1.57 (m, 4 H). **^{13}C NMR (75**

MHz, CD_3CN): δ = 86.3 (2 C), 81.5 (2 C), 72.9 (2 C), 72.2 (2 C), 71.8 (2 C), 70.1 (2 C), 59.3 (2 C), 50.6 (2 C), 27.1 (2 C). **IR (film): ν =** 3392, 2919, 2867, 1445, 1356, 1229, 1122, 1090, 1016, 873, 597 cm^{-1}. **HRMS (ESI):** *m*/*z* calcd. for $C_{18}H_{30}O_8$: 397.1833 [$M+Na^+$]; found: 397.1832.

4,4'-((((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(2-hydroxypropane-3,1-diyl))bis(oxy))bis(but-2-yn-1-ol)



But-2-yne-1,4-diol (2.15 g, 24.96 mmol, 2.5 eq.) and tetrabutylammonium bromide (TBAB, 0.65 g, 1.99 mmol, 0.2 eq.) were taken in an Argon flushed 50 mL three neck round bottom flask. To this, was added 15 mL chlorobenzene and the mixture was heated to 110 °C until the reagents were completely dissolved. A solution of bisphenol-A-diglycidyl ether (3.40 g, 9.98 mmol, 1.0 eq.) in 15 mL chlorobenzene was then added to the above mixture with the help of a syringe and the reaction was heated overnight. Flash chromatography of the crude (silica gel, EtOAc/MeOH = 98:2) gave the pure product (R_f = 0.54 in EtOAc/MeOH = 98:2) as a colourless oil (3.84 g, 75%).

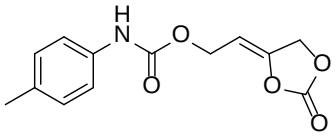
^{1}H NMR (400 MHz, CD_3CN): δ = 7.14 (d, *J* = 8.8 Hz, 4 H), 6.83 (d, *J* = 8.8 Hz, 4 H), 4.18 (m, 8 H), 3.99 (dd, *J* = 18.8 Hz, 13.4 Hz, 4 H), 3.90 (dd, *J* = 9.7 Hz, 6.0 Hz, 2 H), 3.58 (ddd, *J* = 15.7 Hz, 9.9 Hz, 5.2 Hz, 4 H), 3.27 (d, *J* = 4.9 Hz, 2 H), 3.16 (t, *J* = 5.8 Hz, 2 H), 1.61 (s, 6 H). **^{13}C NMR (101 MHz, CD_3CN): δ =** 157.7 (2 C), 144.3 (2 C), 128.6 (4 C), 114.9 (4 C), 86.4 (2 C), 81.4 (2 C), 71.8 (2 C), 70.3 (2 C), 69.7 (2 C), 59.3 (2 C), 50.6 (2 C), 42.3, 31.2 (2 C). **IR (film): ν =** 3379, 2931, 2871, 1607, 1510, 1461, 1361, 1297, 1248, 1184, 1124, 1087, 1013, 830, 575 cm^{-1}. **HRMS (ESI):** *m*/*z* calcd. for $C_{29}H_{36}NaO_8$: 535.2305 [$M+Na^+$]; found: 535.2302.

3.0. General procedure for the carboxylative cyclisation of 1,4-butynediol derivatives

A steel autoclave was charged with Alkynol (5.0 mmol), AgOAc (1 mol% for mono-EVC and 5 mol% for bis-EVCs), Davephos-Ligand (1 mol% for mono-EVC or 5 mol% for bis-EVC) and solvent (10 mL) under atmospheric conditions. The reaction mixture was pressurized with CO_2 (20 bar) and stirred at room temperature for 18 h. Then CO_2 overpressure was carefully released and solvent evaporated. The resulting crude mixture was purified by flash column chromatograph.

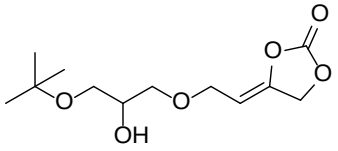
4.0. Characterisation of the isolated exo-vinylene carbonate products

(Z)-2-(2-oxo-1,3-dioxolan-4-ylidene)ethyl *p*-tolylcarbamate



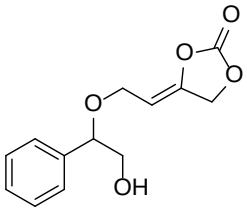
Yellow solid, (1.25 g, **95%**). R_f (EtOAc/PE 1:1) **=** 0.72. **^{1}H NMR (300 MHz, CD_3CN): δ =** 7.62 (br.s, 1 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 7.11 (d, *J* = 8.3 Hz, 2 H), 5.06–5.01 (m, 3 H), 4.73–4.70 (m, 2 H), 2.27 (s, 3 H). **^{13}C NMR (75 MHz, CD_3CN): δ =** 153.6, 147.2 (2 C), 137.0, 133.7, 130.3 (4 C), 98.1, 68.8, 58.9, 20.7. **IR (film): ν =** 3304, 1847 (C=O), 1732, 1704, 1599, 1538, 1455, 1317, 1235, 1130, 1098, 1045, 1007, 820, 763, 688 cm^{-1}. **HRMS (ESI):** *m*/*z* calcd. for $C_{13}H_{13}NO_5$: 549.2542 [2M+Na$^+$]; found: 549.2546.

(*Z*)-4-(2-(3-(tert-butoxy)-2-hydroxypropoxy)ethylidene)-1,3-dioxolan-2-one



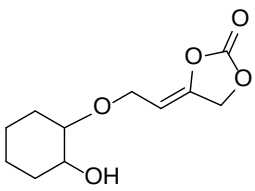
Light yellow liquid, (1.23 g, **95%**). R_f (EtOAc/PE 3:2) **=** 0.30. **^{1}H NMR (400 MHz, $CDCl_3$): δ =** 5.00–4.99 (m, 2 H), 4.96–4.90 (m, 1 H), 4.19–4.15 (m, 2 H), 3.90–3.81 (m, 1 H), 3.53–3.31 (m, 4 H), 2.55–2.54 (m, 1 H), 1.10 (s, 9 H). **^{13}C NMR (101 MHz, $CDCl_3$): δ =** 152.3, 144.1, 100.2, 73.4, 71.9, 69.9, 67.4, 64.4, 62.9, 27.6 (3 C). **IR (film): ν =** 3442, 2975, 2932, 2874, 1834 (C=O), 1724, 1471, 1365, 1296, 1196, 1126, 1086, 1044, 956, 766, 733, 461 cm^{-1}. **HRMS (ESI):** *m*/*z* calcd. for $C_{12}H_{20}O_6$: 283.1152 [M+Na$^+$]; found: 283.1158. Anal. Calcd. for $C_{12}H_{20}O_6$: C 55.37%, H 7.75%, Found: C 55.60%, H 7.74%.

(*Z*)-4-(2-(2-hydroxy-1-phenylethoxy)ethylidene)-1,3-dioxolan-2-one



Light yellow liquid, (1.18 g, **95%**). R_f (EtOAc/PE 3:2) **=** 0.33. **^{1}H NMR (300 MHz, $CDCl_3$): δ =** 7.39–7.28 (m, 5 H), 4.97–4.85 (m, 3 H), 4.44 (dd, *J* = 8.2 Hz, 3.9 Hz, 1 H), 4.15–4.03 (m, 2 H), 3.69 (dd, *J* = 11.7 Hz, 8.2 Hz, 1 H), 3.60 (dd, *J* = 11.7 Hz, 3.8 Hz, 1 H), 2.73 (br.s, 1 H). **^{13}C NMR (75 MHz, $CDCl_3$): δ =** 152.3, 144.0, 138.2, 128.5 (2 C), 128.2, 126.8 (2 C), 99.9, 82.8, 67.3, 67.0, 62.1. **IR (film): ν =** 3424, 2925, 2875, 1831 (C=O), 1724, 1634, 1493, 1454, 1375, 1295, 1212, 1130, 1099, 1046, 870, 762, 703, 637, 539 cm^{-1}. **HRMS (ESI):** *m*/*z* calcd. for $C_{13}H_{14}O_5$: 250.08357 [M$^+$]; found: 250.08439. Anal. Calcd. for $C_{13}H_{14}O_5$: C 62.39%, H 5.64%, Found: C 62.11%, H 5.64%.

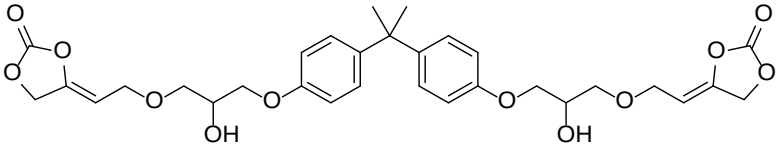
(*Z*)-4-(2-((2-hydroxycyclohexyl)oxy)ethylidene)-1,3-dioxolan-2-one



Colorless liquid, (**1.11 g**, **97%**). R_f (EtOAc/PE 1:1) **=** 0.15. **^{1}H NMR (300 MHz, $CDCl_3$): δ =** 4.97–4.88 (m, 3 H), 4.28–4.21 (m, 1 H), 4.13–4.06 (m, 1 H), 3.39–3.31 (m, 1 H), 3.06–2.99 (m, 1 H), 2.76 (br.s, 1 H), 2.10–1.91 (m, 2 H), 1.68–1.63 (m, 2 H), 1.27–1.09 (m, 4 H). **^{13}C NMR (75 MHz, $CDCl_3$): δ =** 152.3, 143.8, 100.5, 83.2, 73.6, 67.4, 61.7, 32.2, 29.1, 24.1, 23.8. **IR (film): ν =** 3441, 2936, 2864,

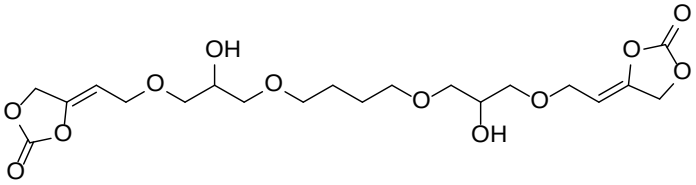
1834 (C=O), 1724, 1634, 1452, 1379, 1297, 1210, 1128, 1084, 1044, 1006, 912, 849, 765, 733, 647, 539 cm^{-1}. **HRMS (ESI):** *m*/*z* calcd. for $C_{11}H_{16}O_5$: 479.1888 [2M+Na^+]; found: 479.1892. Anal. Calcd. for $C_{11}H_{16}O_5$: C 57.89%, H 7.07%, Found: C 57.86%, H 7.18%.

(4Z,4'Z)-4,4'-(((((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(2-hydroxy propane-3,1-diyl))bis(oxy))bis(ethan-2-yl-1-ylidene))bis(1,3-dioxolan-2-one)



Colorless oil, 545 mg (**93%**) for a reaction scale of 0.97 mmol. ***R*f** (EtOAc) **=** 0.59. **^{1}H NMR (300 MHz, $CDCl_3$): δ =** 7.16–7.10 (m, 4 H), 6.84–6.78 (m, 4 H), 5.01–4.88 (m, 6 H), 4.23–4.21 (m, 2 H), 4.20–4.18 (m, 2 H), 4.17–4.09 (m, 2 H), 4.03–3.95 (m, 4 H), 3.67–3.56 (m, 4 H), 2.52 (br.s, 2 H), 1.63 (s, 6 H). **^{13}C NMR (75 MHz, $CDCl_3$): δ =** 156.4 (2 C), 152.3 (2 C), 144.4 (2 C), 143.8 (2 C), 127.9 (4 C), 114.0 (4 C), 99.9 (2 C), 71.3 (2 C), 69.2 (2 C), 68.9 (2 C), 67.4 (2 C), 64.5 (2 C), 41.8, 31.1 (2 C). **IR (film): ν =** 3446, 2964, 2930, 2873, 1832 (C=O), 1724, 1608, 1510, 1463, 1382, 1297, 1249, 1127, 831, 724 cm^{-1}. **HRMS (ESI):** *m*/*z* calcd. for $C_{31}H_{36}O_{12}$: 623.2099 [M+Na^+]; found: 623.2101. Anal. Calcd. for $C_{31}H_{36}O_{12}$: C 61.99%, H 6.04%, Found: C 61.96%, H 6.06%.

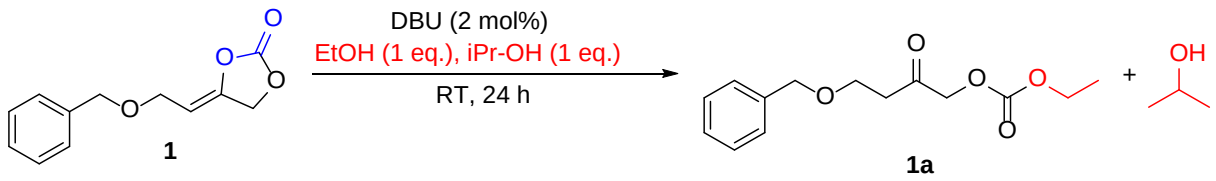
(4*Z*,4'*Z*)-4,4'-(5,14-dihydroxy-3,7,12,16-tetraoxaoctadecane-1,18-diylidene)bis (1,3-dioxolan-2-one)



Colorless liquid, **426 mg** (**95%**) for a reaction scale of 0.97 mmol. ***R*f** (EtOAc/MeCN 96:4) **=** 0.19. **^{1}H NMR (400 MHz, $CDCl_3$): δ =** 5.03–5.02 (m, 4 H), 4.95 (tt, *J* = 7.1 Hz, 2.0 Hz, 2 H), 4.20 (t, *J* = 1.4 Hz, 2 H), 4.18 (t, *J* = 1.3 Hz, 2 H), 3.98–3.91 (m, 2 H), 3.55–3.41 (m, 12 H), 2.68 (br.s, 1 H), 1.67–1.63 (m, 4 H). **^{13}C NMR (100 MHz, $CDCl_3$): δ =** 152.4 (2 C), 144.3 (2 C), 100.1 (2 C), 71.9 (2 C), 71.7 (2 C), 71.4 (2 C), 69.6 (2 C), 67.5 (2 C), 64.4 (2 C), 26.4 (2 C). **IR (film): ν =** 3441, 2919, 2870, 1832 (C=O), 1724, 1465, 1381, 1297, 1214, 1103, 1044, 958, 916, 874, 766, 734, 574 cm^{-1}. **HRMS (ESI):** *m*/*z* calcd. for $C_{20}H_{30}O_{12}$: 485.1629 [M+Na^+]; found: 485.1627. Anal. Calcd. for $C_{20}H_{30}O_{12}$: C 51.95%, H 6.54%, Found: C 51.97%, H 6.54%.

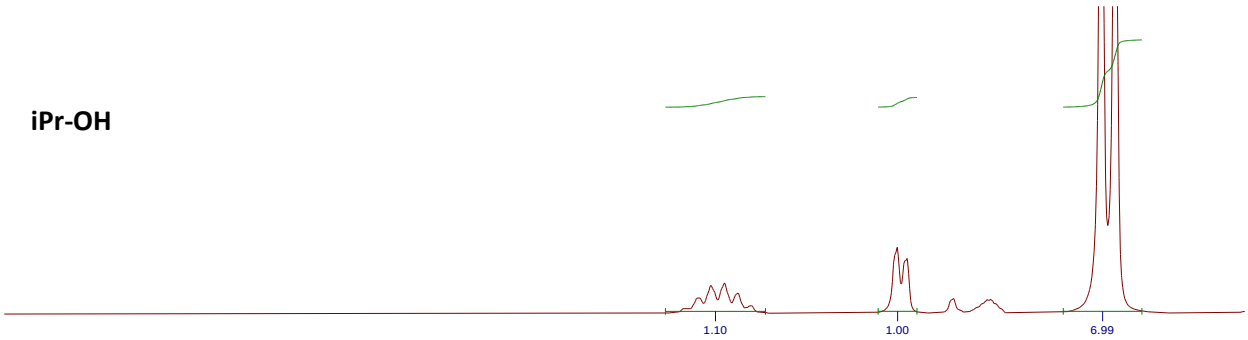
5.0. Nucleophilic ring opening reaction of mono- and bis- EVCs

5.1. Ring opening reaction of EVC 1

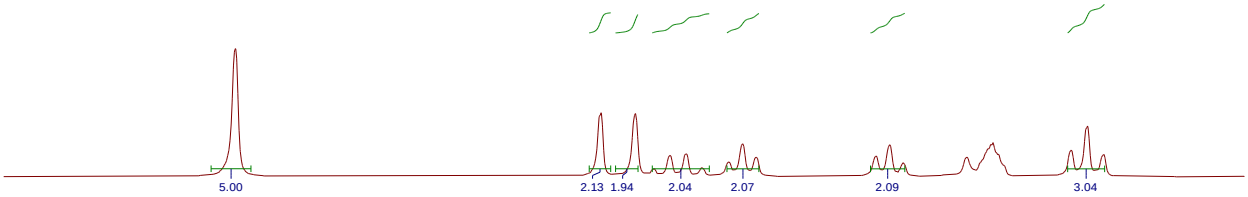


1 **1a**

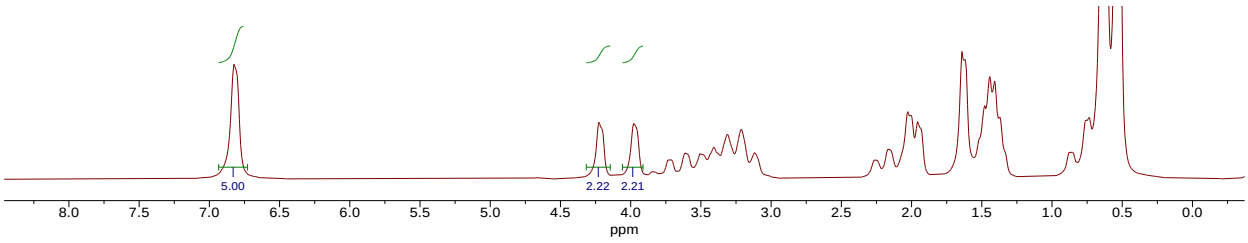
iPr-OH



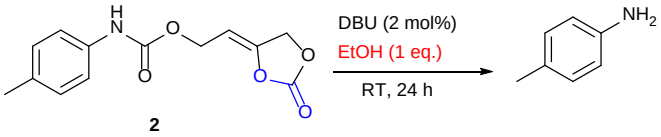
1a

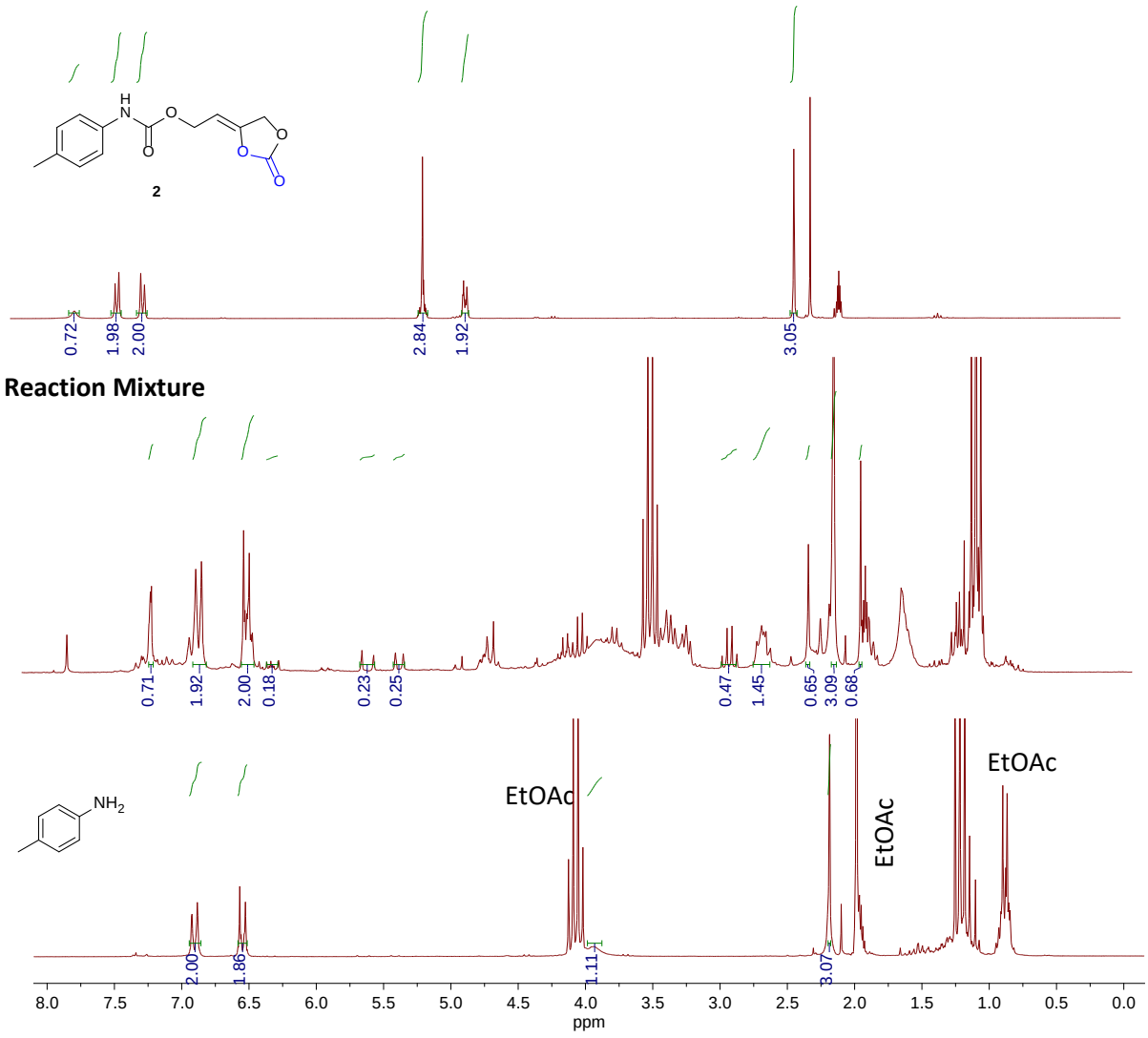


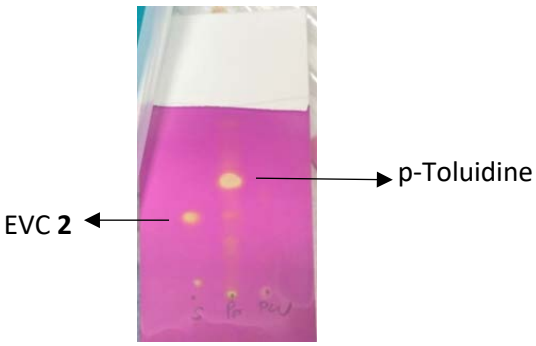
Crude reaction mixture showing exclusive formation of 1a



5.2. Ring opening reaction of EVC 2

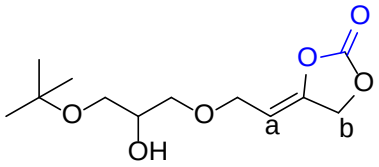






TLC of the crude reaction mixture

5.3. Self-polymerisation of EVC 5a

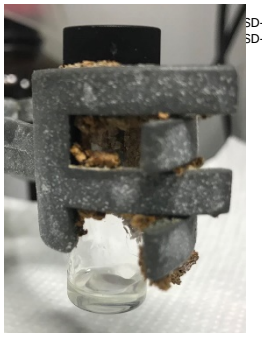


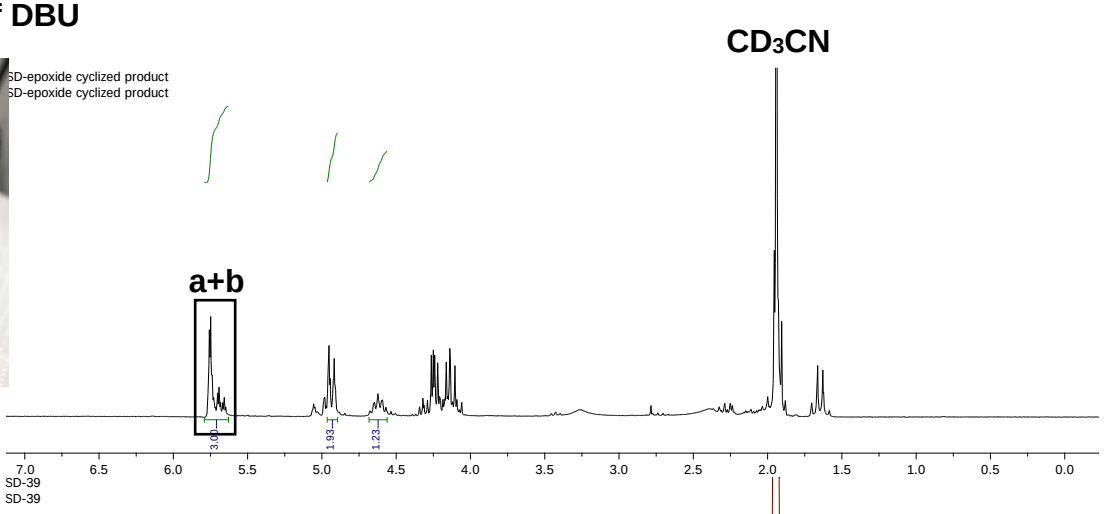
5a

DBU (2 mol%)
15 min, RT

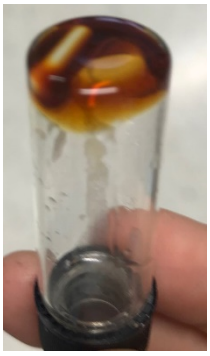
Full conversion to brown sticky product
GPC analysis: Mn = 948, Mw= 2497, Đ = 2.63

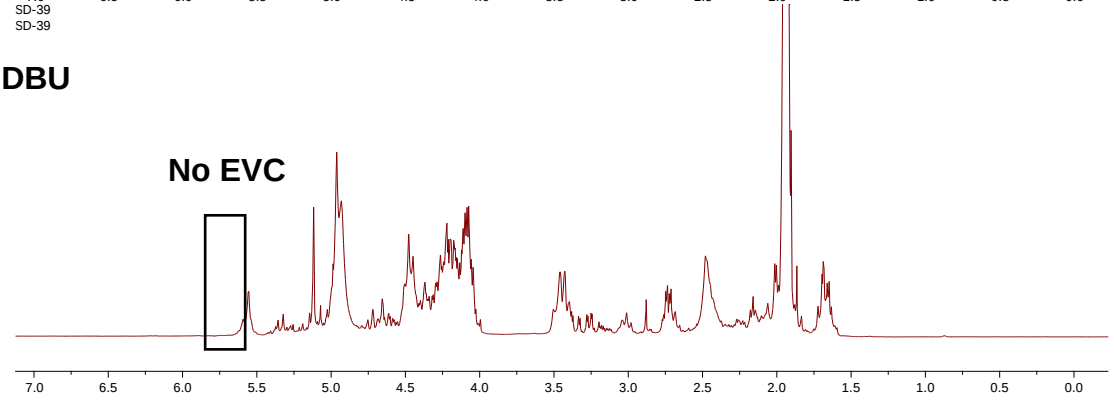
Before addition of DBU



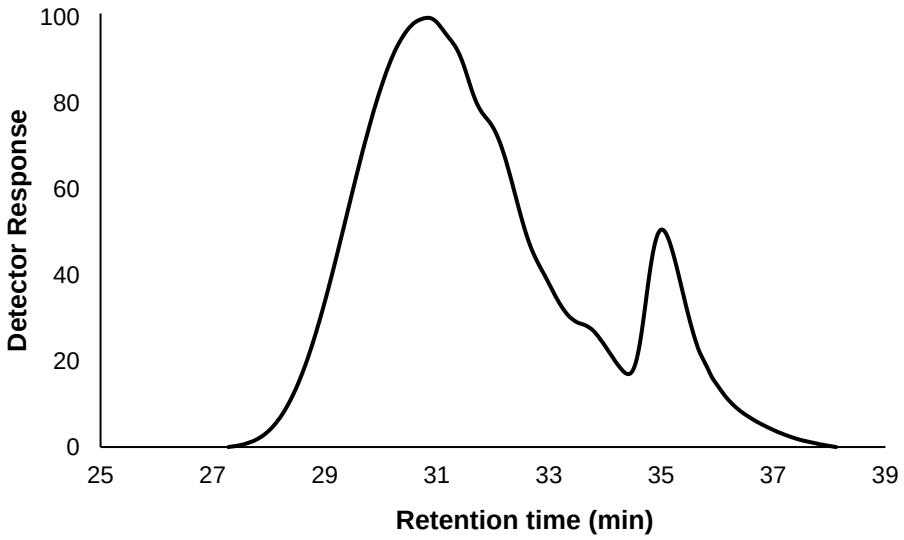


After addition of DBU

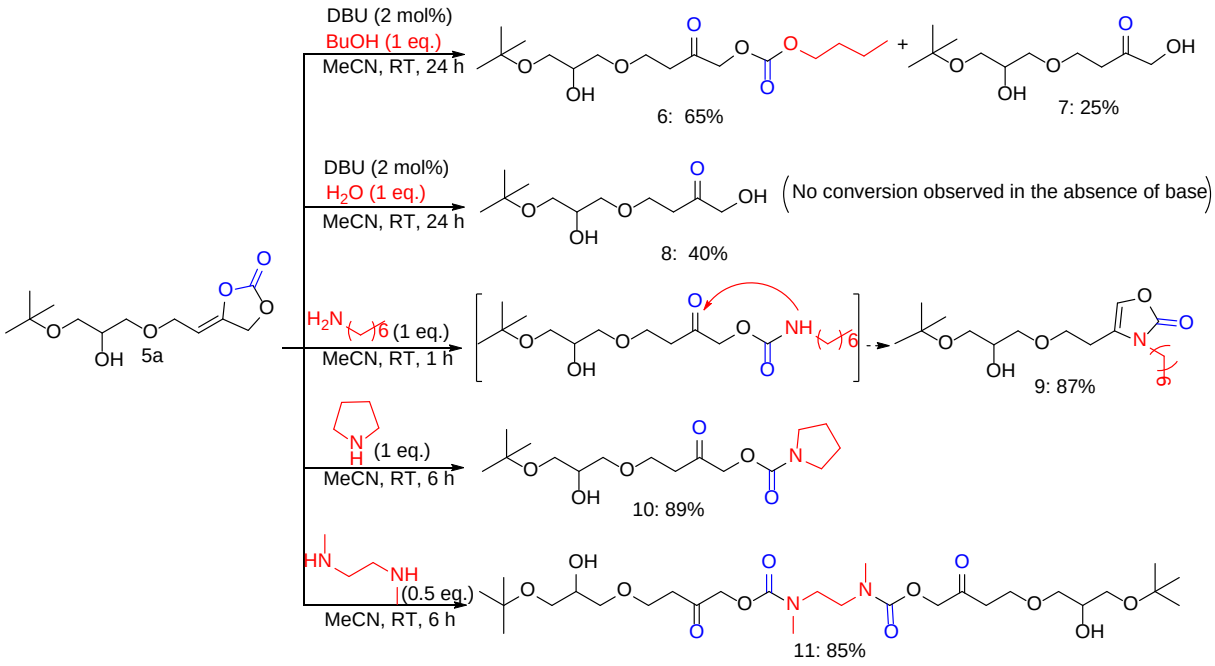




GPC measurements for polymer obtained after self-polymerisation of 5a



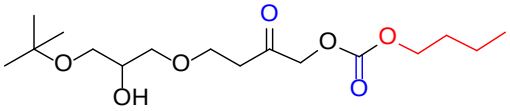
5.4. General reaction procedure for ring opening reaction of mono-EVC 5a



A 5 mL glass vial containing **5a** (50 mg, 0.19 mmol, 1.0 eq.) was charged with equimolar quantities of either alcohol (BuOH) with catalytic amounts of DBU (0.02 eq.) or with equimolar amounts of either primary (1-hexylamine) or secondary amine (pyrrolidine or of *N*,*N*-dimethylethylamine) in the presence of MeCN (1.5 mL). The reaction mixture was stirred at room temperature. The products **6-11** were isolated by column chromatography.

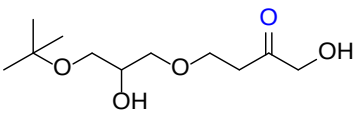
Product characterisation

4-(3-(tert-butoxy)-2-hydroxypropoxy)-2-oxobutyl butyl carbonate



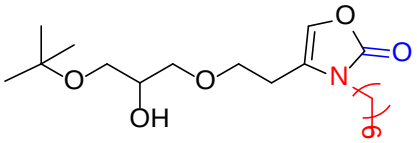
Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$): δ =** 4.70 (s, 2 H), 4.17 (t, *J* = 6.7 Hz, 2 H), 3.82 (br.s, 1 H), 3.78–3.73 (m, 2 H), 3.51 (dd, *J* = 9.9 Hz, 4.3 Hz, 1 H), 3.44 (dd, *J* = 9.9 Hz, 6.2 Hz, 1 H), 3.39–3.31 (m, 2 H), 2.68–2.65 (m, 3 H), 1.70–1.62 (m, 2 H), 1.45–1.35 (m, 2 H), 1.17 (s, 9 H), 0.93 (t, *J* = 7.4 Hz, 3 H). **^{13}C NMR (101 MHz, $CDCl_3$): δ =** 202.4, 155.0, 73.3, 72.8, 71.1, 69.8, 68.7, 66.1, 62.8, 39.3, 30.7, 27.6 (3 C), 19.0, 13.7. **IR (film): ν =** 3484, 2971, 2935, 2875, 1755 (C=O), 1737 (C=O), 1466, 1422, 1390, 1365, 1276, 1197, 1119, 1085, 1021, 946, 788 cm^{-1}. **HRMS (ESI):** *m*/*z* calcd. for $C_{16}H_{30}O_7$: 357.1884 [M+Na^+]; found: 357.1883.

4-(3-(tert-butoxy)-2-hydroxypropoxy)-1-hydroxybutan-2-one



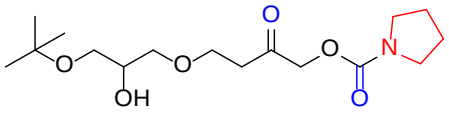
Colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$): δ =** 4.28 (s, 2 H), 3.87–3.77 (m, 3 H), 3.51–3.44 (m, 2 H), 3.40–3.31 (m, 2 H), 3.10 (br.s, 1 H), 2.68 (t, *J* = 6.0 Hz, 1 H), 1.19 (s, 9 H). **^{13}C NMR (75 MHz, $CDCl_3$): δ =** 208.6, 73.4, 72.6, 69.8, 69.0, 66.2, 62.8, 39.1, 27.6 (3 C). **IR (film): ν =** 3423, 2974, 2926, 2874, 1720 (C=O), 1474, 1364, 1237, 1197, 1117, 1083, 885, 558 cm^{-1}. **HRMS (ESI):** *m*/*z* calcd. for $C_{11}H_{22}O_5$: 257.1387 [M+Na^+]; found: 257.1384.

4-(2-(3-(tert-butoxy)-2-hydroxypropoxy)ethyl)-3-hexyloxazol-2(3H)-one



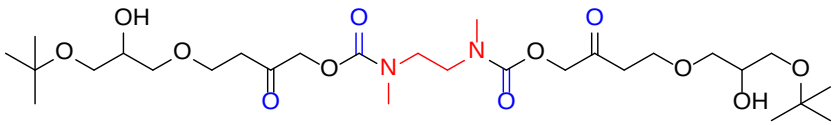
Colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$): δ =** 6.63 (t, *J* = 1.4 Hz, 1 H), 3.86 (t, *J* = 6.1 Hz, 1 H), 3.70–3.31 (m, 8 H), 2.64–2.60 (m, 2 H), 1.64–1.59 (m, 2 H), 1.31–1.27 (m, 6 H), 1.18 (s, 9 H), 0.87 (t, *J* = 6.5 Hz, 3 H).**^{13}C NMR (75 MHz, $CDCl_3$): δ =** 147.2, 125.8, 124.0, 73.4, 72.5, 69.9, 68.6, 62.8, 42.1, 31.5, 29.2, 27.6 (3 C), 26.4, 24.3, 22.6, 14.1. **IR (film): ν =** 3423, 2970, 2930, 2871, 1749 (C=O), 1654, 1460, 1409, 1364, 1236, 1195, 1115, 1081, 884, 731 cm^{-1}. **HRMS (ESI):** *m*/*z* calcd. for $C_{18}H_{33}NO_5$: 366.2248 [M+Na^+]; found: 366.2248.

4-(3-(tert-butoxy)-2-hydroxypropoxy)-2-oxobutyl pyrrolidine-1-carboxylate



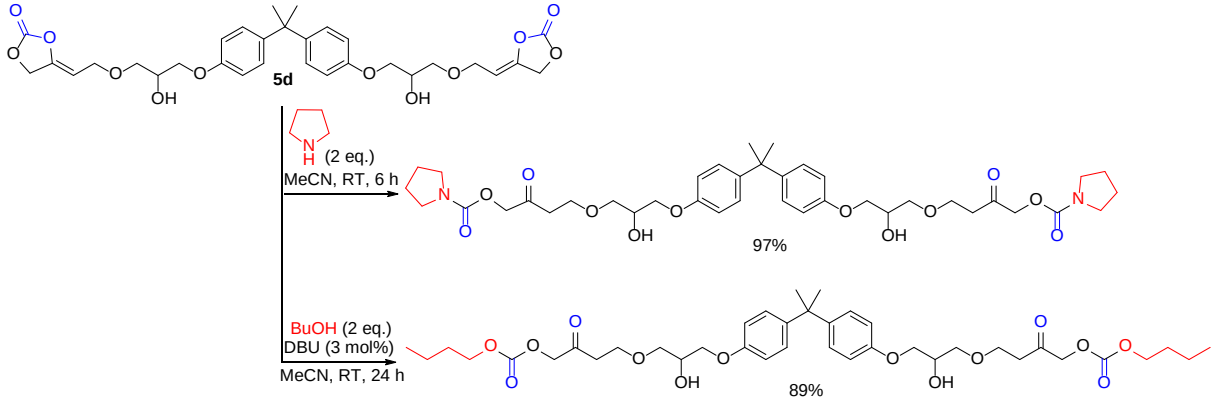
Colorless liquid. ***R*$_f$** (EtOAc/MeOH 99.5:0.5) **=** 0.44. **^{1}H NMR (300 MHz, $CDCl_3$): δ =** 4.66 (s, 2 H), 3.86–3.79 (m, 1 H), 3.77–3.70 (m, 2 H), 3.51 (dd, *J* = 9.9 Hz, 4.1 Hz, 1 H), 3.45–3.37 (m, 5 H), 3.34 (d, *J* = 5.5 Hz, 2 H), 2.75 (br.s, 1 H), 2.67 (t, *J* = 6.1 Hz, 1 H), 1.89-1.84 (m, 4 H), 1.15 (s, 9 H). **^{13}C NMR (101 MHz, $CDCl_3$): δ =** 204.3, 154.1, 73.2, 72.8, 69.8, 69.2, 66.1, 62.8, 46.2 (2 C), 39.2, 27.6 (3 C), 25.4 (2 C).**IR (film): *ν* =** 3463, 2973, 2876, 1709 (br.s, C=O), 1531, 1441 (C-N stretch), 1403, 1364, 1254, 1196, 1108, 1023, 961, 884, 766, 527, 420 cm^{-1}. **HRMS (ESI):** *m*/*z* calcd. for $C_{16}H_{29}NO_6$: 354.1887 [M+Na^+]; found: 354.1886.

4-(3-(tert-butoxy)-2-hydroxypropoxy)-2-oxobutyl(4-(4-(tert-butoxy)-3-hydroxy butoxy)-2-oxobutyl) ethane-1,2-diylbis(methylcarbamate)

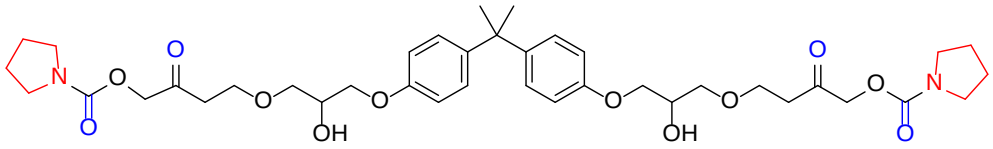


Colorless oil (diastereomeric mixture). ***R*$_f$** (EtOAc/MeOH 98:2) **=** 0.12. **^{1}H NMR (400 MHz, $CDCl_3$): δ =** 4.68–4.64 (m, 4 H), 3.80–3.78 (m, 2 H), 3.74–3.66 (m, 4 H), 3.50–3.38 (m, 8 H), 3.32–3.31 (m, 4 H), 2.99–2.96 (m, 3 H), 2.93 (br.s, 4 H), 2.89 (br.s, 1 H), 2.63 (m, 4 H), 1.13 (s, 18 H). **^{13}C NMR (101 MHz, $CDCl_3$): δ =** 203.7, 203.6, 203.4 (2 diastereomeric C), 155.7, 155.6, 155.3 (2 C), 73.1, 72.7, 69.6, 69.4, 66.0, 62.7, 47.6, 47.3, 46.8, 46.7, 39.0 (2 diastereomeric C), 35.8, 35.6, 35.3, 34.8, 27.4. **IR (film): *ν* =** 3473, 2974, 2913, 2873, 1708 (br.s, C=O), 1482 (C-N), 1402, 1364, 1219, 1196, 1118, 1085, 885, 943, 979, 767, 646 cm^{-1}. **HRMS (ESI):** *m*/*z* calcd. for $C_{28}H_{52}N_2O_{12}$: 631.3412 [M+Na^+]; found: 631.3413.

5.5. General reaction procedure for ring opening reaction of bis-EVC 5d and 5e

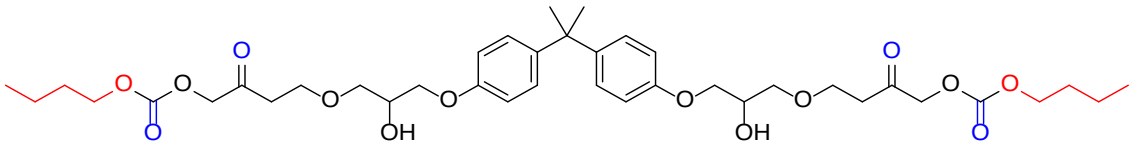


((((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(2-hydroxypropane-3,1-diyl)) bis(oxy))bis(2-oxobutane-4,1-diyl) bis(pyrrolidine-1-carboxylate)

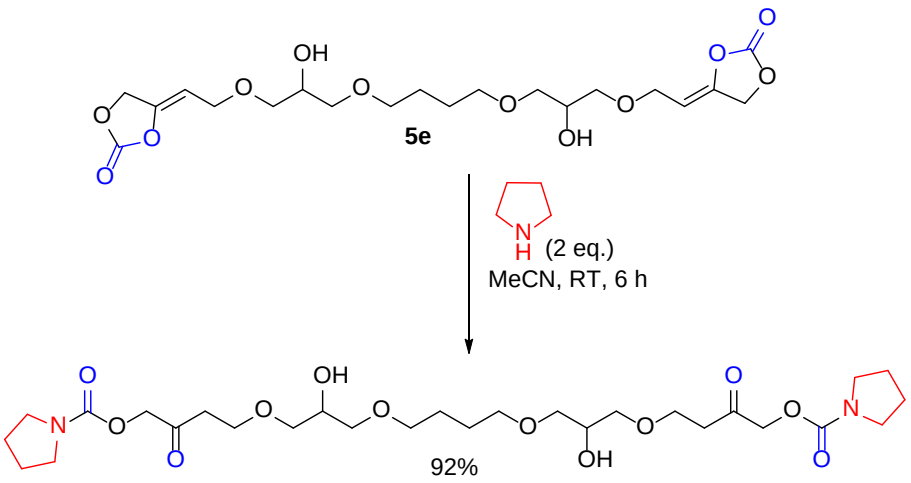


Colorless oil, ^{1}H NMR (400 MHz, CD_3CN): δ = 7.16 (d, *J* = 8.8 Hz, 4 H), 6.85 (d, *J* = 8.8 Hz, 4 H), 4.67 (s, 4 H), 4.01–3.96 (m, 4 H), 3.93–3.89 (m, 2 H), 3.78-3.69 (m, 4 H), 3.56 (dd, *J* = 10.1 Hz, 4.2 Hz, 2 H), 3.50 (dd, *J* = 10.1 Hz, 5.7 Hz, 2 H), 3.42–3.37 (m, 6 H), 3.31 (t, *J* = 6.5 Hz, 4 H), 2.65 (t, *J* = 6.0 Hz, 4 H), 1.91–1.83 (m, 8 H), 1.64 (s, 6 H). **^{13}C NMR (101 MHz, CD_3CN): δ =** 205.4 (2 C), 157.7 (2 C), 154.9 (2 C), 144.3 (2 C), 128.6 (4 C), 114.9 (4 C), 73.0 (2 C), 70.3 (2 C), 69.9 (2 C), 69.7 (2 C), 66.9 (2 C), 47.1 (2 C), 46.7 (2 C), 42.3, 39.7 (2 C), 31.2 (2 C), 26.4 (2 C), 25.5 (2 C). **IR (film): *ν* =** 3451, 2966, 2931, 2876, 1703 (br.s, C=O), 1608, 1510, 1441 (C-N stretch), 1402, 1296, 1250, 1183, 1038, 1108, 831, 765, 730, 576 cm^{-1}. **HRMS (ESI):** *m/z* calcd. for $C_{39}H_{54}N_2O_{12}$: 765.3570 [M+Na$^+$]; found: 765.3569.

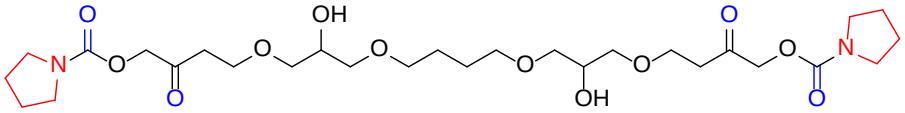
dibutyl (((((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(2-hydroxypropane-3,1-diyl))bis(oxy))bis(2-oxobutane-4,1-diyl)) bis(carbonate)



Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$): δ =** 7.12 (d, *J* = 8.8 Hz, 4 H), 6.80 (d, *J* = 8.8 Hz, 4 H), 4.71 (s, 4 H), 4.18 (t, *J* = 6.7 Hz, 4 H), 4.14–4.09 (m, 3 H), 3.97 (d, *J* = 1.0 Hz, 2 H), 3.96 (d, *J* = 1.4 Hz, 2 H), 3.82–3.76 (m, 5 H), 3.64 (dd, *J* = 9.9 Hz, 4.0 Hz, 2 H), 3.58 (dd, *J* = 9.9 Hz, 6.1 Hz, 2 H), 2.68 (t, *J* = 5.9 Hz, 4 H), 1.70–1.65 (m, 4 H), 1.62 (s, 6 H), 1.44–1.38 (m, 4 H), 0.94 (t, *J* = 7.4 Hz, 6 H). **^{13}C NMR (101 MHz, $CDCl_3$): δ =** 202.4 (2 C), 156.5 (2 C), 155.0 (2 C), 143.7 (2 C), 127.9 (4 C), 114.1 (4 C), 72.4 (2 C), 71.2 (2 C), 69.1 (2 C), 68.8 (4 C), 66.2 (2 C), 41.8, 39.1 (2 C), 31.2 (2 C), 30.7 (2 C), 19.0 (2 C), 13.8 (2 C). **IR (film): *ν* =** 3518, 2963, 2933, 2874, 1808, 1753 (C=O), 1734 (C=O), 1608, 1510, 1462, 1421, 1392, 1254, 1183, 1118, 1040, 943, 831, 787, 735, 558 cm^{-1}. **HRMS (ESI):** *m/z* calcd. for $C_{39}H_{56}O_{14}$: 771.3562 [M+Na$^+$]; found: 771.3562.



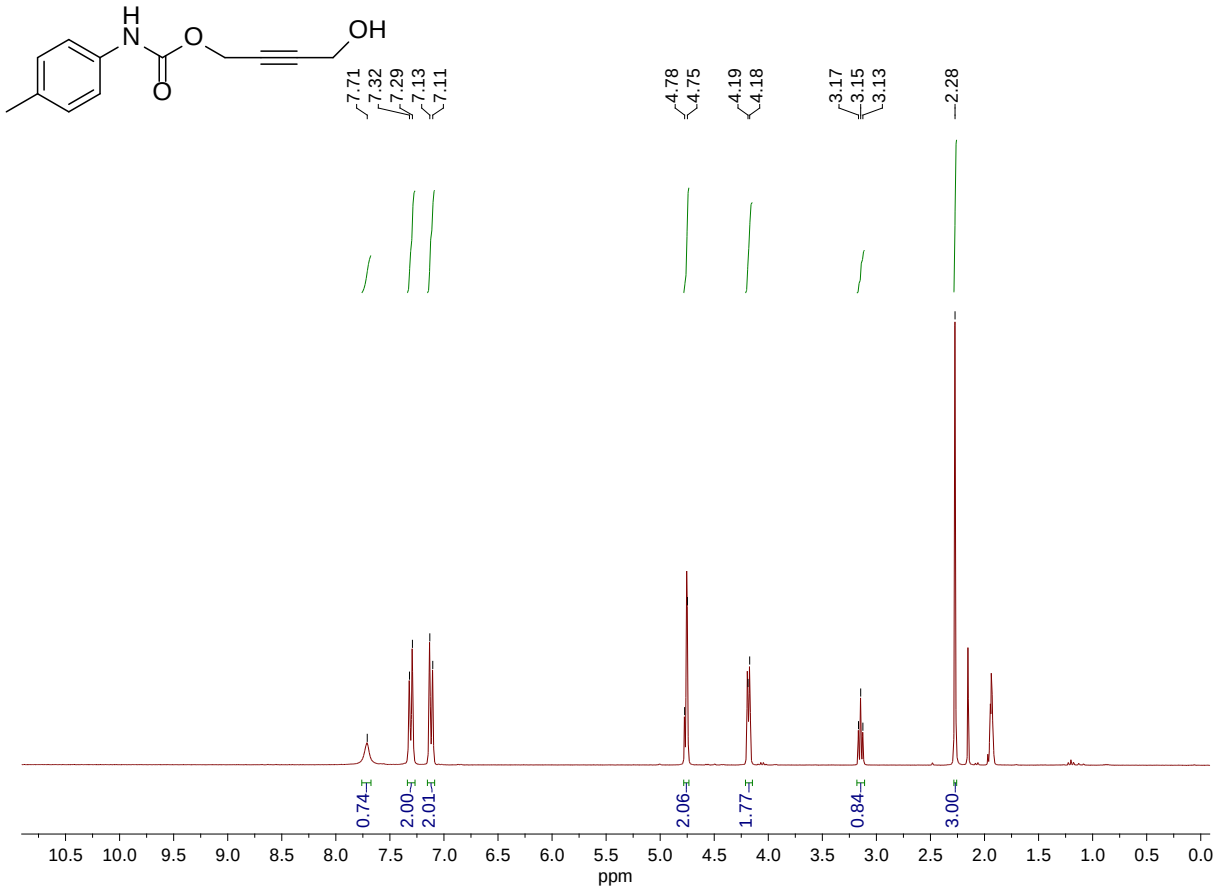
7,16-dihydroxy-2,21-dioxo-5,9,14,18-tetraoxadocosane-1,22-diyl bis(pyrrolidine-1-carboxylate)

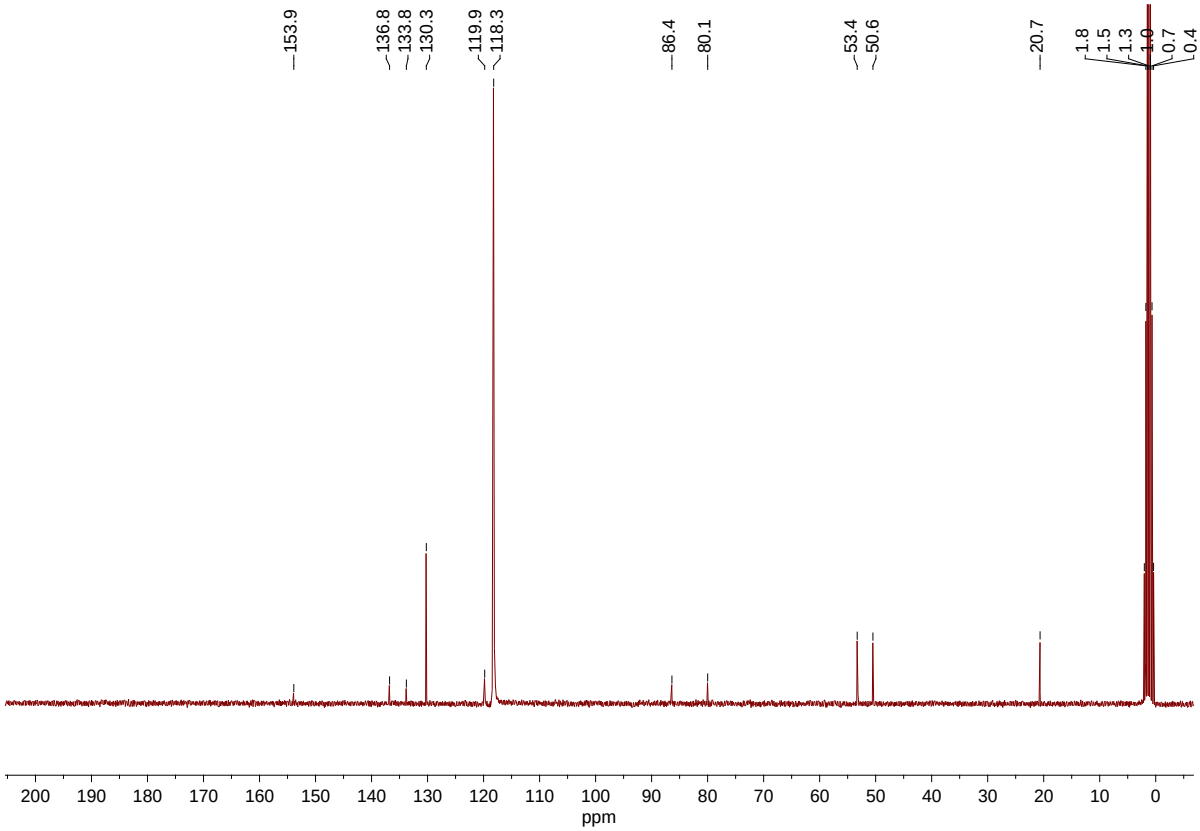


Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.65 (s, 4 H), 3.91–3.86 (m, 2 H), 3.77–3.68 (m, 4 H), 3.49 (dd, *J* = 9.9 Hz, 4.0 Hz, 2 H), 3.45–3.35 (m, 18 H), 2.77 (s, 2 H), 2.65 (t, *J* = 6.1 Hz, 4 H), 1.89–1.80 (m, 8 H), 1.63 – 1.56 (m, 4 H). **^{13}C NMR (101 MHz, $CDCl_3$): δ =** 204.3 (2 C), 154.1 (2 C), 72.7 (2 C), 71.8 (2 C), 71.3 (2 C), 69.4 (2 C), 69.2 (2 C), 66.1 (2 C), 46.4 (2 C), 46.0 (2 C), 39.1 (2 C), 26.4 (2 C), 25.8 (2 C), 25.0 (2 C). **IR (film): ν =** 3454, 2928, 2874, 1703 (br.s, C=O), 1440 (C-N stretch), 1400, 1346, 1254, 1108, 859, 765, 576 cm^{-1}. **HRMS (ESI):** *m/z* calcd. for $C_{28}H_{48}N_2O_{12}$: 627.3099 [$M+Na^+$]; found: 627.3098.

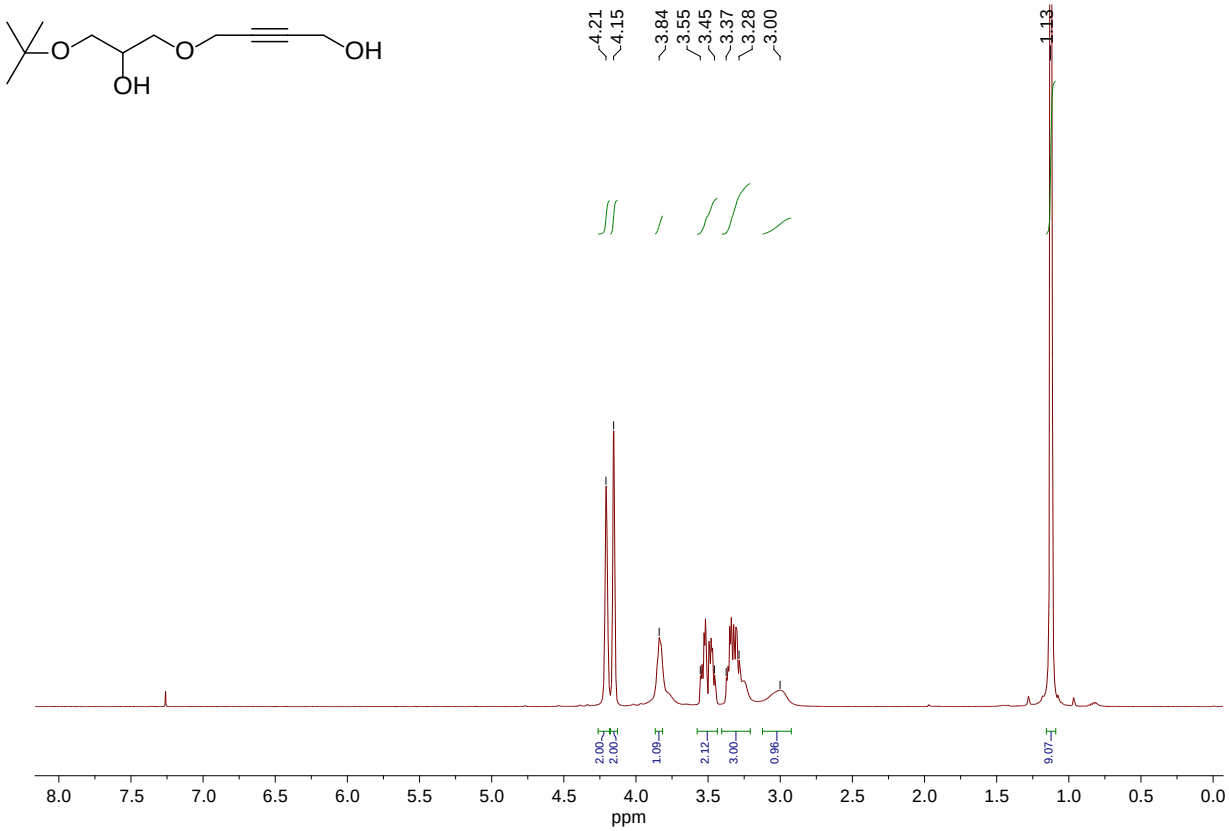
6.0. ^{1}H and ^{13}C NMR spectra of the starting materials and isolated products

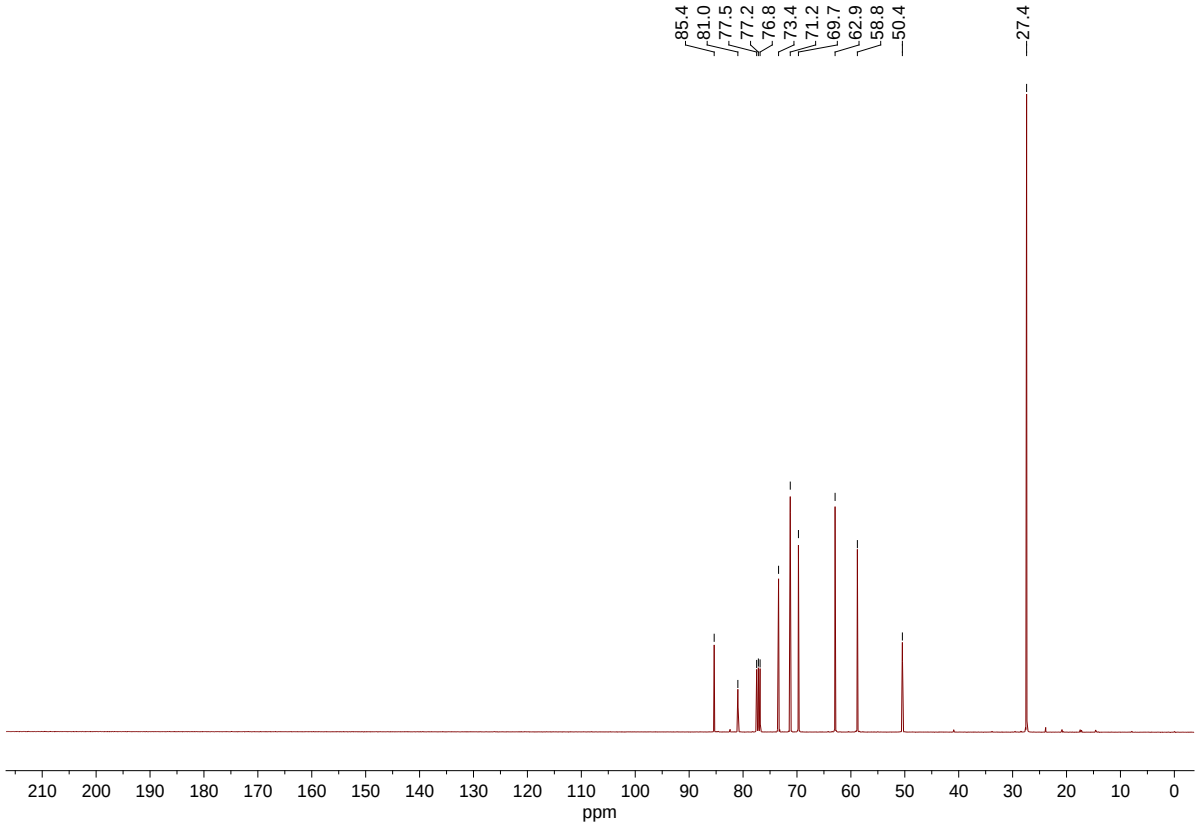
4-hydroxybut-2-yn-1-yl *p*-tolylcarbamate



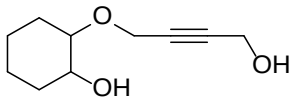


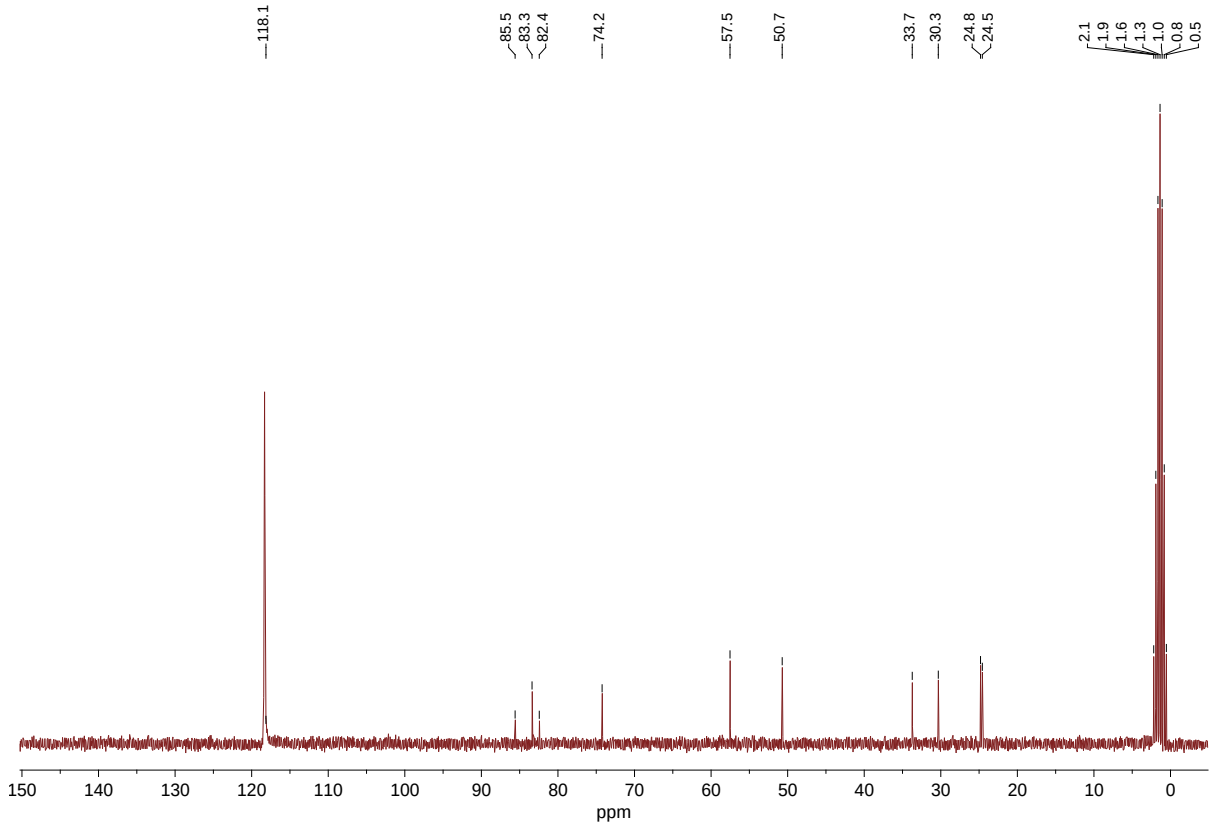
4-(3-(tert-butoxy)-2-hydroxypropoxy)but-2-yn-1-ol



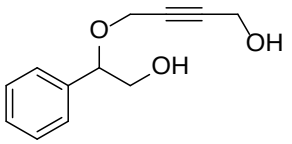


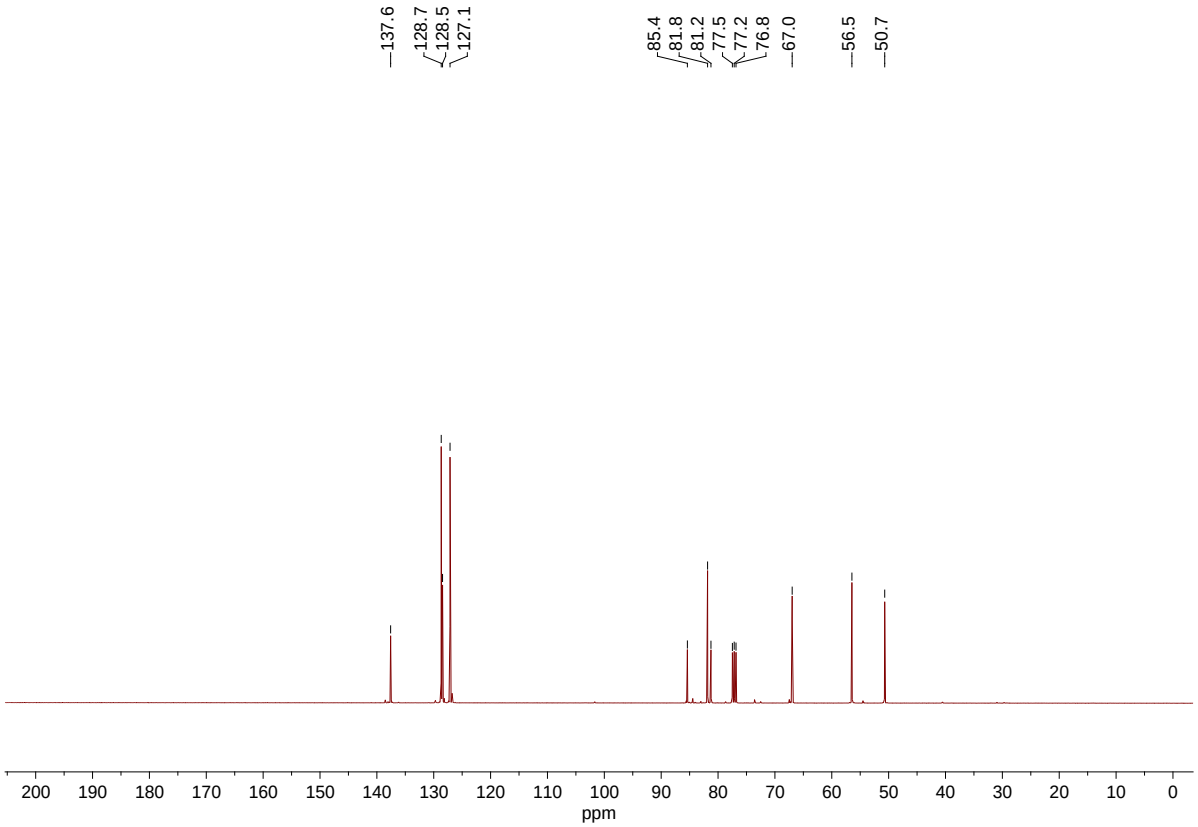
2-((4-hydroxybut-2-yn-1-yl)oxy)cyclohexan-1-ol



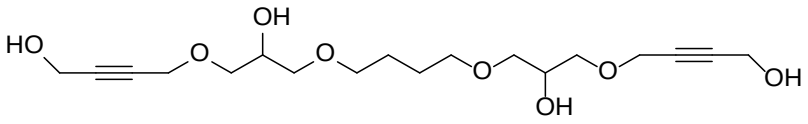


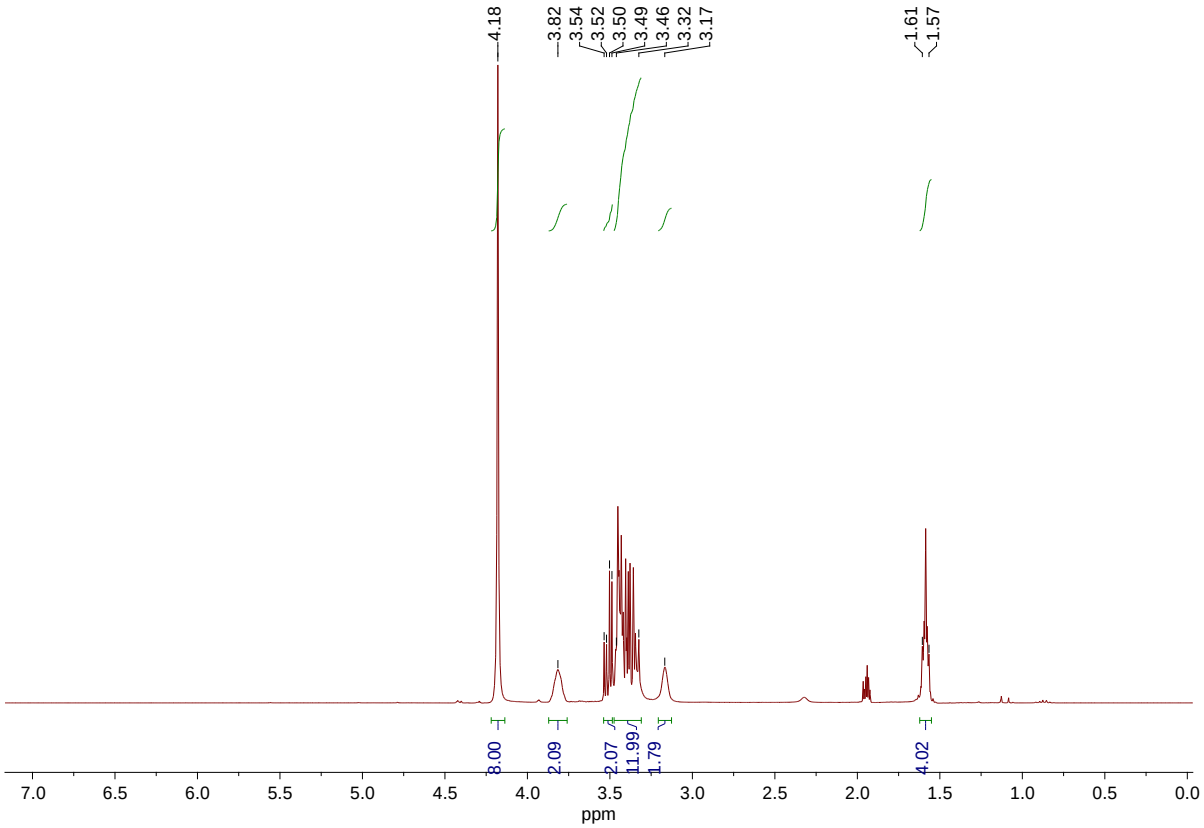
4-(2-hydroxy-1-phenylethoxy)but-2-yn-1-ol

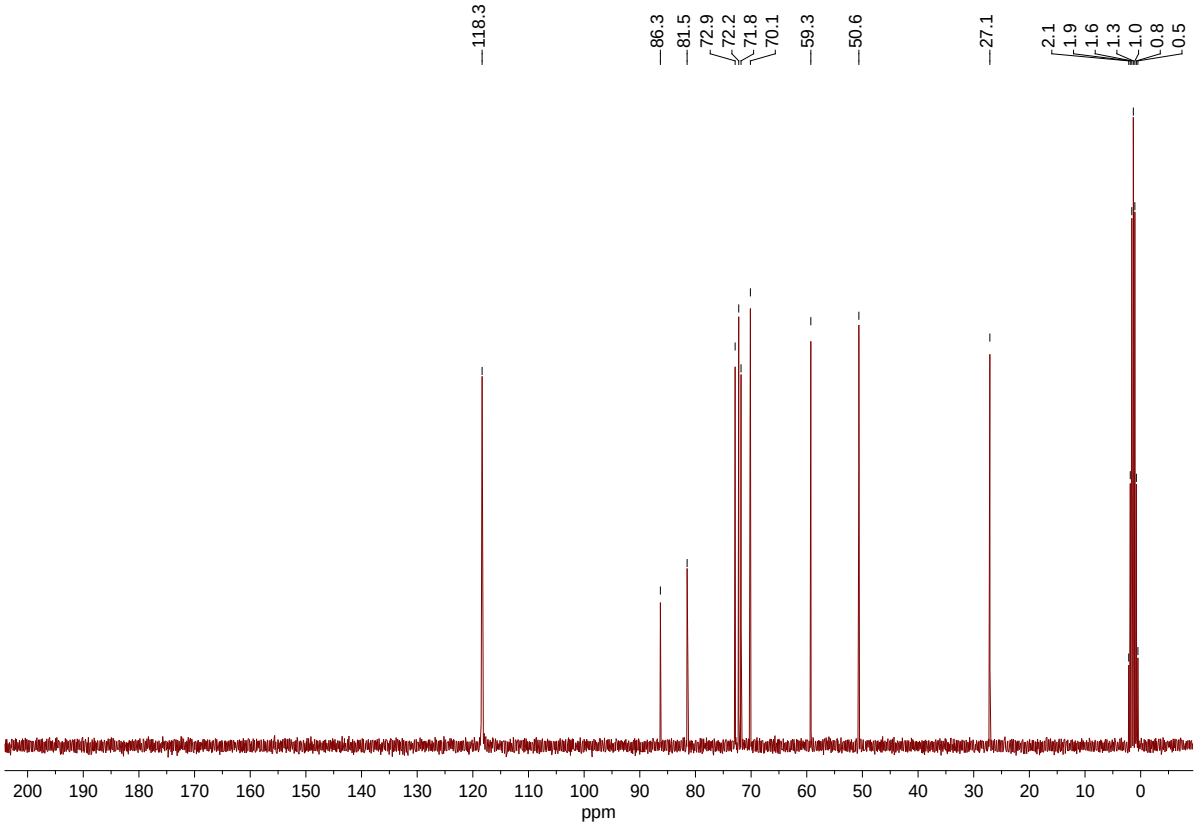




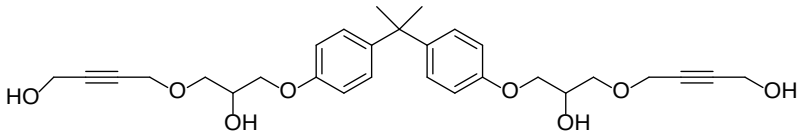
5,9,14,18-tetraoxadocosa-2,20-diyne-1,7,16,22-tetraol

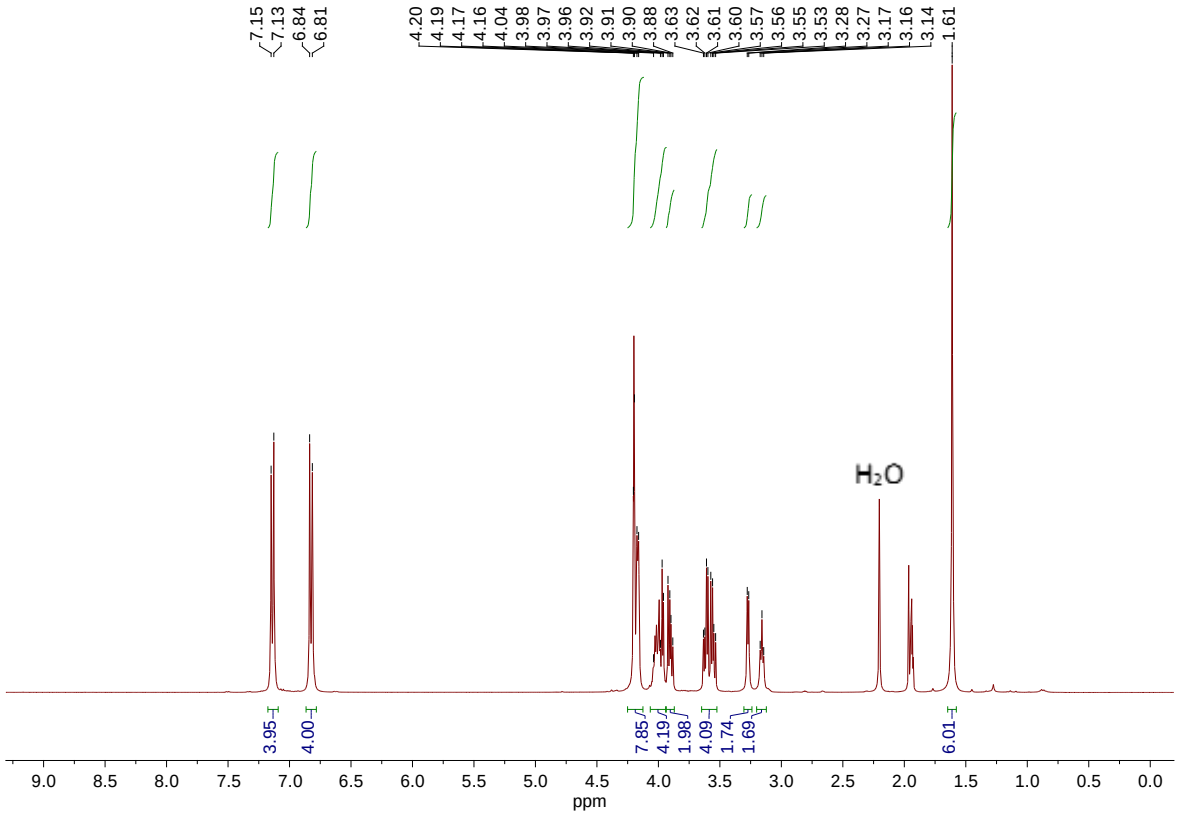


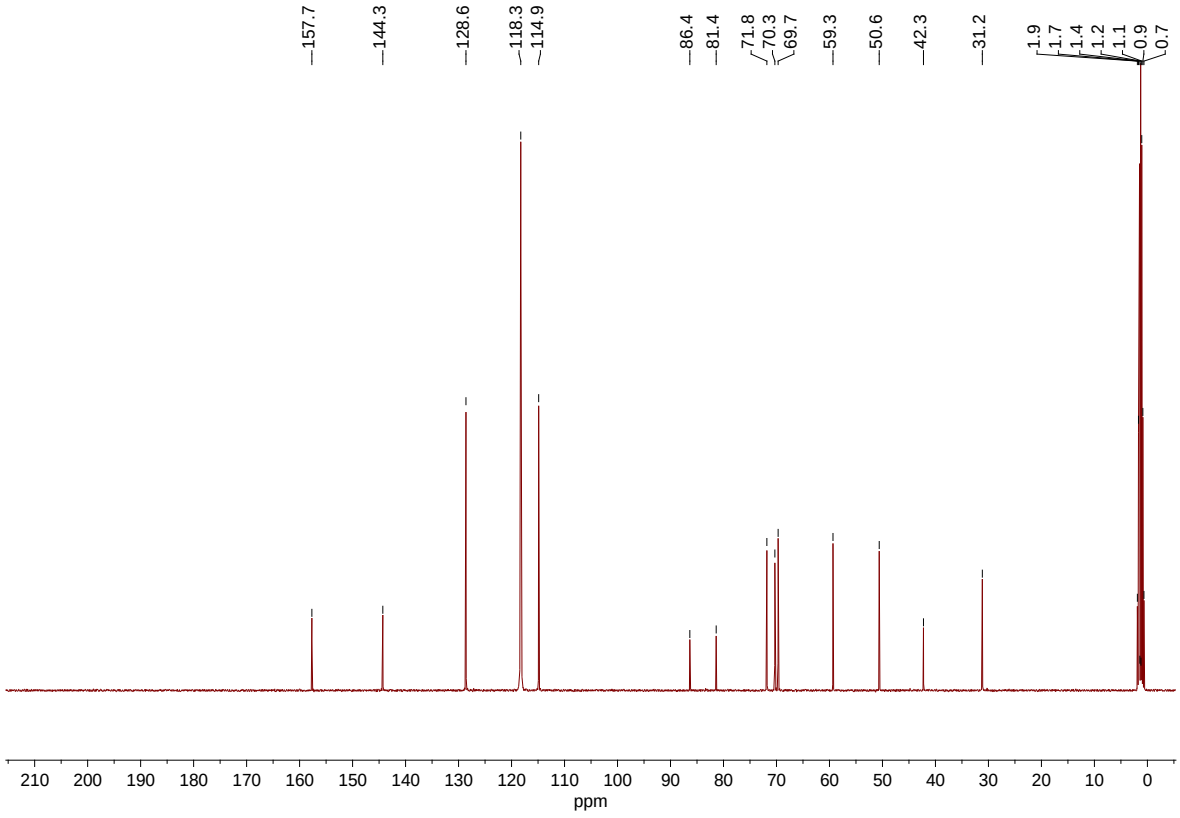




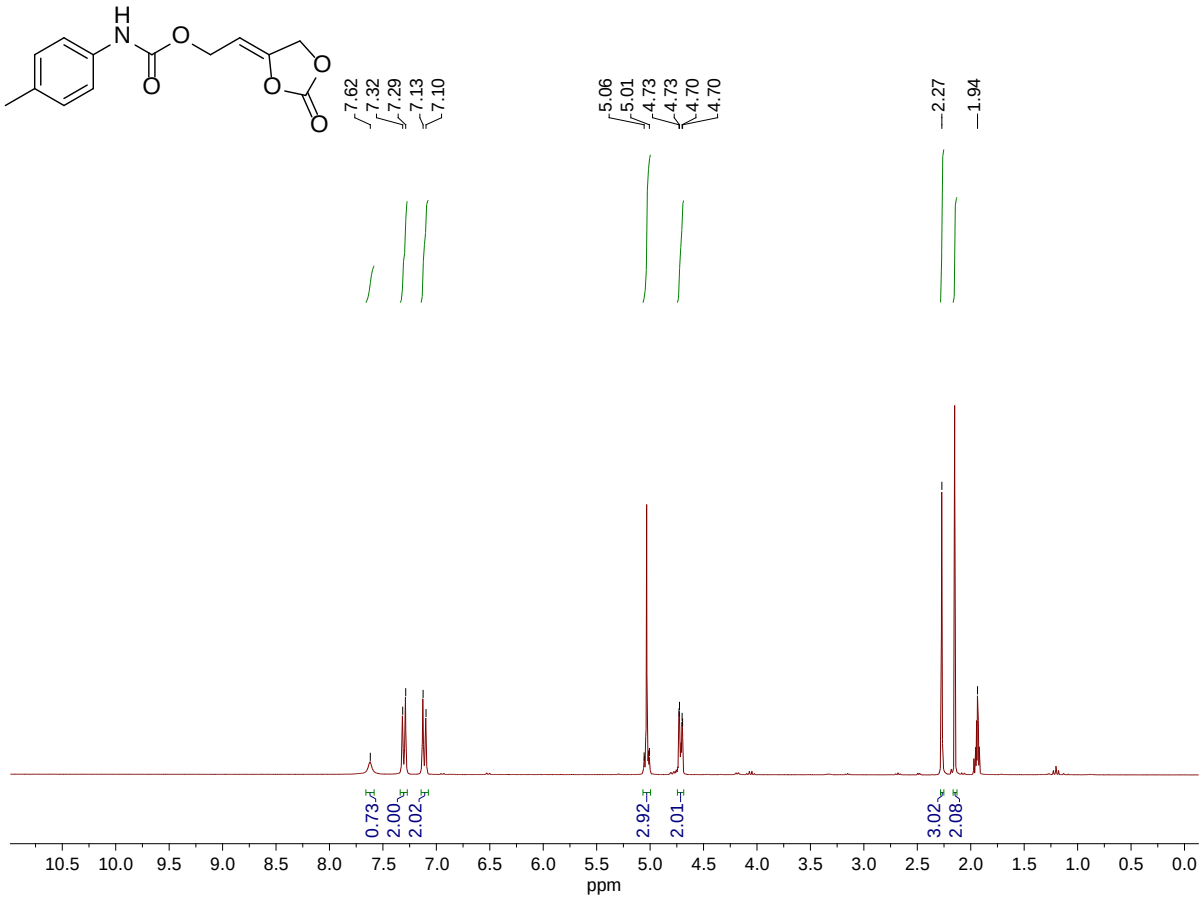
4,4'-((((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(2-hydroxypropane-3,1-diyl))bis(oxy))bis(but-2-yn-1-ol)

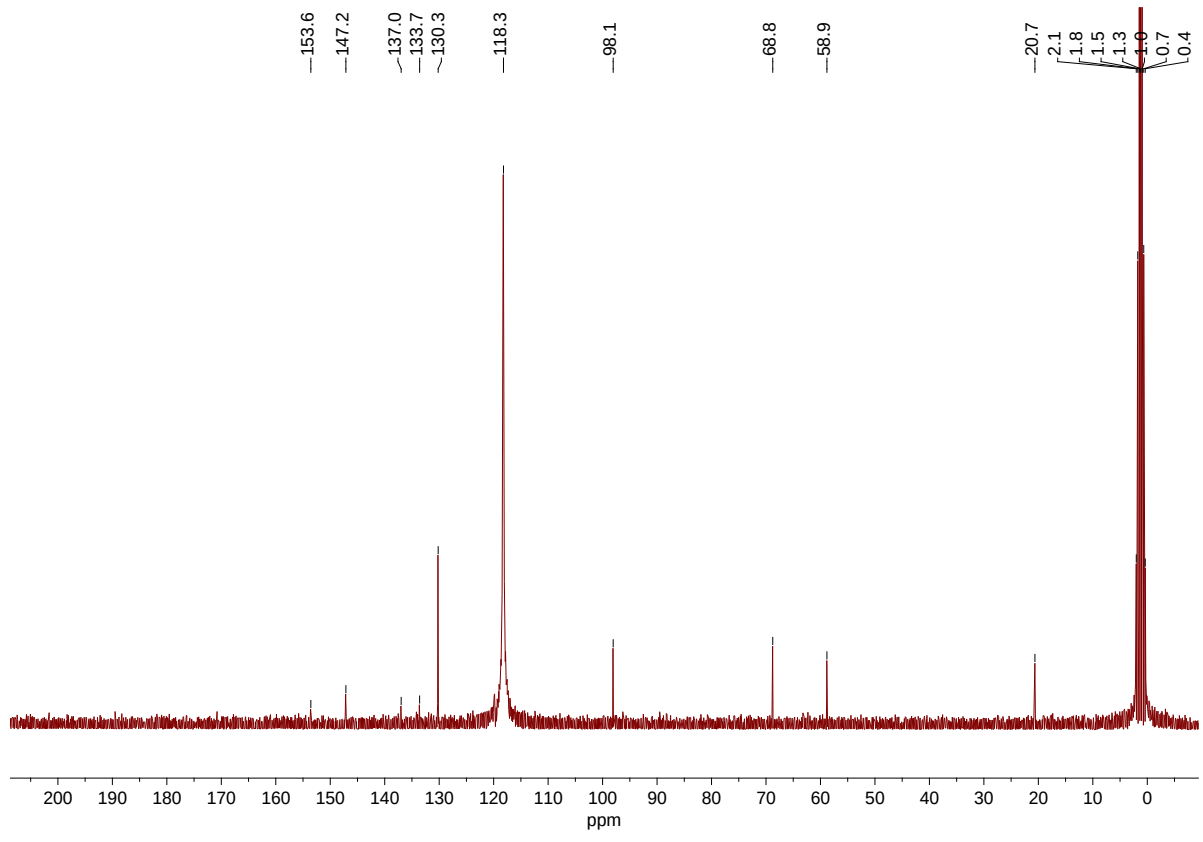




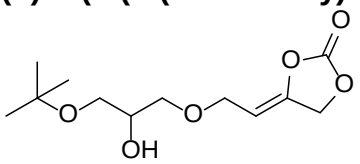


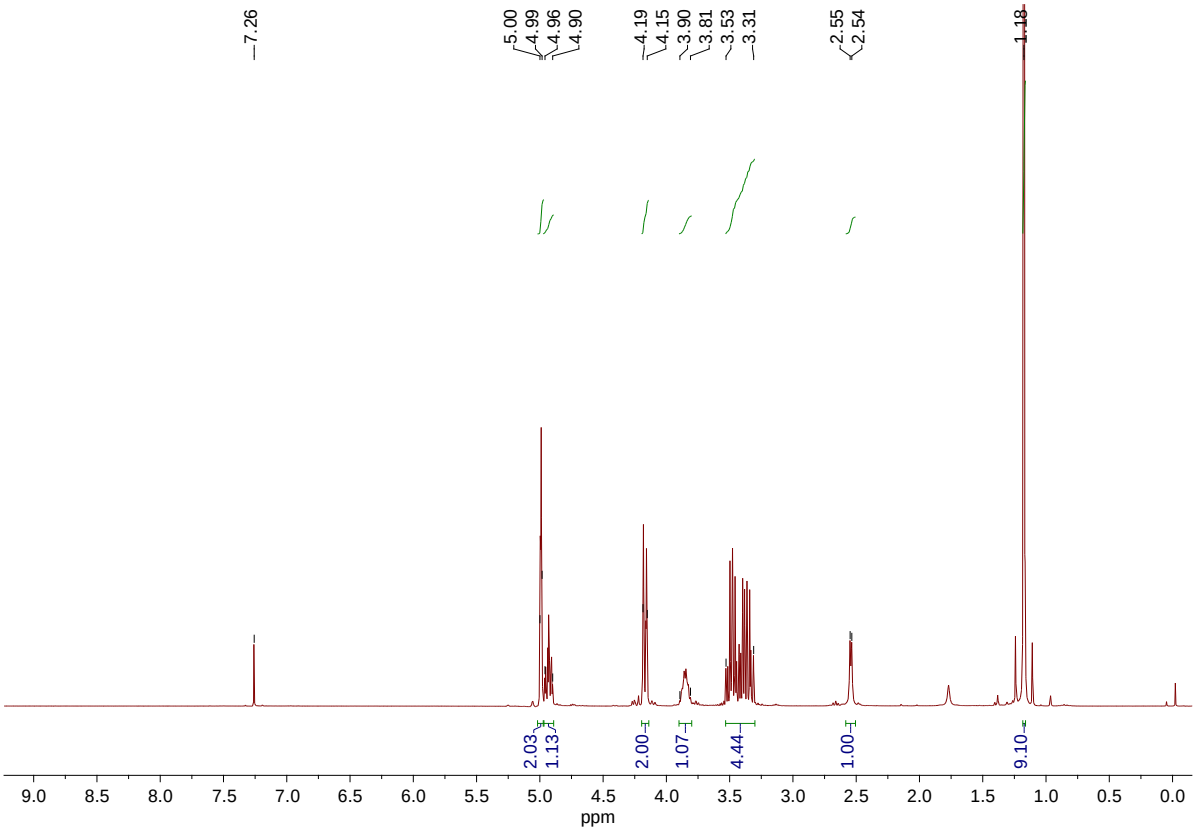
(Z)-2-(2-oxo-1,3-dioxolan-4-ylidene)ethyl *p*-tolylcarbamate

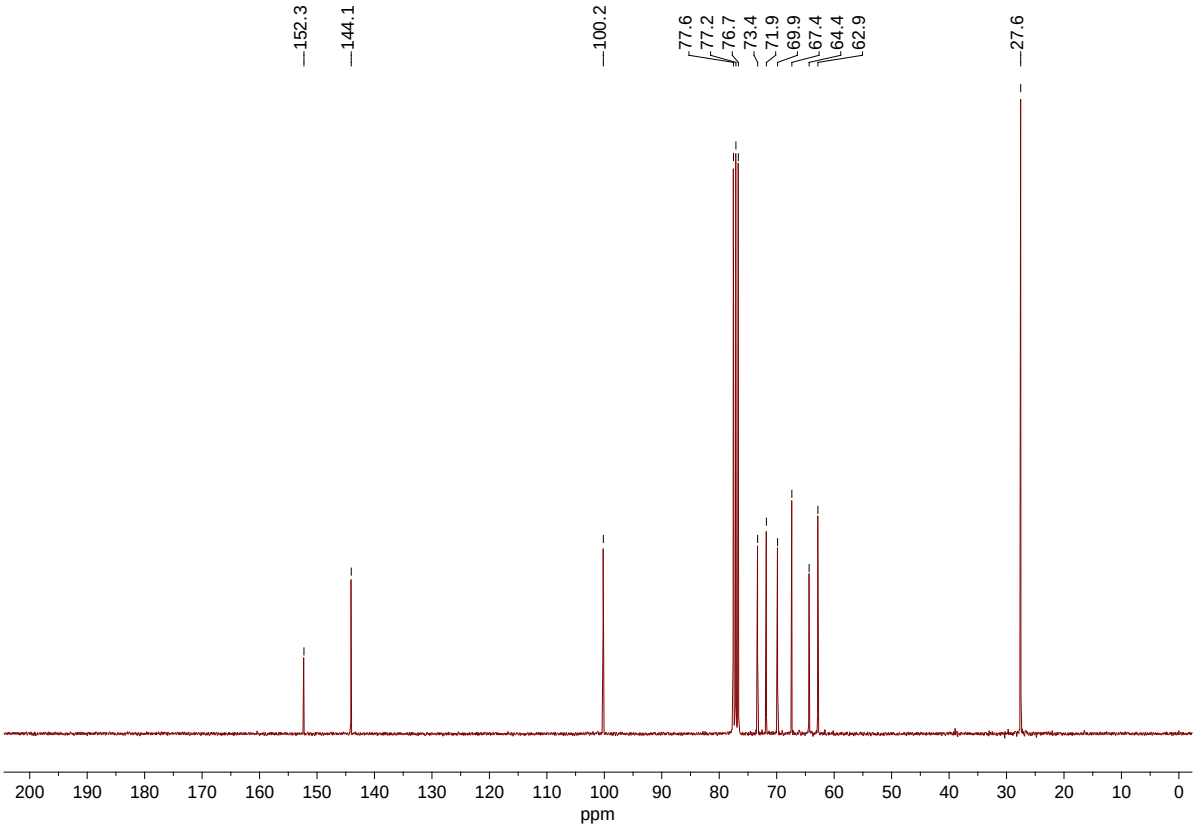




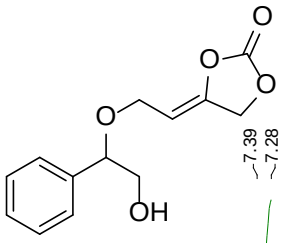
(*Z*)-4-(2-(3-(tert-butoxy)-2-hydroxypropoxy)ethylidene)-1,3-dioxolan-2-one

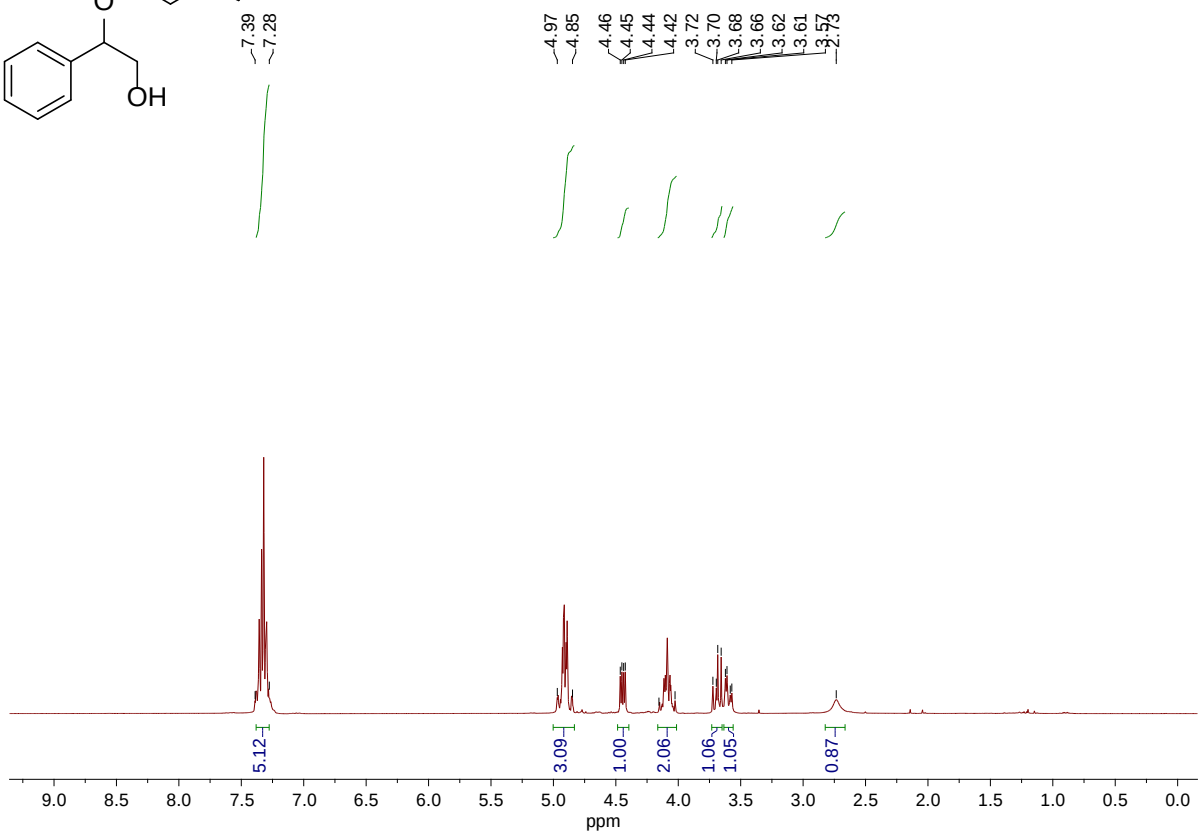


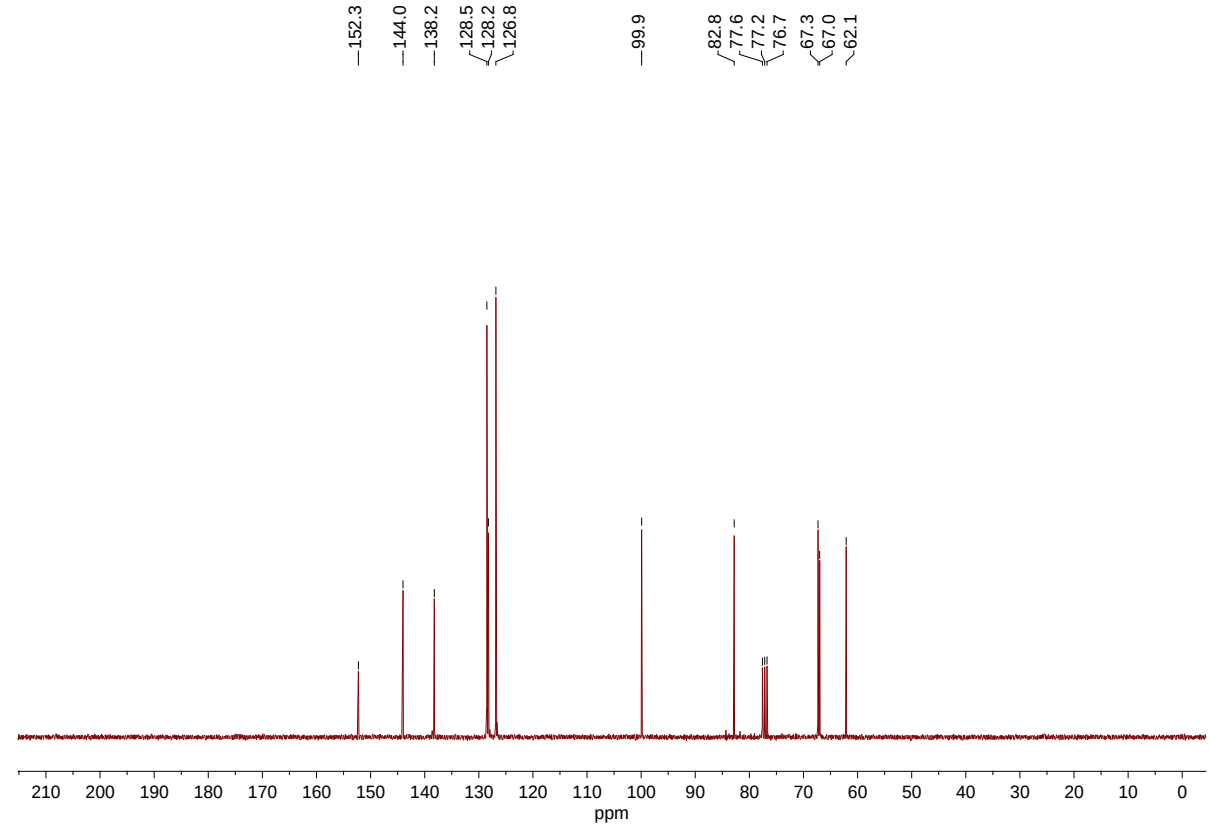




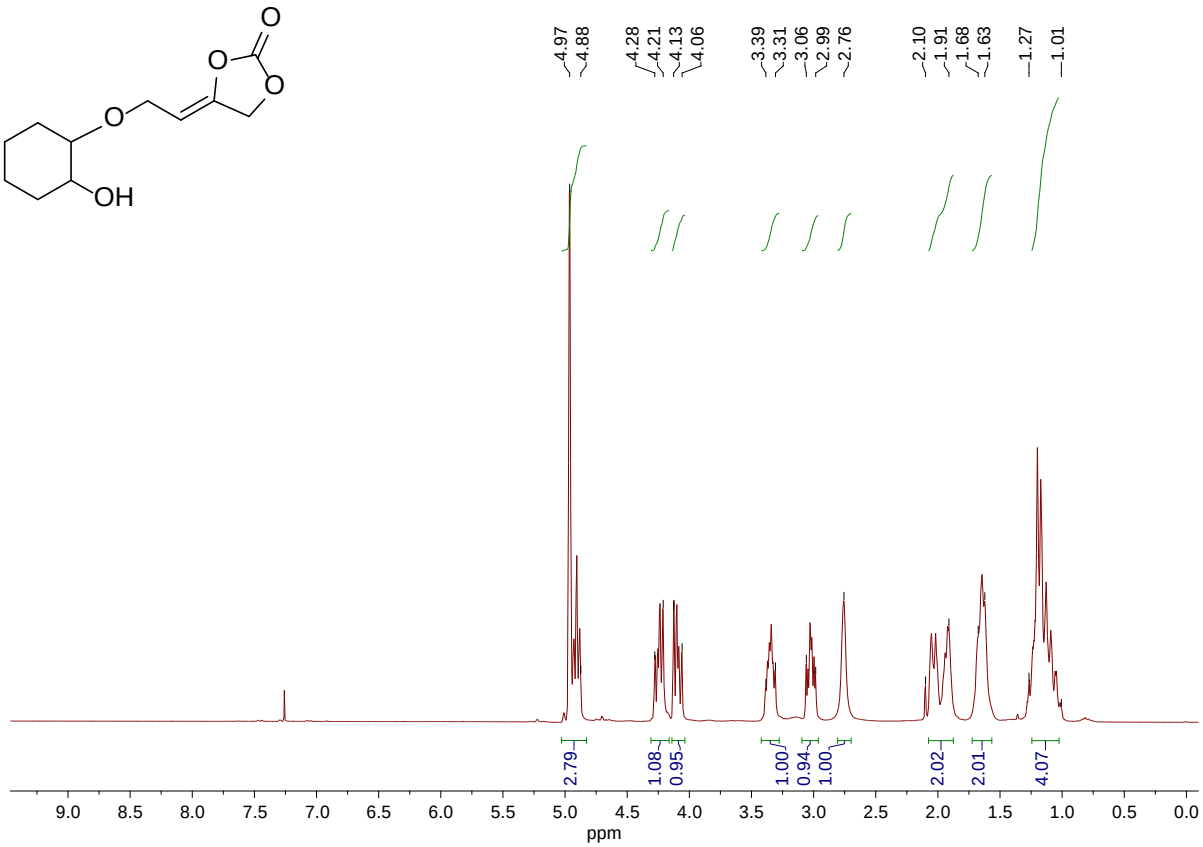
(*Z*)-4-(2-(2-hydroxy-1-phenylethoxy)ethylidene)-1,3-dioxolan-2-one

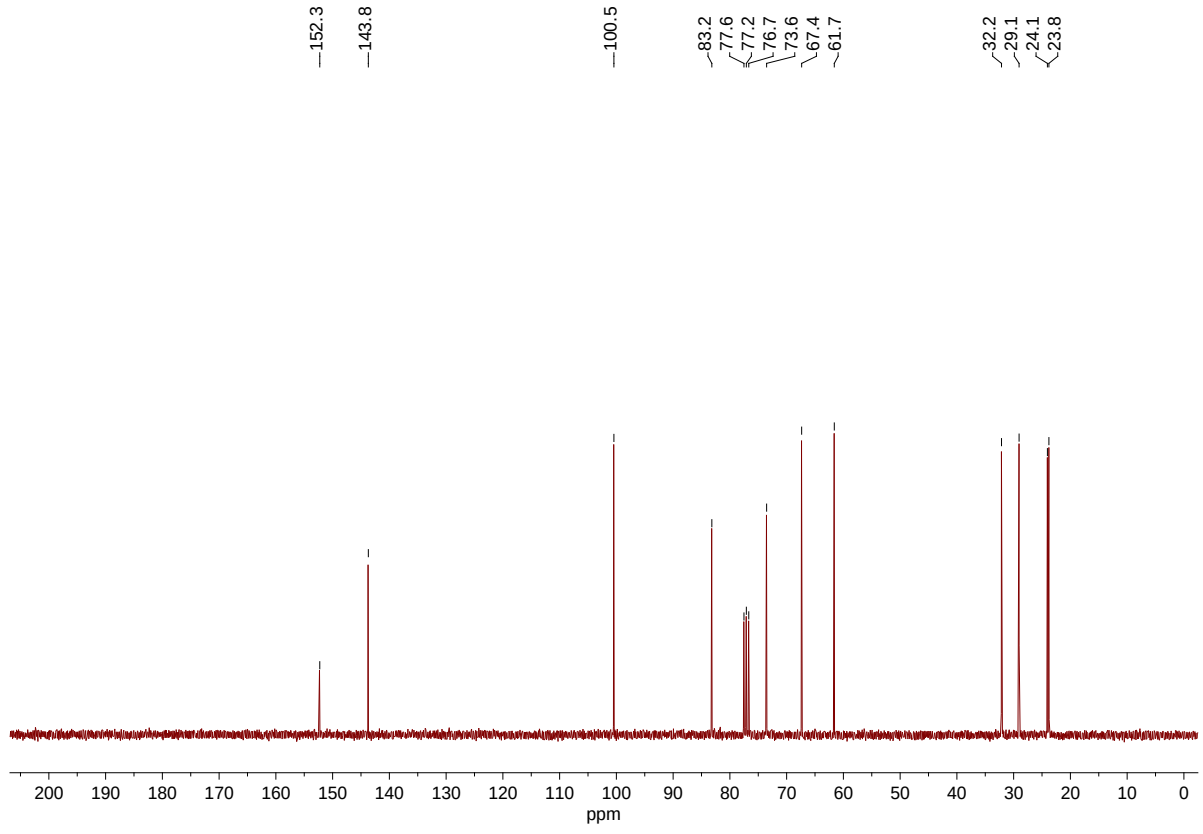




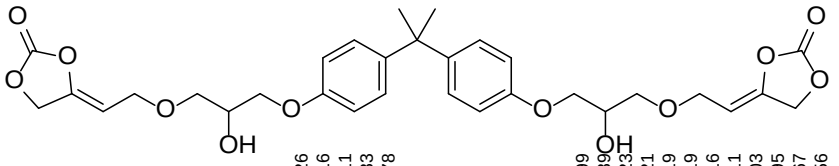


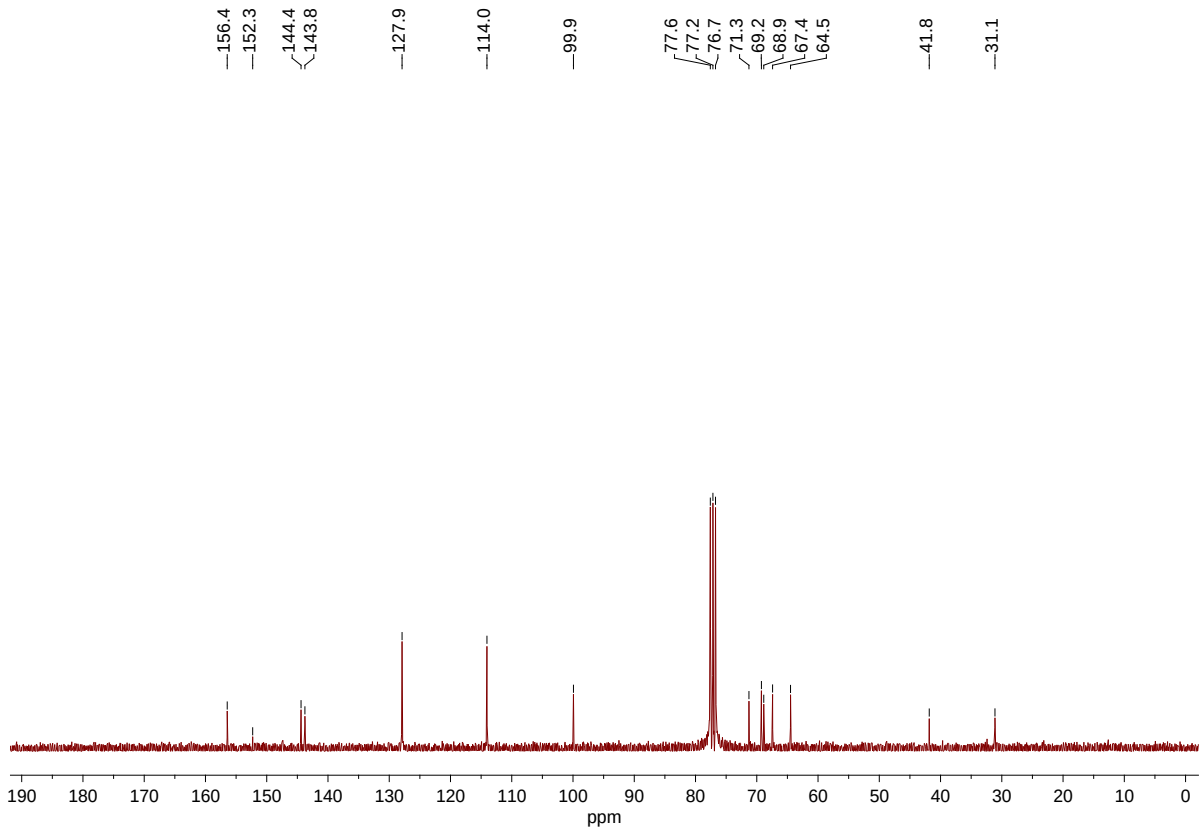
(*Z*)-4-(2-((2-hydroxycyclohexyl)oxy)ethylidene)-1,3-dioxolan-2-one



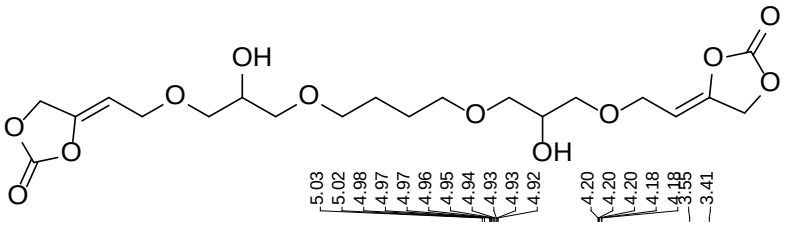


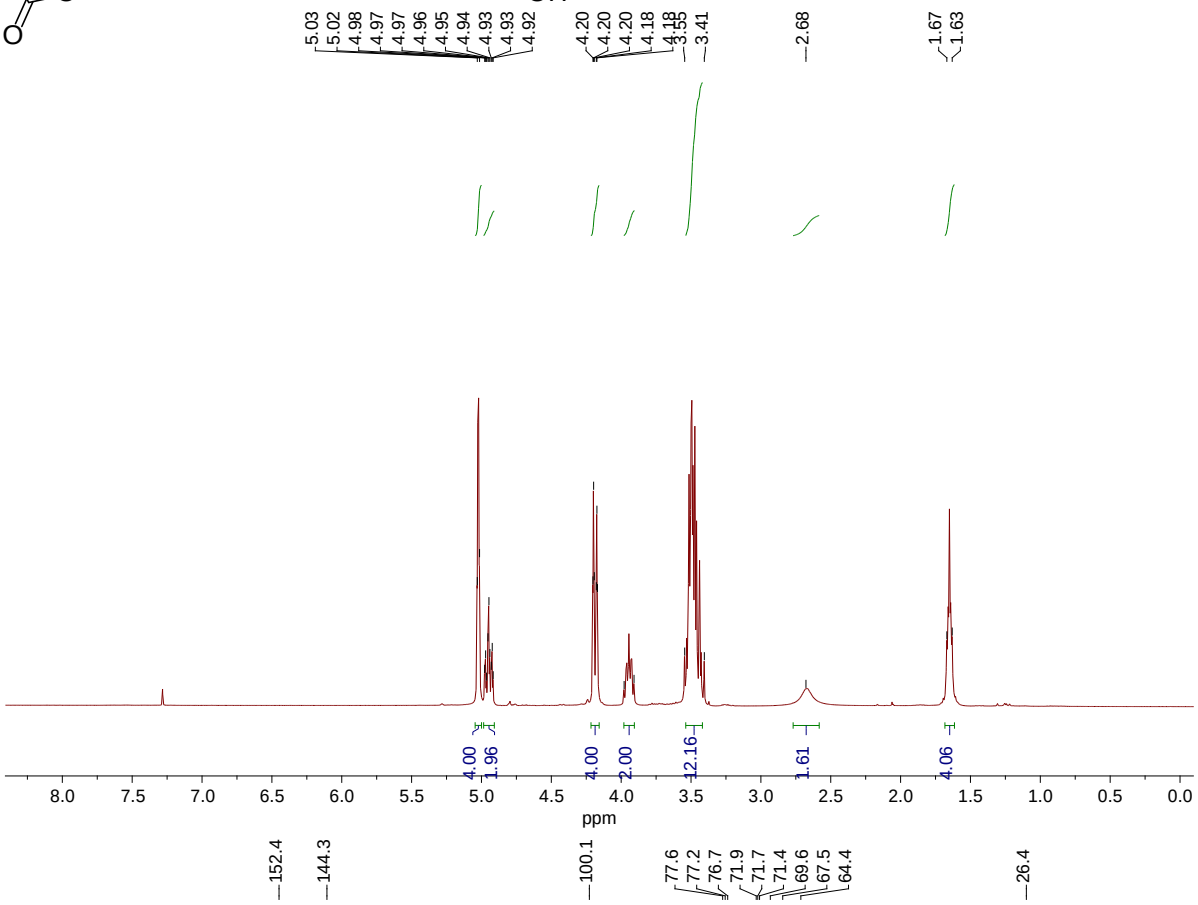
(4Z,4'Z)-4,4'-(((((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(2-hydroxy propane-3,1-diyl))bis(oxy))bis(ethan-2-yl-1-ylidene))bis(1,3-dioxolan-2-one)

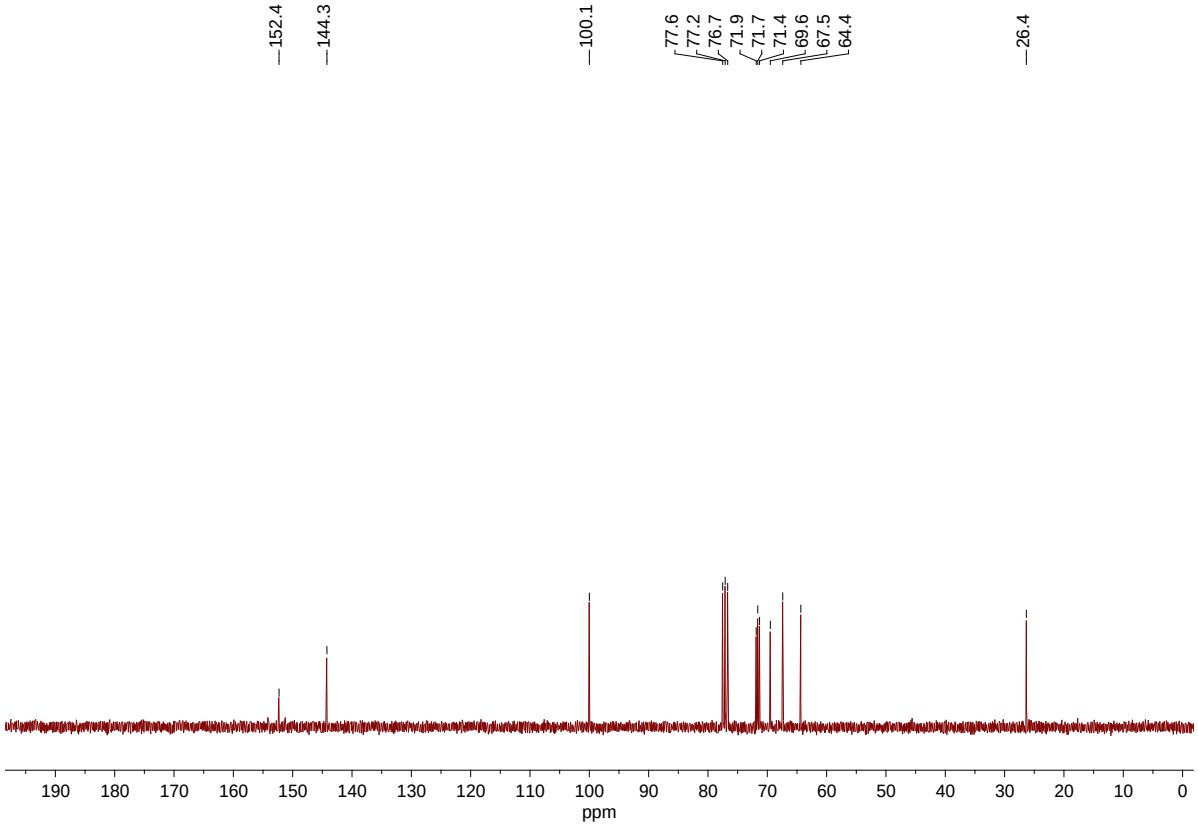




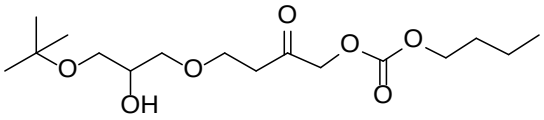
(4*Z*,4'*Z*)-4,4'-(5,14-dihydroxy-3,7,12,16-tetraoxaoctadecane-1,18-diylidene)bis (1,3-dioxolan-2-one)

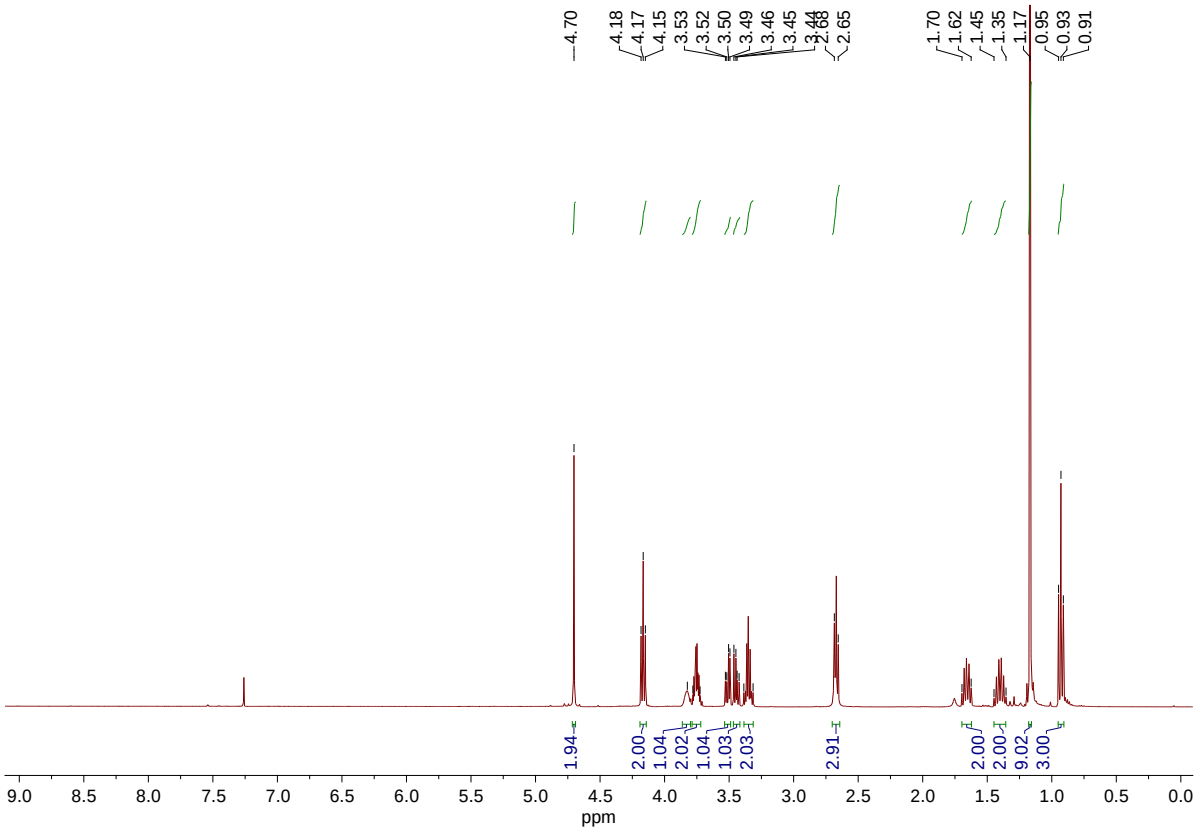


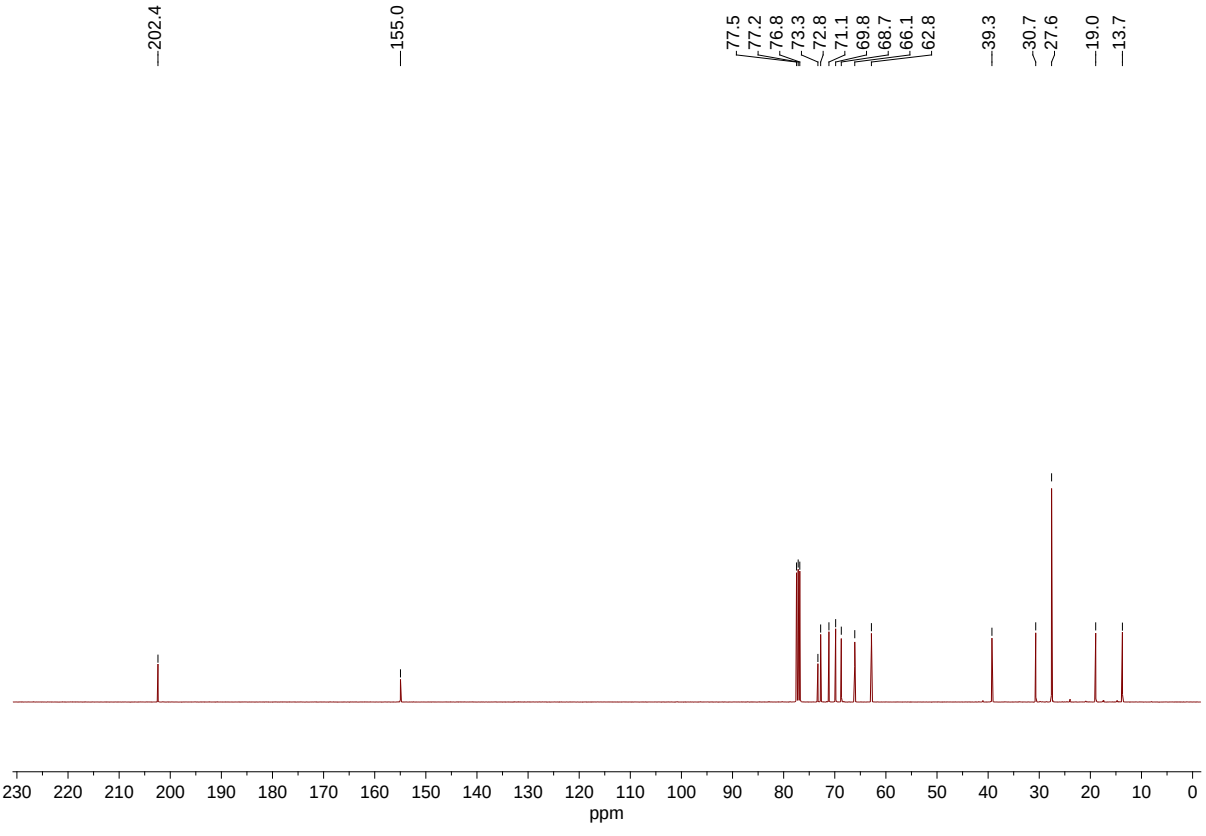




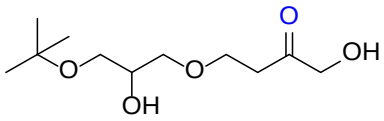
4-(3-(tert-butoxy)-2-hydroxypropoxy)-2-oxobutyl butyl carbonate

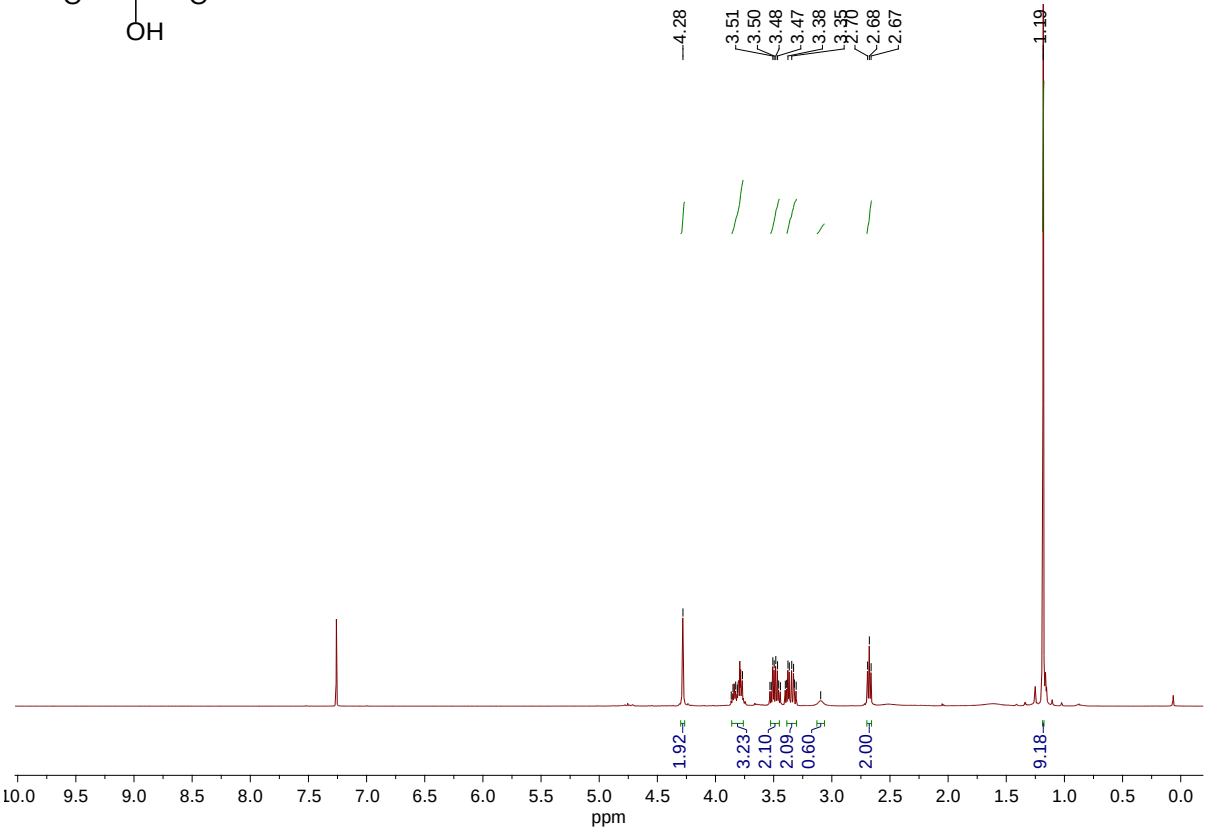


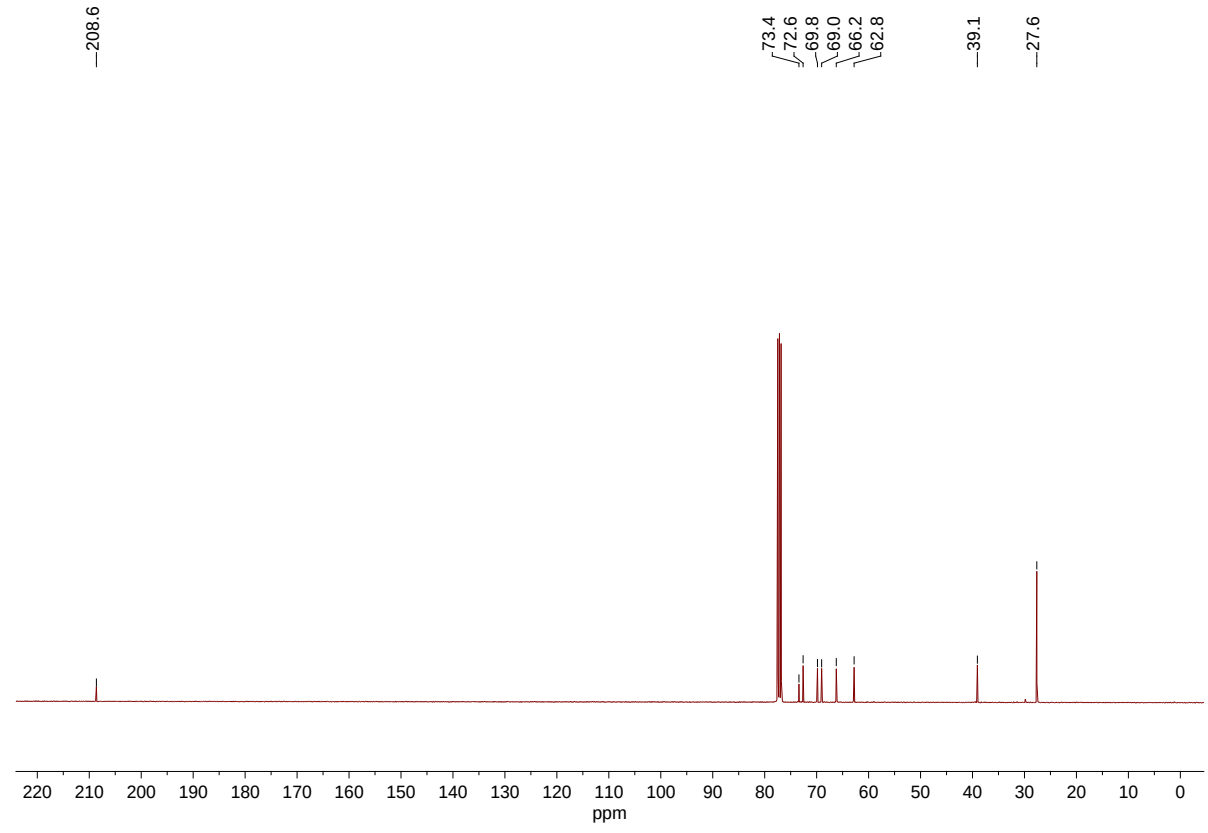




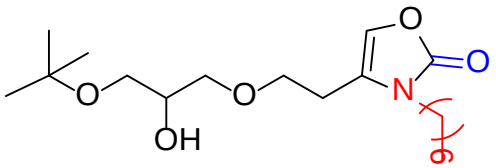
4-(3-(tert-butoxy)-2-hydroxypropoxy)-1-hydroxybutan-2-one

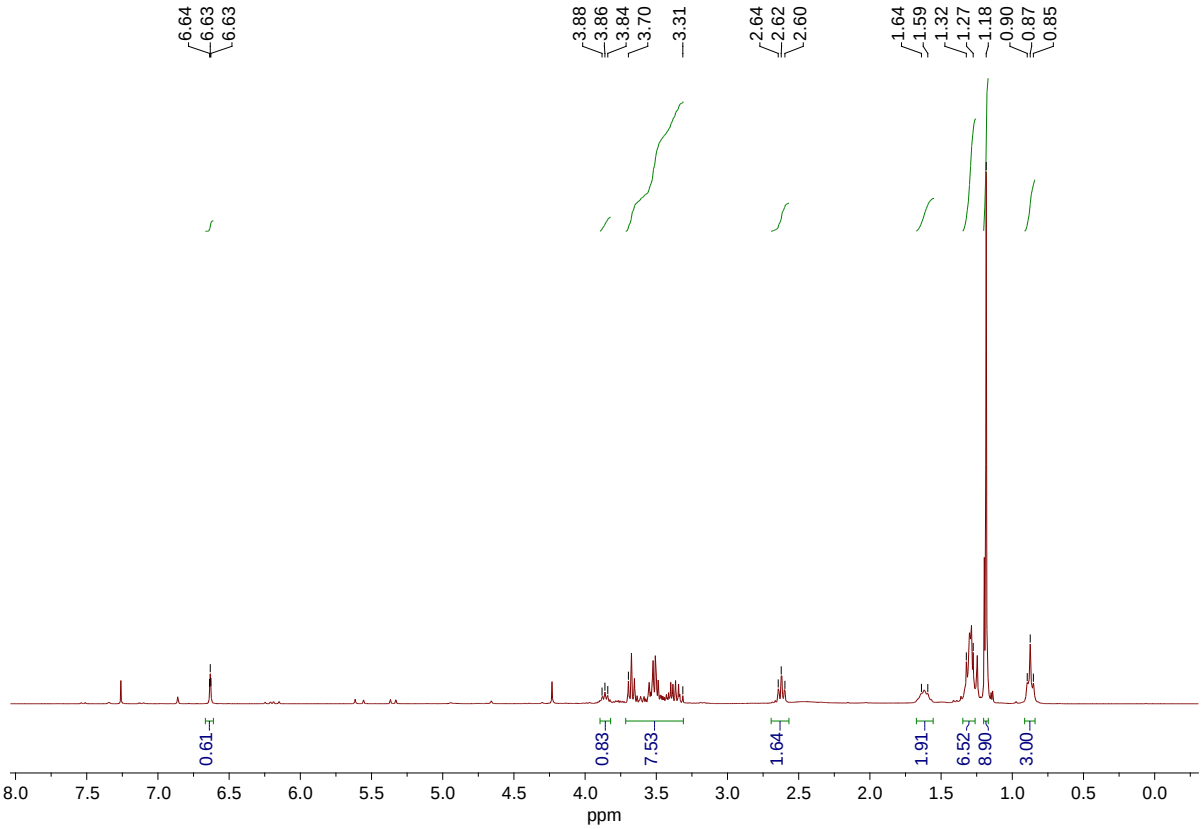


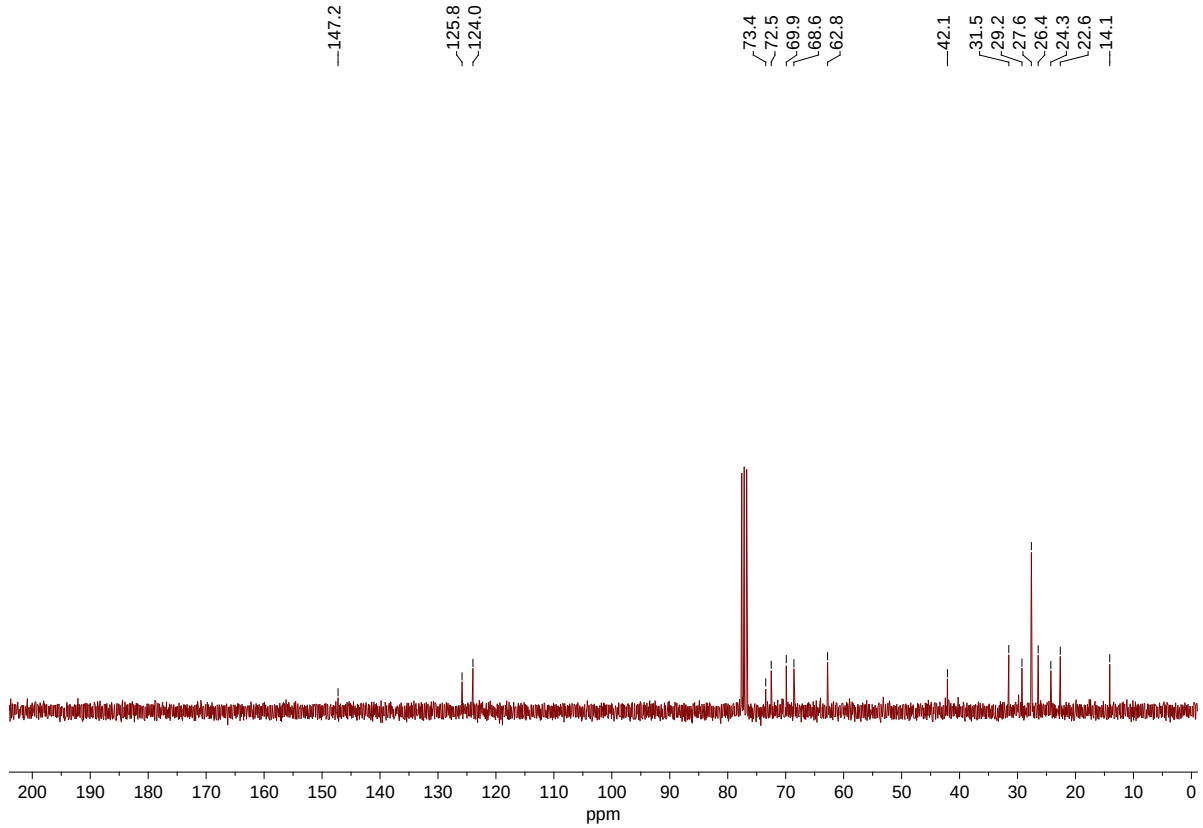




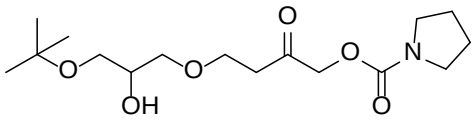
4-(2-(3-(tert-butoxy)-2-hydroxypropoxy)ethyl)-3-hexyloxazol-2(3H)-one

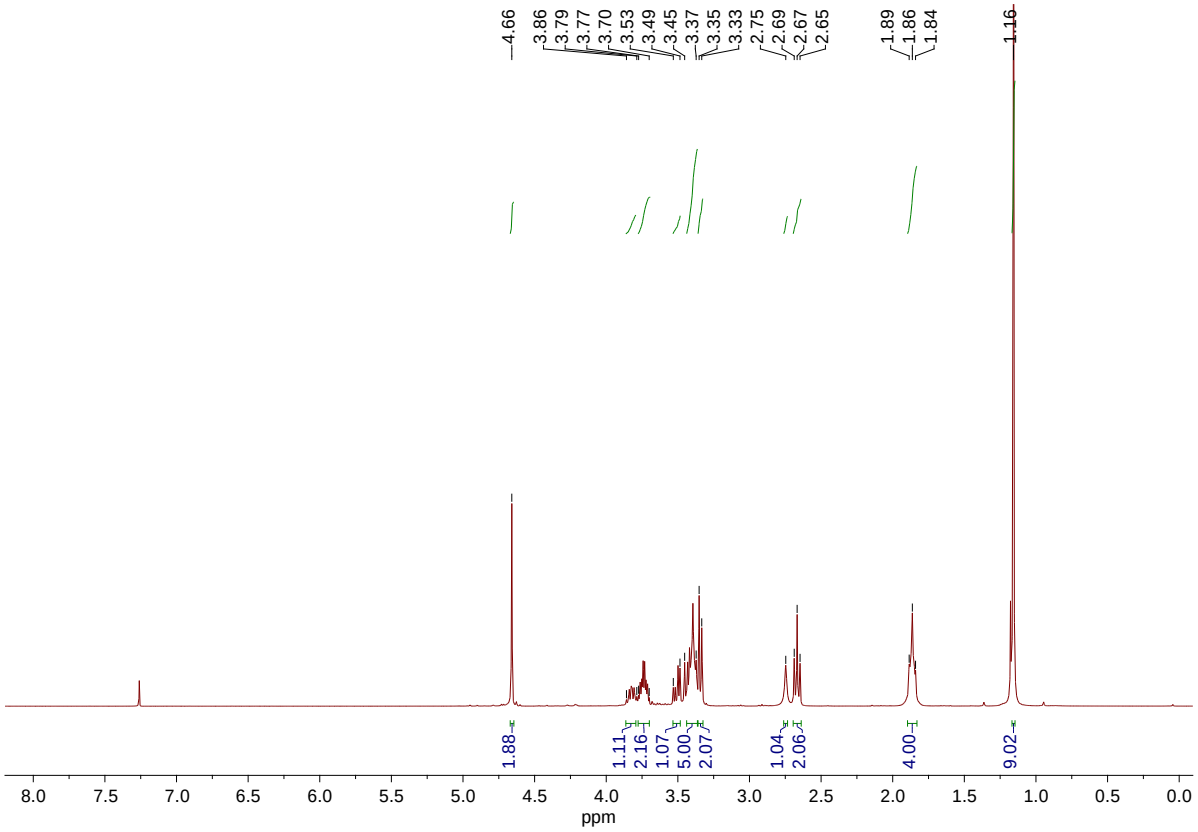


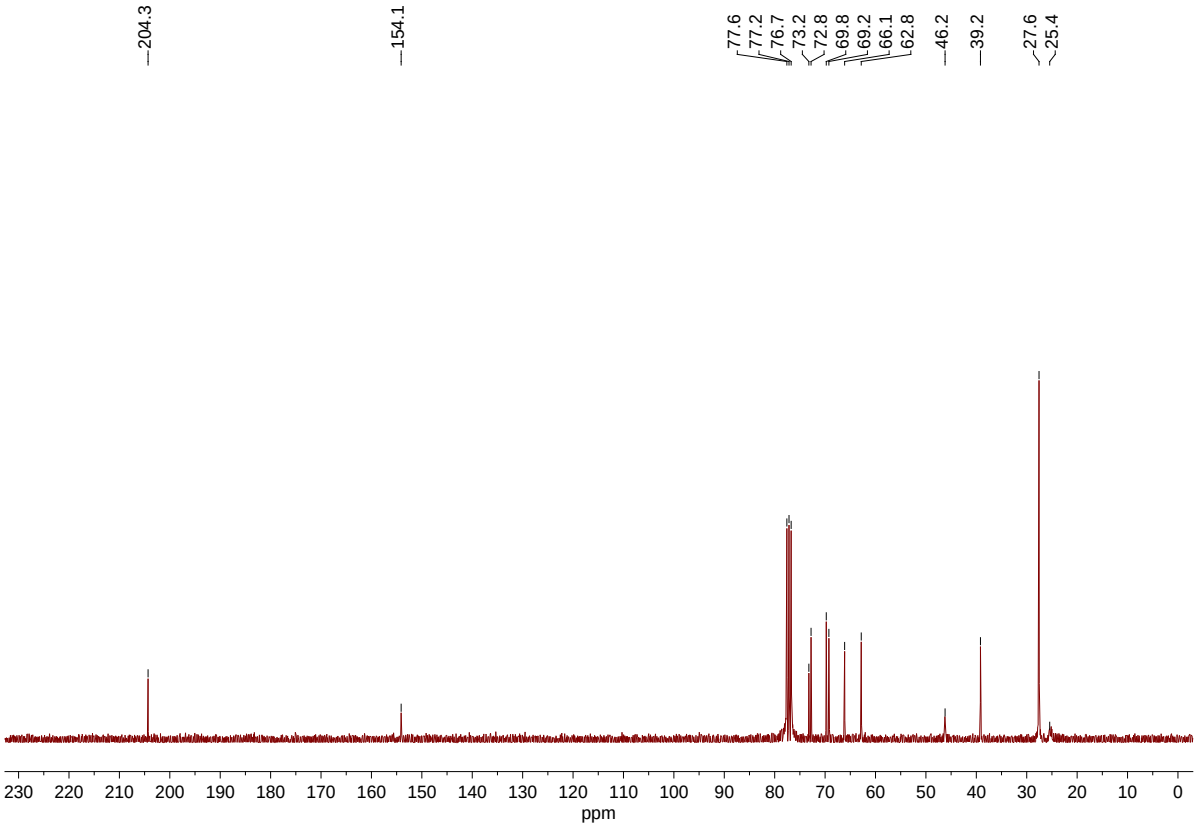




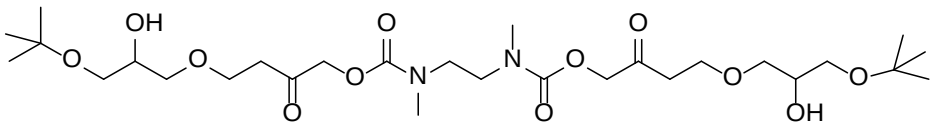
4-(3-(tert-butoxy)-2-hydroxypropoxy)-2-oxobutyl pyrrolidine-1-carboxylate

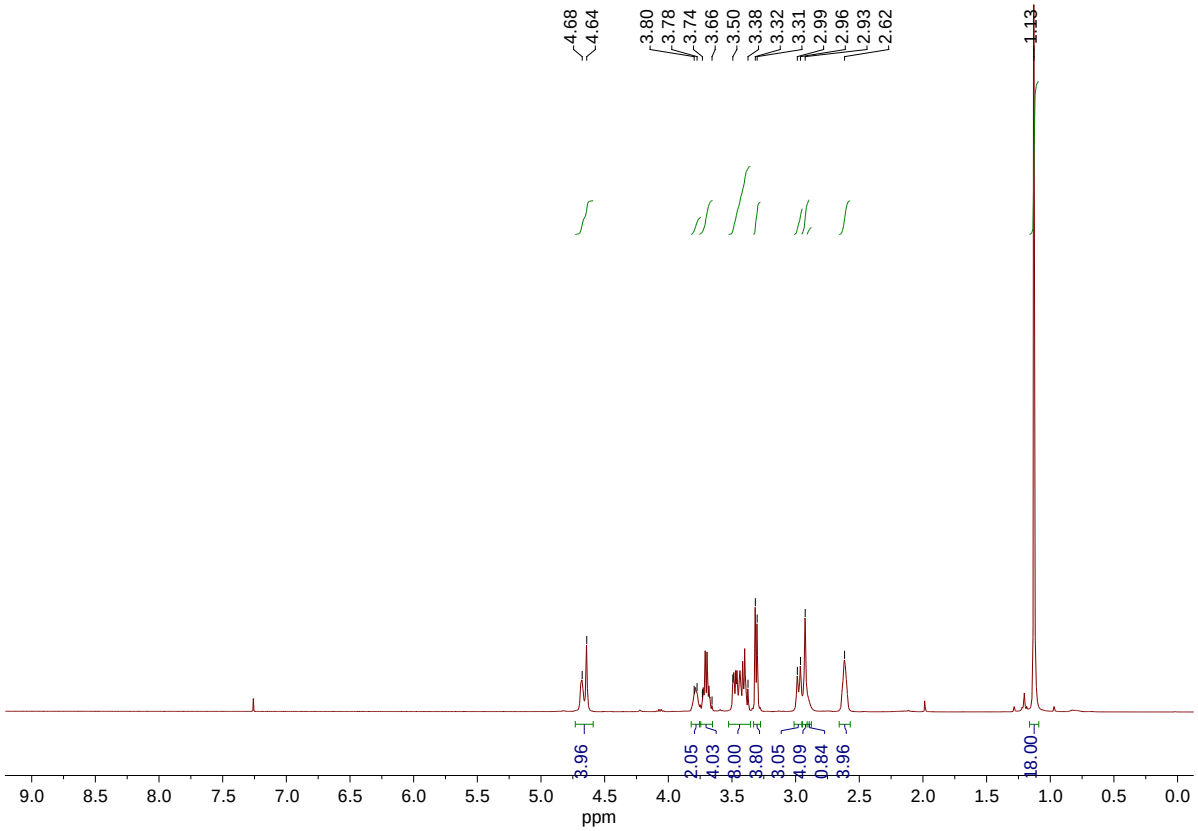


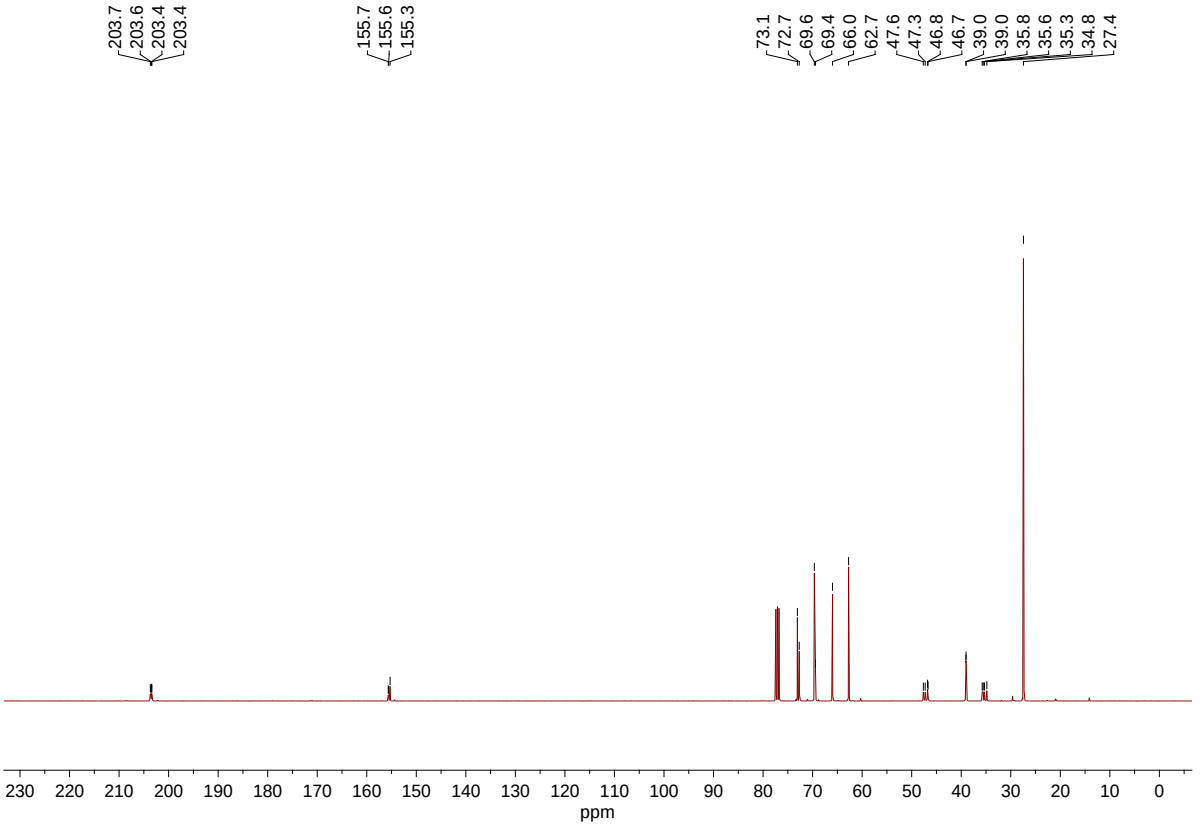




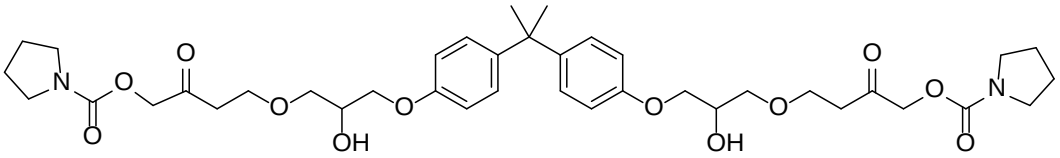
4-(3-(tert-butoxy)-2-hydroxypropoxy)-2-oxobutyl(4-(4-(tert-butoxy)-3-hydroxy butoxy)-2-oxobutyl) ethane-1,2-diylbis(methylcarbamate)

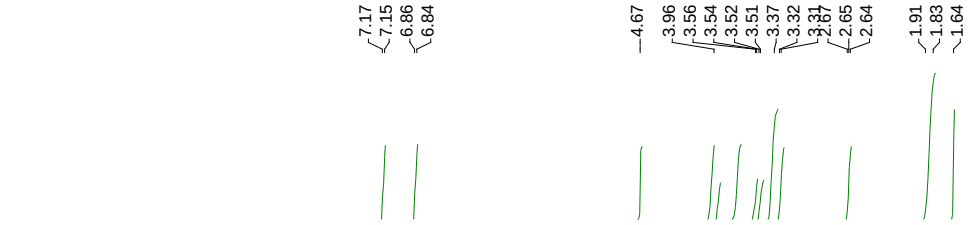


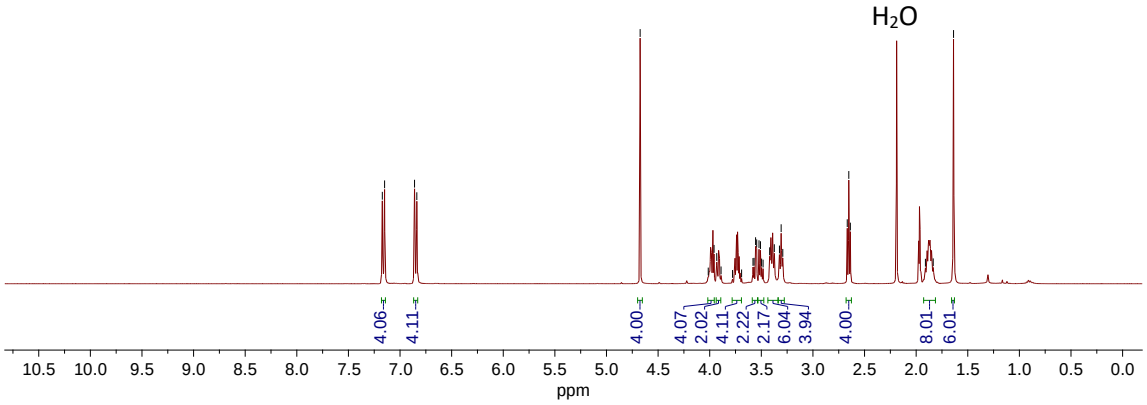


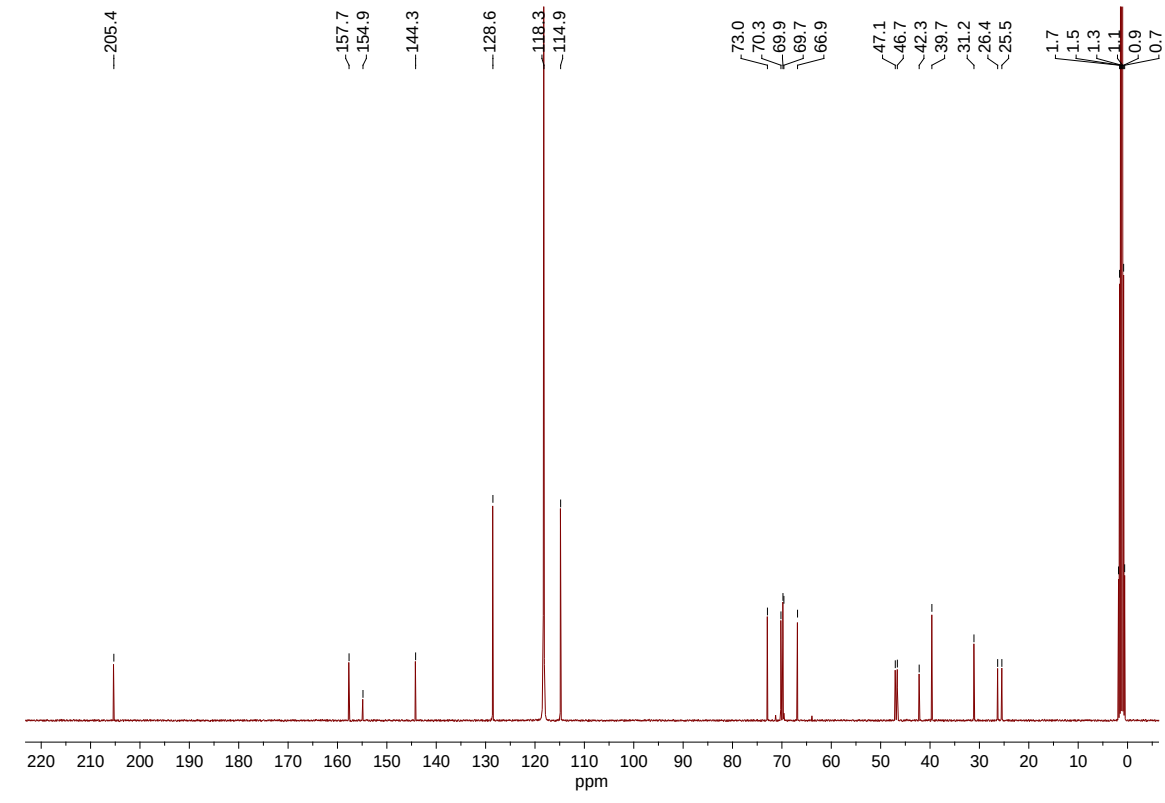


((((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(2-hydroxypropane-3,1-diyl)) bis(oxy))bis(2-oxobutane-4,1-diyl) bis(pyrrolidine-1-carboxylate)

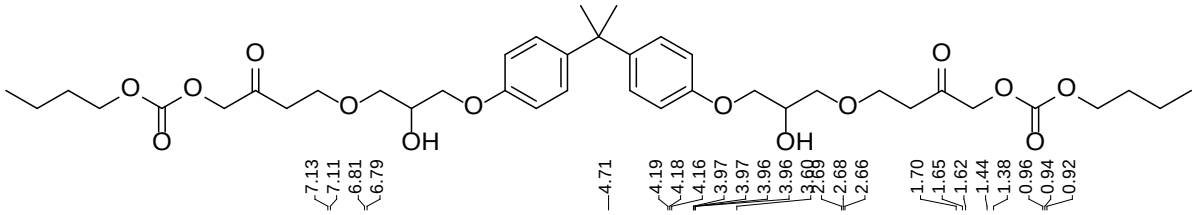


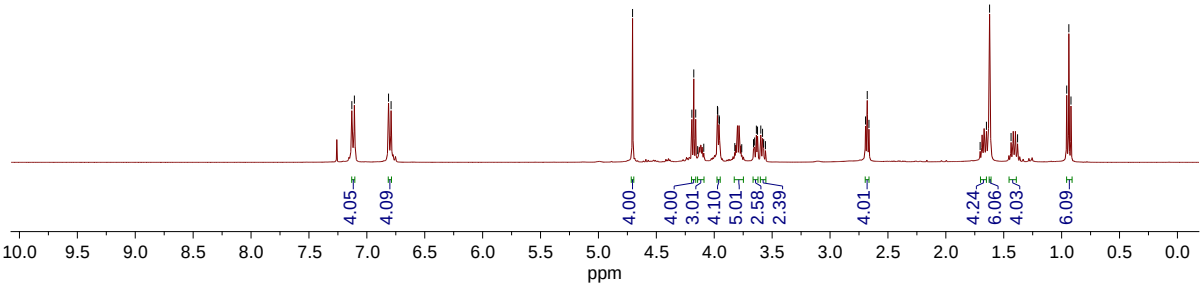


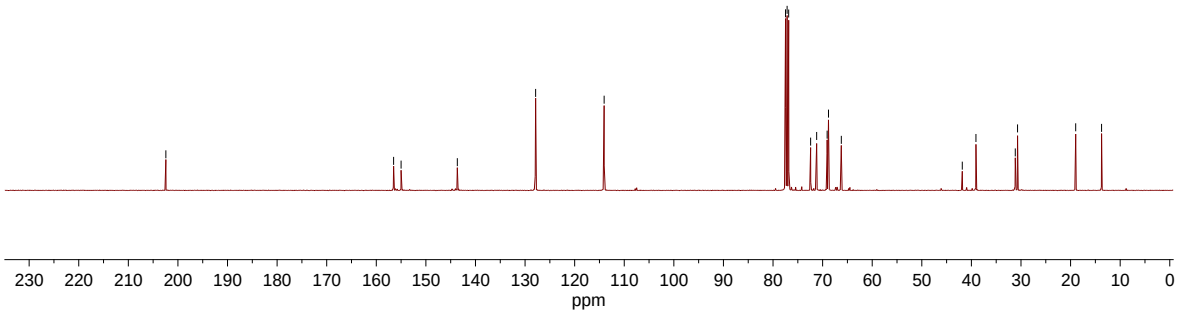




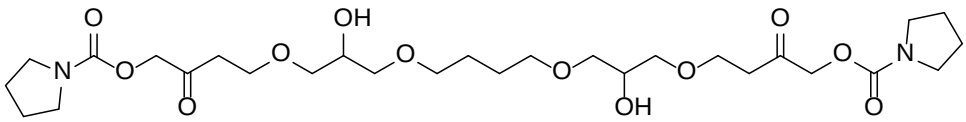
dibutyl ((((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(2-hydroxypropane-3,1-diyl))bis(oxy))bis(2-oxobutane-4,1-diyl)) bis(carbonate)

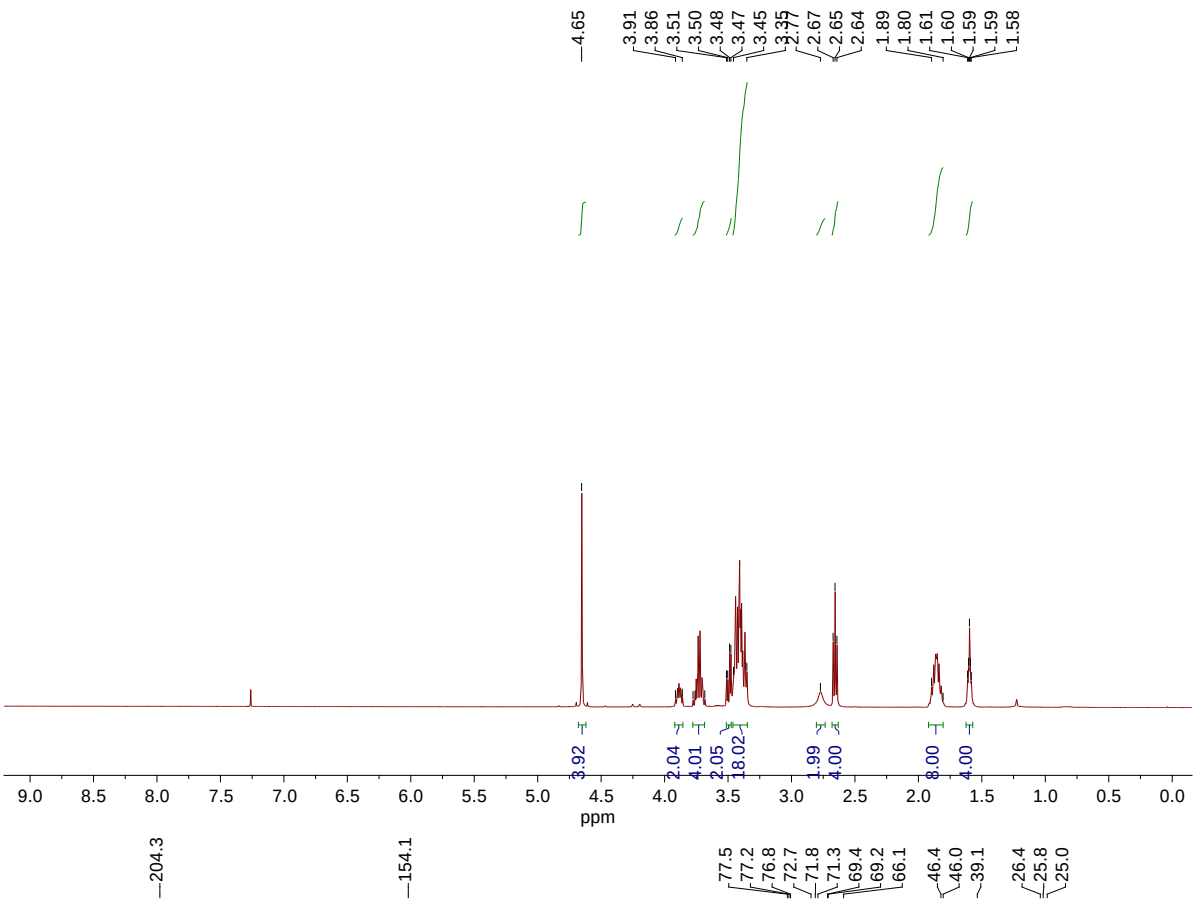


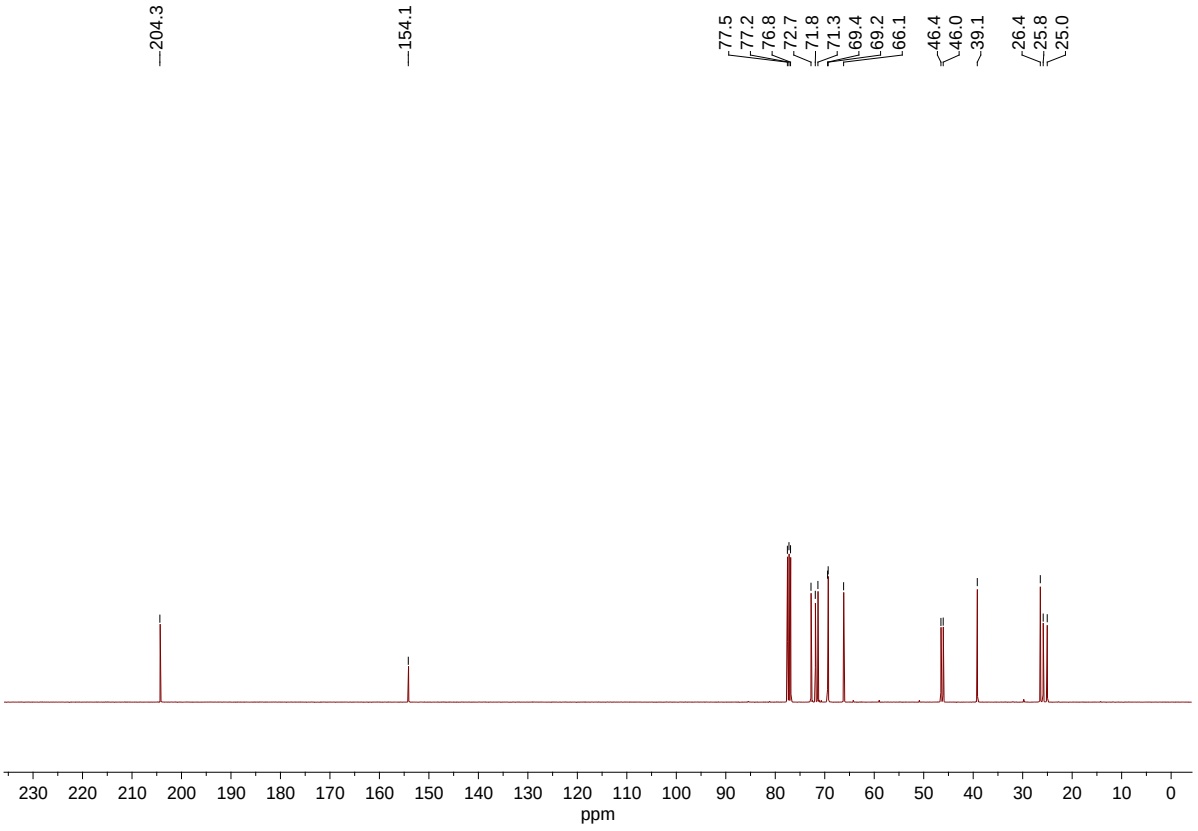




7,16-dihydroxy-2,21-dioxo-5,9,14,18-tetraoxadocosane-1,22-diyl bis(pyrrolidine-1-carboxylate)

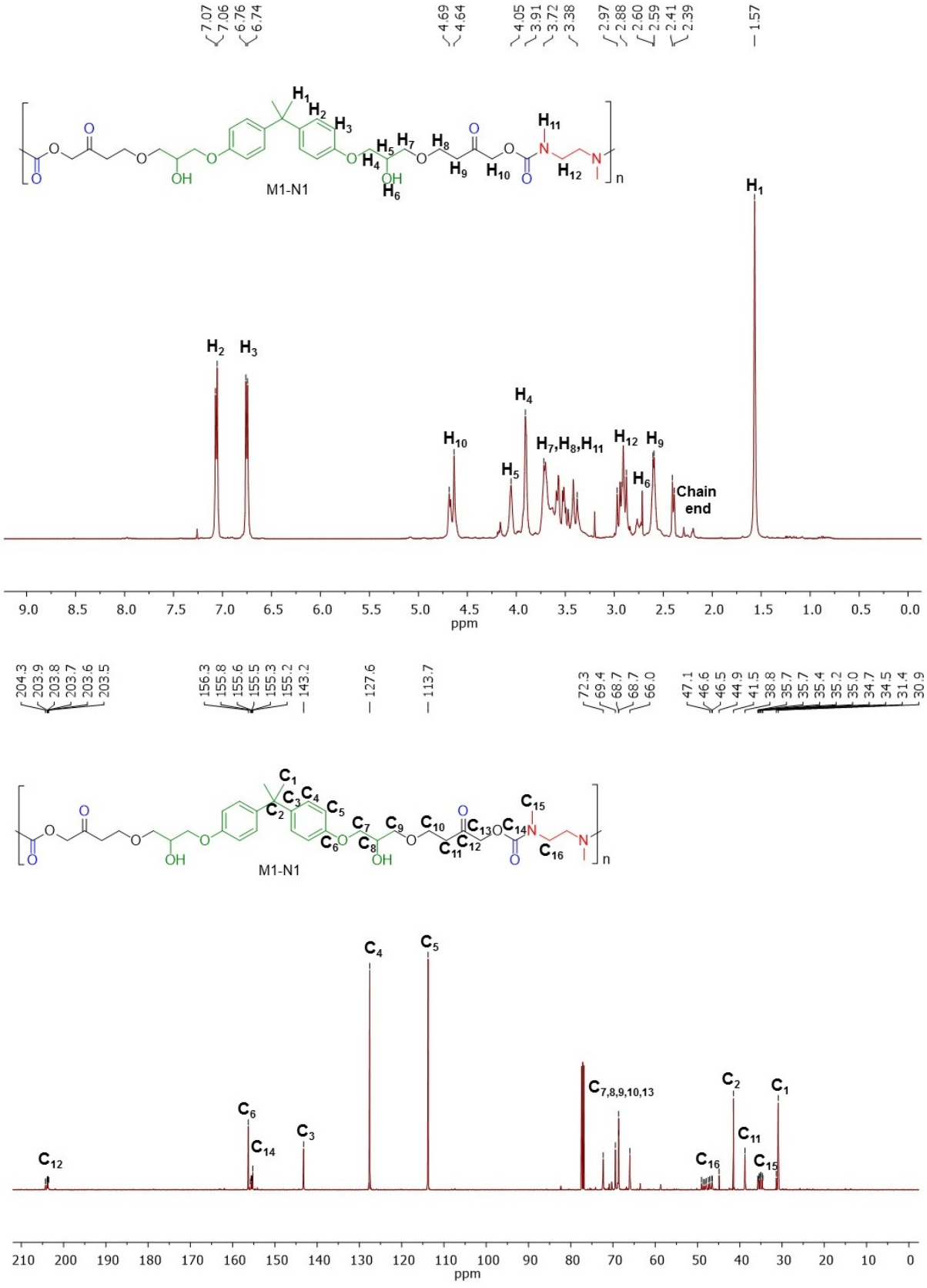






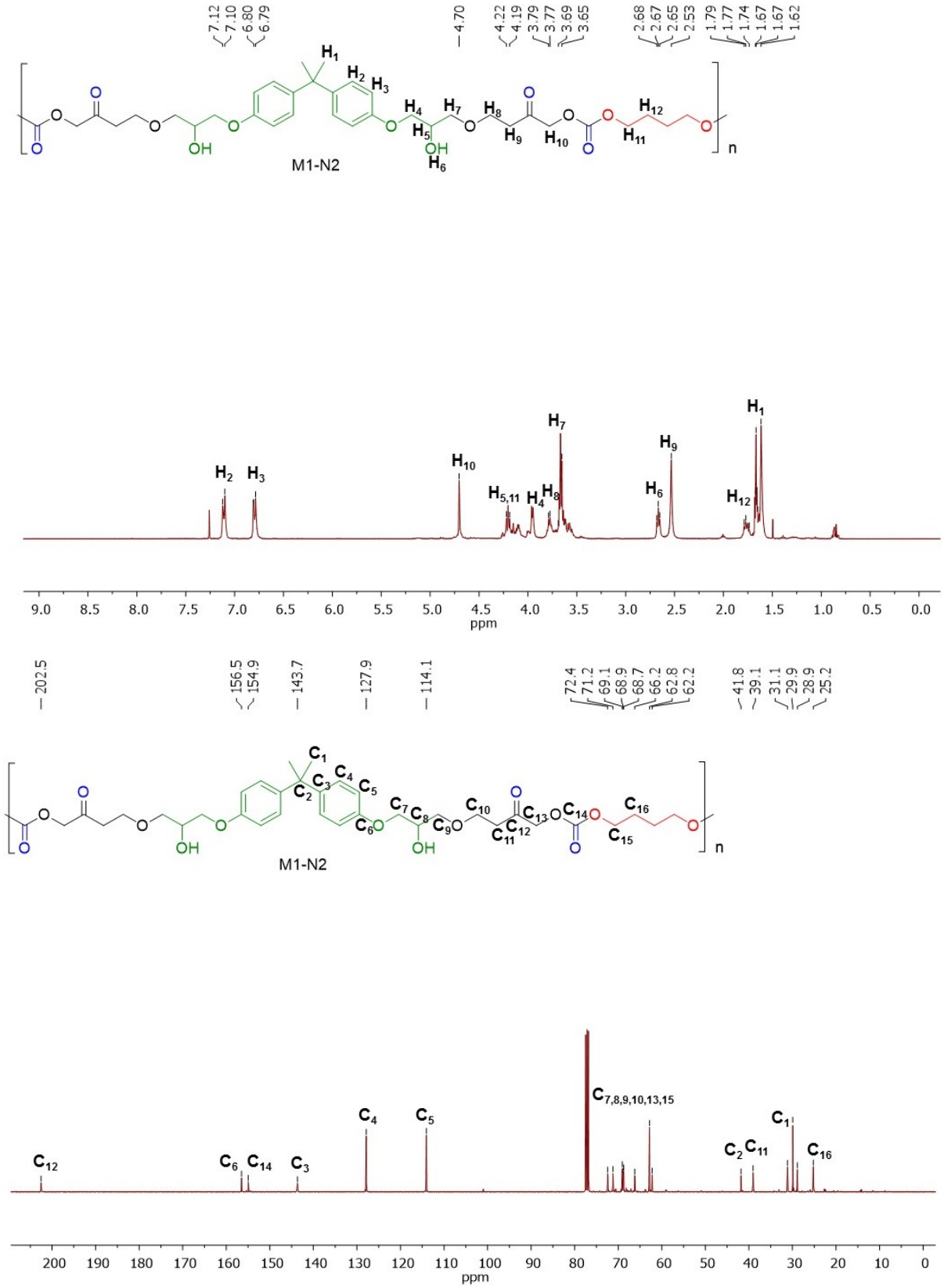
7.0 ^{1}H and ^{13}C NMR spectra of the Polymers

7.1 Polymer of Bisphenol A EVC and *N,N′*-Dimethylenediamine



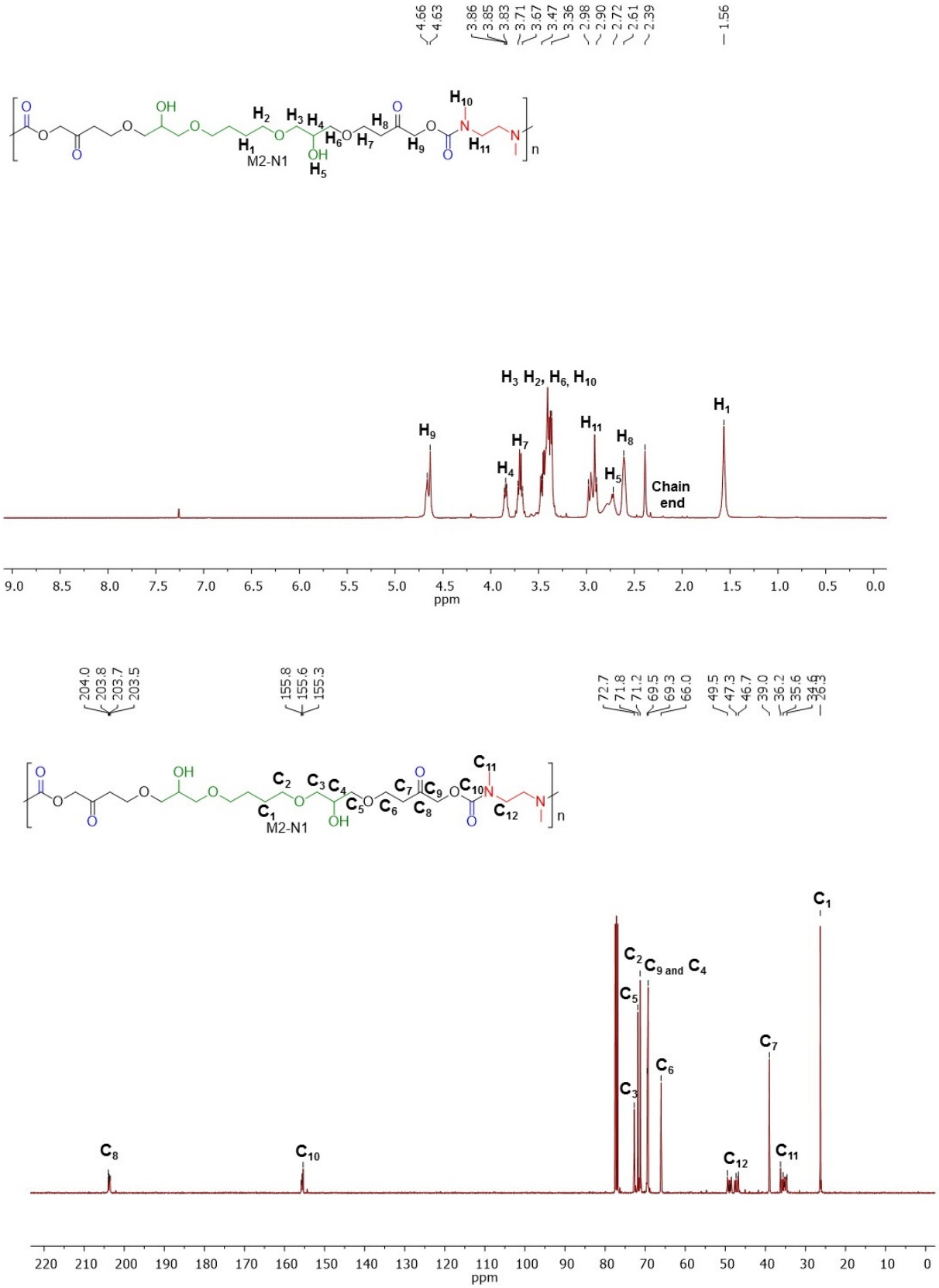
IR (film): ν = 3444 (OH), 2930 (aliphatic C-H), 2873 (aliphatic C-H), 1699 (br.s, C=O), 1607, 1509, 1470, 1409, 1294, 1247, 1182, 1118, 1037, 912, 830, 766, 729, 558 cm^{-1}.

7.2 Polymer of Bisphenol A EVC and 1,4-butanediol



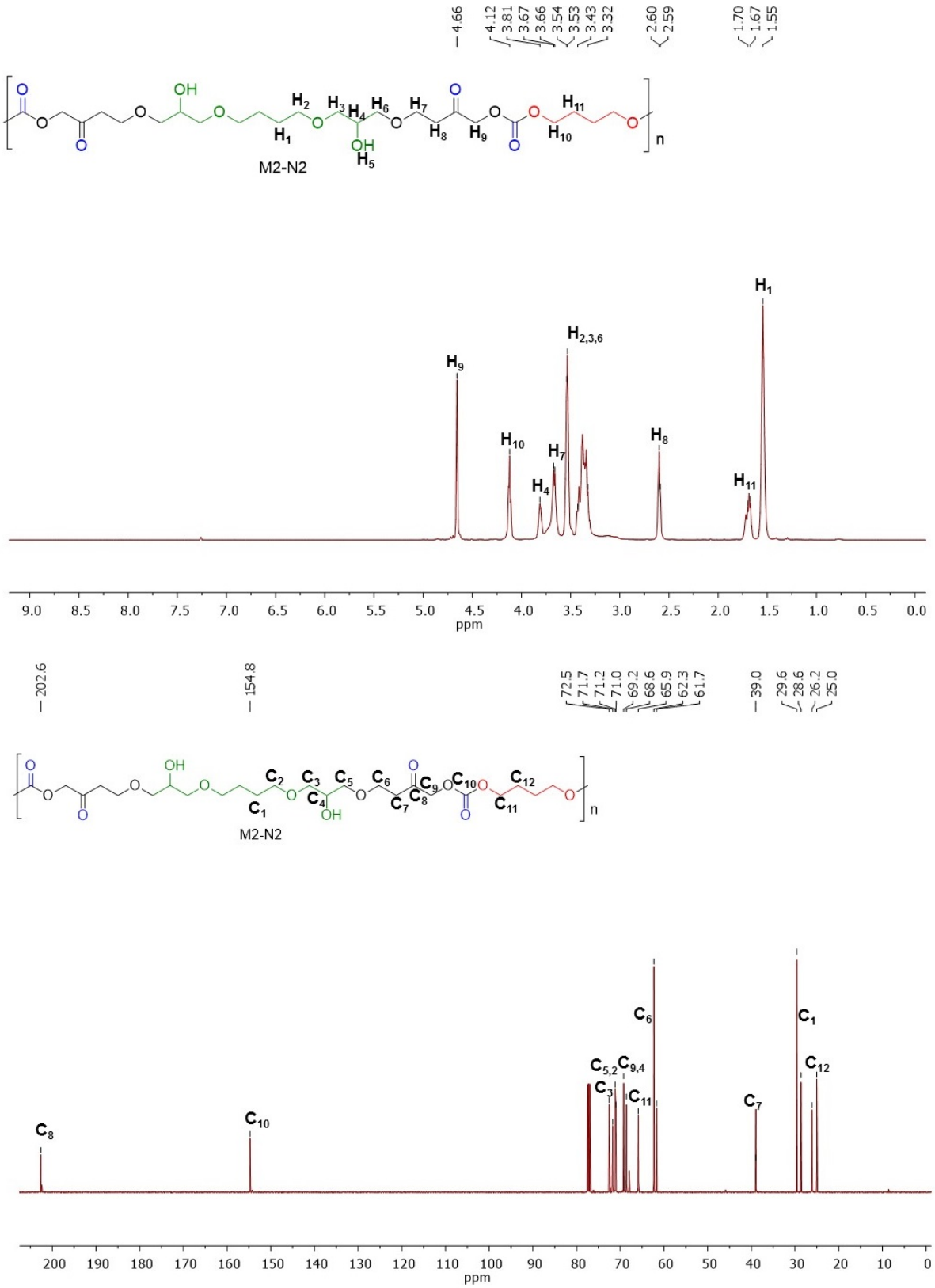
IR (film): ν **=** 3383 (OH), 2938 (aliphatic C-H), 2874 (aliphatic C-H), 1752 (C=O), 1734 (C=O), 1608, 1510, 1461, 1421, 1392, 1252, 1184, 1118, 1044, 831, 787, 731 cm^{-1}.

7.3 Polymer of 1,4-butanedioldiglycidylether EVC and *N,N'*-Dimethylethylene diamine



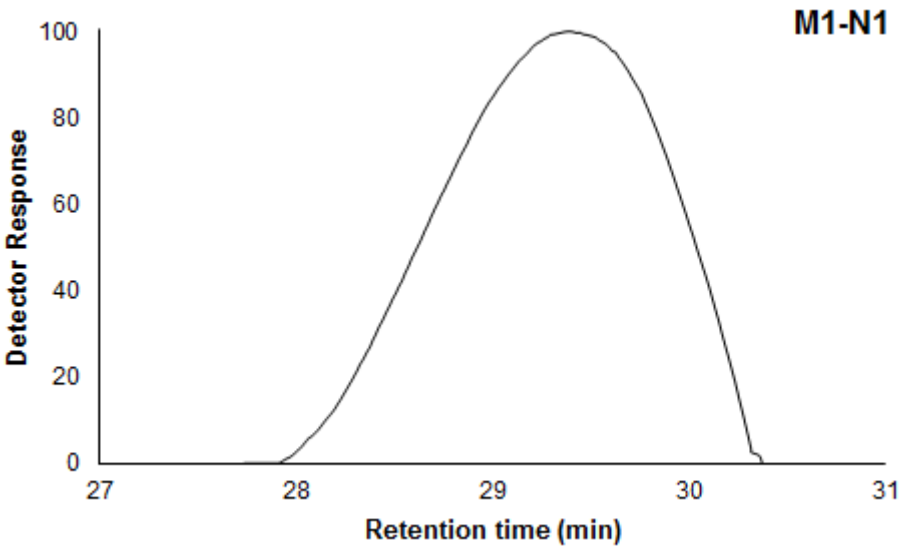
IR (film): ν = 3450 (OH), 2934 (aliphatic C-H), 2869 (aliphatic C-H), 1703 (br.s, C=O), 1483, 1403, 1273, 1218, 919, 766, 731, 646, 571 cm^{-1}.

7.4 Polymer of 1,4-butanedioldiglycidylether EVC and 1,4-butanediol

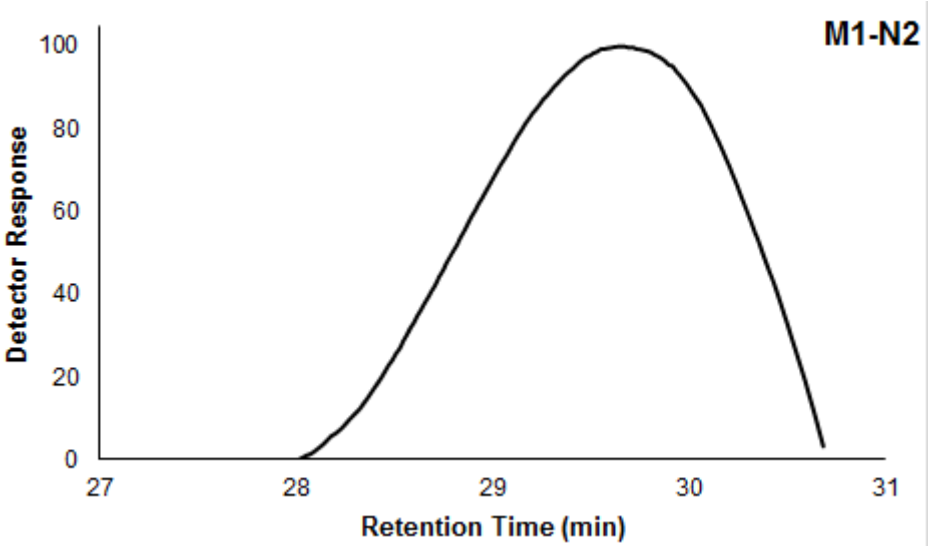


IR (film): ν **=** 3388 (OH), 2937 (aliphatic C-H), 2871 (aliphatic C-H), 1751 (C=O), 1731 (C=O), 1649, 1396, 1268, 1112, 868, 788, 584 cm^{-1}.

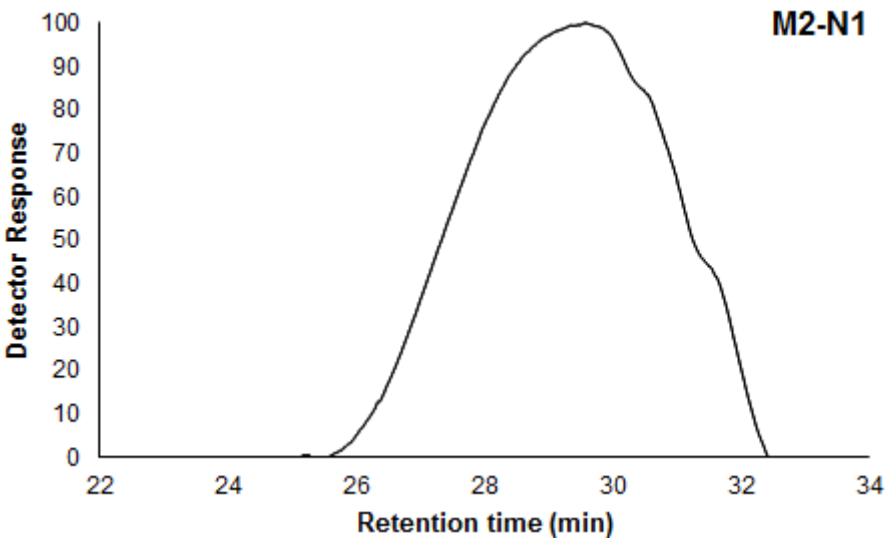
8.0 GPC Measurements of poly(β-oxo-urethane) and poly(β-oxo-carbonate)



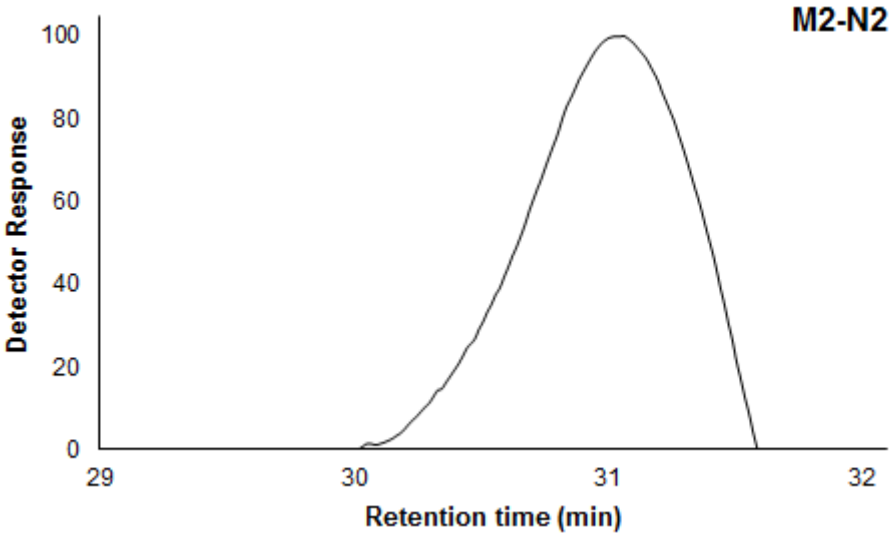
SEC chromatogram of poly(β-oxo-urethane) (M_1-N_1)



SEC chromatogram of poly(β-oxo-carbonate) (M_1-N_2)



SEC chromatogram of poly(β-oxo-urethane) (M_2-N_1)



SEC chromatogram of poly(β-oxo-carbonate) (M_2-N_2)