Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Development of hydroxy-containing imidazole organocatalysts for CO_2 fixation into cyclic carbonates

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Experimental Section

All commercially available epoxide substrates and reagents (Alfa, Aldrich, Fluka) were used as received unless specified otherwise. Epoxides from which cyclic carbonates **11d**–**11h** were synthesized and *N*-butyl-2-hydroxybenzylideneamine were prepared according to previously reported procedures.[1] Carbon dioxide was purchased from Air Liquide and used without further purification. Solvents were distilled from appropriate drying agents and degassed before use. Microanalyses were carried out with a Perkin-Elmer 2400 CHN analyzer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova FT-500 (^{1}H NMR: 500 MHz; ^{13}C NMR: 125 MHz) spectrometer and referenced to the residual deuterated solvent and recorded at room temperature. IR spectra were obtained on a Shimadzu IR Prestige-21 spectrophotometer equipped with a Pike Technology ATR system.

Synthesis of 5-(2-hydroxyphenyl)-1-phenyl-1*H*-imidazole (3). A mixture of commercial salicylidene aniline (3.02 g, 15.31 mmol), TosMIC (3.87 g, 19.82 mmol), K_2CO_3 (6.32 g, 45.73 mmol) and MeOH (60 mL) was heated under reflux with stirring for 3 h. The mixture was allowed to cool, and the solvent was evaporated under reduced pressure to give a dark brown oil that solidified after the addition of water (60 mL). The product was filtered off, washed with CH_2Cl_2, and dried to afford 3.07 g (85%) of the title compound as an orange solid. An analytically pure sample was obtained by recrystallization from ethyl acetate. (3.07 g, 85%). Mp 223–224 ^{o}C. Found: C, 76.31; H, 5.28; N, 11.75. Calc. for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86%. ^{1}H NMR (500 MHz, $CDCl_3$): 6.41 (1H, br s, OH), 6.79 (1H, dt, J=7.5 and 1.0 Hz), 6.91 (1H, dd, *J*=7.5 and 1.5 Hz), 6.94 (1H, d, *J*=8.0 Hz), 7.14-7.17 (2H, m), 7.22 (1H, dt, *J*=7.5 and 1.5 Hz), 7.28 (1H, s, $H4_{Im}$), 7.31-7.38 (3H, m), 7.79 (1H, s, $H2_{Im}$). ^{13}C{^{1}H} NMR and DEPT (125 MHz, $CDCl_3$) 154.2 (C), 138.9 (CH), 136.2 (C), 131.3 (CH), 130.3 (CH), 129.8 (CH), 129.4 (CH), 128.1 (CH), 127.6 (C), 124.9 (CH), 120.2 (CH), 116.0 (CH), 115.6 (C). IR (neat) 3059 (br, OH), 1497, 1279, 754, 694 cm^{-1}.

Synthesis of 5-(2-hydroxyphenyl)-1-butyl-1*H*-imidazole (4). A mixture of *N*-butyl-2-hydroxybenzylideneamine (2.59 g, 14.61 mmol), TosMIC (3.71 g, 18.99 mmol), K_2CO_3 (6.06 g, 43.84 mmol) and MeOH (60 mL) was heated under reflux with stirring for 3 h. The mixture was allowed to cool, and the solvent was evaporated under reduced pressure to give a dark brown oil that solidified after the addition of water (60 mL). The product was filtered off, washed with diethyl ether, and dried to afford 2.82 g (89%) of the title compound as an orange solid. An analytically pure sample was obtained by recrystallization from ethyl acetate. Mp 175-176 ^{o}C. Found: C, 72.25; H, 7.53; N, 12.83. Calc. for $C_{13}H_{16}N_2O$: C, 72.19; H, 7.46; N, 12.95%. ^{1}H NMR (500 MHz, $CDCl_3$) 0.80 (3H, t, *J* = 7.5 Hz, CH_3), 1.18 (2H, m, C$\underline{H_2}$CH$_3$), 1.55 (2H, m, C$\underline{H_2}$CH$_2$CH$_3$), 3.85 (2H, t, *J* = 7.5 Hz, 2H, NCH$_2$), 6.93 (1H, t, *J* = 7.5 Hz, ArH), 6.96 (1H, s, $H5_{im}$), 7.06 (1H, d, *J* = 8.0 Hz ArH), 7.15 (1H, dd, *J* = 7.5 and 1.5 Hz, ArH), 7.31 (1H, dt, *J* = 7.8 and 1.5 Hz, ArH), 6.40 (1H, br s, OH), 7.52 (1H, s, $H2_{im}$). ^{13}C{^{1}H} NMR and DEPT (125 MHz, $CDCl_3$) 55.4 (C), 137.7 (CH), 131.7 (CH), 130.6 (CH), 128.5 (C), 128.2 (CH), 119.9 (CH), 116.6 (CH), 116.4 (C), 45.2 (CH$_2$), 32.7 (CH$_2$), 19.6 (CH$_2$), 13.4 (CH$_3$). IR (neat) 3059 (br, OH), 1497, 1477, 1448, 1435, 1279, 930, 754, 694, 656 cm^{-1}.

Synthesis of 1-butyl-4-(2-hydroxyphenyl)-3-phenyl-1*H*-imidazolium bromide (7). A suspension of bromobutane (10 mL) and 5-(2-hydroxyphenyl)-1-phenyl-1*H*-imidazole (**2**) (600 mg, 2.54 mmol) was heated at 100 ^{o}C for 7 h, resulting in the formation of a brown precipitate. After completion of the reaction, the mixture was cooled to room temperature. The excess bromobutane was evaporated under reduced pressure and the residue was washed with diethyl ether (3 × 20 mL). Pure product was obtained as a yellow solid (673 mg, 71%). An analytically pure sample was obtained by recrystallization from a mixture of chloroform-diethyl ether. Mp 188-190 ^{o}C. Found: C, 61.32; H, 5.81; N, 7.42. Calc. for $C_{19}H_{21}BrN_2O$: C, 61.13; H, 5.67; N, 7.50%. ^{1}H NMR (500MHz, [D$_6$]DMSO) 0.96 (3H, t, *J* = 7.5 Hz, CH_3), 1.40 (2H, m,

C$\underline{H_2}$$CH_3$), 1.93 (2H, m, C$\underline{H_2}$$CH_2CH_3$), 4.30 (2H, t, *J* = 7.5 Hz, NCH_2), 6.82-6.85 (2H, m, ArH), 7.17 (1H, dd, *J* = 7.5 and 1.5 Hz, ArH), 7.27 (1H, dt, *J* = 7.8 and 2.0 Hz, ArH), 7.39-7.41 (2H, m, ArH), 7.47-7.51 (3H, m, ArH), 8.09 (1H, d, *J* = 1.0 Hz, $H5_{im}$), 9.71 (1H, d, *J* = 1.5 Hz, $H2_{im}$), 9.98 (1H, s, OH). $^{13}C\{^1H\}$ NMR and DEPT (125MHz, [D_6]DMSO) 155.6 (C), 136.7 (CH), 134.5 (C), 131.9 (CH), 131.7 (CH), 131.4 (C), 129.8 (CH), 129.5 (CH), 125.1 (CH), 121.5 (CH), 119.1 (CH), 115.8 (CH), 112.2 (C), 49.1 (CH_2), 31.1 (CH_2), 18.9 (CH_2), 13.4 (CH_3). IR (neat) 3055 (br, OH), 1587, 1555, 1454, 1348, 1271, 1177, 762, 692, 635 cm^{-1}.

Synthesis of 1-butyl-4-(2-hydroxyphenyl)-3-phenyl-1*H*-imidazolium iodide (8). A suspension of 1-iodobutane (10 mL) and 5-(2-hydroxyphenyl)-1-phenyl-1*H*-imidazole (3) (544 mg, 2.3 mmol) was heated at 100 °C for 7 h, resulting in the formation of a brown precipitate. The mixture was allowed to cool and the excess 1-iodobutane was evaporated under reduced pressure. The residue was washed with diethyl ether (3 × 20 mL) and filtered off to afford 925 mg (96%) of the title compound as a yellow solid. An analytically pure sample was obtained by recrystallization from a mixture of chloroform-diethyl ether. Mp 179-181 °C. Found: C, 54.10; H, 4.94; N, 6.60. Calc. for $C_{19}H_{21}IN_2O$: C, 54.30; H, 5.04; N, 6.67% ^1H NMR (500MHz, [D_6]DMSO) 0.96 (3H, t, *J* = 7.5 Hz, CH_3), 1.39 (2H, m, C$\underline{H_2}$$CH_3$), 1.91 (2H, m, *C*$\underline{H_2}$$CH_2CH_3$), 4.26 (2H, t, *J* = 7.5 Hz, NCH_2), 6.61 (1H, d, *J* = 8.5 Hz, ArH), 6.66 (1H, t, *J* = 7.5 Hz, ArH), 7.07 (1H, d, *J* = 7.0 Hz, ArH), 7.15 (1H, t, *J* = 7.5 Hz, ArH), 7.41-7.43 (2H, m, ArH), 7.46-7.51 (3H, m, ArH), 8.02 (1H, d, *J* = 1.5 Hz, $H5_{im}$), 9.60 (1H, d, *J* = 1.5 Hz, $H2_{im}$). $^{13}C\{^1H\}$ NMR (125MHz, [D_6]DMSO) 158.8, 136.8, 135.1, 132.9, 132.1, 131.8, 130.2, 129.9, 125.6, 121.6, 117.4, 116.9, 112.7, 49.5, 31.6, 19.4, 13.8. IR (neat) 3100 (br, OH), 1592, 1544, 1494, 1455, 1384, 1176, 761 cm^{-1}.

Synthesis of 1-butyl-4-(2-hydroxyphenyl)-3-butyl-1*H*-imidazolium iodide (9). A suspension of 1-iodobutane (10 mL) and 1-butyl-5-(2-hydroxyphenyl)-1*H*-imidazole (**4**) (560 mg, 2.6 mmol) was heated at 100 °C for 7 h, resulting in the formation of a brown precipitate. The mixture was allowed to cool and the excess 1-iodobutane was evaporated under reduced pressure. The residue was washed with diethyl ether (3 × 20 mL) and filtered off to afford 910 mg (87%) of the title compound as a yellow solid. An analytically pure sample was obtained by recrystallization from ethyl acetate. Mp 126-127 °C. Found: C, 51.18; H, 6.36; N, 6.95. Calc. for $C_{17}H_{25}IN_2O$: C, 51.01; H, 6.30; N, 7.00%. ^1H NMR (500MHz, $CDCl_3$) 0.76 (3H, t, *J* = 7.5 Hz, CH_3), 0.96 (3H, t, *J* = 7.5 Hz, CH_3), 1.16 (2H, m, C$\underline{H_2}$$CH_3$), 1.40 (2H, m, C$\underline{H_2}$$CH_3$), 1.66 (2H, m, *C*$\underline{H_2}$$CH_2CH_3$), 1.92 (2H, m, *C*$\underline{H_2}$$CH_2CH_3$), 4.10 (2H, t, *J* = 7.5 Hz, NCH_2), 4.32 (2H, t, *J* = 7.5 Hz, NCH_2), 6.95 (1H, t, *J* = 7.5 Hz, ArH), 7.14 (1H, dd, *J* = 8.0 and 1.5 Hz, ArH), 7.26 (1H, d, *J* = 2.0 Hz, $H4_{im}$), 7.37 (1H, dt, *J* = 7.5 and 1.5 Hz, ArH), 7.59 (1H, d, *J* = 7.5 Hz, ArH), 8.32 (1H, s, OH), 9.84 (1H, d, *J* = 1.5 Hz, $H2_{im}$). $^{13}C\{^1H\}$ NMR and DEPT (125MHz, $CDCl_3$) 155,3 (C), 135.7 (CH), 133.4 (C), 132.6 (CH), 131.3 (CH), 120.3 (CH), 119.8 CH), 117.6 (CH), 111.7 (C), 49.9 (CH_2), 47.9 (CH_2), 32.1 (CH_2), 31.8 (CH_2), 19.5 (CH_2), 19.4 (CH_2), 13.5 (CH_3), 13.3 (CH_3). IR (neat) 3105 (br, OH), 1599, 1545, 1500, 1450, 1389, 11646, 769 cm^{-1}.

General procedure for synthesis of cyclic carbonates at 10 bar pressure. An epoxide **5a**–**j** or **10a**–**h** (1.66 mmol), a combination of catalysts **3**–**4** (1.6–16.6 μmol) and Bu_4NBr or Bu_4NI (1.6–16.6 μmol) or bifunctional catalysts **7**–**9** (12.4-16.6 μmol) were placed in a stainless steel reactor with a magnetic stirrer bar. The reaction mixture was heated to 80–90 °C, then pressurised to 10 bar of carbon dioxide pressure and stirred for 1–2 h. The conversion of epoxide to cyclic carbonate was then determined by analysis of a sample by ^1H NMR spectroscopy. The remaining sample was filtered through a plug of silica, eluting with CH_2Cl_2 to remove the catalyst. The eluent was evaporated *in vacuo* to give either the pure cyclic carbonate or a mixture of cyclic carbonate and unreacted epoxide. In the latter case, the mixture was purified by flash chromatography using a solvent system of first hexane, then hexane:EtOAc (9:1), then hexane:EtOAc (3:1), then EtOAc to give the pure cyclic carbonate. Cyclic carbonates **6a**–**j** or **11a-h** are all known compounds and the spectroscopic data were consistent with those reported in the literature.[1b,2]

1,2-Hexylene carbonate (**6a**). Obtained as a colourless liquid (214.8 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) 4.61 (1H, qd, *J* = 7.5, and 5.4 Hz, OCH), 4.45 (1H, t, *J* = 8.1 Hz, OCH_2), 4.00 (1H, dd, *J* = 8.4 and 7.2 Hz, OCH_2), 1.60-1.80 (2H, m, CH_2), 1.20-1.40 (4H, m, CH_2), 0.86 (3H, t, *J* = 7.1 Hz, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) 155.1, 77.0, 69.4, 33.5, 26.4, 22.2, 13.7. IR (neat) 2941, 2922, 2899, 1796 cm^{-1}.

Propylene carbonate (**6b**). Obtained as a colourless liquid (121.3 mg, 71%). ^{1}H NMR (500 MHz, $CDCl_3$) 4.80-4.90 (1H, m, OCH), 4.54 (1H, t, *J* = 8.3 Hz, OCH_2), 4.00 (1H, dd, *J* = 8.3 and 7.4 Hz, OCH_2), 1.46 (3H, d, *J* = 6.3 Hz, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) 155.1, 73.6, 70.7, 19.4. IR (neat) 2961, 2902, 1781 cm^{-1}.

1,2-Butylene carbonate (**6c**). Obtained as a colourless liquid (174.8 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) 4.50-4.70 (1H, m, OCH), 4.52 (1H, t, *J* = 8.1 Hz, OCH_2), 4.08 (1H, dd, *J* = 6.3 and 5.3 Hz, OCH_2), 1.70-1.80 (2H, m, CH_2) 1.03 (3H, t, *J* = 7.1 Hz, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) 155.2, 78.1, 69.1, 27.0, 8.6. IR (neat) 2938, 2917, 1801 cm^{-1}.

1,2-Decylene carbonate (**6d**). Obtained as a colourless liquid (286.0 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) 4.60-4.70 (1H, m, OCH), 4.52 (1H, dd, *J* = 8.4 and 7.8 Hz, OCH_2), 4.06 (1H, dd, *J* = 8.4 and 7.2 Hz, OCH_2), 1.60-1.90 (2H, m, CH_2), 1.20-1.60 (12H, m, CH_2), 0.88 (3H, t, *J* = 6.8 Hz, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) 155.0, 77.0, 69.4, 33.8, 31.8, 29.3, 29.2, 29.1, 24.4, 22.7, 14.0. IR (neat) 2916, 2851, 1800 cm^{-1}.

Styrene carbonate (**6e**). Obtained as a white solid. (232.0 mg, 85%). Mp 49-51 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) 7.30-7.50 (5H, m, ArH), 5.68 (1H, t, *J* = 8.0 Hz, PhC<u>H</u>O), 4.81 (1H, t, *J* = 8.4 Hz, OCH_2), 4.35 (1H, t, *J* = 8.6 Hz, OCH_2). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) 154.8, 135.8, 129.7, 129.2, 125.8, 77.9, 71.2. IR (neat) 3060, 3029, 2961, 2903, 1791, 1599 cm^{-1}.

4-Chlorostyrene carbonate (**6f**). Obtained as a white solid. (302.5 mg, 91%). Mp 66-69 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) 7.40 (2H, d, *J* = 8.5 Hz, ArH), 7.29 (2H, d, *J* = 8.5 Hz, ArH), 5.65 (1H, t, *J* = 7.9 Hz, OCH), 4.79 (1H, t, *J* = 8.4 Hz, OCH), 4.29 (1H, t, *J* = 7.8 Hz, OCH_2). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) 154.6, 135.7, 134.3, 129.4, 127.3, 76.8, 71.0. IR (neat) 2973, 2698, 2121, 2017, 1971, 1793 cm^{-1}.

4-Bromostyrene carbonate (**6g**). Obtained as a white solid. (322.40 mg, 96%). Mp 72-75 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) 7.34 (2H, dd, *J* = 8.1 and 2.0 Hz, ArH), 7.23 (2H, dd, *J* = 8.4 and 1.8 Hz, ArH), 5.59 (1H, t, *J* = 7.9 Hz, OCH), 4.73 (1H, t, *J* = 8.4 Hz, OCH_2), 4.23 (1H, t, *J* = 7.8 Hz, OCH_2). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) 154.5, 135.7, 134.2, 129.4, 127.3, 77.2, 71.0. IR (neat) 2951, 2522, 2161, 2017, 1981, 1801, 1771 cm^{-1}.

3-Chloropropylene carbonate (**6h**). Obtained as a colourless liquid. (198.5 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) 4.98 (1H, m, OCH), 4.59 (1H, t, *J* = 8.5 Hz, CH_2Cl), 4.42 (1H, dd, *J* = 9.0 and 8.7 Hz, CH_2Cl), 3.79 (1H, dd, *J* = 12.0 and 6.5 Hz, CH_2O), 3.76 (1H, dd, *J* = 12.5 and 4.0 Hz, CH_2O). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) 154.2, 74.3, 67.0, 43.7. IR (neat) 3451, 1971, 1803 cm^{-1}.

Glycerol carbonate (**6i**). Obtained as a colourless liquid (76.2 mg, 93%). ^{1}H NMR (500 MHz, [D_6]DMSO) 5.23 (1H, t, *J* = 5.5, OH), 4.70-4.80 (1H, m, OCH), 4.47 (1H, t, *J* = 8.3 Hz, CH_2O), 4.26 (1H, dd, *J* = 8.1 and 5.8 Hz, CH_2O), 3.64 (1H, ddd, *J* = 12.5, 5.5 and 2.6 Hz, C<u>H</u>$_2$OH), 3.49 (1H, ddd, *J* =12.6, 5.6 and 3.3 Hz, C<u>H</u>$_2$OH). ^{13}C{^{1}H} NMR (125 MHz, [D_6]DMSO) 155.6, 77.4, 66.3, 61.0. IR 3382, 2901, 1799 cm^{-1}.

3-Phenoxyproplylene carbonate (**6j**). Obtained as a white solid. (305.0 mg, 94%). Mp 94-97 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) 7.20-7.30 (2H, m, ArH), 7.03 (1H, t, *J* = 7.5 Hz, ArH), 6.90-7.00 (2H, m, ArH), 5.00-5.10 (1H, m, OCH), 4.50-4.60 (2H, m, OCH_2), 4.23 (1H, dd, *J* = 10.6 and 4.2 Hz, C<u>H</u>$_2$OPh), 4.15 (1H, dd, *J* =

10.6 and 3.6 Hz, C$\underline{H}_2$OPh). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) 157.7, 154.6, 129.7, 122.0, 114.6, 74.1, 66.9, 66.2. IR (neat) 3429, 3061, 2989, 2924, 2328, 1791 cm^{-1}.

***cis*-1,2-Cyclopentene carbonate** (**11a**). Obtained as a white solid. (169.7 mg, 80%). Mp 30−33 °C. ^1H NMR (400 MHz, $CDCl_3$) 5.10 (m, 2H, CHO), 2.15 (2H, m, CH_2), 1.60–1.80 (4H, m, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) 155.4, 81.8, 32.2, 21.6. IR (neat) 2967, 2871, 1789 cm^{-1}.

***cis*-1,2-Cyclohexene carbonate** (**11b**). Obtained as a white solid. (114.7 mg, 49%). Mp 35−37 °C. ^1H NMR (400 MHz, $CDCl_3$) 4.60–4.70 (m, 2H, CHO), 1.80–1.90 (4H, m, C$\underline{H}_2$CHO), 1.50–1.60 (2H, m, CH_2), 1.40–1.50 (2H, m, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) 155.3, 75.7, 26.7, 19.1. IR (neat) 2933, 2861, 1784 cm^{-1}.

(2-oxo-1,3-dioxolan-4-yl)methyl furan-2-carboxylate (11c). Obtained as a white solid (305.8 mg, 94%). Mp 95-98 ^{0}C. ^1H NMR (400 MHz; $CDCl_3$) 7.61 (s, 1H, OCH=CH), 7.22 (s, 1H, CH=CH), 6.53 (s, 1H, CH=CH), 5.04 (m, 1H, OCH), 4.62 (m, 1H, OCH_2), 4.60-4.40 (m, 2H, CH_2), 4.38 (m, 1H, OCH_2); $^{13}C\{^1H\}$ NMR (100 MHz; $CDCl_3$) 157.8, 154.4, 147.3, 143.3, 119.4, 112.2, 73.8, 66.1, 63.3. IR (neat) 2980, 2860, 1783, 1717 cm^{-1}.

4-(furan-2-ylmethoxy)-1,3-dioxolan-2-one (**11d**). Obtained as a colourless liquid (325.7 mg, 99%). ^1H NMR (400 MHz; $CDCl_3$) 7.48 (s, 1H, OC$\underline{H}$=CH), 6.35 (s, 2H, CH=CH), 4.77 (m, 1H, OCH), 4.30-4.60 (4H, m, OCH_2), 3.60-3.80 (2H, m, CH_2). $^{13}C\{^1H\}$ NMR (100 MHz; $CDCl_3$) 154.8, 150.6, 143.2, 110.4, 110.1, 74.8, 68.4, 66.3, 65.3. IR (neat) 2960, 2899, 1784 cm^{-1}.

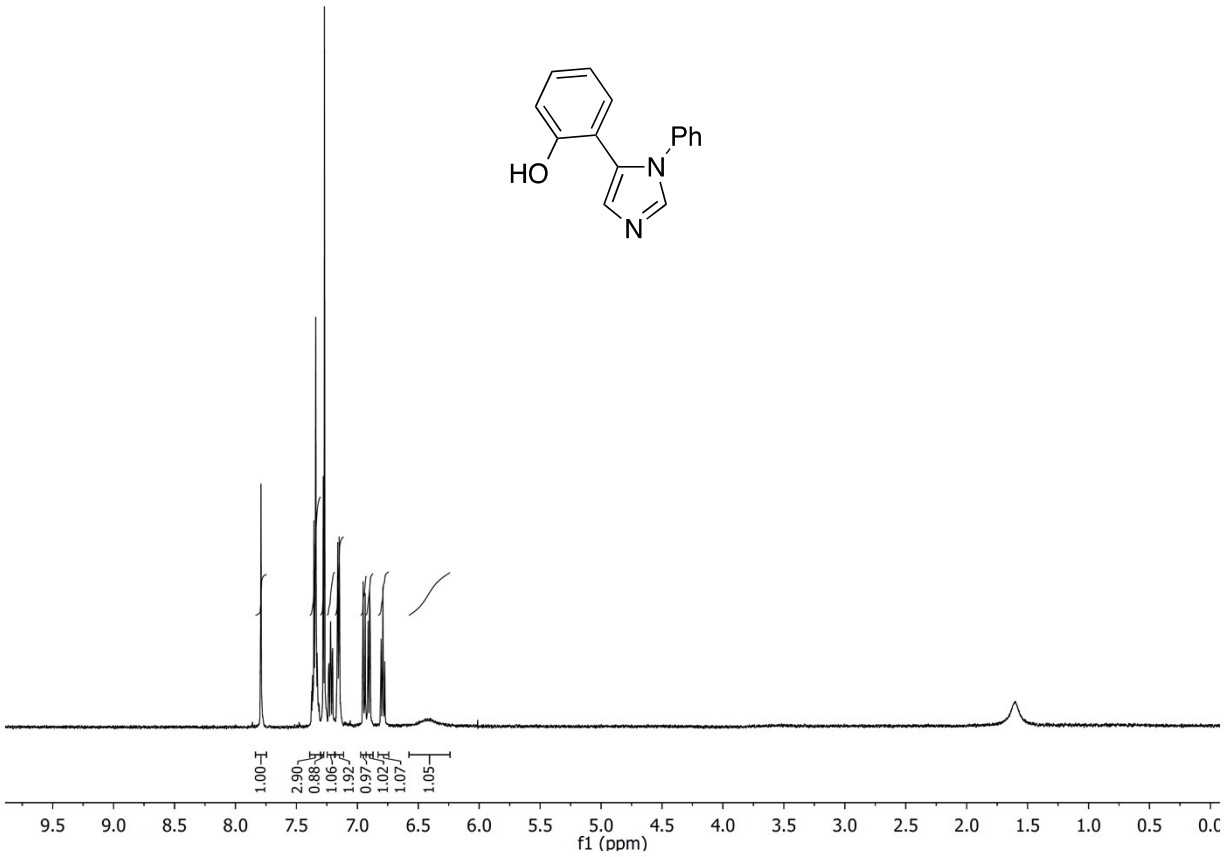
4,4'-((Furan-2,5diylbis(methylene))bis(oxy))bis(1,3-dioxolan-2-one) (**11e**). Obtained as a colourless liquid (485.0 mg, 89%). ^1H NMR (400 MHz; $CDCl_3$) 6.31 (s, 2H, CH=CH), 4.79 (2H, m, OCH), 4.30–4.60 (8H, m, OCH_2), 3.60-3.80 (4H, m, $OCOCH_2$). $^{13}C\{^1H\}$ NMR (100 MHz; $CDCl_3$) 154.9, 151.45, 110.8, 75.0, 68.6, 66.1, 65.3. IR (neat) 2871, 2771, 1789 cm^{-1}.

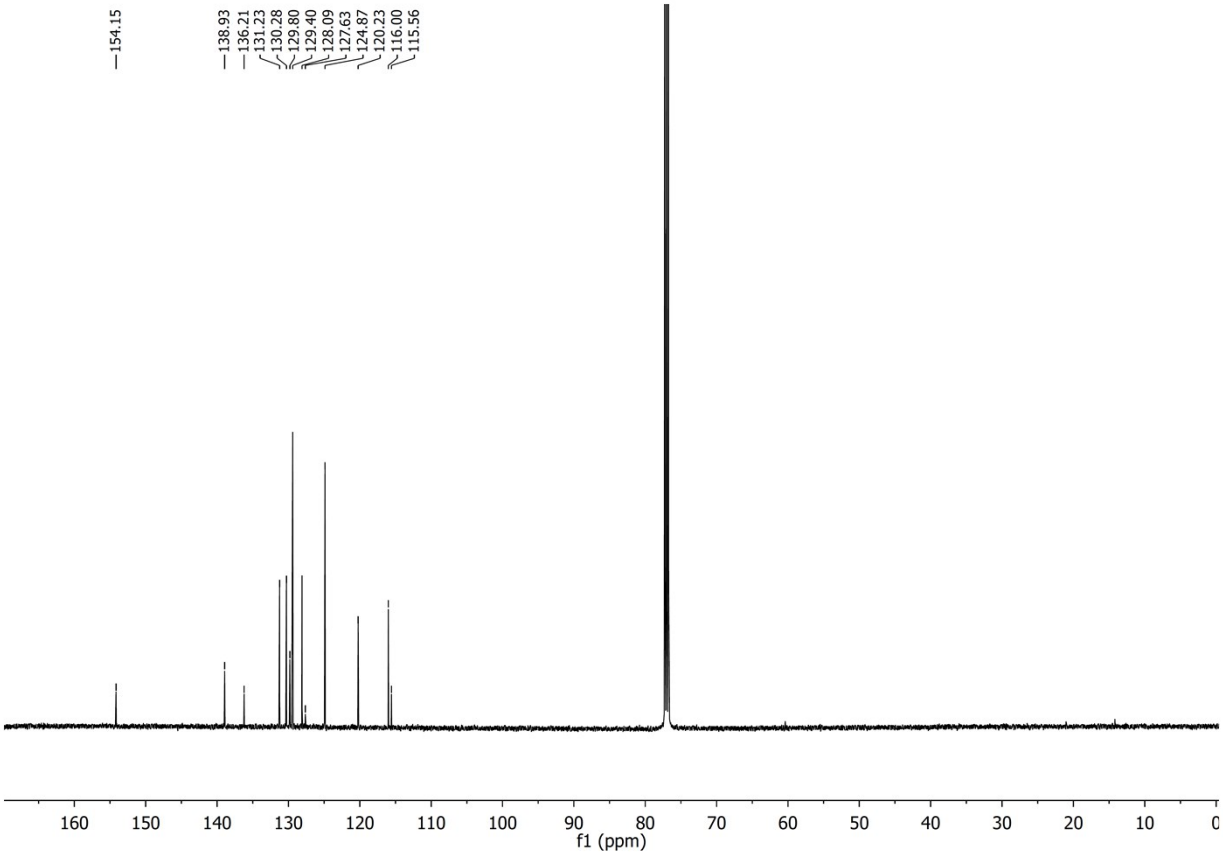
Bis((2-oxo-1,3-dioxolan-4-yl)methyl) fumarate (**11f**). Obtained as a white solid. (446.2 mg, 85%). Mp 135–138 °C. ^1H NMR (400 MHz. [D_6]DMSO) 6.77 (s, 2H, CH=CH), 5.10 (m, 2H, OCH), 4.30-4.60 (m, 8H, OCH_2). $^{13}C\{^1H\}$ NMR (100 MHz. [D_6]DMSO) 164.2, 155.1, 133.5, 74.5, 66.4, 64.9. IR (neat) 1778, 1723 cm^{-1}.

Bis((2-oxo-1,3-dioxolan-4-yl)methyl) succinate (**11g**). Obtained as a white solid. (501.8 mg, 95%). Mp 115–118 °C. ^1H NMR (400 MHz; [D_6]DMSO) 5.05 (2H, m, OCH), 4.20–4.60 (8H, m, OCH_2), 2.63 (4H, br s, $COCH_2$). $^{13}C\{^1H\}$ NMR (100 MHz; [D_6]DMSO) 172.0, 155.1, 74.7, 66.4, 64.0, 28.8. IR (neat) 2910, 2850, 1782, 1731 cm^{-1}.

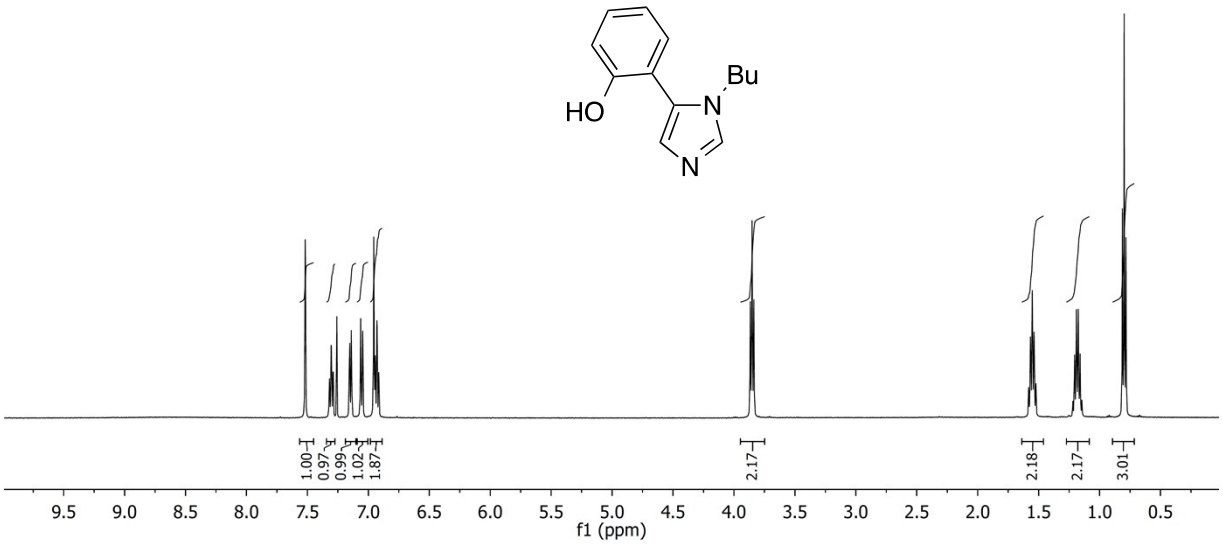
Bis((2-oxo-1,3-dioxolan-4-yl)methyl) glutarate (**11h**). Obtained as a white solid. (508.2 mg, 95%). Mp 105−108 °C. ^1H NMR (400 MHz; [D_6]DMSO) 5.05 (2H, m, OCH), 4.20–4.60 (8H, m, OCH_2), 2.41 (2H, m, $COCH_2$), 1.76 (2H, m, $COCH_2C\underline{H}_2$). $^{13}C\{^1H\}$ NMR (100 MHz; [D_6]DMSO) 172.5, 155.1, 74.7, 66.4, 63.8, 32.6, 20.0. IR (neat) 2855, 1780, 1735 cm^{-1}.

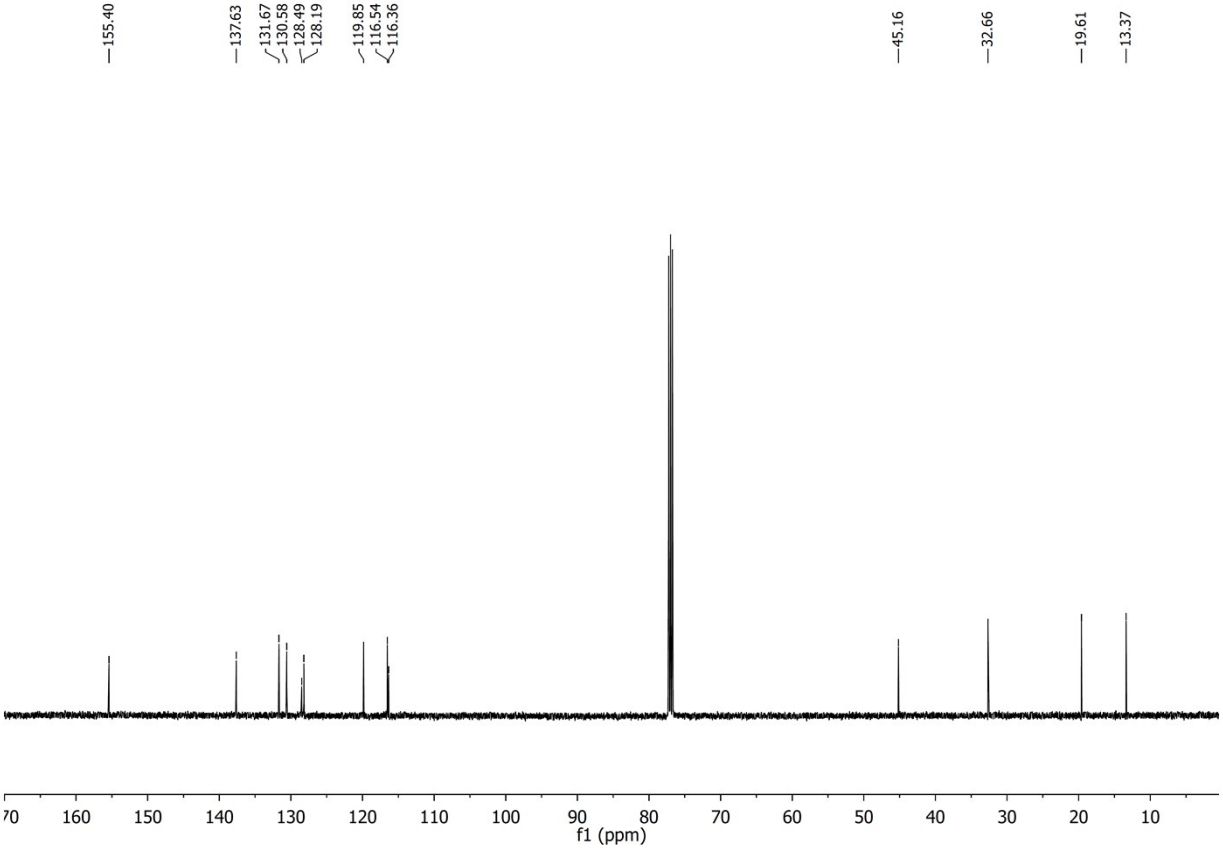
NMR Spectra for 5-(2-Hydroxyphenyl)-1-phenyl-1H-imidazole **3**



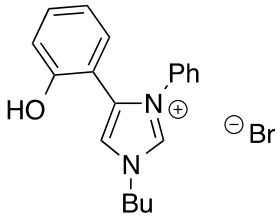


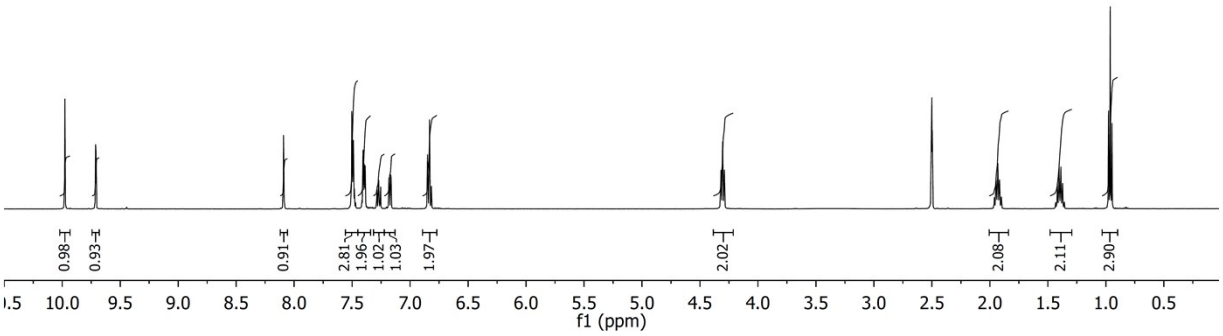
NMR Spectra for 5-(2-Hydroxyphenyl)-1-butyl-1*H*-imidazole **4**

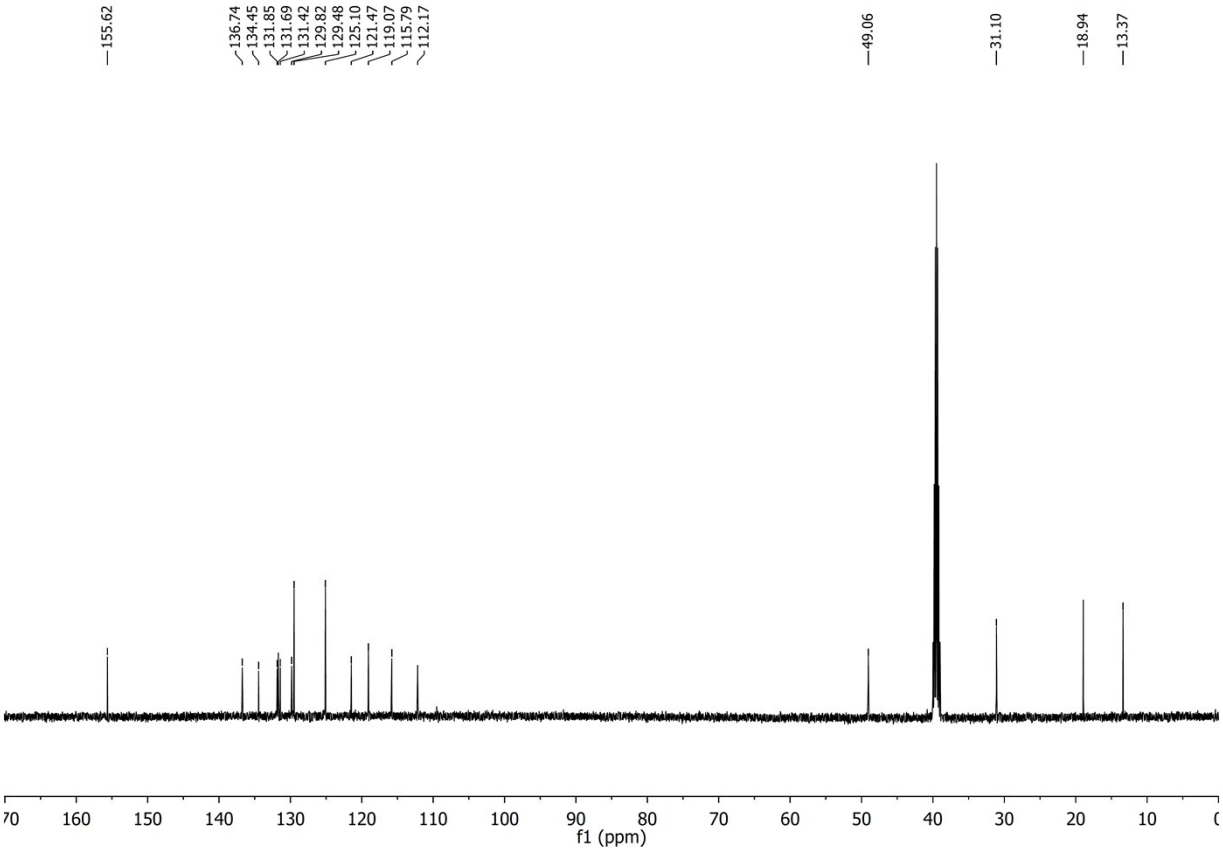




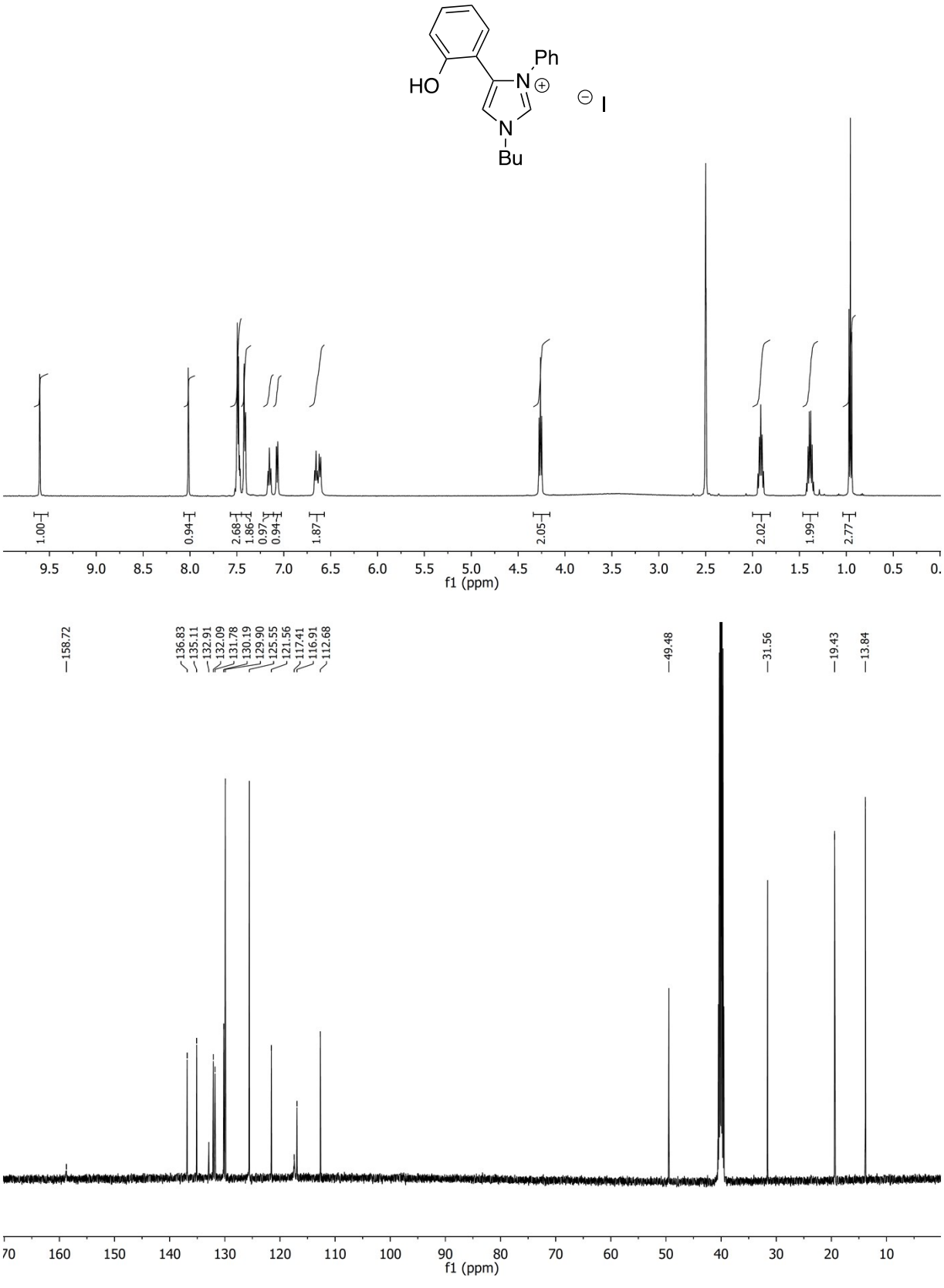
NMR Spectra for 1-butyl-4-(2-Hydroxyphenyl)-3-phenyl-1*H*-imidazolium bromide **7**



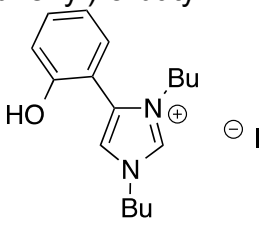


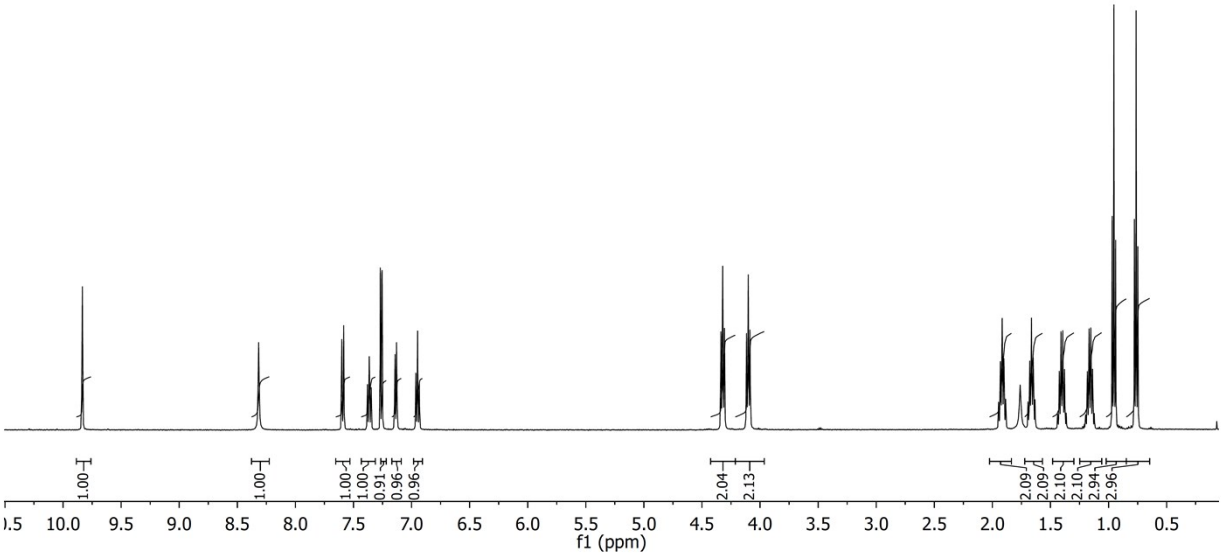


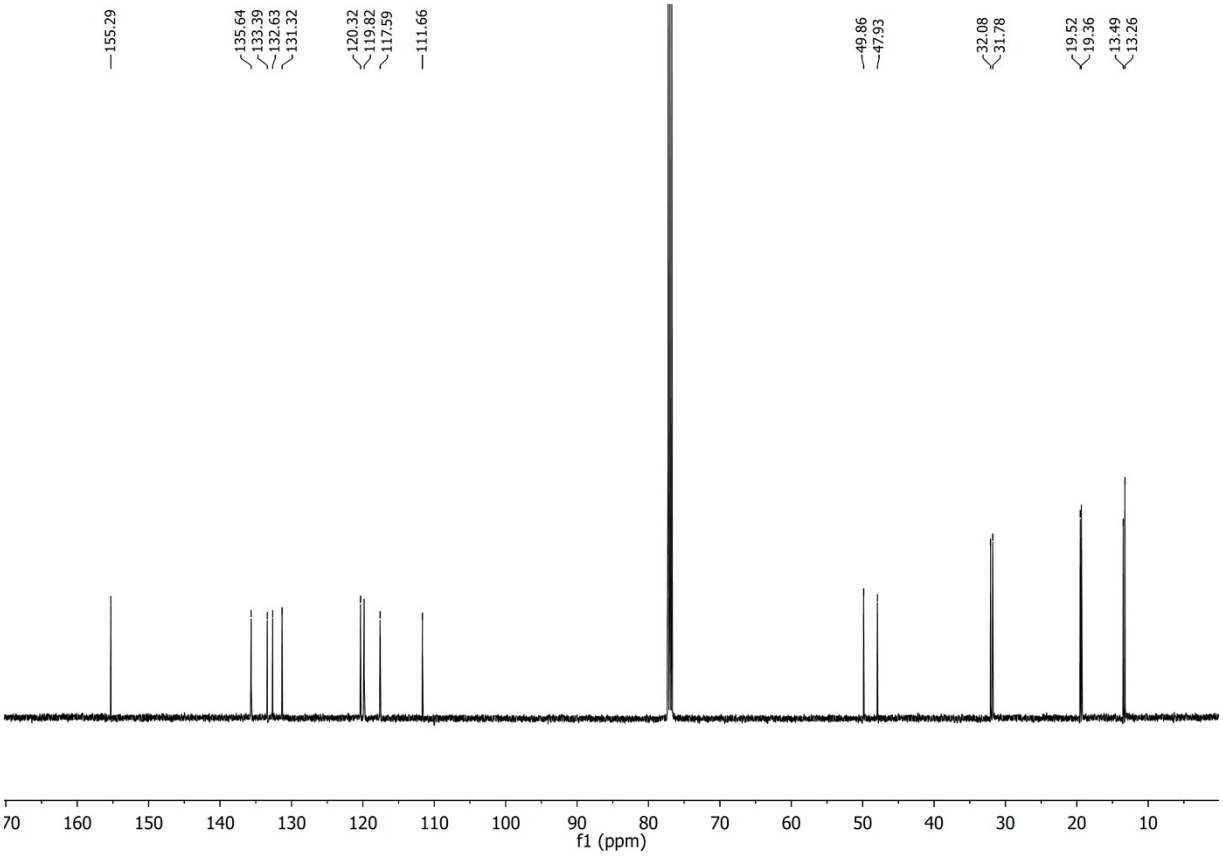
NMR Spectra for 1-butyl-4-(2-Hydroxyphenyl)-3-phenyl-1*H*-imidazolium iodide **8**



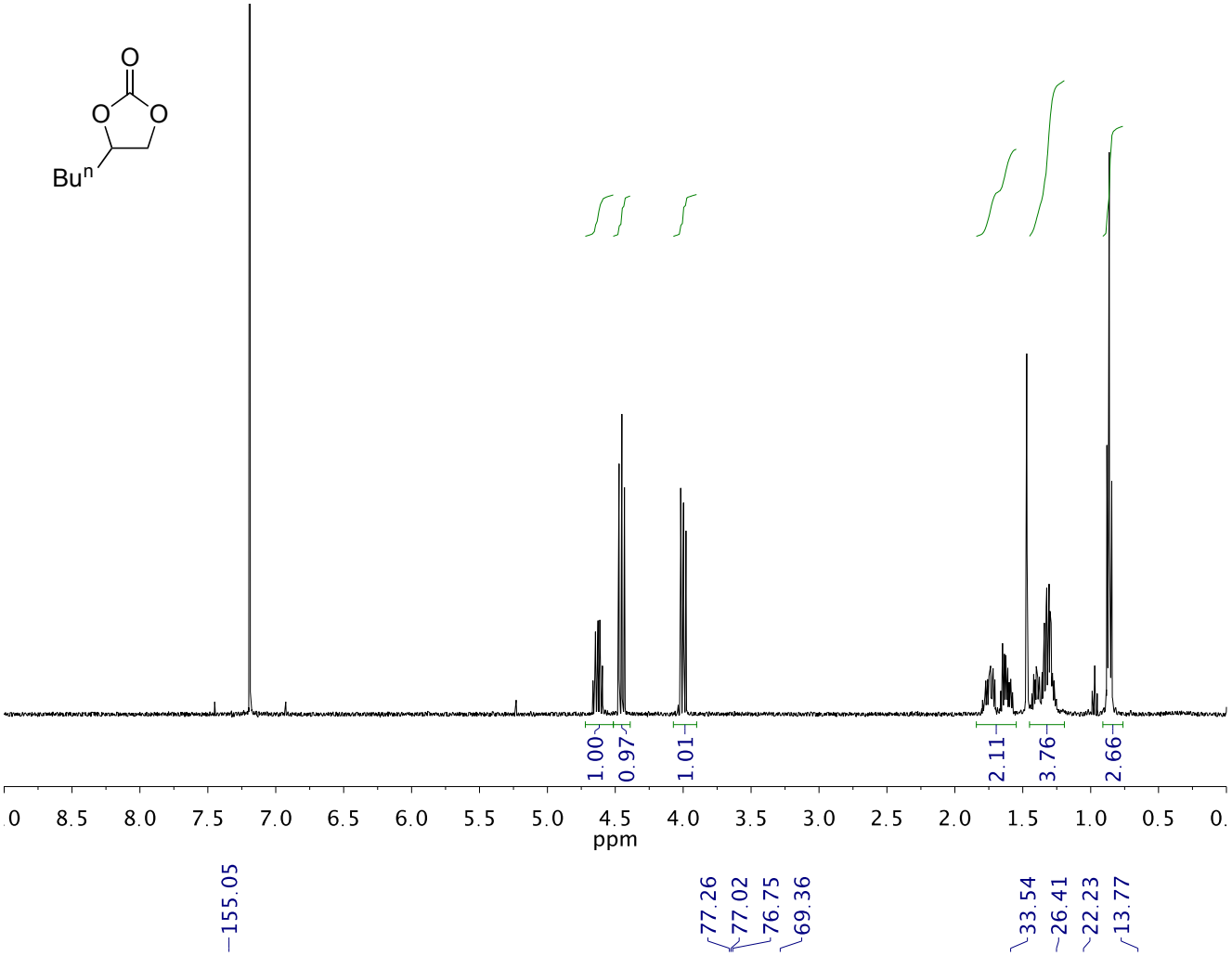
NMR Spectra for 1-butyl-4-(2-Hydroxyphenyl)-3-butyl-1H-imidazolium iodide **9**

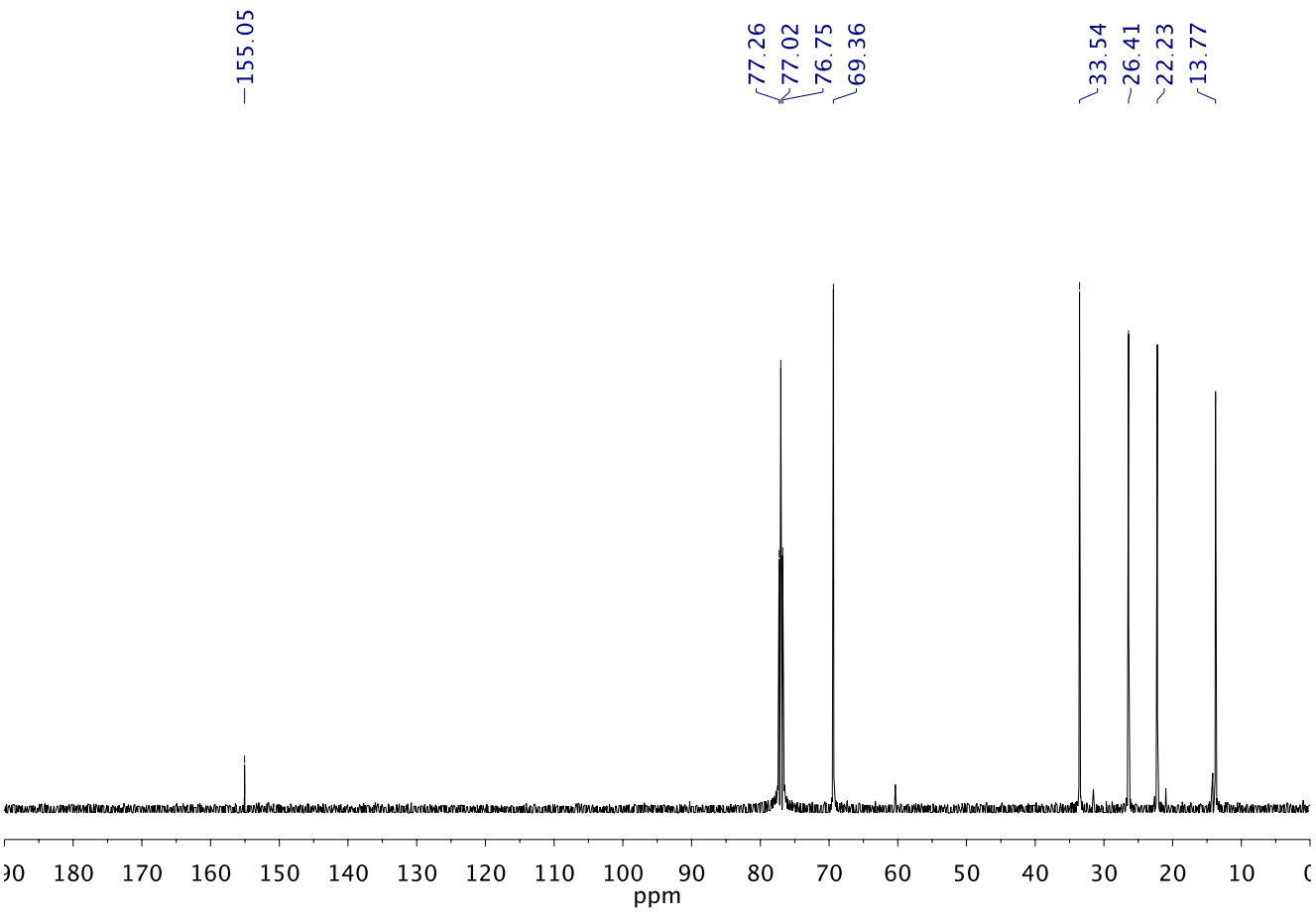




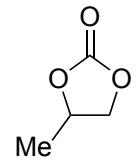


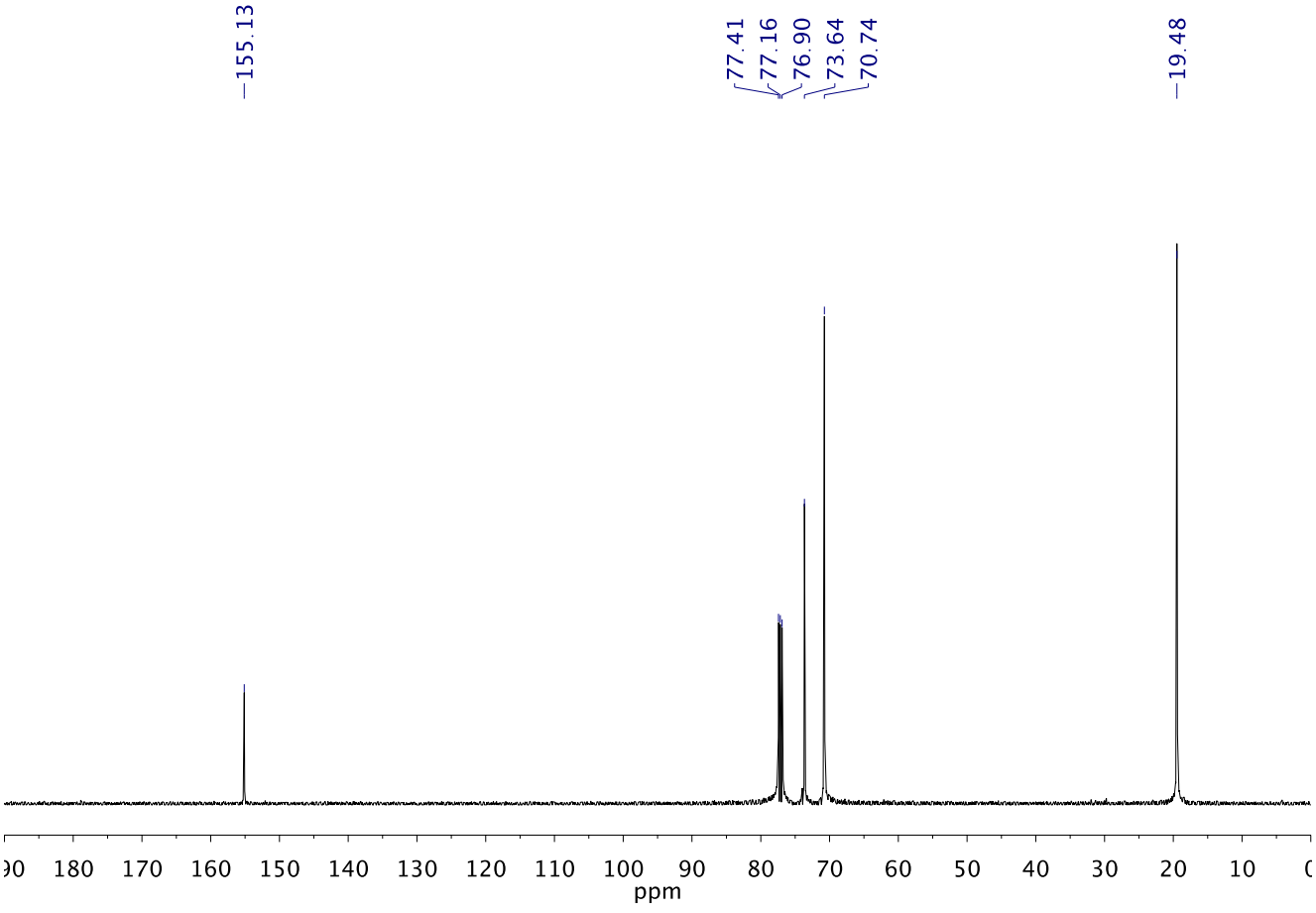
NMR Spectra for 1,2-hexylene carbonate **6a** in $CDCl_3$



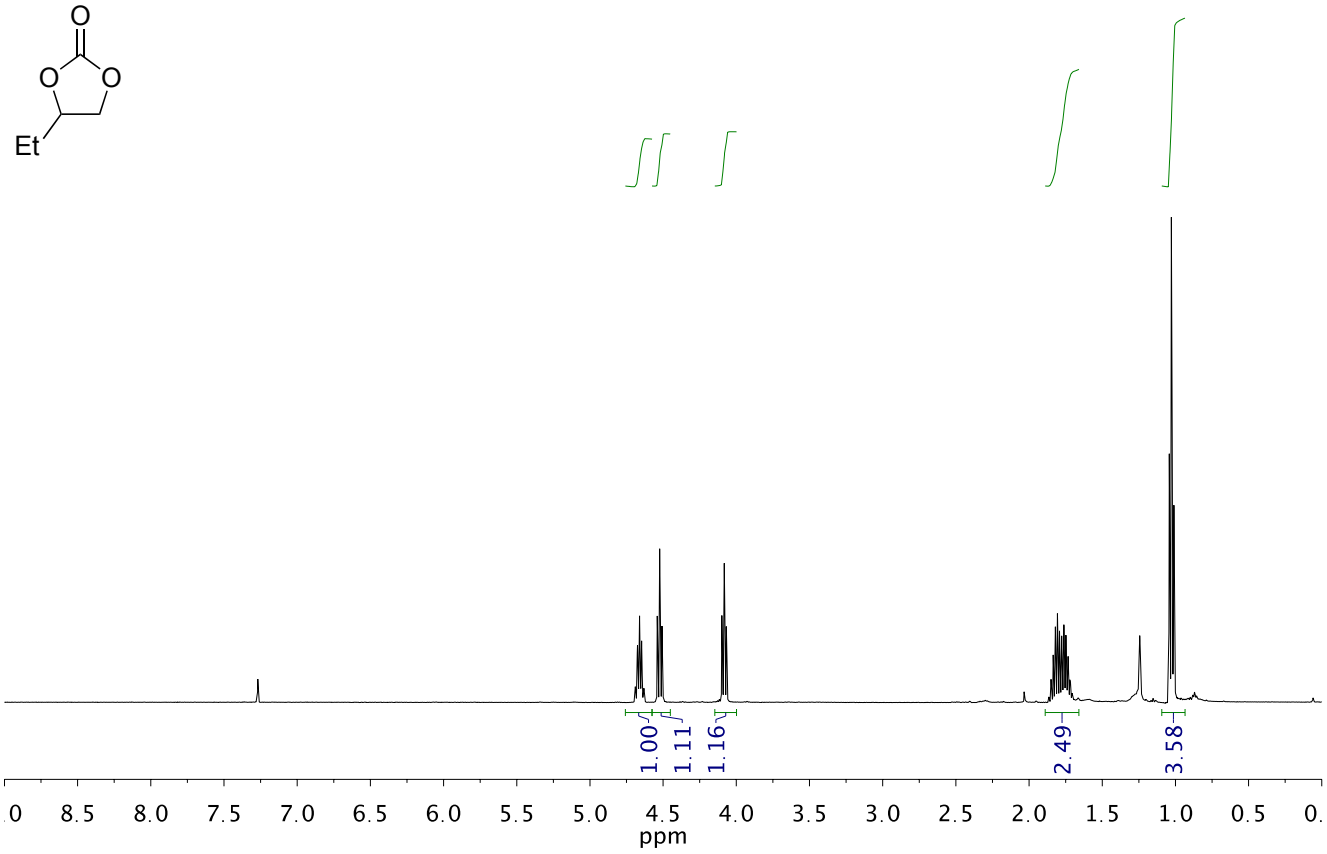


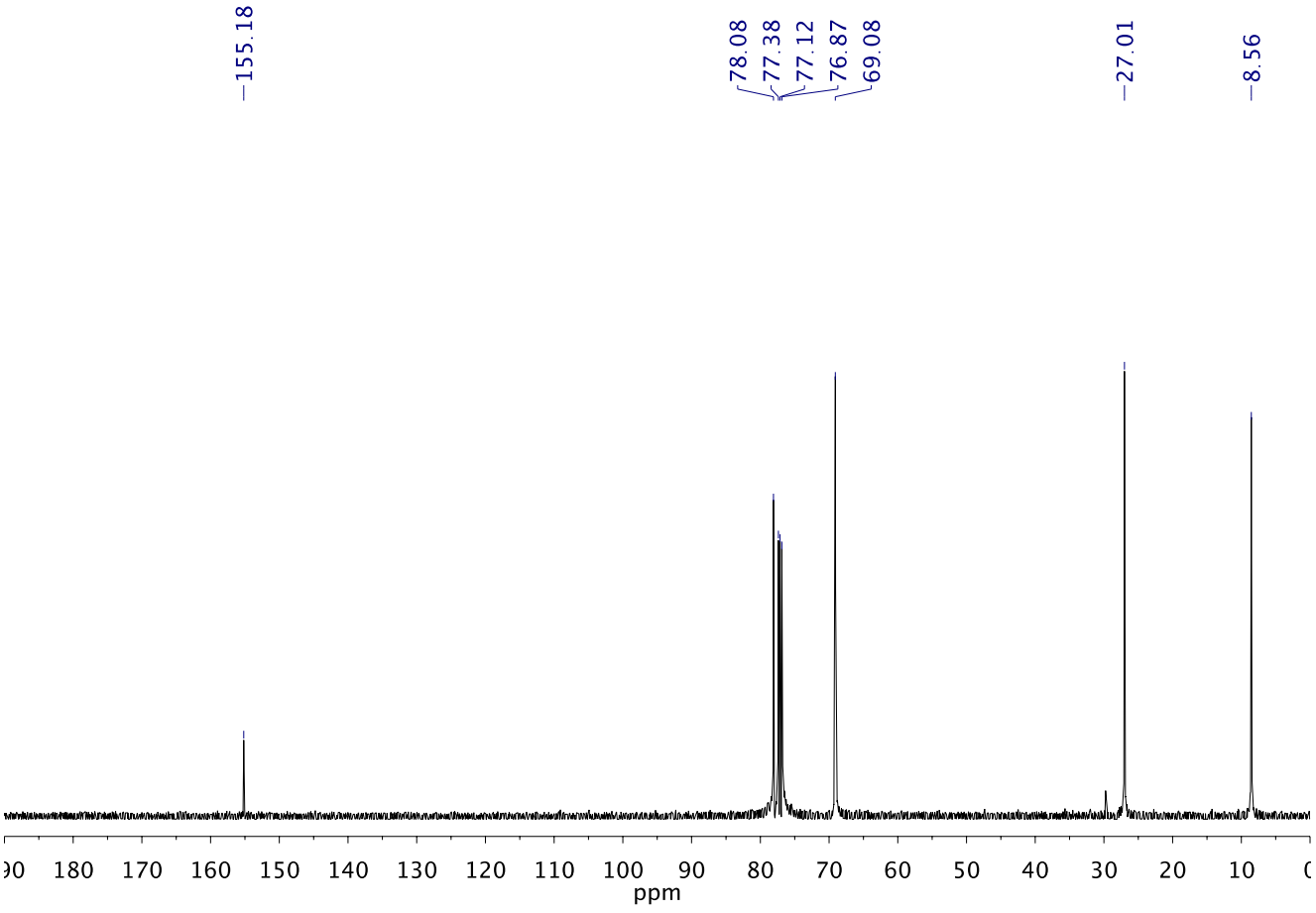
NMR Spectra for propylene carbonate **6b** in $CDCl_3$



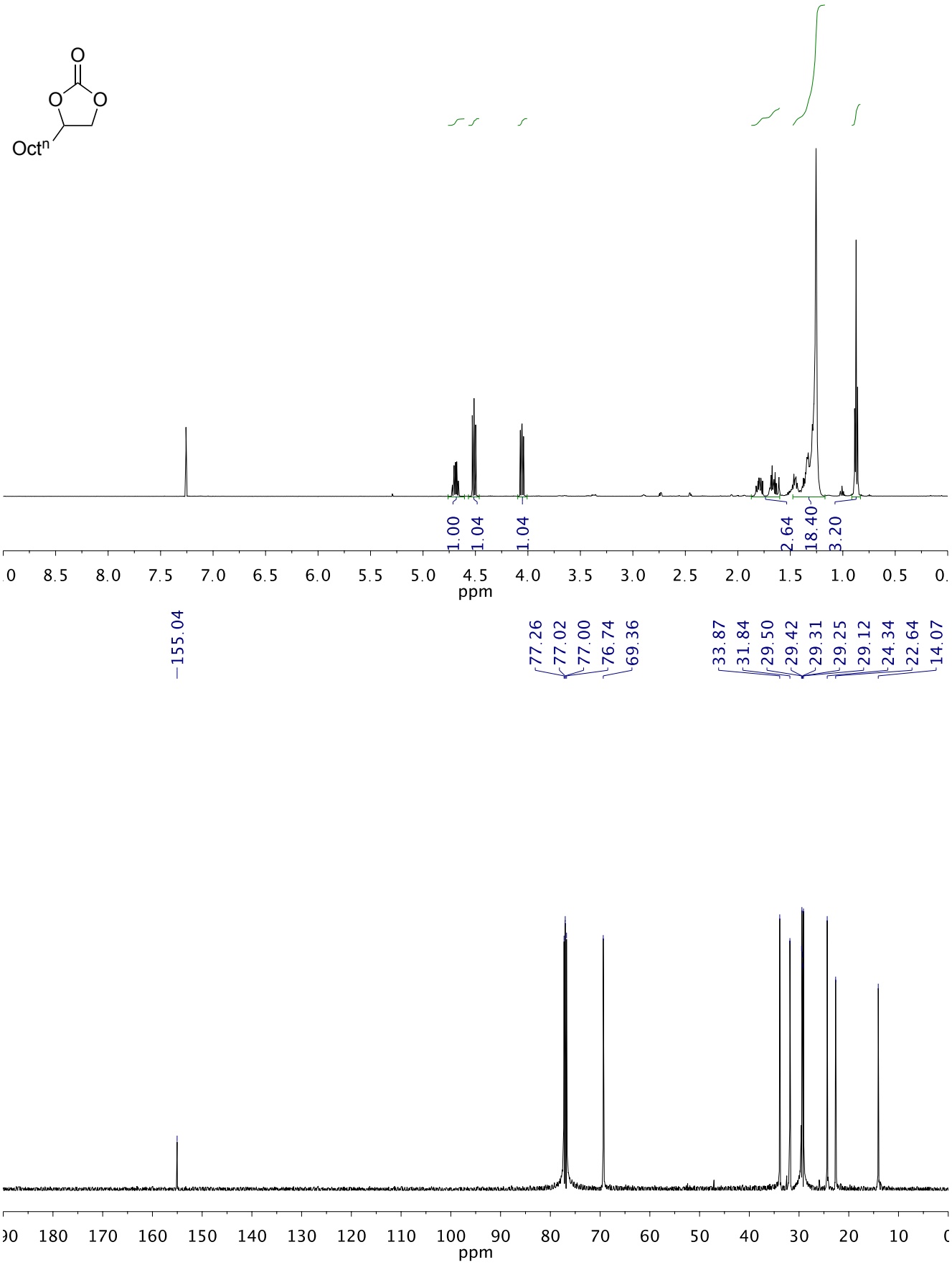


NMR Spectra for 1,2-butylene carbonate **6c** in $CDCl_3$

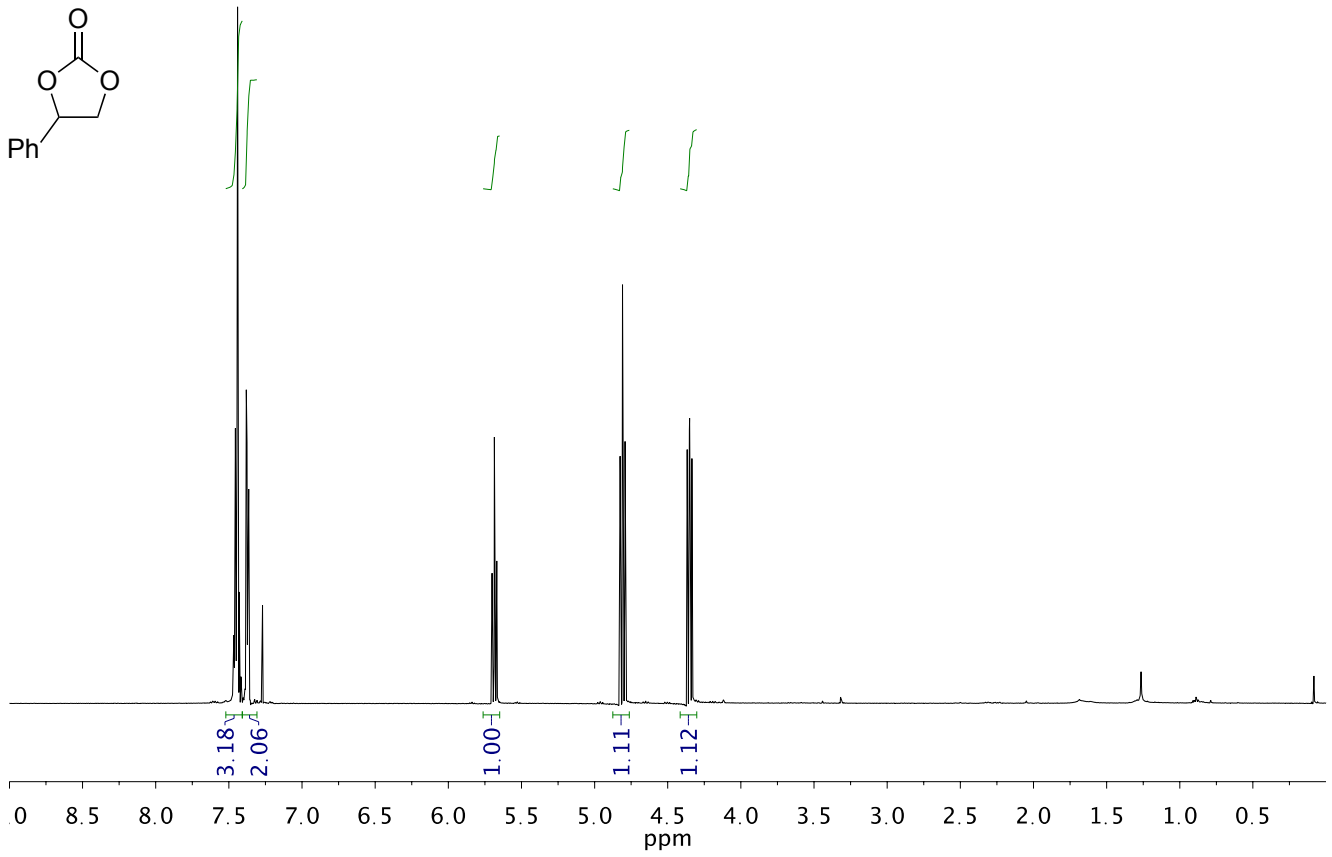


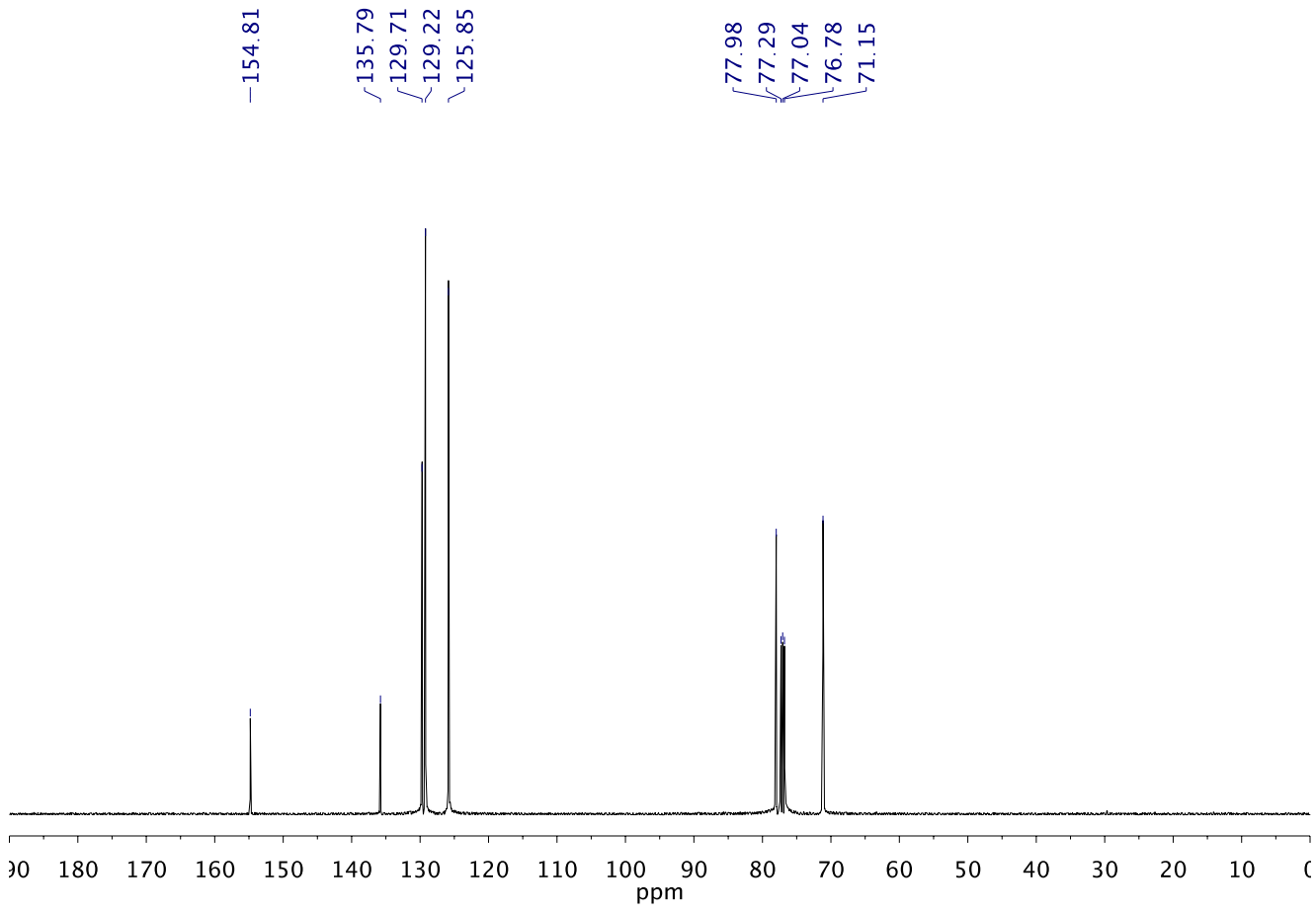


NMR Spectra for 1,2-decylene carbonate **6d** in $CDCl_3$

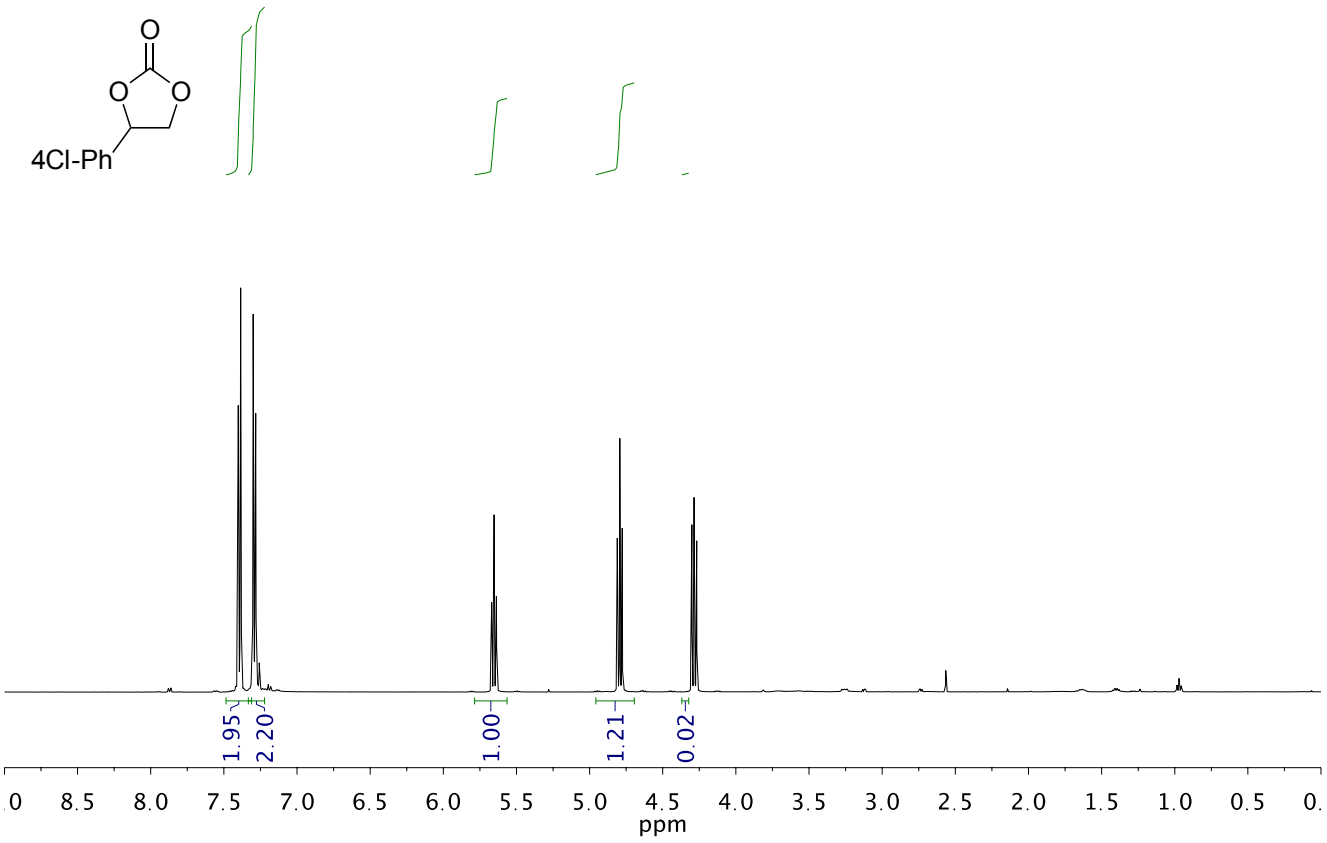


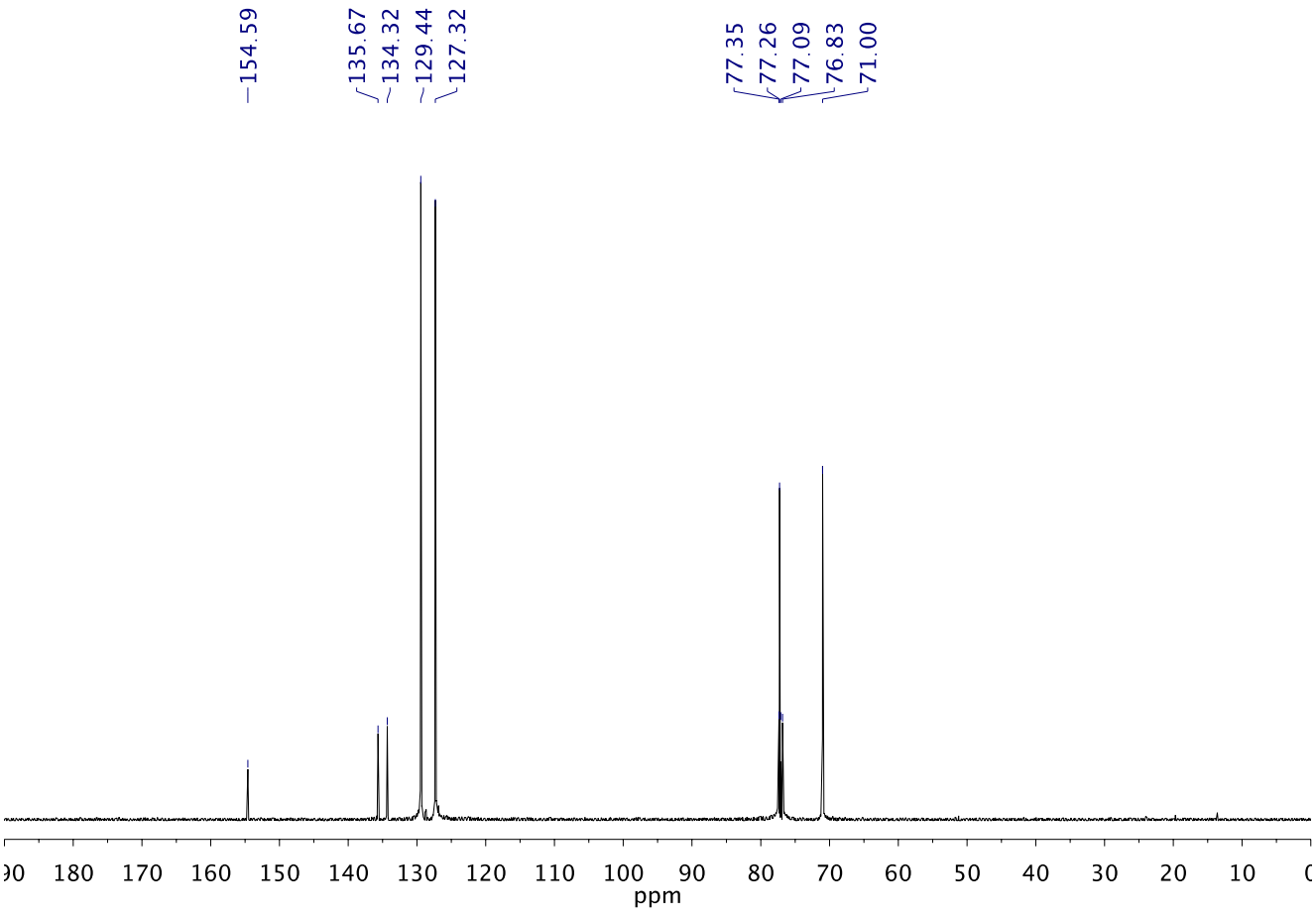
NMR Spectra for styrene carbonate **6e** in $CDCl_3$



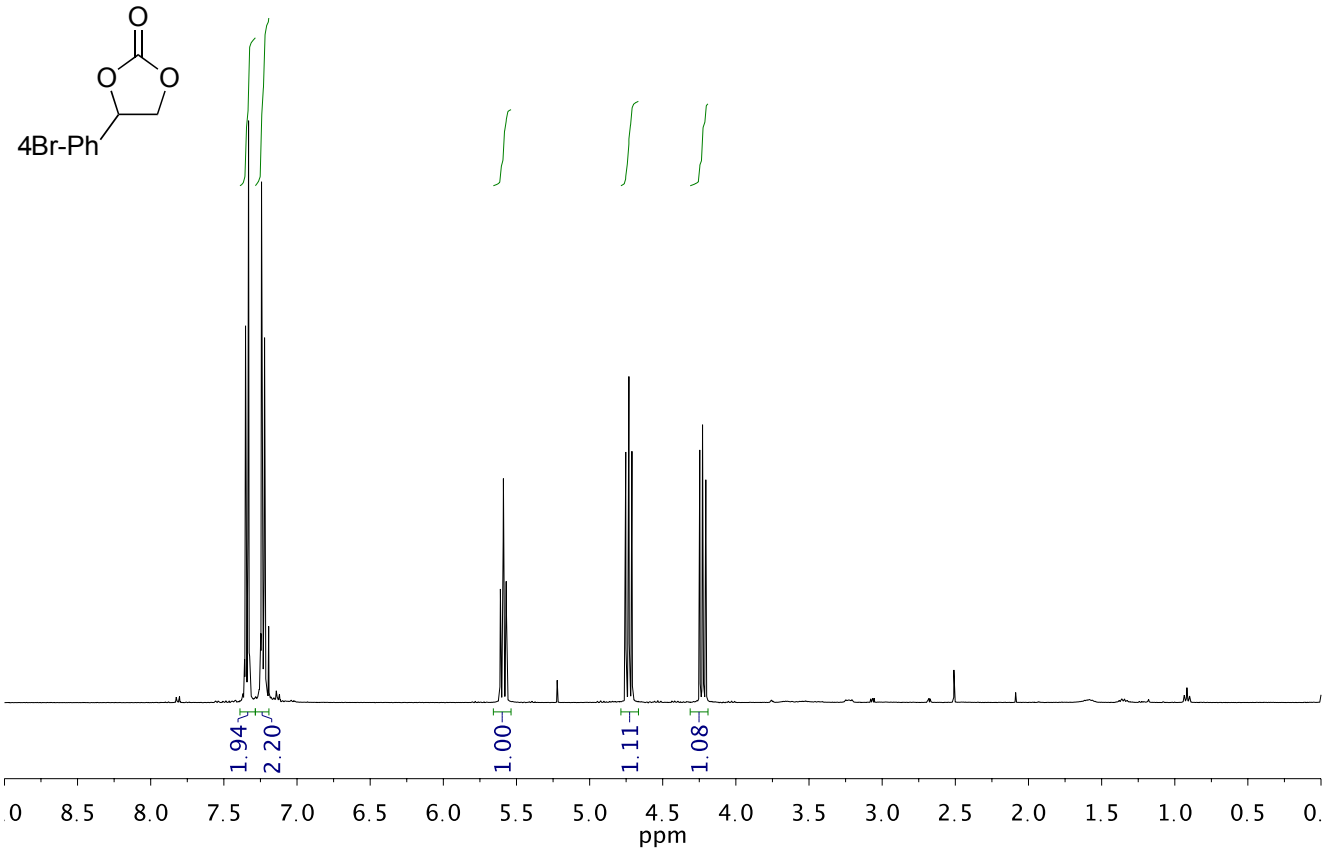


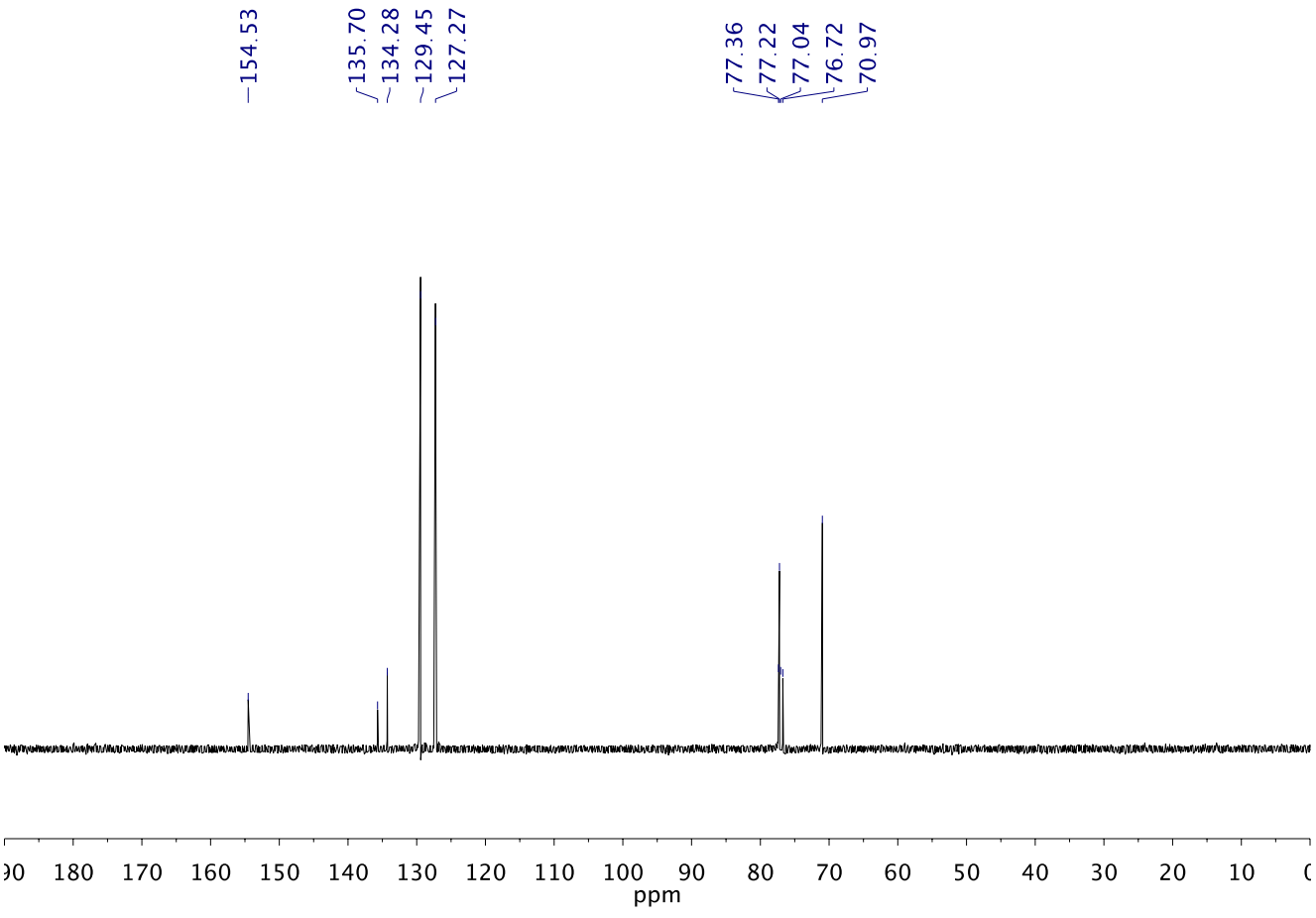
NMR Spectra for 4-chlorostyrene carbonate **6f** in $CDCl_3$



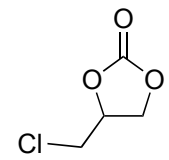


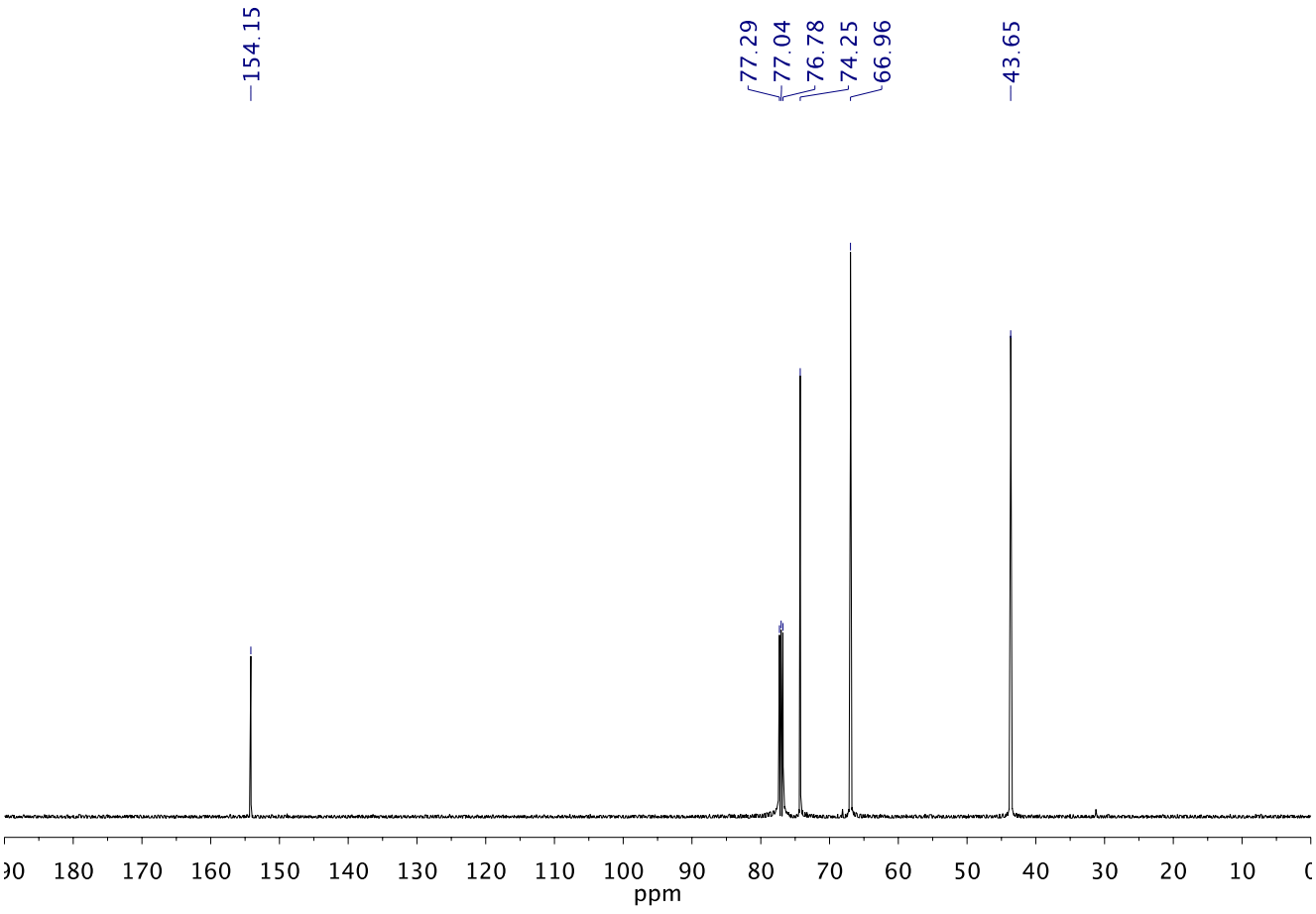
NMR Spectra for 4-bromostyrene carbonate **6g** in $CDCl_3$



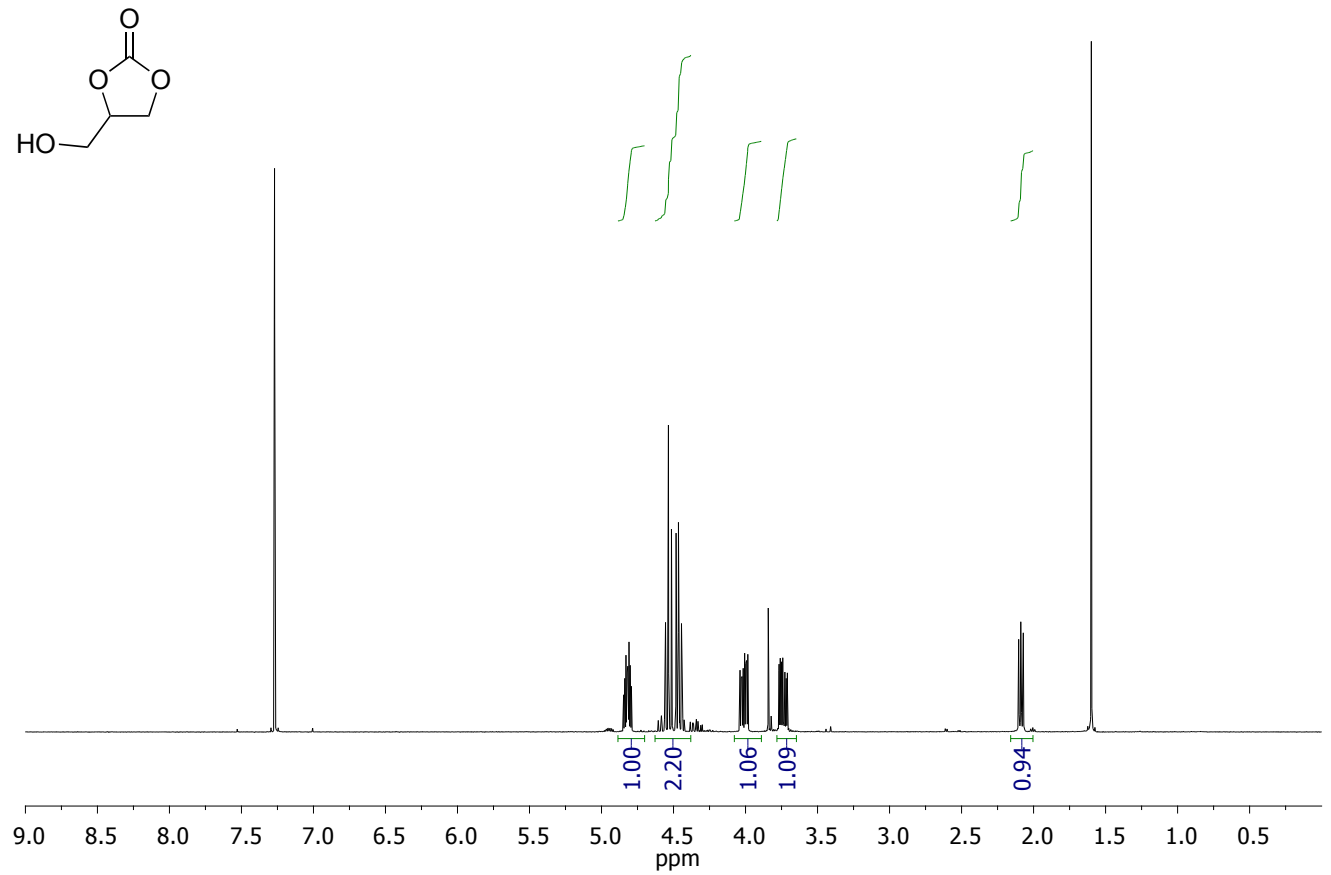


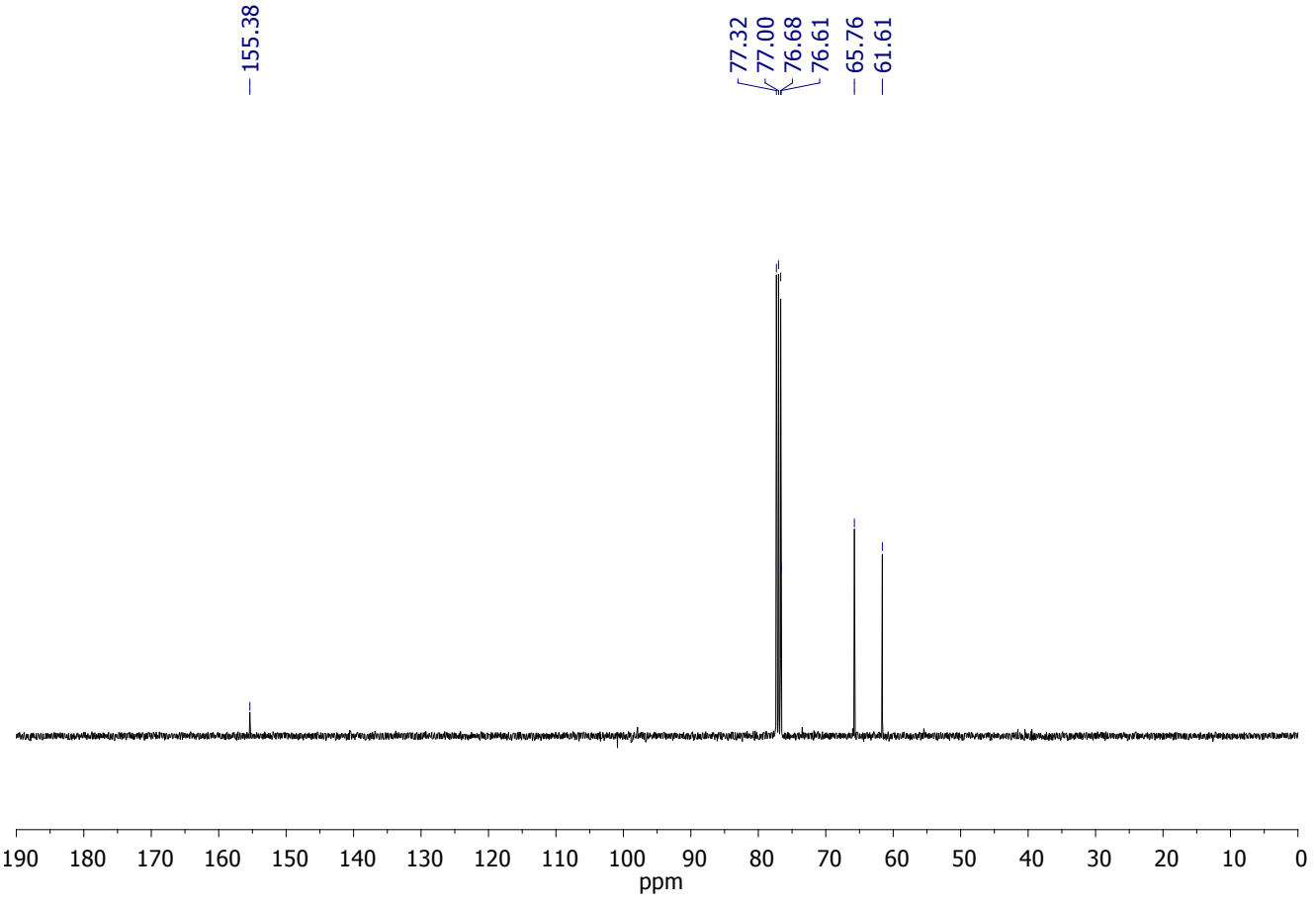
NMR Spectra for 3-chloropropylene carbonate **6h** in $CDCl_3$



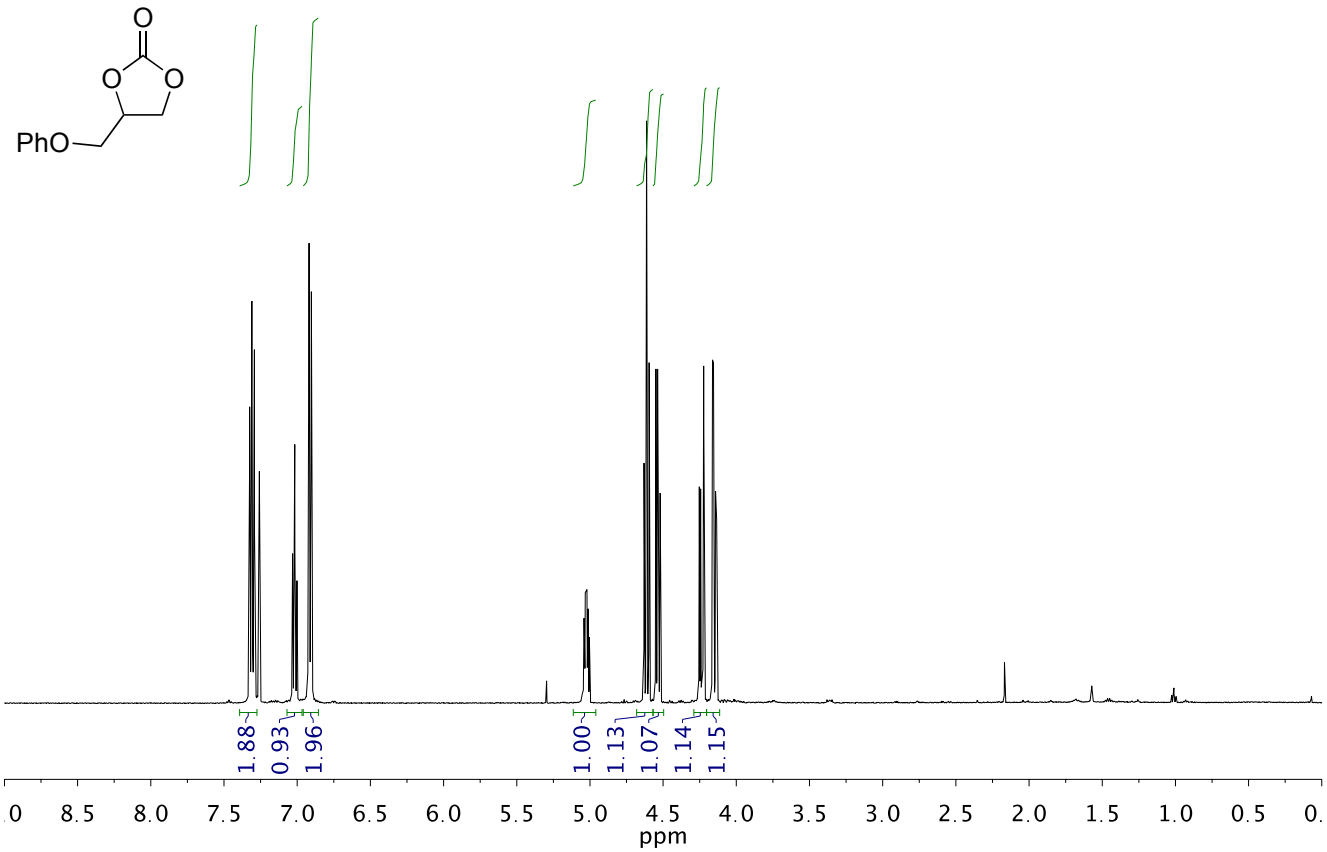


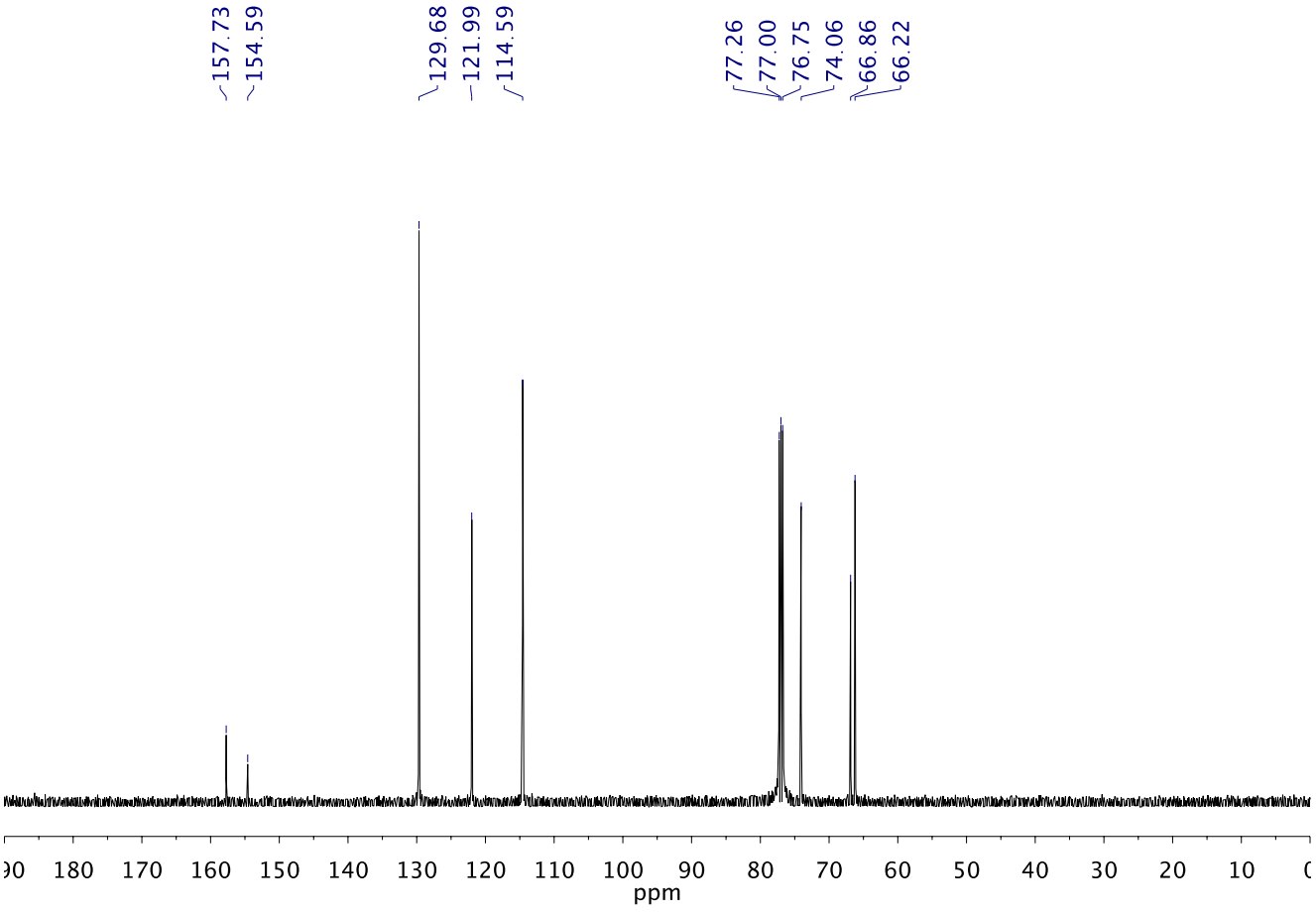
NMR Spectra for glycerol carbonate **6i** in $CDCl_3$



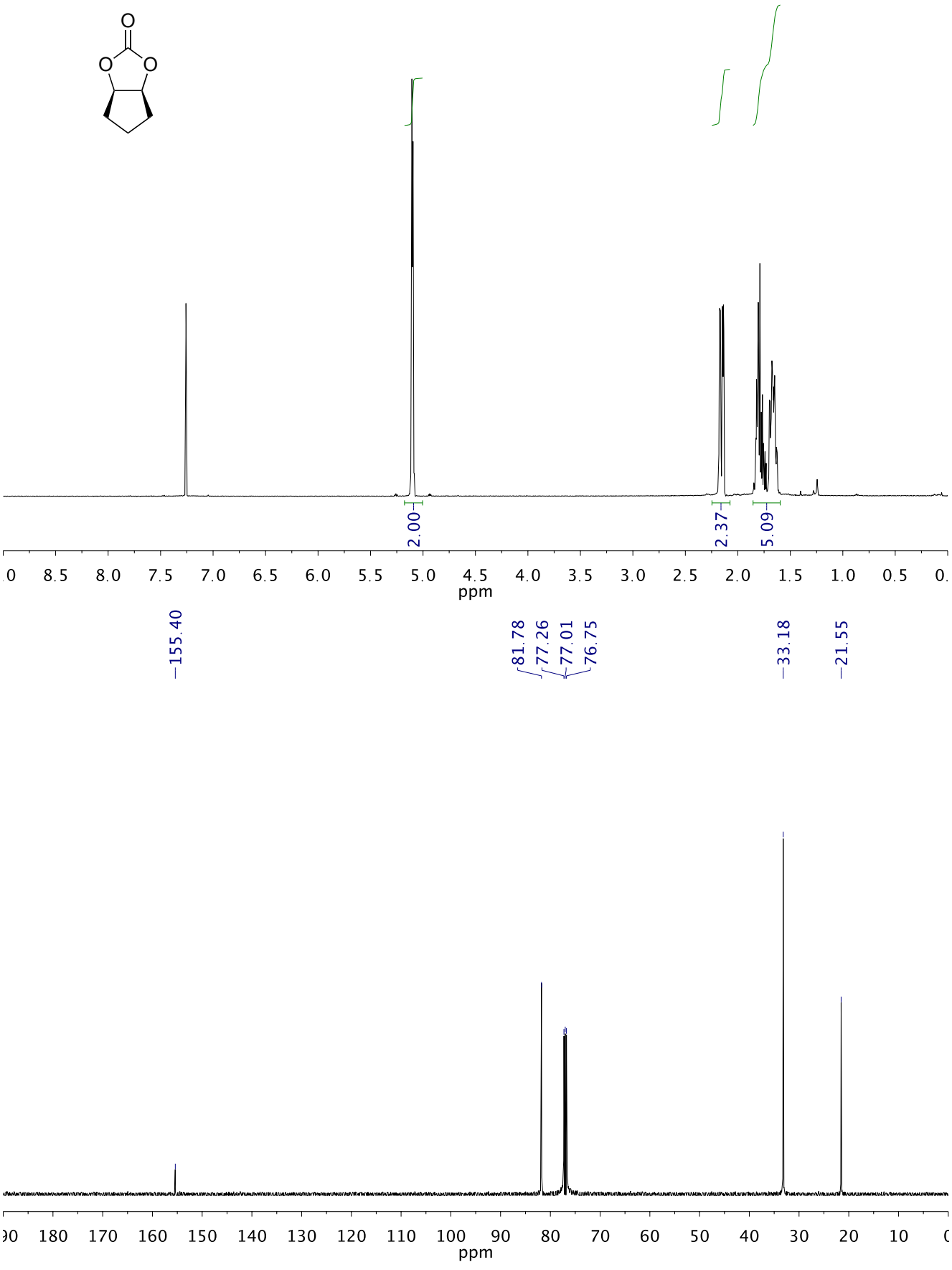


NMR Spectra for 3-phenoxypropylene carbonate **6j** in $CDCl_3$

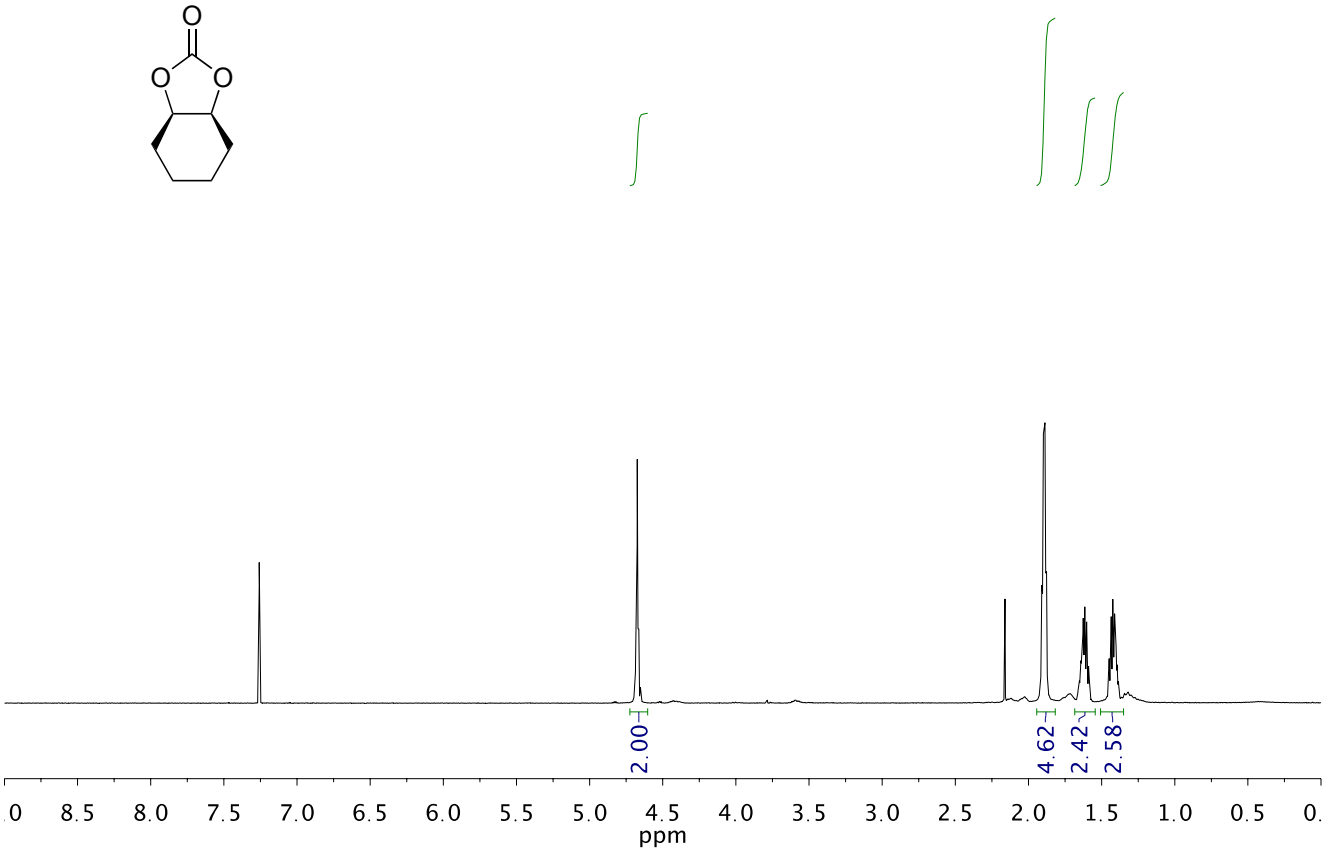


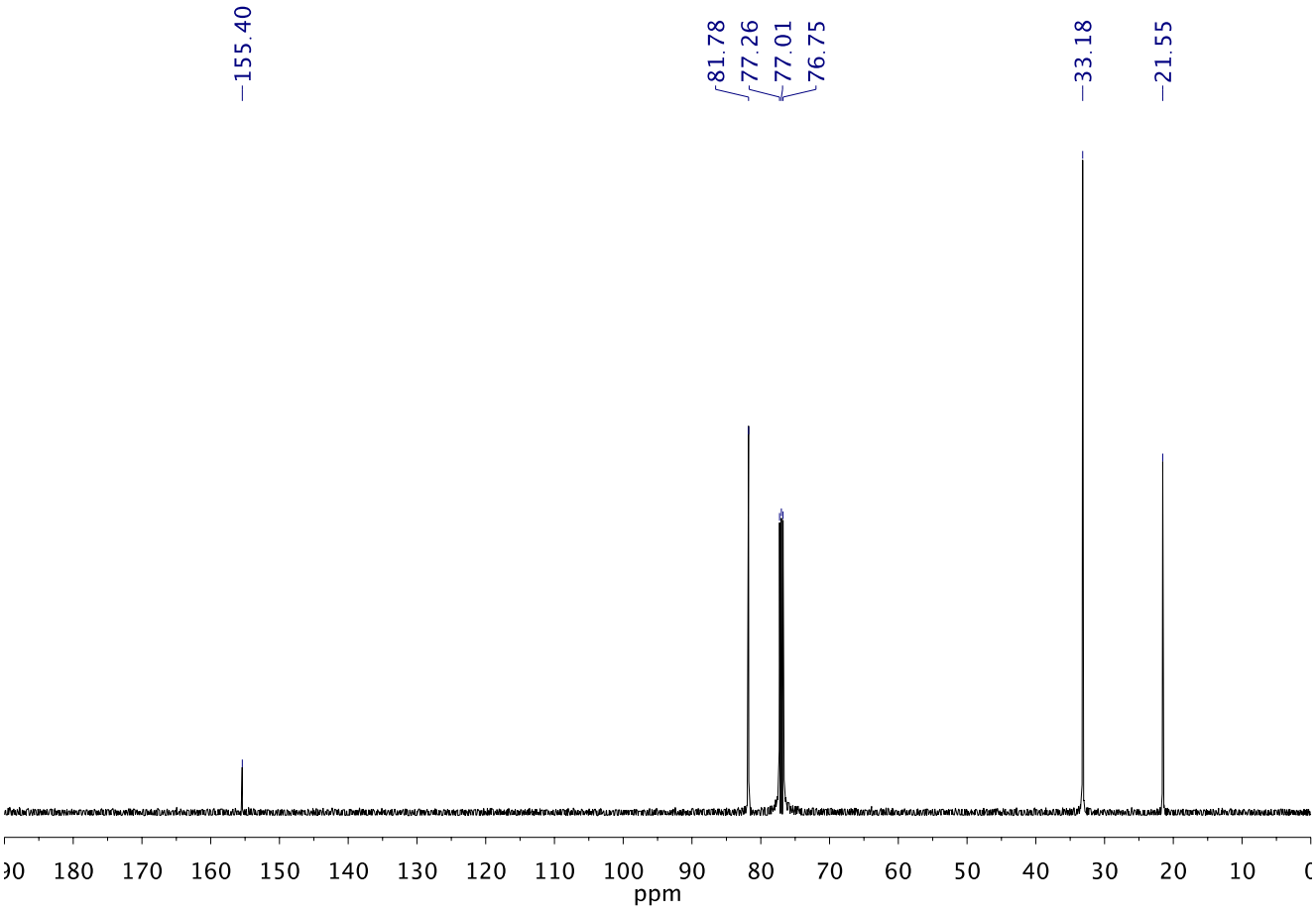


NMR Spectra for *cis*-cyclopentene carbonate **11a** in $CDCl_3$

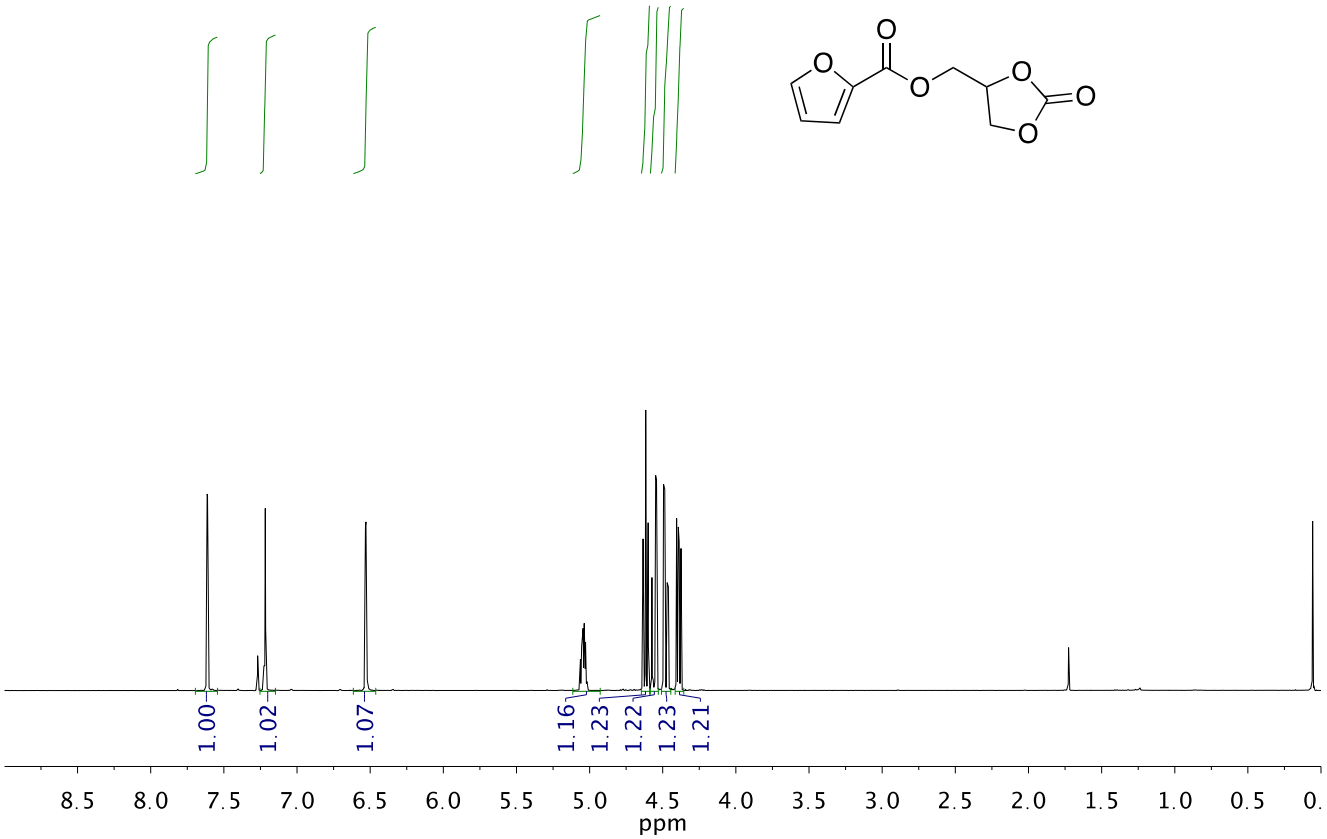


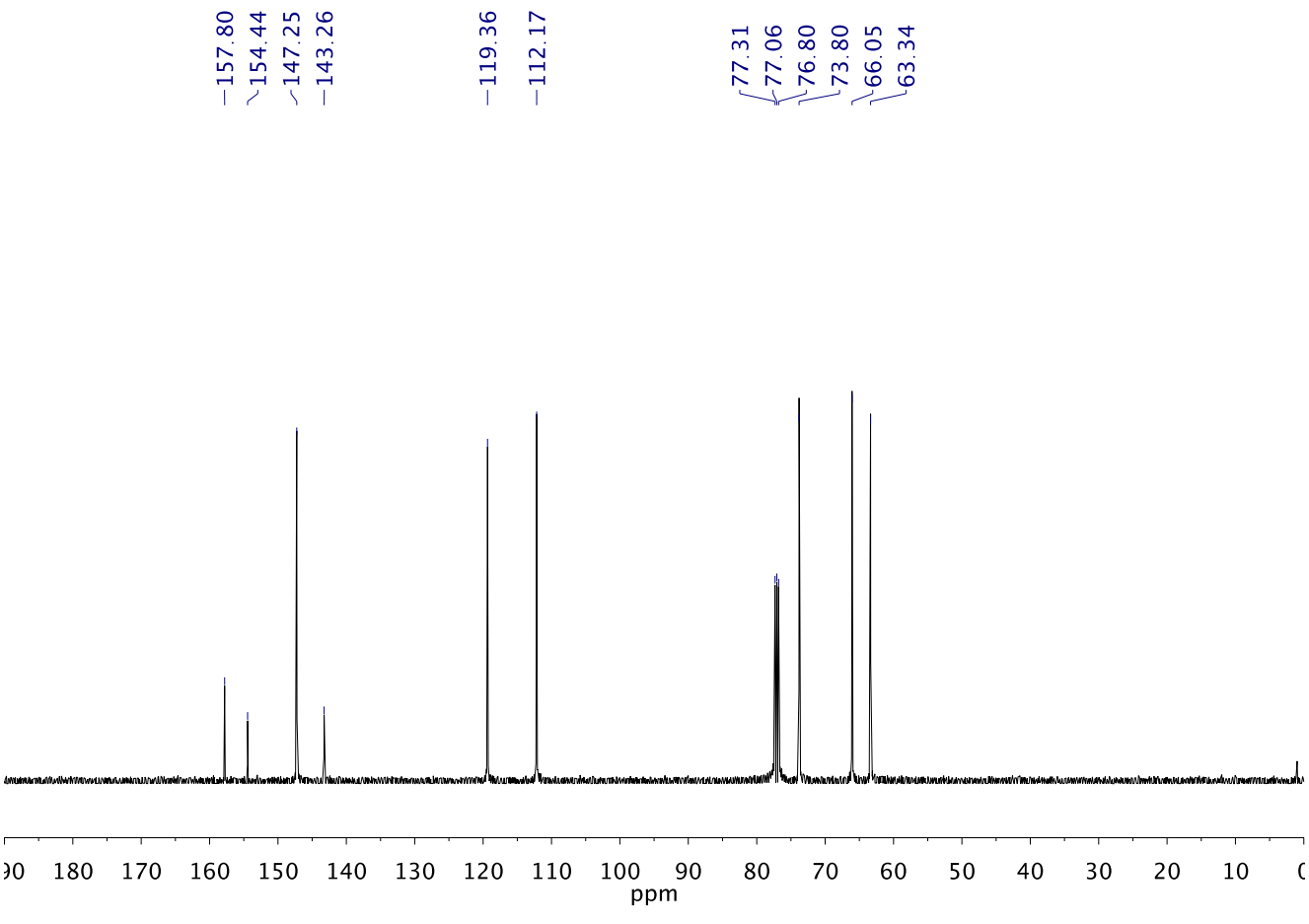
NMR Spectra for *cis*-cyclohexene carbonate **11b** in $CDCl_3$



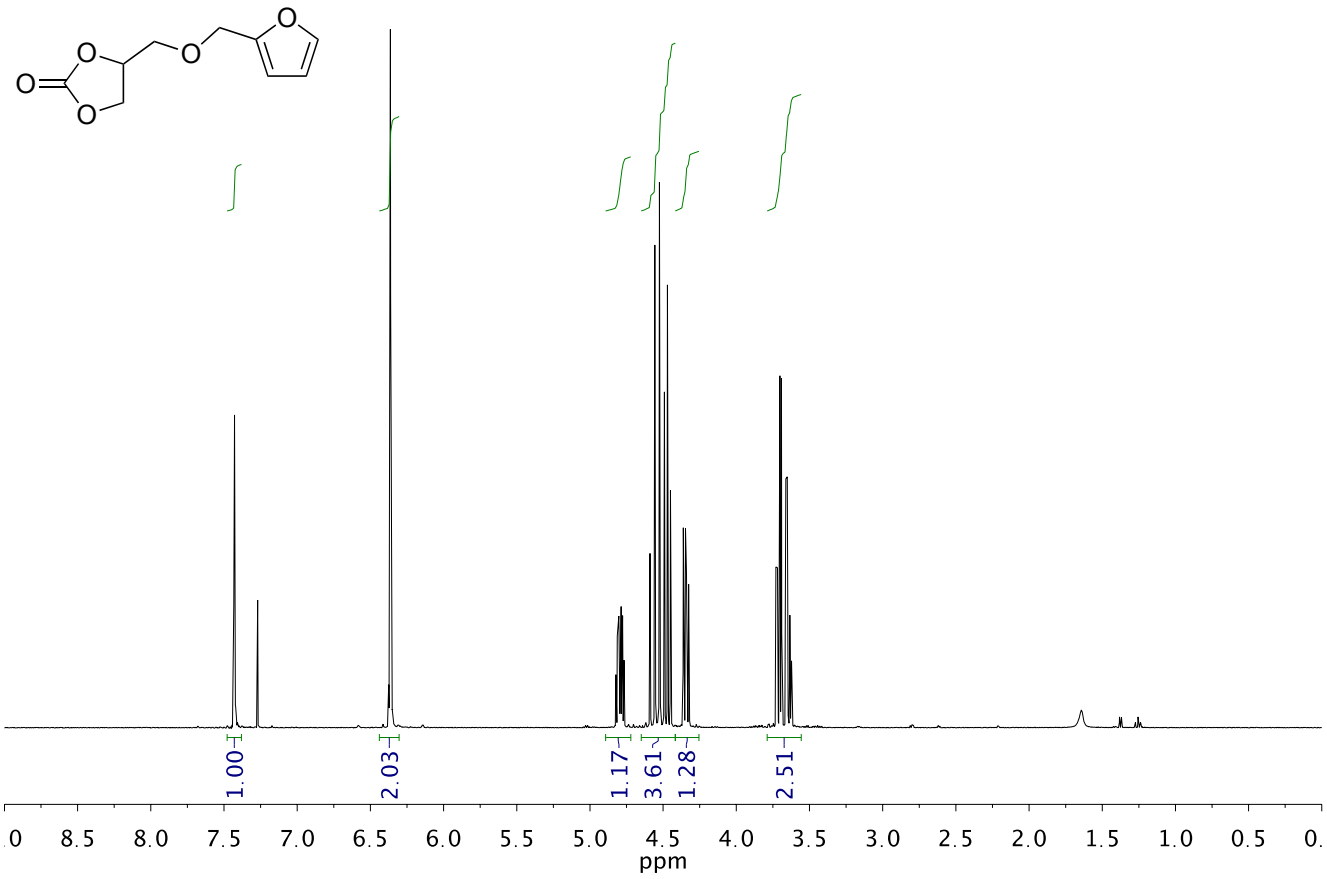


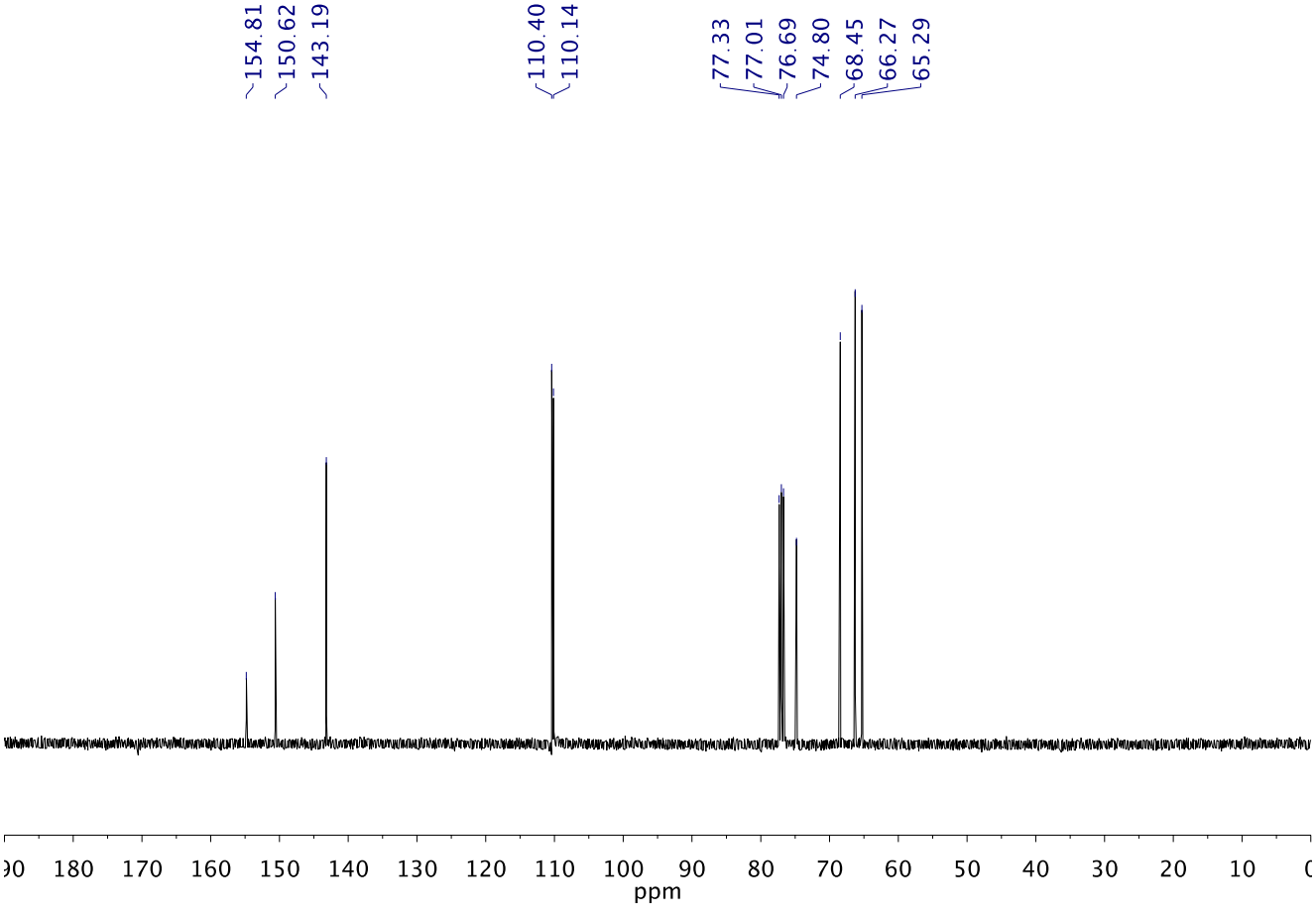
NMR Spectra for (2-oxo-1,3-dioxolan-4-yl)methyl furan-2-carboxylate **11c** in $CDCl_3$



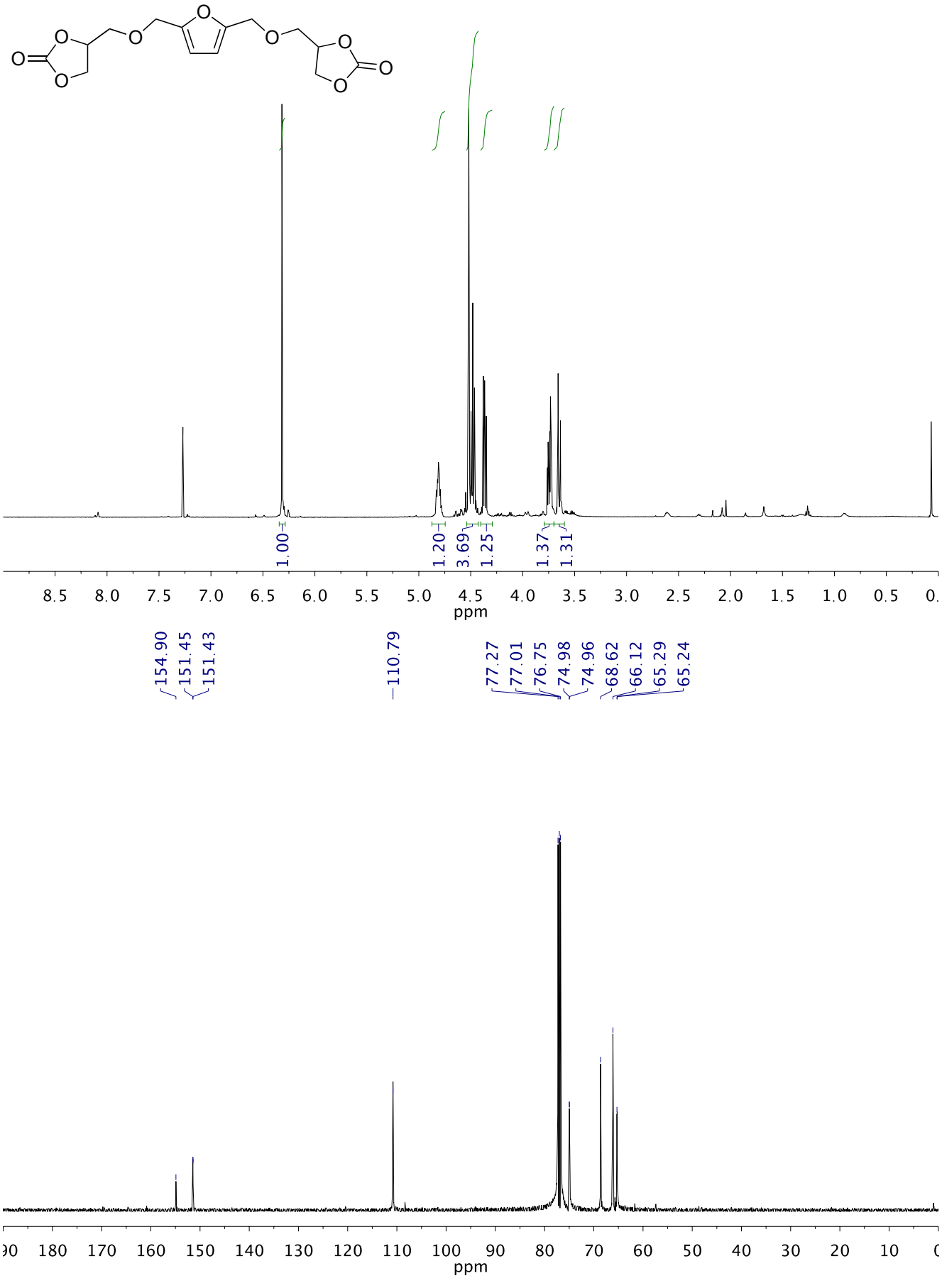


NMR Spectra for 4-(furan-2-ylmethoxy)-1,3-dioxolan-2-one **11d** in $CDCl_3$

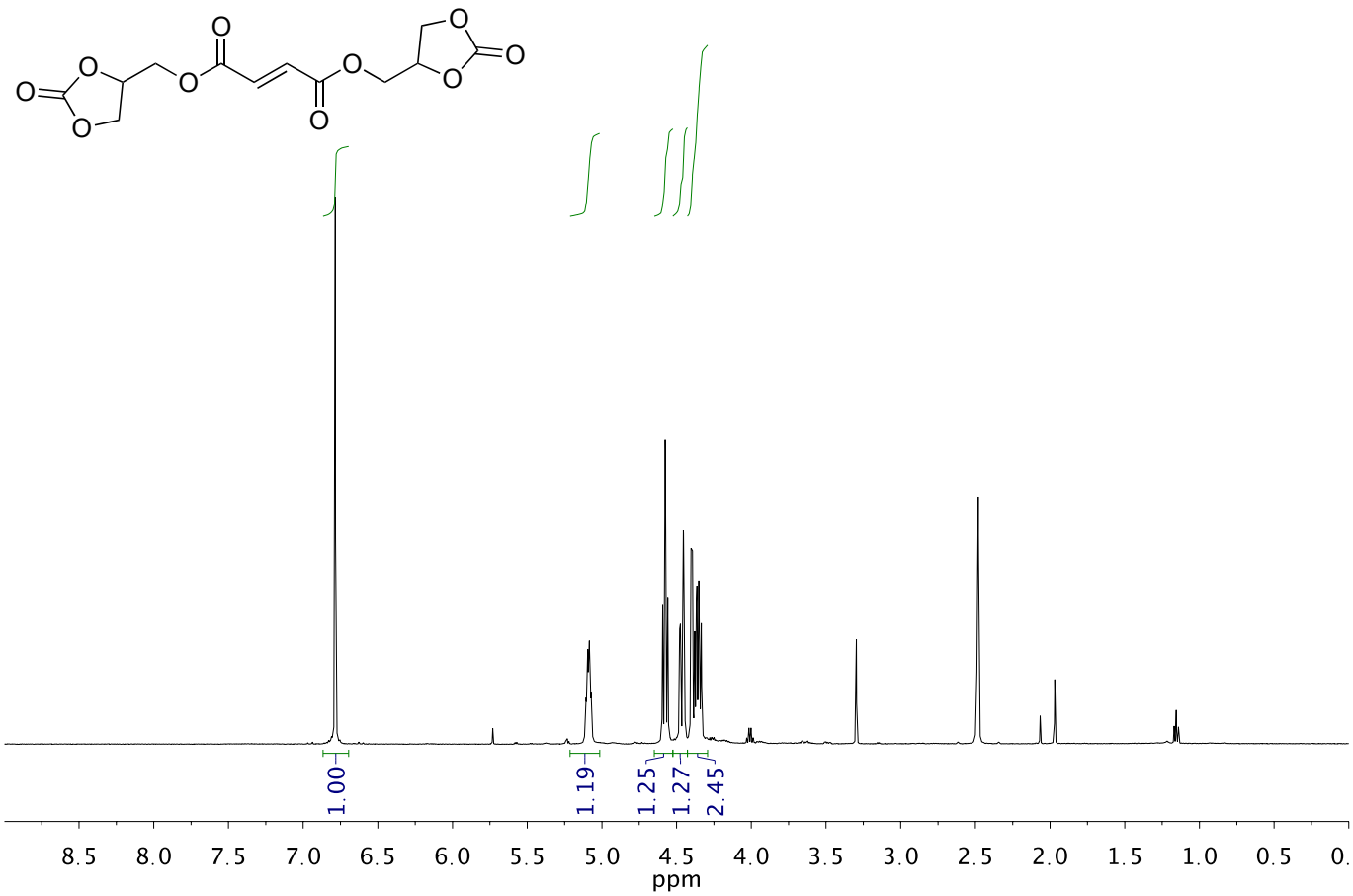


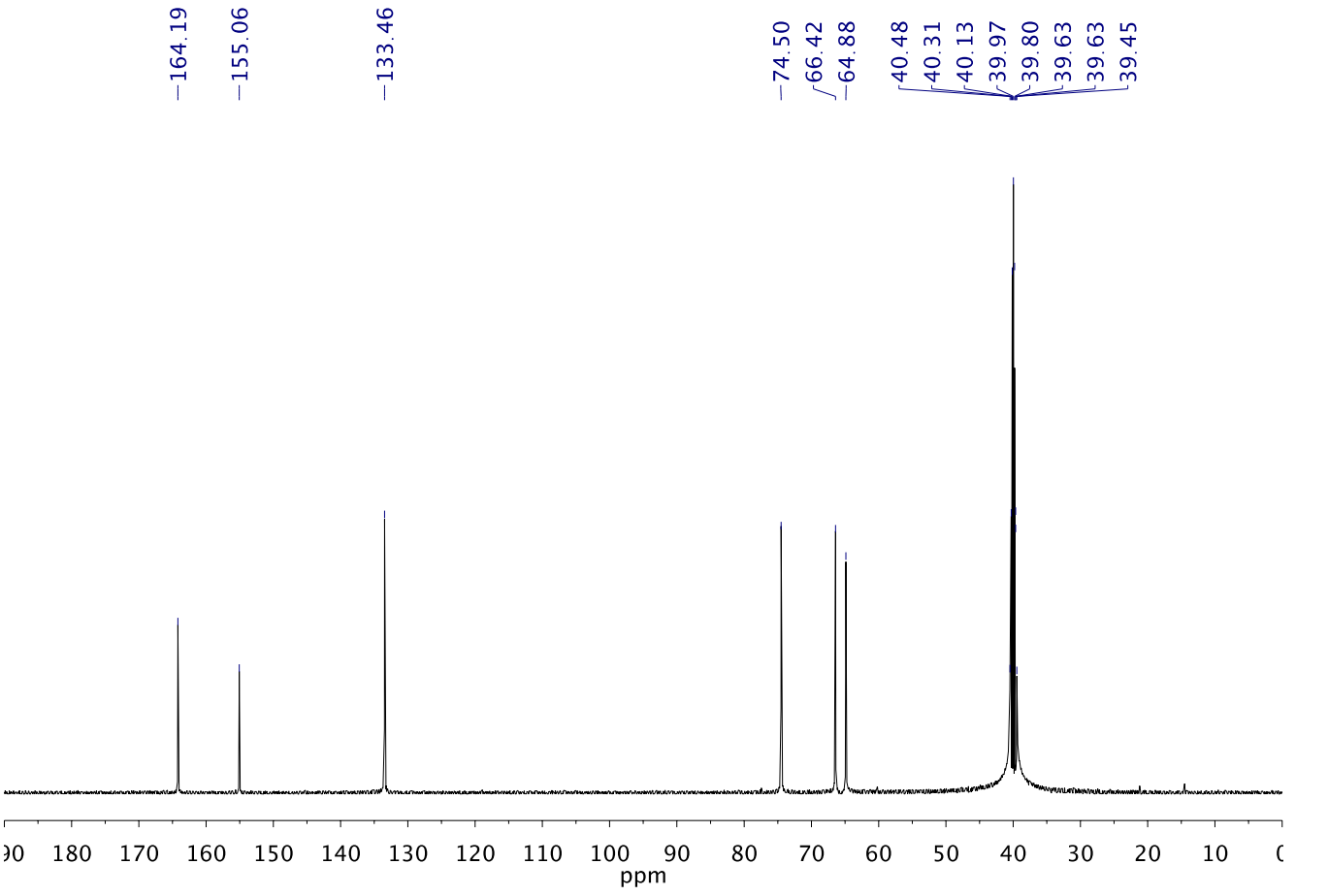


NMR Spectra for 4,4'-((furan-2,5diylbis(methylene))bis(oxy))bis(1,3-dioxolan-2-one) **11e** in $CDCl_3$

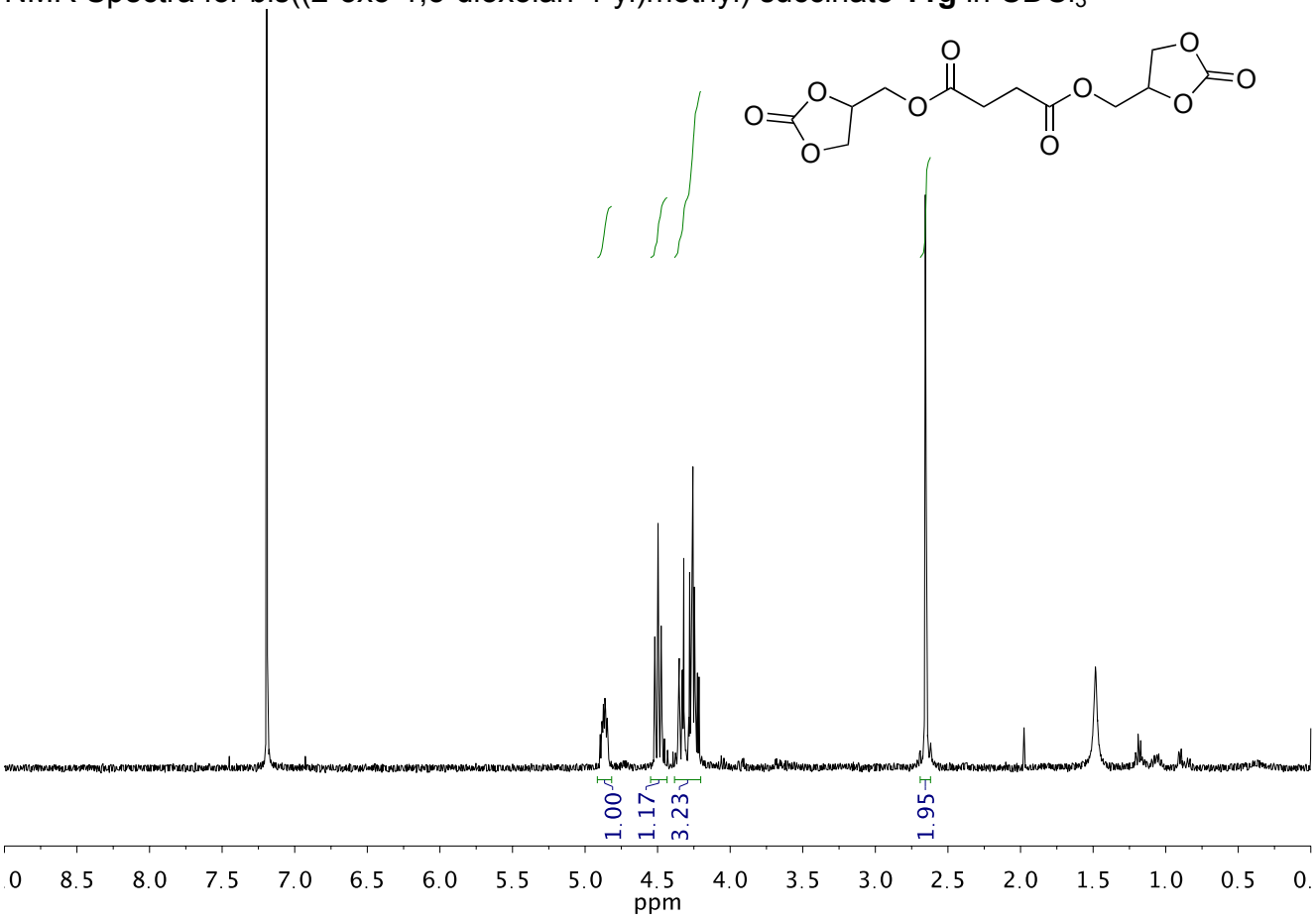


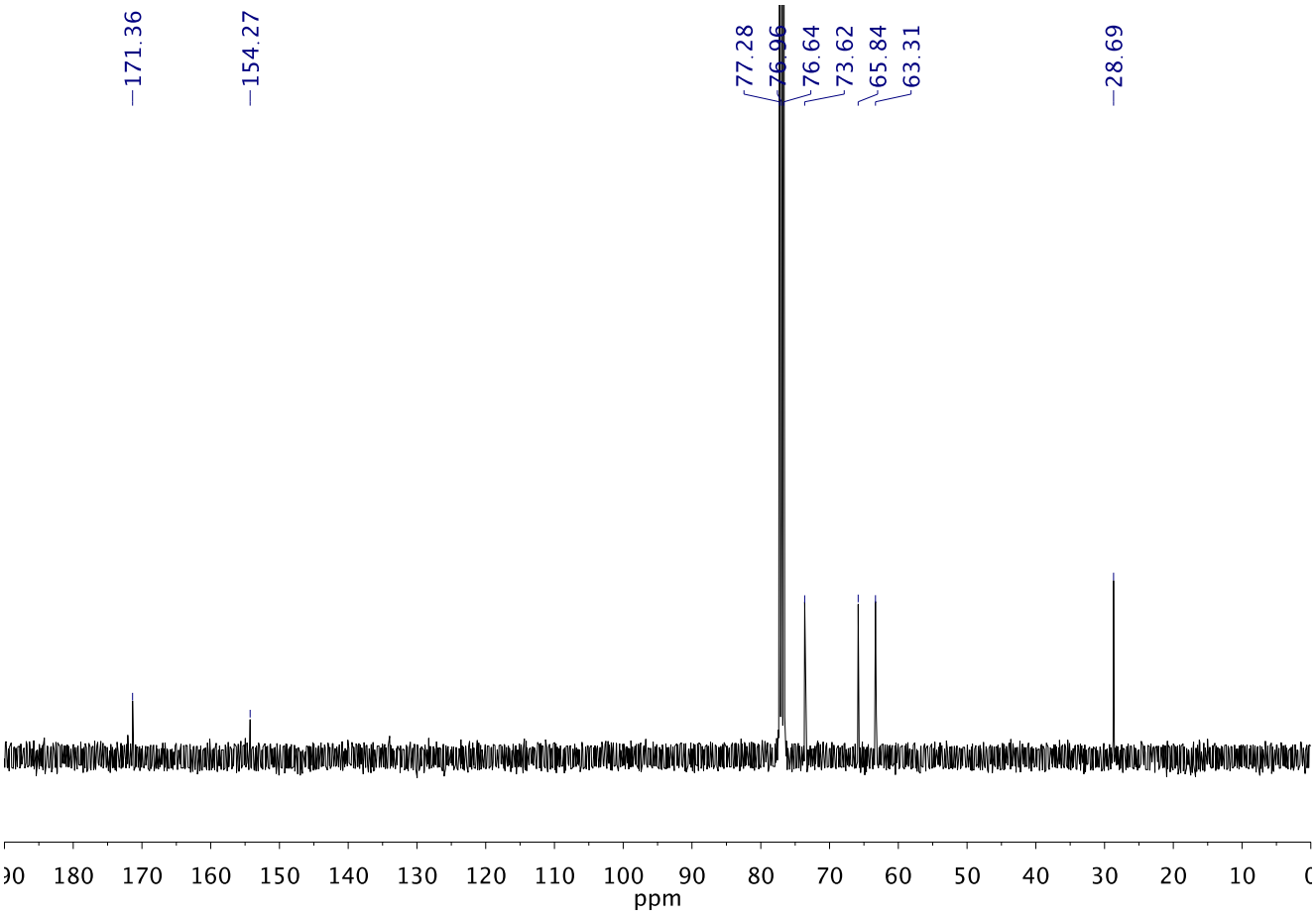
NMR Spectra for bis((2-oxo-1,3-dioxolan-4-yl)methyl) fumarate **11f** in DMSO-d_6



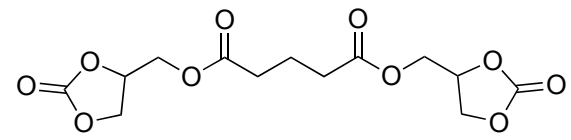


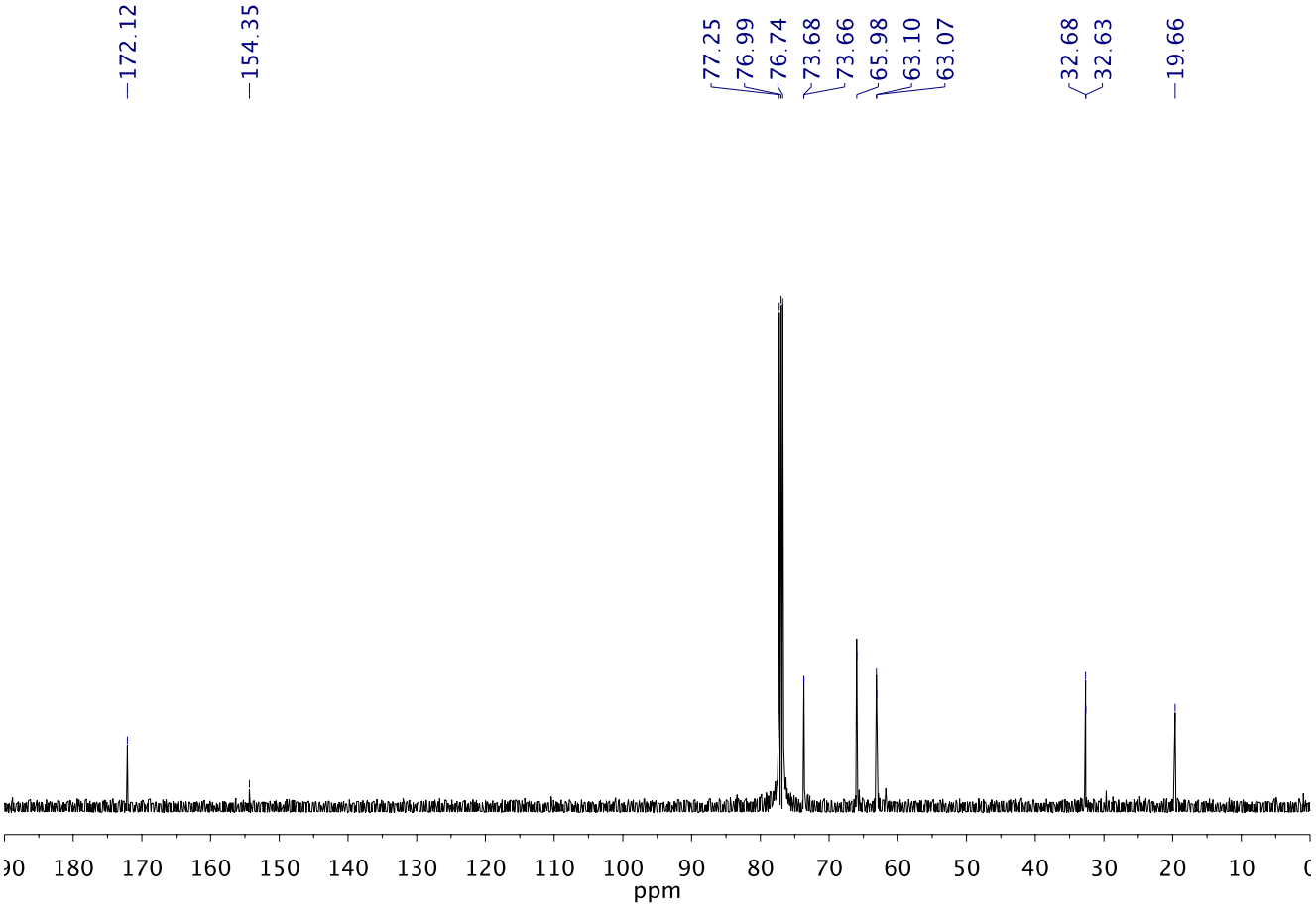
NMR Spectra for bis((2-oxo-1,3-dioxolan-4-yl)methyl) succinate **11g** in $CDCl_3$



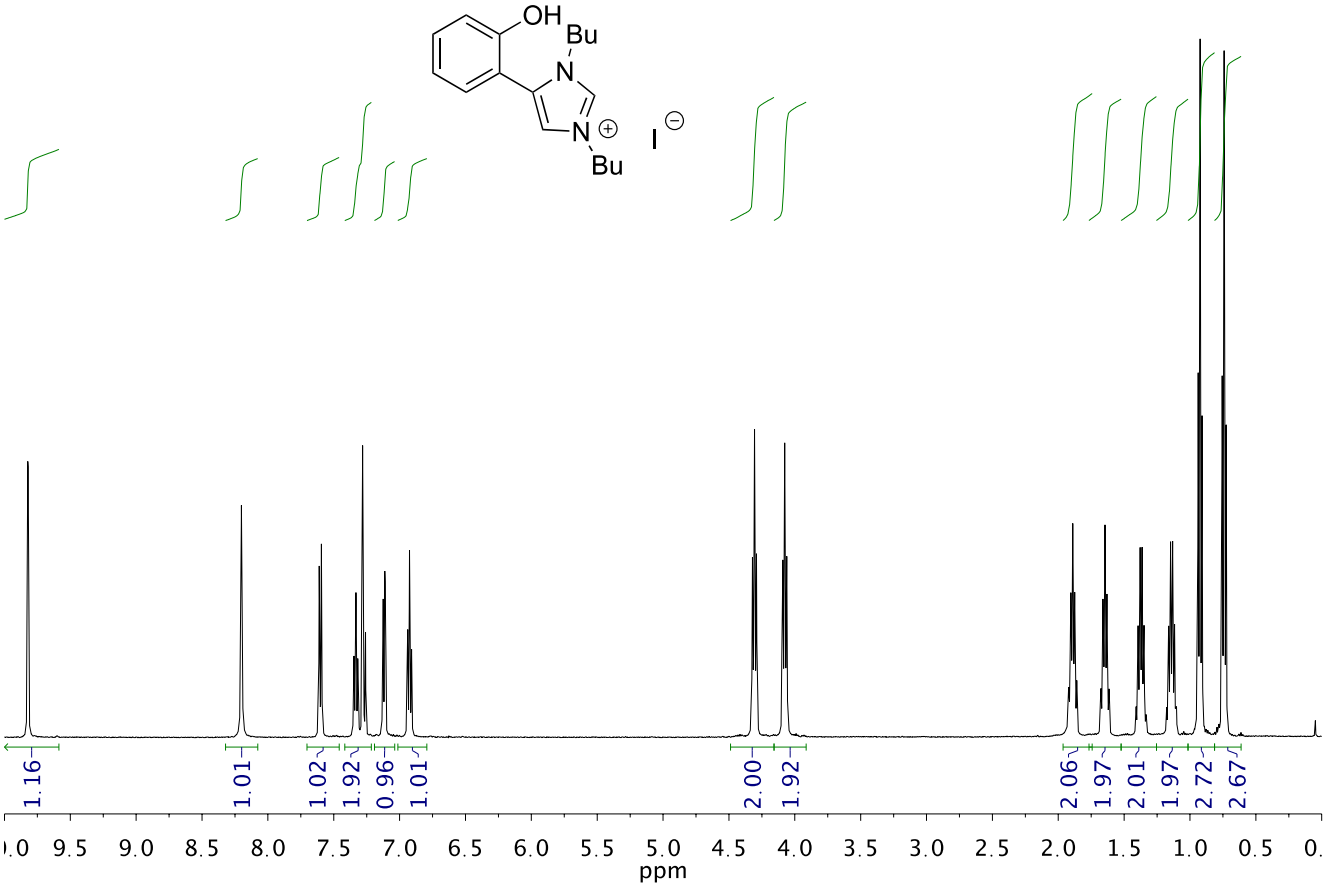


NMR Spectra for bis((2-oxo-1,3-dioxolan-4-yl)methyl) glutarate **11h** in $CDCl_3$

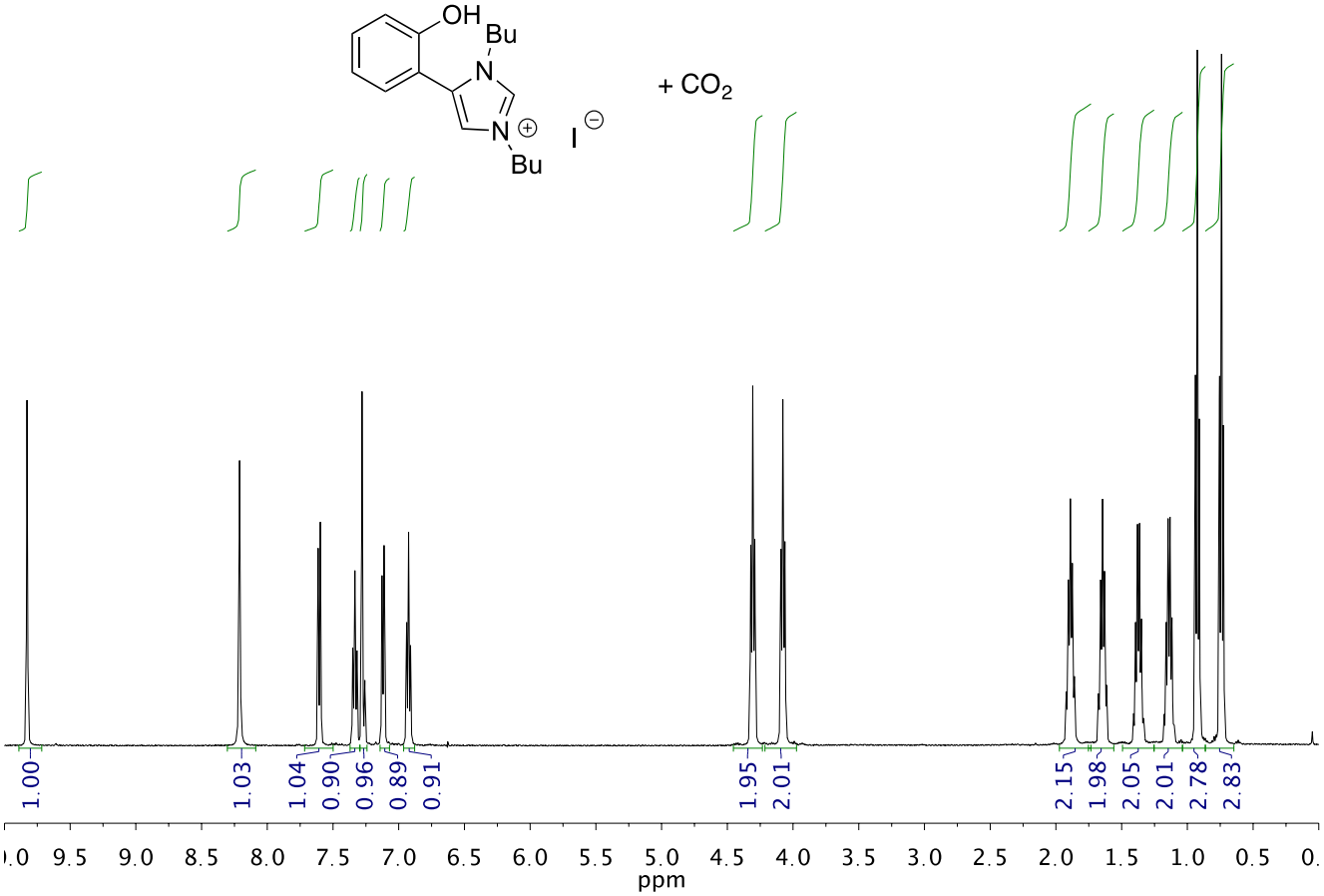




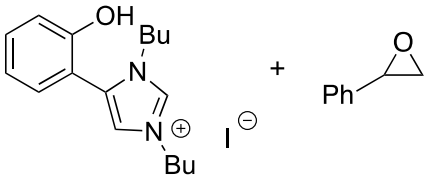
^{1}H-NMR spectrum for compound **9** in $CDCl_3$

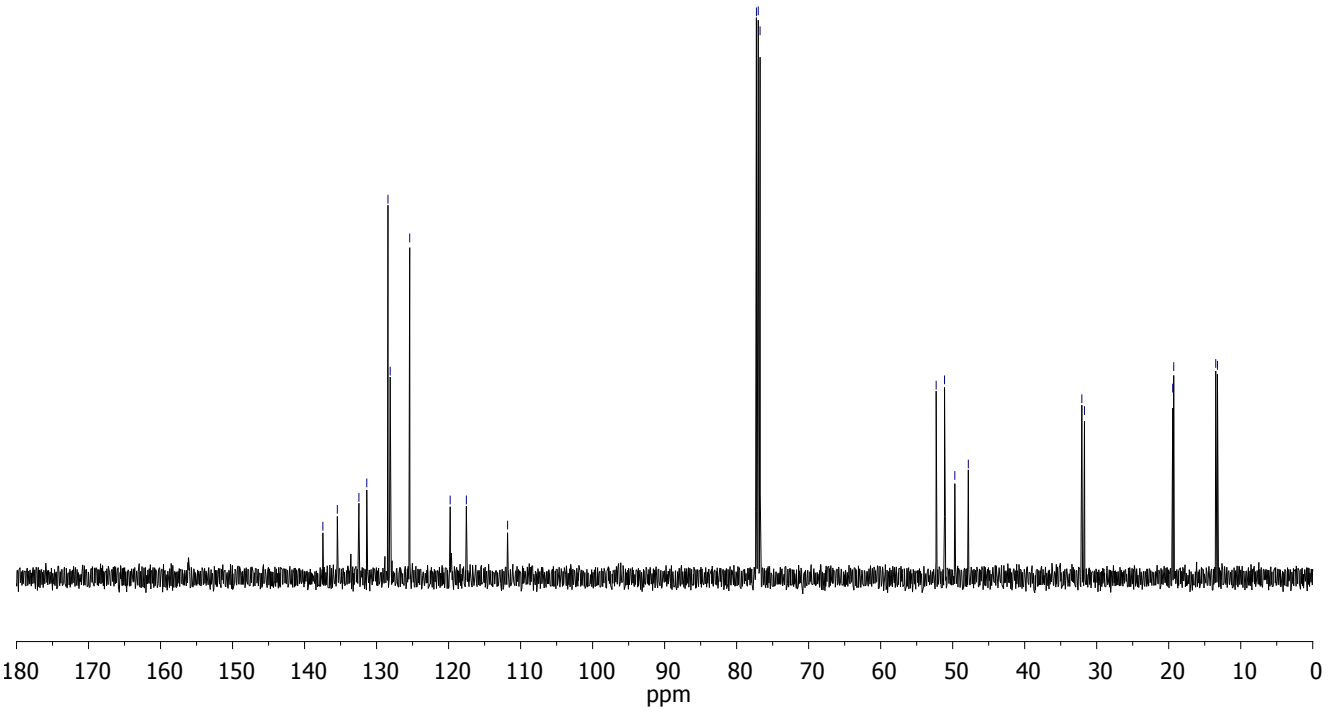


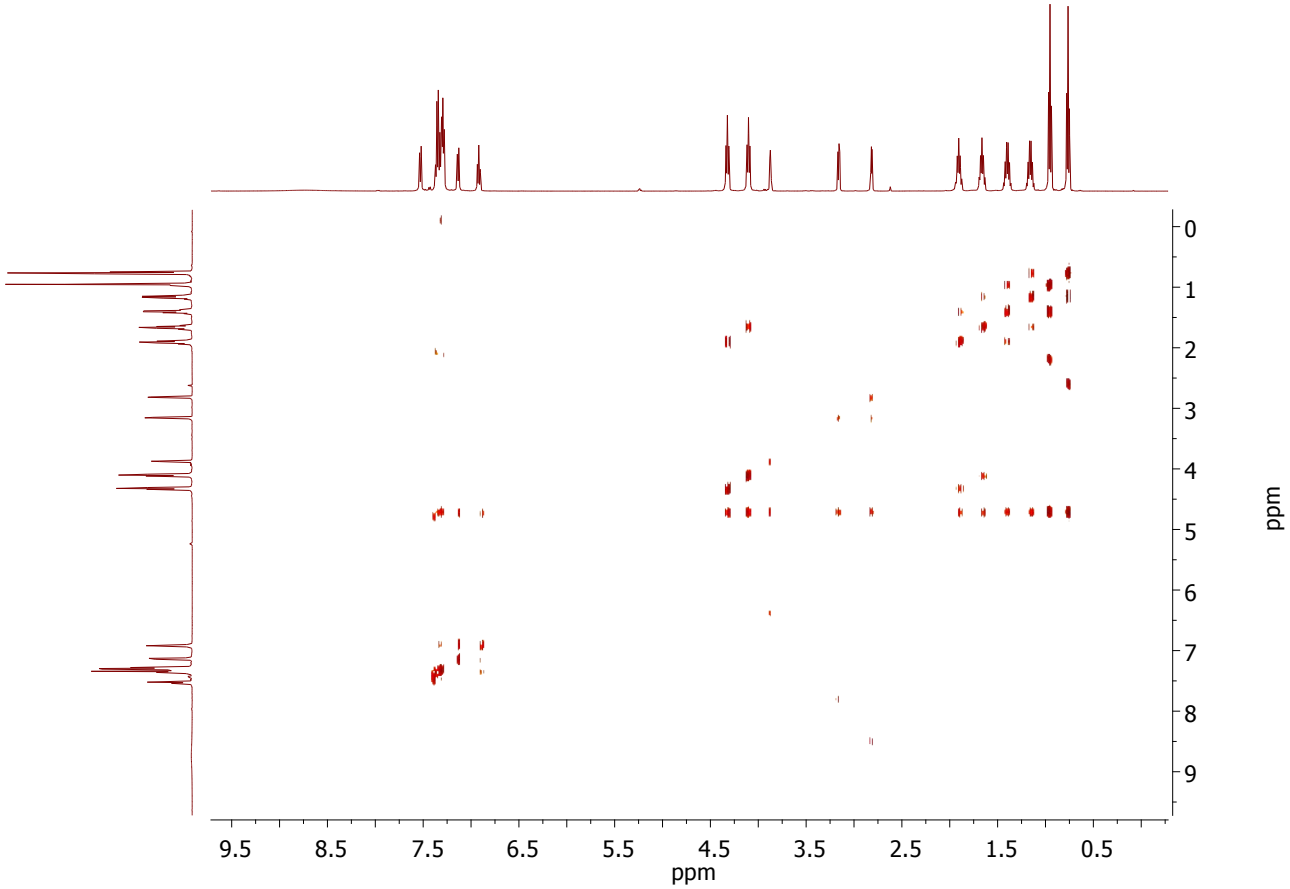
^{1}H-NMR spectrum for compound **9** + CO_2 at 80 °C and t = 24h in $CDCl_3$



NMR spectra for compound **9** + epoxide **5e** at r.t. and t = 0h in $CDCl_3$



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4
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6
7
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7.5
6.5
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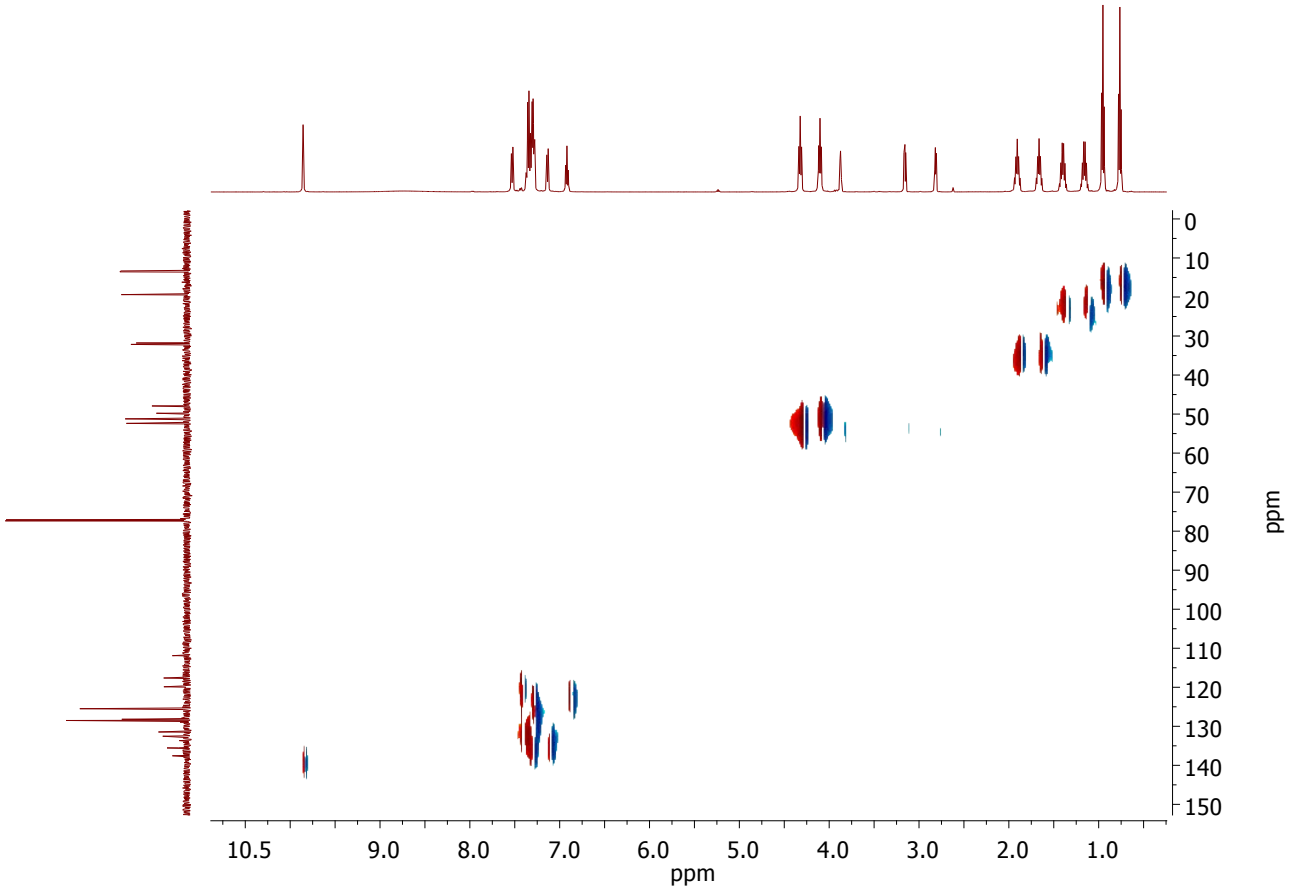
3.5
2.5
1.5
0.5
ppm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30
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90
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110
120
130
140
150
ppm
10.5
9.0
8.0
7.0
6.0
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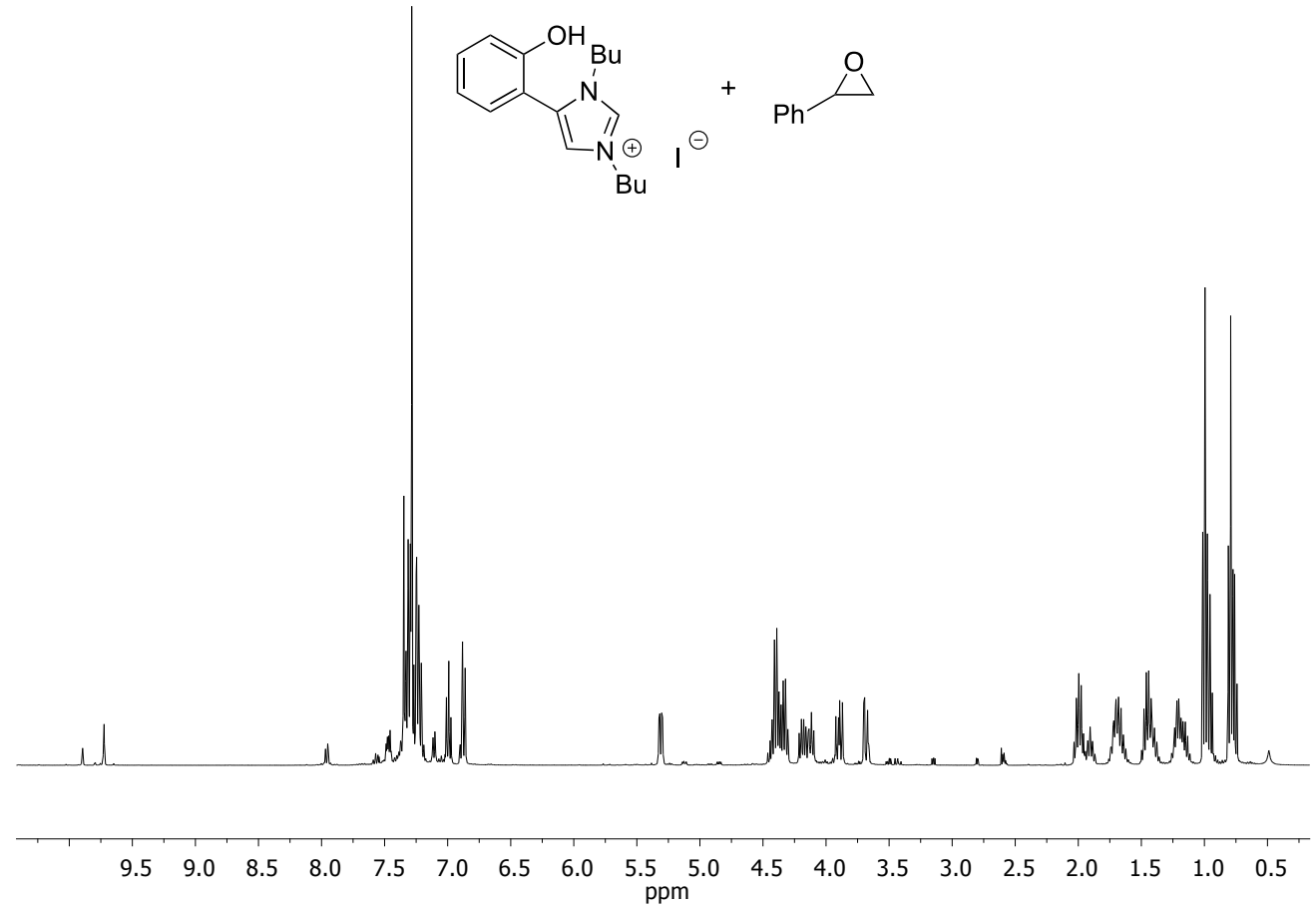
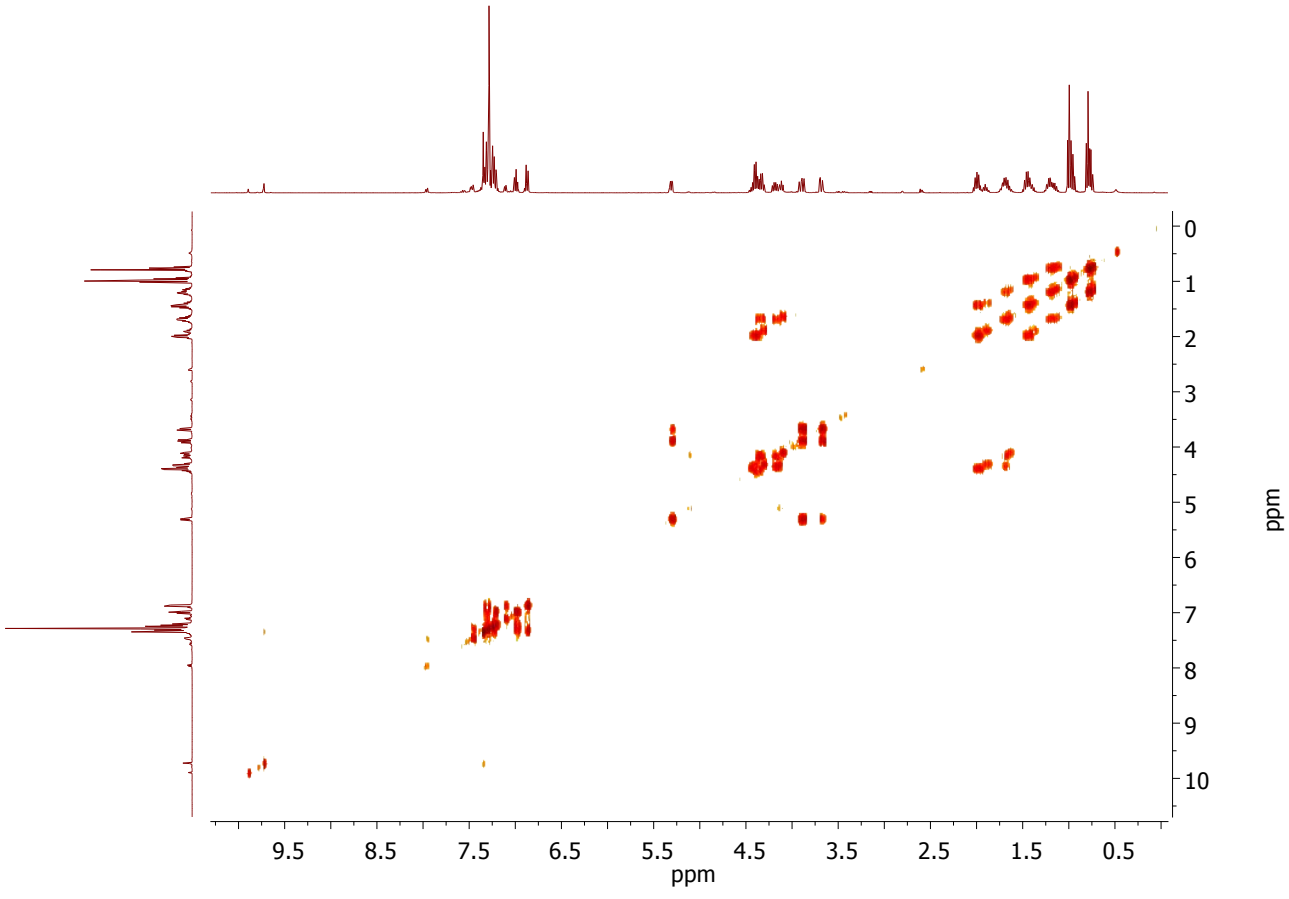
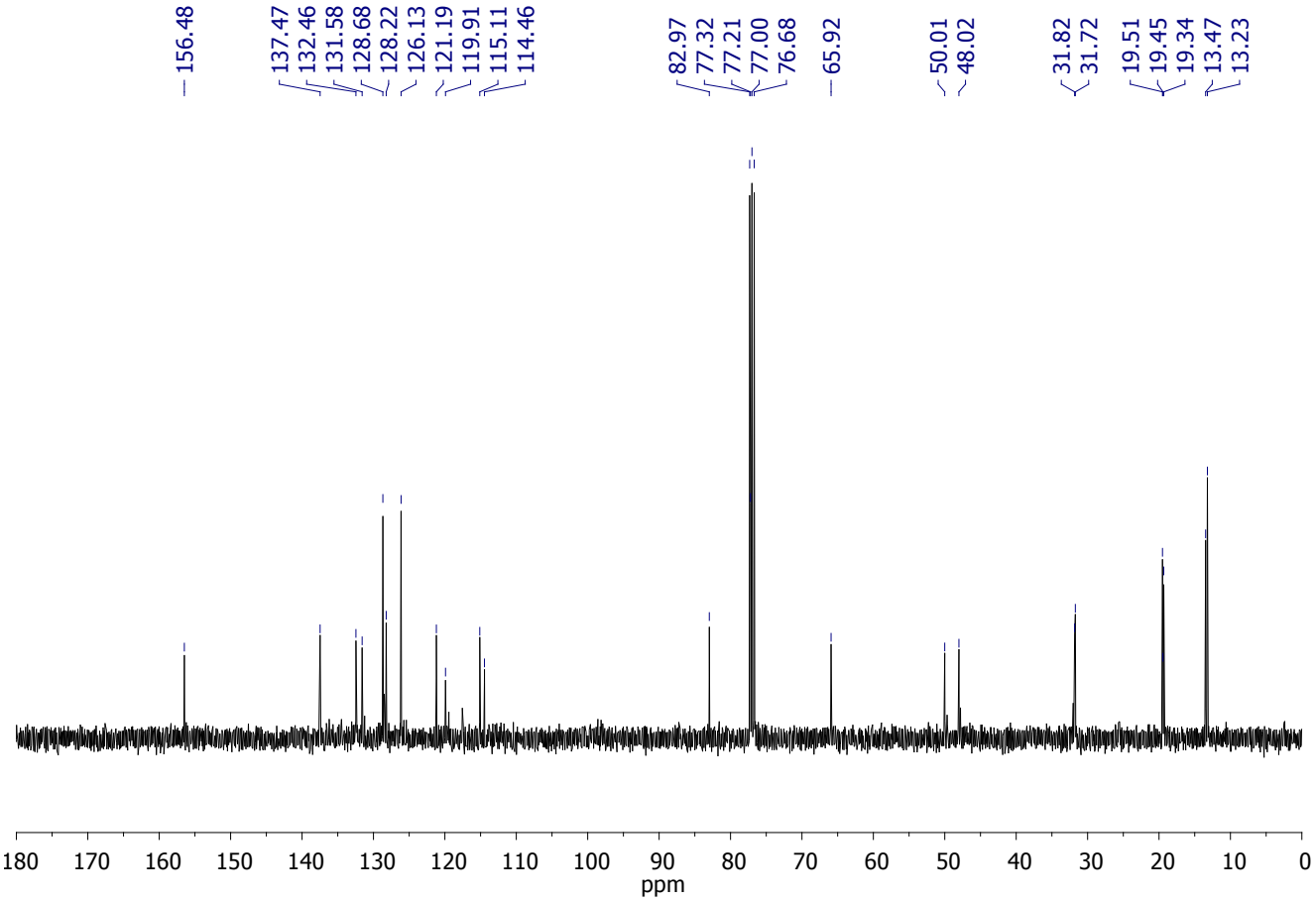
3.0
2.0
1.0
ppm

NMR spectra for compound **9** + epoxide **5e** at 80 °C and t = 1h in $CDCl_3$



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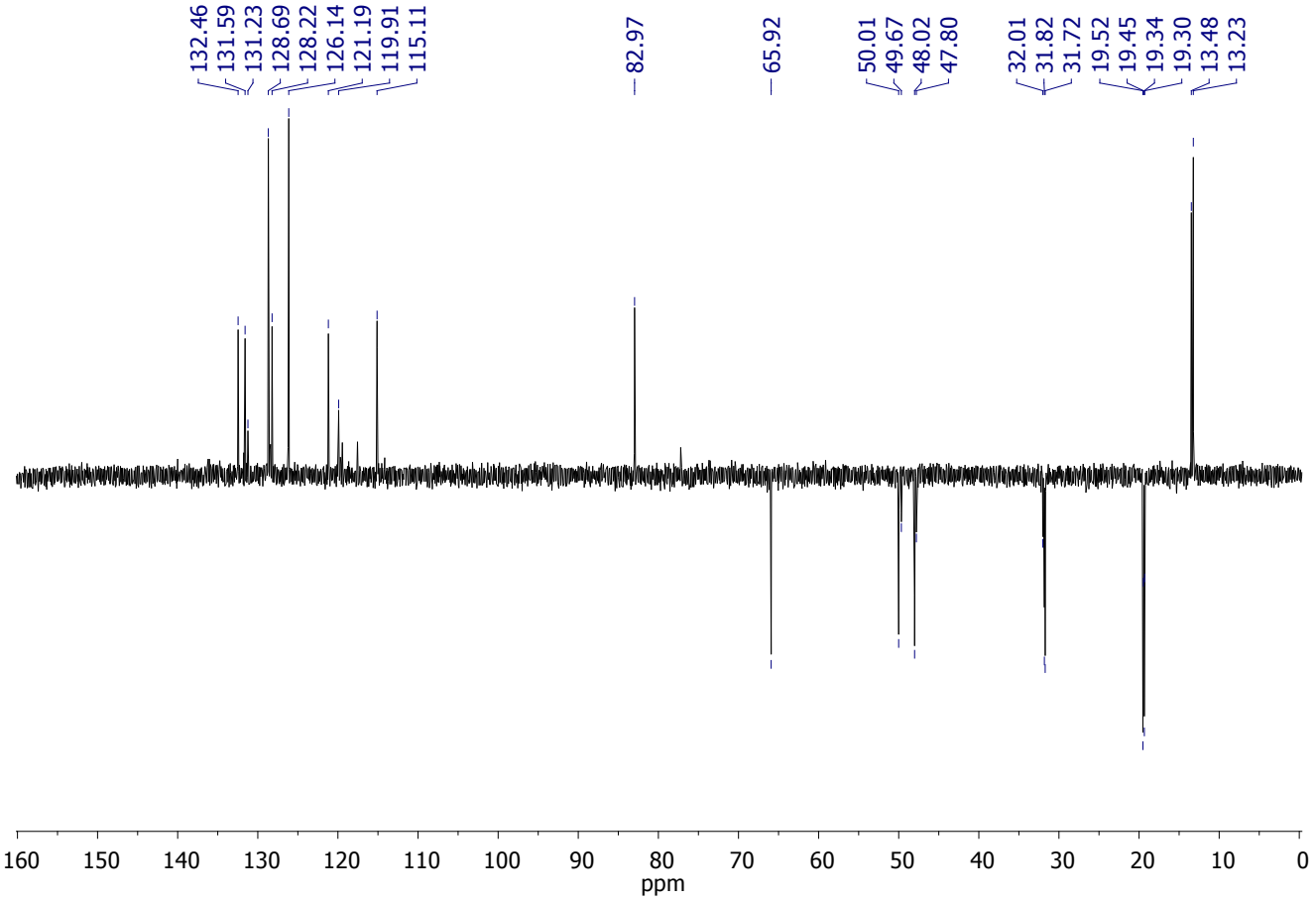
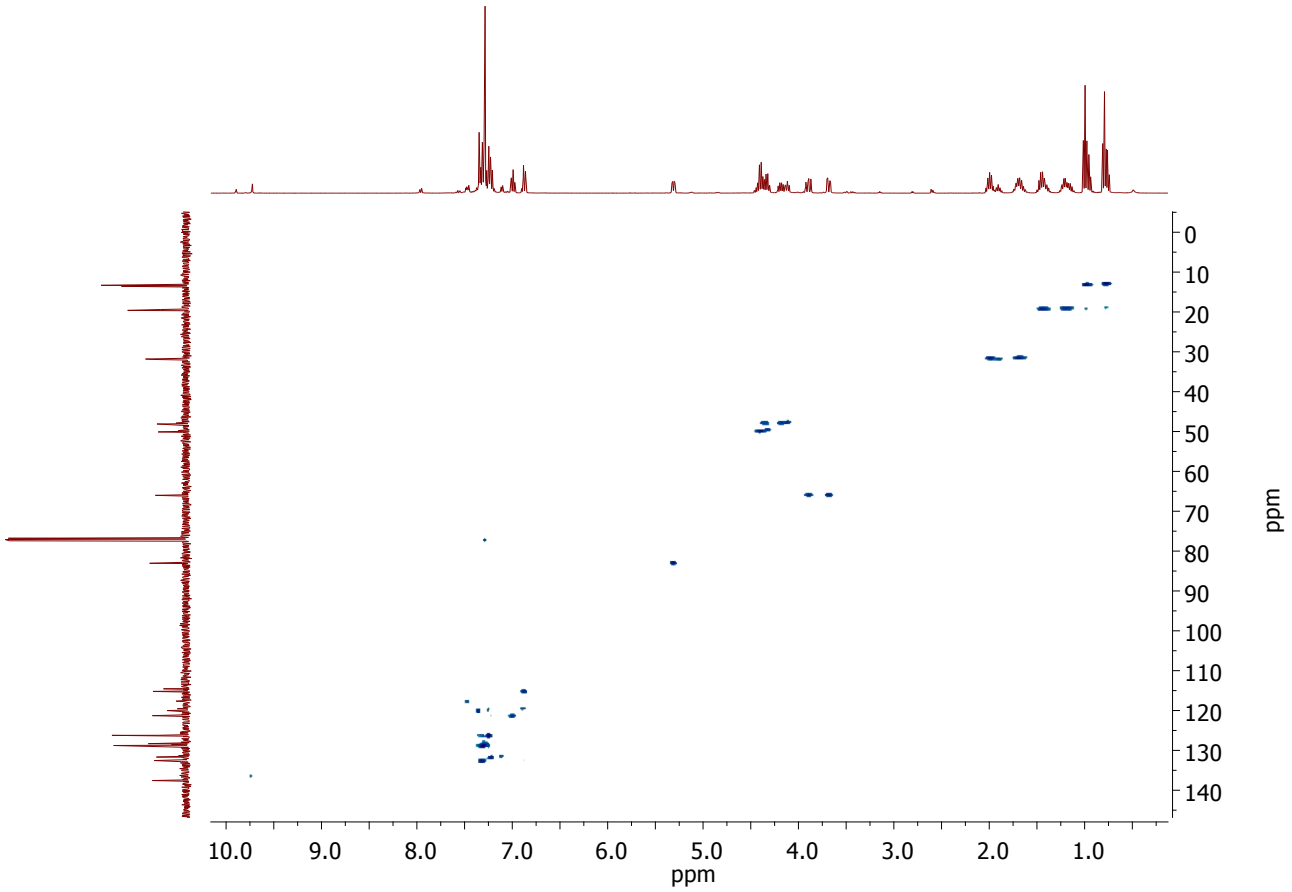
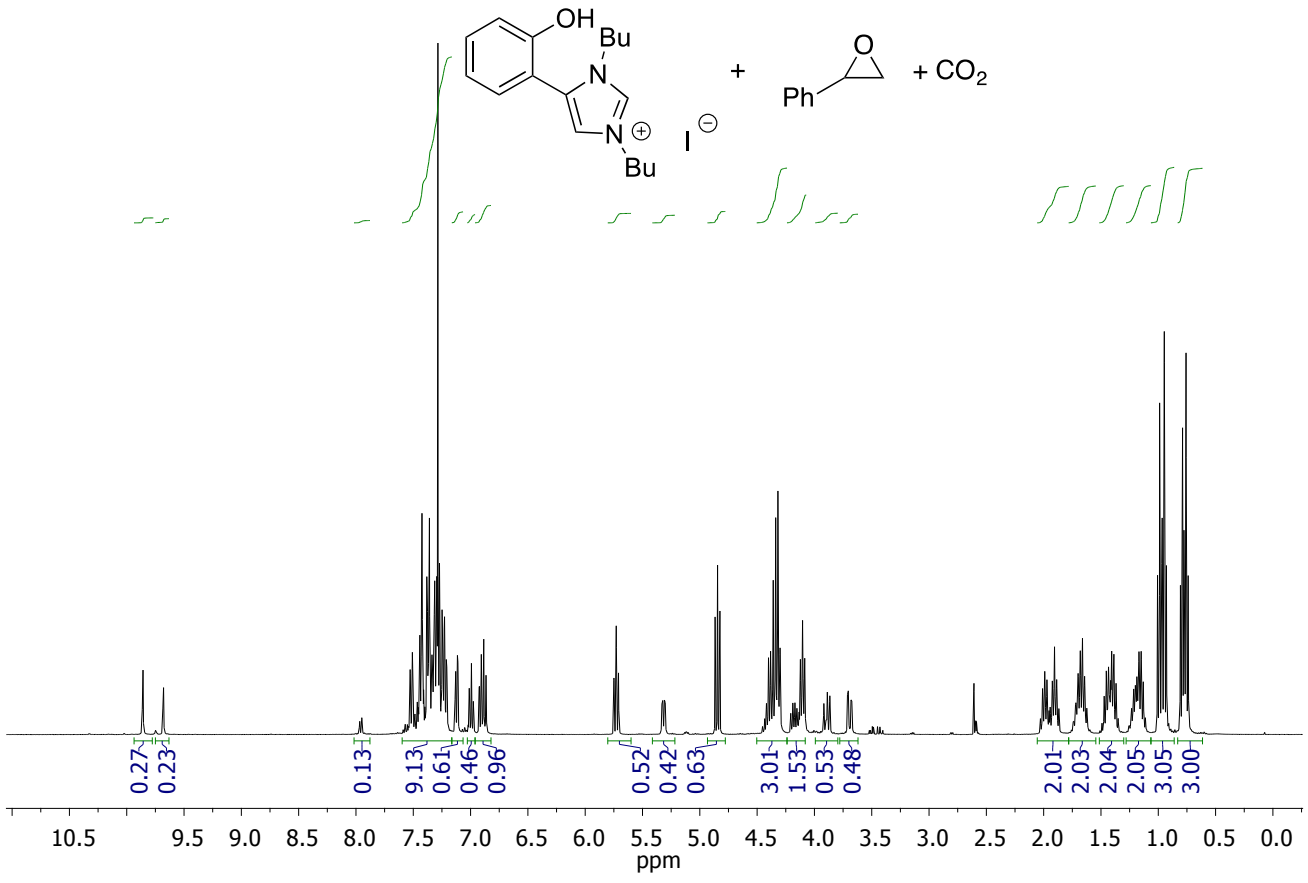
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


132.46
131.59
131.23
128.69
128.22
126.14
121.19
119.91
115.11
82.97
65.92
50.01
49.67
48.02
47.80
32.01
31.82
31.72
19.52
19.45
19.34
19.30
13.48
13.23
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



^{1}H-NMR spectrum for compound **9** + epoxide **5e** + CO_2 at 80 ^{o}C and t = 1h in $CDCl_3$



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