Green Chemistry

Electronic Supplementary Information

Heterogeneously catalyzed etherification of glycerol: new pathways for transformation of glycerol to more valuable chemicals

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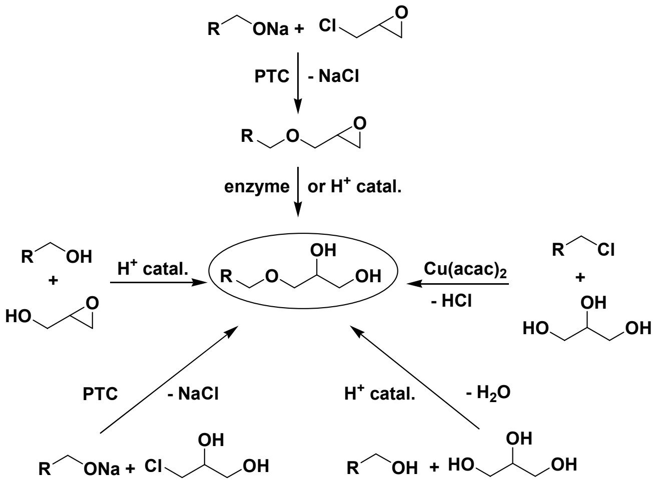
General remarks

Silica gel (60 ACC 40-63 μm, surface area: 550 m^2/g) was purchased from CARLO ERBA REACTIFS-SDS. 3-Mercaptopropyltrimethoxy silane, glycerol, 1-phenyl-1-ethanol, 1-phenyl-1-propanol 1-totyl-1-ethanol, 2-(4-chlorophenyl)propanol, dicyclopentadiene, *exo*-norborneol, hydrogen peroxide aqueous solution (30%), 1-phenyl-1-pentyn-3-ol, α-vinylbenzyl alcohol, 1-dodecanol, 2-dodecanol and *trans*-2-octen-1-ol were purchased from Aldrich Chemical Company. 1-Phenyl-2-propyn-1-ol and benzhydrol were purchased from Alfa Aesar Chemical Company. Dibenzyl ether and norbornylene were purchased from Across Chemical Company. Bis(1-phenylpropyl) ether was synthesized from 1-phenyl-1-propanol by our previous reported method.[1] ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 DPX 300. Chemical shifts are expressed in ppm relative to Me_4Si in $CDCl_3$. IR spectra were recorded on a FT-IR Perkin Elmer (spectrum one) using ATR technology. Elemental analysis were measured on a NA 2100 Instrument. The reaction progress was monitored on a Varian 3300 GPC equipped with a BPX5 column (12m × 0.22 mm; phase thickness: 0.25 μm) supplied by SGE, a Flame Detector Ionization and an injector on column.



Scheme 1 Previous methods for synthesis of MAGEs

Synthesis of covalently anchored sulfonic acid onto silica gel[2]

Silica was activated by an over-night heating at 150 °C. In order to remove trace amount of water, toluene was treated on typical water-carry reflux equipment under refluxed condition before use. Activated silica (2 g) and 3-mercaptopropyltrimethoxy silane (0.2-0.4 g) were added into a 200 ml of round-bottom flask containing 80-150 ml toluene. After 24 h of reflux, the 3-mercaptopropyl silica was filtered off, washed with hot toluene and dried at room temperature for 2 days. The obtained 3-mercaptopropyl silica (2 g) was then mixed with an aqueous solution of hydrogen peroxide (30%, 120 ml). The mixture was stirred at room temperature for 12 h after addition of three drops of conc. H_2SO_4. The solid was then filtered off and washed with distilled water till washings were neutral.

Titration of solid catalysts

0.2 g of acid solid catalysts was suspended in 20mL of aqueous solution of KCl (0.1M) and stirred for 30 mn. Titration of the resulting solution was then carried out with a solution of KOH 0.02M and the pH evolution was monitored by a Metrohm pH meter.

A typical procedure for etherification between glycerol and 1-phenyl-1-propanol

All reactions were conducted in a 10 mL flask with equipped with magnetic stirring. In a typical reaction, Silica-supported sulfonic acid (SiO_2-SO_3H, H^+ exchange ability = 0.32 mmol) (60 mg, 1.7 mol%) was mixed with 1-phenyl-1-propanol (154 mg, 1.13 mmol) and glycerol (437 mg, 4.74 mmol) under air. The mixture was stirred for 4.5 hours at 80 °C. After reaction, products were extracted with ethyl acetate (6 mL × 3) from the glycerol phase.

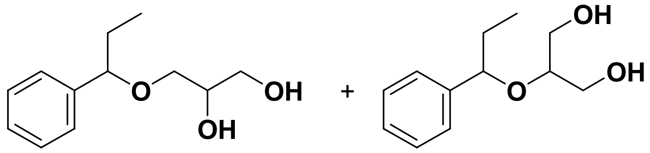
After concentration of organic phase, crude compounds were purified by silica column chromatography using a mixture of ethyl acetate and heptane ($E/H_{v/v}$ = 5/1) as eluting solvent to give color-less liquid. The structure was confirmed as a mixture of 1-phenyl-1-propyl α-glyceryl ether (**1c**) and 1-phenyl-1-propyl β-glyceryl ether(**1d**) (**1c**/**1d** mole ratio is 9/1 determined by ^{1}H NMR) from the spectroscopic data and elemental analysis. (228 mg, 96% yield).

The recovering glycerol phase still contains the solid catalyst. For recycling experiments, glycerol phase (including the SiO_2-SO_3H catalyst) was treated under reduced pressure (15 mmHg) to remove all volatile components and then reactants were directly added for the next catalytic run.

Table 1 reuse of catalyst SiO_2-SO_3H **1**.

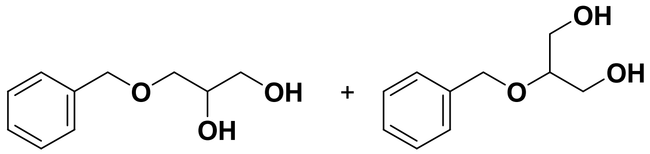
Run	1	2	3	4	5
Yield (%)	96	96	94	95	96

1-Phenyl-1-propyl α-glyceryl ether and 1-phenyl-1-propyl β-glyceryl ether (α/β = 90/10)



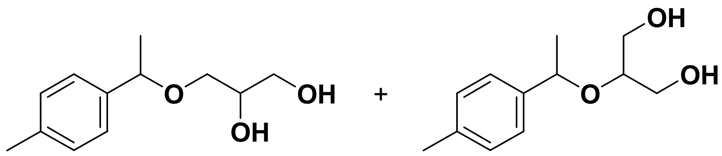
(colorless liquid, heptane/ethyl acetate = 1/5, 96% yield) ^{1}H NMR δ 0.85 (t, J = 7.4 Hz, 3H), 1.59-1.73 (m, 1H), 1.76-1.91 (m, 1H), 3.25-3.35 (m, 2H), 3.46-3.75 (m, 4H), 3.77-3.82 (m, 1H), 4.12 (t, J = 6.7 Hz, 0.9 H), 4.30 (t, J = 6.8 Hz, 0.1 H), 7.21-7.34 (m, 5H); ^{13}C NMR δ 10.2, 10.4, 30.8, 31.0, 61.1, 62.4, 64.0, 64.2, 70.1, 70.2, 70.9, 71.1, 82.8, 84.5, 84.6, 126.7, 126.8, 127.6, 127.8, 128.4, 128.5, 141.9, 142.4. IR (neat) 3381, 2965, 2933, 2876, 1452, 1103, 1042, 727, 755, 700 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.35; H, 8.91.

Benzyl α-glyceryl ether and Benzyl β-glyceryl ether (α/β = 84/16)[3]



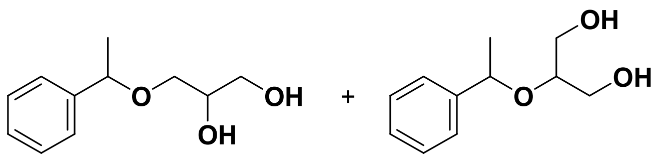
(colorless liquid, heptane/ethyl acetate = 1/5, 76% yield) ^{1}H NMR δ 3.07 (bs, 0.5H), 3.35-3.75 (m, 5H), 3.85 (s, 1.5H), 4.49 (s, 1.67H), 4.58 (s, 0.33 H), 7.15-7.34 (m, 5H); ^{13}C NMR δ 61.7, 63.9, 70.9, 71.6, 71.8, 73.4, 79.2, 127.8, 127.9, 128.4, 128.5, 137.7, 138.0. IR (neat) 3367, 2937, 2868, 1454, 1067, 1040, 1028, 736, 697 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 66.15; H, 7.91.

1-Tolyl-1-ethyl α-glyceryl ether and 1-tolyl-1-ethyl β-glyceryl ether (α/β = 94/6)



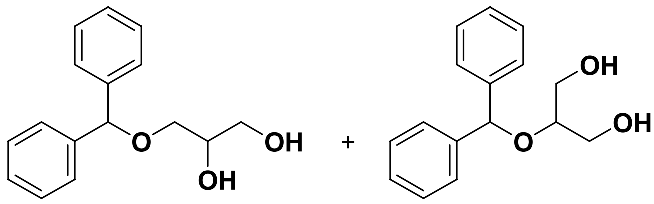
(colorless liquid, heptane/ethyl acetate = 1/5, 94% yield) ^{1}H NMR δ 1.41 (d, J = 0.9 Hz, 1.5H), 1.43 (d, J = 0.9Hz, 1.5H), 2.32 (s, 3H), 3.21-3.37 (m, 2H), 3.44-3.68 (m, 4H), 3.72-3.80 (m, 1H), 4.37 (dd, J_a = 12.2 Hz, J_b = 5.8 Hz, 0.94 H), 4.58 (dd, J_a = 12.9 Hz, J_b = 6.5 Hz, 0.06 H), 7.08-7.24 (m, 4H); ^{13}C NMR δ 21.1, 23.8, 24.1, 61.3, 62.5, 69.9, 70.0, 70.9, 71.0, 76.9, 78.5, 78.8, 126.1, 126.2, 129.2, 129.3137.3, 137.4, 140.1, 140.5. IR (KBr) 3379, 2975, 2926, 2868, 1514, 1370, 1204, 1056, 1085, 816 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.77; H, 8.92.

1-Phenyl-1-ethyl α-glyceryl ether and 1-phenyl-1-ethyl β-glyceryl ether (α/β = 93/7)



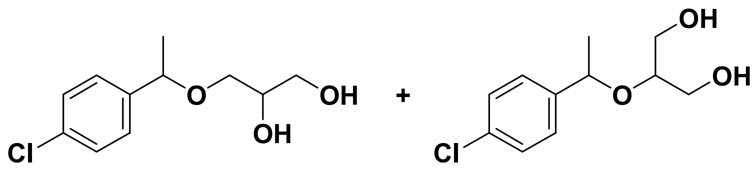
(colorless liquid, heptane/ethyl acetate = 1/5, 85% yield) ^{1}H NMR δ 1.41 (d, J = 1.2 Hz, 1.5H), 1.43 (d, J = 1.2 Hz, 1.5H), 3.26-3.38 (m, 2H), 3.42-3.70 (m, 2H), 3.73-4.05 (m, 3H), 4.39 (dd, J_a = 12.6 Hz, J_b = 6.2 Hz, 0.93 H), 4.60 (dd, J_a = 12.9 Hz, J_b = 6.4 Hz, 0.07 H), 7.20-7.34 (m, 5H); ^{13}C NMR δ 23.8, 24.1, 61.0, 62.2, 63.9, 64.0, 69.9, 70.0, 70.9, 71.1, 76.7, 77.0, 78.5, 78.7, 126.1, 126.2, 127.5, 127.7, 128.5, 143.2, 143.6. IR (neat) 3378, 2975, 2929, 2870, 1451, 1103, 1050, 1029, 760 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.56; H, 8.09.

Benzhydryl α-glyceryl ether and benzhydryl β-glyceryl ether (α/β = 94/6)



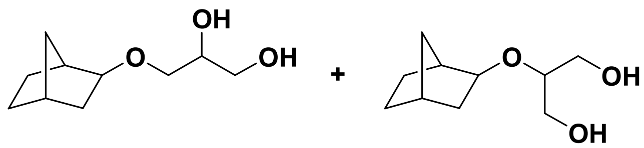
(colorless liquid, heptane/ethyl acetate = 1/5, 96% yield) ^{1}H NMR δ 3.37-3.74 (m, 6H), 3.81-3.87 (m, 1H), 5.32 (s, 0.94 H), 5.55 (s, 0.06 H), 7.16-7.23 (m, 2H), 7.26-7.34 (m, 8H); ^{13}C NMR δ 61.9, 63.9, 70.4, 70.9, 77.4, 82.1, 84.2, 126.9, 127.0, 127.6, 127.7, 128.4, 141.6, 141.7, 142.0. IR (neat) 3371, 3028, 2924, 2870, 1493, 1452, 1066, 1028, 921, 741, 696 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.68; H, 7.27.

1-(4-Chlorophenyl)-1-ethyl α-glyceryl ether and 1-(4-chlorophenyl)-1-ethyl β-glyceryl ether (α/β = 93/7)



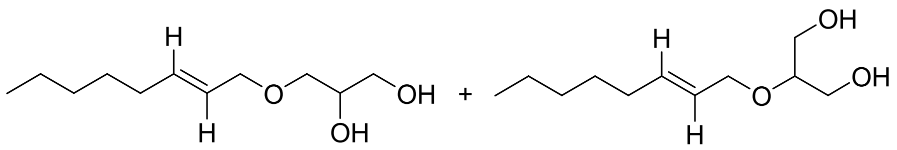
(colorless liquid, heptane/ethyl acetate = 1/5, 89% yield) ^{1}H NMR δ 1.41 (d, J = 0.7 Hz, 1.5H), 1.41 (d, J = 0.9 Hz, 1.5H), 3.24-3.35 (m, 2H), 3.44-3.63 (m, 2H), 3.75-4.09 (m, 3H), 4.38 (dd, J_a = 11.9 Hz, J_b = 5.4 Hz, 0.93 H), 4.60 (dd, J_a = 12.8 Hz, J_b = 6.4 Hz, 0.07 H), 7.20-7.30 (dd, J_a =22.8, J_b = 8.2 Hz, 4H); ^{13}C NMR δ 23.8, 24.0, 61.1, 62.2, 63.9, 64.0, 69.9, 70.0, 76.1, 77.1, 77.9, 78.1, 127.5, 127.7, 128.7, 133.2, 133.3, 141.8, 142.1. IR (neat) 3370, 2975, 2929, 2873, 1597, 1489, 1408, 1100, 1055, 1013,827 cm^{-1}. Anal. Calcd for $C_{11}H_{15}ClO_3$: C, 57.27; H, 6.55. Found: C, 57.49; H, 6.78.

Norbornanyl α-glyceryl ether and norbornanyl β-glyceryl ether (α/β = 89/11, determined by GC)



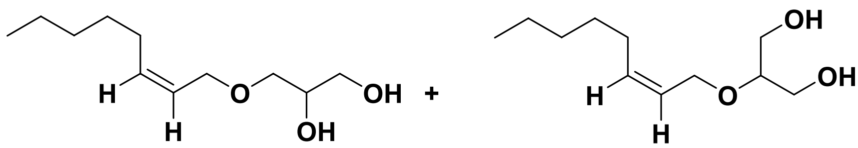
(colorless liquid, heptane/ethyl acetate = 1/5, 83% yield) ^{1}H NMR δ 0.93-1.10 (m, 3H), 1.34-1.58 (m, 5H), 2.23 (s, 1H), 2.31 (d, J = 3.0 Hz, 1H), 3.23-3.49 (m, 3H), 3.57-3.78 (m, 5H); ^{13}C NMR δ 24.5, 24.5, 28.4, 28.5, 34.8, 35.1, 35.2, 39.4, 39.4, 40.0, 40.2, 40.3, 41.1, 61.8, 62.0, 64.2, 64.2, 69.7, 70.8, 70.9, 77.3, 81.5, 83.2, 83.3. IR (neat) 3371, 2953, 2871, 1452, 1352, 1176, 1084, 1065, 988, 919, 731 cm^{-1}. Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.31; H, 9.89.

***trans*-2-Octen-1-yl α-glyceryl ether and *trans*-2-octen-1-yl β-glyceryl ether** (α/β = 76/24)



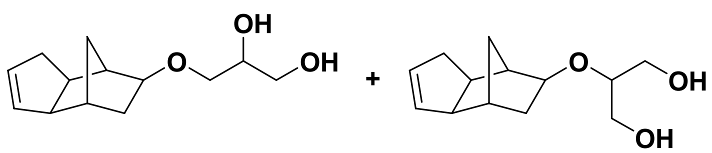
(colorless liquid, heptane/ethyl acetate = 1/5, 41% yield) ^{1}H NMR δ 0.86 (t, J = 6.6 Hz, 3H), 1.21-1.43 (m, 6H), 2.04 (dd, J_a = 13.6 Hz, J_b = 6.6 Hz, 2 H), 3.08-3.30 (m, 1H), 3.41-3.51 (m, 2H), 3.52-3.61 (m, 1H), 3.66-3.73 (m, 2H), 3.83-3.88 (m, 1H), 3.95 (dd, J_a = 6.3 Hz, J_b = 0.80 Hz, 1.52H), 4.06 (dd, J_a = 6.3 Hz, J_b = 0.8 Hz, 0.48H), 5.48-5.60 (m, 1H), 5.65-5.77 (m, 1H); ^{13}C NMR δ 14.0, 22.5, 28.7, 31.4, 32.3, 61.9, 64.1, 70.7, 70.8, 71.3, 72.3, 78.7, 125.7, 126.0, 135.6, 135.6. IR (neat) 3370, 2957, 2925, 2858, 1456, 1379, 1260, 1104, 1048, 970 cm^{-1}. Anal. Calcd for $C_{11}H_{22}O_3$: C, 57.27; H, 6.55. Found: C, 57.49; H, 6.78.

***cis*-2-Octen-1-yl α-glyceryl ether and *cis*-2-octen-1-yl β-glyceryl ether** (α/β = 84/16, determined by GC)



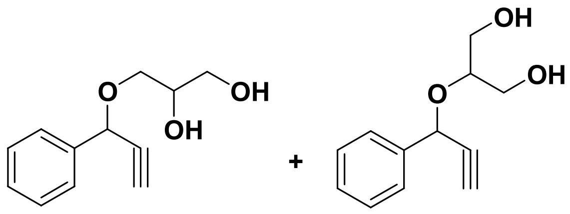
(colorless liquid, heptane/ethyl acetate = 1/5, 20% yield) ^{1}H NMR δ 0.88 (t, J = 6.6 Hz, 3H), 1.24-1.40 (m, 6H), 1.43-1.55 (m, 1H), 1.57-1.70 (m, 1H), 2.72 (bs, 1H), 2.97 (bs, 1H), 3.35 (ddd, J_a = 15.8 Hz, J_b = 9.8 Hz, J_c = 4.1 Hz, 1H), 3.54-3.72 (m, 4H), 3.83-3.87 (m, 1H), 5.16 (dt, J_a = 8.9 Hz, J_b = 0.8 Hz, 1 H), 5.21-5.22 (m, 1H), 5.59-5.73 (m, 1H); ^{13}C NMR δ 14.0, 22.6, 25.0, 25.0, 25.1, 31.8, 35.3, 35.6, 61.8, 62.9, 64.2, 64.4, 70.1, 70.1, 70.7, 70.8, 76.8, 77.3, 80.8, 82.3, 82.5, 117.3, 117.3, 138.7, 139.3. IR (neat) 3382, 2957, 2929, 2860, 1461, 1421, 1258, 1048, 993, 923, 864, 727 cm^{-1}. Anal. Calcd for $C_{11}H_{22}O_3$: C, 57.27; H, 6.55. Found: C, 57.53; H, 6.81.

3a,4,5,6,7,7a-hexahydro-1H-4,7-methanoinden-5-yl α-glyceryl ether and 3a,4,5,6,7,7a-hexahydro-1H-4,7-methanoinden-5-yl β-glyceryl ether (α/β = 74/26, determined by GC**)**



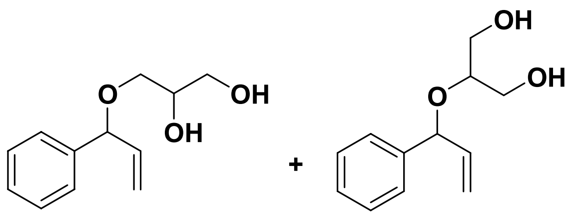
(light brown liquid, heptane/ethyl acetate = 1/5, 64% yield) ^{1}H NMR δ 1.17-1.58 (m, 3H), 1.60-1.68 (m, 1H), 1.85-2.23 (m, 4H), 2.41-2.59 (m, 2H), 2.87-3.00 (m, 1H), 3.32-3.81 (m, 7H), 5.44-5.55 (m, 1H), 5.58-5.69 (m, 1H); ^{13}C NMR δ 28.4, 28.5, 32.6, 39.1, 39.3, 39.6, 41.7, 41.8, 43.2, 43.2, 44.9, 45.8, 51.2, 51.3, 61.9, 64.2, 64.2, 70.0, 70.0, 70.7, 70.8, 77.4, 81.5, 83.2, 83.2, 130.3, 130.9, 131.0, 131.1, 131.4, 131.5, 132.0, 132.1, 132.2, 132.4, 132.5. IR (neat) 3371, 2953, 2871, 1452, 1394, 1352, 1260, 1223, 1176, 1155, 1084, 1065, 988, 919, 881, 846, 731 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.88; H, 9.23.

1-Phenyl-1-ethynyl α-glyceryl ether and 1-phenyl-1-ethynyl β-glyceryl ether (α/β = 90/10)



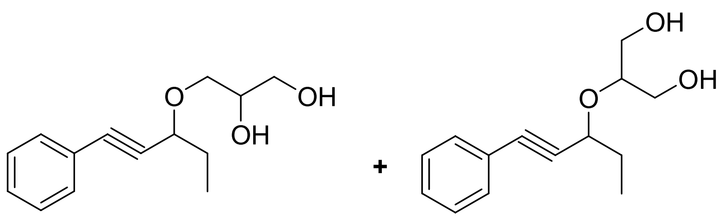
(colorless liquid, heptane/ethyl acetate = 1/5, 70% yield) ^{1}H NMR δ 2.67 (d, J = 2.1 Hz, 1H), 3.09 (bs, 1H), 3.34 (bs, 1H), 3.48-3.57 (m, 2H), 3.61-3.78 (m, 3H), 3.82-3.95 (m, 1H), 5.20 (s, 0.90 H), 5.35 (s, 0.10 H), 7.29-7.39 (m, 3H), 7.48-7.50 (m, 2H); ^{13}C NMR δ 61.9, 62.5, 63.8, 63.9, 69.5, 70.7, 70.8, 71.8, 71.9, 76.1, 76.3, 78.3, 81.1, 127.4, 127.4, 128.6, 128.7, 128.7, 128.8, 137.6, 138.1. IR (neat) 3367, 3285, 2930, 2876, 2113, 1452, 1275, 1055, 1028, 920, 864, 759, 697 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 70.20; H, 7.07.

α-Vinylbenzyl α-glyceryl ether and α-vinylbenzyl β-glyceryl ether (α/β = 92/8)



(colorless liquid, heptane/ethyl acetate = 1/5, 82% yield) ^{1}H NMR δ 2.69 (bs, 2H), 3.52-3.62 (m, 4H), 3.71-3.78 (m, 1H), 3.89-4.15 (m, 1H), 5.22 (s, 0.92), 5.38 (s, 0.08), 7.26-7.39 (m, 4H), 7.49-7.52 (m, 3H); ^{13}C NMR δ 60.5, 62.2, 62.8, 63.9, 63.9, 69.6, 69.9, 70.6, 70.7, 71.9, 72.0, 76.3, 78.5, 81.0, 126.6, 127.4, 128.5, 128.5, 128.6, 128.6, 128.7, 128.8, 128.9, 129.1, 131.3, 137.5. IR (neat) 3386, 2921, 2870, 1641, 1493, 1453, 1355, 1087, 1070, 1042, 992, 916, 758, 700 cm^{-1}. Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.54; H, 7.97.

1-phenyl-1-pentyn-3-yl α-glyceryl ether and 1-phenyl-1-pentyn-3-yl β-glyceryl ether (α/β = 88/12)



(colorless liquid, heptane/ethyl acetate = 1/5, 83% yield) ^{1}H NMR δ 1.06 (t, J = 7.2 Hz, 3H), 1.79-1.98 (m, 2H), 2.53 (bs, 1H), 2.90 (bs, 1H), 3.49-3.77 (m, 3H), 3.85-3.94 (m, 2H), 4.24 (t, J = 6.3 Hz, 0.88 H), 4.39 (t, J = 6.3 Hz, 0.12 H), 7.26-7.33 (m, 3H), 7.40-7.71 (m, 2H); ^{13}C NMR δ 9.75, 9.77, 9.86, 28.9, 29.4, 62.1, 62.9, 64.1, 64.2, 70.4, 70.4, 70.6, 70.8, 71.1, 72.1, 72.3, 77.3, 78.8, 86.0, 86.2, 87.6, 87.6, 88.3, 122.4, 122.5, 128.3, 128.5, 128.5, 131.7, 131.8. IR (neat) 3367, 3285, 2930, 2876, 2113, 1452, 1275, 1055, 1028, 920, 864, 759, 697 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.89; H, 7. 97.

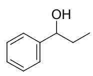
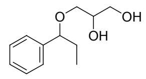
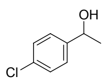
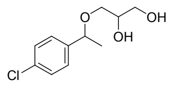
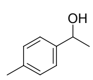
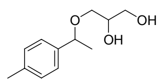
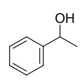
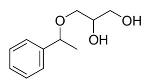
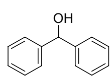
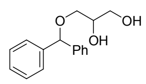
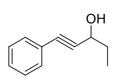
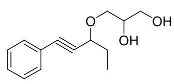
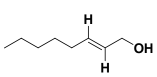
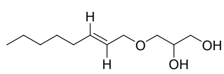
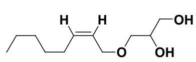
A typical procedure for etherification between glycerol and norbornylene

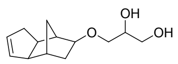
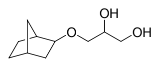
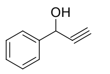
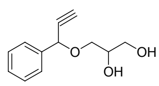
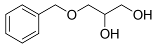
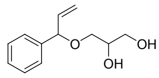
All reactions were conducted in a 10 mL flask with equipped with magnetic stirring. In a typical reaction, Silica-supported sulfonic acid (SiO_2-SO_3H, H^+ exchange ability = 0.57 mmol) (60 mg, 3.4 mol%) was mixed with norbornylene (94 mg, 1.0 mmol) and glycerol (278 mg, 3.02 mmol) under air. The mixture was stirred for 8 hours at 95 ^oC. After reaction, the mixture was extracted with ethyl acetate (6 mL × 3). After concentration of organic phase, the crude compounds were purified by silica column chromatography using a mixture of ethyl acetate and heptane ($E/H_{v/v}$ = 5/1) as eluting solvent to give color-less liquid. The structure was confirmed as a mixture of norbornanyl α-glyceryl ether (***4a***) and norbornanyl β-glyceryl ether (***4b***) (α/β = 89/11, determined by GC) from the spectroscopic data and elemental analysis. (166 mg, 89% yield).

A typical procedure for reaction between glycerol and dibenzyl ether

All reactions were conducted in a 10 mL flask with equipped with magnetic stirring. In a typical reaction, Silica-supported sulfonic acid (SiO_2-SO_3H, H^+ exchange ability = 0.32 mmol) (60 mg, 2.2 mol%) was mixed with dibenzyl ether (173 mg, 0.87 mmol) and glycerol (320 mg, 3.48 mmol) under air. The mixture was stirred for 4 hours at 95 ^oC. After reaction, the mixture was extracted with ethyl acetate (6 mL × 3). After concentration of organic phase, the crude compounds were purified by silica column chromatography using a mixture of ethyl acetate and heptane ($E/H_{v/v}$ = 5/1) as eluting solvent to give color-less liquid. (145.8 mg, 92% yield).

Table 1. GC Response factors of some alcohols and products related to hexadecane

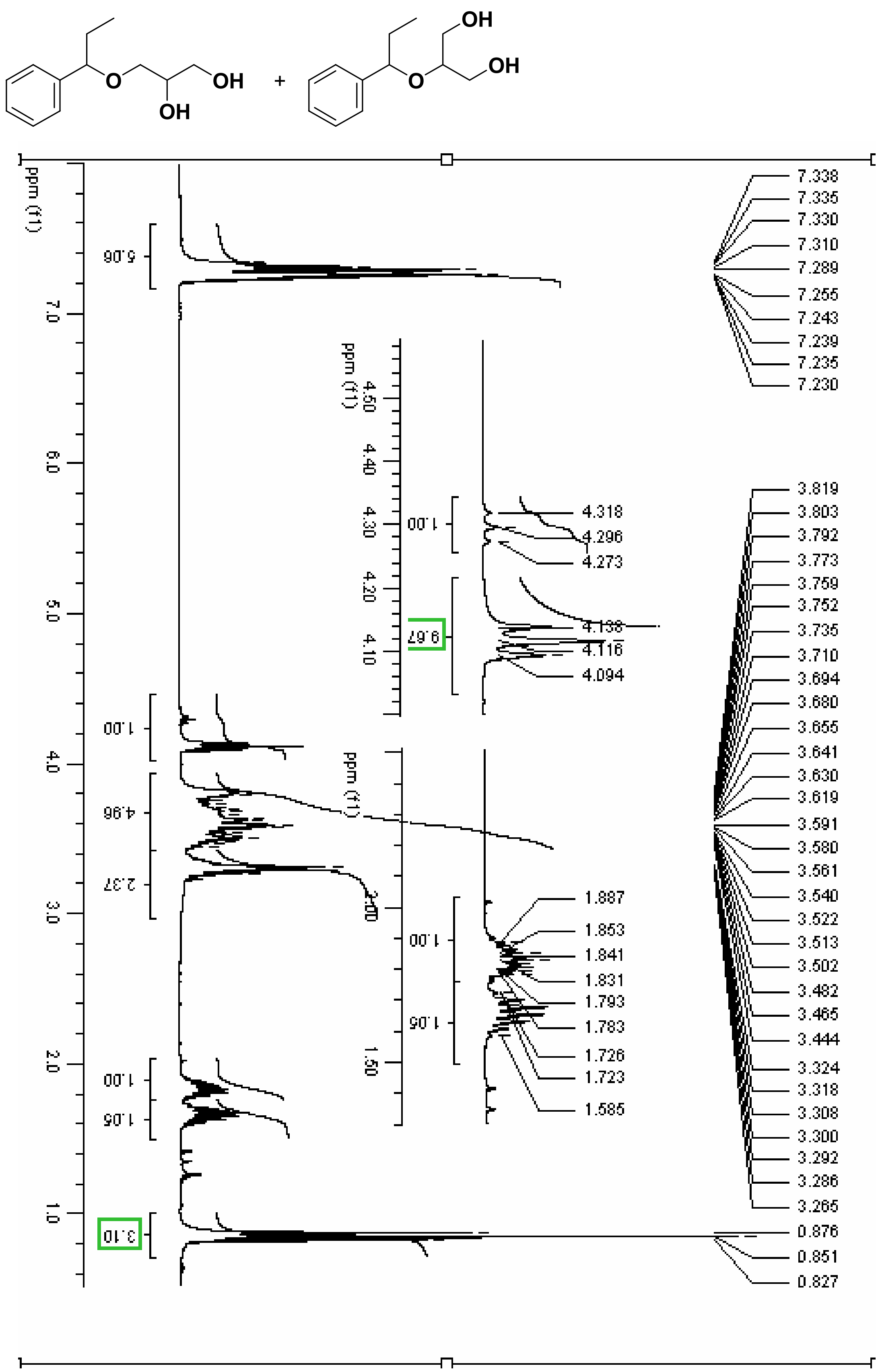
Compound	GC response factors	Compound	GC response factors
	1.3243		0.8413
	0.9252		0.7158
	1.3461		0.7858
	1.2958[a]		0.9463[a]
	1.3312		0.7869
	1.3077		0.5738
	1.4927[b]		1.1901[b]
			1.2716[b]

	0.3903		1.1807[b]
	1.6428[b]		0.8617[b]
	1.0761[b]		0.955[a]

[a]: Dodecane was used as internal standard; [b]: methyl Laurate was used as internal standard.

References

1. Y. Gu, A. Karam, F. Jèrôme, J. Barrault, *Org. Lett*. **2007**, *9(16)*, 3145.
2. A. Karam, Y. Gu, F. Jèrôme, J. –P. Douliez, J. Barrault, *Chem. Commun*. **2007**, 2222.
3. O. Sirkecioglu, B. Karliga, N. Talinli, *Tetrahedron Lett*. **2003**, *44*, 8483-8485.



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7.235
7.230
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3.803
3.792
3.773
3.759
3.752
3.735
3.710
3.694
3.680
3.655
3.641
3.630
3.619
3.591
3.580
3.561
3.540
3.522
3.513
3.502
3.482
3.465
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3.318
3.308
3.300
3.292
3.286
3.265
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0.827
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4.273
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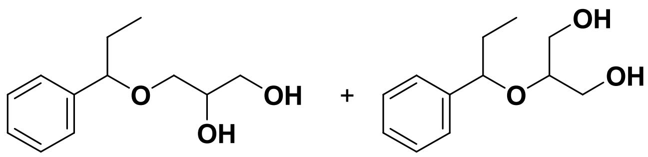
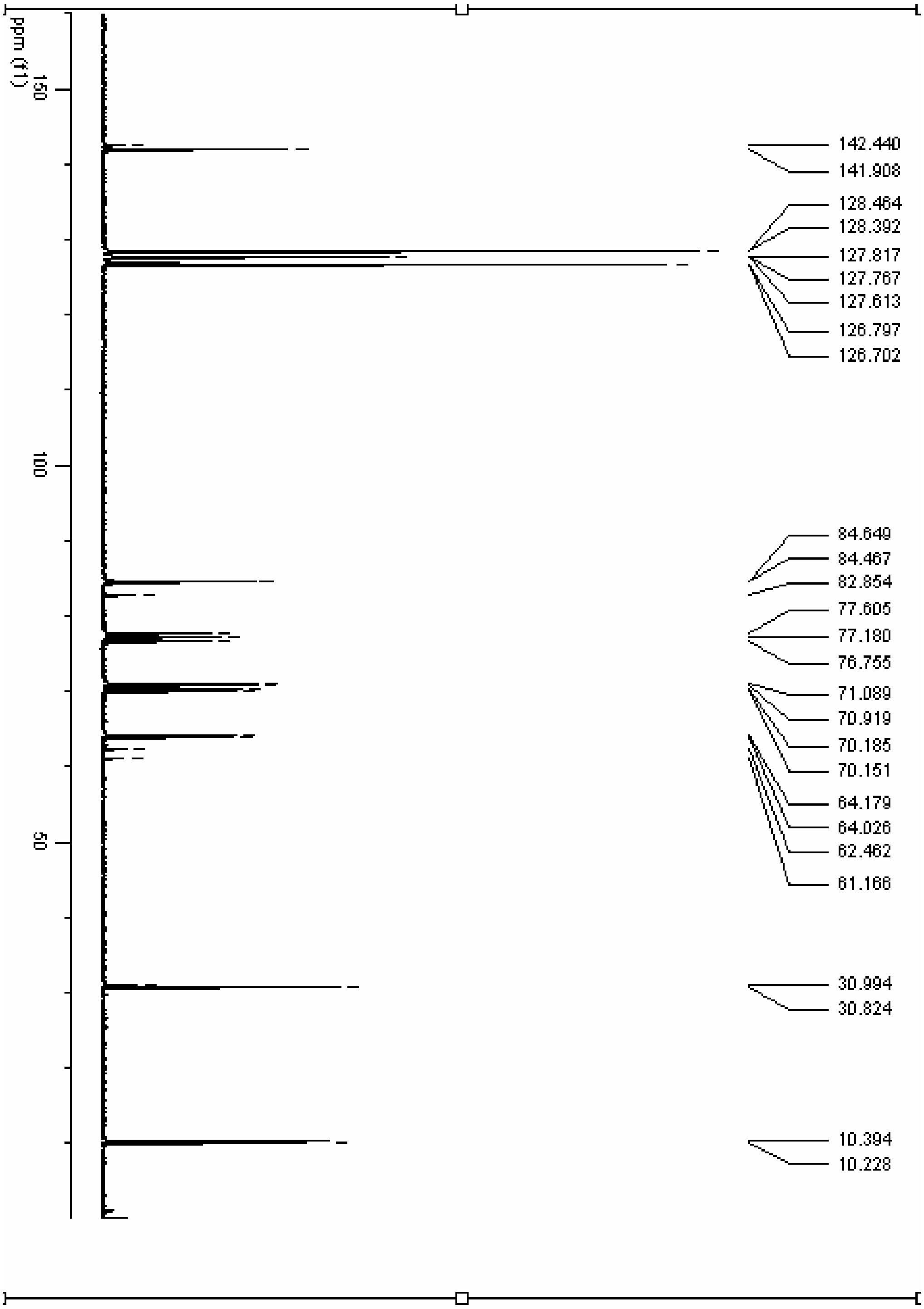
1.585

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82.854
77.605
77.180
76.755
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70.151
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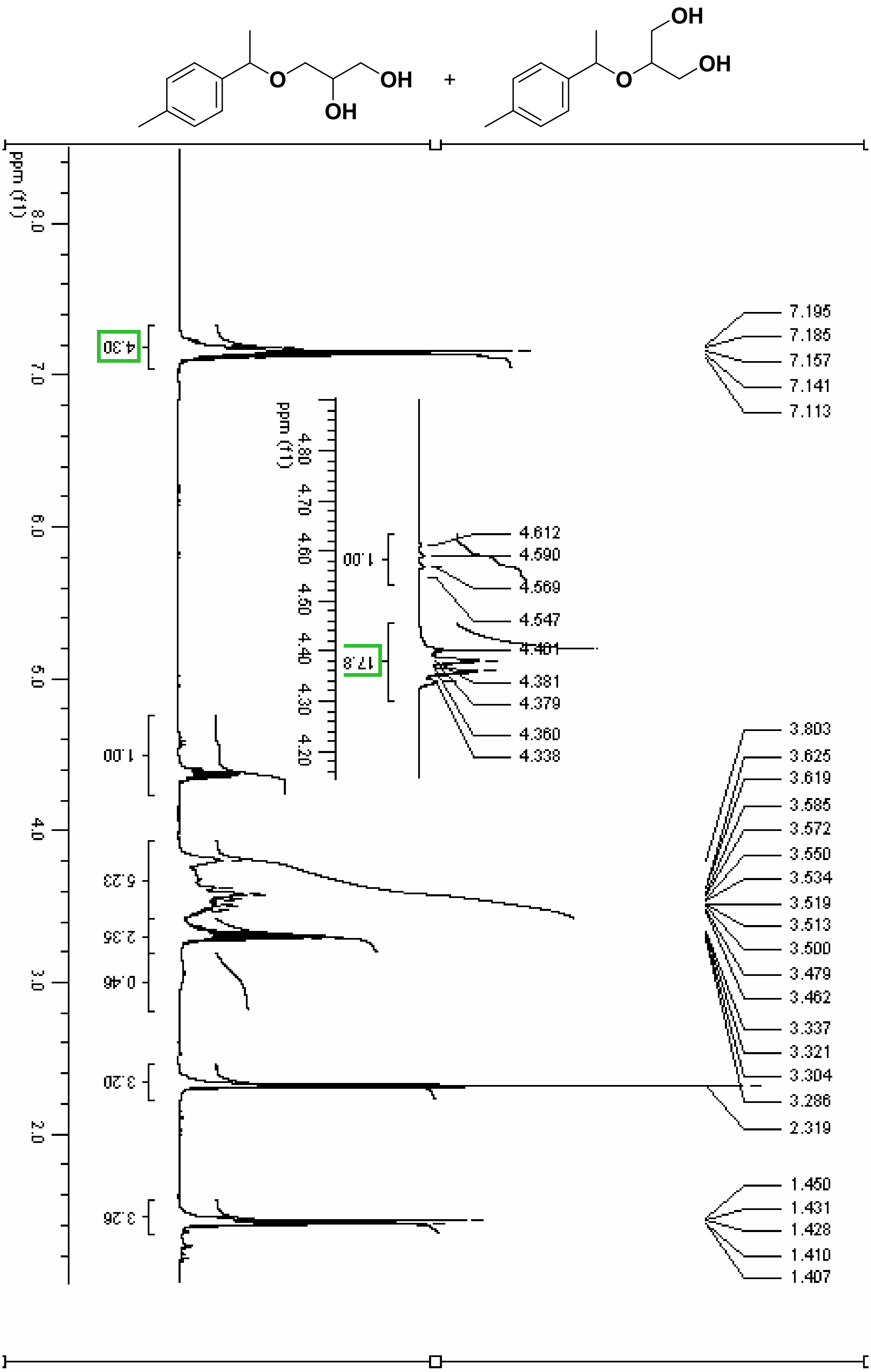
30.824
10.394
10.228



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OH
+
O
OH
OH
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4.30
1.00
5.23
2.35
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3.20
3.26
ppm (f1)
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4.70
4.60
4.50
4.40
4.30
4.20
1.00
17.8
4.612
4.590
4.569
4.547
4.401
4.381
4.379
4.360
4.338
7.195
7.185
7.157
7.141
7.113
3.803
3.625
3.619
3.585
3.572
3.550
3.534
3.519
3.513
3.500
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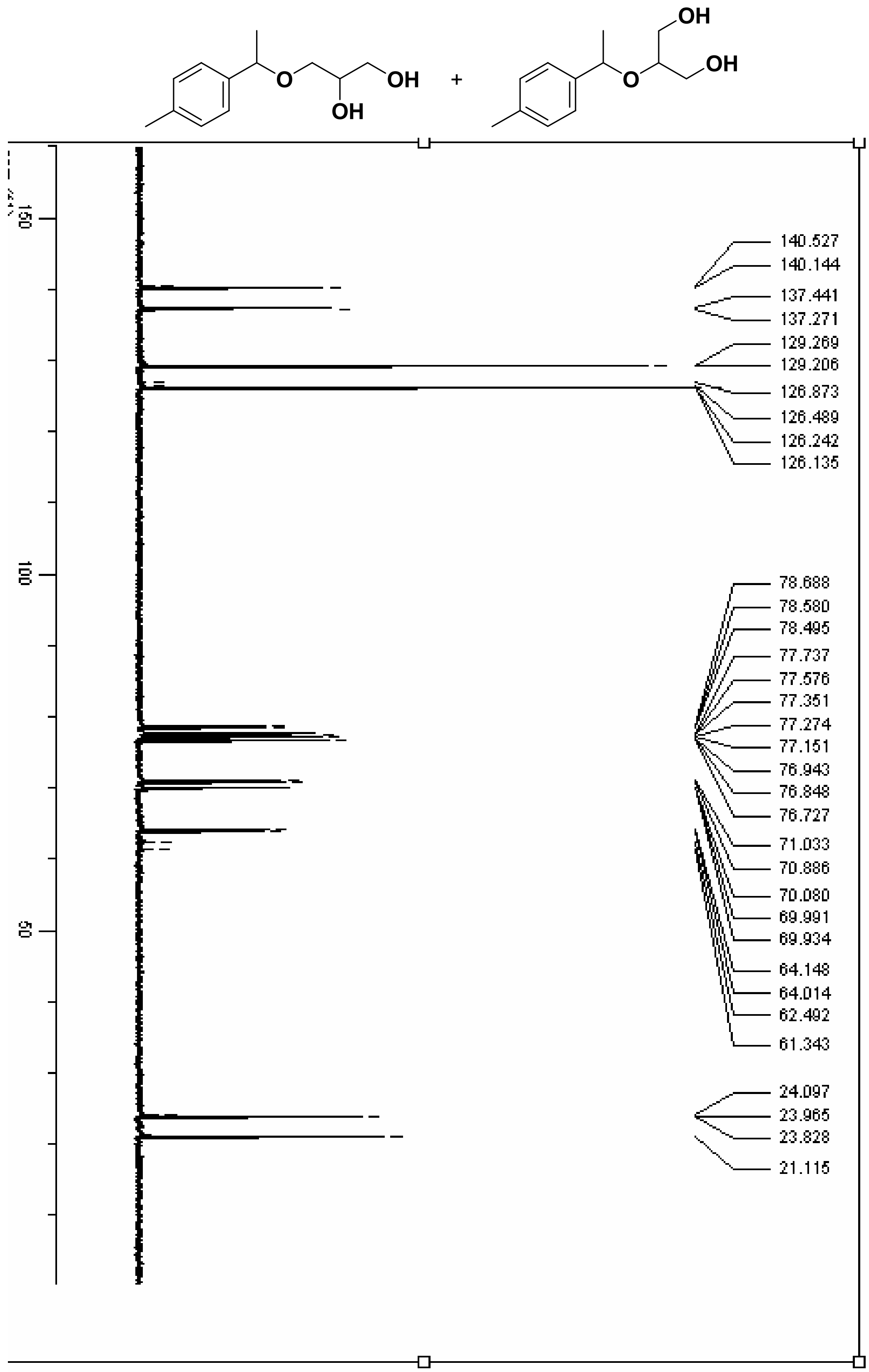
1.410
1.407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OH
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126.489
126.242
126.135
78.688
78.580
78.495
77.737
77.576
77.351
77.274
77.151
76.943
76.848
76.727
71.033
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23.828
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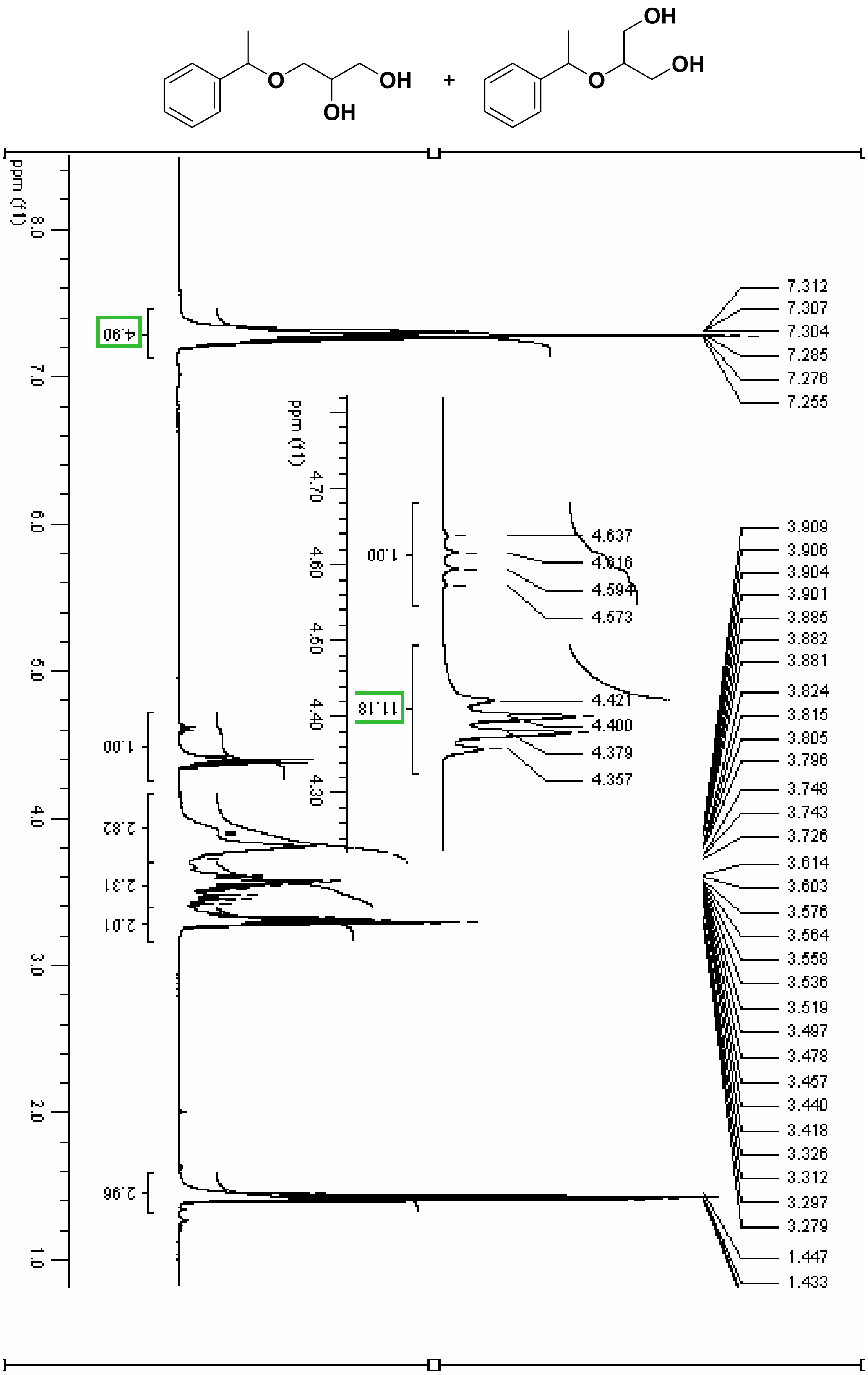

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OH
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4.379
4.357
3.909
3.906
3.904
3.901
3.885
3.882
3.881
3.824
3.815
3.805
3.796
3.748
3.743
3.726
3.614
3.603
3.576
3.564
3.558
3.536
3.519
3.497
3.478
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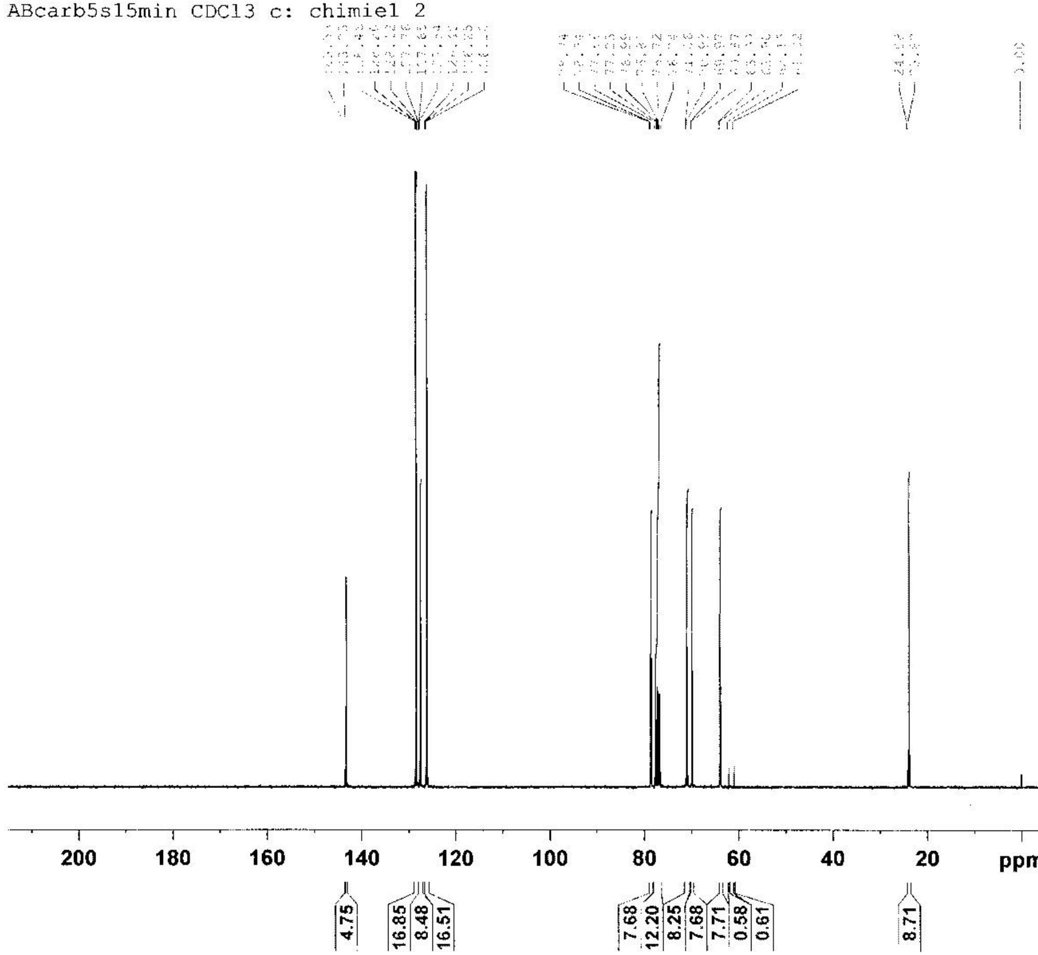
1.433

ABcarb5s15min CDCl3 c: chimiel 2

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PROCNO                  1

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TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                  6502
DW                27.800 usec
DE                 10.00 usec
TE                 300.0 K
D1            5.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.35 usec
PL1                -2.00 dB
SFO1          75.4760204 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               15.00 dB
PL13               15.00 dB
SFO2         300.1312005 MHz

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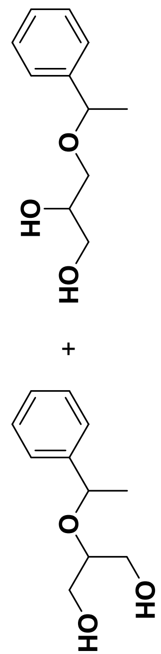

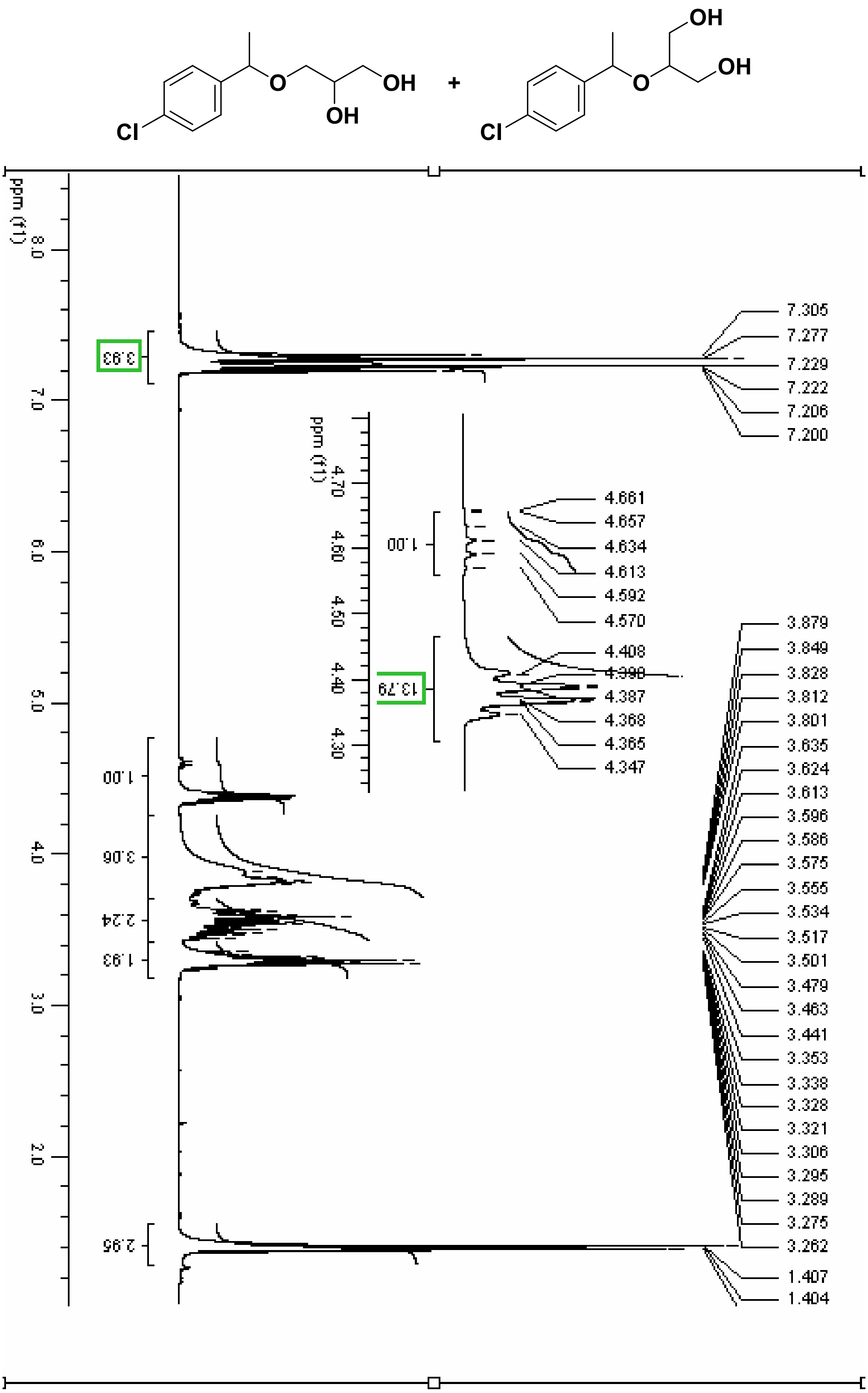

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OH
OH
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Cl
O
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1.00
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2.24
1.93
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4.40
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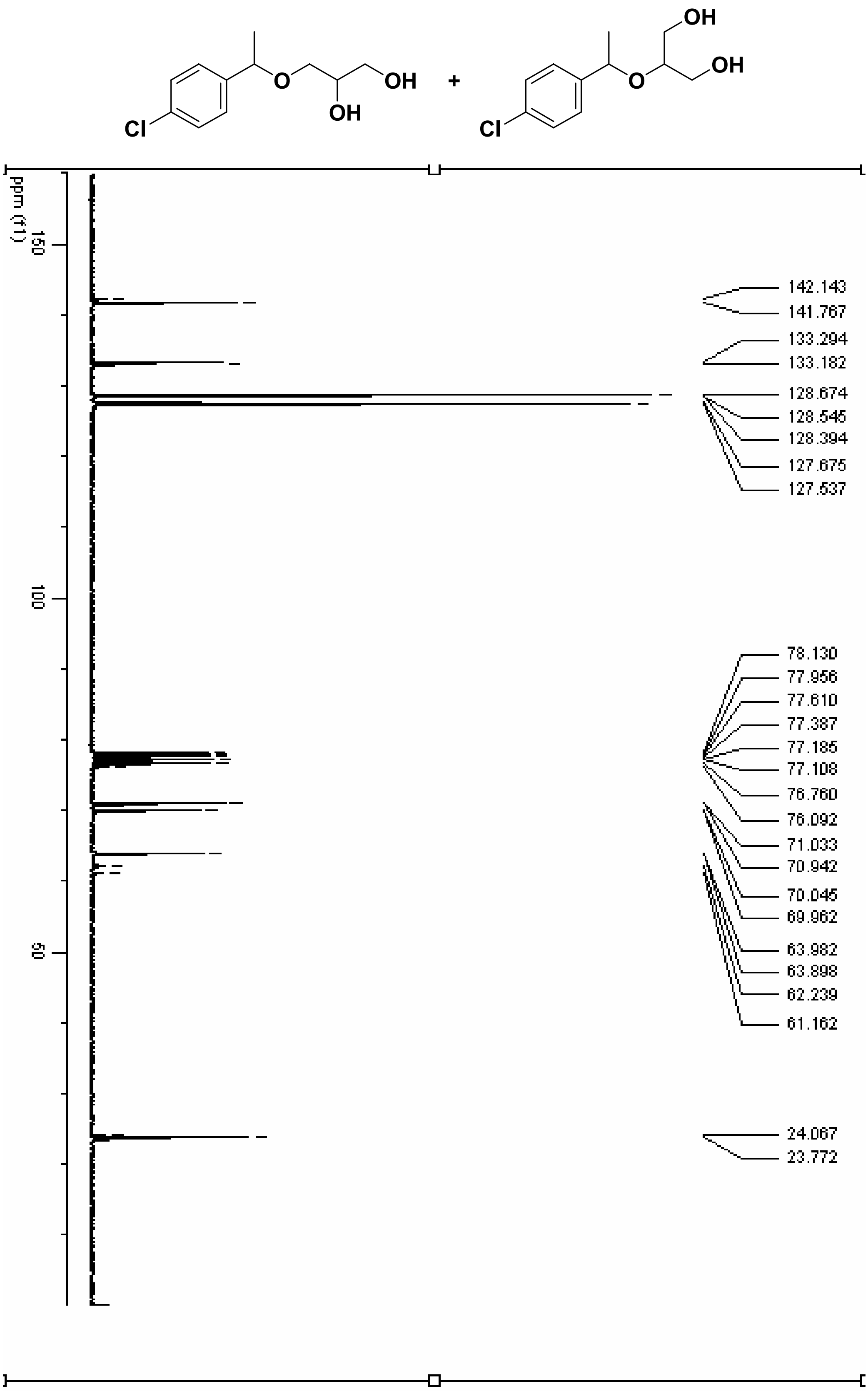
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77.610
77.387
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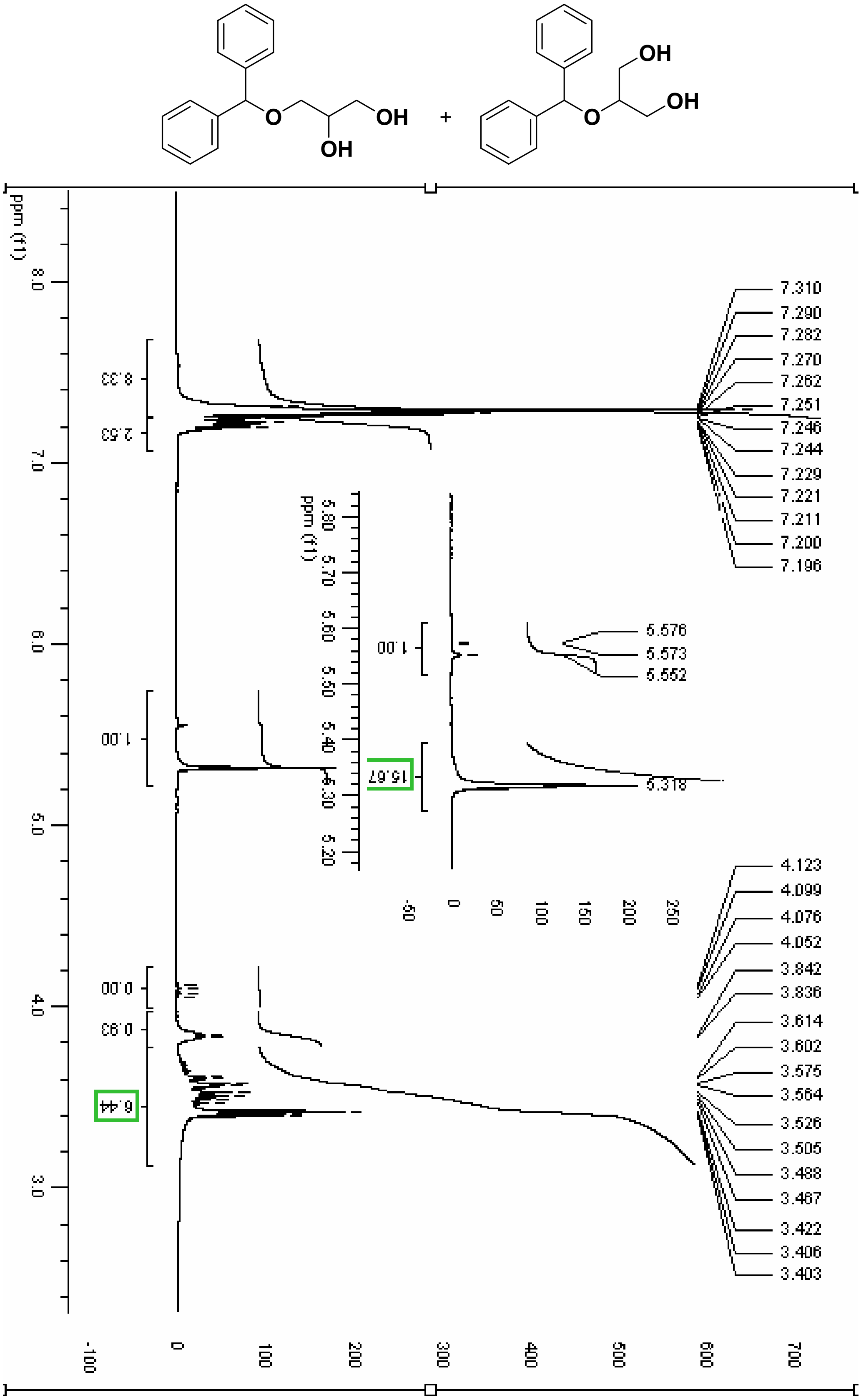
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O
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OH
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15.67
-100
0
100
200
300
400
500
600
700
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7.290
7.282
7.270
7.262
7.251
7.246
7.244
7.229
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7.200
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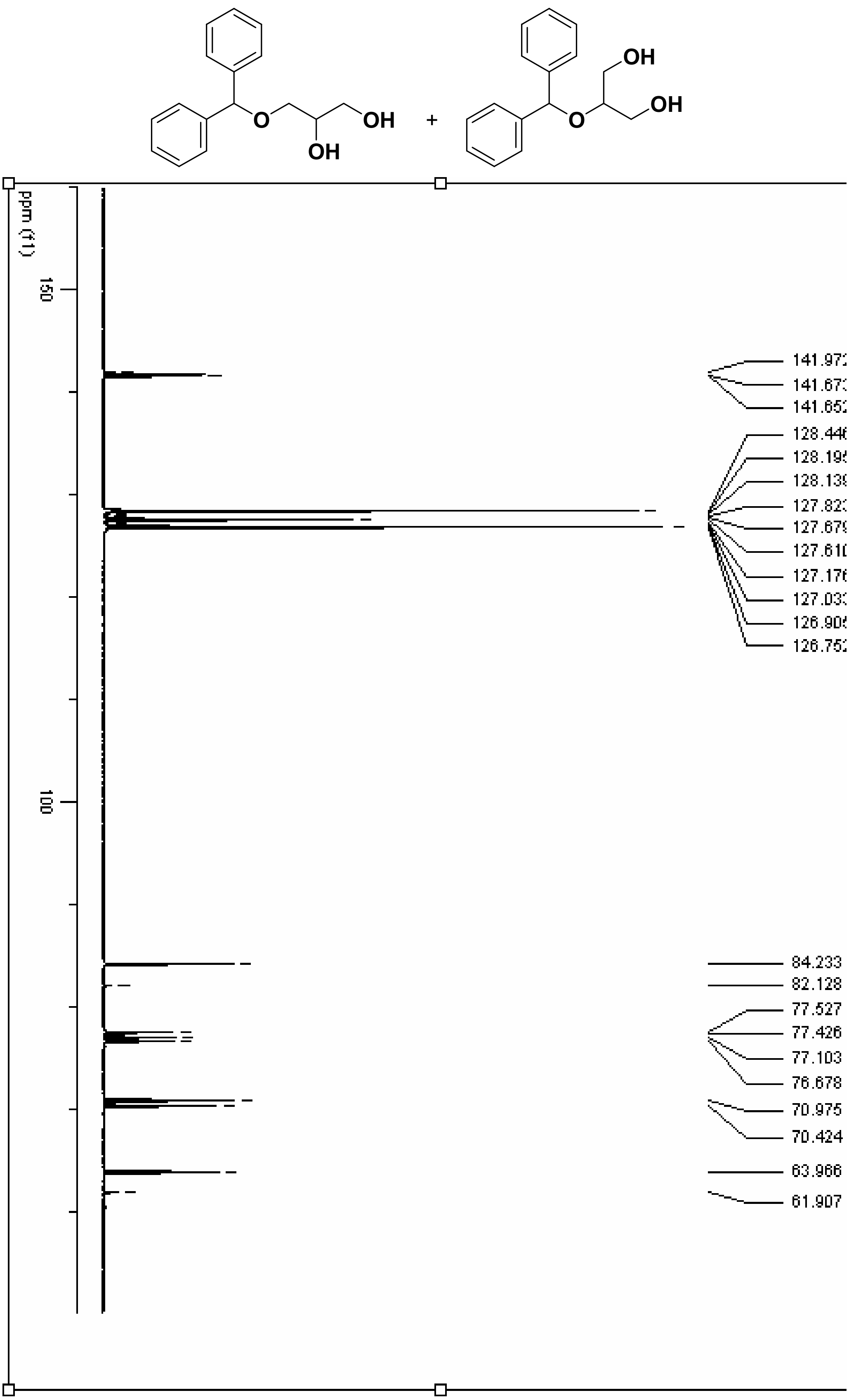

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128.13
127.82
127.67
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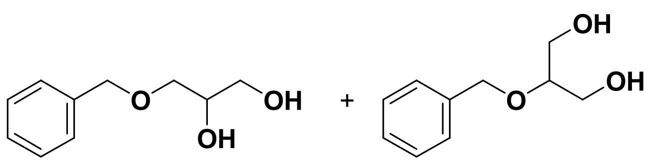
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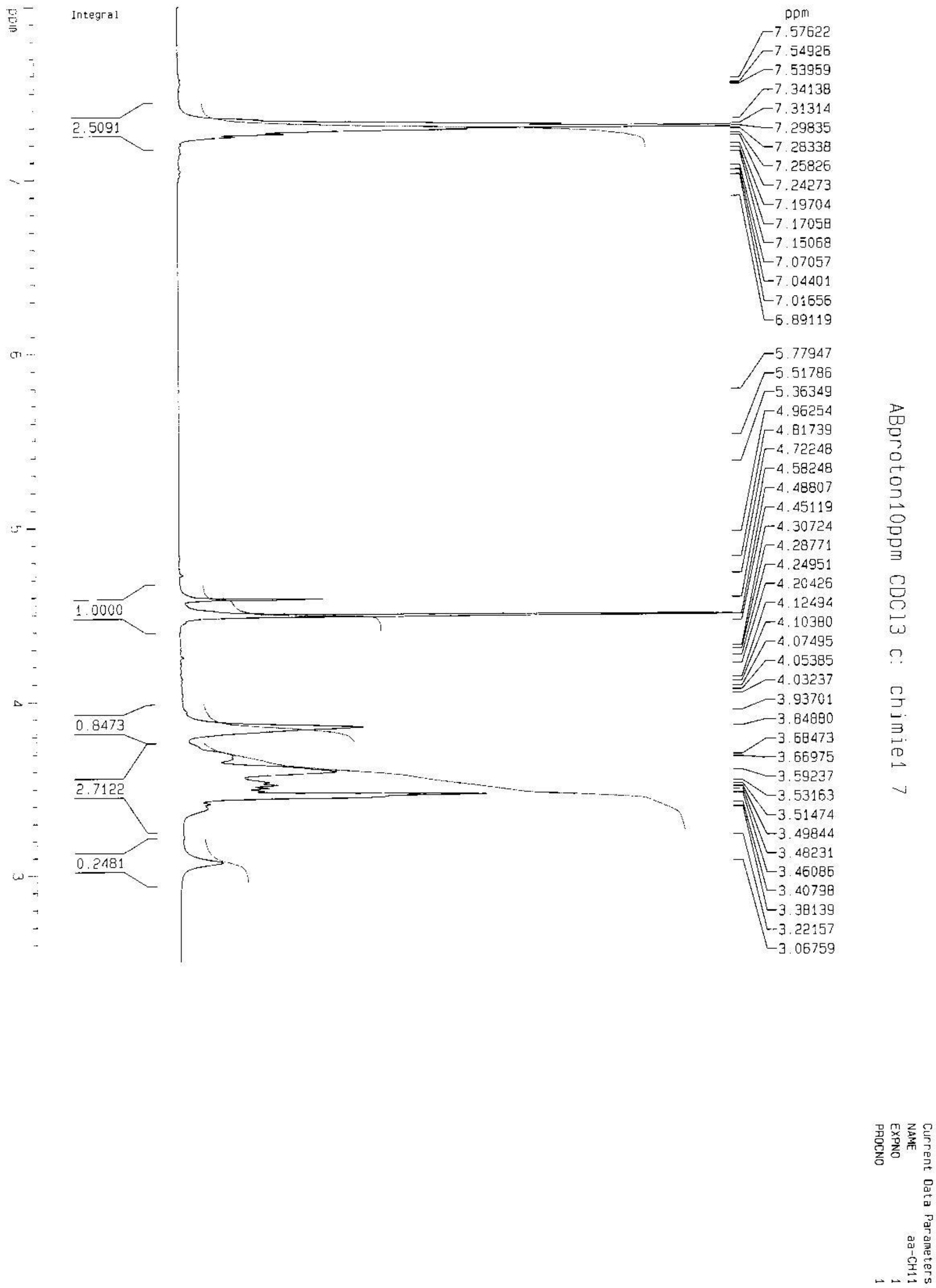
O
O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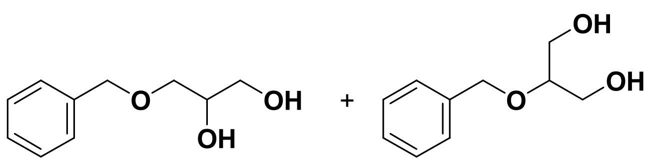
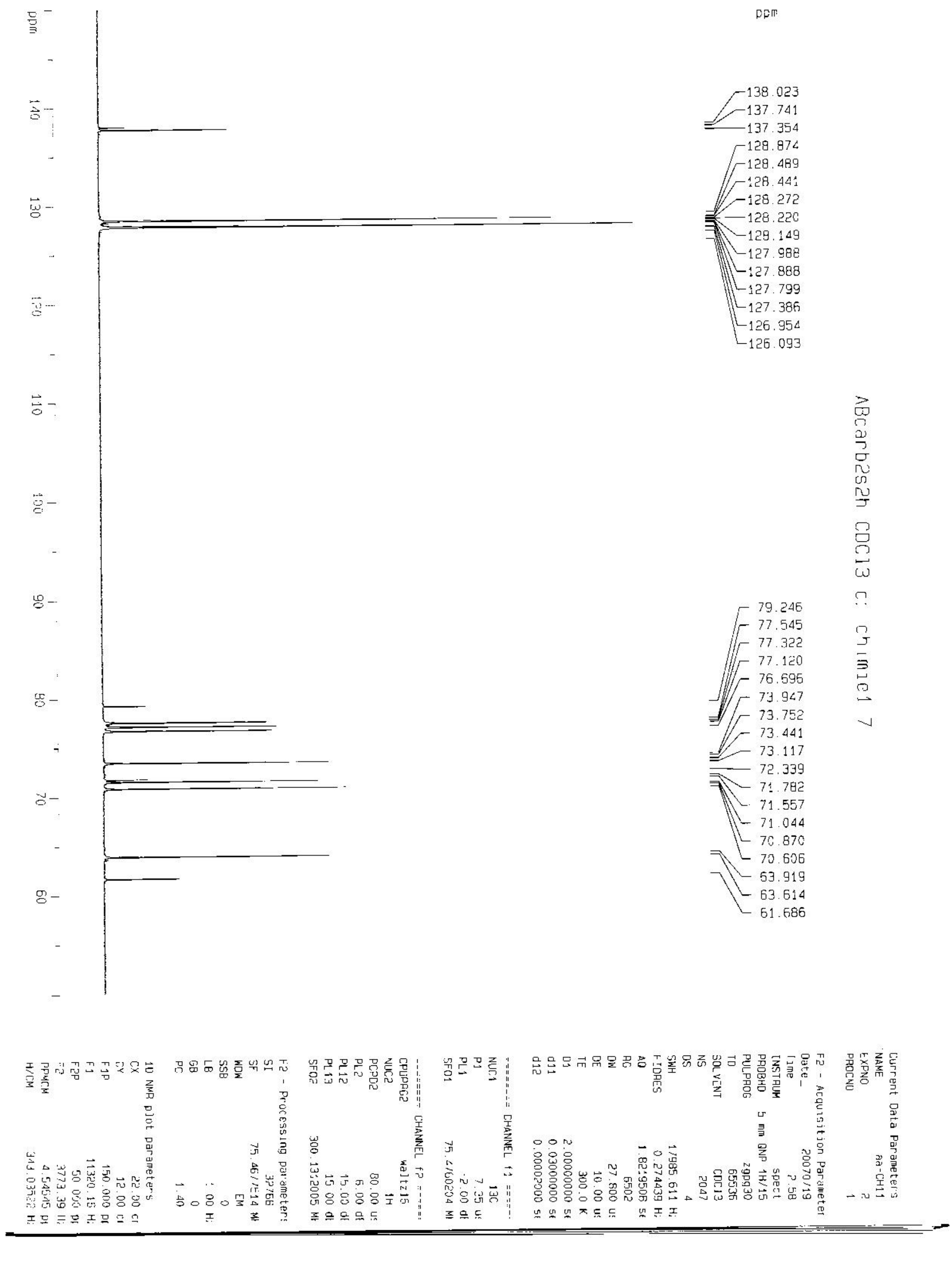
PROCNO 1

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126.954
126.093
79.246
77.545
77.322
77.120
76.696
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73.752
73.441
73.117
72.339
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61.686
ABcarb2s2h CDCl3 C: chimie1 7
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PROCNO 1
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TD 65536
SOLVENT CDCl3
NS 2047
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SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 6502
DW 27.800 usec
DE 10.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 7.35 usec
PL1 -2.00 dB
SFO1 75.4760204 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 6.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677514 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 22.00 cm
CY 12.00 cm
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F2P 50.000 ppm
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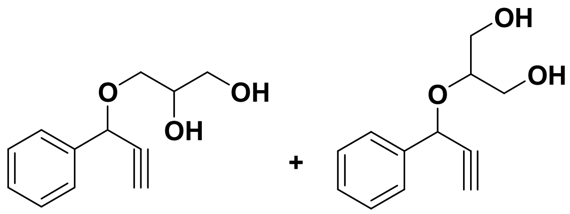

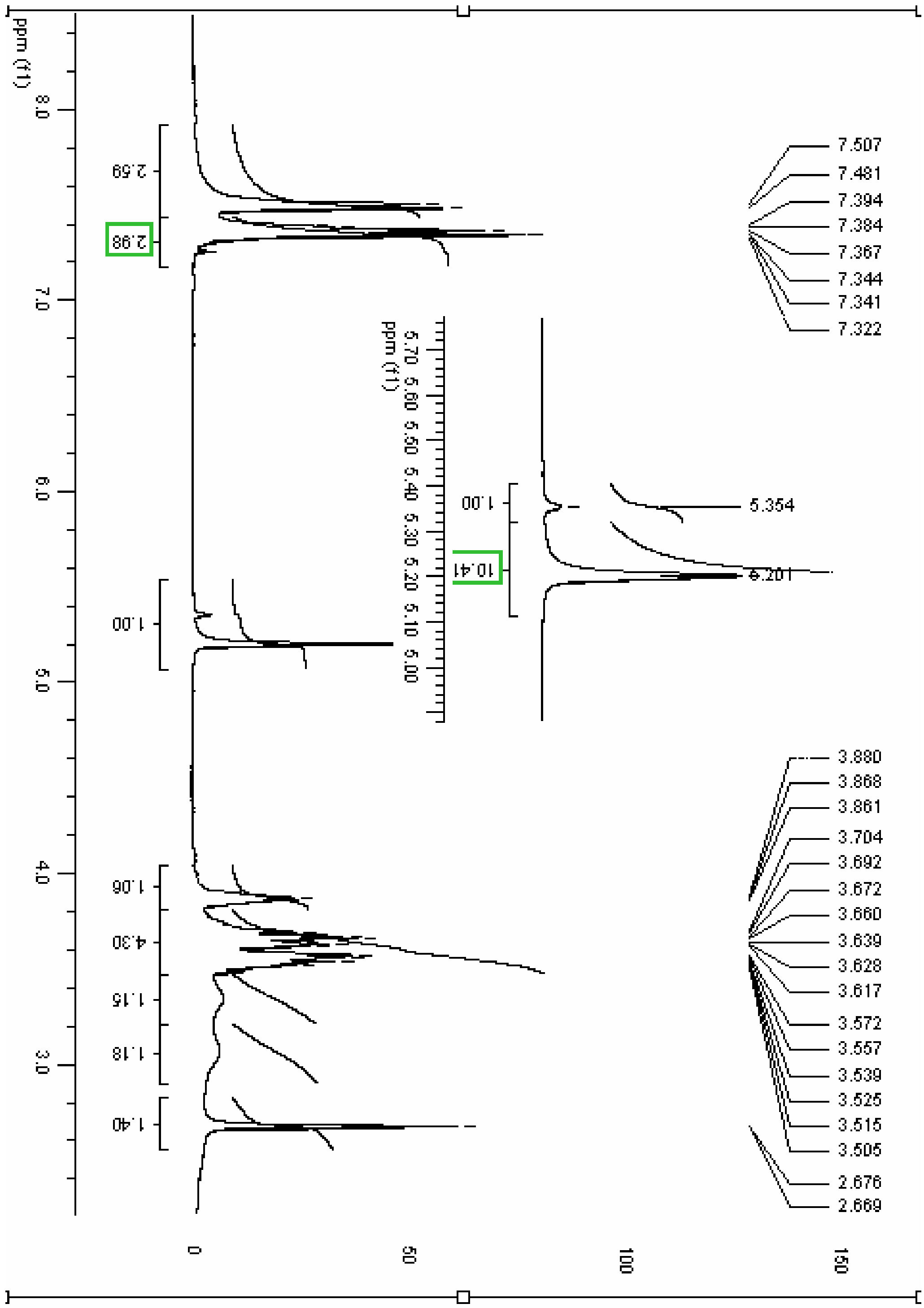
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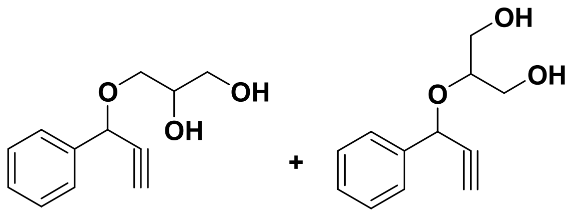
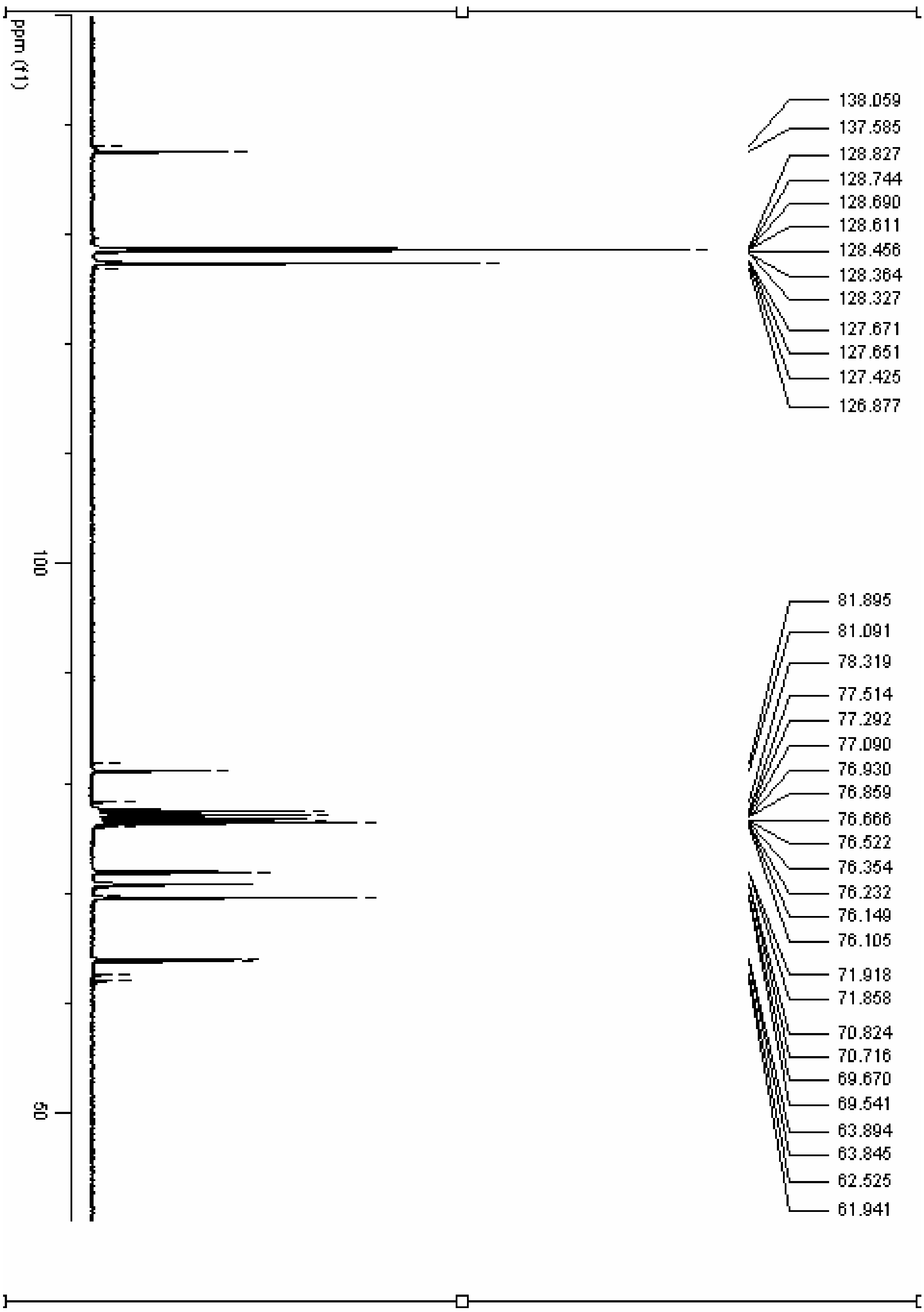
1.15
1.18
1.40
7.507
7.481
7.394
7.384
7.367
7.344
7.341
7.322
5.354
5.201
1.00
10.41
3.880
3.868
3.861
3.704
3.692
3.672
3.660
3.639
3.628
3.617
3.572
3.557
3.539
3.525
3.515
3.505
2.676
2.669
0
50
100
150



OH
OH
OH
O
+
OH
OH
O



ppm (f1)
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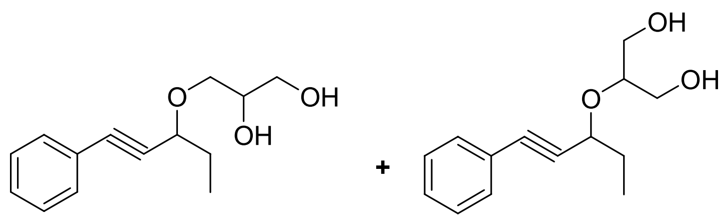
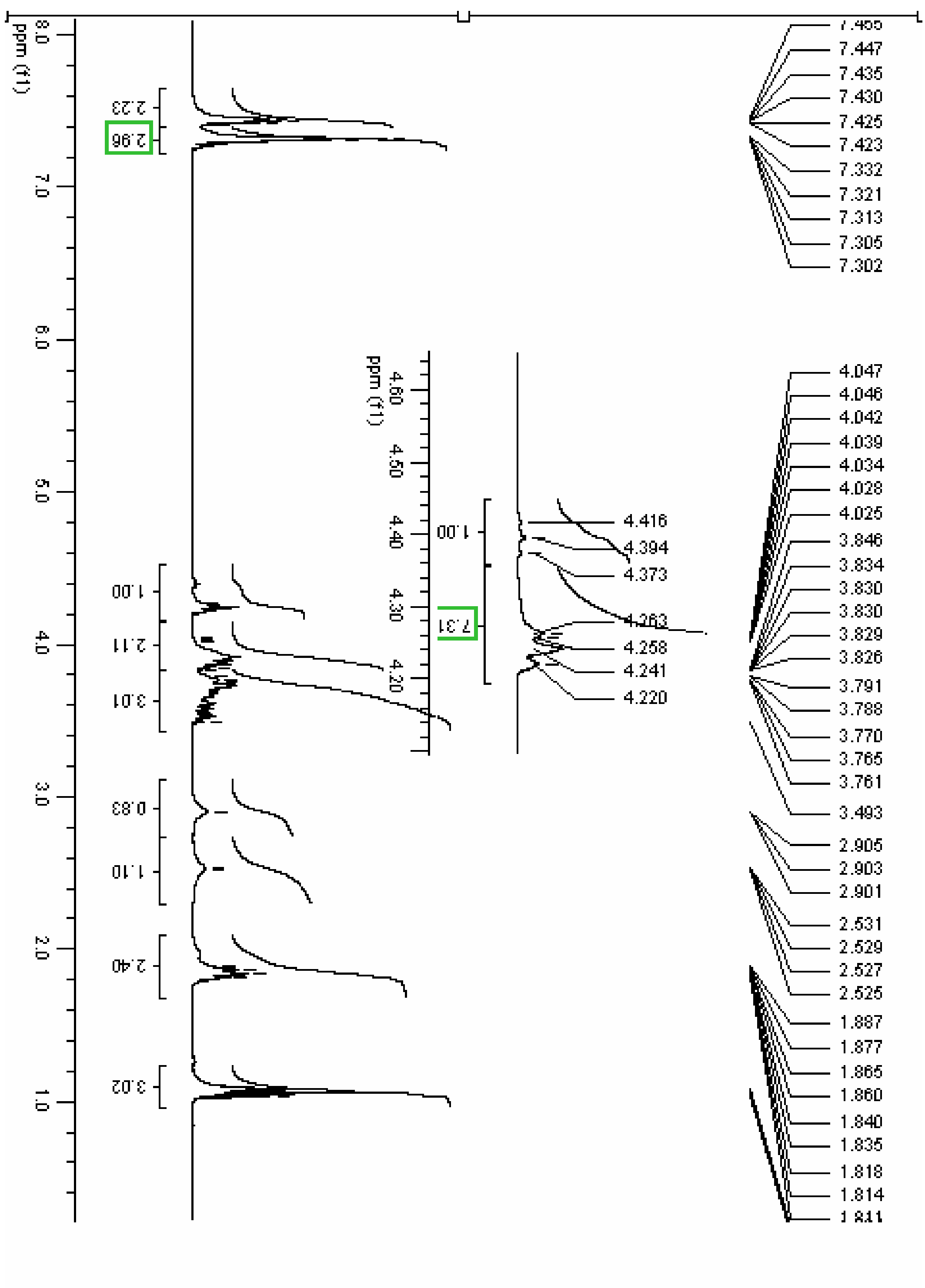
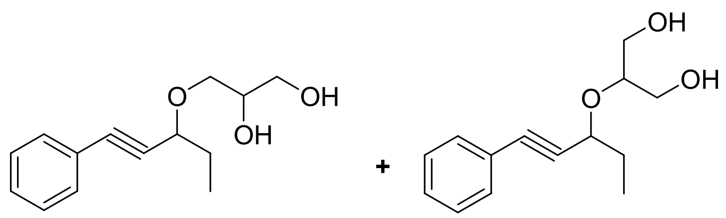
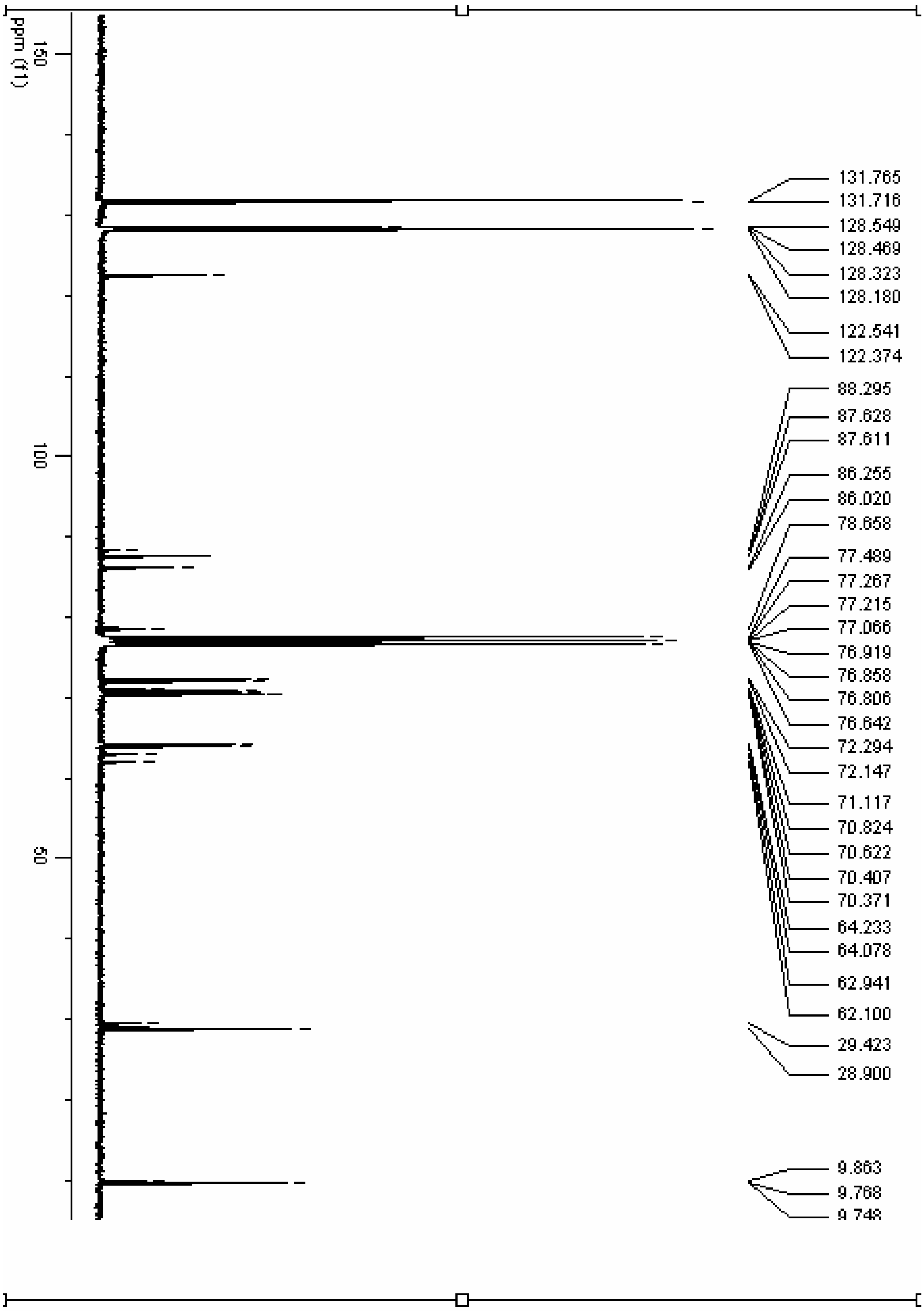
50
138.059
137.585
128.827
128.744
128.690
128.611
128.456
128.364
128.327
127.671
127.651
127.425
126.877
81.895
81.091
78.319
77.514
77.292
77.090
76.930
76.859
76.666
76.522
76.354
76.232
76.149
76.105
71.918
71.858
70.824
70.716
69.670
69.541
63.894
63.845
62.525
61.941




7.447
7.435
7.430
7.425
7.423
7.332
7.321
7.313
7.305
7.302
4.047
4.046
4.042
4.039
4.034
4.028
4.025
3.846
3.834
3.830
3.830
3.829
3.826
3.791
3.788
3.770
3.765
3.761
3.493
2.905
2.903
2.901
2.531
2.529
2.527
2.525
1.887
1.877
1.865
1.860
1.840
1.835
1.818
1.814
4.416
4.394
4.373
4.263
4.258
4.241
4.220
2.23
2.96
1.00
2.11
3.01
0.83
1.10
2.40
3.02
1.00
7.31
ppm (f1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
4.60
4.50
4.40
4.30
4.20


OH
OH
O
+
OH
OH
O


ppm (f1)
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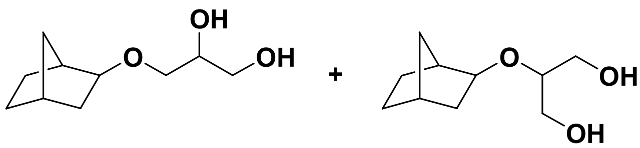
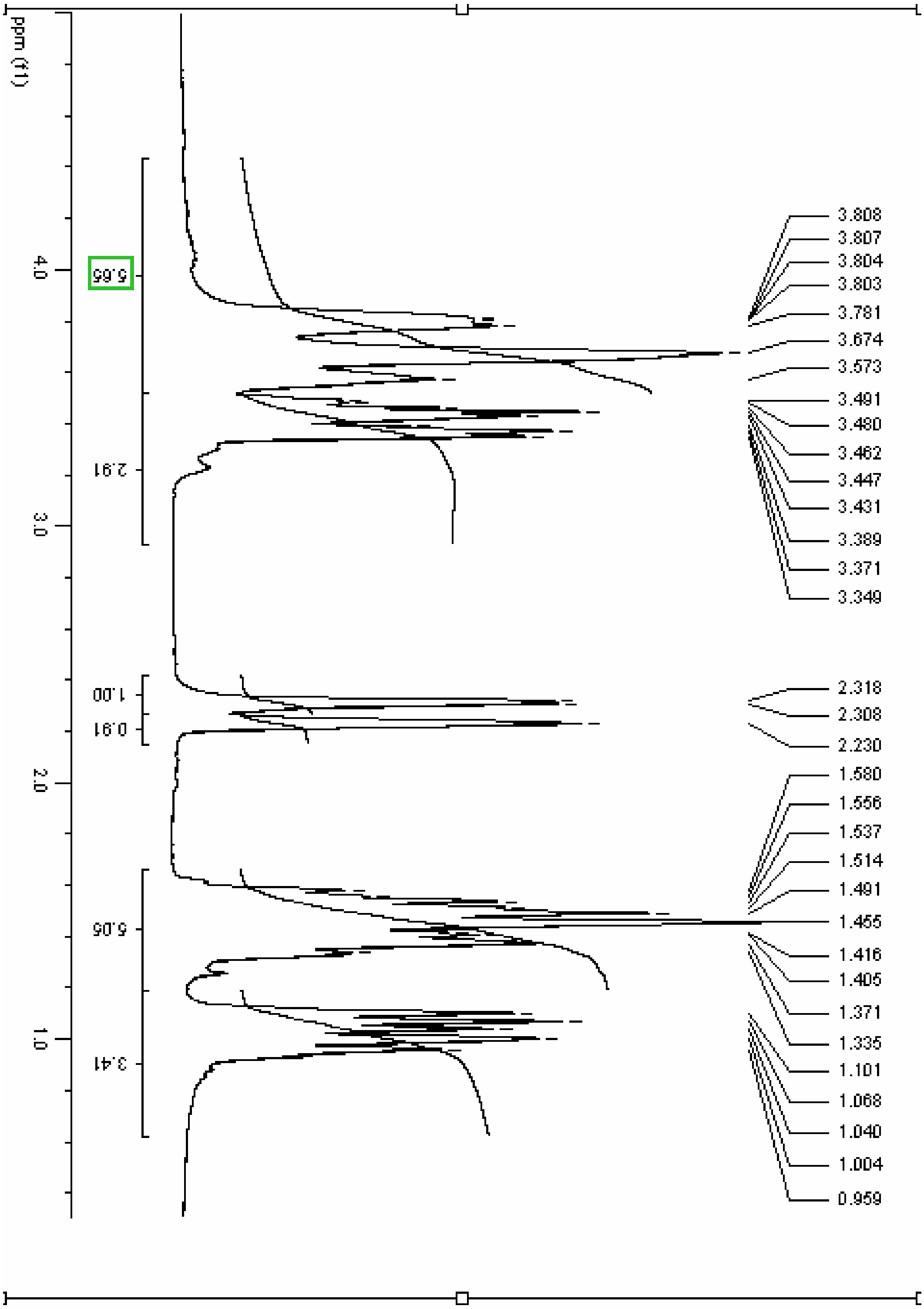
100
50
131.765
131.716
128.549
128.469
128.323
128.180
122.541
122.374
88.295
87.628
87.611
86.255
86.020
78.658
77.489
77.267
77.215
77.066
76.919
76.858
76.806
76.642
72.294
72.147
71.117
70.824
70.622
70.407
70.371
64.233
64.078
62.941
62.100
29.423
28.900
9.863
9.768
9.748


OH
O
OH
+
O
OH
OH


ppm (f1)
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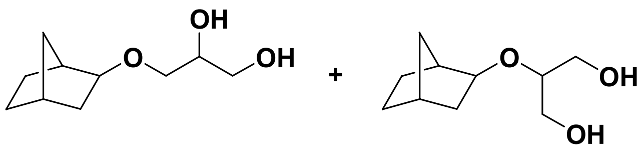
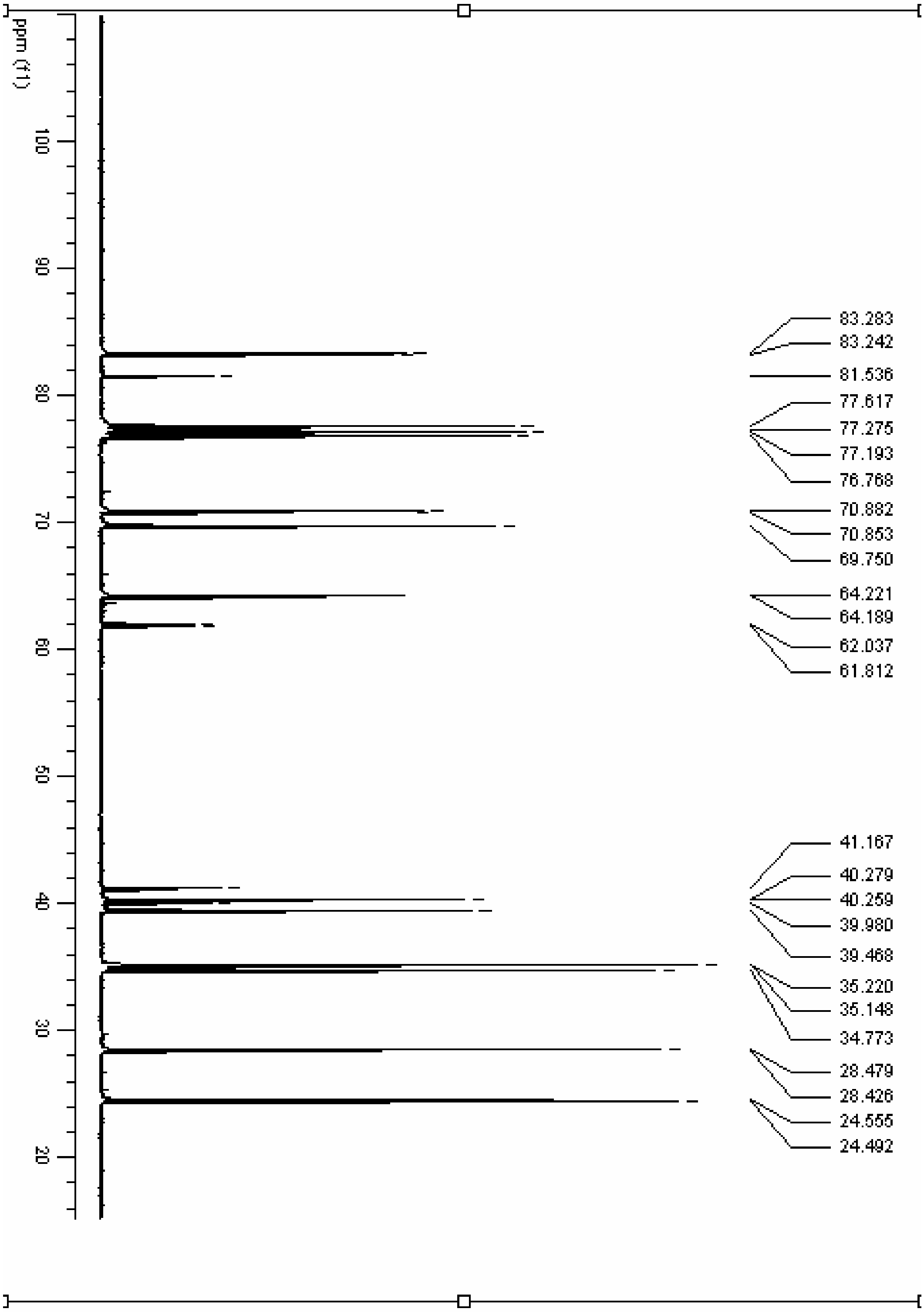
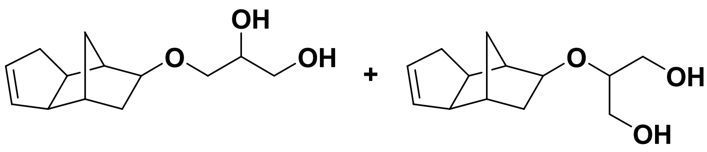
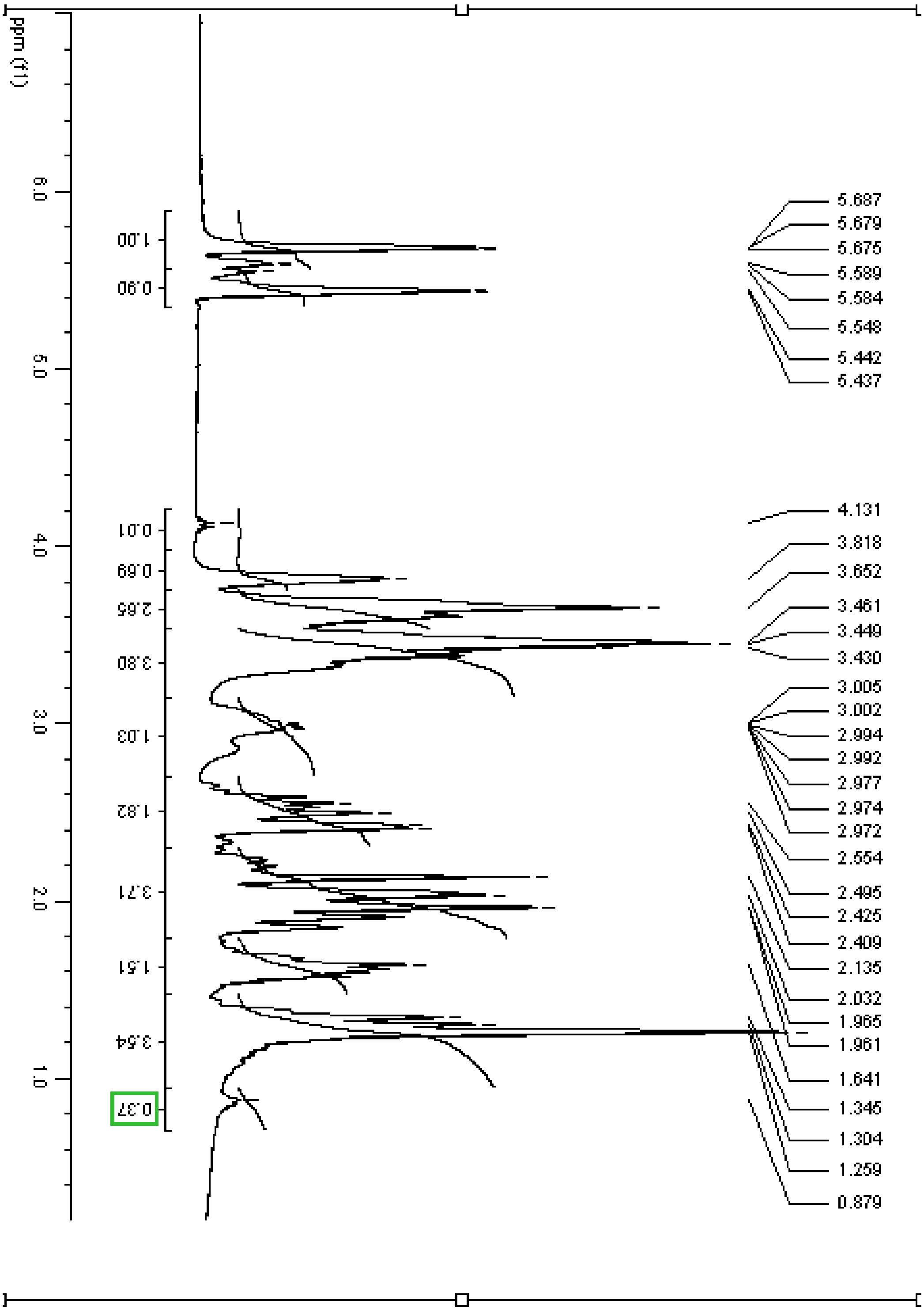
3.0
2.0
1.0
5.65
2.91
1.00
0.91
5.06
3.41
3.808
3.807
3.804
3.803
3.781
3.674
3.573
3.491
3.480
3.462
3.447
3.431
3.389
3.371
3.349
2.318
2.308
2.230
1.580
1.556
1.537
1.514
1.491
1.455
1.416
1.405
1.371
1.335
1.101
1.068
1.040
1.004
0.959

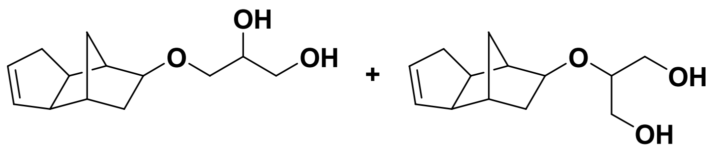

OH
OH
O
+
O
OH
OH


ppm (f1)
100
90
80
70
60
50
40
30
20
83.283
83.242
81.536
77.617
77.275
77.193
76.768
70.882
70.853
69.750
64.221
64.189
62.037
61.812
41.167
40.279
40.259
39.980
39.468
35.220
35.148
34.773
28.479
28.426
24.555
24.492

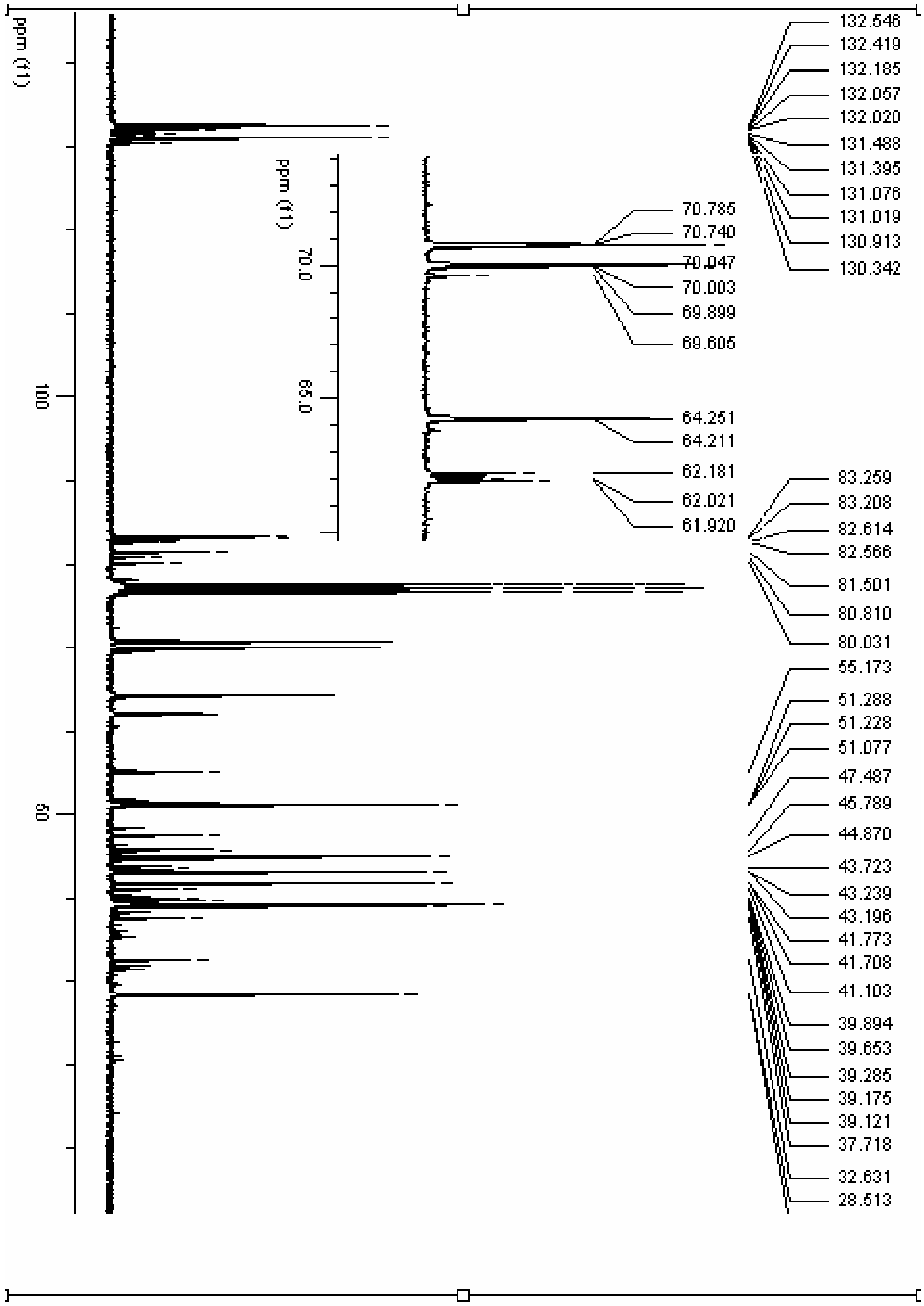


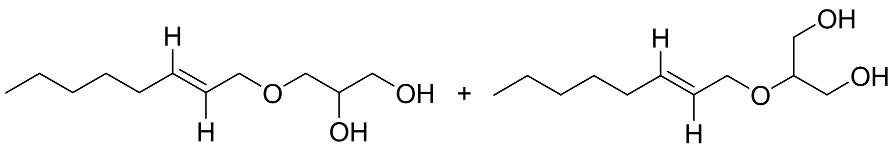
+ diastereoisomers and epimers

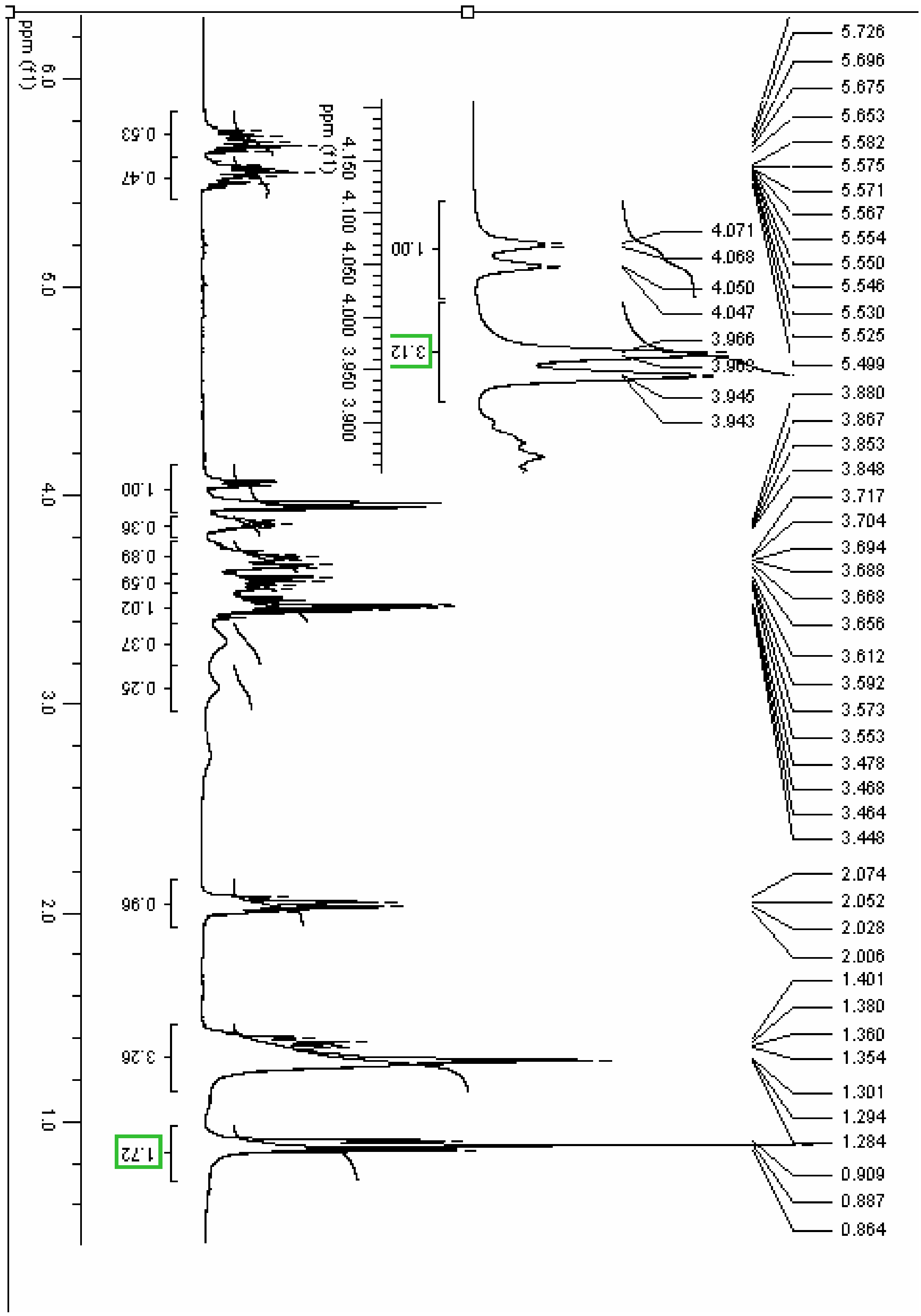




+ diastereoisomers and epimers




OH
OH
OH
OH
+


ppm (f1)
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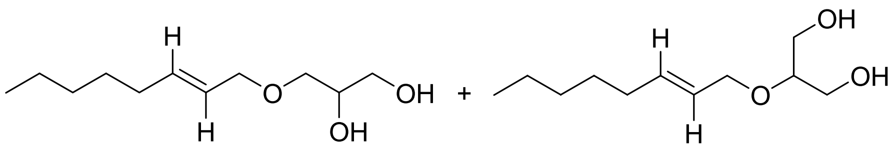
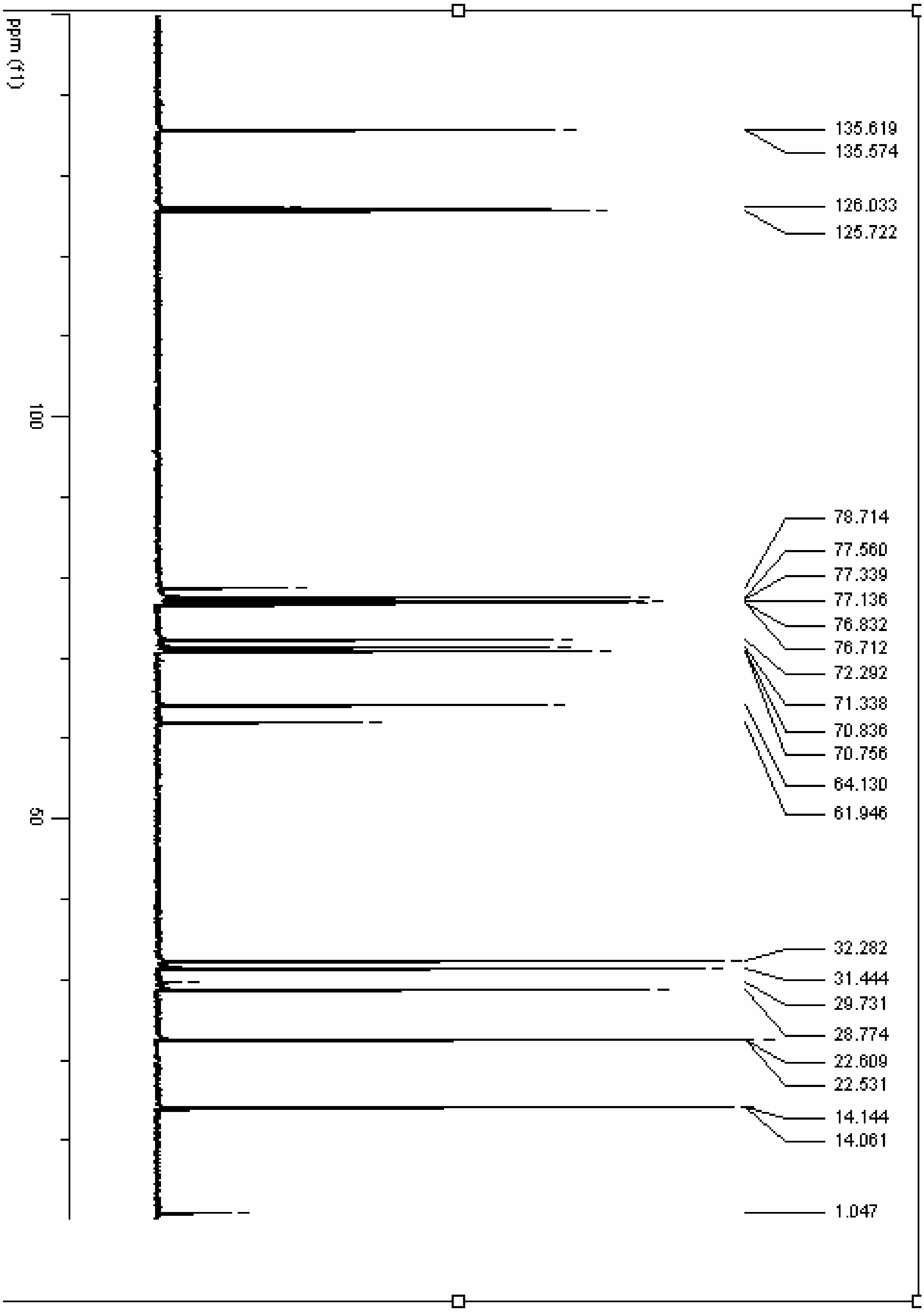
5.0
4.0
3.0
2.0
1.0
0.53
0.47
1.00
0.36
0.89
0.69
1.02
0.37
0.25
0.96
3.26
1.72
3.12
4.150 4.100 4.050 4.000 3.950 3.900
4.071
4.068
4.050
4.047
3.966
3.963
3.945
3.943
5.726
5.696
5.675
5.653
5.582
5.575
5.571
5.567
5.554
5.550
5.546
5.530
5.525
5.499
3.880
3.867
3.853
3.848
3.717
3.704
3.694
3.688
3.668
3.656
3.612
3.592
3.573
3.553
3.478
3.468
3.464
3.448
2.074
2.052
2.028
2.006
1.401
1.380
1.360
1.354
1.301
1.294
1.284
0.909
0.887
0.864


H
H
O
OH
OH
+
H
H
O
OH
OH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126.033
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77.339
77.136
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76.712
72.292
71.338
70.836
70.756
64.130
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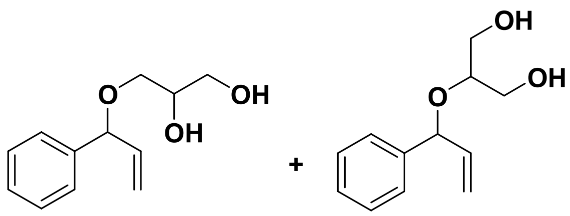
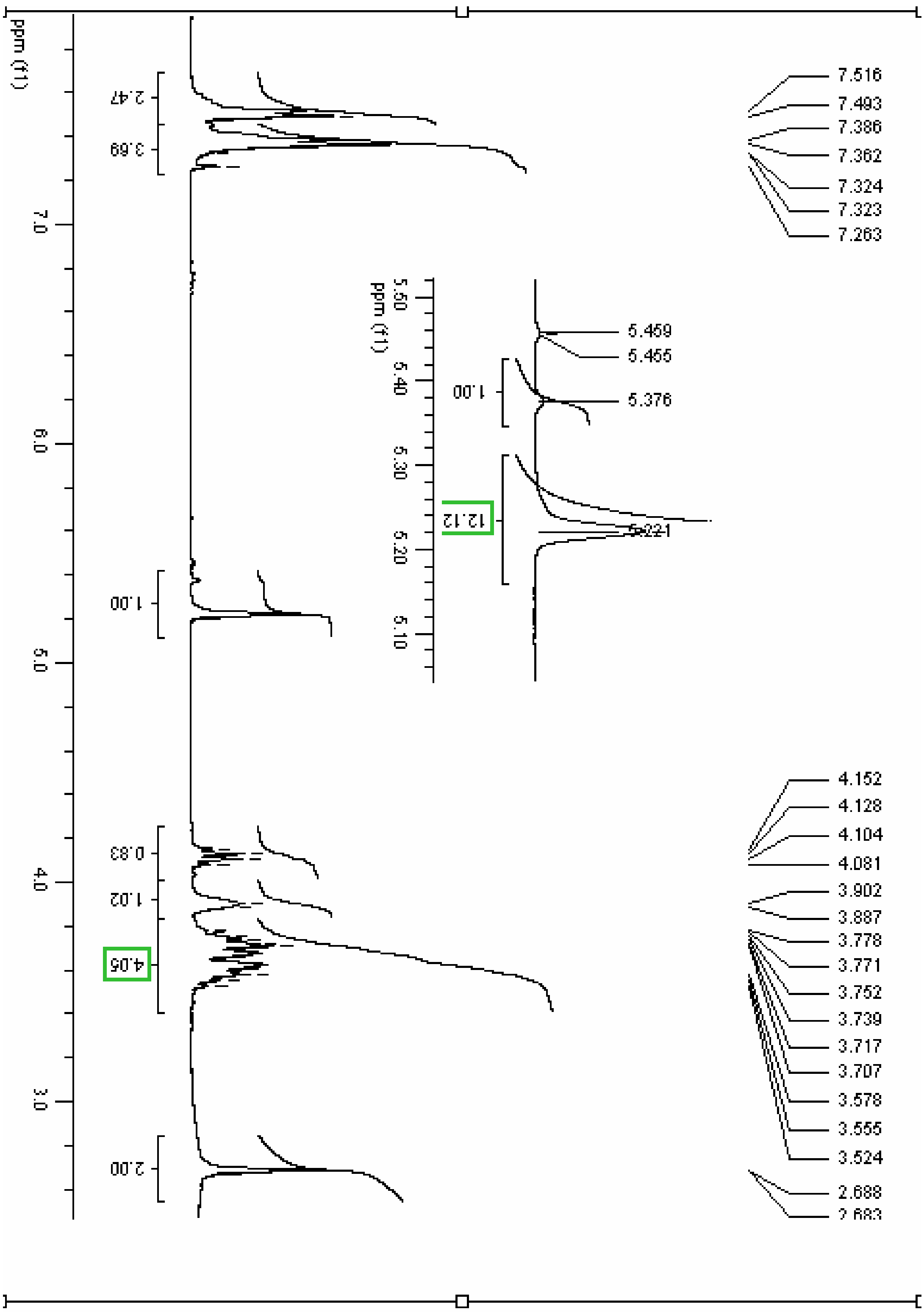
32.282
31.444
29.731
28.774
22.609
22.531
14.144
14.061
1.047


OH
OH
O
OH
+
O
OH
OH


ppm (f1)
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6.0
5.0
4.0
3.0
2.47
3.69
1.00
0.83
1.02
4.06
2.00
7.516
7.493
7.386
7.362
7.324
7.323
7.263
5.459
5.455
5.376
5.221
1.00
12.12
5.60
5.40
5.30
5.20
5.10
4.152
4.128
4.104
4.081
3.902
3.887
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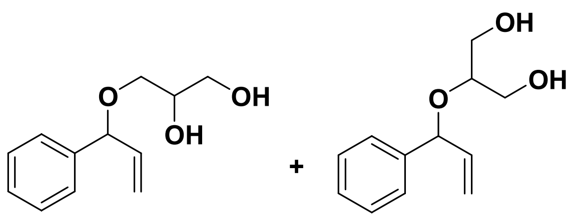
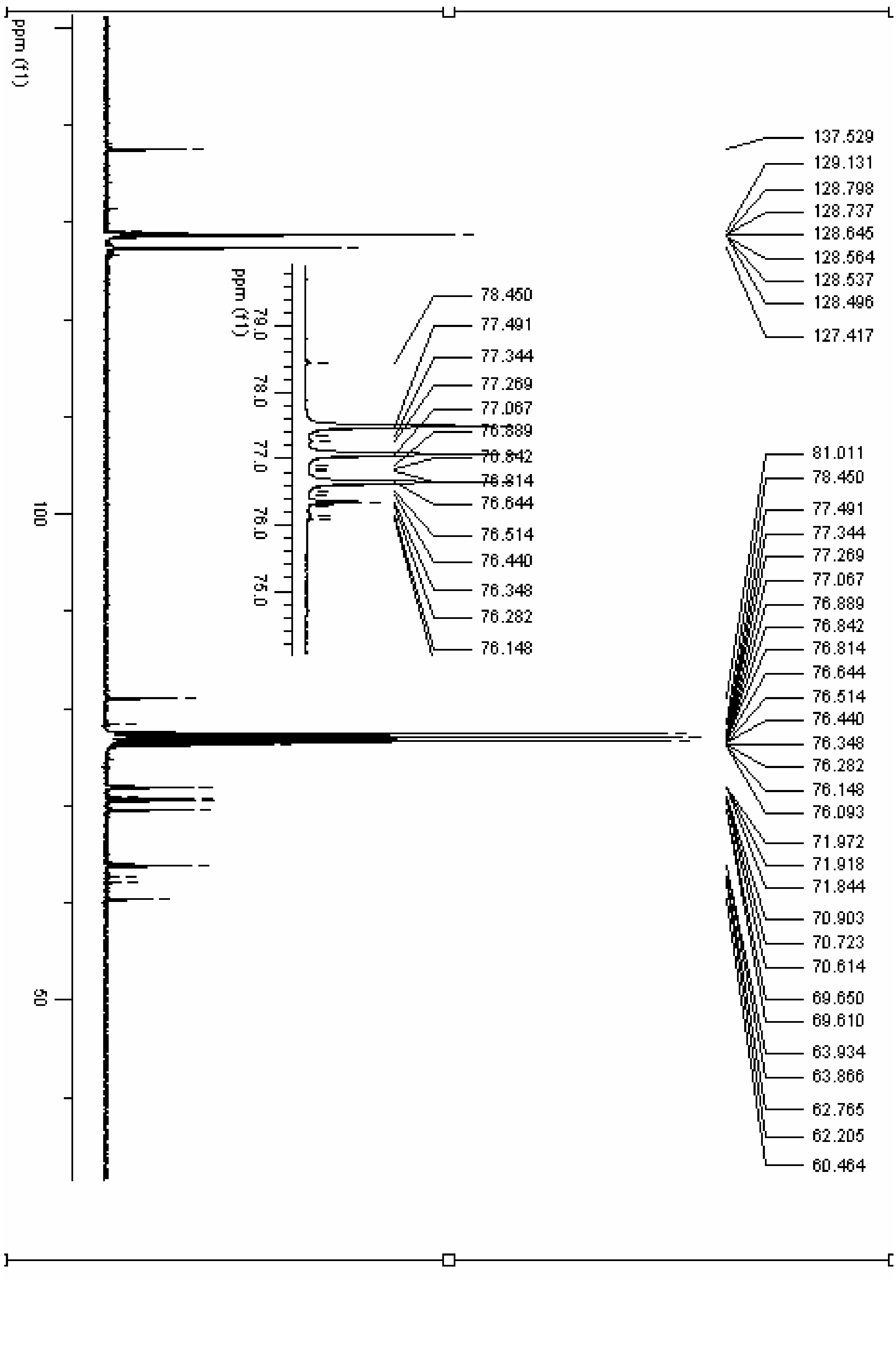
3.752
3.739
3.717
3.707
3.578
3.555
3.524
2.688
2.683


O
OH
OH
+
OH
O
OH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128.537
128.496
127.417
78.450
77.491
77.344
77.269
77.067
76.889
76.842
76.814
76.644
76.514
76.440
76.348
76.282
76.148
81.011
78.450
77.491
77.344
77.269
77.067
76.889
76.842
76.814
76.644
76.514
76.440
76.348
76.282
76.148
76.093
71.972
71.918
71.844
70.903
70.723
70.614
69.650
69.610
63.934
63.866
62.765
62.205
60.464
ppm (f1)
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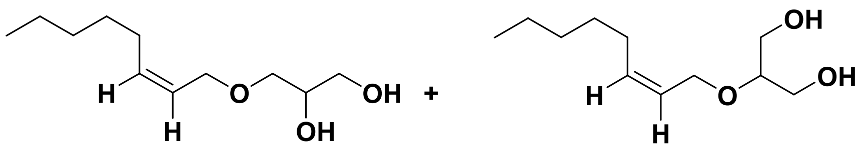
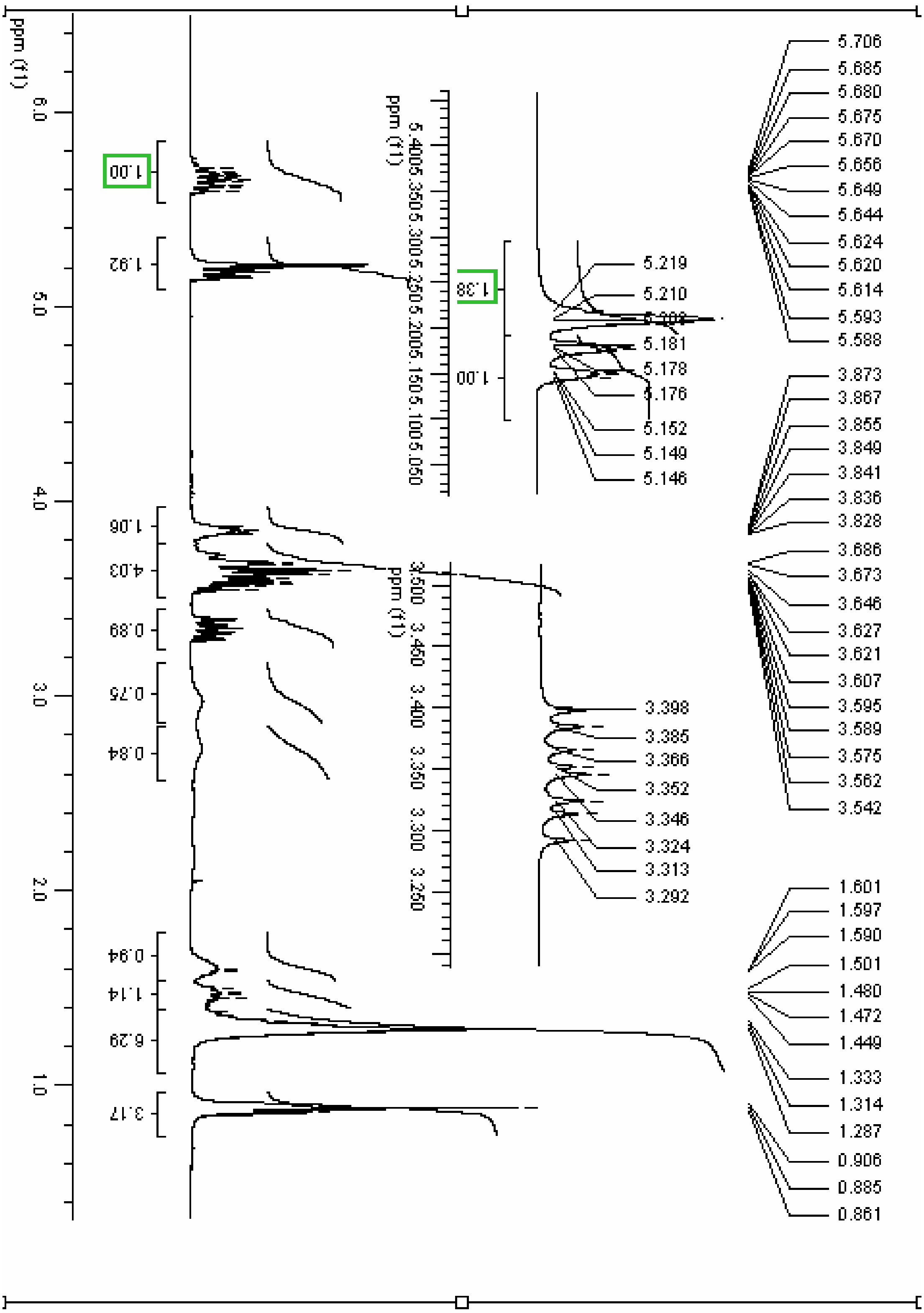
77.0
76.0
75.0




ppm (f1)
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4.0
3.0
2.0
1.0
1.00
1.92
1.06
4.03
0.89
0.75
0.84
0.94
1.14
6.29
3.17
1.38
1.00
5.706
5.685
5.680
5.675
5.670
5.656
5.649
5.644
5.624
5.620
5.614
5.593
5.588
5.219
5.210
5.181
5.178
5.176
5.152
5.149
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3.873
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3.686
3.673
3.646
3.627
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3.589
3.575
3.562
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3.385
3.366
3.352
3.346
3.324
3.313
3.292
1.601
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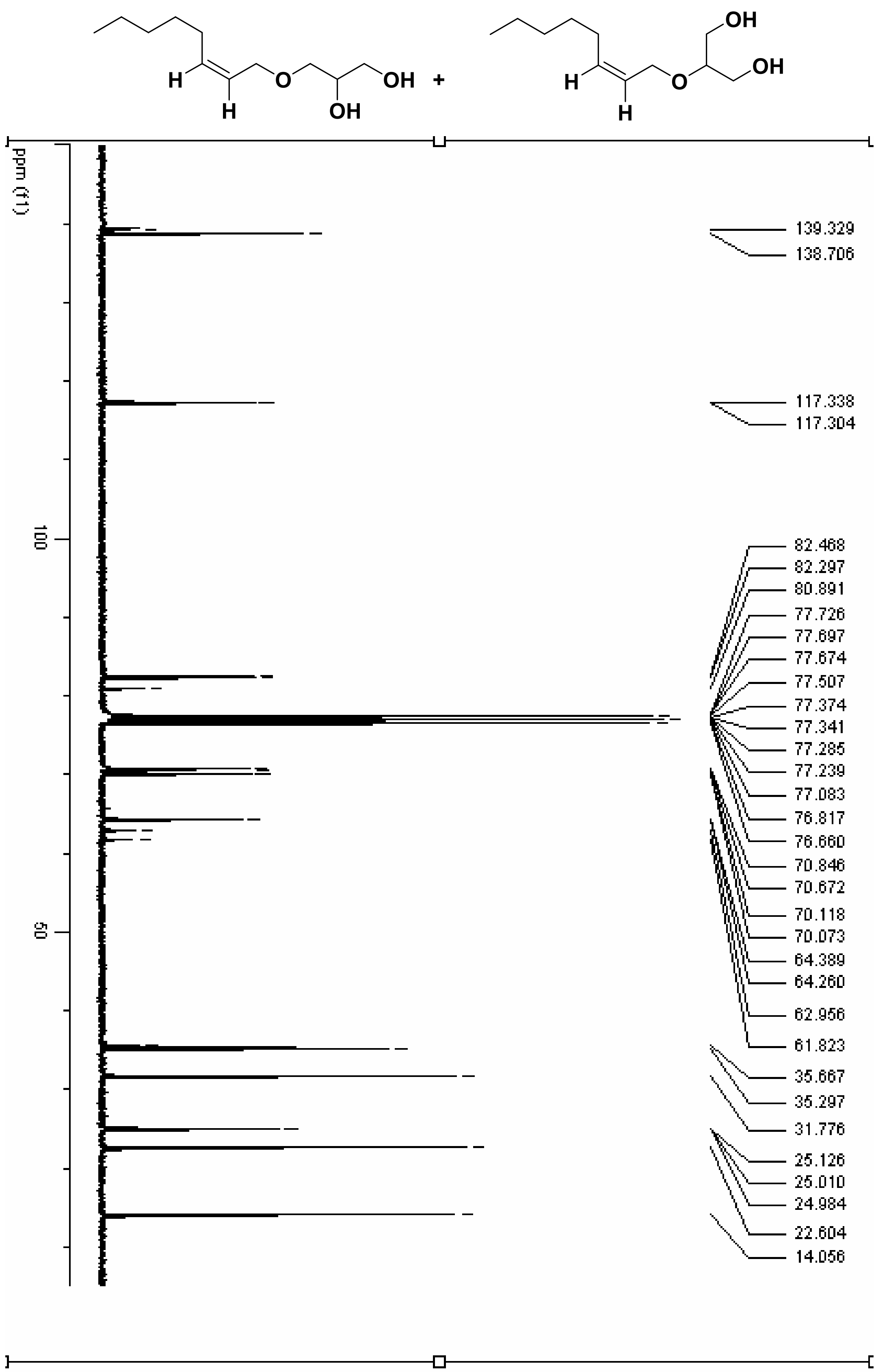

H
H
O
OH
OH
+
H
H
O
OH
OH
ppm (f1)
100
50
139.329
138.706
117.338
117.304
82.468
82.297
80.891
77.726
77.697
77.674
77.507
77.374
77.341
77.285
77.239
77.083
76.817
76.660
70.846
70.672
70.118
70.073
64.389
64.260
62.956
61.823
35.667
35.297
31.776
25.126
25.010
24.984
22.604
14.056