

Direct synthesis of 1-*O*-alkyl (di)glycerolethers from methyl esters and triglycerides by catalytic transesterification and reductive alkylation

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SUPPORTING INFORMATION

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Experimental

General

All reagents were used as received from the chemical company. Glycerol, 99 %, *Reagentplus®* was purchased from Sigma-Aldrich, Diglycerol 80 % from TCI, Pd/C (5%) on activated carbon, reduced and dry (Escat 1431) from Strem Chemicals. Oleic sunflower refined oil ($\geq 90\%$) was provided by our industrial partner and was used without further purification. Amberlyst 15 dry, Amberlyst 36 dry, Amberlyst 35 dry, were bought from Rohm and Haas and the methyl esters were supplied by Acros, Sigma-Aldrich, Alfa Aesar and TCI. The concentration of acid site for each resin used in our report; amberlyst 35 dry (5 eq./Kg), amberlyst 36 dry (5.4 eq./Kg) and amberlyst 15 dry (4.7 eq./Kg). All reagents and reactants were used without further purification. All reductive alkylation reactions were performed in a 300 ml steel Parr autoclave equipped with a mechanical stirrer.

^1H NMR and ^{13}C NMR spectra were recorded on a BRUKER DRX 300 or BRUKER ALS 300 (^1H 300 MHz, ^{13}C 75 MHz) in CDCl_3 (except when mentioned) and chemical shifts are given in ppm. J values are given in Hertz (Hz). Abbreviations are defined as follows: br = broad singlet, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quadruplet, m = multiplet.

IR spectra were recorded on a Spectro Nicolet IS10 Smart ITR with an ATR diamond.

The HRMS-ESI mass spectra were recorded in positive-ion mode on a hybrid quadrupole time-of-flight mass spectrometer (MicroTOFQ-II, Bruker Daltonics, Bremen) with an Electrospray Ionization (ESI) ion source. The flow of spray gas was at 0.6 bar and the capillary voltage was 4.5kV. The solutions were infused at $180\mu\text{L}/\text{h}$ in a mixture of solvents (methanol / dichloromethane / water 45/40/15). The mass range of the analysis was 50-1000m/z and the calibration was done with sodium formate. The HRMS-CI mass spectra were recorded on a double-focusing mass spectrometer (ThermoFinnigan MAT95XL, Bremen, Germany) equipped with a chemical ionization (CI) source. The reagent gas was isobutene and the calibrations for high resolution mass spectra were done with perfluorotrybutylamine (FC43).

Catalyst preparation for the transesterification reactions

The BaO/ Al_2O_3 catalyst was prepared by incipient-wetness impregnation method according the following procedure:ⁱ The Al_2O_3 support was obtained after calcination of basic γ - Al_2O_3 (surface area $\geq 150\text{ m}^2/\text{g}$; Strem Chemicals) at 600 °C for 2h. The barium precursor, $\text{Ba}(\text{NO}_3)_2$, was purchased from Sigma-Aldrich. Alumina impregnation of barium nitrate was performed in two steps (10 wt% of BaO each time), due to its limited solubility in water. In an open reactor with a magnetic stirrer, 1 g of barium nitrate (3.83 mmol) was dissolved in 5.07 g of demineralized water at 80 °C. Then, 5.31 g of alumina (52.1 mmol) was added to the solution. The resulting gel was dried at 120 °C for 3h. A second impregnation of barium

nitrate at 80 °C on the resulting powder was performed following the same procedure before being dried at 120 °C for 3h under reduced pressure. Finally, powder was calcinated at 500 °C for 2h to obtain BaO (22 %) /Al₂O₃ (78 %).

General procedure for reductive alkylation of glycerol with a methyl ester or a monoglyceride using H₂ as a reducing agent

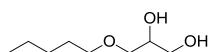
Glycerol (713 mmol, 40 eq.) and methyl ester or α-monoglyceride (17.6 mmol, 1 eq.) were mixed in a 300 ml steel autoclave at room temperature. CSA or Amberlyst 35 (10 wt %) and Pd/C (1 mol % Pd) were then added. The autoclave was first flushed with argon then with hydrogen four times. The solution was stirred (800 rpm) at 120 °C under 50 bar hydrogen for 16 h. After reaction, the medium was dissolved in absolute ethanol and filtered (Millipore Durapore filter 0.01 μm). The solvents were evaporated under reduced pressure and the organic products were extracted four times with dichloromethane or toluene. The crude products were finally purified by silica column chromatography (eluent: cyclohexane/ethyl acetate = 4:1~1:0 for short alkyl chain lengths; cyclohexane/ethyl acetate = 9:1~1:2 for long alkylchain length).

General procedure for transesterification of glycerol with methyl ester or triolein

Glycerol (350 mmol, 20 eq.) and methyl ester (17.5 mmol, 1 eq.) were added in a round bottom flask under inert atmosphere (argon). The mixture was heated to temperature and the mixed metal oxide BaO/Al₂O₃ was added (5 wt%). After 16h under heating and stirring, the reaction mixture was diluted in a minimum of ethanol absolute and filtered off (Millipore Durapore filter 0.01 μm). The solvents were evaporated under reduced pressure and the organic products were extracted three times with dichloromethane or toluene. The mixture was finally purified by silica column chromatography to afford the desired monoglyceride (eluent: cyclohexane/ethyl acetate = 4:1~1:0 for small alkylchains length; cyclohexane/ethyl acetate = 5:1~1:2 for long alkylchain length).

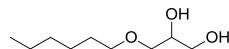
For the transesterification reactions of long alkyl chain methyl esters or triolein with glycerol and diglycerol, the reaction was performed in sealed reactors, under an inert atmosphere of argon. Monoolein **2g** was purified by silica column chromatography (eluent: cyclohexane/ethyl acetate = 5:1~1:2) and for the monoester of diglycerol **7g**, eluent was dichloromethane/methanol 99/1~9/1.

3-(pentyloxy)propane-1,2-diol [22636-32-4] (4a)



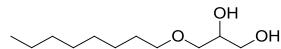
Colorless oil; ^1H NMR: δ = 0.88 (t, J = 7 Hz, 3H, CH_3), 1.28-1.32 (m, 4H, CH_2), 1.54-1.59 (m, 2H, CH_2), 2.65 (br, 2H, OH), 3.43-3.52 (m, 4H, CH_2), 3.59-3.71 (m, 2H, CH_2), 3.82-3.86 (m, 1H, CHOH); ^{13}C NMR: δ = 14.1 (CH_3), 22.6 (CH_2), 28.3 (CH_2), 29.4 (CH_2), 64.3 (CH_2), 70.7 (CHOH), 71.9 (CH_2), 72.5 (CH_2); IR (ATR): $\nu_{\text{max}} = 3373, 2931, 2861, 1458, 1110, 1041 \text{ cm}^{-1}$; HRMS-ESI: m/z [MNa] $^+$ calcd for $\text{C}_8\text{H}_{18}\text{NaO}_3$: 185.1148 found: 185.1147.

3-(hexyloxy)propane-1,2-diol [10305-38-1] (4b)



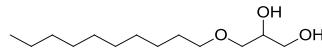
Colorless oil; ^1H NMR: δ = 0.88 (t, J = 6.8 Hz, 3H, CH_3), 1.25-1.35 (m, 6H, CH_2), 1.52-1.59 (m, 2H, CH_2), 2.25 (br, 2H, OH), 3.43-3.52 (m, 4H, CH_2), 3.61-3.74 (m, 2H, CH_2), 3.83-3.88 (m, 1H, CHOH); ^{13}C NMR: δ = 14.1 (CH_3), 22.6 (CH_2), 25.7 (CH_2), 29.5 (CH_2), 31.7 (CH_2), 64.1 (CH_2), 70.8 (CHOH), 71.8 (CH_2), 72.2 (CH_2); IR (ATR): $\nu_{\text{max}} = 3371, 2931, 2859, 1458, 1111, 1041 \text{ cm}^{-1}$; HRMS-ESI: m/z [MNa] $^+$ calcd for $\text{C}_9\text{H}_{20}\text{NaO}_3$: 199.1305 found: 199.1307.

3-(octyloxy)propane-1,2-diol [10438-94-5] (4c)



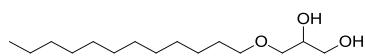
Colorless oil; ^1H NMR: δ = 0.88 (t, J = 6.7 Hz, 3H, CH_3), 1.25-1.35 (m, 10H, CH_2), 1.54-1.60 (m, 2H, CH_2), 2.51 (br, 2H, OH), 3.44-3.56 (m, 4H, CH_2), 3.61-3.74 (m, 2H, CH_2), 3.83-3.89 (m, 1H, CHOH); ^{13}C NMR: δ = 14.2 (CH_3), 22.7 (CH_2), 26.2 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 29.7 (CH_2), 31.9 (CH_2), 64.3 (CH_2), 70.7 (CHOH), 71.9 (CH_2), 72.5 (CH_2); IR (ATR): $\nu_{\text{max}} = 3378, 2924, 2855, 1458, 1378, 1112, 1042 \text{ cm}^{-1}$; HRMS-ESI: m/z [MNa] $^+$ calcd for $\text{C}_{11}\text{H}_{24}\text{NaO}_3$: 227.1618 found: 227.1624.

3-(decyloxy)propane-1,2-diol [10430-97-4] (4d)



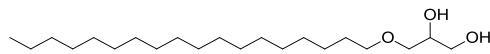
crystalline solid; Mp = < 44 °C; ^1H NMR: δ = 0.87 (t, J = 7 Hz, 3H, CH₃), 1.24-1.36 (m, 14H, CH₂), 1.54-1.60 (m, 2H, CH₂), 2.34 (br, 2H, OH), 3.44-3.55 (m, 4H, CH₂), 3.61-3.74 (m, 2H, CH₂), 3.82-3.87 (m, 1H, CHOH); ^{13}C NMR: δ = 14.2 (CH₃), 22.8 (CH₂), 26.1 (CH₂), 29.4 (CH₂), 29.5 (CH₂), 29.6 (CH₂), 29.7 (CH₂), 29.7 (CH₂), 32.0 (CH₂), 64.2 (CH₂), 70.8 (CHOH), 71.9 (CH₂), 72.3 (CH₂); IR (ATR): ν_{\max} = 3347, 2953, 2917, 2850, 1467, 1324, 1121, 1060 cm⁻¹; HRMS-ESI: m/z [MNa]⁺ calcd for C₁₃H₂₈NaO₃: 255.1931 found: 255.1925.

3-(dodecyloxy)propane-1,2-diol [1561-07-5] (4e)



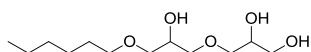
White crystalline solid; Mp = 46 °C; ^1H NMR: δ = 0.88 (t, J = 6.7 Hz, 3H, CH₃), 1.21-1.36 (m, 18H, CH₂), 1.54-1.60 (m, 2H, CH₂), 2.30 (br, 2H, OH), 3.44-3.56 (m, 4H, CH₂), 3.62-3.75 (m, 2H, CH₂), 3.83-3.89 (m, 1H, CHOH); ^{13}C NMR: δ = 14.2 (CH₃), 22.8 (CH₂), 26.2 (CH₂), 29.5 (CH₂), 29.6 (CH₂), 29.7 (CH₂), 29.7 (CH₂), 29.7 (CH₂), 29.8 (CH₂), 32.0 (CH₂), 64.3 (CH₂), 70.7 (CHOH), 71.9 (CH₂), 72.5 (CH₂); IR (ATR): ν_{\max} = 3351, 2954, 2917, 2850, 1469, 1325, 1122, 1094, 1060 cm⁻¹; HRMS-ESI: m/z [MNa]⁺ calcd for C₁₅H₃₂NaO₃: 283.2244 found: 283.2241.

3-(octadecyloxy)propane-1,2-diol [544-62-7] (4f)



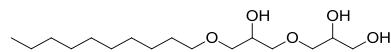
White crystalline solid; Mp = 73 °C; ^1H NMR: δ = 0.88 (t, J = 6.6 Hz, 3H, CH₃), 1.20-1.38 (m, 30H, CH₂), 1.55-1.60 (m, 2H, CH₂), 2.15 (br, 2H, OH), 3.44-3.56 (m, 4H, CH₂), 3.62-3.75 (m, 2H, CH₂), 3.83-3.88 (m, 1H, CHOH); ^{13}C NMR: δ = 14.2 (CH₃), 22.8 (CH₂), 26.2 (CH₂), 29.5 (CH₂), 29.6 (CH₂), 29.7 (CH₂), 29.7 (CH₂), 29.8 (CH₂), 29.8 (CH₂), 32.1 (CH₂), 64.3 (CH₂), 70.7 (CHOH), 72.0 (CH₂), 72.5 (CH₂); IR (ATR): ν_{\max} = 3358, 2954, 2916, 2849, 1471, 1327, 1120, 1060 cm⁻¹; HRMS-ESI: m/z [MNa]⁺ calcd for C₂₁H₄₄NaO₃: 367.3183 found: 367.3165.

3-(3-(hexyloxy)-2-hydroxypropoxy)propane-1,2-diol [146490-38-2] (6b)



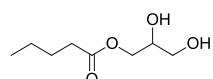
Colorless oil (Mixture of isomers); ^1H NMR: δ = 0.89 (t, J = 6.9 Hz, 3H, CH_3), 1.20-1.39 (m, 6H, CH_2), 1.54-1.60 (m, 2H, CH_2), 2.85 (br, 3H, OH), 3.43-3.75 (m, 10H, CH_2), 3.84-3.92 (m, 1H, CHOH), 3.94-4.00 (m, 1H, CHOH); ^{13}C NMR: δ = 14.1 (CH_3), 22.6 (CH_2), 25.8 (CH_2), 29.5 (CH_2), 31.7 (CH_2), 63.8 (CH_2), 69.4 (C^*HOH), 69.6 (C^*HOH), 70.9 (C^*HOH), 71.1 (C^*HOH), 71.8 (CH_2), 71.8 (CH_2), 72.8 (CH_2), 72.9 (CH_2), 73.1 (CH_2), 73.2 (CH_2); IR (ATR): ν_{max} = 3363, 2928, 2860, 1457, 1378, 1109, 1040 cm^{-1} ; HRMS-ESI: m/z [MNa] $^+$ calcd for $\text{C}_{12}\text{H}_{26}\text{NaO}_5$: 273.1672 found: 273.1668.

3-(3-(decyloxy)-2-hydroxypropoxy)propane-1,2-diol [88456-94-4] (6d)



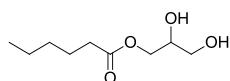
Colorless oil; (Mixture of isomers); ^1H NMR: δ = 0.88 (t, J = 6.7 Hz, 3H, CH_3), 1.20-1.39 (m, 14H, CH_2), 1.54-1.59 (m, 2H, CH_2), 2.42 (br, 1H, OH), 2.91 (br, 1H, OH), 3.25 (br, 1H, OH), 3.42-3.74 (m, 10H, CH_2), 3.87-3.92 (m, 1H, CHOH), 3.94-3.99 (m, 1H, CHOH); ^{13}C NMR: δ = 14.2 (CH_3), 22.7 (CH_2), 26.1 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.7 (CH_2), 31.9 (CH_2), 63.8 (CH_2), 69.4 (C^*HOH), 69.6 (C^*HOH), 70.9 (C^*HOH), 71.1 (C^*HOH), 71.8 (CH_2), 71.8 (CH_2), 72.8 (CH_2), 72.9 (CH_2), 73.1 (CH_2), 73.2 (CH_2); IR (ATR): ν_{max} = 3363, 2922, 2853, 1458, 1378, 1110, 1043 cm^{-1} ; HRMS-ESI: m/z [MNa] $^+$ calcd for $\text{C}_{16}\text{H}_{34}\text{NaO}_5$: 329.2298 found: 329.2288.

2,3-dihydroxypropyl pentanoate [64633-17-6] (2a)



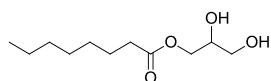
Colorless oil; ^1H NMR: δ = 0.91 (t, J = 7.3 Hz, 3H, CH_3), 1.30-1.40 (m, 2H, CH_2), 1.57-1.65 (m, 2H, CH_2), 2.26 (br, 2H, OH), 2.35 (t, J = 7.5 Hz, 2H, CH_2), 3.56-3.72 (m, 2H, CH_2), 3.90-3.96 (m, 1H, CHOH), 4.11-4.22 (m, 2H, CH_2); ^{13}C NMR: δ = 13.7 (CH_3), 22.3 (CH_2), 27.0 (CH_2), 33.9 (CH_2), 63.4 (CH_2), 65.1 (CH_2), 70.2 (CHOH), 174.5 (C_q); IR (ATR): ν_{max} = 3380, 2958, 2933, 2874, 1717, 1175, 1097, 1048 cm^{-1} ; HRMS-ESI: m/z [MNa] $^+$ calcd for $\text{C}_8\text{H}_{16}\text{NaO}_4$: 199.0946 found: 199.0947.

2,3-dihydroxypropyl hexanoate [502-53-4] (2b)



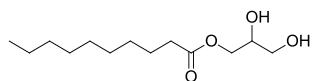
Colorless oil; ^1H NMR: $\delta = 0.90$ (t, $J = 6.9$ Hz, 3H, CH_3), 1.26-1.38 (m, 4H, CH_2), 1.58-1.68 (m, 2H, CH_2), 2.18 (br, 1H, OH), 2.35 (t, $J = 7.5$ Hz, 2H, CH_2), 2.57 (br, 1H, OH), 3.57-3.72 (m, 2H, CH_2), 3.90-3.96 (m, 1H, CHOH), 4.11-4.24 (m, 2H, CH_2); ^{13}C NMR: $\delta = 13.9$ (CH_3), 22.3 (CH_2), 24.6 (CH_2), 31.3 (CH_2), 34.2 (CH_2), 63.5 (CH_2), 65.1 (CH_2), 70.3 (CHOH), 174.5 (C_q); IR (ATR): $\nu_{\text{max}} = 3389, 2956, 2932, 2873, 1719, 1171, 1101, 1046 \text{ cm}^{-1}$; HRMS-ESI: m/z [MNa] $^+$ calcd for $\text{C}_9\text{H}_{18}\text{NaO}_4$: 213.1097 found: 213.1095.

2,3-dihydroxypropyl octanoate [502-54-5] (2c)



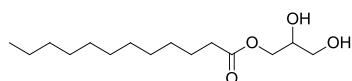
Colorless oil; ^1H NMR: $\delta = 0.88$ (t, $J = 6.8$ Hz, 3H, CH_3), 1.23-1.37 (m, 8H, CH_2), 1.60-1.65 (m, 2H, CH_2), 2.16 (br, 1H, OH), 2.35 (t, $J = 7.5$ Hz, 2H, CH_2), 2.58 (br, 1H, OH), 3.56-3.72 (m, 2H, CH_2), 3.92-3.96 (m, 1H, CHOH), 4.11-4.23 (m, 2H, CH_2); ^{13}C NMR: $\delta = 14.1$ (CH_3), 22.6 (CH_2), 24.9 (CH_2), 28.9 (CH_2), 29.1 (CH_2), 31.7 (CH_2), 34.2 (CH_2), 63.4 (CH_2), 65.0 (CH_2), 70.2 (CHOH), 174.4 (C_q); IR (ATR): $\nu_{\text{max}} = 3375, 2957, 2932, 2874, 1717, 1172, 1100, 1045 \text{ cm}^{-1}$; HRMS-ESI: m/z [MNa] $^+$ calcd for $\text{C}_{11}\text{H}_{22}\text{NaO}_4$: 241.1410 found: 241.1401.

2,3-dihydroxypropyl decanoate [2277-23-8] (2d)



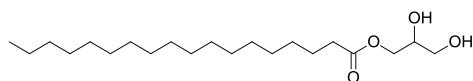
White solid; Mp < 35 °C; ^1H NMR: $\delta = 0.87$ (t, $J = 6.6$ Hz, 3H, CH_3), 1.20-1.37 (m, 12H, CH_2), 1.58-1.66 (m, 2H, CH_2), 2.22 (br, 2H, OH), 2.35 (t, $J = 7.5$ Hz, 2H, CH_2), 3.57-3.72 (m, 2H, CH_2), 3.90-3.96 (m, 1H, CHOH), 4.11-4.24 (m, 2H, CH_2); ^{13}C NMR: $\delta = 14.1$ (CH_3), 22.7 (CH_2), 24.9 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 31.9 (CH_2), 34.2 (CH_2), 63.5 (CH_2), 65.1 (CH_2), 70.3 (CHOH), 174.4 (C_q); IR (ATR): $\nu_{\text{max}} = 3288, 3221, 2954, 2917, 2850, 1729, 1173, 1103, 1047 \text{ cm}^{-1}$; HRMS-ESI: m/z [MNa] $^+$ calcd for $\text{C}_{13}\text{H}_{26}\text{NaO}_4$: 269.1723 found: 269.1721.

2,3-dihydroxypropyl dodecanoate [142-18-7] (2e)



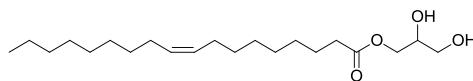
White solid; Mp = 61 °C; ^1H NMR: δ = 0.87 (t, J = 6.7 Hz, 3H, CH₃), 1.20-1.38 (m, 16H, CH₂), 1.58-1.66 (m, 2H, CH₂), 2.16 (br, 1H, OH), 2.35 (t, J = 7.6 Hz, 2H, CH₂), 2.58 (br, 1H, OH), 3.56-3.72 (m, 2H, CH₂), 3.90-3.96 (m, 1H, CHOH), 4.11-4.23 (m, 2H, CH₂); ^{13}C NMR: δ = 14.3 (CH₃), 22.8 (CH₂), 25.0 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 29.5 (CH₂), 29.6 (CH₂), 29.7 (CH₂), 32.0 (CH₂), 34.3 (CH₂), 63.4 (CH₂), 65.3 (CH₂), 70.4 (CHOH), 174.5 (C_q); IR (ATR): ν_{\max} = 3296, 3225, 2958, 2916, 2850, 1729, 1173, 1103, 1047 cm⁻¹; HRMS-ESI: m/z [MNa]⁺ calcd for C₁₅H₃₀NaO₄: 297.2036 found: 297.2030.

2,3-dihydroxypropyl octadecanoate [123-94-4] (2f)



White solid; Mp = 80 °C; ^1H NMR: δ = 0.88 (t, J = 6.6 Hz, 3H, CH₃), 1.18-1.40 (m, 28H, CH₂), 1.57-1.67 (m, 2H, CH₂), 2.08 (br, 2H, OH), 2.35 (t, J = 7.5 Hz, 2H, CH₂), 3.57-3.72 (m, 2H, CH₂), 3.90-3.96 (m, 1H, CHOH), 4.11-4.24 (m, 2H, CH₂); ^{13}C NMR (CDCl₃/MeOD = 9/1): δ = 14.0 (CH₃), 22.6 (CH₂), 24.8 (CH₂), 29.1 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 29.6 (CH₂), 29.6 (CH₂), 29.7 (CH₂), 31.9 (CH₂), 34.1 (CH₂), 63.2 (CH₂), 65.1 (CH₂), 70.0 (CHOH), 174.5 (C_q); IR (ATR): ν_{\max} = 3300, 2954, 2917, 2848, 1730, 1175, 1058, 988 cm⁻¹; HRMS-ESI: m/z [MNa]⁺ calcd for C₂₁H₄₂NaO₄: 381.2975 found: 381.2977.

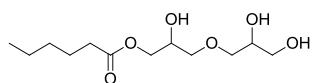
2,3-dihydroxypropyl oleate [111-03-5] (2g)



White wax. ^1H NMR: δ = 0.87 (t, J = 6.7 Hz, 3H, CH₃), 1.20-1.40 (m, 20H, CH₂), 1.58-1.66 (m, 2H, CH₂), 1.96-2.04 (m, 4H, CH₂), 2.35 (t, J = 7.5 Hz, 2H, CH₂), 3.56-3.72 (m, 2H, CH₂), 3.91-3.96 (m, 1H, CHOH), 4.11-4.23 (m, 2H, CH₂), 5.30-5.36 (m, 2H, CH); ^{13}C NMR: δ = 14.2 (CH₃), 22.8 (CH₂), 25.0 (CH₂), 27.2 (CH₂), 27.3 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 29.6 (CH₂), 29.8 (CH₂), 29.8 (CH₂), 32.0 (CH₂), 34.2 (CH₂), 63.5 (CH₂), 65.1 (CH₂), 70.3 (CHOH), 129.8 (CH), 130.1 (CH), 174.5 (C_q); IR (ATR): ν_{\max} = 3314, 2954, 2917, 2848, 1731, 1175, 1116, 1057 cm⁻¹; HRMS-ESI: m/z [MNa]⁺ calcd for

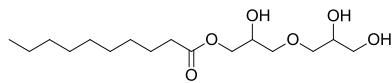
C₂₁H₄₀NaO₄: 379.2819 found: 379.2811.

3-(2,3-dihydroxypropoxy)-2-hydroxypropyl hexanoate [1026295-85-1] (7b)



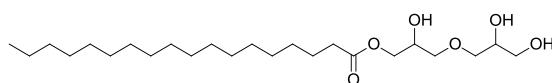
Colorless oil (Mixture of isomers); ¹H NMR: δ = 0.89 (t, *J* = 6.9 Hz, 3H, CH₃), 1.26-1.35 (m, 4H, CH₂), 1.58-1.66 (m, 2H, CH₂), 2.34 (t, *J* = 7.5 Hz, 2H, CH₂), 3.05 (br, 3H, OH), 3.48-3.78 (m, 6H, CH₂), 3.85-3.91 (m, 1H, CHOH), 3.99-4.05 (m, 1H, CHOH), 4.12-4.19 (m, 2H, CH₂); ¹³C NMR: δ = 13.9 (CH₃), 22.3 (CH₂), 24.6 (CH₂), 31.3 (CH₂), 34.1 (CH₂), 63.7 (CH₂), 65.0 (CH₂), 68.6 (C^{*}HOH), 68.7 (C^{*}HOH), 71.0 (C^{*}HOH), 71.1 (C^{*}HOH), 72.6 (CH₂), 72.7 (CH₂), 72.7 (CH₂), 174.1 (C_q); IR (ATR): ν_{max} = 3380, 2954, 2931, 2872, 1733, 1173, 1100, 1041 cm⁻¹; HRMS-ESI: *m/z* [MNa]⁺ calcd for C₁₂H₂₄NaO₆: 287.1465 found: 287.1462.

3-(2,3-dihydroxypropoxy)-2-hydroxypropyl decanoate [156153-06-9] (7d)



White wax. (Mixture of isomers); ¹H NMR: δ = 0.87 (t, *J* = 6.7 Hz, 3H, CH₃), 1.21-1.36 (m, 12H, CH₂), 1.58-1.67 (m, 2H, CH₂), 2.34 (t, *J* = 7.6 Hz, 2H, CH₂), 2.86 (br, 3H, OH), 3.48-3.78 (m, 6H, CH₂), 3.83-3.92 (m, 1H, CHOH), 3.98-4.06 (m, 1H, CHOH), 4.12-4.22 (m, 2H, CH₂); ¹³C NMR: δ = 14.2 (CH₃), 22.7 (CH₂), 24.9 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.5 (CH₂), 31.9 (CH₂), 34.2 (CH₂), 63.7 (CH₂), 65.0 (CH₂), 68.7 (C^{*}HOH), 68.8 (C^{*}HOH), 71.0 (C^{*}HOH), 71.1 (C^{*}HOH), 72.7 (CH₂), 72.7 (CH₂), 72.8 (CH₂), 174.1 (C_q); IR (ATR): ν_{max} = 3368, 2923, 2854, 1736, 1172, 1111, 1043 cm⁻¹; HRMS-ESI: *m/z* [MNa]⁺ calcd for C₁₆H₃₂NaO₆: 343.2091 found: 343.2081.

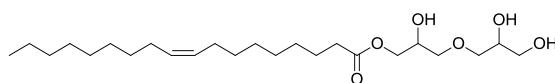
3-(2,3-dihydroxypropoxy)-2-hydroxypropyl octadecanoate [66168-54-5] (7f)



White wax. (Mixture of isomers); ¹H NMR (400 MHz): δ = 0.87 (t, *J* = 6.9 Hz, 3H, CH₃), 1.20-1.37 (m, 28H, CH₂), 1.57-1.67 (m, 2H, CH₂), 2.33 (t, *J* = 6.5 Hz, 2H, CH₂), 2.82 (br, 3H, OH), 3.48-3.75 (m, 6H, CH₂), 3.84-3.91 (m, 1H, CHOH), 3.99-4.06 (m, 1H, CHOH), 4.09-4.19 (m, 2H, CH₂); ¹³C NMR (100

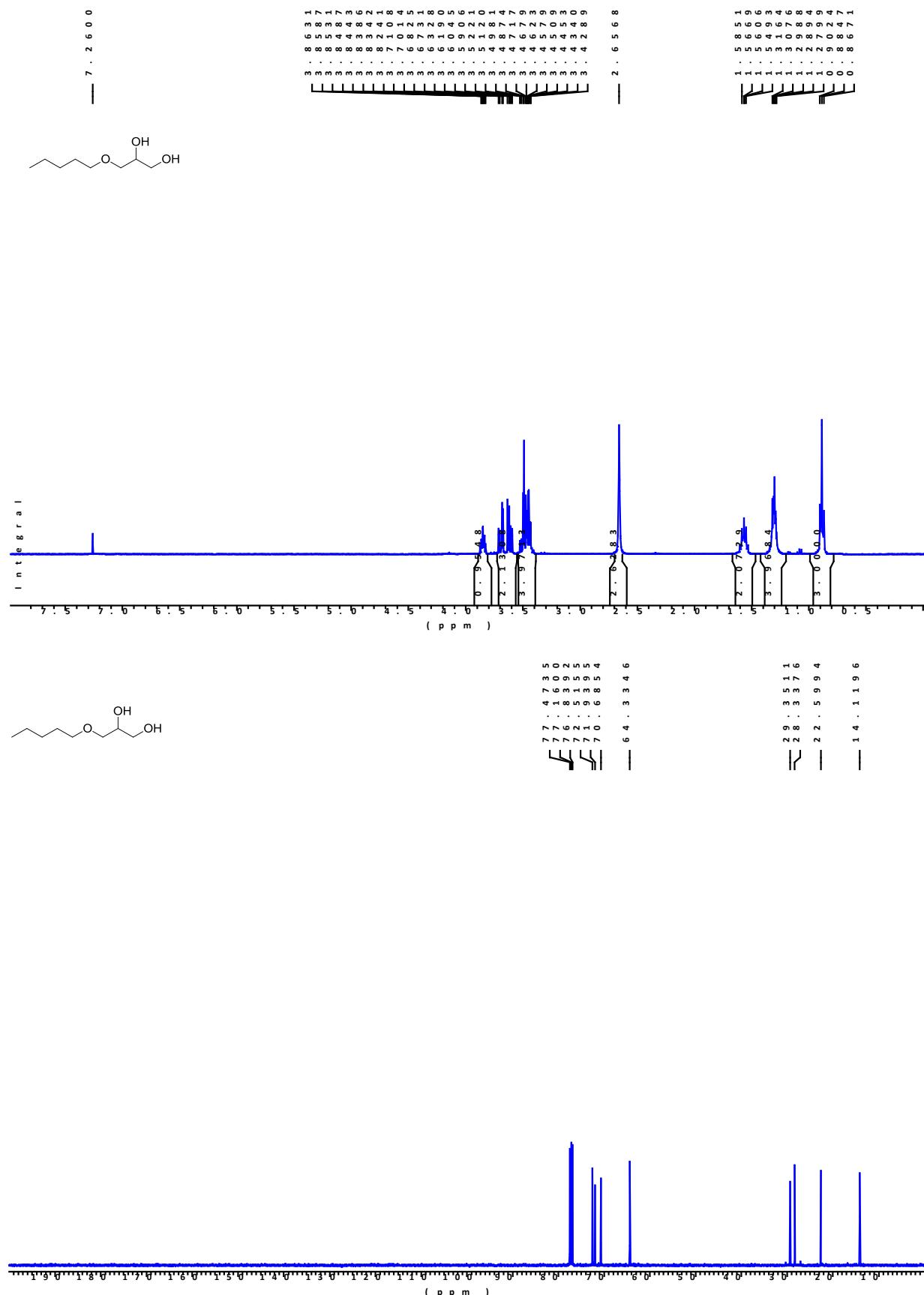
MHz): δ = 14.3 (CH₃), 22.8 (CH₂), 25.0 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 29.5 (CH₂), 29.6 (CH₂), 29.8 (CH₂), 29.8 (CH₂), 32.1 (CH₂), 34.3 (CH₂), 63.9 (CH₂), 65.2 (CH₂), 65.2 (CH₂), 69.0 (C^{*}HOH), 69.1 (C^{*}HOH), 70.9 (C^{*}HOH), 71.0 (C^{*}HOH), 72.6 (CH₂), 72.7 (CH₂), 73.1 (CH₂), 73.1 (CH₂), 174.2 (C_q); IR (ATR): ν_{max} = 3373, 2916, 2849, 1736, 1126, 1044 cm⁻¹; HRMS-ESI: *m/z* [MNa]⁺ calcd for C₂₄H₄₈NaO₆: 455.3343 found: 455.3323.

3-(2,3-dihydroxypropoxy)-2-hydroxypropyl oleate [97605-97-5] (7g)

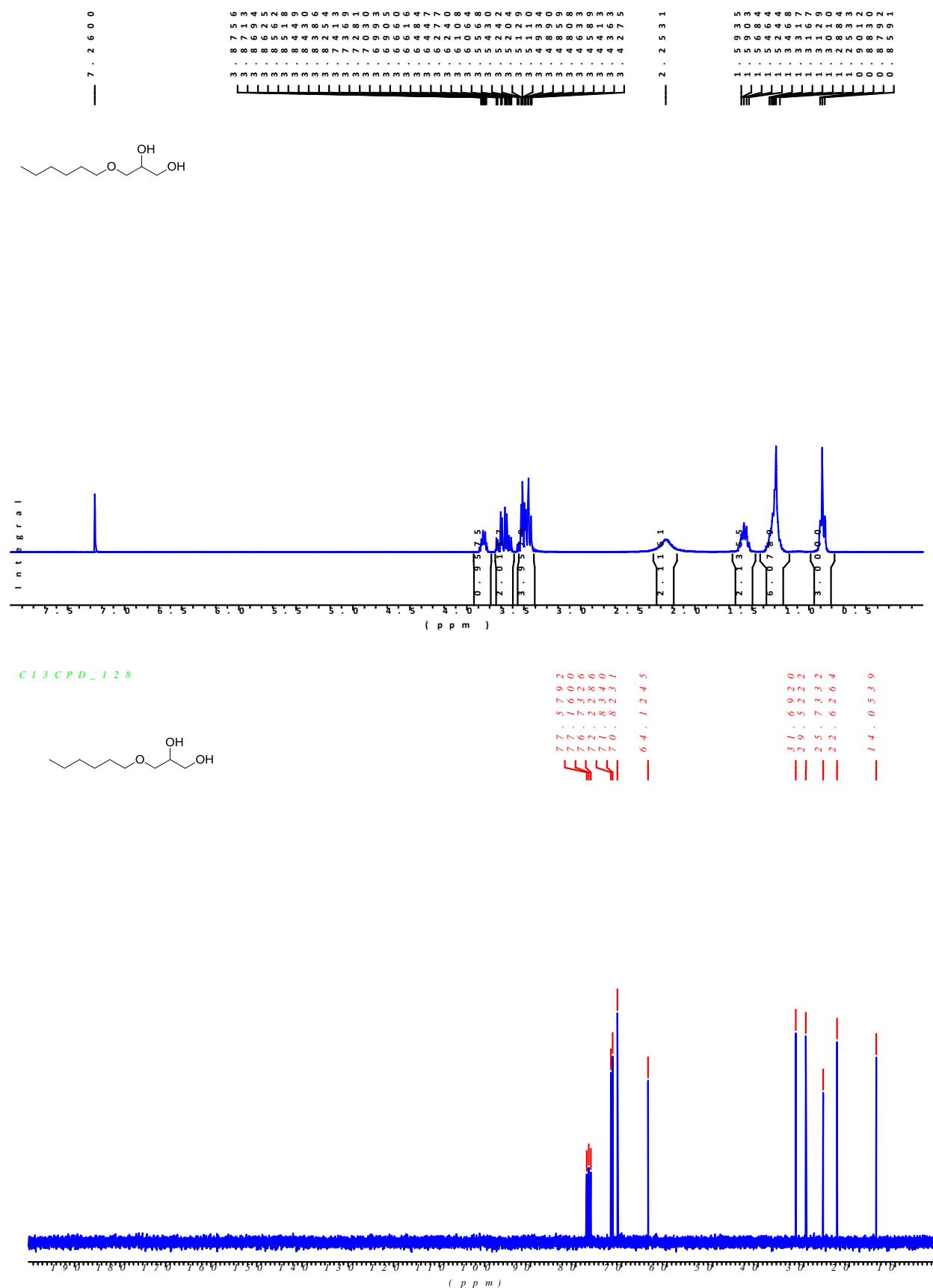


White wax. (Mixture of isomers); ¹H NMR (400 MHz): δ = 0.87 (t, *J* = 6.9 Hz, 3H, CH₃), 1.20-1.39 (m, 20H, CH₂), 1.57-1.66 (m, 2H, CH₂), 1.96-2.03 (m, 4H, CH₂), 2.32 (t, *J* = 7.7 Hz, 2H, CH₂), 2.85 (br, 3H, OH), 3.47-3.77 (m, 6H, CH₂), 3.85-3.90 (m, 1H, CHOH), 4.00-4.04 (m, 1H, CHOH), 4.10-4.17 (m, 2H, CH₂), 5.29-4.36 (m, 2H, CH); ¹³C NMR (100 MHz): δ = 14.3 (CH₃), 22.8 (CH₂), 25.0 (CH₂), 27.3 (CH₂), 27.4 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.5 (CH₂), 29.7 (CH₂), 29.8 (CH₂), 29.8 (CH₂), 29.9 (CH₂), 32.0 (CH₂), 34.3 (CH₂), 63.9 (CH₂), 65.2 (CH₂), 65.2 (CH₂), 69.0 (C^{*}HOH), 69.0 (C^{*}HOH), 70.9 (C^{*}HOH), 71.0 (C^{*}HOH), 72.6 (CH₂), 72.7 (CH₂), 73.1 (CH₂), 129.8 (CH), 130.2 (CH), 174.2 (C_q); IR (ATR): ν_{max} = 3376, 2922, 2853, 1736, 1175, 1119, 1043 cm⁻¹; HRMS-ESI: *m/z* [MNa]⁺ calcd for C₂₄H₄₆NaO₆: 453.3187 found: 453.3168.

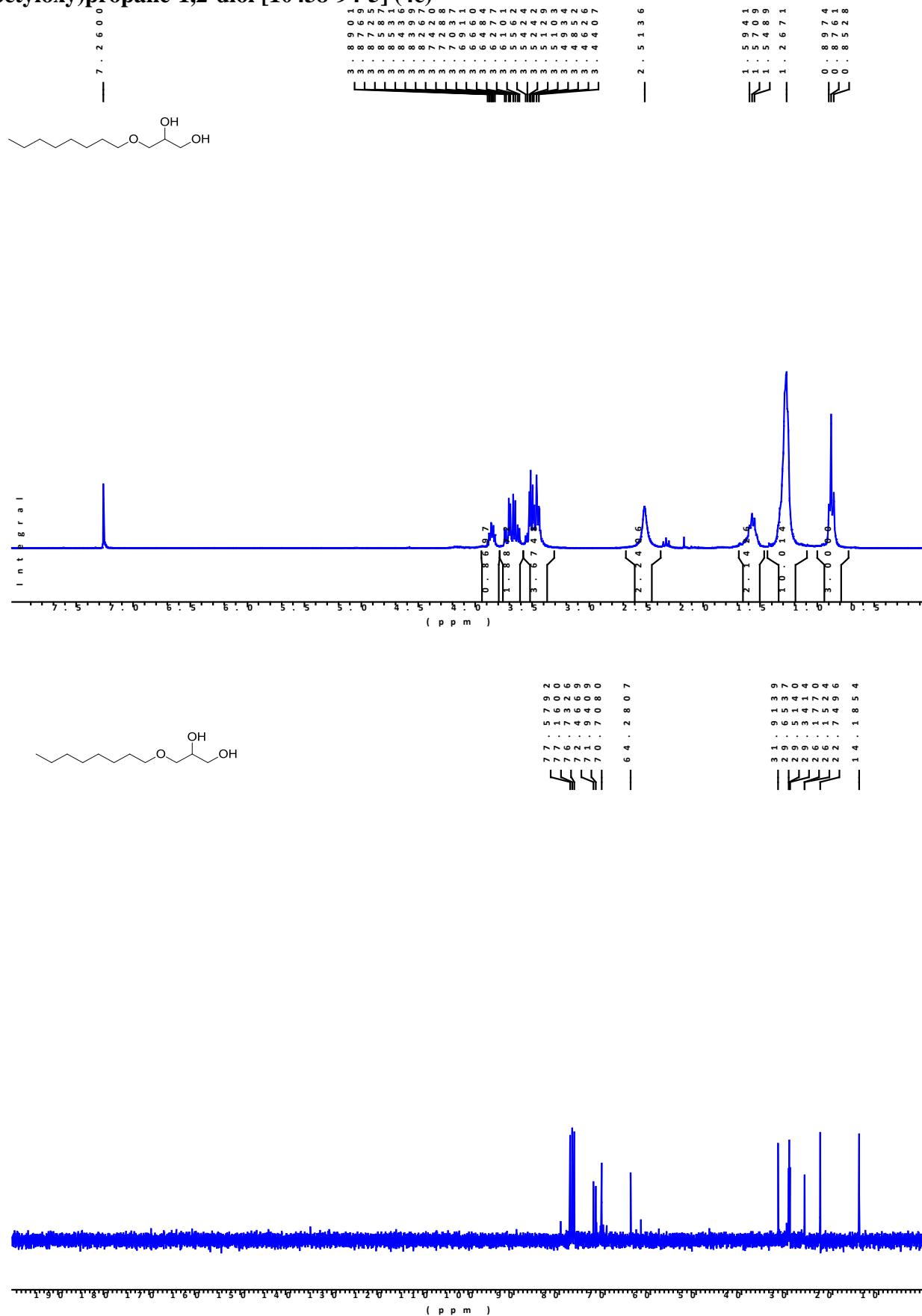
3-(pentyloxy)propane-1,2-diol [22636-32-4] (4a)



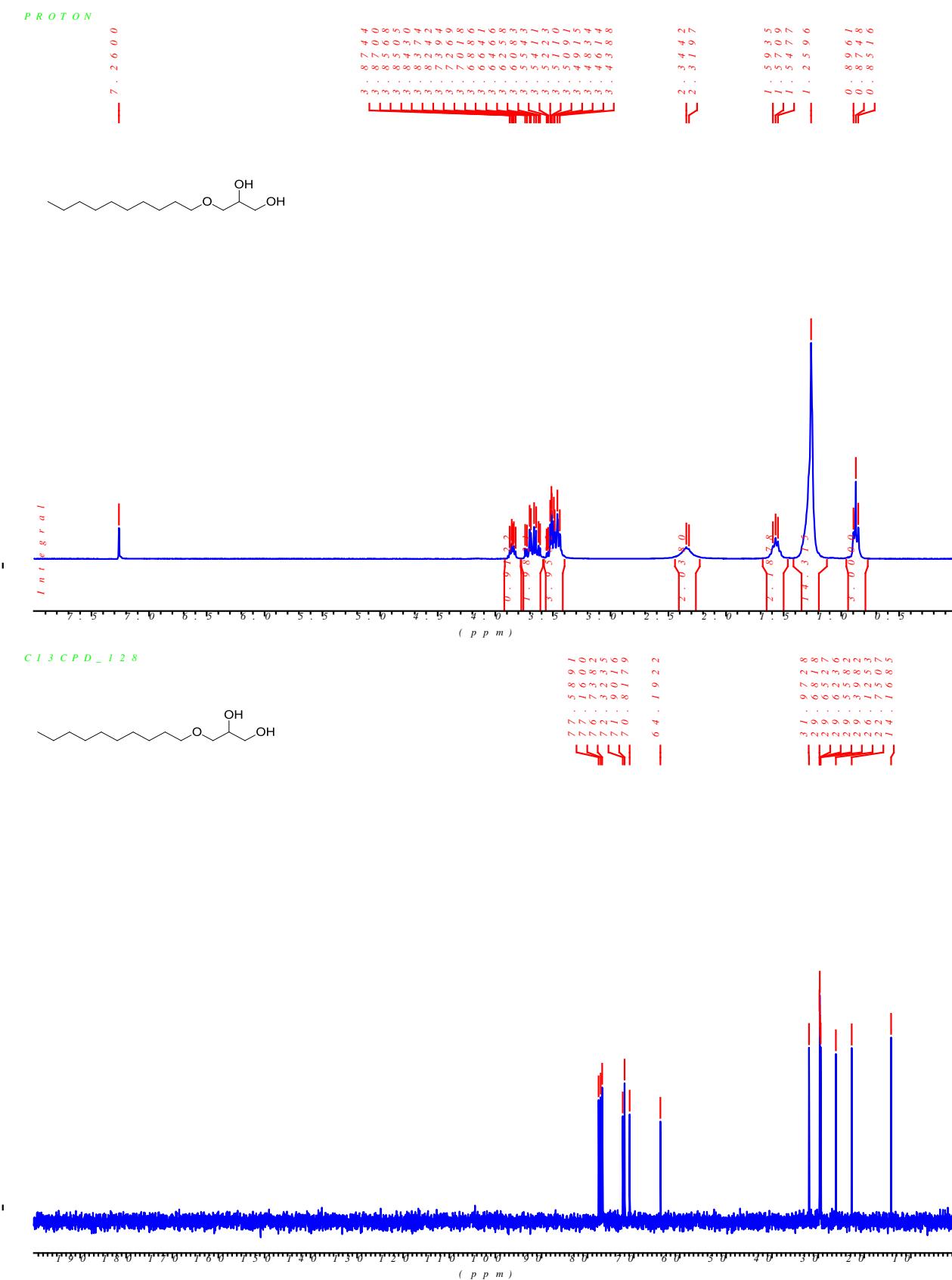
3-(hexyloxy)propane-1,2-diol [10305-38-1] (4b)



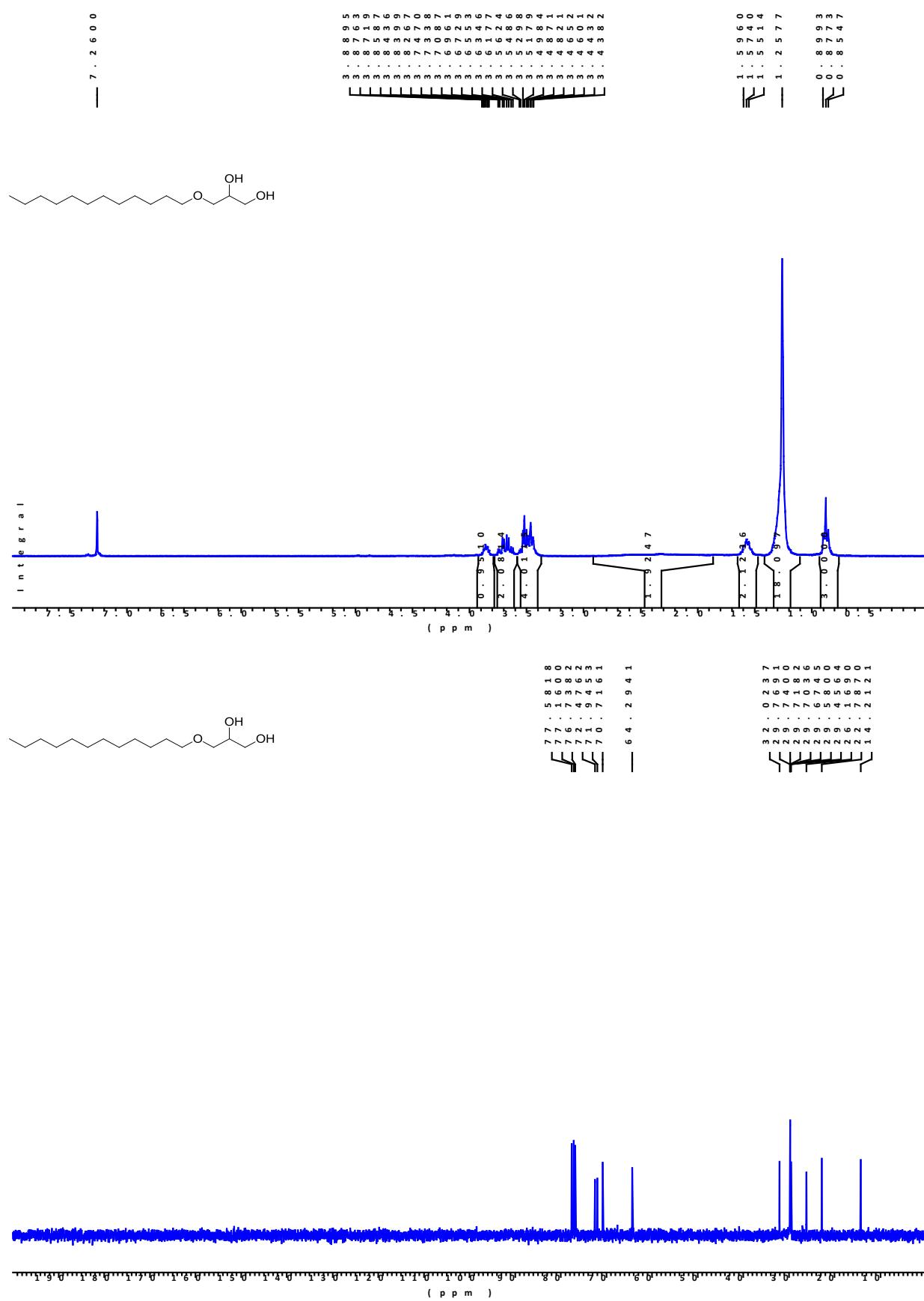
3-(octyloxy)propane-1,2-diol [10438-94-5] (4c)



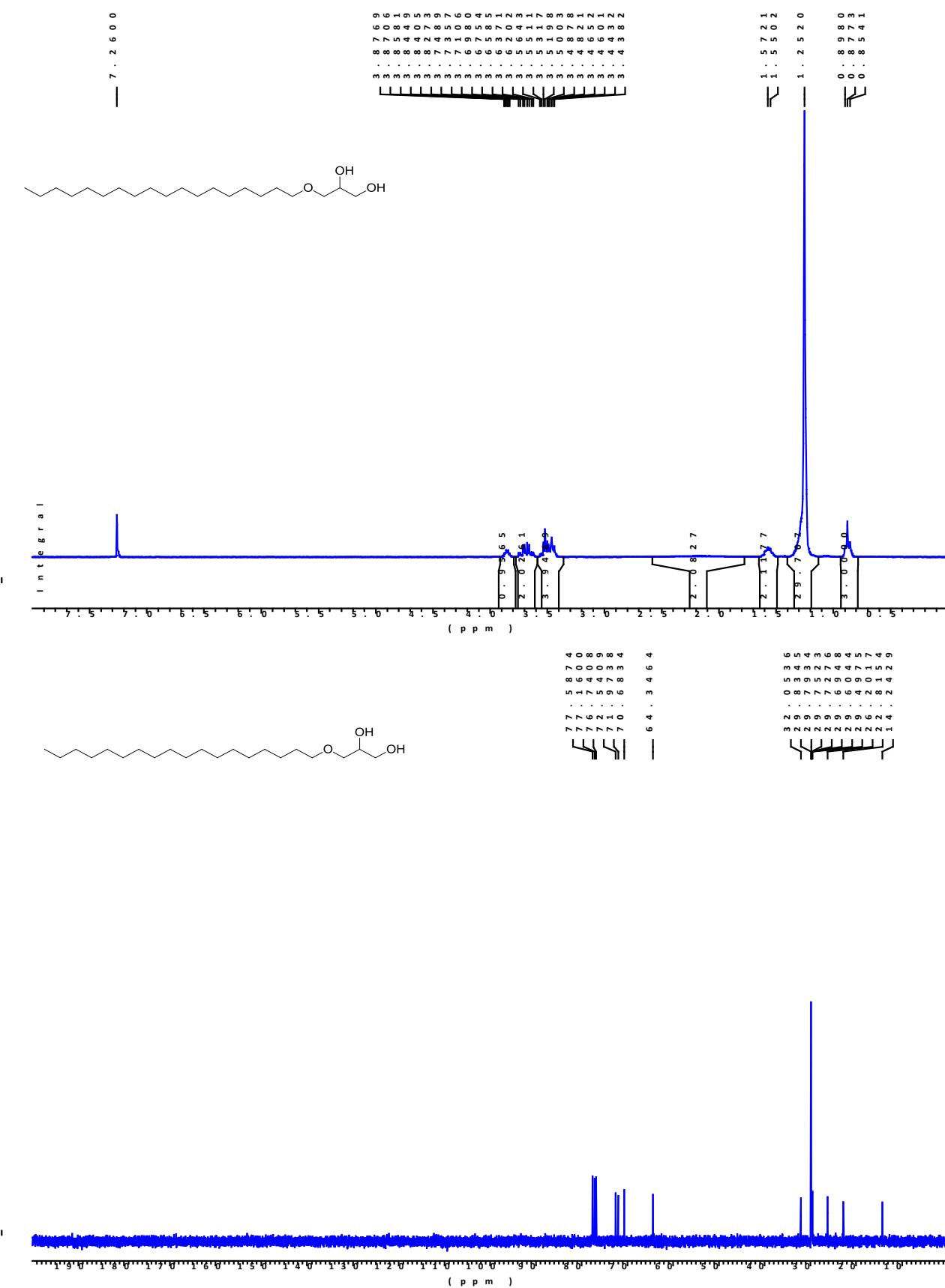
3-(decyloxy)propane-1,2-diol [10430-97-4] (4d)



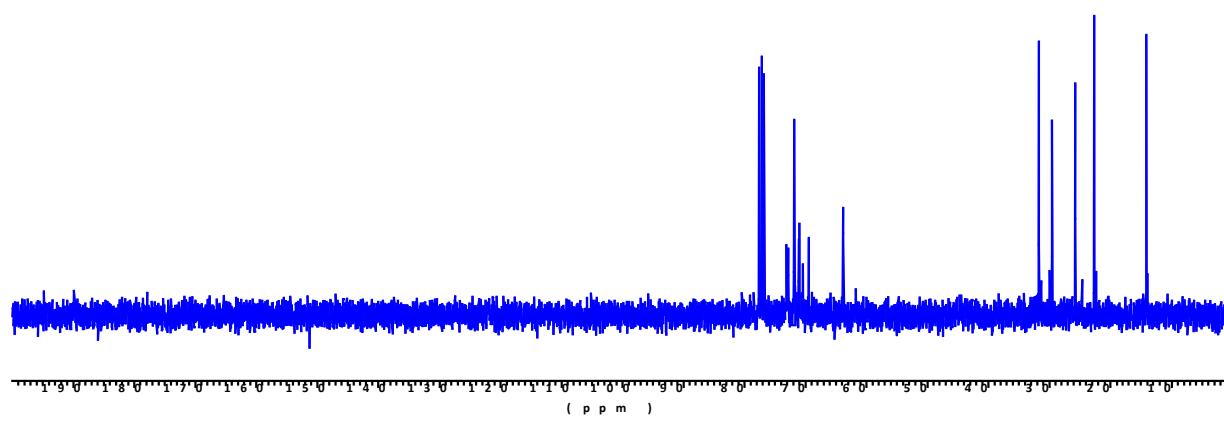
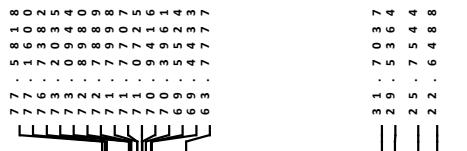
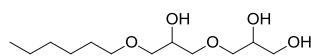
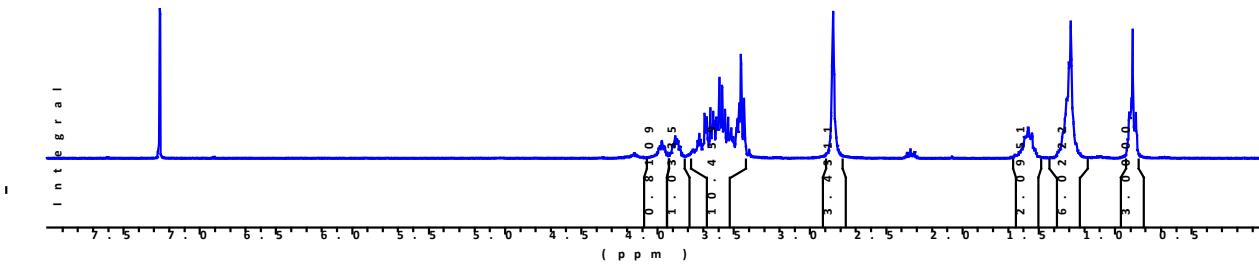
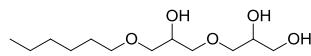
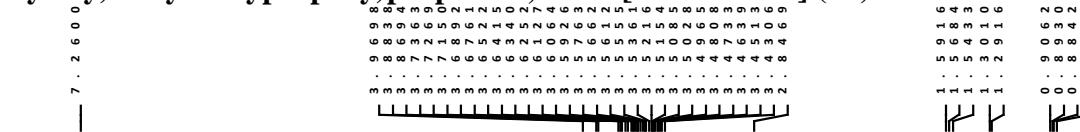
3-(dodecyloxy)propane-1,2-diol [1561-07-5] (4e)



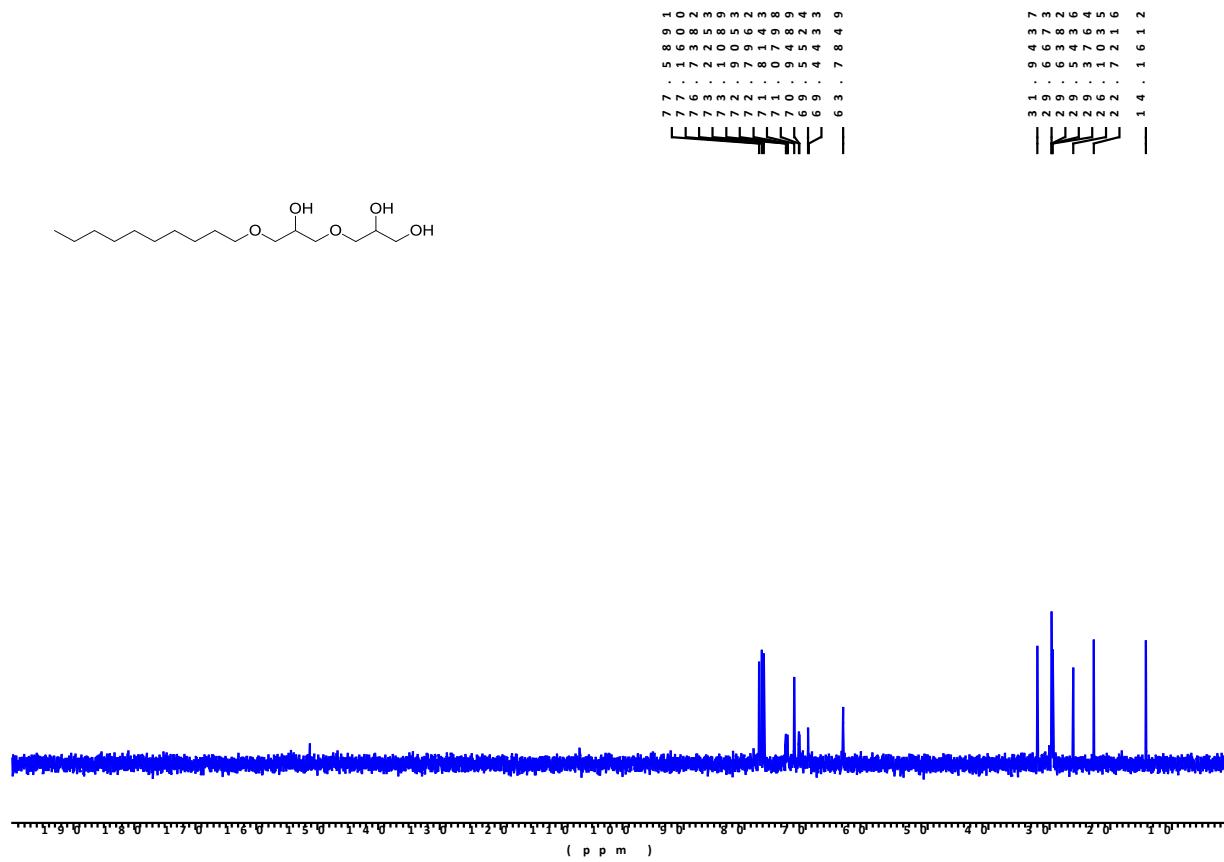
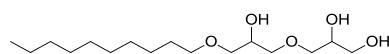
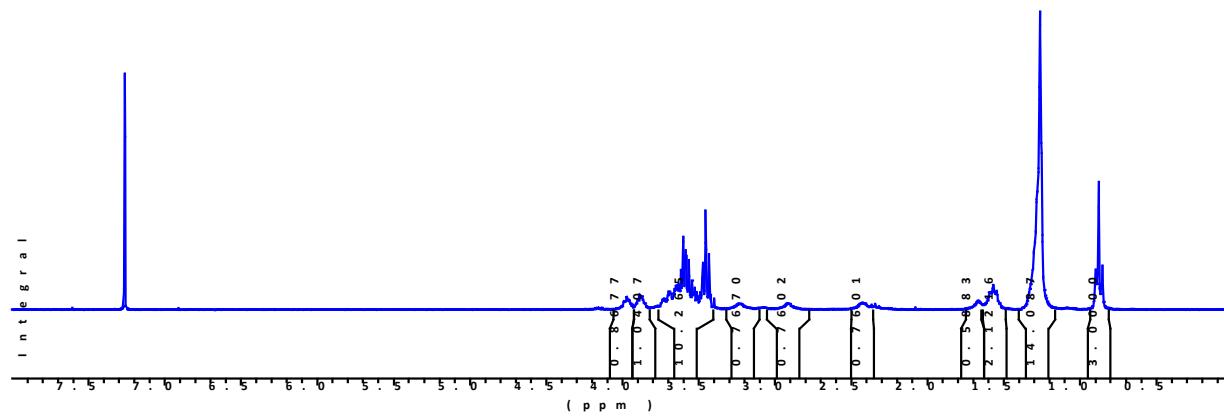
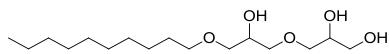
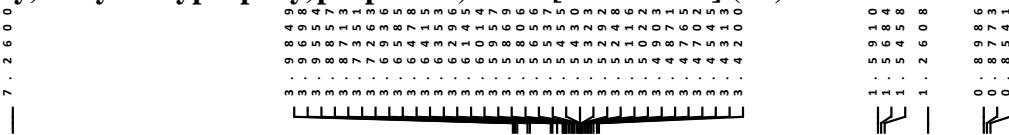
3-(octadecyloxy)propane-1,2-diol [544-62-7] (4f)



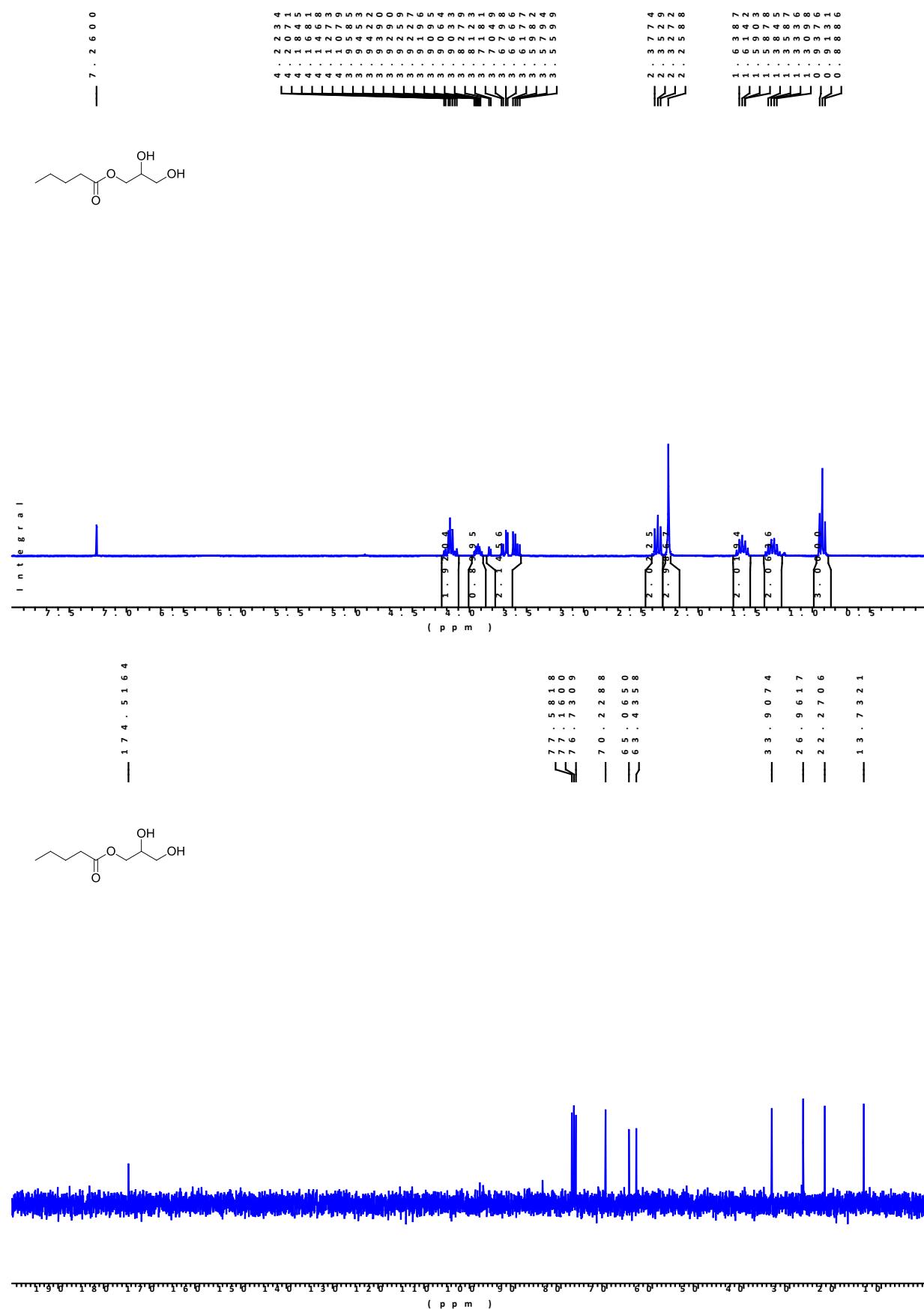
3-(3-(hexyloxy)-2-hydroxypropoxy)propane-1,2-diol [146490-38-2] (6b)



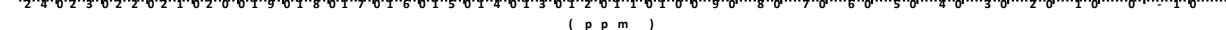
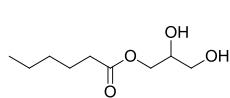
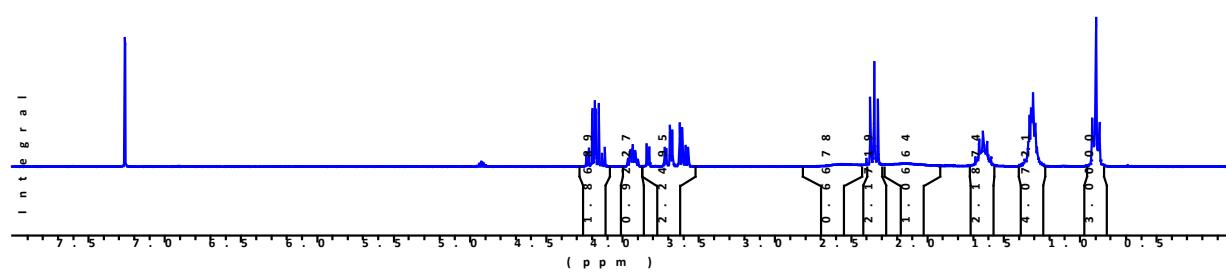
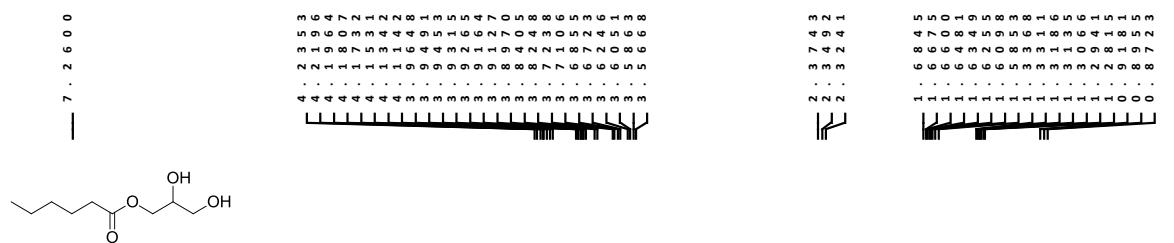
3-(3-(decyloxy)-2-hydroxypropoxy)propane-1,2-diol [88456-94-4] (6d)



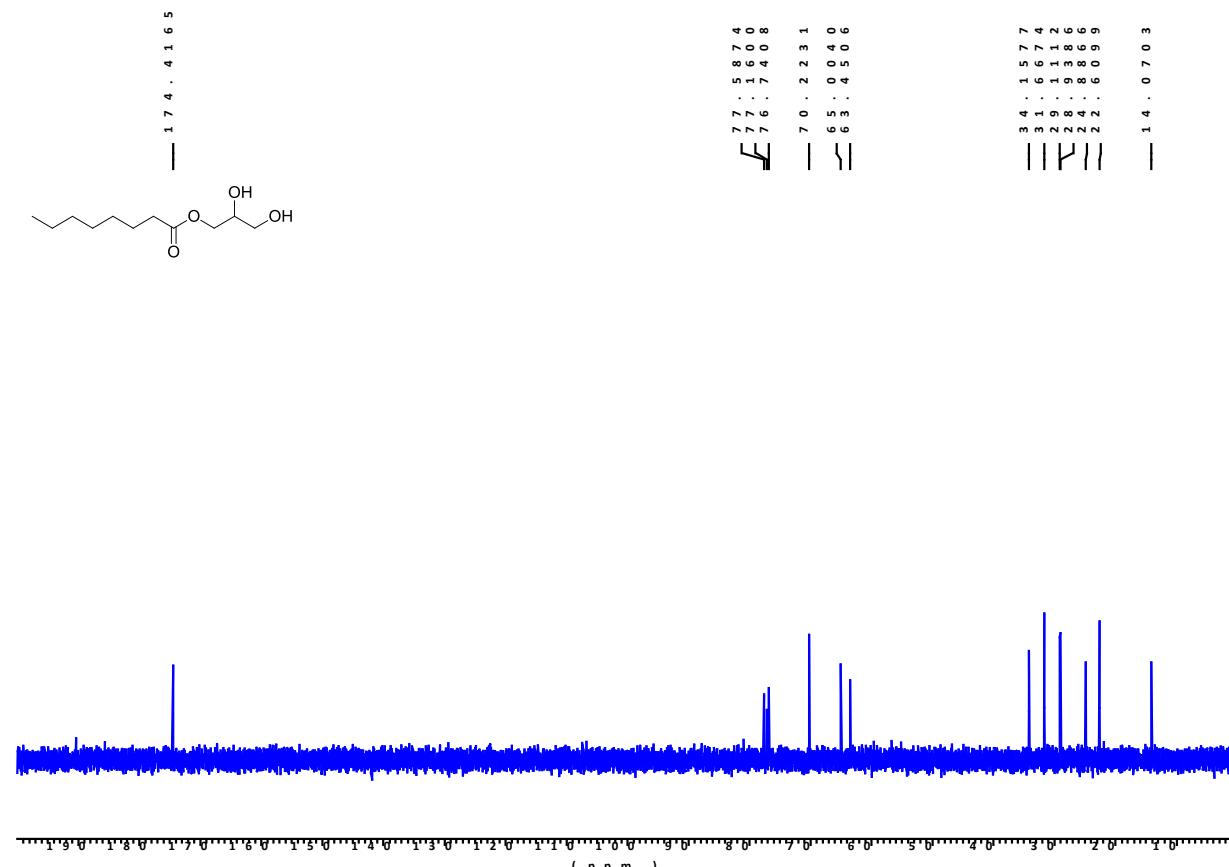
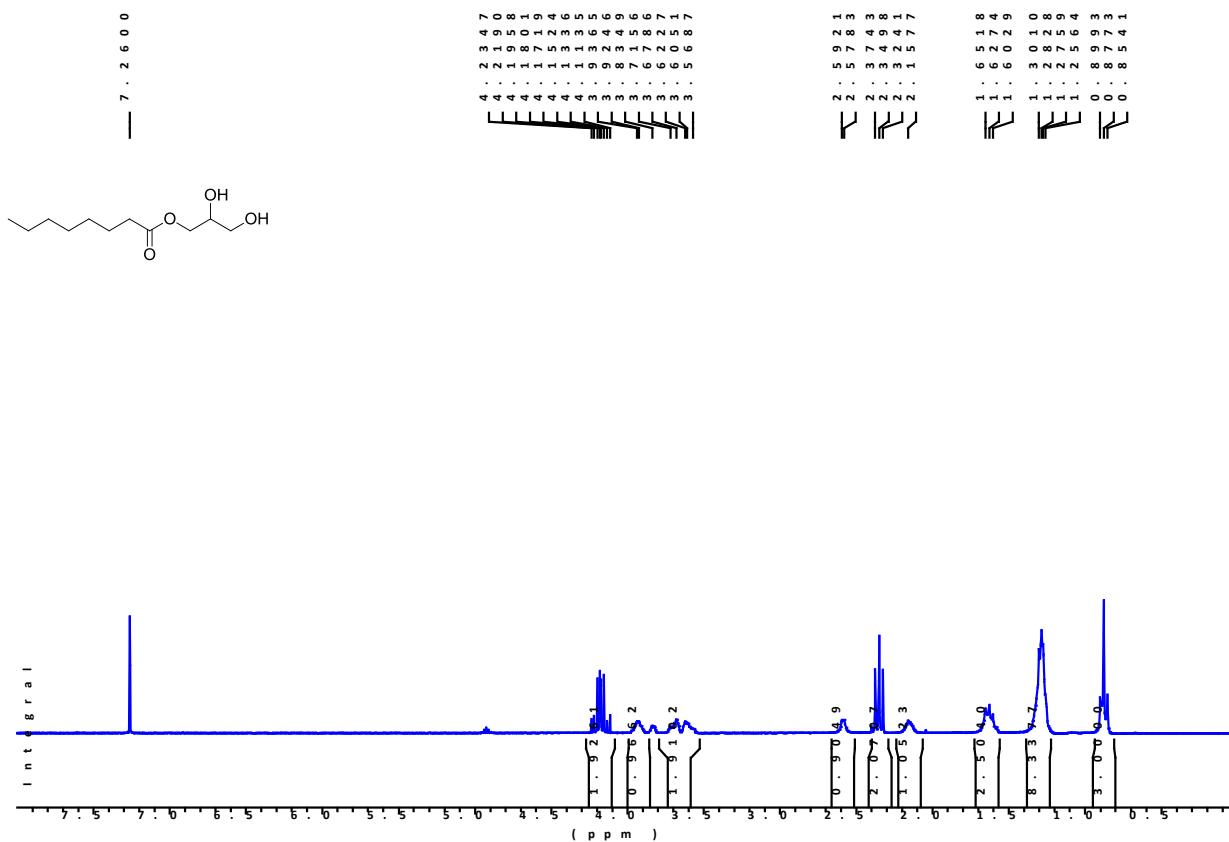
2,3-dihydroxypropyl pentanoate [64633-17-6] (2a)



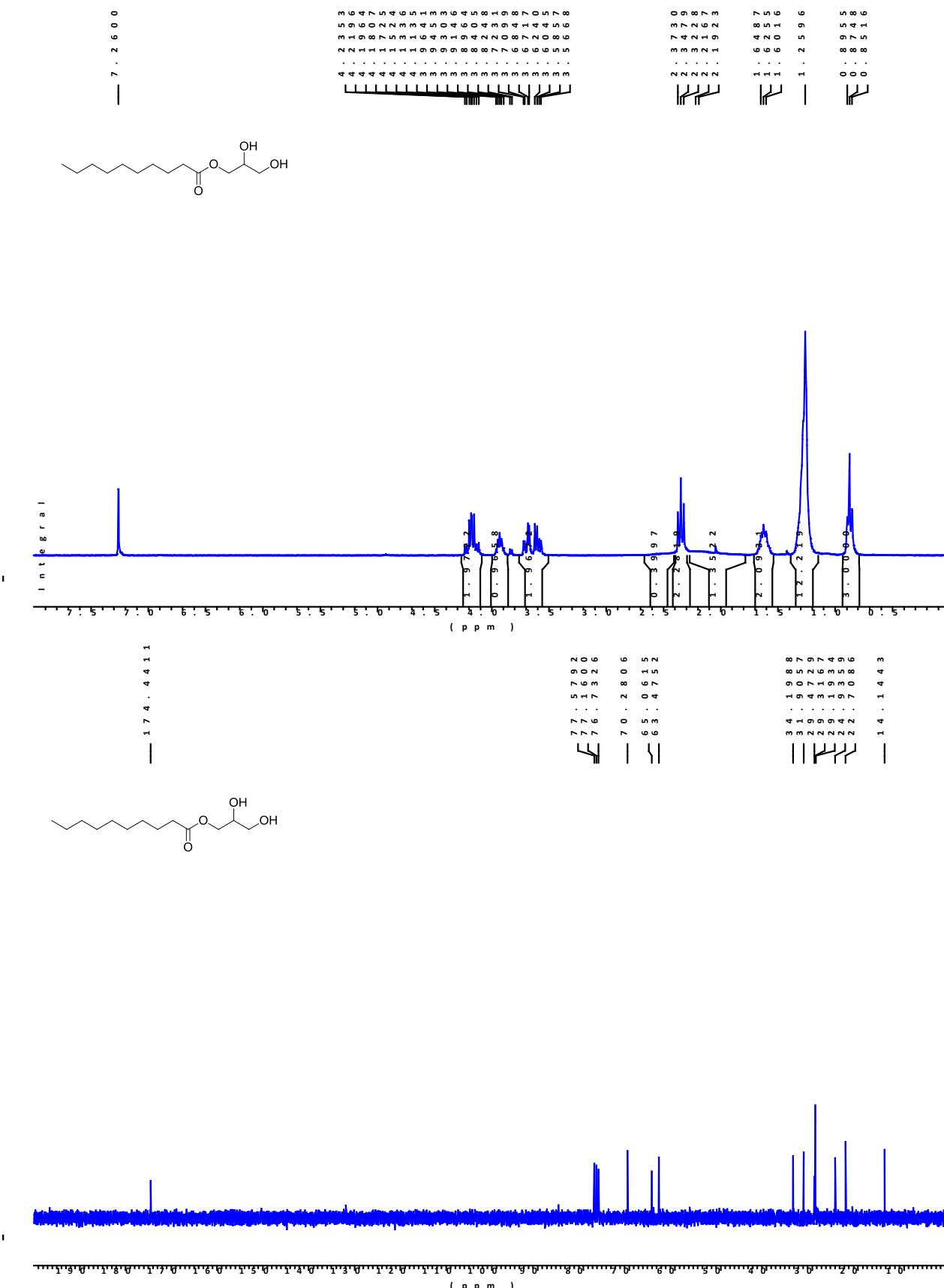
2,3-dihydroxypropyl hexanoate [502-53-4] (2b)



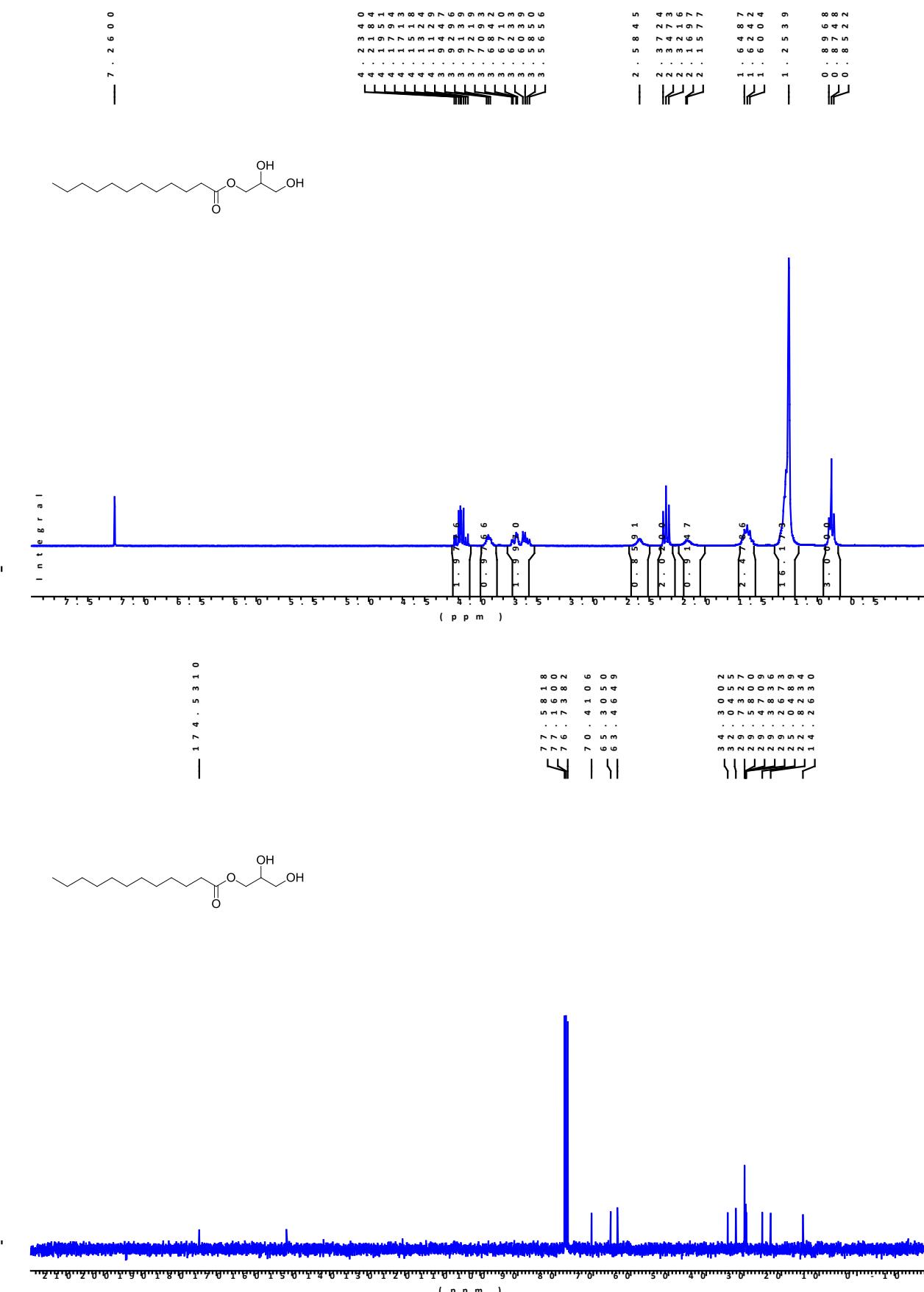
2,3-dihydroxypropyl octanoate [502-54-5] (2c)



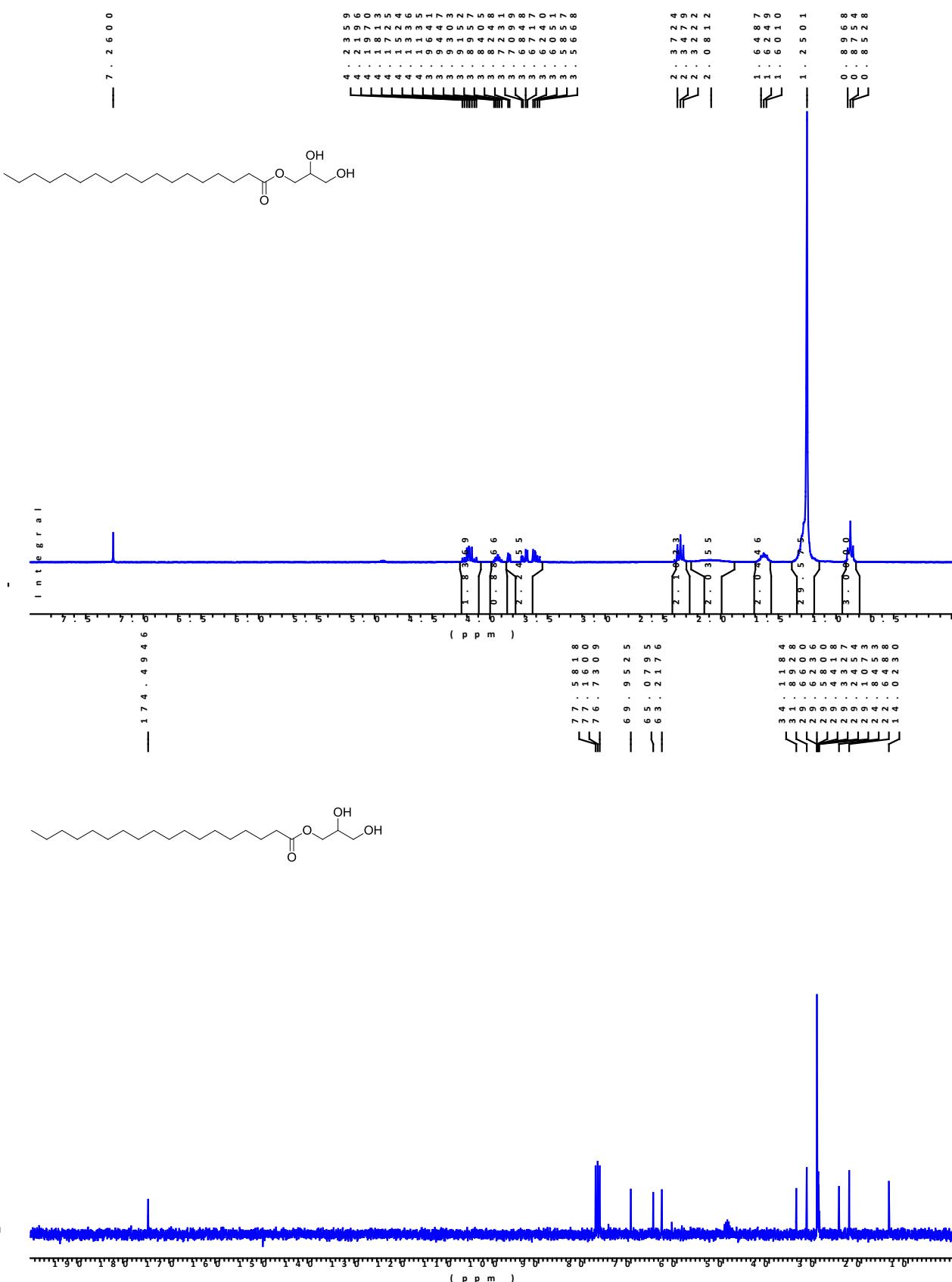
2,3-dihydroxypropyl decanoate [2277-23-8] (2d)



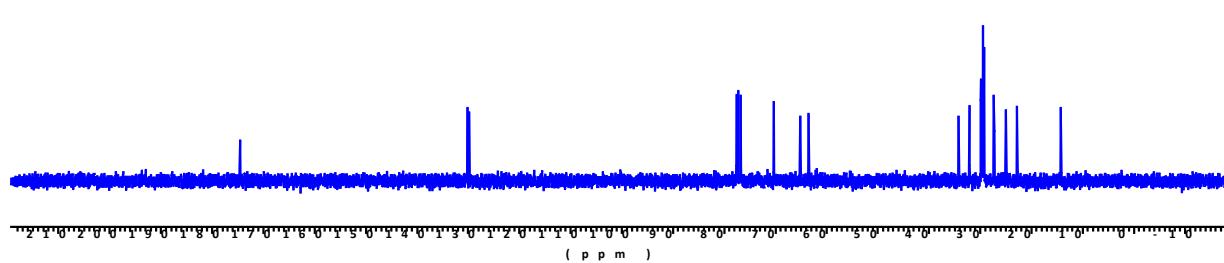
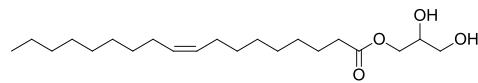
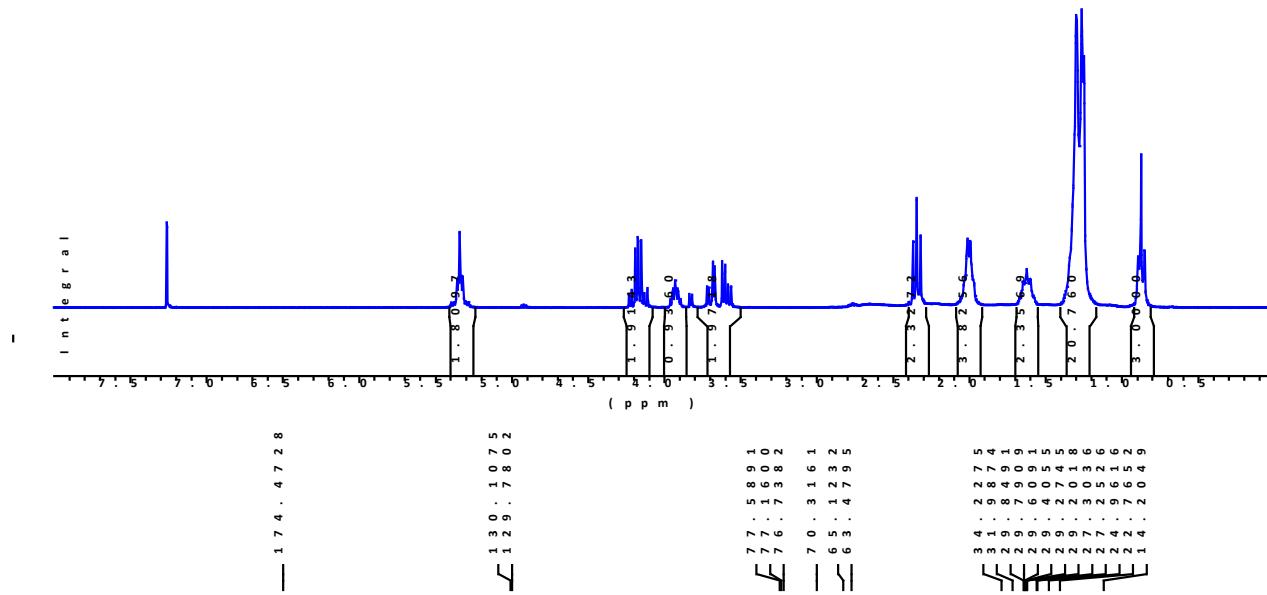
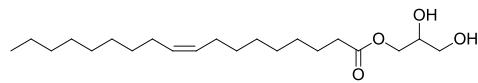
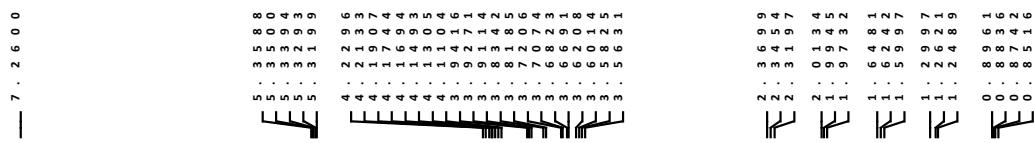
2,3-dihydroxypropyl dodecanoate [142-18-7] (2e)



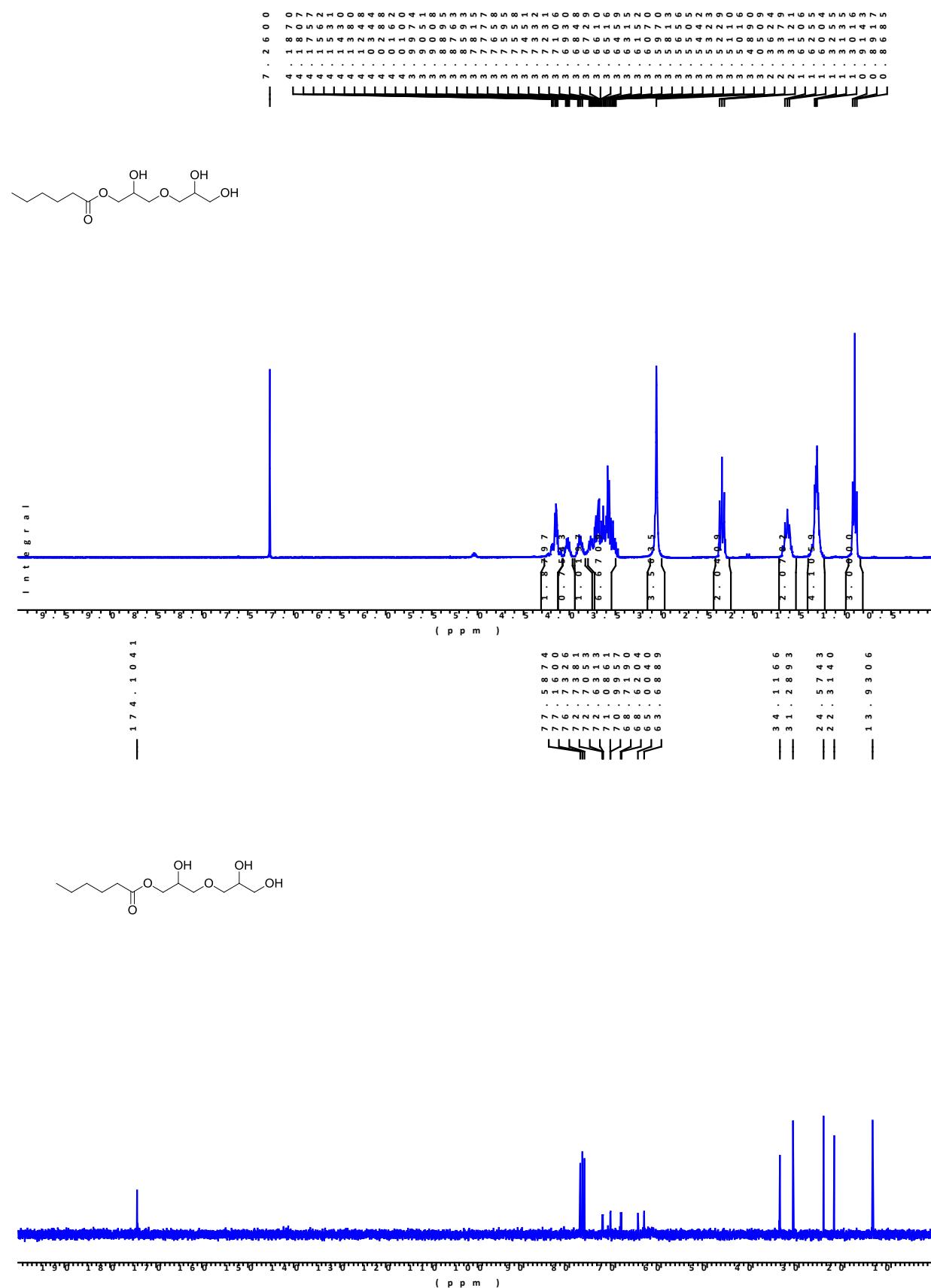
2,3-dihydroxypropyl octadecanoate [123-94-4] (2f)



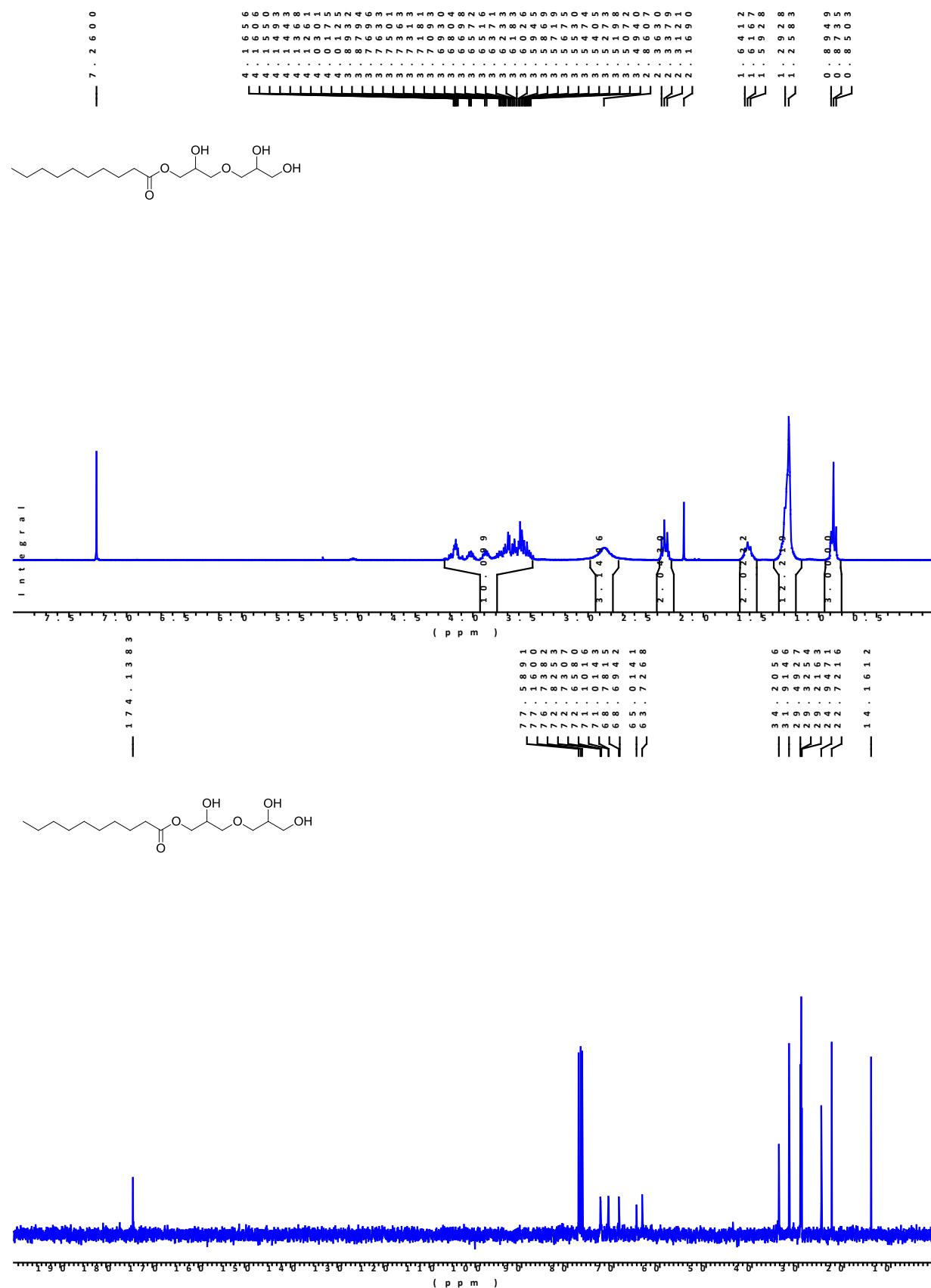
2,3-dihydroxypropyl oleate [111-03-5] (2g)



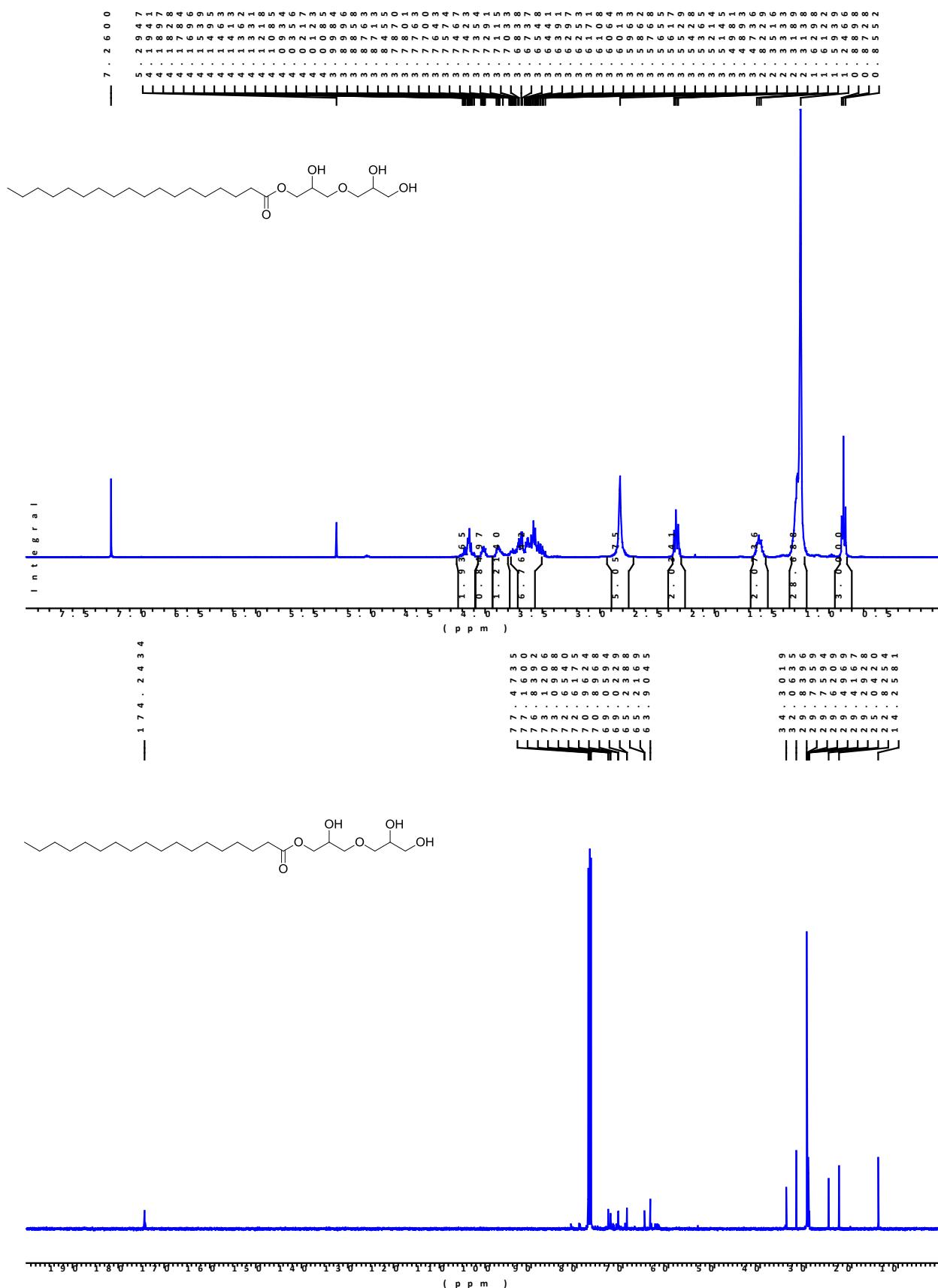
3-(2,3-dihydroxypropoxy)-2-hydroxypropyl hexanoate [1026295-85-1] (7b)



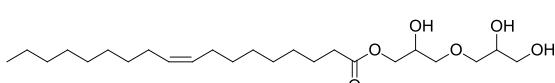
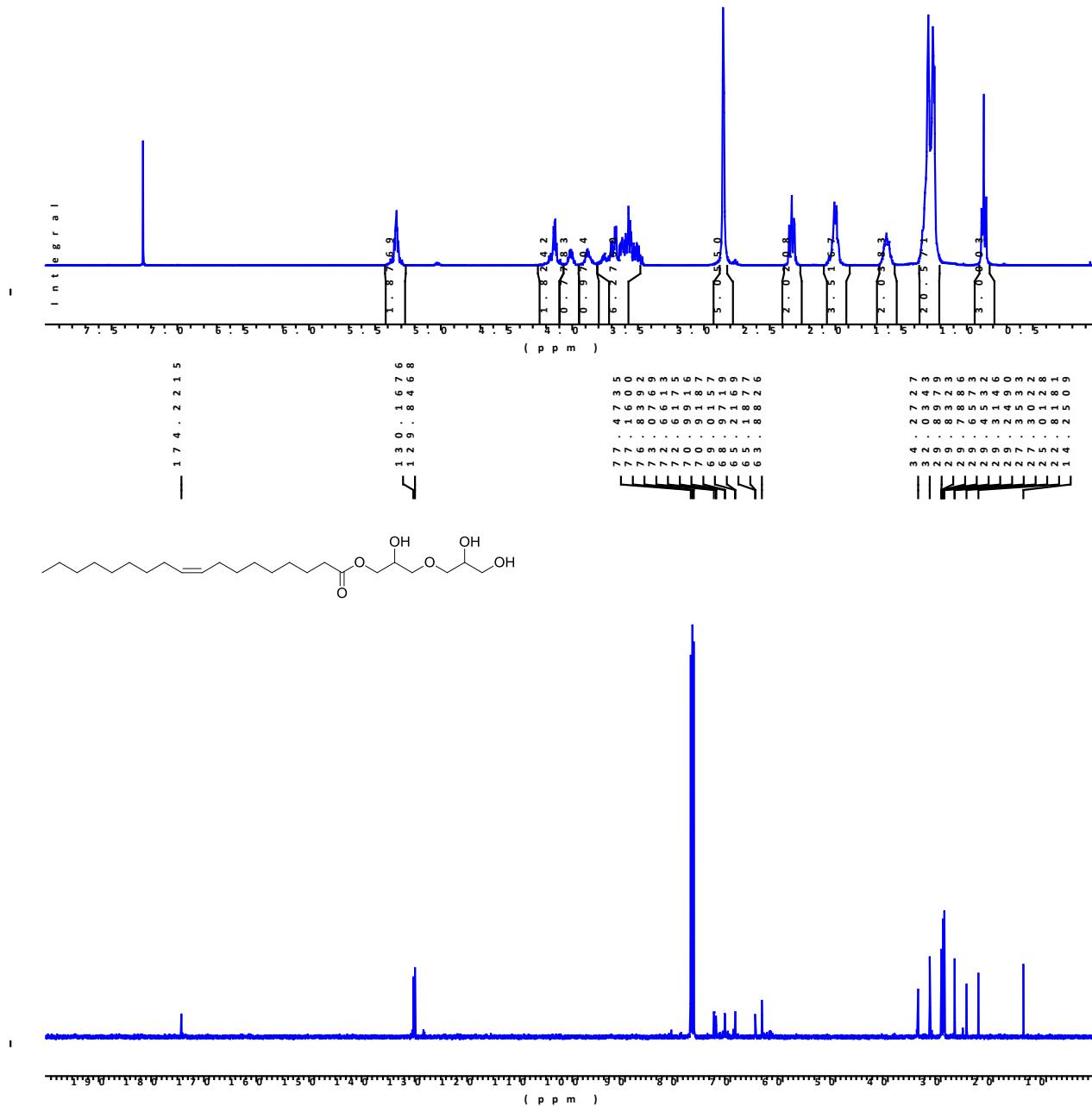
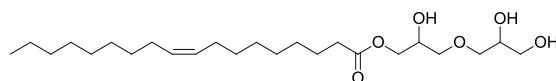
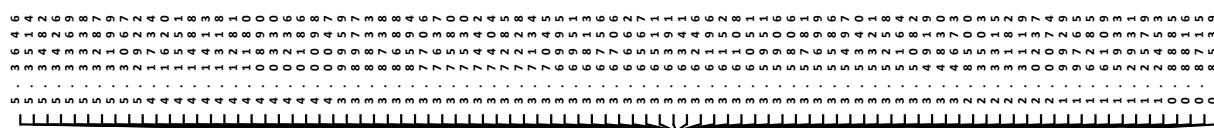
3-(2,3-dihydroxypropoxy)-2-hydroxypropyl decanoate [156153-06-9] (7d)



3-(2,3-dihydroxypropoxy)-2-hydroxypropyl octadecanoate [66168-54-5] (7f)



3-(2,3-dihydroxypropoxy)-2-hydroxypropyl oleate [97605-97-5] (7g)



ⁱ E. Rohart, V. Belliere-Baca, K. Yokota, C. Pitois, *Top. Catal.*, **42-43**, 71-75