Electronic Supplementary Information

Boronic acid-promoted, site-selective Fischer esterification of sugar alcohols

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Materials and Methods

General

All reactions were carried out under an argon atmosphere, unless specifically indicated. Stainless steel needles and gas-tight syringes were used to transfer air- and moisture-sensitive liquids. Flash chromatography was performed using neutral silica gel (Silicycle). Analytical thin layer chromatography (TLC) was carried out using aluminium-backed silica gel 60 F254 plates (EMD), and visualized using short-wave UV light or KMnO4 stain with appropriate heating.

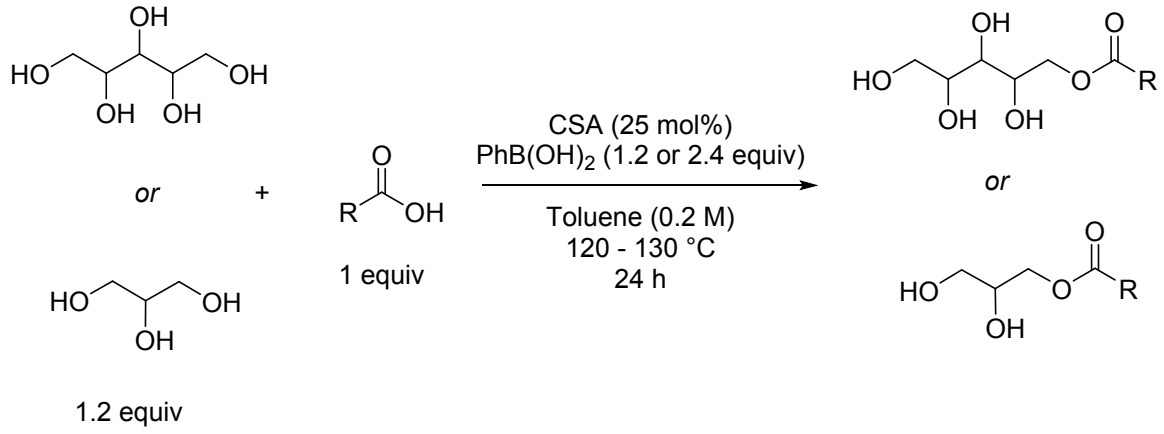
Materials

HPLC grade toluene was dried and purified using a solvent purification system with activated alumina columns under argon (Innovative Technology Inc.). Distilled water was obtained from an in-house supply. Phenylboronic acid purchased from Sigma Aldrich was recrystallized before using. All other reagents and solvents were purchased from Sigma Aldrich, Caledon, Carbosynth or Alfa Aesar and used without further purification. Nuclear magnetic resonance (NMR) solvents were purchased from Cambridge Isotope Laboratories and Sigma Aldrich.

Instrumentation

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions using an Agilent DD2-500 (500 MHz) spectrometer with XSens cryogenic probe. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane with the solvent resonance resulting from incomplete deuteration as the internal standard. Spectral features are tabulated in the following order: chemical shift (δ, ppm); multiplicity (s-singlet, d-doublet, t-triplet, q-quartet, m-complex multiplet, app t–apparent triplet); number of protons; coupling constants (*J*, Hz); assignment. Infared (IR) spectra were obtained on a Perki*n*-Elmer Spectrum 100 instrument equipped with a single-reflection diamond / ZnSe ATR accessory as thin films from CH_2Cl_2. Spectral features are tabulated as follows: wavenumber (cm^{-1}); intensity (s-strong, m-medium, w-weak, br-broad).

General Procedures: Boronic-acid promoted Fischer esterifications



General Procedure A: Boronic acid–promoted Fischer esterification with basic sorbitol workup

To a 25 mL or 50 mL round bottom flask containing a magnetic stir bar was added sugar alcohol (2.4 mmol, 1.2 equivalent), carboxylic acid (2.0 mmol, 1 equivalent), (1S)-(+)-10-Camphorsulphonic acid (CSA) (0.05 mmol, 0.25 equivalents), and phenylboronic acid (2.4 mmol, 1.2 equivalent) or (4.8 mmol, 2.4 equivalents) depending on the sugar alcohol. Anhydrous toluene was added to the flask (0.2 M, 10 mL), and fitted to a Dean Stark apparatus equipped with a reflux condenser. The reaction was purged with argon and all joints were greased and wrapped with Teflon™. The Dean Stark apparatus was wrapped with cotton wool/aluminum foil and the reaction was stirred at 120–130°C. After 24 hours, the solvent was removed by rotary evaporation. The residue was dissolved in roughly 150 mL of diethyl ether (Et_2O). A minimum amount of basic sorbitol solution (1M Na_2CO_3 + 1M D-sorbitol in water) was added (~50 mL for 2 mmol scale) and shaken vigorously in a separatory funnel for 5 minutes. This process was repeated with fresh sorbitol solution. The combined aqueous extracts were back-extracted three times with Et_2O. The combined organic extracts were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The resulting crude reaction mixture was purified by precipitation or recrystallization.

The reaction was also scaled up using 12 mmol sugar alcohol, worked up, and isolated as outlined above for the following substrates with decanoic acid: glycerol, xylitol, and ribitol.

General Procedure B: Boronic acid–promoted Fischer glycosidation with pinacol workup

Reaction parameters were identical to those detailed in *General procedure* A. After 24 hours, the solvent was removed by rotary evaporation. The residue was poured into a separatory funnel to which H_2O (50 mL) and saturated brine solution (50 mL) were added. The aqueous layer was extracted with hexanes (150 mL x 3). The combined organic extracts were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was transferred to a 50 mL round bottom flask equipped with a magnetic stir bar. Pinacol (20 mmol, 10 equivalent) and anhydrous toluene (25 mL, 0.08 M) were added. The reaction flask was fitted to a reflux condenser and stirred overnight at 120–130°C. The solvent was removed by rotary evaporation, and the residue was washed with an abundance of chilled hexanes. The resulting crude reaction mixture was purified by recrystallization in EtOH.

Procedure for recovery of phenylboronic acid after phase switching deprotection.

Decanoic acid (0.50 mmol) was subjected to phenylboronic acid-mediated Fischer esterification using xylitol (1.2 equiv), phenylboronic acid (2.4 equiv) and (S)-CSA (25 mol %) in toluene (2.5 mL), as described in General Procedure A, but in a sealed tube rather than a round-bottomed flask with a Dean–Stark apparatus. The mixture was heated in an oil bath at 125 °C for 24 h, then cooled to room temperature and subjected to workup with aqueous Na_2CO_3/sorbitol as described in General Procedure A. The combined aqueous extracts were acidified to pH 2 and extracted four times with ethyl acetate. The organic extracts were dried over anhydrous magnesium sulfate and concentrated, yielding 123 mg of a white solid (92% purity by mass, as judged by ^1H NMR spectroscopy, with decanoic acid as the impurity; 78% recovery of $PhB(OH)_2$).

Attempted synthesis of secondary monoester sugar alcohols

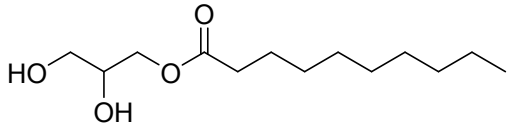
To address if the process of the boronic acid-promoted Fischer esterification is under kinetic or thermodynamic control, the synthesis of a secondary acyl isomer of (±) xylitol monocaprate (**2a**) was attempted. The 1,2:4,5-bis-O-isopropylidene ketal of xylitol was synthesized following a procedure by Miller *et al.*[1] and then subjected to a standard DCC coupling[2] with decanoic acid to yield the 1,2:4,5-bis-O-isopropylidene ketal-protected xylitol ester. Deprotection of the protected xylitol ester in TFA/H_2O resulted in a complex formation of acyl-migrated byproducts that could not be cleanly separated by column chromatography.

Transesterification experiment

As an alternative to investigating the reversibility of the reaction, an equal ratio of (±) ribitol monocaprate (**2c**) and (±) L-arabitol monostearate (**2f**) was subjected to otherwise identical reaction parameters detailed in General Procedure A. An exchange of the ester partners between the sugar alcohols would suggest reversibility. By crude NMR analysis, only 5% L-arabitol monocaprate (**2e**) formation was detected, along with 40% recovered **2c** and <5% recovered **2f**, which suggests that the transformation may not be under thermodynamic control.

Synthesis of monoester sugar alcohols

(±) glycerol monocaprate (3a)



The reaction was set up in toluene at 2.0 mmol according to the General Procedure A. Purification via recrystallization in heptane

[1] K. W. Fiori , A. L. A. Puchlopek and S. J. Miller. *Nat. Chem.* 2009, **1**, 630–634.

[2] F. Chery, L. Cronin, J. L. O'Brien and P. V. Murphy. *Tetrahedron* 2004, **60**, 6597–6608.

provided (±) glycerol monocaprate as a white solid. Yield = 298.1 mg, 1.21 mmol, 61 %. The reaction was also scaled up to 10 mmol according to the General Procedure A and the product was recrystallized three times in heptane, to give a combined yield of 1.602 g (6.50 mmol, 54 %). Spectrum.

^{1}HNMR (500 MHz, DMSO-d_6) δ 4.85 (d, *J* = 5.2 Hz, 1H, O-*H*), 4.61 (dd, *J* = 5.9, 5.5 Hz, 1H, O-*H*), 4.03 (dd, *J* = 11.1, 4.2 Hz, 1H, *H*-1a), 3.89 (dd, *J* = 11.1, 6.5 Hz, 1H, *H*-1b), 3.66–3.59 (m, 1H, *H*-2), 3.38–3.28 (m, 2H, *H*-3a, *H*-3b), 2.28 (t, *J* = 7.4 Hz, 2H), 1.51 (m, 2H), 1.25 (m, 12H), 0.89–0.81 (m, 3H).

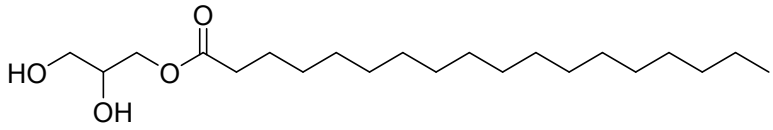
^{13}CNMR (126 MHz, DMSO-d_6) δ 172.9, 69.3, 65.5, 62.6, 33.5, 31.3, 28.8, 28.7, 28.6, 28.5, 24.4, 22.1, 14.0.

IR (thin film, cm^{-1}): 3232 (br, m), 2918 (s), 2851 (s), 1739 (s), 1729 (s), 1171 (s), 1103 (s), 1046 (s), 720 (s).

MP: 53.2–54.3 °C [lit: 51.4 °C][3]

HRMS (DART+): calculated for $C_{13}H_{30}NO_4$ $[M+NH_4]^+$: 264.2175 m/z, found: 264.2171 m/z

(±) glycerol monostearate (3b)



The reaction was set up in toluene at 2.0 mmol according to the General Procedure A. Following the workup, the crude reaction mixture was washed with cold heptane and recrystallized in EtOH to provide (±) glycerol monostearate as a white solid. Yield = 391 mg, 1.09 mmol, 55 %. Spectrum.

^{1}H NMR (500 MHz, DMSO-d_6) δ 4.85 (d, *J* = 5.1 Hz, 1H, O-*H*), 4.61 (t, *J* = 5.6 Hz, 1H, O-*H*), 4.03 (dd, *J* = 11.1, 4.2 Hz, 1H, *H*-1a), 3.89 (dd, *J* = 11.1, 6.5 Hz, 1H, *H*-1b), 3.62 (h, *J* = 5.3 Hz, 1H, *H*-2), 3.39–3.27 (m, 2H, *H*-3a, *H*-3b), 2.28 (t, *J* = 7.4 Hz, 2H), 1.51 (p, *J* = 7.0 Hz, 2H), 1.23 (s, 28H), 0.89–0.82 (m, 3H).

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[3] Averill, H. P. *J. Am. Chem. Soc*. 1929, **51**, 866–872.

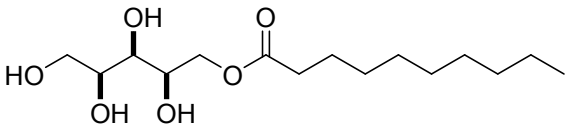
^{13}C NMR (126 MHz, DMSO-d_6) δ 172.9, 69.3, 65.5, 62.6, 33.5, 31.3, 29.0, 29.0, 29.0, 29.0, 29.0, 28.9, 28.7, 28.5, 24.4, 22.1, 13.9.

IR (thin film, cm^{-1}): 3295 (br, m), 3236 (br, m), 2916 (s), 2849 (s), 1730 (s), 1471 (m), 1176 (s), 1048 (s), 720 (s).

MP: 76.2–80.4 °C [lit: 81–81.5 °C][4]

HRMS (DART+): calculated for $C_{21}H_{46}NO_4$ $[M + NH_4]^+$: 376.3427 m/z; found 376.3418 m/z.

(±) xylitol monocaprate (2a)



The reaction was set up in toluene at 2.0 mmol according to the General Procedure A. Purification via recrystallization in EtOH provided (±) xylitol monocaprate as a white solid. Yield = 283 mg, 0.92 mmol, 46%. The reaction was also scaled up to 10 mmol according to the General Procedure A and the product was purified by three separate recyrstallizations in EtOH. Yield = 1.562 g, 5.10 mmol, 43 %. Spectrum.

^{1}H NMR (500 MHz, DMSO-d_6) δ 4.78 (d, *J* = 5.5 Hz, 1H, O-*H*), 4.47 (dd, *J* = 5.9, 5.3 Hz, 1H, O-*H*), 4.42 (d, *J* = 5.5 Hz, 1H, O-*H*), 4.36 (d, *J* = 6.5 Hz, 1H, O-*H*), 4.05 (dd, *J* = 11.2, 4.3 Hz, 1H, *H*-1a), 4.00 (dd, *J* = 11.2, 7.2 Hz, 1H, *H*-1b), 3.73 (m, 1H, *H*-2), 3.53 (m, 1H, *H*-4), 3.46–3.39 (m, 2H, *H*-3, *H*-5a), 3.39–3.33 (m, 1H, *H*-5b), 2.27 (t, *J* = 7.4 Hz, 2H), 1.56–1.47 (m, 2H), 1.25 (m, 12H), 0.90–0.82 (m, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 173.0, 71.7, 70.5, 69.6, 65.7, 62.6, 33.5, 31.3, 28.8, 28.7, 28.6, 28.5, 24.4, 22.1, 13.9.

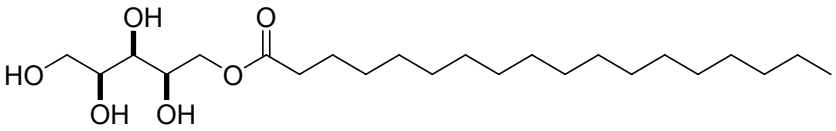
IR (thin film, cm^{-1}): 3410 (br, m), 3301 (br, m), 2919 (s), 2851 (s), 1726 (s), 1391 (m), 1173 (s), 1143 (s), 1027 (s), 720 (s).

MP: 65.5–69.4 °C [lit: 62.3 °C][5]

[4] Hartman, L. *J. Chem. Soc.* **1959**, 4134–4135.

HRMS (DART+): calculated for $C_{15}H_{31}O_6$ $[M+H]^+$: 307.2121 m/z, found: 307.2123 m/z

(±) xylitol monostearate (2b)



The reaction was set up in toluene at 2.0 mmol according to the General Procedure A. Purification via recrystallization in EtOH provided (±) xylitol monostearate as a white solid. Yield = 676.8 mg, 1.62 mmol, 81 %. Spectrum.

^{1}H NMR (500 MHz, DMSO-d_6) δ 4.77 (d, *J* = 5.5 Hz, 1H, O-*H*), 4.47 (app t, *J* = 5.6 Hz, 1H, O-*H*), 4.42 (d, *J* = 5.5 Hz, 1H, O-*H*), 4.36 (d, *J* = 6.4 Hz, 1H, O-*H*), 4.05 (dd, *J* = 11.2, 4.4 Hz, 1H, *H*-1a), 4.00 (dd, *J* = 11.2, 7.2 Hz, 1H, *H*-1b), 3.73 (m, 1H, *H*-2), 3.53 (m, 1H, *H*-4), 3.46–3.39 (m, 2H, *H*-3, *H*-5a), 3.35 (m, 1H, *H*-5b), 2.27 (t, *J* = 7.4 Hz, 2H), 1.51 (m, 2H), 1.23 (m, 28H), 0.88–0.82 (m, 3H).

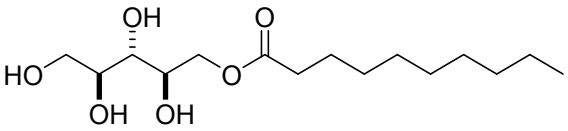
^{13}C NMR (126 MHz, DMSO-d_6) δ 173.0, 71.7, 70.5, 69.6, 65.7, 62.6, 33.5, 31.3, 29.1, 29.0, 29.0, 28.9, 28.8, 28.7, 28.5, 24.5, 22.1, 14.0.

IR (thin film, cm^{-1}): 3408 (br, m), 2916 (s), 2850 (s), 1726 (s), 1472 (m), 1172 (s), 1145 (s), 1028 (s), 717 (s).

MP: 92.4–98.4 °C

HRMS (DART+): calculated for $C_{23}H_{47}O_6$ $[M+H]^+$: 419.3373 m/z, found: 419.3378 m/z

(±) ribitol monocaprate (2c)



The reaction was set up in toluene at 2.0 mmol according to the General Procedure A. Purification via recrystallization in diethyl ether provided (±) ribitol monocaprate as a white solid. Yield = 288.5 mg, 0.94

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[5] J. W. Goodby, J. A. Haley, M. J. Watson, G. Mackenzie, S. M. Kelly, P. Letellier, O. Douillet, P. Gode, G. Goethals, G. Ronco and P. Villa, *Liquid Cryst.*, 1997, **22**, 367–378.

mmol, 47 %. The reaction was also scaled up to 10 mmol according to the General Procedure A and the same product was purified by three separate recyrstallizations in diethyl ether. Yield = 1.618 g, 5.28 mmol, 44 %. Spectrum.

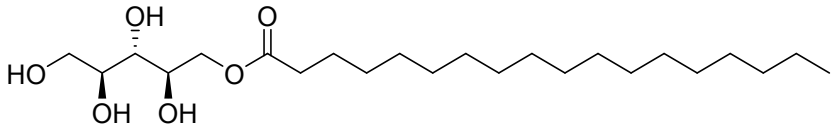
^{1}H NMR (500 MHz, DMSO-d_6) δ 4.83 (d, *J* = 5.5 Hz, 1H, O-*H*), 4.70 (d, *J* = 5.6 Hz, 1H, O-*H*), 4.60 (d, *J* = 5.2 Hz, 1H, O-*H*), 4.37 (t, *J* = 5.6 Hz, 1H, O-*H*), 4.14 (dd, *J* = 11.3, 2.8 Hz, 1H, *H*-1a), 3.98 (dd, *J* = 11.3, 7.5 Hz, 1H, *H*-1b), 3.76 (m, 1H, *H*-2), 3.56 (m, 1H, *H*-5a), 3.50 (m, 1H, *H*-4), 3.38 (m, 2H, *H*-3, *H*-5b), 2.28 (t, *J* = 7.4 Hz, 2H), 1.52 (m, 2H), 1.32–1.19 (m, 12H), 0.89–0.82 (m, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 173.1, 72.7, 72.4, 69.8, 65.9, 63.0, 33.5, 31.3, 28.9, 28.7, 28.6, 28.5, 24.4, 22.1, 14.0.

IR (thin film, cm^{-1}): 3484 (br, m), 3274 (br, m), 2919 (s), 2850 (s), 1702 (s), 1467 (m), 1414 (m), 1378 (m), 1327 (m), 1218 (m), 1189 (m), 1036 (s), 955 (m)
MP: 72.8–76.2 °C

HRMS (DART+): calculated for $C_{15}H_{31}O_6$ $[M+H]^+$: 307.2121 m/z, found: 307.2121 m/z

(±) ribitol monostearate (2d)



The reaction was set up in toluene at 2.0 mmol according to the General Procedure B. Following the workup, the crude reaction mixture was washed with cold heptane and recrystallized in EtOH to provide (±) ribitol monostearate as a white solid. Yield = 372 mg, 0.888 mmol, 44 %. Spectrum.

^{1}H NMR (500 MHz, DMSO-d_6) δ 4.84 (d, *J* = 5.6 Hz, 1H, O-*H*), 4.72 (d, *J* = 5.6 Hz, 1H, O-*H*), 4.62 (d, *J* = 5.2 Hz, 1H, O-*H*), 4.39 (t, *J* = 5.6 Hz, 1H, O-*H*), 4.13 (dd, *J* = 11.3, 2.8 Hz, 1H, *H*-1a), 3.98 (dd, *J* = 11.3, 7.6 Hz, 1H, *H*-1b), 3.76 (dtd, *J* = 7.5, 5.6, 2.8 Hz, 1H, *H*-2), 3.55 (ddd, *J* = 10.9, 5.8, 3.4 Hz, 1H, *H*-5a), 3.50 (tdd, *J* = 6.3, 5.1, 3.5 Hz, 1H, *H*-4), 3.42–3.34 (m, 2H, *H*-3, *H*-5b), 2.28 (t, *J* = 7.4 Hz, 2H), 1.51 (p, *J* = 7.6 Hz, 2H), 1.23 (s, 28H), 0.89–0.81 (m, 3H).

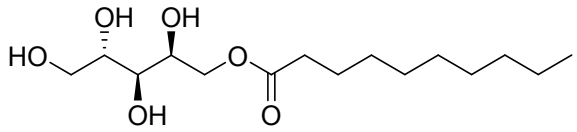
^{13}C NMR (126 MHz, DMSO-d_6) δ 173.5, 73.1, 72.9, 70.3, 66.3, 63.5, 34.0, 31.7, 29.5, 29.4, 29.4, 29.2, 29.1, 29.0, 24.9, 22.5, 14.4.

IR (thin film, cm^{-1}): 3294 (br, m), 3233 (br, m), 2916 (s), 2849 (s), 1730 (s), 1471 (m), 1193 (m), 1176 (s), 1048 (s), 720 (s).

MP: 101.4–104.2 °C

HRMS (DART+): calculated for $C_{23}H_{47}O_6$ $[M+H]^+$ 419.3373 m/z; found 419.3379 m/z.

L-arabitol monocaprate (S,S,S) (2e)



The reaction was set up in toluene at 2.0 mmol according to the General Procedure A. Purification via recrystallization in EtOH provided L-arabitol monocaprate (S,S,S) as a white solid. Yield = 232.9 mg, 0.76 mmol, 38 %. Spectrum.

^{1}H NMR (500 MHz, DMSO-d_6) δ 4.54 (d, *J* = 6.6 Hz, 1H, O-*H*), 4.49 (d, *J* = 5.6 Hz, 1H, O-*H*), 4.42 (d, *J* = 7.6 Hz, 1H, O-*H*), 4.34 (t, *J* = 5.7 Hz, 1H, O-*H*), 4.01 (dd, *J* = 10.8, 7.4 Hz, 1H, *H*-1a), 3.97 (dd, *J* = 10.8, 5.6 Hz, 1H, *H*-1b), 3.88 (m, 1H, *H*-2), 3.59 (m, 1H, *H*-5a), 3.47 (m, 1H, *H*-4), 3.39 (m, 1H, *H*-5b), 3.24 (ddd, *J* = 8.4, 7.6, 1.8 Hz, 1H, *H*-3), 2.28 (t, *J* = 7.4 Hz, 2H), 1.51 (m, 2H), 1.24 (m, 12H), 0.91–0.82 (m, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 172.9, 71.0, 70.6, 67.3, 65.7, 63.6, 33.5, 31.3, 28.8, 28.7, 28.6, 28.5, 24.5, 22.1, 14.0.

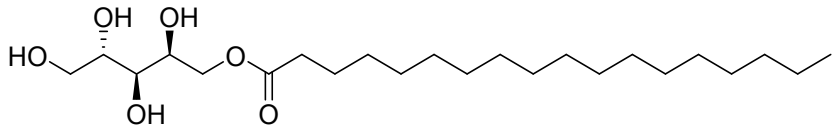
IR (thin film, cm^{-1}): 3374 (br, m), 3250 (br, m), 2921 (m), 1742 (s), 1214 (m), 1164 (s), 1097 (s), 1076 (s), 1041 (s), 722 (m)

MP: 124.0–126.0 °C

Optical Rotation: $[\alpha]_D^{20}$ –3 (*c* 1.0, DMSO)

HRMS (DART+): calculated for $C_{15}H_{31}O_6$ $[M+H]^+$: 307.2121 m/z, found: 307.2119 m/z

L-arabitol monostearate (S,S,S) (2f)



The reaction was set up in toluene at 2.0 mmol according to the General Procedure A. Purification via recrystallization in EtOH provided L-arabitol monostearate as a white solid. Yield = 274 mg, 0.655 mmol, 33 %. Spectrum.

^{1}H NMR (500 MHz, DMSO-d_6) δ 4.68 (d, *J* = 6.8 Hz, 1H, O-*H*), 4.65 (d, *J* = 5.6 Hz, 1H, O-*H*), 4.51 (d, *J* = 7.7 Hz, 1H, O-*H*), 4.43 (t, *J* = 5.8 Hz, 1H, O-*H*), 4.03 – 3.94 (m, 2H, *H*-1a, *H*-1b), 3.89 (m, 1H, *H*-2), 3.57 (m, 1H, *H*-5a), 3.46 (m, 1H, *H*-4), 3.40 (m, 1H, *H*-5b), 3.22 (ddd, *J* = 8.9, 7.8, 1.7 Hz, 1H, *H*-3), 2.27 (t, *J* = 7.4 Hz, 2H), 1.49 (m, 3H), 1.31 – 1.16 (s, 31H), 0.90 – 0.80 (m, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 172.9, 70.9, 70.7, 67.2, 65.8, 63.5, 33.5, 31.3, 29.0, 29.0, 28.9, 28.9, 28.8, 28.7, 28.7, 28.5, 24.5, 22.1, 14.0.

IR (thin film, cm^{-1}): 3399 (br, m), 3293 (br, m), 2919 (s), 2851 (s), 1727 (s), 1472 (m), 1172 (s), 1144 (s), 1028 (s), 719 (s).

MP: 93.0 – 97.0 °C

Optical Rotation: $[\alpha]_D^{20}$ –2.6 (*c* 1.0, DMSO)

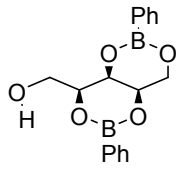
HRMS (DART+): calculated for $C_{23}H_{47}O_6$ $[M+H]^+$:418.3373 m/z; found 418.3529 m/z.

Details of computational modelling

This section will provide more detailed information on the boronate species evaluated. Calculated at the M06-2X/6-311+G(d,p) level of theory in the gas phase.[6] Electronic

[6] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.;

energy (Hartree) for each structure is provided, along with the zero point correction energy (Ezpe), as well as thermal corrections to energy (Ecorr), enthalpy (Hcorr), and Gibbs free energy (Gcorr) in Hartree. The number of imaginary frequencies are given, and the frequency (cm^{-1}) where applicable, for each structure.

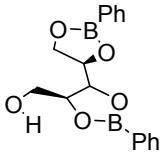


Xylitol bis-boronic ester **A**
Energy: -1084.55660947
Ezpe: -1084.21700547
Ecorr: -1084.19701547
Hcorr: -1084.19607147
Gcorr: -1084.26787547
Imaginary Frequencies: 0

Center Number	Atomic Type	Atomic Center	Coordinates (Angstroms) X	Y	Z
1	0	C	0.404292	3.070376	-1.517556
2	0	H	-0.193508	2.302453	-2.018031
3	0	H	-0.215797	3.957137	-1.367096
4	0	C	0.869703	2.536378	-0.174478
5	0	H	1.482604	3.303331	0.314796
6	0	C	-0.272311	2.164291	0.757144

Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09; Gaussian, Inc.: Wallingford, CT, 2009.

7	0	H	-0.796760	3.079690	1.056272
8	0	C	0.277049	1.466151	1.996772
9	0	H	0.873228	2.174626	2.582794
10	0	C	-0.861519	0.946241	2.852335
11	0	H	-1.381806	1.786723	3.322982
12	0	H	-0.462843	0.295783	3.632069
13	0	O	1.089987	0.364487	1.621803
14	0	O	-1.171856	1.310547	0.068864
15	0	O	1.702671	1.409738	-0.441739
16	0	O	-1.789100	0.189083	2.093516
17	0	O	1.506916	3.464815	-2.303196
18	0	H	2.080337	2.696990	-2.391324
19	0	B	1.773552	0.360344	0.432793
20	0	B	-1.903618	0.363902	0.745834
21	0	C	2.664194	-0.867858	0.083599
22	0	C	2.750517	-1.957130	0.957490
23	0	C	3.403894	-0.904227	-1.103322
24	0	C	3.552600	-3.051737	0.655629
25	0	H	2.179304	-1.940397	1.879332
26	0	C	4.208659	-1.995071	-1.410572
27	0	H	3.345588	-0.066028	-1.789246
28	0	C	4.282821	-3.070100	-0.529314
29	0	H	3.609371	-3.890058	1.340092
30	0	H	4.777373	-2.009960	-2.333005
31	0	H	4.908813	-3.922615	-0.767334
32	0	C	-2.902799	-0.520672	-0.055737
33	0	C	-3.068686	-0.346808	-1.434006
34	0	C	-3.661502	-1.502253	0.590949
35	0	C	-3.968107	-1.130069	-2.148300
36	0	H	-2.485127	0.411903	-1.944764
37	0	C	-4.561972	-2.288907	-0.117995
38	0	H	-3.538254	-1.645323	1.659127
39	0	C	-4.715664	-2.101675	-1.488921
40	0	H	-4.088216	-0.985342	-3.215715
41	0	H	-5.142597	-3.047480	0.393933
42	0	H	-5.417329	-2.713591	-2.044300



Xylitol bis-boronic ester **B**

Energy: -1084.55462353

Ezpe: -1084.21546253

Ecorr: -1084.19558953

Hcorr: -1084.19464553

Gcorr: -1084.26479453

Imaginary Frequencies: 0

Center Number	Atomic Type	Atomic Center	Coordinates (Angstroms) X	Y	Z
1	0	C	-1.785599	-2.852109	0.985599
2	0	H	-2.141816	-2.500093	1.955162
3	0	H	-2.100961	-3.886670	0.833600
4	0	C	-2.238181	-1.930938	-0.168376
5	0	H	-3.031535	-2.373015	-0.776558
6	0	C	-2.653635	-0.540712	0.306149
7	0	H	-3.508139	-0.596826	0.986364
8	0	C	-2.918864	0.429240	-0.872846

9	0	H	-2.906923	-0.100463	-1.830141
10	0	C	-4.204730	1.221863	-0.729910
11	0	H	-5.059894	0.541827	-0.752334
12	0	H	-4.294250	1.915550	-1.573633
13	0	O	-4.259366	1.902695	0.504169
14	0	H	-3.549782	2.552125	0.515172
15	0	O	-1.809811	1.331201	-0.850464
16	0	O	-1.542762	0.020773	1.002019
17	0	O	-1.063891	-1.769676	-0.963575
18	0	O	-0.361813	-2.787069	0.960495
19	0	B	0.012203	-2.108257	-0.166410
20	0	B	-1.007599	1.015155	0.218273
21	0	C	1.468457	-1.684587	-0.469055
22	0	C	1.734646	-0.750953	-1.476699
23	0	C	2.520947	-2.114621	0.346250
24	0	C	3.018041	-0.250918	-1.661423
25	0	H	0.919476	-0.395044	-2.099116
26	0	C	3.809187	-1.628637	0.156116
27	0	H	2.319534	-2.824711	1.141610
28	0	C	4.055444	-0.692166	-0.844720
29	0	H	3.207660	0.489314	-2.429972
30	0	H	4.618697	-1.967233	0.792489
31	0	H	5.056434	-0.298849	-0.982688
32	0	C	0.373558	1.665384	0.467159
33	0	C	1.238723	1.145803	1.437116
34	0	C	0.827306	2.700874	-0.356644
35	0	C	2.525729	1.649533	1.580746
36	0	H	0.904851	0.324040	2.062856
37	0	C	2.111411	3.213280	-0.211083
38	0	H	0.170026	3.094005	-1.125311
39	0	C	2.960801	2.684382	0.756411
40	0	H	3.194404	1.229715	2.323143
41	0	H	2.454320	4.015371	-0.854345
42	0	H	3.966567	3.074777	0.864480

^{1}H, ^{13}C, and 2D NMR Spectra

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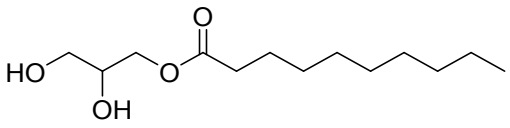
^{1}H NMR (500 MHz, DMSO-d_6) (±) glycerol monocaprate (3a)



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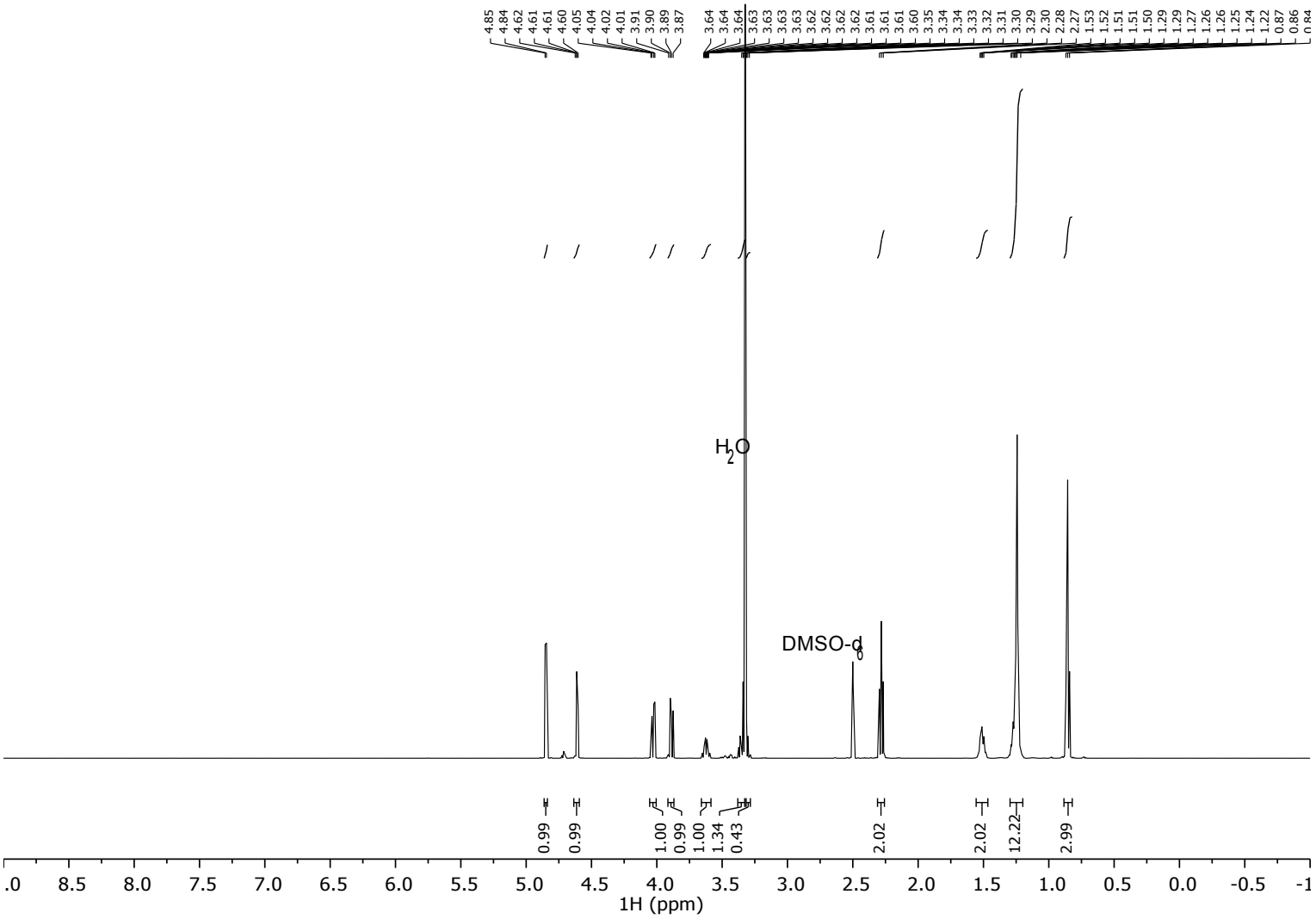
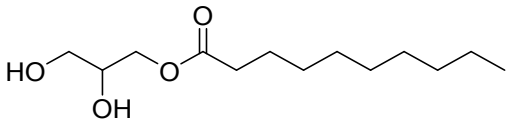
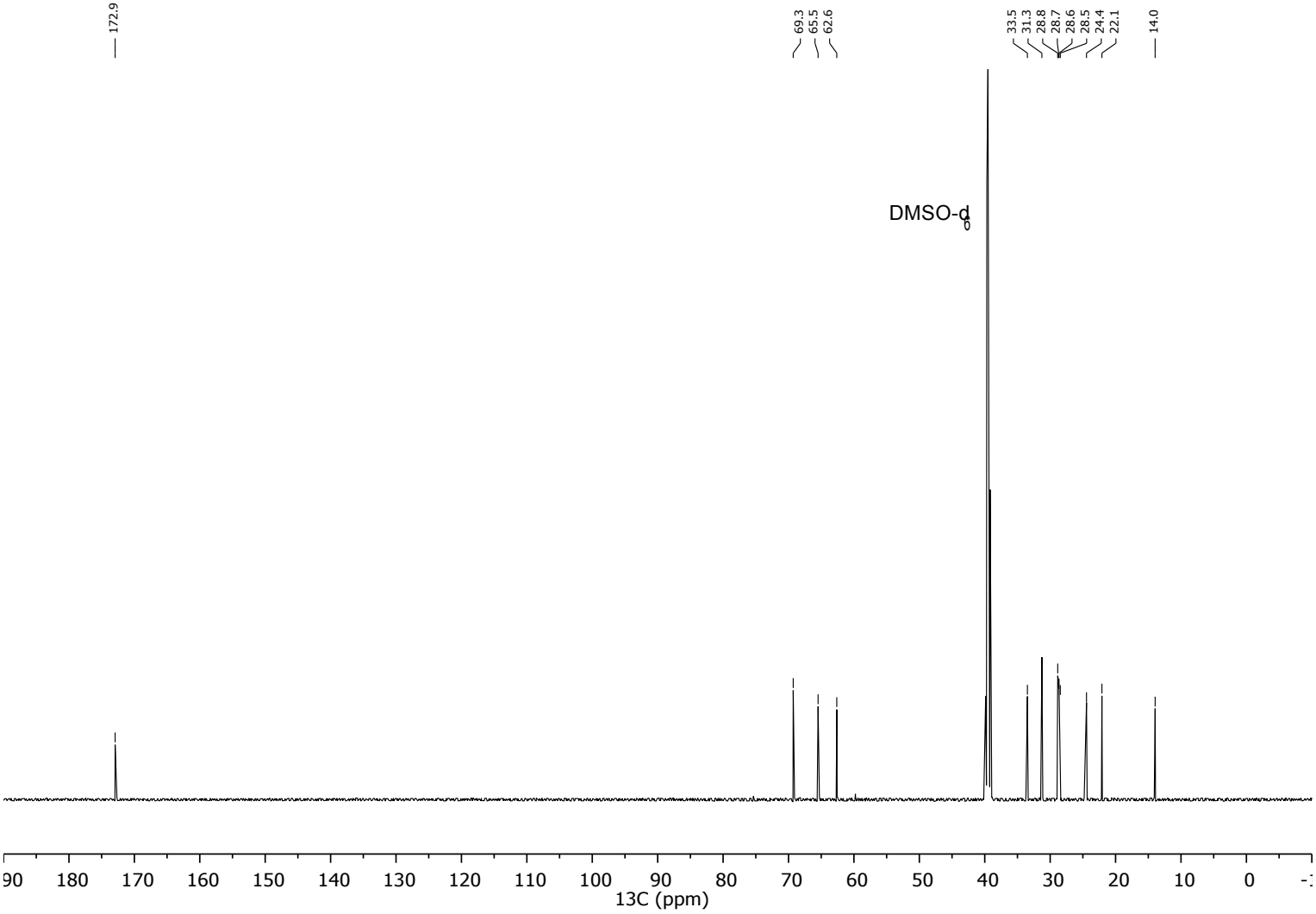
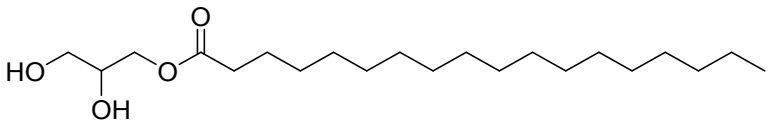


^{13}C NMR (125 MHz, DMSO-d_6) (±) glycerol monocaprate (3a)





^{1}H NMR (500 MHz, DMSO-d_6) (±) glycerol monostearate (3b)



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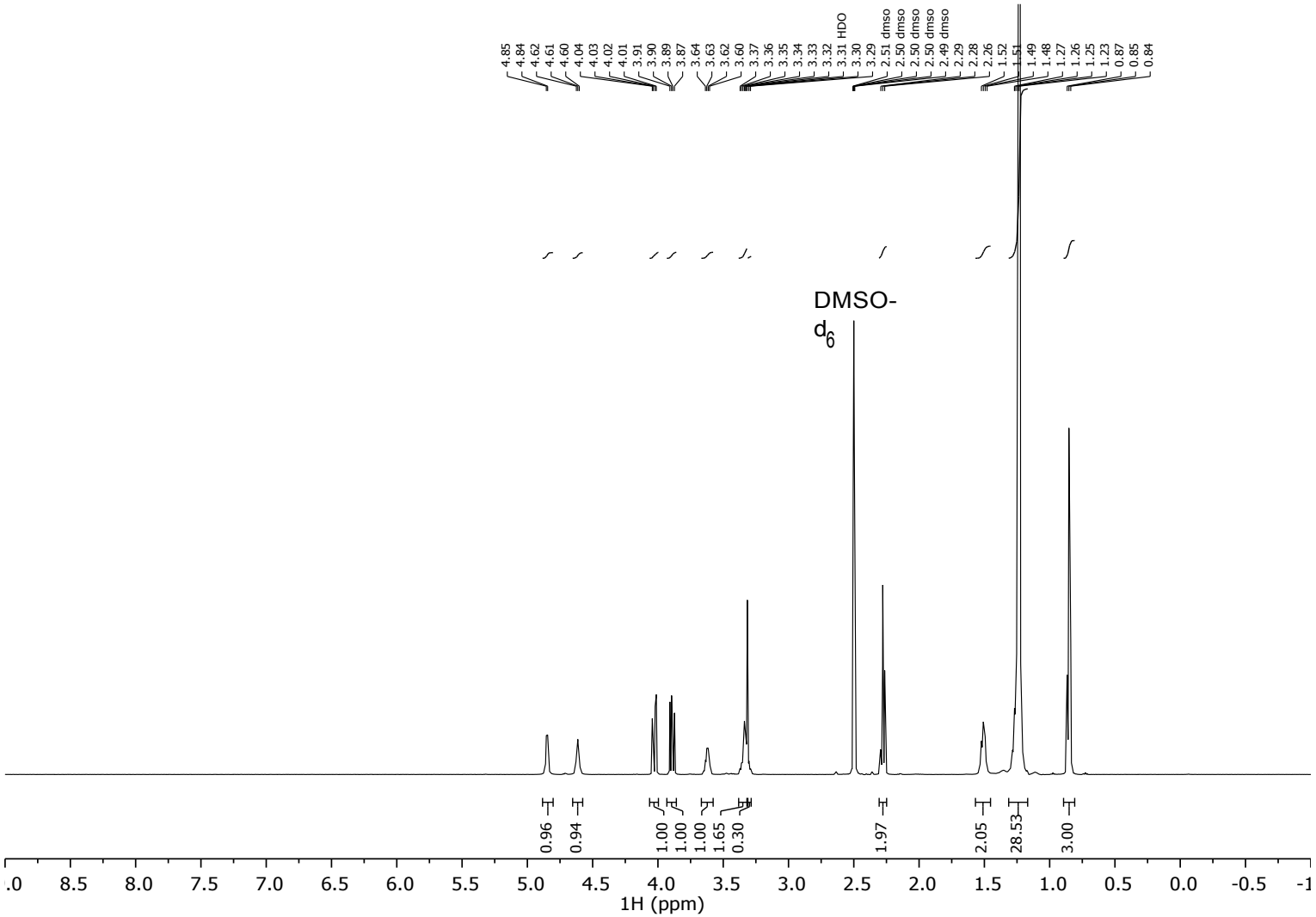
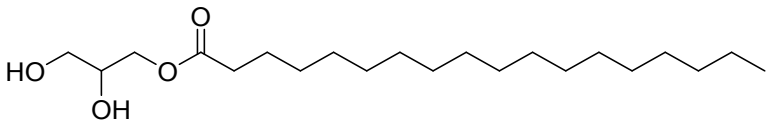
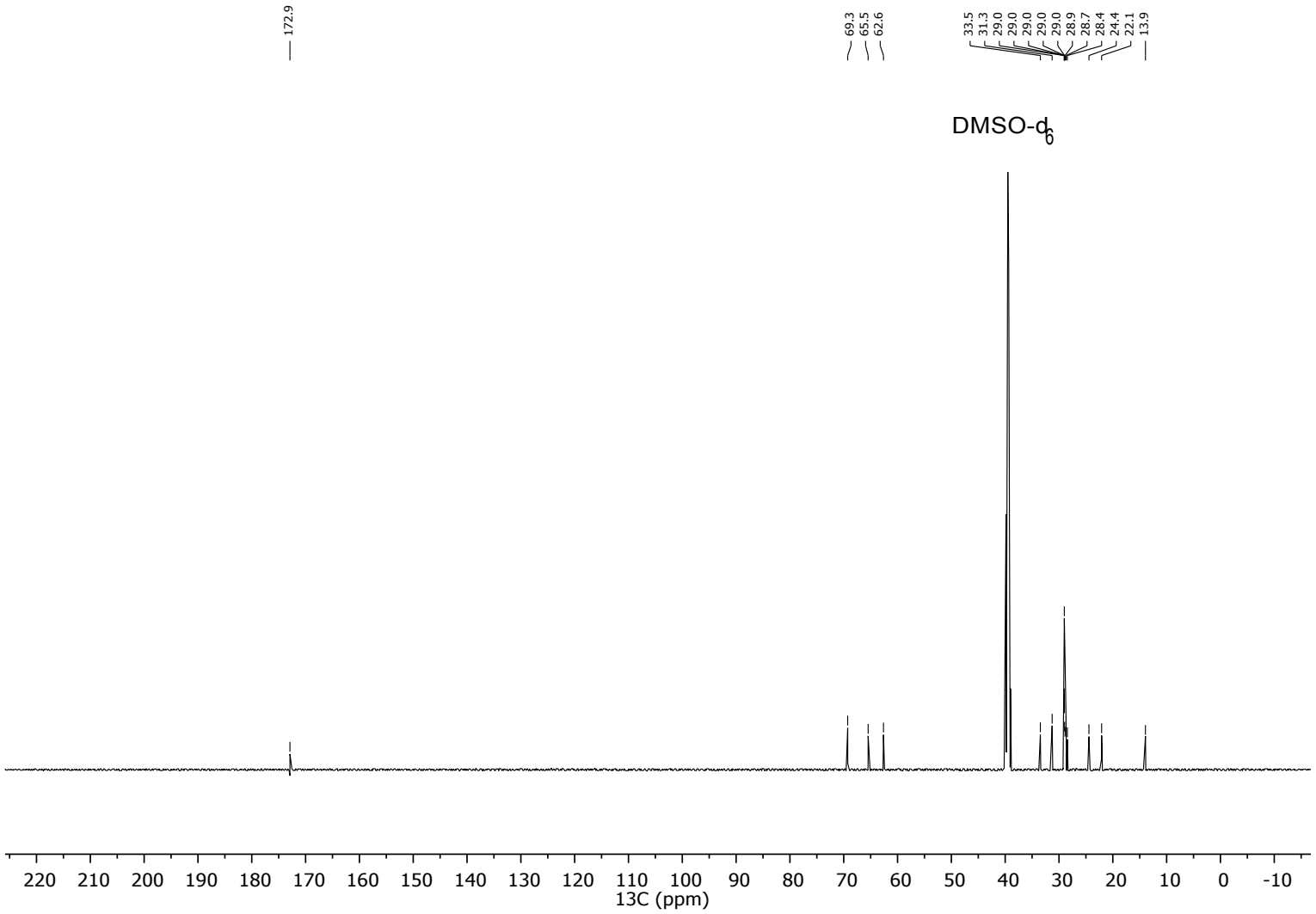
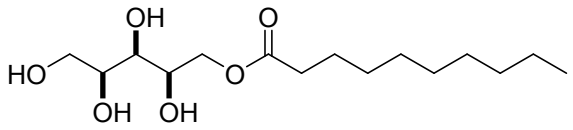


^{13}C NMR (125 MHz, DMSO-d_6) (±) glycerol monostearate (3b)





^{1}H NMR (500 MHz, DMSO-d_6) (±) xylitol monocaprate (2a)



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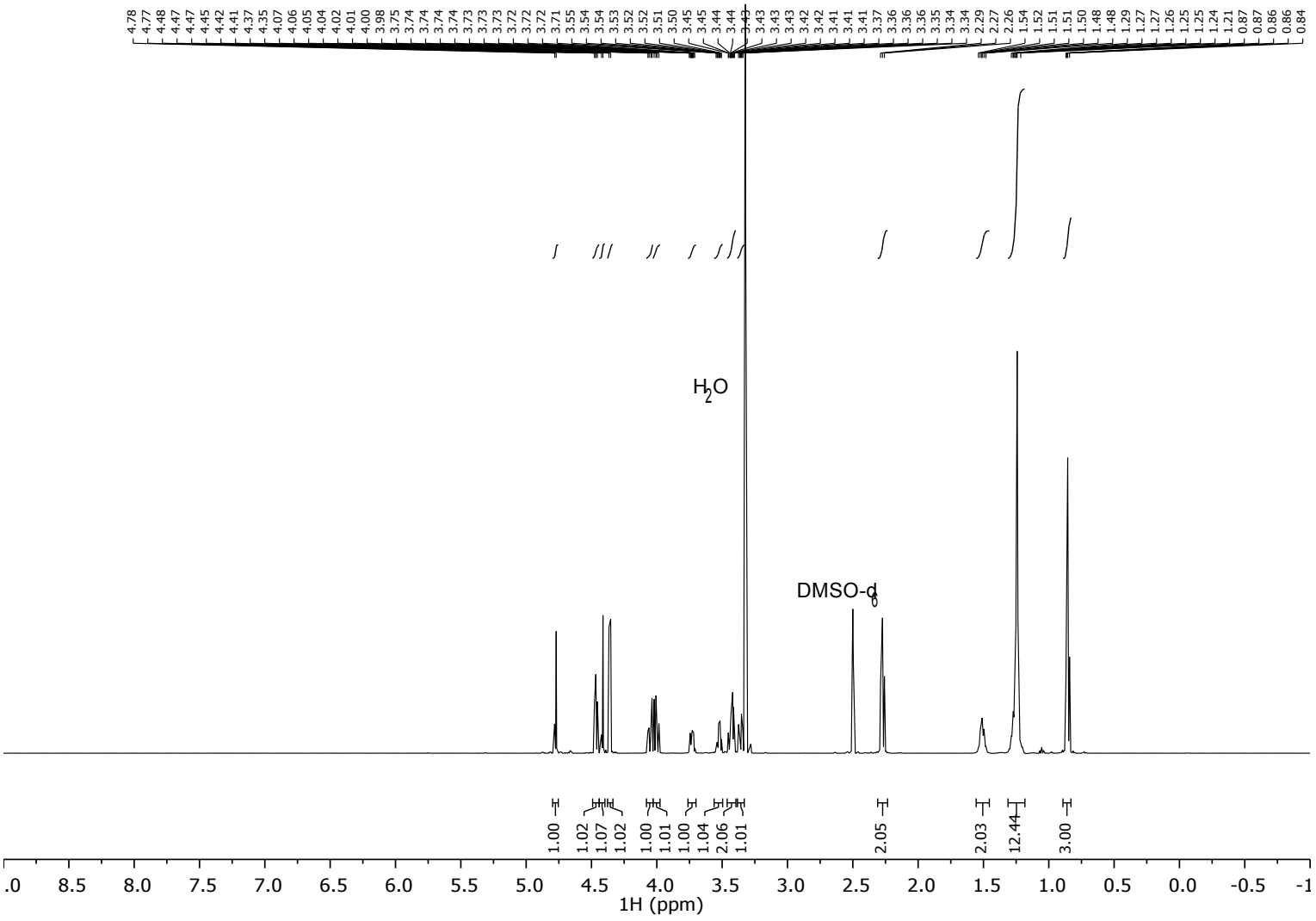
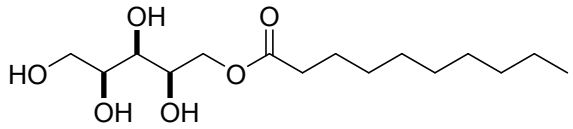
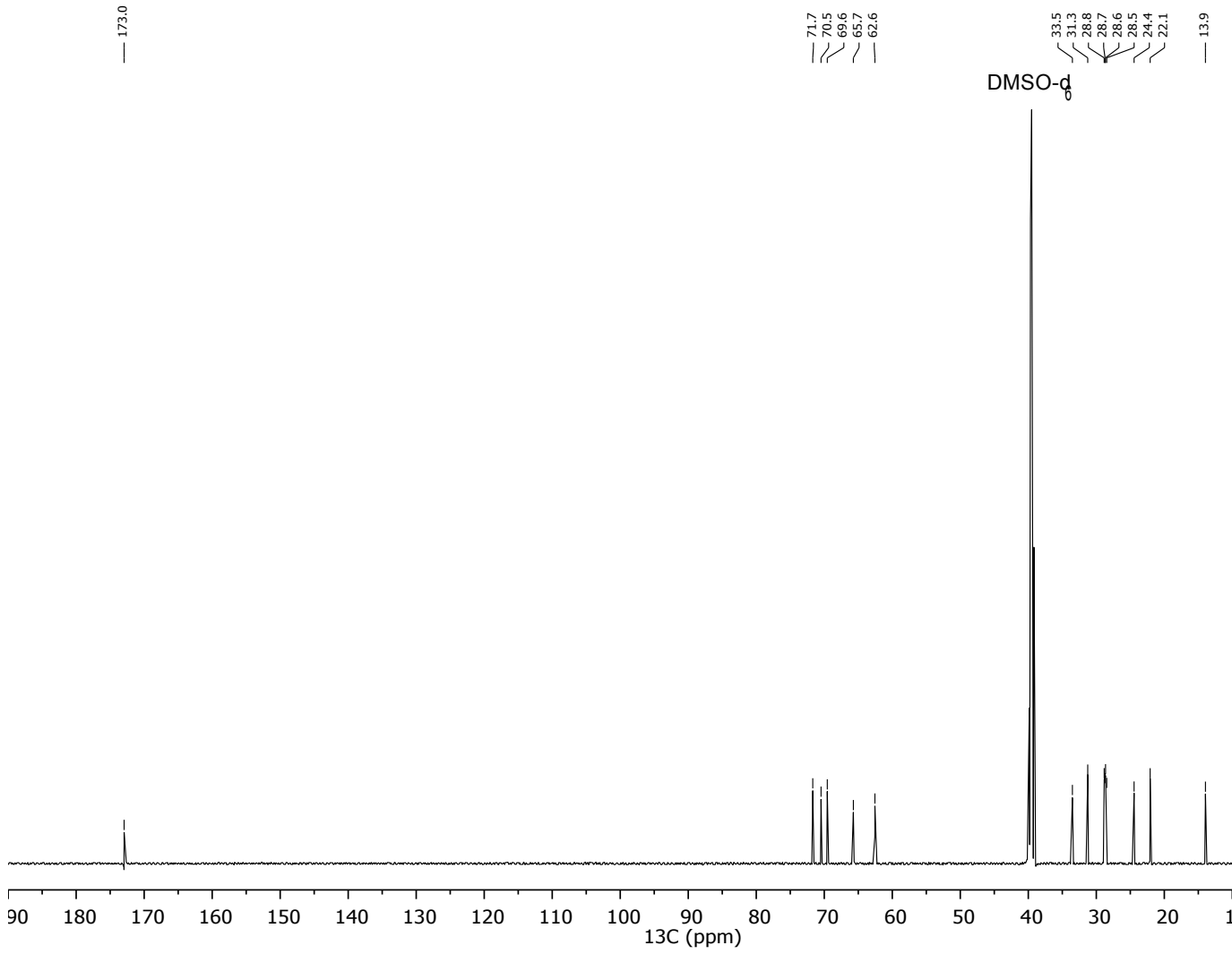
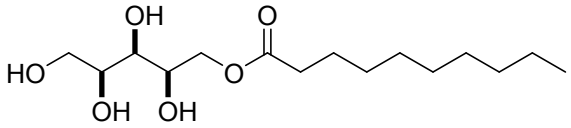


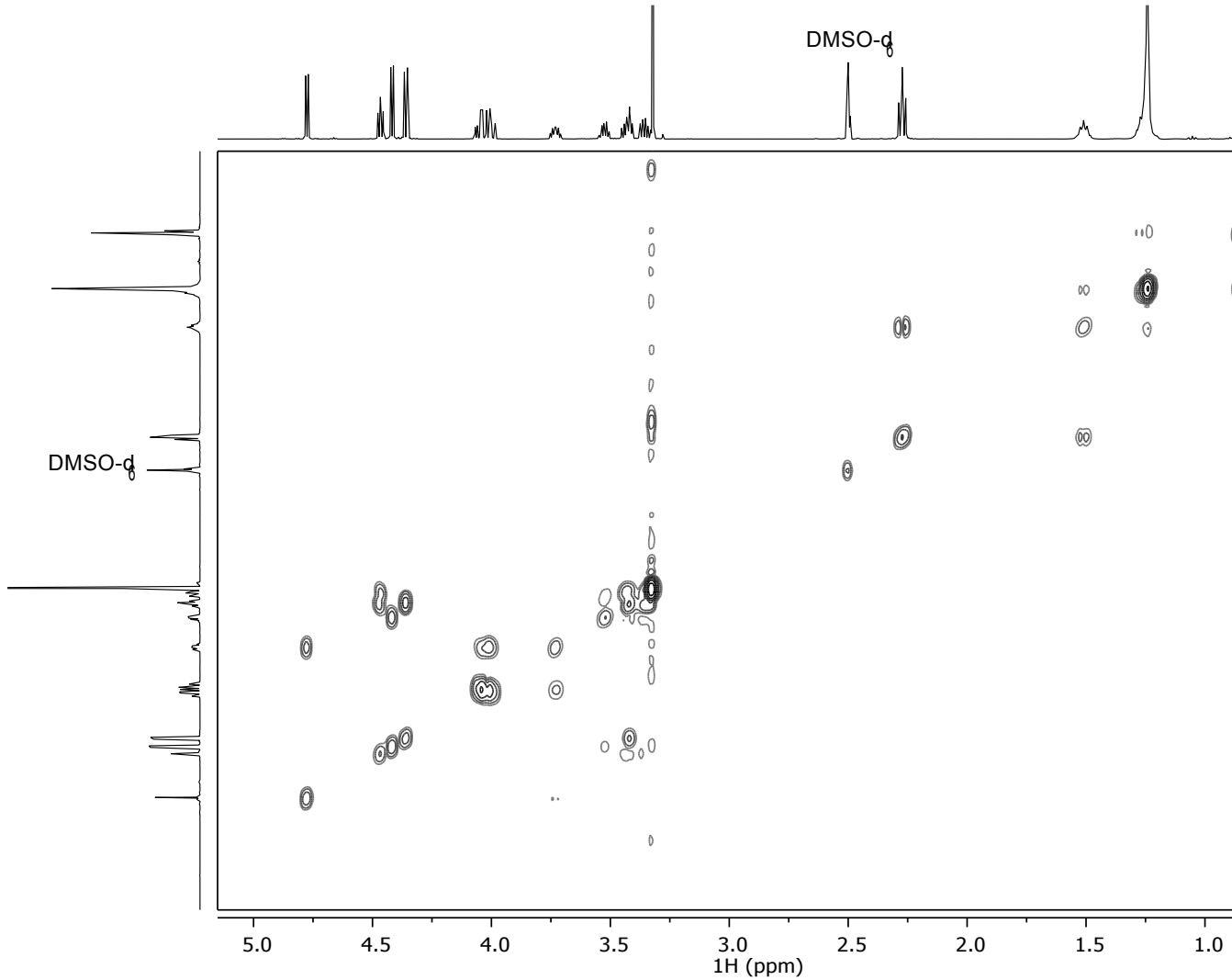
^{13}C NMR (125 MHz, DMSO-d6) (±) xylitol monocaprate (2a)



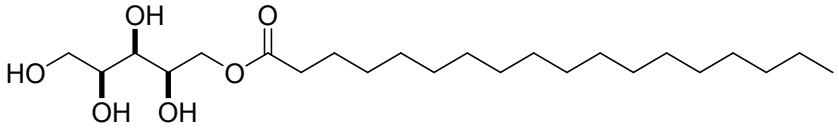


^{1}H-^{1}H COSY NMR (500 MHz, DMSO-d6) (±) xylitol monocaprate (2a)





^{1}H NMR (500 MHz, DMSO-d_6) (±) xylitol monostearate (2b)



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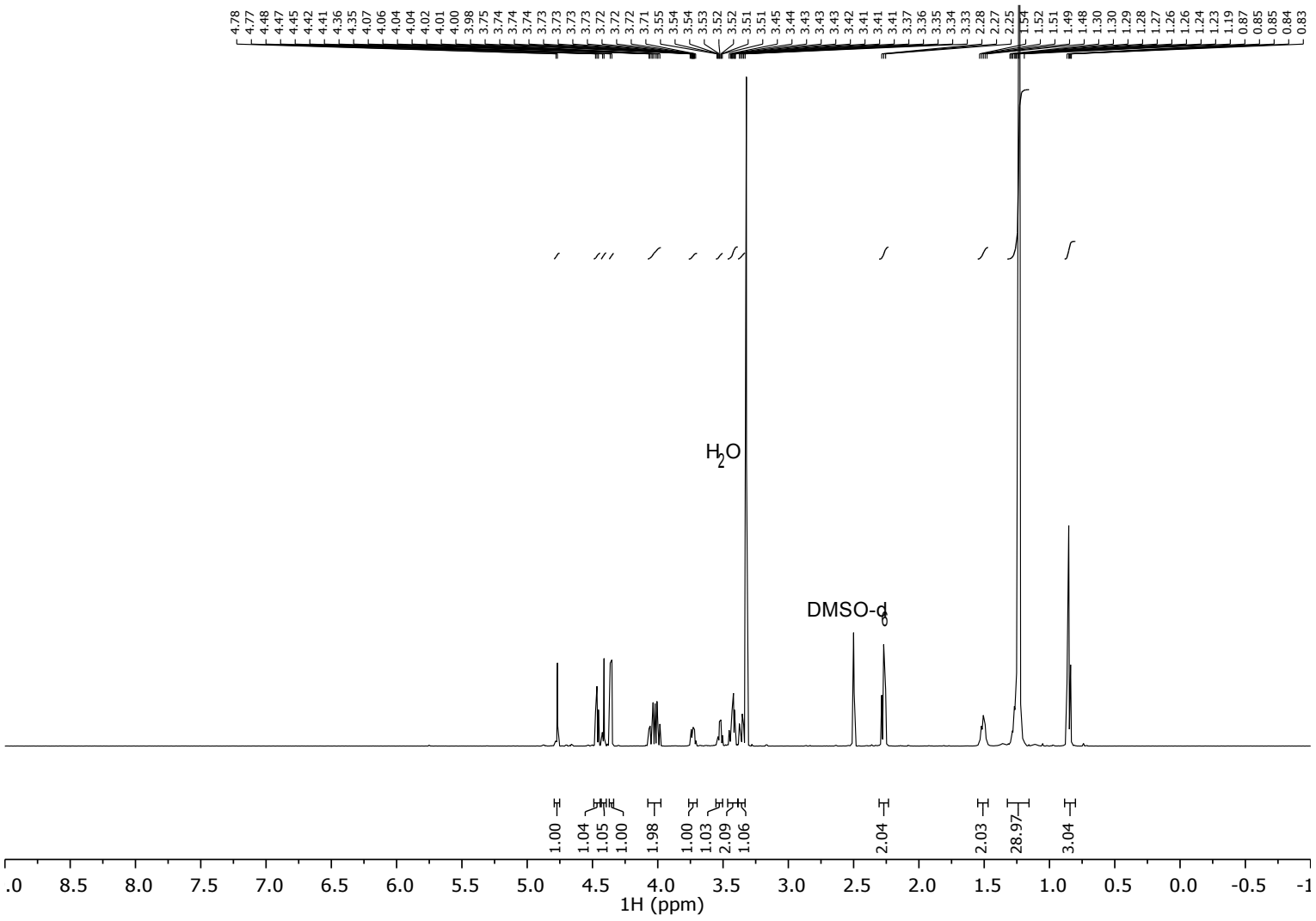
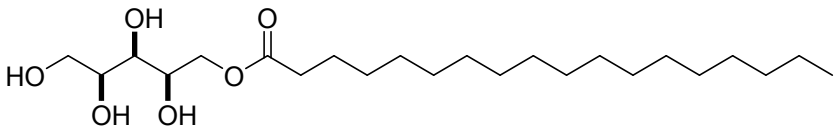
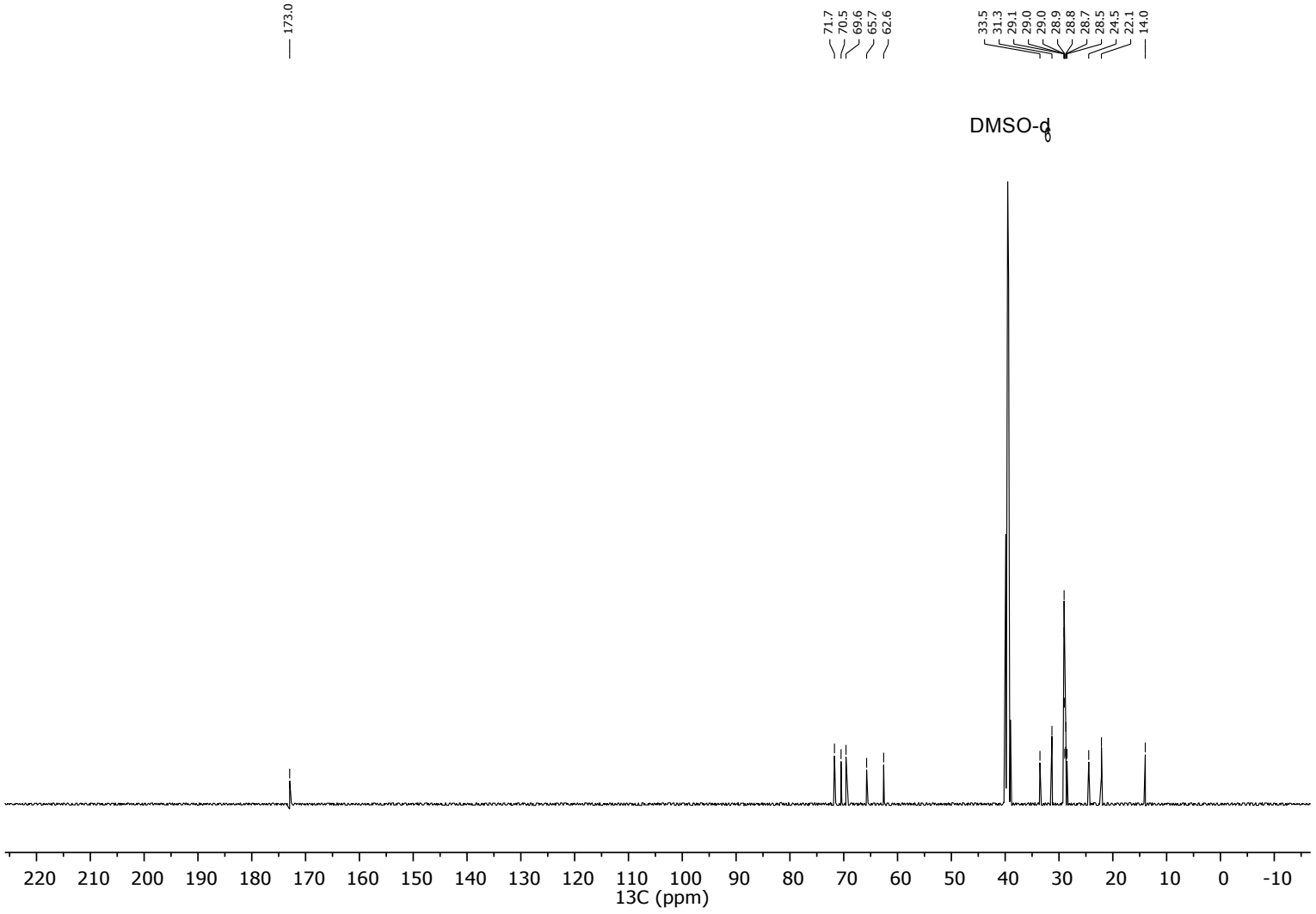
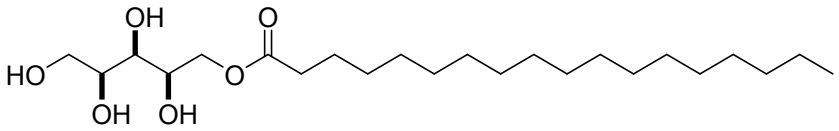


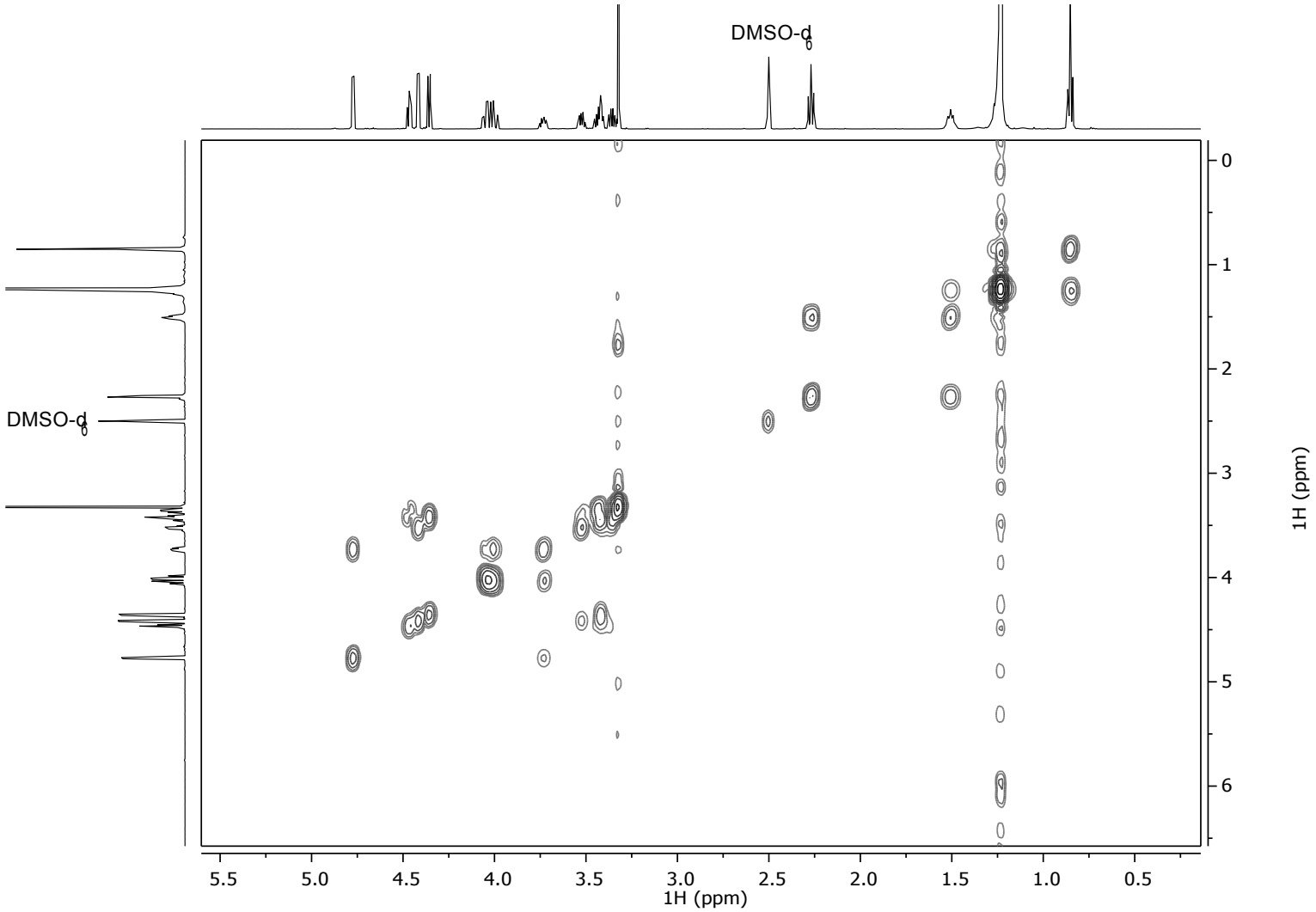
^{13}C NMR (125 MHz, DMSO-d6) (±) xylitol monostearate (2b)



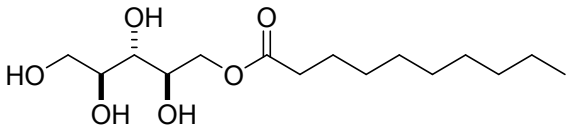


^{1}H-^{1}H COSY NMR (500 MHz, DMSO-d6) (±) xylitol monostearate (2b)





^{1}H NMR (500 MHz, DMSO-d_6) (±) ribitol monocaprate (2c)



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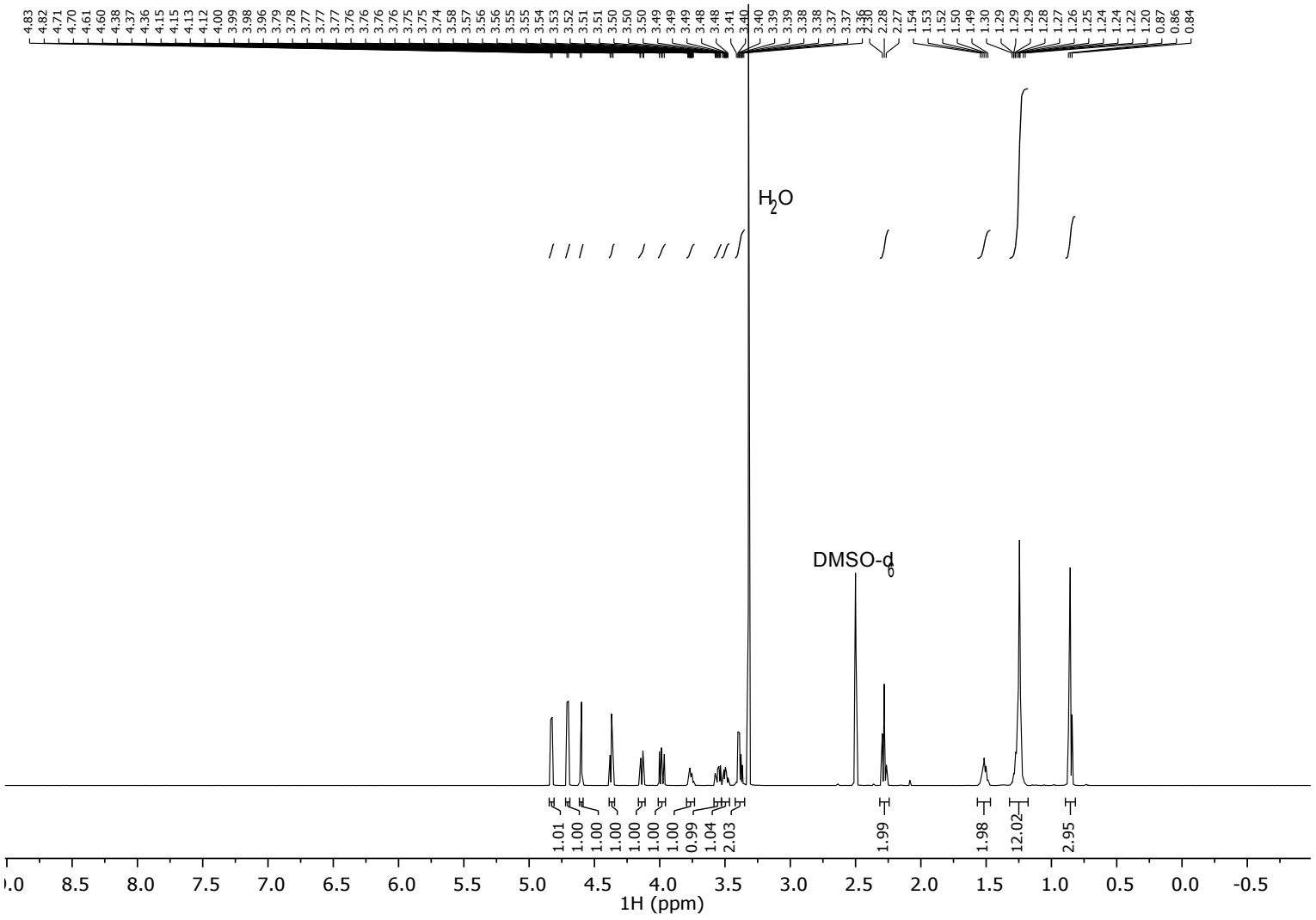
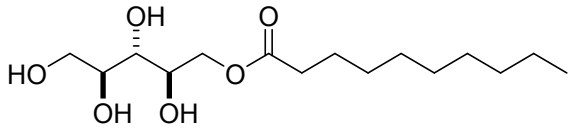
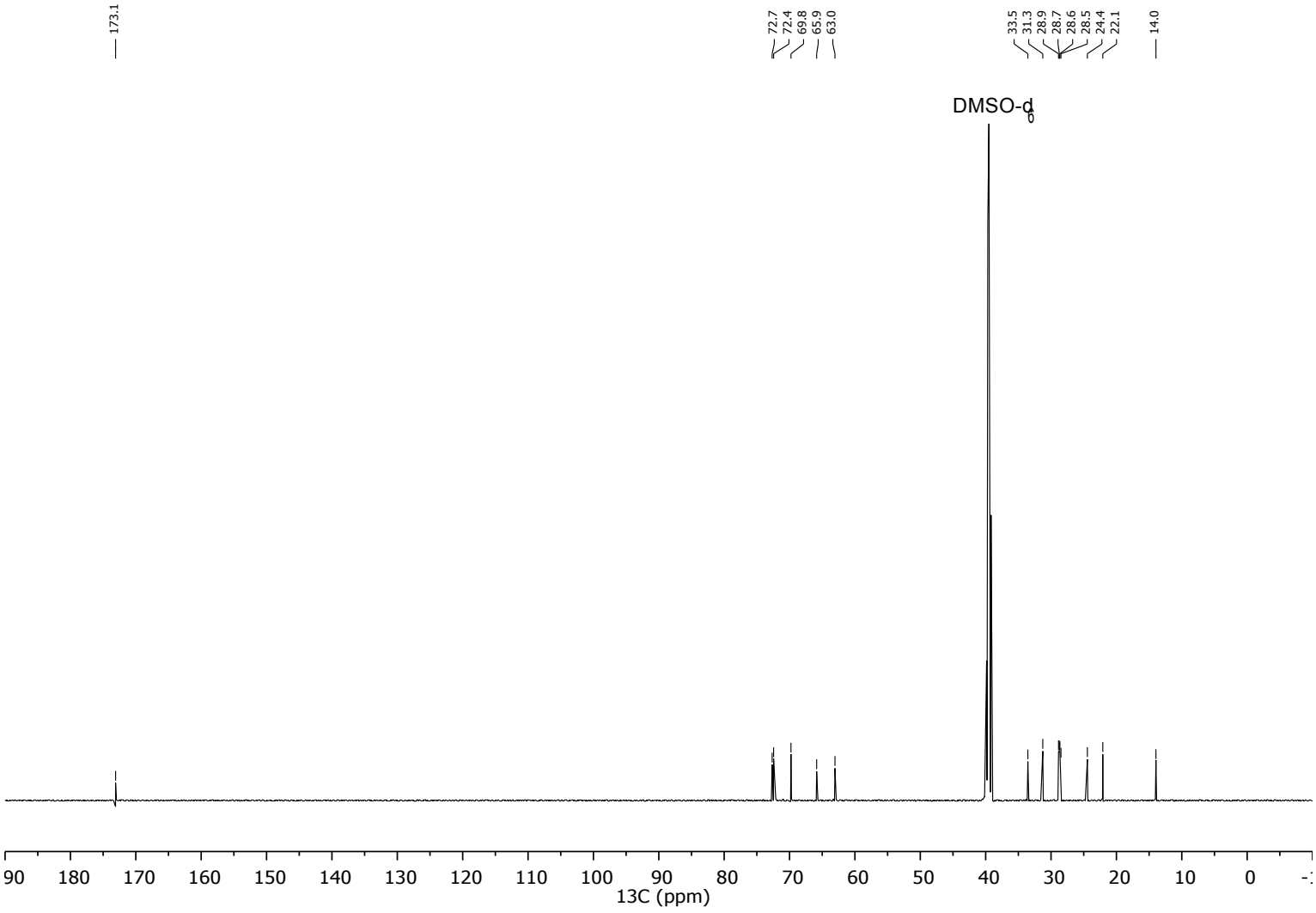
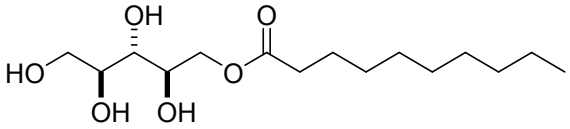


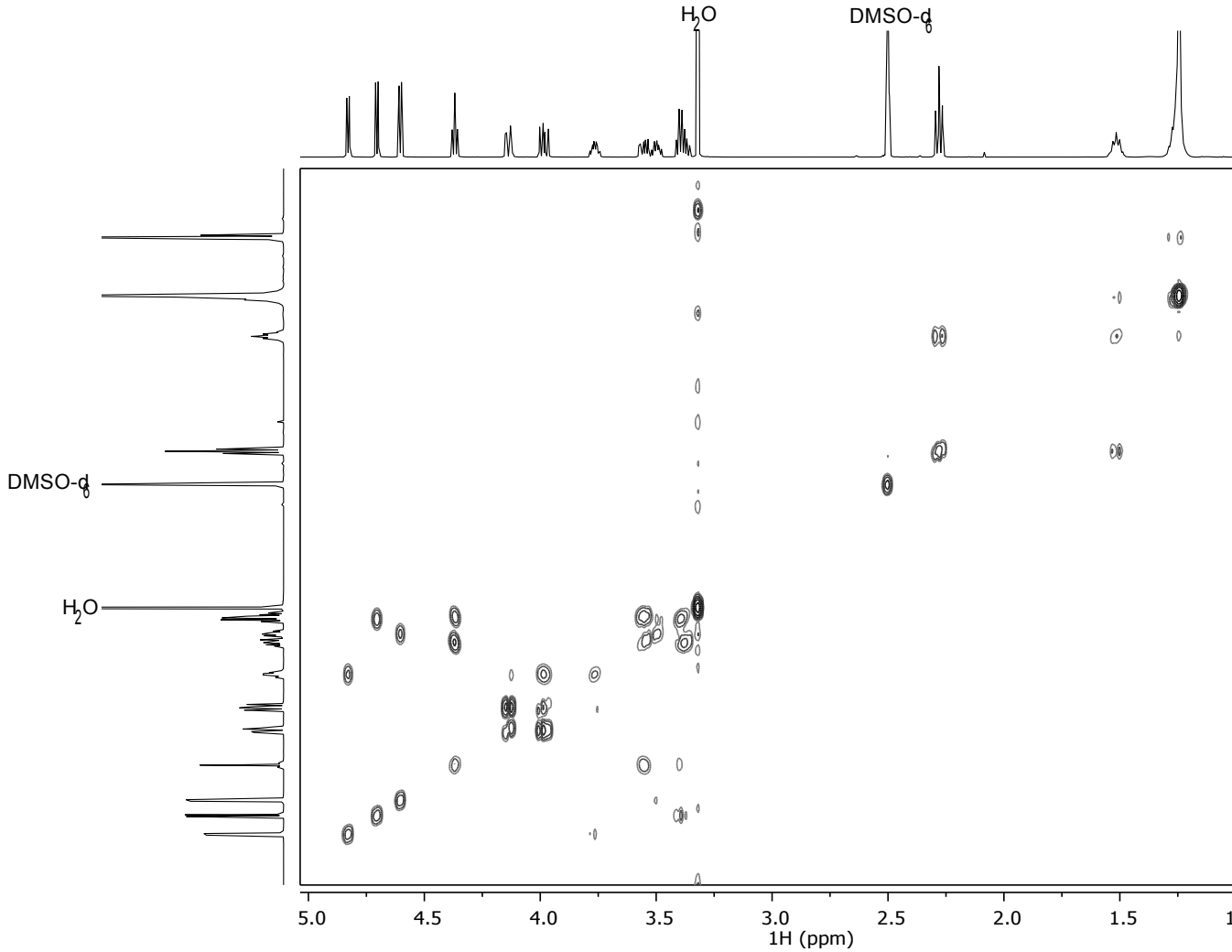
^{13}C NMR (125 MHz, DMSO-d_6) (±) ribitol monocaprate (2c)



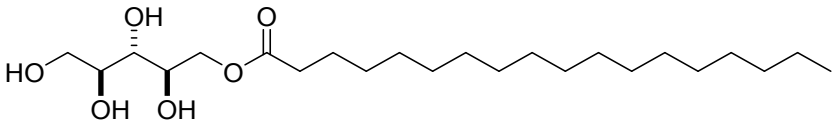


^{1}H-^{1}H COSY NMR (500 MHz, DMSO-d6) (±) ribitol monocaprate (2c)





^{1}H NMR (500 MHz, DMSO-d_6) (±) ribitol monostearate (2d)



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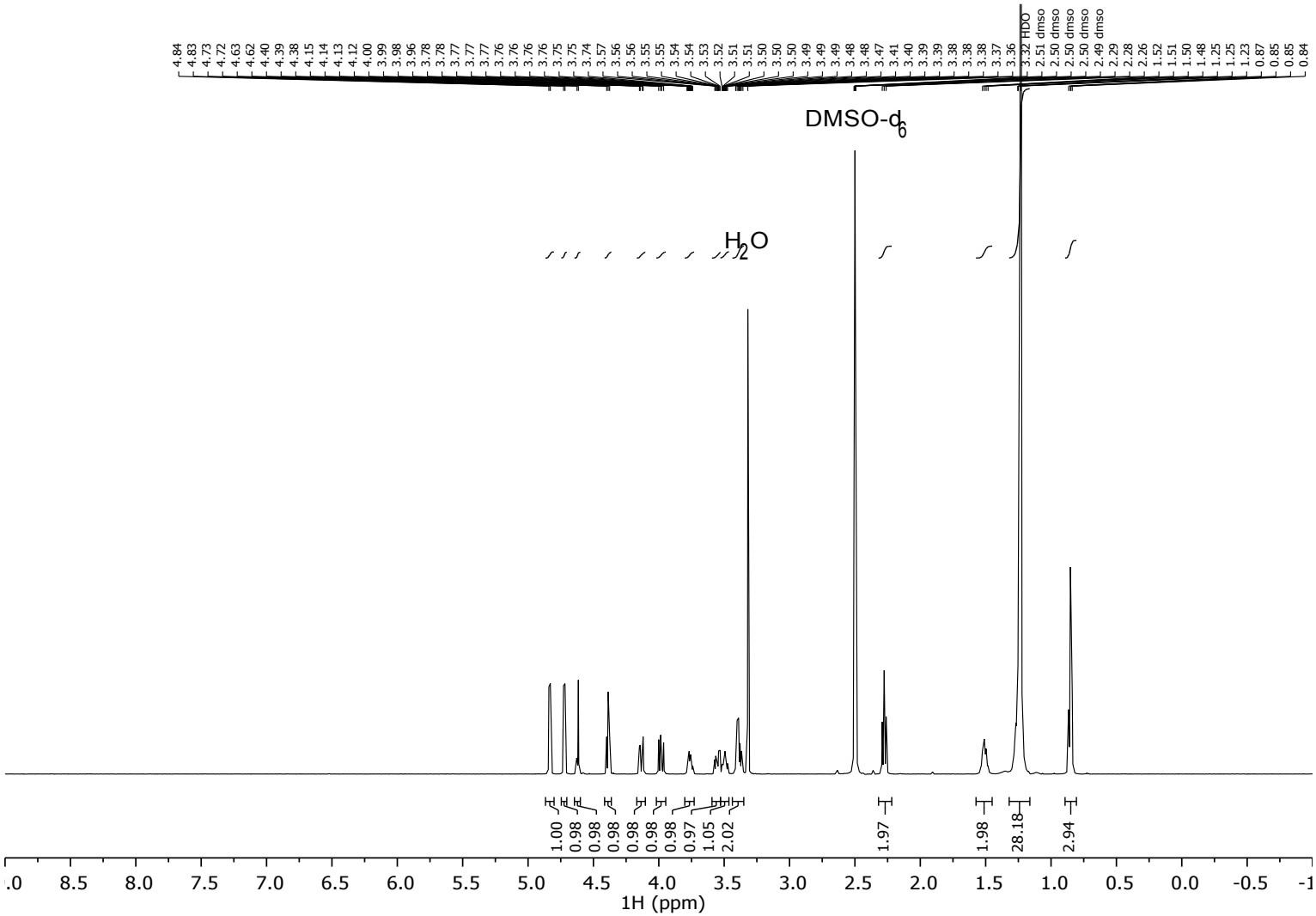
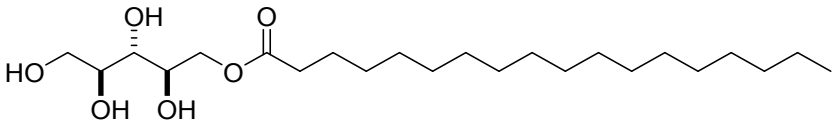
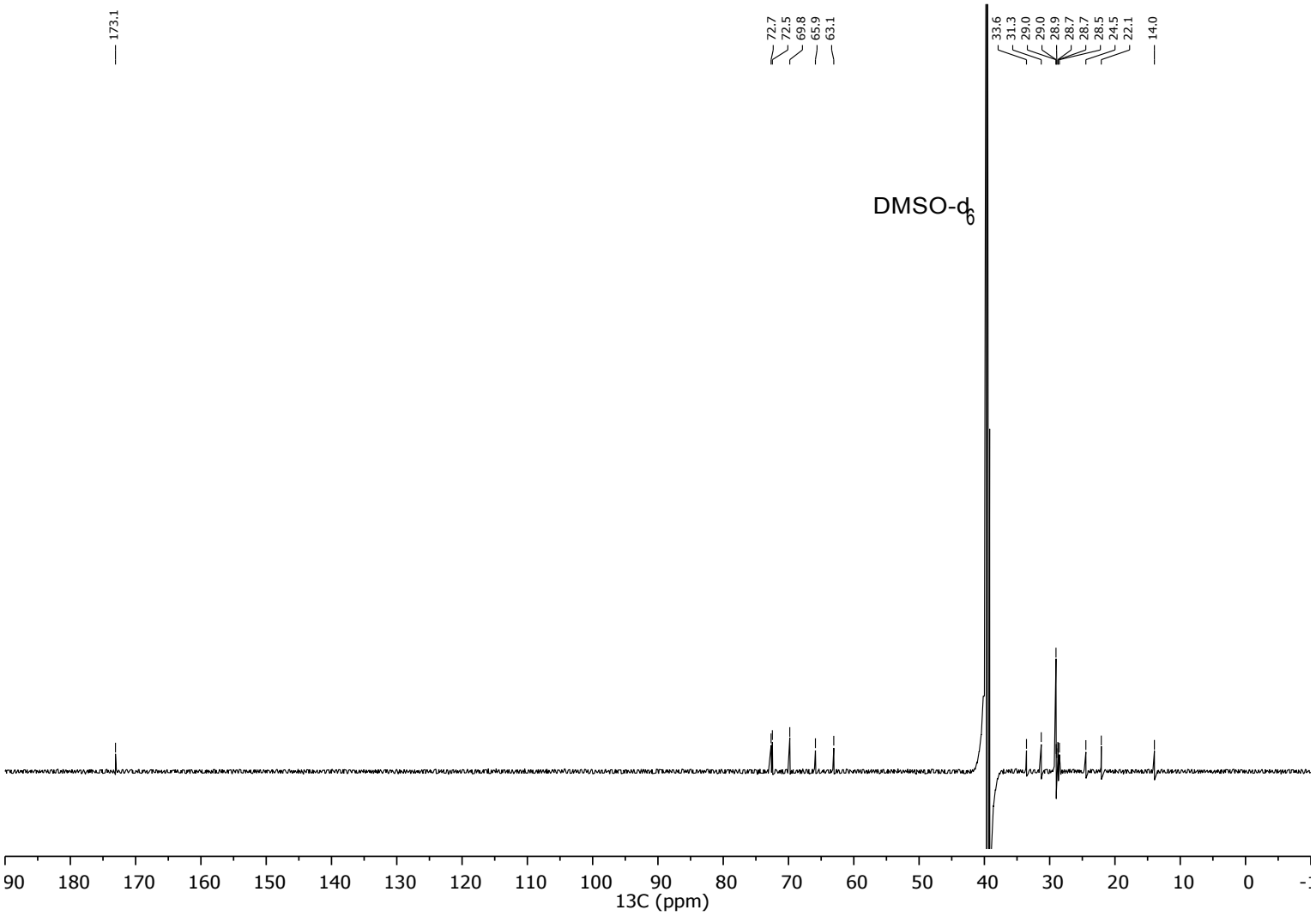
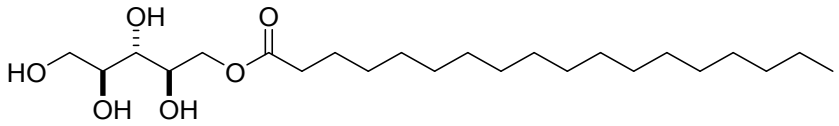


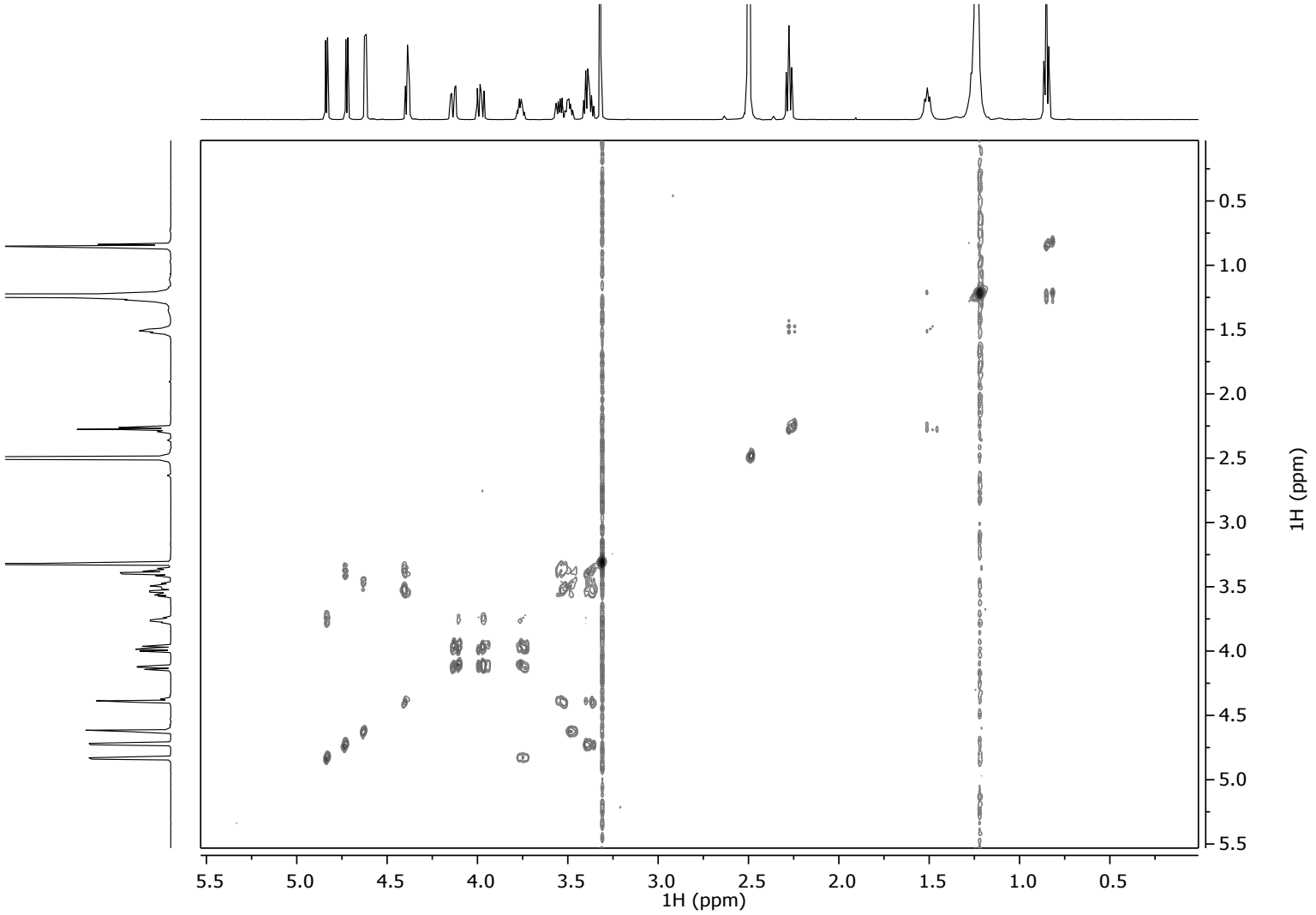
^{13}C NMR (125 MHz, DMSO-d_6) (±) ribitol monostearate (2d)



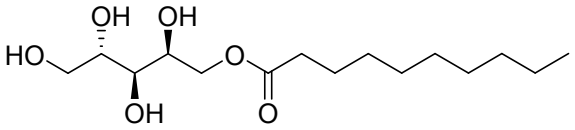


^{1}H-^{1}H COSY NMR (500 MHz, DMSO-d_6) (±) ribitol monostearate (2d)

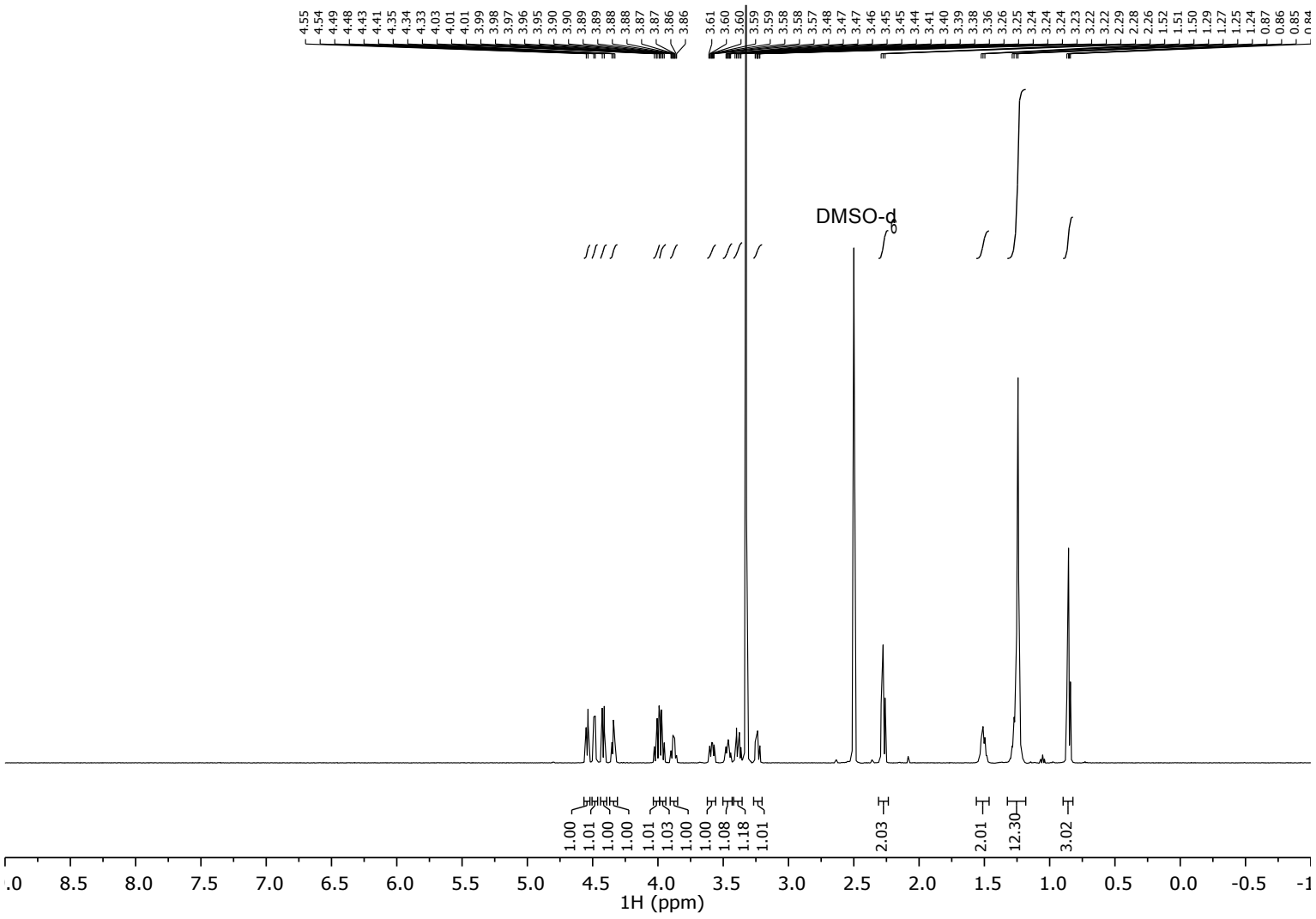




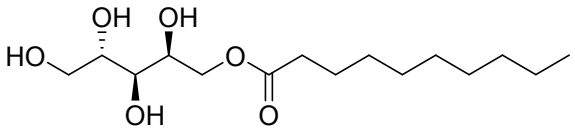
^{1}H NMR (500 MHz, DMSO-d_6) L-arabitol monocaprate (S,S,S) (2e)

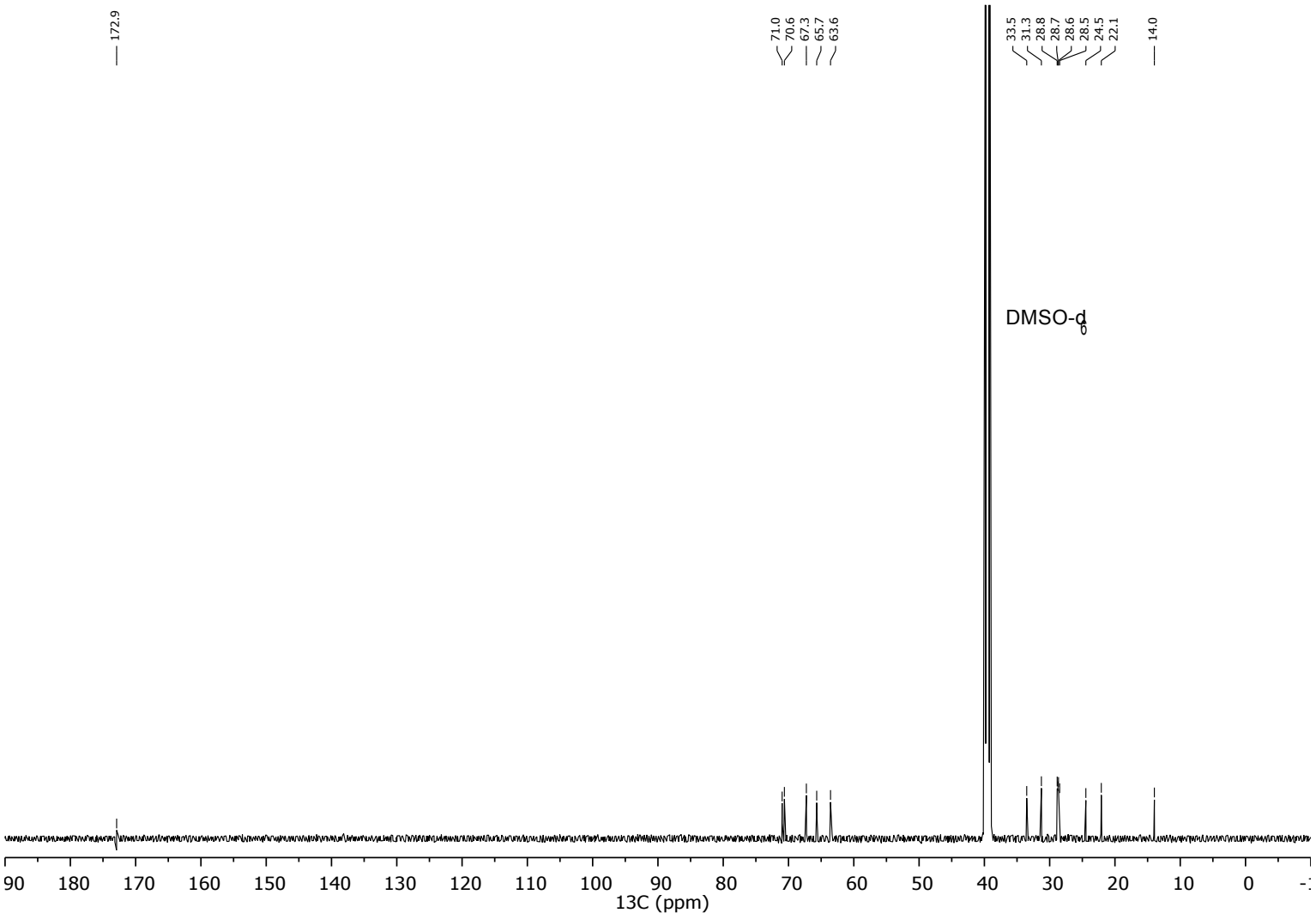


Back to characterization data

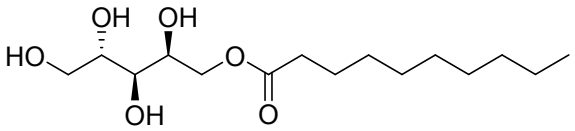


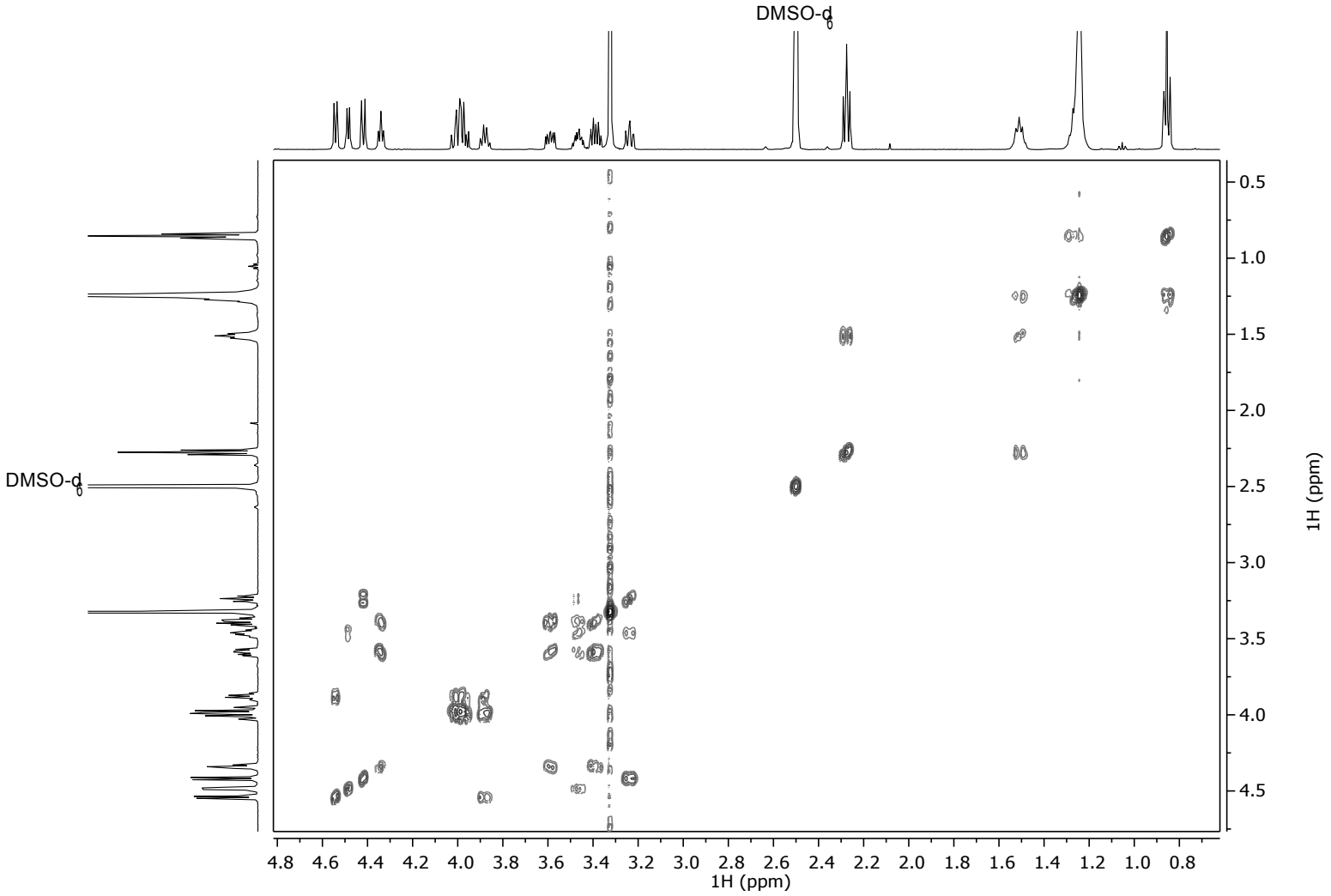
^{13}C NMR (500 MHz, DMSO-d6) L-arabitol monocaprate (S,S,S) (2e)



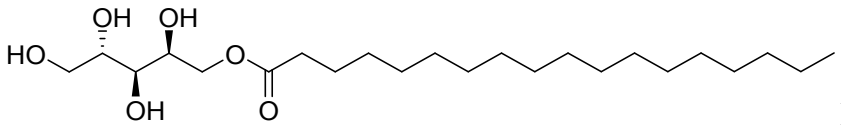


^{1}H-^{1}H COSY NMR (500 MHz, DMSO-d6) L-arabitol monocaprate (S,S,S) (2e)





^{1}H NMR (500 MHz, DMSO-d_6) L-arabitol monostearate (S,S,S) (2f)



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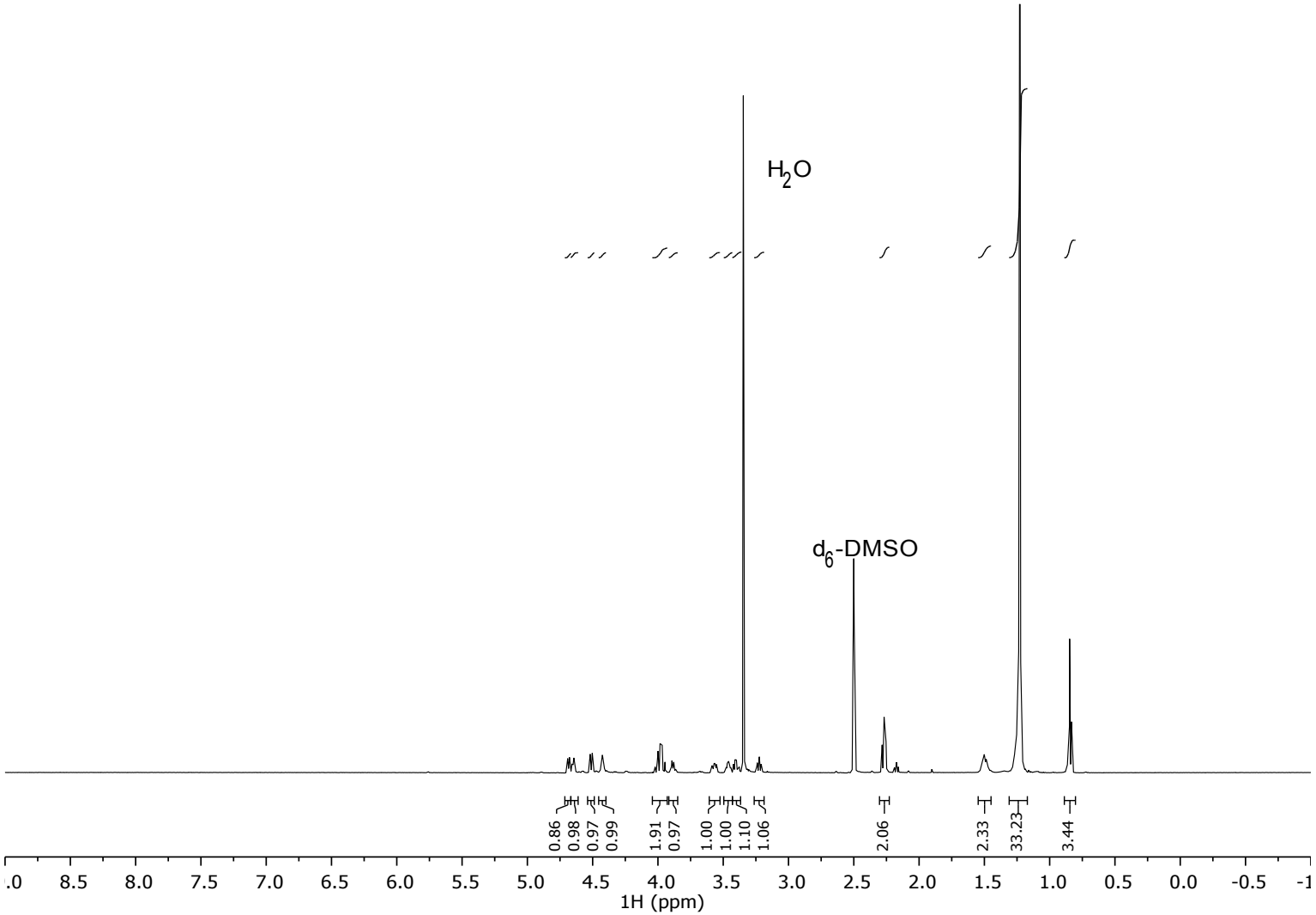

^{13}C NMR (500 MHz, DMSO-d6) L-arabitol monostearate (S,S,S) (2f)