Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFO

Total synthesis of a cyclopropane-fatty acid α-glucosyl diglyceride from *Lactobacillus plantarum* and identification of its ability to signal through Mincle

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Table of Contents

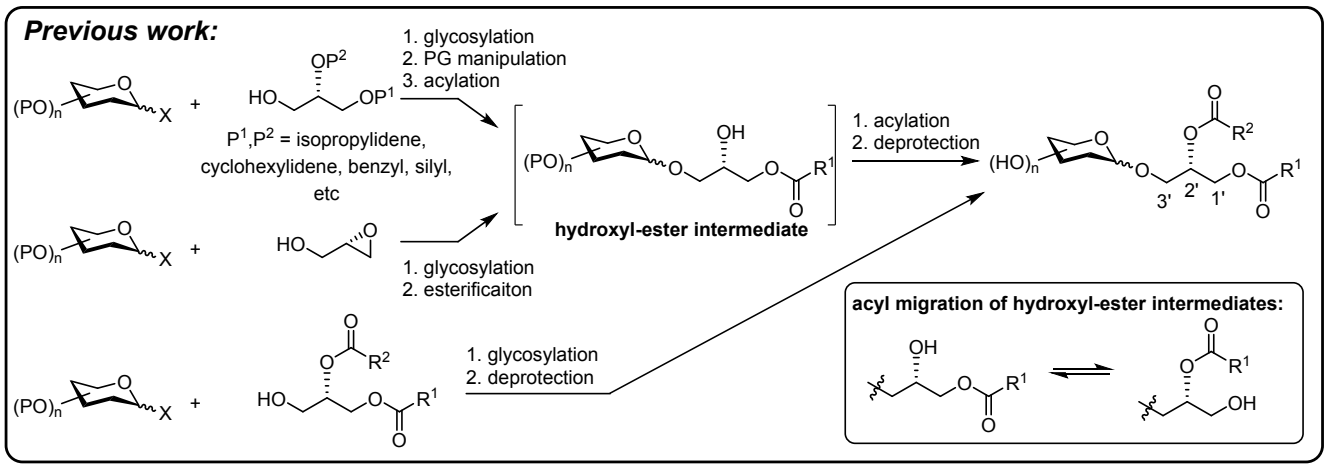
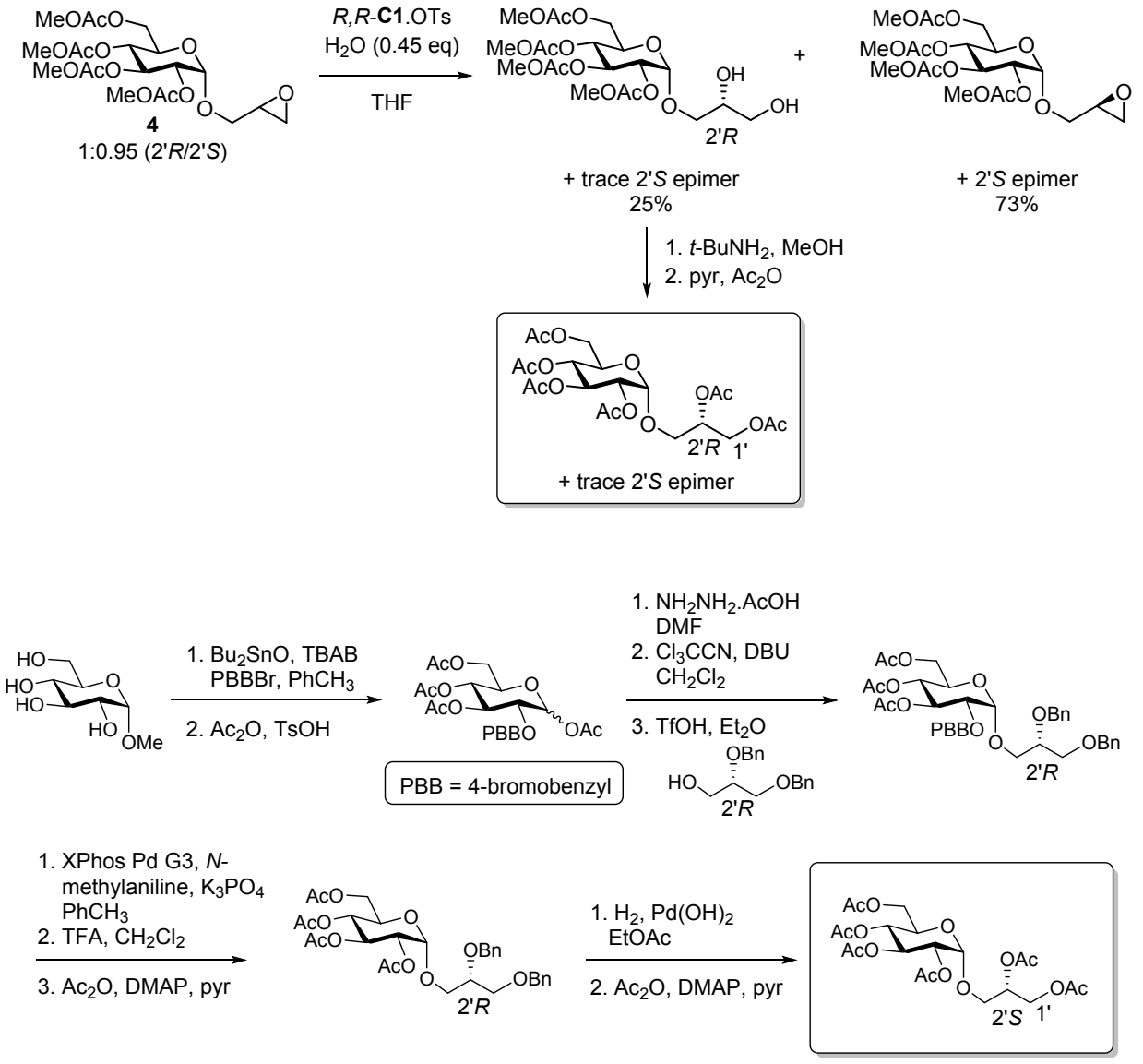


Figure S1. Summary of previous approaches to glycosyl diglycerides.



Characteristic ^{1}H nmr data for hexaacetates:
2'*S* epimer (400 MHz, $CDCl_3$): δ 4.088 (1 H, dd, $J_{1',1'}$ 12.4, $J_{1',2'}$ 2 Hz, H1')
2'*R* epimer (400 MHz, $CDCl_3$): δ 4.104 (0.95 H, dd, $J_{1',1'}$ 12.4, $J_{1',2'}$ 2 Hz, H1')

Figure S2. Summary of method used for stereochemical assignment of Jacobsen hydrolytic kinetic resolution of epoxide 4.

Note: This method was applied to the mixture of epoxides derived from the use of *R*,*R*-**C1**.OTs, which is the enantiomer of that used in the preparation of 2'*R*-**4** in the main paper. Full details will be reported elsewhere.

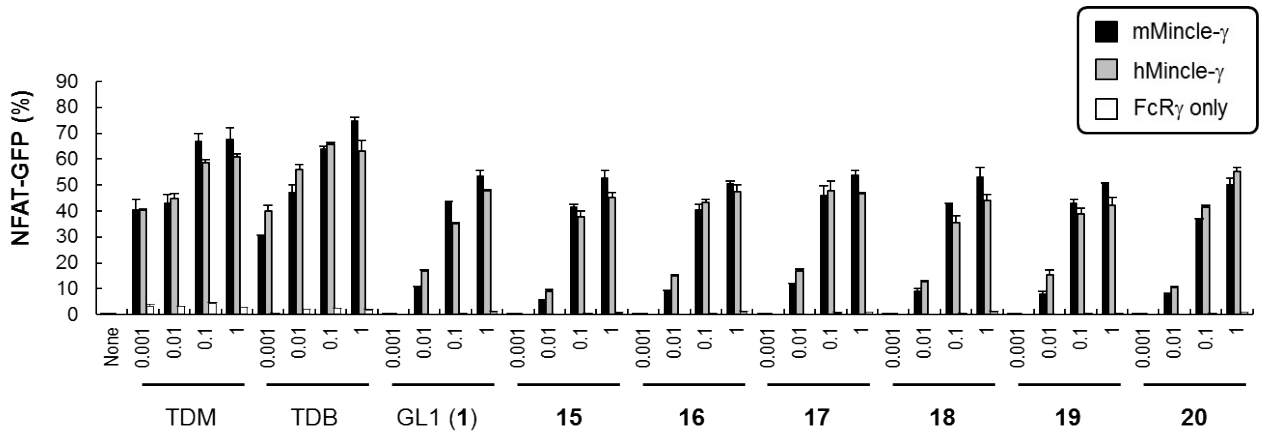


Figure S3. Signalling through Mincle by GL1 and analogues.

NFAT-GFP reporter cells expressing either human Mincle/FcRγ or mouse Mincle/FcRγ, as well as those expressing FcRγ alone were tested for their reactivity to plate-bound trehalose dimycolate (TDM), trehalose dibehenate (TDB), GL1 (**1**) and analogues **15**-**20**. Quantities denote amount in nmol; assays were performed in triplicate; the mean values and standard deviations are shown.

General

Proton nuclear magnetic resonance spectra (^{1}H NMR, 400, 600 MHz) and proton decoupled carbon nuclear magnetic resonance spectra (^{13}C NMR, 100, 150 MHz) were obtained in deuterochloroform, with residual protiated solvent as internal standard. Chemical shifts are followed by multiplicity, coupling constant(s) (*J*, Hz), integration and assignments where possible. Flash chromatography was carried out according to the procedure of Still *et al*.[1] using an automated system. Analytical thin layer chromatography (t.l.c.) was conducted on aluminium-backed 2 mm thick silica gel 60 GF_{254} and chromatograms were visualized with 10% H_2SO_4 in methanol. High resolution mass spectra (HRMS) were obtained by ionizing samples using electron spray ionization (ESI) and a time of flight mass analyzer. Dry THF and CH_2Cl_2 was obtained by the method of Pangborn *et al*.[2] Pet. spirits refers to petroleum ether, boiling range 40–60 °C. All other commercially available reagents were used as received.

Allyl 2,3,4,6-tetra-*O*-methoxyacetyl-α-D-glucopyranoside (3)

Methoxyacetyl chloride (3.32 ml, 36.3 mmol) was added dropwise to a stirred solution of allyl α-D-glucopyranoside (**1**) (1.00 g, 4.54 mmol) in pyridine (30 ml) at 0 °C. The solution was gradually warmed to room temperature and stirring was continued overnight. The reaction mixture was diluted with water and EtOAc, and washed with sat. aq. $CuSO_4$, sat. aq.$NaHCO_3$ and water, dried ($MgSO_4$), filtered and concentrated. Flash chromatography of the residue (EtOAc/pet. spirits 4:1) afforded **3** as a yellow oil (2.26 g, 98%), $[\alpha]_D^{26}$ = +91.7 (*c* 1.19, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.39, 3.40, 3.42, 3.45 (4 × 3 H, 4s, C**H**$_3$OCH$_2$), 3.95–4.14 (2 H, m, H3′,3′), 3.95, 3.99, 4.09 (3 × 2 H, 3s, CH$_3$OC**H**$_2$), 4.02 (2 H, m, CH$_3$OC**H**$_2$), 4.16–4.21 (2 H, m, H5,6), 4.37 (1 H, dd, $J_{5,6}$ 4, $J_{6,6}$ 12 Hz, H6), 4.98 (1 H, dd, $J_{1,2}$ 4, $J_{2,3}$ 10 Hz, H2), 5.13–5.18 (1 H, 2 × d, H1,4), 5.22–5.33 (2 H, m, H1′,1′), 5.58 (1 H, t, $J_{2,3}$ = $J_{3,4}$ 10 Hz, H3), 5.82–5.59 (1 H, m, H2′); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 59.5, 59.6, 59.7, 59.8 (4 C, CH_3), 61.9 (C6), 67.2, 68.7, 69.2, 69.4, 69.5, 69.6, 70.7, 70.9 (8 C, C2,3,4,5,**C**H$_2$OCH$_3$), 94.8 (C1), 118.7, 132.9 (2 C, C=C), 169.3, 169.5, 169.6, 170.1 (4 C, C=O); HRMS (ESI$^+$) calcd for $C_{21}H_{32}O_{14}Na$ (M+Na) 531.1684. Found 531.1677.

2',3'-Epoxypropyl 2,3,4,6-tetra-*O*-methoxyacetyl-α-D-glucopyranoside (4)

A solution of m-chloroperbenzoic acid (1.53 g, 8.85 mmol) and **3** (3.00 g, 5.90 mmol) in dry CH_2Cl_2 (40 ml) was stirred at room temperature overnight. Additional m-CPBA (0.51 g, 2.95 mmol) was added and stirring was continued for another night. The solution was diluted with dichloromethane, washed

successively with aqueous $Na_2S_2O_5$, sat. aq. $NaHCO_3$ and water, dried ($MgSO_4$) and concentrated. Flash chromatography of the residue (EtOAc 100%) afforded **4** (mixture of 2'*R*/2'*S* isomers in a 1:0.95 ratio) as a colourless oil (2.94 g, 95%), $[\alpha]_D^{26}$ = +89.8 (*c* 2.00, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.61 (1 H, dd, $J_{1',1'}$, 4.8, $J_{1',2'}$ 2.4 Hz, H1′, 2′*S* epimer), 2.66 (0.95 H, dd, $J_{1',1'}$, 4.8, $J_{1',2'}$ 2.4 Hz, H1′, 2′*R* epimer), 2.82 (1.95 H, m, H1′,1′), 3.17 (1.95 H, H2′,2′), 3.39, 3.40, 3.45 (3 × 5.85 H, 3 s, C**H**$_3$OCH$_2$), 3.43 (5.85 H, m, C**H**$_3$OCH$_2$), 3.56 (0.95 H, dd, $J_{2',3'}$ 5.6, $J_{3',3'}$ 12 Hz, H3′), 3.88 (0.95 H, dd, $J_{2',3'}$ 2.4, $J_{3',3'}$ 12 Hz, H3′), 3.95, 4.00, 4.00 (3 × 3.90 H, 3 s, CH$_3$OC**H**$_2$), 3.94–4.22 (2 H, m, H3′,3′), 4.08 (3.90 H, m, CH$_3$OC**H**$_2$), 3.95–4.23 (3.90 H, m, H5,6), 4.34–4.39 (1.95 H, m, H6), 4.95–5.01 (1.95 H, m, H2), 5.13–5.20 (3.90 H, m, H1,4), 5.54–5.56 (1.95 H, m, H3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.2, 44.4, 50.2, 50.4 (C1′,2′), 59.5, 59.58, 59.59 (4 C, CH_3), 61.89, 61.94 (C3′), 67.27, 67.30, 68.58, 68.61, 68.9, 69.4, 69.5, 69.6, 69.8, 70.5, 70.6, 70.8, 70.9 (C2,3,4,5,6,**C**H$_2$OCH$_3$), 96.1 (C1), 169.4, 169.7, 169.8, 170.1 (4 C, C=O); HRMS (ESI$^+$) calcd for $C_{21}H_{32}O_{15}Na$ (M+Na) 547.1633. Found 547.1631.

(2'*R*)-2',3'-Epoxypropyl 2,3,4,6-tetra-*O*-methoxyacetyl-α-D-glucopyranoside ((2'*R*)-4) and (2'*S*)-2',3'-Dihydroxypropyl 2,3,4,6-tetra-*O*-methoxyacetyl-α-D-glucopyranoside ((2'*S*)-5)

A mixture of (*S*,*S*)-salen Co(II) (0.046 g, 0.076 mmol) and *p*-toluenesulfonic acid (0.016 g, 0.084 mmol) in CH_2Cl_2 (1 ml) was stirred vigorously open to the atmosphere at room temperature, for 30 min. The solvent was evaporated and the solid was dried under reduced pressure. A solution of the resulting (*S*,*S*)-salen Co(III) complex (*S*,*S*-**C1**.OTs) and the epoxide **4** (2.00 g, 3.81 mmol) in dry THF (2 ml) was cooled to 0 °C and was treated with H_2O (0.038 ml, 2.10 mmol). The mixture was slowly warmed to room temperature and was stirred overnight. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (EtOAc 100%) to afford firstly (2'*R*)-**4** as a colorless liquid (0.94 g, 48%), $[\alpha]_D^{26}$ = +84.8 (*c* 1.51, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.61 (1 H, dd, $J_{1',2'}$ 2.4, $J_{1',1'}$ 4.8 Hz, H1′), 2.82 (1 H, m, H1′), 3.15–3.19 (1 H, m, H2′), 3.39, 3.40, 3.42, 3.44 (4 × 3 H, 4s, C**H**$_3$OCH$_2$), 3.95, 3.99, 4.07 (3 × 2 H, 3s, CH$_3$OC**H**$_2$), 4.03 (2 H, m, CH$_3$OC**H**$_2$), 3.94–4.22 (4 H, m, H5,6,3′,3′), 4.35 (1 H, dd, $J_{5,6}$ 4, $J_{6,6}$ 12 Hz, H6), 4.99 (1 H, dd, $J_{1,2}$ 4, $J_{2,3}$ 10 Hz, H2), 5.15 (1 H, t, $J_{3,4} = J_{4,5}$ 10 Hz, H4), 5.19 (1 H, d, $J_{1,2}$ 4 Hz, H1), 5.56 (1 H, t, $J_{2,3} = J_{3,4}$ 10 Hz, H3); ^{13}C NMR ($CDCl_3$, 100MHz) δ 44.4, 50.4 (C2′,3′), 59.4, 59.53, 59.54 (4 C, CH_3), 62.0 (C3′), 67.3, 68.6, 69.4, 69.5, 69.6, 69.8, 70.5, 70.7 (9 C, C2,3,4,5,6,**C**H$_2$OCH$_3$), 96.1 (C1), 169.3, 169.6, 169.7, 170.1 (4 C, C=O); HRMS (ESI$^+$) calcd for $C_{21}H_{32}O_{15}Na$ (M+Na) 547.1633. Found 547.1631.

Next to elute (EtOAc/MeOH spirits 9:1) was the diol (2'*S*)-**5** as a colourless liquid (1.04 g, 50%), $[\alpha]_D^{25}$= +89.5 (*c* 1.25, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.23 (1 H, br), 2.79 (1 H, br), 3.39, 3.40,

3.42, 3.45 (4 × 3 H, 4s, C**H**$_3$OCH$_2$), 3.58–3.64 (2 H, m, H3′,3′), 3.69–3.77 (2 H, m, H1′,1′), 3.88–3.90 (1 H, m, H2′), 3.95, 4.00 (2 × 2 H, 2s, CH$_3$OC**H**$_2$), 4.03 (2 H, m, CH$_3$OC**H**$_2$), 4.09 (2 H, m, CH$_3$OC**H**$_2$), 4.15–4.24 (2 H, m, H5,6), 4.35 (1 H, dd, $J_{5,6}$ 4, $J_{6,6}$ 12 Hz, H6), 5.00 (1 H, dd, $J_{1,2}$ 4, $J_{2,3}$ 8 Hz, H2), 5.13 (1 H, t, $J_{3,4} = J_{4,5}$ 8 Hz, H4), 5.16 (1 H, d, $J_{1,2}$ 4 Hz, H1), 5.55 (1 H, t, $J_{2,3} = J_{3,4}$ 10 Hz, H3); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 59.5, 59.61, 59.63 (4 C, CH$_3$), 62.0, 63.6 (C1′,6), 67.3, 68.7, 69.4, 69.54, 69.6, 70.2, 70.6, 70.9 (8 C, C2,3,4,5,**C**H$_2$OCH$_3$), 96.1 (C1), 169.3, 169.5, 169.7, 170.1 (4 C, C=O); HRMS (ESI$^+$) calcd for C$_{21}$H$_{35}$O$_{15}$ (M+H) 543.1919. Found 543.1917.

(2'*R*)-3'-Bromo-2'-hydroxypropyl 2,3,4,6-tetra-*O*-methoxyacetyl-α-D-glucopyranoside (6)

Anhydrous LiBr (1.00 g, 11.5 mmol) and NiBr$_2$ (1.25 g, 5.72 mmol) were stirred for 48 h in dry THF (13.7 ml) at room temperature. Stirring was stopped and undissolved material was allowed to settle, affording a clear dark blue/green solution of Li$_2$NiBr$_4$ (~ 0.4 M). Excess Li$_2$NiBr$_4$ (0.4 ml) in THF was added to a solution of (2'*R*)-**4** (0.051 g, 0.104 mmol) in dry THF (1 ml) and the solution was stirred overnight. The reaction mixture was treated with phosphate buffer (1 ml, pH 7) and extracted with CH$_2$Cl$_2$. The organic layer was washed with water, dried (Na$_2$SO$_4$), filtered and concentrated. Flash chromatography of the residue (EtOAc/pet. spirits 8:2) afforded **6** as a colourless oil (0.057 g, 98%), $[\alpha]_D^{24}$ = +67.4 (*c* 1.35, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.39, 3.41, 3.43, 3.45 (4 × 3 H, 4s, C**H**$_3$OCH$_2$), 3.45–3.54 (1 H, m, H2′), 3.60 (1 H, dd, $J_{1',1'}$ 10.4, $J_{1',2'}$ 6 Hz, H1′), 3.87 (1 H, dd, $J_{1',1'}$ 10.4, $J_{1',2'}$ 6 Hz, H1′), 3.96, 4.00, 4.02, 4.00 (4 × 2 H, 4s, CH$_3$OC**H**$_2$), 3.96–4.23 (4 H, m, H5,6,3′,3′), 4.37 (1 H, dd, $J_{5,6}$ 4, $J_{6,6}$ 12 Hz, H6), 5.01 (1 H, dd, $J_{1,2}$ 4, $J_{2,3}$ 10 Hz, H2), 5.11–5.16 (2 H, m, H1,4), 5.54 (1 H, t, $J_{2,3} = J_{3,4}$ 10 Hz, H3); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 34.5 (C1′), 59.5, 59.59, 59.61, 59.7 (4 C, CH$_3$), 62.0, 67.4, 68.6, 69.5, 69.6, 69.68, 69.71, 70.6, 70.8 (9 C, C2,3,4,5,6,**C**H$_2$OCH$_3$), 70.9 (C2′), 96.6 (C1), 169.3, 169.5, 169.7, 170.0 (4 C, C=O); HRMS (ESI$^+$) calcd for C$_{21}$H$_{33}$BrO$_{15}$Na (M+Na) 627.0895. Found 627.0892.

(2'*R*)-3'-Bromo-2'-oleoyloxypropyl 2,3,4,6-tetra-*O*-methoxyacetyl-α-D-glucopyranoside (7)

Oleoyl chloride (0.044 ml, 0.132 mmol) was added to a stirred solution of **6** (0.040 g, 0.066 mmol) in dry CH$_2$Cl$_2$ (1 ml) and pyridine (0.053 ml, 0.66 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirring was continued overnight. The reaction mixture was diluted with CH$_2$Cl$_2$, washed sequentially with water, sat. aq. CuSO$_4$ and sat. aq. NaHCO$_3$. The combined organic layers were dried (MgSO$_4$), filtered and concentrated under reduced pressure. Flash chromatography of the residue (EtOAc/pet. spirits 1:1) afforded **7** as colorless oil (0.053 g, 93%), $[\alpha]_D^{25}$ = +55.8 (*c* 1.15,

$CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz) δ 0.88 (3 H, t, J = 8 Hz, $CH_2C\mathbf{H}_3$), 1.24–1.31 (20 H, m, alkyl), 1.59–1.65 (2 H, m, β-CH_2) 1.98–2.04 (4 H, m, $\mathbf{H}_2CCH{=}CHC\mathbf{H}_2$), 2.33–2.37 (2 H, m, α-$CH_2$), 3.39, 3.41, 3.43, 3.45 (4 × 3 H, 4s, $C\mathbf{H}_3OCH_2$), 3.52 (1 H, dd, $J_{1',2'}$ 6, $J_{1',1'}$ 10.8 Hz, H1′), 3.60 (1 H, dd, $J_{1',2'}$ 6, $J_{1',1'}$ 10.8 Hz, H1′), 3.73 (1 H, dd, $J_{2',3'}$ 4.8, $J_{3',3'}$ 10.8 Hz, H3′), 3.89 (1 H, dd, $J_{2',3'}$ 4.8, $J_{3',3'}$ 10.8 Hz, H3′), 3.96, 4.00, 4.10 (3 × 2 H, 3s, $CH_3OC\mathbf{H}_2$), 4.02 (2 H, m, $CH_3OC\mathbf{H}_2$), 4.07–4.13 (1 H, m, H6), 4.20 (1 H, m, H5), 4.38 (1 H, dd, $J_{5,6}$ 4, $J_{6,6}$ 12 Hz, H6), 5.00 (1 H, dd, $J_{1,2}$ 4, $J_{2,3}$ 10.4 Hz, H2), 5.09–5.17 (3 H, m, H1,2′,4), 5.30–5.38 (2 H, m, HC=CH), 5.53 (1 H, t, $J_{2,3}$ 9.6, $J_{3,4}$ 10 Hz, H3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2 ($CH_2\mathbf{C}H_3$), 22.8, 25.0, 27.3, 27.4, 29.20, 29.24, 29.3, 29.43, 29.44, 29.6, 29.8, 29.9, 30.0, 32.0, 34.3, 59.5, 59.56, 59.57, 59.59 (4 C, OCH_3), 61.8, 67.40, 67.44, 68.5, 69.41, 69.42, 69.5, 69.6, 70.4, 70.5, 70.7, 96.2 (C1), 129.8, 130.2 (2C, HC=CH), 169.3, 169.6, 169.7, 170.1 (4 C, $MeOCH_2\mathbf{C}{=}O$), 172.9 (sn2–CO_2); HRMS (ESI^+) calcd for $C_{39}H_{65}BrO_{16}Na$ (M+Na) 891.3348. Found 891.3346.

1-*O*-(9*S*,10*R*-Dihydrosterculyl)-2-*O*-oleoyl-sn-glyceryl 2,3,4,6-tetra-*O*-methoxyacetyl-α-D-glucopyranoside (8)

Tetrabutylammonium hydroxide solution in H_2O (1.5 M, 0.040 ml, 0.061 mmol) was added to a suspension of 9*S*,10*R*-dihydrosterculic acid (0.020 g, 0.068 mmol) in H_2O. The resulting mixture was vigorously stirred at rt overnight. The solvent was evaporated and the crude residue was co-evaporated with toluene several times to give the tetrabutylammonium salt of dihydrosterculic acid. A mixture of tetrabutylammonium dihydrosterculate (0.043 g, 0.081 mmol) and **7** (0.035 g, 0.040 mmol) in toluene (0.5 ml) was heated to 85 °C and stirred vigorously for 25 min. The solvents were evaporated under high vacuum. Flash chromatography of the residue (EtOAc/pet spirits 2:3) afforded **8** as a colourless oil (0.018 g, 55%), $[\alpha]_D^{26}$ = +24.1 (*c* 0.28, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz) δ –0.32 (1 H, ddd, J_{gem} = J_{trans} 4 Hz, cyclopropane CH_2), 0.53–0.58 (1 H, m, cyclopropane CH_2), 0.59–0.64 (2 × 1 H, m, cyclopropane CH), 0.88–0.93 (2 × 3 H, m, $CH_2C\mathbf{H}_3$), 1.25–1.42 (44 H, m, alkyl), 1.53–1.64 (4 H, m, β-CH_2), 1.98–2.01 (4 H, m, $\mathbf{H}_2CHC{=}CHC\mathbf{H}_2$), 2.29–2.34 (2 × 2 H, m, α-CH_2), 3.39, 3.41, 3.43, 3.45 (4 × 3 H, 4s, CH_3O), 3.64 (1 H, dd, $J_{2',3'}$ 4.8, $J_{3',3'}$ 10.8 Hz, H3′), 3.81 (1 H, dd, $J_{2',3'}$ 4.8, $J_{3',3'}$ 10.8 Hz, H3′), 3.96, 4.00, 4.09 (3 × 2 H, 3s, $CH_3OC\mathbf{H}_2$), 4.04 (2 H, m, $CH_3OC\mathbf{H}_2$), 4.06–4.08 (1 H, m, H5), 4.11–4.20 (2 H, m, H1′,6), 4.31–4.41 (2 H, m, H1′,6), 4.98 (z1 H, dd, $J_{1,2}$ 4, $J_{2,3}$ 10.4 Hz, H2), 5.12–5.23 (3 H, m, H1,2′,4), 5.30–5.39 (2 H, m, HC=CH), 5.52 (1 H, t, $J_{2,3}$ 9.6, $J_{3,4}$ 10 Hz, H3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.1 (cyclopropane CH_2), 14.3 (2 × $CH_2\mathbf{C}H_3$), 15.8, 15.9 (2 C, cyclopropane CH), 22.81, 22.83, 25.0, 27.3, 27.4, 28.8, 28.9, 29.2, 29.3, 29.4, 29.45, 29.5, 29.6, 29.7, 29.87, 29.90, 30.3, 30.4,

32.0, 32.1, 34.2, 34.3, 59.48, 59.55, 59.56, 59.57 (4 C, OCH_3), 61.7, 62.1, 67.1, 67.4, 68.5, 69.3, 69.4, 69.5, 69.8, 70.5, 70.7, 96.3 (C1), 129.8, 130.2 (2 C, HC=CH), 169.3, 169.6, 169.7, 170.1 (4 C, $MeOCH_2$**C**=O), 173.0, 173.7 (sn1–CO_2, sn2–CO_2); HRMS (ESI^+) calcd for $C_{58}H_{100}O_{18}Na$ (M+Na) 1107.6802. Found 1107.6793.

1-*O*-(9*S*,10*R*-Dihydrosterculyl)-2-*O*-oleoyl-sn-glyceryl α-D-glucopyranoside (1; GL1)

A solution of *t*-butylamine (0.077 ml, 0.74 mmol) and **8** (0.016 g, 0.015 mmol) in $CHCl_3$ (0.16 ml) and MeOH (0.38 ml) was stirred at 0 °C for 10 min and then at 10 °C for 1 h at which time tlc indicated that the starting material was completely consumed. The solvents were evaporated under high vacuum without heating. Flash chromatography of the residue (MeOH/$CHCl_3$ 5:95) afforded GL1 (**1**) as a white semisolid (0.010 g, 84%), $[\alpha]_D^{26}$ = +45.4 (*c* 0.6, $CHCl_3$). ^{1}H NMR ($CDCl_3$, CD_3OD 2:1, 600 MHz) δ –0.33 (1 H, ddd, $J_{gem} = J_{trans}$ = 4 Hz, cyclopropane CH_2), 0.55–0.58 (1 H, m, cyclopropane CH_2), 0.62–0.65 (2 H, m, cyclopropane CH), 0.83–0.89 (2 × 3 H, m, CH_3), 1.60–1.62 (44 H, m, alkyl), 2.01–2.04 (2 × 2 H, m, β-CH_2), 2.31–2.34 (4 H, m, $\mathbf{H}_2$CHC=CHC$\mathbf{H}_2$), 2.09–2.12 (2 × 2 H, m, α-CH_2), 3.39 (1 H, t, $J_{3,4}$ 9.6, $J_{4,5}$ 9 Hz, H4), 3.44 (1 H, dd, $J_{1,2}$ 4.2, $J_{2,3}$ = 10.2 Hz, H2), 3.55–3.57 (1 H, m, H5), 3.62–3.66 (2 H, m, H3,3′), 3.74–3.80 (2 H, H6,6), 3.84 (1 H, dd, $J_{3',3'}$ 10.8, $J_{2',3'}$ 5.4 Hz, H3′), 4.18 (1 H, dd, $J_{1',2'}$ 6.6, $J_{1',1'}$ 12 Hz, H1′), 4.41–4.44 (1 H, m, H1′), 4.82 (1 H, d, $J_{1,2}$ 3.6 Hz, H1), 5.25–5.26 (1 H, m, H2′), 5.34–5.37 (2 H, m, HC=CH); ^{13}C NMR ($CDCl_3$, CD_3OD 2:1, 150 MHz) δ 10.5 (cyclopropane-CH_2), 13.7 (2 × CH_3), 15.4, 15.5 (2 C, cyclopropane-CH), 22.38, 22.39, 24.61, 24.62, 26.9, 27.0, 28.4, 28.5, 28.8, 28.9, 29.0, 29.02, 29.04, 29.1, 29.21, 29.23, 29.9, 31.6, 31.7, 33.8, 34.0 (2 C, C-α), 61.6, 62.4, 65.8, 69.8 (4 C, C6,1′,2′,3′), 69.9 (C4), 71.8 (C5), 72.0 (C2), 73.5 (C3), 99.1 (C1), 129.4, 129.7 (2 C, HC=CH), 173.4, 173.8 (C=O); HRMS (ESI^+) calcd for $C_{46}H_{84}O_{10}Na$ (M+Na) 819.5957. Found 819.5952. The ^{1}H and ^{13}C NMR were in good agreement with that reported in the literature.[3]

Preparation of GL1 analogues

General procedure for preparation of tetrabutylammonium salt

Tetrabutylammonium hydroxide solution in H_2O (1.5 M, 1 eq.) was added to a suspension of carboxylic acid (1.1 eq.) in H_2O (1 ml). The resulting mixture was vigorously stirred at rt overnight. The solvent was evaporated and the crude residue was co-evaporated with toluene several times to give the crude tetrabutylammonium salt.

General procedure for substitution of tetrabutylammonium carboxylate salt

A mixture of tetrabutylammonium carboxylate (2 eq.) and bromide **7** (1 eq.) in toluene (0.5 ml) was heated at 85 °C and stirred vigorously for 25 min. The solvents were then evaporated under reduced pressure. The residue was purified by flash chromatography.

General procedure for deprotection of methoxyacetyl groups

A solution of *t*-butylamine (50 eq.) and protected glucopyranoside (1 eq.) in $CHCl_3$:MeOH (1: 2.5) was stirred at 0 °C for 10 min followed by stirring at 10 °C for 1 h. The solvents were evaporated under reduced pressure without heating, and the residue purified by flash chromatography.

1-*O*-(9*R*,10*S*-Dihydrosterculyl)-2-*O*-oleoyl-sn-glyceryl 2,3,4,6-tetra-*O*-methoxyacetyl-α-D-glucopyranoside (9)

The General Procedure for Substitution conducted with **7** (0.025 g, 0.028 μmol) and tetrabutylammonium 9*R*,10*S*-dihydrosterculate (0.031 g, 0.576 μmol), and purified by flash chromatography (8–15% EtOAc/hexanes) afforded **9** as a colorless oil (0.014 g, 49%), $[\alpha]_D^{26} = +23.8$ (*c* 0.15, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ –0.34 (1 H, ddd, $J_{gem} = J_{trans}$ 4 Hz, cyclopropane CH_2), 0.53–0.65 (1 H, m, cyclopropane CH_2), 0.59–0.65 (2 H, m, cyclopropane CH), 0.83–0.97 (2 × 3 H, m, $CH_2C\mathbf{H}_3$), 1.18–1.35 (44 H, m, alkyl), 1.55–1.67 (4 H, m, β-CH_2), 1.97–2.05 (4 H, m, $\mathbf{H}_2CHC{=}CHC\mathbf{H}_2$), 2.28–2.33 (2 × 2 H, m, α-CH_2), 3.39, 3.40, 3.42, 3.43 (4 × 3 H, 4s, $C\mathbf{H}_3OCH_2$), 3.64 (1 H, dd, $J_{2',3'}$ 4.8, $J_{3',3'}$ 10.8 Hz, H3′), 3.82 (1 H, dd, $J_{2',3'}$ 4.8, $J_{3',3'}$ 10.8 Hz, H3′), 3.95, 3.99, 4.08 (3 × 2 H, 3s, $CH_3OC\mathbf{H}_2$), 4.02 (2 H, m, $CH_3OC\mathbf{H}_2$), 4.04–4.06 (1 H, m, H5), 4.10–4.19 (2 H, m, H1′,6), 4.31–4.40 (2 H, m, H1′,6), 4.97 (1 H, dd, $J_{1,2}$ 4, $J_{2,3}$ 10.4 Hz, H2), 5.11–5.22 (3 H, m, H1,2′,4), 5.29–5.38 (2 H, m, HC=CH), 5.51 (1 H, t, $J_{2,3}$ 9.6, $J_{3,4}$ 10 Hz, H3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.1 (cyclopropane CH_2), 14.3 (2 C, $CH_2\mathbf{C}H_3$), 15.89, 15.91 (2 C, cyclopropane CH), 22.82, 22.83, 25.0, 27.3, 27.4, 28.85, 28.86, 29.2, 29.3, 29.4, 29.45, 29.47, 29.49, 29.65, 29.66, 29.80, 29.83, 29.88, 29.90,

30.3, 30.4, 32.0, 32.1, 34.2, 34.3, 59.5, 59.55, 59.56, 59.58 (4 C, OCH_3), 61.7, 62.1, 67.1, 67.4, 68.5, 69.35, 69.42, 69.5, 69.6, 69.8, 70.5, 70.7, 96.3 (C1), 129.8, 130.2 (2 C, HC=CH), 169.3, 169.6, 169.7, 170.1 (4 C, $MeOCH_2$**C**=O), 173.0, 173.4 (sn1–CO_2, sn2–CO_2); HRMS (ESI^+) calcd for $C_{58}H_{100}O_{18}Na$ (M+Na) 1107.6802. Found 1107.6792.

1-*O*-(9*R*,10*S*-Dihydrosterculyl)-2-*O*-oleoyl-sn-glyceryl α-D-glucopyranoside (15)

The General Procedure for Deprotection conducted with **9** (0.010 g, 0.009 μmol), and purified by flash chromatography (MeOH/$CHCl_3$ 5:95) afforded **15** as a colorless oil (0.006 g, 94%), $[\alpha]_D^{25}$ = +44.8 (*c* 0.19, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ –0.34 (1 H, ddd, J_{gem} = J_{trans} 4 Hz, cyclopropane CH_2), 0.54–0.58 (1 H, m, cyclopropane CH_2), 0.59–0.65 (2 H, m, cyclopropane CH), 0.83–0.89 (2 × 3 H, m, CH_3), 1.25–1.37 (44 H, m, alkyl), 1.58–1.62 (2 × 2 H, m, β-CH_2), 1.99–2.03 (4 H, m, **H**$_2$CHC=CHC**H**$_2$), 2.30–2.34 (2 × 2 H, m, α-CH_2), 3.45–3.64 (4 H, m, H2,4,5,3′), 3.72 (1 H, t, $J_{2,3}$ = $J_{3,4}$ 9.2 Hz, H3), 3.83–3.85 (3 H, m, H3′,6,6), 4.15 (1 H, dd, $J_{1',2'}$ 6.5, $J_{1',1'}$ 12 Hz, H1′), 4.40 (1 H, dd, $J_{1',2'}$ 6.6, $J_{1',1'}$ 12 Hz, H1′), 4.86 (1 H, d, $J_{1,2}$ 3.6 Hz, H1), 5.24–5.26 (1 H, m, H2′), 5.32–5.36 (2 H, m, HC=CH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.1 (cyclopropane CH_2), 14.2, 14.3 (2 × CH_3), 15.87, 15.92 (2 C, cyclopropane-CH), 22.8, 22.9, 25.0, 27.3, 27.4, 28.8, 28.9, 29.2, 29.30, 29.32, 29.4, 29.47, 29.49, 29.52, 29.6, 29.7, 29.85, 29.88, 29.92, 30.3, 30.4 (2 C, C-α), 62.1, 62.3, 66.6, 66.8 (4 C, C6,1′,2′,3′), 69.9, 70.5, 71.8, 72.4(4 C, C2,3,4,5), 99.1 (C1), 129.8, 130.2 (2 C, HC=CH), 173.5, 173.9 (C=O); HRMS (ESI^+) calcd for $C_{46}H_{84}O_{10}Na$ (M+Na) 819.5957. Found 819.5952.

1-*O*-(9*R*,10*S*-Methylenehexadecanoyl)-2-*O*-oleoyl-sn-glyceryl 2,3,4,6-tetra-*O*-methoxyacetyl-α-D-glucopyranoside (10)

The General Procedure for Substitution conducted with **7** (0.051 g, 0.058 μmol) and tetrabutylammonium 9*R*,10*S*-methylhexadecanoate (0.061 g, 0.115 μmol), and purified by flash chromatography (EtOAc/hexanes 40:60) afforded **10** as a colorless oil (0.027 g, 47%), $[\alpha]_D^{25}$ = +24.9 (*c* 0.19, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ –0.34 (1 H, ddd, J_{gem} = J_{trans} 4 Hz, cyclopropane CH_2), 0.53–0.64 (3 H, m, cyclopropane CH,CH_2), 0.82–0.90 (2 × 3 H, m, CH_2C**H**$_3$), 1.12–1.42 (40 H, m, alkyl), 1.55–1.67 (4 H, m, β-CH_2), 1.98–2.01 (4 H, m, **H**$_2$CHC=CHC**H**$_2$), 2.29–2.34 (2 × 2 H, m, α-CH_2), 3.39, 3.41, 3.43, 3.45 (4 × 3 H, 4s, C**H**$_3$O), 3.63 (1 H, dd, $J_{2',3'}$ 4.8, $J_{3',3'}$ 10.8 Hz, H3′), 3.81 (1 H, dd, $J_{2',3'}$ 4.8, $J_{3',3'}$ 10.8 Hz, H3′), 3.96, 4.00, 4.09 (3 × 2 H, 3s, CH_3OC**H**$_2$), 4.04 (2 H, m, CH_3OC**H**$_2$), 4.06–4.08 (1 H, m, H5), 4.11–4.20 (2 H, m, H1′,6), 4.31–4.41 (2 H, m, H1′,6), 4.97 (1 H, dd, $J_{1,2}$ 4, $J_{2,3}$ 10.4 Hz, H2), 5.12–5.23 (3 H, m, H1,2′,4), 5.30–5.39 (2 H, m, HC=CH), 5.52 (1 H, t, $J_{2,3}$ 9.6, $J_{3,4}$ 10

Hz, H3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.1 (cyclopropane CH_2), 14.3 (2 × CH_2**C**H_3), 15.85, 15.90 (2 × cyclopropane CH), 22.81, 22.83, 25.0, 27.3, 27.4, 28.8, 28.9, 29.2, 29.3, 29.4, 29.45, 29.5, 29.6, 29.7, 29.87, 29.90, 30.3, 30.4, 32.0, 32.1, 34.2, 34.3, 59.48, 59.55, 59.56, 59.57 (4 C, OCH_3), 61.7, 62.1, 67.1, 67.4, 68.5, 69.3, 69.4, 69.5, 69.8, 70.5, 70.7, 96.3 (C1), 129.8, 130.2 (2 C, HC=CH), 169.3, 169.6, 169.7, 170.1 (4 C, $MeOCH_2$**C**=O), 173.0, 173.4 (sn1–CO_2, sn2–CO_2); HRMS (ESI$^+$) calcd for $C_{54}H_{96}O_{18}Na$ (M+Na) 1079.6494. Found 1079.6485.

1-*O*-(9*R*,10*S*-Methylenehexadecanoyl)-2-*O*-oleoyl-sn-glyceryl α-D-glucopyranoside (16)

The General Procedure for Deprotection conducted with **10** (0.022 g, 0.021 μmol), and purified by flash chromatography (MeOH/$CHCl_3$ 5:95) afforded **16** as a colorless oil (0.014 g, 89%), $[\alpha]_D^{24}$ = +48.1 (*c* 0.6, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ –0.35 (1 H, ddd, J_{gem} = J_{trans} 4 Hz, cyclopropane CH_2), 0.55–0.58 (1 H, m, cyclopropane CH_2), 0.59–0.64 (2 H, m, cyclopropane CH), 0.83–0.90 (2 × 3 H, m, CH_3), 1.25–1.44 (40 H, m, alkyl), 1.59–1.63 (2 × 2 H, m, β-CH_2), 1.85–2.05 (4 H, m, **H**$_2$CHC=CHC**H**$_2$), 2.30–2.34 (2 × 2 H, m, α-CH_2), 2.26–2.78 (1 H, br s), 3.24 (1 H, br s), 3.39 (1 H, br s), 3.47–2.49 (1 H, br s), 3.53–3.65 (4 H, m, H2,4,5,3′), 3.72 (1 H, t, $J_{2,3}$ = $J_{3,4}$ 9.2 Hz, H3), 3.82–3.85 (3 H, m, H3′,6, 6), 4.14 (1 H, dd, $J_{1',2'}$ 6.5, $J_{1',1'}$ 12 Hz, H1′), 4.40 (1 H, dd, $J_{1',2'}$ 6.6, $J_{1',1'}$ 12 Hz, H1′), 4.86 (1 H, d, $J_{1,2}$ 3.6 Hz, H1), 5.22–5.26 (1 H, m, H2′), 5.30–5.38 (2 H, m, HC=CH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.3 (cyclopropane CH_2), 14.1, 14.3 (2 × CH_3), 15.87, 15.92 (2 C, cyclopropane CH), 22.8, 22.9, 25.0, 27.3, 27.4, 28.8, 28.9, 29.2, 29.31, 29.32, 29.4, 29.47, 29.49, 29.52, 29.6, 29.7, 29.85, 29.88, 29.92, 30.3, 30.4 (2 C, C-α), 62.3, 66.6, 69.9, 70.5, 71.8, 72.4 (8 C, C2,3,4,5,6,1′,2′,3′), 99.1 (C1), 129.8, 130.2 (2 C, HC=CH), 173.5, 173.8 (C=O); HRMS (ESI$^+$) calcd for $C_{44}H_{80}O_{10}Na$ (M+Na) 791.5649. Found 791.5641.

1-*O*-(11*R*,12*S*-Lactobacillyl)-2-*O*-oleoyl-sn-glyceryl 2,3,4,6-tetra-*O*-methoxyacetyl-α-D-glucopyranoside (11)

The General Procedure for Substitution conducted with **7** (0.042 g, 0.046 μmol) and tetrabutylammonium 11*R*,12*S*-lactobacillate (0.052 g, 0.092 μmol), and purified by flash chromatography (EtOAc/hexanes 40:60) afforded **11** as a colorless oil (0.027 g, 55%), $[\alpha]_D^{25}$ = +24.3 (*c* 0.25, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ –0.34 (1 H, ddd, J_{gem} = J_{trans} 4 Hz, cyclopropane CH_2), 0.52–0.65 (3 H, m, cyclopropane CH,CH_2), 0.82–0.97 (2 × 3 H, m, CH_2C**H**$_3$), 1.18–1.35 (44 H, m, alkyl), 1.25–1.67 (4 H, m, β-CH_2), 1.97–2.05 (4 H, m, **H**$_2$CHC=CHC**H**$_2$), 2.28–2.33 (4 H, m, α-CH_2),

3.39, 3.40, 3.42, 3.44 (4 × 3 H, 4s, C**H**$_3$OCH$_2$), 3.63 (1 H, dd, $J_{2',3'}$ 4.6, $J_{3',3'}$ 10.6 Hz, H3′), 3.81 (1 H, dd, $J_{2',3'}$ 4.6, $J_{3',3'}$ 10.7 Hz, H3′), 3.95, 3.99, 4.08 (3 × 2 H, 3s, CH$_3$OC**H**$_2$), 4.02 (2 H, m, CH$_3$OC**H**$_2$), 4.04–4.06 (1 H, m, H5), 4.10–4.19 (2 H, m, H1′,6), 4.31–4.40 (2 H, m, H1′,6), 4.97 (1 H, dd, $J_{1,2}$ 3.8, $J_{2,3}$ 10.1 Hz, H2), 5.11–5.22 (3 H, m, H1,2′,4), 5.29–5.38 (2 H, m, HC=CH), 5.51 (1 H, t, $J_{2,3}$ 10, $J_{3,4}$ 9.8 Hz, H3); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 11.1 (cyclopropane CH$_2$), 14.3 (2 × CH$_2$**C**H$_3$), 15.89, 15.91 (2 × cyclopropane CH), 22.82, 22.83, 25.0, 27.3, 27.4, 28.85, 28.86, 29.2, 29.3, 29.4, 29.45, 29.47, 29.49, 29.65, 29.66, 29.80, 29.83, 29.88, 29.90, 30.3, 30.4, 32.0, 32.1, 34.2, 34.3, 59.5, 59.55, 59.56, 59.58 (4 C, OCH$_3$), 61.7, 62.1, 67.1, 67.4, 68.5, 69.35, 69.42, 69.5, 69.6, 69.8, 70.5, 70.7, 96.3, 129.8, 130.2 (2 C, HC=CH), 169.3, 169.6, 169.7, 170.1 (4 C, MeOCH$_2$**C**=O), 173.0, 173.4 (sn1–CO$_2$, sn2–CO$_2$); HRMS (ESI$^+$) calcd for $C_{58}H_{100}O_{18}Na$ (M+Na) 1107.6802. Found 1107.6793.

1-*O*-(11*R*,12*S*-Lactobacillyl)-2-*O*-oleoyl-sn-glyceryl α-D-glucopyranoside (17)

The General Procedure for Deprotection conducted with **11** (0.020 g, 0.019 μmol), and purified by flash chromatography (MeOH/CHCl$_3$ 5:95) afforded **17** as a colorless oil (0.015 g, 99%), $[\alpha]_D^{25}$ = +45 (*c* 0.6, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 400 MHz) δ –0.34 (1 H, ddd, $J_{gem} = J_{trans}$ 4 Hz, cyclopropane CH$_2$), 0.52–0.57 (1 H, m, cyclopropane CH$_2$), 0.58–0.65 (2 H, m, cyclopropane CH), 0.82–0.97 (2 × 3 H, m, CH$_3$), 1.15–1.37 (44 H, m, alkyl), 1.59–1.61 (2 × 2 H, m, β-CH$_2$), 1.99–2.05 (4 H, m, **H**$_2$CHC=CHC**H**$_2$), 2.29–2.33 (2 × 2 H, m, α-CH$_2$), 2.70 (1 H, br s), 3.21 (1 H, br s), 3.51–3.53 (1 H, br s), 3.54–3.62 (4 H, m, H2,4,5,3′), 3.73 (1 H, t, $J_{2,3} = J_{3,4}$ 9.2 Hz, H3), 3.80–3.85 (3 H, m, H3′,6,6), 4.15 (1 H, dd, $J_{1',2'}$ 6.6, $J_{1',1'}$ 11.8 Hz, H1′), 4.40 (1 H, dd, $J_{1',2'}$ 6.6, $J_{1',1'}$ 11.8 Hz, H1′), 4.86 (1 H, d, $J_{1,2}$ 3.8 Hz, H1), 5.23–5.27 (1 H, m, H2′), 5.30–5.37 (2 H, m, HC=CH); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 11.1 (cyclopropane CH$_2$), 14.3 (2 × CH$_3$), 15.8, 15.9 (2 C, cyclopropane CH), 22.8, 25.0, 27.3, 27.4, 28.9, 29.2, 29.3, 29.4, 29.5, 29.7, 29.8, 29.87, 29.92, 30.3, 30.4, 32.06, 32.2, 34.3, 34.4 (2 C, C-α), 62.3, 66.6, 69.9, 70.5, 71.8, 72.4, 74.7 (8 C, C2,3,4,5,6,1′,2′,3′), 99.1 (C1), 129.8, 130.2 (2 C, HC=CH), 173.5, 173.8 (2 C, C=O); HRMS (ESI$^+$) calcd for $C_{46}H_{84}O_{10}Na$ (M+Na) 819.5957. Found 819.5952.

1-*O*-(11*S*,12*R*-Lactobacillyl)-2-*O*-oleoyl-sn-glyceryl 2,3,4,6-tetra-*O*-methoxyacetyl-α-D-glucopyranoside (12)

The General Procedure for Substitution conducted with **7** (0.015 g, 0.017 μmol) and tetrabutylammonium 11*S*,12*R*-lactobacillate (0.019 g, 0.035 μmol), and purified by flash chromatography (EtOAc/hexanes 40:60) afforded **12** as a colorless oil (0.002 g, 8%), $[\alpha]_D^{25}$ = +24.2 (*c* 0.28, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 400 MHz) δ –0.34 (1 H, ddd, $J_{gem} = J_{trans}$ 4 Hz, cyclopropane CH$_2$),

0.52–0.65 (3 H, m, cyclopropane CH,CH_2), 0.82–0.97 (2 × 3 H, m, $CH_2C\mathbf{H}_3$), 1.12–1.35 (44 H, m, alkyl), 1.55–1.67 (4 H, m, β-CH_2), 1.97–2.05 (4 H, m, $\mathbf{H}_2CHC{=}CHC\mathbf{H}_2$), 2.28–2.33 (α-$CH_2$), 3.39, 3.40, 3.42, 3.44 (4 × 3 H, 4s, $C\mathbf{H}_3OCH_2$), 3.63 (1 H, dd, $J_{2',3'}$ 4.4, $J_{3',3'}$ 10.4 Hz, H3′), 3.81 (1 H, dd, $J_{2',3'}$ 4.4, $J_{3',3'}$ 10.5 Hz, H3′), 3.95, 3.99, 4.08 (3 × 2 H, 3s, $CH_3OC\mathbf{H}_2$), 4.02 (2 H, m, $CH_3OC\mathbf{H}_2$), 4.04–4.06 (1 H, m, H5), 4.10–4.19 (2 H, m, H1′,6), 4.31–4.40 (2 H, m, H1′,6), 4.97 (1 H, dd, $J_{1,2}$ 4, $J_{2,3}$ 10.4 Hz, H2), 5.11–5.22 (3 H, m, H1,2′,4), 5.29–5.38 (2 H, m, HC=CH), 5.51 (1 H, t, $J_{2,3}$ 9.6, $J_{3,4}$ 10 Hz, H3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.1 (cyclopropane CH_2), 14.3 (2 × $CH_2\mathbf{C}H_3$), 15.89, 15.91 (2 × cyclopropane CH), 22.82, 22.83, 25.0, 27.3, 27.4, 28.85, 28.86, 29.2, 29.3, 29.4, 29.45, 29.47, 29.49, 29.65, 29.66, 29.80, 29.83, 29.88, 29.90, 30.3, 30.4, 32.0, 32.1, 34.2, 34.3, 59.5, 59.55, 59.56, 59.58 (4C, OCH_3), 61.7, 62.1, 67.1, 67.4, 68.5, 69.35, 69.42, 69.5, 69.6, 69.8, 70.5, 70.7, 96.3 (C1), 129.8, 130.2 (2 C, HC=CH), 169.3, 169.6, 169.7, 170.1 (4 C, $MeOCH_2\mathbf{C}$=O), 173.0, 173.4 (sn1–CO_2, sn2–CO_2); HRMS (ESI$^+$) calcd for $C_{58}H_{100}O_{18}Na$ (M+Na) 1107.6802. Found 1107.6793.

1-*O*-(11*S*,12*R*-Lactobacillyl)-2-*O*-oleoyl-sn-glyceryl α-D-glucopyranoside (18)

The General Procedure for Deprotection conducted with **12** (0.015 g, 0.014 μmol), and purified by flash chromatography (MeOH/$CHCl_3$ 5:95) afforded **18** as a colorless oil (0.0006 g, 65%), $[\alpha]_D^{26}$ = +43.5 (*c* 0.25, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ –0.34 (1 H, ddd, $J_{gem} = J_{trans}$ 4 Hz, cyclopropane CH_2), 0.52–0.56 (1 H, m, cyclopropane CH_2), 0.58–0.65 (2 H, m, cyclopropane CH), 0.82–0.97 (2 × 3 H, m, CH_3), 1.12–1.37 (44 H, m, alkyl), 1.59–1.61 (4 H, m, β-CH_2), 1.99–2.05 (4 H, m, $\mathbf{H}_2CHC{=}CHC\mathbf{H}_2$), 2.29–2.33 (4 H, m, α-$CH_2$), 2.70 (1 H, br s), 3.21 (1 H, br s), 3.51–3.53 (1 H, br s), 3.54–3.62 (4 H, m, H2,4,5,3′), 3.73 (1 H, t, $J_{2,3} = J_{3,4}$ 9.2 Hz, H3), 3.80–3.85 (3 H, m, H3′,6,6), 4.15 (1 H, dd, $J_{1',2'}$ 6.6, $J_{1',1'}$ 12 Hz, H1′), 4.40 (1 H, dd, $J_{1',2'}$ 6.6, $J_{1',1'}$ 12 Hz, H1′), 4.86 (1 H, d, $J_{1,2}$ 3.6 Hz, H1), 5.23–5.27 (1 H, m, H2′), 5.30–5.37 (2 H, m, HC=CH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.1 (cyclopropane CH_2), 14.3 (2 × CH_3), 15.8, 15.9 (2 × cyclopropane CH), 22.8, 25.0, 27.3, 27.4, 28.9, 29.2, 29.3, 29.4, 29.5, 29.7, 29.8, 29.87, 29.92, 30.3, 30.4, 32.06, 32.11, 34.3, 34.4 (2 C, C-α), 62.3, 66.6, 69.9, 70.5, 71.8, 72.4, 74.7 (8 C, C2,3,4,5,6,1′,2′,3′), 99.1 (C1), 129.8, 130.2 (2 C, HC=CH), 173.5, 173.8 (C=O); HRMS (ESI$^+$) calcd for $C_{46}H_{84}O_{10}Na$ (M+Na) 819.5957. Found 819.5952.

1,2-Di-*O*-oleoyl-sn-glyceryl 2,3,4,6-tetra-*O*-methoxyacetyl-α-D-glucopyranoside (13)

The General Procedure for Substitution conducted with **7** (0.102 g, 0.121 mmol) and tetrabutylammonium oleate (0.091 g, 0.171 mmol), and purified by flash chromatography (EtOAc/hexanes 40:60) afforded **13** as a colorless oil (0.060 g, 62%), $[\alpha]_D^{25}$ = +27 (*c* 0.95, $CHCl_3$). ^{1}H

NMR ($CDCl_3$, 400 MHz) δ 0.83–0.90 (2 × 3 H, m, $CH_2C\mathbf{H}_3$), 1.25–1.30 (42 H, m, alkyl), 1.55–1.64 (4 H, m, β-CH_2), 2.00–2.04 (2 × 4 H, m, $\mathbf{H}_2CHC{=}CHC\mathbf{H}_2$), 2.28–2.33 (4 H, m, α-$CH_2$), 3.39, 3.41, 3.43, 3.45 (4 × 3 H, 4s, $C\mathbf{H}_3O$), 3.64 (1 H, dd, $J_{2',3'}$ 4.4, $J_{3',3'}$ 10.4 Hz, H3′), 3.81 (1 H, dd, $J_{2',3'}$ 4.4, $J_{3',3'}$ 10.4 Hz, H3′), 3.95, 4.00, 4.09 (3 × 2 H, 3s, $CH_3OC\mathbf{H}_2$), 4.03 (2 H, m, $CH_3OC\mathbf{H}_2$), 4.05–4.07 (1 H, m, H5), 4.11–4.20 (2 H, m, H1′,6), 4.31–4.41 (2 H, m, H1′,6), 4.98 (1 H, dd, $J_{1,2}$ 4, $J_{2,3}$ 10.4 Hz, H2), 5.11–5.23 (3 H, m, H1,2′,4), 5.30–5.39 (2 × 2 H, m, HC=CH), 5.52 (1 H, t, $J_{2,3}$ 9.8, $J_{3,4}$ 10 Hz, H3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.3 (2 × $CH_2\mathbf{C}H_3$), 22.8, 25.0, 25.1, 27.3, 27.4, 29.3, 29.4, 29.5, 29.7, 29.9, 32.1, 34.2, 34.3, 59.5, 59.6 , 61.7, 62.1, 67.1, 67.4, 68.5, 69.3, 69.4, 69.5, 69.6, 69.8, 70.6, 70.8, 96.3 (C1), 129.8, 130.2 (4 C, 2 × HC=CH), 169.3, 169.6, 169.7, 170.1 (4 C, $MeOCH_2\mathbf{C}$=O), 173.1, 173.4 (sn1–CO_2, sn2–CO_2); HRMS (ESI^+) calcd for $C_{57}H_{98}O_{18}Na$ (M+Na) 1093.6651. Found 1093.6648.

1,2-Di-*O*-oleoyl-sn-glyceryl α-D-glucopyranoside (19)

The General Procedure for deprotection conducted with **13** (0.061 g, 0.056 μmol), and purified by flash chromatography (MeOH/$CHCl_3$ 5:95) afforded **19** as a colorless oil (0.038 g, 82%), $[\alpha]_D^{25}$ = +45 (*c* 1.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.86–0.89 (2 × 3 H, m, CH_3), 1.26–1.29 (42 H, m, alkyl), 1.58–1.61 (4 H, m, β-CH_2), 1.98–2.02 (2 × 4 H, m, $\mathbf{H}_2CHC{=}CHC\mathbf{H}_2$), 2.28–2.33 (4 H, m, α-$CH_2$), 3.45–3.64 (4 H, m, H2,4,5,3′), 3.72 (1 H, t, $J_{2,3}$ 10, $J_{3,4}$ 9.4 Hz, H3), 3.85–3.81 (3 H, m, H3′,6, 6), 4.15 (1 H, dd, $J_{1',2'}$ 6.4, $J_{1',1'}$ 12 Hz, H1′), 4.39 (1 H, dd, $J_{1',2'}$ 6.4, $J_{1',1'}$ 12 Hz, H1′), 4.85 (1 H, d, $J_{1,2}$ 3.6 Hz, H1), 5.21–5.27 (1 H, m, H2′), 5.29–5.38 (2 × 2 H, m, HC=CH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.3 (2 × CH_3), 22.8, 25.0, 27.35, 27.38, 29.27, 29.29, 29.34, 29.4, 29.5, 29.7, 29.9, 32.1, 34.3, 34.4, 61.9, 62.6, 66.4, 70.1, 72.0, 72.2, 74.3, 99.3 (C1), 129.8, 130.2 (4 C, 2 × HC=CH), 173.4, 173.9 (2 C, 2 × C=O); HRMS (ESI^+) calcd for $C_{45}H_{82}O_{10}Na$ (M+Na) 805.5800. Found 805.5806.

1-*O*-Stearyl-2-*O*-oleoyl-sn-glyceryl 2,3,4,6-tetra-*O*-methoxyacetyl-α-D-glucopyranoside (14)

The General Procedure for Substitution conducted with **7** (0.091 g, 0.103 μmol) and tetrabutylammonium stearate (0.110 g, 0.207 μmol), and purified by flash chromatography (EtOAc/hexanes 40:60) afforded **14** as a colorless oil (0.069 g, 64%), $[\alpha]_D^{24}$ = +26.3 (*c* 0.35, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.86–0.89 (2 × 3 H, m, $CH_2C\mathbf{H}_3$), 1.25–1.31 (44 H, m, alkyl), 1.58–1.62 (4 H, m, β-CH_2), 2.00–2.04 (4 H, m, $\mathbf{H}_2CHC{=}CHC\mathbf{H}_2$), 2.28–2.34 (4 H, m, α-$CH_2$), 3.39, 3.40, 3.42, 3.45 (4 × 3 H, 4s, $C\mathbf{H}_3OCH_2$), 3.64 (1 H, dd, $J_{2',3'}$ 4.4, $J_{3',3'}$ 10.4 Hz, H3′), 3.81 (1 H, dd, $J_{2',3'}$ 4.4, $J_{3',3'}$ 10.4 Hz, H3′), 3.95, 4.00, 4.08 (3 × 2 H, 3s, $CH_3OC\mathbf{H}_2$), 4.03 (2 H, m, $CH_3OC\mathbf{H}_2$), 4.05–4.07 (1 H, m,

H5), 4.12 (1 H, m, H5), 4.14–4.20 (2 H, m, H1′,6), 4.31–4.40 (2 H, m, H1′,6), 4.97 (1 H, dd, $J_{1,2}$ 4, $J_{2,3}$ 10.1 Hz, H2), 5.11–5.22 (3 H, m, H1,2′,4), 5.30–5.38 (2 H, m, HC=CH), 5.52 (1 H, t, $J_{2,3}$ 9.8, $J_{3,4}$ 10 Hz, H3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.3 (2 × CH_2**C**H_3), 22.8, 25.0, 27.3, 27.4, 29.26, 29.30, 29.4, 29.47, 29.51, 29.7, 29.85, 29.91, 32.1, 34.2, 34.3, 59.5, 59.6, 61.7, 62.1, 67.1, 67.4, 68.5, 69.36, 69.43, 69.5, 69.6, 69.8, 70.6, 70.8, 96.3 (C1), 129.8, 130.2 (2 × HC=CH), 169.3, 169.6, 169.7, 170.1 (4 C, MeOCH_2**C**=O), 173.1, 173.4 (sn1–CO_2, sn2–CO_2); HRMS (ESI$^+$) calcd for $C_{57}H_{100}O_{18}$ (M+H) 1073.6943. Found 1073.6913.

1-*O*-Stearyl-2-*O*-oleoyl-sn-glyceryl α-D-glucopyranoside (20)

The General Procedure for Deprotection conducted with **14** (0.052 g, 0.047 μmol), and purified by flash chromatography (MeOH/$CHCl_3$ 5:95) afforded **20** as a colorless oil (0.040 g, 86%), $[\alpha]_D^{24} = +42.4$ (*c* 0.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.83–0.89 (2 × 3 H, m, CH_3), 1.18–1.30 (44 H, m, alkyl), 1.59–1.71 (4 H, m, β-CH_2), 1.98–2.03 (4 H, m, **H**$_2$CHC=CHC**H**$_2$), 2.29–2.34 (4 H, m, α-CH_2), 3.45–3.64 (4 H, m, H2,4,5,3′), 3.72 (1 H, t, $J_{2,3}$ 10, $J_{3,4}$ *J* 9.8 Hz, H3), 3.85–3.81 (3 H, m, H3′,6,6), 4.14 (1 H, dd, $J_{1',2'}$ 6.4, $J_{1',1'}$ 12 Hz, H1′), 4.40 (1 H, dd, $J_{1',2'}$ 6.4, $J_{1',1'}$ 12 Hz, H1′), 4.85 (1 H, d, $J_{1,2}$ 3.8 Hz, H1), 5.23–5.26 (1 H, m, H2′), 5.32–5.37 (2 H, m, HC=CH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.3 (2 × CH_3), 22.8, 25.0, 27.3, 27.4, 29.25, 29.30, 29.4, 29.49, 29.52, 29.7, 29.9, 32.1, 34.3, 34.4, 59.6, 62.2, 62.4, 66.7, 69.9, 70.6, 71.8, 72.4, 74.8, 99.1 (C1), 129.8, 130.2 (2 × HC=CH), 173.4, 173.8 (2 × C=O); HRMS (ESI$^+$) calcd for $C_{45}H_{84}O_{10}Na$ (M+Na) 807.5956. Found 807.5969.

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1 W. C. Still, M. Kahn and A. M. Mitra, *J. Org. Chem.*, 1978, **43**, 2923.

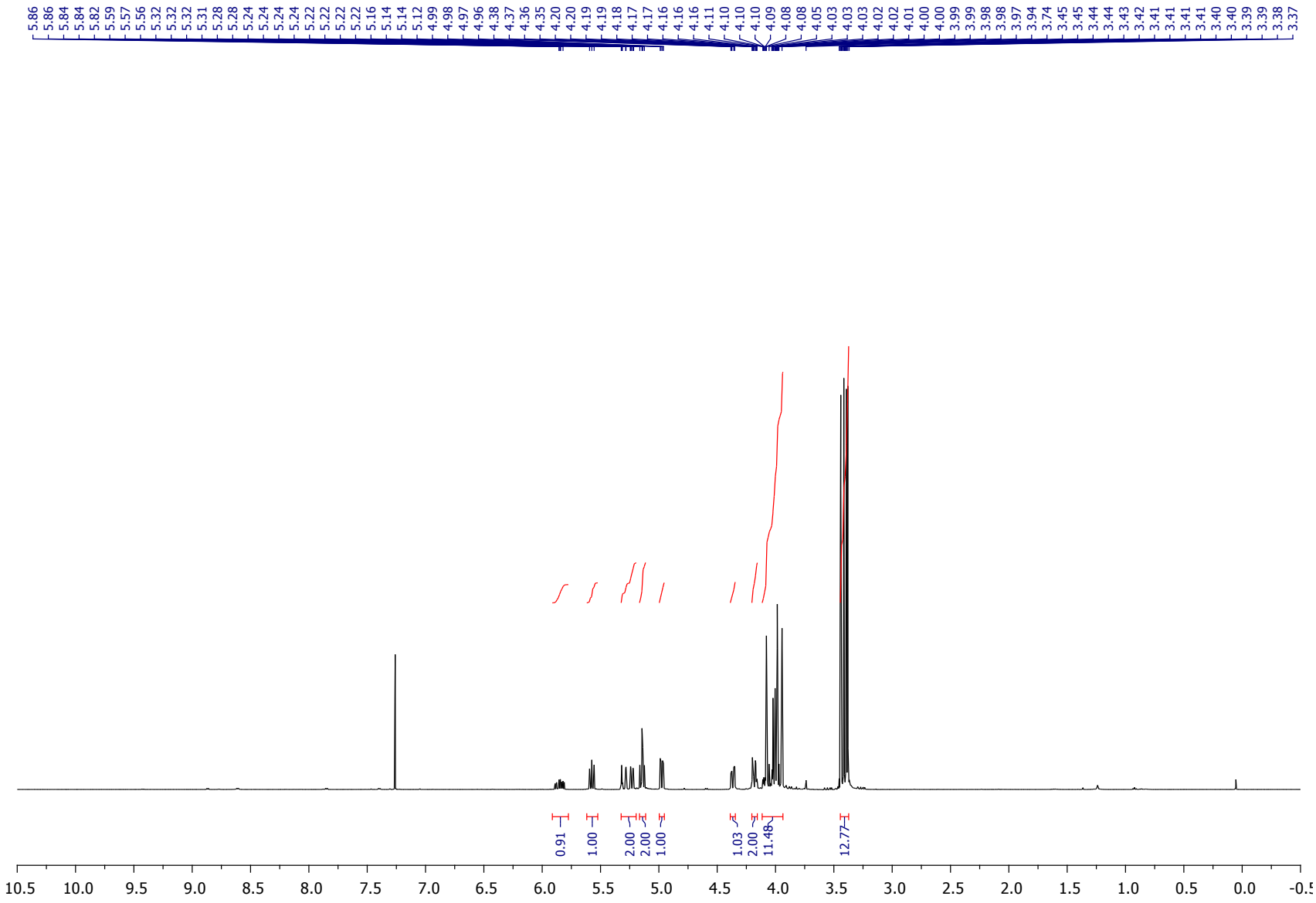
2 A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.

3 J. Sauvageau, J. Ryan, K. Lagutin, I. M. Sims, B. L. Stocker and M. S. Timmer, *Carbohydr. Res.*, 2012, **357**, 151.

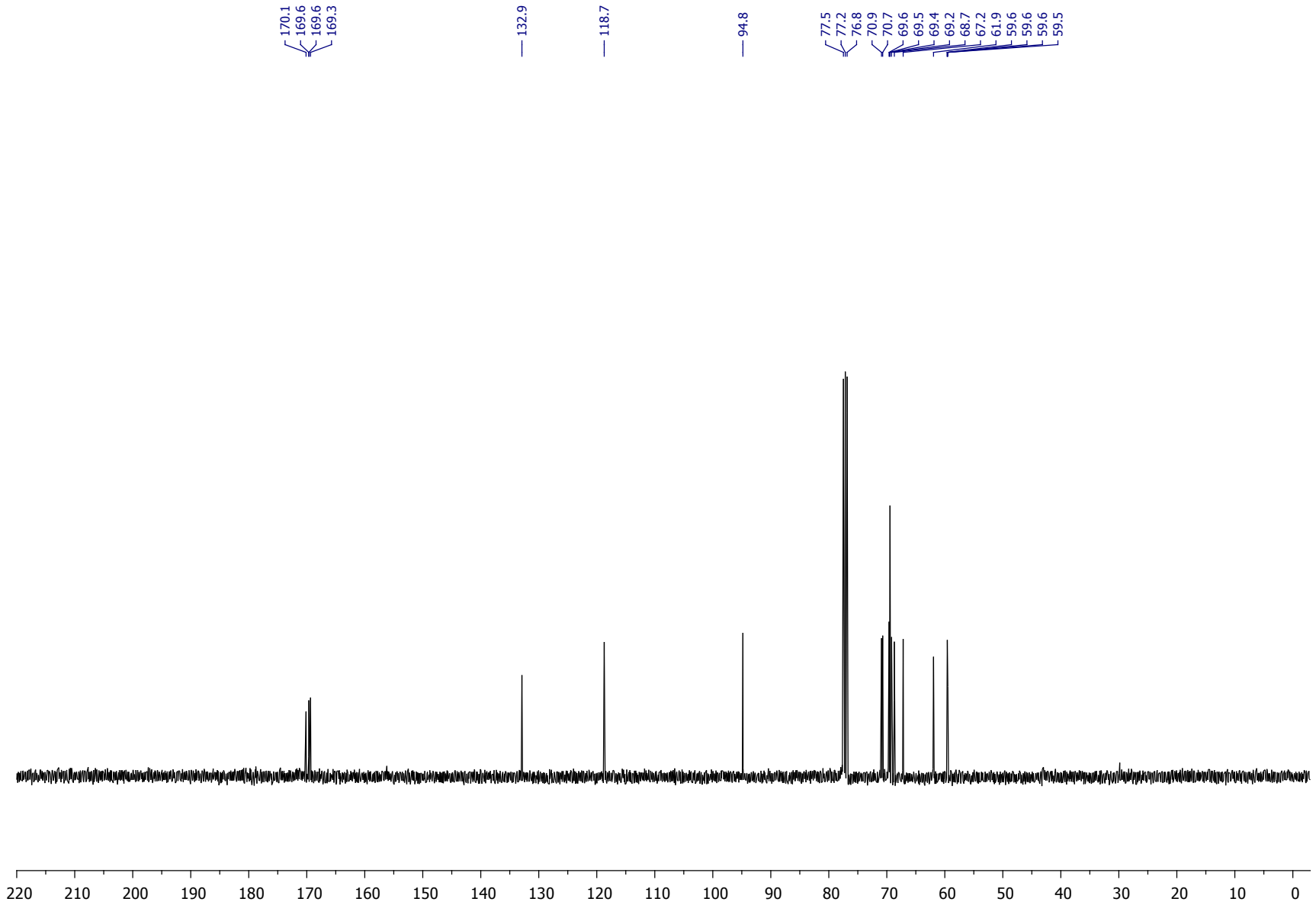
Spectral Data

Allyl 2,3,4,6-tetra-O-methoxyacetyl-α-D-glucopyranoside (3)

^{1}H NMR ($CDCl_3$, 400 MHz)

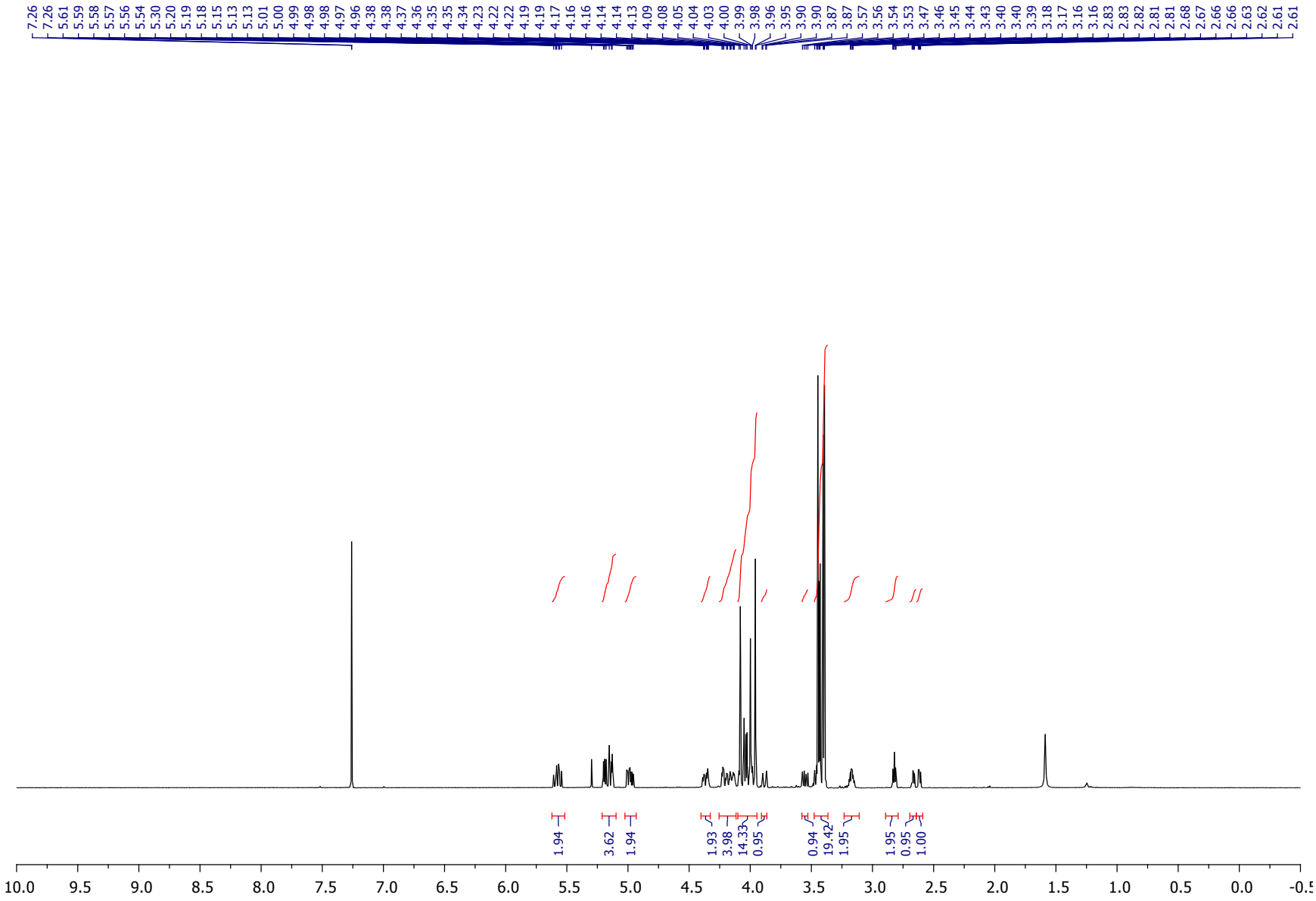


^{13}C NMR ($CDCl_3$, 100 MHz)

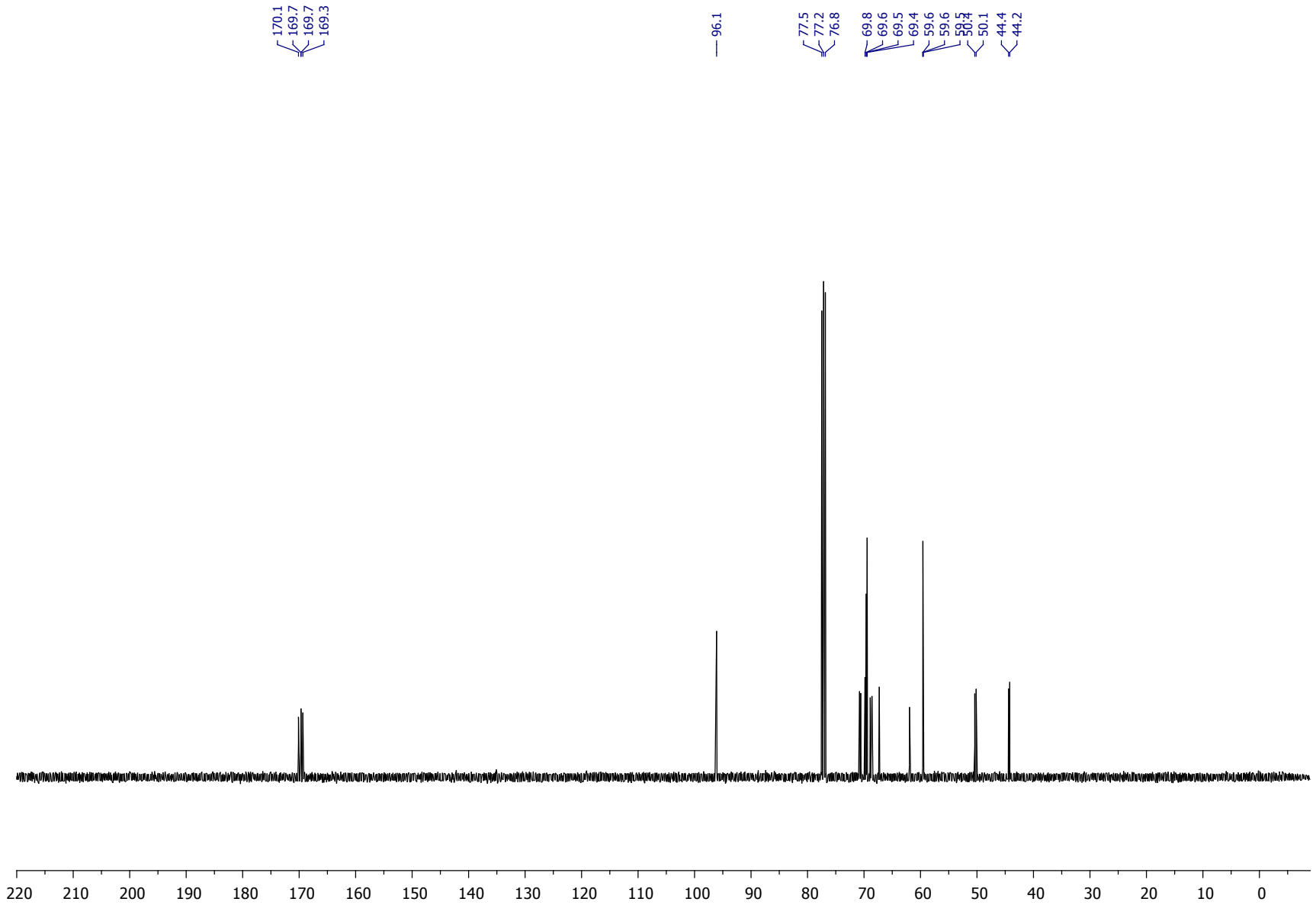


2',3'-Epoxypropyl 2,3,4,6-tetra-O-methoxyacetyl-α-D-glucopyranoside (4)

^{1}H NMR ($CDCl_3$, 400 MHz)

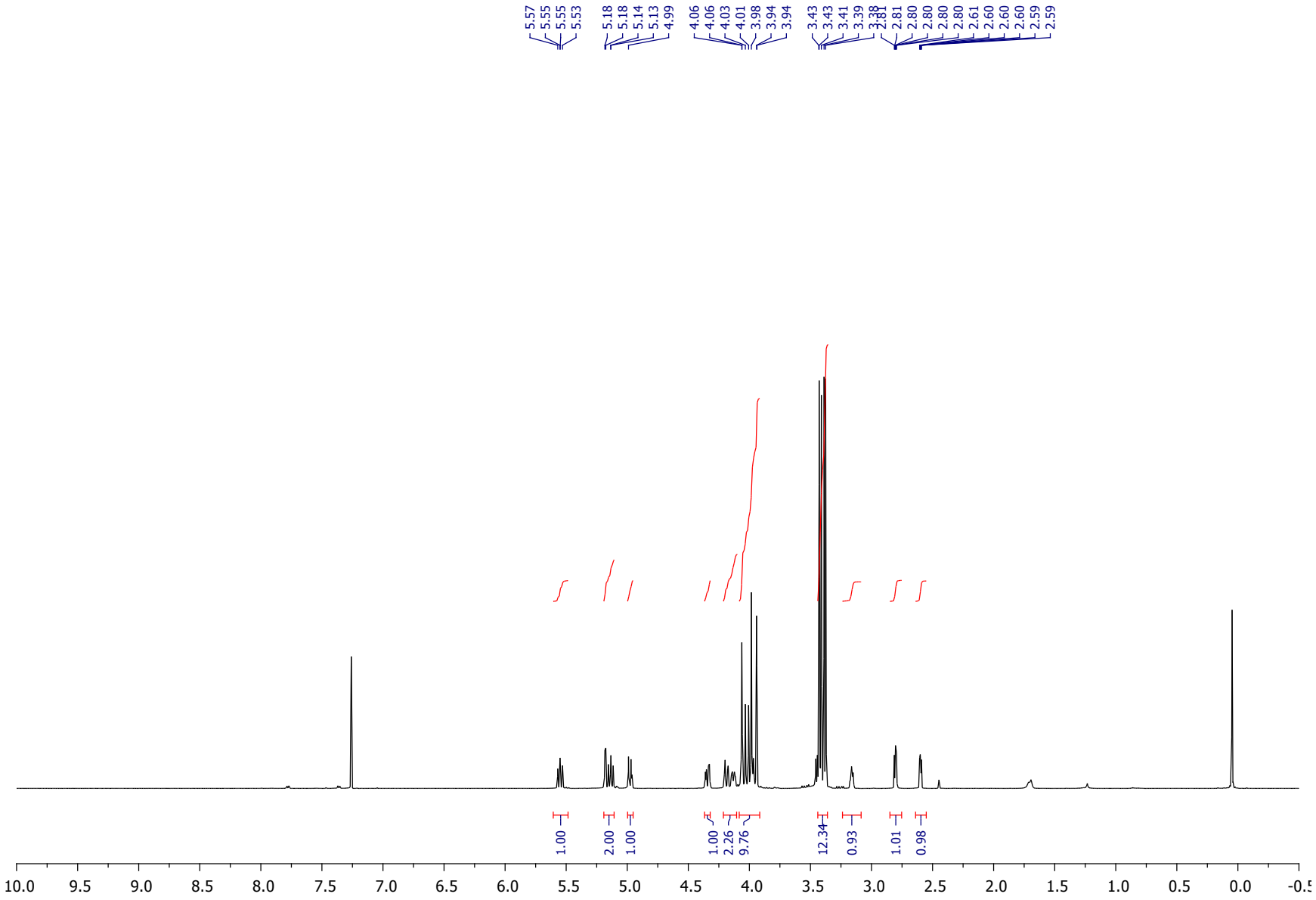


^{13}C NMR ($CDCl_3$, 100 MHz)

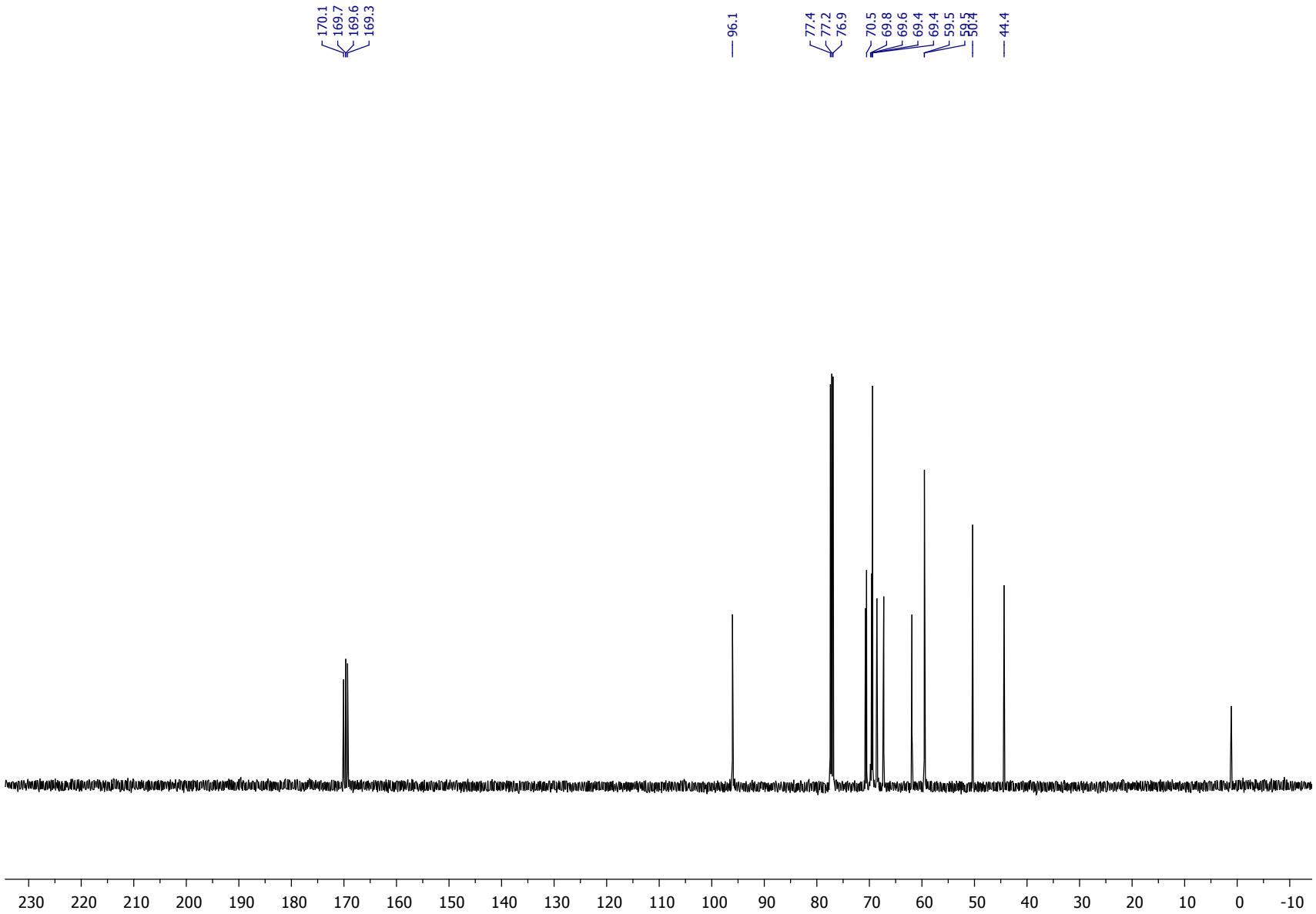


(2'R)-2',3'-Epoxypropyl 2,3,4,6-tetra-O-methoxyacetyl-α-D-glucopyranoside ((2'R)-4)

^{1}H NMR ($CDCl_3$, 400 MHz)

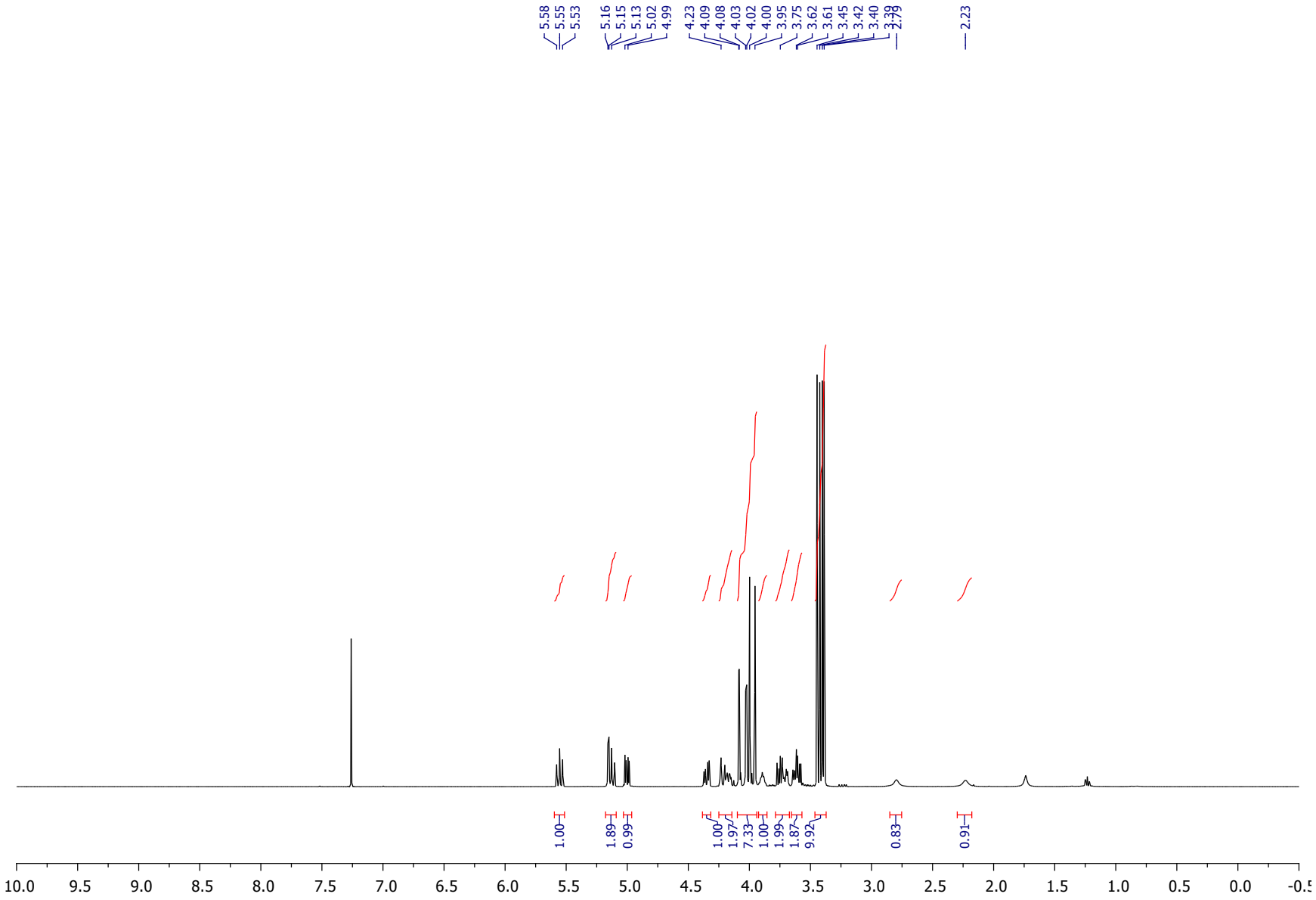


^{13}C NMR ($CDCl_3$, 100 MHz)

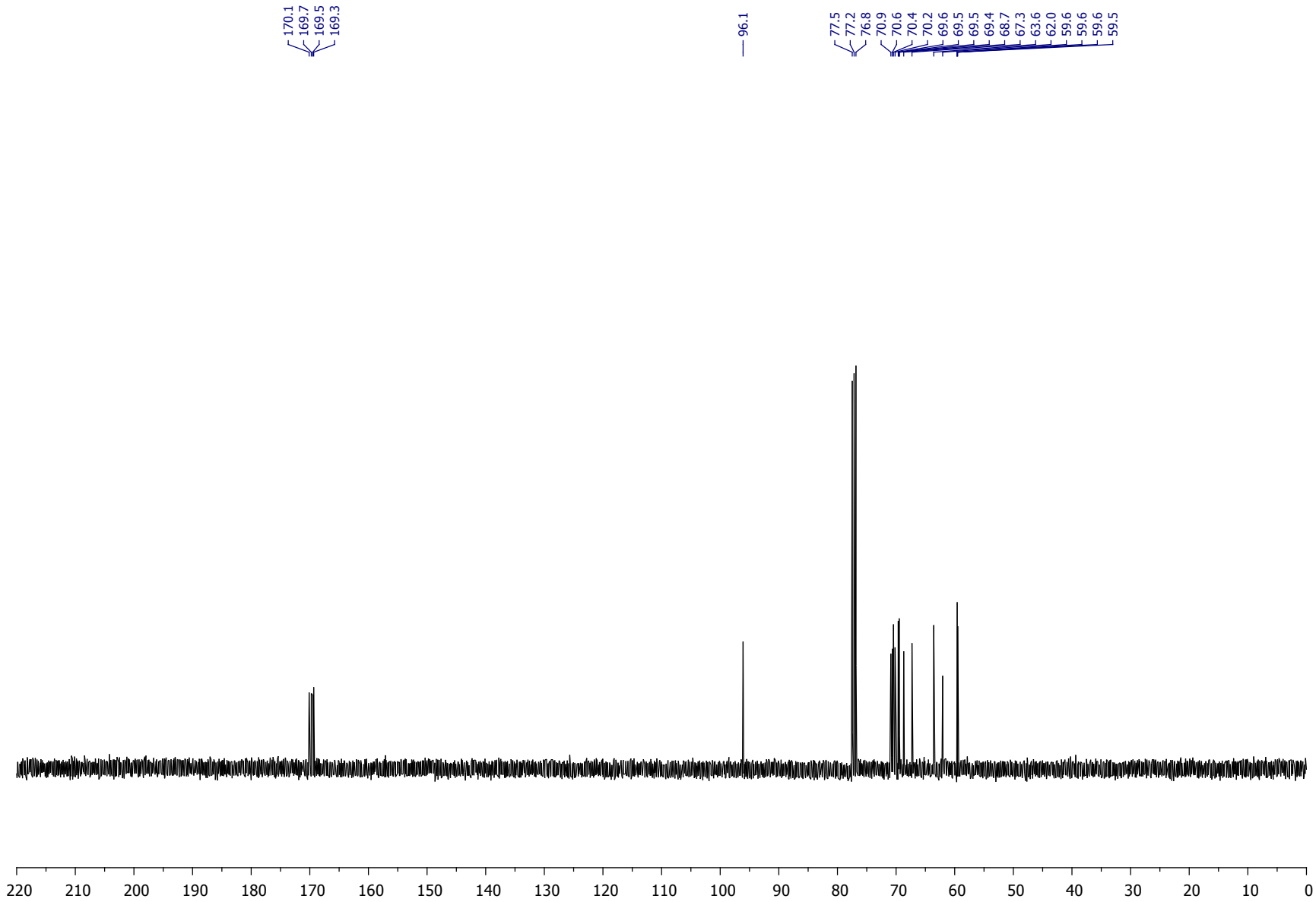


(2'S)-2',3'-Dihydroxypropyl 2,3,4,6-tetra-O-methoxyacetyl-α-D-glucopyranoside ((2'S)-5)

^{1}H NMR ($CDCl_3$, 400 MHz)

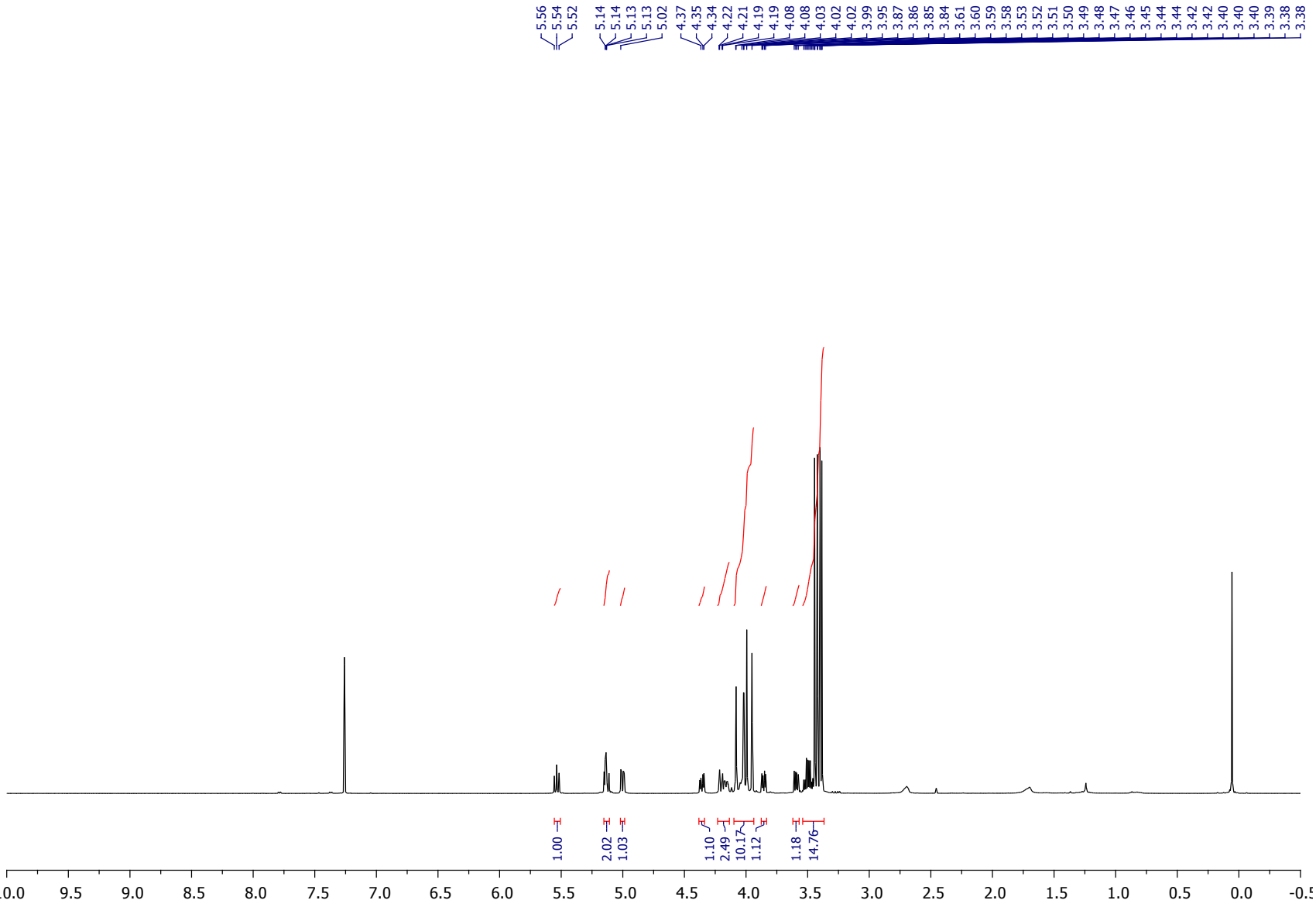


^{13}C NMR ($CDCl_3$, 100 MHz)

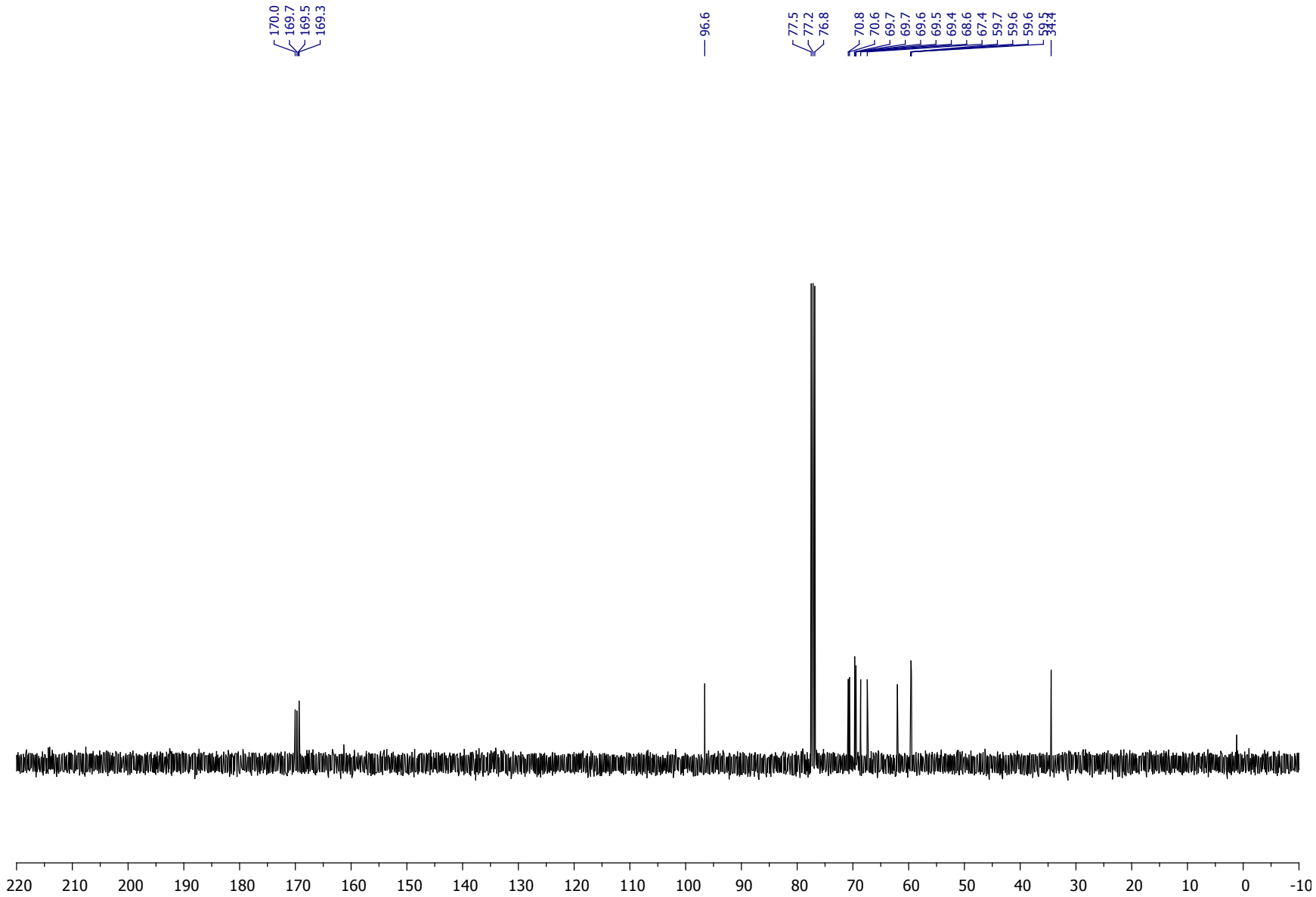


(2'R)-3'-Bromo-2'-hydroxypropyl 2,3,4,6-tetra-O-methoxyacetyl-α-D-glucopyranoside (6)

^{1}H NMR ($CDCl_3$, 400 MHz)

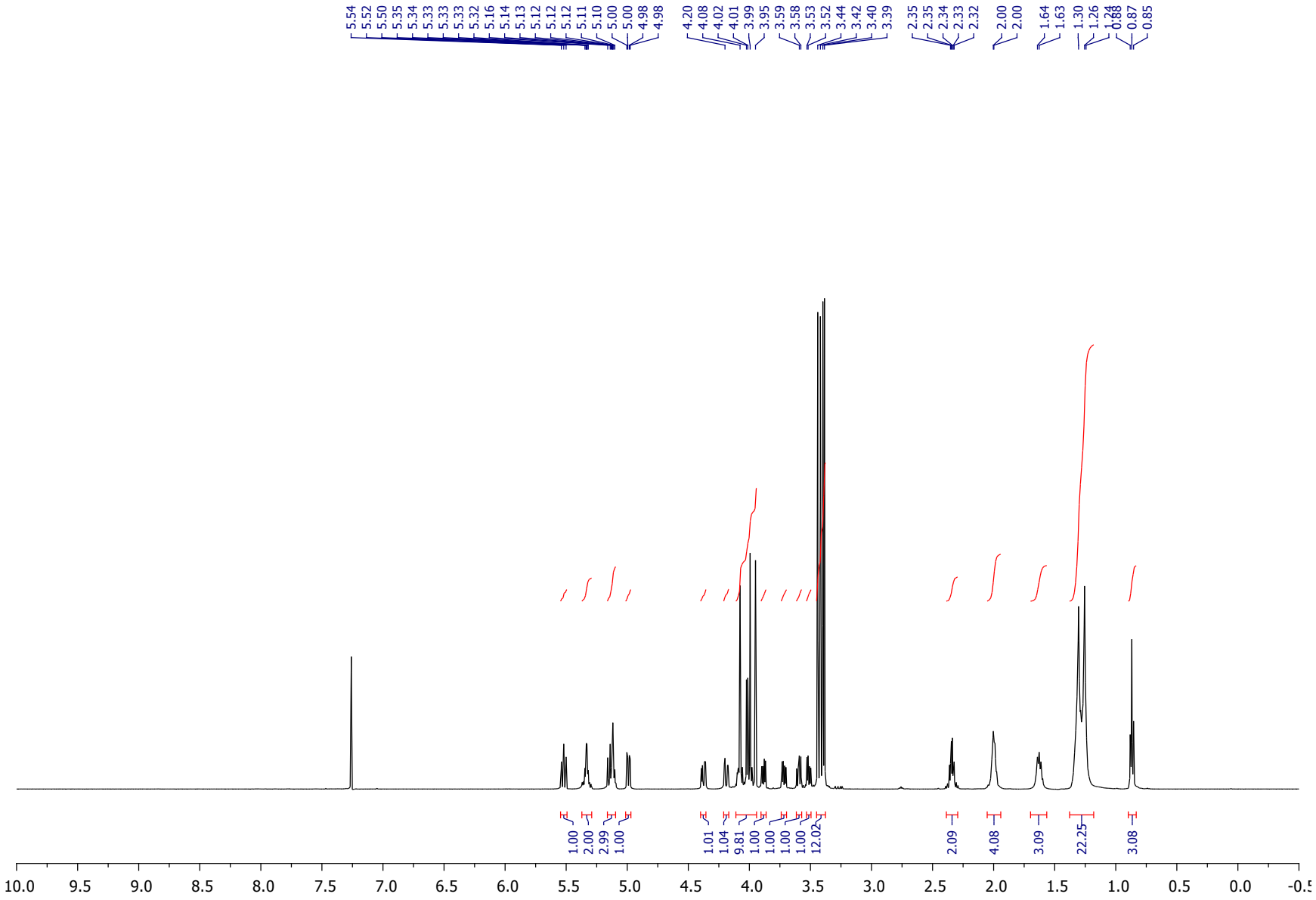


^{13}C NMR ($CDCl_3$, 100 MHz)

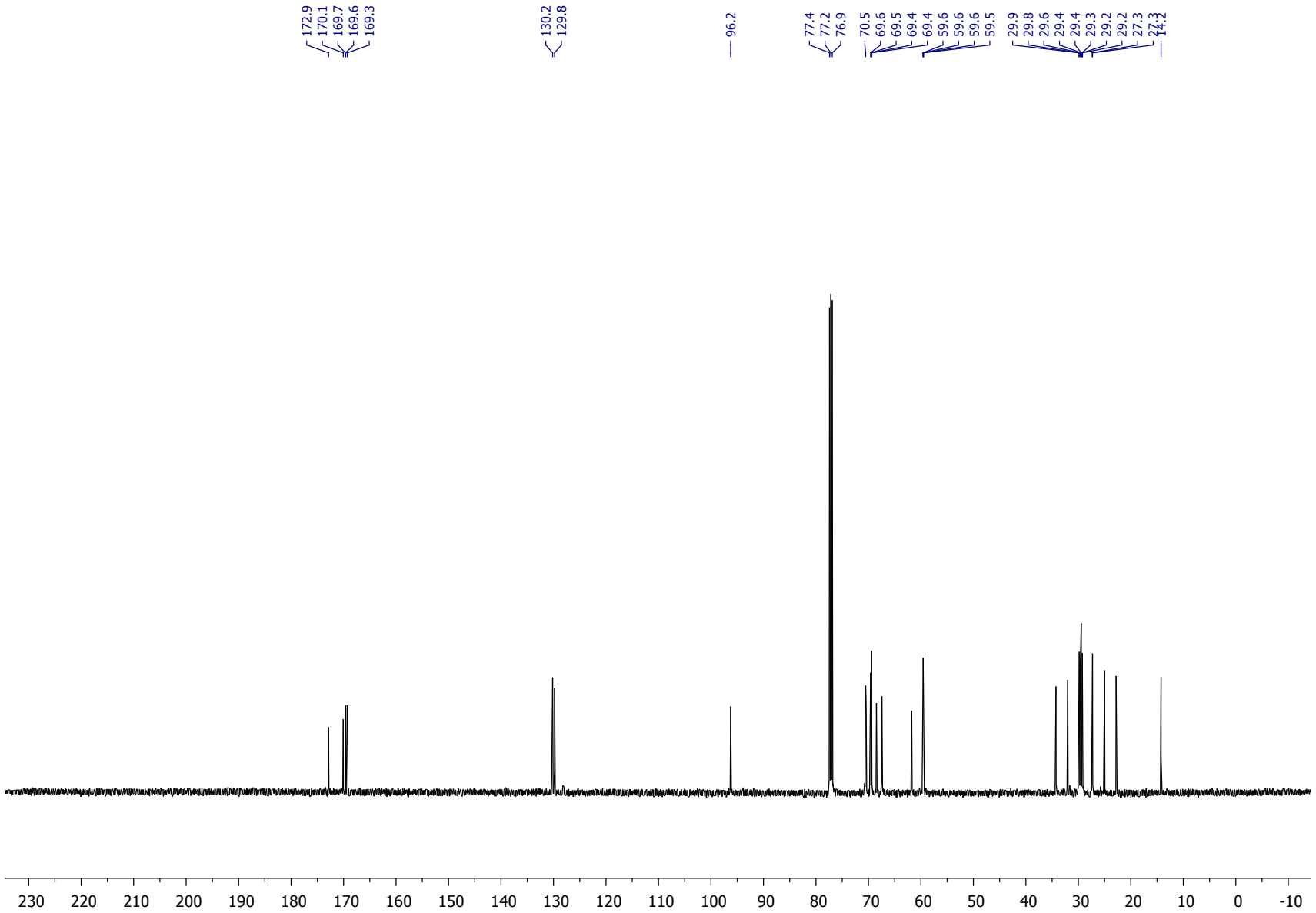


(2'R)-3'-Bromo-2'-oleoyloxypropyl 2,3,4,6-tetra-O-methoxyacetyl-α-D-glucopyranoside (7)

^{1}H NMR ($CDCl_3$, 400 MHz)

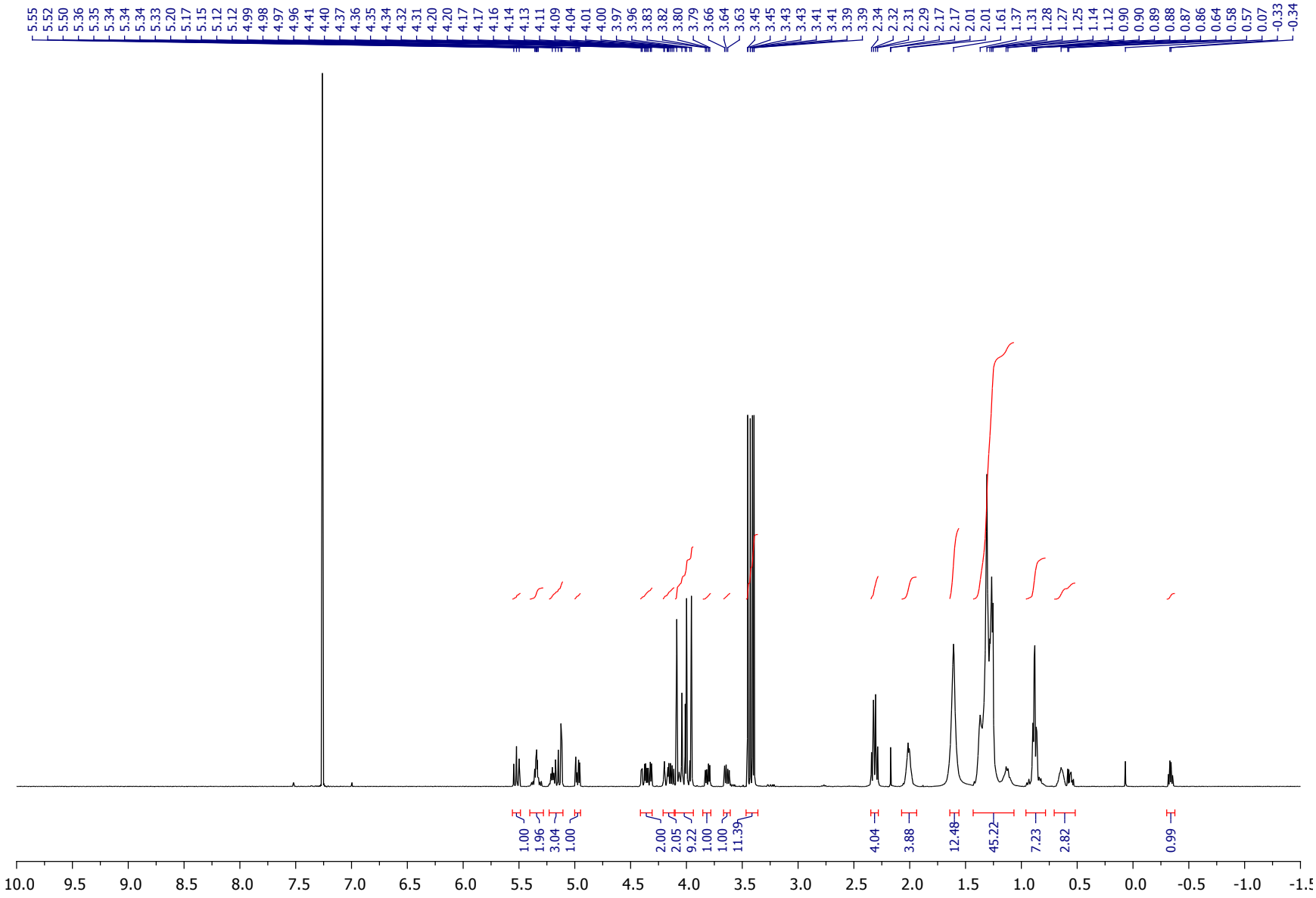


^{13}C NMR ($CDCl_3$, 100 MHz)

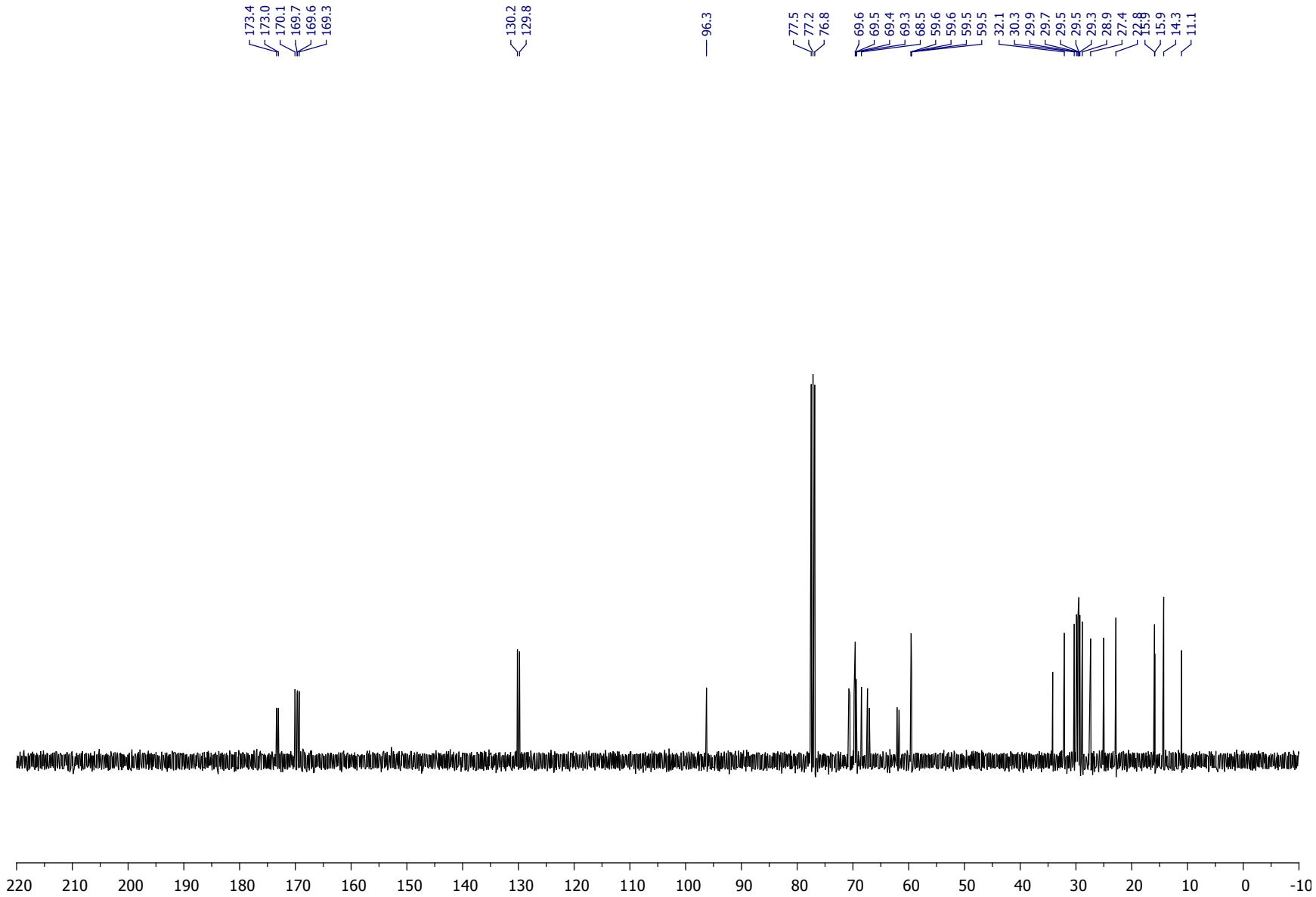


1-O-(9S,10R-Dihydrosterculyl)-2-O-oleoyl-sn-glyceryl 2,3,4,6-tetra-O-methoxyacetyl-α-D-glucopyranoside (8)

^{1}H NMR ($CDCl_3$, 400 MHz)

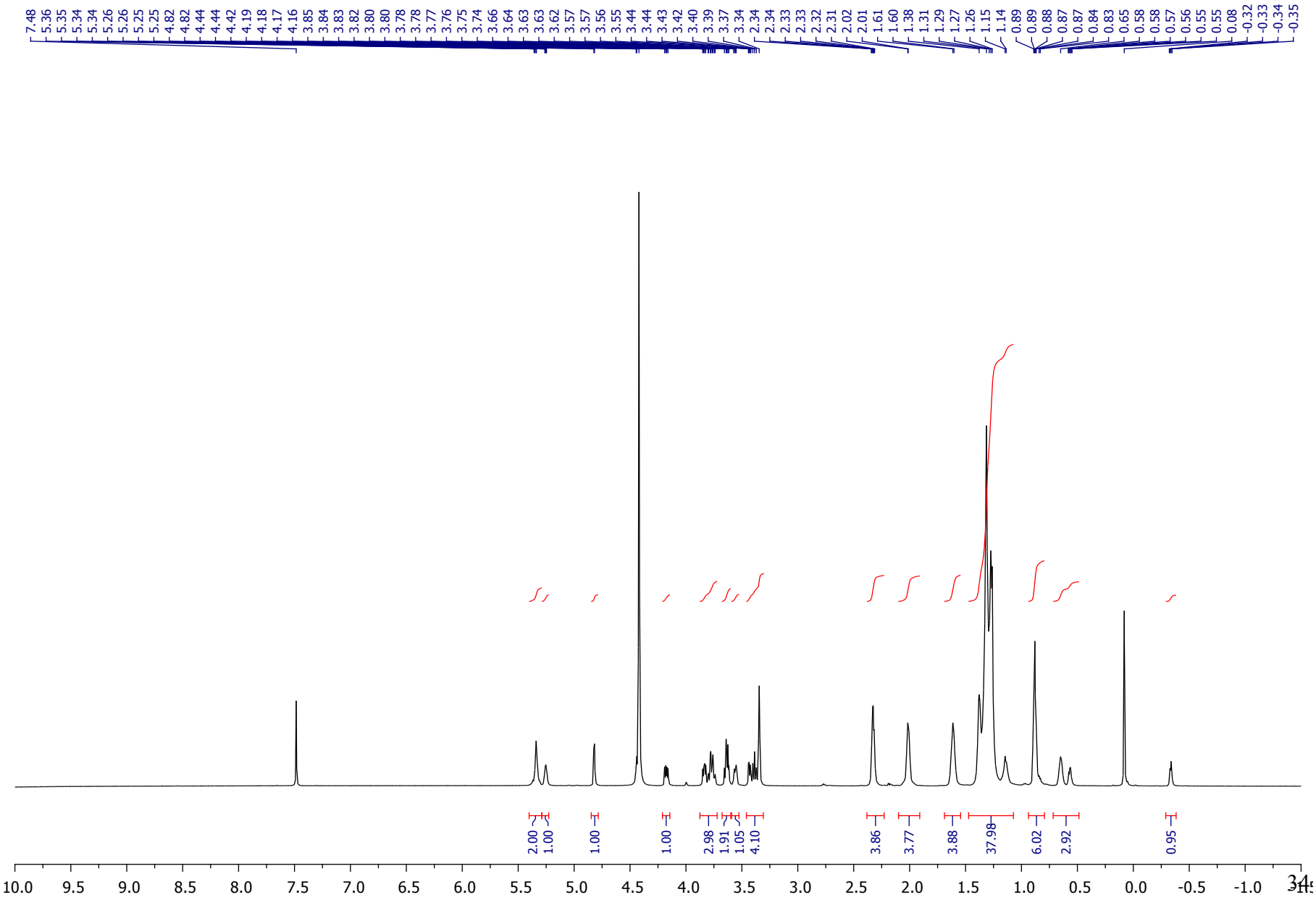


^{13}C NMR ($CDCl_3$, 100 MHz)

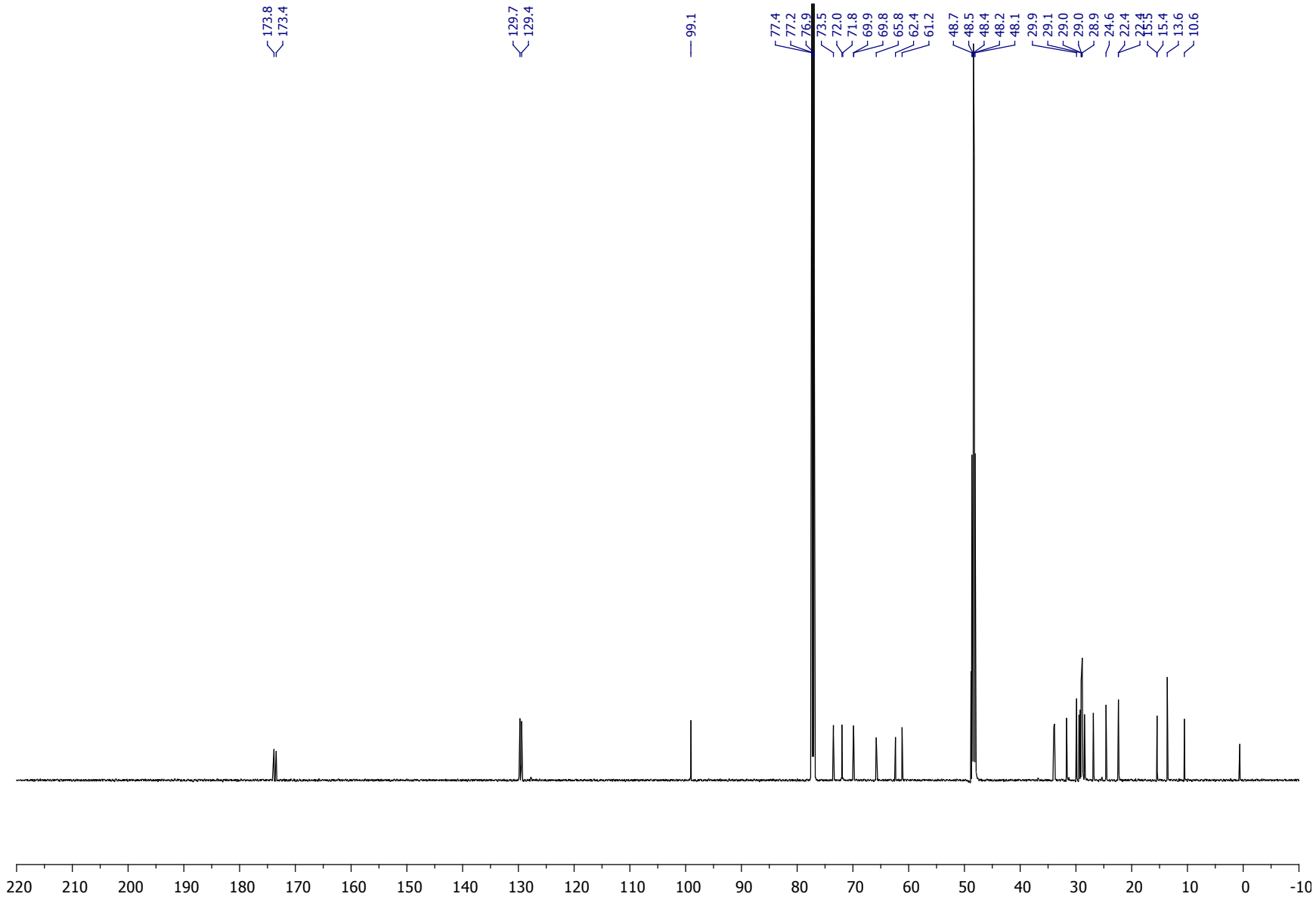


1-O-(9S,10R-Dihydrosterculyl)-2-O-oleoyl-sn-glyceryl α-D-glucopyranoside (1; GL1)

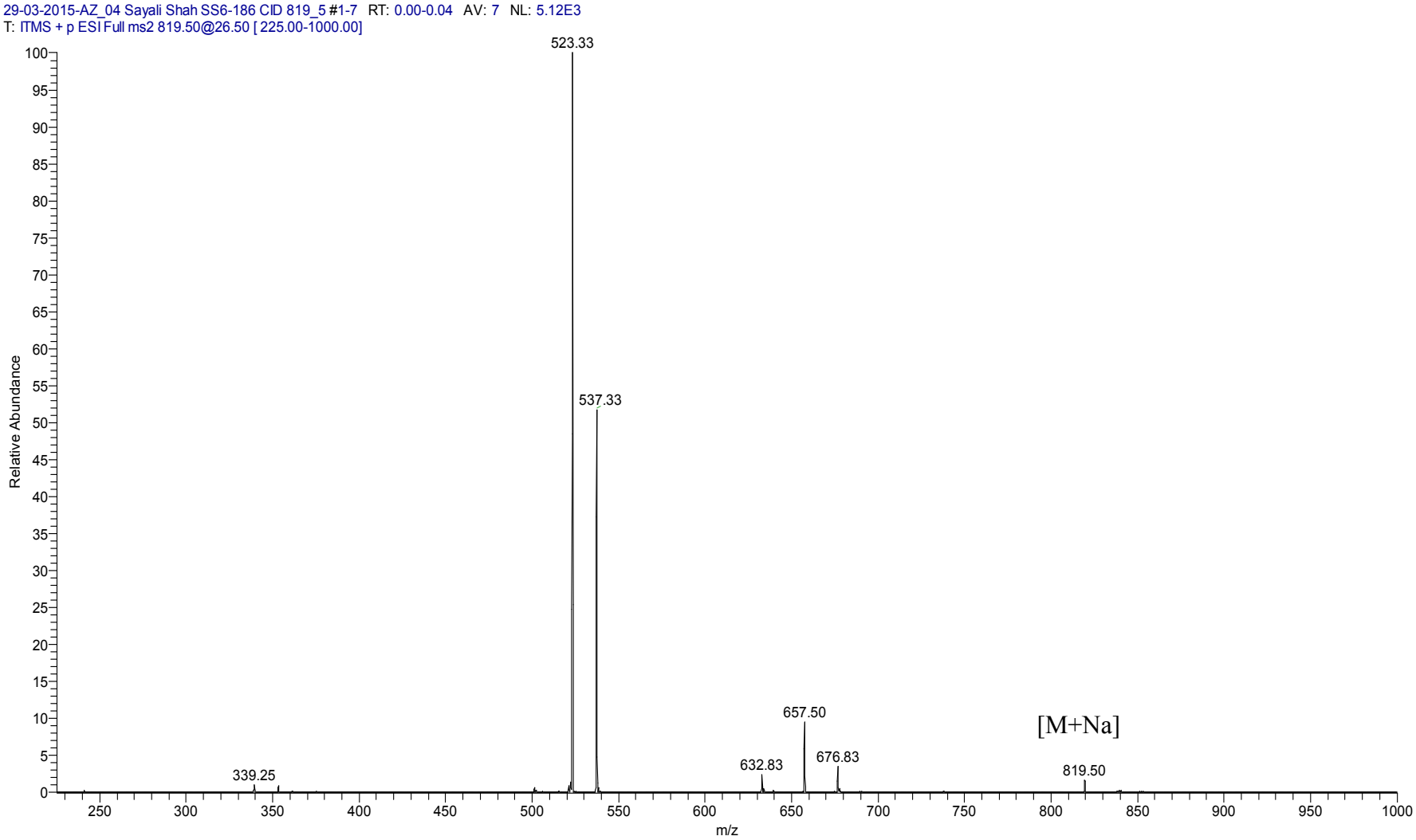
^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 100 MHz)

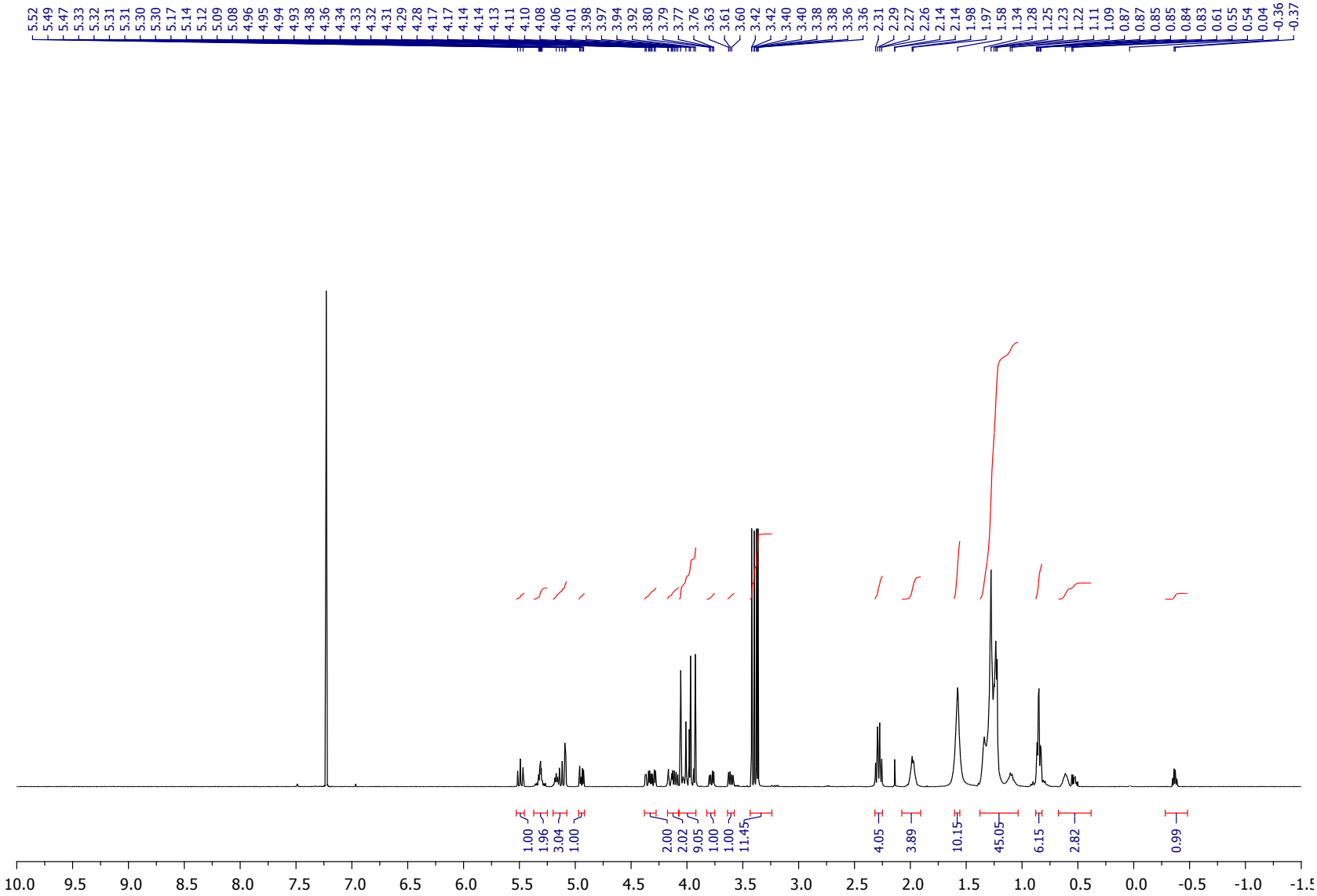


ESI MS^2 data (positive ion mode)

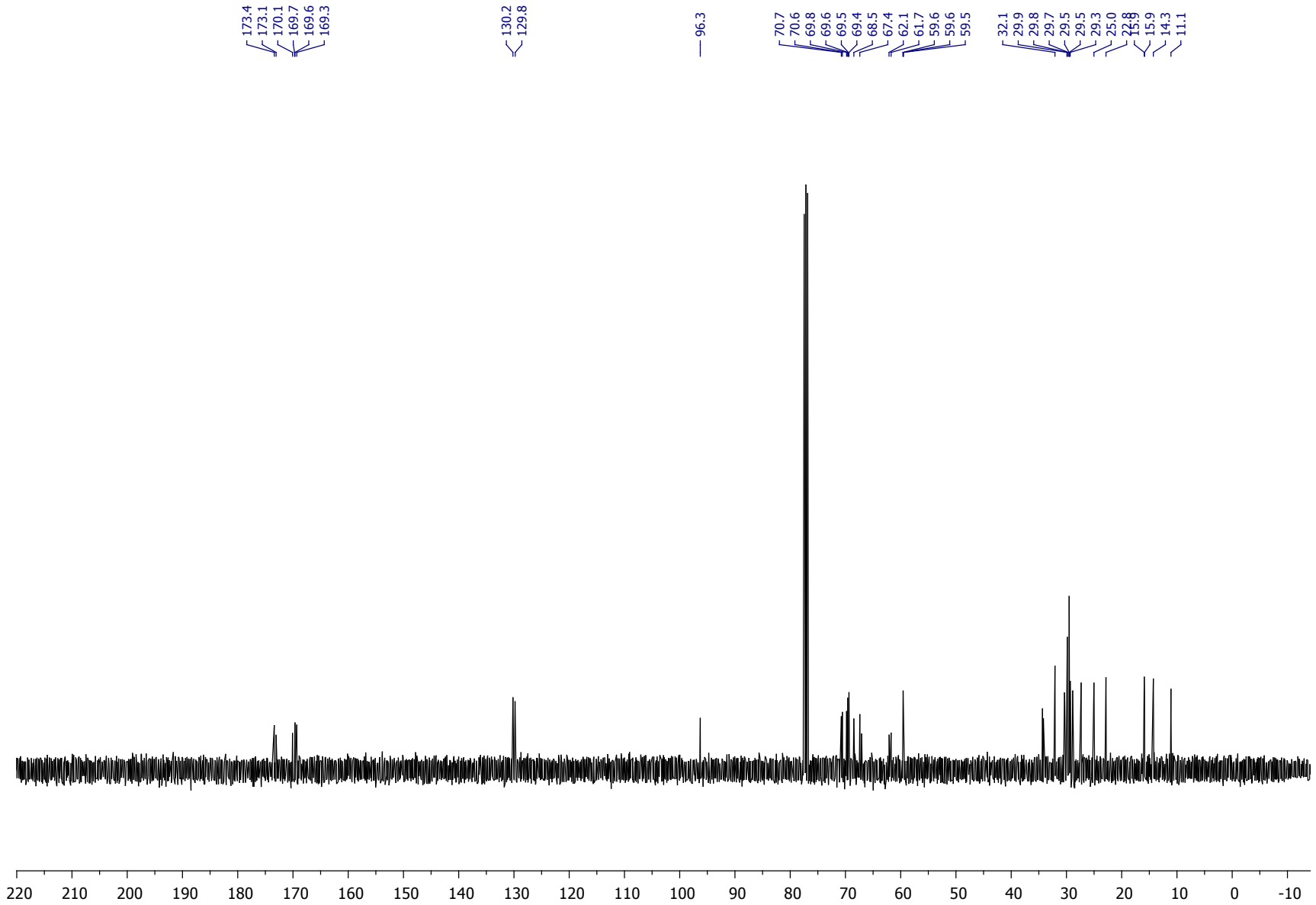


1-O-(9R,10S-Dihydrosterculyl)-2-O-oleoyl-sn-glyceryl 2,3,4,6-tetra-O-methoxyacetyl-α-D-glucopyranoside (9)

^{1}H NMR ($CDCl_3$, 400 MHz)

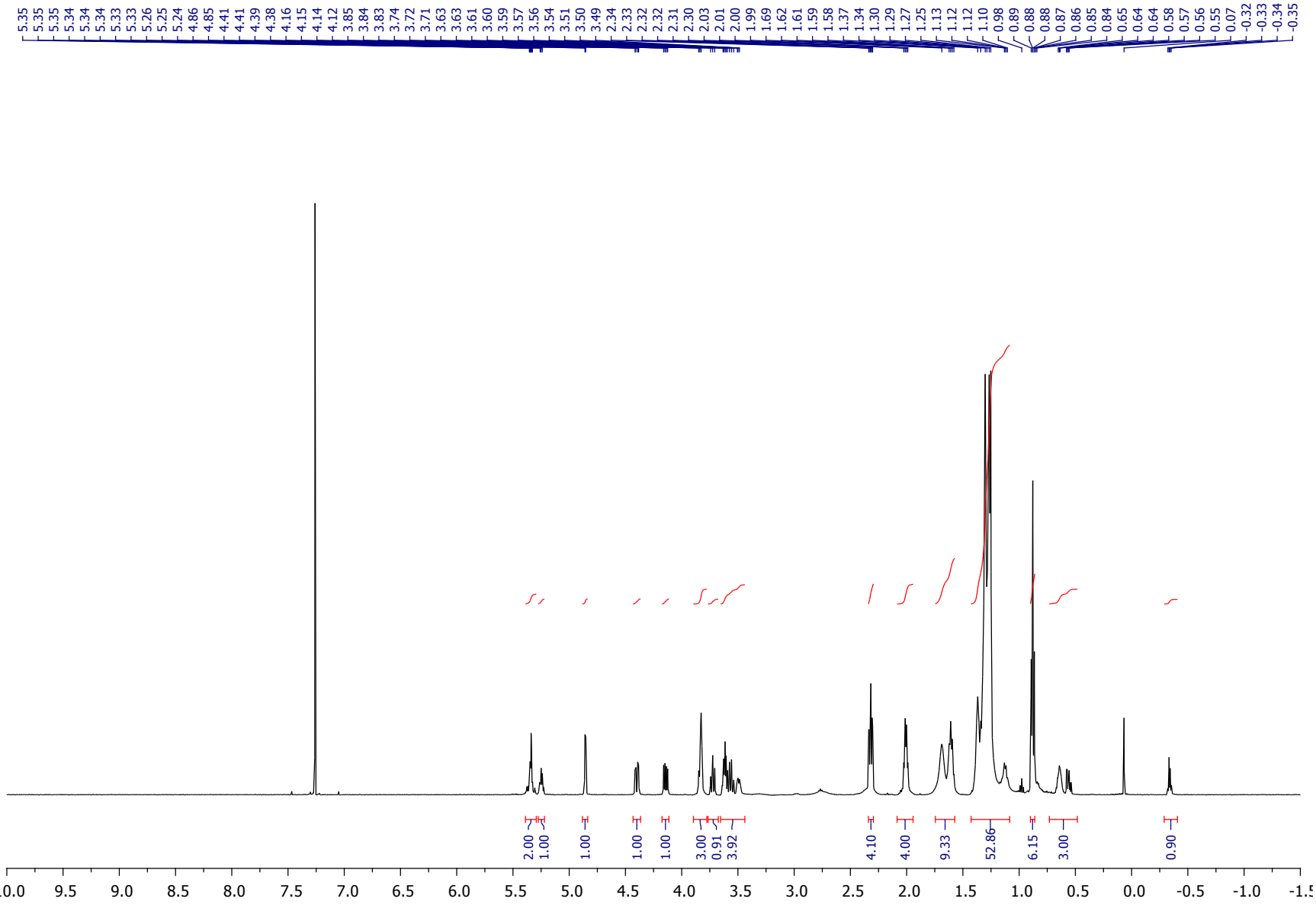


^{13}C NMR ($CDCl_3$, 100 MHz)

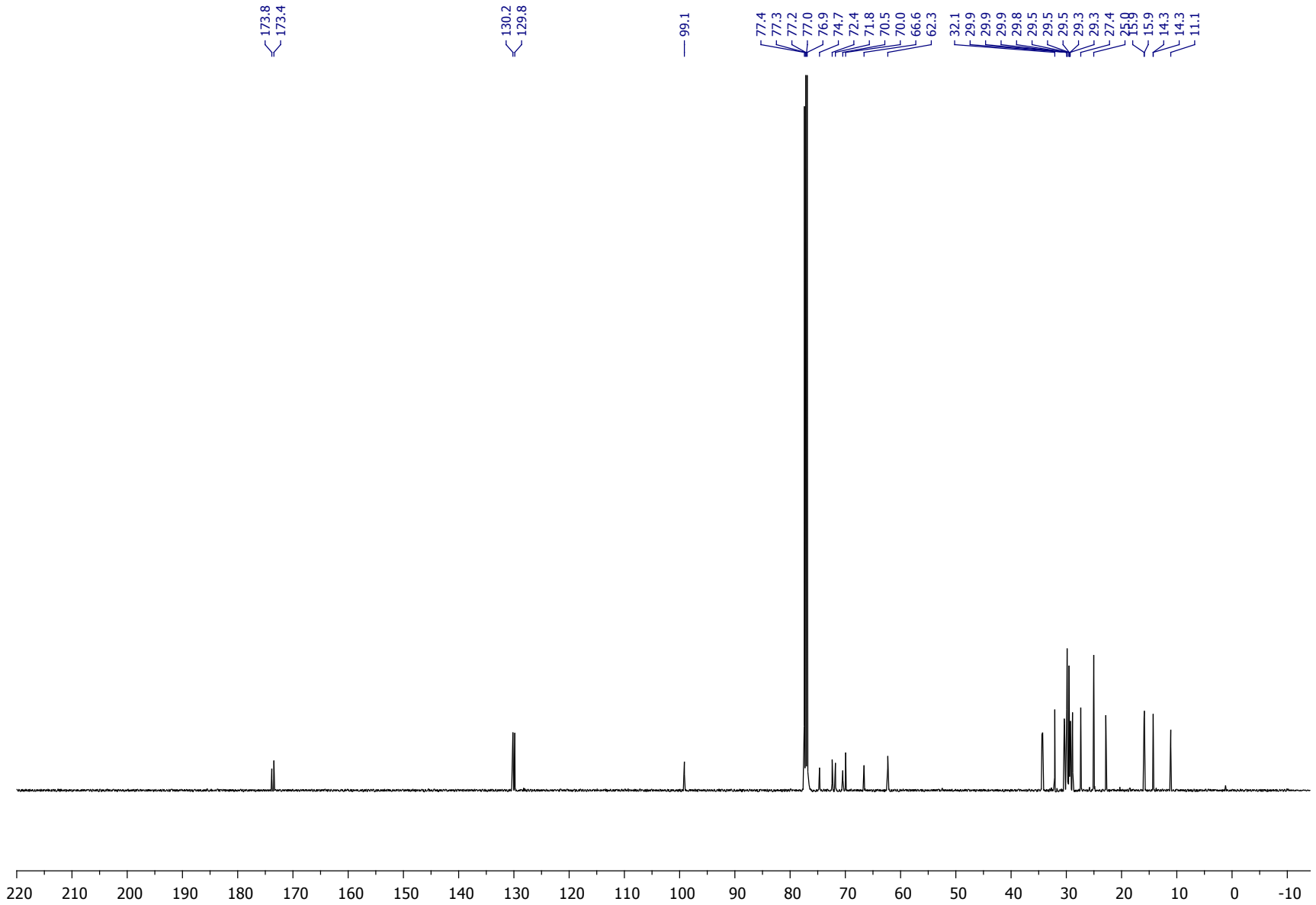


1-O-(9R,10S-Dihydrosterculyl)-2-O-oleoyl-sn-glyceryl α-D-glucopyranoside (15)

^{1}H NMR ($CDCl_3$, 400 MHz)

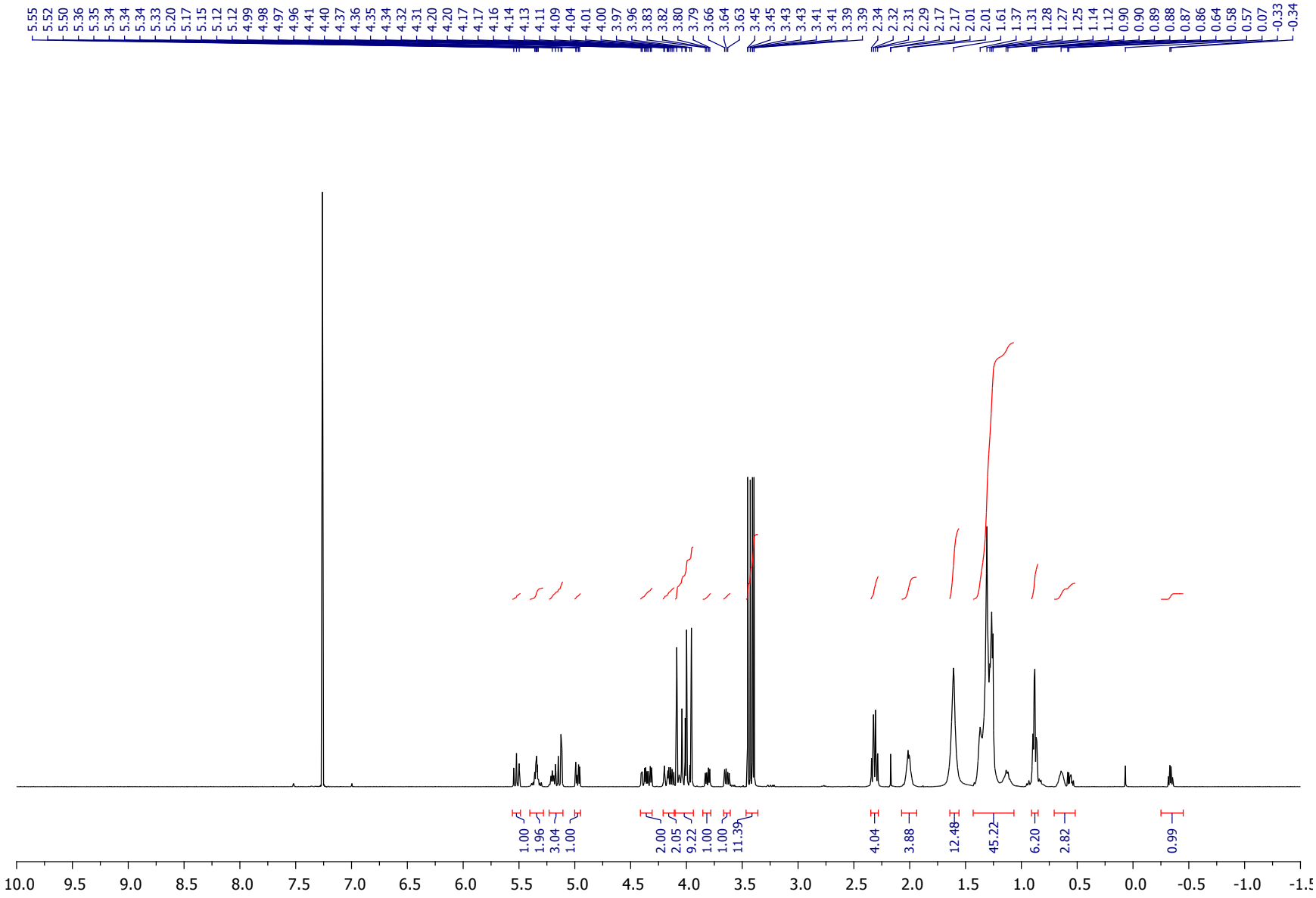


^{13}C NMR ($CDCl_3$, 100 MHz)

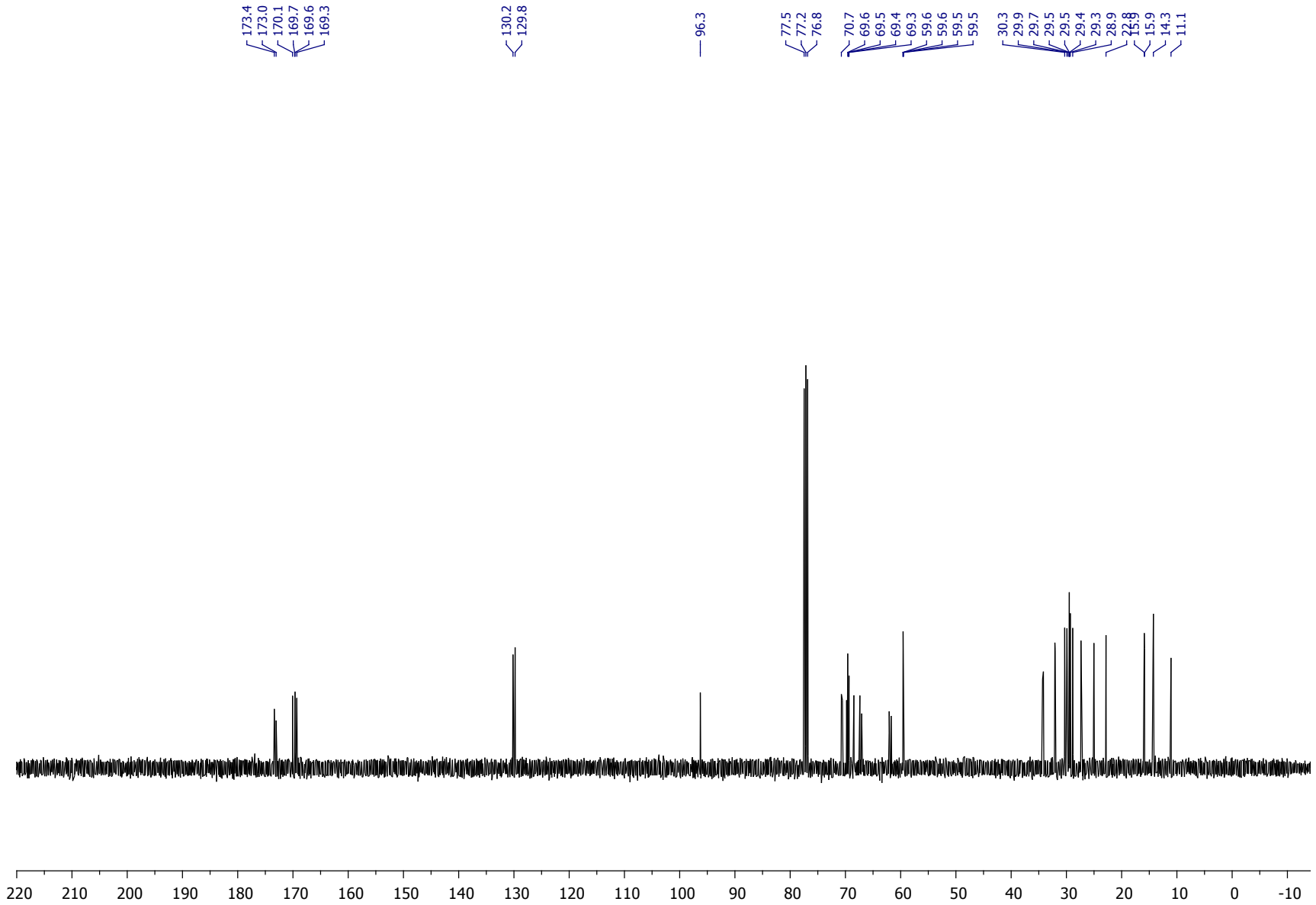


1-O-(9R,10S-Methylenehexadecanoyl)-2-O-oleoyl-sn-glyceryl 2,3,4,6-tetra-O-methoxyacetyl-α-D-glucopyranoside (10)

^{1}H NMR ($CDCl_3$, 400 MHz)

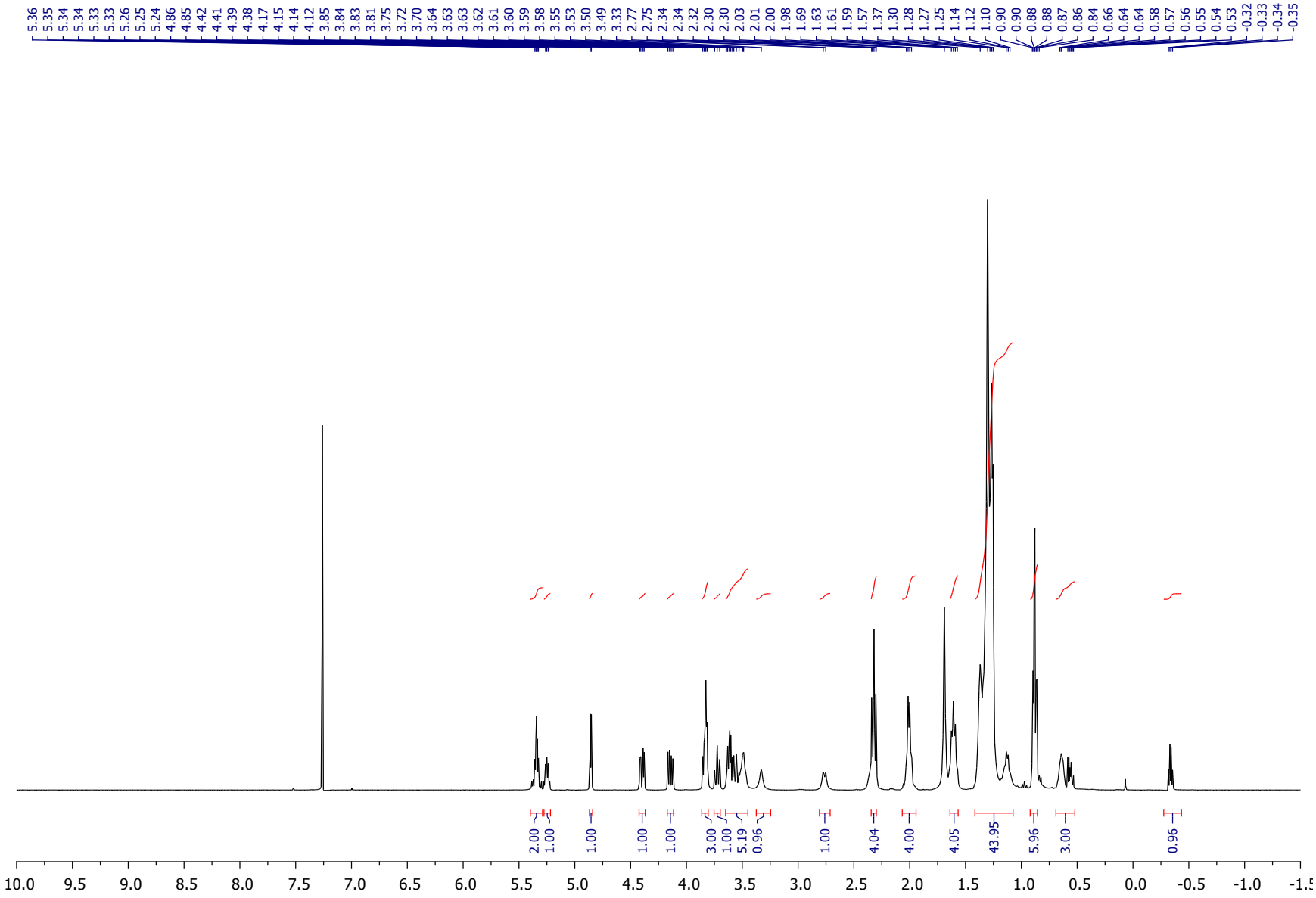


^{13}C NMR ($CDCl_3$, 100 MHz)

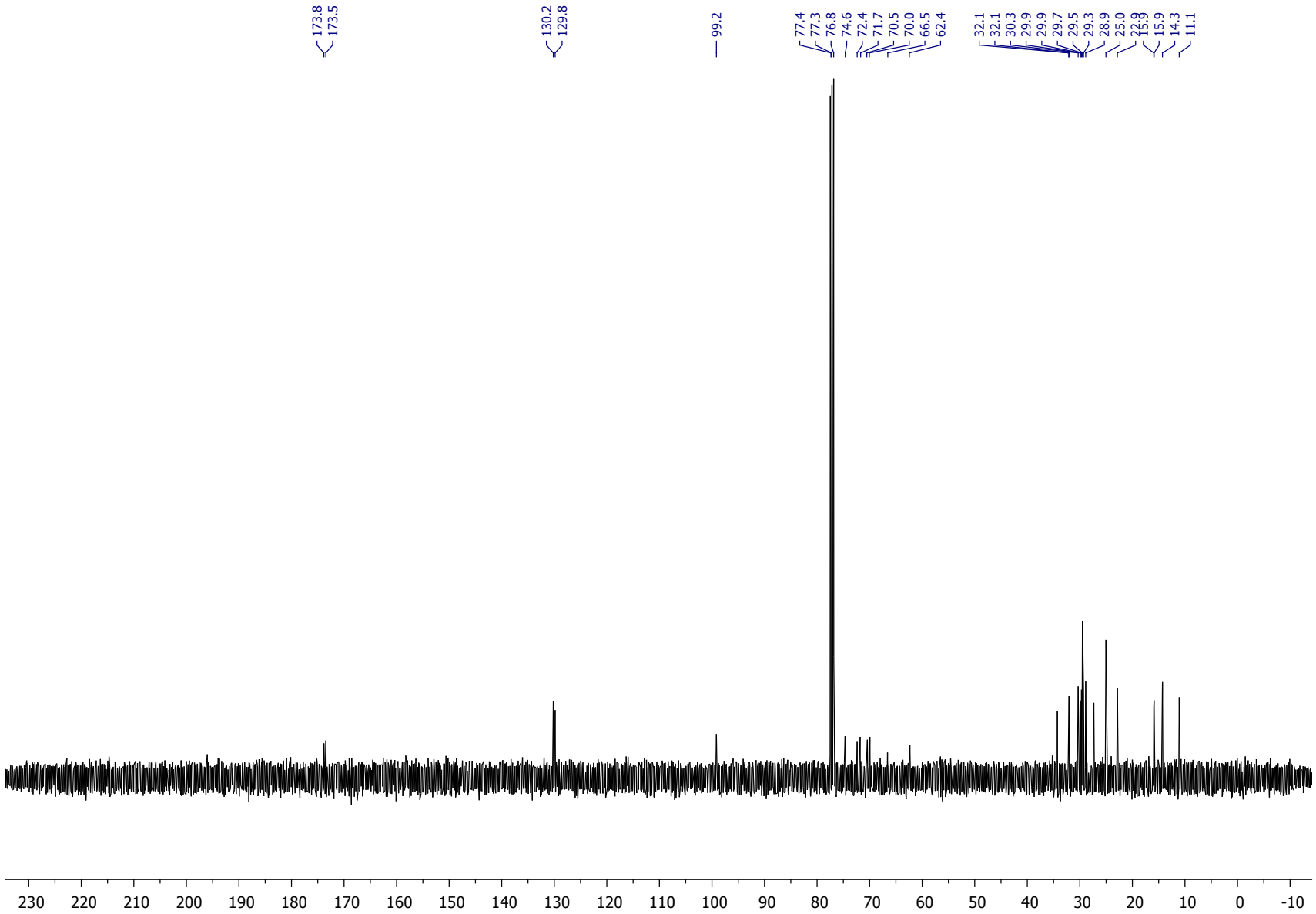


1-O-(9R,10S-Methylenehexadecanoyl)-2-O-oleoyl-sn-glyceryl α-D-glucopyranoside (16)

^{1}H NMR ($CDCl_3$, 400 MHz)

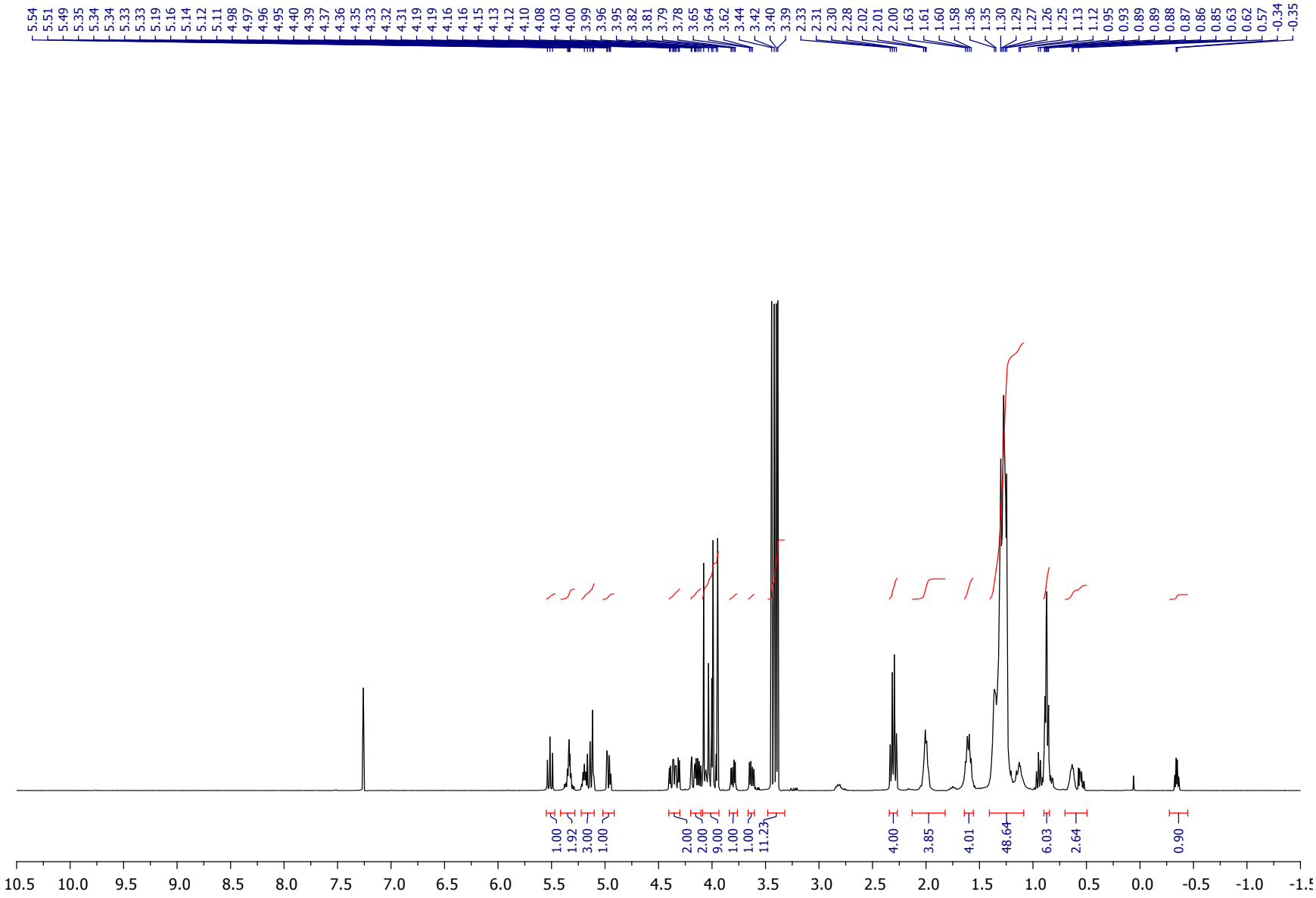


^{13}C NMR ($CDCl_3$, 100 MHz)

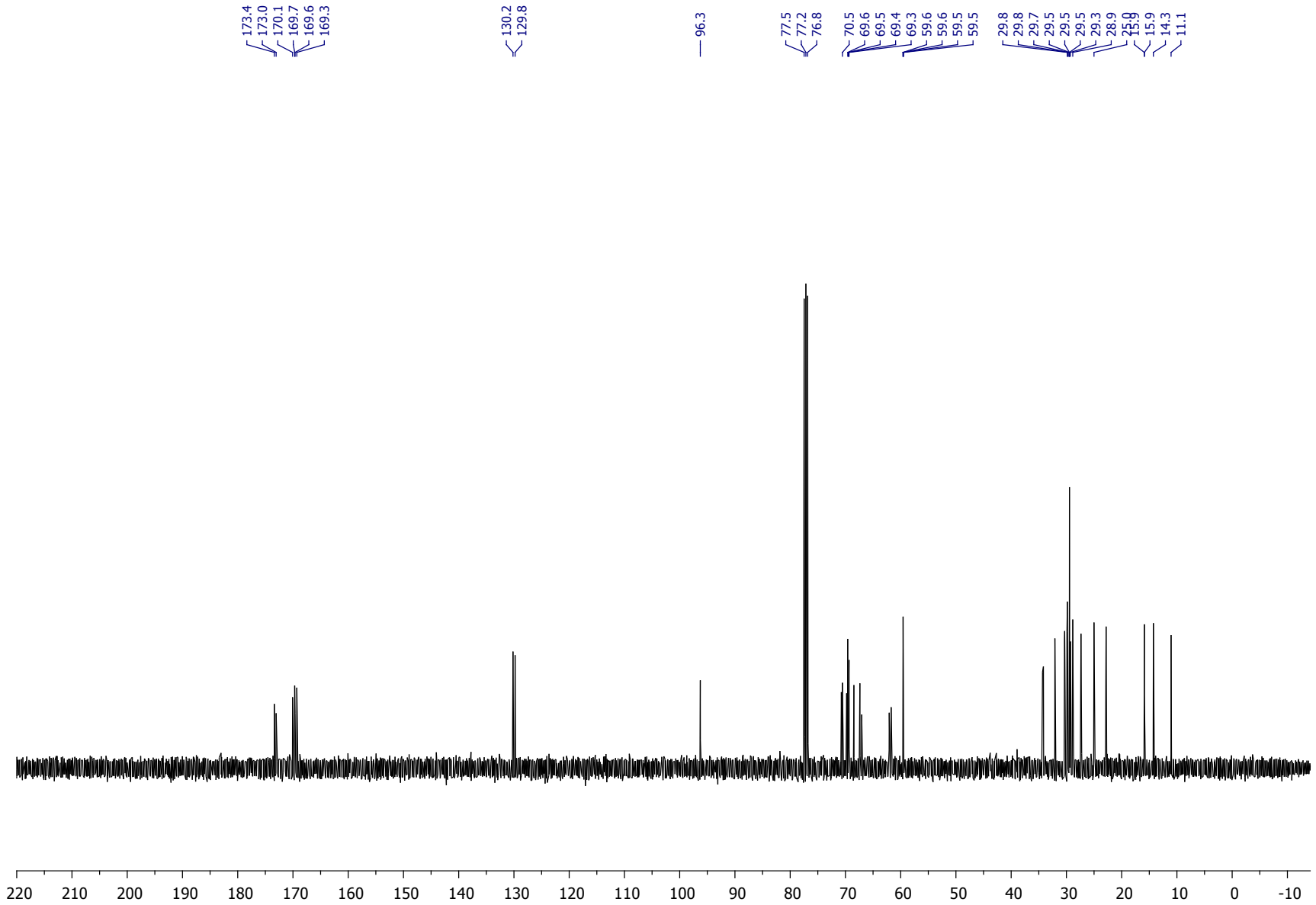


1-O-(11R,12S-Lactobacillyl)-2-O-oleoyl-sn-glyceryl 2,3,4,6-tetra-O-methoxyacetyl-α-D-glucopyranoside (11)

^{1}H NMR ($CDCl_3$, 400 MHz)

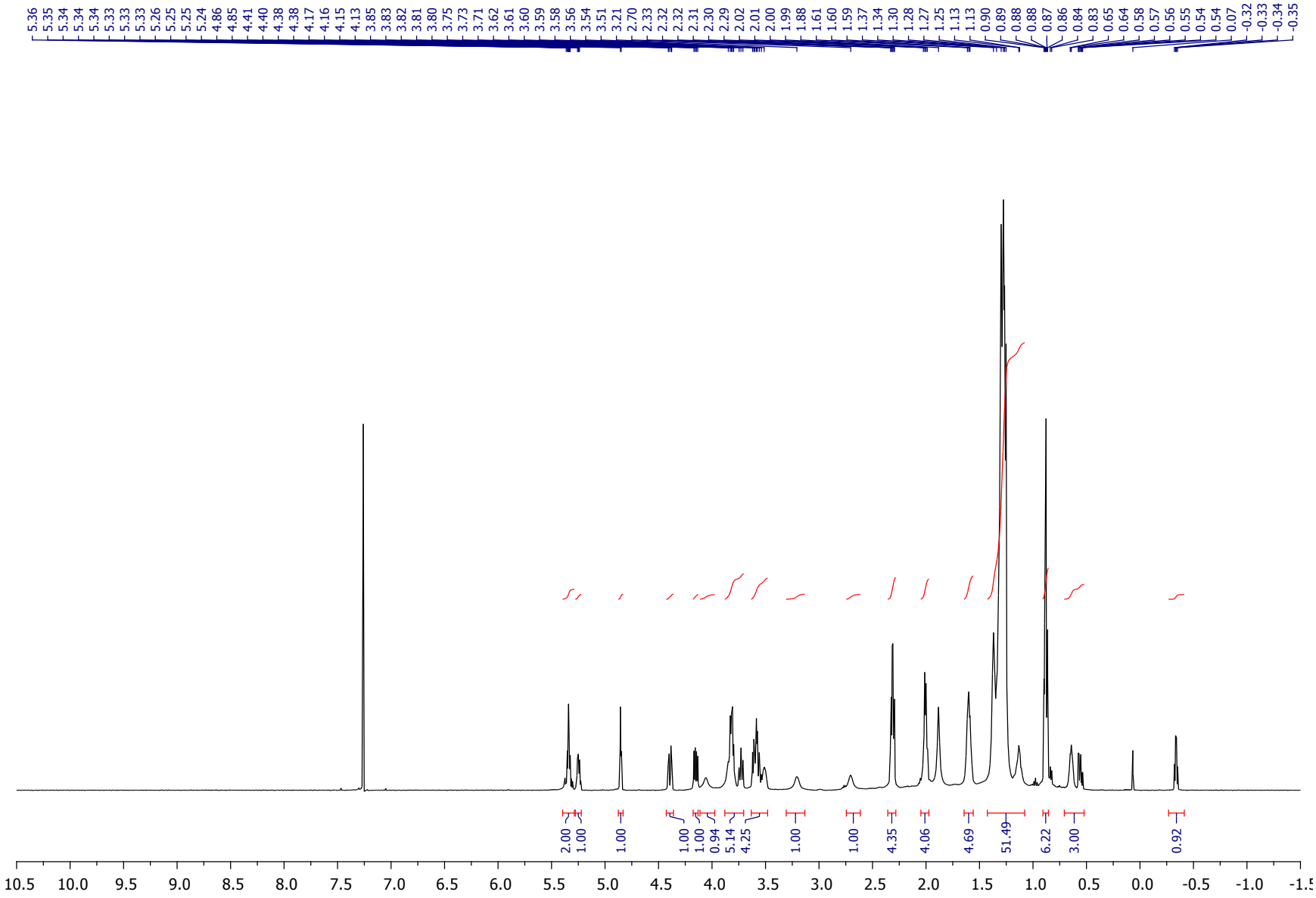


^{13}C NMR ($CDCl_3$, 100 MHz)

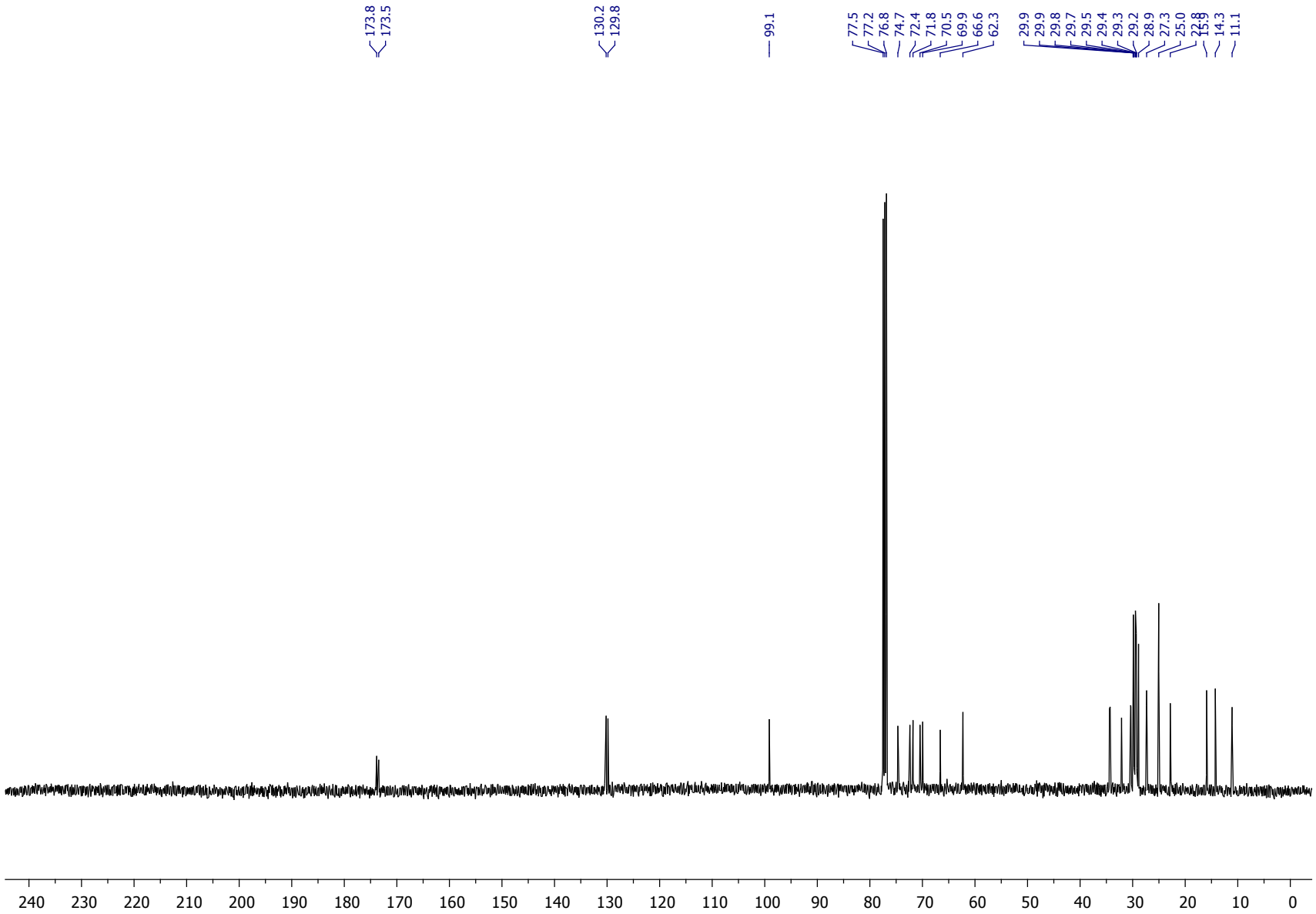


1-O-(11R,12S-Lactobacillyl)-2-O-oleoyl-sn-glyceryl α-D-glucopyranoside (17)

^{1}H NMR ($CDCl_3$, 400 MHz)

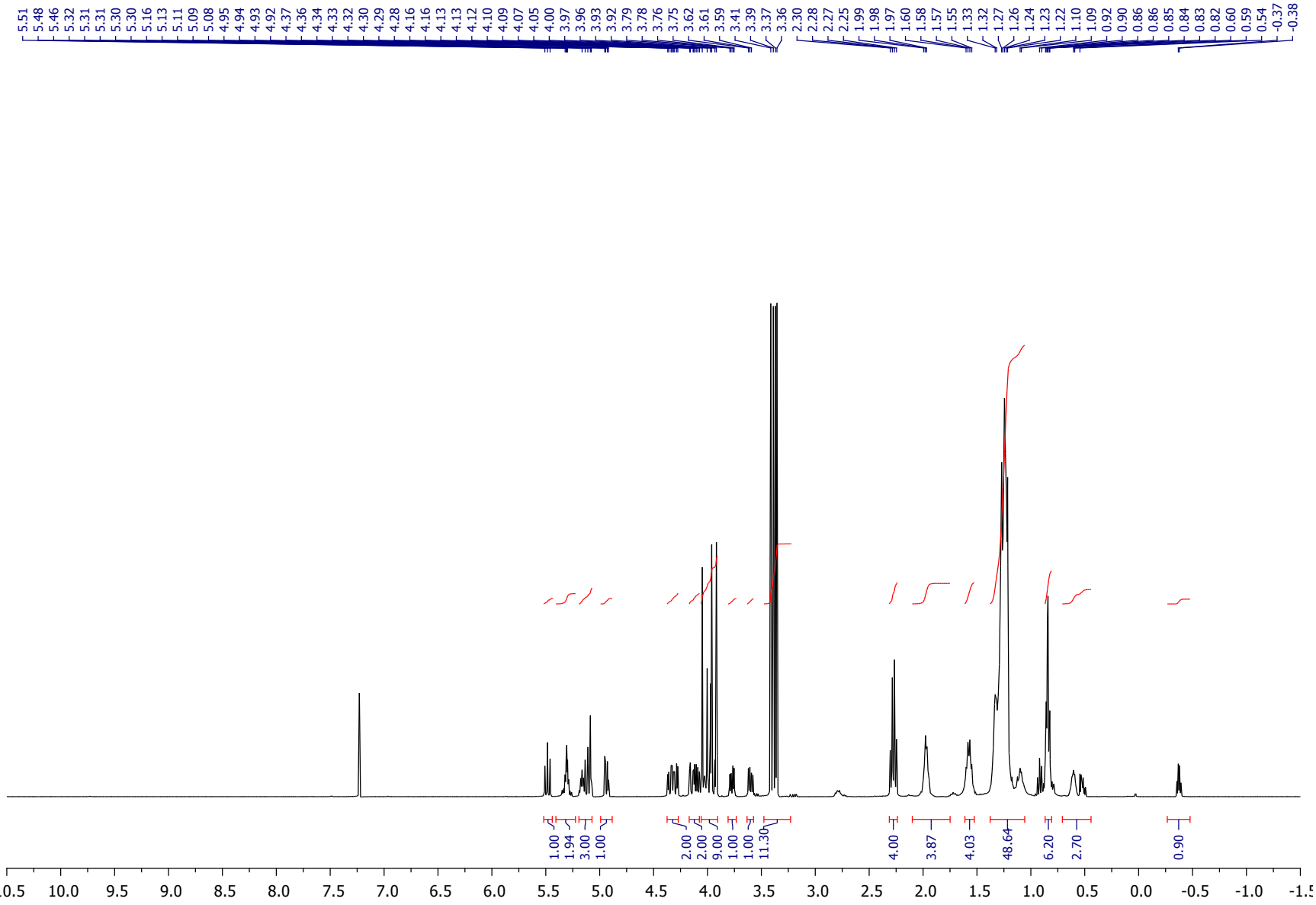


^{13}C NMR ($CDCl_3$, 100 MHz)

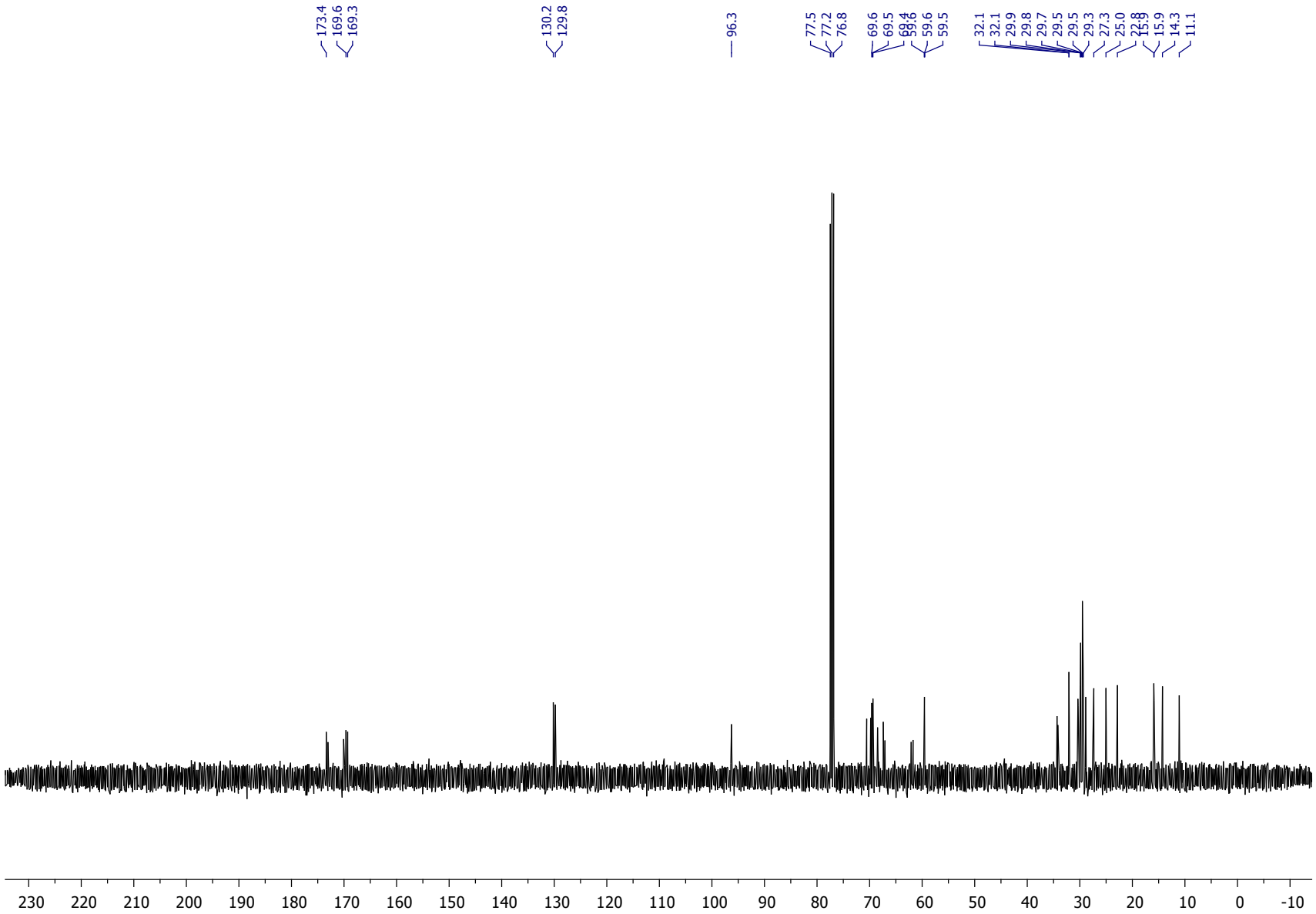


1-O-(11S,12R-Lactobacillyl)-2-O-oleoyl-sn-glyceryl 2,3,4,6-tetra-O-methoxyacetyl-α-D-glucopyranoside (12)

^{1}H NMR ($CDCl_3$, 400 MHz)

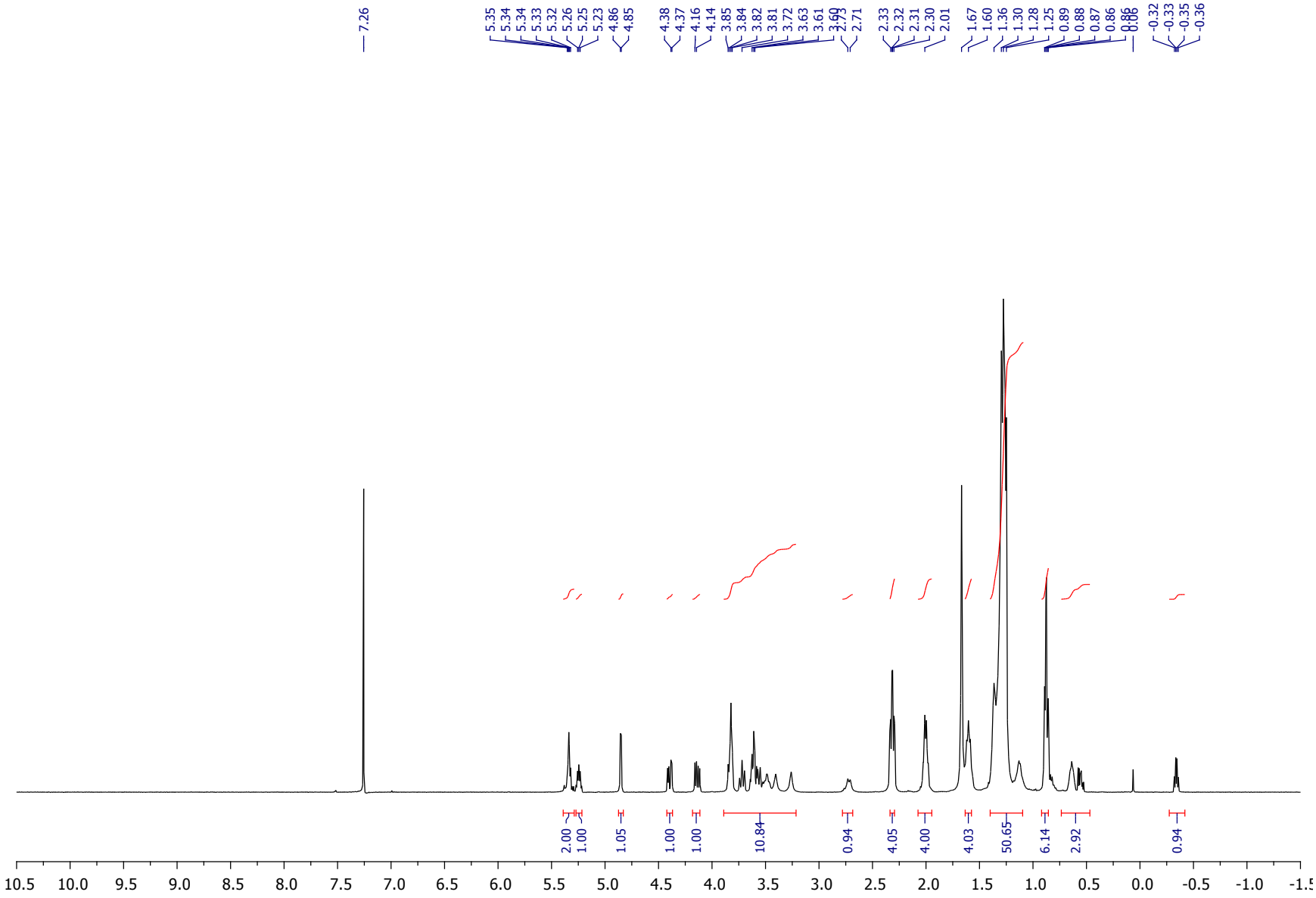


^{13}C NMR ($CDCl_3$, 100 MHz)

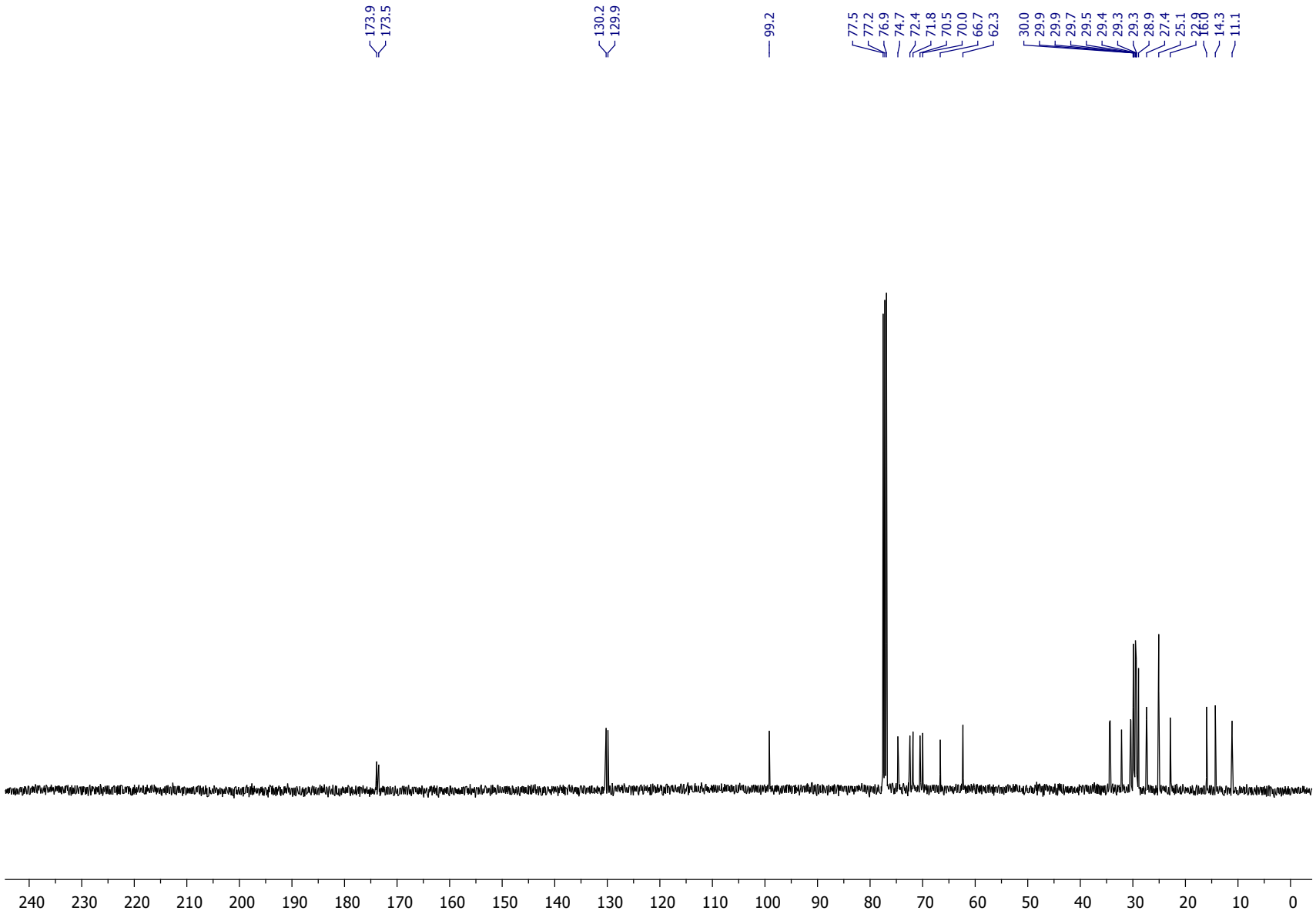


1-O-(11S,12R-Lactobacillyl)-2-O-oleoyl-sn-glyceryl α-D-glucopyranoside (18)

^{1}H NMR ($CDCl_3$, 400 MHz)

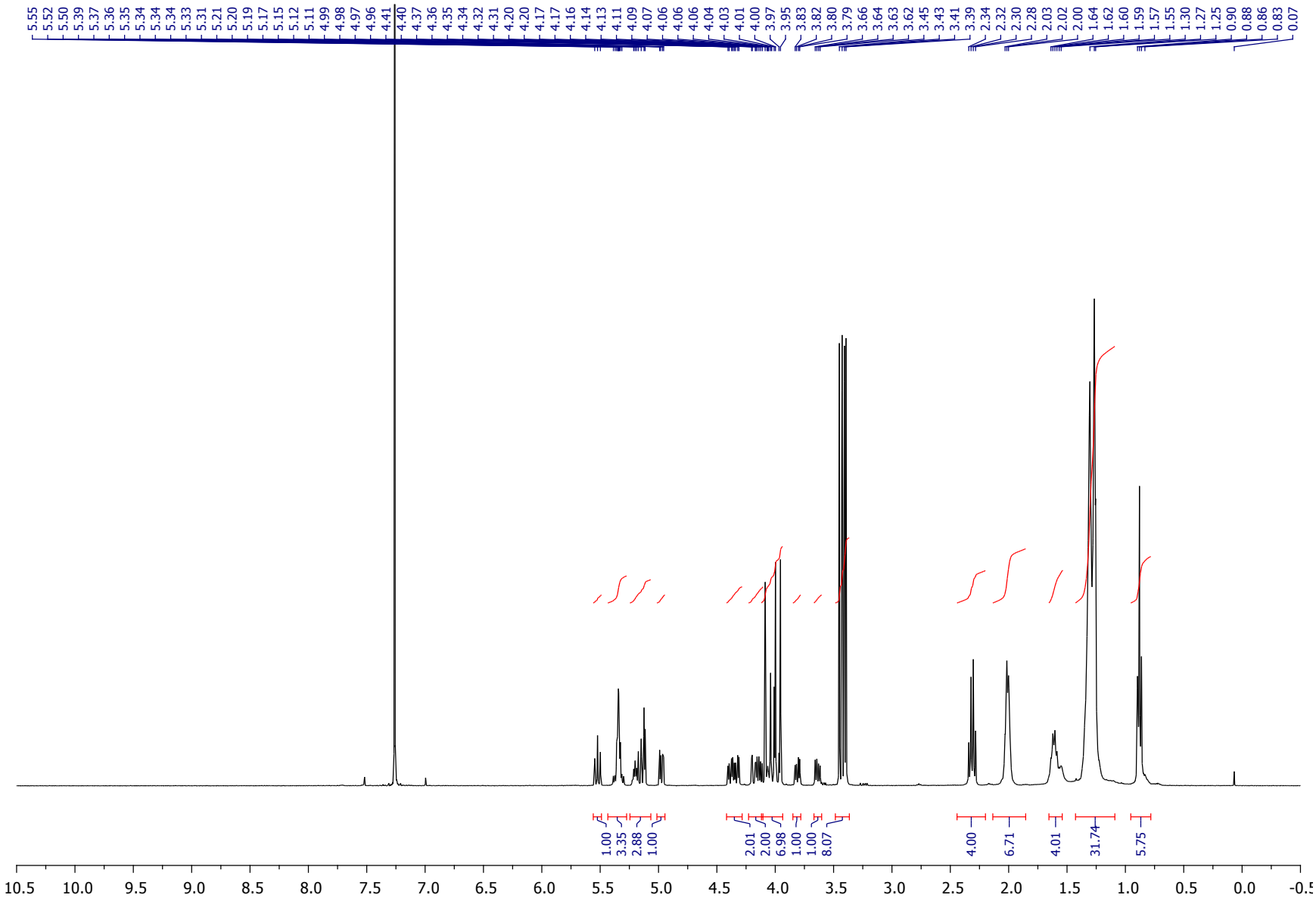


^{13}C NMR ($CDCl_3$, 100 MHz)

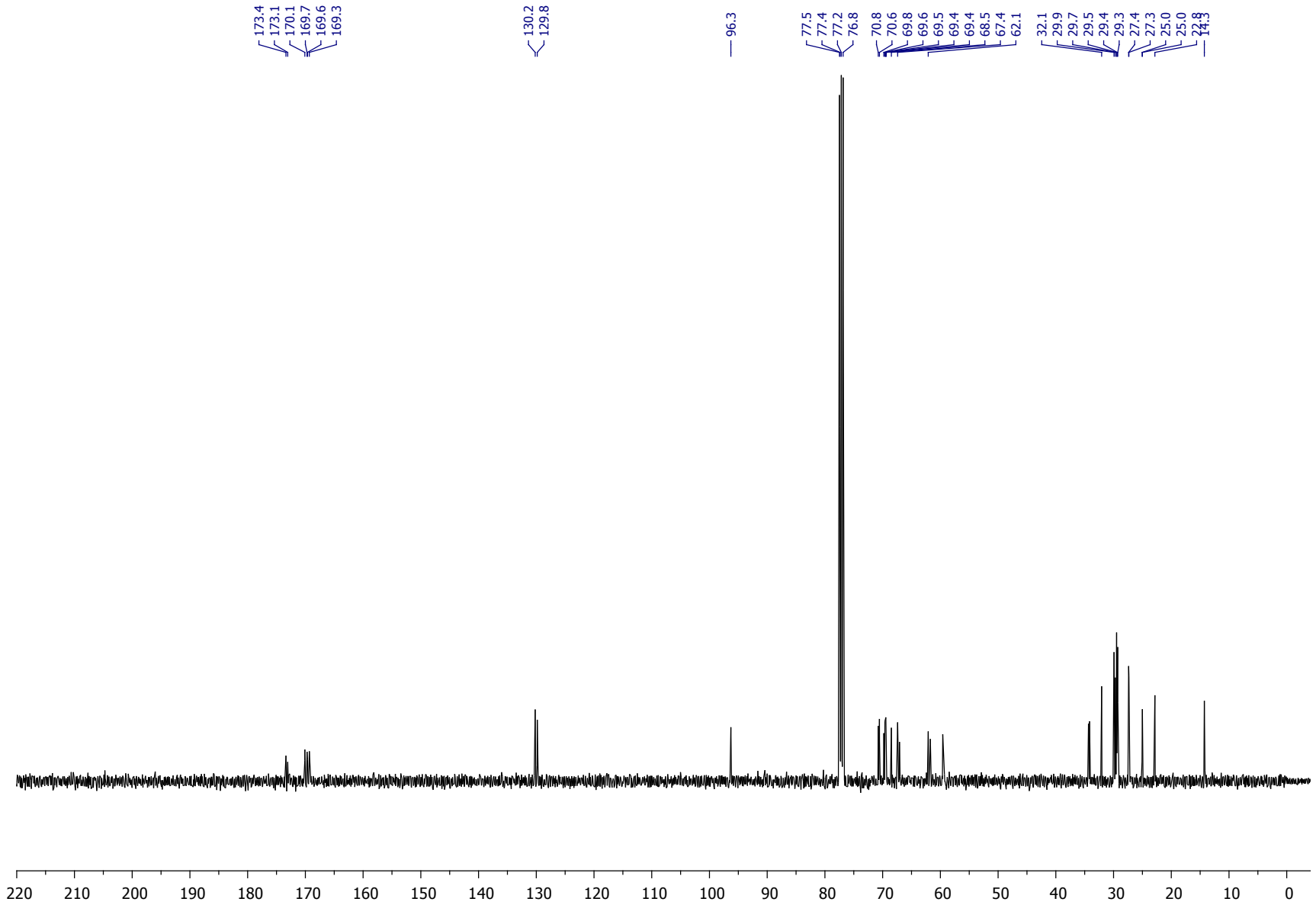


1,2-Di-O-oleoyl-sn-glyceryl 2,3,4,6-tetra-O-methoxyacetyl-α-D-glucopyranoside (13)

^{1}H NMR ($CDCl_3$, 400 MHz)

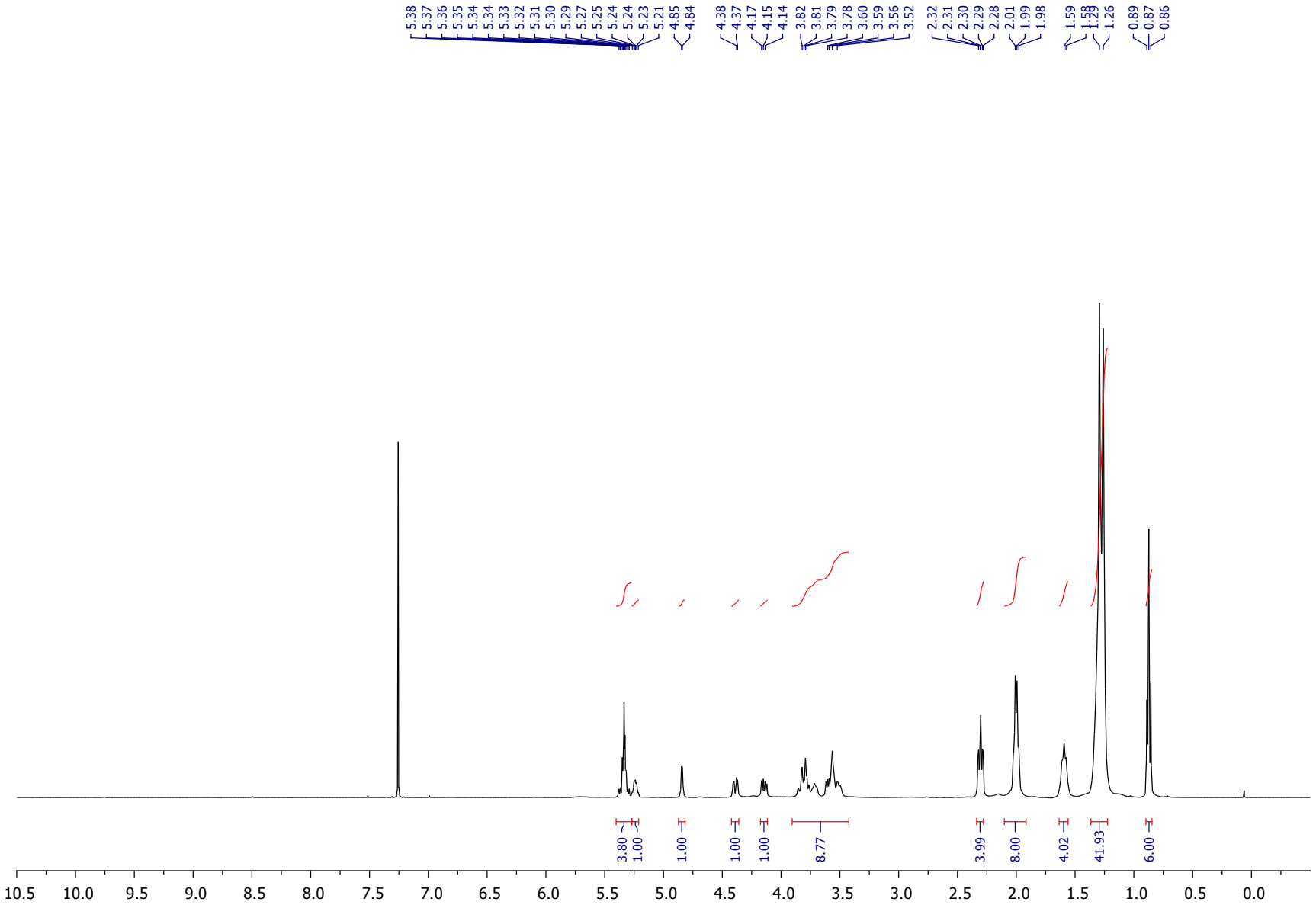


^{13}C NMR ($CDCl_3$, 100 MHz)

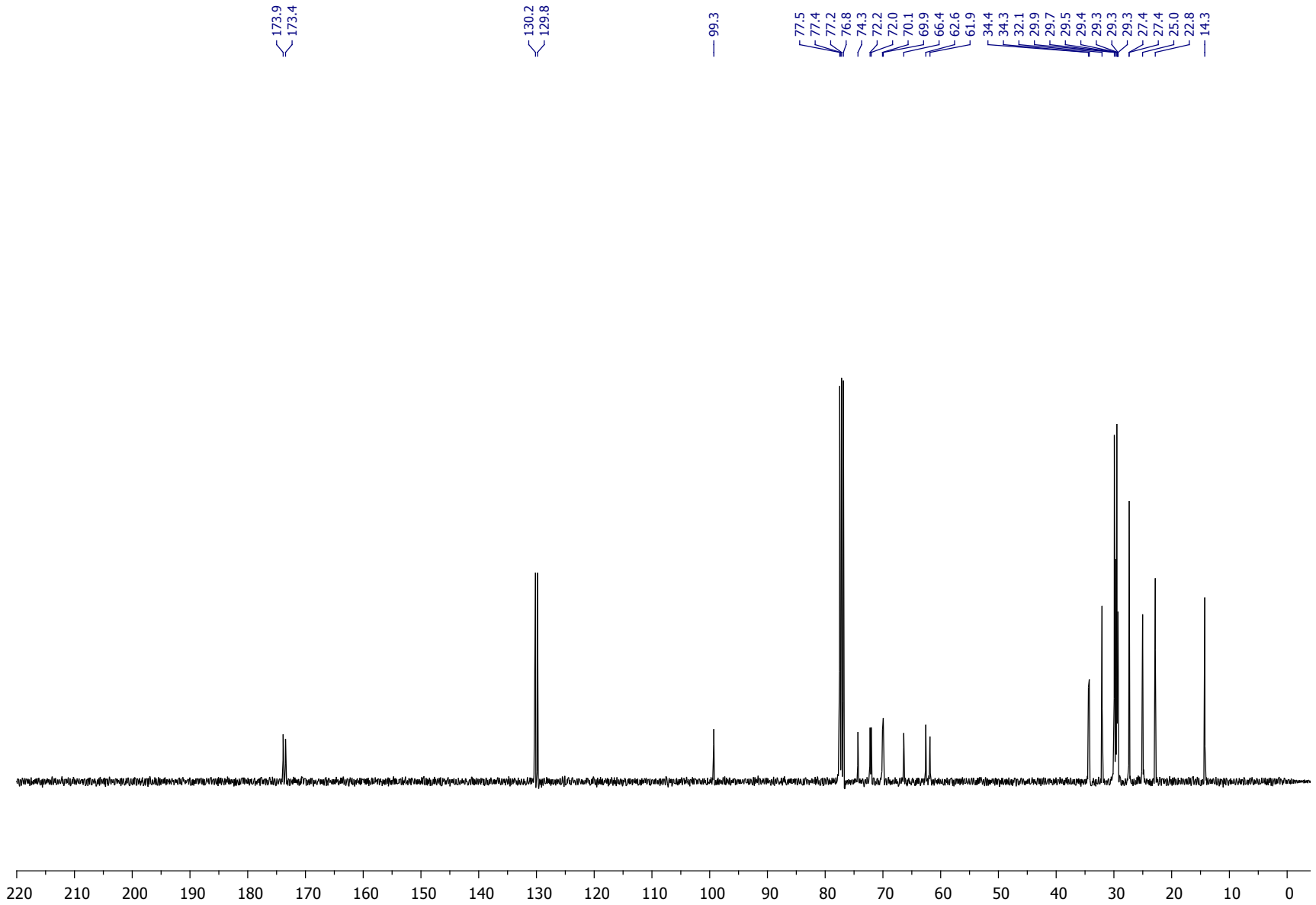


1,2-Di-O-oleoyl-sn-glyceryl α-D-glucopyranoside (19)

^{1}H NMR ($CDCl_3$, 400 MHz)

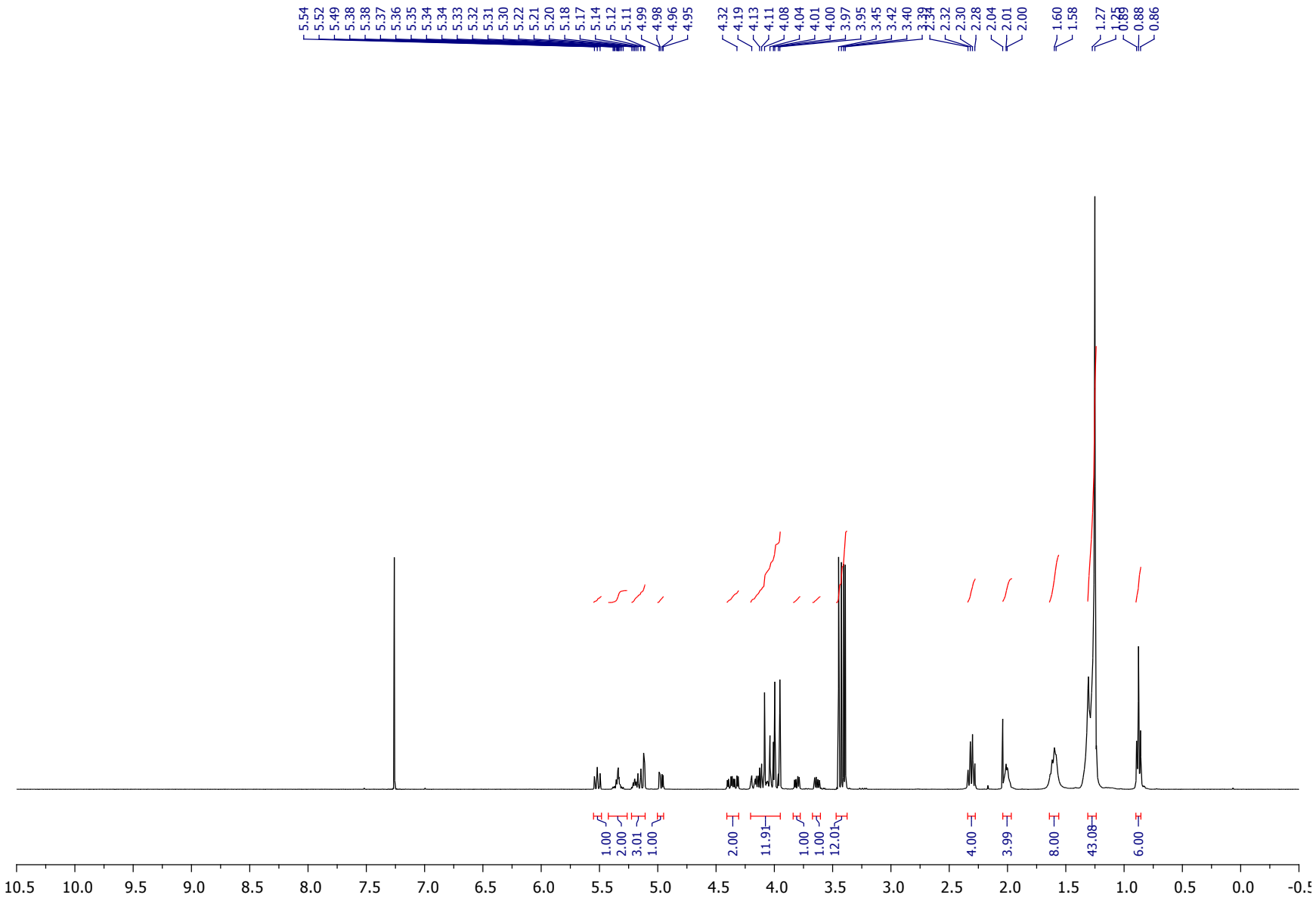


^{13}C NMR ($CDCl_3$, 100 MHz)

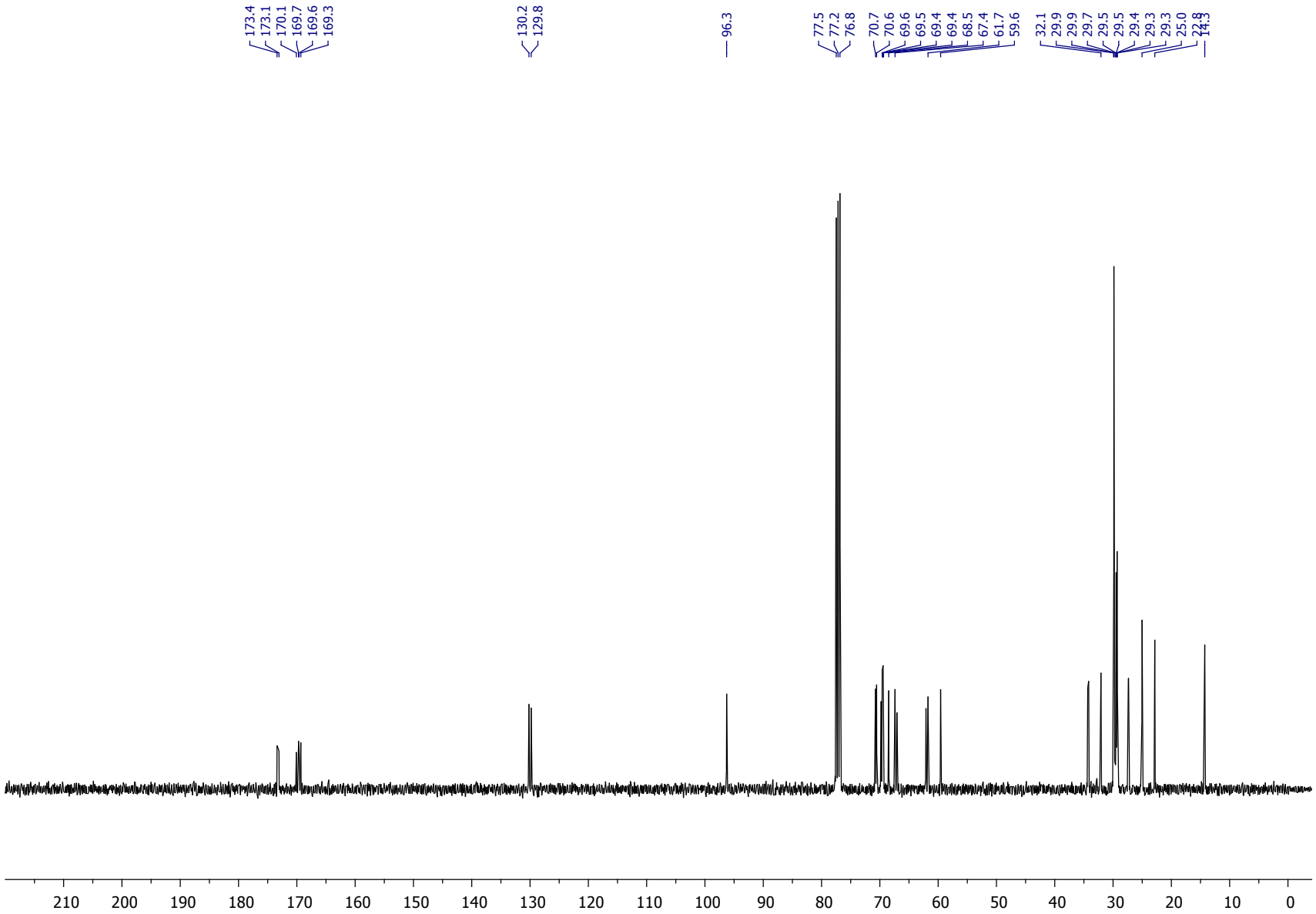


1-O-Stearyl-2-O-oleoyl-sn-glyceryl 2,3,4,6-tetra-O-methoxyacetyl-α-D-glucopyranoside (14)

^{1}H NMR ($CDCl_3$, 400 MHz)

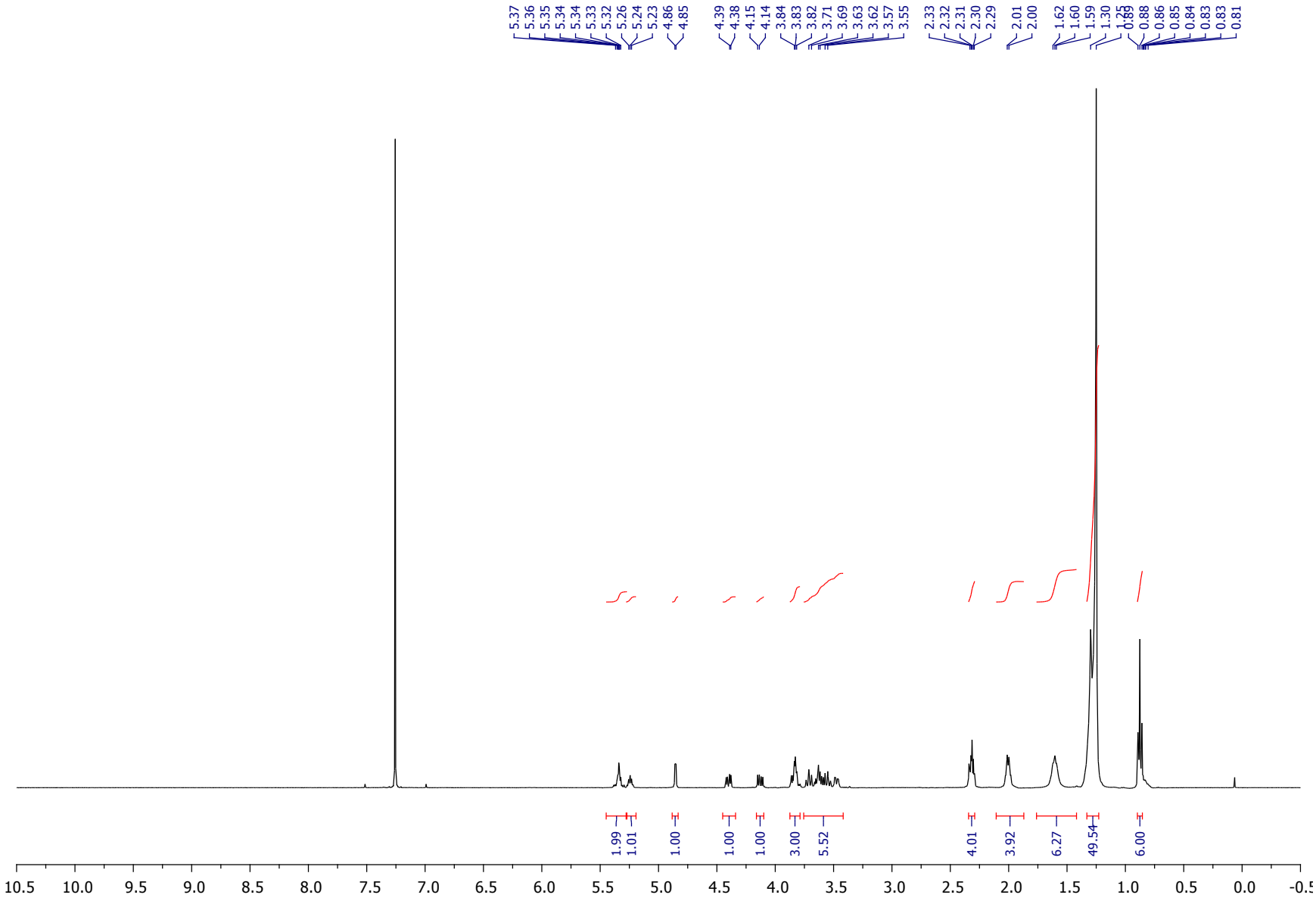


^{13}C NMR ($CDCl_3$, 100 MHz)



1-O-Stearyl-2-O-oleoyl-sn-glyceryl α-D-glucopyranoside (20)

^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 100 MHz)