Electronic Supplementary Material (ESI) for Soft Matter.

Sweet Surfactants: Packing Parameter-Invariant Amphiphiles as Emulsifiers and Capping Agents for Morphology Control of Inorganic Particles

Michael Voggel,[a] Rebecca M. Meinusch,[a] Vanessa Siewert,[a] Marius Kunkel,[a] Valentin Wittmann[a]* and Sebastian Polarz[a]*

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Electronic Supporting Information - Additional synthetic details

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Synthesis and characterization of glycosurfactants

GalαC$_6$

GalαC$_6$ was synthesized according to general procedure 2.2.2 in diethyl ether at 0 °C and purified by FC (petroleum ether/ethyl acetate = 18:1) to yield 44 % of the benzylated α-compound (β-compound could not be separated from impurities), which was consecutively deprotected by hydrogenation in 97 % yield to give **GalαC$_6$** as white solid. R_f = 0.35 (CH_2Cl_2/MeOH 12:1); ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 4.60 (d, *J* = 3.5 Hz, 1 H, H-1), 4.51–4.49 (m, 2 H, OH-3, OH-6), 4.37 (d, *J* = 6.2 Hz, 1 H, OH-2), 4.31 (d, *J* = 4.2 Hz, 1 H, OH-4), 3.69 (t, *J* = 3.1 Hz, 1 H, H-4), 3.60–3.47 (m, 5 H, H-7a, H-2, H-5, H-3, H-6a), 3.42 (dt, *J* = 6.0 Hz, 5.5 Hz, 1 H, H-6b), 3.31 (m, H-7b), 1.52 (m, 2 H, H-8), 1.35–1.21 (m, 6 H, H-9, H-10, H-11), 0.86 (t, *J* = 6.4 Hz, 3 H, H-12); ^{13}C NMR (101 MHz, DMSO-d$_6$): δ = 99.3 (C1), 71.7 (C2/3/5), 70.1 (C2/3/5), 69.3 (C2/3/5), 68.9 (C4), 67.4 (C7), 61.1 (C6), 31.6 (C9–11), 29.6 (C8), 25.9 (C9–11), 22.6 (C9–11), 14.4 (C12) ppm.

GalβC$_6$

GalβC$_6$ was synthesized according to general procedure 2.2.2 in CH_2Cl_2 at -78 °C and purified by FC (petroleum ether/ethyl acetate = 24:1) to yield 72 % of the benzylated β-compound as yellow oil, which was consecutively deprotected by hydrogenation in 58 % yield to give **GalβC$_6$** as white solid. R_f = 0.34 (CH_2Cl_2/MeOH 12:1); ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 4.76 (d, *J* = 4.2 Hz, 1 H, OH-2), 4.66 (s, 1 H, OH-3), 4.53 (t, *J* = 5.6 Hz, 1 H, OH-6), 4.32 (d, *J* = 4.3 Hz, 1 H, OH-4), 4.04 (d, *J* = 4.5 Hz, 1 H, H-1), 3.72 (dt, *J* = 9.4 Hz, 6.9 Hz, 1 H, H-7a), 3.61 (s, 1 H, H-4), 3.58–3.37 (m, 3 H, H-6, H-7b), 3.01 (m, 1 H, H-5), 3.26–3.24 (m, 2 H, H-2, H-3), 1.51 (p, *J* = 6.9 Hz, 2 H, H-8), 1.34–1.21 (m, 6 H, H-9, H-10, H-11), 0.86 (t, *J* = 7.0 Hz, 3 H, H-12) ppm; ^{13}C NMR (101 MHz, DMSO-d$_6$): δ = 103.4 (C1), 75.1 (C5), 73.5 (C2/3), 70.5 (C2/3), 68.3 (C7), 68.1 (C4), 60.4 (C6), 31.1 (C9–11), 29.3 (C8), 25.2 (C9–11), 22.1 (C9–11), 13.9 (C12) ppm.

Galα/βC$_8$

Galα/βC$_8$ was synthesized according to general procedure 2.2.2 in diethyl ether at 0 °C and purified by FC (petroleum ether/ethyl acetate = 40:1 to 30:1) to yield 3 % of the benzylated α-compound and 11 % of the benzylated β-compound (overall yield of reaction: 76 %; α/β-ratio: 1.09:1). The benzylated compounds were consecutively deprotected by hydrogenation to give **GalαC$_8$** in quantitative yield and **GalβC$_8$** in 95 % as white solids. R_f(α) = 0.6 (CH_2Cl_2/MeOH 6:1); ^{1}H NMR (α) (400 MHz, DMSO-d$_6$): δ = 4.62 (d, *J* = 3.4 Hz, 1 H, H-1), 4.53–4.49 (m, 2 H, OH-3, OH-6), 4.37 (d, *J* = 6.3 Hz, 1 H, OH-2), 4.32 (d, *J* = 4.2 Hz, 1 H, OH-4), 3.70 (t, *J* = 3.6 Hz, 1 H, H-4), 3.60–3.40 (m, 6 H, H-2, H-3, H-5, H-6, H-7a), 3.30–3.28 (m, 1 H, H-7b), 1.56–1.49 (m, 2 H, H-8), 1.33–1.26 (m, 10 H, H-9, H-10, H-11, H-12, H-13), 0.86 (t, *J* = 6.6 Hz, 3 H, H-14) ppm; ^{13}C NMR (α) (101 MHz, DMSO-d$_6$): δ = 98.8 (C1), 71.2 (C2/3/5), 69.6 (C2/3/5), 68.8 (C2/3/5), 68.4 (C4), 66.4 (C7), 60.6 (C6), 31.2 (C9–13), 29.1 (C9–13), 28.8 (C8), 28.7 (C9–13), 25.7 (C9–13), 22.1 (C9–13), 13.9 (C14) ppm.
R_f(β) = 0.63 (CH_2Cl_2/MeOH 5:1); ^{1}H NMR (β) (400 MHz, DMSO-d$_6$): δ = 4.76 (d, *J* = 4.3 Hz, 1 H, OH-2), 4.64 (d, *J* = 4.9 Hz, 1 H, OH-3), 4.53 (t, *J* = 5.6 Hz, 1 H, OH-6), 4.31 (d, *J* = 4.4 Hz, 1 H,

OH-4), 4.05 (d, *J* = 7.5 Hz, 1 H, H-1), 3.73 (dt, *J* = 9.9 Hz, 7.0 Hz, 1 H, H-7a), 3.63 (s, 1 H, H-4), 3.59–3.38 (m, 3 H, H-6, H-7b), 3.30 (s, 1 H, H-5), 3.27–3.25 (m, 2 H, H-2, H-3), 1.51 (m, 2 H, H-8), 1.35–1.26 (m, 10 H, H-9, H-10, H-11, H-12, H-13), 0.86 (t, *J* = 7.1 Hz, 3 H, H-14) ppm; ^{13}C NMR (β) (101 MHz, DMSO-d_6): δ = 103.4 (C1), 75.1 (C5), 73.5 (C2/3), 70.5 (C2/3), 68.4 (C7), 68.1 (C4), 60.4 (C6), 31.2 (C9–13), 29.3 (C8), 28.9 (C9–13), 28.7 (C9–13), 25.5 (C9–13), 22.1 (C9–13), 13.9 (C14) ppm.

Galα/βC$_{10}$

Galα/βC$_{10}$ was synthesized according to general procedure 2.2.2 in diethyl ether at 0 °C and purified by FC (petroleum ether/ethyl acetate = 40:1 to 30:1) to yield 13 % of the benzylated α-compound and 17 % of the benzylated β-compound (overall yield of reaction: 68 %; α/β-ratio: 1.36:1). The benzylated compounds were consecutively deprotected by hydrogenation to give **GalαC$_{10}$** in 87 % yield and **GalβC$_{10}$** in quantitative yield as white solids.
R_f(α) = 0.21 (CH_2Cl_2/MeOH 10:1); ^{1}H NMR (α) (400 MHz, DMSO-d_6): δ = 4.61 (d, *J* = 3.3 Hz, 1 H, H-1), 4.51–4.48 (m, 2 H, OH-6, OH-3), 4.36 (d, *J* = 6.1 Hz, 1 H, OH-2), 4.31 (d, *J* = 4.2 Hz, 1 H, OH-4), 3.69 (t, *J* = 3.1 Hz, 1 H, H-4), 3.59–3.39 (m, 6 H, H-7a, H-2, H-5, H-3, H-6), 3.29–3.27 (m, 1 H, H-7b), 1.55–1.48 (m, 2 H, H-8), 1.32–1.25 (m, 14 H, H-9, H-10, H-11, H-12, H-13, H-14, H-15), 0.85 (t, *J* = 6.5 Hz, 3 H, H-16) ppm; ^{13}C NMR (α) (101 MHz, DMSO-d_6): δ = 98.8 (C1), 71.1 (C2/3/5), 69.6 (C2/3/5), 68.8 (C2/3/5), 68.4 (C4), 66.9 (C7), 60.5 (C6), 31.3 (C9–15), 29.1 (C8), 29.03 (C9–15), 28.97 (C9–15), 28.9 (C9–15), 28.7 (C9–15), 25.7 (C9–15), 22.1 (C9–15), 14.0 (C16) ppm.
R_f(β) = 0.19 (CH_2Cl_2/MeOH 10:1); ^{1}H NMR (β) (400 MHz, DMSO-d_6): δ = 4.75 (d, *J* = 4.1 Hz, 1 H, OH-2), 4.64 (d, *J* = 4.5 Hz, 1 H, OH-3), 4.52 (t, *J* = 6.0 Hz, 1 H, OH-6), 4.30 (d, *J* = 4.5 Hz, 1 H, OH-4), 4.04 (d, *J* = 7.6 Hz, 1 H, H-1), 3.71 (dt, *J* = 9.5 Hz, 6.8 Hz, 1 H, H-7a), 3.62 (s, 2 H, H-4), 3.57–3.36 (m, 3 H, H-6, H-7b), 3.30–3.25 (m, 1 H, H-5), 3.26–3.24 (m, 2 H, H-2, H-3), 1.50 (m, 2 H, H-8), 1.31–1.25 (m, 14 H, H-9, H-10, H-11, H-12, H-13, H-14,H-15), 0.85 (t, *J* = 6.6 Hz, 3 H, H-16) ppm; ^{13}C NMR (β) (101 MHz, DMSO-d_6): δ = 103.4 (C1), 75.1 (C5), 73.5 (C3), 70.5 (C2), 68.4 (C7), 68.1 (C4), 60.4 (C6), 31.2 (C9–15) 31.1 (C9–15), 29.3 (C8), 29.02 (C9–15), 28.96 (C9–15), 28.91 (C9–15), 28.7 (C9–15), 22.1 (C9–15), 13.9 (C16) ppm.

Galα/βC$_{12}$

Galα/βC$_{12}$ was synthesized according to general procedure 2.2.2 in diethyl ether at 0 °C and purified by FC (petroleum ether/ethyl acetate = 20:1) to yield 18 % of the benzylated α-compound and 21 % of the benzylated β-compound (overall yield of reaction: 62 %; α/β-ratio: 0.55:1). The benzylated compounds were consecutively deprotected by hydrogenation to give **GalαC$_{12}$** in 95 % yield and **GalβC$_{12}$** in 99 % yield as white solids. R_f(α) = 0.46 (CH_2Cl_2/MeOH 5:1); ^{1}H NMR (α) (400 MHz, DMSO-d_6): δ = 4.61 (d, *J* = 3.5 Hz, 2 H, H-1), 4.53-4.45 (m, 2 H, OH), 4.35 (d, *J* = 6.2 Hz, 1 H, OH), 4.31 (d, *J* = 4.2 Hz, 1 H, OH), 3.70 (m, 1 H, H-3), 3.60-3.46 (m, 5 H, H-2, H-4, H-5, H-7a, H-6a), 3.45-3.38 (m, 1 H, H-6b), 3.33-3.25 (m, 1-H, H-7b), 1.51 (m, 2 H, H-8), 1.35-1.19 (m, 18 H, H-9 - H-17), 0.85 (t, *J* = 6.5 Hz, 3 H, H-18) ppm; ^{13}C NMR (α) (101 MHz, DMSO-d_6): δ = 96.8 (C1), 71.1 (C2/3/5), 69.6 (C2/3/5), 68.8 (C2/3/5), 68.4 (C4), 66.9 (C7), 60.5 (C6), 31.3, 29.1, 29.0, 28.9, 28.7, 25.7 (C8-16), 22.1 (C17), 13.9 (C18) ppm.

R_f(β) = 0.41 (CH_2Cl_2/MeOH 5:1); ^{1}H NMR (β) (400 MHz, DMSO-d_6): δ = 4.04 (d, *J* = 7.5 Hz, 1 H, H-1), 4.30-3.78 (brs, 4 H, OH), 3.76-3.67 (m, 1 H, H-7a), 3.64-3.61 (m, 1 H, H-3), 3.59-3.44 (m, 2 H, H-6), 3.42-3.36 (m, 1 H, H-7b), 3.33-3.28 (m, 1 H, H-5), 3.28-3.22 (m, 2 H, H-2, H-4), 1.57-1.45 (m, 2 H, H-8), 1.34-1.19 (m, 18 H, H-9 - H-17), 0.86 (t, *J* = 6.8 Hz, H-18) ppm; ^{13}C NMR (β) (101 MHz, DMSO-d_6): δ = 103.4 (C1), 75.1 (C5), 73.5 (C4), 71.1 (C2), 68.8 (C7), 68.1 (C3), 60.4 (C6), 31.3, 29.3, 29.1-29.85, 28.9, 28.7, 25.5 (C8-16), 22.1 (C17), 13.9 (C18) ppm.

ManαC_6

ManαC_6 was prepared according to general procedure 2.2.1. The acetylated product was purified by FC (petroleum ether/ethyl acetate =10:1) to yield 26 % of the acetylated α-product as yellow oil. After deprotection following the Zemplén protocol, **ManαC_6** was obtained in 95 % yield as white solid. R_f = 0.37 (CH_2Cl_2/MeOH 5:1); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.72 (brs, 1 H, OH), 4.66 (brs, 1 H, OH), 4.57 (d, *J* = 1.5 Hz, 1 H, H-1), 4.40 (t, *J* = 5.7 Hz, 1 H, OH-6), 4.09 (d, *J* = 5.0 Hz, 1 H, OH), 3.67-3.61 (m, 1 H, H-6a), 3.60-3.55 (m, 2 H, H-7a, H-2), 3.48-3.40 (m, 2 H, H-3, H-6b), 3.40-3.33 (m, 1 H, H-4), 3.33-3.25 (m, 2 H, H-7b, H-5), 1.54-1.43 (m, 2 H, H-8), 1.35-1.20 (m, 6 H, H-9 - H-11), 0.86 (t, *J* = 6.9 Hz, 3 H, H-12) ppm.

Manα/βC_8

Manα/βC_8 was prepared according to general procedure 2.2.1 at 0 °C. The acetylated product was purified by FC (petroleum ether/ethyl acetate =10:1) to yield 25 % of the acetylated α-product and 11 % of the acetylated β-product as yellow oils. After deprotection following the Zemplén protocol, **ManαC_8** was obtained in 72 % yield and **ManβC_8** in 95 % yield as slightly yellow solids. R_f (α)= 0.40 (CH_2Cl_2/MeOH 5:1); ^{1}H NMR (α) (400 MHz, DMSO-d_6): δ = 4.68 (d, *J* = 5.2 Hz, 1 H, OH-4), 4.65 (d, *J* = 4.6 Hz, 1 H, OH-2), 4.57 (d, *J* = 1.3 Hz, 1 H, H-1), 4.51 (d, *J* = 6.1 Hz, 1 H, OH-3), 4.40 (t, *J* = 5.9 Hz, 1 H, OH-6), 3.67-3.62 (m, 1 H, H-6a), 3.62-3.54 (m, 2 H, H-7a, H-2), 3.47-3.39 (m, 2 H, H-3, H-6b), 3.39-3.33 (m, 1 H, H-4), 3.32-3.24 (m, 2 H, H-7b, H-5), 1.57-1.40 (m, 2 H, H-8), 1.36-1.19 (m, 10 H, H-9 - H-13), 0.86 (t, *J* = 6.9 Hz, 3 H, H-14) ppm.
R_f (β)= 0.41 (CH_2Cl_2/MeOH 5:1); ^{1}H NMR (β) (400 MHz, DMSO-d_6): δ = 4.68 (d, *J* = 5.2 Hz, 1 H, OH-4), 4.49 (d, *J* = 6.1 Hz, 1 H, OH-3), 4.40 (t, *J* = 5.9 Hz, 1 H, OH-6), 4.33 (d, *J* = 0.6 Hz, 1 H, H-1), 4.24 (d, *J* = 5.0 Hz, 1 H, OH-2), 3.79-3.71 (m, 1 H, H-7a), 3.70-3.63 (m, 1 H, H-6a), 3.63-3.58 (m, 1 H, H-2), 3.49-3.36 (m, 2 H, H-6b, H-7b), 3.32-3.19 (m, 2 H, H-4, H-3), 3.04-2.97 (m, 1 H, H-5), 1.57-1.44 (m, 2 H, H-8), 1.33-1.17 (m, 10 H, H-9 - H-13), 0.86 (t, *J* = 7.0 Hz, 3 H, H-14) ppm.

Manα/βC_{10}

Manα/βC_{10} was prepared according to general procedure 2.2.1 at 0 °C. The acetylated product was purified by FC (petroleum ether/ethyl acetate =20:1) to yield 54 % of the acetylated α-product and 13 % of the acetylated β-product as yellow oils. After deprotection following the Zemplén protocol, **ManαC_{10}** was obtained in 66 % yield and **ManβC_{10}** in 86 % yield as slightly yellow solids. R_f (α)= 0.46 (CH_2Cl_2/MeOH 5:1); ^{1}H NMR (α) (400 MHz, DMSO-d_6): δ = 4.67 (d, *J* = 5.0 Hz, 1 H, OH-4), 4.64 (d, *J* = 4.4 Hz, 1 H, OH-2), 4.58 (s, 1 H, H-1), 4.49

(d, *J* = 5.7 Hz, 1 H, OH-3), 4.37 (t, *J* = 5.7 Hz, 1 H, OH-6), 3.68-3.61 (m, 1 H, H-6a), 3.61-3.54 (m, 2 H, H-7a, H-2), 3.49-3.41 (m, 2 H, H-6a, H-3), 3.41-3.35 (m, 1 H, H-4), 3.35-3.25 (m, 2 H, H-7b, H-5), 1.56-1.44 (m, 2 H, H-8), 1.35-1.18 (m, 14 H, H-9 - H-15), 0.86 (t, *J* = 6.9 Hz, 3 H, H-16) ppm; ^{13}C NMR (α) (101 MHz, DMSO-d_6): δ = 99.7 (C1), 73.9 (C5), 71.0 (C3), 70.4 (C2), 76.0 (C4), 66.2 (C7), 61.3 (C6), 31.3, 29.1-28.9, 28.8, 28.7 (C8-13), 25.7 (C14), 22.1 (C15), 13.9 (C16) ppm.
R_f (β)= 0.49 (CH_2Cl_2/MeOH 5:1); ^{1}H NMR (β) (400 MHz, DMSO-d_6): δ = 4.33 (s, 1 H, H-1), 4.07-3.80 (brs, 4 H, OH), 3.78-3.70 (m, 1 H, H-7a), 3.70-3.64 (m, 1 H, H-6a), 3.60 (d, *J* = 2.7 Hz, 1 H, H-2), 3.48-3.34 (m, 2 H, H-6b, H-7b), 3.32-3.18 (m, 2 H, H-4, H-3), 3.03-2.96 (m, 1 H, H-5), 1.56-1.44 (m, 2 H, H-8), 1.33-1.18 (m, 14 H, H-9 - H-15), 0.86 (t, *J* = 6.9 Hz, 3 H, H-16) ppm; ^{13}C NMR (β) (101 MHz, DMSO-d_6): δ = 100.2 (C1), 77.5 (C5), 73.7 (C3), 70.6 (C2), 68.4 (C7), 67.2 (C4), 61.4 (C6), 31.3, 29.2, 29.1-28.8, 25.6 (C8-14), 22.1 (C15), 13.9 (C16) ppm.

Manα/βC$_{12}$

Manα/βC$_{12}$ was prepared according to general procedure 2.2.1 at -50 °C. The acetylated product was purified by FC (petroleum ether/ethyl acetate =5:1) to yield 73 % of the acetylated α-product and 1 % of the acetylated β-product as yellow oils. After deprotection following the Zemplén protocol, **ManαC$_{12}$** was obtained in 94 % yield and **ManβC$_{12}$** in 92 % yield as white solids. R_f (α)= 0.32 (CH_2Cl_2/MeOH 10:1); ^{1}H NMR (α) (400 MHz, DMSO-d_6): δ = 4.66 (d, *J* = 5.3 Hz, 1 H, OH-4), 4.63 (d, *J* = 4.4 Hz, 1 H, OH-2), 4.58 (d, *J* = 1.3 Hz, 1 H, H-1), 4.48 (d, *J* = 6.2 Hz, 1 H, OH-3), 4.36 (d, *J* = 6.0 Hz, 1 H, OH-6), 3.67-3.60 (m, 1 H, H-6a), 3.60-3.54 (m, 2 H, H-7a, H-2), 3.48-3.40 (m, 2 H, H-6b, H-3), 3.40-3.32 (m, 1 H, H-4), 3.32-3.25 (m, 1 H, H-7b, H-5), 1.55-1.43 (m, 2 H, H-8), 1.35-1.19 (m, 18 H, H-9 - H17), 0.86 (t, *J* = 6.9 Hz, 3 H, H-18) ppm; ^{13}C NMR (α) (101 MHz, DMSO-d_6): δ = 99.7 (C1), 73.9 (C5), 71.0 (C3), 70.4 (C2), 67.0 (C4), 66.2 (C7), 61.3 (C6), 31.2, 29.0-28.6 (C8-15), 25.7 (C16), 22.0 (C17), 13.9 (C18) ppm.
R_f (β)= 0.34 (CH_2Cl_2/MeOH 10:1); ^{1}H NMR (β) (400 MHz, DMSO-d_6): δ = 4.33 (s, 1 H, H-1), 4.17-3.79 (brs, 4 H, OH), 3.79-3.71 (m, 1 H, H-7a), 3.71-3.64 (m, 1 H, H-6a), 3.62-3.59 (m, 1 H, H-2), 3.48-3.34 (m, 2 H, H-6b, H-7b), 3.32-3.20 (m, 2 H, H-4, H-3), 3.04-2.97 (m, 1 H, H-5), 1.55-1.44 (m, 2 H, H-8), 1.31-1.19 (m, 18 H, H-9 - H-17), 0.86 (t, *J* = 6.9 Hz, 3 H, H-18) ppm; ^{13}C NMR (β) (101 MHz, DMSO-d_6): δ = 100.2 (C1), 77.5 (C5), 73.7 (C3), 70.6 (C2), 68.3 (C7), 67.2 (C4), 61.4 (C5), 31.3, 29.00-28.87, 28.7, 25.6 (C8-16), 22.0 (C17), 13.9 (C18) ppm.

Glcα/βC$_{12}$

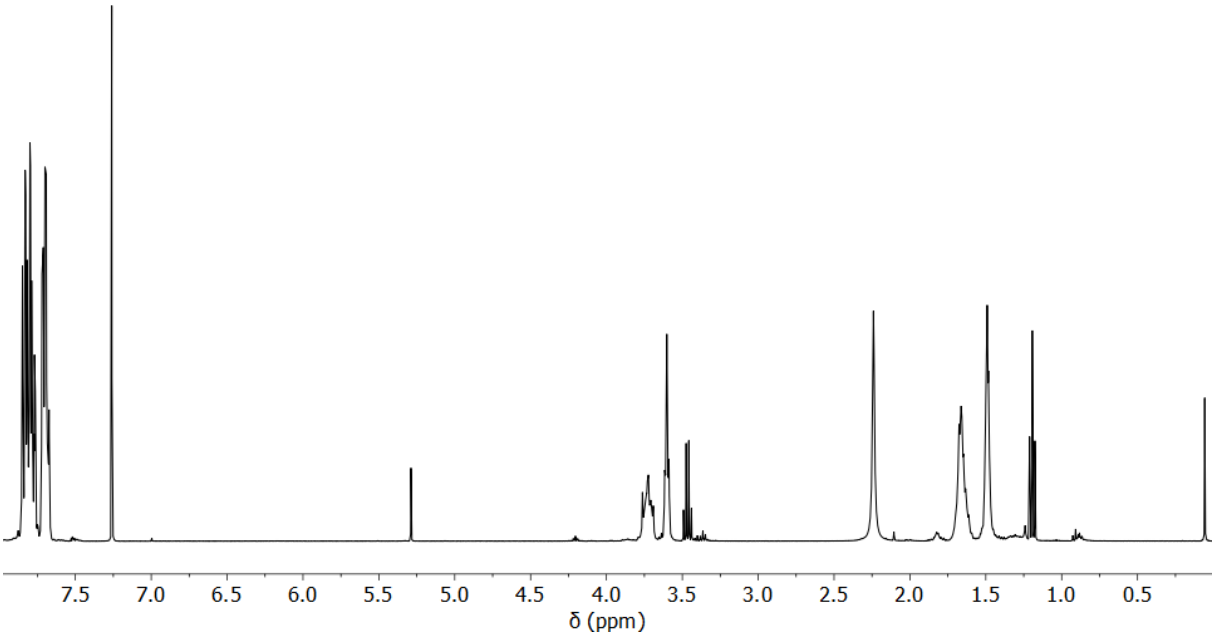
Glcα/βC$_{12}$ was prepared according to general procedure 2.2.1 at -50 °C. The acetylated product was purified by FC (petroleum ether/ethyl acetate =5:1) to yield 14 % of the acetylated α-product and 62 % of the acetylated β-product as yellow oils. After deprotection following the Zemplén protocol, **GlcαC$_{12}$** was obtained in 96 % yield and **GlcβC$_{12}$** in 99 % yield as white solids. R_f (α)= 0.50 (CH_2Cl_2/MeOH 5:1); ^{1}H NMR (α) (400 MHz, DMSO-d_6): δ = 4.84-4.36 (brs, 4 H, OH), 4.60 (d, *J* = 3.7 Hz, 1 H, H-1), 3.63-3.54 (m, 2 H, H-6a, H-7a), 3.47-3.25 (m, 4 H, H-6b, H-3, H-5, H7b), 3.21-3.13 (dd, *J* = 9.7, 3.7 Hz, 1 H, H-2), 3.05 (d, *J* = 9.1 Hz, 1 H, H-4), 1.57-1.45 (m, 2 H, H-8), 1.36-1.18 (m, 18 H, H-9 - H-17), 0.85 (t, *J* = 0.69 Hz, 3 H, H-18) ppm; ^{13}C NMR (α) (101 MHz, DMSO-d_6): δ = 98.5 (C1), 73.3 (C3), 72.7 (C5), 72.0 (C2), 70.3 (C4), 66.8 (C7), 60.9 (C6), 31.3, 29.16-28.81, 28.7, 25.7 (C8-16), 22.1 (C17), 13.9 (C18) ppm.

R_f (β)= 0.47 (CH_2Cl_2/MeOH 5:1); ^{1}H NMR (β) (400 MHz, DMSO-d_6): δ = 5.05-4.64 (brs, 4 H, OH), 4.09 (d, *J* = 7.7 Hz, 1 H, H-1), 3.78-3.70 (m, 1 H, H-7a), 3.68-3.62 (m, 1 H, H-6a), 3.46-3.36 (m, 2 H, H-6b, H-7b), 3.14-2.99 (m, 3 H, H-3, H-5, H-4), 2.95-2.89 (m, 1 H, H-2), 1.55-1.45 (m, 2 H, H-8), 1.33-1.18 (m, 18 H, H-9 - H-17), 0.85 (t, *J* = 6.9 Hz, 3 H, H-18) ppm; ^{13}C NMR (β) (101 MHz, DMSO-d_6): δ = 102.8 (C1), 76.8, 76.8 (C3, C5), 73.4 (C2), 70.1 (C4), 68.5 (C7), 61.1 (C6), 31.3, 29.3, 29.08-28.98, 28.9, 28.7, 25.5 (C8-16), 22.1 (C17), 13.9 (C18) ppm.

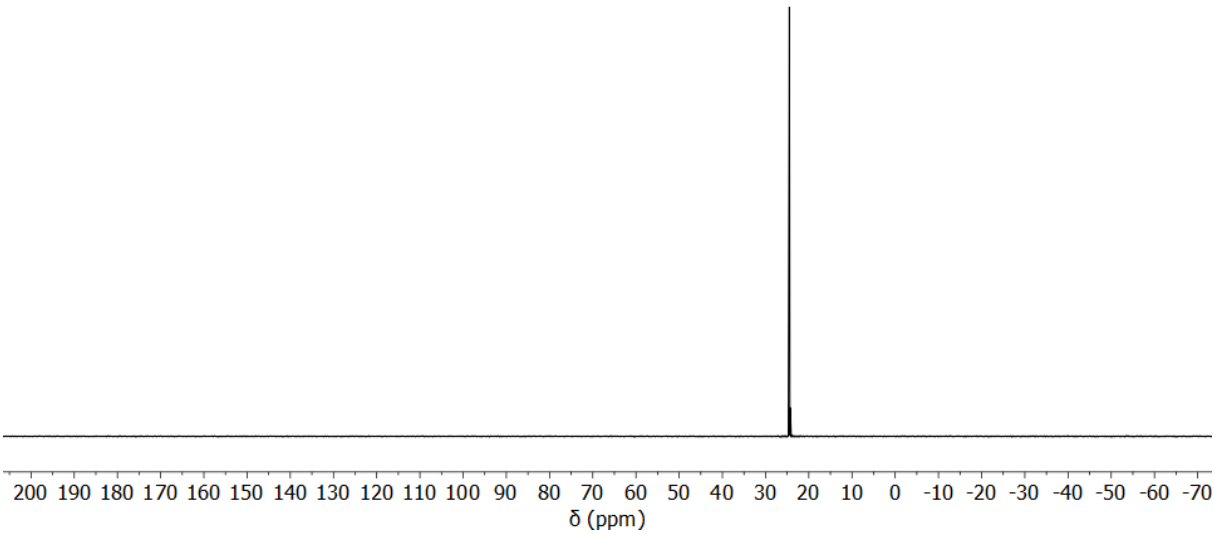
Xylα/βC$_{12}$

Xylα/βC$_{12}$ was prepared according to general procedure 2.2.3. The acetylated product was purified by FC (petroleum ether/ethyl acetate =10:1) to yield 21 % of the acetylated α-product and 10 % of the acetylated β-product as yellow oils. After deprotection following the Zemplén protocol, **XylαC$_{12}$** was obtained in 96 % yield and **XylβC$_{12}$** in 85 % yield as white solids. R_f (α)= 0.52 (CH_2Cl_2/MeOH 5:1); ^{1}H NMR (α) (400 MHz, DMSO-d_6): δ = 4.87 (d, *J* = 4.1 Hz, 1 H, OH-3), 4.74 (d, *J* = 4.7 Hz, 1 H, OH-4), 4.57 (d, *J* = 6.4 Hz, 1 H, OH-2), 4.55 (d, *J* = 3.7 Hz, 1 H, H-1), 3.58-3.49 (m, 1 H, H-6a), 3.41-3.29 (m, 3 H, H-5a, H-4, H-6b), 3.28-3.22 (m, 2 H, H-3, H-5b), 3.19-3.13 (m, 1 H, H-2), 1.57-1.46 (m, 2 H, H-7), 1.36-1.19 (m, 18 H, H-8 - H-16), 0.86 (t, *J* =6.9 Hz, 3 H, H-17) ppm.
R_f (β)= 0.62 (CH_2Cl_2/MeOH 5:1); ^{1}H NMR (β) (400 MHz, DMSO-d_6): δ = 4.91-4.85 (m, 3 H, OH), 4.06 (d, *J* = 7.6 Hz, 1 H, H-1), 3.71-3.62 (m, 2 H, H-5a, H-6a), 3.44-3.36 (m, 1 H, H-6b), 3.28-3.21 (m, 1 H, H-4), 3.11-3.04 (m, 1 H, H-3), 3.04-2.97 (m, 1 H, H-5b), 2.97-2.89 (m, 1 H, H-2), 1.55-1.44 (m, 2 H, H-7), 1.34-1.17 (m, 18 H, H-8 - H-16), 0.86 (t, *J* = 6.9 Hz, 3 H, H-17) ppm; ^{13}C NMR (β) (101 MHz, DMSO-d_6): δ = 103.6 (C1), 76.6 (C3), 73.2 (C2), 69.6 (C4), 68.5 (C6), 65.6 (C5), 31.2, 29.3, 29.0-28.9, 28.8, 28.6, 25.5 (C7-15), 22.0 (C16), 13.9 (C17) ppm.

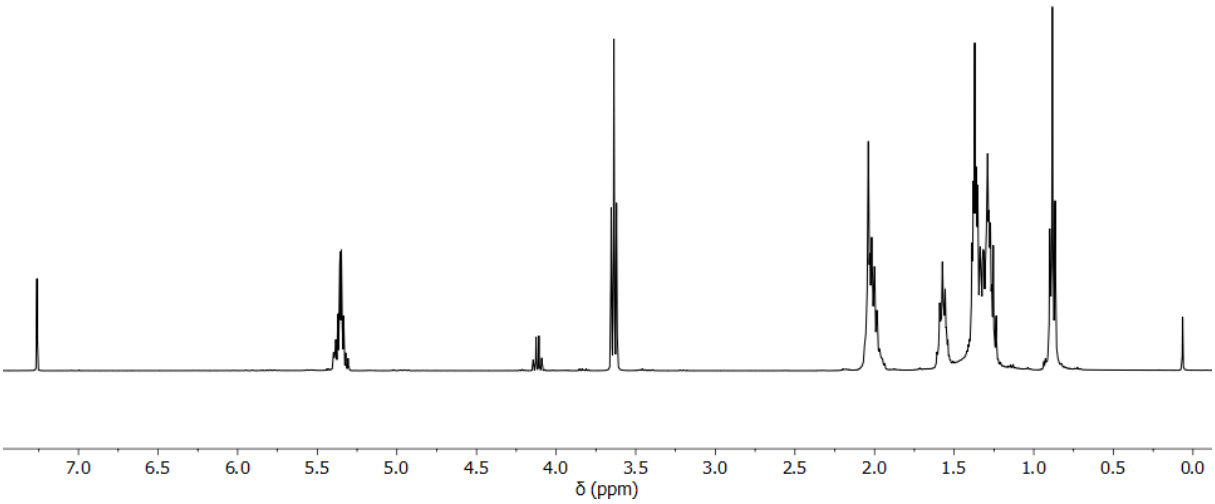
NMR and mass spectra



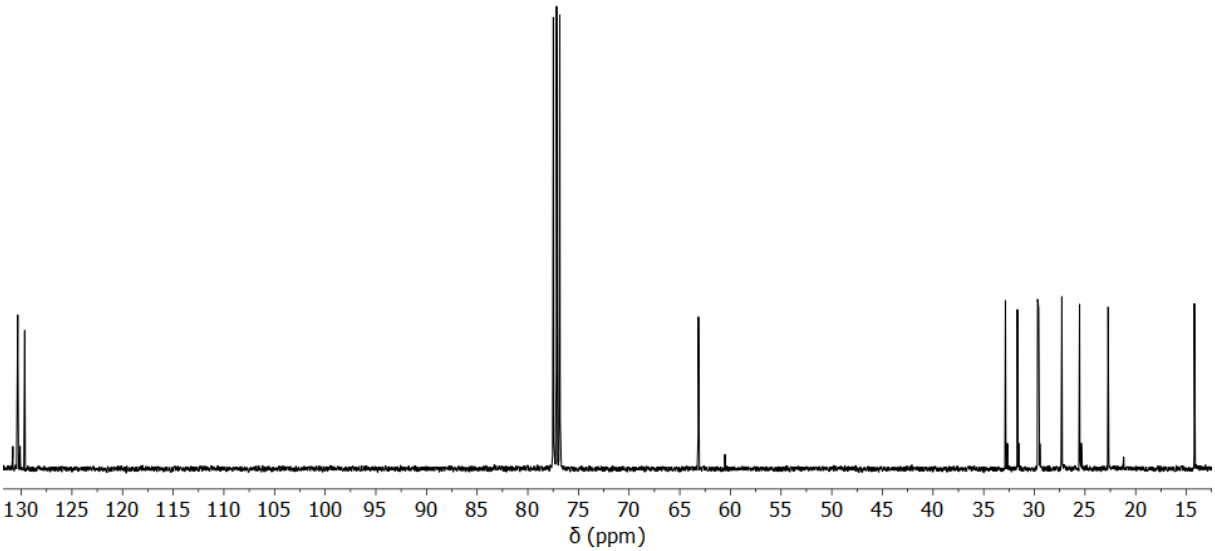
^{1}H NMR ($CDCl_3$, 400 MHz) of (6-hydroxyhexyl)-triphenylphosphonium bromide



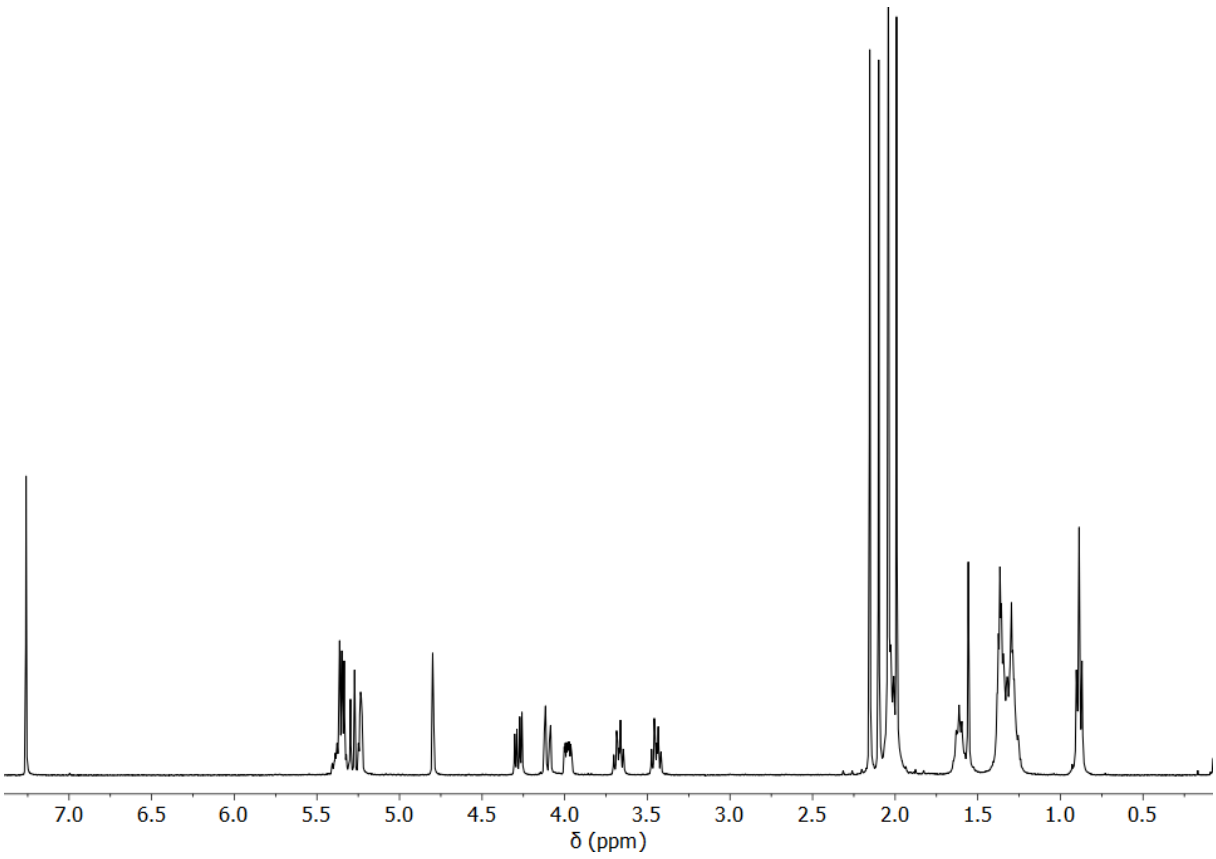
^{31}P NMR ($CDCl_3$, 161.8 MHz) of (6-hydroxyhexyl)-triphenylphosphonium bromide



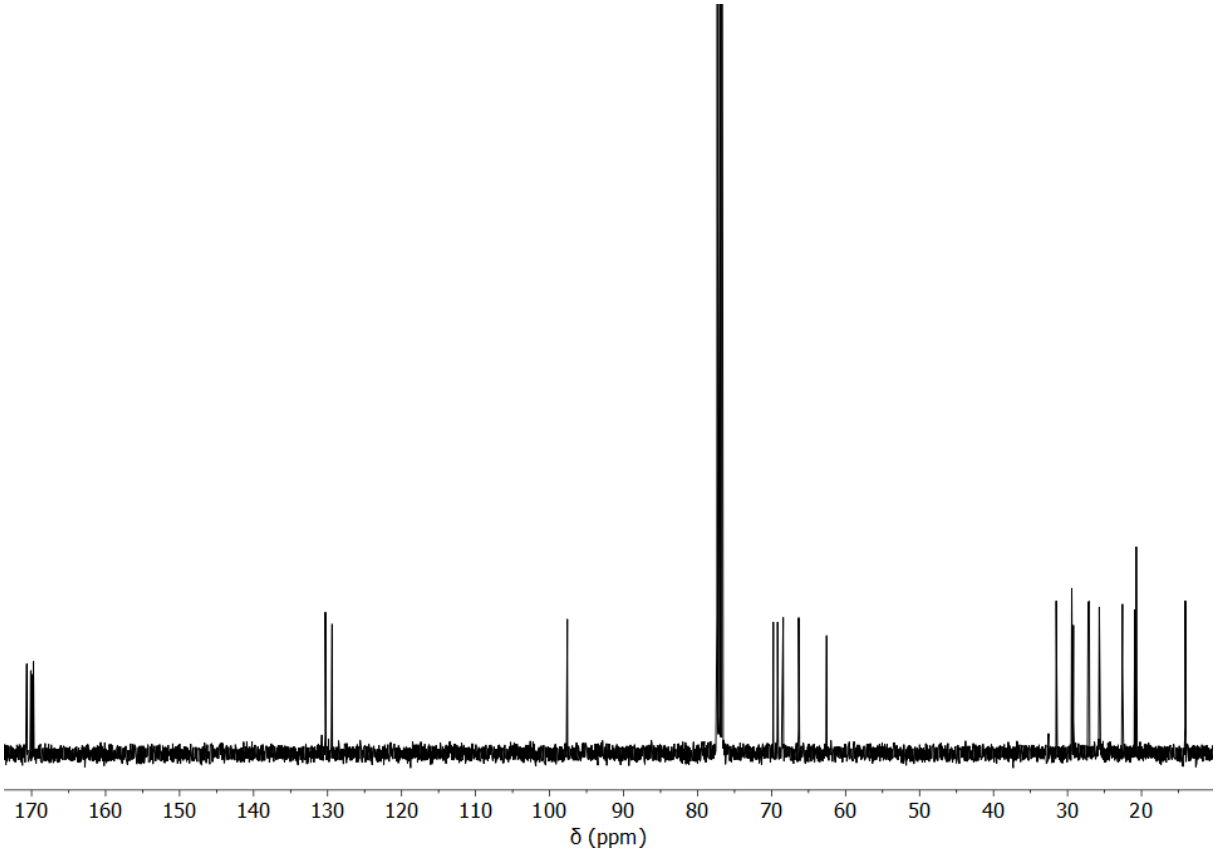
^{1}H NMR ($CDCl_3$, 400 MHz) of **3**



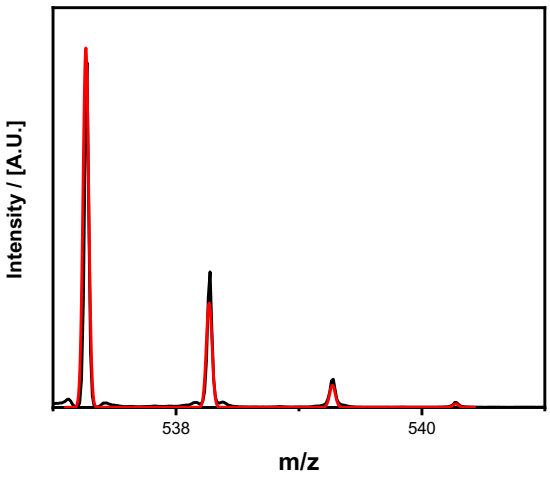
^{13}C NMR ($CDCl_3$, 100.5 MHz) of **3**



^{1}H NMR ($CDCl_3$, 400 MHz) of **4α**

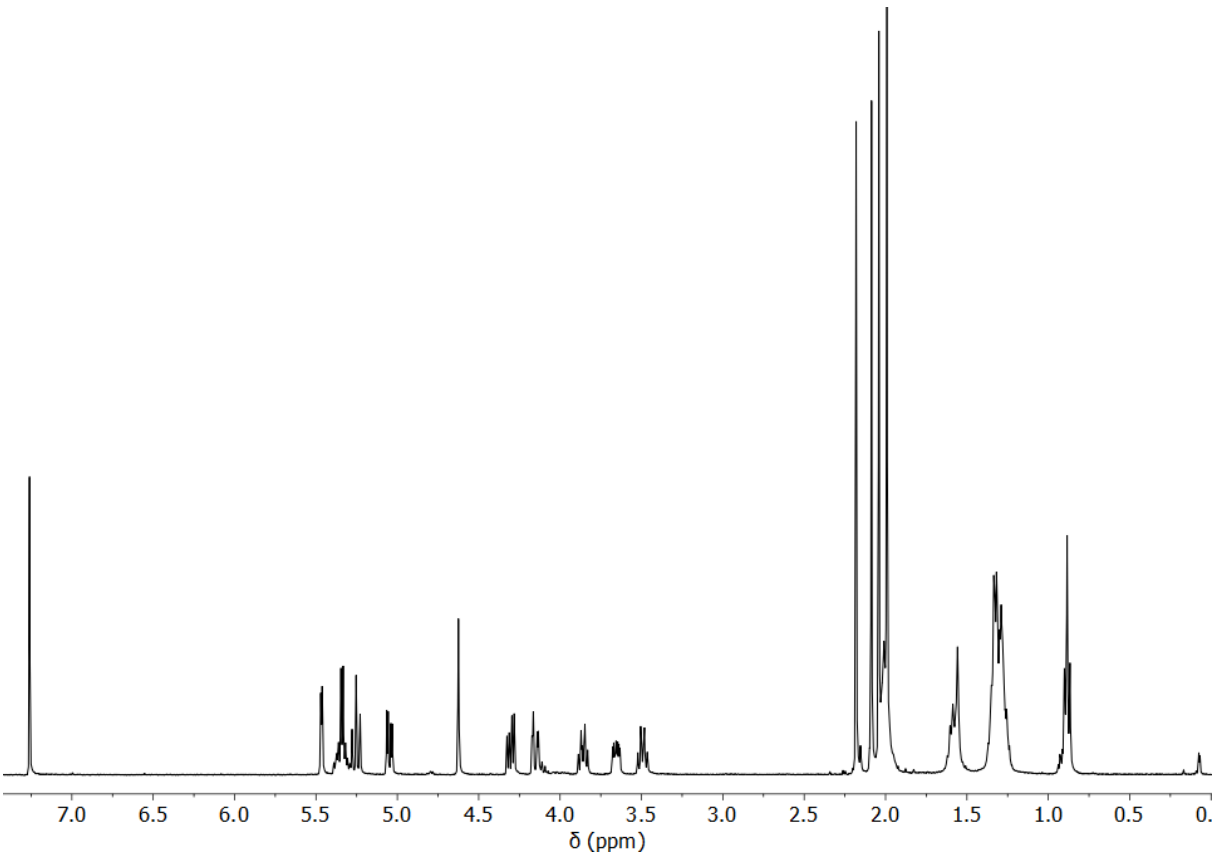


^{13}C NMR ($CDCl_3$, 100.5 MHz) of **4α**

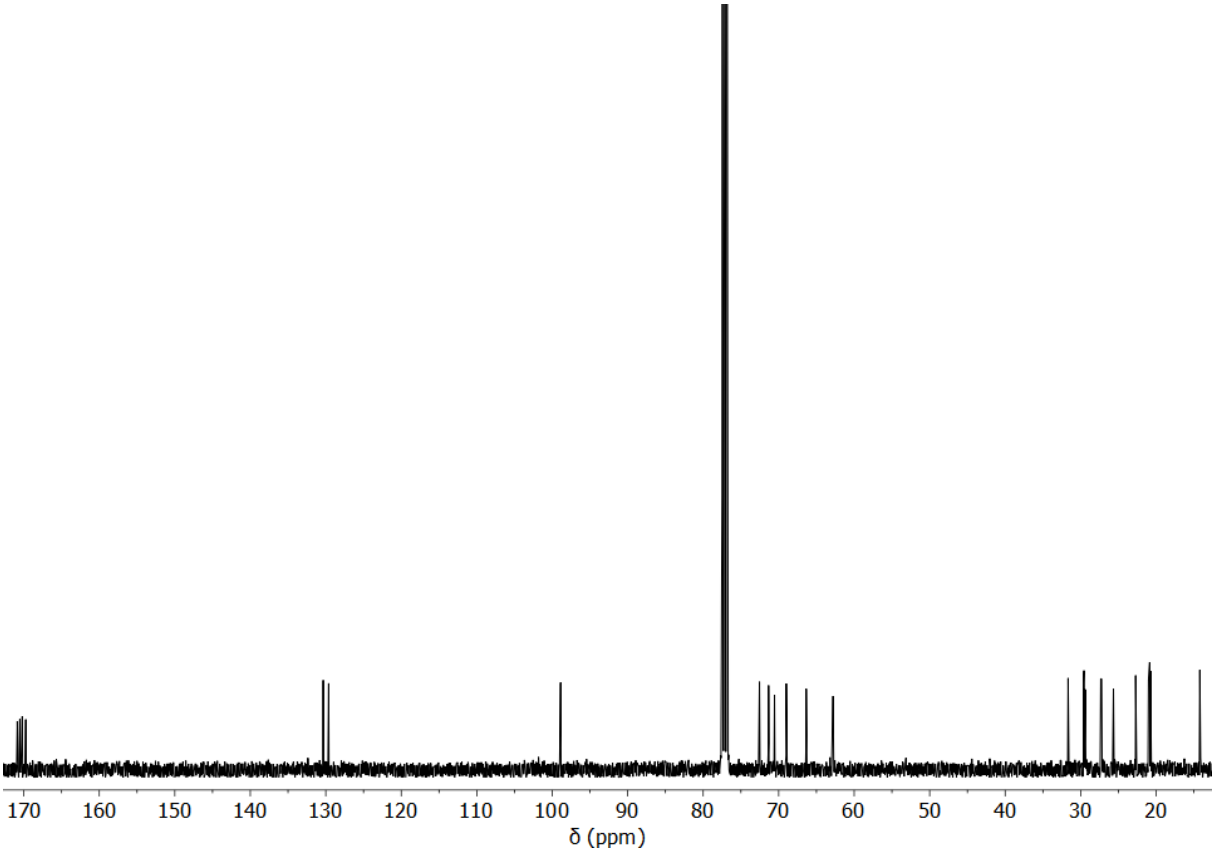


calcd (red) for $C_{26}H_{42}O_{10}Na$ $[M+Na]^+$: 537.2669;
found (black): 537.2762

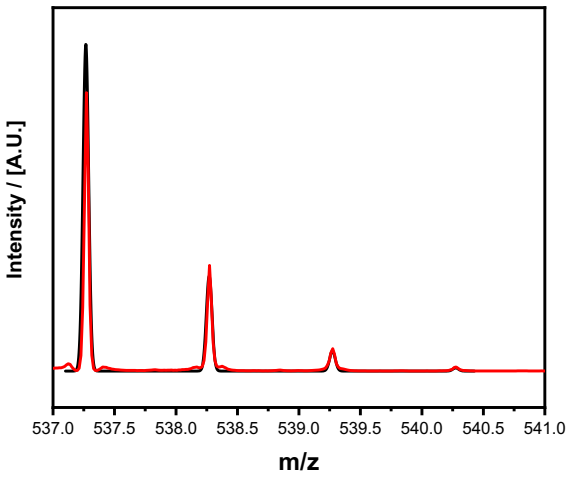
ESI-HRMS of **4α**



^{1}H NMR ($CDCl_3$, 400 MHz) of **4β**

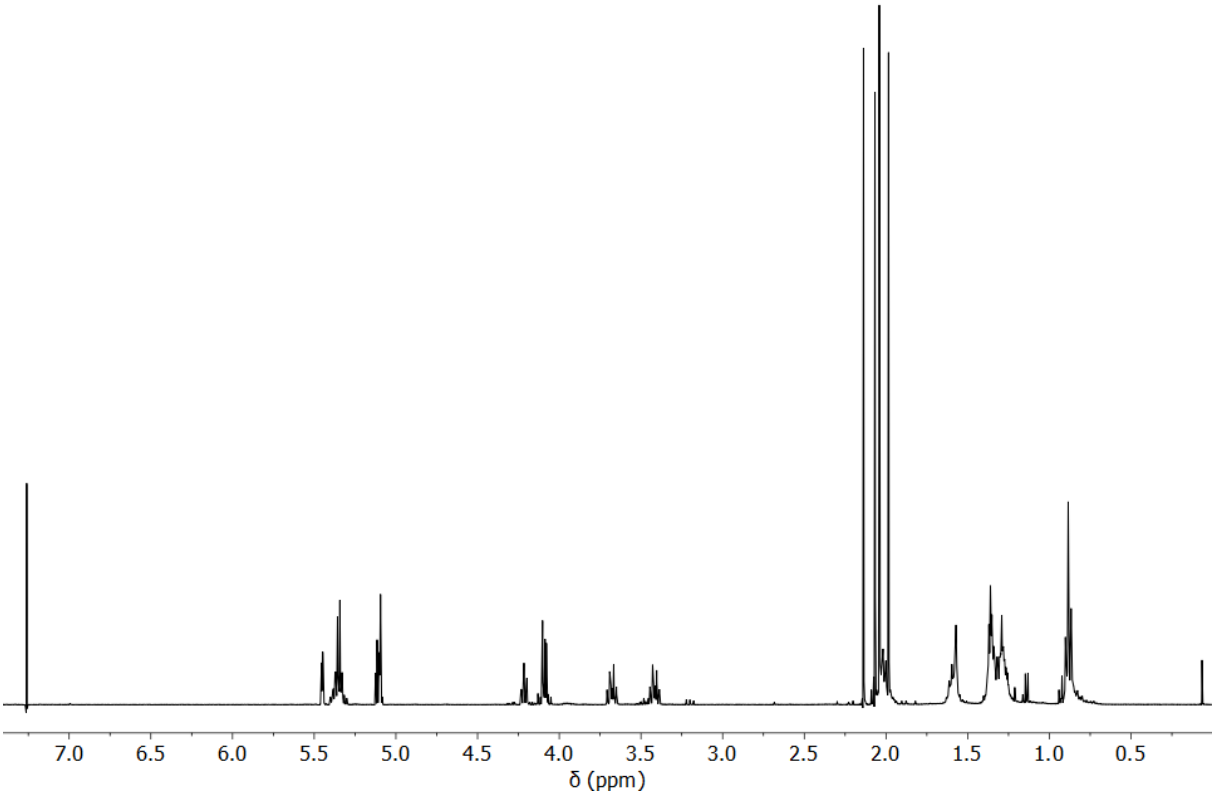


^{13}C NMR ($CDCl_3$, 100.5 MHz) of **4β**

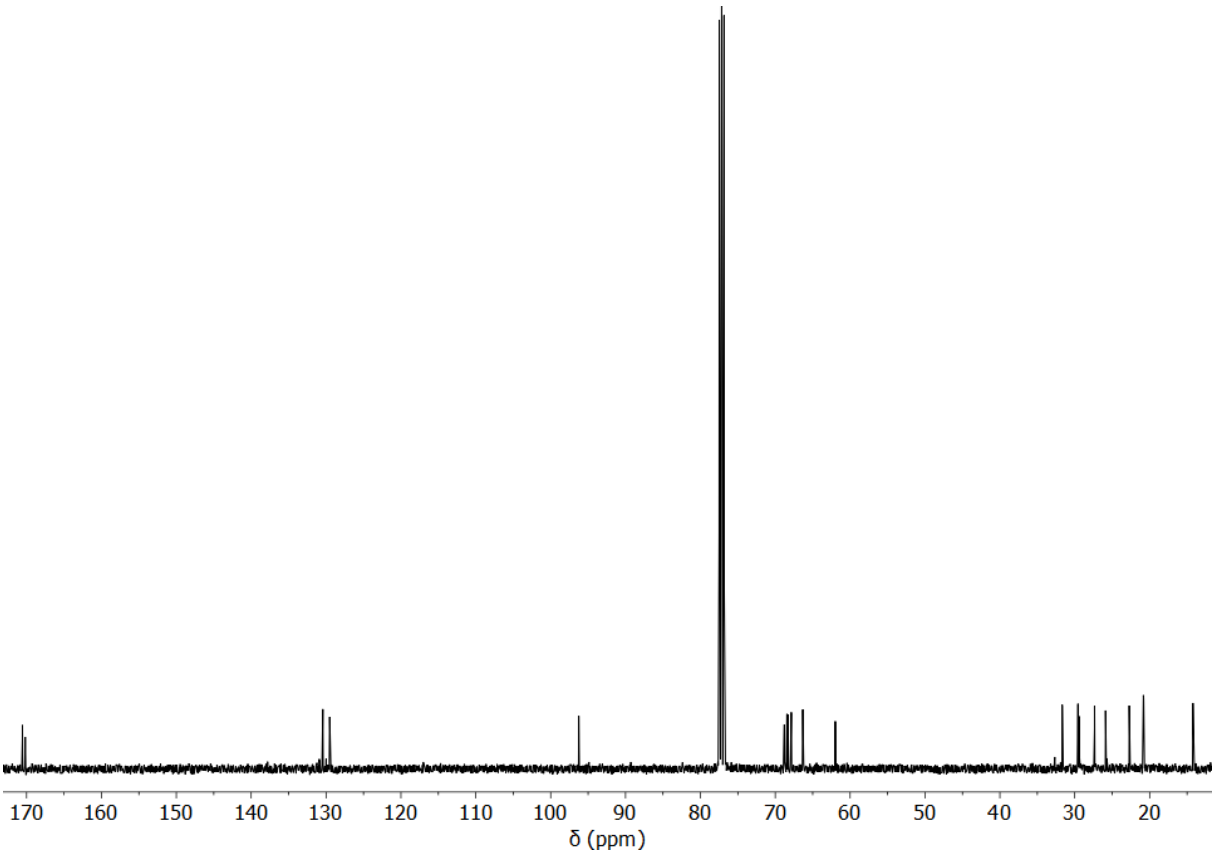


calcd (red) for $C_{26}H_{42}O_{10}Na$ $[M+Na]^+$: 537.2669;
found (black): 537.2672

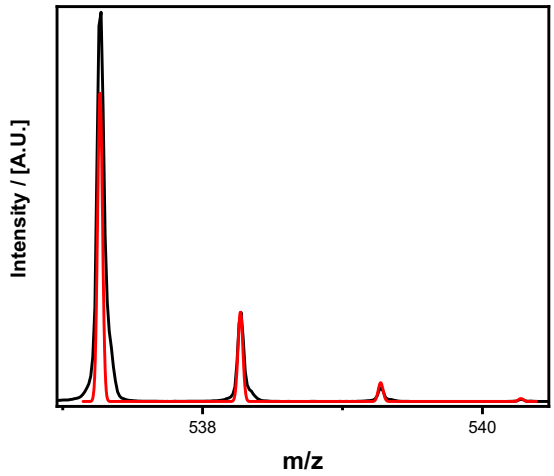
ESI-HRMS of **4β**



^{1}H NMR ($CDCl_3$, 400 MHz) of **5α**

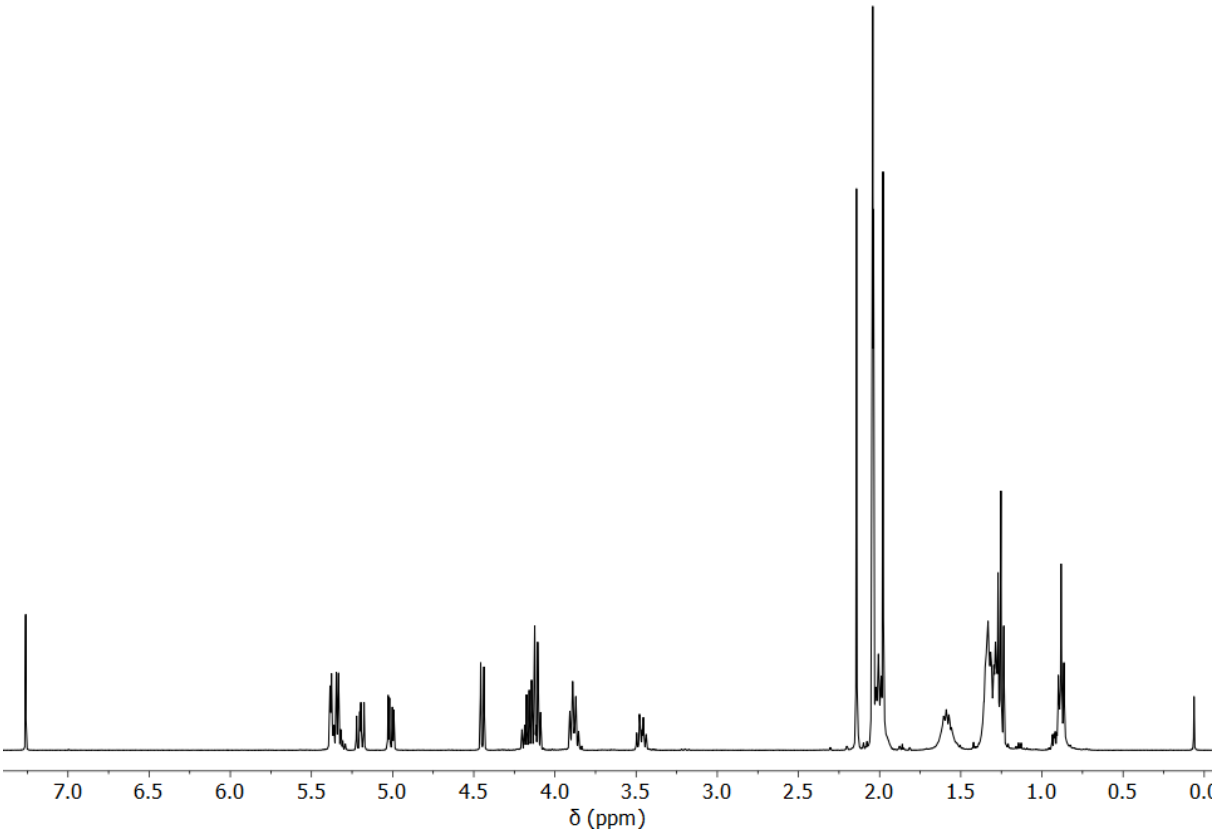


^{13}C NMR ($CDCl_3$, 100.5 MHz) of **5α**

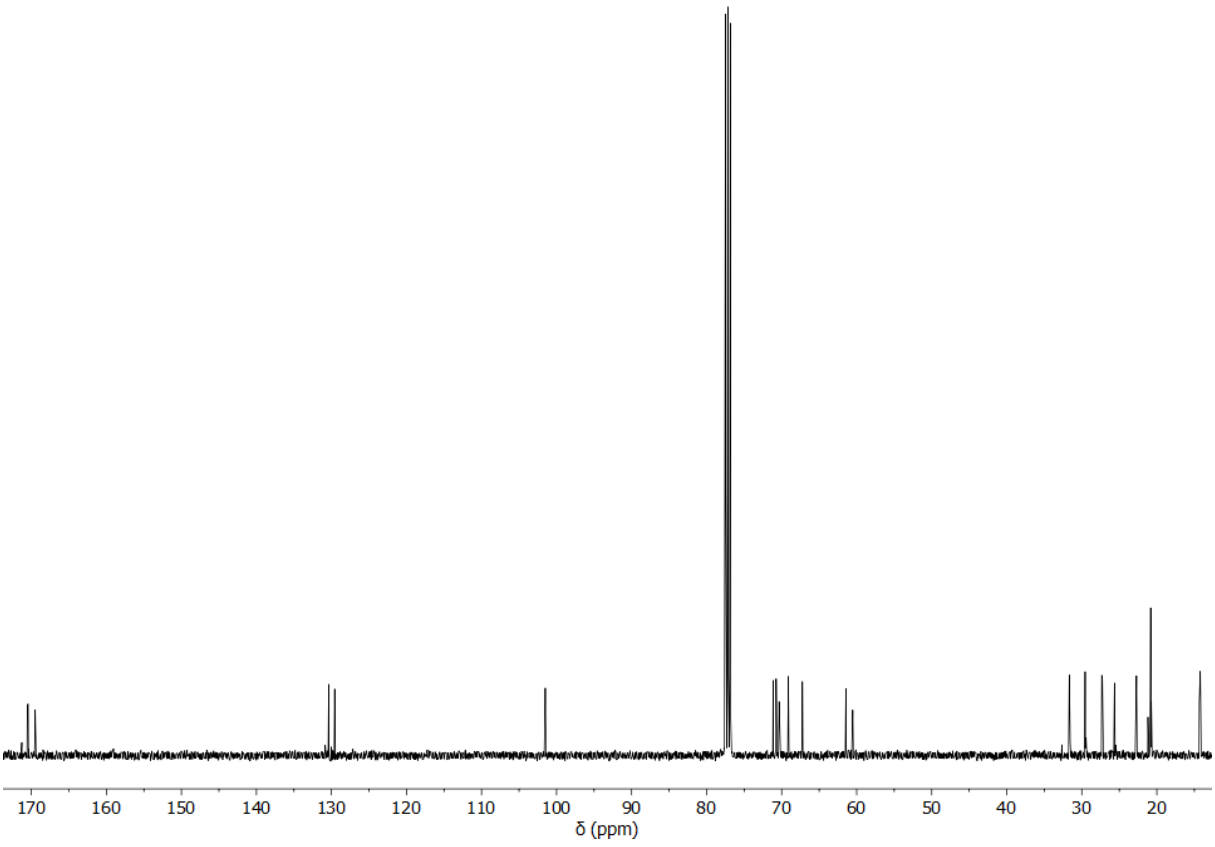


calcd (red) for $C_{26}H_{42}O_{10}Na$ $[M+Na]^+$: 537.2669;
found (black): 537.2742

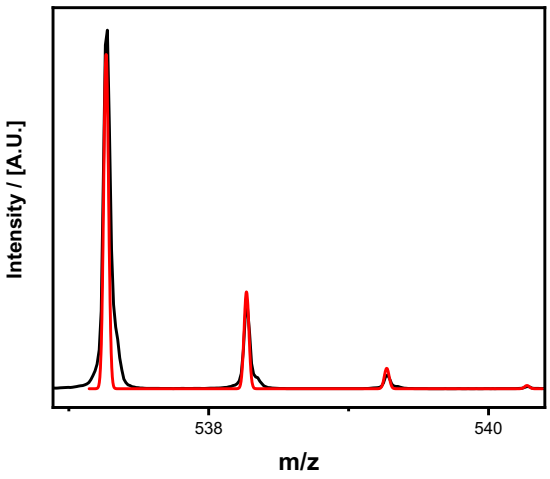
ESI-HRMS of **5α**



^{1}H NMR ($CDCl_3$, 400 MHz) of **5β**

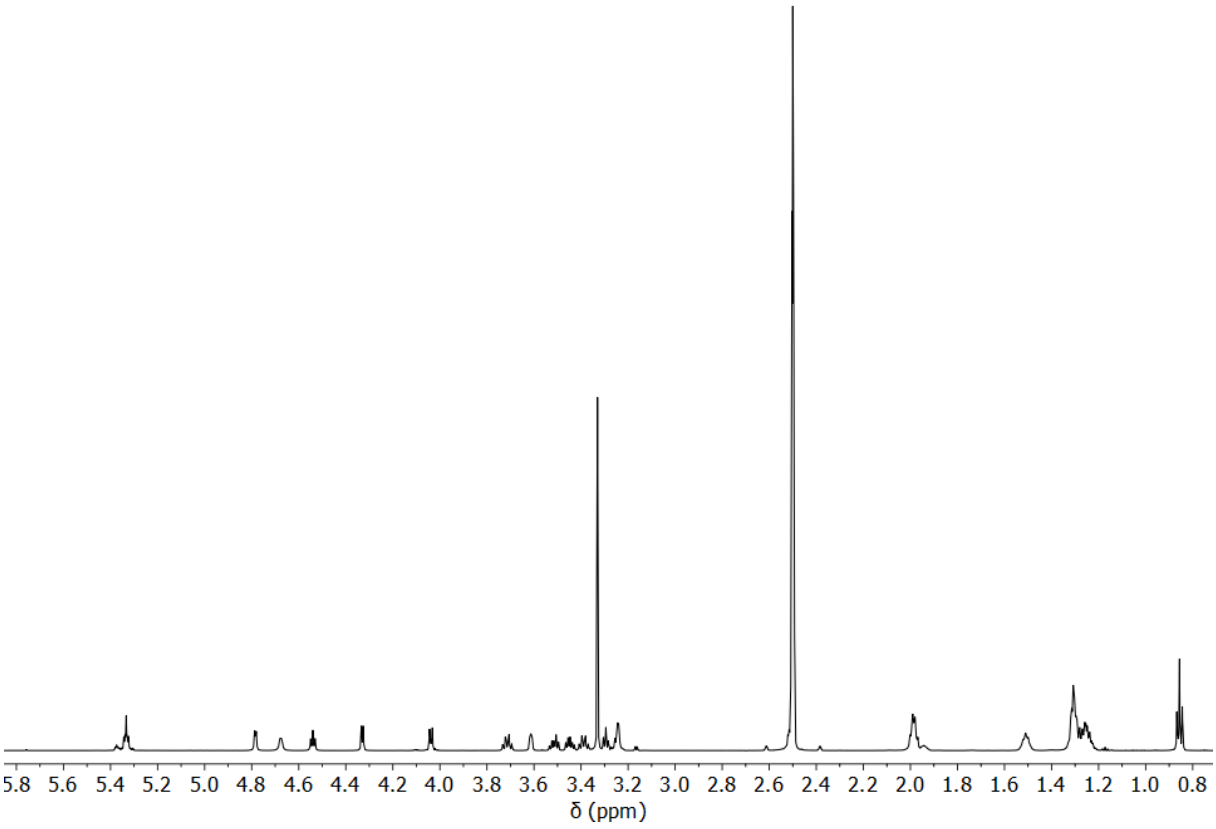


^{13}C NMR ($CDCl_3$, 100.5 MHz) of **5β**

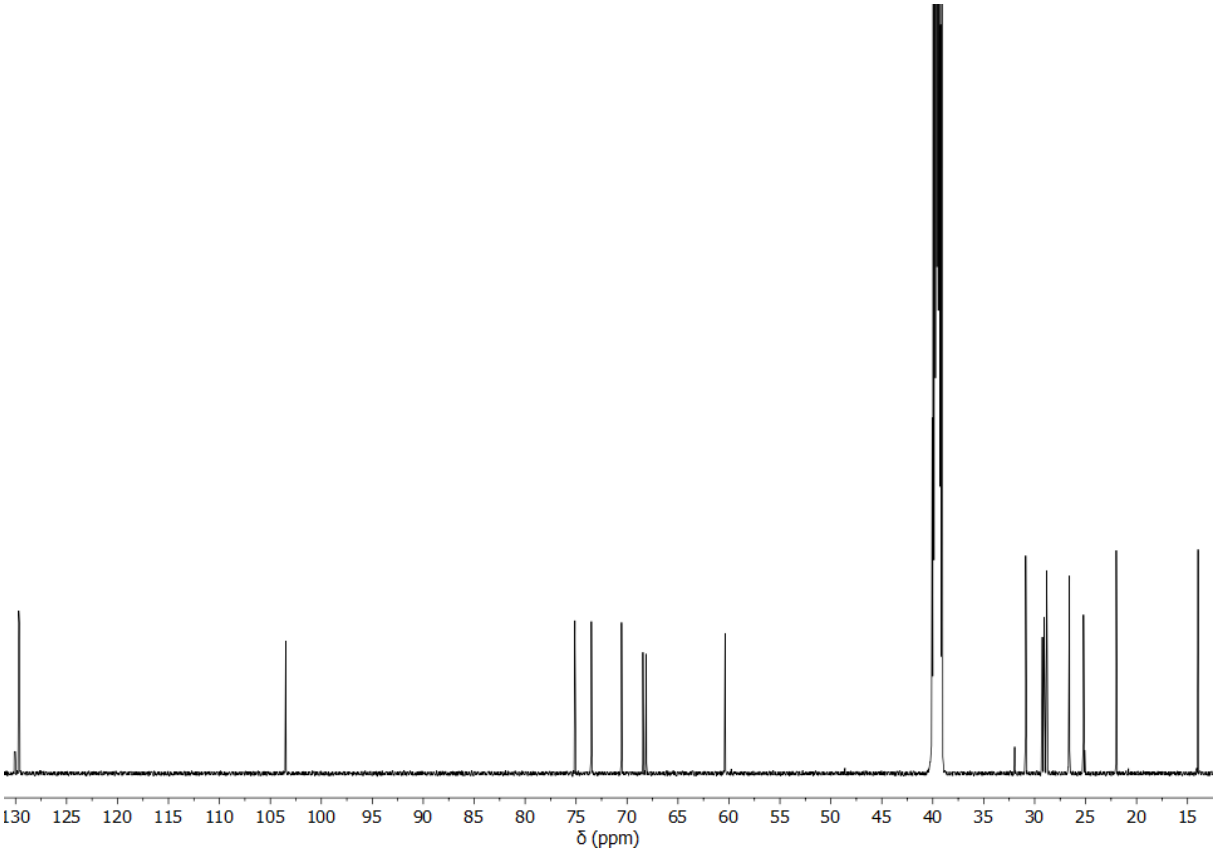


calcd (red) for $C_{26}H_{42}O_{10}Na$ $[M+Na]^+$: 537.2669;
found (black): 537.2761

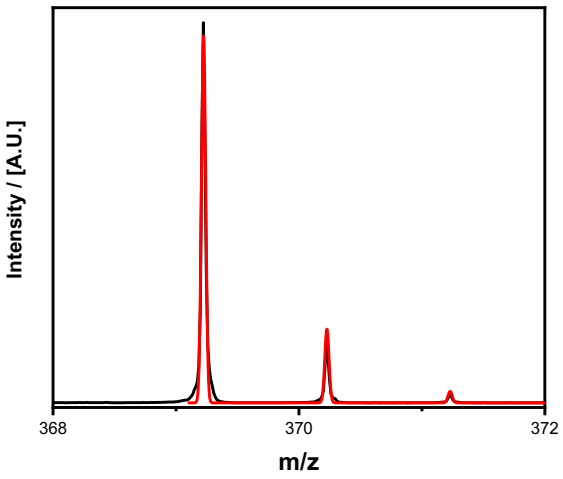
ESI-HRMS of **5β**



^{1}H NMR (DMSO-d$_6$, 600 MHz) of **GalαC$^{uns}_{12}$**

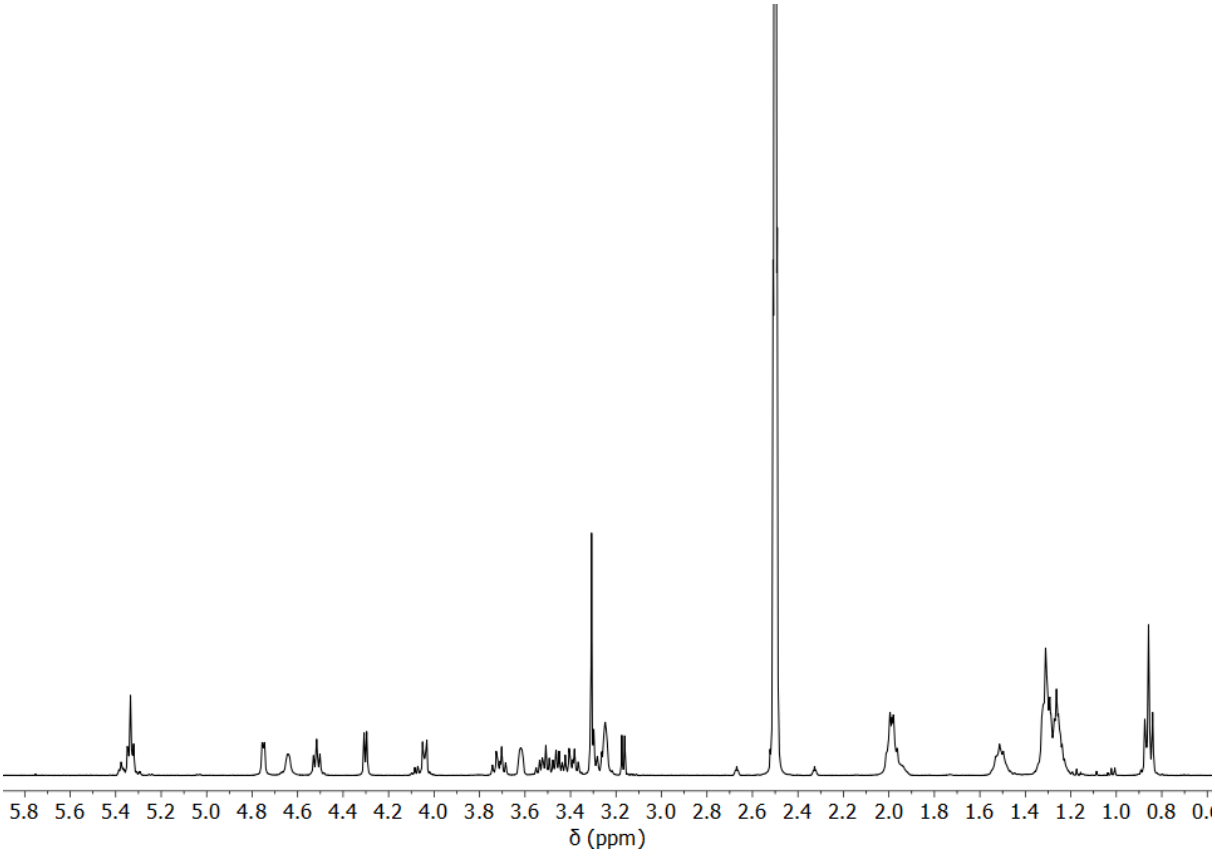


^{13}C NMR (DMSO-d$_6$, 151 MHz) of **GalαC$^{uns}_{12}$**

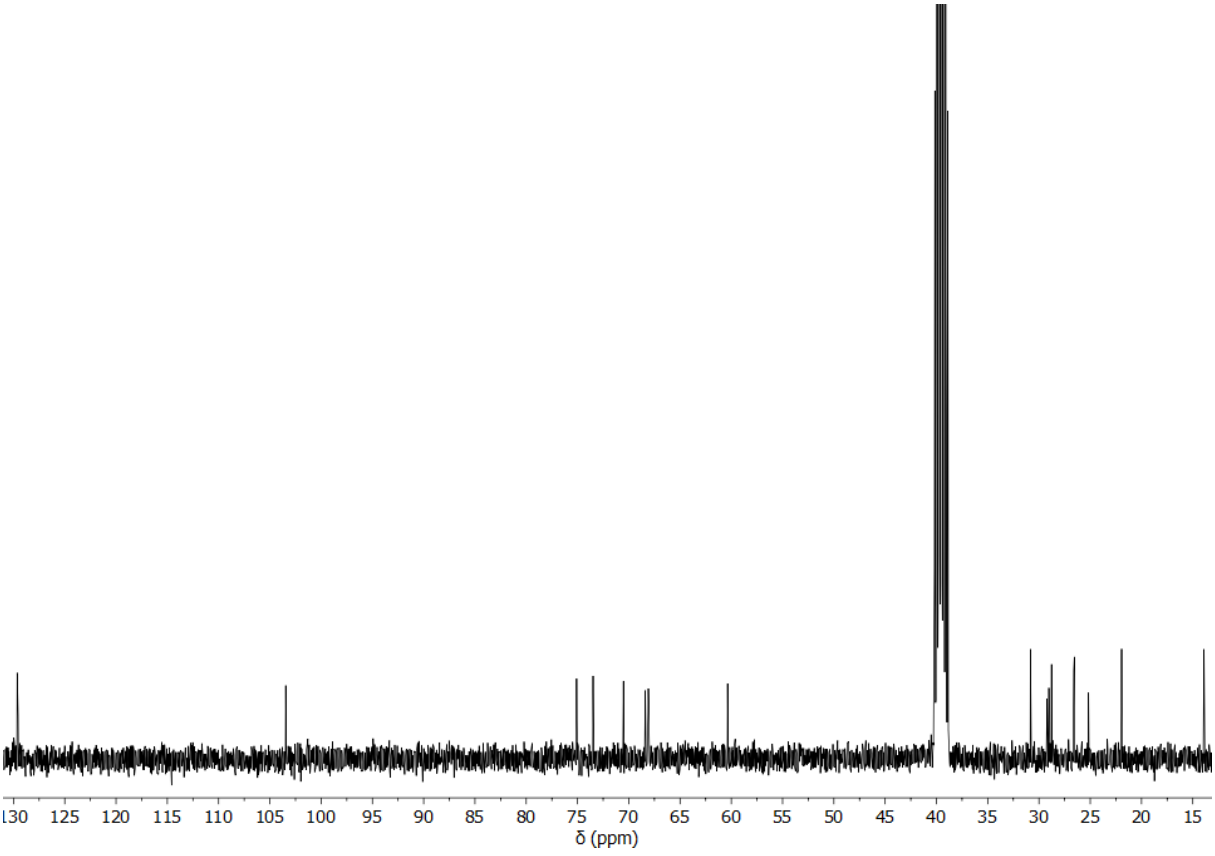


calcd (red) for $C_{18}H_{34}O_6Na$ $[M+Na]^+$: 369.2246;
found (black): 369.2226

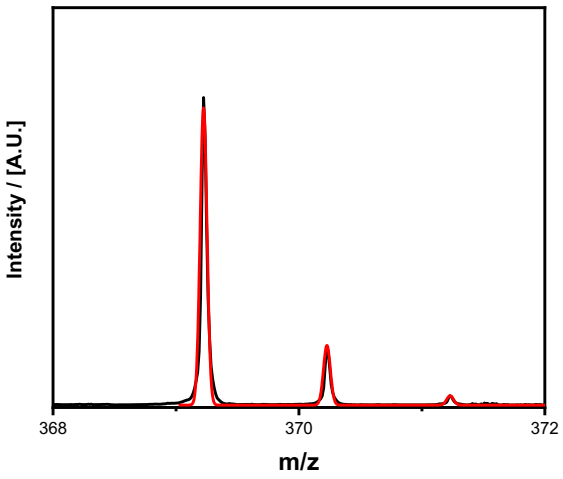
ESI-HRMS of **GalαC$^{uns}_{12}$**



^{1}H NMR (DMSO-d$_6$, 400 MHz) of **GalβC$^{uns}_{12}$**

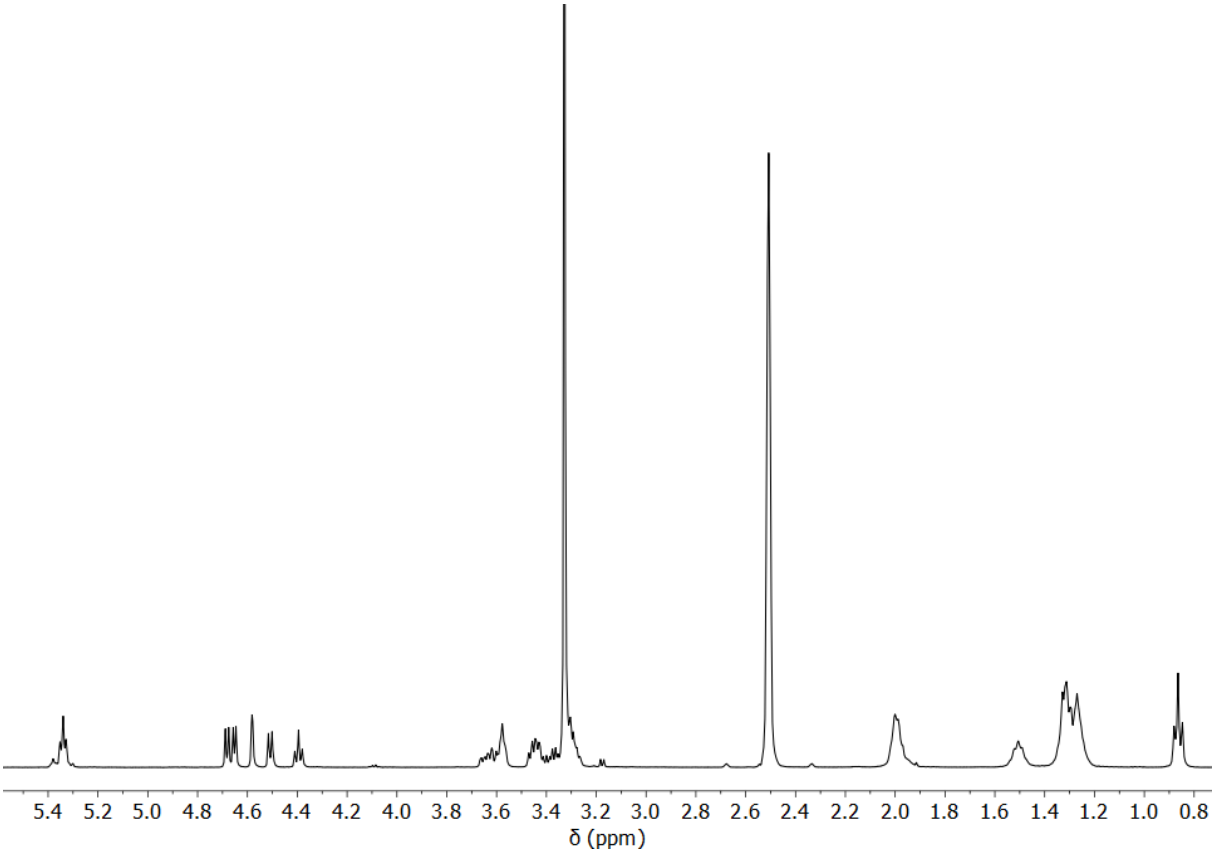


^{13}C NMR (DMSO-d$_6$, 100.5 MHz) of **GalβC$^{uns}_{12}$**

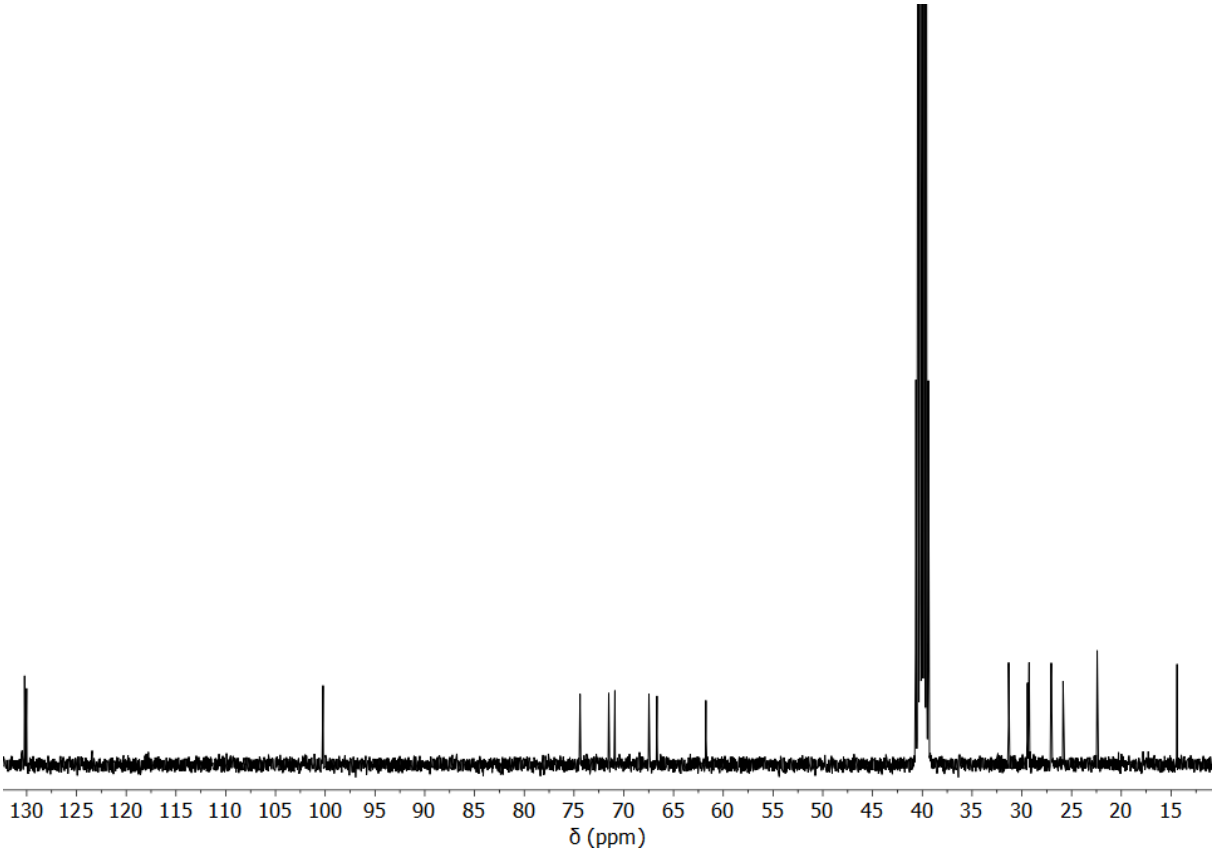


calcd (red) for $C_{18}H_{34}O_6Na$ $[M+Na]^+$: 369.2246;
found (black): 369.2250

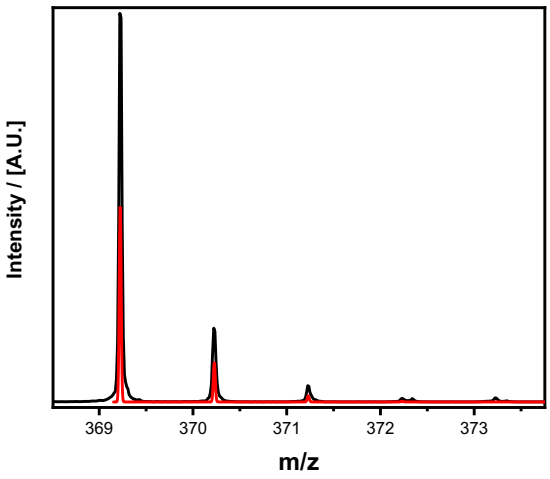
ESI-HRMS of **GalβC$^{uns}_{12}$**



^{1}H NMR (DMSO-d_6, 400 MHz) of **ManαC$^{uns}_{12}$**

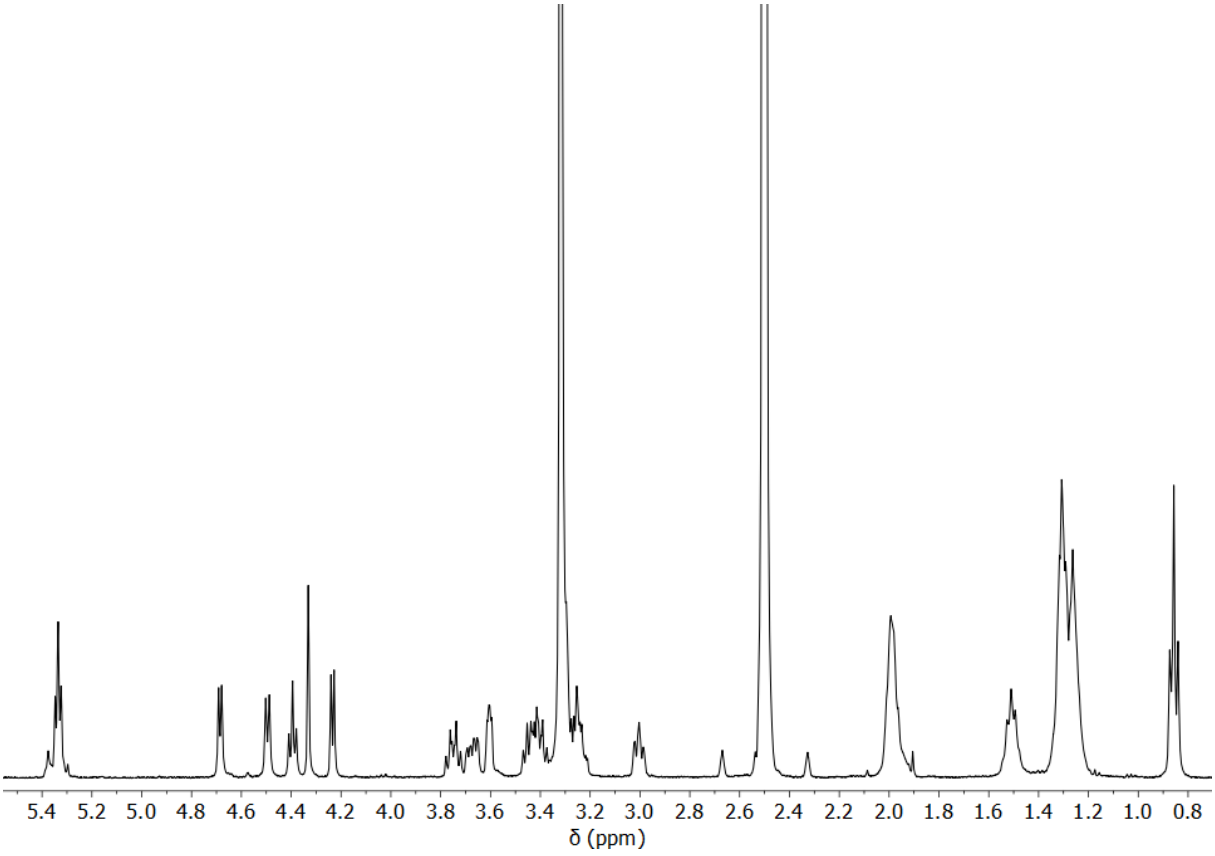


^{13}C NMR (DMSO-d_6, 100.5 MHz) of **ManαC$^{uns}_{12}$**

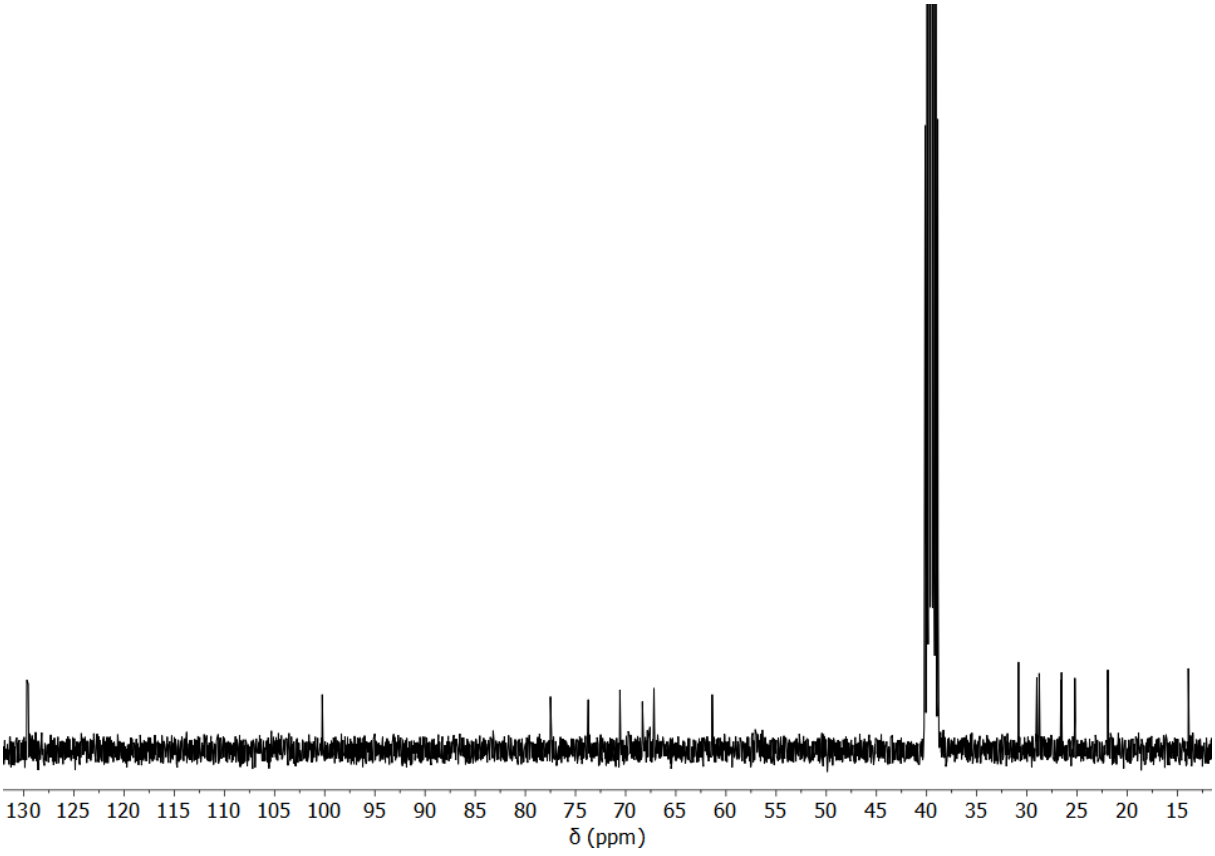


calcd (red) for $C_{18}H_{34}O_6Na$ $[M+Na]^+$: 369.2246;
found (black): 369.2208

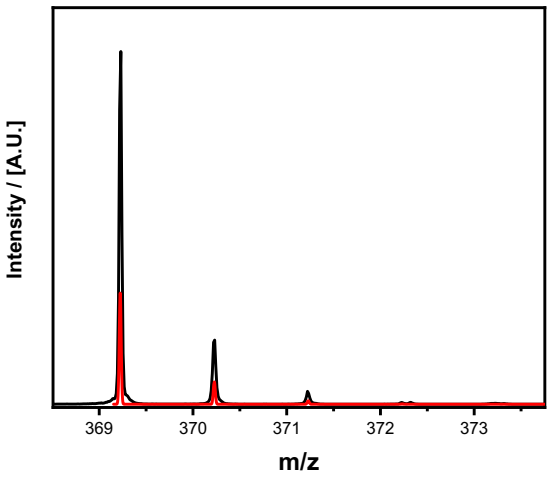
ESI-HRMS of **ManαC$^{uns}_{12}$**



^{1}H NMR (DMSO-d_6, 400 MHz) of **ManβC$^{uns}_{12}$**



^{13}C NMR (DMSO-d_6, 100.5 MHz) of **ManβC$^{uns}_{12}$**



calcd (red) for $C_{18}H_{34}O_6Na$ $[M+Na]^+$: 369.2246;
found (black): 369.2307

ESI-HRMS of **ManβC$^{uns}_{12}$**