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Synthesis of Oligosaccharides of the Linkage Region of Proteoglycans using Regioselective Glycosylation.

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Experimental procedures

2-Naphthylmethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (11): A mixture of donor 10[11] (10.5 g, 21.32 mmol), 2-naphthylmethanol (4.1 g, 25.9 mmol) in dry CH_2Cl_2 (100 mL) and 4 Å powdered molecular sieves (1.5 g) was stirred for 1 h at RT under dry argon then was cooled at 0 °C. TMSOTf (1.2 mL, 6.4 mmol) was added and the mixture was stirred for 40 min at 0°C, then was quenched with NEt_3 (7.8 mL), filtered and concentrated. Flash silica chromatography (petroleum ether/AcOEt 3:2 containing 0.1% of Et_3N) afforded the saccharide **11** (8.5 g, 82%) as a white foam. $[\alpha]_D$ = -18.3 (*c* = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7,84-7,39 (m, 7H, arom. H), 5,39 (dd, $J_{3,4}$ 3,0, $J_{4,5}$ < 1,0 Hz, 1H, H-4), 5,33-5,28 (m, 1H, H-2), 4,98 (dd, $J_{2,3}$ 10,0, $J_{3,4}$ 3,0 Hz, 1H, H-3), 4,92 (ABq, 2H, CH_2-Ar), 4,56 (d, $J_{1,2}$ 8,0 Hz, 1H, H-1), 4,26-4,19 (m, 2H, H-6a,b), 3,91-3,88 (m, 1H, H-5), 2,17, 2,07, 2,01, 1,97 (4s, 12H, OC(O)CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.53, 170.4, 170.24, 169.55 (4C, C=O), 134.36, 133.36, 133.26, 128.49, 128.06, 127.85, 127.53, 126.35, 126.33, 126.26 (10C, arom. C), 99.90 (1C, C-1), 71.07 (1C, C-3), 70.97 (1C, CH_2-Ar), 70.88 (1C, C-5), 69.03 (1C, C-2), 67.21 (1C, C-4), 61.47 (1C, C-6), 20.91, 20.82, 20.81, 20.70 (4C, C(O)O*C*H_3); ESI$^+$ HRMS [M+Na]$^+$ m/z 511.157468 calcd. for $C_{25}H_{28}NaO_{10}$, found: 511.157362.

2-Naphthylmethyl 3,4-*O*-isopropyliden-6-*O*-(2-methoxy-2-propyl)-β-D-galactopyranoside (13): A solution of **11** (7,9g, 16 mmol) in MeOH (150 mL) was treated for 3h with methanolic sodium methoxide (1M, 5mL), then was deionized with Amberlite IR-120[H+] resin, filtered, and concentrated to give quantitatively the corresponding tetrol **12**. ^{1}H NMR (400 MHz, CD_3OD): δ = 7,90-7,45 (m, 7H, arom. H), 4,80 (ABq, 2H, CH_2-Ar), , 4,38 (d, $J_{1,2}$ 7.5 Hz, 1H, H-1), 3.85 (dd, $J_{3,4}$ 3,0, $J_{4,5}$ < 1,0 Hz, 1H, H-4), 3.82-3.73 (m, 2H, H-6a,b), 3.66 (dd, $J_{1,2}$ 7.5, $J_{2,3}$ 9,5 Hz, H-2), 3.56 (m, 1H, H-5), 3.50 (dd, $J_{2,3}$ 9.5, $J_{3,4}$ 3,0 Hz, 1H, H-3). A mixture of the tetrol **12** (5.1 g, 15.6 mmol) and CSA (190 mg) in 2,2-dimethoxypropane (150 mL) was stirred for 60 h at rt. NEt_3 (2 mL) was added and the mixture was concentrated. Flash silica chromatography (CH_2Cl_2/acetone 12:1 containing 0.2% of Et_3N) afforded the saccharide **13** (4.47 g, 65%) as a white foam. $[\alpha]_D$ = -14.4 (*c* = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7,89-7,51 (m, 7H, arom. H), 4.95 (ABq, 2H, CH_2-Ar), 4.30 (d, $J_{1,2}$ 8.5 Hz, 1H, H-1), 4.18 (dd, $J_{3,4}$ 5.5, $J_{4,5}$ 2.0 Hz, 1H, H-4), 4.05 (dd, $J_{3,4}$ 5.5, $J_{2,3}$ 8.0Hz, 1H, H-3), 3.87 (m, 1H, H-5), 3.82-3.74 (m, 2H, H-6a,b), 3.68 (dd, $J_{1,2}$ 8.5, $J_{2,3}$ 8.0 Hz, 1H, H-2), 3.29 (s, 3H, OCH_3), 1.56, 1.43, 1.42, 1.36 (4s, 12H, C(CH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.36, 133.36, 133.26, 128.49, 128.06, 127.85, 127.53, 126.35, 126.33, 126.26 (10C, arom. C),110.27 (1C, *C*(CH$_3$)$_2$), 100.90 (1C, C-1), 100.32 (1C, *C*(CH$_3$)$_2$), 78.87 (1C, C-3), 73.97 (1C, C-2), 73.95 (1C, C-4), 72.86 (1C, C-5), 70.92 (1C, *C*H$_2$-Ar), 60.54 (1C, C-6), 48.72 (1C, O*C*H$_3$), 28.32, 26.40, 24.63, 24.57 (4C, C(*C*H$_3$)$_2$); HRMS [M+Na]$^+$ m/z 455.204024 calcd. for $C_{24}H_{32}NaO_7$, found: 455.204473.

2-Naphthylmethyl 2-*O*-benzoyl-3,4-*O*-isopropylidene-6-*O*-(2-methoxy-2-propyl)-β-D-galactopyranoside (14): BzCl (0.5 mL, 4.16 mmol) was added to a solution of saccharide **13** (1 g, 2.77 mmol) in CH_2Cl_2/Pyridine (3:1, 40 mL) cooled a 0°C. The reaction mixture was stirred for 1 h at rt and then quenched with MeOH, diluted with CH_2Cl_2 and washed with water, sat. $NaHCO_3$ and water. The organic phase was dried ($MgSO_4$) and concentrated. Flash silica chromatography (petroleum ether/ AcOEt 2:1 containing 0.2% of Et_3N) afforded the saccharide **14** (745 mg, 60%) as a white foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03-7.30 (m, 12H, arom. H), 5.36 (dd, $J_{1,2}$ 8.5, $J_{2,3}$ 7.0 Hz, 1H, H-2), 4.95 (ABq, 2H, CH_2-Ar), 4.50 (d, $J_{1,2}$ 8.5 Hz, 1H, H-1), 4.25 (dd, $J_{3,4}$ 5.5, $J_{2,3}$ 7.0 Hz, 1H, H-3), 4.22 (dd, $J_{3,4}$ 5.5, $J_{4,5}$ 2.0 Hz, 1H, H-4), 3.89 (m, 1H, H-5), 3.86-3.74 (m, 2H, H-6a,b), 3.29 (s, 3H, OCH_3), 1.65, 1.43, 1.41, 1.34 (4s, 12H, C(CH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.55 (1C, C=O), 134.63, 133.27, 133.15, 130.19, 130.06, 128.42, 128.23, 127.99, 127.76, 126.86, 126.17, 126.05, 125.98 (14C, arom. C),110.69, 100.37 (2C, *C*(CH$_3$)$_2$), 98.70 (1C, C-1), 77.35 (1C, C-3), 74.08 (1C, C-4), 73.81 (1C, C-2), 72.64 (1C, C-5), 69.99 (1C, CH_2-Ar), 60.50 (1C, C-6), 48.77 (1C, OCH3), 27.93, 26.46, 24.65, 24.59 (4C, C(*C*H$_3$)$_2$).

2-Naphthylmethyl 2-*O*-benzoyl-4,6-*O*-di-*tert*-butylsilylene-β-D-galactopyranoside (15): A solution of **14** (500 mg, 0.76 mmol) in AcOH/$H_2$0 (2:1, 50 mL) was heated at 100°C for 20 min then was diluted with water, concentrated, evaporated with water (3 x 10 mL) and dried to give quantitatively the corresponding triol. Di-*tert*-butylsilylditriflate (0.37 mL, 1.14 mmol) was added at 0°C to a suspension of the triol and 2,6-lutidine (307 µL, 2.65 mmol) in CH_2Cl_2 (30 mL) and the mixture was stirred for 3h at 0°C. The solution was washed with water, HCl 1M, sat. $NaHCO_3$ and

water. The organic phase was dried ($MgSO_4$) and concentrated. Flash silica chromatography (petroleum ether/ AcOEt 4:1) afforded the saccharide **15** (420 mg, 80%) as a yellowish foam. $[\alpha]_D$ = +20.1 (*c* = 1.02 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11-7.18 (m, 12H, arom. HAr), 5.52 (dd, $J_{1,2}$ 8.5, $J_{2,3}$ 10.0 Hz, 1H, H-2), 4.95 (ABq, 2H, CH_2-Ar), 4.63 (d, $J_{1,2}$ 8.5 Hz, 1H, H-1), 4.46 (dd, $J_{3,4}$ 3.5, $J_{4,5}$ <1.0 Hz, 1H, H-4), 4.41-4.31 (m, 2H, H-6a,b), 3.73-3.64 (m, 1H, H-3), 3.49-3.46 (m, 1H, H-5), 2.83 (d, $J_{3,OH}$ 11.0 Hz, 1H, O*H*), 1.12, 1.07 (2s, 18H, C(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.39 (1C, C=O), 134.95, 133.21, 133.16, 133.04, 130.14, 130.03, 128.41, 128.16, 127.92, 127.73, 126.56, 126.12, 125.97, 125.84 (16C, arom. C), 99.24 (1C, C-1), 73.12 (1C, C-4), 72.95 (1C, C-2), 72.88 (1C, CH-3), 71.54 (1C, C-5), 70.13 (1C, CH_2-Ar), 66.96 (1C, C-6), 27.60 (6C, C(*C*H$_3$)$_3$), 23.50, 20.93 (2C, *C*(CH$_3$)$_3$); HRMS $[M+H]^+$ m/z 565.261607 calcd. for $C_{32}H_{41}O_7Si$, found: 565.262216.

2-Naphthylmethyl *O*-(methyl 2,3-di-*O*-benzoyl-4-*O*-levulinoyl-β-D-glucopyranosyluronate)-(1→3)-2-*O*-benzoyl-4,6-*O*-di-*tert*-butylsilylene-β-D-galactopyranoside (17): <u>From **15**</u>: A mixture of imidate **16**[4f] (606 mg, 0.92 mmol) and alcohol **15** (401 mg, 0.71 mmol) in dry CH_2Cl_2 (7 mL) and 4 Å powdered molecular sieves (0.5 g) was stirred for 1 h at RT under dry argon then was cooled at 0 °C. $BF_3.Et_2O$ (185 μL, 0,18 mmol) was added and the mixture was stirred for 1h from 0°C to rt, then was quenched with NEt_3 (0.3 mL), filtered and concentrated. Flash silica chromatography (petroleum ether/AcOEt 1:1 containing 0.1% of Et_3N) afforded the disaccharide **17** (655 mg, 87%) as a white foam. <u>From **19**:</u> Disaccharide **19** (143 mg, 0.15 mmol) was submitted to the same procedure as described for the preparation of **14** (with an overnight stirring). Flash silica chromatography (petroleum ether/AcOEt 1:1) afforded the disaccharide **17** (151 mg, 95%) as a white foam. $[\alpha]_D$ = +74.6 (*c* = 1.02 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83-7.07 (m, 22H, arom. H), 5.63 (dd, 1H, $J_{1,2}$ = $J_{2,3}$ = 8.0 Hz, Gal H-2), 5.51 (dd, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, GlcA H-3), 5.45-5.38 (m, 2H, GlcA H-2, H-4), 5.01 (d, 1H, $J_{1,2}$ = 7.5 Hz, GlcA H-1), 4.84 (ABq, 2H, CH_2Ar), 4.66 (dd, 1H , $J_{3,4}$ = 3.0, $J_{4,5}$ < 1.0 Hz, Gal H-4), 4.49 (d, 1H, $J_{1,2}$ = 8.0 Hz, Gal H-1), 4.30-4.29 (m, 2H, Gal H-6a,b), 4.10 (d, 1H, $J_{4,5}$ = 9.5 Hz, GlcA H-5), 3.86 (dd, 1H, $J_{2,3}$ = 8.0, $J_{3,4}$ = 3.0 Hz, Gal H-3), 3.74 (s, 3H, OCH_3), 3.41-3.40 (m, 1H, Gal H-5), 2.62-2.30 (m, 4H, CH_2CO), 2.04 (s, 3H, COCH_3), 1.09,1.07 (2s, 18H, C(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.75, 171.13, 167.10, 165.65, 164.81, 164.75 (6C, GlcA C-6, C=O), 134.80, 133.42, 133.10, 132.91, 132.85, 132.79, 129.90, 129.83, 129.68, 129.61, 128.89, 128.81, 128.40, 128.34, 128.06, 128.00, 127.86, 127.64, 126.53, 125.98, 125.84, 125.83 (28C, arom. C), 101.50 (1C, GlcA C-1), 99.47 (1C, Gal C-1), 79.70 (1C, Gal C-3), 72.90 (2C, Gal C-4, C-5), 72.50 (1C, GlcA C-3), 71.77 (1C, GlcA C-2), 71.60 (1C, GlcA C-5), 70.73 (1C, Gal C-2), 69.86 (Ar-*C*H$_2$), 69.74 (1C, GlcA C-4), 67.04 (1C, Gal C-6), 53.05 (1C, OCH$_3$), 37.69, 27.76 (2C, *C*H$_2$CO), 29.63 (1C, CO*C*H$_3$), 27.59, 27.53, 27.49 (6C, C(*C*H$_3$)$_3$), 23.47, 20.80 (2C, *C*(CH$_3$)$_3$); HRMS $[M+Na]^+$ m/z 1083.380498 calcd. for $C_{58}H_{64}NaO_{17}Si$, found: 1083.380188.

2-Naphthylmethyl 4,6-O-di-*tert*-butylsilylene-β-D-galactopyranoside (18): Tetrol **12** (1.2 g, 3.74 mmol) was treated as described for the preparation of **15**. Flash silica chromatography (petroleum ether/AcOEt 4:1) gave the compound **18** (1.62 g, 94% yield). $[\alpha]_D$ = +2.1 (*c* = 1.02 in $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92-7.32 (m, 7H, arom. H), 4.95 (ABq, 2H, CH_2Ar), 4.40 (m, 2H, H-1, H-5), 4.29 (m, 2H, H-6a,b), 3.77 (dd, $J_{1,2}$ = 8.5, $J_{2,3}$ 11.0 Hz, 1H, H-2), 3.52 (m, 1H, H-3), 3.44 (m, 1H, H-4), 2.65 (d, $J_{OH,3}$ = 10.5 Hz, 1H, O*H*), 2.52-2.38 (m, 1H, O$H_{(2)}$), 1.08, 1.07 (2s, 18H, C(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$); δ = 134.94, 133.38, 133.22, 128.38, 128.05, 127.86, 127.11, 126.29, 126.16 (10C, arom. C), 101.84 (1C, C-1), 74.02 (1C, C-3), 72.75 (1C, C-5), 72.39 (1C, C-2), 71.66 (1C, C-4), 70.94 (1C, *C*H$_2$-Ar), 67.09 (1C, *C*H$_2$-6), 27.64, 27.54 (6C, C(*C*H$_3$)$_3$), 23.52, 20.95 (2C, *C*(CH$_3$)$_3$).
HRMS $[M+Na]^+$ m/z 483,217336 calcd. for $C_{25}H_{36}NaO_6Si$, found : 483,216817.

2-Naphthylmethyl *O*-(methyl 2,3-di-*O*-benzoyl-4-*O*-levulinoyl-β-D-glucopyranosyluronate)-(1→3)-2,6-di-*O*-benzoyl-β-D-galactopyranoside (23): A mixture of **21** (97 mg, 0.105 mmol) and benzoyl cyanide (28 mg, 0.214 mmol) in pyridine (1.5 mL) was stirred overnight at rt. Methanol was added and the mixture was diluted in dichloromethane, washed with water and $NaHCO_3$. The organic phases were dried with $MgSO_4$, filtered and concentrated. Flash silica chromatography (CH_2Cl_2/Acetone 12:1) gave **23** (81 mg, 75%) as a white powder. Mp = 231 °C (from hot EtOAc); $[\alpha]_D$ = +49.9 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.14-7.08 (m, 27H, arom. H), 5.62-5.54 (m, 2H, Gal H-2, GlcA H-3), 5.46-5.36 (m, 2H, GlcA H-2, H-4), 4.95-4.91 (d, 1H, $J_{1,2}$ = 7.0 Hz, GlcA H-1), 4.84 (ABq, 2H, Ar-CH_2), 4.79-4.70 (m, 2H, Gal H-6a,b), 4.48 (d, 1H, $J_{1,2}$ = 8.0 Hz, Gal H-1), 4.27 (dd, 1H, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1.0 Hz, Gal H-4), 4.18 (d, 1H, $J_{4,5}$ = 9.5 Hz, GlcA H-5), 3.93-3.86 (m, 2H, Gal H-3, H-5), 3.71 (s, 3H, OCH_3), 3.09 (bs, 1H, O*H*), 2.61-2.30 (m, 4H, CH_2CO), 2.03 (s, 3H, COCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.61, 171.14, 167.02, 166.38, 165.48, 164.63, 164.58 (7C, GlcA C-6, *C*=O), 134.24, 133.44, 133.26, 132.89, 132.74, 129.90, 129.85, 129.82, 129.77, 129.58, 129.54, 129.47, 128.55, 128.51, 128.48, 128.45, 128.38, 128.17, 128.08, 127.79, 127.54, 126.82, 125.93, 125.85 (34C, arom. C), 101.28 (1C, GlcA C-1), 98.70 (1C, Gal C-1), 80.97, 72.12 (2C, Gal C-3, GlcA C-5), 72.39 (1C, Gal C-5), 71.77, 70.52 (2C, Gal C-2, GlcA C-3), 71.31, 69.29 (2C, GlcA C-2, C-4), 69.62 (Ar-*C*H$_2$), 68.41 (1C, Gal C-4), 63.53 (1C, Gal C-6), 53.13 (1C, OCH$_3$), 37.62, 27.71 (2C, *C*H$_2$CO), 29.56 (1C, CO*C*H$_3$); HRMS $[M+Na]^+$ calcd for $C_{57}H_{52}NaO_{18}$ 1047.304586, found:1047.304732;

2-Naphthylmethyl *O*-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-2-*O*-benzoyl-4,6-*O*-di-*tert*-butylsilylene-β-D-galactopyranoside (25): A freshly prepared solution of pyridine/acetic acid/hydrazine (12: 8: 1, 2.5 mL) was added to a solution of disaccharide **17** (250 mg, 0,236 mmol) in pyridine (2,5 mL) and the mixture was stirred for 8 min at rt then was diluted with CH_2Cl_2 (50 mL), washed with water, saturated $NaHCO_3$ solution and water, dried ($MgSO_4$) and concentrated. Flash silica chromatography (petroleum ether/AcOEt 3:2) afforded **25** as a white solid (199 mg, 88%). $[\alpha]_D$ = +42.1 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$)**:** δ =7.92-7.04 (m, 22H, arom. H), 5.63 (dd, $J_{1,2} = J_{2,3}$ = 8.5Hz, 1H, Gal H-2), 5.41 (dd, $J_{1,2}$ = 7.5, $J_{2,3}$ = 9.0Hz, 1H, GlcA H-2), 5.29 (dd, $J_{2,3} = J_{3,4}$ = 9.0 Hz, 1H, GlcA H-3), 4.97 (d, $J_{1,2}$ = 7.5 Hz, 1H, GlcA H-1), 4.81 (ABq, 2H, CH_2-Ar), 4.69 (dd, 1H, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1.0 Hz, Gal H-4), 4.50 (d, $J_{1,2}$ = 8.5 Hz, 1H, Gal H-1), 4.30 (s, 2H, Gal H-6a,b), 4.19 (m, 1H, GlcA H-4), 3.98 (d, $J_{4,5}$ = 10.0 Hz, 1H, GlcA H-5), 3.86 (dd, 1H, $J_{2\text{-}3}$ = 10.0, $J_{3,4}$ = 3.0 Hz, Gal H-3), 3.81 (s, 3H, OCH_3), 3.38 (m, 2H, Gal H-5, OH), 1.08,1.05 (2s, 18H, C(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.00, 166.98, 164.97, 164.89 (4C, GlcA C-6, C=O) 134.87, 133.57, 133.16, 132.98, 132.93, 132.87, 130.07, 129.91, 129.74, 129.66, 129.00, 128.95, 128.49, 128.41, 128.14, 128.07, 127.92, 127.71, 126.61, 126.04, 125.91 (28C, arom.C), 101.72 (1C, GlcA C-1), 99.49 (1C, Gal C-1), 79.78 (1C, Gal C-3), 75.67 (1C, GlcA C-3), 74.70 (1C, GlcA C-5), 72.90 (1C, Gal C-4), 71.66 (1C, Gal C-5), 71.37 (1C, GlcA C-2), 70.85 (1C, GlcA C-4), 70.63 (1C, Gal C-2), 69.89 (1C, *C*H$_2$-Ar), 67.14 (1C, Gal C-6), 53.00 (1C, O*C*H$_3$), 27.61 (6C, C(*C*H$_3$)$_3$), 23.51, 20.84 (2C, *C*(CH$_3$)$_3$); HRMS [M+Na]$^-$ calcd for $C_{53}H_{58}NaO_{15}Si$ 985.344273, found: 985.343553

2-Naphthylmethyl *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-trichloroacetamido-β-D-galactopyranosyl-(1→4)-*O*-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-2-*O*-benzoyl-4,6-*O*-di-*tert*-butylsilylene-β-D-galactopyranoside (27): A mixture of imidate **26**[15] (160 mg, 0.27 mmol) and disaccharide **25** (199 mg, 0.21 mmol) in dry CH_2Cl_2 (2.5 mL) and 4 Å powdered molecular sieves (0.3 g) was stirred for 30 min at RT under dry argon. A solution of TMSOTf in toluene (1M, 67 μL) was added and the mixture was stirred for 45 min at rt, then was quenched with NEt_3 (0.5 mL), filtered and concentrated. Flash silica chromatography (petroleum ether/AcOEt 1:1 containing 0.1% of Et_3N) afforded the trisaccharide **27** (235 mg, 82%) as a white foam. $[\alpha]_D$ = +13.6 (*c* 0.97 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$)**:** δ = 7.89-6.99 (m, 22H, arom. H), 6.65 (d, J_{2NH} 8.5 Hz, 1H, NH), 5.61 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 9.5 Hz, 1H, Gal H-2), 5.49 (dd, $J_{2,3} = J_{3,4}$ = 9.5 Hz, 1H, GlcA H-3), 5.39 (dd, $J_{1,2}$ = 8.5, $J_{2,3}$ = 9.5 Hz, 1H, GlcA H-2), 5.11 (m, 1H, GlcA H-4), 5.08 (dd, $J_{2,3}$ = 10.0, $J_{3,4}$ = 3.5 Hz, 1H, GalN H-3), 4.97 (d, $J_{1,2}$ = 7.5 Hz, 1H, GlcA H-1), 4.84 (ABq, 2H, Ar-CH_2), 4.86 (d, $J_{1,2}$ = 8.5 Hz, 1H, GalN H-1), 4.64 (m, 1H, Gal H-4), 4.49 (d, $J_{1,2}$ = 8.0 Hz, 1H, Gal H-1), 4.31-4.27 (m, 2H, GalN H-6a,b), 4.24 (m, 1H, GlcA H-4), 4.02 (d, $J_{4,5}$ = 9.5 Hz, 1H, GlcA H-5), 3.90 (ddd, $J_{1,2} = J_{2,NH}$ = 8.5, $J_{2\text{-}3}$ = 10.0 Hz, 1H, GalN H-2), 3.82 (dd, $J_{2,3}$ = 9.5, $J_{3,4}$ = 3.0 Hz, 1H, Gal H-3), 3.78 (s, 3H, OCH_3), 3.67-3.62 (m, 1H, Gal H-5), 3.44-3.39 (m, 1H, GalN H-5), 3.21 (m, 2H, Gal H-6a,b), 2.00, 1.95, 1.92 (3s, 9H, OC(O)CH_3), 1.10, 1.05 (2s, 18H, C(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.31, 170.11, 170.01, 168.82, 165.36, 164.97, 164.82, 161.70 (8C, GlcA C-6, *C*=O), 134.82, 133.31, 133.15, 132.98, 132.88, 132.81, 129.89, 129.73, 129.61, 128.94, 128.39, 128.33, 128.12, 128.07, 127.90, 127.71, 126.61, 126.05, 125.92, 125.88 (28C, arom. C), 102.25 (1C, GlcA C-1), 99.93 (1C, GalN C-1), 99.50 (1C, Gal C-1), 80.47 (1C, Gal C-3), 76.19 (1C, GlcA C-4), 73.94 (1C, GlcA C-5), 72.88 (1C, Gal C-4), 72.54 (1C, GlcA C-3), 71.62 (1C, GalN C-5), 71.33 (1C, GlcA C-2), 70.91 (1C, Gal C-5), 70.58 (1C, Gal C-2), 69.90 (1C, GalN C-3), 69.86 (Ar-*C*H$_2$), 67.20 (1C, GalN C-6), 66.27 (1C, GalN C-4), 60.28 (1C, Gal C-6), 53.31 (O*C*H$_3$), 53.07 (1C, GalN C-2), 27.65, 27.56 (6C, C(*C*H$_3$)$_3$), 23.56, 20.87 (2C, *C*(CH$_3$)$_3$), 20.79, 20.58, 20.55 (3C, OC(O)*C*H$_3$); HRMS [M+H]$^+$ calcd for $C_{67}H_{75}Cl_3NO_{23}Si$ 1394.355924, found: 1394.355047.

2-Naphthylmethyl *O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-*O*-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-2-*O*-benzoyl-4,6-*O*-di-*tert*-butylsilylene-β-D-galactopyranoside (28): A solution of trisaccharide **27** (114 mg, 0.082 mmol) in acetic acid (1.5 mL) was heated at 50°C under Ar. Zn-Cu couple (155 mg, 1.21 mmol) was then added in five portions at 1 h intervals and then stirred for 20 h at 55°C. The mixture was then cooled, filtered through a Celite pad and concentrated. Flash silica chromatography (CH_2Cl_2/MeOH 19:1) gave the trisaccharide **28** (89 mg, 84%) as a white powder. $[\alpha]_D$ = +19.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87-7.02 (m, 22H, arom. H), 5.63 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0 Hz, Gal H-2), 5.50-5.44 (m, 2H, GlcA H-3, NH), 5.38 (dd, 1H, $J_{1,2} = J_{2,3}$ = 7.0 Hz, GlcA H-2), 5.13-5.06 (m, 2H, GalN H-3, H-4), 5.00 (d, 1H, $J_{1,2}$ = 7.0 Hz, GlcA H-1), 4.84 (ABq, 2H, Ar-CH_2), 4.66 (d, 1H, $J_{1,2}$ = 8.0 Hz, GalN H-1), 4.62 (dd, 1H, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1.0 Hz, Gal H-4), 4.48 (d, 1H, $J_{1,2}$ = 8.0 Hz, Gal H-1), 4.29-4.24 (m, 3H, Gal H6a,b, GlcA H-4), 4.07 (d, 1H, $J_{4\text{-}5}$ = 10.0 Hz, GlcA H-5), 3.83-3.78 (m, 4H, Gal H-3, OCH_3), 3.78-3.67 (m, 1H, GalN H-2), 3.52 (m, 1H, GalN H-5), 3.41 (m, 1H, Gal H-5), 3.29-3.25 (m, 2H, GalN H-6a,b), 1.92, 1.91, 1.90, 1.89 (4s, 12H, OC(O)CH_3, NHC(O)CH_3), 1.11, 1.07 (2s, 18H, (CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.47, 170.41, 170.14, 170.08, 168.27, 165.27, 164.93, 164.87 (8C, GlcA C-6, *C*=O), 134.80, 133.33, 133.13, 132.96, 132.84, 132.81, 129.86, 129.70, 129.62, 128.93, 128.37, 128.35, 128.09, 128.05, 127.89, 127.69, 126.57, 126.02, 125.89, 125.85 (28C, arom. C), 102.04 (1C, GlcA C-1), 100.53 (1C, GalN C-1), 99.53 (1C, Gal C-1), 80.38 (1C, Gal C-3), 76.60 (1C, GlcA C-4), 74.39 (1C, GlcA C-5), 72.93 (1C, Gal C-4), 72.72 (1C, GlcA C-3), 71.56 (2C, GlcA C-2, GalN C-5), 70.54 (1C, Gal C-5), 70.52 (1C, Gal C-2), 69.92 (1C, GalN C-3), 69.88 (1C, Ar-*C*H$_2$), 67.12 (1C, Gal C-6), 66.21 (1C, GalN C-4), 60.34 (1C, GalN C-6), 53.19 (1C, O*C*H$_3$), 51.73 (1C, GalN C-2), 27.64, 27.57 (6C, C(*C*H$_3$)$_3$), 23.56, 20.86

(2C, *C*(CH_3)$_3$), 23.48 (1C, NHC(O)*C*H_3), 20.73, 20.71, 20.61 (3C, OC(O)*C*H_3) ppm; HRMS [M+H]$^+$ calcd for $C_{67}H_{78}NO_{23}Si$ 1292.472841, found: 1292.471422.

2-Naphthylmethyl *O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-*O*-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-2-*O*-benzoyl-β-D-galactopyranoside (29): Compound **28** (137 mg, 0106 mmol) was treated as described for the preparation of **21**. Flash silica chromatography (CH_2Cl_2/acetone 17:1) afforded the diol **29** (78 mg, 64%) as a white foam. $[\alpha]_D$ = +23.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87-7.07 (m, 22H, arom. H), 6.02 (d, $J_{NH\text{-}2}$ = 8.5 Hz, 1H, NH), 5.58 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0 Hz, Gal H-2), 5.54 (dd, $J_{2,3}$ = 7.5, $J_{3,4}$ = 8.5 Hz, 1H, GlcA H-3), 5.38 (dd, $J_{1,2}$ = 7.0, $J_{2,3}$ = 7.5 Hz, 1H, GlcA H-2), 5.07 (m, 1H, GalN H-4), 5.05 (m, 1H, GalN H-3), 4.96 (d, $J_{1,2}$ 7.0 Hz, 1H, GlcA H-1), 4.86 (ABq, 2H, Ar-CH2), 4.75 (d, $J_{1,2}$ = 8.5 Hz, 1H, GalN H-1), 4.54 (d, $J_{1,2}$ 8.0 Hz, 1H, Gal H-1), 4.47 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, 1H, GlcA H-4), 4.27 (m, 1H, Gal H-4), 4.23 (d, $J_{4,5}$ = 9.0 Hz, 1H, GlcA H-5), 4.08-4.01 (m, 2H, Gal H-6a,b), 3.95 (m, 1H, GalN H-2), 3.88 (m, 1H, Gal H-3), 3.84 (s, 3H, OCH_3), 3.63 (m, 1H, GalN H-5), 3.57-3.50 (m, 1H, Gal H-5), 3.36-3.12 (m, 2H, Gal H-6a,b),1.94, 1.93, 1.91, 1.89 (4s, 12H, OC(O)CH_3, NHC(O)CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.66, 170.58, 170.20, 170.02, 168.92, 165.14, 165.10 (8C GlcA C-6, *C*=O), 134.40, 133.35, 133.06, 133.03, 132.96, 132.87, 129.65, 129.58, 129.42, 129.36, 128.58, 128.39, 128.29, 128.21, 128.11, 127.89, 127.63, 126.81, 126.05, 125.95, 125.91 (28C, arom. C), 101.60 (1C, GlcA C-1), 101.16 (1C, GalN C-1), 99.33 (1C, Gal C-1), 81.90 (1C, Gal C-3), 76.47 (1C, GlcA C-4), 74.57 (1C, GalN C-5), 73.80 (1C, GlcA C-5), 72.84 (1C, GlcA C-3), 71.49 (1C, GlcA C-2), 70.57 (1C, Gal C-2), 70.48 (1C, GalN C-3), 70.36 (1C, Gal C-5), 70.08 (1C, Ar-*C*H_2), 68.71 (1C, Gal C-4), 66.11 (1C, GalN C-4), 61.96 (1C, GalN C-6), 60.26 (1C, Gal C-6), 53.46 (1C, O*C*H_3), 51.08 (1C, GalN C-2), 23.38 (1C, NHC(O)*C*H_3), 20.68, 20.61, 20.59 (3C, OC(O)*C*H_3) ppm; HRMS [M+H]$^+$ calcd for $C_{59}H_{62}NO_{23}$ 1152.370714, found: 1152.368605.

2-Naphthylmethyl *O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-*O*-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-2,6-di-*O*-benzoyl-β-D-galactopyranoside (30): Compound **29** (95 mg, 0.082 mmol) was treated as described for the preparation of **23**. Flash silica chromatography (CH_2Cl_2/Acetone 12:1) gave **30** (74 mg, 71%) as a white foam. $[\alpha]_D$ = +14.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.12-7.12 (m, 27H, arom. H), 5.66 (d, 1H, $J_{NH\text{-}2}$ = 9.0 Hz, N*H*), 5.58 (dd, 1H, $J_{1,2}$ = $J_{2,3}$ = 8.5 Hz, Gal H-2), 5.51 (dd, 1H, $J_{2,3}$ = $J_{3,4}$ = 8.0 Hz, GlcA H-3), 5.29 (dd, 1H, $J_{1,2}$ = $J_{2,3}$ = 8.0 Hz, GlcA H-2), 5.08 (dd, 1H, $J_{3,4}$ = 2.5, $J_{4,5}$ < 1.0 Hz, GalN H-4), 5.03 (dd, 1H, $J_{2,3}$ = 10.5, $J_{3,4}$ = 2.5 Hz, GalN H-3), 4.93 (d, 1H, $J_{1,2}$ = 8.0 Hz, GlcA H-1), 4.85 (ABq, 2H, Ar-CH_2), 4.71-4.69 (m, 3H, Gal H-6a,b, GalN H-1), 4.50 (d, 1H, $J_{1,2}$ = 8.5 Hz, Gal H-1), 4.41 (dd, 1H, $J_{3,4}$ = $J_{4,5}$ = 8.0 Hz, GlcA H-4), 4.23-4.18 (m, 2H, Gal H-4, GlcA H-5), 3.93-3.86 (m, 3H, Gal H-3, H-5, GalN H-2), 3.75 (s, 3H, O*C*H_3), 3.51-3.48 (m, 1H, GalN H-5), 3.45-3.40 (m, 1H, GalN H-6a), 3.28 (dd, 1H, $J_{5,6b}$ = 5.5, $J_{6a,6b}$ = 10.5 Hz, GalN H-6b), 1.93, 1.91 (4s, 12H, NHC(O)CH_3, OC(O)CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.72, 170.61, 170.36, 170.26, 169.13, 166.70, 165.29, 165.11 (9C, GlcA C-6, *C*=O), 134.52, 133.64, 133.61, 133.33, 133.29, 133.24, 133.11, 130.31, 130.04, 129.94, 129.90, 129.86, 129.71, 129.55, 128.92, 128.85, 128.65, 128.51, 128.47, 128.37, 128.10, 127.88, 127.14, 126.28, 126.20, 126.13 (34C, arom. C), 101.54 (1C, Gal C-1), 101.25 (1C, GalN C-1), 99.09 (1C, GlcA C-1), 81.72 (1C, Gal C-3), 76.52 (1C, GlcA C-4), 74.01 (1C, GlcA C-5), 73.06 (1C, GlcA C-3), 72.54 (1C, Gal C-5), 71.79 (1C, GlcA C-2), 70.88, 70.72, 70.57 (1C, Gal C-2, GlaN C-3, C-5), 70.06 (1C, Ar-*C*H_2), 68.57 (1C, Gal C-4), 66.39 (1C, GalN C-4), 63.97 (1C, Gal C-6), 60.66 (1C, GalN C-6), 53.58 (1C, O*C*H_3), 51.50 (1C, GalN C-2), 23.67 (1C, NHC(O)*C*H_3), 20.90, 20.88, 20.81 (3C, OC(O)*C*H_3); HRMS [M+H]$^+$ calculated for $C_{66}H_{66}NO_{24}$ 1256.396928, found: 1256.396769.

2-Naphthylmethyl *O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-*O*-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-sodium 2,6-di-*O*-benzoyl-4-*O*-sulfonato-β-D-galactopyranoside (31): Compound **30** (56 mg, 0.045 mmol) was treated with $Me_3N.SO_3$ (25 eq.) as described for the preparation of **24** to give the sodium salt **31** (36 mg, 59%) as a white foam. $[\alpha]_D$ = +51.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.14-7.04 (m, 27H, arom. *H*), 6.86 (d, 1H, $J_{NH\text{-}2}$ = 10.0 Hz, N*H*), 5.78-5.62 (m, 2H, GlcA H-2, H-3), 5.47 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0 Hz, Gal H-2), 5.19 (d, 1H, $J_{1,2}$ = 8.5 Hz, GalN H-1), 5.15 (dd, 1H, $J_{3,4}$ = 3.0, $J_{4,5}$ < 1.0 Hz, Gal H-4), 4.98-4.63 (m, 6H, Gal H-6a,b, GlcA H-1, H-4, GalN H-3, H-4), 4.83 (ABq, 2H, Ar-CH_2), 4.43 (d, 1H, $J_{1,2}$ = 8.0 Hz, Gal H-1), 4.26-4.21 (m, 2H, GlcA H-5, GalN H-2), 3.90 (s, 3H, O*C*H_3), 3.88-3.68 (m, 3H, Gal H-3, H-5, GalN H-6a), 3.23 (dd, 1H, $J_{5,6a}$ = 5.0, $J_{6a,6b}$ = 11.0 Hz, GalN H-6b), 2.91-2.88 (m, 1H, GalN H-5), 2.04, 2.02, 1.77, 1.67 (4s, 12H, NHC(O)CH_3, OC(O)CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.56, 170.99, 170.30, 170.22, 169.75, 166.83, 166.47, 165.15, 164.88 (9C, GlcA C-6, C=O), 133.92, 133.59, 133.40, 133.34, 133.07, 133.04, 132.98, 130.02, 129.85, 129.60, 129.03, 128.61, 128.22, 128.18, 127.84, 127.66, 126.11, 126.09, 126.01 (34C, arom. C), 103.86 (1C, GlcA C-1), 101.54 (1C, GalN C-1), 98.34 (1C, Gal C-1), 80.11 (1C, Gal C-3), 77.36 (1C, Gal C-4), 76.86, 72.13, 65.80 (3C, GlcA C-4, GalN C-3, C-4), 74.13 (1C, GlcA C-5), 72.79 (1C, Gal C-5), 71.28 (2C, GlcA C-2, C-3), 70.79 (1C, GalN C-5), 70.37 (1C, Gal C-2), 69.72 (1C, Ar-*C*H_2), 64.59 (1C, Gal C-6), 59.91 (1C, GalN C-6), 54.00 (1C, O*C*H_3), 50.50 (1C, GalN C-2), 23.41 (1C, NHC(O)*C*H_3), 20.82, 20.54, 20.33 (3C, OC(O)*C*H_3); HRMS [M-Na]$^-$ calcd for $C_{66}H_{64}NO_{27}S$ 1334.339190, found: 1334.339067.

2-Naphthylmethyl *O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-*O*-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-sodium 4-*O*-acetyl-2-*O*-benzoyl-6-*O*-sulfonato-β-D-galactopyranoside (32): Compound **29** (78 mg, 0.068 mmol) was treated as described for the preparation of **22** to give the sodium salt **32** (61 mg, 70%) as a white solid. $[\alpha]_D$ = +18.1 (*c* 1.0, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ = 7.87-7.07 (m, 22H, arom. H), 5.59 (dd, 1H, $J_{3,4}$ = 3.5, $J_{4,5}$ < 1.0 Hz, Gal H-4), 5.51 (dd, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, GlcA H-3), 5.44-5.39 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0 Hz, Gal H-2), 5.23 (dd, 1H, $J_{1,2}$ = $J_{2,3}$ = 7.5 Hz, GlcA H-2), 5.09 (dd, 1H, $J_{3,4}$ = 3.5, $J_{4,5}$ < 1.0 Hz, GalN H-4), 5.00 (dd, 1H, $J_{2,3}$ = 11.0, $J_{3,4}$ = 3.5 Hz, GalN H-3), 4.95 (d, 1H, $J_{1,2}$ = 7.5 Hz, GlcA H-1), 4.85 (ABq, 2H, Ar-CH_2), 4.67-4.64 (m, 2H, Gal H-1, GalN H-1), 4.33 (dd, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, GlcA H-4), 4.19-4.11 (m, 5H, Gal H-3, H-5, H-6a,b, GlcA H-5), 3.91 (s, 3H, OCH_3), 3.80 (dd, 1H, $J_{1,2}$ = 8.5, $J_{2,3}$ = 11.0 Hz, GalN H-2), 3.60-3.56 (m, 1H, GalN H-5), 3.41 (dd, 1H, $J_{5,6a}$ = 8.0, $J_{6a,6b}$ = 11.0 Hz, GalN H-6a), 3.28 (dd, 1H, $J_{5,6b}$ = 6.0, $J_{6a,6b}$ = 11.0 Hz, GalN H-6b), 2.19 (s, 3H, NHC(O)CH_3), 1.95, 1.93, 1.92, 1.91 (4s, 12H, OC(O)CH_3); ^{13}C NMR (100 MHz, CD_3OD) δ = 173.00, 171.53, 171.36, 171.25, 171.21, 169.07, 166.08, 166.04, 165.81 (9C, GlcA C-6, *C*=O), 134.92, 134.10, 133.84, 133.77, 133.69, 133.63, 130.16, 130.14, 130.01, 129.87, 129.29, 129.03, 128.95, 128.75, 128.62, 128.47, 128.10, 127.39, 126.55, 126.49, 126.32 (28C, arom. C), 101.76 (1C, GlcA C-1), 101.52 (1C, Gal C-1), 100.20 (1C, GalN C-1), 77.58 (1C, Gal C-3), 76.90 (1C, GlcA C-4), 74.55 (1C, Gal C-5), 73.72 (1C, GlcA C-3), 72.80 (1C, GlcA C-5), 72.44 (1C, GlcA C-2), 71.91 (1C, Gal C-2), 71.23 (1C, Ar-*C*H_2), 70.86 (1C, GalN C-5), 70.79 (1C, GalN C-3), 70.49 (1Cn, Gal C-4), 66.84 (1C, GalN C-4), 66.75 (1C, Gal C-6), 61.16 (1C, GalN C-6), 53.61 (1C, O*C*H_3), 51.36 (1C, GalN C-2), 23.05 (1C, NHC(O)*C*H_3), 20.90, 20.66, 20.60, 20.49 (4C, OC(O)*C*H_3); HRMS $[M+2H-Na]^+$ calcd for $C_{61}H_{64}NO_{27}S$ 1274.338093, found: 1274.337931.

2-Naphthylmethyl *O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl-(1→4)-*O*-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-2-*O*-benzoyl-β-D-galactopyranoside (36): Compound **31** (113 mg, 0.087 mmol) was treated as described for the preparation of **21**. Flash silica chromatography (CH_2Cl_2/acetone 17:1) afforded the diol **36** (88 mg, 87%) as a white foam. $[\alpha]_D$ = +74.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77-7.06 (m, 22H, arom. H), 5.57-5.54 (m, 2H, Gal H-2, GlcA H-3), 5.48 (d, 1H, $J_{2,NH}$ = 9.5 Hz, N*H*), 5.34 (dd, 1H, $J_{1,2}$ = 7.5, $J_{2,3}$ = 9.5 Hz, GlcA H-2), 5.08-5.07 (m, 2H, GlcN H-3, H-4), 5.01 (d, 1H, $J_{1,2}$ = 3.5 Hz, GlcN H-1), 4.97 (d, 1H, $J_{1,2}$ = 7.5 Hz, GlcA H-1), 4.85 (ABq, 2H, Ar-CH_2), 4.54-4.48 (m, 2H, Gal H-1, GlcA H-4), 4.26-4.24 (m, 1H, GlcA H-5), 4.20-4.10 (m, 4H, Gal H-4, GlcN H-2, H-6a,b), 4.08-4.03 (m , 1H, Gal H-6a), 3.90-3.87 (m, 2H, Gal H-3, H-6b), 3.83 (s, 3H, OCH_3), 3.77-3.74 (m, 1H, GlcN H-5), 3.62-3.59 (m, 1H, Gal H-5), 3.28 (brs, 1H, O*H*), 2.58-2.55 (m, 1H, O*H*), 2.10, 2.00, 1.95 (3s, 9H, OC(O)CH_3), 1.60 (s, 3H, NHC(O)CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.31, 170.92, 169.94, 169.17, 168.10, 165.93, 164.84, 164.80 (8C, GlcA C-6, *C*=O), 134.52, 134.07, 133.12, 133.09, 133.00, 132.89, 129.84, 129.70, 129.59, 129.53, 128.74, 128.47, 128.29, 128.21, 128.14, 128.09, 127.94, 127.68, 126.80, 126.09, 125.99, 125.93 (28C, arom.C), 101.65 (1C, GlcA C-1), 99.36 (1C, Gal C-1), 98.54 (1C, GlcN C-1), 81.28 (1C, Gal C-3), 75.33 (1C, GlcA C-4), 74.64 (1C, GlcA C-5), 74.42 (1C, Gal C-5), 74.12 (1C, Gal C-2), 71.24 (1C, GlcA C-2), 70.78 (1C, GlcN C-3), 70.67 (1C, GlcA C-3), 70.14 (1C, Ar-*C*H_2), 69.11 (1C, Gal C-4), 69.01 (1C, GlcN C-5), 67.72 (1C, GlcN C-4), 62.36 (1C, Gal C-6), 61.48 (1C, GlcN C-6), 53.36 (1C, O*C*H_3), 51.36 (1C, GlcN C-2), 22.66 (1C, NHC(O)*C*H_3), 20.84, 20.74, 20.67 (3C, OC(O)*C*H_3); HRMS $[M+H]^+$ calcd for $C_{59}H_{62}NO_{23}$ 1152.370714, found: 1152.370483.

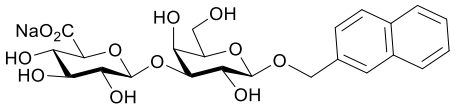
2-Naphthylmethyl *O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl-(1→4)-*O*-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-2,6-di-*O*-benzoyl-β-D-galactopyranoside (37): Compound **36** (46 mg, 0.039 mmol) was treated as described for the preparation of **23**. Flash silica chromatography (CH_2Cl_2/Acetone 12:1) gave **37** (41 mg, 81%) as a white foam. $[\alpha]_D$ = +63.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.13-7.08 (m, 27H, arom. H), 5.59-5.54 (m, 2H, Gal H-2, GlcA H-3), 5.42 (d, 1H, $J_{2,NH}$ = 9.5 Hz, N*H*), 5.31 (dd, 1H, $J_{1,2}$ = 7.0, $J_{2,3}$ = 9.5 Hz, GlcA H-2), 5.07-5.04 (m, 2H, GlcN H-3, H-4), 5.01 (d, 1H, $J_{1,2}$ = 3.5 Hz, GlcN H-1), 4.95 (d, 1H, $J_{1,2}$ = 7.0 Hz, GlcA H-1), 4.84 (ABq, 2H, Ar-CH_2), 4.72-4.69 (m, 2H, Gal H-6a,b), 4.50-4.46 (m, 2H, Gal H-1, GlcA H-4), 4.23-4.16 (m, 4H, Gal H-4, GlcA H-5, GlcN H-2, H-6a), 4.09 (dd, 1H, $J_{5,6}$ = 12.5, $J_{6a,6b}$ = 2.5 Hz, GlcN H-6b), 3.89-3.85 (m, 2H, Gal H-3, H-5), 3.75 (s, 3H, OCH_3), 3.74-3.71 (m, 1H, GlcN H-5), 3.06 (brs, 1H, O*H*), 2.10, 2.00, 1.95 (3s, 9H, OC(O)CH_3), 1.61 (s, 3H, NHC(O)CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.32, 170.90, 169.89, 169.16, 168.02, 166.52, 165.90, 164.77, 164.71 (9C, GlcA C-6, *C*=O), 133.44, 133.11, 130.08, 129.97, 129.72, 129.61, 128.77, 128.68, 128.30, 128.23, 128.16, 127.91, 127.67, 127.00, 126.08, 126.01, 125.99 (34C, arom. C), 101.62 (1C, GlcA C-1), 98.75 (1C, Gal C-1), 98.51 (1C, GlcN C-1), 81.17 (1C, Gal C-3), 75.17 (1C, GlcA C-4), 74.60 (1C, GlcA C-5), 74.03 (1C, Gal C-2), 72.19 (1C, Gal C-5), 71.33 (1C, GlcA C-2), 70.77 (1C, GlcN C-3), 70.61 (1C, GlcA C-3), 69.77 (1C, Ar-*C*H_2), 69.05 (1C, GlcN C-5), 68.59 (1C, Gal C-4), 67.66 (1C, GlcN C-4), 63.65 (1C, Gal C-6), 61.44 (1C, GlcN C-6), 53.29 (1C, O*C*H_3), 51.35 (1C, GlcN C-2), 31.35 (1C, NHC(O)*C*H_3), 20.85, 20.75, 20.69 (3C, OC(O)*C*H_3); HRMS $[M+H]^+$ calcd for $C_{66}H_{66}NO_{24}$ 1256.396928, found: 1256.397059.

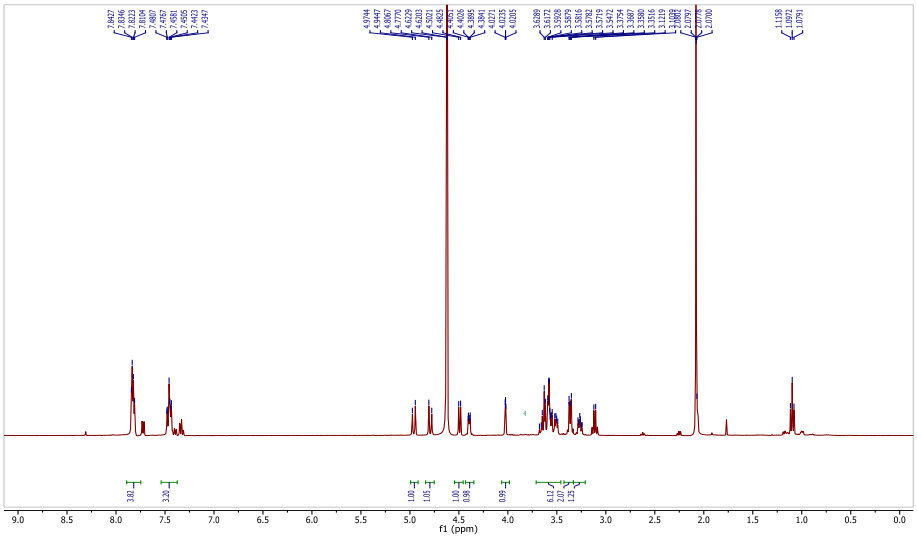
2-Naphthylmethyl *O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl-(1→4)-*O*-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-sodium 2,6-di-*O*-benzoyl-4-*O*-sulfonato-β-D-galactopyranoside (38): Compound **37** (41 mg, 0.033 mmol) was treated with $Me_3N.SO_3$ (25 eq.) as described for the preparation of **24** to give the sodium salt **38** (42 mg, 95%) as a white foam. $[\alpha]_D$ = +53.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, CD_3OD) δ = 8.14-7.07 (m, 27H, arom. H), 5.84-5.79 (m, 1H, GlcA H-3), 5.46-5.39 (m, 2H, Gal H-2, GlcA H-2), 5.13 (d, $J_{1,2}$ = 7.5 Hz, 1H, GlcA H-1), 5.11-5.06 (m, 3H, Gal H-4, GlcN H-1, H-3), 4.91 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, 1H, GlcN H-4), 4.72 (ABq, 2H, Ar-CH_2), 4.77-4.75 (m, 2H, Gal H-6a,b), 4.64 (d, $J_{1,2}$ = 7.5 Hz, 1H, Gal H-1), 4.56 (dd, $J_{3,4}$ = $J_{4,5}$ = 7.5 Hz, 1H, GlcA H-4), 4.40-4.38 (m, 1H, GlcA H-5), 4.27 (dd, $J_{2,3}$ = 10.0, $J_{3,4}$ = 3.5 Hz, 1H, Gal H-3), 4.20-4.18 (m, 2H, GlcN H-6a,b), 4.11-4.09 (m, 1H, Gal H-5), 4.02 (dd, $J_{1,2}$ = 3.5, $J_{2,3}$ = 11.0 Hz, 1H, GlcN H-2), 3.83 (s, 3H, OCH_3), 3.78-3.74 (m, 1H, GlcN H-5), 2.06, 1.97, 1.89 (3s, 9H, OC(O)CH_3), 1.74 (s, 3H, NHC(O)CH_3); ^{13}C NMR (100 MHz, CD_3OD) δ = 174.11, 173.33, 172.74, 171.97, 171.06, 168.66, 167.64, 167.54, 167.50 (9C, GlcA C-6, *C*=O), 136.56, 135.59, 135.30, 135.22, 135.19, 135.01, 132.38, 131.65, 131.62, 131.56, 131.54, 131.48, 130.87, 130.78, 130.54, 130.46, 130.37, 130.03, 129.83, 129.60, 129.41, 128.49, 127.86, 127.79, 127.57 (34C, arom. C), 103.90 (1C, GlcA C-1), 101.61 (1C, Gal C-1), 99.19 (1C, GlcN C-1), 80.07 (1C, Gal C-3), 78.03, 72.65 (2C, Gal C-4, GlcN C-3), 77.28 (1C, GlcA C-3), 75.78 (1C, GlcA C-5), 75.19 (1C, GlcA C-4), 74.78, 74.63, 73.38 (3C, Gal C-2, C-5, GlcA C-2), 72.10 (1C, Ar-*C*H_2), 70.69, 70.54 (2C, GlcN C-4, C-5), 66.27 (1C, Gal C-6), 63.61 (1C, GlcN C-6), 54.51 (1C, O*C*H_3), 53.02 (1C, GlcN C-2), 23.39 (1C, NHC(O)*C*H_3), 21.58, 21.41, 21.36 (3C, OC(O)*C*H_3); HRMS [M-Na]$^-$ calcd for $C_{66}H_{64}NO_{27}S$ 1334.339190, found: 1334.338801.

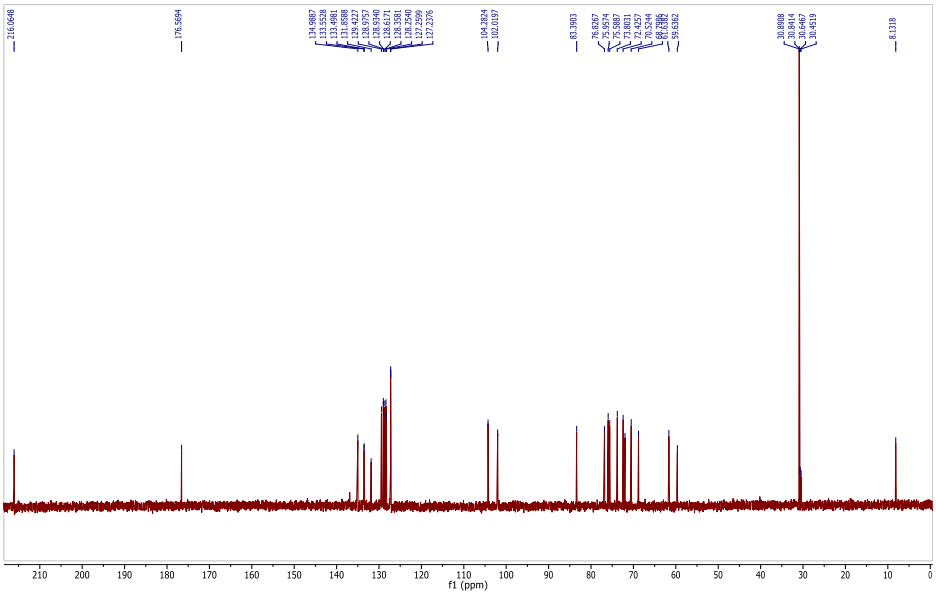
2-Naphthylmethyl *O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl-(1→4)-*O*-(methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyluronate)-(1→3)-sodium 4-*O*-acetyl-2-*O*-benzoyl-6-*O*-sulfonato-β-D-galactopyranoside (39): Compound **36** (44 mg, 0.038 mmol) was treated as described for the preparation of **22** to give the sodium salt **39** (20 mg, 40%) as a white solid. $[\alpha]_D$ = +116.1 (c 1.0, MeOH); ^{1}H NMR (250 MHz, CD_3OD) δ = 7.73-7.02 (m, 22H, arom. H), 5.79 (dd, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, GlcA H-3), 5.53 (dd, 1H, $J_{3,4}$ = 3.5, $J_{4,5}$ < 1.0 Hz, Gal H-4), 5.36 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.0 Hz, Gal H-2), 5.20-5.03 (m, 4H, GlcA H-1, H-2, GlcN H-1, H-3), 4.95 (dd, 1H, $J_{3,4}$ = 2.5, $J_{4,5}$ < 1.0 Hz, GlcN H-4), 4.80 (ABq, 2H, Ar-CH_2), 4.67 (d, 1H, $J_{1,2}$ = 8.0 Hz, Gal H-1), 4.45-4.30 (m, 2H, GlcA H-4, H-5), 4.27-4.24 (m, 1H, Gal H-3), 4.22-4.18 (m, 3H, Gal H-6a, GlcN H-6a,b), 4.14-4.10 (m, 1H, Gal H-5), 4.05-3.97 (m, 2H, Gal H-6b, GlcN H-2), 3.89 (s, 3H, OCH_3), 3.73-3.67 (m, 1H, GlcN H-5), 2.16, 2.08, 1.99, 1.89 (4s, 12H, OC(O)CH_3), 1.75 (s, 3H, NHC(O)CH_3); ^{13}C NMR (62.5 MHz, CD_3OD) δ = 173.27, 172.44, 171.97, 171.83, 171.13, 169.84, 166.62, 166.54, 166.11 (9C, GlcA C-6, *C*=O), 135.78, 134.72, 134.52, 134.34, 134.16, 130.59, 130.53, 130.41, 129.83, 129.59, 129.37, 129.13, 128.95, 128.50, 127.82, 126.93, 126.86, 121.38 (28C, arom. C), 102.08 (1C, GlcA C-1), 100.83 (1C, Gal C-1), 98.34 (1C, GlcN C-1), 79.77 (1C, Gal C-3), 76.17 (1C, GlcA C-3), 74.85, 74.49 (2C, GlcA C-4, C-5), 73.70 (1C, Gal C-5), 73.16 (1C, GlcA C-2), 72.34 (1C, Gal C-2), 71.77 (1C, GlcN C-3), 71.62 (1C, Ar-*C*H_2), 71.00 (1C, Gal C-4), 69.80, 69.70 (2C, GlcN C-4, C-5), 68.01 (1C, Gal C-6), 62.73 (1C, GlcN C-6), 53.65 (1C, O*C*H_3), 52.12 (1C, GlcN C-2), 22.51 (1C, NHC(O)*C*H_3), 20.83, 20.69, 20.55, 20.49 (4C, OC(O)*C*H_3); HRMS [M-Na]$^-$ calcd for $C_{61}H_{62}NO_{27}S$ 1272.323540, found: 1272.323707.

^{1}H and ^{13}C NMR Spectra of new compounds

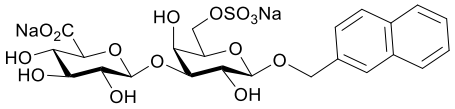
^{1}H NMR (400 MHz, D_2O) and ^{13}C NMR (100 MHz, D_2O) for compound **1**

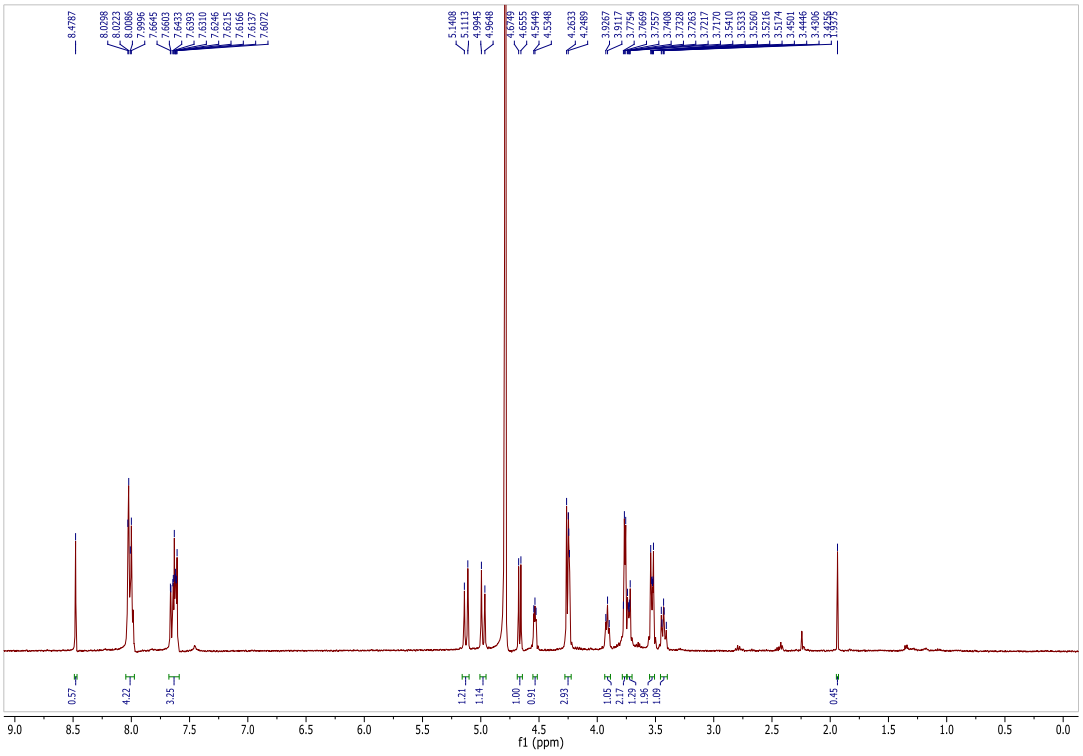


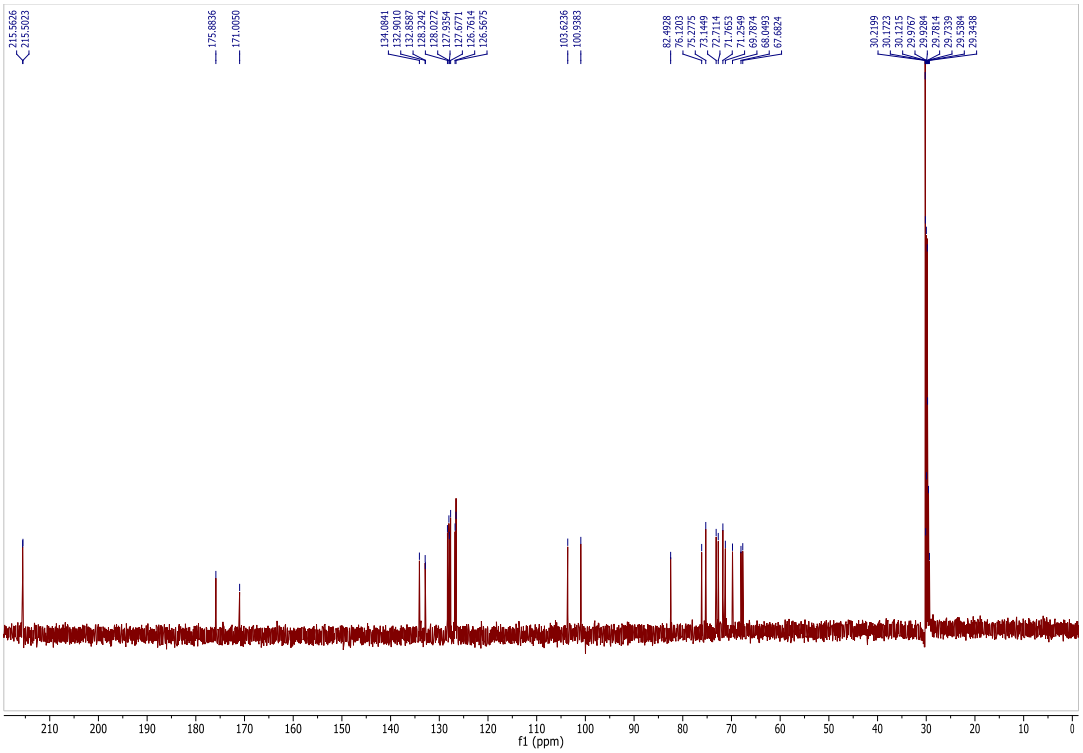




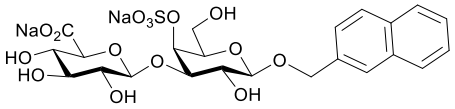
^{1}H NMR (400 MHz, D_2O) and ^{13}C NMR (100 MHz, D_2O) for compound **2**

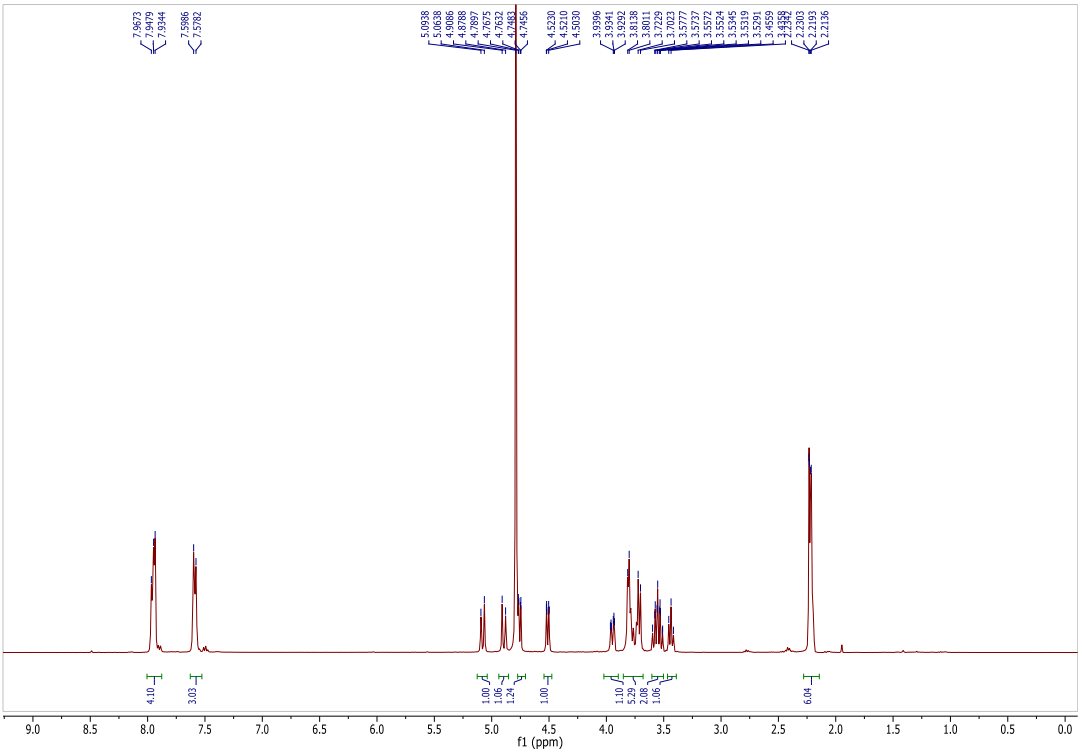


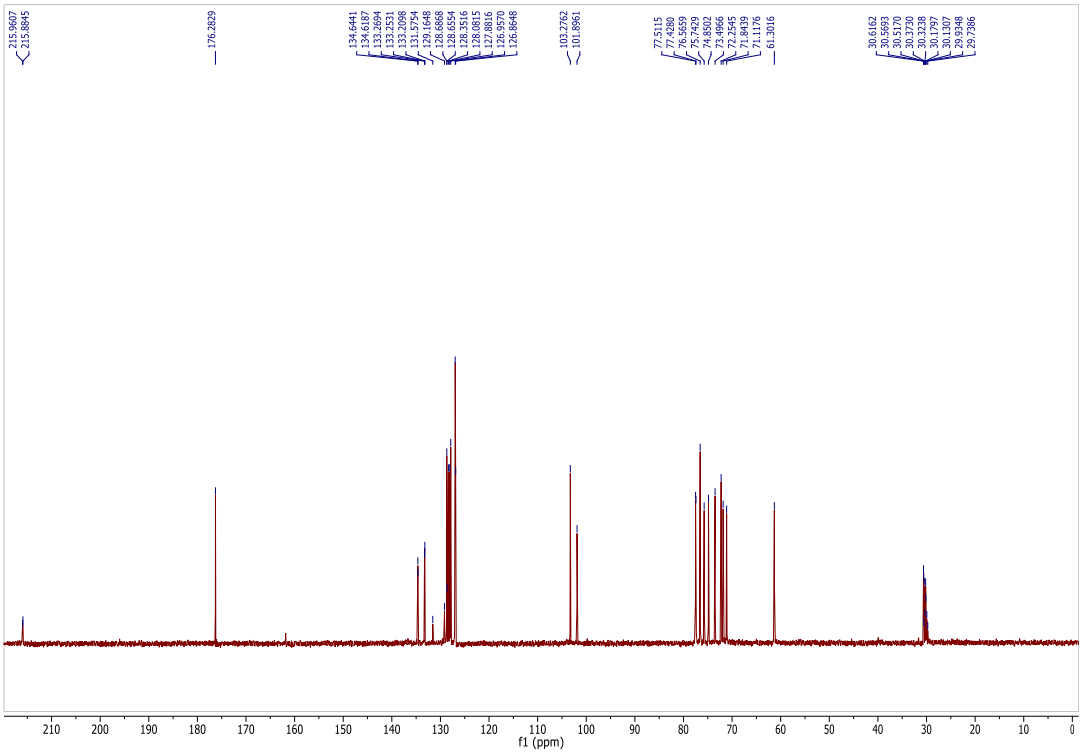




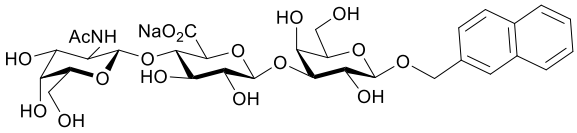
^{1}H NMR (400 MHz, D_2O) and ^{13}C NMR (100 MHz, D_2O) for compound **3**

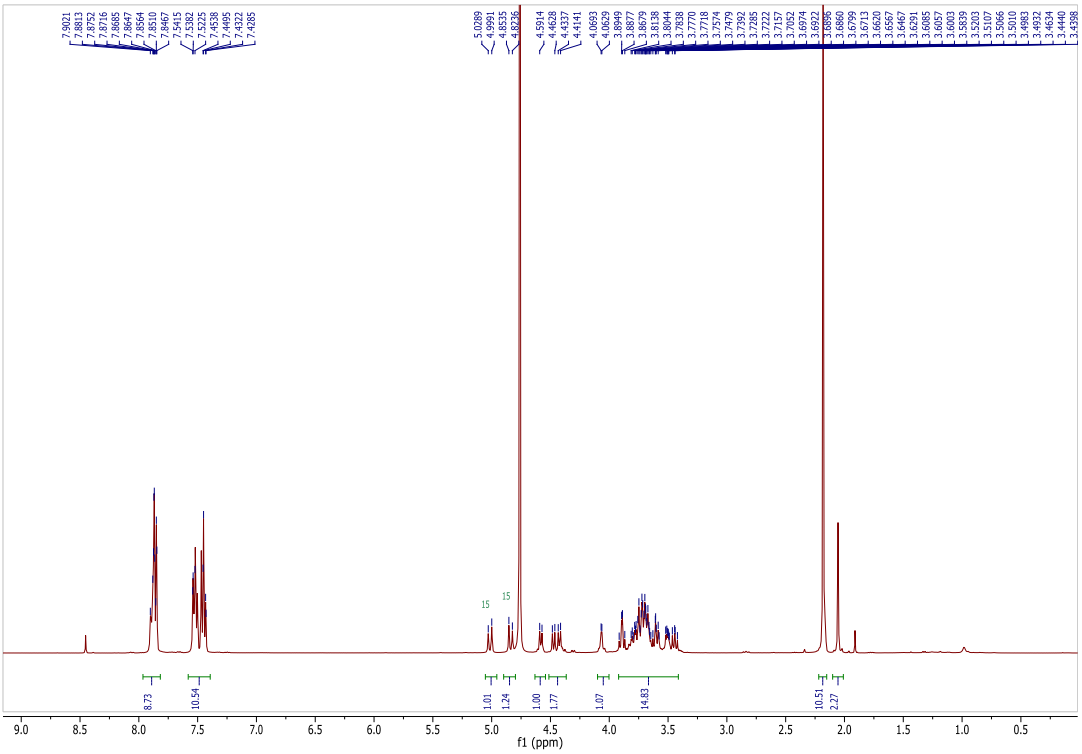


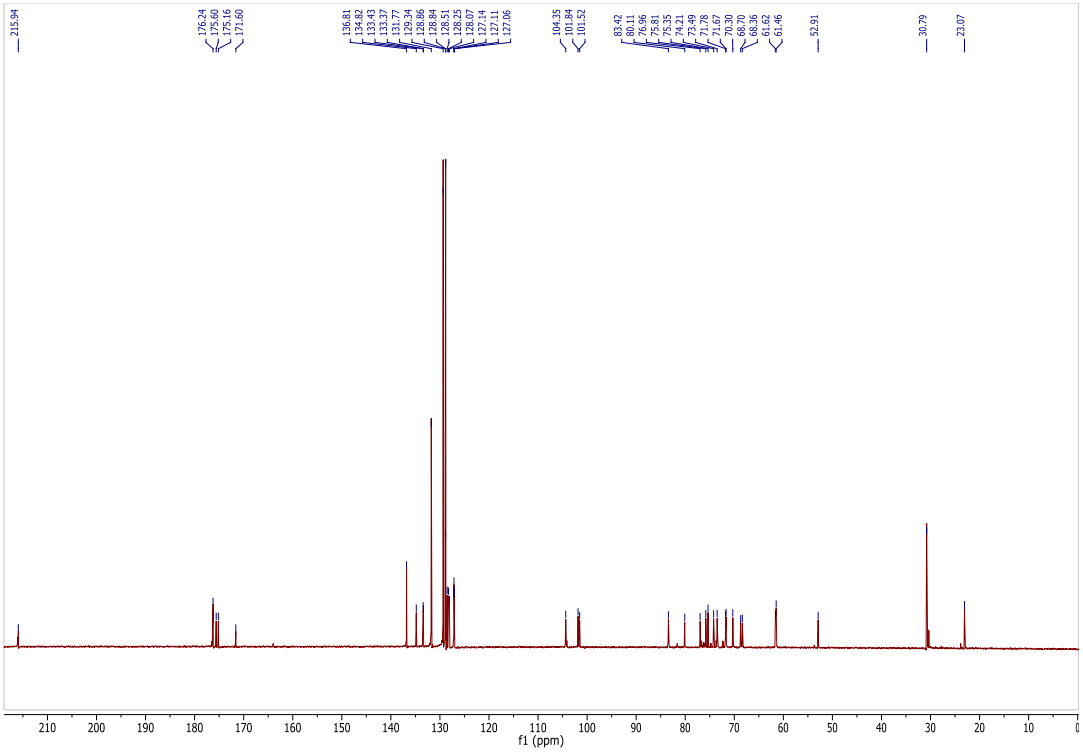




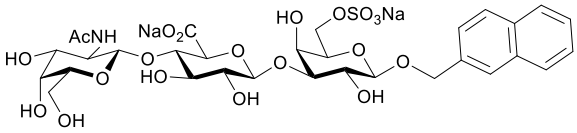
^{1}H NMR (400 MHz, D_2O) and ^{13}C NMR (100 MHz, D_2O) for compound **4**

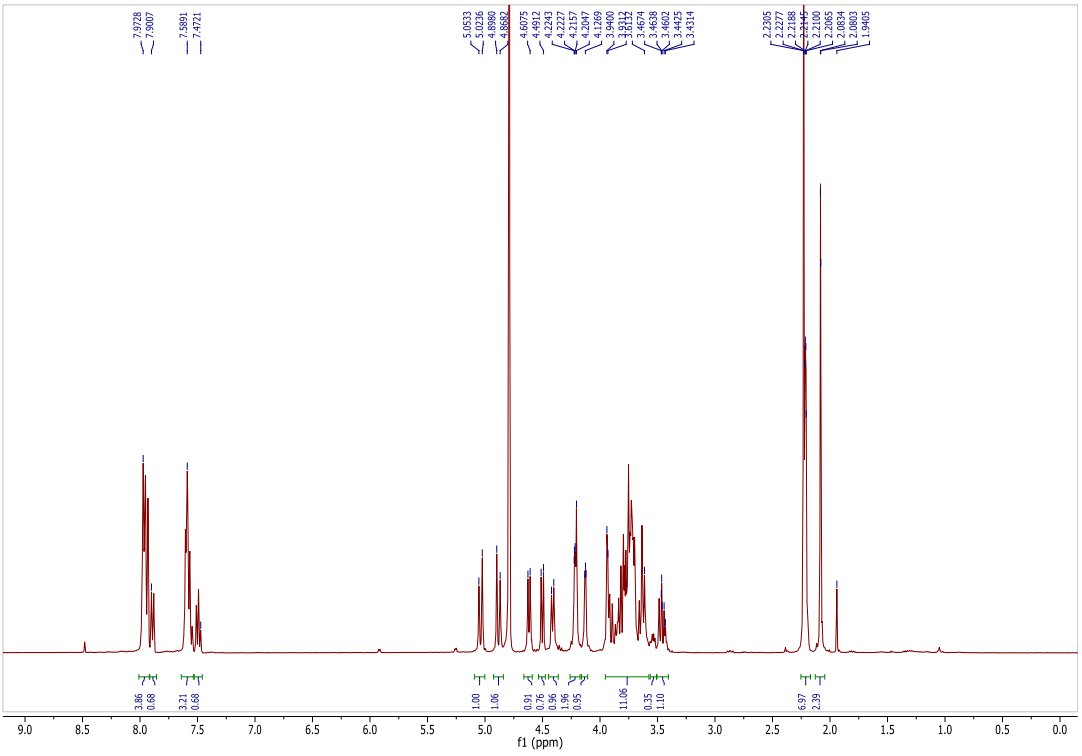


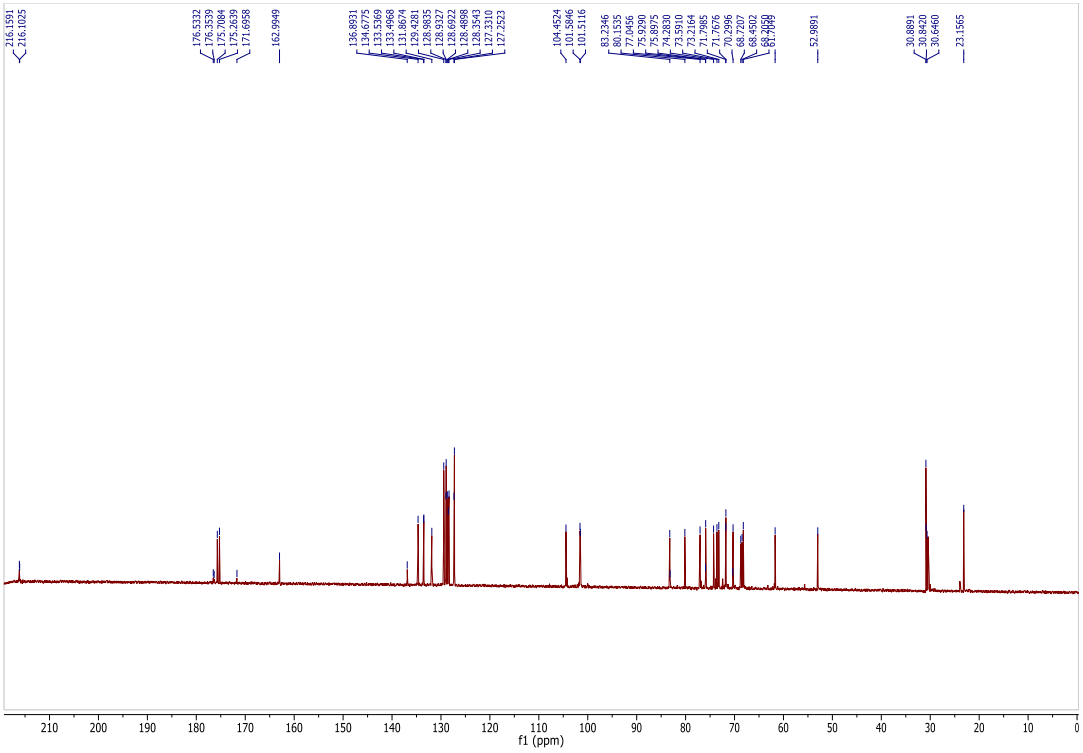




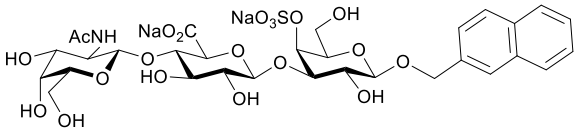
^{1}H NMR (400 MHz, D_2O) and ^{13}C NMR (100 MHz, D_2O) for compound **5**

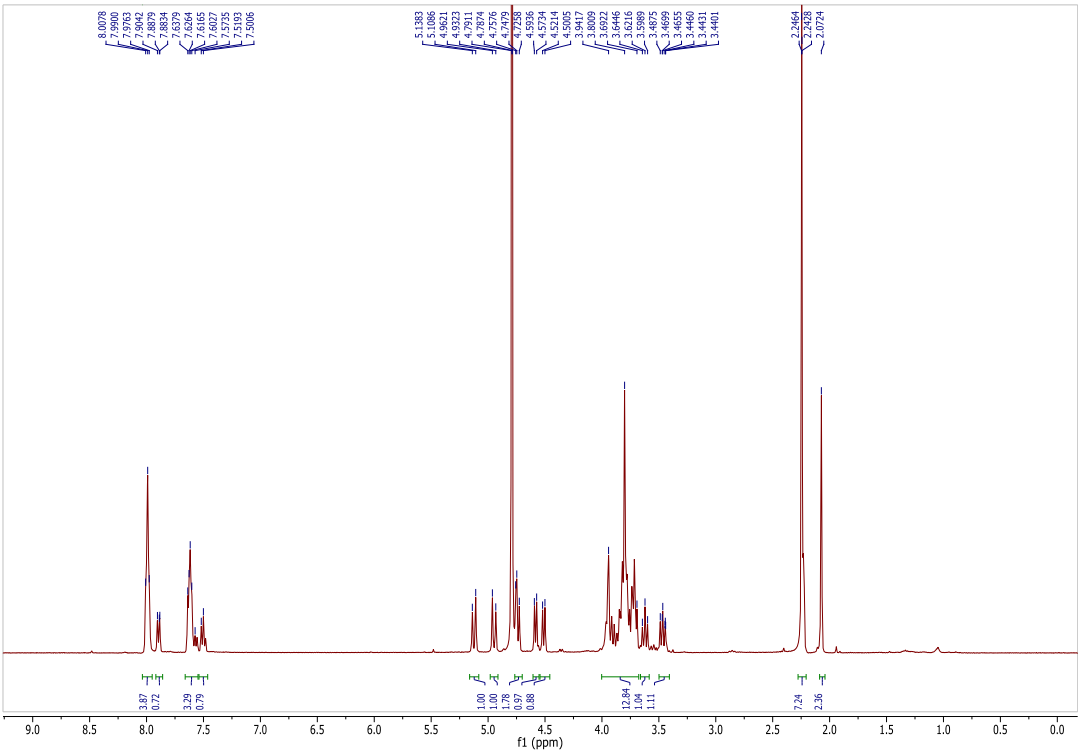


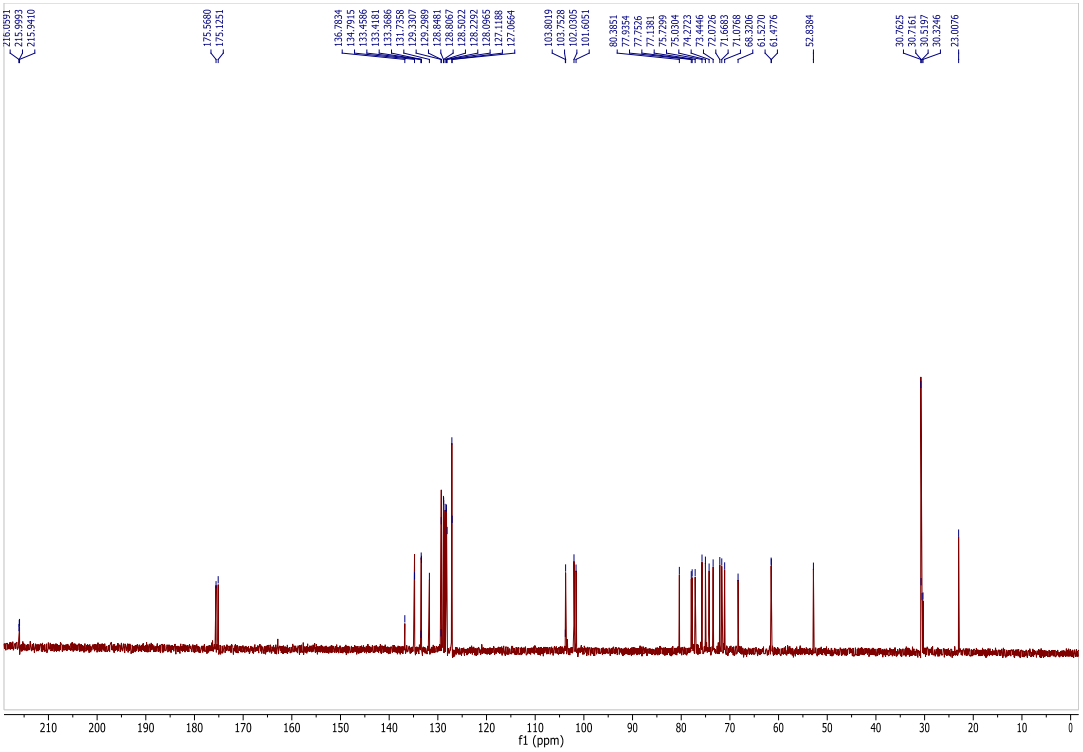




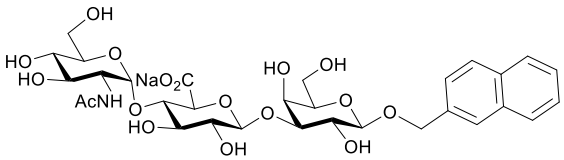
^{1}H NMR (400 MHz, D_2O) and ^{13}C NMR (100 MHz, D_2O) for compound **6**

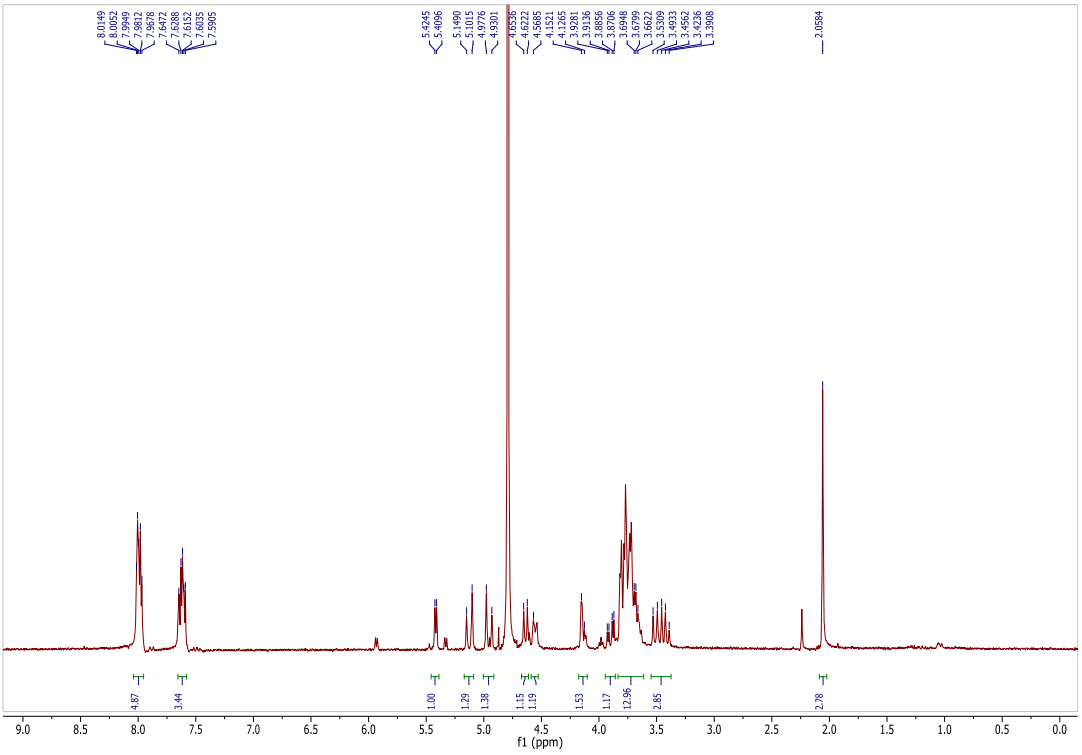


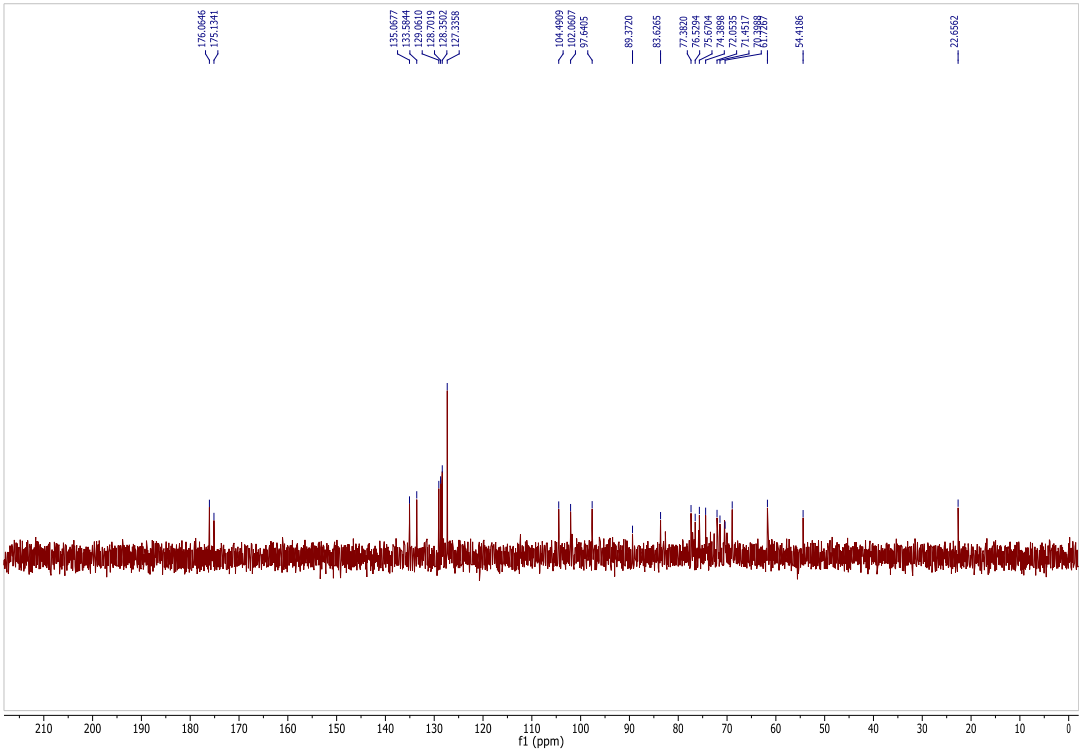




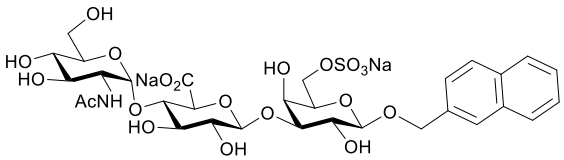
^{1}H NMR (250 MHz, D_2O) and ^{13}C NMR (62.5 MHz, D_2O) for compound **7**

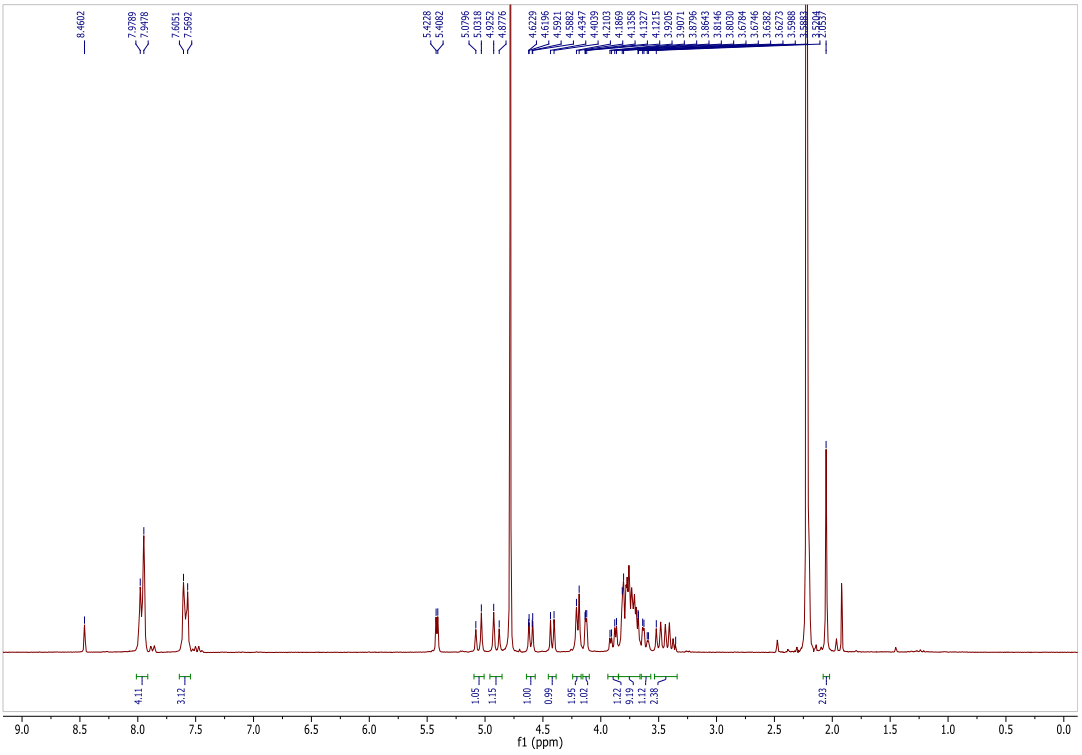


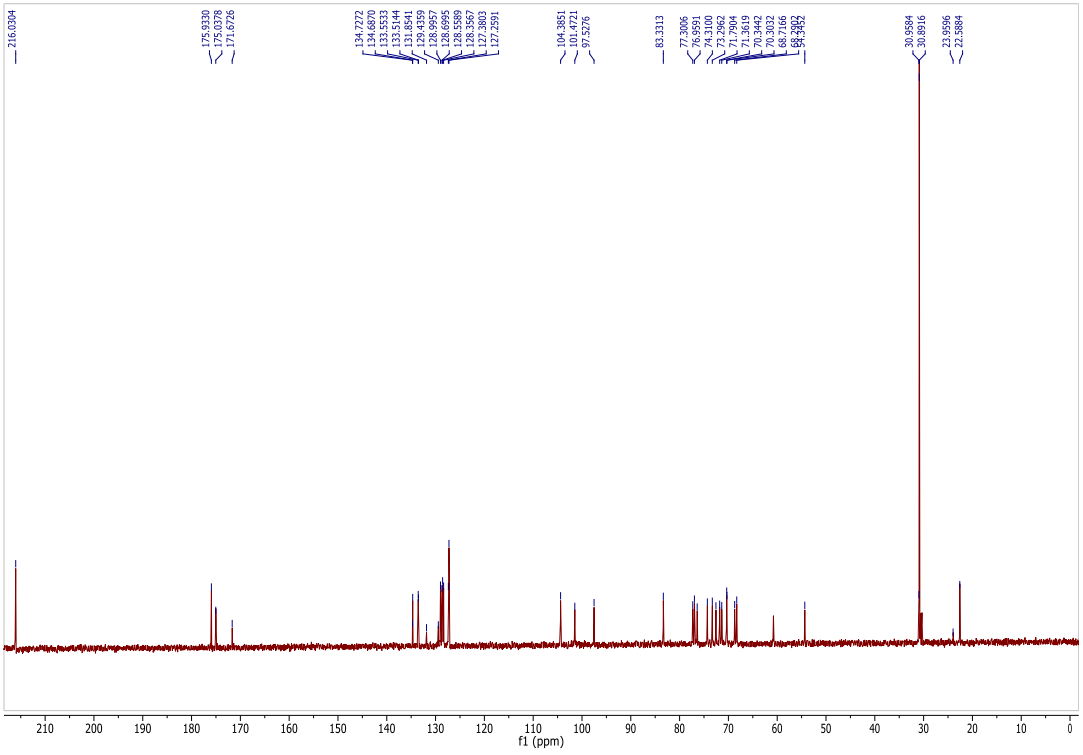




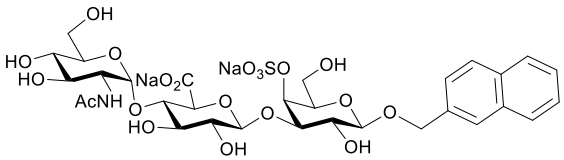
^{1}H NMR (250 MHz, D_2O) and ^{13}C NMR (62.5 MHz, D_2O) for compound **8**

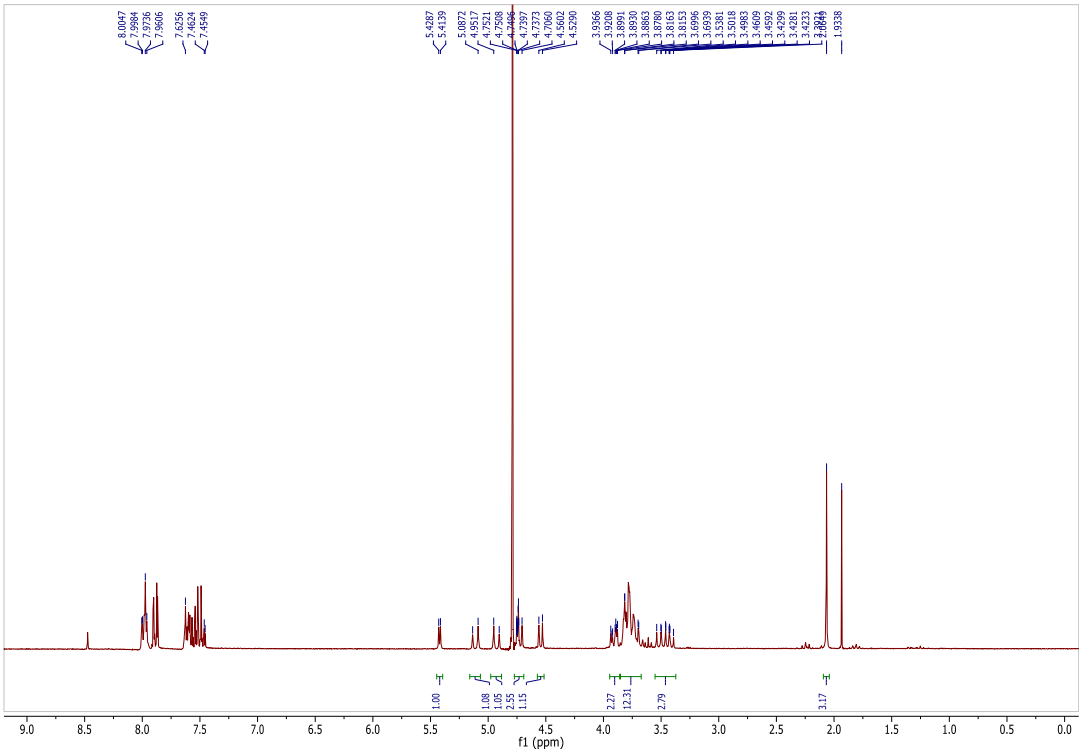


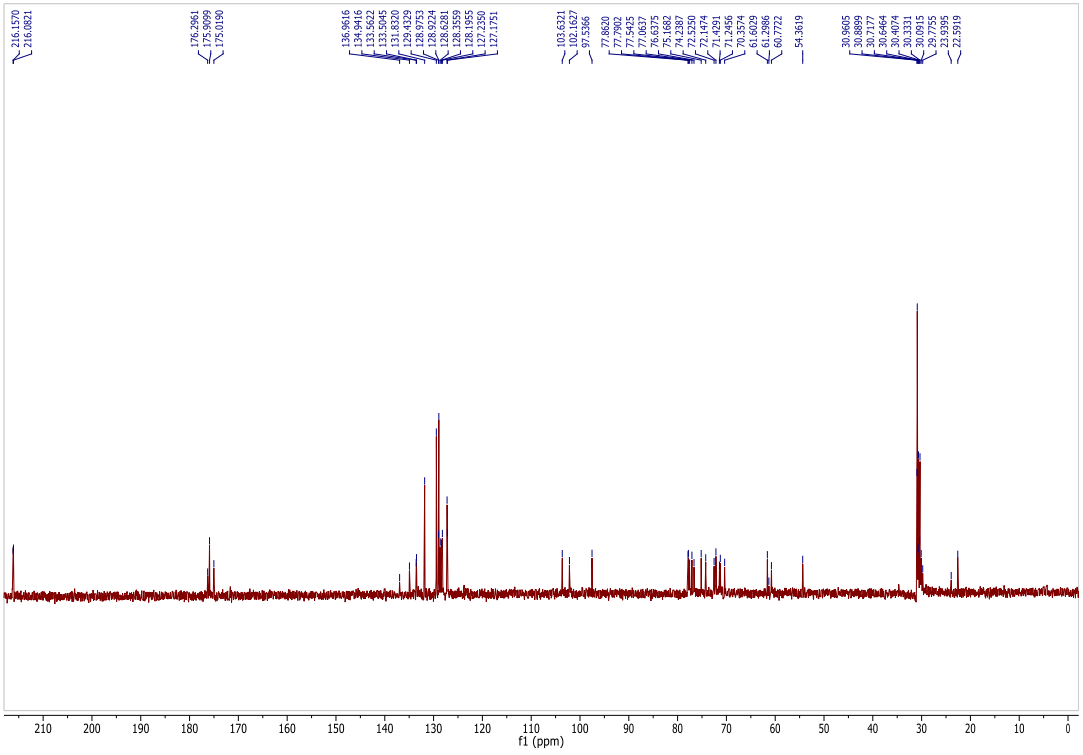




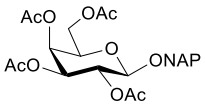
^{1}H NMR (250 MHz, D_2O) and ^{13}C NMR (62.5 MHz, D_2O) for compound **9**

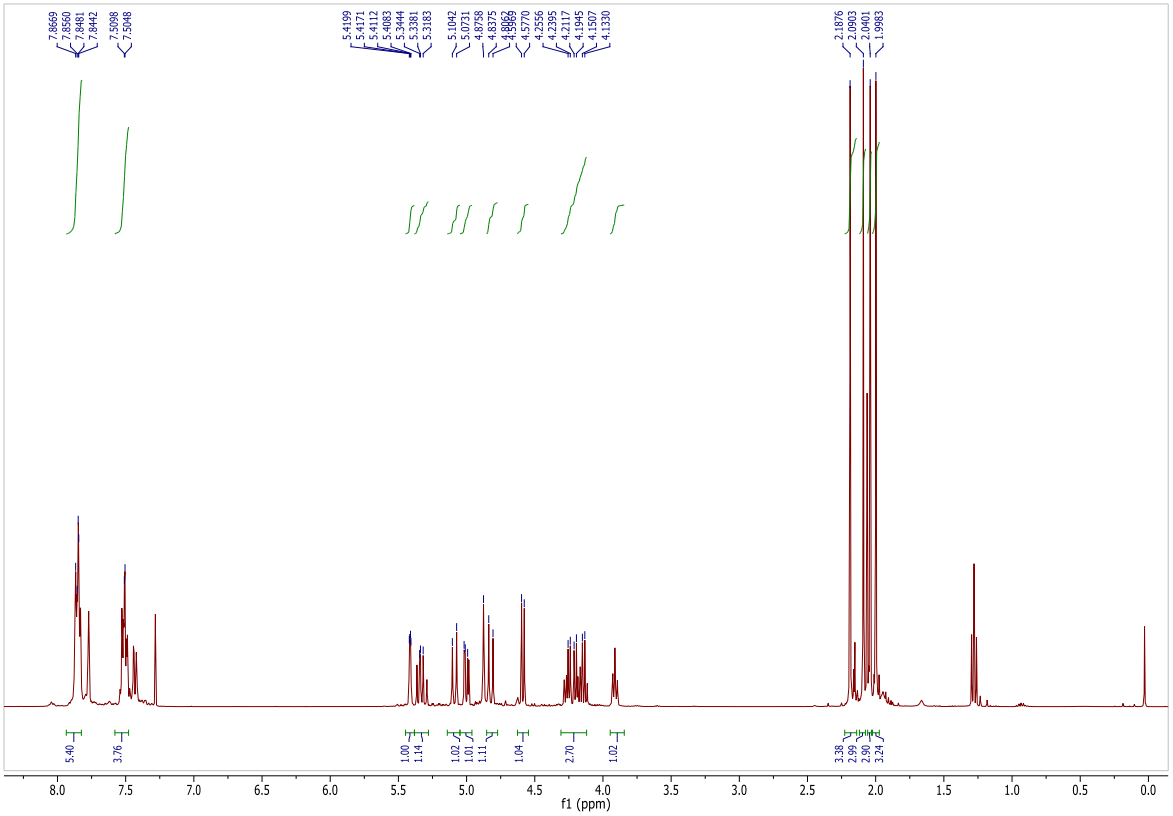


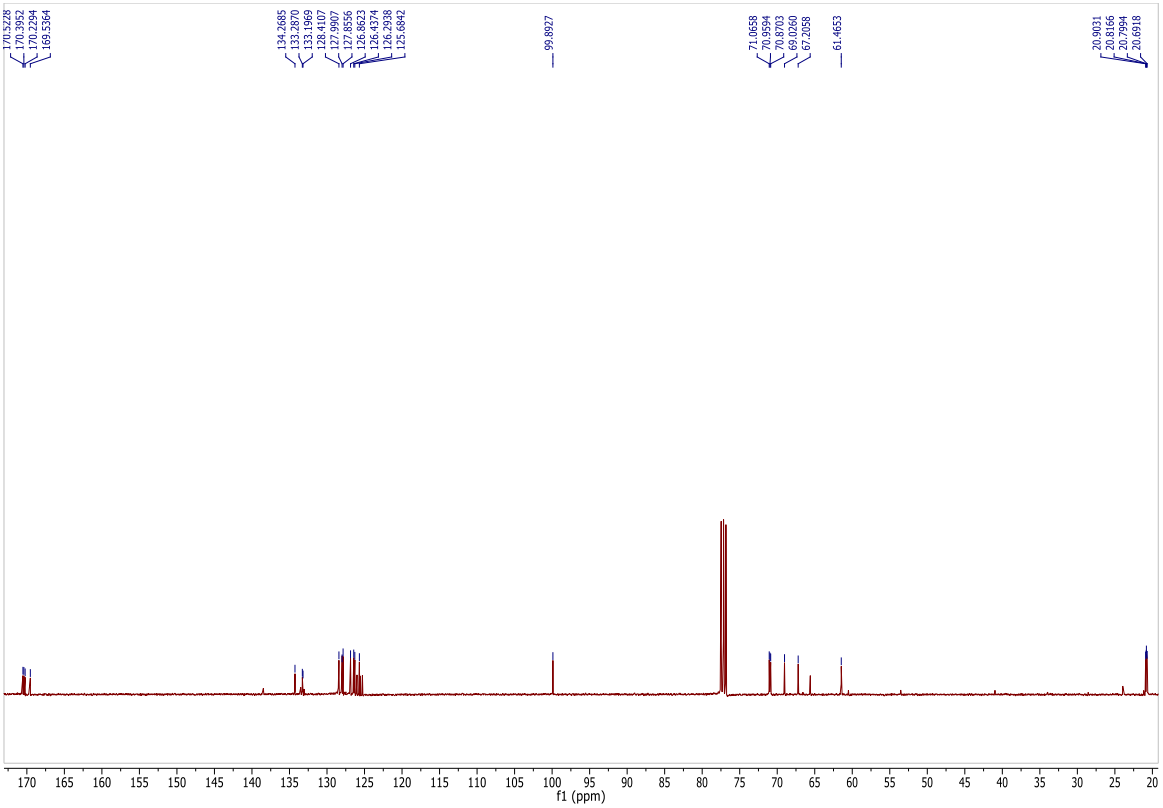




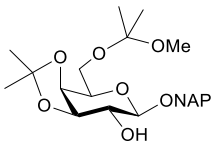
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for compound **11**

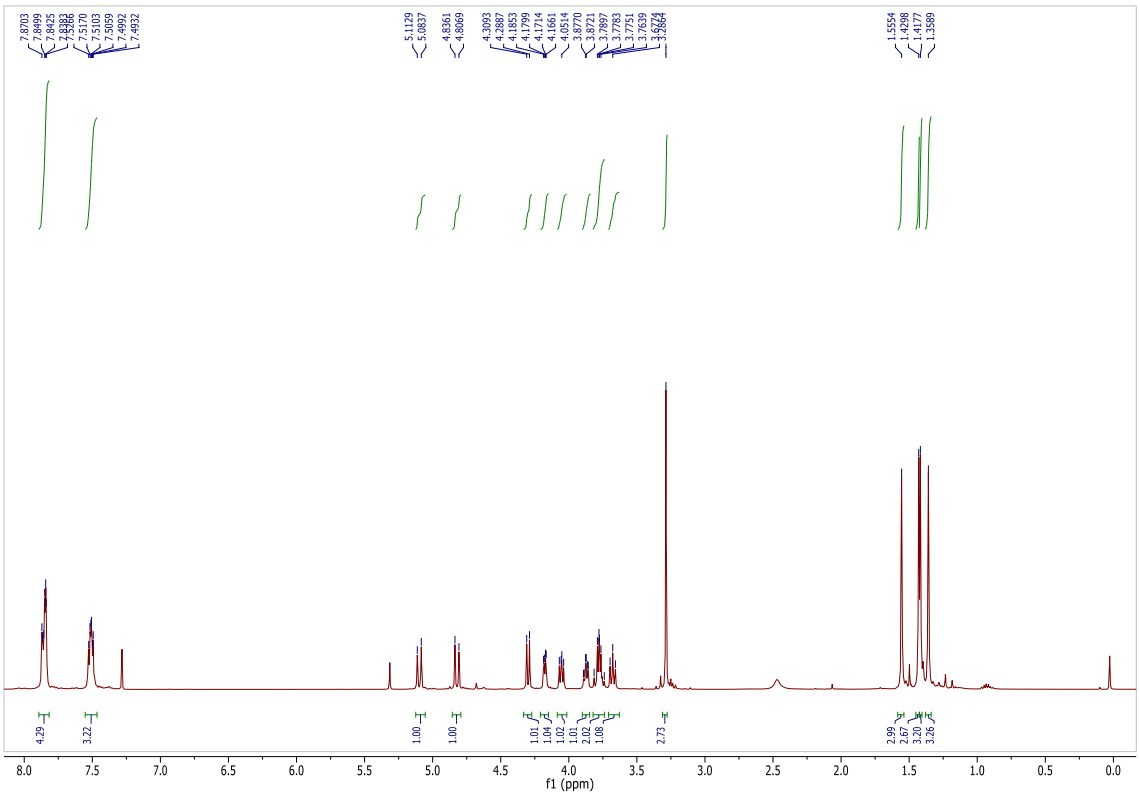


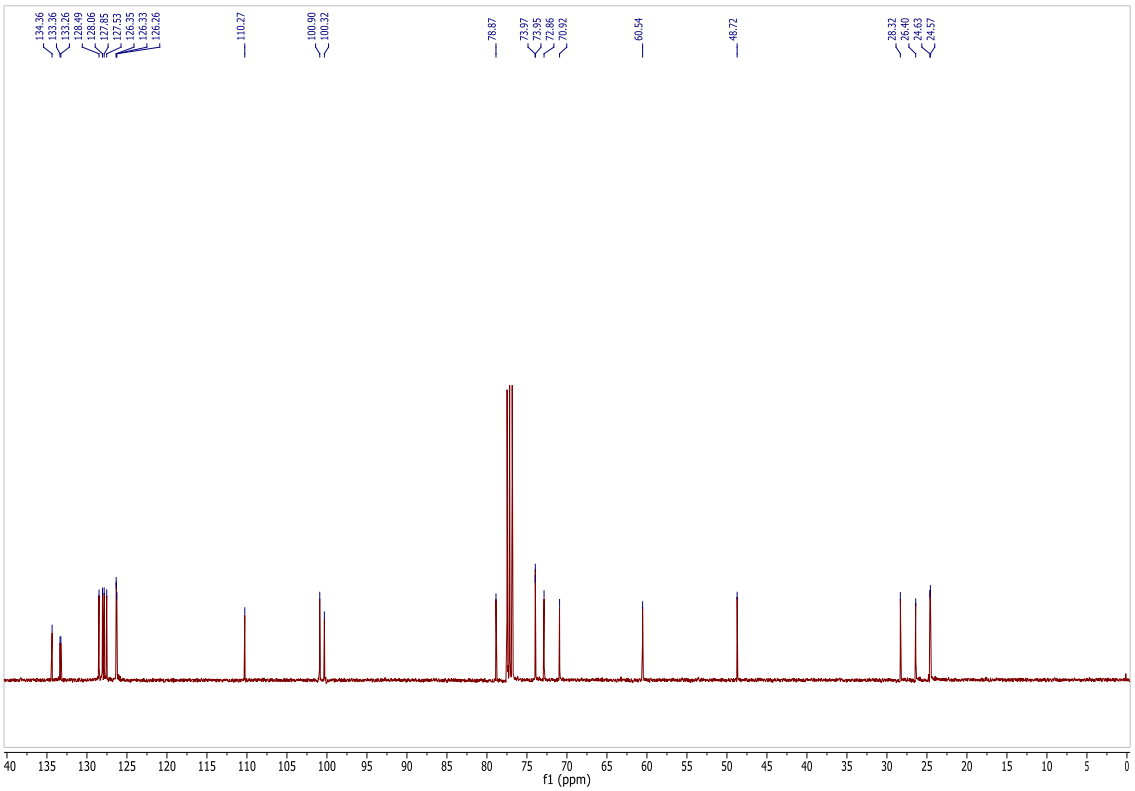




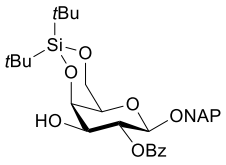
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for compound **13**

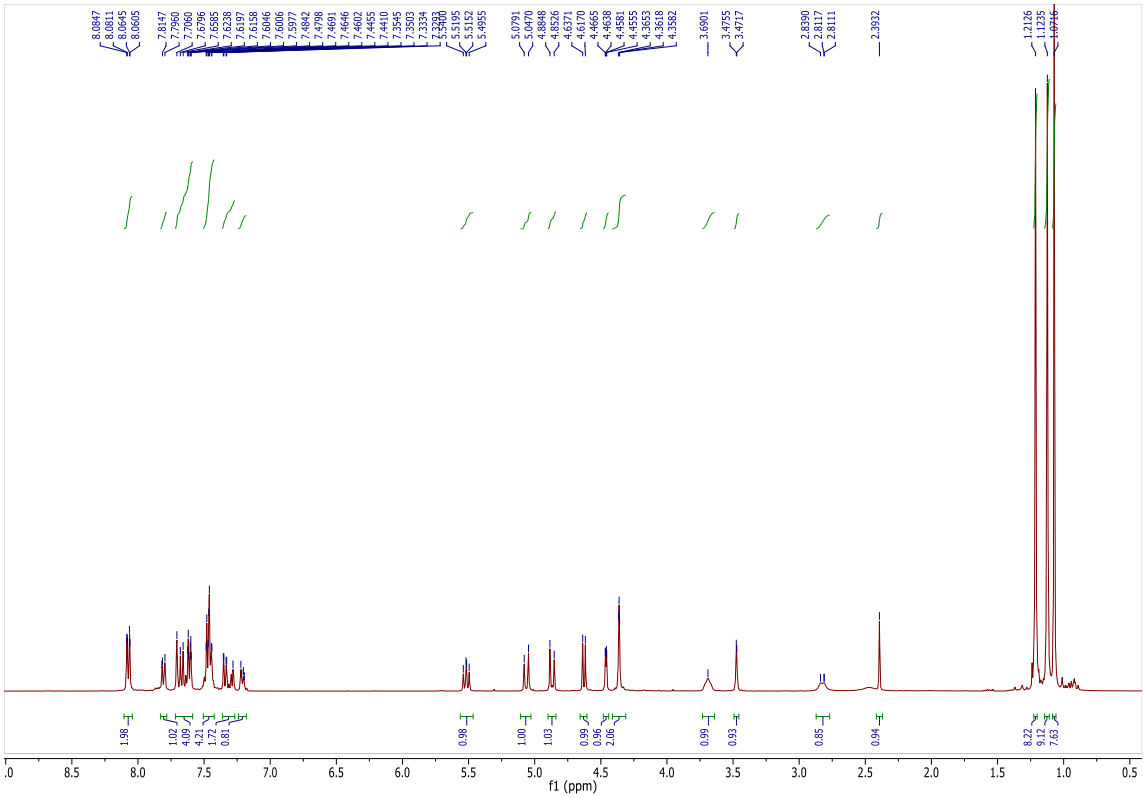


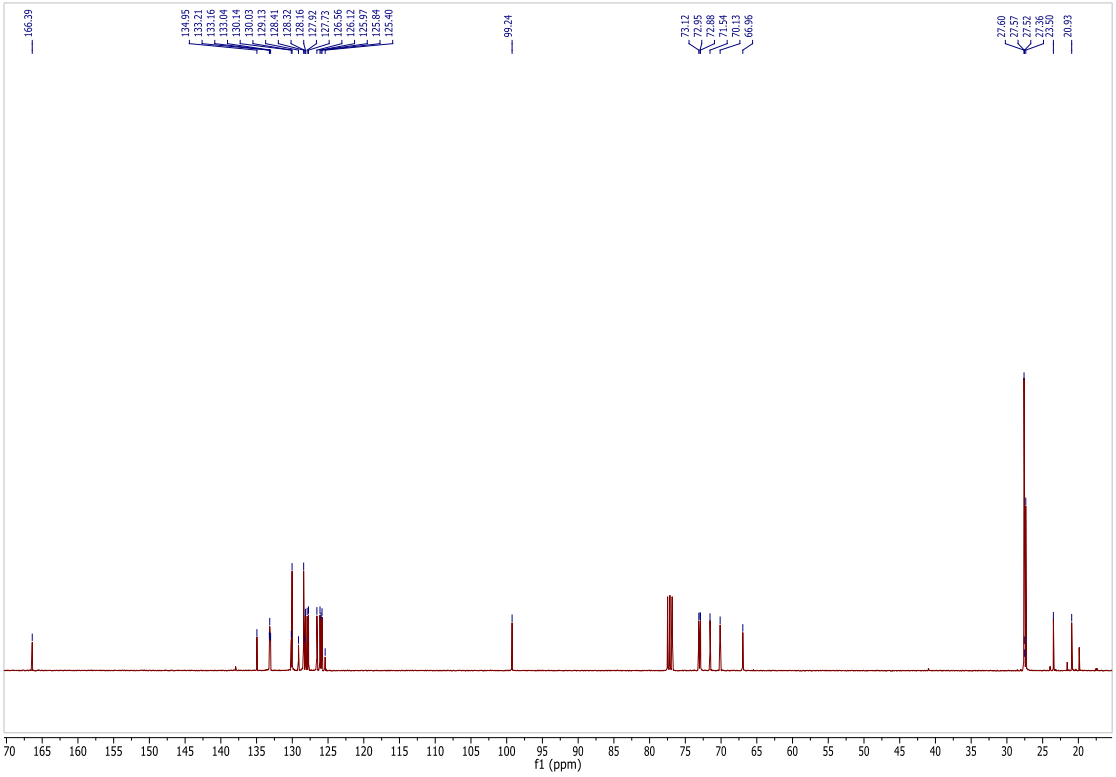




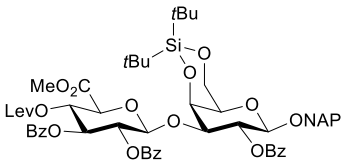
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for compound **15**

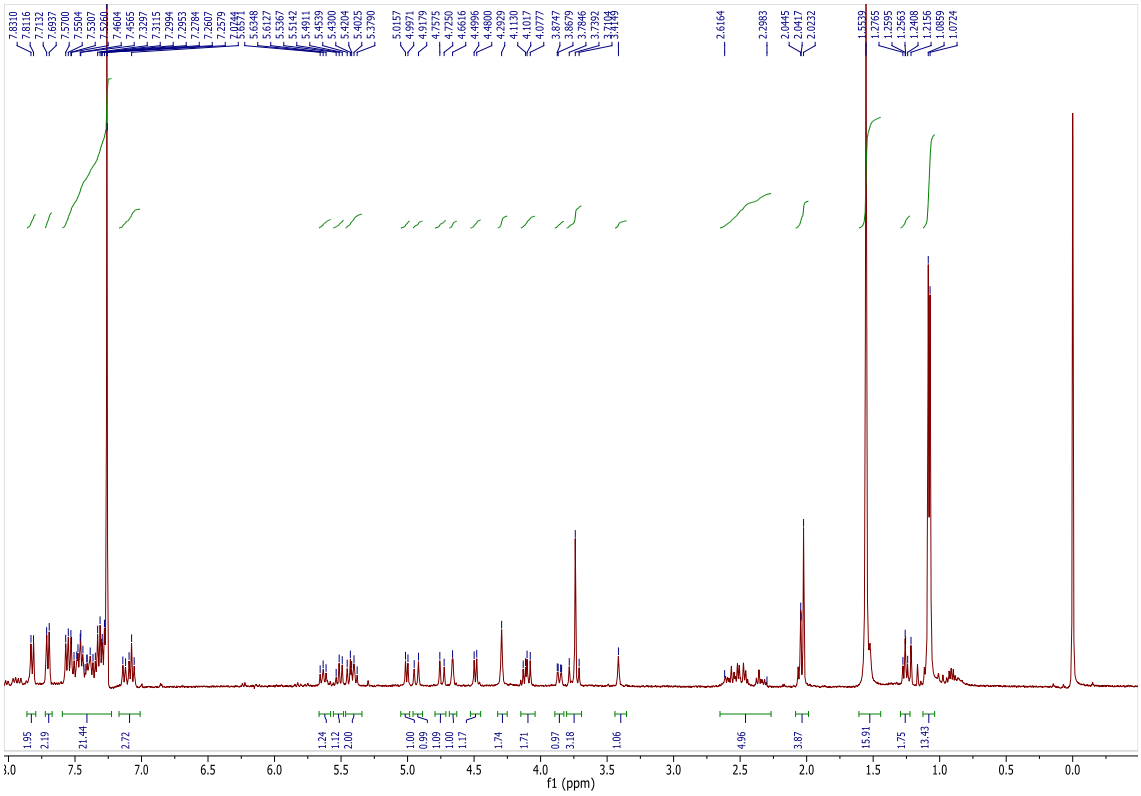


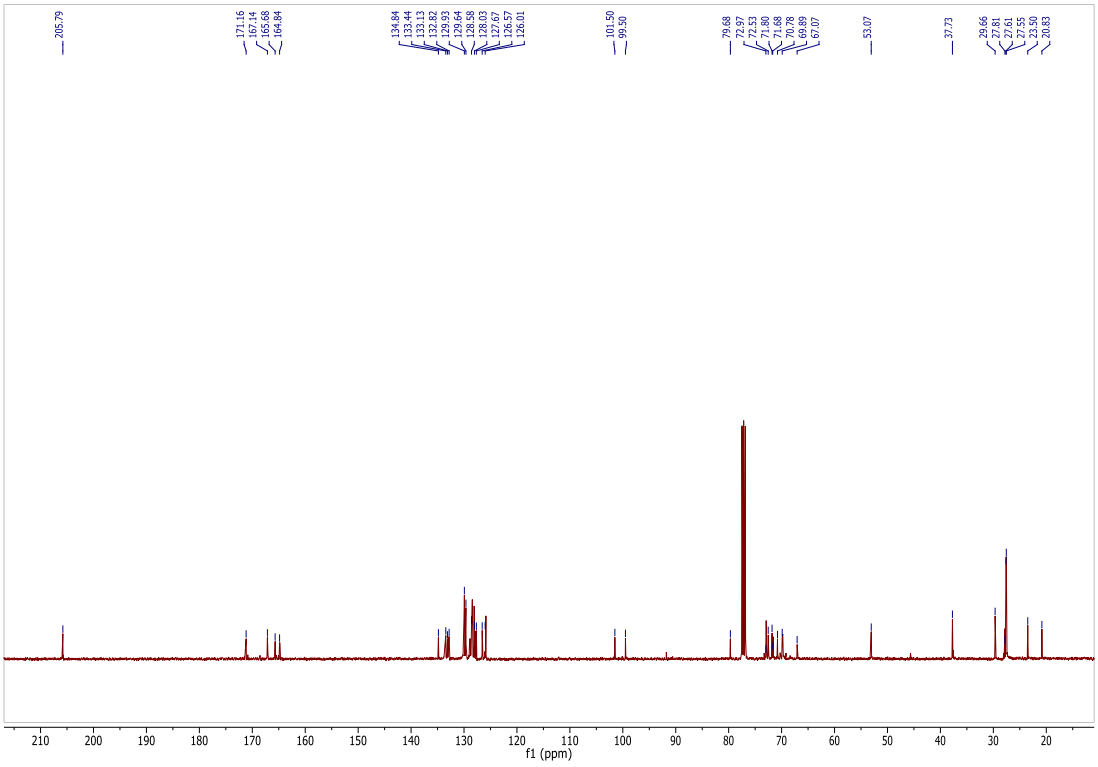




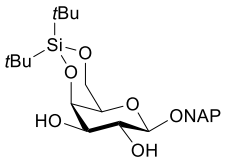
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for compound **17**

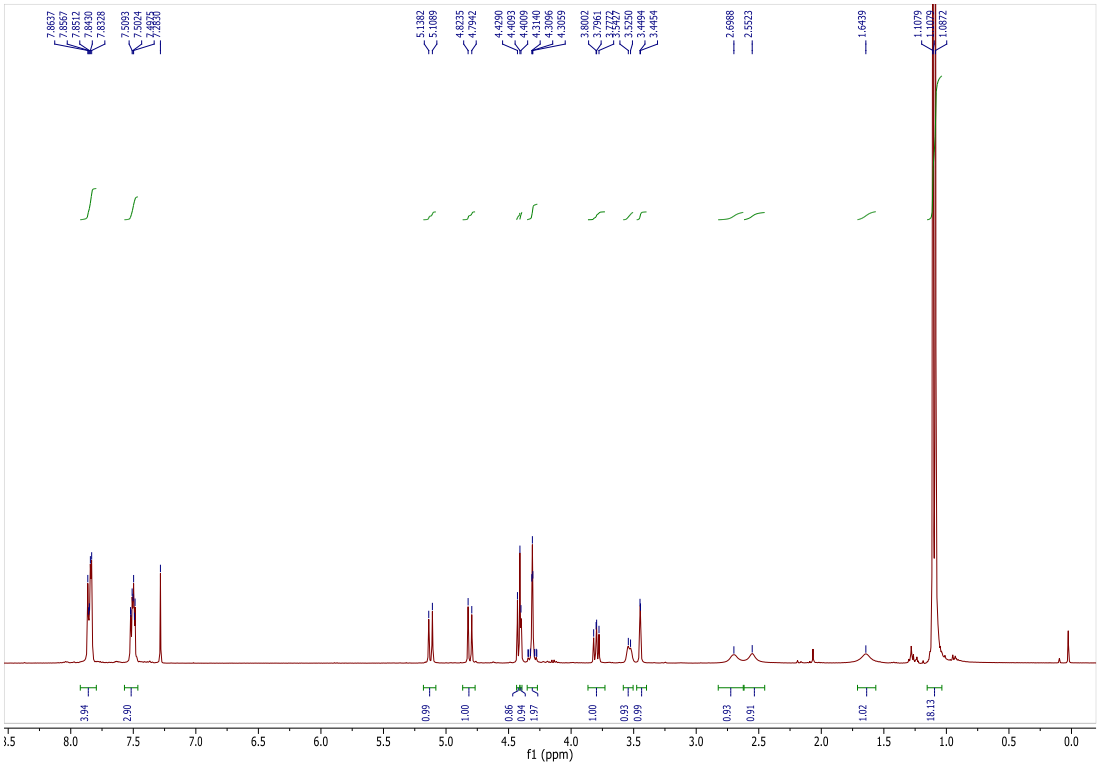


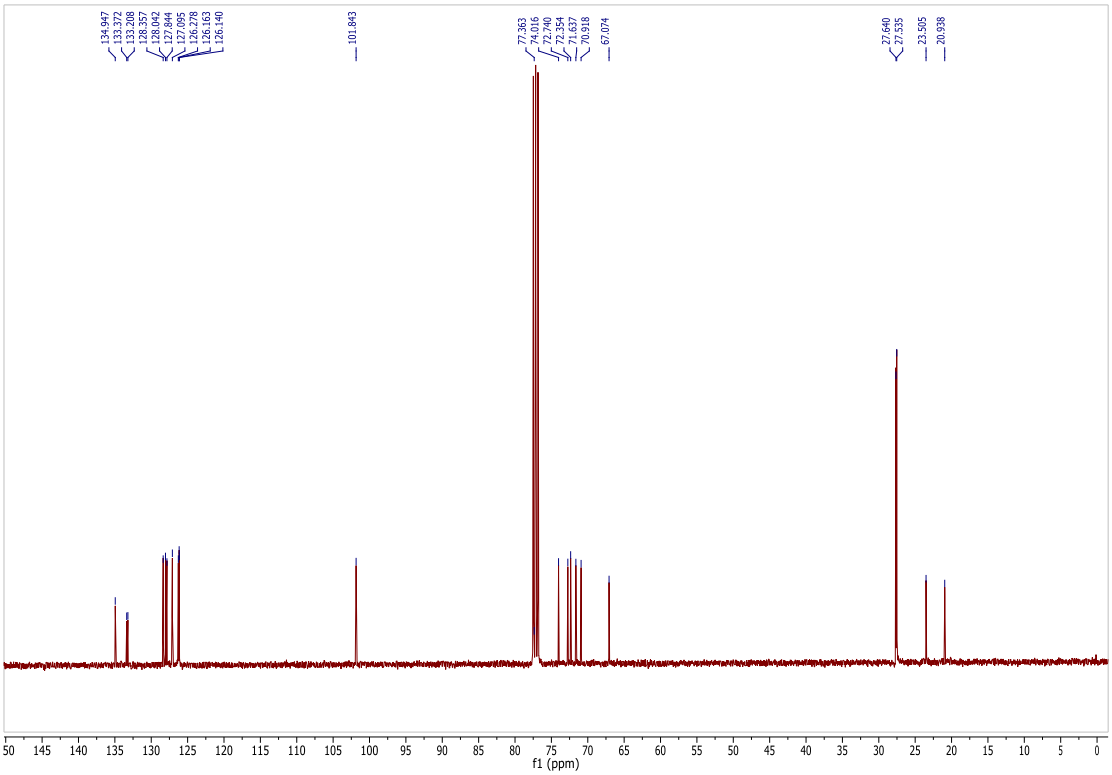




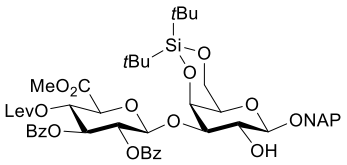
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for compound **18**

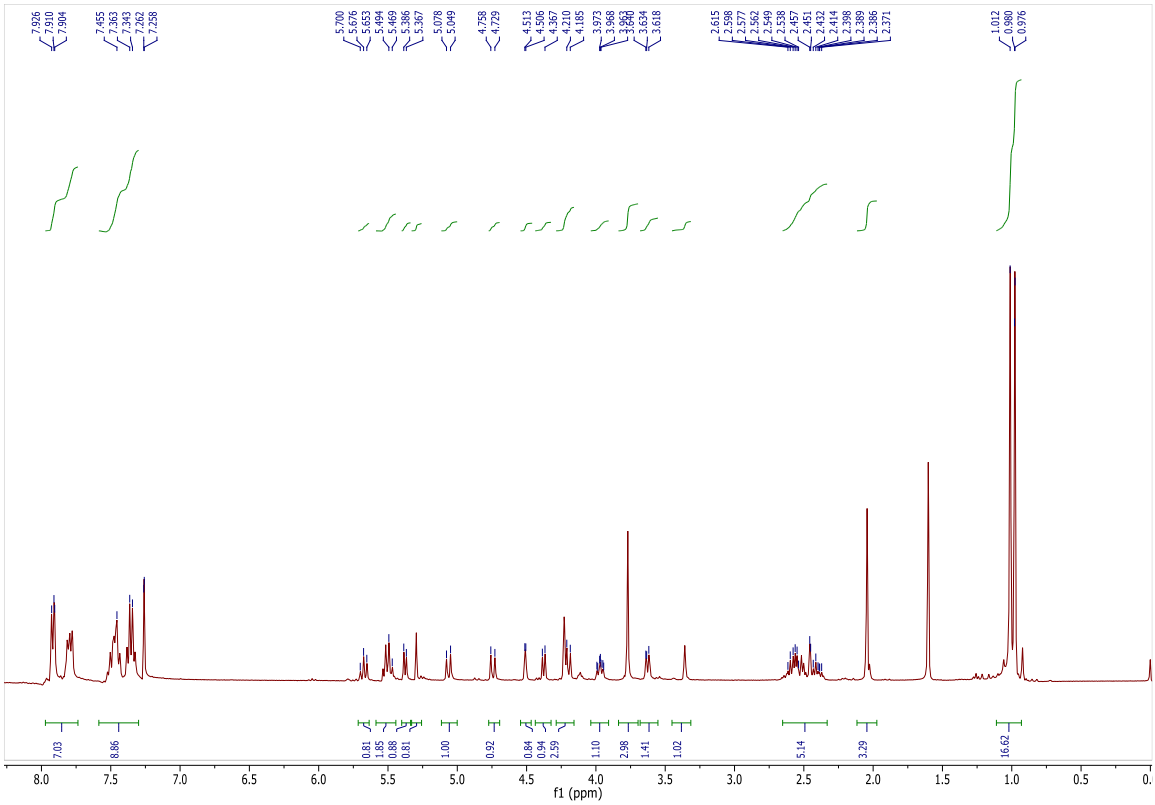


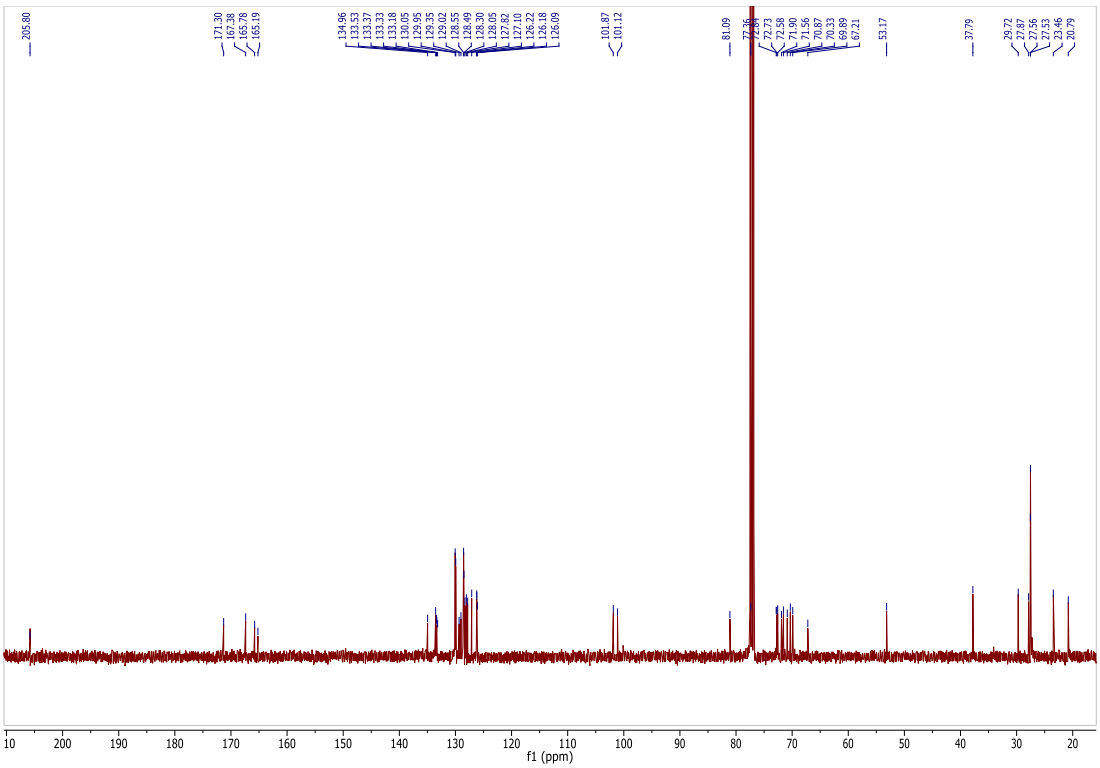




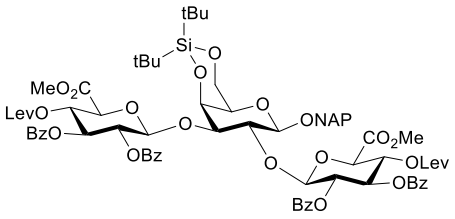
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for compound **19**

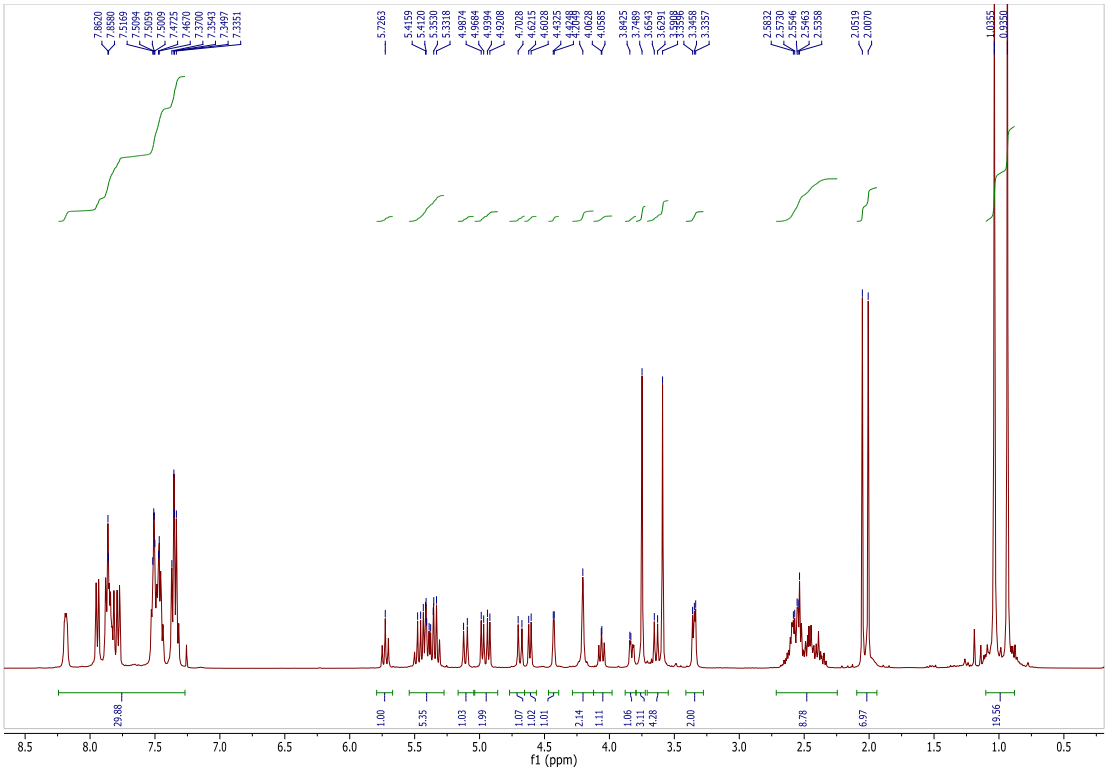


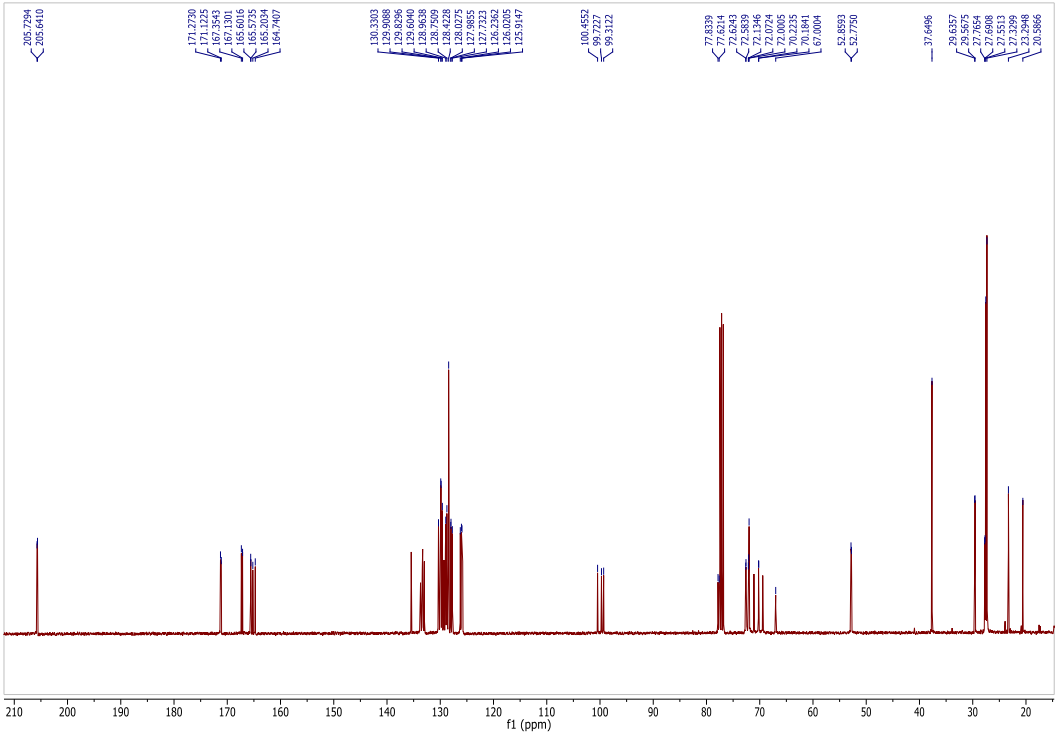




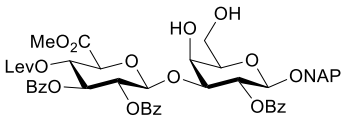
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for compound **20**

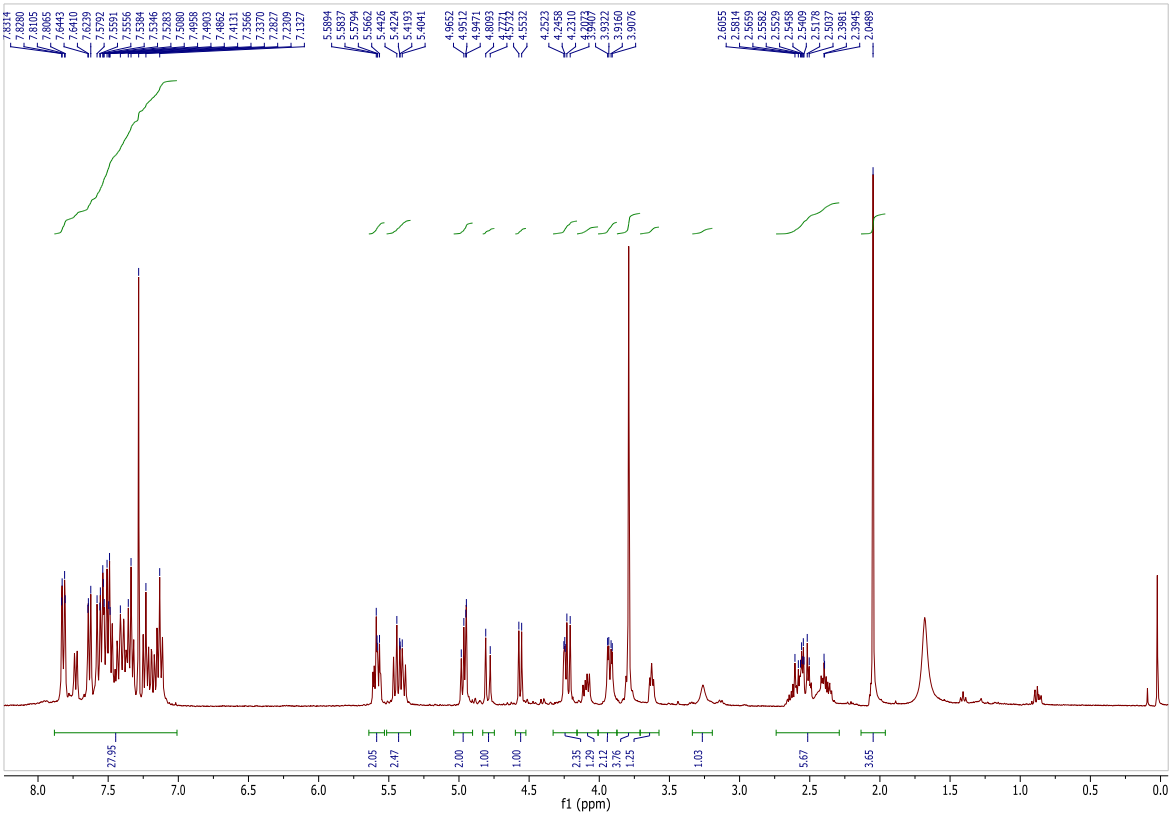


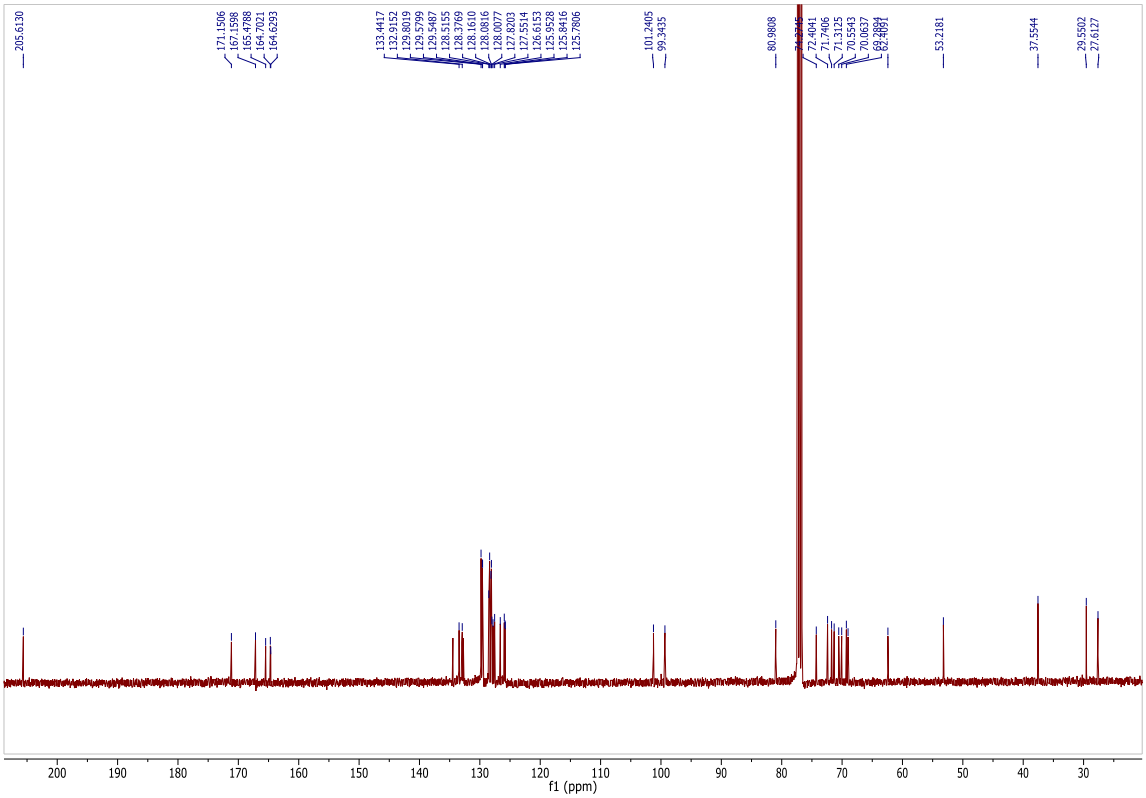




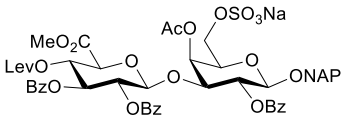
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for compound **21**

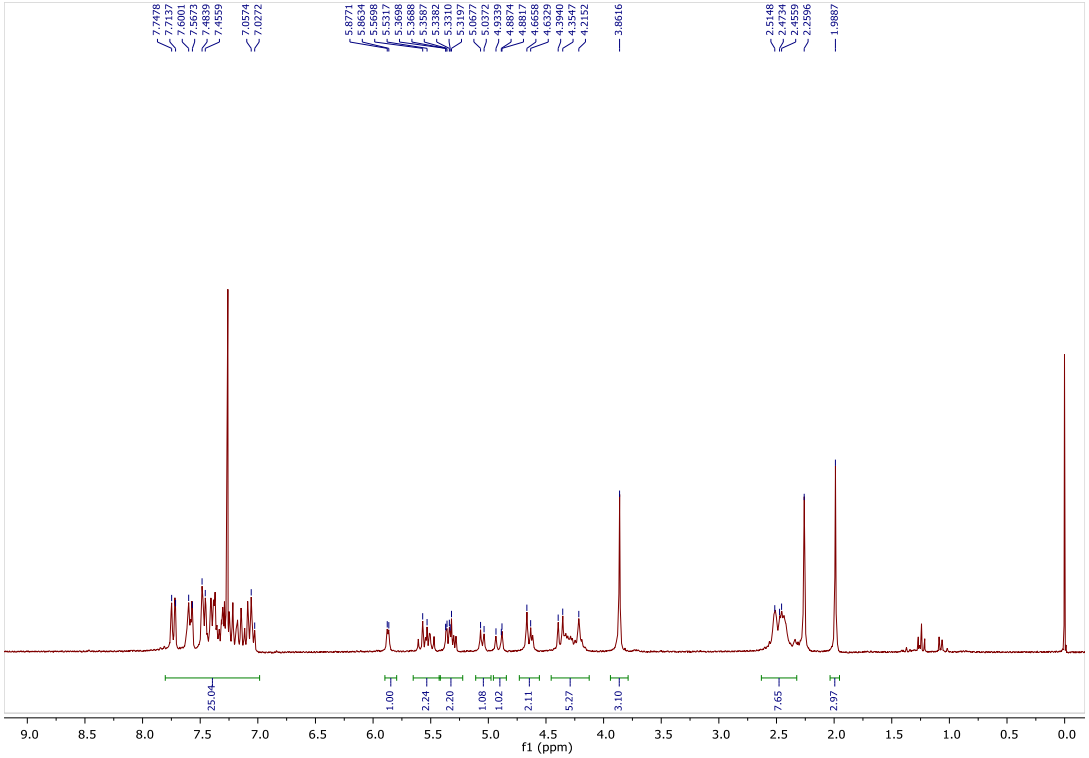


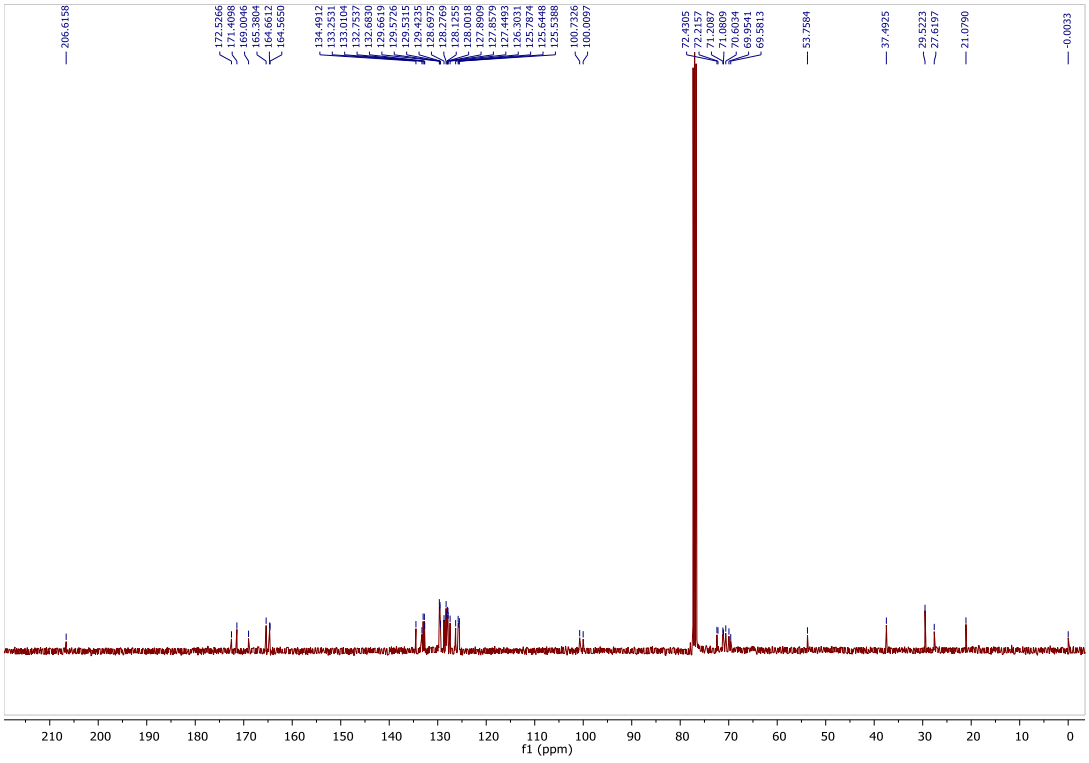




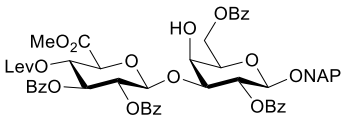
^{1}H NMR (250 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for compound **22**

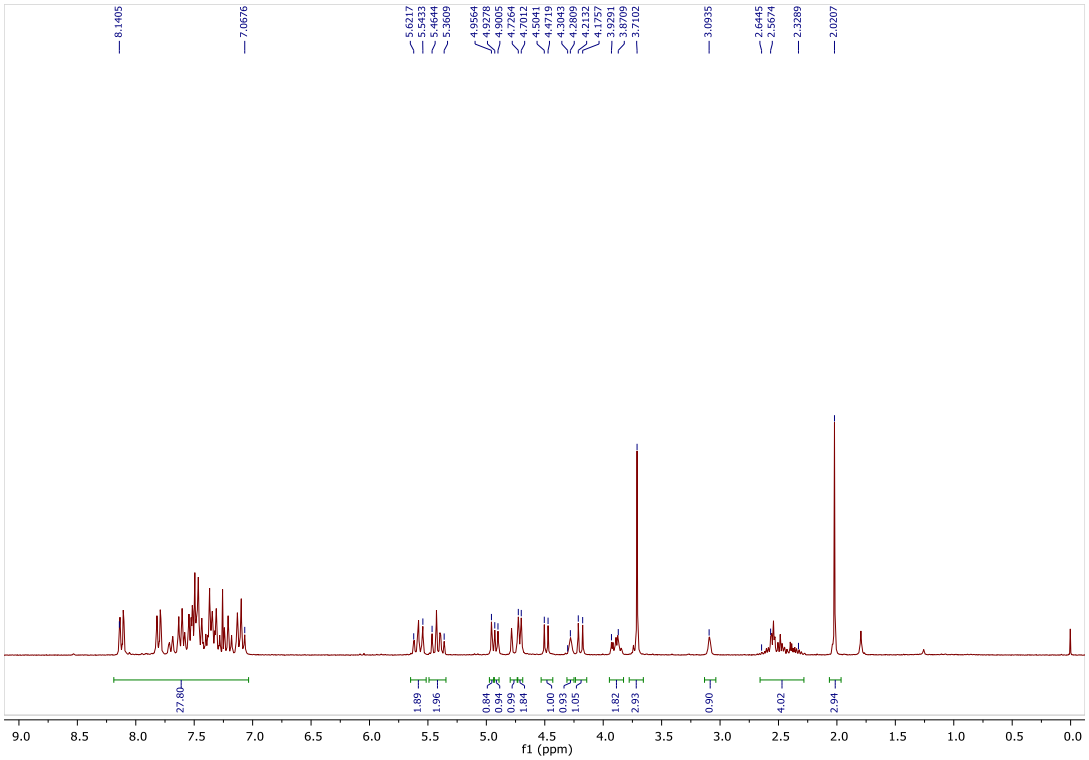


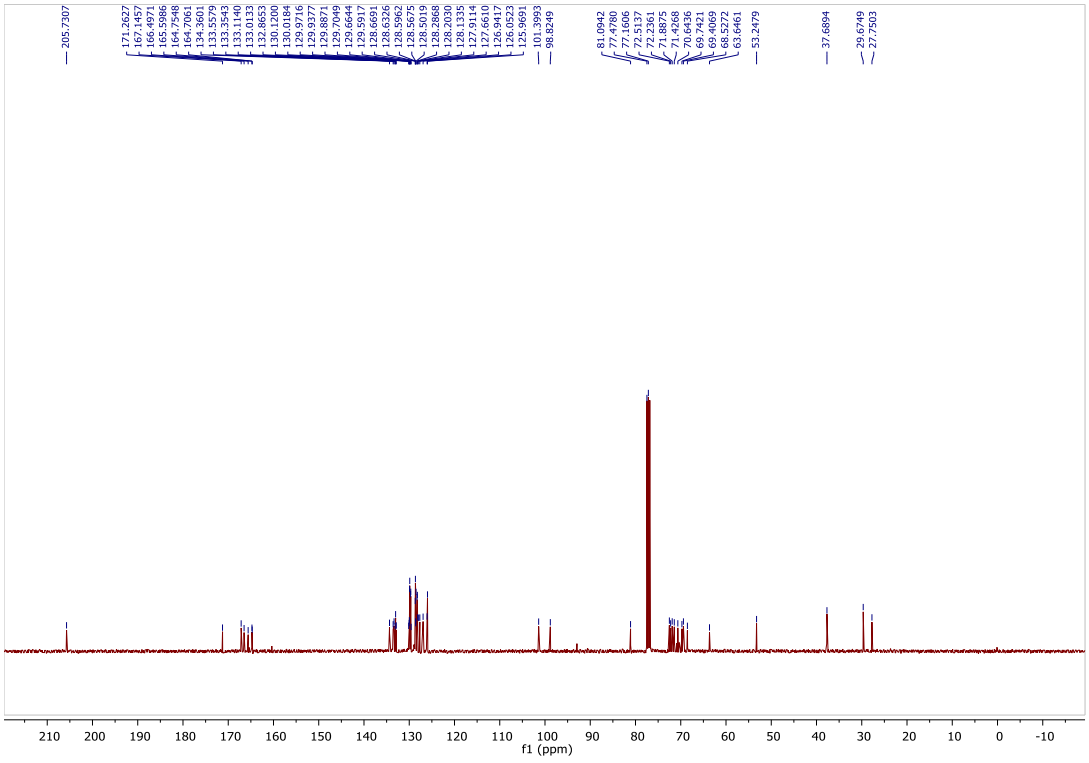




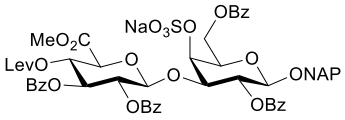
^{1}H NMR (250 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for compound **23**

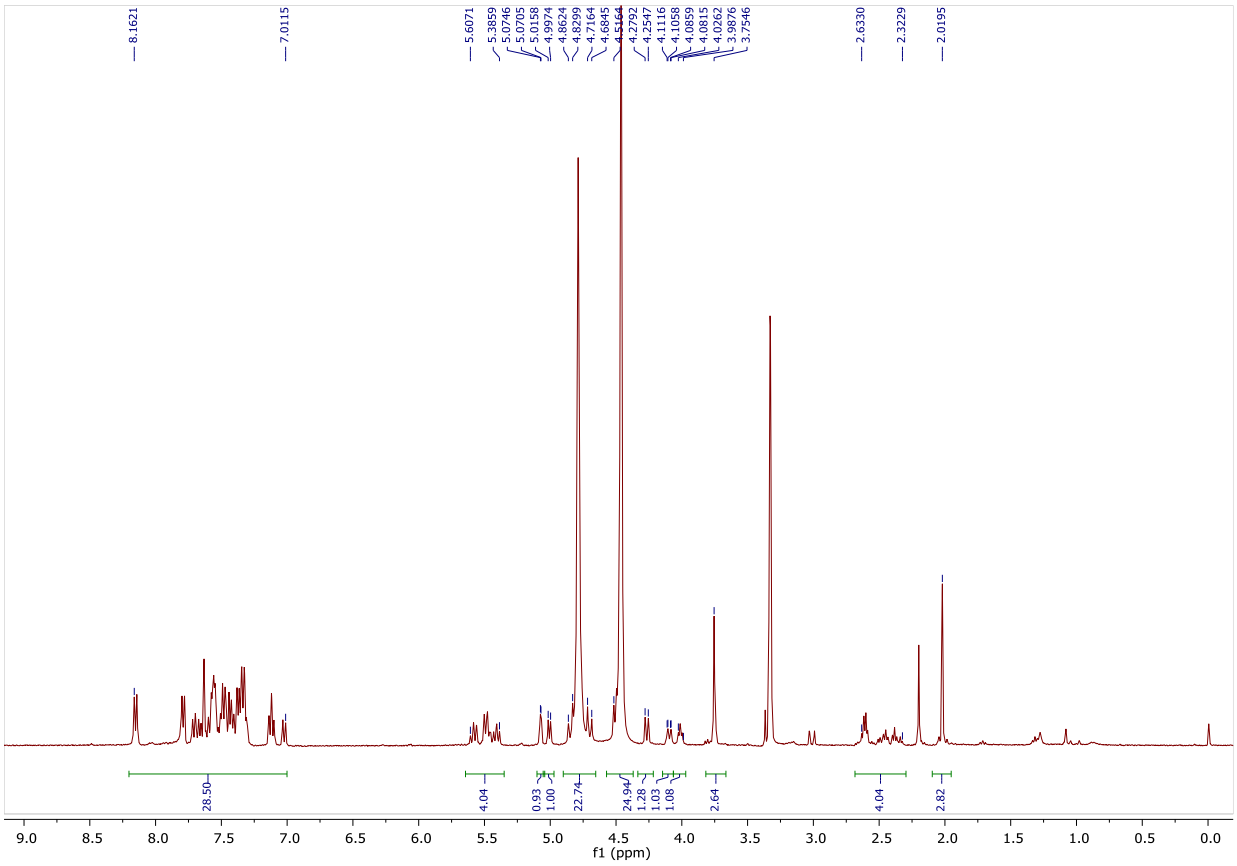


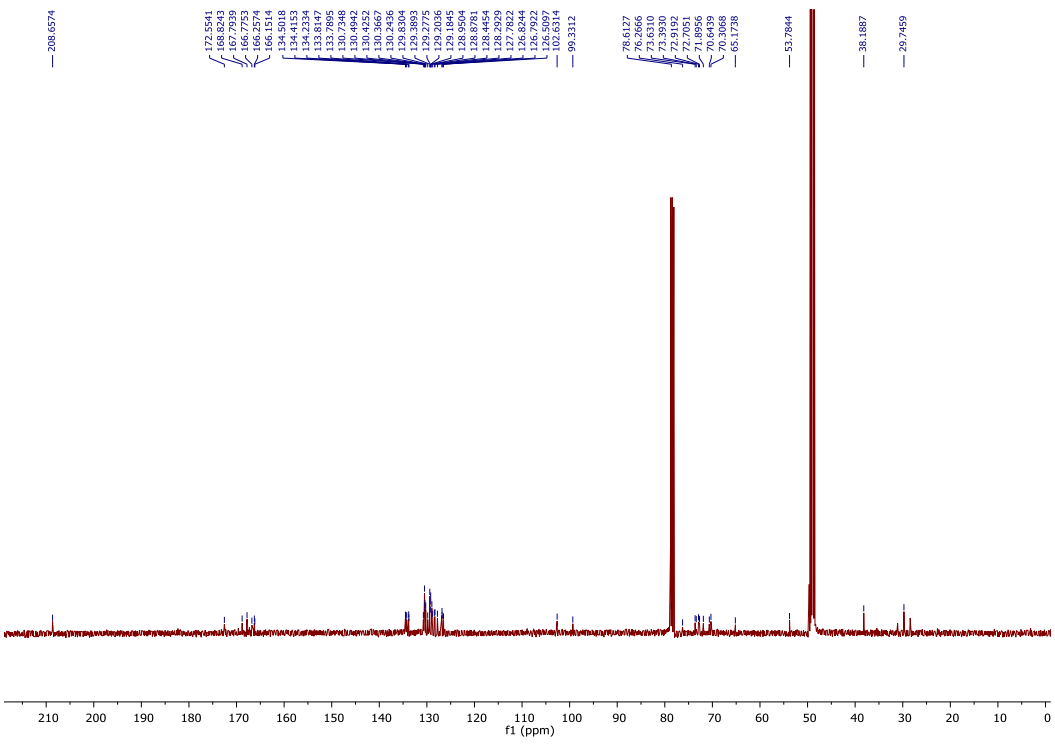




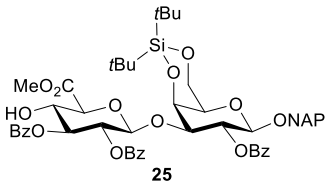
^{1}H NMR (250 MHz, $CDCl_3/CD_3OD/D_2O$) and ^{13}C NMR (100 MHz, $CDCl_3/CD_3OD/D_2O$) for compound **24**



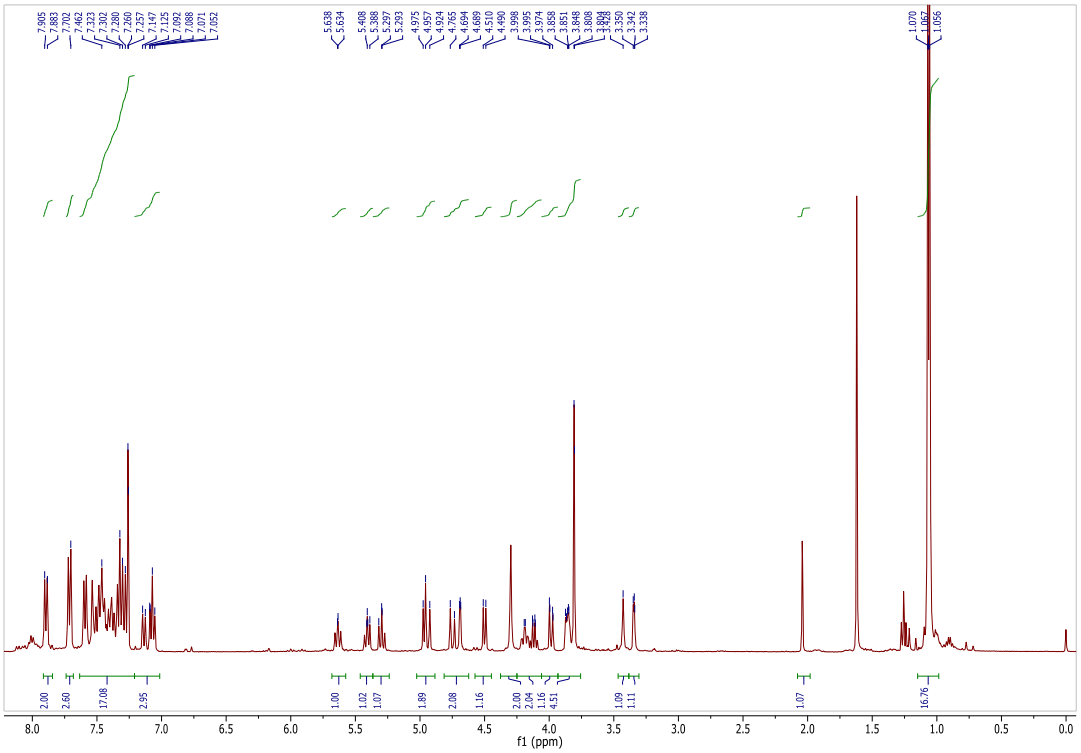


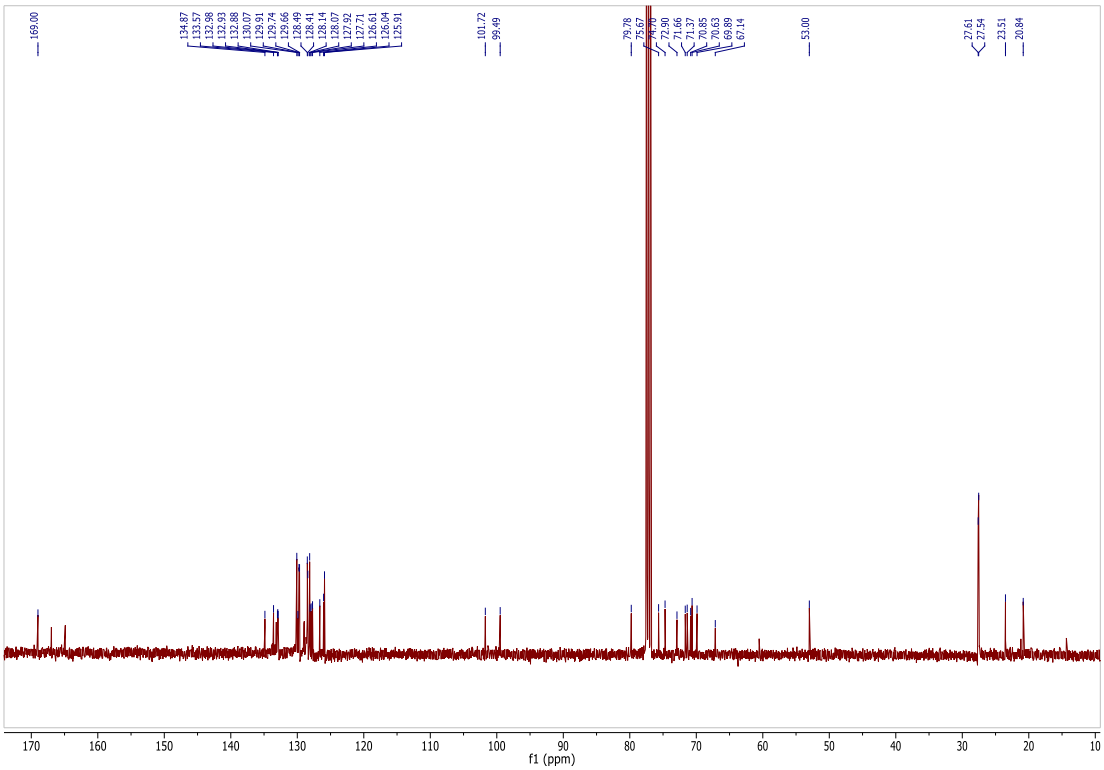


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for compound **25**

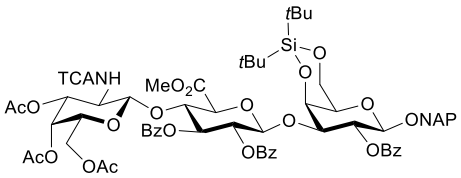


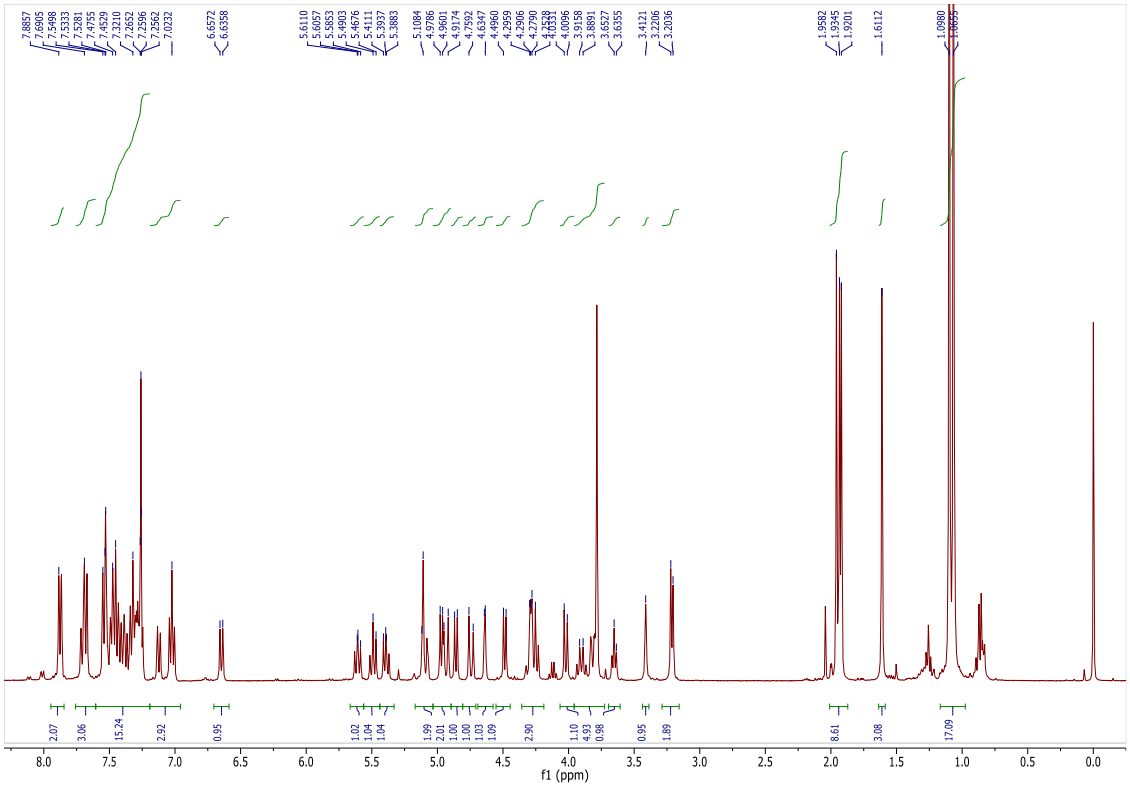
25

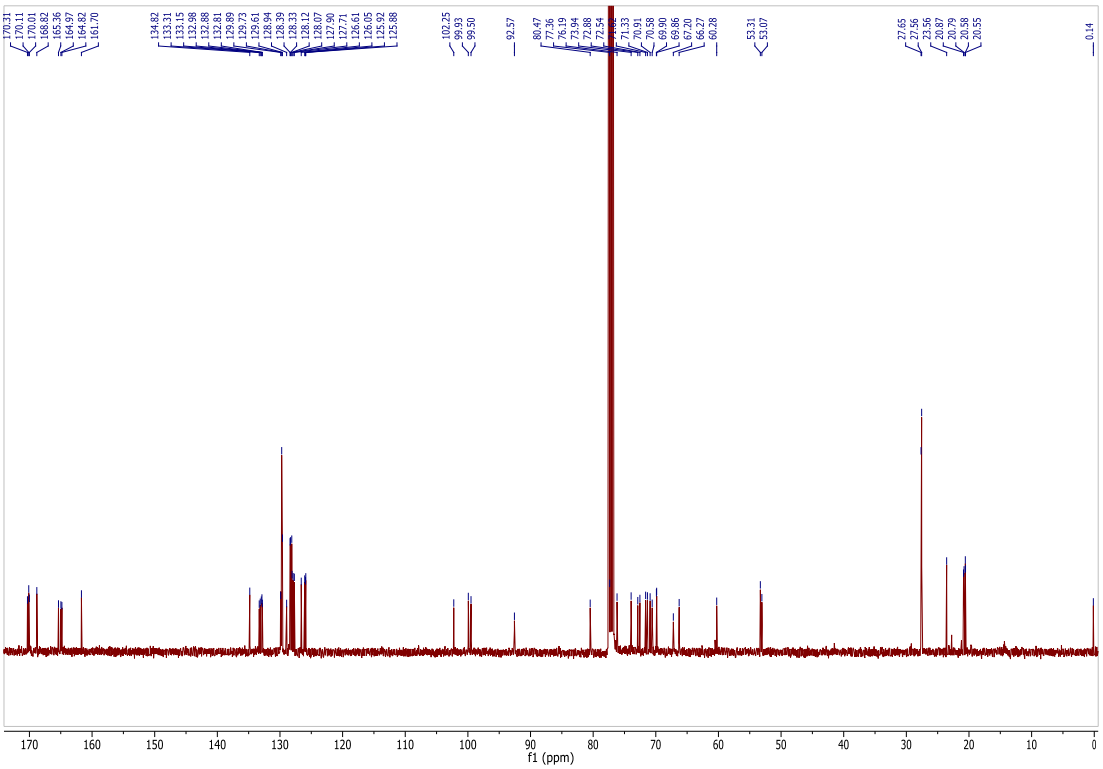




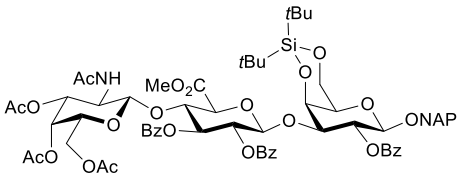
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for compound **27**

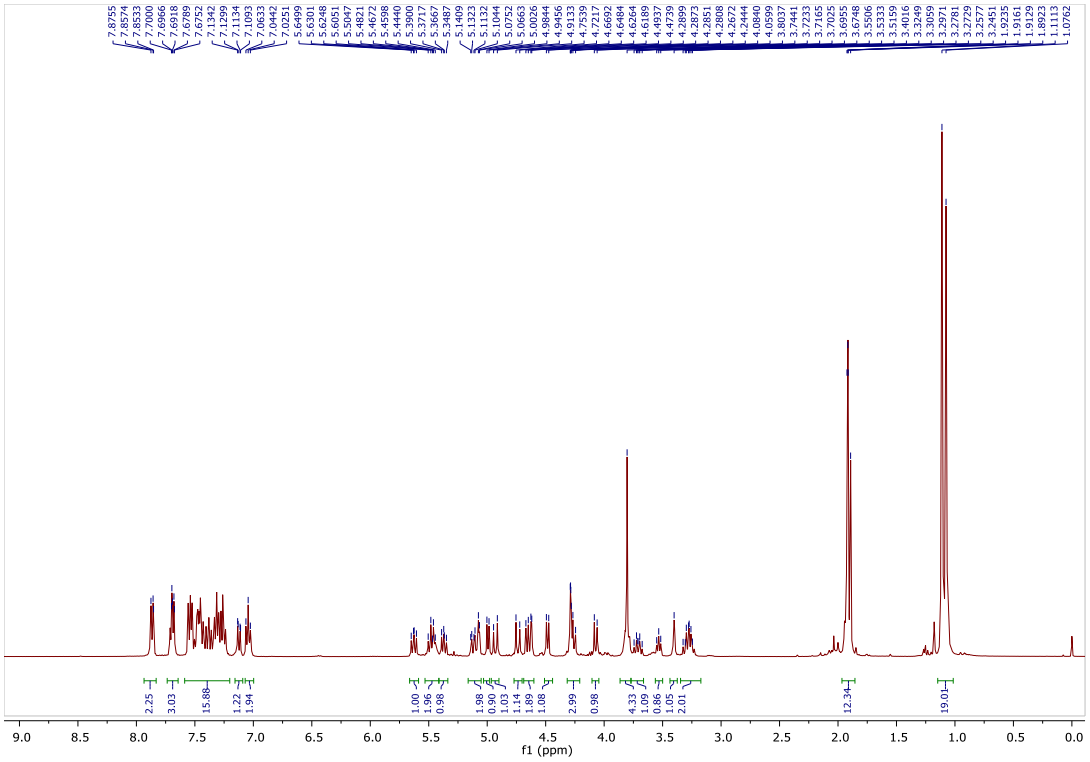


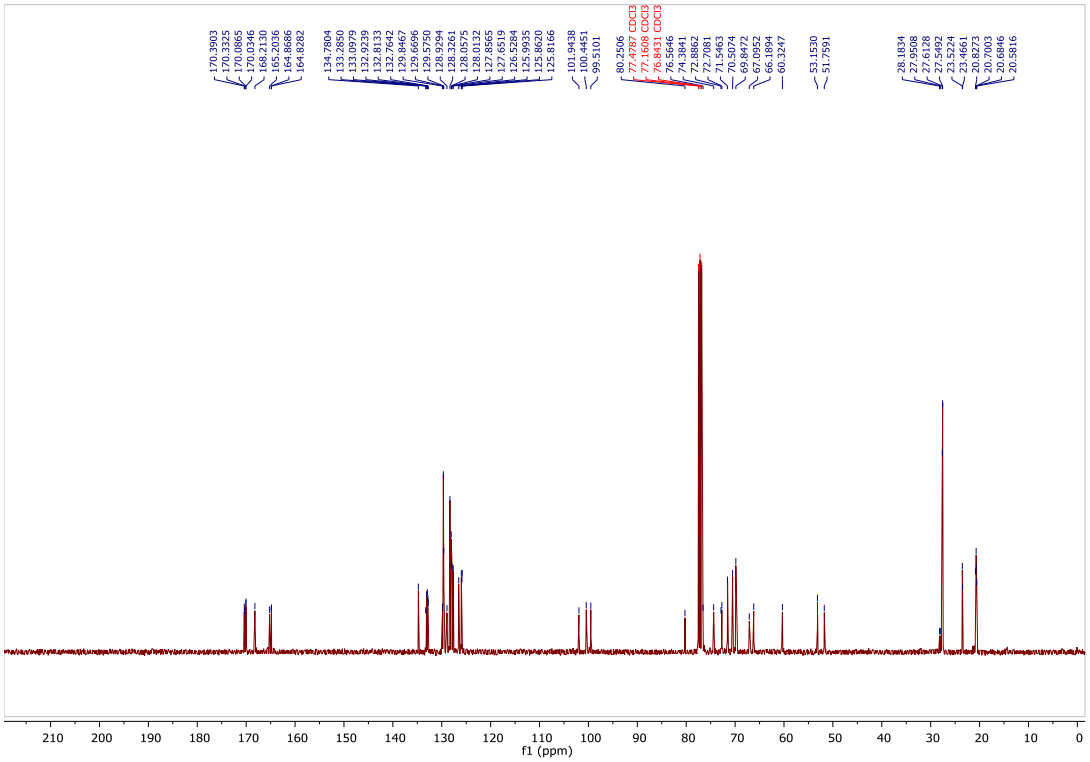




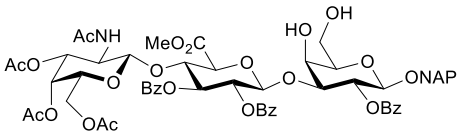
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for compound **28**

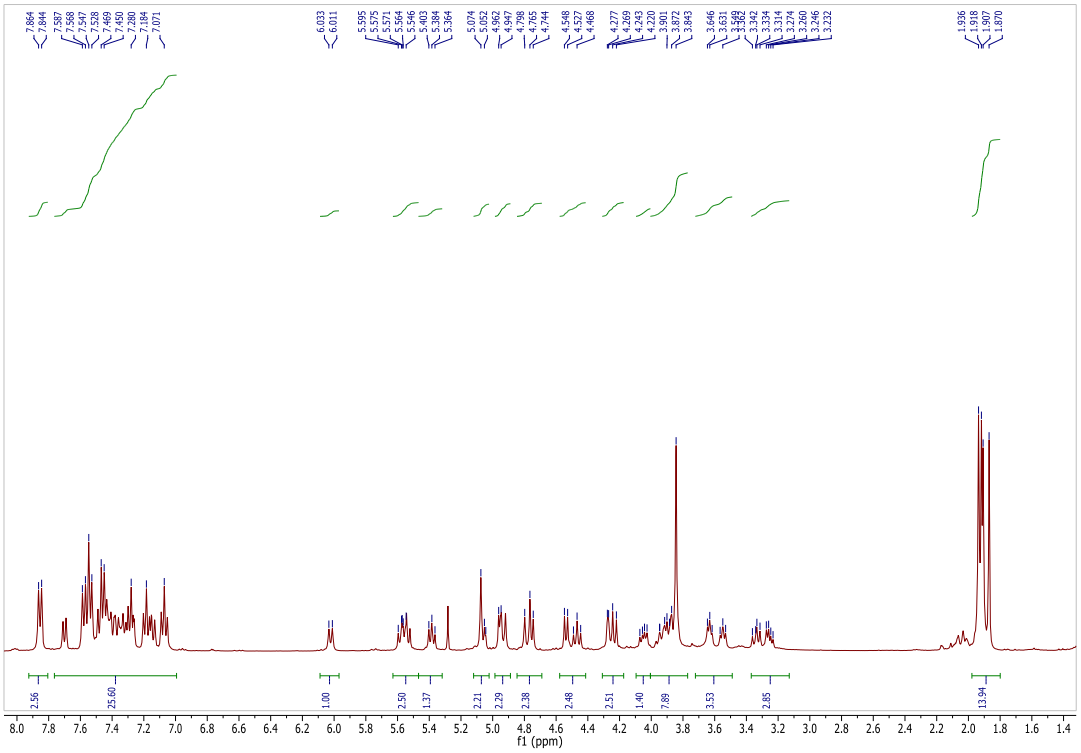


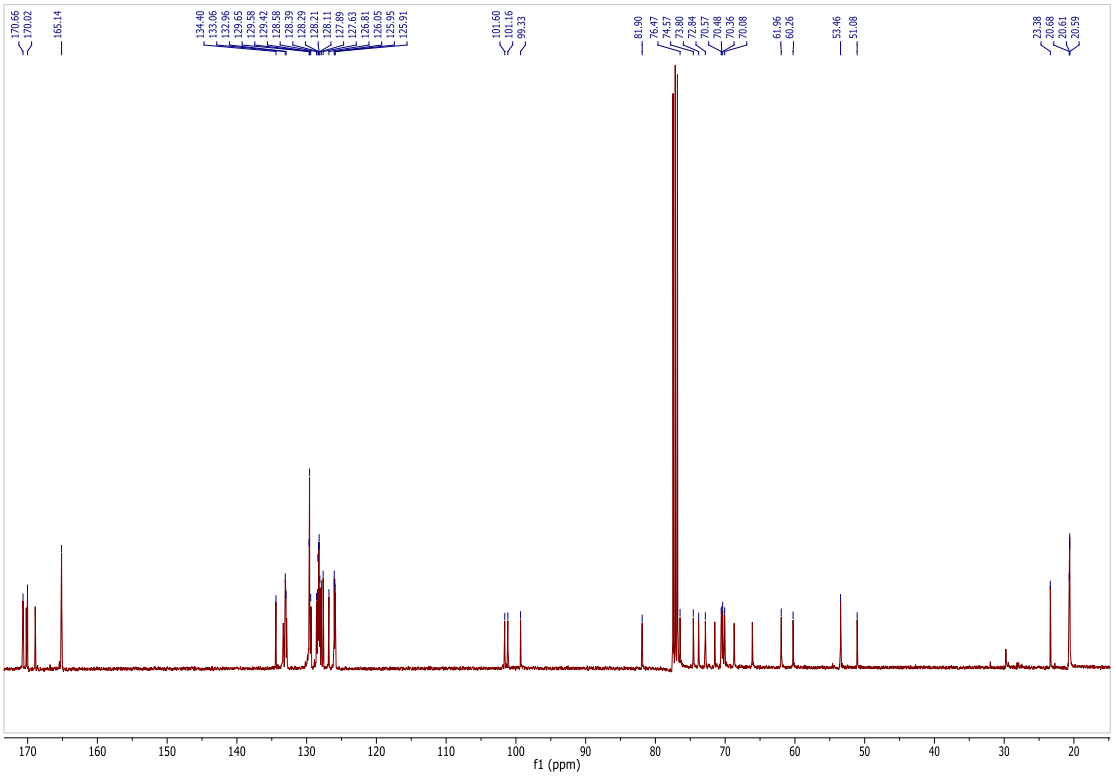




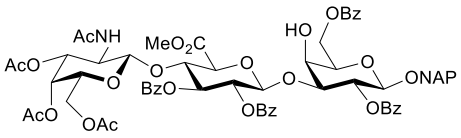
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for compound **29**

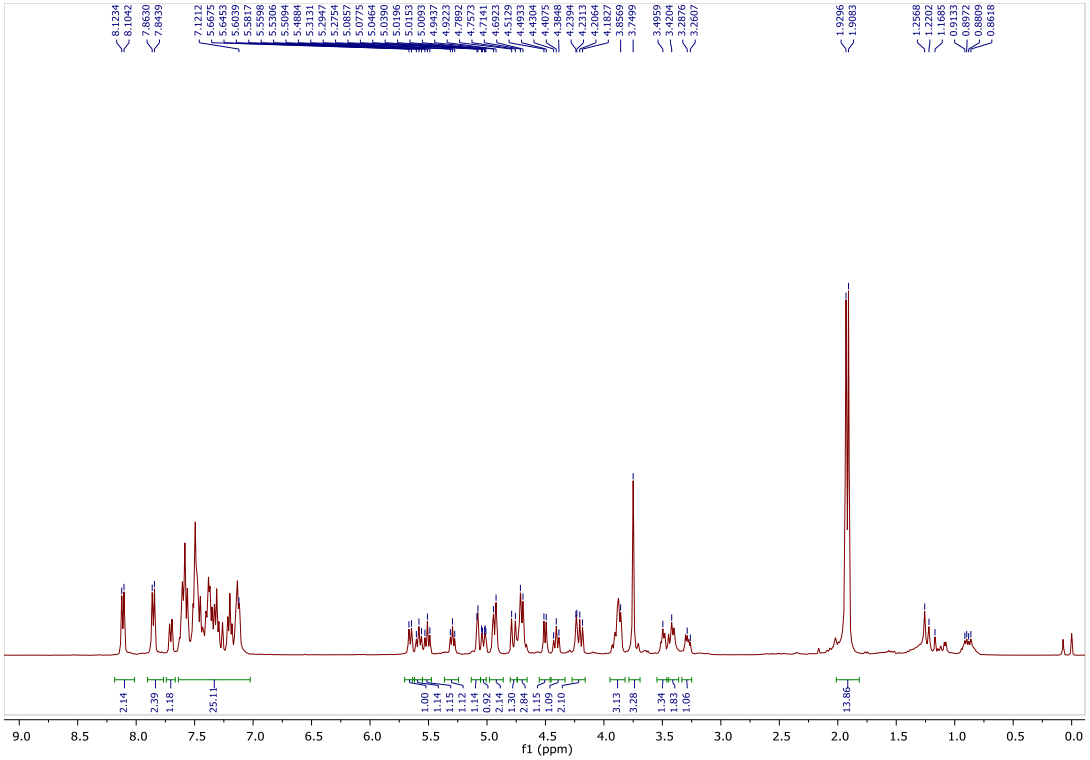


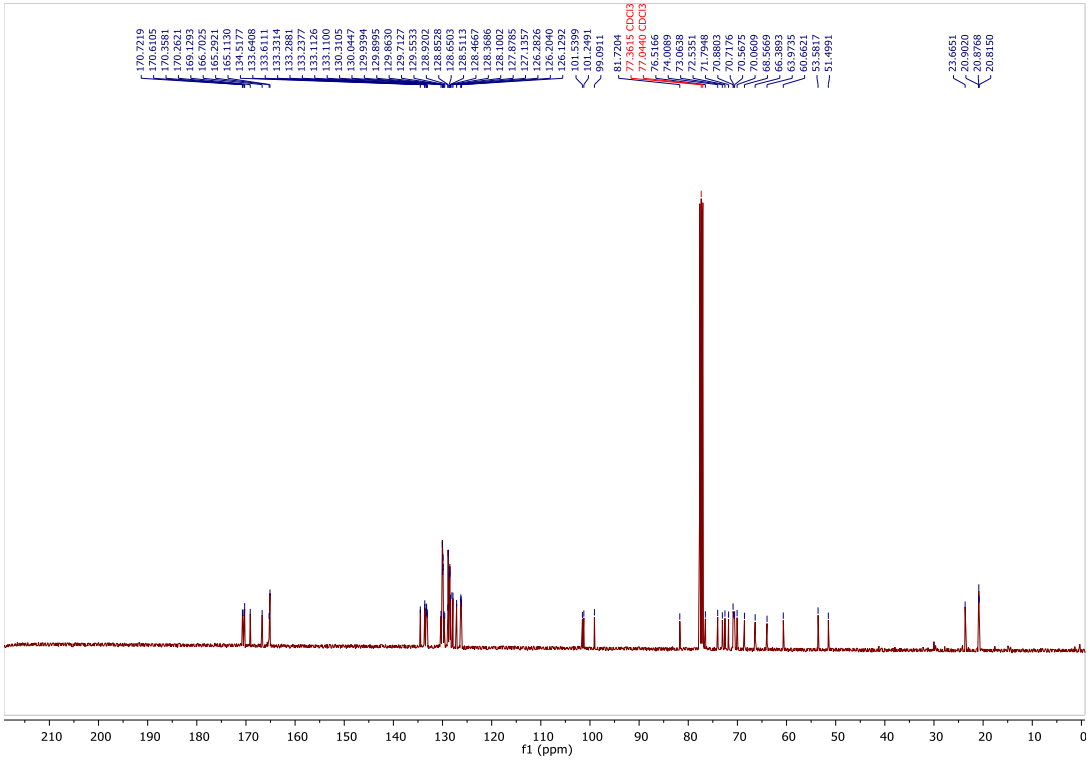




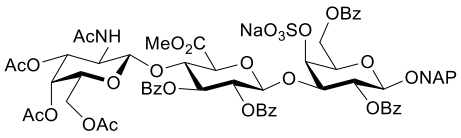
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for compound **30**

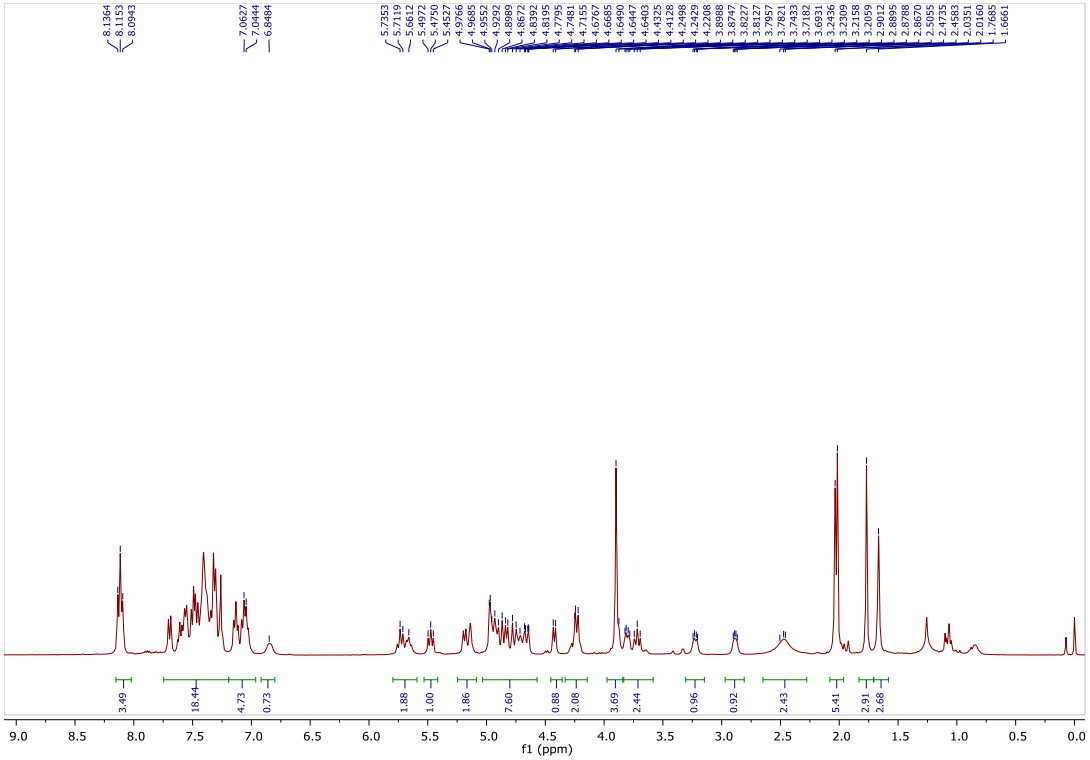


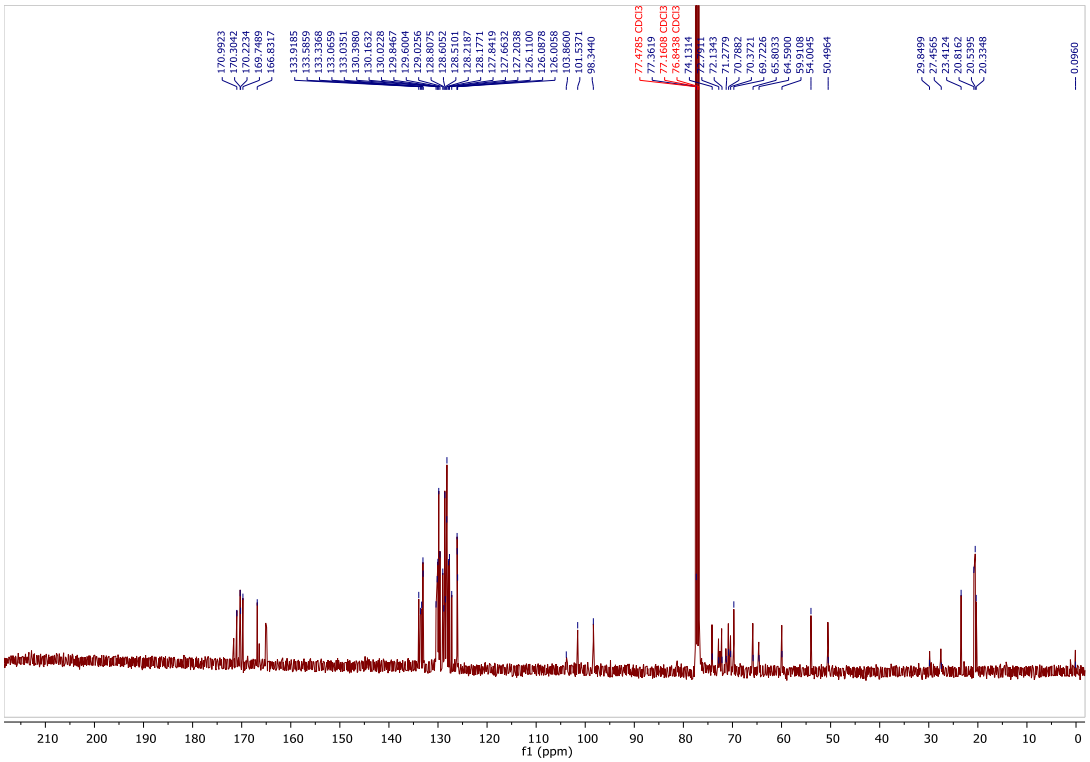




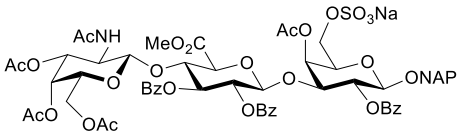
^{1}H NMR (250 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for compound **31**

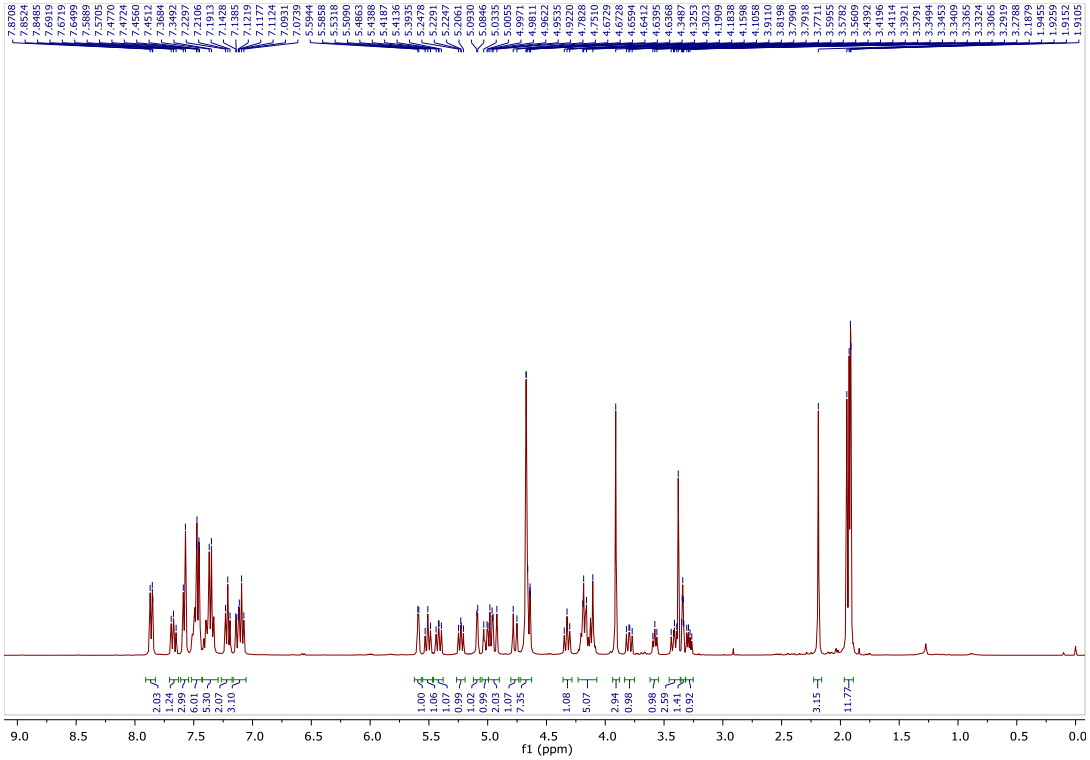


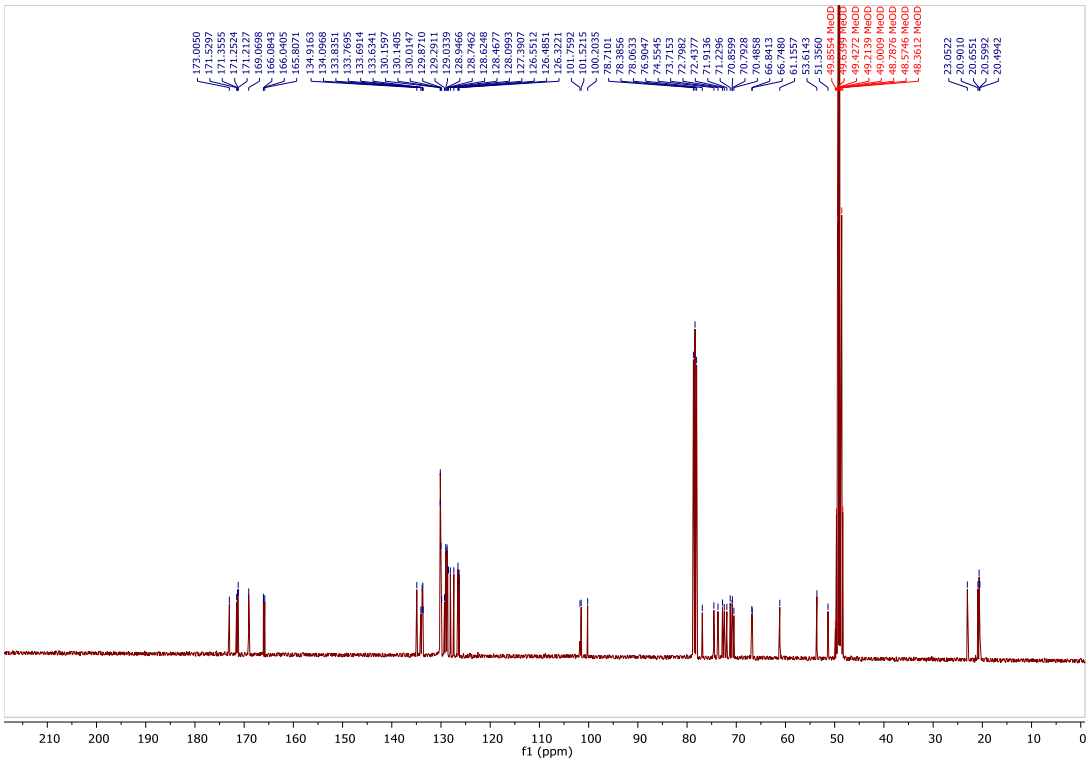




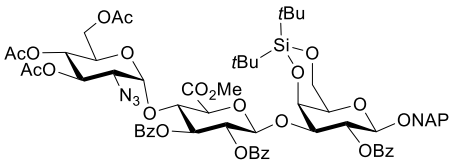
^{1}H NMR (400 MHz, CD_3OD) and ^{13}C NMR (100 MHz, CD_3OD) for compound **32**

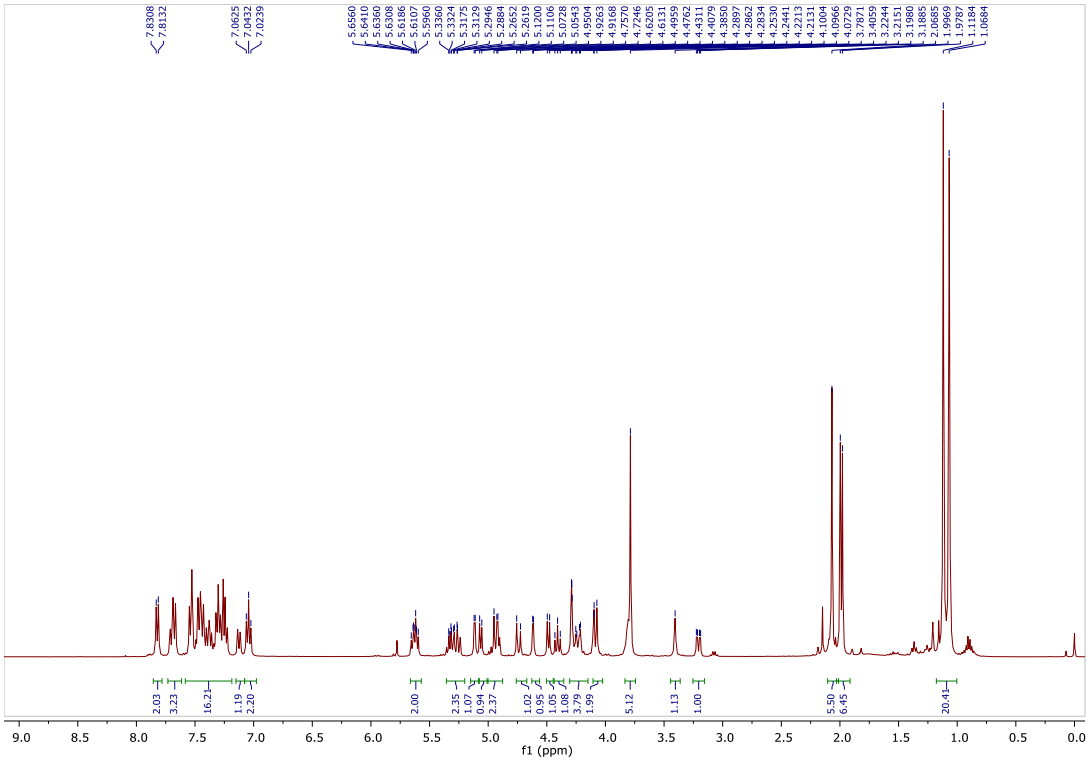


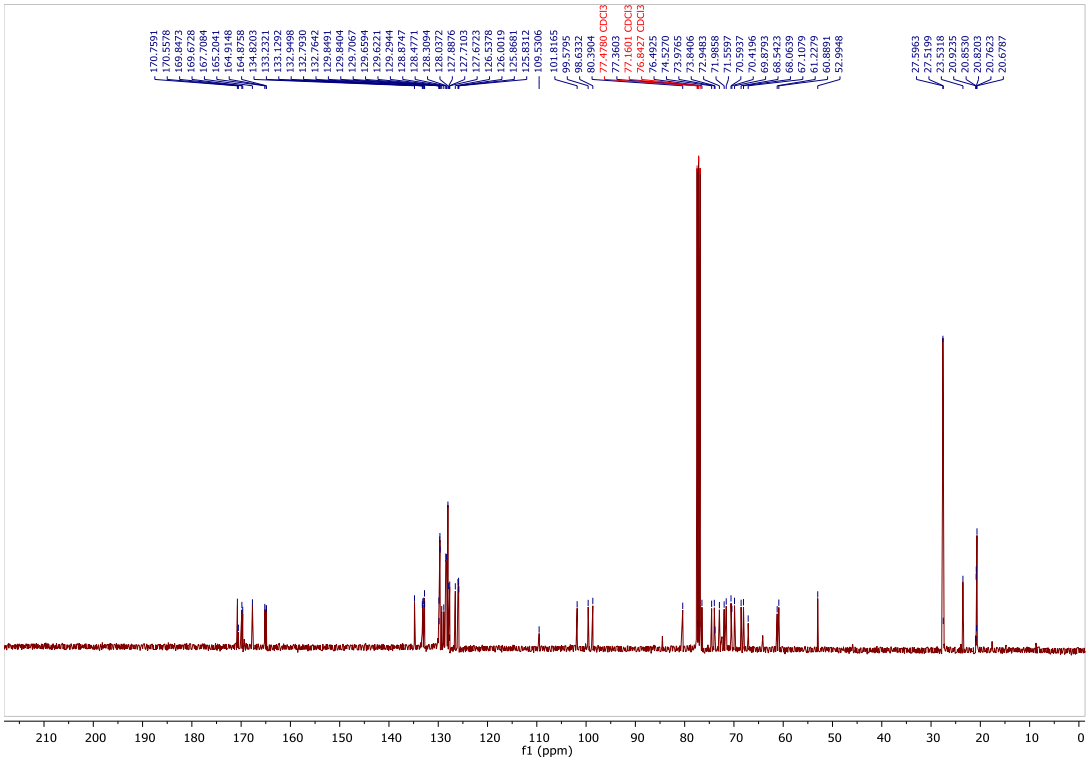




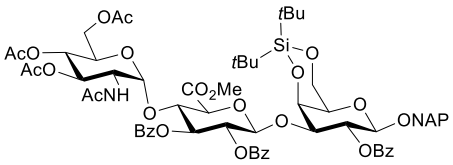
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for compound **34**

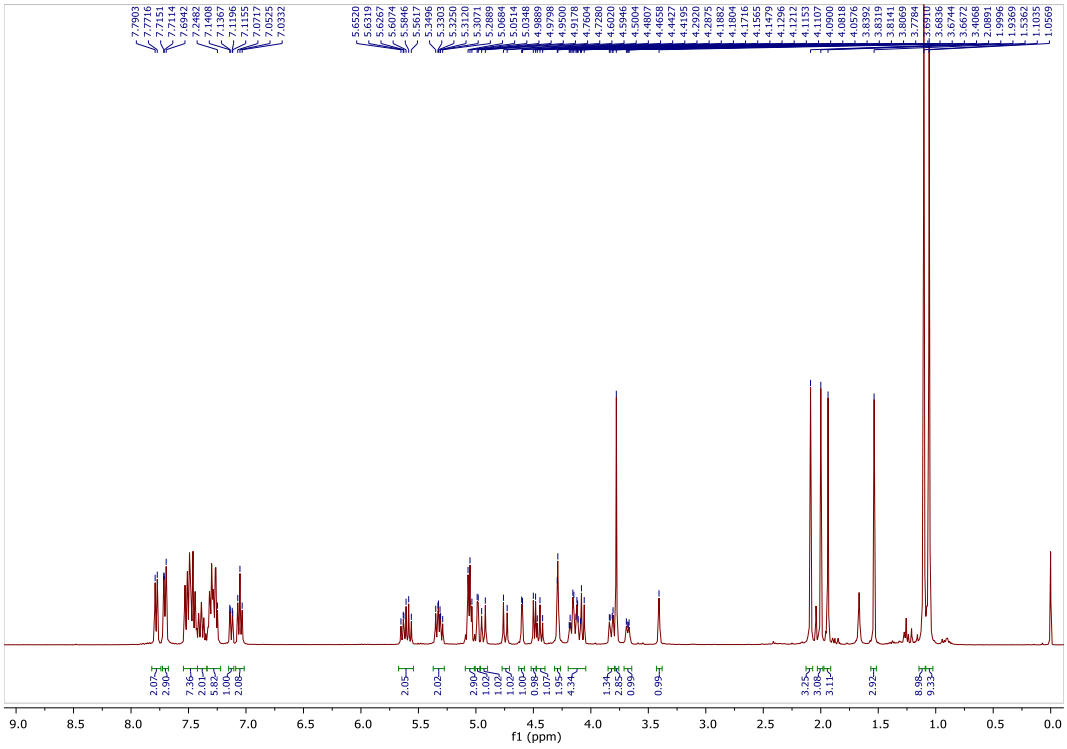


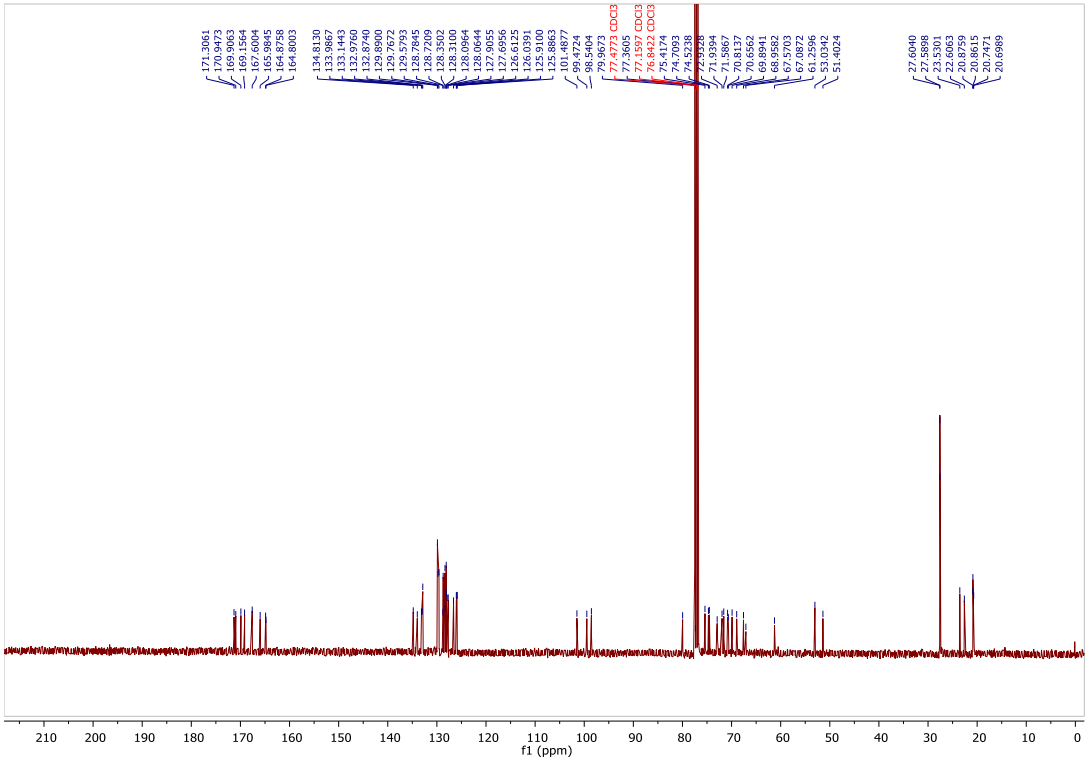




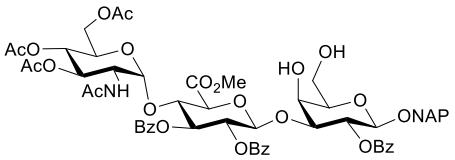
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for compound **35**

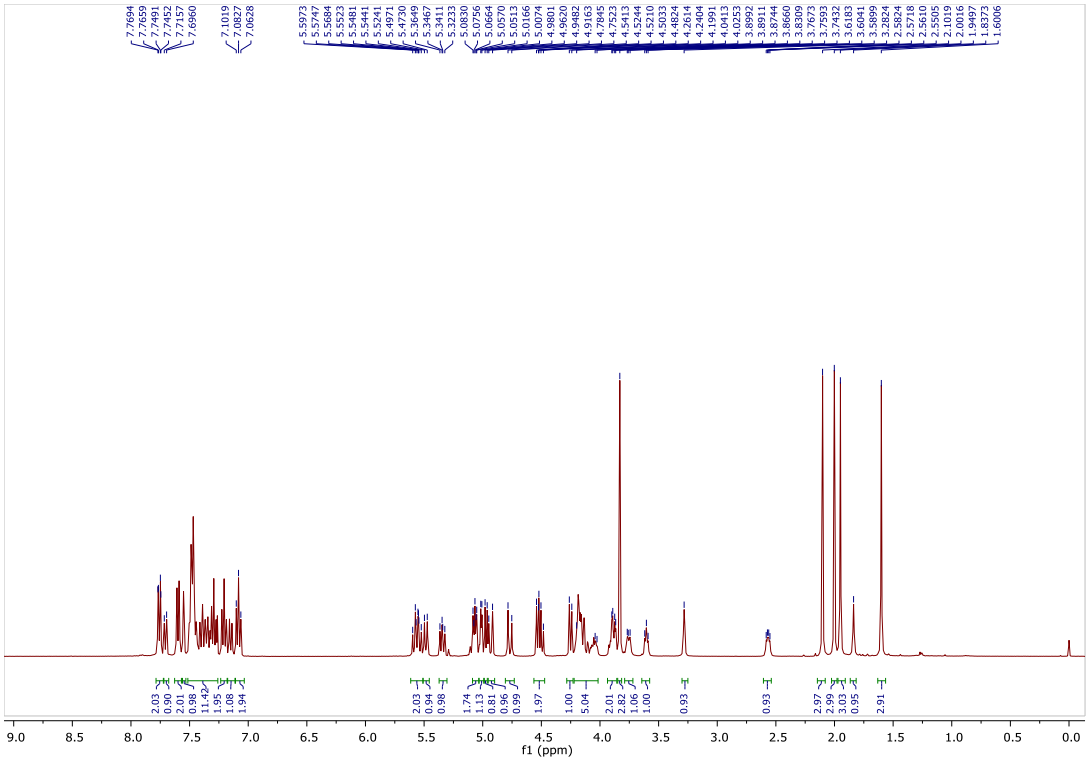


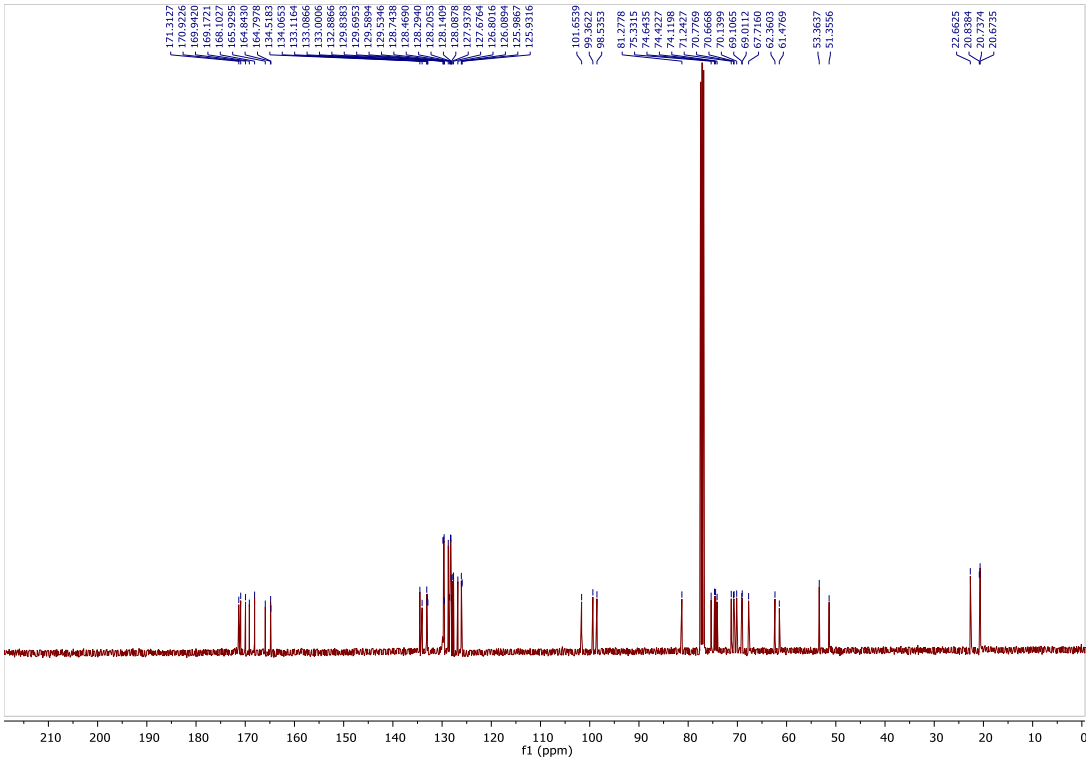




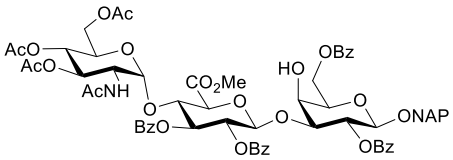
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for compound **36**

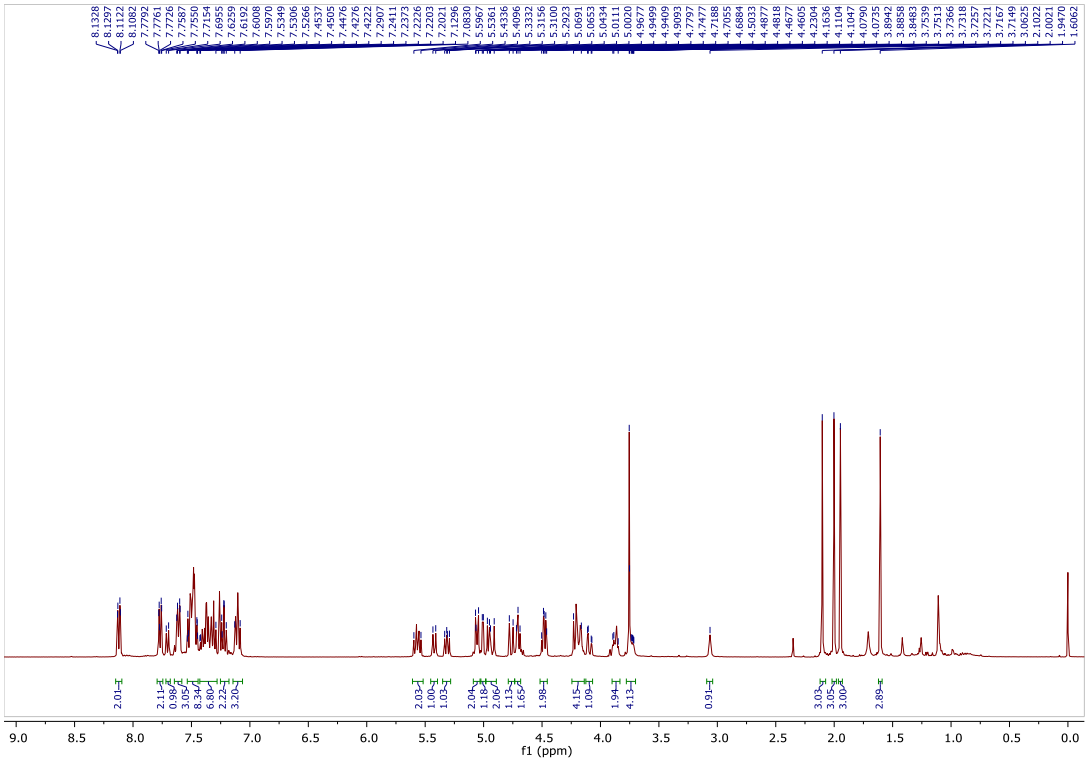


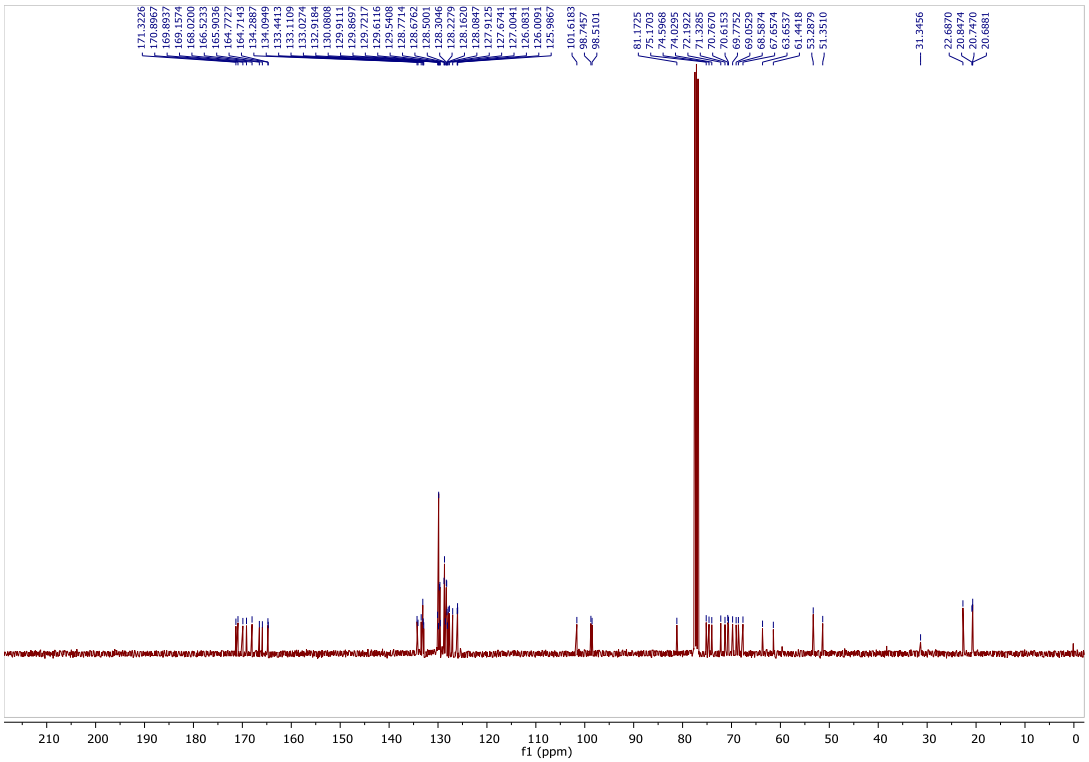




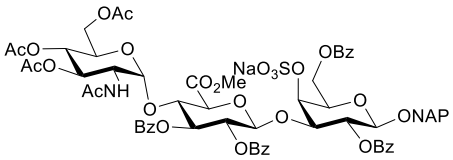
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) for compound **37**

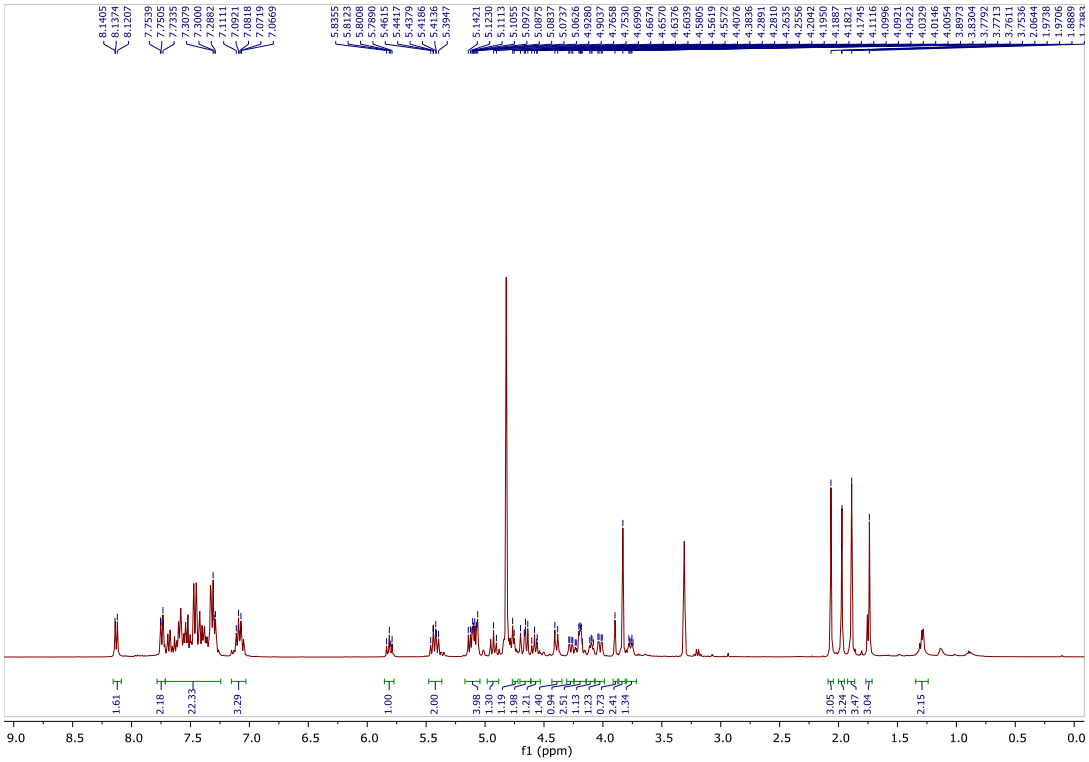


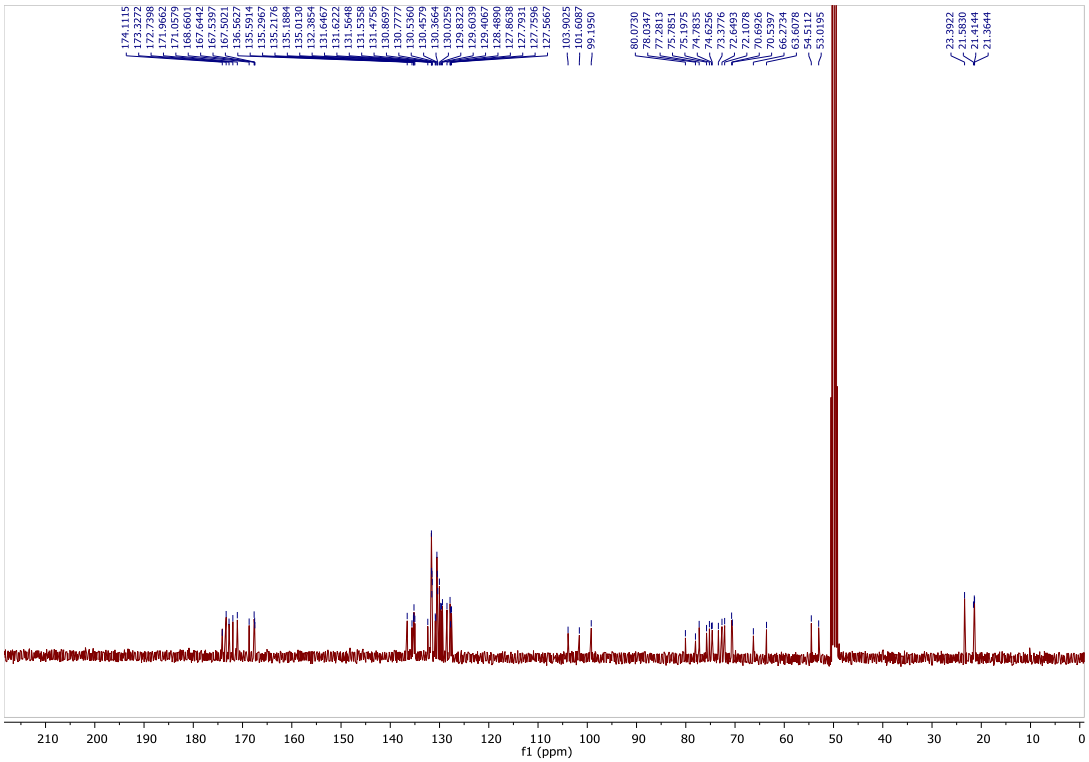




^{1}H NMR (400 MHz, CD_3OD) and ^{13}C NMR (100 MHz, CD_3OD) for compound **38**







^{1}H NMR (250 MHz, CD_3OD) and ^{13}C NMR (62.5 MHz, CD_3OD) for compound **39**