Supporting Information

STICS: Surface-Tethered Iterative Carbohydrate Synthesis

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Contents:

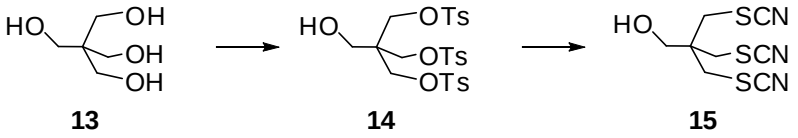
1. General

Column chromatography was performed on silica gel 60 (EM Science, 70-230 mesh), reactions were monitored by TLC on Kieselgel 60 F_{254} (EM Science). The compounds were detected by examination under UV light and by charring with 10% sulfuric acid in methanol or potassium permanganate solution. Solvents were removed under reduced pressure at <40 ^{o}C. Dichloromethane was distilled from CaH_2 directly prior to application. Methanol was dried by refluxing with magnesium methoxide, distilled and stored under argon. Pyridine was dried by refluxing with CaH_2 and then distilled and stored over molecular sieves (3Å). Reagent grade solvents, such as N,N-dimethylformamide (DMF) and tetrahydrofuran (THF) were purchased from Acros. Molecular sieves (3Å), used for reactions, were crushed and activated *in vacuo* at 390°C during 8 h in the first instance and then for 2-3 h at 390°C directly prior to application.

10 carat white gold sheets were purchased from Hoover and Strong, Richmond, VA. Concentrated nitric acid (trace metal grade, Fisher Scientific) was used for dealloying. Optical rotations were measured at 'Jasco P-1020' polarimeter. ^{1}H-NMR spectra were recorded at 300MHz, ^{13}C-NMR spectra were recorded at 75MHz (Bruker Avance). HRMS determinations were made with the use of JEOL MStation (JMS-700) Mass Spectrometer.

2. Synthesis of anchors

2.1 Tripod



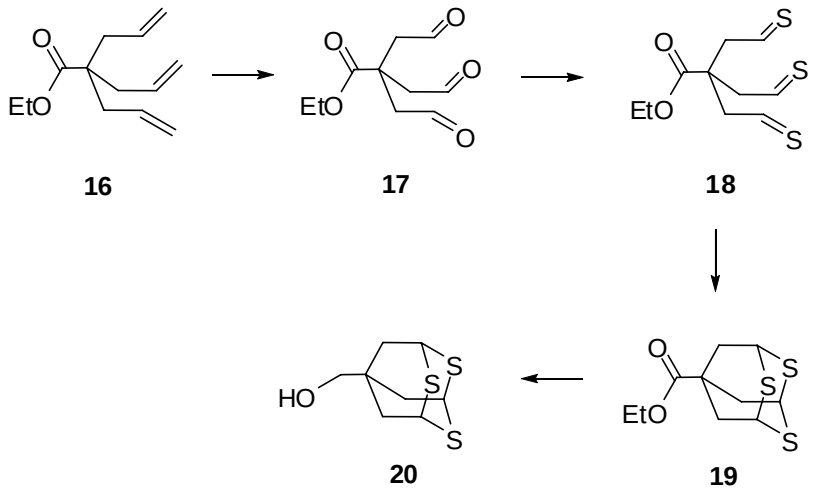
13 **14** **15**

Tris(*p*-toluenesulfonyl) pentaerythritol (14). Toluenesulfonyl chloride (28 g, 0.15 mol) was added to a stirred solution of pentaerythritol (**13**, 5.0 g, 37 mmol) in dry pyridine (100 mL) and the resulting mixture was stirred under argon for 16 h at rt. After that, the reaction mixture was concentrated under reduced pressure, the residue was dissolved in CH_2Cl_2 (600 mL) and washed successively with water (150 mL), sat. aq. $NaHCO_3$ (150 mL), and water (2 x 150 mL). The organic phase was separated, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (acetone-toluene gradient elution) to give the title compound as a white solid (35 g, 80% yield). Analytical data for **14** were in a good agreement with those reported previously.[1]

2,2,2-Tris(thiocyanatomethyl)ethanol (15). Potassium thiocyanate (1.81 g, 18.6 mmol) was added to a stirred solution of **14** (858 mg, 1.4 mmol) in dry DMF (5 mL) under argon at rt. The reaction mixture was stirred at 140 ^oC for 8 h. After that, the resulting dark solution was poured into cold water, left for 16 h at 5 ^oC, and then extracted with CH_2Cl_2 (3 x 100 mL). The combined organic phase was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate-toluene gradient elution) to give

the compound **2** as colorless syrup (313 mg, 71% yield). Analytical data for **15** were in a good agreement with those reported previously.[2]

2.2 Thiaadamantane



16 **17** **18** **20** **19**

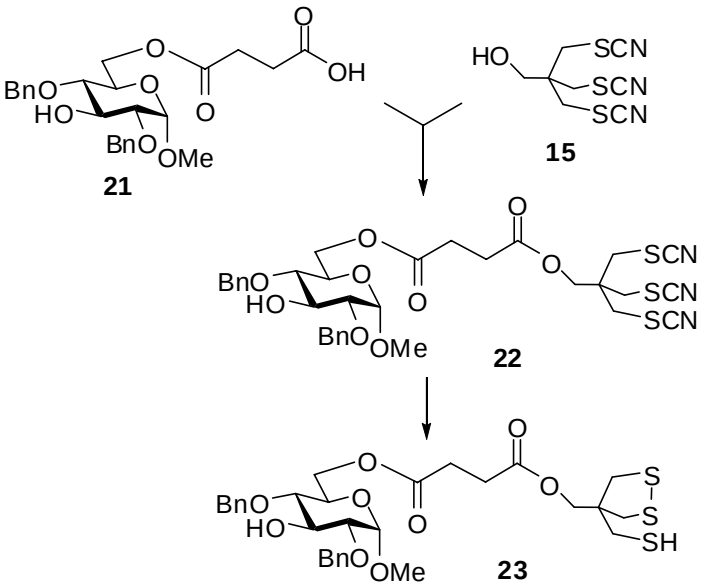
7-Ethoxycarbonyl-2,4,9-trithiaadamantane (19). A flow of ozone/oxygen obtained from ozone generator was bubbled through a solution of ethyl triallylacetate[3] (**16**, 1.76 g, 8.46 mmol) in dry CH_2Cl_2 (60 mL) at –78 ^oC. The bubbling was continued until the reaction mixture displayed a light blue color (~3 h). The excess of ozone was then removed by bubbling argon through the mixture for 10 min. After that, dimethyl sulfide (1.86 mL, 25.4 mmol) was added dropwise at –78 ^oC. The reaction mixture was gradually warmed to rt and kept for additional 16 h. After that, the reaction mixture was concentrated under reduced pressure and dried in vacuo to obtain crude **17** as a colorless syrup (1.8 g, 99% yield). The latter was dissolved in 1,4-dioxane (50 mL) and Lawesson's reagent (12.2 g, 30.3 mmol) was added under argon at rt. The resulting mixture was stirred at 80 ^oC for 6 h. After that, the reaction mixture was cooled to rt, filtered through a pad of Celite, concentrated under reduced pressure, and dried to give crude compound

18 as a colorless syrup (2.1 g, 95%). The latter was dissolved in CH_2Cl_2 (100 mL), BF_3-Et_2O (3.6 mL, 25.2 mmol) was added dropwise, and the resulting mixture was kept at reflux for 20 h. After that, the reaction mixture was cooled to rt, diluted with CH_2Cl_2 (400 mL) and washed successively with 5M K_2CO_3 (50 mL) and water (3 x 50 mL). The organic phase was separated, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (acetone/toluene) to afford the title compound **19** as a pale yellow solid (940 mg, 42% yield). Analytical data for **19** were in a good agreement with those reported previously.[4]

7-Hydroxymethyl-2,4,9-trithiaadamantane (20). A solution of **19** (250 mg, 0.95 mmol) in THF (2 mL) was added to a stirred suspension of $LiAlH_4$ (72 mg, 1.9 mmol) in dry THF (1 mL) and the resulting mixture was stirred under argon for 30 min at rt. After that, sat. aq. NH_4Cl (~5 mL) was added until two phases were clearly seen. The aqueous layer was separated and extracted with CH_2Cl_2 (3 x 50 mL). The organic phase and the extracts were combined, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (acetone-toluene gradient elution) to afford the title compound as white solid (112 mg, 53% yield). Analytical data for **20**: R_f = 0.58 (acetone/toluene, 1/1, v/v); ^{1}H-n.m.r.: δ, 1.68 (bs, 1H, OH), 2.57 (d, 6H, J = 2.8 Hz, CCH_2C), 3.63 (s, 1H, CH_2OH), 4.33 (t, 3H, SCH) ppm; ^{13}C-n.m.r.: δ, 32.3, 40.8, 42.3, 73.8 ppm; HR-FAB MS $[M+H]^+$ calcd for $C_8H_{13}OS_3$ 221.0129, found 221.0121

3. Synthesis of acceptor-linker-anchor conjugates

3.1 Tripod



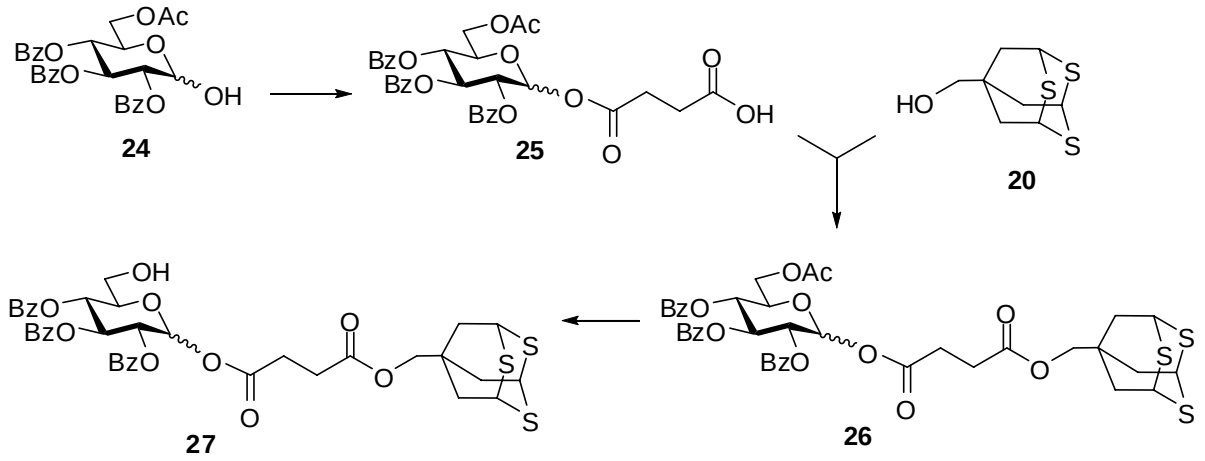
Methyl 2,4-di-*O*-benzyl-6-*O*-[3-(2,2,2-tris(thiocyanatomethyl)ethoxycarbonyl)propanoyl]-α-D-glucopyranoside (22). A mixture of *N*,*N*'-dicyclohexylcarbodiimide (DCC, 0.93 g, 4.5 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (DMAP, 118 mg, 0.96 mmol) in dry CH_2Cl_2 (10 mL) was added to a stirred solution of methyl 2,4-di-*O*-benzyl-6-*O*-(3-hydroxycarbonylpropanoyl)-α-D-glycopyranoside[5] (**21**, 1.82 g, 3.85 mmol) and anchor **15** (0.98 g, 3.2 mmol) in dry CH_2Cl_2 (20 mL) under argon at 0 ^{o}C. The reaction mixture was gradually warmed up and stirred for 1 h at rt. After that, the reaction mixture was diluted with CH_2Cl_2 (200 mL) and washed successively with water (3 x 40 mL). The organic phase was separated, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (acetone-toluene gradient elution) to afford the title compound as a white solid (1.47 g, 80% yield). Analytical

data for **22**: R_f = 0.4 (acetone/toluene, 1/4, v/v), $[\alpha]_D^{21}$ +44.6° (c = 1, $CHCl_3$); ^{1}H-n.m.r.: δ, 2.66 (d, 4H, $COCH_2CH_2CO$), 2.75 (d, 1H, OH), 3.25 (s, 6H, 3 x CH_2SCN), 3.34 (s, 3H, OCH_3), 3.37-3.43 (m, 2H, H-2, 4), 3.79 (m, 1H, H-5), 4.10 (dd, 1H, $J_{3,4}$ = 8.4 Hz, H-3), 4.23 (s, 2H, OCH_2C), 4.30 (d, 2H, H-6a, 6b), 4.62 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.65-4.70 (m, 3H, C*H*$_2$Ph), 4.91 (d, 1H, C*H*$_2$Ph), 7.27-7.46 (m, 10H, aromatic) ppm; ^{13}C-n.m.r.: δ, 14.3, 21.1, 28.9, 29.1, 36.8, 45.5, 55.4, 60.5, 63.5, 63.8, 68.3, 73.2, 73.7, 74.5, 79.7, 97.5, 111.4, 128.0, 128.2 (x 4), 128.2, 128.6 (x 3), 128.7 (x 3), 138.0, 138.3, 171.5, 172.4 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{33}H_{37}N_3O_9S_3Na$ 738.1590, found 738.1568.

Methyl 2,4-di-*O*-benzyl-6-*O*-[3-(4-mercaptomethyl-1,2-dithiolan-4-yl)methoxycarbonyl) propanoyl]-α-D-glucopyranoside (23). A solution of **22** (380 mg, 0.50 mmol) in diethyl ether/THF (10 mL, 1/1, v/v) was added to a stirred suspension of $LiAlH_4$ (38 mg, 1.0 mmol) in diethyl ether (3 mL) and the resulting mixture was stirred under argon for 1 h at rt. After that, sat. aq. NH_4Cl (~10 mL) was added until two phases were clearly seen. The aqueous layer was separated and extracted with diethyl ether (3 x 50 mL). The organic phase and the extracts were combined, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (acetone-toluene gradient elution) to afford the title compound as a pale-yellow syrup (212 mg, 62% yield). Analytical data for **23**: R_f= 0.5 (1/4 acetone/toluene), $[\alpha]_D^{20}$ +45.8° (c = 1, $CHCl_3$); ^{1}H-n.m.r.: δ, 1.19 (dd, 1H, SH), 2.56 (s, 4H, $COCH_2CH_2CO$), 2.96 (s, 4H, CH_2SSCH_2), 3.18 (s, 2H, C*H*$_2$SH), 3.26 (s, 3H, OCH_3), 3.28-3.36 (m, 2H, H-2, 4), 3.72 (m, 1H, H-5), 4.04 (dd, 1H, $J_{3,4}$ = 8.7 Hz, H-3), 4.14 (s, 2H, OCH_2C), 4.22 (d, 2H, H-6a, 6b), 4.54 (d, 1H, $J_{1,2}$ = 4.4 Hz, H-1), 4.55-4.67 (m, 3H, C*H*$_2$Ph), 4.85 (d, 1H, C*H*$_2$Ph), 7.19-7.36 (m, 10H, aromatic) ppm; ^{13}C-n.m.r.: δ, 28.9, 29.0, 39.7, 45.9, 45.9, 55.3, 55.4, 63.6, 66.0, 68.2, 73.2,

73.7, 74.5, 77.0, 79.6, 127.9, 128.2 (x2), 128.2 (x3), 128.5 (x2), 128.7 (x2), 138.0, 138.2, 171.6, 172.0 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{30}H_{38}O_9S_3Na$ 661.1576, found 661.1535.

3.2 Thiaadamantane



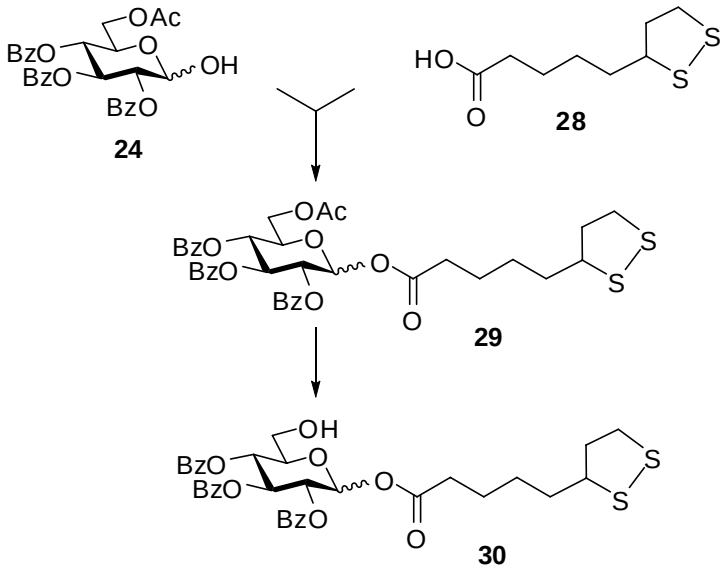
6-*O*-Acetyl-2,3,4-tri-*O*-benzoyl-1-*O*-(3-hydroxycarbonylpropanoyl)-α/β-D-glycopyranose (25). DMAP (33 mg, 0.27 mmol) and succinic anhydride (108 mg, 1.08 mmol) were added to a solution of 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-α/β-D-glycopyranose[6] (**24**, 289 mg, 0.54 mmol) in dry pyridine (4 mL) and the resulting mixture was stirred under argon for 3 h at rt. After that, the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate-hexane gradient elution) to afford the title compound as a colorless syrup (277 mg, 80% yield, α/β = 1.5/1). Analytical data for **α-25**; R_f = 0.37 (acetone/toluene, 3/7, v/v); ^{1}H-n.m.r.: δ, 2.08 (s, 3H, $COCH_3$), 2.23 (s, 4H, $COCH_2CH_2CO$), 4.02 (dd, 1H, $J_{5,6b}$ = 2.0 Hz, H-6b), 4.10 (dd, 1H, $J_{5,6a}$ = 4.0 Hz, H-6a), 4.22 (m, 1H, H-5), 5.31 (dd, 1H, $J_{2,3}$ = 11.5 Hz, H-2), 5.50 (dd, 1H, $J_{4,5}$ = 9.8 Hz, H-4), 5.93 (dd, 1H, $J_{3,4}$ = 10.1 Hz, H-3), 6.47 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 7.05-8.00 (m, 15H, aromatic) ppm; ^{13}C-n.m.r. (α/β): δ, 20.9, 28.6,

28.7, 28.9, 29.2, 53.6, 68.6, 68.8, 70.2, 70.4, 70.4, 70.5, 89.9, 90.0, 128.6, 128.7, 128.7, 128.8, 128.9, 129.0, 129.0, 129.9, 129.9, 130.0, 130.0, 130.2, 133.6, 133.7, 133.8, 134.2, 164.7, 165.3, 165.3, 165.5, 166.0, 166.1, 170.2, 170.8, 170.9, 171.1, 177.0, 177.2 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{33}H_{30}O_{13}Na$ 657.1584, found 657.1568

6-*O*-Acetyl-2,3,4-tri-*O*-benzoyl-1-*O*-[3-(2,4,9-trithiaadamantane-7-yl)methoxycarbonyl propanoyl]-α/β-D-glycopyranose (26). A solution of DCC (72 mg, 0.35 mmol) and DMAP (14.2 mg, 0.12 mmol) in dry CH_2Cl_2 (1 mL) was added to a stirred solution of **25** (147 mg, 0.23 mmol) and **20** (47 mg, 0.21 mmol) in dry CH_2Cl_2 (2 mL) was added under argon at 0 ^oC. The resulting mixture was warmed to rt and stirred for 1 h, after that, it was diluted with CH_2Cl_2 (30 mL) and washed with water (3 x 10 mL). The organic phase was separated, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate-hexane gradient elution) to afford the title compound as a white foam (102 mg, 76% yield). Analytical data for **α-26**: R_f= 0.5 (ethyl acetate/hexane, 1/1, v/v); ^{1}H-n.m.r.: δ, 2.06 (s, 3H, $COCH_3$), 2.45 (d, 6H, J = 3.2 Hz, 3 x SCH*C*H_2S), 2.51 (s, 4H, $COCH_2CH_2CO$), 3.58 (dd, 2H, OCH_2C), 4.20-4.32 (m, 5H, H-6a,6b, 3 x SCHS), 4.44 (m, 1H, H-5), 5.50 (dd, 1H, $J_{2,3}$ = 3.7 Hz, H-2), 5.67 (dd, 1H, $J_{4,5}$ = 10.0 Hz, H-4), 6.10 (dd, 1H, $J_{3,4}$ = 10.1 Hz, H-3), 6.69 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 7.27-7.95 (m, 15H, aromatic) ppm; ^{13}C-n.m.r.: δ, 20.9, 25.1, 25.8, 28.9, 29.0, 30.9, 34.2, 40.3, 42.1, 42.2, 49.4, 62.1, 68.8, 70.2, 70.4, 70.6, 73.6, 77.0, 77.2, 77.5, 90.0, 128.7, 128.7, 128.9, 129.0, 129.1, 129.2, 130.0, 130.3, 133.7, 133.8, 134.2, 164.7, 165.4, 165.0, 170.8, 171.3, 171.6 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{41}H_{40}O_{13}S_3Na$ 859.1529, found 859.1501

2,3,4-Tri-*O*-benzoyl-1-*O*-[3-(2,4,9-trithiaadamantane-7-yl)methoxycarbonylpropanoyl]-α/β-D-glycopyranose (27). Acetyl chloride (0.1 mL) was added to a solution of compound **26** (137 mg, 0.16 mmol) in CH_2Cl_2/methanol (3 mL, 1/1, v/v) and the resulting mixture was stirred for 2 h at rt. After that, the reaction mixture was neutralized by addition of triethylamine (~0,5 mL) and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate-hexane gradient elution) to afford the title compound as a white foam (80 mg, 61% yield). For characterization purposes, the anomers could be obtained individually in nearly equal amounts. Analytical data for **α–27**: R_f= 0.30 (ethyl acetate/hexane, 1/1, v/v); ^{1}H-n.m.r.: δ, 2.44 (d, 6H, J= 3.5 Hz, 3 x SCH*C*H_2C), 2.51 (s, 4H, $COCH_2CH_2CO$), 2.70 (bs, 1H, OH), 3.58 (dd, 2H, OCH_2C), 3.72 (dd, 1H, $J_{6a,6b}$ = 13.1 Hz, H-6a), 3.80 (dd, 1H, H-6b), 4.24 (m, 4H, H-5, 3 x SCHS), 5.50 (dd, 1H, $J_{2,3}$ = 3.7 Hz, H-2), 5.58 (dd, 1H, $J_{4,5}$ = 9.8 Hz, H-4), 6.17 (dd, 1H, $J_{3,4}$ = 10.0 Hz, H-3), 6.71 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 7.36-8.20 (m, 15H, aromatic) ppm; ^{13}C-n.m.r.: δ, 25.1, 25.8, 28.8, 29.0, 30.9, 34.1, 40.2, 42.1, 49.3, 61.0, 69.1, 70.2, 70.2, 73.0, 73.6, 90.1, 128.6, 128.7 (x 2), 128.7 (x 3), 129.0, 129.2, 129.2, 130.0 (x 2), 130.2 (x 4), 133.6, 134.0, 134.2, 164.7, 166.0, 166.3, 171.3, 171.6 ppm. Analytical data for **β–27**: R_f= 0.23 (ethyl acetate/hexane, 1/1, v/v); ^{1}H-n.m.r.: δ, 2.54 (d, 6H, J= 3.5 Hz, 3 x SCH*C*H_2C), 2.68-2.84 (m, 4H, $COCH_2CH_2CO$), 3.75 (dd, 1H, H-6a), 3.80 (dd, 2H, OCH_2C), 3.83 (dd, 1H, H-6b), 4.20 (m, 1H, H-5), 4.28 (m, 3H, 3 x SCHS), 5.52 (dd, 1H, $J_{2,3}$ = 3.8 Hz, H-2), 5.60 (dd, 1H, $J_{4,5}$ = 10.0 Hz, H-4), 6.21 (dd, 1H, $J_{3,4}$ = 10.0 Hz, H-3), 6.65 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1), 7.27-8.00 (m, 15H, aromatic) ppm; ^{13}C-n.m.r.: δ, 28.9, 29.2, 31.0, 40.2 (x 2), 42.1, 61.1, 69.0, 70.2, 70.5, 72.8, 73.9, 90.0, 128.6 (x 2), 128.6, 128.7 (x 2), 128.7 (x 5), 128.8, 128.8, 129.0, 129.9 (x 3), 130.1 (x 2), 130.2 (x 2), 133.6, 133.7, 134.0, 165.5, 166.0, 166.3, 170.6, 172.0 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{39}H_{38}O_{12}S_3Na$ 817.1423, found 817.1420.

3.3 Lipoic Acid conjugates



6-*O*-Acetyl-2,3,4-tri-*O*-benzoyl-1-*O*-[5-(1,2-dithiolan-3-yl)pentanoyl]-α/β-D-glycopyranose (29). A solution of DCC (194 mg, 0.94 mmol) and DMAP (34 mg, 0.28 mmol) in dry CH_2Cl_2 (2 mL) was added to a stirred solution of hemiacetal **24** (350 mg, 0.66 mmol) and lipoic [5-(1,2-dithiolan-3-yl)pentanoic] acid (**28**, 162 mg, 0.79 mmol) in CH_2Cl_2 (4 mL) at 0 ^oC under argon. The resulting solution was warmed to rt and stirred for 16 h. After that, the reaction mixture was diluted with CH_2Cl_2 (50 mL), washed with water (10 mL), sat. aq. $NaHCO_3$ (10 mL), and water (2 x 10 mL). The organic phase was separated, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate-hexane gradient elution) to afford the title compound as a white foam (340 mg, 72% yield, α/β = 1.4/1). Analytical data for α-**29**: R_f= 0.25 (ethyl acetate/hexane, 3/7, v/v); ^{1}H-n.m.r.: δ, 1.20-3.30 (m, 13H, lipoic aglycone protons), 2.07 (s, 3H, $COCH_3$), 4.24 (dd, 1H, $J_{5,6b}$ = 2.8 Hz, H-6b), 4.30 (dd, 1H, $J_{5,6a}$ = 3.9 Hz, H-6a), 4.42 (m, 1H, H-5), 5.43 (dd, 1H, $J_{2,3}$ = 3.8 Hz, H-2), 5.60 (dd, 1H,

$J_{4,5}$ = 9.9 Hz, H-4), 6.20 (dd, 1H, $J_{3,4}$ = 10.2 Hz, H-3), 6.62 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1), 7.36-8.20 (m, 15H, aromatic) ppm; ^{13}C-n.m.r. (α/β): δ, 20.9, 20.9, 24.6, 24.8, 28.5, 28.5, 28.8, 28.8, 33.8, 33.8, 34.1, 34.5, 34.7, 38.6, 38.6, 40.2, 40.4, 40.4, 56.1, 56.3, 56.4, 62.1, 62.2, 68.7, 68.8, 69.8, 70.3, 70.5, 70.6, 89.3, 90.1, 128.6, 128.7, 128.7, 128.9, 128.9, 128.9, 129.0, 129.0, 129.1, 129.9, 130.0, 130.1, 130.2, 133.5, 133.7, 134.2, 164.7, 165.3, 165.4, 165.4, 165.9, 166.0, 170.8, 170.8, 171.4, 172.4 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{37}H_{38}O_{11}S_2Na$ 745.1753, found 745.1750.

2,3,4-Tri-*O*-benzoyl-1-*O*-[5-(1,2-dithiolan-3-yl)pentanoyl]-α/β-D-glycopyranose (30). The title compound was prepared from **29** (201 mg, 61% yield, α/β = 1.4/1) as described for the synthesis of **27**. Analytical data for **α-30**: R_f= 0.58 (ethyl acetate/hexane, 1/1, v/v); ^{1}H-n.m.r.: δ, 3.50-3.80 (m, 2H, H-6a, 6b), 4.10 (m, 1H, H-5), 5.42-5.52 (m, 2H, H-2, 4), 6.13 (dd, 1H, H-2), 6.63 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 7.27-8.20 (m, 15 H, aromatic) ppm; ^{13}C-n.m.r. (α/β): δ, 21.5, 24.8, 25.0, 28.7, 29.0, 34.0, 34.4, 34.7, 34.9, 38.8, 38.9, 40.4, 40.6, 40.6, 56.3, 56.5, 56.6, 60.8, 61.2, 61.3, 69.2, 69.3, 70.0, 70.3, 70.5, 70.9, 73.0, 73.2, 89.6, 90.4, 128.6, 128.8, 128.9, 128.9, 129.0, 129.0, 129.2, 129.3, 130.1, 130.2, 130.4, 130.4, 130.5, 133.8, 134.0, 134.2, 134.4, 165.0, 165.7, 166.1, 166.3, 166.5, 166.6, 171.8, 172.6 ppm; HR-FAB MS $[M]^+$ calcd for $C_{35}H_{36}O_{10}S_2$ 680.1750, found 680.1729.

4. Synthesis of other building blocks

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(3-hydroxycarbonylpropanoyl)-α-D-glycopyranoside (31). The title compound was obtained from methyl 2,3,4-tri-*O*-benzyl-α-D-glycopyranoside (**32**)[7] in 93% yield as described for the synthesis of compound **25**. Analytical data for **31**: R_f= 0.57 (acetone/toluene, 1/1, v/v); $[\alpha]_D^{18}$ = 17.7° (c = 1, $CHCl_3$); ^{1}H-n.m.r.: δ, 2.50 (s, 4H, $COCH_2CH_2CO$), 3.28 (s, 3H, OCH_3), 3.39 (dd, 1H, $J_{4,5}$ = 9.5 Hz, H-4), 3.46 (dd, 1H, $J_{2,3}$ = 3.4 Hz, H-2), 3.73 (m, 1H, H-5), 3.93 (dd, 1H, $J_{3,4}$ = 9.2 Hz, H-3), 4.22 (m, 2H, H-6a, 6b), 4.45-4.60 (m, 3H, $J_{1,2}$ = 3.4 Hz, H-1, CH_2Ph), 4.68-4.94 (m, 4H, CH_2Ph), 7.10-7.30 (m, 15H, aromatic), 10.1 (bs, 1H, COOH) ppm; ^{13}C-n.m.r.: δ, 55.3, 63.3, 68.6, 73.4, 75.1, 75.9, 77.4, 79.9, 82.1, 98.1, 127.8, 128.0, 128.0, 128.1, 128.2, 128.5, 128.5, 128.6, 137.9, 138.1, 138.6, 171.9, 177.7 ppm; HR-FAB MS $[M]^+$ calcd for $C_{32}H_{36}O_9Na$ 587.2257, found 587.2247.

2-Benzoxazolyl 2,3,4-tri-O-benzoyl-6-O-(*tert*-butyldiphenylsilyl)-1-thio-β-D-glucopyranoside (10). *Tert*-butyldiphenylsilyl chloride (0.19 mL, 0.72 mmol) and imidazole (81 mg, 1.2 mmol) were added to a solution of 2-benzoxazolyl 2,3,4-tri-O-benzoyl-1-thio-β-D-glucopyranoside[8] (300 mg, 0.48 mmol) in DMF (2 mL). The resulting mixture was stirred for 8 h at rt, after that the volatiles were removed under reduced pressure and the residue was purified by column chromatography on silica gel (ethyl acetate-hexane gradient elution) to afford the title compound as a white foam (399 mg, 96% yield). Analytical data for **10**: R_f = 0.3 (ethyl acetate/hexane, 1/4, v/v); $[\alpha]_D^{20}$ = 65.7° (c = 1, $CHCl_3$); ^{1}H-n.m.r.: δ, 0.91 (s, 9H, $C(CH_3)_3$), 3.82 (m, 2H, H-6a,6b), 4.09 (m, 1H, H-5), 5.65-5.80 (m, 2H, H-2, 4), 5.94-6.05 (m, 2H, H-1, 3), 7.10-

7.87 (m, 29H, aromatic) ppm; ^{13}C-n.m.r.: δ, 19.5, 26.9, 63.1, 69.1, 71.2, 74.7, 77.6, 80.2, 84.1, 110.5, 119.4, 124.8, 124.9, 127.9, 128.0, 128.7, 128.8, 128.8, 129.1, 129.2, 129.5, 129.9, 130.0, 130.2, 130.3, 133.3, 133.6, 133.7, 133.9, 136.0, 136.1142.0, 152.3, 161.6, 165.3, 165.7, 166.2 ppm; HR-FAB MS $[M]^+$ calcd for $C_{50}H_{45}NO_9SNa$ 886.2482, found 886.2470.

5. General procedure for preparing nanoporous gold (NPG) plates

A 10 carat white gold sheet of 0.25 mm thickness was cut into 8mm x 8mm pieces, which were then dealloyed by immersion in concentrated nitric acid for 72 h and then thorough rinsed with milli-Q water. NPG pieces were previously characterized using field-emission SEM, tapping mode AFM, electrochemistry, and BET adsorption isotherm measurements for determination of surface area. Energy dispersed spectroscopy confirmed the presence of only gold after the dealloying. The BET measurements gave a surface area of 6.5 m^2 g^{-1} for the NPG prepared from these alloy sheets.[9]

6. General procedure for loading glycosyl acceptor on gold plates. Preparation of 5-7.

Single NPG plate was immersed in a 5 mM solution of glycosyl acceptor-linker-anchor conjugate (**23**, **27** or **30**) in CH_2Cl_2 (1.0 mL) for 48 h at rt. Similarly, ten-plate assembly was immersed in a 5 mM solution of conjugate **27** in CH_2Cl_2 (7.0 mL). After that, the excess reagents was rinsed by repeatedly dipping the plate or the conjugate in CH_2Cl_2 (3-5 x 1 or 7 mL, respectively), and the solvent excess was removed under reduced pressure (2 h) to afford anchored glycosyl acceptors **5-7**. The loading was determined by comparing the results of gravimetric analysis of plates prior and after the loading procedure. The Table 1 summarizes the results obtained.

Table 1. Determination of the surface coverage

Acceptor	# plates	Loading, mg Max/aver	Loading, μmol Max/aver	Plate weight, mg	Surface coverage Max/aver
23 → 5	1 [a]	1.03 0.97	1.50 1.41	126.76 129.85	1.82 μmol/m^2 1.67 μmol/m^2
27 → 6	1 [a]	1.05 0.90	1.33 1.18	133.79 132.14	1.53 μmol/m^2 1.37 μmol/m^2
27 → 6	10 [b]	7.20 7.00	9.10 8.85	na	na
30 → 7	1 [b]	0.71 0.58	1.04 0.85	83.36 85.75	1.92 μmol/m^2 1.53 μmol/m^2

[a] - 10 x 10 mm plates were used

[b] - 8 x 8 mm plates were used

7. Synthesis of disaccharides 8 and 9 by glycosylation of NPG-supported glycosyl acceptors 5-7 on a single NPG plate

Method A: *General procedure for MeOTf-promoted glycosylation.* A mixture of the glycosyl donor (**1**, **3** or **4**, 9.0 μmol, 6 mg), acceptor conjugate (**5**, **6** or **7**, 0.9 μmol, 0.6 mg), and freshly activated molecular sieves (3Å, 20 mg) in dry CH_2Cl_2 (1.0 mL) was agitated under argon for 2-3 h. MeOTf (0.017 mmol, 3 μL) was added and the reaction mixture was agitated under argon for 16-48 h at rt. After that, the excess reagents was removed by repeatedly dipping the plate in CH_2Cl_2 (3-5 x 1 mL), and the solvent excess was removed by briefly drying the plate under reduced pressure (10 min – 1 h). The NPG plate covered with bound disaccharides was then agitated in 1N solution of NaOMe in methanol (1.0 mL) for 16 h at rt, while maintaining the pH = 8-9. The reaction mixture was then neutralized with Dowex (H^+) and the NPG plate was removed and rinsed by dipping in MeOH (3-5 x 1 mL). Dowex (H^+) was filtered off and washed successively with methanol (5 x 2 mL). The combined methanol filtrate and washings were combined and concentrated under reduced pressure and dried in *vacuo*. The resulting crude mixture containing fully or partially deprotected disaccharides was dissolved in pyridine (0.5 mL), cooled to 0 ^oC and benzoyl chloride (10 μL) was added. The reaction mixture was stirred under argon for 5 h at rt, then quenched with methanol (1 mL) and the volatiles were evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel (ethyl acetate-hexane gradient elution) to allow the corresponding disaccharides **8** or **9**. The yield of disaccharide was obtained using standardized HPLC calibration plots (see Charts 1 and 2).

Method B: *General procedure for TMSOTf-promoted glycosylation.* A mixture of the glycosyl donor (**2** or **4**, 11.0 μmol, 8 mg), acceptor conjugate (**5**, **6** or **7**, 1.0 μmol, 0.7 mg), and freshly activated molecular sieves (3Å, 20 mg) in dry CH_2Cl_2 (1.0 mL) was agitated under argon for 2-3 h. TMSOTf (0.017 mmol, 4 μL) was added and the reaction mixture was agitated under argon for 16-48 h at rt. After that, the excess reagents was removed by repeatedly dipping the plate in CH_2Cl_2 (3-5 x 1 mL), and the solvent excess was removed by briefly drying the plate under reduced pressure (10 min – 1 h). The NPG plate covered with bound disaccharides was then agitated in 1N solution of NaOMe in methanol (1.0 mL) for 16 h at rt, while maintaining the pH = 8-9. The reaction mixture was then neutralized with Dowex (H^+) and the NPG plate was removed and rinsed by dipping in MeOH (3-5 x 1 mL). Dowex (H^+) was filtered off and washed successively with methanol (5 x 2 mL). The combined methanol filtrate and washings were combined and concentrated under reduced pressure and dried in *vacuo*. The resulting crude mixture containing fully or partially deprotected disaccharides was dissolved in pyridine (0.5 mL), cooled to 0 ^oC and benzoyl chloride (10 μL) was added. The reaction mixture was stirred under argon for 5 h at rt, then quenched with methanol (1 mL) and the volatiles were evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel (ethyl acetate-hexane gradient elution) to allow the corresponding disaccharides **8** or **9**. The yield of disaccharide was obtained using standardized HPLC calibration plots (see Charts 1 and 2).

Chart 1. HPLC calibration plot for **8**.

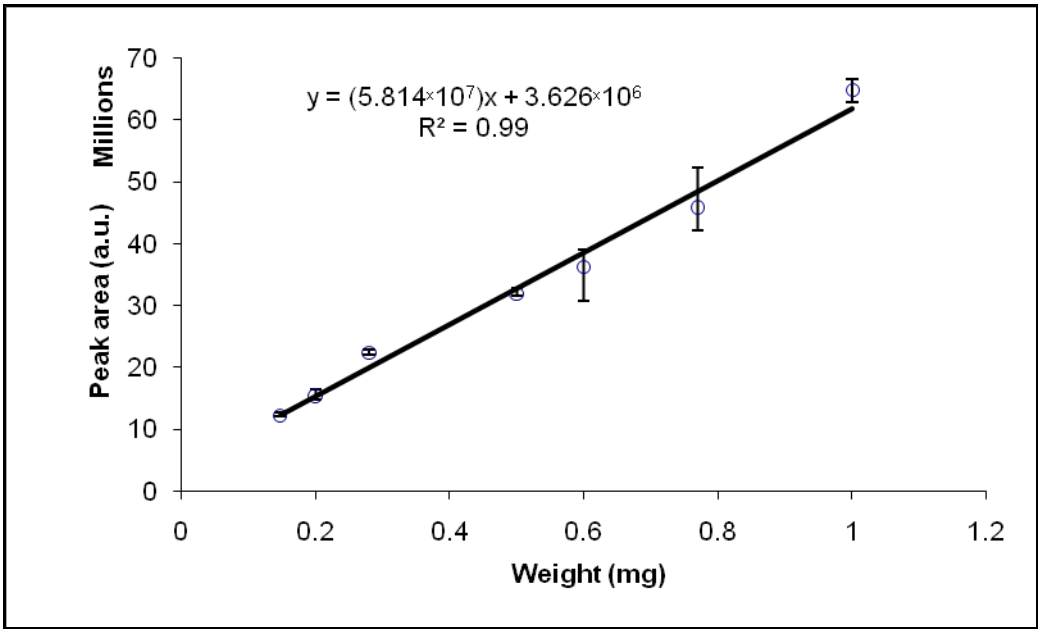
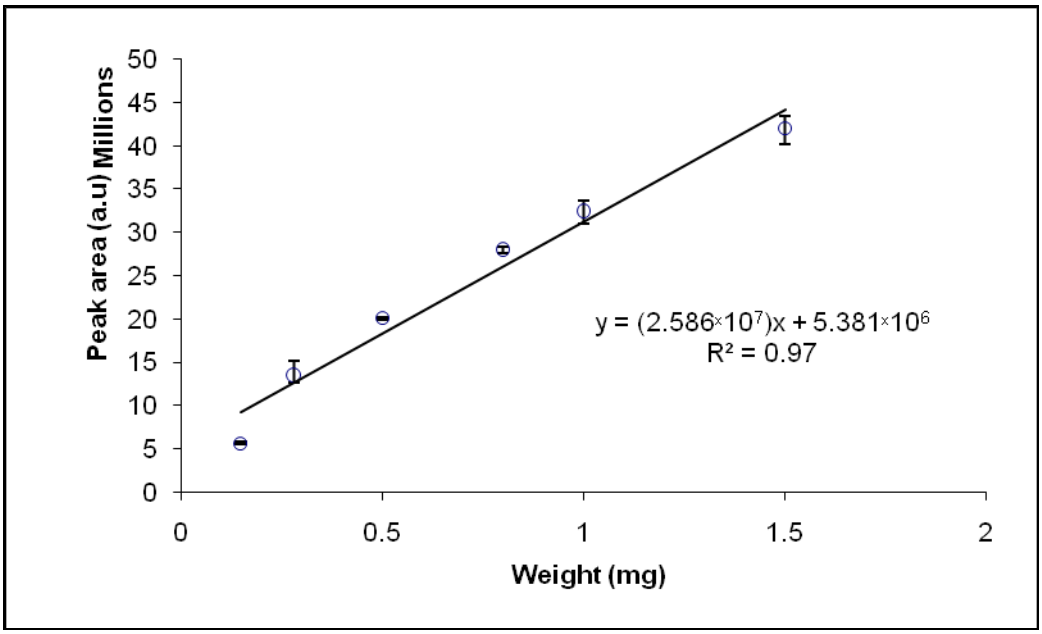


Chart 2. HPLC calibration plot for **9**.



Methyl 6-O-benzoyl-3-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-2,4-di-O-benzyl-α-D-glucopyranoside (8). The title compound was obtained from acceptor 5 and donors **1** (Method A, 31%), **2** (Method B, 39%), **3** (Method A, 32%) or **4** (Method A, 42%). Analytical data for **8**: R_f= 0.25 (ethyl acetate/hexanes, 3/7, v/v), $[\alpha]_D^{24}$ = -0.94^o (c = 1, $CHCl_3$); ^{1}H-n.m.r: δ, 3.30 (s, 3H, OCH_3), 3.41 (dd, 1H, $J_{2,3}$ = 3.6 Hz, H-2), 3.56 (dd, 1H, $J_{4,5}$ = 8.8 Hz, H-4), 3.89 (m, 1H, H-5), 4.20-4.25 (m, 2H, H-3', 5'), 4.35 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.40 (dd, 1H, $J_{5,6a}$ = 5.2 Hz, $J_{6a,6b}$ = 11.9 Hz, H-6a), 4.46-4.58 (m, 3H, H-3, 6a', 6b), 4.61 (dd, 1H, $H_{5',6b'}$ = 3.1 Hz, $H_{6a',6b'}$ = 12.0 Hz, H-6b'), 4.73 (dd, 2H, H-2', 4'), 5.20 (d, 1H, $J_{1',2'}$ = 11.0 Hz, H-1'), 5.60 (d, 1H, CH_2Ph), 5.72-5.80 (m, 2H, CH_2Ph), 6.00 (d, 1H, CH_2Ph), 7.15-8.20 (m, 35H, aromatic) ppm; ^{13}C-n.m.r.: δ, 55.1, 60.5, 63.3, 63.7, 68.6, 70.0, 72.1, 72.7, 73.3, 73.9, 74.9, 75.4, 79.5, 80.8, 97.6, 101.2, 127.8, 127.9, 128.2, 128.3, 128.4, 128.4, 128.4, 128.5, 128.6, 128.6, 128.9, 129.4, 129.7, 129.8, 129.9, 130.0, 130.1, 133.0, 133.1, 133.3, 133.5, 133.5, 138.0, 138.1, 148.7, 165.3, 165.4, 166.0,166.2, 166.3 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{62}H_{56}O_{16}Na$ 1079.3466, found 1079.3446

1,2,3,4-Tetra-O-benzoyl-6-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-α/β-D-glucopyranose (9). The title compound was obtained from acceptors **6** or **7** and donors **1-4** as shown in Table 1 of the article. Analytical data for **9** was in a good agreement to those reported previously.[6]

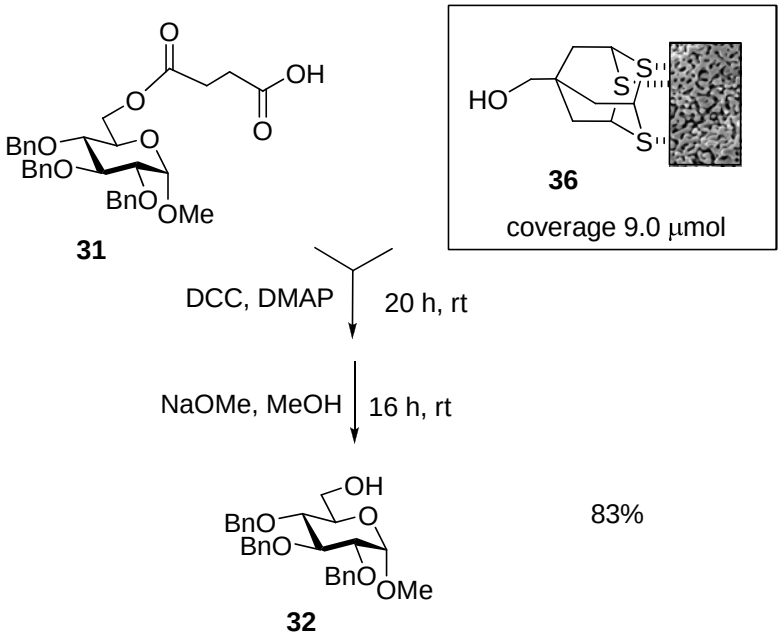
8. Synthesis of trisaccharides 12 and 34 by sequential glycosylation of NPG-supported glycosyl acceptor 6 on a NPG 10-plate assembly.

O-(2,3,4,6-Tetra-O-benzoyl-β-D-glucopyranosyl)-(1→6)-O-(2,3,4-tri-O-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzoyl-α/β-D-glucopyranose (12). NPG stick containing glycosyl acceptor conjugate **6** (7 mg, 9.0 μmol) was placed into the reaction vessel containing a mixture of the glycosyl donor **10** (39 mg, 0.05 mmol) and freshly activated molecular sieves (3Å, 120 mg) in dry CH_2Cl_2 (7.0 mL). The assembly was agitated under argon for 3 h, MeOTf (17 μL, 0.14 mmol) was added and the reaction vessel was agitated under argon for 20 h at rt. The excess reagents was removed by repeatedly dipping the stick in CH_2Cl_2 (3-5 x 7 mL), and the solvent excess was removed by drying the stick under reduced pressure (1 – 2 h). After that, the NPG stick was placed into the reaction vessel containing a solution of 1M Bu_4NF (27 μL, 0.03 mmol) in THF (7 mL). The reaction vessel was agitated at rt for 16 h. The excess reagents was removed by repeatedly dipping the stick in CH_2Cl_2 (3-5 x 7 mL), and the solvent excess was removed by drying the stick under reduced pressure (1 – 2 h). After that, the NPG stick was placed into the reaction vessel containing a mixture of the glycosyl donor **4** (33 mg, 0.05 mmol) and freshly activated molecular sieves (3Å, 100 mg) in dry CH_2Cl_2 (7.0 mL). The assembly was agitated under argon for 3 h, MeOTf (17 μL, 0.14 mmol) was added and the reaction vessel was agitated under argon for 20 h at rt. The excess reagents was removed by repeatedly dipping the stick in CH_2Cl_2 (3-5 x 7 mL), and the solvent excess was removed by drying the stick under reduced pressure (1 – 2 h). After that, the NPG stick covered with bound trisaccharides was agitated in 1N solution of NaOMe in methanol (7.0 mL) for 16 h at rt, while maintaining the pH

= 8-9. The reaction mixture was then neutralized with Dowex (H^+) and the NPG stick was removed and rinsed by dipping in MeOH (3-5 x 7.0 mL). Dowex (H^+) was filtered off and washed successively with methanol (5 x 2 mL). The combined methanol filtrate and washings were combined and concentrated under reduced pressure and dried in *vacuo*. The resulting crude mixture containing fully deprotected trisaccharides was dissolved in pyridine (0.5 mL), cooled to 0 ^oC and benzoyl chloride (30 μL) was added. The reaction mixture was stirred under argon for 5 h at rt, then quenched with methanol (1 mL) and the volatiles were evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel (ethyl acetate-hexane gradient elution) to allow the title trisaccharides **12** as a colorless foam in 52% yield (α/β = 3.3/1). Analytical data for **12**: R_f= 0.5 (1/1 ethyl acetate/hexanes), ^{1}H-n.m.r: (α-**12**); δ, 3.50 (dd, 1H, $J_{5,6a}$= 4.1 Hz, $J_{6a,6b}$= 11.0 Hz, H-6a), 3.88 (d, 2H, H-5',6b'), 4.00 (d, 1H, H-6a'), 4.04 (dd, 1H, $J_{5,6b}$= 4.0 Hz, H-6b), 4.30 (m, 1H, H-5), 4.42-4.52 (m, 2H, H-5'',6b''), 4.56 (d, 1H, $J_{1',2'}$=7.7 Hz, H-1'), 4.66 (d, 1H, H-6a''), 5.05 (dd, 1H, $J_{4',5'}$= 9.5 Hz, H-4'), 5.16 (dd, 1H, $J_{2',3'}$= 7.7 Hz, H-2'), 5.25 (d, 1H, $J_{1'',2''}$= 7.9 Hz, H-1''), 5.51 (dd, 1H, $J_{2'',3''}$= 7.9 Hz, H-2''), 5.62-5.72 (m, 2H, H-3',4''), 5.75 (dd, 1H, $J_{2,3}$= 3.7 Hz, H-2), 5.80 (dd, 1H, $J_{4,5}$= 9.9 Hz, H-4), 6.17 (dd, 1H, $J_{3'',4''}$=9.8 Hz, H-3''), 6.27 (dd, 1H, $J_{3,4}$= 10.0 Hz, H-3), 6.86 (d, 1H, $J_{1,2}$= 3.7 Hz, H-1), 7.15-8.12 (m, 55H, aromatic) ppm; ^{13}C-n.m.r.: δ, 29.9, 31.1, 63.5, 68.1, 68.6, 69.7, 69.8, 70.3, 70.5, 70.8, 71.3, 72.0, 72.4, 72.5, 72.8, 72.9, 74.8, 77.6, 90.3, 100.6, 101.6, 128.4, 128.5, 128.5, 128.5, 128.6, 128.6, 128.7, 128.7, 128.9, 129.1, 129.1, 129.1, 129.3, 129.3, 129.5, 129.5, 129.9, 130.0, 130.0, 130.1, 130.3, 130.5, 133.1, 133.3, 133.3, 133.5, 133.5, 133.6, 133.7, 133.9, 164.7, 165.2, 165.4, 165.5, 165.5, 165.6, 165.8, 166.0, 166.1, 166.4 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{95}H_{76}O_{27}Na$ 1671.4472, found 1671.4425. Also obtained herein was compound **9** in 20% yield.

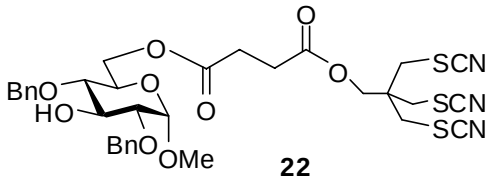
O-(2,3,4,6-Tetra-O-benzoyl-β-D-galactopyranosyl)-(1→6)-O-(2,3,4-tri-O-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzoyl-α/β-D-glucopyranose (34). The title compound was obtained from The title compound was obtained from building blocks **6**, **10,** and 2-benzoxazolyl 2,3,4,6-tetra-O-benzoyl-1-thio-β-D-galactopyranoside (**33**)[10] as a pale yellow foam in 31% yield (α/β = 4.1/1). Analytical data for **34**: R_f= 0.5 (1/1 ethyl acetate/hexanes), ^{1}H-n.m.r.; δ, 3.54 (dd, 1H, $J_{5,6a}$= 3.5 Hz, $J_{6a,6b}$= 10.8 Hz, H-6a), 3.90 (m, 1H, H-5''), 3.97-4.01 (m, 2H, H-6a'',6b''), 4.10 (dd, 1H, $J_{5,6b}$= 3.4 Hz, H-6b), 4.35 (m, 1H, H-5), 4.48 (dd, 1H, $J_{5',6a'}$= 6.0 Hz, H-5'), 4.53 (d, 1H, $J_{1',2'}$= 7.6 Hz, H-1'), 4.60 (dd, 1H, H-6b'), 4.65 (dd, 1H, $J_{6a',6b'}$= 10.8 Hz, H-6a'), 5.15 (dd, 1H, $J_{4',5'}$= 9.7 Hz, H-4'), 5.29 (dd, 2H, $J_{1'',2''}$= 8.0 Hz, $J_{2',3'}$= 9.8 Hz, H-1'',2'), 5.68 (m, 2H, H-2,3'), 5.78 (m, 2H, H-2'',4), 5.91 (dd, 1H, H-3''), 6.14 (d, 1H, $J_{4'',5''}$= 3.2 Hz, H-4''), 6.28 (dd, 1H, $J_{3,4}$= 10.0 Hz, H-3), 6.84 (d, 1H, $J_{1,2}$= 3.7 Hz, H-1), 7.20-8.14 (m, 55H, aromatic) ppm; ^{13}C-n.m.r.: δ, 62.5, 67.7, 68.3, 69.2, 69.6, 70.6, 70.8, 71.3, 71.5, 71.8, 71.9, 72.9, 75.3, 76.6, 90.4, 100.5, 101.9, 128.4, 128.4, 128.5, 128.5, 128.6, 128.6, 128.7, 128.7, 128.9, 128.9, 128.9, 129.0, 129.1, 129.2, 129.3, 129.3, 129.5, 129.6, 129.7, 129.9, 129.9, 130.1, 130.2, 130.3, 130.3, 130.4, 133.0, 133.3, 133.4, 133.4, 133.5, 133.6, 133.7, 133.9, 134.0, 164.9, 165.2, 165.2, 165.3, 165.4, 165.6, 165.7, 165.8, 165.9, 165.9, 166.2, 166.3, 171.4 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{95}H_{76}O_{27}Na$ 1671.4472, found 1671.4425. Also obtained herein were compound **9** and 1,2,3,4-Tetra-O-benzoyl-6-O-(2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl)-α/β-D-glucopyranose (**35**) in 26% and 8% yield, respectively. Analytical data for **35** was in a good agreement to those reported previously.[11]

9. Reusing the anchored NPG plates



The adamantine monolayer covered NPG 10-plate assembly (**36**) left over after the cleavage of trisaccharide **11** (see the synthesis of **12**) was investigated with the purpose of direct reapplication. For this purpose DCC/DMAP mediated coupling with model compound **31** was performed as described for the solution phase couplings (see for example the synthesis of compound **26**. After agitating for 20 h (1 h for the synthesis of **26**) and washing-drying sequence, the stick was subjected to the treatment with NaOMe in MeOH (16 h) as described for the synthesis of compounds **8** or **9**. As a result, compound **32** was obtained in 83% yield (3.5 mg, 7.47 μmol). Analytical data for **32** was in a good agreement to those reported previously.[7]

10. Copies of NMR spectra for all new compounds



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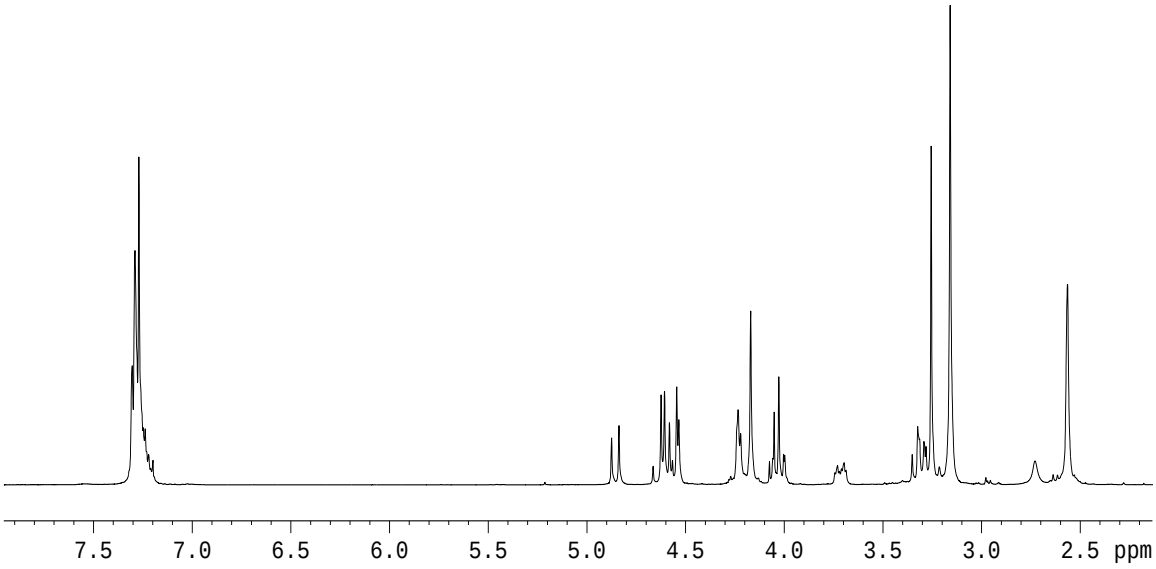

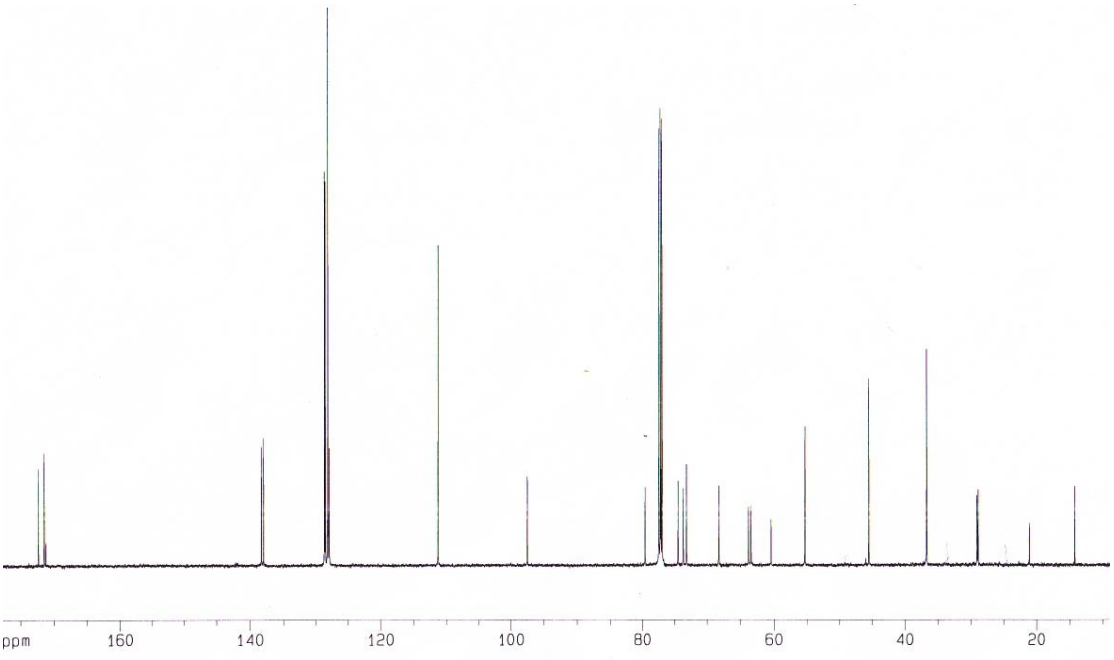

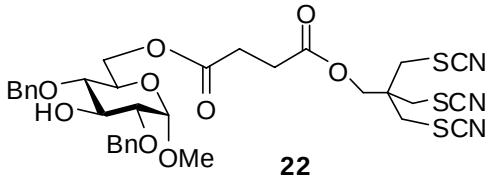
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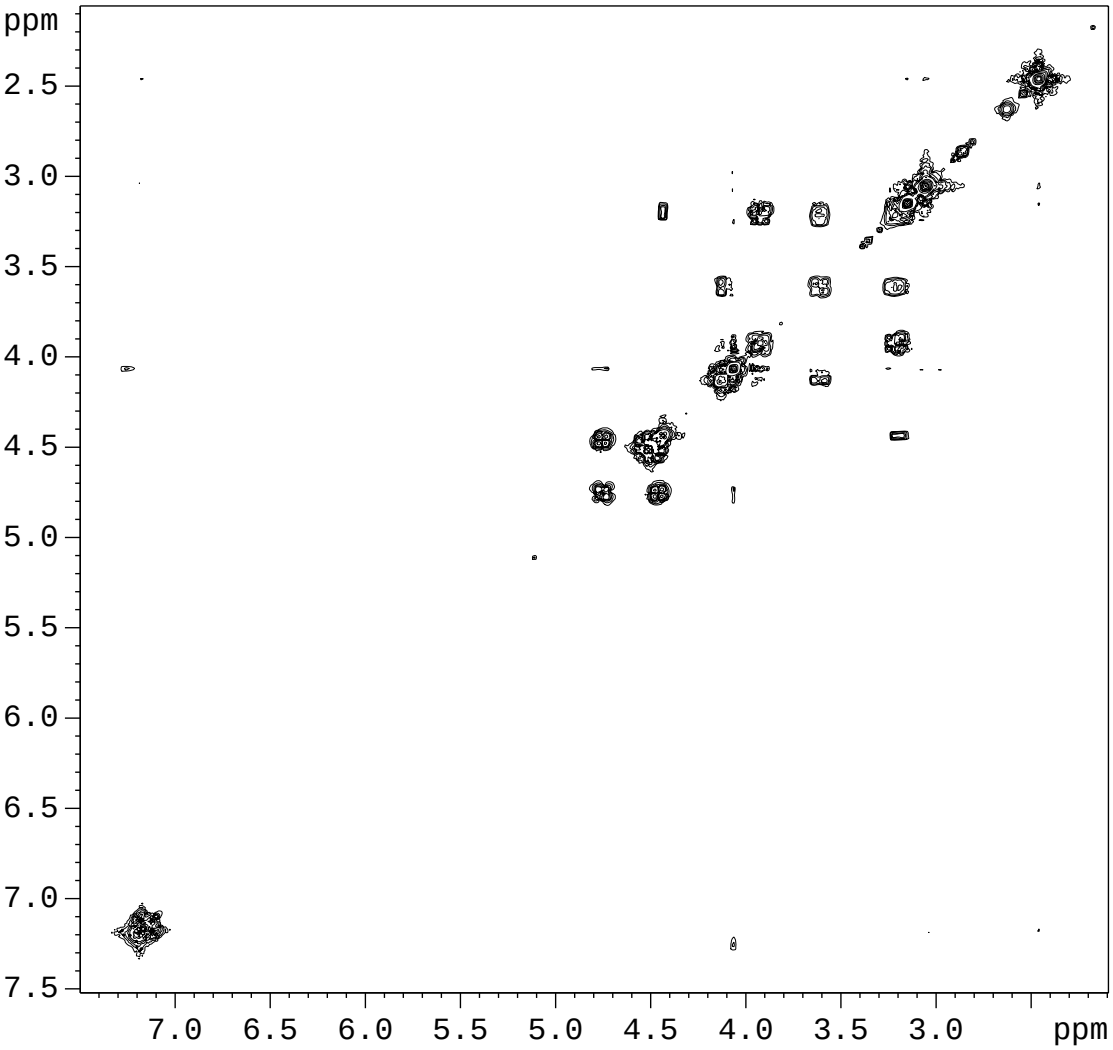
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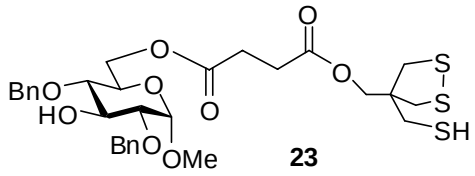
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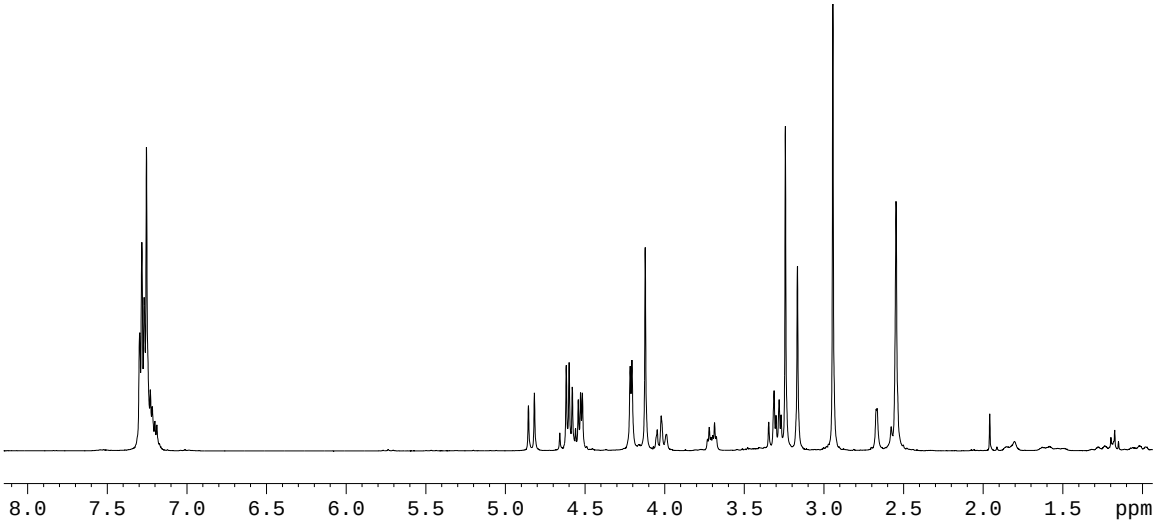
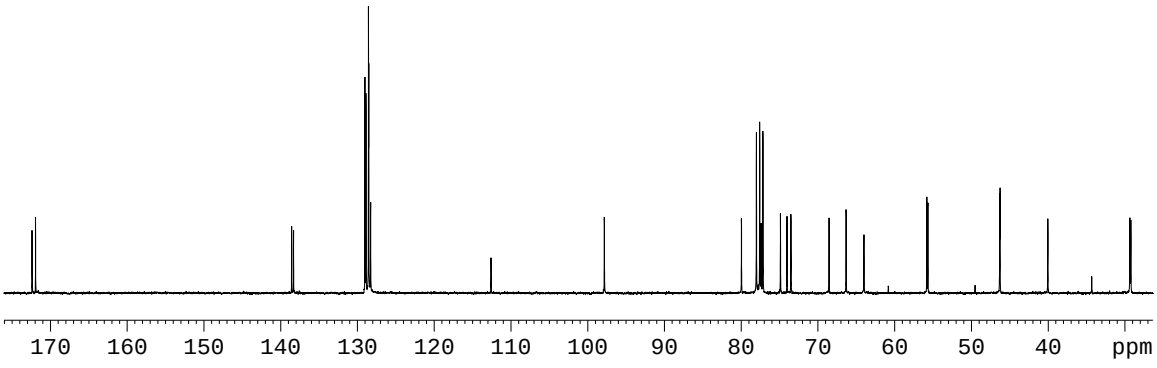
O
HO
O
O
S
O
S
SH
BnO
OMe

23


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


170
160
150
140
130
120
110
100
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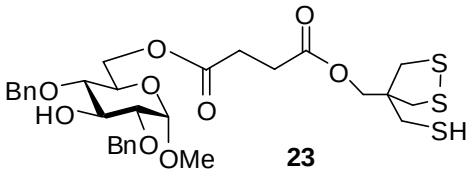
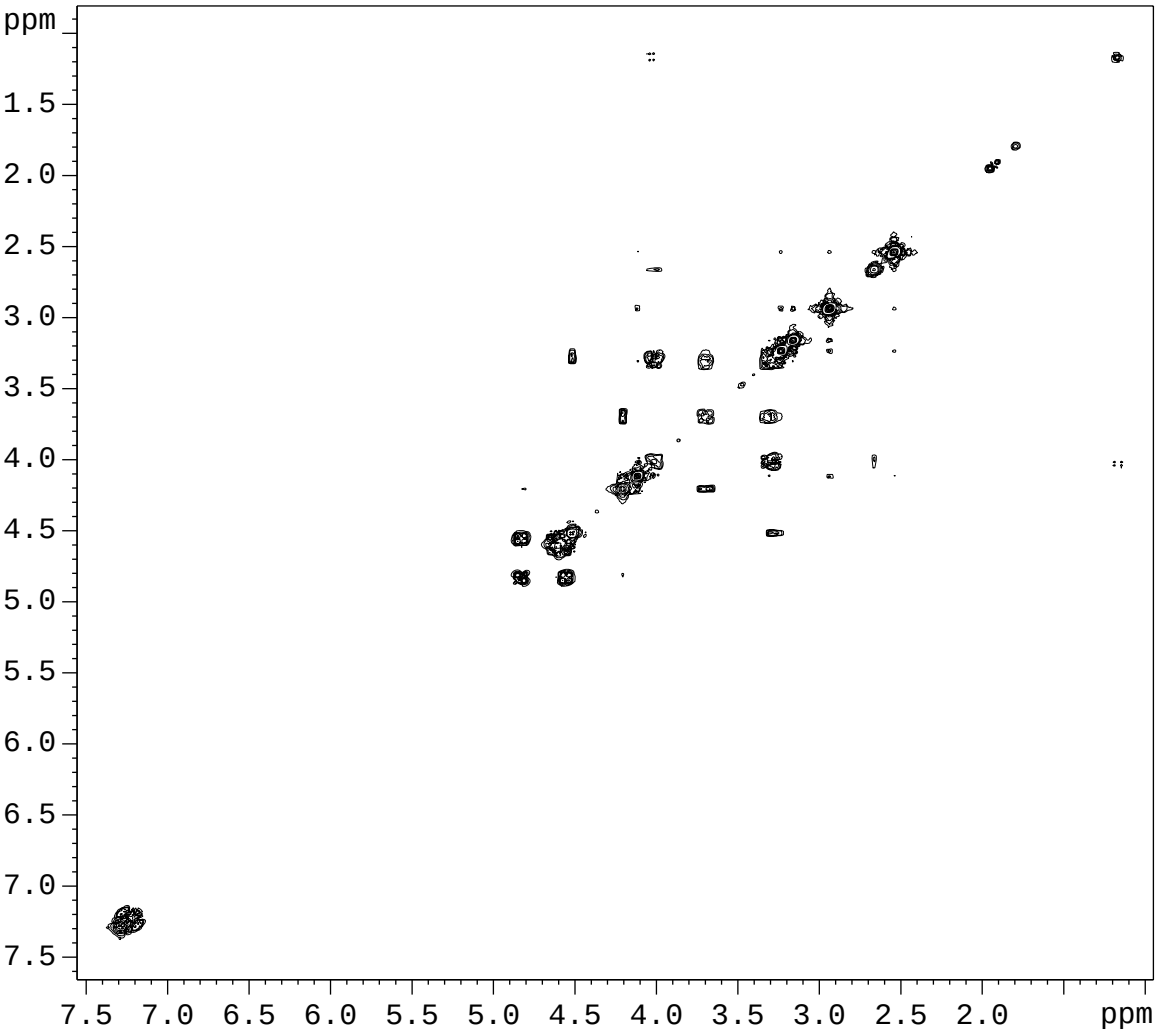
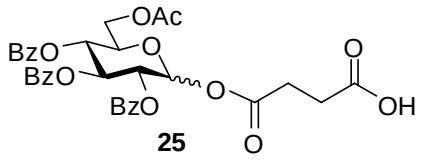
60
50
40
ppm

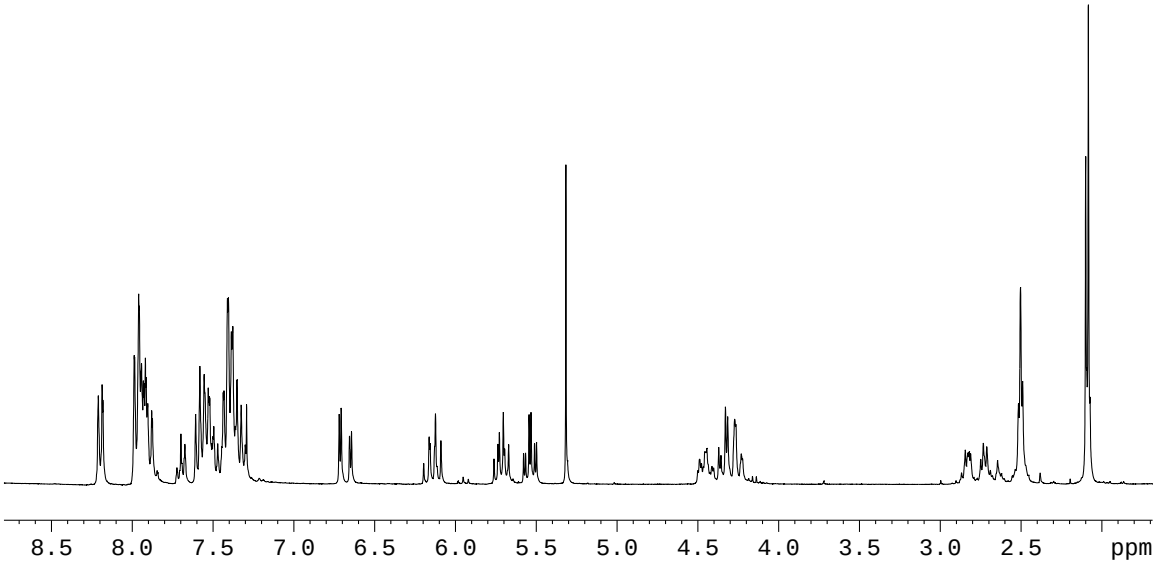

O
O
BnO
HO
O
O
O
S
S
SH
BnO
OMe

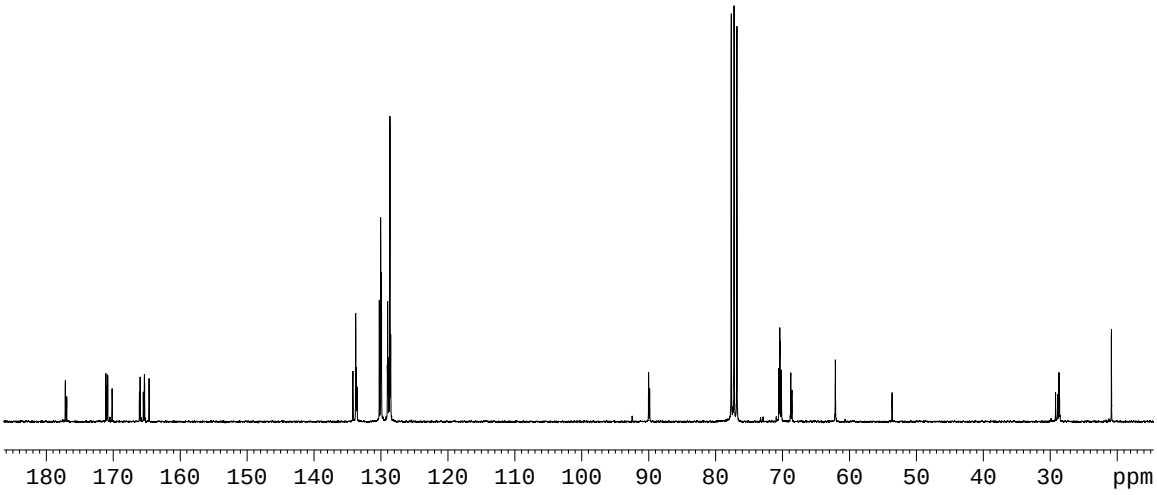
23

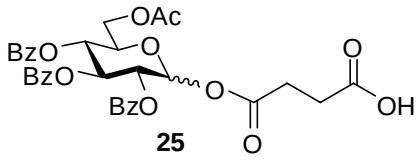

ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0
ppm


OAc
BzO
BzO
BzO
O
O
O
O
OH
O

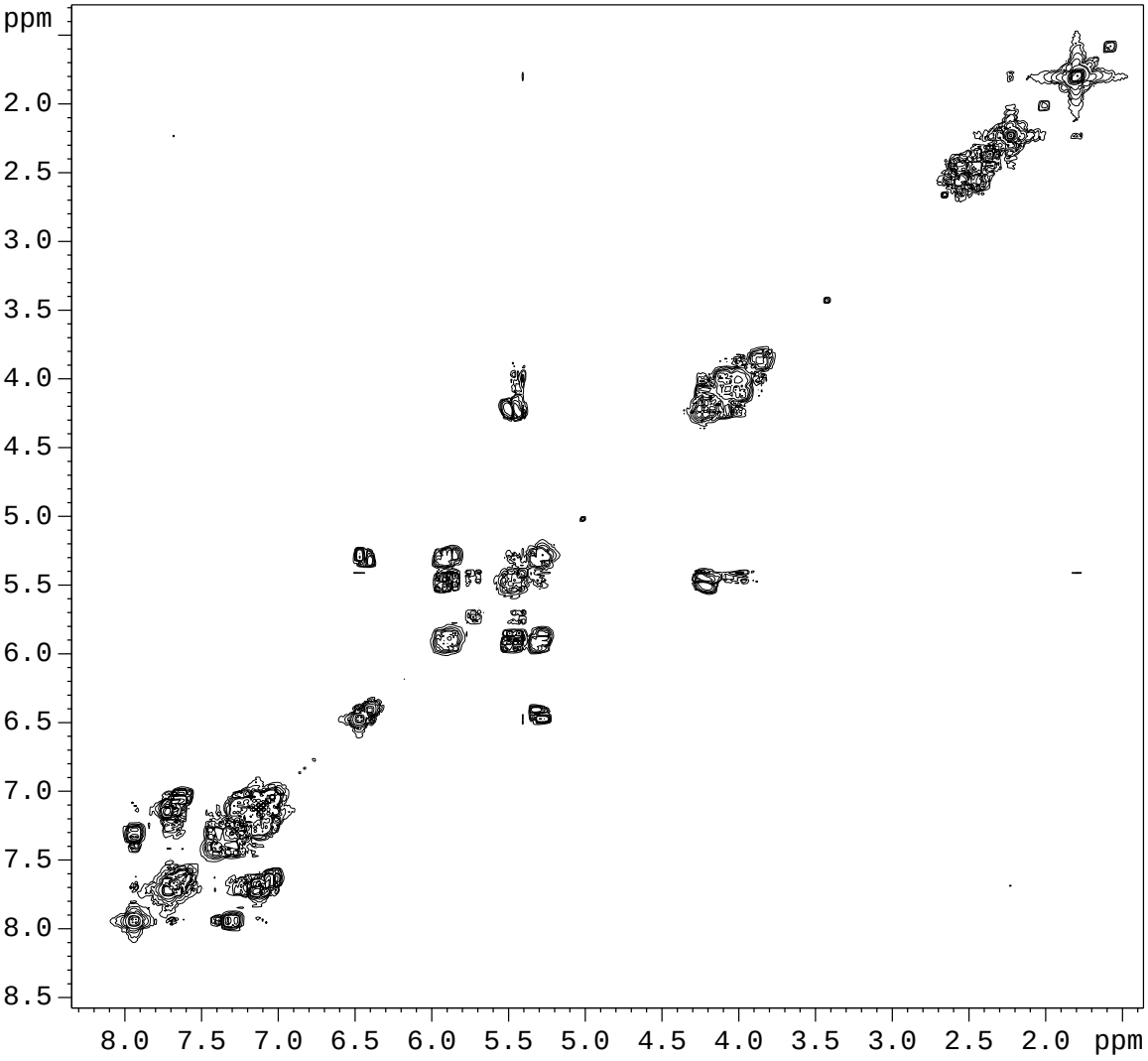
25

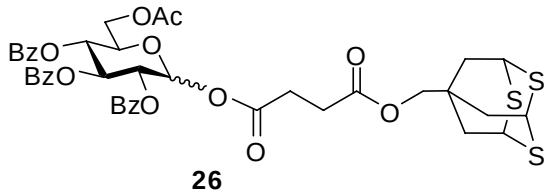

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

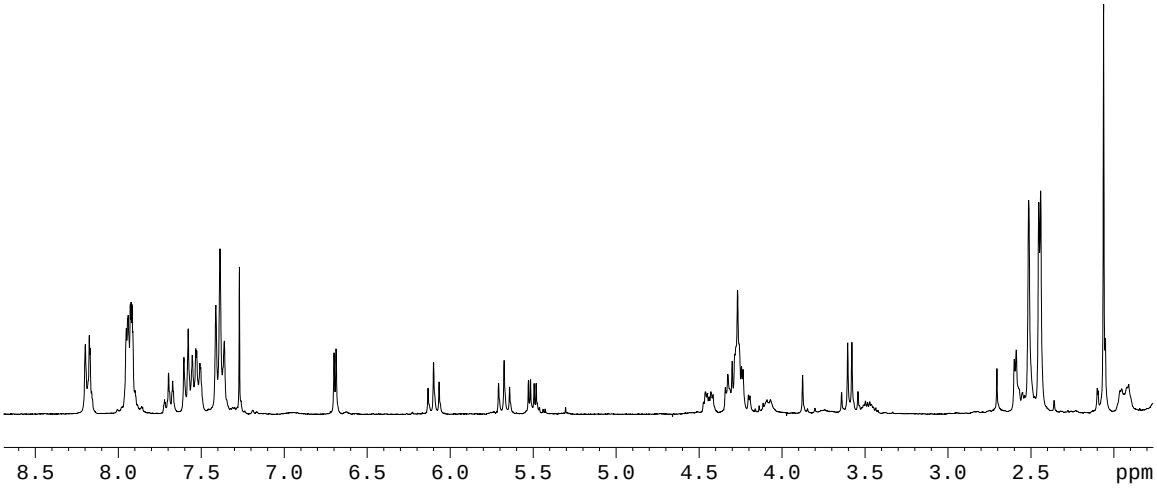

OAc
BzO
O
BzO
BzO
O
O
OH
O

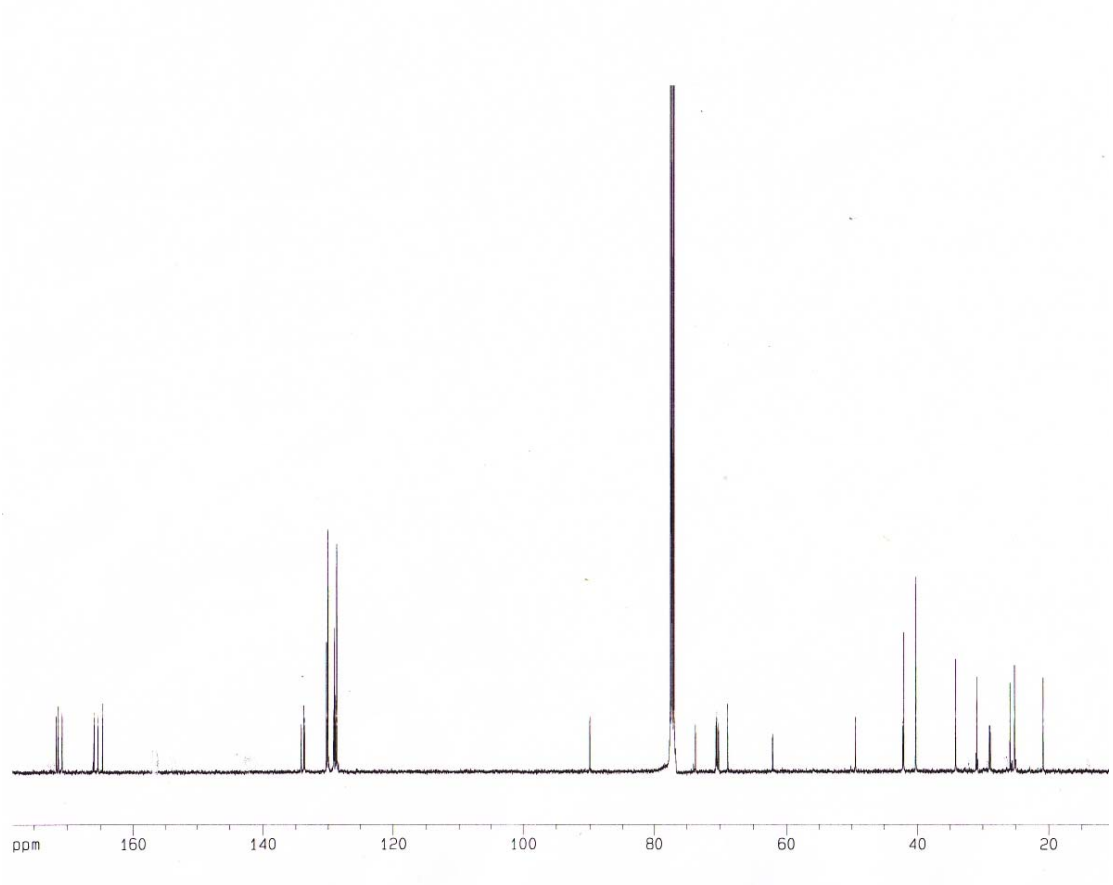
25

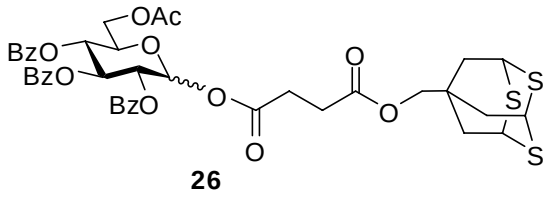

ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm


OAc
BzO
BzO
BzO
O
O
O
O
O
S
S
S

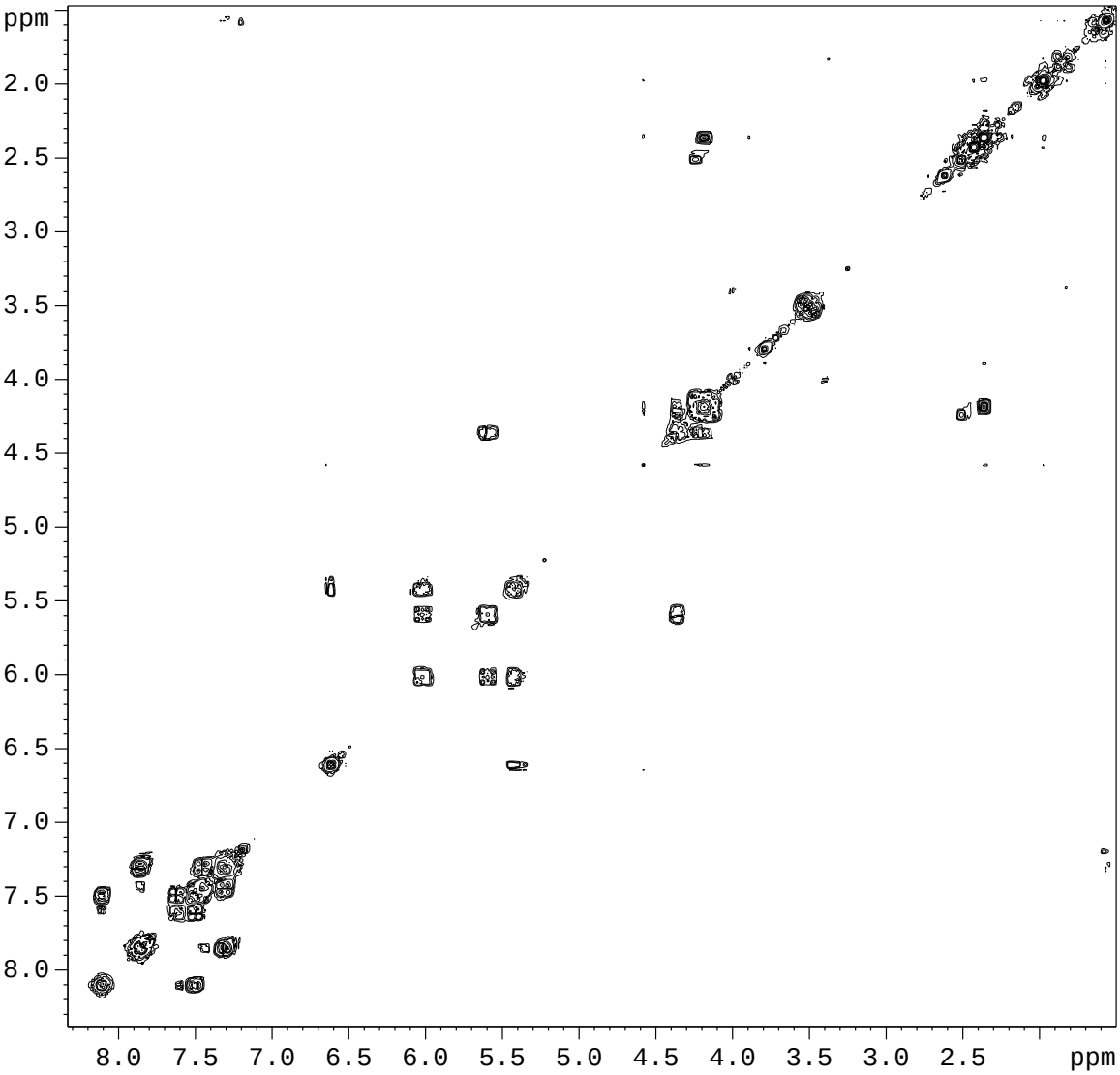
26

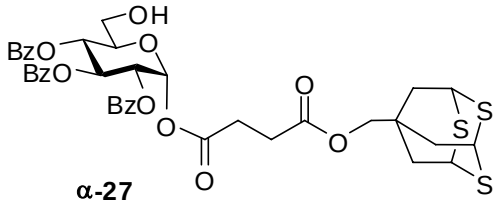

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm


ppm
160
140
120
100
80
60
40
20

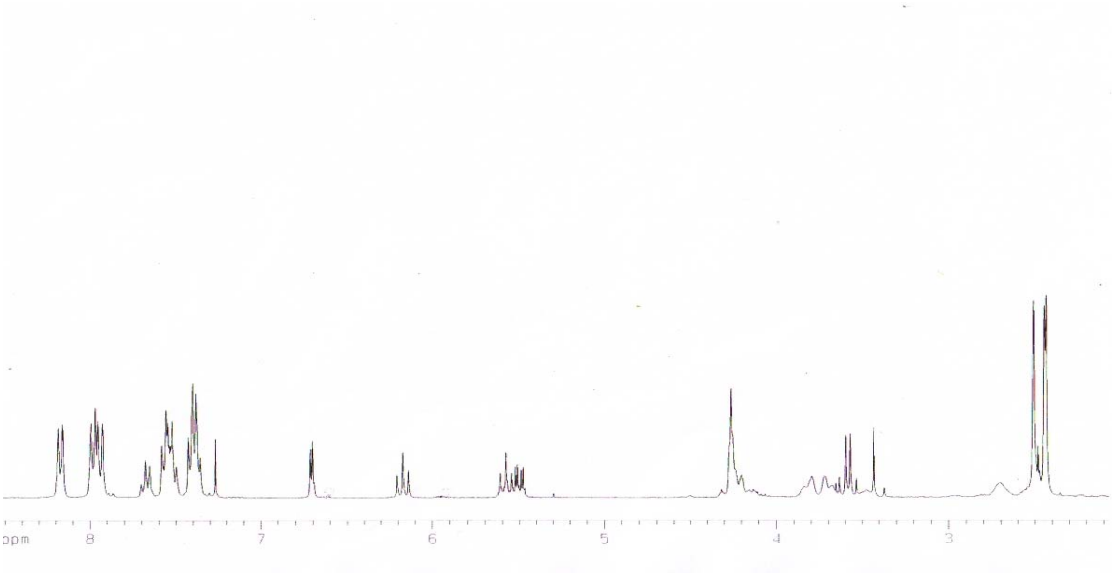

OAc
BzO
BzO
BzO
O
O
O
O
O
S
S
S

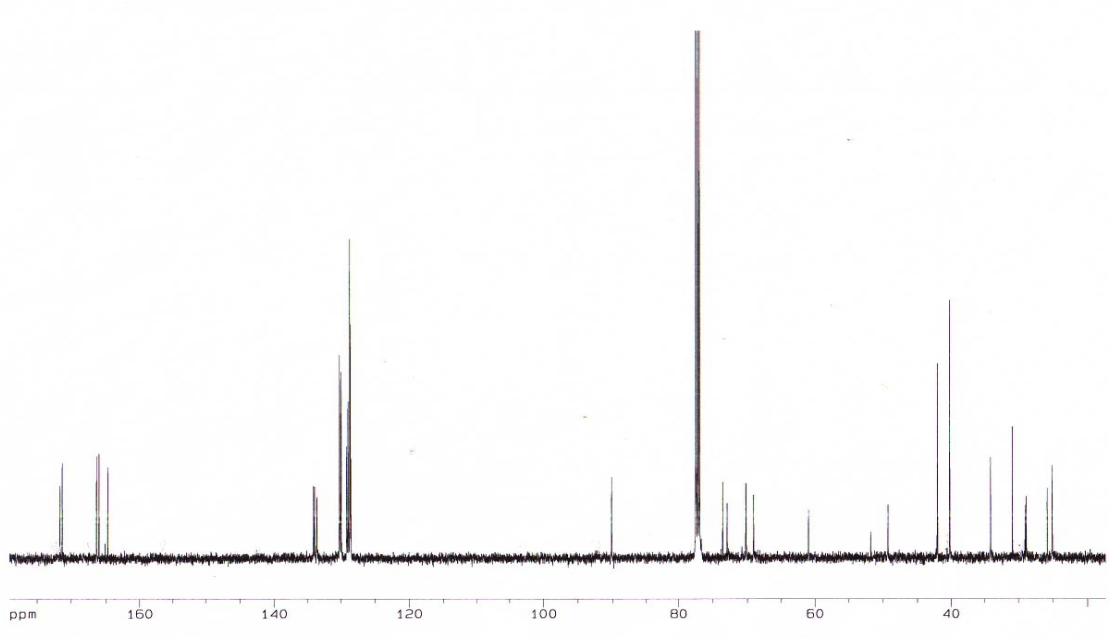
26

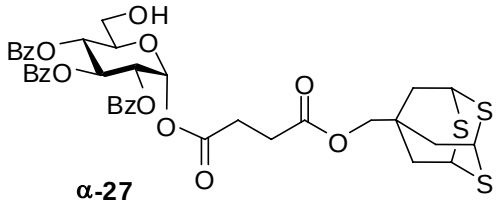

ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm



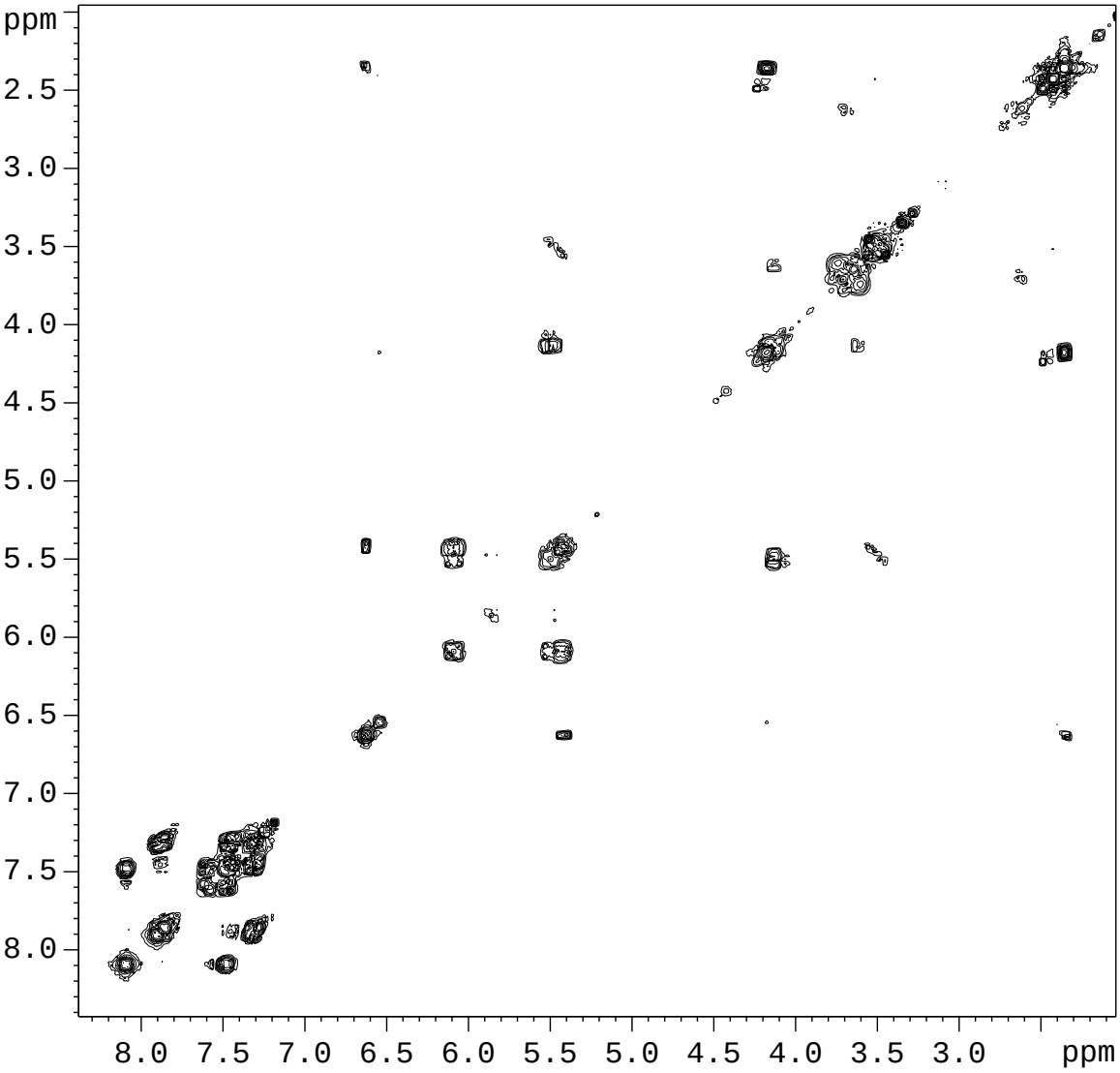
α-27

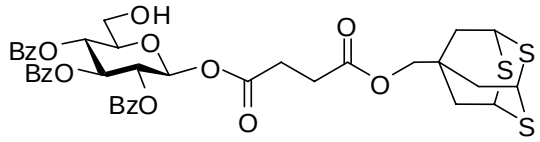




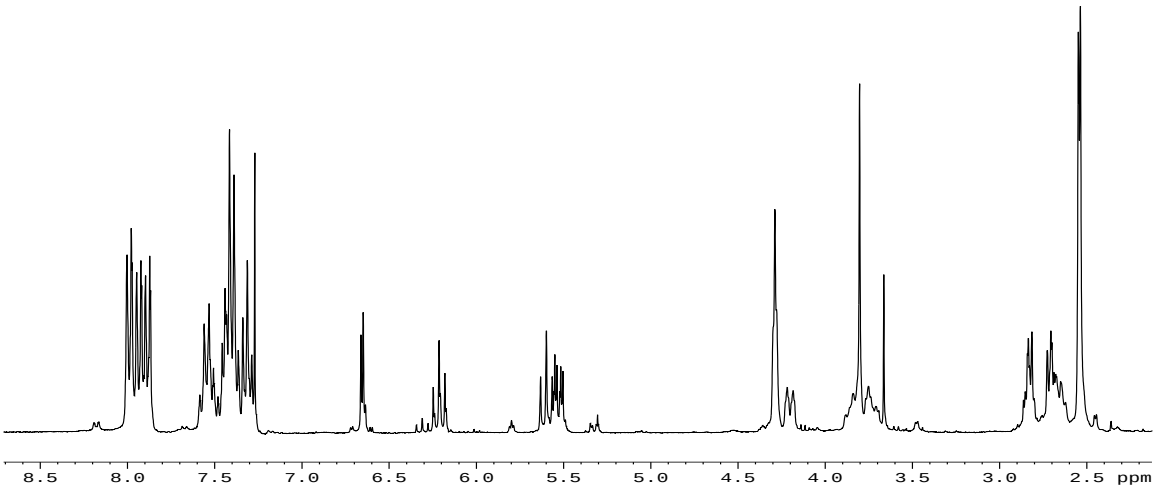

OH
O
BzO
BzO
BzO
O
O
O
O
S
S
S

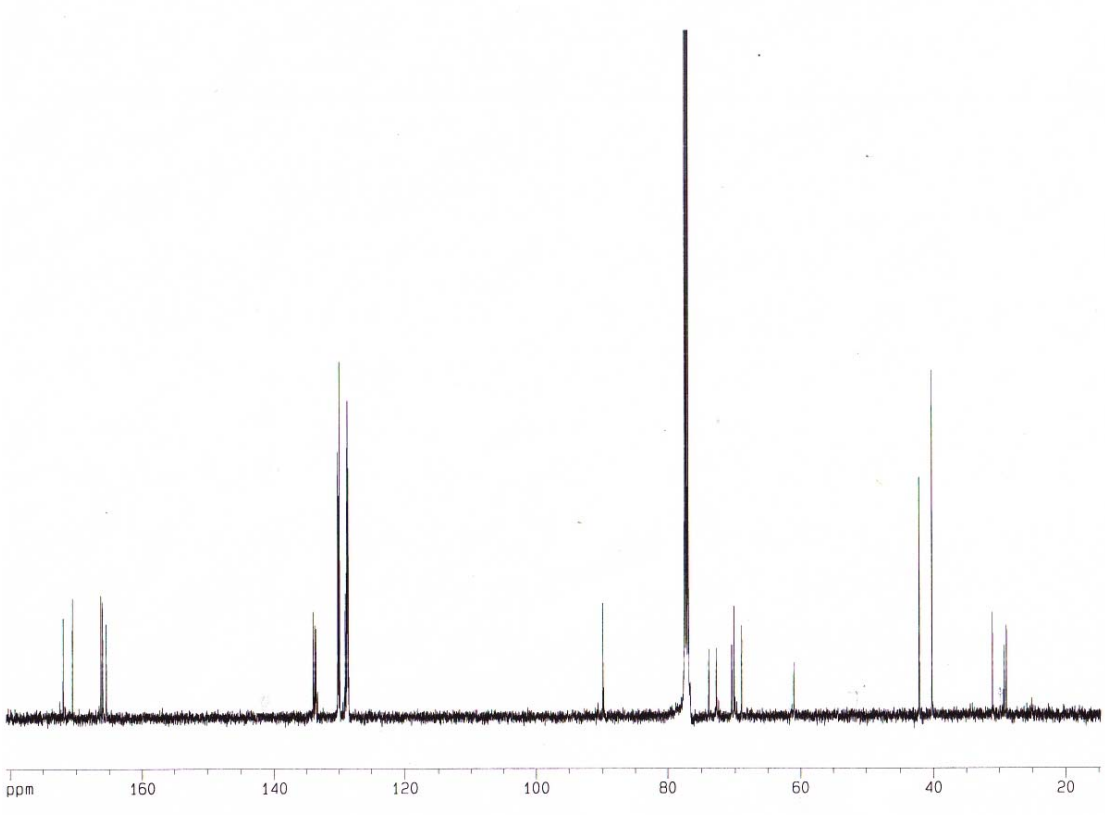
α-27

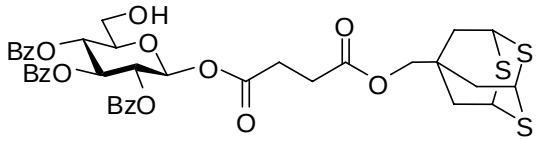

ppm
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 ppm


OH
O
BzO
BzO
BzO
O
O
O
O
S
S
S

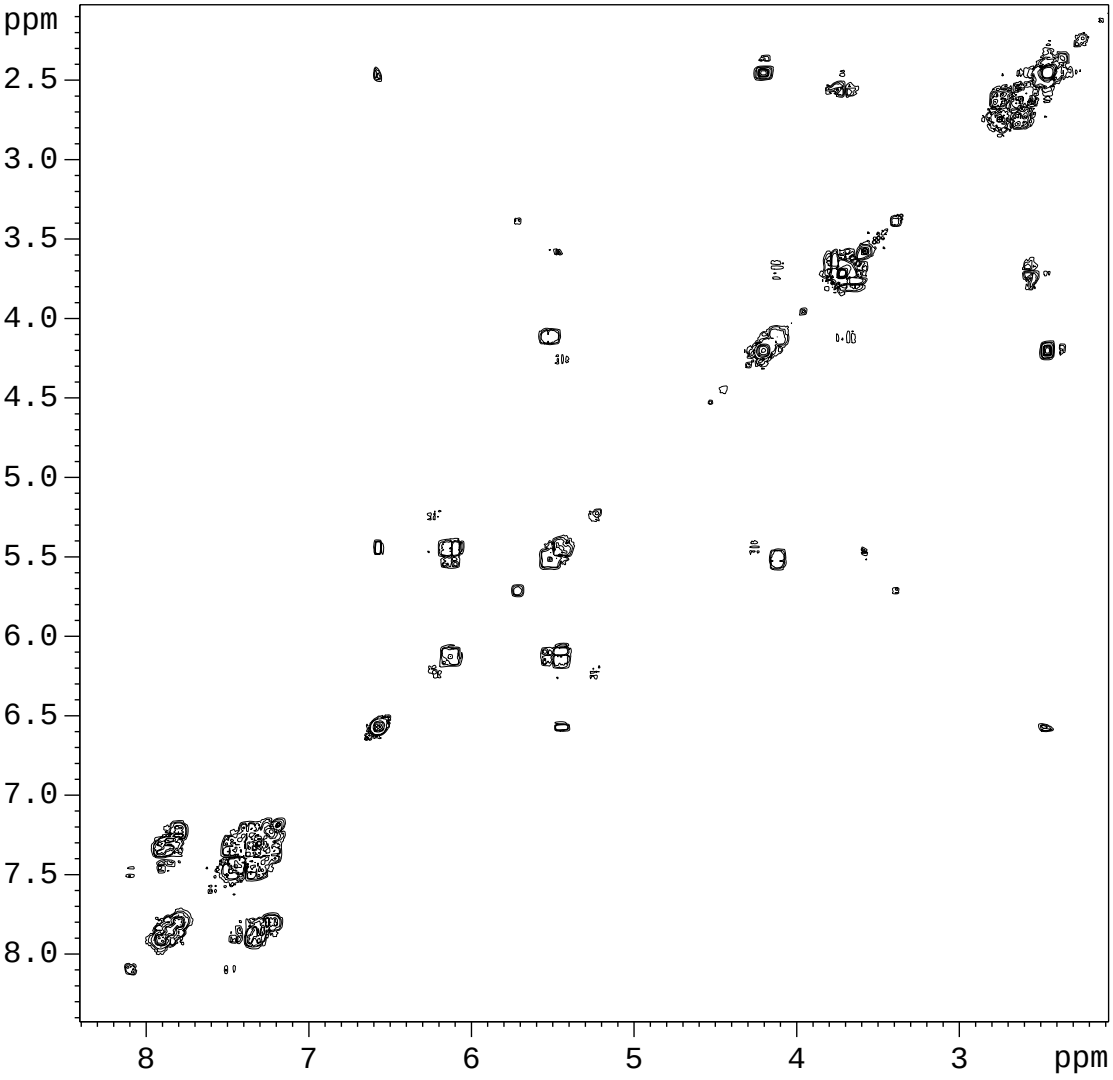
β-27

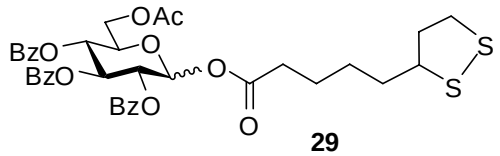

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5 ppm


ppm
160
140
120
100
80
60
40
20

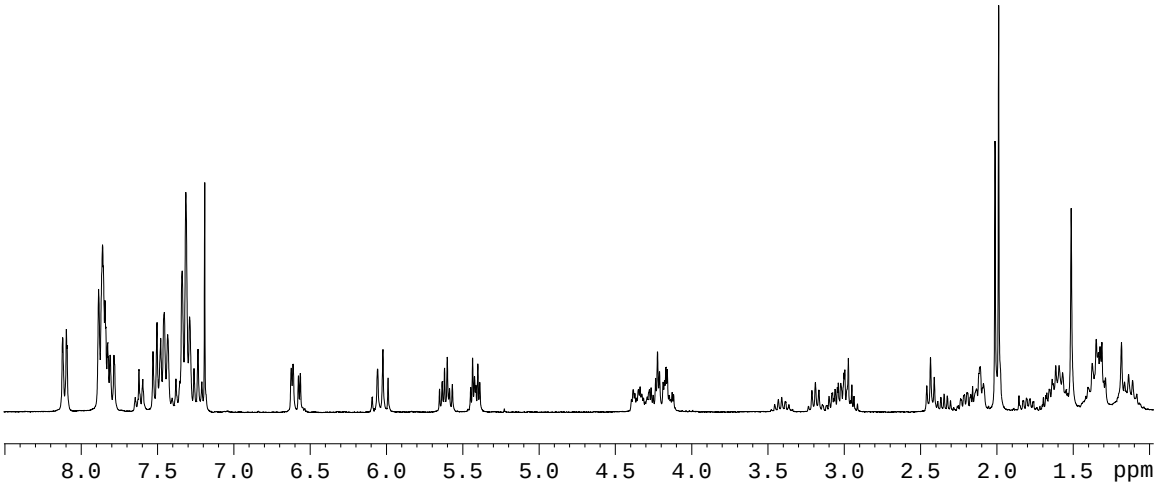

OH
O
BzO
BzO
BzO
O
O
O
O
S
S
S

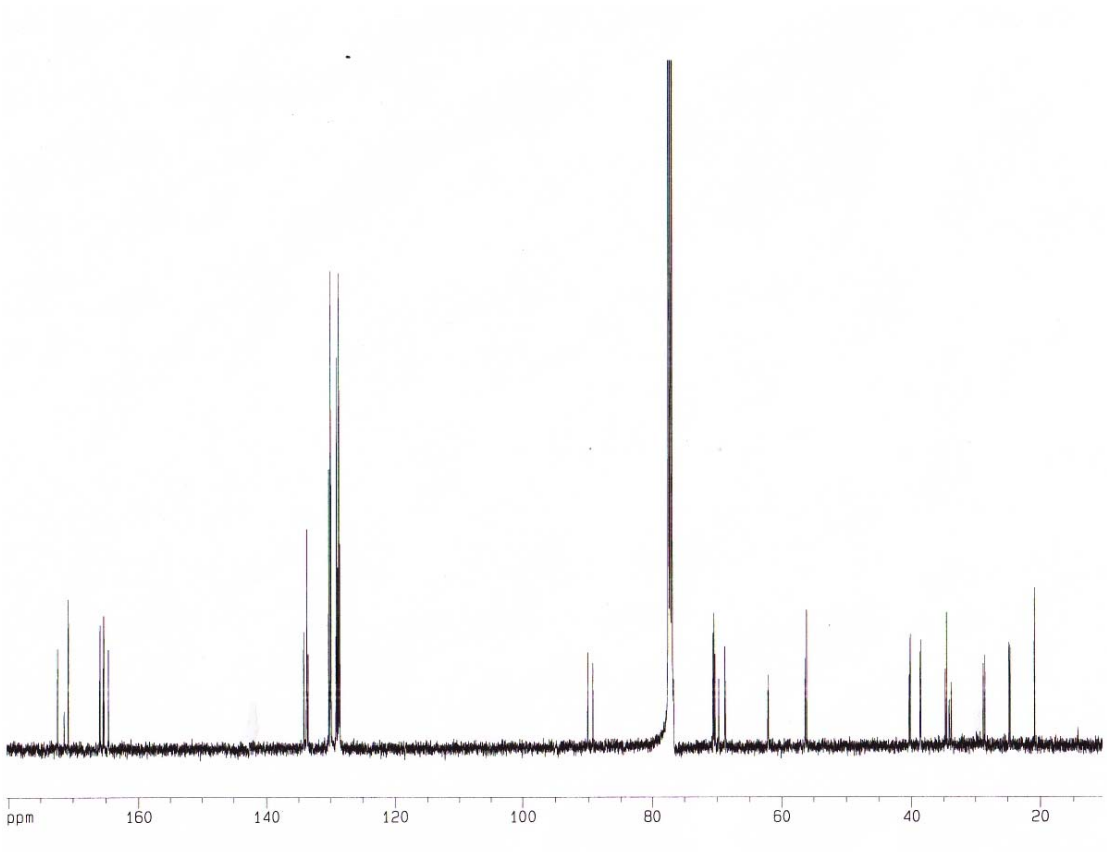
β-27

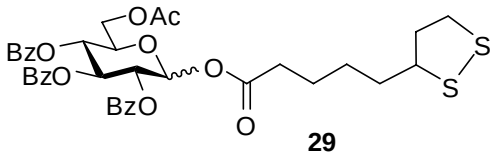

ppm
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8
7
6
5
4
3
ppm


OAc
BzO
O
BzO
O
BzO
O
S
S
O

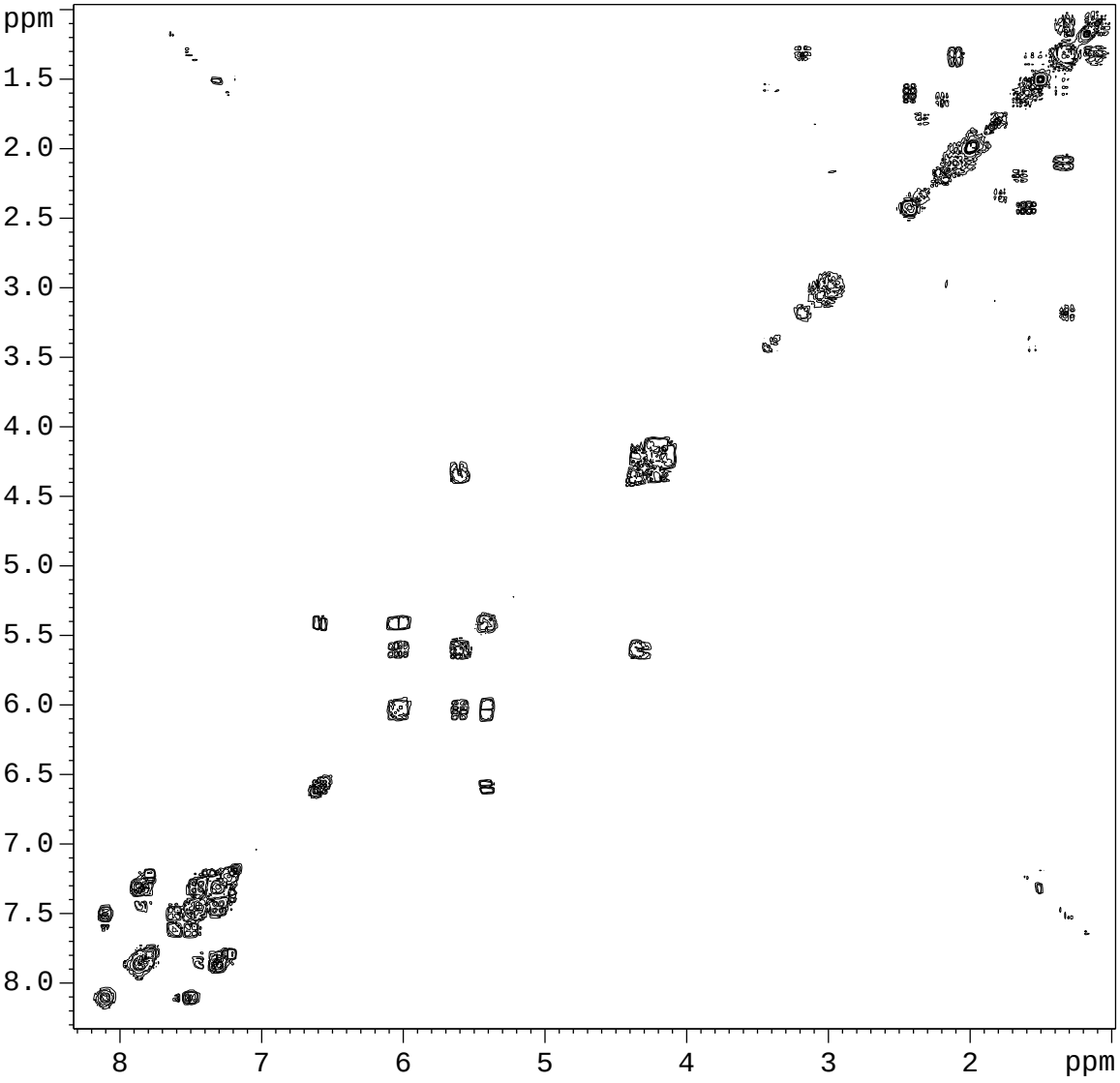
29

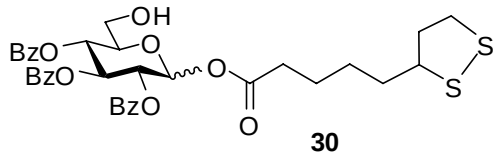

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


ppm
160
140
120
100
80
60
40
20

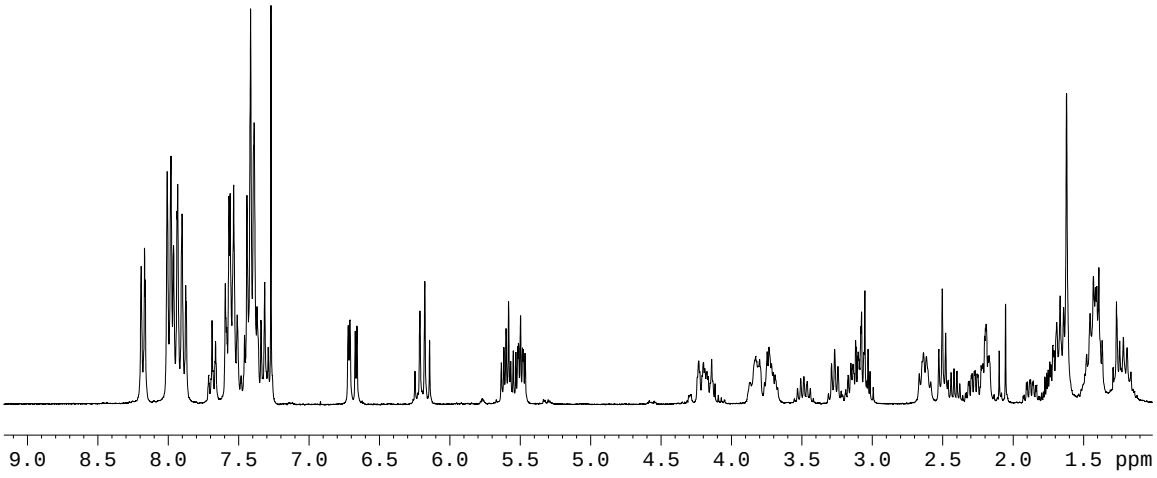

OAc
O
BzO
BzO
BzO
O
O
S
S

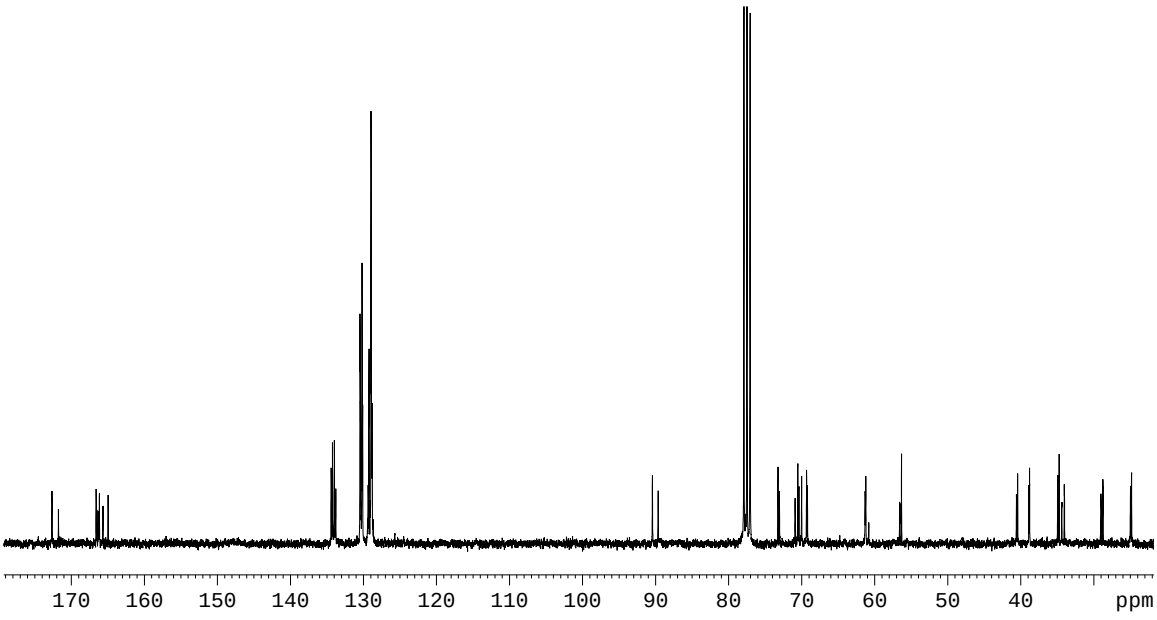
29

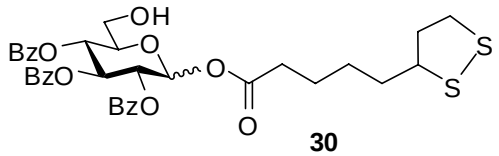

ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8
7
6
5
4
3
2
ppm


OH
O
BzO
BzO
BzO
O
O
S
S

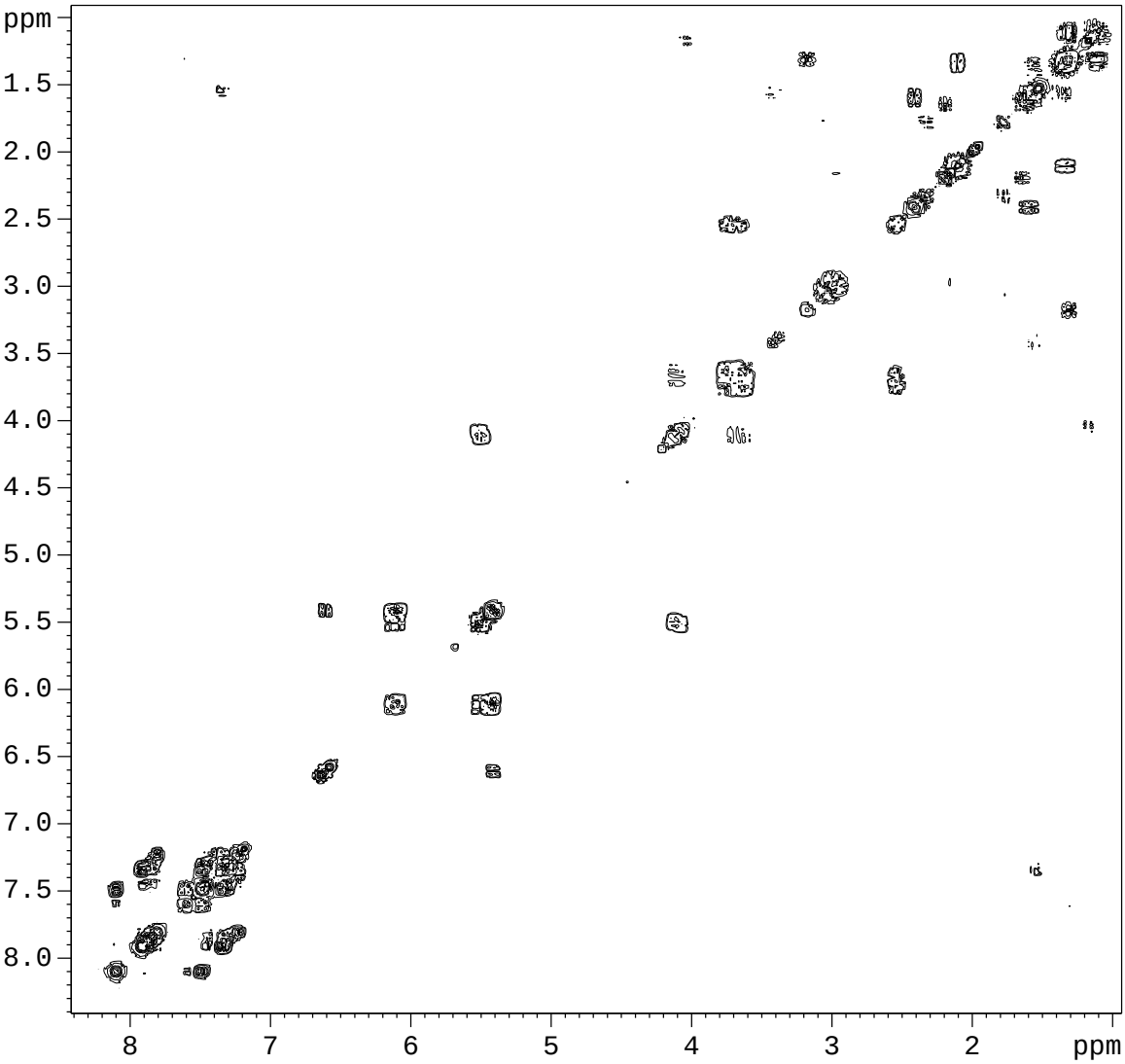
30

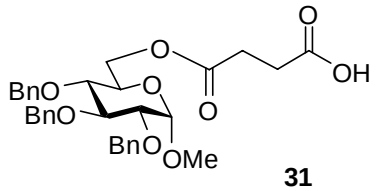

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm


170 160 150 140 130 120 110 100 90 80 70 60 50 40 ppm

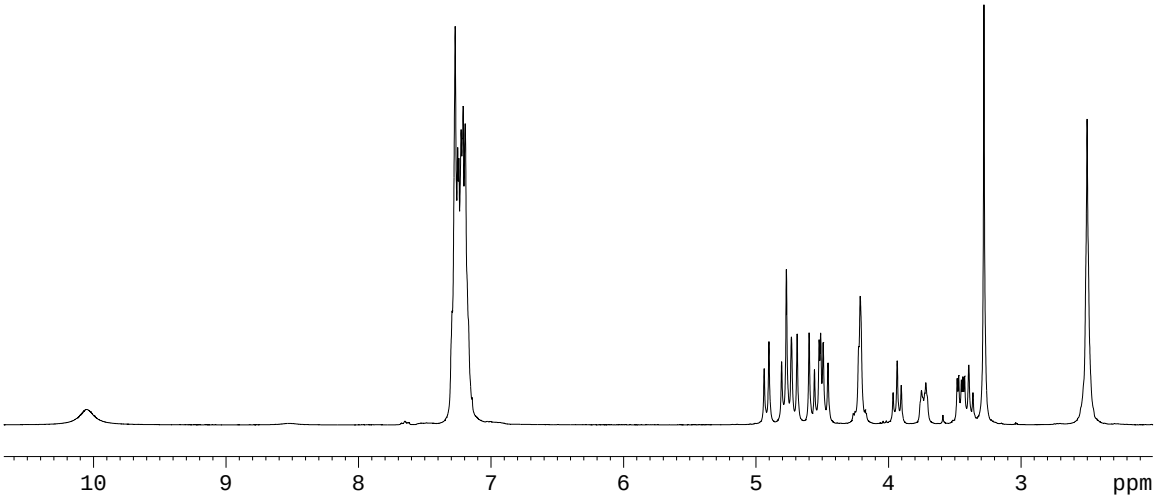

OH
O
BzO
BzO
BzO
O
O
S
S

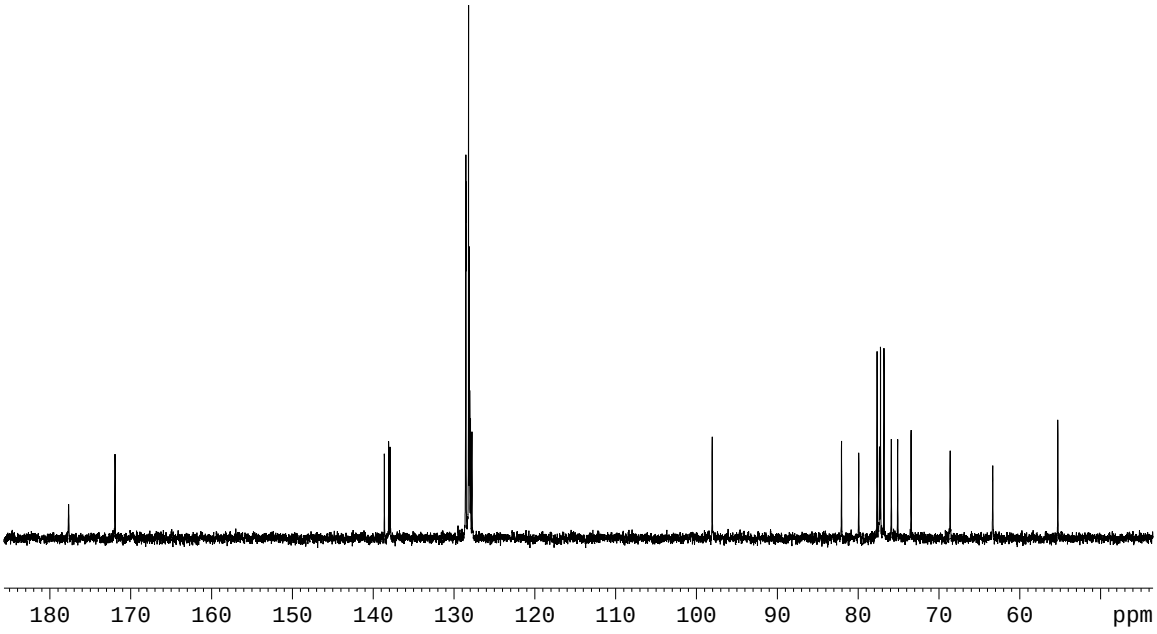
30

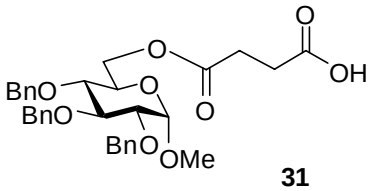

ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8
7
6
5
4
3
2
ppm


O
O
OH
BnO
O
BnO
O
BnO
OMe

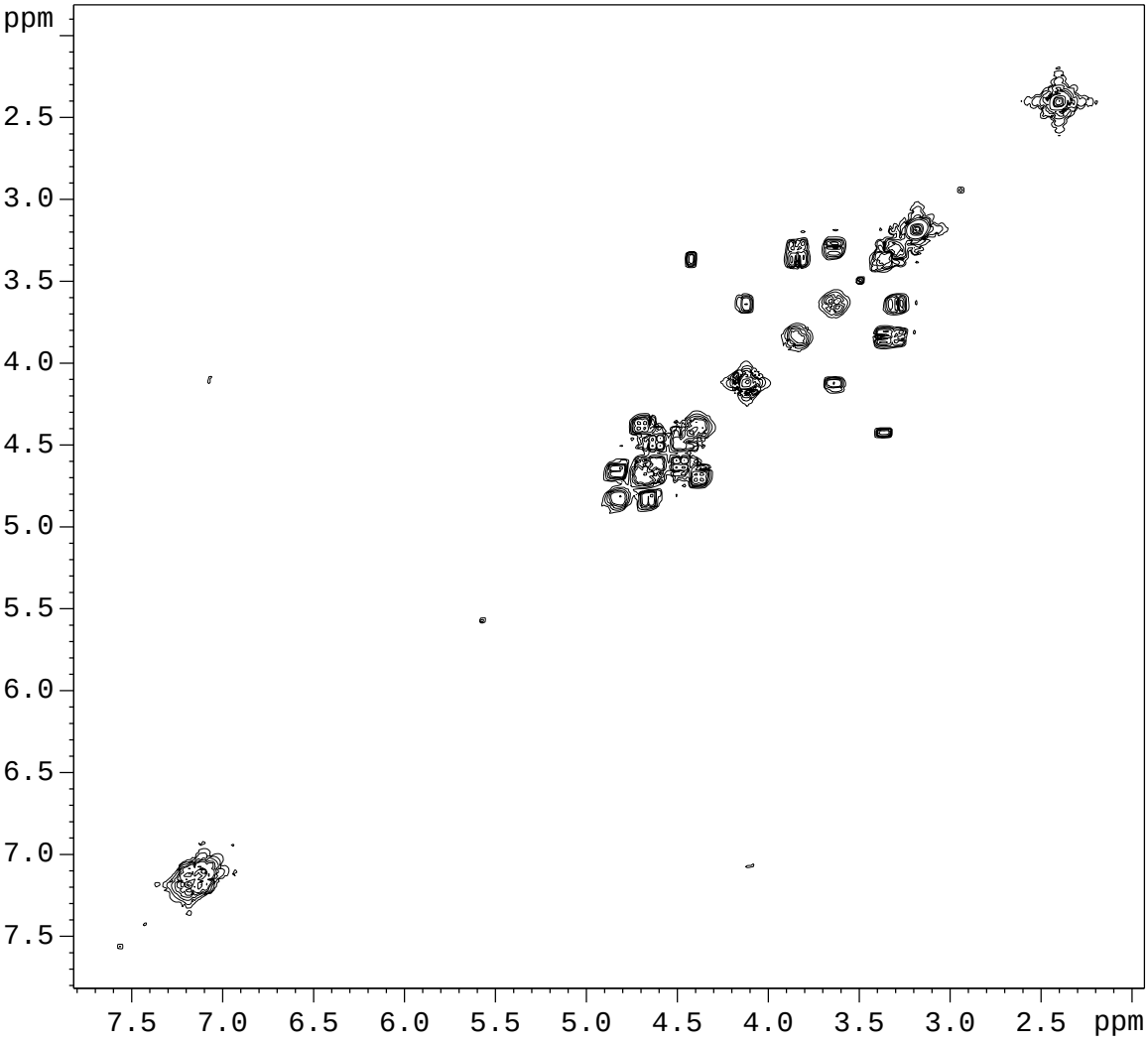
31

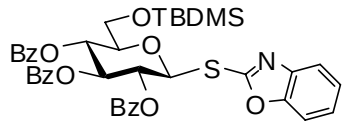

10
9
8
7
6
5
4
3
ppm


180
170
160
150
140
130
120
110
100
90
80
70
60
ppm

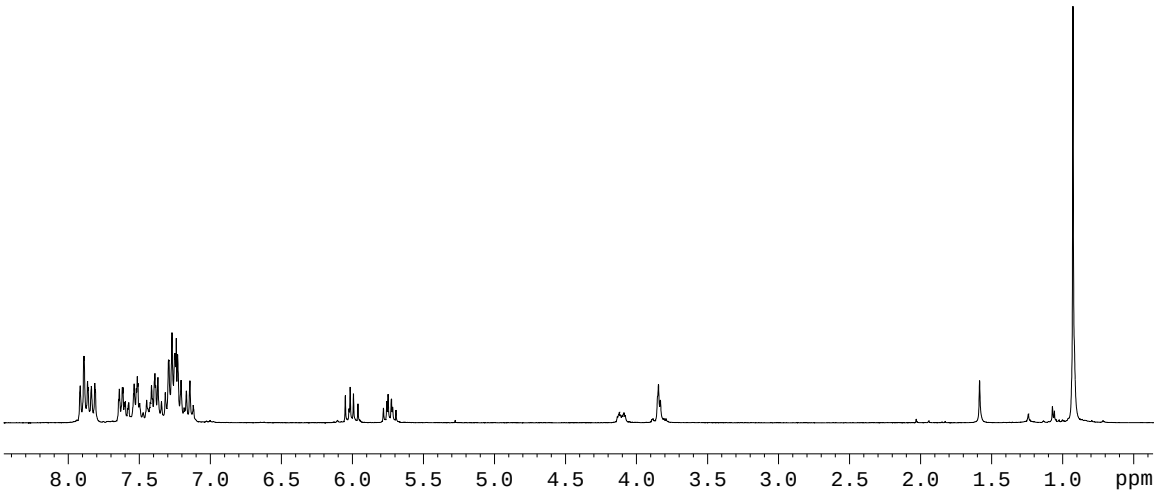

O
O
OH
BnO
O
BnO
O
BnO
OMe

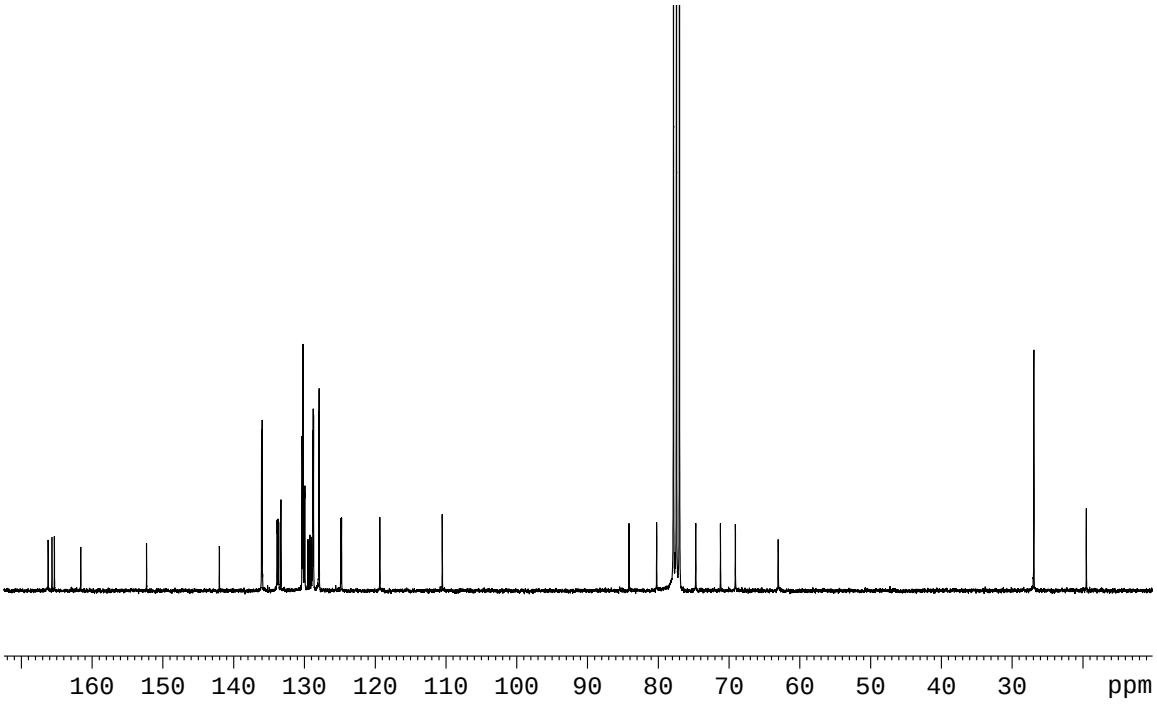
31

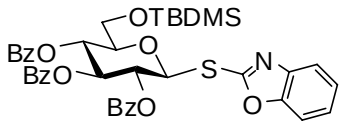

ppm
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm


OTBDMS
O
BzO
BzO
BzO
S
N
O

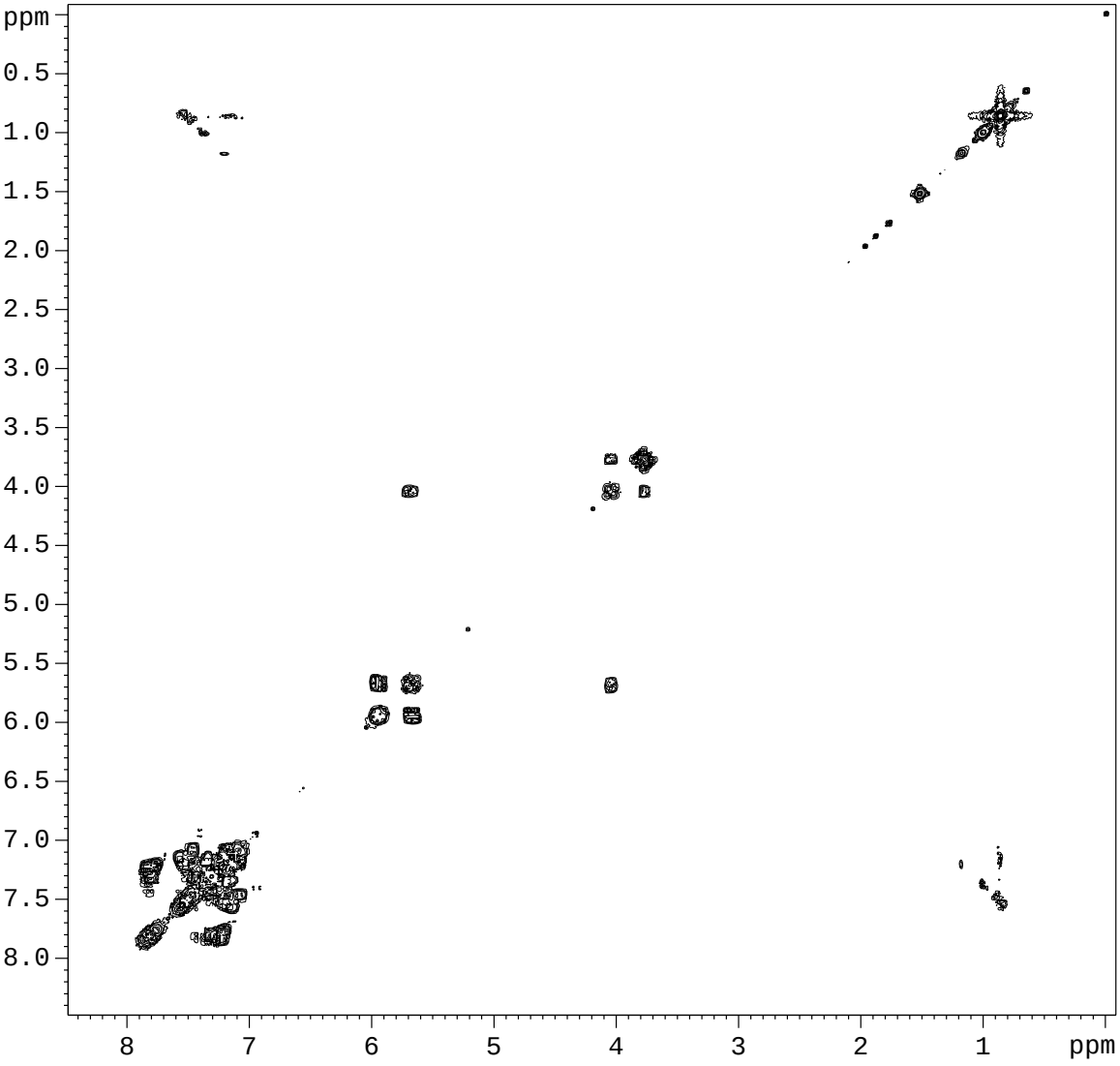
32

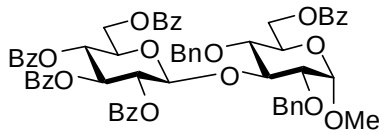

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


OTBDMS
O
BzO
BzO
BzO
S
N
O

32


ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8
7
6
5
4
3
2
1
ppm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BnO
OBz
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BzO
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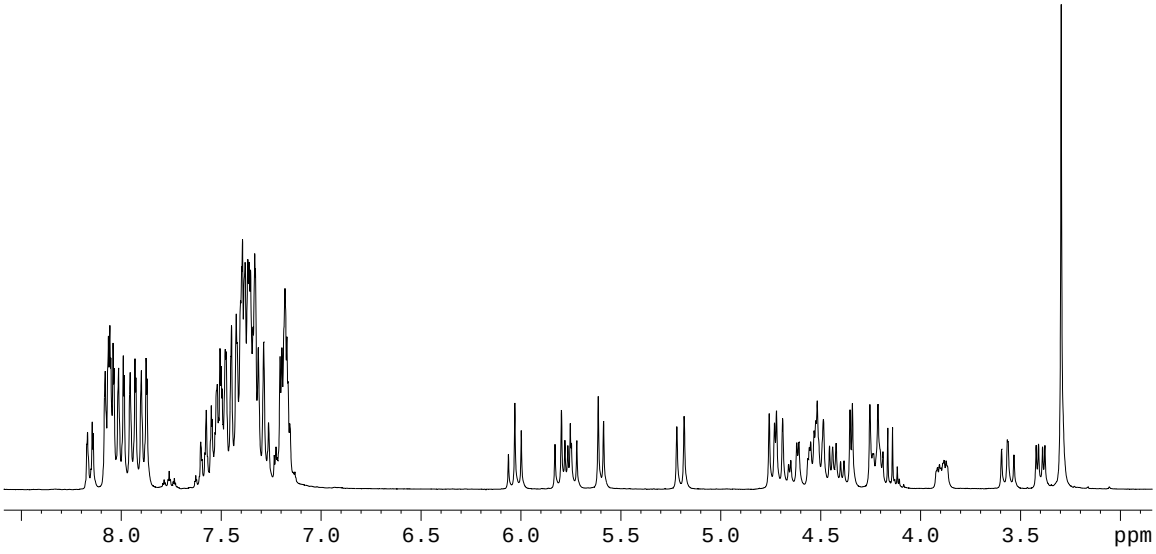
BzO
BnO
OMe

8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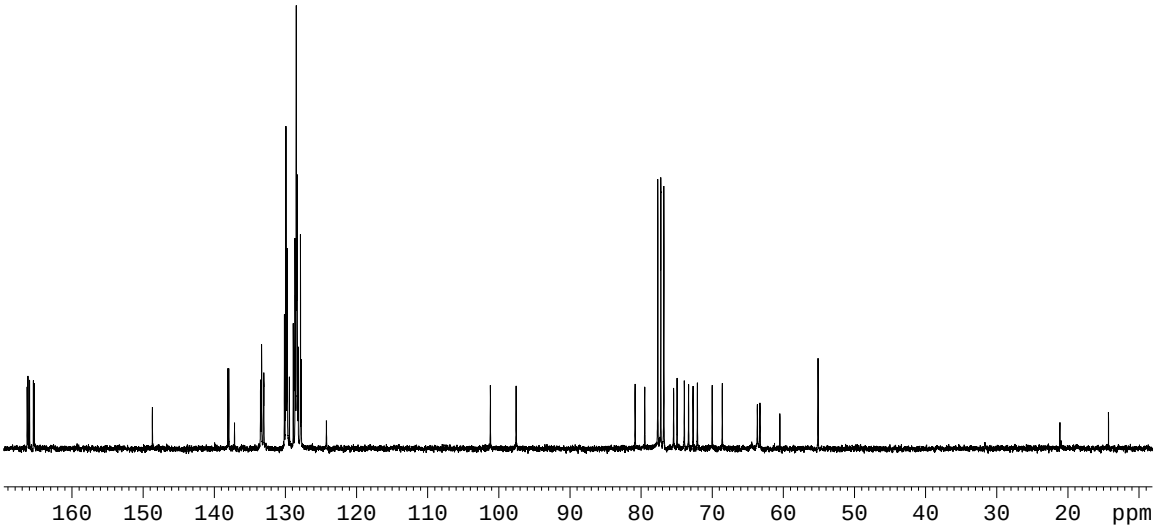
5.0
4.5
4.0
3.5
ppm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150
140
130
120
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100
90
80
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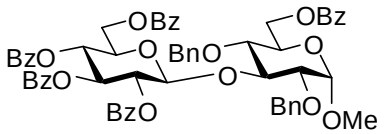
40
30
20
ppm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BnO
BzO
BzO
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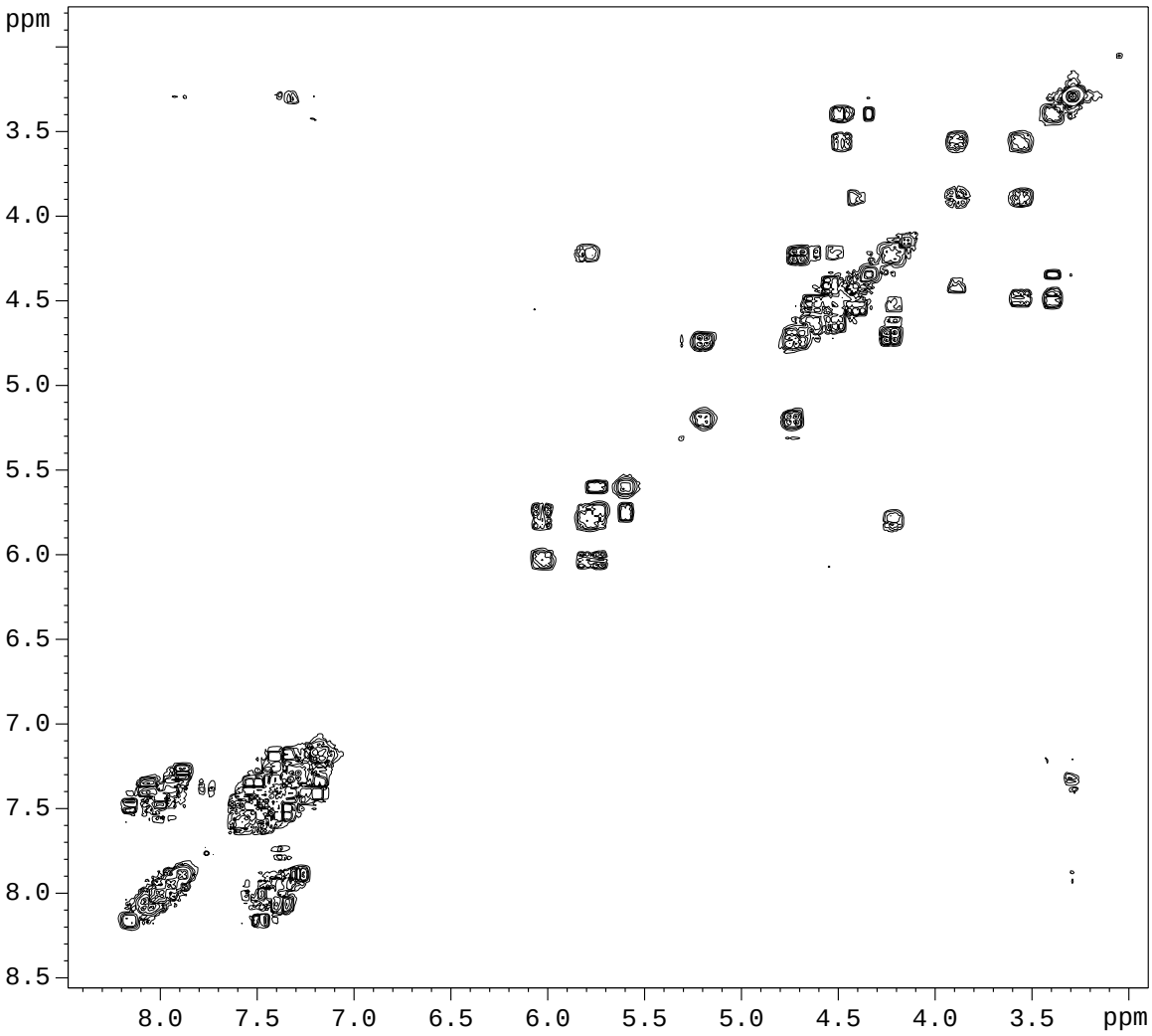
BnO
OMe
BzO

8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6.5
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5.0
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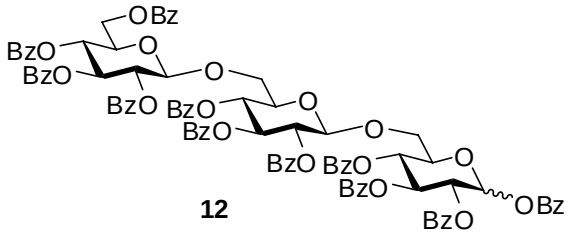
4.0
3.5
ppm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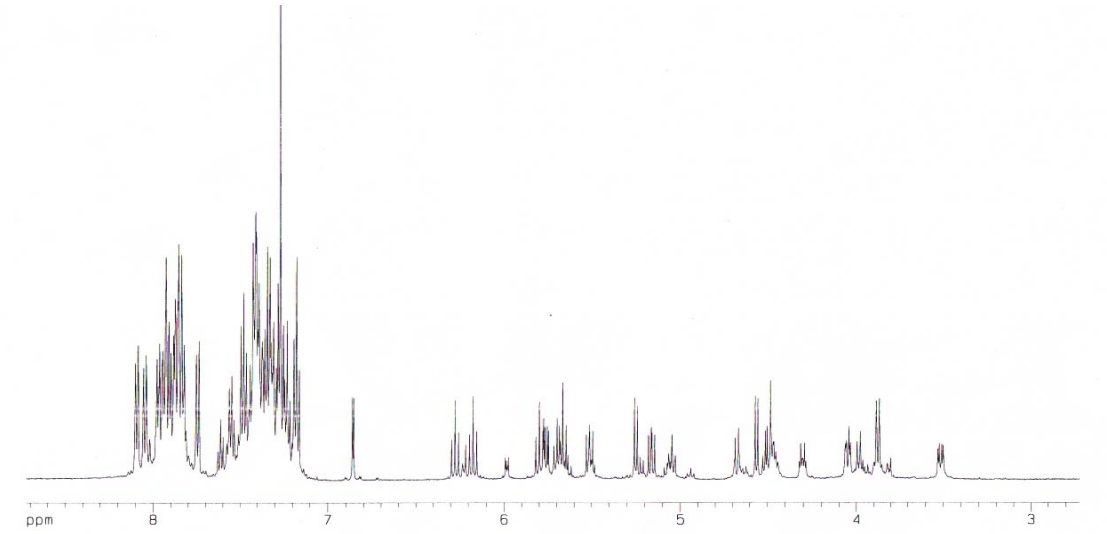
BzO
OBz
BzO

12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6
5
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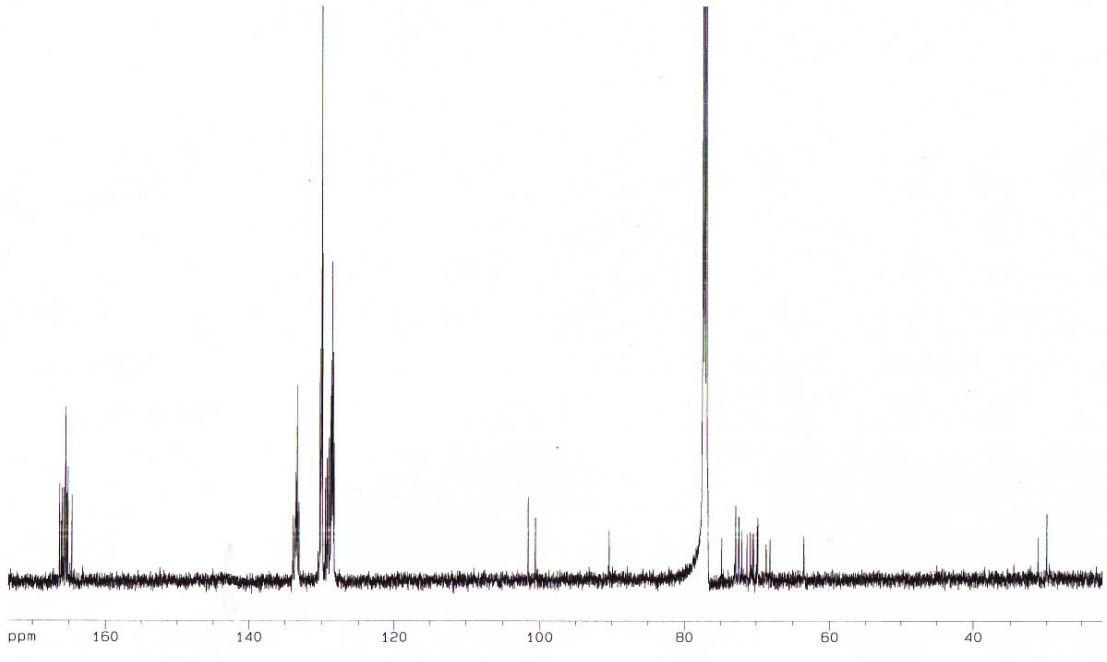
3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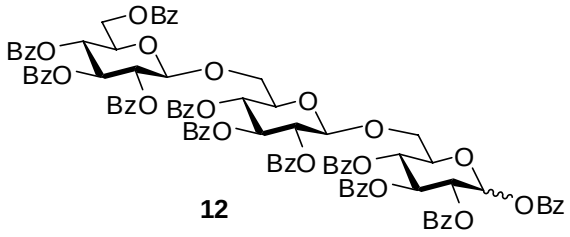
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BzO
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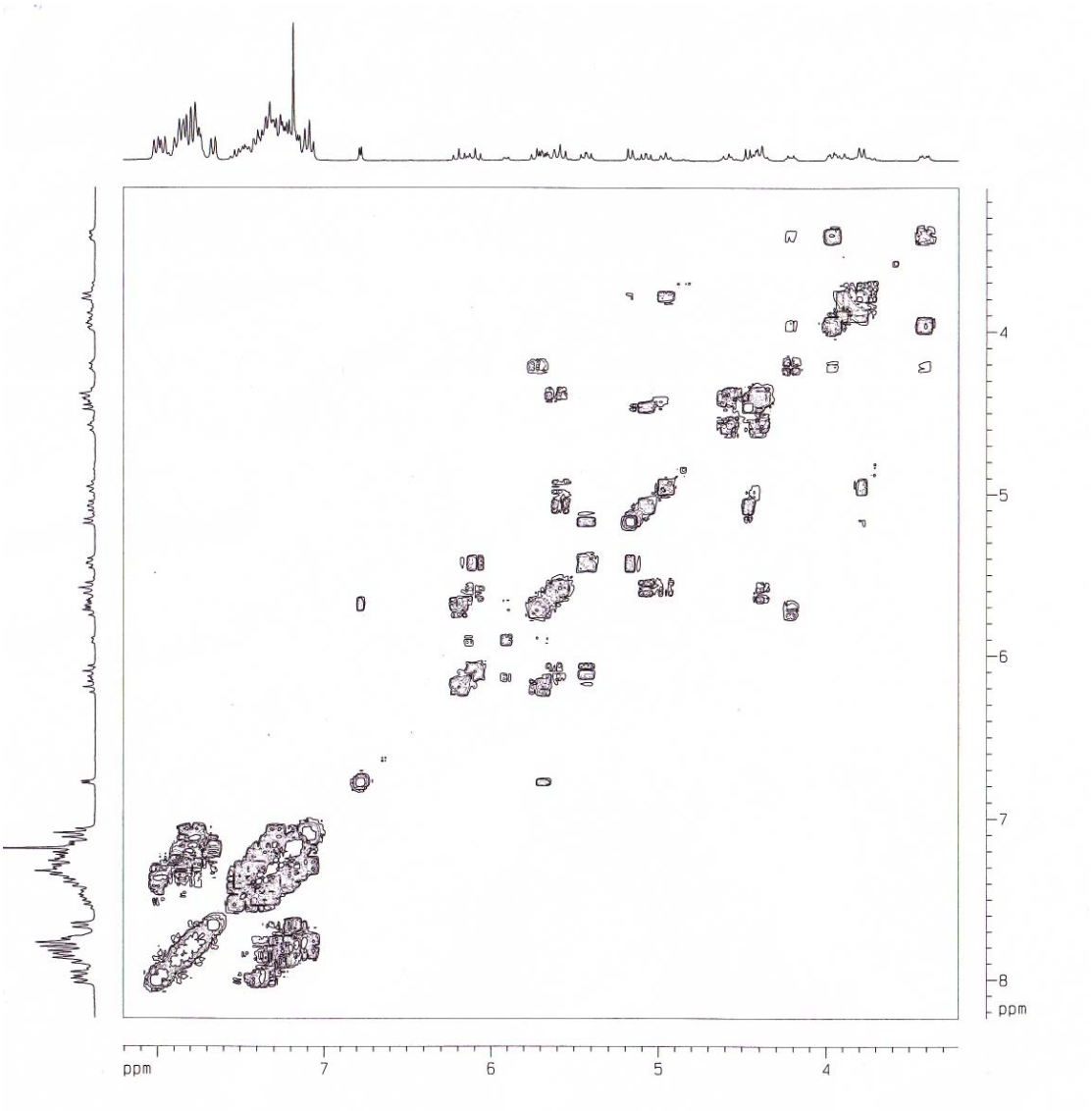
BzO
OBz
BzO

12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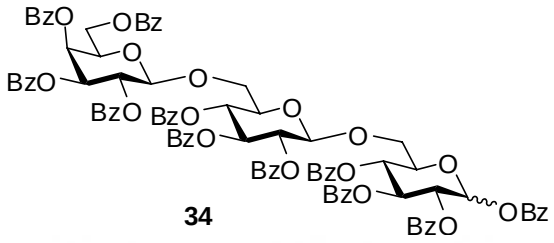
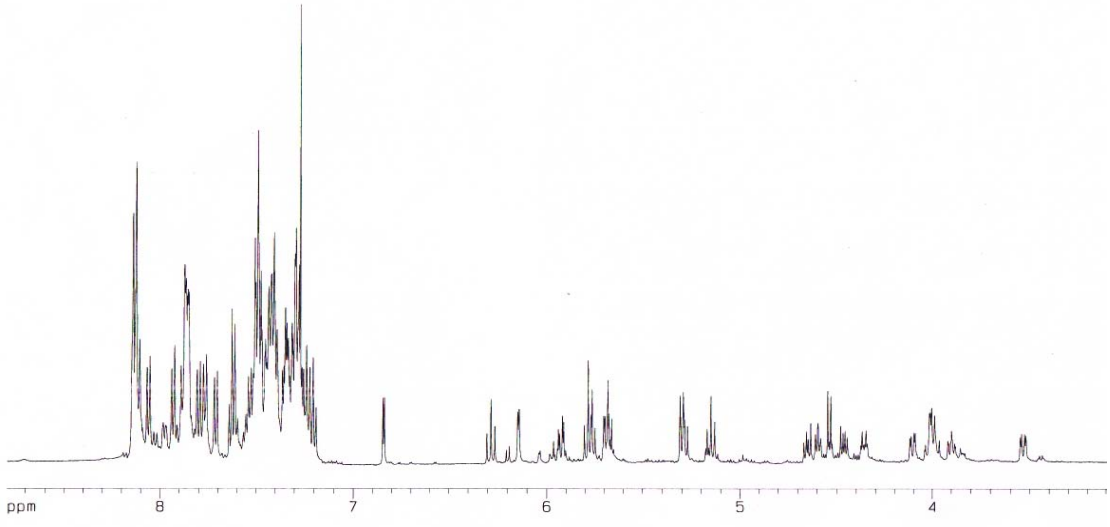
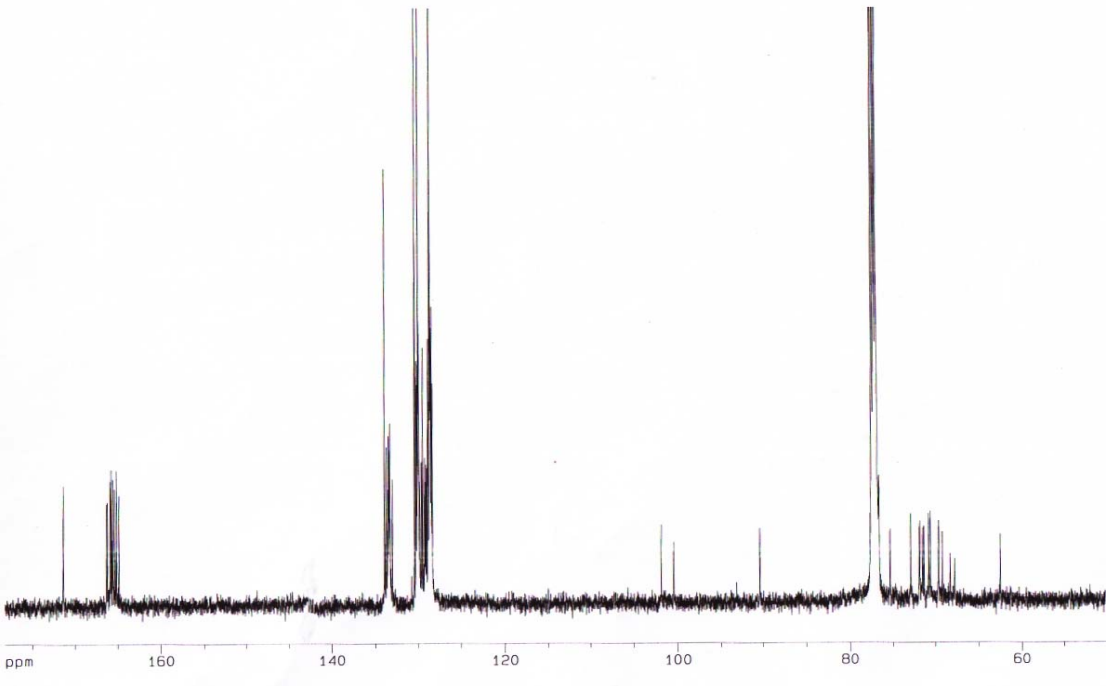
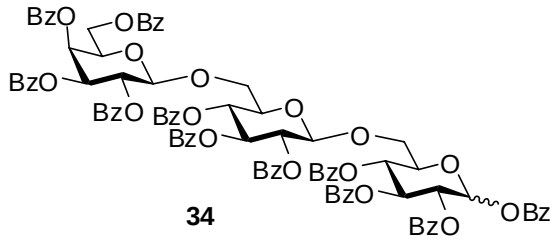
6
7
8
ppm
ppm
7
6
5
4



34



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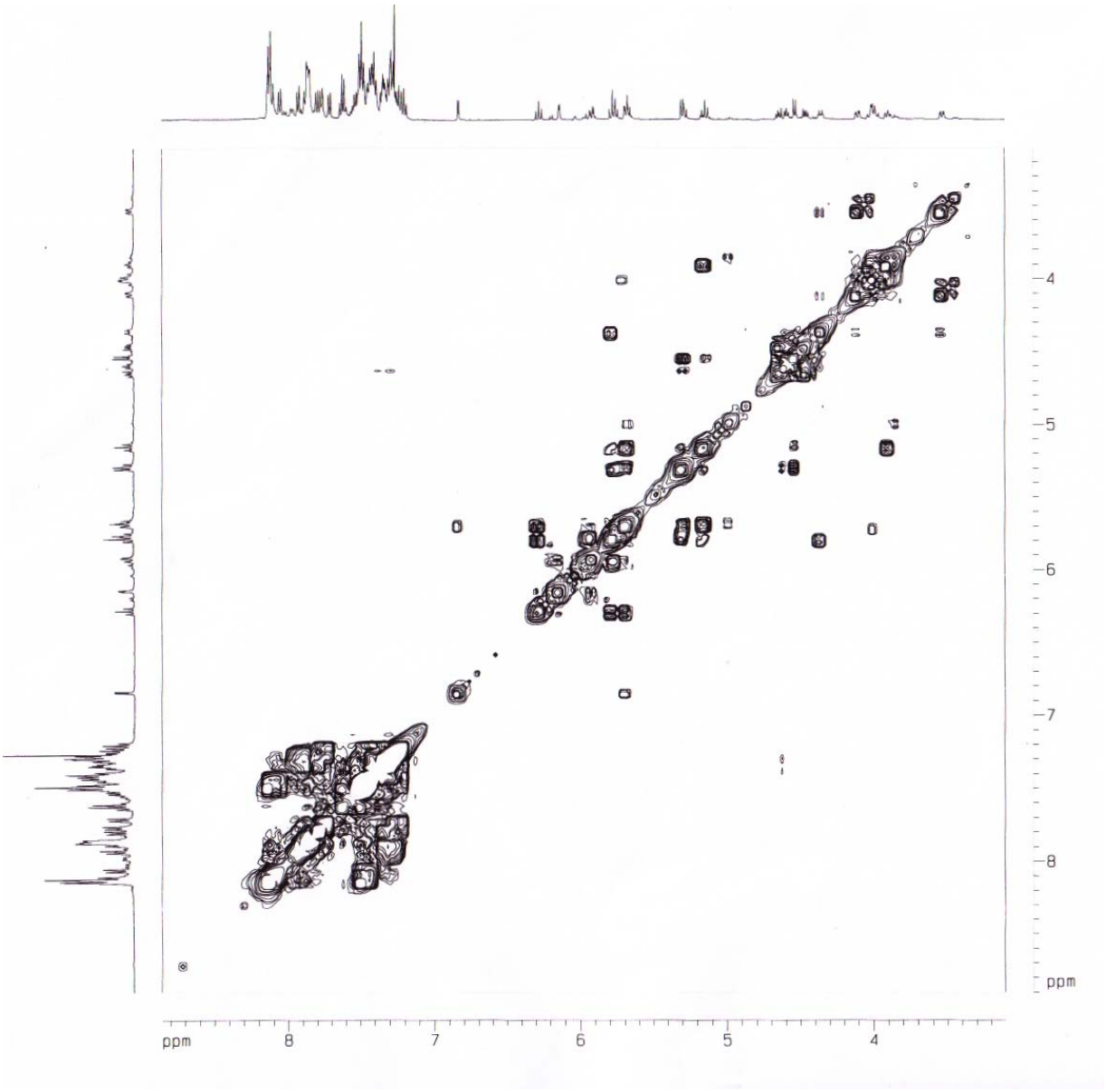
OBz
BzO

34


4
5
6
7
8
ppm
ppm
8
7
6
5
4

11. References

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