Supporting information

Silver(I) Tetrafluoroborate as a Potent Promoter for Chemical Glycosylation

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Contents:

General Methods. Column chromatography was performed on silica gel 60 (70-230 mesh), reactions were monitored by TLC on Kieselgel 60 F_{254}. The compounds were detected by examination under UV light and by charring with 10% sulfuric acid in methanol. Solvents were removed under reduced pressure at <40 ^{o}C. Dichloromethane and 1,2-dichloroethane were 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). 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. $AgBF_4$ was used as received. Optical rotations were measured at 'Jasco P-1020' polarimeter. ^{1}H-NMR spectra were recorded at 500MHz, ^{13}C-NMR spectra were recorded at 125MHz. HRMS determinations were made with the use of JEOL MStation (JMS-700) Mass Spectrometer.

Transformation of the STaz moiety into other leaving groups: synthesis of glycosyl donors

1-O-Acetyl-2,3,4,6-tetra-O-benzyl-D-glucopyranose (1). $Pd(OAc)_2$ (35 mg, 0.156 mmol) was added to a mixture of 2-thiazolinyl 2,3,4,6-tetra-O-benzyl-1-thio-β-D-glucopyranoside (**5a**, 50 mg, 0.078 mmol) and activated molecular sieves 3Å (150 mg) in dry $(ClCH_2)_2$ (0.5 mL). The reaction mixture was stirred under argon for 24 h at 55 °C. Upon completion, the solid was filtered-off and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate/ hexane gradient elution) to afford 1-O-acetate **1** as colorless syrup in 72% yield (α/β = 1.6/1). Analytical data for **1** were essentially the same as reported previously.[1]

2-Benzoxazolyl 2,3,4,6-tetra-O-benzyl-1-thio-β-D-glucopyranoside (3a). A mixture of **5a** (50 mg, 0.078 mmol) and activated molecular sieves 3Å (40 mg) in dry CH_2Cl_2 (1.2 mL) was stirred under argon for 1 h. Freshly prepared solution of Br_2 in dry CH_2Cl_2 (0.75 mL, 1/165, v/v) was then added dropwise over the period of 5 min at rt. Quantitative TLC estimates were made based on the accumulation of 2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl bromide **2a**. After that, the solvent was evaporated under the reduced pressure at rt. The residue containing crude **2a** was then treated dissolved in dry acetone (0.5 mL) and potassium salt (KSBox,[2] 22 mg, 0.117 mmol) and 18-crown-6 (4 mg, 0.012 mmol) were added. The reaction mixture was stirred under argon for 1 h at rt. After that, the mixture was diluted with CH_2Cl_2 (20 mL) and washed with water (10 mL), 1% aq. NaOH (10 mL) and water (3 x 10 mL), the organic phase was separated, dried, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/hexane gradient elution) to afford the title compound **3a** as a white foam in 82% yield. Analytical data for **3a** were essentially the same as reported previously.[2]

2-Benzothiazolyl 2,3,4,6-tetra-O-benzyl-1-thio-β-D-glucopyranoside (4a). Crude glycosyl bromide **2a** (~48 mg, 0.078 mmol), obtained as described for the synthesis of **3a**, was dissolved in dry acetone (0.5 mL) and potassium salt of 2-mercaptobenzotriazole[3] (24 mg, 0.117 mmol) and 18-crown-6 (4 mg, 0.012 mmol) were added. The reaction mixture was stirred under argon for 1 h at rt, then diluted with CH_2Cl_2 (20 mL) and washed with water (10 mL), 1% aq. NaOH (10 mL), and water (3 x 10 mL). The organic phase was separated, dried, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/hexane gradient elution) to afford the title compound **4a** as a white foam in 75% yield. Analytical data for **4a** were essentially the same as reported previously.[4]

Ethyl 2,3,4,6-tetra-O-benzyl-1-thio-β-D-glucopyranoside (6). A mixture of ethane thiol (17 μL, 0.225 mmol) and sodium hydride (1.0 mg, 0.025 mmol) was added to a solution of **2a** (~95 mg, 0.15 mmol), prepared as described for the synthesis of **3a**, in dry CH_2Cl_2 (1.0 mL) at 0 °C and the resulting mixture was stirred under argon for 1 h at rt. The reaction mixture was then diluted with CH_2Cl_2 (20 mL) and washed with water (10 mL), 20% aq. $NaHCO_3$ (10 mL), and water (3 x 10 mL), the organic phase was separated, dried, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/hexane gradient elution) to afford the title thioglycoside **6** as a white foam in 92% yield. Analytical data for **6** were essentially the same as reported previously.[5]

2,3,4,6-Tetra-O-benzyl-α-D-glucopyranosyl chloride (8). To a stirred solution of **5a** (100 mg, 0.15 mmol) and dimethylformamide (6 μL, 0.075 mmol) in dry CH_2Cl_2 (1.2 mL) under argon thionyl chloride (34 μL, 0.45 mmol) was added dropwise. The reaction mixture was kept for 1 h and then concentrated under the reduced pressure. The residue was purified by short-path silica gel column chromatography (ethyl acetate/hexane gradient elution) to afford the title compound **8** as a colorless syrup in 84% yield. Analytical data for **8** were essentially the same as reported previously.[6]

2,3,4,6-Tetra-O-benzyl-D-glucopyranosyl fluoride (9). To a stirred solution of **5a** (100 mg, 0.15 mmol) in THF (1.2 mL) diethylaminosulfur trifluoride (DAST, 72 μL, 0.55 mmol) was added at -30 °C under argon. The external cooling was then removed and the reaction mixture was stirred for 24 h at rt. After that, the solution was cooled to -30 °C and methanol (0.1 mL) was added, the resulting mixture was warmed to rt and the volatiles were evaporated off *in vacuo*. The residue was dissolved in CH_2Cl_2 (20 mL) and washed successively with water (10 mL), 20% aq. $NaHCO_3$ (10 mL), and water (3 x 10 mL). The

organic phase was separated, dried, and concentrated *in vacuo*. The residue was purified by short-path silica gel column chromatography (ethyl acetate/hexane gradient elution) to afford the title fluoride **9** as a white foam in 88% yield (α/β = 1/2.8). Analytical data for **9** were essentially the same as reported previously.[7,8]

2,3,4,6-Tetra-O-benzyl-D-glucopyranose (10). A solution of **5a** (65 mg, 0.10 mmol) and N-bromosuccinimide (45 mg, 0.20 mmol) in acetone/water (1.5 mL, 9/1, v/v) was stirred for 16 h at rt. The reaction mixture was then diluted with CH_2Cl_2 (20 mL) and washed with water (10 mL), 20% aq. $NaHCO_3$ (10 mL), and water (3 x 10 mL). The organic phase was separated, dried, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/hexane gradient elution) to afford the title hemiacetal **10** as a colorless syrup in 90% yield (α/β = 1/1). Analytical data for **10** were essentially the same as for the commercial sample.

2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl trichloroacetimidate (11). NaH (8 mg, 0.37 mmol) was added portionwise to a stirred solution of compound **10** (100 mg, 0.185 mmol) and trichloroacetonitrile (85 μL, 0.84 mmol) in dry CH_2Cl_2 (2 mL). After stirring for 3 h at rt, the reaction mixture was concentrated under the reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate/ hexane gradient elution) to afford the title compound **11** as a colorless syrup in 82% yield. Analytical data for **11** were essentially the same as reported previously.[9]

General Glycosylation Procedures: Synthesis of O-Glycosides and Oligosaccharides.

Method A – Activation with $AgBF_4$. (see the article)

*Method B – Activation of glycosyl donor **1** with $BF_3{\cdot}Et_2O$.* A mixture containing the glycosyl donor (0.11 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (3Å, 200 mg) in $(ClCH_2)_2$ (2mL) was stirred under argon for 1.5 h. $BF_3{\cdot}Et_2O$ (40 μL, 0.33 mmol) was added and the reaction mixture was stirred for 16 h at rt. It was then diluted with CH_2Cl_2, the solid was filtered-off and the residue was washed with CH_2Cl_2. The combined filtrate (30 mL) was washed with 20% aq. $NaHCO_3$ (10 mL) and water (3 x 10 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to afford a disaccharide derivative.

*Method C- Activation of **1** with $BF_3{\cdot}Et_2O/AgBF_4$.* A mixture of the glycosyl donor (0.11 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (3 Å, 200 mg) in $(ClCH_2)_2$ (2 mL) was stirred under argon for 1.5 h. $BF_3{\cdot}Et_2O$ (40 μL, 0.33 mmol) and $AgBF_4$ (10 mg, 0.05 mmol) were added and the reaction mixture was stirred for 5 h at rt. Upon completion, it was diluted with CH_2Cl_2, the solid was filtered-off and the residue was washed with CH_2Cl_2. The combined filtrate (30 mL) was washed with 20% aq. $NaHCO_3$ (10 mL) and water (3 x 10 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to afford a disaccharide derivative.

*Method D - Activation of **6** and **7** with NIS.* A mixture of the glycosyl donor (0.11 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (3 Å, 200 mg) in

$(ClCH_2)_2$ (2 mL) was stirred for 1.5 h under argon. NIS (50 mg, 0.22 mmol) was then added and the reaction mixture was stirred for 24 h at rt. Upon completion, the solid was filtered-off and the residue was washed with CH_2Cl_2. The combined filtrate (30 mL) was washed with 20% aq. $Na_2S_2O_3$ (10 mL) and 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 a disaccharide derivative.

*Method E - Activation of **6** and **7** with NIS/$AgBF_4$.* A mixture of the glycosyl donor (0.11 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (3 Å, 200 mg) in $(ClCH_2)_2$ (2 mL) was stirred for 1.5 h under argon. NIS (50 mg, 0.22 mmol) and $AgBF_4$ (10 mg, 0.05 mmol) were added and the reaction mixture was stirred for 10-20 min at rt. Upon completion, the solid was filtered-off and the residue was washed with CH_2Cl_2. The combined filtrate (30 mL) was washed with 20% aq. $Na_2S_2O_3$ (10 mL) and 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 a disaccharide derivative.

Pent-4-en-1-yl 2,3,4,6-tetra-O-benzyl-1-thio-β-D-glucopyranoside (7). The title compound was synthesized from glycosyl bromide **2a**, obtained as described for the synthesis of **3a**, and 4-penten-1-ol by Method A in 89% yield as a white foam. Analytical data for **7** were essentially the same as reported previously.[10]

Methyl 4-O-(2,3,4,6-tetra-O-benzyl-D-glucopyranosyl)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (16a). The title compound was obtained by Method A from **8** and **12**[11] in

91% yield (α/β = 1/3.4) or **11** and **12** in 65% yield (α/β = 1/5.4). Analytical data for **16a** were essentially the same as reported previously.[12]

Methyl 6-O-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (17a). The title compound was obtained by Method A from glycosyl donors **2a, 3a, 5a, 8, 9** or **11** and glycosyl acceptor **13** [13] in 92% (α/β = 2.4/1), 89% (α/β = 1.2/1), 95% (α/β = 1.3/1), 97% (α/β = 1.6/1), 81% (α/β = 2/1) or 80% (α/β = 1.5/1) yield, respectively. In addition, the title compound was obtained by Method B from **1** and **13** in 91% yield (α/β = 1.4/1), by Method C - from **1** and **13** in 95% yield (α/β = 2/1), by Method D - from **6** or **7** and **13** in 91% (α/β = 1.2/1) or 89% (α/β = 1/1), and by Method E - from **6** or **7** and **13** in 92% (α/β = 1.2/1) or 76% (α/β = 1.2/1), respectively. Analytical data for **17a** were essentially the same as reported previously.[14]

Methyl 2-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-3,4,6-tri-O-benzyl-α-D-glucopyranoside (17b). The title compound was obtained by Method A from **2b** and **14** [15] in 99% yield. Analytical data for **17b** were essentially the same as reported previously.[16]

Methyl 6-O-(3,4,6-tri-O-acetyl-2-O-benzyl-D-glucopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (17c). The title compound was obtained by Method A from **3c** or **5c** and **13** in 91% (α/β = 1.6/1) or 75% yield (α/β = 1.2/1), respectively. Analytical data for **17c** were essentially the same as reported previously.[17]

Methyl 2-O-(2,3,4,6-tetra-O-benzyl-D-glucopyranosyl)-3,4,6-tri-O-benzyl-α-D-glucopyranoside (18a). The title compound was obtained by Method A from **5a** and **14** in

92% yield (α/β = 1.4/1). Analytical data for **18a** were essentially the same as reported previously.[17]

Methyl 2-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-3,4,6-tri-O-benzyl-α-D-glucopyranoside (18b). This compound was obtained by Method A from **2b** and **14** in 82% yield. Analytical data for **19a** were essentially the same as reported previously.[17]

Methyl 2-O-benzyl-3-O-(2,3,4,6-tetra-O-benzyl-D-glucopyranosyl)-4,6-O-benzylidene-α-D-glucopyranoside (19a). This compound was obtained by Method A from **4a** or **9** and **15** [18] in 87% (α/β = 7.4/1) or 81% yield (α/β = 2.3/1), respectively. Analytical data for **19a** were essentially the same as reported previously.[19]

Pent-4-en-1-yl 3-O-(2,3,4,6-tetra-O-benzyl-D-glucopyranosyl)-4,6-O-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbamoyl)-β-D-galactopyranoside (21). This compound was obtained by Method A from **3a, 4a, 5a,** or **9** and **20**[20] in 86% (α/β = 1.1/1), 85% (α/β = 3.3/1), 83% (α/β = 1/1.2), or 65% yield (α/β = 1.6/1), respectively. Analytical data for **21** were essentially the same as reported previously.[17]

Ethyl 6-O-(2,3,4,6-tetra-O-benzyl-D-glycopyranosyl)-2,3,4-tri-O-benzyl-1-thio-β-D-glucopyranoside (23). This compound was obtained by Method A from **2a, 3a, 5a, 8** or **9** and **22**[21] in 84% (α/β = 1.6/1), 87% (α/β = 2/1), 89% (α/β = 2.4/1), 84% (α/β = 2.2/1) or 83% yield (α/β = 2.4/1), respectively. Analytical data for **23** were essentially the same as reported previously.[22]

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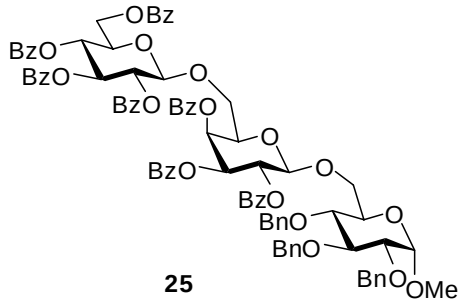
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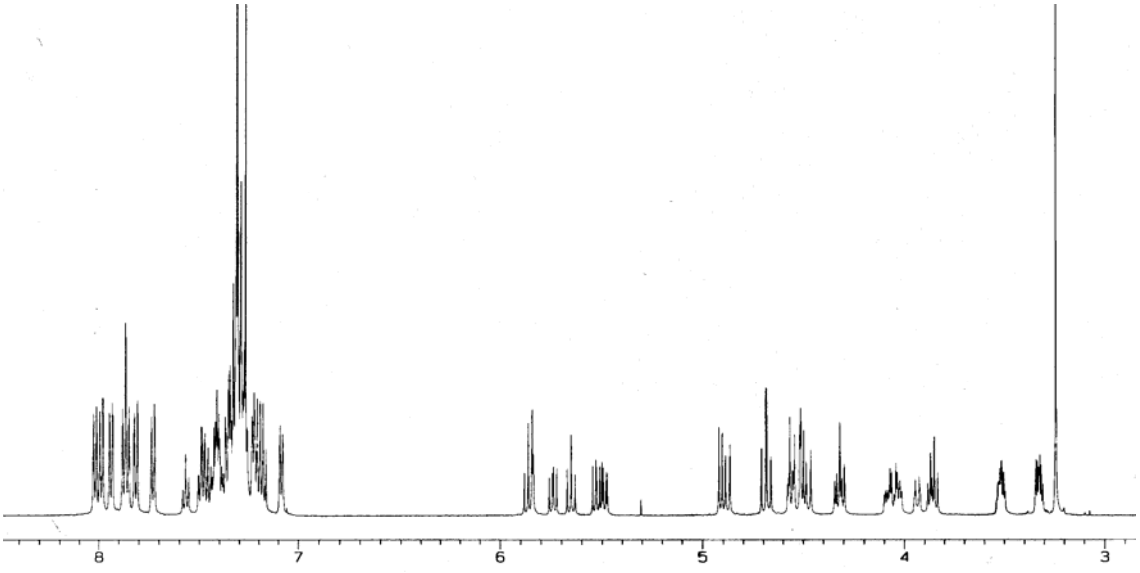
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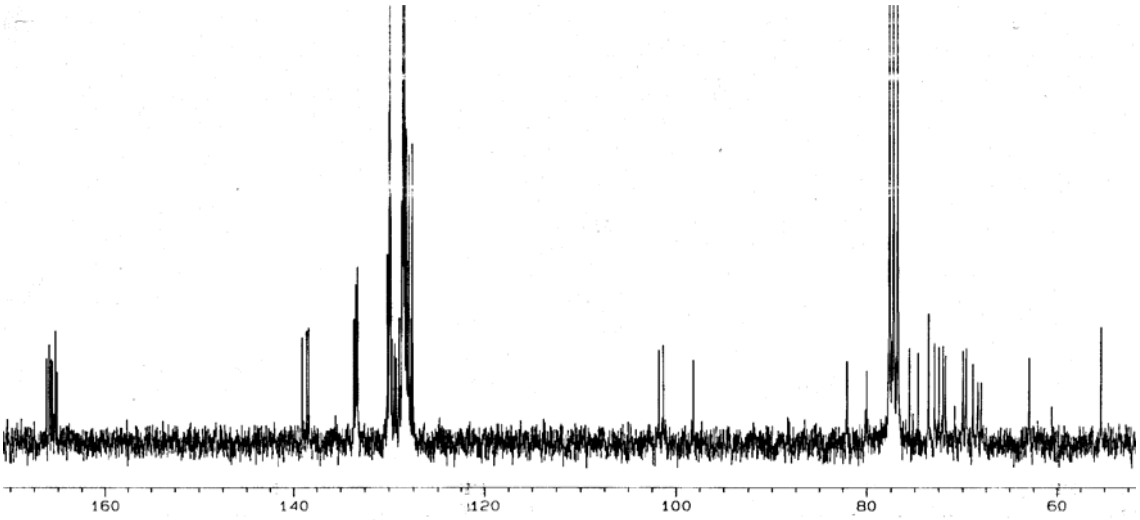
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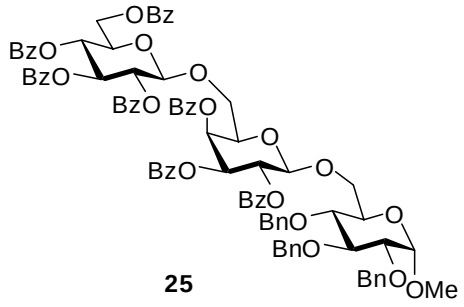

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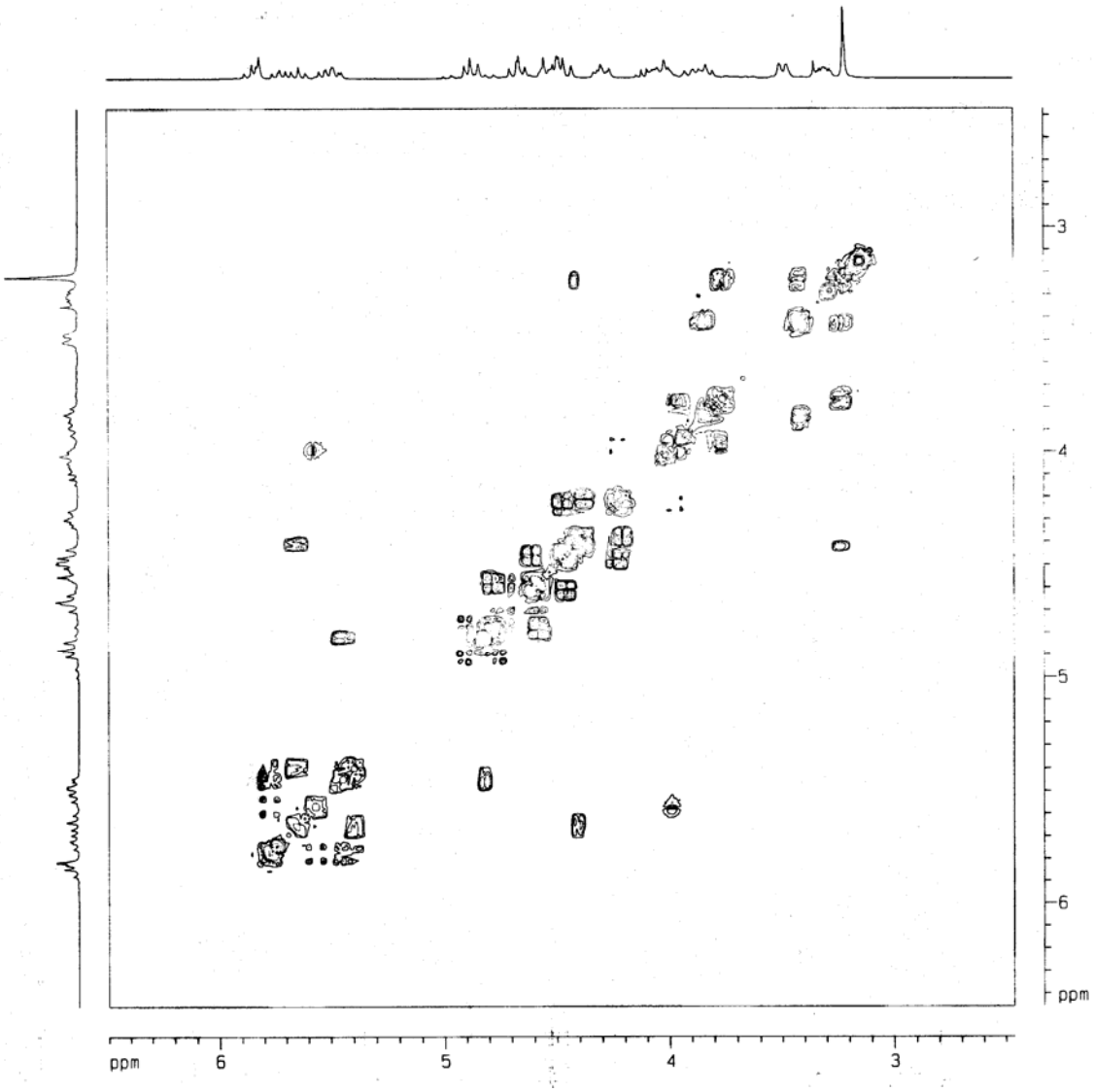

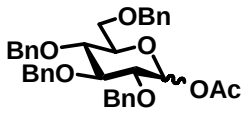
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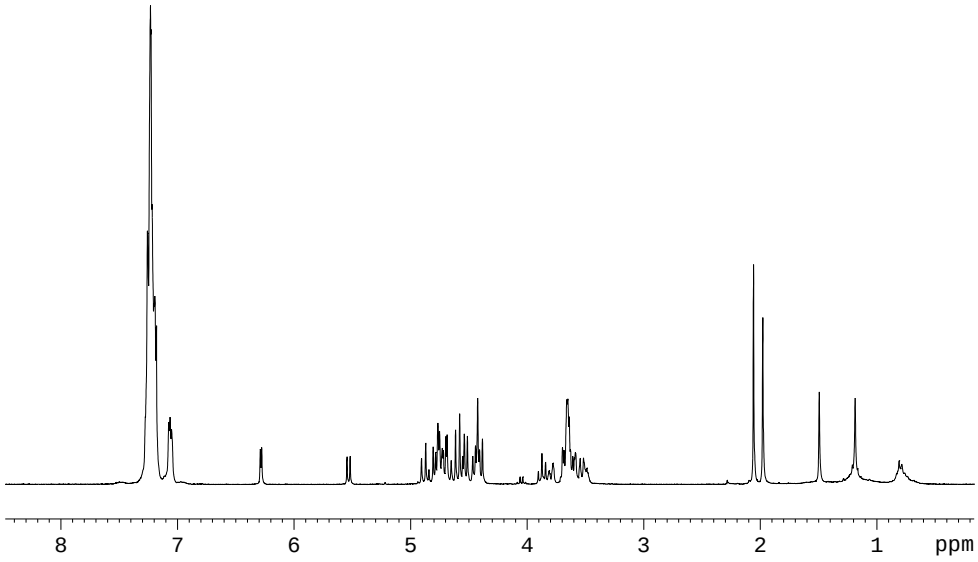
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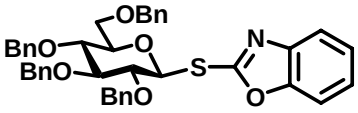
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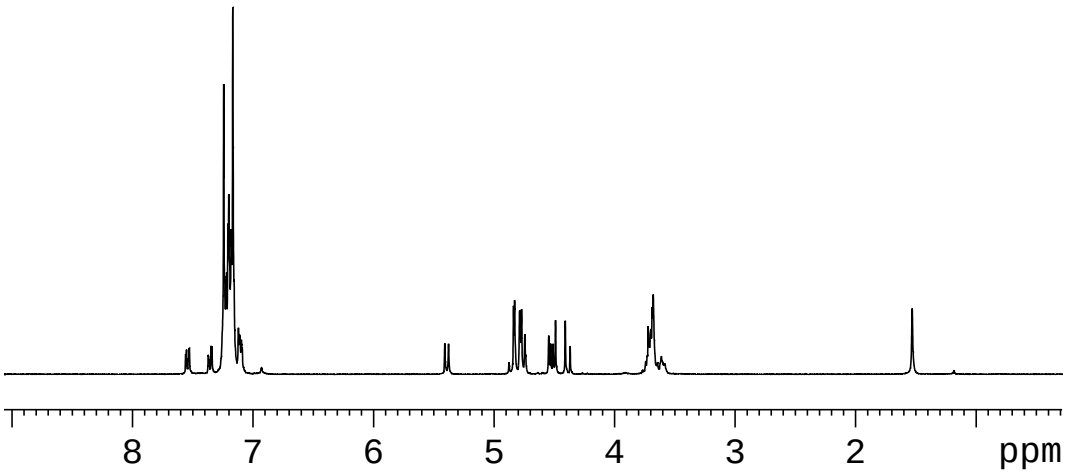
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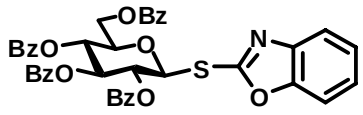

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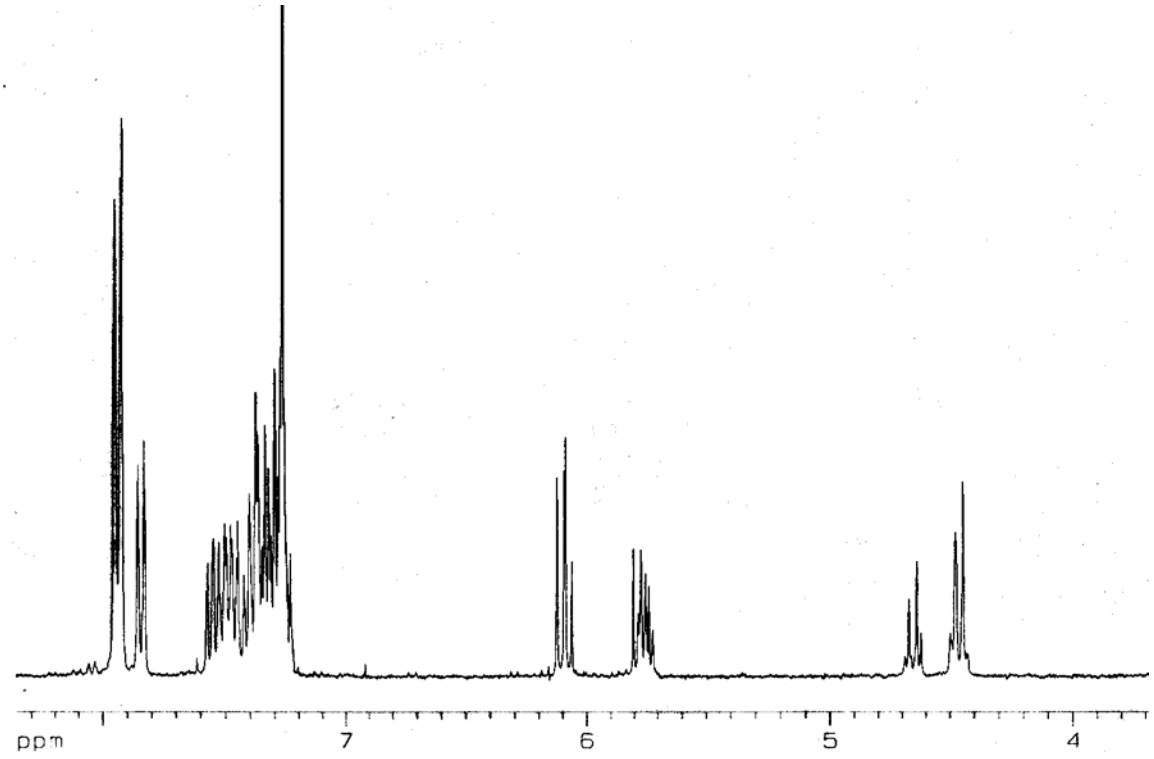

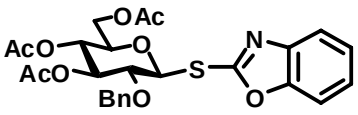

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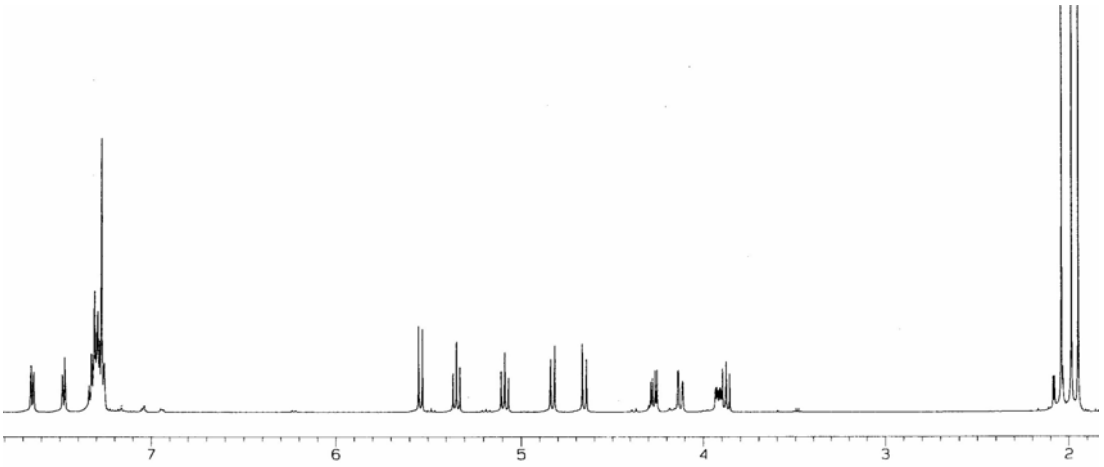

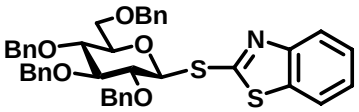
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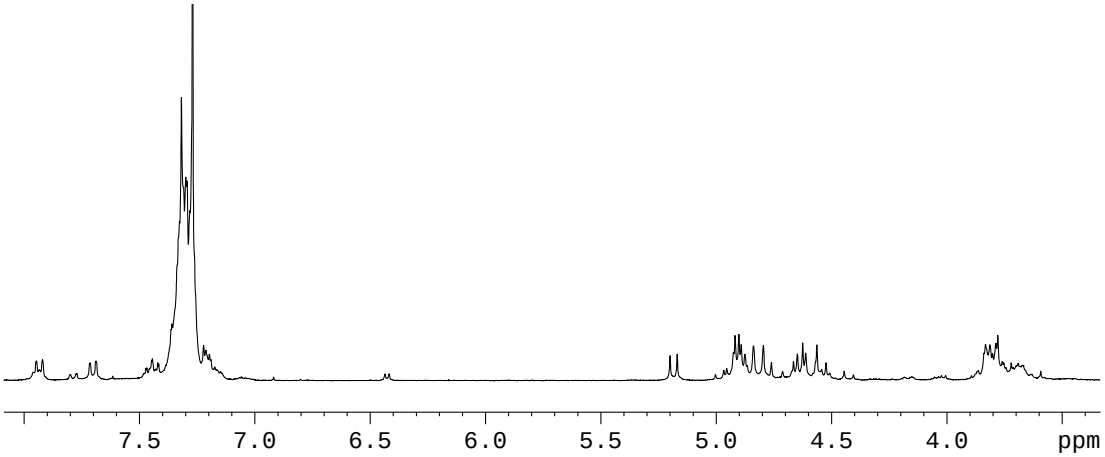
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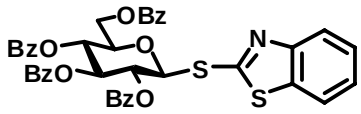
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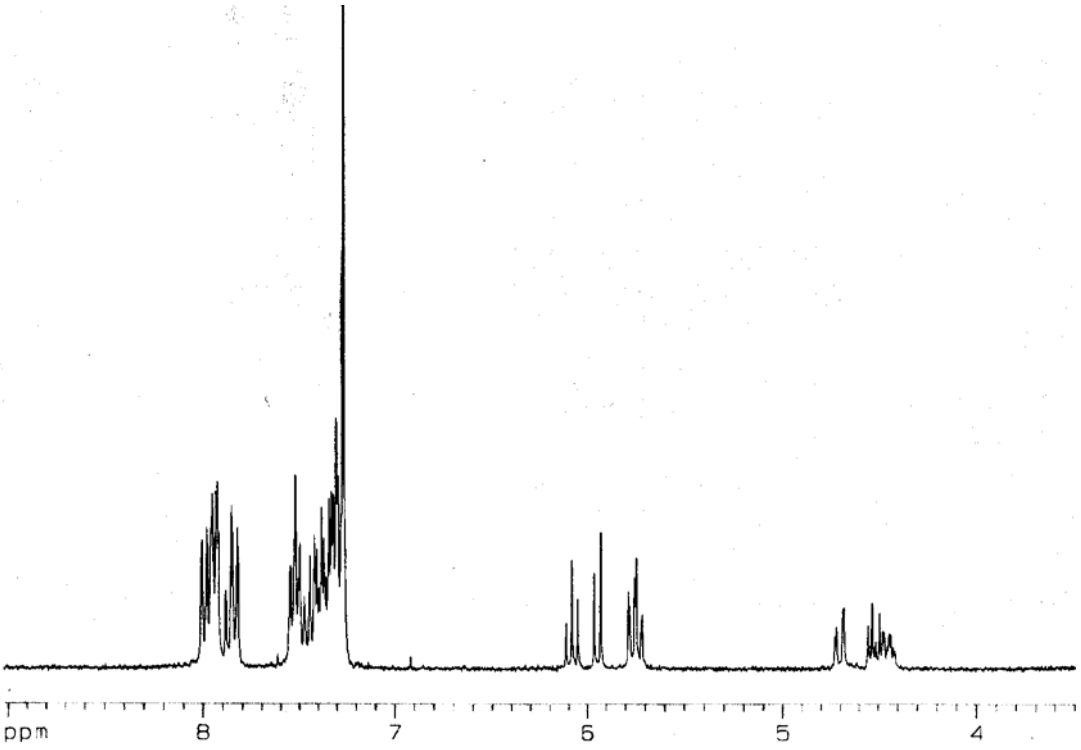
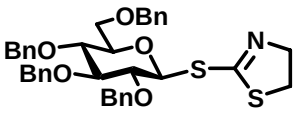
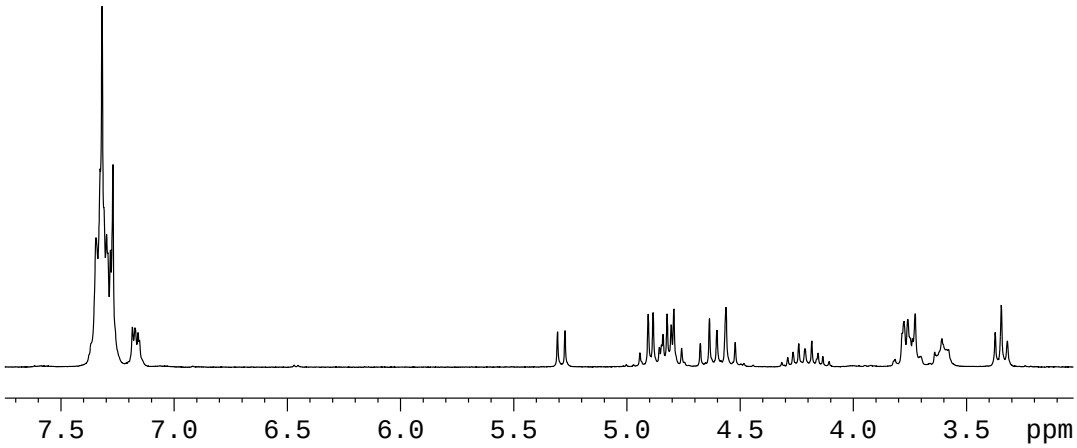
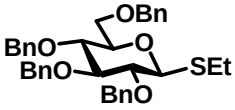
4b


ppm
8
7
6
5
4

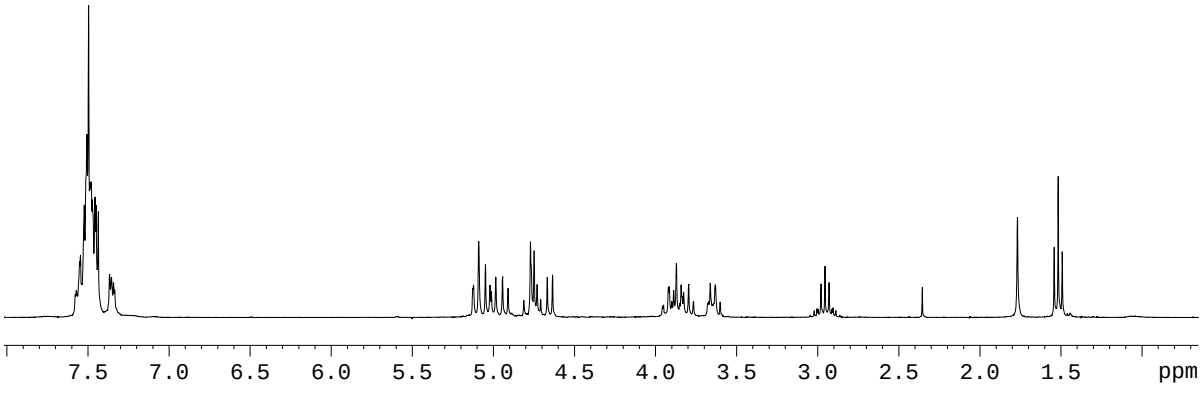

OBn
BnO
BnO
BnO
O
S
N
S

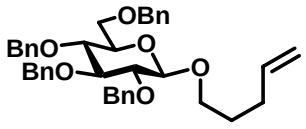
5a


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

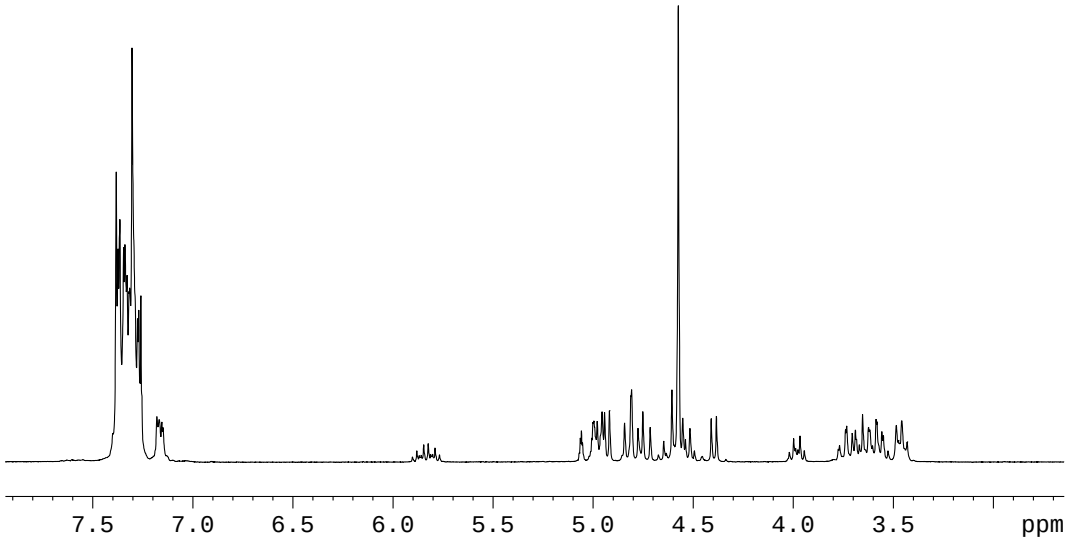

OBn
BnO
BnO
BnO
O
SEt

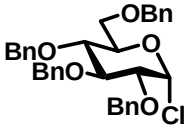
6


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

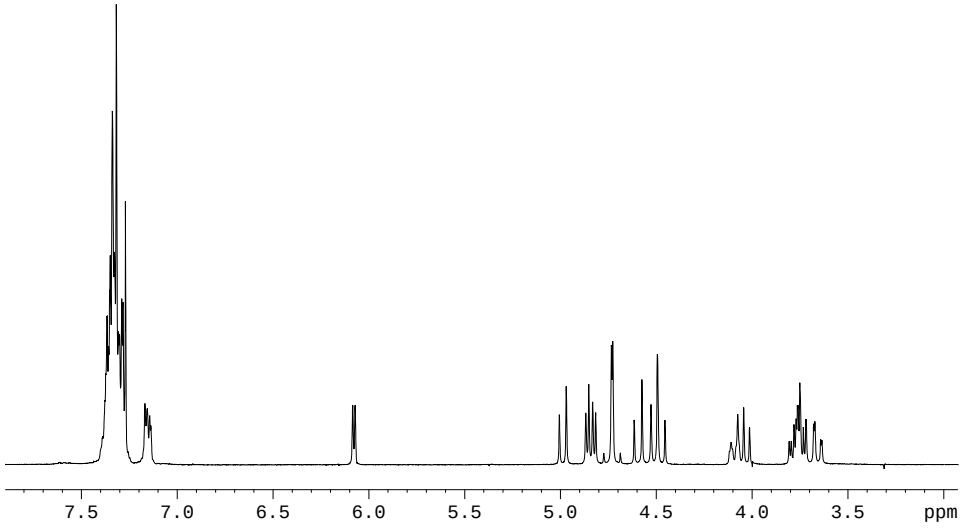

OBn
BnO
BnO
BnO
O
O

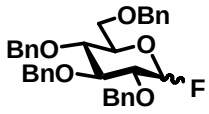
7


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

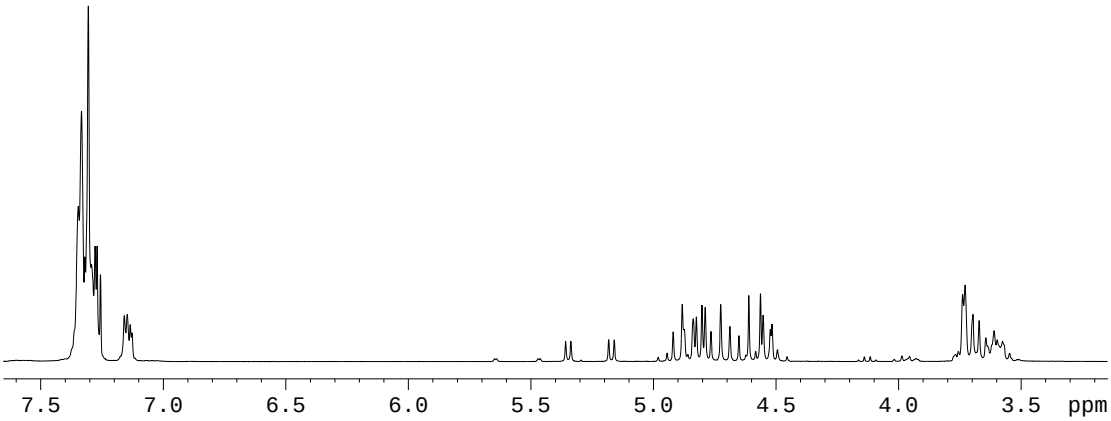

OBn
BnO
BnO
BnO
Cl
O

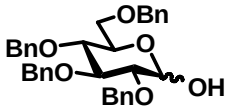
8


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

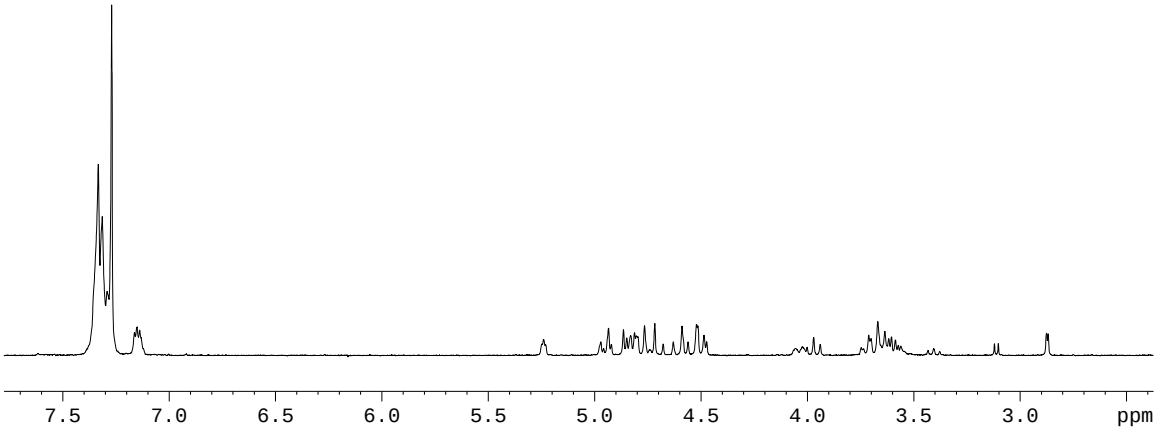

OBn
O
BnO
BnO
BnO
F

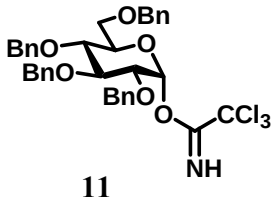
9


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

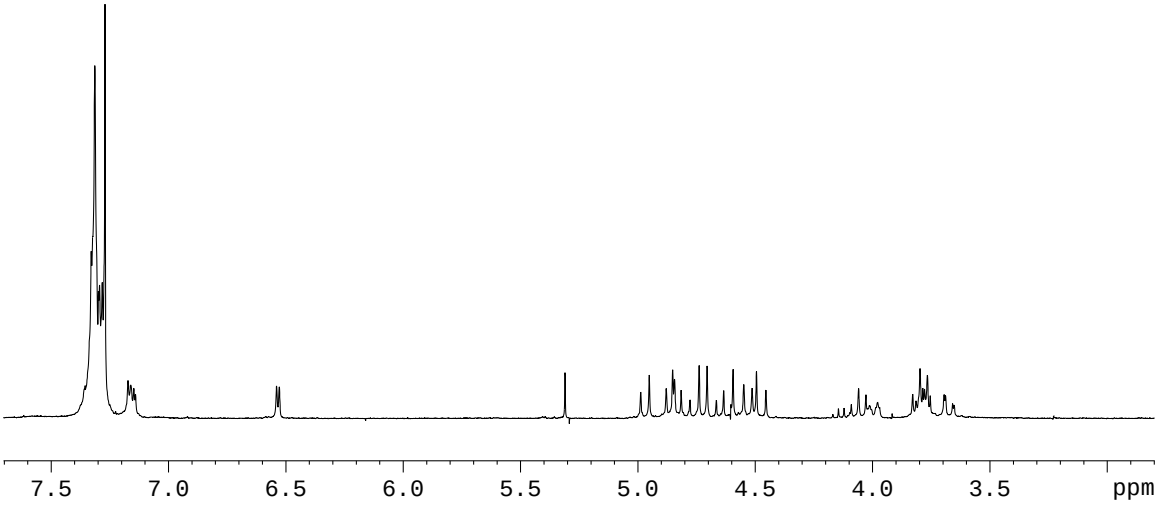

OBn
O
BnO
BnO
BnO
OH

10


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm


OBn
BnO
O
BnO
BnO
O
CCl3
NH

11


7.5
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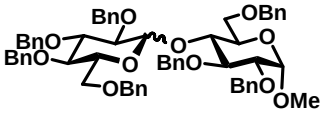
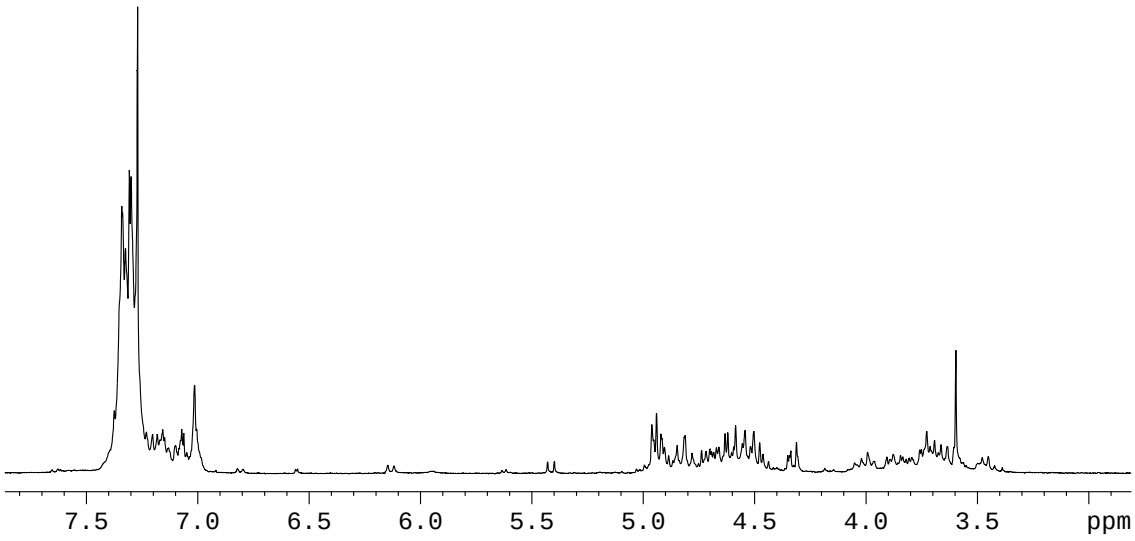
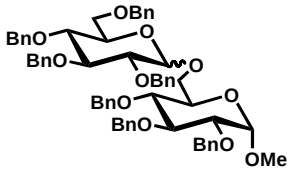
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

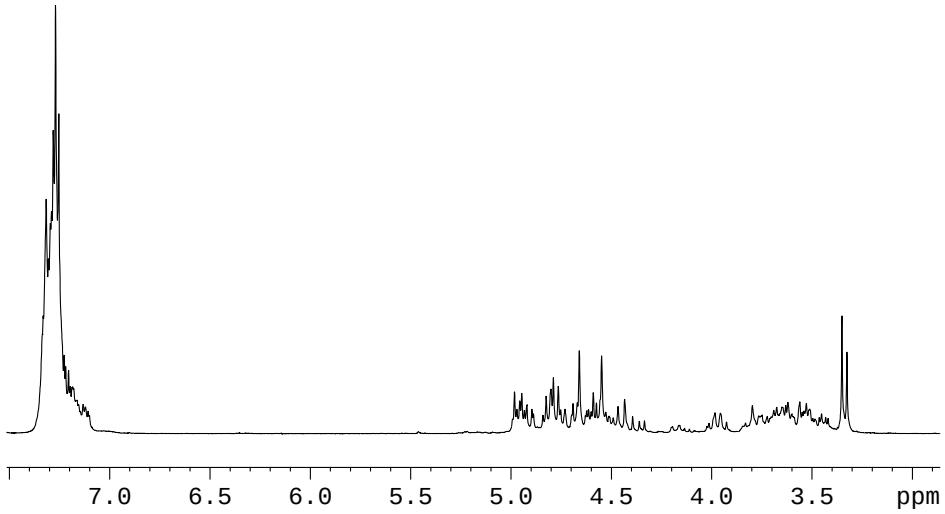

BnO
OBn
BnO
O
O
BnO
O
BnO
OBn
BnO
OMe

16a


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm


OBn
BnO
BnO
O
O
OBn
BnO
BnO
BnO
O
OMe

17a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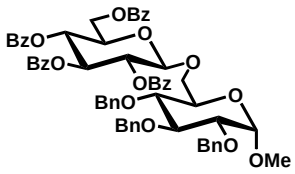
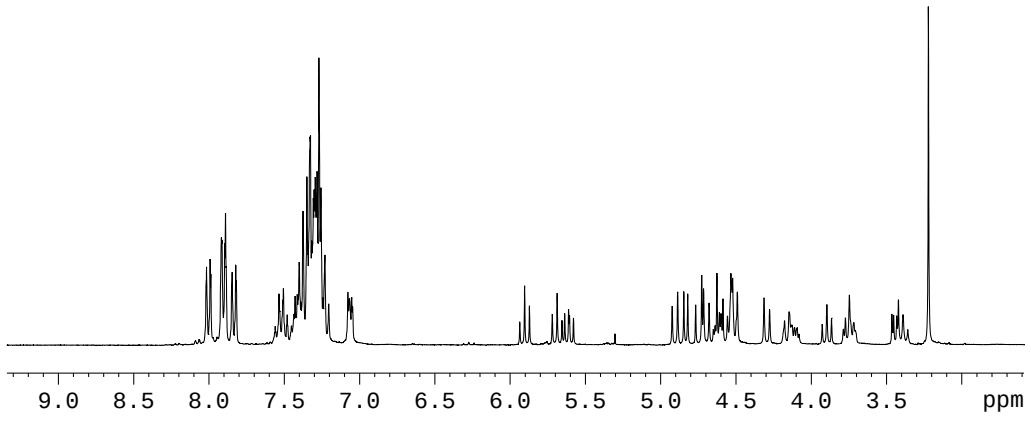
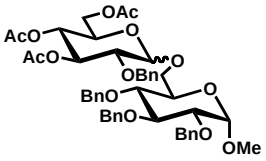
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

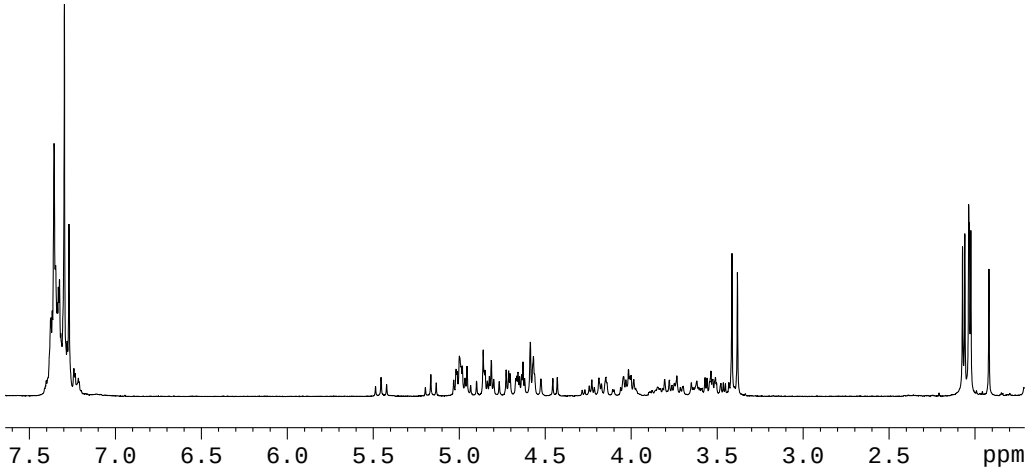

OBz
BzO
BzO
O
O
OBz
BnO
BnO
BnO
O
OMe

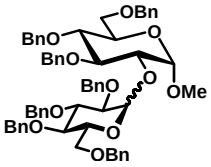
17b


9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

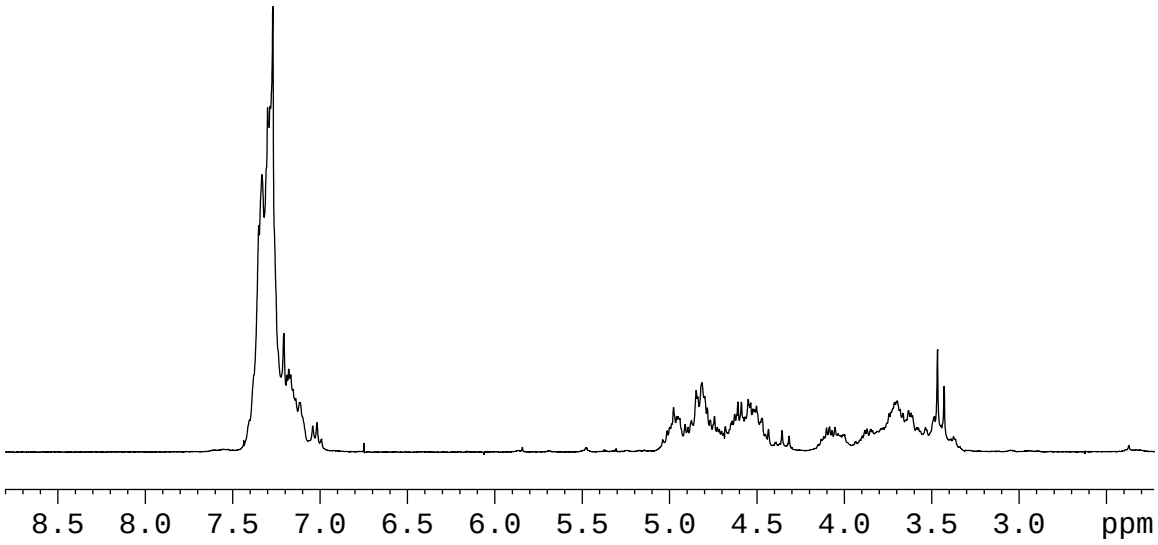

OAc
AcO
AcO
O
O
OBn
BnO
BnO
BnO
O
OMe

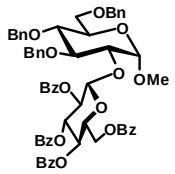
17c


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

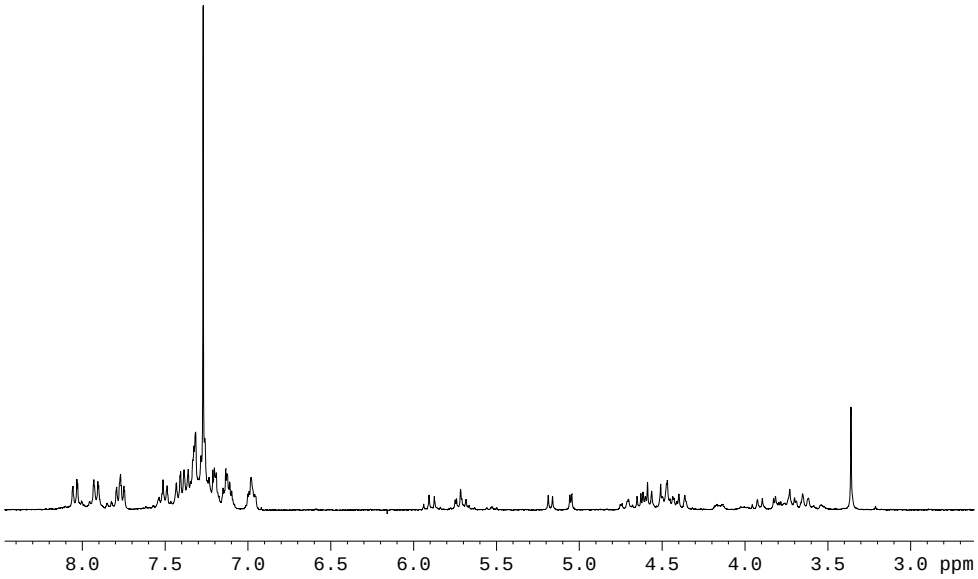

OBn
BnO
BnO
O
BnO
O
OMe
BnO
BnO
O
OBn

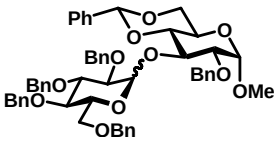
18a


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

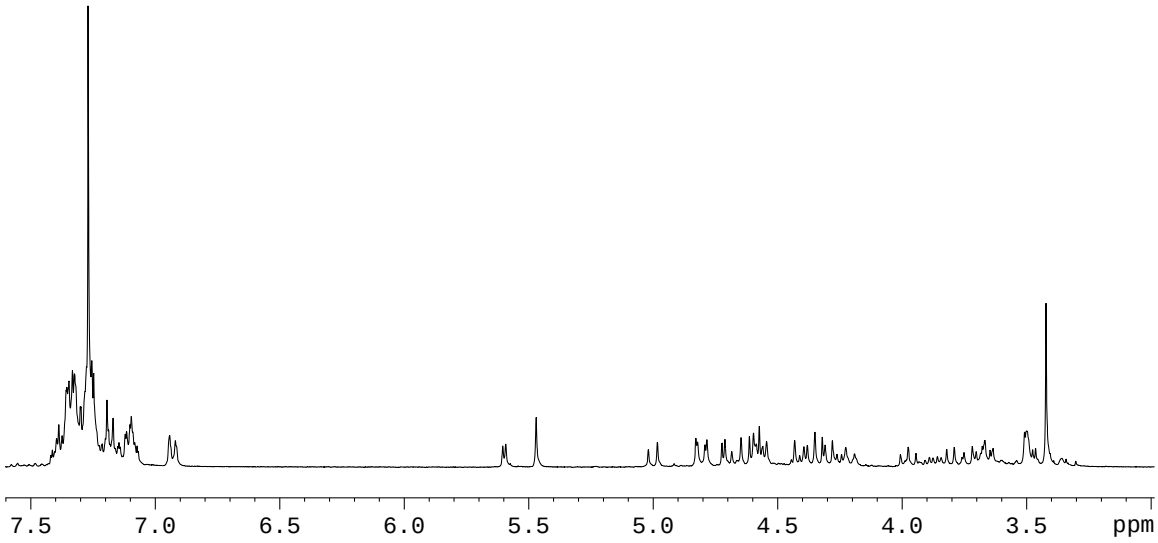

OBn
BnO
BnO
O
OMe
BzO
O
OBz
BzO
BzO

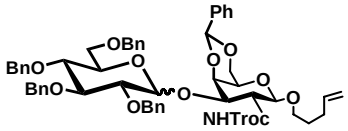
18b


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

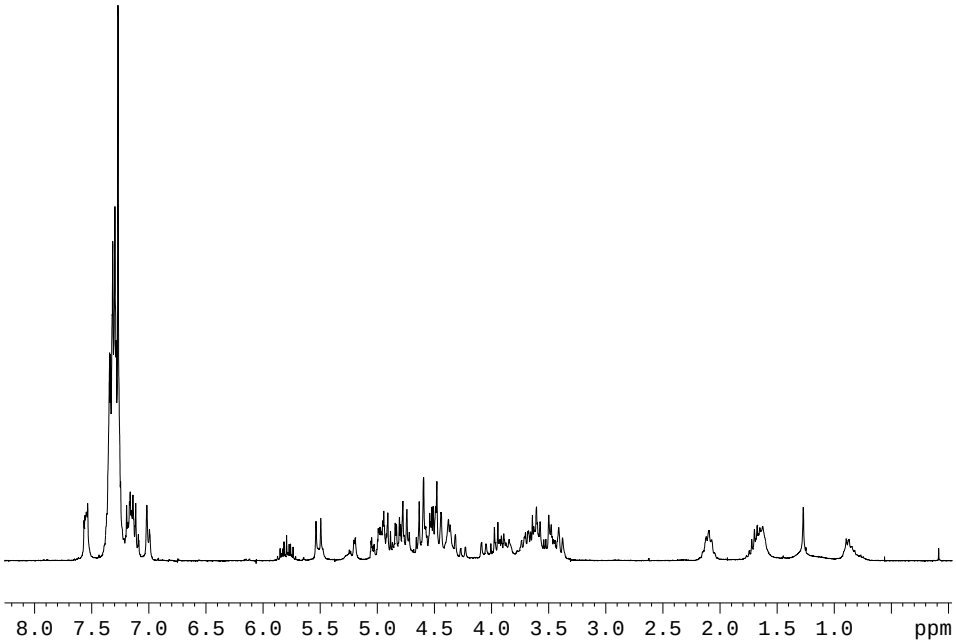

Ph
O
O
O
BnO
O
BnO
OMe
BnO
BnO
O
OBn

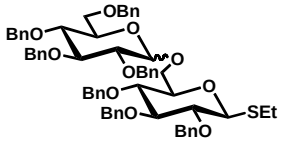
19a


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

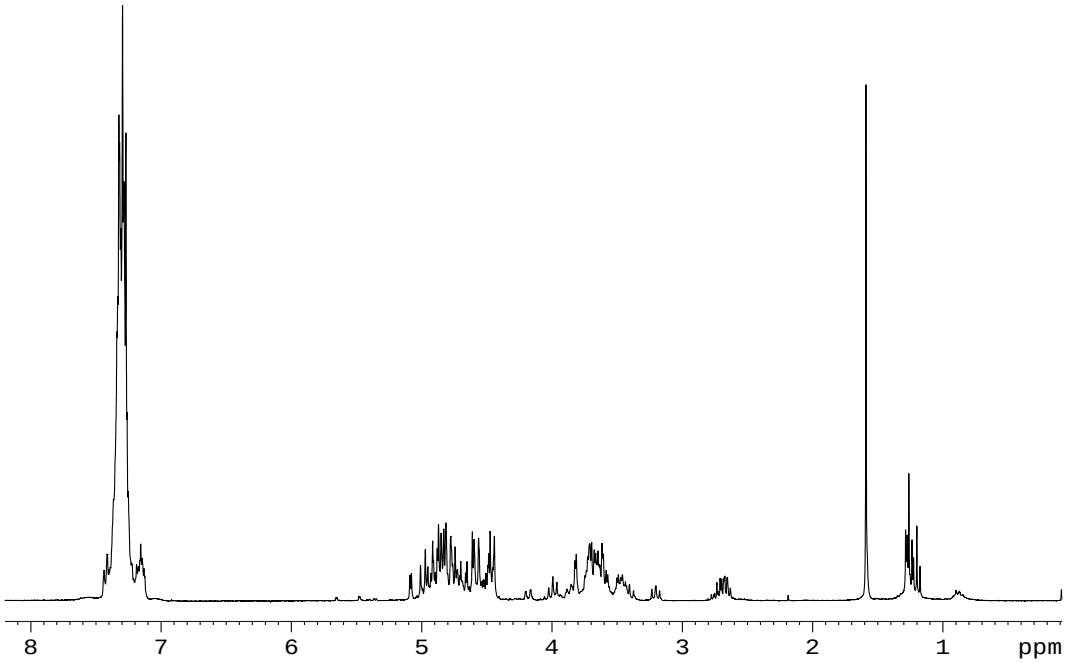

Ph
OBn
BnO
BnO
OBn
NHTroc

21


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


OBn
BnO
BnO
OBn
BnO
BnO
BnO
SEt

23


8 7 6 5 4 3 2 1 ppm