Supporting information

How the Arming Participating Moieties can Broaden the Scope of Chemoselective Oligosaccharide Synthesis by Allowing the Inverse Armed-Disarmed Approach

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Content:

General. 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. CH_2Cl_2, $ClCH_2CH_2Cl$, CH_3CN, toluene 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 (3 Å). 1,4-Dioxane and acetone were dried and stored over molecular sieves 3 Å and K_2CO_3, respectively. Anhydrous DMF was used as is. Molecular sieves (3 Å or 4 Å), 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. AgOTf was co-evaporated with toluene (3 x 10 mL) and dried *in vacuo* for 2-3 h directly prior to application. $Cu(OTf)_2$ was dried *in vacuo* during 2-3 h prior to application. Optical rotations were measured at 'Jasco P-1020' polarimeter. Unless noted otherwise, ^{1}H-n.m.r. spectra were recorded in $CDCl_3$ at 300 or 500 MHz, ^{13}C-NMR spectra were recorded in $CDCl_3$ at 75 or 125 MHz.

Additional experimental procedures

3,4,6-Tri-*O*-benzyl-1,2-*O*-(1-thioethyl)ethylidene-α-D-glucopyranose (2a). To a stirred solution of 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-thioethyl)ethylidene-α-D-glucopyranose[1,2] (**1a**, 3.0 g, 7.65 mmol) in methanol (25 mL) NaOMe (41 mg, 0.765 mmol) was added and the reaction mixture was stirred under argon for 1 h at rt. The volatiles were then evaporated off, the residue was co-evaporated with dry CH_2Cl_2 (3 x 10 mL) and dried *in vacuo*. The resulting solid was dissolved in dry DMF (18 mL) and benzyl bromide (4.6 mL, 38.2 mmol) was added. The resulting solution was added dropwise to a stirred solution of NaH (60 % in mineral oil, 1.84 g, 45.9 mmol) in DMF (25 mL) at –30 ^oC over 15 min. The stirred reaction mixture was then allowed to warm to rt over 16 h. Upon completion, the reaction was poured on crushed ice (5 g) and stirred until cessation of H_2 evolution. The mixture was then extracted with ethyl acetate/diethyl ether (1/1, v/v, 3 x 50 mL) and the combined organic layer was washed with water (3 x 40 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 /toluene gradient elution) to afford the title compound as colorless syrup (3.65 g, 89%). Analytical data for **2a**: R_f = 0.44 (ethyl acetate-hexane, 1/4, v/v); $[\alpha]_D^{24}$ = +17.6 (c = 1, $CHCl_3$); ^{1}H-n.m.r: δ, 1.26 (t, 3H, SCH_2CH_3), 1.88 (s, 3H, CCH_3), 2.58 (q, 2H, SCH_2CH_3), 3.60 (m, 2H, H-6a, 6b), 3.67 (dd, 1H, $J_{4,5}$ = 9.4 Hz, H-4), 3.78 (m, 1H, H-5), 3.88 (dd, 1H, $J_{3,4}$ = 3.1 Hz, H-3), 4.28-4.68 (m, 7H, $J_{2,3}$ = 3.1 Hz, H-2, 3 x CH_2Ph), 5.74 (d, 1H, $J_{1,2}$ = 5.4 Hz, H-1), 7.10-7.34 (m, 15H, aromatic) ppm; ^{13}C-n.m.r.: δ, 15.4, 25.1, 28.1, 69.3, 70.3, 7.0, 72.7, 73.6, 74.8, 75.3, 77.2, 98.4, 115.9, 127.8, 128.0, 128.1, 128.1, 128.2, 128.2, 128.2, 128.2, 128.2, 128.5, 128.5, 128.6, 128.6,

128.7, 128.7, 137.8, 138.0, 138.3 ppm; HR-FAB MS $[M+H]^+$ calcd for $C_{31}H_{37}O_6S$ 537.2311, found 537.2317.

Ethyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (3). A mixture of **2a** (5.64 g, 8.87 mmol), mercaptoethanol (0.644 mL, 8.868 mmol), and freshly activated molecular sieves (4Å, 6.1 g) in CH_2Cl_2 (200 mL) was stirred under argon for 45 min at rt. TMSOTf (0.154 mL, 0.8868 mmol) was added and the reaction mixture was stirred for 1.5 h at rt. Upon completion, the reaction was quenched with Et_3N (0.5 mL), solid was filtered off and the filtrate was diluted with CH_2Cl_2 (200 mL) and washed water (2 x 100 mL). The organic layer was separated, dried with $MgSO_4$, filtered and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate-toluene gradient elution) to afford the title compound as white solids (4.9 g, 87%). The spectroscopic and analytical data for **3** were in good agreement with those reported previously.[1]

Ethyl 3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (4). To a solution of **3** (4.65 g, 8.68 mmol) in dry methanol (200 mL), NaOMe (240 mg, 4.34 mmol) was added. The reaction mixture was stirred for 40 h at rt. The reaction was then neutralized with Dowex (H^+), filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate-hexane gradient elution) to yield the title compound as colorless syrup (3.67 g, 86%). The spectroscopic and analytical data for **4** were in good agreement with those reported previously.[1]

Thiazolinyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (14a). A mixture of **2a** (7.50 g, 14.1 mmol), 2-mercaptothiazoline (13.44 g, 0.113 mol), and freshly activated molecular sieves (4Å, 8.25 g) in CH_2Cl_2 (200 mL) was stirred under argon for 45 min at rt. TMSOTf (0.63 mL, 3.52 mmol) was added and the reaction mixture was stirred for 2 h at rt. Upon completion, the reaction was quenched with Et_3N (2 mL), solid was filtered off and the filtrate was washed with 1 % aq. NaOH (3 x 80 mL) and water (3 x 50 mL). The organic layer was separated, dried with $MgSO_4$, filtered and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate-toluene gradient elution) to afford the title compound as white amorphous solid (7.54 g, 90%). Analytical data for **14a**: R_f = 0.23 (ethyl acetate-hexane, 3/7, v/v); $[\alpha]_D^{24}$ = +24.0^o (c = 1, $CHCl_3$); ^{1}H-n.m.r: δ, 1.95 (s, 3H, $COCH_3$), 3.34 (t, 2H, CH_2S), 3.58 (m, 1H, H-5), 3.67-3.82 (m, 4H, H-3, 4, 6a, 6b), 4.18 (m, 2H, CH_2N), 4.50-4.84 (m, 6H, C*H*$_2$Ph), 5.12 (dd, 1H, $J_{2,3}$ = 8.7 Hz, H-2), 5.31 (d, 1H, $J_{1,2}$ = 10.4 Hz, H-1), 7.12-7.36 (m, 15H, aromatic) ppm; ^{13}C-n.m.r.: δ, 21.1, 35.3, 64.4, 68.6, 71.6, 73.6, 75.3, 75.5, 77.7, 79.9, 83.5, 84.5, 127.8, 128.0, 128.0, 128.1, 128.5, 128.6, 128.6, 138.1, 138.3, 138.3, 163.7, 169.8 ppm; HR-FAB MS $[M+H]^+$ calcd for $C_{32}H_{36}NO_6S_2$ 594.1984, found 594.1991.

Thiazolinyl 3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (15a). A solution of NaOMe in MeOH (0.1 M, 11.1 mL, 1.11 mmol of MeONa) was added to a stirred suspension of **14a** (6.65 g, 11.1 mmol) in dry methanol (185 mL) and the reaction mixture was stirred for 40 h at rt. The reaction was then neutralized with Dowex (H^+), filtered, and concentrated in vacuo. The residue **15a** was purified by column chromatography on silica gel (ethyl acetate-hexane gradient elution) to yield the title compound as colorless syrup (5.87 g, 95%). Analytical data for **15a**: R_f = 0.38 (ethyl acetate/hexane, 1/1, v/v); $[\alpha]_D^{24}$ = +18.4 (c = 1, $CHCl_3$); ^{1}H-n.m.r.: δ, 3.31 (t, 2H, SCH_2),

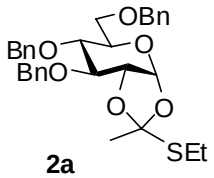
3.49-3.75 (m, 6H, H-2, 3, 4, 5, 6a, 6b), 4.14 (m, 2H, CH_2N), 4.45-4.94 (m, 6H, C*H*$_2$Ph), 5.13 (d, 1H, $J_{1,2}$ = 9.5 Hz, H-1), 7.09-7.33 (m, 15H, aromatic) ppm; ^{13}C-n.m.r.: δ, 35.7, 64.1, 68.8, 73.7, 75.0, 75.2, 75.6, 77.1, 80.1, 85.6, 86.7, 127.8, 128.0, 128.1, 128.1, 128.2, 128.5, 128.6, 128.7, 138.3, 138.3, 138.8, 165.5 ppm; HR-FAB MS $[M+H]^+$ calcd for $C_{30}H_{34}NO_5S_2$ 552.1878, found 552.1871.

3,4,6-Tri-*O*-benzyl-2-*O*-picolyl-α/β-D-glucopyranose (30). To a suspension of the **8** or **16a** (0.171 mmol) in wet CH_2Cl_2 (0.75 mL) the promoter was added: DMTST (0.359 mmol for **8**) or $Cu(OTf)_2$ (0.428 mmol for **16a**) and the reaction mixture was stirred for 20 h at 42 °C. The reaction was quenched with TEA, stirred for 30 min, and 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 water (4 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 yield the title compound as colorless syrup (81-85%, α/β = 4/1). Analytical data for α-**30**: R_f = 0.10 (ethyl acetate-hexane, 35/65, v/v); ^{1}H-n.m.r.: δ, 3.38-3.51 (m, 1H, H-4), 3.54-3.68 (m, 4H, H-2, 3, 5, 6a), 4.02 (dd, 1H, H-6b), 4.37-4.57 (m, 4H, C*H*$_2$Ph), 4.76-5.05 (m, 4H, C*H*$_2$Ph), 5.35 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1), 6.95-7.30 (m, 17H, aromatic), 7.57 (m, 1H, aromatic), 8.52 (d, 1H, aromatic) ppm; ^{13}C-n.m.r.; δ, 68.9, 69.1, 70.4, 72.9, 73.5, 73.6, 73.7, 75.1, 75.1, 75.8, 78.5, 81.5, 81.9, 84.2, 85.7, 90.8, 97.2, 121.6, 122.1, 122.9, 122.9, 127.7, 127.7, 127.8, 127.9, 128.0, 128.1, 128.1, 128.5, 128.6, 137.3, 137.5, 138.2, 138.3, 138.3, 138.5, 138.8, 139.1, 148.5, 149.0, 158.0 ppm; HR-FAB MS calc for $C_{33}H_{35}NO_6Na$ $[M+Na]^+$: 564.2362, found 564.2357.

Thiazolinyl 3,4-di-*O*-benzoyl-2-*O*-benzyl-6-*O*-trityl-1-thio-β-D-glucopyranoside (37a). A solution of NaOMe in MeOH (0.1 M, 11.1 mL, 1.11 mmol of MeONa) was added to a stirred suspension of thiazolinyl 3,4,6-tri-O-acetyl-2-*O*-benzyl-1-thio-β-D-glucopyranoside (**37**)[3] (338 mg, 0.68 mmol) in dry methanol (10 mL) and the reaction mixture was stirred for 2 h at rt. The reaction was then neutralized with Dowex (H^+), filtered, and concentrated in vacuo. The crude residue containing thiazolinyl 2-*O*-benzyl-1-thio-β-D-glucopyranoside (250 mg, 0.68 mmol) was dissolved in pyridine (5.0 mL) and TrCl (380 mg, 1.360 mmol) was added. The reaction mixture was stirred under an atmosphere of argon for 40 h at rt, cooled to 0 ^oC BzCl (320 μL, 2.72 mmol) was added. The reaction mixture was stirred for 16 h at rt. Upon completion, the reaction was quenched with methanol (1.0 mL), the volatiles were evaporated off, the residue was dissolved in CH_2Cl_2 (15mL) and washed successively with water (15 mL) sat. $NaHCO_3$ (15 mL), water (15 mL), 1N HCl (15 mL) and water (3 x 15 mL). The organic phase was separated, dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/hexane gradient elution) to afford the title compound as off-white foam in 98% yield. Analytical data for **37a**: R_f = 0.40 (ethyl acetate-hexane, 3/7, v/v); $[\alpha]_D^{24}$ = +13.4^o (c = 1, $CHCl_3$); ^{1}H-n.m.r.: δ, 3.36 (m, 2H, H-6a, 6b), 3.27 (t, 2H, $J_{CH2CH2N}$ = 8.0, SC*H*$_2$CH$_2$), 3.71-3.91 (m, 2H, H-2, 5), 4.11- 4.19 (m, 2H, C*H*$_2$N), 4.52 (d, 1H, C*H*$_2$Ph), 4.70 (d, 1H, C*H*$_2$Ph), 5.34-5.41 (m, 2H, C*H*$_2$Ph), 5.61 (dd, 1H, $J_{3,4}$ = 9.1, H-3), 7.03-7.35 (m, 26H, aromatic), 7.60 (dd, 2H, aromatic), 7.82 (dd, 2H, aromatic) ppm; ^{13}C-n.m.r.; δ, 35.1, 53.6, 63.2, 64.5, 69.5, 75.3, 76.3, 77.4, 78.3, 78.6, 84.7, 86.9, 127.0, 127.9, 128.1, 128.4, 128.5, 128.5, 128.6, 128.8, 128.9, 129.3, 129.6, 129.9, 130.0, 133.0, 133.2, 133.3, 137.1, 143.9, 165.2, 165.8 ppm; HR-FAB MS calc for $C_{49}H_{43}NO_7S_2Na$ $[M+Na]^+$: 844.2379 found 844.2375.

Thiazolinyl 2-*O*-benzyl-2,3-di-*O*-benzoyl-1-thio-β-D-glucopyranoside (38). To a stirred solution of **37a** (82 mg, 0.0997 mmol) in wet CH_2Cl_2 (2 mL), water (50 μL) and 10% TFA/CH_2Cl_2 (1/9, v/v, 10 μL) were added at rt. The reaction mixture was stirred for 30 min, then diluted with CH_2Cl_2 (15mL) and washed with water (15 mL), sat. $NaHCO_3$ (15 mL), and water (2 x 15 mL). The organic phase was separated, dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/toluene gradient elution) to afford the title compound as white amorphous solid in 80% yield. Analytical data for **38**: R_f = 0.17 (ethyl acetate-hexane, 2/3, v/v); $[\alpha]_D^{24} = +19.4^o$ (c = 1, $CHCl_3$); ^{1}H-n.m.r: δ, 2.88 (bs, 1H, OH), 3.49 (t, 2H, $J_{CH2CH2N}$ = 7.6, SC*H*$_2$CH$_2$), 3.78 (dd, 1H, J = 4.9, H-6a), 3.90-4.01 (m, 3H, H-2, 5, 6a), 4.17-4.46 (m, 2H, C*H*$_2$N), 4.67 (d, 1H, C*H*$_2$Ph), 4.85 (d, 1H, C*H*$_2$Ph), 5.49 (dd, 1H, J = 9.7, H-4), 5.60 (d, 1H, $J_{1,2}$ = 10.0, H-1), 5.92 (dd, 1H, $J_{2,3}$ = 9.2 Hz, H-3), 7.19-7.24 (m, 5H, aromatic), 7.42-7.48 (m, 4H, aromatic), 7.60 (t, 2H, aromatic), 8.02 (t, 4H, aromatic) ppm; ^{13}C-n.m.r.; δ, 28.2, 35.4, 50.9, 61.1, 61.7, 64.5, 69.5, 72.9, 75.1, 75.3, 75.8, 77.4, 78.4, 79.0, 83.7, 84.7, 128.2, 128.3, 128.5, 127.6, 128.7, 128.8, 128.8, 129.5, 129.9, 130.1, 130.2, 133.4, 133.6, 133.8, 134.0, 136.9, 137.3, 163.2, 165.7, 166.2; FAB MS $[M+Na]^+$ HR-FAB MS calc for $C_{30}H_{29}NO_7S_2Na$: 602.1283 found 602.1270.

Copies of NMR spectra



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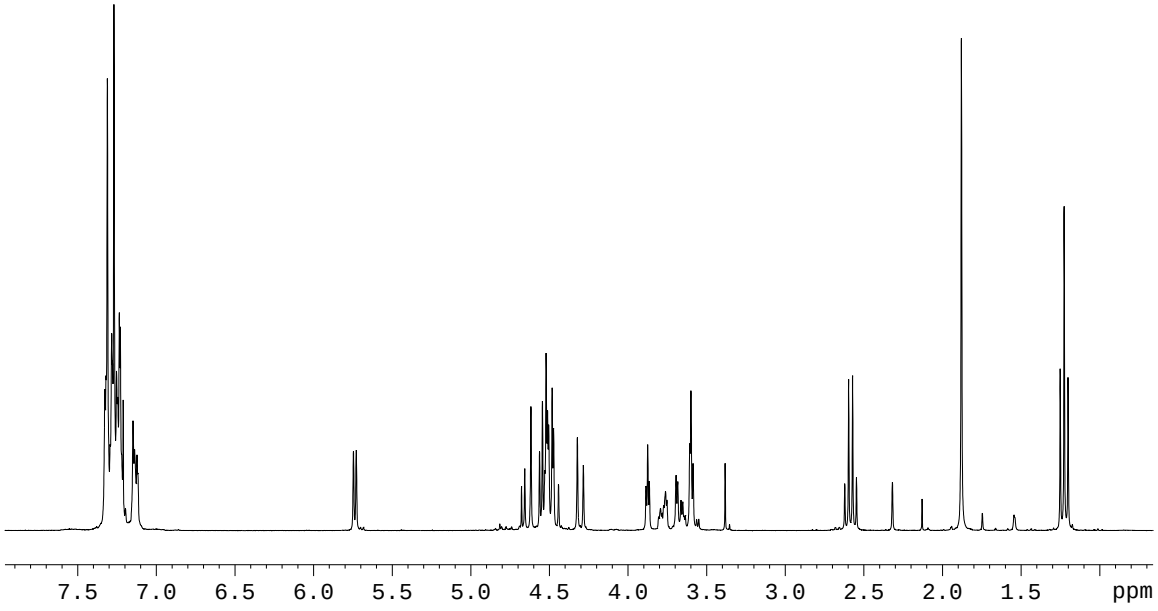

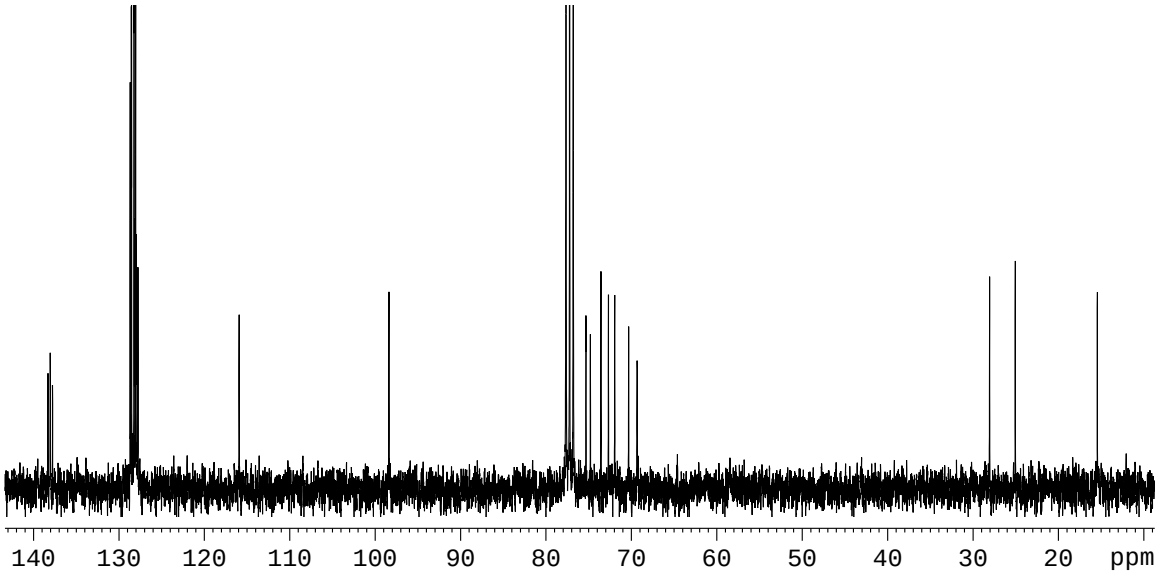

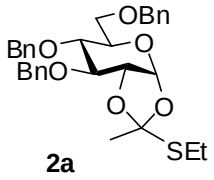
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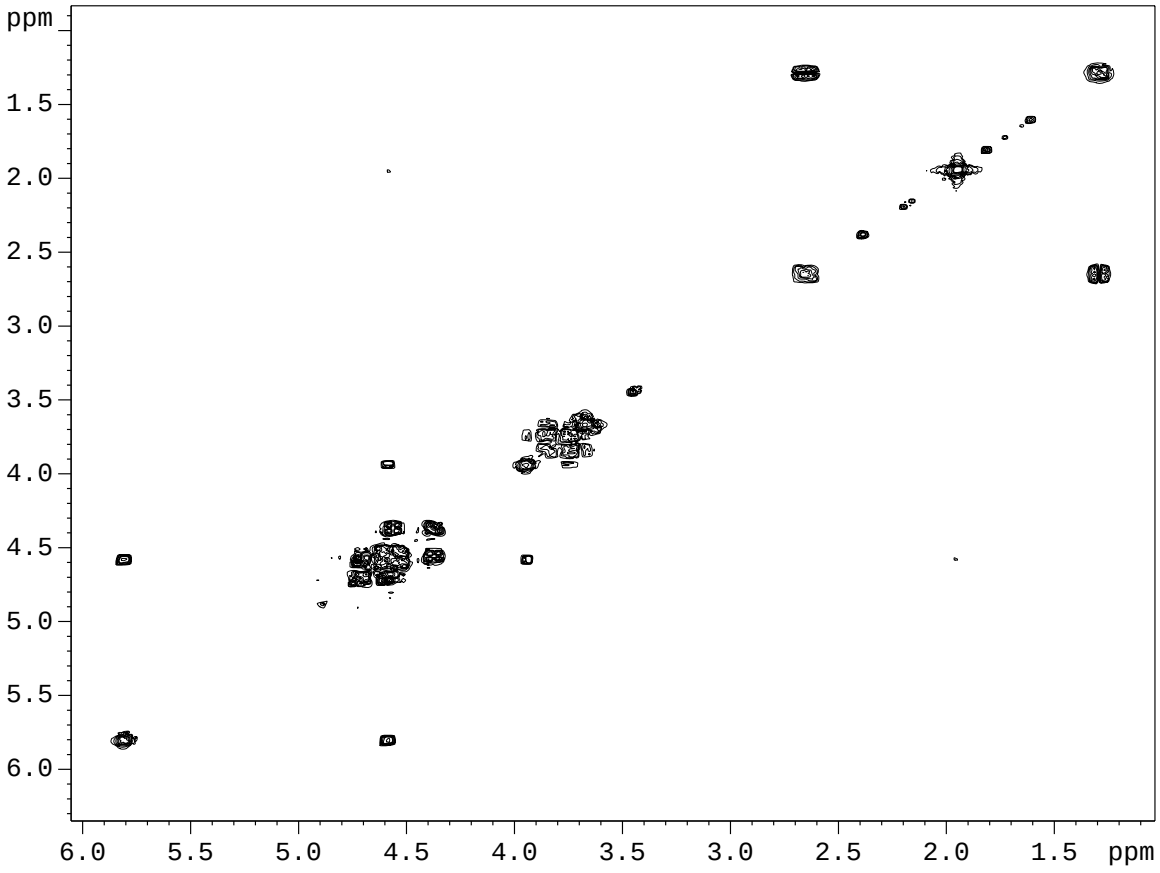
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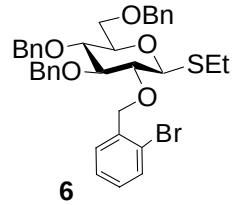
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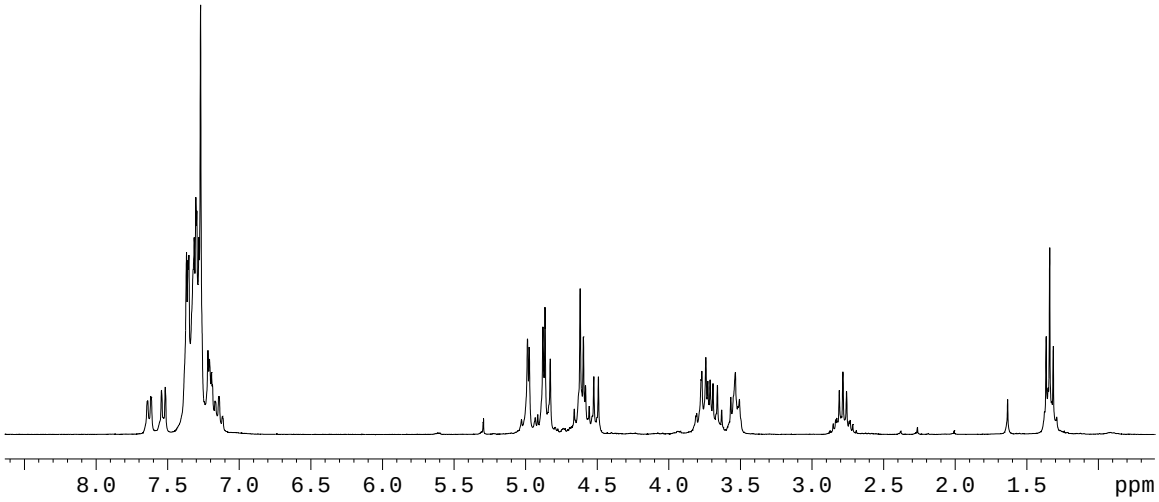
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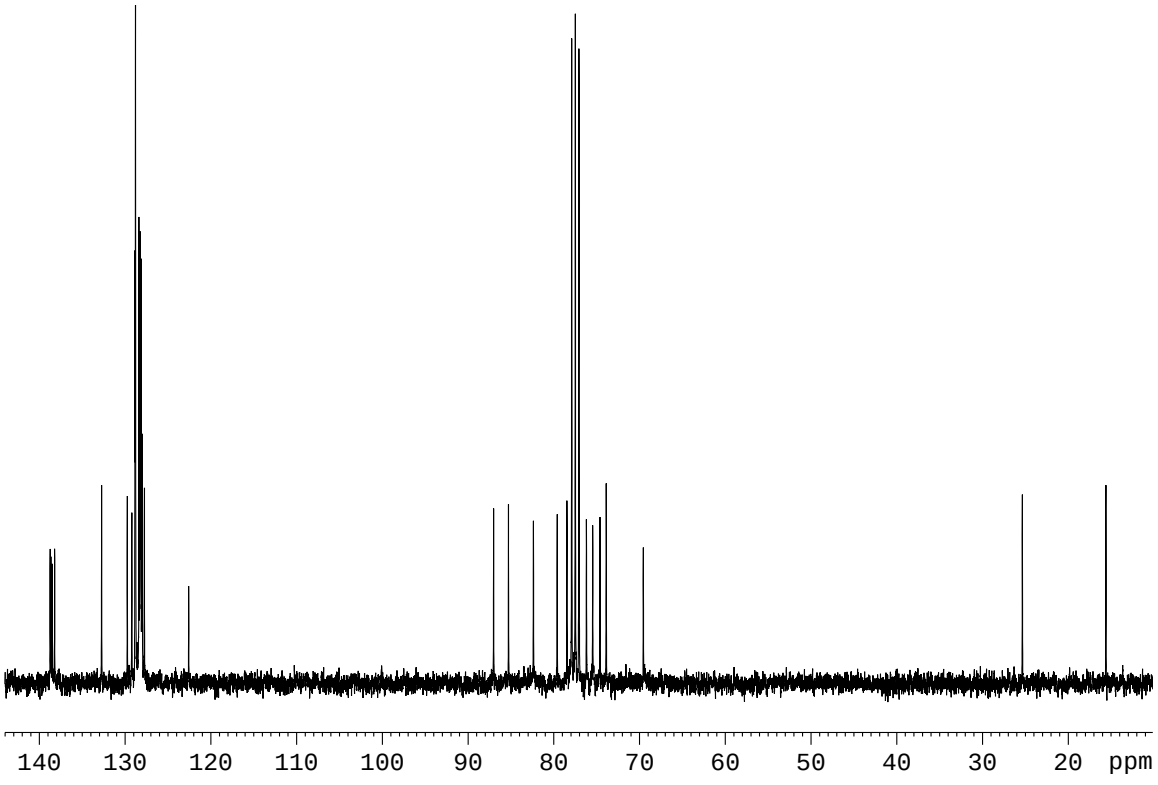
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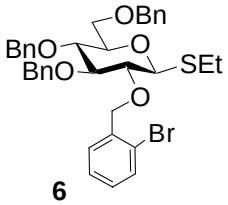
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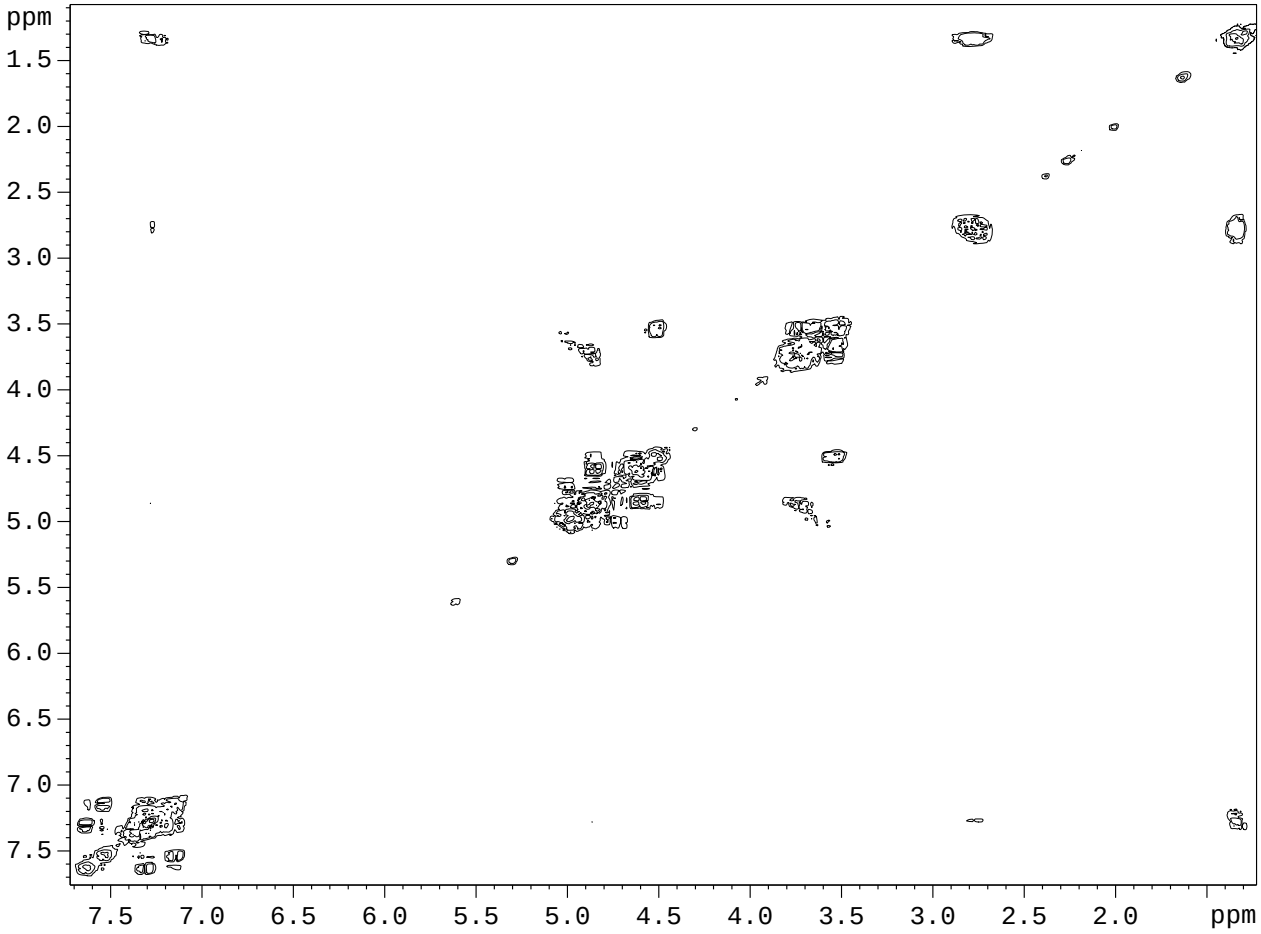
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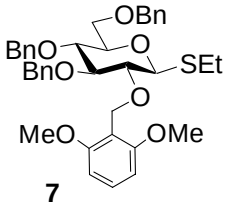
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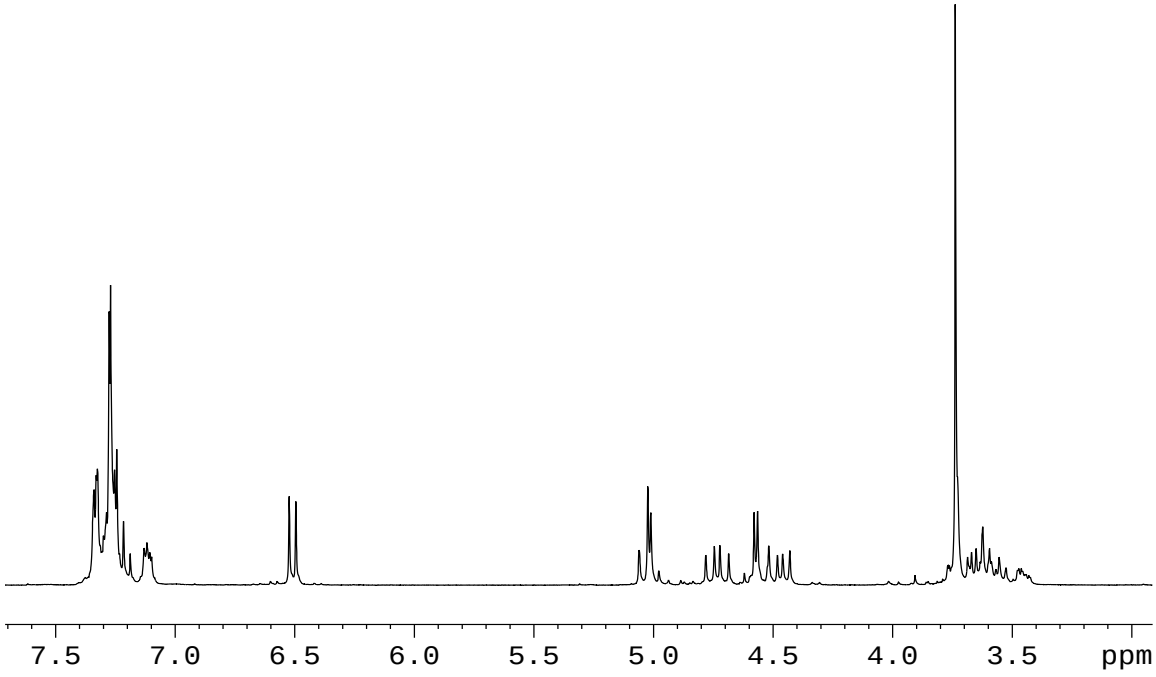
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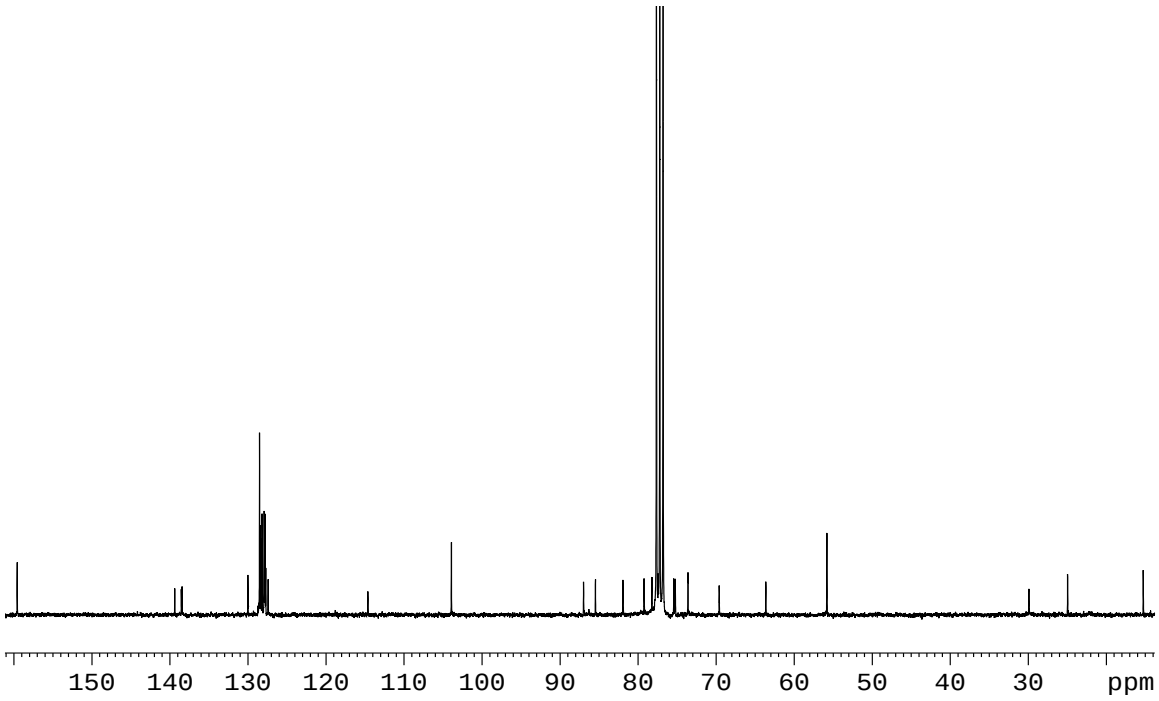
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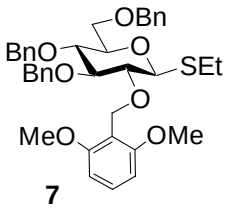
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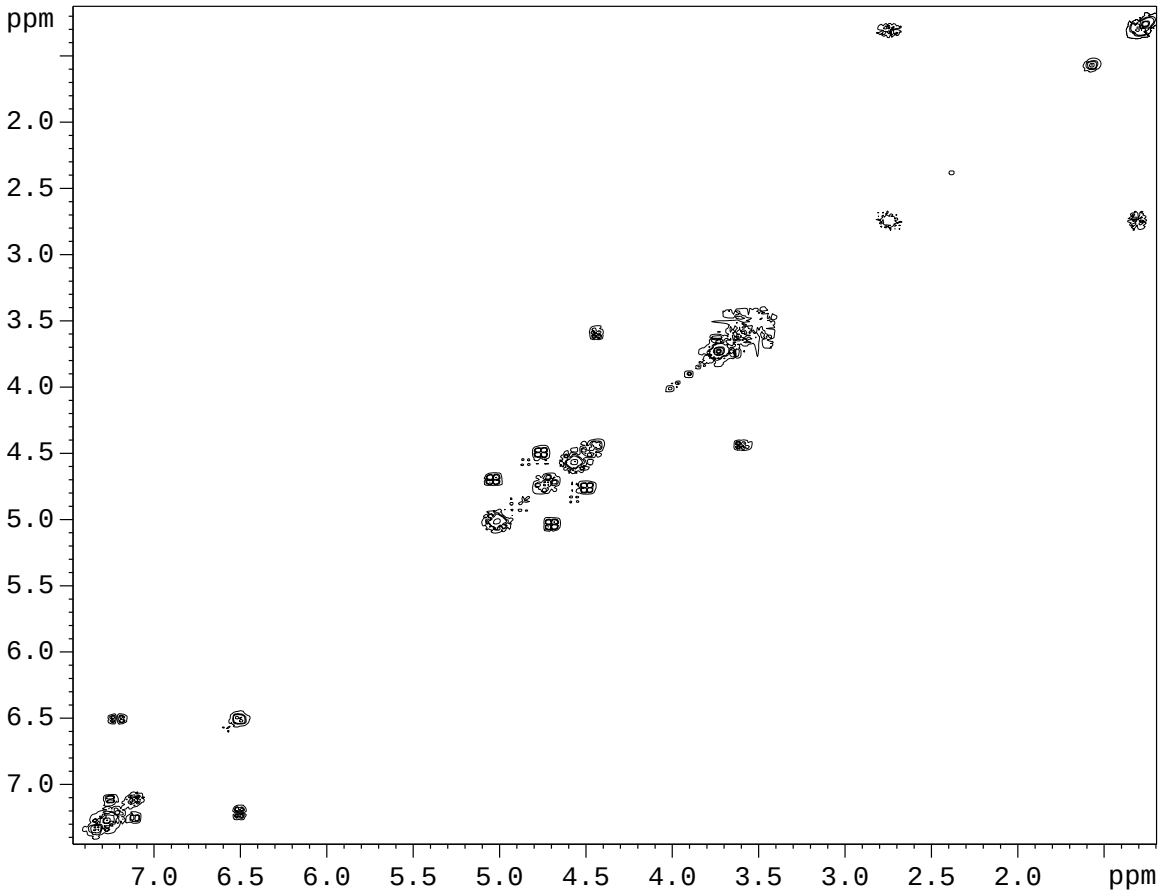
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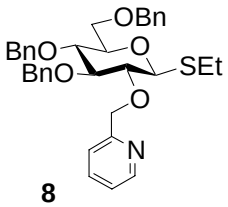
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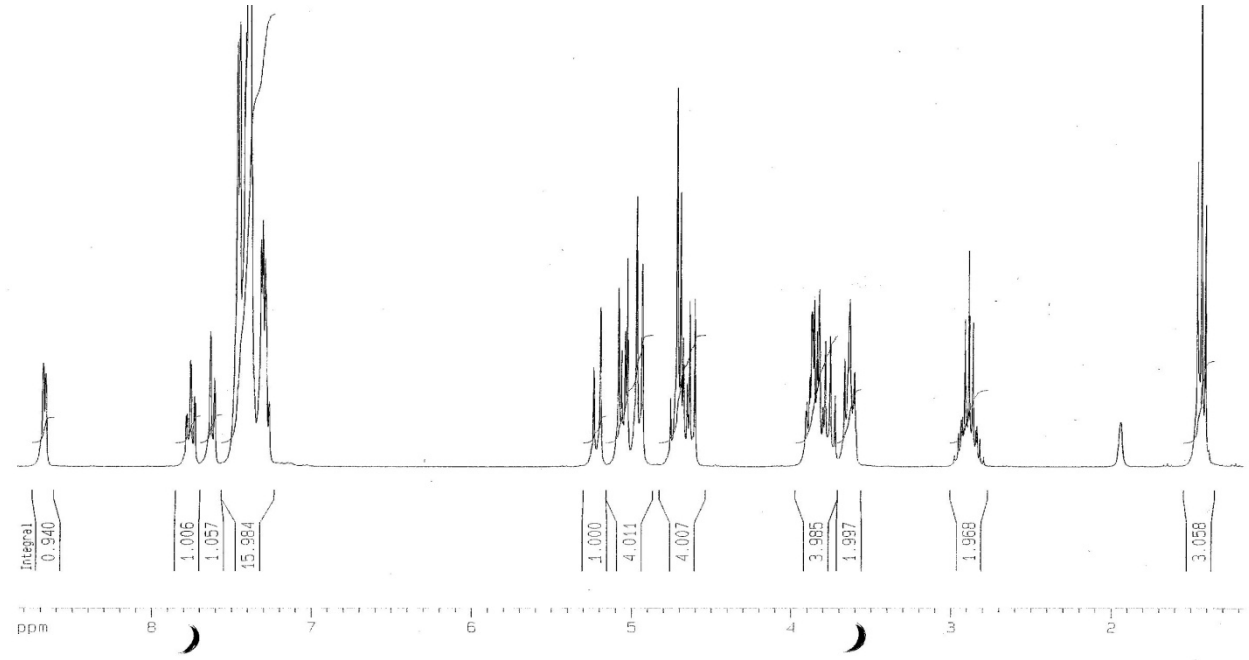
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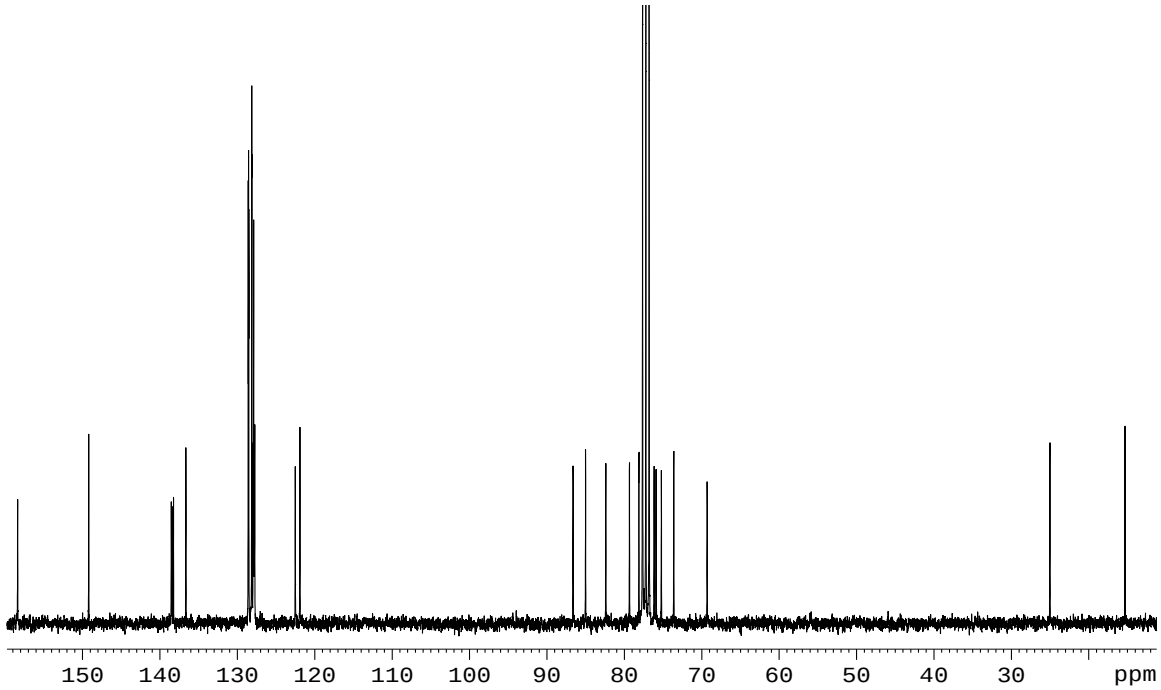
0.940
1.006
1.057
15.984
1.000
4.011
4.007
3.985
1.997
1.968
3.058
ppm
8
7
6
5
4
3
2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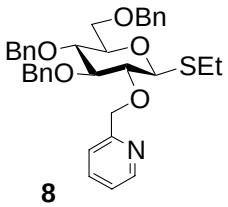
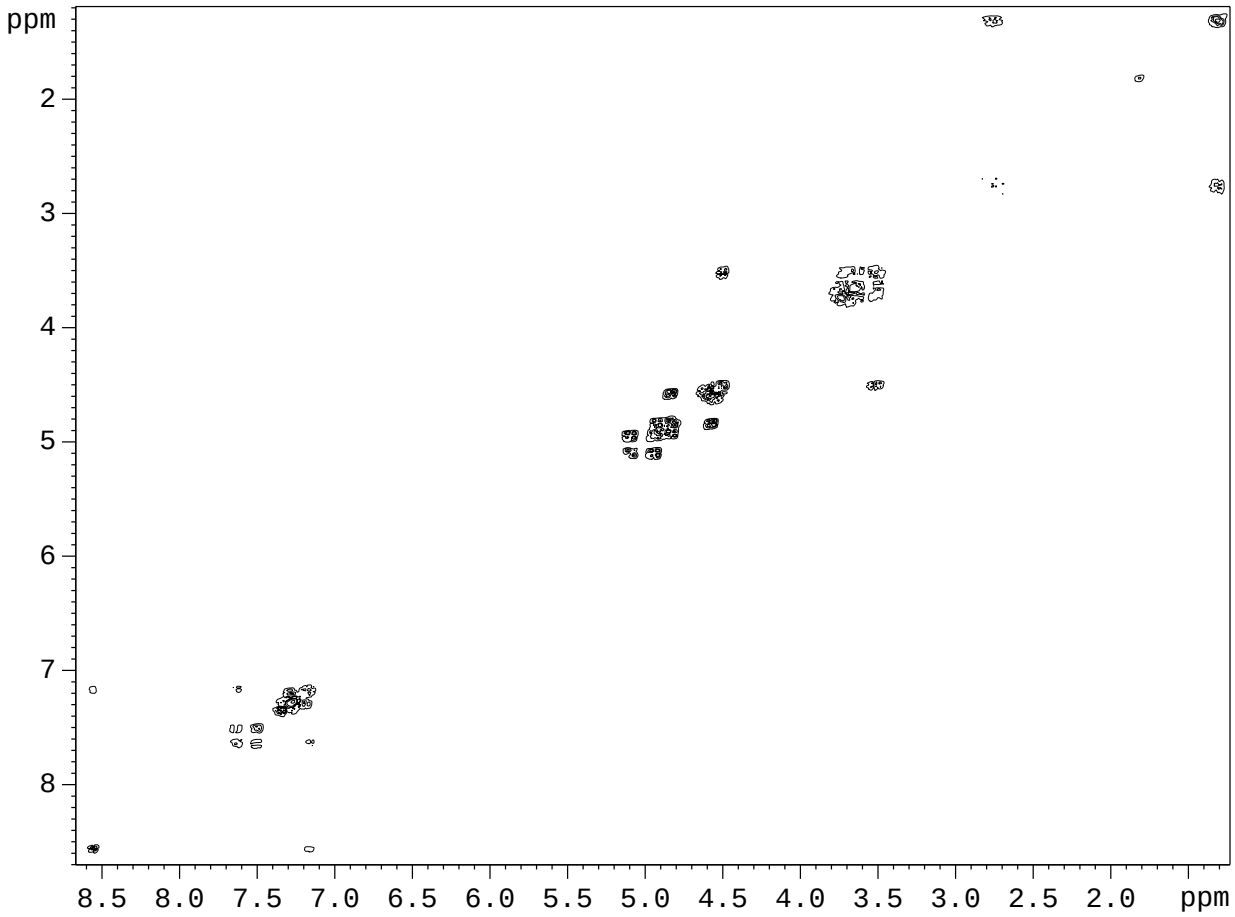
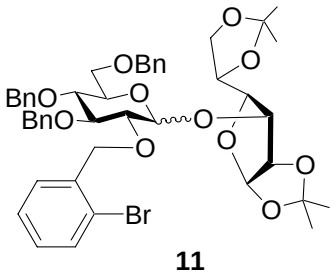
140
130
120
110
100
90
80
70
60
50
40
30
ppm

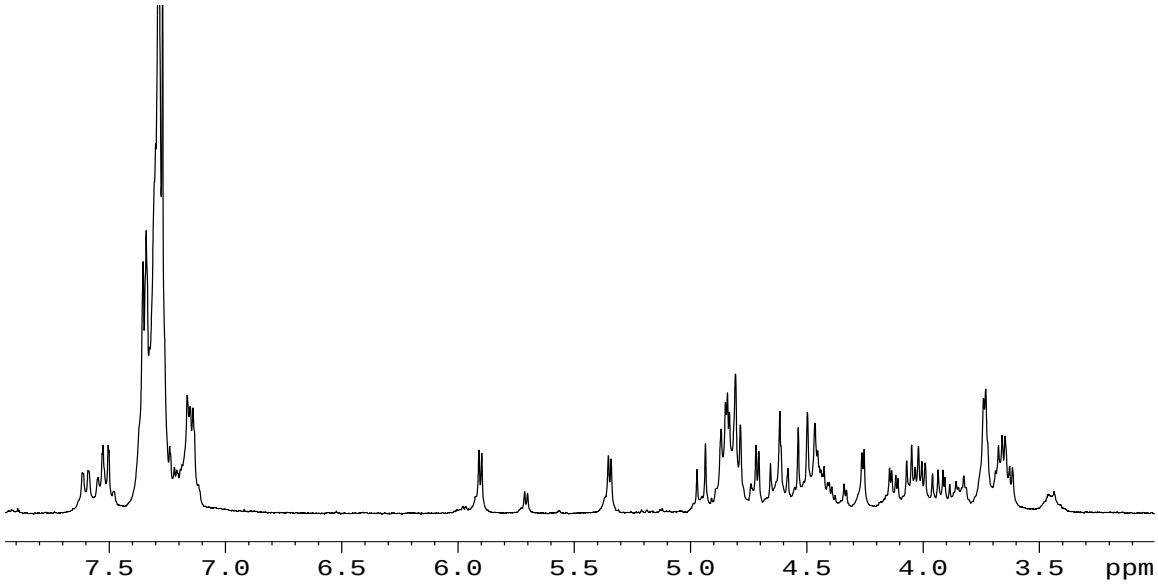

OBn
BnO
O
BnO
SEt
O
N

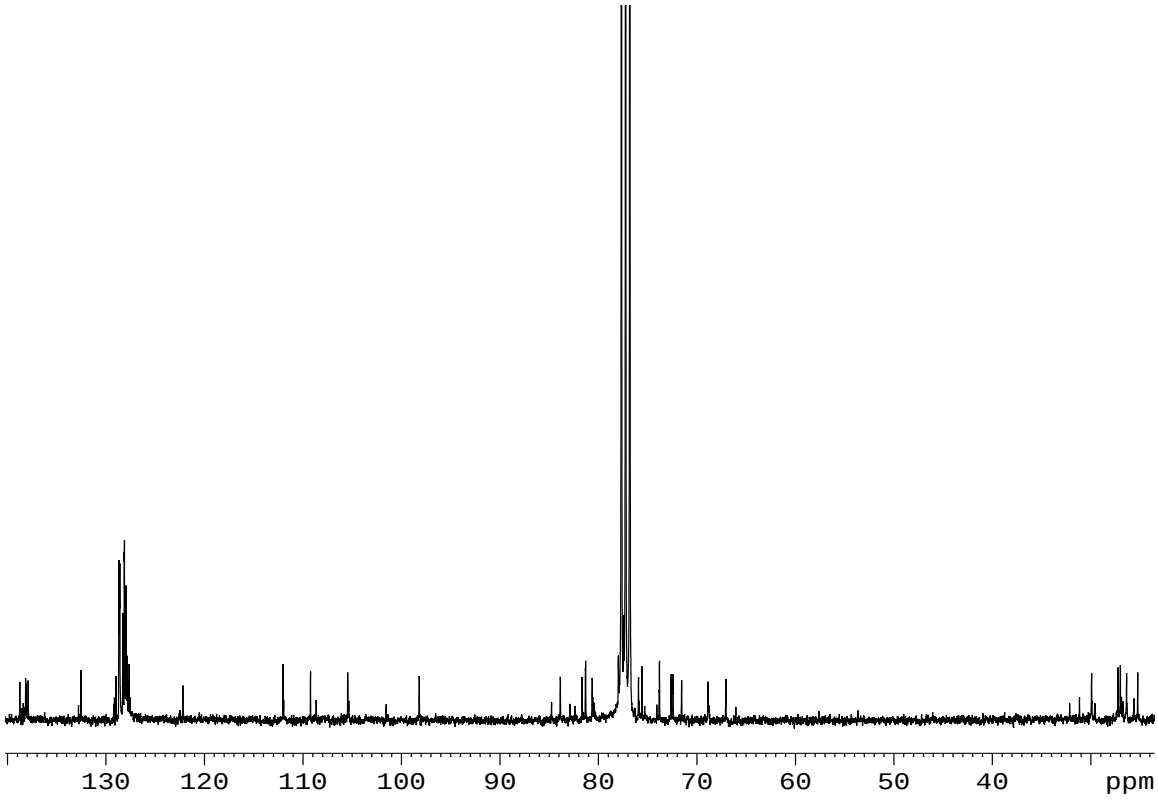
8

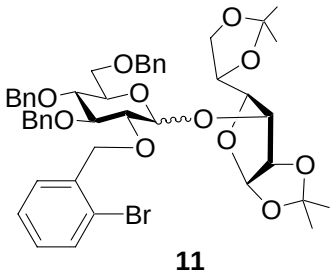

ppm
2
3
4
5
6
7
8
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm


OBn
BnO
BnO
O
O
O
O
O
O
O
O
Br

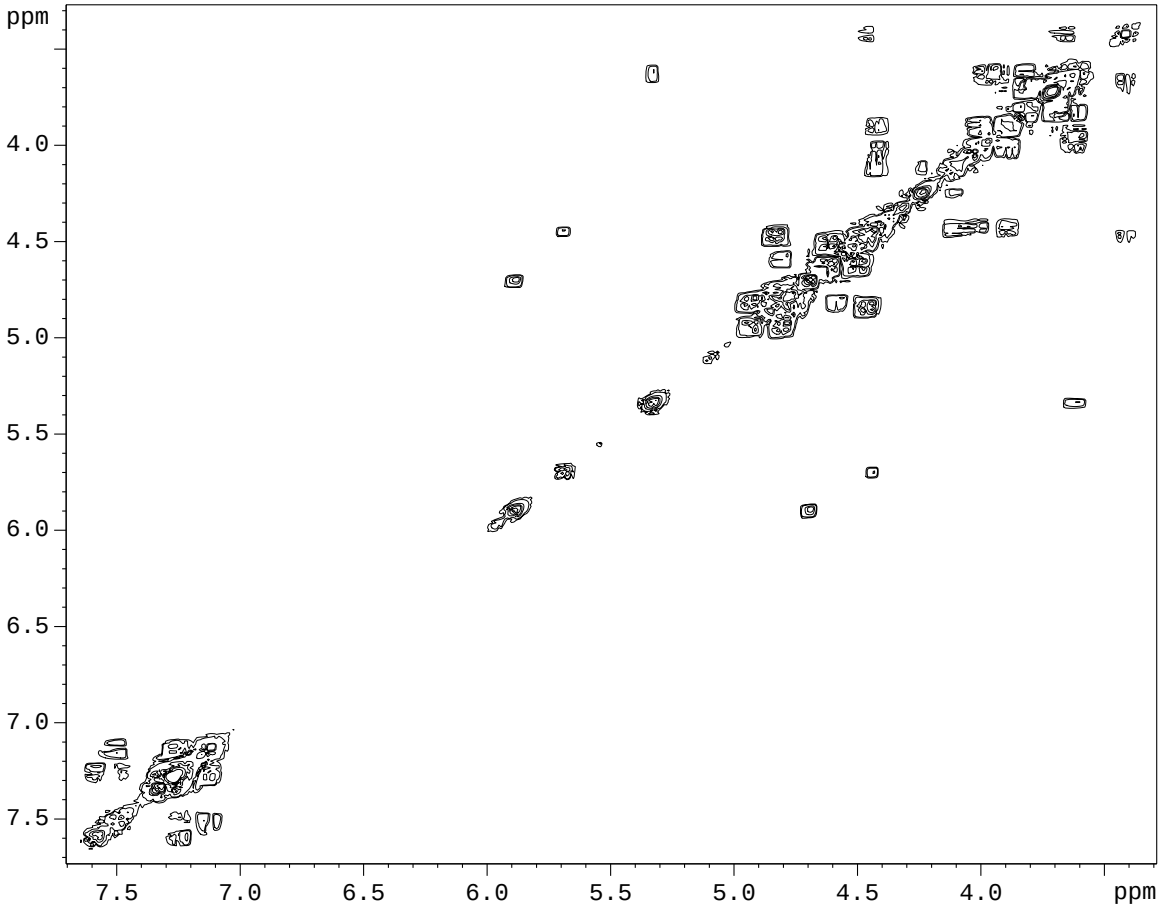
11

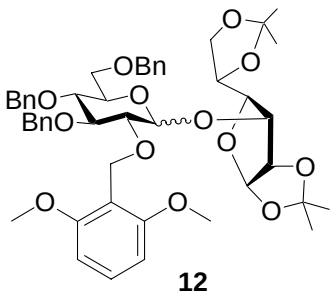

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm


130
120
110
100
90
80
70
60
50
40
ppm

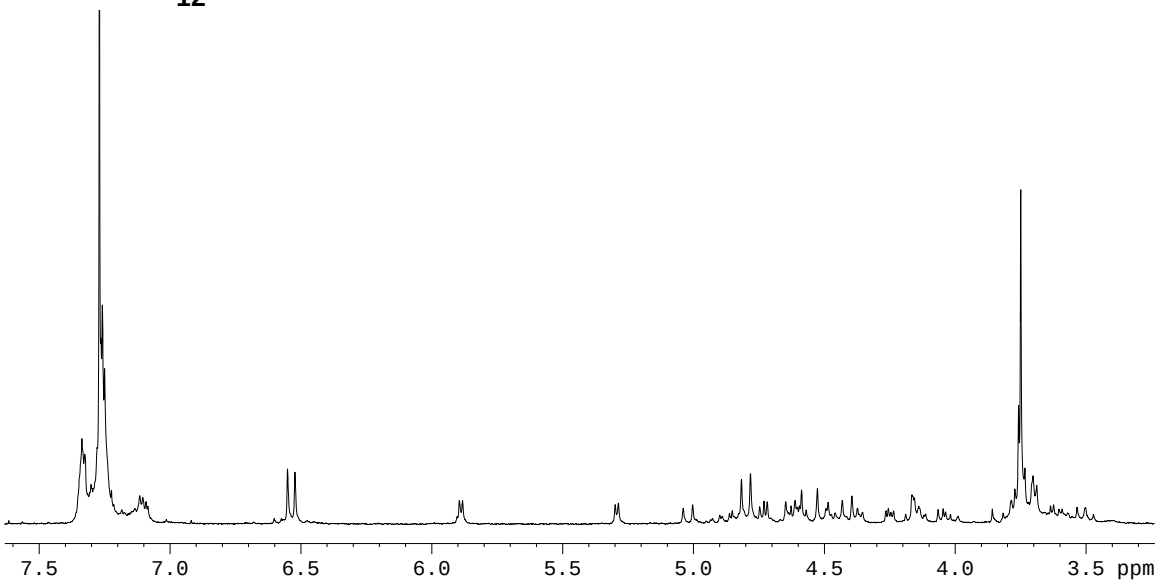

OBn
BnO
BnO
O
O
O
O
O
O
O
Br

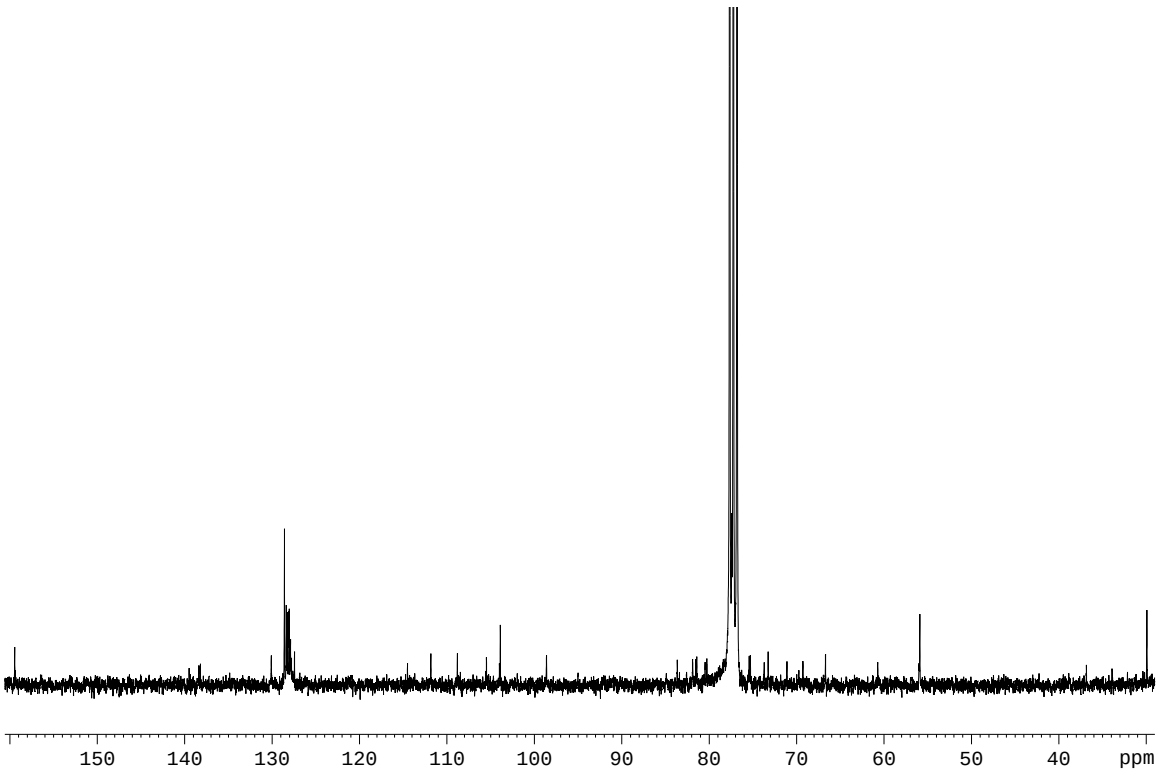
11

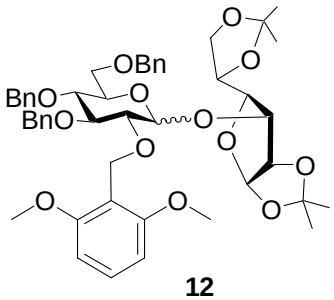

ppm
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm


OBn
BnO
BnO
O
O
O
O
O
O
O
O
O

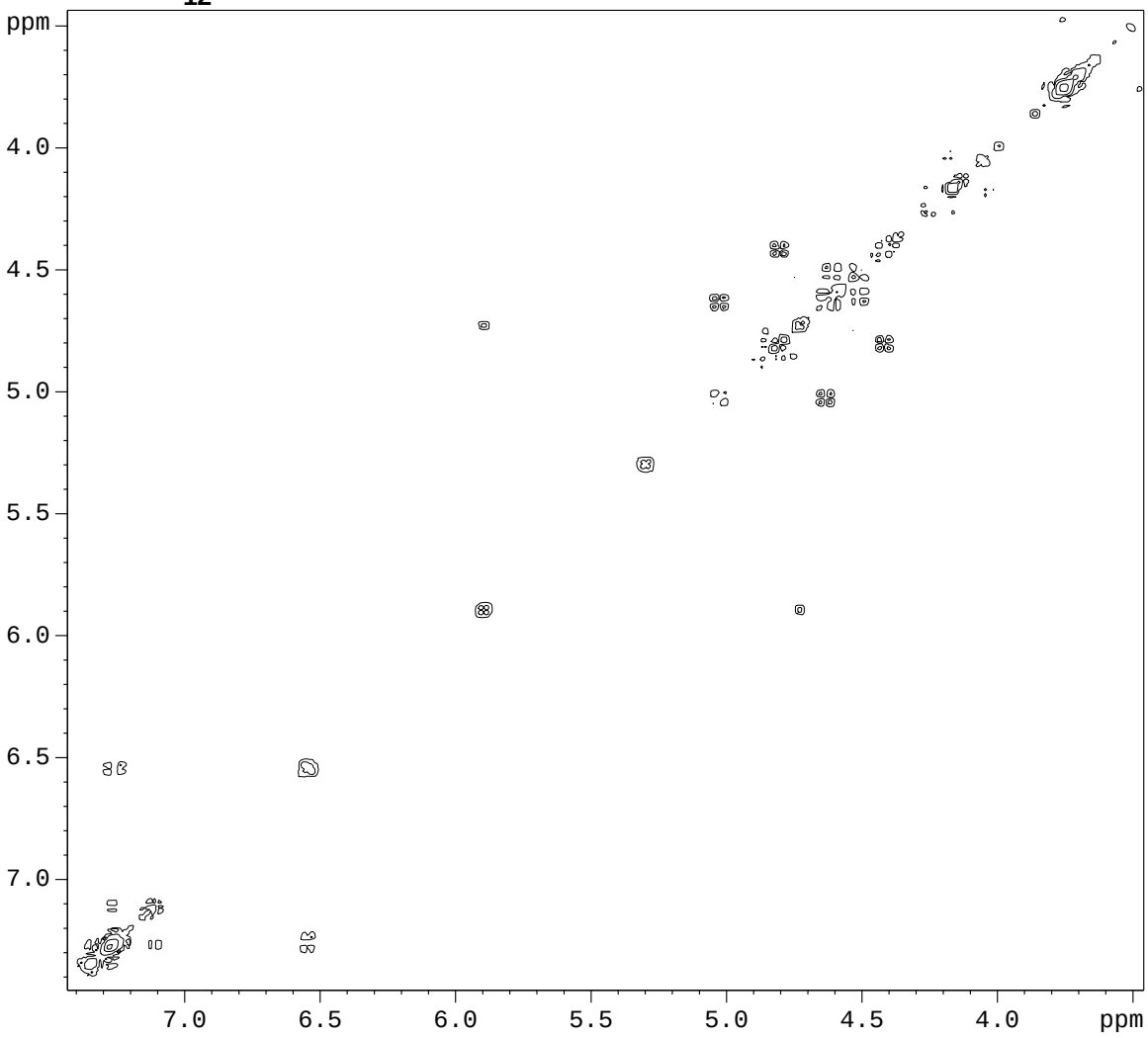
12

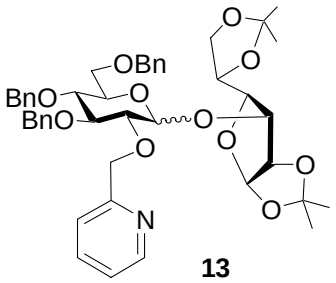

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5 ppm


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

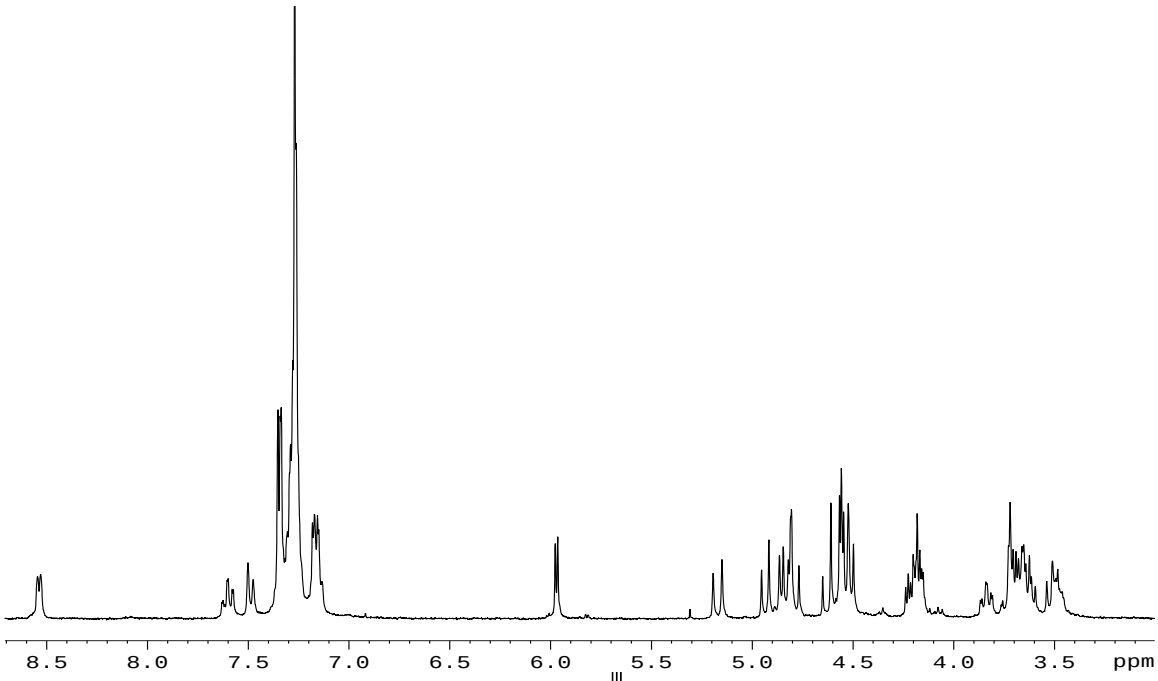


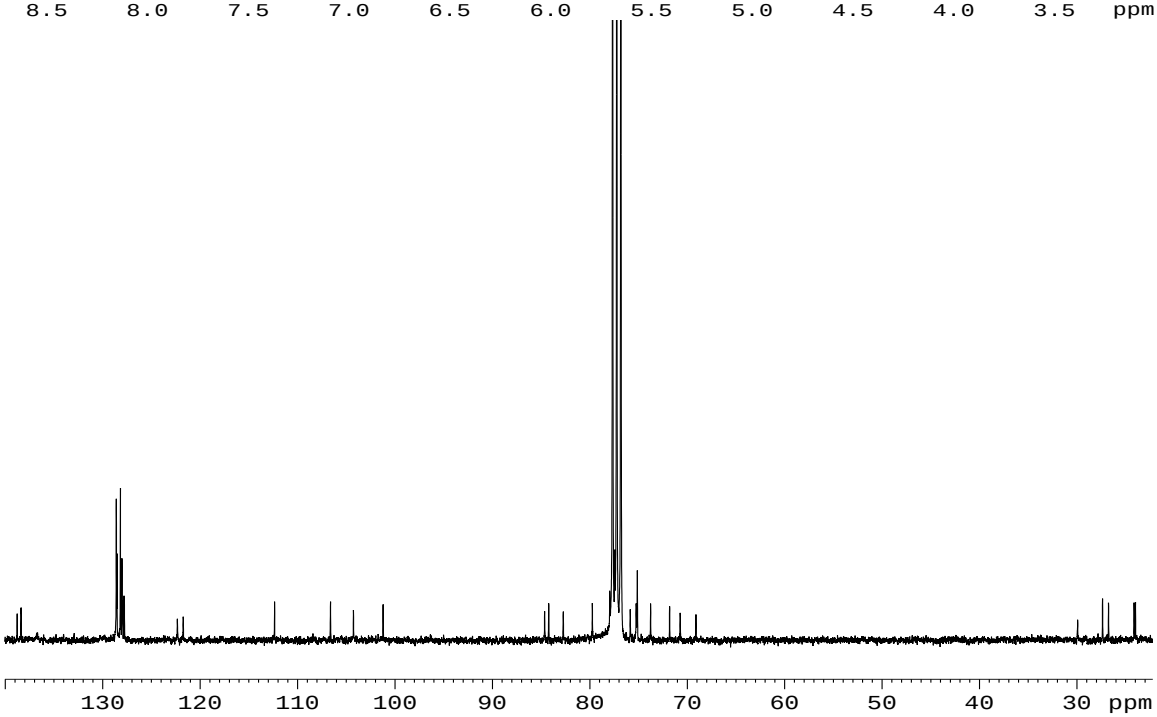
12

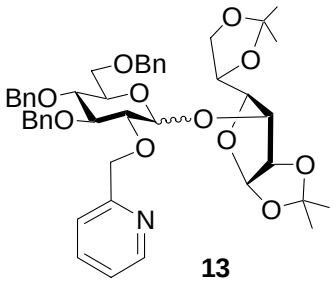



OBn
BnO
BnO
O
O
O
O
O
O
O
O
N

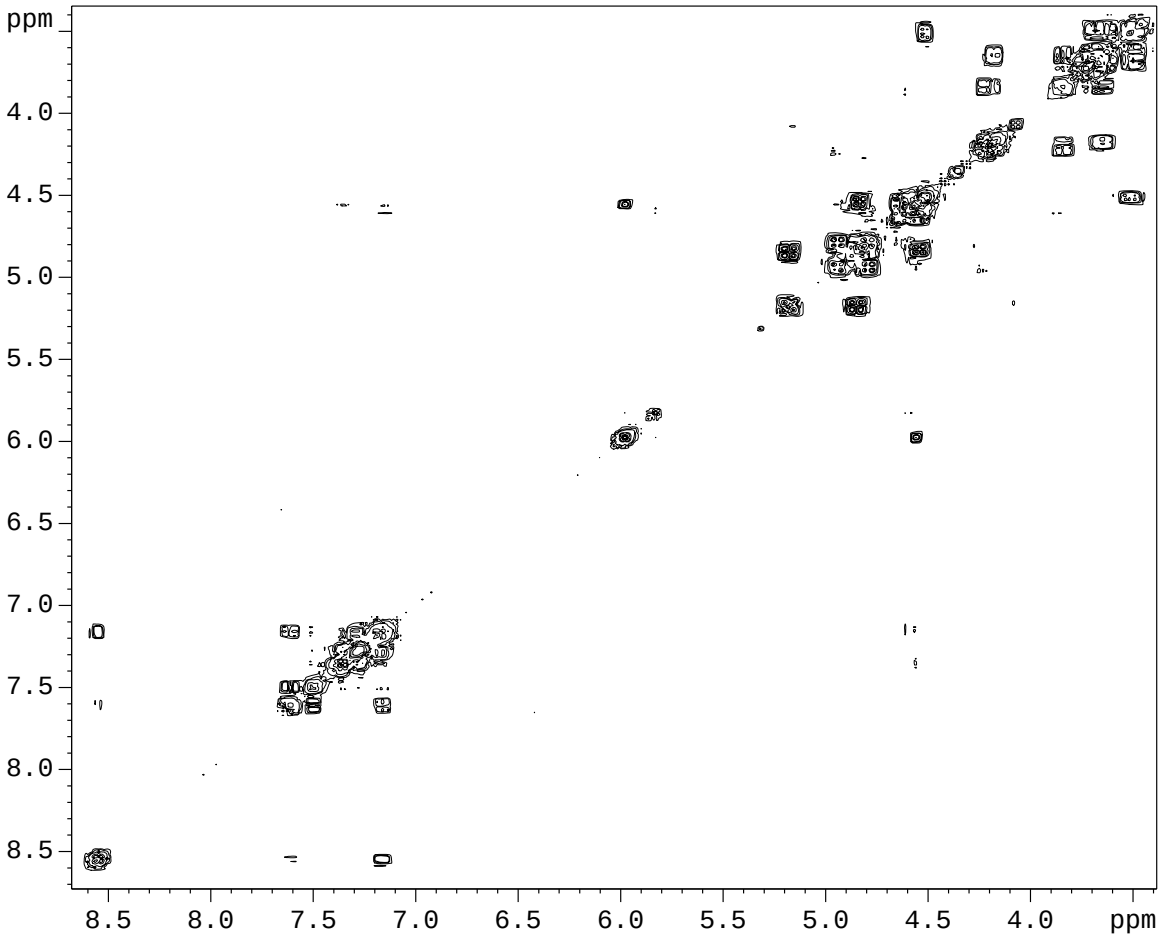
13

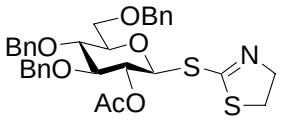

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm


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

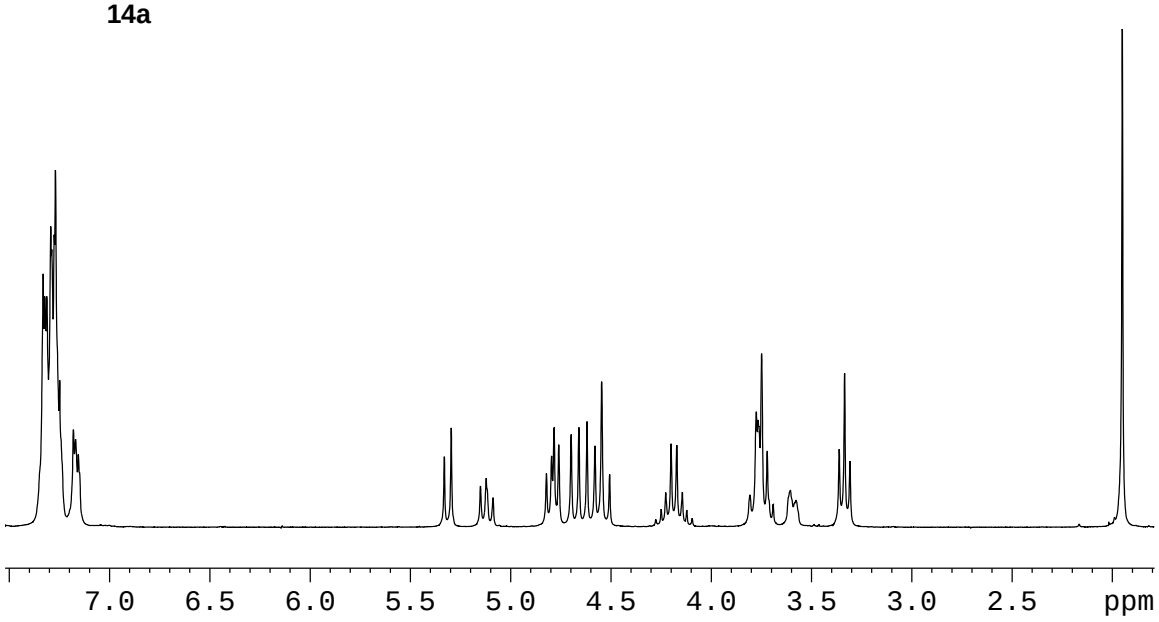

OBn
BnO
BnO
O
O
O
O
O
O
O
O
N

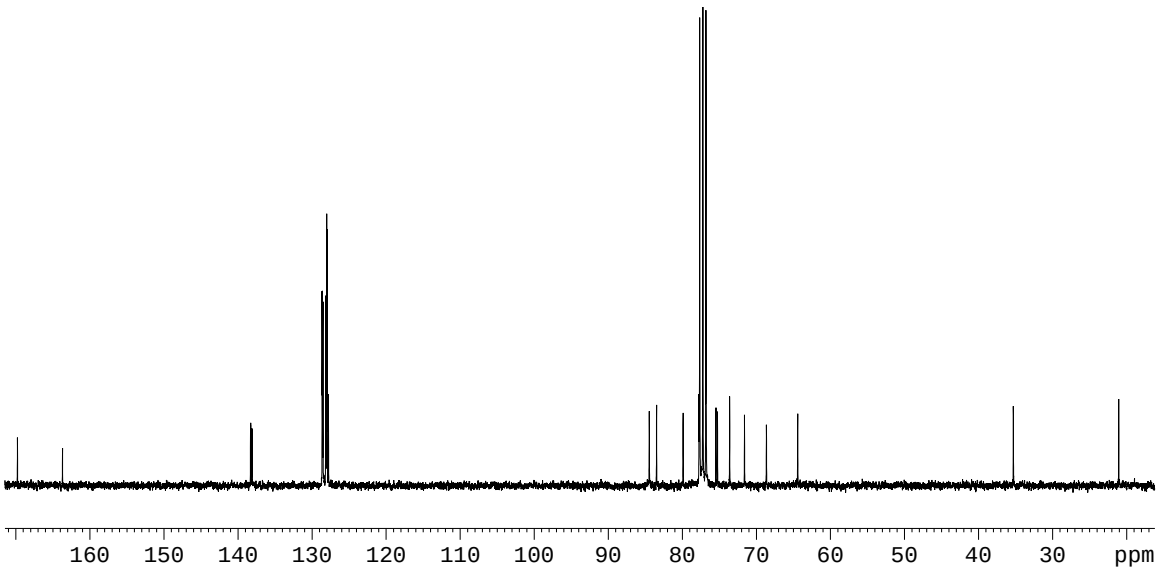
13

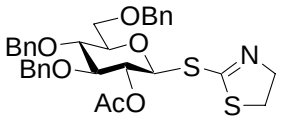

ppm
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm


OBn
BnO
O
BnO
S
N
AcO
S

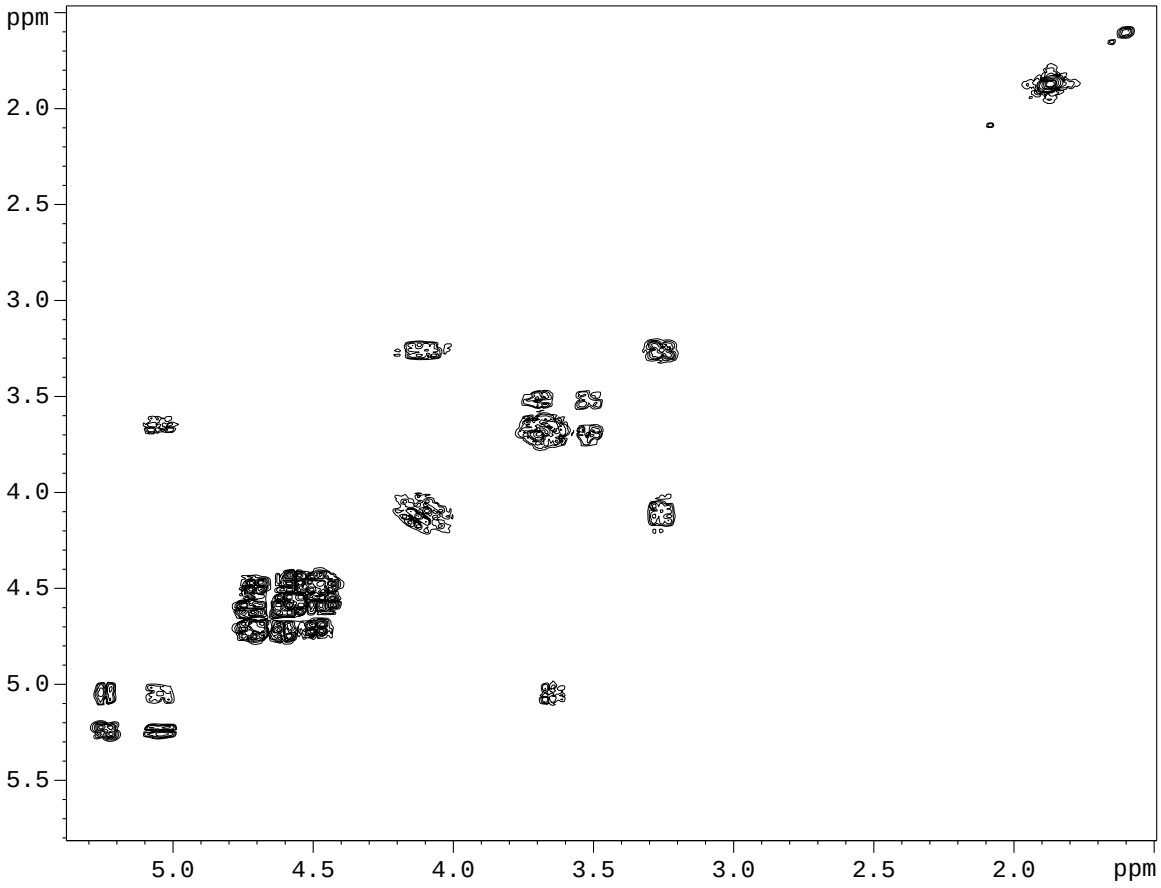
14a

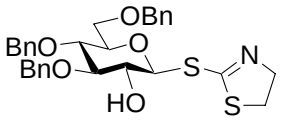

7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm


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

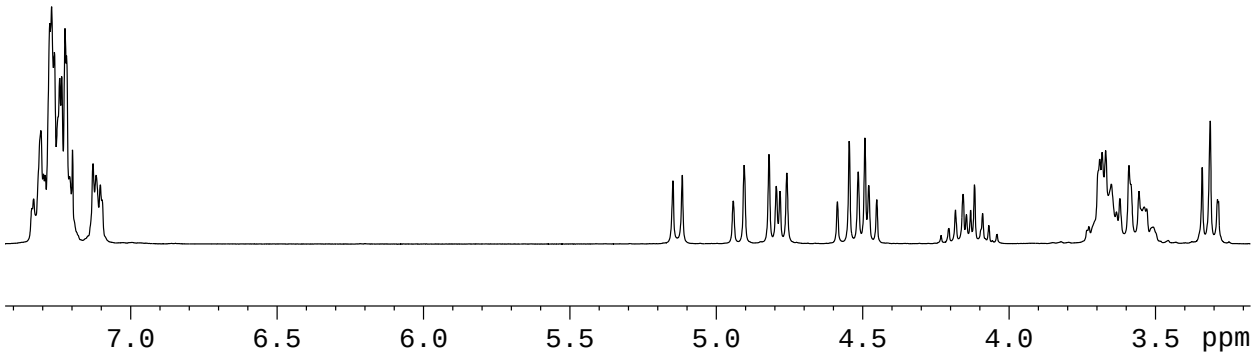

OBn
BnO
O
BnO
S
N
AcO
S

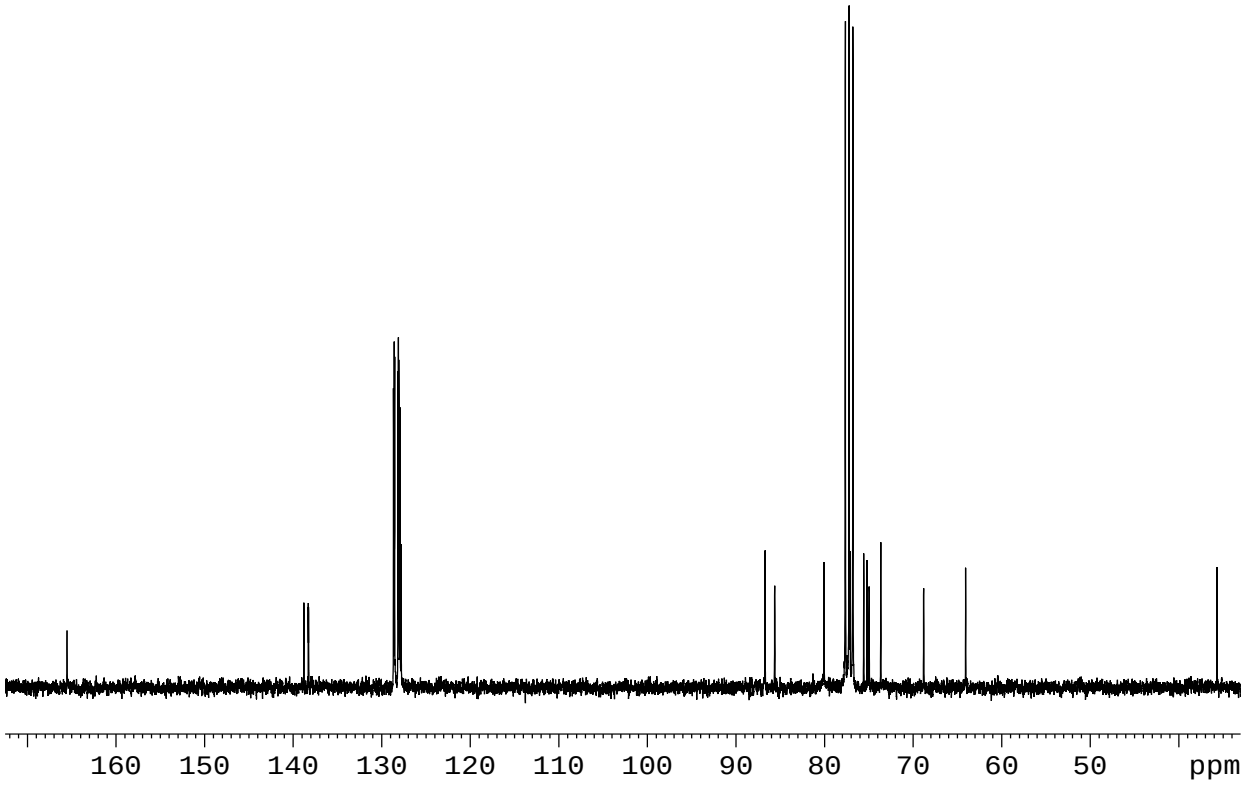
14a

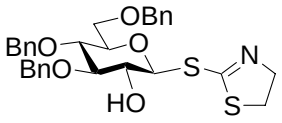

ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm


OBn
BnO
O
BnO
S
N
HO
S

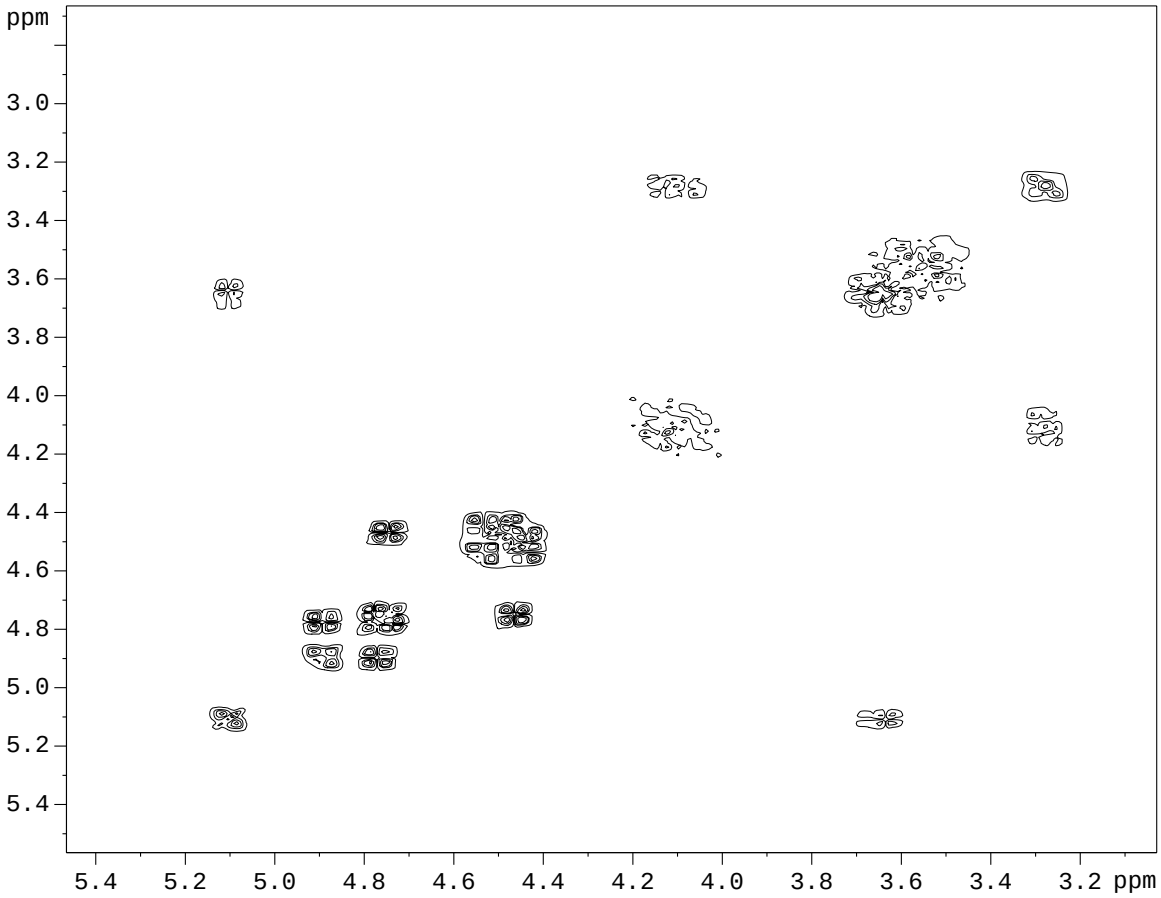
15a

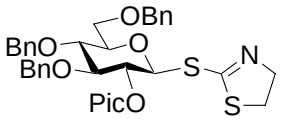

7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm


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

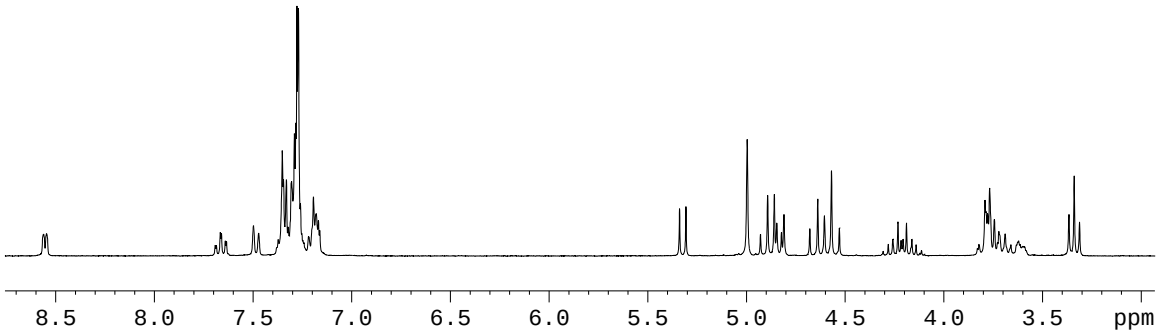

OBn
BnO
O
BnO
S
N
HO
S

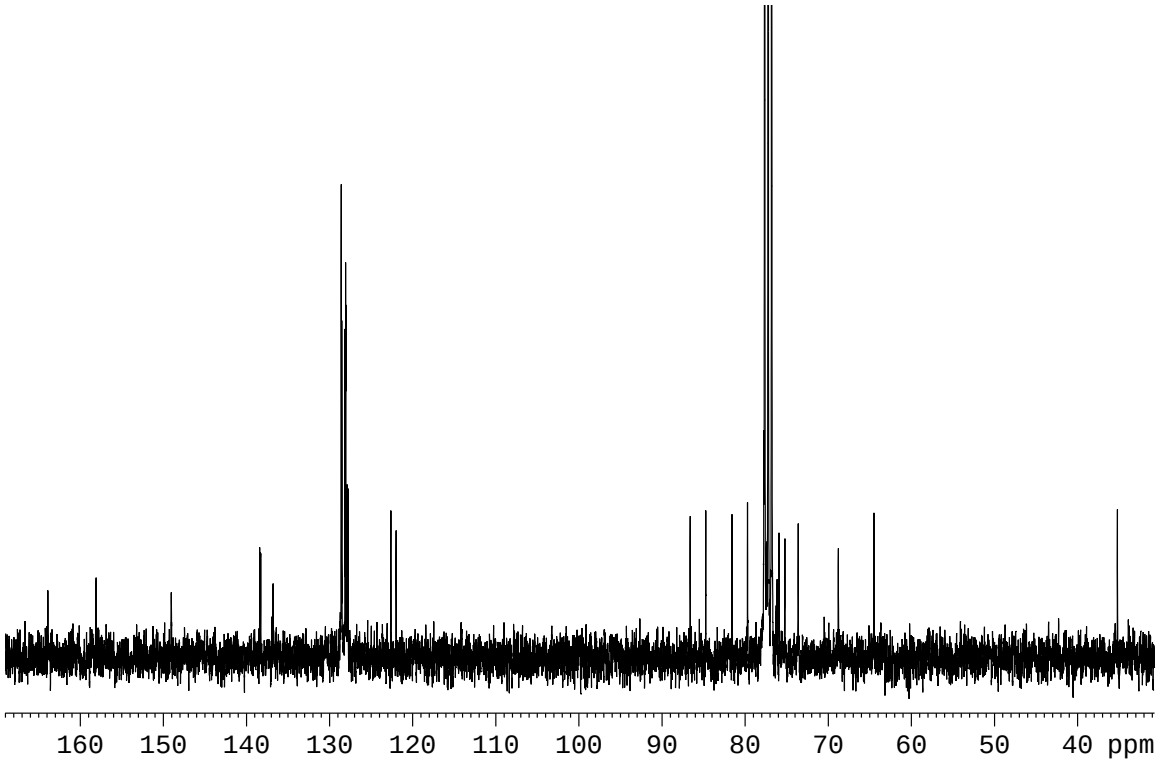
15a

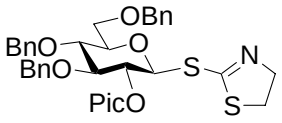

ppm
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2 ppm


OBn
O
BnO
BnO
S
N
PicO
S

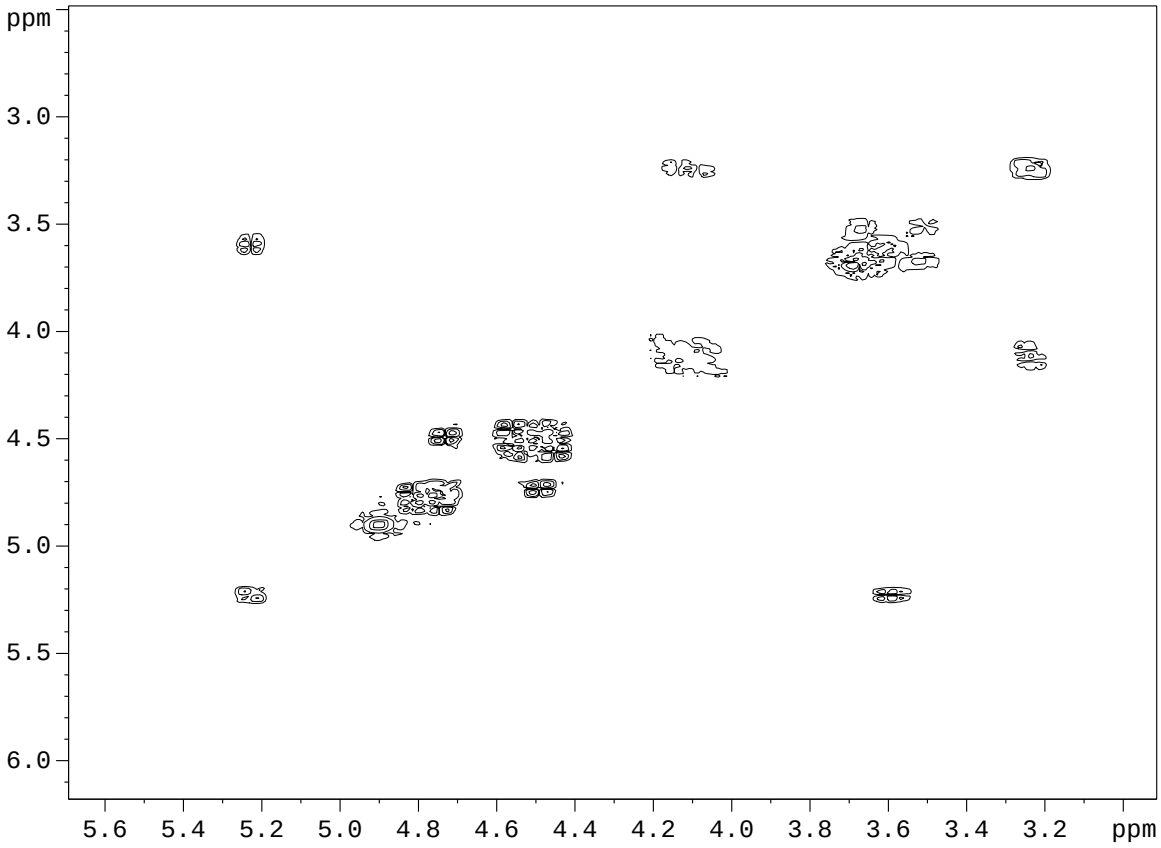
16a

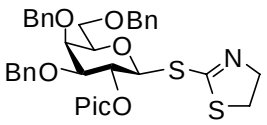

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm


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

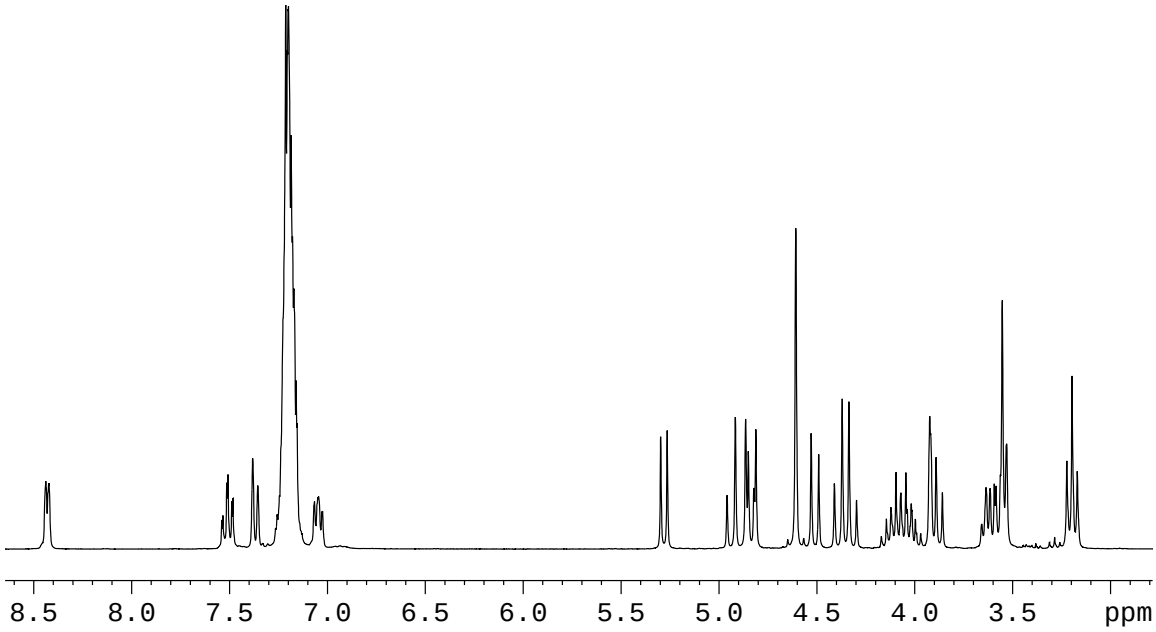

OBn
BnO
O
BnO
S
N
PicO
S

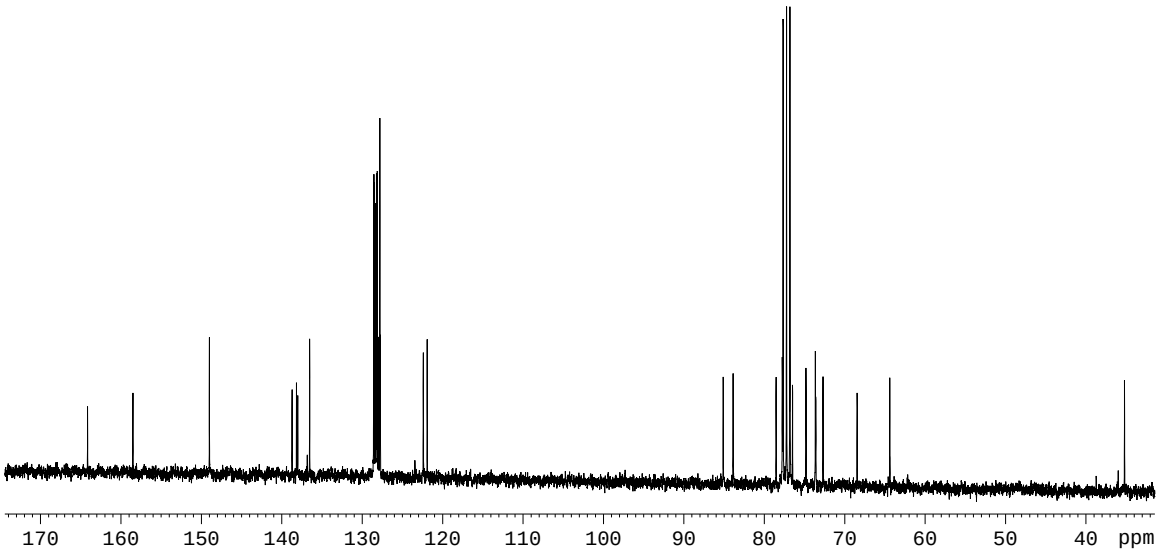
16a

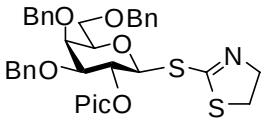

ppm
3.0
3.5
4.0
4.5
5.0
5.5
6.0
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm


BnO
OBn
O
BnO
S
N
PicO
S

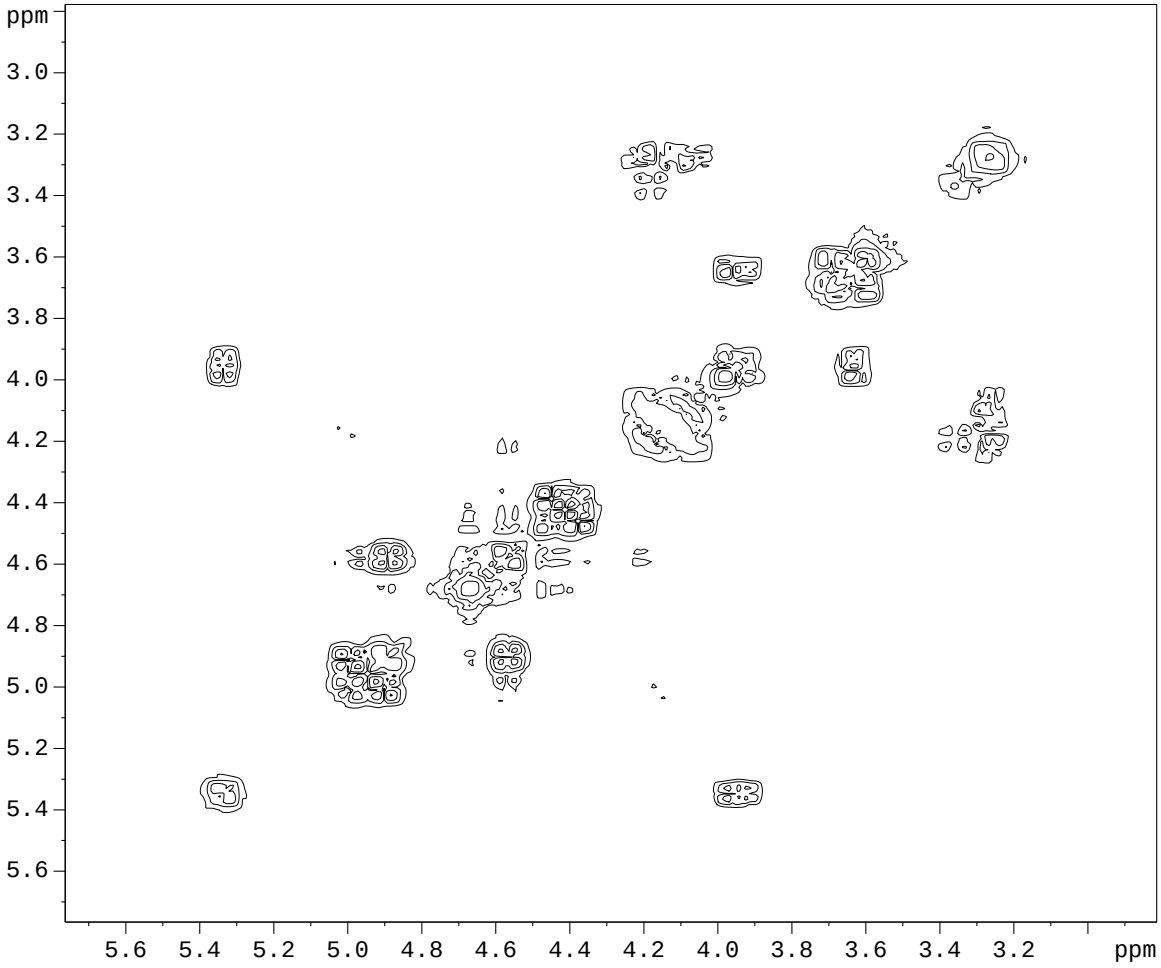
16b

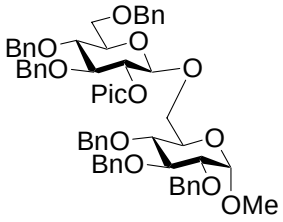

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm


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

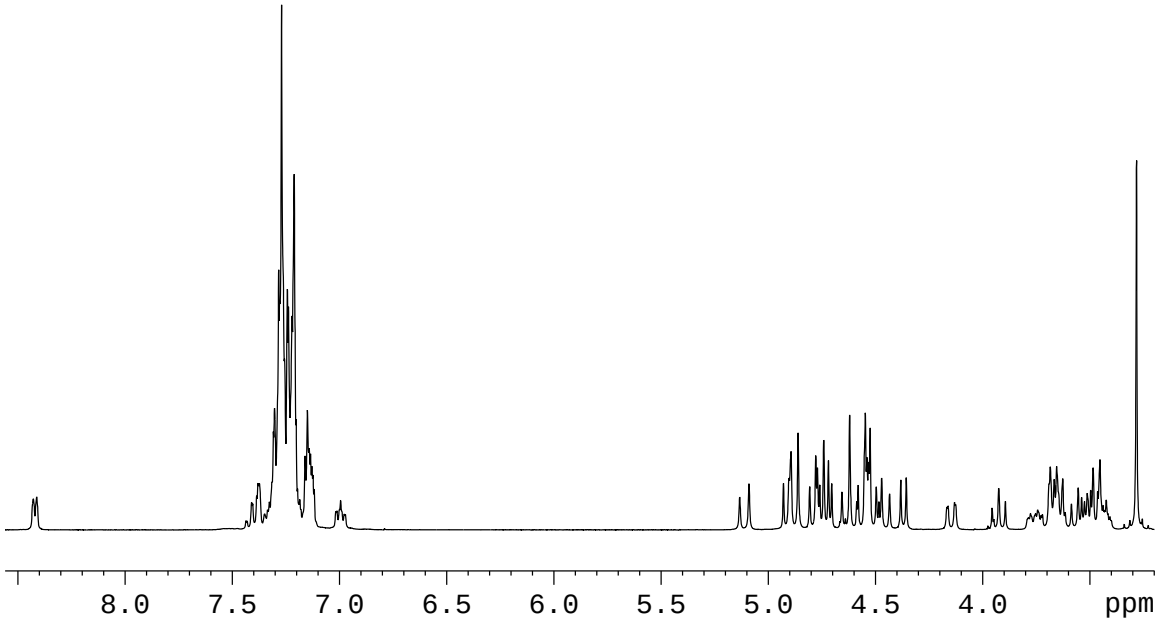

BnO
OBn
O
BnO
S
N
PicO
S

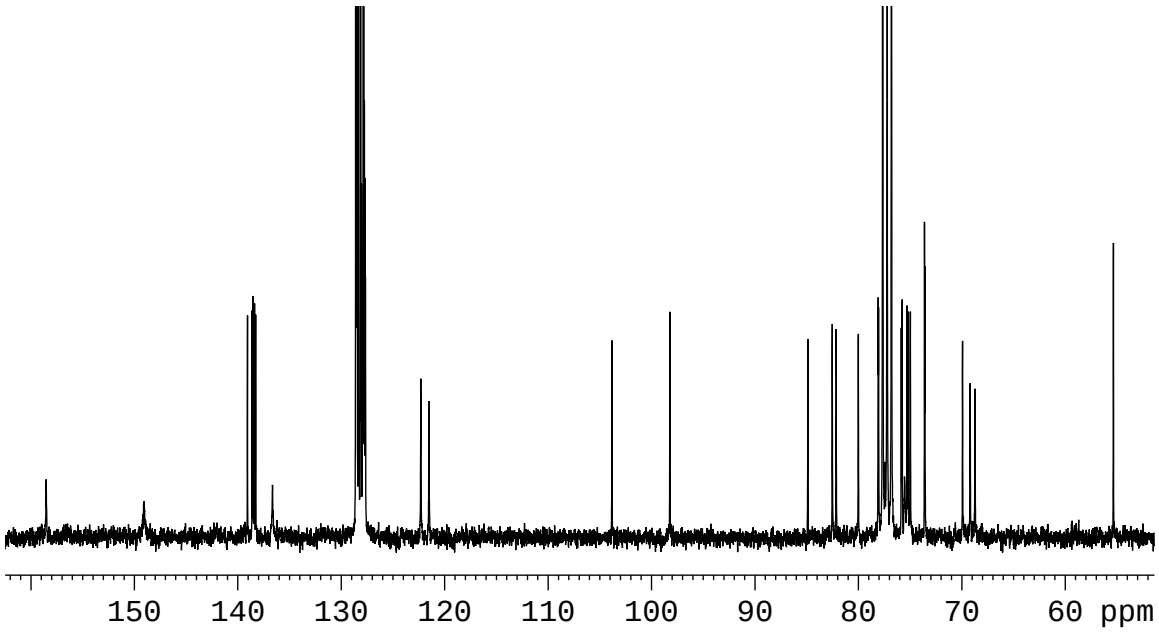
16b

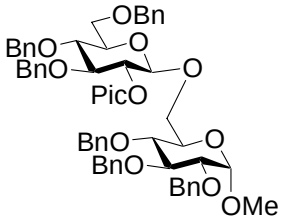

ppm
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 ppm


OBn
O
BnO
BnO
O
PicO
BnO
O
BnO
BnO
OMe

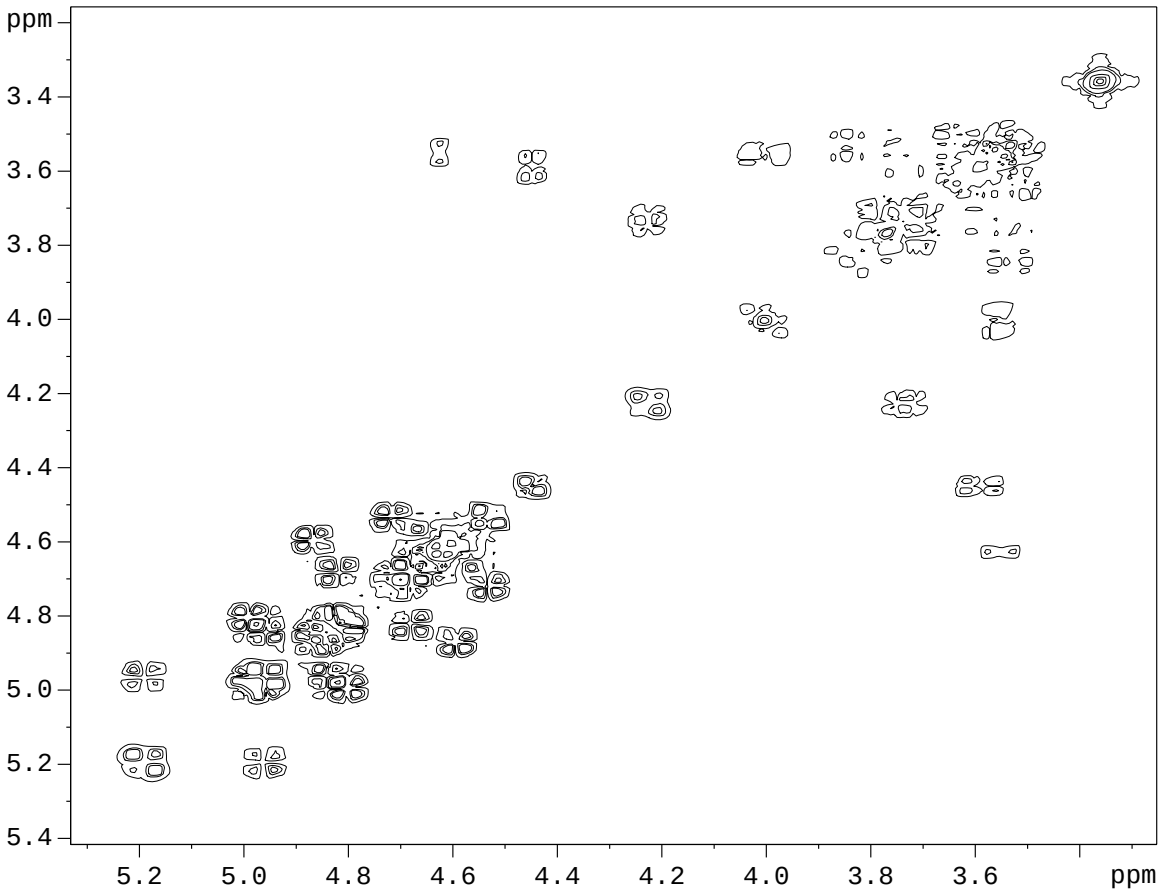
23

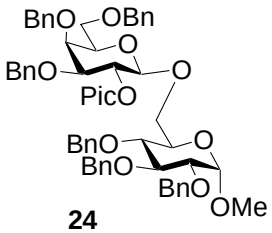

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm


150
140
130
120
110
100
90
80
70
60
ppm

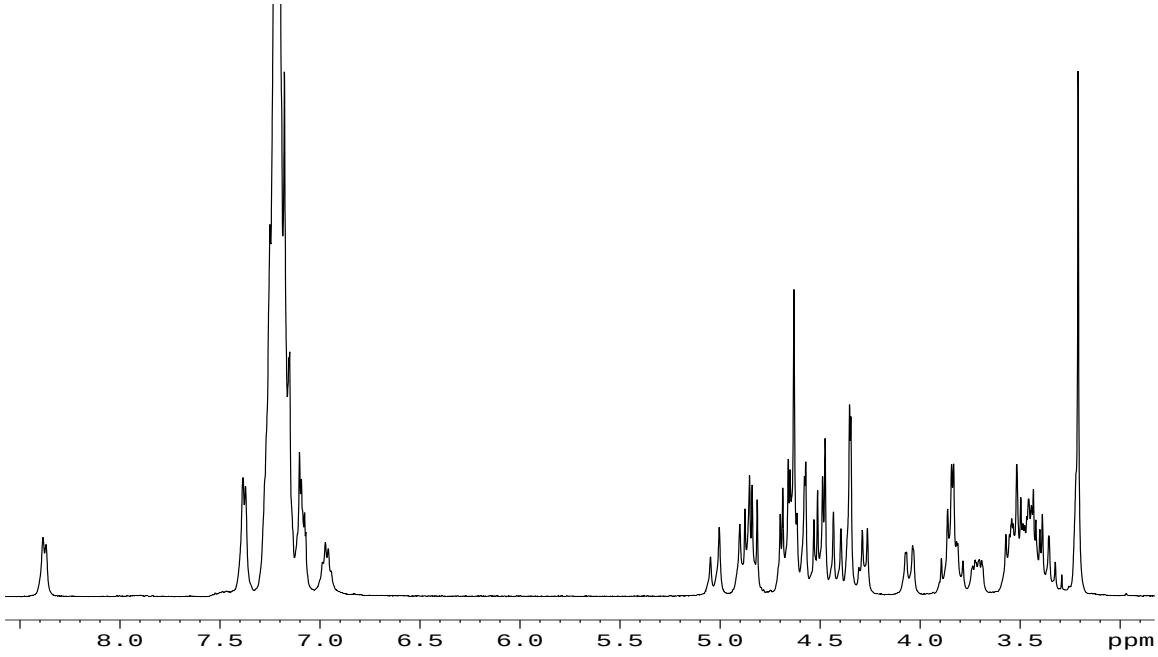

OBn
O
BnO
BnO
O
PicO
BnO
O
BnO
BnO
OMe

23


ppm
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
ppm


BnO
OBn
O
BnO
O
PicO
BnO
O
BnO
BnO
OMe

24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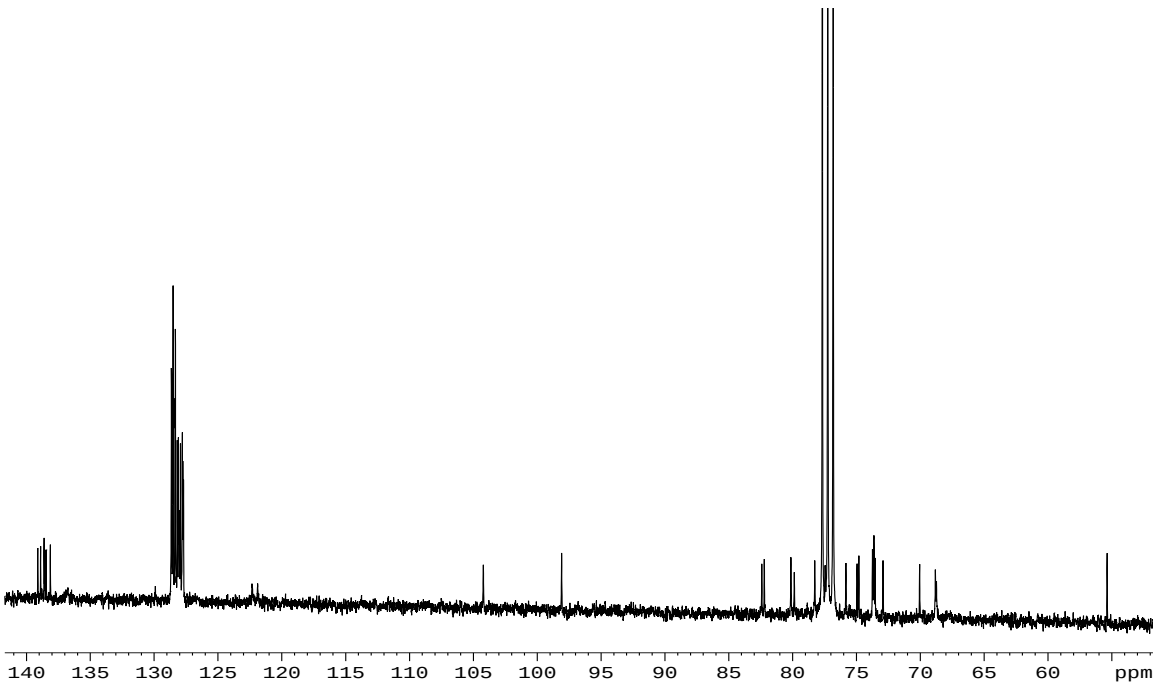
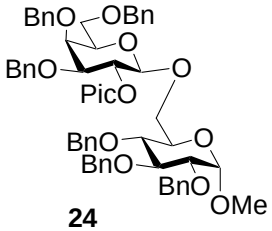
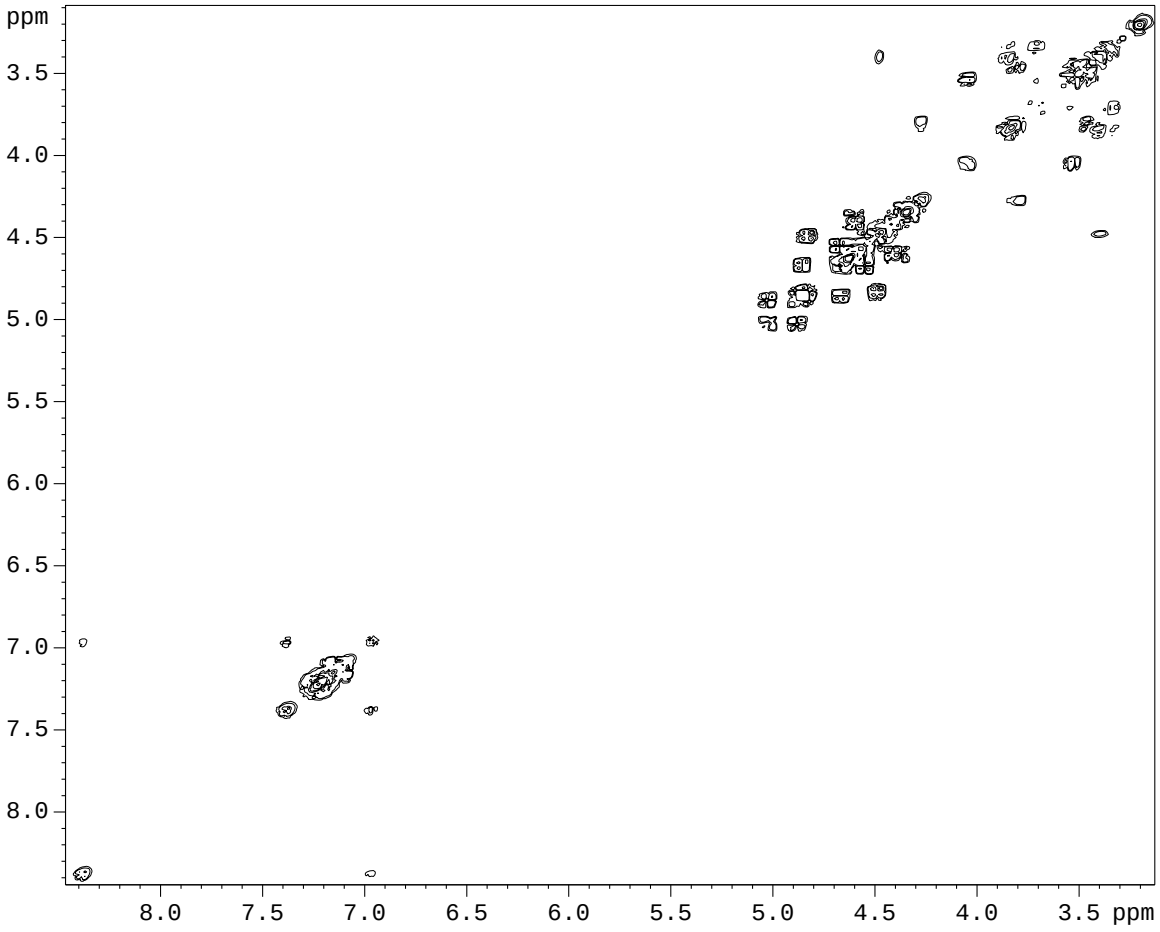
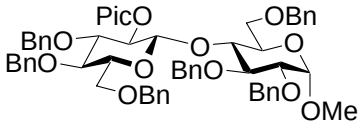
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm


140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
ppm

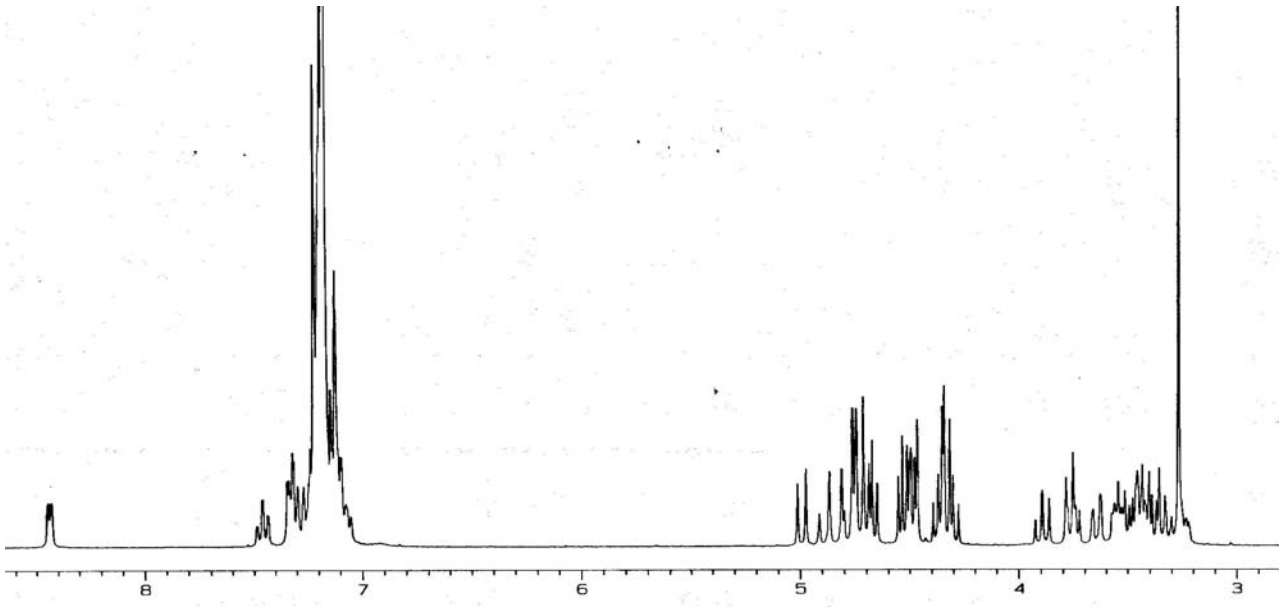

BnO
OBn
O
BnO
O
PicO
BnO
O
BnO
BnO
OMe

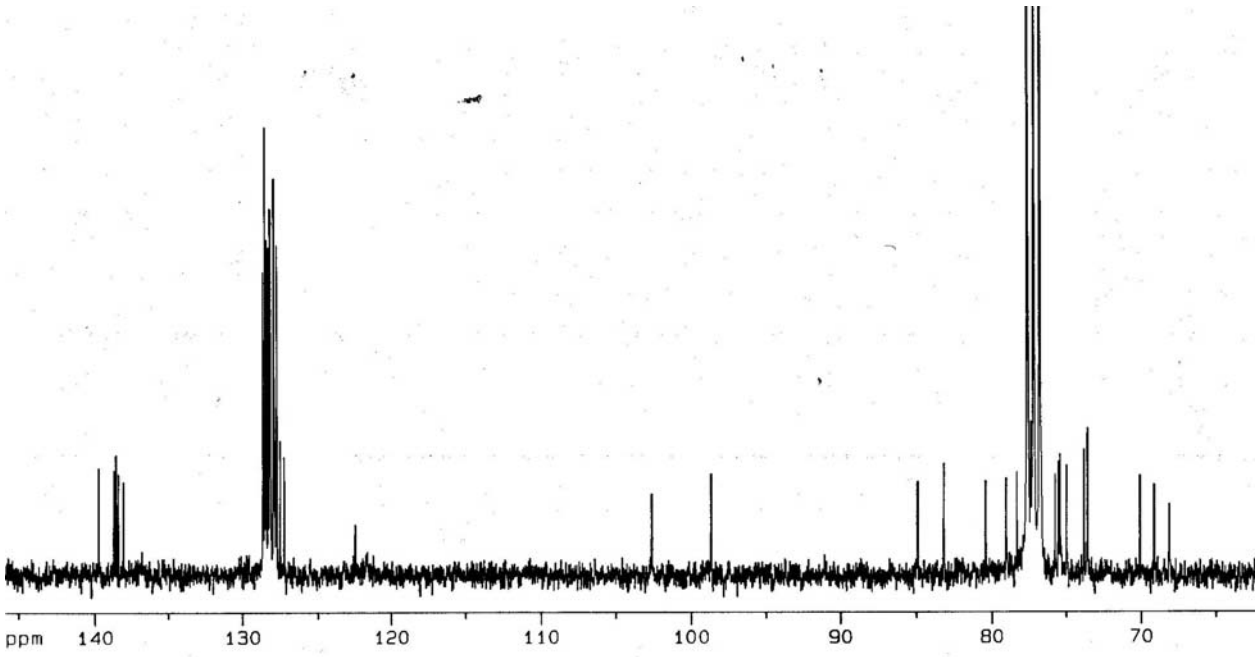
24


ppm
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 ppm


PicO
OBn
BnO
BnO
O
O
BnO
O
OBn
BnO
OMe

25


8
7
6
5
4
3


ppm
140
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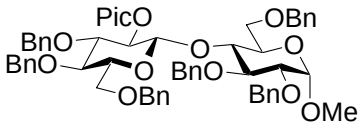
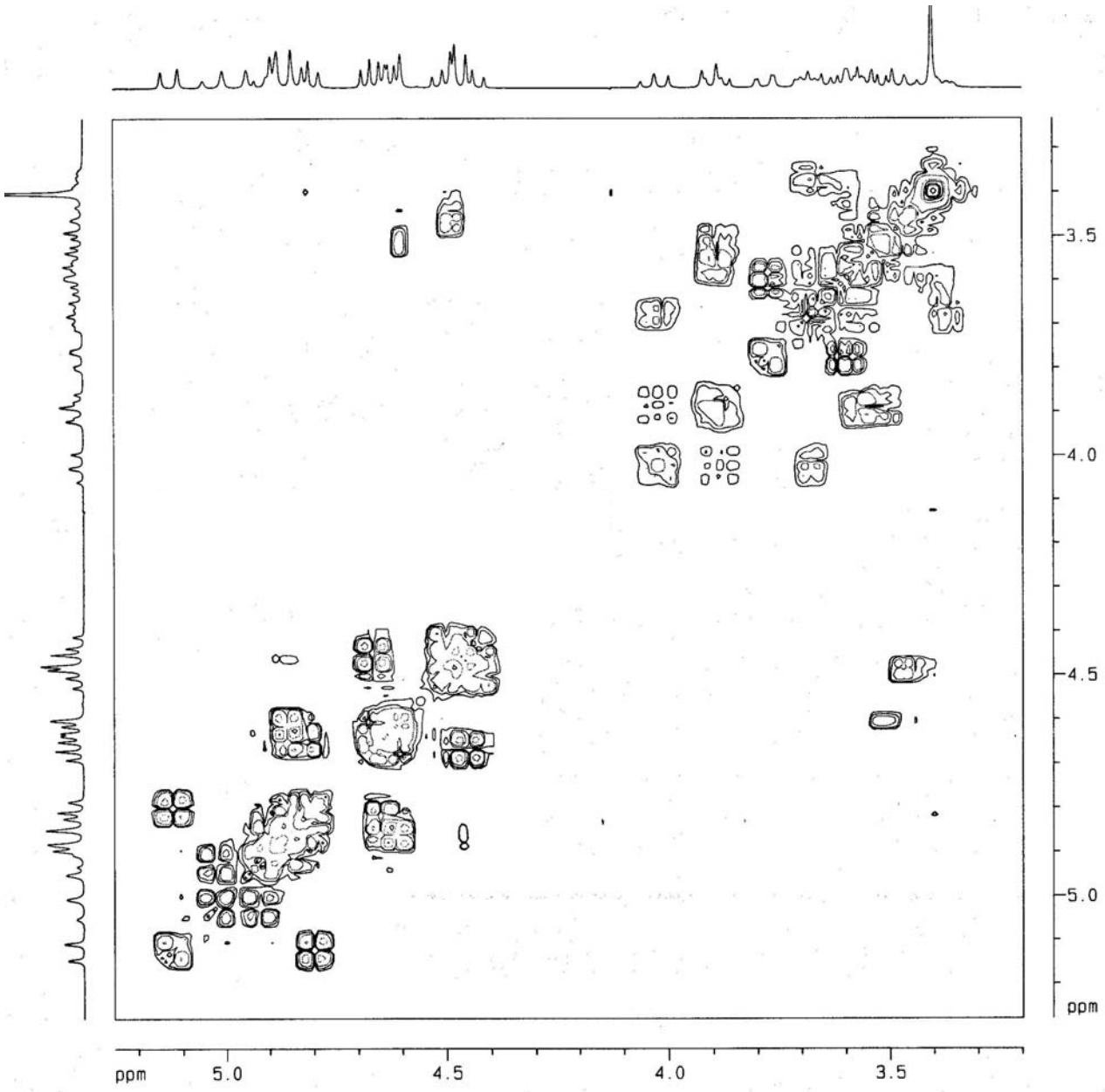
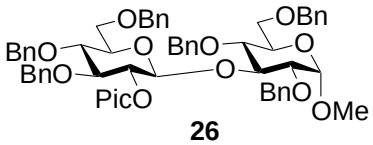
110
100
90
80
70

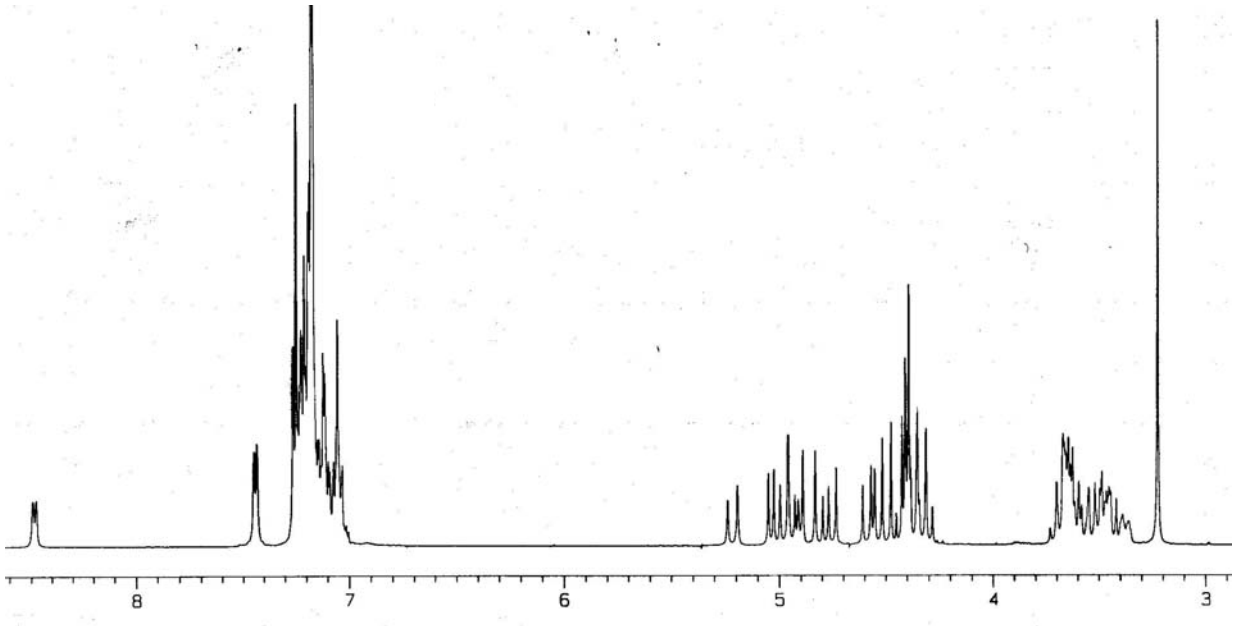

PicO
BnO
BnO
O
OBn
O
BnO
OBn
O
BnO
OMe

25


3.5
4.0
4.5
5.0
ppm
ppm
5.0
4.5
4.0
3.5


OBn
BnO
O
BnO
BnO
PicO
OBn
BnO
O
O
BnO
OMe

26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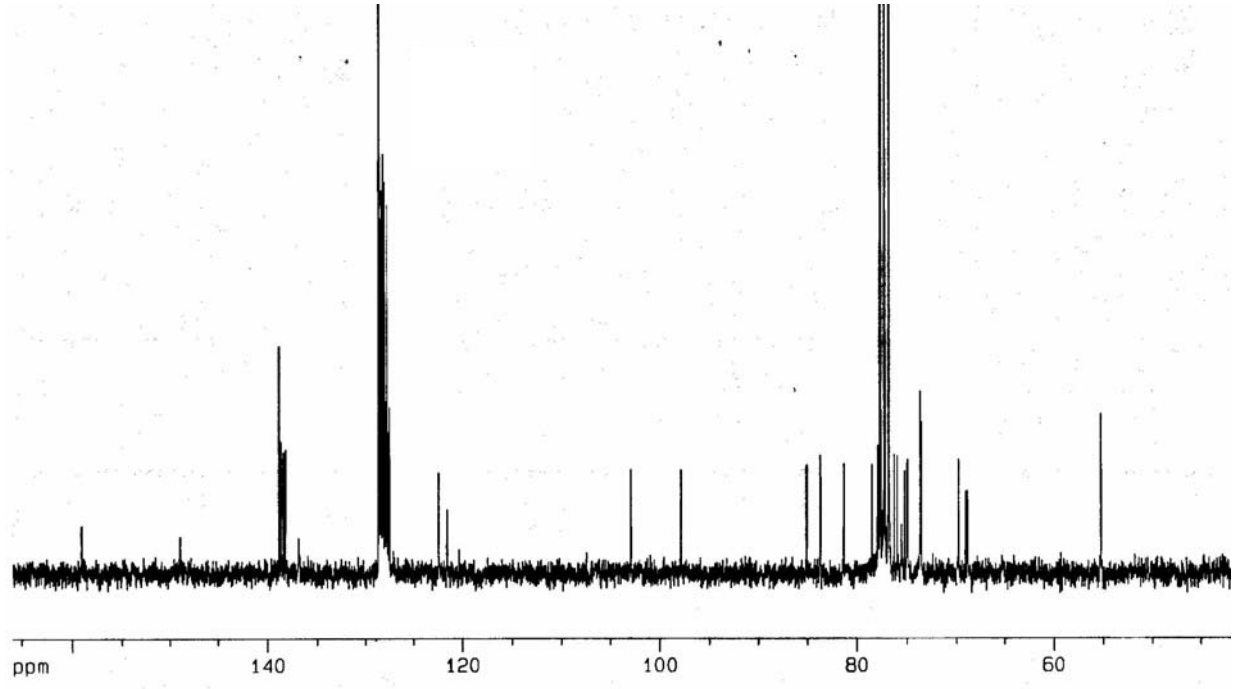
6
5
4
3


ppm
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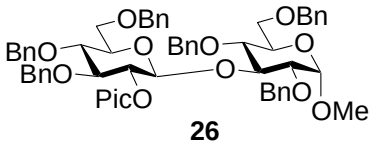
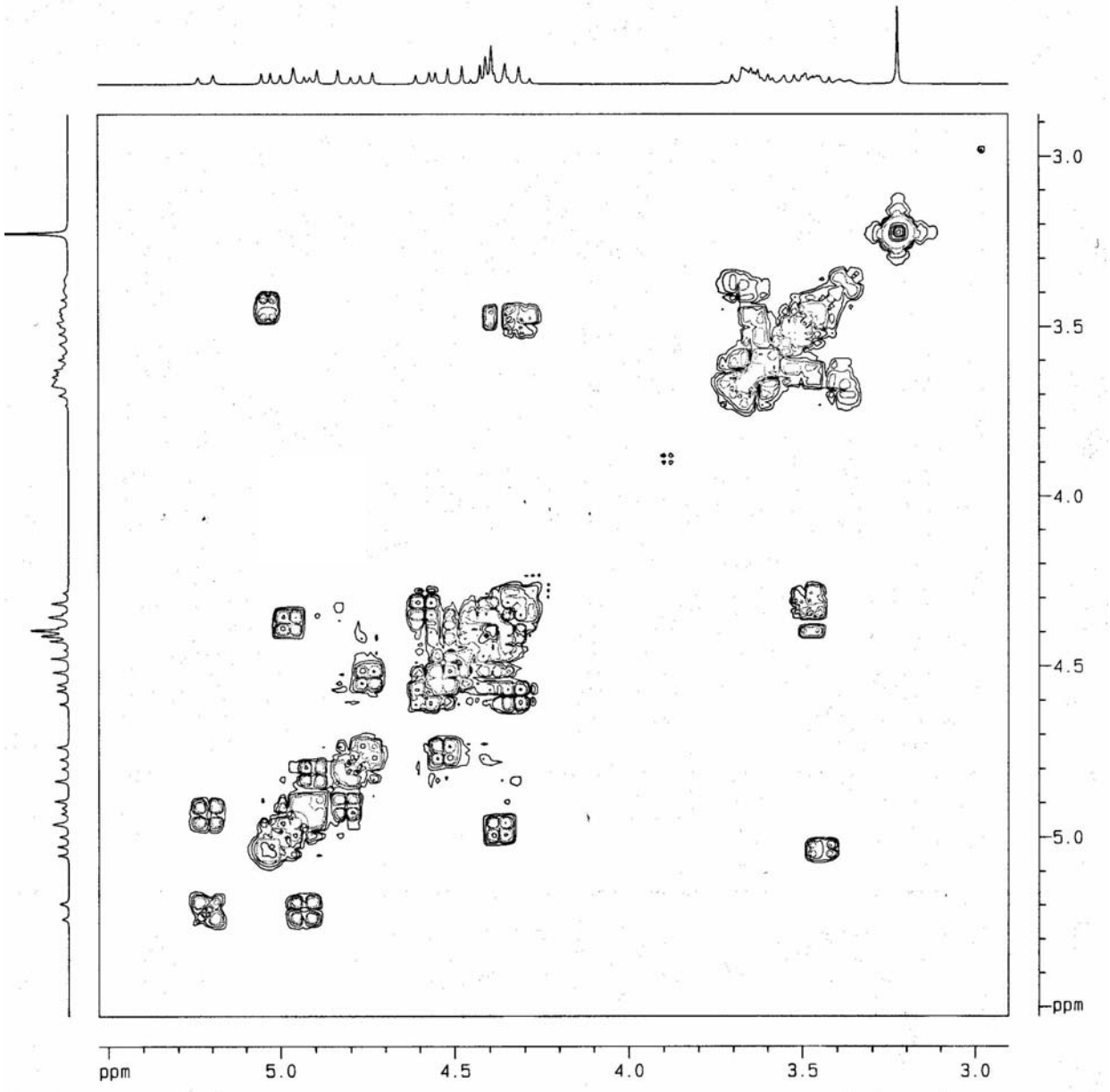
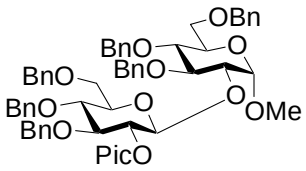
120
100
80
60

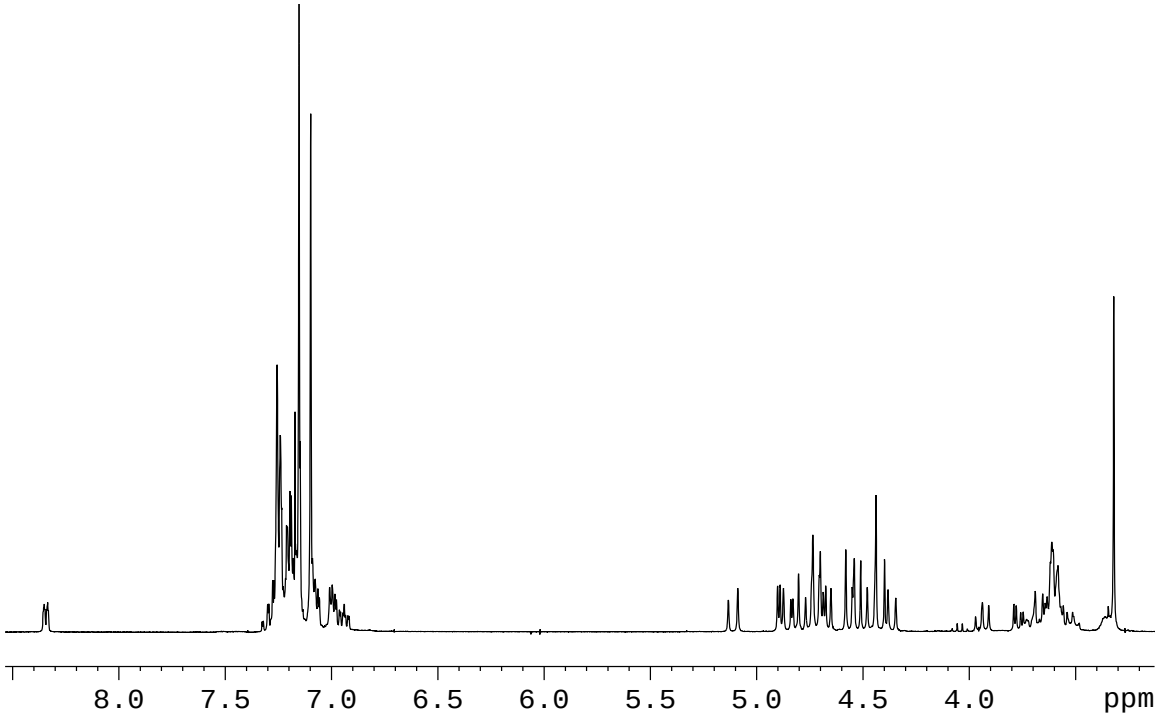

OBn
BnO
O
BnO
BnO
O
PicO
OBn
O
BnO
OMe

26


3.0
3.5
4.0
4.5
5.0
ppm
ppm
5.0
4.5
4.0
3.5
3.0


OBn
BnO
O
BnO
BnO
O
O
OMe
BnO
BnO
PicO

27


8.0
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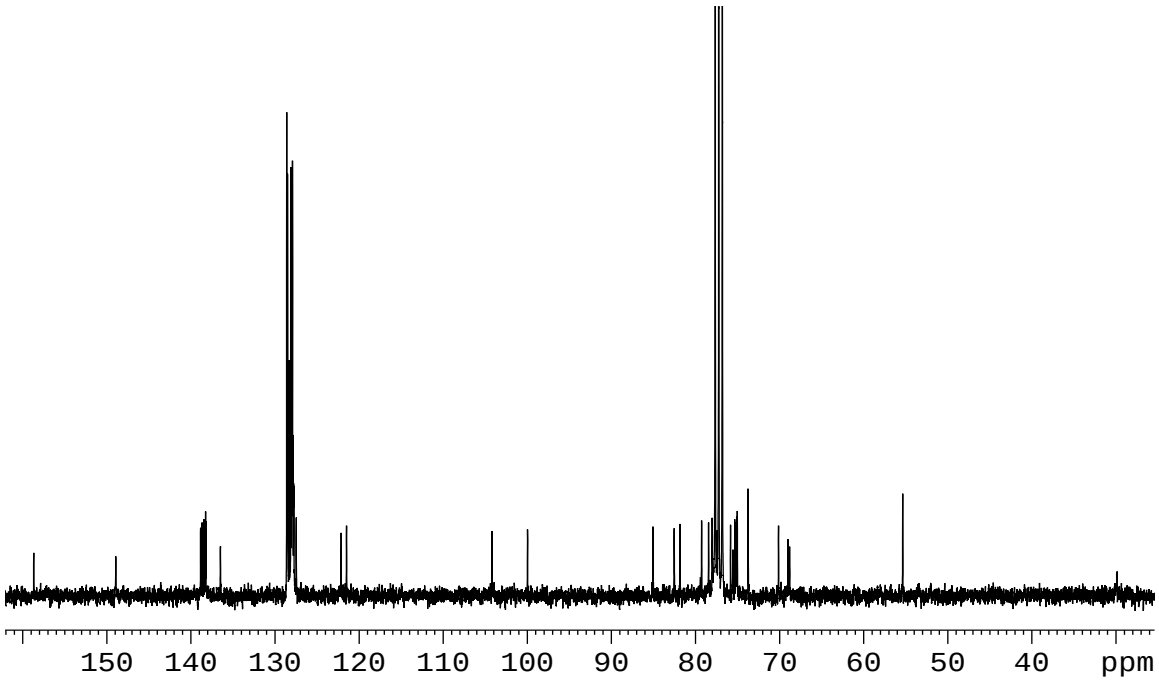
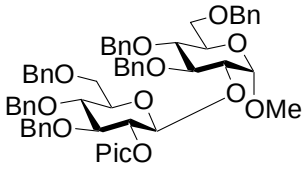
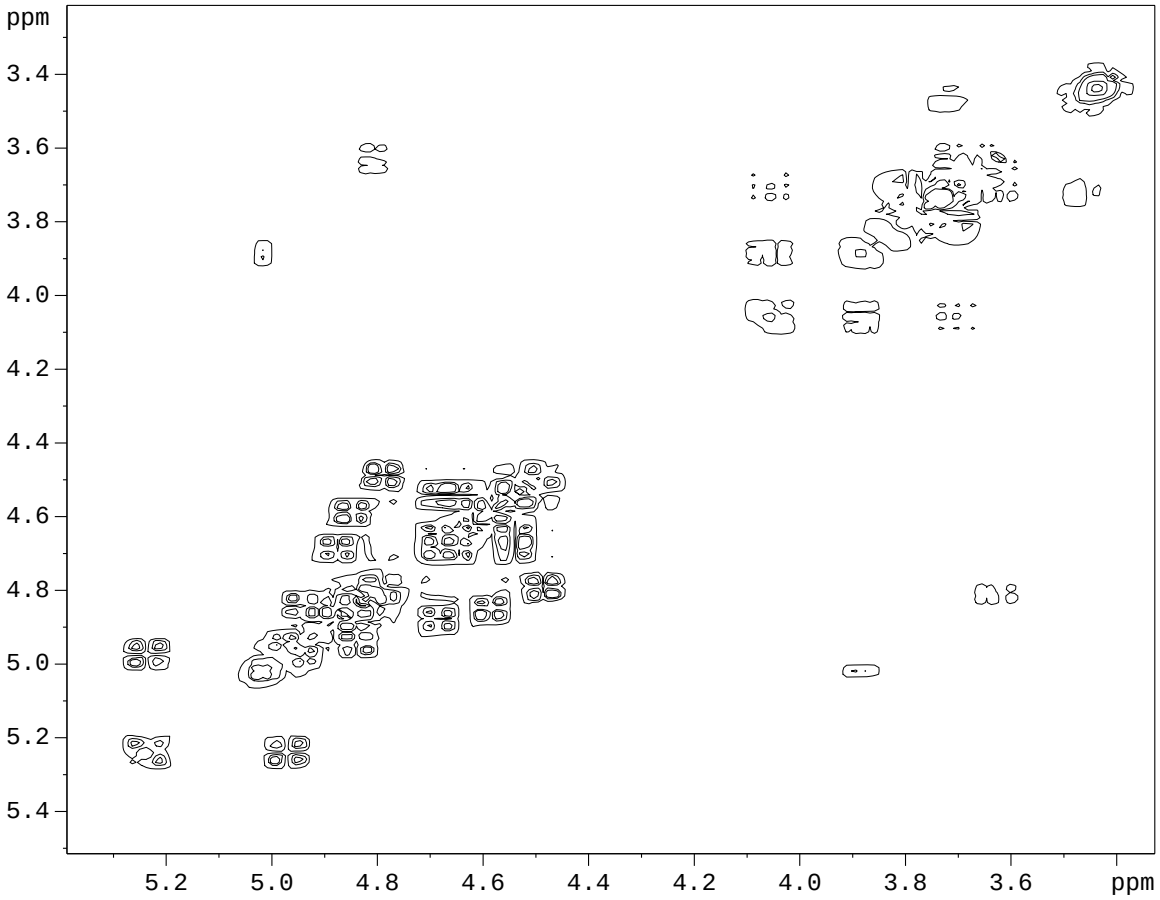
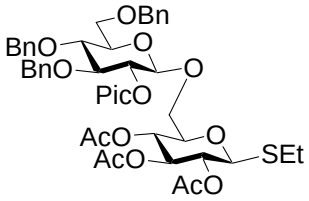
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm


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

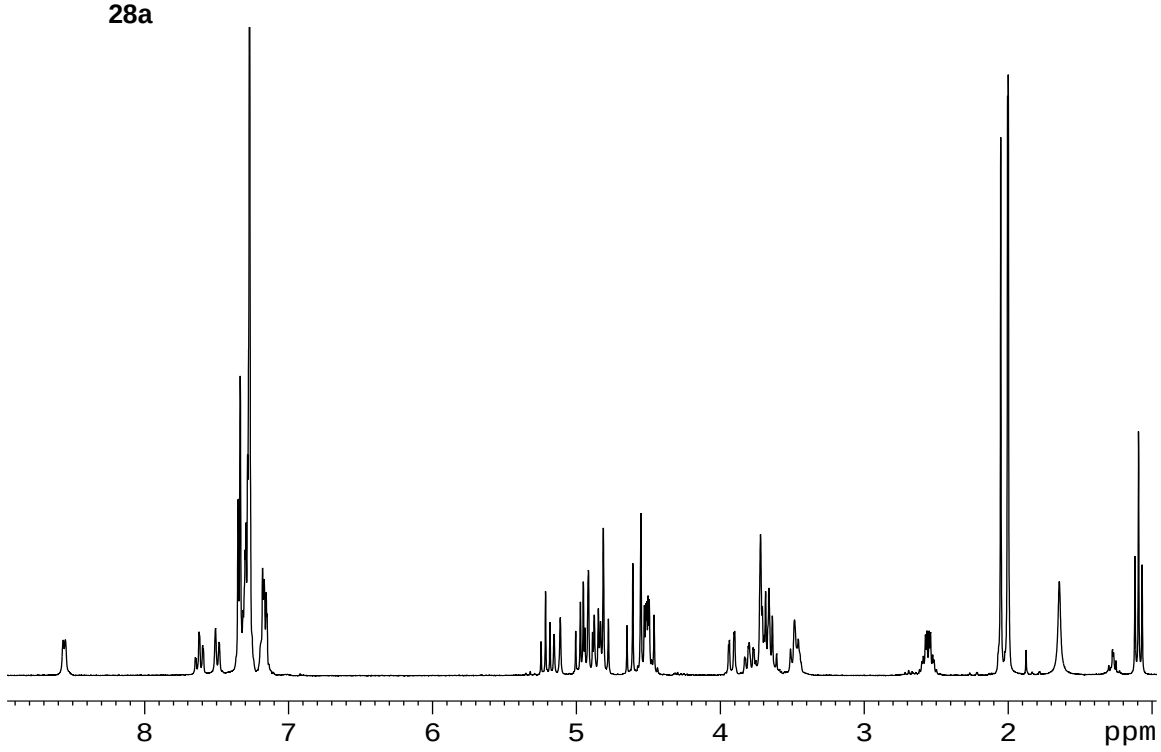

OBn
BnO
O
BnO
BnO
O
O
OMe
BnO
BnO
PicO

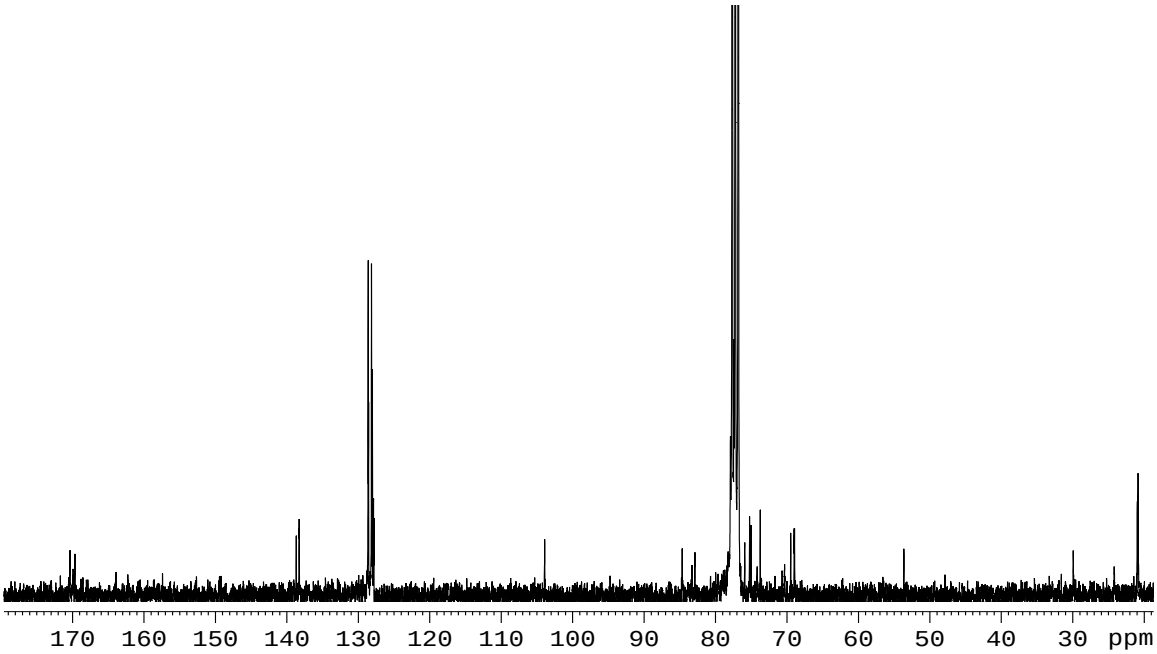
27

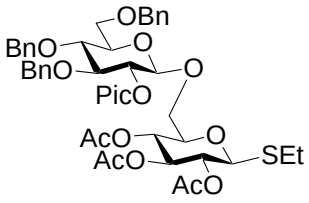

ppm
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
ppm


OBn
BnO
O
BnO
O
PicO
AcO
O
AcO
SEt
AcO

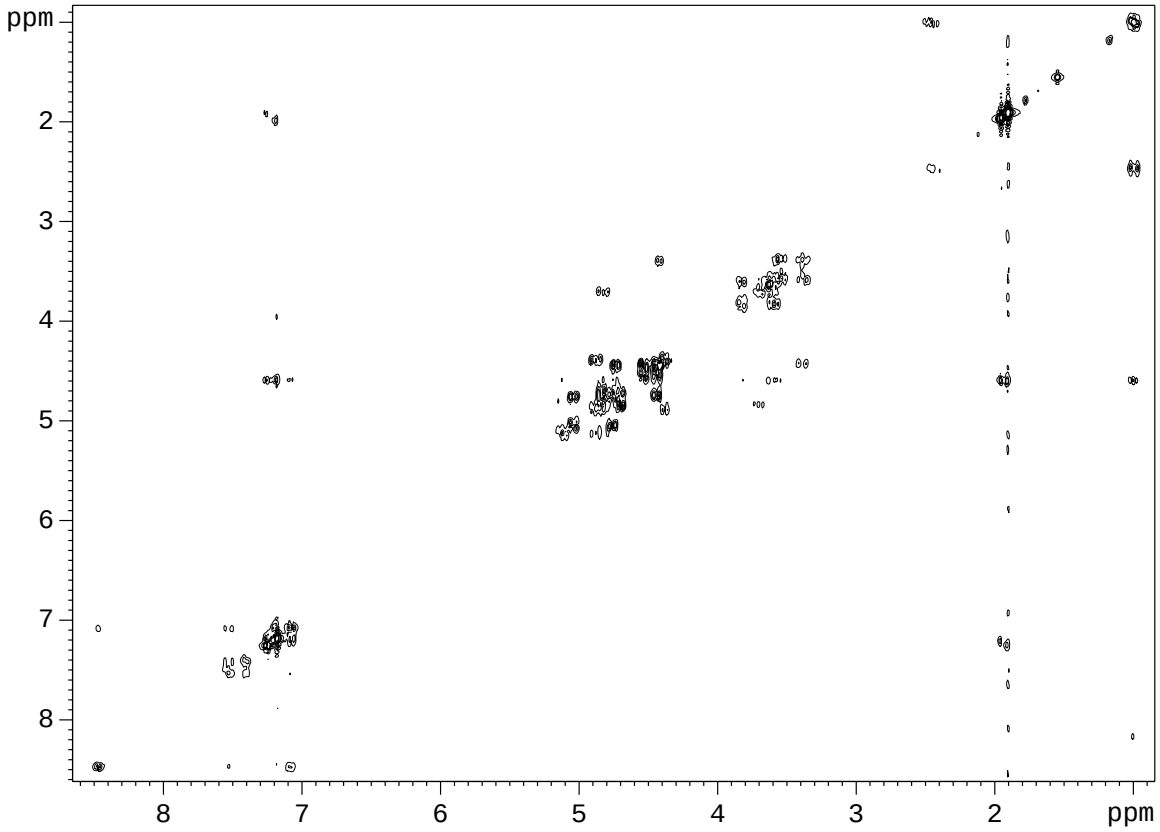
28a

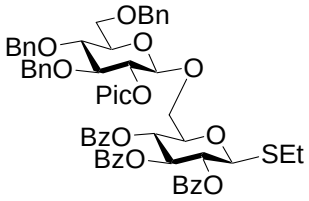

8
7
6
5
4
3
2
ppm


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

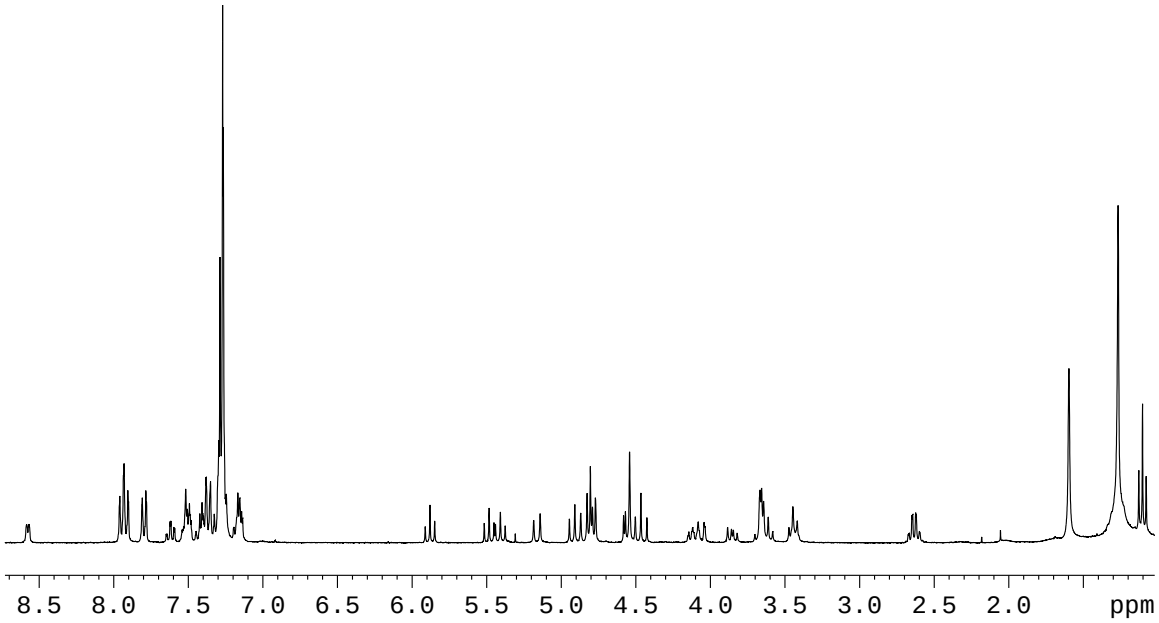


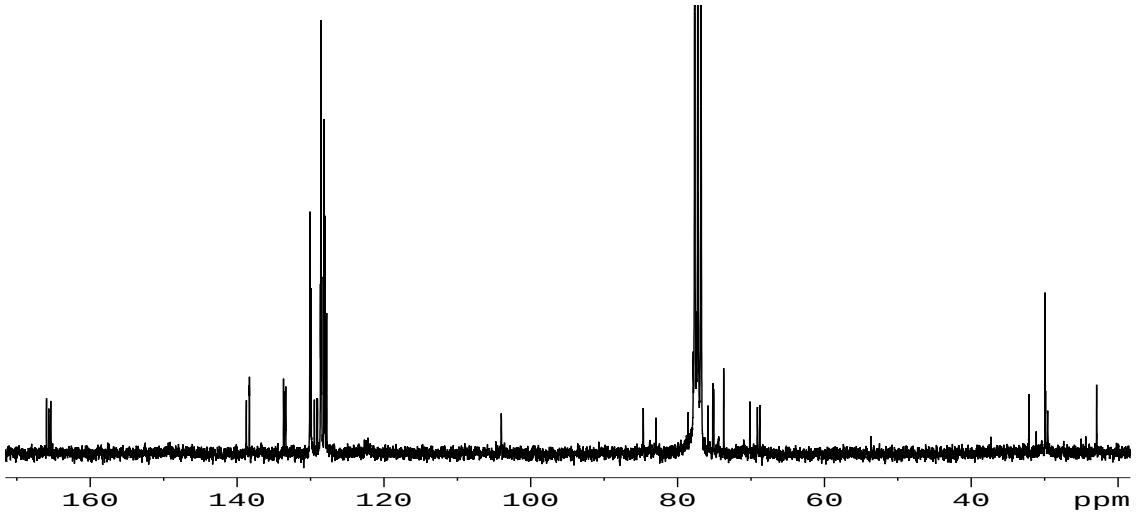
28a

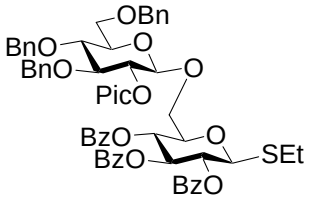



OBn
BnO
O
BnO
O
PicO
BzO
O
BzO
SEt
BzO

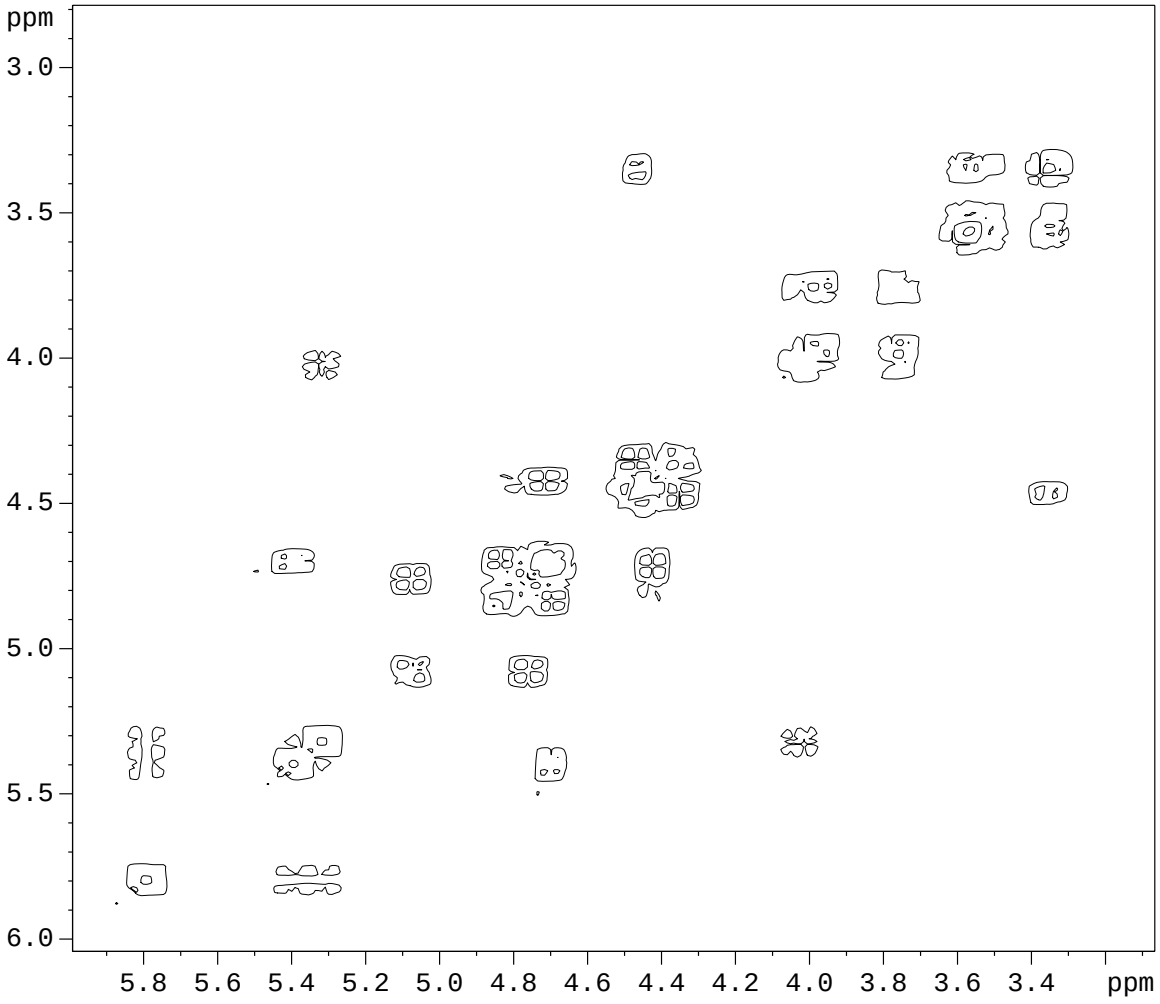
28b

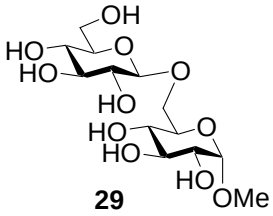

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm


160 140 120 100 80 60 40 ppm

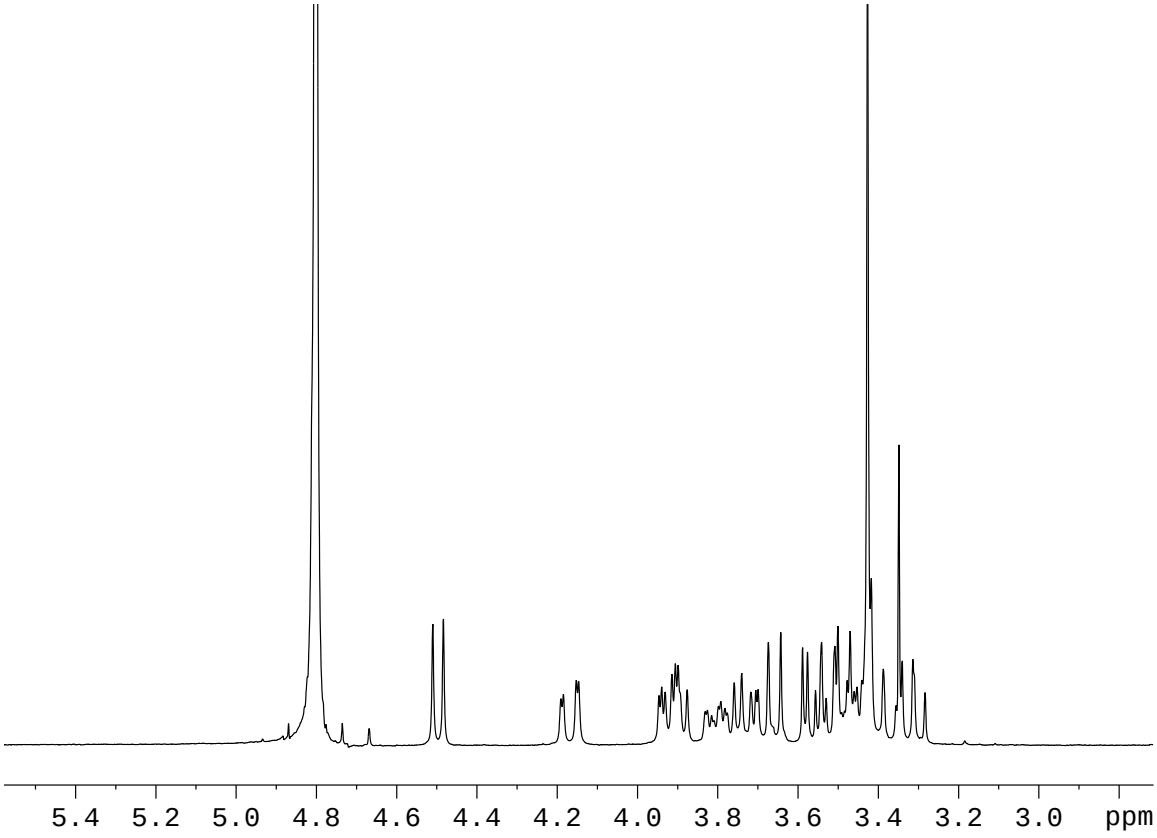

OBn
BnO
O
BnO
O
PicO
BzO
O
BzO
SEt
BzO

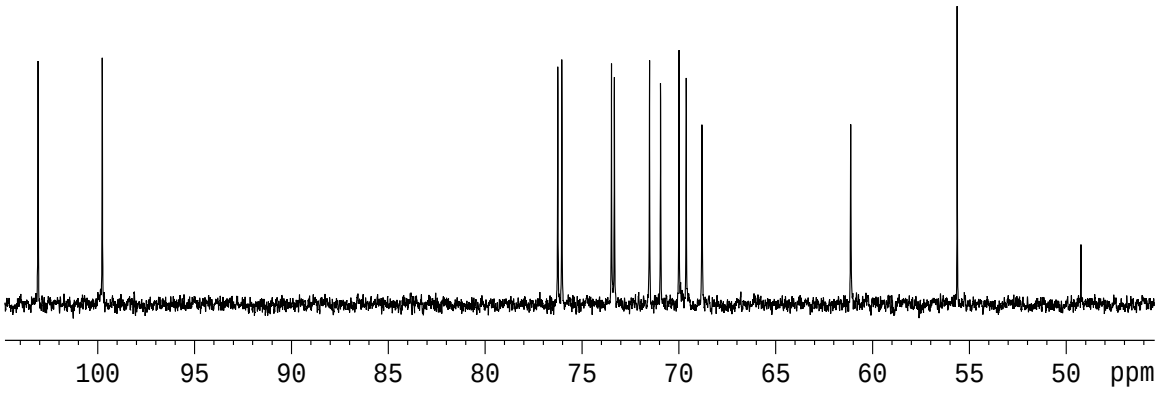
28b

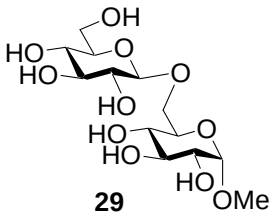

ppm
3.0
3.5
4.0
4.5
5.0
5.5
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
ppm


OH
HO
O
HO
O
HO
HO
O
HO
HO
OMe

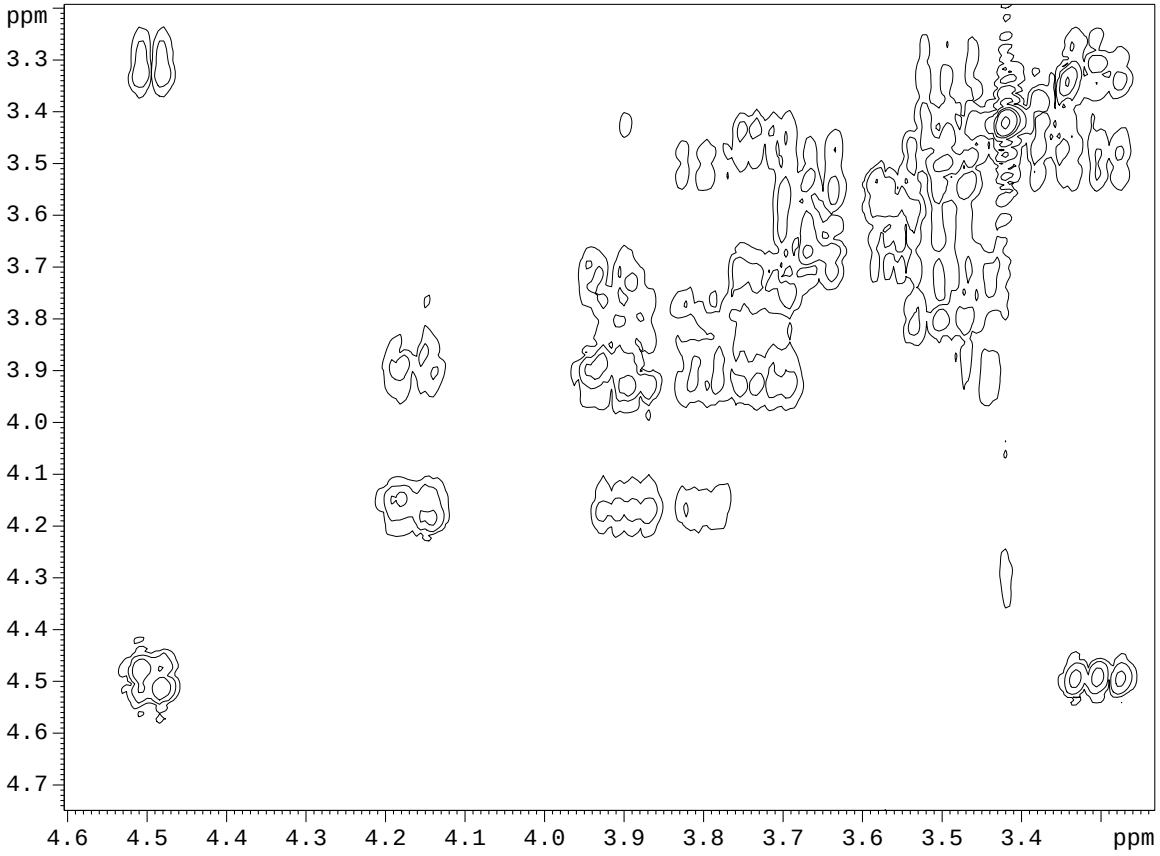
29

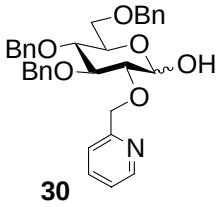

5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
ppm


100
95
90
85
80
75
70
65
60
55
50
ppm

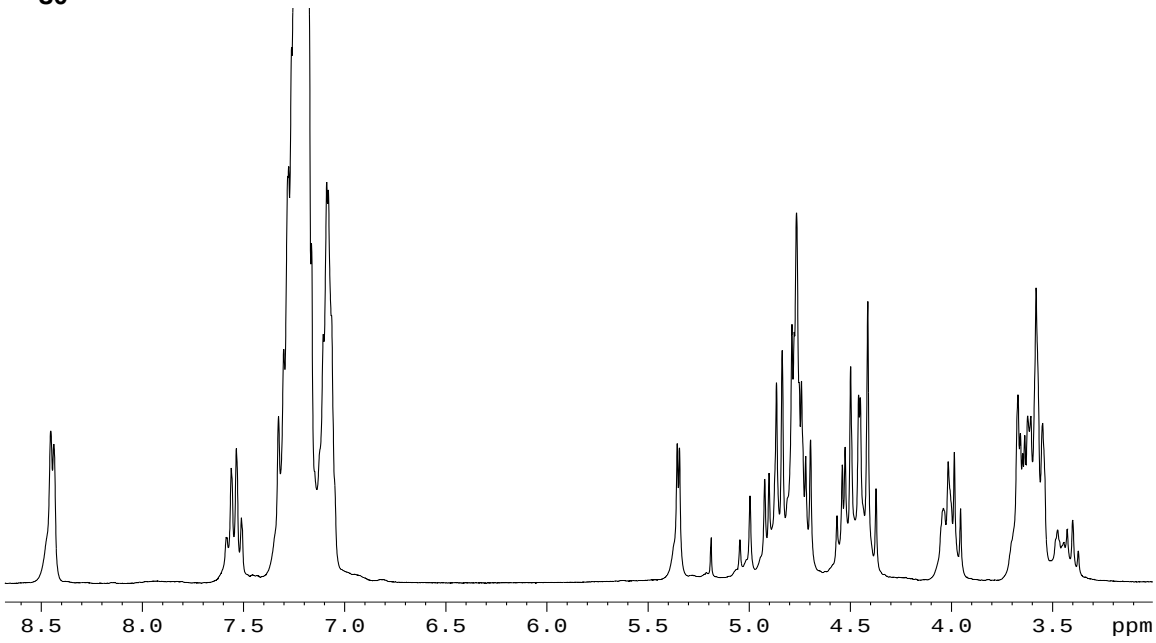

OH
HO
O
HO
O
HO
HO
O
HO
HO
OMe

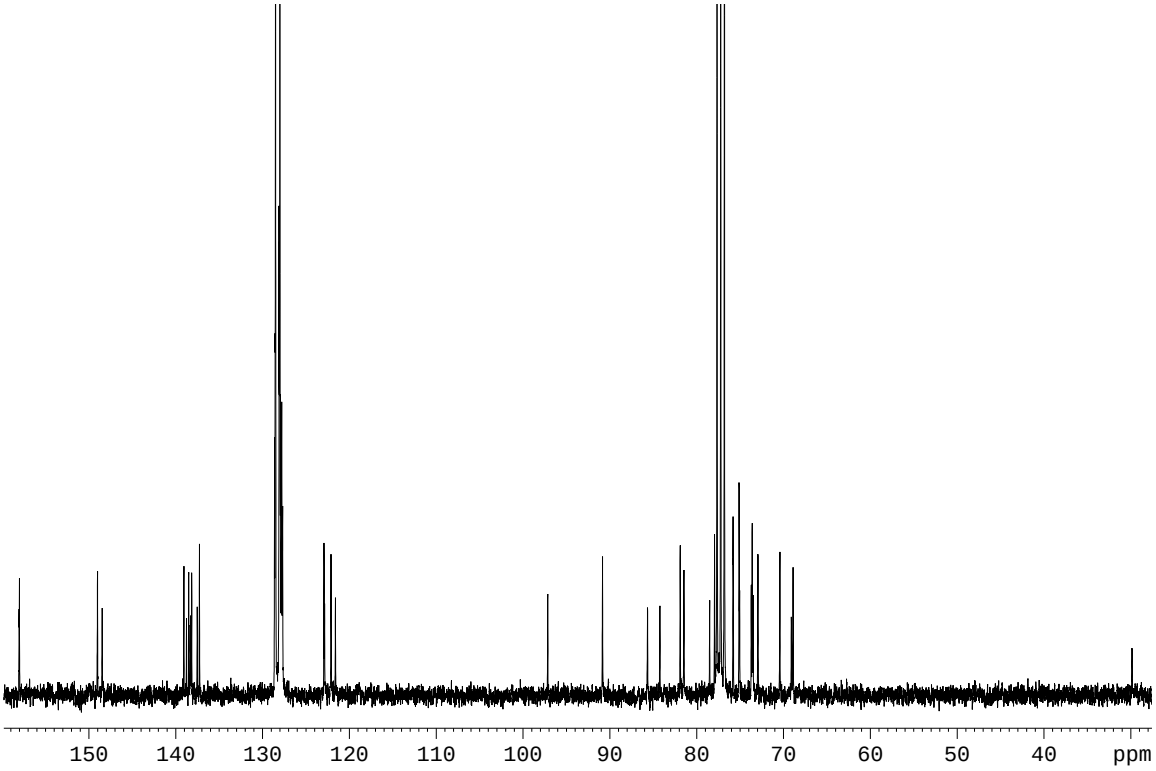
29

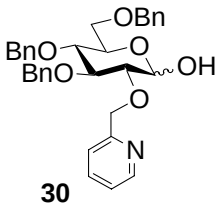

ppm
3.3
3.4
3.5
3.6
3.7
3.8
3.9
4.0
4.1
4.2
4.3
4.4
4.5
4.6
4.7
4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 ppm


OBn
BnO
O
BnO
OH
O
N

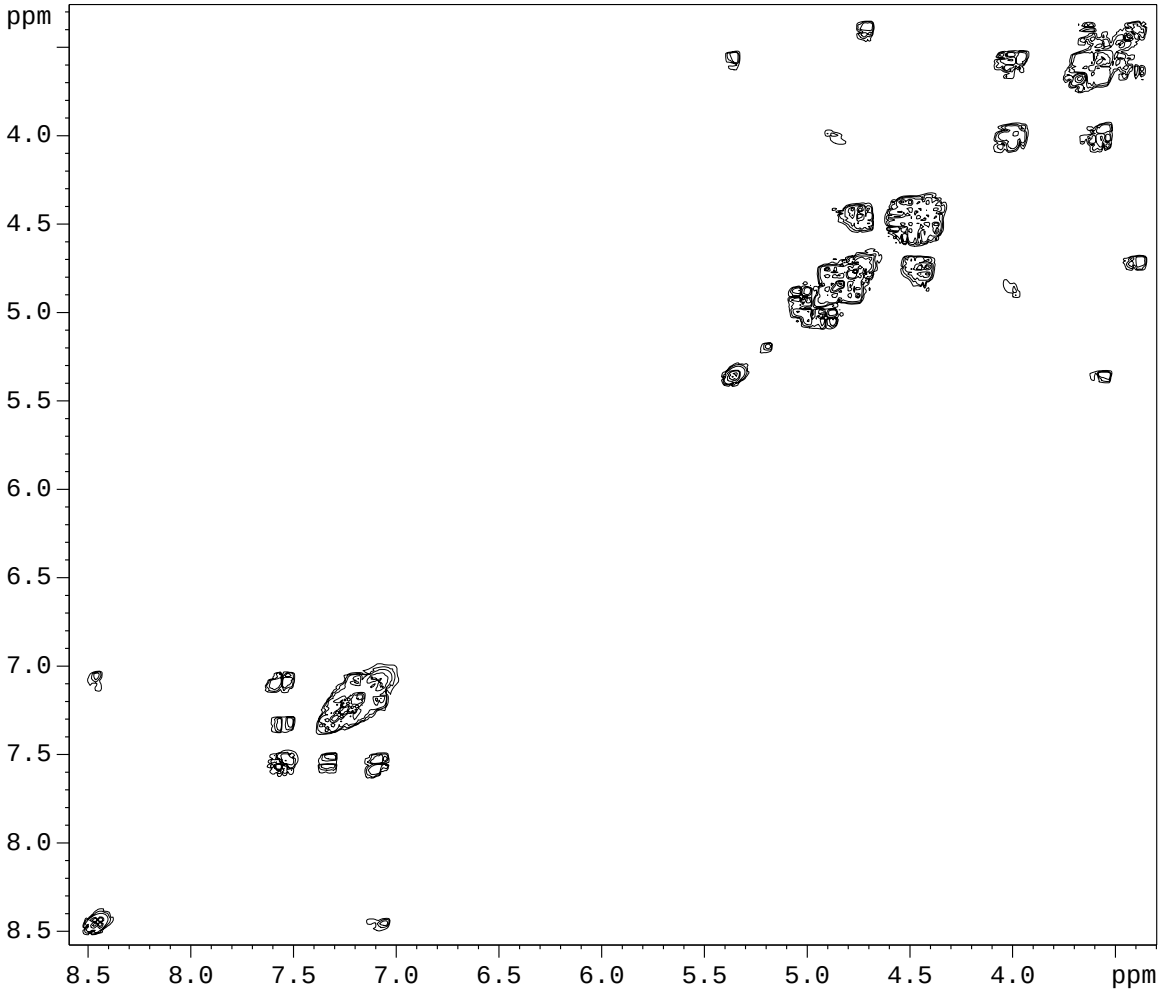
30

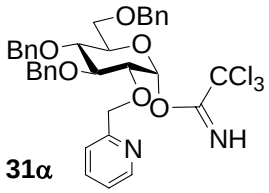

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm


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

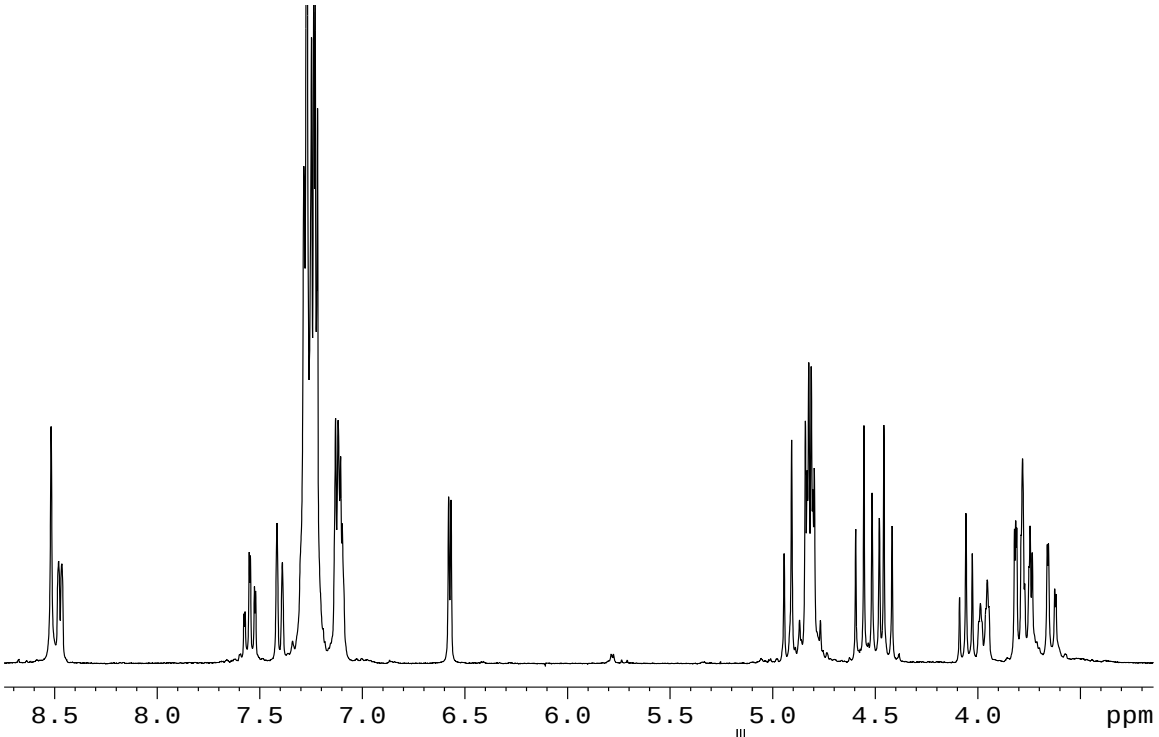

OBn
BnO
O
BnO
OH
O
N

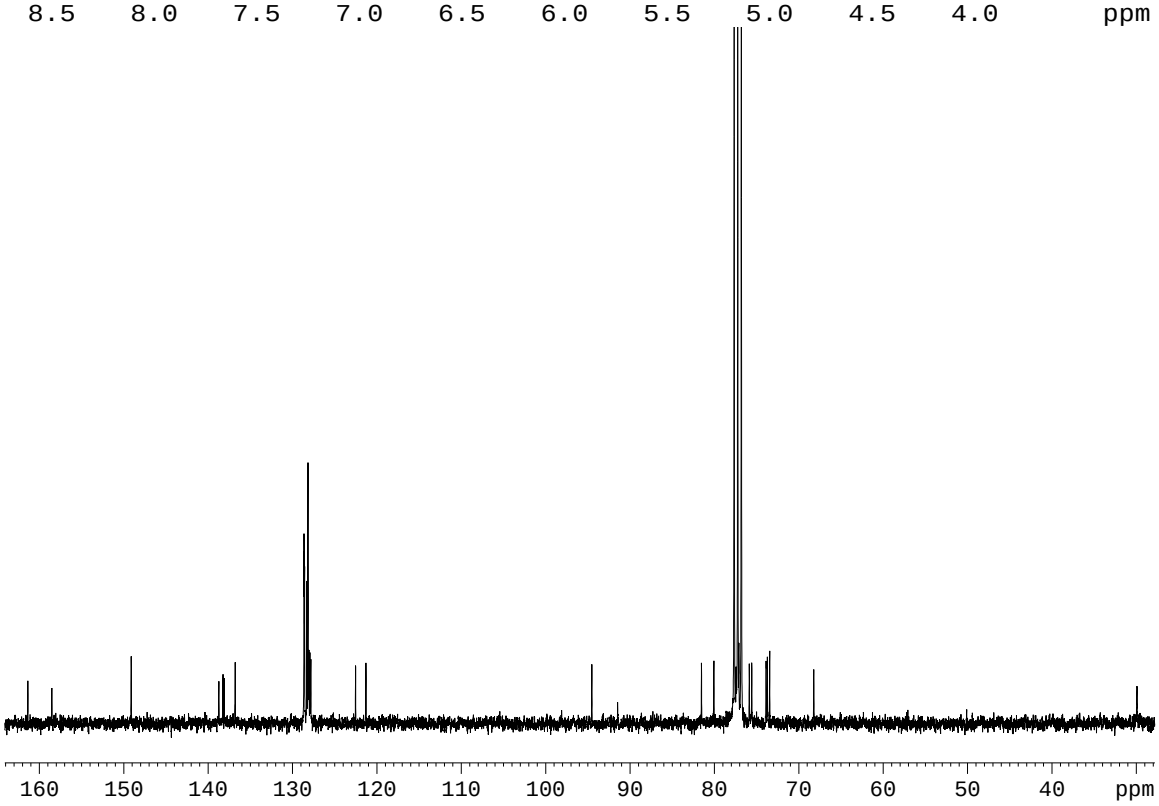
30

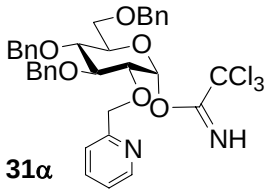

ppm
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm


OBn
BnO
BnO
O
O
O
CCl3
NH
N

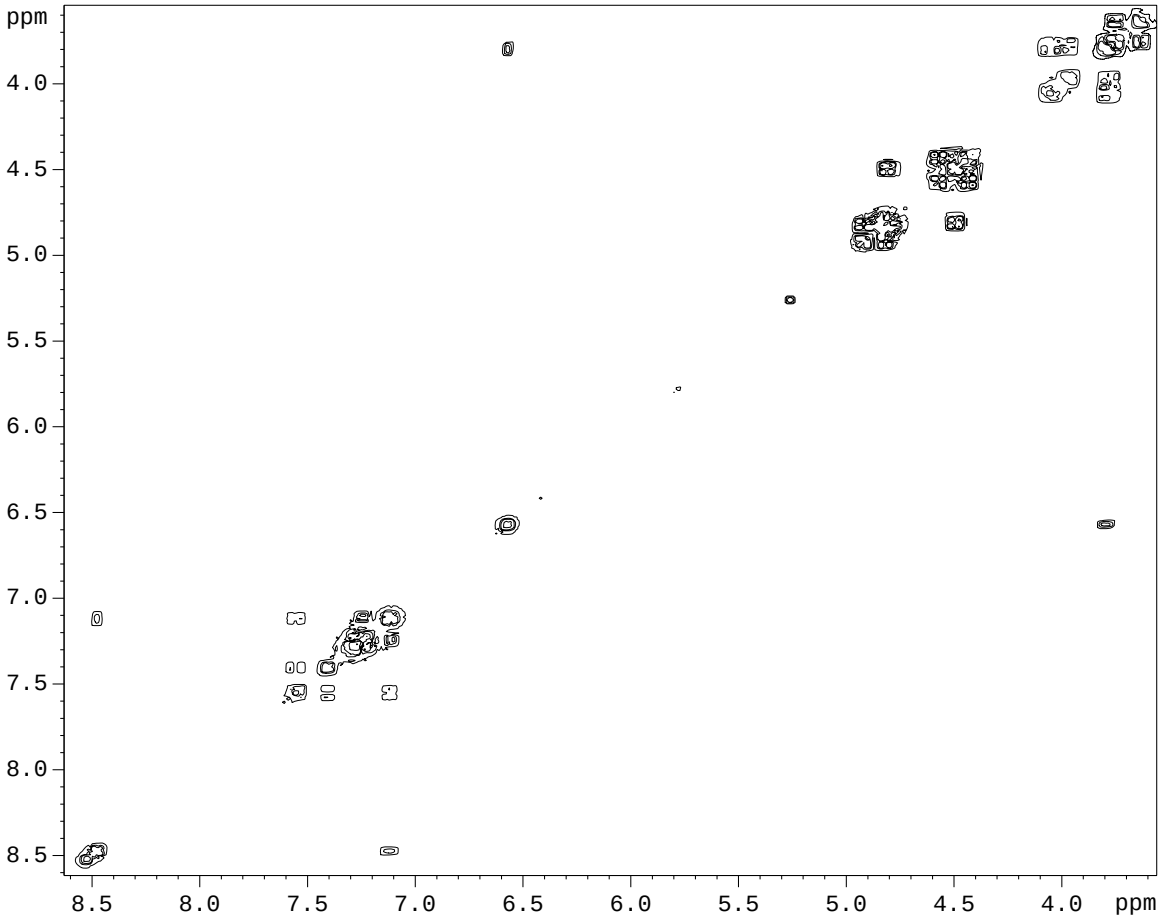
31α

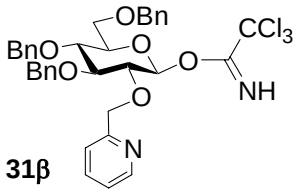

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm


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

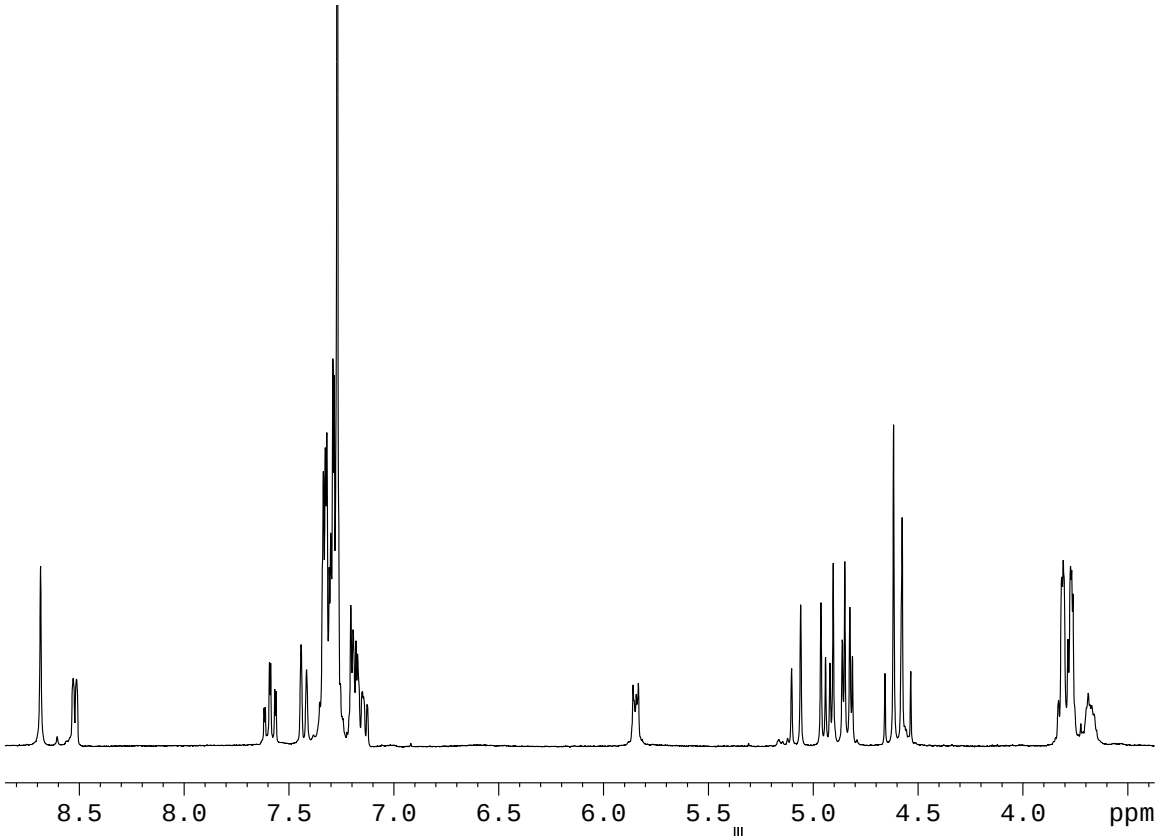

OBn
BnO
BnO
O
O
O
CCl3
NH
N

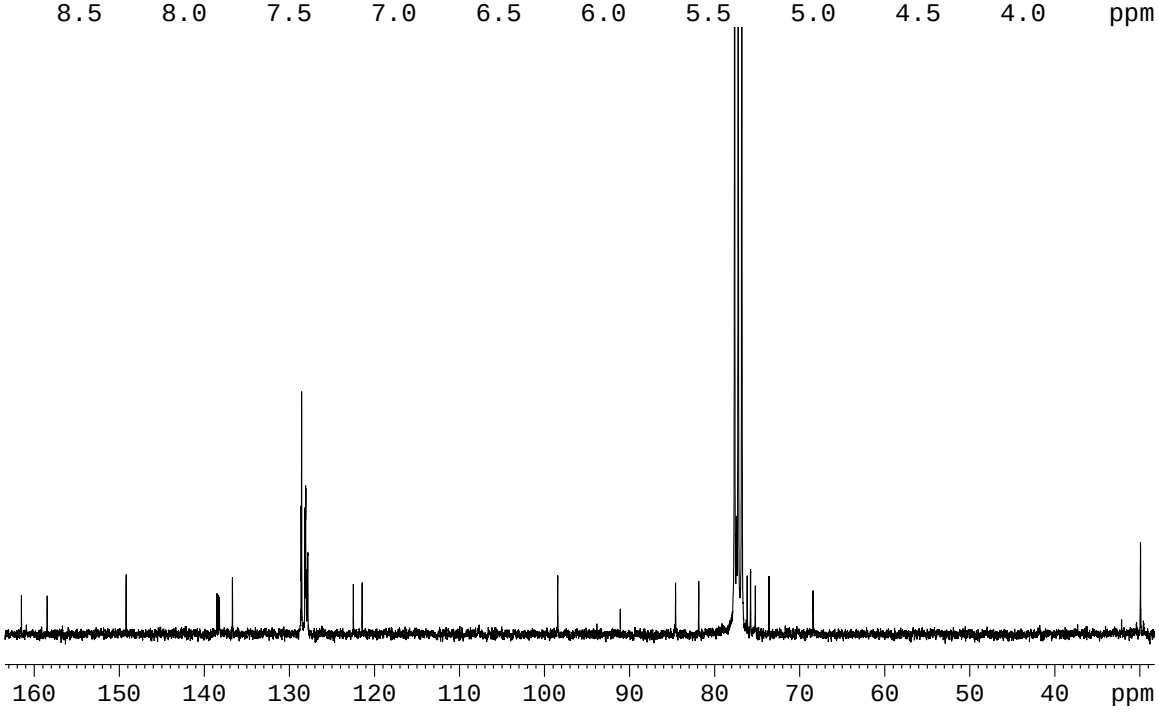
31α

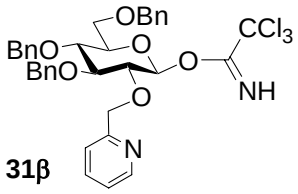

ppm
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm


OBn
BnO
BnO
O
O
CCl3
NH
O
N

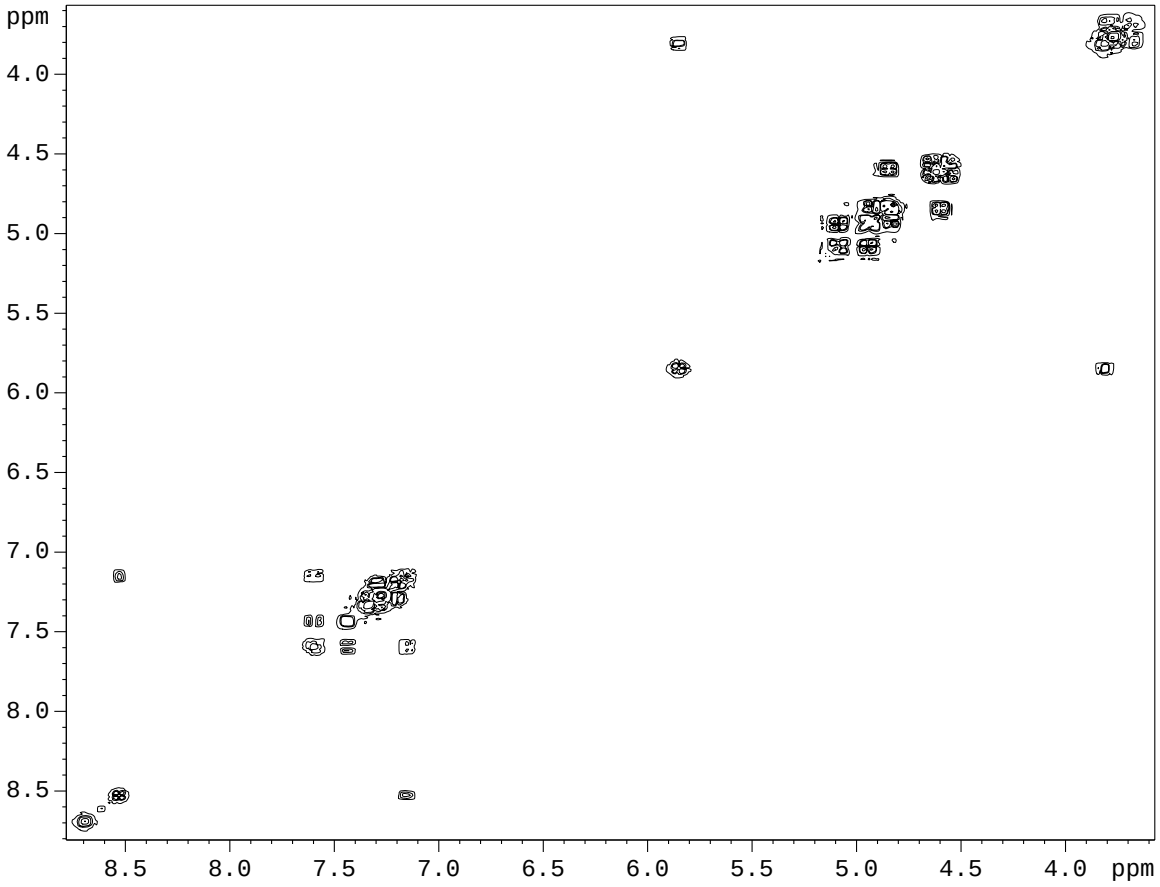
31β

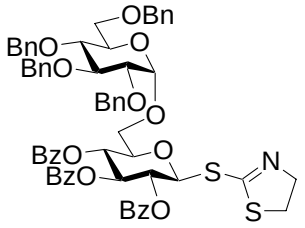

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm


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

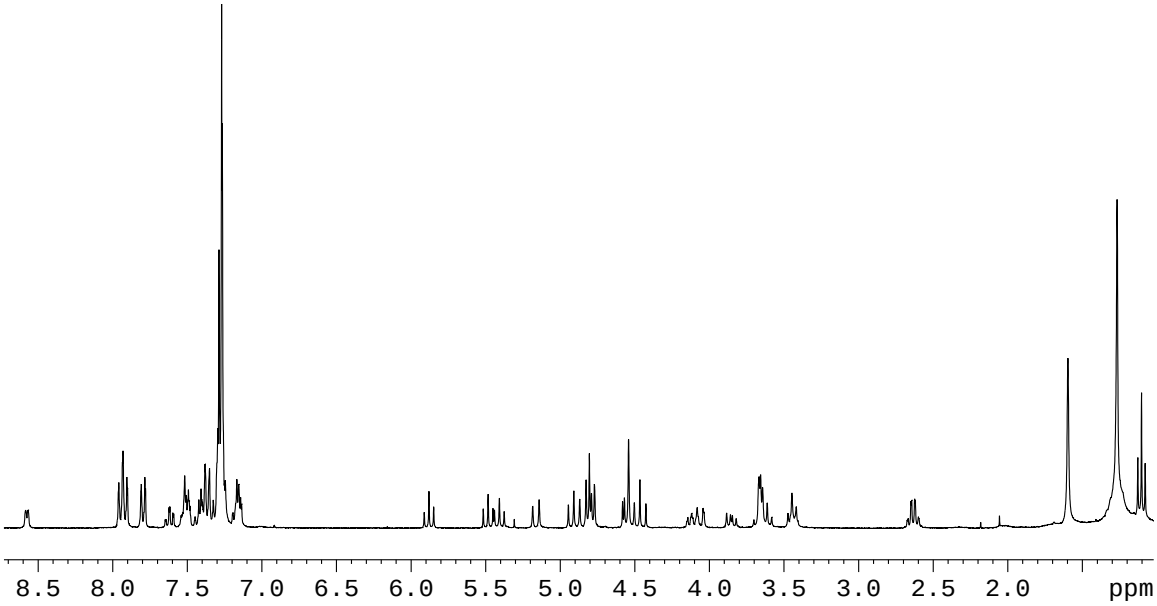

OBn
BnO
BnO
O
O
CCl3
NH
O
N

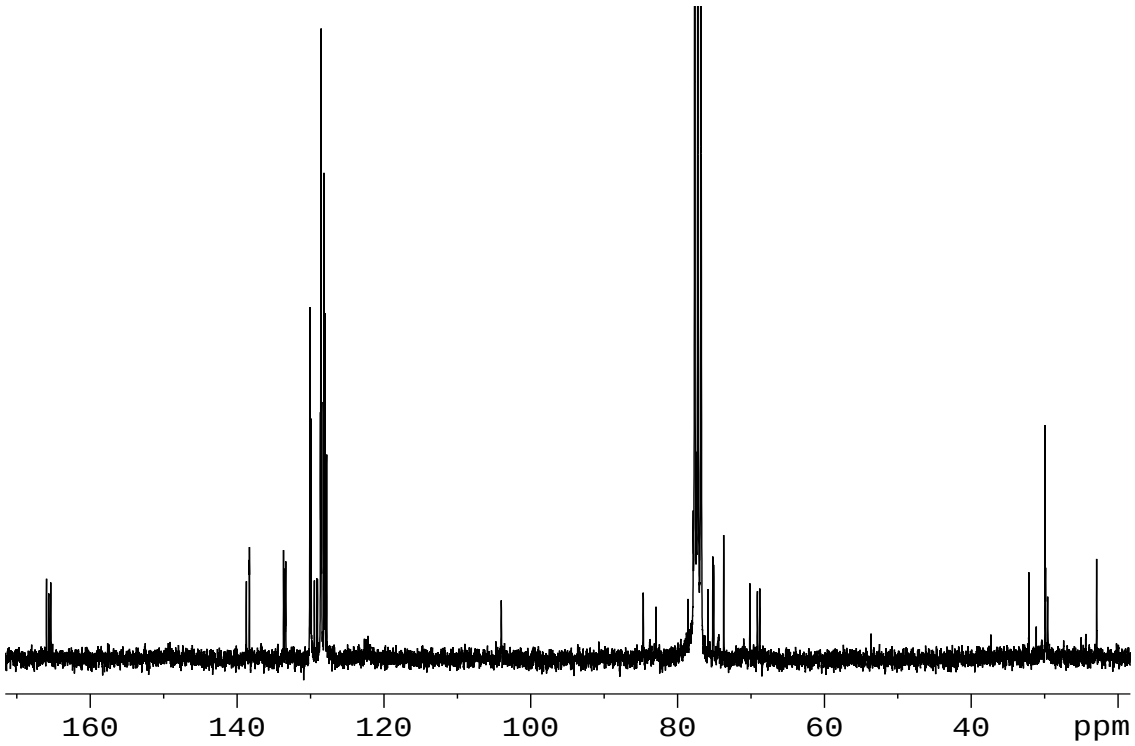
31β

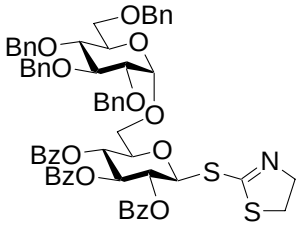

ppm
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm


OBn
BnO
O
BnO
BnO
O
BzO
O
S
N
BzO
BzO
S

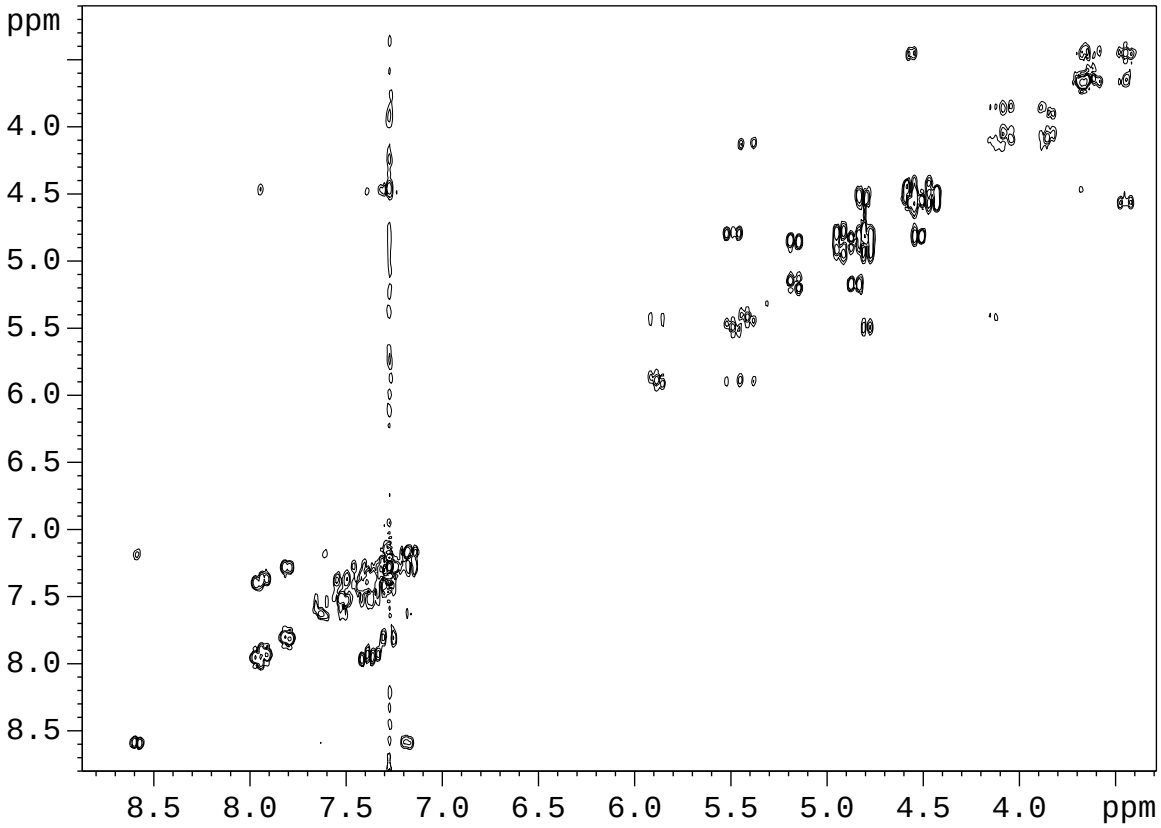
33

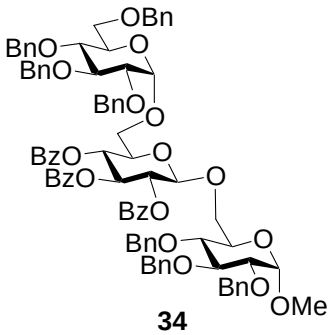

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm


160 140 120 100 80 60 40 ppm

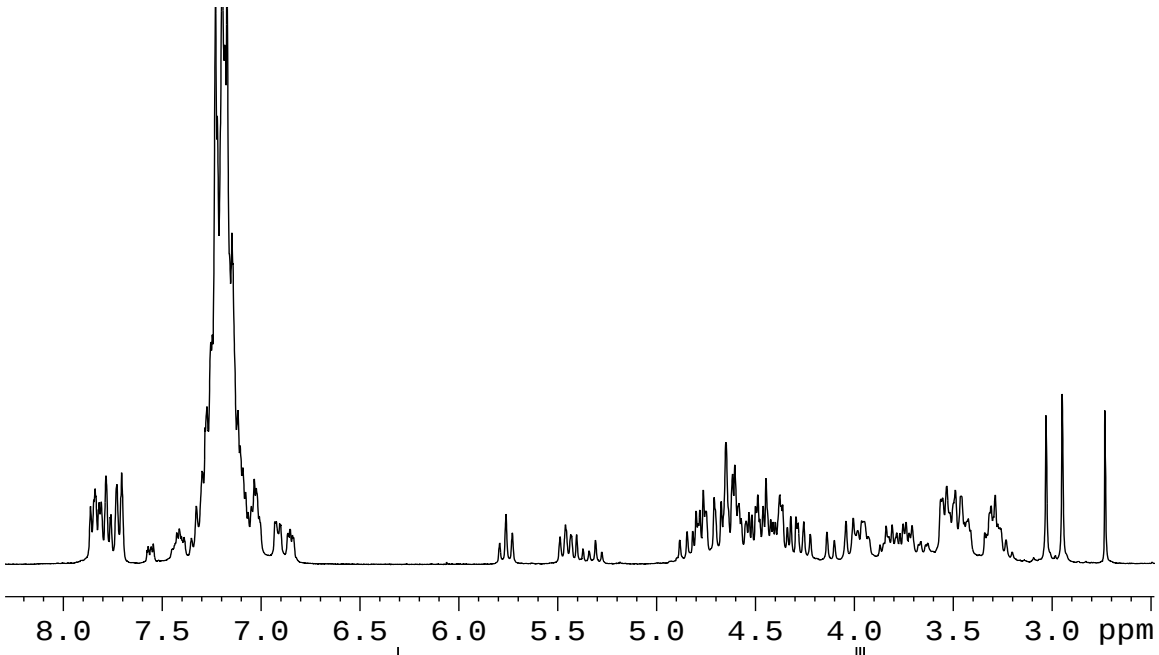

OBn
BnO
BnO
BnO
O
O
BzO
BzO
BzO
O
S
N
S

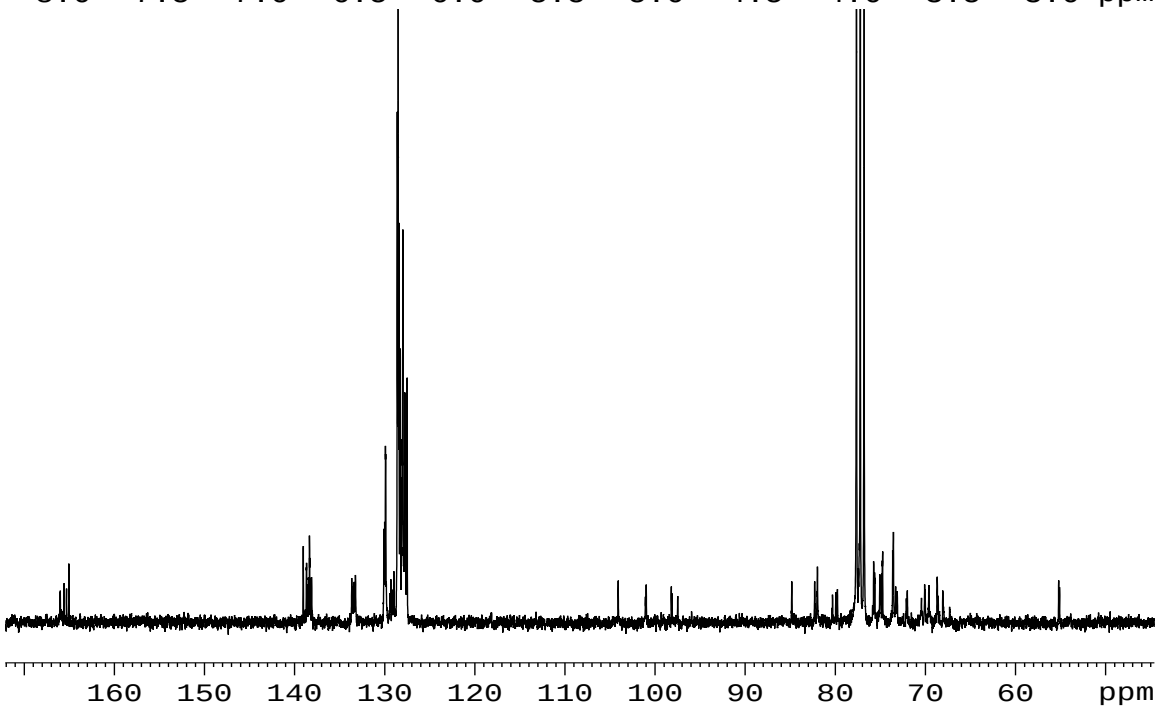
33

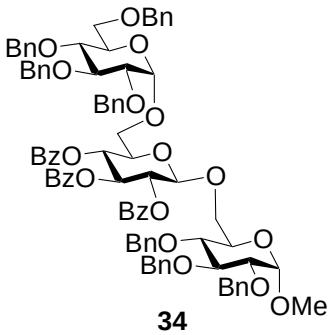

ppm
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 ppm


OBn
BnO
O
BnO
BnO
O
BzO
O
BzO
O
BzO
BnO
O
BnO
BnO
OMe

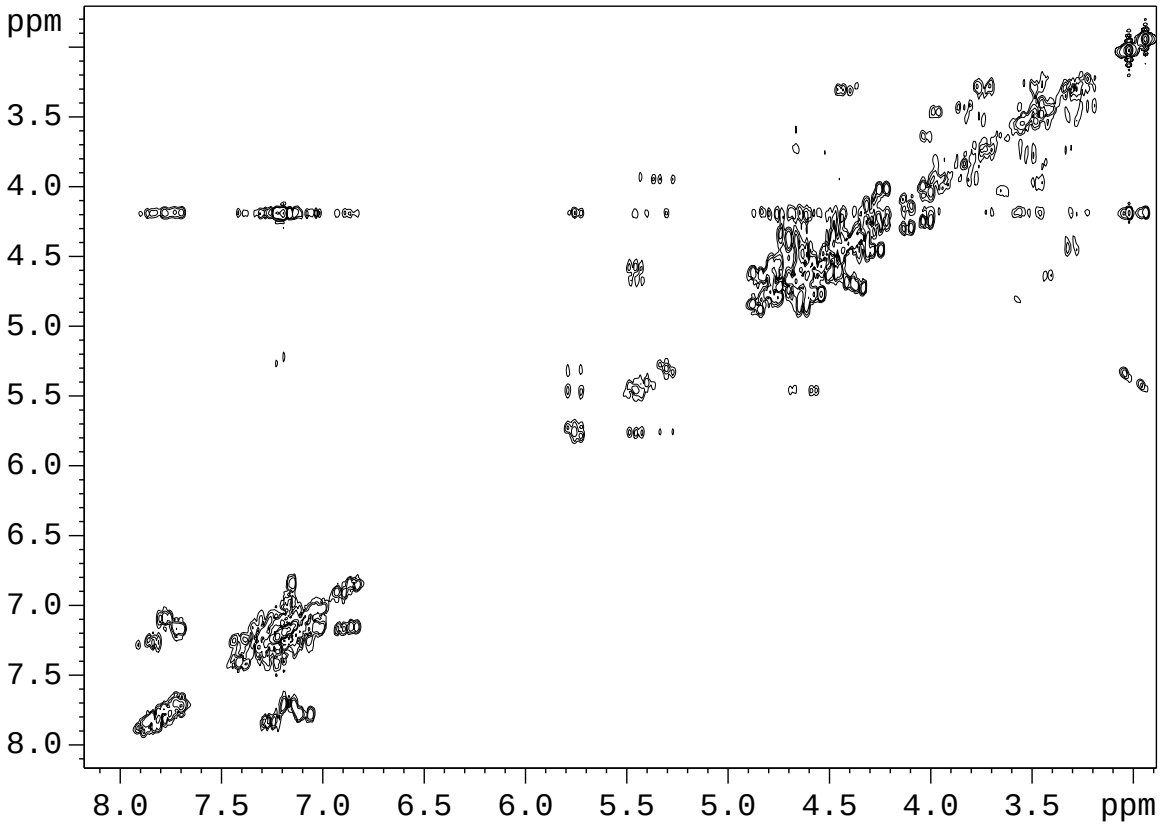
34

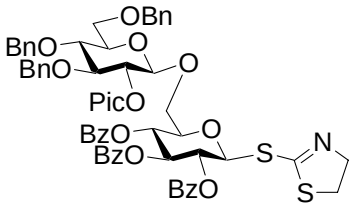

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm


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

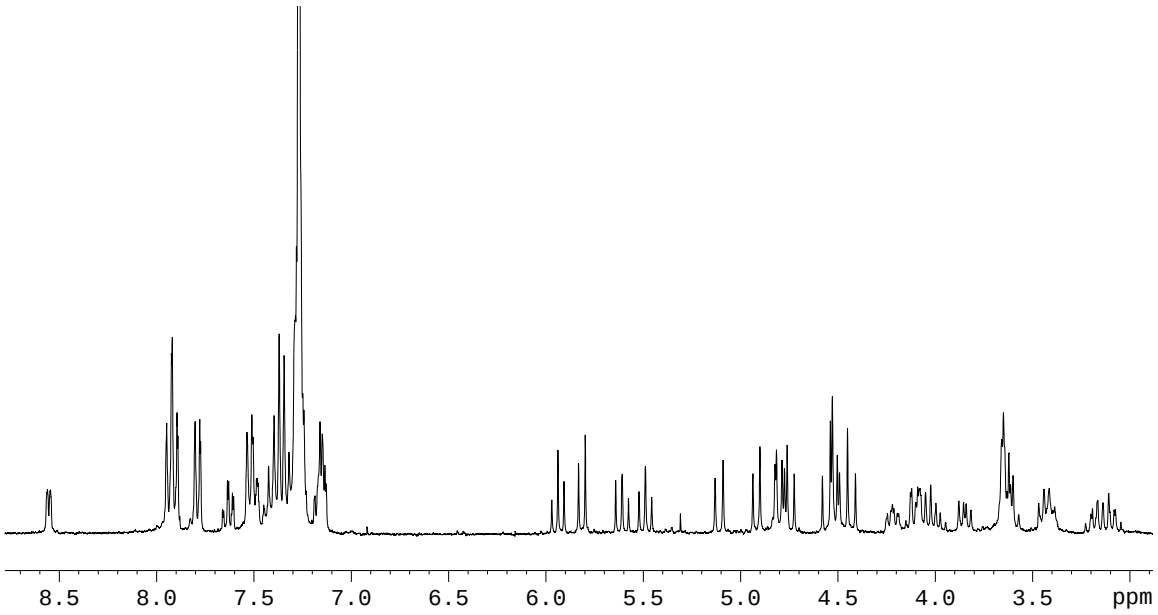

OBn
BnO
O
BnO
BnO
O
BzO
O
BzO
O
BzO
BnO
O
BnO
BnO
OMe

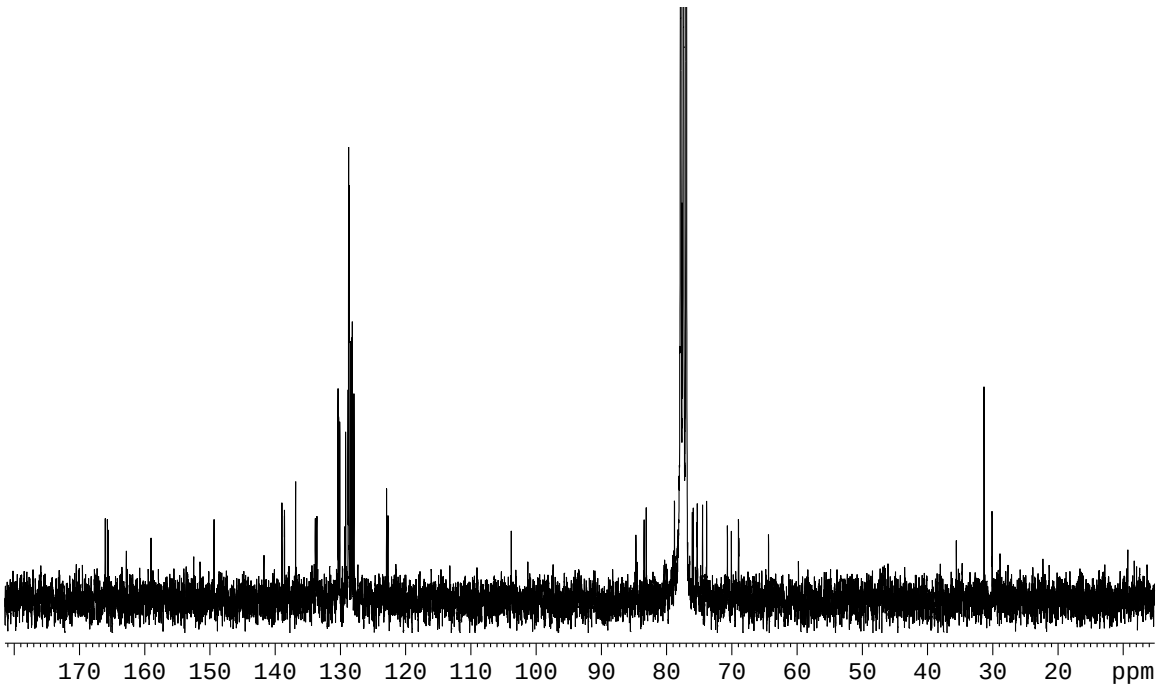
34

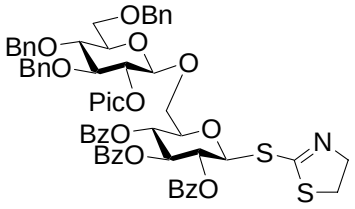

ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 ppm


OBn
BnO
O
BnO
O
PicO
BzO
O
BzO
S
N
S
BzO

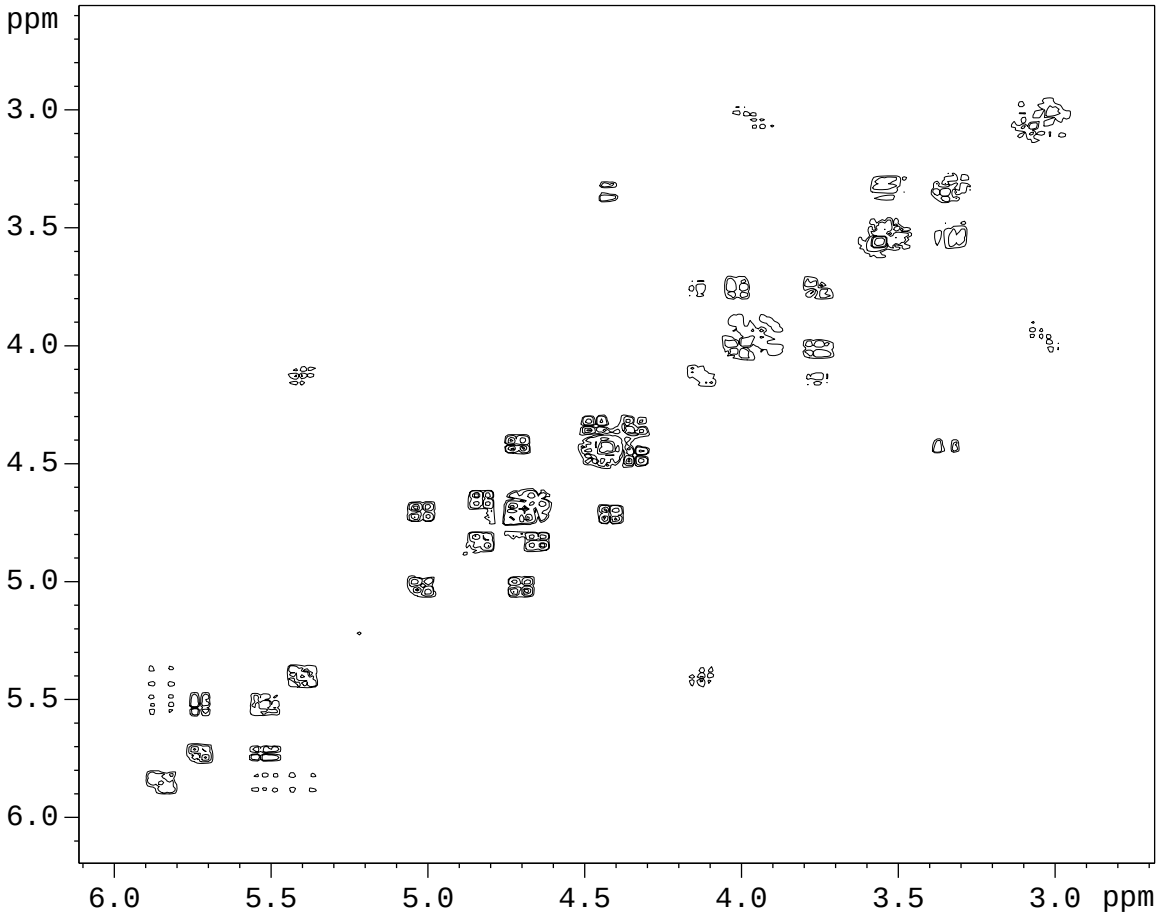
35

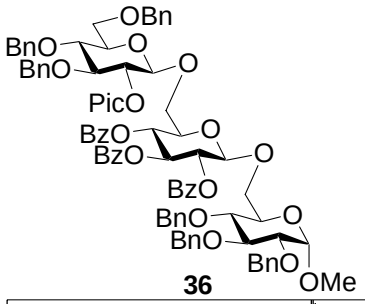

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

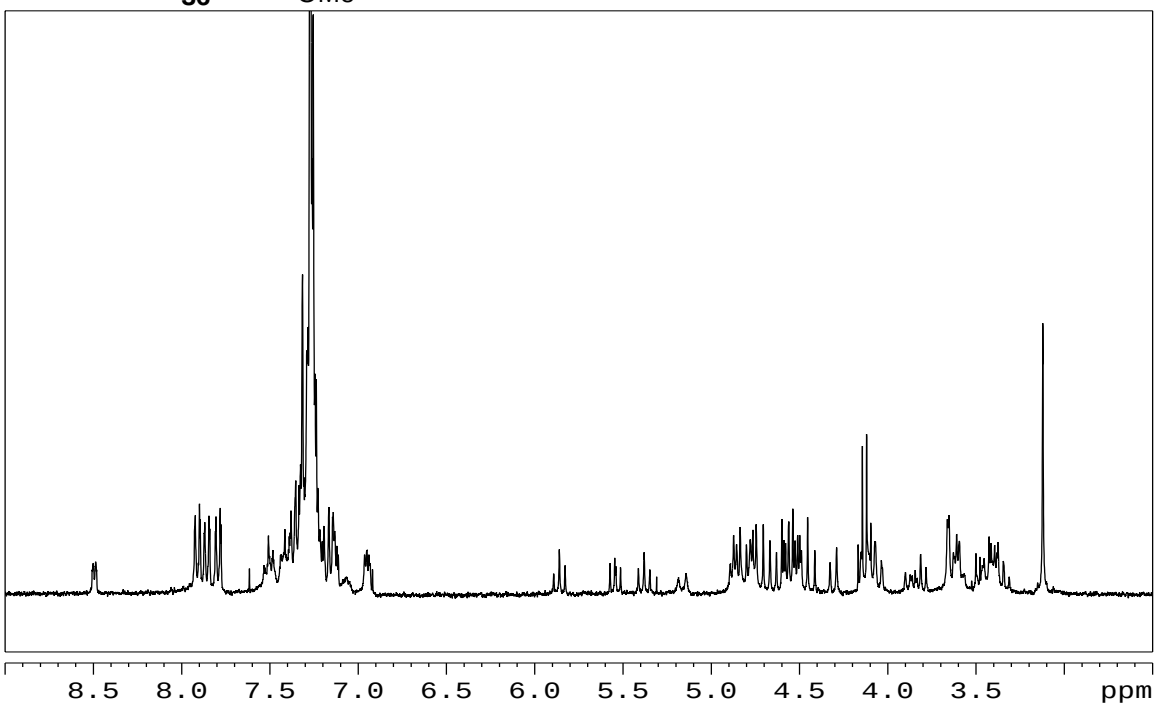

OBn
BnO
O
BnO
O
PicO
BzO
O
BzO
S
N
BzO
S

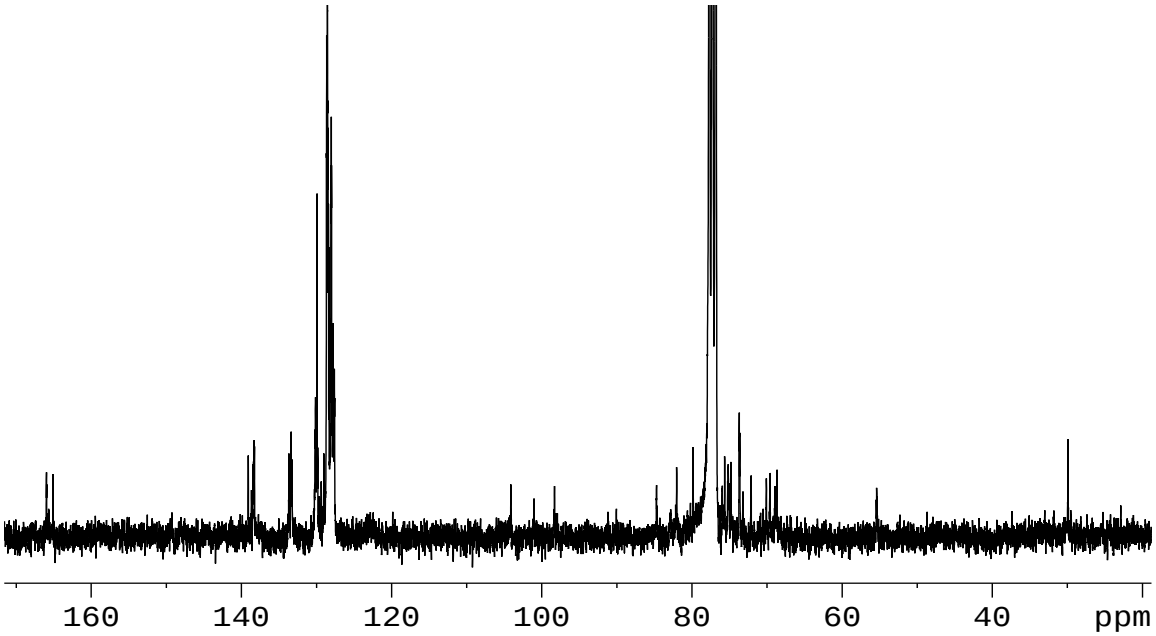
35

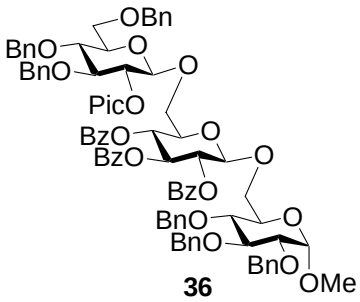

ppm
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm


OBn
BnO
O
BnO
O
PicO
BzO
O
BzO
O
BzO
BnO
O
BnO
BnO
OMe

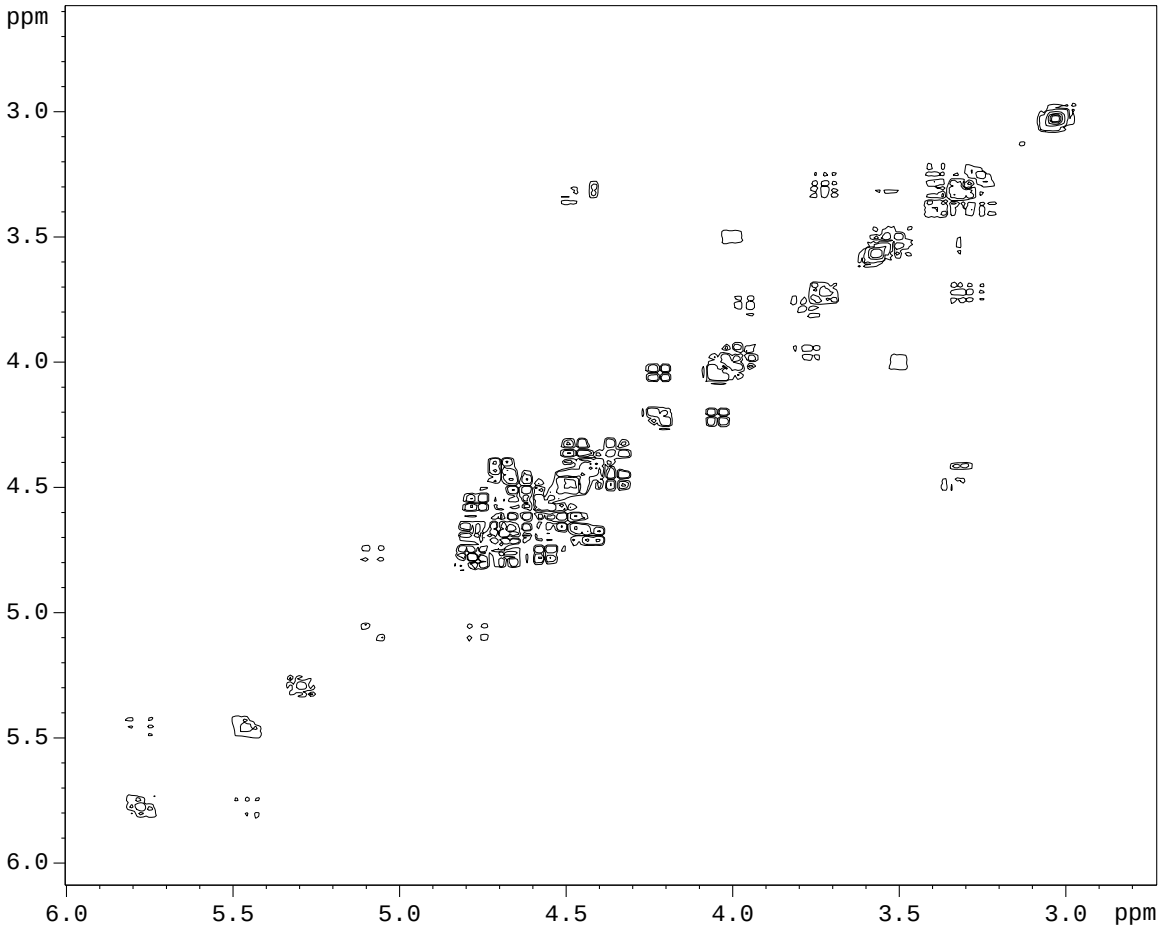
36

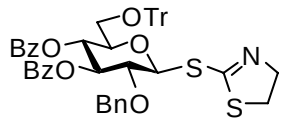

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm


160
140
120
100
80
60
40
ppm

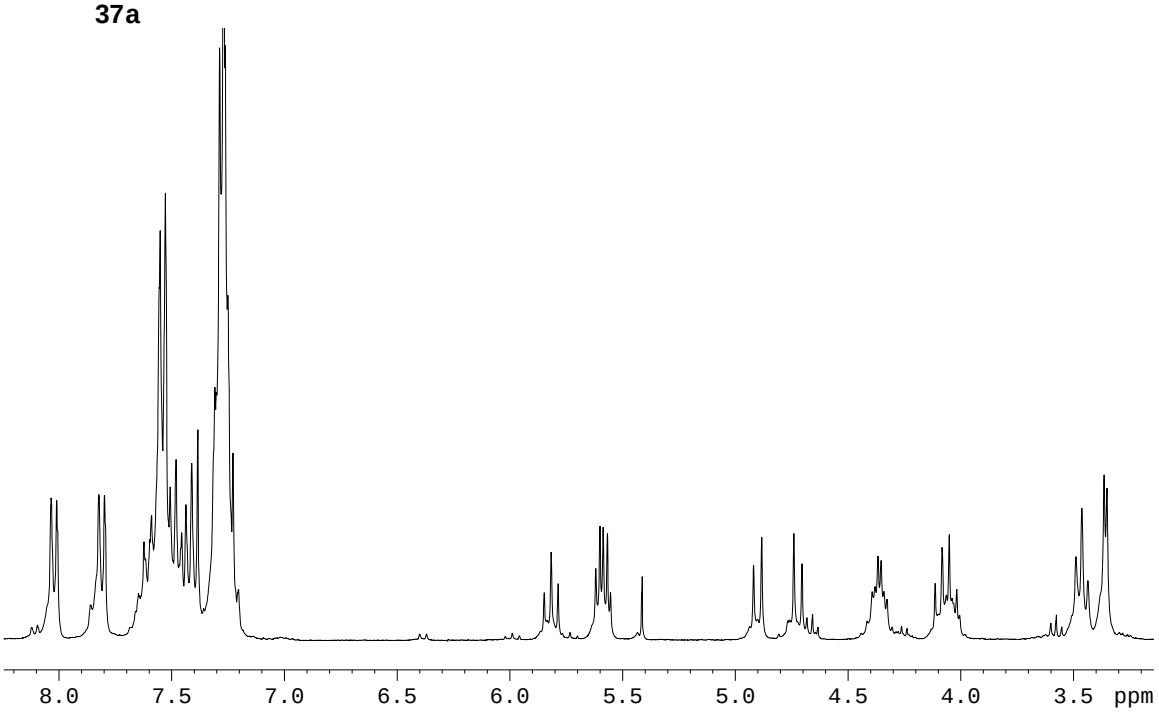

OBn
BnO
O
BnO
O
PicO
BzO
O
BzO
O
BzO
BnO
O
BnO
BnO
OMe

36


ppm
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm


OTr
BzO
O
BzO
S
N
BnO
S

37a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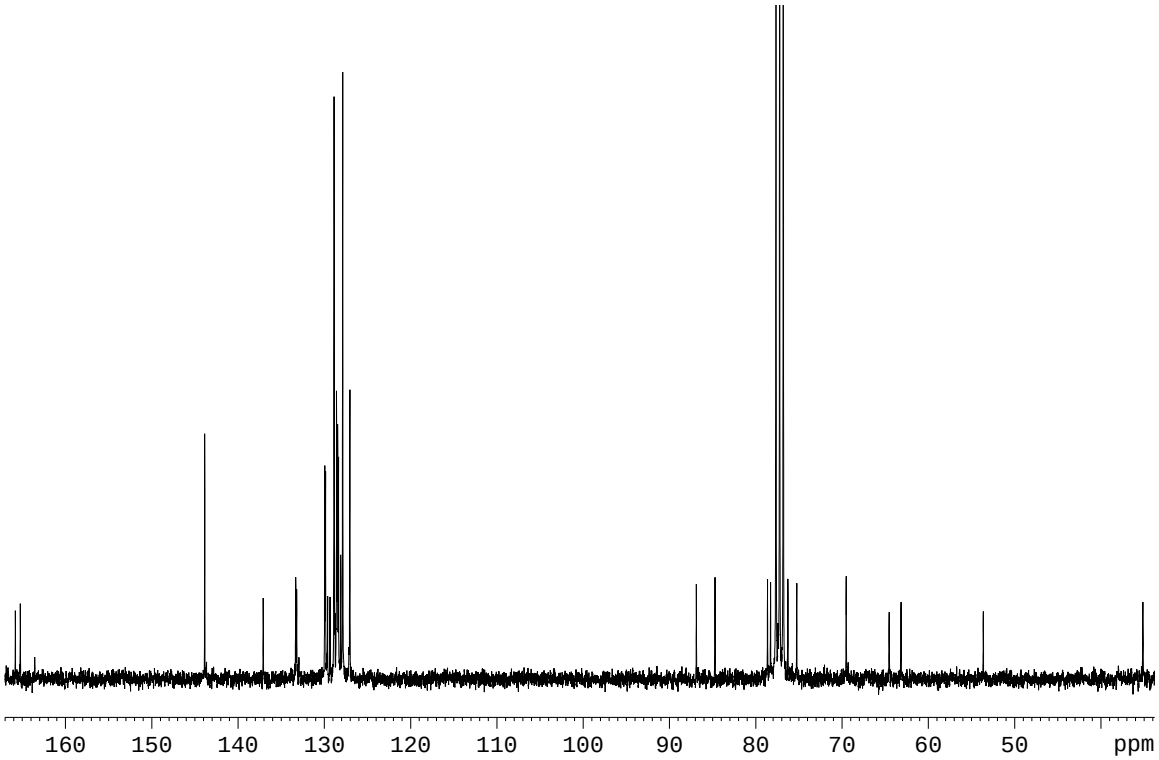
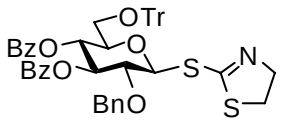
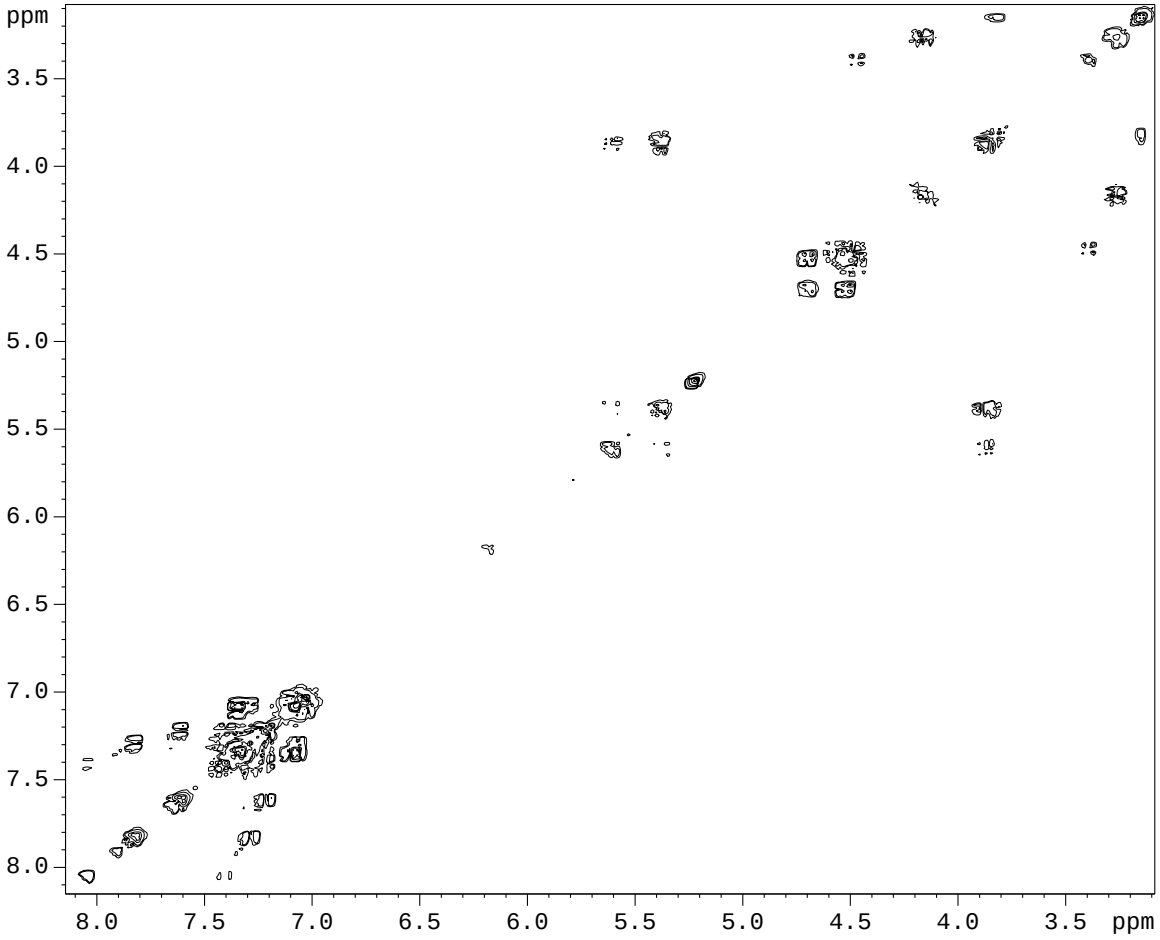
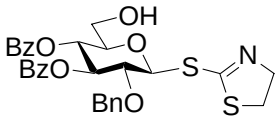
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm


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

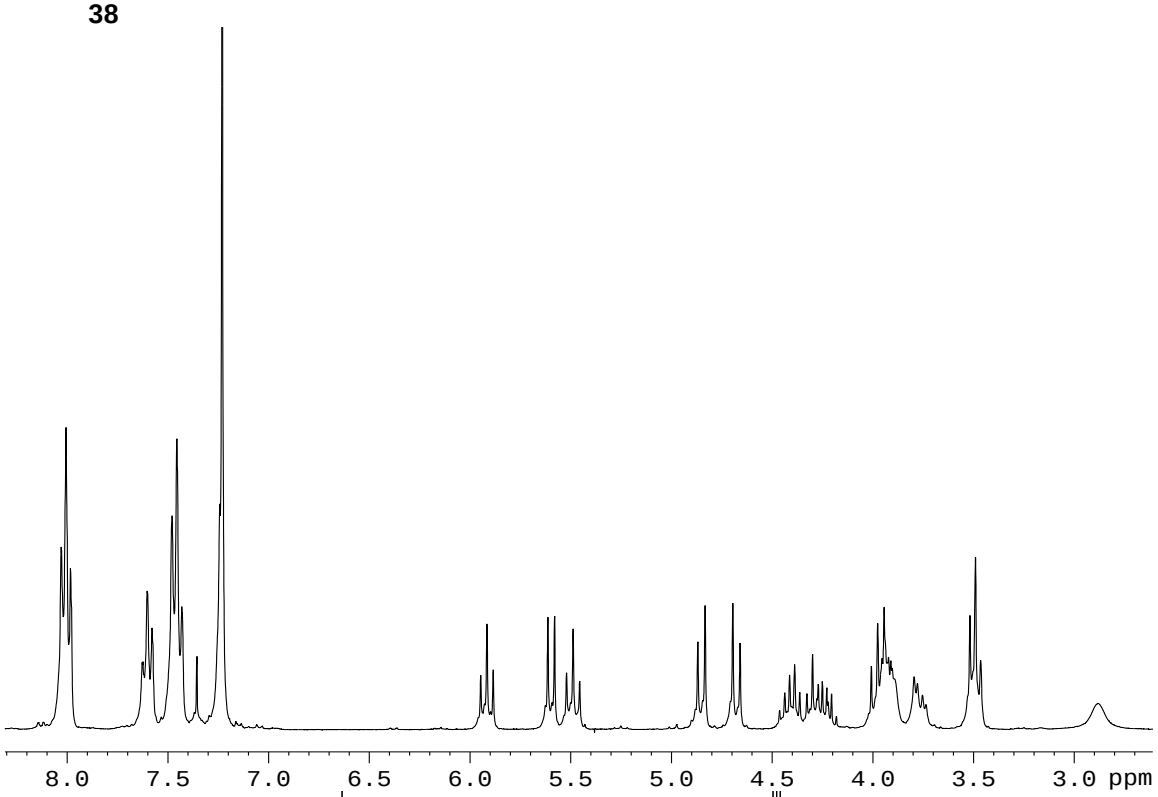

OTr
O
BzO
BzO
S
N
S
BnO

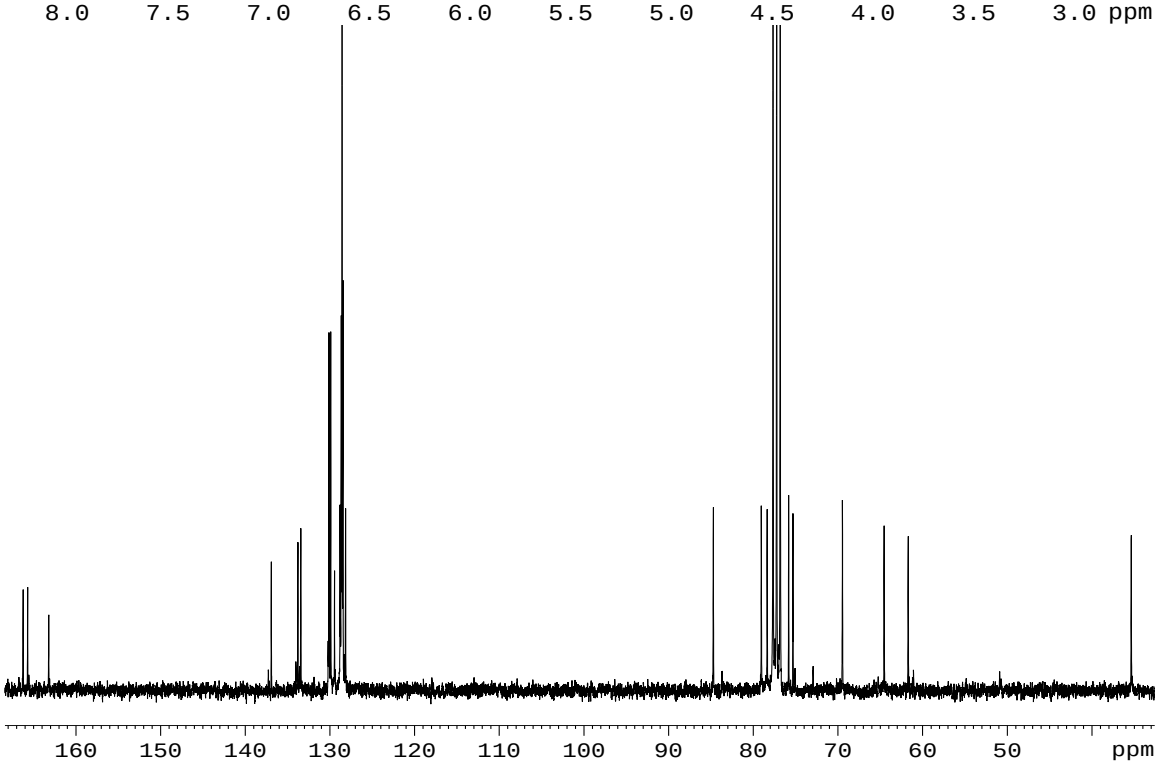
37a

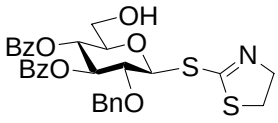

ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm


OH
BzO
O
S
N
BzO
BnO
S

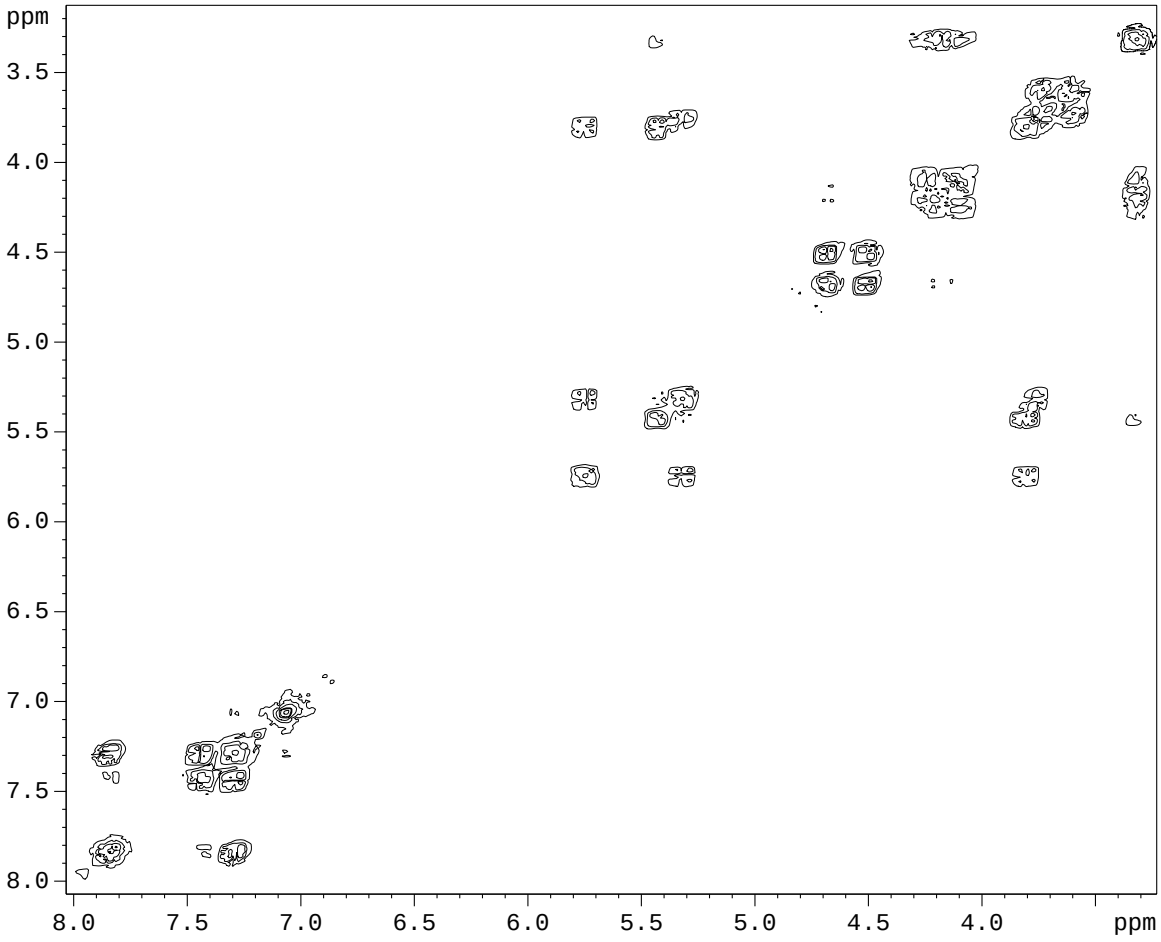
38

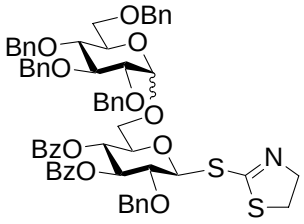

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0 ppm


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

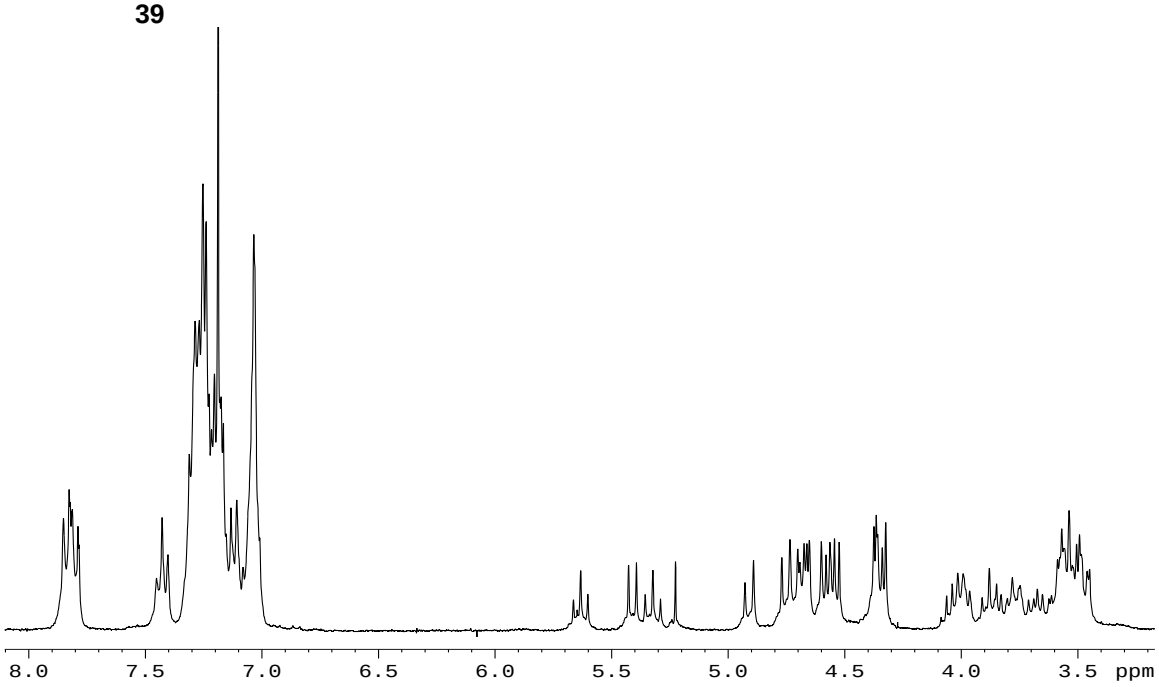

OH
O
BzO
BzO
S
N
BnO
S

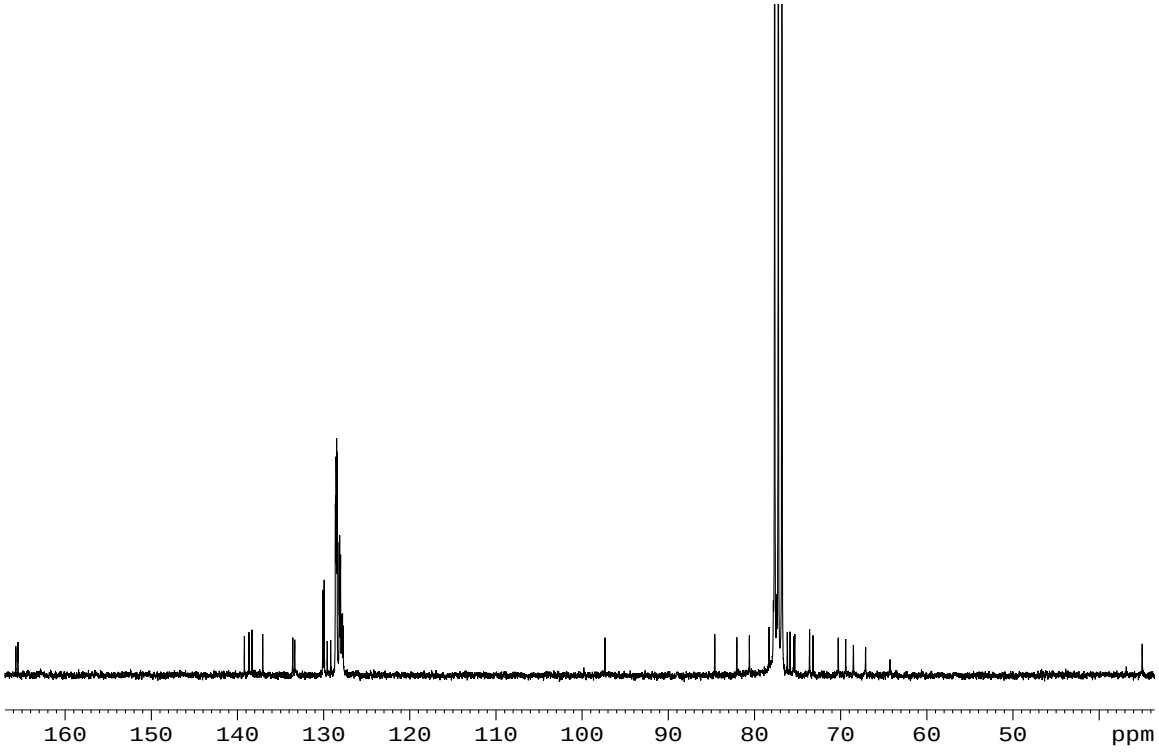
38

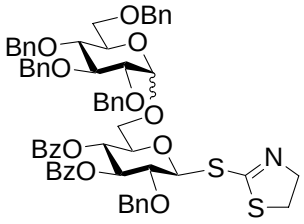

ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm


OBn
BnO
O
BnO
BnO
O
BzO
O
BzO
S
N
S
BnO

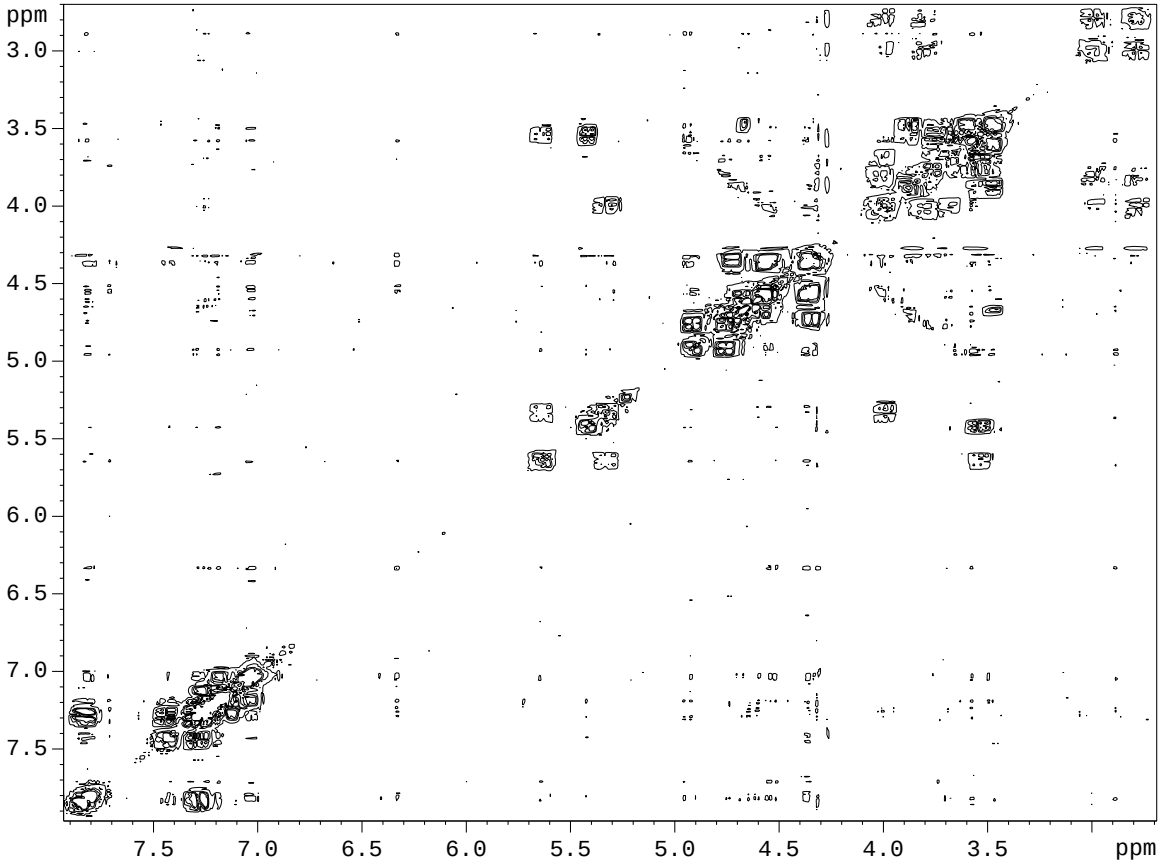
39

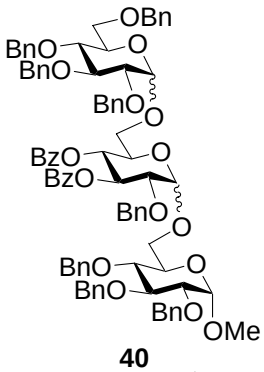

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm


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

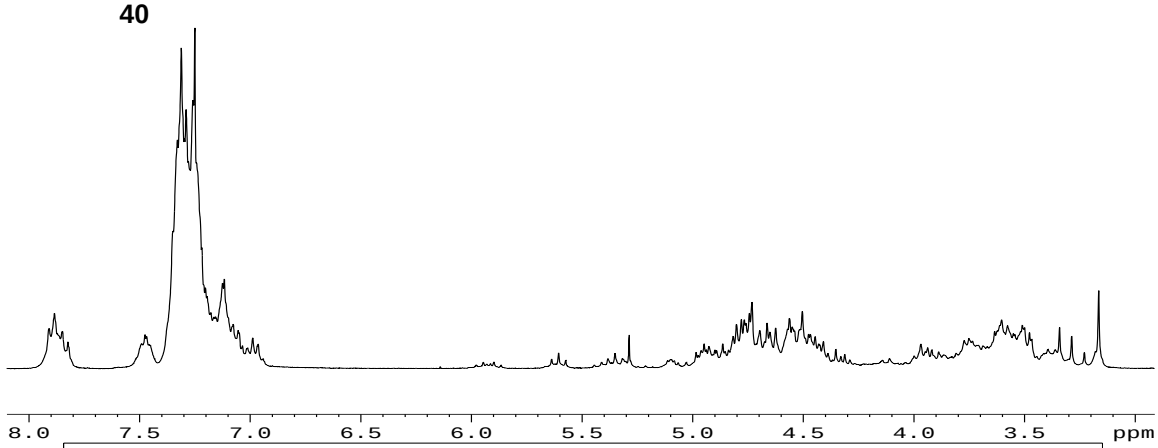

OBn
BnO
O
BnO
BnO
O
BzO
O
BzO
S
N
BnO
S

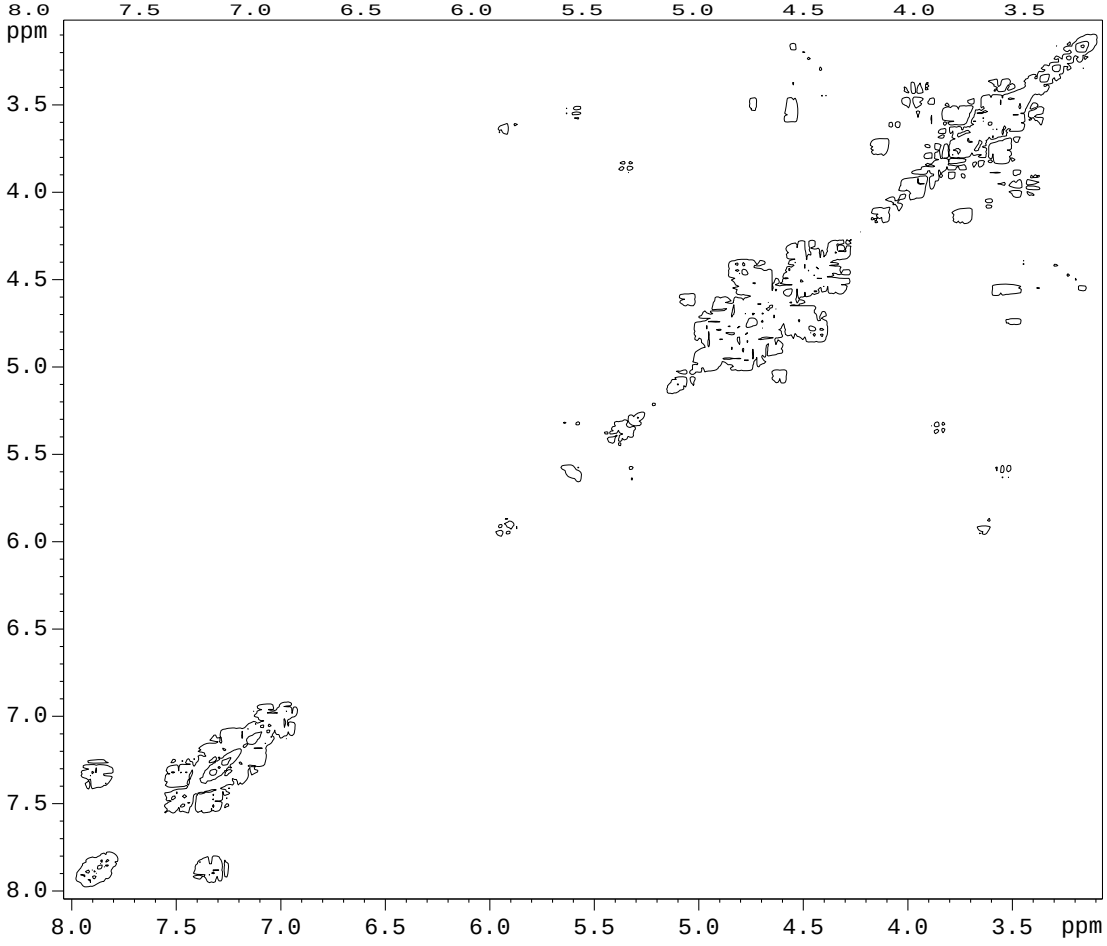
39


ppm
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
ppm


OBn
BnO
BnO
O
BnO
O
BzO
BzO
O
BnO
O
BnO
BnO
O
BnO
OMe

40


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm


ppm
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
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6.0
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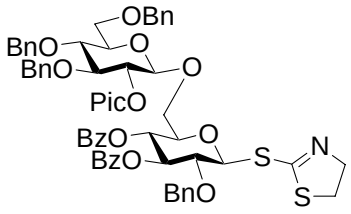
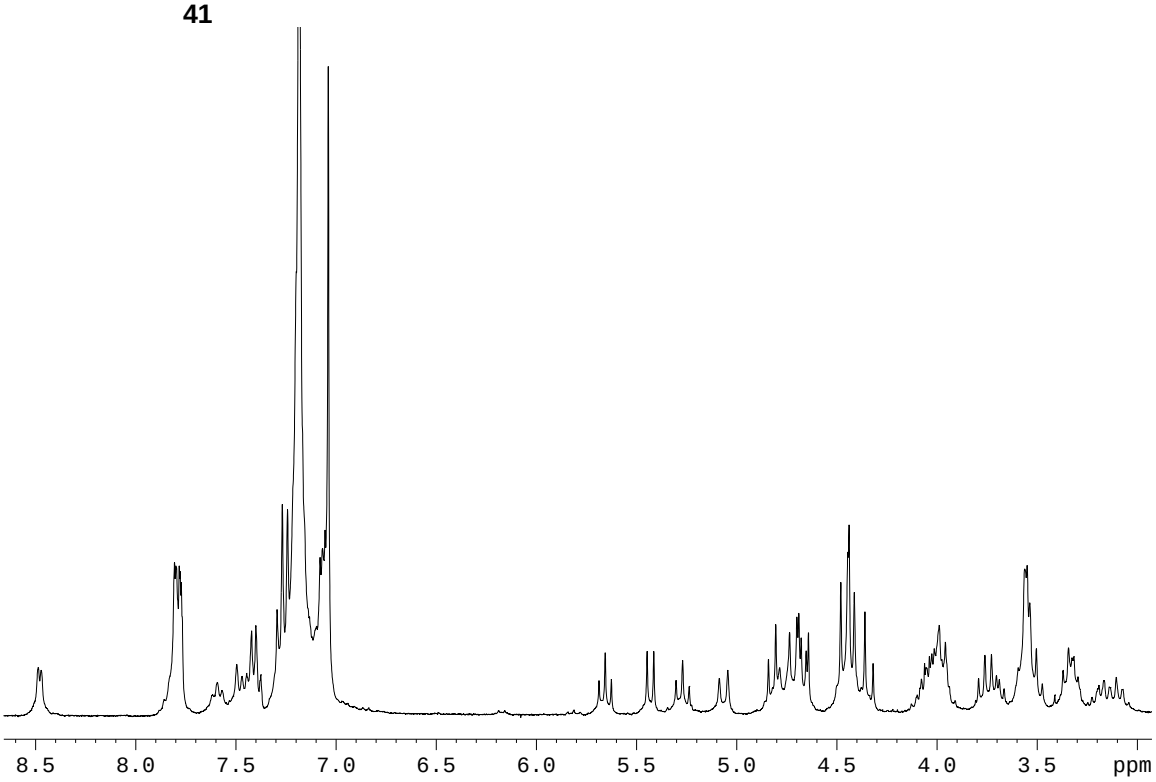
5.0
4.5
4.0
3.5
ppm


OBn
BnO
O
BnO
O
PicO
BzO
O
BzO
S
N
S
BnO

41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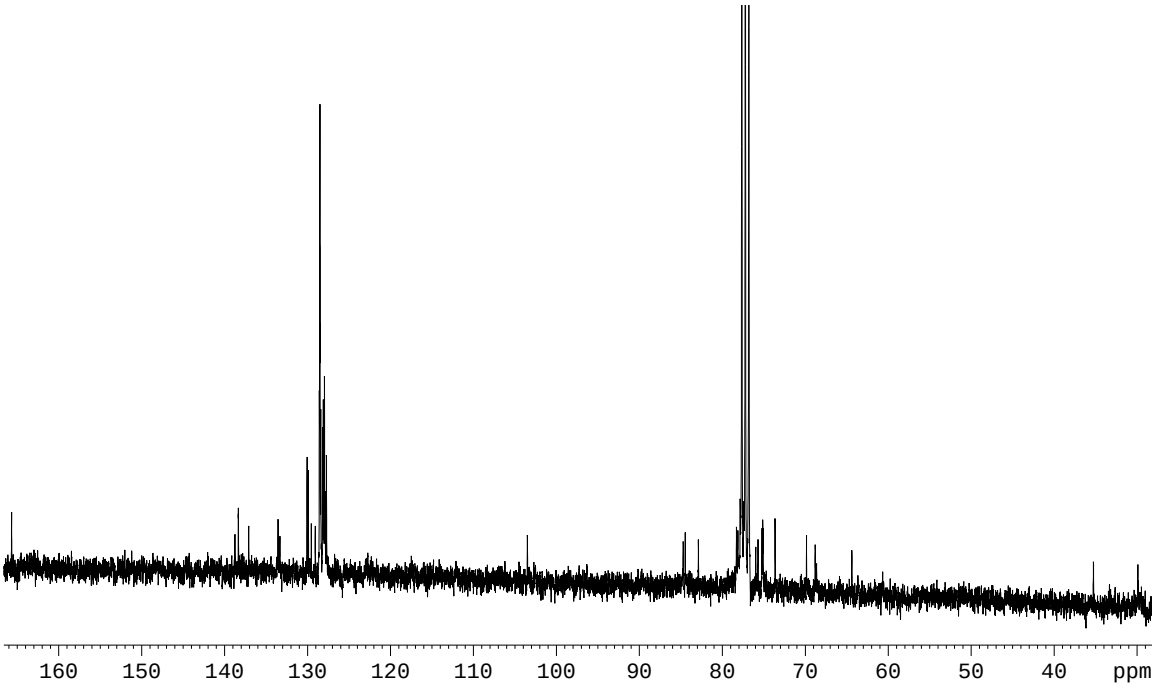
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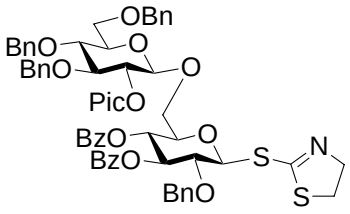
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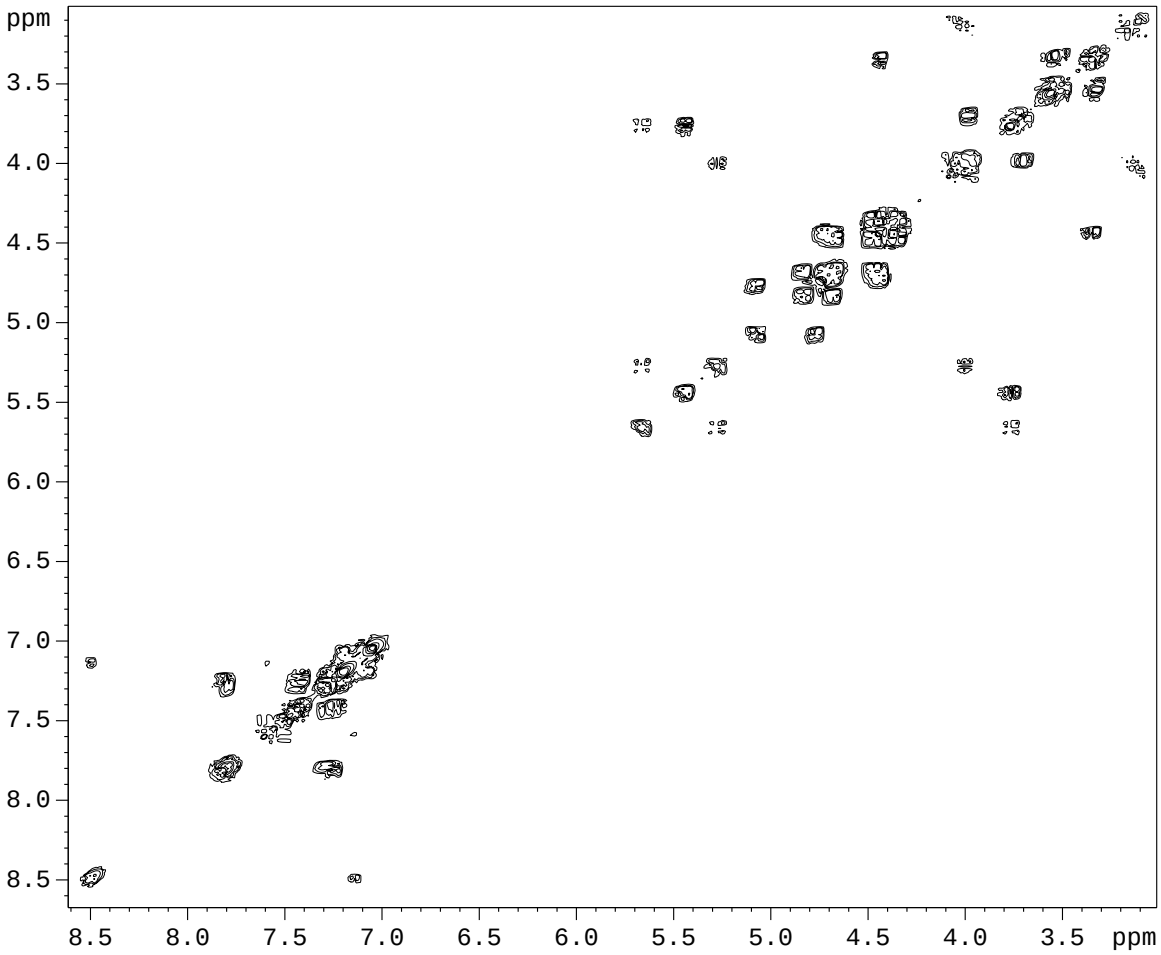
BnO
S

41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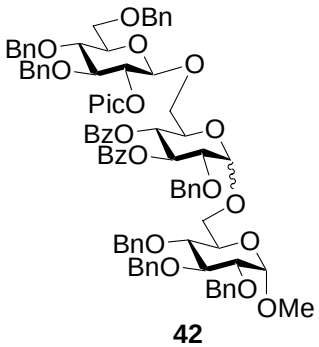
OBn
BnO
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BnO
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PicO
BzO
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BnO
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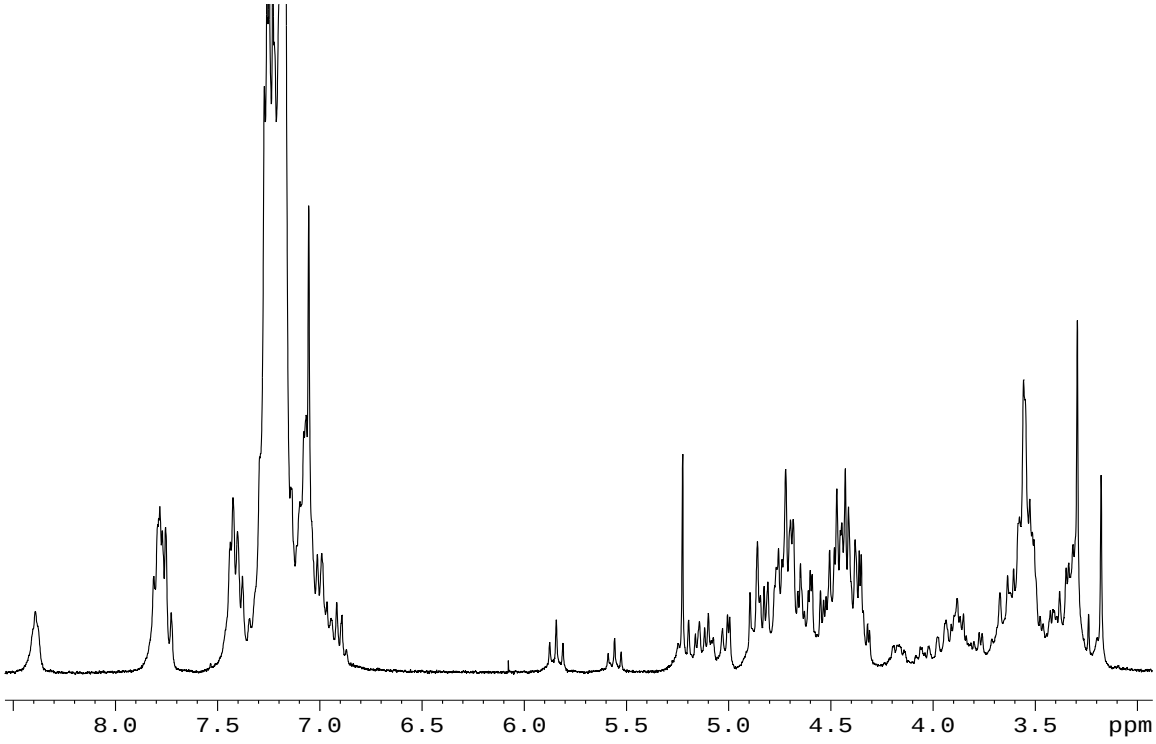
BnO
BnO
OMe

42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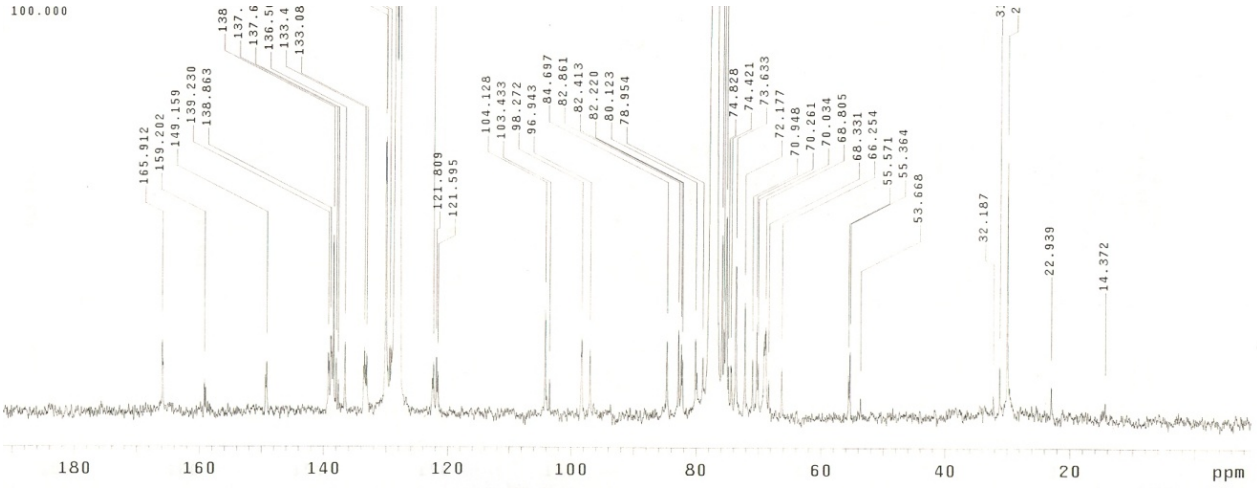
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70.261
70.034
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20
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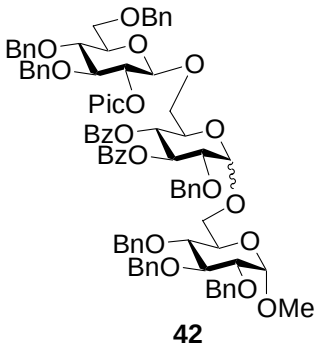
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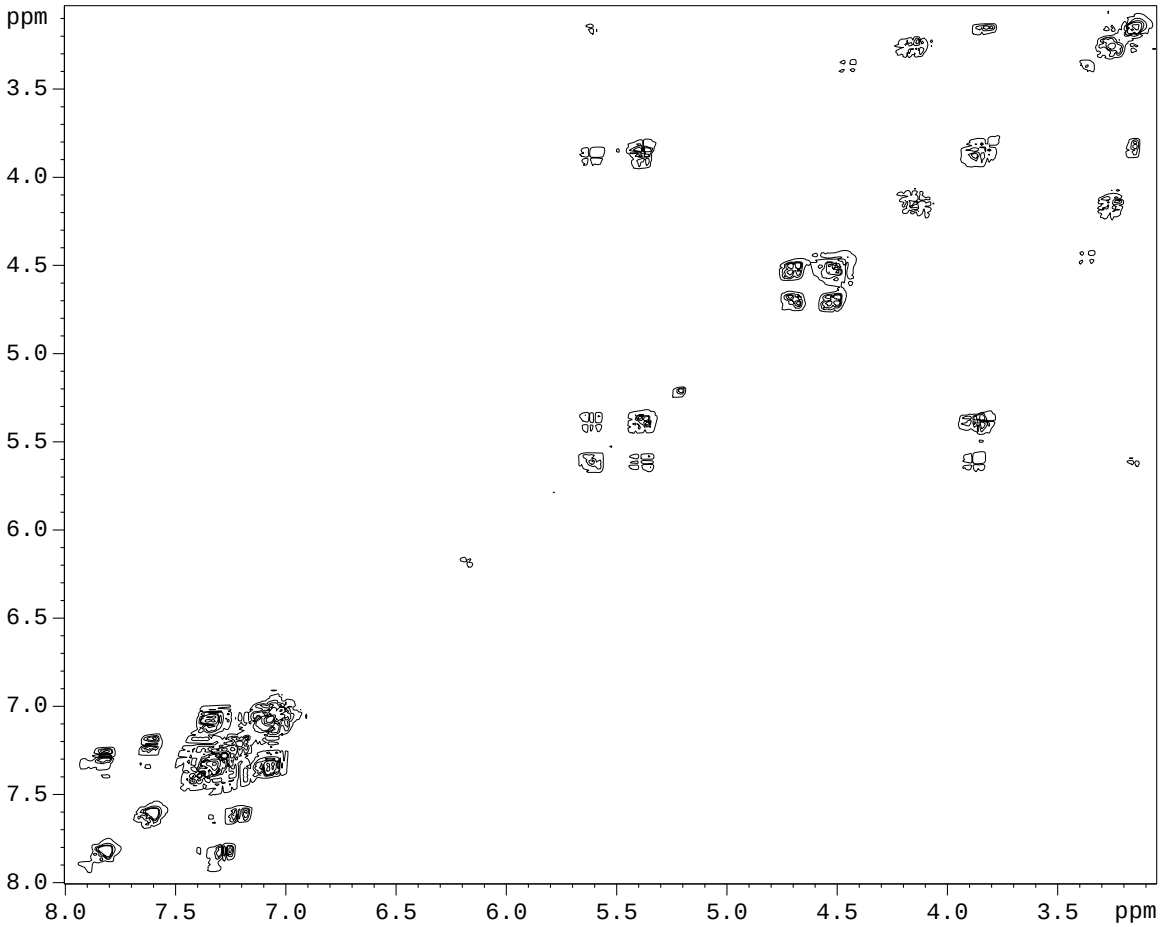
BnO
OMe

42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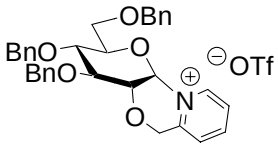

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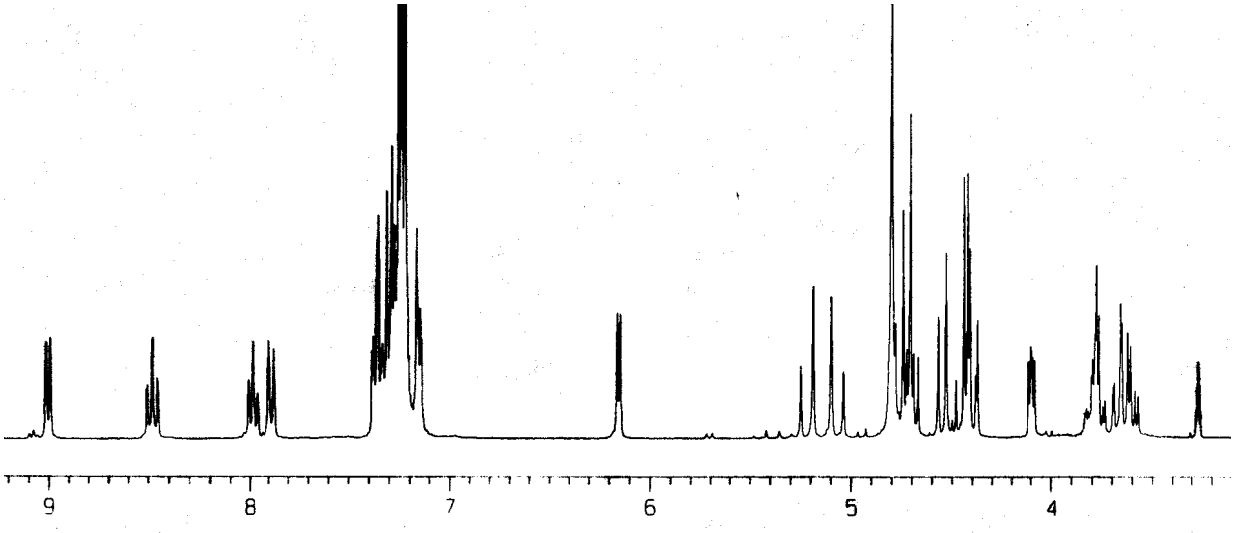

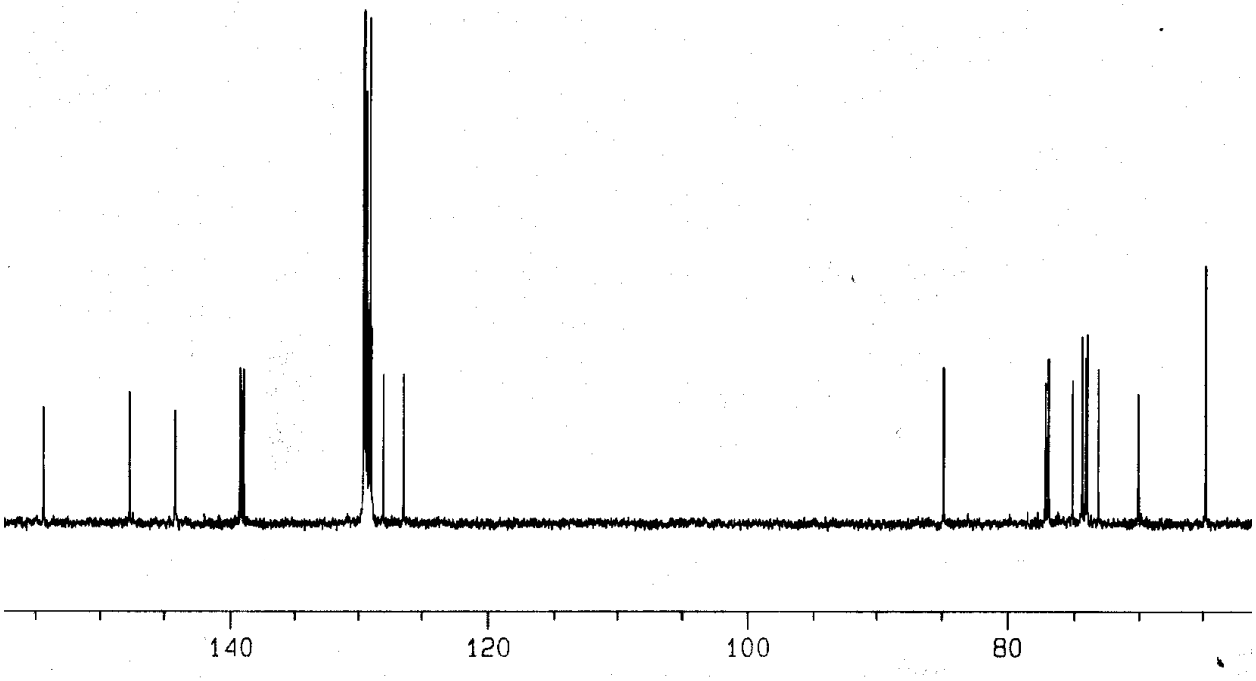

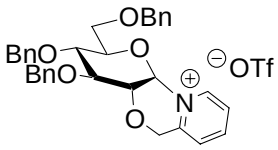

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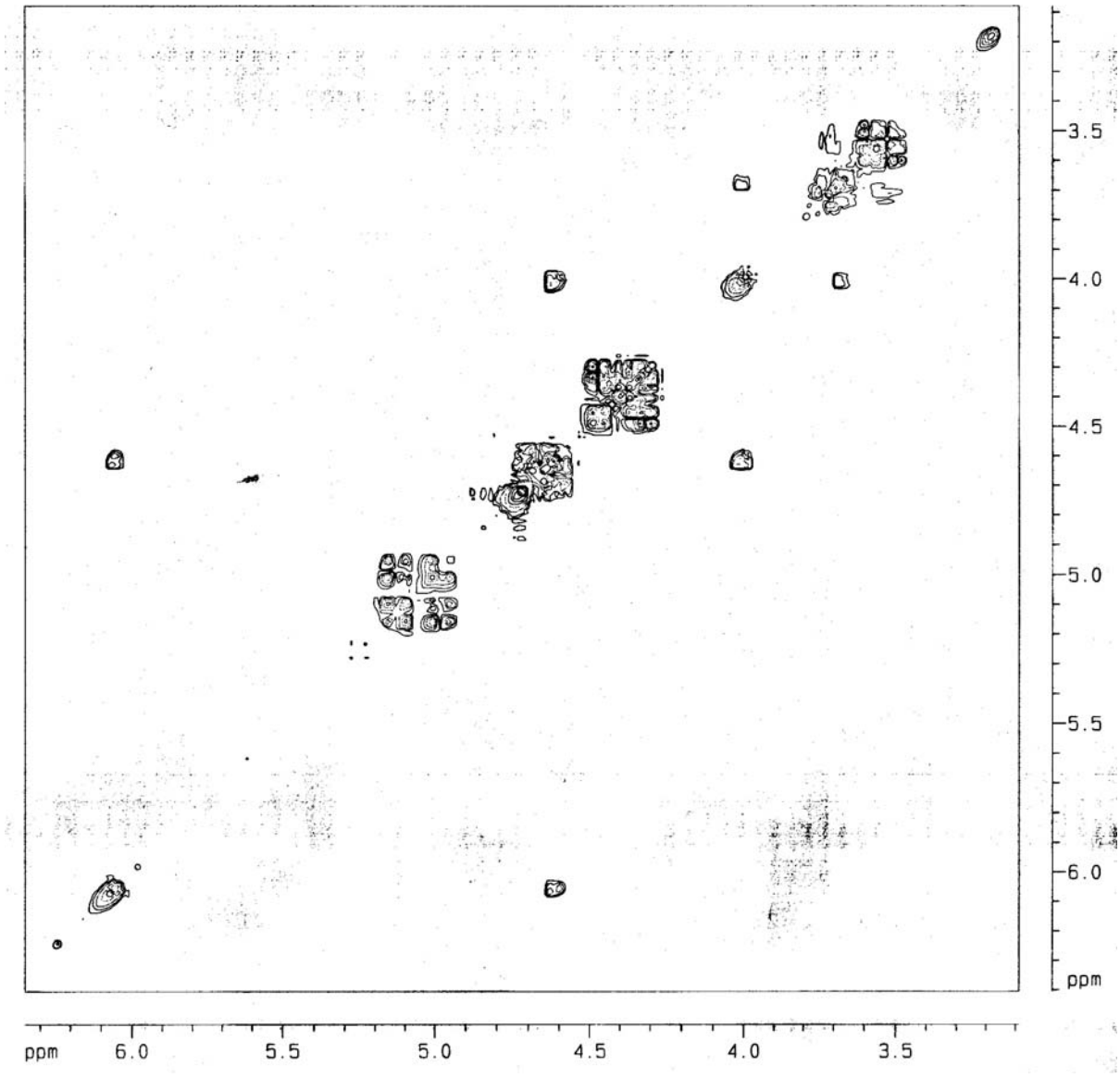

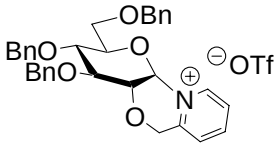

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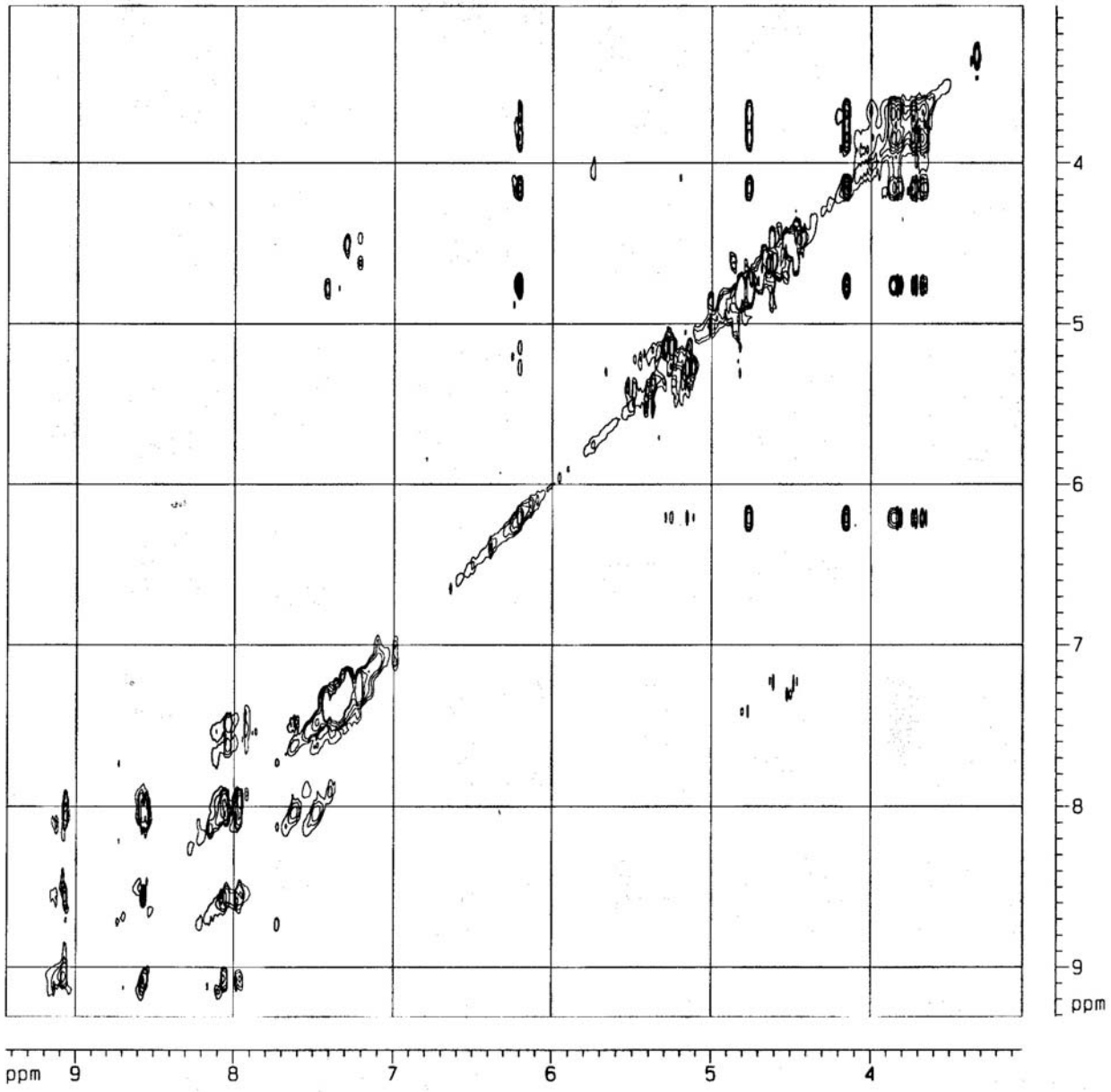

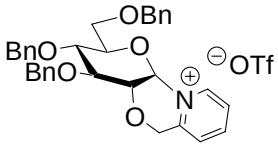

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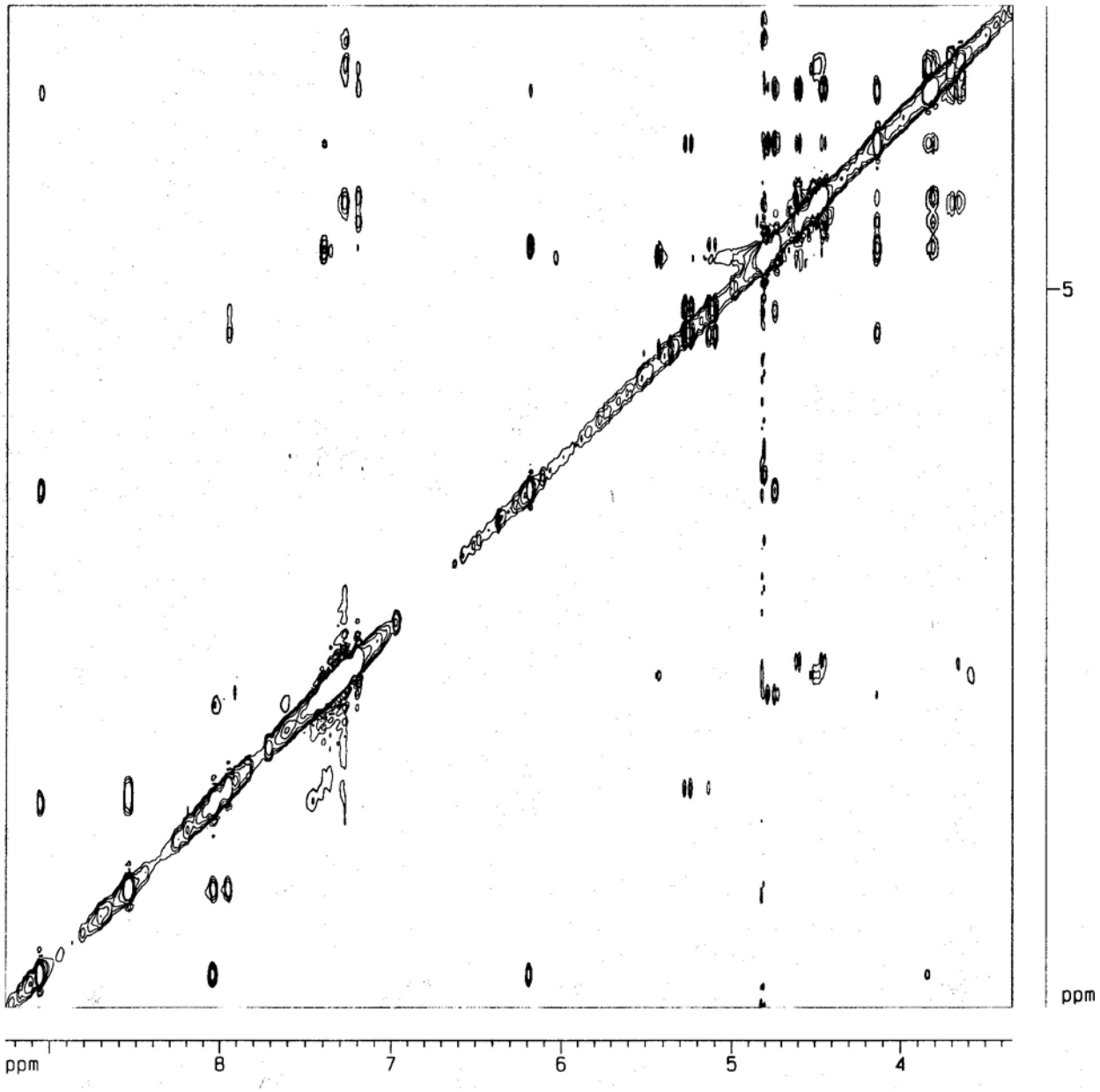

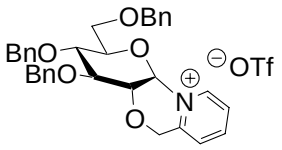

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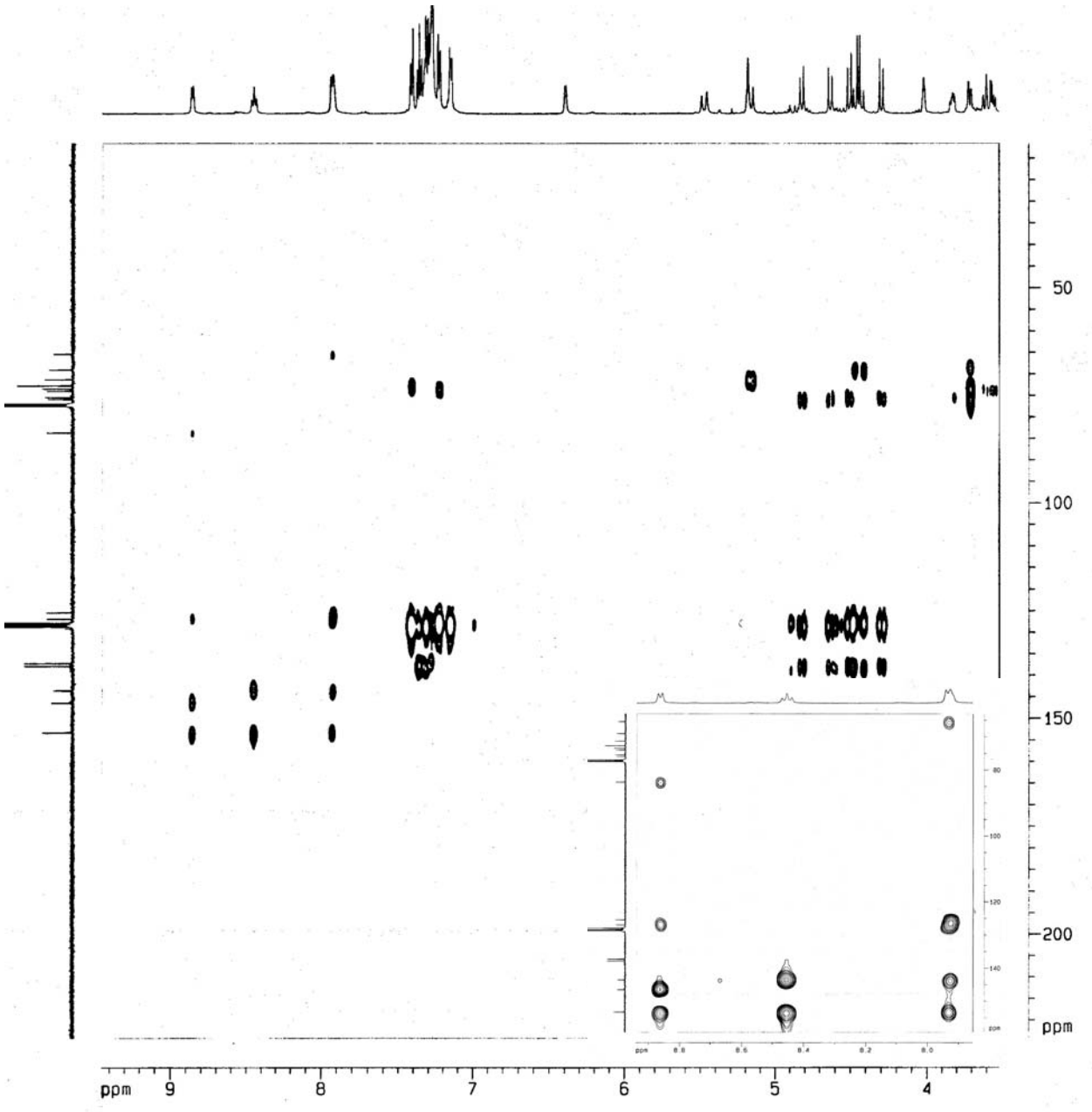

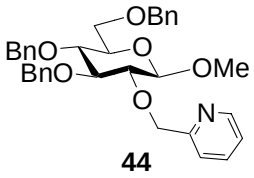

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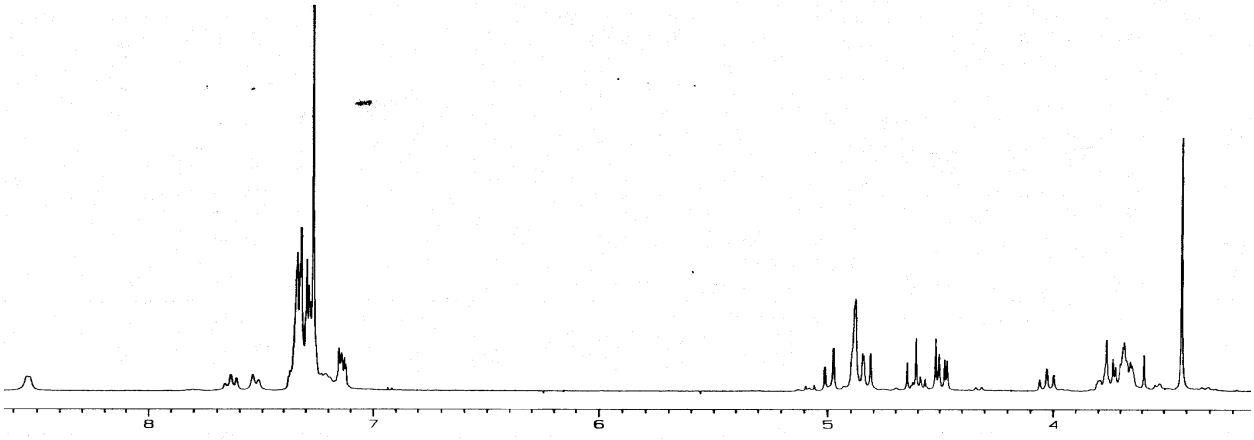

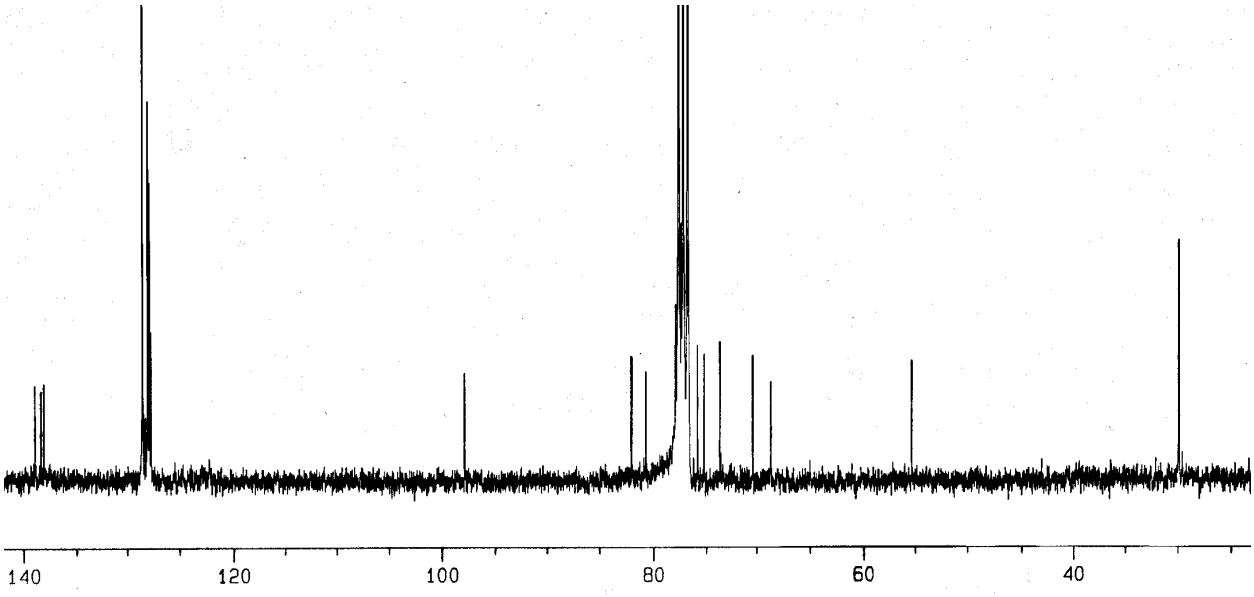

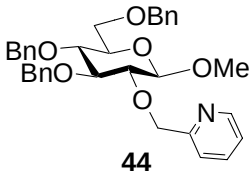

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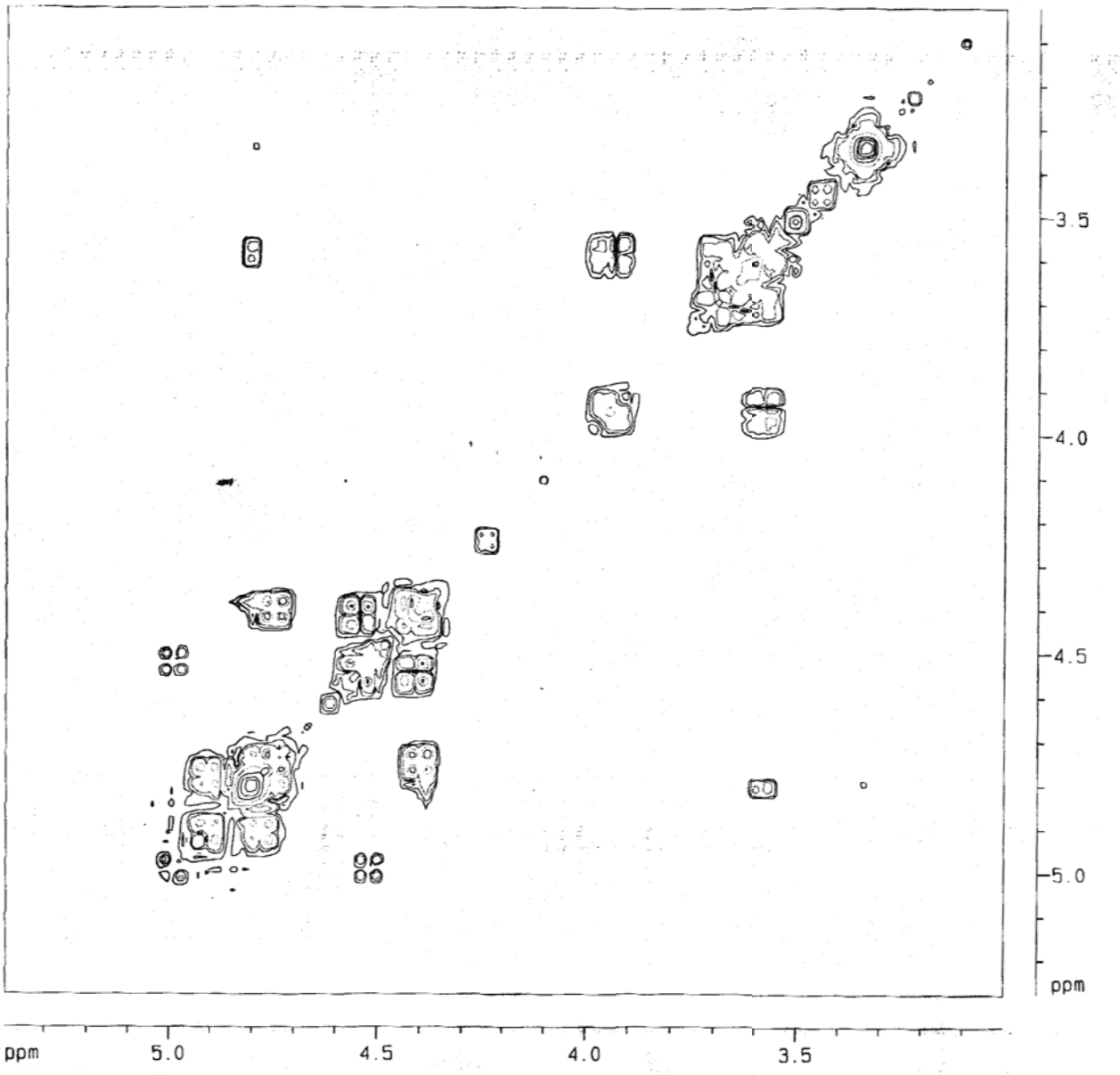

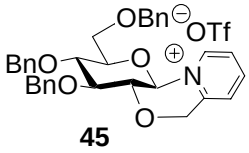

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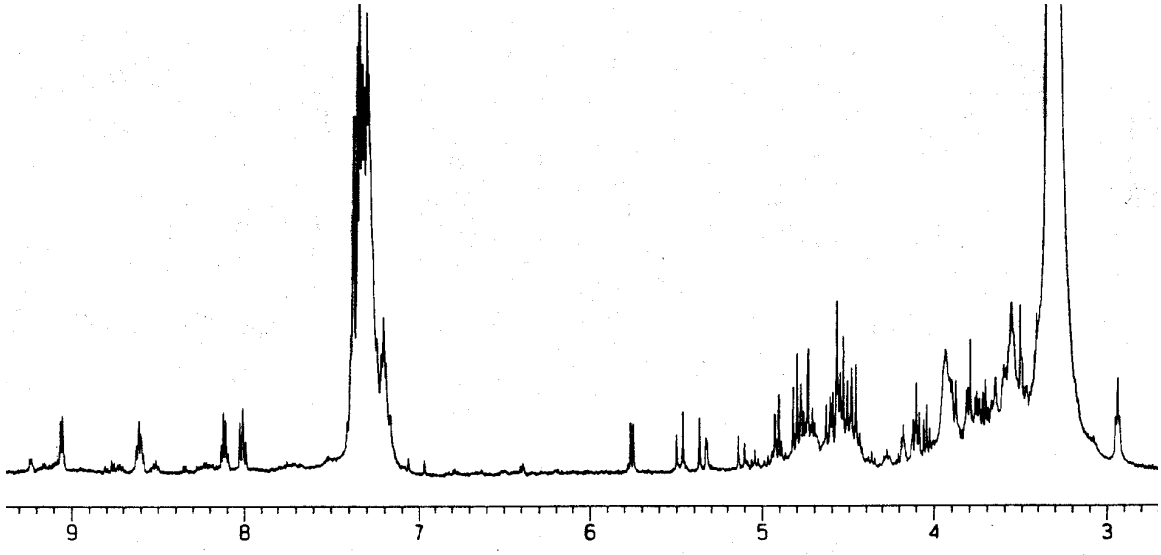

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(1) Thijssen, M. J. L.; Halkes, K. M.; Kamerling, J. P.; Vliegenthart, J. F. G. *Bioorg. Med. Chem.* **1994**, *2*, 1309-1317.

(2) Kochetkov, N. K.; Backinowsky, L. V.; Tsvetkov, Y. E. *Tetrahedron Lett.* **1977**, *41*, 3681-3684.

(3) Pornsuriyasak, P.; Demchenko, A. V. *Chem. Eur. J.* **2006**, *12*, 6630-6646.