Supporting information

Comparison of the Armed/Disarmed Building Blocks of the D-Gluco and D-Glucosamino Series in the Context of Chemoselective Oligosaccharide Synthesis

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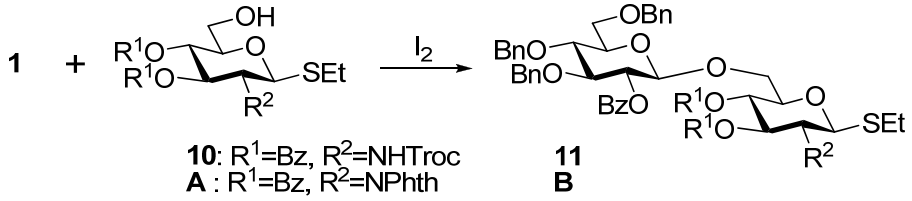
Contents:

Table SI. Chemoselective activations



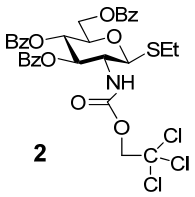
Entry	Acceptor	Conditions	Time	Product	Yield
1	**10**	I_2, rt	5 min	**11**	38%
2	**10**	I_2, -20 ^oC	3 h	**11**	77%
3	**A**	I_2, rt	5 min	**B**	59%
4	**A**	I_2, -20 ^oC	3 h	**B**	61%

General remarks

Column chromatography was performed on silica gel 60 (EM Science, 70-230 mesh), reactions were monitored by TLC on Kieselgel 60 F254 (EM Science). 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 ^oC. CH_2Cl_2 and $ClCH_2CH_2Cl$ were distilled from CaH_2 directly prior to application. Anhydrous DMF (EM Science) was used as is. Pyridine was dried by refluxing with CaH_2 and then distilled and stored over molecular sieves (3 Å). 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. Optical rotations were measured at 'Jasco P-1020' polarimeter. ^{1}H-n.m.r. spectra were recorded in $CDCl_3$ at 300 MHz, ^{13}C-NMR spectra were recorded in $CDCl_3$ at 75 MHz (Bruker Avance) unless otherwise noted. HRMS determinations were made with the use of JEOL MStation (JMS-700) Mass Spectrometer.

*Synthesis of glycosyl donors **2** and **3**.*

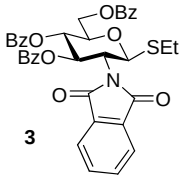
Ethyl 3,4,6-tri-O-benzoyl-2-deoxy-1-thio-2-(2,2,2-trichloroethoxy)carbamoyl-β-D-glucopyranoside (2):



2

Ethyl 2-deoxy-1-thio-2-(2,2,2-trichloroethoxy)carbamoyl-β-D-glucopyranoside[1] (398 mg, 1.00 mmol) was dissolved in pyridine (1.25 mL) and the mixture was cooled to 0 °C. Benzoyl chloride (0.52 mL, 4.51 mmol) was added, and the reaction mixture was stirred under argon for 16 h at rt. Upon completion, the reaction was quenched by addition of MeOH (~1.5 mL), co-evaporated with toluene (3 x 10 mL), then diluted with CH_2Cl_2 (30 mL), washed with 1N aq. HCl (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 column chromatography on silica gel (ethyl acetate/ hexanes gradient elution) to afford the title compound **2** as a white amorphous solid in 67% yield. Analytical for data **2**: R_f = 0.57 (ethyl acetate-hexanes, 2/3, v/v); $[\alpha]_D^{23}$ = -30.1° (c= 1, $CHCl_3$); ^{1}H–n.m.r.: δ, 1.26 (t, 3H, CH_2CH_3), 2.68-2.80 (m, 2H, CH_2CH_3), 4.04-4.11 (m, 2H, H-2, H-5), 4.46 (dd, $J_{5,6a}$ = 5.5 Hz, 1H, H-6a), 4.56 (dd, 1H, $J_{6a,6b}$ = 9.1 Hz, H-6b), 4.60 (q, 2H, CH_2CCl_3), 4.79 (d, 1H, $J_{1,2}$ = 10.3 Hz, H-1), 5.33 (d, 1H, NH), 5.61-5.71 (m, 2H, H-3, H-4), 7.24-7.99 (m, 15H, aromatic) ppm; ^{13}C-n.m.r.: δ, 15.1, 24.5, 55.7, 63.6, 69.9, 74.2, 74.5, 76.3, 84.8, 95.4, 128.5 (x 3), 128.6, 128.7, 128.8, 128.9, 129.7 (x 3), 129.8, 129.9, 130.1 (x 3), 133.3, 133.6, 133.8, 154.5, 165.4, 166.3, 166.8 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{32}H_{30}Cl_3NO_9SNa$ 732.0605, found 732.0635.

Ethyl 3,4,6-tri-O-benzoyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (3).

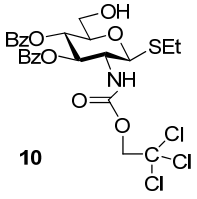


3

Ethyl 2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside[2] (1.59 g, 4.50 mmol) was benzoylated as described for synthesis of **2** to afford the title compound **3** as a white amorphous solid in 71% yield. Analytical data for **3**: R_f = 0.48 (ethyl acetate-hexanes, 3/7, v/v); $[\alpha]_D^{23}$ = +58.4° (c= 1,$CHCl_3$); ^{1}H –n.m.r.: δ, 1.21 (t, 3H, CH_2CH_3), 2.64-2.77 (m, 2H, CH_2CH_3), 4.27-4.29 (m, 1H, H-5), 4.50 (dd, 1H, $J_{5,6a}$ = 12.2 Hz, H-6a), 4.59 (d, 1H, $J_{6a,6b}$ = 3.5 Hz, H-6b), 4.64 (dd, 1H, $J_{2,3}$= 2.1 Hz, H-2), 5.64-5.71 (m, 2H, H-1, H-4), 6.30 (dd, 1H, $J_{3,4}$ = 9.9 Hz, H-3), 7.22-8.00 (m, 20H, aromatic) ppm; ^{13}C - n.m.r.: δ, 15.2, 24.6, 54.2, 63.6, 70.3, 72.1, 81.5, 123.9, 128.4 (x 3), 128.5 (x 4), 128.7 (x 2), 128.9, 129.8 (x 3), 129.9 (x 3), 129.1 (x 3), 131.3, 133.3, 133.5, 133.6, 134.5, 165.4 (x 2), 165.8 (x 2), 166.3 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{37}H_{31}NO_9SNa$ 688.1617 found 688.1589.

*Synthesis of glycosyl acceptors **10** and **12**.*

Ethyl 3,4-di-O-benzoyl-2-deoxy-1-thio-2-(2,2,2-trichloroethoxy)carbamoyl-β-D-glucopyranoside (10).

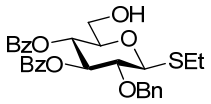


10

Ethyl 2-deoxy-1-thio-2-(2,2,2-trichloroethoxy)carbamoyl-β-D-glucopyranoside[1] (430 mg, 1.22 mmol) was dissolved in pyridine (2.15 mL), trityl chloride (0.68 g, 2.44 mmol) was added and the

reaction mixture was stirred under argon for 16 h. Upon completion as indicated by TLC, the mixture was cooled to 0 ^{o}C. Benzoyl chloride (0.42 g, 3.65 mmol) was then added, and the reaction mixture was stirred under argon for 16 h at rt. The reaction was quenched by addition of MeOH (~1.5 mL), then co-evaporated with toluene (3 x 10 mL). The residue was diluted with CH_2Cl_2 (30 mL) and washed with 1N aq. HCl (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 column chromatography on silica gel (ethyl acetate/ hexanes gradient elution). The product was dissolved in CH_2Cl_2 (30 mL) and 30% soln. of trifluoroacetic acid in CH_2Cl_2 (~1.5 mL) was added dropwise until the reaction was completed, as indicated by TLC, at which point yellow color was persistent. The mixture was diluted with CH_2Cl_2 (30 mL) and washed with 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 column chromatography on silica gel (ethyl acetate/ hexanes gradient elution) to afford the title compound **10** as a white amorphous solid in 35% overall yield over three steps. Analytical data for **10**: R_f = 0.48 (ethyl acetate-hexanes, 2/3, v/v); $[\alpha]_D^{23}$ = -103.3^{o} (c= 1, $CHCl_3$); ^{1}H–n.m.r.: δ, 1.38 (t, 3H, CH_2CH_3), 2.64-2.72 (m, 2H, CH_2CH_3), 3.64 (d, 1H, $J_{6a,6b}$ =7.8 Hz, H-6b), 3.66-3.77 (m, 2H, H-6a, H-5), 3.97-4.04 (m, 1H, $J_{2,3}$ = 7.1 Hz, H-2), 4.50 (q, 2H, CH_2CCl_3), 4.74 (d, 1H, $J_{1,2}$ = 10.3 Hz, H-1), 5.39 (dd, 1H, $J_{4,5}$ = 9.6 Hz, H-4), 5.71 (dd, 1H, $J_{3,4}$ = 9.9 Hz, H-3), 5.79 (d, 1H, NH), 7.16-7.82 (m, 10H, aromatic) ppm; ^{13}C-n.m.r.: δ, 15.2, 24.6, 55.9, 62.0, 69.9, 74.3, 74.8, 79.1, 84.9, 95.7, 128.8 (x 2), 128.9 (x 2), 129.0, 129.1, 130.2 (x 2), 130.3 (x 2), 133.9, 134.1, 154.7, 166.3, 166.9 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{25}H_{26}Cl_3NO_8SNa$ 628.0342, found 628.0322.

Ethyl 3,4-di-O-benzoyl-2-O-benzyl-1-thio-β-D-glucopyranoside (12).



12

Ethyl 2-O-benzyl-1-thio-β-D-glucopyranoside[3] was tritylated, benzoylated and detritylated as described for the synthesis of **10** to afford the title compound **12** as a white amorphous solid in 59% overall yield. Analytical data for **12**: R_f = 0.43 (ethyl acetate-hexanes, 2/3, v/v); $[\alpha]_D^{25}$ = -84.7° (c= 1, $CHCl_3$); ^{1}H–n.m.r.: δ, 1.31-1.37 (t, 3H, CH_2CH_3), 2.48-2.50 (m, 1H, OH), 2.77-2.83 (m, 2H, CH_2CH_3), 3.63-3.69 (m, 3H, H-2, H-5, H-6a), 3.74-3.83 (m, 1H, H-6b), 4.57 (d, 1H, ½ CH_2 -Ph), 4.69 (d, 1H, $J_{1,2}$ = 9.7 Hz, H-1), 4.81 (d, 1H, ½ CH_2Ph), 5.32 (dd, 1H, $J_{3,4}$ = 9.5 Hz, H-3), 5.74 (dd, 1H, $J_{4,5}$ = 9.3 Hz, H-4), 7.11-7.91 (m, 15H, aromatic) ppm; ^{13}C-n.m.r.: δ, 15.2, 25.5, 61.8, 69.7, 75.3, 75.7, 78.6, 79.2, 85.5, 128.2, 128.6 (x 4), 128.8 (x 4), 128.9, 129.1, 129.8 (x 2), 130.1, 133.3, 133.6, 134.0, 137.5, 166.1, 166.6 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{29}H_{30}Cl_3O_7SNa$ 545.1610, found 545.1601.

*Preparation of di- and trisaccharides (**6, 7, 8, 9, 11** and **13**)*

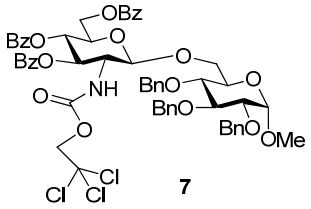
Method A: Typical NIS/TfOH-Promoted Glycosylation Procedure. A mixture containing the glycosyl donor (0.11 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (4 Å, 30 mg) in 1,2-dichloroethane (DCE, 0.5 mL) was stirred under argon for 1 h. The mixture was kept at room temperature or chilled at -20 °C (see Table 1), NIS (0.22 mmol) and TfOH (0.022 mmol) were added, and upon completion (~5 min) the mixture was diluted with CH_2Cl_2, the solid was filtered off, and the residue was rinsed successively with CH_2Cl_2. The combined filtrate (30mL) was washed with 10%$Na_2S_2O_3$ (10 mL) and water (3 x 10 mL). The

organic phase was separated, dried, and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel as indicated to obtain the corresponding disaccharide.

Method B: Typical MeOTf-Promoted Glycosylation Procedure. A mixture containing the glycosyl donor (0.11 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (3Å, 90mg) in DCE (0.5 mL) was stirred under argon for 1 h. MeOTf (0.33 mmol) was added, and the reaction mixture was stirred for 2-6 h (see Table 1). Upon completion, the mixture was diluted with CH_2Cl_2, the solid was filtered off, and the residue was rinsed successively with CH_2Cl_2. The combined filtrate (30 mL) was washed with 10% $Na_2S_2O_3$ (10 mL) and water (3 x 10 mL). The organic phase was separated, dried, and concentrated in vacuo. The residue was purified by column chromatography on silica gel as indicated to obtain the corresponding disaccharide.

Method C: Typical Iodine-Promoted Glycosylation Procedure. A mixture containing the glycosyl donor (0.11 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (3Å, 90 mg) in DCE (0.5 mL) was stirred under argon for 1 h. Iodine (0.33 mmol) was then added, and the reaction mixture was stirred for 1-24 h at room temperature (or at 50 °C Table 1, 2 and 3). Upon completion, the mixture was quenched with Et_3N and diluted with CH_2Cl_2, the solid was filtered off, and the residue was rinsed successively with CH_2Cl_2 .The combined filtrate (30 mL) was washed with 10% $Na_2S_2O_3$ and water (3 x10 mL). The organic phase was separated, dried, and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel as indicated to obtain the corresponding di- or trisaccharide.

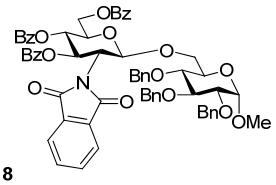
Methyl O-(3,4,6-tri-O-benzoyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbamoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-β-D-glucopyranoside (7).



7

The title compound was obtained from **2** and **5** by Method A, B or C as a white amorphous solid in 72 - 98% (see Table 1). Analytical data for **7**: R_f = 0.50 (ethyl acetate-hexanes, 2/3, v/v); $[\alpha]_D^{25}$ = +10.9° (c= 1, $CHCl_3$); ^{1}H–n.m.r.: δ, 3.27 (s, 3H, OC*H*$_3$), 3.40-3.43 (m, 2H, H-2, H-4), 3.65-3.69 (m, 2H, H-5, H-6b), 3.83-3.95 (m, 3H, H-5′, H-2′, H-3), 4.03 (d, 1H, $J_{6a,6b}$ = 8.7 Hz, H-6a), 4.36-4.58 (m, 7H, H-6a′, H-6b′, H-1, H-1′, *CH*$_2$Ph, ½ *CH*$_2$$CCl_3$), 4.68-4.92 (m, 6H, 2 x C*H*$_2$Ph, ½ *CH*$_2$$CCl_3$, NH), 5.46-5.62 (m, 2H, H-4′, H-3′), 7.18-7.90 (m, 30H, aromatic) ppm; ^{13}C-n.m.r.: δ, 55.6, 63.6, 69.9, 70.1, 72.5, 73.8, 75.0, 76.1, 80.1, 82.5, 95.5 (x 2), 98.5 (x 2), 128.0, 128.4, 128.6, 128.7, 128.8 (x 4), 128.9 (x 4), 129.0 (x 5), 129.1 (x 5), 129.2 (x 4), 129.9 (x 4), 130.1 (x 4), 130.2, 130.3, 133.5, 133.9, 138.5, 138.9, 139.1, 155.1, 165.6, 166.5, 166.7 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{58}H_{56}Cl_3NO_{15}Na$ 1134.2613, found 1134.2610.

Methyl O-(3,4,6-tri-O-benzoyl-2-deoxy-phthalimido-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-β-D-glucopyranoside (8).

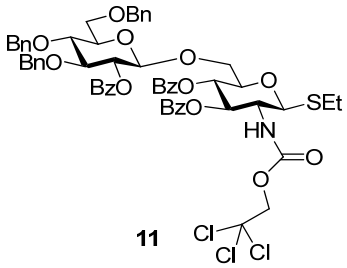


8

The title compound was obtained from **3** and **5** by Method A, B, or C as a white amorphous solid in 61-86% (see Table 1). Analytical data for **8**: R_f = 0.48 (ethyl acetate-hexanes, 3/7, v/v); $[\alpha]_D^{25}$ =

-36.5° (c= 1,$CHCl_3$); ^{1}H–n.m.r.: δ, 3.14 (s, 3H, OCH_3), 3.19 (dd, 1H, $J_{4,5}$ = 9.2 Hz, H-4), 3.35 (dd, 1H, $J_{2,3}$ = 5.1 Hz, H-2), 3.60-3.69 (m, 2H, H-5, H-6a), 3.77 (dd, 1H, $J_{3,4}$ = 9.3 Hz, H-3), 4.07 (d, 1H, $J_{6a,6b}$ = 10.8 Hz, H-6b), 4.18-4.20 (m, 1H, H-5), 4.32 (m, 2H, H-1, ½ CH_2Ph), 4.45-4.71 (m, 7H, H-6a′, H-6b′, H-2′, 2 x CH_2Ph), 4.78 (d, 1H, ½ CH_2Ph), 5.56-5.71 (m, 2H, H-1′, H-4′), 6.23 (dd, 1H, $J_{2',3'}$ = 9.3 Hz, H-3′), 7.05-8.03 (m, 35H, aromatic) ppm: ^{13}C-n.m.r.: δ, 21.7, 29.9, 63.5, 65.6, 68.9, 69.4, 70.6, 71.3, 72.4, 73.6, 74.9, 75.8, 77.9, 79.9, 82.0, 98.1, 98.8, 123.7 (x 2), 127.8, 127.9 (x 4), 128.1 (x 4), 128.2, 128.3, 128.4 (x 4), 128.5 (x 4), 128.6 (x 5), 128.7 (x 4), 129.0 (x 4), 129.2, 129.8, 129.9, 130.0, 133.4, 137.9, 138.3, 165.4, 165.9 (x 2), 166.3 (x 2) ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{63}H_{57}ClNO_{15}Na$ 1090.3626, found 1090.3607.

Ethyl O-(2-O-benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→6)-3,4-di-O-benzoyl-2 deoxy-1-thio-2-(2,2,2-trichloroethoxy)carbamoyl-β-D-glucopyranoside (11).

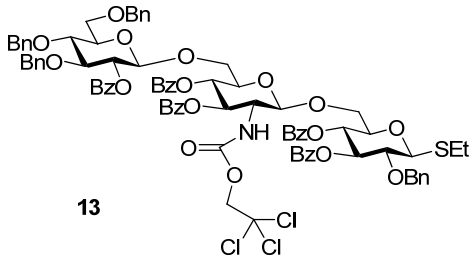


11

The title compound was obtained from **1** and **10** by Method C as a syrup in 77% yield. Analytical data for **11**: R_f = 0.35 (ethyl acetate-hexanes, 3/7, v/v); $[\alpha]_D^{25}$ = -5.78° (c= 1, $CHCl_3$); ^{1}H–n.m.r.: δ, 1.04 (t, 3H, CH_2CH_3), 2.36-2.58 (m, 2H, CH_2CH_3), 3.47-3.50 (m, 1H, H-5), 3.64-3.80 (m, 4H, H-3′, H-4′, H-6a′, H-6b′), 3.82-3.95 (m, 4H, H-2, H-5, H-6a, H-6b), 4.39 (d, 1H, $J_{1,2}$ = 12.1 Hz, H-1), 4.47-4.48 (m, 9H, 3 x CH_2Ph, CH_2CCl$_3$, H-1′), 5.00 (d, 1H, NH), 5.21-5.28 (m, 2H, H-2′, H-4), 5.43 (dd, 1H, $J_{3,4}$ = 4.0 Hz, H-3), 7.03-8.04, (m, 30H, aromatic) ppm; ^{13}C-n.m.r.: δ, 14.9, 24.1, 55.6, 68.8, 69.7, 73.7 (x 2), 73.8, 74.1, 74.6, 75.2, 75.3, 75.4, 78.2, 83.0 (x 2), 84.3, 95.4, 101.3,

127.8 (x 4), 127.9 (x 4), 128.0 (x 4), 128.1 (x 4), 128.2 (x 4) , 128.4, 128.5, 128.6, 128.9, 129.9 (x 4), 130.0, 130.1, 130.2, 133.7 (x 2), 137.9, 138.1, 138.2, 154.8, 165.3, 165.6, 166.5 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{59}H_{58}ClNO_{14}SNa$ 1164.2541, found 1164.2493.

Ethyl O-(2-O-benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→6)-(2,3-di-O-benzoyl-2 deoxy-2-(2,2,2-trichloroethoxy)carbarmoyl-β-D-glucopyranosyl)-(1→6)-2-O-benzyl-3,4-di-O-benzoyl-1-thio-β-D-glucopyranoside (13).

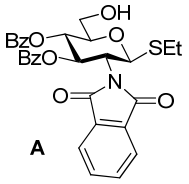


13

The title compound was obtained from **11** and **12** by Method C as a syrup in 60 % yield. Analytical data for **13**: R_f = 0.35 (ethyl acetate-hexanes, 3/7, v/v); $[\alpha]_D^{25}$ = -0.7° (c= 0.6, $CHCl_3$); ^{1}H–n.m.r.: δ, 1.31, (t, 3H, CH_2CH_3), 2.73-2.82 (m, 2H, CH_2CH_3), 3.13-3.18 (m, 1H, H-5″), 3.36-3.42 (m, 1H, H-5), 3.47-3.52 (m, 1H, H-6a′), 3.58-3.95 (m, 10H, H-2, H-6a, H-6b, H-5′, H-6b′, H-4″, H-6″a, H-6″b, H-3″, H-2′), 4.28 (d, 1H, $J_{1',2'}$ = 8.4 Hz, H-1′), 4.40 (d, $J_{1,2}$ = 12.2 Hz, H-1), 4.49-4.80 (m, 11H, 4 x CH_2Ph, CH_2CCl_3, H-1″), 5.12-5.18 (m, 2H, H-4′, H-2″), 5.24-5.44 (m, 2H, H-3′, H-4), 5.59 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-3), 5.77 (d, 1H, NH), 7.08-8.01 (m, 45H, aromatic) ppm; ^{13}C-n.m.r.: δ, 15.5, 30.1, 68.8, 69.7, 70.2, 73.8 (x 3), 74.3 (x 2), 74.4, 75.4 (x 3), 75.5, 76.2, 78.3, 79.0, 83.1 (x 3), 85.4 (x 2), 101.6, 128.0 (x 4), 128.1 (x 4), 128.2 (x 4), 128.3 (x 4), 128.4 (x 4), 128.6 (x 4), 128.7 (x 4) 128.8 (x 4), 128.9 (x 4), 129.0 (x 4), 130.1 (x 3), 130.2 (x 3), 130.3 (x 3), 130.4 (x 3), 137.6, 138.4 (x 3), 155.0, 165.4, 165.8, 166.1, 166.2 (x 2) ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{86}H_{82}Cl_3NO_{15}Na$ 1624.4312, found 1624.4063.

*Synthesis of compounds **A** and **B**.*

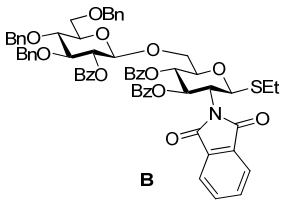
Ethyl 3,4-di-O-benzoyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (A).



A

Ethyl 2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside[2] was tritylated, benzoylated and detritylated as described for the synthesis of **10** to obtain the title compound **A** as a white amorphous solid in 37% overall yield**.** Analytical data for **A**: R_f = 0.51 (ethyl acetate-hexanes, 1/1, v/v); $[\alpha]_D^{23}$ = +30.4^o (c= 1,$CHCl_3$); ^{1}H–n.m.r.: δ, 1.23 (t, 3H, CH_2CH_3), 2.65-2.78 (m, 2H, CH_2CH_3), 3.73 (dd, 1H, $J_{6a,6b}$ = 7.2 Hz, H-6b), 3.90-3.94 (m, 2H, H-5, H-6a), 4.61 (dd, 1H, $J_{2,3}$= 10.4 Hz, H-2), 5.51 (dd, 1H, $J_{4,5}$ = 9.6 Hz, H-4), 5.62 (d, 1H, $J_{1,2}$ = 10.5 Hz, H-1), 6.34 (dd, 1H, $J_{3,4}$ = 10.2 Hz, H-3), 7.24-7.93 (m, 15H, aromatic) ppm; ^{13}C-n.m.r.: δ, 15.1, 24.3, 54.1, 61.7, 70.1, 71.9, 78.8, 81.3, 123.9, 128.5 (x 3), 128.6, 128.7, 128.8, 129.9 (x 3), 130.1 (x 3), 131.3, 131.7, 133.4, 133.8, 134.3, 134.5, 165.8, 166.1, 167.3; HR-FAB MS $[M+Na]^+$ calcd for $C_{30}H_{27}NO_8SNa$ 584.1355, found 584.1366.

Ethyl O-(2-O-benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→6)-3,4-di-O-benzoyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (B).

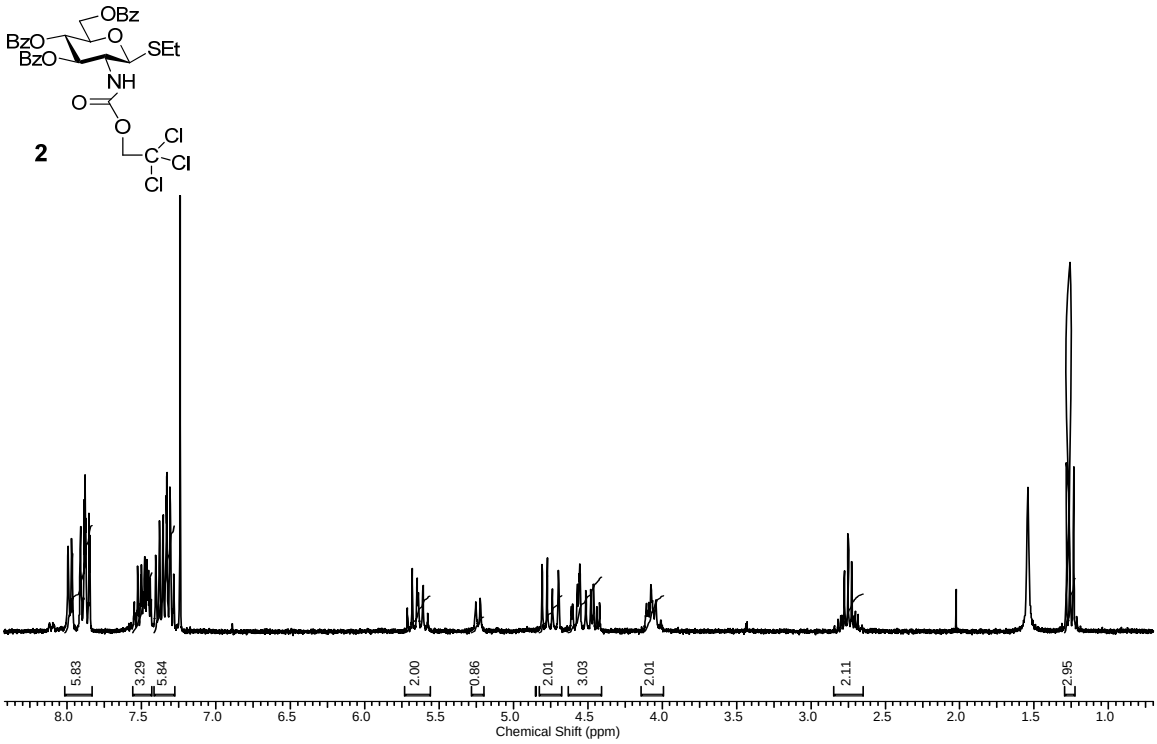


B

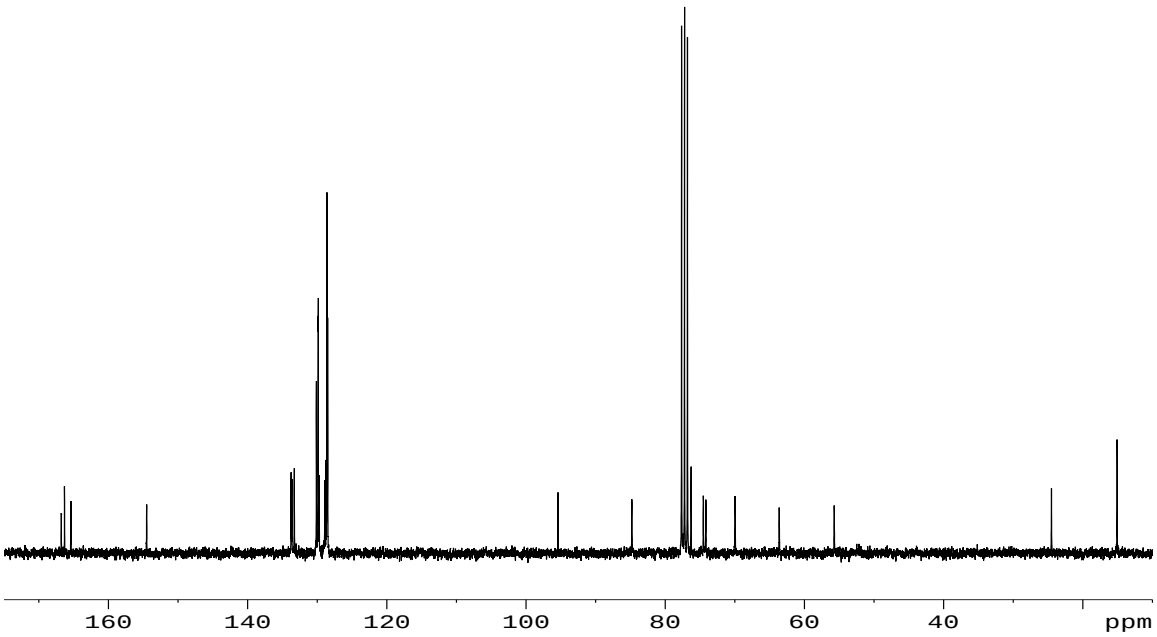
The title compound was obtained from **1** and **A** by Method C as a syrup in 61% overall yield. Analytical data for **B**: R_f = 0.48 (ethyl acetate-hexanes, 2/3, v/v); $[\alpha]_D^{25}$ = +16.60^o (c= 1,$CHCl_3$);

^{1}H–n.m.r.: δ, 0.96 (t, 3H, CH_2CH_3), 2.30-2.44 (m, 2H, CH_2CH_3), 3.44-3.47 (m, 1H, H-5′), 3.65-3.76 (m, 5H, H-3′, H-4′, H-6a′, H-6b′, H-6b), 3.95-4.10 (m, 2H, H-5, H-6a), 4.42-4.76 (m, 8H, 3 x CH_2Ph, H-2, H-1′), 5.27 (dd, 1H, $J_{2,3}$ = 9.9 Hz, H-2′), 5.38 (d, 1H, $J_{4,5}$ = 9.9 Hz, H-4), 5.47 (d, 1H, $J_{1,2}$ = 10.5 Hz, H-1), 6.15 (dd, 1H, $J_{3,4}$ = 10.1 Hz, H-3), 7.05-8.10 (m, 35H, aromatic) ppm; ^{13}C-n.m.r.: δ, 15.3, 24.3, 68.5, 68.9, 70.6, 72.4, 73.9, 74.1, 75.4, 75.5, 75.7, 78.3, 78.5, 81.1, 83.3, 101.4, 124.0, 127.7, 128.0, 128.2 (x 4), 128.3, 128.4 (x 4), 128.6 (x 4), 128.7 (x 4), 128.8 (x 4), 129.0, 129.2, 133.51 (x 4), 133.6 (x 4), 133.8 (x 4), 134.5, 134.6, 138.2, 138.4, 138.5, 165.6, 165.8, 165.9, 167.5, 168.2 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{64}H_{59}NO_{14}SNa$ 1120.3554, found 1120.3573.

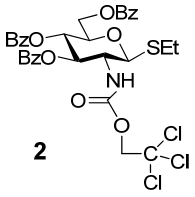
NMR spectra



$CDCl_3$ at 300 MHz



$CDCl_3$ at 75 MHz



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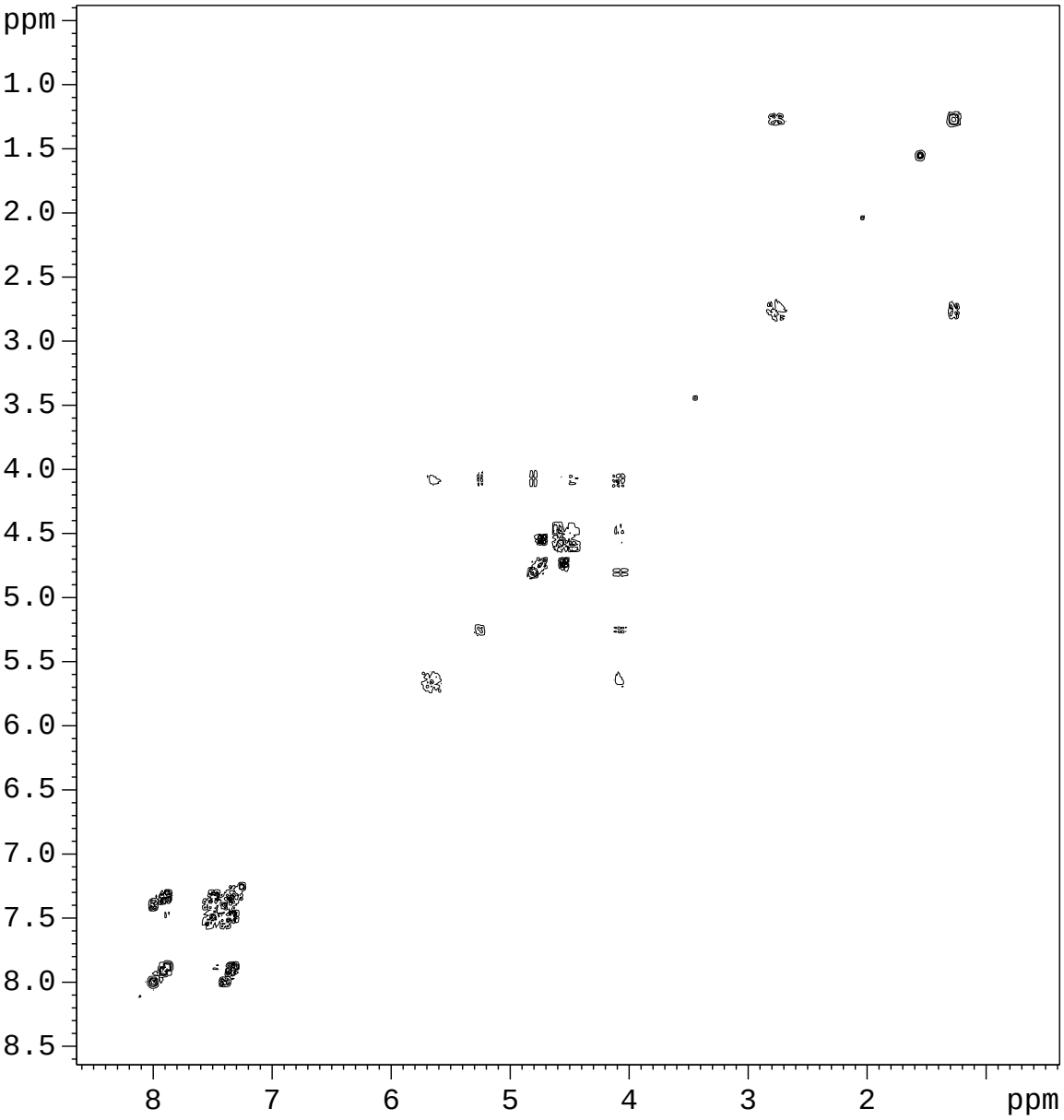

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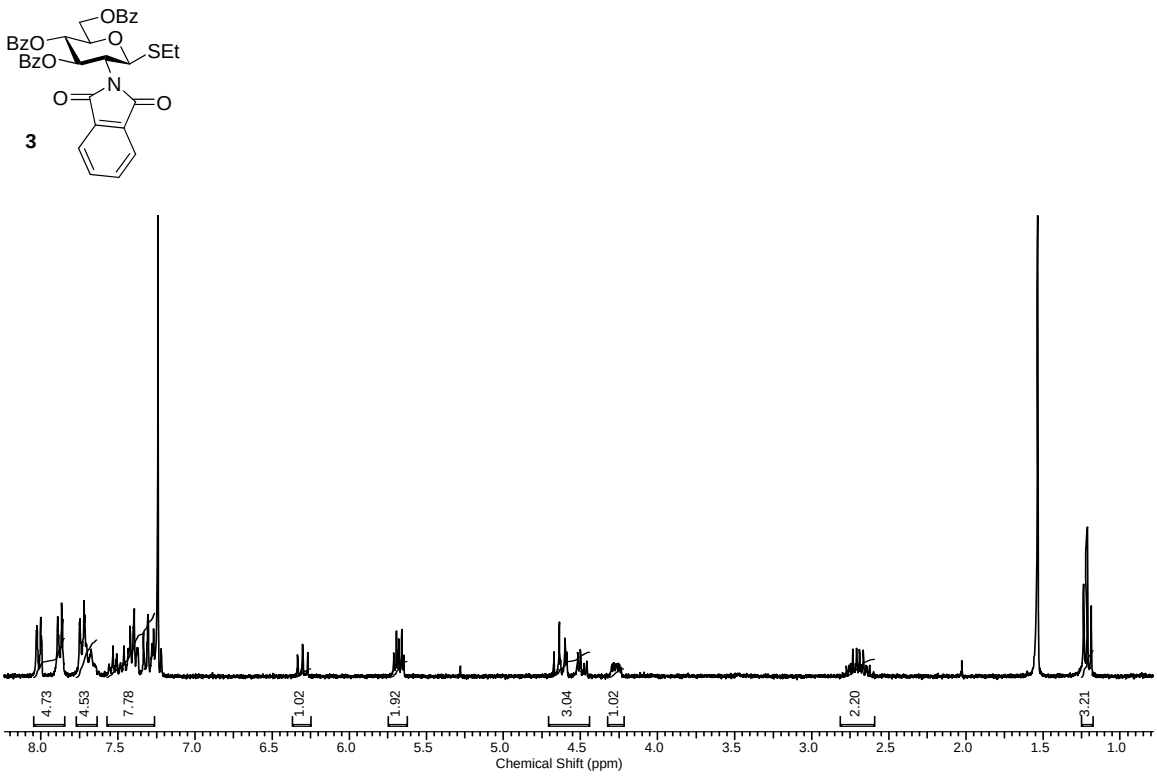

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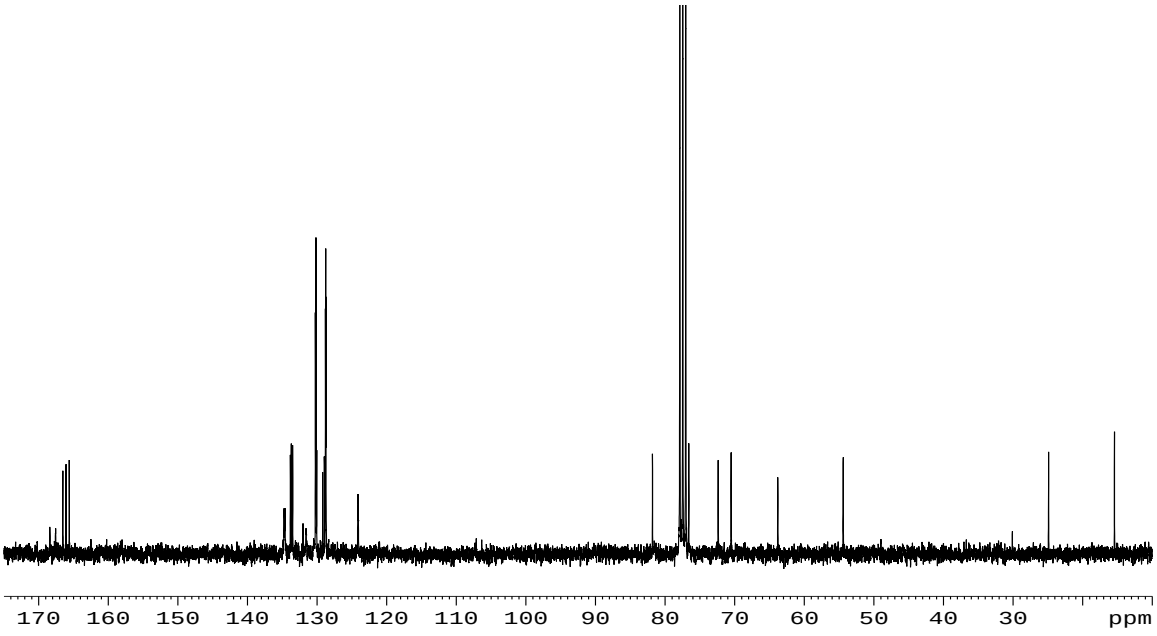

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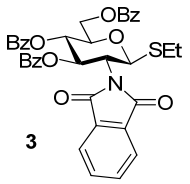

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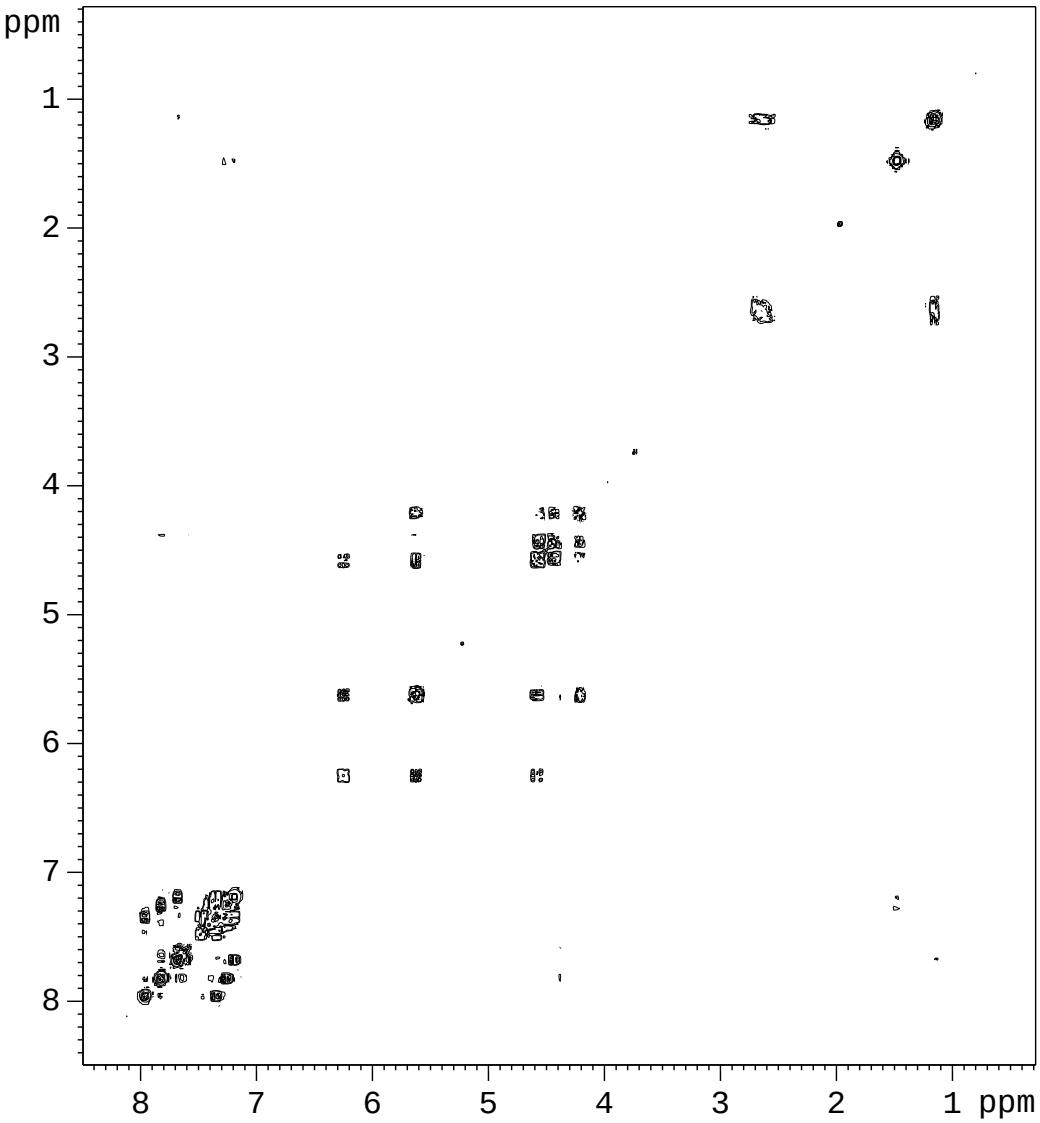

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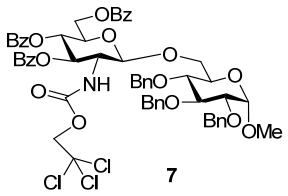

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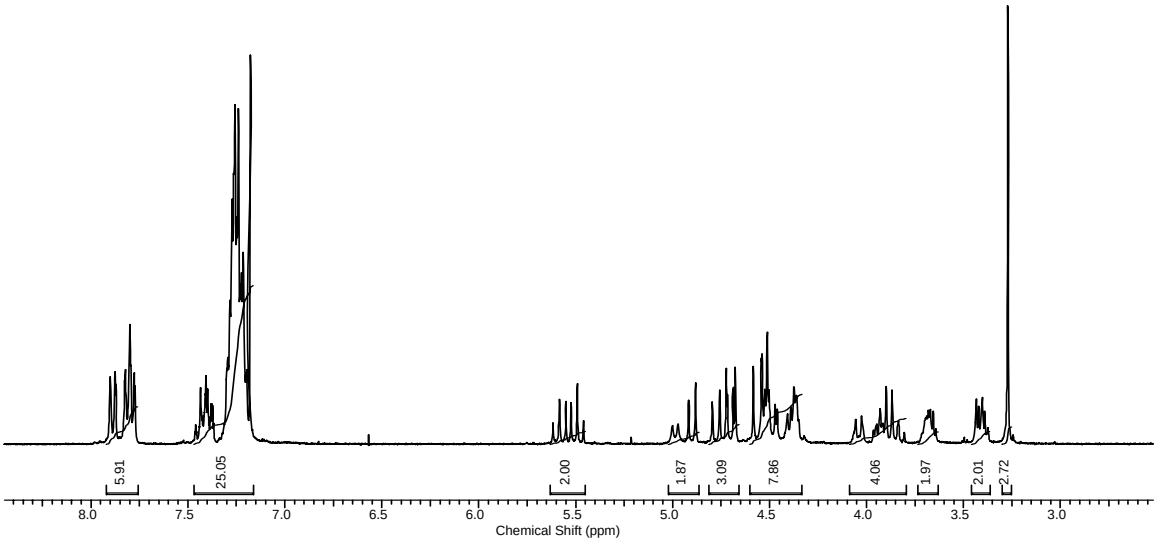

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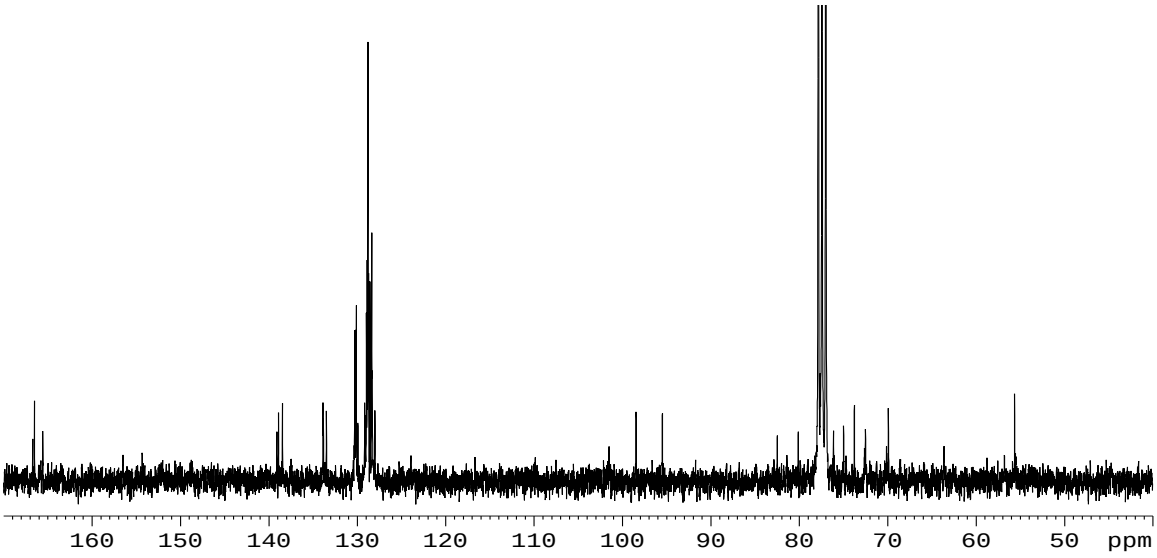

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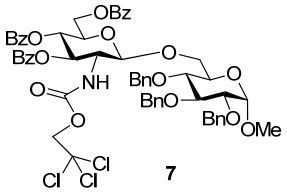

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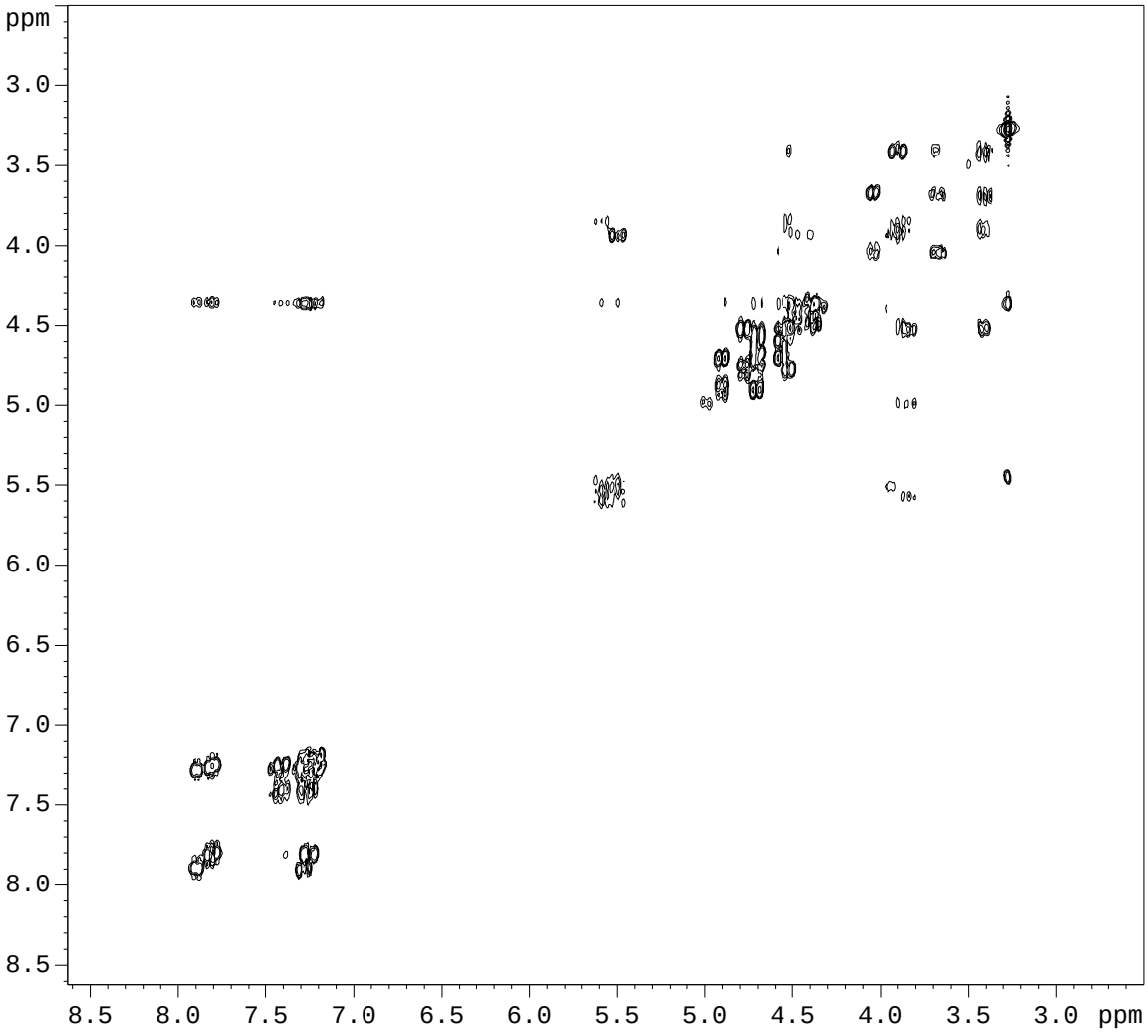

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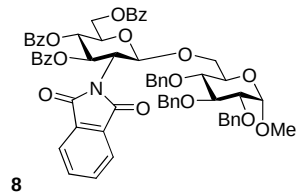

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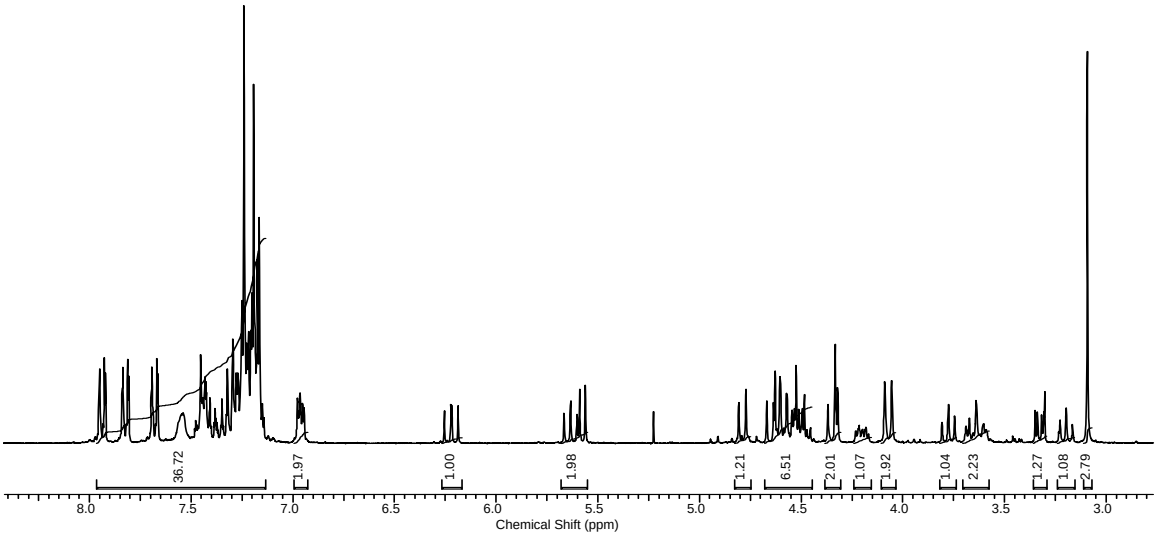

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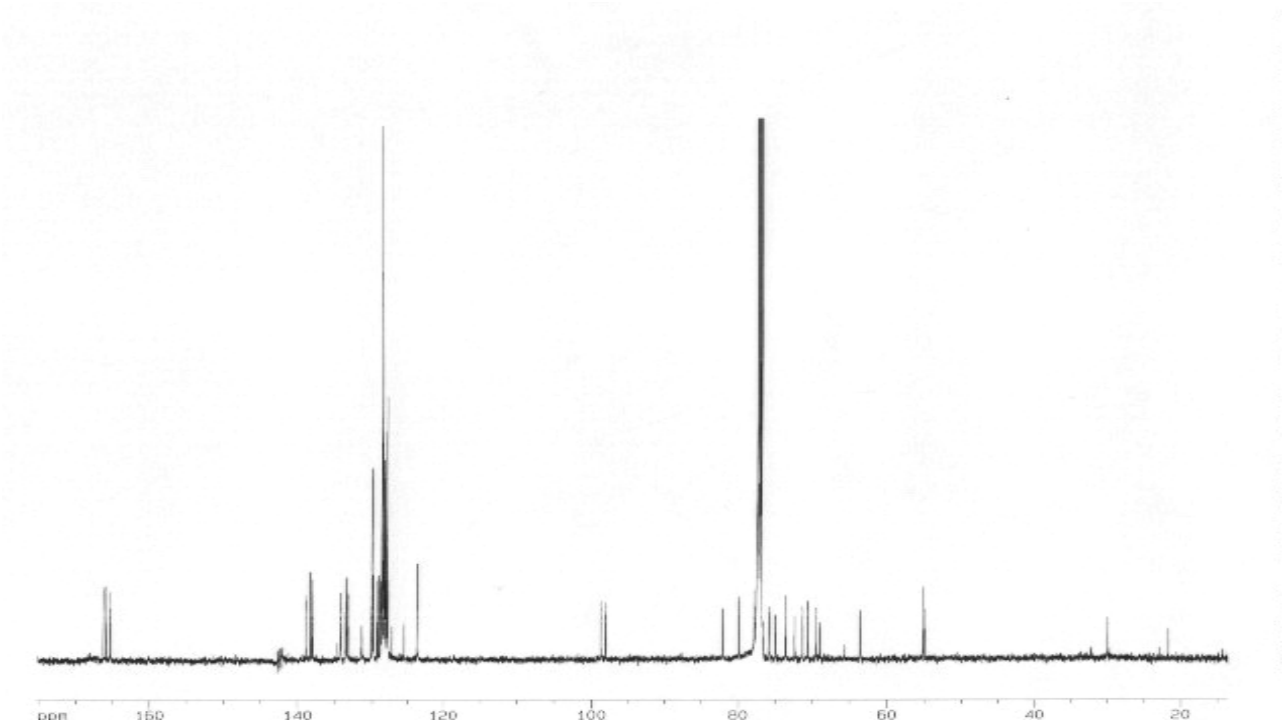
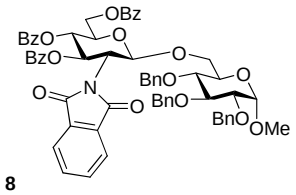


$CDCl_3$ at 125 MHz



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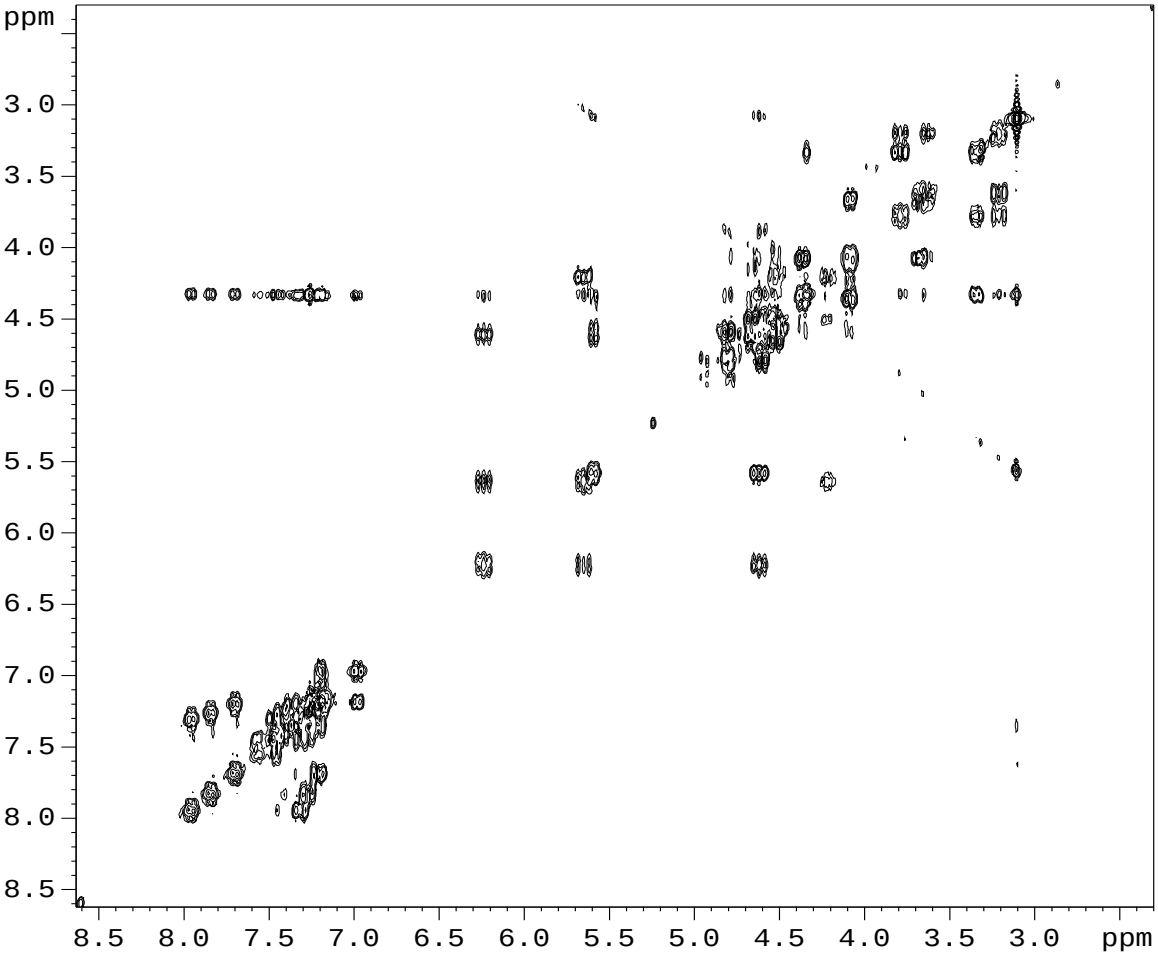

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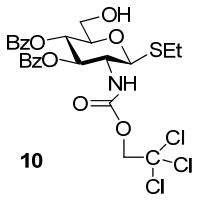

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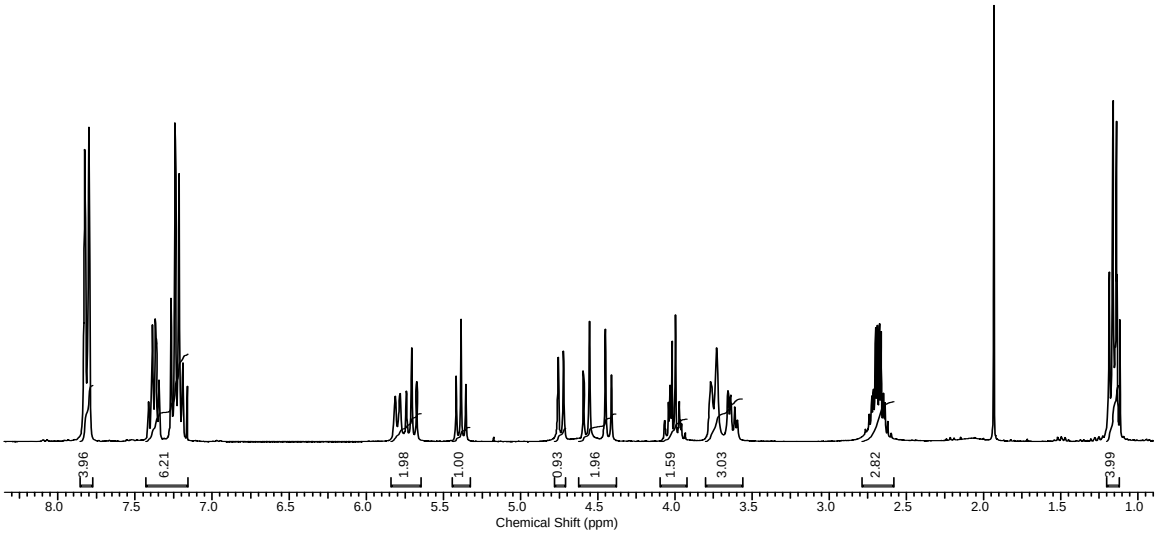

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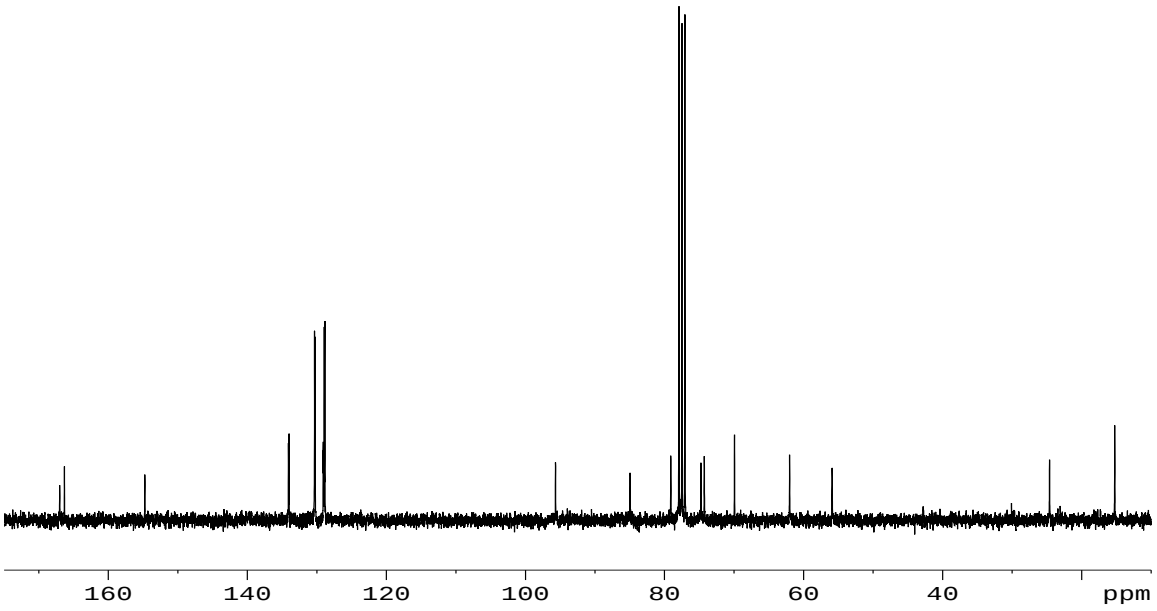

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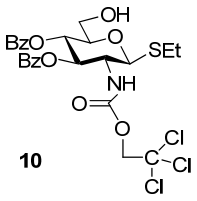

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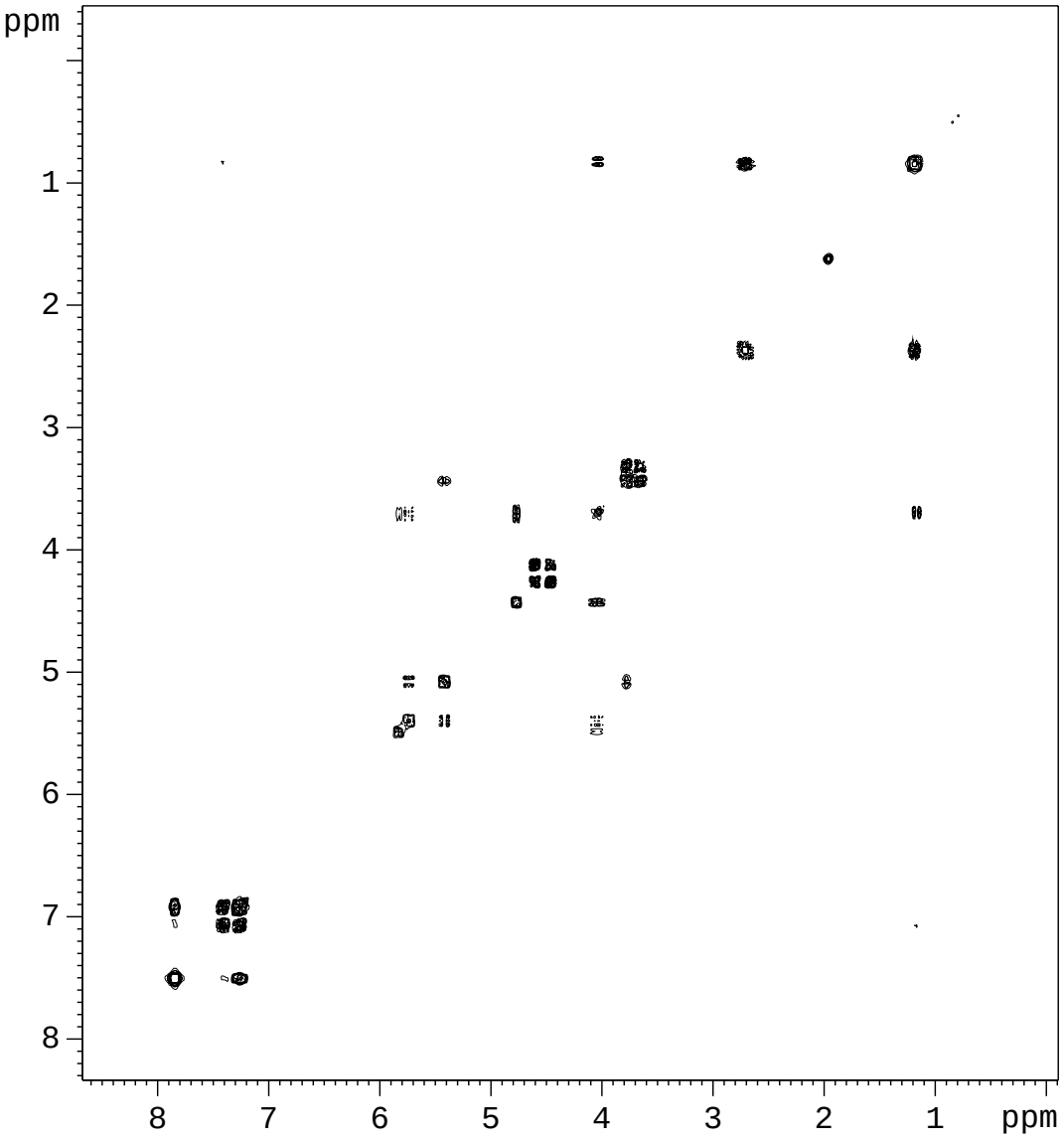

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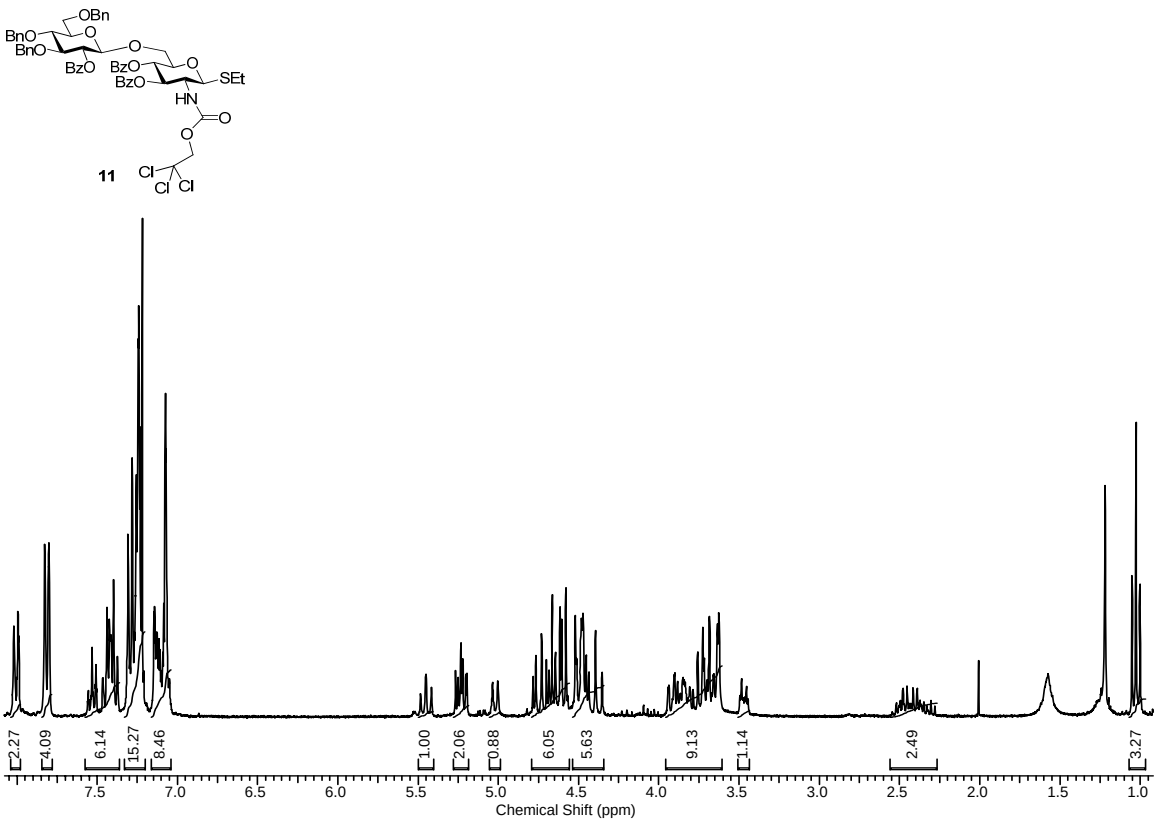

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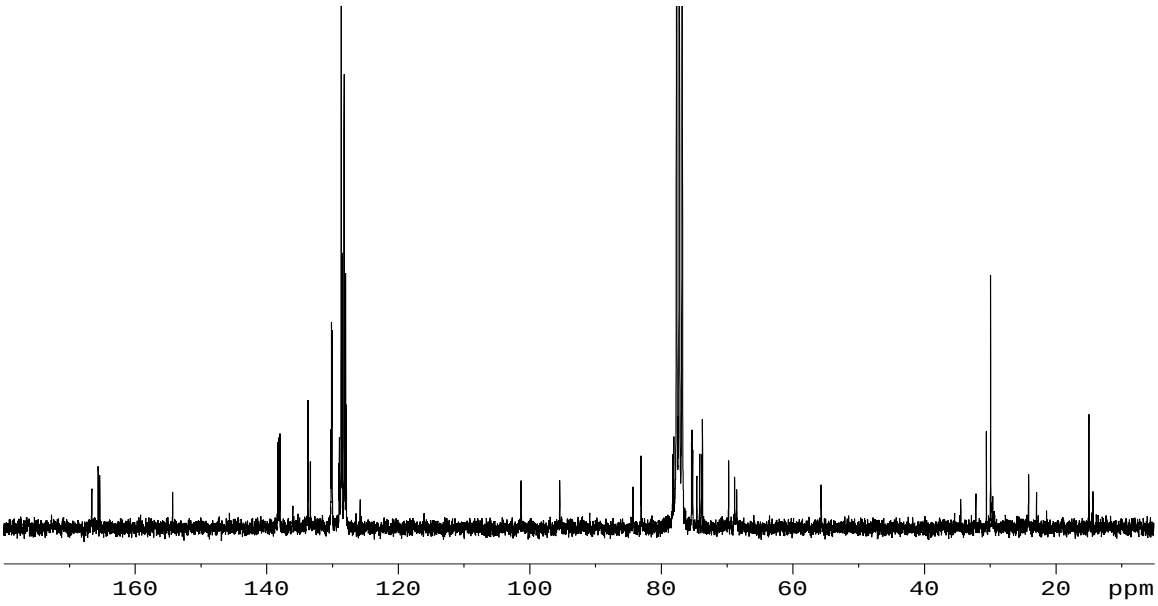

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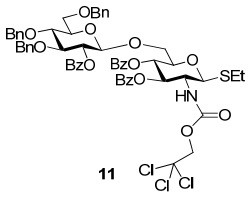

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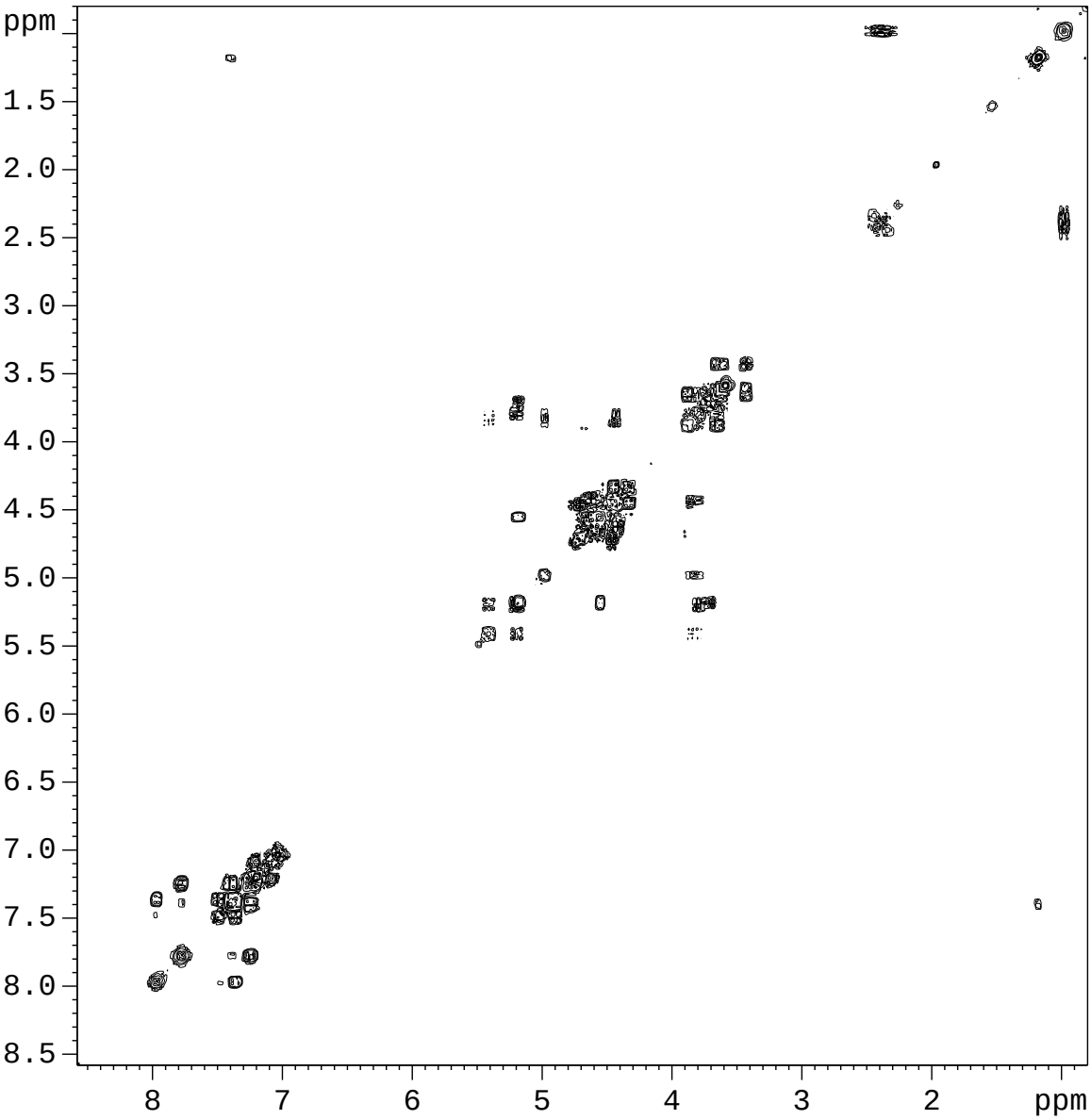

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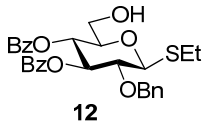

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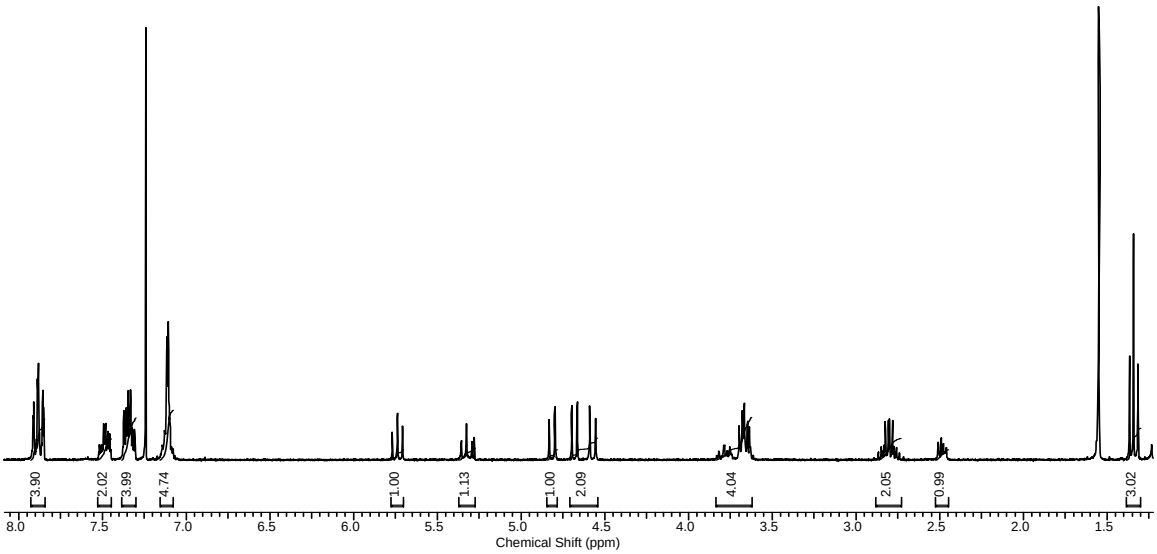

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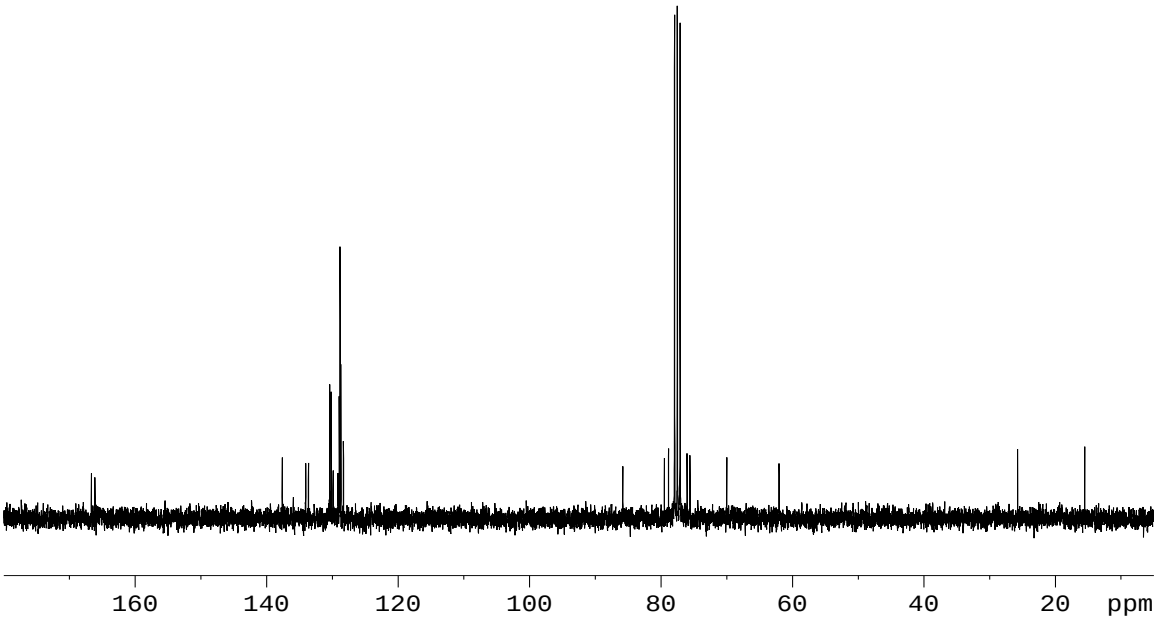

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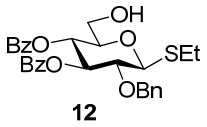

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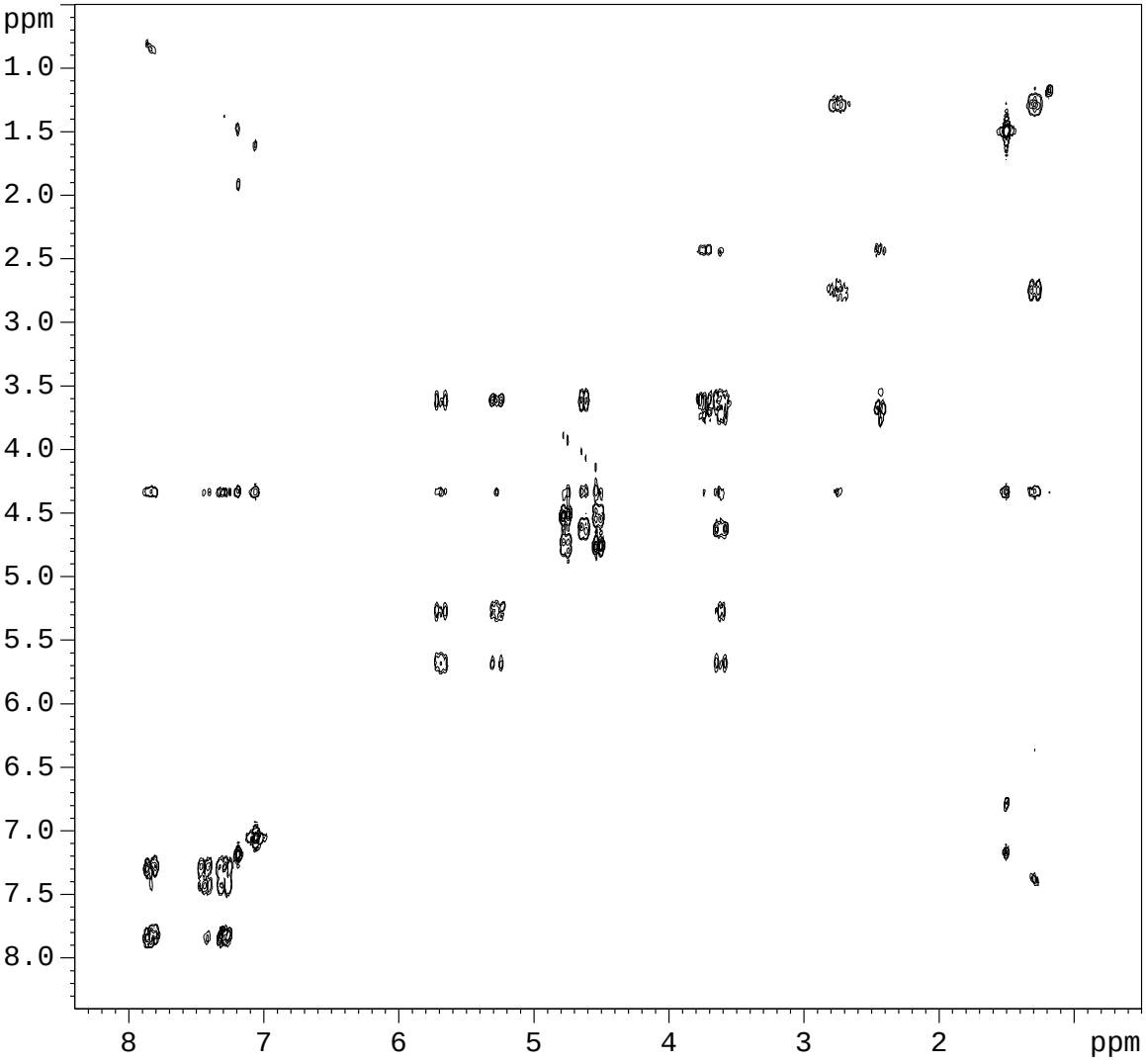

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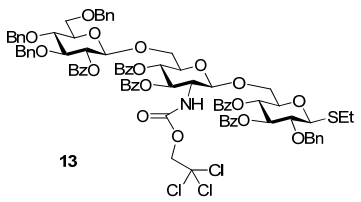

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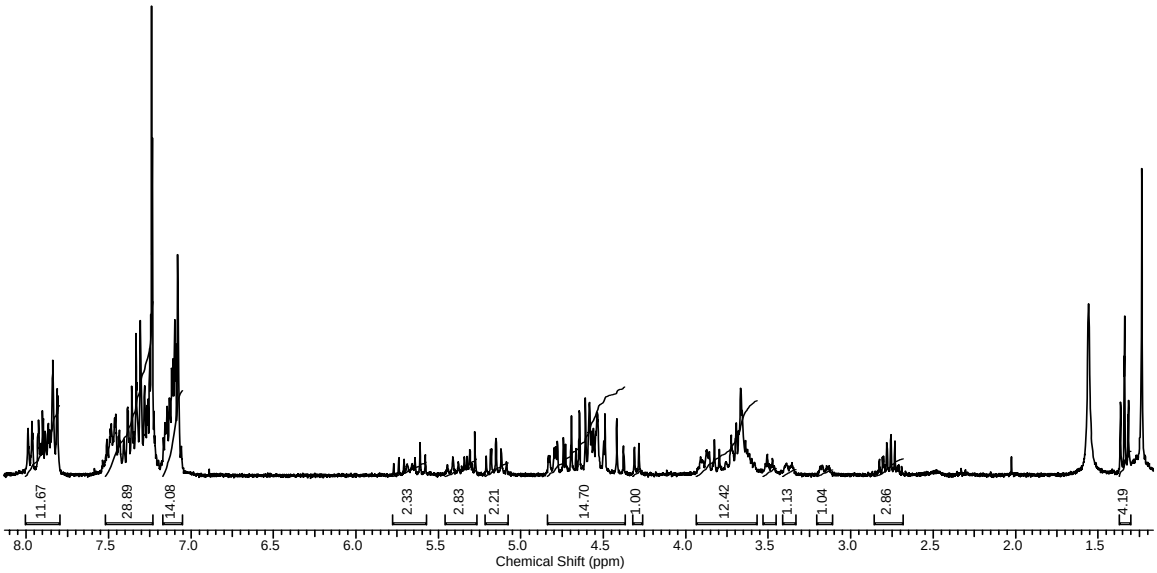

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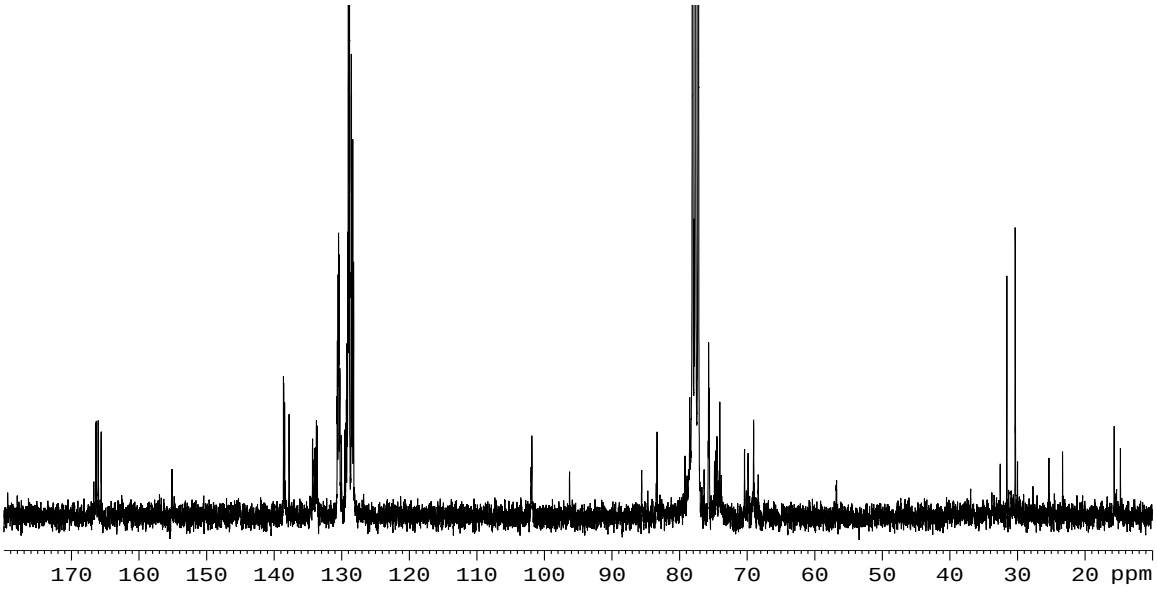

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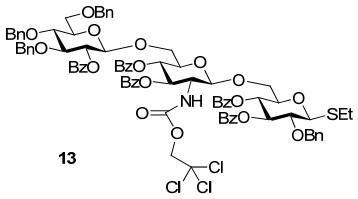

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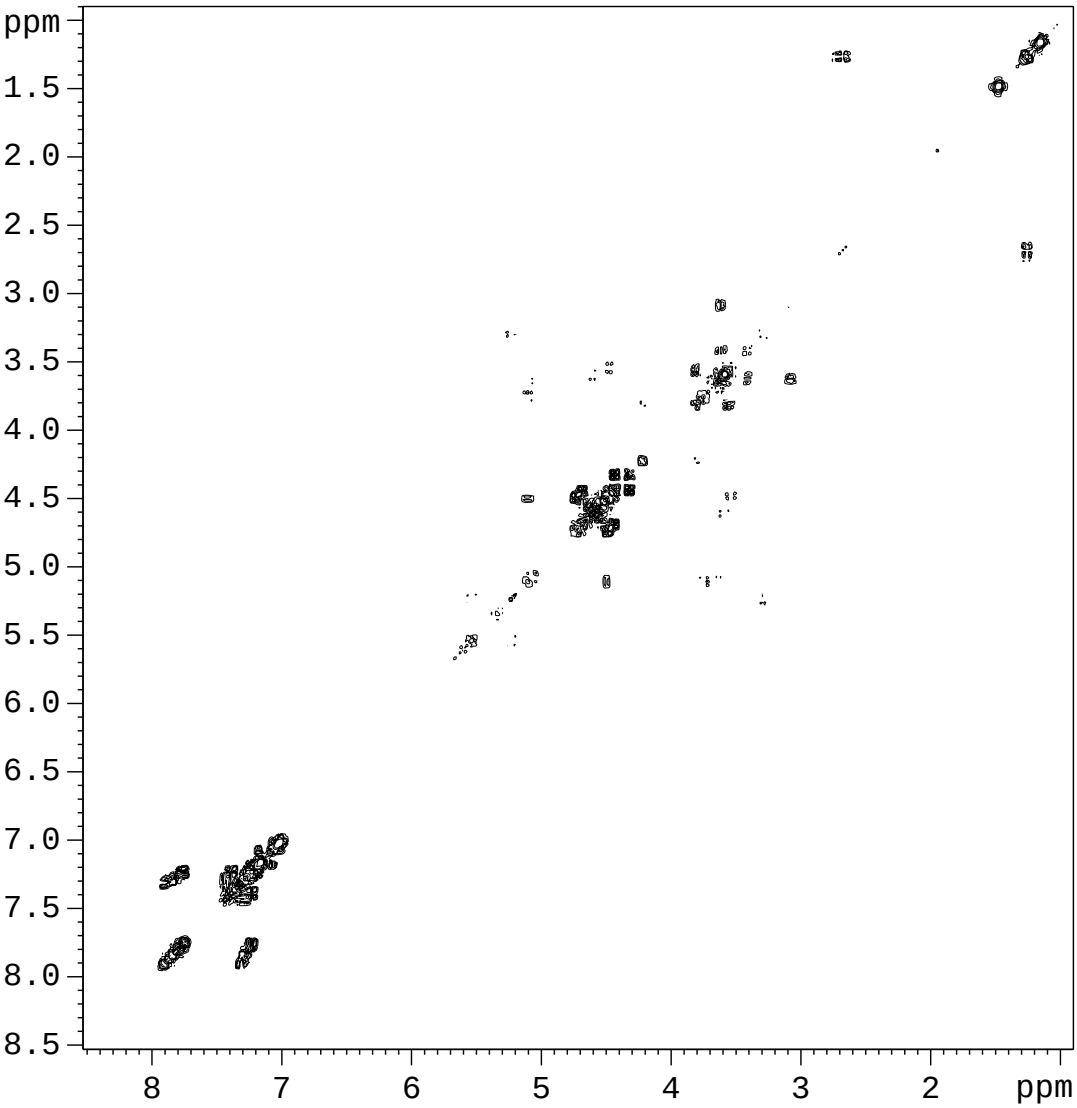

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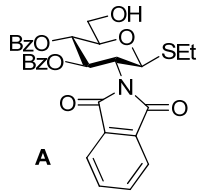

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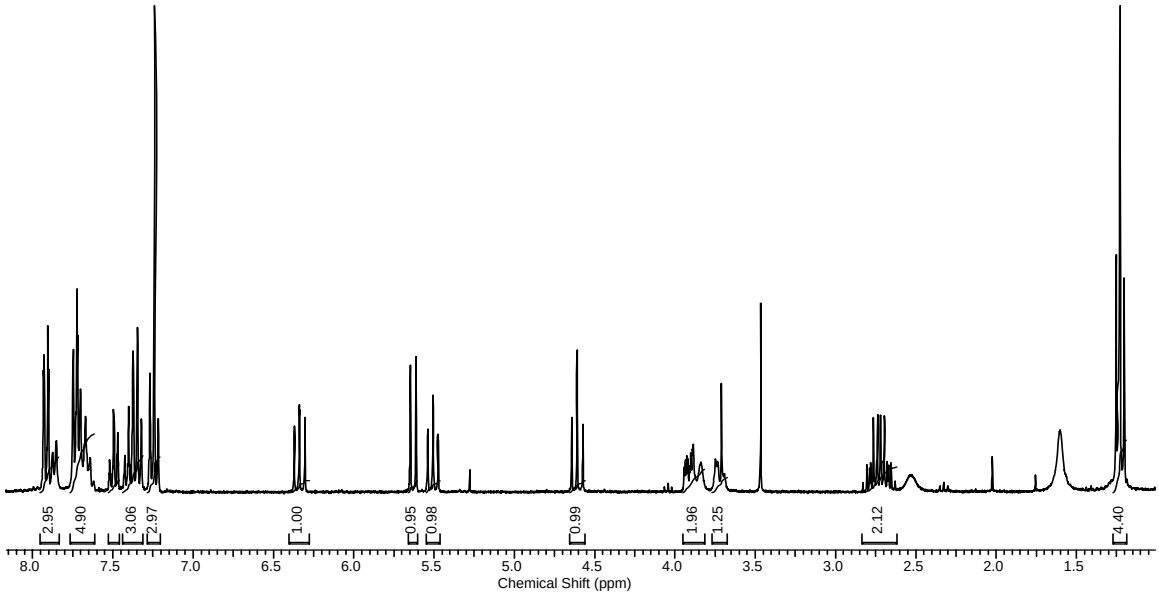

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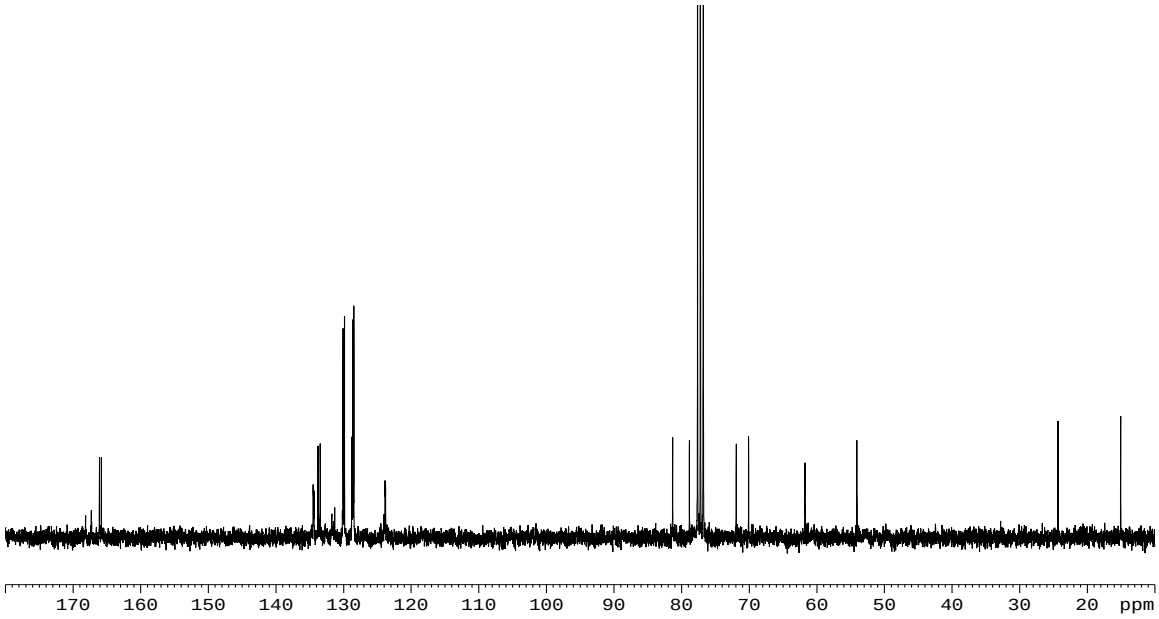

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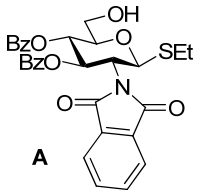

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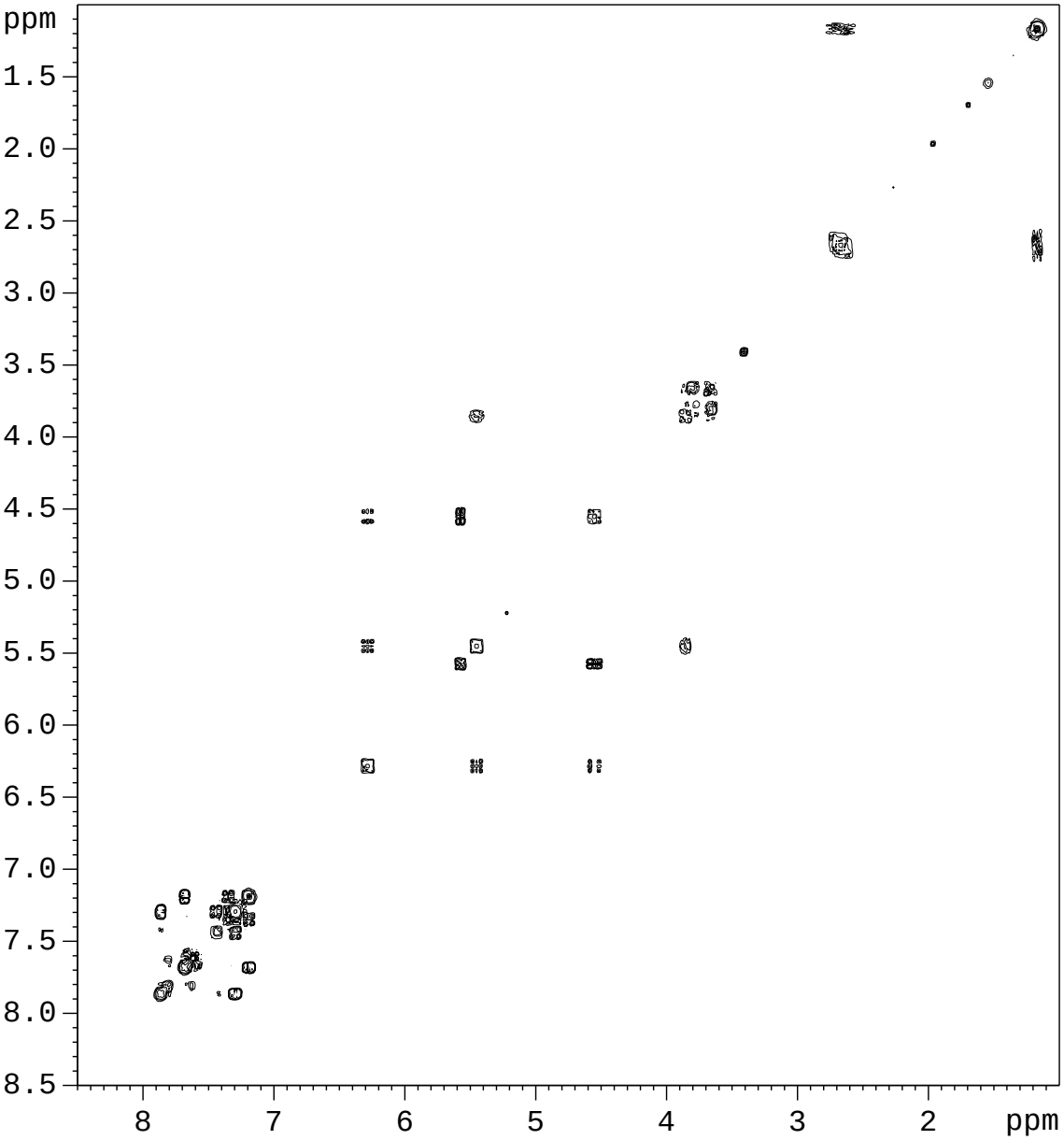

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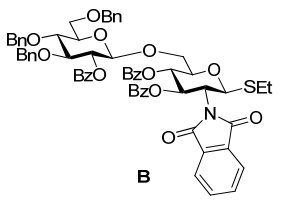

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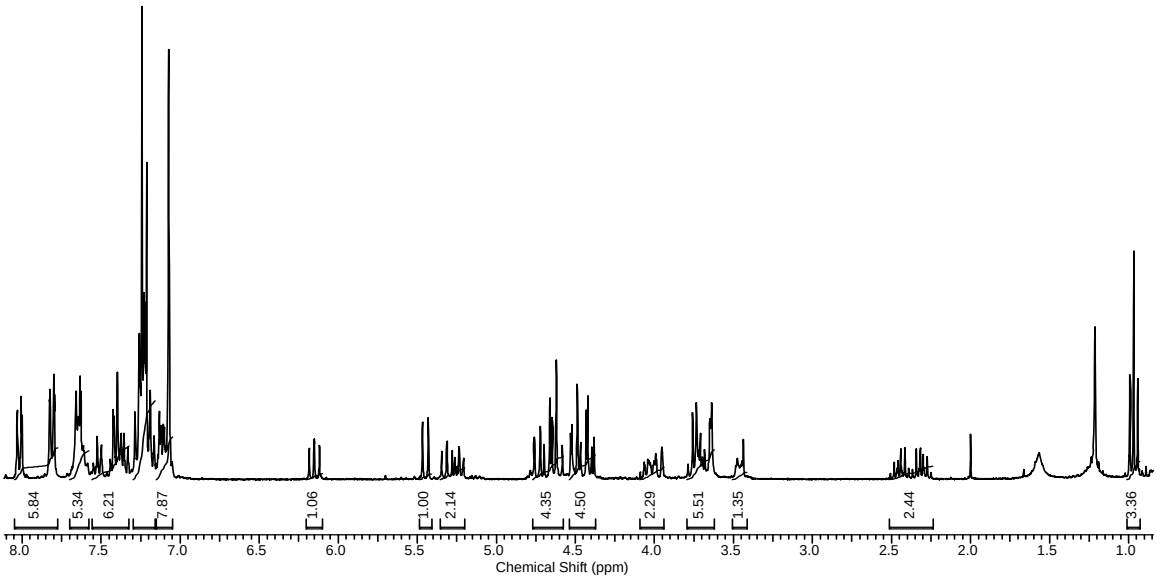

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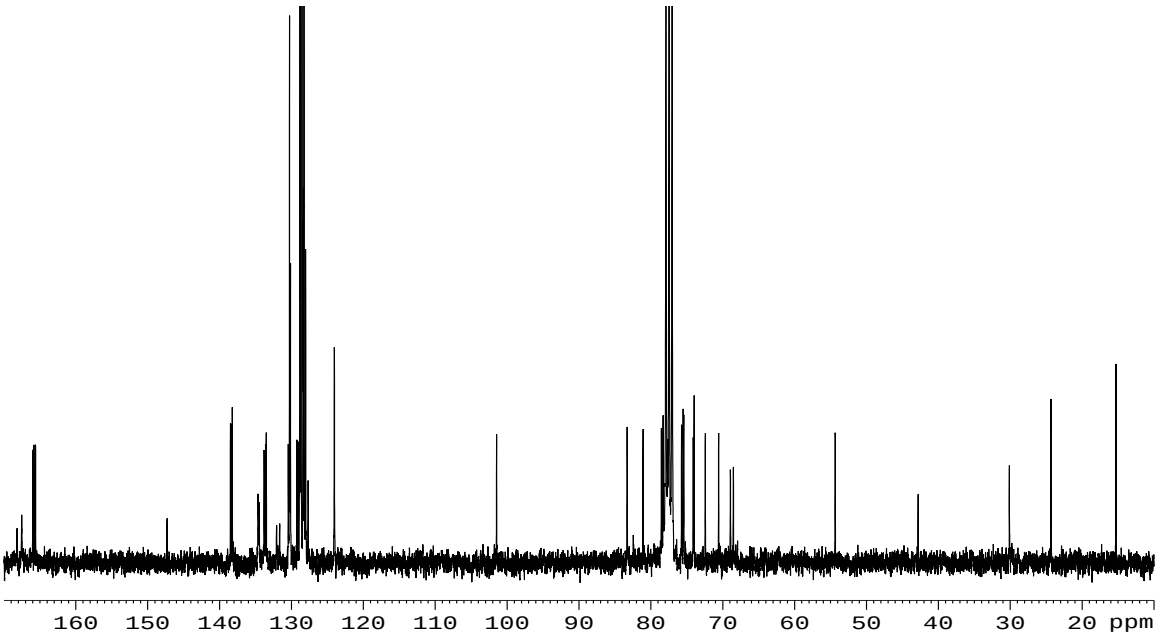

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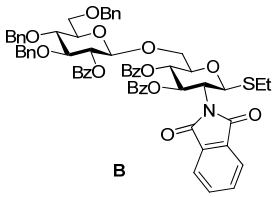

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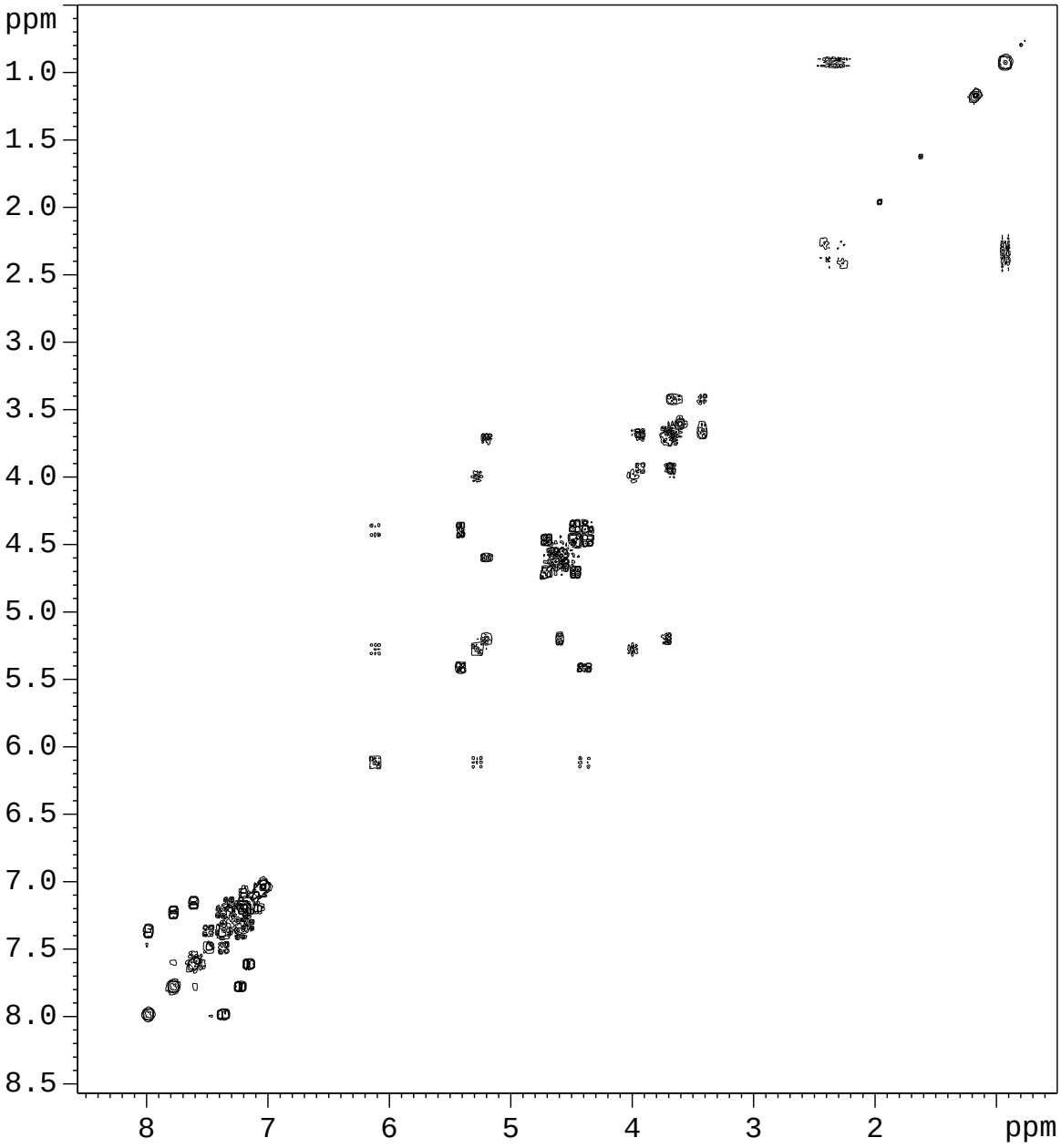

$CDCl_3$ at 300 MHz

References

(1) Ellervik, U.; Grundberg, H.; Magnusson, G. *J. Org. Chem.* **1998**, *63*, 9323-9338.

(2) Lonn, H. *Carbohydr. Res.* **1985**, *139*, 105-113.

(3) Ekelof, K.; Oscarson, S. *Carbohydr. Res.* **1995**, *278*, 289-300.