Supporting information

Direct Synthesis of Diastereomerically Pure Glycosyl Sulfonium Salts

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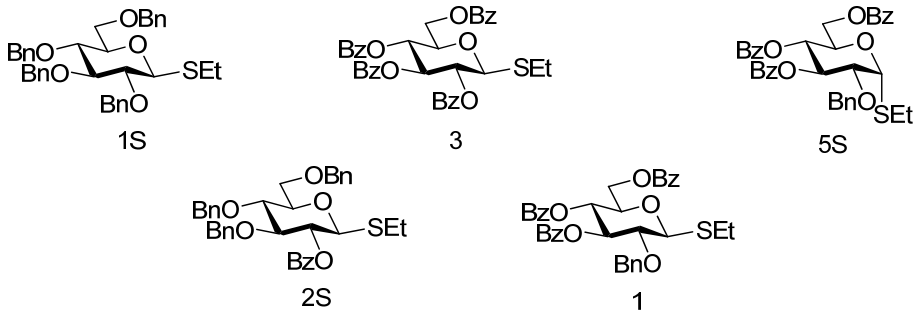
General experimental remarks.

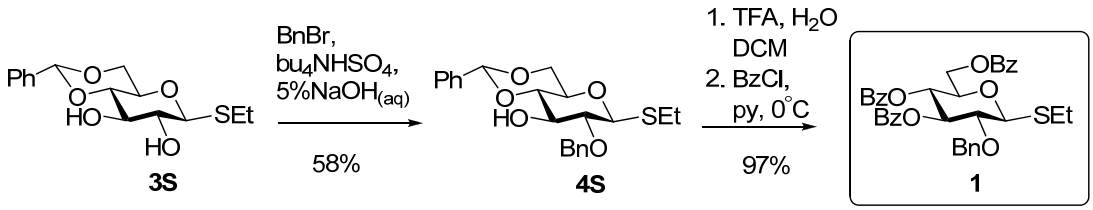
Column chromatography was performed on silica gel 60 (70-230 mesh), reactions were monitored by TLC on Kieselgel 60 F_{254}. Preparative layer chromatography was performed on PLC silica gel 60 glass plates, Kieselgel 60 F_{254}, 1 mm. The compounds were detected by examination under UV light and by charring with 10% sulfuric acid in methanol. Solvents were removed under reduced pressure at < 40 ^{o}C. CH_2Cl_2 and $ClCH_2CH_2Cl$ were distilled from CaH_2 directly prior to application. 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. AgOTf was co-evaporated with toluene (3 x 10 mL) and dried *in vacuo* for 2-3 h directly prior to application. DMTST was prepared in accordance to previously reported methods.[1] 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. HR FAB-MS determinations were made with the use of JEOL MStation (JMS-700) Mass Spectrometer, matrix *m*-nitrobenzyl alcohol, with NaI as necessary.

Synthesis of glycosyl donors.



Glycosyl donors **1S**,[2] **2S**,[3] and **3**[4] were obtained in accordance with the reported protocols.

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



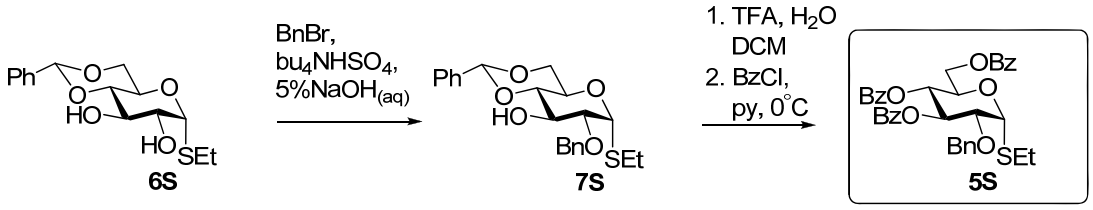
Compound **3S** was converted into **4S** as described for the synthesis of **5S** (vide infra).

To a stirred solution of ethyl 2-O-benzyl-4,6-O-benzylidene-1-thio-β-D-glucopyranoside[5] (**4S**, 1.57 g, 3.91 mmol) in wet CH_2Cl_2 (25 mL) was added dropwise a solution of trifluoroacetic acid in CH_2Cl_2, (5 mL; 1/20, v/v). Upon reaction completion (2h), the reaction was neutralized with triethylamine, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (methanol – dichloromethane gradient elution) to afford ethyl 2-O-benzyl-1-thio-β-D-glucopyranoside in 98% yield. R_f = 0.40 (methanol-dichloromethane, 1/9, v/v); ^{1}H NMR (MeOD): δ, 1.30 (t, 3H, SCH_2CH_3), 2.66-2.87 (m, 2H, SCH_2CH_3), 3.20 (dd, 1H, $J_{2,3}$ = 8.7 Hz, H-2), 3.23-3.37 (m, 2H, H-4, H-5), 3.52 (dd, 1H, $J_{3,4}$ = 8.7 Hz, H-3), 3.67 (dd, 1H, $J_{6a,5}$ = 5.5 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6a), 3.88 (dd, 1H, $J_{6b,5}$ = 2.1 Hz, H-6b), 4.48 (d, 1H, $J_{1,2}$ = 9.6 Hz, H-1), 4.8 (br s, 2H, CH_2Ph), 7.27-7.36 (m, 3H, aromatic), 7.43-7.46 (m, 2H, aromatic) ppm; ^{13}C NMR

(MeOD): δ, 15.5, 25.5, 63.0, 71.8, 76.2, 79.8, 82.0, 82.9, 85.9, 128.8, 129.3 (x2), 129.5 (x2), 139.9 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{15}H_{22}O_5SNa^+$ 337.1086, found 337.1089.

Ethyl 2-O-benzyl-1-thio-β-D-glucopyranoside (**A**, 1.53g, 4.88 mmol) was dissolved in anhydrous pyridine (25 mL) under argon at 0°C, whereupon benzoyl chloride (2.55 mL, 21.93 mmol) was added dropwise. After 15 min, the reaction mixture was brought to room temperature, and allowed to stir for 16h. The reaction was then cooled to 0 ˚C, quenched with dry MeOH (0.5 mL), and concentrated in vacuo. The residue was then diluted with CH_2Cl_2 (50 mL) and washed successively with H_2O (10 mL), saturated aq. $NaHCO_3$ (2 x 10 mL), H_2O (10 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – hexane gradient elution) to afford the title compound **1** as colorless crystals in quantitative yield. Analytical data for **1**: R_f = 0.55 (ethyl acetate-toluene, 1/9, v/v); $[\alpha]_D^{23.9}$ = -19.81^o (c = 1, $CHCl_3$); m.p. +124-126 ^{o}C (hexanes – diethyl ether); ^{1}H NMR ($CDCl_3$): δ, 1.31 (t, 3H, SCH_2CH_3), 2.75-2.81 (m, 2H, SCH_2CH_3), 3.70 (dd, 1H, $J_{2,3}$ = 9.3 Hz, H-2), 4.00-4.07 (m, 1H, H-5), 4.40-4.47 (dd, 1H, J = 6.0 Hz, J = 12.1 Hz, H-6a), 4.51-4.59 (m, 2H, H-6b, J = 10.9 Hz, $PhCH_2^a$), 4.72 (d, 1H, $J_{1,2}$ = 9.7 Hz, H-1), 4.81 (d, 1H, J = 10.8 Hz, $PhCH_2^b$), 5.47 (dd, 1H, $J_{4,5}$ = 9.8 Hz, H-4) 5.72 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-3), 7.06-7.15 (m, 5H, aromatic), 7.28-7.38 (m, 6H, aromatic), 7.43-7.54 (m, 3H, aromatic), 7.85-7.89 (m, 4H, aromatic), 7.94-7.98 (m, 2H, aromatic) ppm; ^{13}C NMR ($CDCl_3$): δ, 15.3, 25.5, 63.9, 70.1, 75.3, 75.9, 76.1, 79.3, 85.5, 128.0, 128.4, 128.5, 128.5, 128.6, 129.0, 129.6, 129.9, 129.9, 130.0, 133.2, 133.3, 133.5, 137.3, 165.6, 165.8, 166.3 ppm. HR-FAB MS $[M+Na]^+$ calcd for $C_{36}H_{34}O_8SNa^+$ 649.1872, found 649.1871.

Ethyl 2-O-benzyl-3,4,6-tri-O-benzoyl-1-thio-α-D-glucopyranoside (5S).



Ethyl 2-O-benzyl-4,6-benzylidene-1-thio-α-D-glucopyranoside (7S). Similar to a previously reported synthesis,[6] a stirred solution of ethyl 4,6-O-benzylidene-1-thio-α-D-glucopyranoside[7] (**6S**, 1.00 g, 3.21 mmol) in CH_2Cl_2 (100 mL), was added sequentially tetrabutylammonium hydrogen sulfate (0.54 g, 1.60 mmol, benzyl bromide (0.42 mL, 3.53 mmol), and 5% aq. NaOH (8.33mL). The reaction mixture was heated to 45 °C and allowed to reflux for 16 h, whereupon the reaction was brought to room temperature. The organic and aqueous phases were then separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 5 mL). The organic fractions were then combined and washed with saturated aq. $NaHCO_3$ (20 mL), brine (20 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – toluene gradient elution) to afford compound **7S** as the major regioisomer in 59% yield. Analytical data for **7S**: R_f = 0.39 (ethyl acetate-toluene, 3/17, v/v); $[\alpha]_D^{27.0}$ = +163.9^o (c = 1, $CHCl_3$); (diethyl ether); ^{1}H NMR ($CDCl_3$): δ, 1.3 (t, 3H, SCH_2CH_3), 2.46-2.65 (m, 2H, SCH_2CH_3), 3.52 (dd, 1H, $J_{4,5}$ = 9.2 Hz, H-4), 3.69-3.77 (m, 2H, H-2, H-6a), 4.03 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-3), 4.20-4.30 (m, 2H, H-5, H-6b), 4.59 (d, 1H, $^2J_{HH}$ = 11.5 Hz, CH_2^aPh), 4.76 (d, 1H, $^2J_{HH}$ = 11.5 Hz, CH_2^bPh), 5.41 (d, 1H, $J_{1,2}$ = 5.5 Hz, H-1), 5.51 (s, 1H, CHPh), 7.30-7.51 (m, 10H, aromatic) ppm; ^{13}C NMR ($CDCl_3$): δ, 15.0, 24.1, 62.7, 69.0, 70.8, 72.4, 79.2, 81.2, 83.6, 102.2, 126.6 (x2), 128.3, 128.4 (x2), 128.5 (x2), 128.7 (x2), 129.4, 137.2, 137.5 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{22}H_{26}O_5SNa^+$ 425.1399, found 425.1396.

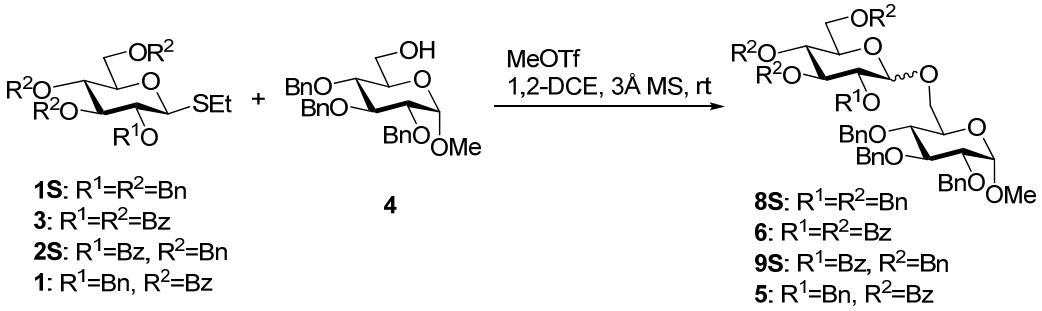
Ethyl 2-O-benzyl-1-thio-α-D-glucopyranoside **(B)** was obtained from **7S** as described for the synthesis of **1**as a colorless solid in 97% yield. Analytical data for ethyl 2-O-benzyl-1-thio-α-D-glucopyranoside (**B**): R_f = 0.51 (methanol-dichloromethane, 1/9, v/v); $[\alpha]_D^{25.8}$ = +197.4^o (c = 1, MeOD); ^{1}H NMR ($CDCl_3$): δ, 1.26 (t, 3H, SCH_2CH_3), 2.05 (br t, 1H, CH_2OH), 2.46-2.59 (m, 2H, SCH_2CH_3), 2.88 (br s, 1H, 3-OH), 2.92 (br s, 1H, 4-OH), 3.52-3.61 (m, 2H, H-2, H-4), 3.76-3.83 (m, 3H, H-6a, H-6b, H-3), 3.99-4.05 (m, 1H, H-5), 4.51 (d, 1H, J = 11.5 Hz, CH_{2a}), 4.72 (d, 1H, J = 11.5 Hz, CH_{2b}), 5.40 (d, 1H, $J_{1,2}$ = 5.5 Hz, H-1), 7.26-7.40 (m, 5H, aromatic) ppm; ^{13}C NMR (MeOD): δ, 15.3, 24.4, 62.7, 71.8, 73.1, 73.7, 75.0, 80.4, 83.9, 128.9, 129.4 (x2), 129.4 (x2), 139.6 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{15}H_{22}O_5SNa^+$ 337.1086, found 337.1079.

The title compound **5S** was obtained as described for the synthesis of **1** as colorless crystals from Ethyl 2-O-benzyl-1-thio-α-D-glucopyranoside in quantitative yield. Analytical data for **5S**: R_f = 0.59 (ethyl acetate-toluene, 1/9, v/v); $[\alpha]_D^{27.1}$ = +81.27 ^{o} (c = 1, $CHCl_3$); m.p. +138-140 ^{o}C (hexanes - diethyl ether); ^{1}H NMR ($CDCl_3$): δ, 1.27 (t, 3H, SCH_2CH_3), 2.54-2.64 (m, 2H, SCH_2CH_3), 4.02 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2), 4.41-4.55 (m, 3H, H-6a, H-6b, $phCH_2^a$), 4.66 (d, 1H, J = 12.5 Hz, $phCH_2^b$), 4.73-4.80 (m, 1H, H-5), 5.44 (dd, 1H, $J_{4,5}$ = 10.0 Hz, H-4), 5.53 (d, 1H, $J_{1,2}$ = 5.6 Hz, H-1), 5.85 (dd, 1H, J = 9.6 Hz, H-3) 7.13-7.25 (m, 5H, aromatic), 7.29-7.41 (m, 6H, aromatic), 7.42-7.57 (m, 3H, aromatic), 7.89-7.92 (m, 4H, aromatic), 7.98-8.00 (m, 2H, aromatic) ppm; ^{13}C NMR ($CDCl_3$): δ, 14.7, 23.8, 63.4, 68.2, 70.0, 72, 2, 72.6, 76.3, 82.9, 128.1, 128.1, 128.4, 128.5, 128.5, 129.1, 129.7, 129.8, 129.9, 130.1, 133.2, 133.2, 133.5, 137.3, 165.6, 165.7, 166.3 ppm. HR-FAB MS $[M+Na]^+$ calcd for $C_{36}H_{34}O_8SNa^+$ 649.1872, found 649.1877.

Typical MeOTf-promoted glycosylation procedure.

A mixture containing the glycosyl donor (0.048 mmol), glycosyl acceptor (0.044 mmol), and freshly activated molecular sieves (3 Å, 105 mg) in 1,2-DCE (0.5 mL) was stirred under argon for 1 h. MeOTf (0.131 mmol) was added and the reaction mixture was stirred for 2-6 h. The mixture was then diluted with CH_2Cl_2, the solid was filtered-off and the combined filtrate (15 mL) was washed with sat. $NaHCO_3$ (5 mL) and H_2O (5 mL). The organic phase was separated, dried and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate-toluene gradient elution).

Comparative glycosidations of glycosyl donors with acceptor **4**



1S: R^1=R^2=Bn
3: R^1=R^2=Bz
2S: R^1=Bz, R^2=Bn
1: R^1=Bn, R^2=Bz

4

8S: R^1=R^2=Bn
6: R^1=R^2=Bz
9S: R^1=Bz, R^2=Bn
5: R^1=Bn, R^2=Bz

entry	donor	time	product	yield
1	**1S**	2h	**8S**	80%
2	**3**	4h	**6**	84%
3	**2S**	2h	**9S**	80%
4	**1**	4h*	**5**	53%

* time at which the incomplete reaction was quenched; when repeated, the reaction required an additional 2 h (6 h total) in order for the baseline spot to completely disappear/react. Resultantly, disaccharide **5** was isolated is a significantly improved yield of 87%.

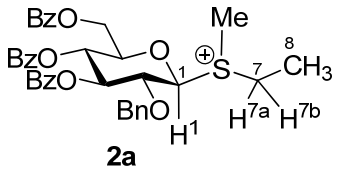
Methyl 2,3,4-tri-O-benzyl-6-O-(2-O-benzyl-3,4,6-tri-O-benzoyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (5) was obtained from glycosyl donor **1** and glycosyl acceptor **4**[8,9] in 87% yield. Selected analytical data for **5α**: R_f = 0.43 (ethyl acetate-toluene, 1/9, v/v); ^{1}H NMR ($CDCl_3$): δ, 3.43 (s, 3H, OCH_3), 5.06 (d, 1H, $J_{1,2}$= 3.5 Hz, H-1'), 5.41 (dd, 1H, $J_{4,5}$ = 9.7 Hz, H-4'), 5.94 (dd, 1H, $J_{3,4}$ = 9.7 Hz, H-3') ppm; ^{13}C NMR ($CDCl_3$): δ, 55.4, 63.4, 66.3, 67.9, 70.0, 70.6, 72.0, 72.3, 73.5, 75.2, 75.9, 78.0, 80.0, 82.3, 96.8, 98.1, 127.7, 127.9, 127.9, 128.0, 128.1, 128.5, 128.6, 128.6, 129.2, 129.9, 130.0, 130.0, 133.2, 133.2, 133.5, 137.8, 138.3, 138.6, 139.0, 165.7, 165.9, 166.3 ppm. HR-FAB MS calcd. for $C_{62}H_{60}O_{14}Na^+$ 1051.3881, found 1051.3890. Selected analytical data for **5β**: R_f = 0.43 (ethyl acetate-toluene, 1/9, v/v); ^{1}H NMR ($CDCl_3$): δ, 3.34 (s, 3H, OCH_3), 5.47 (dd, 1H, H-4'), 5.66 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-3') ppm; ^{13}C NMR ($CDCl_3$): δ, 98.3, 104.0 ppm;

Methyl 6-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (6) was obtained by *method A* from **3** and **4** as a clear foam in 84% yield. Analytical data for **6** was the same as reported previously.[10]

Methyl 6-O-(2,3,4,6-tetra-O-benzyl-α/β-D-glucopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (8S) was obtained from **1S** and **4** as a clear foam in 80% yield. Analytical data for **8S** was the same as reported previously.[10,11]

Methyl 6-O-(2-O-benzoyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (9S) was obtained from **2S** and **4** as a clear film in 80% yield. Analytical data for **9S** was the same as reported previously.[11]

Formation, isolation and characterization of sulfonium ion 2a



2a

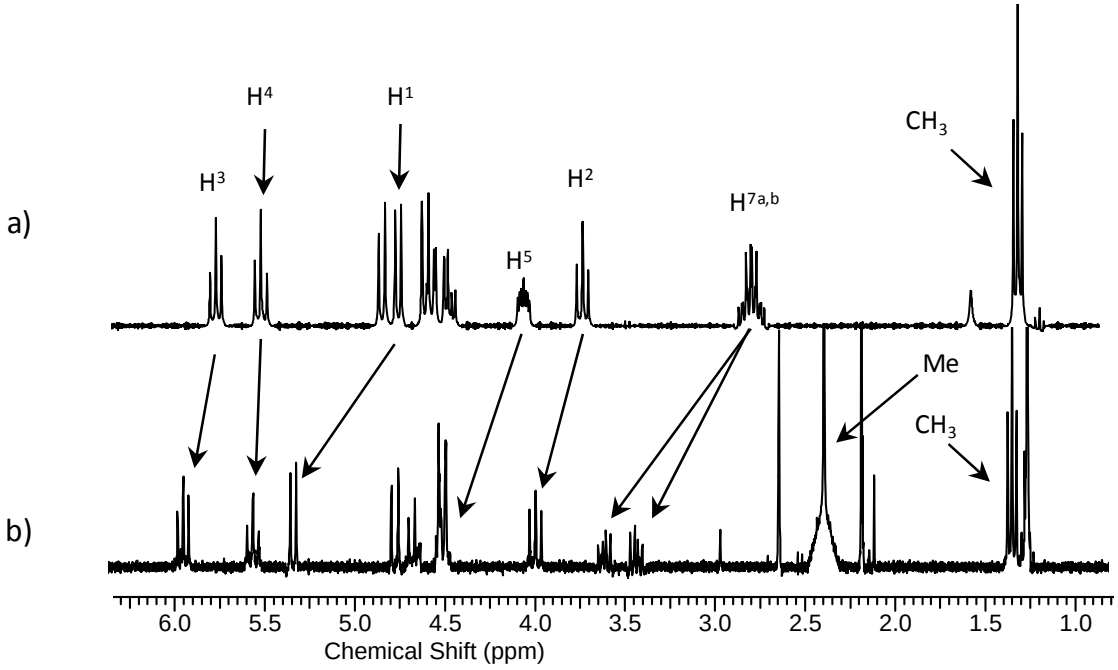
To isolate sulfonium salt **2a**, glycosyl donor **1** was treated with MeOTf (3 equiv.) in the absence of glycosyl acceptor in the presence of molecular sieves in 1,2-dichloroethane (DCE) at rt. Salt **2a** corresponding to glycosyl donor **1** was formed cleanly, in approximately 1 h, at which point the reaction mixture was worked up and attempts were made to purify and characterize the unknown polar compound. Anticipating the lability of this compound, attempts to purify this compound from the reaction mixture were approached with care. As it was assumed that it may not survive column chromatography, compound **2a** was purified by preparative TLC, using anhydrous solvents. This separation was immediately followed by spectral analysis, whereupon ^{1}H-NMR spectral data confirmed the existence of a new compound.

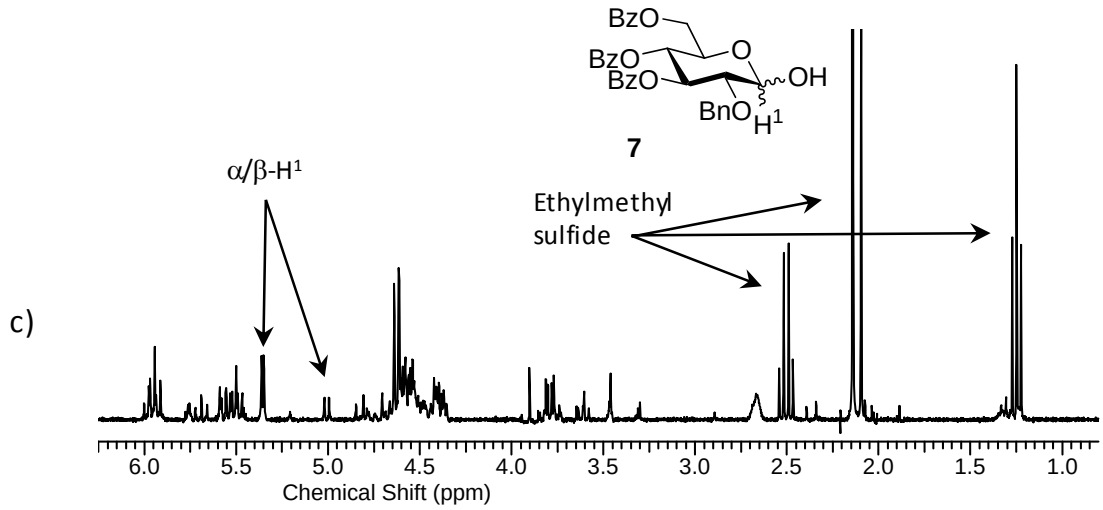
As can be seen from the ^{1}H-NMR spectra below, a number of signals have shifted downfield; however, the most significant shifts were those of the H-1 and *S*-ethyl protons. Thus, the H-1 peak was shifted from 4.72 ppm to 5.31 ppm, while retaining its β-configuration ($J_{1,2}$ = 9.8 Hz), and the methylene hydrogens (H-7a,b, Figure 3Sa) were both shifted and split due to the chiral environment created by the addition of a methyl group. Importantly, the appearance of a singlet at 2.44 ppm, integrating to 3 protons, was evidence of the newly acquired methyl group (Me). It is possible that the additional singlet at about 2.17 ppm corresponds to the residual acetone carried over from the separation step using preparative TLC.

In addition, a follow-up spectrum taken after 16 h revealed that the compound had hydrolyzed and consisted of only hemiacetal **7** (Figure 3Sc) and liberated ethylmethylsulfide, as confirmed

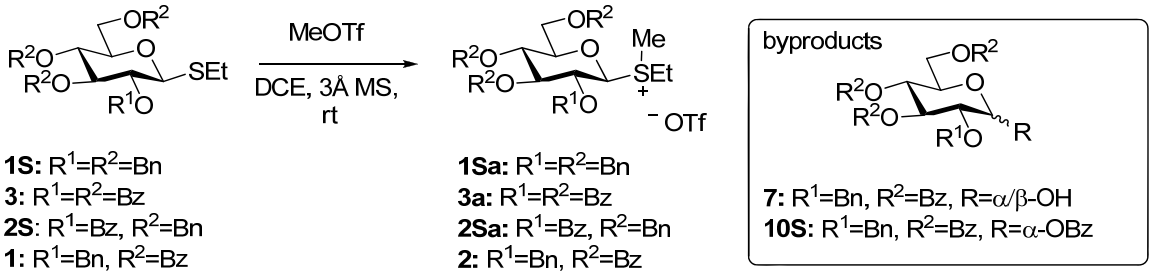
through comparison with authentic samples. Furthermore, the ^{13}C-NMR spectra also reinforced these findings, as various carbon shifts were observed. This includes the anomeric carbon (C-1), which was found to shift only slightly from the original anomeric signal at 85.5 ppm to 82.3 ppm, and the ethyl carbons were found to diverge, C-7 moving downfield by 10.6 ppm and C-8 moving upfield by 6.1 ppm. In addition, a new methyl peak appeared at 16.3 ppm. Mass spectral data was also consistent with the anticipated compound **2**, exhibiting an ion peak at m/z equal to 641.2219 (calculated for $C_{37}H_{37}O_8S^+$, 641.2209)

^{1}H NMR of (**a**) starting material **1**, (**b**) β-sulfonium ion **2**, (**c**) hydrolysis product **7**

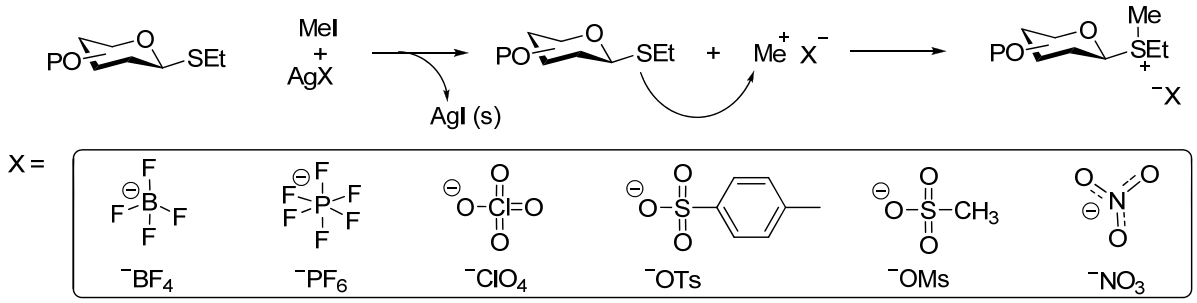


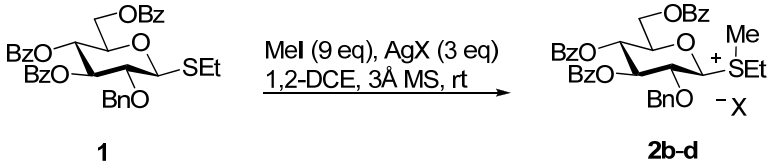


In our attempt to isolate other sulfonium salts, glycosyl donors were each treated with 3 equivalents of MeOTf in the presence of molecular sieves in 1,2-dichloroethane (DCE) at room temperature. Consistent with earlier observations, neither the superarmed (**2S**) nor the armed (**1S**) glycosyl donors yielded a sulfonium salt, and again the less reactive disarmed glycosyl donor (**3**) showed only nominal signs of "salt" formation. While efforts were made to isolate this sulfonium salt, the high lability of this species, rendered all attempts unsuccessful.



Investigation of the counter-anion. Synthesis of salts 2b-d



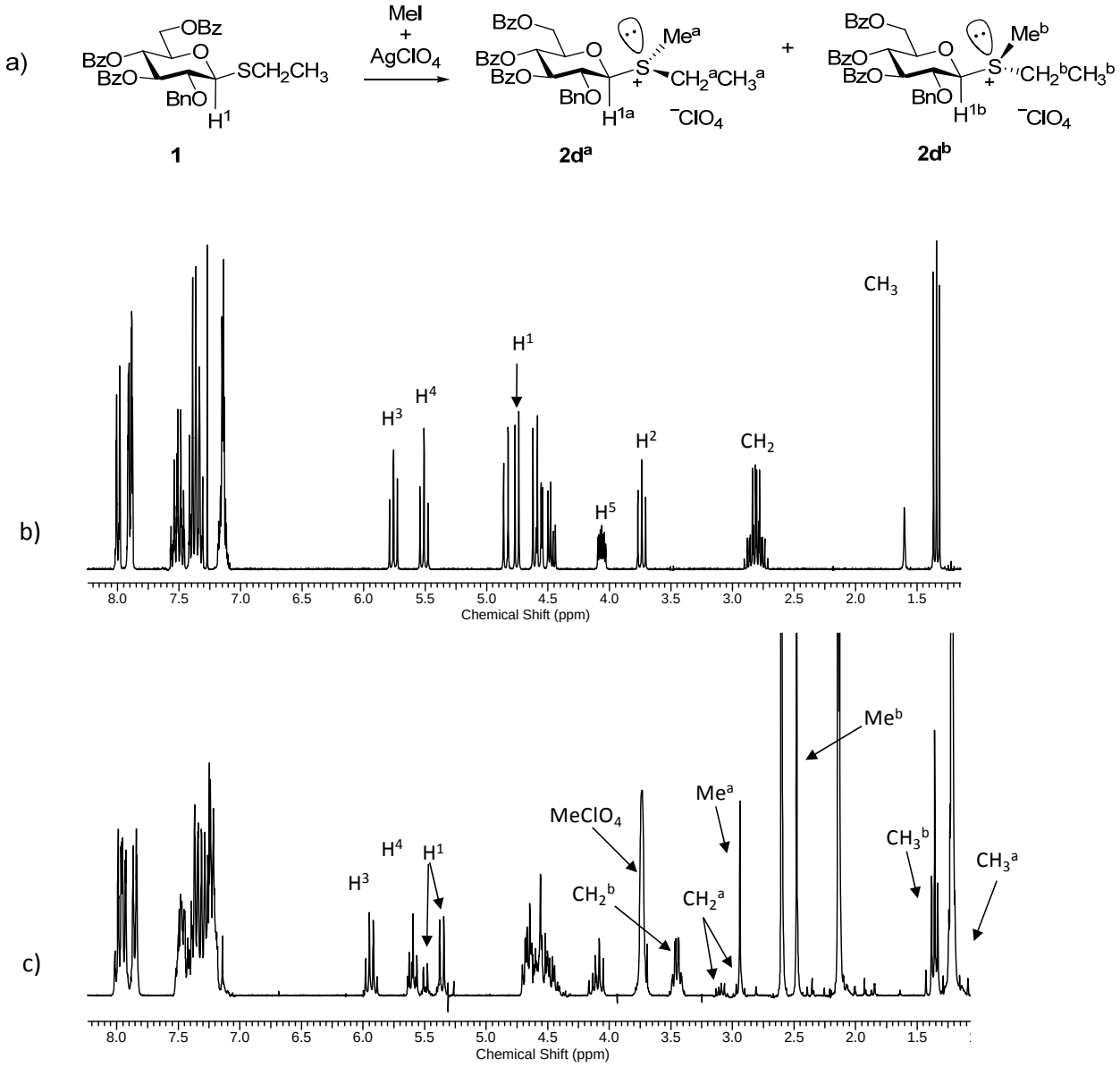


entry	AgX	*in situ* promoters		time to salt formation[a]	*β*-sulfonium ion
1	$AgBF_4$	**b**	$MeBF_4$	0.5 h	**2b**
2	$AgPF_6$	**c**	$MePF_6$	0.5 h	**2c**
3	$AgClO_4$	**d**	$MeClO_4$	0.5 h	**2d**
4	AgOTs	**e**	MeOTs	--	none
5	AgOMs	**f**	MeOMs	--	none
6	$AgNO_3$	**g**	$MeNO_3$	--	none

[a] time at which significant amount of salt formation was detected

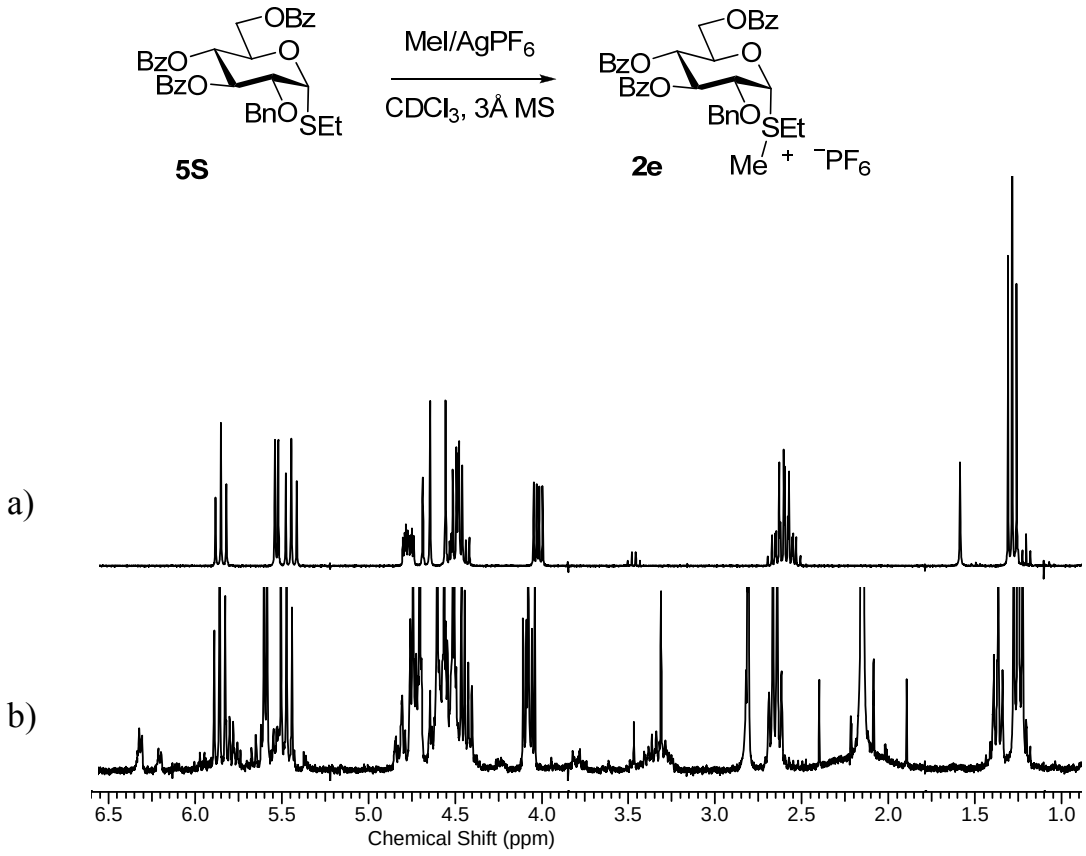
(a) Reaction of glycosyl donor **1** with MeI/$AgClO_4$; (b) ^{1}H NMR spectrum of glycosyl donor **1**;

(c) ^{1}H NMR spectrum of resulting diastereomeric β-sulfonium ions **2d^a** and **2d^b**



Investigation of superdisarmed α-ethylthio glycosyl donor. Observation of 2e

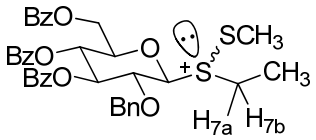
α-SEt **5S** and sulfonium salt **2e** (a) ^{1}H NMR of α-SEt starting material **5S** (b) ^{1}H NMR of diastereomeric salt formation **2e**



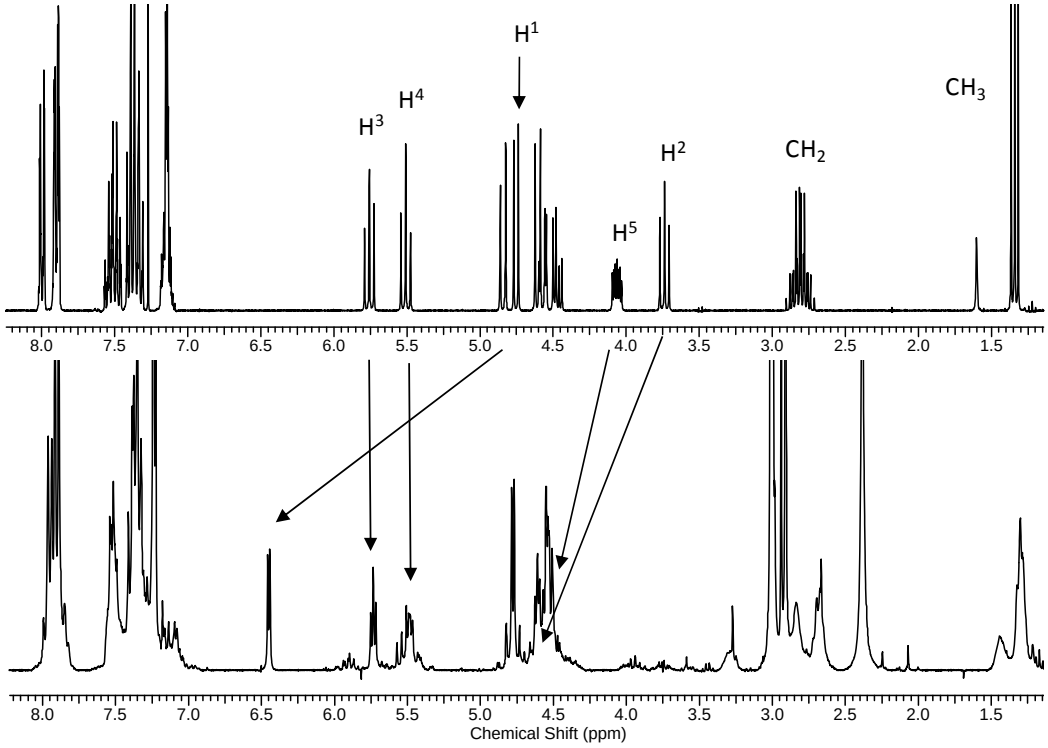
Dimethyl(thiomethyl)sulfonium triflate (DMTST) generated sulfonium ion 2f

(a) proposed thiomethylated *β*-sulfonium ion **2f**, (b) starting material **1**, (c) *in situ* NMR of **2f**

a)



2f



Experimental procedures for the synthesis of sulfonium salts and characterization data thereof

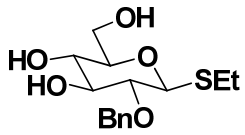
A mixture containing the glycosyl donor (0.05 mmol), and freshly activated molecular sieves (3Å, 105 mg) in DCE (0.5 mL) was stirred under argon for 1 h. The specified amount of promoter was added and the reaction mixture was monitored for donor disappearance and concomitant salt formation. *MeOTf promoter*: 0.14 mmol, reaction was stirred for 1 h; *MeI/AgX promoters (X = BF_4, PF_6, ClO_4, OTs, OMs, or NO_3)*: MeI (0.43 mmol) was added, after 0.5 h AgX (0.14 mmol) was added, and the reaction was allowed to stirred for 1-16 h; *DMTST promoter*: 0.10 mmol, reaction was stirred for 0.5 h. Upon formation of the sulfonium salt, the reaction mixture was then diluted with anhydrous DCE (5 mL), filtered and worked up following one of three procedures: (1) the crude residue was concentrated *in vacuo*, whereupon was dissolved in CDCl3 and subsequent NMR spectral data was obtained; (2) the crude residue was purified by PLC (acetone:DCM, 3.5/6.5, v/v); or (3) the crude residue was washed with cold water (5 mL), and the organic phase was separated, dried and concentrated *in vacuo* before purifying by PLC (acetone:DCM, 3.5/6.5, v/v).

Analytical data for compound **2a**: ^{1}H NMR ($CDCl_3$): δ, 1.32 (t, 3H, SCH_2CH_3), 2.36 (s, 3H, SCH_3), 3.37-3.47 (m, 1H, $SCH_2^aCH_3$), 3.53-3.63 (m, 1H, $SCH_2^bCH_3$), 3.97 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2), 4.47-4.51 (m, 3H, H-5, H-6a, $phCH_2^a$), 4.66 (dd, 1H, H-6b), 4.75 (d, 1H, ^2J = 11.5 Hz, $phCH_2^b$), 5.31 (d, 1H, $J_{1,2}$ = 9.8 Hz, H-1), 5.54 (dd, 1H, $J_{4,5}$ = 9.6 Hz, H-4), 5.93 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-3), 7.24-7.60 (m, 14H, aromatic), 7.88-8.01 (m, 6H, aromatic) ppm; Selected data for

^{13}C NMR ($CDCl_3$): δ, 9.3 (CH_3), 16.3 (SCH_3), 36.1 (SCH_2), 82.3 (C-1), 133.7, 134.0, 135.5, 165.3, 165.4, 166.2 ppm; HR-FAB MS calcd. for $C_{37}H_{37}O_8S^+$ 641.2209, found 641.2219.

Analytical data given for diastereomeric compounds **2c^a** and **2c^b** (crude sample): Data for compound **2c^a**: ^{1}H NMR ($CDCl_3$): δ, 1.18 (t, 3H, SCH_2CH_3), 2.83-2.92 (s, m, 4H, SCH_3, $SCH_2^aCH_3$), 2.97-3.09 (m, 1H, $SCH_2^bCH_3$), 4.13 (dd, 1H, H-2), 4.42-4.67 (m, 5H, H-5, H-6a, H-6b, $phCH_2$), 5.21 (d, 1H, $J_{1,2}$ = 9.8 Hz, H-1), 5.61 (dd, 1H, H-4), 5.88 (dd, 1H, H-3), 7.14-7.46 (m, 14H, aromatic), 7.82-7.85 (dd, 2H, aromatic), 7.94-8.00 (m, 4H, aromatic) ppm; Selected data for ^{13}C NMR ($CDCl_3$): δ, 8.9 (CH_3), 20.5 (SCH_3), 31.8 (SCH_2), 62.0, 68.0, 74.5, 74.6, 75.8, 85.3 (C-1) ppm; Data for compound **2c^b**: ^{1}H NMR ($CDCl_3$): δ, 1.32 (t, 3H, SCH_2CH_3), 2.44, (s, 3H, SCH_3), 3.26-3.46 (m, 2H, SCH_2CH_3), 4.09 (dd, 1H, $J_{2,3}$ = 9.4 Hz, H-2), 4.42-4.67 (m, 5H, H-5, H-6a, H-6b, $phCH_2$), 5.17 (d, 1H, $J_{1,2}$ = 9.8 Hz, H-1), 5.61 (dd, 1H, H-4), 5.91 (dd, 1H, H-3), 7.14-7.46 (m, 14H, aromatic), 7.82-7.85 (dd, 2H, aromatic), 7.94-8.00 (m, 4H, aromatic) ppm; Selected data for ^{13}C NMR ($CDCl_3$): δ, 9.0 (CH_3), 15.8 (SCH_3), 35.7 (SCH_2), 73.6, 74.8, 75.7, 82.4 (C-1), 133.5, 133.8, 135.4, 165.1, 165.3, 166.1 ppm.

NMR spectra



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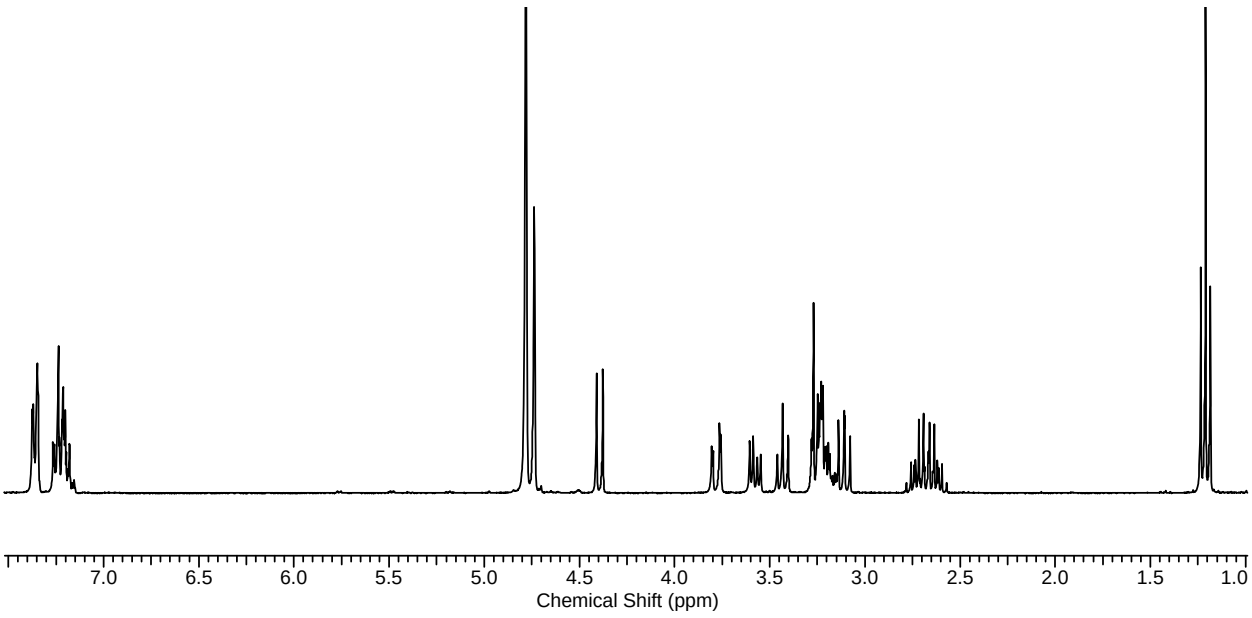
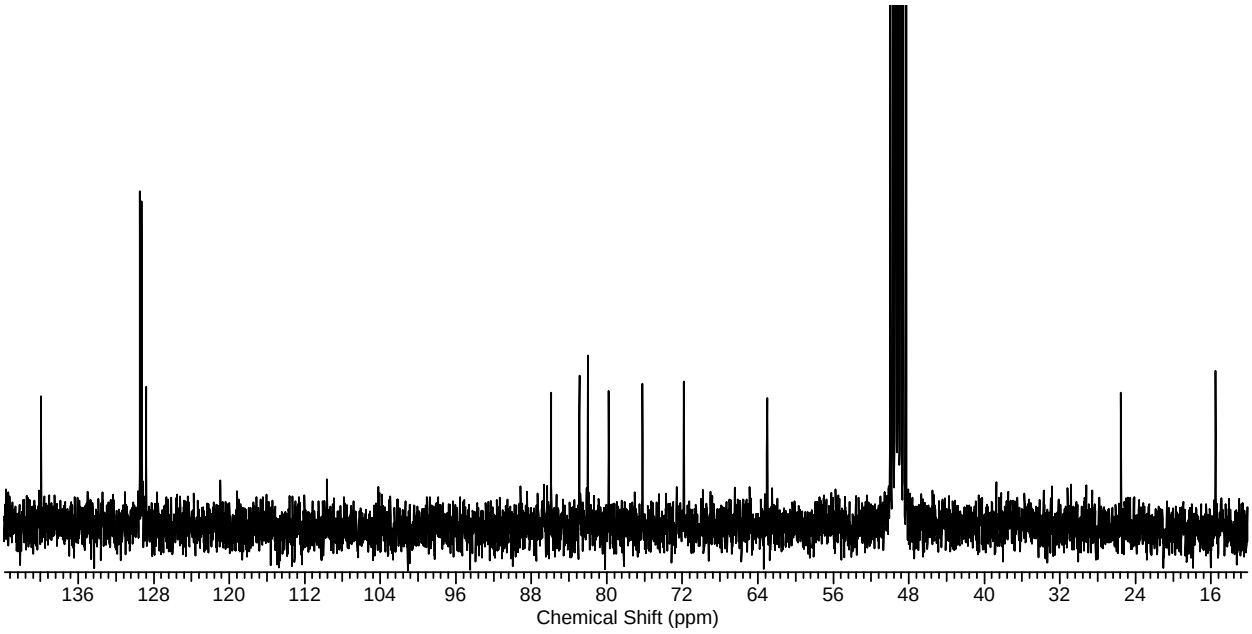
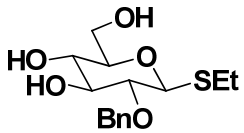


$CDCl_3$ at 300 MHz



$CDCl_3$ at 75 MHz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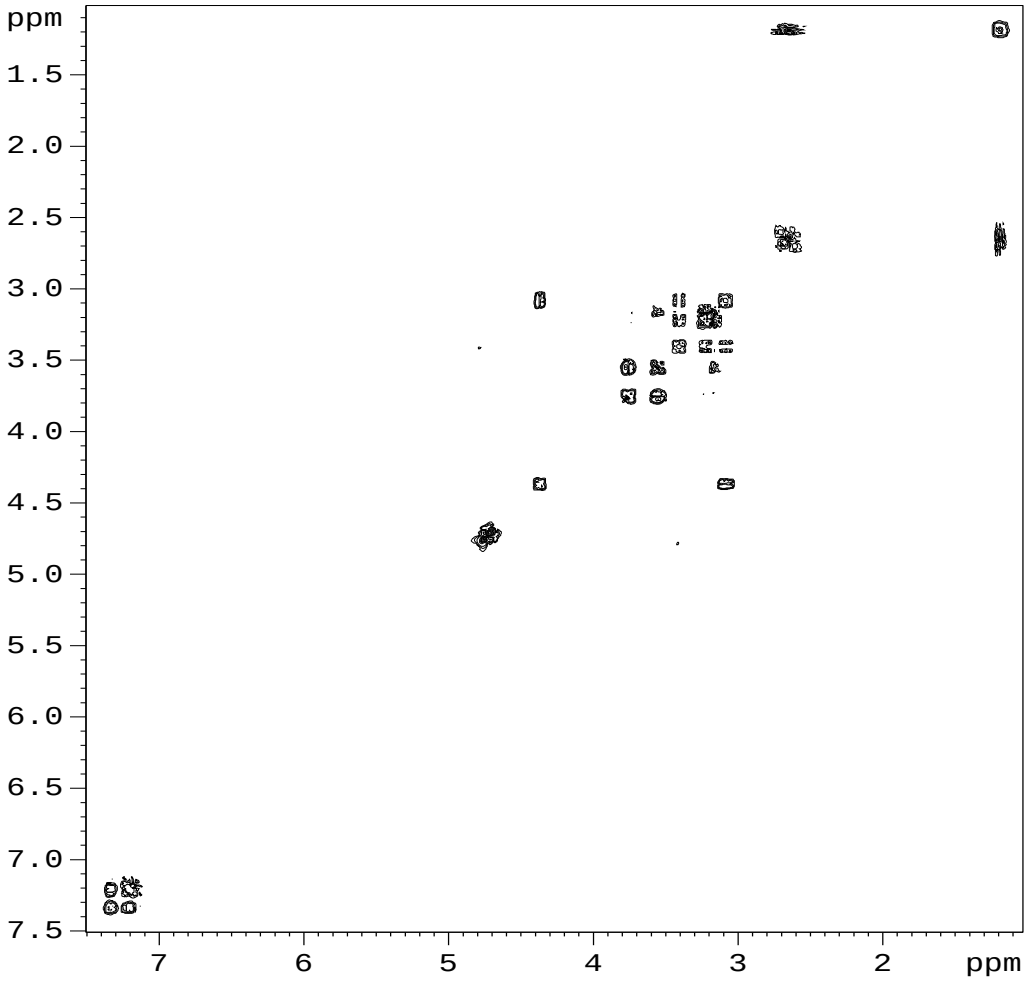
SEt
HO
BnO

A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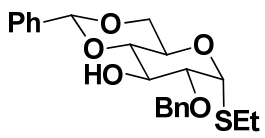

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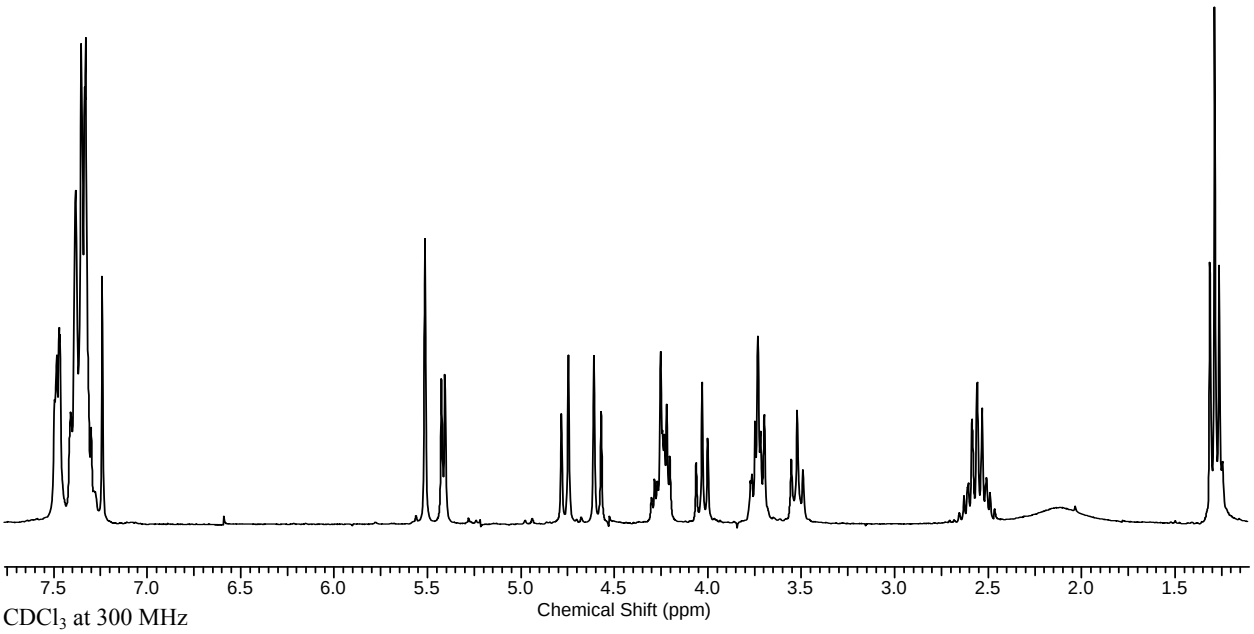

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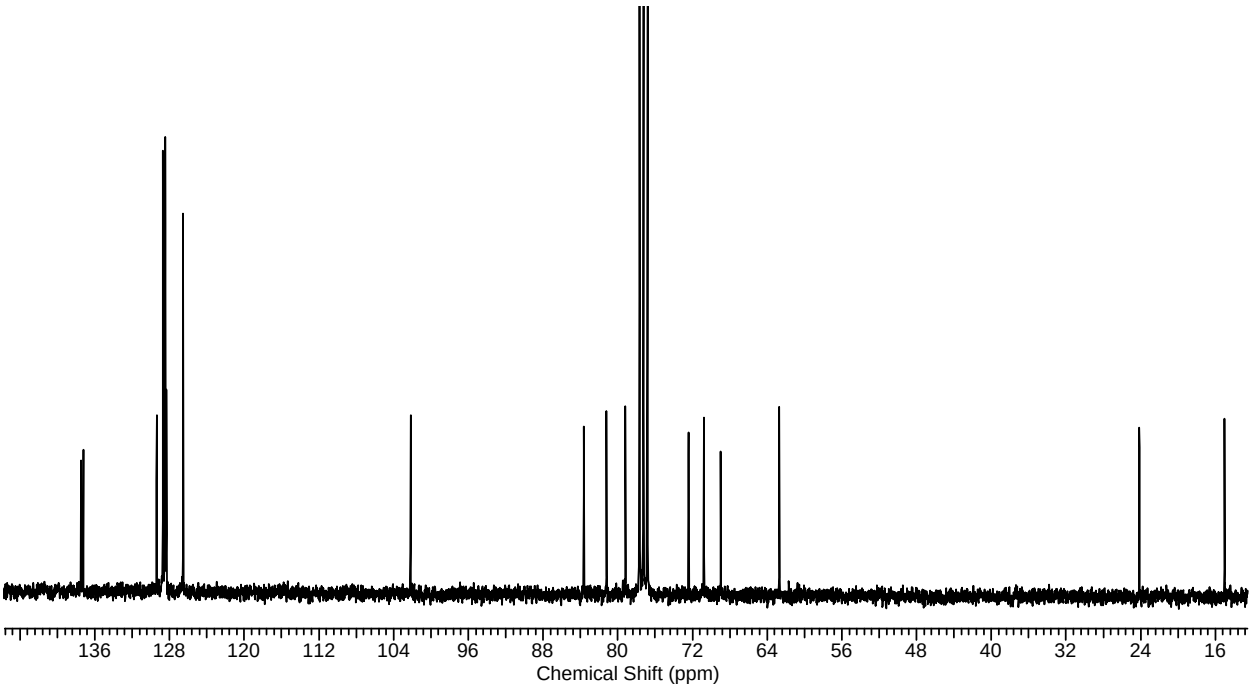
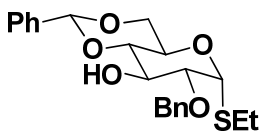


$CDCl_3$ at 75 MHz



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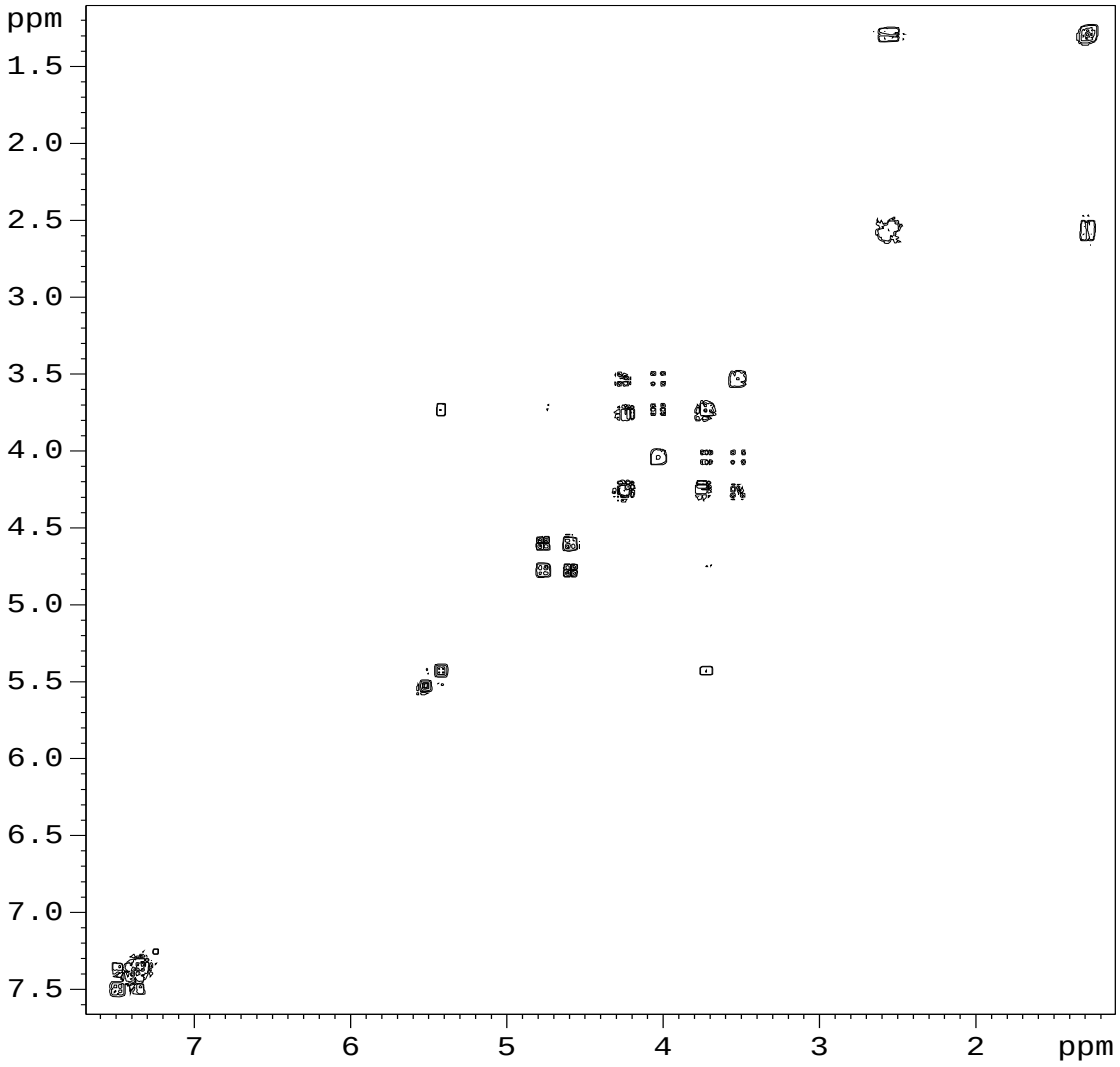

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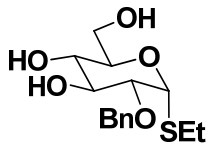

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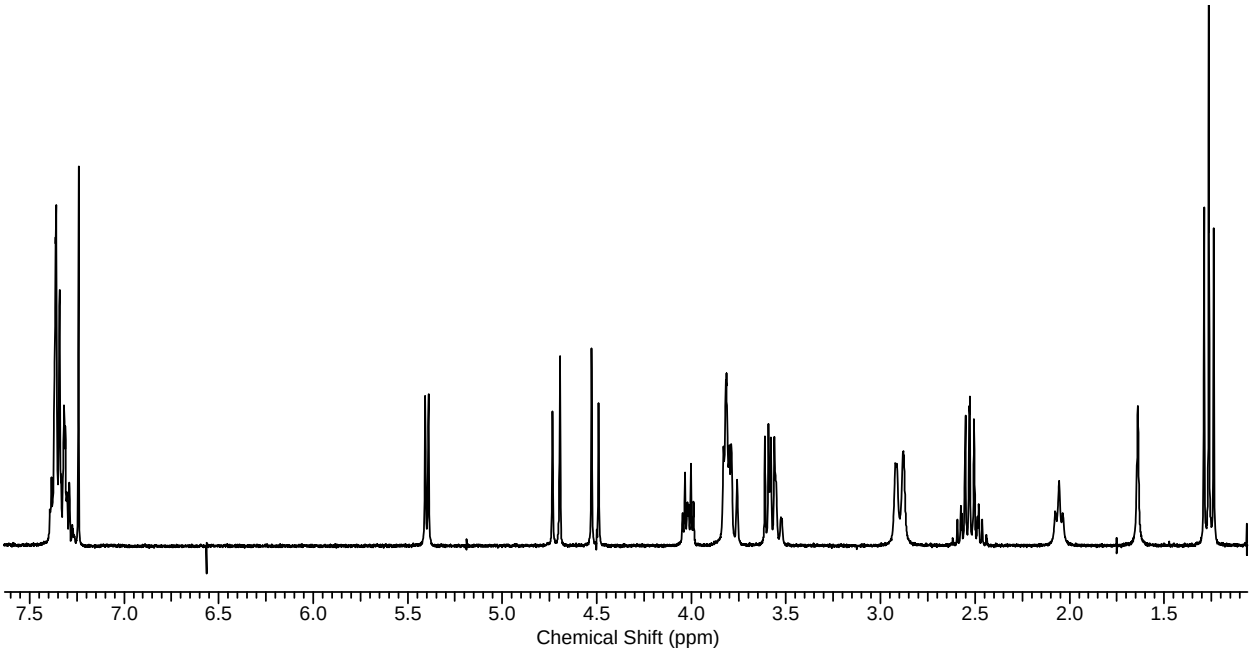

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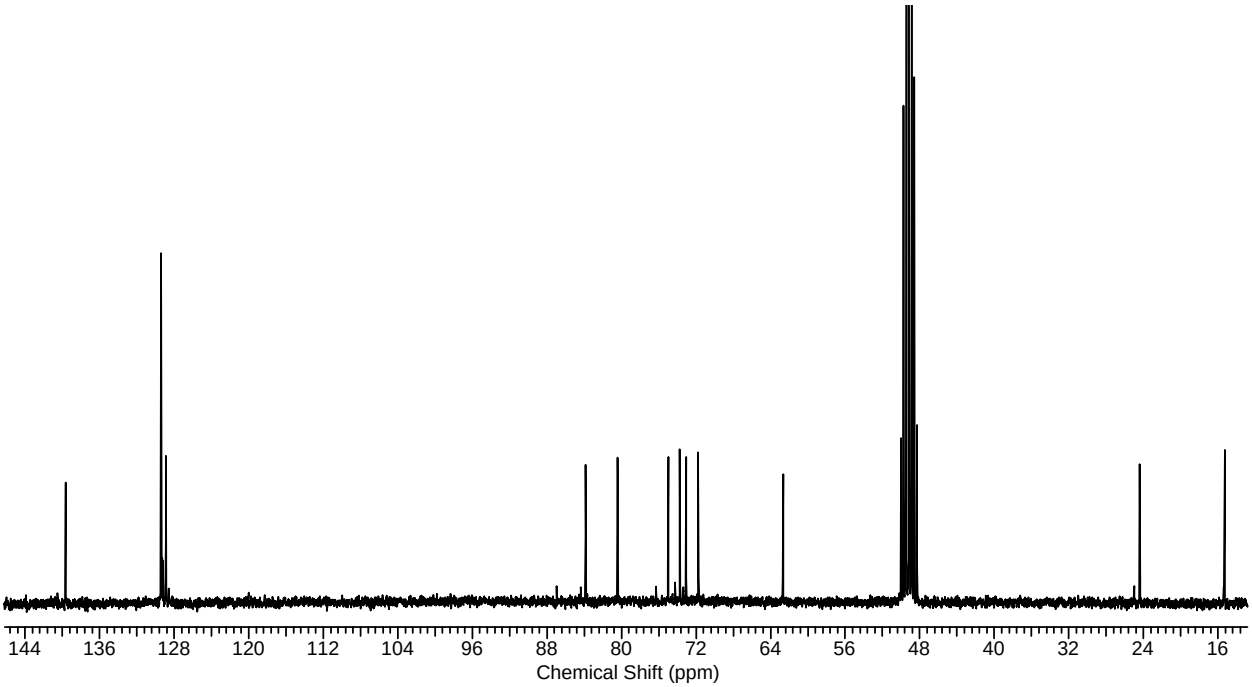

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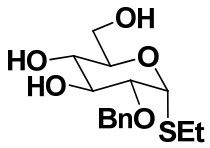
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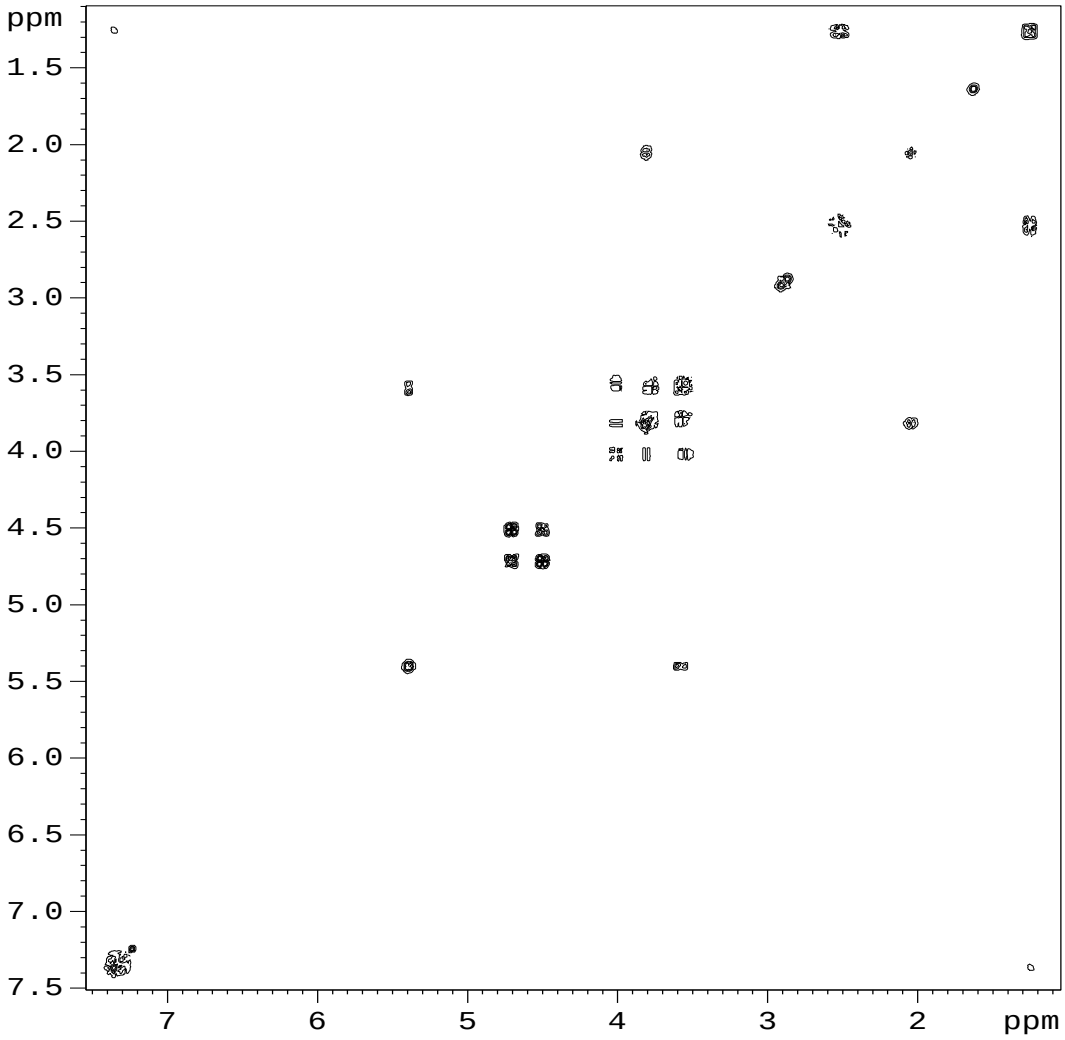
HO
BnO
SEt

B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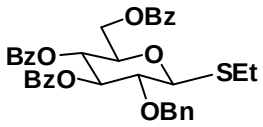

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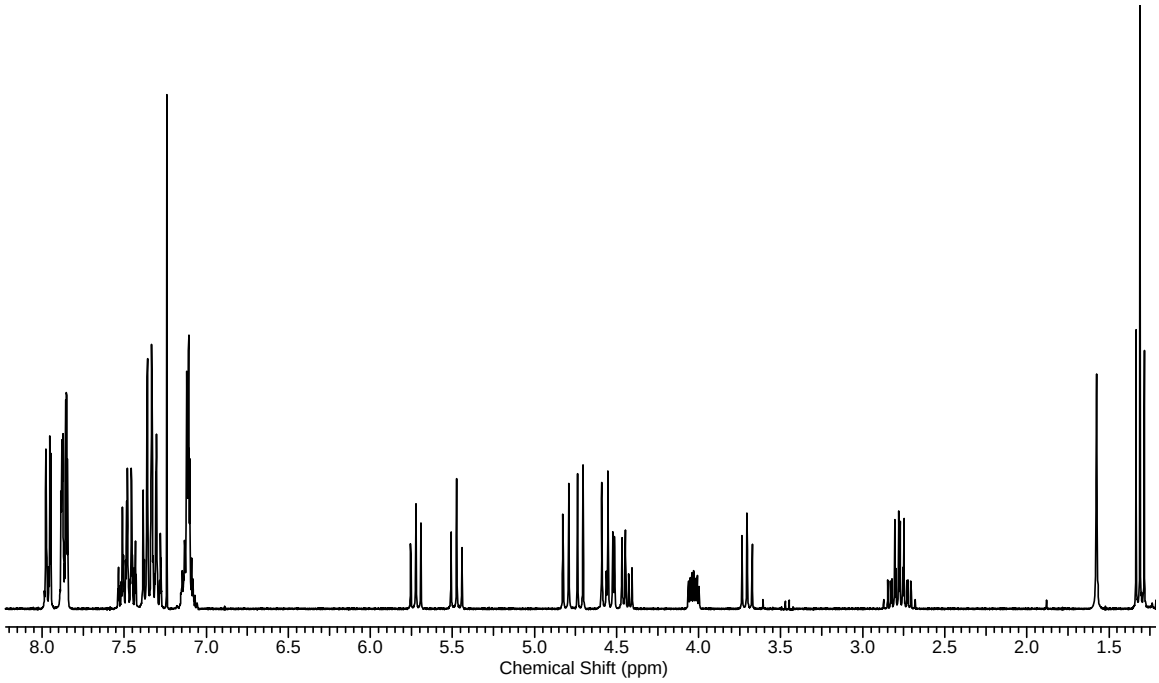

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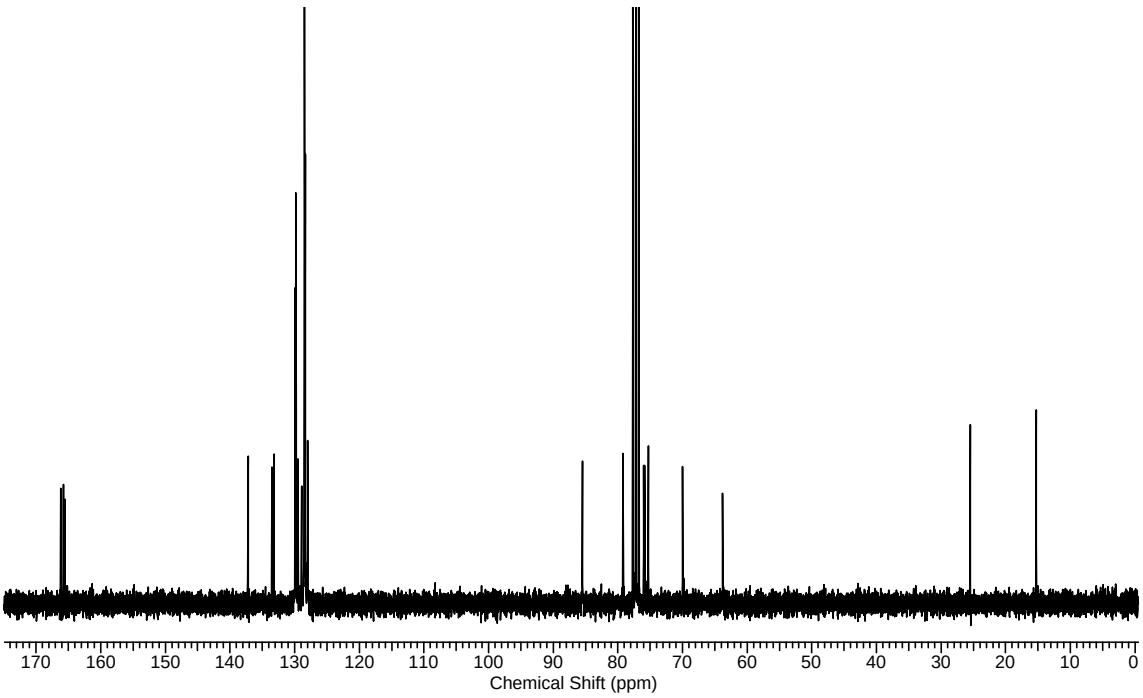

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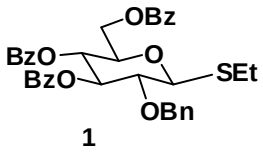
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SEt
BzO
OBn

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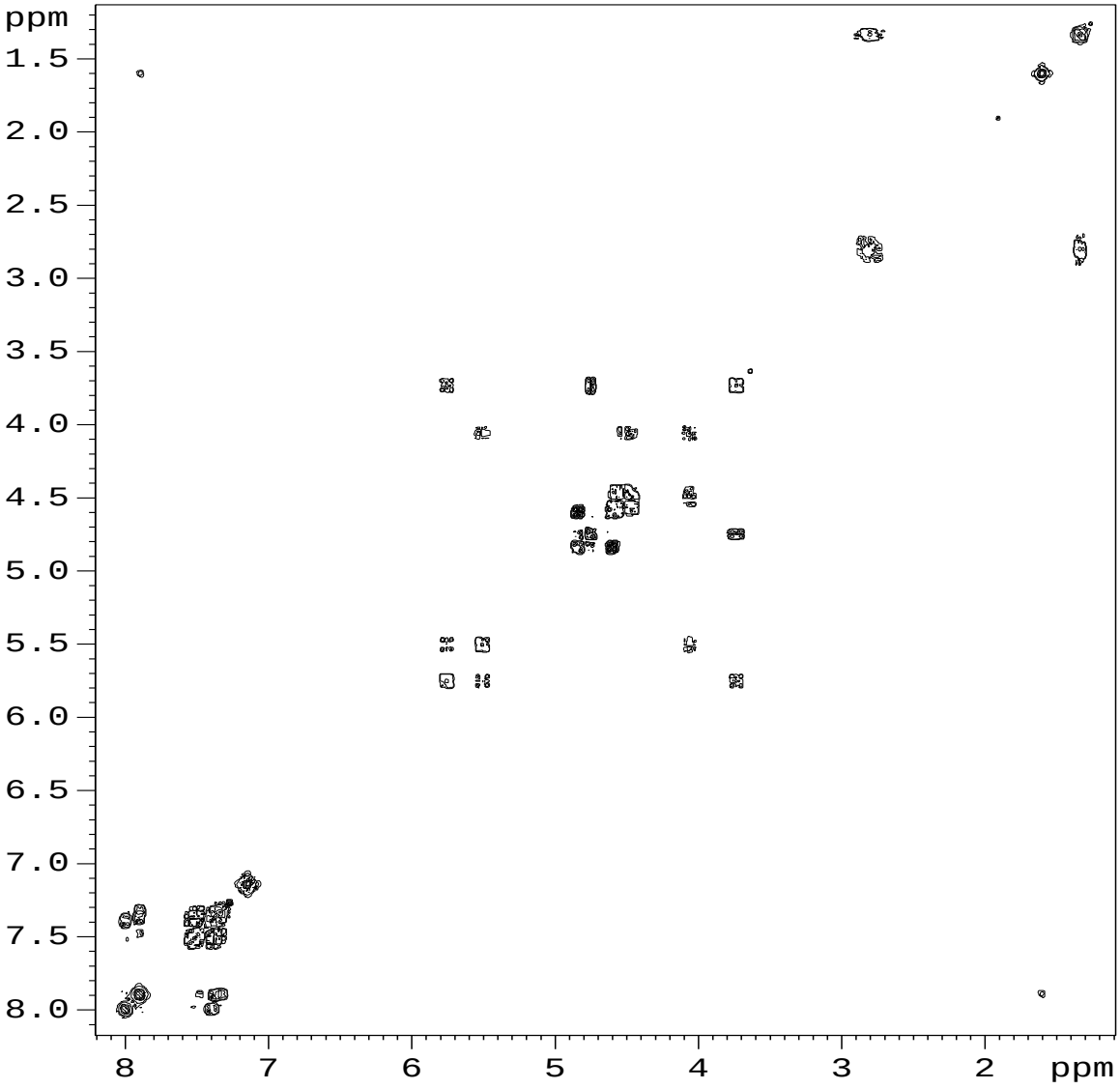
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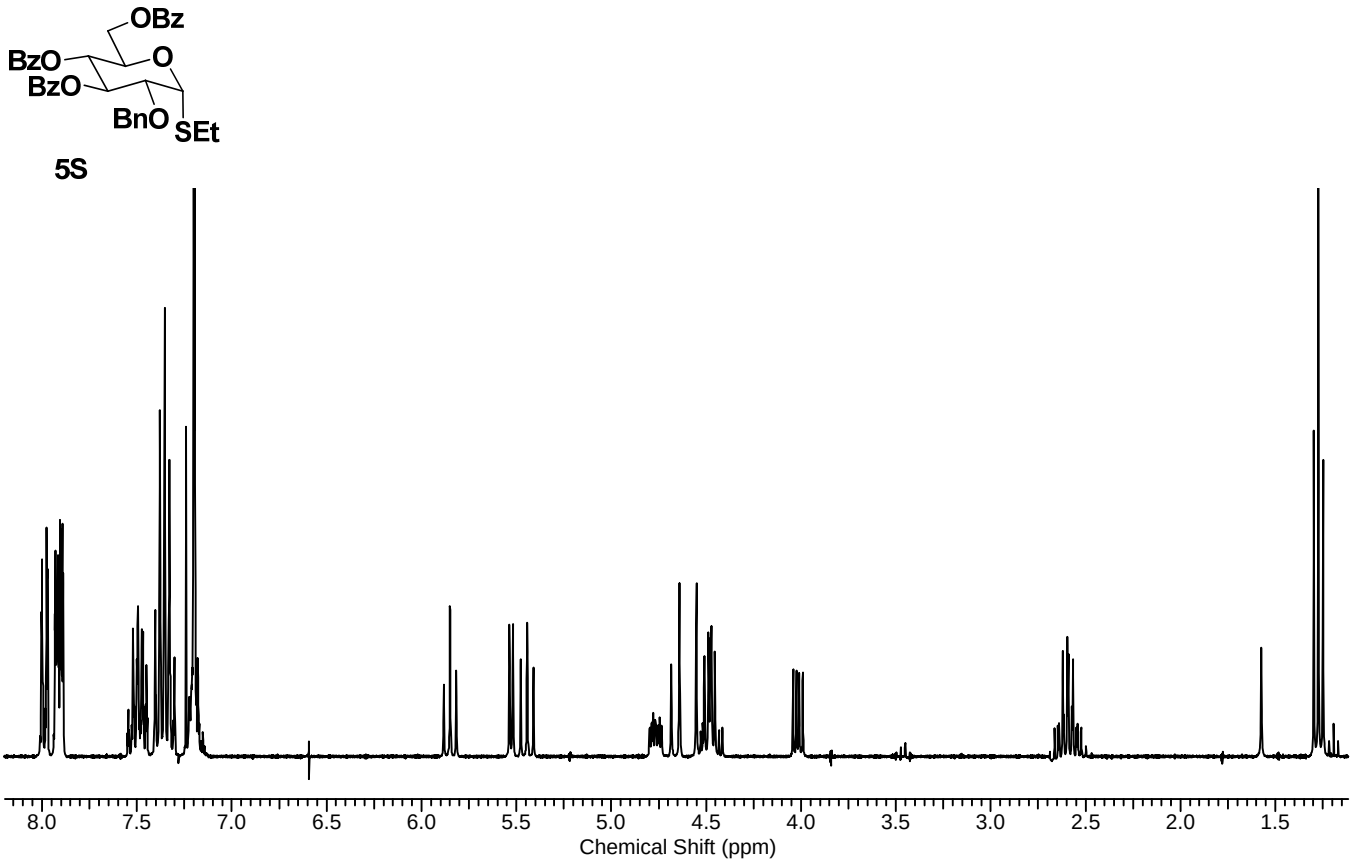

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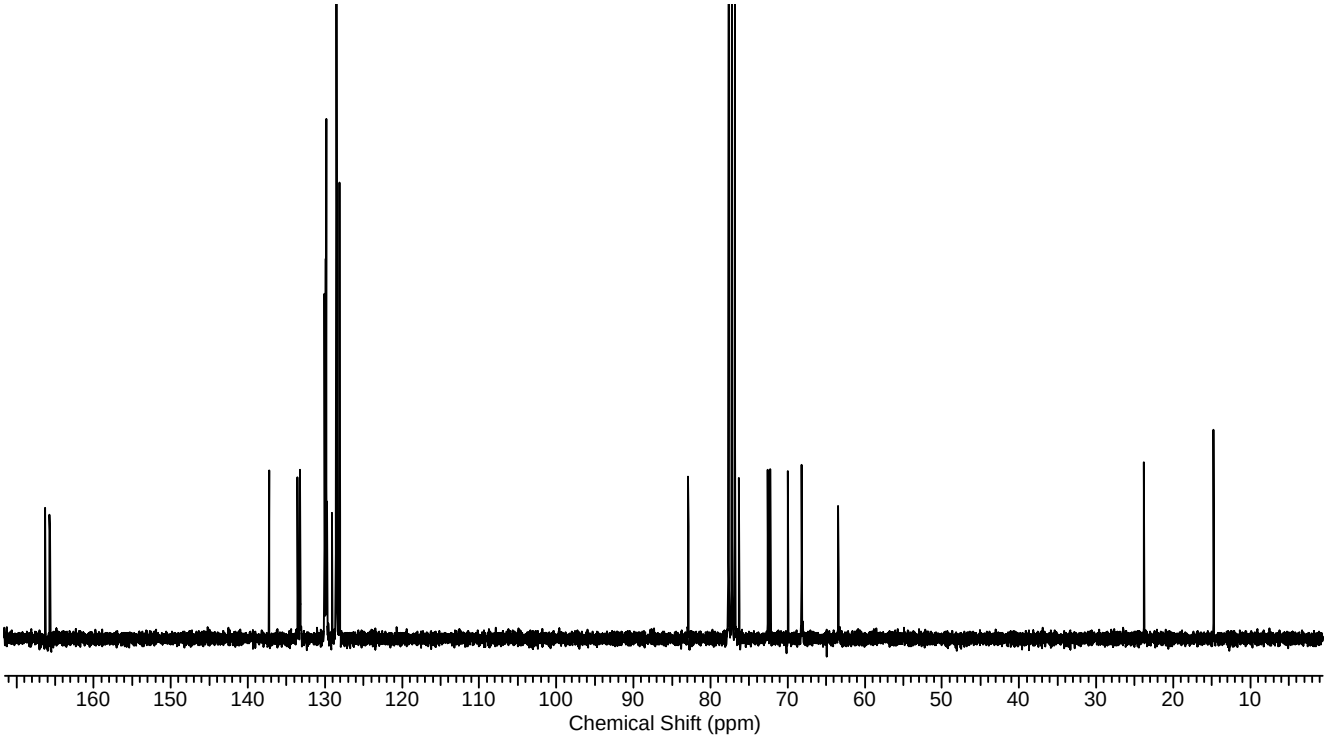

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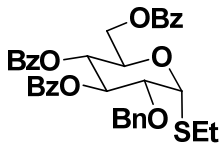

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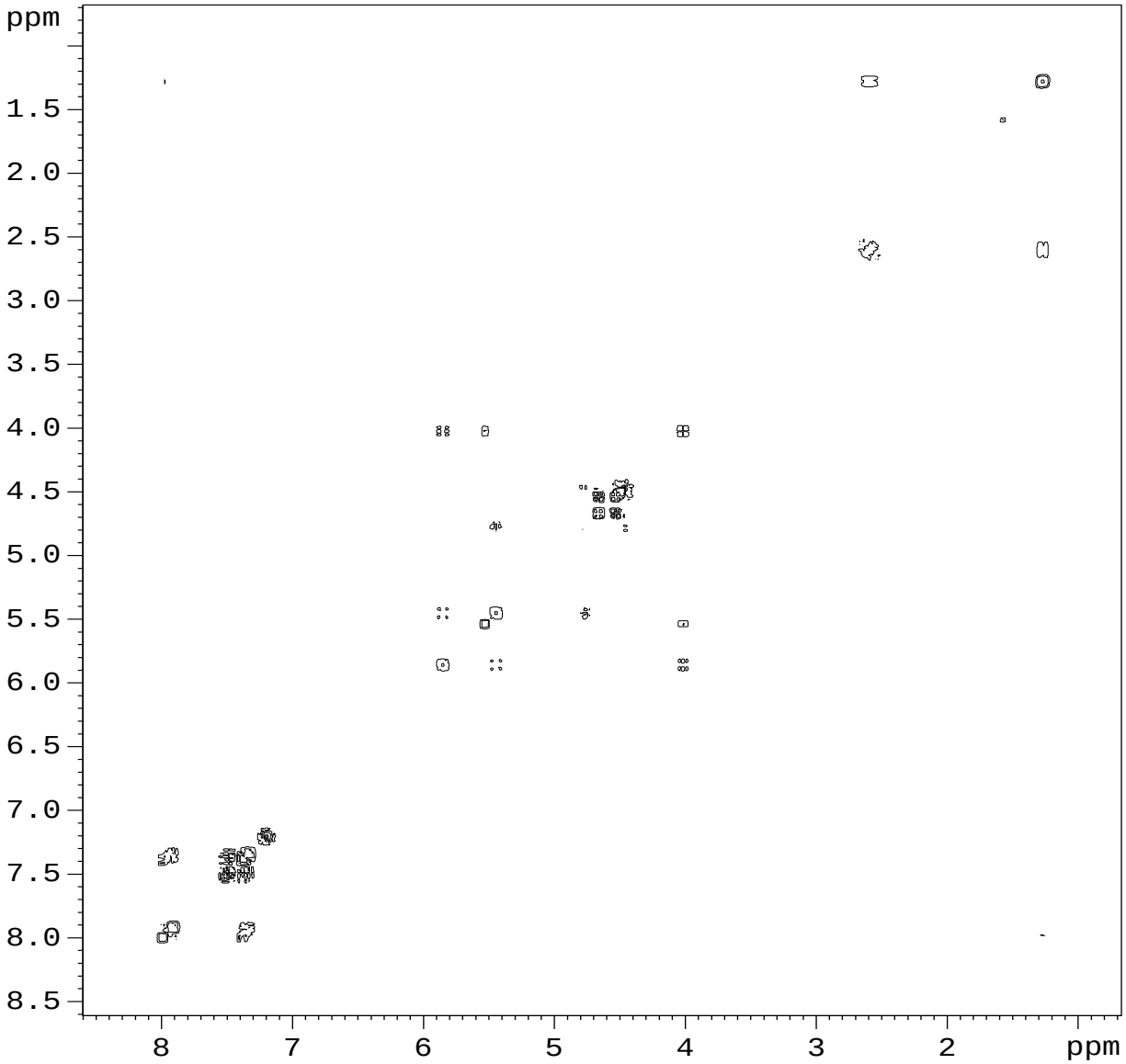

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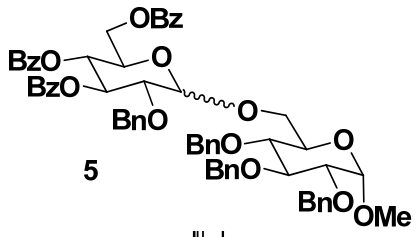

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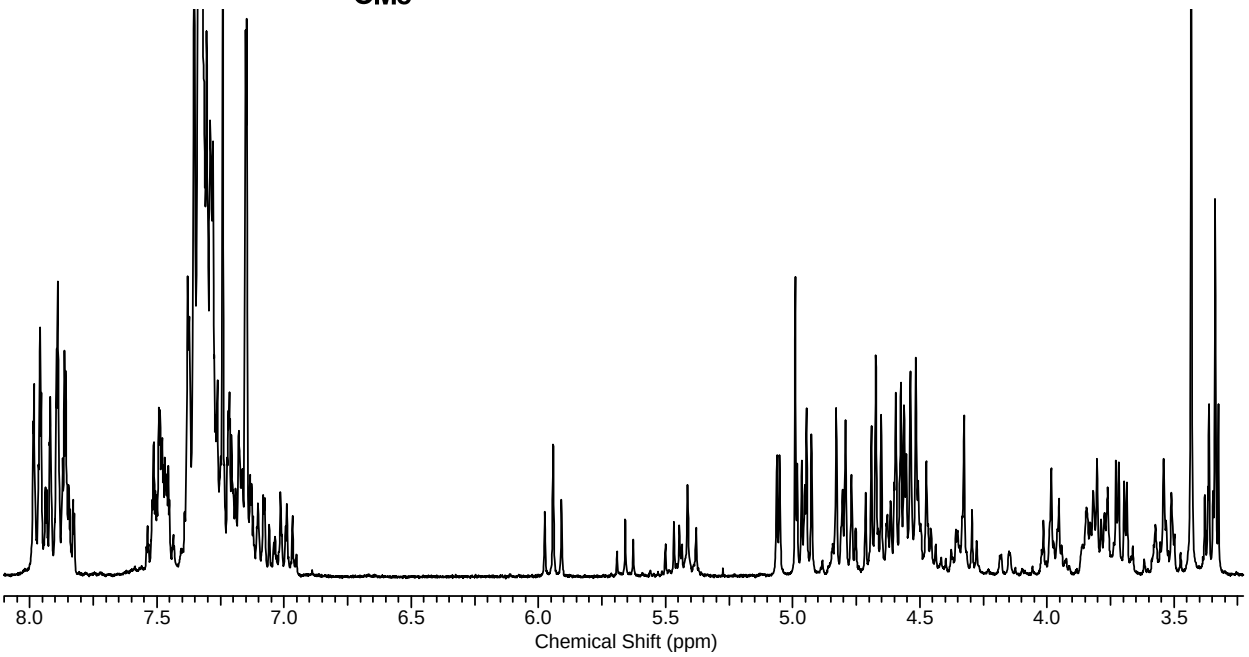

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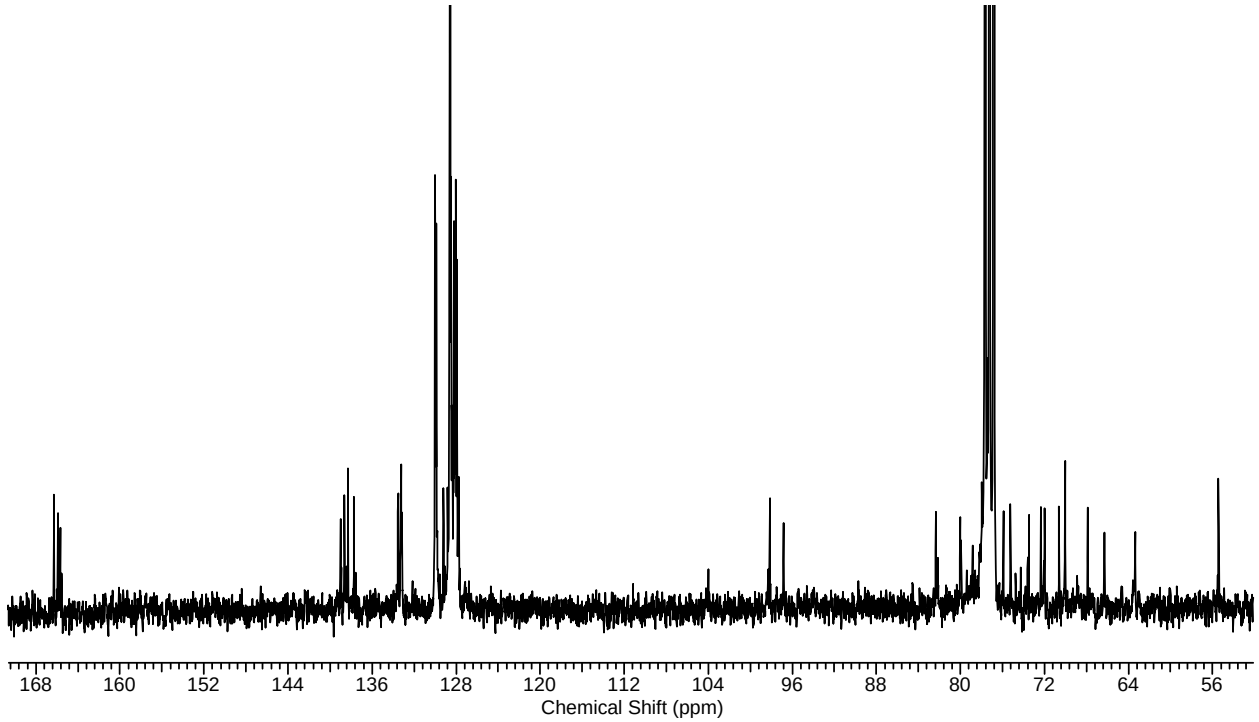

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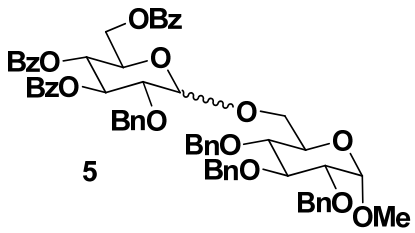

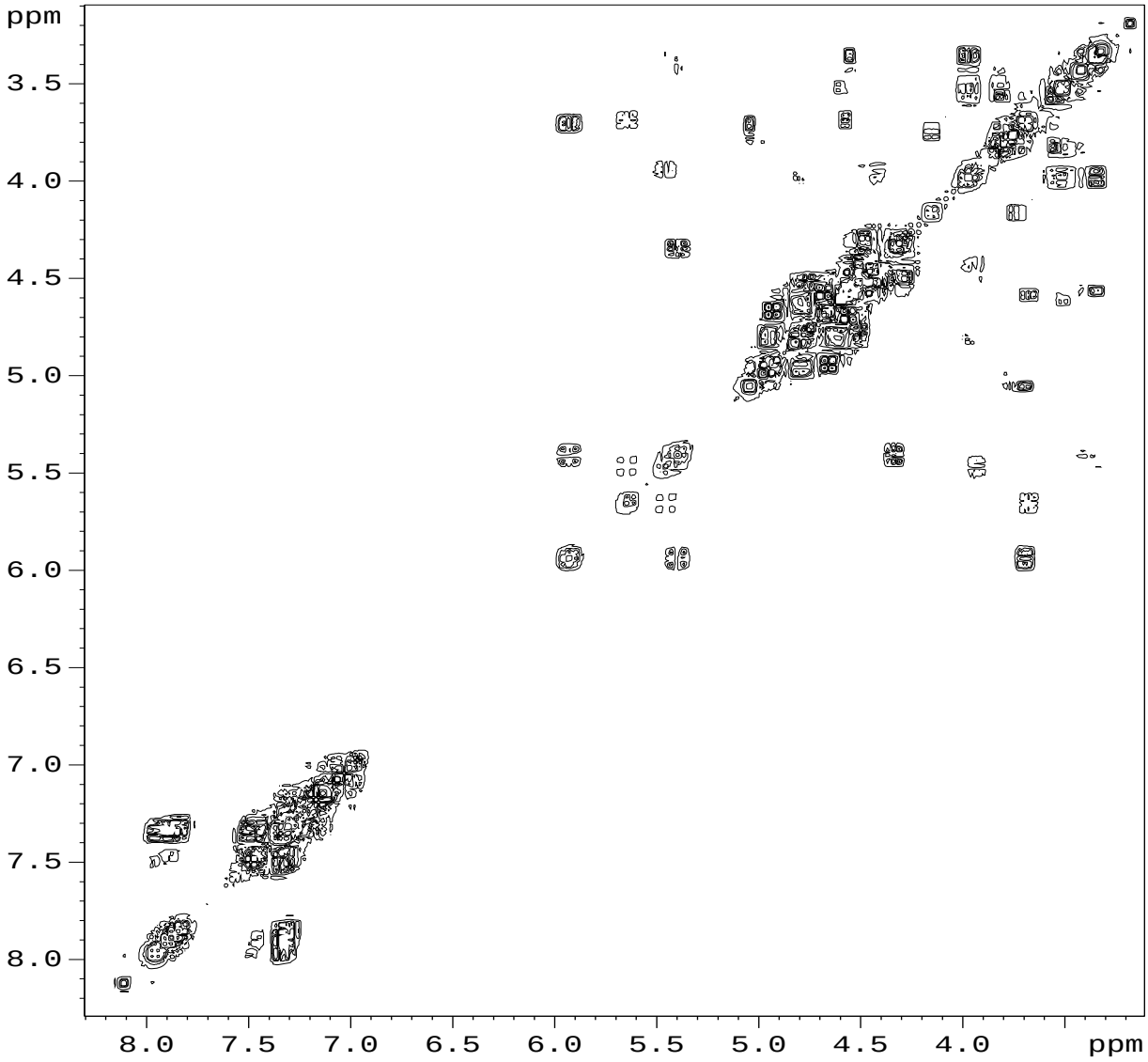

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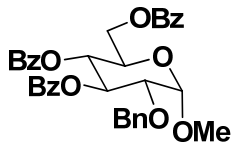

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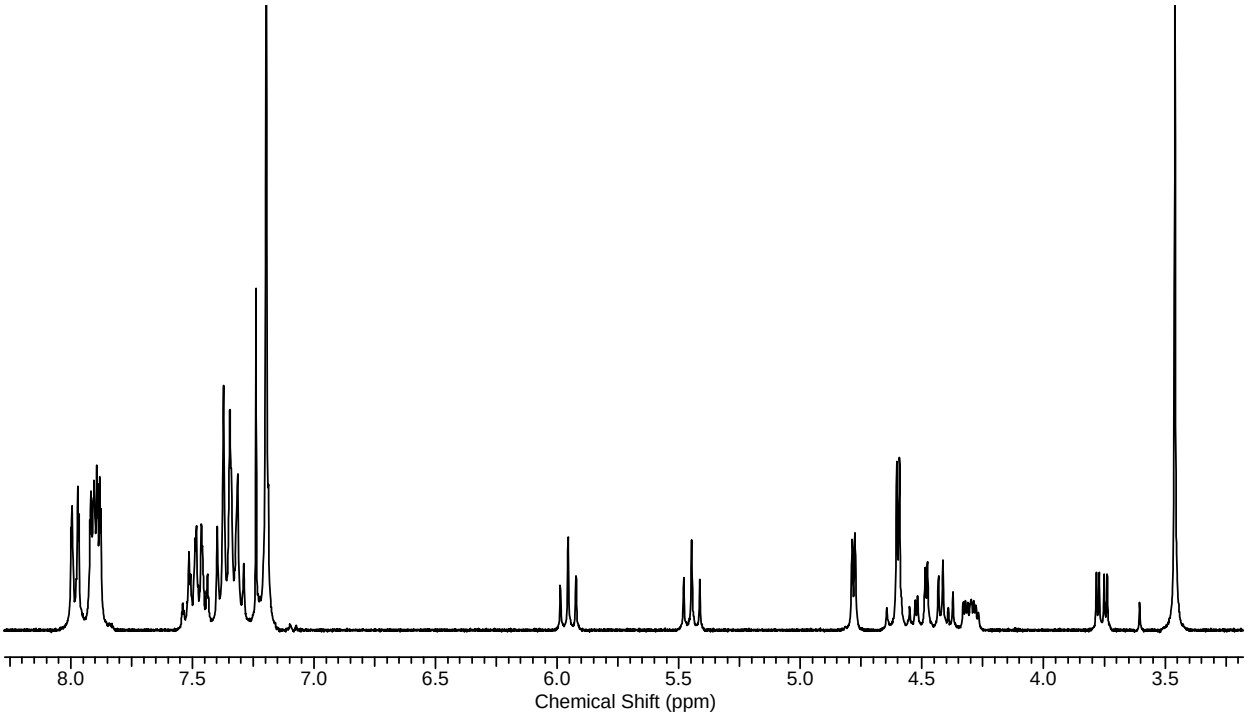

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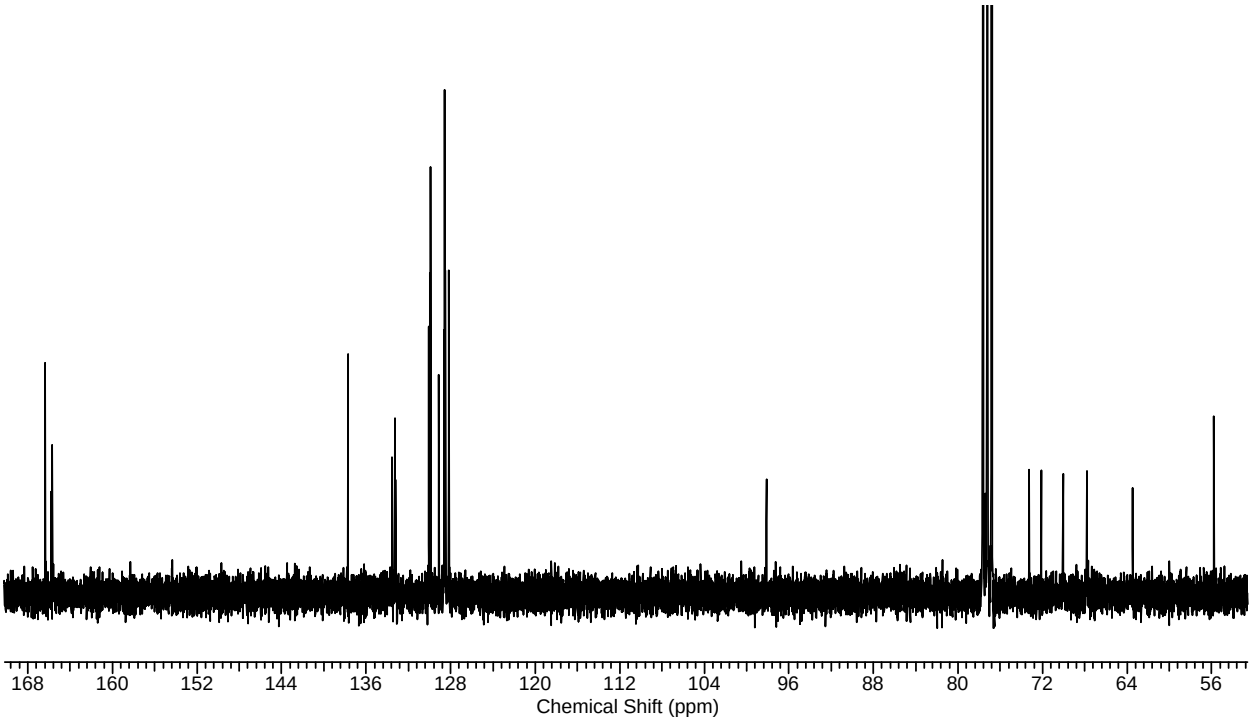

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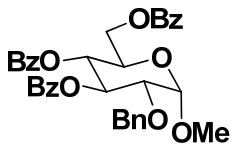

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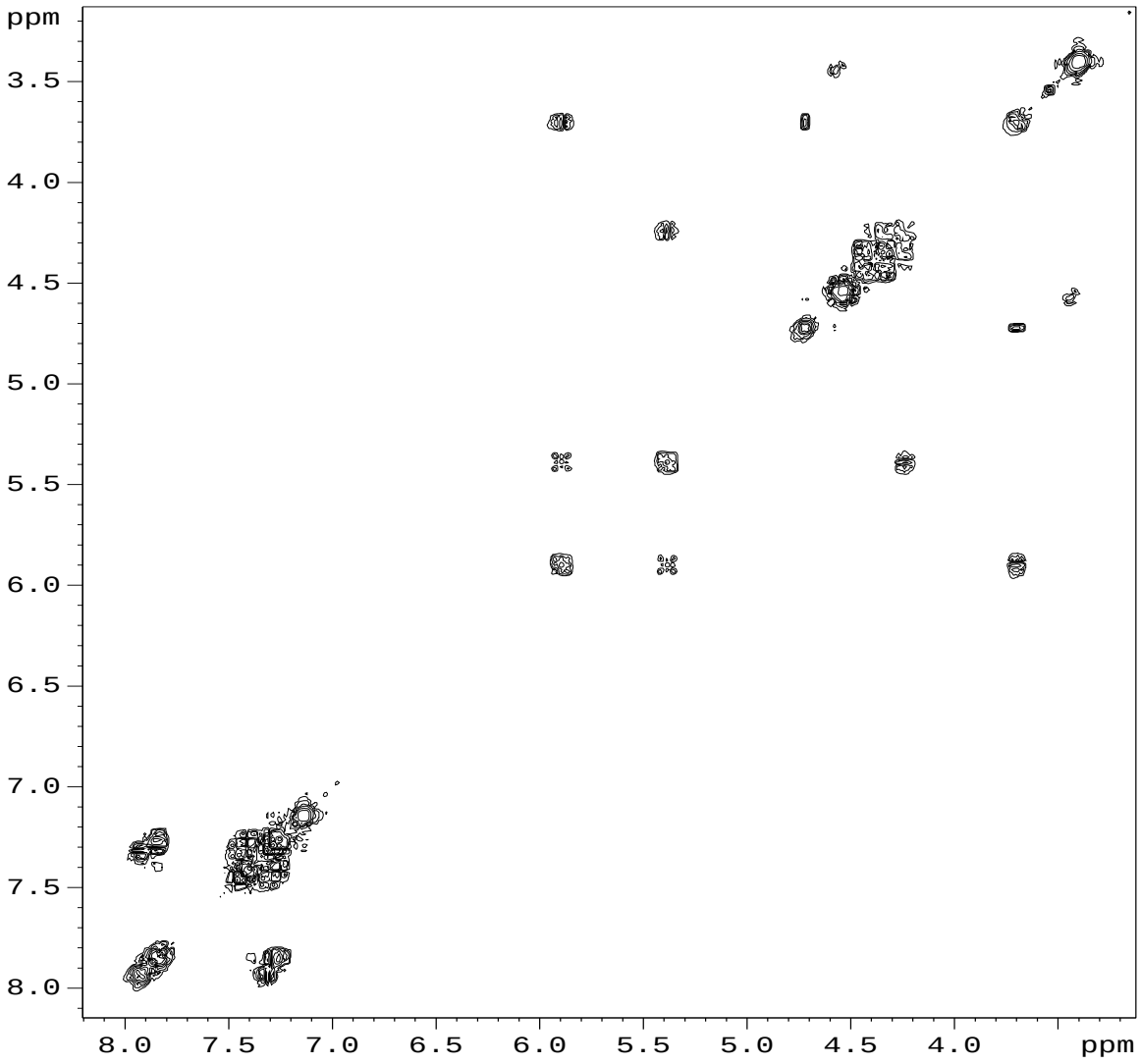

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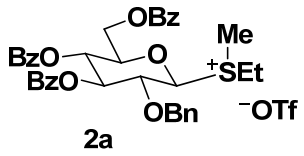

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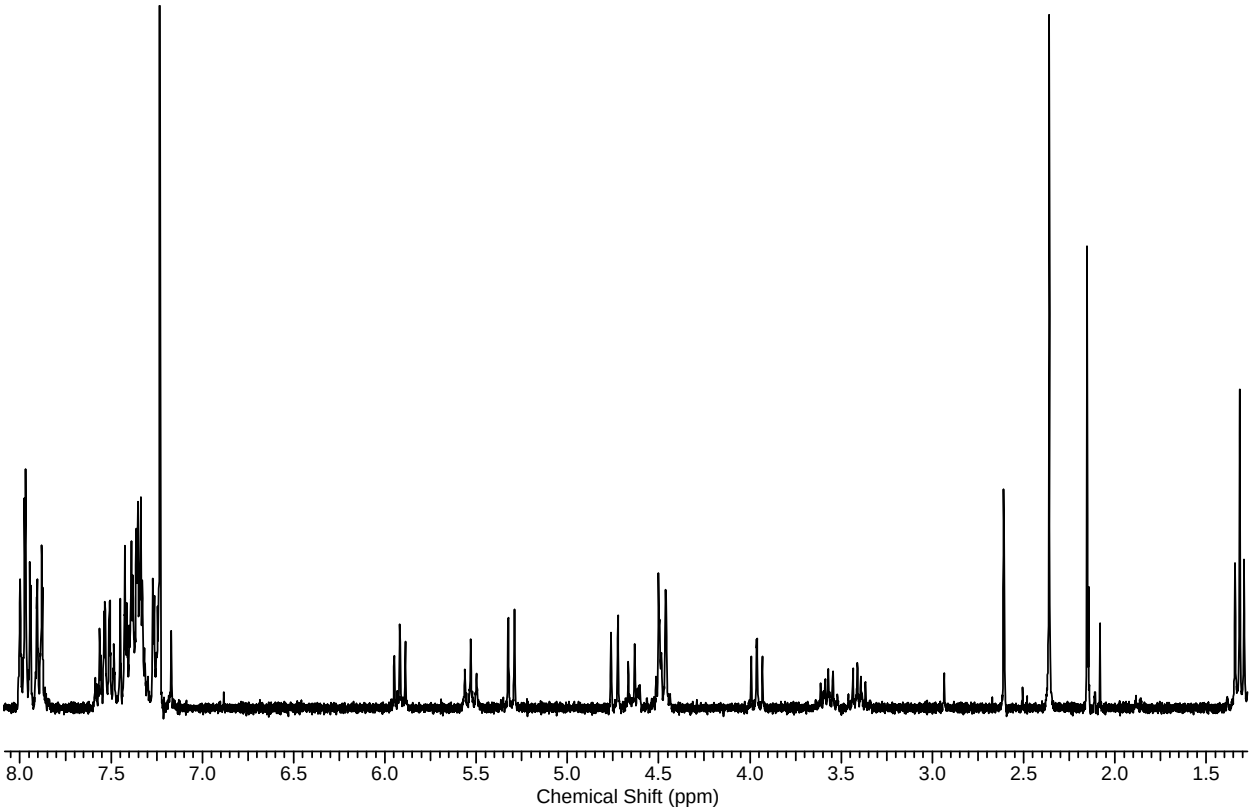

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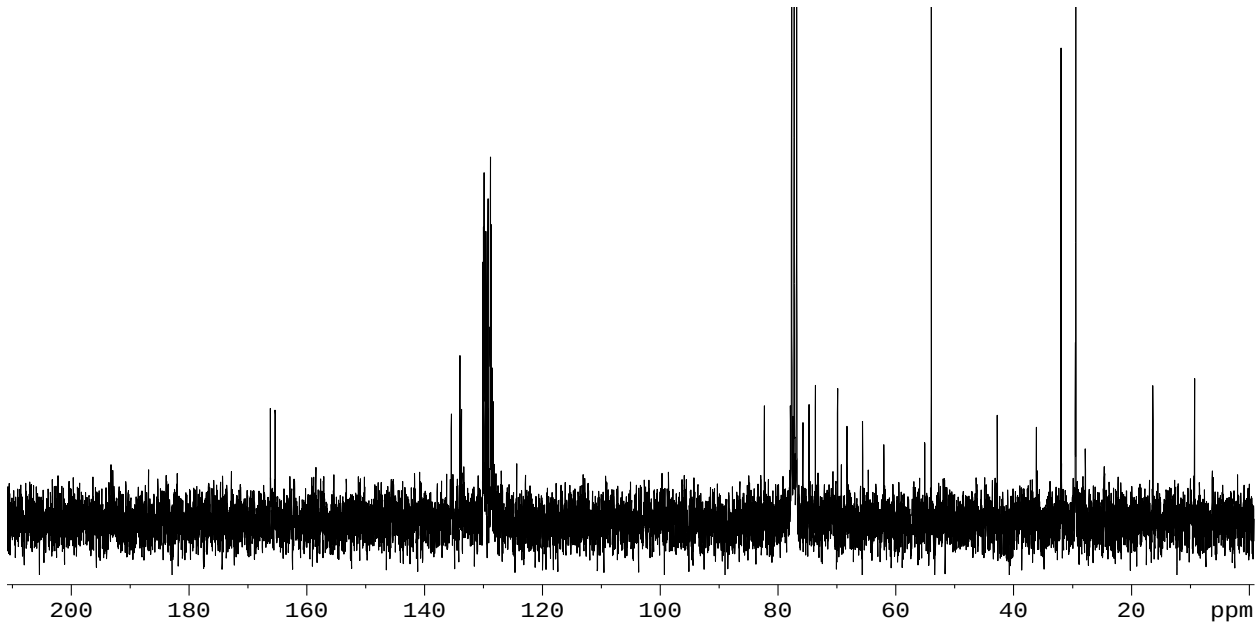
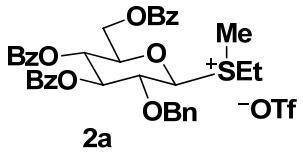


$CDCl_3$ at 75 MHz



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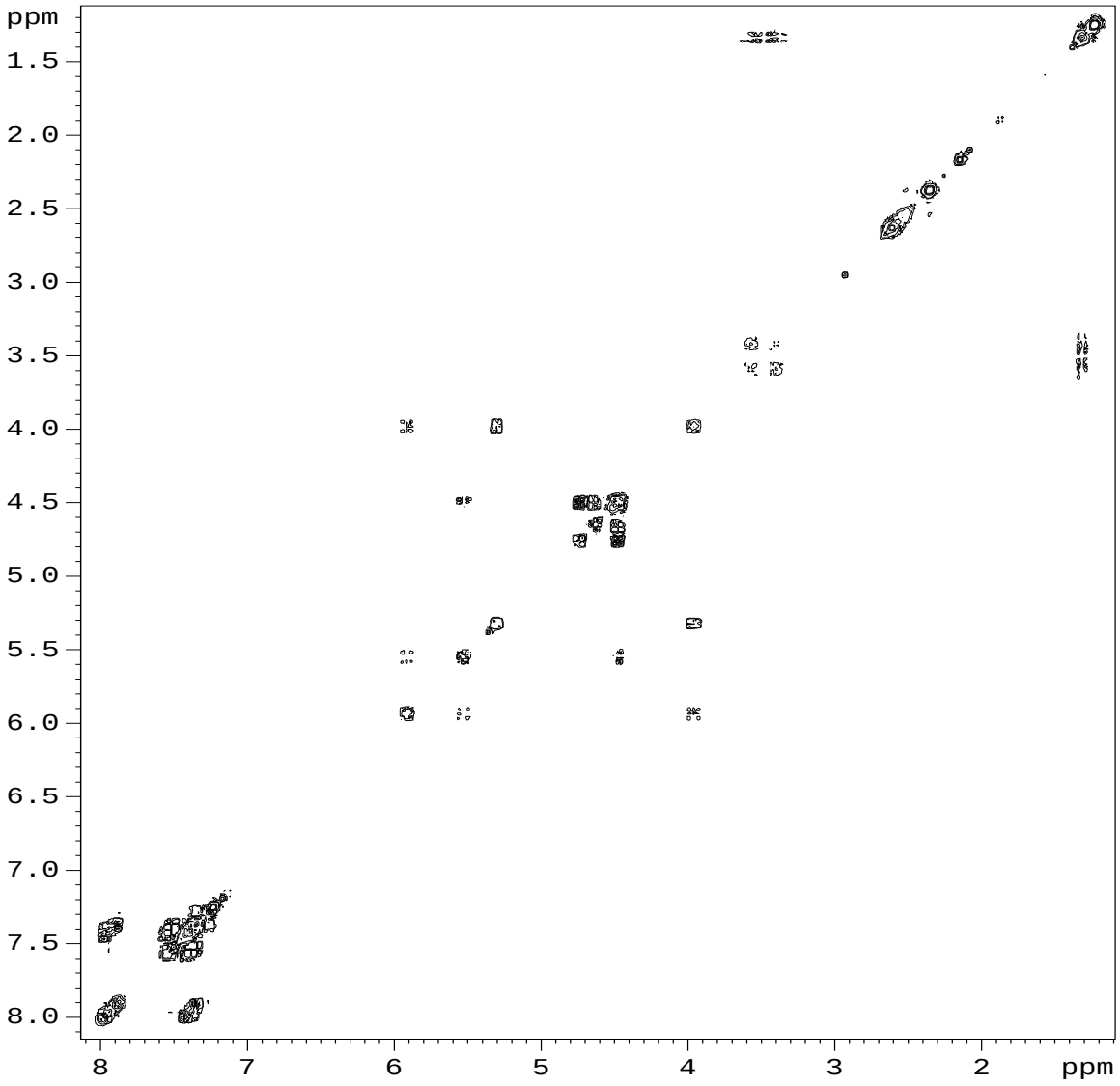
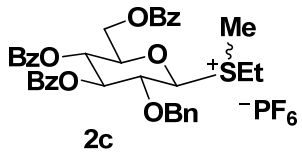
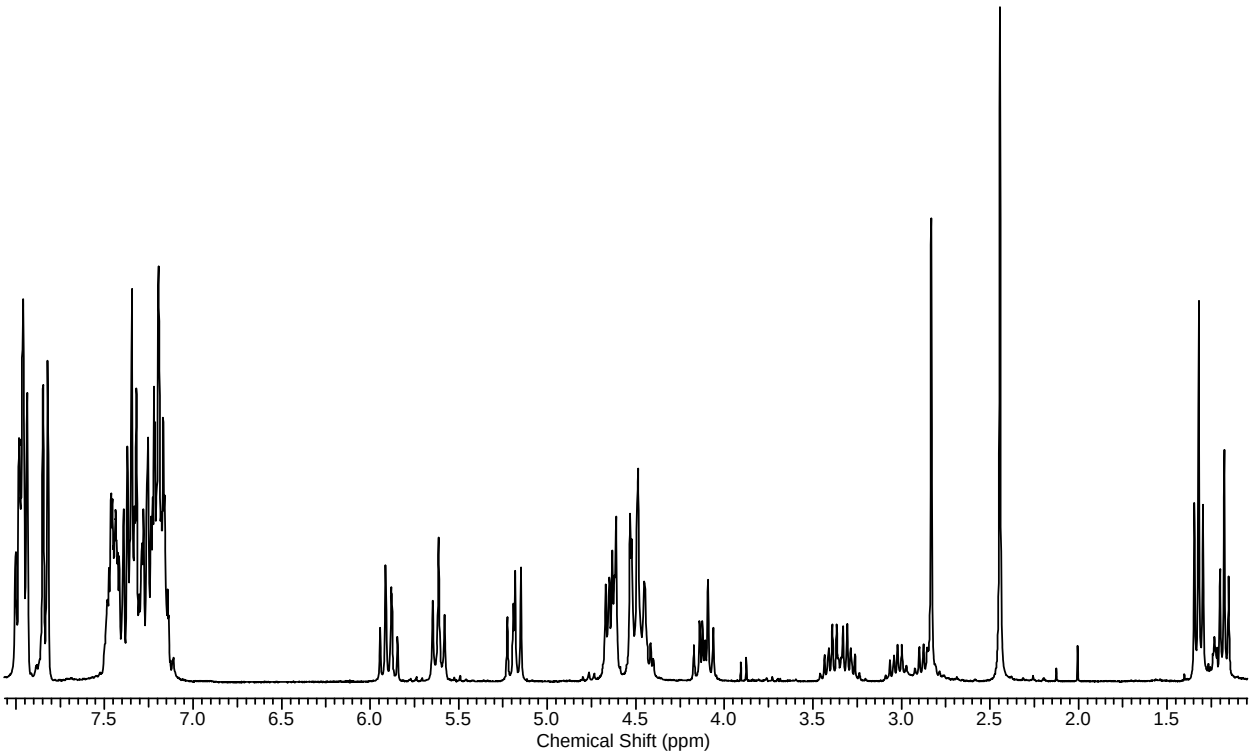


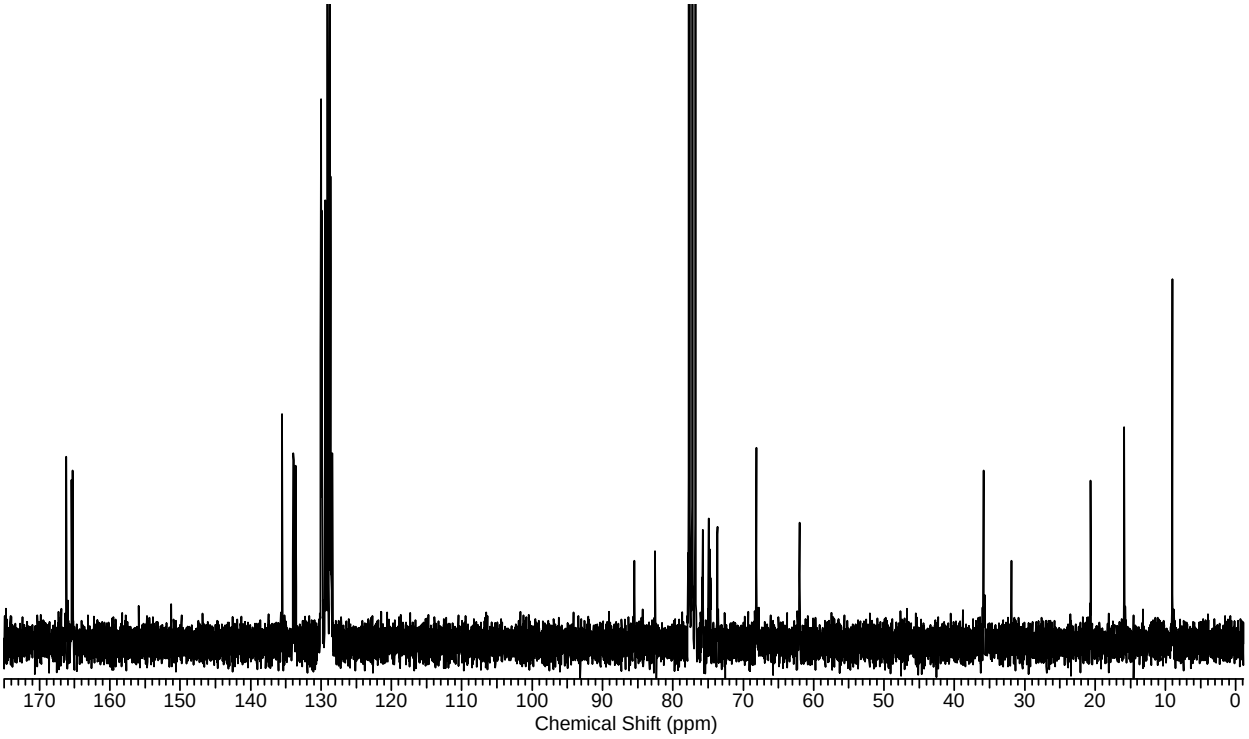
$CDCl_3$ at 300 MHz



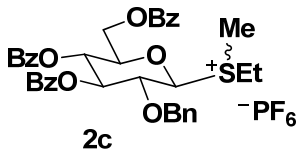
2c



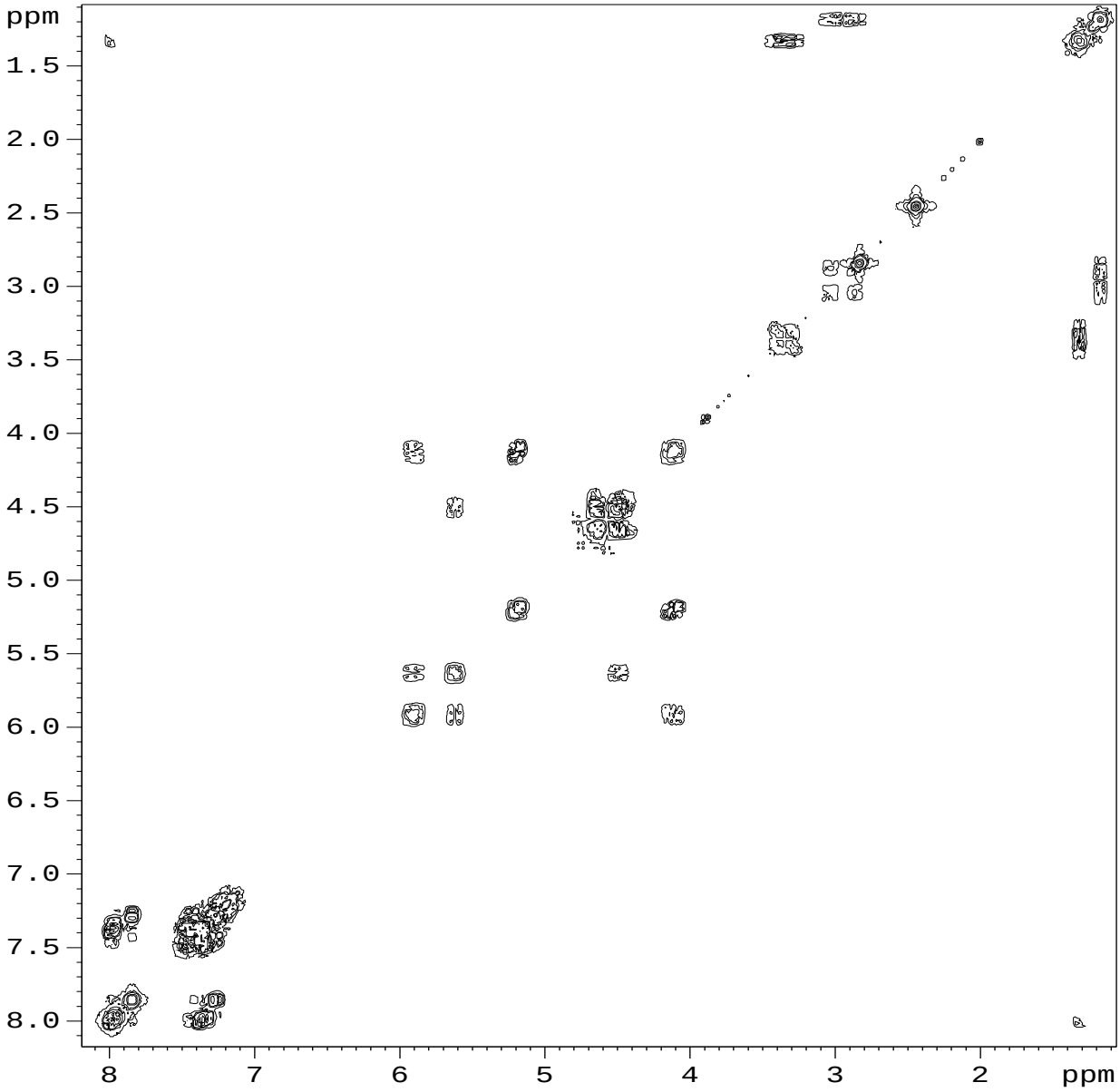
$CDCl_3$ at 300 MHz



$CDCl_3$ at 75 MHz



2c



$CDCl_3$ at 300 MHz

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