Supporting information

The effect of remote picolinyl and picoloyl substituents on the stereoselectivity of chemical glycosylation

Jagodige P. Yasomanee and Alexei V. Demchenko*

Department of Chemistry and Biochemistry, University of Missouri – St. Louis
One University Boulevard, St. Louis, MO 63121, USA
Fax: (+) 1-314-516-5342;E-mail: demchenkoa@umsl.edu

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Table 1S. Comparison of glycosyl donors **1c** and **S2** to understand the effect of the pyranose ring rigidity on stereoselectivity.

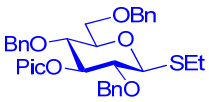
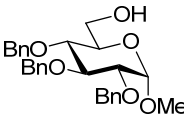
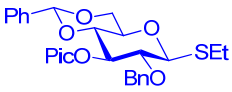
Entry	*Donor (conc.)*	*Acceptor*	*Time*	*Temp, °C*	*Yield*	*Product*	*α/β Ratio*
1	 **1c** (50 mM)	 **2**	4 h	-30 → 42	84%	**3c**	1/5.8
2	**1c** (5 mM)	**2**	3 h	-30 → 42	85%	**3c**	1/15.6
3	 **S2** (50 mM)	**2**	18 h	-30 → 42	76%	**S8**	1/2.4
4	**S2** (5 mM)	**2**	20 h	-30 → 42	77%	**S8**	1/2.1

Table 2S. The effect of the anomeric configuration on the stereoselectivity of glycosidation of picolinylated and benzylated glycosyl donors.

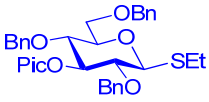
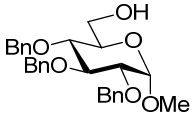
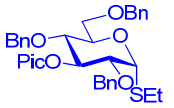
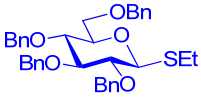
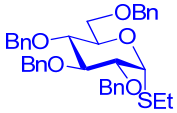
Entry	*Donor (conc.)*	*Acceptor*	*Time*	*Temp, °C*	*Yield*	*Product*	*α/β Ratio*
1	 **1c** (50 mM)	 **2**	4 h	-30 → 42	84%	**3c**	1/5.8
2	**1c** (5 mM)	**2**	3 h	-30 → 42	85%	**3c**	1/15.6
3	 α-**1c** (50 mM)	**2**	3.5 h	-30 → 42	89%	**3c**	1/14.5
4	 **1a** (50 mM)	**2**	15 min	-30	92%	**3a**	1/1.9
5	**1a** (5 mM)	**2**	2 h	-30 → rt	90%	**3a**	1/1.0
6	 *α*-**1a** (50 mM)	**2**	15 min	-30	96%	**3a**	1/1.3

Table 3S. The effect of dilution and temperature on the stereoselectivity of glycosidation of donors **1a** and **1c**.

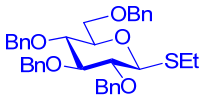
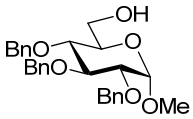
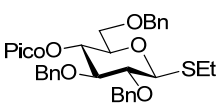
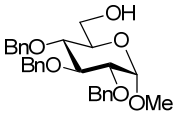
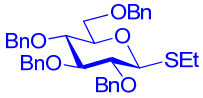
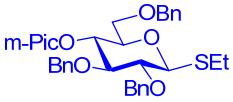
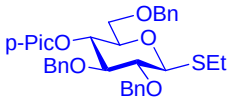
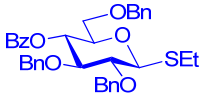
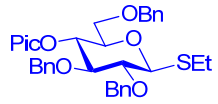
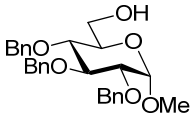
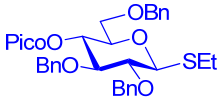
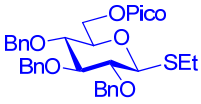
Entry	*Donor (conc.)*	*Acceptor*	*Time*	*Temp, °C*	*Yield*	*Product*	*α/β Ratio*
1	 **1a** (50 mM)	 **2**	15 min	-30	92%	**3a**	1 / 1.9
2	**1a** (50 mM)	**2**	10 min	rt	89%	**3a**	1 / 1.2
3	**1a** (5 mM)	**2**	2 h	-30 → rt	90%	**3a**	1 / 1.0
4	**1a** (1 mM)	**2**	16 h	-30 → rt	<5%	**3a**	n/a
5	 **1c** (50 mM)	**2**	4 h	-30 → 42	84%	**3c**	1 / 5.8
6	**1c** (50 mM)	**2**	1 ½ h	rt → 42	87%	**3c**	1 / 5.0
7	**1c** (5 mM)	**2**	3 h	-30 → 42	85%	**3c**	1 / 15.6
8	**1c** (5 mM)	**2**	18 h	50	64%	**3c**	1 / 7.1
9	**1c** (1 mM)	**2**	2 ½ h	-30 → 42	82%	**3c**	1 / 15.8

Table 4S. The effect of non-assisting protecting groups at C-4 on stereoselectivity.[a]

Entry	*Donor (conc.)*	*Acceptor*	*Time*	*Temp, °C*	*Yield*	*Product*	*α/β Ratio*
1	 **1f** (5 mM)	 **2**	4 h	-30 → rt	73%	**3f**	>25 / 1
2	 **1a** (50 mM)	**2**	15 min	-30	92%	**3a**	1 / 1.9
3	**1a** (5 mM)	**2**	2 h	-30 → rt	90%	**3a**	1 / 1.0
4	 **S14** (50 mM)	**2**	5 ½ h	-30 → rt	87%	**S15**	1 / 1.1
5	**S14** (5 mM)	**2**	10 h	-30 → rt	82%	**S15**	1.5 / 1
6	 **S16**(50 mM)	**2**	6 ½ h	-30 → rt	82%	**S17**	1 / 1.6
7	**S16** (5 mM)	**2**	10 h	-30 → rt	74%	**S17**	1.3 / 1
8	 **S18** (50 mM)	**2**	2 h	-30 → rt	97%	**S19**	1 / 2.5
9	**S18** (5 mM)	**2**	5 h	-30 → rt	93%	**S19**	1 / 2.6

[a] - Reactions with m- and p-picoloyl protected donors were sluggish, low yielding, and non-stereoselective (no experimental data has been provided)

Table 5S. The effect of donor and acceptor mixing time, before adding promoter, on the stereoselectivity.

Entry	*Donor (Conc.)*	*Acceptor*	*Mixing Time*	*Temp, °C*	*Yield*	*Product*	*α/β Ratio*
1	 **1d** (5 mM)	 **2**	0 [a]	-30 → rt	63%	**3d**	3.4 / 1
2	**1d** (5 mM)	**2**	1 h	-30 → rt	86%	**3d**	5.3 / 1
3	 **1f** (5 mM)	**2**	0 [a]	-30 → rt	67%	**3f**	11.3 / 1
4	**1f** (5 mM)	**2**	1 h	-30 → rt	73%	**3f**	>25 / 1
5	 **1g** (5 mM)	**2**	0 [a]	-30 → rt	86%	**3g**	1 / 13
6	**1g** (5 mM)	**2**	1 h	-30 → rt	92%	**3g**	>1 / 25

[a] - acceptor and DMTST were added concomitantly to a solution of the donor and sieves in $(ClCH_2)_2$

Table 6S. Glycosylation of 6-OTMS acceptor **S23**[1] on the stereoselectivity of glycosidation of donors **1a**, **1c**, and **1g**.

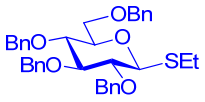
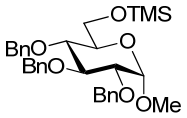
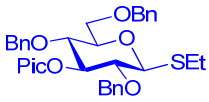
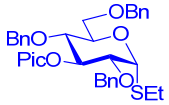
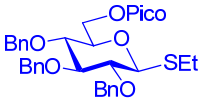
Entry	*Donor (Conc.)*	*Acceptor*	*Time*	*Temp, °C*	*Yield*	*Product*	*α/β Ratio*
1	 **1a** (50 mM)	 **S23**	1 ½ h	-30 → rt	87%	**3a**	1 / 1.8
2	 **1c** (5 mM)	**S23**	8 h	-30 → rt	76%	**3c**	1 / 2.0
3	 **α-1c** (50 mM)	**S23**	6 ½ h	-30 → rt	70%	**3c**	1 / 3.0
4	 **1g** (50 mM)	**S23**	5 h	-30 → rt	77%	**3g**	1 / 5.6

Table 7S. The effect of excess DMTST (6 equiv. with respect to the donor) on the stereoselectivity of glycosidation of donors **1c** and **1g**.

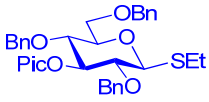
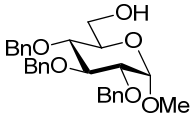
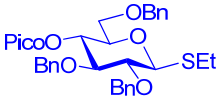
Entry	*Donor (Conc.)*	*Acceptor*	*Time*	*Temp, °C*	*Yield*	*Product*	*α/β Ratio*
1	 **1c** (5 mM)	 **2**	16 h	-30 → 42	89%	**3c**	1 / 9.8
2	 **1f** (5 mM)	**2**	6 h	-30 → rt	83%	**3g**	4.2 / 1

Table 8S. The effect of TfOH (1 equiv. with respect to the donor) added along with DMTST on the stereoselectivity of glycosidation of donors **1c** and **1g**.

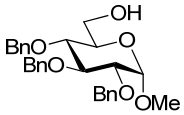
Entry	*Donor (Conc.)*	*Acceptor*	*Time*	*Temp, °C*	*Yield*	*Product*	*α/β Ratio*
1	 **1c** (5 mM)	 **2**	4 ½ h	-30 → 42	84%	**3f**	1 / 8.1
2	 **1g** (50 mM)	**2**	2 h	-30 → rt	93%	**3g**	1.7 / 1
3	 **1g** (5 mM)	**2**	3 ½ h	-30 → rt	87%	**3g**	2.3 / 1

Table 9S. The effect of DMSO on stereoselectivity of glycosidation of donors **1a**, **1c**, and **1f**.

*Although DMSO is an α-directing solvent, herein it still reduces high α-selectivity achieved with donor **1f**.*

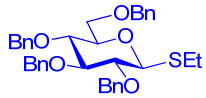
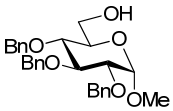
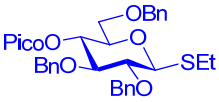
Entry	*Donor (conc.)*	*Acceptor*	*Temp, °C, Time*	*Donor : DMSO Molar Ratio*	*Product*	*α/β Ratio*
1	 **1a** (50 mM)	 **2**	-30 → rt, 15 min	1 : 0	**3a**	1 / 1.9
2	**1a** (5 mM)	**2**	-30 → rt, 2 h	1 : 0	**3a**	1 / 1.0
3	**1a** (50 mM)	**2**	-30 → rt, 30 min	1 : 1	**3a**	1.1 / 1
4	**1a** (5 mM)	**2**	-30 → rt, 4 h	1 : 1	**3a**	1.6 / 1
5	**1a** (50 mM)	**2**	-30 → rt, 7 h	1 : 5	**3a**	1.6 / 1
6	 **1c** (50 mM)	**2**	-30→42, 4 h	1 : 0	**3c**	1 / 5.8
7	**1c** (5 mM)	**2**	-30→42, 3h	1 : 0	**3c**	1 / 15.6
8	**1c** (50 mM)	**2**	-30 42, 16 h	1 : 1	**3c**	1 / 1.3
9	**1c** (5 mM)	**2**	-30→42, 24 h	1 : 1	**3c**	1 / 4.9
10	**1c** (50 mM)	**2**	-30→42, 24 h	1 : 5	**3c**	2.3 / 1
11	 **1f** (50 mM)	**2**	-30→rt, 3 ½ h	1 : 0	**3f**	2.8 / 1
12	**1f** (5 mM)	**2**	-30 → rt, 4 h	1 : 0	**3f**	>25 / 1
13	**1f** (50 mM)	**2**	-30 → rt, 5 h	1 : 1	**3f**	2.4 / 1
14	**1f** (5 mM)	**2**	-30 → rt, 6 h	1 : 1	**3f**	5.6 / 1
15	**1f** (50 mM)	**2**	-30 → rt, 16 h	1 : 5	**3f**	3.1 / 1

Table 10S. Additional results on glycosylation with galactosyl, mannosyl, and rhamnosyl donors.

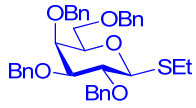
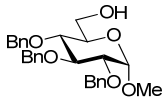
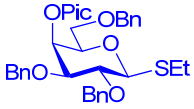
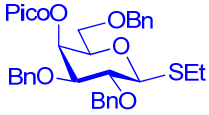
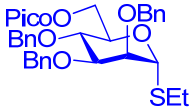
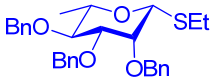
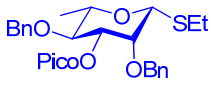
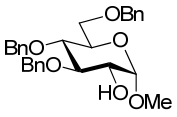
Entry	*Donor (conc.)*	*Acceptor*	*Time*	*Temp, °C*	*Yield*	*Product*	*α/β Ratio*
1	 **1h** (50 mM)	 **2**	45 min	-30 → rt	87%	**3h**	1 / 1.0
2	 **1i** (50 mM)	**2**	1½ h	-30 → rt	89%	**3i**	1 / 10
3	**1i** (5 mM)	**2**	3 h	-30 → rt	83%	**3i**	>1 / 25
4	 **1j** (50 mM)	**2**	1 h	-30 → rt	96%	**3j**	1 / 24
5	**1j** (5 mM)	**2**	1½ h	-30 → rt	95%	**3j**	>1 / 25
6	 **1k** (50 mM)	**2**	4 h	-30 → rt	89%	**3k**	1 / 3.5
7	**1k** (5 mM)	**2**	4 h	-30 → rt	86%	**3k**	1 / 4.5
8	**1k** (1 mM)	**2**	6 h	-30 → rt	89%	**3k**	1 / 6.5
9	**1k** (50 mM)	**2** (NIS/TfOH)	1 h	-30 → rt	91%	**3k**	1 / 5.3
10	**1k** (5 mM)	**2** (NIS/TfOH)	2½ h	-30 → rt	87%	**3k**	1 / 9.5
11	 **S20** (50 mM)	**2**	45 min	-30 → rt	85%	**S21**	1.1 / 1
12	 **1l** (50 mM)	 **4**	1 h	-30 → rt	90%	**S22**	>1 / 25

Chart 1S. Concentration dependence of OH chemical shift of **2** in the presence of donor **1d** (or **1f)** at 24℃.

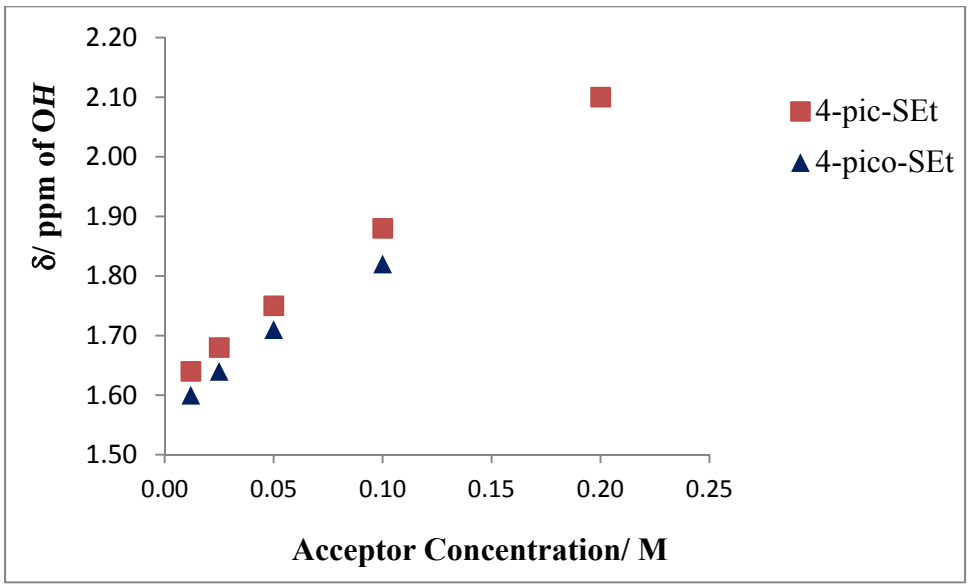
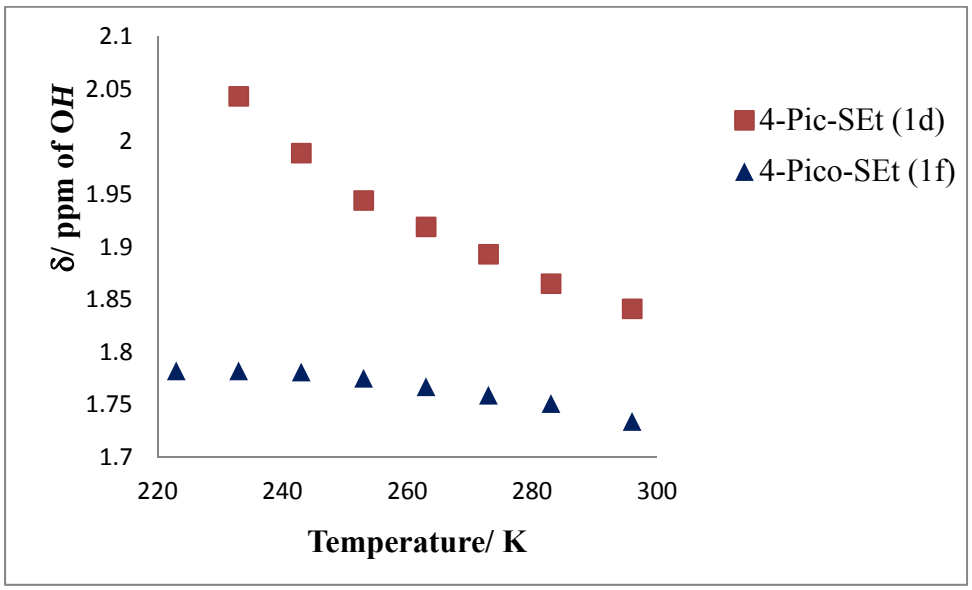


Chart 2S. Temperature dependence of OH chemical shift of **2** in the presence of equimolar amount of donor **1d** (or **1f)** in 0.05 M solution.



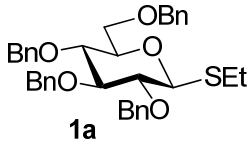
Reduced temperature coefficient ($\Delta\delta/\Delta T$) of **1d** is 3.1 $ppbK^{-1}$ and that of **1f** is 0.9 $ppbK^{-1}$.

General Experimental

Column chromatography was performed on silica gel 60 (70-230 mesh), reactions were monitored by TLC on Kieselgel 60 F254. 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 °C. CH_2Cl_2 and $ClCH_2CH_2Cl$ (1,2-DCE) 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). Anhydrous DMF was used as it 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. Optical rotations were measured at '*J*asco P-1020' polarimeter. Unless noted otherwise, ^{1}H-NMR spectra were recorded in $CDCl_3$ at 300 or 600 MHz, ^{13}C-NMR spectra were recorded in $CDCl_3$ at 75 MHz. Two-dimensional heteronuclear *J*-resolved spectra (HETERO2DJ)[2-4] were recorded in $CDCl_3$at 600 MHz .

Synthesis of Glycosyl Donors

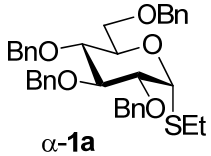
Ethyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (1a).



1a

The title compound was synthesized according to the standard procedure and the analytical data for **1a** was essentially the same as reported previously.[5]

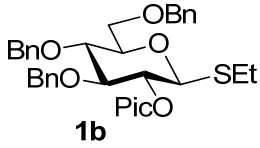
Ethyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-α-D-glucopyranoside (α-1a).



α-**1a**

The title compound was synthesized according to the standard procedure and the analytical data for α-**1a** was essentially the same as reported previously.[6]

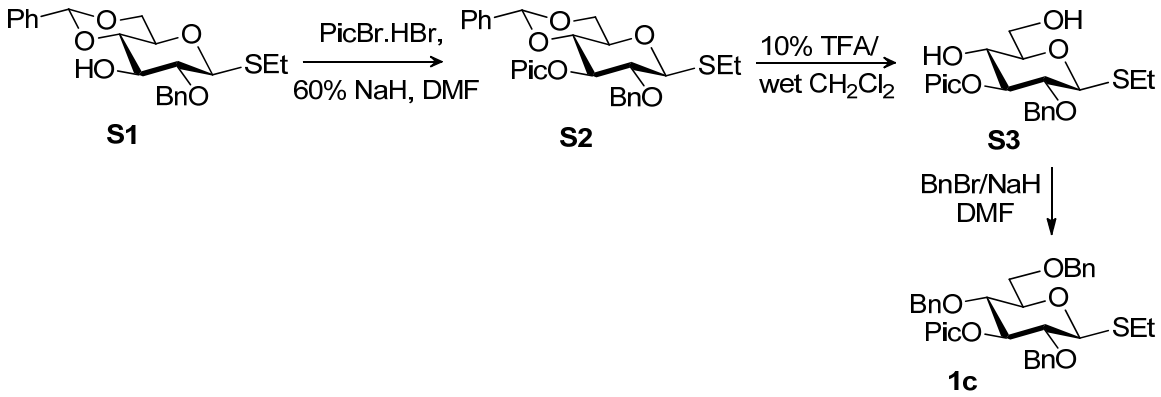
Ethyl 3,4,6-Tri-*O*-benzyl-2-*O*-picolinyl-1-thio-β-D-glucopyranoside (1b).



1b

The title compound was synthesized according to the standard procedure and the analytical data for **1b** was essentially the same as reported previously.[7]

Ethyl 2,4,6-Tri-*O*-benzyl-3-*O*-picolinyl-1-thio-β-D-glucopyranoside (1c).



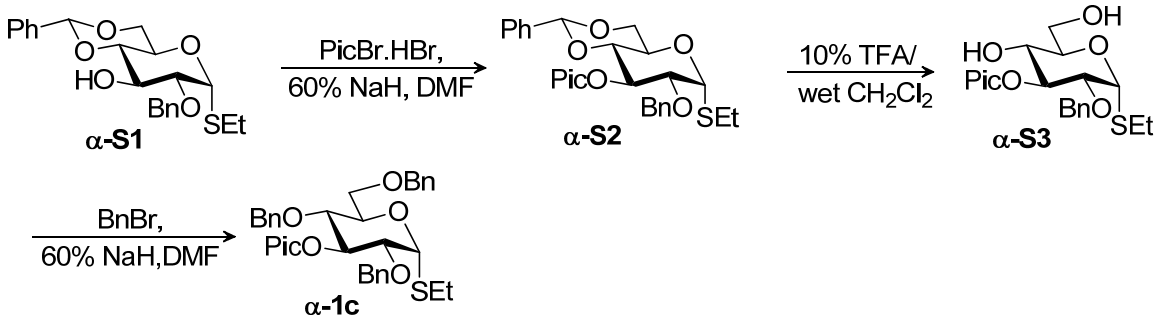
Ethyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-*O*-picolinyl-1-thio-β-D-glucopyranoside (S2). To a solution of ethyl 2-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside[8] (**S1**, 1.0 g, 2.48 mmol) in DMF (10 mL) NaH (60% in mineral oil, 0.2 g, 5.00 mmol) and picolinyl bromide hydrobromide (0.94 g, 3.73 mmol) were added at rt. The reaction mixture was stirred for 1.5 h, quenched with ice-water (~10 mL, 30 min) and then extracted with ethyl acetate /diethyl ether (1/1, v/v, 3 × 50 mL). The combined organic extract (~150 mL) was washed with cold water (3 × 30 mL). The organic phase was separated, dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to give the title compound as a white amorphous solid in 90% yield (1.1g, 2.23 mmol). Analytical data for **S2**: R_f = 0.58 (ethyl acetate/hexane, 1/1, v/v); $[\alpha]_D^{26}$ -50.4 (*c* = 1.0, $CHCl_3$); ^{1}H-NMR: δ, 1.21 (t, 3H, *J* = 7.4 Hz, SCH_2CH_3), 2.65 (m, 2H, SCH_2CH_3), 3.35 (m, 1H, H-5), 3.41 (dd, 1H, $J_{2,3}$ = 8.3 Hz, H-2), 3.59-3.71 (m, 2H, H-4, 6a), 3.73 (dd, 1H, $J_{3,4}$ = 9.2 Hz, H-3), 4.24 (dd, 1H, $J_{5,6b}$ = 5.0 Hz $J_{6a,6b}$ = 10.4 Hz, H-6b), 4.47 (d, 1H, $J_{1,2}$ = 9.8 Hz, H-1), 4.76 (dd, 2H, ^2J = 10.2 Hz, CH_2Ph), 4.92 (dd, 2H, ^2J = 13.4 Hz, CH_2Ph), 5.44 (s, 1H, >C*H*Ph), 6.90-7.50 (m, 13H, aromatic), 8.40 (d, 1H, aromatic) ppm; ^{13}C-NMR: δ, 15.2, 25.3, 68.8, 70.3, 75.6, 76.0, 81.4, 81.5, 83.7, 85.9, 101.3, 121.6, 122.3, 126.1 (×2), 128.0, 128.3 (×2), 128.5 (×4), 129.1, 136.6, 137.2, 137.9, 149.0, 158.8 ppm; HR FAB MS $[M+H]^+$ calcd for $C_{28}H_{32}NO_5S$ 494.2001, found 494.2005.

Ethyl 2-*O*-Benzyl-3-*O*-picolinyl-1-thio-β-D-glucopyranoside (**S3**). To a stirring mixture of **S2** (0.5 g, 1.00 mmol) in CH_2Cl_2 (10 mL), water (150 μL) and trifluoroacetic acid (TFA)/CH_2Cl_2 (1/9, v/v, 1.0 mL) were added at rt. The reaction mixture was stirred for 3 h, then neutralized with Et_3N (3 mL) and then diluted with dichloromethane (200 mL) and washed with cold water (20 mL), sat. aq. $NaHCO_3$ (20 mL), and cold water (20 mL). The organic phase was separated, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (methanol - dichloromethane gradient elution) to afford the title compound as a white amorphous solid in 92% yield (0.38 g, 0.93 mmol). Analytical data for **S3**: R_f = 0.40 (methanol/dichloromethane, 1/9, v/v); $[\alpha]_D^{25}$ -34.6 (*c* = 1.0, $CHCl_3$); ^{1}H-NMR: δ, 1.25 (t, 3H, *J* = 7.4 Hz, SCH_2CH_3), 2.70 (m, 2H, SCH_2CH_3), 3.28-3.42 (m, 3H, H-2, 5, OH), 3.52 (dd, 1H, $J_{3,4}$ = 8.7 Hz, H-3), 3.67 (dd, 1H, $J_{4,5}$ = 9.1 Hz, H-4), 3.78 (dd, 1H, $J_{5,6b}$ = 5.5 Hz, $J_{6a,6b}$ = 11.7 Hz, H-6b), 3.93 (dd, 1H, $J_{5,6a}$ = 3.4 Hz, H-6a), 4.46 (d, 1H, $J_{1,2}$ = 9.7 Hz, H-1), 4.71 (d, 1H, ^2J = 10.6 Hz, ½ CH_2Ph), 4.81-4.98 (m, 3H, 1½ × CH_2Ph), 7.05-7.70 (m, 8H, aromatic), 8.51 (d, 1H, *J*

= 4.9 Hz, aromatic) ppm; ^{13}C NMR: δ, 15.1, 24.9, 62.9, 71.0, 74.0, 75.4, 79.9, 81.4, 85.0, 89.1, 121.6, 122.8, 127.8, 128.1 (×2), 128.3 (×2), 137.3, 138.1, 148.6, 158.0 ppm; HR FAB MS $[M+Na]^+$ calcd for $C_{21}H_{27}NO_5SNa$ 428.1508, found 428.1912.

Ethyl 2,4,6-Tri-*O*-benzyl-3-*O*-picolinyl-1-thio-β-D-glucopyranoside (1c). To a solution of **S3** (0.38 g, 0.93 mmol) in DMF (5.0 mL), NaH (60% in mineral oil, 0.19 g, 4.69 mmol) and benzyl bromide (0.33 mL, 2.79 mmol) were added at rt. The reaction mixture was stirred for 2 h, then quenched with ice water (15 mL, 30 min) and extracted with ethyl acetate/ diethyl ether (1/1, v/v, 3 × 30 mL). The combined organic extract (~90 mL) was washed with cold water (3 × 10 mL). The organic phase was separated, dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to give the title compound as a white amorphous solid in 87% yield (0.48 g, 0.82 mmol). Analytical data for **1c**: R_f = 0.47 (ethyl acetate/hexane, 2/3, v/v); $[\alpha]_D^{25}$ +0.10 (*c* = 1.2, $CHCl_3$); ^{1}H NMR: δ, 1.24 (t, 3H, *J* = 7.4 Hz, SCH_2CH_3), 2.68 (m, 2H, SCH_2CH_3), 3.36-3.47 (m, 2H, H-2, 4), 3.52-3.74 (m, 4H, H-3, 5, 6a, 6b), 4.39 (d, 1H, $J_{1,2}$ = 9.7 Hz, H-1), 4.49 (dd, 2H, ^2J = 12.2 Hz, CH_2Ph), 4.59 (dd, 2H, ^2J = 10.7 Hz, CH_2Ph), 4.73 (dd, 2H, ^2J = 10.1 Hz, CH_2Ph), 4.95 (dd, 2H, ^2J = 12.8 Hz, CH_2Ph), 7.05-7.70 (m, 18H, aromatic), 8.48 (d, 1H, *J* = 4.8 Hz, aromatic) ppm; ^{13}C NMR: δ, 15.3, 25.2, 69.2, 73.6, 75.2, 75.6, 76.3, 78.0, 79.2, 81.7, 85.2, 87.1, 121.5, 122.4, 127.8, 127.9 (×2), 128.0, 128.3 (×2), 128.5 (×7), 128.6 (×2), 136.7, 138.0, 138.1, 138.3, 149.3, 158.7 ppm; HR FAB MS $[M+H]^+$ calcd for $C_{35}H_{40}NO_5S$ 586.2627, found 586.2612.

Ethyl 2,4,6-Tri-*O*-benzyl-3-*O*-picolinyl-1-thio-α-D-glucopyranoside (α-1c).



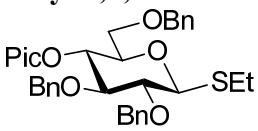
Ethyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-*O*-picolinyl-1-thio-α-D-glucopyranoside (α-S2). To a solution of ethyl 2-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-glucopyranoside[8] (α-**S1**, 1.0 g, 2.48 mmol) in DMF (10 mL), NaH (60% in mineral oil, 0.2 g, 5.00 mmol) and picolinyl bromide hydrobromide (0.94 g, 3.73 mmol) were added at rt. The reaction mixture was stirred for 1 h, then quenched with ice water (20 mL, 30 min) and extracted with ethyl acetate/ diethyl ether (1/1, v/v, 3 × 50 mL). The combined organic extract (~ 150 mL) was washed with cold water (3 × 30 mL). The organic phase was separated, dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/ hexane gradient elution) to give the title compound as a white amorphous solid in 91% yield (1.1g, 2.26 mmol). Analytical data for α-**S2**: R_f = 0.53 (ethyl acetate/hexane, 1/1, v/v); $[\alpha]_D^{25}$ +175.7 (*c* = 1.0, $CHCl_3$); ^{1}H NMR: δ, 1.27 (t, 3H, *J* = 7.4 Hz, SCH_2CH_3), 2.54 (m,

SC*H*$_2$CH$_3$), 3.64 (dd, 1H, $J_{4,5}$ = 9.2 Hz, H-4), 3.74 (m, 1H, H-6b), 3.83-3.40 (m, 2H, H-2, 3), 4.18-4.36 (m, 2H, H-5, 6a), 4.71 (dd, 2H, ^2J = 11.8 Hz, C*H*$_2$Ph), 4.99 (dd, 2H, ^2J = 14.0 Hz, C*H*$_2$Ph), 5.40 (d, 1H, $J_{1,2}$ = 5.4 Hz, H-1), 5.54 (s, 1H, >C*H*Ph), 7.00-7.65 (m, 13H, aromatic), 8.47 (d, 1H, aromatic) ppm; ^{13}C NMR: δ, 15.0, 23.9, 62.9, 69.0, 72.7, 75.8, 79.0, 81.9, 84.1, 101.6, 121.6, 122.2, 126.3 (×2), 128.0, 128.2 (×2), 128.4 (×2), 128.5 (×2), 129.1, 136.5, 137.4, 137.8, 148.9, 159.3 ppm; HR FAB MS [M+H]$^+$ calcd for $C_{28}H_{32}NO_5S$ 494.2001, found 494.1963.

Ethyl 2-*O*-Benzyl-3-*O*-picolinyl-1-thio-α-D-glucopyranoside (α-S3). To a stirred solution of α-**S2** (0.5 g, 1.00 mmol) in CH_2Cl_2 (10 mL), water (150 μL) and 10% TFA/CH_2Cl_2 (1/9, v/v, 1.0 mL) were added at rt. The reaction mixture was stirred for 3 h, neutralized with Et_3N (~3 mL) and then diluted with CH_2Cl_2 (200 mL) and washed with cold water (20 mL), sat. aq. $NaHCO_3$ (20 mL), and water (20 mL). The organic phase was separated, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (methanol - dichloromethane gradient elution) to afford the title compound as a white amorphous solid in 91% yield (0.37 g, 0.91 mmol). Analytical data for: R_f = 0.44 (methanol/ dichloromethane, 1/9, v/v); $[\alpha]_D^{22}$ +99.2 (*c* = 1.0, $CHCl_3$); ^{1}H NMR: δ, 1.23 (t, 3H, *J* = 7.4 Hz, SCH$_2$C*H*$_3$), 2.51 (m, 2H, SC*H*$_2$CH$_3$), 2.90 (br. s, 1H, OH), 3.61-3.94 (m, 5H, H-2, 3, 4, 6a, 6b), 4.02(m, 1H, H-5), 4.67 (dd, 1H, ^2J= 11.8 Hz, C*H*$_2$Ph), 4.94 (dd, 2H, ^2J= 15.2 Hz, C*H*$_2$Ph), 5.38 (d, 1H, $J_{1,2}$ = 5.2 Hz, H-1), 7.05-7.80 (m, 8H, aromatic), 8.48 (d, 1H, *J* = 4.6 Hz, aromatic) ppm; ^{13}C NMR: δ, 14.8, 23.6, 62.9, 70.9, 72.0, 72.2, 73.6, 79.3, 82.9, 84.6, 121.6, 122.8, 128.0, 128.1 (×2), 128.5 (×2), 137.3, 138.0, 148.6, 158.5 ppm; HR FAB MS [M+H]$^+$ calcd for $C_{21}H_{28}NO_5S$ 406.1688, found 406.1697.

Ethyl 2,4,6-Tri-*O*-benzyl-3-*O*-picolinyl-1-thio-α-D-glucopyranoside (α-1c). To a solution of α-**S3** (0.37 g, 0.91 mmol) in DMF (5 mL), NaH (60% in mineral oil, 0.18 g, 4.56 mmol) and benzyl bromide (0.33 mL, 2.73 mmol) were added at rt. The reaction mixture was stirred for 2 h, then quenched with ice water (15 mL, 30 min) and extracted with ethyl acetate/ diethyl ether (1/1, v/v, 3 × 30 mL). The combined organic extract (~90 mL) was washed with cold water (3 × 10 mL). The organic phase was separated, dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to give the title compound as a white amorphous solid in 85% yield (0.45 g, 0.77 mmol). Analytical data for α-**1c**: R_f = 0.49 (ethyl acetate/hexane, 2/3, v/v); $[\alpha]_D^{25}$ +128.9 (*c* = 1.0, $CHCl_3$); NMR: δ, 1.23 (t, 3H, *J* = 7.4 Hz, SCH$_2$C*H*$_3$), 2.47 (m, 2H, SC*H*$_2$CH$_3$), 3.30-3.94 (m, 5H, H-2, 3, 4, 6a, 6b), 4.15 (m, 1H, H-5), 4.53 (dd, 2H, ^2J= 11.9 Hz, C*H*$_2$Ph), 4.56 (dd, 2H, ^2J= 10.2 Hz, C*H*$_2$Ph), 4.59 (dd, 2H, ^2J= 10.7 Hz, C*H*$_2$Ph), 4.96 (dd, 2H, ^2J= 12.9 Hz, C*H*$_2$Ph), 5.37 (d, 1H, $J_{1,2}$ = 4.7 Hz, H-1), 6.92-7.63 (m, 18H, aromatic), 8.47 (d, 1H, *J* = 4.8 Hz, aromatic) ppm; ^{13}C NMR: δ, 14.8, 23.7, 68.5, 70.4, 72.2, 73.5, 75.0, 76.2, 77.5, 79.2, 83.0, 83.1, 121.6, 122.2, 127.7, 127.8, 127.9, 128.0 (×4), 128.1 (×2), 128.3 (×2), 128.4 (×4), 136.4, 137.8, 137.9, 138.2, 149.1, 158.9 ppm; HR FAB MS [M+H]$^+$ calcd for $C_{35}H_{40}NO_5S$ 586.2627, found 586.2735.

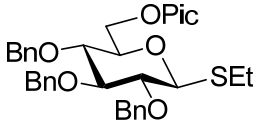
Ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-picolinyl-1-thio-β-D-glucopyranoside (1d).



1d

To a solution of ethyl 2,3,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside[9] (**S4**, 0.5 g, 1.01 mmol) in DMF (5 mL), NaH (60% in mineral oil, 0.12 g, 3.03 mmol) and picolinyl bromide hydrobromide (0.51 g, 2.02 mmol) were added at rt. The reaction mixture was stirred for 2.5 h, then quenched with ice water (15 mL, 30 min) and extracted with ethyl acetate/ diethyl ether (1/1, v/v, 3 × 50 mL). The combined organic extract (~150 mL) was washed with cold water (3 × 15 mL). The organic phase was separated, dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to give the title compound as a white amorphous solid in 88% yield (0.51 g, 0.87 mmol). Analytical data for **1d**: R_f = 0.48 (ethyl acetate/hexane, 1/1, v/v); $[\alpha]_D^{25}$ +1.5 (*c* = 1.0, $CHCl_3$); ^{1}H NMR: δ, 1.31 (t, 3H, *J* = 7.4 Hz, SCH_2CH_3), 2.75 (m, 2H, SCH_2CH_3), 3.44 (dd, 1H, $J_{2,3}$ = 8.9 Hz, H-2), 3.50 (m, 1H, H-5), 3.60-3.79 (m, 4H, H-3, 4, 6a, 6b), 4.46 (d, 1H, $J_{1,2}$ = 9.8 Hz, H-1), 4.54 (dd, 2H, ^2J = 12.1 Hz, CH_2Ph), 4.72 (dd, 2H, ^2J = 11.4 Hz, CH_2Ph), 4.84 (dd, 2H, ^2J = 10.9 Hz, CH_2Ph), 4.90 (dd, 2H, ^2J = 12.6 Hz, CH_2Ph), 7.05-7.65 (m, 18H, aromatic), 8.51 (d, 1H, *J* = 4.8 Hz, aromatic) ppm; ^{13}C NMR: δ, 15.3, 25.1, 69.3, 73.5, 75.6, 75.8, 75.9, 78.7, 79.2, 81.8, 85.1, 121.5, 122.5, 127.6, 127.8 (×3), 128.0 (×2), 128.4 (×4), 128.5 (×3), 128.5 (×2), 136.6, 138.1, 138.3, 138.5, 149.2, 158.3 ppm; HR FAB MS $[M+H]^+$ calcd for $C_{35}H_{40}NO_5S$ 586.2627, found 586.2619.

Ethyl 2,3,4-Tri-*O*-benzyl-6-*O*-picolinyl-1-thio-β-D-glucopyranoside (1e).

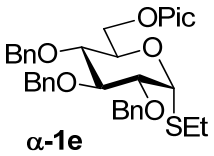


1e

To a solution of ethyl 2,3,4-tri-*O*-benzyl-1-thio-β-D-glucopyranoside[10] (**S5**, 0.5 g, 1.01 mmol) in DMF (5 mL), NaH (60% in mineral oil, 0.12 g, 3.03 mmol) and picolinyl bromide hydrobromide (0.51 g, 2.02 mmol) were added at rt. The reaction mixture was stirred for 2.5 h, then quenched with ice water (15 mL, 30 min) and extracted with ethyl acetate/ diethyl ether (1/1, v/v, 3 × 50 mL). The combined organic extract (~150 mL) was washed with cold water (3 × 15 mL). The organic phase was separated, dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to give the title compound as a white amorphous solid in 87% yield (0.52 g, 0.89 mmol). Analytical data for **1e**: R_f = 0.42 (ethyl acetate/hexane, 1/1, v/v); $[\alpha]_D^{24}$ +4.3 (*c* = 1.0, $CHCl_3$); ^{1}H NMR: δ, 1.33 (t, 3H, *J* = 7.4 Hz, SCH_2CH_3), 2.78 (m, 2H, SCH_2CH_3), 3.47 (dd, 1H, $J_{2,3}$ = 8.7 Hz, H-2), 3.53 (m, 1H, H- 5), 3.66 (dd, 1H, $J_{4,5}$ = 8.9 Hz, H-4), 3.72 (dd, 1H, $J_{3,4}$ = 8.6 Hz, H-3), 3.78 (dd, 1H, $J_{6a,6b}$ = 10.9 Hz, H-6a), 3.84 (dd, 1H, $J_{5,6b}$ = 1.9 Hz, H-6b), 4.50 (d, 1H, $J_{1,2}$ = 9.7 Hz, H-1), 4.70 (d, 2H, ^2J = 4.4 Hz, CH_2Ph), 4.74 (dd, 2H, ^2J = 9.7 Hz, CH_2Ph), 4.83 (dd, 2H, ^2J = 10.2 Hz, CH_2Ph), 4.91 (dd, 2H, ^2J = 13.2 Hz, CH_2Ph), 7.05-7.50 (m, 17H, aromatic), 7.66 (dd, 1H, *J* = 7.7 Hz, aromatic), 8.53 (d, 1H, *J* = 4.8 Hz, aromatic) ppm; ^{13}C NMR: δ, 15.3, 25.1, 70.0, 74.3, 75.2, 75.7, 75.9, 78.0, 79.1, 81.9, 85.2, 86.8, 121.4, 122.4, 127.8,

127.9 (×2), 128.0 (×2), 128.1 (×2), 128.5 (×4), 128.6 (×4), 136.7, 138.1 (×2), 138.6, 149.1, 158.7 ppm; HR FAB MS $[M+H]^+$ calcd for $C_{35}H_{40}NO_5S$ 586.2627, found 586.2695.

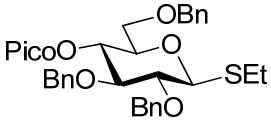
Ethyl 2,3,4-Tri-*O*-benzyl-6-*O*-picolinyl-1-thio-α-D-glucopyranoside (α-1e).



α-1e

To a solution of ethyl 2,3,4-tri-*O*-benzyl-1-thio-α-D-glucopyranoside[11] (α-**S5**, 0.5 g, 1.01 mmol) in DMF (5 mL), NaH (60% in mineral oil, 0.12 g, 3.03 mmol) and picolinyl bromide hydrobromide (0.51 g, 2.02 mmol) were added at rt. The reaction mixture was stirred for 2 h, then quenched with ice water (15 mL) and extracted with ethyl acetate/ diethyl ether (1/1, v/v, 3 × 50 mL). The combined organic extract (~150 mL) was washed with cold water (3 × 15 mL). The organic phase was separated, dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to give the title compound as a white amorphous solid in 94% yield (0.56 g, 0.95 mmol). Analytical data for α–**1e**: R_f = 0.38 (ethyl acetate/hexane, 1/1, v/v); $[\alpha]_D^{24}$ +146.9 (*c* = 1.0, $CHCl_3$); ^{1}H NMR: δ, 1.32 (t, 3H, *J* = 7.4 Hz, SCH_2CH_3), 2.59 (m, 2H, SCH_2CH_3), 3.72 (dd, 1H, $J_{4,5}$ = 8.5 Hz, H-4), 3.78 (dd, 1H, $J_{5,6a}$ = 1.8 Hz, $J_{6a,6b}$ = 10.8 Hz, H- 6a), 3.85-3.93 (m, 2H, H-2, 6b), 3.94 (dd, 1H, $J_{3,4}$ = 9.5 Hz, H-3), 4.29 (m, 1H, H-5), 4.69 (dd, 2H, ^2J = 13.6 Hz, CH_2Ph), 4.75 (dd, 2H, ^2J = 11.5 Hz, CH_2Ph), 4.77 (dd, 2H, ^2J = 11.0 Hz, CH_2Ph), 4.92 (dd, 2H, ^2J = 10.8 Hz, CH_2Ph), 5.47 (d, 1H, $J_{1,2}$ = 4.8 Hz, H-1), 7.10-7.50 (m, 17H, aromatic), 7.65 (dd, 1H, *J* = 7.7 Hz, aromatic), 8.54 (d, 1H, *J* = 4.2 Hz, aromatic) ppm; ^{13}C NMR: δ, 14.9, 23.8, 69.5, 70.5, 72.4, 74.3, 75.1, 75.8, 77.6, 79.6, 82.7, 83.2, 121.3, 122.4, 127.7, 127.8, 127.9 (×2), 128.0, 128.2 (×4), 128.5 (×6), 136.6, 137.9, 138.4, 138.8, 149.0, 158.4 ppm; HR FAB MS $[M+H]^+$ calcd for $C_{35}H_{40}NO_5S$ 586.2627, found 586.2702.

Ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-picoloyl-1-thio-β-D-glucopyranoside (1f).

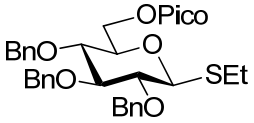


1f

To a solution of ethyl 2,3,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside[11] (**S4**, 0.5 g, 1.01 mmol) in CH_2Cl_2 (10 mL), picolinic acid (0.19 g, 1.52 mmol), *N*,*N*′-dicyclohexylcarbodiimide (0.31 g, 1.52 mmol), and 4-dimethylaminopyridine (25 mg, 0.20 mmol) were added at rt. The reaction mixture was stirred for 15 min under argon, the solid was filtered off and rinsed successively with CH_2Cl_2. The combined filtrate (~100 mL) was washed with brine (2 x 10 mL). The organic phase was separated, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to give the title compound as a white amorphous solid in 89% yield (0.54 g, 0.90 mmol). Analytical data for **1f**: R_f = 0.44 (ethyl acetate/hexane, 1/1, v/v); $[\alpha]_D^{25}$ -38.7 (*c* = 1.0, $CHCl_3$); ^{1}H NMR: δ, 1.50 (t, 3H, *J* = 7.4 Hz, SCH_2CH_3), 2.95 (m, 2H, SCH_2CH_3), 3.74 (dd, 1H, $J_{2,3}$ = 9.3 Hz, H-2), 3.80-3.85 (m, 2H, H- 6a, 6b), 4.02 (m, 1H, H-5), 4.10 (dd, 1H, $J_{3,4}$ = 9.1 Hz, H-3), 4.63 (s, 2H, CH_2Ph), 4.74 (d, 1H, $J_{1,2}$ =9.8 Hz, H-1), 4.92 (dd, 2H, ^2J = 11.3 Hz, CH_2Ph), 5.01 (dd, 2H, ^2J =10.3 Hz, CH_2Ph), 5.58 (dd, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 7.15-7.65 (m, 16H, aromatic), 7.89 (dd, 1H,

J = 7.7 Hz, aromatic), 8.14 (d, 1H, J = 7.7 Hz, aromatic), 8.87 (d, 1H, J = 3.9 Hz, aromatic) ppm; ^{13}C NMR: δ, 15.1, 24.9, 69.6, 72.3, 73.4, 75.4, 77.2, 81.5, 83.6, 85.1, 125.5, 126.9, 127.3, 127.4, 127.5 (×2), 127.8 (×2), 127.9, 128.1 (×5), 128.3 (×3), 136.9, 137.7, 137.8, 137.9, 147.4, 149.7, 164.1 ppm; HR FAB MS $[M+H]^+$ calcd for $C_{35}H_{38}NO_6S$ 600.2420, found 600.2427.

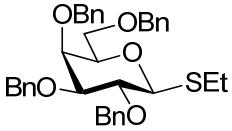
Ethyl 2,3,4-Tri-*O*-benzyl-6-*O*-picoloyl-1-thio-β-D-glucopyranoside (1g).



1g

To a solution of ethyl 2,3,4-tri-*O*-benzyl-1-thio-β-D-glucopyranoside[10] (**S5**, 0.5 g, 1.01 mmol) in CH_2Cl_2 (10 mL), picolinic acid (0.19 g, 1.52 mmol), *N*,*N*′-dicyclohexylcarbodiimide (0.31 g, 1.52 mmol), and 4-dimethylaminopyridine (25 mg, 0.20 mmol) were added at rt. The reaction mixture was stirred 10 min under argon, the solid was filtered off and rinsed successively with CH_2Cl_2. The combined filtrate (~100 mL) was washed with brine (2 x 10 mL). The organic phase was separated, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to give the title compound as a white amorphous solid in 87% yield (0.53 g, 0.88 mmol). Analytical data for **1g**: R_f = 0.47 (ethyl acetate/hexane, 1/1, v/v); $[\alpha]_D^{24}$ +18.7 (c = 1.2, $CHCl_3$); ^{1}H NMR: δ, 1.23 (t, 3H, J = 7.4 Hz, SCH_2CH_3), 2.69 (m, 2H, SCH_2CH_3), 3.46 (dd, 1H, $J_{2,3}$ = 9.4 Hz, H-2), 3.63 (dd, 1H, $J_{4,5}$ = 9.4 Hz, H-4), 3.70 (m, 1H, H-5), 3.72 (dd, 1H, $J_{3,4}$ = 8.6 Hz, H-3), 4.51 (d, 1H, $J_{1,2}$ = 9.7 Hz, H-1), 4.53-4.68 (m, 3H, H-6a, 6b, ½ CH_2Ph), 4.73 (d, 1H, ^2J = 10.2 Hz, ½ CH_2Ph), 4.80-5.00 (m, 4H, 2 × CH_2Ph), 7.10-7.50 (m, 16H, aromatic), 7.78 (dd, 1H, J = 7.7 Hz, aromatic), 8.02 (d, 1H, J = 7.8 Hz, aromatic), 8.81 (dd, 1H, J = 4.7 Hz, aromatic) ppm; ^{13}C NMR: δ, 15.3, 25.2, 64.6, 75.2, 75.7, 76.0, 77.0, 78.0, 81.9, 85.2, 86.7, 125.2, 127.0, 127.9 (×2), 128.0, 128.1, 128.2 (×2), 128.4 (×2), 128.5 (×2), 128.6 (×4), 137.0, 137.7, 137.9, 138.3, 147.9, 150.1, 164.7 ppm; HR FAB MS $[M+H]^+$ calcd for $C_{35}H_{38}NO_6S$ 600.2420, found 600.2430.

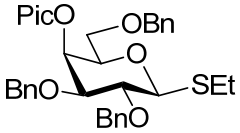
Ethyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-β-D-galactopyranoside (1h).



1h

The title compound was synthesized according to the standard procedure and the analytical data for **1h** was essentially the same as reported previously.[12]

Ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-picolinyl-1-thio-β-D-galactopyranoside (1i).

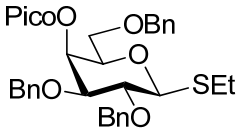


1i

To a solution of ethyl 2,3,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside[13] (**S6**, 0.5 g, 1.01 mmol) in DMF (5 mL), NaH (60% in mineral oil, 0.12 g, 3.03 mmol) and picolinyl bromide hydrobromide (0.51 g, 2.02 mmol) were added at rt. The reaction mixture was stirred for 1.5 h,

then quenched with ice water (15 mL, 30 min) and extracted with ethyl acetate/ diethyl ether (1/1, v/v, 3 × 50 mL). The combined organic extract (~150 mL) was washed with cold water (3 × 15 mL). The organic phase was separated, dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to give the title compound as a white amorphous solid in 90% yield (0.53 g, 0.90 mmol). Analytical data for **1i**: R_f = 0.46 (ethyl acetate/hexane, 1/1, v/v); $[\alpha]_D^{25}$ -5.9 (*c* = 1.0, $CHCl_3$); ^{1}H NMR: δ, 1.31 (t, 3H, *J* = 7.4 Hz, SCH_2CH_3), 2.75 (m, 2H, SCH_2CH_3), 3.54-3.75 (m, 4H, H-3, 5, 6a, 6b), 3.82 (dd, 1H, $J_{2,3}$ = 9.4 Hz, H-2), 4.06 (d, 1H, $J_{4,5}$ = 2.8 Hz, H-4), 4.39-4.53 (m, 3H, H-1, CH_2Ph), 4.67-4.53 (m, 4H, 2 × CH_2Ph), 4.88 (d, 1H, ^2J = 10.2 Hz, ½ CH_2Ph), 5.12 (d, 1H, ^2J = 13.4 Hz, ½ CH_2Ph), 7.05-7.80 (m, 18H, aromatic), 8.51 (d, 1H, *J* = 4.8 Hz, aromatic) ppm; ^{13}C NMR: δ, 15.2, 25.0, 68.6, 72.8, 73.7, 75.2, 75.8, 75.9, 77.1, 78.5, 83.7, 85.5, 121.7, 122.3, 127.8, 127.9 (×4), 128.1 (×2), 128.5 (×6), 128.6 (×2), 136.7, 137.8, 138.3, 138.4, 148.6, 159.2 ppm; HR FAB MS $[M+H]^+$ calcd for $C_{35}H_{40}NO_5S$ 586.2627, found 586.2612.

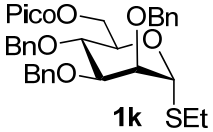
Ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-picoloyl-1-thio-β-D-galactopyranoside (1j).



1j

To a solution of ethyl 2,3,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside[13] (**S6**, 0.5 g, 1.01 mmol) in CH_2Cl_2 (10 mL), picolinic acid (0.19 g, 1.52 mmol), *N*,*N*′-dicyclohexylcarbodiimide (0.31 g, 1.52 mmol), and 4-dimethylaminopyridine (25 mg, 0.20 mmol) were added at rt. The reaction mixture was stirred 10 min under argon, the solid was filtered off and rinsed successively with CH_2Cl_2. The combined filtrate (~100 mL) was washed with brine (2 x 10 mL). The organic phase was separated, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to give the title compound as a colorless syrup in 91% yield (0.55 g, 0.90 mmol). Analytical data for **1j**: R_f = 0.56 (ethyl acetate/ hexane, 1/1, v/v); $[\alpha]_D^{25}$ +23.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR: δ, 1.35 (t, 3H, *J* = 7.5 Hz, SCH_2CH_3), 2.80 (m, 2H, SCH_2CH_3), 3.53-3.69 (m, 2H, H-6a, 6b), 3.69 (dd, 1H, $J_{2,3}$ = 9.2 Hz, H-2), 3.76 (dd, 1H, $J_{3,4}$ = 3.1 Hz, H-3), 3.87 (dd, 1H, H-5), 4.47 (dd, 2H, ^2J = 11.7 Hz, CH_2Ph), 4.57 (d, 1H, $J_{1,2}$ = 9.3 Hz, H-1), 4.58 (d, 1H, ^2J = 11.3 Hz, ½ CH_2Ph), 4.80 (dd, 1H, ^2J = 10.2 Hz, CH_2Ph), 4.89 (d, 1H, ^2J = 11.3 Hz, ½ CH_2Ph), 5.97 (dd, 1H, $J_{4,5}$ = 2.8 Hz, H-4), 7.10-7.50 (m, 16H, aromatic), 7.79 (dd, 1H, aromatic), 8.07 (d, 1H, *J* = 7.8 Hz, aromatic), 8.81 (dd, 1H, *J* = 4.8 Hz, aromatic) ppm; ^{13}C NMR: δ, 15.2, 25.1, 68.2, 68.5, 72.1, 73.8, 75.9, 76.0, 77.9, 81.1, 85.6, 125.5, 127.8 (×2), 127.9, 128.1 (×2), 128.4 (×11), 137.0, 137.5, 137.6, 138.1, 147.6, 150.3, 163.9 ppm; HR FAB MS $[M+H]^+$ calcd for $C_{35}H_{38}NO_6S$ 600.2420, found 600.2431.

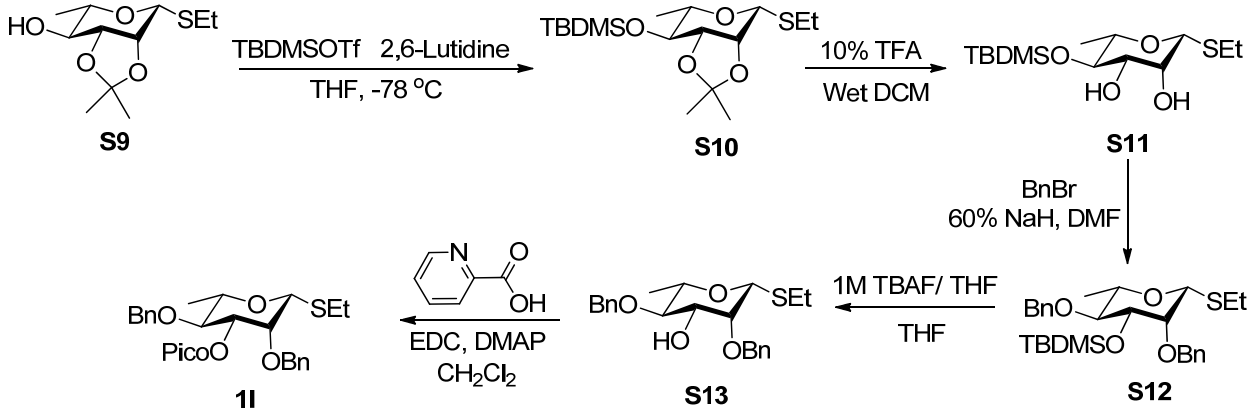
Ethyl 2,3,4-Tri-*O*-benzyl-6-*O*-picoloyl-1-thio-α-D-mannopyranoside (1k).



To a solution of ethyl 2,3,4-tri-*O*-benzyl-1-thio-α-D-mannopyranoside[14] (**S7**, 0.5 g, 1.01 mmol) in CH_2Cl_2 (10 mL), picolinic acid (0.19 g, 1.52 mmol), *N*,*N*′-dicyclohexylcarbodiimide (0.31 g,

1.52 mmol), and 4-dimethylaminopyridine (25 mg, 0.20 mmol) were added at rt. The reaction mixture was stirred 10 min under argon, the solid was filtered off and rinsed successively with CH_2Cl_2. The combined filtrate (~100 mL) was washed with brine (2 x 10 mL). The organic phase was separated, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to give the title compound as colorless syrup in 91% yield (0.55 g, 0.92 mmol). Analytical data for **1k**: R_f = 0.39 (ethyl acetate/hexane, 1/1, v/v); $[\alpha]_D^{24}$ +93.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR: δ, 1.18 (t, 3H, *J* = 7.4 Hz, SCH_2CH_3), 2.52 (m, 2H, SCH_2CH_3), 3.82-3.93 (m, 2H, H-2, 3), 4.03 (dd, 1H, $J_{3,4}$ = 9.3 Hz, $J_{4,5}$ = 9.2 Hz, H-4), 4.28 (m, 1H, H-5), 4.50-4.70 (m, 7H, H-6a, 6b, 2 ½ × CH_2Ph), 4.90 (d, 1H, ^2J = 10.9 Hz, ½ CH_2Ph), 5.34 (s, 1H, H-1), 7.05-7.60 (m, 17H, aromatic), 7.92 (d, 1H, *J* = 7.8 Hz, aromatic), 8.64 (d, 1H, *J* = 1.7 Hz, aromatic) ppm; ^{13}C NMR: δ, 14.8, 25.2, 64.1, 70.1, 71.7, 71.8, 74.1, 74.8, 76.2, 80.1, 81.6, 124.9, 126.5, 127.4 (×2), 127.5 (×3), 127.6 (×2), 127.8 (×2), 128.1 (×5), 128.2 (×2), 136.5, 137.8 (×2), 147.5, 149.7, 164.2 ppm; HR FAB MS $[M+H]^+$ calcd for $C_{35}H_{38}NO_6S$ 600.2420, found 600.2426.

Ethyl 2,4-Di-*O*-benzyl-3-*O*-picoloyl-1-thio-β-L-rhamnopyranoside (1l).



Ethyl 4-*O*-*tert*-butyldimethylsilyl-2,3-*O*-isopropylidene-1-thio-β-L-rhamnopyranoside (S10). 2,6-Lutidine (0.79 mL, 7.2 mmol) was added to a soln. of ethyl 2,3-*O*-isopropylidene-1-thio-β-L-rhamnopyranoside[15] (**S9**, 0.9 g, 3.6 mmol) in anhydrous THF (10 mL) and the resulting mixture was stirred under argon for 10 min at rt. After that, the mixture was cooled to -78 °C, TBDMSOTf (5.5 mmol, 1.2 mL) was added. The resulting reaction mixture was stirred for 15 min at -78 °C and the volatiles were evaporated *in vacuo*. The residue was diluted with CH_2Cl_2 (~200 mL) and washed with 20% aq. $NaHCO_3$ (40 mL) and water (3 x 40 mL). The organic phase was separated, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to afford the title compound in 89% yield (1.2 g, 2.7 mmol) as a white amorphous solid. Analytical data for **S10**: R_f = 0.69 (ethyl acetate/hexane, 1/4, v/v); $[\alpha]_D^{22}$ +62.3 (c = 1.0, $CHCl_3$); ^{1}H NMR: δ, 0.03, 0.09 (2s, 6H, 2 × $Si(CH_3)_3$), 0.84 (s, 9H, 3 × $C(CH_3)_3$), 1.18-1.35 (m, 6H, C-6, SCH_2CH_3), 1.31, 1.50 (2s, 6H, 2 × $C(CH_3)_2$), 2.71 (q, 2H, *J* = 7.5 Hz, SCH_2CH_3), 3.10-3.25 (m, 1H, H-5), 3.38 (dd, 1H, $J_{4,5}$ = 9.1 Hz, H-4), 3.89 (dd, 1H, $J_{3,4}$ = 6.6 Hz, H-3), 4.20 (dd, 1H, $J_{2,3}$ = 5.6 Hz, H-2), 4.77 (d, 1H, $J_{1,2}$ = 2.1 Hz, H-1) ppm; ^{13}C NMR: δ -4.9, -3.9, 14.9, 18.2, 18.4, 25.9, 26.0 (× 3), 26.6, 28.2, 75.8, 76.0, 76.6, 80.7, 80.9, 110.1 ppm; HR-FAB MS $[M+H]^+$ calcd for $C_{17}H_{35}O_4SSiNa$ 363.2025, found 363.2113.

Ethyl 4-O-*tert*-butyldimethylsilyl-1-thio-β-L-rhamnopyranoside (S11). To a stirring mixture of ethyl 2,3-*O*-isopropylidene-4-*O*-*tert*-butyldimethylsilyl-1-thio-β-L-rhamnopyranoside (**S10**, 0.42 g, 1.2 mmol) in CH_2Cl_2 (10 mL), water (150 μL) and a soln. of TFA in CH_2Cl_2 (1/9, v/v, 1.2 mL) were added at rt. The reaction mixture was stirred for 30 min, then neutralized with Et_3N (~3.0 mL), diluted with CH_2Cl_2 (~200 mL) and washed with water (20 mL), sat. aq. $NaHCO_3$ (20 mL), and water (3 x 20 mL). The organic phase was separated, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (methanol - dichloromethane gradient elution) to afford the title compound in 83% yield (0.31 g, 0.9 mmol) as a white amorphous solid. Analytical data for **S11**: R_f = 0.36 (ethyl acetate/hexane, 3/7, v/v); $[\alpha]_D^{22}$ +63.0 (c = 1.0, $CHCl_3$); ^{1}H NMR: δ, 0.05, 0.10 (2s, 6H, 2 × $Si(CH_3)_3$), 0.85 (s, 9H, 3 × $C(CH_3)_3$), 1.20-1.35 (m, 6H, C-6, SCH_2CH_3), 2.51 (br. s, 1H, OH), 2.67 (m, 2H, SCH_2CH_3), 3. 22 (m, 1H, H-5), 3.32-3.45 (m, 2H, H-3, 4), 3.96 (s, 1H, H-2), 4.59 (d, 1H, $J_{1,2}$ = 0.9 Hz, H-1) ppm; ^{13}C NMR: δ, -4.4, -3.6, 15.2, 18.4, 18.5, 25.4, 26.1 (× 3), 72.7, 75.0, 75.5, 77.4, 83.8 ppm; $^1J_{C1,H1}$ = 151.7 Hz; HR-FAB MS $[M+Na]^+$ calcd for $C_{14}H_{30}O_4SSiNa$ 345.1532, found 345.1687.

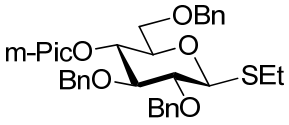
Ethyl 2,4-di-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-1-thio-β-L-rhamnopyranoside (S12). NaH (60% in mineral oil, 0.23 g, 5.8 mmol) and benzyl bromide (0.46 mL, 3.9 mmol) were added to a solution of ethyl 4-*O*-*tert*-butyldimethylsilyl-1-thio-β-L-rhamnopyranoside (**S11**, 0.31 g, 0.96 mmol) in DMF (5.0 mL) and the resulting mixture was stirred for 1.5 h at rt. After that, the reaction mixture was poured into ice-water (~20 mL), stirred for 30 min, and extracted with ethyl acetate/ diethyl ether (1/1, v/v, 3 × 50 mL). The combined organic extract (~150 mL) was washed with cold water (3 × 15 mL). The organic phase was separated, dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to give the title compound in 81% yield (0.39 g, 0.78 mmol) as a white amorphous solid. Analytical data for **S12**: R_f = 0.66 (ethyl acetate/hexane, 1/4, v/v); $[\alpha]_D^{21}$ +47.8 (c = 1.0, $CHCl_3$); ^{1}H NMR: δ, 0.00, 0.05 (2s, 6H, $Si(CH_3)_3$), 0.85 (s, 9H, $C(CH_3)_3$), 1.10-1.25 (m, 6H, C-6, SCH_2CH_3), 2.60 (q, 2H, J = 7.4 Hz, SCH_2CH_3), 3. 22 (m, 1H, H-5), 3.44 (dd, 1H, $J_{4,5}$ = 8.9 Hz, H-4), 3.63-3.72 (m, 2H, H-2, 3), 4.42-4.56 (m, 2H, H-1, ½ CH_2Ph), 4.78 (d, 1H, ^2J = 11.3 Hz, ½ CH_2Ph), 4.79 (dd, 2H, ^2J = 11.2 Hz, CH_2Ph), 7.15-7.45 (m, 10H, aromatic) ppm; ^{13}C NMR: δ, -4.7, -4.0, 15.2, 18.1, 18.2, 25.8, 26.1 (× 3), 75.4, 75.8, 76.4, 77.7, 80.7, 82.0, 84.4, 127.4, 127.6, 127.8 (× 4), 128.1 (× 2), 128.2 (× 2), 138.4, 138.8 ppm; HR-FAB MS $[M+H]^+$ calcd for $C_{28}H_{42}O_4SSiNa$ 525.2573, found 525.2463.

Ethyl 2,4-di-*O*-benzyl-1-thio-β-L-rhamnopyranoside (S13). 1M soln. of *tert*-butylammonium fluoride in THF (0.5 mL, 0.5 mmol) was added to a solution of ethyl 2,4-di-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-1-thio-β-L-rhamnopyranoside (**S12**, 0.25 g, 0.50 mmol) in THF (3.0 mL) and the resulting mixture was stirred for 30 min at rt. After that, the reaction mixture was neutralized with Et_3N (~0.5 mL), diluted with CH_2Cl_2 (~150 mL) and washed with cold water (15 mL), sat. aq. $NaHCO_3$ (15 mL), and water (3 x 15 mL). The organic phase was separated, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to afford the title compound in 93% yield (0.18 g, 0.46 mmol) as a white amorphous solid. Analytical data for **S13**: R_f = 0.43 (ethyl acetate/hexane, 3/7, v/v); $[\alpha]_D^{21}$ +132.3 (c = 1.0, $CHCl_3$); ^{1}H NMR: δ, 1.30 (t, 3H, J = 7.5 Hz, SCH_2CH_3), 1.37 (d, 3H, $J_{5,6}$= 5.7 Hz, C-6), 2.17 (d, 1H, J = 8.7 Hz, OH), 2.74

(q, 2H, J = 7.4 Hz, SCH_2CH$_3$), 3.25-3.37 (m, 2H, H-4, 5), 3.64 (m, 1H, H-3), 3.86 (d, 1H, $J_{2,3}$ = 3.2 Hz, H-2), 4.57 (d, 1H, $J_{1,2}$ = 0.6 Hz, H-1), 4.73 (dd, 2H, ^2J = 11.1 Hz, CH_2Ph), 4.82 (dd, 2H, ^2J = 11.5 Hz, CH_2Ph), 7.16-7.50 (m, 10H, aromatic) ppm; ^{13}C NMR: δ, 15.2, 18.4, 26.1, 75.3, 75.6, 76.1, 76.2, 80.9, 81.9, 84.3, 128.0, 128.2 (× 3), 128.5 (× 2), 128.6 (× 2), 128.7 (× 2), 138.2, 138.4 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{22}H_{28}O_4SNa$ 411.1606, found 411.1713.

Ethyl 2,4-Di-*O*-benzyl-3-*O*-picoloyl-1-thio-β-L-rhamnopyranoside (1l). Picolinic acid (95 mg, 0.77 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (197 mg, 1.03 mmol), and 4-dimethylaminopyridine (12.6 mg, 0.10 mmol) were added to a solution of ethyl 2,4-di-*O*-benzyl-1-thio-β-L-rhamnopyranoside (**S13**, 200 mg, 0.52 mmol) in CH_2Cl_2 (6.0 mL) and the resulting mixture was stirred under argon for 45 min at rt. The reaction mixture was diluted with CH_2Cl_2 (~100 mL) and washed with 20% brine solution (2 x 10 mL). The organic phase was separated, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/ hexane gradient elution) to give the title compound in 90% yield (229 mg, 0.46 mmol) as a colorless syrup. Analytical data for **1l**: R_f = 0.44 (ethyl acetate/hexane, 2/3, v/v); $[\alpha]_D^{22}$ +122.0 (c = 1.0, $CHCl_3$); ^{1}H NMR: δ, 1.31 (t, 3H, J = 7.4 Hz, SCH$_2$CH_3), 1.42 (d, 3H, $J_{5,6}$ = 6.1 Hz, C-6), 2.74 (q, 2H, J = 7.5 Hz, SCH_2CH$_3$), 3.51 (m, 1H, H-5), 3.90 (dd, 1H, $J_{4,5}$ = 9.4 Hz, H-4), 4.21 (d, 1H, $J_{2,3}$ = 3.2 Hz, H-2), 4.63- 4.87 (m, 5H, H-1, 2 × CH_2Ph), 5.22 (dd, 1H, $J_{3,4}$ = 9.8 Hz, H-3), 7.02-7.50 (m, 12H, aromatic), 7.75 (m, 1H, aromatic), 7.91 (m, 1H, aromatic), 7.87 (d, 1H, J = 4.0 Hz, aromatic) ppm; ^{13}C NMR: δ, 15.2, 18.3, 25.9, 75.3, 75.7, 76.3, 78.0, 78.3, 78.5, 84.2, 125.2, 127.1, 127.6, 127.7, 128.0 (× 2), 128.1 (× 2), 128.3 (× 2), 128.5 (× 2), 136.9, 137.8, 138.0, 147.5, 150.1, 164.4 ppm; HR-FAB MS $[M+H]^+$ calcd for $C_{28}H_{32}O_5$ 494.2001, found 494.2005.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(pyrid-3-ylmethyl)-1-thio-β-D-glucopyranoside (S14).

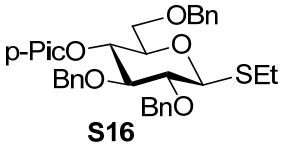


S14

NaH (60% in mineral oil, 40.8 mg, 1.02 mmol) and 3-(bromomethyl)pyridine hydrobromide (191.8 mg, 0.76 mmol) were added to a solution of ethyl 2,3,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside[9] (**S4**, 250 mg, 0.51 mmol) in DMF (3 mL) and the resulting mixture was stirred for 6.5 h at rt. After that, the reaction mixture was poured into ice-water (10 mL), stirred for 30 min, and extracted with ethyl acetate/ diethyl ether (1/1, v/v, 3 × 30 mL). The combined organic extract (~90 mL) was washed with cold water (3 × 10 mL). The organic phase was separated, dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/ hexane gradient elution) to give the title compound in 89% yield (265 mg, 0.45 mmol) as a white amorphous solid. Analytical data for **S14**: R_f = 0.38 (ethyl acetate/hexane, 1/1, v/v); $[\alpha]_D^{21}$ +5.0 (c = 1.0, $CHCl_3$); ^{1}H NMR: δ, 1.93 (t, 3H, J = 7.4 Hz, SCH$_2$CH_3), 2.83 (m, 2H, SCH_2CH$_3$), 3.45-3.58 (m, 2H, H-2, 5), 3.67-3.85 (m, 4H, H-3, 4, 6a, 6b), 4.53 (d, 1H, $J_{1,2}$ = 9.8 Hz, H-1), 4.64 (dd, 2H, ^2J = 11.3 Hz, CH_2Ph), 4.72 (dd, 2H, ^2J = 12.1 Hz, CH_2Ph), 4.90 (dd, 2H, ^2J = 10.6 Hz, CH_2Ph), 4.92 (dd, 2H, ^2J = 11.7 Hz, CH_2Ph), 7.15-7.52 (m, 17H, aromatic), 8.44 (d, 1H, J = 0.9 Hz, aromatic), 8.55 (d, 1H, J = 4.7 Hz, aromatic) ppm; ^{13}C NMR: δ, 15.3, 25.1, 68.9, 72.4, 73.6, 75.6, 75.8, 78.0, 79.0, 81.9, 85.2, 86.7, 123.4, 127.7 (× 2), 127.8 (× 3), 127.9 (× 2), 128.0, 128.4 (× 2), 128.5(× 3), 128.6 (× 2),

133.6, 135.5, 138.0, 138.1, 138.5, 149.2 (× 2) ppm; HR FAB MS $[M+H]^+$ calcd for $C_{35}H_{40}NO_5S$ 586.2627, found 586.2673.

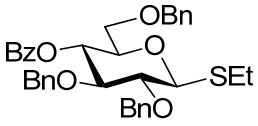
Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(pyrid-4-ylmethyl)-1-thio-β-D-glucopyranoside (S16).



S16

NaH (60% in mineral oil, 40.8 mg, 1.02 mmol) and 4-(bromomethyl)pyridine hydrobromide (191.8 mg, 0.76 mmol) were added to a solution of ethyl 2,3,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside[9] (**S4**, 250 mg, 0.51 mmol) in DMF (3 mL) and the resulting mixture was stirred for 6 h at rt. After that, the reaction mixture was poured into ice-water (10 mL), stirred for 30 min, and extracted with ethyl acetate/ diethyl ether (1/1, v/v, 3 × 30 mL). The combined organic extract (~90 mL) was washed with cold water (3 × 10 mL). The organic phase was separated, dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/ hexane gradient elution) to give the title compound 91% yield (269 mg, 0.45 mmol) as a white amorphous solid. Analytical data for **S16**: R_f = 0.35 (ethyl acetate/hexane, 1/1, v/v); $[\alpha]_D^{21}$ +2.5 (c = 1.0, $CHCl_3$); ^{1}H NMR: δ, 1.39 (t, 3H, *J* = 7.4 Hz, SCH_2CH_3), 2.82 (m, 2H, SCH_2CH_3), 3.45-3.56 (m, 2H, H-2, 4), 3.62-3.85 (m, 4H, H-5, 6a, 6b), 4.53 (d, 1H, $J_{1,2}$ = 9.7 Hz, H-1), 4.61 (dd, 2H, ^2J = 12.2 Hz, CH_2Ph), 4.71 (dd, 2H, ^2J = 12.9 Hz, CH_2Ph), 4.88 (dd, 2H, ^2J = 11.1 Hz, CH_2Ph), 4.88 (dd, 2H, ^2J = 10.2 Hz, CH_2Ph), 7.05-7.52 (m, 17H, aromatic), 8.53 (d, 2H, *J* = 5.7 Hz, aromatic) ppm; ^{13}C NMR: δ, 15.3, 25.2, 69.0, 73.1, 73.6, 75.6, 75.9, 78.3, 79.0, 82.0, 85.3, 86.7, 121.7 (× 2), 127.8 (× 3), 127.9 (× 3), 128.1, 128.5 (× 4), 128.6 (× 4), 138.0, 138.1, 138.4, 147.4, 149.9 (× 2) ppm; HR FAB MS $[M+H]^+$ calcd for $C_{35}H_{40}NO_5S$ 586.2627, found 586.2681.

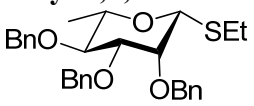
Ethyl 4-*O*-Benzoyl-2,3,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (S18).



S18

The title compound was synthesized according to standard procedures and the analytical data for **S18** was essentially same as previously reported.[16]

Ethyl 2,3,4-tri-*O*-benzyl-1-thio-β-L-rhamnopyranoside (S20).



S20

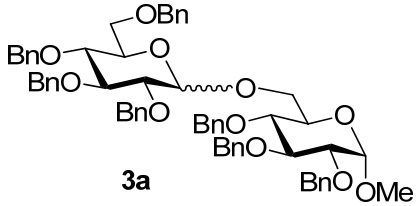
NaH (60% in mineral oil, 0.43 g, 10.8 mmol) and benzyl bromide (0.86 mL, 7.2 mmol) were added to a solution of ethyl 1-thio-β-L-rhamnopyranoside[15] (0.25 g, 1.2 mmol) in DMF (5.0 mL) and the resulting mixture was stirred for 2 h at rt. After that, the reaction mixture was poured into ice-water (30 mL), stirred for 30 min, and extracted with ethyl acetate/ diethyl ether (1/1, v/v, 3 × 50 mL). The combined organic extract (~150 mL) was washed with cold water (3 × 15 mL). The organic phase was separated, dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/ hexane gradient

elution) to give the title compound in 89% yield (0.51 g, 1.1 mmol) as a white amorphous solid. Analytical data for **S20**: R_f = 0.61 (ethyl acetate/hexane, 2/3, v/v); $[\alpha]_D^{22}$ +80.8 (c = 1.0, $CHCl_3$); ^{1}H NMR: δ, 1.27 (t, 3H, *J* = 7.4 Hz, SCH_2CH_3), 1.35 (d, 3H, $J_{5,6}$ = 6.2 Hz, C-6), 2.68 (q, 2H, *J* = 7.4 Hz, SCH_2CH_3), 3.33 (m, 1H, H-5), 3.55 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-3), 3.67 (dd, 1H, $J_{4,5}$ = 9.2 Hz, H-4), 3.96 (d, 1H, $J_{2,3}$ = 2.5 Hz, H-2), 4.51 (s, 1H, H-1), 4.60- 4.75 (m, 3H, 1½ × CH_2Ph), 4.89 (dd, 2H, ^2J = 11.6 Hz, CH_2Ph), 4.93 (d, 1H, ^2J = 10.8 Hz, ½ CH_2Ph), 7.15-7.55 (m, 15H, aromatic) ppm; ^{13}C NMR: δ, 15.2, 18.3, 25.9, 72.3, 75.1, 75.6, 76.5, 77.3, 80.1, 84.3, 84.4, 127.7 (× 3), 127.8, 127.9, 128.2 (× 2), 128.3 (× 2), 128.5 (× 4), 128.6 (× 2), 138.4, 138.5 (× 2) ppm; HR-FAB MS $[M+H]^+$ calcd for $C_{29}H_{35}O_4S$ 479.2256, found 479.2586.

Synthesis of Disaccharides

General procedure for glycosylation in the presence of DMTST. A mixture of a glycosyl donor (0.13 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (4 Å, 200 mg) in $(ClCH_2)_2$ (2.6 mL, 50 mM or 26 mL, 5 mM) was stirred under argon for 1 h. The mixture was cooled to -30 °C, DMTST[17] (0.26 mmol) was added, and the resulting mixture was allowed to warm to rt over a period of 1 h. The external heating was then applied and the reaction mixture was stirred at 42 °C for the time specified in tables. *Alternative procedure involved stirring at rt as indicated in tables.* Upon completion, Et_3N (0.3 mL) was added and the resulting mixture was stirred for 30 min. The mixture was then diluted with CH_2Cl_2 (10 mL, in case of 50 mM experiment only), the solid was filtered off, and the residue was washed sucessively with CH_2Cl_2. The combined filtrate (~30-40 mL) was washed with 20% aq. $NaHCO_3$ (10 mL) and water (3 x 10 mL). The organic phase was separated, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution). Anomeric ratios (or anomeric purity) were determined by comparison of the integral intensities of relevant signals in ^{1}H NMR spectra.

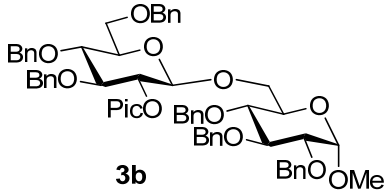
Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (3a).



3a

The title compound was obtained as a white amorphous solid from glycosyl donor **1a** and acceptor **2** in 92% (α/β = 1/1.9, 50 mM) and 85% yield (α/β = 1/1, 5 mM) under regular and high dilution reaction conditions, respectively. Analytical data for **3a** was in accordance with that reported previously.[18]

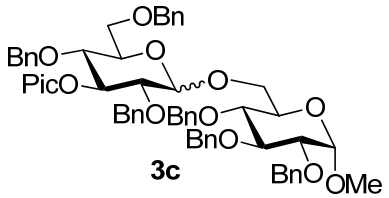
Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(3,4,6-tri-*O*-benzyl-2-*O*-picolinyl-β-D-glucopyranosyl)-α-D-glucopyranoside (3b).



3b

The title compound was obtained as a white amorphous solid from glycosyl donor **1b** and acceptor **2** in 83% yield (β only, 50 mM). Analytical data for **3b** was essentially the same as reported previously.[19]

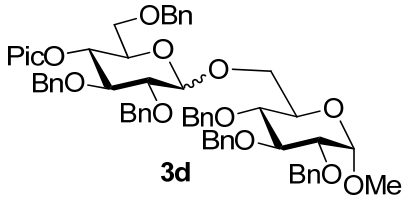
Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,4,6-tri-*O*-benzyl-3-*O*-picolinyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (3c).



3c

The title compound was obtained as a white amorphous solid from glycosyl donor **1c** and acceptor **2** in 84% (α/β = 1/5.8, 50 mM) and 85% yield (α/β = 1/15.6, 5 mM) under regular and high dilution reaction conditions, respectively. Analytical data for **β-**isomer of **3c**: R_f = 0.63 (ethyl acetate/hexane, 1/1, v/v); ^{1}H NMR: δ, 3.25(s, 3H, OCH_3), 3.28-3.66 (m, 9H, H-2, 2', 3', 4, 4', 5, 6a, 6a', 6b'), 3.76 (m, 1H, H-5'), 3.92 (dd, 1H, $J_{3,4}$ = 9.3 Hz, H-3), 4.11 (dd, 1H, $J_{5,6b}$ = 1.8 Hz, $J_{6a,6b}$ = 10.8 Hz, H-6b), 4.27 (d, 1H, $J_{1',2'}$ = 7.8 Hz, H-1'), 4.49 (dd, 2H, ^2J = 13.2 Hz, CH_2Ph), 4.53 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.54 (dd, 2H, ^2J = 9.8 Hz, CH_2Ph), 4.58 (dd, 2H, ^2J = 10.7 Hz, CH_2Ph), 4.64 (dd, 2H, ^2J = 12.4 Hz, CH_2Ph), 4.75 (dd, 2H, ^2J = 9.8 Hz, CH_2Ph), 4.80 (dd, 2H, ^2J = 10.8 Hz, CH_2Ph), 4.93 (dd, 2H, ^2J = 12.9 Hz, CH_2Ph), 7.00-7.90 (m, 32H, aromatic), 7.47 (dd, 1H, J = 7.7 Hz, aromatic), 8.46 (dd, 1H, J = 4.1 Hz, aromatic) ppm; ^{13}C NMR: δ, 55.3, 68.6, 69.0, 70.0, 73.3, 73.5, 74.8, 74.9, 75.0, 75.0 (× 2), 75.5, 76.2, 77.8, 78.1, 79.8, 81.7, 82.0, 85.3, 98.1, 103.8, 121.4, 122.2, 127.5, 127.6, 127.7 (× 5), 127.8, 127.9 (× 3), 128.0 (× 2), 128.1 (× 2), 128.2 (× 2), 128.3 (× 2), 128.4 (× 9), 128.5 (× 2), 136.5, 138.0, 138.2, 138.3 (× 2), 138.4, 138.9, 149.1, 158.7 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{61}H_{65}NO_{11}Na$ 1010.4455, found 1010.4442.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,6-tri-*O*-benzyl-4-*O*-picolinyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (3d).

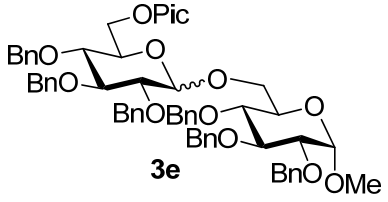


3d

The title compound was obtained as a white amorphous solid from glycosyl donor **1d** and acceptor **2** in 88% (α/β = 1.2/1, 50 mM) and 86% yield (α/β = 5.3/1, 5 mM) under regular and high dilution reaction conditions, respectively. Analytical data for **α** isomer of **3d**: R_f = 0.59 (ethyl acetate/hexane, 1/1, v/v); ^{1}H NMR: δ, 3.31 (s, 3H, OCH_3), 3.39 (dd, 1H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$

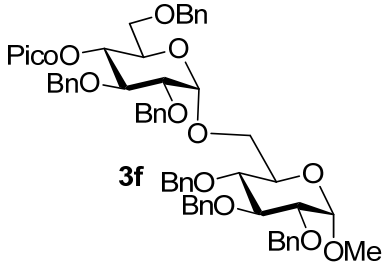
= 9.6 Hz, H-2), 3.45-3.83 (m, 9H, H-2', 4, 4', 5, 5', 6a, 6a', 6b, 6b'), 3.92 (dd, 1H, $J_{3',4'}$ = 9.2 Hz, H-3'), 3.94 (dd, 1H, $J_{3,4}$ = 9.2 Hz, H-3), 4.44 (dd, 2H, ^2J = 12.1 Hz, CH_2Ph), 4.60 (dd, 2H, ^2J = 12.1 Hz, CH_2Ph), 4.51 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1), 4.56-4.67 (m, 2H, CH_2Ph), 4.69 (d, 1H, ^2J = 10.9 Hz, ½ CH_2Ph), 4.71 (dd, 2H, ^2J = 10.8 Hz, CH_2Ph), 4.76 (dd, 1H, ^2J = 10.8 Hz, ½ CH_2Ph), 4.84-4.98 (m, 5H, H-1', 2 × CH_2Ph), 7.05-7.56 (m, 33H, aromatic), 8.47 (d, 1H, J = 4.8 Hz, aromatic) ppm; ^{13}C NMR: δ, 55.4, 66.3, 68.7, 70.4, 70.5, 72.6, 73.6 (× 2), 75.2, 75.6, 75.7, 75.9, 78.0, 78.3, 80.2, 80.3, 81.5, 82.3, 97.5, 98.2, 121.3, 122.3, 127.6, 127.7, 127.8 (× 4), 128.0 (× 4), 128.1, 128.2 (× 4), 128.3 (× 2), 128.4 (× 5), 128.6 (× 8), 136.6, 138.1, 138.4, 138.6, 138.8, 139.0, 149.1, 158.8 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{61}H_{65}NO_{11}Na$ 1010.4455, found 1010.4476.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzyl-6-*O*-picolinyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (3e).



The title compound was obtained as a white amorphous solid from glycosyl donor **1e** and acceptor **2** in 93% (α/β = 1/2.4, 50 mM) and 84% yield (α/β = 1.1/1, 5 mM) under regular and high dilution reaction conditions, respectively. Selected analytical data for **β**-isomer of **3e**: R_f = 0.44 (ethyl acetate/hexane, 1/1, v/v); ^{1}H NMR: δ, 3.36 (s, 3H, OCH_3), 4.22 (dd, 1H, $J_{5,6b}$ = 1.7 Hz, $J_{6a,6b}$ = 10.6 Hz, H-6b), 4.24 (dd, 1H, $J_{5',6b'}$ = 5.0 Hz, $J_{6a',6b'}$ = 10.5 Hz, H-6b'), 4.39 (d, 1H, $J_{1',2'}$ = 7.7 Hz, H-1') ppm; ^{13}C NMR: δ, 98.2, 104.0 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{61}H_{65}NO_{11}Na$ 1010.4455, found 1010.4523.

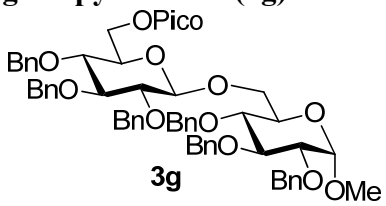
Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,6-tri-*O*-benzyl-4-*O*-picoloyl-α-D-glucopyranosyl)-α-D-glucopyranoside (3f).



The title compound was obtained as a colorless syrup from glycosyl donor **1f** and acceptor **2** in 85% (α/β = 2.8/1, 50 mM) and 73% yield (α/β > 25/1, 5 mM) under regular and high dilution reaction conditions, respectively. Analytical data for **3f**: R_f = 0.50 (ethyl acetate/hexane, 1/1, v/v); $[\alpha]_D^{23}$ +42.3 (*c* = 1.0, $CHCl_3$); ^{1}H NMR: δ, 3.30 (s, 3H, OCH_3), 3.38 (dd, 1H, $J_{2,3}$ = 9.6 Hz, H-2), 3.42-3.60 (m, 2H, H-6a', 6b'), 3.55-3.67 (m, 2H, H-4, 2'), 3.69-3.82 (m, 3H, H- 5, 6a, 6b), 3.93 (dd, 1H, $J_{3,4}$ = 9.1 Hz, H-3), 4.03 (m, 1H, H- 5'), 4.07 (dd, 1H, $J_{3',4'}$ = 9.5 Hz, H-3'), 4.37 (dd, 2H, ^2J = 10.5 Hz, CH_2Ph), 4.50 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1), 4.60 (s, 2H, CH_2Ph), 4.62 (dd, 2H, ^2J = 10.1 Hz, CH_2Ph), 4.65 (dd, 2H, ^2J = 11.4 Hz, CH_2Ph), 4.74 (dd, 2H, ^2J = 11.1 Hz, CH_2Ph), 4.83 (dd, 2H, ^2J = 10.9 Hz, CH_2Ph), 5.00 (d, 1H, $J_{1',2'}$ = 3.4 Hz, H-1'), 5.34 (dd, 1H, $J_{4',5'}$ = 9.7 Hz, H-4'), 6.85-7.70 (m, 31H, aromatic), 7.67 (dd, 1H, J = 7.7 Hz, aromatic), 7.82 (d, 1H, J = 7.8 Hz, aromatic), 8.66 (d, 1H, J = 3.3 Hz, aromatic) ppm; ^{13}C NMR: δ, 55.3, 66.1, 68.9,

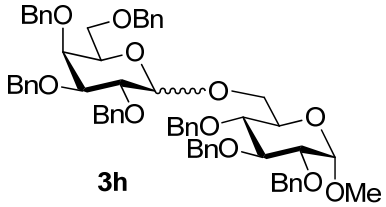
70.7, 72.0, 72.7, 73.6, 73.7, 75.1, 75.2, 75.9, 77.4, 77.9, 78.6, 79.9, 80.3, 82.3, 97.5, 98.1, 125.6, 127.0, 127.4, 127.5, 127.7, 127.8 (× 3), 127.9 (× 2), 128.1 (× 4), 128.2 (× 7), 128.3 (× 2), 128.5 (× 3), 128.6 (× 6), 137.0, 138.0, 138.3, 138.4, 138.5, 138.6, 139.0, 147.9, 150.0, 164.1 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{61}H_{63}O_{12}NNa$ 1024.4248, found 1024.4273.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzyl-6-*O*-picoloyl-β-D-glucopyranosyl)-α-D-glucopyranoside (3g).



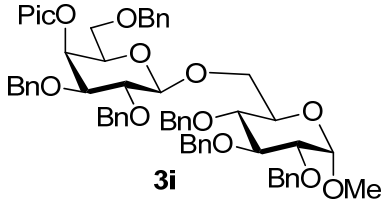
The title compound was obtained as a colorless syrup from glycosyl donor **1g** and acceptor **2** in 96% (α/β > 1/25, 50 mM) and 92% yield (α/β > 1/25, 5 mM) under regular and high dilution reaction conditions, respectively. Analytical data for **3g**: R_f = 0.57 (ethyl acetate/hexane, 3/2, v/v); $[\alpha]_D^{23}$ +32.5 (*c* = 1.0, $CHCl_3$); ^{1}H NMR: δ, 3.27 (s, 3H, OCH_3), 3.46-3.57 (m, 3H, H-2, 2', 6b), 3.59-3.71 (m, 4H, H-3', 4, 4', 5'), 3.76 (m, 1H, H-5), 3.94 (dd, 1H, $J_{3,4}$ = 9.3 Hz, H-3), 4.11 (dd, 1H, $J_{5,6b}$ = 1.5 Hz, $J_{6a,6b}$ = 9.3, H-6b), 4.37 (d, 1H, $J_{1',2'}$ = 7.8 Hz, H-1'), 4.44 (d, 1H, ^2J = 11.2 Hz, ½ CH_2Ph), 4.48-4.69 (m, 6H, H-1, 6a', 6b', 1½ × CH_2Ph), 4.70- 4.85 (m, 4H, 2 × CH_2Ph), 4.93 (dd, 4H, ^2J = 10.6 Hz, 2 × CH_2Ph), 7.05-7.52 (m, 31H, aromatic), 7.73 (dd, 1H, *J* = 7.7 Hz, aromatic), 7.99 (d, 1H, *J* = 7.7 Hz, aromatic), 8.72 (d, 1H, *J* = 3.9 Hz, aromatic) ppm; ^{13}C NMR: δ, 55.4, 64.5, 68.8, 69.9, 73.1, 73.6, 75.1, 75.2, 75.3, 75.9, 76.1, 77.4, 78.1, 79.9, 82.1, 82.2, 85.0, 98.2, 104.0, 125.4, 127.1, 127.8 (× 5), 128.0 (× 3), 128.1 (× 2), 128.2 (× 4), 128.3 (× 2), 128.4 (× 2), 128.5 (× 2), 128.6 (× 4), 128.7 (× 6), 137.0, 137.9, 138.3, 138.4, 138.5 (× 2), 139.0, 147.9, 150.2, 164.8 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{61}H_{63}O_{12}NNa$ 1024.4248, found 1024.4246.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl)-α-D-glucopyranoside (3h).



The title compound was obtained as a white amorphous solid from glycosyl donor **1h** and acceptor **2** in 87% yield (α/β = 1/1.0, 50 mM). Analytical data for **3h** was in accordance with that reported previously.[20,21]

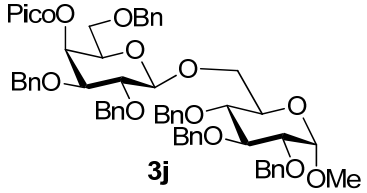
Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,6-tri-*O*-benzyl-4-*O*-picolinyl-β-D-galactopyranosyl)-α-D-glucopyranoside (3i).



3i

The title compound was obtained as a white amorphous solid from glycosyl donor **1i** and acceptor **2** in 89% (α/β = 1/10, 50 mM) and 83% yield (α/β > 1/25, 5 mM) under regular and high dilution reaction conditions, respectively. Analytical data for **3i**: R_f = 0.54 (ethyl acetate/hexane, 1/1, v/v); $[\alpha]_D^{23}$ +19.9 (*c* = 1.0, $CHCl_3$); ^{1}H NMR: δ, 3.23 (s, 3H, OCH_3), 3.35-3.64 (m, 7H, H-2, 3', 4, 5, 5', 6a, 6a'), 3.71-3.81 (m, 2H, H-2', 3), 3.85-3.96 (m, 2H, H-4', 6b'), 4.07 (dd, 1H, $J_{5,6b}$ = 1.6 Hz, $J_{6a,6b}$ = 10.8 Hz, H-6b), 4.22 (d, 1H, $J_{1',2'}$ = 7.7 Hz, H-1'), 4.37 (s, 2H, CH_2Ph), 4.51 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.53 (dd, 2H, ^2J = 11.2 Hz, CH_2Ph), 4.63 (dd, 2H, ^2J = 12.2 Hz, CH_2Ph), 4.70 (d, ^2J = 10.2 Hz, CH_2Ph), 4.77 (dd, 2H, ^2J = 10.6 Hz, CH_2Ph), 4.79 (dd, 2H, ^2J = 10.7 Hz, CH_2Ph), 4.83 (dd, 2H, ^2J = 13.3 Hz, CH_2Ph), 7.00-7.55 (m, 33H, aromatic), 8.40 (d, 1H, *J* = 4.7 Hz, aromatic) ppm; ^{13}C NMR: δ, 55.3, 68.5, 68.8, 70.1, 72.9, 73.4, 73.5, 73.7, 75.0, 75.1, 75.3, 75.8, 76.0, 78.2, 79.3, 80.0, 82.0, 82.2, 98.1, 104.5, 121.8, 122.2, 127.5, 127.7 (× 3), 127.8 (× 4), 127.9, 128.0 (× 3), 128.1 (× 2), 128.2 (× 2), 128.3 (× 2), 128.4 (× 2), 128.5 (× 8), 128.6 (× 4), 136.6, 137.9, 138.3, 138.4, 138.5, 138.8, 139.0, 148.6, 159.2 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{61}H_{65}NO_{11}Na$ 1010.4455, found 1010.4503.

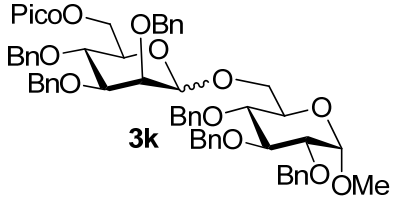
Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,6-tri-*O*-benzyl-4-*O*-picoloyl-β-D-galactopyranosyl)-α-D-glucopyranoside (3j).



3j

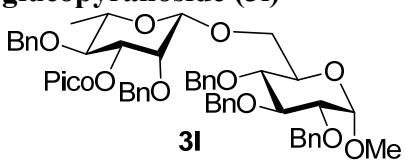
The title compound was obtained as a colorless syrup from glycosyl donor **1j** and acceptor **2** in 96% (α/β = 1/24, 50 mM) and 95% yield (α/β > 1/25, 5 mM) under regular and high dilution reaction conditions, respectively. Analytical data for **3j**: R_f = 0.43 (ethyl acetate/hexane, 1/1, v/v); $[\alpha]_D^{23}$ +36.9 (*c* = 1.0, $CHCl_3$); ^{1}H NMR: δ, 3.25 (s, 3H, OCH_3), 3.41-3.72 (m, 8H, H-2, 2', 3', 4, 5', 6a, 6a', 6b'), 3.75 (m, 1H, H-5), 3.91 (dd, 1H, $J_{3,4}$ = 9.2 Hz, H-3), 4.09 (dd, 1H, $J_{6a,6b}$ = 11.0 Hz, $J_{5,6b}$ = 1.8 Hz, H-6b), 4.26 (d, 1H, $J_{1',2'}$ = 7.5 Hz, H-1'), 4.37 (dd, 2H, ^2J = 11.8 Hz, CH_2Ph), 4.52 (dd, 2H, ^2J = 11.3 Hz, CH_2Ph), 4.54 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 4.64 (dd, 2H, ^2J = 12.3 Hz, CH_2Ph), 4.65 (dd, 2H, ^2J = 11.5 Hz, CH_2Ph), 4.73 (dd, 2H, ^2J = 10.8 Hz, CH_2Ph), 4.79 (dd, 2H, ^2J = 10.9 Hz, CH_2Ph), 5.79 (dd, 1H, $J_{4',5'}$ = 2.7 Hz, H-4'), 7.05-7.45 (m, 33H, aromatic), 7.69 (dd, 1H, *J* = 7.7 Hz, aromatic), 7.95 (d, 1H, *J* = 7.8 Hz, aromatic), 8.70 (d, 1H, *J* = 3.4 Hz, aromatic) ppm; ^{13}C NMR: δ, 55.4, 68.2, 68.4, 69.0, 70.1, 72.3, 72.5, 73.6, 73.9, 75.0, 75.5, 75.8, 78.0, 78.9, 79.6, 80.0, 82.2, 98.3, 104.5, 125.7, 127.1, 127.6, 127.7 (× 2), 127.8 (× 3), 127.9, 128.1 (× 5), 128.2 (× 2), 128.3 (× 2), 128.4 (× 4), 128.5 (× 7), 128.6 (× 2), 137.0, 137.7, 137.8, 138.3, 138.5, 138.6, 139.0, 147.8, 150.4, 164.2 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{61}H_{63}O_{12}NNa$ 1024.4248, found 1024.4271.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzyl-6-*O*-picoloyl-α/β-D-mannopyranosyl)-α-D-glucopyranoside (3k).



The title compound was obtained as a colorless syrup from glycosyl donor **1k** and acceptor **2** in 89% (α/β > 1/3.5, 50 mM) and 86% yield (α/β > 1/4.5, 5 mM) under regular and high dilution reaction conditions, respectively. Alternatively, the title compound was prepared as follows. A mixture of glycosyl donor **1k** (0.13 mmol), glycosyl acceptor **2** (0.10 mmol), and freshly activated molecular sieves (4 Å, 200 mg) in $(ClCH_2)_2$ (2.6 mL, 50 mM or 26 mL, 5 mM) was stirred under an argon for 1 h. The mixture was cooled to -30 °C, NIS (0.26 mmol) and TfOH (0.026 mmol) were added, and the reaction mixture was allowed to warm to rt and stirred until the completion (see tables). The resulting mixture was diluted with CH_2Cl_2 (~10 mL), the solid was filtered off and the residue was washed with CH_2Cl_2. The combined filtrate (~30 mL) was washed with 10% aq. $Na_2S_2O_3$ (10 mL) and water (3 x 10 mL). The organic phase was separated, dried with $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - hexane gradient elution) to afford the title compound in 91% (α/β = 1/5.3, 50 mM) and 87% yield (α/β = 1/9.5, 5 mM). Analytical data for β–isomer of **3k**: R_f = 0.46 (ethyl acetate/hexane, 3/2, v/v); ^{1}H NMR: δ, 3.20 (s, 3H, OCH_3), 3.31 (dd, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 3.36- 3.47 (m, 3H, H-2, 3', 6a), 3.53 (m, 1H, H-5'), 3.65-3.77 (m, 2H, H- 5, 2'), 3.84-3.96 (m, 2H, H-3, 4'), 4.06 (dd, 1H, $J_{5,6b}$ = 1.7 Hz, $J_{6a,6b}$ = 10.5 Hz, H-6b), 4.13 (s, 1H, H-1'), 4.45-4.58 (m, 3H, H-1, 6a', 6b'), 4.51 (dd, 2H, ^2J = 4.4 Hz, CH_2Ph), 4.56 (dd, 2H, ^2J = 11.3 Hz, CH_2Ph), 5.63 (dd, 2H, ^2J = 12.3 Hz, CH_2Ph), 5.71 (dd, 2H, ^2J = 10.8 Hz, CH_2Ph), 5.77 (dd, 2H, ^2J = 12.3 Hz, CH_2Ph), 5.82 (dd, 2H, ^2J = 10.9 Hz, CH_2Ph), 7.05-7.43 (m, 31H, aromatic), 7.49 (dd, 1H, J = 7.8 Hz, aromatic), 7.90 (d, 1H, J = 7.8 Hz, aromatic), 8.64 (d, 1H, J = 3.9 Hz, aromatic) ppm; ^{13}C NMR: δ, 55.2, 65.2, 68.6, 69.9, 71.8, 73.5, 73.7, 73.9, 74.0, 74.8, 75.0, 75.4, 76.0, 77.9, 80.0, 82.2, 82.3, 98.0, 101.8 ($^1J_{C1,H1}$ = 165.2 Hz, $^1J_{C1',H1'}$ = 154.6 Hz), 125.6, 126.9, 127.6, 127.7, 127.8 (× 3), 127.9 (× 2), 128.0, 128.2 (× 3), 128.2 (× 2), 128.4 (× 5), 128.5 (× 2), 128.6 (× 8), 128.7 (× 2), 137.1, 138.1, 138.2 (× 2), 138.4, 138.9, 139.0, 150.1, 164.8 ppm. Selected analytical data for α–isomer of **3k**: R_f = 0.46 (ethyl acetate/hexane, 3/2, v/v); $^1J_{C1,H1}$ = 164.0 Hz, $^1J_{C1',H1'}$ = 171.0 Hz. HR-FAB MS $[M+Na]^+$ calcd for $C_{61}H_{63}O_{12}NNa$ 1024.4248, found 1024.4293.

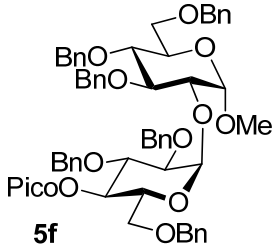
Methyl 2,3,4-Tri-O-benzyl-6-O-(2,4-di-O-benzyl-3-O-picoloyl-β-L-rhamnopyranosyl)-α-D-glucopyranoside (3l)



The title compound was obtained as a colorless syrup from glycosyl donor **1l** and acceptor **2** in 94% yield (α/β > 1/25, 50 mM). Analytical data for **3l**: R_f = 0.47 (acetone/toluene, 3/17, v/v); $[\alpha]_D^{22}$ +79.9 (c = 1.0, $CHCl_3$); ^{1}H NMR: δ, 1.33 (d, 3H, $J_{5,6}$ = 6.0 Hz, C-6), 3.30 (s, 3H, OCH_3), 3.36-3.50 (m, 2H, H-2, 5'), 3.56 (dd, 1H, m, 1H, $J_{4,5}$ = 9.3 Hz, H-4), 3.62-3.73 (m, 2H, H-5, 6a),

3.77 (dd, 1H, $J_{4',5'}$ = 9.4 Hz, H-4'), 3.92 (dd, 1H, $J_{3,4}$ = 9.2 Hz, H-3), 4.11 (d, 1H, $J_{2',3'}$ = 3.2 Hz, H-2'), 4.20 (dd, 1H, $J_{5,6b}$ = 3.3 Hz, $J_{6a,6b}$ = 11.3 Hz, H-6b), 4.53-4.79 (m, 9H, H-1, 1', 3½ × CH_2Ph), 4.85 (dd, 2H, ^2J = 10.9 Hz, CH_2Ph), 4.85 (dd, 1H, ^2J = 12.2 Hz, ½ CH_2Ph), 6.78-7.45 (m, 26H, aromatic), 7.70 (dd, 1H, J = 7.7 Hz, aromatic), 7.85 (d, 1H, J = 7.8 Hz, aromatic), 8.46 (d, 1H, J = 4.1 Hz, aromatic) ppm; ^{13}C NMR: δ, 18.1, 55.4, 67.6, 70.2, 72.0, 73.6, 74.9, 75.4 (× 2), 75.6, 75.9, 77.3, 78.0, 78.7, 80.2, 82.0, 98.3, 101.2 ($^1J_{C1,H1}$ = 167.5 Hz, $^1J_{C1',H1'}$ = 155.1 Hz), 125.4, 127.1, 127.6, 127.7, 127.8, 127.9, 128.0 (× 2), 128.1 (× 2), 128.2 (× 2), 128.3 (× 2), 128.3 (× 3), 128.4 (× 3), 128.5 (× 5), 128.6 (× 2), 137.0, 138.2, 138.3, 138.4, 138.5, 139.0, 147.8, 150.2, 164.2 ppm; HR-FAB MS [M+Na]$^+$ calcd for $C_{54}H_{57}NaO_{11}$ 918.3829, found 918.3774.

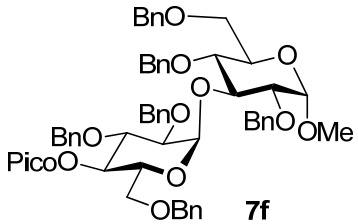
Methyl 3,4,6-Tri-*O*-benzyl-2-*O*-(2,3,6-tri-*O*-benzyl-4-*O*-picoloyl-α-D-glucopyranosyl)-α-D-glucopyranoside (5f).



5f

The title compound was obtained as a colorless syrup from glycosyl donor **1f** and acceptor **4** in 93% yield (α/β > 25/1, 50 mM). Analytical data for **5f**: R_f = 0.40 (ethyl acetate/hexane, 1/1, v/v); $[\alpha]_D^{23}$ +79.4 (c = 1.0, $CHCl_3$); ^{1}H NMR: δ, 3.30 (dd, 1H, $J_{5',6b'}$ = 3.8 Hz, $J_{6a',6b'}$ = 11.0 Hz, H-6b'), 3.41 (m, 1H, H-6a'), 3.45 (s, 3H, OCH_3), 3.57-3.83 (m, 5H, H-2, 4, 5, 6a, 6b), 3.87 (dd, 1H, $J_{2',3'}$ = 9.8 Hz, H-2'), 4.08 (dd, 1H, $J_{3,4}$ = 9.2 Hz, H-3), 4.15 (dd, 1H, $J_{3',4'}$ = 9.2 Hz, H-3'), 4.25 (m, 1H, H-5'), 4.37 (dd, 2H, ^2J = 11.9 Hz, CH_2Ph), 4.56 (dd, 2H, ^2J = 12.1 Hz, CH_2Ph), 4.60 (dd, 2H, ^2J = 10.9 Hz, CH_2Ph), 4.73 (dd, 2H, ^2J = 11.8 Hz, CH_2Ph), 4.74 (dd, 2H, ^2J = 13.5 Hz, CH_2Ph), 4.91 (dd, 2H, ^2J = 11.3 Hz, CH_2Ph), 4.94 (d,1H, $J_{1',2'}$ = 3.4 Hz, H-1'), 4.95 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 5.46 (dd, 1H, $J_{4',5'}$ = 9.8 Hz, H-4'), 6.65-7.70 (m, 33H, aromatic), 8.70 (d, 1H, J = 4.6 Hz, aromatic) ppm; ^{13}C NMR: δ, 55.1, 68.3, 68.7, 68.9, 70.4, 71.5, 73.2, 73.6, 73.7, 75.2, 75.3, 75.5, 75.8, 78.2, 79.1, 79.3, 81.0, 94.8, 96.7, 126.8, 127.5 (× 2), 127.7 (× 2), 127.9 (× 2), 128.0 (× 2), 128.1 (× 4), 128.2 (× 2), 128.3 (× 5), 128.5 (× 4), 128.6 (× 4), 137.0, 137.9 (× 2), 138.1, 138.3 (× 2), 138.4 (× 2), 138.9, 147.8, 150.1, 163.7 ppm; HR-FAB MS [M+Na]$^+$ calcd for $C_{61}H_{63}O_{12}NNa$ 1024.4248, found 1024.4248.

Methyl 2,4,6-Tri-*O*-benzyl-3-*O*-(2,3,6-tri-*O*-benzyl-4-*O*-picoloyl-α-D-glucopyranosyl)-α-D-glucopyranoside (7f).

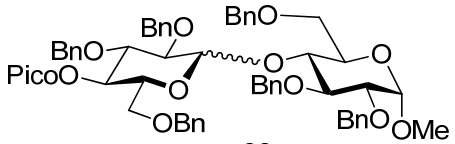


7f

The title compound was obtained as a colorless syrup from glycosyl donor **1f** and acceptor **6** in 87% (α/β = 10/1, 50 mM) and 81% yield (α/β > 25/1, 5 mM) under regular and high dilution reaction conditions, respectively. Analytical data for **7f**: R_f = 0.44 (ethyl acetate/hexane, 1/1, v/v); $[\alpha]_D^{23}$ +53.9 (c = 1.0, $CHCl_3$); ^{1}H NMR: δ, 3.36 (s, 3H, OCH_3), 3.41 (dd, 1H, $J_{6a',6b'}$ = 10.9

Hz, H-6b'), 3.58 (dd, 1H, $J_{5',6a'}$ = 2.5 Hz, H-6a'), 3.63-3.93 (m, 6H, H-2, 2', 4, 5, 6a, 6b), 4.31 (dd, 1H, $J_{3',4'}$ = 9.4 Hz, H-3'), 4.33 (dd, 1H, $J_{3,4}$ = 9.2 Hz, H-3), 4.49 (dd, 2H, ^2J = 11.9 Hz, CH_2Ph), 4.59 (dd, 2H, ^2J = 12.0 Hz, CH_2Ph), 4.64 (m, 2H, H-1, 5'), 4.69 (dd, 2H, ^2J = 11.8 Hz, CH_2Ph), 4.73 (dd, 2H, ^2J = 11.7 Hz, CH_2Ph), 4.76 (dd, 2H, ^2J = 11.3 Hz, CH_2Ph), 4.78 (dd, 2H, ^2J = 11.3 Hz, CH_2Ph), 5.56 (dd, 1H, $J_{4',5'}$ = 10.1 Hz, H-4'), 5.69 (d,1H, $J_{1',2'}$ = 3.5 Hz, H-1'), 7.05-7.60 (m, 31H, aromatic), 7.80 (dd, 1H, J = 7.7 Hz, aromatic), 7.90 (d, 1H, J = 7.8 Hz, aromatic), 8.79 (d, 1H, J = 3.2 Hz, aromatic) ppm; ^{13}C NMR: δ, 55.3, 68.7, 68.8, 69.0, 69.0, 69.6, 72.3, 73.3, 73.7, 73.8, 74.1, 75.4, 77.5, 78.1, 78.5, 79.1, 79.5, 79.9, 97.7 (× 2), 125.5, 127.0, 127.3 (× 2), 127.5 (× 2), 127.8, 128.0, 128.1 (× 5), 128.2 (× 3), 128.3 (× 6), 128.4 (× 2), 128.5 (× 4), 128.6 (× 4), 128.9 (× 2), 137.0, 138.1 (× 2), 138.2, 138.4, 138.5 (× 2), 148.2, 150.1, 164.2 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{61}H_{63}O_{12}NNa$ 1024.4248, found 1024.4239.

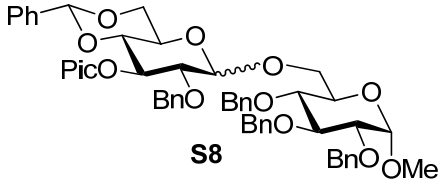
Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2,3,6-tri-*O*-benzyl-4-*O*-picoloyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (9f).



9f

The title compound was obtained as a colorless syrup from glycosyl donor **1f** and acceptor **8** in 94% (α/β = 12/1, 50 mM) and 81% yield (α/β = 21/1, 5 mM) under regular and high dilution reaction conditions, respectively. Analytical data for α-isomer of **9f**: R_f = 0.47 (ethyl acetate/hexane, 1/1, v/v); ^{1}H NMR: δ, 3.36-3.54 (m, 5H, H-6a', 6b', OCH_3), 3.58- 3.67 (m, 2H, H-2, 2'), 3.72 (dd, 1H, $J_{5,6b}$ = 3.8 Hz, $J_{6a,6b}$ = 10.7 Hz, H-6b), 3.87 (m, 1H, H-5), 4.00 (dd, 1H, $J_{5,6a}$ = 1.6 Hz, $J_{6a,6b}$ = 10.7 Hz, H-6a), 4.08 (dd, 1H, $J_{4,5}$ = 8.3 Hz, H-4), 4.12-4.24 (m, 3H, H-3, 3', 5'), 4.39 (dd, 2H, ^2J = 11.9 Hz, CH_2Ph), 4.48-4.71 (m, 7H, H-1, 3 × CH_2Ph), 4.76 (d, 1H, ^2J = 12.2 Hz, ½ CH_2Ph), 4.81 (d, 1H, ^2J = 11.3 Hz, ½ CH_2Ph), 4.99 (dd, 2H, ^2J = 11.5 Hz, CH_2Ph), 5.43 (dd, 1H, $J_{4',5'}$ = 9.7 Hz, H-4'), 5.57 (d, 1H, $J_{1',2'}$ = 3.6 Hz, H-1'), 7.05-7.60 (m, 31H, aromatic), 7.80 (dd, 1H, J = 7.8 Hz, aromatic), 7.98 (d, 1H, J = 7.9 Hz, aromatic), 8.77 (d, 1H, J = 4.0 Hz, aromatic) ppm; ^{13}C NMR: δ, 55.4, 69.0, 69.4, 69.6, 69.9, 72.3, 73.4 (× 2), 73.6, 73.7, 74.9, 75.3, 75.4, 79.2, 79.4, 80.1, 81.8, 97.7, 98.0, 125.6, 127.3, 127.5, 127.6, 127.7, 127.8, 127.9 (× 4), 128.0 (× 2), 128.1, 128.3 (× 4), 128.4 (× 8), 128.5 (× 2), 128.6 (× 2), 137.0, 138.0, 138.1, 138.3, 138.4 (× 2), 139.3, 148.0, 150.0, 164.2 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{61}H_{63}O_{12}NNa$ 1024.4248, found 1024.4242.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-picolinyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (S8).

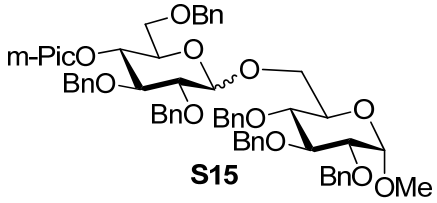


S8

The title compound was obtained as a white amorphous solid from glycosyl donor **S2** and acceptor **2** in 76% (α/β = 1/2.4, 50 mM) and 77% yield (α/β = 1/2.1, 5 mM) under regular and high dilution reaction conditions, respectively. Selected analytical data for β–isomer of **S8**: R_f = 0.64 (ethyl acetate/hexane, 1/1, v/v); ^{1}H NMR: δ, 3.34 (s, 3H, OCH_3), 3.35-3.41 (m, 1H, H-6'a),

3.50-3.58 (m, 3H, H-2, 2', 4), 3.67-3.74 (m, 2H, H-4', 6a), 3.75-3.82 (m, 3H, H-3', 5, 5'), 4.00 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-3), 4.13 (dd, 1H, $J_{5,6b}$ = 1.9 Hz, $J_{6a,6b}$ = 10.8 Hz, H-6b), 4.32 (dd, 1H, $J_{5',6b'}$ = 5.0 Hz, $J_{6a',6b'}$ = 10.5 Hz, H-6b'), 4.47 (d, 1H, $J_{1',2'}$ = 8.2 Hz, H-1'), 4.61(d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.62 (dd, 2H, ^2J = 11.2 Hz, CH_2Ph), 4.63-4.72 (m, 2H, CH_2Ph), 4.77-4.84 (m, 2H, CH_2Ph), 4.88-4.95 (m, 2H, CH_2Ph), 5.00 (dd, 2H, ^2J = 13.5 Hz, CH_2Ph), 5.53 (s, 1H, >C*H*Ph), 7.05 (m, 28H, aromatic), 8.50 (m, 1H, aromatic) ppm; ^{13}C NMR: δ, 55.4, 62.7, 66.2, 68.9 (× 2), 69.9, 73.6, 75.1, 75.5, 75.8, 75.9, 78.0, 79.9, 81.4, 81.9, 82.1, 98.3, 101.4, 104.2, 121.7, 122.4, 126.2 (× 2), 126.3, 127.7, 127.8 (× 2), 128.1 (× 6), 128.3 (× 2), 128.4 (× 2), 128.5 (× 2), 128.6 (× 5), 128.7, 129.2, 136.7, 137.3, 138.2, 138.3, 138.5, 138.9, 148.9, 159.0 ppm. Selected analytical data for α–isomer of **S8**: R_f = 0.64 (ethyl acetate/hexane, 1/1, v/v); ^{1}H NMR: δ, 3.35 (s, 3H, OCH_3), 3.43 (dd, 1H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 9.6Hz, H-2), 3.56-3.66 (m, 3H, H-2', 4, 4'), 3.69-3.74 (m, 1H, H-5'), 3.65- .74 (m, 2H, H-4', 6a), 3.75- 3.83 (m, 1H, H-5), 3.91 (m, 1H, H-6a'), 3.97-4.06 (m, 2H, H-3, 3'), 4.22 (dd, 1H, $J_{5',6b'}$ = 4.9 Hz, $J_{6a',6b'}$ = 10.2 Hz, H-6b'), 4.44- 5.08 (m, 12H, H-1, 1', 5 × CH_2Ph), 5.53 (s, 1H, >C*H*Ph), 7.05 (m, 28H, aromatic), 8.50 (m, 1H, aromatic) ppm; ^{13}C NMR: δ, 55.4, 62.5, 66.5, 69.3, 70.6,72.9, 75.2, 75.6, 75.9, 77.8, 79.0, 79.4, 80.2, 82.1, 82.2, 82.3, 98.2 (× 2), 101.6 ppm; HR-FAB MS $[M+H]^+$ calcd for $C_{54}H_{58}NO_{11}$ 896.4010, found 896.4050.

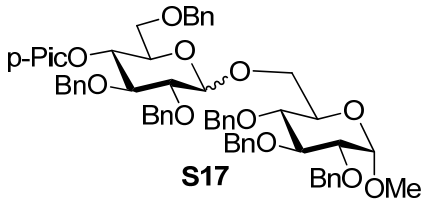
Methyl 2,3,4-Tri-O-benzyl-6-O-(2,3,6-tri-O-benzyl-4-O-(pyrid-3-ylmethyl)-α/β-D-glucopyranosyl)-α-D-glucopyranoside (S15).



S15

The title compound was obtained as a white amorphous solid from glycosyl donor **S14** and acceptor **2** by in 87% (α/β = 1.1/1, 50 mM) and 82% yield (α/β = 1.5/1, 5 mM) under regular and high dilution reaction conditions, respectively. Selected analytical data for **S15**: R_f = 0.45 (acetone/toluene, 3/17, v/v). Selected ^{1}H NMR data for β-isomer of **S15**: δ, 3.34 (s, 3H, OCH_3), 3.41 (m, 1H, H-5'), 3.48- 3.58 (m, 3H, H-2, 2', 4), 3.59-3.88 (m, 6H, H-3', 4', 5, 6a, 6'a, 6'b), 3.97-4.40 (m, 1H, H-3), 4.19 (dd, 1H, $J_{6a,\ 6b}$ = 11.2 Hz, H-6b), 4.36 (d, 1H, $J_{1',2'}$ = 7.6 Hz, H-1'), 4.39 (d, 1H, ^2J = 11.2 Hz, ½ CH_2Ph), 4.90-5.40 (m, 14H, H-1, 6½ × CH_2Ph), 7.10-7.50 (m, 32H, aromatic), 8.28-8.56 (m, 2H, aromatic) ppm. Selected ^{1}H NMR data for α-isomer of **S15**: δ, 3.37 (s, 3H, OCH_3), 3.45 (dd, 1H, $J_{2,3}$ = 10.0 Hz, H-2), 3.48-3.58 (m, 2H, H-2', 5'), 3.59-3.88 (m, 7H, H- 4, 4', 5, 6a, 6b, 6'a, 6'b), 3.94 (dd, 1H, $J_{3',4'}$ = 9.0 Hz, H-3'), 3.97-4.40 (m, 1H, H-3), 4.40 (d, 1H, ^2J = 12.3 Hz, ½ CH_2Ph), 4.90-5.40 (m, 15H, H-1, 1', 6½ × CH_2Ph), 7.10-7.50 (m, 32H, aromatic), 8.28-8.56 (m, 2H, aromatic) ppm. Selected ^{13}C NMR data for the sugar region of α/β-**S15**: δ, 55.3, 55.4, 66.3, 68.3, 68.8, 68.9, 70.0, 70.2, 70.5, 72.4 (× 2), 72.5, 73.6 (× 2), 73.7 (× 2), 75.0, 75.1 (× 3), 75.7, 75.9 (× 2), 76.0, 77.4, 77.9, 78.1, 78.2, 79.9, 80.2, 80.3, 81.7, 82.2, 82.3 (× 2), 84.9, 97.4, 98.2 (× 2), 104.0 ppm. HR-FAB MS $[M+Na]^+$ calcd for $C_{61}H_{65}NO_{11}Na$ 1010.4455, found 1010.4521.

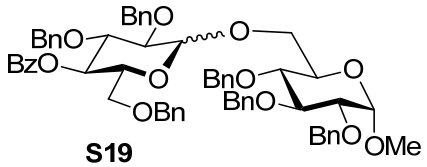
Methyl 2,3,4-Tri-O-benzyl-6-O-(2,3,6-tri-O-benzyl-4-O-(pyrid-3-ylmethyl)-α/β-D-glucopyranosyl)-α-D-glucopyranoside (S17).



S17

The title compound was obtained as a white amorphous solid from glycosyl donor **S16** and acceptor **2** in 82% (α/β = 1/1.6, 50 mM) and 74% yield (α/β = 1.3/1, 5 mM) under regular and high dilution reaction conditions, respectively. Selected analytical data of **S16**: R_f = 0.49 (acetone/toluene, 3/17, v/v). Selected ^{1}H NMR data for β-isomer of **S17**: δ, 3.34 (s, 3H, OCH_3), 3.43 (m, 1H, H-5'), 3.45- 3.60 (m, 7H, H-2, 2', 4, 5, 6b, 6'a, 6'b), 3.84-3.89 (m, 1H, H-3), 4.01 (m, 1H, H-3), 4.19 (dd, 1H, $J_{6a, 6b}$ = 10.9 Hz, H-6b), 4.35- 4.41 (m, 2H, H-1', ½ CH_2Ph), 4.48-5.40 (m, 14H, H-1, 6½ × CH_2Ph), 6.90-7.55 (m, 32H, aromatic), 8.45-8.55 (m, 2H, aromatic) ppm. Selected ^{1}H NMR data for α-isomer of **S17**: δ, 3.38 (s, 3H, OCH_3), 3.45-3.60 (m, 6H, H-2, 2', 4, 4', 6a', 6b'), 3.84-3.89 (m, 1H, H-5'), 3.95 (dd, 1H, $J_{3',4'}$ = 9.1 Hz, H-3'), 4.01 (m, 1H, H-3), 4.36-4.41 (m, 1H, ½ CH_2Ph), 4.48-5.40 (m, 15H, H-1, 1', 6½ × CH_2Ph), 6.90-7.55 (m, 32H, aromatic), 8.45-8.55 (m, 2H, aromatic) ppm. Selected ^{13}C NMR data for the sugar region of α/β-**S17**: δ, 55.3, 55.4, 66.4, 68.3, 68.8, 68.9, 70.0, 70.2, 70.5, 72.5, 73.0, 73.1, 73.6 (× 3), 73.7, 75.0 (× 3), 75.1, 75.7, 75.9 (× 2), 76.0, 77.4, 77.9, 78.2, 78.3, 79.9, 80.1, 80.3, 81.6, 82.1, 82.2, 82.3, 84.8, 97.4, 98.2 (× 2), 104.0 ppm. HR-FAB MS $[M+Na]^+$ calcd for $C_{61}H_{65}NO_{11}Na$ 1010.4455, found 1010.4732.

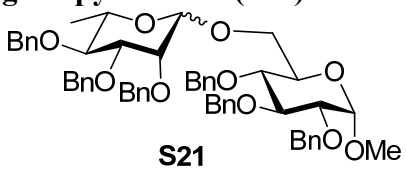
Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(4-*O*-benzoyl-2,3,6-tri-*O*-benzyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (S19).



S19

The title compound was obtained as a colorless syrup from glycosyl donor **S18** and acceptor **2** in 97% (α/β = 1/2.5, 50 mM) and 93% yield (α/β > 1/2.6, 5 mM) under regular and high dilution reaction conditions, respectively. Analytical data for the title compound was in accordance with that reported previously.[16]

Methyl 2,3,4-Tri-O-benzyl-6-O-(2,3,4-tri-O-benzyl-α/β-L-rhamnopyranosyl)-α-D-glucopyranoside (S21).

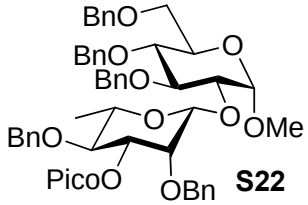


S21

The title compound was obtained as a colorless syrup from glycosyl donor **S20** and acceptor **2** in 85% yield (α/β = 1.1/1, 50 mM). Analytical data for **S21**: R_f = 0.59 (ethyl acetate/hexane, 2/3,

v/v). Selected ^{1}H NMR data for β-isomer of **S21**: δ, 1.36 (d, 3H, $J_{5',6'}$ = 5.9 Hz, C-6'), 3.27 (s, 3H, OCH_3), 3.30-3.36 (m, 1H, H-5'), 3.42-3.52 (m, 2H, H-2, 3'), 3.57-3.73 (m, 3H, H-4, 4', 6a), 3.75 (m, 1H, H-5), 3.93- 4.20 (m, 2H, H-2', 3), 4.29 (dd, 1H, $J_{5,6b}$ = 3.5 Hz, $J_{6a,6b}$ = 11.2 Hz, H-6b), 4.44 (s, 1H, H-1'), 4.36- 5.02 (m, 13H, H-1, 6 × CH_2Ph), 7.15-7.50 (m, 30H, aromatic) ppm; Selected ^{1}H NMR data for α-isomer of **S21**: δ, 1.31 (d, 3H, $J_{5',6'}$ = 5.9 Hz, C-6'), 3.20-3.85 (m, 4H, H-4, OCH_3), 3.42-3.52 (m, 2H, H-2, 3'), 3.57-3.73 (m, 3H, H-5, 5', 6a), 3.81-3.86 (m, 2H, H-4', 6b), 3.93-4.20 (m, 1H, H-3), 4.36-5.02 (m, 14H, H-1, 1', 6 × CH_2Ph), 7.15-7.50 (m, 30H, aromatic). Selected ^{13}C NMR data for the sugar region of α/β-**S21**: δ,18.1, 18.2, 55.2, 55.4, 66.2, 67.4, 68.2, 70.0, 70.2, 71.5, 72.2, 72.5, 72.9, 73.5, 73.7, 74.2, 74.4, 75.1, 75.2, 75.4, 75.6, 75.7, 75.9, 76.0, 77.4, 78.0 (× 2), 79.9, 80.0, 80.1, 80.4, 80.8, 82.1 (× 2), 97.9, 98.4, 98.5, 101.6 ppm. HR-FAB MS $[M+Na]^+$ calcd for $C_{55}H_{60}NaO_{10}$ 903.4084, found 903.4221.

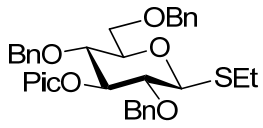
Methyl 3,4,6-Tri-O-benzyl-2-O-(2,4-di-O-benzyl-3-O-picoloyl-β-L-rhamnopyranosyl)-α-D-glucopyranoside (S22).



S22

The title compound was obtained as colorless syrup from glycosyl donor **3l** and acceptor **4** in 90% yield (α/β > 1:25, 50 mM). Analytical data for **S22**: R_f = 0.49 (acetone/toluene, 3/17, v/v); $[\alpha]_D^{22}$ +65.4 (c = 1.0, $CHCl_3$); ^{1}H NMR: δ, 1.45 (d, 3H, $J_{5',6'}$ = 6.1 Hz, C-6'), 3.42-3.55 (m, 4H, H-5', OCH_3), 3.68-3.87 (m, 4H, H-4, 5, 6a, 6b), 3.56 (dd, 1H, $J_{4,5}$ = 9.3 Hz, H-4), 3.62-3.73 (m, 2H, H-5, 6b), 3.77 (dd, 1H, $J_{4',5'}$ = 9.4 Hz, H-4'), 3.91(dd, 1H, $J_{4',5'}$ = 9.5 Hz, H-4'), 3.95-4.18 (m, 2H, H-2, 3), 4.20 (d, 1H, $J_{2',3'}$ = 3.2 Hz, H-2'), 4.61 (dd, 2H, ^2J = 12.2 Hz, CH_2Ph), 4.70 (dd, 2H, ^2J = 10.9 Hz, CH_2Ph), 4.78 (s, 1H, H-1'), 4.79 (dd, 2H, ^2J = 10.8 Hz, CH_2Ph), 4.85(dd, 2H, ^2J = 12.8 Hz, CH_2Ph), 4.92 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1), 5.12-5.25 (m, 2H, H-3', CH_2Ph), 6.90-7.65 (m, 26H, aromatic), 7.82 (dd, 1H, J = 7.5 Hz, aromatic), 7.97 (d, 1H, J = 7.8 Hz, aromatic), 8.84 (d, 1H, J = 4.5 Hz, aromatic) ppm; ^{13}C NMR: δ, 18.2, 55.3, 68.7, 70.2, 72.2, 73.7, 74.7, 75.2, 75.3, 75.5, 75.7, 77.3 (× 2), 78.2, 78.8, 81.1, 97.6, 99.1 ($^1J_{C1,H1}$ = 166.9 Hz, $^1J_{C1',H1'}$ = 152.6 Hz), 125.4, 127.1, 127. 5 (× 2), 127.8, 127.9 (× 2), 128.0 (× 2), 128.1 (× 5), 128.3 (× 2), 128.5 (× 9), 128.6 (× 2), 137.0, 138.2 (× 2), 138.4, 138.6, 139.2, 147.8, 150.2, 164.3 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{54}H_{57}NaO_{11}$ 918.3829, found 918.3891.

NMR Spectra



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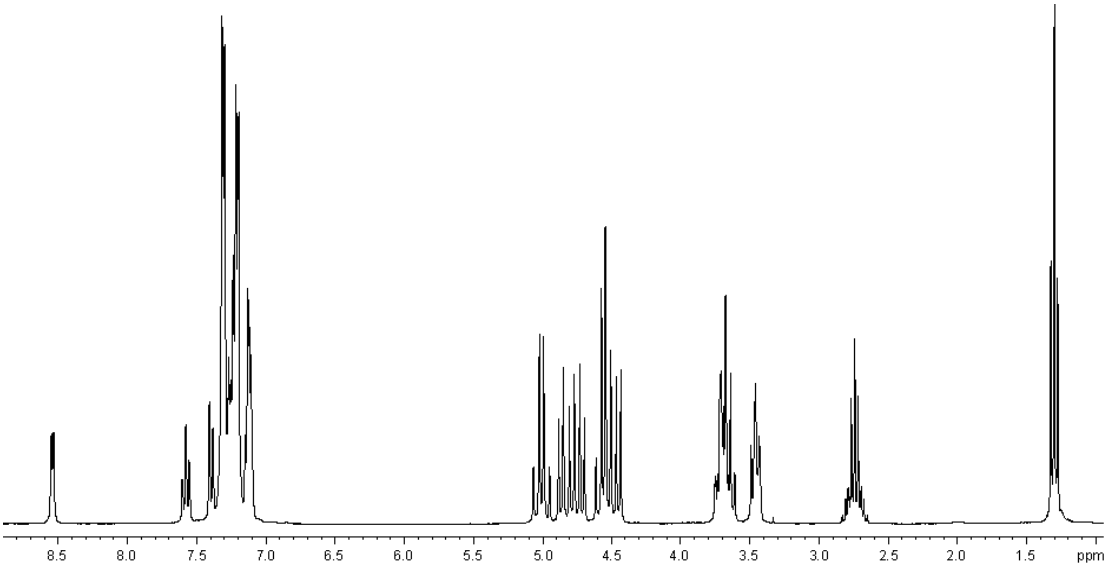

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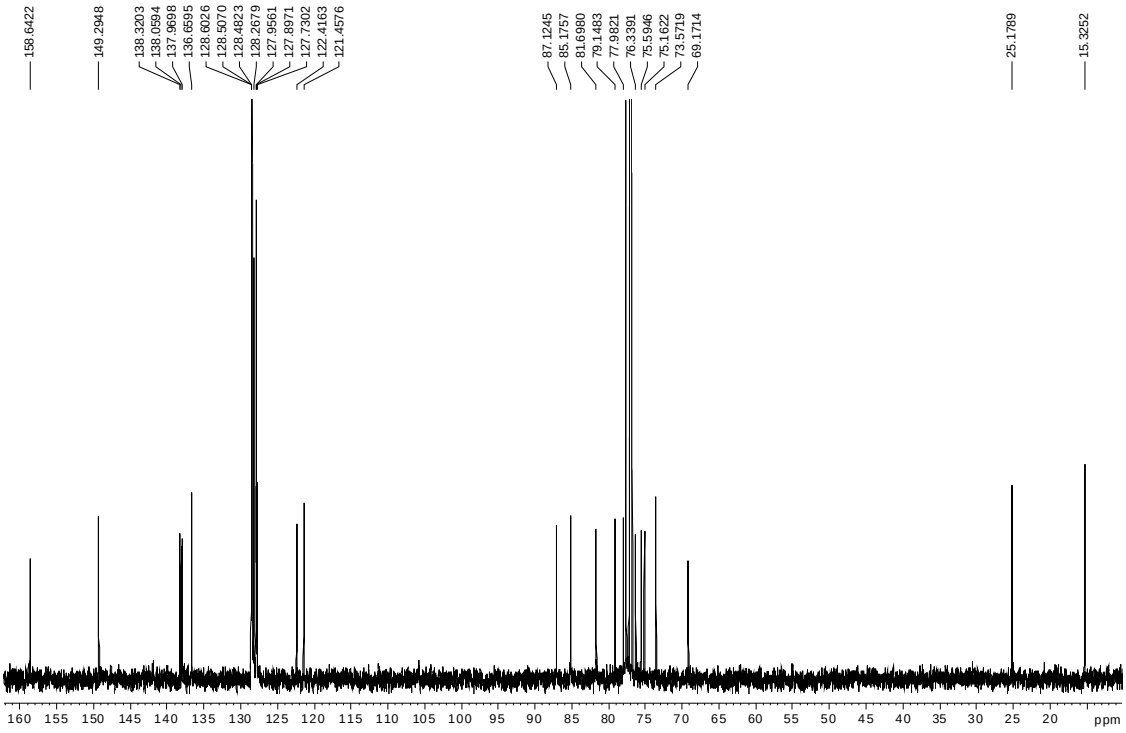

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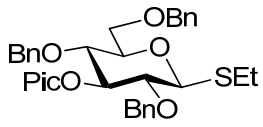

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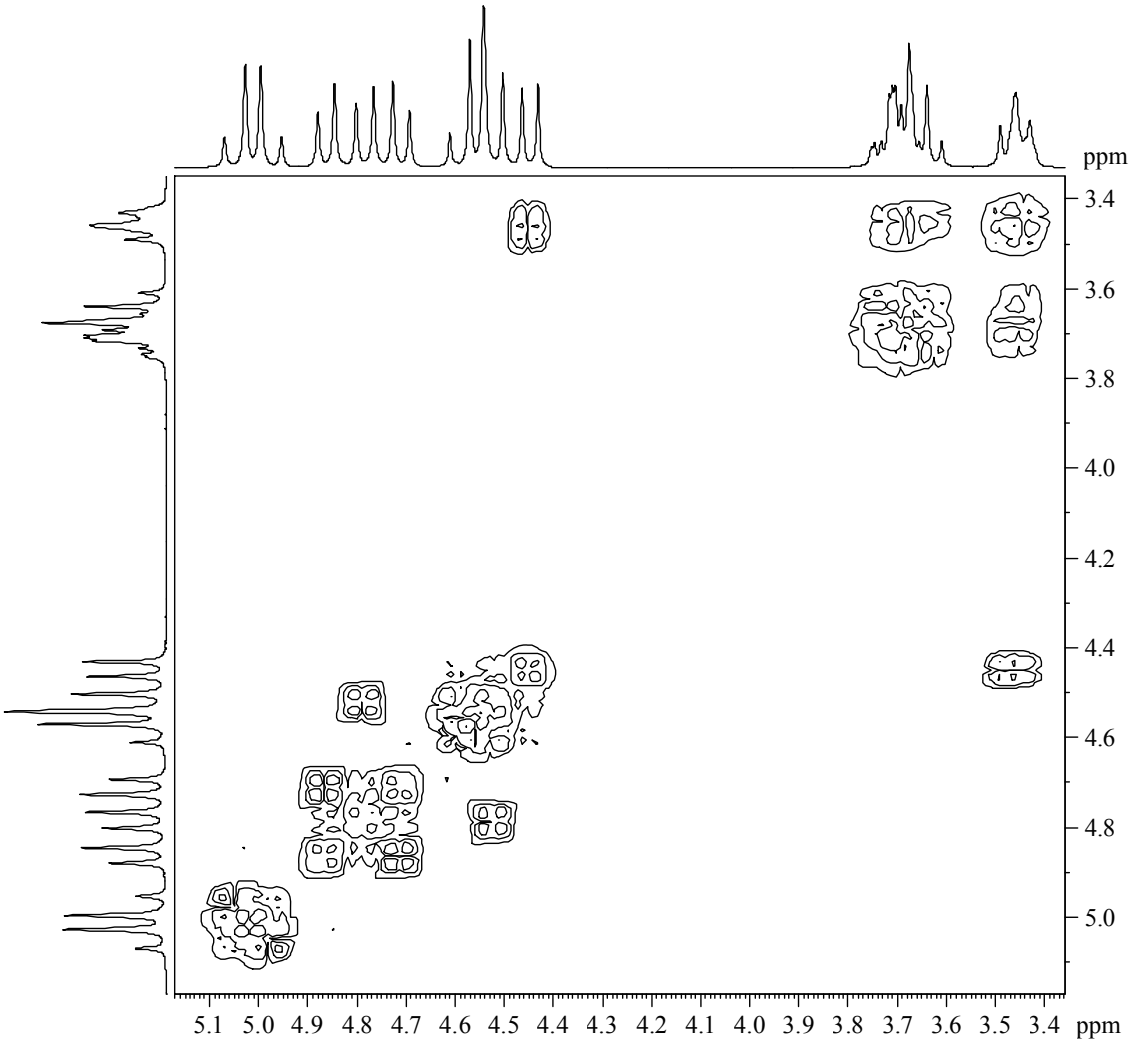

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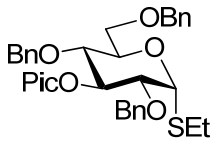
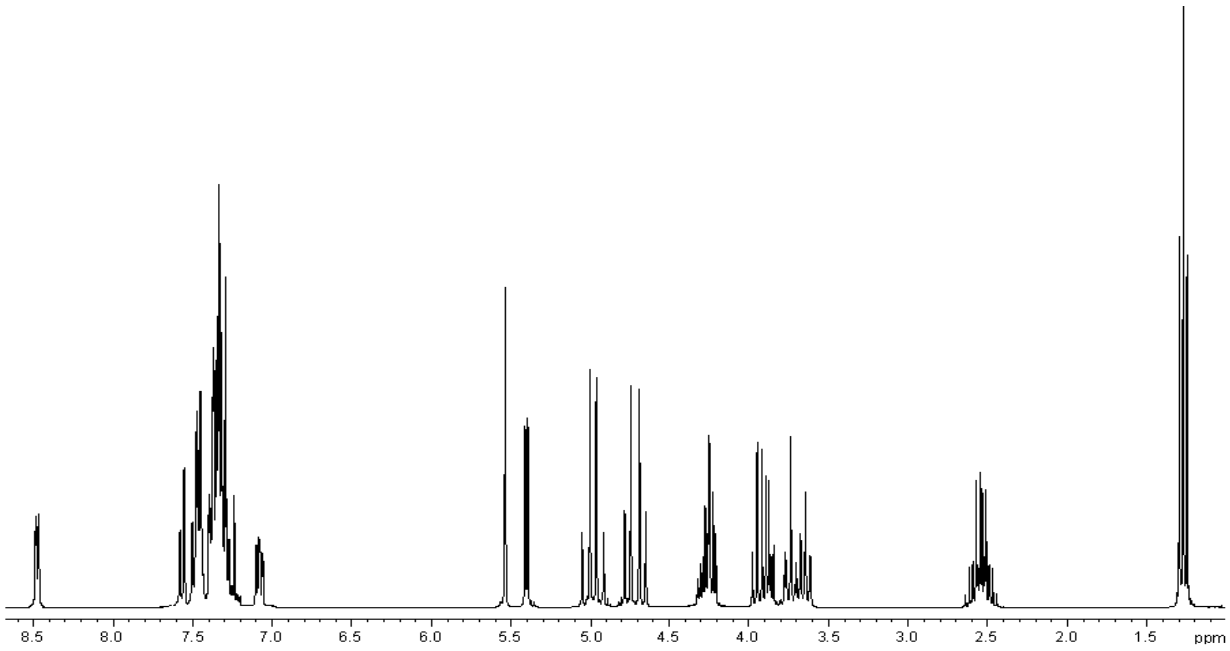


α-1c



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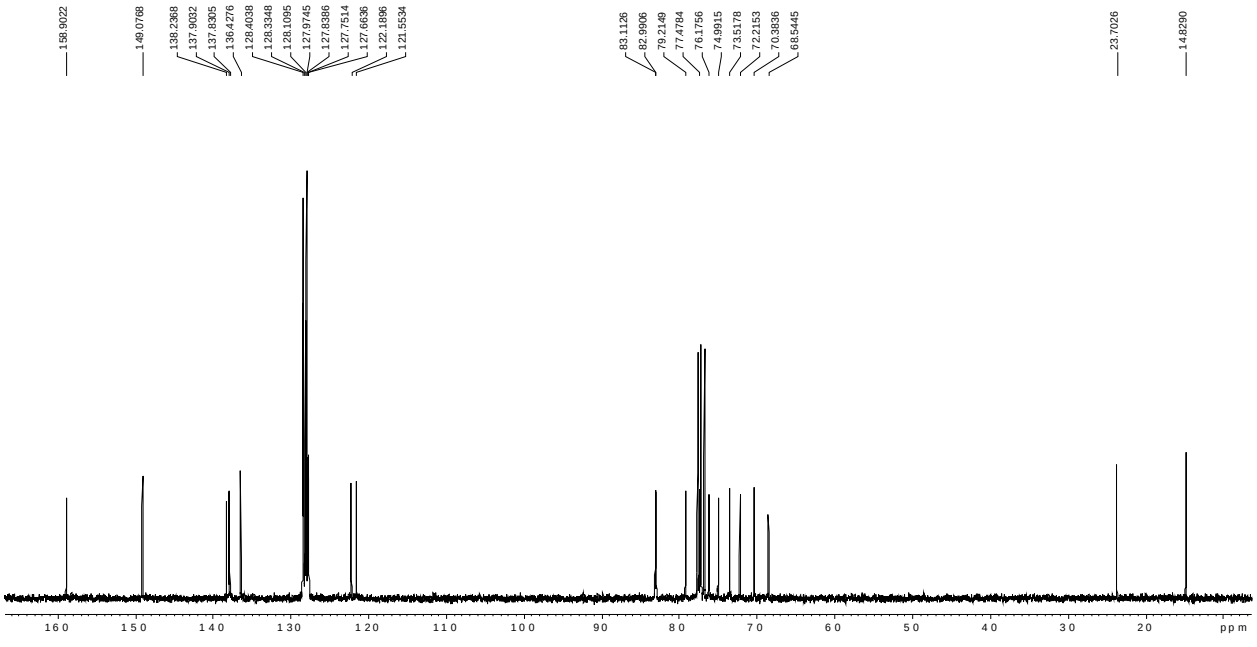

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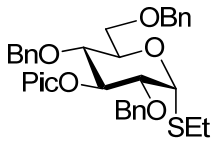
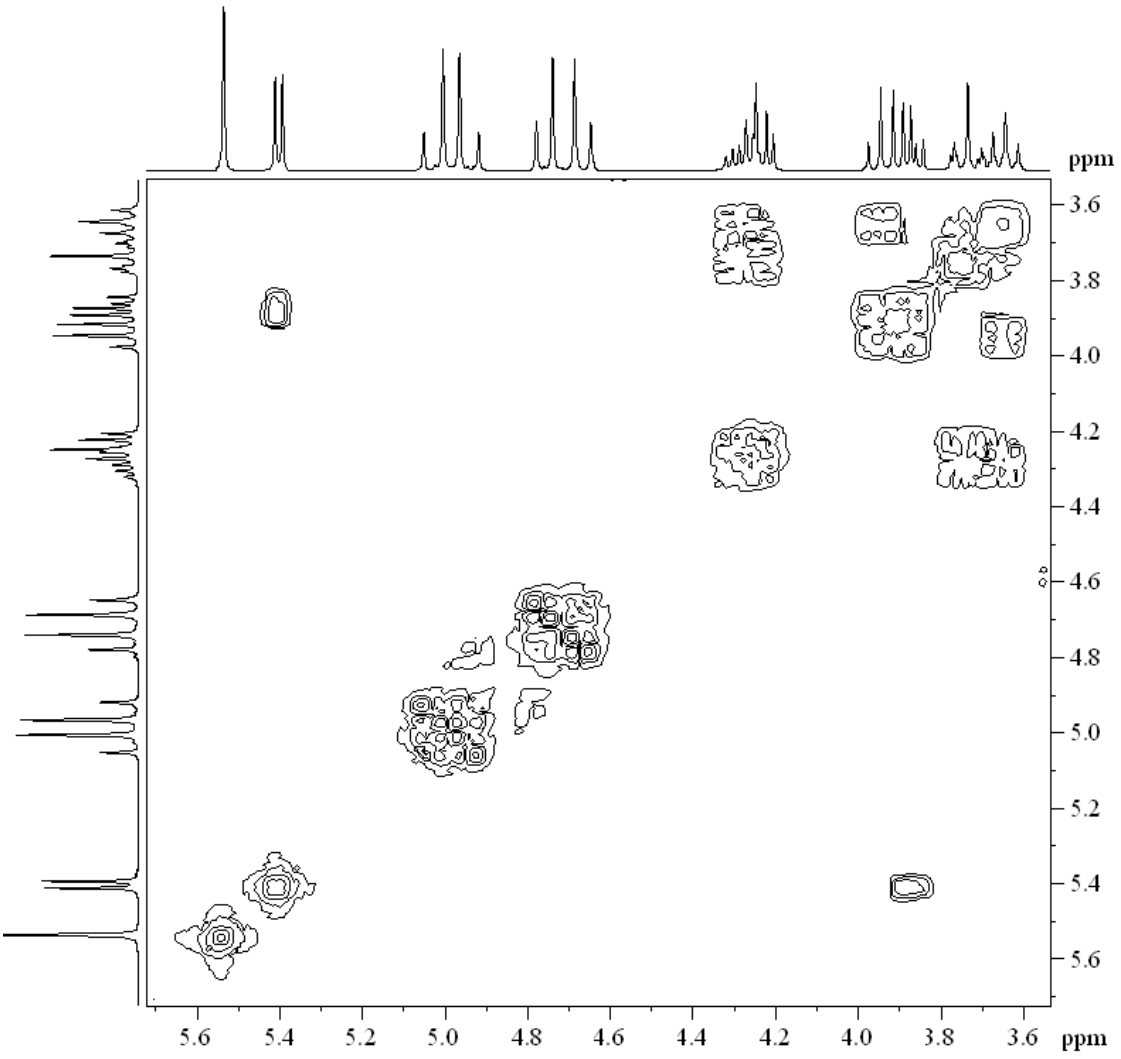


α-1c



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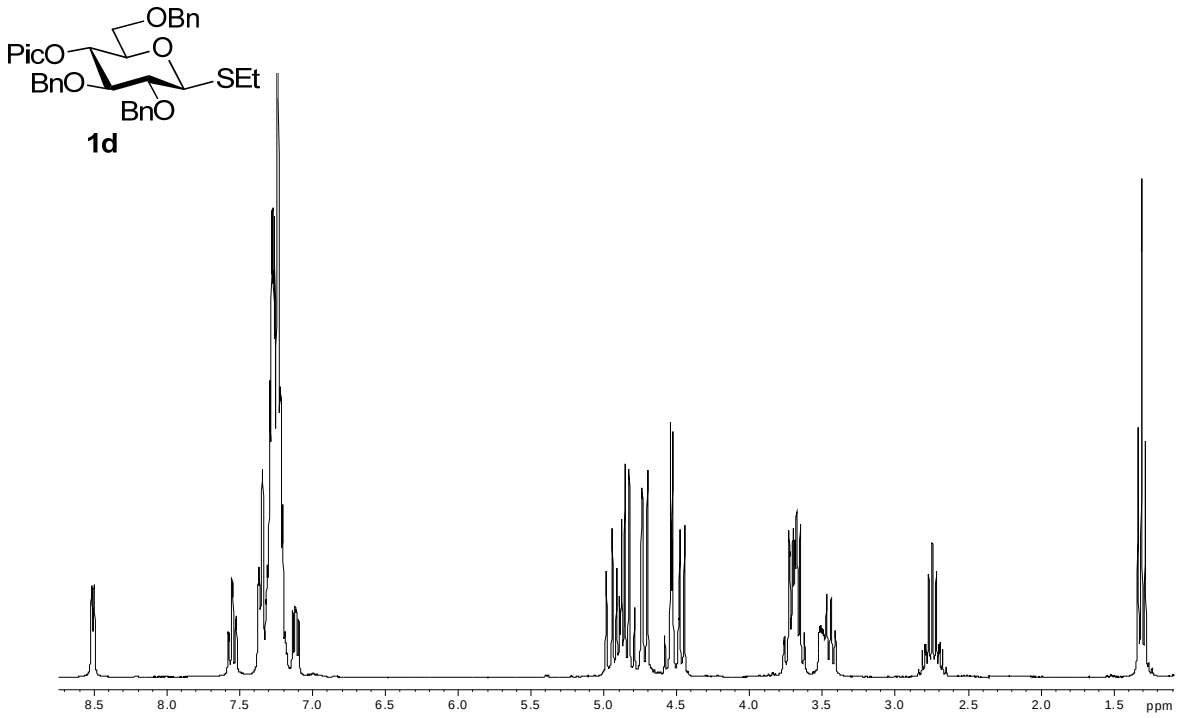

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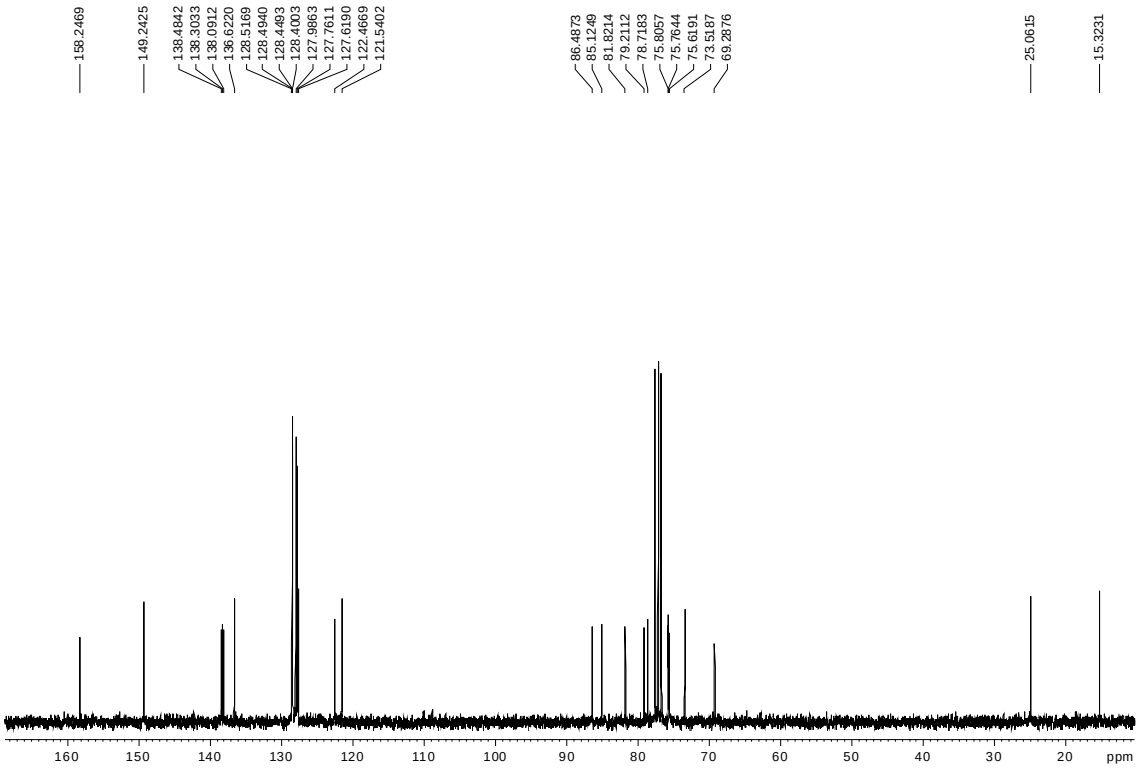

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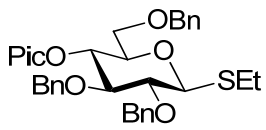

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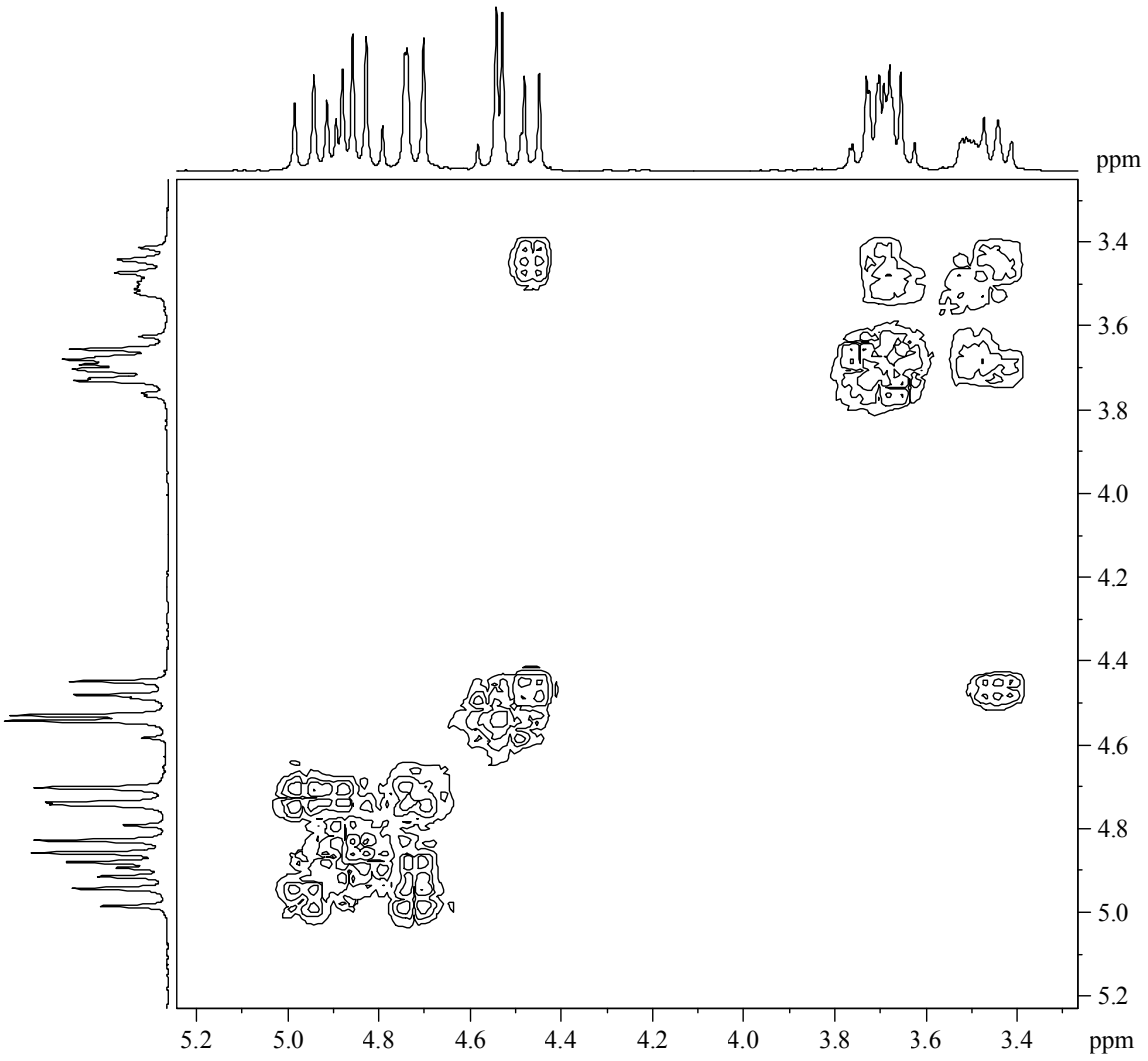

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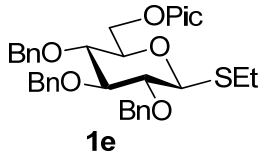

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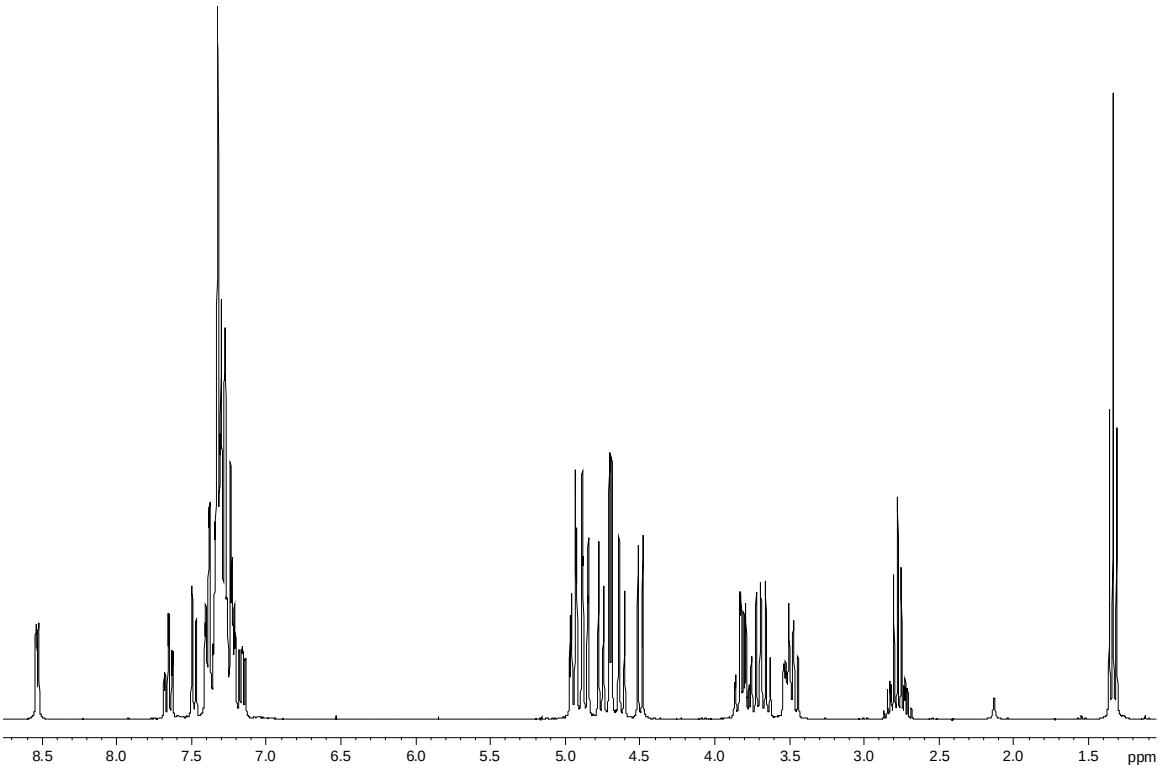

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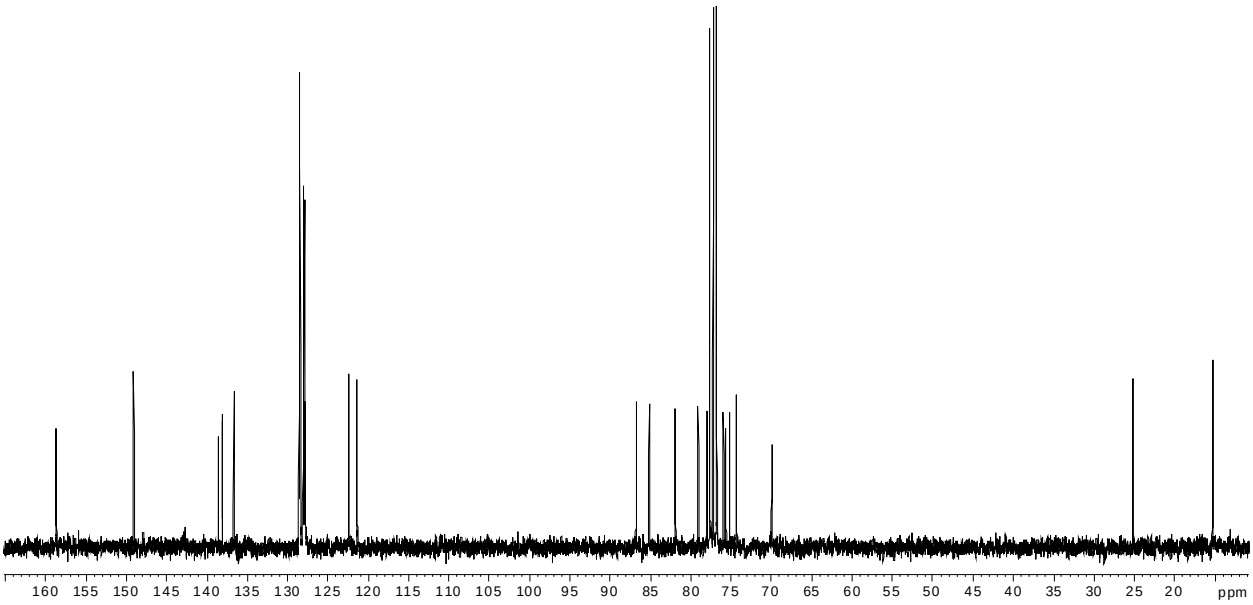

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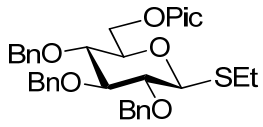

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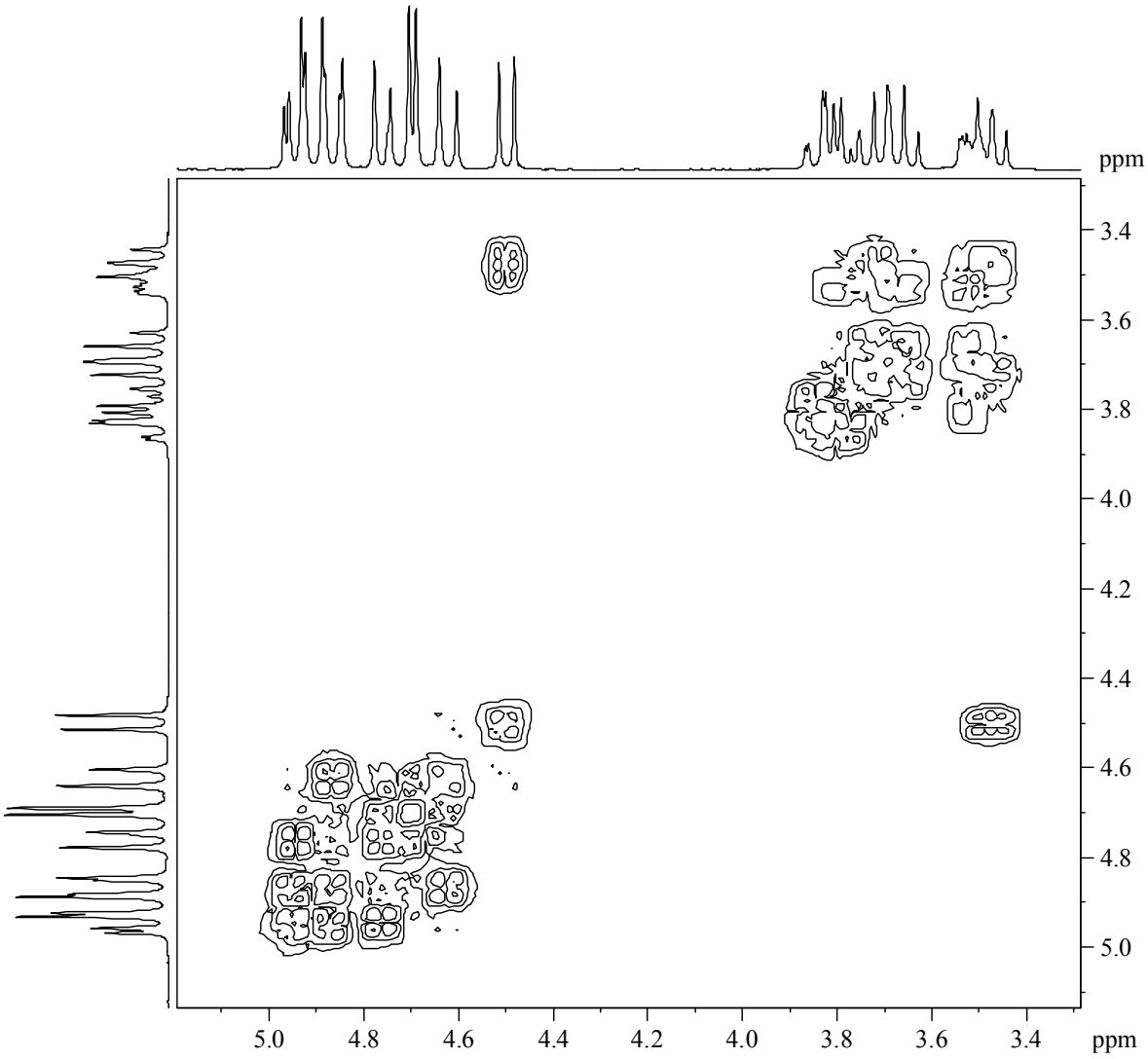

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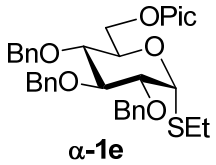
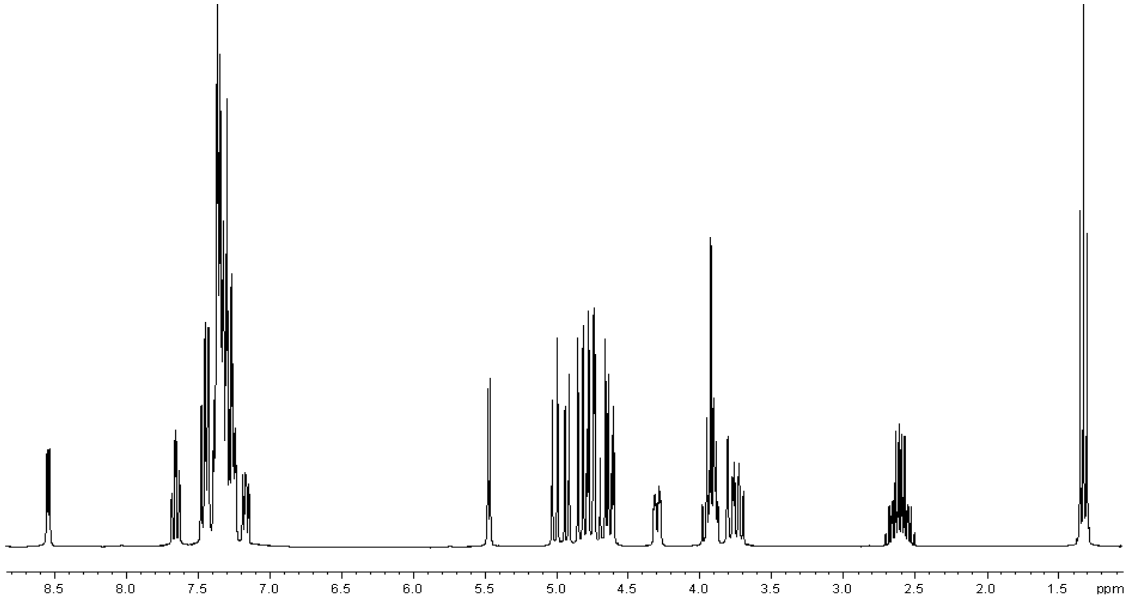


α-1e



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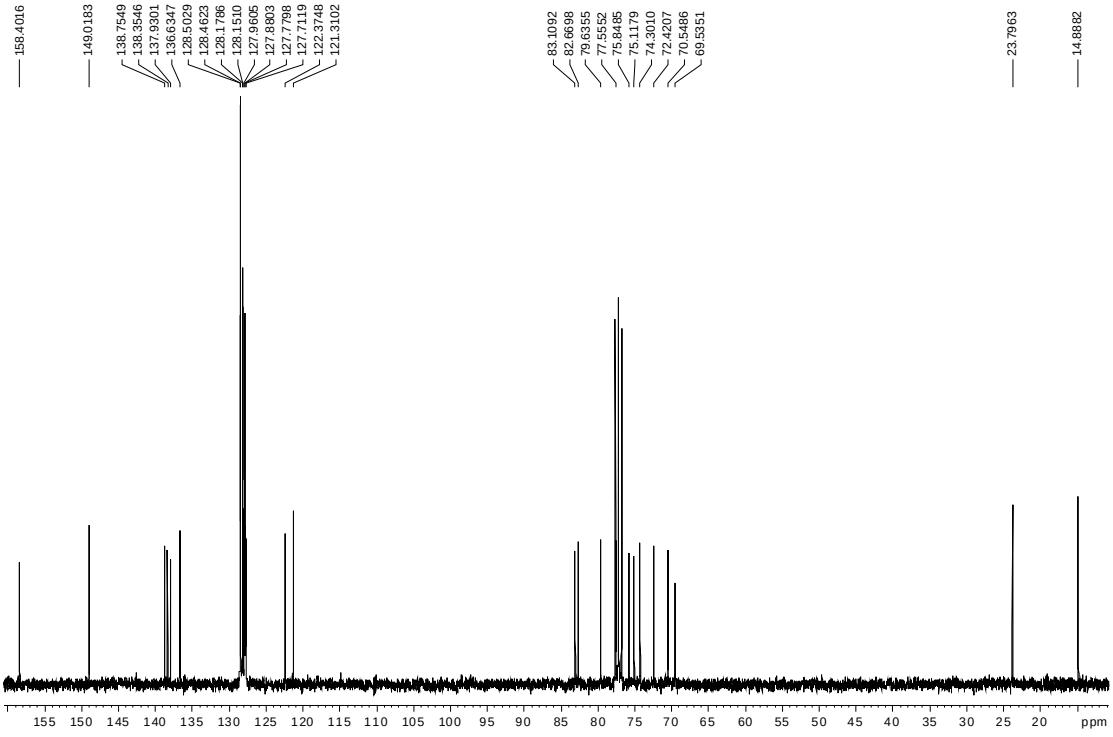

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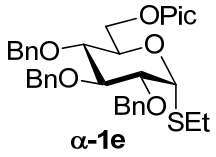
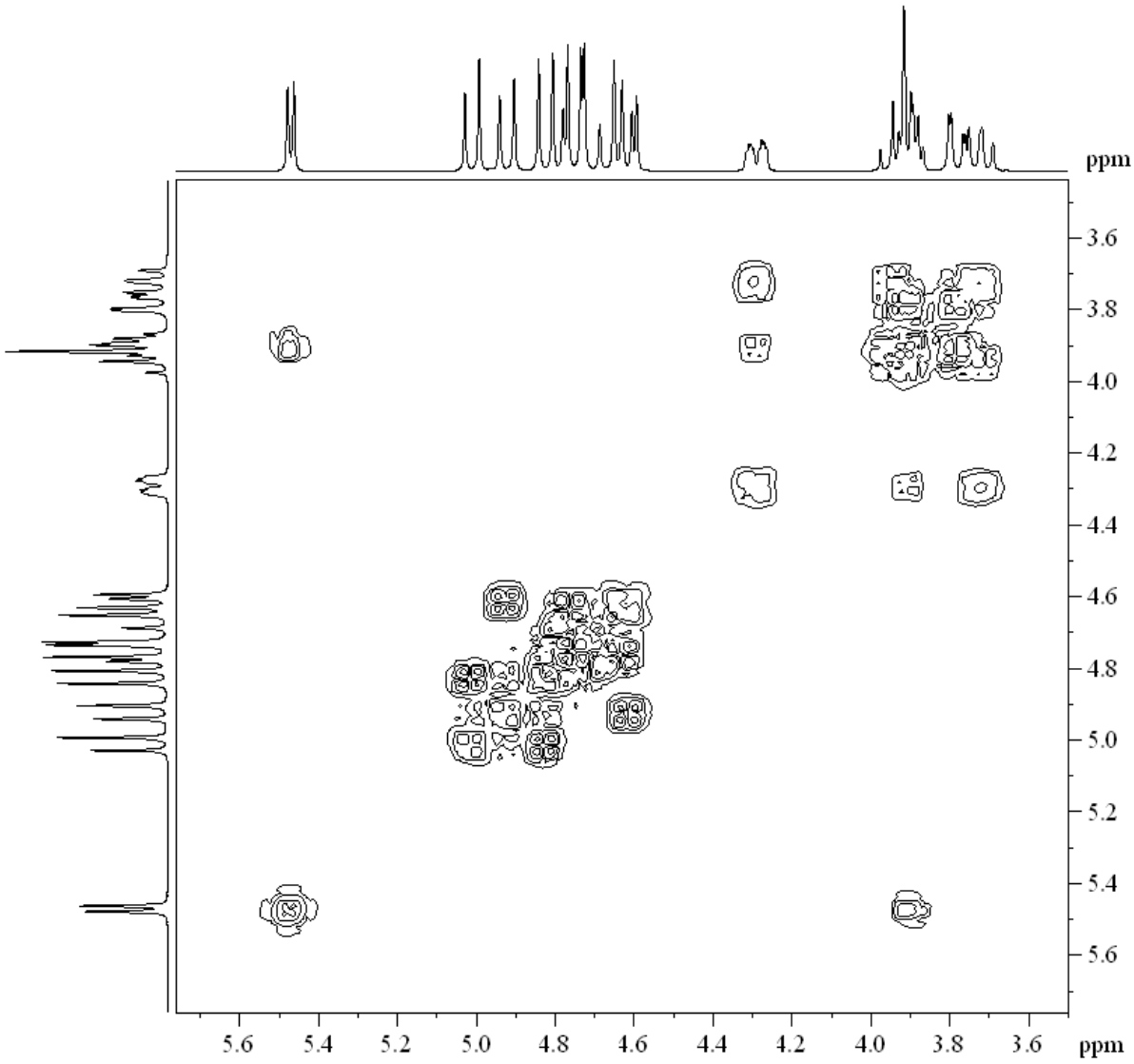


α-1e



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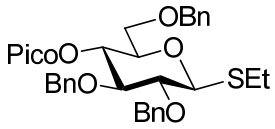

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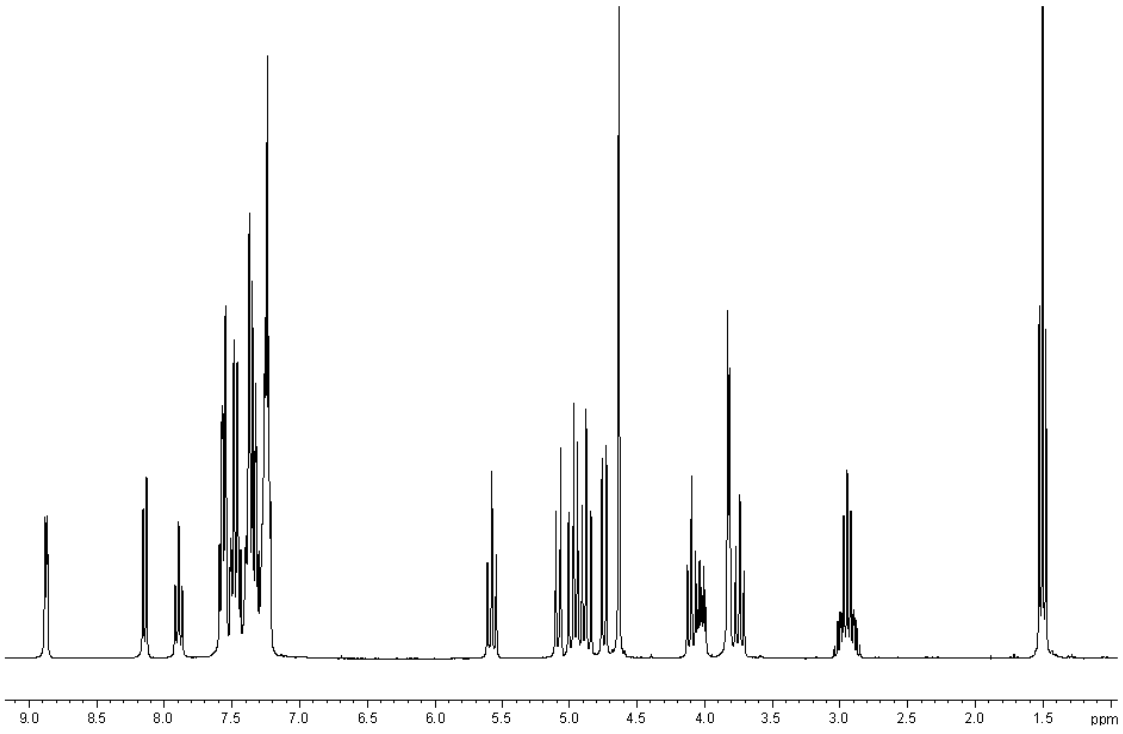

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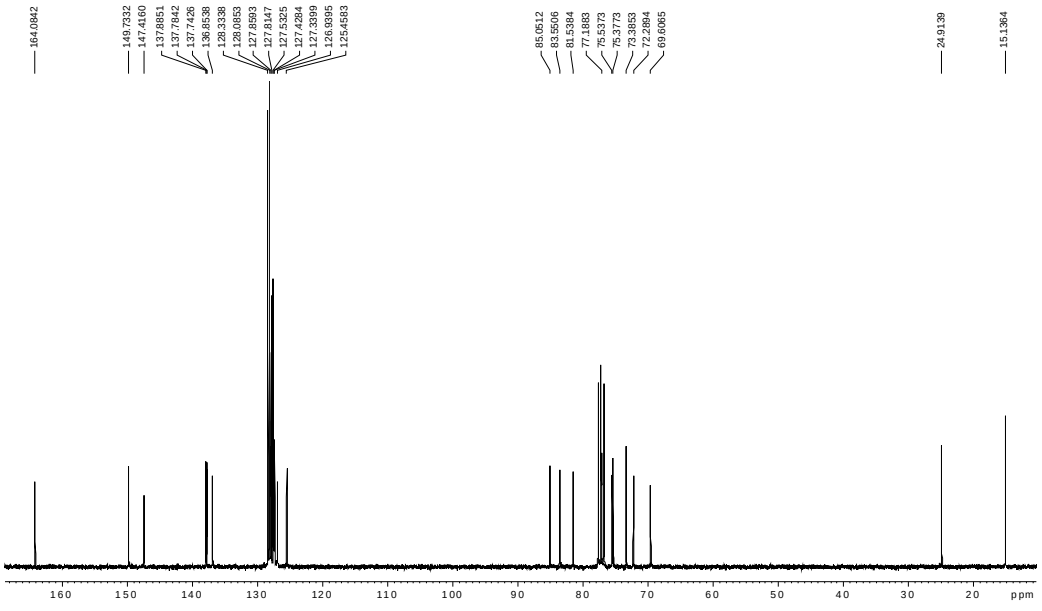

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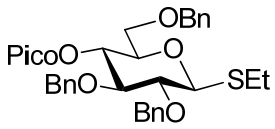

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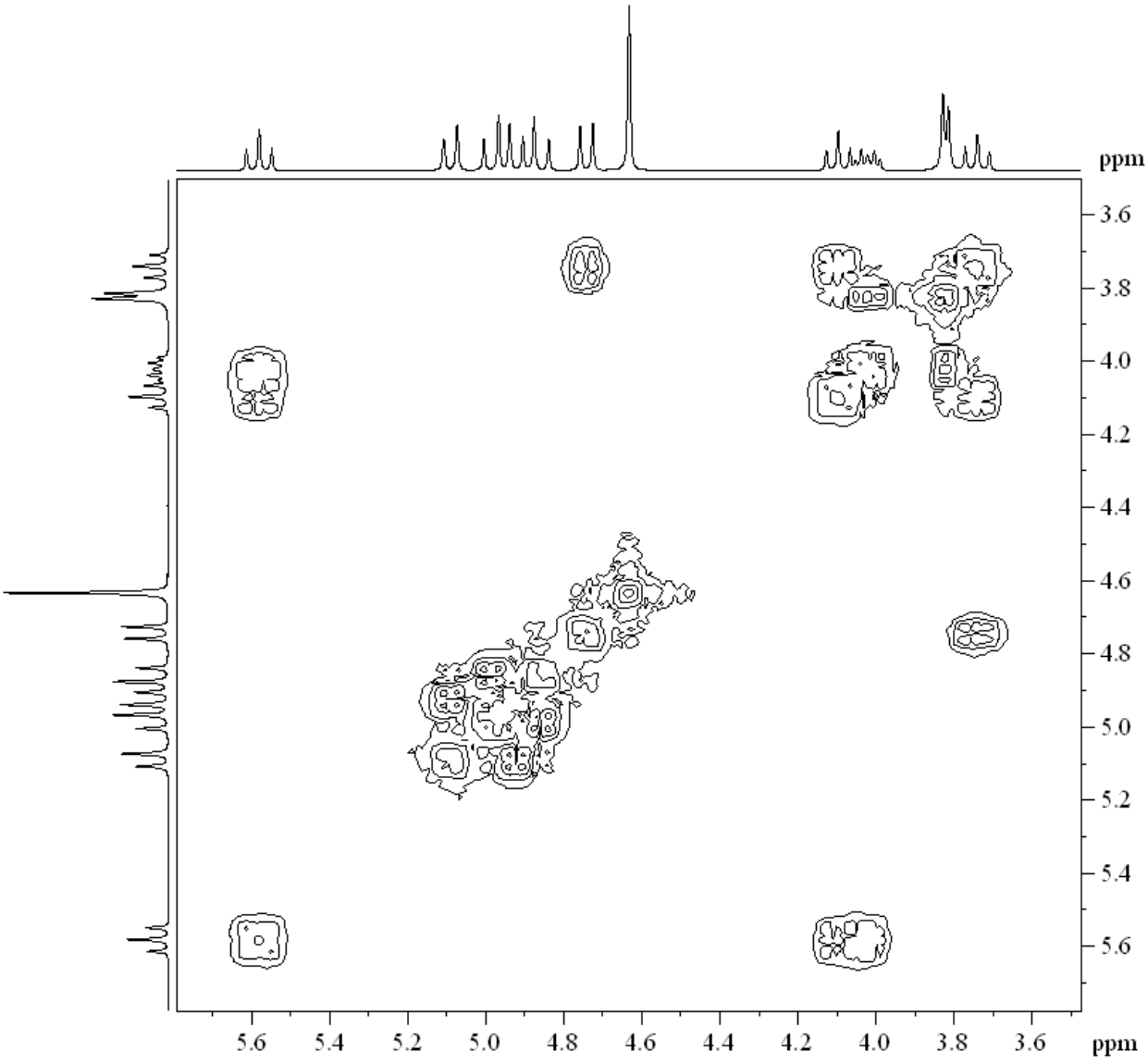

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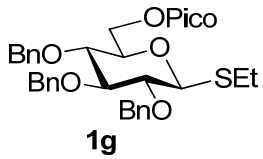

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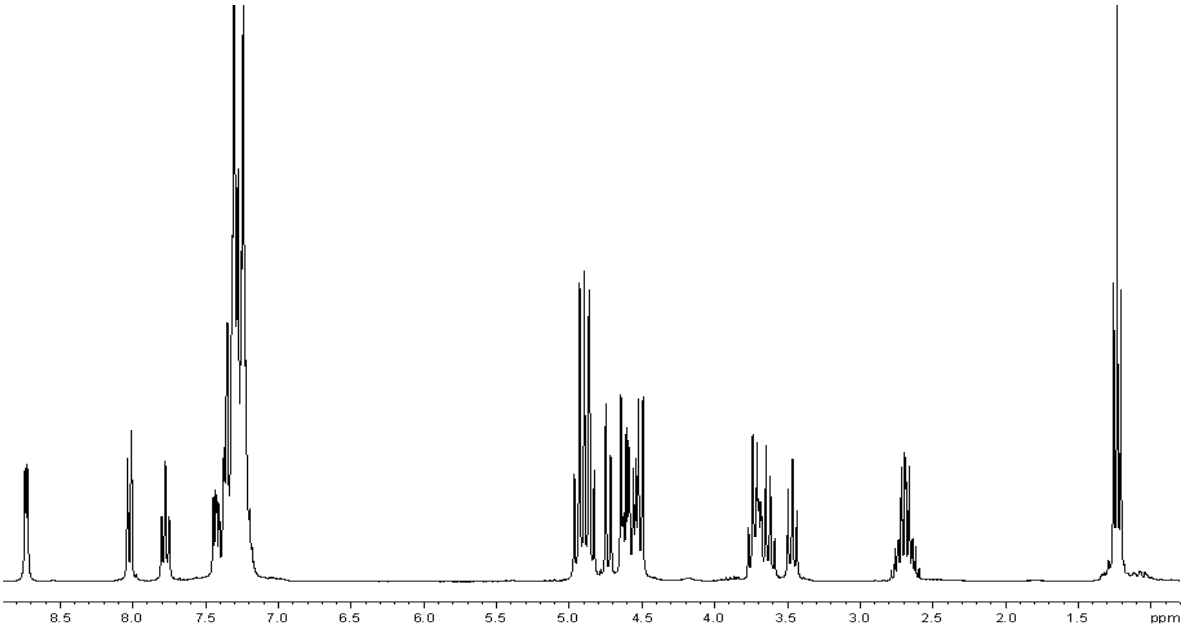

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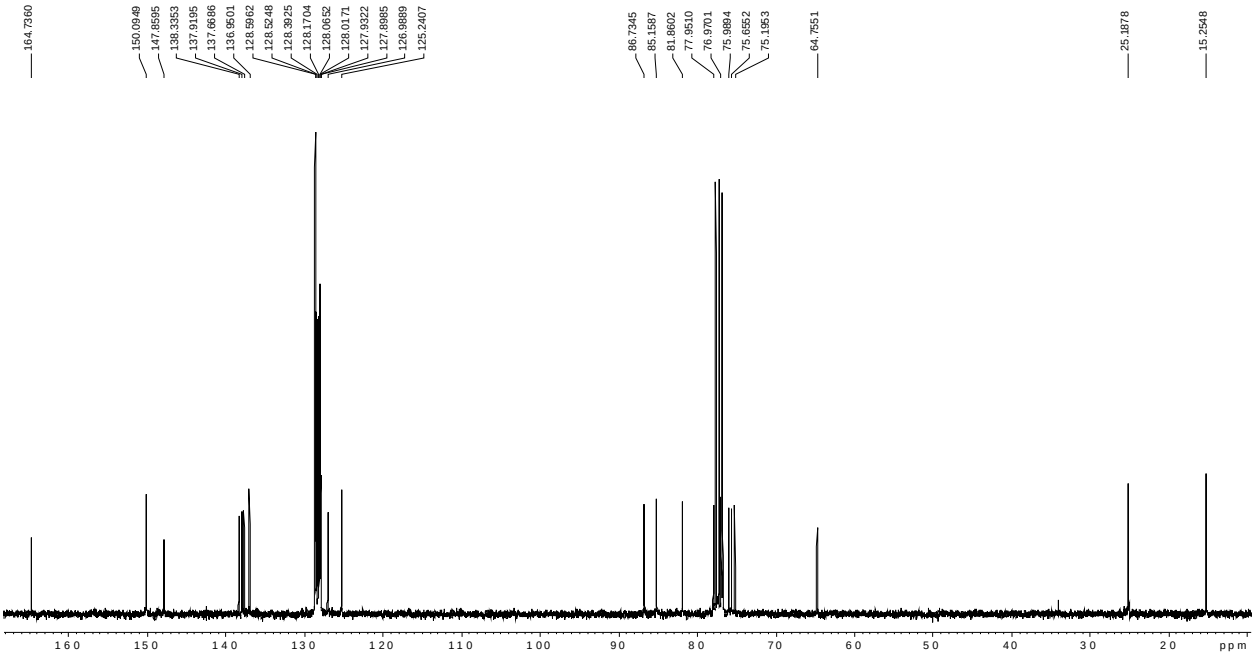

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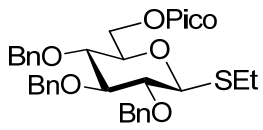

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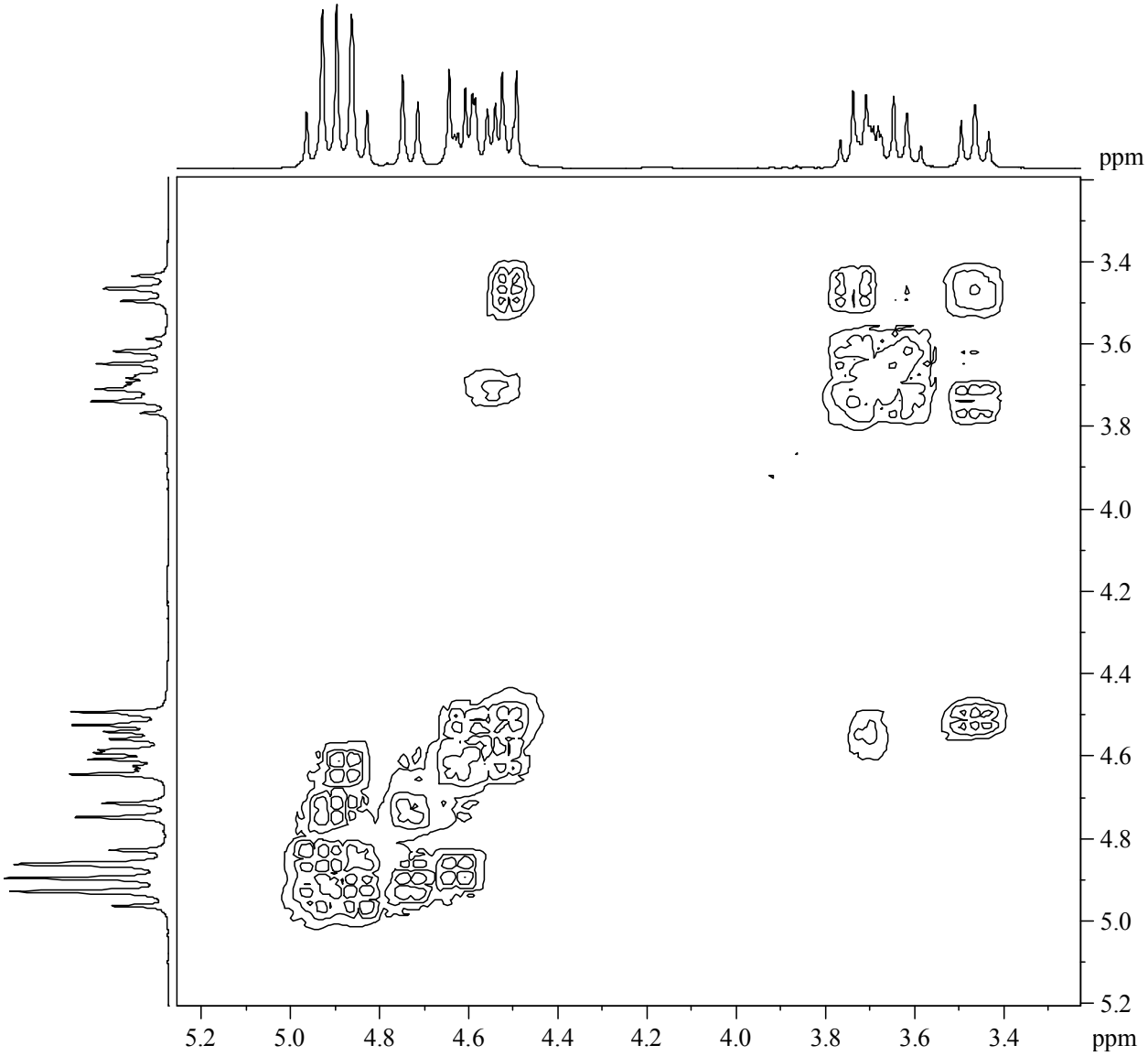

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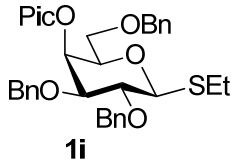

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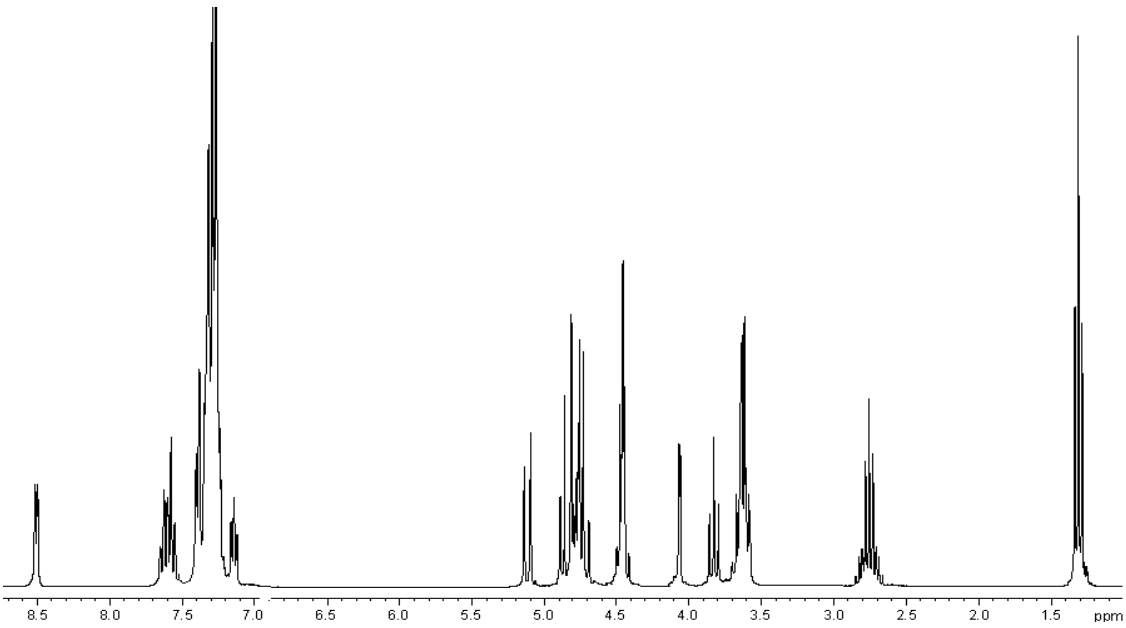

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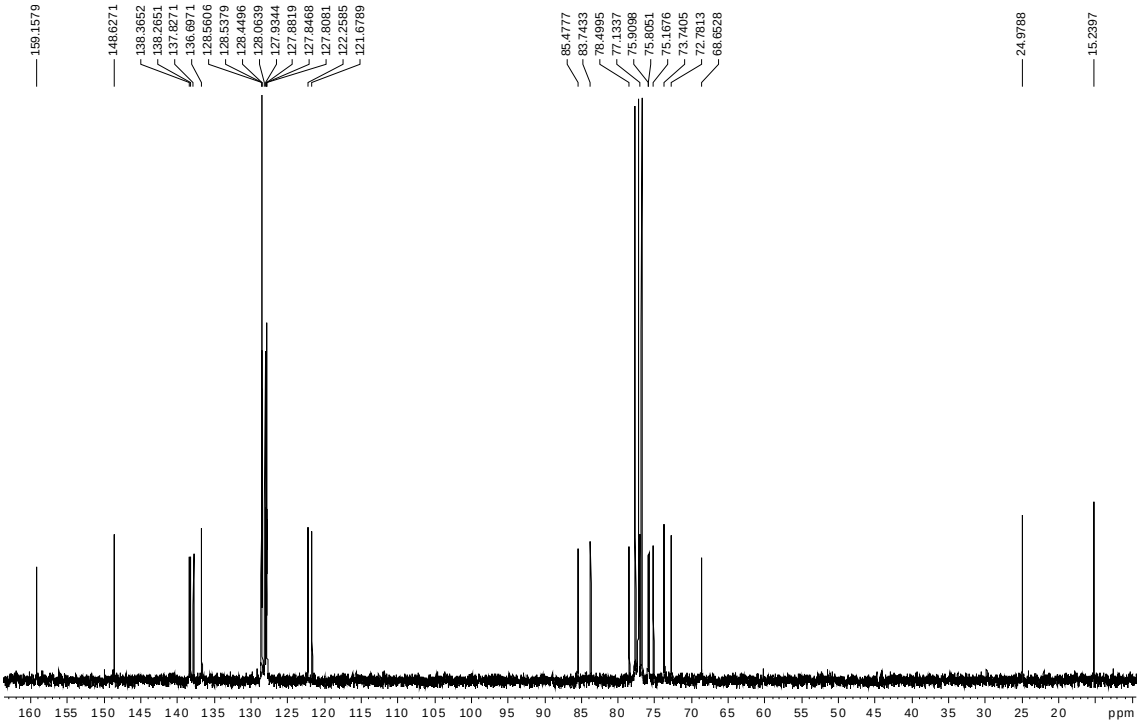

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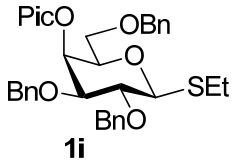

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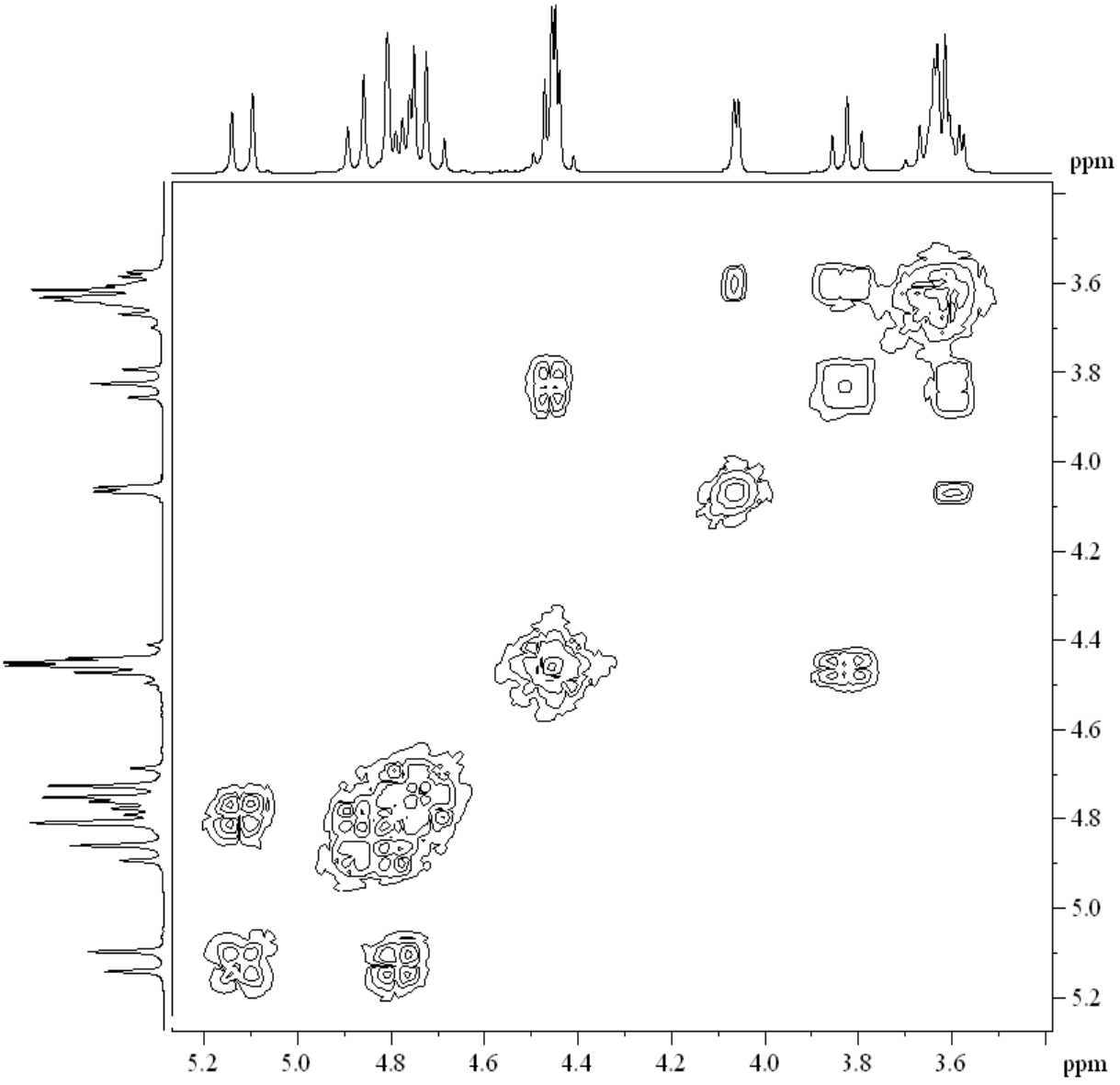

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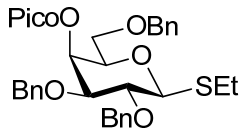

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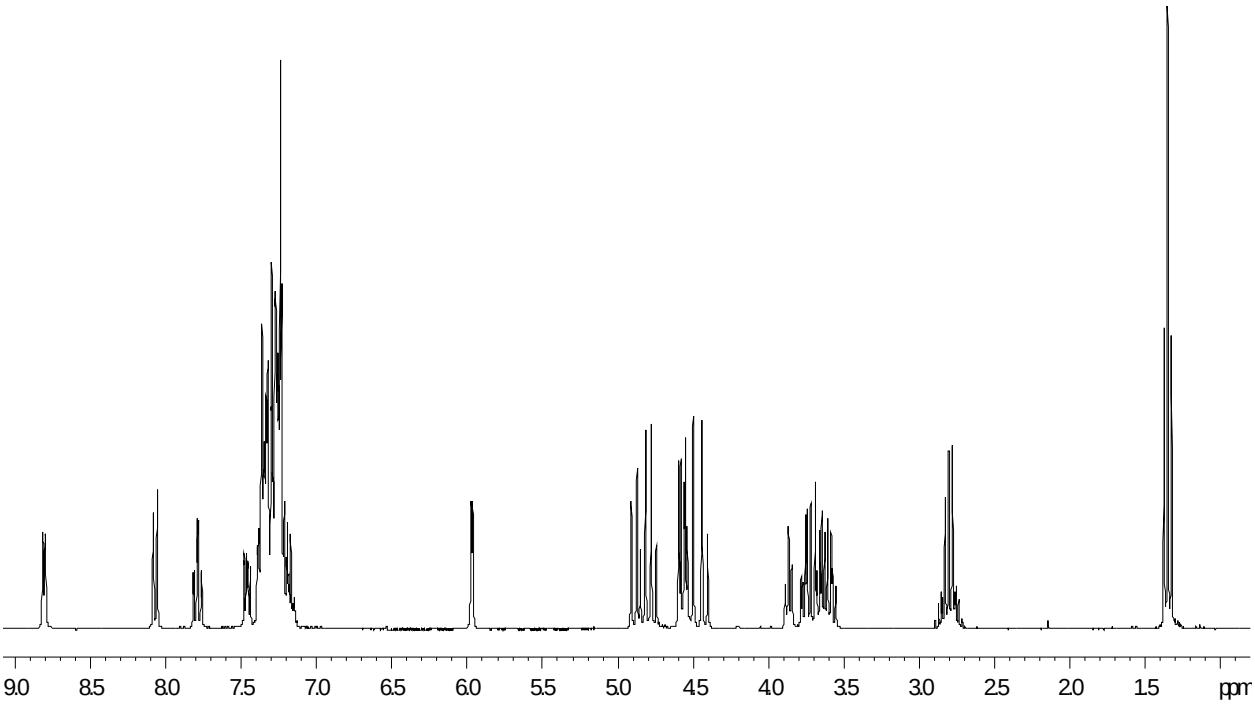

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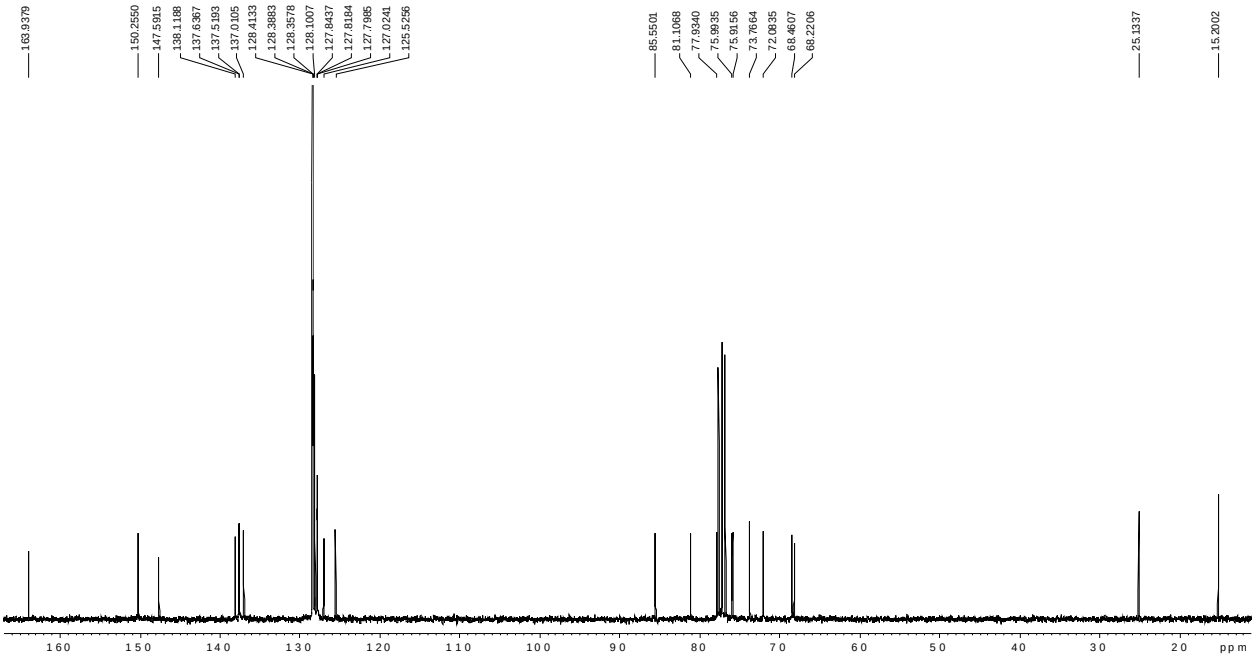

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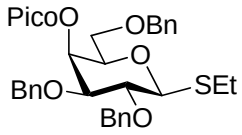

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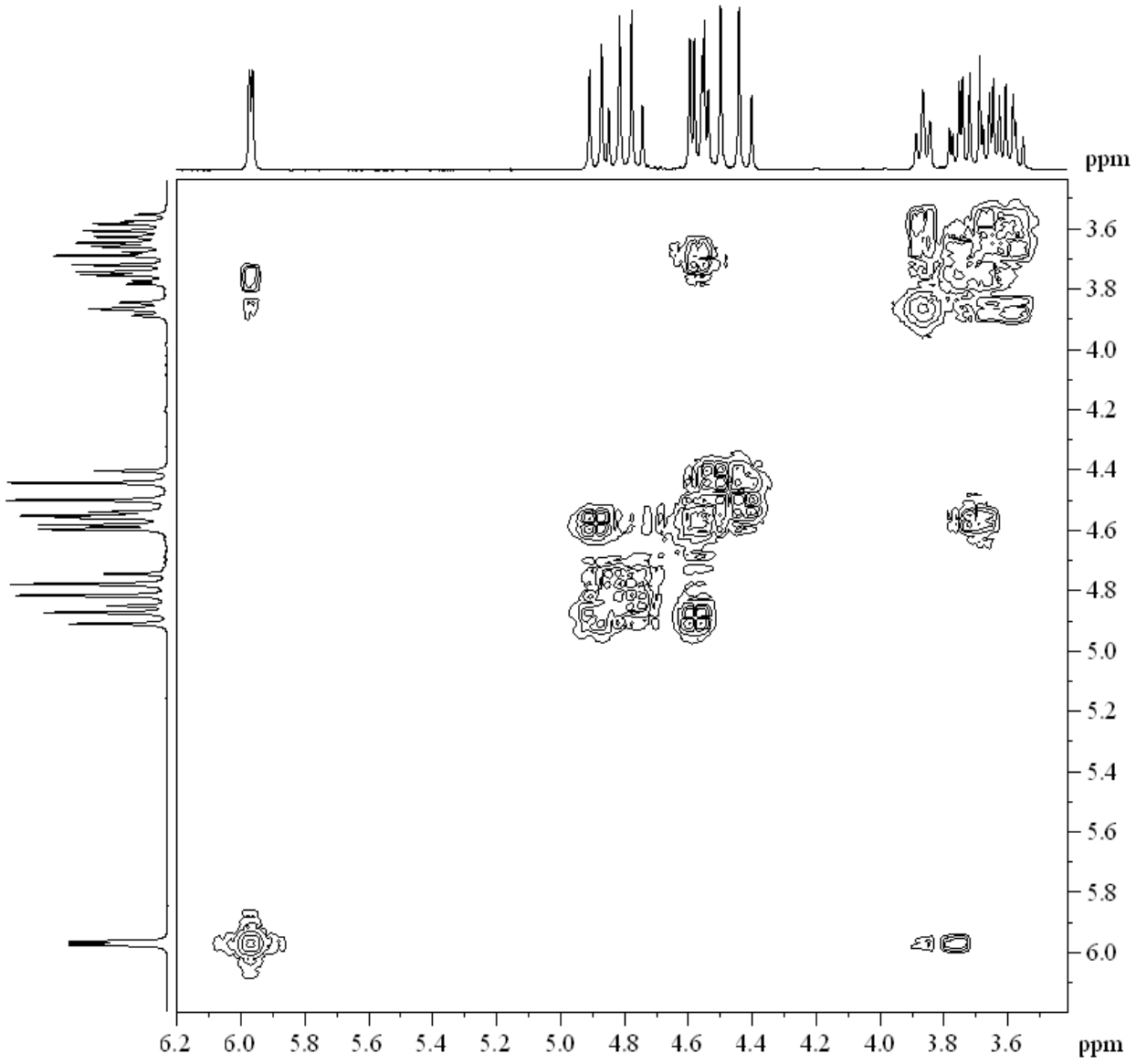

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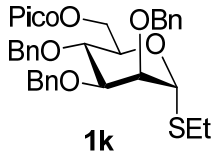

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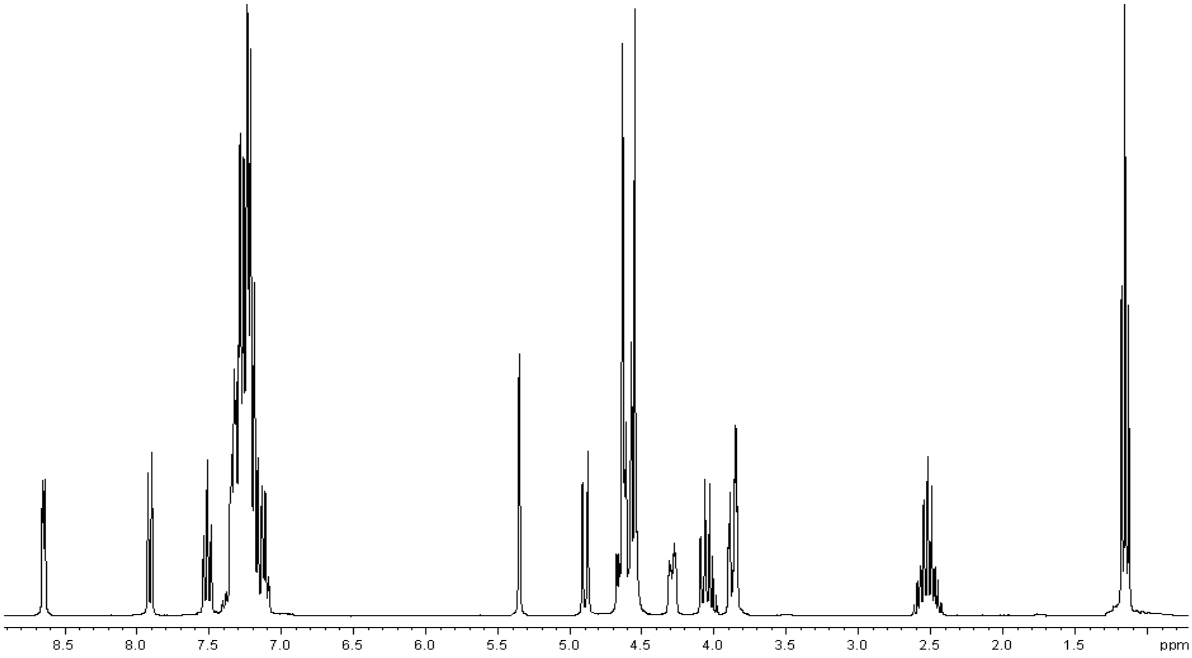

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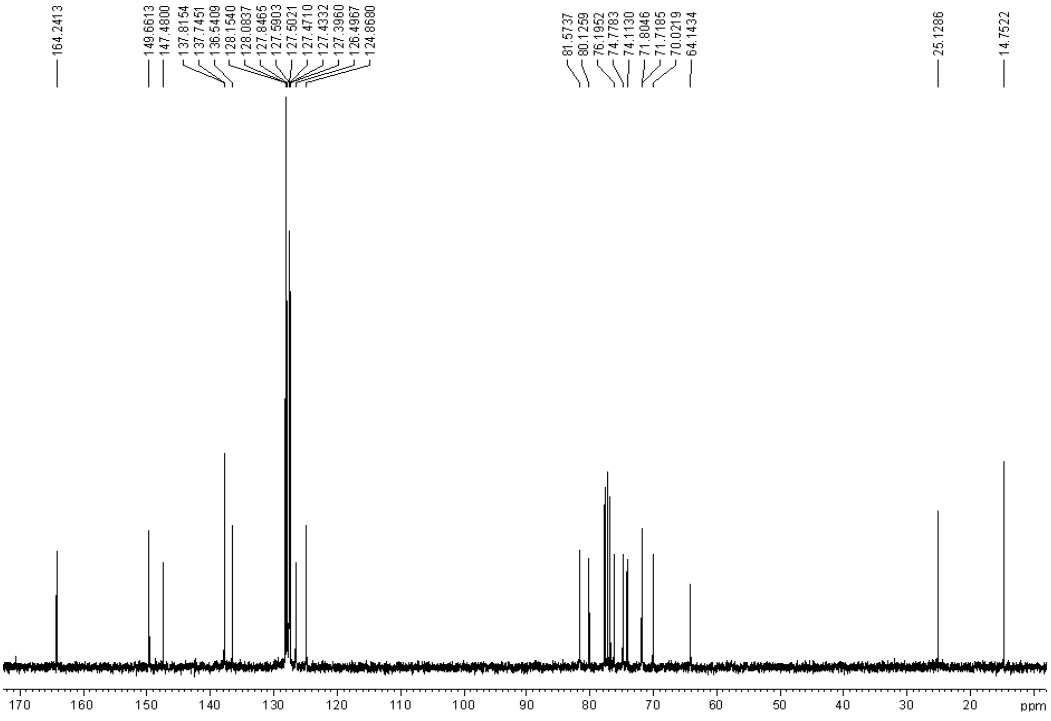
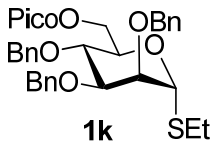
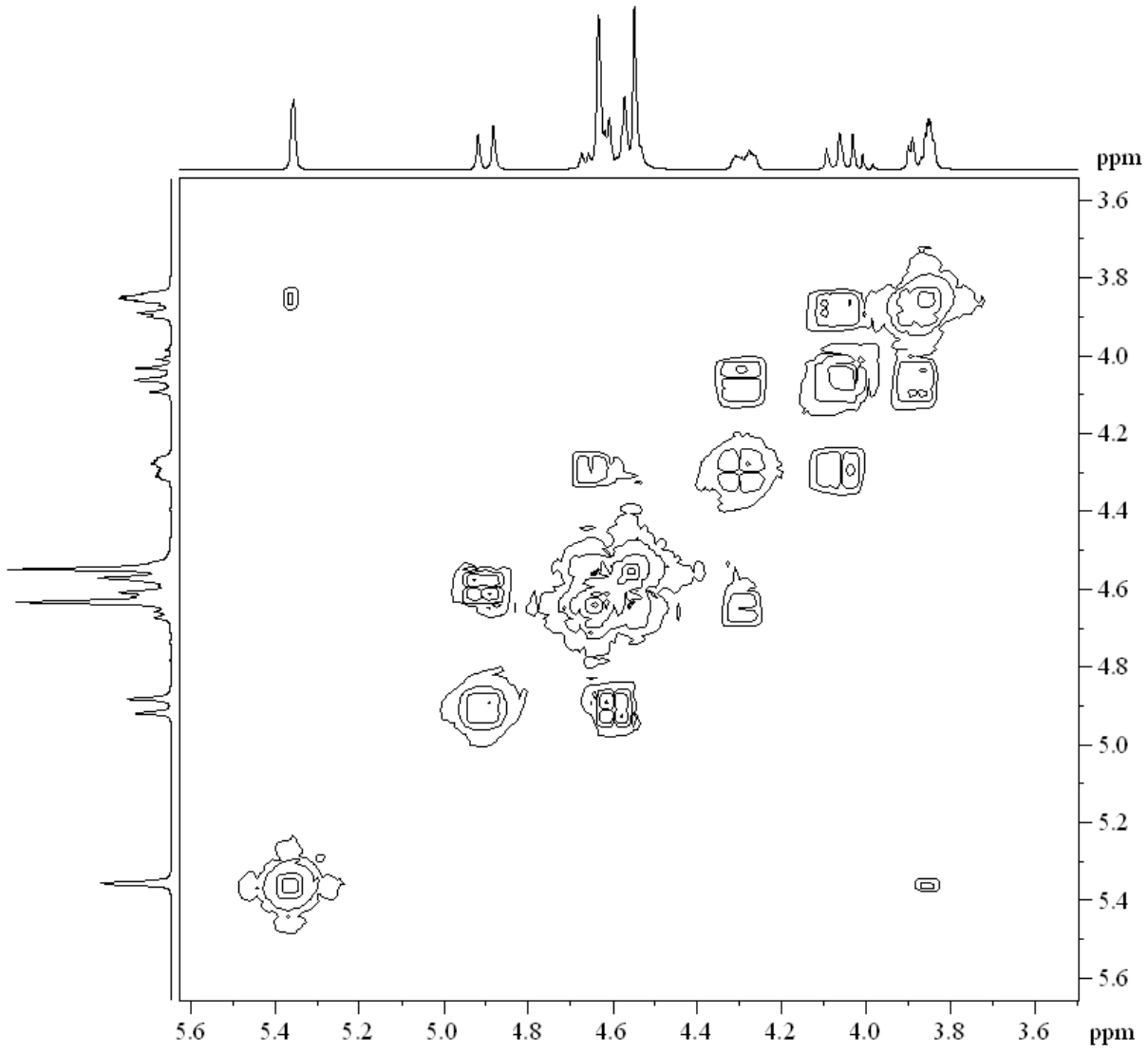


$CDCl_3$ 75 MHz





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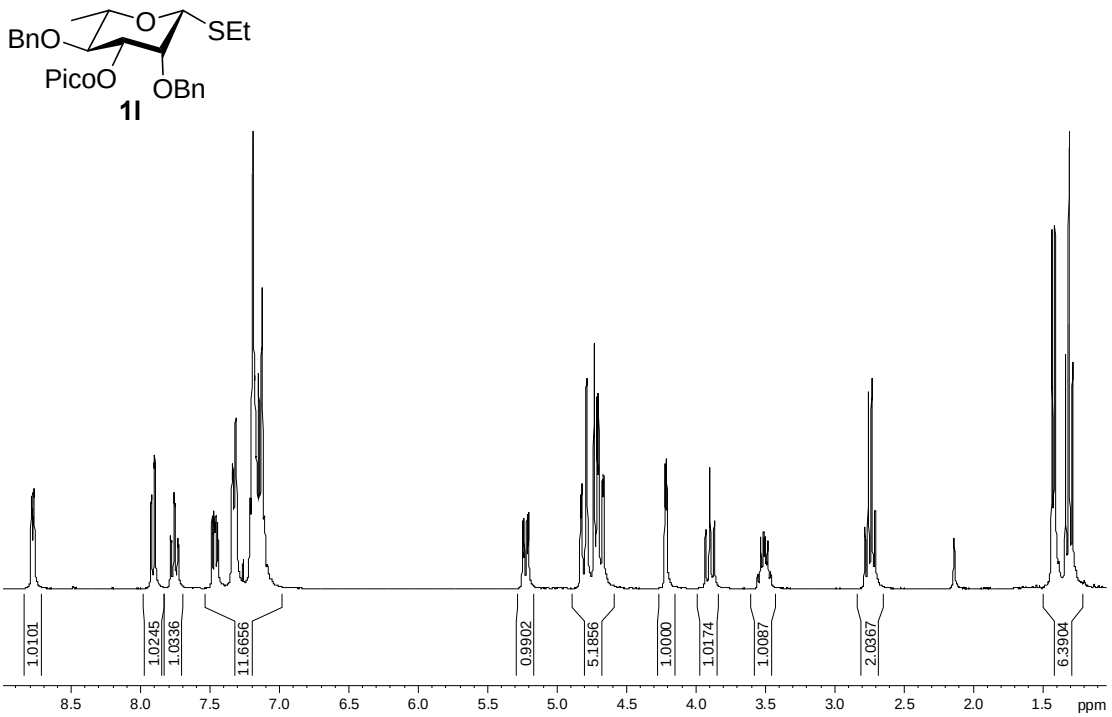

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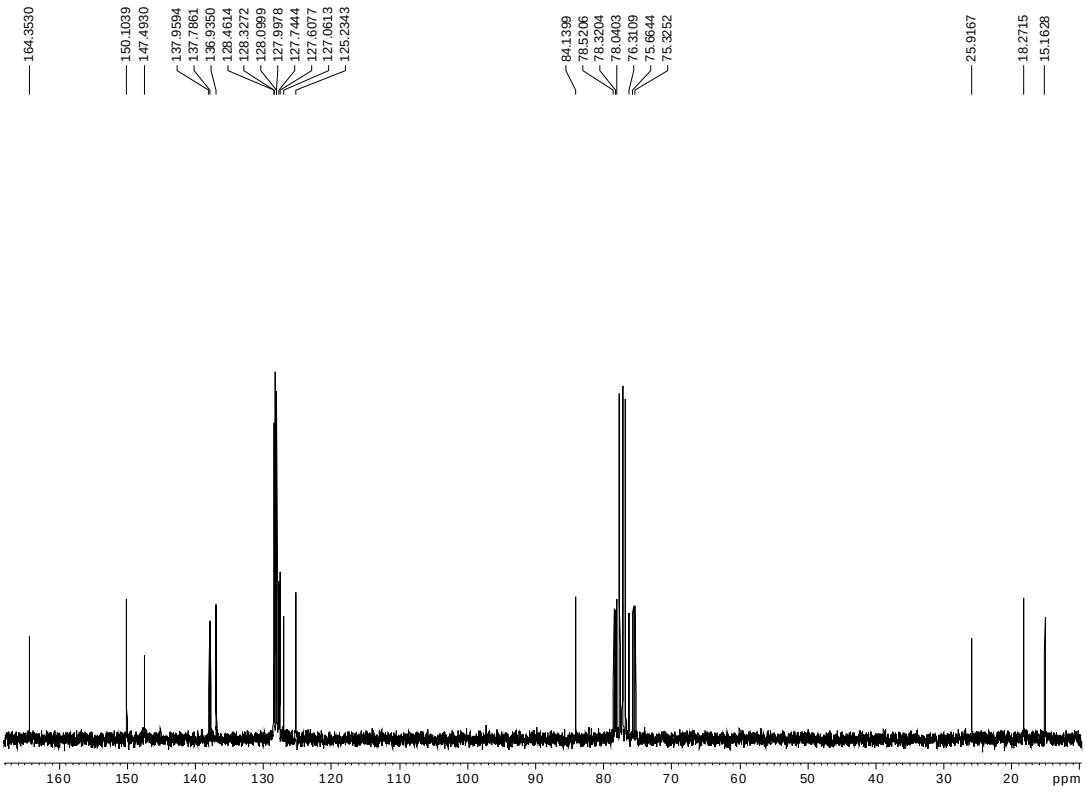

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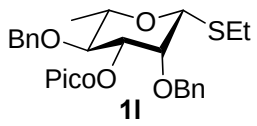
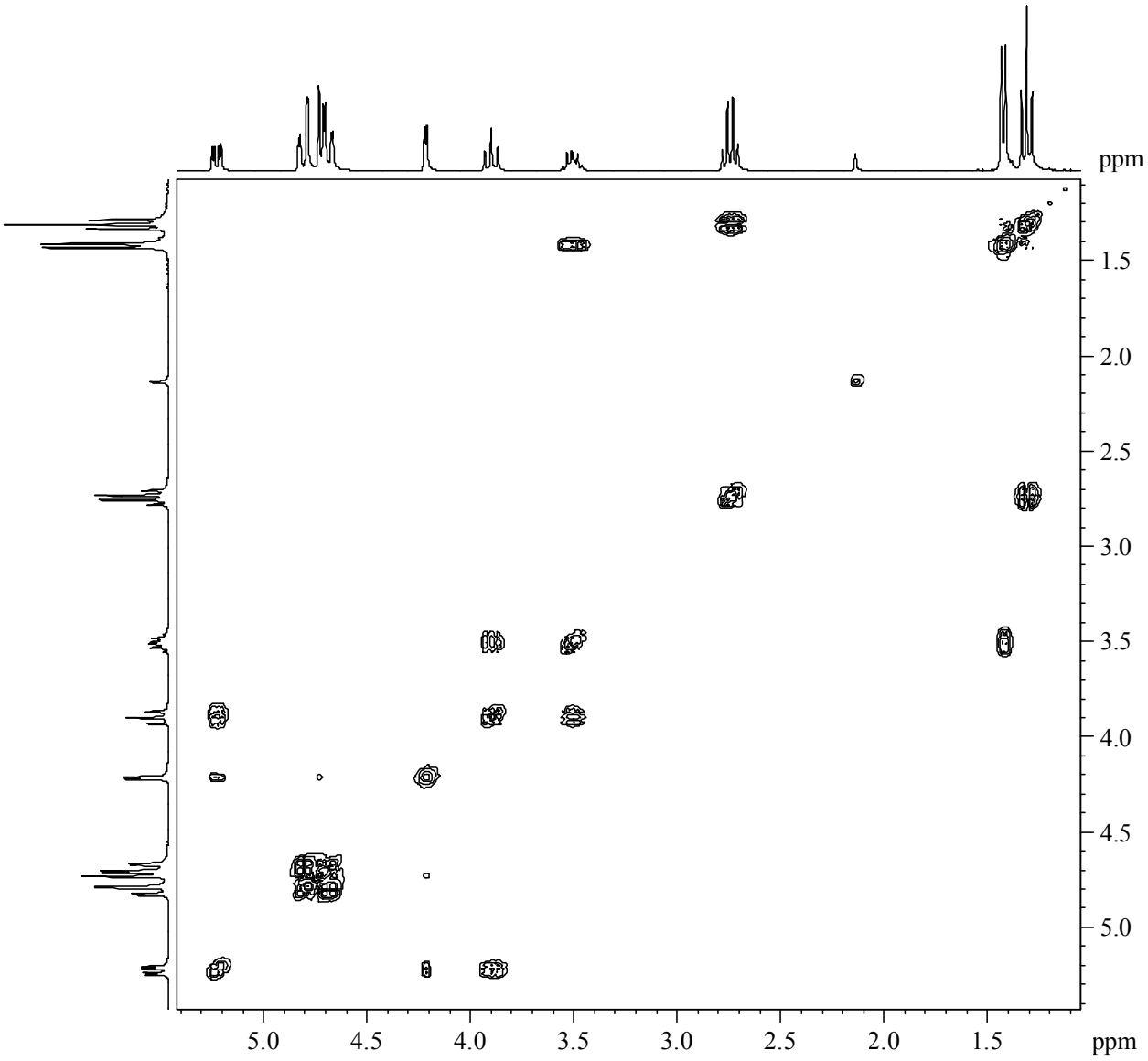


1l



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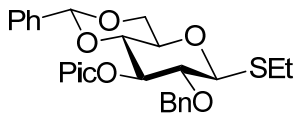
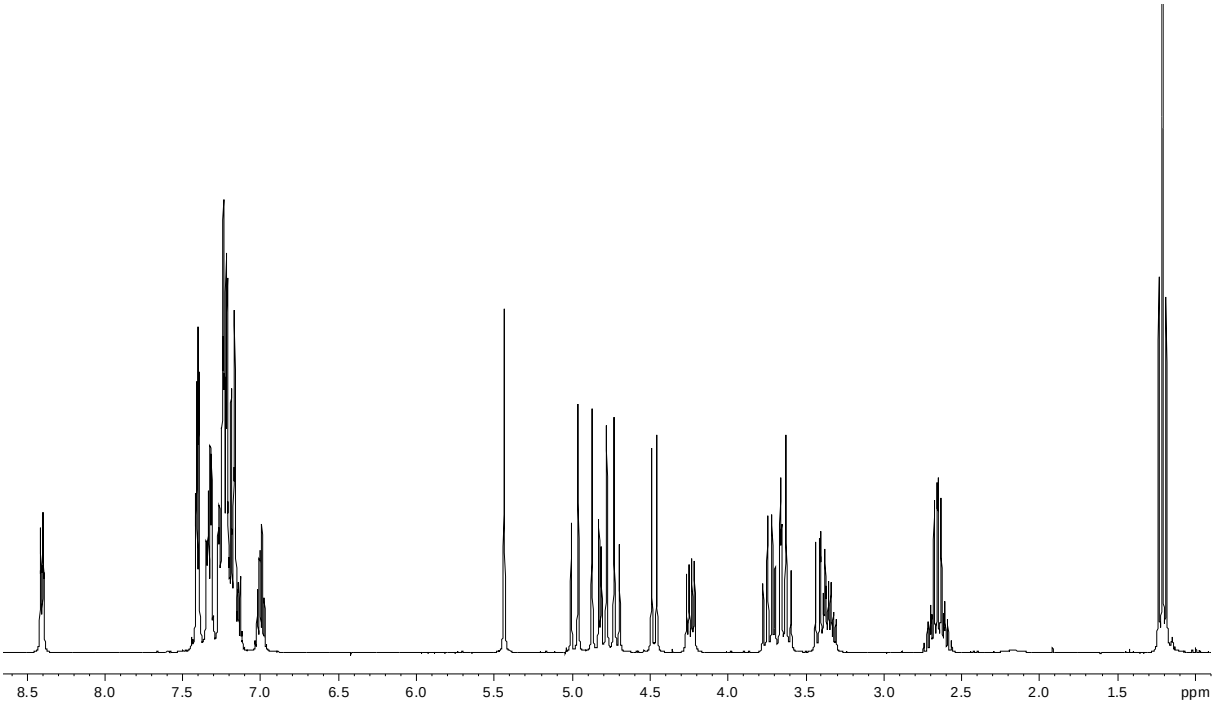


S2



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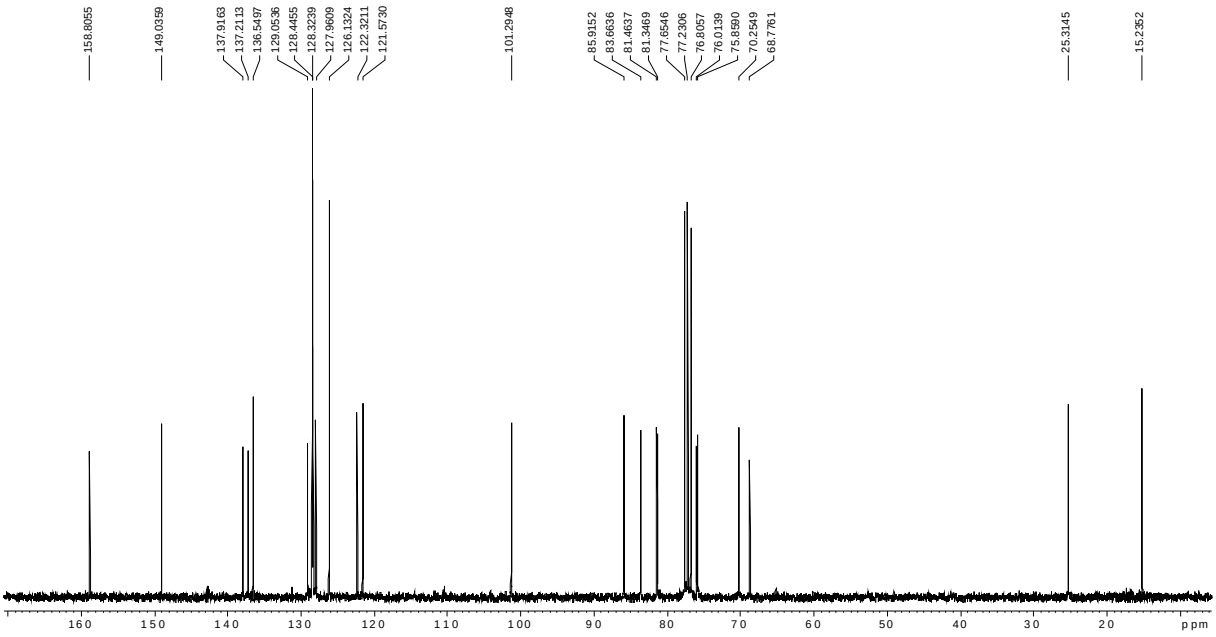

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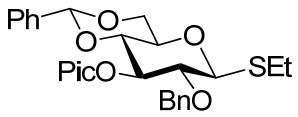
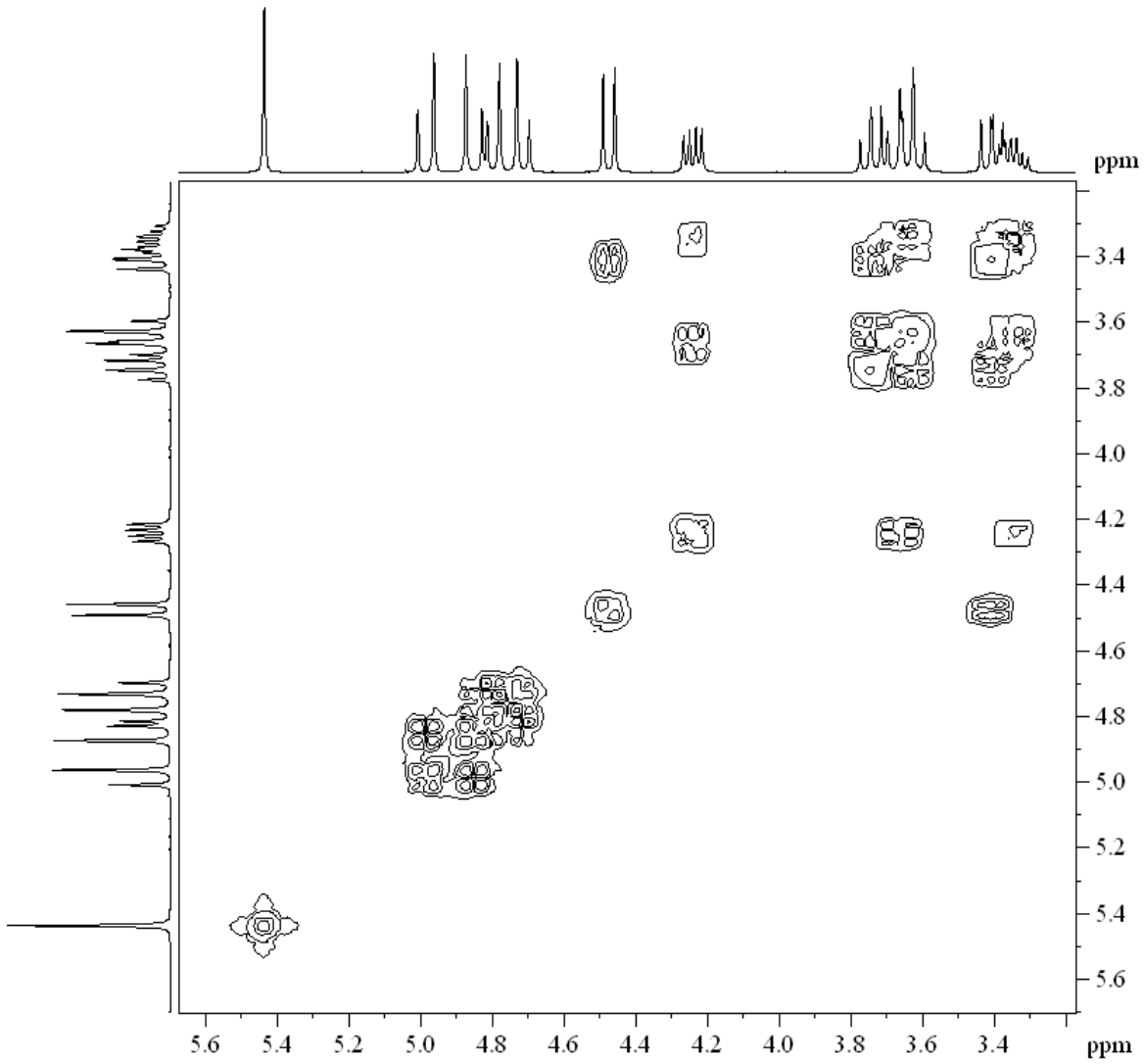


S2



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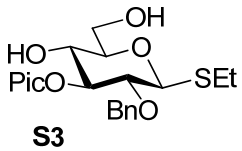
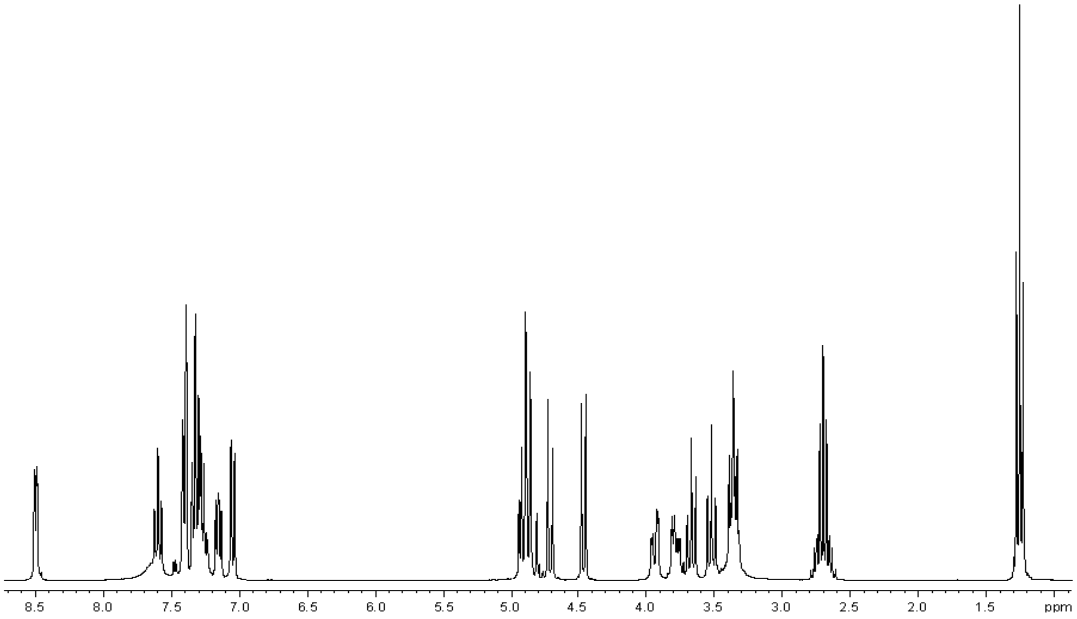


S3



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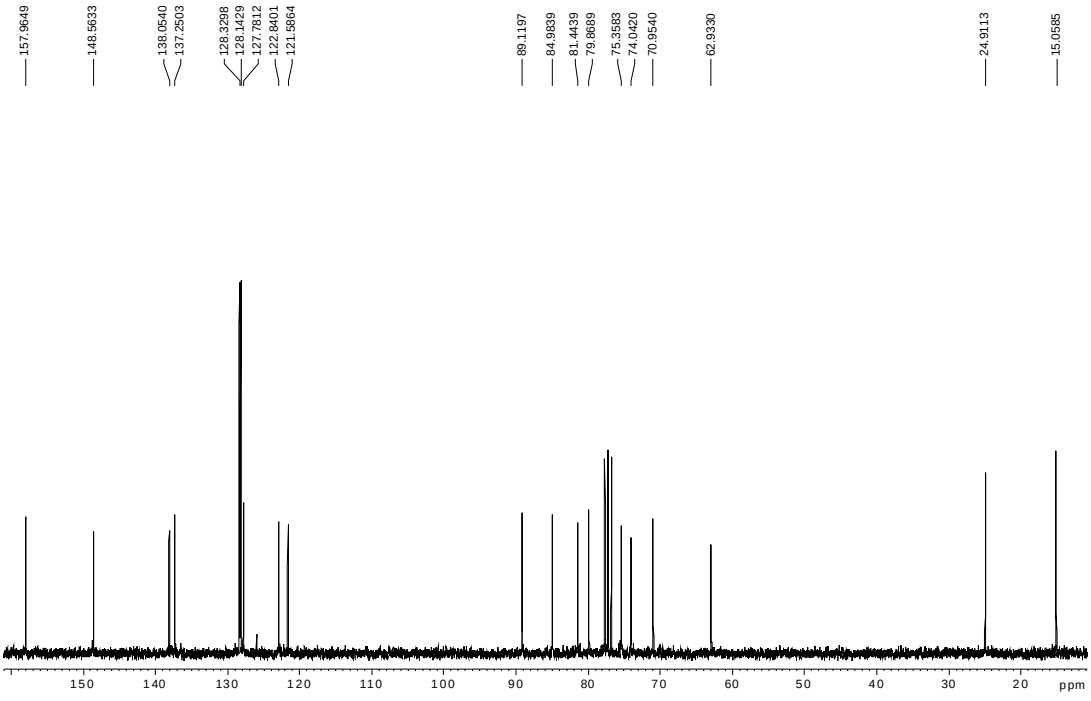

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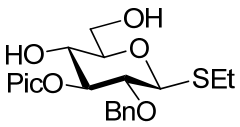
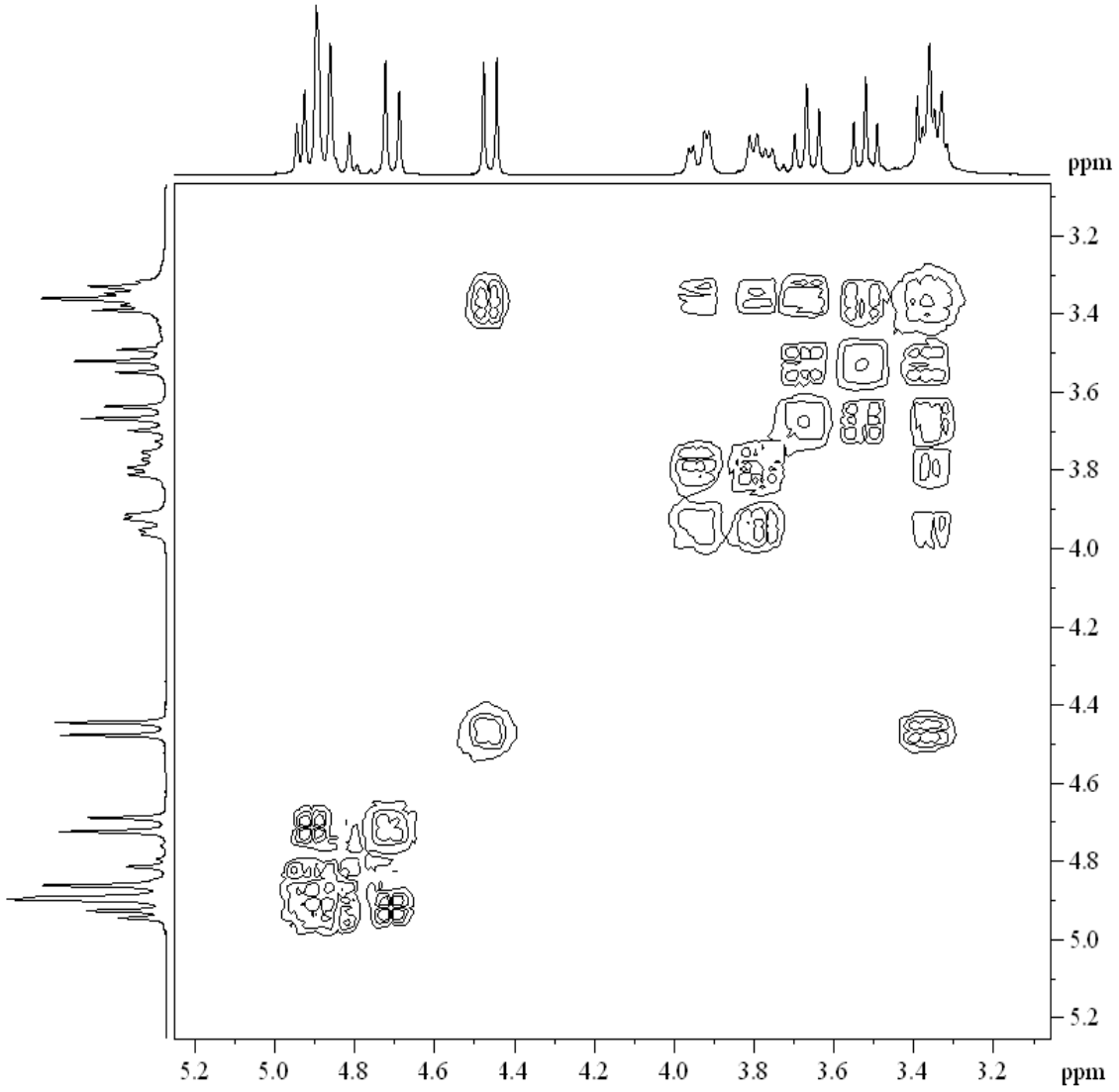


S3



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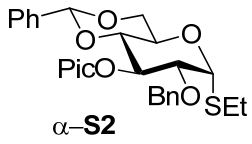
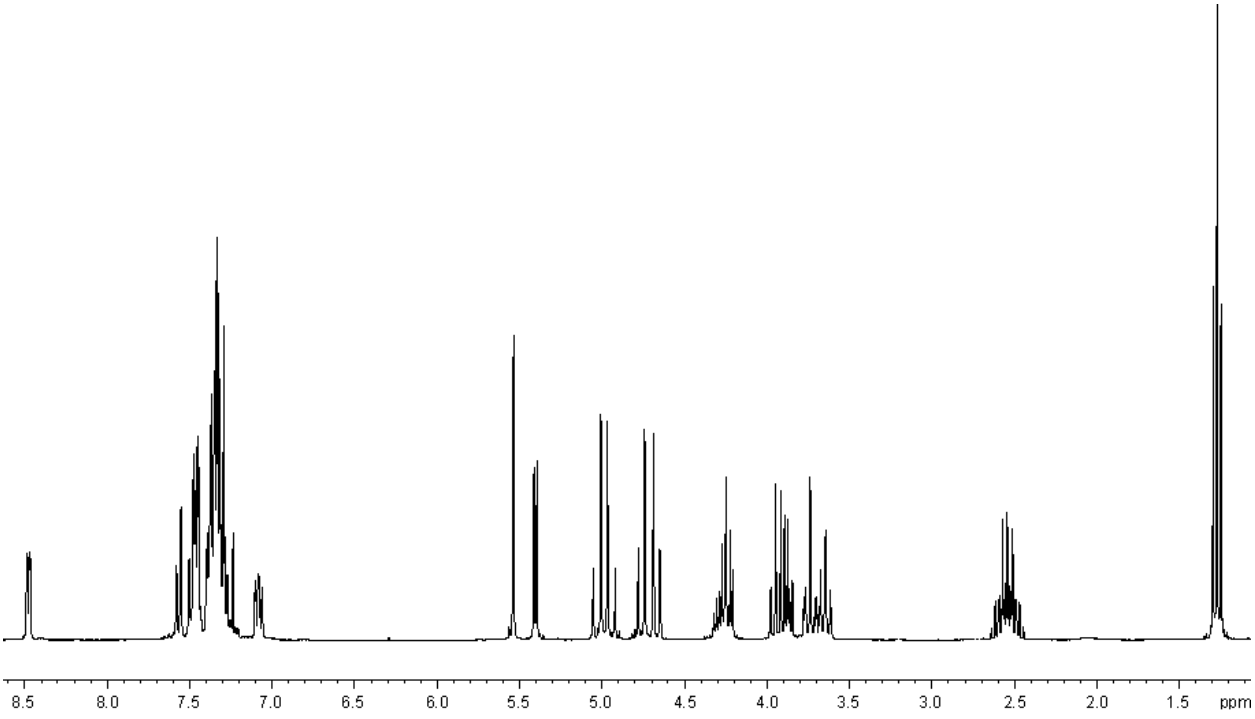


α–**S2**



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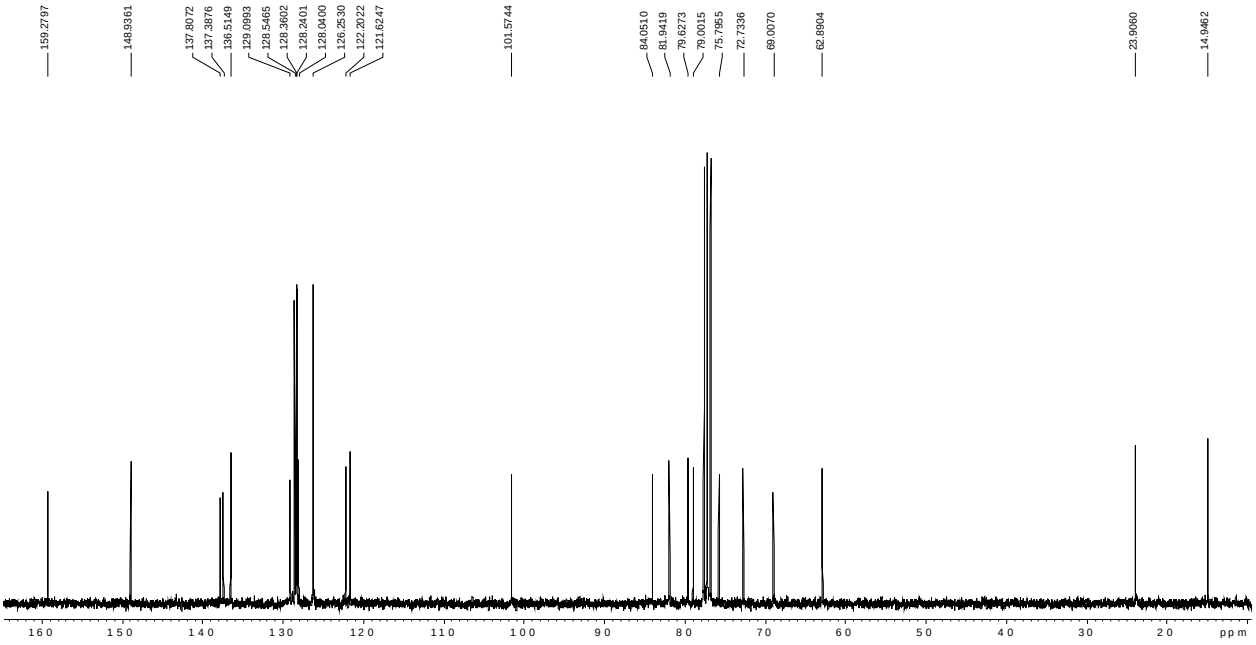
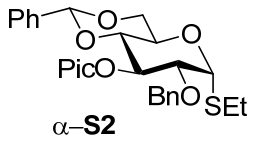
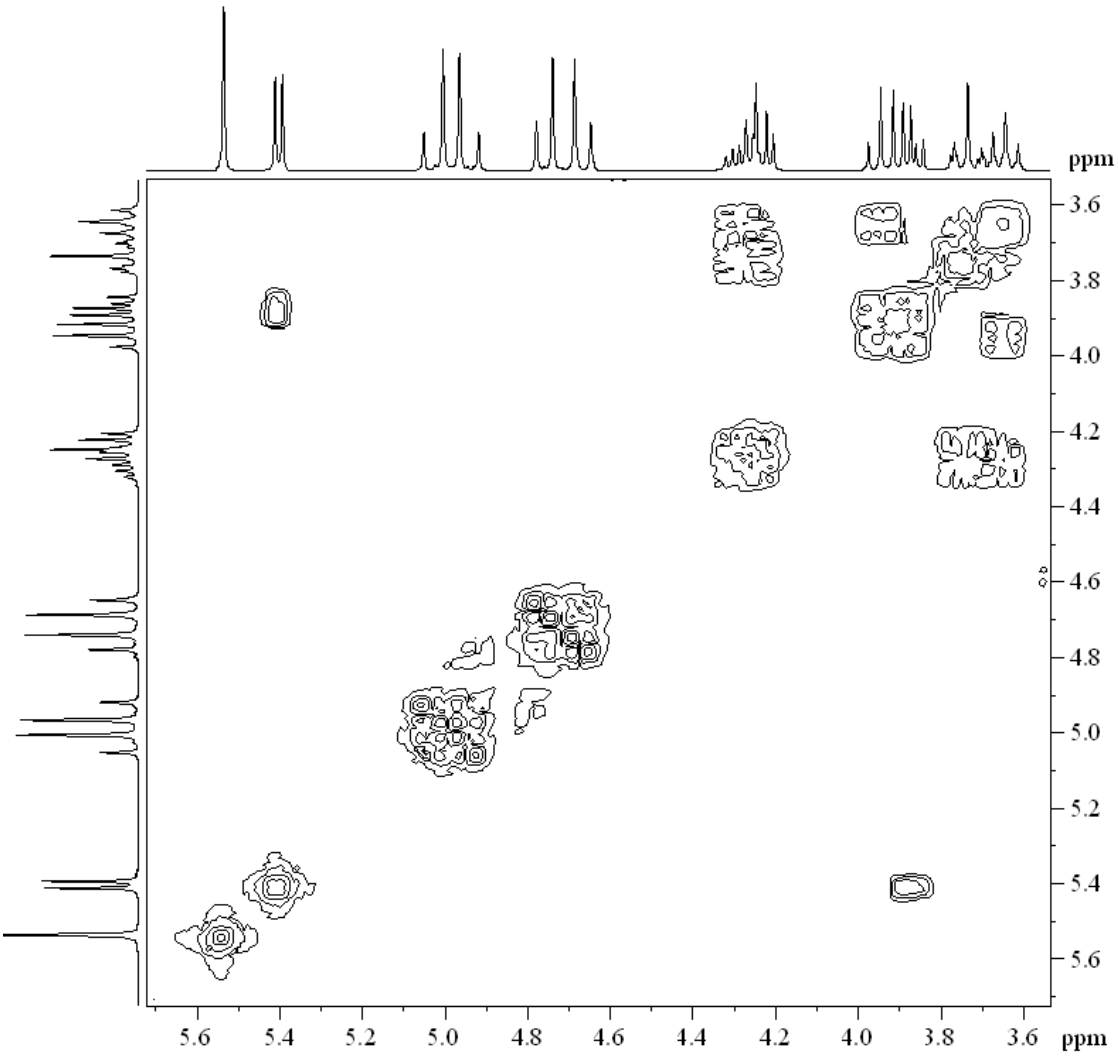


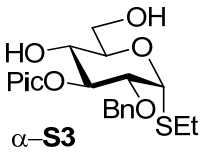
$CDCl_3$ 75 MHz



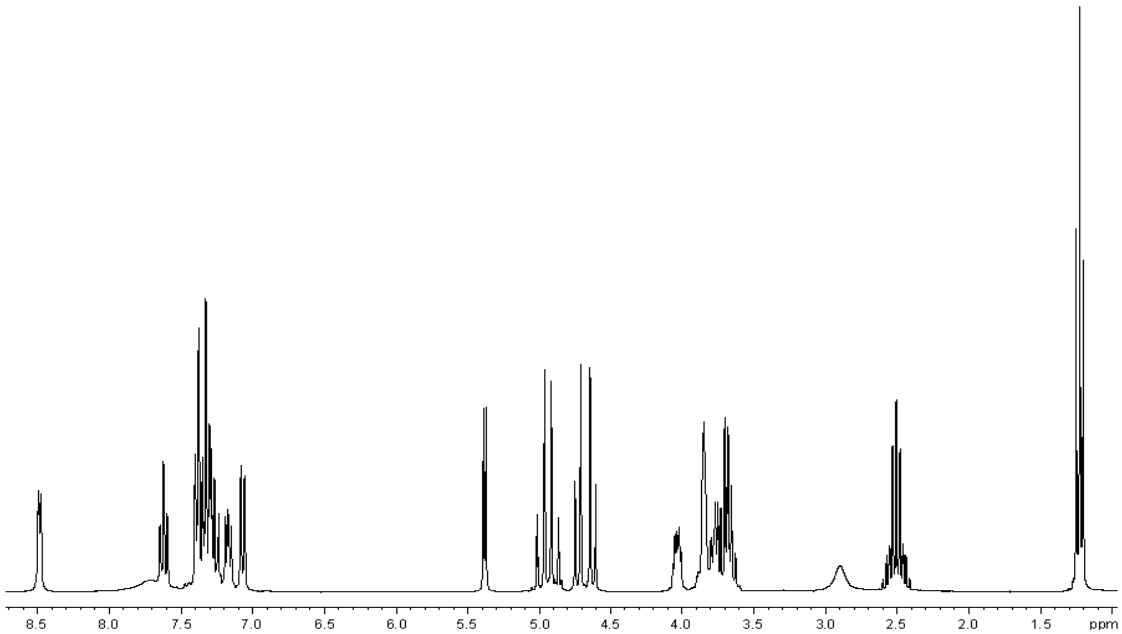
α–**S2**



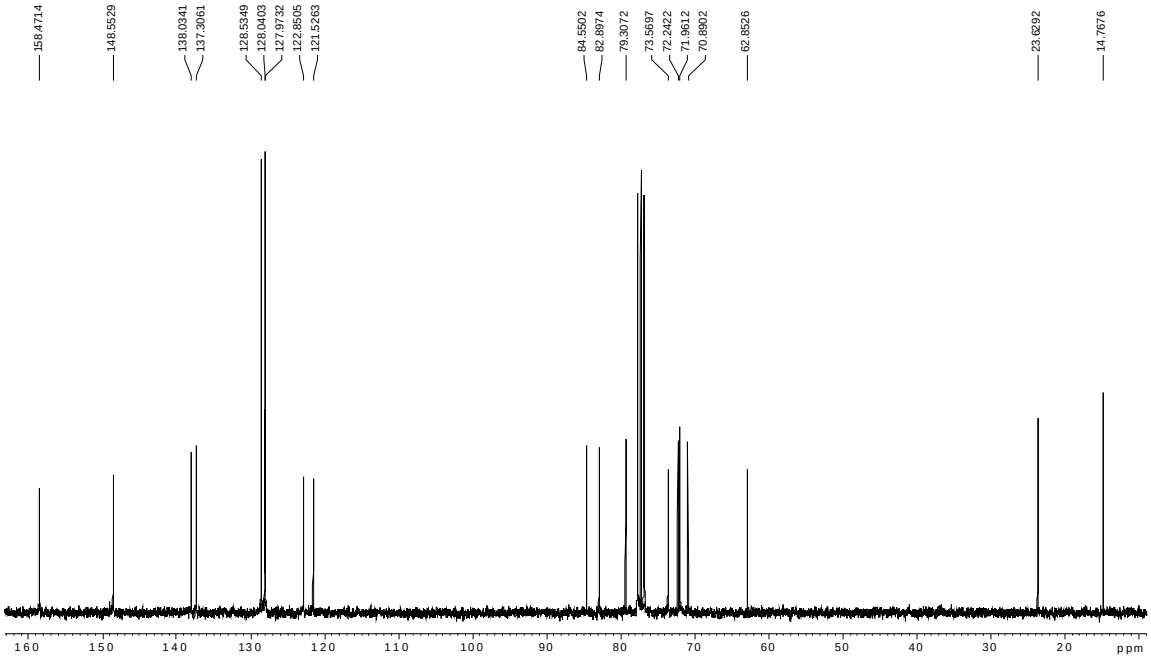
$CDCl_3$ 300 MHz



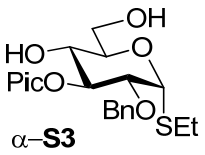
α–**S3**



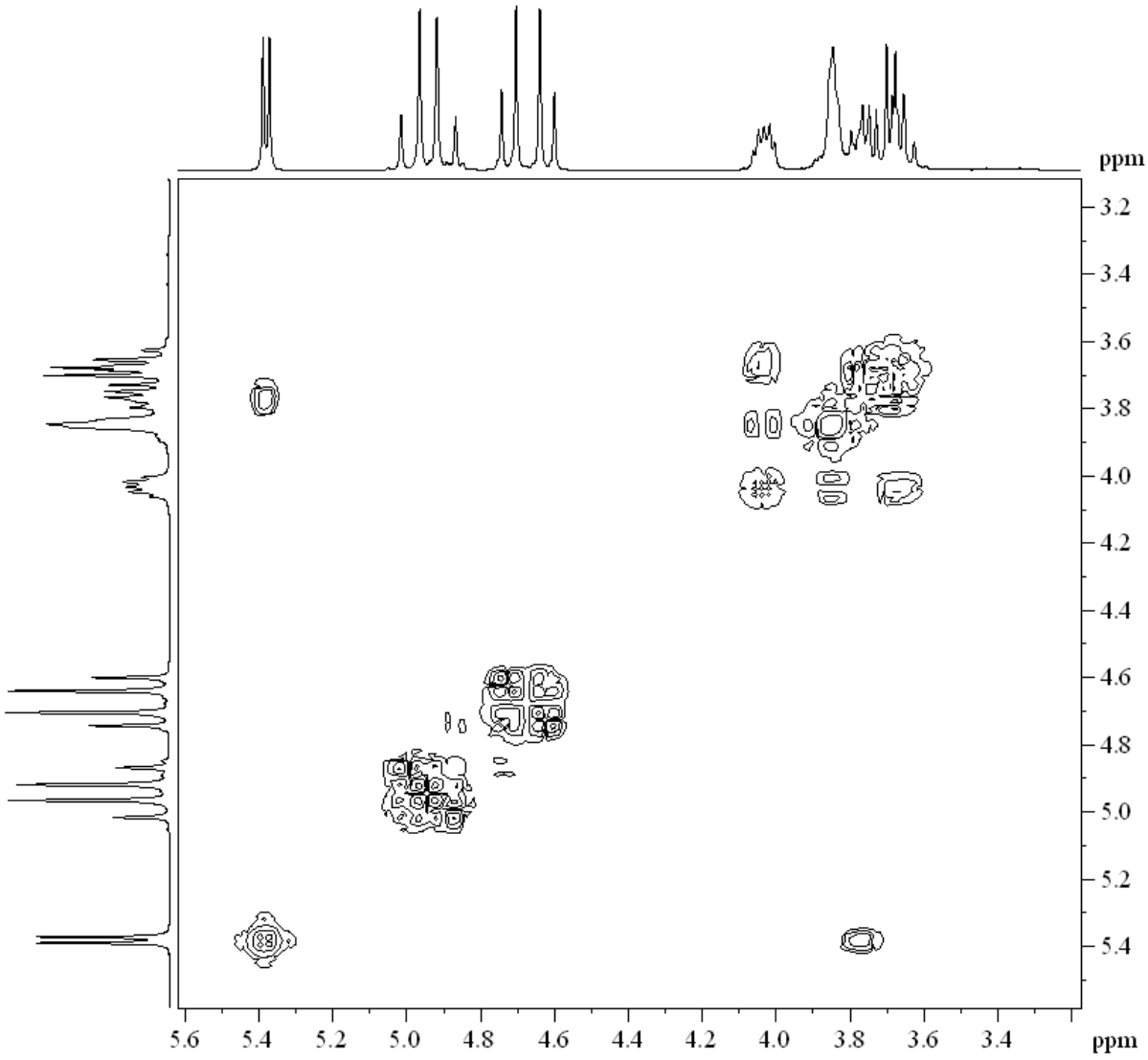
$CDCl_3$ 300 MHz



$CDCl_3$ 75 MHz



α–**S3**



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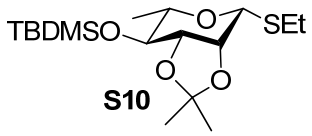

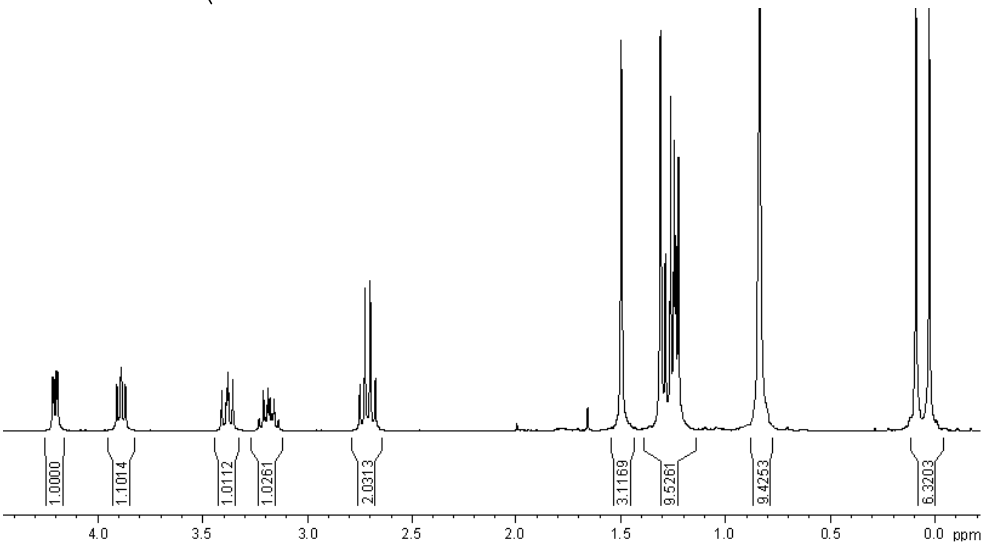

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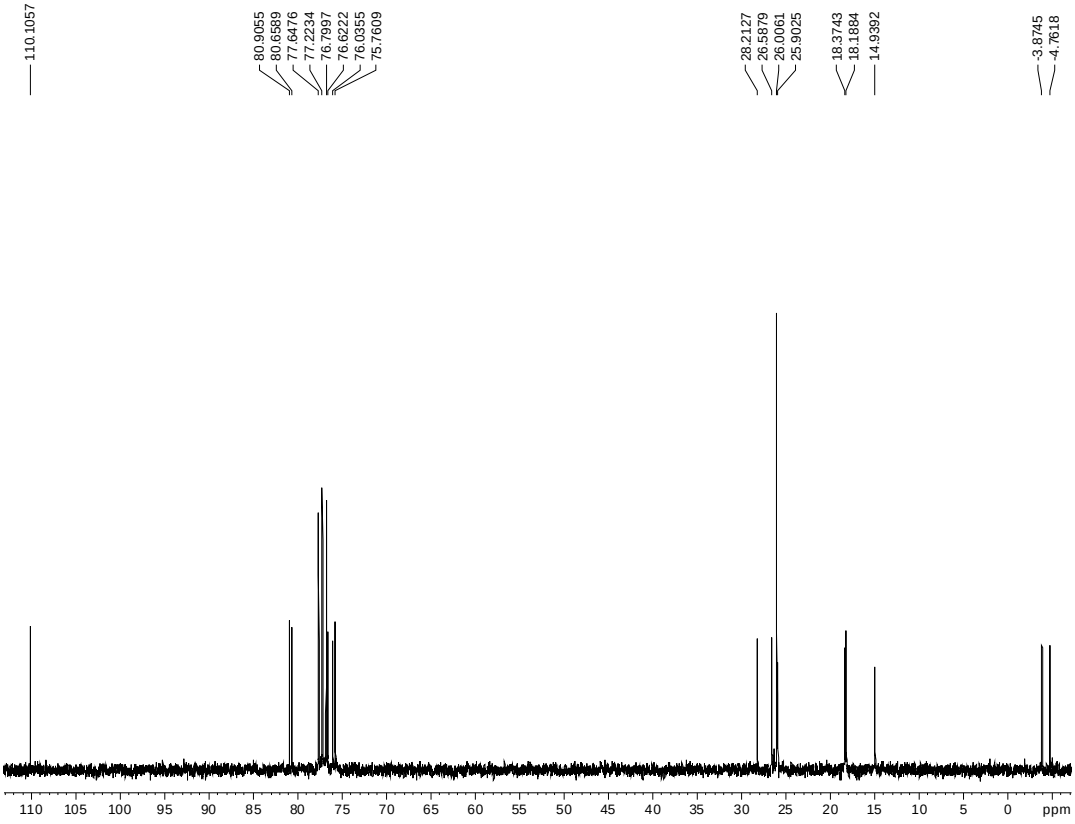

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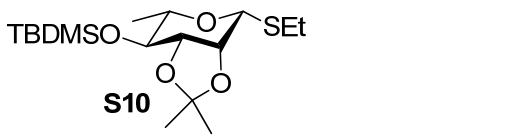

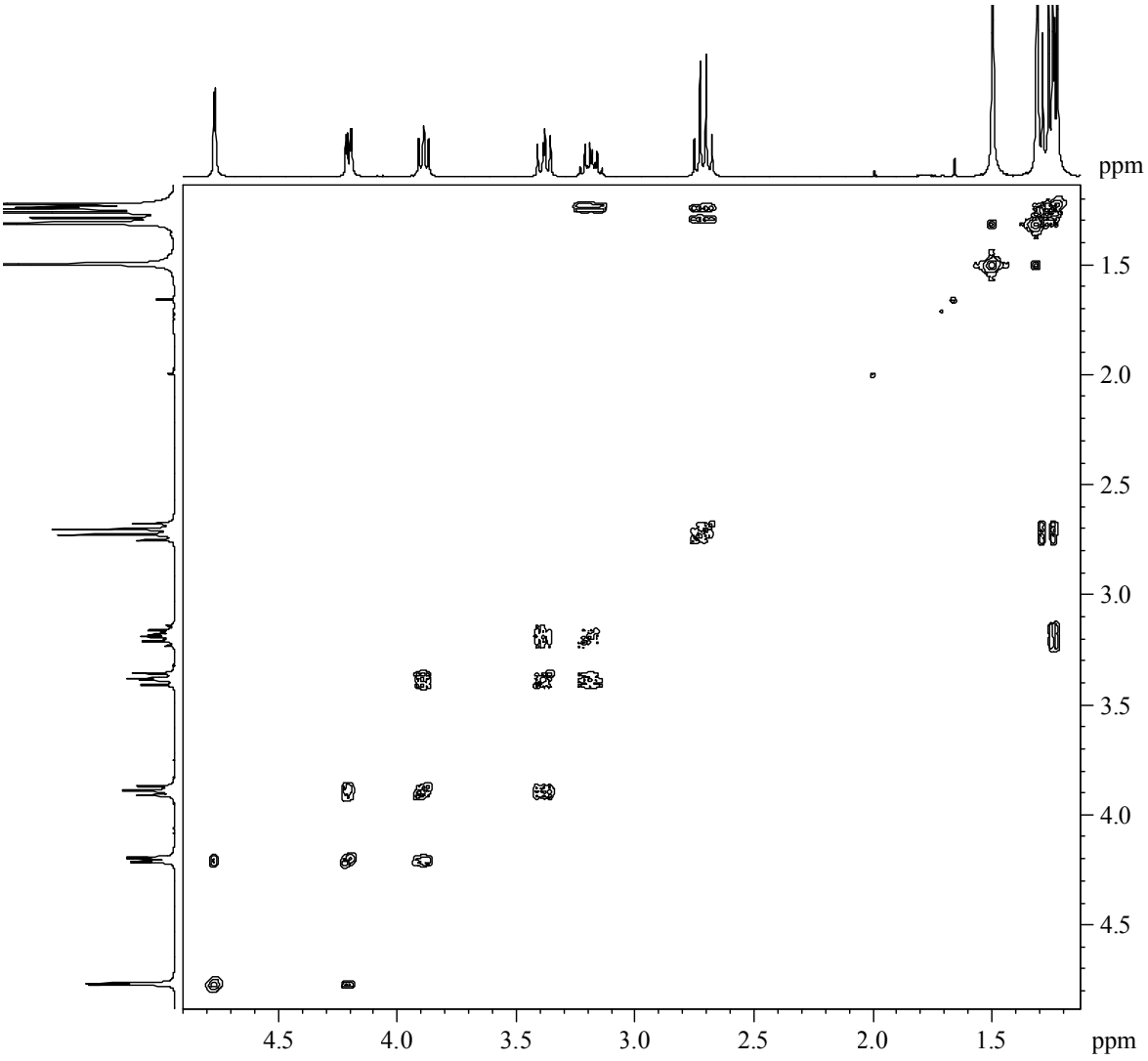

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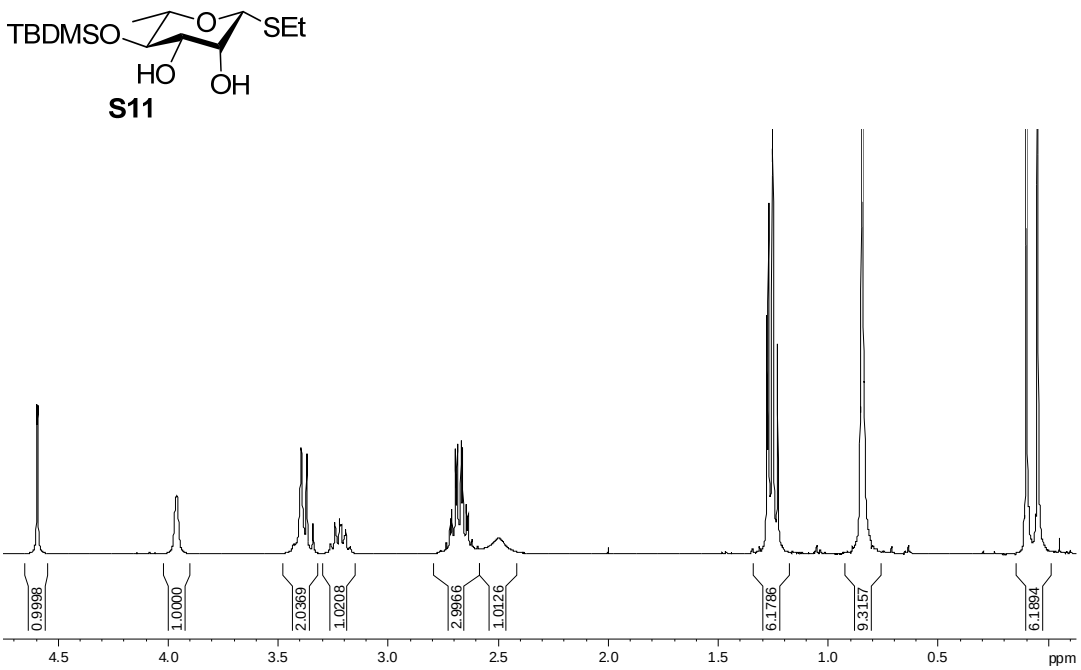

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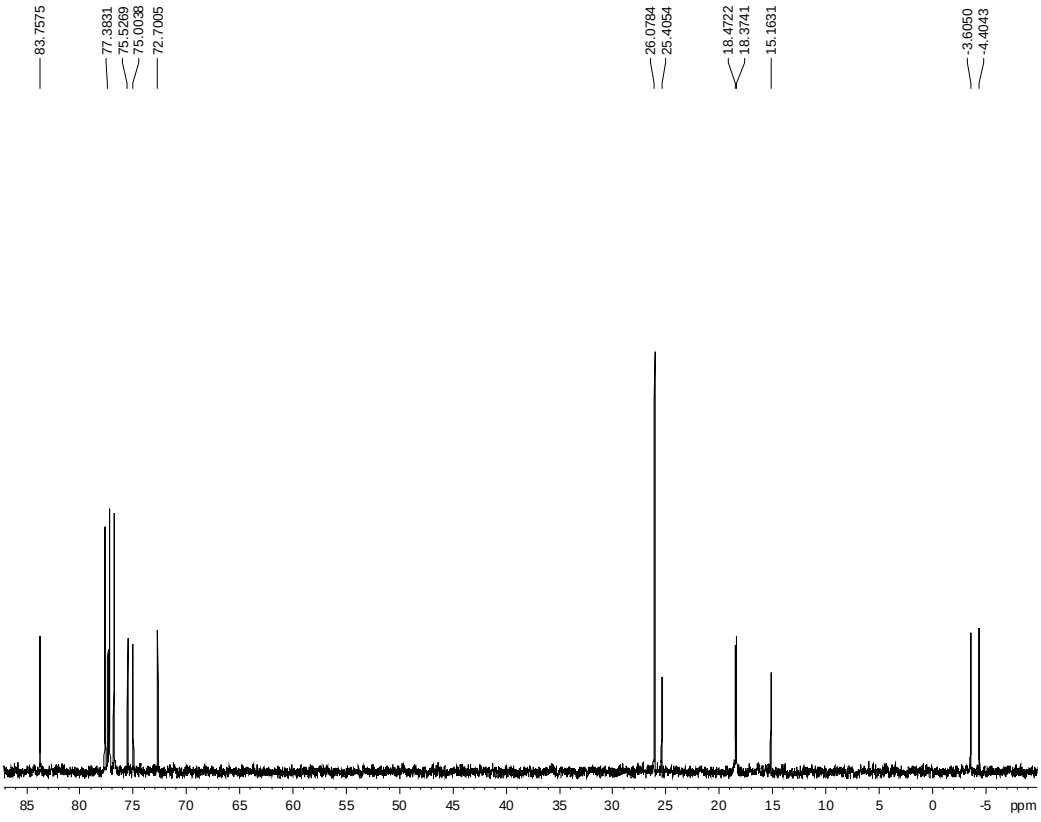

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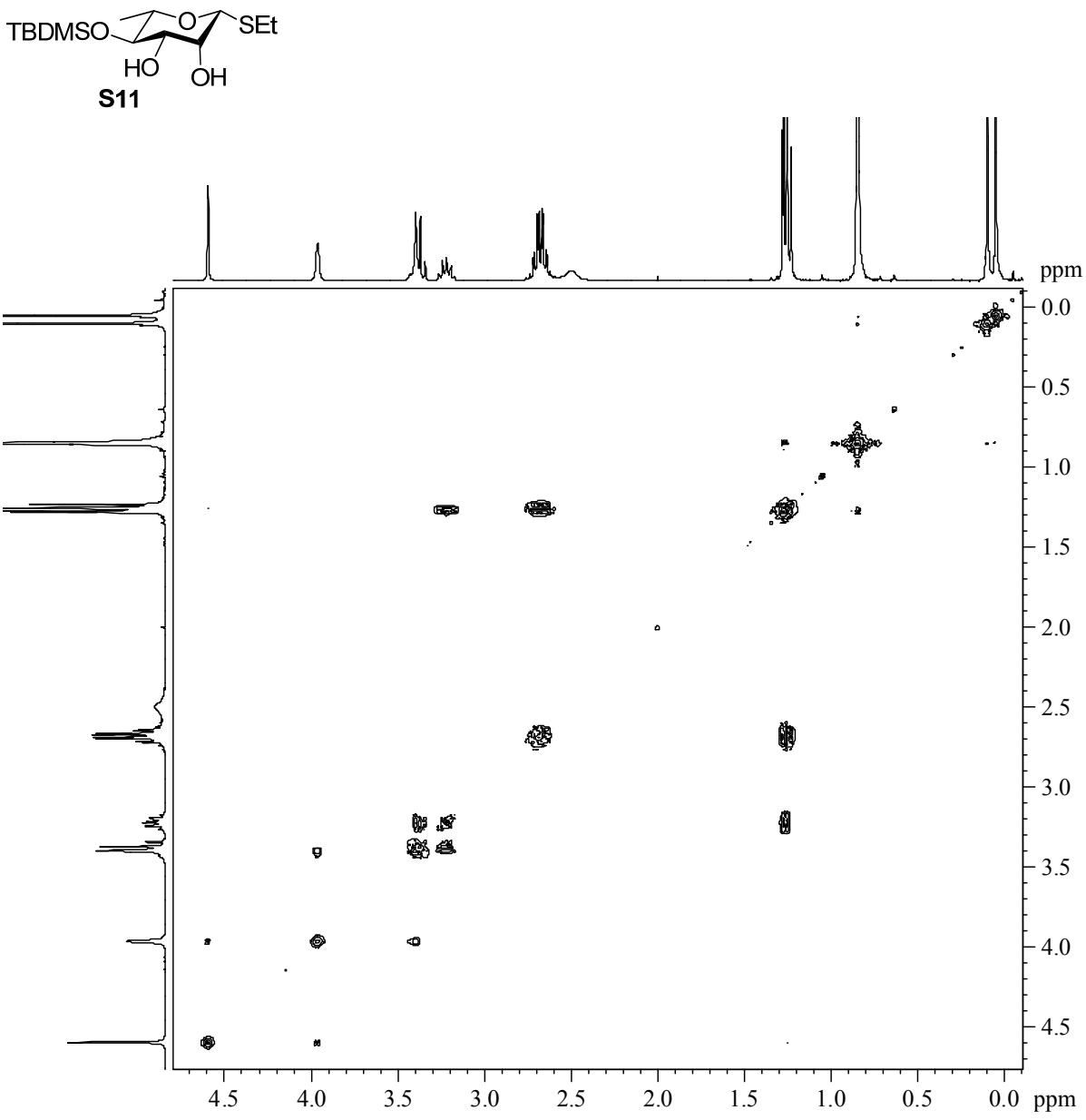

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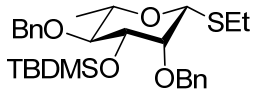
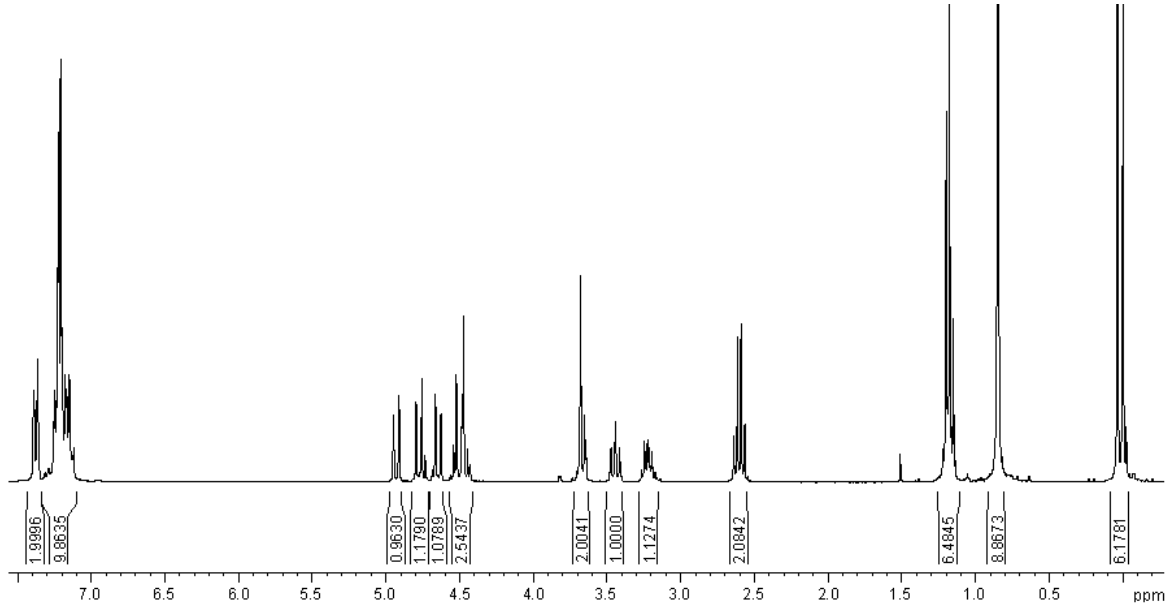
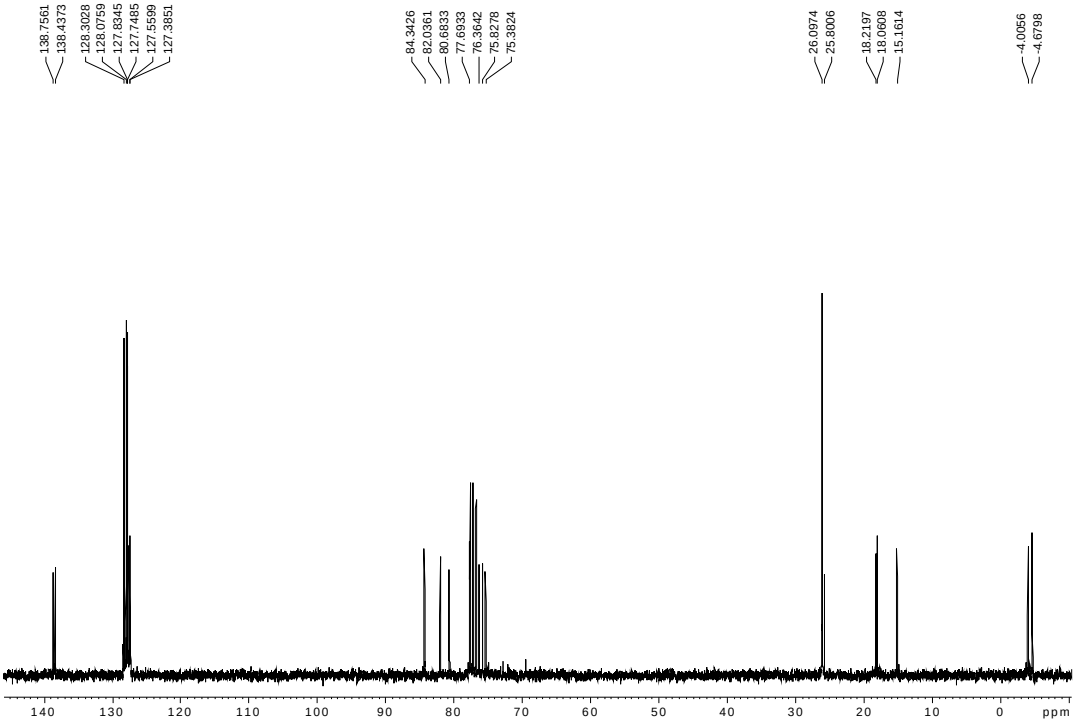


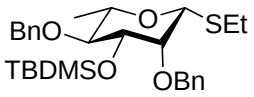
S12



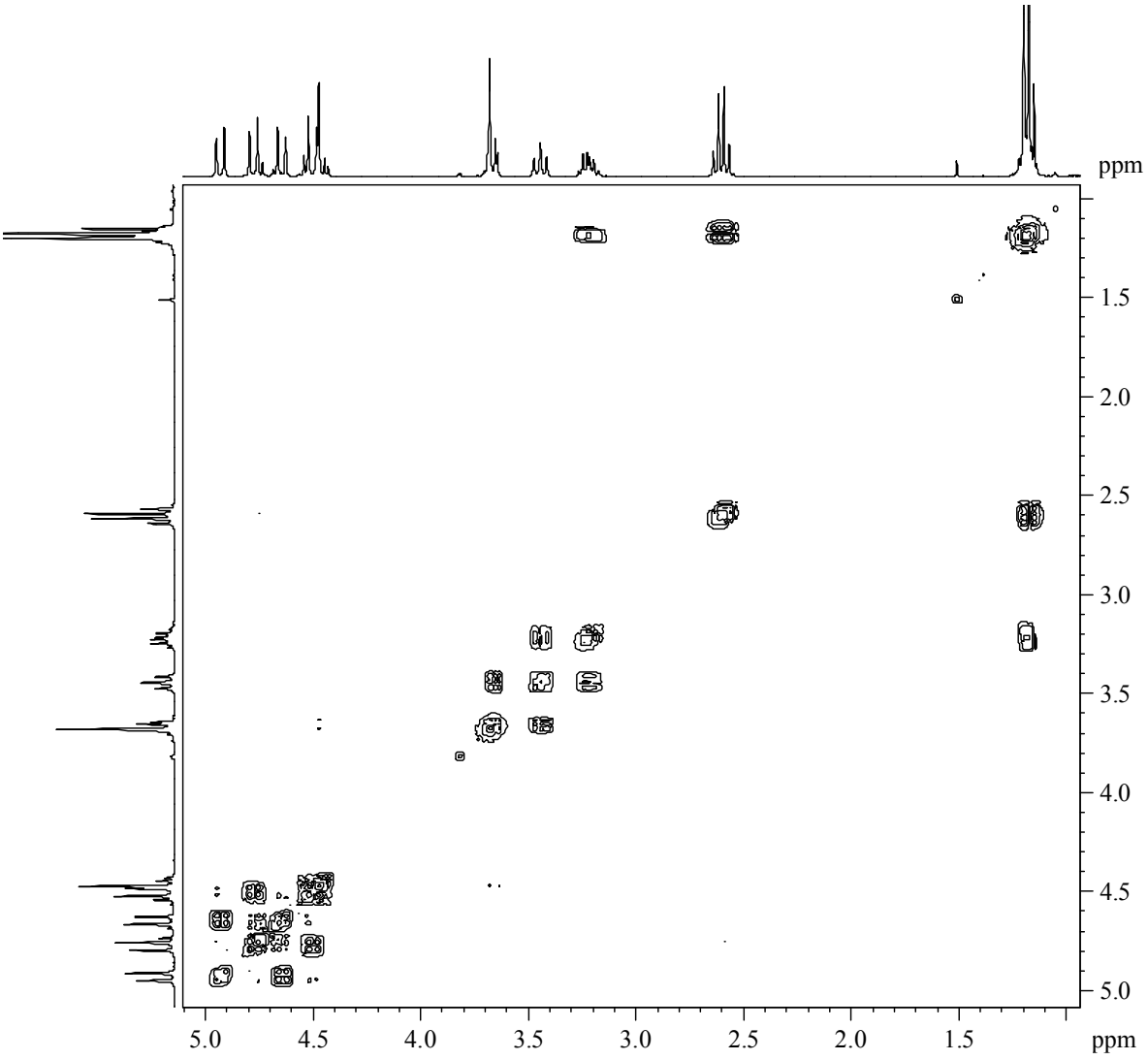
$CDCl_3$ 300 MHz



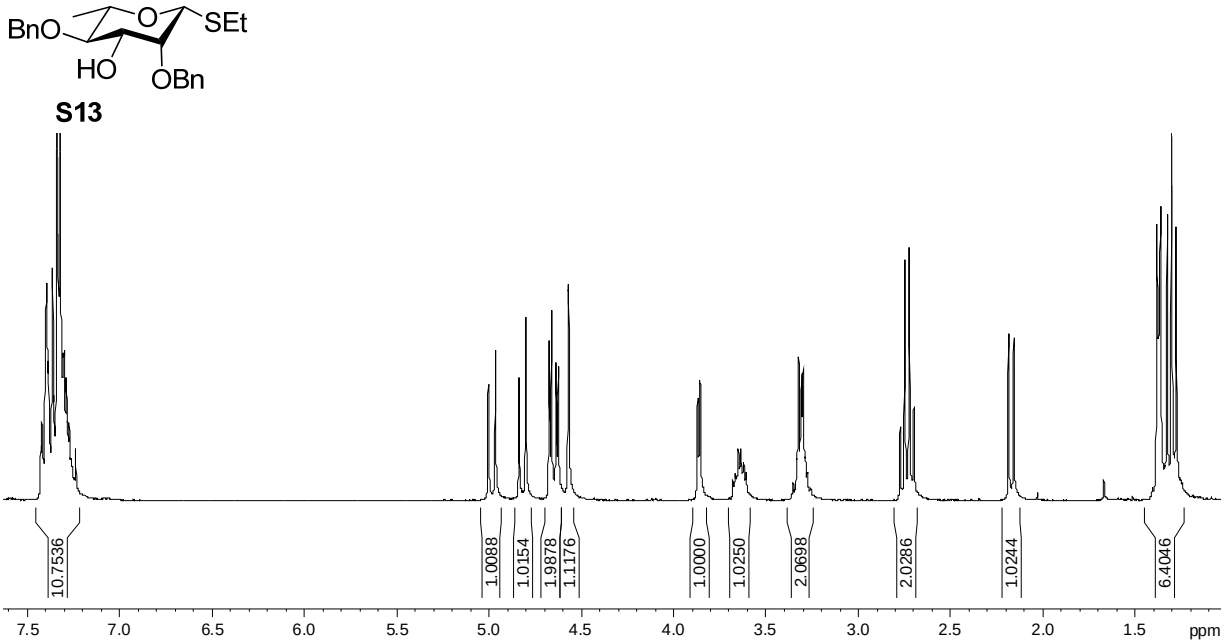
$CDCl_3$ 75 MHz



S12



$CDCl_3$ 300 MHz



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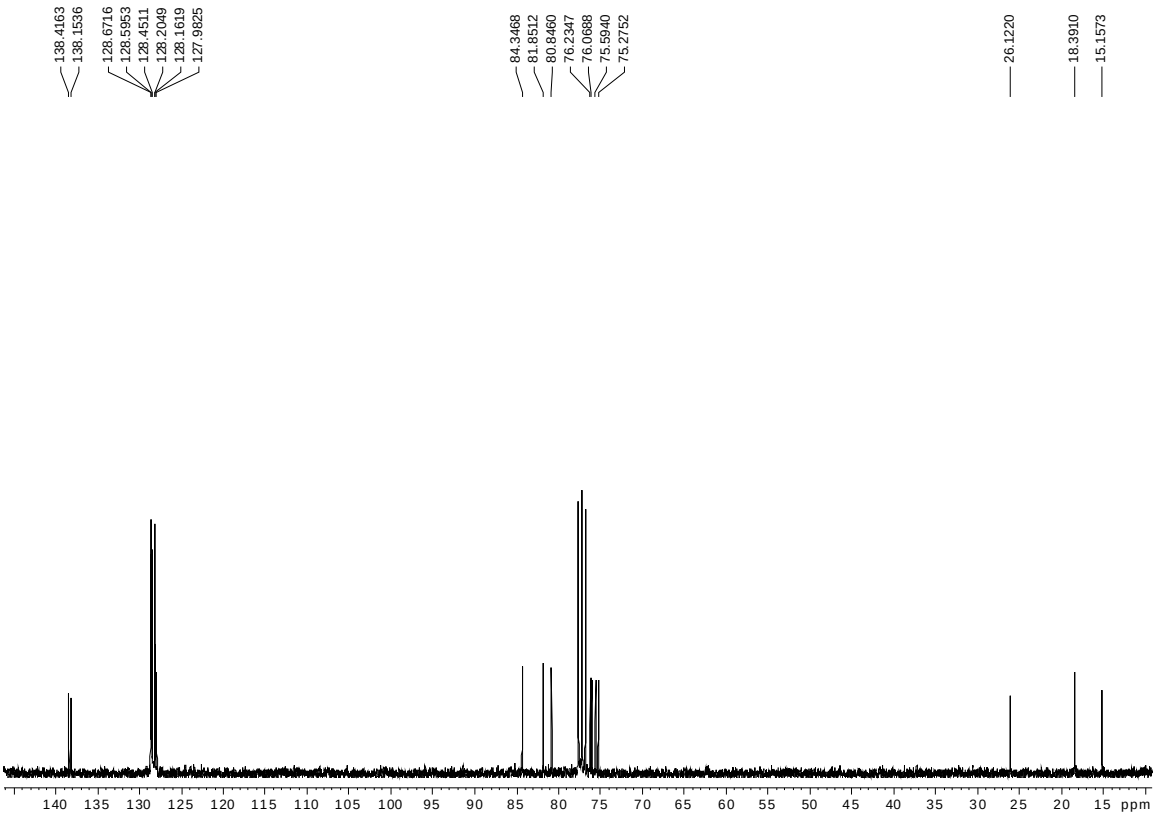
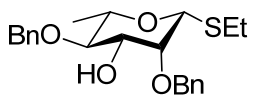
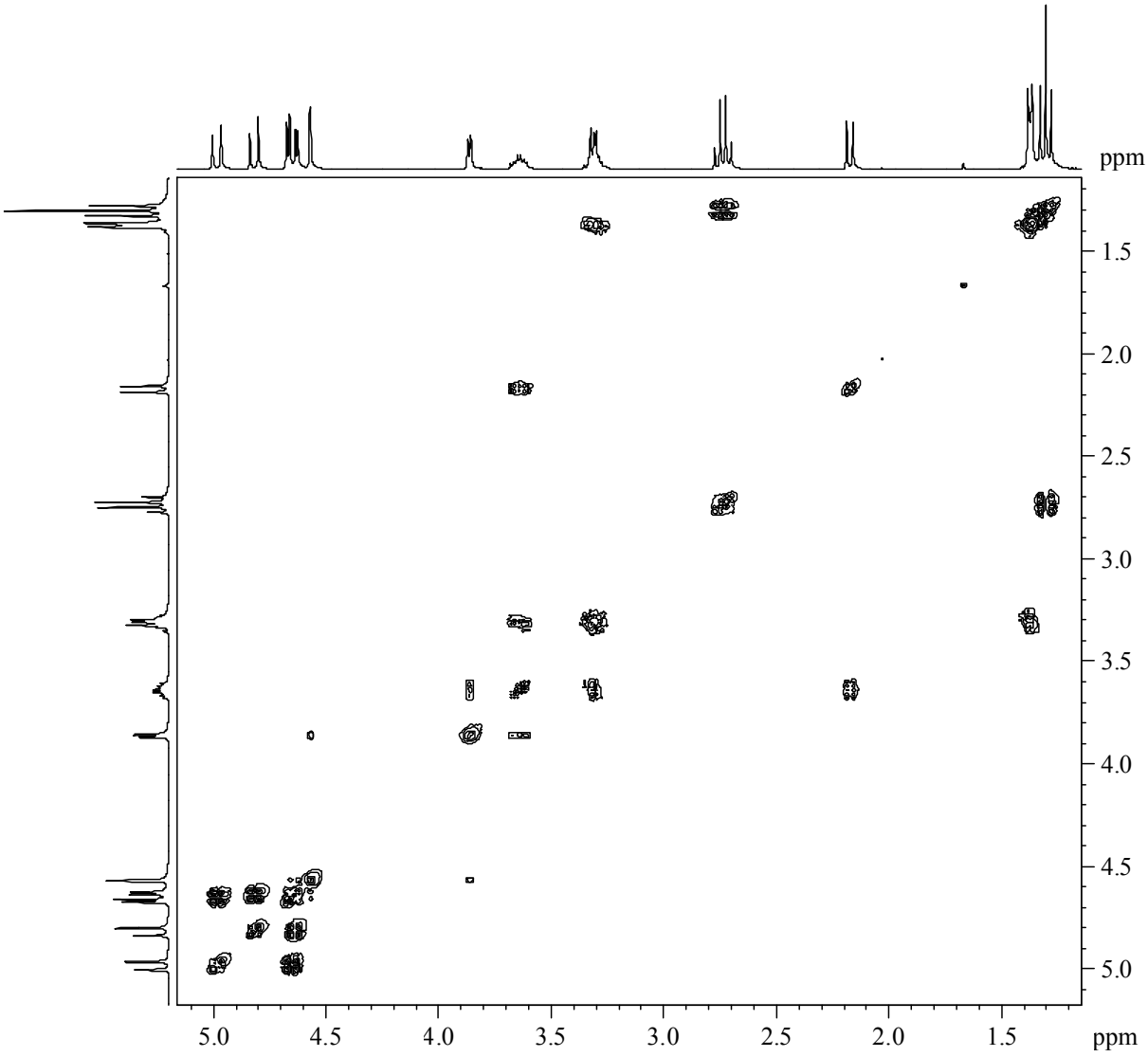


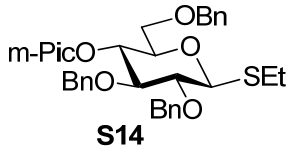
$CDCl_3$ 75 MHz



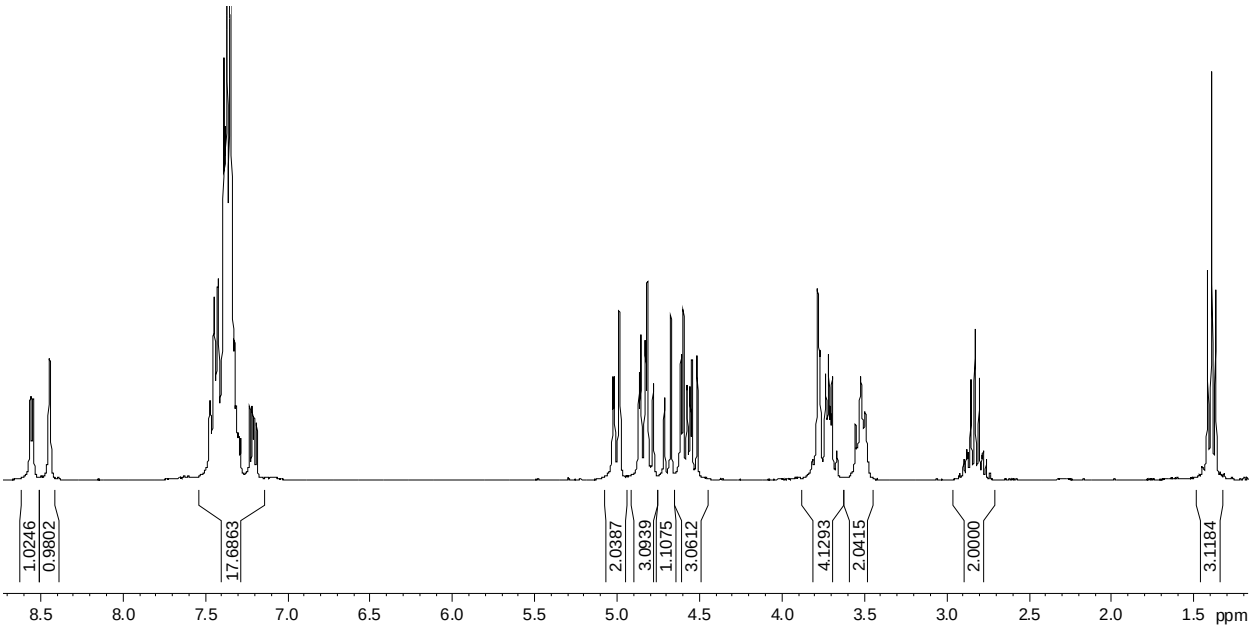
S13



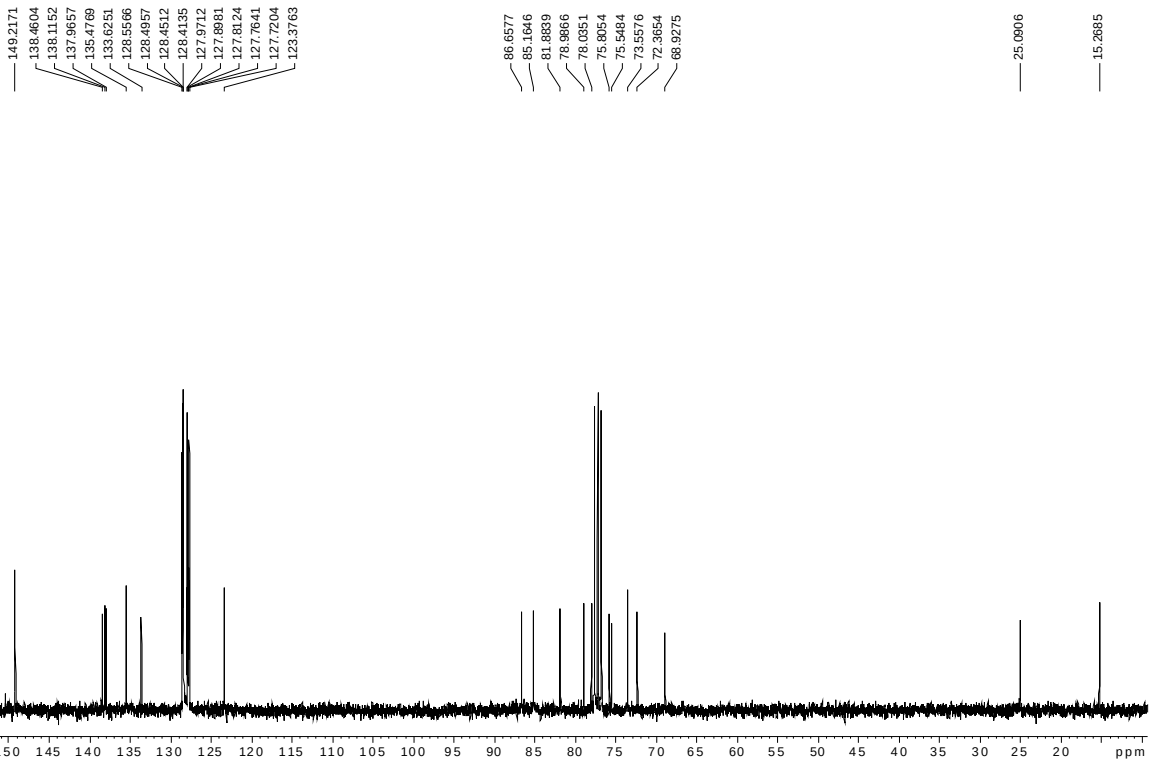
$CDCl_3$ 300 MHz



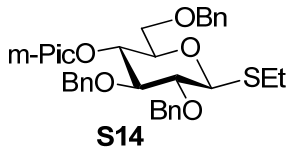
S14



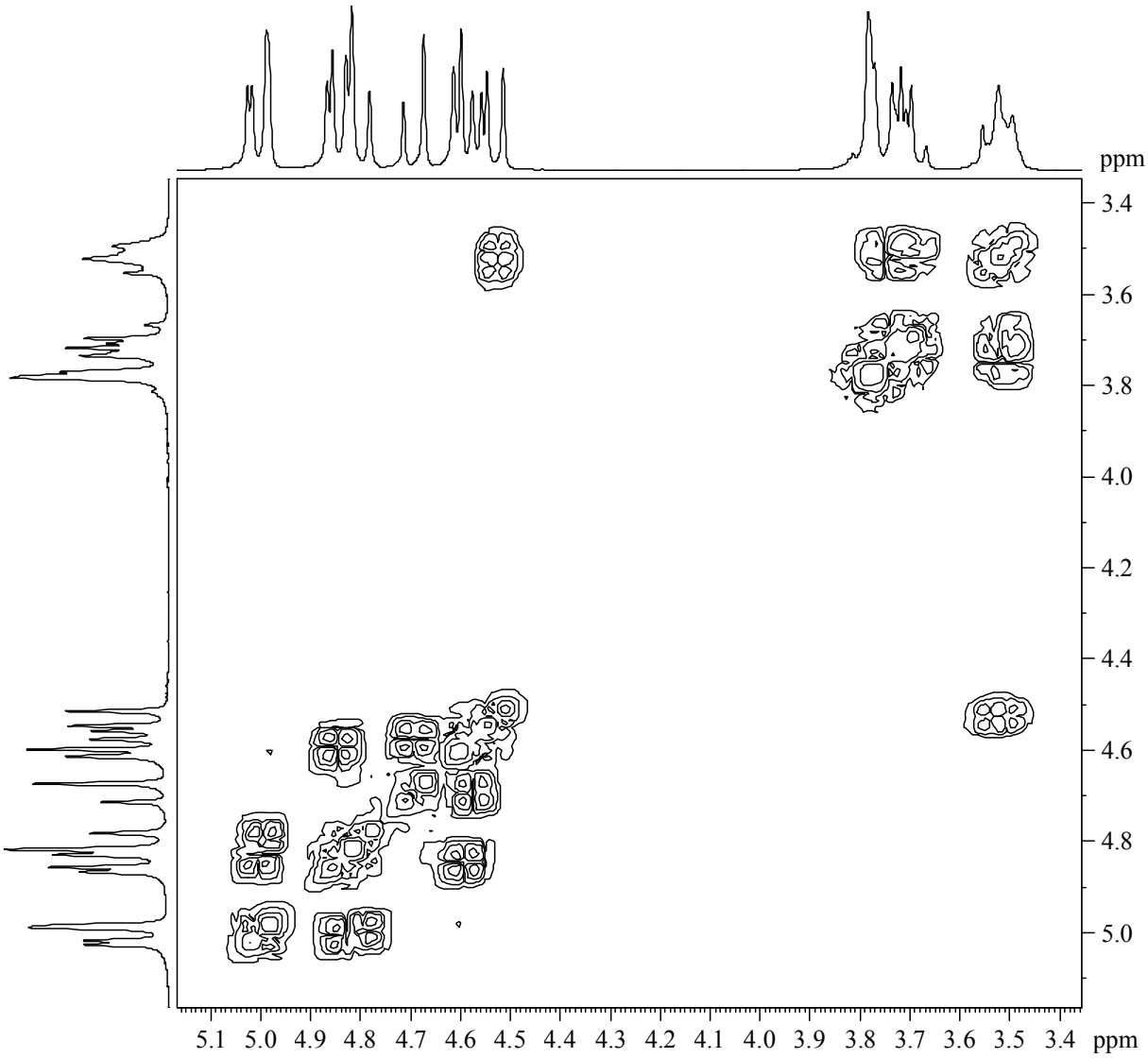
$CDCl_3$ 300 MHz



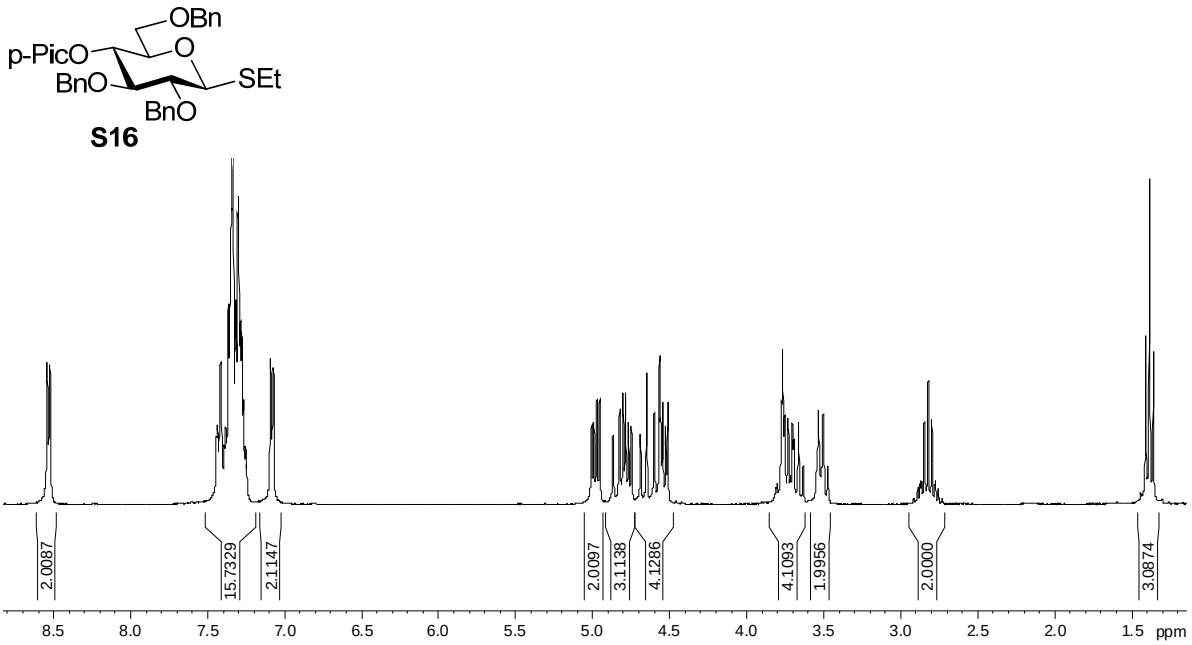
$CDCl_3$ 75 MHz



S14



$CDCl_3$ 300 MHz



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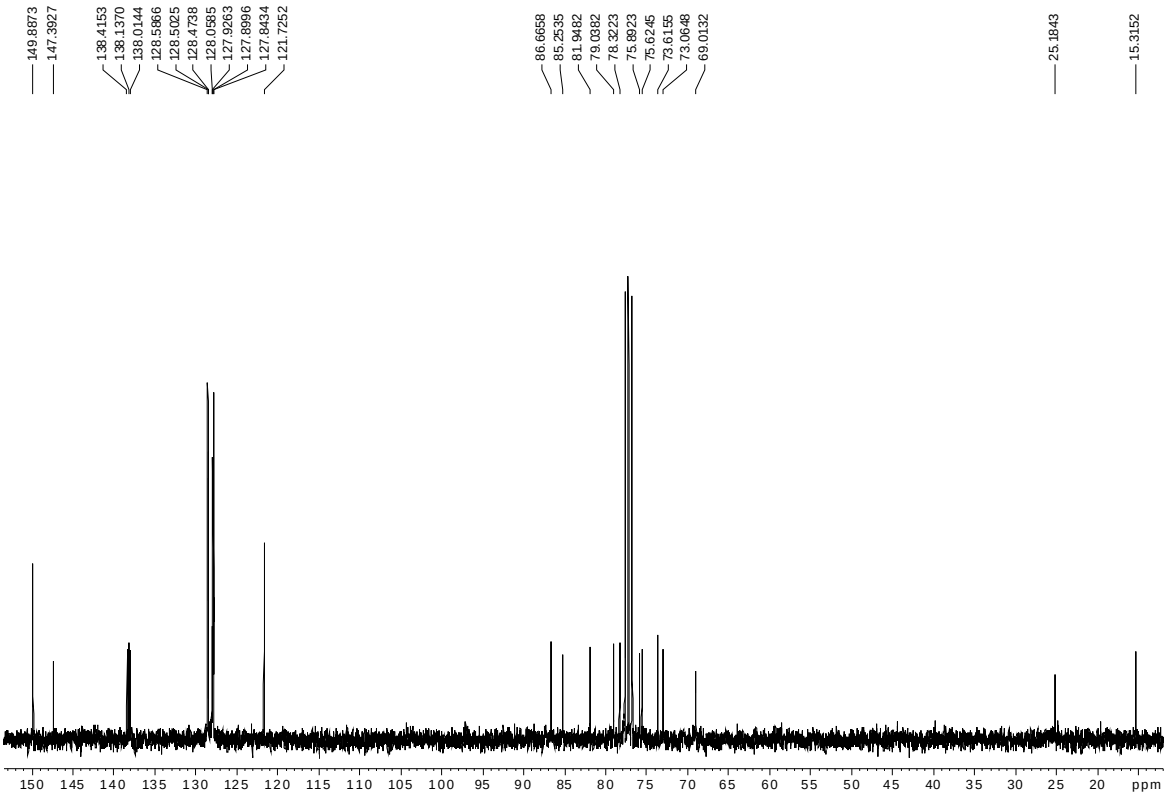

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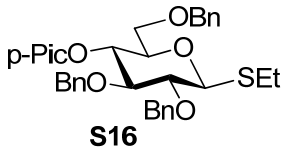
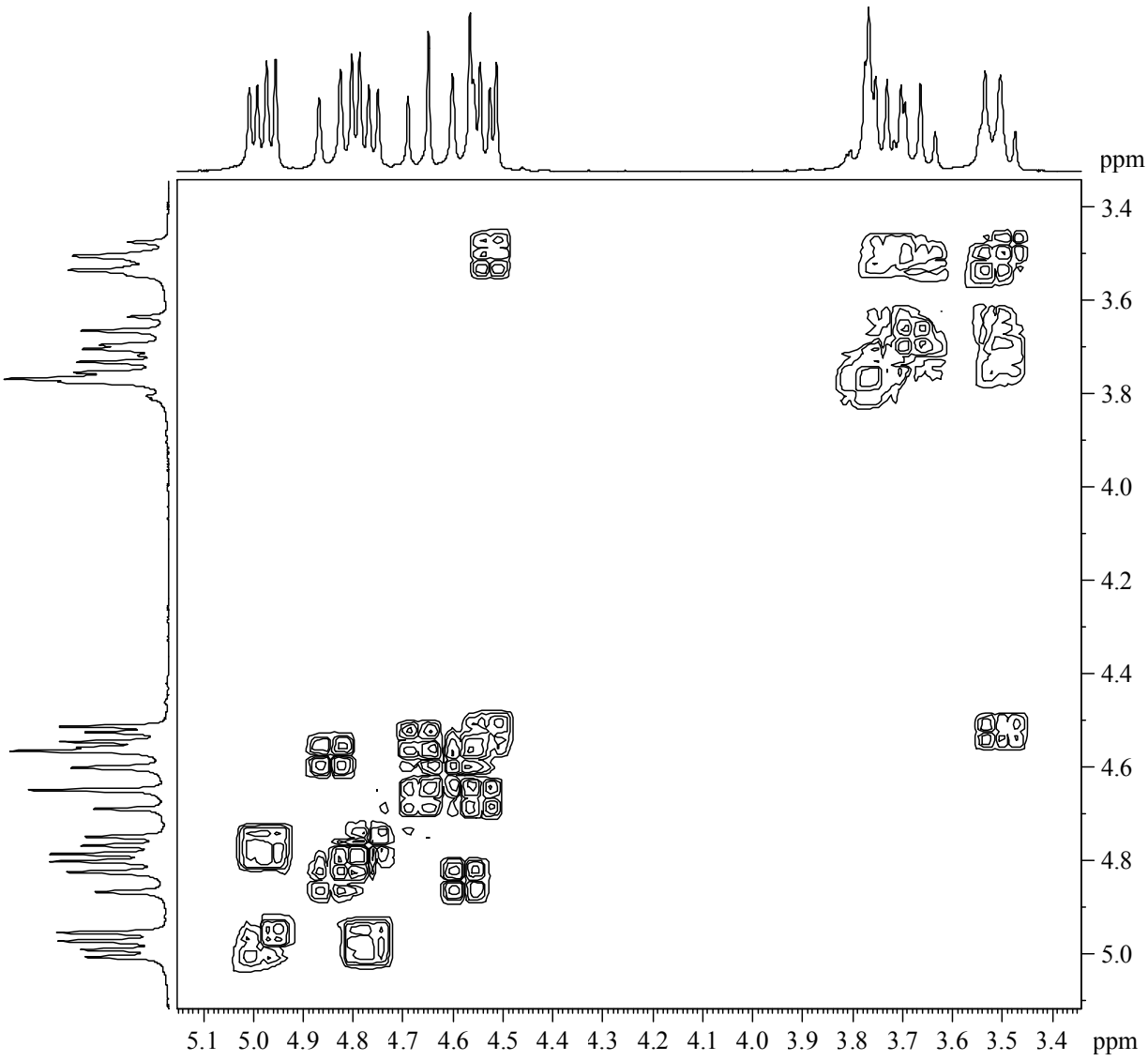


S16



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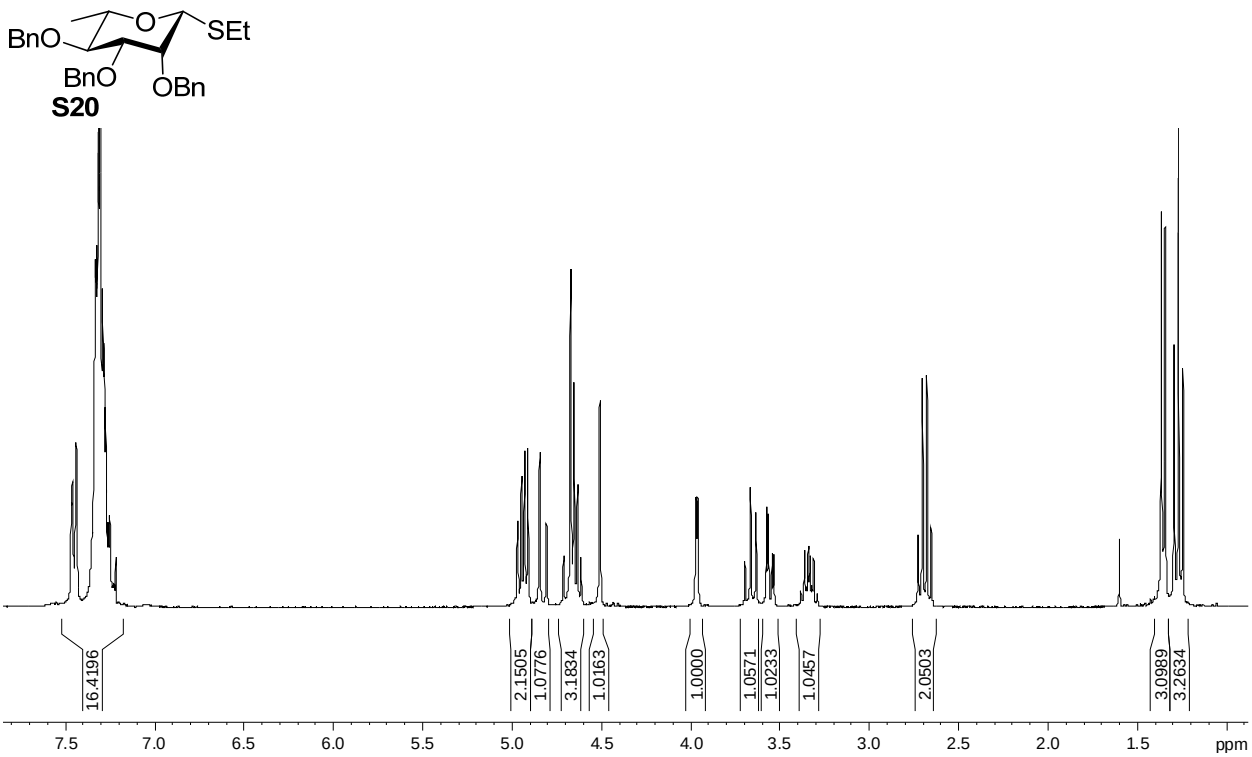

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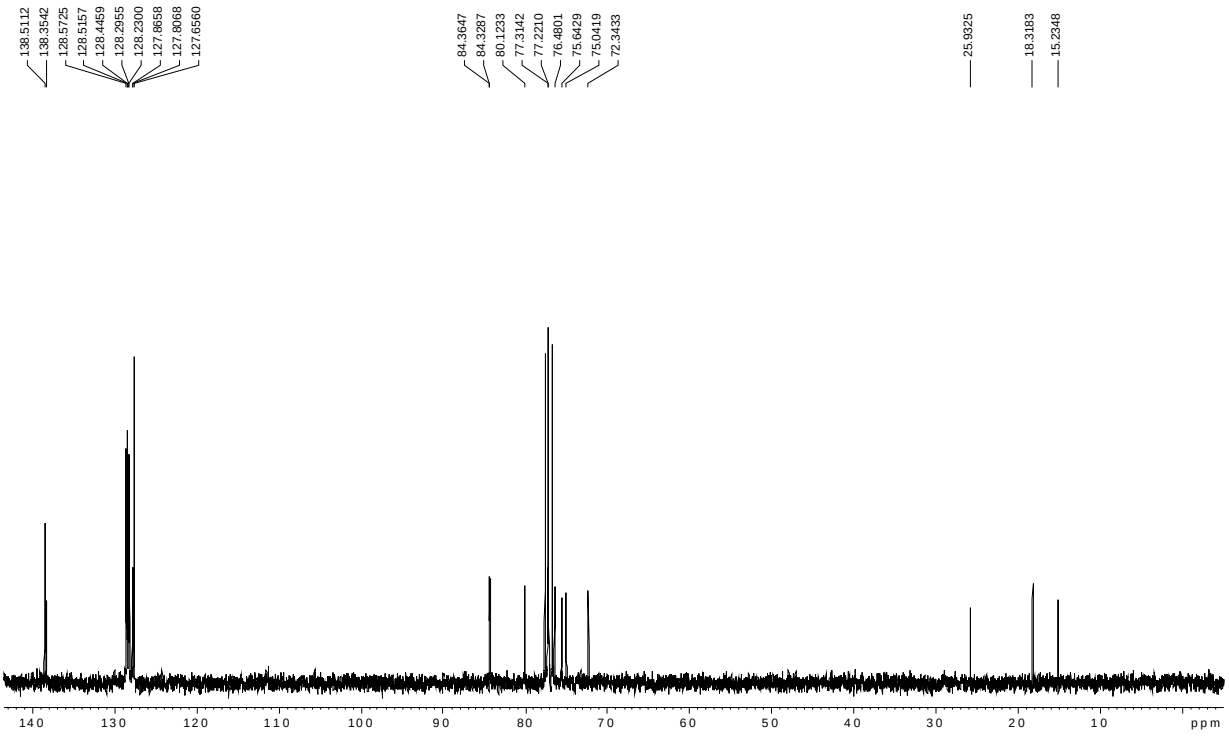

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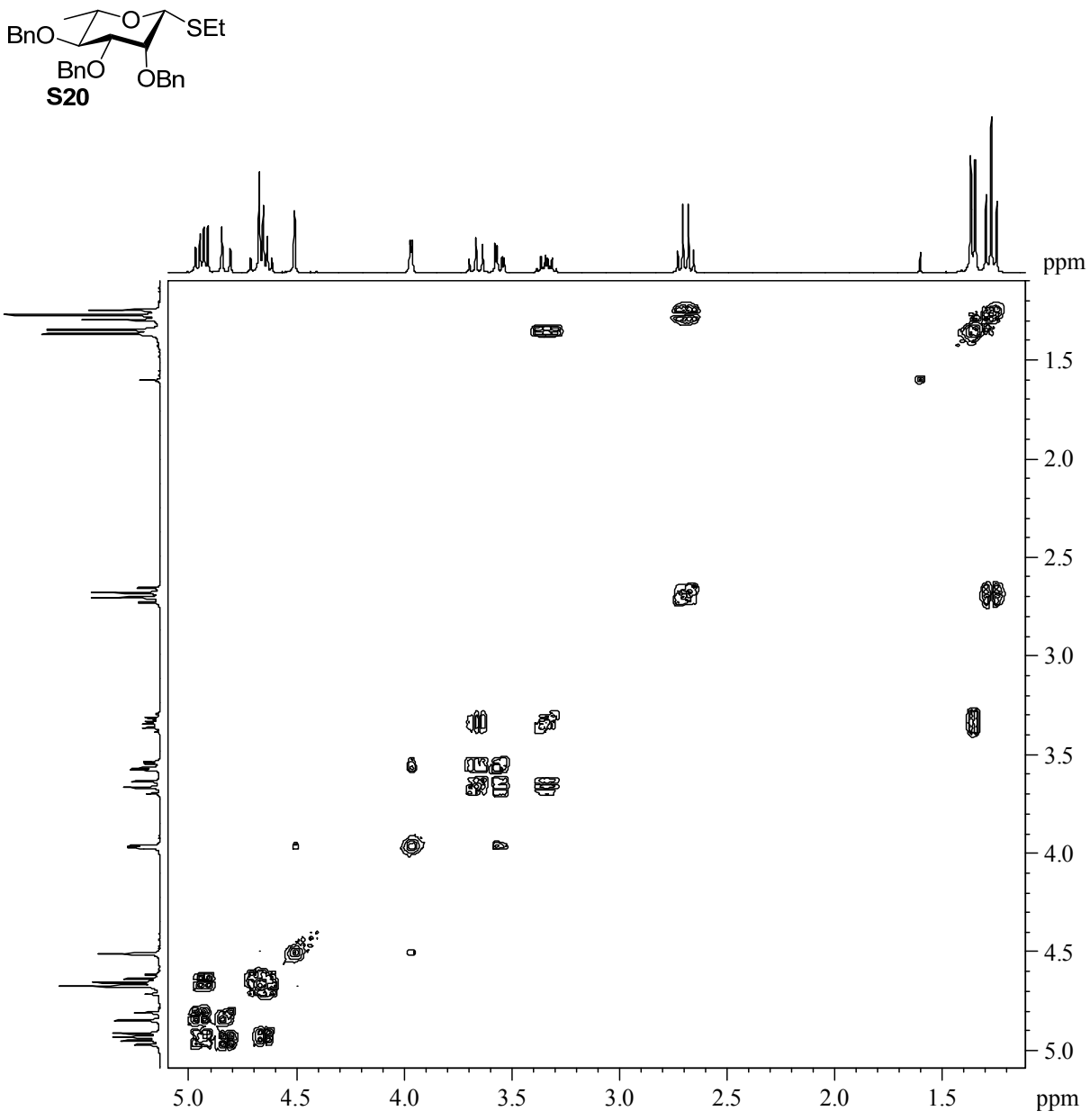

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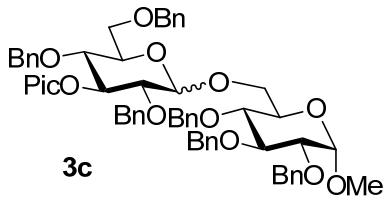
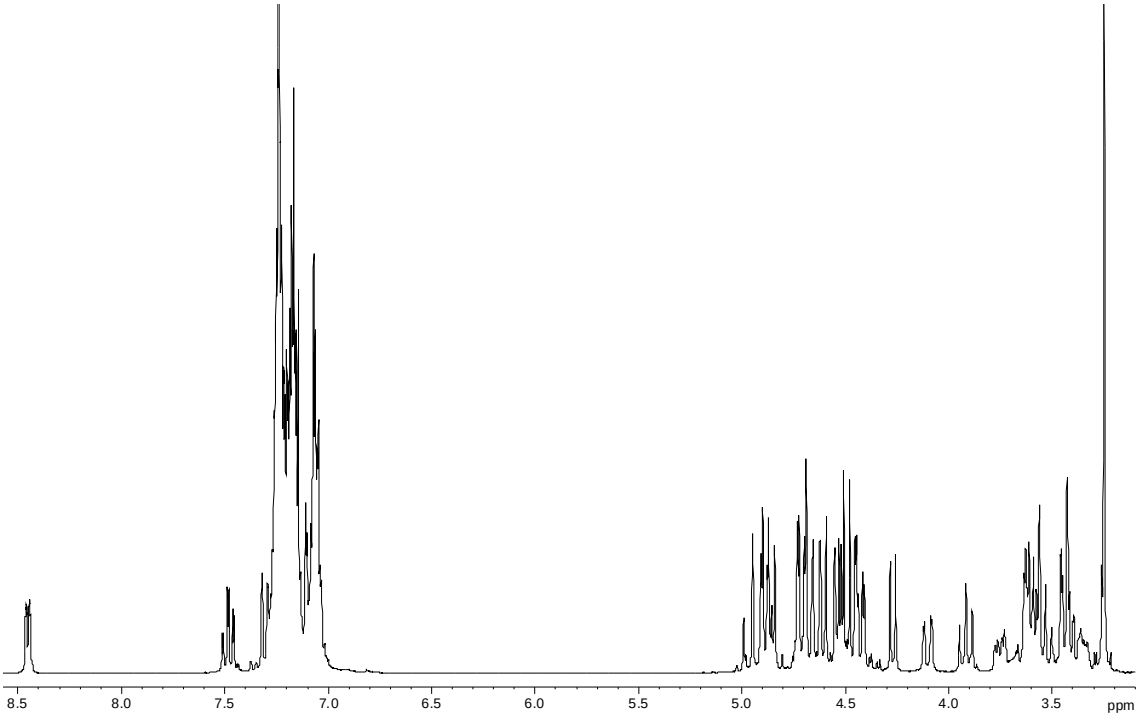


3c



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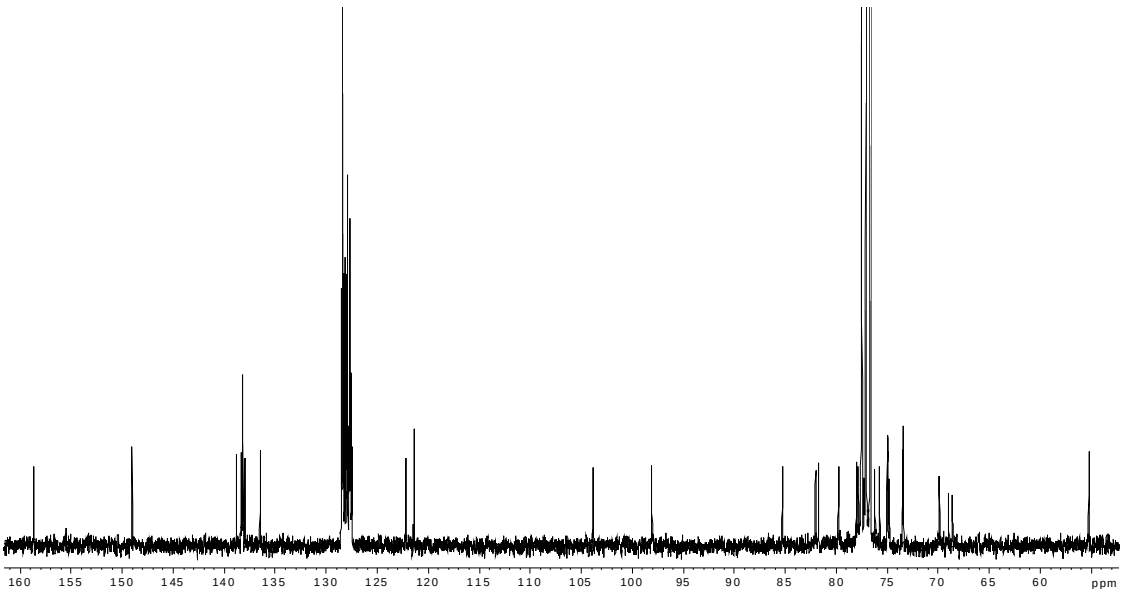

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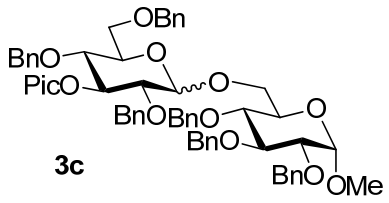

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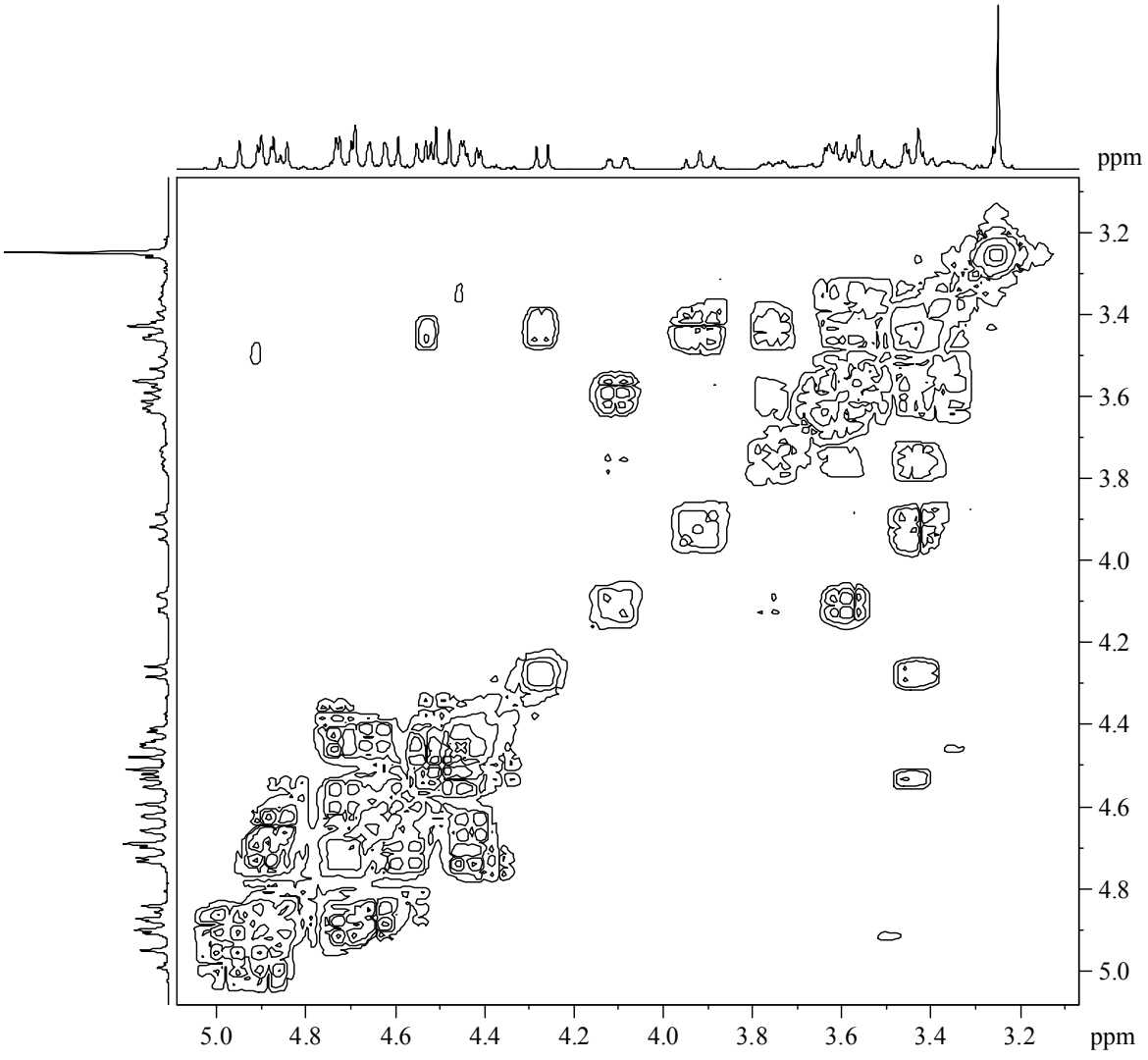

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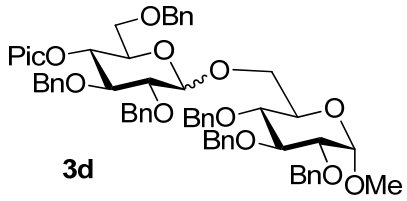

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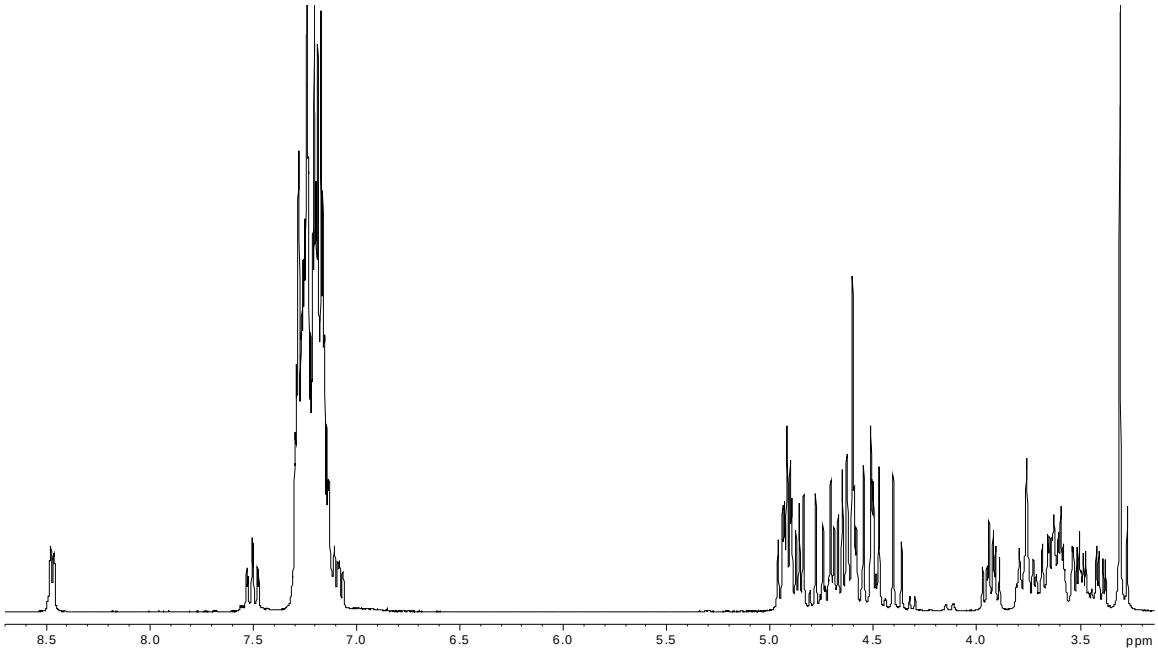

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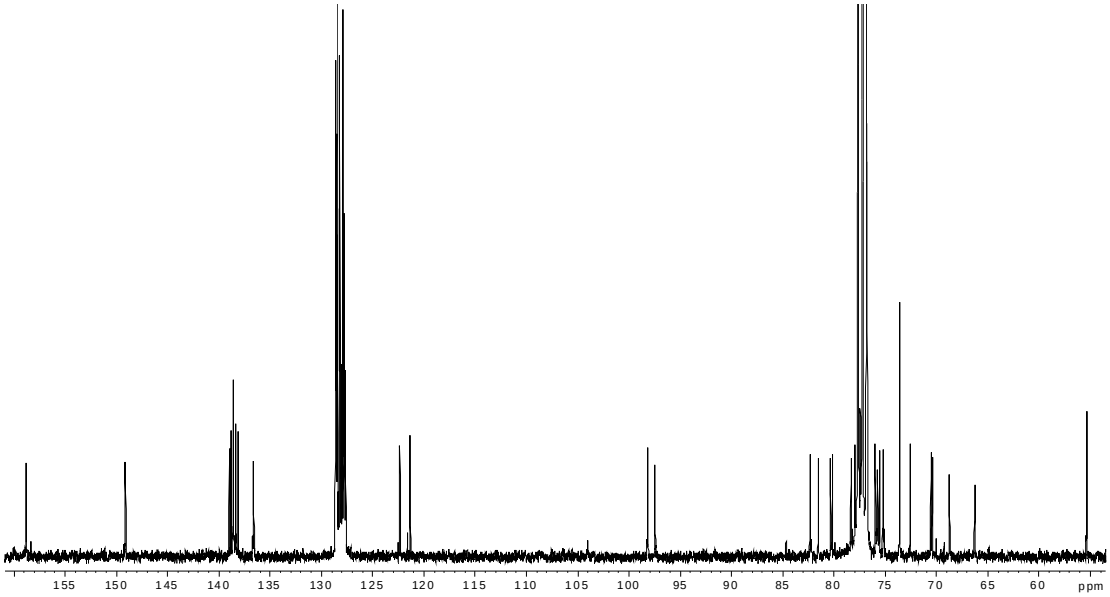

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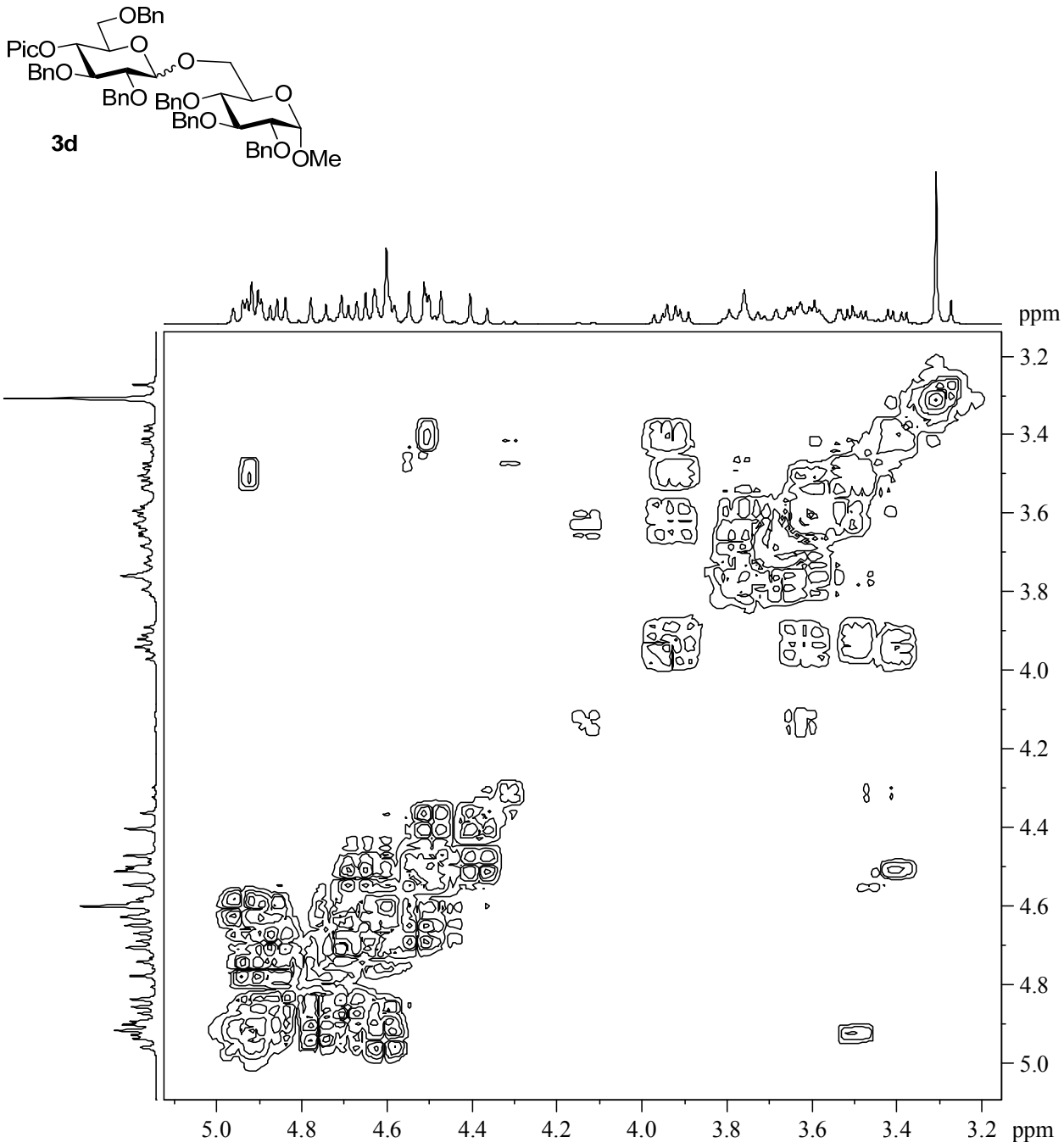

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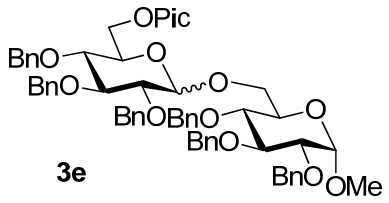

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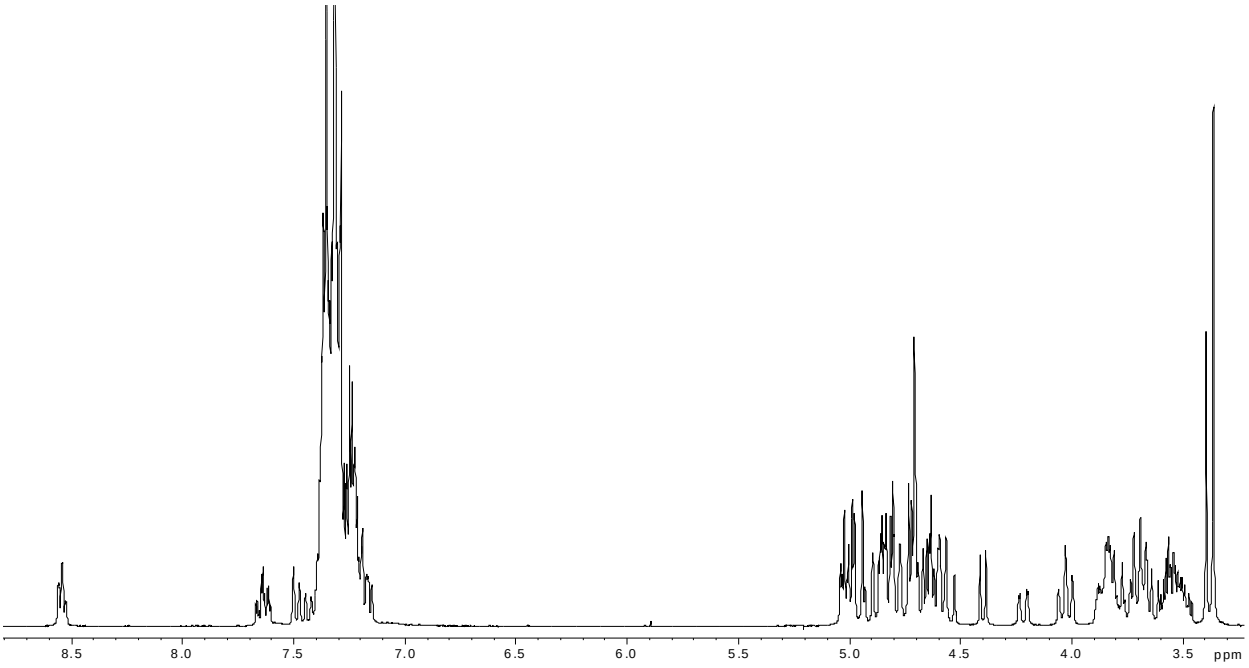

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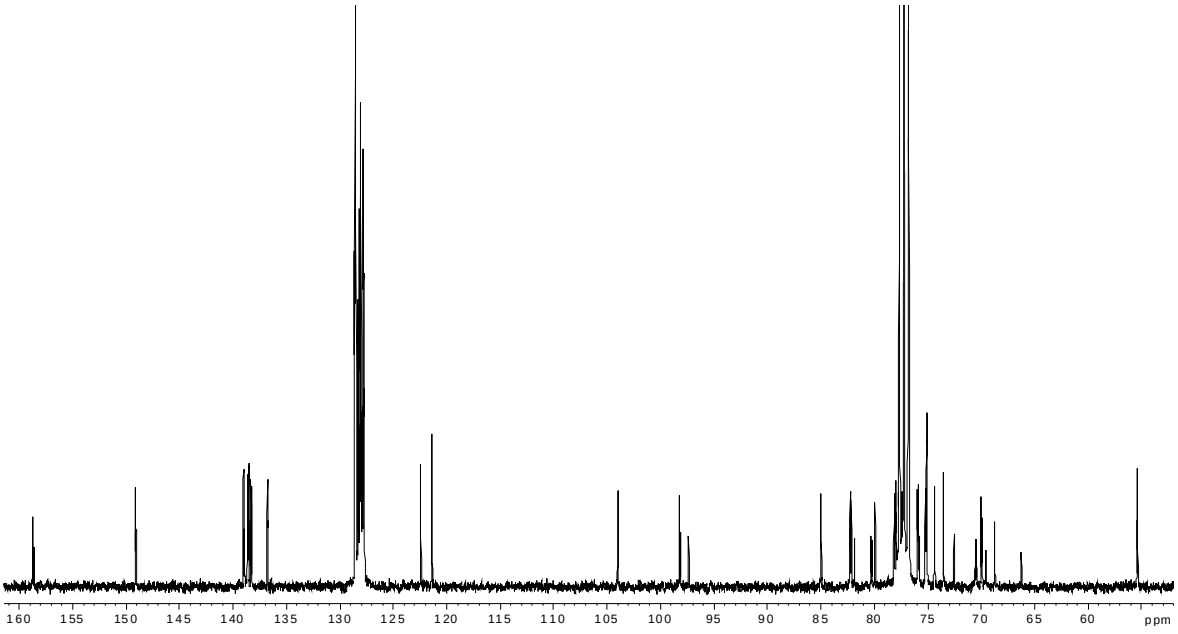

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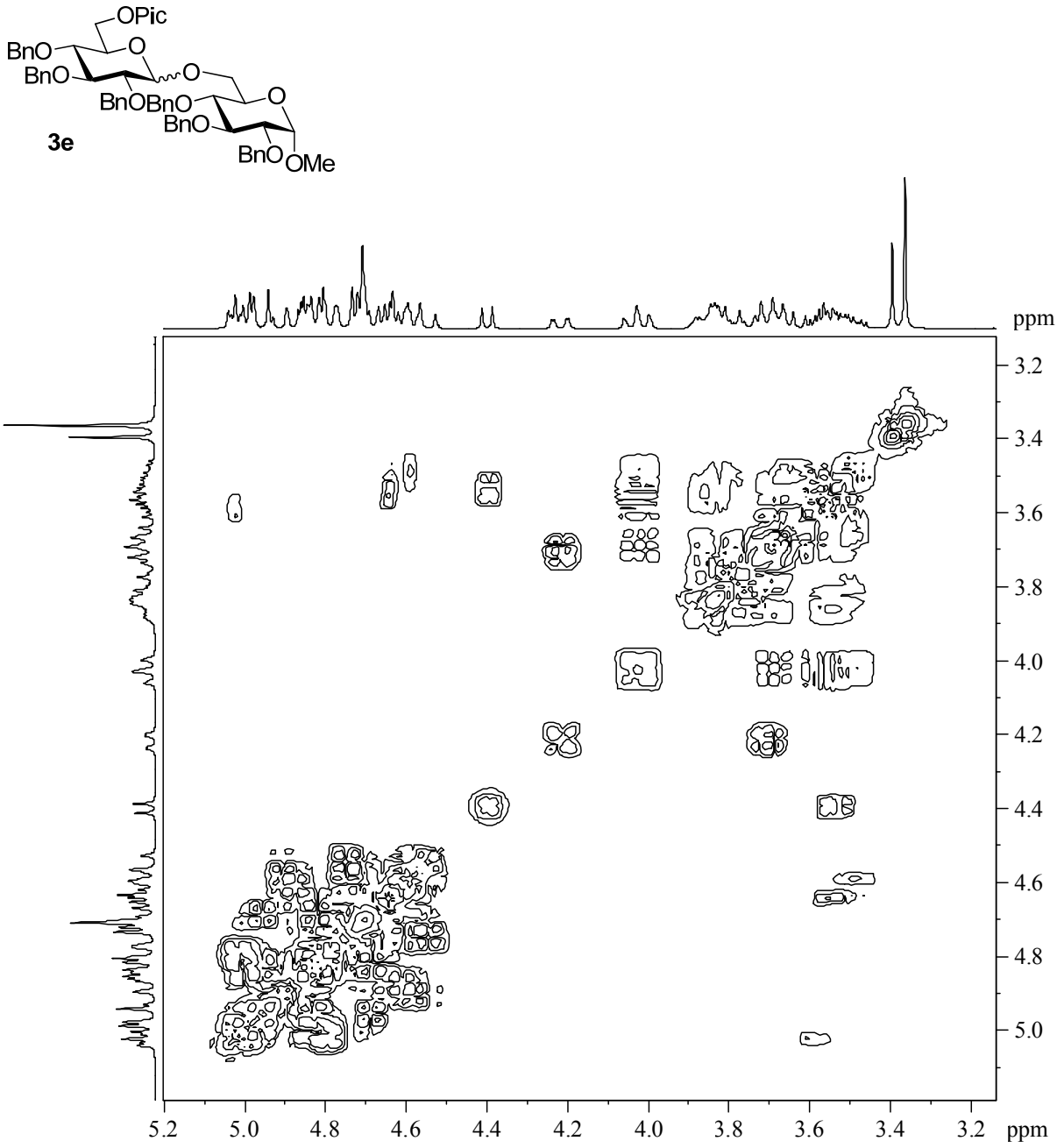

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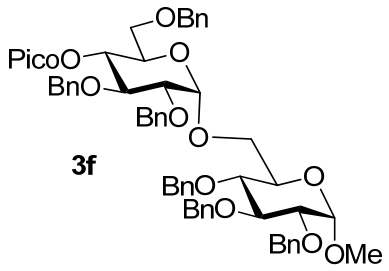

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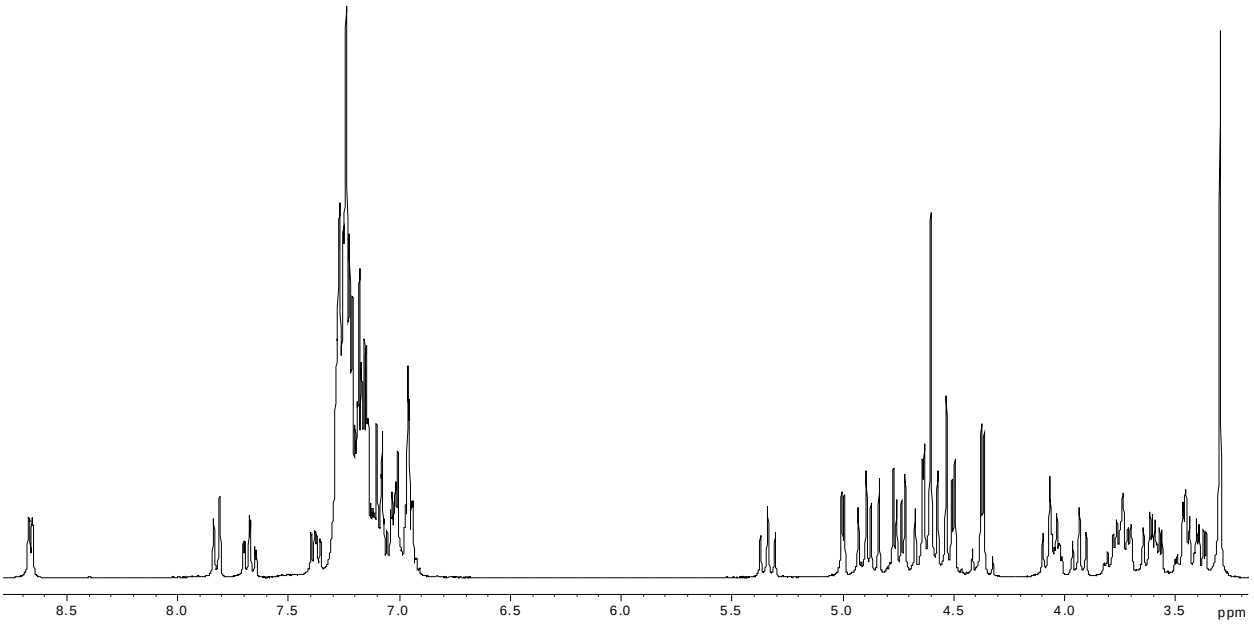

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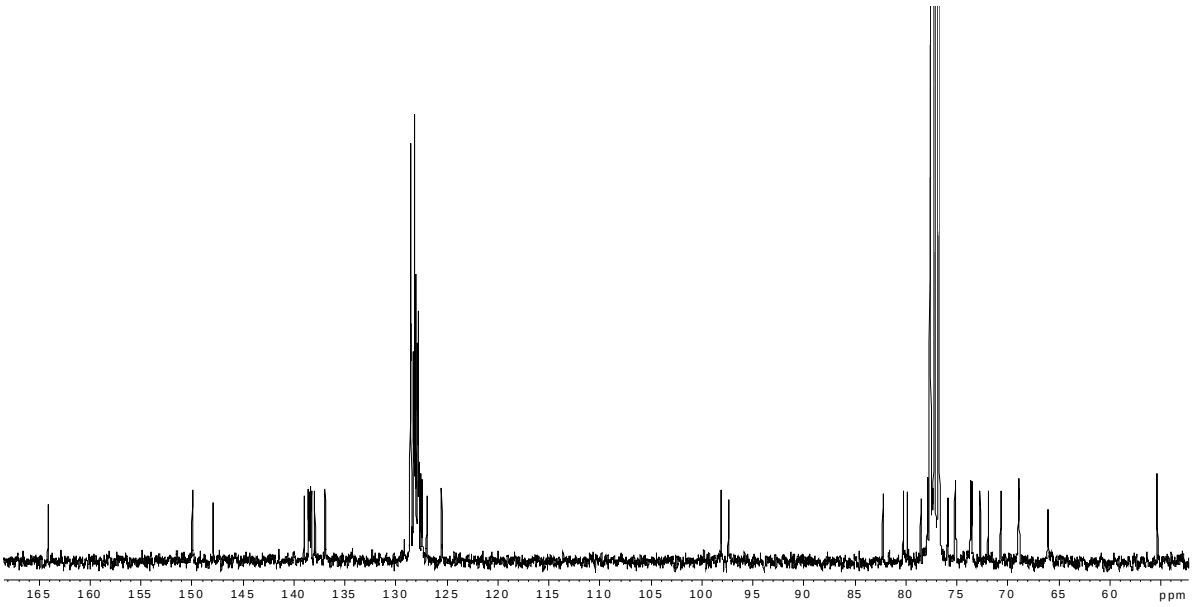

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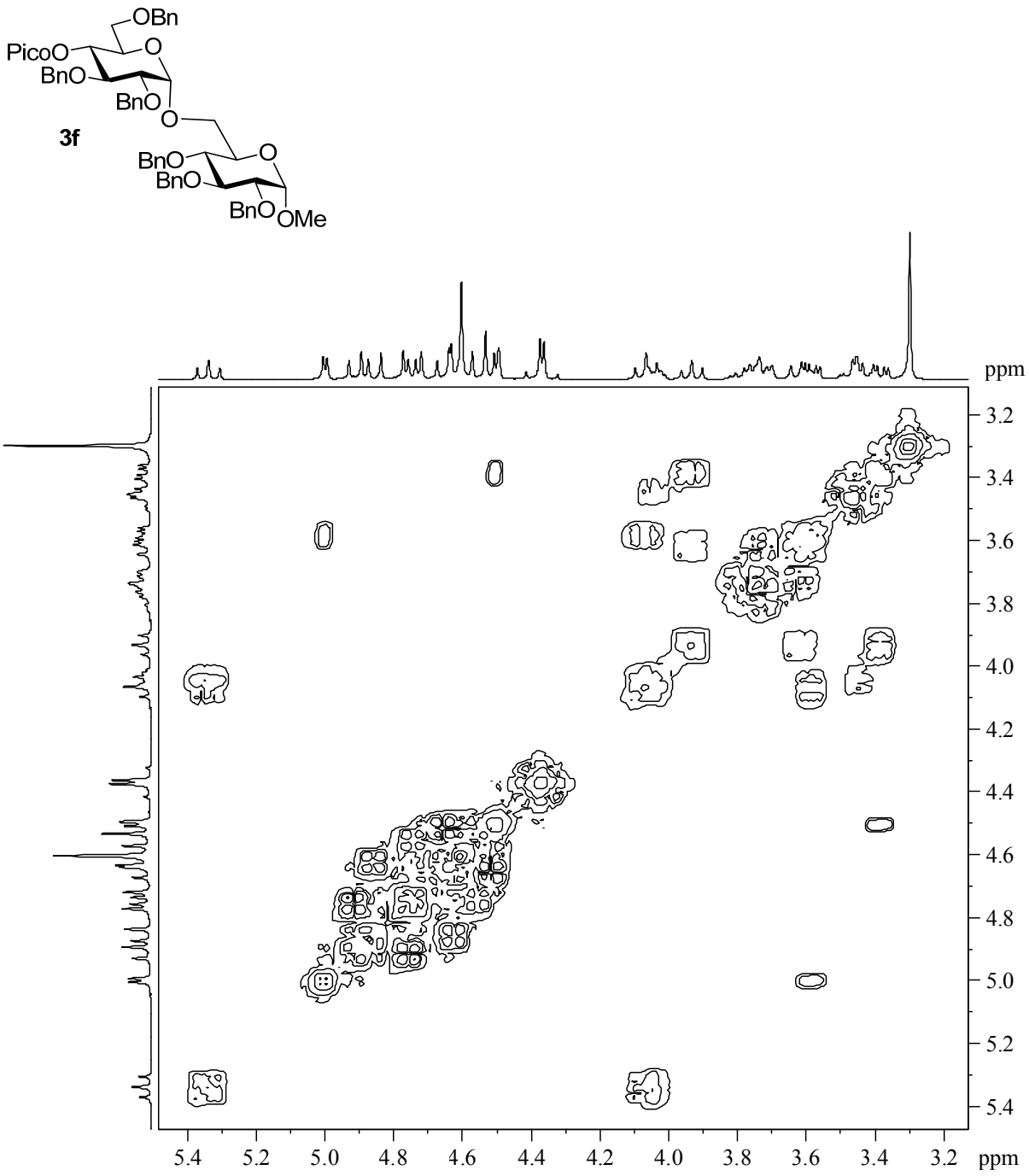

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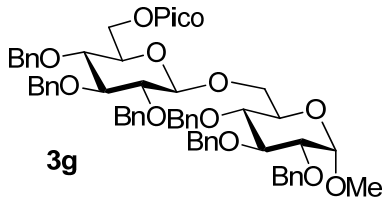

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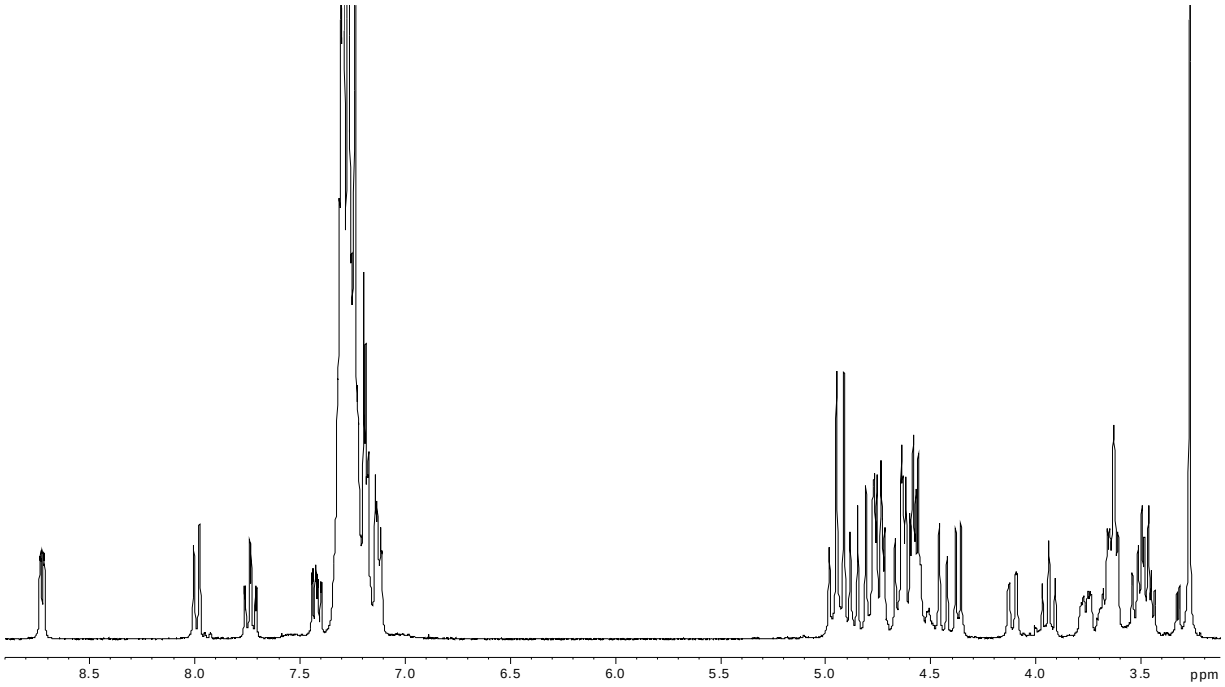

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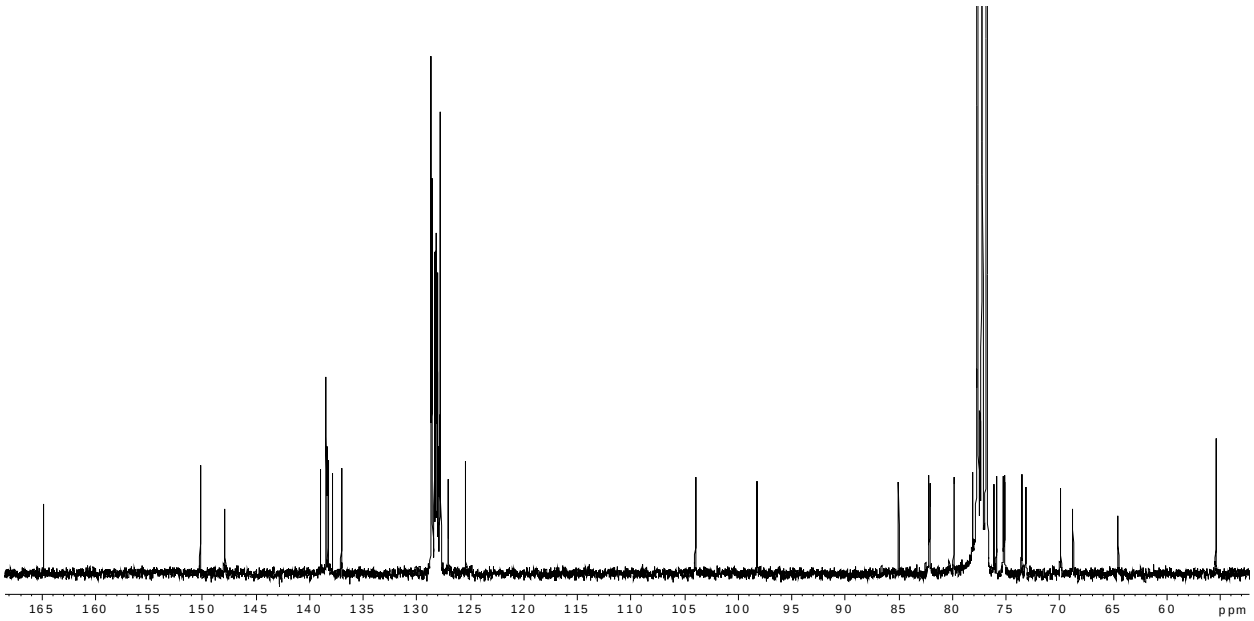

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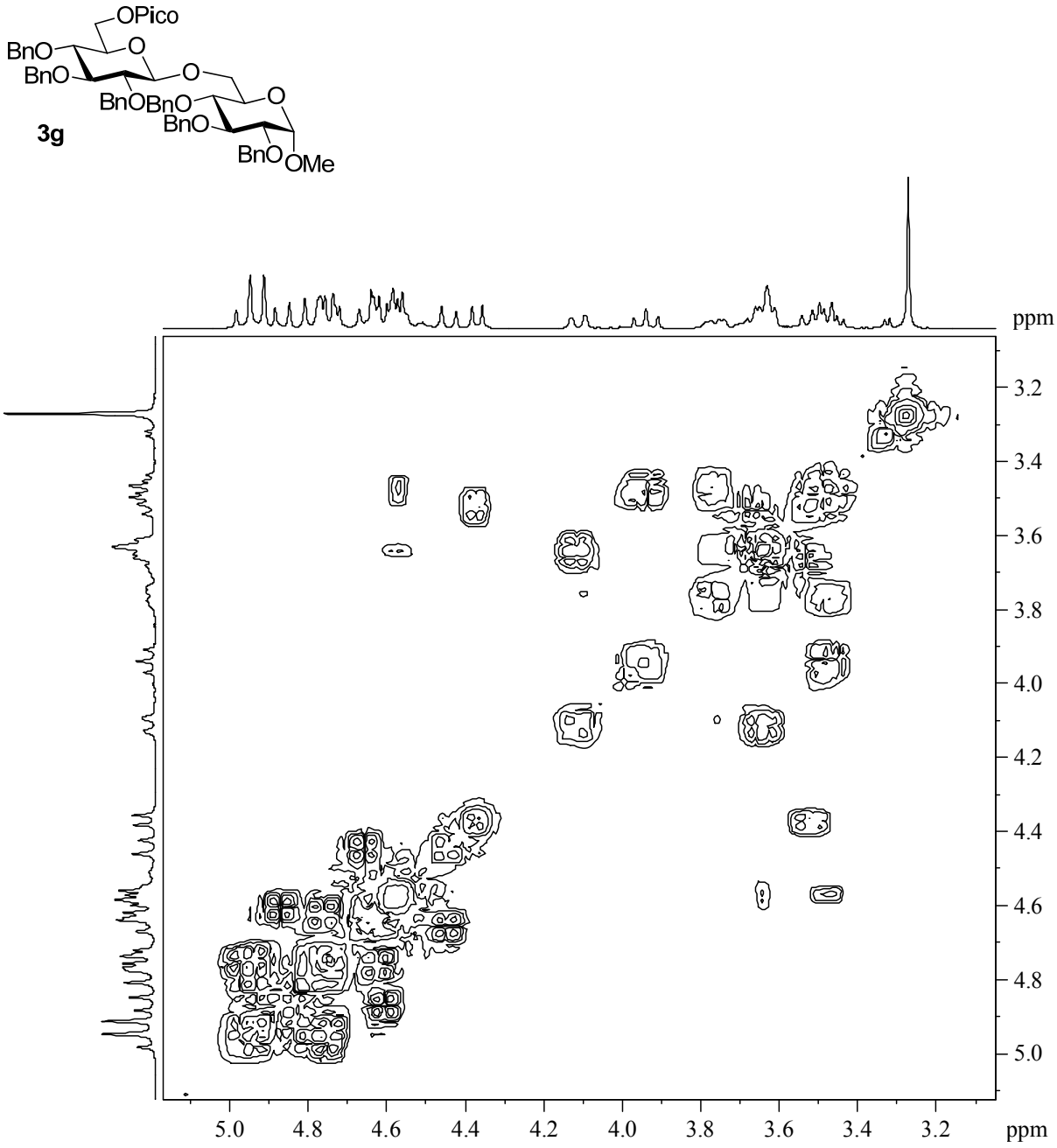

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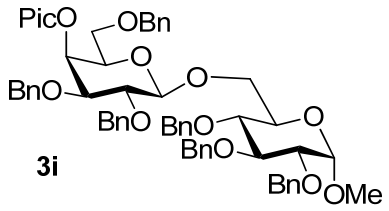

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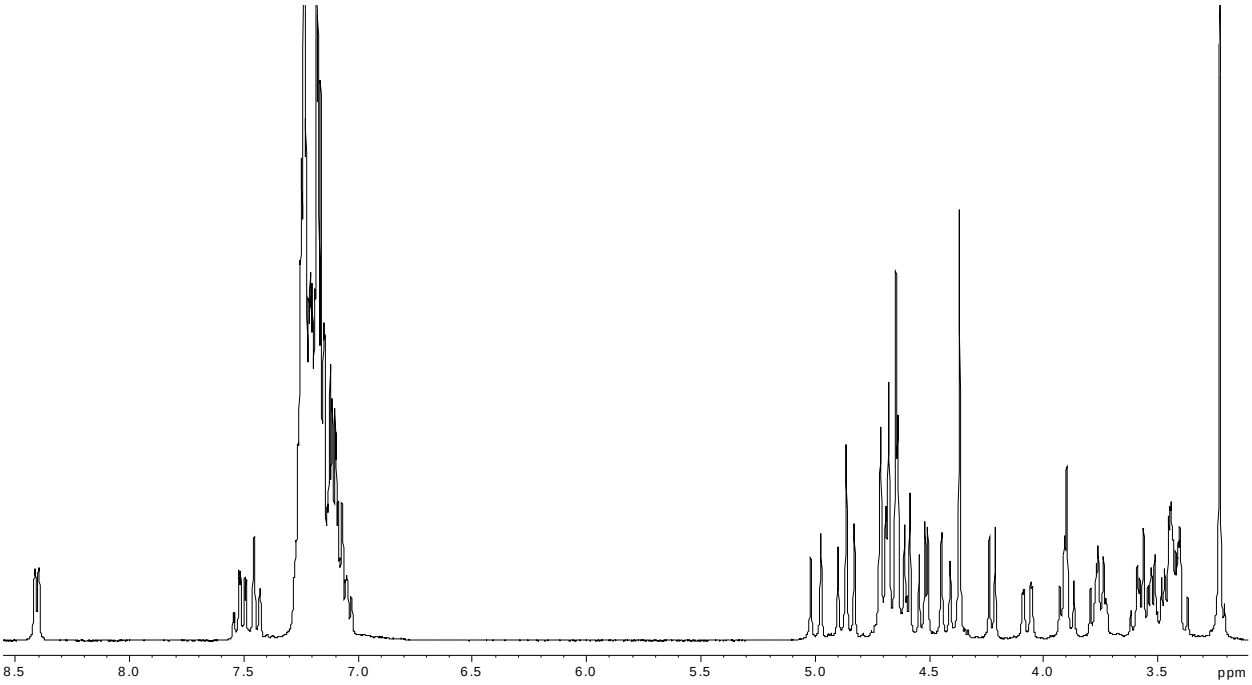

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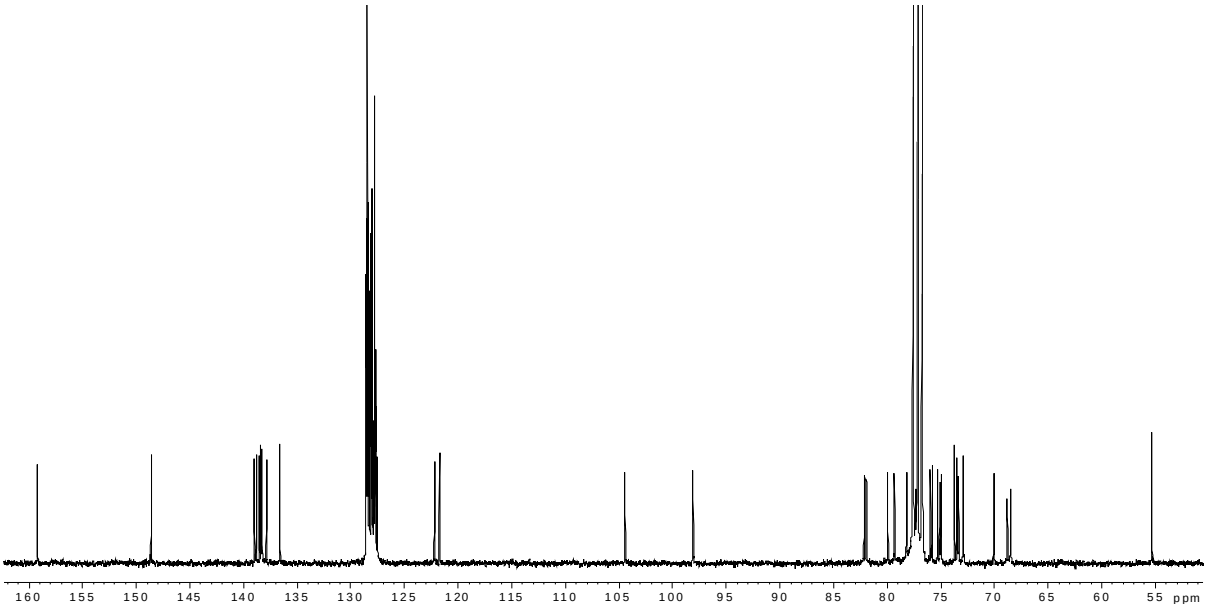

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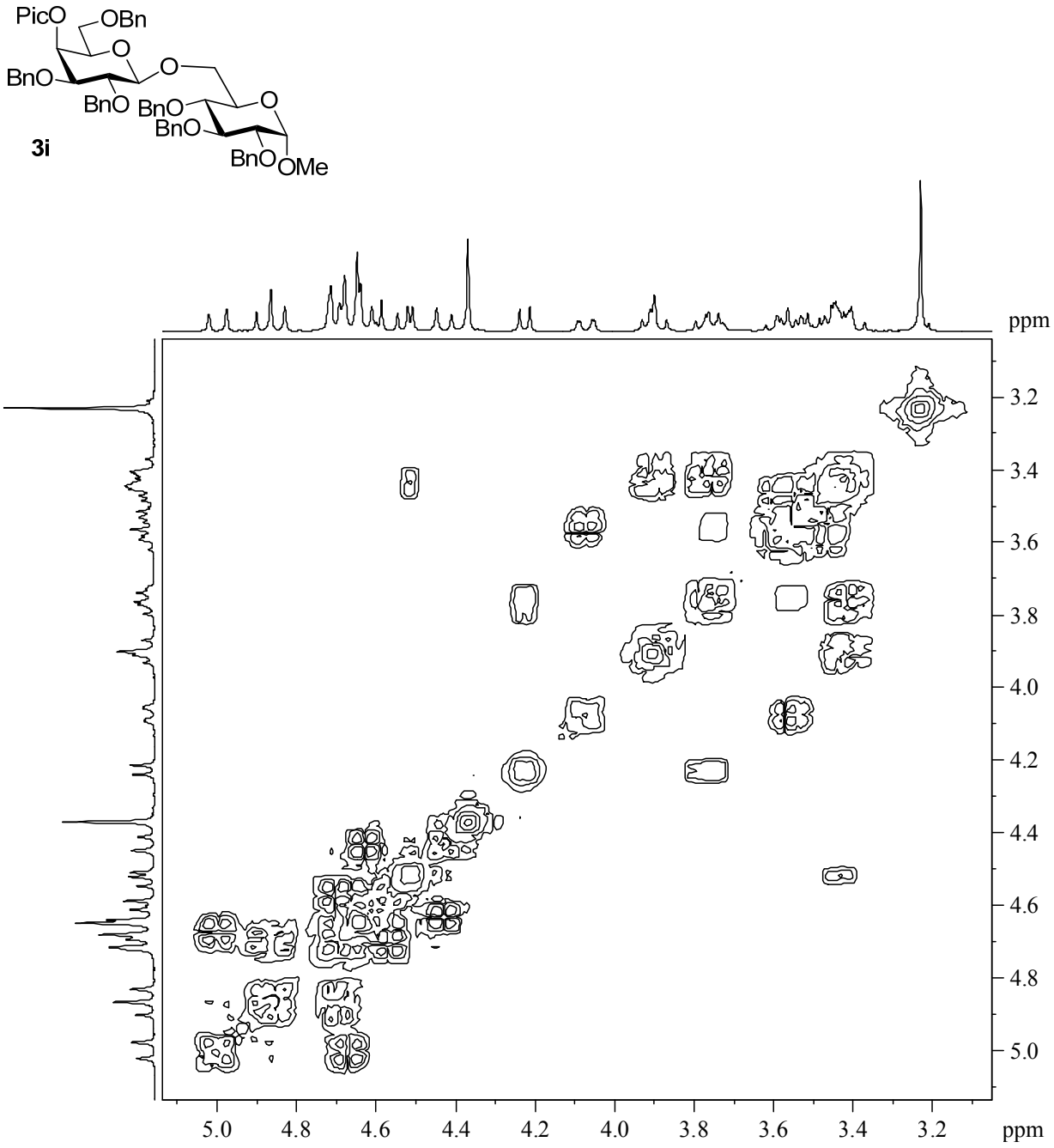

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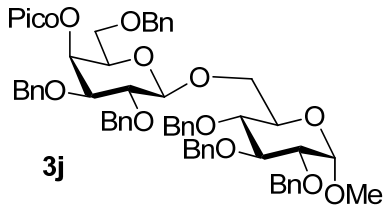

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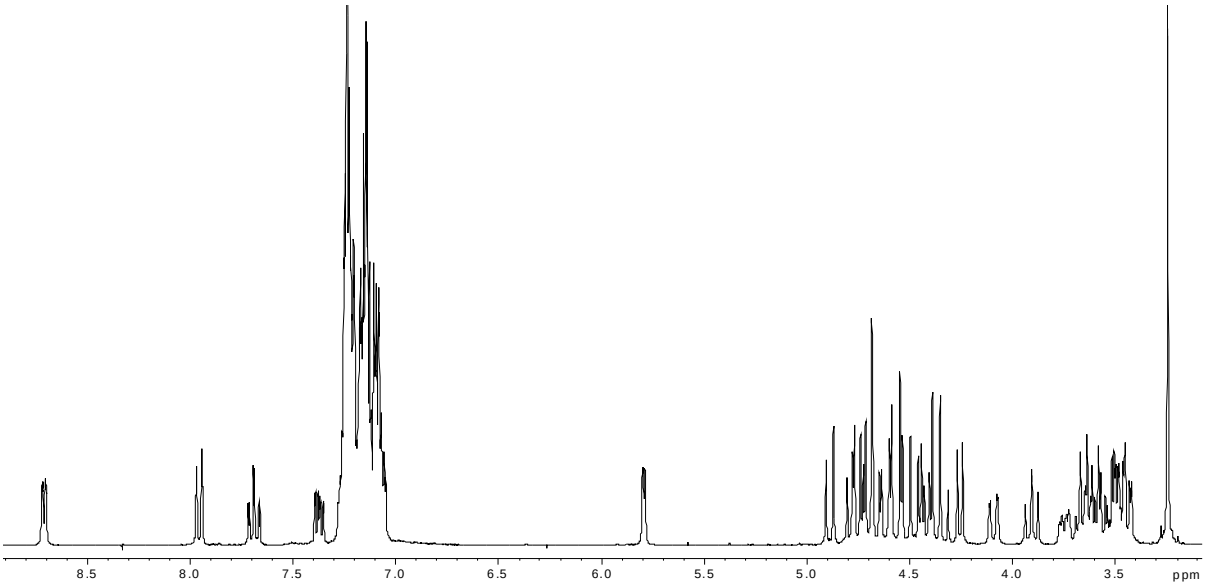

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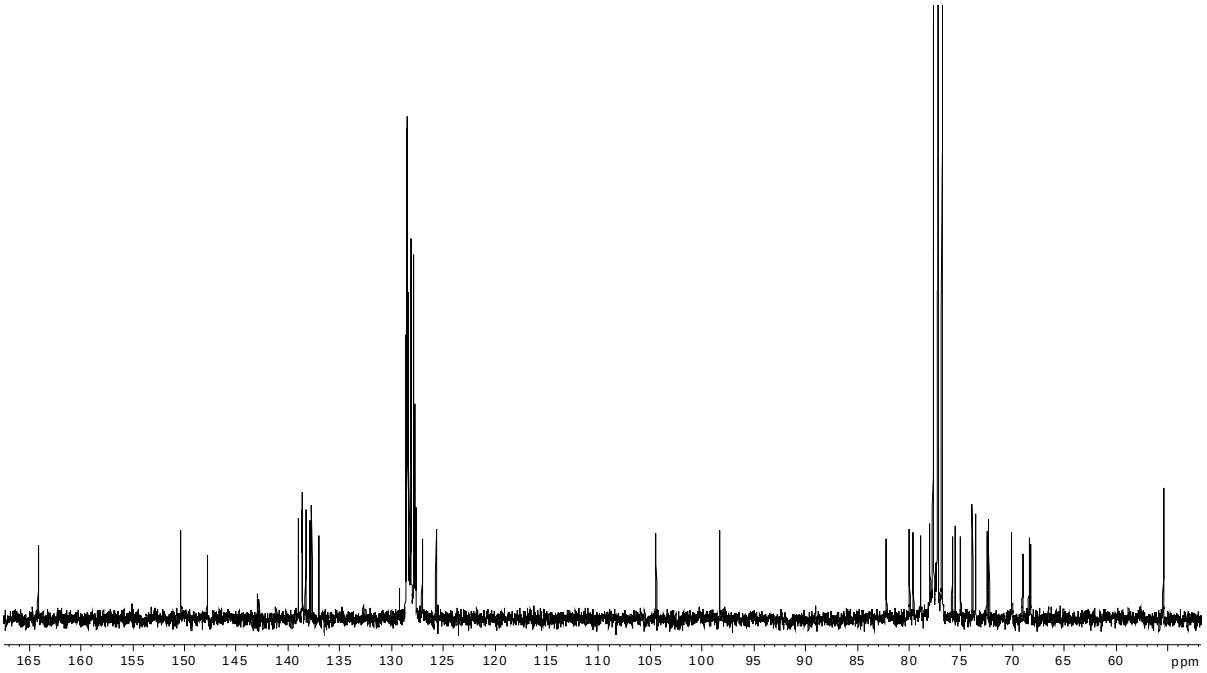

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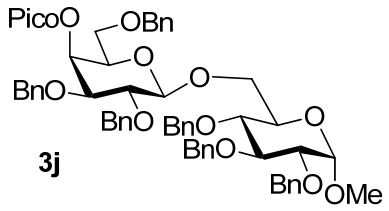

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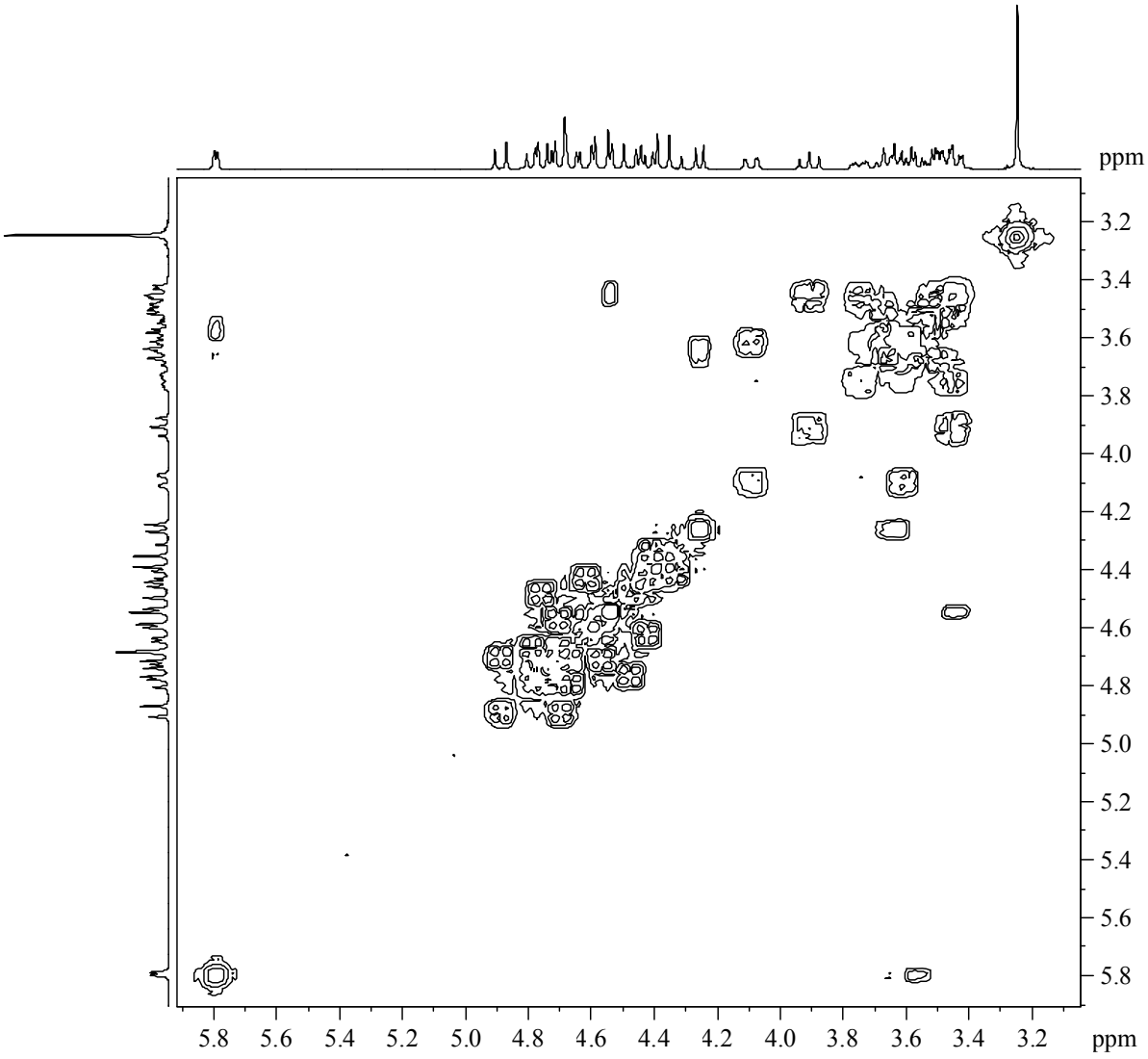

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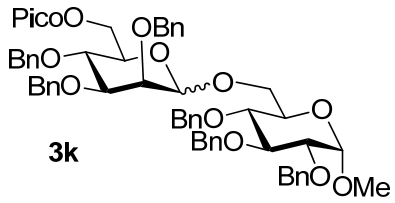

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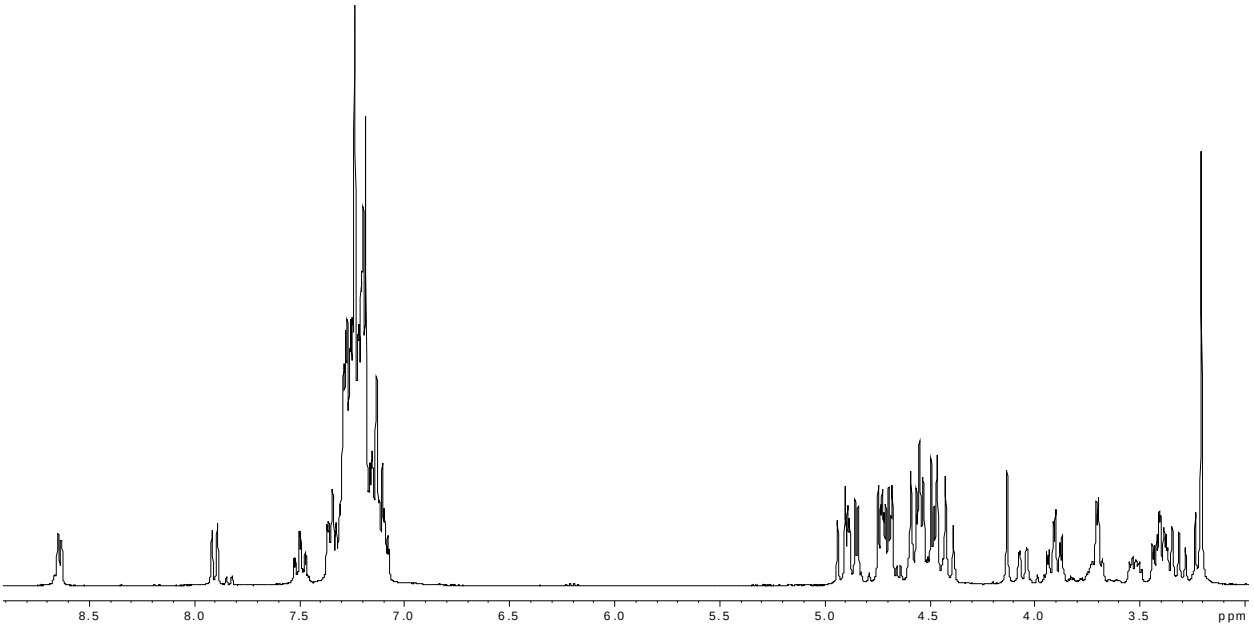

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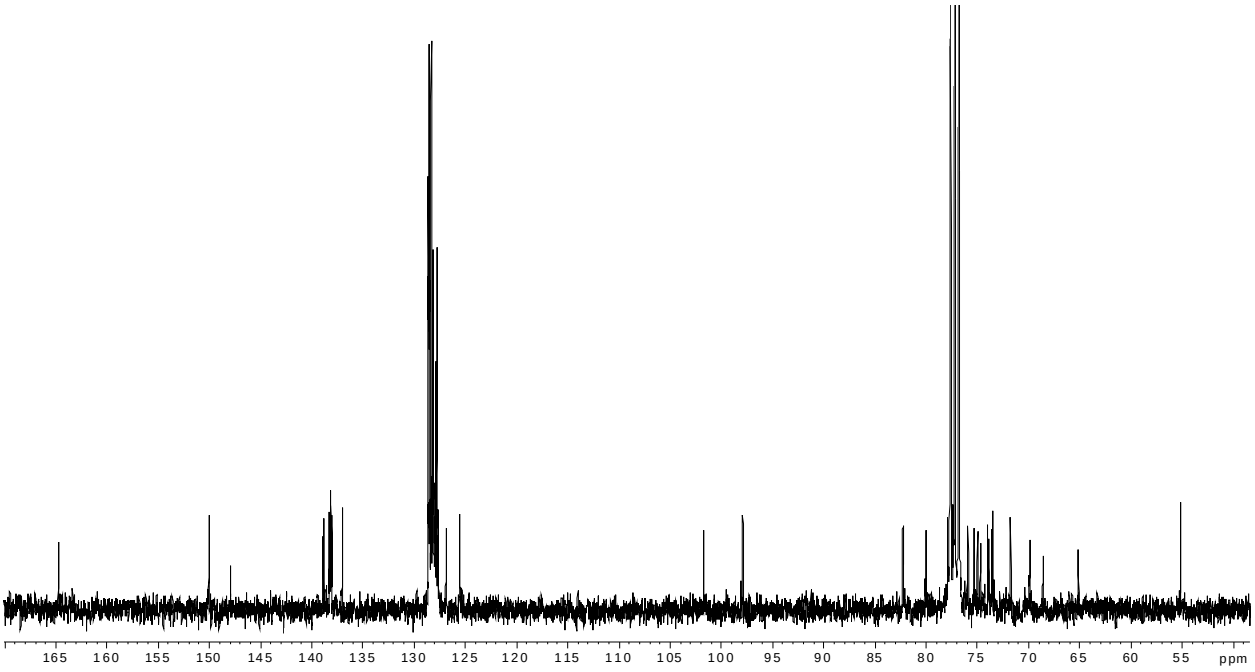

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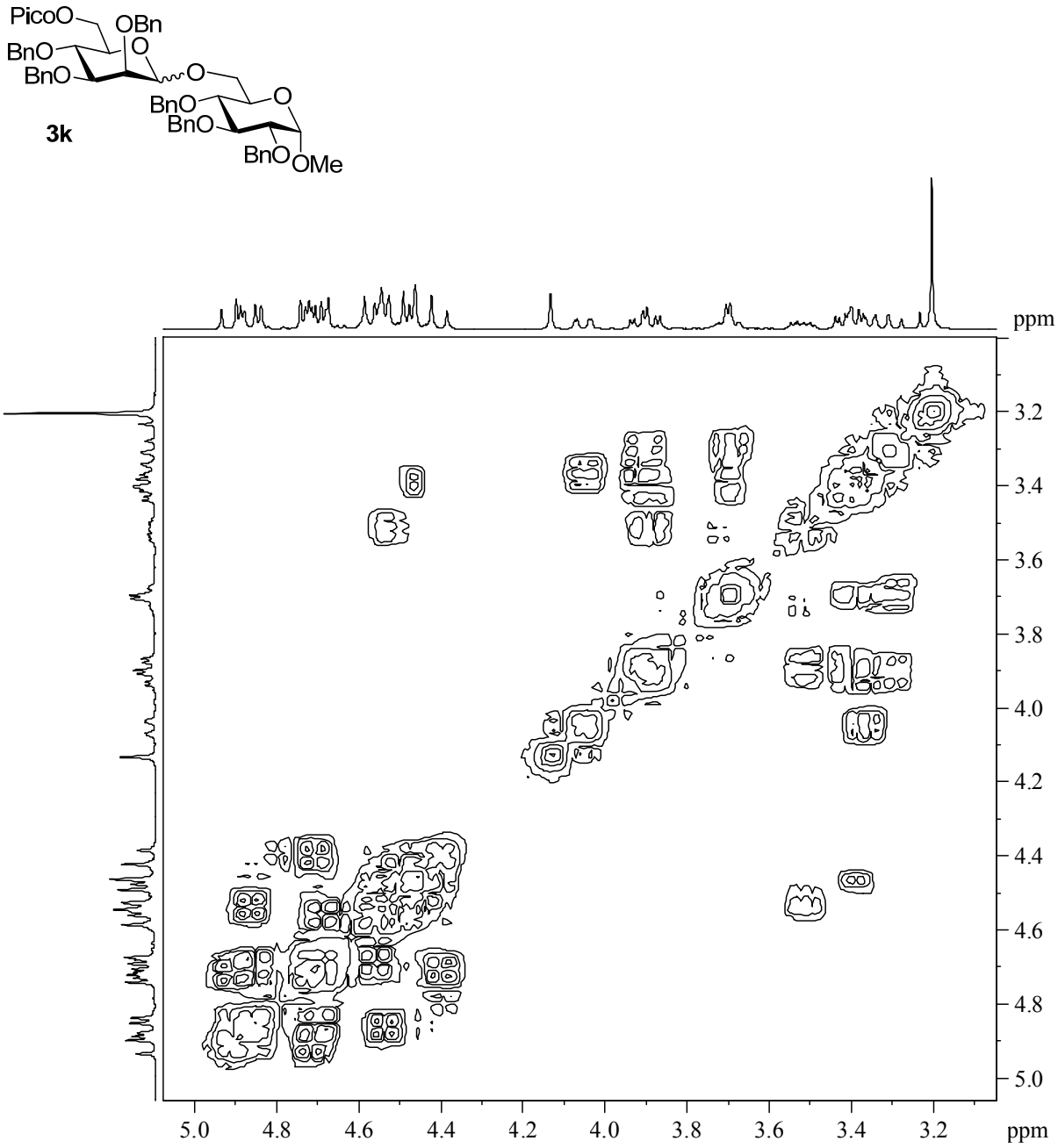

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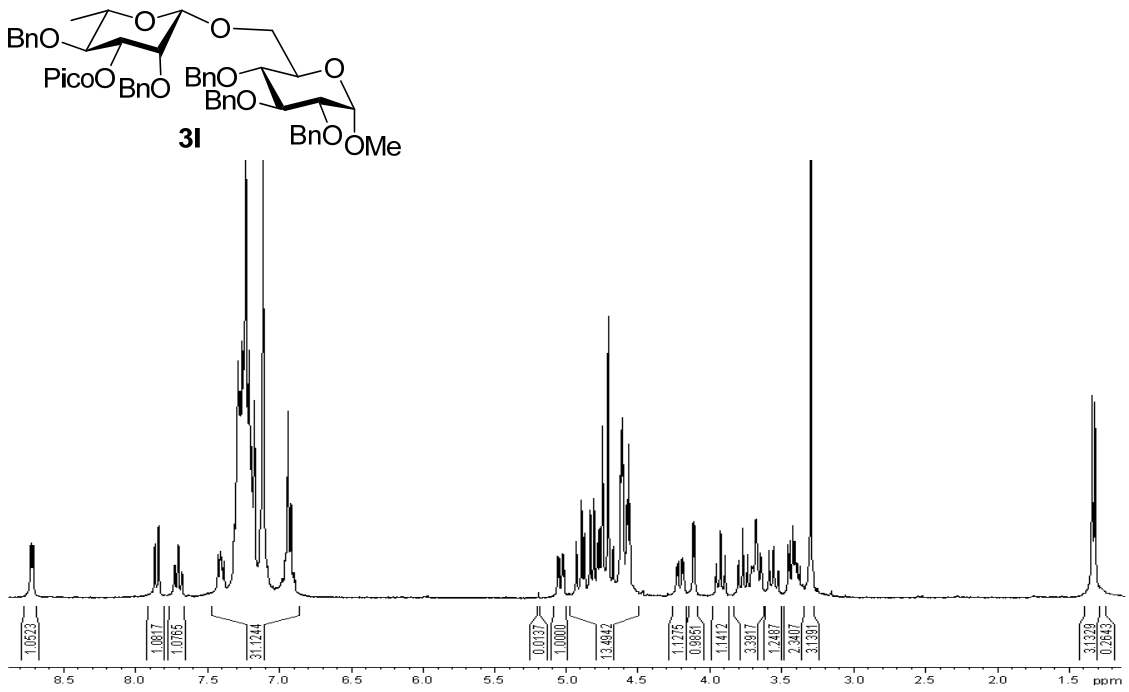

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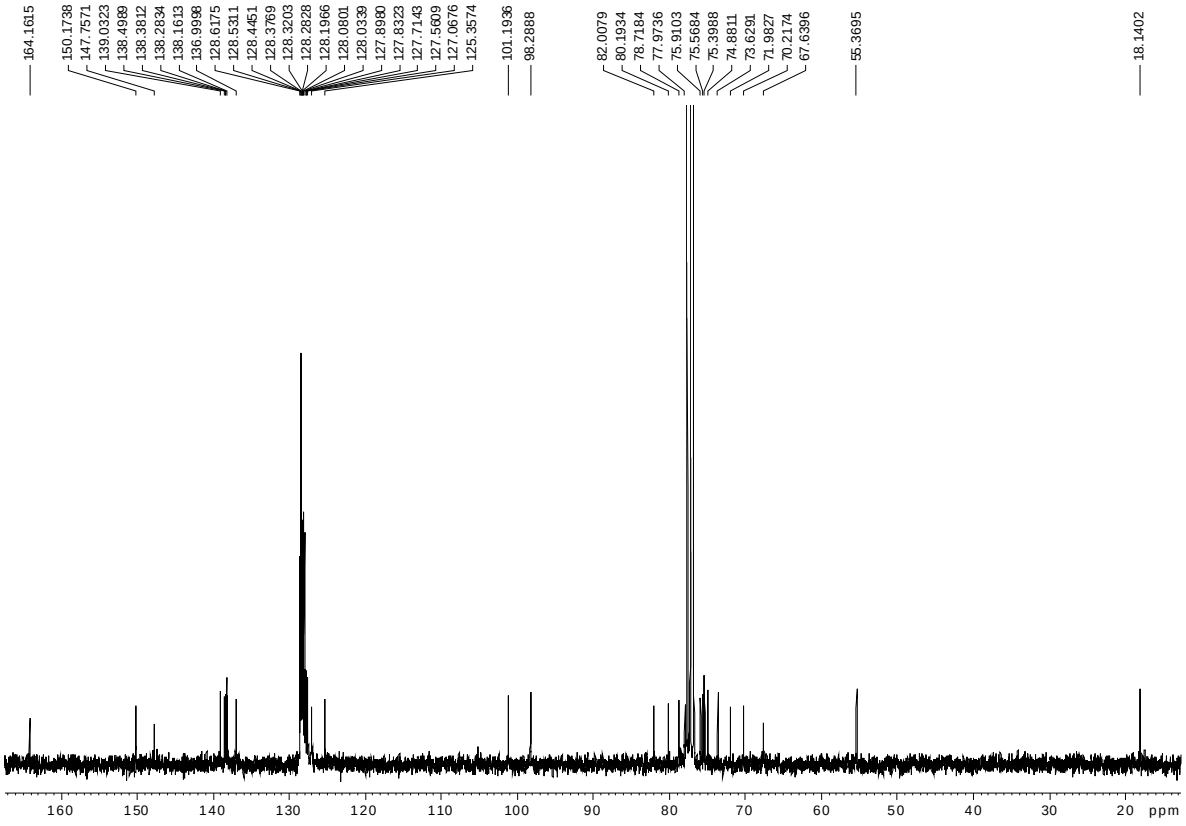

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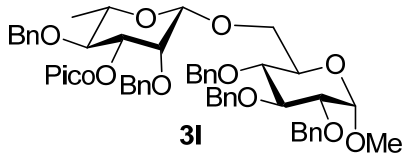

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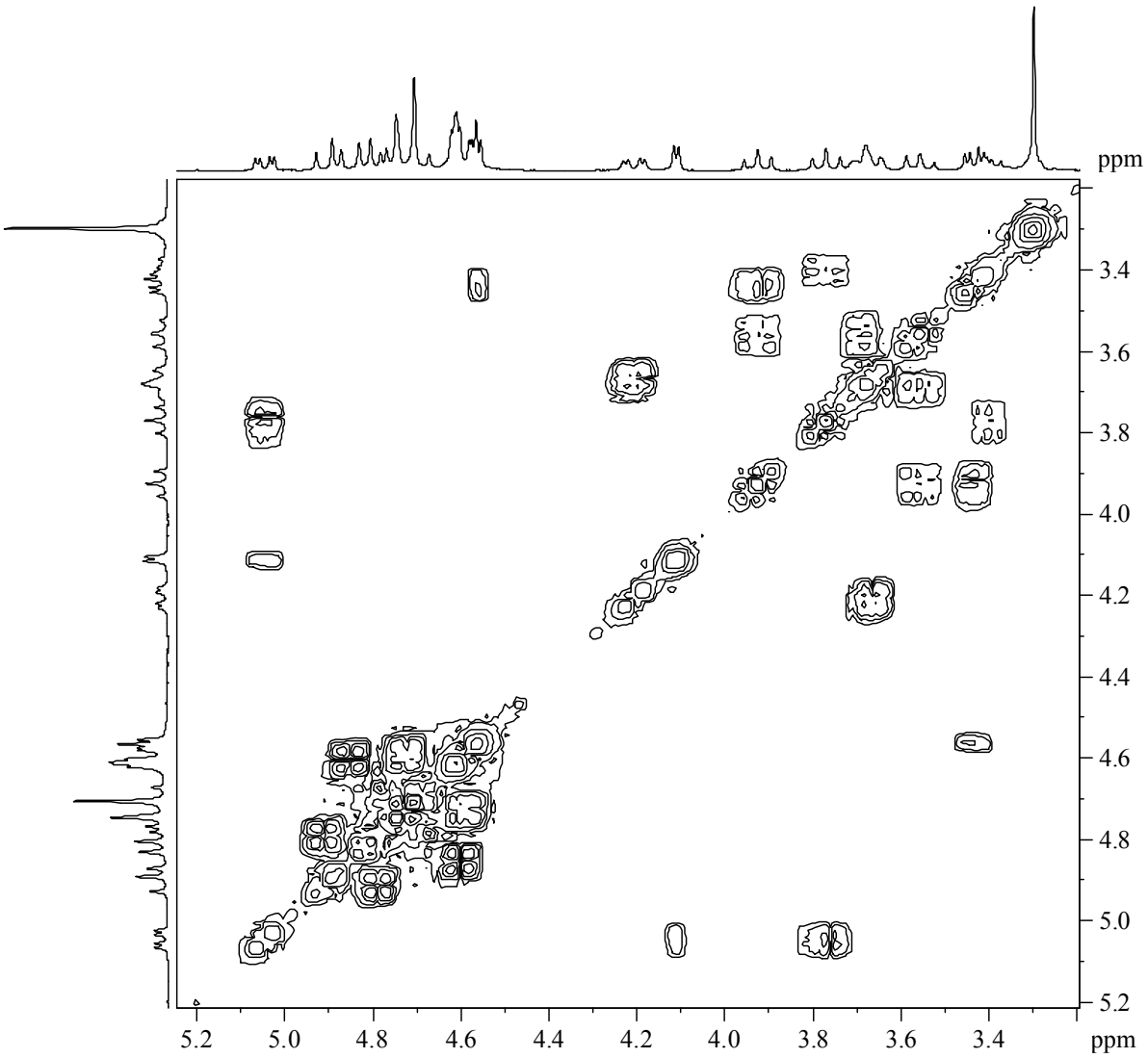

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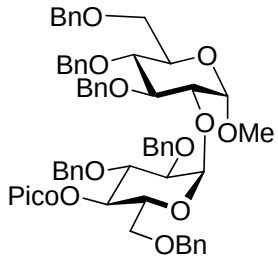

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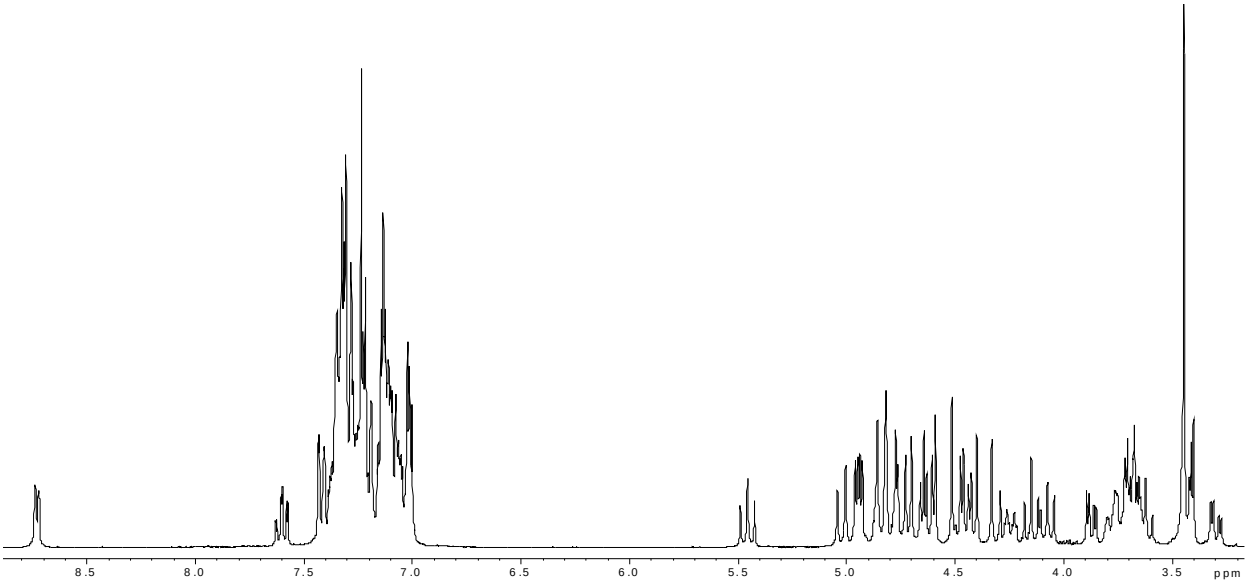

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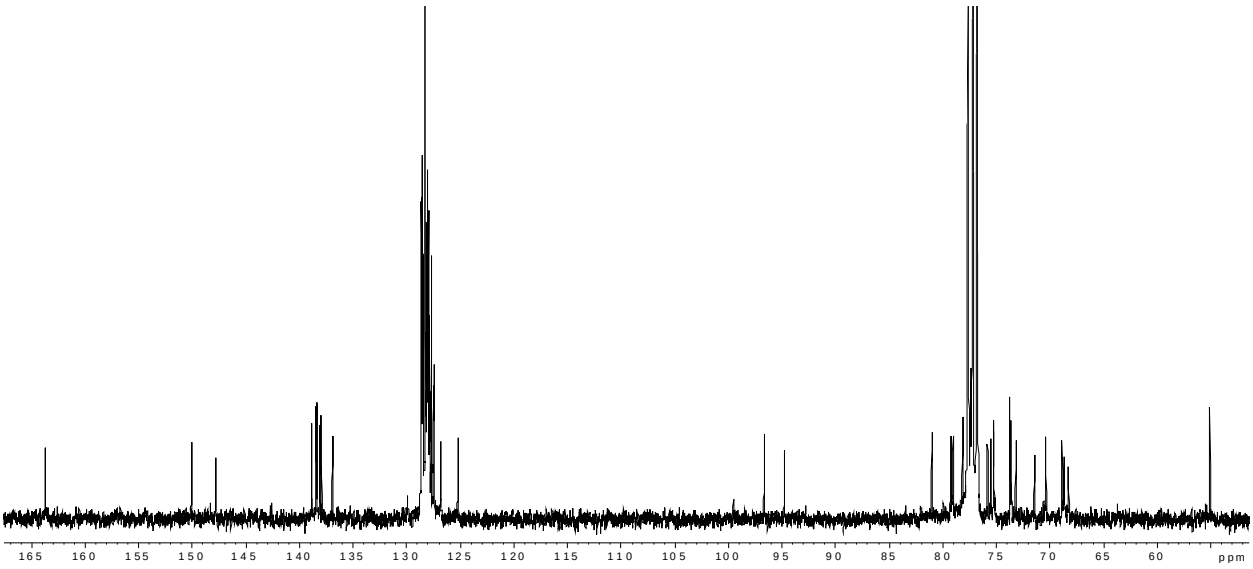

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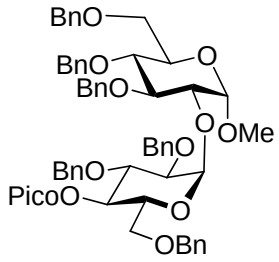

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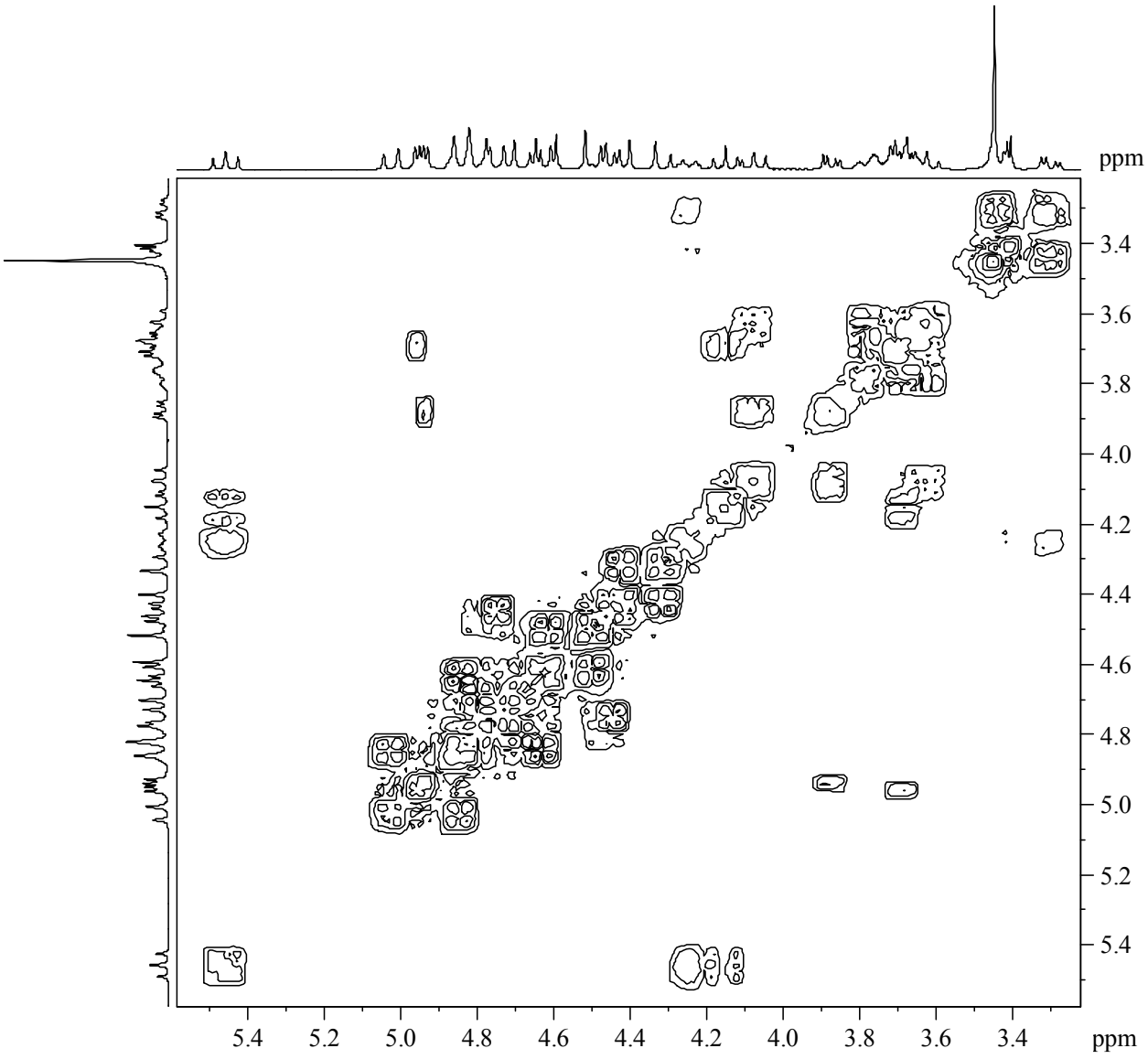

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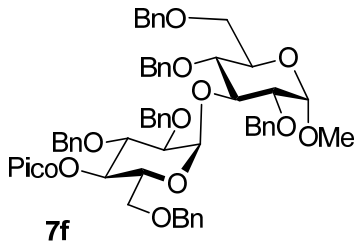
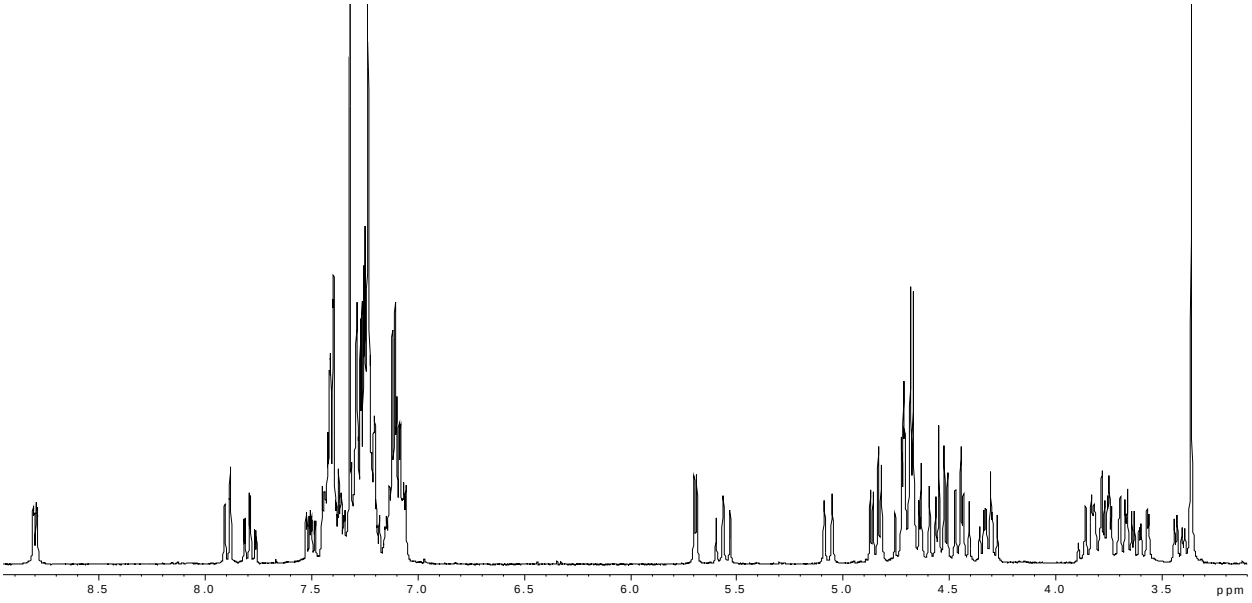


7f



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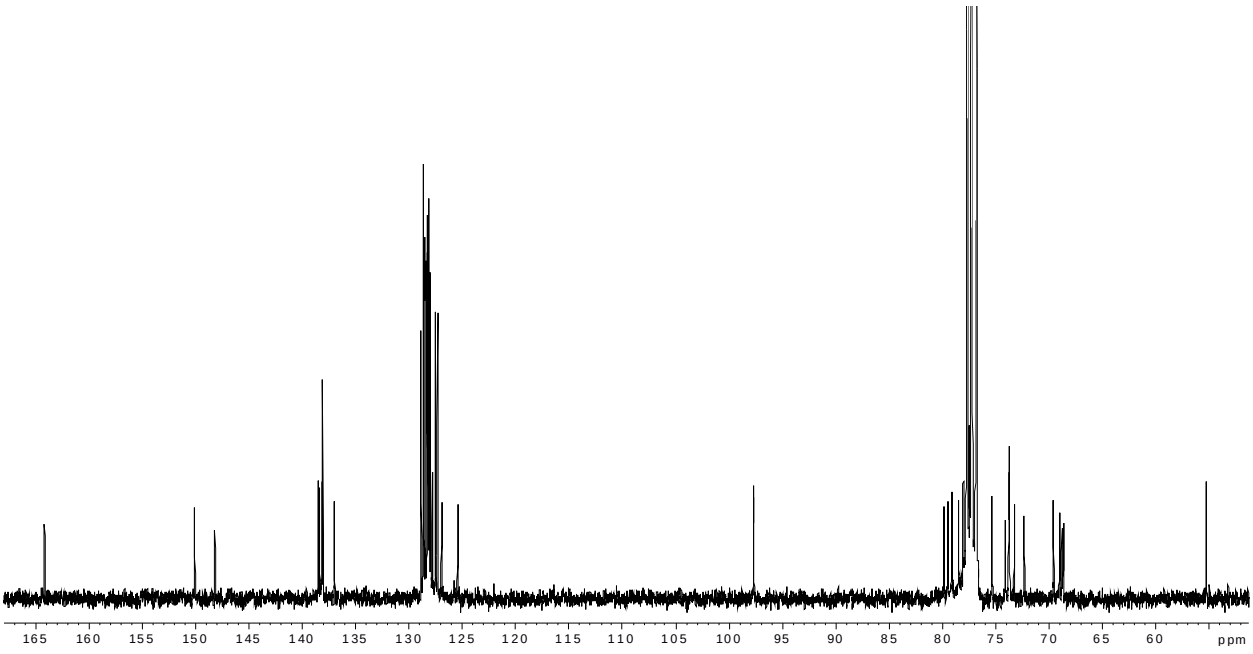

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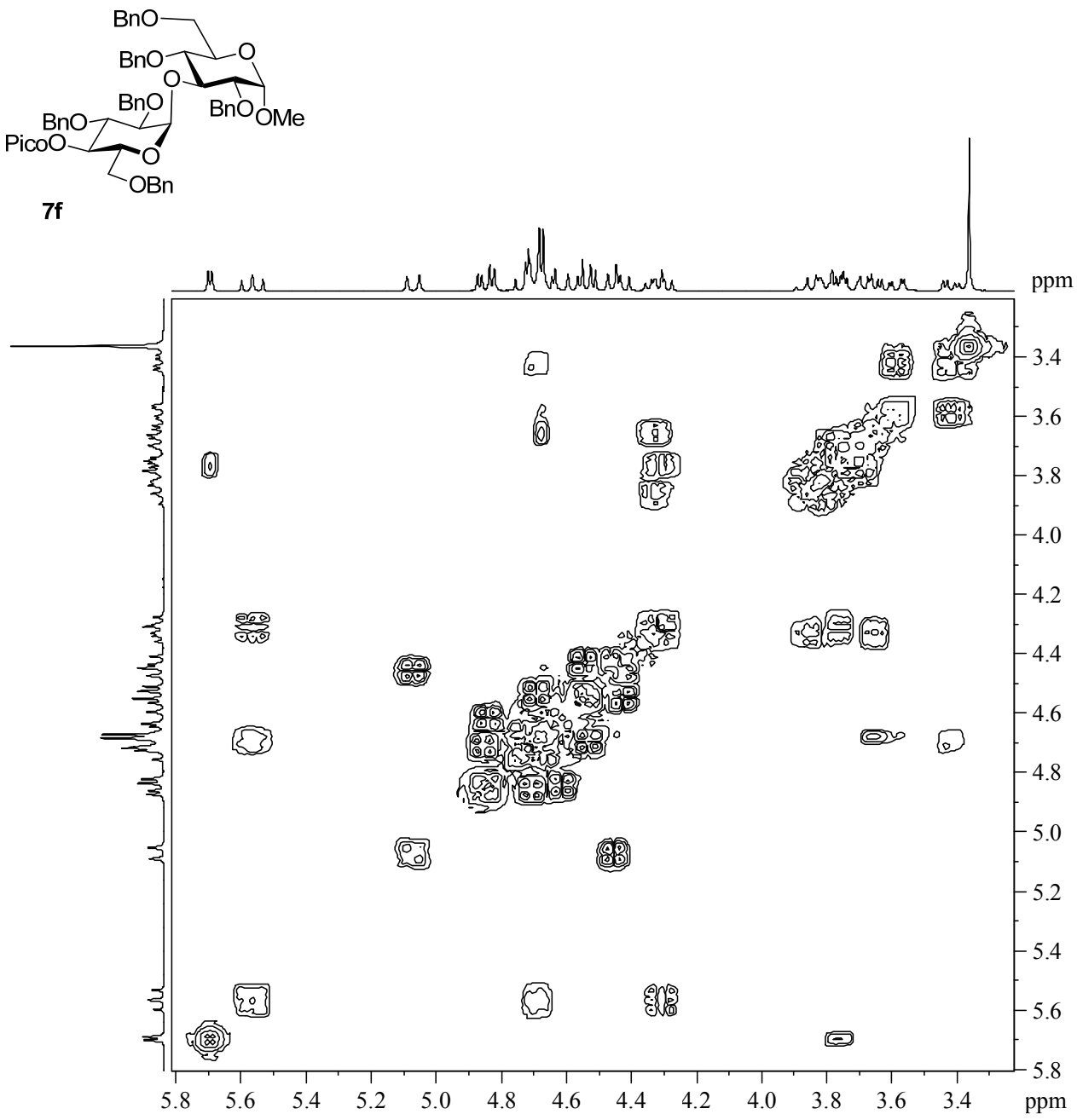

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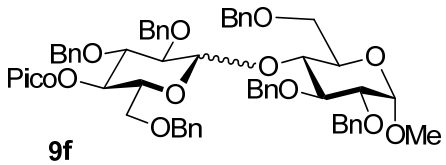

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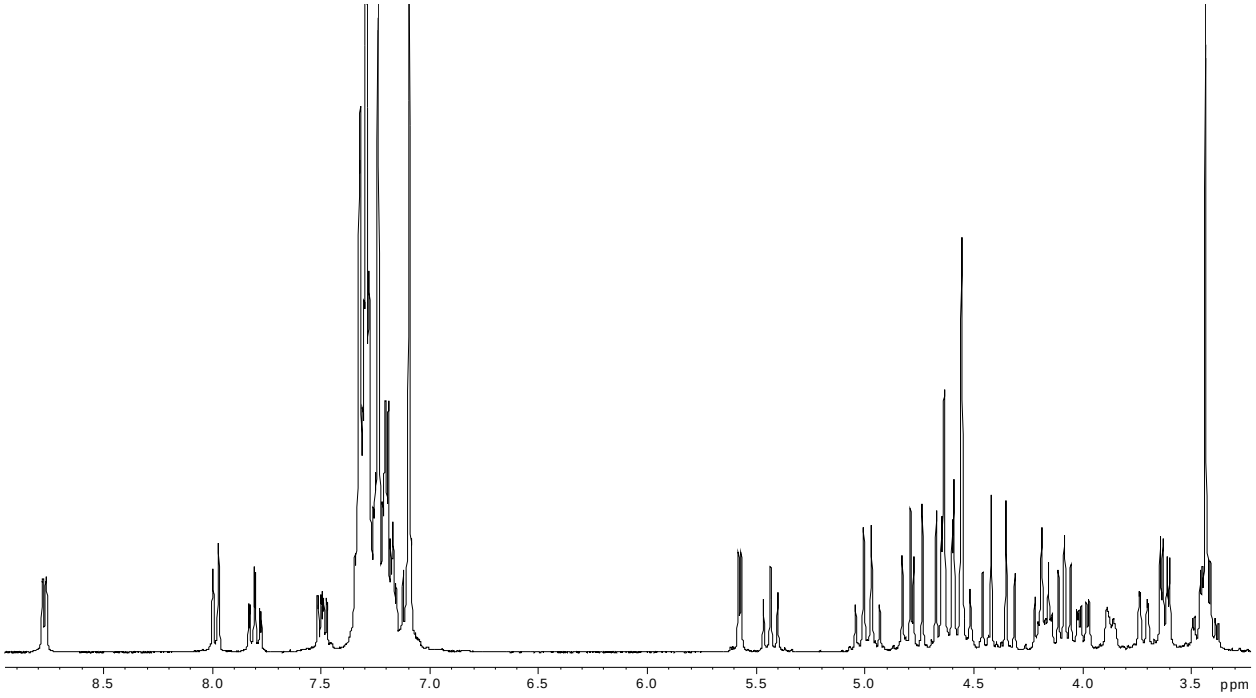

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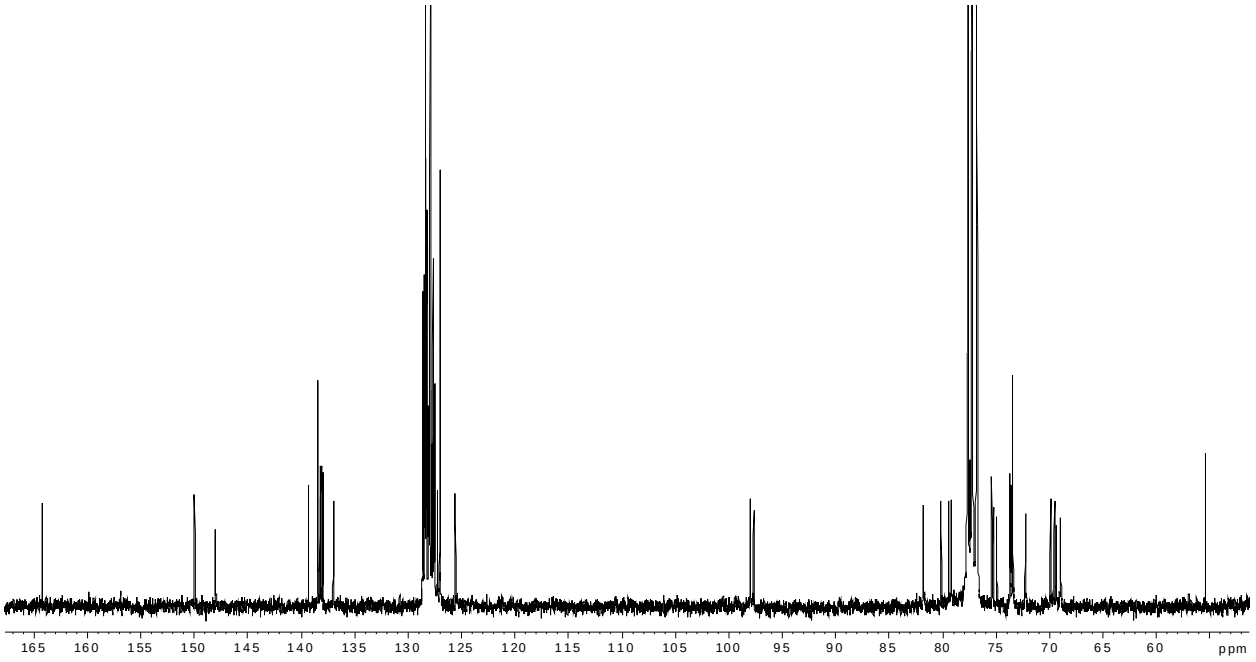

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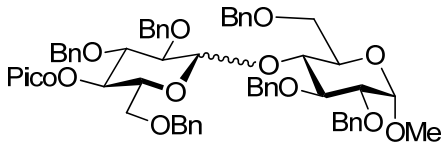

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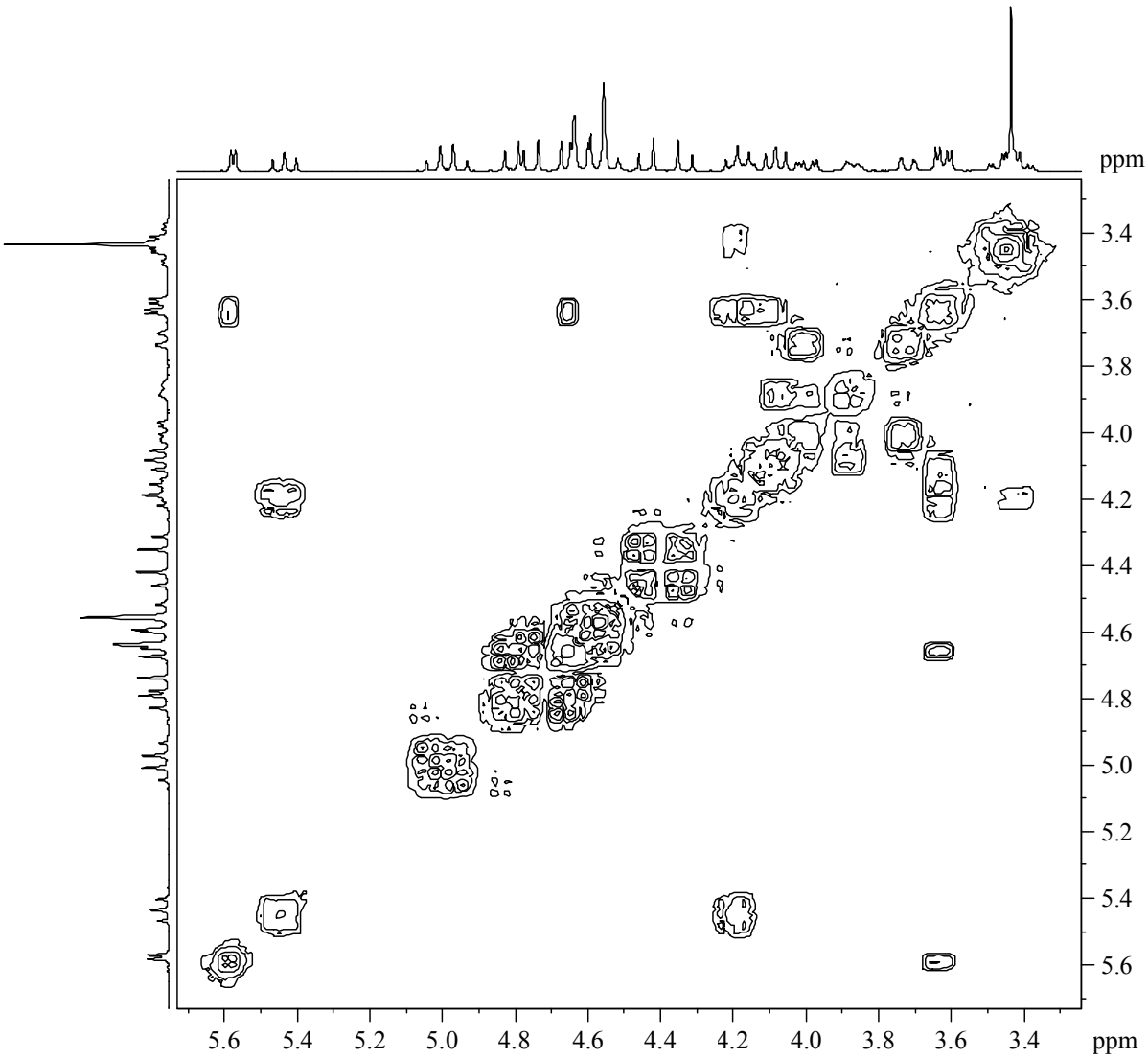

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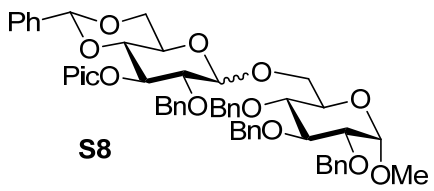
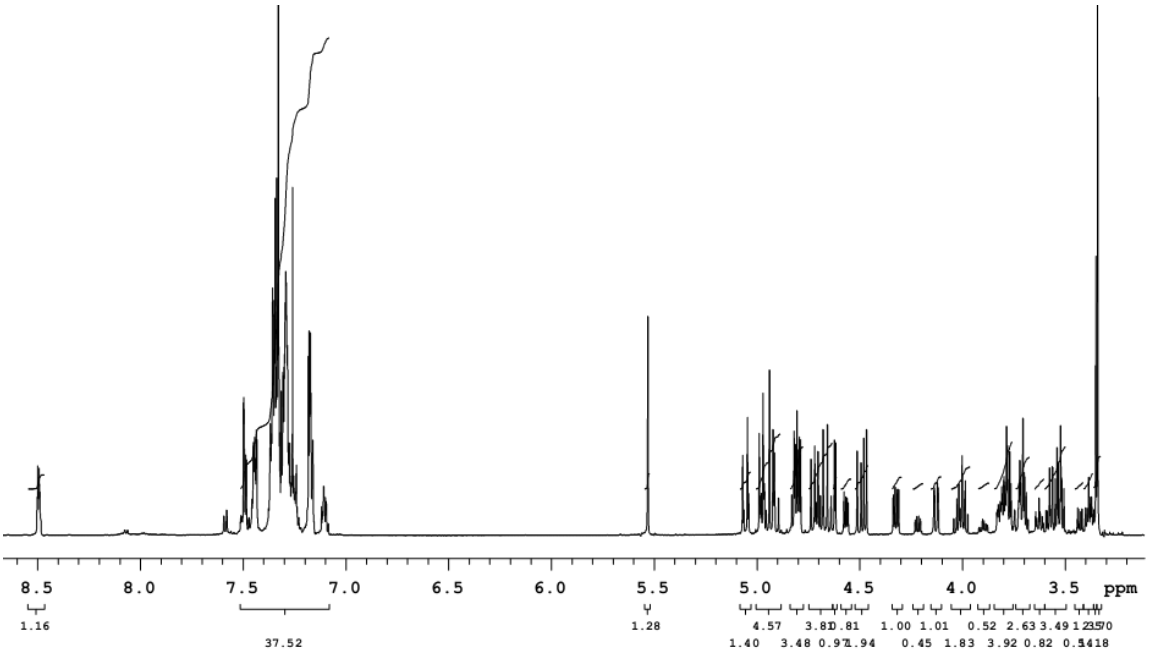


S8



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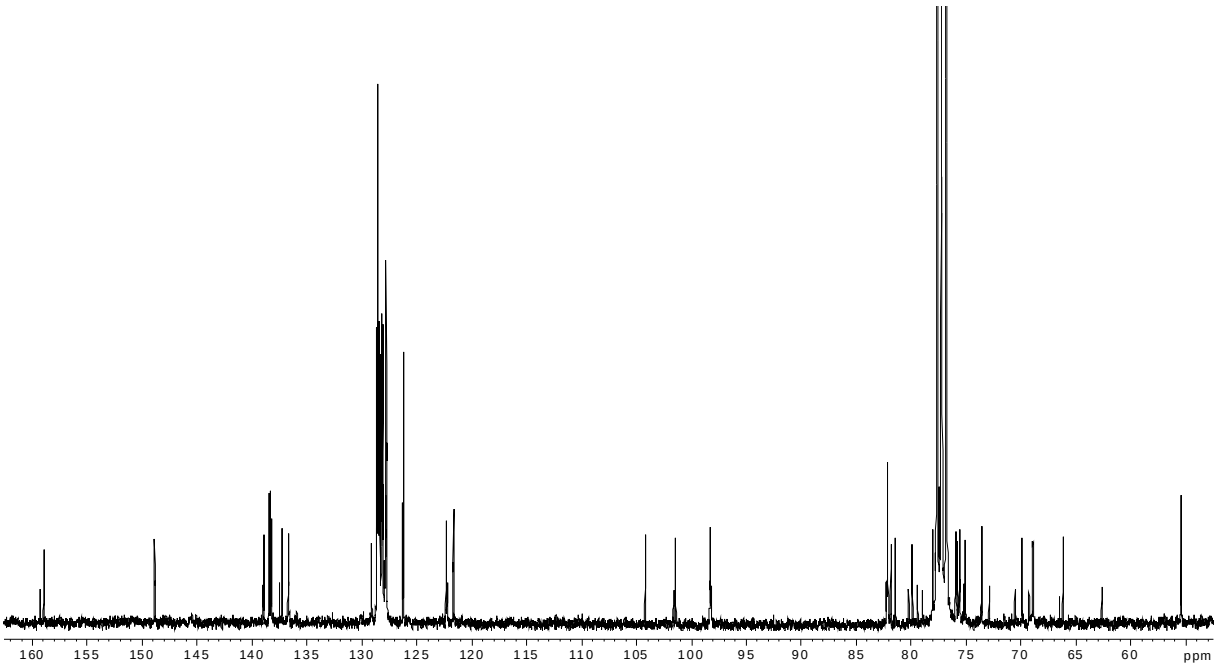

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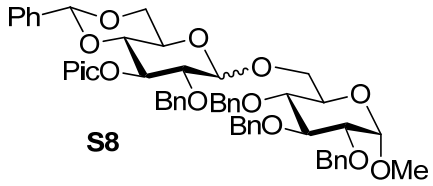
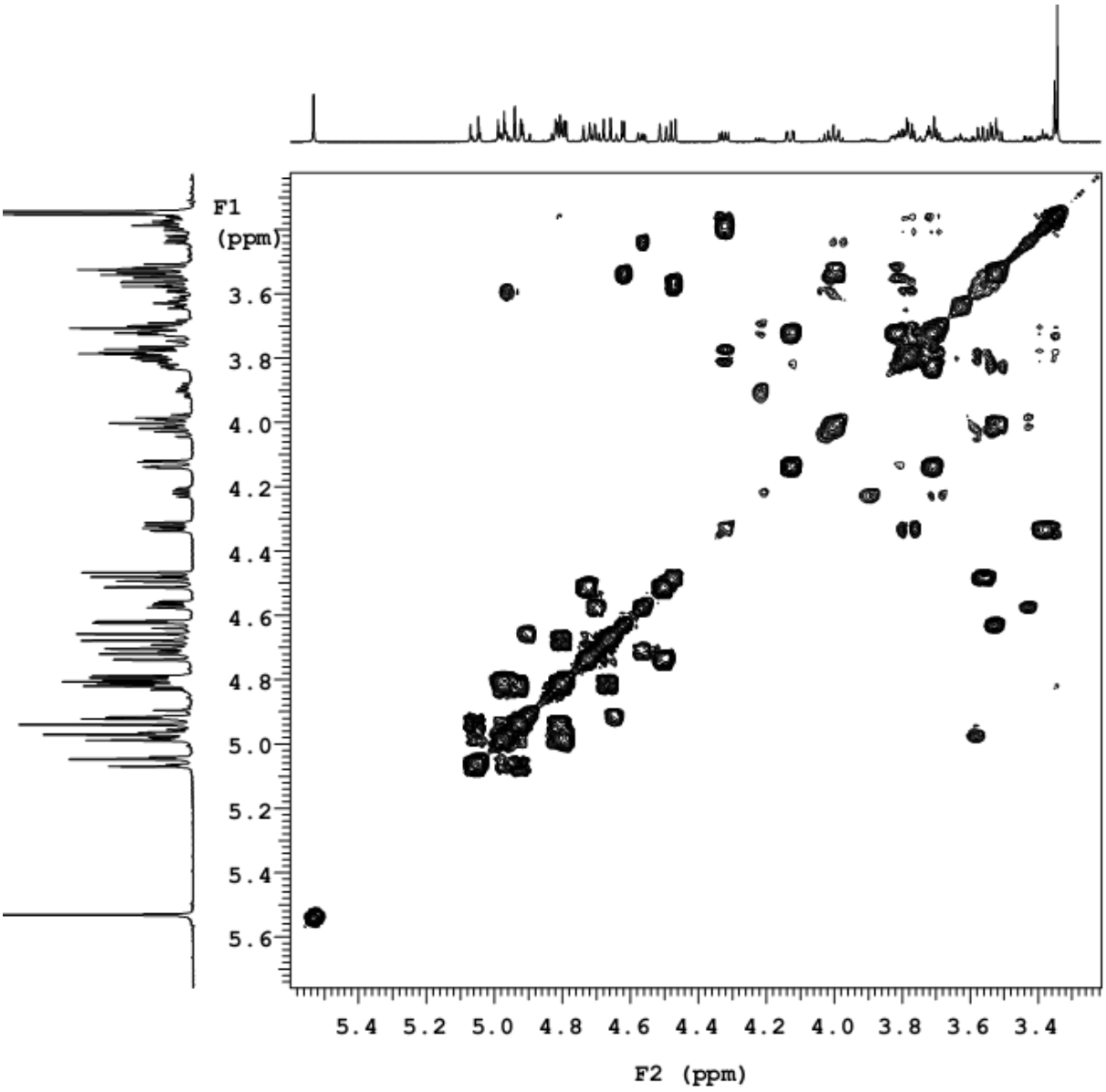


S8



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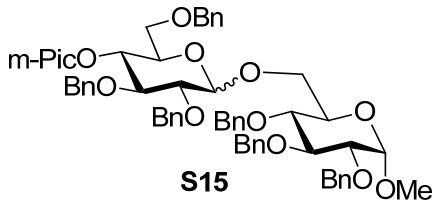
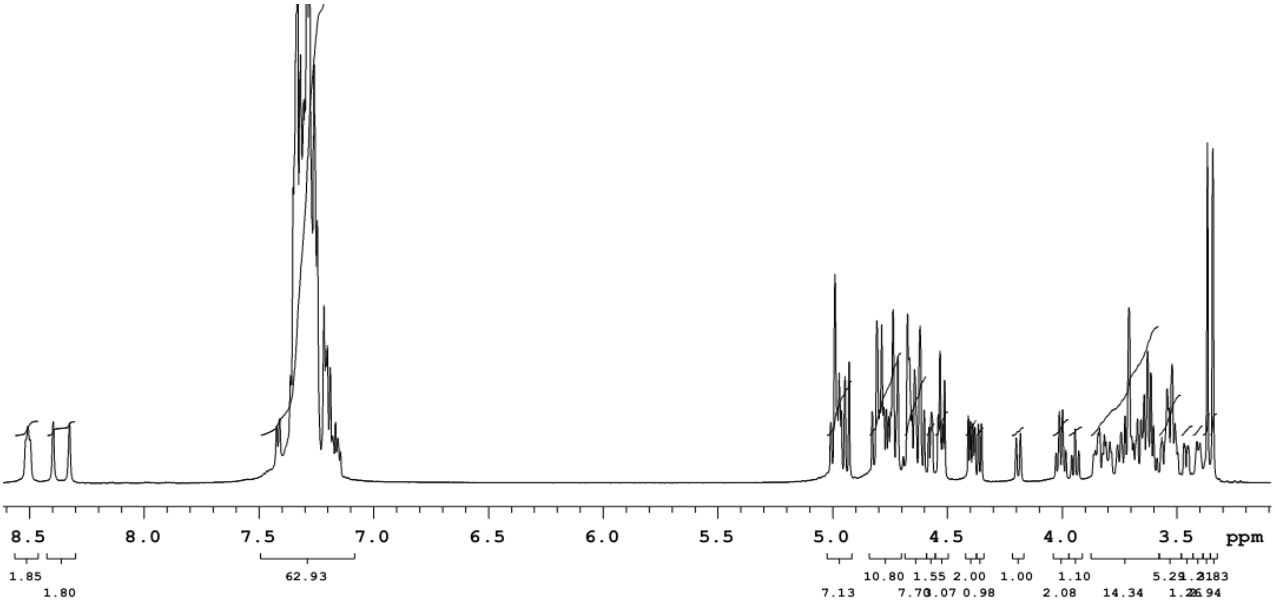
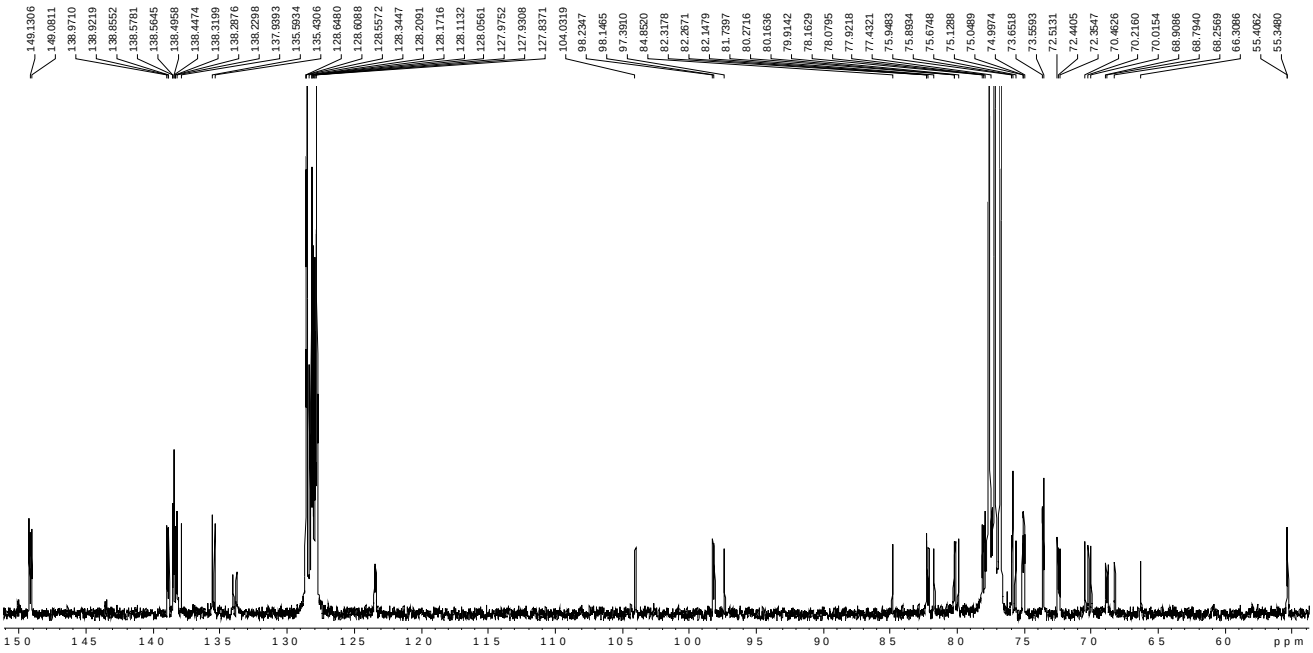


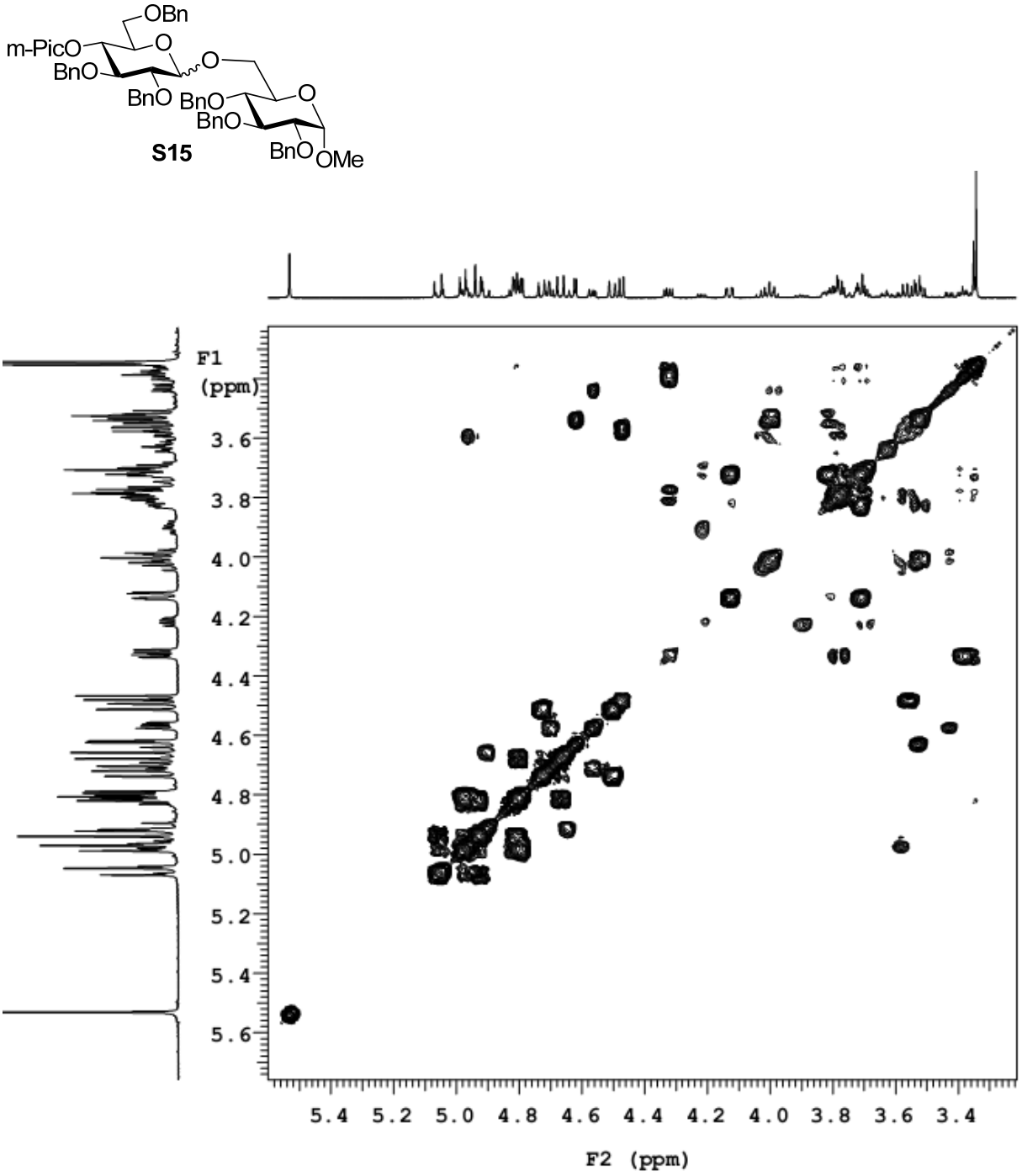
S15



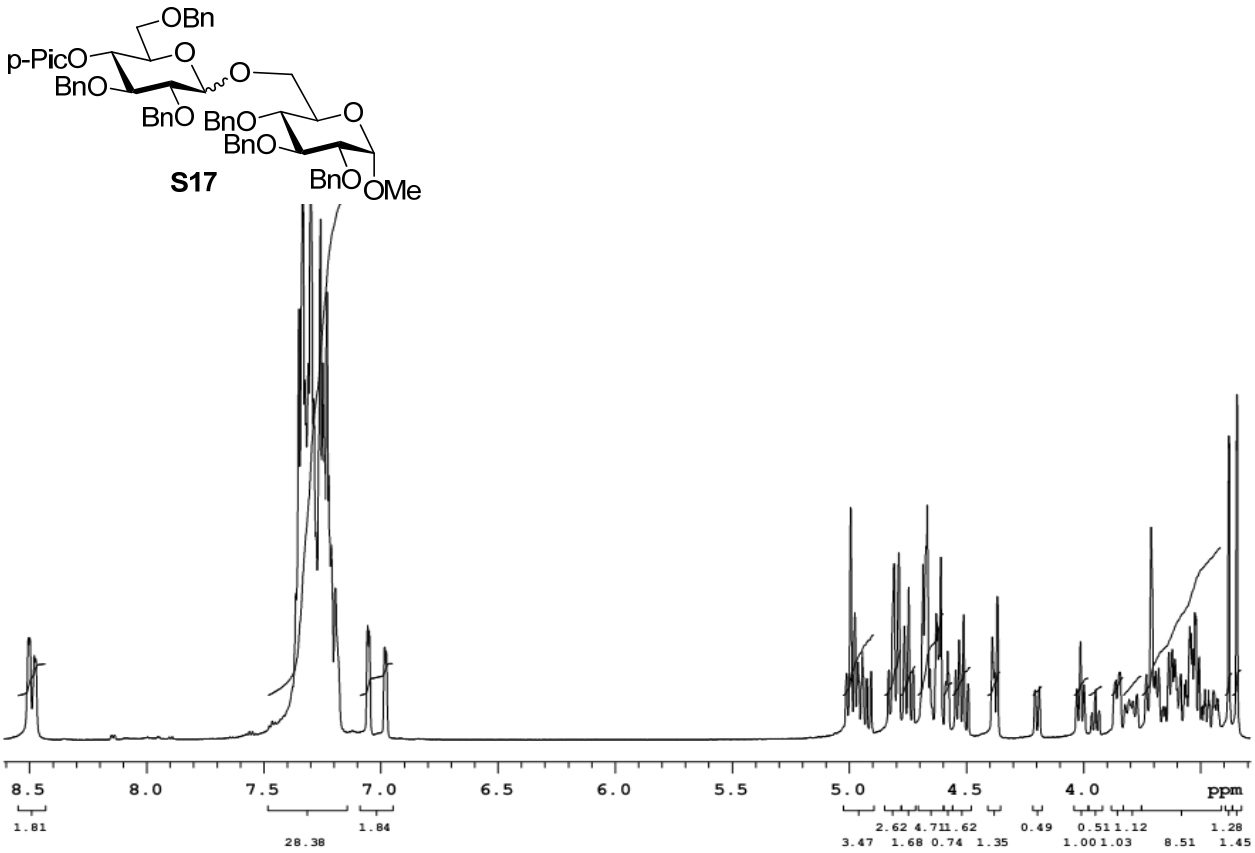
$CDCl_3$ 600 MHz



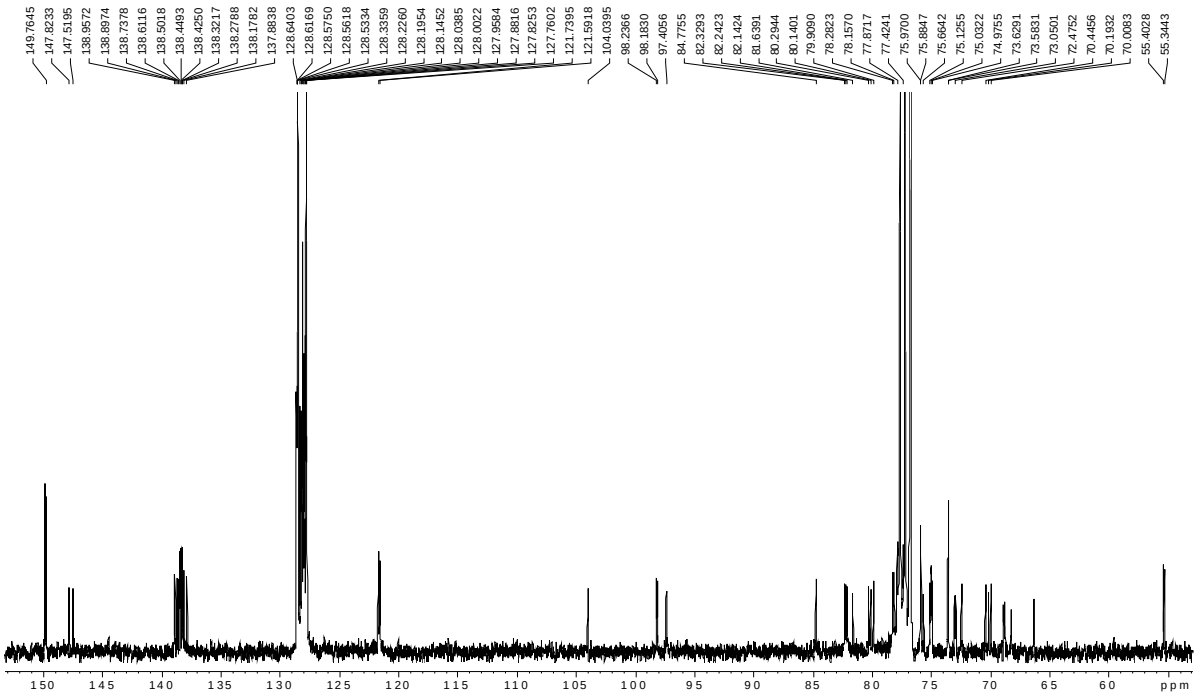
$CDCl_3$ 75 MHz



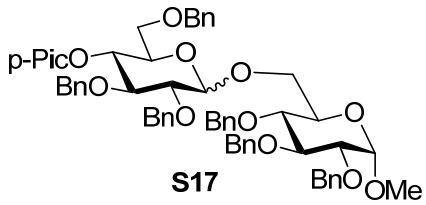
$CDCl_3$ 600 MHz



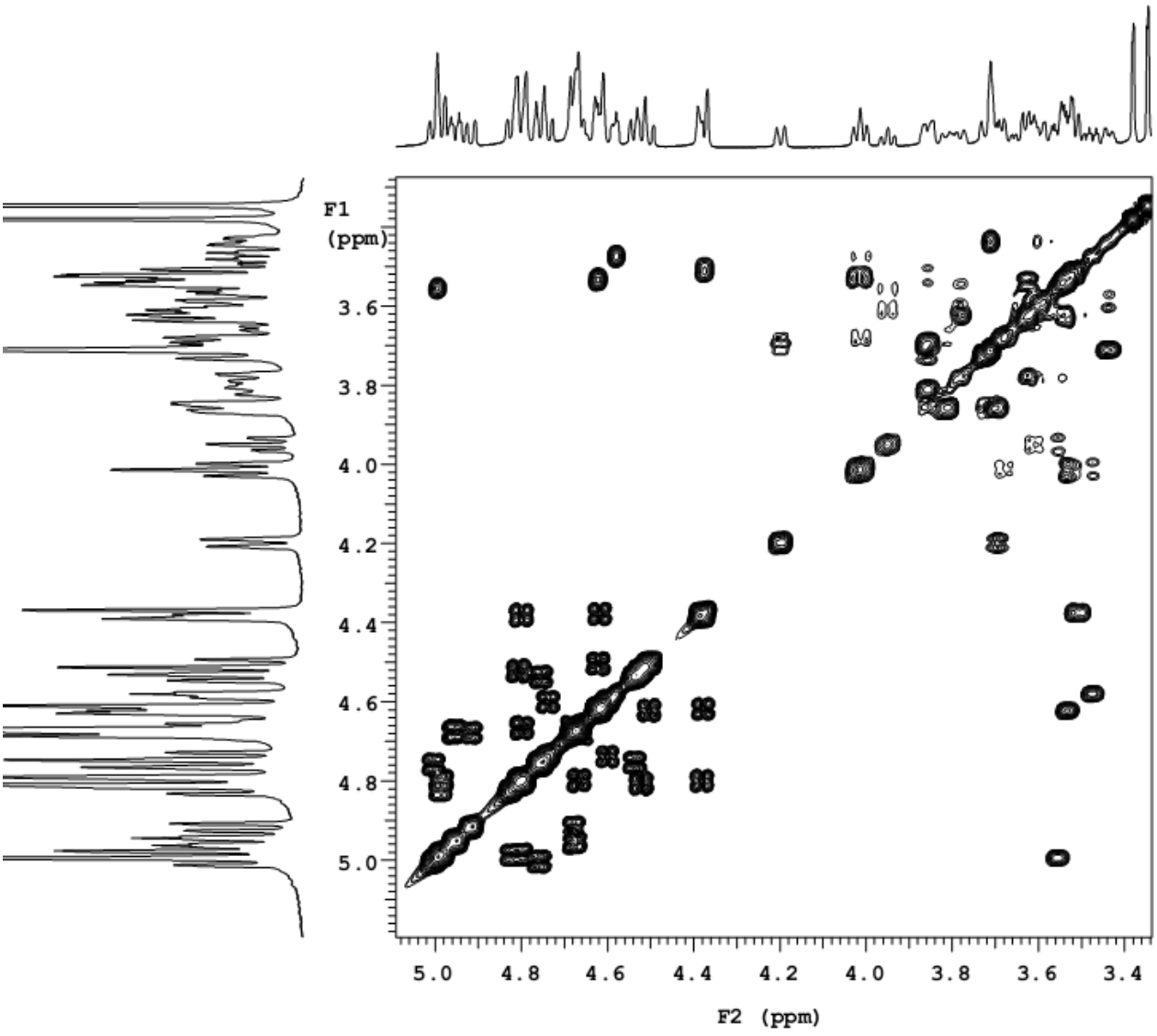
$CDCl_3$ 600 MHz



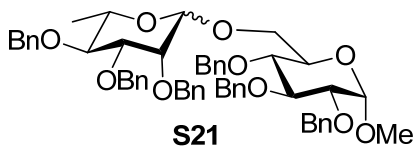
$CDCl_3$ 75 MHz



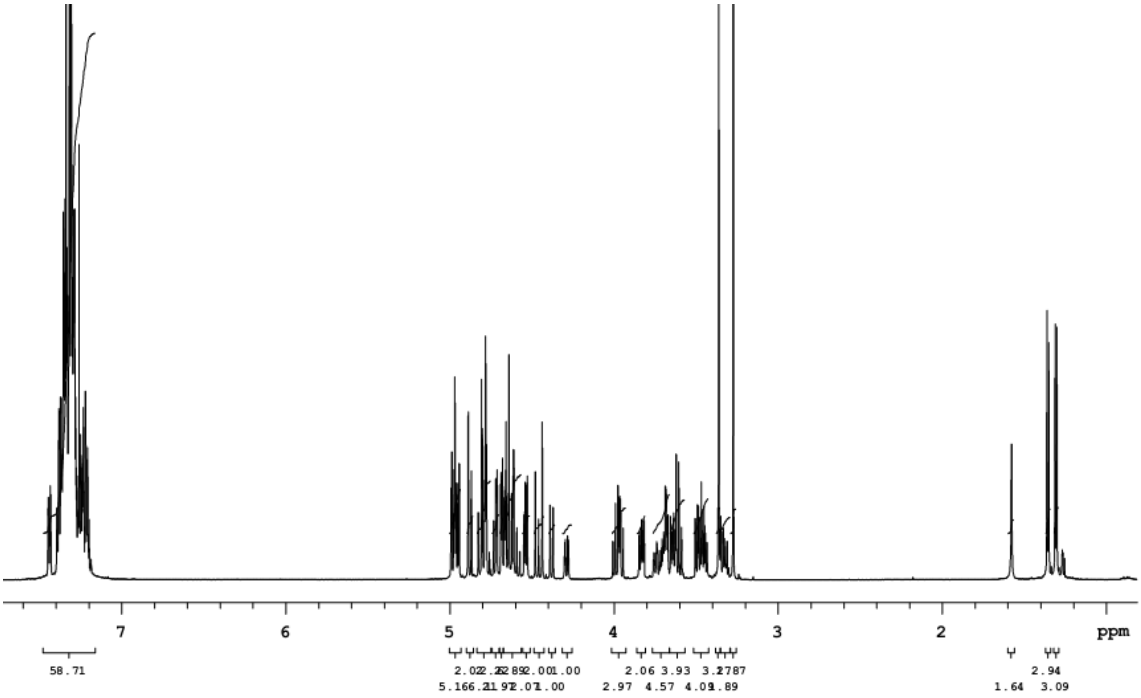
S17



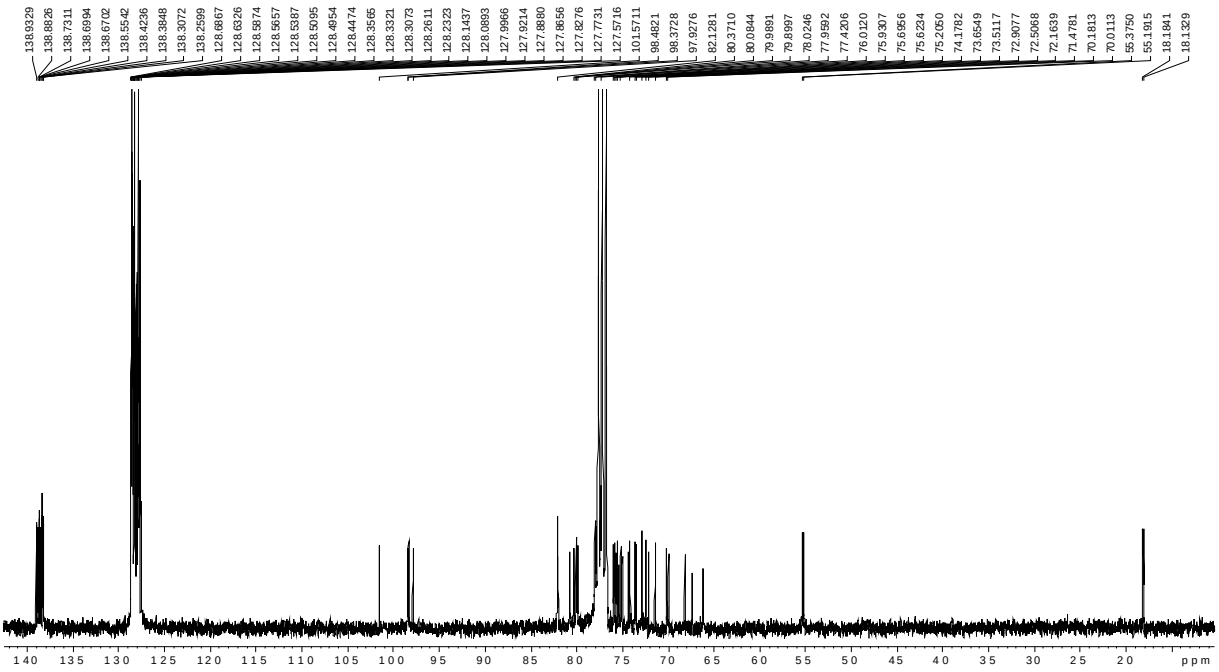
$CDCl_3$ 600 MHz



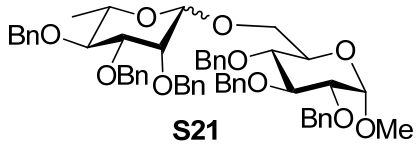
S21



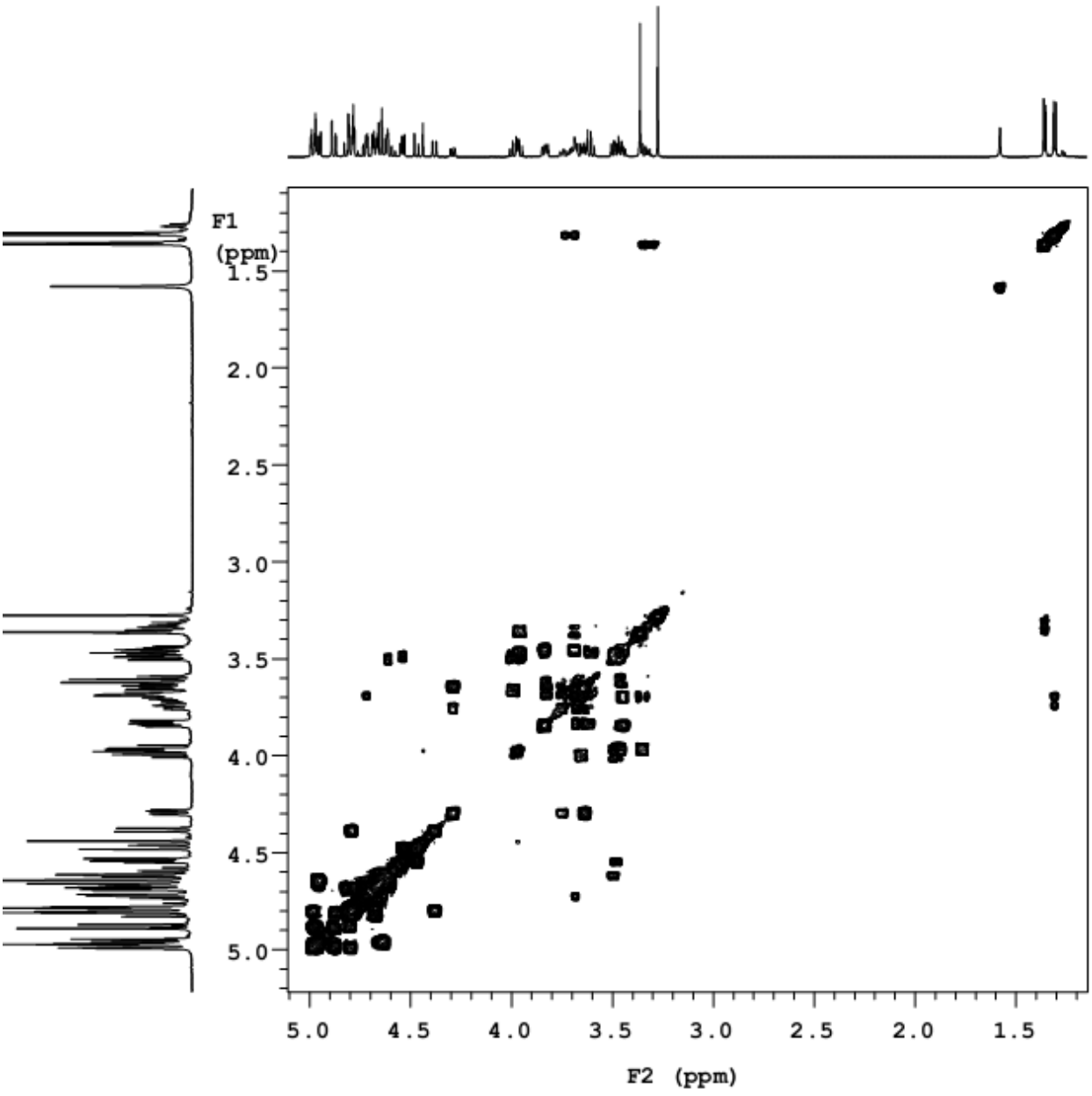
$CDCl_3$ 600 MHz



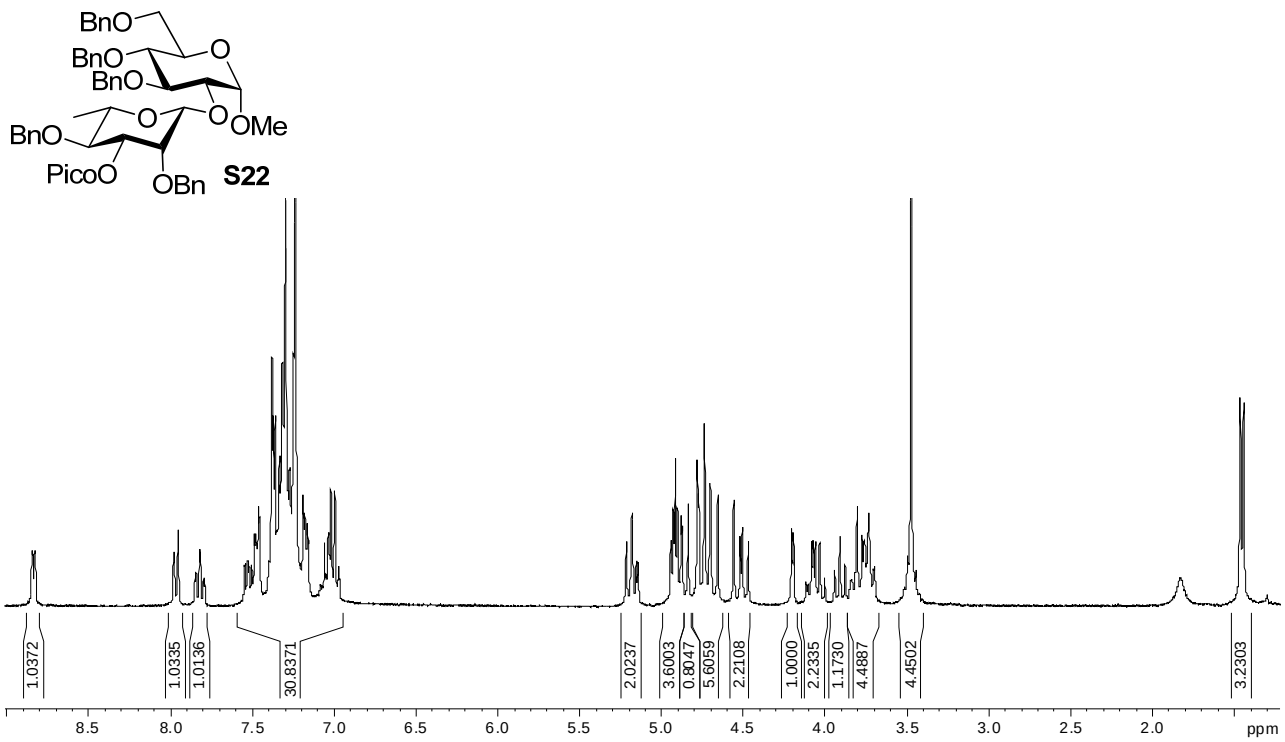
$CDCl_3$ 75 MHz



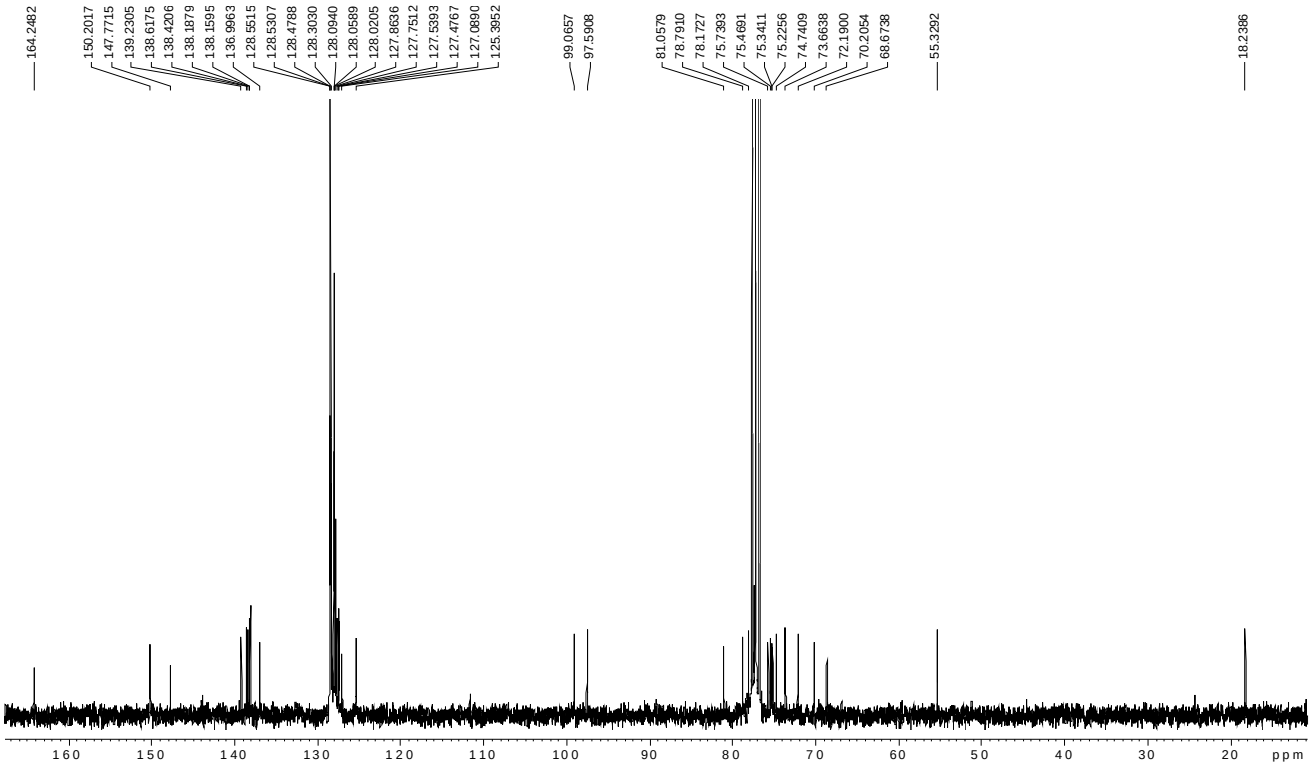
S21



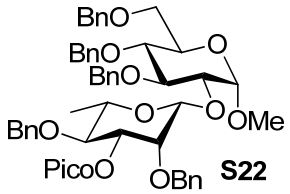
$CDCl_3$ 600 MHz



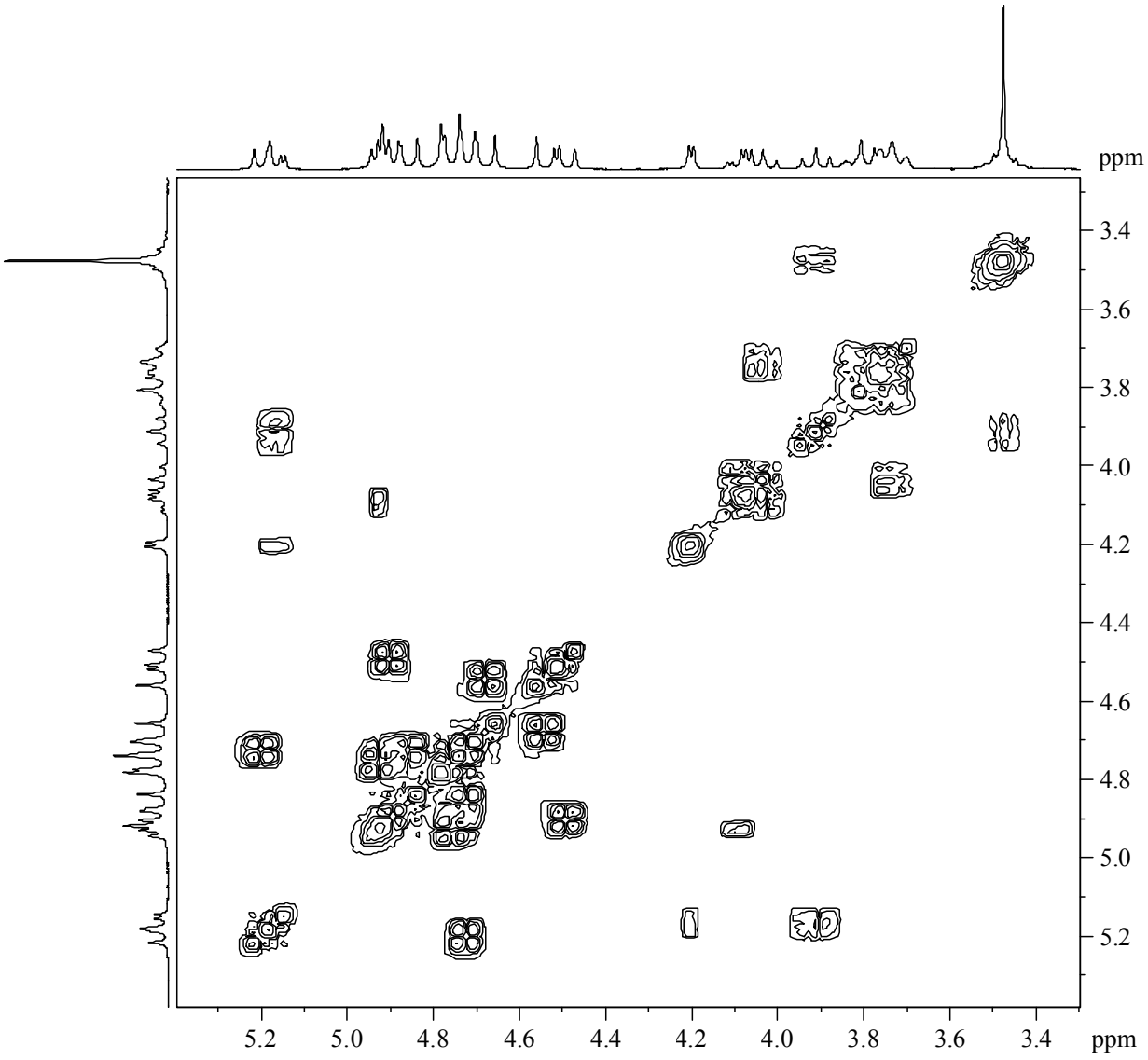
$CDCl_3$ 300 MHz



$CDCl_3$ 75 MHz



S22



$CDCl_3$ 300 MHz

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