Supporting information

Superarming Common Glycosyl Donors by Simple 2-O-Benzoyl-3,4,6-tri-O-benzyl Protection.

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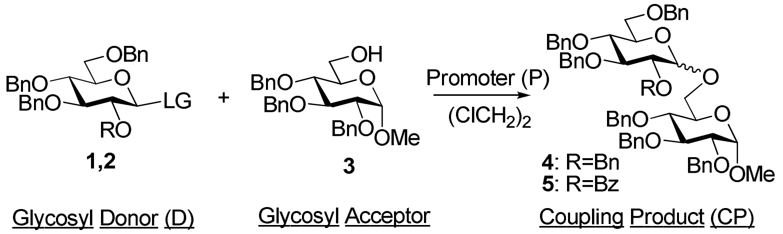
Content:

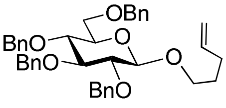
Additional experimental data

Table SI: Comparative glycosylations of O-pentenyl and S-ethyl glycosides



Armed Series

Superarmed Series



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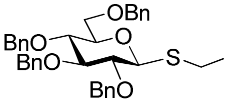

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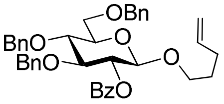

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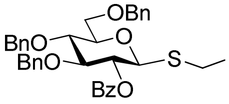


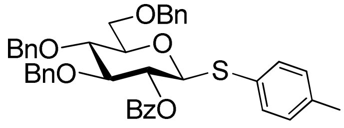
2c

Entry	*Donor*	*promoter*	*Temp*	*Time*	*Product*	*Yield*	*Ratio*
1	**1b**	NBS	45 °C	2 days	**4**	62 %	3:1
2	**2b**	NBS	45 °C	24 h	**5**	50 %	β only
3	**1b**	NIS	rt	3 days	**4**	62 %	1:1
4	**2b**	NIS	rt	2 days	**5**	81 %	β only
5	**1b**	NIS/TfOH	-20 °C	5 min	**4**	50 %	2:1
6	**2b**	NIS/TfOH	-20 °C	5 min	**5**	68 %	β only
7	**1b**	IDCP	rt	10 min	**4**	62%	3:1
8	**2b**	IDCP	rt	10 min	**5**	50%	β only
9	**1c**	DMTST	0 °C	5 min	**4**	96 %	1.25:1
10	**2c**	DMTST	0 °C	5 min	**5**	96 %	β only
11	**1c**	I_2	50 °C	10 min	**4**	98 %	1:1
12	**2c**	I_2	50 °C	10 min	**5**	98 %	β only
13	**1c**	I_2	rt	15 min	**4**	97 %	1:1
14	**2c**	I_2	rt	15 min	**5**	97 %	β only
15	**1c**	I_2	0 °C	45 min	**4**	97 %	1:2
16	**2c**	I_2	0 °C	25 min	**5**	98 %	β only
17	**1c**	I_2	-10 °C	90 min	**4**	92 %	1:3
18	**2c**	I_2	-10 °C	90 min	**5**	89 %	β only
19	**1c**	I_2	-35 °C	10 h	**4**	92 %	1:4
20	**2c**	I_2	-35 °C	7 h	**5**	97 %	β only

General Experimental Procedures

Column chromatography was performed on silica gel 60 (70-230 mesh), reactions were monitored by TLC on Kieselgel 60 F_{254}. The compounds were detected by examination under UV light and by charring with 10% sulfuric acid in methanol. Solvents were removed under reduced pressure at < 40 ^{o}C. CH_2Cl_2, $ClCH_2CH_2Cl$, CH_3CN were distilled from CaH_2 directly prior to application. 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. $Cu(OTf)_2$ was dried *in vacuo* during 2-3 h prior to application. ^{1}H-n.m.r. spectra were recorded in $CDCl_3$ at 300 MHz, ^{13}C-NMR spectra were recorded in $CDCl_3$ at 75 MHz.

Copies of NMR spectra



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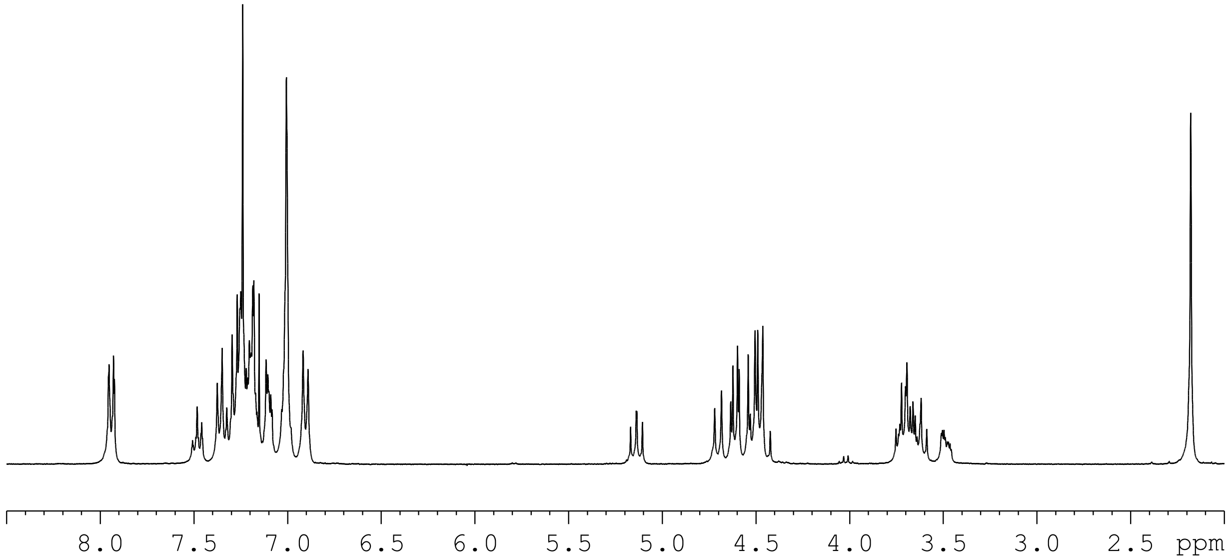

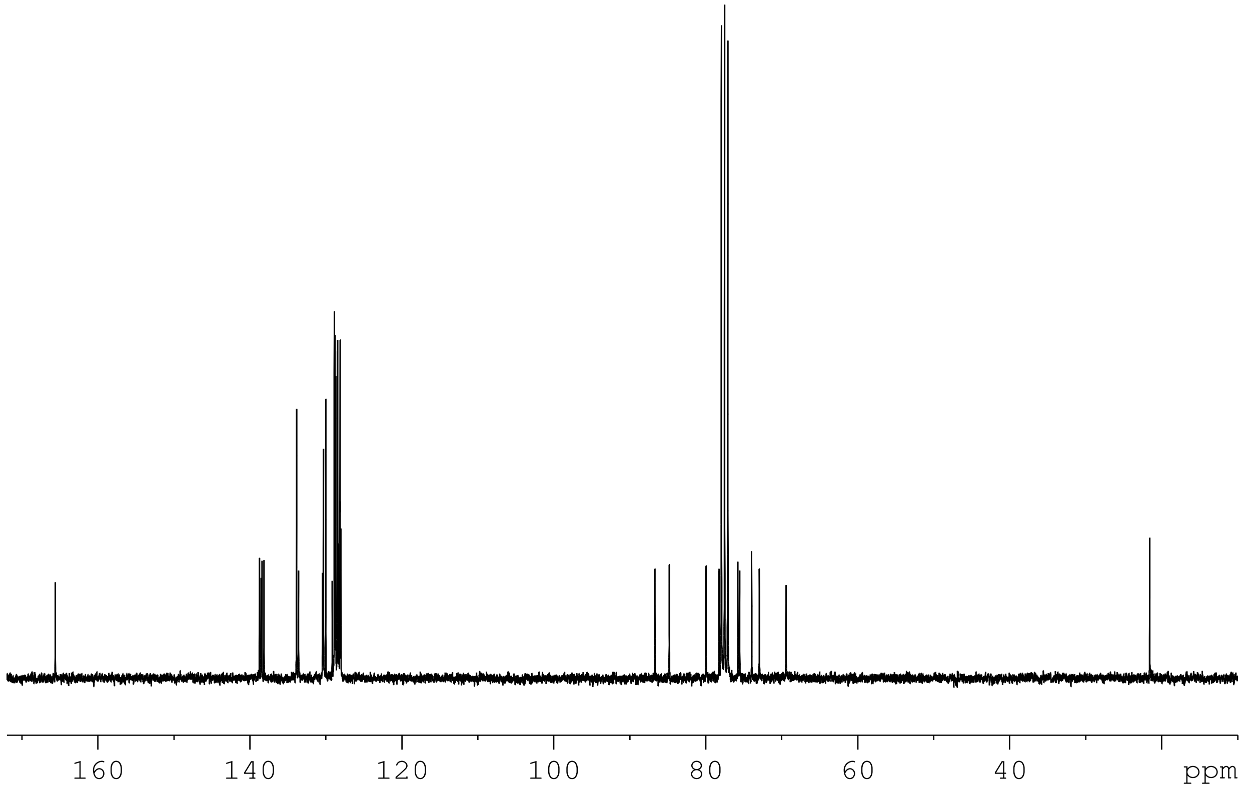

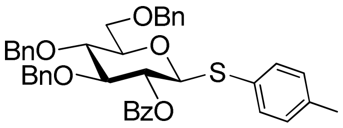

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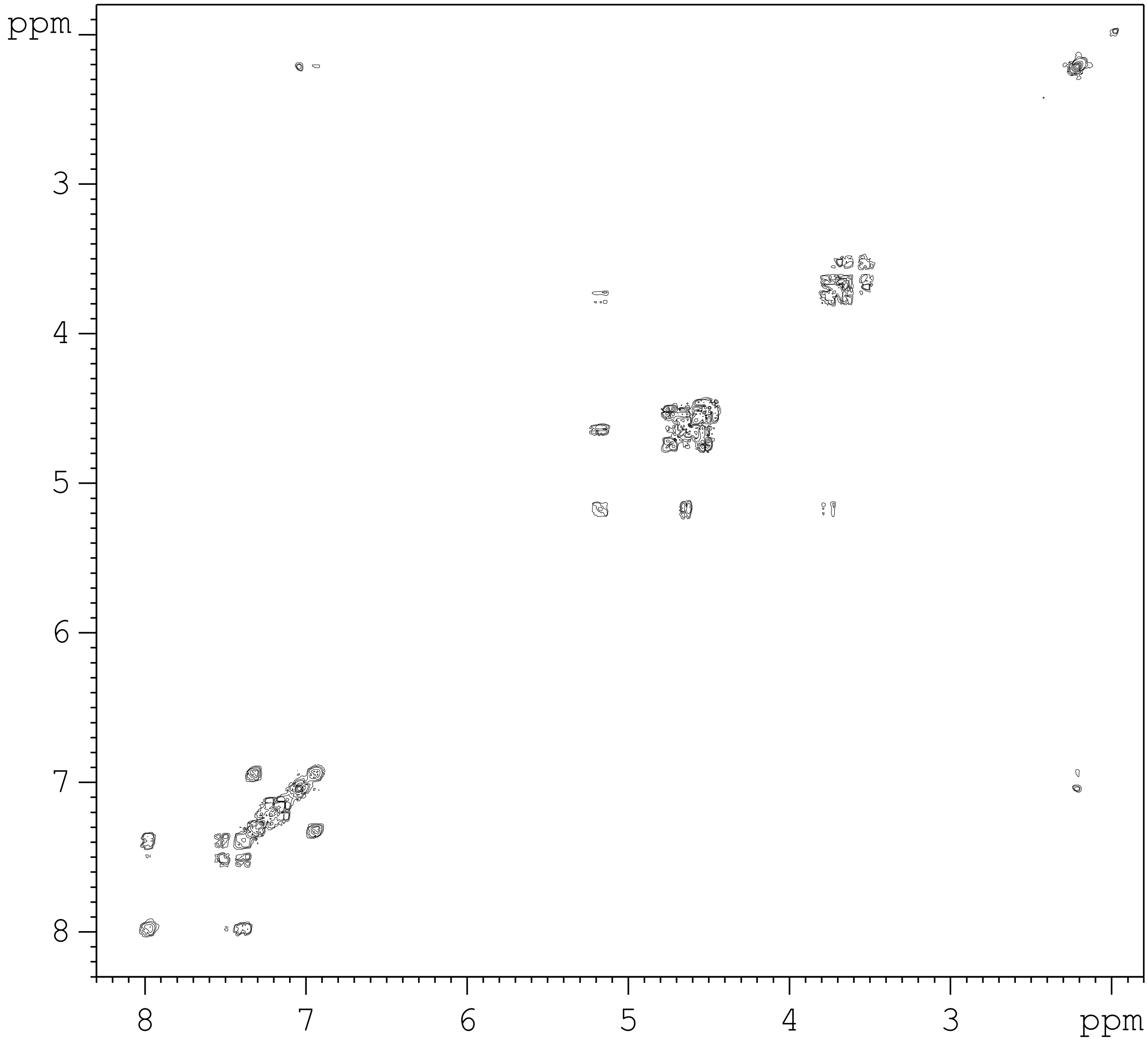

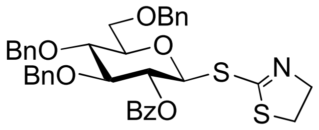
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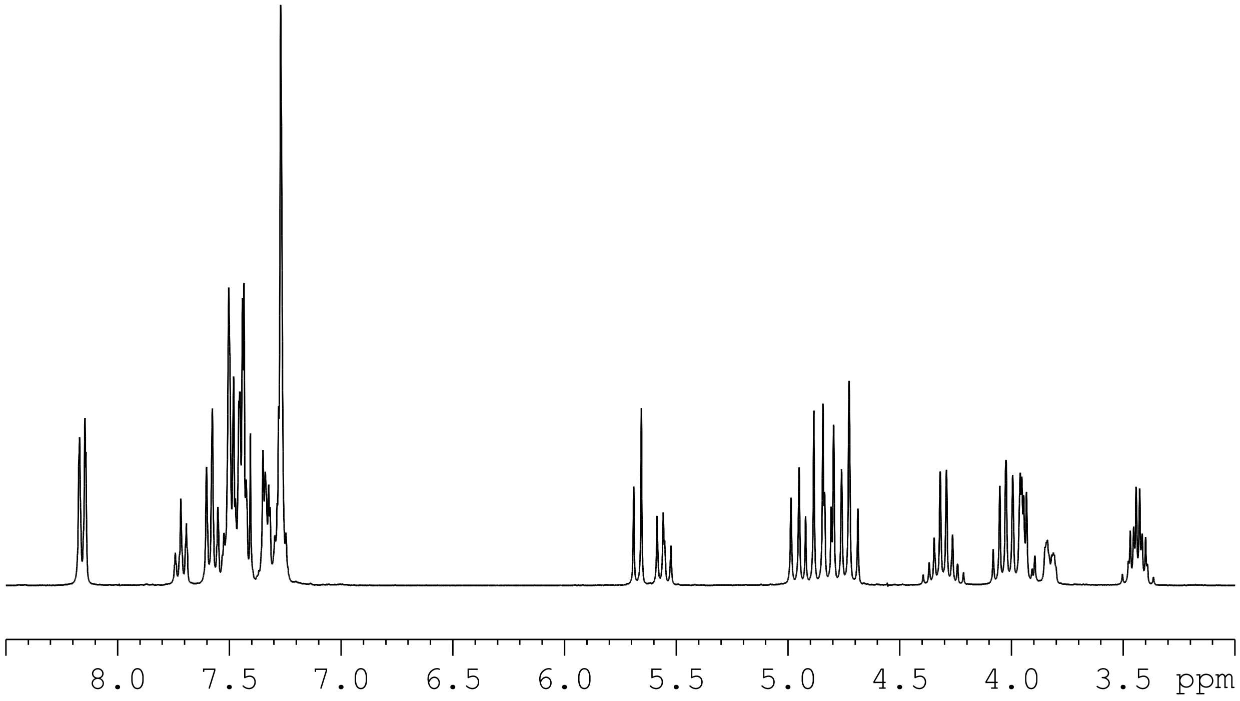
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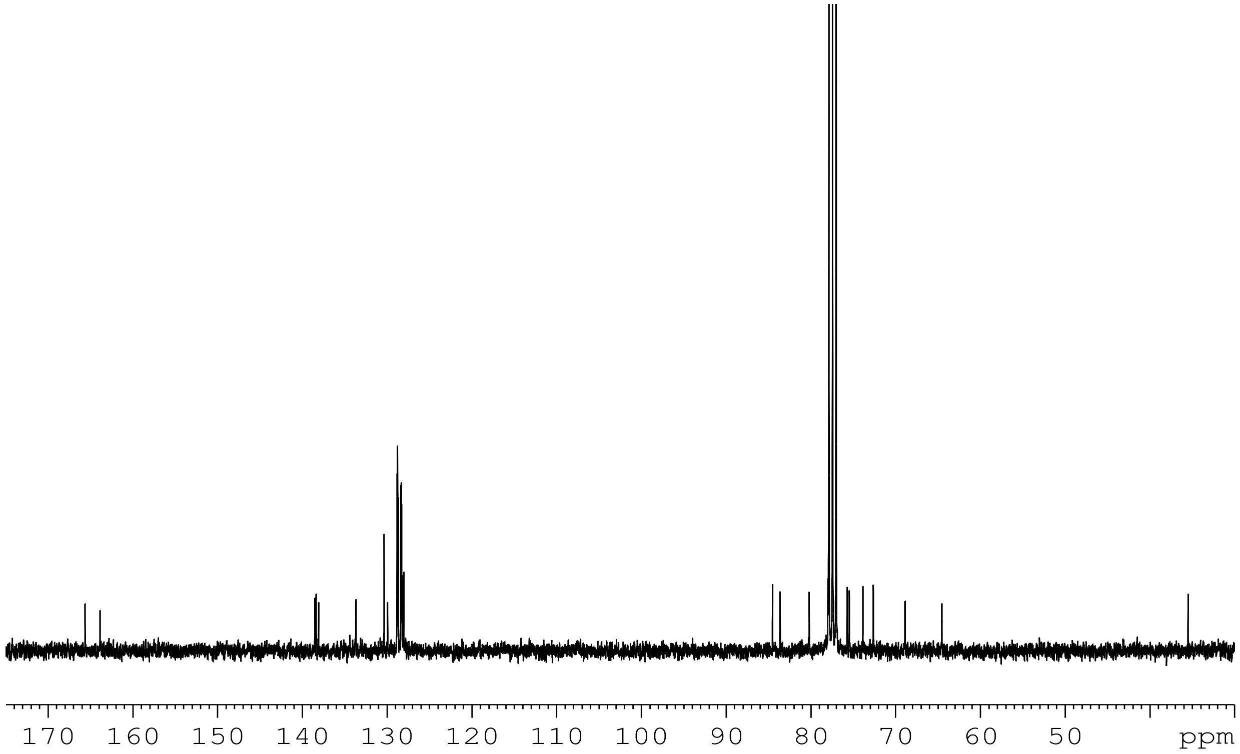
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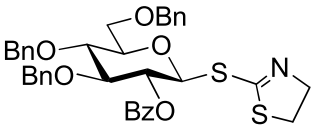
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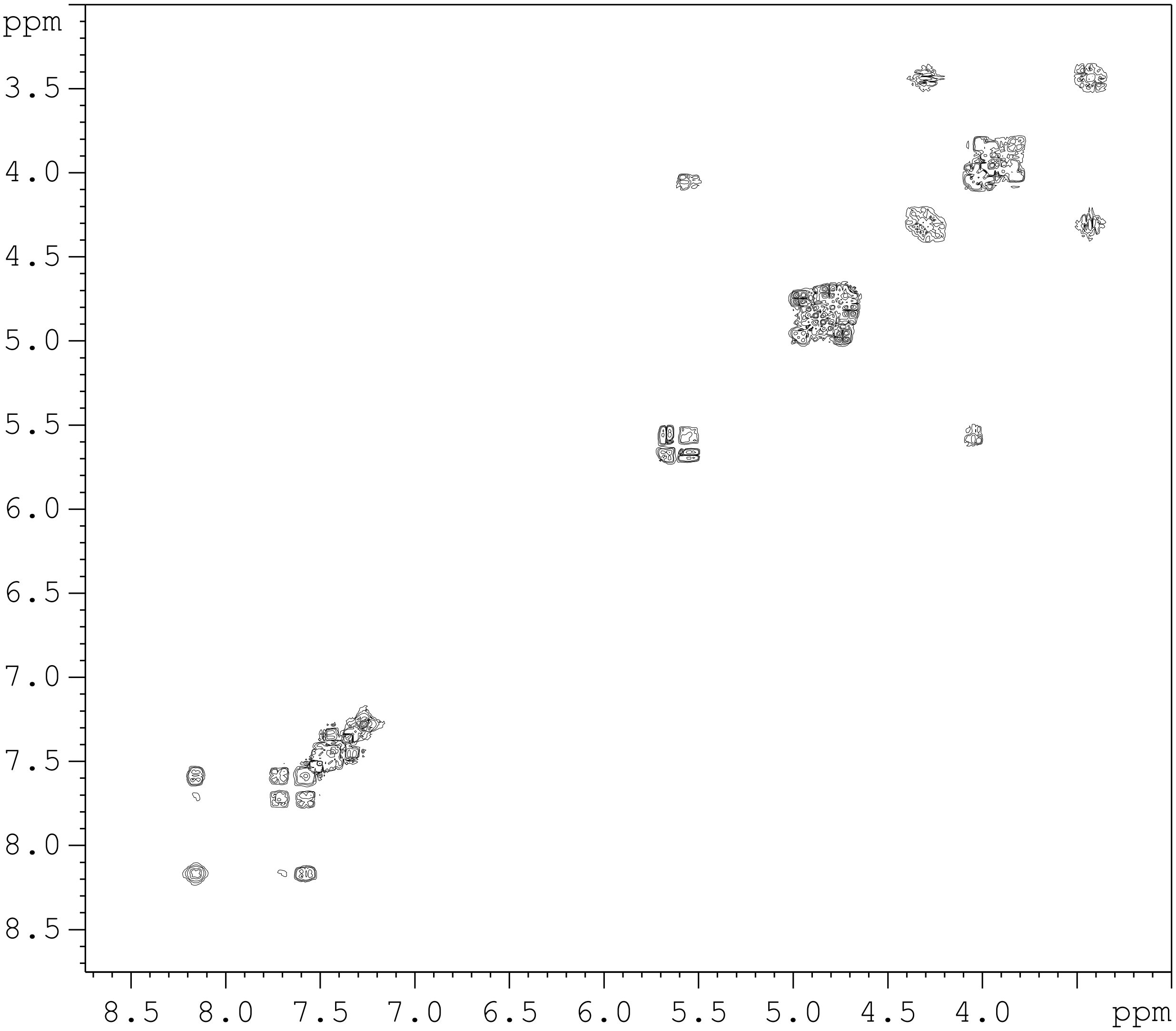
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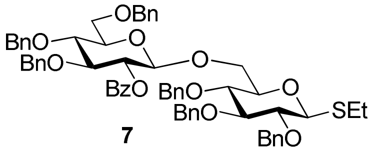
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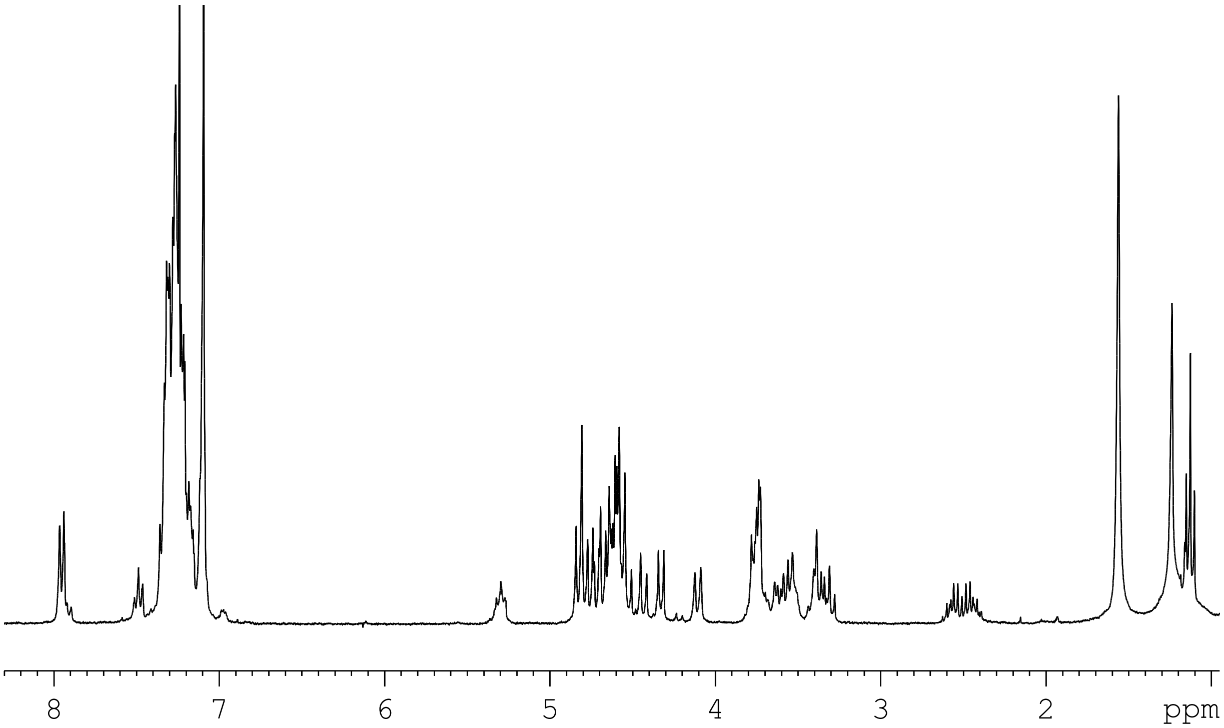
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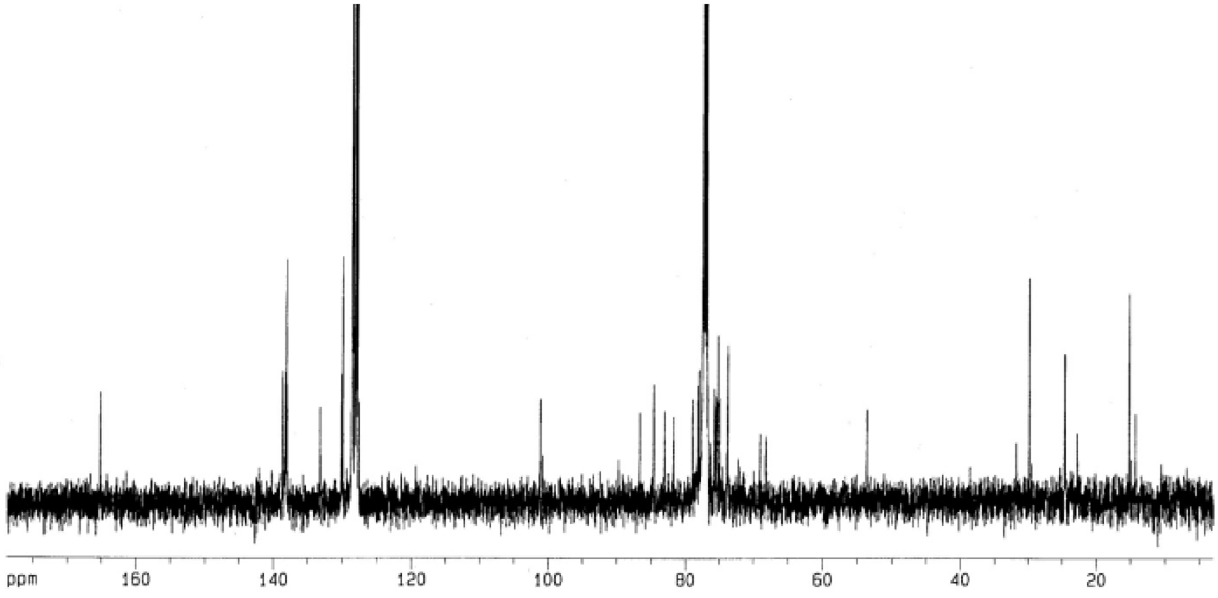
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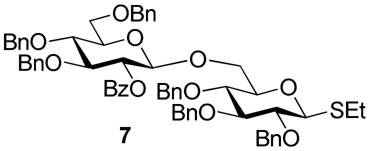

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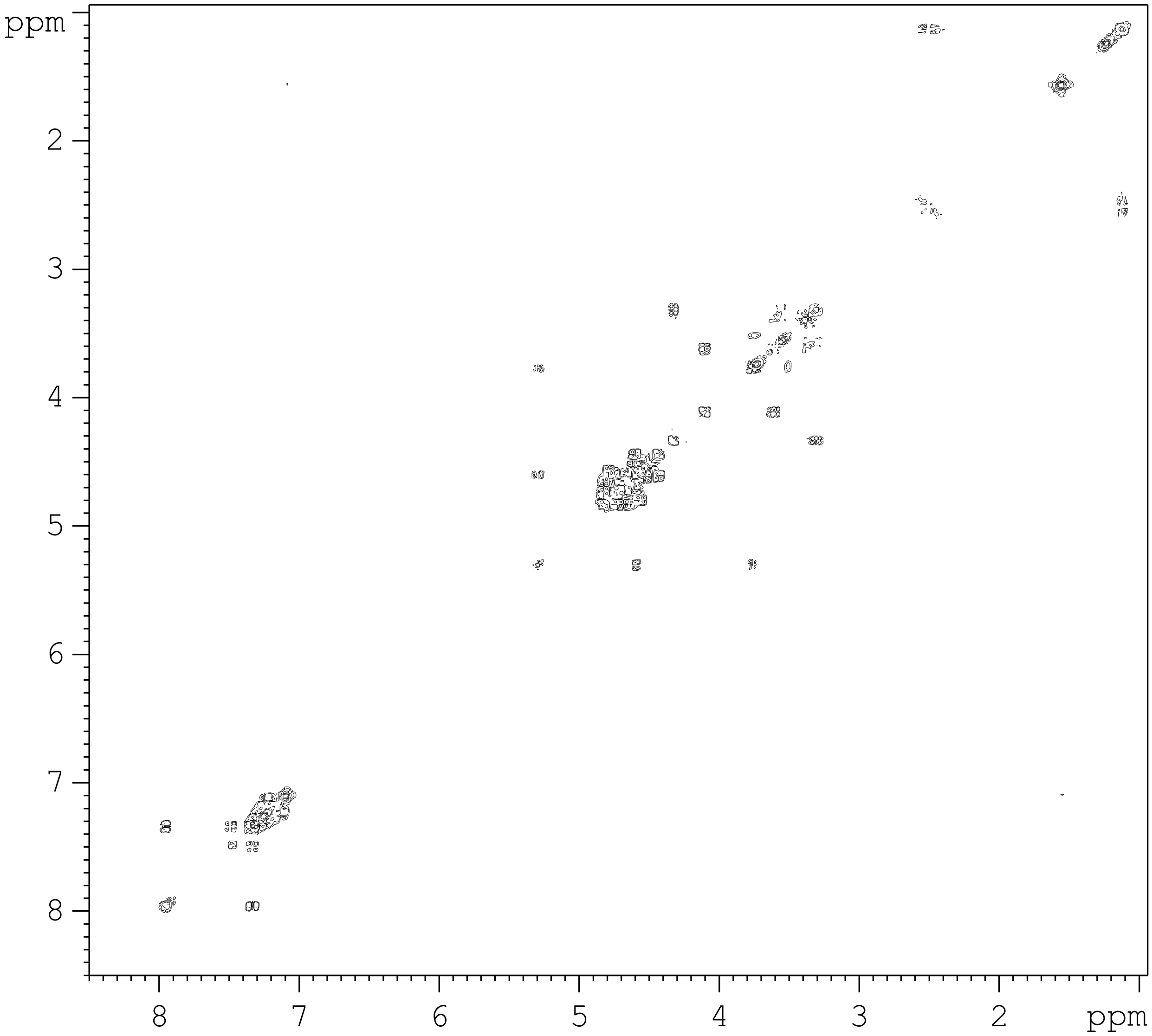

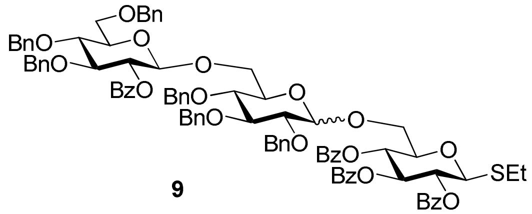
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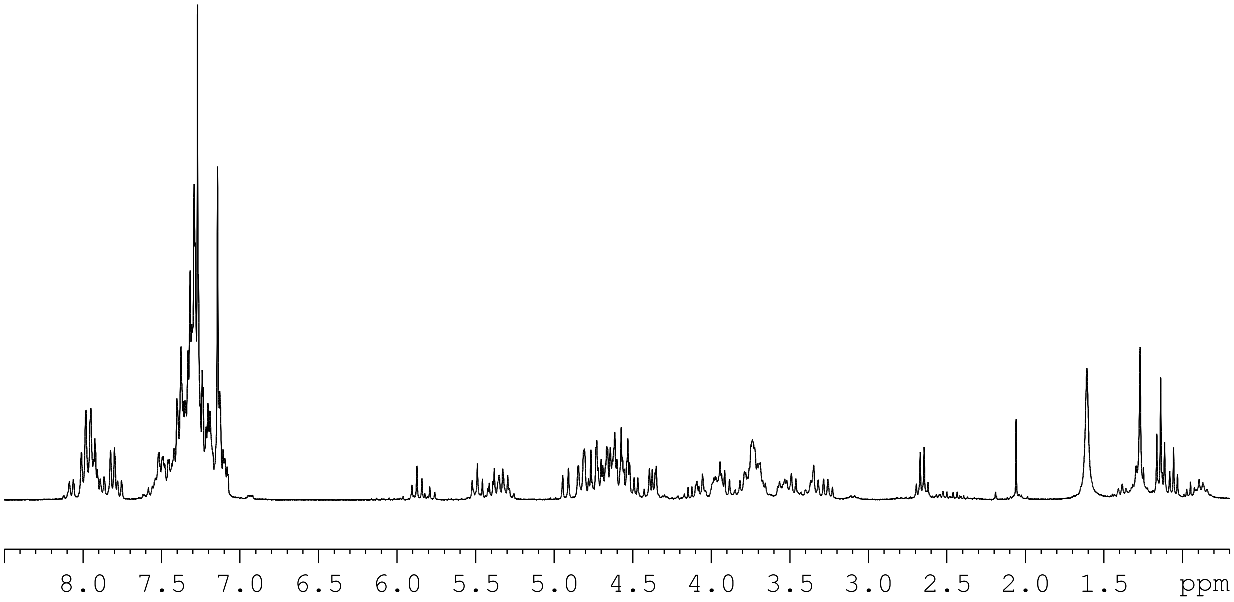
9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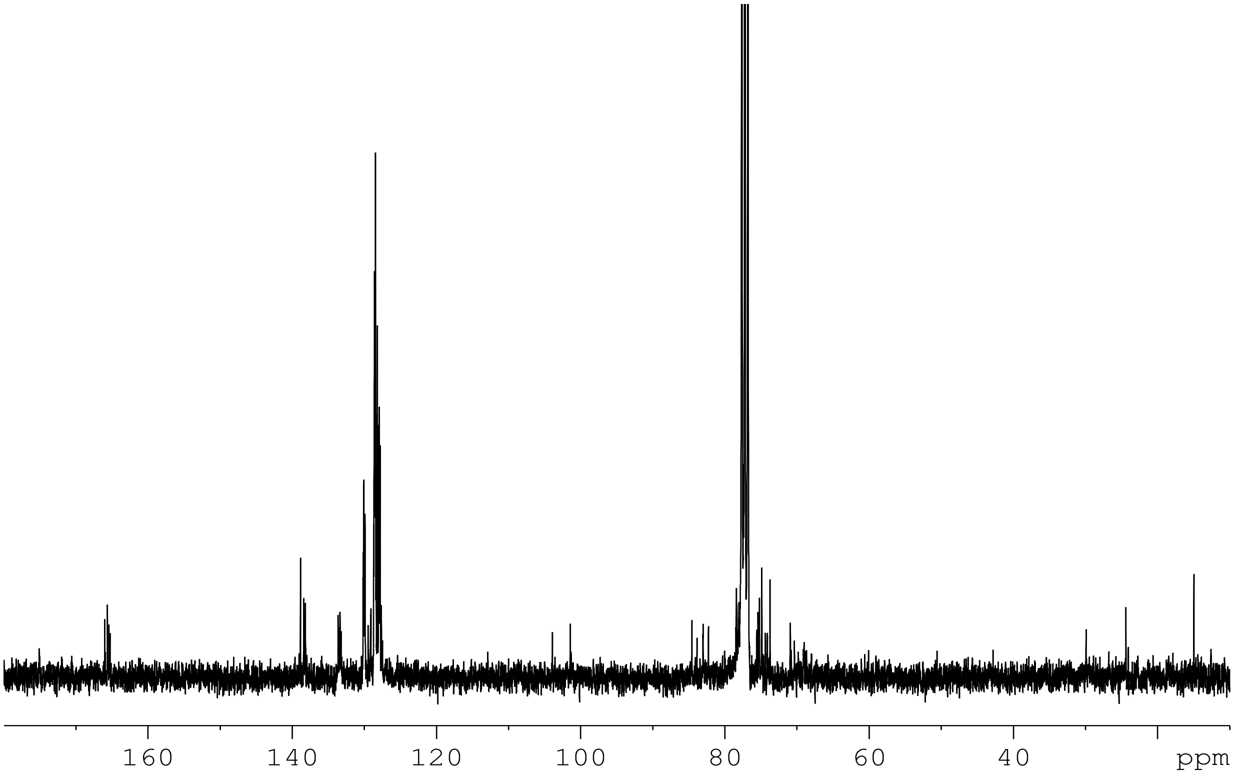
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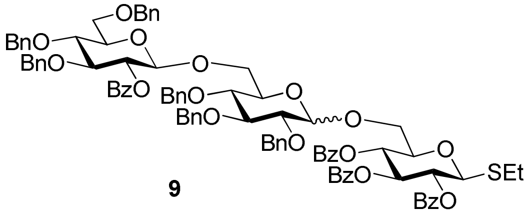
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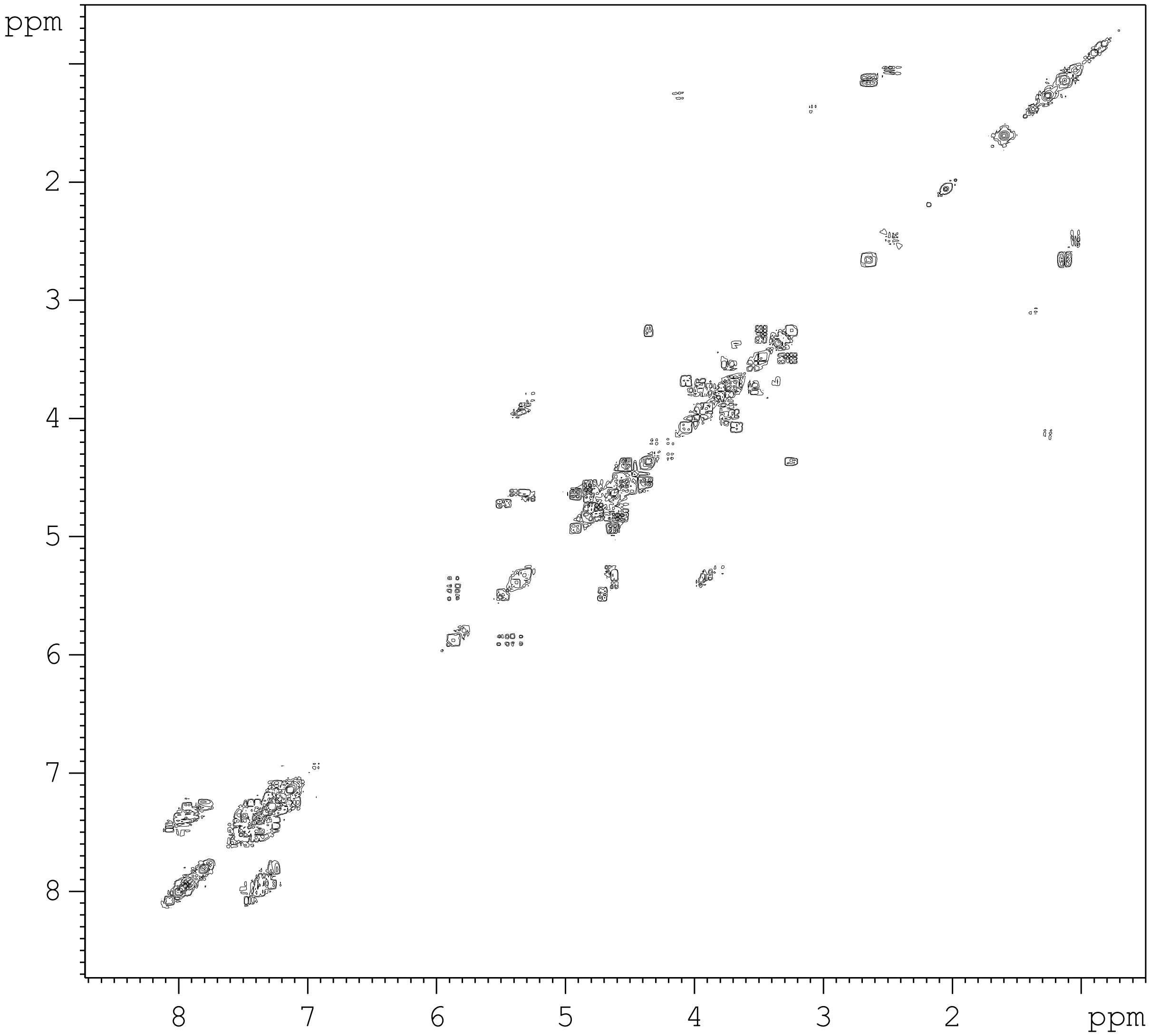
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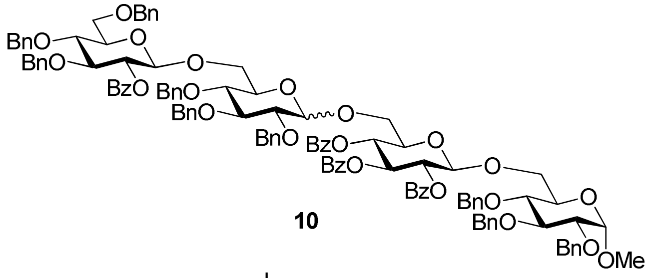

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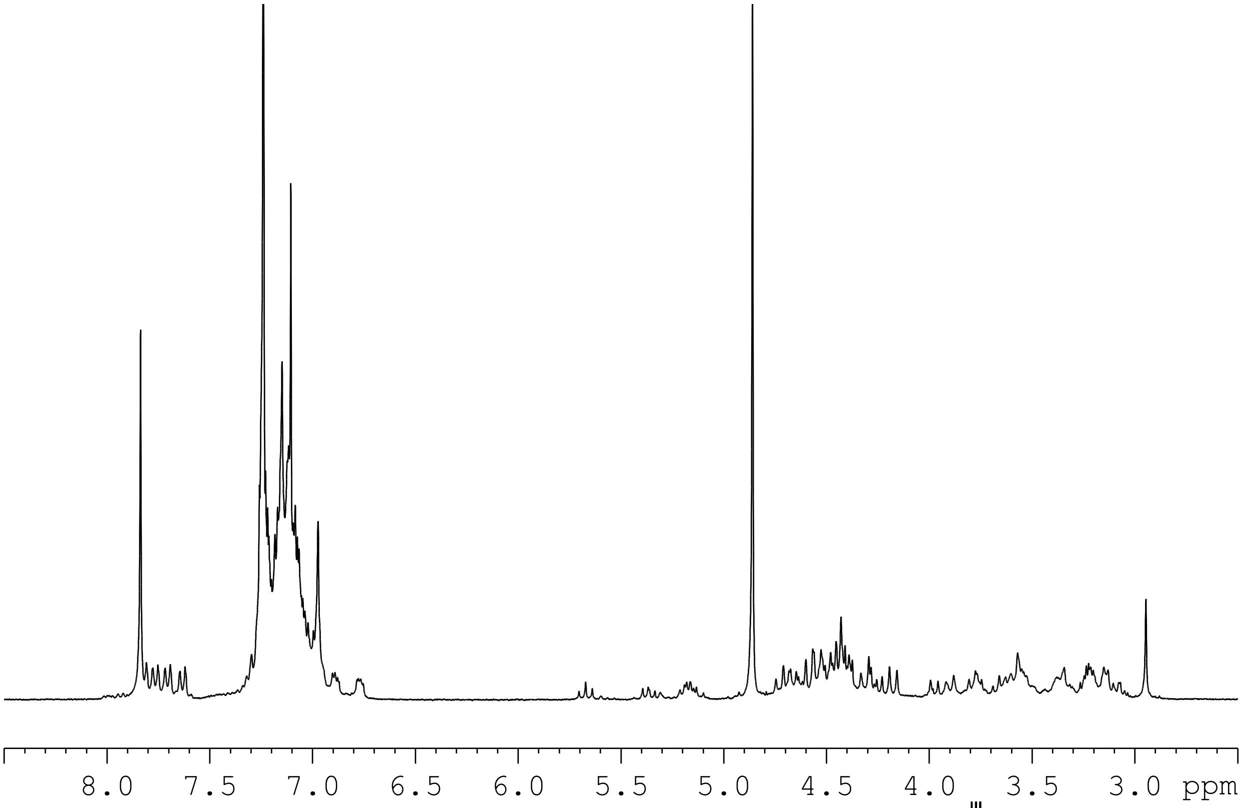
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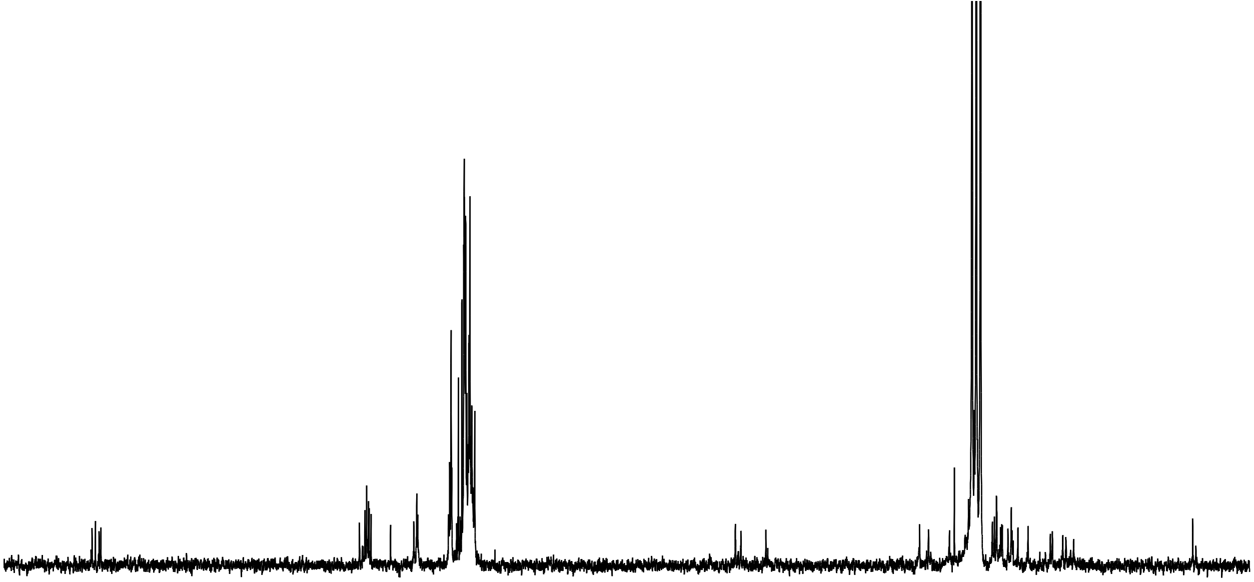
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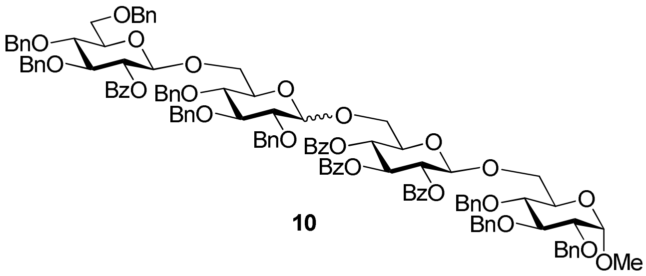

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