Electronic Supplementary Material (ESI) for CrystEngComm.

ELECTRONIC SUPPLEMENTARY INFORMATION

Hydrogen bonding induced conformational change in crystalline sugar derivative

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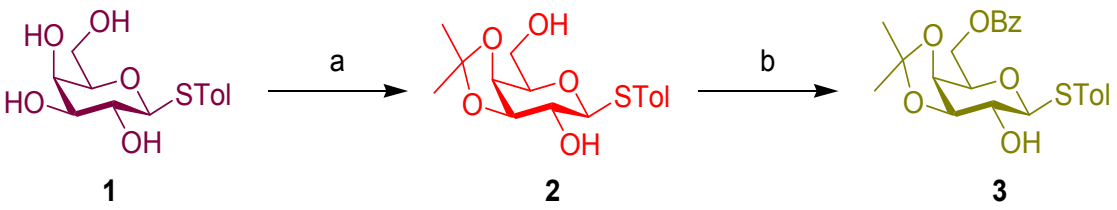
Synthetic scheme:



Scheme S1: Synthesis of the compounds 2 and 3. **Reagents and condition:** a) Acetone, H_2SO_4-silica, rt b) Et_3N, BzCN, rt

Synthesis, purification and NMR Characterization:

***p*-tolyl-1-thio-β-D-galactopyranoside (1):**

Compound **1** was synthesized following the literature procedure.[1]

$[\alpha]_D^{25}$ +121 (c 1.1, CH_3OH). ^1H NMR (CD_3OD, 500 MHz) δ: 7.44, 6.88 (2 dd, 4H, *J* 6.5 Hz, ArH), 4.52 (d, 1H, $J_{1,2}$9.5 Hz, H-1), 3.89 (dd, 1H, $J_{3,4}$,$J_{4,5}$3.0 Hz, H-4), 3.76 (dd, 1H, $J_{5,6a}$6.5 Hz, $J_{6a,6b}$11.5 Hz,H-6a), 3.70 (dd, 1H, $J_{5,6b}$5.5 Hz, $J_{6a,6b}$11.5 Hz,H-6b), 3.59 (t, 1H, $J_{1,2}$9.5 Hz, $J_{2,3}$9.0 Hz, H-2), 3.53 (t, 1H, *J* 6.5 Hz, H-5), 3.50 (dd, 1H, $J_{2,3}$9.0 Hz, $J_{3,4}$3.0 Hz, H-3), 2.28 (s, 3H, S-C_6H_4-CH_3). ^{13}C NMR (CD_3OD, 125 MHz) δ: 138.2, 132.7(2), 131.9, 130.4(2), 90.4 (C-1), 80.3 (C-5), 76.1 (C-3), 70.9 (C-2), 70.2 (C-4), 62.4 (C-6), 21.0 (S-C_6H_4-CH_3). HRMS calcd. for $C_{13}H_{18}O_5SNa$ $(M^+Na)^+$: 309.0773, found: 309.0771.

***p*-tolyl-3,4-*O*-isopropylidene-1-thio-β-D-galactopyranoside (2):**

Compound **2** was synthesized following the literature procedure.[2]

$[\alpha]_D^{25}$ +103 (c 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz) δ: 7.41, 7.09 (2 dd, 4H, *J* 6.5 Hz, ArH),4.39 (d, 1H, $J_{1,2}$10.0 Hz, H-1), 4.13 (dd, 1H, $J_{3,4}$ 5.5, $J_{4,5}$ 2.0 Hz, H-4), 4.43 (dd, 1H, $J_{2,3}$ 7.0 Hz, $J_{3,4}$ 5.5 Hz, H-3), 3.94 (dd, 1H, $J_{5,6a}$7.0 Hz, $J_{6a,6b}$11.0 Hz,H-6a), 3.77 (m, 1H, H-5), 3.62 (dd, 1H, $J_{5,6b}$6.0 Hz, $J_{6a,6b}$11.0 Hz,H-6a), 3.52 (m, 1H, H-2), 2.90, 2.55 (2 bs, 2H, 2×O*H*), 2.30 (s, 3H, S-C_6H_4-CH_3), 1.39, 1.30 (2s, 6H, $C(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 138.2, 132.8(2), 129.7(2), 128.0, 110.3 [$C(CH_3)_2$], 87.8 (C-1), 79.1 (C-3), 76.9 (C-5), 73.7 (C-4), 71.3 (C-2), 62.4 (C-6), 27.9, 26.2 [$C(CH_3)_2$], 21.0 (S-C_6H_4-CH_3). HRMS calcd. for $C_{16}H_{22}O_5SNa$ $(M^+Na)^+$: 349.1086, found: 349.1083.

***p*-tolyl-6-*O*-bezoyl-3,4-*O*-isopropylidene-1-thio-β-D-galactopyranoside (3):**

To a solution of **3** (3.0g, 7.66 mmol) in CH_3CN (30 mL), BzCN (0.91 mL, 7.66 mmol) was added followed by Et_3N (0.1 mL) and the mixture was stirred at 0–5 °C for 10 min until the starting material had completely disappeared (TLC) and the excess BzCN was neutralized with MeOH . Then organic solvent was removed directly under reduced pressure.Further purification was achieved on a flash chromatography with silica gel and *n*-hexane: EtOAc (2:1) with a high yield (3.0g, 92%) of the desired compound**3**. $[\alpha]_D^{25}$ +87 (c 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.05-6.88 (m, 9H, ArH), 4.63 (dd, 1H, $J_{5,6a}$ 4.0 Hz, $J_{6a,6b}$ 12.0 Hz, H-6a), 4.57 (dd, 1H, $J_{5,6b}$ 8.5 $J_{6a,6b}$ 12.0 Hz, H-6b), 4.43 (d, 1H, $J_{1,2}$ 10.0 Hz, H-1), 4.23 (dd, 1H, $J_{3,4}$ 5.5 Hz, $J_{4,5}$ 2.5 Hz, H-4), 4.10 (m, 2H, H-3, H-5), 3.62 (t, 1H, $J_{2,3}$ 10.0 Hz, $J_{3,4}$ 8.0 Hz, H-2), 3.03 (bd, 1H, $J_{2,OH}$ 1.5 Hz, O*H*), 2.22 (s, 3H, S-C_6H_4-CH_3), 1.46, 1.34 [2s, 6H, C(CH_3)$_2$]. ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 166.1 (*C*OC_6H_5), 137.8, 133.0, 132.5(2), 129.7(2), 129.6, 129.4(2), 128.6(2), 128.2(2) (ArC), 110.3 (*C*(CH_3)$_2$), 88.1 (C-1), 79.1 (C-3), 74.2 (C-5), 73.4 (C-4), 71.5 (C-2), 64.0 (C-6), 27.8, 26.1 [C(*C*H_3)$_2$], 20.9 (S-C_6H_4-*C*H_3). HRMS calcd. for $C_{23}H_{26}O_6SNa$ $(M^+Na)^+$: 453.1348, found: 453.1345.

Powder X-Ray Diffraction (PXRD): The PXRD patterns of compound **1**, **2** and **3** in different states, bulk solid, xerogel and precipitate, were collected on a Rigaku SmartLab with a Cu Kα radiation (1.540 Å). The tube voltage and amperage were set at 40 kV and 50 mA respectively. Each sample was scanned between 2º and 50º (2θ) with a step size of 0.02º. The instrument was previously calibrated using a silicon standard.

Figure S1: Plot of gel-sol transition temperature (T_{gel}) against gelator concentration of 1,3-dichlorobenzene gel of compound **1**

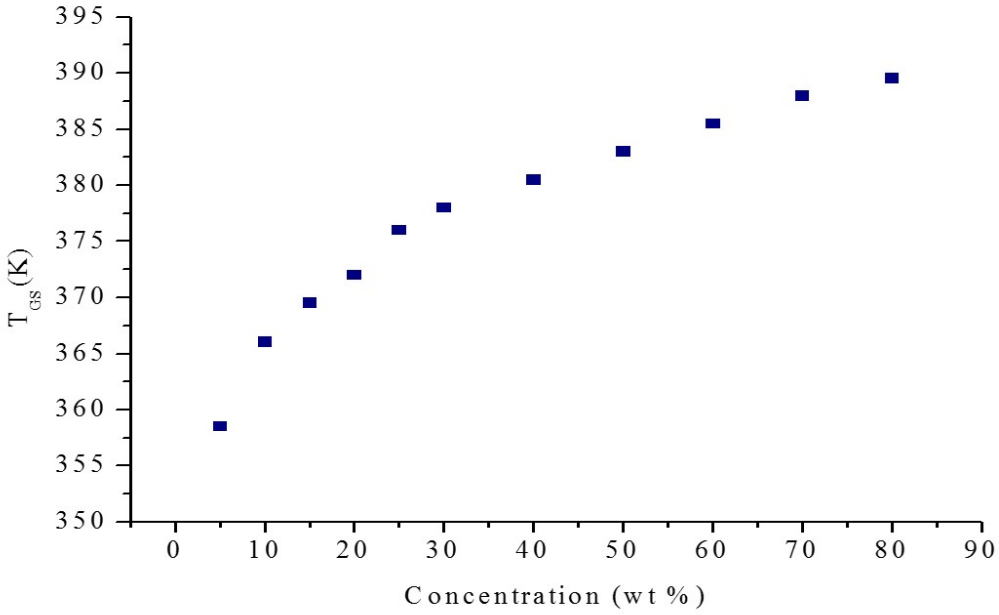
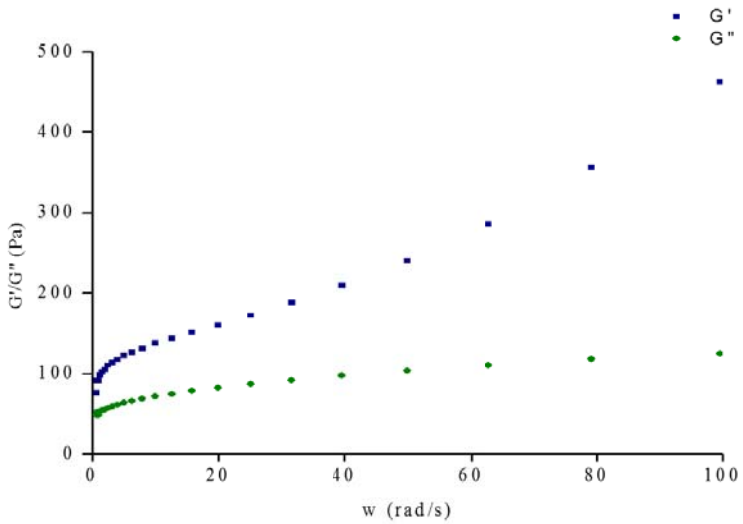


Figure S2: Dynamic rheology of the organogel containing 1.2% w/v compound **1** in (a) 1,2-dichlorobenzene, (b) chlorobenzene and (c) bromobenzene as a function of angular frequency (rad s^{-1}) at 15 °C



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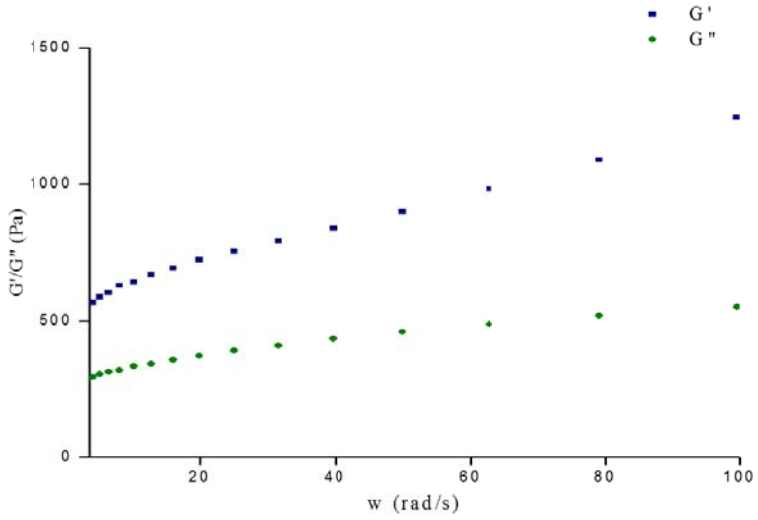

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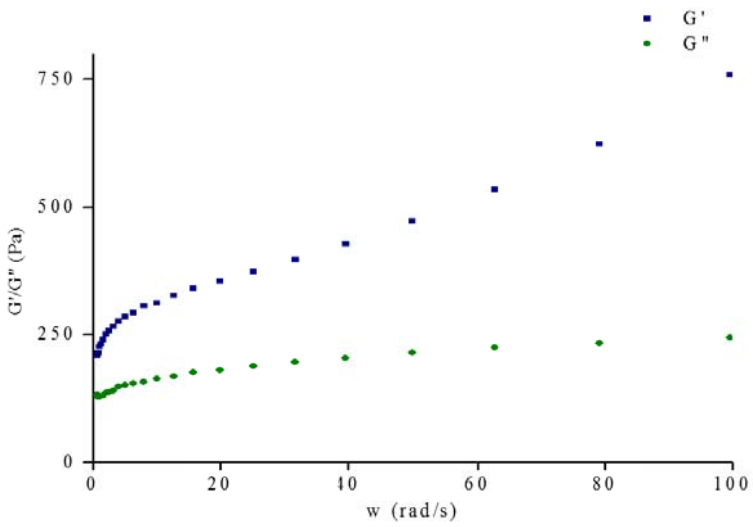


(c)

Table S1. Crystallographic data and Structure Refinement Parametersfor the galactosides**1**, **2** and **3**

Crystals	**1**	**2**	**3**
Empirical formula	$C_{13}H_{18}O_5S$	$2(C_{16}H_{22}O_5S), H_2O$	$C_{23}H_{26}O_6S$
Formula weight	286.33	670.81	430.50
Colour	colourless	colourless	colourless
Crystal morphology	block	needle	rod
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1$	$P2_1$	$P2_12_12_1$
***T*/K**	292 K	100 K	100 K
***a*/Å**	5.1361(3)	11.1679(8)	5.8253(7)
***b*/Å**	8.6117(5)	7.7832(5)	8.3302(5)
***c*/Å**	15.7890(8)	19.3582(13)	42.609(2)
***α*/°**	90	90	90
***β*/°**	96.403(5)	100.192(7)	90
***γ*/°**	90	90	90
Z	2	2	4
***V*/Å^3**	694.00(7)	1656.09(19)	2067.6(3)
D_{calc}/g cm^{-3}	1.370	1.345	1.383
μ/mm^{-1}	0.246	0.220	0.195
***F* (000)**	304.0	716.0	912.0
***θ* (min, max)**	2.587, 27.312	1.955, 25.611	2.486, 27.512
Reflections collected	2594	7409	5264
Unique reflections	2029	5657	3638
Observed reflections	1906	4532	3363
R_1 [I >2σ(I)]	0.109	0.069	0.051
wR_2 [all]	0.042	0.137	0.105
Goodness-of-fit	1.088	1.046	1.169
Value of Flack parameter	0.02(9)	-0.01(10)	0.02(13)
CCDC	1052160	1411666	1052154

Table S2. Inter-molecular and intra-molecular interactions in the crystal structure of galactoside**1**, **2** and **3**

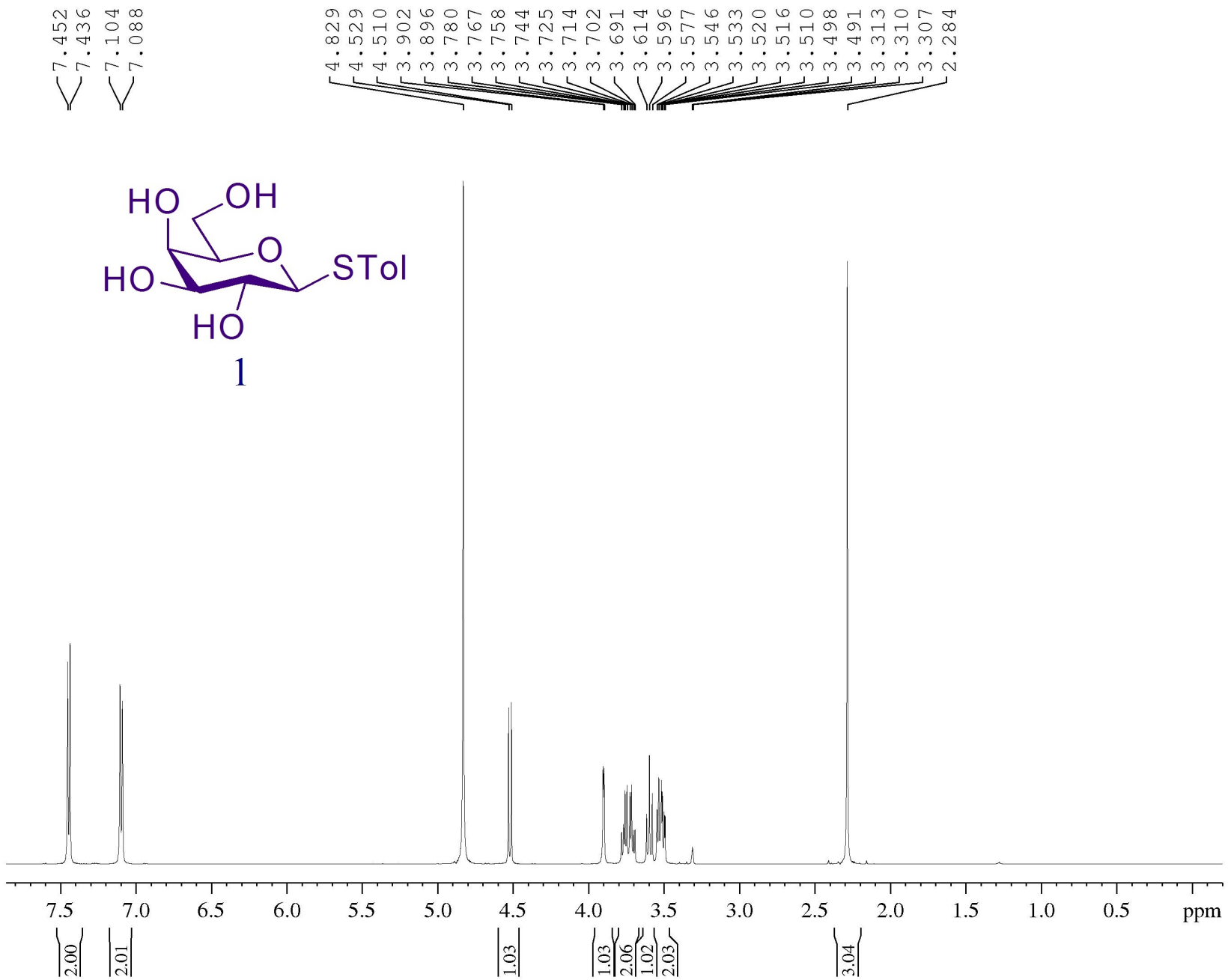
Crystal	D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)	Symmetry codes
1	O–H···O					
	O2–H2···O4	0.82	2.01	2.798(3)	160	– 1 – x, ½ +y, – z
	O3–H3···O5	0.82	2.02	2.825(3)	166	– x, ½ +y, – z
	O4–H4···O3	0.82	1.95	2.746(3)	164	– 1 – x, –½ +y, – z
	O5–H5···O2	0.82	2.07	2.763(3)	142	x, – 1+y,z
2	O–H···O					
	O2–H2···O11	0.84	1.95	2.667(5)	143	x, – 1+y,z
	O5–H5···O2	0.84	1.90	2.724(5)	167	x, 1 + y, z
	O7–H7A···O5	0.84	1.86	2.691(6)	171	– x, – ½ + y, – 1 – z
	O10–H10A···O7	0.84	1.93	2.759(5)	168	x, 1 + y, z
	O11–H11A···O1	0.85	2.16	2.994(5)	169	—
	O11–H11B···O10	0.85	1.95	2.803(5)	177	– 1 – x, – ½ + y, – 1 – z
	C–H···O					
	C12–H12A···O3	0.98	2.46	3.366(6)	154	– 1 – x, ½ + y, – 1 – z
	C22–H22···O6 (intra)	0.95	2.52	3.222(5)	131	—
	C17–H17A···O5	0.98	2.53	3.468(6)	160	x,y , – 1+z
	C29–H29A···O9	0.98	2.45	3.341(5)	151	– x, – ½ + y, – 1 – z
3	O–H···O					
	O2–H2···O1	0.82	2.06	2.858(3)	165	– 1 + x , y , z
	C–H···O					
	C15–H15···O2(intra)	0.98	2.46	2.937(4)	110	—
	C23–H23···O5(intra)	0.93	2.41	2.728(5)	100	—

Reference:

1. (a) B. Yang, K. Yoshida, Z. Yin, H. Dai, H. Kavunja, M. H. El-Dakdouki, S. Sungsuwan, S. B. Dulaney, X. Huang, *Angew. Chem. Int. Ed.*, 2012, **51**, 10185-10189; (b) K.-K.T. Mong and C.-H. Wong, *Angew. Chem. Int.*

Ed., 2002, **41**, 4087-4090; (c) M. Wilstermann, J. Balogh, G. Magnusson, *J. Org. Chem.*, 1997, **62**, 3659-3665; (d) C.-M. Huang, R.-S. Liu, T.-S. Wuc, W.-C. Cheng, *Tetrahedron Lett.*, 2008, **49**, 2895-2898; (e) C. Wang, Q. Li, H. Wang, L.-H. Zhang and X.-S. Ye, *Tetrahedron*, 2006, **62**, 11657-11662; (f) M.-Y. Chen, L. N. Patkar, K.-C. Lu, A. S.-Y Lee, C.-C. Lin, *Tetrahedron*, 2004, **60**, 11465–11475.

2. (a) A. K. Choudhury, N. Roy, *J. Carbohydr. Chem.*, 1997, **16**, 1363-1371; (b) N. Khiar, B. Suárez, M. Stiller, V. Valdivia, I. Fernández, *Synlett*, 2005, **180**, 1253-1258.



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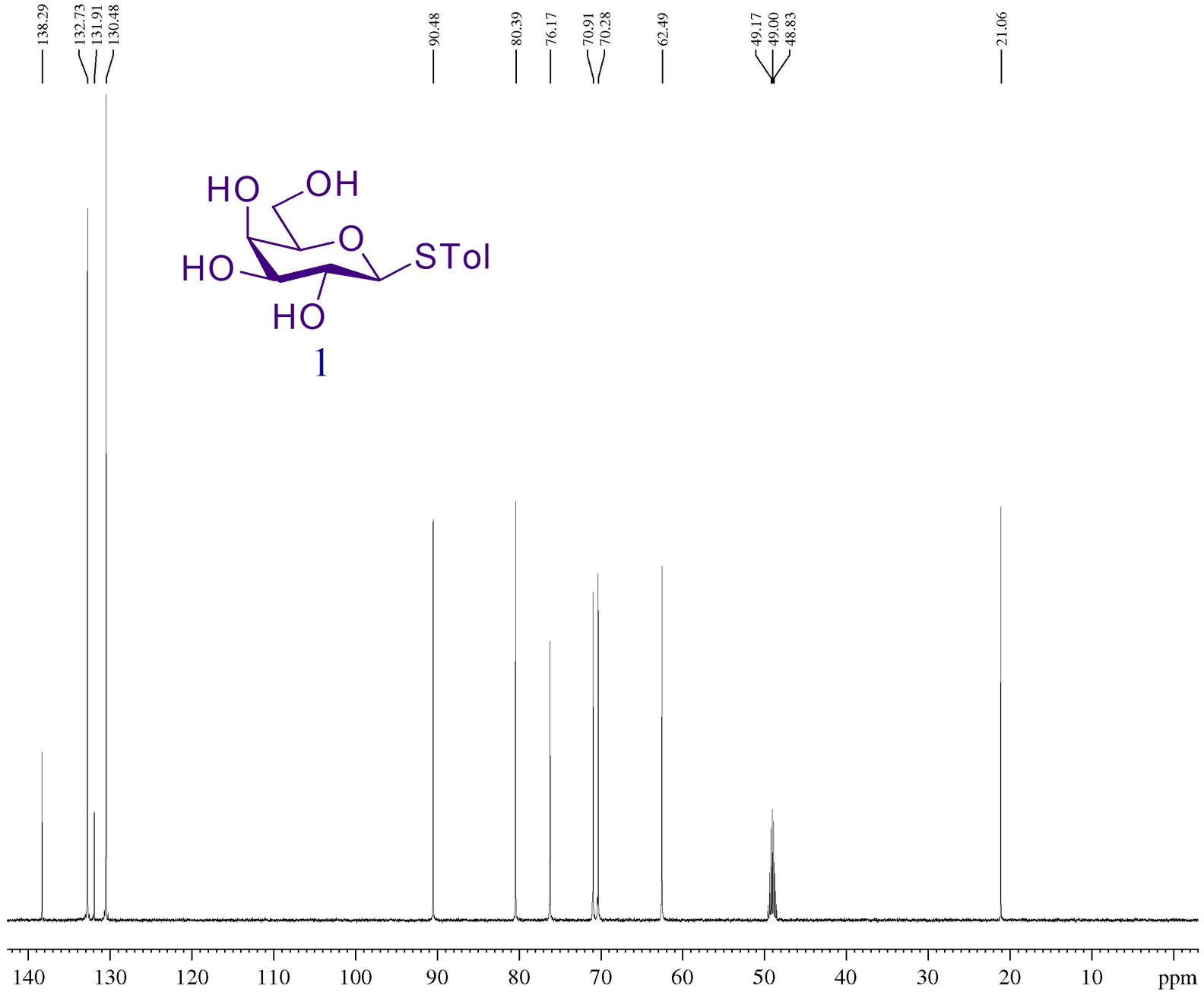

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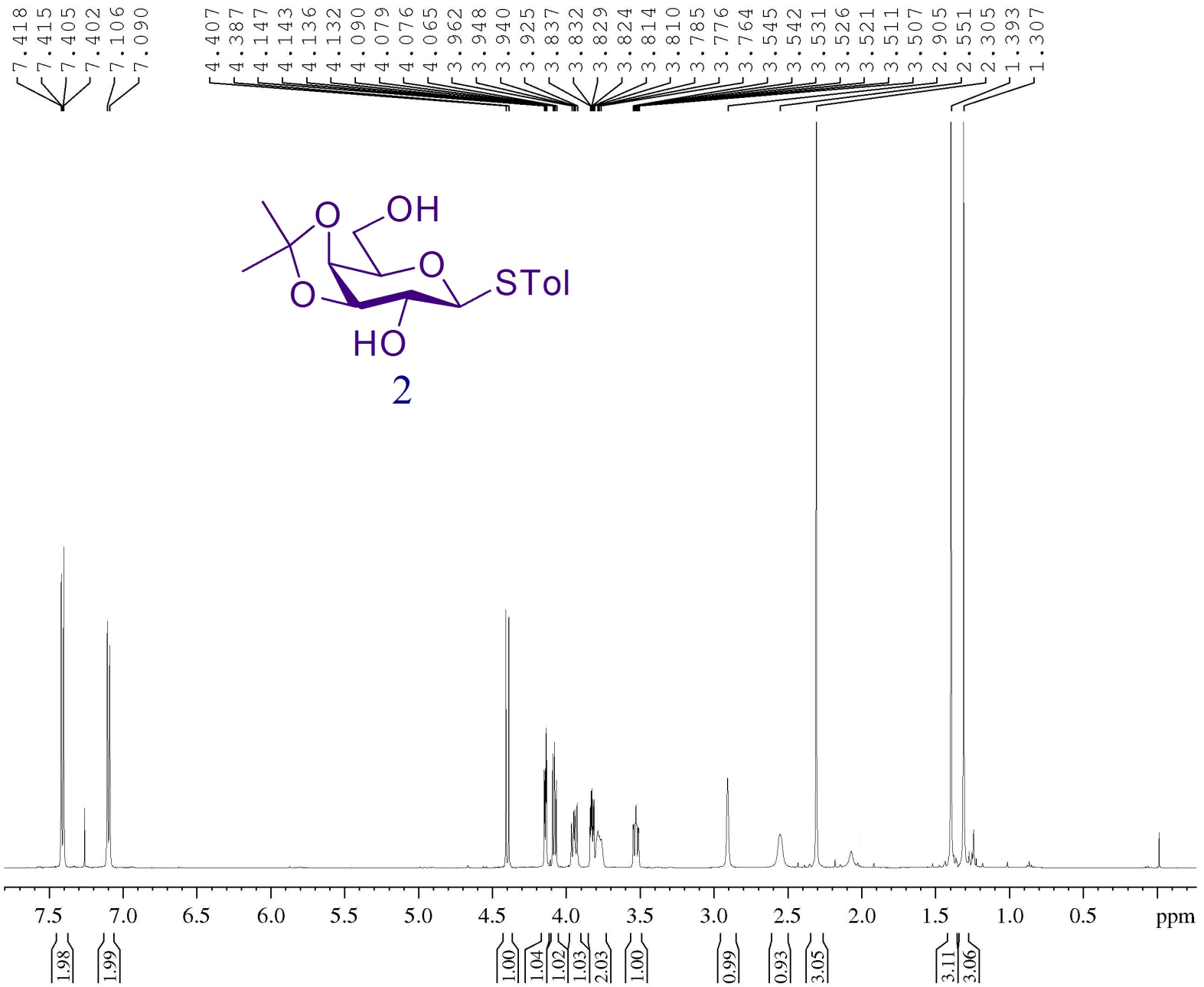

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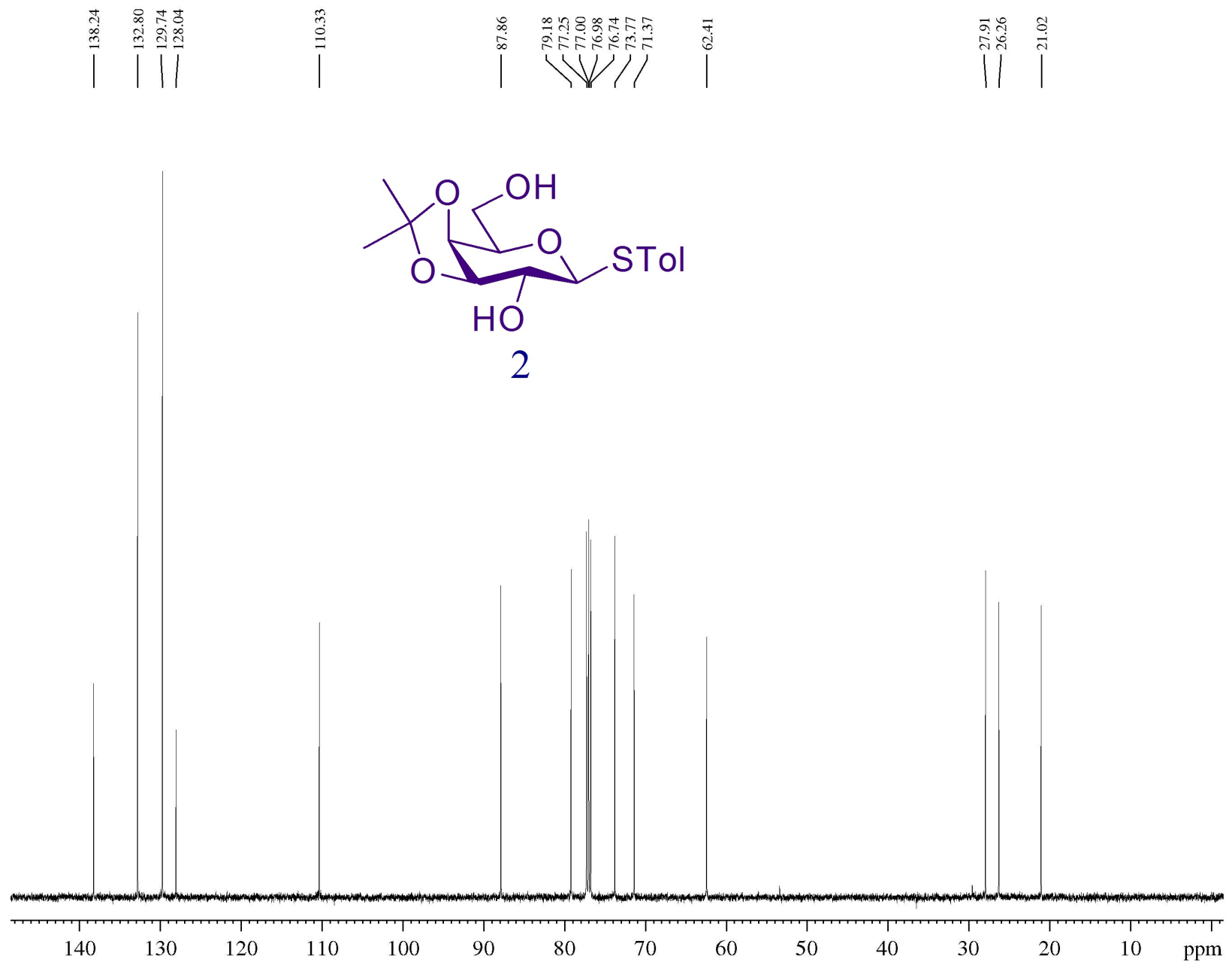

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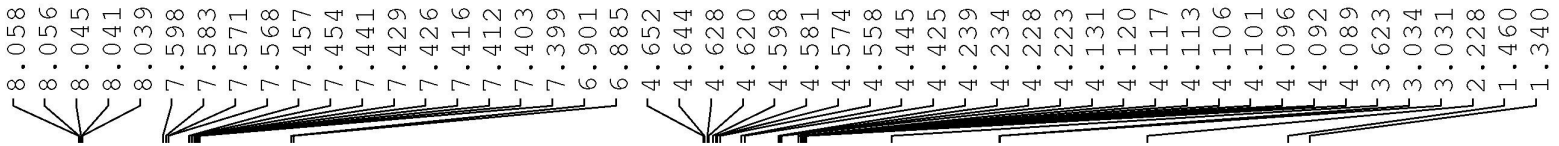

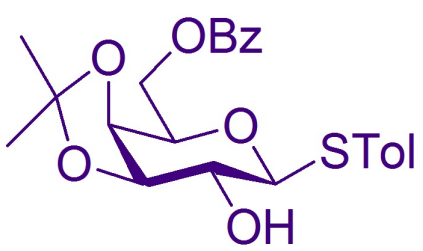

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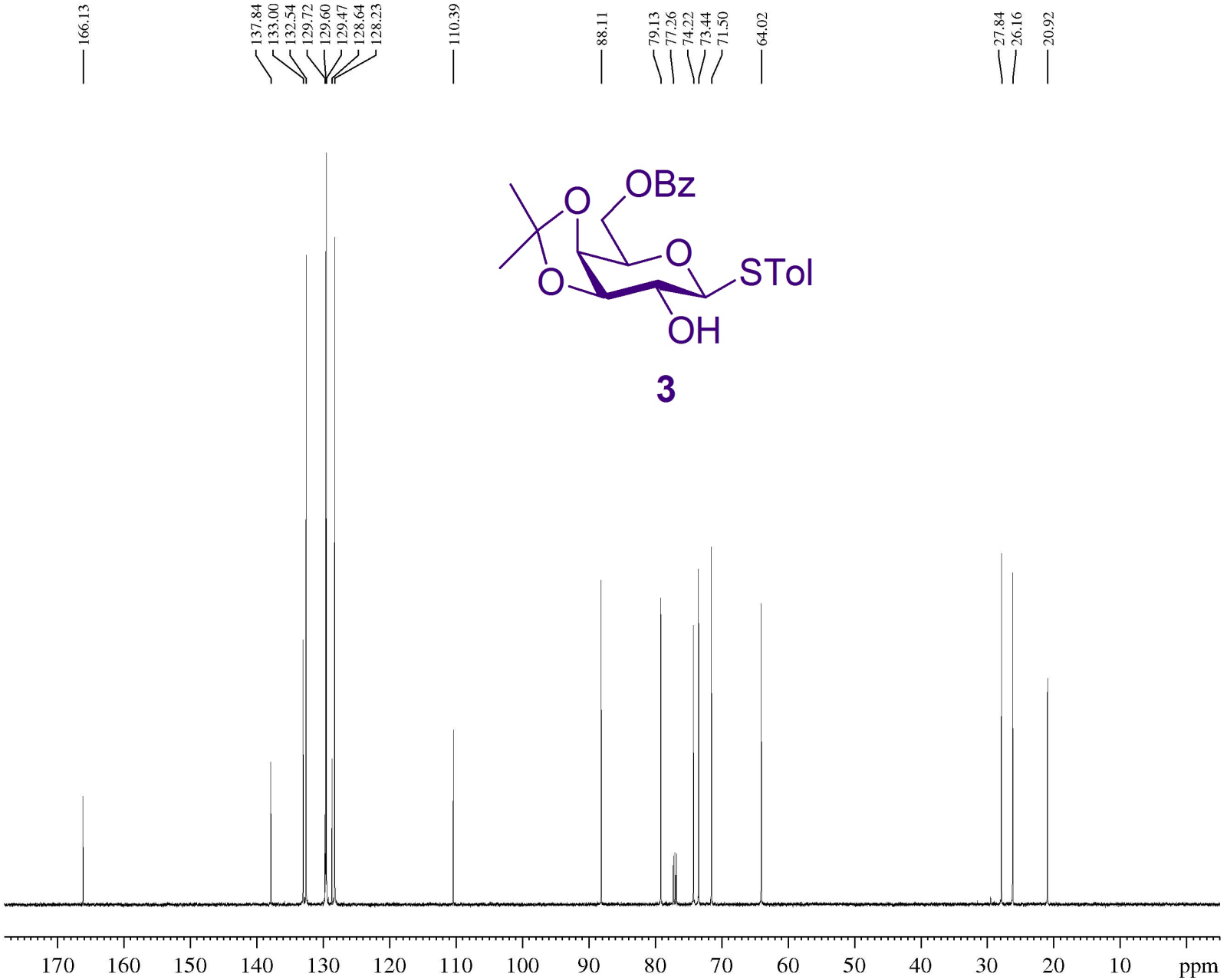

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