

Electronic Supplementary Information

for

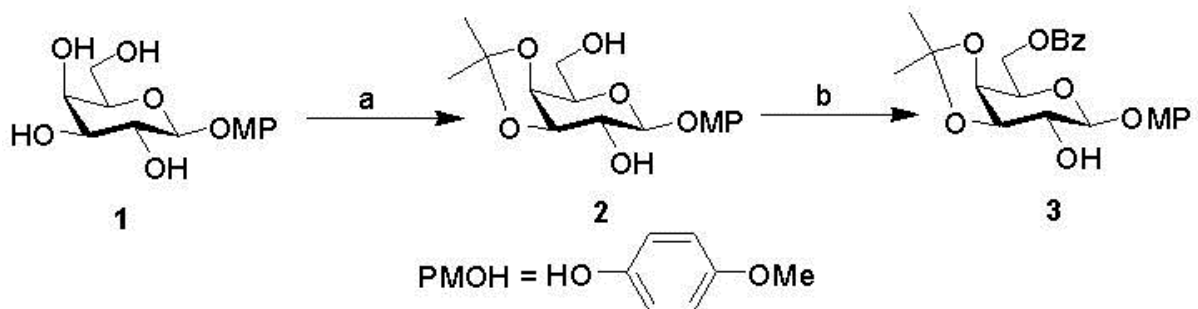
A correlation study between hydrogen bonded network and gelation ability of three galactose derivatives

Somnath Mukherjee*, G. Rama Krishna, Balaram Mukhopadhyay and C. Malla
Reddy*

Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur Campus,
Mohanpur 741246, India. E-mail: cmallareddy@gmail.com, E-mail: carbo.som@gmail.com;

Fax: +91 33 25873020

1. Synthetic scheme:



Scheme S1: Synthesis of the compounds **2** and **3**. **Reagents and condition:** a) acetone, H₂SO₄-silica, rt b) Et₃N, BzCN, rt

2. NMR Characterization:

Compound 1:

¹H NMR (500 MHz, CD₃OD) δ : 7.07-6.8 (m, 4H, ArH), 4.86 (CD₃OD-H₂O peak), 4.73 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 3.89 (dd, 1H, $J_{1,2}$ = 0.5 Hz, $J_{3,4}$ = 1Hz, H-4), 3.79-3.75 (m, 3H, H-2, H-6a, H-6b), 3.74 (s, 3H, C₆H₄-OCH₃), 3.63 (m, 1H, H-5), 3.56 (dd, 1H, $J_{1,2}$ 3.5, $J_{3,4}$ 3.0 Hz, H-3), 3.31 (solvent residual peak).

¹³C NMR (125 MHz, CD₃OD) δ : 156.59, 153.31(ArC-O), 119.26(2), 115.42(2) (ArC), 104.08 (C-1), 76.86, 74.87, 72.36, 70.21, 62.40 (CH₂), 56.05 (C₆H₄-OCH₃). [49.513-48.492 = NMR solvent signal]

Compound 2:

¹H NMR (500 MHz, CDCl₃) δ : 7.26 (solvent residual peak), 6.99-6.80 (m, 4H, ArH), 4.70 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.20-4.16 (m, 2H, H-3, H-4), 4.01-3.93 (m, 2H, H-5, H-6a), 3.86-3.79 (m, 2H, H-6b, H-2), 3.76 (s, 3H, C₆H₄-OCH₃), 2.70 (s, 1H, 2-OH), 2.22 (d, 1H, $J_{1,2}$ 6.0 Hz, 6-OH), 1.69 (CDCl₃- H₂O peak), 1.55, 1.36 (2s, 6H, 2 x isopropylidene-CH₃).

^{13}C NMR (125 MHz, CDCl_3) δ : 155.66, 151.03 (ArC-O), 118.38(2), 114.81(2) (ArC), 110.80 [$\text{C}(\text{CH}_3)_2$], 101.52 (C-1), 79.01, 73.93, 73.87, 73.54, 62.46 (CH_2), 55.78 ($\text{C}_6\text{H}_4\text{-OCH}_3$), 28.24, 26.46 (2 x isopropylidene- CH_3). [77.414-76.906 = NMR solvent signal]

Compound 3:

^1H NMR (500 MHz, CDCl_3) δ : 8.05–6.654 (m, 9H, ArH), 7.26 (solvent residual peak), 4.70 (dd, 1H, $J_{1,2}$, $J_{3,4}$ 4.0 Hz, H-6a), 4.65 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.60 (dd, 1H, $J_{1,2}$, $J_{3,4}$ 8.5 Hz, H-6b), 4.27 (dd, 1H, $J_{1,2}$, $J_{3,4}$ 2.0 Hz, H-5), 4.23-4.19 (m, 2H, H-3, H-4), 3.87-3.84 (m, 1H, H-2), 3.71 (s, 3H, $\text{C}_6\text{H}_4\text{-OCH}_3$), 2.72 (d, 1H, $J_{1,2}$ 2.5 Hz, 2-OH), 1.69 ((CDCl_3 - H_2O peak), 1.57, 1.38 (2s, 6H, 2 x isopropylidene- CH_3).

^{13}C NMR (125 MHz, CDCl_3) δ : 166.38 (COPh), 155.64, 151.13 (ArC-O), 133.34, 130.00, 129.87(2), 128.55(2), 118.76(2), 114.56(2) (ArC), 110.98 [$\text{C}(\text{CH}_3)_2$], 101.78 (C-1), 79.03, 73.53, 73.49, 71.60, 63.81 (CH_2), 55.68 ($\text{C}_6\text{H}_4\text{-OCH}_3$), 28.20, 26.46 (2 x isopropylidene- CH_3). [77.413-76.906 = NMR solvent signal]

3. Determination of gel-sol transition temperature (T_{gel}):

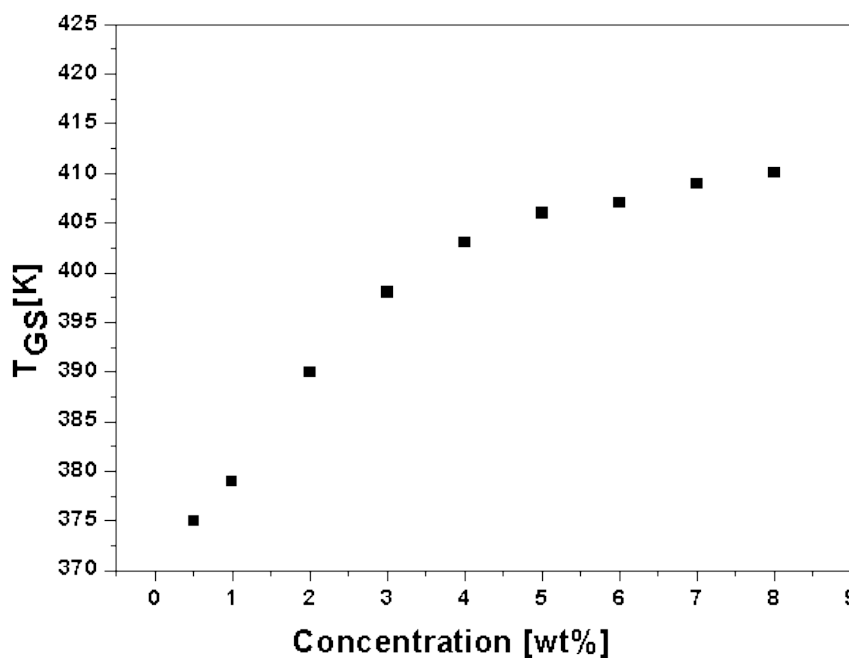


Figure S1: Plot of gel-sol transition temperature (T_{gel}) against gelator concentration of 1,2-dichlorobenzene gel of compound **1**.

4. DFT calculation: The optimized geometry and vibrational transitions of galactoside **1** were evaluated using DFT calculations on B3LYP/6-31 G(d) level¹ with GAUSSIAN 03.² The starting point for the optimization process was the crystal structure of gelator molecule.

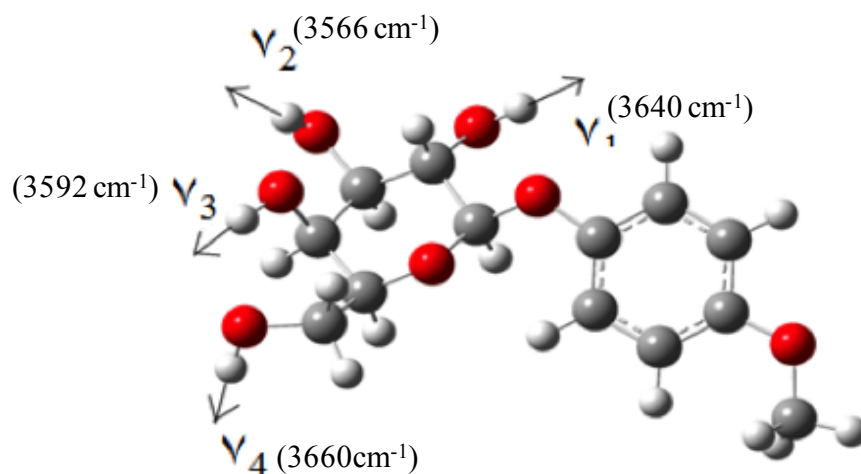


Figure S2: The calculated molecular conformation of compound **1** together with the assigned OH stretching modes ν_1 , ν_2 , ν_3 , and ν_4 .

5. 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 $K\alpha$ radiation (1.540 Å). The tube voltage and amperage were set at 40 kV and 50 mA respectively. Each sample was scanned between 2° and 50° (2 θ) with a step size of 0.02°. The instrument was previously calibrated using a silicon standard.

Table S1. Crystallographic Data and Structure Refinement Parameters of galactose derived crystals:

Formula	C₁₃H₁₈O₇ (1)	C₁₆H₂₂O₇ (2)	C₂₃ H₂₆O₈ (3)
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)	P2(1)	C2
<i>a</i> [Å]	4.8576(6)	9.292(5)	20.410(4)
<i>b</i> [Å]	9.2069(12)	7.698(3)	5.8212(10)
<i>c</i> [Å]	14.7648(19)	12.322(5)	18.903(4)
<i>α</i> [°]	90	90	90
<i>β</i> [°]	95.696(8)	111.34(3)	95.216(7)
<i>γ</i> [°]	90	90	90
<i>V</i> [Å³]	657.07(15)	821.0(6)	2236.6(7)
<i>Z</i>	2	2	4
<i>λ</i> [Å]	0.71073	0.71073	0.71073
<i>ρ</i>_{calcd} [gcm⁻³]	1.447	1.320	1.278
<i>F</i>[000]	304	348	912
<i>μ</i> [mm⁻¹]	0.118	0.104	0.097
<i>θ</i> [°]	2.61-34.20	2.35-31.43	2.16- 18.20
index range	-5 ≤ <i>h</i> ≤ 6 -11 ≤ <i>k</i> ≤ 11 -18 ≤ <i>l</i> ≤ 18	-8 ≤ <i>h</i> ≤ 11 -9 ≤ <i>k</i> ≤ 9 -15 ≤ <i>l</i> ≤ 15	-23 ≤ <i>h</i> ≤ 9 -5 ≤ <i>k</i> ≤ 4 -19 ≤ <i>l</i> ≤ 21
<i>T</i> [K]	298(2)	298(2)	298(2)
<i>R</i>1	0.0550	0.0480	0.0344

wR2	0.1834	0.1403	0.0649
R_{merge}	0.0578	0.0568	0.0535
Parameters	186	213	284
GOF	1.367	1.059	1.100
reflns total	4793	6979	6471
unique reflns	2593	3420	1552
obsd reflns	2442	2995	8540
CCDC^[a]	865731	865732	865730

Hydrogen Bond Parameters:

Table S2. (Galactoside 1)

D -- H ...A ^a	D -- H	H ... A	D -- A	(D—H... A)/°
O4 -- H4 ..O6 #1	0.820	1.980	2.785(3)	166.0
O5 -- H5A .. O6 #2	0.820	2.040	2.857(3)	172.0
O6 -- H6A .. O5	0.820	2.360	2.762(3)	111.0
O6 -- H6A .. O4 #3	0.820	2.050	2.805(3)	153.0
O7 -- H7 .. O4 #4	0.820	2.190	2.884(3)	142.0
C10 -- H10 .. O5 #5	0.980	2.2900	3.175(4)	149.0

^aSymmetry transformation code: #1=1-x,1/2+y,-z #2= 2-x,1/2+y,-z #3 = 2-x,-1/2+y,-z #4 = x,-1+y,z #5 = -1+x,y,z

Table S3. (Galactoside 2)

D -- H ... A ^a	D -- H	H ... A	D -- A	(D—H... A)/°
O3 -- H3A .. O1 #1	0.820	2.090	2.857(3)	156.0
O5 -- H5A .. O3 #2	0.820	2.020	2.833(3)	168.0
C3 -- H3 .. O7 #3	0.930	2.520	3.275(4)	139.0
C12 -- H12 .. O5 #4	0.980	2.590	3.335(3)	133.0

^aSymmetry transformation code: #1 = 1+x,y,z #2 = x,-1+y,z #3 = -1+x,y,z #4= -x,1/2+y,-z

Table S4. (Galactoside 3)

D -- H ... A ^a	D -- H	H ... A	D -- A	(D—H... A)/°
O4 -- H5 .. O5 #1	0.820	2.000	2.777(5)	159.0
C6 -- H6 .. O3	0.930	2.440	2.961(7)	115.0
C10 -- H10 .. O2 #2	0.980	2.560	3.525(6)	170.0
C16 -- H16A .. O8	0.970	2.290	2.712(7)	105.0
C23 -- H23 .. O7	0.930	2.380	2.699(8)	100.0

^aSymmetry transformation code: #1 = 1/2-x,1/2+y,-z #2 = x,-1+y,z

6. NMR spectra of compounds 1, 2 and 3:

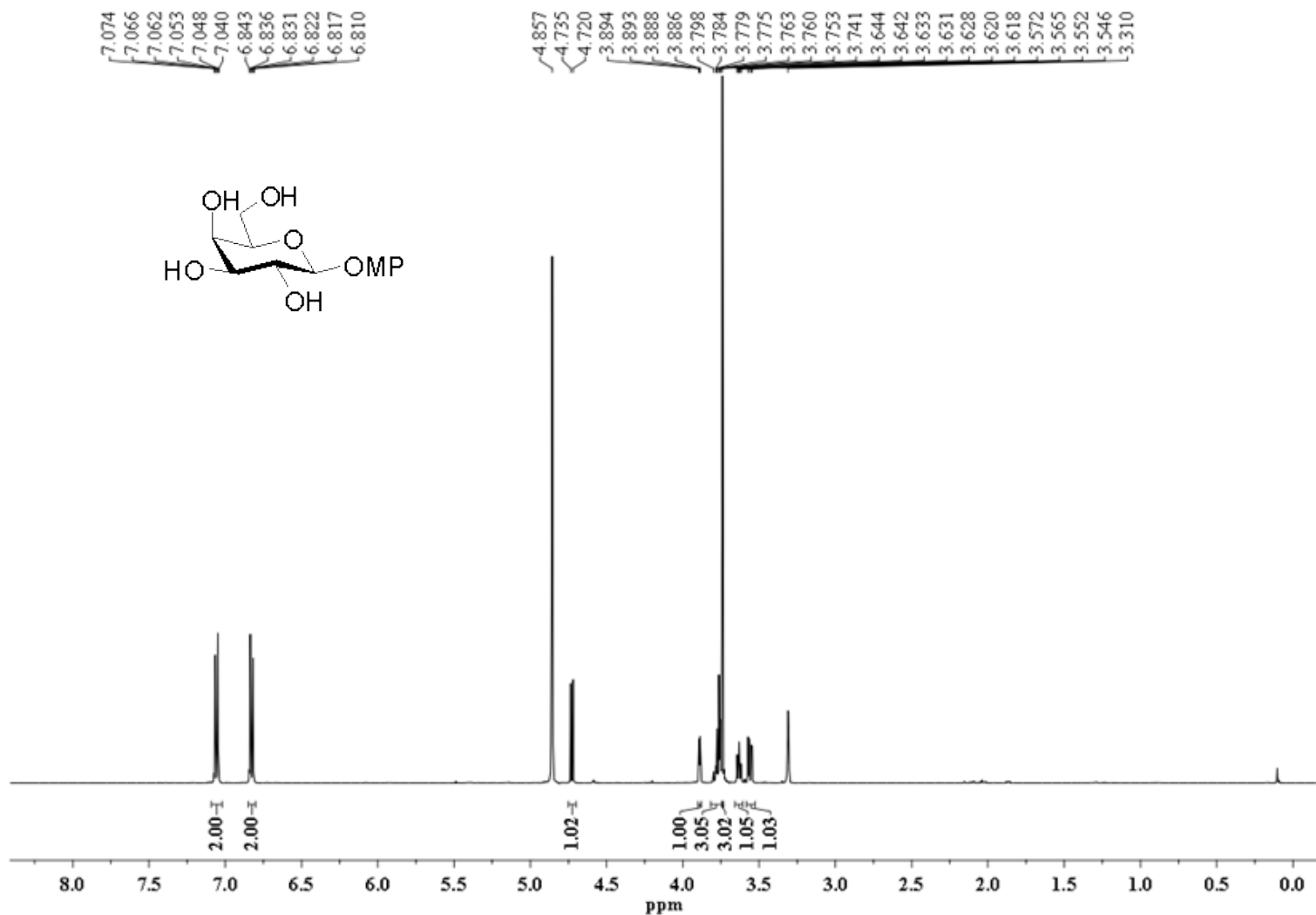


Figure S3: Proton NMR spectrum of compound **1** in CD₃OD.

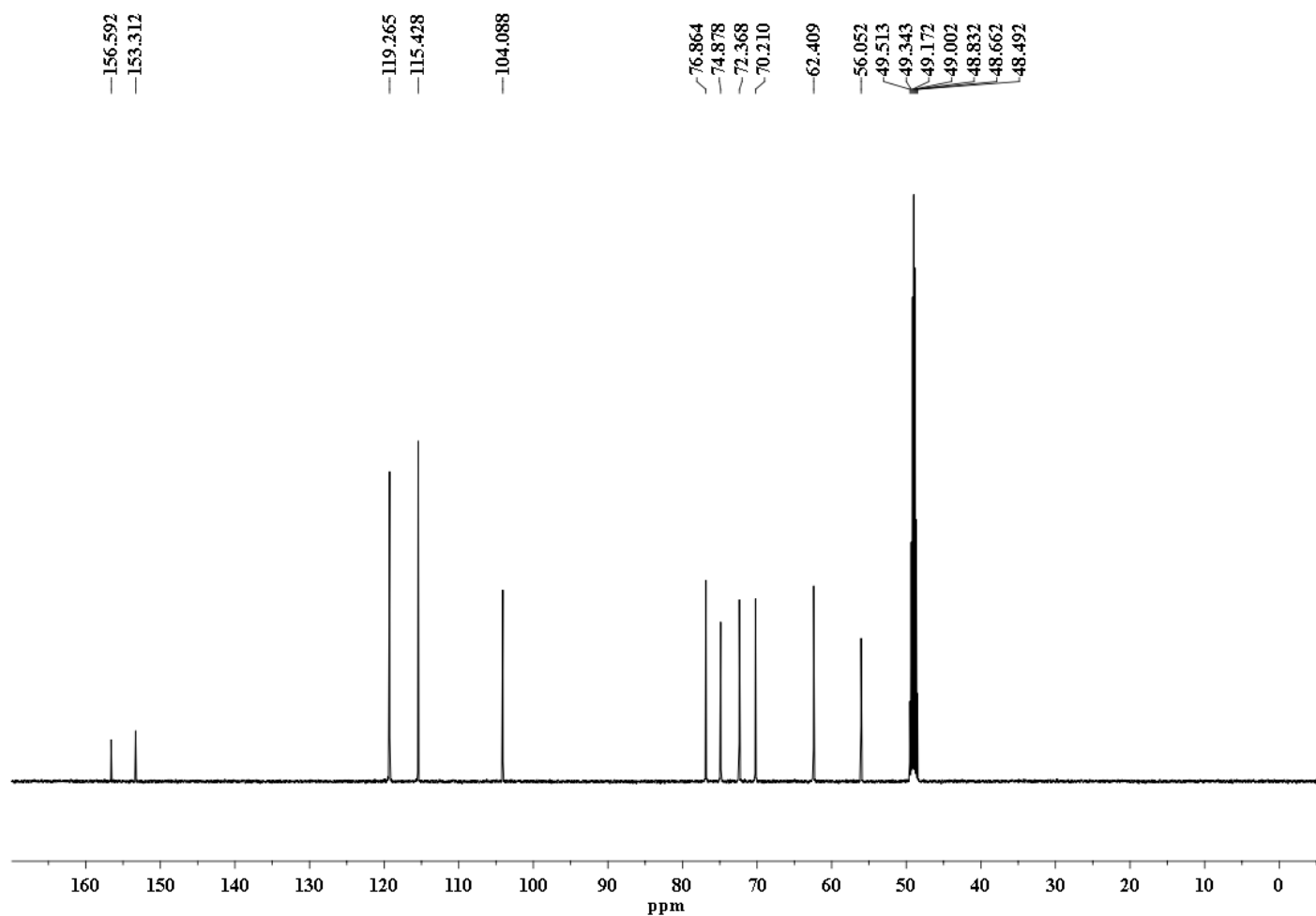


Figure S4: Carbon NMR spectrum of compound **1** in CD₃OD.

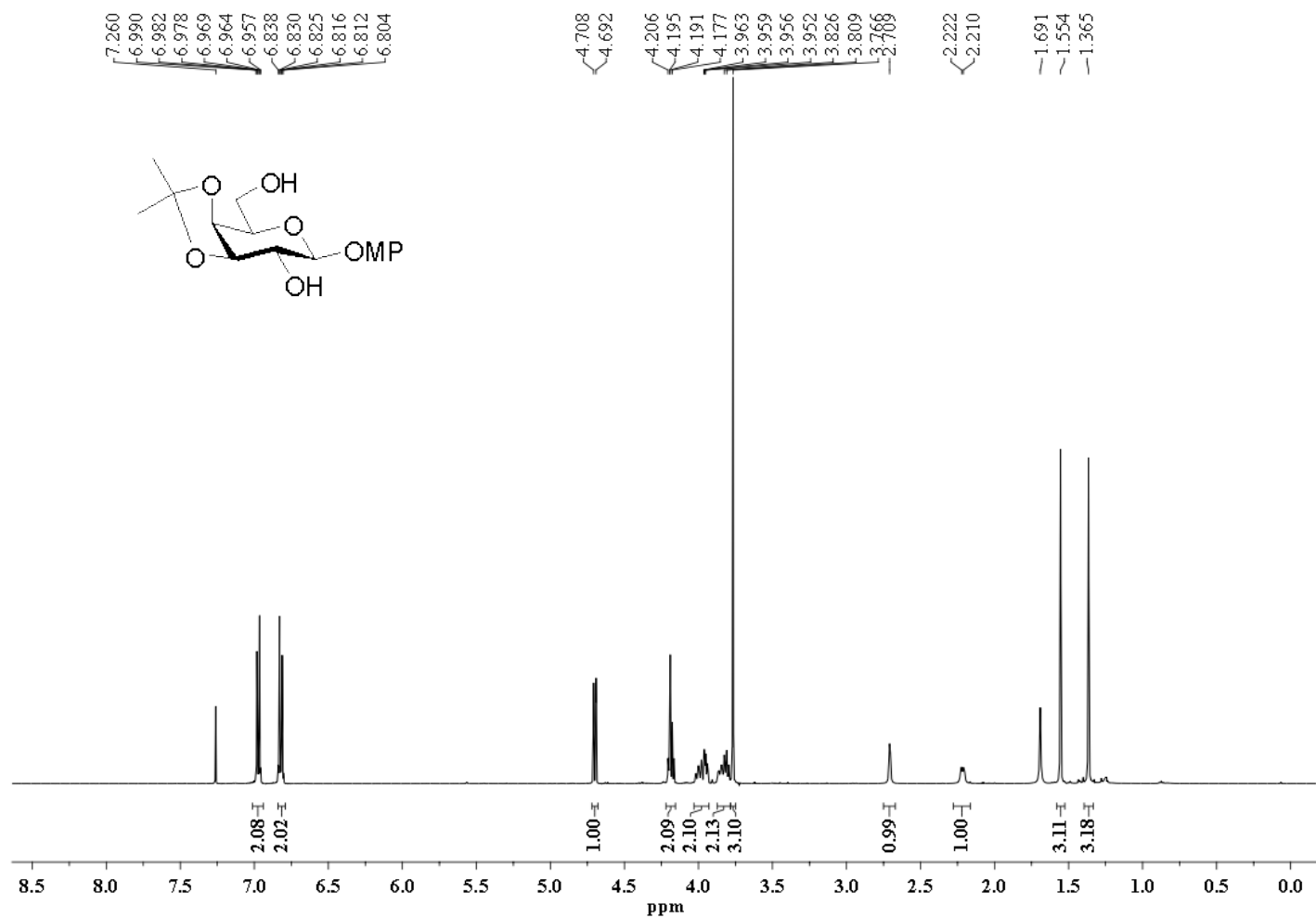


Figure S5: Proton NMR spectrum of compound **2** in CDCl₃.

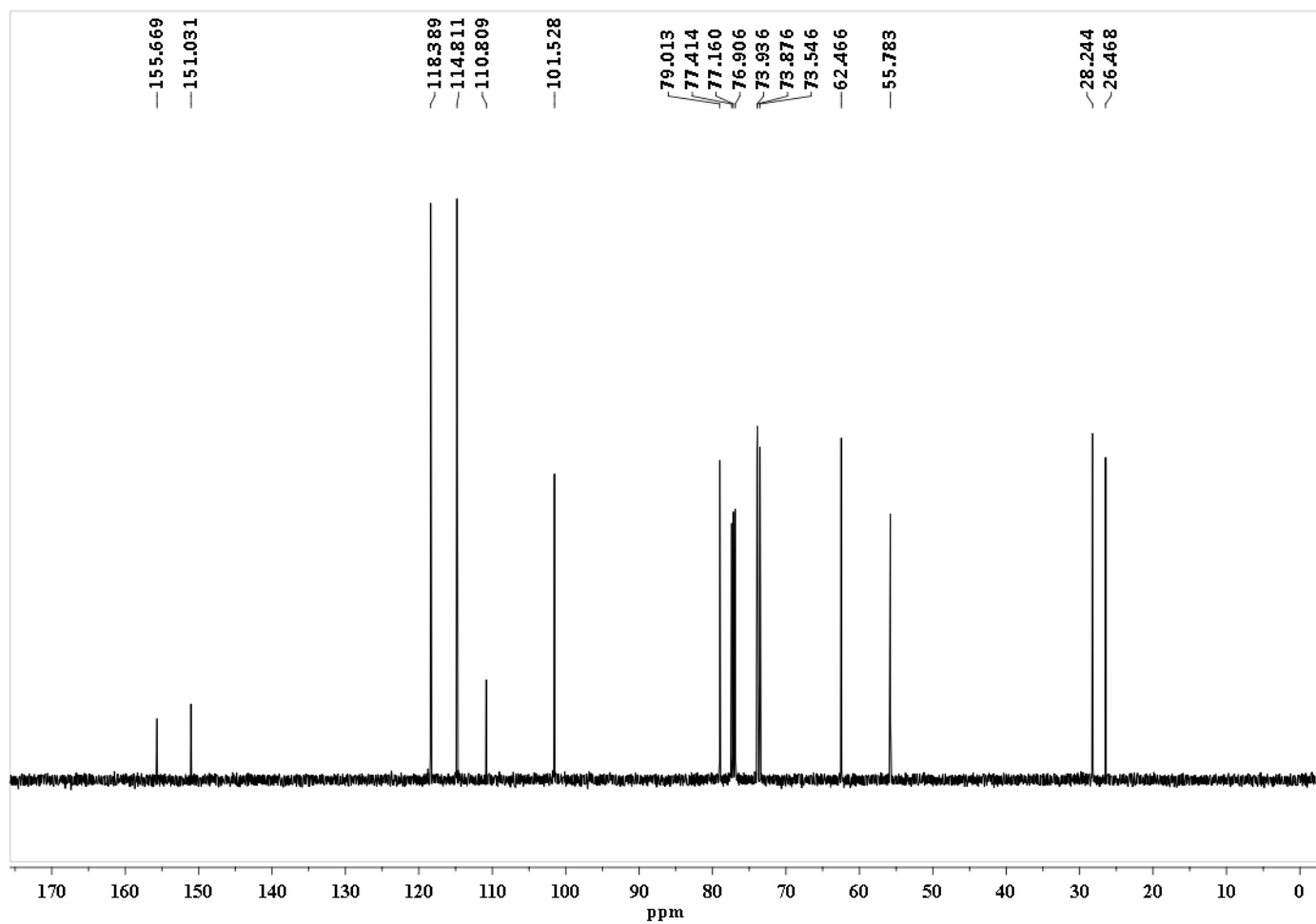


Figure S6: Carbon NMR spectrum of compound **2** in CDCl₃.

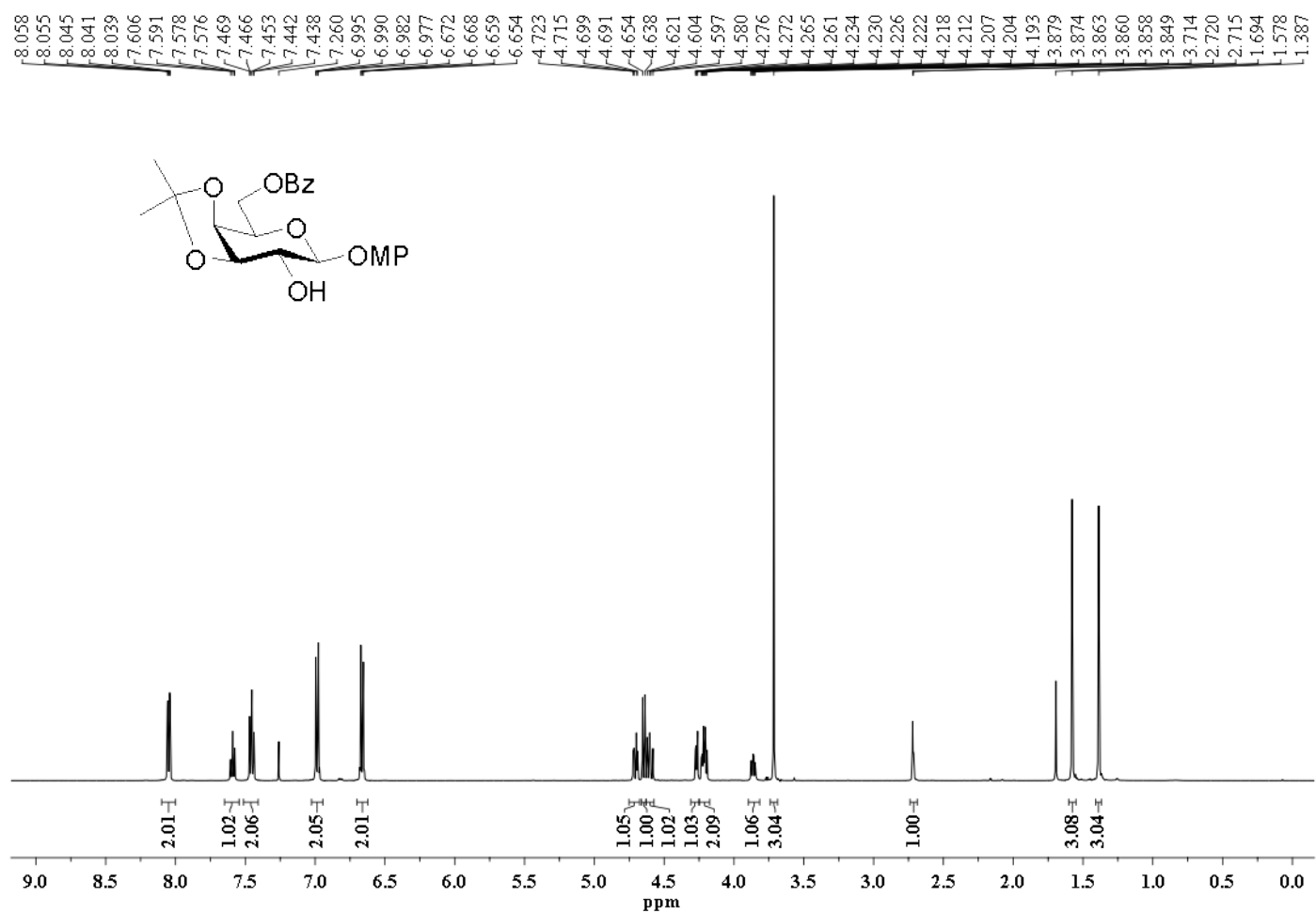


Figure S7: Proton NMR spectrum of compound **3** in CDCl_3 .

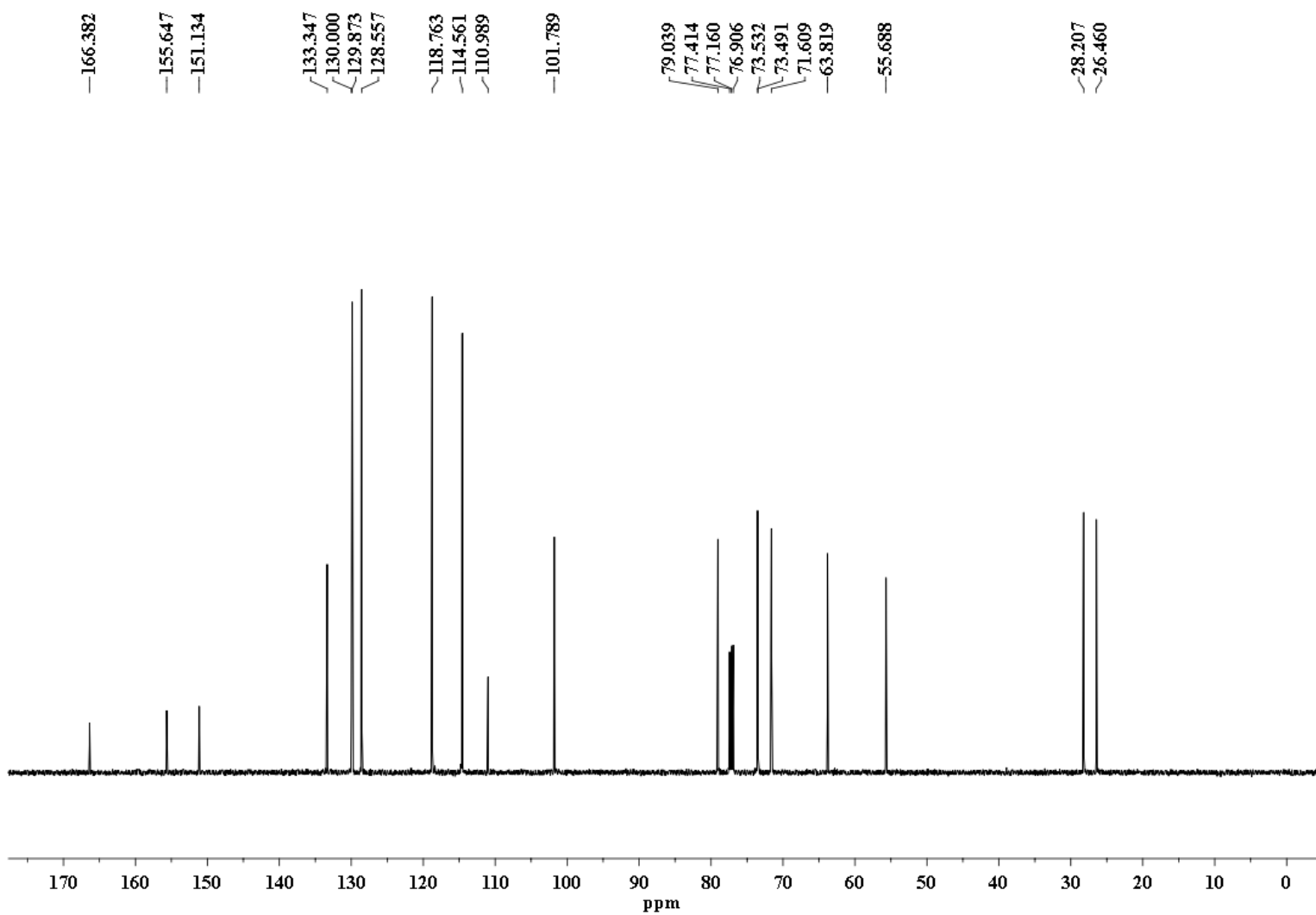


Figure S8: Carbon NMR spectrum of compound **3** in CDCl_3 .

6. Mass spectra of compounds 1, 2 and 3:

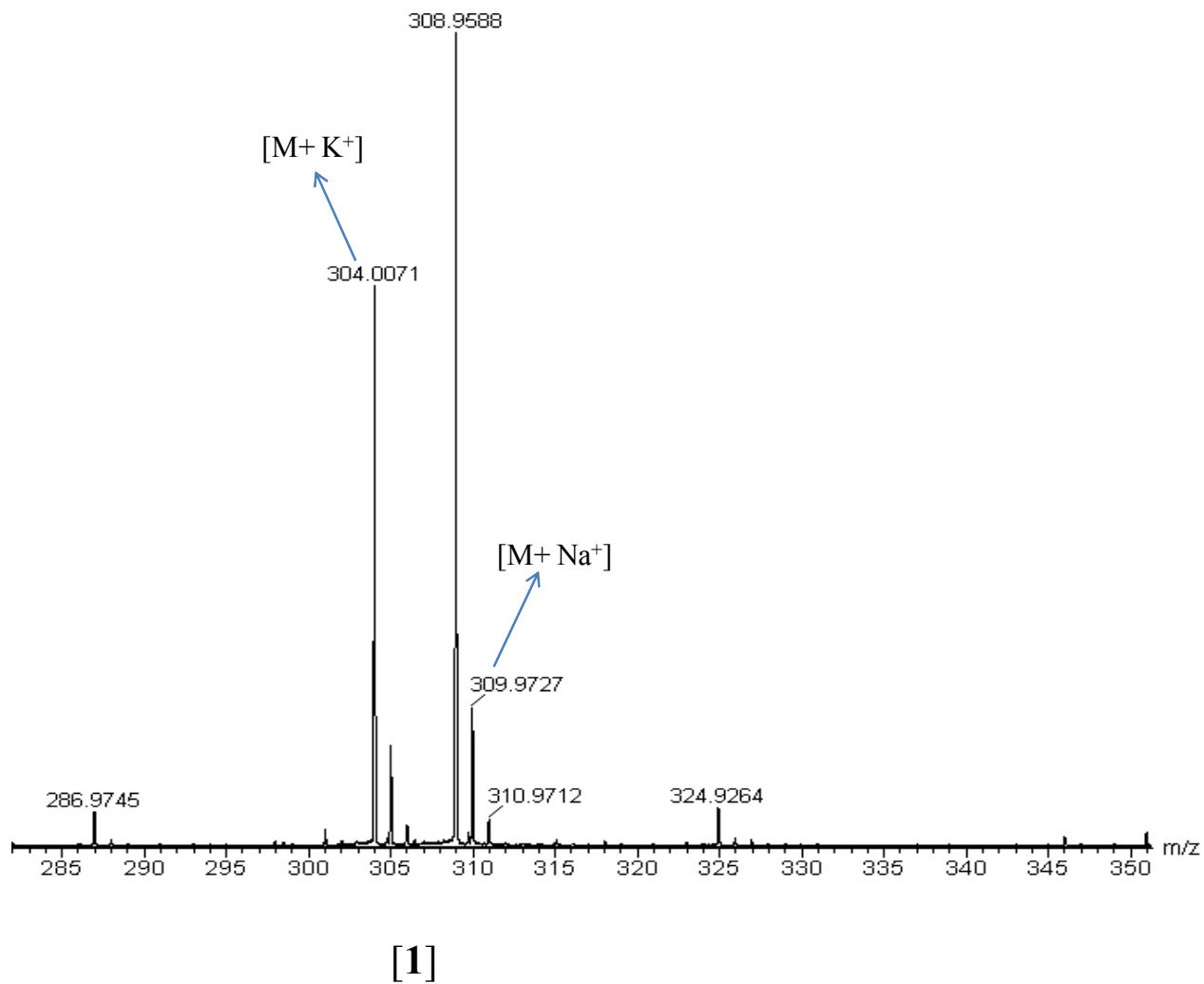
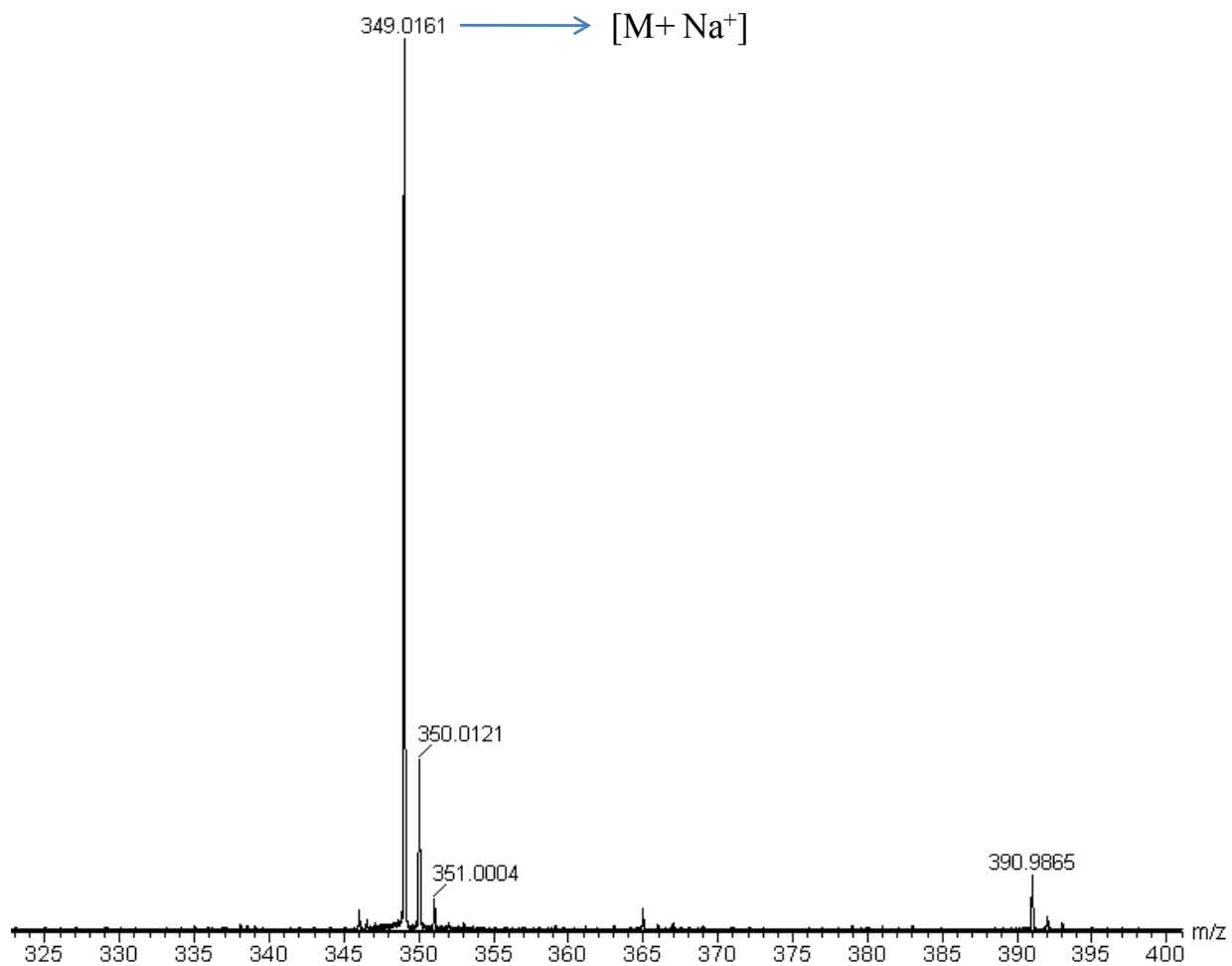
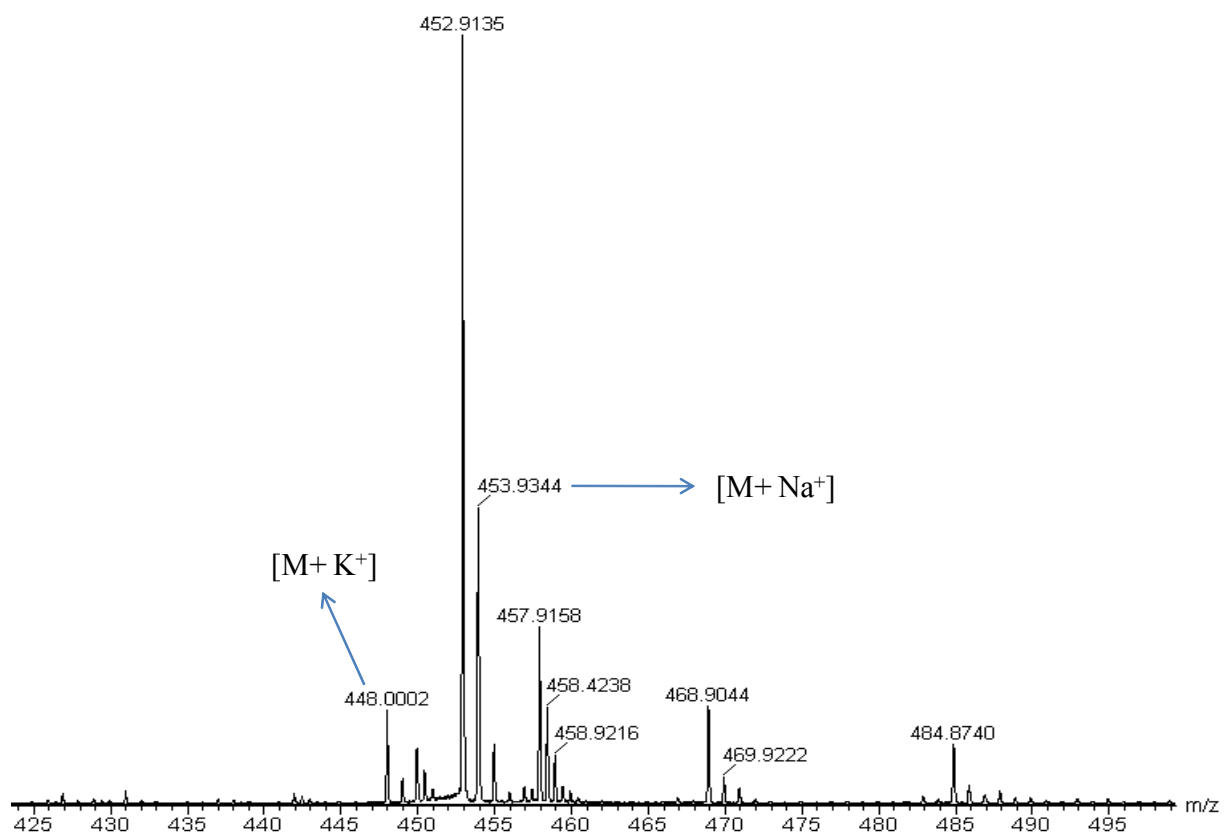


Figure S9: Mass spectrum of compound 1.



[2]

Figure S10: Mass spectrum of compound 2.



[3]

Figure S11: Mass spectrum of compound 3.

References:

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, G. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, C. Y. Al-Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, GAUSSIAN 03, Revision B.05, Gaussian, Inc., Pittsburgh, PA, 2003.
2. (a) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098-3100; (b) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652; (c) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789; (d) A. P. Scott and L. Radom, *J. Phys. Chem.*, 1996, **100**, 16502–16513.