Electronic Supplementary Information for the New Journal of Chemistry article, NJ-ART-11-2014-002103, entitled "Synthesis, NMR and mass spectrometric study of ammonioacetohydrazones of formylphenylboronic acids, novel ionic prospective sugar receptors" by Grażyna Bartkowiak, Łukasz Popenda, Stefan Jurga and Grzegorz Schroeder

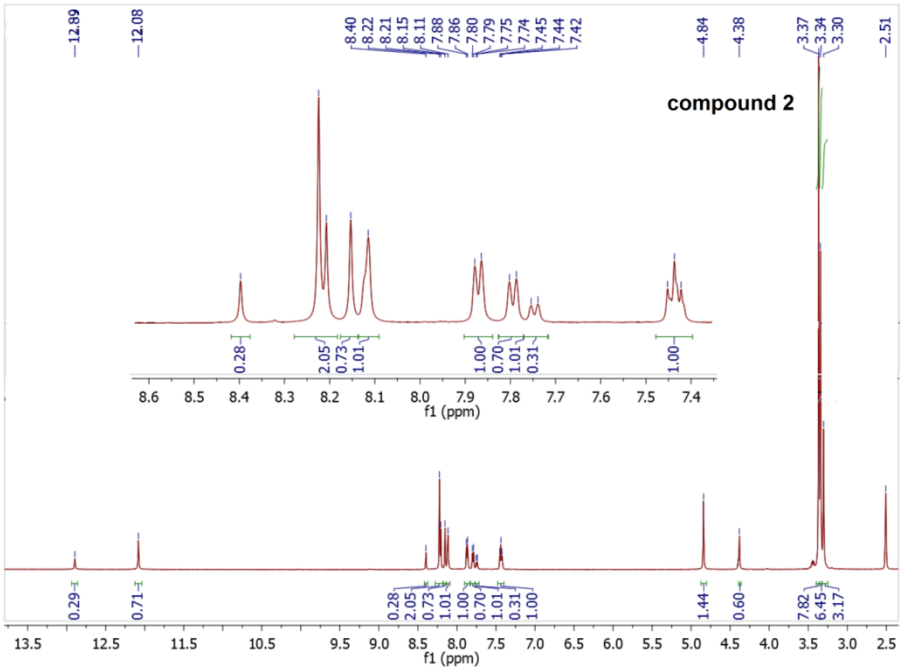


Fig. S1. ^{1}H NMR (800 MHz, solvent DMSO-d6) spectrum of compound **2** with expanded region 7.4-8.6 ppm (inset).

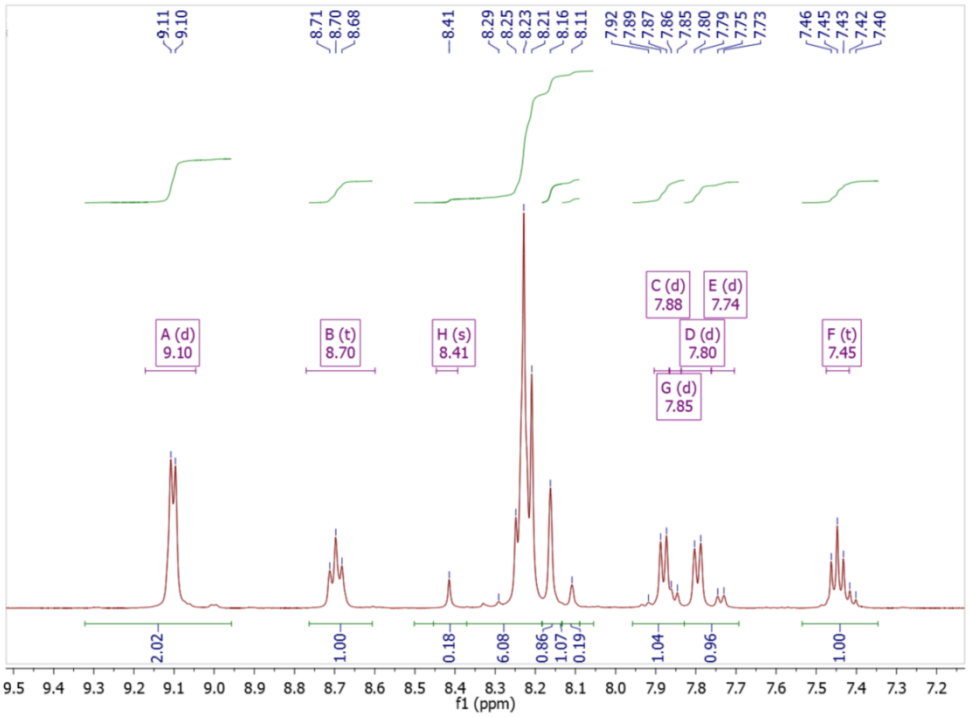


Figure S2. ^{1}H NMR spectrum of **5** (800 MHz, DMSO-d6), at the range 7.1-9.5 ppm, 25^{0}C (*meta* isomer).

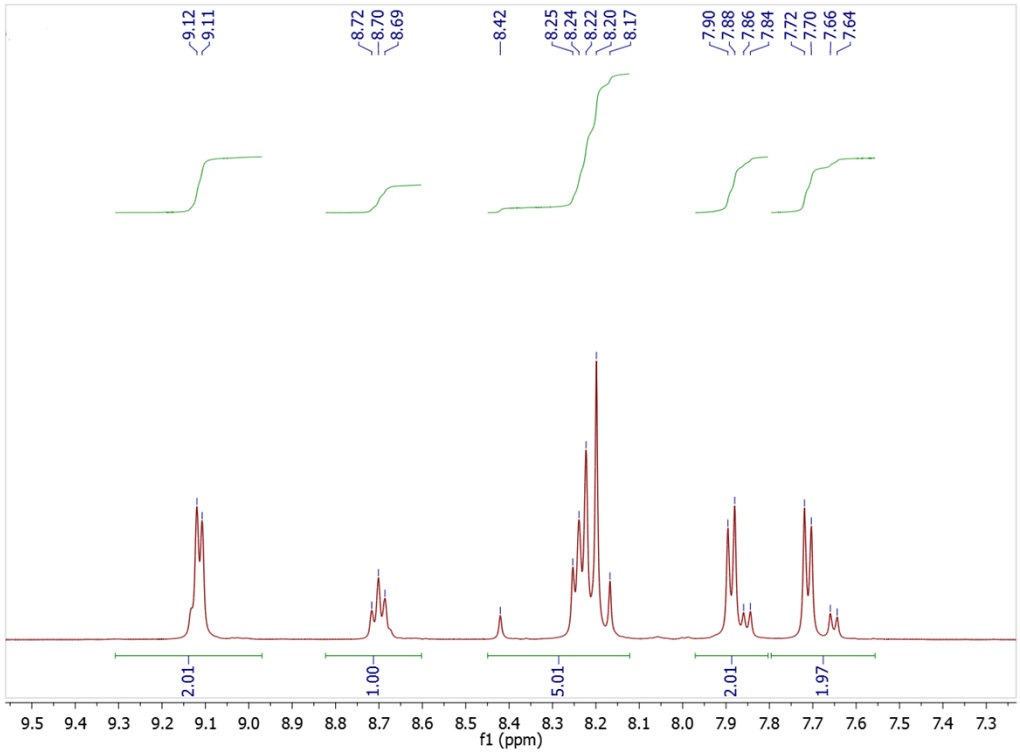


Figure S3. ^{1}H NMR spectrum of **6** (800 MHz, DMSO-d6),at the range 7.3 – 9.5 ppm, 25^{0}C (*para* isomer)

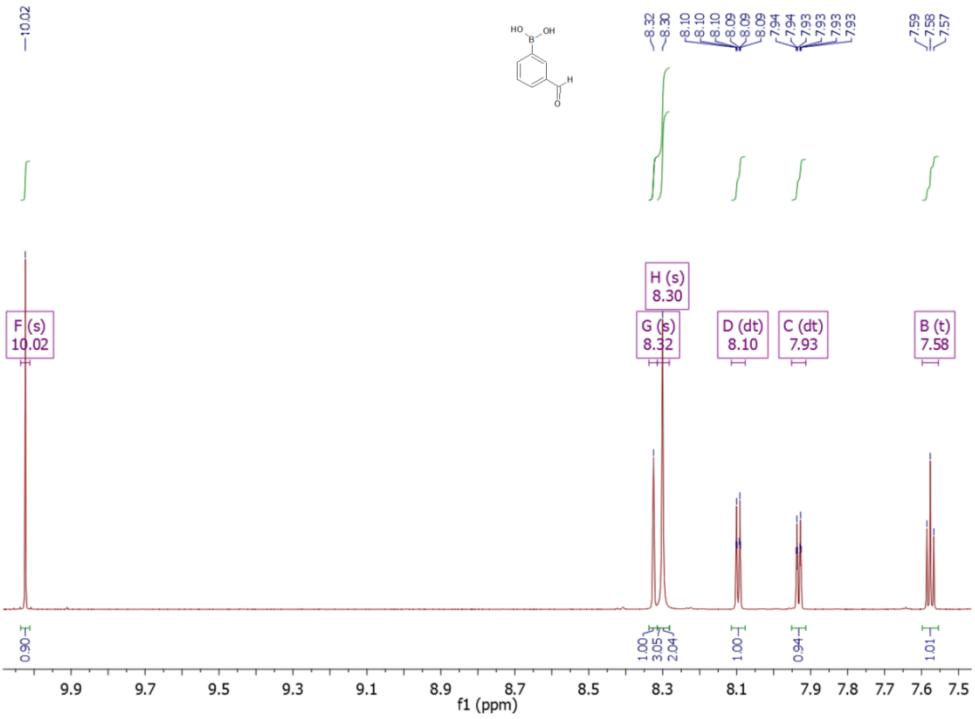


Fig. S4A. ^{1}H NMR spectrum of *m*-formylphenylboronic acid in DMSO-d_6 without D_2O

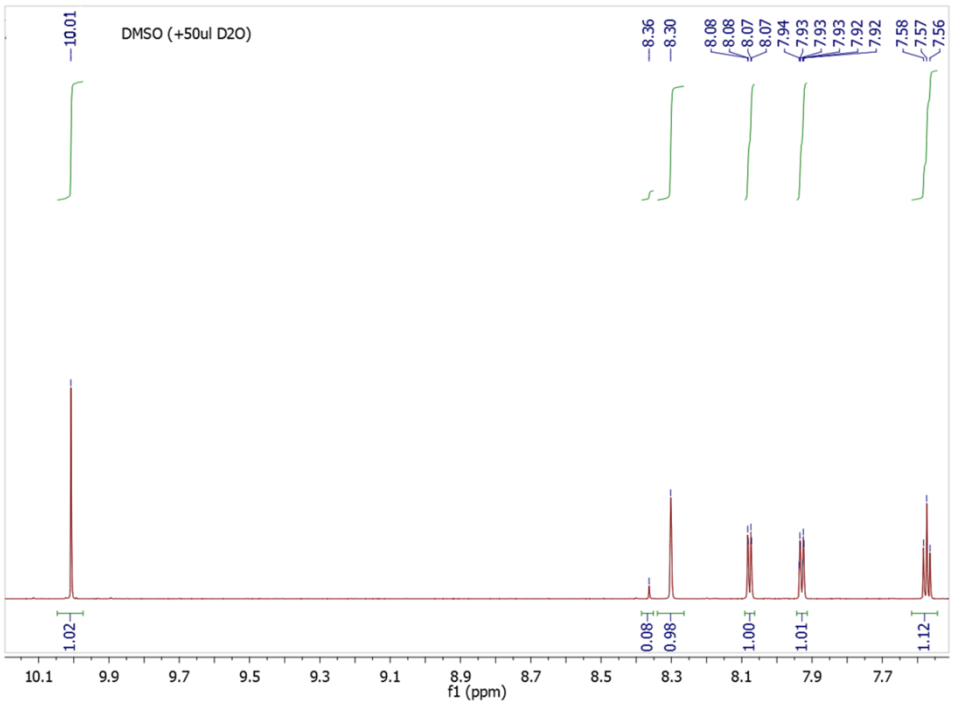


Fig. S4B. ^{1}H NMR spectrum of *m*-formylphenylboronic acid in DMSO-d_6 after addition of 50 µL D_2O

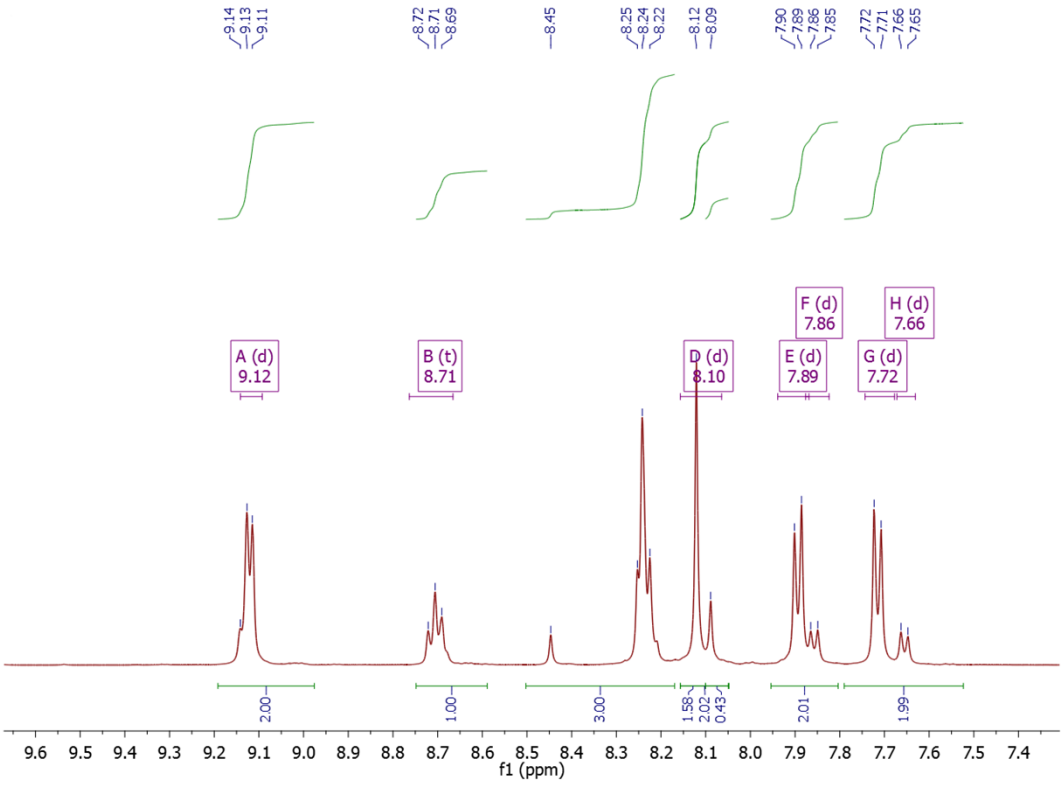


Fig. S5. ^{1}H NMR spectrum of **6** at **40^{o}C**, in the range 7.4-9.6 ppm.

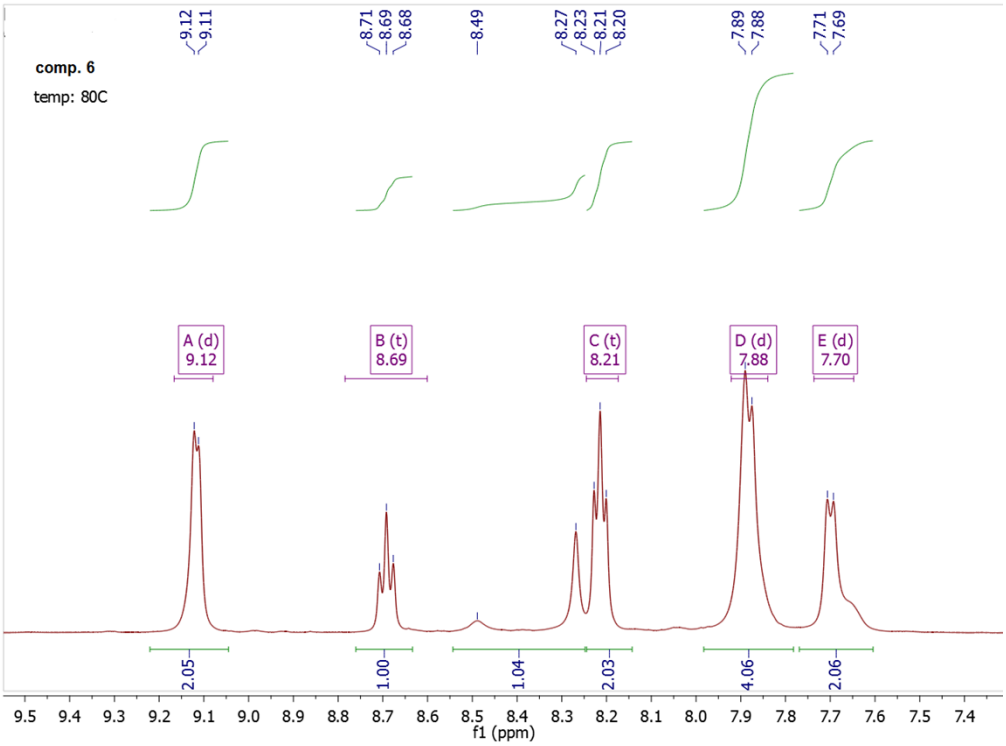


Fig. S6. ^{1}H NMR spectrum of compound **6** in the range 7.4-9.5 ppm at the temperature of **80** ^{o}C.

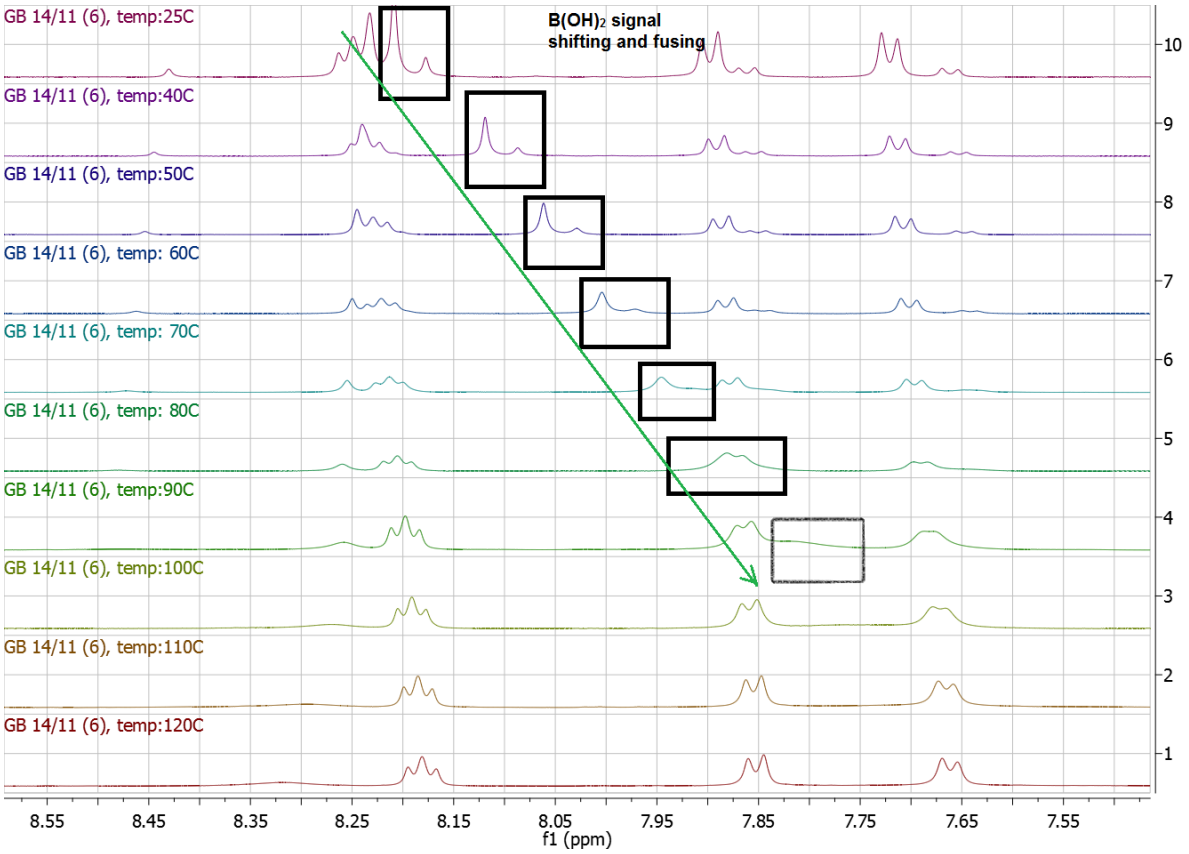


Fig. S7. ^{1}H NMR temperature-dependent (25 – 120 °C) spectra of compound **6** (in the range 7.50 – 8.60 ppm) show B-OH protons signal upfield shift and fusing with increasing temperature.

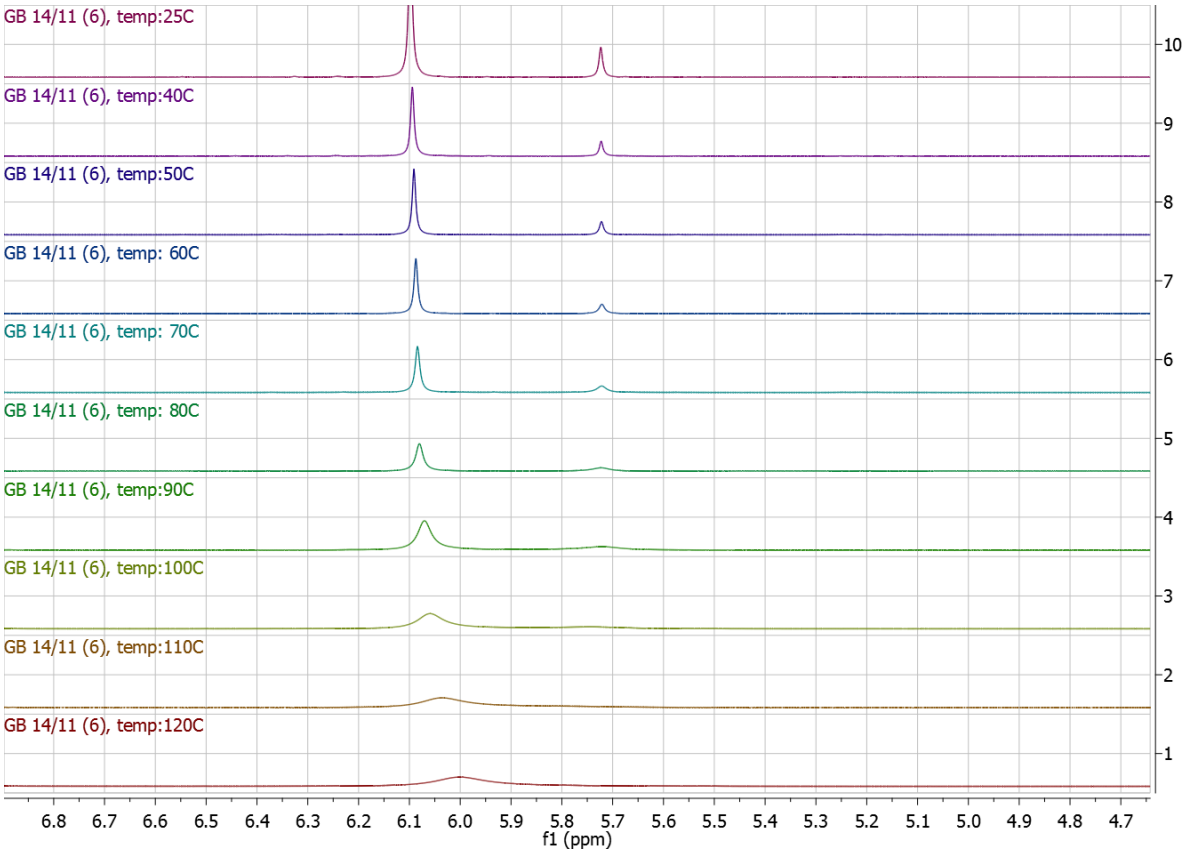
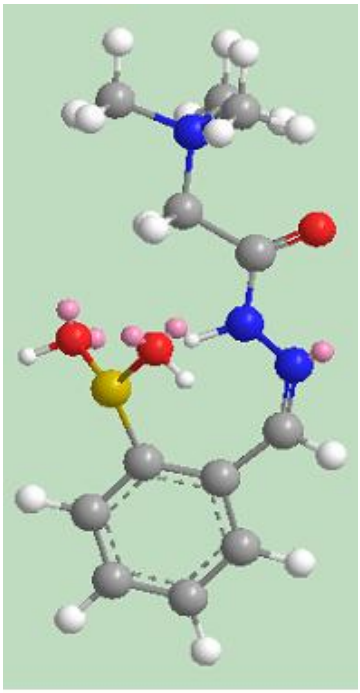


Fig. S8.The double CH_2 signals in ^1H NMR temperature-dependent spectra (25-120 °C, chemical shift range 4.6-6.9 ppm) fuse with the temperature increase, they are merged at 110^0C .



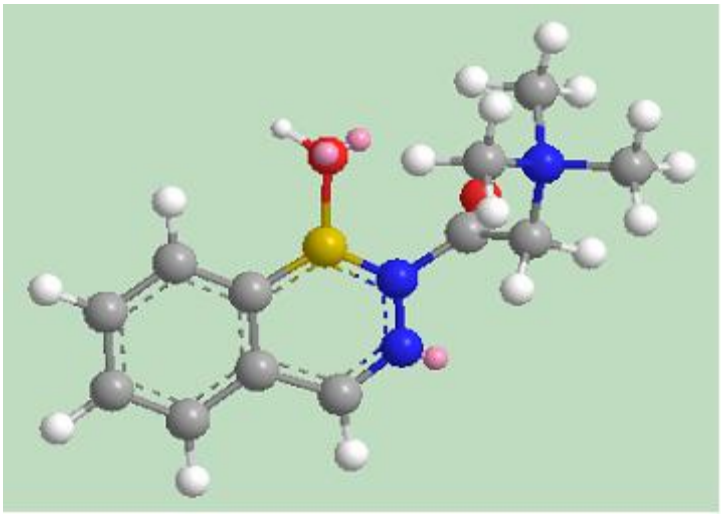


Fig. S9. 3D models of compounds **1** (left) and **1a** (right). Close proximity of OH and NH groups in a molecule of compound **1** enables cyclization.

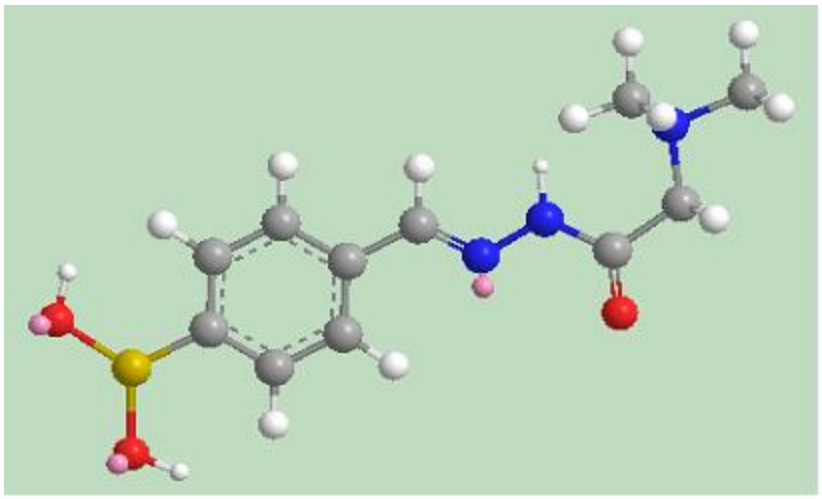


Fig. S10. 3D model of compound **3**. The distance between the CON**H** proton and B-O**H** hydroxyl prevents cyclization.

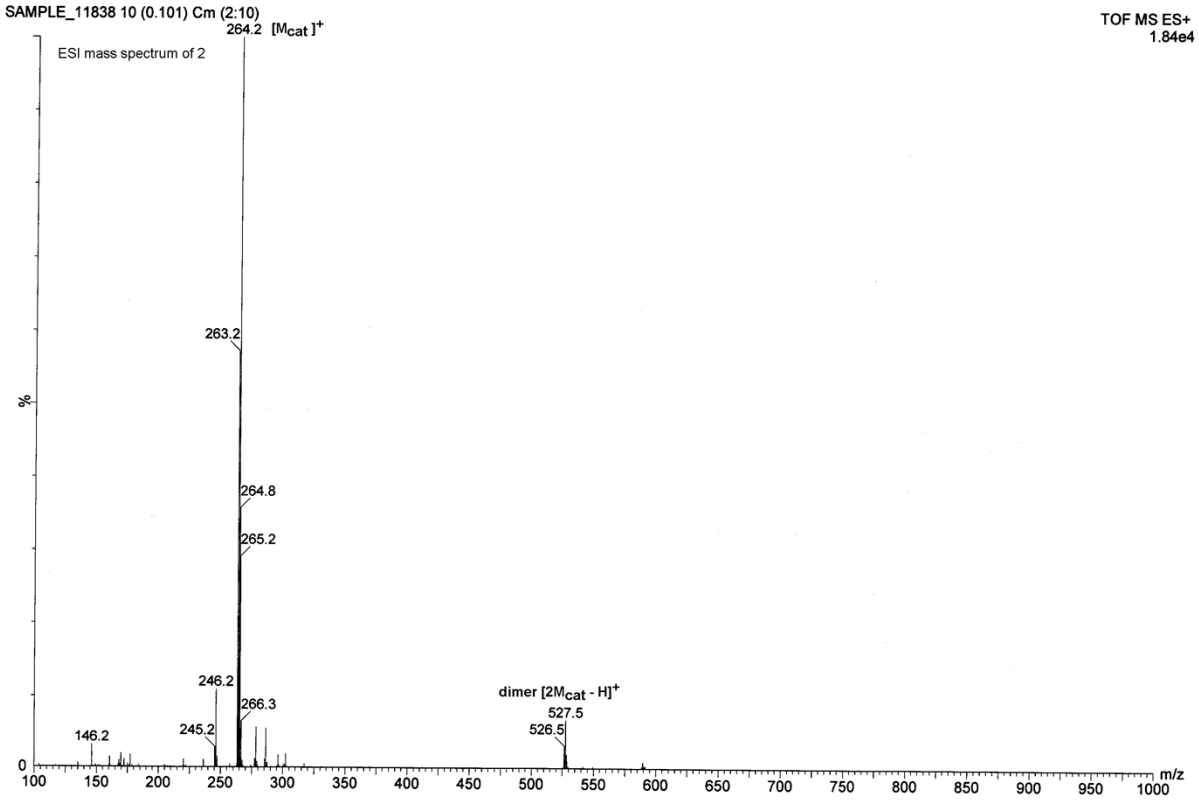


Fig. S11. Electrospray ionization mass spectrum of compound **2** in positive ion mode; at *m*/*z* 264 cation of **2**; at *m*/*z* 527 dimeric ion $[2M_{cat}\text{-}H]^+$, 2x264-1=527u.

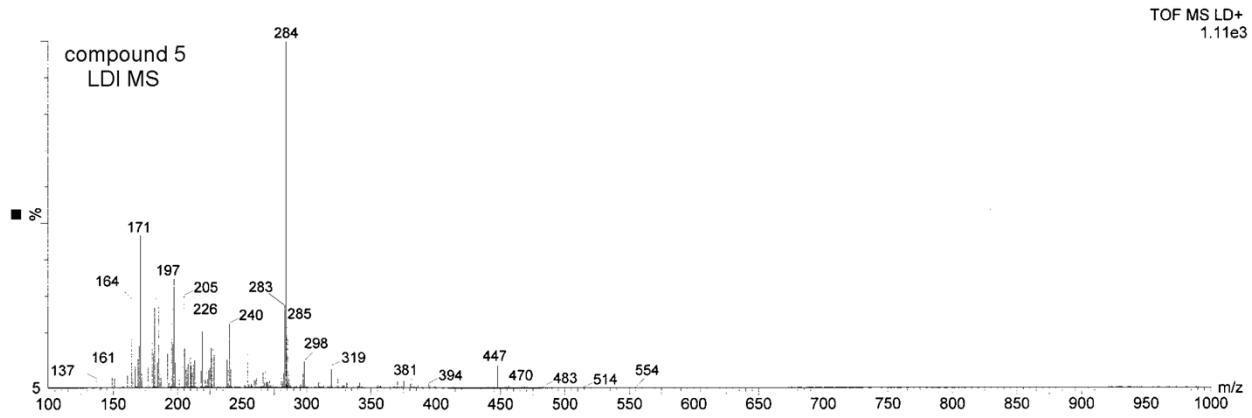


Fig. S12. Laser desorption/ionization (LDI, without matrix) TOF mass spectrum of compound **5** ; ion at *m/z* 284 corresponds to the cation of **5**. Spectrum measured without matrix shows a great number of noises.

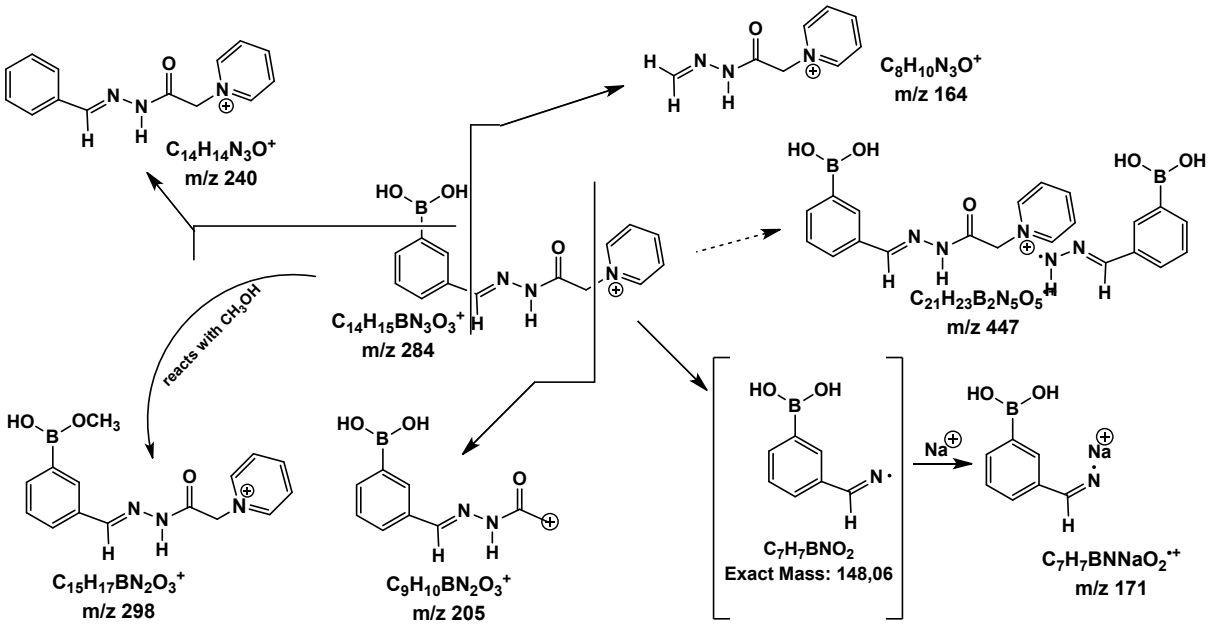


Fig. S12A. Proposed fragmentation pathways of **5** in LDI conditions showing possible origin of ions at m/z 164, 171, 205, 240 and 447. The ion at m/z 298 is from methyl monoester of **5** (esterified boronic group).

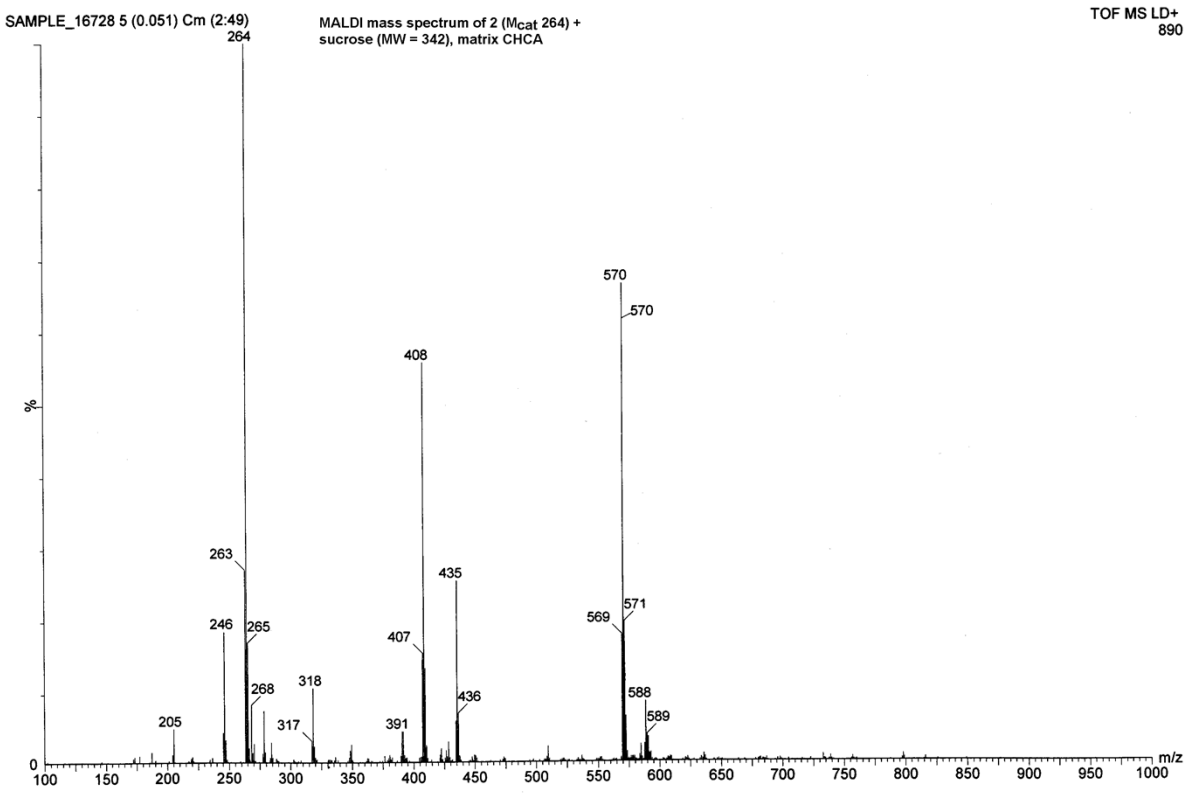


Fig. S13. MALDI TOF mass spectrum of the mixture of compound **2** and sucrose (with excess of **2**), matrix CHCA. (*m/z* 570 = **2**+ sucrose – $2H_2O$; *m/z* 588 = 2 + sucrose – H_2O; *m/z* 408 = 570 – 162 (162 – monosaccharide unit).

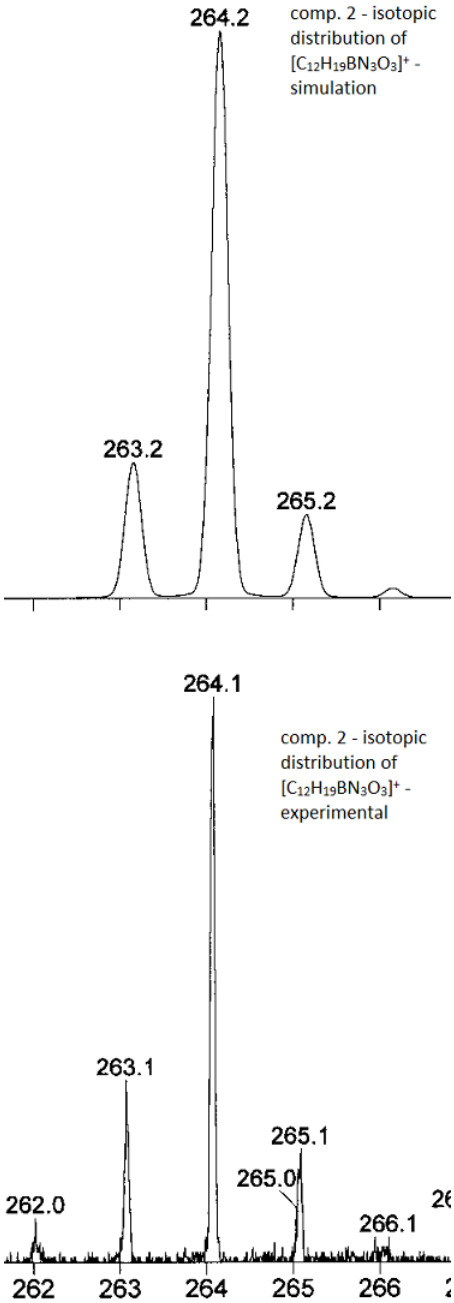


Fig. S13A – Comparison of theoretical (top) and experimental (bottom) isotopic patterns of cation $C_{12}H_{19}BN_3O_3$ (*m/z* 264).

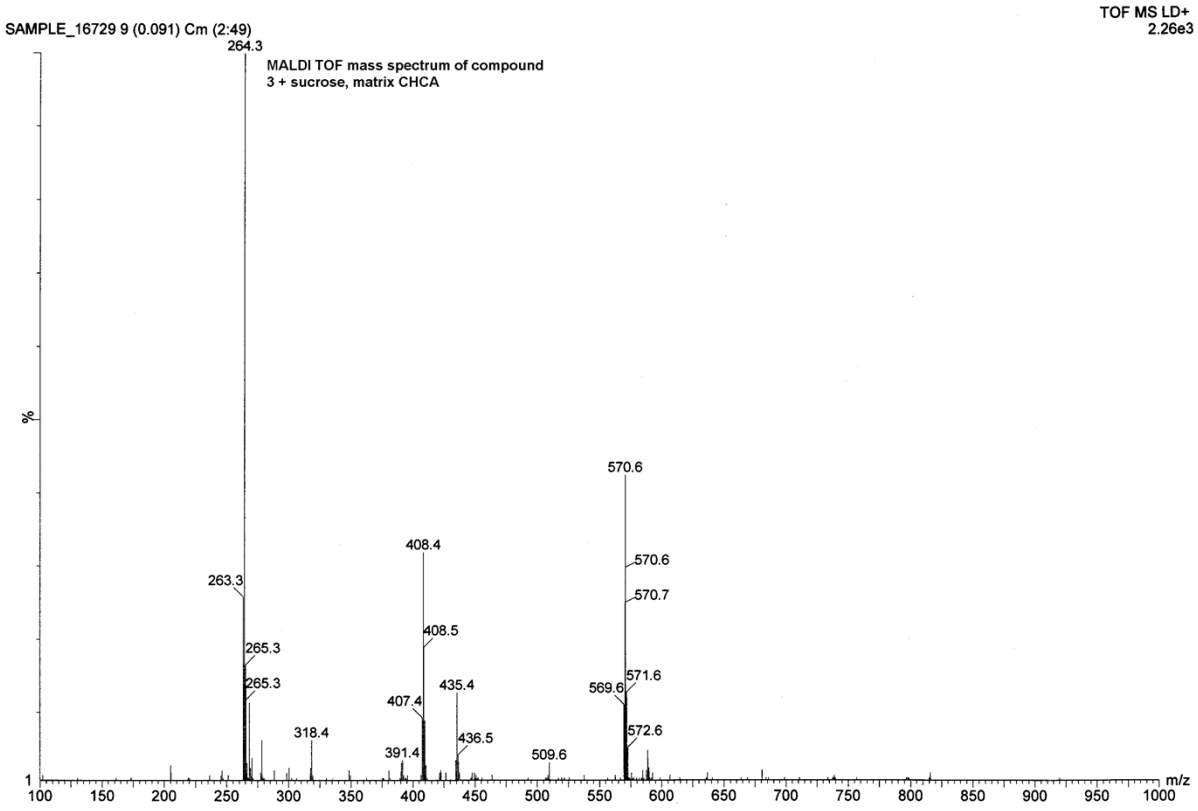


Fig. S14. MALDI TOF mass spectrum of the mixture of compound **3** and sucrose, matrix CHCA. (*m*/*z* 570 = **3**+ sucrose – $2H_2O$; *m*/*z* 408 = 570 – 162 (162 – monosaccharide unit), *m*/*z* 264 M_{cation} of **3**.

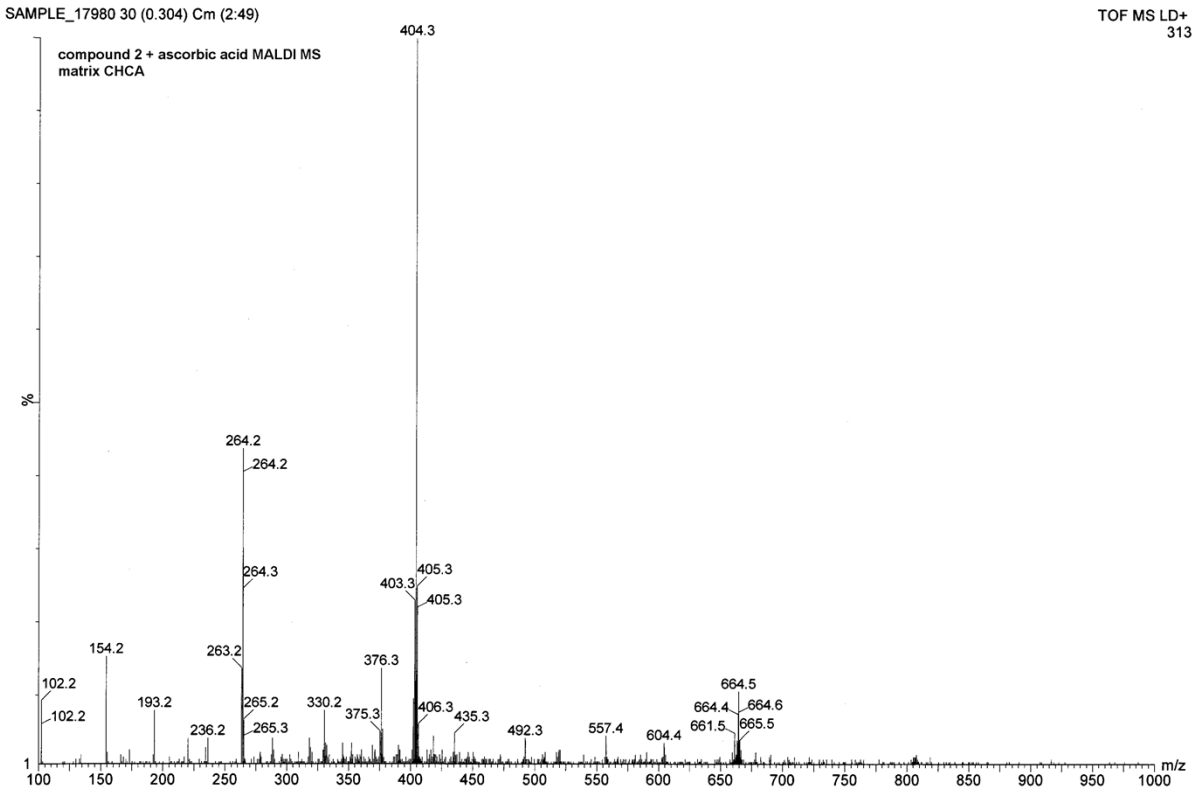


Fig. S15. MALDI TOF mass spectrum of the mixture of compound **2** and ascorbic acid, matrix CHCA; the base peak observed at m/z 404 corresponds to the cation [**2**+ascorbic acid – 2 H_2O]$^+$.

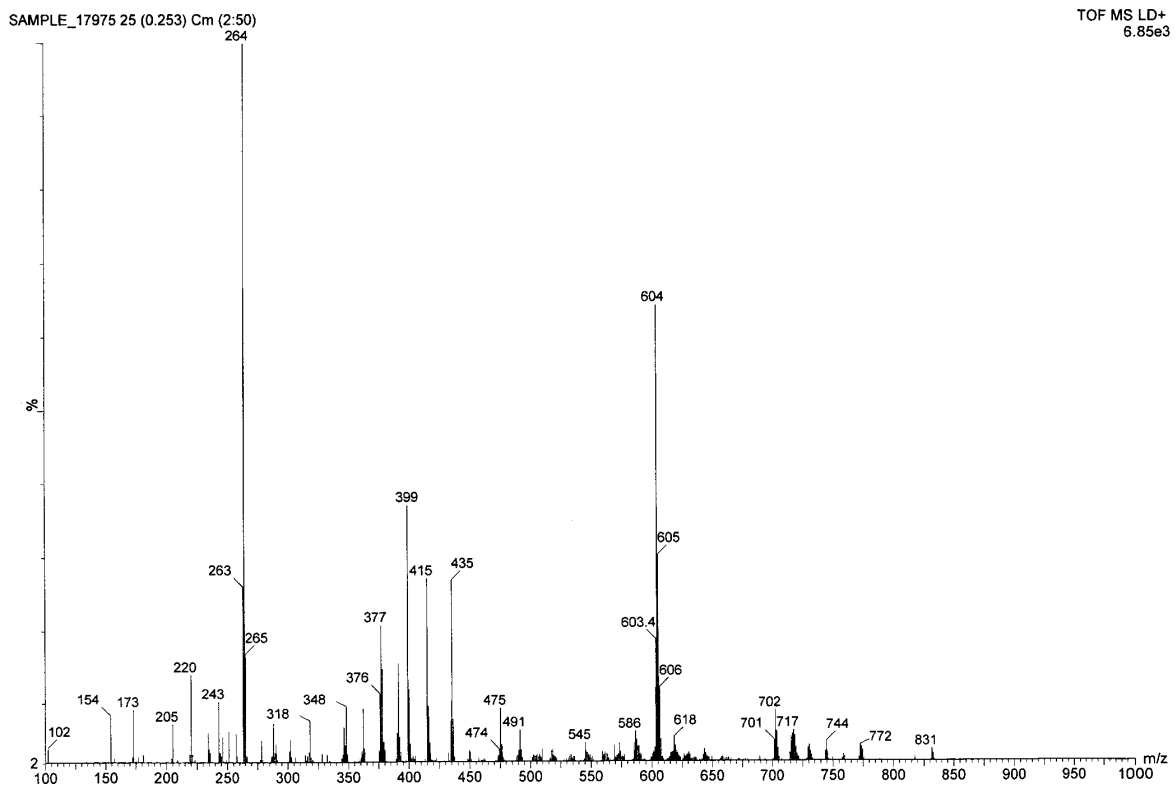


Fig. S16. MALDI TOF mass spectrum of the mixture of compound **2** and ryboflavin, matrix CHCA; the peak observed at m/z 604 corresponds to the cation [**2**+ryboflavin – 2 H_2O]$^+$.

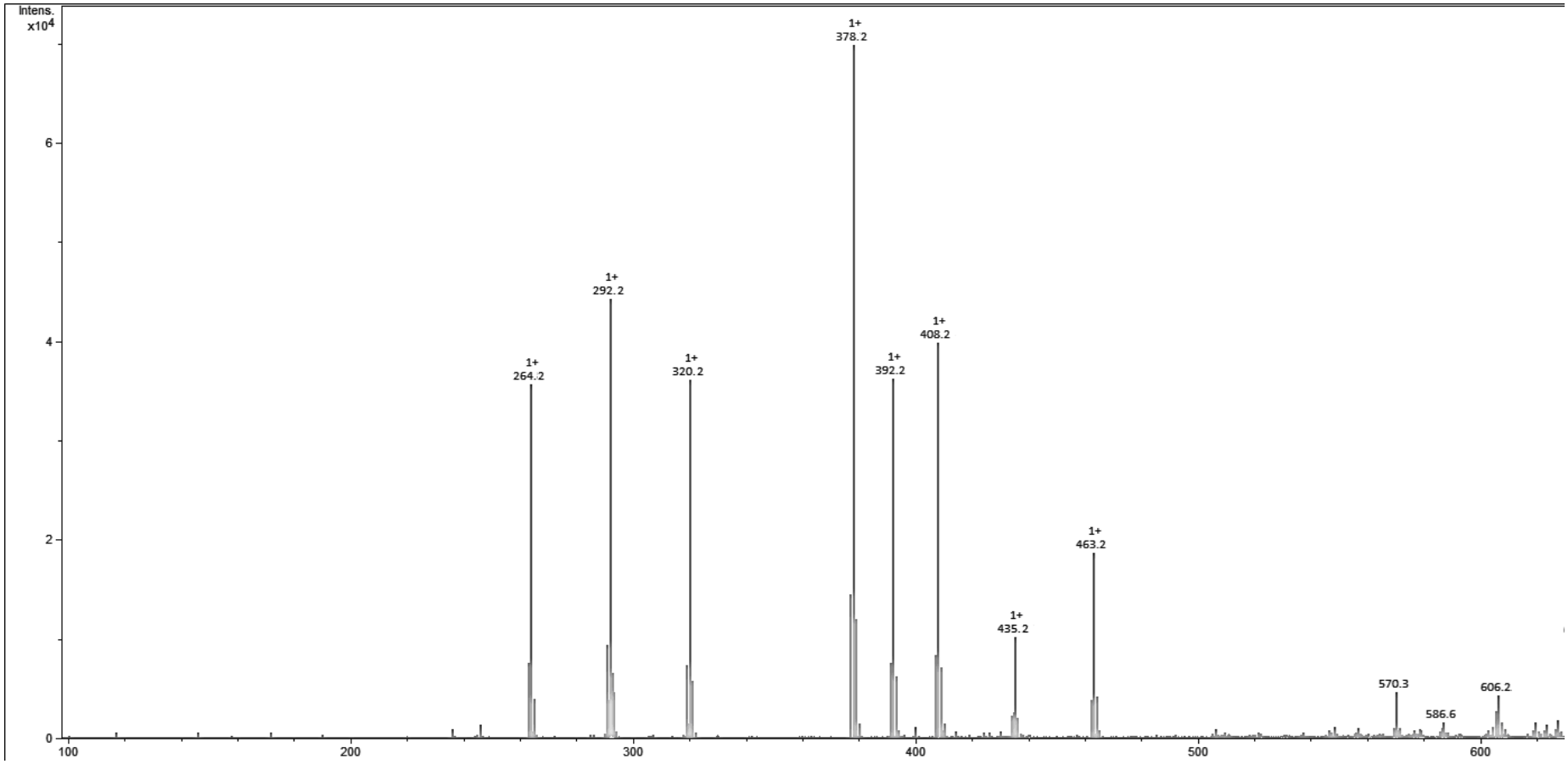


Fig. S17. MALDI TOF mass spectrum of compound **2** after the reaction with a mixture of sugars (lyxose $C_5H_{10}O_5$, monoisotopic mass Mm 150.0528; rhamnose $C_6H_{12}O_5$, Mm 164.0685; glucose $C_6H_{12}O_6$, Mm 180.0634; sucrose $C_{12}H_{22}O_{11}$, Mm = 342.1162), matrix CHCA ($C_{10}H_7NO_3$, Mm = 189.0426). Expected m/z values for compound **2**-sugar conjugate are: **2**+ lyxose-$2H_2O$ = 378.18, **2**+ rhamnose – $2H_2O$ = 392.20; **2** + glucose – 2 H_2O = 408.19; **2** + sucrose – 2 H2O = 570.25. Boronic acid moiety in **2** reacts easily also with ethanol to form ethyl esters (monoester gives signal at m/z 292.2 and diester at m/z 320.2) and with α-cyano-4-hydroxycinnamic acid, yielding product ions [**2**+CHCA-H_2O]$^+$ m/z 435; [**2**+CHCA+ EtOH – $2H_2O$]$^+$ m/z 463 and [2+2CHCA-$2H_2O$]$^+$ m/z 606.

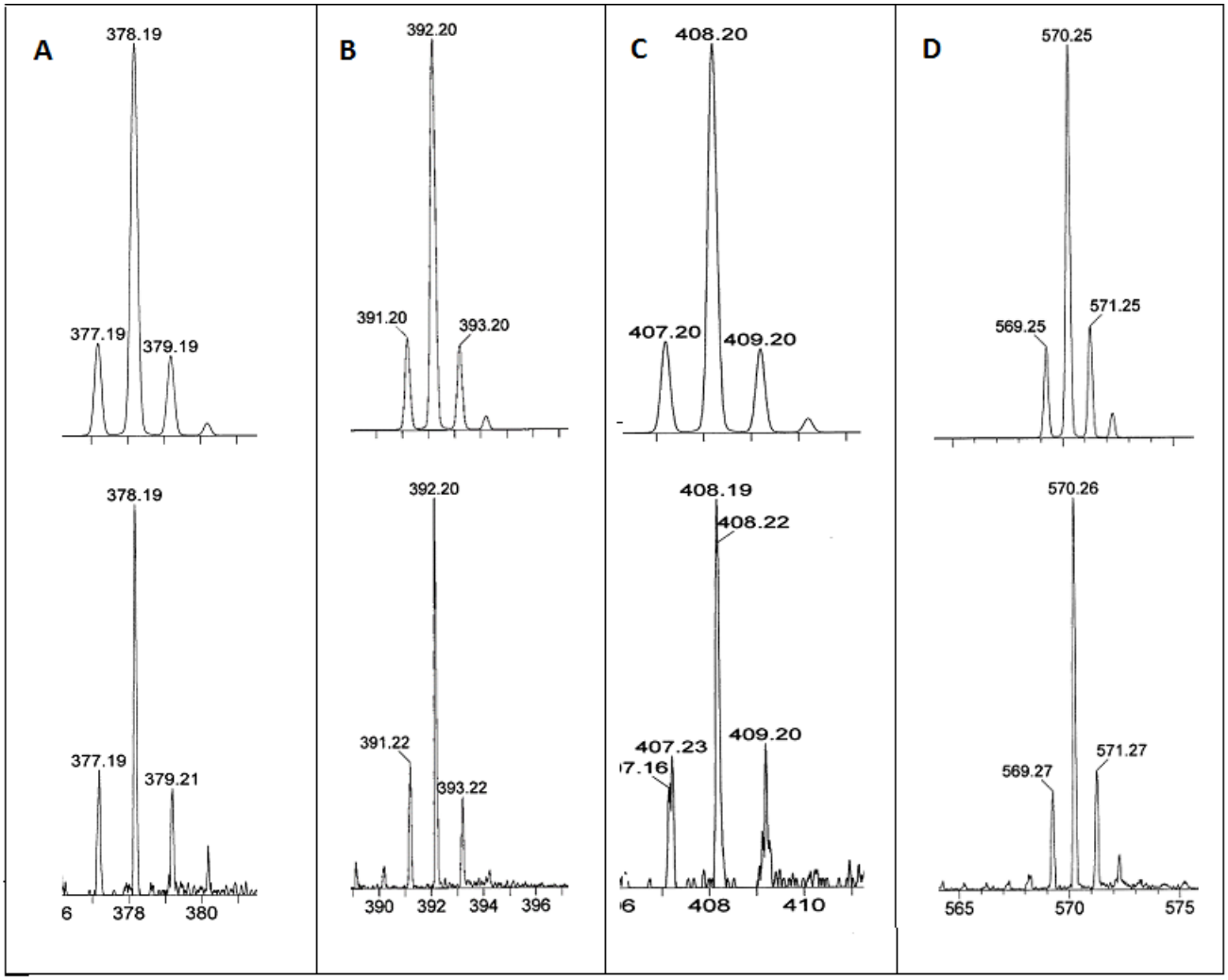


Fig. S18. Isotopic patterns of [**2**+sugar-$2H_2O$]$^+$ ions predicted theoretically (top) and seen in MALDI TOF mass spectra (bottom), where sugar = lyxose (**A**), rhamnose (**B**), glucose (**C**) and sucrose (**D**), respectively.

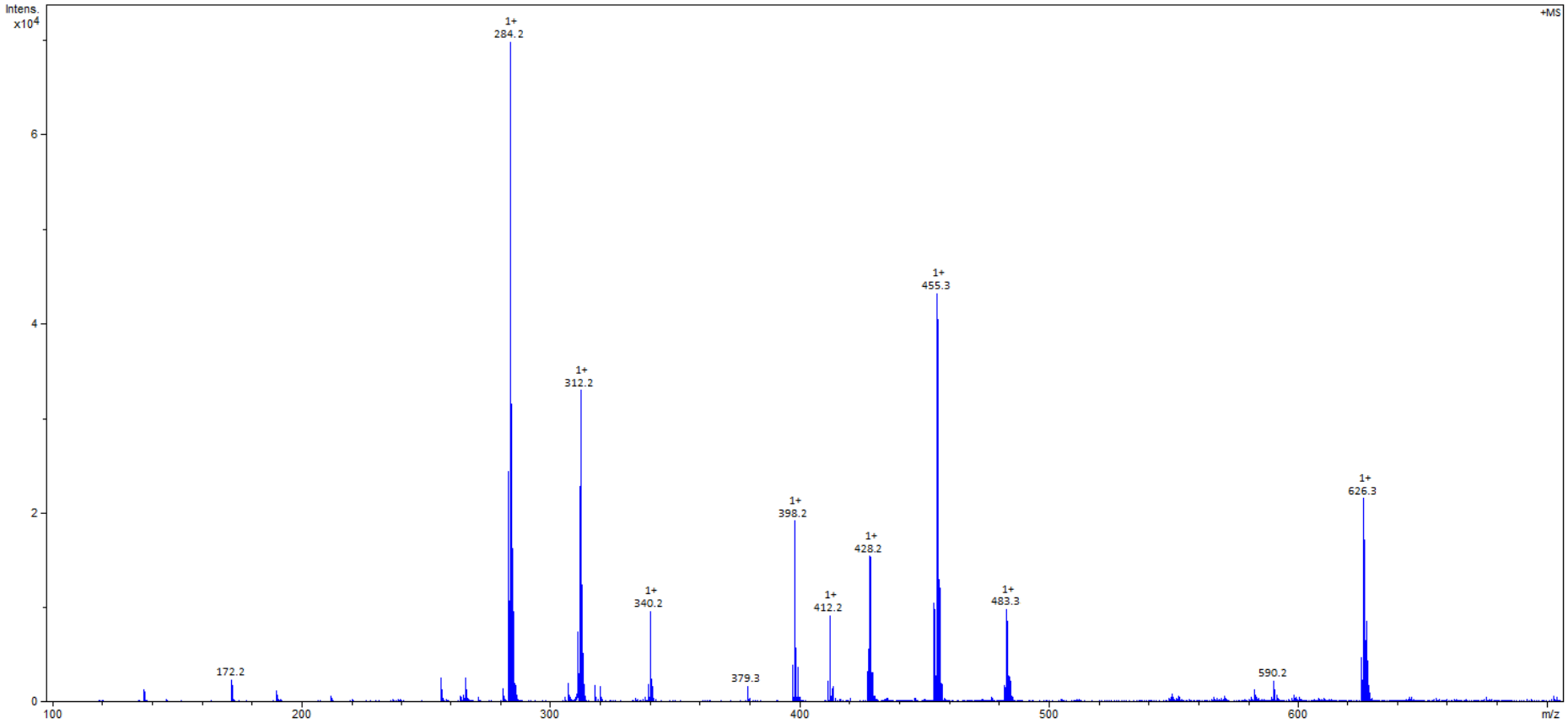


Fig. S19. MALDI TOF mass spectrum of compound **5** after the reaction with a mixture of sugars (lyxose $C_5H_{10}O_5$, monoisotopic mass M_m 150.0528; rhamnose $C_6H_{12}O_5$, M_m 164.0685; glucose $C_6H_{12}O_6$, M_m 180.0634; sucrose, $C_{12}H_{22}O_{11}$, M_m = 342.1162), matrix CHCA.