



J. Serb. Chem. Soc. 00(0) S1-S5 (2024)

Journal of  
the Serbian  
Chemical Society

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Supplementary material

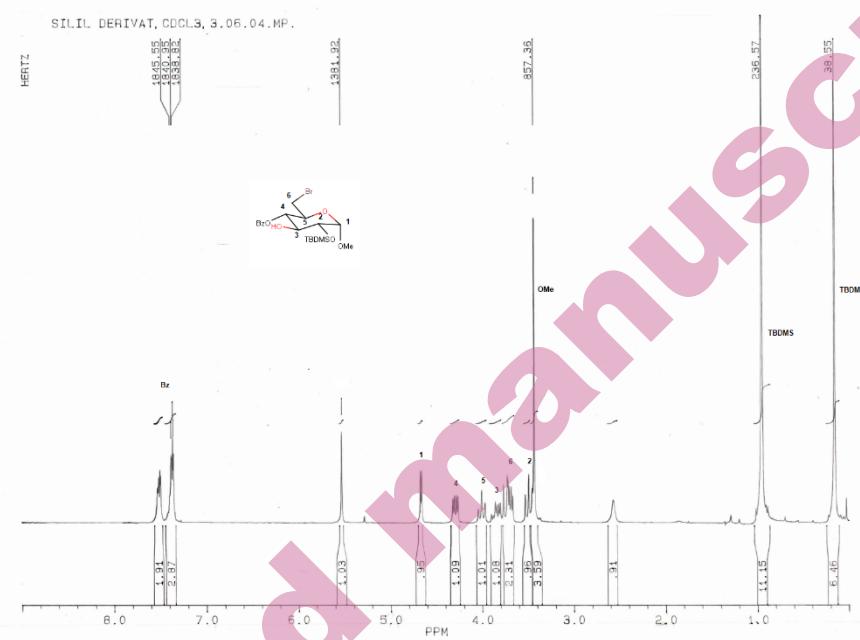
SUPPLEMENTARY MATERIAL TO  
**Synthesis of methyl 3,4-anhydro-6-bromo-2-O-*tert*-butyldimethylsilyl-6-deoxy- $\alpha$ -D-allopyranoside from  $\alpha$ -D-glucose**

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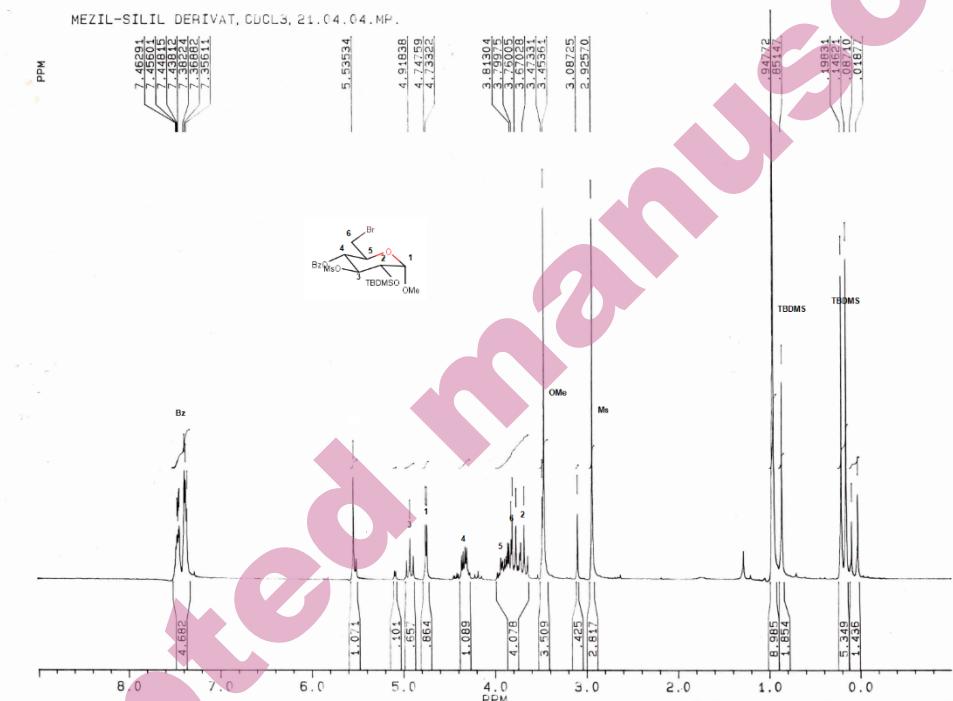
Accepted manuscript

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<https://doi.org/10.2298/JSC230831049G>



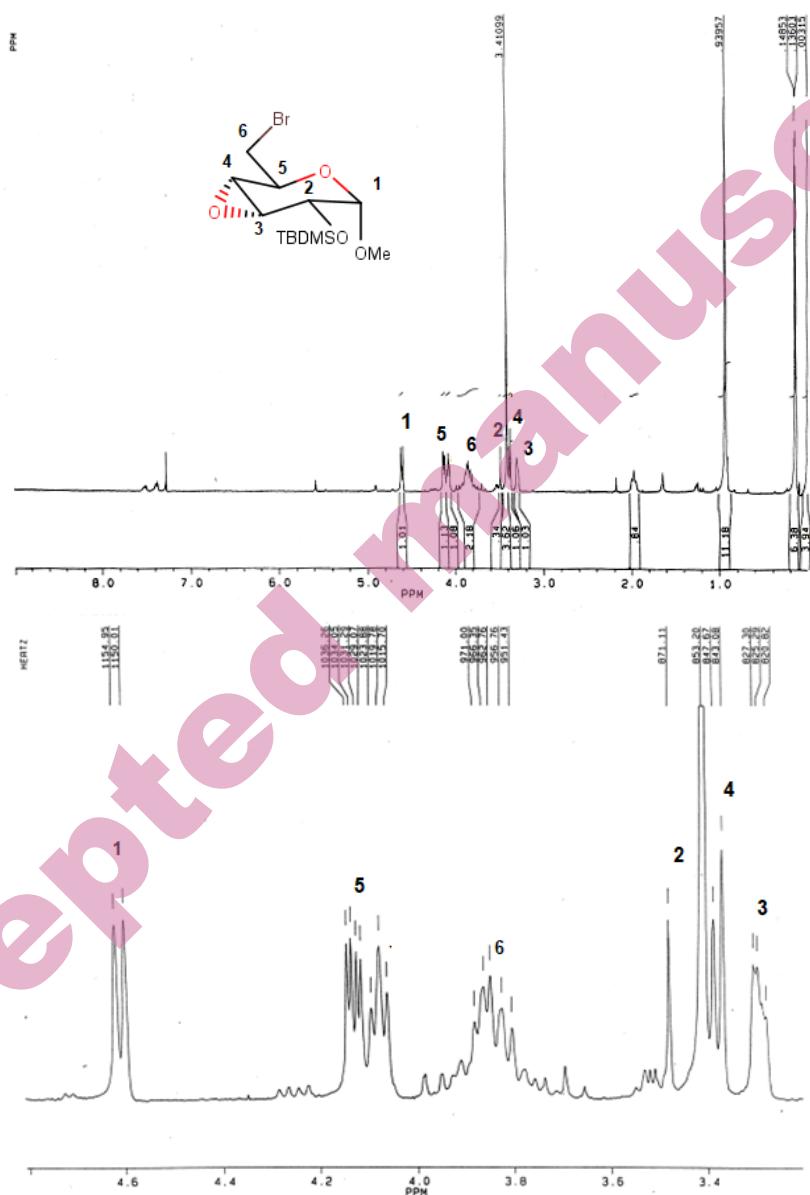
**Figure S1.** <sup>1</sup>H NMR spectra with proton assignments for methyl 4-O-benzoyl-6-bromo-2-O-*tert*-butyldimethylsilyl-6-deoxy- $\alpha$ -D-glucopyranoside (**4**).

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  7.36-7.60 (m, 5 H, OBz), 4.65 (d, 1 H, H-1), 4.35 (dd, 1 H, H-4), 3.81 (t, 1 H, H-5), 3.8-3.9 (m, 1 H, H-3), 3.65-3.80 (m, 2 H, H-6), 3.50 (m, 1 H, H-2), 3.43 (s, 3 H, OMe), 0.95 (s, 9 H, *tert*-butyl), 0.15 (s, 6 H, dimethylsilyl).



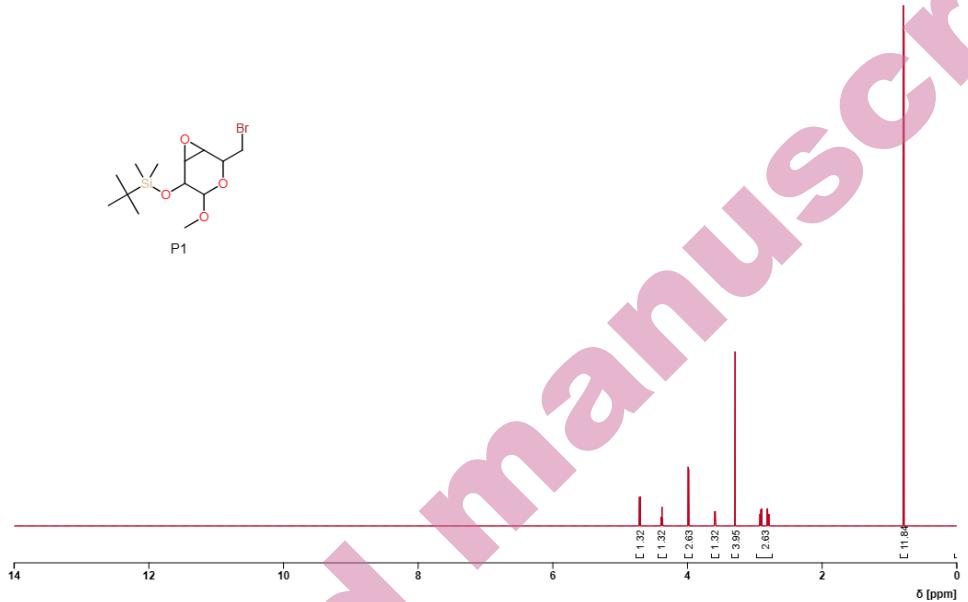
**Figure S2.** <sup>1</sup>H NMR spectra with proton assignments for methyl 4-*O*-benzoyl-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-3-*O*-mesyl- $\alpha$ -D-glucopyranoside (**6**).

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  7.41 (m, 5 H, OBz), 4.92 (t, 1 H, H-3), 4.74 (d, 1 H, J=3.6 Hz, H-1), 4.2-4.4 (dd, 1 H, H-4), 3.81 (t, 1 H, J=3.3 Hz, H-5), 3.76 (m, 2 H, H-6), 3.67 (dd, 1 H, H-2), 3.46 (s, 3 H, OMe), 2.93 (s, 3 H, OMs), 0.95 (s, 9 H, *tert*-butyl), 0.17 (s, 6 H, dimethylsilyl).



**Figure S3.** <sup>1</sup>H NMR spectra with proton assignments for methyl 3,4-anhydro-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy- $\alpha$ -D-allopyranoside (**8**).

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  4.61 (d, 1 H, H-1), 4.14 (m, 1 H, H-5), 3.85 (m, 2 H, H-6), 3.41 (d, 1 H, H-2), 3.41 (s, 3 H, OMe), 3.38 (m, 1 H, H-4), 3.30 (m, 1 H, H-3), 0.94 (s, 9 H, *tert*-butyl), 0.14 (s, 6 H, dimethylsilyl).



**Figure S4.** Simulated  $^1\text{H}$  NMR spectrum of methyl 3,4-anhydro-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy- $\alpha$ -D-allopyranoside (**8**) using NMRium.