

SUPPLEMENTARY MATERIAL TO
**Synthesis of methyl 3,4-anhydro-6-bromo-2-*O*-*tert*-
butyldimethylsilyl-6-deoxy- α -D-glucopyranoside from α -D-glucose**

ĐORĐE GLIŠIN, OLGA JOVANOVIĆ, GORDANA STOJANOVIĆ, ALEKSANDRA ŽIVKOVIĆ, DRAGAN STOJANOVIĆ, MARINA PAVLOVIĆ AND BILJANA ARSIĆ *

*Department of Chemistry, Faculty of Sciences and Mathematics, University of Niš,
Višegradska 33, 18000 Niš, Republic of Serbia.*

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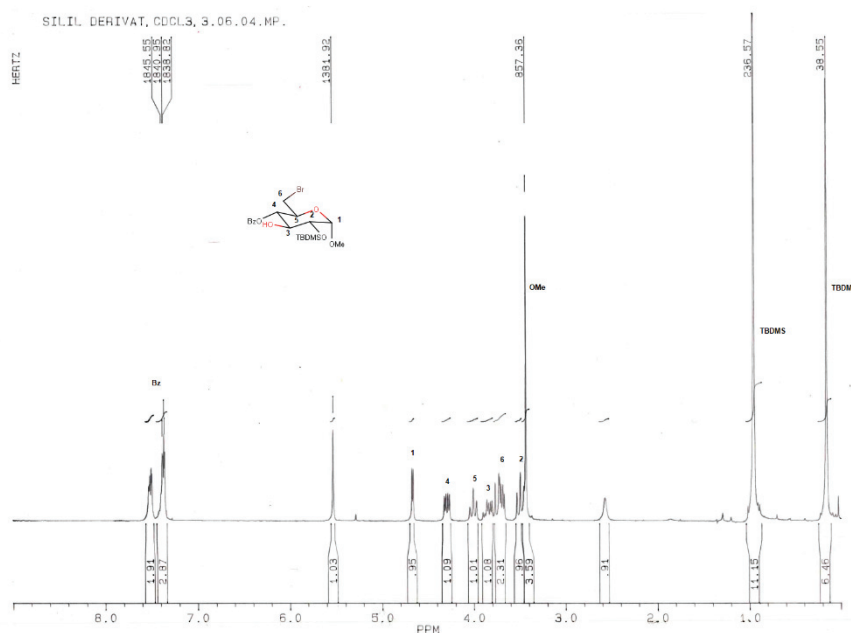


Figure S-1. ^1H NMR spectrum with proton assignments for methyl 4-*O*-benzoyl-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy- α -D-glucopyranoside (**4**).

^1H NMR (250 MHz, CDCl_3): δ 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,

* Corresponding author. E-mail: biljana.arsic@pmf.edu.rs

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).

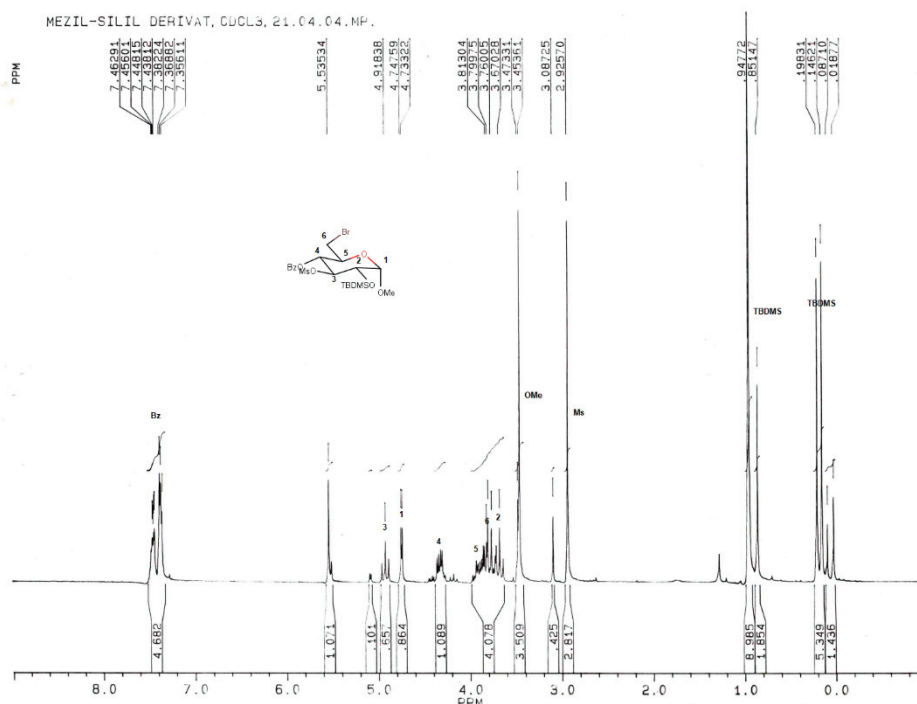


Figure S-2. ^1H NMR spectrum with proton assignments for methyl 4-*O*-benzoyl-6-bromo-2-*O*-*tert*-butyl dimethylsilyl-6-deoxy-3-*O*-mesyl- α -D-glucopyranoside (6).

^1H NMR (250 MHz, CDCl_3): δ 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).

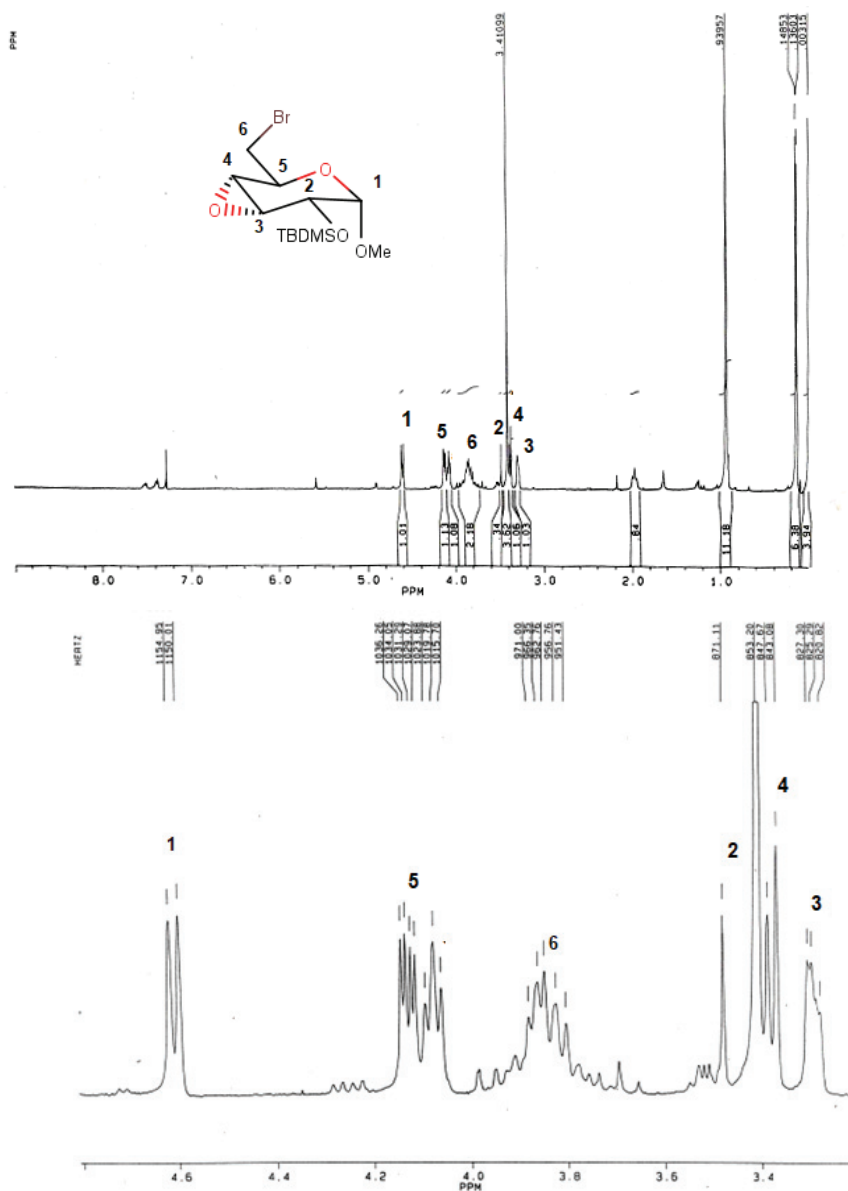


Figure S-3. ^1H NMR spectra with proton assignments for methyl 3,4-anhydro-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy- α -D-allopyranoside (**8**).

^1H NMR (250 MHz, CDCl_3): δ 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).

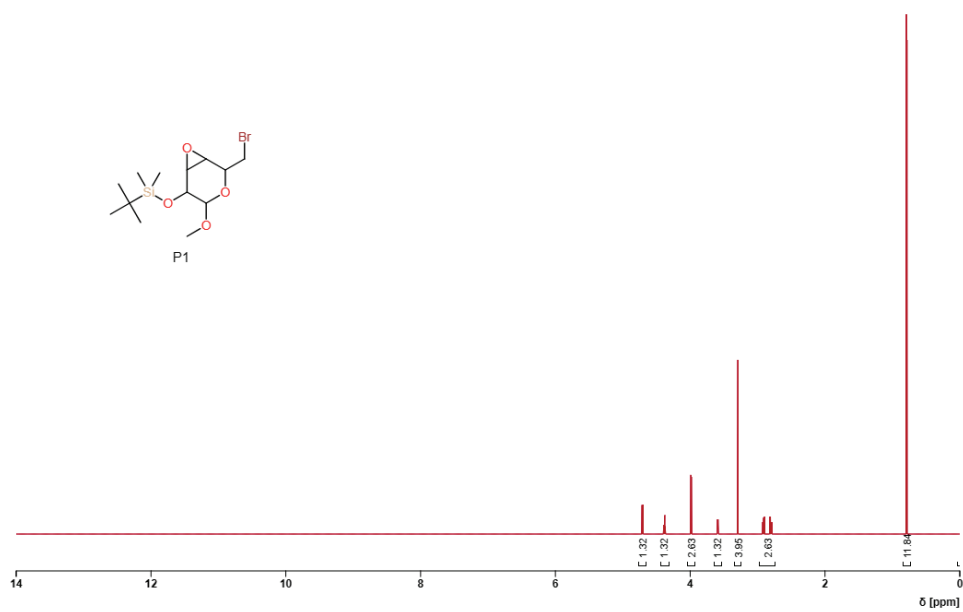


Figure S-4. Simulated ^1H NMR spectrum of methyl 3,4-anhydro-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy- α -D-allopyranoside (**8**) using NMRium.