

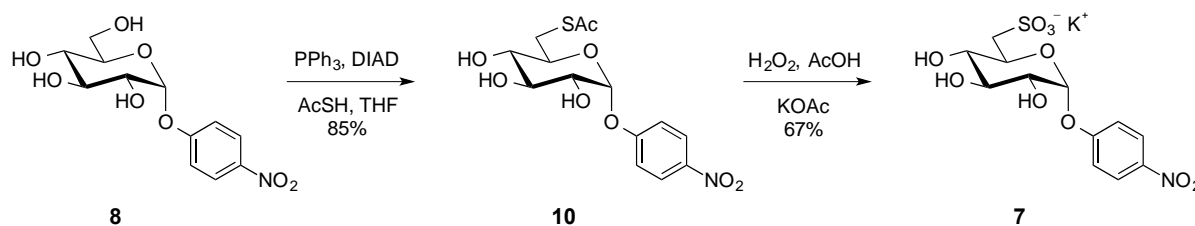
Supplementary Notes

Chemical synthesis of PNPSQ (7)

General

All chemical reagents were purchased from Sigma-Aldrich at >95% purity unless otherwise stated. ^1H and ^{13}C NMR spectra were recorded using a 400 MHz instrument. All signals were referenced to solvent peaks (d_4 -MeOH: δ 3.49 ppm for ^1H or 49.0 ppm for ^{13}C). TLC analysis used aluminium backed Merck Silica Gel 60 F₂₅₄ sheets, detection was achieved using UV light, 5% H_2SO_4 in MeOH, or ceric ammonium molybdate solution with heating as necessary. Flash chromatography was performed using Geduran silica gel according to the method of Still *et al.*¹ Dry THF was obtained from a dry solvent apparatus (Glass Contour of SG Water, Nashua, U.S.A.).² Melting points were obtained using a hot-stage microscope. $[\alpha]_D$ values are given in deg $10^{-1} \text{ cm}^2 \text{ g}^{-1}$.

Synthetic scheme



4-Nitrophenyl 6-S-acetyl-6-thio- α -D-glucopyranoside (**10**)

A solution of 4-nitrophenyl α -D-glucopyranoside **8** (0.10 g, 0.33 mmol) and thioacetic acid (28 μl , 0.40 mmol) in dry THF (2.0 ml) at 0 $^\circ\text{C}$ was added to a mixture of PPh_3 (0.10 g, 0.40 mmol) and DIAD (80 μl , 0.40 mmol) in THF (1.0 ml) at 0 $^\circ\text{C}$. The reaction mixture was allowed to warm to r.t. and stirred overnight. The mixture was concentrated and the residue was purified by flash chromatography (EtOAc/hexane, 40-100%), to afford the thioacetate **10** (0.10 g, 0.28 mmol, 85%) as a white crystalline solid. A small portion was recrystallized (m.p. 122-123 $^\circ\text{C}$, EtOAc); $[\alpha]_D^{23} +1.2^\circ$ (c 0.55, CH_3OH); ^1H NMR (400 MHz, CD_3OD) δ 2.21 (3 H, s, CH_3), 2.93 (1 H, dd, $J_{6,6} = 13.9$, $J_{5,6} = 8.6$ Hz, H6a), 3.27 (1 H, dd, $J_{3,4} = 9.3$, $J_{4,5} = 9.3$ Hz, H4), 3.51 (1 H, dd, $J_{5,6} = 2.7$ Hz, H6b), 3.66–3.58 (2 H, m, H2,5), 3.86–3.77 (1 H, dd, $J_{2,3} = 9.3$ Hz, H3), 5.64 (1 H, d, $J_{1,2} = 3.7$ Hz, H1), 7.34–7.28 (2 H, m, Ar), 8.29–8.23 (2 H, m, Ar); ^{13}C NMR (101 MHz, CD_3OD) δ 30.25 (CH_3), 31.80 (C6), 73.03 (C2), 73.31 (C5), 74.56 (C3), 74.67 (C4), 98.76 (C1), 118.08, 126.54, 143.91, 163.12 (4C, Ar), 196.68 (C=O); HRMS (ESI)⁺ m/z 360.0760 [$\text{C}_{14}\text{H}_{17}\text{NO}_8\text{S}$ ($\text{M} + \text{H}$)⁺ requires 360.0753].

Potassium 4-nitrophenyl 6-deoxy-6-sulfonato- α -D-glucopyranoside (PNPSQ, 7)

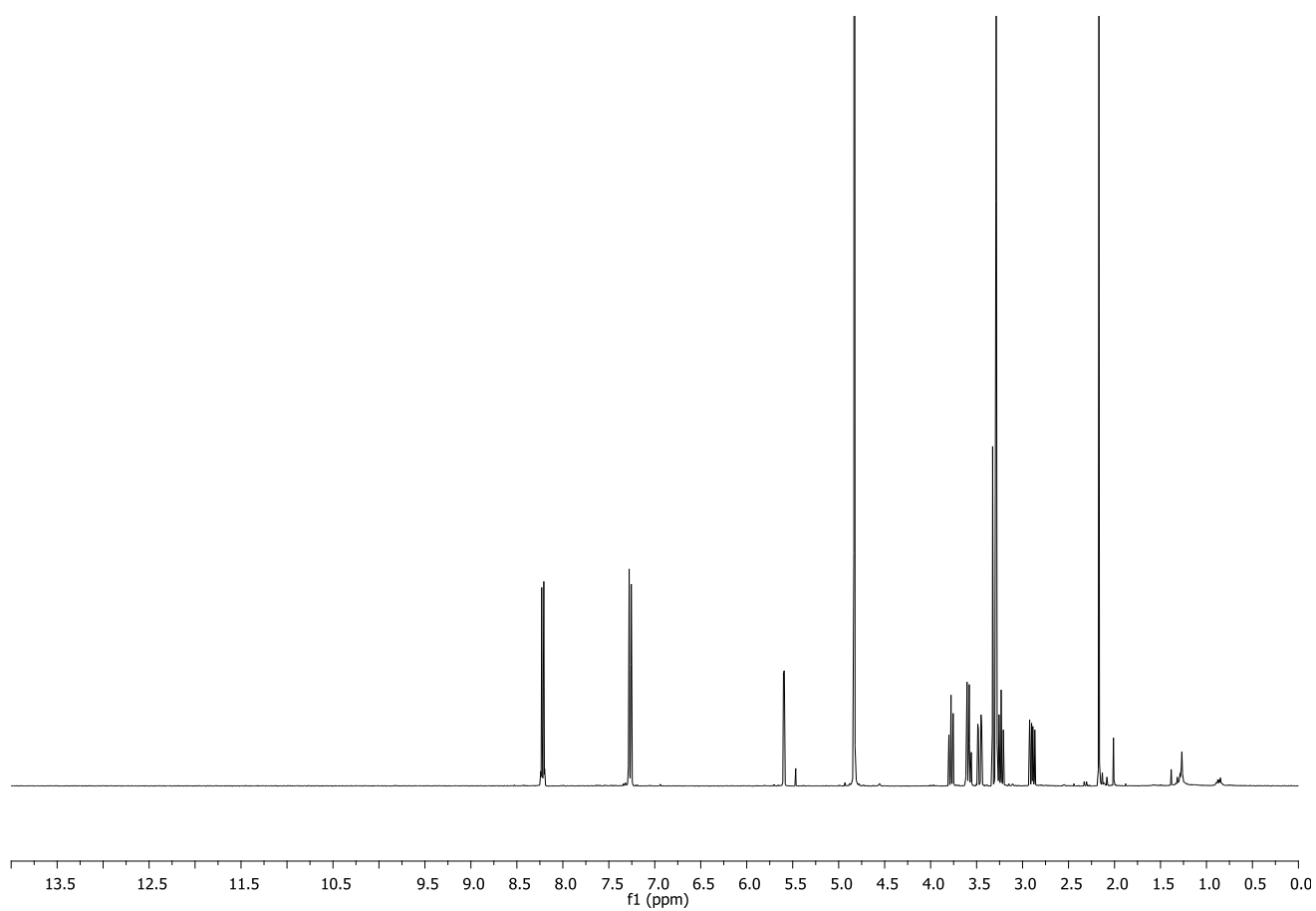
30% H₂O₂ (0.70 ml) was added to a solution of 4-nitrophenyl 6-S-acetyl-6-thio- α -D-glucopyranoside **10** (50 mg, 0.14 mmol) and KOAc (15 mg, 0.16 mmol) in glacial AcOH (0.70 ml). The mixture was stirred at 50 °C for 24 h then diluted with water and quenched by the addition of PPh₃ in Et₂O (2.0 M, 3.0 ml). The aqueous phase was separated, and the organic phase was extracted twice with water. The combined aqueous phases were concentrated and the residue purified by flash chromatography (EtOAc/MeOH/H₂O, 19:2:1→7:2:1) and C₁₈ reversed phase chromatography (H₂O/CH₃CN, 95:5), affording PNPSQ **7** (38 mg, 0.094 mmol, 67%) as a white solid. $[\alpha]_D^{23} +1.3^\circ$ (*c* 0.91, CH₃OH); ¹H NMR (400 MHz, CD₃OD) δ 3.01 (1 H, dd, $J_{6,6} = 14.4$, $J_{5,6} = 8.5$ Hz, H6a), 3.27 (1 H, dd, $J_{3,4} = 9.7$, $J_{4,5} = 9.0$ Hz, H4), 3.36 (1 H, dd, $J_{5,6b} = 2.5$ Hz, H6b), 3.64 (1 H, dd, $J_{2,3} = 9.8$, $J_{1,2} = 3.7$ Hz, H2), 3.86 (1 H, dd, H3), 4.16 (1 H, ddd, H5), 5.51 (1 H, d, H1), 7.47–7.39 (2 H, m, Ar), 8.26–8.18 (2 H, m, Ar); ¹³C NMR (101 MHz, CD₃OD) δ 53.09 (C6), 69.78 (C5), 71.59 (C2), 73.02 (C3), 73.43 (C4), 98.52 (C1), 117.51, 125.04, 142.61, 162.65 (4C, Ar); HRMS (ESI)[−] *m/z* 364.0340 [C₁₂H₁₄NO₁₀S (M – H)[−] requires 364.0343].

References

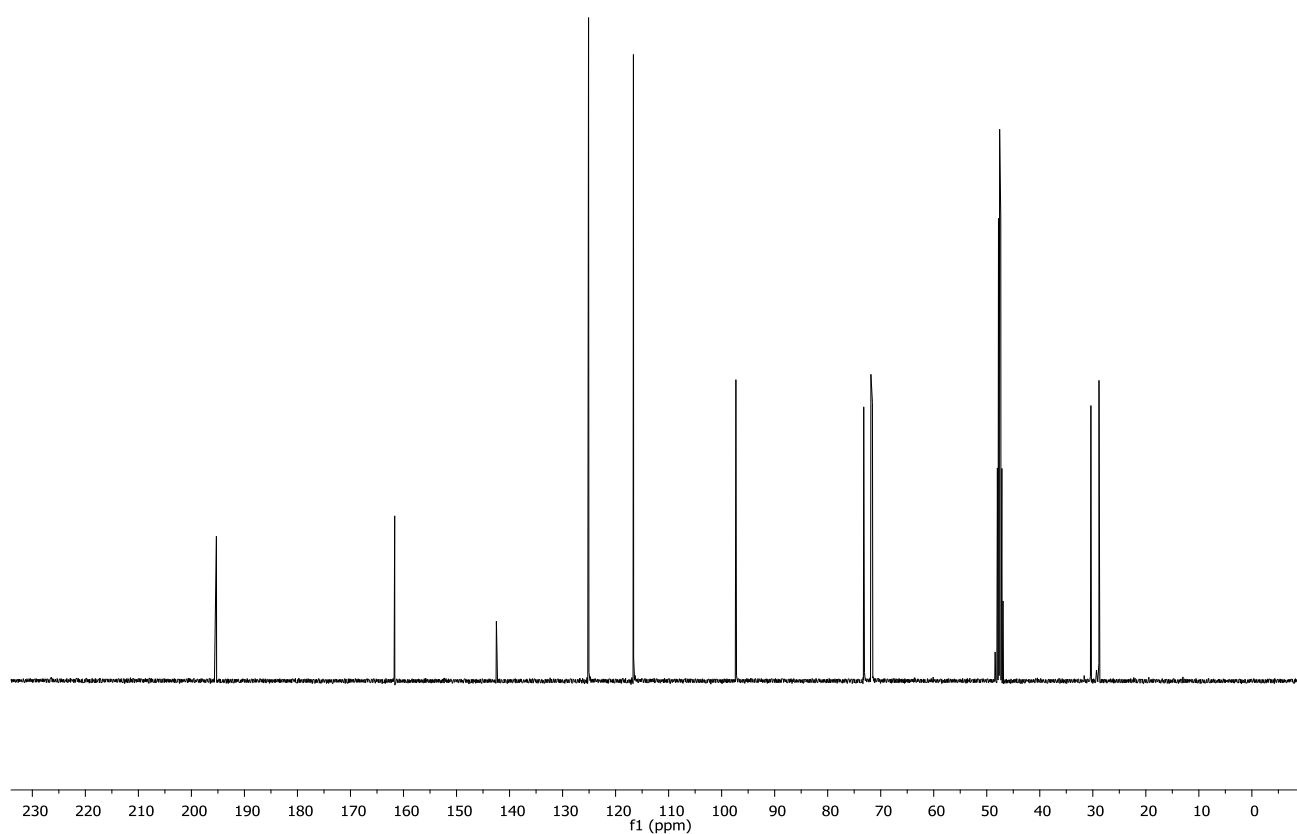
- 1 Still, W. C., Kahn, M. & Mitra, A. M. Rapid chromatographic technique for preparative separations with moderate resolution. *J. Org. Chem.* **43**, 2923-2925, (1978).
- 2 Pangborn, A. B., Giardello, M. A., Grubbs, R. H., Rosen, R. K. & Timmers, F. J. Safe and convenient procedure for solvent purification. *Organometallics* **15**, 1518-1520, (1996).

4-Nitrophenyl 6-S-acetyl-6-thio- α -D-glucopyranoside (10)

^1H NMR

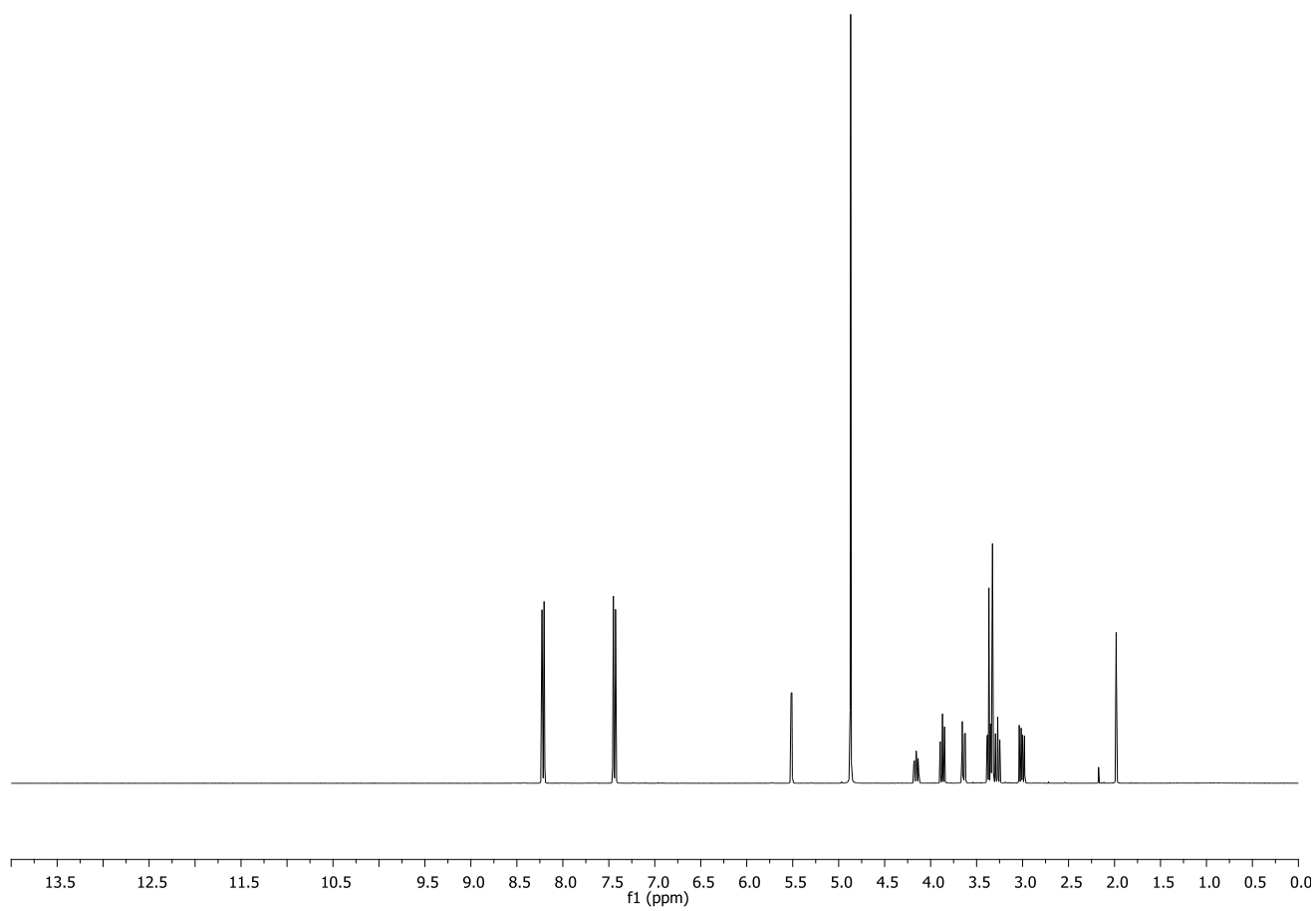


^{13}C NMR



Potassium 4-nitrophenyl 6-deoxy-6-sulfonato- α -D-glucopyranoside (PNPSQ, 7)

^1H NMR



^{13}C NMR

