

Supplementary Material 7. NMR signals for Resorufinyl 2,3,6-tri-*O*-acetyl-4-*S*-(2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranosyl)-4-thio- β -D-glucopyranoside and Resorufinyl 4-*S*-(β -D-glucopyranosyl)-4-thio- β -D-glucopyranoside (Glc-*S*-Glc- β -Res).

Resorufinyl 2,3,6-tri-O-acetyl-4-S-(2,3,4,6-tetra-O-acetyl- β -D-glucopyranosyl)-4-thio- β -D-glucopyranoside. ¹H-NMR (CDCl₃, 500 MHz): δ (ppm) 7.64 (d, 1H, $J = 9.1$ Hz), 7.35 (d, 1H, $J = 9.8$ Hz), 6.93 (m, 2H), 6.92 (d, 1H, $J = 2.5$ Hz), 6.78 (dd, 1H, $J_1 = 9.8$ Hz, $J_2 = 2.0$ Hz), 6.22 (d, 1H) (6H of resorufin), 5.21 (dd, 1H, $J_{3,4} = 10.6$ Hz, H-3), 5.17 (dd, 1H, $J_{2,3} = 8.8$ Hz, H-2), 5.16 (d, 1H, $J_{3',4'} = 9.7$ Hz, H-3'), 5.12 (d, 1H, $J_{1,2} = 7.7$ Hz, H-1), 4.99 (t, 1H, $J_{4',5'} = 9.9$ Hz, H-4'), 4.88 (dd, 1H, $J_{2',3'} = 9.1$ Hz, H-2'), 4.71 (d, 1H, $J_{1',2'} = 10.0$ Hz, H-1'), 4.64 (dd, 1H, $J_{6a,6b} = 12.1$ Hz, H-6a), 4.31 (dd, 1H, H-6b), 4.23 (dd, 1H, $J_{6'a,6'b} = 12.4$ Hz, H-6'a), 4.08 (dd, 1H, H-6'b), 4.02 (ddd, 1H, $J_{5,6a} = 2.1$ Hz, $J_{5,6b} = 6.0$ Hz, H-5), 3.70 (ddd, 1H, $J_{5',6'a} = 2.4$ Hz, $J_{5',6'b} = 5.1$ Hz, H-5'), 2.97 (dd, 1H, $J_{4,5} = 10.7$ Hz, H-4), 2.05, 2.04, 2.03, 2.01, 1.98, 1.96, 1.93 (7 \times CH₃). ¹³C-NMR (CDCl₃, 125 MHz): δ (ppm) 170.39, 170.20, 170.04, 170.01, 169.36, 169.33, 169.19 (7 \times CO-Ac), 186.22, 159.92, 149.52, 146.89, 145.11, 134.81, 134.70, 131.58, 129.58, 115.10, 106.93, 103.55 (12 \times C-Ar), 98.31 (C-1), 81.71 (C-1'), 75.93, 74.67, 73.59, 72.36, 70.34, 70.04, 68.14 (C-2, C-2', C-3, C-3', C-4', C-5, C-5'), 63.46, 62.12 (C-6, C-6'), 45.91 (C-4), 21.45, 20.73, 20.72, 20.66, 20.59, 20.55, 20.54, 20.49 (7 \times CH₃-Ac). ESI Q-TOF HRMS (m/z): 870,1907 (870,1891 calculated for C₃₈H₄₁NNaO₁₉S [M+Na]⁺).

*Resorufinyl 4-S-(β -D-glucopyranosyl)-4-thio- β -D-glucopyranoside (Glc-*S*-Glc- β -Res).* ¹³C-NMR (DMSO-d₆, 125 MHz): δ (ppm) 185.36, 160.82, 149.64, 145.75, 144.90, 134.92, 133.86, 131.21, 128.45, 114.67, 105.71, 102.50 (12C of resorufin), 99.35 (C-1), 83.22 (C-1'), 80.58, 77.52, 76.81, 74.02, 73.30, 72.51, 69.78 (C-2, C-2', C-3, C-3', C-4', C-5, C-5'), 61.04, 60.79 (C-6, C-6'), 45.24 (C-4). ESI Q-TOF HRMS (m/z): 576,1132 (576,1152 calculated for C₂₄H₂₇NNaO₁₂S [M+Na]⁺).

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