

Supporting Information
for
Appel-reagent-mediated transformation of glycosyl hemiacetal
derivatives into thioglycosides and glycosyl thiols

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Spectral data of synthesized compounds:

Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio- β -D-glucopyranoside (10)¹: White solid; mp 117–118 °C; $[\alpha]_D^{25} -15$ (c 1.2, CHCl₃); IR (KBr): 3024, 1750, 1477, 1436, 1371, 1237, 1067, 917, 763 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.51-7.29 (m, 5 H, Ar-H), 5.22-5.13 (t, J = 9.2 Hz each, 1 H, H-3), 5.08-5.02 (t, J = 9.7 Hz each, 1 H, H-2), 4.98-4.92 (t, J = 9.2 Hz each, 1 H, H-4), 4.70 (d, J = 9.9 Hz, 1 H, H-1), 4.21-4.18 (m, 2 H, H-6_{a,b}), 3.80-3.65 (m, 1 H, H-5), 2.08, 2.07, 2.01, 1.98 (4 s, 12 H, 4 COCH₃); ¹³C NMR (CDCl₃, 75 MHz): δ 170.3, 170.1, 169.2, 169.0, 133.7-128.7 (Ar-C), 85.9, 76.2, 74.4, 70.3, 68.5, 62.3, 20.9 (2 C), 20.8 (2 C); ESIMS: 463.1 [M + Na]⁺; Anal. calcd for C₂₀H₂₄O₉S (440.11): C, 54.54; H, 5.49; found: C, 54.40; H, 5.70.

4-Methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-1-thio- β -D-glucopyranoside (11)²: White solid; mp 164–165 °C; $[\alpha]_D^{25} -22$ (c 1.2, CHCl₃); ¹H NMR (CDCl₃, 500 MHz): δ 7.44 (d, J = 9.2 Hz, 2 H, Ar-H), 6.84 (d, J = 9.2 Hz, 2 H, Ar-H), 5.19 (t, J = 9.2 Hz each, 1 H, H-3), 4.99 (t, J = 9.8 Hz each, 1 H, H-2), 4.89 (t, J = 9.2 Hz each, 1 H, H-4), 4.54 (d, J = 9.8 Hz, 1 H, H-1), 4.22-4.15 (m, 2 H, H-6), 3.81 (s, 3 H, OCH₃), 3.69-3.65 (m, 1 H, H-5), 2.10, 2.07, 2.01, 1.98 (4 s, 12 H, 4 COCH₃); ¹³C NMR (CDCl₃, 125 MHz): δ 170.6, 170.2, 169.4, 169.2 (4 COCH₃), 160.4-114.4 (Ar-C), 85.6 (C-1), 75.7, 74.0, 69.8, 68.2, 62.0 (C-6), 55.3 (OCH₃), 20.8, 20.7 (2 C), 20.6 (4 COCH₃); ESIMS: 493.1 [M + Na]⁺; Anal. calcd for C₂₁H₂₆O₁₀S (470.12): C, 53.61; H, 5.57; found: C, 53.42; H, 5.64.

***p*-Methylphenyl 2,3,4,6-tetra-*O*-acetyl-1-thio- β -D-glucopyranoside (12)³:** White solid; mp 117–118 °C; $[\alpha]_D^{25} -22$ (c 1.2, CHCl₃); IR (KBr): 2925, 2363, 1749, 1221, 771 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.41-7.37 (m, 2 H, Ar-H), 7.14-7.10 (m, 2 H, Ar-H), 5.25-5.16 (t, J = 9.2 Hz each, 1 H), 5.07-4.97 (t, J = 9.8, 9.5 Hz, 1 H), 4.98-4.88 (t, J = 9.8 Hz each, 1 H), 4.63 (d, J = 9.9 Hz, 1 H), 4.21-4.13 (m, 2 H, H-6_{a,b}), 3.74-3.65 (m, 1 H, H-5), 2.35, 2.09, 2.07, 2.01, 1.98 (5 s, 15 H); ¹³C NMR (CDCl₃, 50 MHz): δ 170.9, 170.5, 169.7, 169.6, 139.1-127.9 (Ar-C), 86.2, 76.1, 74.4, 70.3, 68.6, 62.5, 21.6, 21.2, 21.1, 20.9 (2 C); ESIMS: 477.1 [M + Na]⁺; Anal. calcd for C₂₁H₂₆O₉S (454.12): C, 55.50; H, 5.77; found: C, 55.33; H, 5.62.

1-Phenyl-1*H*-tetrazol-5-yl 2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranoside (13)⁴: Yellow oil; $[\alpha]_D^{25} -8$ (c 1.2, CHCl₃); IR (neat): 3110, 2840, 1610, 1520, 1460, 910, 696 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.58-7.52 (m, 5 H, Ar-H), 5.78 (d, J = 10.0 Hz, 1 H, H-1), 5.31 (t, J = 9.0 Hz each, 1 H, H-3), 5.18 (t, J = 10.0 Hz each, 1 H, H-2), 5.12 (t, J = 10.0 Hz each, 1 H, H-4), 4.29-4.07 (m, 2 H, H-6_{ab}), 3.92-3.89 (m, 1 H, H-5), 2.06, 2.05, 2.04, 2.01 (4 s, 12 H, 4 COCH₃); ¹³C NMR (125 MHz, CDCl₃): δ 170.3, 169.7, 169.3, 169.2 (4 COCH₃), 133.3-124.0 (Ar-C), 83.7 (C-1), 76.5 (C-5), 73.6

(C-3), 69.8 (C-4), 67.7 (C-2), 61.3 (C-6), 20.7, 20.6, 20.5, 20.4 (4 COCH₃); ESIMS: 531.1 [M + Na]⁺; Anal. calcd for C₂₁H₂₄N₄O₉S (508.12): C, 49.60; H, 4.76; found: C, 49.45; H, 4.90.

2-Naphthyl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranoside (14)⁵: White solid; mp 110–112 °C; [α]_D²⁵ −18 (c 1.2, CHCl₃); IR (KBr): 1747, 1594, 1381, 1225, 1045 cm^{−1}; ¹H NMR (CDCl₃, 200 MHz): δ 7.97 (bs, 1 H), 7.82–7.73 (m, 3 H), 7.56–7.45 (m, 3 H), 5.19 (t, *J* = 9.1 Hz each, 1 H, H-2), 4.99 (t, *J* = 9.6 Hz each, 1 H, H-3), 4.96 (t, *J* = 9.5 Hz each, 1 H, H-4), 4.73 (d, *J* = 9.9 Hz, 1 H, H-1), 4.21–4.10 (m, 2 H, H-6_{ab}), 3.73–3.65 (m, 1 H, H-5), 2.10, 2.02, 2.0, 1.97 (4 s, 12 H, 4 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 170.4, 170.1, 169.3, 169.1, 133.8, 133.3, 130.8, 129.0, 128.7, 128.1 (2 C), 127.0 (2 C), 126.9, 85.9, 76.3, 74.3, 70.4, 68.5, 62.3, 21.0, 20.9, 20.8 (2 C); ESIMS: 513.1 [M + Na]⁺; Anal. calcd for C₂₄H₂₆O₉S (490.12): C, 58.77; H, 5.34; found: C, 58.60; H, 5.50.

Phenyl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-galactopyranoside (15)⁶: Yellow oil; [α]_D²⁵ +3 (c 1.5, CHCl₃); IR (neat): 2363, 1594, 1353, 1051 cm^{−1}; ¹H NMR (CDCl₃, 300 MHz): δ 7.54–7.29 (m, 5 H, Ar-H), 5.42 (d, *J* = 3.1 Hz, 1 H, H-4), 5.29–5.19 (t, *J* = 10.7, 9.8 Hz, 1 H, H-2), 5.09–5.02 (dd, *J* = 9.9, 3.2 Hz, 1 H, H-3), 4.75 (d, *J* = 9.8 Hz, 1 H, H-1), 4.18–4.10 (m, 2 H, H-6_{ab}), 3.98–3.91 (m, 1 H, H-5), 2.11, 2.09, 2.03, 1.97 (4 s, 12 H, 4 COCH₃); ¹³C NMR (CDCl₃, 75 MHz): δ 170.7, 170.5, 170.3, 169.7, 132.9–128.5 (Ar-C), 86.9, 74.8, 72.4, 67.7 (2 C), 62.0, 21.2 (2 C), 20.9 (2 C); ESIMS: 463.1 [M + Na]⁺; Anal. calcd for C₂₀H₂₄O₉S (440.11): C, 54.54; H, 5.49; found: C, 54.38; H, 5.70.

***p*-Methylphenyl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-galactopyranoside (16)**³: Yellow oil; [α]_D²⁵ −5 (c 1.0, CHCl₃); IR (neat): 2928, 2367, 1741, 1597, 1353, 1227, 1048, 768 cm^{−1}; ¹H NMR (CDCl₃, 300 MHz): δ 7.43–7.39 (d, *J* = 8.1 Hz, 2 H, Ar-H), 7.14–7.10 (d, *J* = 8.0 Hz, 2 H, Ar-H), 5.41–5.39 (d, *J* = 3.1 Hz, 1 H, H-4), 5.27–5.17 (t, *J* = 9.8 Hz each, 1 H, H-2), 5.06–5.00 (dd, *J* = 9.8, 3.2 Hz, 1 H, H-3), 4.67–4.62 (d, *J* = 9.8 Hz, 1 H, H-1), 4.24–4.06 (m, 2 H, H-6_{ab}), 3.94–3.88 (t, *J* = 6.5 Hz each, 1 H, H-5), 2.34 (s, 3 H, PhCH₃), 2.11, 2.10, 2.04, 1.97 (4 s, 12 H, 4 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 170.7, 170.6, 170.4, 169.8, 138.8–129.0 (Ar-C), 87.3, 74.7, 72.4, 67.7, 67.6, 61.9, 21.5, 21.2, 20.9 (3 C); ESIMS: 477.1 [M + Na]⁺; Anal. calcd for C₂₁H₂₆O₉S (454.12): C, 55.50; H, 5.77; found: C, 55.35; H, 5.60.

2-Benzothiazolyl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-galactopyranoside (18)⁷: Yellow oil; [α]_D²⁵ +34 (c 1.0, CHCl₃); IR (neat): 2908, 2377, 1751, 1600, 1343, 1236, 1054, 767 cm^{−1}; ¹H NMR (CDCl₃, 300 MHz): δ 7.94–7.33 (m, 4 H, Ar-H), 5.57 (d, *J* = 10.5 Hz, 1 H, H-1), 5.49 (d, *J* = 3.5 Hz, 1 H, H-4), 5.40 (t, *J* = 10.0 Hz, 1 H, H-2), 5.17 (dd, *J* = 10.0, 3.5 Hz, 1 H, H-3), 4.18–4.10 (m, 3 H, H-5, H-6_{ab}), 2.18, 2.04, 2.00, 1.99 (4 s, 12 H, 4 COCH₃); ¹³C NMR (125 MHz, CDCl₃): δ 170.3, 170.1, 170.0, 169.9 (4 COCH₃), 126.3–120.9 (Ar-C), 84.5 (C-1), 74.9 (C-3), 71.8 (C-4), 67.1 (C-2),

66.9 (C-5), 61.2 (C-6), 20.7, 20.6 (2 C), 20.5 (4 COCH₃); ESIMS: 520.1 [M + Na]⁺; Anal. calcd for C₂₁H₂₃NO₉S₂ (497.08): C, 50.69; H, 4.66; found: C, 50.53; H, 4.80.

2-Naphthyl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-galactopyranoside (19)⁵: White solid; mp 114–116 °C; [α]_D²⁵ +5 (c 1.2, CHCl₃); IR (KBr): 1743, 1592, 1375, 1224, 1043 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz): δ 7.99 (bs, 1 H), 7.82–7.74 (m, 3 H), 7.57–7.44 (m, 3 H), 5.36 (d, *J* = 2.8 Hz, 1 H, H-4), 5.20 (t, *J* = 9.8 Hz each, 1 H, H-2), 5.02 (dd, *J* = 9.6, 3.2 Hz, 1 H, H-3), 4.75 (d, *J* = 9.7 Hz, 1 H, H-1), 4.19–4.06 (m, 2 H, H-6_{a,b}), 3.92–3.89 (m, 1 H, H-5), 2.11, 2.03, 2.0, 1.96 (4 s, 12 H, 4 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 170.7, 170.5, 170.4, 169.8, 133.8, 133.1, 132.3, 130.1, 129.9, 128.8, 128.1, 128.0, 127.0 (2 C), 86.9, 74.9, 72.4, 67.7, 67.6, 62.1, 21.2, 21.0, 20.9 (2 C); ESIMS: 513.1 [M + Na]⁺; Anal. calcd for C₂₄H₂₆O₉S (490.12): C, 58.77; H, 5.34; found: C, 58.58; H, 5.52.

Phenyl 2,3,4,6-tetra-O-acetyl-1-thio-α-D-mannopyranoside (21)⁶: Yellow oil; [α]_D²⁵ +118 (c 1.5, CHCl₃); IR (neat): 2930, 2121, 1753, 1370, 1220, 1052, 769 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.51–7.46 (m, 2 H, Ar-H), 7.32–7.26 (m, 3 H, Ar-H), 5.49 (bs, 2 H, H-1 and H-2), 5.39–5.26 (m, 2 H, H-3, H-4), 4.62–4.44 (m, 1 H, H-5), 4.35–4.06 (ddd, *J* = 12.1, 2.16, 2.24 Hz, 2 H, H-6_{a,b}), 2.15, 2.07, 2.05, 2.02 (4 s, 12 H, 4 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 170.9, 170.5, 170.1 (2 C), 133.0–128.5 (Ar-C), 86.0, 71.3, 69.9 (2 C), 66.7, 62.8, 21.3, 21.1, 21.0 (2 C); ESIMS: 463.1 [M + Na]⁺; Anal. calcd for C₂₀H₂₄O₉S (440.11): C, 54.54; H, 5.49; found: C, 54.40; H, 5.70.

Phenyl 2,3,4-tri-O-acetyl-1-thio-α-L-rhamnopyranoside (22)⁸: Yellow oil; [α]_D²⁵ +76 (c 1.5, CHCl₃); IR (neat): 2354, 1763, 1220, 1067, 770 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.52–7.28 (m, 5 H, Ar-H), 5.66 (d, *J* = 2.8 Hz, 1 H), 5.13–5.03 (t, *J* = 9.3 Hz each, 1 H), 5.03–4.98 (dd, *J* = 8.0, 3.3 Hz, 1 H), 4.90 (br s, 1 H), 3.59–3.51 (m, 1 H), 2.19, 2.04, 1.97 (3 s, 9 H, 3 COCH₃), 1.30 (d, *J* = 6.1 Hz, 3 H); ¹³C NMR (CDCl₃, 75 MHz): δ 170.5, 170.4, 170.1, 133.7–128.2 (Ar-C), 85.7, 75.3, 72.2, 71.4, 70.6, 21.1, 20.9 (2 C), 18.1; ESIMS: 405.1 [M + Na]⁺; Anal. calcd for C₁₈H₂₂O₇S (382.10): C, 56.53; H, 5.80; found: C, 56.35; H, 6.00.

Phenyl 2,3,4-tri-O-acetyl-1-thio-β-L-fucopyranoside (24)⁹: Yellow oil; [α]_D²⁵ –8 (c 1.5, CHCl₃); IR (neat): 2360, 1767, 1232, 1066, 772 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.53–7.29 (m, 5 H, Ar-H), 5.27 (br s, 1 H, H-4), 5.22 (t, *J* = 9.8 Hz each, 1 H, H-2), 5.06 (dd, *J* = 9.8, 3.2 Hz, 1 H, H-3), 4.72 (d, *J* = 9.8 Hz, 1 H, H-2), 3.87–3.81 (m, 1 H, H-5), 2.14, 2.07, 1.96 (3 s, 9 H, 3 COCH₃), 1.25 (d, *J* = 6.0 Hz, 3 H, CCH₃); ¹³C NMR (75 MHz): δ 170.9, 170.5, 169.8 (3 COCH₃), 133.2–128.3 (Ar-C), 86.7 (C-1), 73.5 (C-3), 72.8 (C-4), 70.7 (C-2), 67.8 (C-5), 21.2, 20.9 (2 C) (3 COCH₃), 16.8 (CCH₃); ESIMS: 405.1 [M + Na]⁺; Anal. calcd for C₁₈H₂₂O₇S (382.10): C, 56.53; H, 5.80; found: C, 56.37; H, 6.00.

Phenyl 2,3,5-tri-*O*-benzoyl-1-thio- β -D-ribofuranoside (25)¹⁰: Yellow oil; $[\alpha]_D^{25} +16$ (*c* 1.5, CHCl₃); IR (neat): 2324, 1760, 1200, 1069, 776 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 8.06-7.32 (m, 20 H, Ar-H), 5.73 (t, *J* = 5.0 Hz each, 1 H, H-2), 5.68 (t, *J* = 5.0 Hz each, 1 H, H-3), 5.62 (d, *J* = 4.9 Hz, 1 H, H-1), 4.68-4.62 (m, 2 H, H-4, H-5_a), 4.52 (dd, *J* = 11.5, 4.1 Hz, 1 H, H-5_b); ¹³C NMR (125 MHz, CDCl₃): δ 166.6, 165.7, 165.5 (3 C_{OPh}), 134.1-128.8 (Ar-C), 88.5 (C-1), 80.8 (C-3), 75.0 (C-2), 72.7 (C-4), 64.6 (C-5); ESIMS: 577.1 [M + Na]⁺; Anal. calcd for C₃₂H₂₆O₇S (554.14): C, 69.30; H, 4.73; found: C, 69.13; H, 4.95.

Phenyl 2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-acetyl-1-thio- β -D-glucopyranoside (26)¹¹: White solid, mp 165–166 °C; $[\alpha]_D^{25} -19$ (*c* 1.5, CHCl₃); IR (KBr): 2930, 1753, 1365, 1038, 752 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.47-7.44 (m, 2 H, Ar-H), 7.31-7.27 (m, 3 H, Ar-H), 5.32 (dd, *J* = 3.4 and 1.0 Hz, 1 H), 5.19 (dd, *J* = 9.2 and 9.1 Hz, 1 H), 5.08 (dd, *J* = 10.5 and 7.9 Hz, 1 H), 4.92 (t, *J* = 10.5 Hz each, 1 H), 4.88 (dd, *J* = 10.0 and 9.2 Hz, 1 H), 4.65 (d, *J* = 10.1 Hz, 1 H), 4.56 (dd, *J* = 11.9 and 2.0 Hz, 1 H), 4.44 (d, *J* = 7.9 Hz, 1 H), 4.10 (dd, *J* = 10.2 and 6.7 Hz, 1 H), 4.08 (dd, *J* = 11.9 and 5.6 Hz, 1H), 4.04 (dd, *J* = 10.2 and 7.2 Hz, 1 H), 3.86-3.83 (m, 1 H), 3.72 (dd, *J* = 9.9 and 9.1 Hz, 1 H), 3.67-3.60 (m, 1 H), 2.12, 2.08, 2.07, 2.02, 2.01, 2.00, 1.94 (7 s, 21 H, 7 COCH₃); ¹³C NMR (75 MHz, CDCl₃): δ 170.3, 170.2, 170.1, 170.0, 169.7, 169.5, 169.0, 133.0-128.7 (Ar-C), 101.0, 85.5, 76.6, 76.1, 73.8, 70.9, 70.8, 70.2, 69.0, 66.6, 62.1, 60.8, 20.8 (2 C), 20.7 (2 C), 20.6 (2 C), 20.5; ESIMS: 751.1 [M+Na]⁺; Anal. Calcd. for C₃₂H₄₀O₁₇S (728.19): C, 52.74; H, 5.53; found: C, 52.55; H, 5.75.

4-Methoxyphenyl (2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-acetyl-1-thio- β -D-glucopyranoside (27)²: White solid; mp 167–168 °C; $[\alpha]_D^{25} -21$ (*c* 1.2, CHCl₃); IR (KBr): 2936, 1766, 1367, 1042, 756 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ 7.42 (d, *J* = 9.2 Hz, 2 H, Ar-H), 6.84 (d, *J* = 9.2 Hz, 2 H, Ar-H), 5.33 (br s, 1 H, H-4_B), 5.18 (t, *J* = 9.2 Hz each, 1 H, H-3_A), 5.08 (dd, *J* = 7.9, 7.9 Hz, 1 H, H-2_A), 4.94 (dd, *J* = 10.3, 3.4 Hz, 1 H, H-3_B), 4.80 (t, *J* = 9.7 Hz each, 1 H, H-2_B), 4.55-4.52 (dd, *J* = 11.9, 1.7 Hz, 1 H, H-6_{aA}), 4.50 (d, *J* = 10.0 Hz, 1 H, H-1_B), 4.44 (d, *J* = 7.9 Hz, 1 H, H-1_A), 4.13-4.0 (m, 3 H, H-6_{abB} and H-6_{bA}), 3.86-3.82 (m, 1 H, H-5_A), 3.80 (s, 3 H, OCH₃), 3.70 (t, *J* = 9.8 Hz each, 1 H, H-4_A), 3.59-3.56 (m, 1 H, H-5_B), 2.14, 2.10, 2.03, 2.02, 2.00, 1.95 (6 s, 21 H, 7 COCH₃); ¹³C NMR (CDCl₃, 125 MHz): δ 170.3, 170.2, 170.1, 170.0, 169.7, 169.5, 169.0 (7 COCH₃), 160.3-114.3 (Ar-C), 100.0 (C-1'), 85.4 (C-1), 76.6, 76.0, 73.9, 70.9, 70.6, 70.2, 69.0, 66.6, 61.9 (C-6), 60.7 (C-6'), 55.3 (OCH₃), 20.9, 20.8, 20.7, 20.6 (3 C), 20.5 (7 COCH₃); ESIMS: 781.2 [M + Na]⁺; Anal. calcd for C₃₃H₄₂O₁₈S (758.20): C, 52.24; H, 5.58; found: C, 52.10; H, 5.75.

Phenyl 2,3,4,6-tetra-*O*-acetyl- α -D-glucopyranosyl-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-acetyl-1-thio- β -D-

glucopyranoside (28)¹¹: White solid; mp 82–84 °C; $[\alpha]_D^{25} +47$ (c 1.5, CHCl₃); IR (KBr): 2927, 1763, 1365, 1030, 756 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.48–7.45 (m, 2 H, Ar-H), 7.32–7.24 (m, 3 H, Ar-H), 5.39–5.29 (m, 3 H), 5.08 (t, J = 9.8 Hz each, 1 H), 4.88–4.75 (m, 3 H), 4.50 (d, J = 9.8 Hz, 1 H), 4.25–4.20 (m, 2 H), 4.07 (br s, 1 H), 4.01–3.88 (m, 2 H), 3.75–3.73 (m, 1 H), 2.08, 2.06, 2.05, 2.03, 2.02, 2.01, 1.98 (7 s, 21 H, 7 COCH₃); ¹³C NMR (75 MHz, CDCl₃): δ 170.4, 170.2, 170.1 (2 C), 169.8, 169.4, 169.3, 133.3–128.4 (Ar-C), 95.5, 85.0, 76.4, 76.0, 72.4, 70.6, 69.9, 69.2, 68.5, 67.9, 62.7, 61.4, 20.8 (2 C), 20.7 (2 C), 20.6 (2 C), 20.5; ESIMS: 751.1 [M + Na]⁺; Anal. calcd for C₃₂H₄₀O₁₇S (728.19): C, 52.74; H, 5.53; found: C, 52.57; H, 5.72.

Phenyl 2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranosyl-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-acetyl-1-thio- β -D-

glucopyranoside (29)¹¹: White solid; mp 223–225 °C; $[\alpha]_D^{25} -29$ (c 1.5, CHCl₃); IR (KBr): 2928, 1753, 1235, 1038, 760 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.46–7.43 (m, 2 H, Ar-H), 7.31–7.26 (m, 3 H, Ar-H), 5.18 (dd, J = 9.1 and 9.0 Hz, 1 H), 5.12 (dd, J = 9.4 and 9.1 Hz, 1 H), 5.04 (dd, J = 9.5 and 9.3 Hz, 1 H), 4.90 (dd, J = 9.2 and 8.0 Hz, 1 H), 4.89 (dd, J = 10.0 and 9.2 Hz, 1 H), 4.64 (d, J = 10.2 Hz, 1 H), 4.54 (dd, J = 11.9 and 1.9 Hz, 1 H), 4.47 (d, J = 7.8 Hz, 1 H), 4.36 (dd, J = 12.5 and 4.3 Hz, 1 H), 4.07 (dd, J = 11.9 and 5.4 Hz, 1 H), 4.00 (dd, J = 12.6 and 2.2 Hz, 1 H), 3.71 (dd, J = 10.0 and 9.0 Hz, 1 H), 3.65–3.60 (m, 2 H), 2.09, 2.06, 2.04, 2.00, 1.98, 1.96 (6 s, 21 H, 7 COCH₃); ¹³C NMR (75 MHz, CDCl₃): δ 170.5, 170.3, 169.8, 169.6, 169.4 (2 C), 169.1, 133.0–128.3 (Ar-C), 100.7, 85.4, 76.6, 76.2, 73.4, 72.8, 71.8, 71.4, 70.0, 67.5, 61.8, 61.3, 20.6 (2 C), 20.5 (2 C), 20.4 (2 C), 20.3; ESIMS: 751.1 [M + Na]⁺; Anal. calcd for C₃₂H₄₀O₁₇S (728.19): C, 52.74; H, 5.53; found: C, 52.59; H, 5.70.

2,3,4,6-Tetra-*O*-acetyl-1-thio- β -D-glucopyranose (30)¹²: Yellow oil; $[\alpha]_D^{25} +13.3$ (c 1.0, CHCl₃);

¹H NMR (500 MHz, CDCl₃): δ 5.15 (t, J = 9.5 Hz each, 1 H, H-2), 5.09 (t, J = 10 Hz each, 1 H, H-3), 4.96 (t, J = 9.5 Hz, 1 H, H-4), 4.52 (t, J = 9.0 Hz each, 1 H, H-1), 4.25 (dd, J = 12.5, 5.0 Hz, 1 H, H-6_a), 4.11 (dd, J = 12.5, 2.0 Hz, 1 H, H-6_b), 3.71–3.69 (m, 1 H, H-5), 2.28 (d, J = 10.0 Hz, 1 H, SH), 2.09, 2.07, 2.02, 2.01 (4 s, 12 H, 4 COCH₃); ¹³C NMR (125 MHz, CDCl₃): δ 170.4, 169.9, 169.4, 169.1 (4 COCH₃), 78.7 (C-1), 76.1 (C-2), 73.6 (2 C, C-3, C-4), 68.1 (C-6), 20.7, 20.6 (2 C), 20.5 (4 COCH₃); ESIMS: 387.0 [M + Na]⁺; Anal. calcd for C₁₄H₂₀O₉S (364.08): C, 46.15; H, 5.53; found: C, 46.0; H, 5.70.

2,3,4,6-Tetra-*O*-acetyl-1-thio- β -D-galactopyranose (31)¹³: Yellow oil; $[\alpha]_D^{25} +104.7$ (c 1.0,

CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 5.39 (d, J = 3.0 Hz, 1 H, H-4), 5.13 (t, J = 9.5 Hz each, 1 H, H-2), 4.98 (dd, J = 10.5, 3.5 Hz, 1 H, H-3), 4.90 (t, J = 10.0 Hz each, 1 H, H-1), 4.11–4.09 (m, 2

H, H-6_{ab}), 3.93-3.90 (m, 1 H, H-5), 2.30 (d, $J = 10.0$ Hz, 1 H, *SH*), 2.15, 2.07, 2.02, 1.96 (4 s, 12 H, 4 COCH₃); ¹³C NMR (125 MHz, CDCl₃): δ 170.1, 170.0, 169.7, 169.6 (4 COCH₃), 79.2 (C-1), 74.9 (C-2), 71.6 (C-3), 70.9 (C-4), 67.2 (C-5), 61.3 (C-6), 20.8, 20.6, 20.5 (2 C), (4 COCH₃); ESIMS: 387.0 [M + Na]⁺; Anal. calcd. for C₁₄H₂₀O₉S (364.08): C, 46.15; H, 5.53; found: C, 46.0; H, 5.75.

2,3,4,6-Tetra-O-acetyl-1-thio- β -D-mannopyranose (32)¹⁴: White solid; mp 146 °C; $[\alpha]_D^{25} -4.9$ (c 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 5.41 (d, $J = 3.5$ Hz, 1 H, H-2), 5.19 (t, $J = 10.0$ Hz each, 1 H, H-4), 5.05 (dd, $J = 10.0, 3.5$ Hz, 1 H, H-3), 4.87 (d, $J = 10.0$ Hz, 1 H, H-1), 4.23 (dd, $J = 12.5, 5.0$ Hz, 1 H, H-6_a), 4.10 (dd, $J = 12.5, 2.0$ Hz, 1 H, H-6_b), 3.69-3.66 (m, 1 H, H-5), 2.50 (d, $J = 10.0$ Hz, 1 H, *SH*), 2.23, 2.09, 2.03, 1.97 (4 s, 12 H, 4 COCH₃); ¹³C NMR (125 MHz, CDCl₃): δ 169.9, 169.8, 169.4 (2 C) (4 COCH₃), 76.9 (C-1), 76.4 (C-2), 72.0 (C-3), 71.6 (C-4), 65.2 (C-5), 62.0 (C-6), 20.8, 20.7, 20.6, 20.5 (4 COCH₃); ESIMS: 387.0 [M + Na]⁺; Anal. calcd for C₁₄H₂₀O₉S (364.08): C, 46.15; H, 5.53; found: C, 46.02; H, 5.72.

2,3,4-Tri-O-acetyl-1-thio- β -L-rhamnopyranose (33)¹⁵: Yellow oil; $[\alpha]_D^{25} +46.3$ (c 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 5.32 (br s, 1 H, H-2), 4.94-4.93 (m, 2 H, H-3, H-4), 4.78 (d, $J = 10.0$ Hz each, 1 H, H-1), 3.49-3.46 (m, 1 H, H-5), 2.39 (d, $J = 10.0$ Hz, 1 H, *SH*), 2.15, 1.97, 1.90 (3 s, 9 H, 3 COCH₃), 1.19 (d, $J = 6.0$ Hz, 3 H, CCH₃); ¹³C NMR (125 MHz, CDCl₃): δ 170.0, 169.8, 169.7 (3 COCH₃), 75.9 (C-1), 75.3 (C-3), 72.0 (C-4), 71.9 (C-2), 69.9 (C-5), 20.7, 20.6, 20.5 (COCH₃), 17.7 (CCH₃); ESIMS: 329.0 [M + Na]⁺; Anal. calcd for C₁₂H₁₈O₇S (306.07): C, 47.05; H, 5.92; found: C, 46.90; H, 6.10.

2,3,4-Tri-O-acetyl-1-thio- β -L-fucopyranose (34)¹²: White solid; mp 108–110 °C; $[\alpha]_D^{25} -2.5$ (c 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 5.26 (d, $J = 3.5$ Hz, 1 H, H-4), 5.11 (t, $J = 10.0$ Hz each, 1 H, H-2), 4.98 (dd, $J = 10.0, 3.5$ Hz, 1 H, H-3), 4.46 (t, $J = 10.0$ Hz, 1 H, H-1), 3.85-3.79 (m, 1 H, H-5), 2.28 (d, $J = 10.0$ Hz, 1 H, *SH*), 2.18, 2.06, 1.96 (3 s, 9 H, 3 COCH₃), 1.21 (d, $J = 6.0$ Hz, 3 H, CCH₃); ¹³C NMR (125 MHz, CDCl₃): δ 170.4, 169.8, 169.7 (3 COCH₃), 78.9 (C-1), 73.8 (C-3), 72.0 (C-4), 71.0 (C-2), 70.3 (C-5), 20.8, 20.7, 20.6 (3 COCH₃), 16.4 (CCH₃); ESIMS: 329.0 [M + Na]⁺; Anal. calcd for C₁₂H₁₈O₇S (306.07): C, 47.05; H, 5.92; found: C, 46.88; H, 6.14.

(2,3,4,6-Tetra-O-acetyl- β -D-galactopyranosyl)-(1→4)-2,3,6-tri-O-acetyl-1-thio- β -D-glucopyranose (35)¹⁶: Yellow oil; $[\alpha]_D^{25} +0.2$ (c 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 5.32 (d, $J = 3.0$ Hz, 1 H, H-4_B), 5.16 (t, $J = 9.5$ Hz each, 1 H, H-3_A), 5.07 (t, $J = 8.0$ Hz each, 1 H, H-2_A), 4.93 (dd, $J = 10.5, 3.5$ Hz, 1 H, H-3_B), 4.85 (t, $J = 9.5$ Hz each, 1 H, H-2_B), 4.50 (t, $J = 9.5$ Hz each, 1 H, H-1_A), 4.45 (d, $J = 8.0$ Hz, 1 H, H-1_B), 4.42 (dd, $J = 12.0, 1.5$ Hz, 1 H, H-6_{ab}), 4.13-4.05 (m, 3 H, H-6_{abA}, H-6_{abB}), 3.87-3.84 (m, 1 H, H-5_B), 3.78 (t, $J = 10.0$ Hz each, 1 H, H-4_A), 3.63-3.61 (m, 1

H, H-5_A), 2.23 (d, $J = 10.0$ Hz, 1 H, *SH*), 2.15, 2.13, 2.07, 2.06, 2.04, 1.96 (6 s, 21 H, 7 COCH₃); ¹³C NMR (125 MHz, CDCl₃): δ 170.2, 170.1, 169.9, 169.8, 169.7, 169.4, 168.9 (7 COCH₃), 101.1 (C-1_B), 78.5 (C-1_A), 77.1 (C-5_A), 76.1 (C-4_A), 73.9 (C-3_A), 73.5 (C-2_B), 70.9 (C-3_B), 70.7 (C-5_B), 69.0 (C-2_A), 66.5 (C-4_B), 62.2 (C-6_B), 60.7 (C-6_A), 20.8, 20.7 (2 C), 20.6 (2 C), 20.5, 20.4 (7 COCH₃); ESIMS: 675.1 [M + Na]⁺; Anal. calcd for C₂₆H₃₆O₁₇S (652.16): C, 47.85; H, 5.56; found: C, 47.70; H, 5.74.

(2,3,4,6-Tetra-O-acetyl- α -D-glucopyranosyl-(1 $\rightarrow$ 4)-2,3,6-tri-O-acetyl-1-thio- β -D-

glucopyranoside (36)¹⁷: White solid; mp 156–157 °C; [α]_D²⁵ +70.7 (*c* 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 5.32 (d, $J = 4.0$ Hz, 1 H, H-1_B), 5.25 (t, $J = 10.0$ Hz each, 1 H, H-3_A), 5.15 (t, $J = 9.0$ Hz each, 1 H, H-2_A), 4.95 (t, $J = 10.0$ Hz each, 1 H, H-3_B), 4.76 (dd, $J = 10.5, 4.0$ Hz, 1 H, H-2_B), 4.69 (t, $J = 9.5$ Hz each, 1 H, H-4_B), 4.50 (t, $J = 9.5$ Hz each, 1 H, H-1_A), 4.35 (dd, $J = 12.0, 2.5$ Hz, 1 H, H-6_{aA}), 4.16–4.12 (m, 2 H, H-6_{abB}), 3.97 (dd, $J = 12.0, 1.5$ Hz, 1 H, H-6_{bA}), 3.92 (t, $J = 10.0$ Hz each, 1 H, H-4_A), 3.88–3.84 (m, 1 H, H-5_A), 3.63–3.60 (m, 1 H, H-5_B), 2.15 (d, $J = 10.0$ Hz, 1 H, *SH*), 2.08, 2.02, 1.97, 1.96, 1.94, 1.93, 1.92 (7 s, 21 H, 7 COCH₃); ¹³C NMR (125 MHz, CDCl₃): δ 170.4, 170.3, 170.2, 169.9, 169.7, 169.6, 169.2 (7 COCH₃), 95.6 (C-1_B), 78.2 (C-1_A), 76.6 (C-2_A), 76.1 (C-5_B), 74.4 (C-4_B), 72.6 (C-4_A), 70.0 (C-2_B), 69.3 (C-3_A), 68.6 (C-3_B), 68.0 (C-5_A), 63.0 (C-6_A), 61.4 (C-6_B), 20.8, 20.7 (2 C), 20.6, 20.5 (3C) (7 COCH₃); ESIMS: 675.1 [M + Na]⁺; Anal. calcd for C₂₆H₃₆O₁₇S (652.16): C, 47.85; H, 5.56; found: C, 47.68; H, 5.75.

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NMR spectra of new compounds:

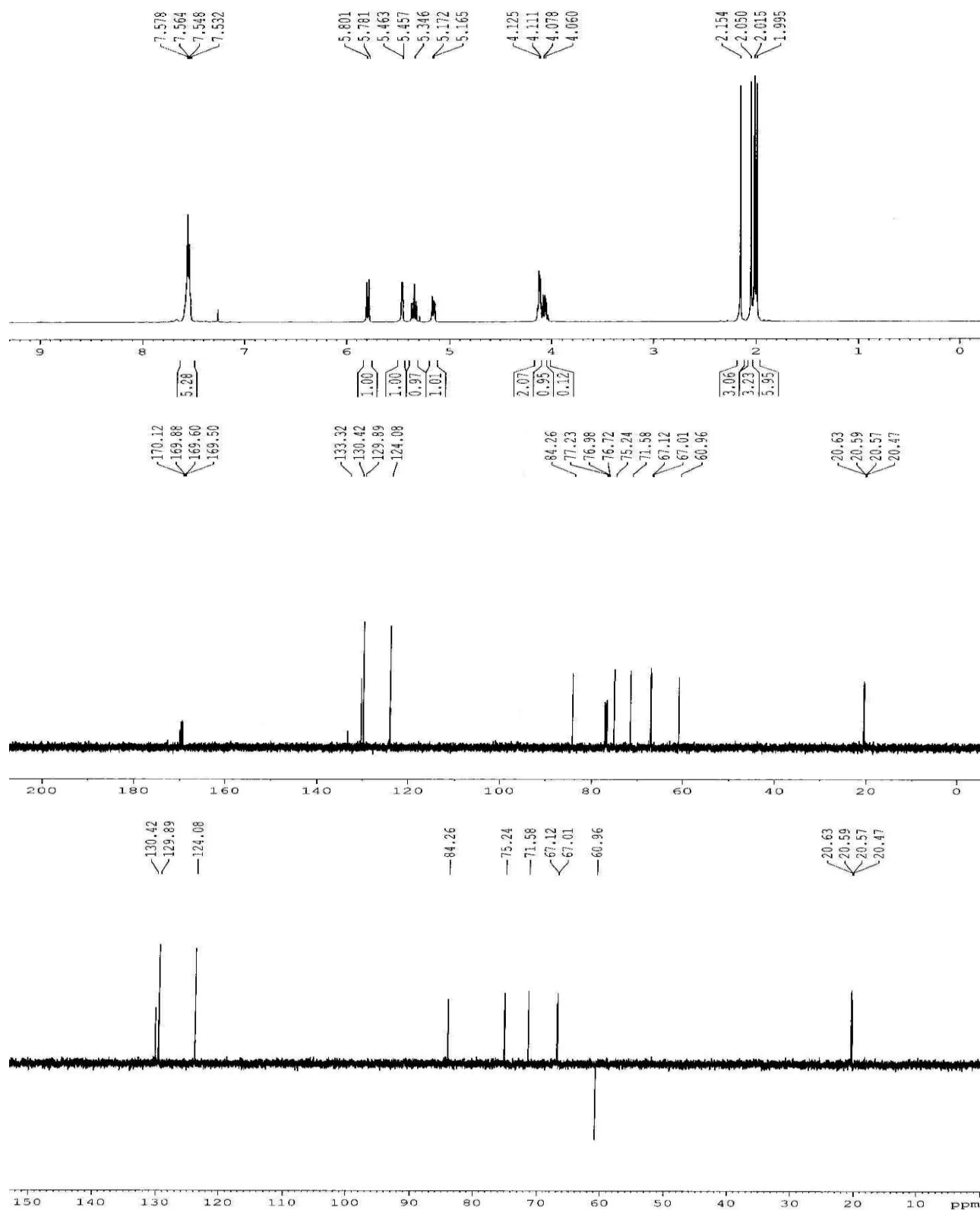


Figure S1: ^1H , ^{13}C and ^{13}C DEPT 135 NMR spectra of 1-phenyl-1*H*-tetrazol-5-yl 2,3,4,6-tetra-*O*-acetyl-1-thio- β -D-galactopyranoside (**17**).

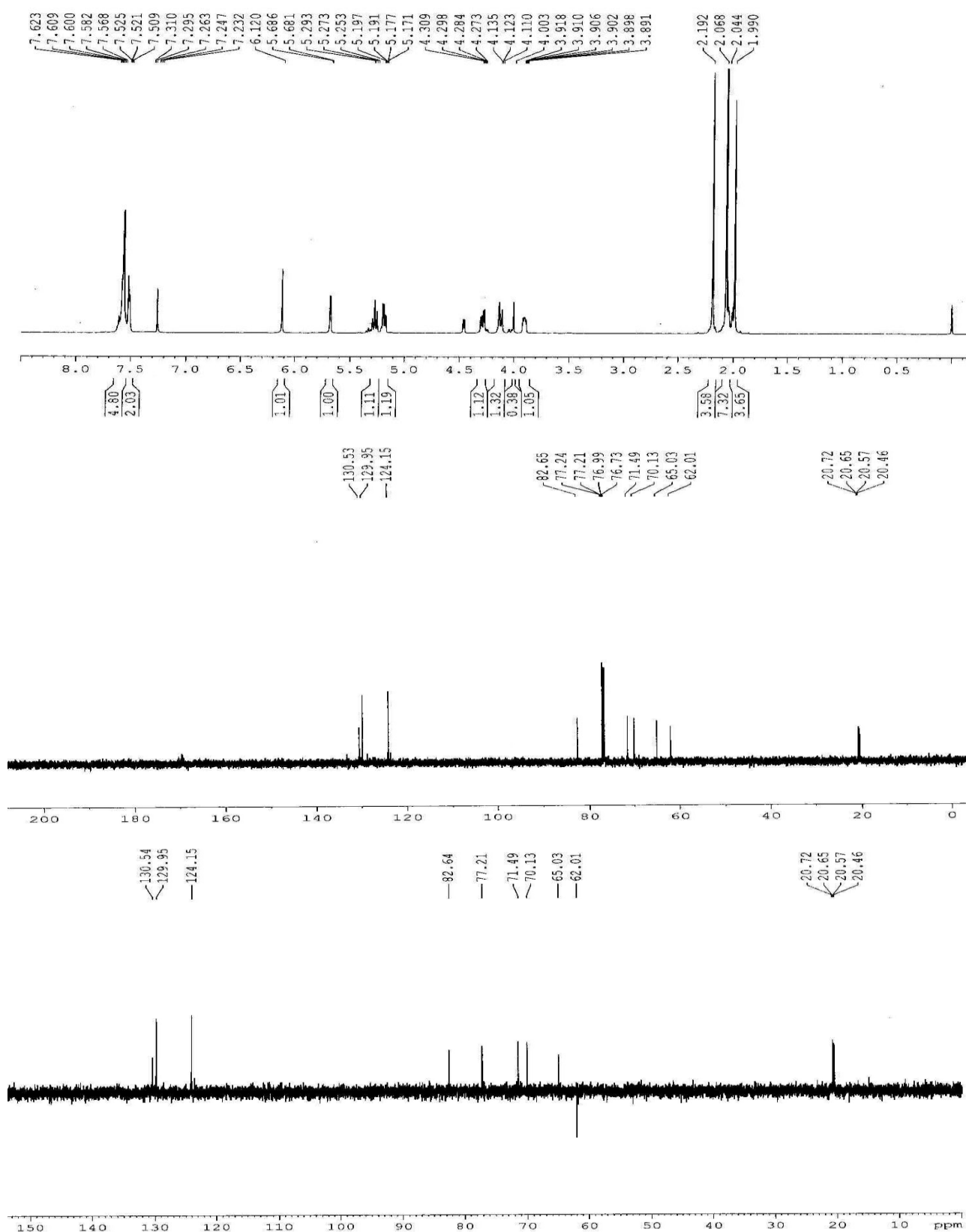


Figure S2: ^1H , ^{13}C and ^{13}C DEPT 135 NMR spectra of 1-phenyl-1H-tetrazol-5-yl 2,3,4,6-tetra-O-acetyl-1-thio- α -D-mannopyranoside (**20**).

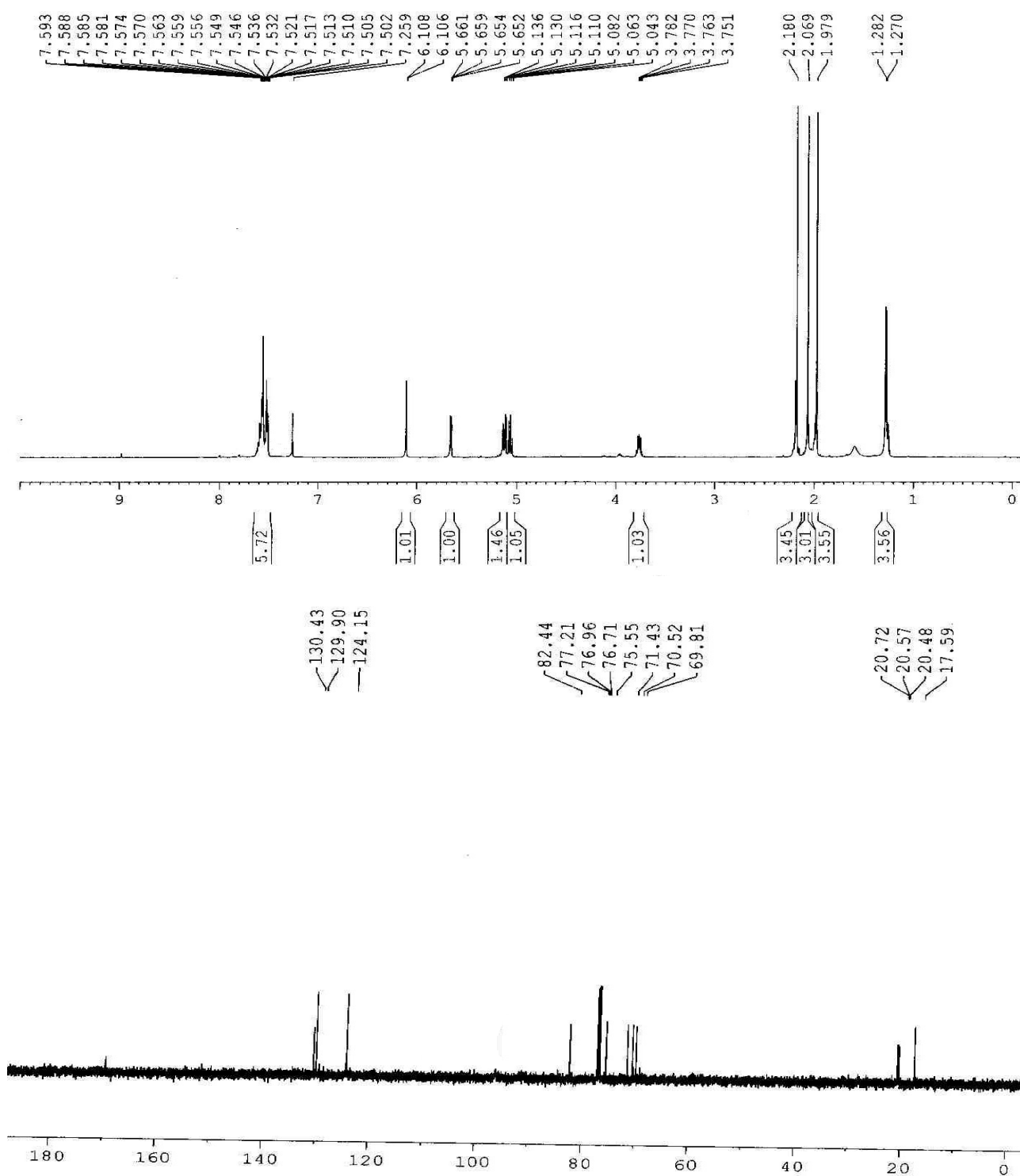


Figure S3: ¹H, ¹³C and ¹³C DEPT 135 NMR spectra of 1-phenyl-1*H*-tetrazol-5-yl 2,3,4-tri-*O*-acetyl-1-thio- α -L-rhamnopyranoside (**23**).