Supporting Information

Pd-Catalyzed Functionalization of Benzo-2,1,3-thiadiazole at C-5-Position using 1-Thiosugars

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1. **General Procedures**: All reactions were carried out using chemical reagents and solvents without any specific treatment. The respective reactions were monitored by Thin Layer Chromatography (TLC) MACHEREY-NAGEL (SIL G/UV254) and were visualized by fluorescence quenching with UV light at 254 nm. The purification of the compounds was performed by column chromatography using hexane/ethyl acetate. $^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$ on Bruker (300 MHz and 75 MHz respectively) spectrometer. $^1$H NMR data are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (J) and assignment.

2. **Typical Procedure for Pd-Catalyzed Coupling of Thiosugars (1a–h) with BTD (2a)**: In a 5 mL round bottle flask were added palladium catalyst (4 mol %), thiosugar$^1$ (0.2 mmol, 1.2 equiv.), BTD (0.17 mmol, 1.0 equiv.), and Et$_3$N (0.26 mmol, 1.5 equiv.). The mixture was magnetically stirred in 1,4-dioxane (1.5 mL) under N$_2$ atmosphere at 90 ºC for 2 h. The progress of the reaction was monitored by TLC (eluent: hexane/ethyl acetate, 70:30). After this time, the solution was cooled to room temperature, diluted with ethyl acetate (20 mL), and washed with water (3x20 mL). The organic phase was separated, dried over Na$_2$SO$_4$, and concentrated under vacuum. The obtained products were purified by column chromatography using hexane/ethyl acetate, 70:30 as the eluent.

3. **Typical Procedure for the Synthesis of Unprotected S-Linked Saccharides**: In a small balloon was placed a mixture of S-linked saccharides (0.06 mmol) and K$_2$CO$_3$ (0.3 equiv) in methanol (0.6 mL), and the mixture was stirred under N$_2$ atmosphere at room temperature for 3 h. The crude mixture was then filtered through Celite and washed with 10 mL of methanol. The filtrate was concentrated under reduced pressure at 25 ºC to afford the desired product.
(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(benzo[c][1,2,5]thiadiazol-5-ylthio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3a):

Light yellow solid (85 mg, >99%). MW: 498.52 g/mol. C_{20}H_{22}N_{2}O_{9}S_{2}. \textbf{^1H NMR} (300 MHz, CDCl_{3}) \delta ppm 8.13 (d, J = 0.9 Hz, 1H), 7.93 (d, J = 8.8 Hz, 1H), 7.59 (dd, J_1 = 9.2 Hz, J_2 = 1.7 Hz, 1H), 5.30 (t, J = 9.3 Hz, 1H), 5.10 (td, J_1 = 9.8 Hz, J_2 = 3.2 Hz, 2H), 4.93 (d, J = 10.1 Hz, 1H), 4.25 (d, J = 4.0 Hz, 2H), 3.88 (dt, J_1 = 9.9 Hz, J_2 = 4.0 Hz, 1H), 2.16 (s, 3H), 2.11 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H). \textbf{^13C NMR} (75 MHz, CDCl_{3}) \delta ppm 170.9, 170.3, 169.6, 169.5, 155.0, 154.1, 135.8, 132.6, 122.7, 121.4, 85.0, 76.2, 73.9, 69.8, 68.2, 62.3, 21.0, 20.9, 20.7. \textbf{HRMS} (ESI-TOF) calcd. for C_{20}H_{23}N_{2}O_{9}S_{2} (M + 1)^+: m/z 499.0845. Found: 499.0816.

(2R,3S,4S,5R,6S)-2-(acetoxymethyl)-6-(benzo[c][1,2,5]thiadiazol-5-ylthio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3b):

Light yellow solid (85 mg, >99%). MW: 498.52 g/mol. C_{20}H_{23}N_{2}O_{9}S_{2}. \textbf{^1H NMR} (300 MHz, CDCl_{3}) \delta ppm 8.18 (s, 1H), 7.92 (d, J = 9.2 Hz, 1H), 7.59 (dd, J_1 = 9.2 Hz, J_2 = 1.3 Hz, 1H), 5.50 (d, J = 2.8 Hz, 1H), 5.36 (q, J = 10.0 Hz, 1H), 5.13 (dd, J_1 = 9.9 Hz, J_2 = 3.2 Hz, 1H), 4.93 (d, J = 10.0 Hz, 1H), 4.26–4.18 (m, 2H), 4.10 (dd, J_1 = 12.3 Hz, J_2 = 6.7 Hz, 1H), 2.17 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H), 1.99 (s, 3H). \textbf{^13C NMR} (75 MHz, CDCl_{3}) \delta ppm 170.7, 170.3, 170.2, 169.6, 155.0, 154.0, 136.4, 132.1, 121.8, 121.3, 85.5, 75.0, 72.0, 67.4, 66.9, 62.1, 20.9, 20.8, 20.7. \textbf{HRMS} (ESI-TOF) calcd. for C_{20}H_{23}N_{2}O_{9}S_{2} (M + 1)^+: m/z 499.0845. Found: m/z 499.0820.

(2S,3R,4S,5R)-2-(benzo[c][1,2,5]thiadiazol-5-ylthio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3c):
Light yellow solid (73 mg, >99%). MW: 426.46 g/mol. C\textsubscript{17}H\textsubscript{18}N\textsubscript{2}O\textsubscript{7}S\textsubscript{2}.

\textbf{\textsuperscript{1}H NMR} (300 MHz, CDCl\textsubscript{3}) δ ppm 8.10 (d, J = 0.7 Hz, 1H), 7.93 (d, J = 9.1 Hz, 1H), 7.60 (dd, J\textsubscript{1} = 9.2 Hz, J\textsubscript{2} = 1.5 Hz, 1H), 5.23 (t, J = 7.4 Hz, 1H), 5.12–4.91 (m, 3H), 4.36 (dd, J\textsubscript{1} = 11.9 Hz, J\textsubscript{2} = 4.7 Hz, 1H), 3.56 (dd, J\textsubscript{1} = 11.9 Hz, J\textsubscript{2} = 8.2 Hz, 1H), 2.10 (d, J = 12.5 Hz, 9H).

\textbf{\textsuperscript{13}C NMR} (75 MHz, CDCl\textsubscript{3}) δ ppm 169.8, 169.8, 169.4, 154.8, 154.0, 136.1, 132.3, 122.5, 121.5, 85.3, 71.3, 69.5, 68.1, 64.9, 20.8, 20.8.

\textbf{HRMS} (ESI-TOF) calcd. for C\textsubscript{17}H\textsubscript{19}N\textsubscript{2}O\textsubscript{7}S\textsubscript{2} (M + 1): m/z 427.0634. Found: m/z 427.0610.

(2S,3R,4S,5S)-2-(benzo[c][1,2,5]thiadiazol-5-ylthio)tetrahydro-2H-pyran-3,4,5-triyi triacetate (3e):

Yellow oil (57 mg, 79%). MW: 426.46 g/mol. C\textsubscript{17}H\textsubscript{18}N\textsubscript{2}O\textsubscript{7}S\textsubscript{2}. \textbf{\textsuperscript{1}H NMR} (300 MHz, CDCl\textsubscript{3}) δ ppm 8.16 (s, 1H), 7.92 (d, J = 9.0 Hz, 1H), 7.61 (dd, J\textsubscript{1} = 9.1 Hz, J\textsubscript{2} = 1.1 Hz, 1H), 5.35 (dd, J\textsubscript{1} = 14.1 Hz, J\textsubscript{2} = 6.3 Hz, 2H), 5.19 (dd, J\textsubscript{1} = 8.3 Hz, J\textsubscript{2} = 3.1 Hz, 1H), 5.05 (d, J = 7.6 Hz, 1H), 4.24 (dd, J\textsubscript{1} = 12.7 Hz, J\textsubscript{2} = 4.3 Hz, 1H), 3.81 (d, J = 12.3 Hz, 1H), 2.15 (s, 3H), 2.13 (s, 3H), 2.08 (s, 3H).

\textbf{\textsuperscript{13}C NMR} (75 MHz, CDCl\textsubscript{3}) δ ppm 170.3, 169.9, 169.5, 154.9, 153.9, 136.9, 132.1, 121.8, 121.4, 85.5, 70.3, 68.1, 67.3, 65.4, 21.0, 20.9, 20.8. \textbf{HRMS} (ESI-TOF) calcd. for C\textsubscript{17}H\textsubscript{19}N\textsubscript{2}O\textsubscript{7}S\textsubscript{2} (M + 1): m/z 427.0634. Found: m/z 427.0650.
(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(((2R,3R,4S,5R,6S)-4,5-diacetoxy-2-(acetoxymethyl)-6-(benzo[c][1,2,5]thiadiazol-5-ylthio)tetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3g):

![Chemical structure of 3g]

White solid (134 mg, >99%). MW: 786.77 g/mol. C\textsubscript{32}H\textsubscript{38}N\textsubscript{2}O\textsubscript{17}S\textsubscript{2}. \textsuperscript{1}H NMR (300 MHz, CD\textsubscript{3}CN) δ ppm 8.23 (d, \(J = 0.9\) Hz, 1H), 8.10 (d, \(J = 9.1\) Hz, 1H), 7.76 (dd, \(J_1 = 9.2\) Hz, \(J_2 = 1.6\) Hz, 1H), 5.62–5.51 (m, 1H), 5.42 (td, \(J_1 = 16.2\) Hz, \(J_2 = 10.1\) Hz, 3H), 5.25–5.01 (m, 3H), 4.76 (d, \(J = 11.9\) Hz, 1H), 4.36 (dd, \(J_1 = 12.3\) Hz, \(J_2 = 4.6\) Hz, 2H), 4.26–4.13 (m, 4H), 2.23–2.10 (m, 21H). \textsuperscript{13}C NMR (75 MHz, CD\textsubscript{3}CN) δ ppm 170.4, 170.3, 170.2, 170.0, 169.8, 169.6, 169.5, 154.8, 153.7, 136.2, 131.7, 121.2, 120.9, 96.3, 83.4, 76.2, 75.1, 73.9, 70.0, 69.9, 69.0, 68.7, 67.9, 62.9, 61.5, 20.2, 20.1, 20.0, 19.9, 19.9, 19.9. HRMS (ESI-TOF) calcd. for C\textsubscript{32}H\textsubscript{38}N\textsubscript{2}O\textsubscript{17}S\textsubscript{2}(M + Na): m/z 809.1510. Found: m/z 809.1470.

(2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-(((2R,3R,4S,5R,6S)-4,5-diacetoxy-2-(acetoxymethyl)-6-(benzo[c][1,2,5]thiadiazol-5-ylthio)tetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3h):

![Chemical structure of 3h]

Yellow solid (126 mg, 95%). MW: 786.77 g/mol. C\textsubscript{32}H\textsubscript{38}N\textsubscript{2}O\textsubscript{17}S\textsubscript{2}. \textsuperscript{1}H NMR (300 MHz, CD\textsubscript{3}CN) δ ppm 8.09 (s, 1H), 7.96 (d, \(J = 9.1\) Hz, 1H), 7.63 (dd, \(J_1 = 9.1\) Hz, \(J_2 = 0.8\) Hz, 1H), 5.38–5.17 (m, 3H), 5.13–4.90 (m, 3H), 4.64 (d, \(J = 7.9\) Hz, 1H), 4.52 (d, \(J = 11.0\) Hz, 1H), 4.21–4.00 (m, 4H), 3.93 (dd, \(J_1 = 17.0\) Hz, \(J_2 = 8.2\) Hz, 2H), 2.17–1.91 (m, 21H). \textsuperscript{13}C NMR (75 MHz, CD\textsubscript{3}CN) δ ppm 170.5, 170.1, 169.8, 169.6, 169.4, 154.8, 153.7, 136.5, 131.5, 121.2, 120.5, 100.5, 83.6, 76.5, 75.9, 73.1,
(2R,3R,4S,5R,6S)-2-((acetoxymethyl)-6-(((2-cyanophenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (4a):

Yellow oil (41 mg, 52%). MW: 465.47 g/mol. C_{21}H_{23}NO_{9}S. \textit{^1H NMR} (300 MHz, CDCl\textsubscript{3}) \(\delta\) ppm 7.82 (d, \(J = 7.8\) Hz, 1H), 7.70 (d, \(J = 7.6\) Hz, 1H), 7.58 (t, \(J = 7.7\) Hz, 1H), 7.48 (t, \(J = 7.1\) Hz, 1H), 5.24 (t, \(J = 9.3\) Hz, 1H), 5.04 (t, \(J = 9.8\) Hz, 1H), 4.94 (t, \(J = 9.6\) Hz, 1H), 4.76 (d, \(J = 10.0\) Hz, 1H), 4.22 (dt, \(J_1 = 24.3\) Hz, \(J_2 = 8.4\) Hz, 2H), 3.81–3.71 (m, 1H), 2.15 (s, 3H), 2.10 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H). \textit{^13C NMR} (75 MHz, CDCl\textsubscript{3}) \(\delta\) ppm 170.7, 170.2, 169.7, 169.6, 135.4, 134.9, 133.9, 133.0, 129.4, 118.2, 117.1, 85.2, 76.1, 73.9, 69.5, 68.1, 62.1, 20.9, 20.9, 20.7. \textit{HRMS} (ESI-TOF) calcd. for C_{21}H_{23}NO_{9}S (M + K)^+: m/z 504.0731. Found: m/z 504.0710.

2-((acetoxymethyl)-6-(((2-formylphenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (5a):

Colorless oil (68 mg, 85%). MW: 468.47 g/mol. C_{21}H_{24}O_{10}S. \textit{^1H NMR} (300 MHz, CDCl\textsubscript{3}) \(\delta\) ppm 10.49 (s, 1H), 7.93 (d, \(J = 6.8\) Hz, 1H), 7.65 (d, \(J = 7.3\) Hz, 1H), 7.54 (dt, \(J_1 = 15.1\) Hz, \(J_2 = 6.7\) Hz, 2H), 5.20 (t, \(J = 9.3\) Hz, 1H), 4.96 (td, \(J_1 = 9.5\) Hz, \(J_2 = 6.1\) Hz, 2H), 4.70 (d, \(J = 10.0\) Hz, 1H), 4.10 (d, \(J = 6.0\) Hz, 2H), 3.72–3.69 (m, 1H), 2.09 – 1.97 (m, 12H). \textit{^13C NMR} (75 MHz, CDCl\textsubscript{3}) \(\delta\) ppm 191.84, 170.59, 170.12, 169.34, 169.27, 137.80, 135.67, 134.17, 134.02, 129.46, 129.40, 84.59, 75.79, 73.78, 69.88, 67.93, 61.94, 20.70, 20.63, 20.55. \textit{HRMS} (ESI-TOF) calcd. for C_{21}H_{24}KO_{10}S (M + K)^+: m/z 507.0727. Found: m/z 507.0740.
(2S,3R,4S,5S)-2-(2-formylphenylthio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (4e):

Colorless oil (59 mg, 88%). MW: 396.41 g/mol. C<sub>18</sub>H<sub>20</sub>O<sub>8</sub>S. ¹H NMR (300 MHz, CDCl<sub>3</sub>) δ ppm 10.50 (s, 1H), 7.92 (d, J = 7.1 Hz, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.4 Hz, 1H), 5.26 (t, J = 7.8 Hz, 2H), 5.12 (dd, J<sub>1</sub> = 8.1 Hz, J<sub>2</sub> = 2.9 Hz, 1H), 4.84 (d, J = 7.6 Hz, 1H), 4.20–4.06 (m, 2H), 3.68 (d, J = 12.6 Hz, 1H), 2.09 (dd, J<sub>1</sub> = 13.5 Hz, J<sub>2</sub> = 8.4 Hz, 9H). ¹³C NMR (75 MHz, CDCl<sub>3</sub>) δ ppm 192.0, 170.3, 170.1, 169.5, 136.9, 136.8, 134.4, 134.3, 130.0, 128.7, 86.0, 70.4, 68.6, 67.4, 65.3, 60.5, 21.0, 21.0, 20.9. HRMS (ESI-TOF) calcd. for C<sub>18</sub>H<sub>20</sub>KO<sub>8</sub>S (M + K)<sup>+</sup>: m/z 435.0516. Found: m/z 435.0530.

(2S,3R,4S,5S)-2-(((E)-styryl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (5e):

Yellow oil (50 mg, 75%). MW: 394.43 g/mol. C<sub>19</sub>H<sub>22</sub>O<sub>7</sub>S. ¹H NMR (300 MHz, CDCl<sub>3</sub>) δ ppm 7.39–7.19 (m, 5H), 6.77 (d, J = 3.2 Hz, 2H), 5.33 (t, J = 8.1 Hz, 2H), 5.12 (dd, J<sub>1</sub> = 8.7 Hz, J<sub>2</sub> = 3.3 Hz, 1H), 4.75 (d, J = 8.1 Hz, 1H), 4.18–4.11 (m, 1H), 3.73 (d, J = 12.9 Hz, 1H), 2.08 (dd, J<sub>1</sub> = 18.7 Hz, J<sub>2</sub> = 5.5 Hz, 9H). ¹³C NMR (75 MHz, CDCl<sub>3</sub>) δ ppm 170.48, 170.20, 169.67, 136.55, 133.50, 128.86, 127.97, 126.30, 120.04, 84.54, 70.74, 68.34, 67.81, 21.13, 21.03, 20.92. HRMS (ESI-TOF) calcd. for C<sub>19</sub>H<sub>22</sub>NaO<sub>7</sub>S (M + Na)<sup>+</sup>: m/z 417.0978. Found: m/z 417.1000.

(2S,3R,4S,5S)-2-((2-(phenylcarbamoyl)phenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (6e):
Yellow oil (72 mg, 87%). MW: 487.52 g/mol. C_{24}H_{25}NO_{8}S. \textbf{^1H NMR} (300 MHz, CDCl_3) δ ppm 8.81 (s, 1H), 7.73 – 7.66 (m, 4H), 7.43 – 7.41 (m, 2H), 7.32 (t, J = 7.7 Hz, 2H), 7.11 (t, J = 7.3 Hz, 1H), 5.08 (dd, J_1 = 9.0 Hz, J_2 = 2.9 Hz, 1H), 4.84 (d, J = 8.8 Hz, 1H), 4.12 – 4.05 (m, 3H), 3.63 (d, J = 12.6 Hz, 1H), 2.01 – 1.97 (m, 9H). \textbf{^{13}C NMR} (75 MHz, CDCl_3) δ ppm 170.27, 170.13, 169.79, 166.27, 141.52, 138.42, 135.72, 131.14, 129.82, 129.50, 129.15, 124.55, 119.96, 88.46, 70.94, 68.25, 67.80, 53.65, 21.06, 20.88, 20.82. \textbf{HRMS} (ESI-TOF) calcd. for C_{24}H_{26}NO_{8}S (M + 1)^+: m/z 488.1374. Found: m/z 488.1370.

(2S,3R,4S,5S)-2-(((2-(2-methoxyphenyl)carbamoyl)phenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (7e):

Yellow oil (55 mg, 63%). MW: 517.55 g/mol. C_{25}H_{27}NO_{9}S. \textbf{^1H NMR} (300 MHz, CDCl_3) δ ppm 8.52 (d, J = 7.3 Hz, 1H), 8.41 (s, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.44-7.39 (m, 2H), 7.05 (dt, J_1 = 14.5 Hz, J_2 = 7.0 Hz, 2H), 6.92 (d, J = 7.9 Hz, 1H), 5.30-5.22 (m, 3H), 5.08 (dd, J_1 = 8.3 Hz, J_2 = 3.0 Hz, 1H), 4.88 (d, J = 7.8 Hz, 1H), 3.87 (s, 3H), 3.64 (d, J = 11.4 Hz, 1H), 2.05 (t, J = 11.4 Hz, 9H). \textbf{^{13}C NMR} (75 MHz, CDCl_3) δ ppm 170.40, 170.14,
169.77, 166.28, 148.40, 140.57, 134.21, 131.30, 130.80, 128.56, 128.45, 127.82, 124.36, 121.31, 120.27, 110.26, 86.85, 70.58, 68.43, 67.65, 55.94, 21.25, 21.07, 20.85, 20.72. **HRMS** (ESI-TOF) calcd. for C_{25}H_{28}NO_{9}S (M + 1)^+: m/z 518.1479. Found: m/z 518.1449.

2-(benzo[c][1,2,5]thiadiazol-5-ylthio)-6-(hydroxymethyl)tetrahydro-2H-pyran-3,4,5-triol (6a):

White solid (20 mg, >99%). MW: 330.37 g/mol. C_{12}H_{14}N_{2}O_{5}S_{2}. **^1H NMR** (300 MHz, DMSO-d_{6}) δ ppm 8.05 (s, 1H), 8.00 (d, J = 9.2 Hz, 1H), 7.69 (d, J = 9.2 Hz, 1H), 4.93 (d, J = 9.7 Hz, 2H), 3.70 (d, J = 11.4 Hz, 1H), 3.40 – 3.08 (m, 7H). **^1^C NMR** (75 MHz, DMSO-d_{6}) δ ppm 154.69, 153.15, 138.79, 131.67, 121.29, 118.57, 86.06, 80.68, 77.86, 72.39, 69.85, 61.15. **HRMS** (ESI-TOF) calcd. for C_{12}H_{14}N_{2}NaO_{5}S_{2} (M + Na)^+: m/z 353.0236. Found: m/z 353.0232.

(2S,3R,4S,5R,6R)-2-(benzo[c][1,2,5]thiadiazol-5-ylthio)-6-(hydroxymethyl)tetrahydro-2H-pyran-3,4,5-triol (4b):

White solid (18 mg, 90%). MW: 330.37 g/mol. C_{12}H_{14}N_{2}O_{5}S_{2}. **^1H NMR** (300 MHz, DMSO-d_{6}) δ ppm 8.06 (s, 1H), 7.99 (d, J = 9.0 Hz, 1H), 7.67 (d, J = 9.1 Hz, 1H), 5.04 – 4.77 (m, 2H), 3.82 – 3.41 (m, 9H). **^1^C NMR** (75 MHz, DMSO-d_{6}) δ ppm 154.75, 153.10, 139.25, 131.55, 121.26, 118.18, 86.54, 79.36, 74.50, 68.78, 61.14. **HRMS** (ESI-TOF) calcd. for C_{12}H_{14}N_{2}NaO_{5}S_{2} (M + Na)^+: m/z 353.0236. Found: m/z 353.0244.
(2S,3R,4S,5S)-2-(benzo[c][1,2,5]thiadiazol-5-ylthio)tetrahydro-2H-pyran-3,4,5-triol (8e):

White solid (16 mg, 76%). MW: 300.34 g/mol. C_{11}H_{12}N_{2}O_{4}S_{2}. \textbf{H NMR} (300 MHz, DMSO-d$_6$) $\delta$ ppm 8.00 (d, $J = 9.4$ Hz, 2H), 7.66 (d, $J = 8.8$ Hz, 1H), 5.12 (d, $J = 5.4$ Hz, 1H), 3.87 – 3.57 (m, 8H). \textbf{C NMR} (75 MHz, DMSO-d$_6$) $\delta$ ppm 154.69, 153.13, 139.34, 131.68, 121.38, 118.39, 86.52, 72.98, 69.99, 67.69. \textbf{HRMS} (ESI-TOF) calcd. for C$_{11}$H$_{13}$N$_2$O$_4$S$_2$ (M + 1)$^+$: m/z 301.0311. Found: m/z 301.0296.

2-(hydroxymethyl)tetrahydro-2H-pyran-3-yloxy)-6-(hydroxymethyl)tetrahydro-2H-pyran-3,4,5-triol (4g):

White solid (30 mg, >99%). MW: 492.51 g/mol. C$_{18}$H$_{24}$N$_2$O$_{10}$S$_2$. \textbf{H NMR} (300 MHz, DMSO-d$_6$) $\delta$ ppm 8.07 (s, 1H), 8.01 (d, $J = 9.2$ Hz, 1H), 7.70 (d, $J = 9.2$ Hz, 1H), 6.21 – 5.91 (m, 3H), 5.32 (d, $J = 48.2$ Hz, 2H), 5.06 – 5.01 (m, 2H), 4.69 (s, 2H), 3.78 – 3.46 (m, 9H), 3.25 (t, $J = 9.1$ Hz, 2H), 3.08 (t, $J = 9.1$ Hz, 1H). \textbf{C NMR} (75 MHz, DMSO-d$_6$) $\delta$ ppm 154.69, 153.18, 138.60, 131.70, 121.34, 118.70, 85.91, 79.13, 77.95, 73.31, 72.06, 69.90, 61.94, 60.85, 54.65. \textbf{HRMS} (ESI-TOF) calcd. for C$_{18}$H$_{24}$N$_2$NaO$_{10}$S$_2$ (M + Na)$^+$: m/z 515.0765. Found: m/z 515.0747.
4. Copy of $^1$H and $^{13}$C-NMR spectra
Supplementary References