Supporting Information

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

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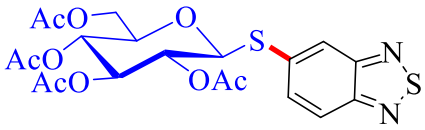
1. General Procedures: All reactions were carried out using chemical reagents and solvents without any specific treatment. The respective reactions were monitored by Thin Layer Chromatography (TLC) MACHEREY-NAGEL (SIL G/UV_{254}) and were visualized by fluorescence quenching with UV light at 254 nm. 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_3N (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_2SO_4, and concentrated under vacuum. The obtained products were purified by column chromatography using hexane/ethyl acetate, 70:30 as the eluent.

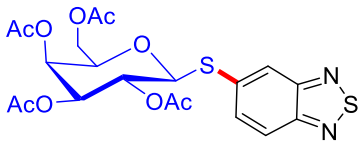
3. Typical Procedure for the Synthesis of Unprotected S-Linked Saccharides: In a small balloon was placed a mixture of S-linked saccharides (0.06 mmol) and K_2CO_3 (0.3 equiv) in methanol (0.6 mL), and the mixture was stirred under N_2 atmosphere at room temperature for 3 h. The crude mixture was then filtered through Celite and washed with 10 mL of methanol. The filtrate was concentrated under reduced pressure at 25 °C 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**):*



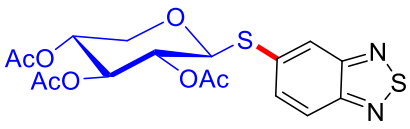
Light yellow solid (85 mg, >99%). MW: 498.52 g/mol. $C_{20}H_{22}N_2O_9S_2$. **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 8.13 (d, *J* = 0.9 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.59 (dd, J_1 = 9.2 Hz, J_2 = 1.7 Hz, 1H), 5.30 (t, *J* = 9.3 Hz, 1H), 5.10 (td, J_1 = 9.8 Hz, J_2 = 3.2 Hz, 2H), 4.93 (d, *J* = 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). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 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. **HRMS** (ESI-TOF) calcd. for $C_{20}H_{23}N_2O_9S_2$ $(M + 1)^+$: 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**):*



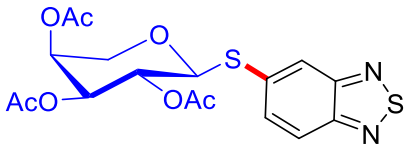
Light yellow solid (85 mg, >99%). MW: 498.52 g/mol. $C_{20}H_{22}N_2O_9S_2$. **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 8.18 (s, 1H), 7.92 (d, *J* = 9.2 Hz, 1H), 7.59 (dd, J_1 = 9.2 Hz, J_2 = 1.3 Hz, 1H), 5.50 (d, *J* = 2.8 Hz, 1H), 5.36 (q, *J* = 10.0 Hz, 1H), 5.13 (dd, J_1 = 9.9 Hz, J_2 = 3.2 Hz, 1H), 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). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 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, 20.9, 20.8, 20.7. **HRMS** (ESI-TOF) calcd. for $C_{20}H_{23}N_2O_9S_2$ $(M + 1)^+$: 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**):*



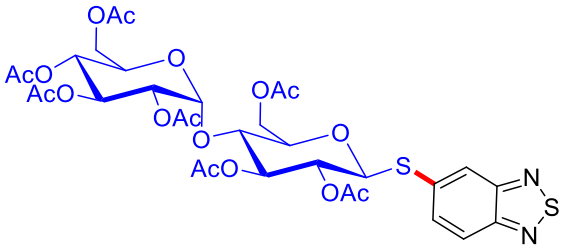
Light yellow solid (73 mg, >99%). MW: 426.46 g/mol. $C_{17}H_{18}N_2O_7S_2$. **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 8.10 (d, *J* = 0.7 Hz, 1H), 7.93 (d, *J* = 9.1 Hz, 1H), 7.60 (dd, J_1 = 9.2 Hz, J_2 = 1.5 Hz, 1H), 5.23 (t, *J* = 7.4 Hz, 1H), 5.12–4.91 (m, 3H), 4.36 (dd, J_1 = 11.9 Hz, J_2 = 4.7 Hz, 1H), 3.56 (dd, J_1 = 11.9 Hz, J_2 = 8.2 Hz, 1H), 2.10 (d, *J* = 12.5 Hz, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) 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. **HRMS** (ESI-TOF) calcd. for $C_{17}H_{19}N_2O_7S_2$ $(M + 1)^+$: 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-triyl triacetate (**3e**):*



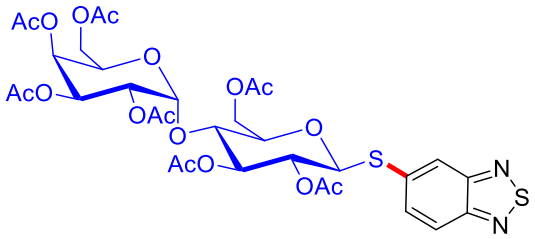
Yellow oil (57 mg, 79%). MW: 426.46 g/mol. $C_{17}H_{18}N_2O_7S_2$. **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 8.16 (s, 1H), 7.92 (d, *J* = 9.0 Hz, 1H), 7.61 (dd, J_1 = 9.1 Hz, J_2 = 1.1 Hz, 1H), 5.35 (dd, J_1 = 14.1 Hz, J_2 = 6.3 Hz, 2H), 5.19 (dd, J_1 = 8.3 Hz, J_2 = 3.1 Hz, 1H), 5.05 (d, *J* = 7.6 Hz, 1H), 4.24 (dd, J_1 = 12.7 Hz, J_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). **^{13}C NMR** (75 MHz, $CDCl_3$) 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. **HRMS** (ESI-TOF) calcd. for $C_{17}H_{19}N_2O_7S_2$ $(M + 1)^+$: 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**):*



White solid (134 mg, >99%). MW: 786.77 g/mol. $C_{32}H_{38}N_2O_{17}S_2$. **^{1}H NMR** (300 MHz, CD_3CN) 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). **^{13}C NMR** (75 MHz, CD_3CN) 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 $C_{32}H_{38}N_2NaO_{17}S_2$ $(M + Na)^+$: m/z 809.1510. Found: m/z 809.1470.

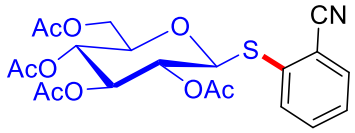
*(2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-(((2R,3R,4S,5R,6S)-4,5-diacetoxy-2-(acetoxymethyl)-6-(benzo[c][1,2,5]thiadiazol-5-ylthio)tetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**3h**):*



Yellow solid (126 mg, 95%). MW: 786.77 g/mol. $C_{32}H_{38}N_2O_{17}S_2$. **^{1}H NMR** (300 MHz, CD_3CN) 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). **^{13}C NMR** (75 MHz, CD_3CN) 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,

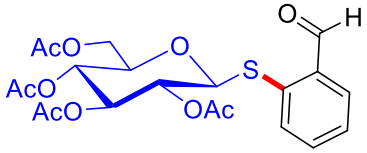
70.6, 70.5, 69.5, 68.9, 67.1, 62.1, 61.0, 20.1, 19.9, 19.9, 19.8. **HRMS** (ESI-TOF) calcd. for $C_{32}H_{38}N_2NaO_{17}S_2$ $(M + Na)^+$: m/z 809.1510. Found: m/z 809.1521.

*(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((2-cyanophenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**4a**):*



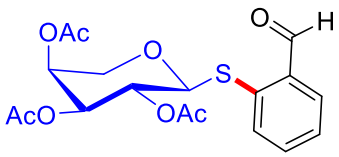
Yellow oil (41 mg, 52%). MW: 465.47 g/mol. $C_{21}H_{23}NO_9S$. **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 7.82 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.1 Hz, 1H), 5.24 (t, *J* = 9.3 Hz, 1H), 5.04 (t, *J* = 9.8 Hz, 1H), 4.94 (t, *J* = 9.6 Hz, 1H), 4.76 (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). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 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. **HRMS** (ESI-TOF) calcd. for $C_{21}H_{23}NKO_9S$ $(M + K)^+$: m/z 504.0731. Found: m/z 504.0710.

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



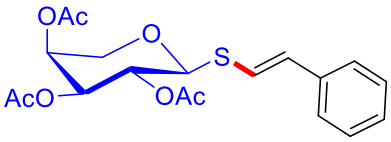
Colorless oil (68 mg, 85%). MW: 468.47 g/mol. $C_{21}H_{24}O_{10}S$. **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 10.49 (s, 1H), 7.93 (d, *J* = 6.8 Hz, 1H), 7.65 (d, *J* = 7.3 Hz, 1H), 7.54 (dt, J_1 = 15.1 Hz, J_2 = 6.7 Hz, 2H), 5.20 (t, *J* = 9.3 Hz, 1H), 4.96 (td, J_1 = 9.5 Hz, J_2 = 6.1 Hz, 2H), 4.70 (d, *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). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 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. **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-formylphenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**4e**):*



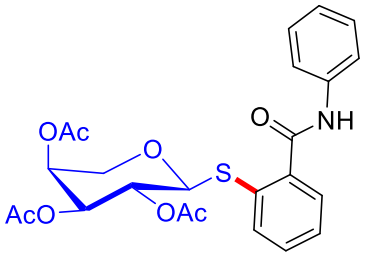
Colorless oil (59 mg, 88%). MW: 396.41 g/mol. $C_{18}H_{20}O_8S$. **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 10.50 (s, 1H), 7.92 (d, *J* = 7.1 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 5.26 (t, *J* = 7.8 Hz, 2H), 5.12 (dd, J_1 = 8.1 Hz, J_2 = 2.9 Hz, 1H), 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_1 = 13.5 Hz, J_2 = 8.4 Hz, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) 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 $C_{18}H_{20}KO_8S$ $(M + K)^+$: 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**):*



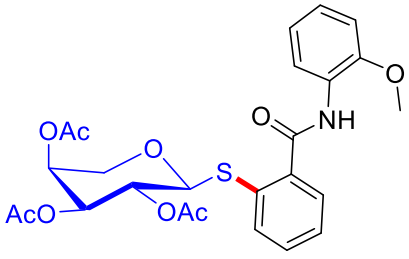
Yellow oil (50 mg, 75%). MW: 394.43 g/mol. $C_{19}H_{22}O_7S$. **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 7.39–7.19 (m, 5H), 6.77 (d, *J* = 3.2 Hz, 2H), 5.33 (t, *J* = 8.1 Hz, 2H), 5.12 (dd, J_1 = 8.7 Hz, J_2 = 3.3 Hz, 1H), 4.75 (d, *J* = 8.1 Hz, 1H), 4.18–4.11 (m, 1H), 3.73 (d, *J* = 12.9 Hz, 1H), 2.08 (dd, J_1 = 18.7 Hz, J_2 = 5.5 Hz, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) 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 $C_{19}H_{22}NaO_7S$ $(M + Na)^+$: 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. $C_{24}H_{25}NO_8S$. **^{1}H 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). **^{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. **HRMS** (ESI-TOF) calcd. for $C_{24}H_{26}NO_8S$ $(M + 1)^+$: m/z 488.1374. Found: m/z 488.1370.

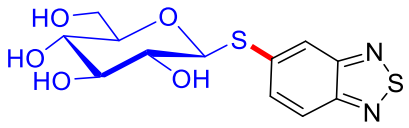
*(2S,3R,4S,5S)-2-((2-((2-methoxyphenyl)carbamoyl)phenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**7e**):*



Yellow oil (55 mg, 63%). MW: 517.55 g/mol. $C_{25}H_{27}NO_9S$. **^{1}H 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). **^{13}C NMR** (75 MHz, $CDCl_3$) δ ppm 170.40, 170.14,

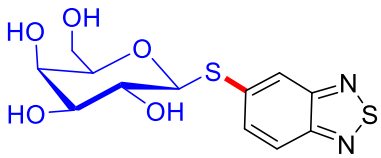
169.77, 166.28, 148.40, 140.57, 134.21, 131.30, 130.80, 128.56, 128.45, 127.82, 124.36, 121.31, 120.27, 110.26, 86.85, 70.58, 68.43, 67.65, 55.94, 21.25, 21.07, 20.85, 20.72. **HRMS** (ESI-TOF) calcd. for $C_{25}H_{28}NO_9S$ $(M + 1)^+$: m/z 518.1479. Found: m/z 518.1449.

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



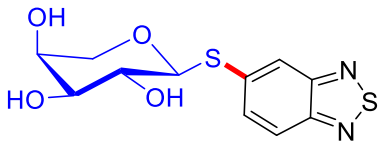
White solid (20 mg, >99%). MW: 330.37 g/mol. $C_{12}H_{14}N_2O_5S_2$. **^{1}H NMR** (300 MHz, DMSO-d_6) δ ppm 8.05 (s, 1H), 8.00 (d, *J* = 9.2 Hz, 1H), 7.69 (d, *J* = 9.2 Hz, 1H), 4.93 (d, *J* = 9.7 Hz, 2H), 3.70 (d, *J* = 11.4 Hz, 1H), 3.40 – 3.08 (m, 7H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ ppm 154.69, 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 $C_{12}H_{14}N_2NaO_5S_2$ $(M + Na)^+$: 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***):



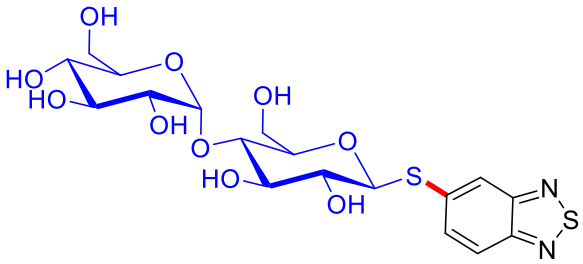
White solid (18 mg, 90%). MW: 330.37 g/mol. $C_{12}H_{14}N_2O_5S_2$. **^{1}H NMR** (300 MHz, DMSO-d_6) δ ppm 8.06 (s, 1H), 7.99 (d, *J* = 9.0 Hz, 1H), 7.67 (d, *J* = 9.1 Hz, 1H), 5.04 – 4.77 (m, 2H), 3.82 – 3.41 (m, 9H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ ppm 154.75, 153.10, 139.25, 131.55, 121.26, 118.18, 86.54, 79.36, 74.50, 68.78, 61.14. **HRMS** (ESI-TOF) calcd. for $C_{12}H_{14}N_2NaO_5S_2$ $(M + Na)^+$: 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**)*:



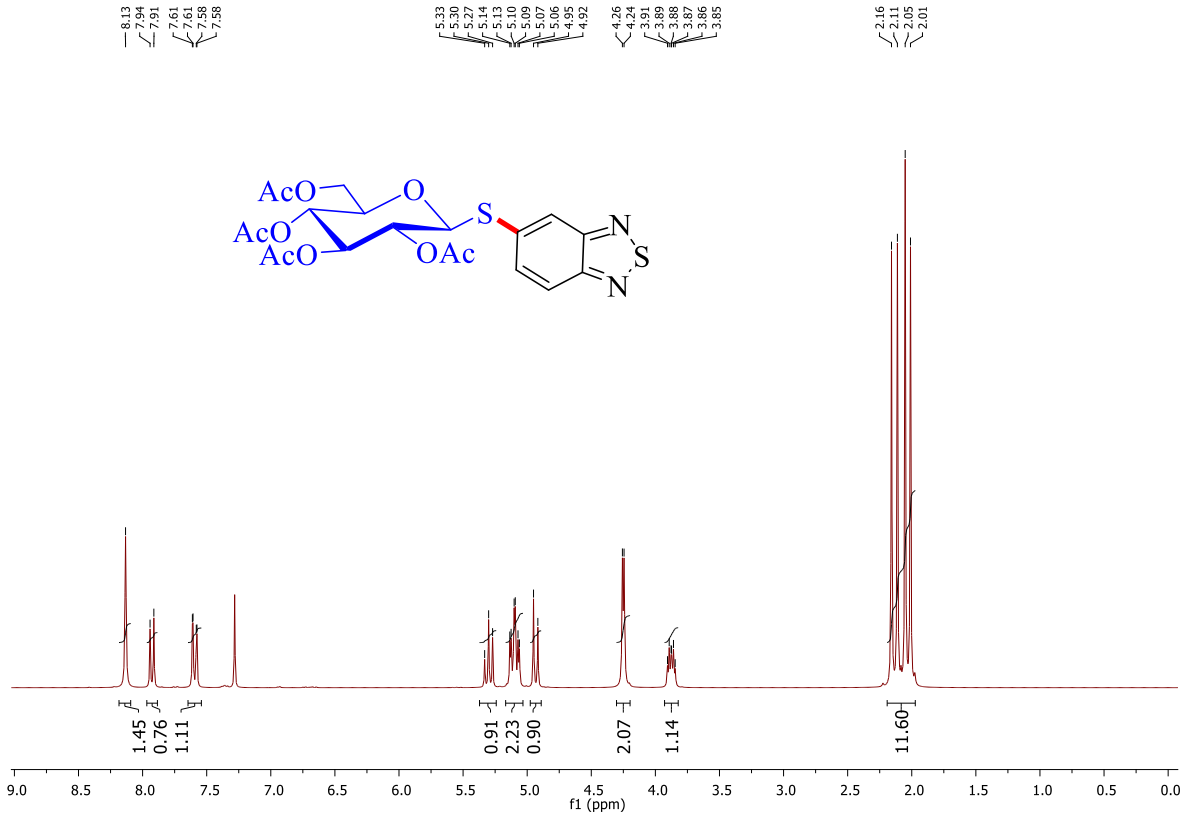
White solid (16 mg, 76%). MW: 300.34 g/mol. $C_{11}H_{12}N_2O_4S_2$. **^{1}H NMR** (300 MHz, DMSO-d_6) δ ppm 8.00 (d, *J* = 9.4 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 1H), 5.12 (d, *J* = 5.4 Hz, 1H), 3.87 – 3.57 (m, 8H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ ppm 154.69, 153.13, 139.34, 131.68, 121.38, 118.39, 86.52, 72.98, 69.99, 67.69. **HRMS** (ESI-TOF) calcd. for $C_{11}H_{13}N_2O_4S_2$ $(M + 1)^+$: m/z 301.0311. Found: m/z 301.0296.

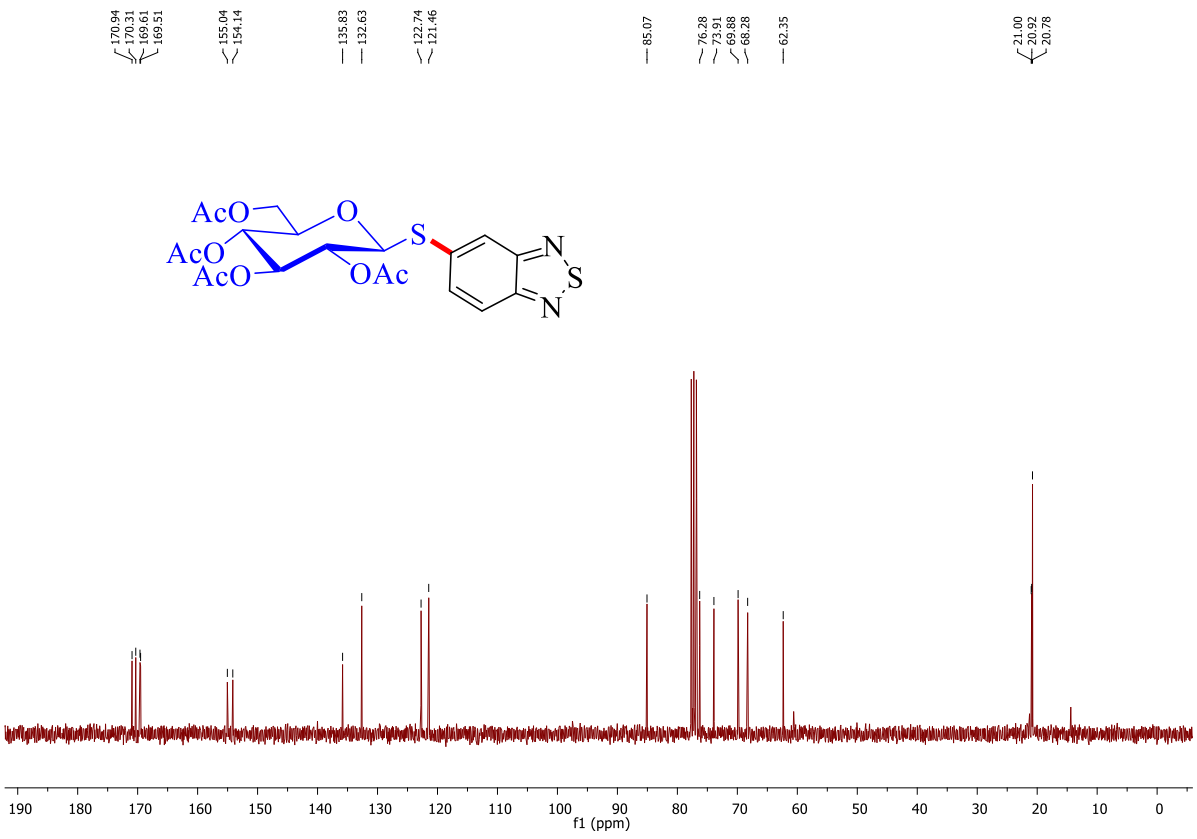
*2-(hydroxymethyl)tetrahydro-2H-pyran-3-yl)oxy)-6-(hydroxymethyl)tetrahydro-2H-pyran-3,4,5-triol (**4g**)*:

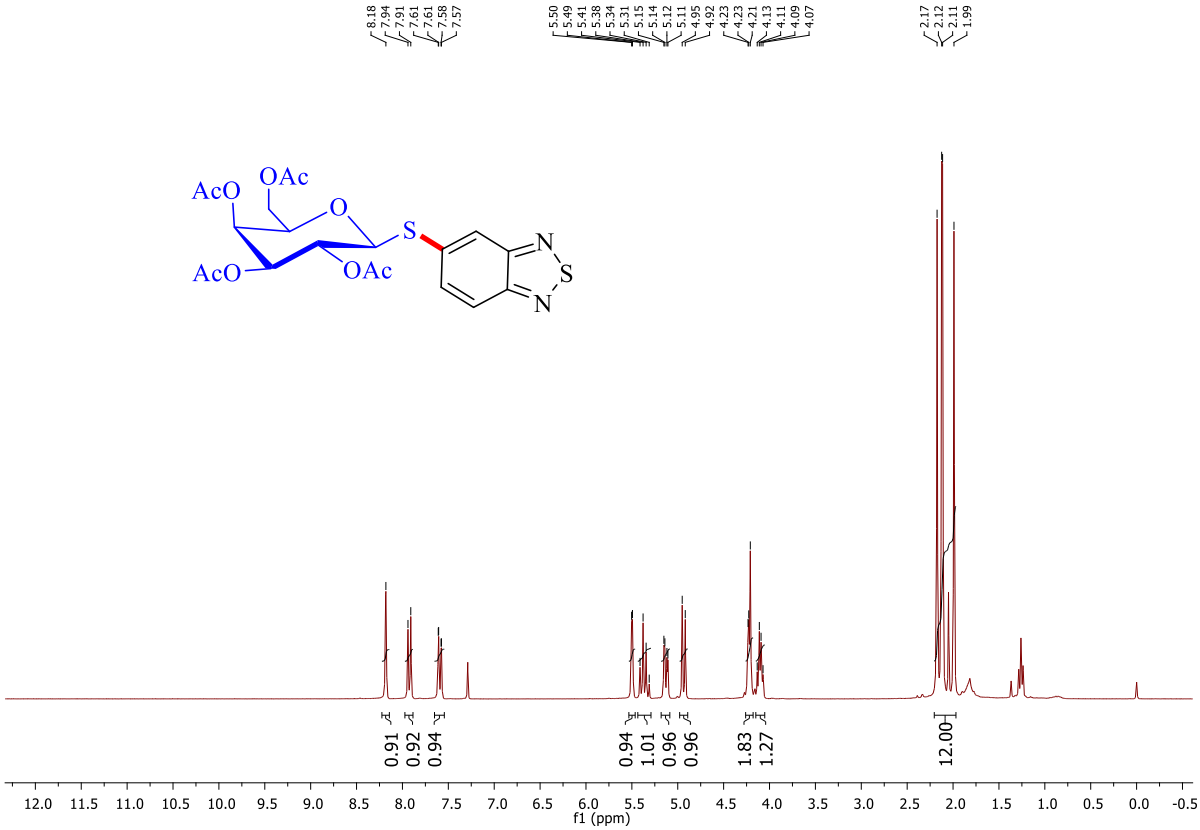


White solid (30 mg, >99%). MW: 492.51g/mol. $C_{18}H_{24}N_2O_{10}S_2$. **^{1}H NMR** (300 MHz, DMSO-d_6) δ ppm 8.07 (s, 1H), 8.01 (d, *J* = 9.2 Hz, 1H), 7.70 (d, *J* = 9.2 Hz, 1H), 6.21 – 5.91 (m, 3H), 5.32 (d, *J* = 48.2 Hz, 2H), 5.06 – 5.01 (m, 2H), 4.69 (s, 2H), 3.78 – 3.46 (m, 9H), 3.25 (t, *J* = 9.1 Hz, 2H), 3.08 (t, *J* = 9.1 Hz, 1H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ 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. **HRMS** (ESI-TOF) calcd. for $C_{18}H_{24}N_2NaO_{10}S_2$ $(M + Na)^+$: m/z 515.0765. Found: m/z 515.0747.

4. Copy of ^{1}H and ^{13}C-NMR spectra



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5.15
5.14
5.12
5.11
4.95
4.92
4.23
4.23
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4.13
4.11
4.09
4.07
2.17
2.12
2.11
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OAc
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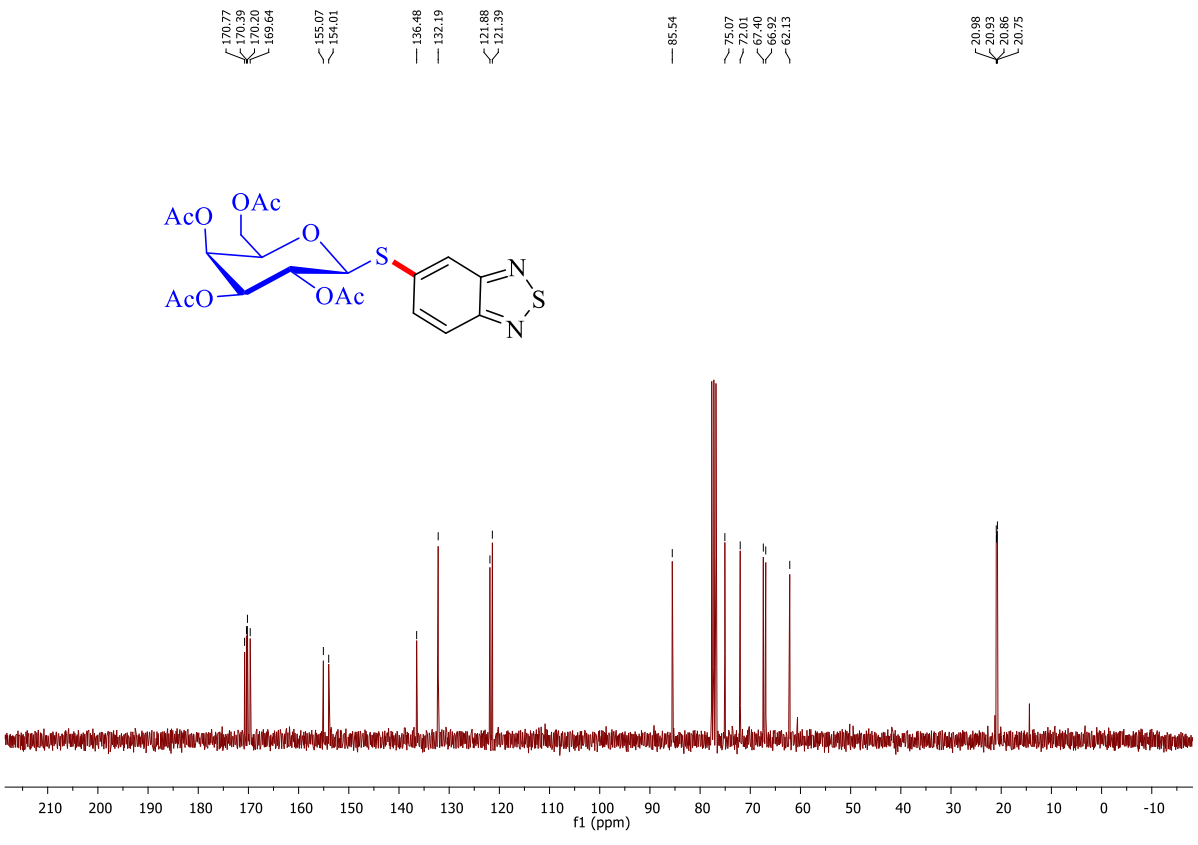
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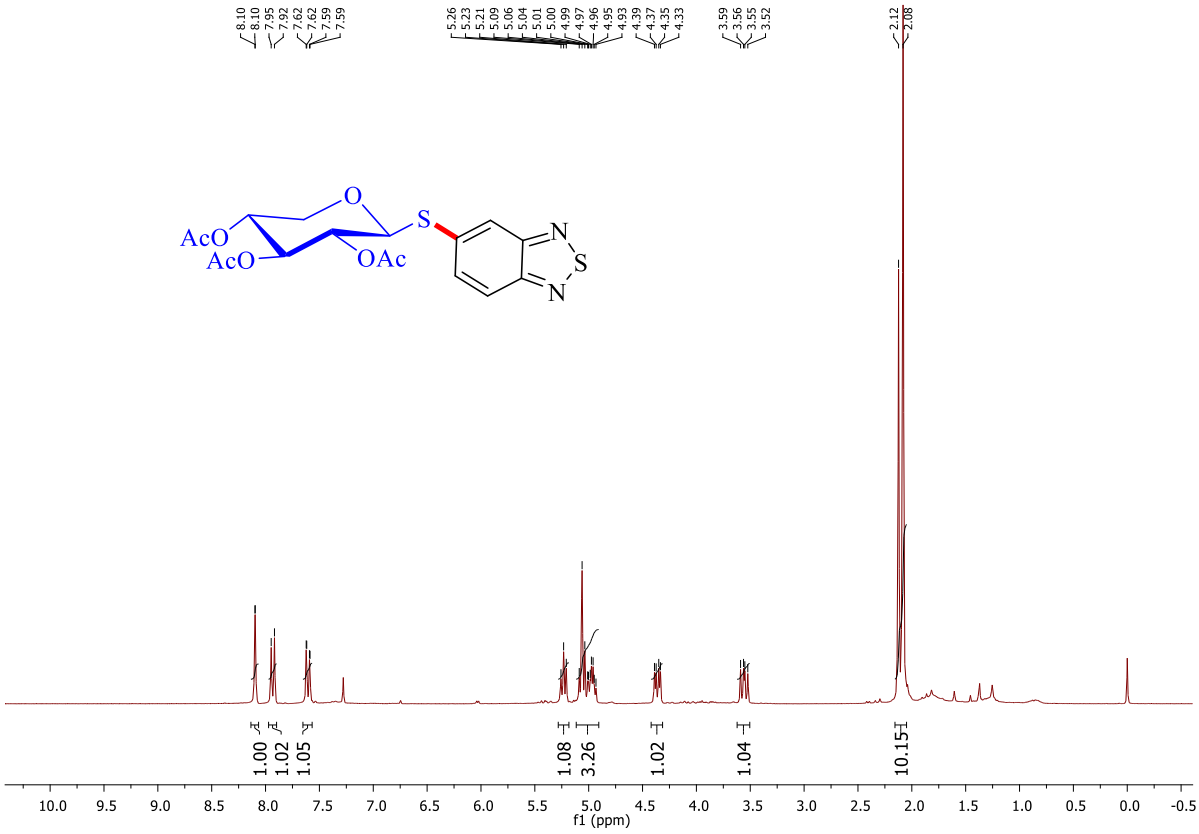
S
N
f1 (ppm)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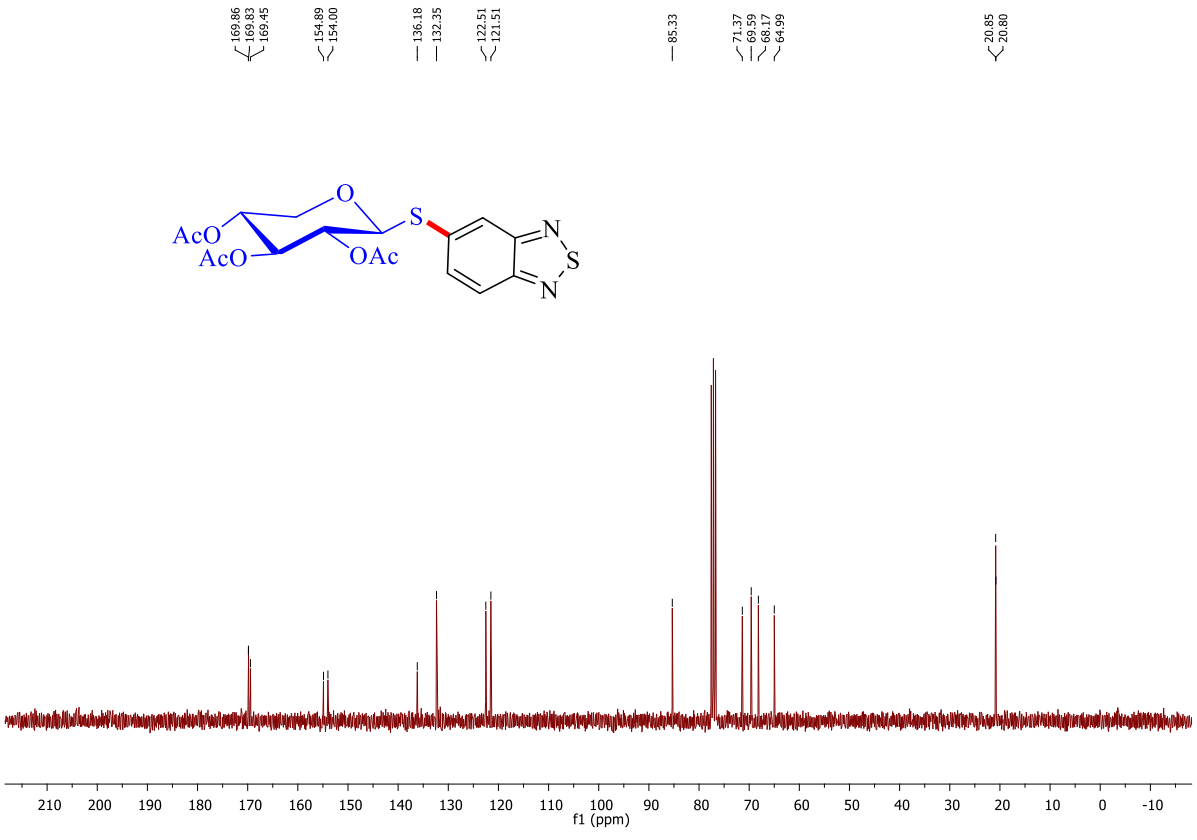
f1 (ppm)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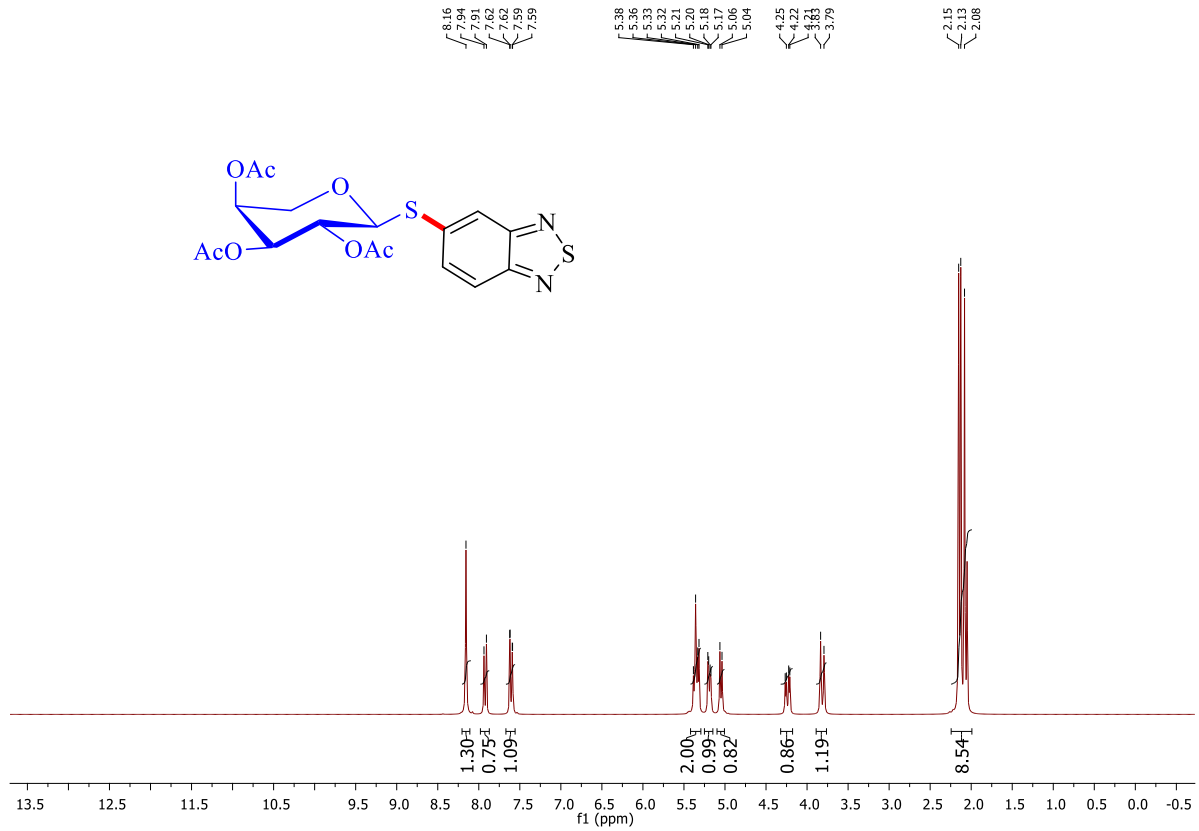
N
f1 (ppm)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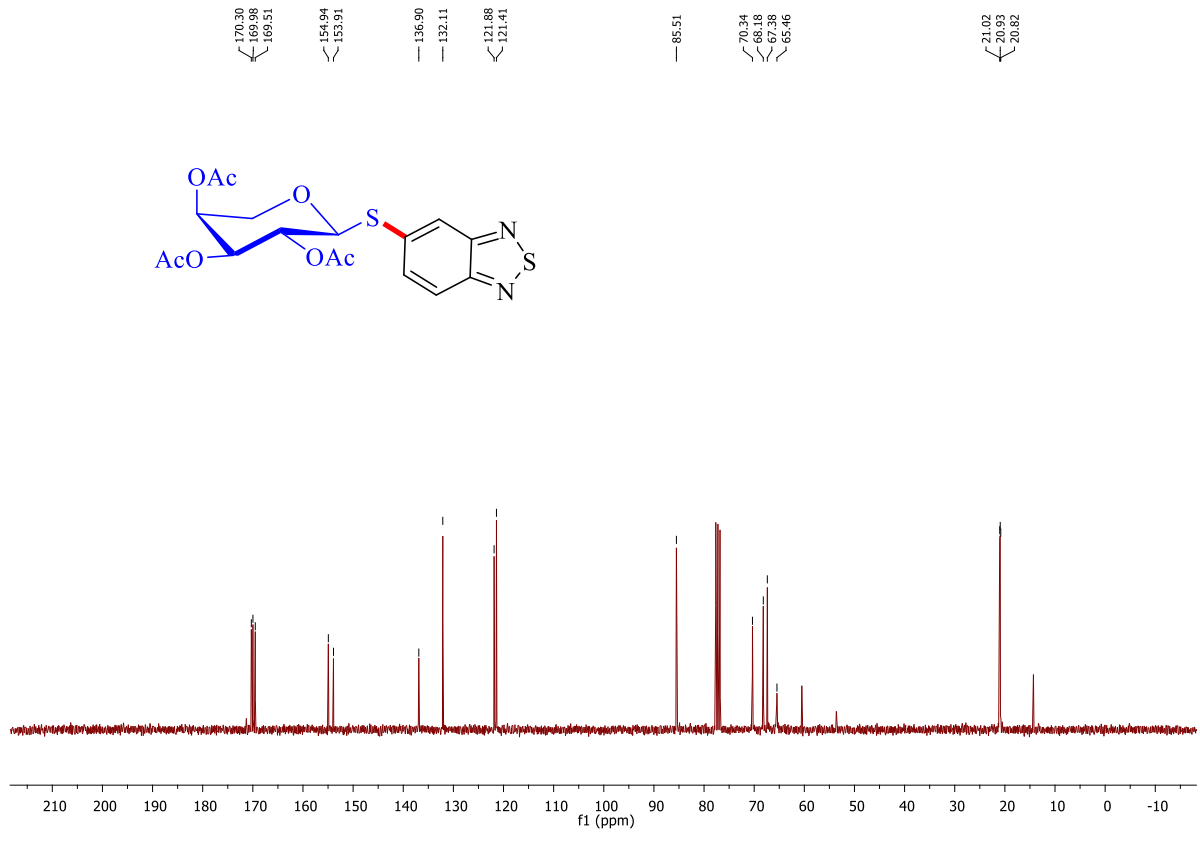
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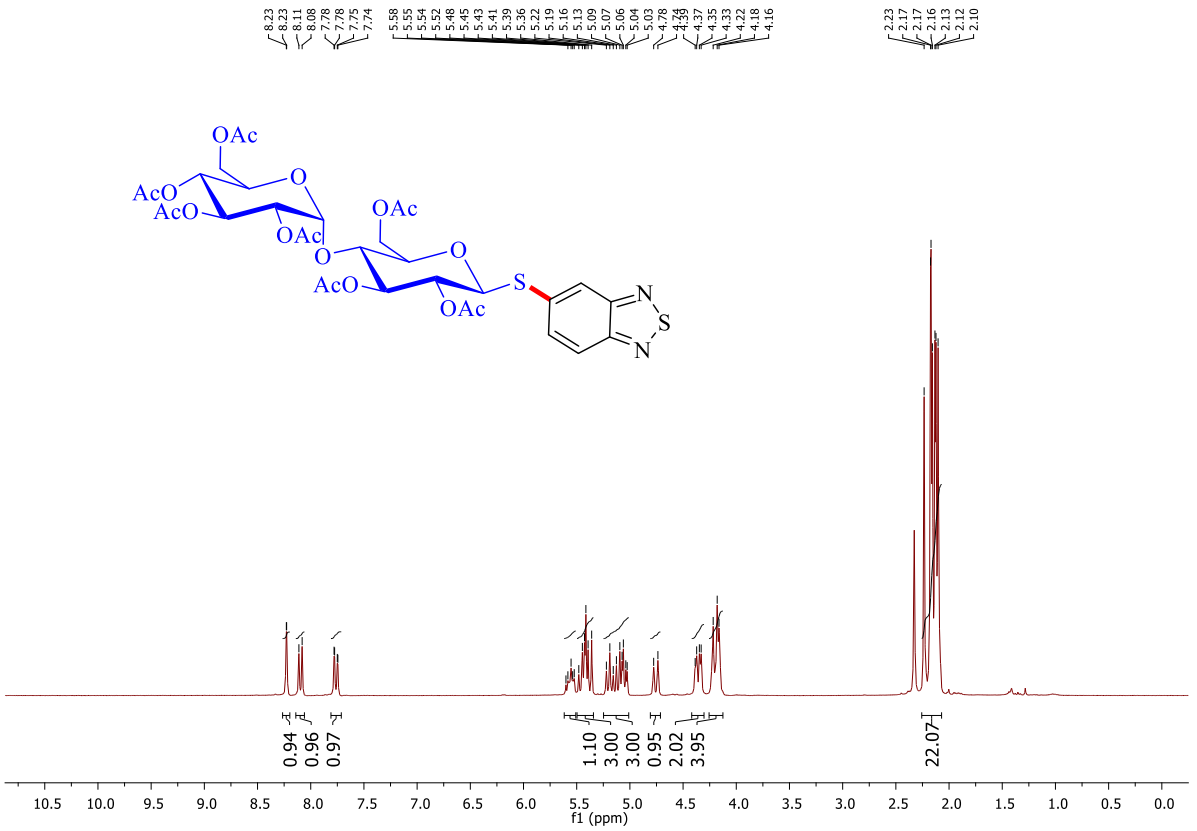
f1 (ppm)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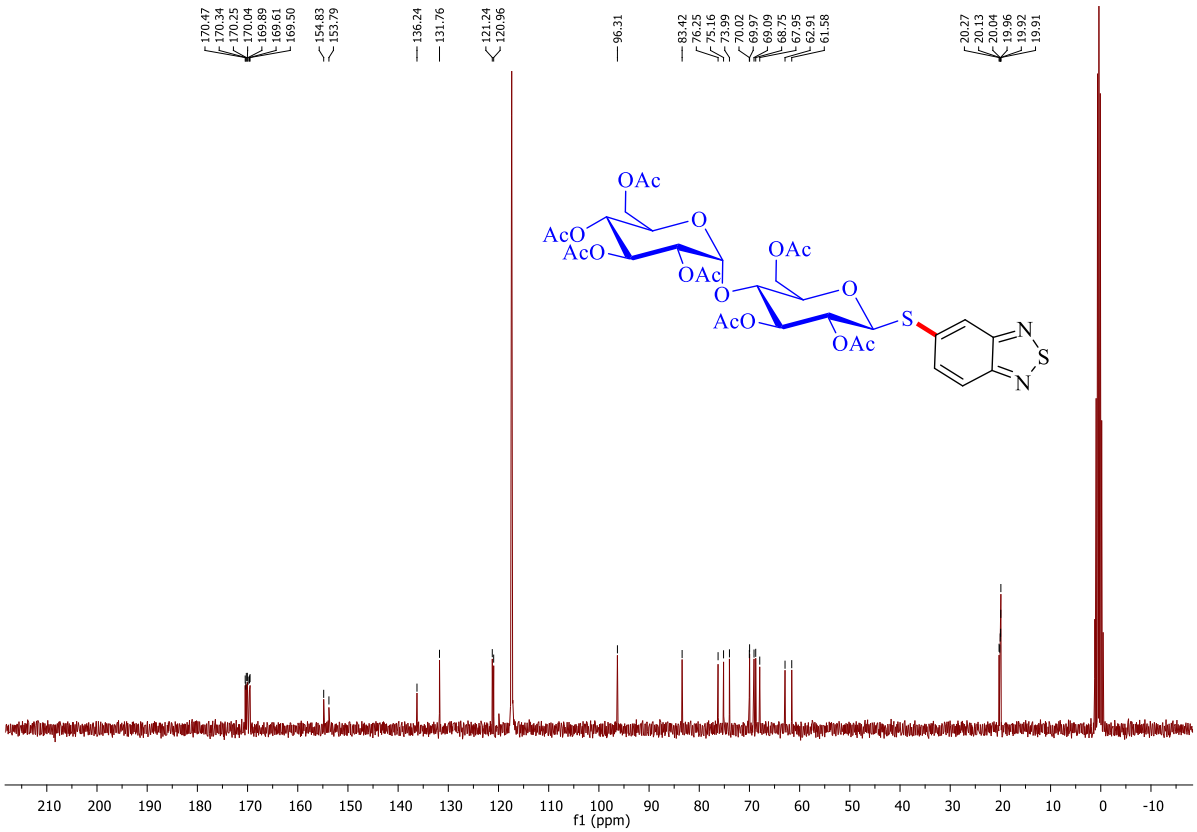
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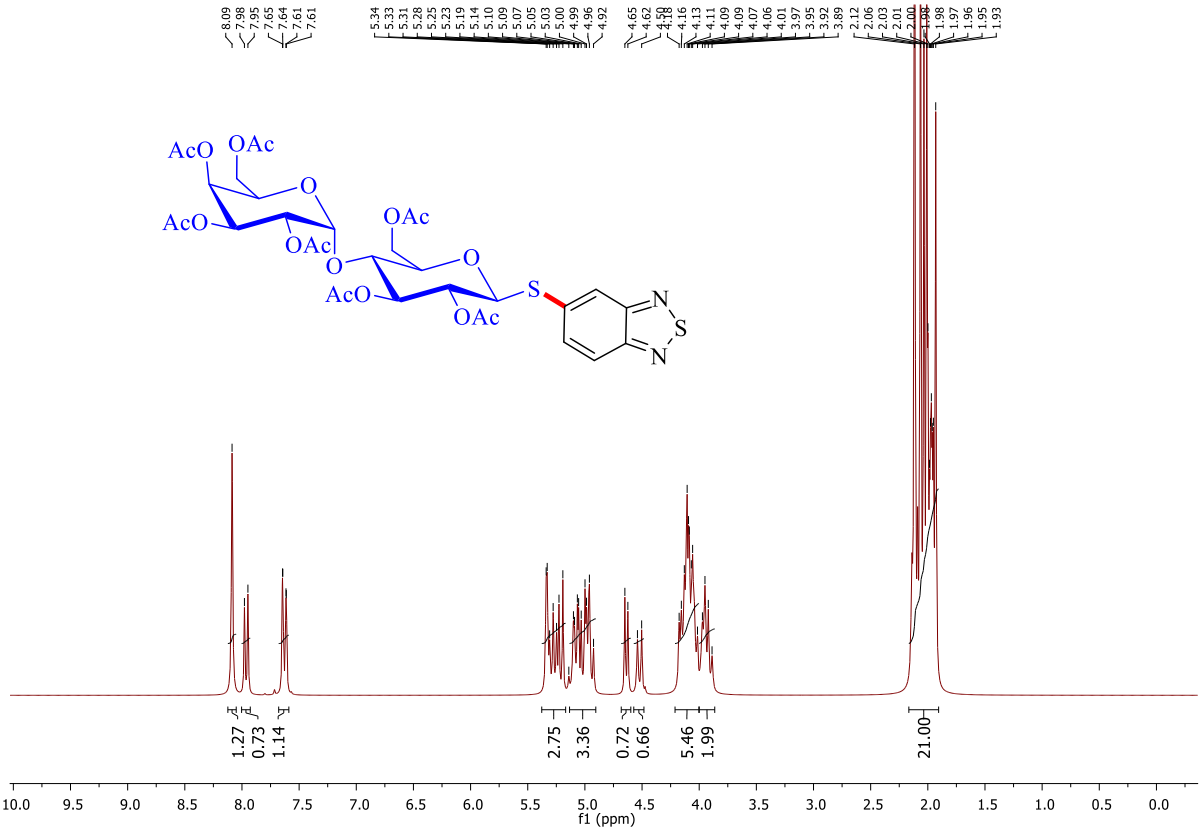
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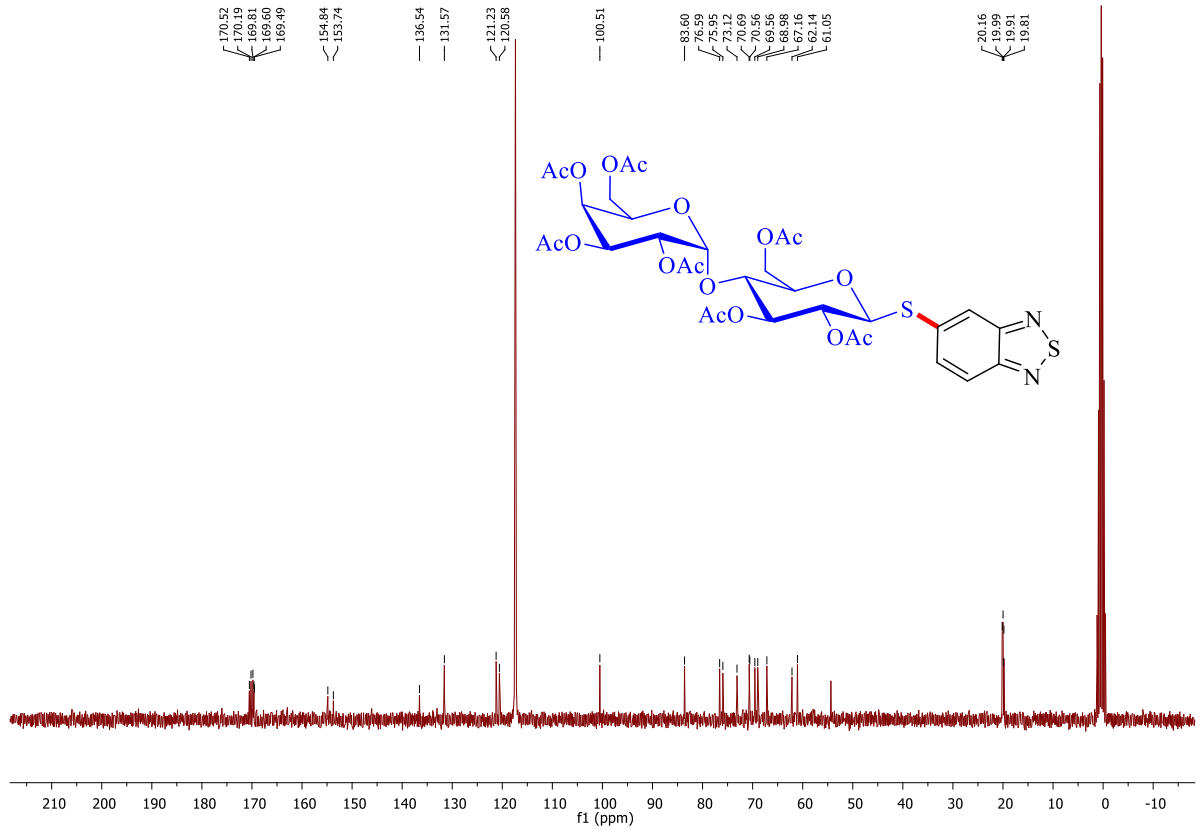
f1 (ppm)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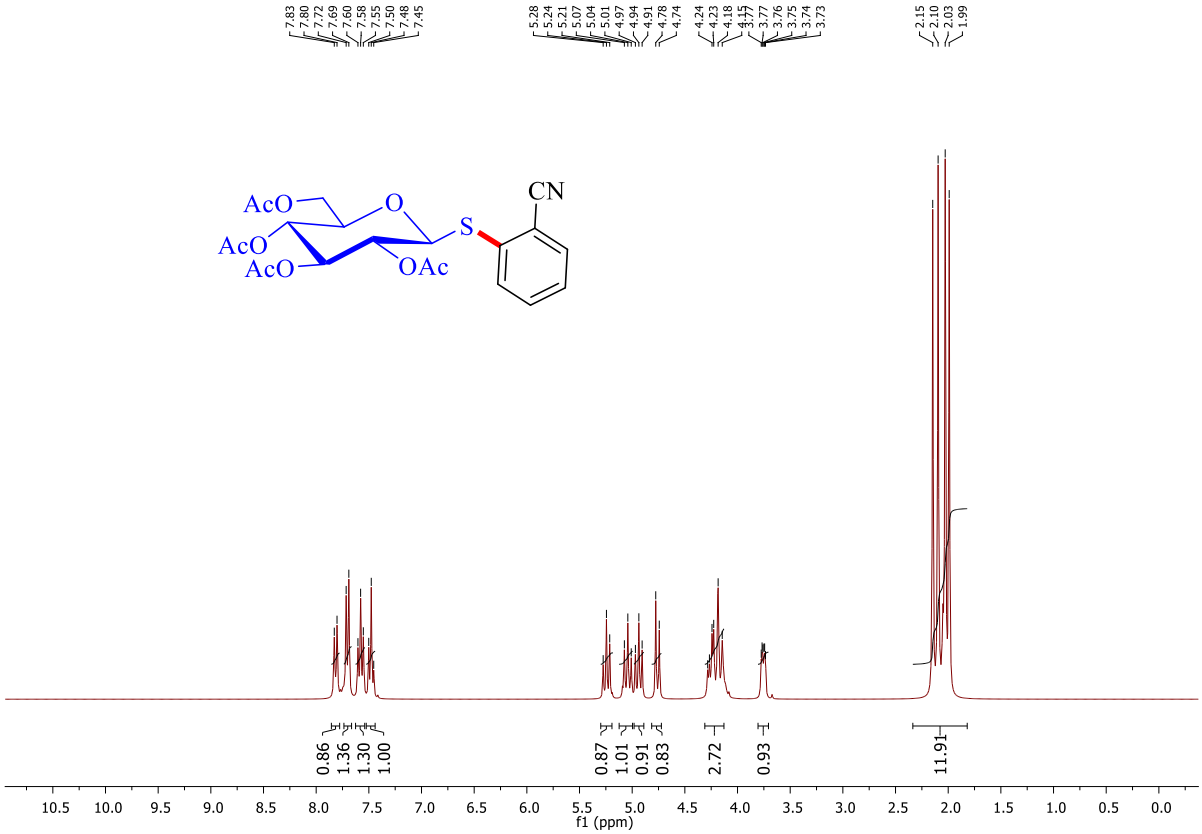
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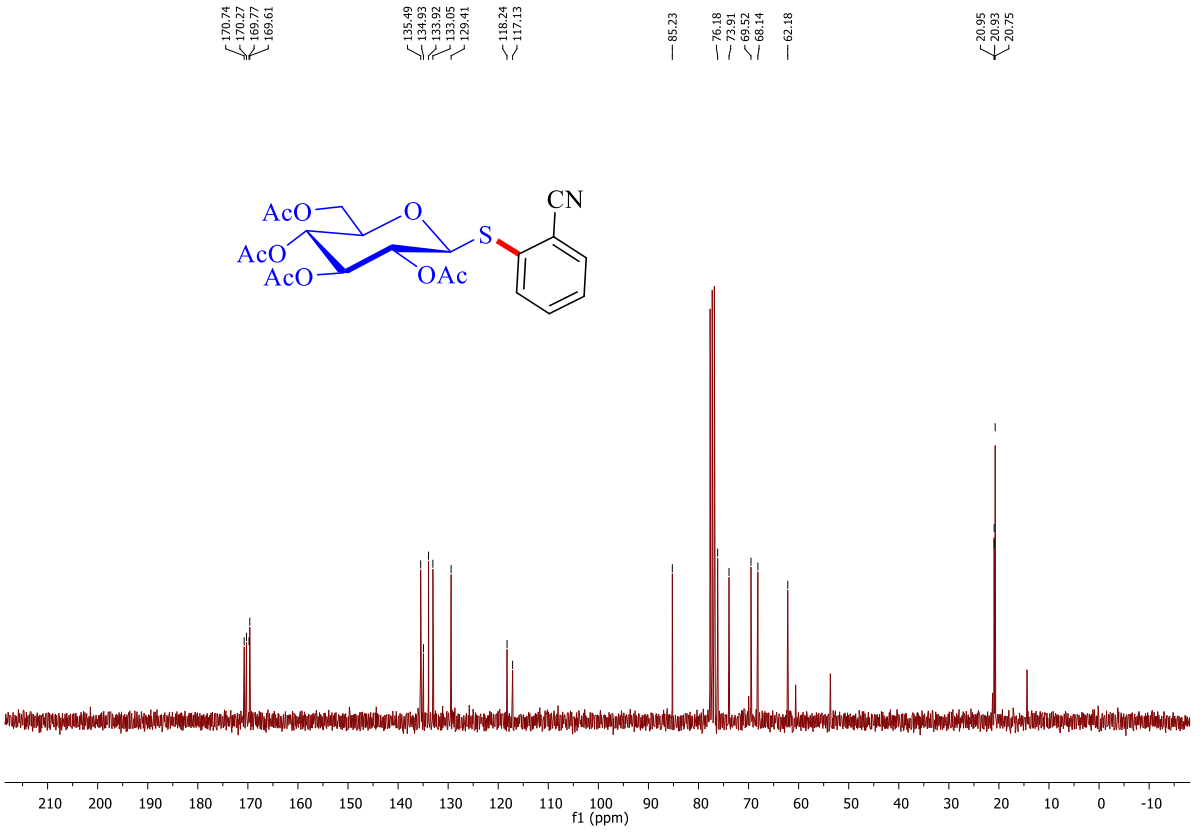
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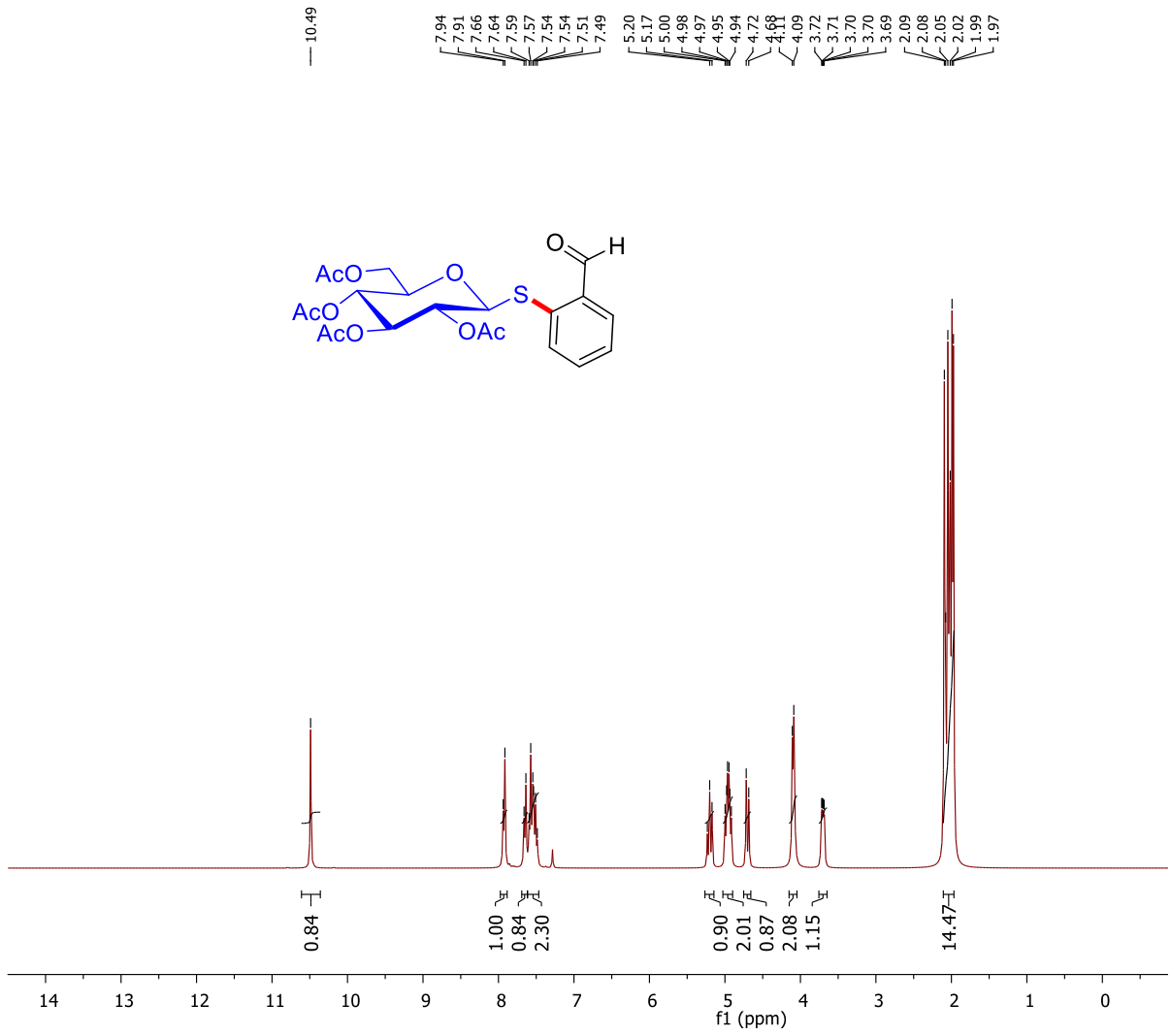
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O
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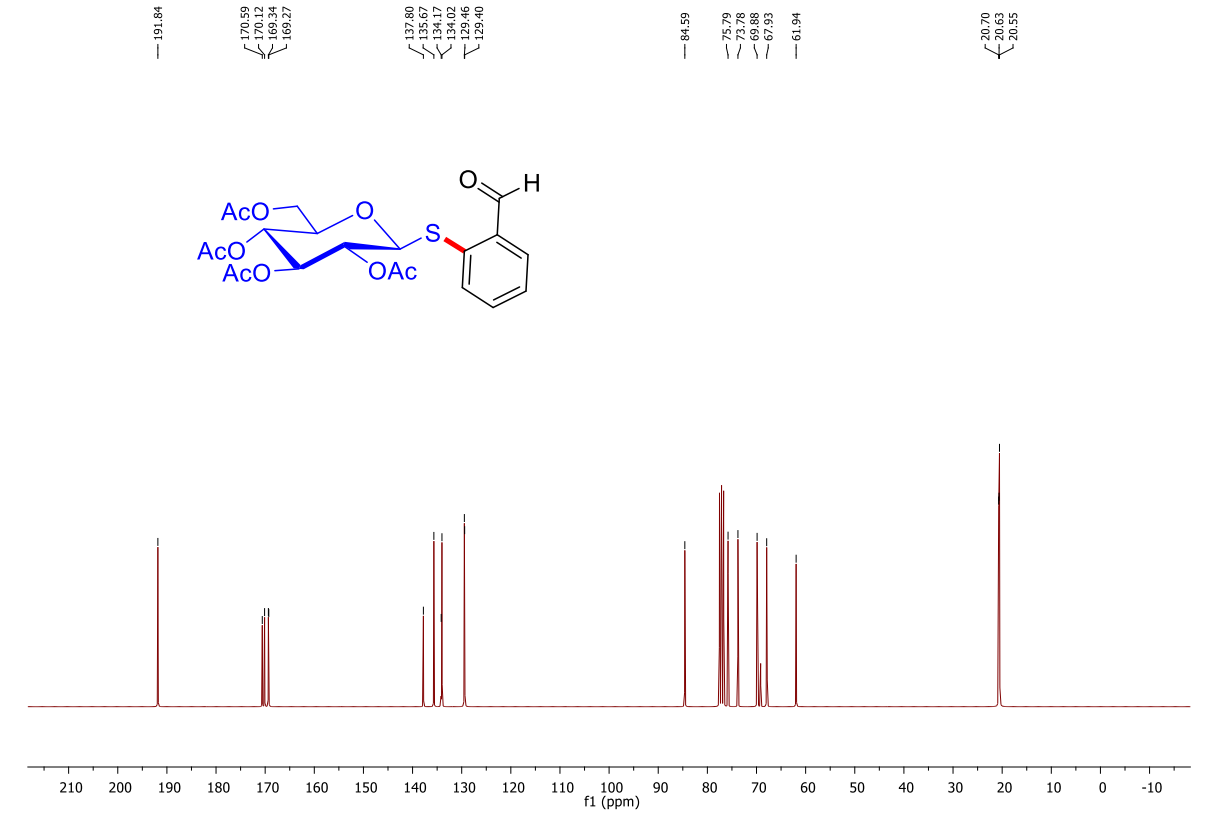
f1 (ppm)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67.93
61.94
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20.63
20.55
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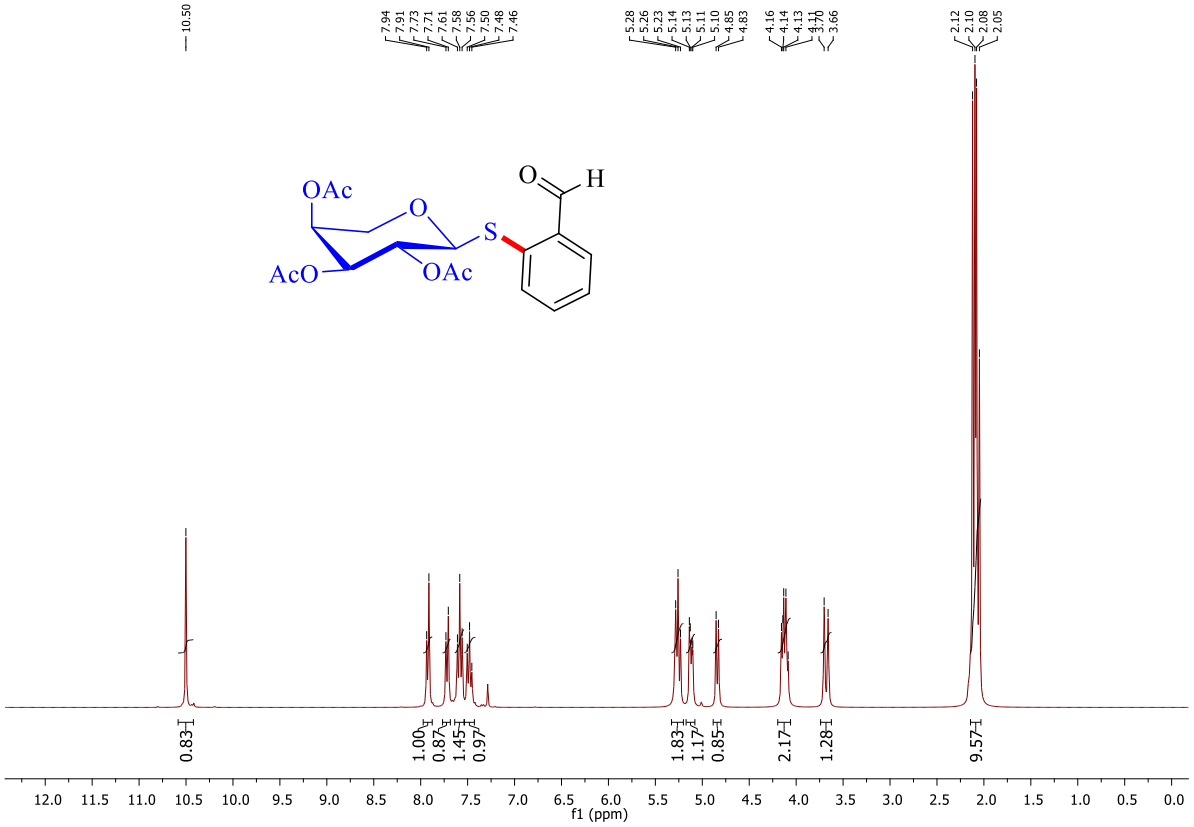
f1 (ppm)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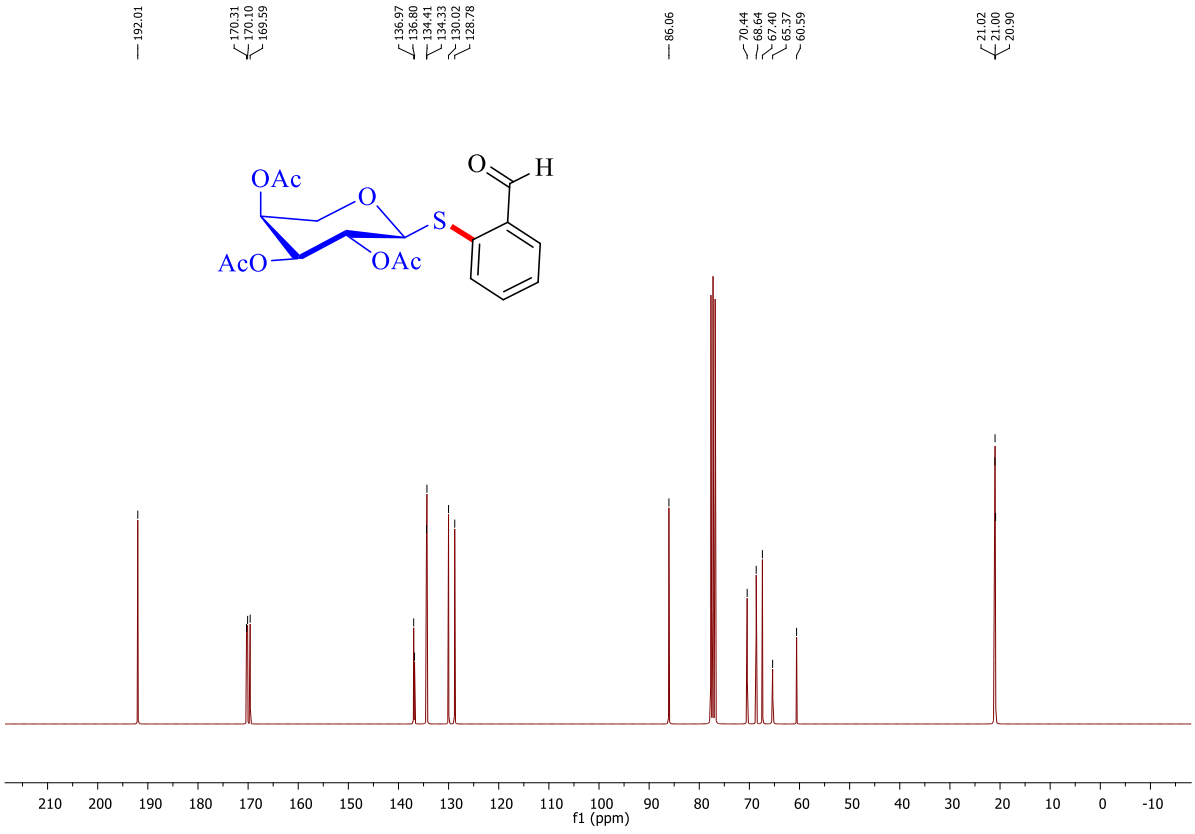
9.57
f1 (ppm)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OAc
O
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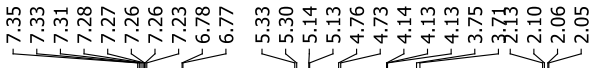
f1 (ppm)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5.14
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4.14
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3.71
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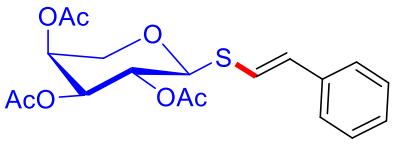
2.10
2.06
2.05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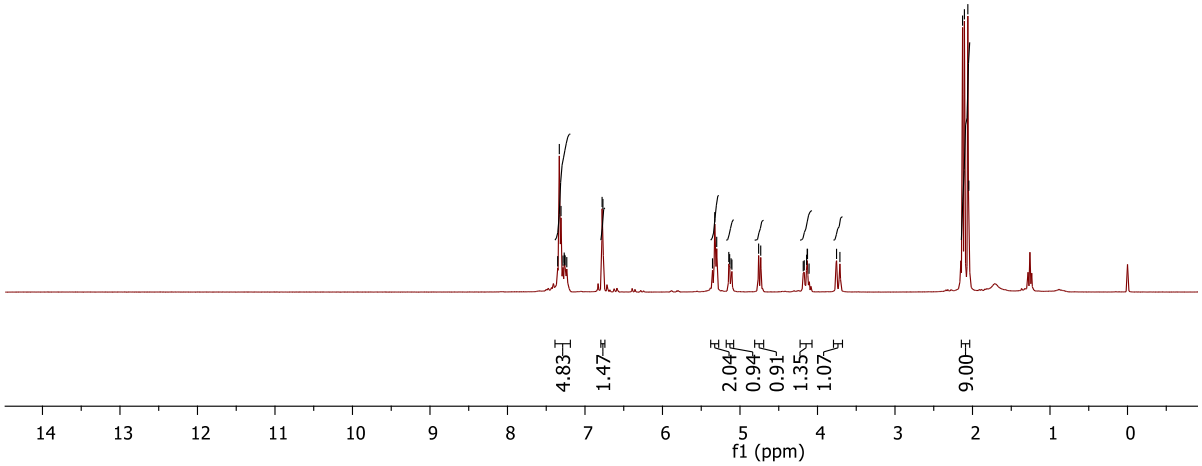
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9.00
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10
9
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7
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5
4
3
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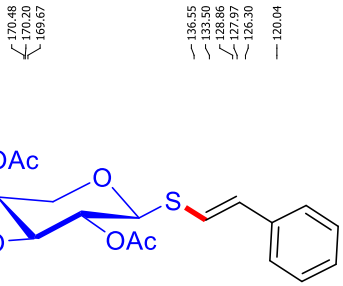
1
0
f1 (ppm)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21.03
20.92

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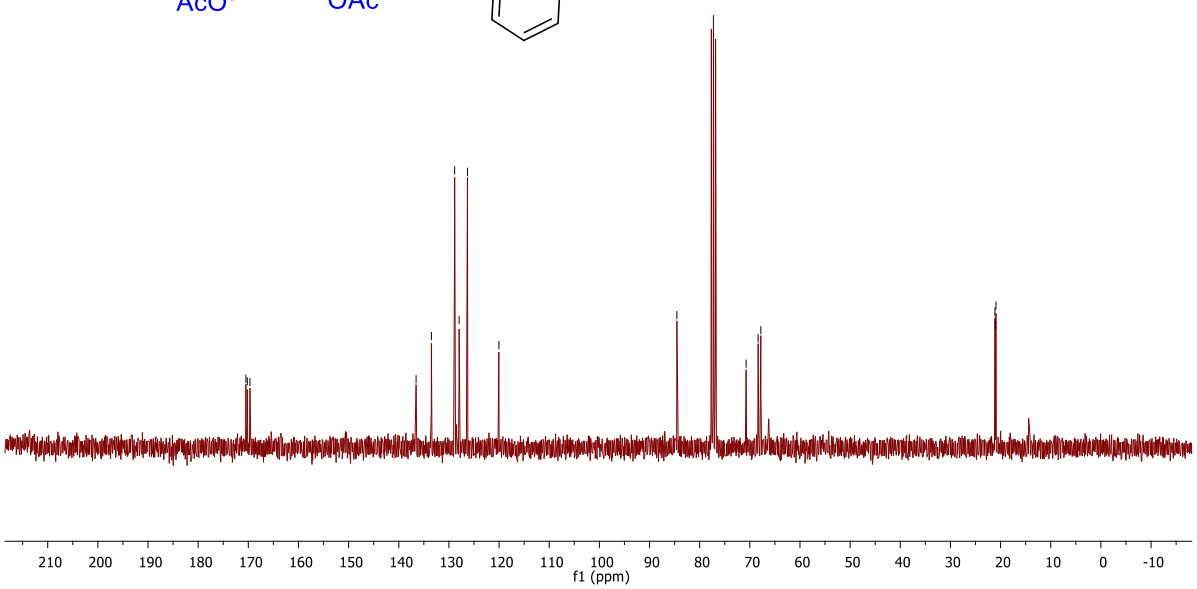
S
AcO
OAc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100
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80
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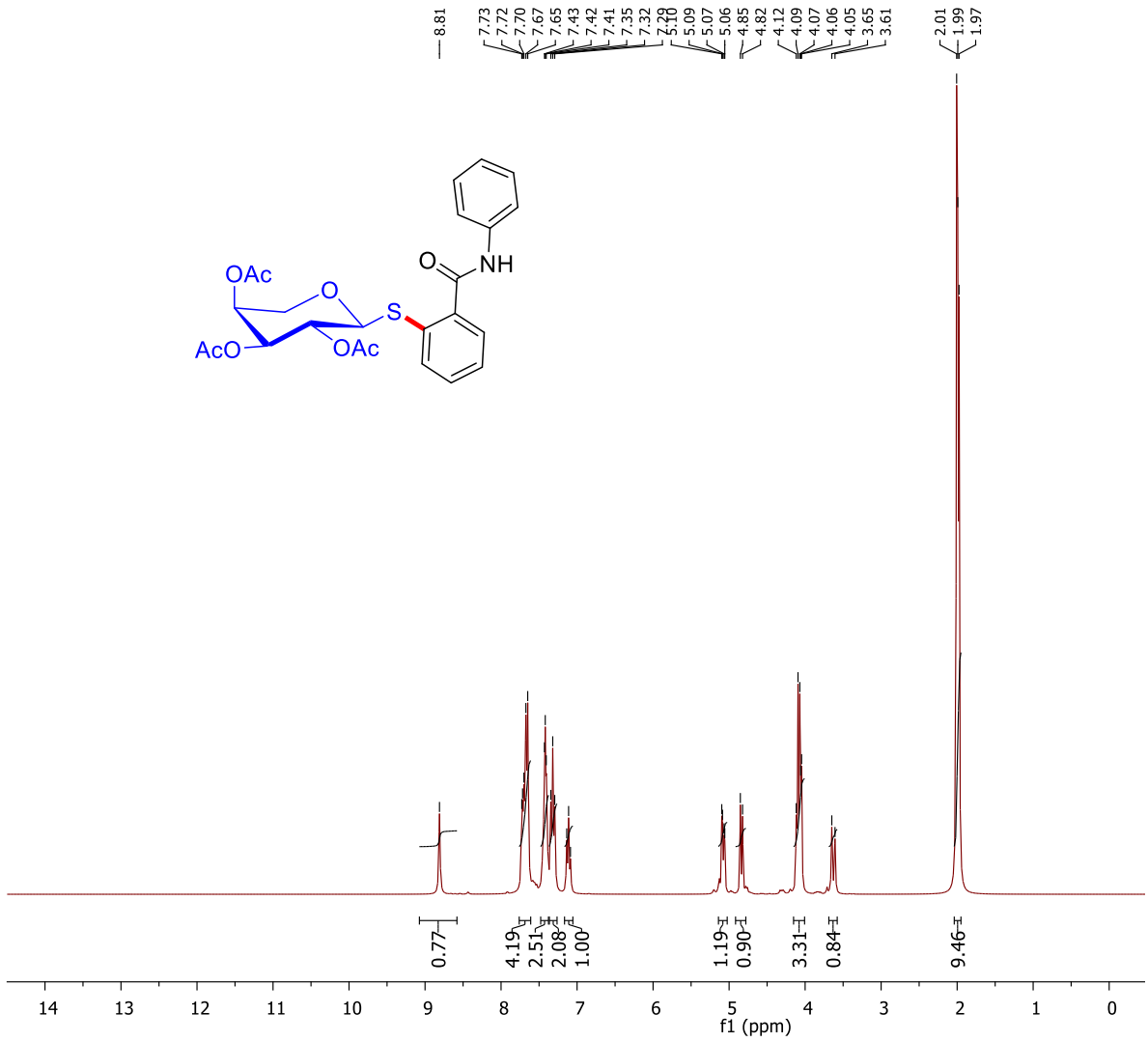
f1 (ppm)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7.42
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7.32
7.29
5.10
5.09
5.07
5.06
4.85
4.82
4.12
4.09
4.07
4.06
4.05
3.65
3.61
2.01
1.99
1.97
OAc
O
S
AcO
OAc
O
NH
0.77
4.19
2.51
2.08
1.00
1.19
0.90
3.31
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13
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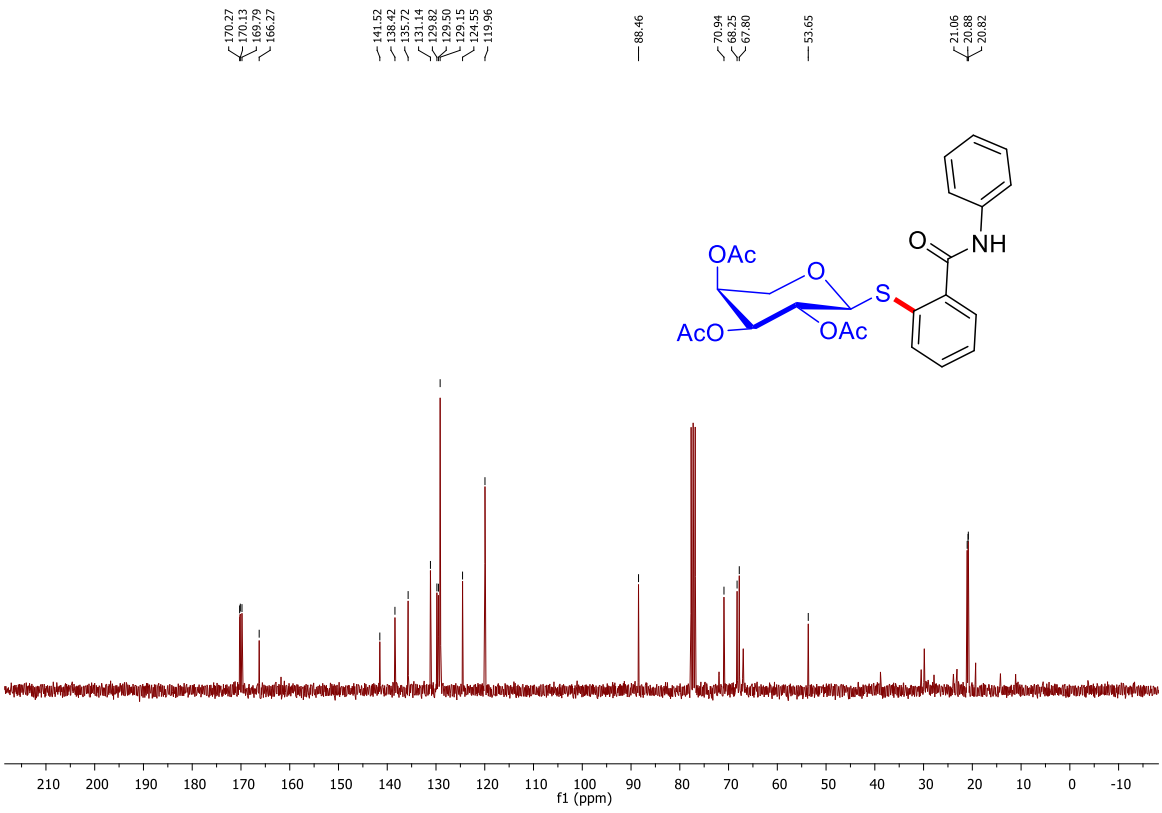
0
f1 (ppm)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138.42
135.72
131.14
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119.96
88.46
70.94
68.25
67.80
53.65
21.06
20.88
20.82
OAc
O
S
AcO
OAc
O
NH
210
200
190
180
170
160
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140
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100
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80
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60
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30
20
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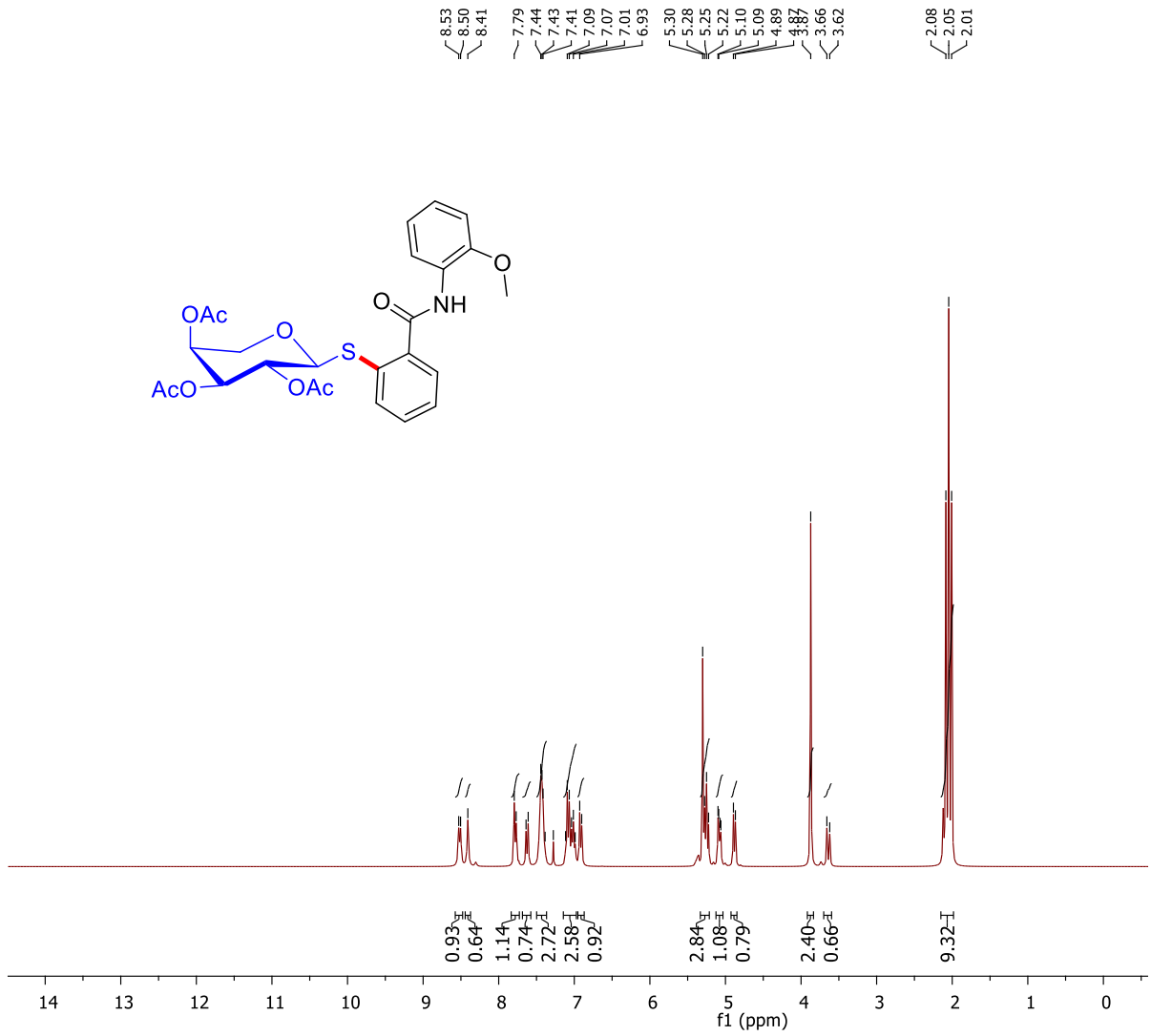
0
-10
f1 (ppm)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7.43
7.41
7.09
7.07
7.01
6.93
5.30
5.28
5.25
5.22
5.10
5.09
4.89
3.87
3.66
3.62
2.08
2.05
2.01
OAc
O
S
AcO
OAc
O
NH
O
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0.64
1.14
0.74
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2.58
0.92
2.84
1.08
0.79
2.40
0.66
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13
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11
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9
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5
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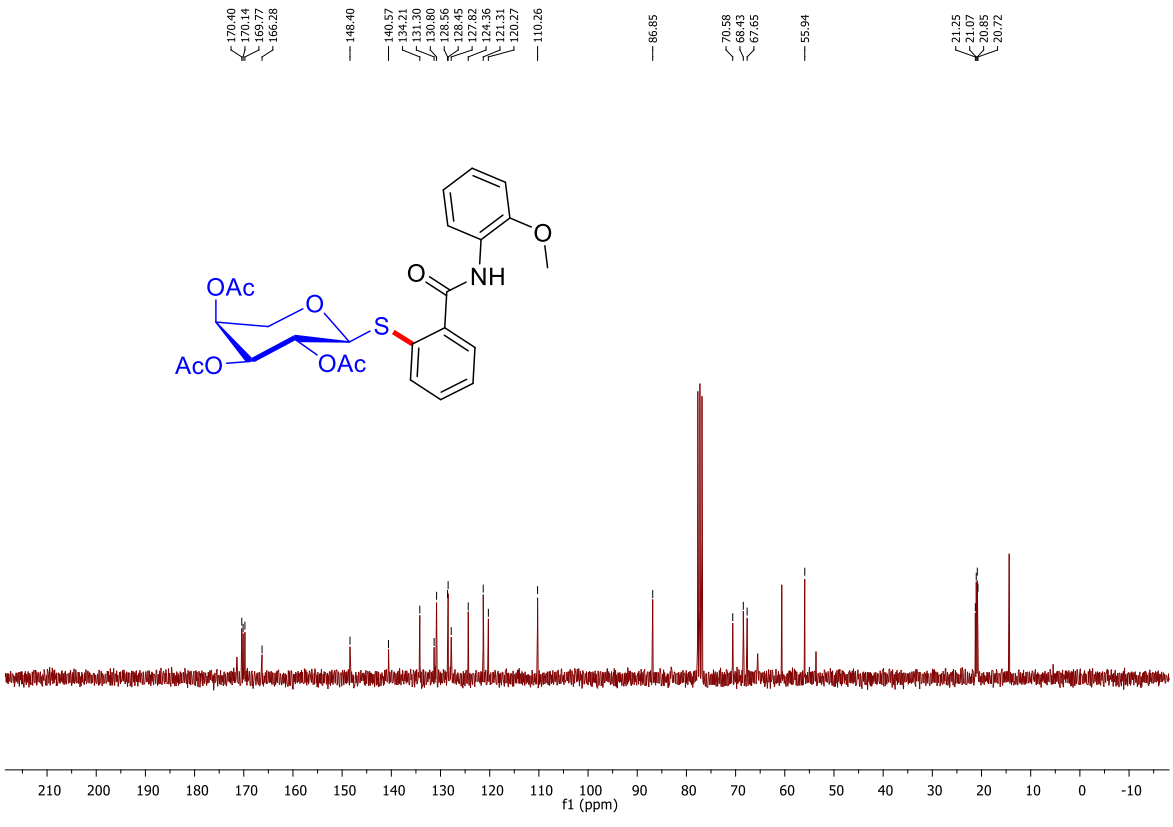
f1 (ppm)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128.45
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124.36
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86.85
70.58
68.43
67.65
55.94
21.25
21.07
20.85
20.72
OAc
O
S
AcO
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O
NH
O
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200
190
180
170
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120
110
100
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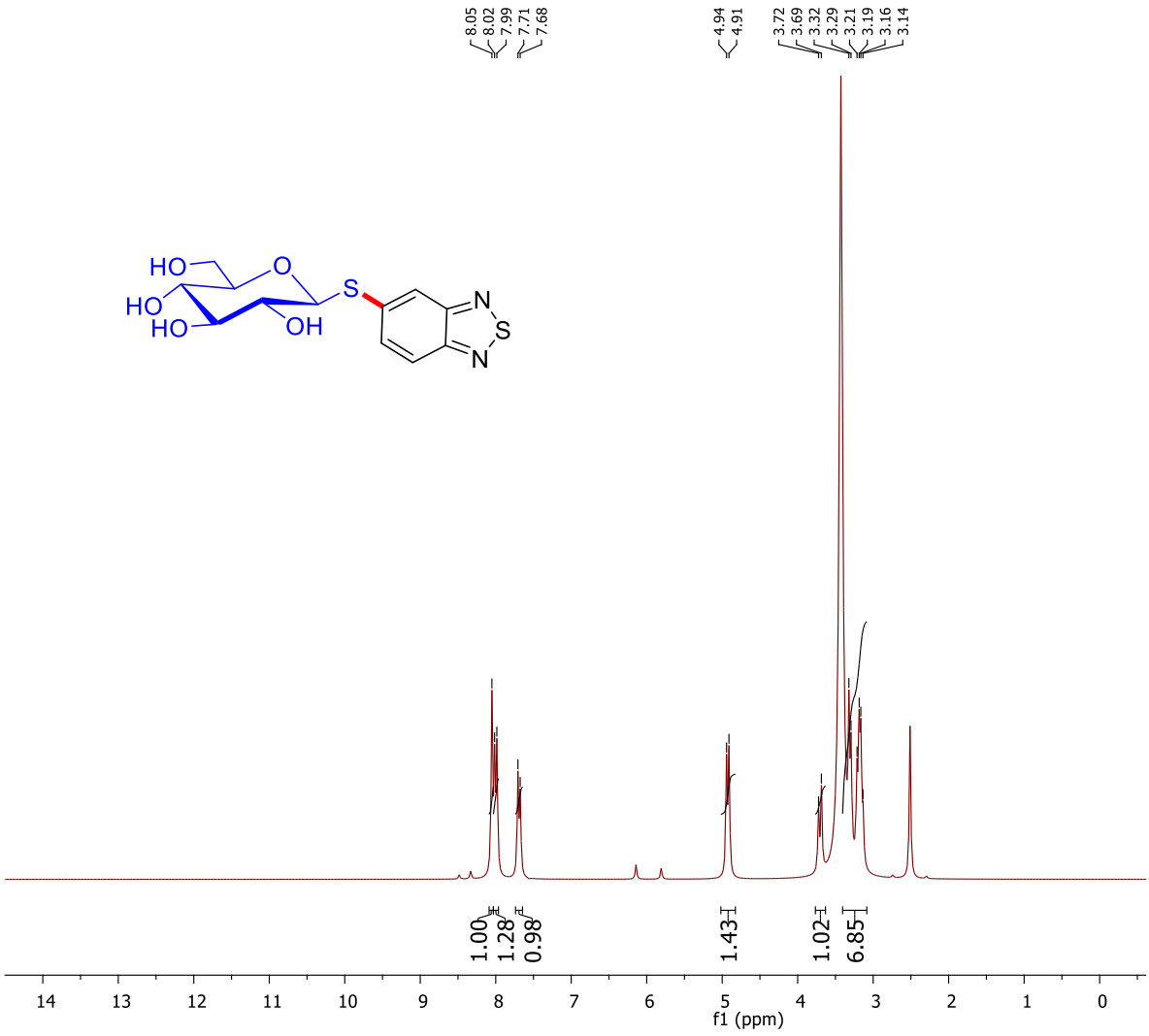
f1 (ppm)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4.94
4.91
3.72
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3.32
3.29
3.21
3.19
3.16
3.14
HO
O
S
HO
HO
OH
N
S
N
1.00
1.28
0.98
1.43
1.02
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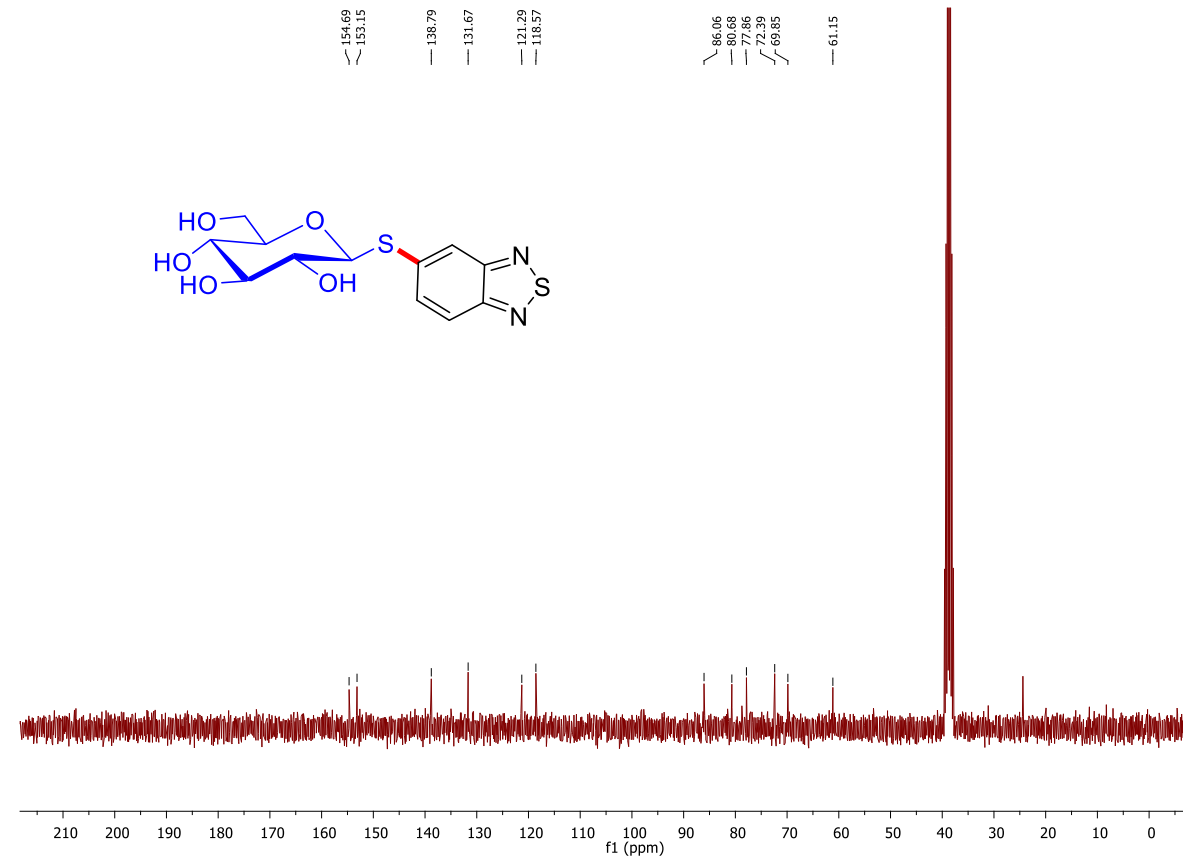
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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69.85
61.15
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O
S
HO
HO
OH
N
S
N
210
200
190
180
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150
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130
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110
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90
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70
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50
40
30
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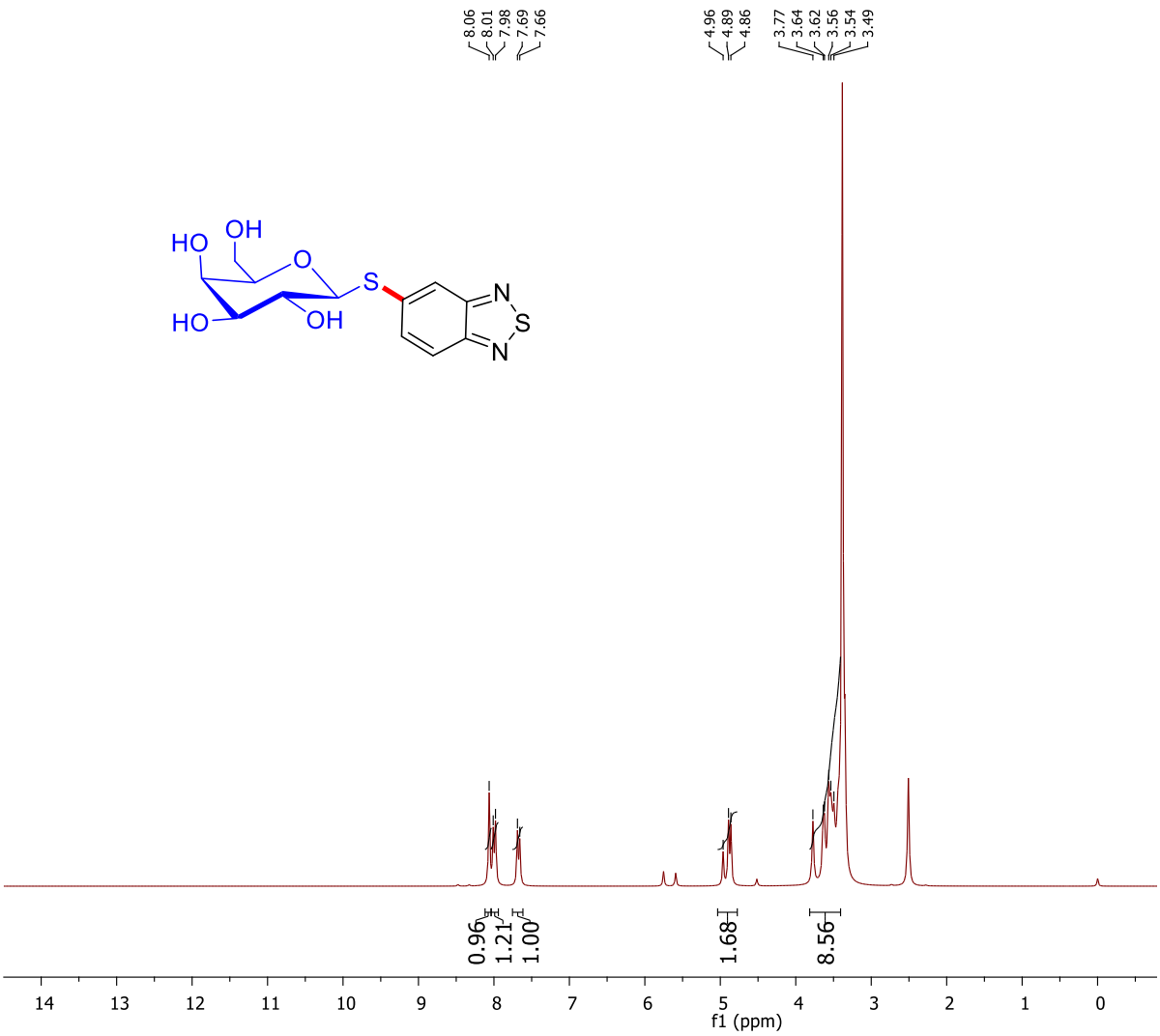
10
0
f1 (ppm)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3.64
3.62
3.56
3.54
3.49
HO
OH
O
S
HO
OH
N
S
N
0.96
1.21
1.00
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13
12
11
10
9
8
7
6
5
4
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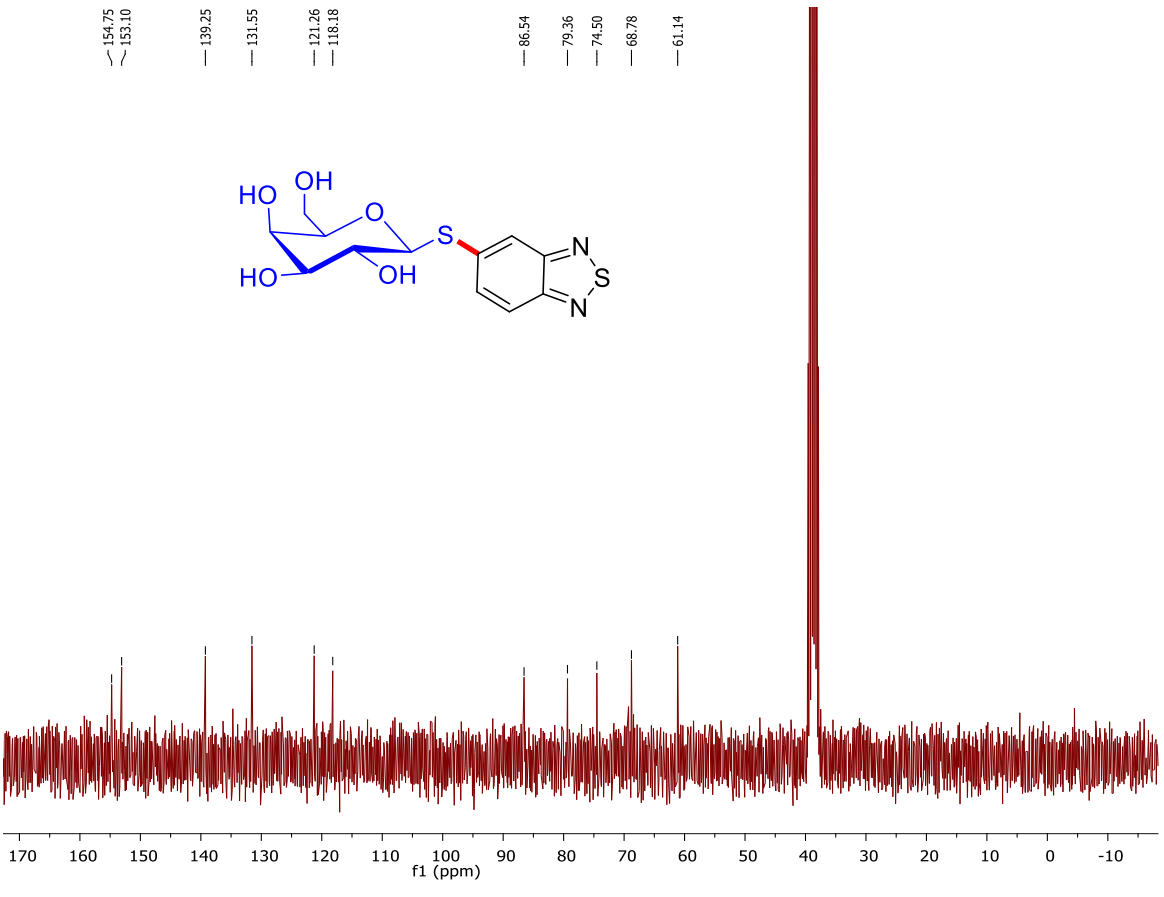
2
1
0
f1 (ppm)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S
HO
OH
N
S
N
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100
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30
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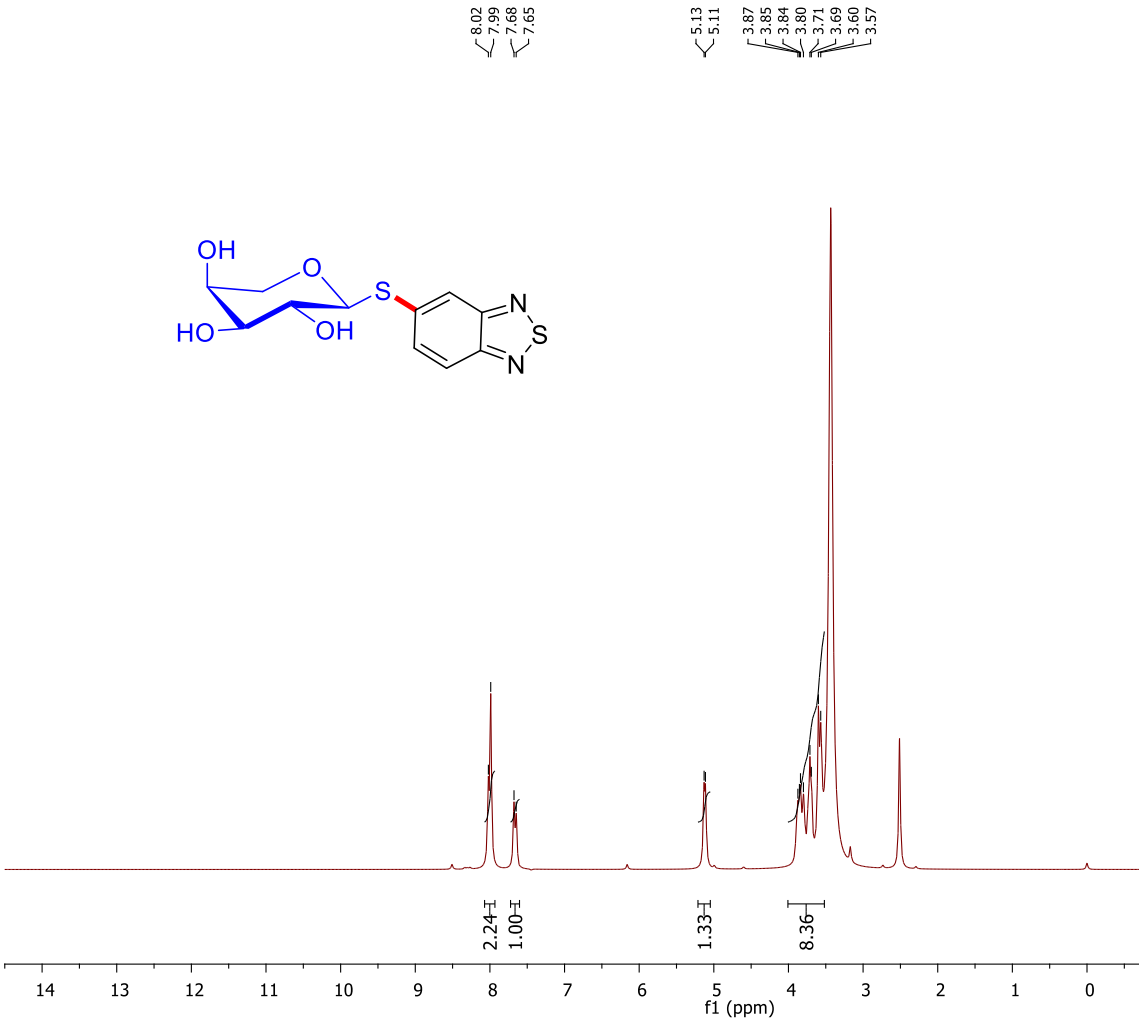
-10
f1 (ppm)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3.60
3.57
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O
S
HO
OH
N
S
N
2.24
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12
11
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9
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5
4
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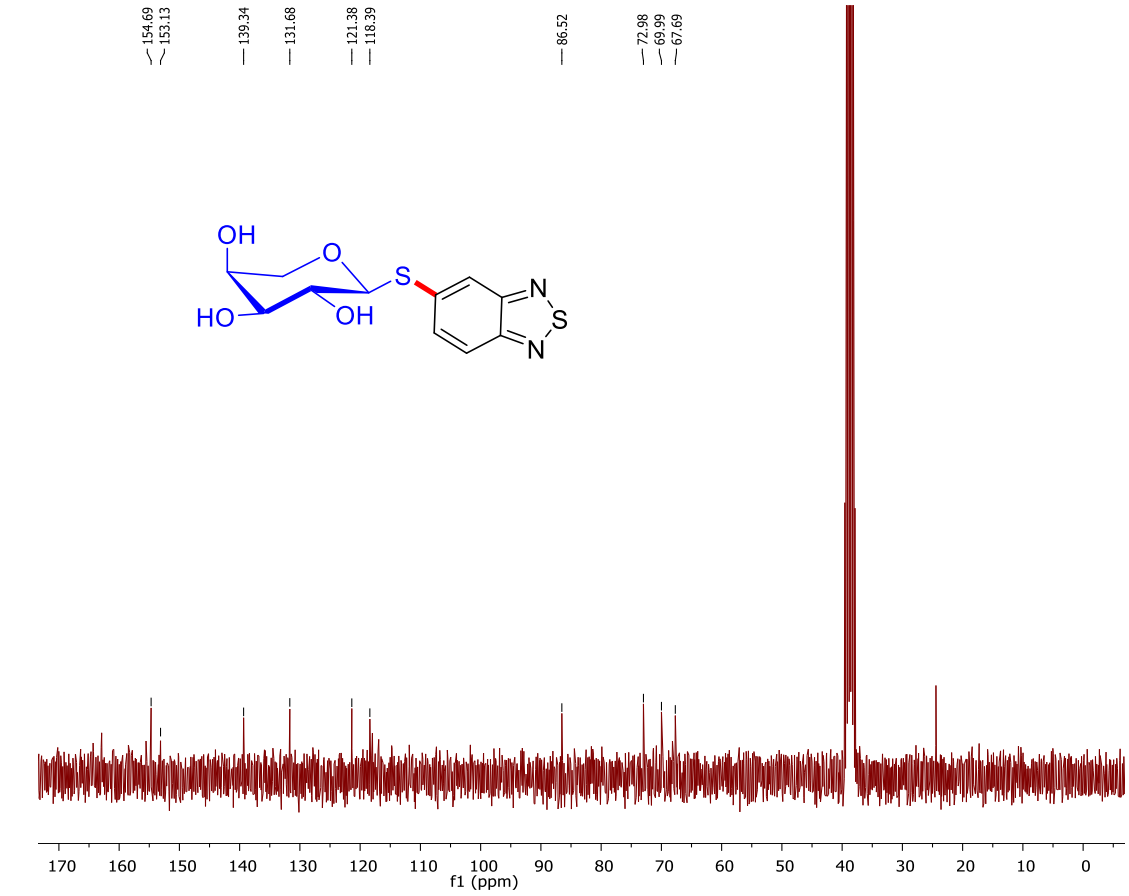
f1 (ppm)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HO
OH
N
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50
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10
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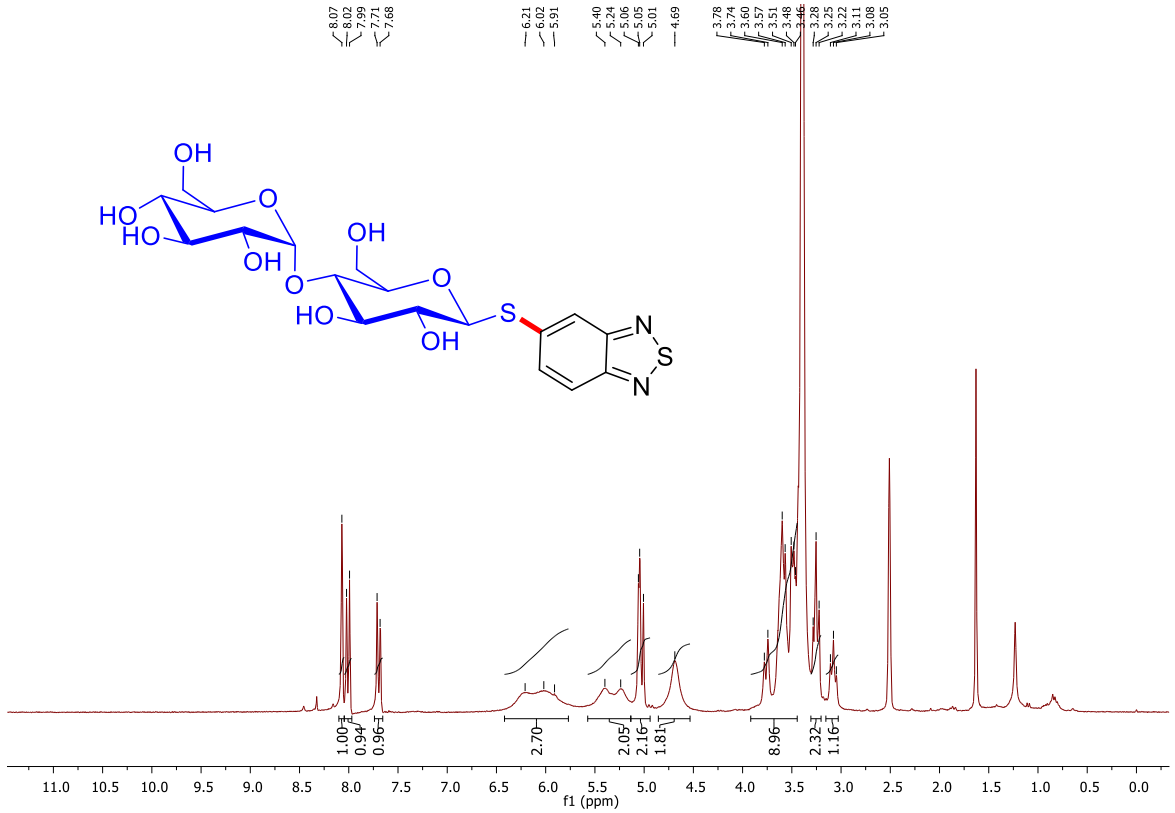
f1 (ppm)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3.74
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3.46
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3.05
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HO
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OH
O
HO
OH
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N
S
N
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0.94
0.96
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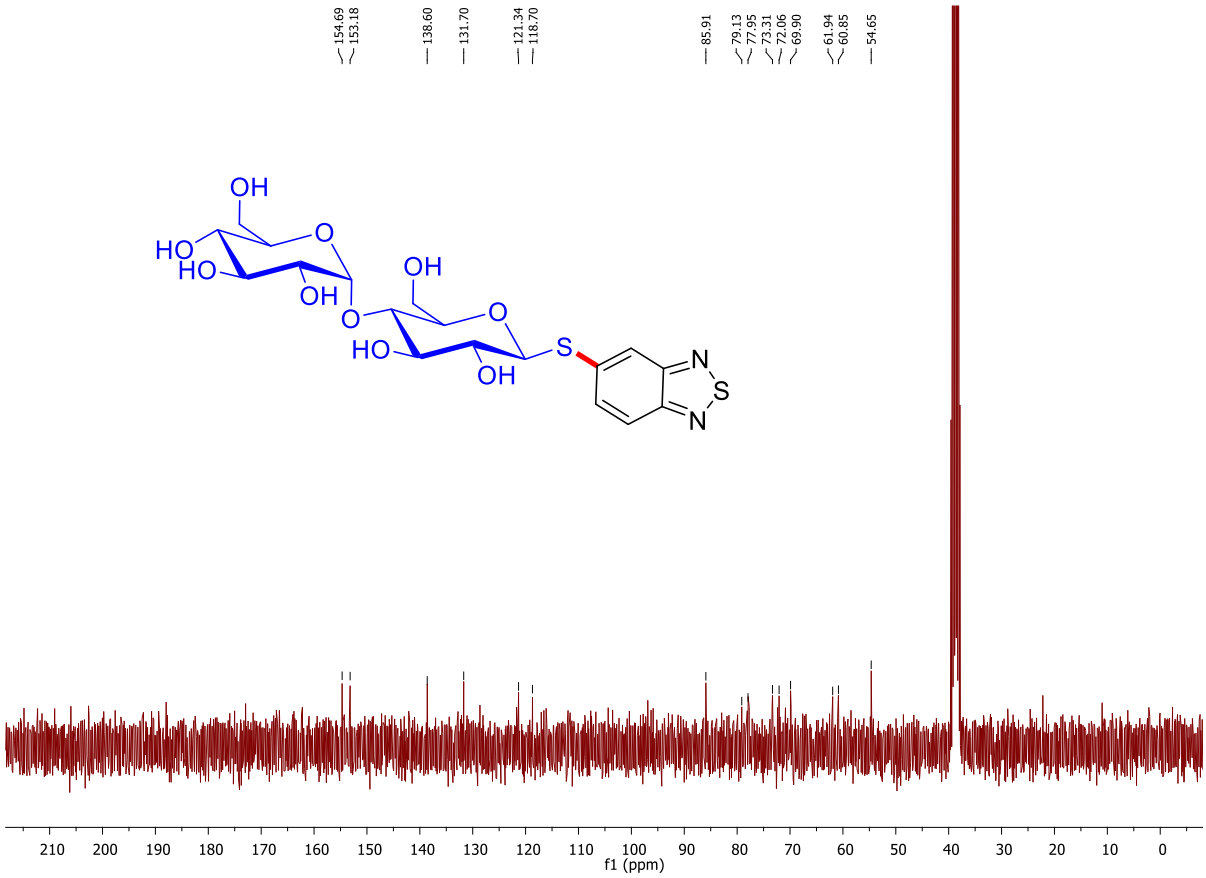
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61.94
60.85
54.65
OH
HO
HO
O
OH
O
OH
O
HO
OH
S
N
S
N
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200
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180
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150
140
130
120
110
100
90
80
70
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30
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10
0
f1 (ppm)

Supplementary References

1. (a) Haydl, A. M.; Breit, B. *Angew. Chem.* **2015**, *127*, 15750. (b) Gao, M.; Chen, Y.; Tan, S.; Reibenspies, J. H.; Zingaro, R. A. *Heteroat. Chem.* **2008**, *19*, 199. (c) Pearson, S.; Scarano, W.; Stenzel, M. H. *Chem. Commun.* **2012**, *48*, 4695.