Supporting information

Triflic Acid-Mediated Synthesis of Thioglycosides

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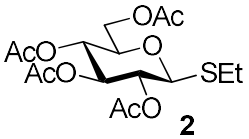
Contents:

General Experimental

The reactions were performed using commercial reagents. Column chromatography was performed on silica gel 60 (70-230 mesh), reactions were monitored by TLC on Kieselgel 60 F254. The compounds were detected by examination under UV light and by charring with 10% sulfuric acid in methanol. Solvents were removed under reduced pressure at <40 °C. CH_2Cl_2 was distilled from CaH_2 directly prior to application. Molecular sieves (3 Å), used for reactions, were crushed and activated *in vacuo* at 390 °C during 8 h in the first instance and then for 2-3 h at 390 °C directly prior to application. ^{1}H-NMR spectra were recorded in $CDCl_3$ at 300 MHz.

Synthesis of Thioglycosides

Ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (2).



2

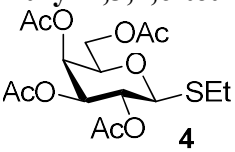
A mixture of per-acetate **1** (0.43 g, 1.10 mmol), ethanethiol (0.16 mL, 2.20 mmol), and freshly activated molecular sieves (3 Å, 0.21 g) in anhydrous CH_2Cl_2 (34 mL) was stirred under argon for 15 min at rt. The mixture was cooled to 0 °C, TfOH (78.2 μL, 0.88 mmol) was added dropwise, and the resulting mixture was stirred for 1 h at 0 °C. After that, the solids were filtered off through a pad of Celite and washed successively with CH_2Cl_2. The combined filtrate (~200 mL) was washed with sat. aq. $NaHCO_3$ (70 mL) and water (3 × 70 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated in *vacuo*. Crystallization (Et_2O-hexanes) for 16 h at 4 °C afforded the title compound (0.39 g, 90%) as a white crystalline solid. The analytical data for **2** was in agreement with that reported previously.[1,2]

*A large-scale synthesis of **2***. A mixture of per-acetate **1** (15.0 g, 38.4 mmol), ethanethiol (5.55 mL, 76.8 mmol), and freshly activated molecular sieves (3 Å, 2.25 g) in anhydrous CH_2Cl_2 (300

mL) was stirred under argon for 15 min at rt. The mixture was cooled to 0 °C, TfOH (2.72 mL, 30.7 mmol) was added dropwise, and the resulting mixture was stirred for 30 min at 0 °C. After that, the solids were filtered off through a pad of Celite and washed successively with CH_2Cl_2. The combined filtrate (~500 mL) was washed with sat. aq. $NaHCO_3$ (100 mL) and water (3 × 100 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated in *vacuo*. Crystallization (Et_2O-hexane) for 16 h at 4 °C afforded the title compound (13.2 g, 87%) as a white solid.

The analytical data for **2** was in agreement with that reported previously.[1,2] Spectral data for **2**: ^{1}H NMR ($CDCl_3$): δ, 1.25 (t, 3H, CH_2CH_3), 2.01, 2.03, 2.06, 2.08 (4 s, 12H, 4 × $COCH_3$), 2.69-2.75 (m, 2H, CH_2CH_3), 3.69–3.75 (m, 1H, $J_{5,6a}$ = 5.0 Hz, H-5), 4.15 (dd, 1H, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.22 (dd, 1H, H-6b), 4.46 (d, 1H, $J_{1,2}$ = 10.0 Hz, H-1), 5.04 (dd, 1H, $J_{2,3}$ = 9.9 Hz, H-2), 5.09 (dd,1H, $J_{4,5}$ = 9.6 Hz, H-4), 5.20 (dd, 1H, $J_{3,4}$ = 8.9 Hz, H-3) ppm; ^{13}C-NMR ($CDCl_3$): δ, 14.8, 20.6, 20.7, 20.8, 24.2, 62.1, 68.2, 69.7, 73.8, 75.8, 76.6, 83.5, 169.4, 169.5, 170.2, 170.7 ppm.

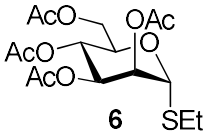
Ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (4).



4

The title compound was synthesized as described for the synthesis of **2**. The analytical data for **4** was in agreement with that reported previously.[3,4] Spectral data for **4**: ^{1}H NMR ($CDCl_3$): δ, 1.25 (t, 3H, CH_2CH_3), 1.98, 2.03, 2.05, 2.13 (4 s, 12H, 4 × $COCH_3$), 2.73 (m, 2H, CH_2CH_3), 3.89 (dt, 1H, $J_{5,6}$ = 6.6 Hz, H-5), 4.12 (m, 2H, H-6a, 6b), 4.8 (d, 1H, $J_{1,2}$ = 9.9 Hz, H-1), 4.98 (dd, 1H, $J_{3,4}$ = 3.3 Hz, H-3), 5.23 (dd, 1H, $J_{2,3}$ = 10.0 Hz, H-2), 5.42 (dd, 1H, $J_{4,5}$ = 1.0 Hz, H-4) ppm; ^{13}C NMR ($CDCl_3$): δ 14.8, 20.6, 20.7, 20.8, 24.4, 61.3, 67.0, 67.1, 71.8, 74.3, 84.0, 169.4, 169.6, 170.1, 170.2, 170.4 ppm.

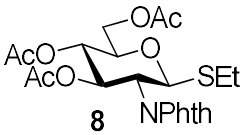
Ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside (6).



6

The title compound was synthesized as described for the synthesis of **2.** The analytical data for **6** was in agreement with that reported previously.[4,5] Spectral data for **6**: ^{1}H NMR ($CDCl_3$): δ, 1.30 (t, 3H, CH_2CH_3), 1.99, 2.03, 2.04, 2.11 (4 s, 12H, 4 × $COCH_3$), 2.59-2.72 (m, 2H, CH_2CH_3), 4.09 (dd, 1H), 4.31 (dd, 1H), 4.49 (m, 1H), 5.24-5.37 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$): δ, 14.8, 20.6, 20.7, 20.8, 25.4, 62.3, 66.3, 68.8, 69.4, 71.1, 76.6, 82.8, 169.7, 169.8, 170.0, 170.6 ppm.

Ethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (8).

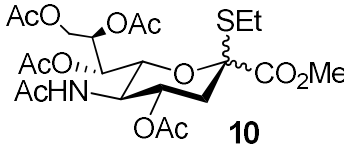


8

The title compound was synthesized as described for the synthesis of **2**. The analytical data for **8** was in agreement with that reported previously.[6,7] Spectral data for **8**: ^{1}H NMR ($CDCl_3$): δ, 1.22 (t, 3H, CH_2CH_3), 1.87, 2.04, 2.11 (3 s, 9H, 3 × $COCH_3$), 2.72 (m, 2H, CH_2CH_3), 3.90 (m, 1H, H-

5), 4.18 (dd, 1H, H-6a), 4.28-4.44 (m, 2H, H-2, 6b), 5.20 (dd, 1H, H-4), 5.50 (d, 1H, $J_{1,2}$ = 10.6 Hz, H-1), 5.85 (dd, 1H, H-2), 7.74 – 7.90 (m, 4H, aromatic) ppm; ^{13}C NMR ($CDCl_3$): δ 14.8, 20.4, 20.6, 20.8, 24.3, 53.6, 62.2, 68.8, 71.5, 75.8, 81.1, 123.74, 131.1, 131.5, 134.3, 134.4, 167.1, 167.8, 169.5, 170.1, 170.7 ppm.

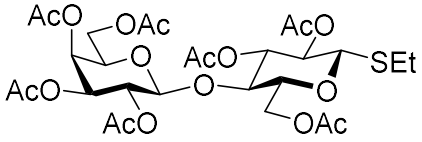
Methyl (ethyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-glycero-D-galacto-non-2-ulopyranosid)onate (10).



10

The title compound was synthesized as described for the synthesis of **2**. The analytical data for **10** was in agreement with that reported previously.[8,9] Selected spectral data for **10**: ^{1}H NMR ($CDCl_3$); δ, 2.70 (dd, $J_{3eq,3ax}$ =12.3 Hz, H-3eq$^{\alpha}$), 2.57 (dd, $J_{3eq,3ax}$ =13.1 Hz, H-3eq$^{\beta}$) ppm.

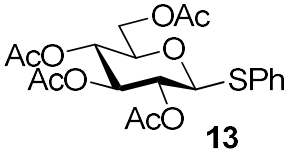
Ethyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside (12).



12

The title compound was synthesized as described for the synthesis of **2**. The analytical data for **12** was in agreement with that reported previously.[10] Spectral data for **12**: ^{1}H NMR ($CDCl_3$): δ, 1.25 (t, 3H, CH_2CH_3), 1.96-2.16 (7 s, 21H, 7 × $COCH_3$), 2.68 (m, 2H, CH_2CH_3), 3.62 (m, 1H, H-5), 3.80 (dd, 1H, H-4), 3.87 (m, 1H, H-5'), 4.05-4.16 (m, 3H), 4.44-4.51 (m, 3H), 4.90-4.98 (dt, 2H, H-3, 3'), 5.11 (dd, 1H, H-2'), 5.22 (dd, 1H, H-2), 5.35 (dd, 1H, H-4') ppm; ^{13}C NMR ($CDCl_3$): δ, 14.8, 20.5, 20.6 (×2), 20.7, 20.8, 22.6, 24.2, 60.7, 62.2, 66.5, 69.0, 70.2, 70.6, 70.9, 71.4, 73.7, 76.2, 76.6, 83.4, 101.0, 168.9, 169.0, 169.7 (×2), 170.0, 170.1, 170.6 ppm.

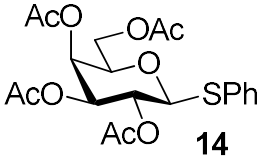
Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (13).



13

The title compound was synthesized as described for the synthesis of **2**. The analytical data for **13** was in agreement with that reported previously.[1] Spectral data for **13**: ^{1}H NMR ($CDCl_3$): δ, 1.96, 1.98, 2.02, 2.04 (4 s, 12 H, 4 × $COCH_3$), 3.68-3.73 (m, 1H, $J_{5,6a}$ = 5.1 Hz, H-5), 4.15 (dd, 1H, $J_{6a,6b}$ = 12.1 Hz, H-6a), 4.21 (dd, 1H, H-6b), 4.66 (d, 1H, $J_{1,2}$ = 10.1 Hz, H-1), 4.91 (dd, 1H, $J_{2,3}$ = 9.2 Hz, H-2), 5.01 (dd, 1H, $J_{4,5}$ = 9.9 Hz, H-4), 5.23 (dd, 1H, $J_{3,4}$ = 9.3 Hz, H-3), 7.26-7.49 (m, 5H, aromatic) ppm; ^{13}C NMR ($CDCl_3$): δ, 20.8 (×2), 20.9 (×2), 62.3, 68.4, 70.1, 74.1, 75.9, 85.9, 128.6, 129.1 (×2), 131.8, 133.3 (×2), 169.4, 169.6, 170.3, 170.7 ppm.

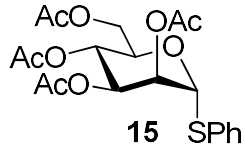
Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (14).



14

The title compound was synthesized as described for the synthesis of **2**. The analytical data for **14** was in agreement with that reported previously.[4,11] Spectral data for **14**: ^{1}H NMR ($CDCl_3$): δ, 1.96, 2.02, 2.08, 2.10 (4 s, 12H, 4 × $COCH_3$), 3.93 (m, 1H, $J_{5,6}$ = 6.6 Hz, H-5), 4.12 (m, 2H, H-6a,b), 4.7 (d, 1H, $J_{1,2}$ = 9.9 Hz, H-1), 5.03 (dd, 1H, $J_{3,4}$ = 3.3 Hz, H-3), 5.23 (dd, 1H, $J_{2,3}$ = 10.0 Hz, H-2), 5.42 (dd, 1H, $J_{4,5}$ = 1.0 Hz, H-4), 7.28-7.52 (m, 5H, aromatic) ppm; ^{13}C NMR ($CDCl_3$): δ, 20.6 (×2), 61.6, 67.1, 71.9, 71.3, 76.6, 86.5, 128.1, 128.8 (×2), 132.4 (×2), 132.5, 169.4, 169.6, 170.1, 170.2, 170.4 ppm.

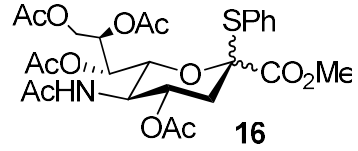
Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside (15).



15

The title compound was synthesized as described for the synthesis of **2**. The analytical data for **15** was in agreement with that reported previously.[11,12] Spectral data for **15**: ^{1}H NMR ($CDCl_3$): δ, 2.01, 2.05, 2.08, 2.16 (4 s, 12H, 4 × $COCH_3$), 4.10 (m, 1H), 4.30 (dd, 1H), 4.51-4.57 (m, 1H), 5.29-5.36 (m, 2H, H-2, 3), 5.50 (d, 1H, H-1), 5.42 (dd, 1H, H-4), 7.28-7.52 (m, 5H, aromatic) ppm; ^{13}C NMR ($CDCl_3$): δ, 20.6 (×2), 20.8, 62.3, 66.2, 70.8, 71.7, 85.6, 128.1, 129.0 (×2), 132.0 (×2), 133.2, 169.6, 169.7 (×2), 169.8, 170.4 ppm.

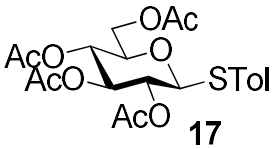
Methyl (phenyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-glycero-D-galacto-non-2-ulopyranosid)onate (16).



16

The title compound was synthesized as described for the synthesis of **2**. The analytical data for **16** was in agreement with that reported previously.[13,14] Selected spectral data for β-**16**: ^{1}H NMR: δ, 1.90, 1.96, 2.04, 2.07, 2.10 (5 s, 15H, 5 × $COCH_3$), 2.68 (dd, $J_{3eq,3ax}$ =14.0 Hz, H-3eq), 2.00 (dd, 1H, H-3ax), 4.49 (dd, 1H, $J_{9a,9b}$ = 10.4 Hz, H-9a), 4.60 (dd, H-9b), 5.40 (n, 1H, H-4), 5.60 (d, 1H, $J_{5,NH}$ = 10.7 Hz, NH), 7.20-7.60 (m, 5H, aromatic) ppm; Selected spectral data for β-**16**: ^{1}H NMR: δ, 2.81 (dd, $J_{3eq,3ax}$ = 13.1 Hz, H-3eq), 2.09 (dd, 1H, H-3ax).

***p*-Methylphenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (17).**

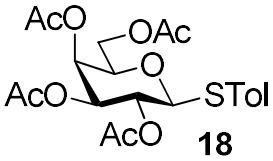


17

The title compound was synthesized as described for the synthesis of **2**. The analytical data for **17** was in agreement with that reported previously.[1,5,15] Spectral data for **17**: ^{1}H NMR ($CDCl_3$):

δ, 1.98, 2.01, 2.08, 2.09 (4 s, 12H, 4 × $COCH_3$), 2.35 (s, 3H, CH_3Ar), 3.67-3.74 (m, 1H, $J_{5,6a}$ = 5.2 Hz, H-5), 4.17 (dd, 1H, $J_{6a,6b}$ = 12.0 Hz, H-6a), 4.20 (dd, 1H, H-6b), 4.61 (d, 1H, $J_{1,2}$ = 10.1 Hz, H-1), 4.91 (dd, 1H, $J_{2,3}$ = 9.3 Hz, H-2), 5.03 (dd, 1H, $J_{4,5}$ = 9.6 Hz, H-4), 5.18 (dd, 1H, $J_{3,4}$ = 9.3 Hz, H-3), 7.10-7.42 (m, 4H, aromatic) ppm; ^{13}C NMR ($CDCl_3$): δ, 20.6, 20.7, 20.8, 21.2, 62.1, 68.3, 69.9, 74.1, 75.8, 76.7, 85.8, 127.6, 129.7 (×2), 133.9 (×2), 138.8, 169.3, 169.4, 170.2, 170.6 ppm.

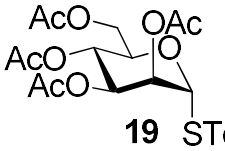
***p*-Methylphenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (18).**



18

The title compound was synthesized as described for the synthesis of **2**. The analytical data for **18** was in agreement with that reported previously.[15,16] Spectral data for **18**: ^{1}H NMR ($CDCl_3$): δ, 1.97, 2.05, 2.10, 2.12 (4 s, 12H, 4 × $COCH_3$), 2.34 (s, 3H, CH_3Ar), 3.91 (m, 1H, $J_{5,6}$ = 6.6 Hz, H-5), 4.14 (m, 2H, H-6a, 6b), 4.65 (d, 1H, $J_{1,2}$ = 9.9 Hz, H-1), 5.03 (dd, 1H, $J_{3,4}$ = 3.3 Hz, H-3), 5.22 (dd, 1H, $J_{2,3}$ = 10.0 Hz, H-2), 5.41 (dd, 1H, $J_{4,5}$ = 1.0 Hz, H-4), 7.10-7.45 (m, 4H, aromatic) ppm; ^{13}C NMR ($CDCl_3$): δ, 20.7 (x2), 20.9, 21.2, 61.6, 67.3, 72.0, 74.3, 86.9, 128.6, 129.6 (×2), 133.1 (×2), 138.4, 169.3, 170.1, 170.2, 170.3 ppm.

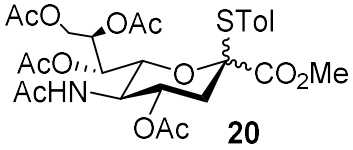
***p*-Methylphenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside (19).**



19

The title compound was synthesized as described for the synthesis of **2**. The analytical data for **19** was in agreement with that reported previously.[17,18] Spectral data for **19**: ^{1}H NMR ($CDCl_3$): δ, 1.99, 2.08, 2.10, 2.14 (4 s, 12H, 4 × $COCH_3$), 2.35 (s, 3H, CH_3Ar), 4.03 (dd, 1H), 4.30 (dd, 1H), 4.50 (m, 1H), 5.29-5.35 (m, 2H), 5.40 (d, 1H, $J_{1,2}$ = 1.0 Hz, H-1), 5.47 (dd, 1H), 7.10-7.45 (m, 4H, aromatic) ppm; ^{13}C NMR ($CDCl_3$): δ, 20.6, 20.7 (×2), 20.8, 21.1, 62.4, 66.3, 69.3, 70.8, 85.9, 128.7, 129.9 (×2), 132.6 (×2), 138.4, 169.7, 169.8, 169.9, 170.1, 170.5 ppm.

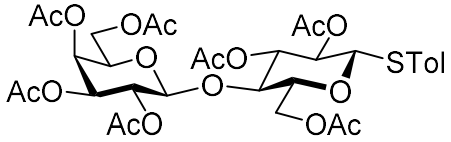
Methyl (*p*-methylphenyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-glycero-D-galacto-non-2-ulopyranosid)onate (20).



20

The title compound was synthesized as described for the synthesis of **2**. The analytical data for **20** was in agreement with that reported previously.[18] Selected spectral data for β-**20**: ^{1}H NMR ($CDCl_3$): δ, 1.90, 1.96, 2.04, 2.08, 2.11 (5 s, 15H, 5 × $COCH_3$), 2.34 (s, 3H, CH_3Ar), 2.65 (dd, $J_{3eq,3ax}$ = 9.5 Hz, H-3eq), 3.61 (s, 3H, OCH_3), 5.39 (m, 1H, H-4), 6.02 (d, 1H, NH), 7.14-7.33 (d, 4H, aromatic) ppm; ^{13}C NMR ($CDCl_3$): δ, 20.7, 20.8 (×2), 21.0, 21.1, 23.2, 29.2, 37.2, 49.2, 49.4, 52.6, 52.7, 62.2, 67.5, 67.6, 68.7, 68.9, 69.9, 73.0, 76.5, 87, 88.7, 128.7, 128.8, 128.9 (×3), 136.6 (×3), 168.2, 170.1, 170.2, 170.3, 170.8, 171.0 ppm.

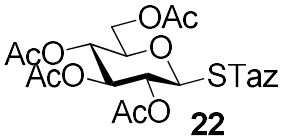
***p*-Methylphenyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside (21).**



21

The title compound was synthesized as described for the synthesis of **2**. The analytical data for **21** was in agreement with that reported previously.[18] Spectral data for **21**: ^{1}H NMR ($CDCl_3$): δ, 1.92-2.14 (7 s, 21H, 7 × $COCH_3$), 2.31 (s, 3H, C*H*$_3$Ar), 3.63 (m, 1H), 3.72 (dd, 1H), 3.84 (dd, 1H), 4.09-4.22 (m, 3H), 4.48-4.75 (m, 3H), 4.83 (m, 1H), 4.93 (dd, 1H), 5.11 (dd, 1H), 5.21 (dd, 1H), 5.33 (dd, 1H), 7.09-7.49 (m, 4H, aromatic) ppm; ^{13}C NMR ($CDCl_3$): δ, 14.8, 20.5, 20.6 (×2), 20.8 (×2), 21.0, 21.1, 29.6, 60.2, 62.0, 66.5, 68.6, 70.9, 73.8, 75.4, 85.9, 101.0, 127.6, 129.8 (×2), 133.3 (×2), 138.6, 169.0, 169.3, 169.5, 169.7, 170.1 (×2) ppm.

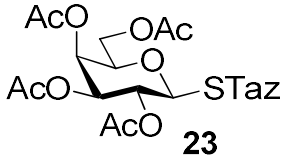
1,3-Thiazolin-2-yl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (22).



22

The title compound was synthesized as described for the synthesis of **2**. The analytical data for **22** was in agreement with that reported previously.[1,19] Spectral data for **22**: ^{1}H NMR ($CDCl_3$): δ, 1.98, 2.01, 2.03, 2.06 (4 s, 12H, 4 × CH_3CO), 3.35 (t, 2H, CH_2N), 3.76-3.83 (m, 1H, $J_{5,6a}$ = 2.3 Hz, $J_{5,6b}$ = 4.5 Hz, H-5), 4.09-4.30 (m, 4H, H-6a, 6b, CH_2S), 5.08 (dd, 1H, $J_{4,5}$ = 9.5 Hz, H-4), 5.13 (dd, 1H, $J_{2,3}$ = 8.3 Hz, H-2), 5.21 (dd, 1H, $J_{3,4}$ = 8.3 Hz, H-3), 5.41 (d, 1H, $J_{1,2}$ = 10.4 Hz, H-1) ppm; ^{13}C NMR ($CDCl_3$): δ, 20.5 (×2), 20.6, 20.7, 35.3, 61.7, 64.2, 68.1, 67.8, 69.3, 73.8, 76.0, 83.0, 162.7, 169.5, 170.1,170.6 ppm.

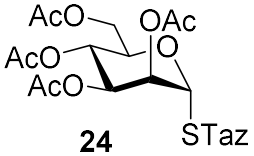
1,3-Thiazolin-2-yl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (23).



23

The title compound was synthesized as described for the synthesis of **2**. The analytical data for **23** was in agreement with that reported previously.[19] Spectral data for **23**: ^{1}H NMR ($CDCl_3$): δ, 1.99, 2.04, 2.06, 2.13 (4 s, 12H, 4 × $COCH_3$), 3.40 (t, 2H, CH_2N), 4.02 (m, 1H, H-5), 4.10- .35 (m, 4H, H-6a, 6b, CH_2S), 5.10 (dd, 1H, $J_{3,4}$ = 3.4 Hz, H-3), 5.31 (dd, 1H, $J_{2,3}$ = 10.1 Hz, H-2), 5.45 (s, 1H, H-4), 5.46 (d, 1H, $J_{1,2}$ = 10.0 Hz, H-1) ppm; ^{13}C NMR ($CDCl_3$): δ, 20.5, 20.6, 20.7, 20.8, 35.2, 61.1, 64.1, 66.7, 67.0, 71.7, 74.7, 83.4, 162.8, 169.6, 169.9, 170.2, 170.3 ppm.

1,3-Thiazolin-2-yl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside (24).



24

The title compound was synthesized as described for the synthesis of **2**. The analytical data for **24** was in agreement with that reported previously.[19] Spectral data for **24**: ^{1}H NMR ($CDCl_3$): δ, 1.96, 2.01, 2.05, 2.13 (4 s, 12H, 4 × $COCH_3$), 3.39 (t, 2H, CH_2N), 4.04-4.13 (m, 2H, H-5, H-6b), 4.16-4.38 (m, 3H, H-6a, CH_2S), 5.11 (dd, 1H, H-3), 5.32 (dd, 1H, H-4), 5.42 (dd, $J_{2,3}$ = 3.2 Hz, 1H, H-2), 6.20 (d, $J_{1,2}$ = 1.3 Hz, 1H, H-1) ppm; ^{13}C NMR ($CDCl_3$): δ, 20.6, 20.7 (×2), 20.8, 35.5, 62.0, 64.0, 65.7, 69.3, 70.6, 71.39, 82.6, 161.2, 169.3, 169.5 (×2), 170.6 ppm.

References

(1) Parameswar, A. R.; Imamura, A.; Demchenko, A. V.: Synthesis of thioglycosides and thioimidates from peracetates. In *Carbohydrate Chemistry: Proven Synthetic Methods*; Kovac, P., Ed.; CRC Press, 2012; Vol. 1; pp 187-196.

(2) Contour, M. O.; Defaye, J.; Little, M.; Wong, E. Zirconium (IV) chloride-catalyzed synthesis of 1,2-trans-thioglycopyranosides. *Carbohydr. Res.* **1989**, *193*, 283-287.

(3) Ibatullin, F. M.; Selivanov, S. I.; Shavva, A. G. A general procedure for conversion of S-glycosyl isothiourea derivatives into thioglycosides, thiooligosaccharides and glycosyl thioesters. *Synthesis* **2001**, 419-422.

(4) Valerio, S.; Iadonisi, A.; Adinolfi, M.; Ravida, A. Novel Approaches for the Synthesis and Activation of Thio- and Selenoglycoside Donors. *J. Org. Chem.* **2007**, *72*, 6097-6106.

(5) Mukhopadhyay, B.; Kartha, K. P. R.; Russell, D. A.; Field, R. A. Streamlined Synthesis of Per-O-acetylated Sugars, Glycosyl Iodides, or Thioglycosides from Unprotected Reducing Sugars. *J. Org. Chem.* **2004**, *69*, 7758-7760.

(6) McGeary, R. P.; Wright, K.; Toth, I. Conversion of Glucosamine to Galactosamine and Allosamine Derivatives: Control of Inversions of Stereochemistry at C-3 and C-4. *J. Org. Chem.* **2001**, *66*, 5102-5105.

(7) Landström, J.; Bergström, M.; Hamark, C.; Ohlson, S.; Widmalm, G. Combining weak affinity chromatography, NMR spectroscopy and molecular simulations in carbohydrate-lysozyme interaction studies. *Org. Biomol. Chem.* **2012**, *10*, 3019-3032.

(8) Tsvetkov, Y. E.; Nifantiev, N. E. Enhanced Sialylating activity of O-chloroacetylated 2-thioethyl sialosides. *Synlett* **2005**, *9*, 1375-1380.

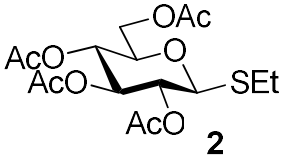
(9) Marra, A.; Sinay, P. Stereoselective synthesis of 2-thioglycosides of N-acetylneuraminic acid. *Carbohydr. Res.* **1989**, *187*, 35-42.

(10) Niggemann, J.; Kamerling, J. P.; Vliegenthart, J. F. G. Application of b-1,4-galactosyltransferase in the synthesis of complex branched-chain oligosaccharide mimics of fragments of the capsular polysaccharide of Streptococcus pneumoniae type 14. *J. Chem. Soc., Perkin Trans. 1* **1998**, 3011-3020.

(11) Weng, S.-S.; Lin, Y.-D.; Chen, C.-T. Highly Diastereoselective Thioglycosylation of Functionalized Peracetylated Glycosides Catalyzed by MoO2Cl2. *Org. Lett.* **2006**, *8*, 5633-5636.

(12) Ahmadipour, S.; Pergolizzi, G.; Rejzek, M.; Field, R. A.; Miller, G. J. Chemoenzymatic Synthesis of C6-Modified Sugar Nucleotides To Probe the GDP-d-Mannose Dehydrogenase from Pseudomonas aeruginosa. *Org. Lett.* **2019**, *21*, 4415-4419.
(13) Parameswar, A. R.; Mueller, D.; Liu, L.; Meo, C. D.; Demchenko, A. V.: Synthesis of thioglycosides and thioimidates from glycosyl halides In *Carbohydrate Chemistry: Proven Synthetic Methods*; Kovac, P., Ed.; CRC Press, 2012; Vol. 1; pp 181-186.
(14) Kirchner, E.; Thiem, F.; Dernick, R.; Heukeshoven, J.; Thiem, J. Studies on the glycosylation of N-acetylneuraminic acid. *J. Carbohydr. Chem.* **1988**, *7*, 453-486.
(15) Kondo, H.; Aoki, S.; Ichikawa, Y.; Halcomb, R. L.; Ritzen, H.; Wong, C. H. Glycosyl phosphites as glycosylation reagents: scope and mechanism. *J. Org. Chem.* **1994**, *59*, 864-877.
(16) Panza, M.; Mannino, M. P.; Baryal, K. N.; Demchenko, A. V.: A facile synthesis and characterization of p-tolyl 2,3,4,6-tetra-O-benzoyl-1-thio-β-D-galactopyranoside. In *Carbohydrate Chemistry: Proven Synthetic Methods*; Wrodnigg, T., Ed.; CRC Press, 2019; Vol. 5; pp in press.
(17) Chatterjee, D.; Paul, A.; Rajkamal, R.; Yadav, S. Cu(ClO4)2·6H2O catalyzed solvent free per-O-acetylation and sequential one-pot conversions of sugars to thioglycosides. *RSC Adv.* **2015**, *5*, 29669-29674.
(18) Chao, C.-S.; Chen, M.-C.; Lin, S.-C.; Mong, K.-K. T. Versatile acetylation of carbohydrate substrates with bench-top sulfonic acids and application to one-pot syntheses of peracetylated thioglycosides. *Carbohydr. Res.* **2008**, *343*, 957-964.
(19) Pornsuriyasak, P.; Demchenko, A. V. S-Thiazolinyl (STaz) glycosides as versatile building blocks for convergent selective, chemoselective, and orthogonal oligosaccharide synthesis. *Chem. Eur. J.* **2006**, *12*, 6630-6646.

NMR Spectra



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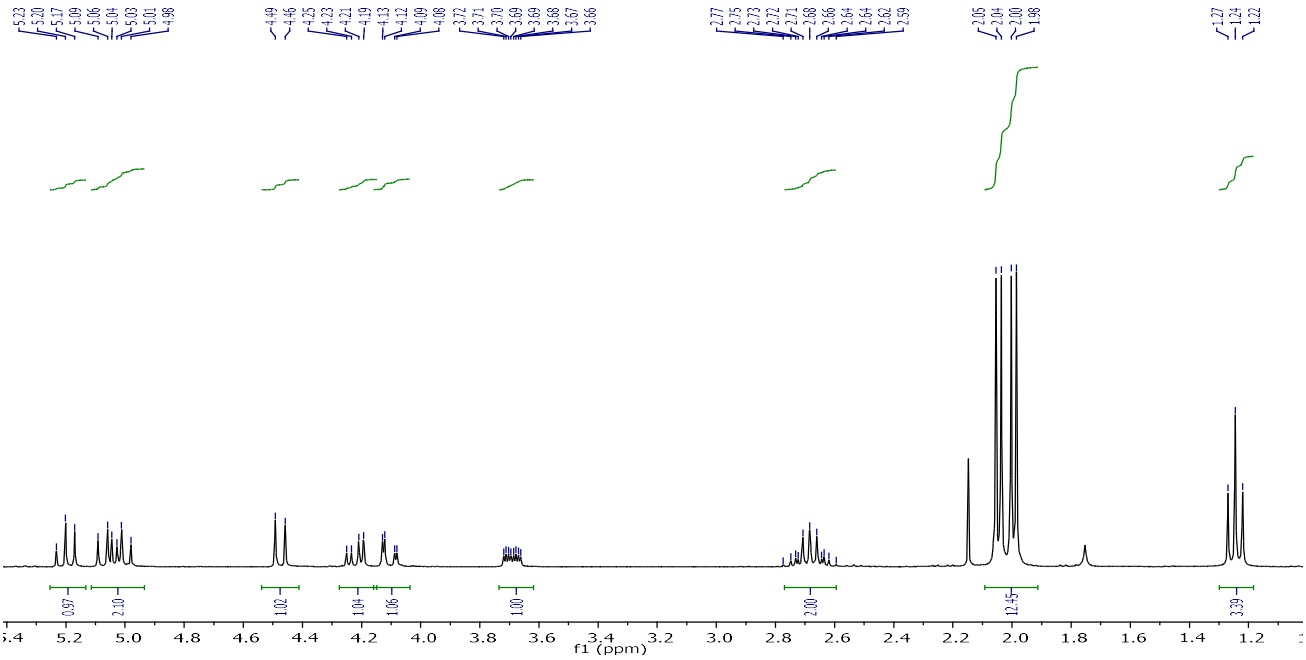

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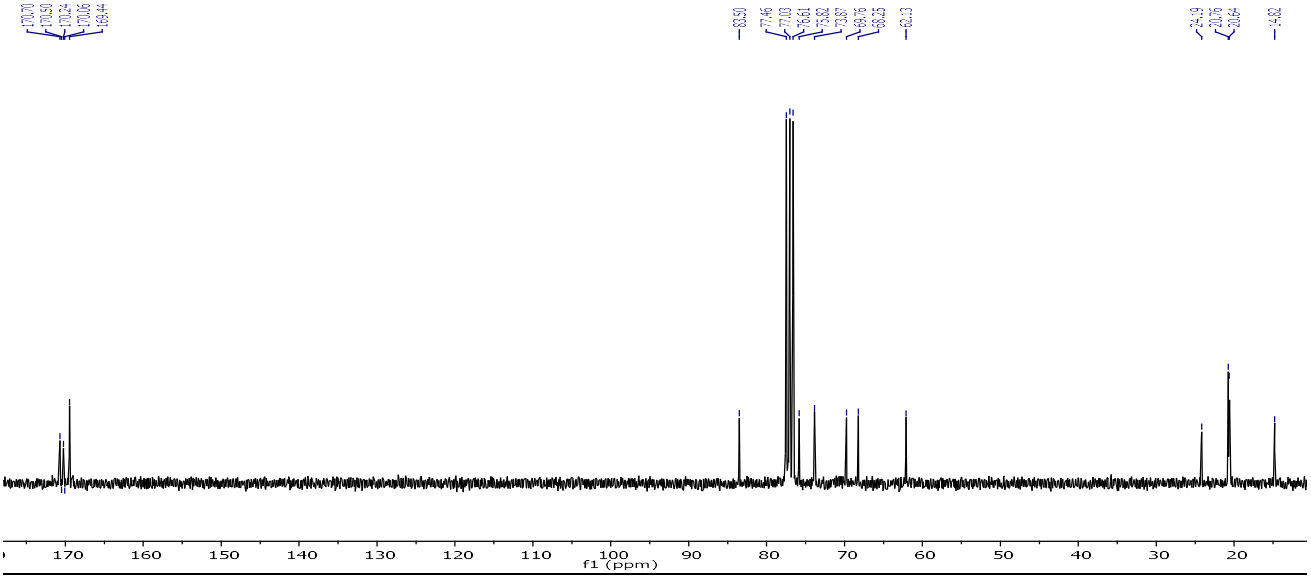

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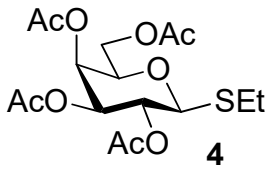

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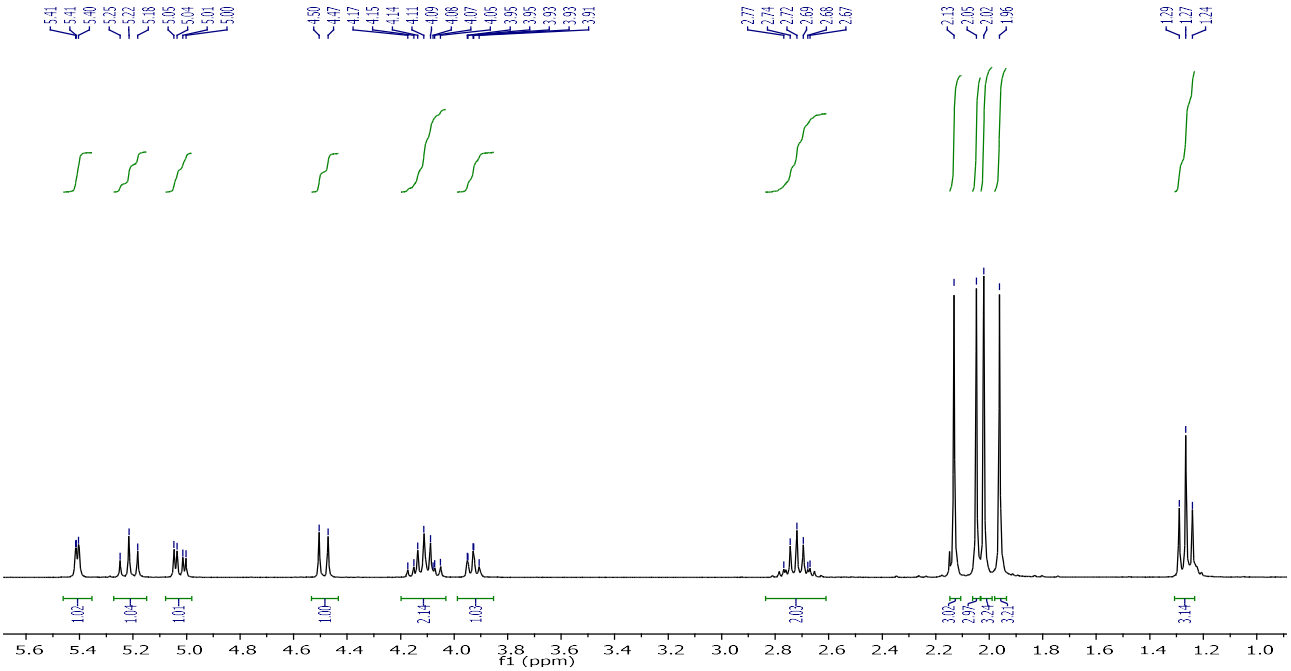

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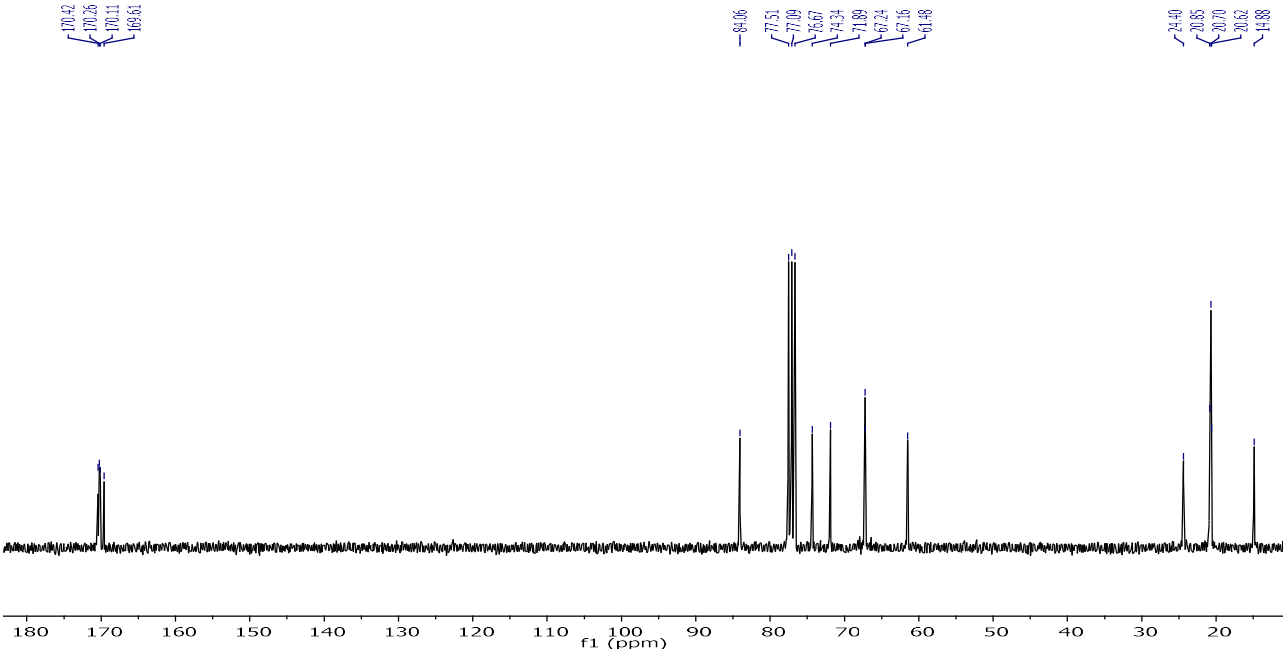

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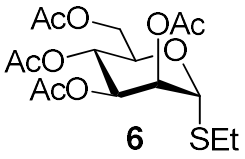

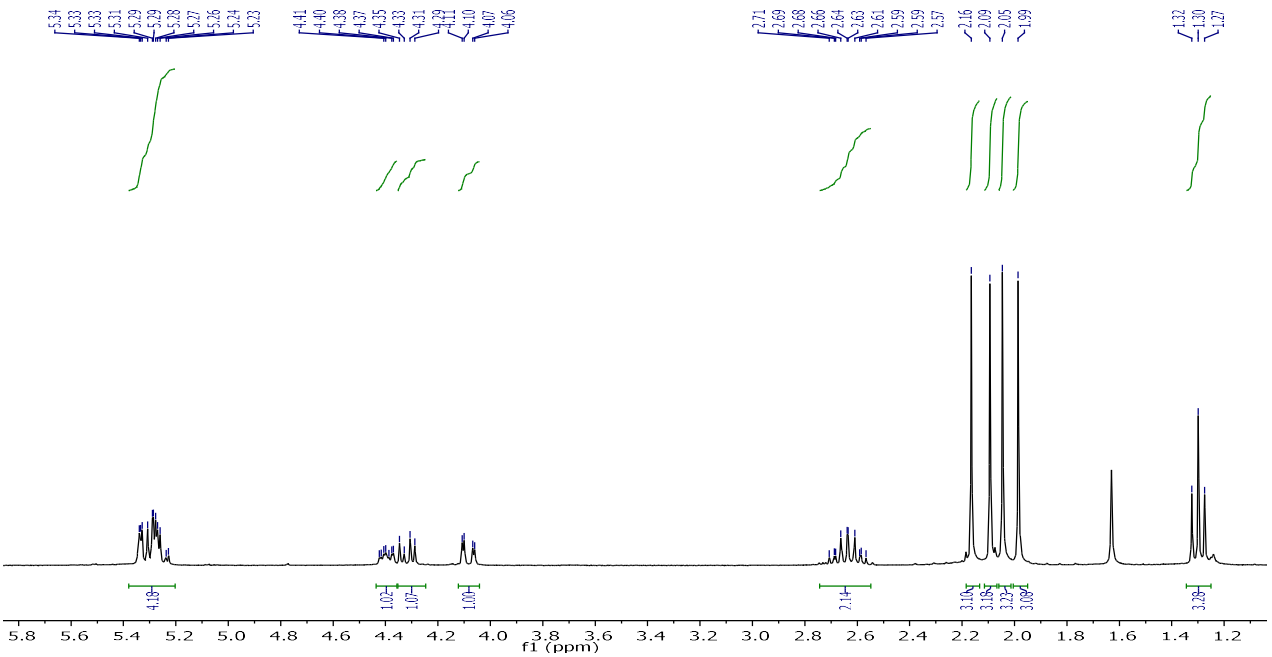

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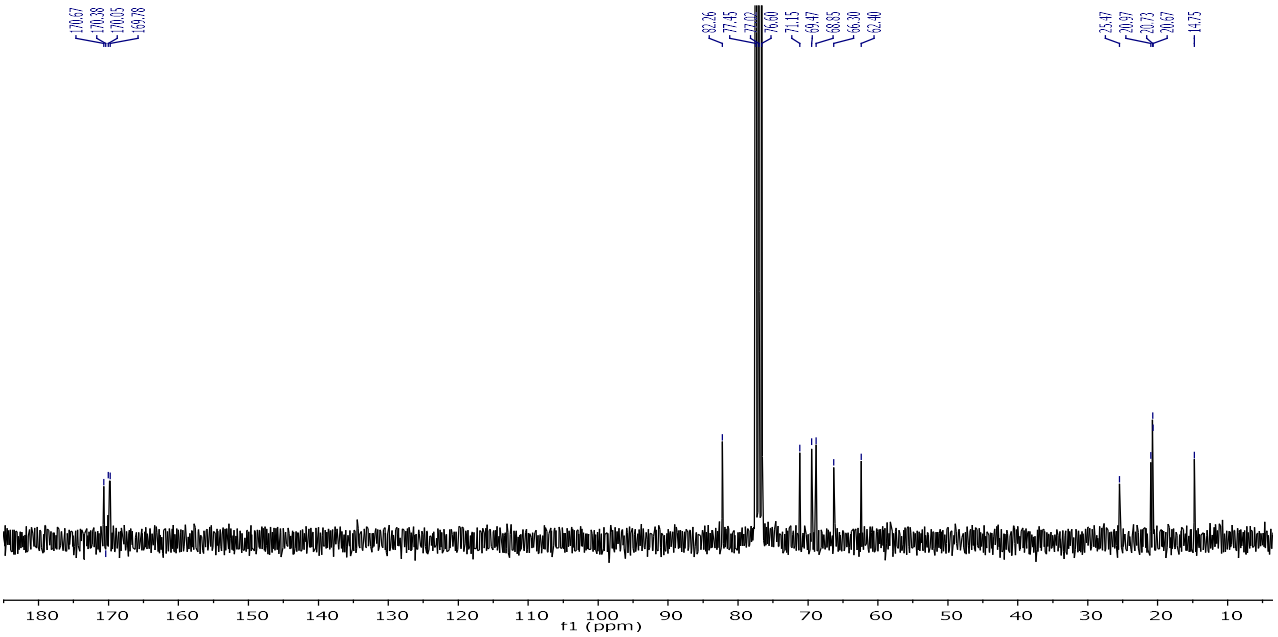

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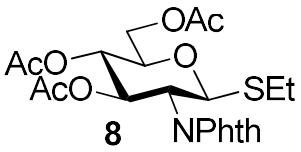

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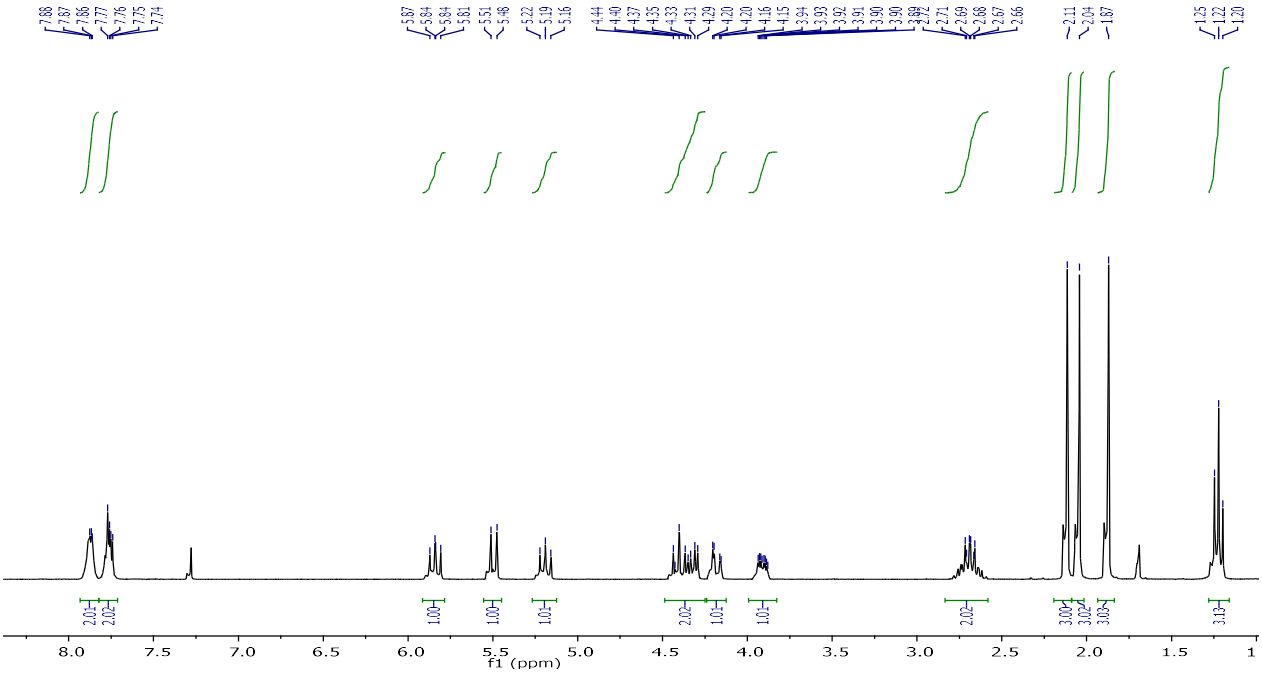

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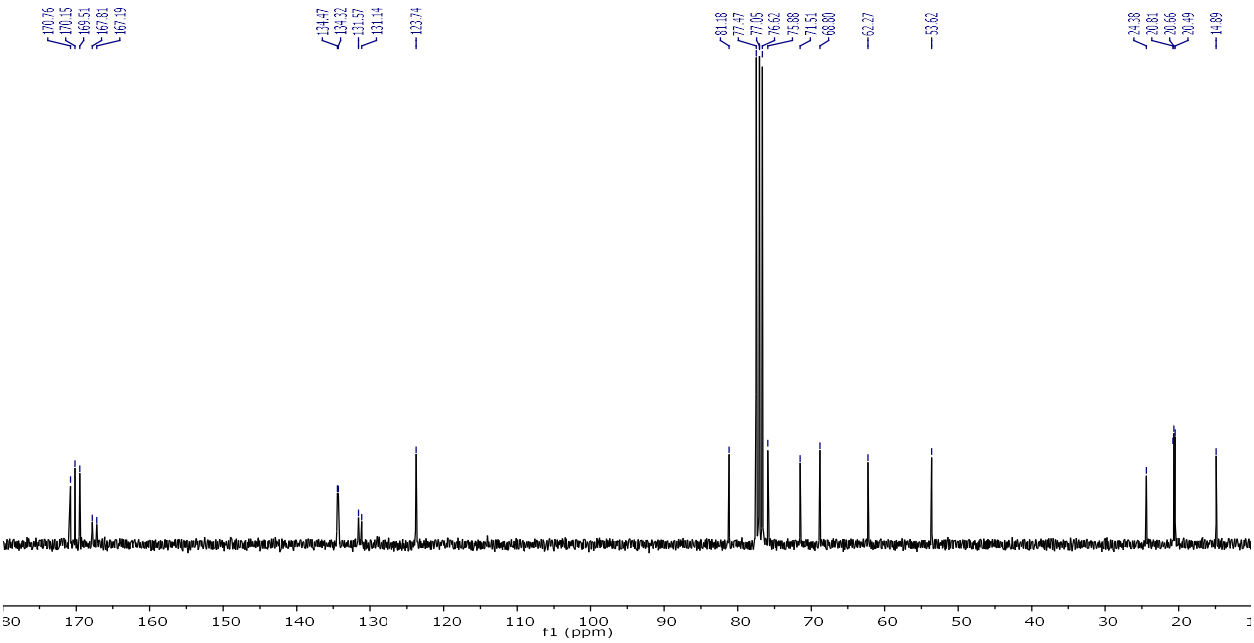

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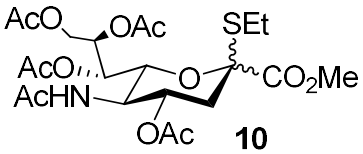

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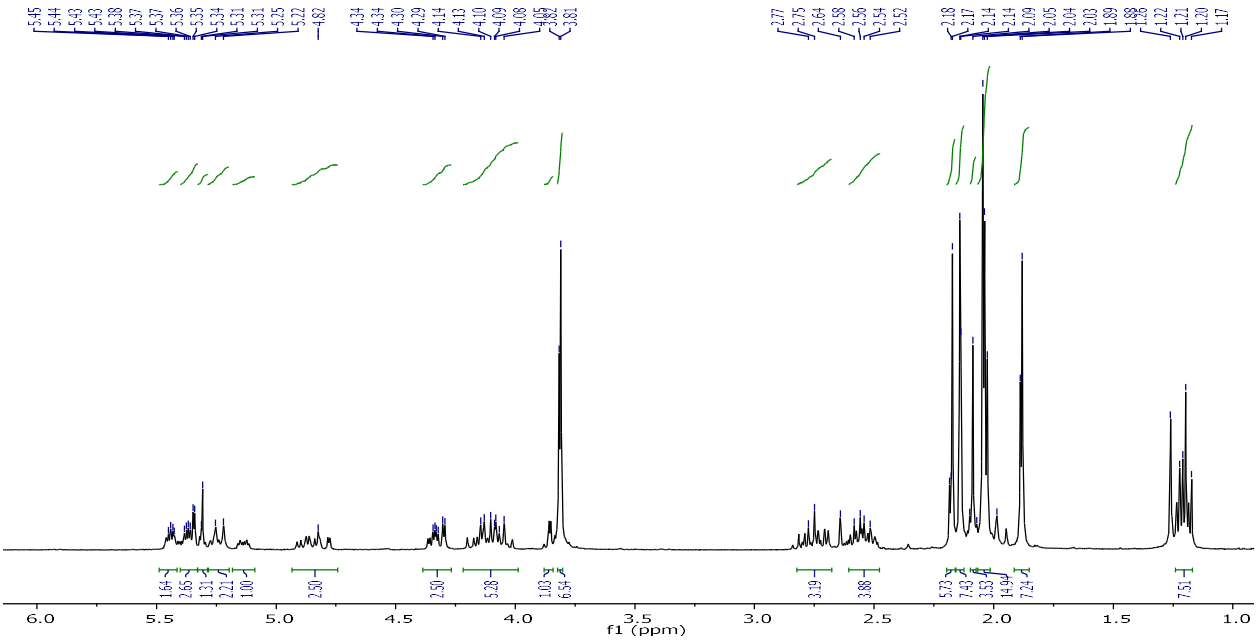

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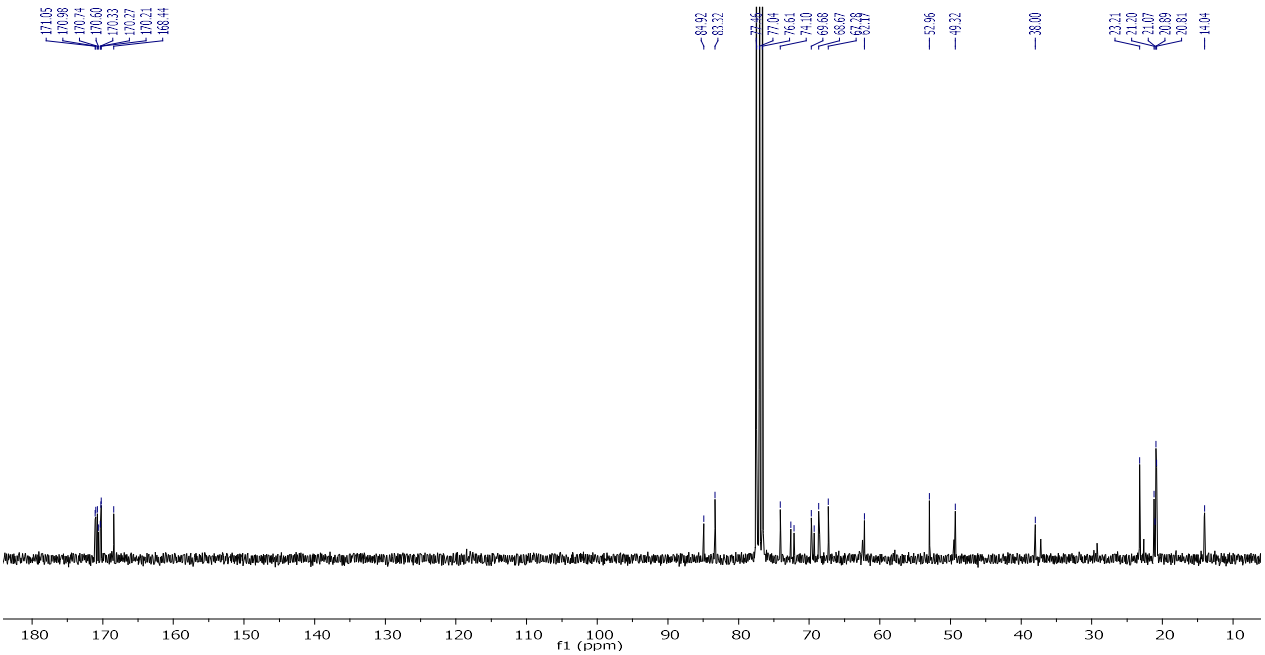

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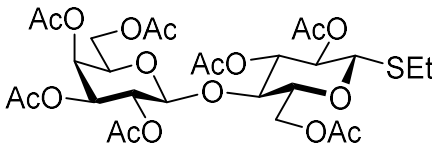

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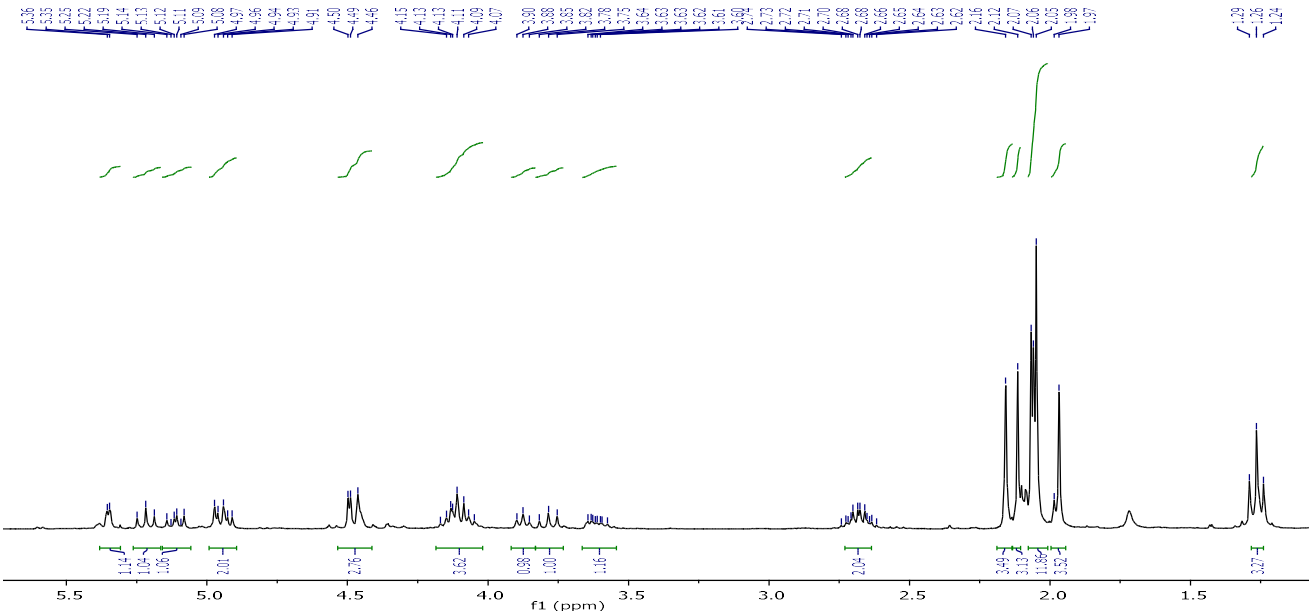

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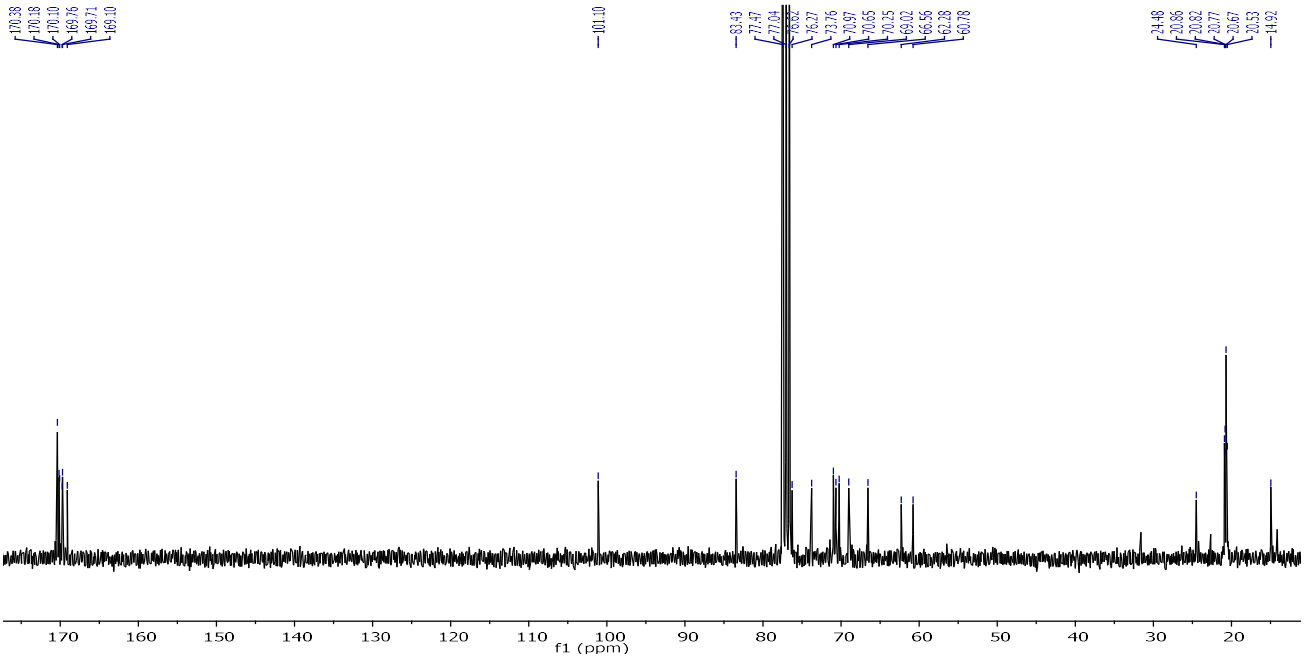

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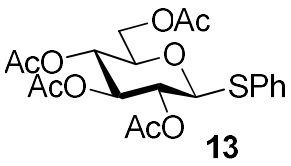

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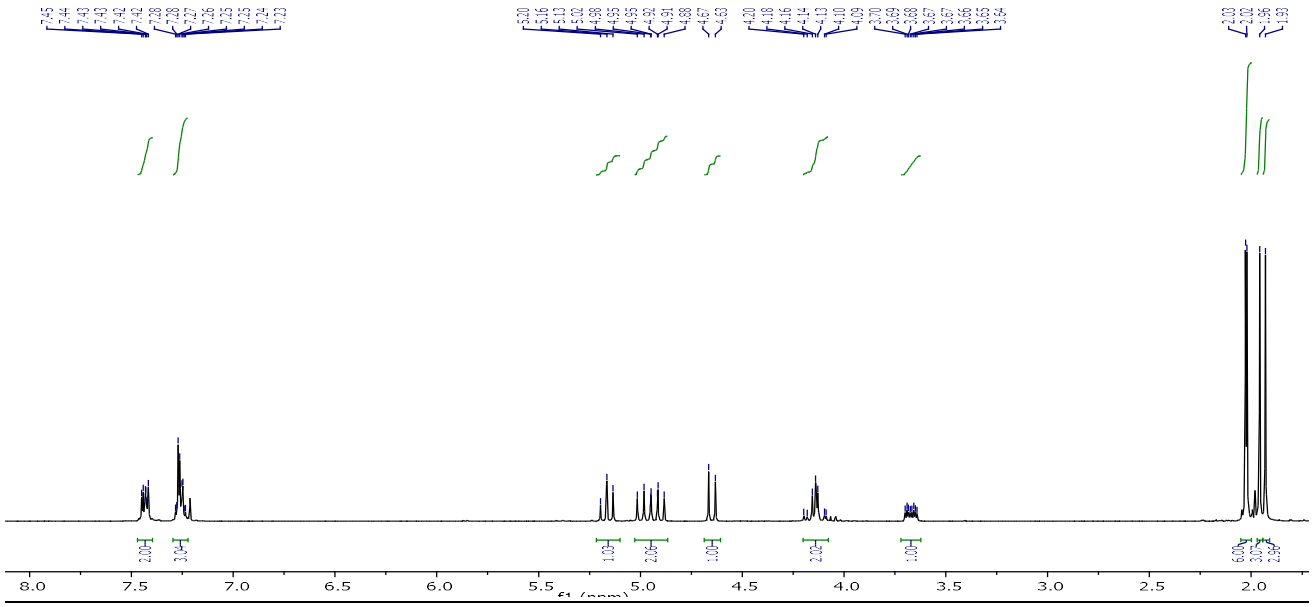

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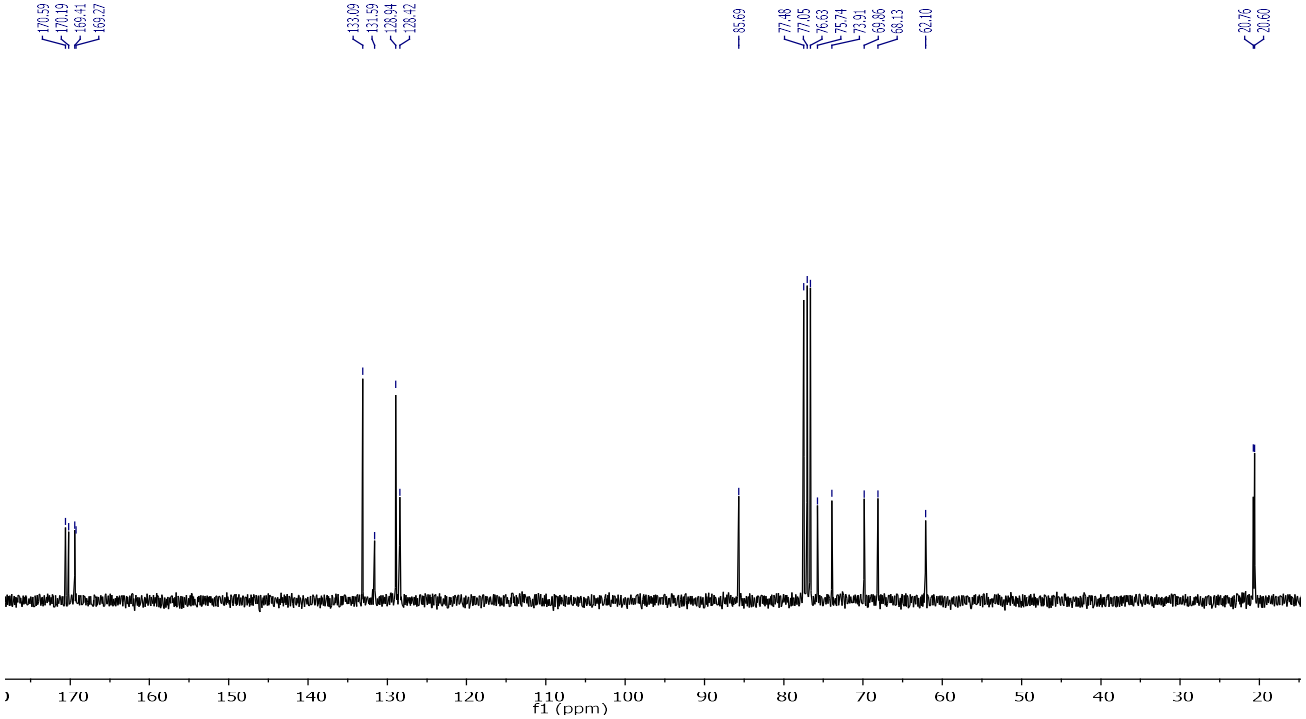

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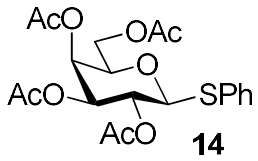

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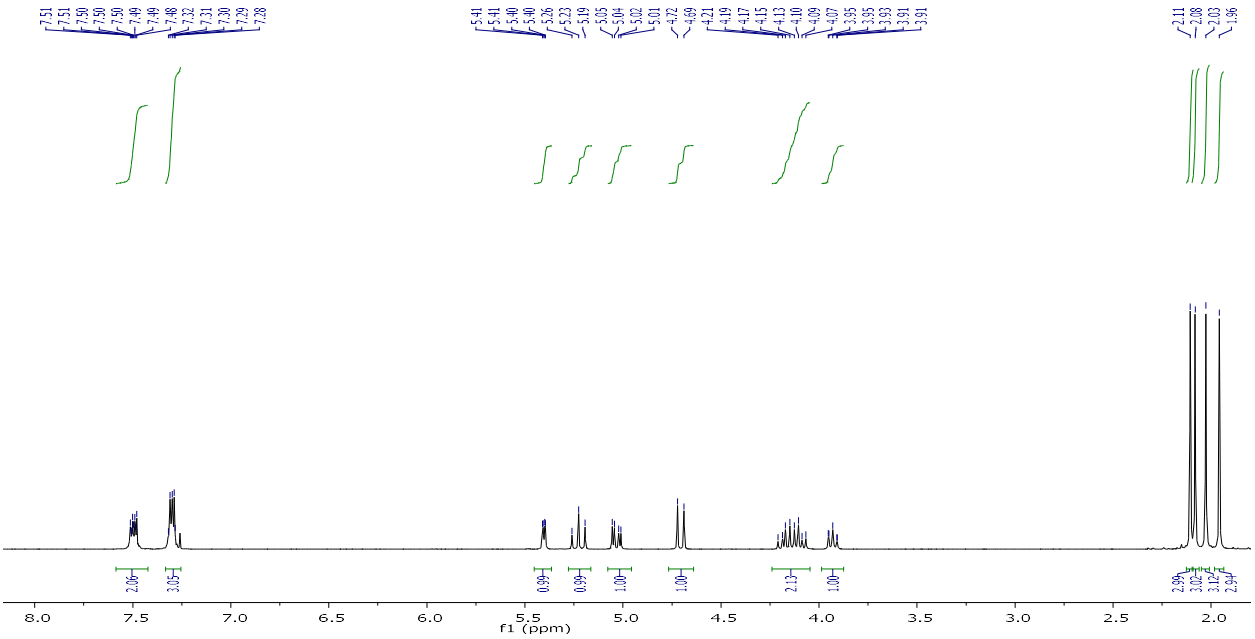

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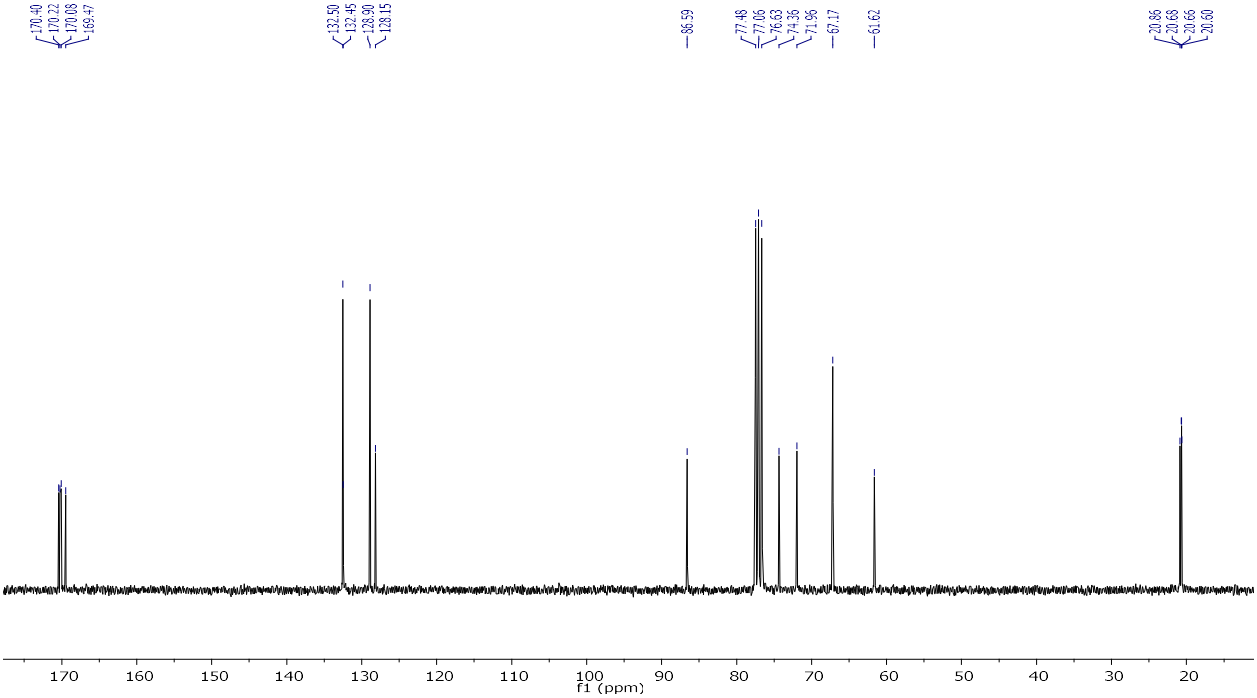

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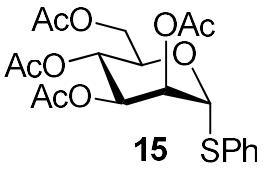

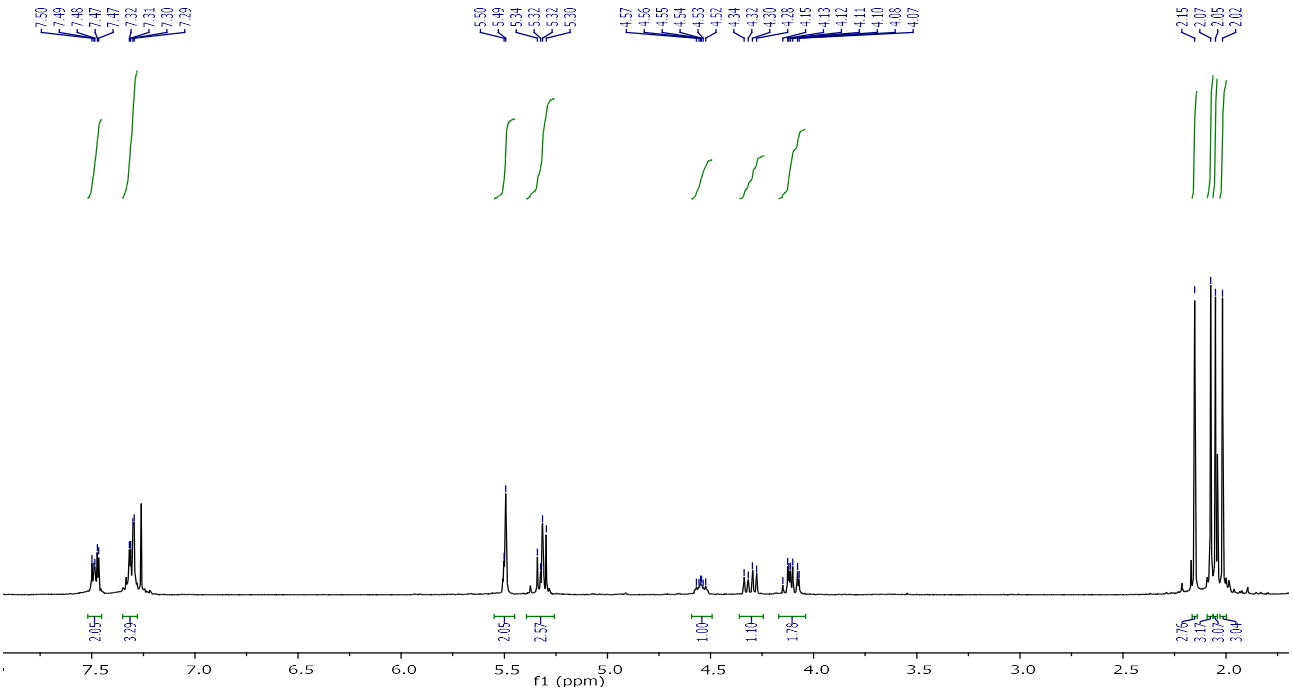

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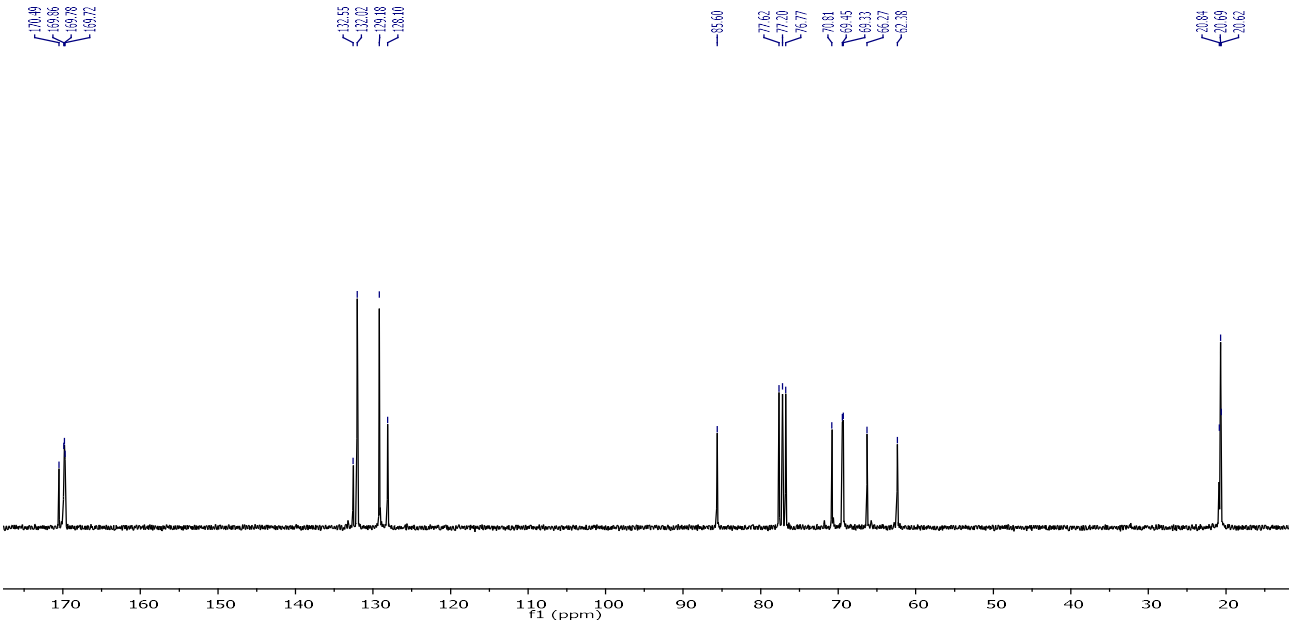

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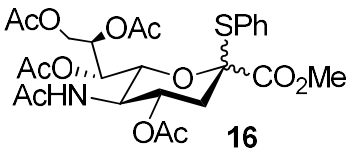

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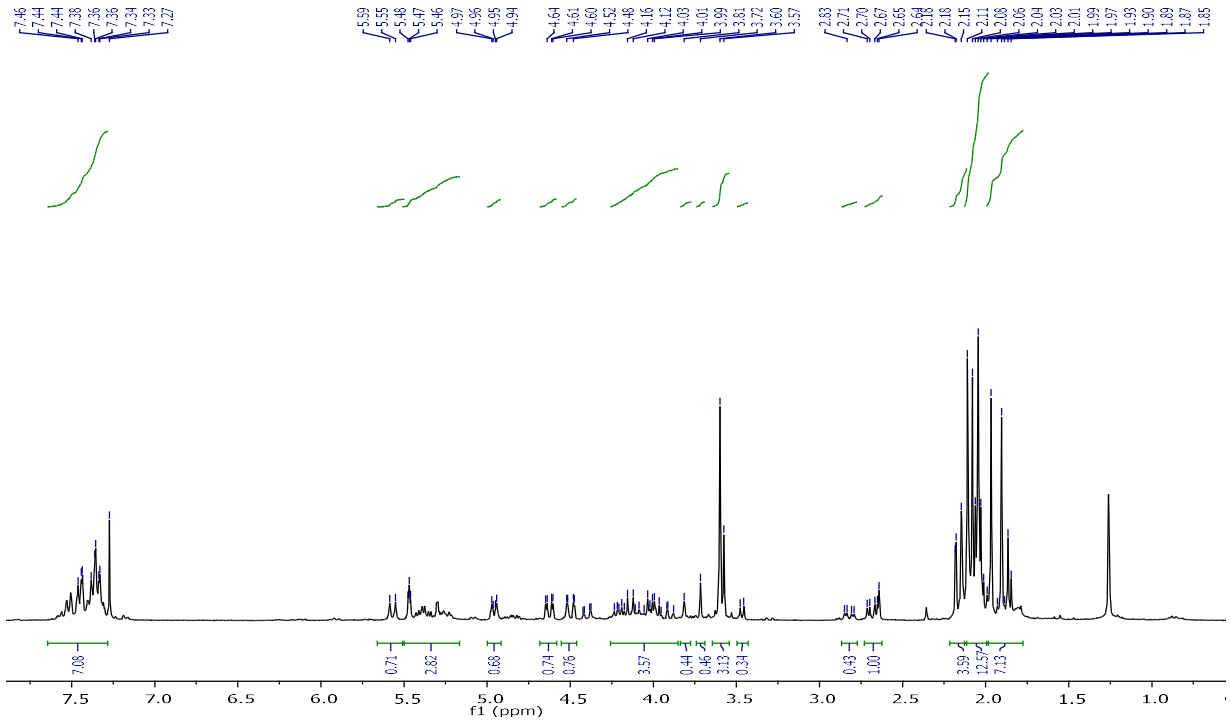

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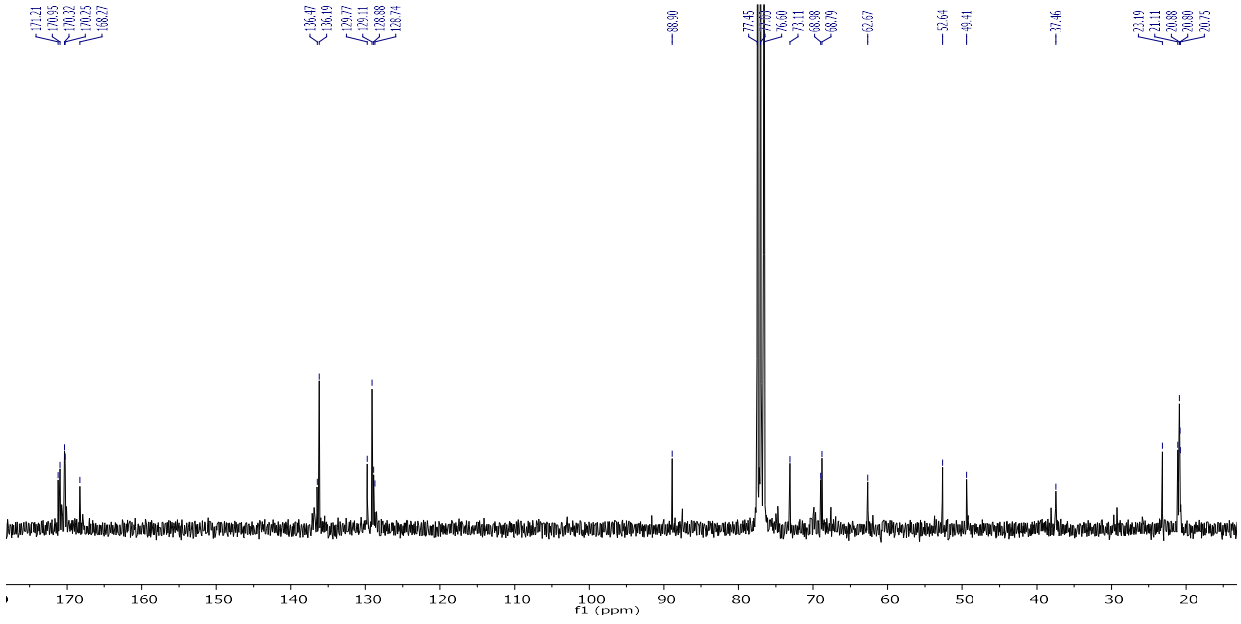

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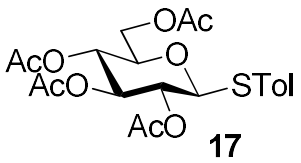

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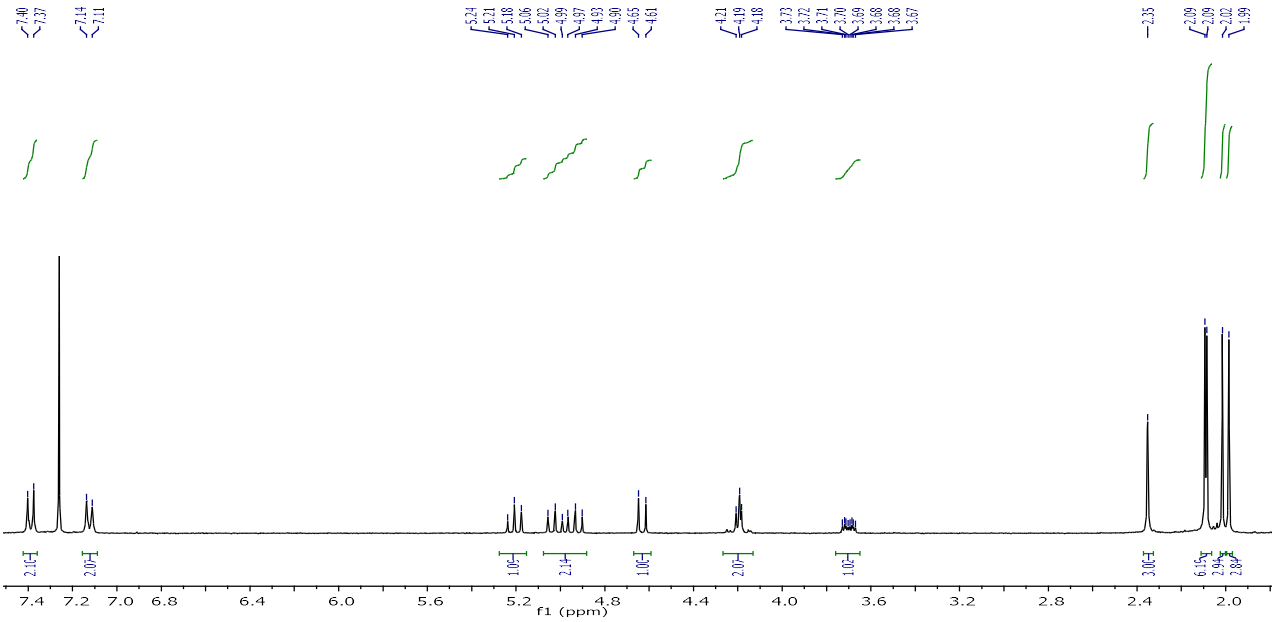

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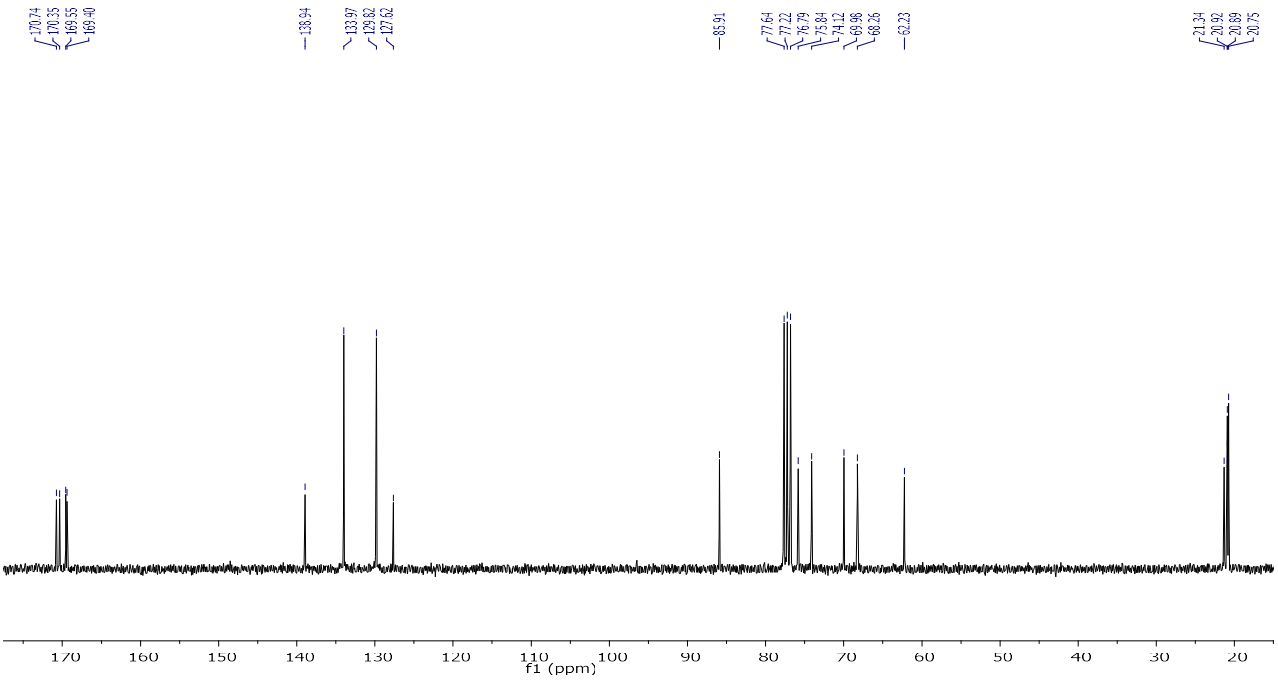

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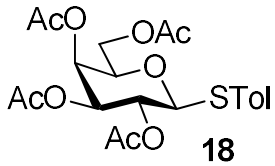
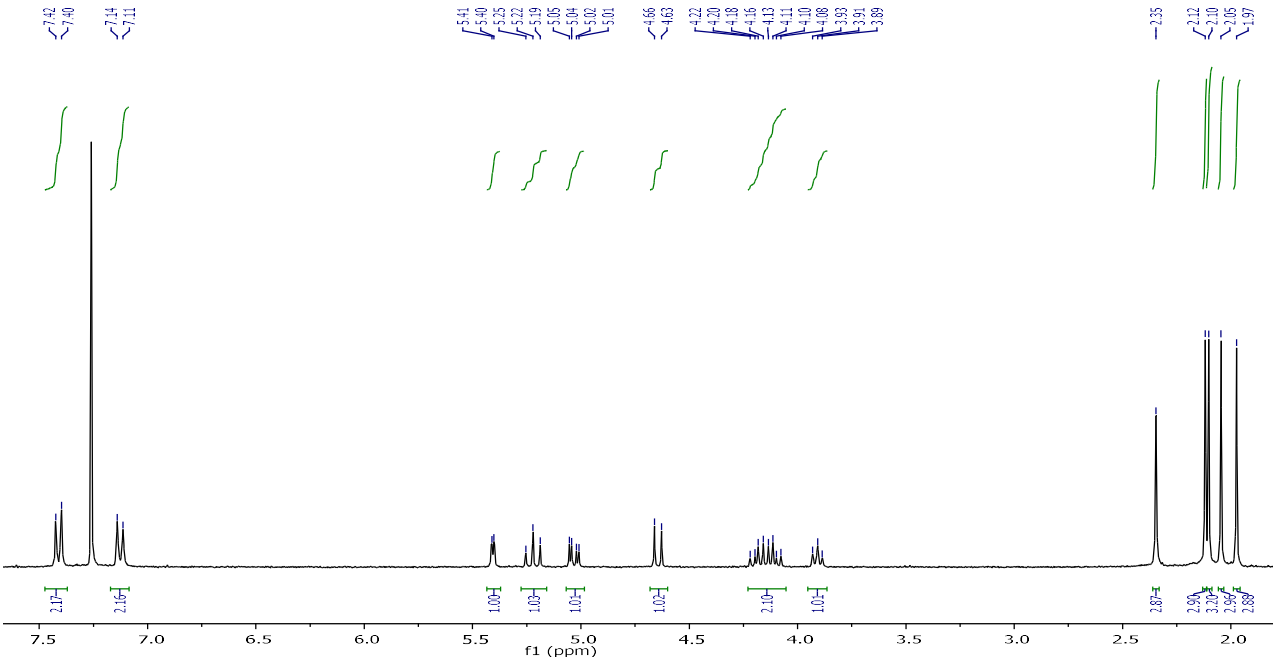
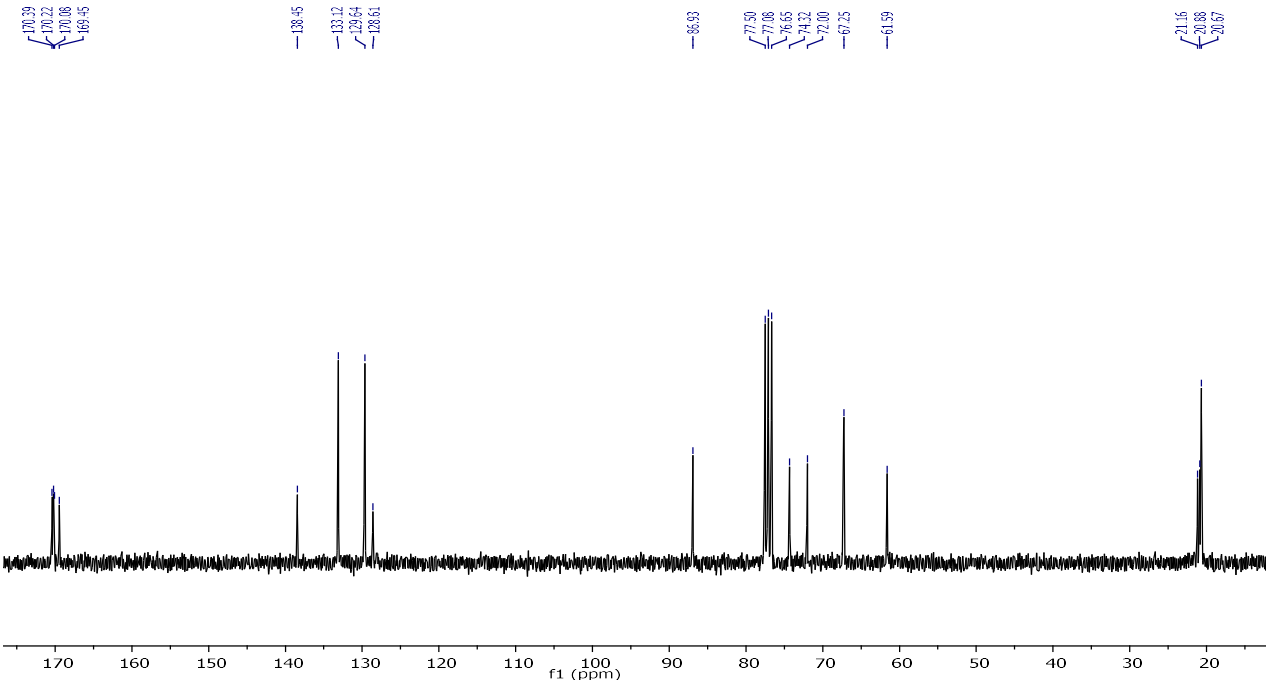


18



$CDCl_3$ 300 MHz



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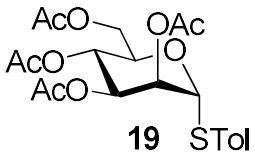

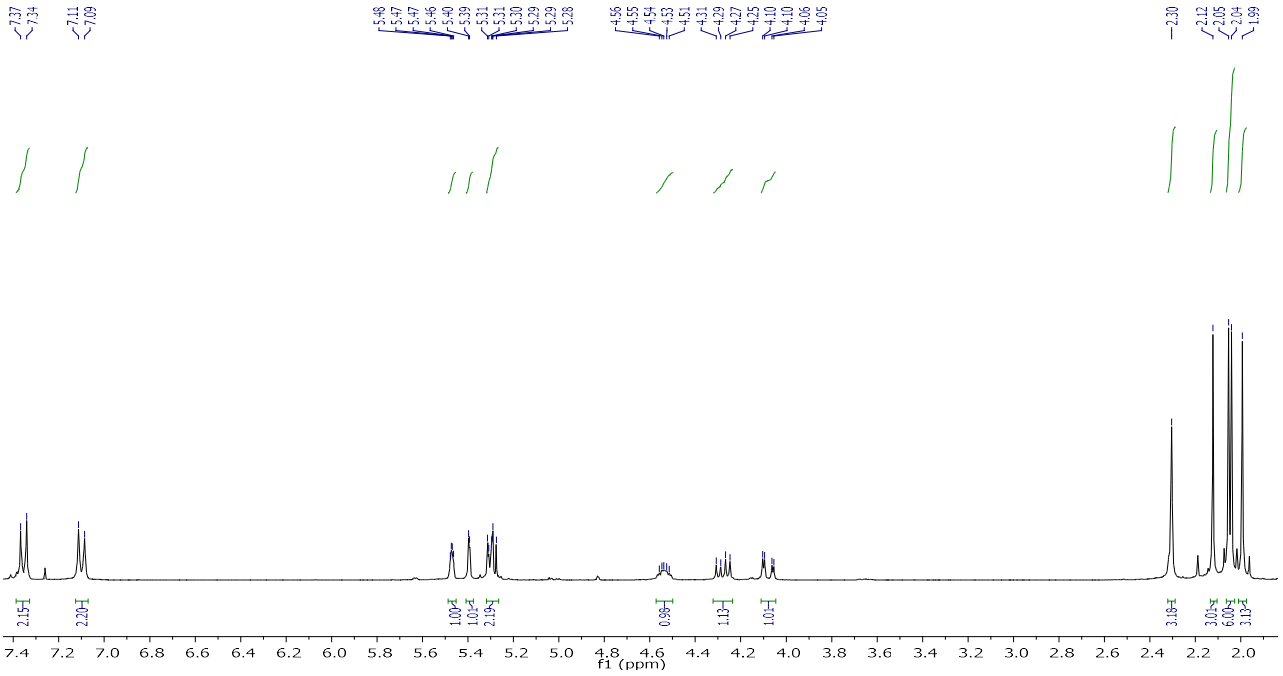

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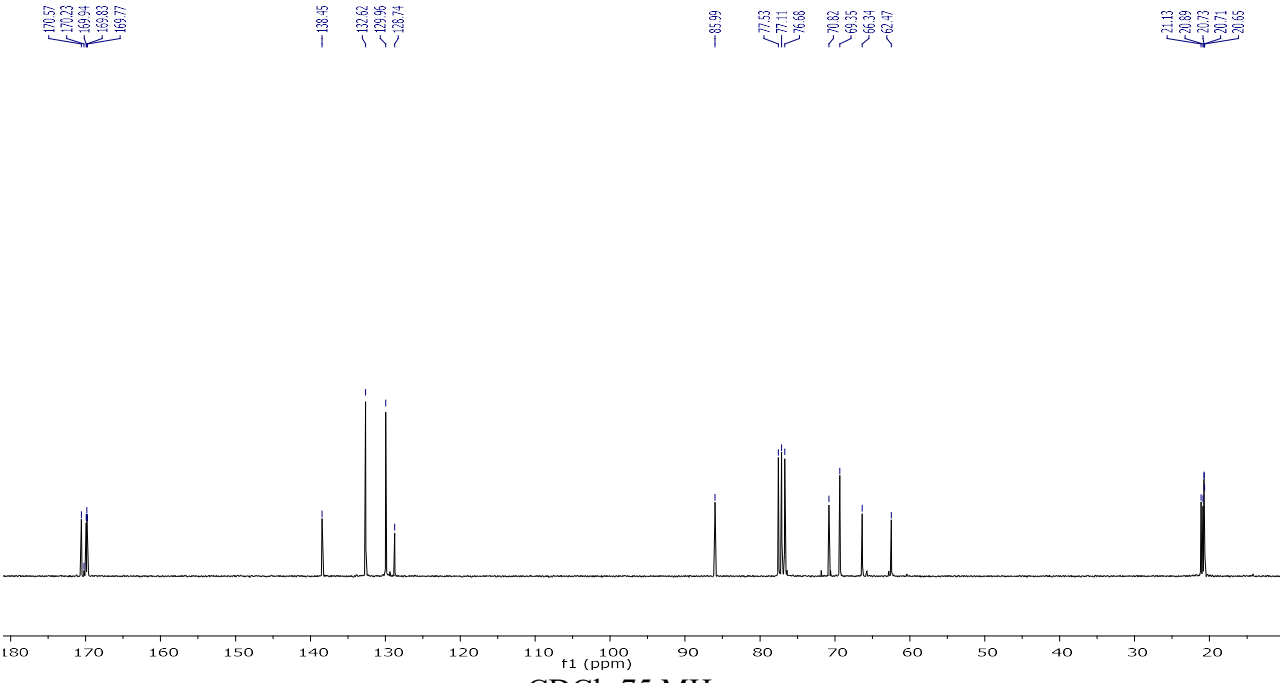

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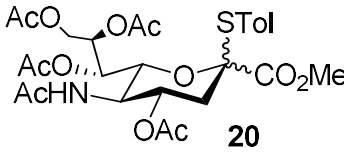
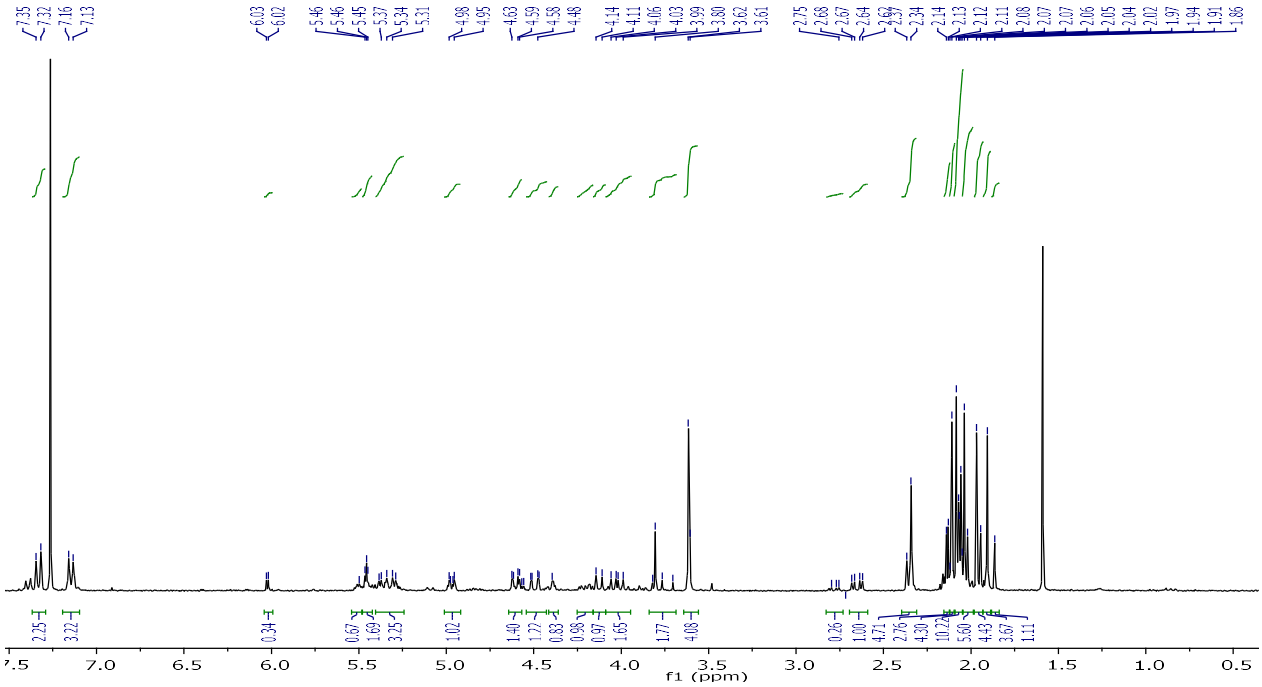
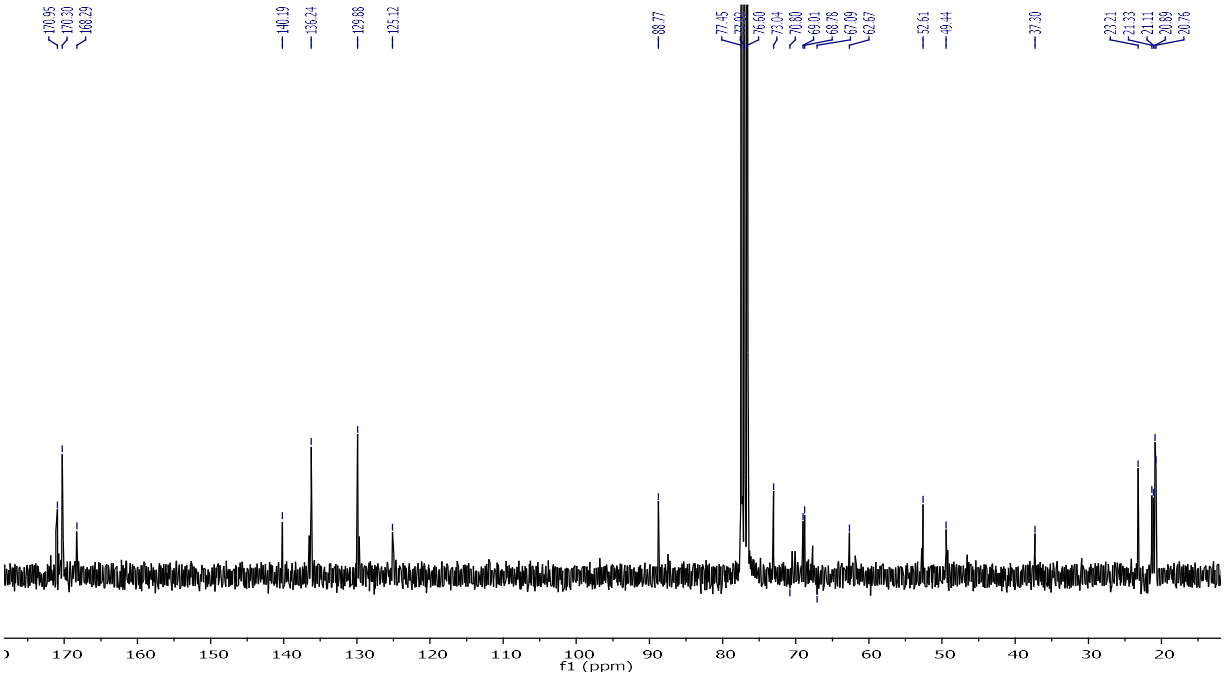


20



$CDCl_3$ 300 MHz



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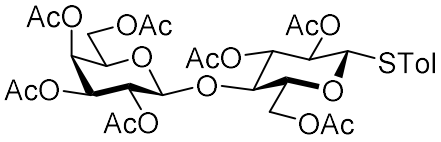

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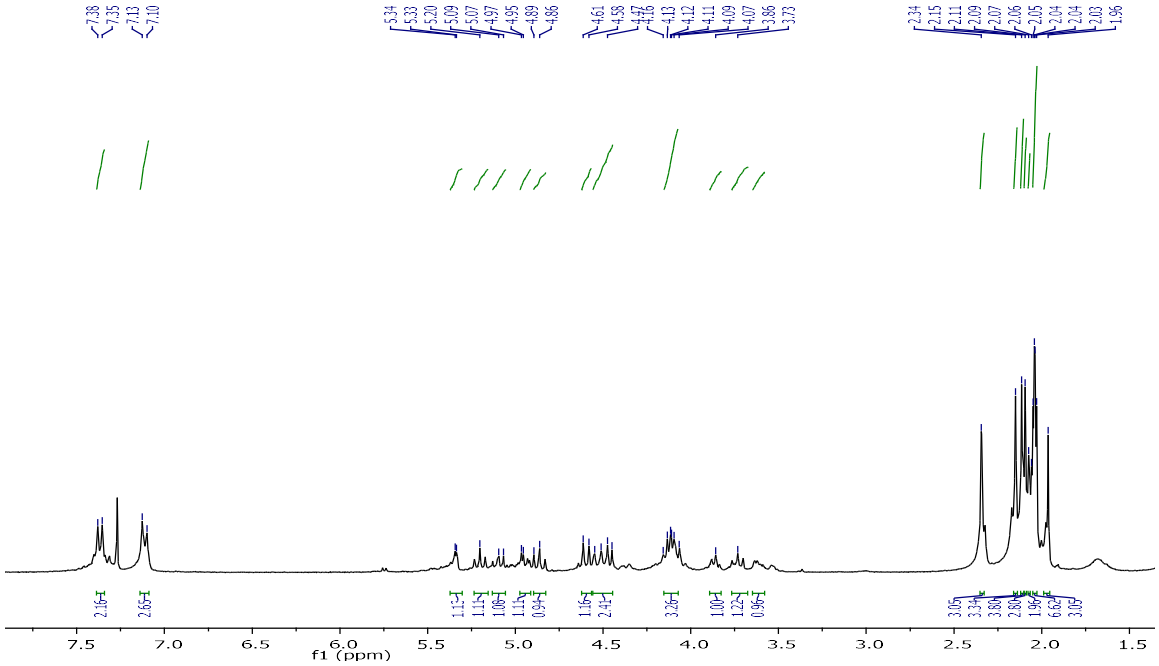
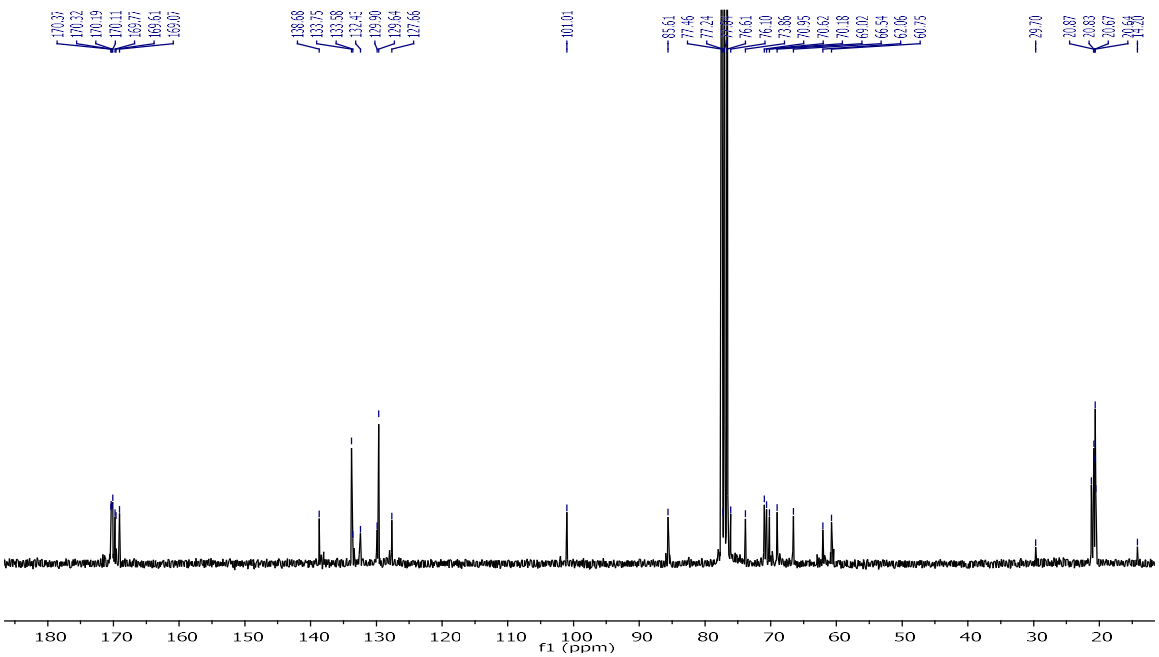


$CDCl_3$ 300 MHz



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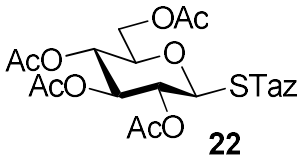

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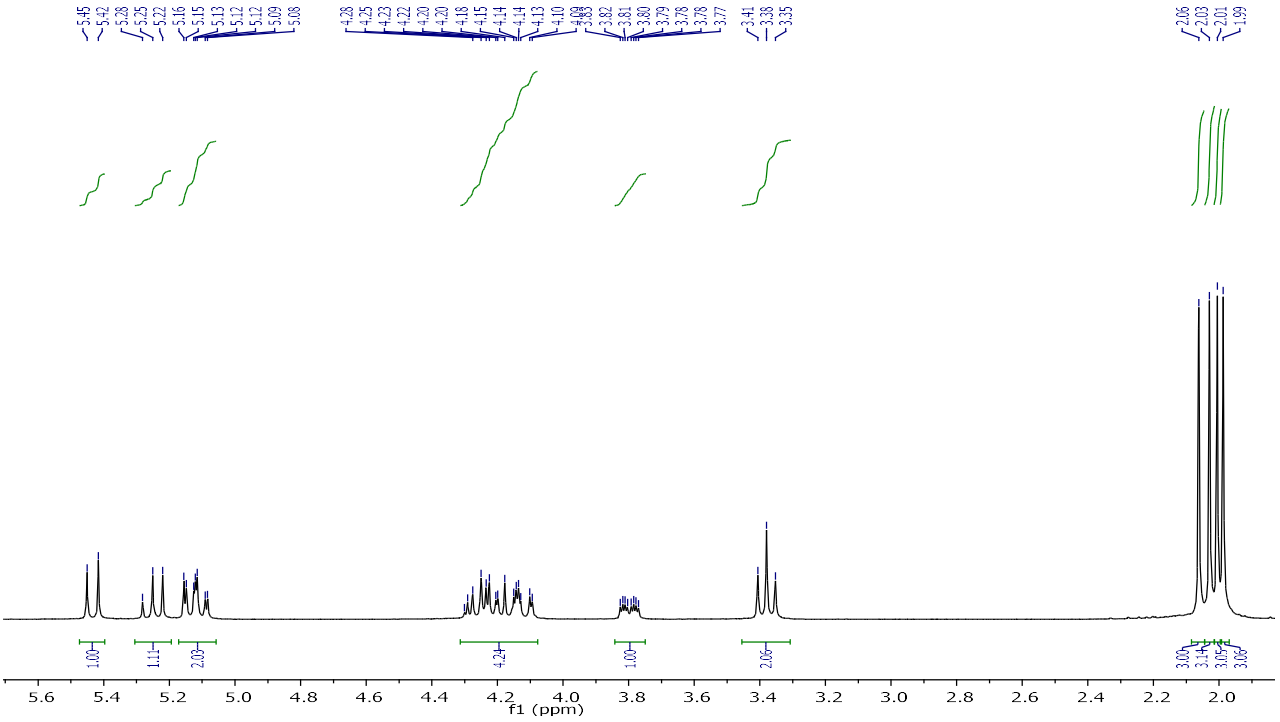

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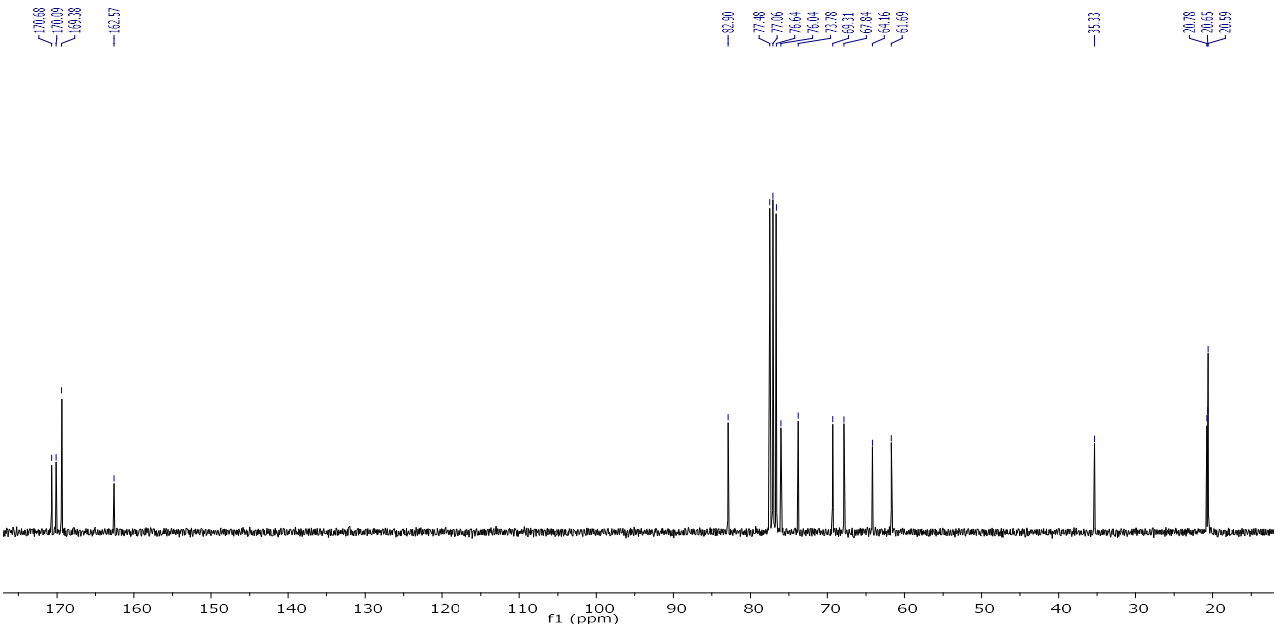

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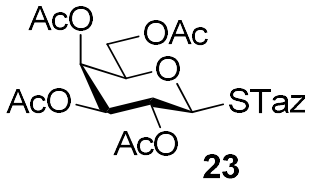
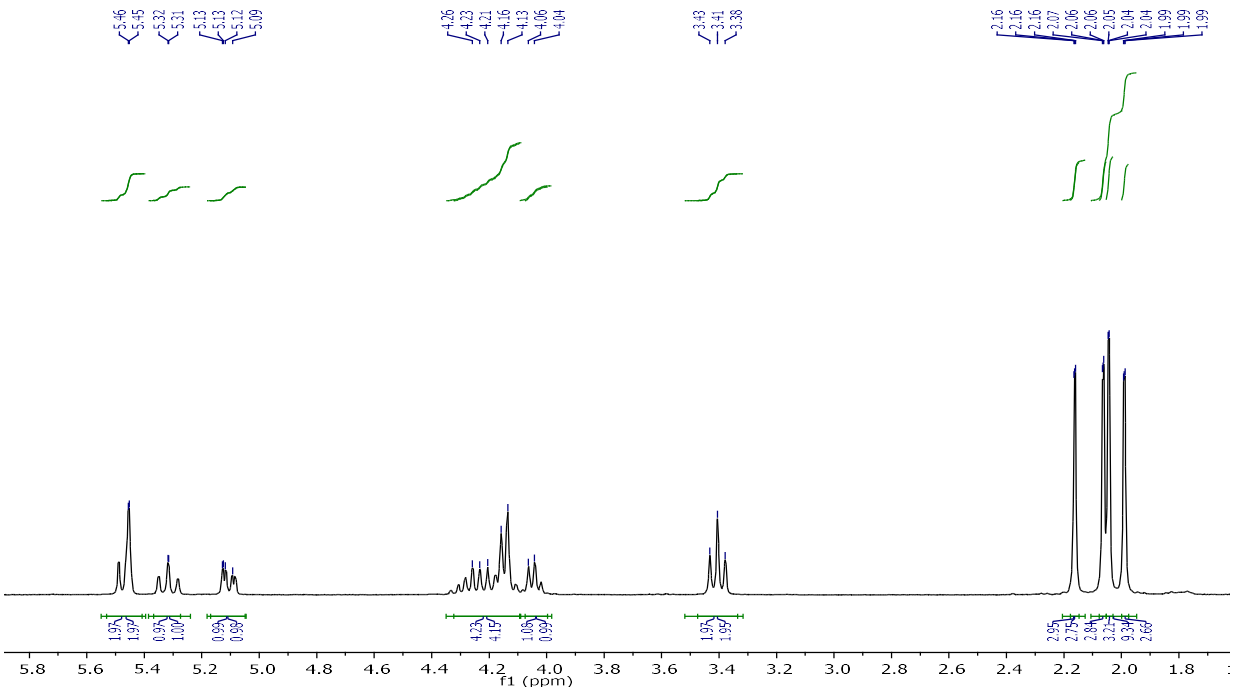


23



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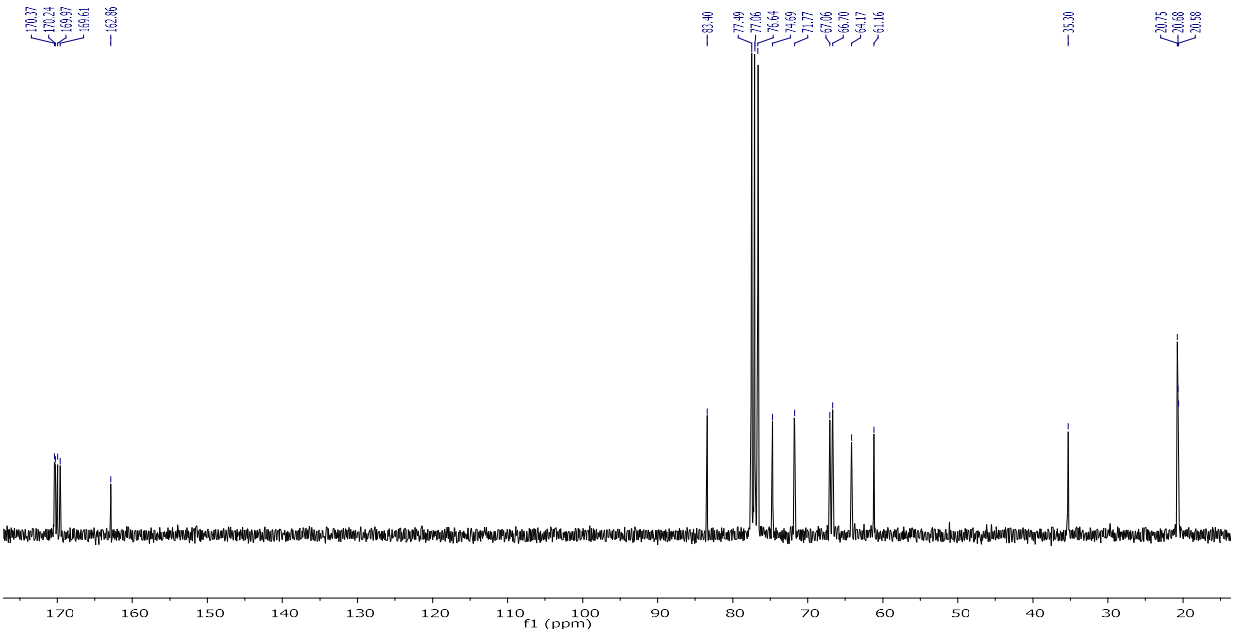

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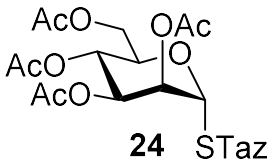

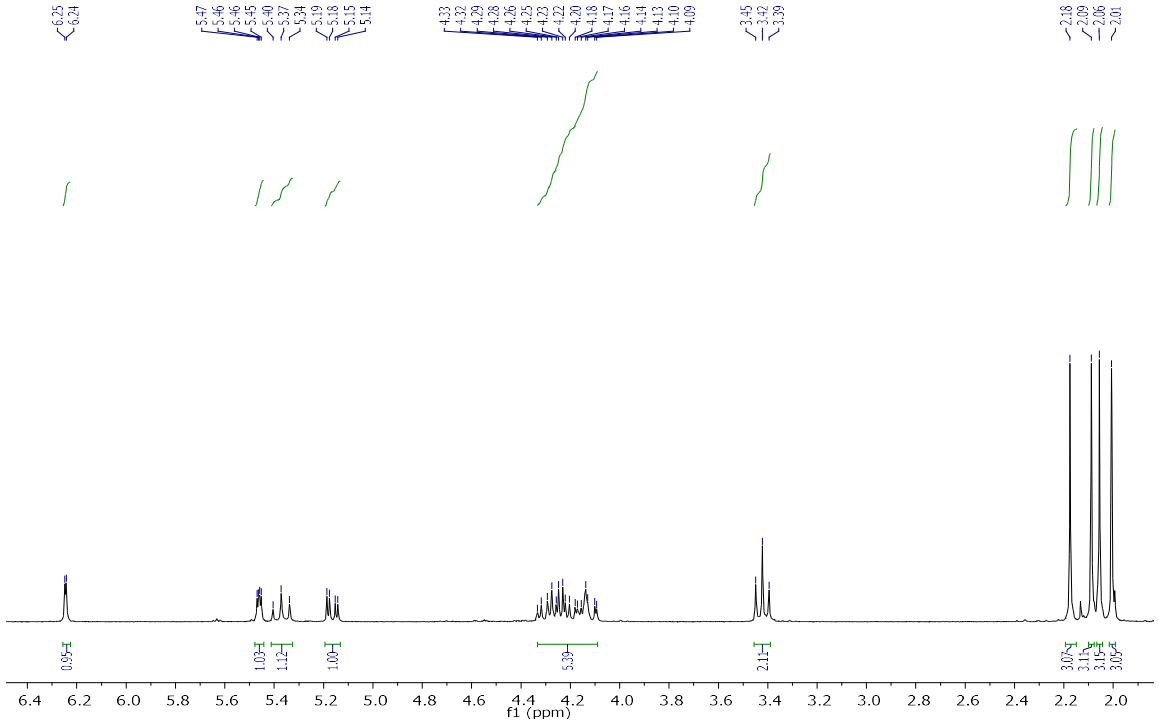

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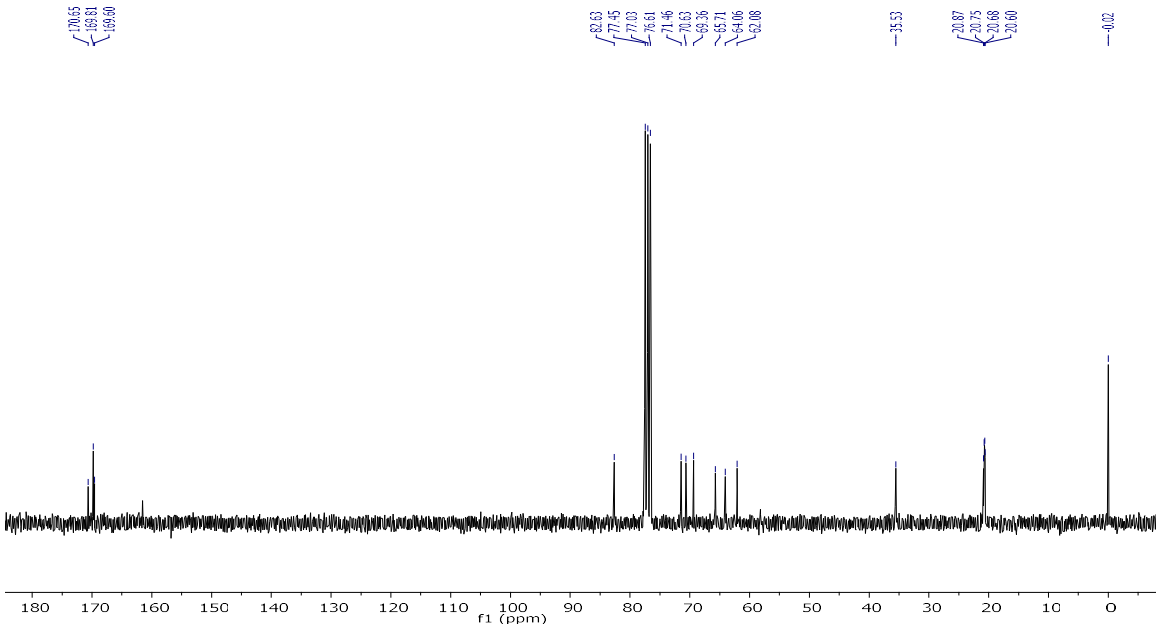

$CDCl_3$ 75 MHz