SUPPORTING INFORMATION

I - Experimental procedures :

General procedure 1: tetraacetylated (4-bromophenyl)-α-D-mannopyranoside **9-10** (1 equiv.), 4- or 3-formylphenyl boronic acid (3 equiv.), caesium carbonate (3 equiv.), and tetrakis(triphenylphosphine)palladium (10 mol%) were heated at 80°C in dioxane/water (84/16, 0.055 M) for 1 h, under argon atmosphere. The solvent was removed under reduced pressure and the crude was purified by silica gel column chromatography (PE/EA: 100/0 to 40/60).

General procedure 2: ammonium acetate (1.1 equiv.) was added to a solution of mannoside **11**-**13** (1 equiv.) in nitromethane (0.08 M). The reaction mixture was heated for 2 to 24h. The solvent was removed under reduced pressure and the crude was purified by silica gel column chromatography (PE/EA : 100/0 to 40/60) (compound **16**). For compounds **14** and **15**, the residue obtained after evaporation was taken up with ethyl acetate and washed 2 times with saturated aqueous NH_4Cl, dried over $MgSO_4$, filtered and the solvent evaporated under reduced pressure to give the desired product which was used in the next step without any further purification.

General procedure 3, thiohydroximate formation: titanium tetrachloride (2.2 equiv.) was added dropwise to a stirred solution of triethylsilane (2.1 equiv.) and biphenylnitrovinyl derivative **14-16** (1 equiv.) in anhydrous dichloromethane (0.06 M) under argon atmosphere. The mixture was stirred at room temperature overnight. The reaction mixture was quenched by addition of water, then the aqueous phase was extracted 2 times with dichloromethane. The combined organic phases were dried over $MgSO_4$ and the solvent evaporated under reduced pressure. The residue was taken up with anhydrous dichloromethane (0.06 M) and 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose (1.2 equiv.) and triethylamine (3 equiv.) were sequentially added and the reaction mixture was stirred for 3h at rt. The solvent was evaporated under reduced pressure and the crude residue was purified by silica gel column chromatography (PE/EA: 100/0 to 50/50) to give the desired product.

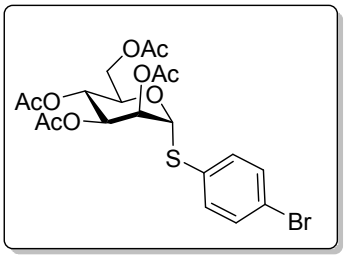
General Procedure 4, sulfation: sulfur trioxide-pyridine complex (5 equiv.) was added to a solution of thiohydroximate (1 equiv.) in anhydrous DMF (0.4 M). The suspension was heated at 50°C overnight. It was then cooled at 0°C, quenched by addition of a 0.5M aqueous $KHCO_3$ solution (10 equiv.) and then stirred for 30 minutes at room temperature. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography (EA/MeOH 9/1).

General procedure 5: potassium methoxide (0.4 equiv.) was added to a solution of acetylated compound (1 equiv.) in anhydrous methanol (0.15 M). The reaction mixture was stirred at room temperature during 6h. The solvent was then evaporated under reduced pressure and the crude product was purified using Reveleris® column chromatography on C-18 reverse phase (H_2O/MeOH : 100/0 to 0/100).

General Procedure 6: 0.67 U of myrosinase from *Sinapis alba* (white mustard) seed (10 U/mL) solution was added to a solution of glucosinolate (0.1 mmol, 1 equiv.) and benzylmercaptan (0.3 mmol, 3 equiv.), in a mixture of water/phosphate buffer pH = 7 (2/1) (0.029 M). The

mixture was stirred at 37°C for 24h, then purified using Reveleris® column chromatography on C-18 reverse phase (H_2O/MeOH : 100/0 to 0/100).

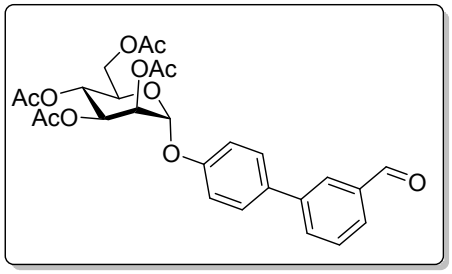
4-Bromophenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside 10:[11d]



2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-manno pyranoside **8** (2.4 g, 6.6 mmol, 0.96 equiv.), 1-bromo-4-iodobenzene (1.95 g, 6.9 mmol, 1 equiv.), xantphos (100 mg, 0.17 mmol, 2.5 mol%), palladium(II) acetate (78 mg, 0.35 mmol, 5 mol%) were added in the reaction vessel. The solid mixture was put under vacuum and backfilled with dry argon three times, then anhydrous dioxane (40 mL), anhydrous triethylamine (960 µL, 6.9 mmol, 1 equiv.) were sequentially added. The solution was heated at 100°C for 1 h. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (PE/EA : 100/0 to 50/50) to give the desired product **10** as a mixture of α/β-anomers (80/20) as a brown foam (3.11 g, 87%).

R_f = 0.8 (DCM/MeOH : 96/4); δ_H (400 MHz, $CDCl_3$) 7.44 (2.2 H, d, ^3J 8.4 Hz, CH_{Ar}), 7.40 - 7.33 (2.2 H, m, CH_{Ar}), 5.64 (0.2 H, d, $^3J_{2\text{-}3}$ 3.4 Hz, H-2_β), 5.51 - 5.43 (2H, m, H-1_α, H-3_α), 5.36 - 5.22 (2.2 H, m, H-2_α, H-4_α, H-$4_{\beta)}$, 5.05 (0.2 H, dd, $^3J_{3\text{-}4}$ 10.1 Hz, $^3J_{2\text{-}3}$ 3.3 Hz, H-3_β), 4.87 (0.2H, s, H-1_β), 4.51 - 4.45 (1H, m, H-5_α), 4.29 (1 H, dd, $^2J_{6a\text{-}6b}$ 12.2 Hz, $^3J_{6a\text{-}5}$ 5.9 Hz, H-$6_{a\alpha}$), 4.27 - 4.23 (0.2H, m, H-$6_{a\beta}$), 4.17 (0.2 H, dd, $^2J_{6b\text{-}6a}$ 12.1 Hz, $^3J_{6\text{-}5}$ 1.9 Hz, $H_{6b\beta}$), 4.10 (1 H, dd, $^2J_{6b\text{-}6a}$ 12.2 Hz, $^3J_{6b\text{-}5}$ 1.5 Hz, H-$6b_\alpha$), 3.72 - 3.62 (0.2 H, m, H-5_β), 2.20 (0.7 H, s, CH_3Ac_β), 2.15 (3H, s, CH_3Ac_α), 2.09 (0.7 H, s, CH_3Ac_β), 2.07, 2.05, (6H, 2 x s, CH_3Ac_α), 2.04 (1.4 H, bs, CH_3Ac_β), 2.01 (3H, s, CH_3Ac_α), 1.98 (0.7H, s, CH_3Ac_α); δ_C (100 MHz, $CDCl_3$) 170.64 ($C{=}O_\beta$), 170.59 ($C{=}O_\alpha$), 170.2, 170.1 ($C{=}O_\beta$), 170.0, 169.9, 169.8 ($C{=}O_\alpha$), 169.7 ($C{=}O_\beta$), 133.8 ($CH_{Ar\,\beta}$), 133.6 ($CH_{Ar\,\alpha}$), 132.4 ($CH_{Ar\,\alpha}$), 132.3 ($CH_{Ar\,\beta}$), 131.9 ($Cq_{Ar\,\alpha}$), 122.7 ($Cq_{Ar\,\beta}$), 122.6 ($Cq_{Ar\,\alpha}$), 85.6 (C-1_α), 85.5 (C-1_β), 76.6 (C-5_β), 71.9 (C-3_β), 70.9 (C-3_α), 70.5 (C-2_β), 69.8 (C-5_α), 69.4 (C-4_α or C-2_α), 66.4 (C-2_α or C-4_α), 65.8 (C-4_β), 62.9 (C-6_β), 62.6 (C-6_α), 21.0 ($CH_{3\,Ac\,\beta}$), 20.9 ($CH_{3\,Ac\,\alpha}$), 20.8, 20.76 ($CH_{3\,Ac\,\beta}$), 20.7 ($CH_{3\,Ac\,\alpha}$), 20.68; IR (neat) ν (cm^{-1}) = 1750 (C=O), 1666 (C=C), 1474 ($C{=}C_{Ar}$), 1215 (C-O), 815 (C_{sp2}-H_{Ar}); ESI^+ HRMS $[M+H]^+$ *m/z* calcd. 519.0319 for $C_{20}H_{24}BrO_9S$, found 519.0314.

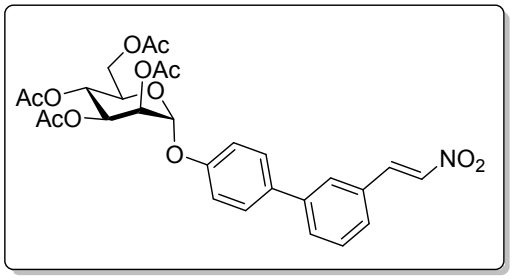
[4'-(2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyloxy)biphenyl-3-yl]carboxaldehyde 13:



General procedure 1 was followed with tetraacetylated 4-bromophenyl-α-D-mannoside **9** (2.35 g), 3-formylphenylboronic acid (1.43 g), caesium carbonate (3.11 g), and tetrakis(triphenylphosphine)palladium (356 mg) in dioxane/water (84/16) (85 mL). The desired product **13** was obtained as a yellow foam (1.97 g, 80%).

R_f = 0.72 (PE/EA : 5/5); $[\alpha]_D^{20}$ +92.5 (*c* 0.13 in MeOH); δ_H (400 MHz, $CDCl_3$) 10.04 (1H, s, HC=O), 8.02 (1H, s, H $_{Ar}$), 7.79 (2H, t, ^3J 7.7 Hz, H $_{Ar}$), 7.58 - 7.51 (3H, m, H $_{Ar}$), 7.17 (2H,d, ^3J 8.6 Hz, H $_{Ar}$), 5.59 - 5.54 (m, 2H, H_1, H_3), 5.45 (bs, 1H, H_2), 5.37 (1H, t, $^3J_{4\text{-}3}$ $^3J_{4\text{-}5}$ 10.2 Hz, H_4), 4.27 (1H,dd, $^2J_{6a\text{-}6b}$ 12.4 Hz, $^3J_{6a\text{-}5}$ 5.4 Hz, H_{6a}), 4.14 - 4.04 (2H, m, H_{6b}, H_5), 2.18 (3H, s, CH_3 $_{Ac}$), , 2.04, 2.02, 2.01 (9H, 3 x s, CH_3 $_{Ac}$); δ_C (100 MHz, $CDCl_3$) 192.3 (HC=O), 170.5, 170.0, 169.9, 169.7 (C=O), 155.6, 141.3, 137.0, 134.6 (Cq $_{Ar}$), 132.7, 129.5, 128.5, 128.4, 127.7, 117.0 (CH $_{Ar}$), 95.9 (C-1), 69.4 (C-2 or C-5), 69.3 (C-5 or C-2), 68.9 (C-3), 66.0 (C-4), 62.1 (C-6), 20.9, 20.7 (CH_3 $_{Ac}$); IR (neat) ν (cm^{-1}) = 1744 (C=O), 1696 (C=O ald), 1605), 1514 (C=C $_{Ar}$), 1215 (C-O), 836 (C_{sp2}-H $_{Ar}$); ESI$^+$ HRMS $[M+H]^+$ *m/z* calcd. 551.1524 for $C_{27}H_{29}NaO_{11}$, found 551.1524.

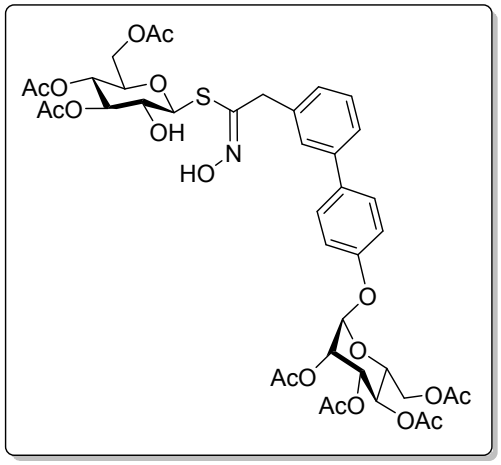
([3'-((*E*)-2-Nitrovinyl)biphenyl]-4-yl) 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside 16 :



General procedure 2 was followed with mannoside **13** (2.12 g), ammonium acetate (340 mg) in nitromethane (57 mL) for 24h at 50°C. The desired product **16** was obtained as a yellow foam after purification (1.66 g, 72%).

R_f =0.80 (PE/EA : 6/4); $[\alpha]_D^{20}$ +78.0 (*c* 0.7 in MeOH); δ_H (400 MHz, $CDCl_3$) 8.04 (1H, d, ^3J $_{trans}$ 13.7 Hz, CH=CH), 7.69-7.60 (3H, m, H $_{Ar}$, CH=CH), 7.54-7.48 (4H, m, H $_{Ar}$), 7.18 (1H, d, ^3J 8.6 Hz, H $_{Ar}$), 5.60 - 5.55 (2H, m, H_1, H_3), 5.47 (1H, bs, H_2), 5.39 (1H, t, $^3J_{4\text{-}3}$ ^3J $_{4\text{-}5}$ 10.2 Hz, H_4), 4.29 (1H, dd, $^2J_{6a\text{-}6b}$ 12.4 Hz, $^3J_{6a\text{-}5}$ 5.3 Hz, H_{6a}), 4.14-4.06 (2H, m, H_{6b}, H_5), 2.20 (3H, s, CH_3), 2.05, 2.04, 2.03 (9H, 3 x s, CH_3 $_{Ar}$); δ_C (100 MHz, $CDCl_3$) 170.6, 170.1, 170.0, 169.8 (C=O), 155.7 (Cq $_{Ar}$), 141.8 (Cq $_{Ar}$), 139.0 (CH=CH), 137.5 (CH=CH), 134.6 (Cq $_{Ar}$), 130.7 (Cq $_{Ar}$), 130.6 (CH $_{Ar}$), 129.9 (CH $_{Ar}$), 128.4 (CH $_{Ar}$), 127.6 (CH $_{Ar}$), 127.59 (CH $_{Ar}$), 117.1 (CH $_{Ar}$), 95.9 (C-1), 69.4 (C-2 or C-5), 69.38 (C-5 or C-2), 68.9 (C-3), 66.0 (C-4), 62.2 (C-6), 20.9, 20.8 (CH_3 $_{Ac}$); IR (neat) ν (cm^{-1}) = 1742 (C=O), 1697 (C=O), 1606, 1516, 1479 (C=C $_{Ar}$), 1213 (C-O), 836, 795 (C_{sp2}-H $_{Ar}$); ESI$^+$ HRMS $[M+Na]^+$ *m/z* calcd. 594.1583 for $C_{28}H_{29}NNaO_{12}$, found 594.1582.

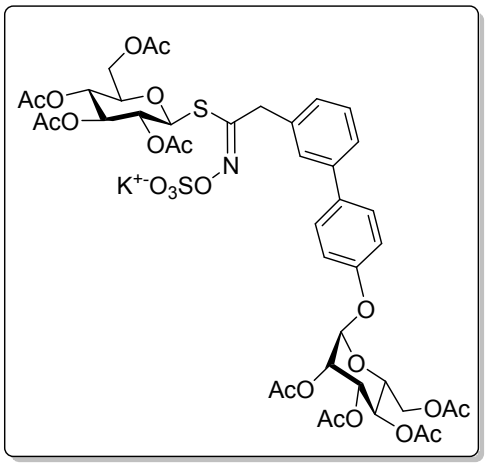
***(Z)*-*S*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)[4'-(2,3,4,6-tetra-*O*-acetyl-α-D-manno pyranosyloxy)biphenyl-3-yl]aceto thiohydroximate 21:**



General procedure 3 was followed from biphenyl nitrovinyl derivative **16** (1.3 g), titanium tetrachloride (554 µL.) and triethylsilane (764 µL) in anhydrous dichloromethane (38 mL). For the second step, were used 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose (746 mg, 0.9 equiv.) and triethylamine (670 µL) and 38 mL of anhydrous dichloromethane. The desired product **21** was obtained after purification (PE/EA: 100/0 to 30/70) as a white foam (1.48 g, 70%).

R_f=0.2 (PE/EA : 5/5); $[\alpha]_D^{20}$ +36.9 (*c* 0.13 in MeOH); δ_H (400 MHz, $CDCl_3$) 8.84 (1H, bs, NOH), 7.49 (2H, d, ^3J 8.7 Hz, H $_{Ar}$), 7.46-7.35 (3H, m, H $_{Ar}$), 7.19 (1H, d, ^3J 7.5 Hz, H $_{Ar}$), 7.13 (2H,d, ^3J 8.7 Hz, H $_{Ar}$), 5.59-5.53 (2H, m, H_{3M}, H_{1M}), 5.45 (1H, bs, H_{2M}), 5.37 (1H, t, $^3J_{4-5}$ $^3J_{4-3}$ 10.0 Hz, H_{4M}), 5.07-4.91 (3H, m, H_{2G}, H_{3G}, H_{4G}), 4.84 (1H, d, $^3J_{1-2}$ 9.9 Hz, H_{1G}), 4.27 (1H, dd, $^2J_{6a-6b}$ 12.3 Hz, $^3J_{6a-5}$ 5.1 Hz, H_{6aM}), 4.14-3.91 (6H, m, CH_2C=N, H_{6bM}, $H_{5M,}$ H_{6G}), 3.51-3.45 (1H, m, H_{5G}), 2.19 (3H, s, CH_3), 2.04, 2.03, 2.02, 2.01 (12H, 4s, CH_3), 1.97 (3H, s, CH_3), 1.94 (3H, s, CH_3), 1.90 (3H, s, CH_3) ; δ_C (100 MHz, $CDCl_3$) 170.7, 170.6, 170.3, 170.1, 170.09, 169.9, 169.4, 169.2 (C=O), 155.3 (Cq $_{Ar}$), 150.9 (C=N), 141.2 (Cq $_{Ar}$), 136.5 (Cq $_{Ar}$), 135.7 (Cq $_{Ar}$), 129.4 (CH $_{Ar}$), 128.4 (CH $_{Ar}$), 126.9 (CH $_{Ar}$), 126.5 (CH $_{Ar}$), 126.0 (CH $_{Ar}$), 116.9 (CH $_{Ar}$), 95.9 (C-1_M), 79.6 (C-1_G), 75.7 (C-5_G), 73.8, 70.1, 69.5, 69.3, 69.0 (C-3_M), 68.1, 66.0 (C-4_M), 62.2 (C-6_G or C-6_M), 62.17 (C-6_M or C-6_G), 38.9 (CH_2C=N), 20.9, 20.8, 20.59, 20.57 ($CH_{3\ Ac}$); IR (neat) ν (cm^{-1}) = 1742 (C=O), 1607, 1479 (C=C $_{Ar}$), 1213, 1031 (C-O), 795 (C_{sp2}-H $_{Ar}$); ESI$^+$ HRMS $[M+H]^+$ *m/z* calcd. 920.2641 for $C_{42}H_{50}NO_{20}S$, found 920.2636.

(*Z*)-*S*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)[4'-(2,3,4,6-tetra-*O*-acetyl-α-D-manno pyranosyloxy)biphenyl-3-yl]aceto thiohydroximate *N*,*O*-sulfate potassium salt 24:

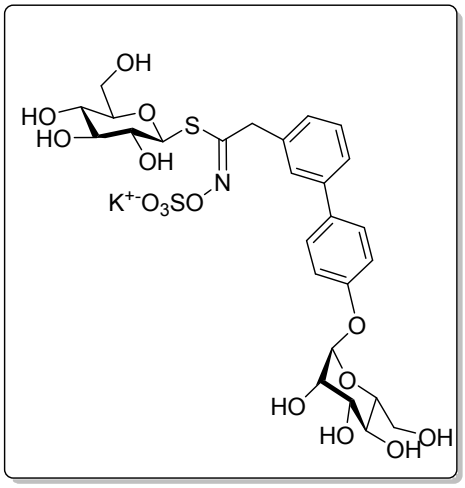


General procedure 4 was followed from thiohydroximate **21** (1.3 g) and sulfur trioxide-pyridine complex (1.12 g) in anhydrous DMF (22 mL). After 16h at 50°C, sulfur trioxide-pyridine complex (560 mg) was added again, and the reaction mixture was heated for an additional 8h. The desired compound **24** was obtained as a white foam (1.26 g, 86%).

R_f = 0.38 (EA/MeOH : 9/1); $[\alpha]_D^{20}$ + 32.7 (*c* 0.18 in MeOH); δ_H (400 MHz, CD_3OD) 7.68-7.62 (3H, m, CH $_{Ar}$), 7.53 (1H, d, ^3J 7.7 Hz, H $_{Ar}$), 7.44 (1H, t, ^3J 7.6 Hz, H $_{Ar}$), 7.36 (1H, d, ^3J 7.5 Hz, H $_{Ar}$), 7.23 (2H, d, ^3J 8.5 Hz, H $_{Ar}$), 5.67 (1H, s, H_{1M}), 5.53-5.46 (2H, m, H_{3M}, H_{2M}), 5.32 (1H, t, $^3J_{4-3}$ $^3J_{4-5}$ 9.8 Hz, H_{4M}), 5.15-5.08 (2H, m, H_{1G}, H_{2G}), 4.97 (1H, t, $^3J_{4-3}$ $^3J_{4-5}$ 9.7 Hz, H_{4G}), 4.87 (1H, t, $^3J_{3-2}$ $^3J_{3-4}$ 9.6 Hz, H_{3G}), 4.24 (1H, dd, $^2J_{6a-6b}$ 11.9 Hz, $^3J_{6a-5}$ 5.3 Hz, H_{6aM}), 4.20-4.05 (5H, m, H_{5M}, H_{6aG}, H_{6bM}, CH_2C=N), 3.83 (1H, bd, $^2J_{6b-6a}$ 11.9 Hz, H_{6bG}), 3.71-3.64 (1H, m, H_{5G}), 2.19 (3H, s, CH_3), 2.06 (3H, s, CH_3), 2.01 (6H, s, CH_3), 1.97 (6H, s, CH_3), 1.93 (3H, s, CH_3), 1.86 (3H, s, CH_3); δ_C (100 MHz, CD_3OD) 172.3, 172.1, 171.6, 171.55, 171.52, 171.4, 171.1, 170.8 (C=O), 158.1 (C=N or Cq $_{Ar}$), 156.5 (Cq $_{Ar}$ or C=N), 142.2 (Cq $_{Ar}$), 137.7 (Cq $_{Ar}$), 136.8 (Cq $_{Ar}$), 130.5 (CH $_{Ar}$), 129.4 (CH $_{Ar}$), 128.1 (CH $_{Ar}$), 127.5 (CH $_{Ar}$), 126.7 (CH $_{Ar}$), 118.3 (CH $_{Ar}$), 97.1 (C-1_M), 80.9 (C-1_G), 76.6 (C-5_G), 74.9 (C-2_G), 71.2

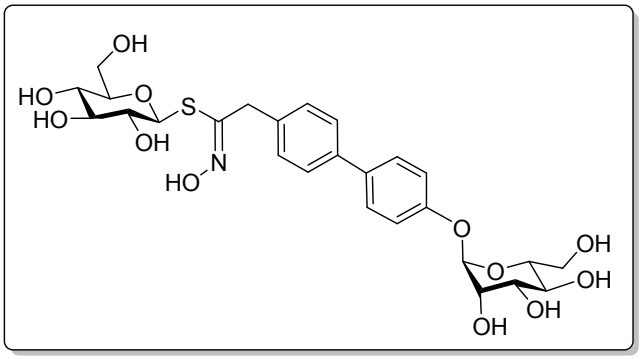
(C-3_G), 70.64, 70.61, 70.4 (C-5_M, C-3_M, C-2_M), 69.2 (C-4_G), 67.1 (C-4_M), 63.3 (C-6_M or C-6_G), 63.1 (C-6_G or C-6_M), 39.2 (CH_2), 20.7, 20.63, 20.6, 20.58, 20.49, 20.44, 20.42 ($CH_{3\ Ac}$); IR (neat) ν (cm^{-1}) = 1742 (C=O), 1697 (C=C), 1606, 1515 (C=C $_{Ar}$), 1213, 1031 (C-O), 836 (C_{sp2}-H $_{Ar}$); ESI^+ HRMS $[M\text{-}K+2H]^+$ *m/z* calcd. 1000.2206 for $C_{42}H_{50}NO_{23}S_2$, found 1000.2207.

***(Z)-S*-(β-D-Glucopyranosyl)[4'-(α-D-mannopyranosylsulfanyl)biphenyl-3-yl]acetothiohydroximate *N*,*O*-sulfate potassium salt 6:**



General procedure 5 was followed from acetylated compound **24** (1.16 g, 1.12 mmol, 1 equiv.) to give product **6** as a white resin (655 mg, 84%).

$[\alpha]_D^{20}$ +77.4 (*c* 0.17 in MeOH); δ_H (400 MHz, D_2O) 7.66-7.60 (3H, m, H_{Ar}), 7.57 (1H, d, ^3J 7.8 Hz, H_{Ar}), 7.50 (1H, t, ^3J 7.6 Hz, H_{Ar}), 7.38 (1H, d, ^3J 7.5 Hz, H_{Ar}), 7.23 (1H, d, ^3J 8.6 Hz, H_{Ar}), 5.66 (1H, bs, H_{1M}), 4.79-4.77 (1H, m, H_{1G}), 4.25-4.16 (3H, m, $CH_2C{=}N$, H_{2M}), 4.10 (1H, dd, $^3J_{3\text{-}4}$ 9.1 Hz, $^3J_{3\text{-}2}$ 3.3 Hz, H_{3M}), 3.85-3.72 (4H, m, H_{4M}, H_{5M}, H_{6M}), 3.62-3.51 (2H, m, H_{6G}), 3.45-3.30 (3H, m, H_{2G}, H_{3G}, H_{4G}), 3.18-3.12 (1H, m, H_{5G}); δ_C (100 MHz, D_2O internal acetone) 163.2 (C=N), 155.9 (Cq $_{Ar}$), 141.2 (Cq $_{Ar}$), 136.5 (Cq $_{Ar}$), 135.3 (Cq $_{Ar}$), 130.4 (CH $_{Ar}$), 128.9 (CH $_{Ar}$), 127.5 (CH $_{Ar}$), 126.8 (CH $_{Ar}$), 126.3 (CH $_{Ar}$), 118.1 (CH $_{Ar}$), 98.8 (C-1_M), 82.2 (C-1_G), 80.4 (C-5_G), 77.6, 74.0, 72.4 (C-4_M or C-5_M), 71.1, 70.6 (C-3_M), 69.2 (C-2_M), 67.2 (C-5_M or C-4_M), 61.3 (C-6_M), 60.7 (C-6_G), 38.9 (CH_2CN); IR (neat) ν (cm^{-1}) = 3380 (O-H), 1515 (C=C), 1230, 1055 (C-O); ESI^- HRMS $[M\text{-}K]^-$ *m/z* calcd. 662.1219 for $C_{26}H_{32}NO_{15}S_2$, found 662.1213.

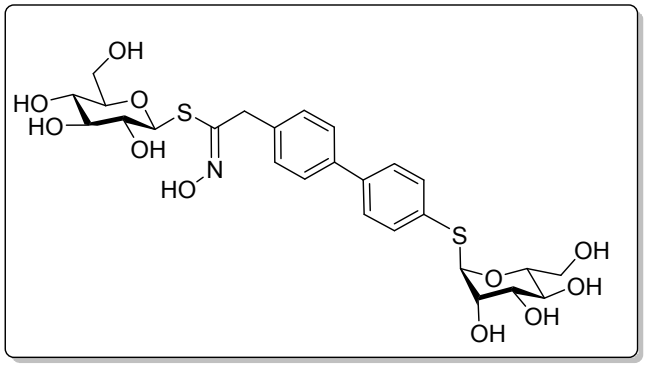


(*Z*)-*S*-(β-D-Glucopyranosyl)[4'-(α-D-mannopyranosyloxy)biphenyl-4-yl]acetothiohydroximate 26:

General procedure 5 was followed from acetylated compound **19** (135 mg, 0.147 mmol, 1 equiv.) to give product **26** as a white resin (74 mg, 84 %).

$[\alpha]_D^{20}$ +34.8 (*c* 0.9 in MeOH); δ_H (400 MHz, CD_3OD) 7.57-7.52 (4H, m, H_{Ar}), 7.39 (2H, d, ^3J 7.6 Hz, H_{Ar}), 7.18 (2H, d, ^3J 7.6 Hz, H_{Ar}), 5.53 (1H, bs, H_{1M}), 4.60-4.54 (1H, m, H_{1G}), 4.16 (1H, d, ^2J 16.2 Hz, CH_2C=N), 4.03 (1H, bs, H_{2M}), 4.01-3.91 (2H, m, H_{3M}, CH_2C=N), 3.87-3.71 (4H, m, H_{6aM}, H_{6bM}, H_{4M}, H_{6aG}), 3.67-3.59 (2H, m, H_{6bG}, H_{4G}), 3.28-3.13 (4H, m, H_{3G}, H_{5G}, H_{5M}, H_{2G}); δ_C (100 MHz, CD_3OD) 157.4 (Cq $_{Ar}$), 153.4 (C=N), 140.5 (Cq $_{Ar}$), 137.1 (Cq $_{Ar}$), 136.2 (Cq $_{Ar}$), 129.7 (CH $_{Ar}$), 128.9 (CH $_{Ar}$), 127.9 (CH $_{Ar}$), 118.1 (CH $_{Ar}$), 100.2 (C-1_M), 82.7 (C-1_G), 82.1 (C-5_G or C-3_G), 79.5 (C-2_G or C-5_M), 75.4 (C-4_G), 74.4 (C-5_M or C-2_G), 72.4 (C-3_M), 72.0 (C-3_G or C-5_G), 71.2 (C-2_M), 68.3 (C-4_M), 62.7 (C-6_G or C-6_M), 62.6 (C-6_M or C-6_G), 39.1 (CH_2C=N); IR (neat) ν (cm^{-1}) = 3310 (O-H), 1606, 1497 (C=C), 1231 (C-O); ESI$^+$ HRMS $[M+H]^+$ *m/z* calcd. 584.1796 for $C_{26}H_{34}NO_{12}S$, found 584.1798.

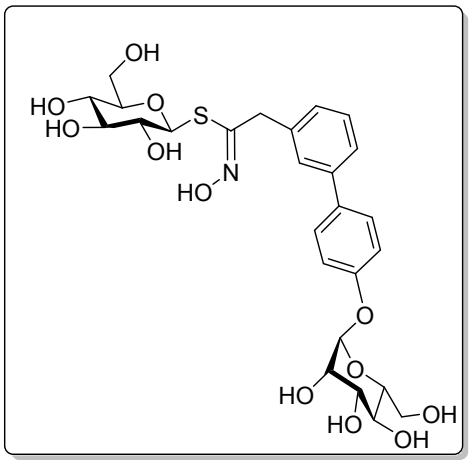
***(Z)-S*-(β-D-Glucopyranosyl)[4'-(α-D-mannopyranosylsulfanyl)biphenyl-4-yl]acetothio hydroximate 27:**



General procedure 5 was followed from acetylated compound **20** (300 mg, 0.32 mmol, 1 equiv.) to give product **27** as a white resin (90 mg, 50%).

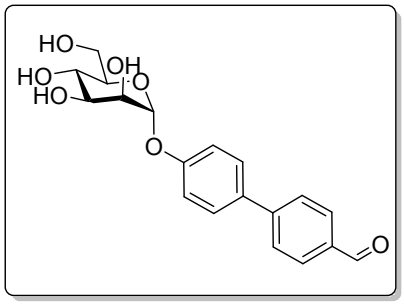
$[\alpha]_D^{20}$ +77.5 (*c* 0.54 in MeOH); δ_H (400 MHz, CD_3OD) 7.66-7.55 (6H, m, CH_{Ar}), 7.50 (2H, d, ^3J 8.2 Hz, CH_{Ar}), 5.48 (1H, d, $^3J_{1\text{-}2}$ 1.5 Hz, H_{1M}), 4.59-4.53 (1H, m, H_{1G}), 4.30 (1H, d, ^2J 16.1 Hz, CH_2CN), 4.13-4.03 (2H, m, H_{2M}, $H_{4M,}$), 3.90 (1H, d, ^2J 16.2Hz, CH_2CN), 3.89-3.68 (5H, m, H_{3M}, H_{5M}, H_{6aG}, H_{6M}), 3.60 (1H, dd, $^3J_{6a\text{-}6b}$ 12.2 Hz, $^3J_{6b\text{-}5}$ 5.8 Hz, H_{6bG}), 3.27-3.13 (4H, m, H_{3G}, H_{2G}, H_{4G}, H_{5G}); δ_C (100 MHz, CD_3OD) 159.1(C=N), 139.8, 139.0, 135.5, 133.5 (Cq $_{Ar}$), 131.9, 128.6, 127.0, 126.9 (CH $_{Ar}$), 89.0 (C-1_M), 81.5 (C-1_G), 80.8, 78.0, 74.3(C-3_M), 72.8, 72.3 (C-2_M), 71.8, 69.8, 67.3, 61.4 (C-6), 61.2 (C-6), 37.9 (CH_2CN); IR (neat) ν (cm^{-1}) = 3320 (O-H), 1484 (C=C $_{Ar}$), 1274, 1220 (C-OH), 1057, 1003 (C_{sp2}-H $_{Ar}$); ESI$^+$ HRMS $[M+H]^+$ *m/z* calcd. 600.1568 for $C_{26}H_{34}NO_{11}S_2$, found 600.1568.

***(Z)-S*-(β-D-Glucopyranosyl)[4'-(α-D-mannopyranosyloxy)biphenyl-3-yl]acetothiohydroximate 28:**



General procedure 5 was followed from acetylated compound **21** (120 mg, 0.128 mmol, 1 equiv.) to give product **28** as a white resin (48 mg, 64%).

$[\alpha]_D^{20}$ + 86.7 (*c* 0.14 in MeOH); δ_H (400 MHz, D_2O) 7.48-7.39 (3H, m, H_{Ar}), 7.34 (2H, bd, ^3J 4.4 Hz, H_{Ar}), 7.27-7.20 (1H, m, H_{Ar}), 7.10 (2H, d, ^3J 8.5 Hz, H_{Ar}), 5.58 (1H, s, H_{1M}), 4.74 (1H, d, $^3J_{1\text{-}2}$ 9.1 Hz, H_{1G}), 4.16 (1H, bs, H_{2M}), 4.07 (1H, dd, $^3J_{3\text{-}4}$ 9.6 Hz, $^3J_{3\text{-}2}$ 3.3 Hz, H_{3M}), 4.02 (1H, d, ^2J 17.2 Hz, $CH_2C{=}N$), 3.98 (1H, d, ^2J 17.2 Hz, $CH_2C{=}N$), 3.82 (1H, t, $^3J_{4\text{-}5}$ $^3J_{4\text{-}3}$ 9.7 Hz, H_{4M}), 3.78-3.74 (2H, m, H_{6M}), 3.73-3.67 (1H, m, H_{5M}), 3.61-3.51 (2H, m, H_{6G}), 3.46-3.37 (1H, m, H_{4G}), 3.38-3.30 (2H, m, H_{2G}, H_{3G}), 3.15-3.08 (1H, m, H_{5G}); δ_C (100 MHz, D_2O internal acetone) 155.8 (Cq $_{Ar}$ or C=N), 154.8 (C=N or Cq $_{Ar}$), 141.0 (Cq $_{Ar}$), 137.3 (Cq $_{Ar}$), 135.2 (Cq $_{Ar}$), 130.2 (CH $_{Ar}$), 128.7 (CH $_{Ar}$), 127.5 (CH $_{Ar}$), 126.7 (CH $_{Ar}$), 126.0 (CH $_{Ar}$), 117.9 (CH $_{Ar}$), 98.8 (C-1_M), 82.0 (C-1_G), 80.4 (C-5_G), 77.7 (C-2_G or C-3_G), 74.0 (C-5_M), 72.7 (C-3_G or C-2_G), 71.2 (C-3_M), 70.6 (C-2_M), 69.3 (C-4_G), 67.1 (C-4_M), 61.2 (C-6_G or C-6_M), 60.8 (C-6_M or C-6_G), 38.7 ($CH_2C{=}N$); IR (neat) ν (cm^{-1}) = 3323 (O-H), 1605, 1514 (C=C), 1228 (C-OH); ESI$^+$ HRMS $[M+H]^+$ *m/z* calcd. 584.1796 for $C_{26}H_{34}NO_{12}S$, found 584.1804.

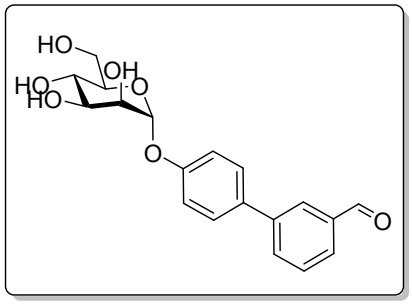


[4'-(α-D-Mannopyranosyloxybiphenyl-4-yl]carboxaldehyde 17:

General procedure 5 was followed from acetylated compound **11** (200 mg, 0.38 mmol, 1 equiv.) to give product **17** as an uncoloured resin (68 mg, 50%).

$[\alpha]_D^{20}$ +160.9 (*c* 0.4 in MeOH); δ_H (400 MHz, CD_3OD) 10.00 (1H, s, HCO), 7.96 (2H, d, ^3J 8.2 Hz, H_{Ar}), 7.80 (2H, d, ^3J 8.3 Hz, H_{Ar}), 7.66 (2H, d, ^3J 8.7 Hz, H_{Ar}), 7.24 (2H, d, ^3J 8.7 Hz, H_{Ar}), 5.56 (1H, d, $^3J_{1\text{-}2}$ 1.8 Hz, H_1), 4.06-4.02 (1H, m, H_2), 3.93 (1H, dd, $^3J_{3\text{-}4}$ 9.4 Hz, $^3J_{3\text{-}2}$ 3.4 Hz, H_3), 3.81-3.70 (3H, m, H_4, H_{6a}, H_{6b}), 3.65-3.57 (1H, m, H_5); δ_C (100 MHz, CD_3OD) 193.8 (HC=O), 158.4 (Cq $_{Ar}$), 148.0 (Cq $_{Ar}$), 136.4 (Cq $_{Ar}$), 134.9 (Cq $_{Ar}$), 131.3 (CH $_{Ar}$), 129.5 (CH $_{Ar}$), 128.2 (CH $_{Ar}$), 118.3 (CH $_{Ar}$), 100.1 (C-1), 75.5 (C-5), 72.4 (C-3), 71.9 (C-2), 68.3 (C-4), 62.7 (C-6); IR (neat) ν (cm^{-1}) = 3341 (O-H), 1691 (C=O), 1599 (C=C), 1113 (C-O); ESI$^+$ HRMS $[M+H]^+$ *m/z* calcd. 361.1282 for $C_{19}H_{21}O_7$, found 361.1281.

[4'-(α-D-Mannopyranosyloxybiphenyl-3-yl]carboxaldehyde 18:



General procedure 5 was followed from acetylated compound **13** (130 mg, 0.245 mmol, 1 equiv.) to give product **18** as a white resin (70 mg, 79%).
$[\alpha]_D^{20}$ + 160.9 (*c* 0.35 in MeOH); δ_H (400 MHz, CD_3OD) 10.04 (1H, s, HC=O), 8.10 (1H, s, CH_{Ar}), 7.91 (1H, d, ^3J 7.7 Hz, CH_{Ar}), 7.86 (1H, d, ^3J 7.7 Hz, CH_{Ar}), 7.71-7.52 (3H, m, CH_{Ar}), 7.26-7.19 (2H, m, CH_{Ar}), 5.60-5.50 (1H, m, H_1), 4.04 (1H, bs, H_2), 3.94 (1H, dd, $^3J_{3-4}$ 9.5 Hz, $^3J_{3-2}$ 3.4 Hz, H_3), 3.82-3.69 (3H, m, H_4, H_6), 3.67-3.59 (1H, m, H_5); δ_C (100 MHz, CD_3OD) 194.3 (HC=O), 158.0 (Cq_{Ar}), 142.9 (Cq_{Ar}), 138.6 (Cq_{Ar}), 135.0 (Cq_{Ar}), 133.7 (CH_{Ar}), 130.7 (CH_{Ar}), 129.2 (CH_{Ar}), 129.0 (CH_{Ar}), 128.7 (CH_{Ar}), 118.3 (CH_{Ar}), 100.1 (C-1), 75.5 (C-5), 72.4 (C-3), 72.0 (C-2), 68.3 (C-4), 62.7 (C-6); IR (neat) ν (cm^{-1}) = 3341 (O-H), 1599, 1524 (C=C), 1185 (C-OH); ESI^+ HRMS $[M+H]^+$ *m/z* calcd. 361.1282 for $C_{19}H_{21}O_7$, found 361.1281.

II - Glycoprofiles:

The Glycoprofile was realised by the GLYcoDIAG Company using known procedure. Lectin array interaction analysis was performed by using customized 96-wells plates functionalized with plant or human recombinant lectins (LEctPROFILE® plates, GLYcoDiag). The principle of the analysis is based on a competition assay between the compound and a specific tracer ligand known to be well recognized by the corresponding lectin. Briefly, a mix of the fluorescein-conjugated tracer (fixed concentration) and the inhibitor (range of concentrations) prepared in PBS supplemented with 1 mM $CaCl_2$ and 0.5 mM $MgCl_2$ is deposed in each well (100 µl) in triplicates and incubated two hours at room temperature. After washing with PBS buffer the readout is performed with a fluorescence reader (Fluostar, BMG labtech, Offenburg, Germany). The signal intensity is inversely correlated with the capacity of the inhibitor to be recognized by the lectin and expressed as inhibition percentage with comparison with the corresponding tracer ligand alone. Glycoprofiles for Glucosinolates **4** and **6** and glucomoringin **1d** have been realised on the inhibition of the interaction using three different concentrations of glucosinolate (2mM, 1mM and 0.5 mM) with 19 lectins listed below. Each experiment has been set in triplicate. Details regarding the source of lectins are listed in the table below (see also http://www.glycodiag.com/products/lectin/):

Lectin		Common Name	Type	Main Carbohydrate inhibitor	Tracer ligand
ConA	Concanavalin A	Canavalia Ensiformis	v	Glc Man GlcNAc	Neoglycoprotein BSA-Man
LcH	Lens Culinaris Agglutinin	Len culinaris	v		Lactoferin from human milk
PSA	Pisum Sativum Agglutinin	Pisum sativum	v		

VFA	Vicia Faba Agglutinin	Vicia faba	v		Neoglycoprotein BSA-Man
GLN/GNA	Galanthus Nivalis Agglutinin	Galanthus nivalis	v	Man	
HHA	Hippeastrum Hybrid Agglutinin	Hippeastrum hybrid	v		
BC2LA	Burkholderia cenocepacia lectin	Burkholderia cenocepacia lectin A	b		
FimH	E. coli Type I fimbrial lectin FimH	E. coli Type I fimbrial lectin FimH	b		
DC-SIGN	DC-SIGN extracellular domain	DC-SIGN extracellular domain	h		
Langerin	Langerin extracellular domain	Langerin extracellular domain	h	Man GlcNAc Fuc	
AIA	Artocarpus intergrifolia Agglutinin (Jacalin)	Artocarpus intergrifolia	v	Gal	Neoglycoprotein BSA-Galactose (Gal)
PNA	Peanut Agglutinin	Arachis hypogaea	v	β-Gal	Neoglycoprotein BSA-lactose (GlcNAc)
GSLII	Griffonia Simplicifolia Lectin II	Griffonia simplicifolia	v	GlcNAc	Neoglycoprotein BSA-N-acetyl-glucosamine (GlcNAc)
WGA	Wheat Germ Agglutinin	Triticum vulgare	v	GlcNAc NeuAc	
AAL	Aleuria Aurantia Lectin	Aleuria aurantia	m	Fuc	Neoglycoprotein BSA-Fucose (Fuc)
UEA-I	Ulex Europeus Agglutinin	Ulex europeus Fuc	v		
MAA	Maackia amurensis Agglutinin	Maackia amurensis	v	NeuAc	Bovine fetuin
SNA	Elderberry Lectin	Sambucus nigra	v		Human transferin
CorM	Coregonus lavaretus marenae	Coregonus lavaretus marenae	v	Rha	Neoglycoprotein BSA-Rhamnose (Rha)

v = vegetal; h = human; b = bacteria; m = mushroom.

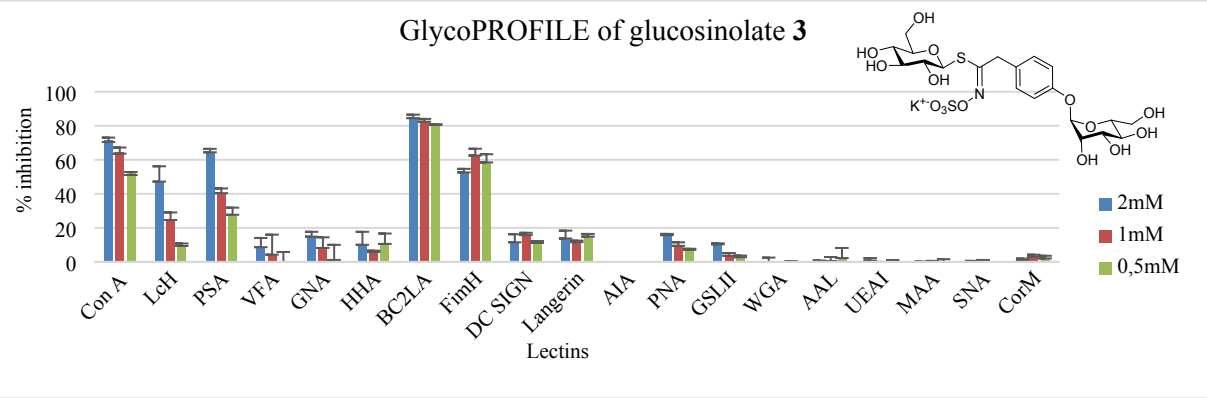
Man = mannose; Gal = galactose; Glc = glucose; GlcNAc = *N*-acetylglucosamine; Fuc = fucose; NeuAc = *N*-acetyl neuraminic acid; Rha = rhamnose.

References:

1 - Landemarre, L.; Duverger, E. Lectin Glycoprofiling of Recombinant Therapeutic Interleukin-7. In *Glycosylation Engineering of Biopharmaceuticals: Methods and Protocols*; Beck, A., Ed.; Humana Press: Totowa, NJ, 2013; pp 221–226.

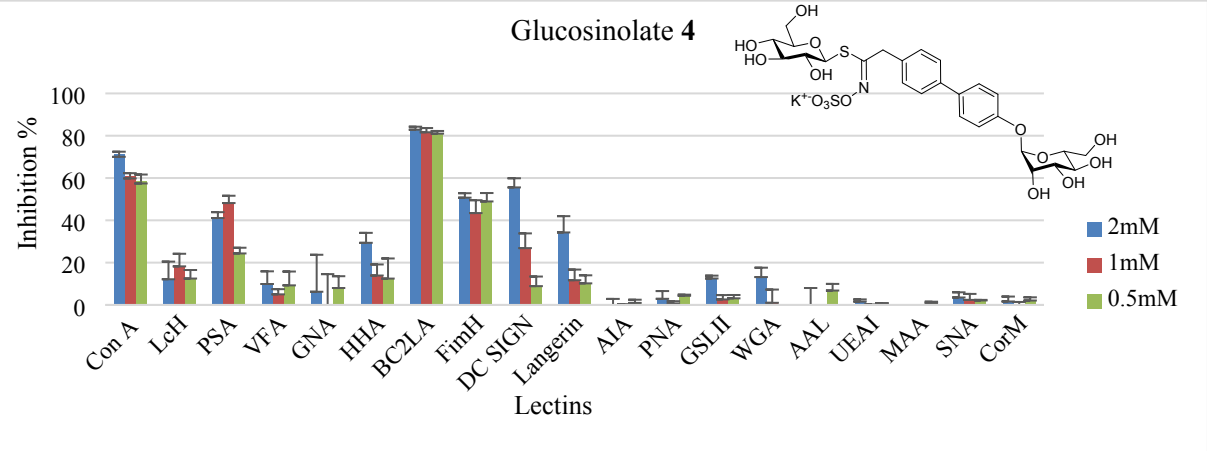
2 - Landemarre, L.; Cancellieri, P.; Duverger, E. Cell Surface Lectin Array: Parameters Affecting Cell Glycan Signature. *Glycoconjugate Journal* **2013**, *30* (3), 195–203.

GlycoProfile for Glucosinolate 3 :



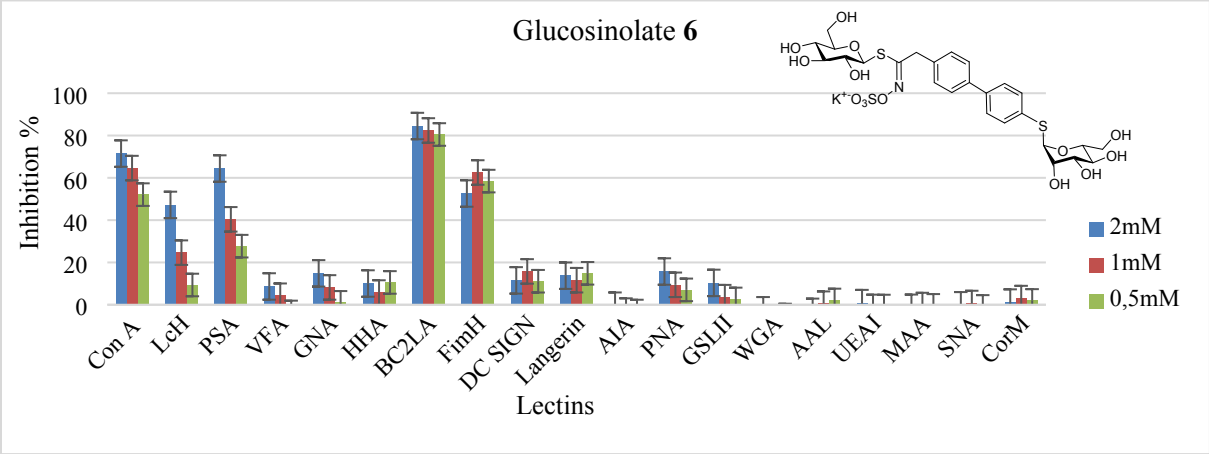
Glucosinolates 3																			
% Inhibition	Con A	LcH	PSA	VFA	GNA	HHA	BC2LA	FimH	DC SIGN	Langerine	AIA	PNA	GSLII	WGA	AAL	UEAI	MAA	SNA	CorM
2mM	40.253	18.905	56.495	-49.541	-28.323	-46.588	76.486	40.507	22.649	10.834	-4.690	4.530	5.450	12.750	-8.440	-0.840	-3.230	3.270	0.780
1mM	46.740	20.011	49.993	-29.292	-2.177	-0.389	78.172	43.306	11.859	10.385	-2.930	-0.820	2.440	5.470	-10.590	0.960	-1.940	3.630	3.400
0,5mM	39.075	20.242	37.128	-10.436	6.216	5.313	75.023	44.375	12.412	5.848	-2.950	-1.330	1.250	4.190	-9.960	0.610	-1.890	3.520	-0.020

GlycoProfile for Glucosinolate 4 :



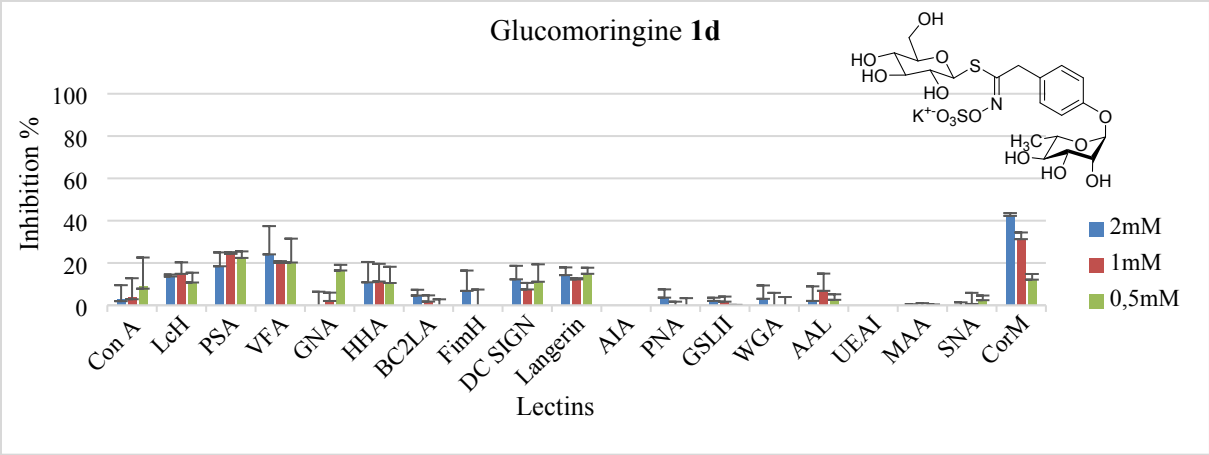
Glucosinolates 4																			
% Inhibition	Con A	LcH	PSA	VFA	GNA	HHA	BC2LA	FimH	DC SIGN	Langerine	AIA	PNA	GSLII	WGA	AAL	UEAI	MAA	SNA	CorM
2mM	71.472	47.199	64.400	8.639	14.836	10.040	84.491	52.590	11.519	13.741	-0.44	15.71	10.33	-2.62	-3.35	0.78	-1.44	-0.26	1.03
1mM	64.608	24.634	40.381	4.267	8.187	5.776	82.395	62.522	15.757	11.605	-2.76	9.43	3.59	-6.2	0.51	-1.02	-0.14	0.82	3.15
0,5mM	52.066	9.336	27.695	-3.406	1.133	10.547	80.487	58.460	11.117	14.862	-2.97	7.03	2.75	-4.85	2.26	-0.61	-0.29	-0.79	2.04

GlycoProfile for Glucosinolate 6 :



Glucosinolate 6																			
% Inhibition	Con A	LcH	PSA	VFA	GNA	HHA	BC2LA	FimH	DC SIGN	Langerine	AIA	PNA	GSLII	WGA	AAL	UEAI	MAA	SNA	CorM
2mM	71.028	12.139	41.077	9.896	6.232	29.366	82.847	50.711	55.559	34.273	-0.12	2.89	12.5	13.17	-2.44	1.59	-0.91	3.52	1.64
1mM	60.817	18.229	48.165	5.001	-2.238	13.903	81.628	43.431	26.857	11.689	-1.85	0.7	2.6	1	-3.1	-1.94	-1.27	2.38	-1.28
0,5mM	58.427	12.473	24.345	9.254	7.999	12.455	80.986	48.926	8.883	10.196	0.95	4.33	3.12	-9.57	6.8	0.76	0.94	2.11	2.08

GlycoProfile for Glucomoringin 1d



Glucomorigin																			
% Inhibition	Con A	LcH	PSA	VFA	GNA	HHA	BC2LA	FimH	DC SIGN	Langerine	AIA	PNA	GSLII	WGA	AAL	UEAI	MAA	SNA	CorM
2mM	2.949	13.621	18.443	24.072	-0.533	10.855	4.614	6.804	12.265	14.261	-4.07	3.61	2.07	3.06	2.06	-7.63	-2	-0.26	42.26
1mM	3.857	14.840	24.297	20.007	2.033	11.236	1.756	-3.284	7.483	12.246	-2.99	-1.25	1.72	-2.27	6.82	-4.29	-1.16	0.62	31.27
0,5mM	8.848	10.765	22.391	20.218	16.441	10.533	-1.091	-15.048	11.117	14.873	-4.3	-0.7	-0.14	-1.57	2.57	-6.19	-0.93	2.41	12.12

III - Docking Tables :

Table S1. Scoring values for docking if compounds **4**, **6**, **26**, **28**, **17**, **18** and the **MeMan** reference into the open gate crystal structure of FimH.

Ligand	docking score	XP GScore	glide gscore	glide evdw	glide ecoul	glide energy	glide einternal	glide emodel	XP HBond
4	-10,082	-10,082	-10,082	-25,653	-36,673	-62,326	8,895	-86,237	-5,659
4	-9,554	-9,554	-9,554	-25,325	-37,515	-62,84	6,101	-85,078	-5,659
4	-9,513	-9,513	-9,513	-25,554	-36,972	-62,525	6,608	-83,601	-5,659
4	-9,08	-9,08	-9,08	-17,155	-39,634	-56,789	8,308	-85,055	-5,659
4	-9,063	-9,063	-9,063	-25,902	-37,791	-63,693	9,974	-96,051	-5,659
6	-11,677	-11,677	-11,677	-24,423	-44,543	-68,966	9,313	-98,085	-7,334
6	-10,823	-10,823	-10,823	-24,512	-41,946	-66,458	8,496	-97,168	-7,334
6	-10,759	-10,759	-10,759	-25,43	-43,871	-69,301	8,875	-96,86	-7,334
6	-10,299	-10,299	-10,299	-26,243	-42,26	-68,503	7,012	-101,536	-7,334
6	-9,854	-9,854	-9,854	-24,174	-41,938	-66,112	11,745	-100,456	-7,334
24	-9,85	-9,851	-9,851	-25,68	-42,789	-68,469	8,622	-105,558	-7,344
24	-9,366	-9,367	-9,367	-23,789	-36,674	-60,463	9,404	-106,132	-7,344
24	-8,786	-8,787	-8,787	-26,041	-35,027	-61,069	8,158	-108,112	-7,344
24	-8,342	-8,342	-8,342	-26,27	-31,729	-57,999	0	-106,996	-7,344
24	-8,136	-8,136	-8,136	-23,766	-36,11	-59,876	9,81	-103,482	-7,344
26	-11,101	-11,101	-11,101	-24,939	-43,289	-68,228	9,146	-103,876	-6,997
26	-10,922	-10,922	-10,922	-26,387	-41,669	-68,057	6,228	-104,487	-6,997
26	-10,567	-10,567	-10,567	-26,204	-38,541	-64,746	3,999	-104,334	-6,997
26	-10,293	-10,293	-10,293	-25,493	-41,197	-66,69	7,553	-103,299	-6,997
26	-10,274	-10,275	-10,275	-25,925	-41,883	-67,809	0	-104,032	-6,997
27	-8,032	-8,032	-8,032	-19,983	-32,62	-52,603	0	-85,597	-5,601
27	-8,781	-8,781	-8,781	-17,242	-34,314	-51,556	3,5	-77,72	-5,601
27	-8,552	-8,552	-8,552	-17,737	-33,829	-51,565	3,856	-78,118	-5,601
28	-8,847	-8,847	-8,847	-19,212	-33,497	-52,709	4,094	-76,789	-5,55
28	-8,824	-8,824	-8,824	-18,488	-34,101	-52,59	3,503	-76,751	-5,55
28	-8,561	-8,561	-8,561	-17,704	-33,896	-51,6	3,904	-77,218	-5,55
28	-8,556	-8,556	-8,556	-18,141	-34,125	-52,266	3,99	-79,144	-5,55
28	-7,826	-7,826	-7,826	-20,722	-33,469	-54,191	4,485	-84,553	-5,55
MeMan	-8,514	-8,514	-8,514	-11,607	-34,657	-46,264	0	-67,48	-5,652
MeMan	-8,398	-8,398	-8,398	-12,084	-32,112	-44,197	4,994	-66,926	-5,652

Table S2. Scoring values for docking if compounds **4**, **6**, **26**, **28**, **17**, **18** and the **MeMan** reference into the closed gate crystal structure of FimH.

Ligand	docking score	XP GScore	glide gscore	glide evdw	glide ecoul	glide energy	glide einternal	glide emodel	XP HBond
4	-9,81	-9,81	-9,81	-25,344	-36,795	-62,139	5,922	-97,717	-5,801
4	-9,665	-9,665	-9,665	-25,97	-34,382	-60,351	9,253	-98,103	-5,801
4	-9,563	-9,563	-9,563	-26,043	-34,502	-60,546	8,362	-97,315	-5,801
4	-9,531	-9,531	-9,531	-26,073	-31,89	-57,963	8,696	-99,607	-5,801
4	-9,481	-9,481	-9,481	-25,852	-34,664	-60,515	8,692	-98,664	-5,801
6	-10,971	-10,971	-10,971	-24,798	-37,687	-62,485	0	-102,352	-7,178
6	-10,833	-10,833	-10,833	-25,852	-38,123	-63,975	7,647	-96,365	-7,178
6	-9,662	-9,662	-9,662	-31,154	-32,473	-63,628	9,391	-95,539	-7,178
6	-9,444	-9,444	-9,444	-26,839	-34,483	-61,322	11,969	-99,109	-7,178
6	-9,42	-9,42	-9,42	-26,952	-34,997	-61,949	11,548	-99,691	-7,178
24	-9,067	-9,067	-9,067	-20,369	-39,024	-59,393	8,839	-104,296	-6,795
24	-8,917	-8,917	-8,917	-21,625	-39,414	-61,039	8,829	-100,699	-6,795
24	-8,737	-8,737	-8,737	-21,648	-39,11	-60,758	8,319	-101,891	-6,795
24	-8,555	-8,555	-8,555	-23,254	-39,303	-62,557	10,468	-102,976	-6,795
24	-8,529	-8,529	-8,529	-21,692	-38,435	-60,127	9,986	-99,797	-6,795
26	-8,88	-8,881	-8,881	-25,769	-36,775	-62,544	3,938	-107,503	-6,515
26	-8,781	-8,781	-8,781	-28,738	-32,618	-61,357	7,427	-102,998	-6,515
26	-8,77	-8,77	-8,77	-28,901	-32,244	-61,145	8,156	-102,342	-6,515
26	-8,769	-8,77	-8,77	-27,505	-33,869	-61,374	6,67	-102,381	-6,515
26	-8,657	-8,657	-8,657	-28,348	-32,583	-60,931	8,344	-101,93	-6,515
27	-8,557	-8,557	-8,557	-20,571	-31,156	-51,727	2,265	-81,163	-4,743
28	-9,785	-9,785	-9,785	-20,965	-30,257	-51,222	4,198	-86,955	-4,74
28	-9,147	-9,147	-9,147	-20,224	-32,719	-52,943	7,182	-79,047	-4,74
28	-8,875	-8,875	-8,875	-22,001	-31,274	-53,275	3,749	-84,055	-4,74
28	-8,529	-8,529	-8,529	-20,159	-31,156	-51,315	3,372	-82,163	-4,74
28	-8,504	-8,504	-8,504	-21,115	-31,121	-52,236	0,999	-83,788	-4,74
MeMan	-8,212	-8,212	-8,212	-9,057	-33,702	-42,759	4,087	-60,99	-4,561
MeMan	-8,08	-8,08	-8,08	-9,425	-32,564	-41,989	1,381	-61,958	-4,561
MeMan	-7,437	-7,437	-7,437	-11,947	-31,006	-42,952	0	-62,139	-4,561
MeMan	-7,434	-7,434	-7,434	-11,914	-31,025	-42,94	0	-63,362	-4,561

Table S3. Values of the binding energies obtained by MM-GBSA calculation for compounds **4**, **6**, **26**, **28**, **17**, **18** and the **MeMan** reference into the open gate crystal structure of FimH. The docking score corresponding to each written pose is given in the first column for comparison.

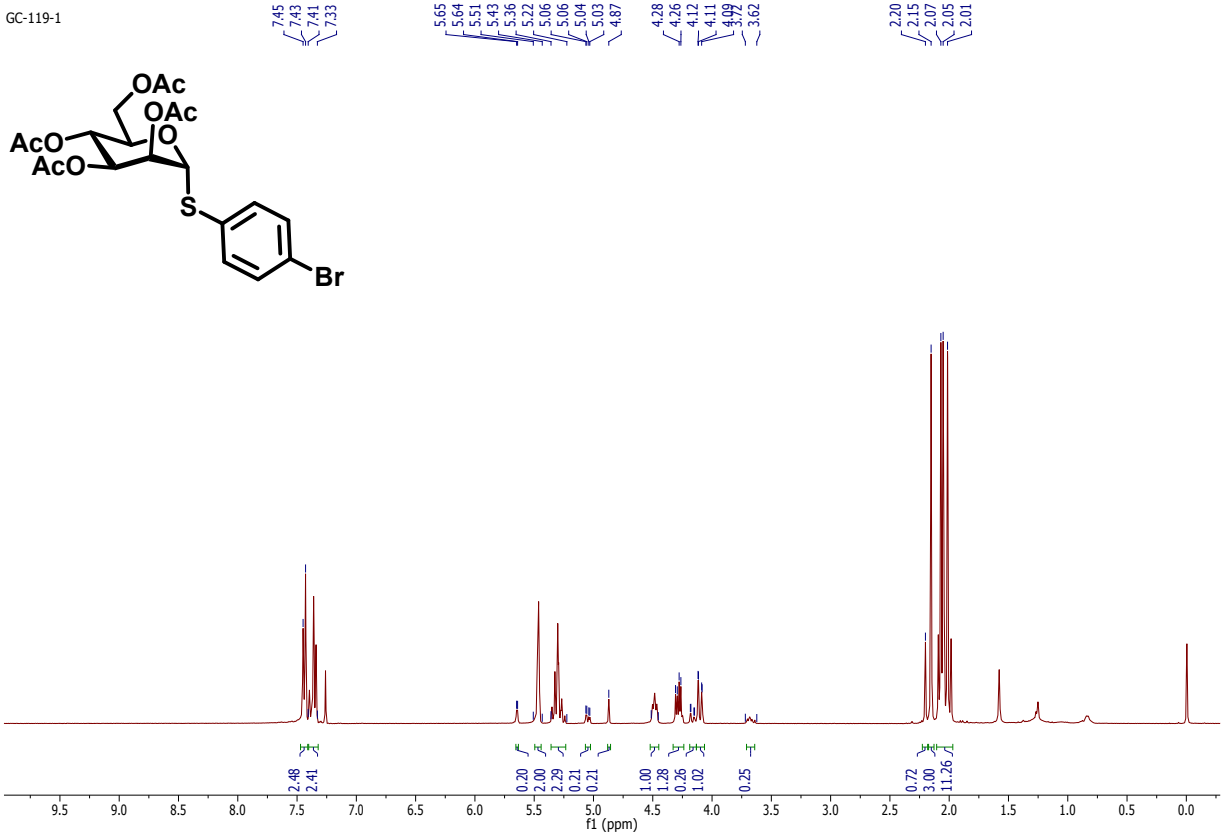
Ligand	docking score	dG Bind	dG Bind Coulomb	dG Bind Covalent	dG Bind Hbond	dG Bind Lipo	dG Bind Packing	dG Bind Solv GB	dG Bind vdW
4	-10,082	-87,681	-49,996	7,115	-7,4	-26,279	-3,496	34,637	-42,263
4	-9,554	-77,209	-33,553	4,606	-7,849	-26,016	-3,36	30,956	-41,992
4	-8,709	-76,768	-51,159	-6,828	-8,442	-10,932	-0,771	31,575	-30,212
4	-9,513	-75,558	-36,659	0,765	-7,246	-22,435	-3,26	32,286	-39,009
4	-7,761	-74,18	-47,475	0,011	-6,794	-18,574	-3,589	29,886	-27,646
6	-11,677	-86,179	-58,346	7,353	-9,202	-25,308	-2,052	36,316	-34,94
6	-10,299	-86,176	-58,218	7,228	-9,203	-25,289	-2,052	36,239	-34,881
6	-10,759	-86,074	-58,319	8,253	-9,239	-25,172	-1,878	35,572	-35,29
6	-9,854	-78,949	-51,488	8,169	-9,157	-25,147	-2,01	34,268	-33,585
6	-8,639	-70,837	-45,589	6,697	-6,856	-17,892	-0,291	29,54	-36,445
24	-8,064	-64,511	-54,312	9,79	-7,268	-13,473	-1,605	34,02	-31,663
24	-7,857	-64,498	-49,584	1,324	-6,218	-11,282	-0,541	32,048	-30,246
24	-9,85	-63,876	-37,897	10,947	-8,571	-18,266	-0,825	27,507	-36,772
24	-8,136	-63,844	-53,993	9,536	-6,748	-13,413	-1,577	34,181	-31,83
24	-7,591	-62,902	-48,62	-0,325	-7,551	-10,466	-0,558	31,895	-27,277
26	-10,922	-89,092	-62,787	3,289	-9,25	-21,332	-2,029	34,365	-31,347
26	-10,274	-84,225	-55,348	6,201	-9,181	-22,673	-3,197	33,181	-33,208
26	-10,567	-82,563	-49,223	2,32	-8,609	-22,616	-2,009	34,003	-36,429
26	-11,101	-81,678	-45,421	-3,601	-9,185	-18,628	-3,182	28,445	-30,105
26	-9,075	-65,073	-49,194	-0,28	-8,887	-11,618	-0,272	33,535	-28,358
27	-8,552	-70,932	-38,258	5,358	-6,203	-21,312	-3,193	25,05	-32,374
27	-8,781	-70,758	-38,22	5,428	-6,186	-21,272	-3,169	25,074	-32,413
27	-8,032	-69,622	-37,423	3,985	-6,217	-20,955	-3,783	25,56	-30,788
28	-8,556	-73,013	-44,736	5,989	-6,758	-20,593	-2,557	27,162	-31,52
28	-8,824	-72,995	-44,771	5,933	-6,748	-20,638	-2,55	27,185	-31,406
28	-8,561	-71,776	-37,519	3,757	-6,251	-20,638	-3,906	24,482	-31,7
28	-8,847	-71,731	-43,059	4,585	-6,222	-20,226	-3,034	28,377	-32,152
28	-7,826	-70,679	-41,484	2,187	-6,162	-19,411	-3,174	26,03	-28,663
MeMan	-8,398	-53,44	-38,07	0,408	-6,265	-8,766	-0,391	20,09	-20,446

Table S4. Values of the binding energies obtained by MM-GBSA calculation for compounds **4**, **6**, **26**, **28**, **17**, **18** and the **MeMan** reference into the closed gate crystal structure of FimH. The docking score corresponding to each written pose is given in the first column for comparison.

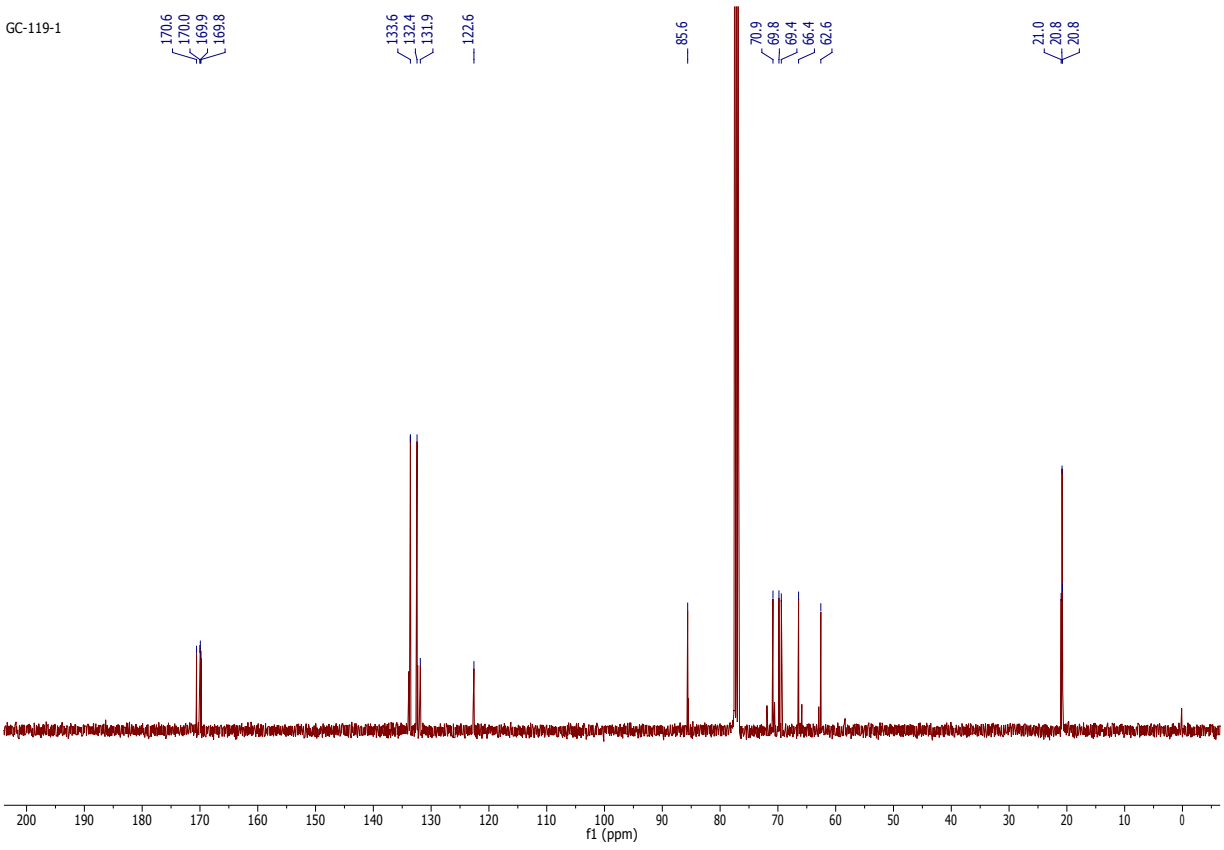
Ligand	docking score	dG Bind	dG Bind Coulomb	dG Bind Covalent	dG Bind Hbond	dG Bind Lipo	dG Bind Packing	dG Bind Solv GB	dG Bind vdW
4	-9,81	-85,935	-42,018	-2,705	-6,429	-24,64	-2,715	34,885	-42,313
4	-9,531	-82,898	-45,075	-0,456	-7,547	-23,493	-2,283	33,703	-37,747
4	-9,194	-82,185	-44,57	-5,858	-6,16	-20,46	-2,43	31,82	-34,527
4	-9,273	-81,631	-46,317	-0,907	-6,088	-23,435	-2,427	35,859	-38,315
4	-9,244	-81,067	-45,523	-5,186	-6,816	-20,426	-2,549	32,754	-33,322
6	-10,833	-91,79	-64,154	2,996	-8,4	-23,348	-2,424	40,436	-36,896
6	-10,971	-86,366	-58,02	-2,872	-8,394	-20,022	-2,445	37,899	-32,512
6	-9,103	-85,031	-41,34	-2,085	-7,22	-22,452	-2,231	26,307	-36,009
6	-9,444	-84,144	-46,435	1,328	-6,613	-23,457	-3,088	29,513	-35,391
6	-8,95	-79,572	-48,021	1,927	-7,753	-20,034	-3,083	38,542	-41,149
24	-8,373	-72,885	-55,65	3,812	-8,451	-15,213	-0,762	37,295	-33,916
24	-8,737	-69,814	-53,725	4,775	-8,081	-15,592	-0,941	38,136	-34,386
24	-8,529	-67,873	-46,961	-5,287	-8,448	-9,38	-0,771	32,384	-29,41
24	-9,067	-64,714	-54,667	10,651	-6,216	-17,008	-0,231	40,064	-37,308
24	-8,917	-64,682	-54,111	7,043	-7,952	-14,557	-0,342	39,84	-34,603
26	-8,88	-92,167	-56,272	-0,672	-8,045	-23,348	-2,753	35,014	-36,091
26	-7,795	-69,562	-51,603	-6,184	-8,037	-10,077	-0,573	39,208	-32,296
26	-7,801	-69,429	-57,941	-4,583	-8,037	-9,061	-0,564	40,491	-29,734
26	-8,769	-63,829	-42,704	-4,769	-8,035	-9,045	-0,568	33,066	-31,774
26	-8,36	-61,571	-40,638	-1,77	-8,014	-10,19	-0,658	34,006	-34,307
27	-8,557	-74,287	-40,61	-0,029	-6,304	-20,159	-2,597	26,619	-31,208
28	-8,875	-77,781	-46,775	-1,543	-6,709	-19,766	-2,74	29,689	-29,935
28	-9,785	-74,861	-45,654	0,802	-6,74	-20,096	-2,693	29,676	-30,156
28	-8,504	-74,531	-39,348	0,849	-6,403	-20,313	-2,789	24,5	-31,028
28	-9,147	-74,435	-42,029	0,771	-6,396	-20,46	-2,753	26,835	-30,404
28	-8,529	-74,263	-35,394	-3,456	-5,78	-19,835	-2,669	25,012	-32,142
MeMan	-8,514	-53,356	-38,063	0,413	-6,171	-8,768	-0,397	20,073	-20,442
MeMan	-8,08	-53,634	-38,968	0,407	-6,393	-8,64	-0,199	21,754	-21,596
MeMan	-7,437	-53,232	-38,994	0,462	-6,097	-8,62	-0,263	21,958	-21,679
MeMan	-8,212	-52,63	-38,064	-2,112	-6,12	-7,401	-0,072	22,168	-21,029
MeMan	-7,434	-52,537	-38,021	-2,066	-6,08	-7,409	-0,069	22,159	-21,051

IV - ^{1}H & ^{13}C NMR Spectra:

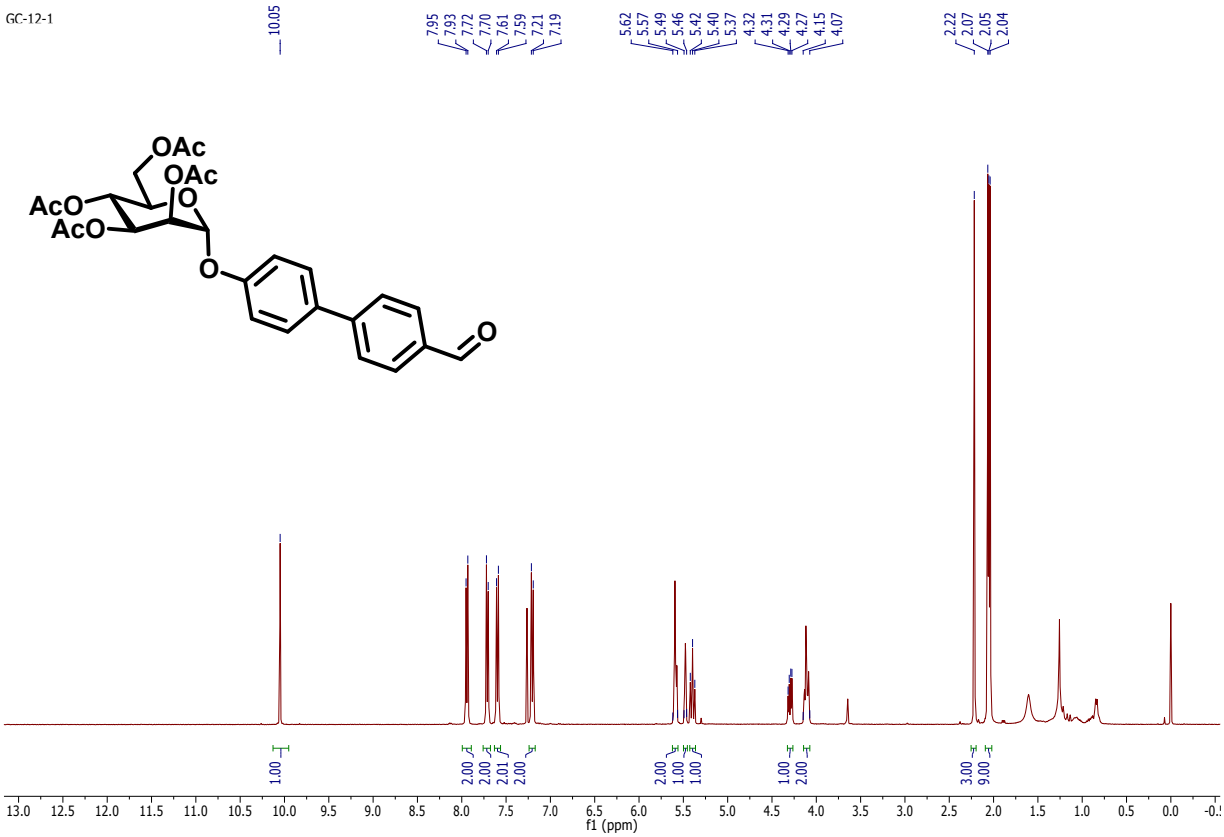
4-Bromophenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside 10: ^{1}H NMR (400 MHz, $CDCl_3$):



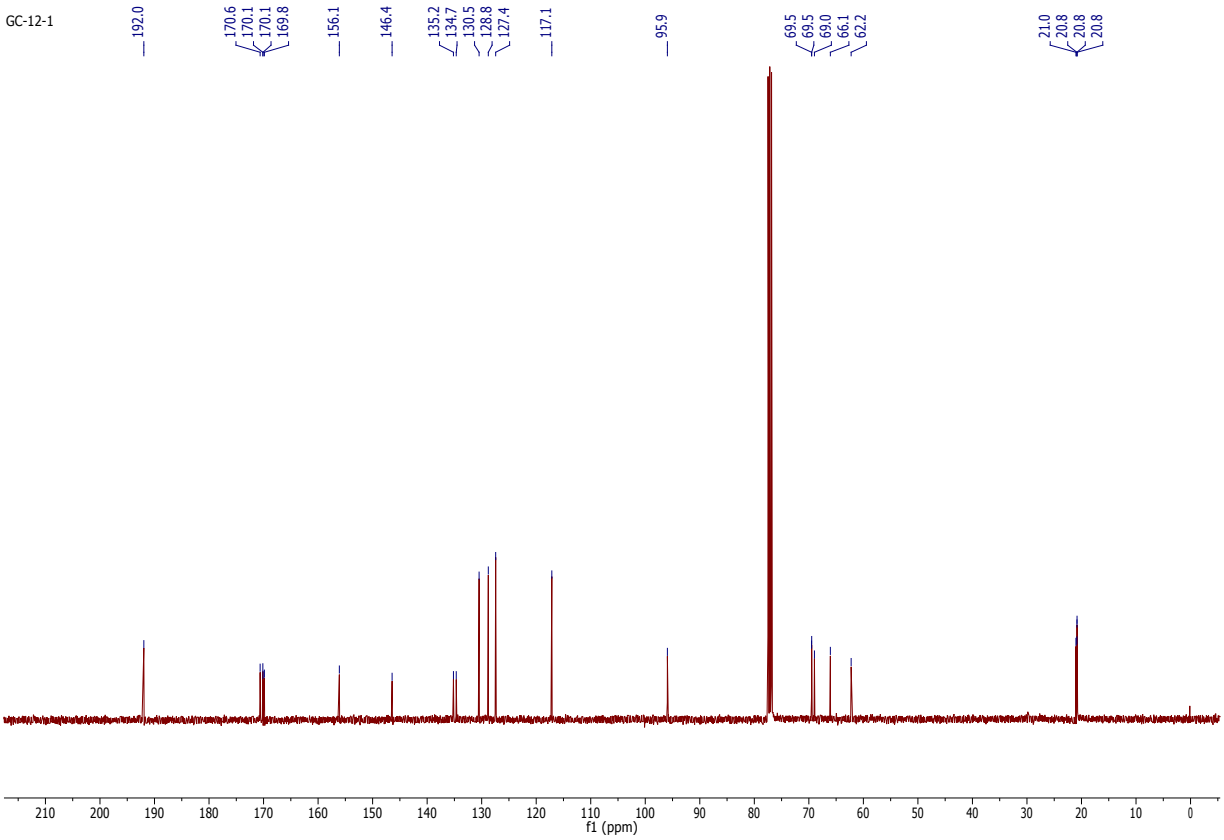
^{13}C NMR (100 MHz, $CDCl_3$) :



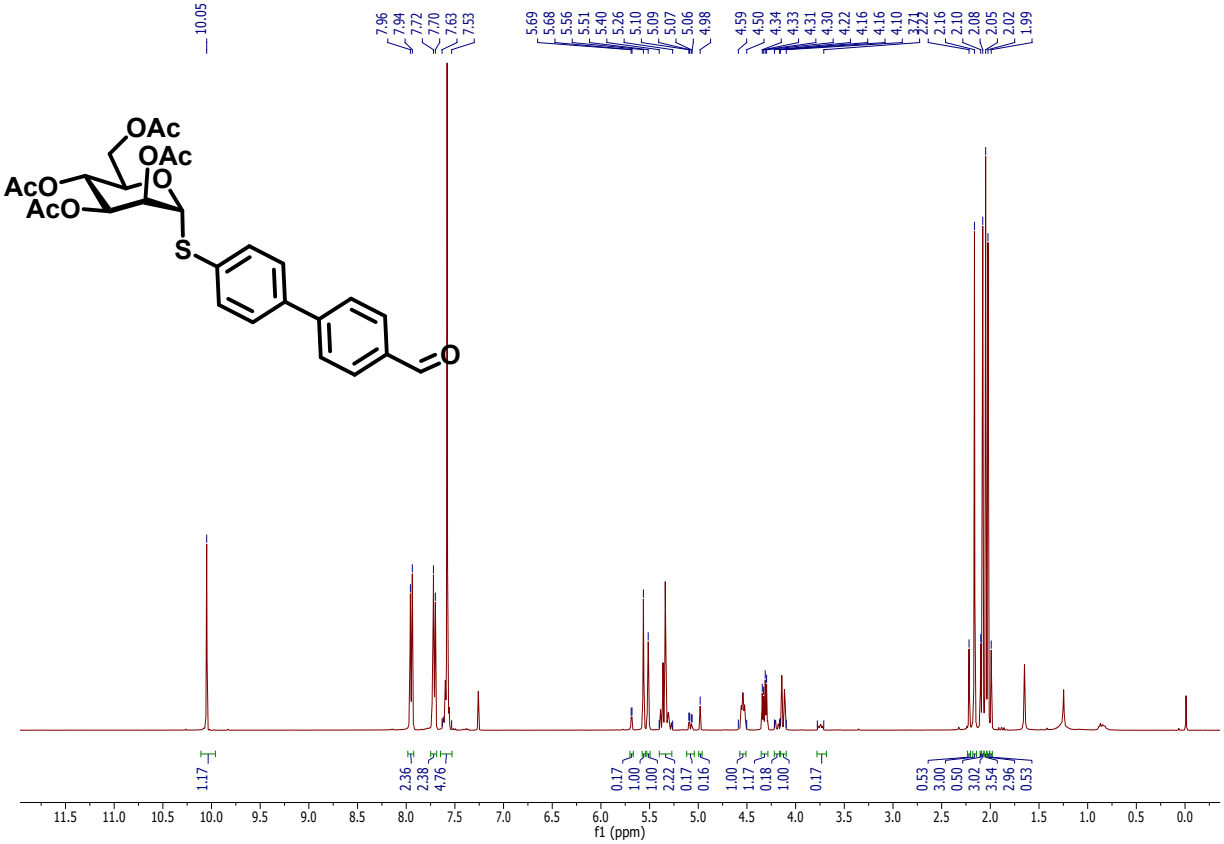
[4'-(2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyloxy)biphenyl-4-yl]carboxaldehyde 11: ^{1}H NMR (250 MHz, $CDCl_3$) :



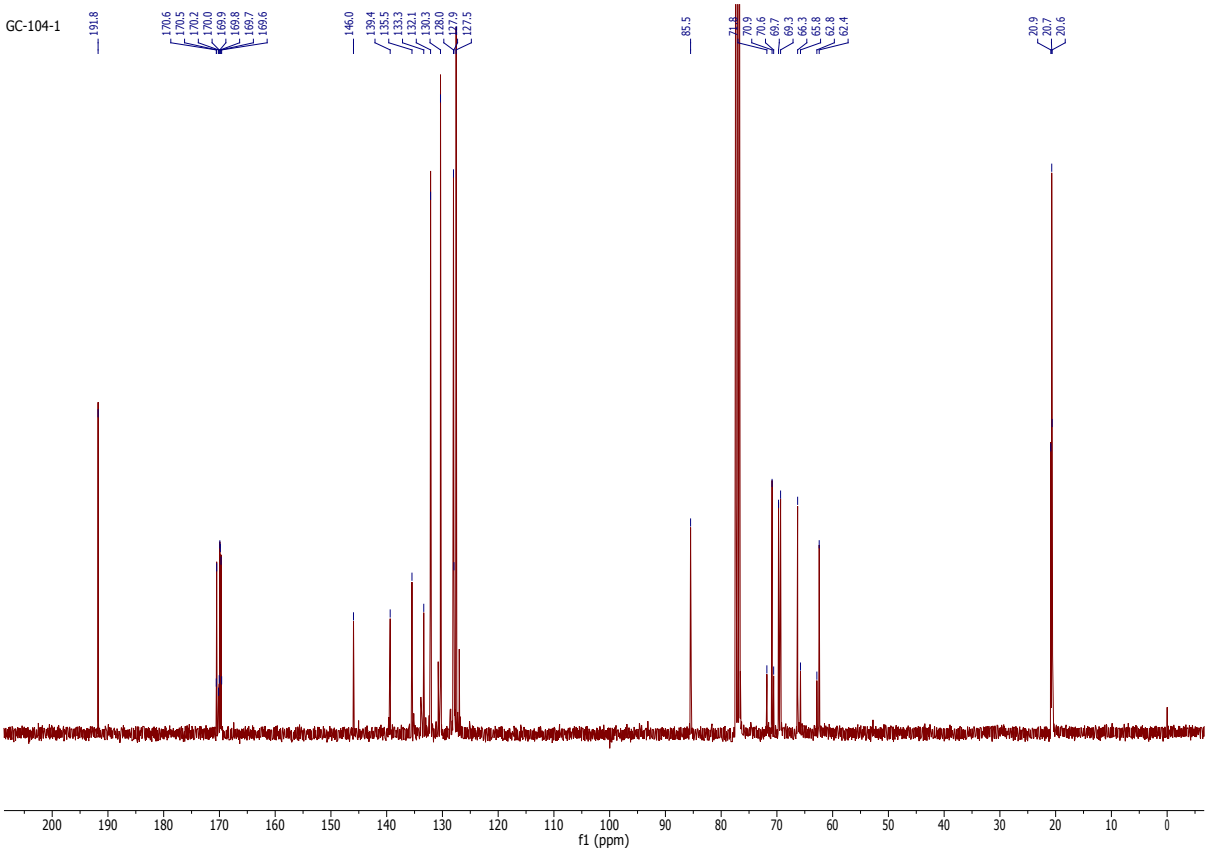
^{13}C NMR (100 MHz, $CDCl_3$):



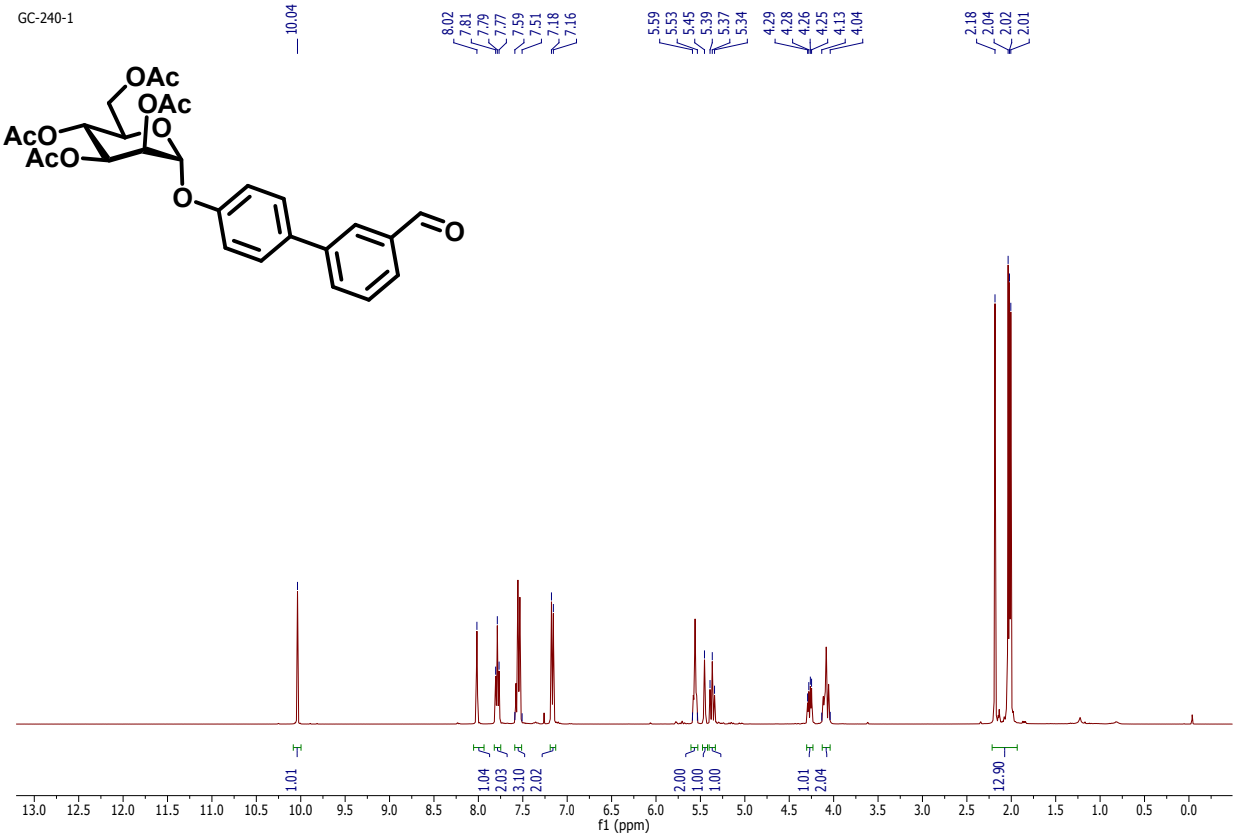
[4'-(2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosylsulfanyl)biphenyl-4-yl]carboxaldehyde 12: ^{1}H NMR (250 MHz, $CDCl_3$) :



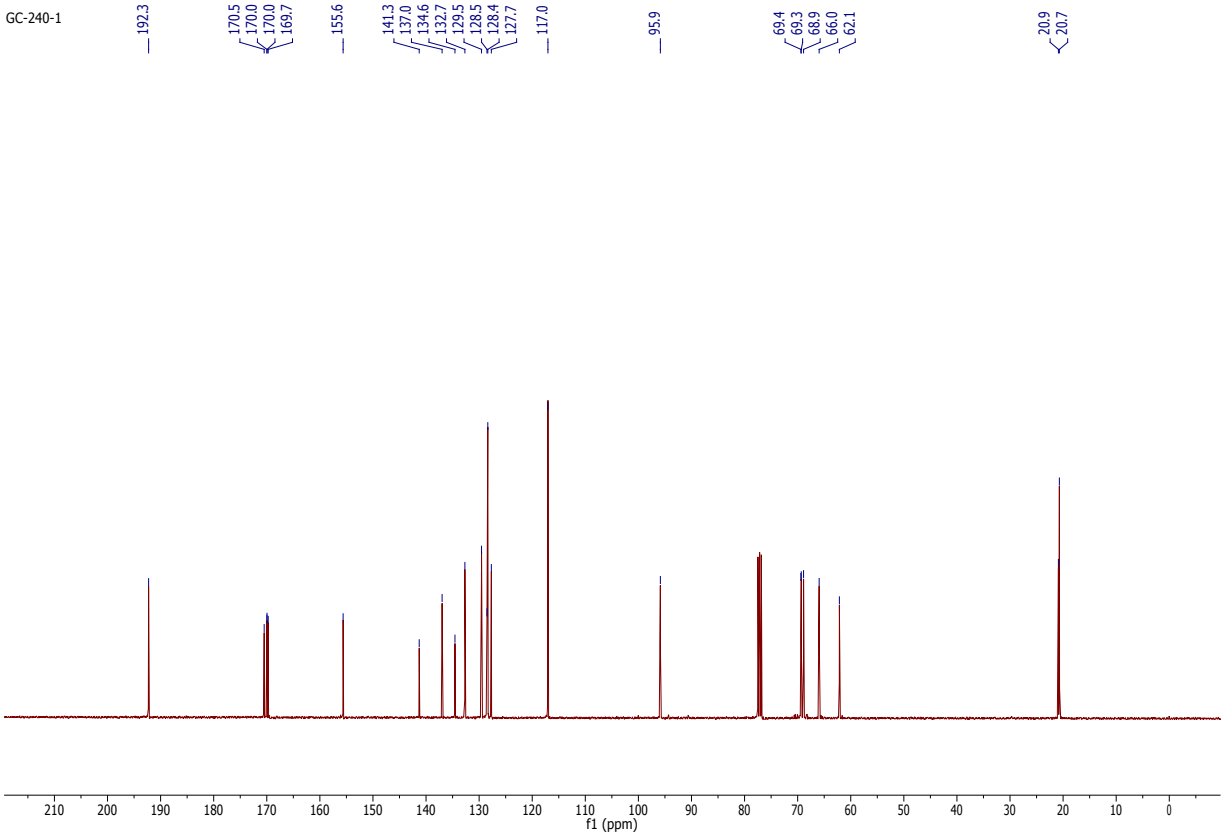
^{13}C NMR (100 MHz, $CDCl_3$) :



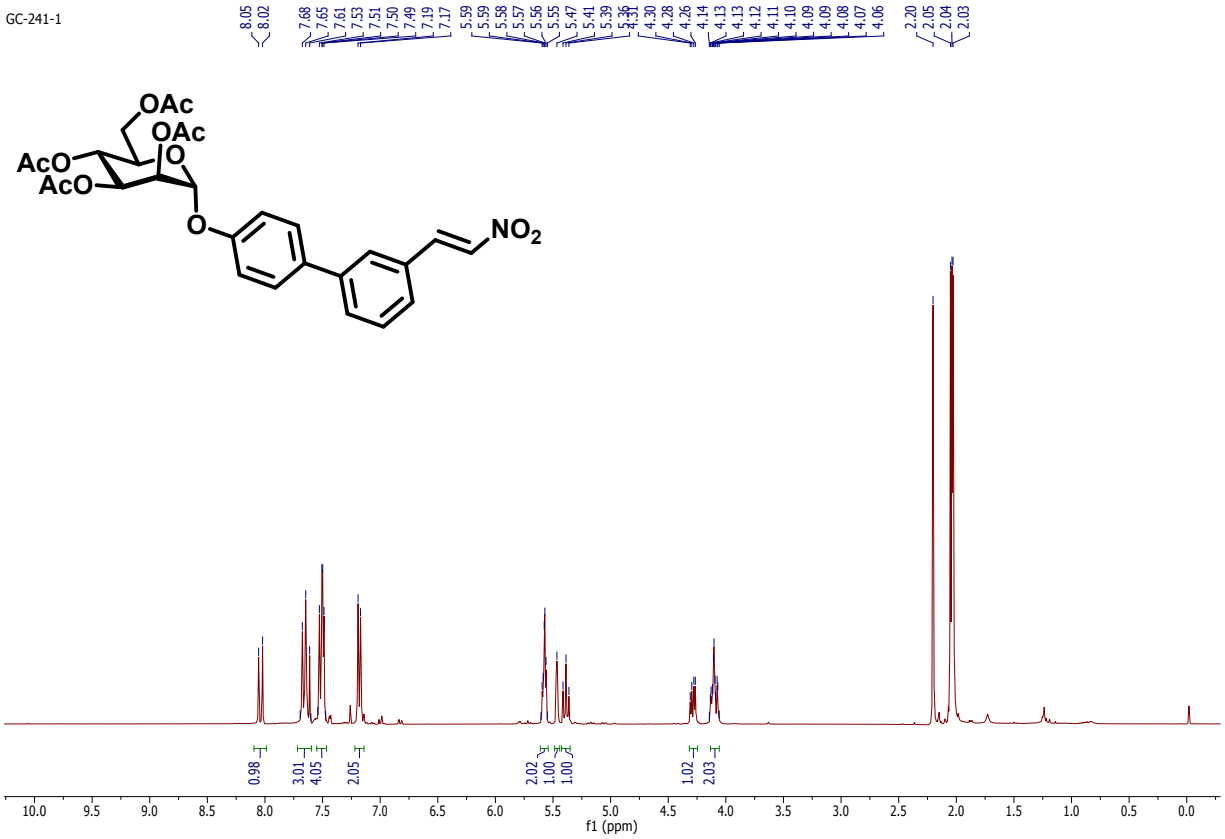
[4'-(2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyloxy)biphenyl-3-yl]carboxaldehyde 13: ^{1}H NMR (400 MHz, $CDCl_3$) :



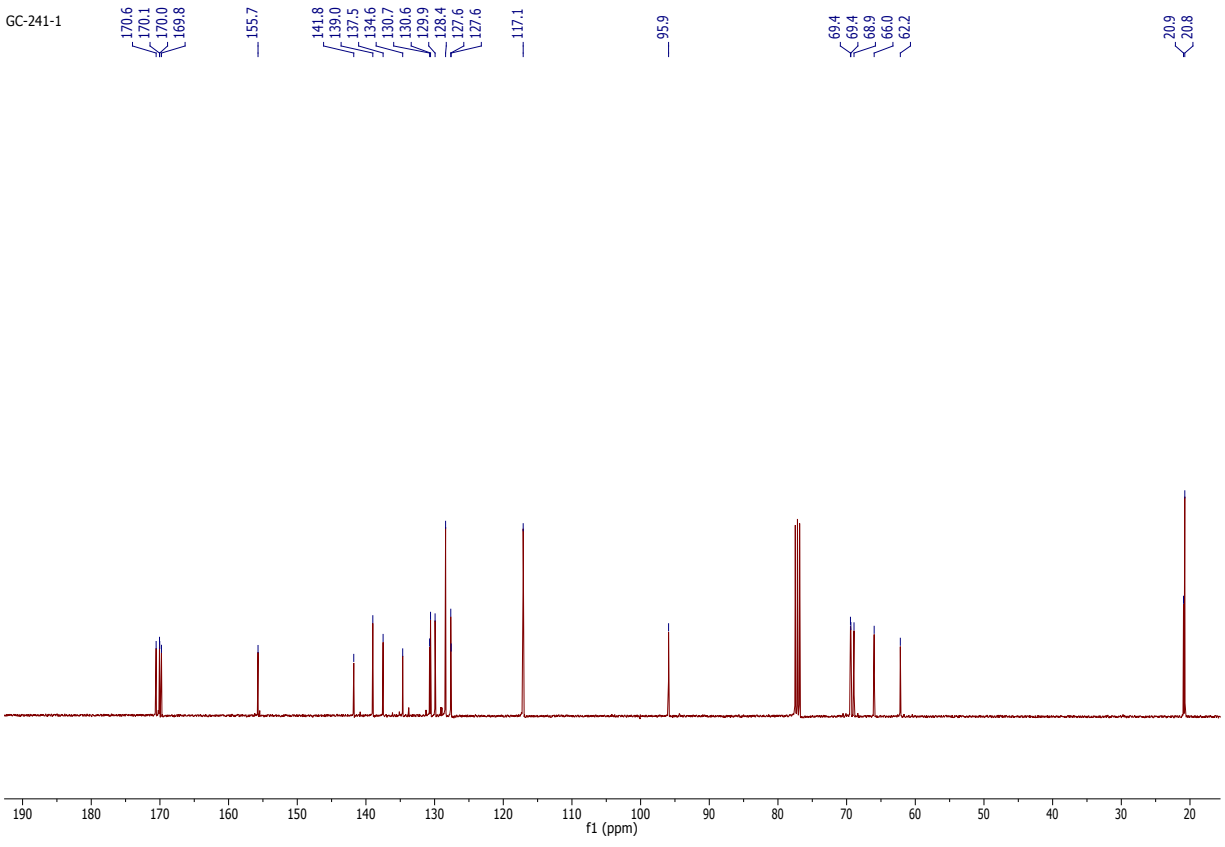
^{13}C NMR (100 MHz, $CDCl_3$) :



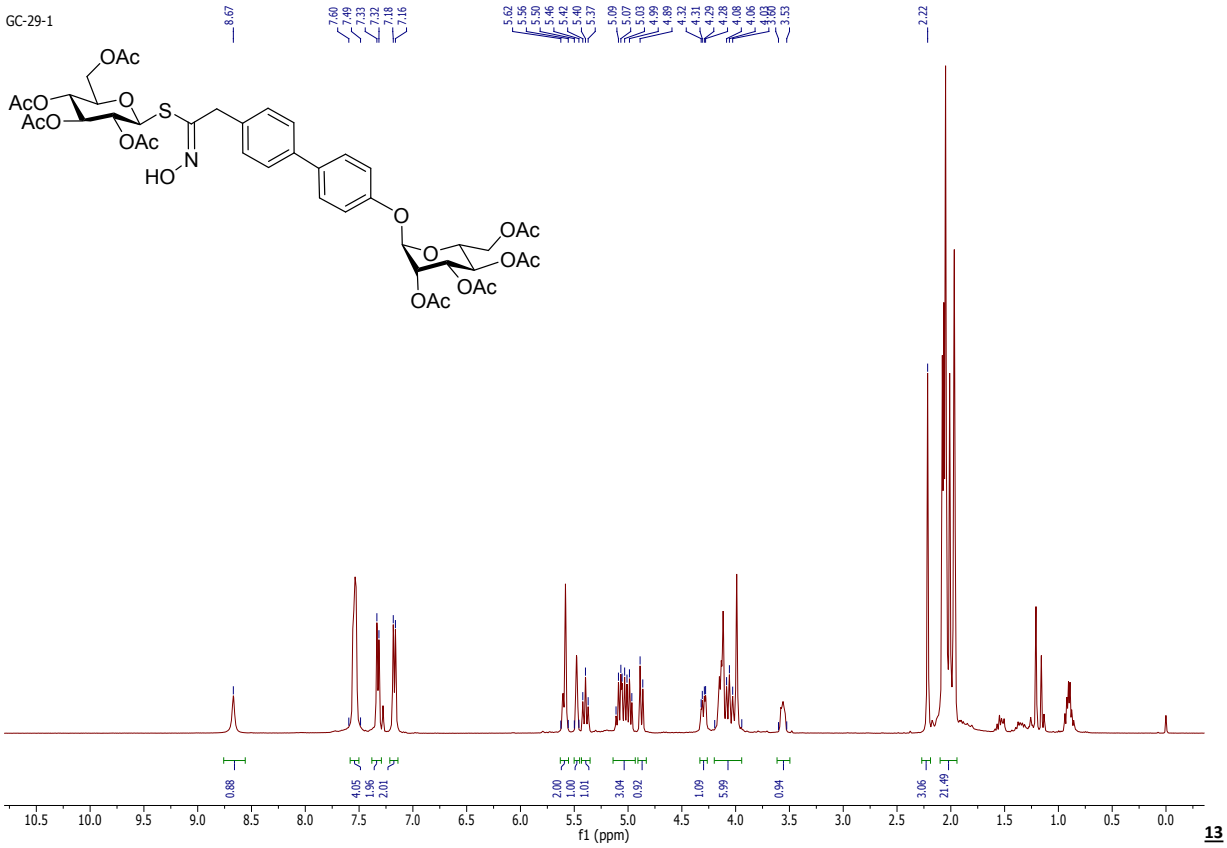
([3'-((*E*)-2-Nitrovinyl)biphenyl]-4-yl) 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside 16 : ^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$) :

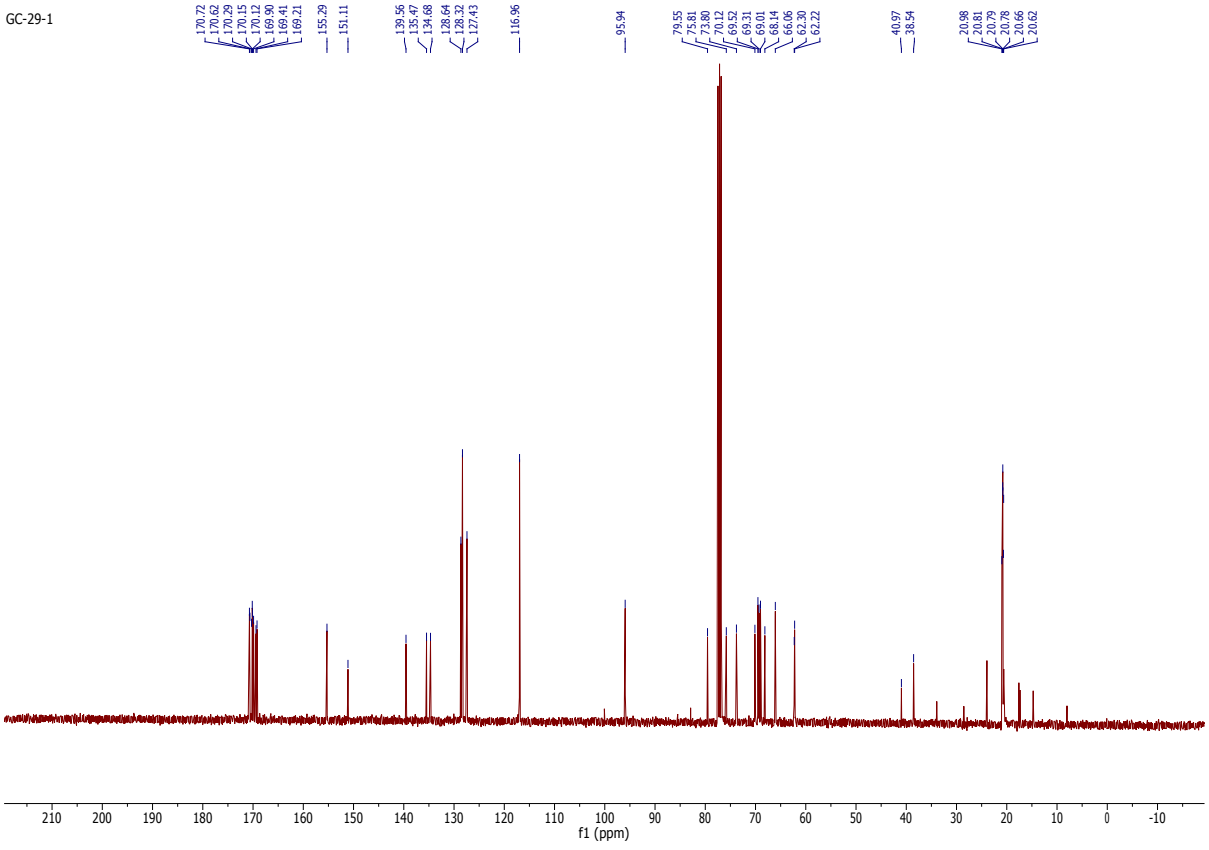


***(Z)-S-*(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl) [4'-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl oxy)biphenyl-4-yl]acetothiohydroximate 19: ^{1}H NMR (400 MHz, $CDCl_3$) :**

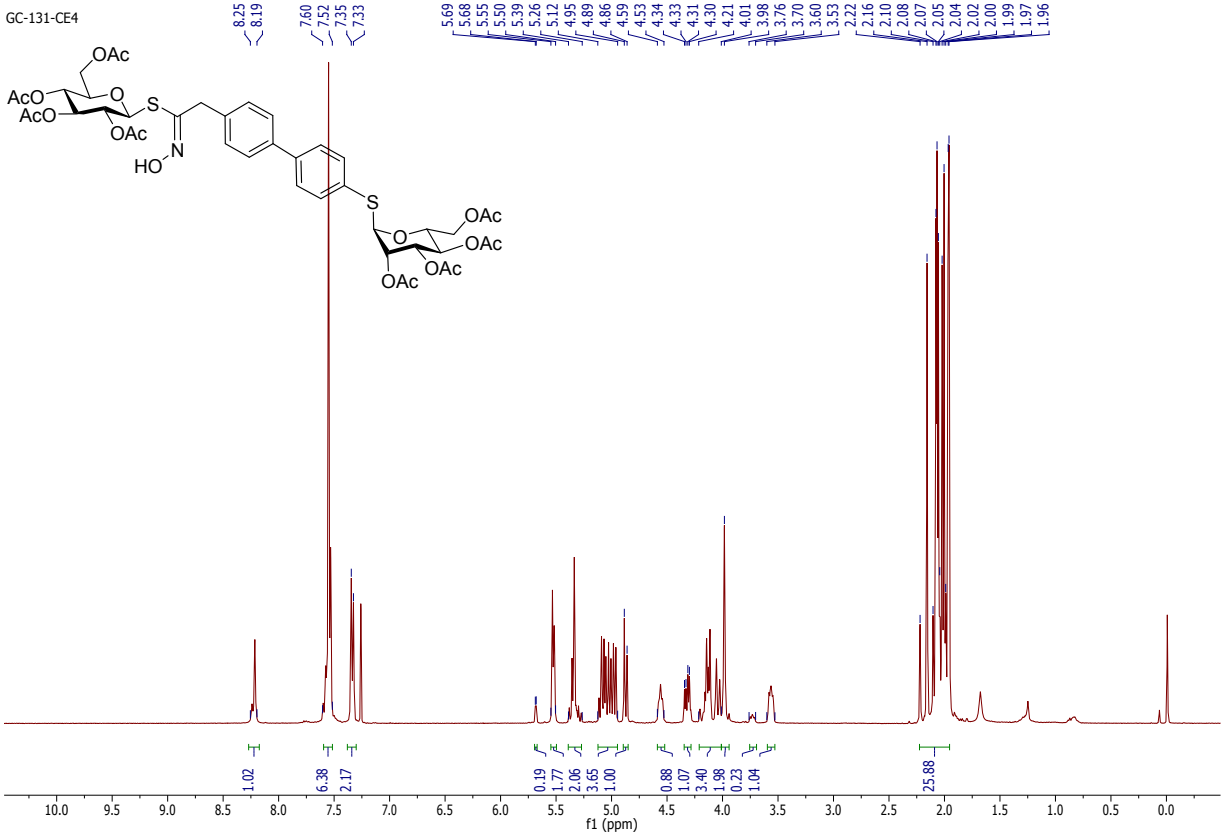


13

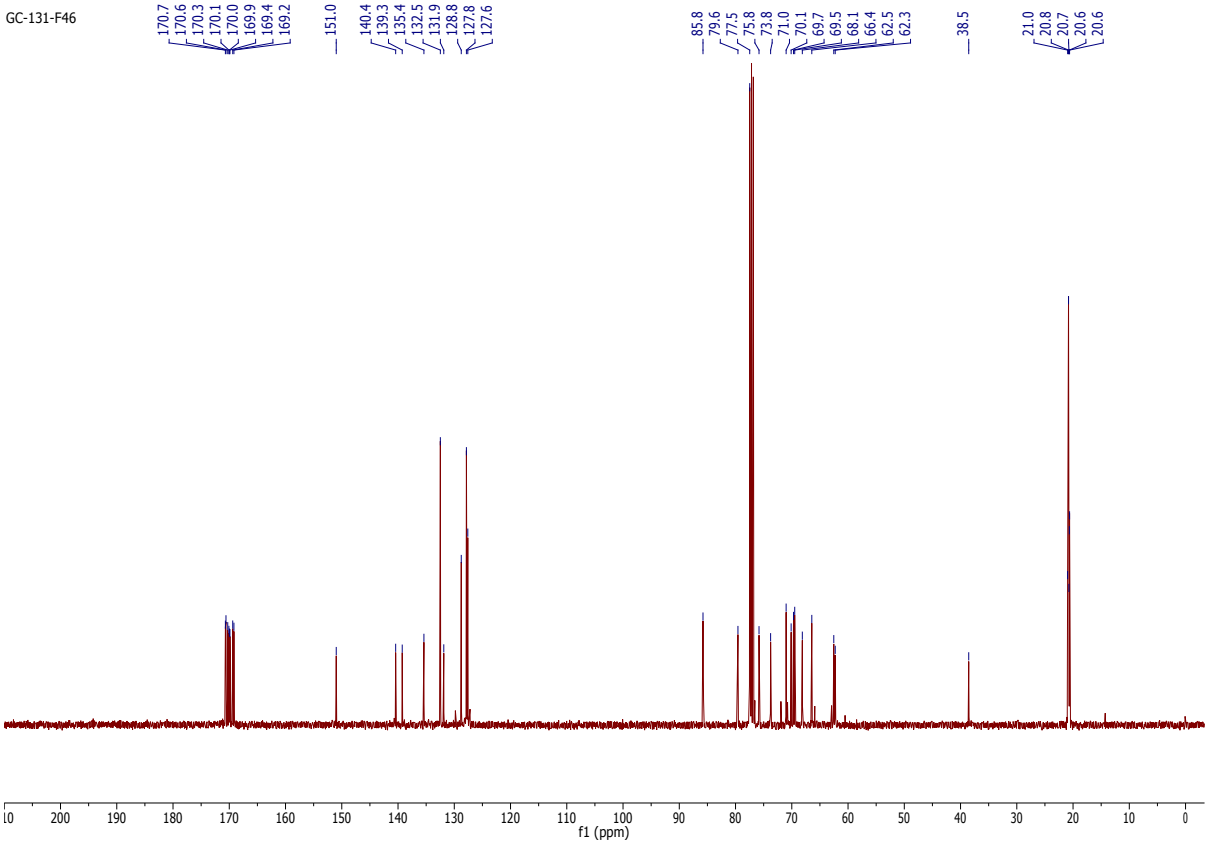
C NMR (100 MHz, $CDCl_3$):



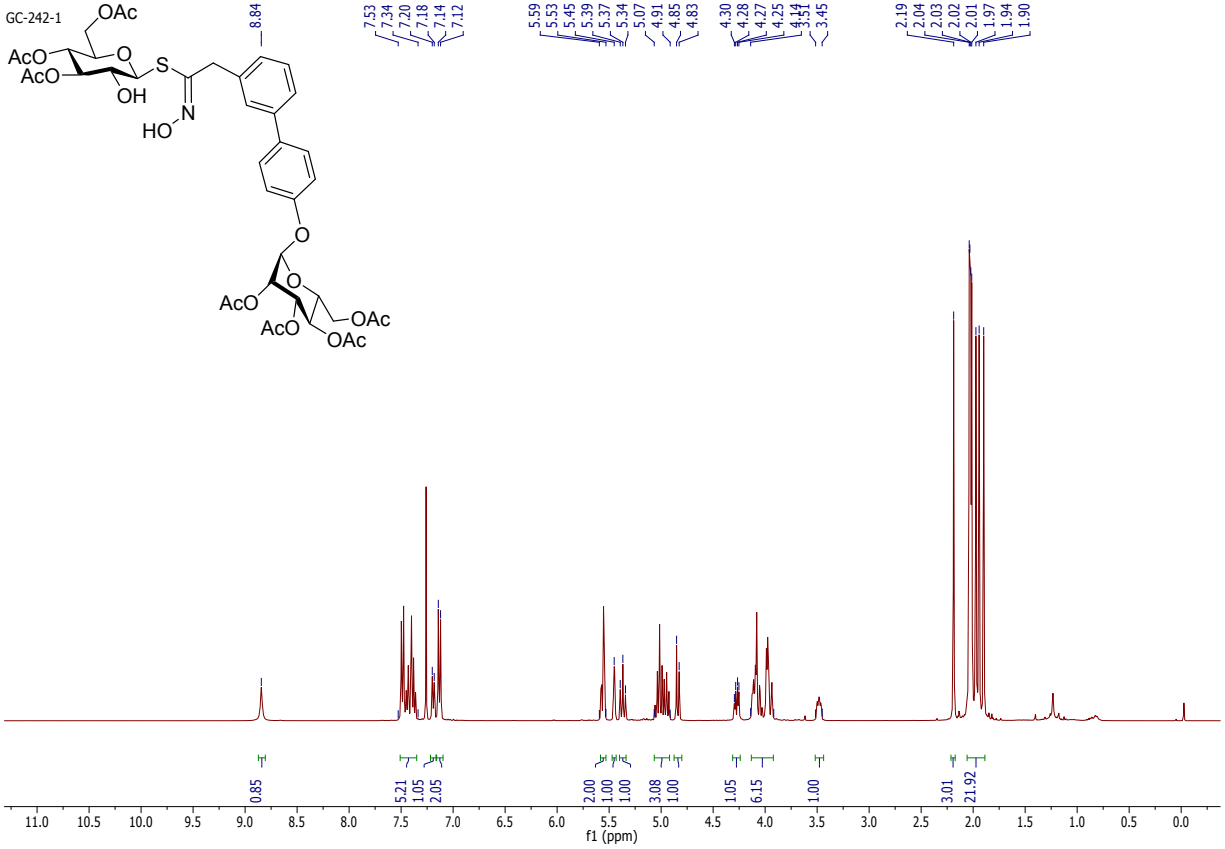
***(Z)-S-*(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl) [4'-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl sulfanyl)biphenyl-4-yl]acetothiohydroximate 20 : ^{1}H NMR (400 MHz, $CDCl_3$):**



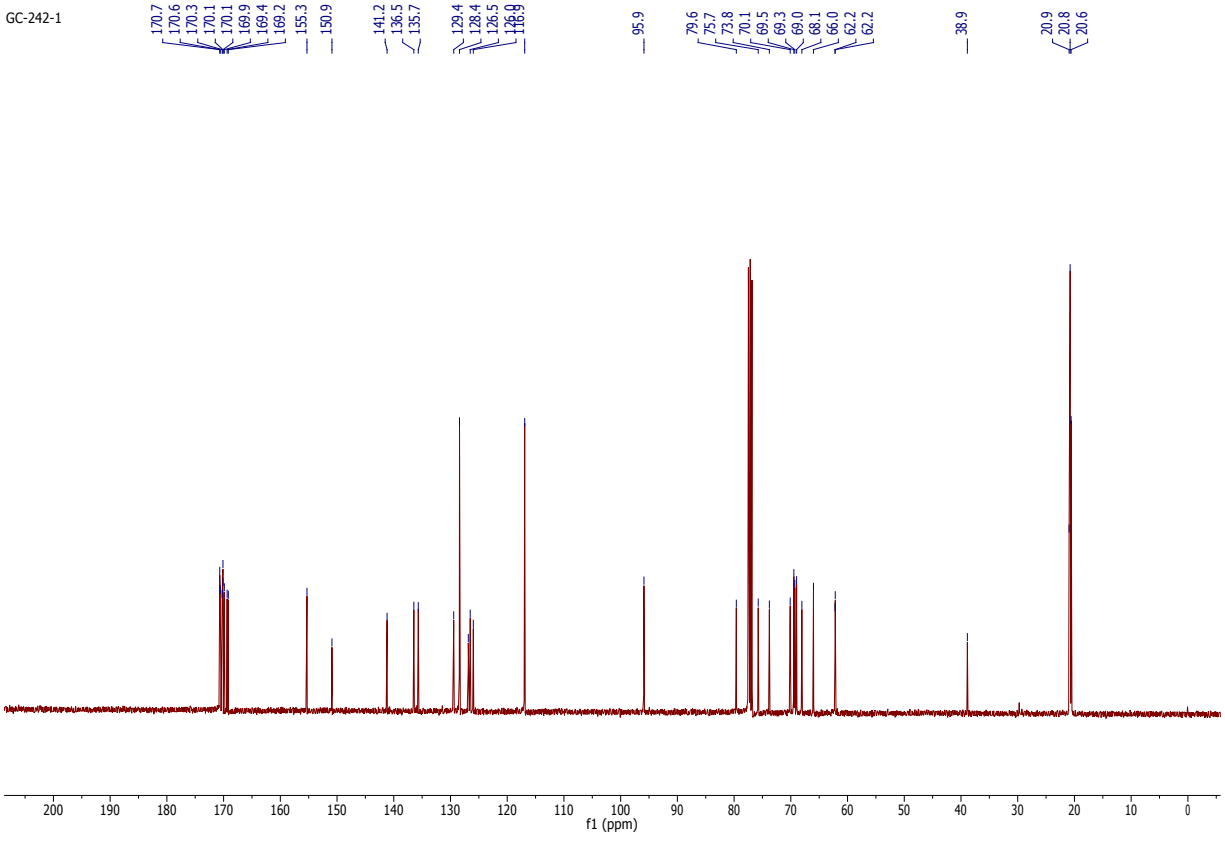
^{13}C NMR (100 MHz, $CDCl_3$) :



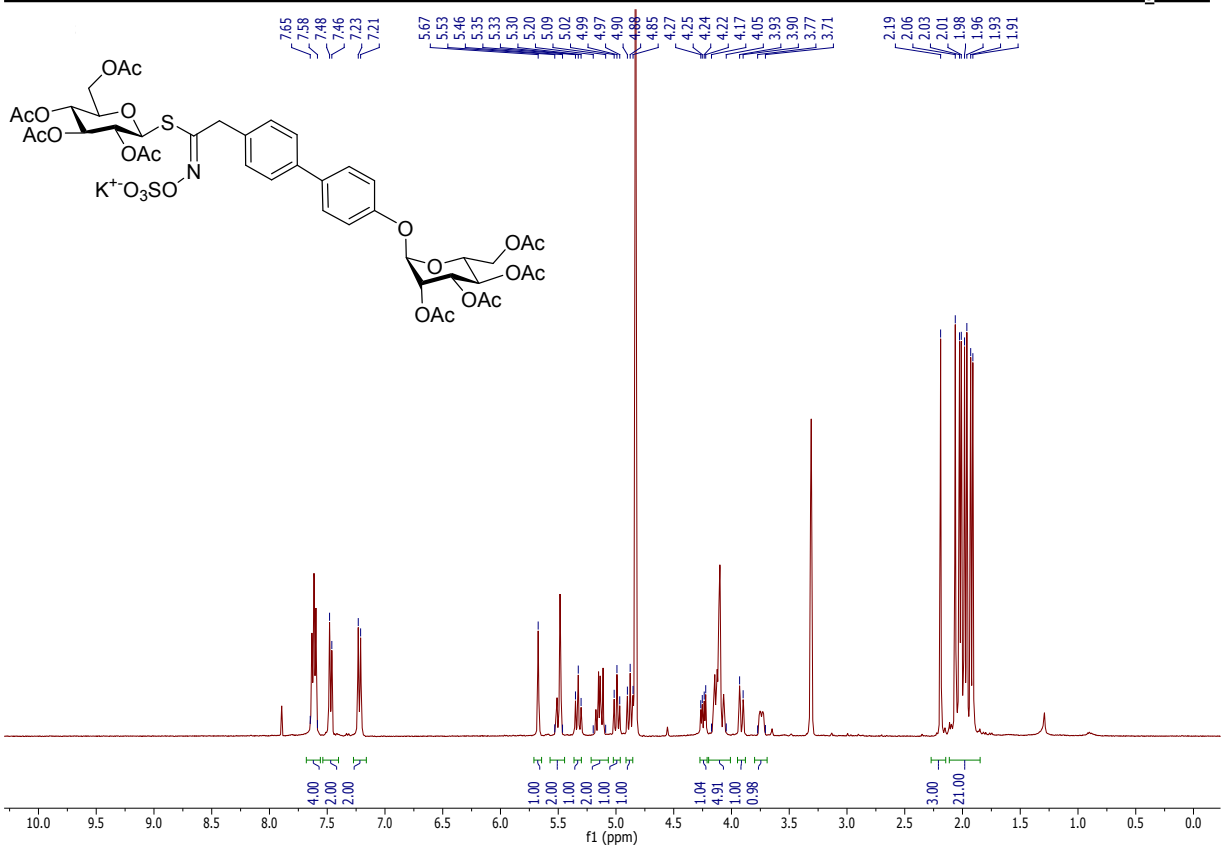
***(Z)-S-*(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl) [4'-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxy)biphenyl-3-yl]acetothiohydroximate 21 : ^{1}H NMR (400 MHz, $CDCl_3$):**



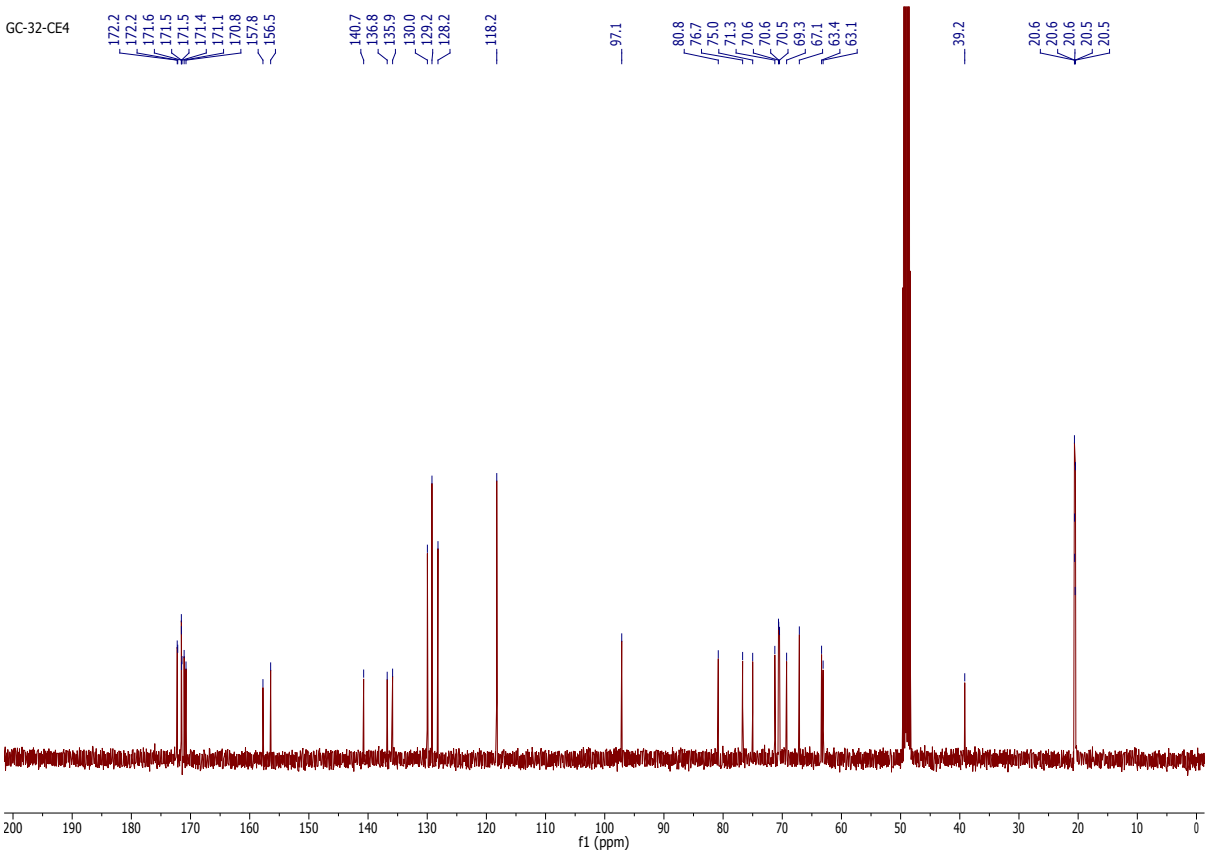
^{13}C NMR (100 MHz, $CDCl_3$) :



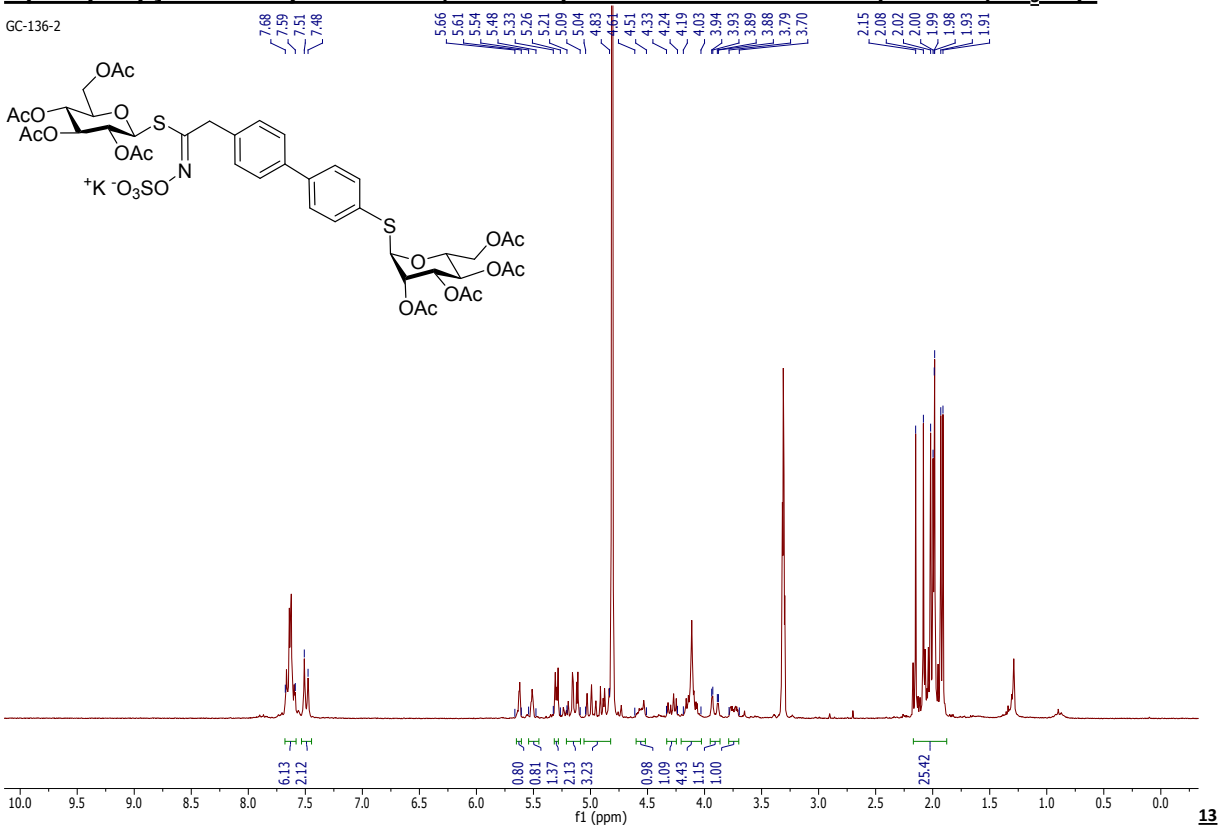
***(Z)-S*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl) [4'-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl oxy)biphenyl-4-yl]acetothiohydroximate *N,O*-sulfate potassium salt 22: ^{1}H NMR (400 MHz, CD_3OD):**



^{13}C NMR (100 MHz, CD_3OD) :

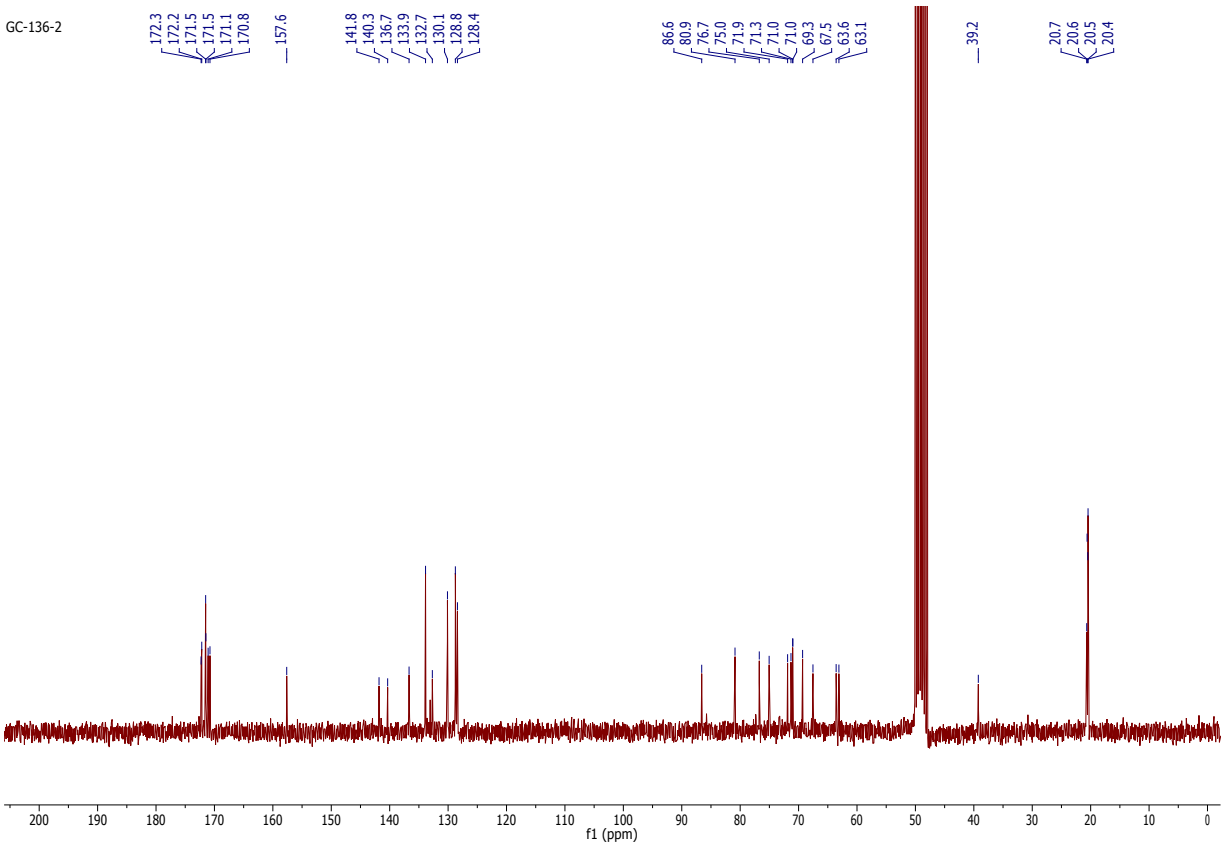


***(Z)*-*S*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl) [4'-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl sulfanyl) biphenyl-4-yl]acetothiohydroximate *N,O*-sulfate potassium salt 23 : ^{1}H NMR (250 MHz, CD_3OD) :**

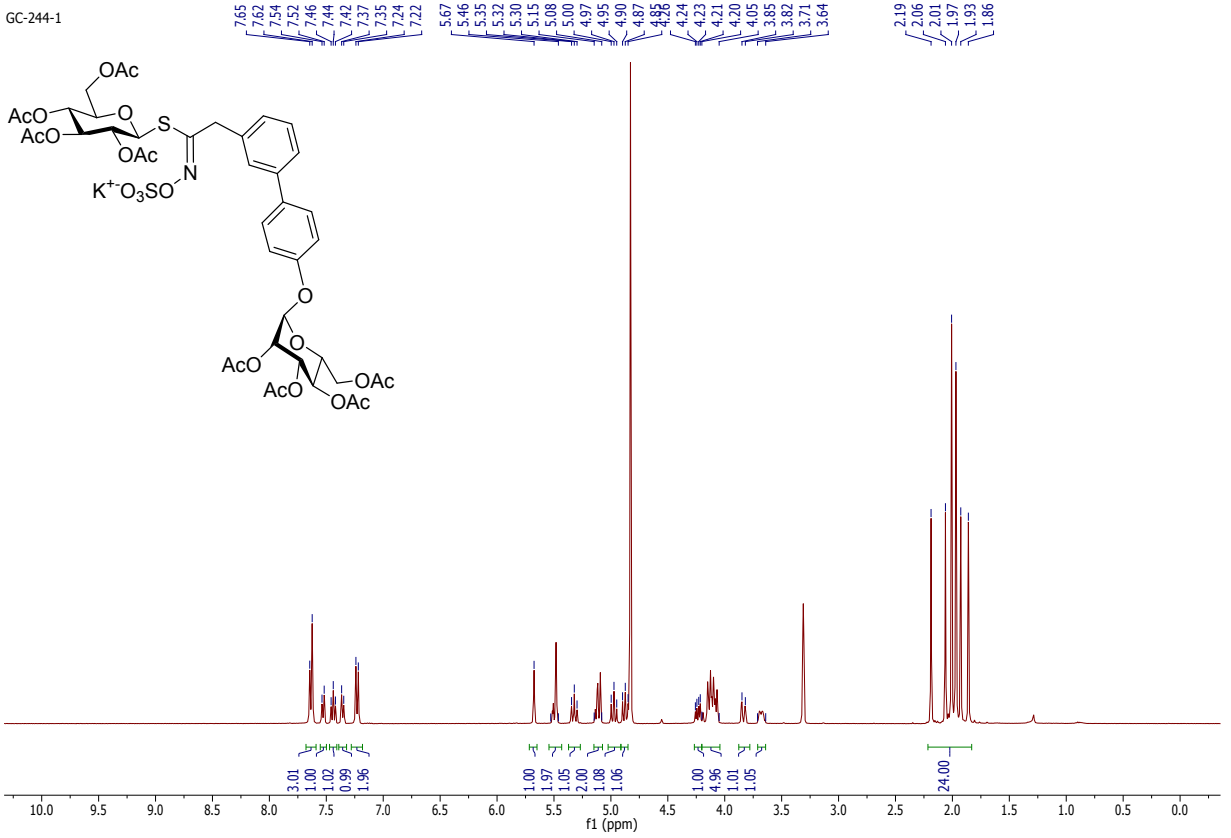


13

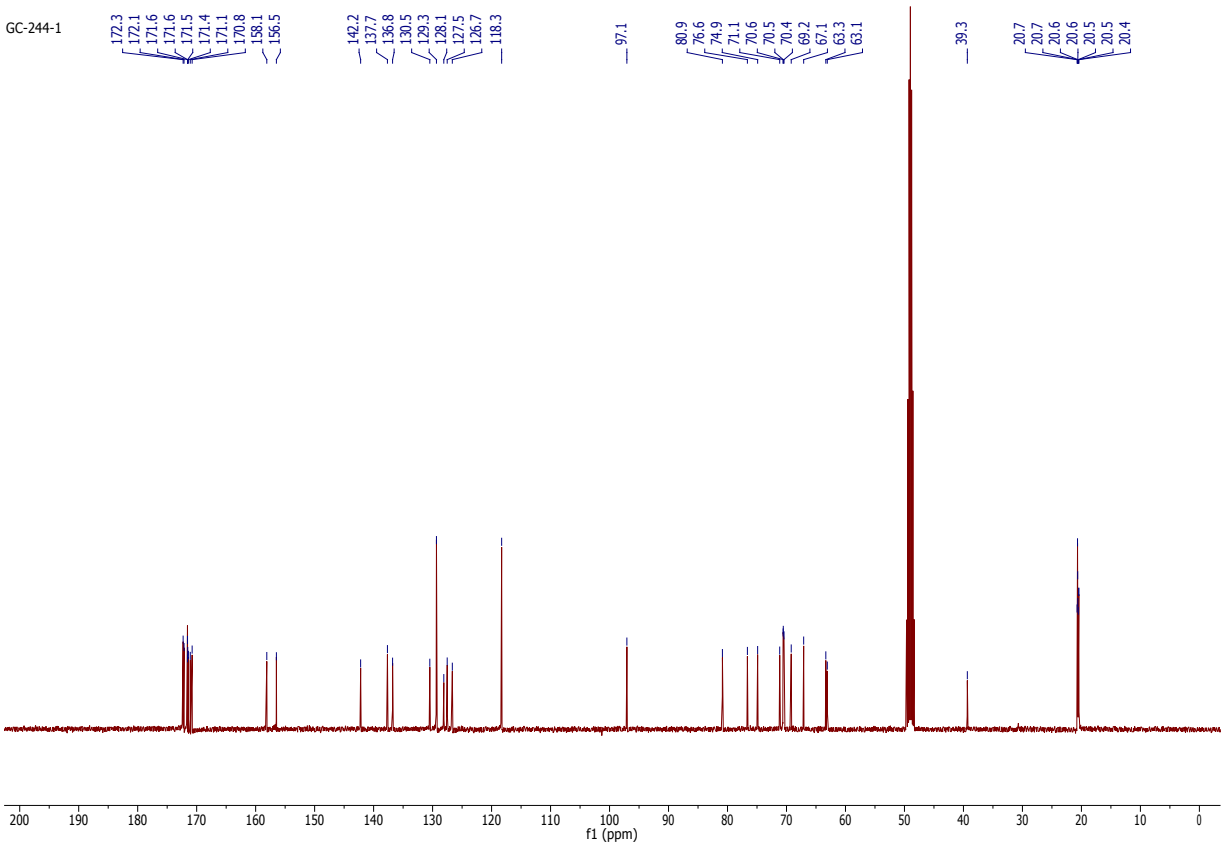
C NMR (62.5 MHz, CD_3OD) :



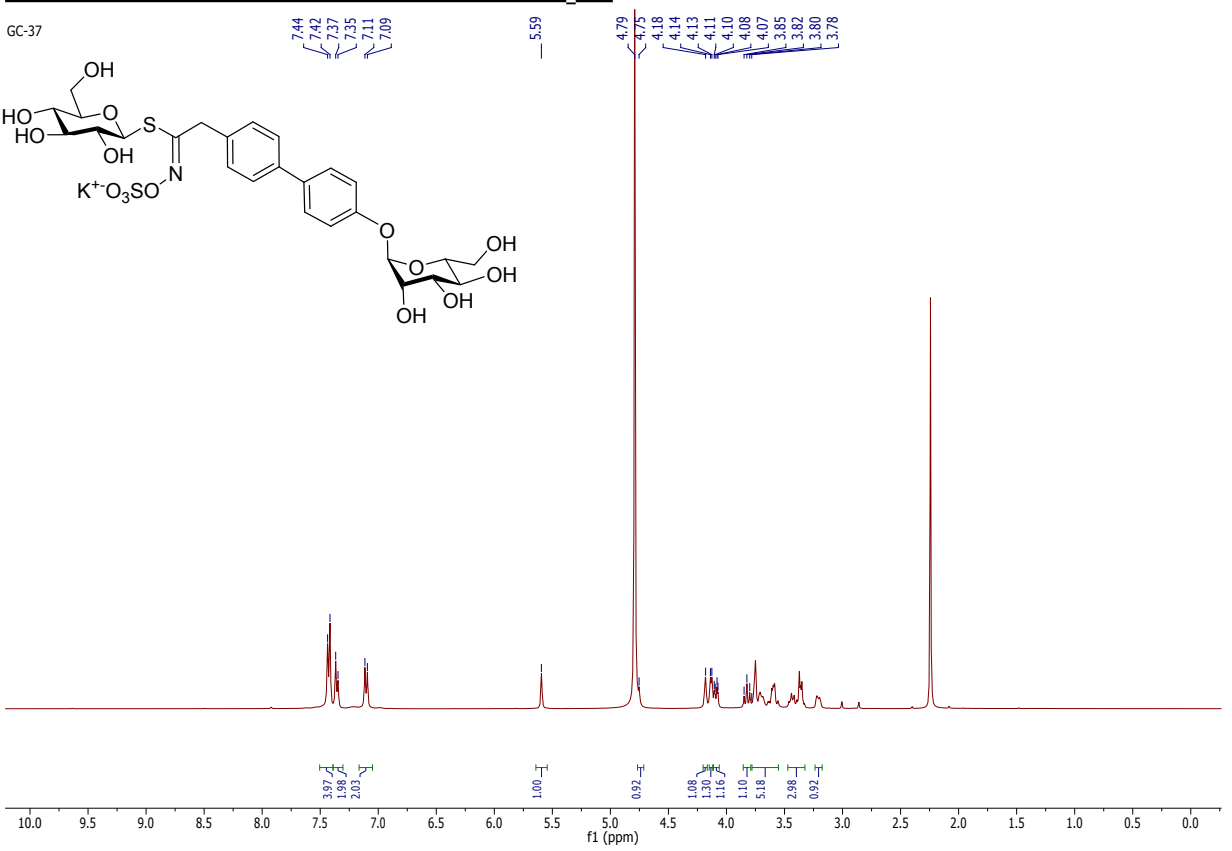
***(Z)-S*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl) [4'-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyloxy)biphenyl-3-yl]acetothiohydroximate *N,O*-sulfate potassium salt 24 : ^{1}H NMR (400 MHz, $CDCl_3$):**



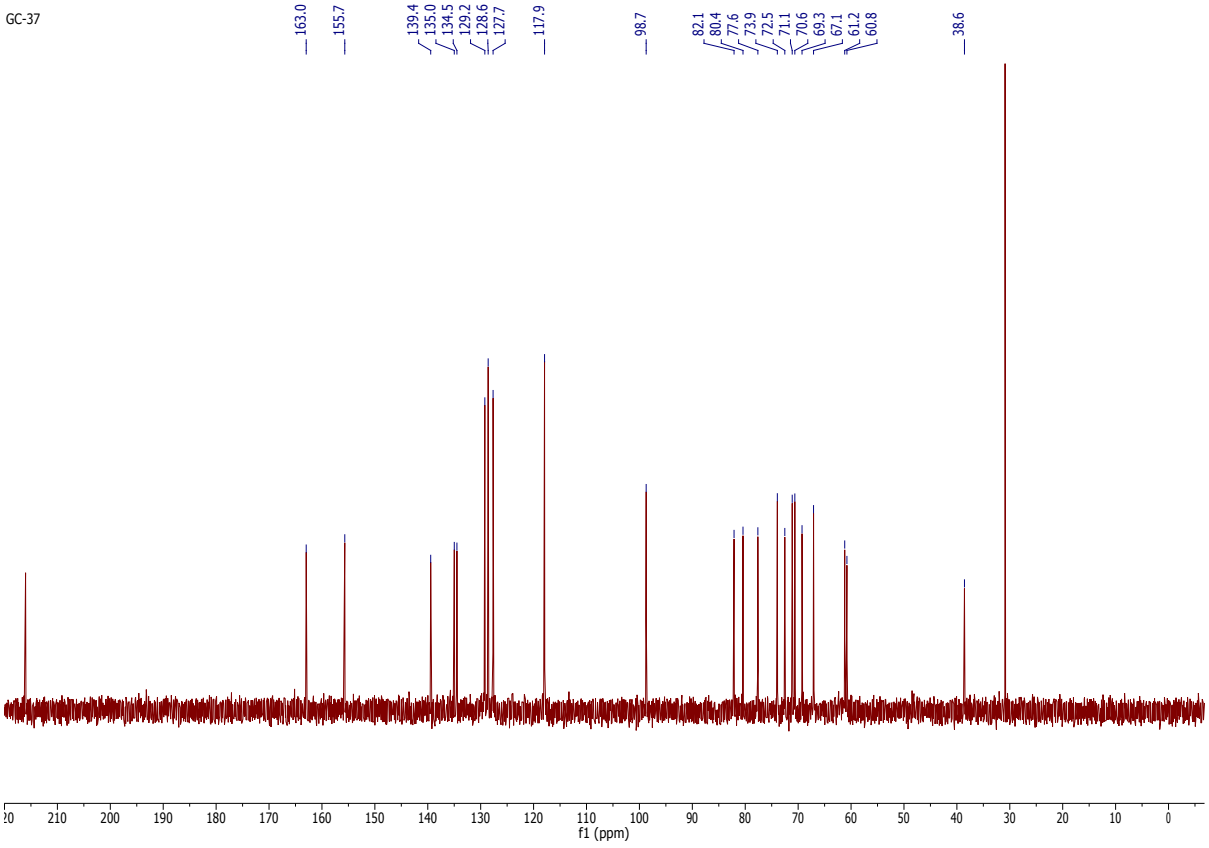
^{13}C NMR (100 MHz, $CDCl_3$) :



***(Z)-S*-(β-D-Glucopyranosyl) [4'-(α-D-mannopyranosyloxy)biphenyl-4-yl]acetothiohydroximate *N,O*-sulfate potassium salt 4 : ^{1}H NMR (400 MHz, D_2O):**

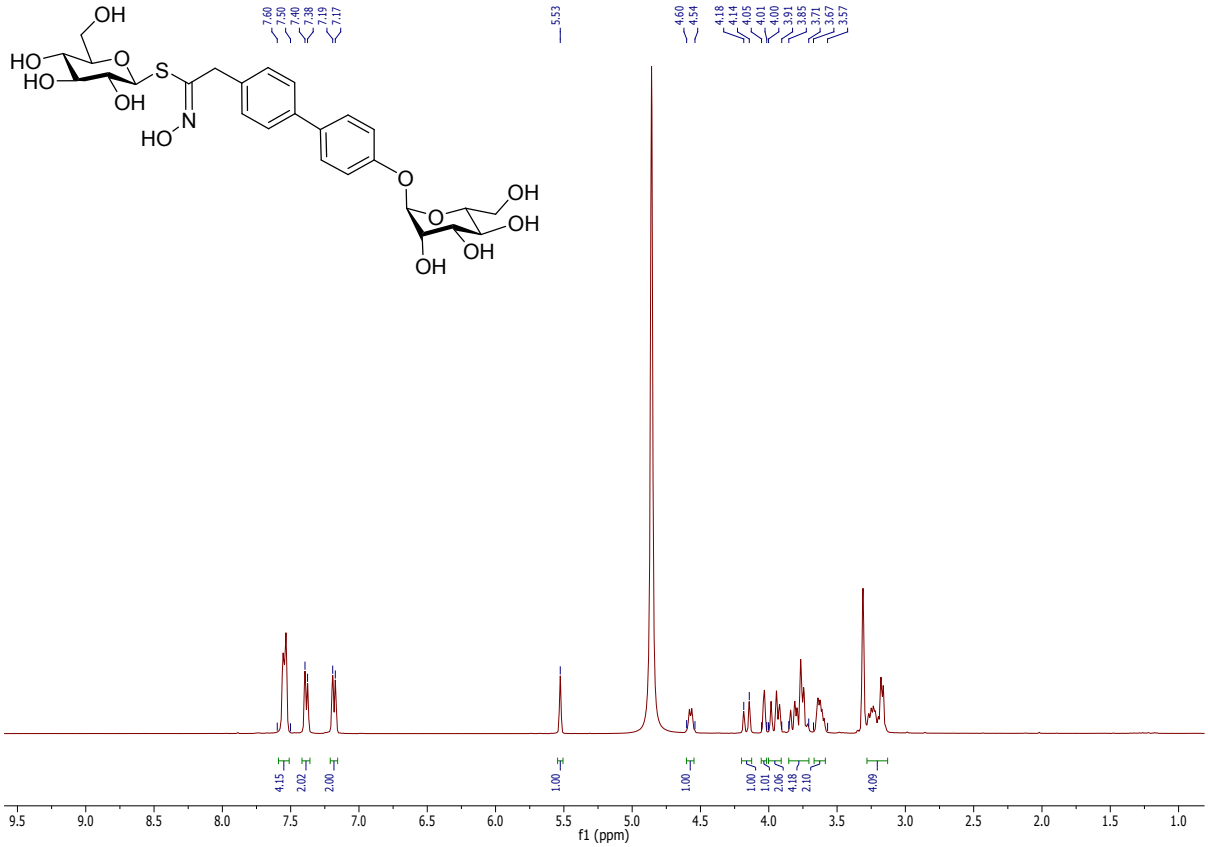


^{13}C NMR (100 MHz, D_2O, internal acetone) :

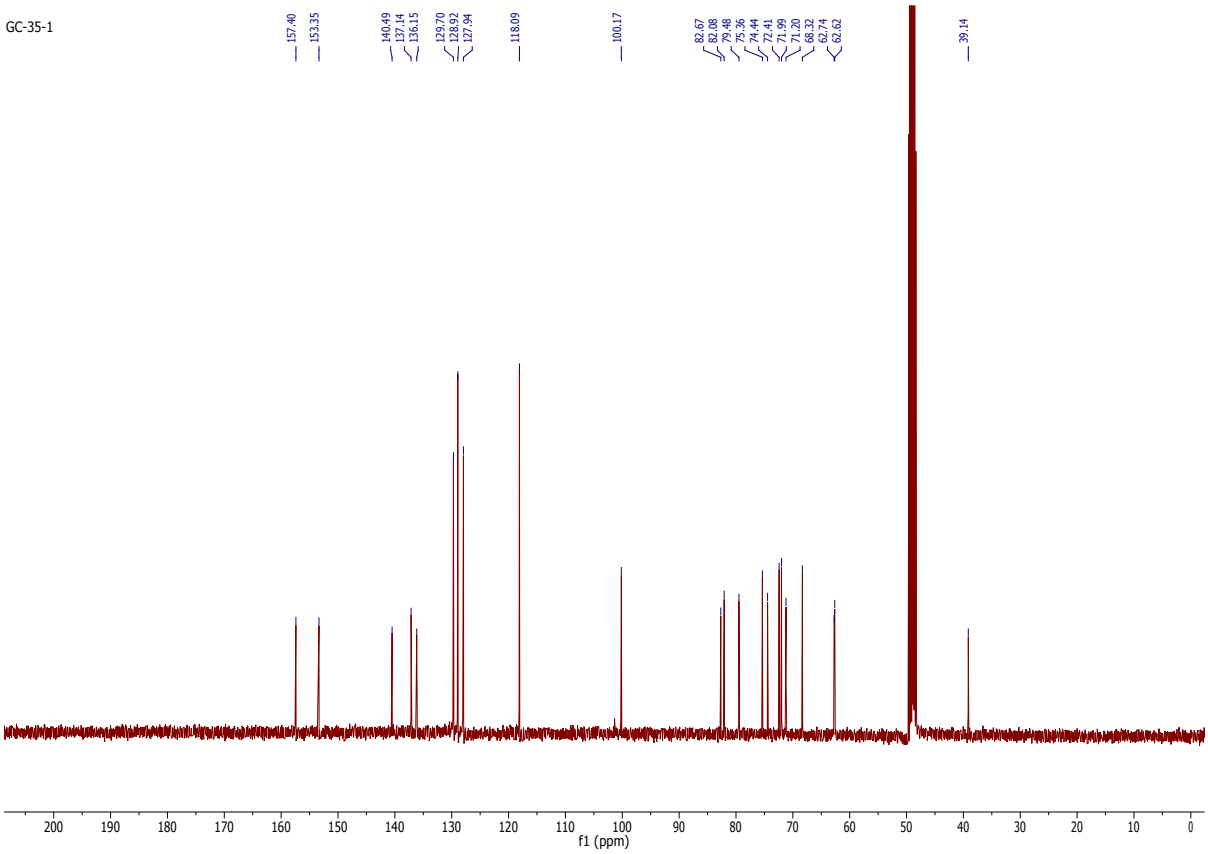


***(Z)*-*S*-(β-D-Glucopyranosyl) [4'-(α-D-mannopyranosyloxy)biphenyl-4-yl]acetothiohydroximate 26:**

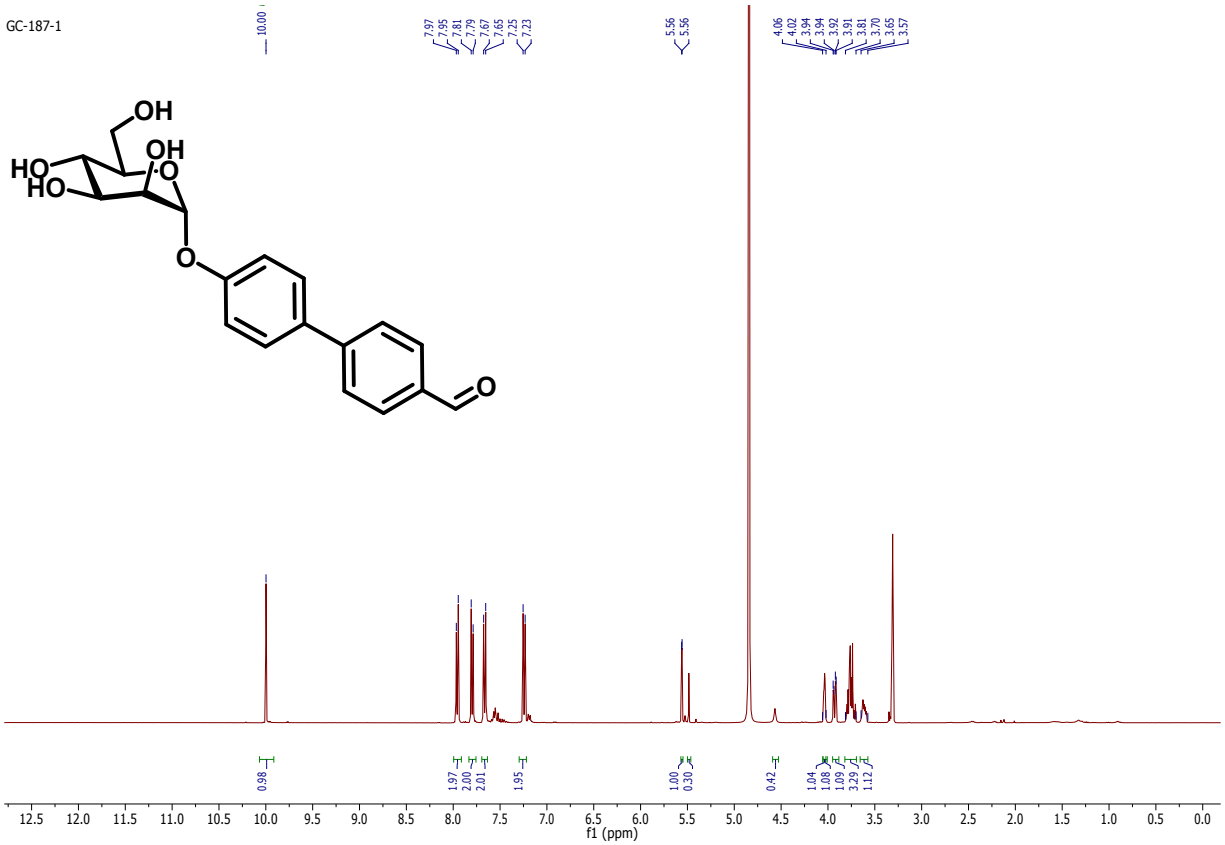
^{1}H NMR (400 MHz, CD_3OD):



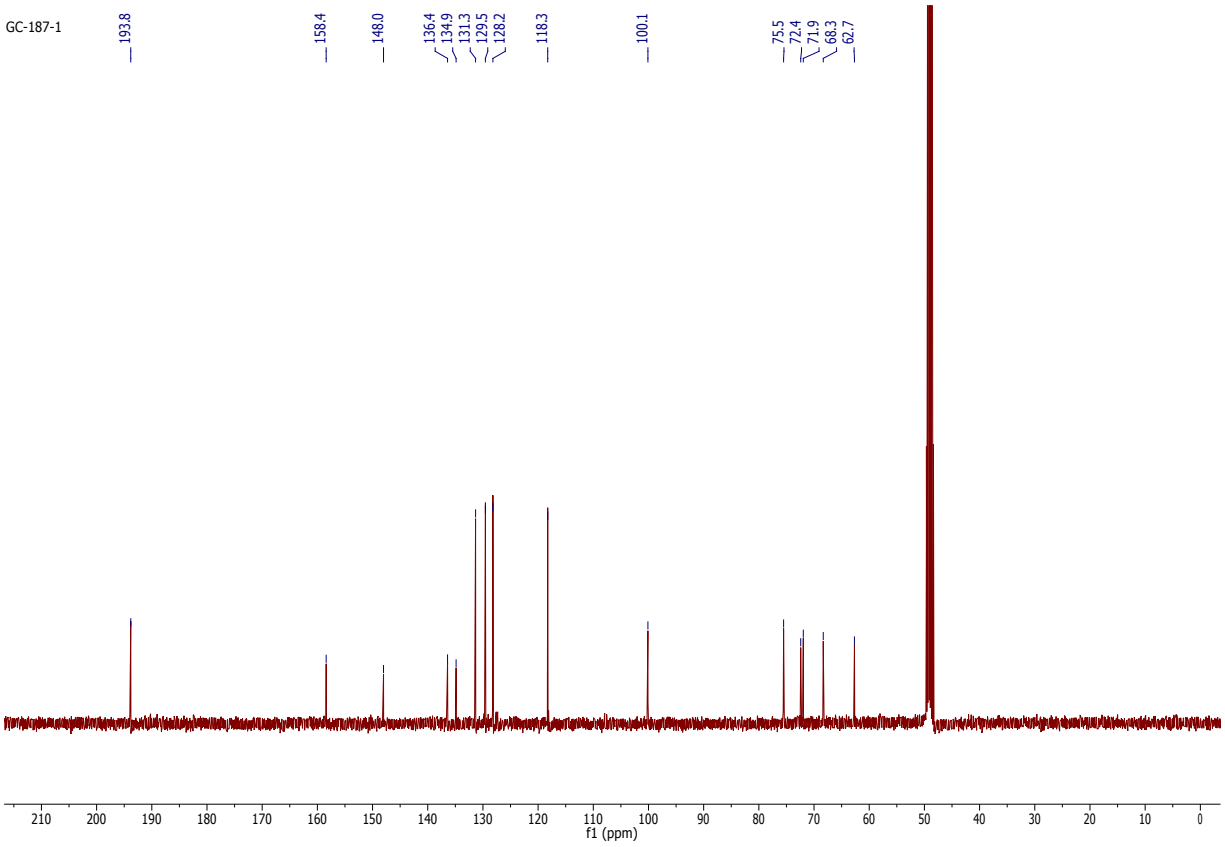
^{13}C NMR (100 MHz, CD_3OD):



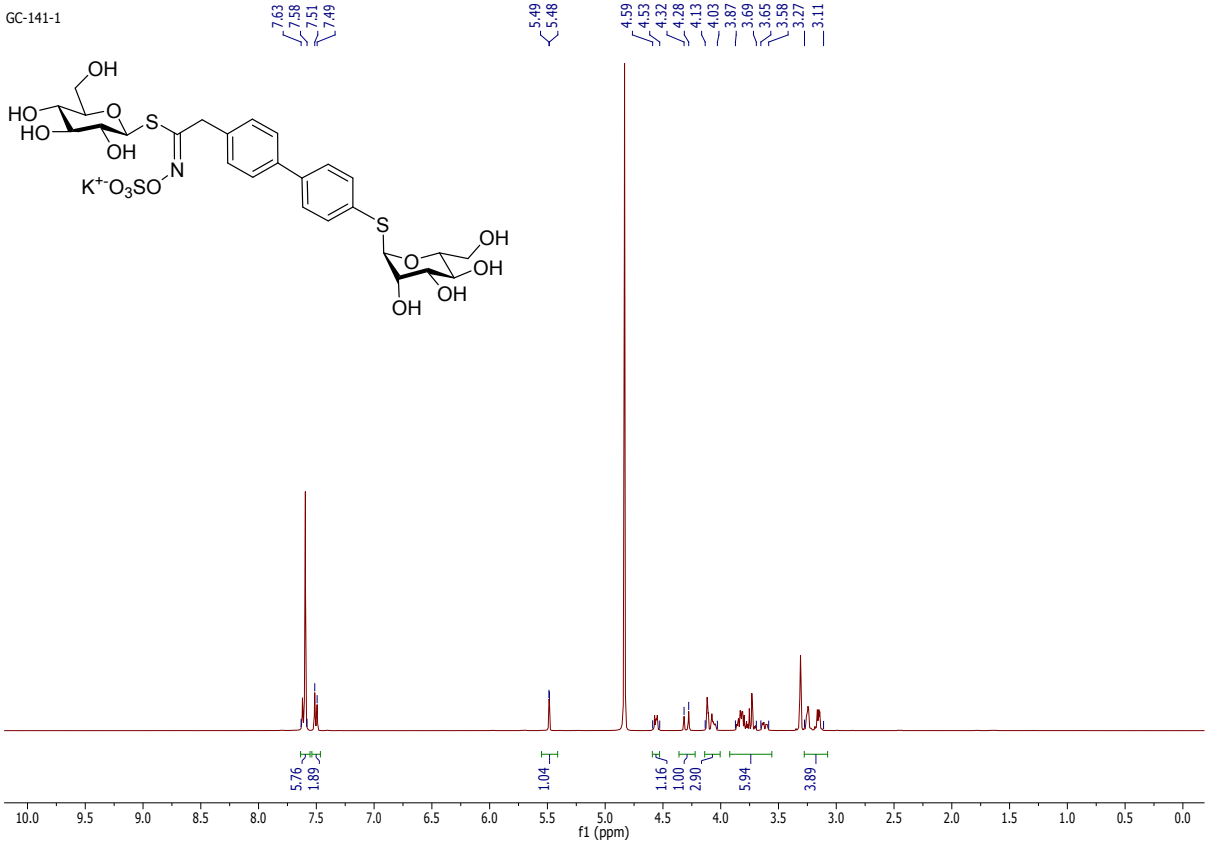
[4'-(α-D-Mannopyranosyloxy)biphenyl-4-yl]carboxaldehyde 17 : ^{1}H NMR (400 MHz, CD_3OD):



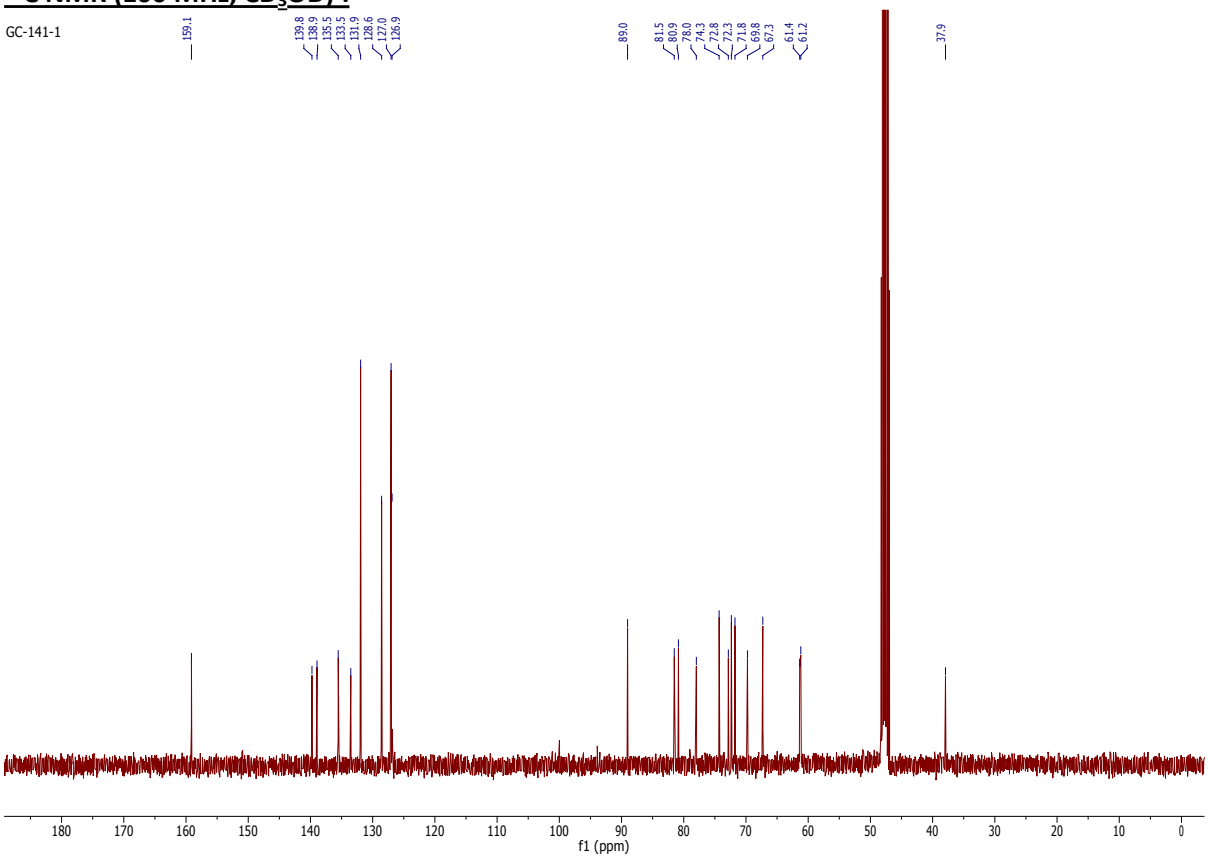
^{13}C NMR (100 MHz, CD_3OD):



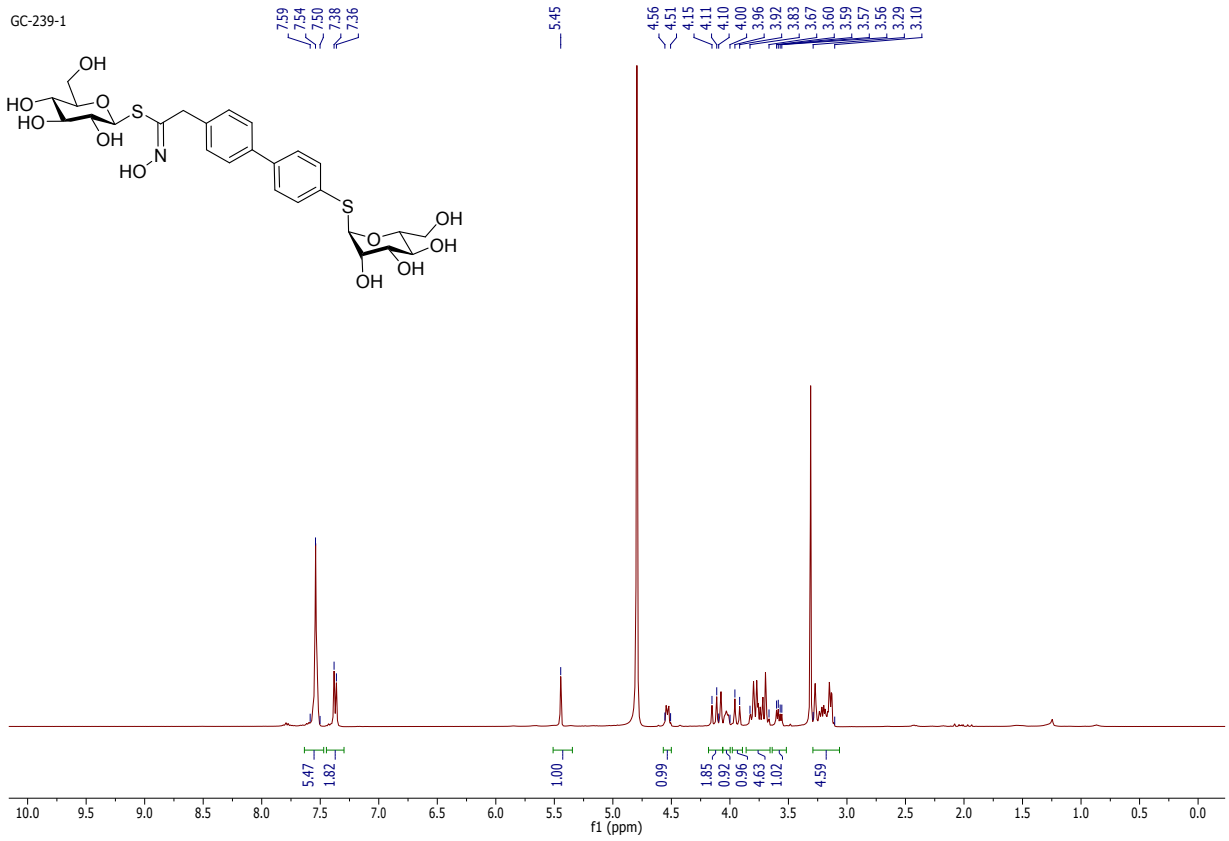
***(Z)*-*S*-(β-D-Glucopyranosyl) [4'-(α-D-mannopyranosylsulfanyl)biphenyl-4-yl]acetothiohydroximate *N*,*O*-sulfate potassium salt 5 : ^{1}H NMR (400 MHz, CD_3OD):**



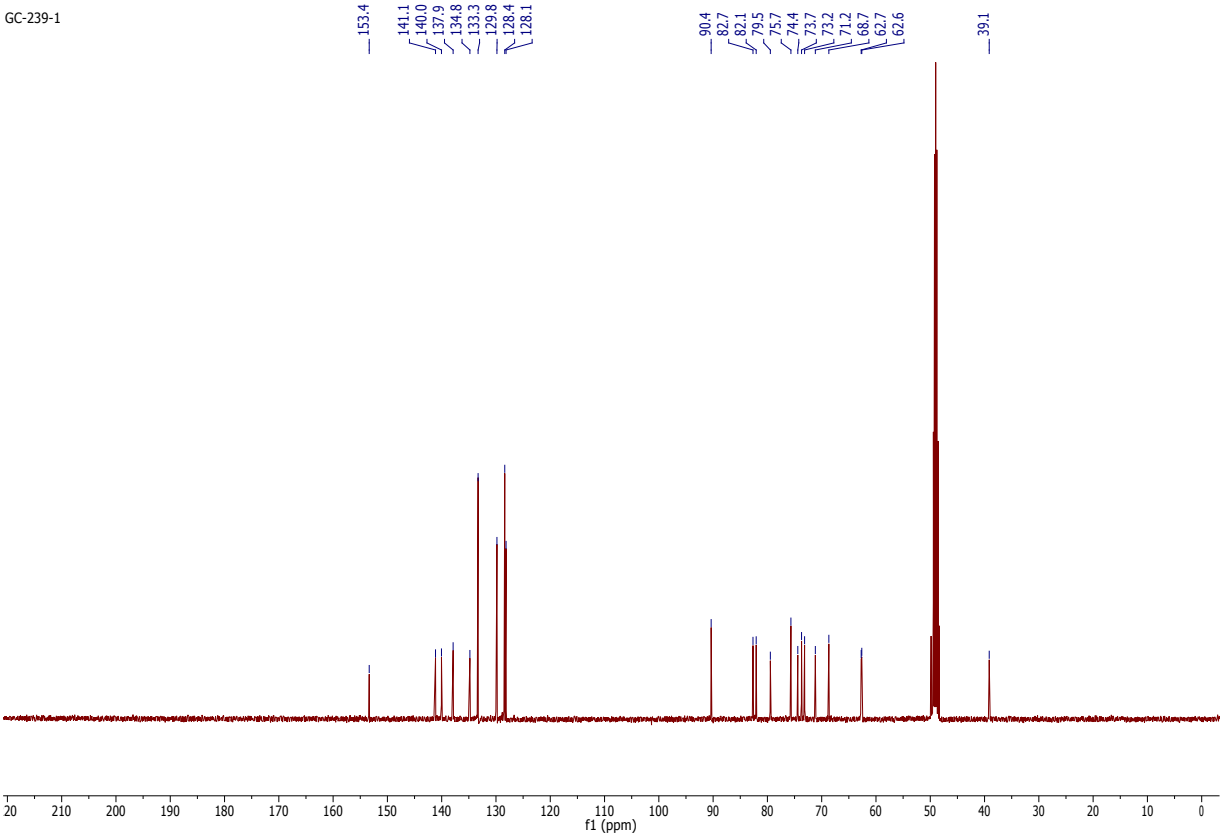
^{13}C NMR (100 MHz, CD_3OD) :



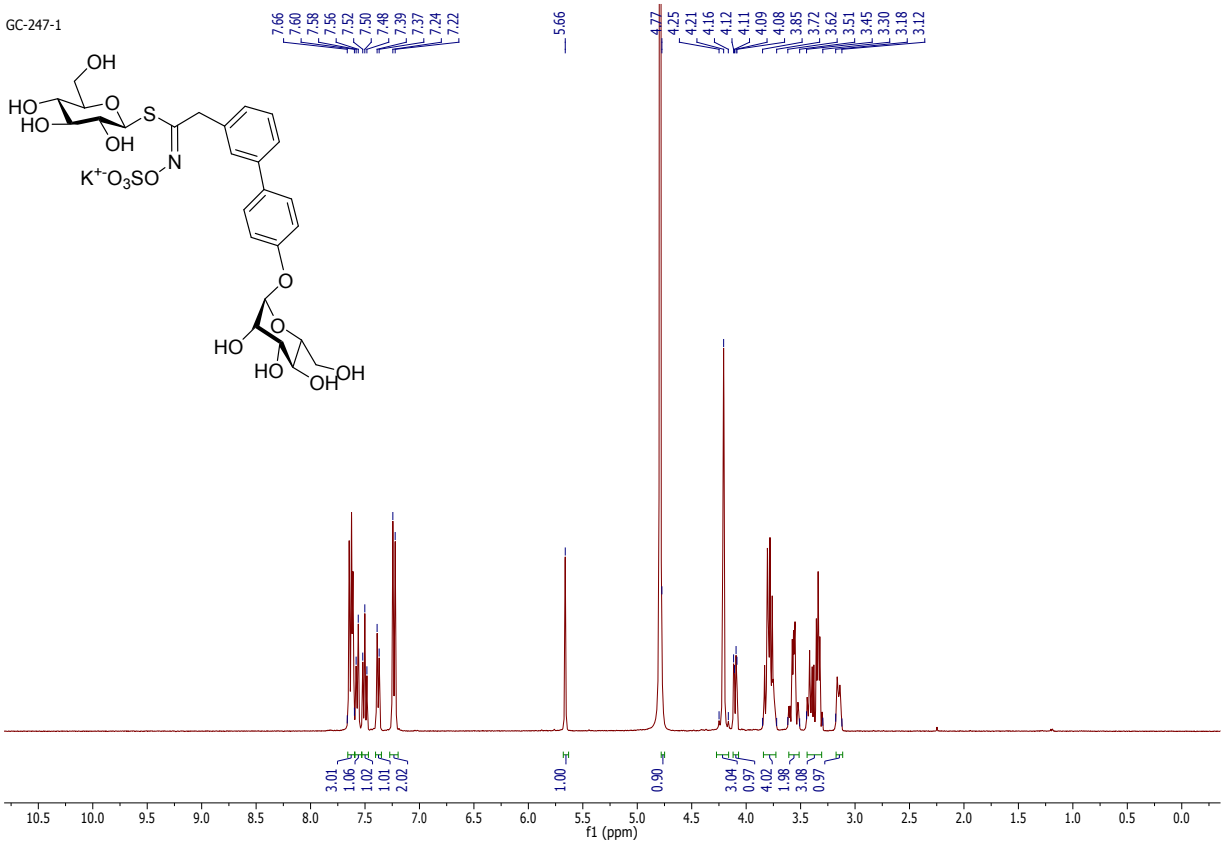
***(Z)-S*-(β-D-Glucopyranosyl) [4'-(α-D-mannopyranosylsulfanyl)biphenyl-4-yl]acetothiohydroximate 27 : ^{1}H NMR (400 MHz, CD_3OD):**



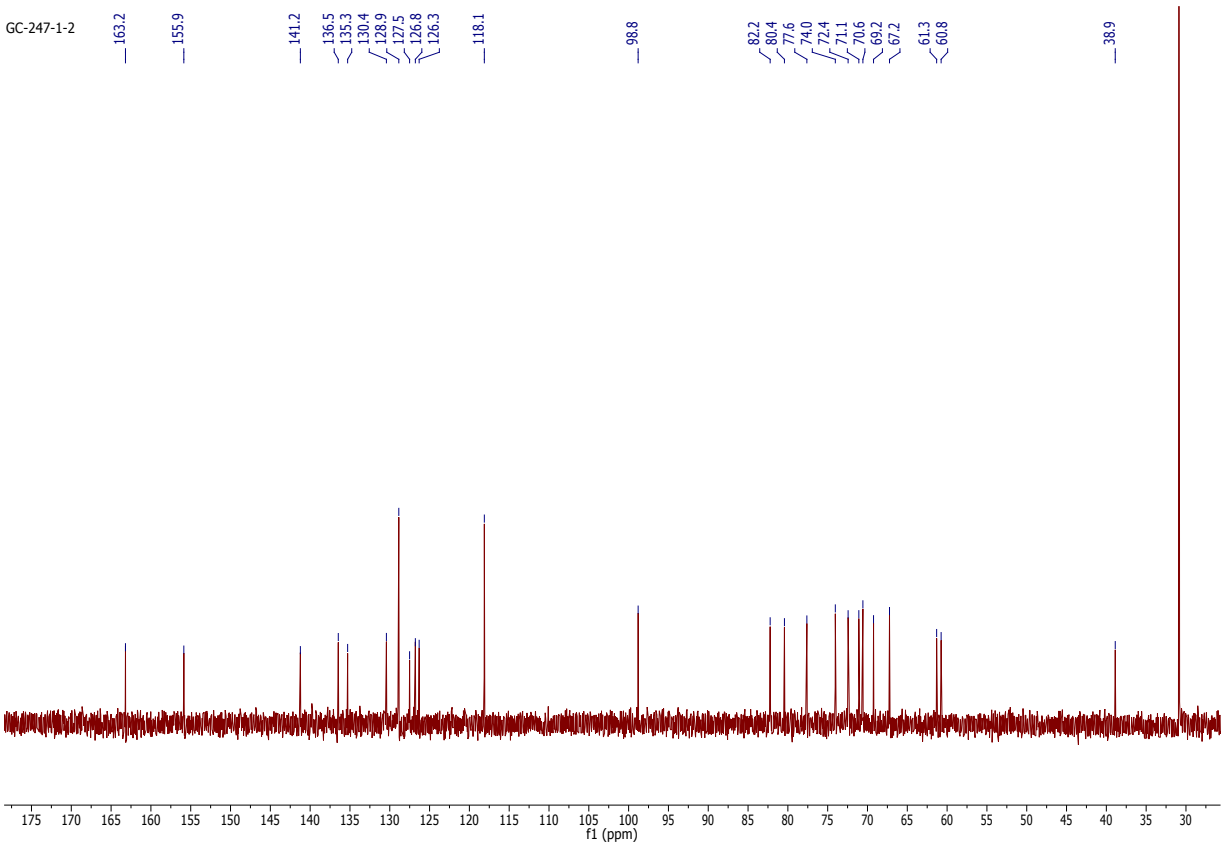
^{13}C NMR (100 MHz, CD_3OD):



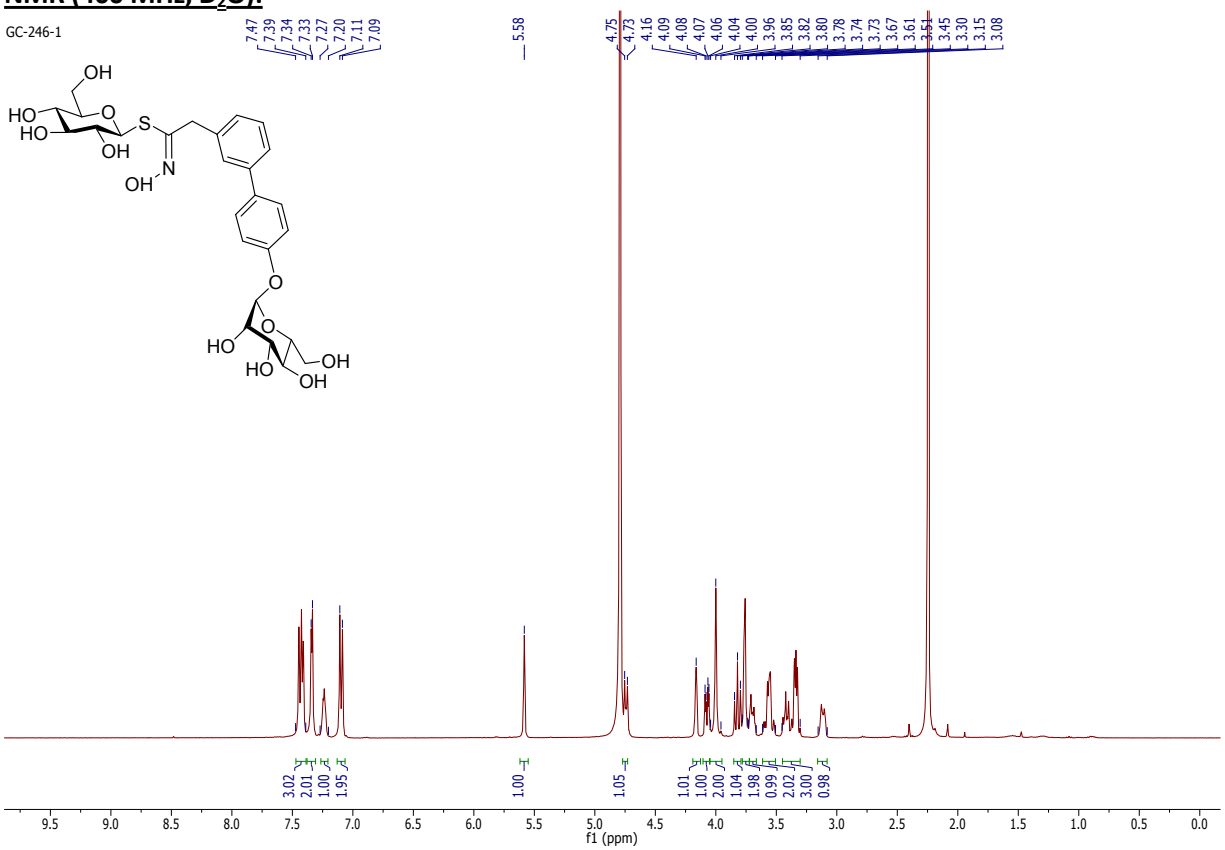
***(Z)*-*S*-(β-D-Glucopyranosyl) [4'-(α-D-mannopyranosylsulfanyl)biphenyl-3-yl]acetothiohydroximate *N*,*O*-sulfate potassium salt 6: ^{1}H NMR (400 MHz, D_2O):**



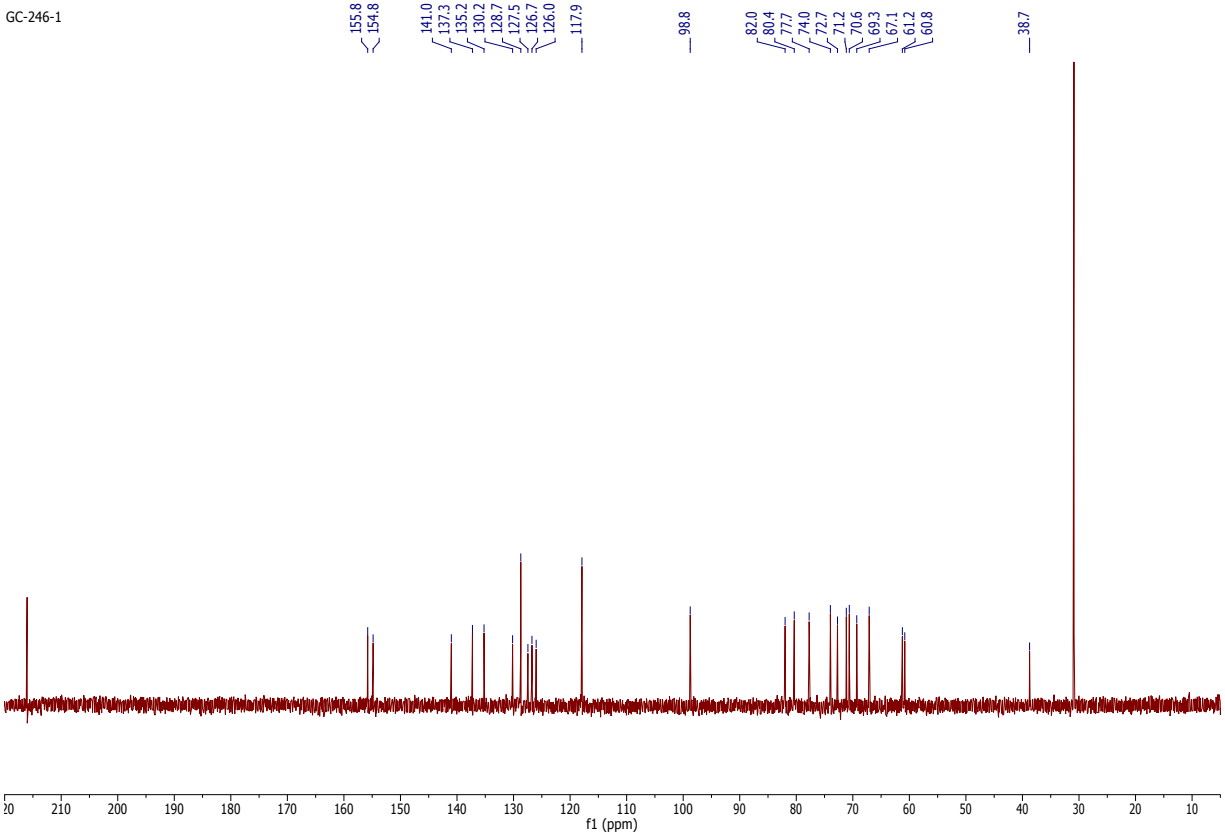
^{13}C NMR (100 MHz, D_2O, internal acetone) :



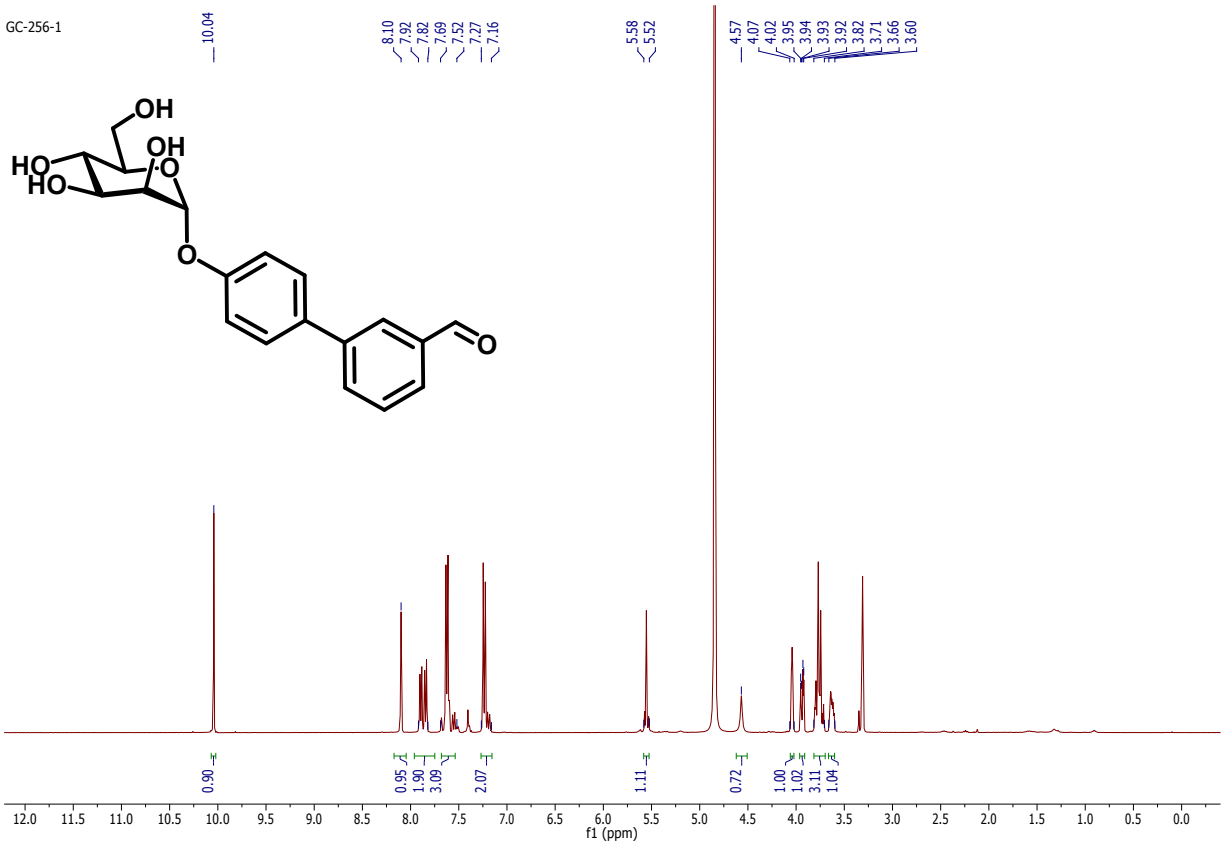
***(Z)-S*-(β-D-Glucopyranosyl) [4'-(α-D-mannopyranosyloxy)biphenyl-3-yl]acetothiohydroximate 28 : ^{1}H NMR (400 MHz, D_2O):**



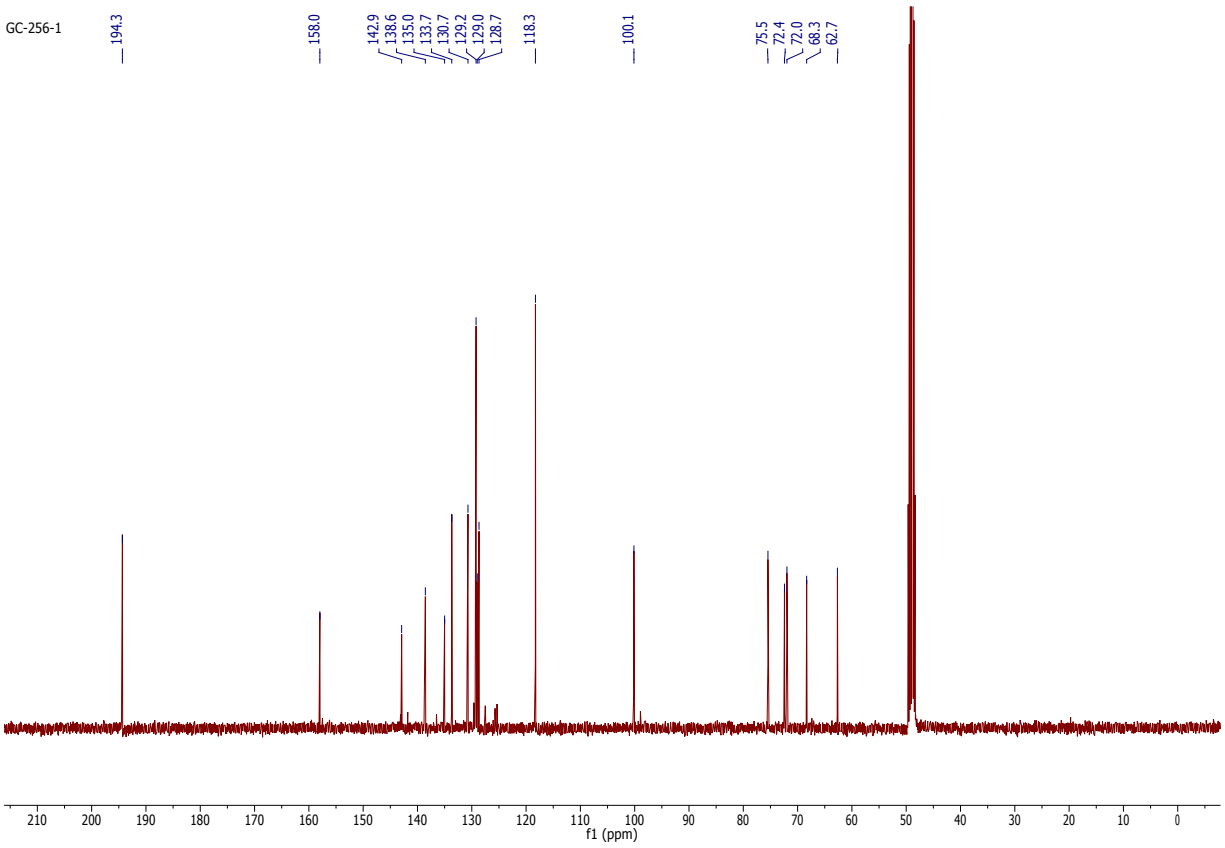
^{13}C NMR (100 MHz, D_2O, internal acetone) :



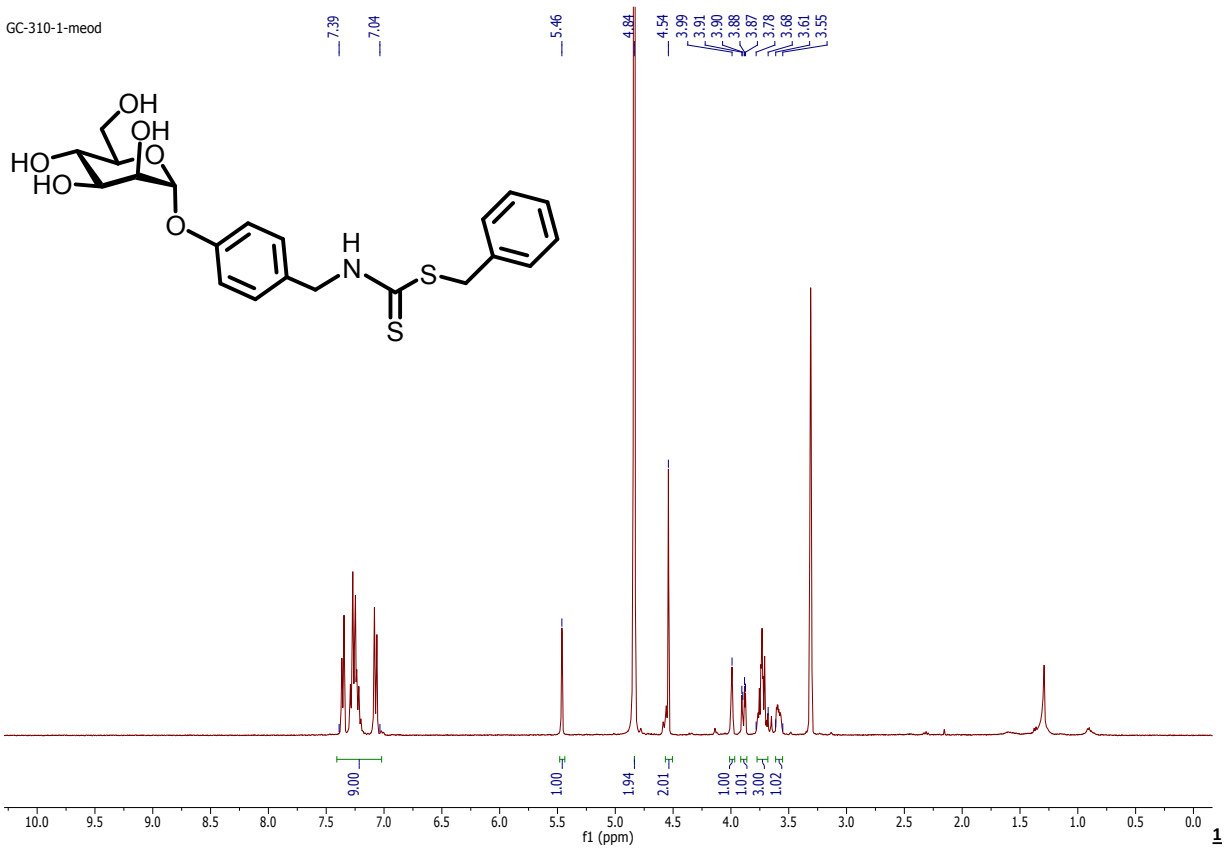
[4'-(α-D-Mannopyranosyloxy)biphenyl-3-yl]carboxaldehyde 18 : ^{1}H NMR (400 MHz, CD_3OD):



^{13}C NMR (100 MHz, CD_3OD):

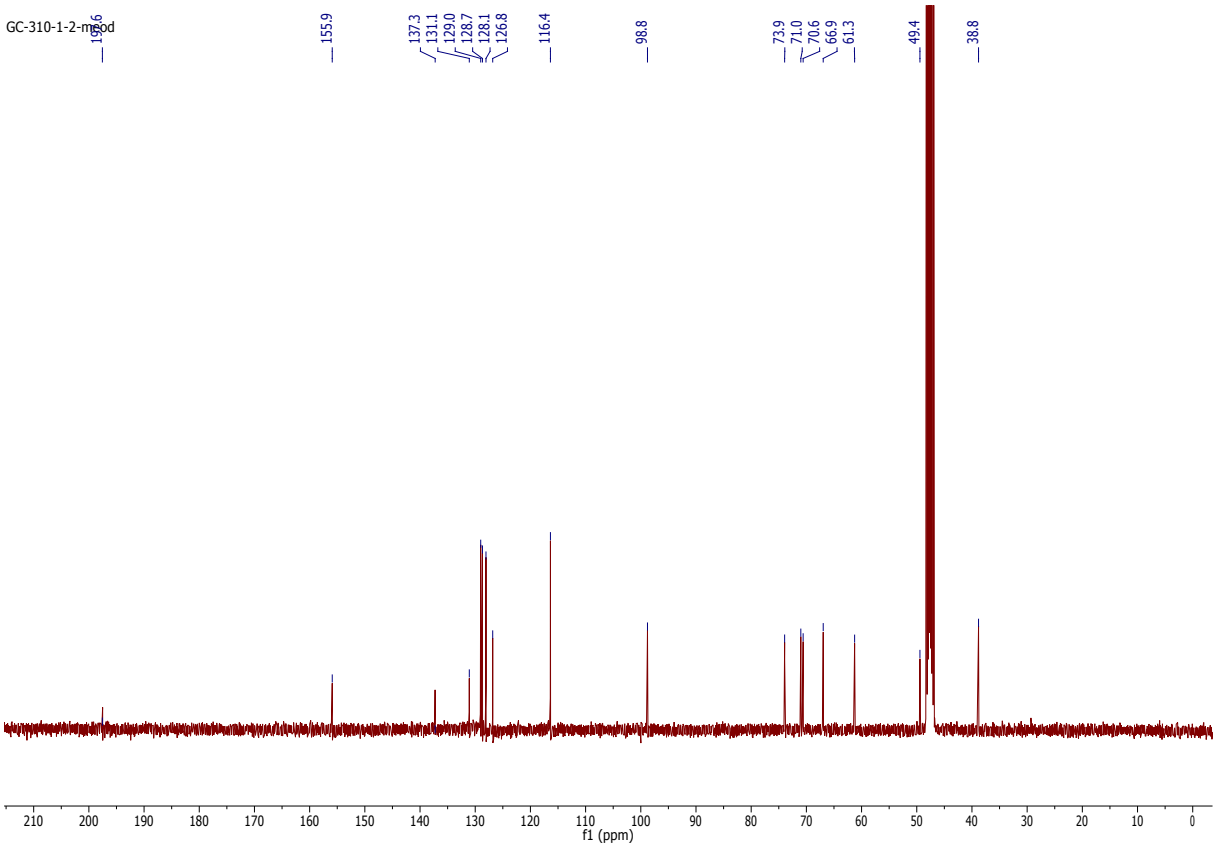


_S_-Benzyl-_N_-(4-(α-D-mannopyranosyloxy)benzyl)dithiocarbamate 31: ^{1}H NMR (400 MHz, CD_3OD):

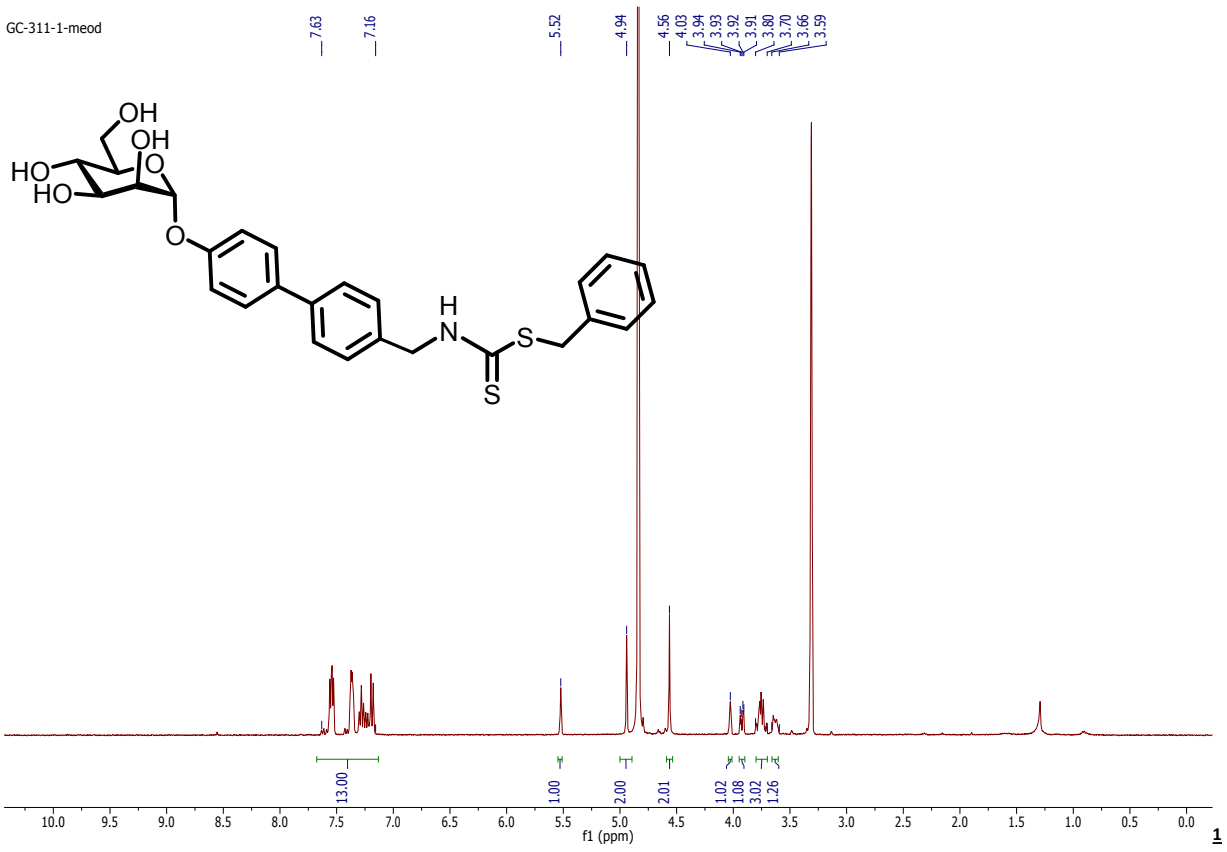


1

^{3}C NMR (100 MHz, CD_3OD):

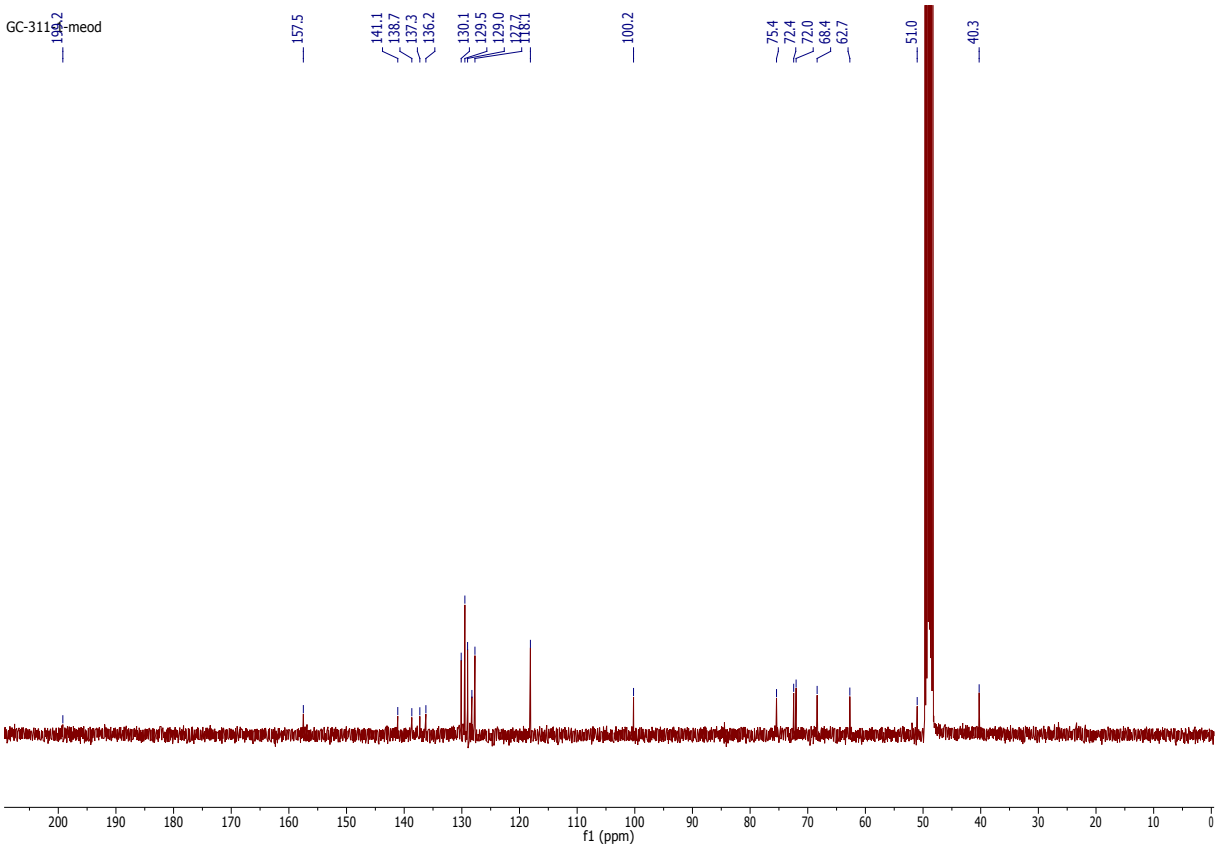


_S_-Benzyl-_N_-(4'-(α-D-mannopyranosyloxybiphenyl))-4-methyldithiocarbamate 32: ^{1}H NMR (400 MHz, CD_3OD):

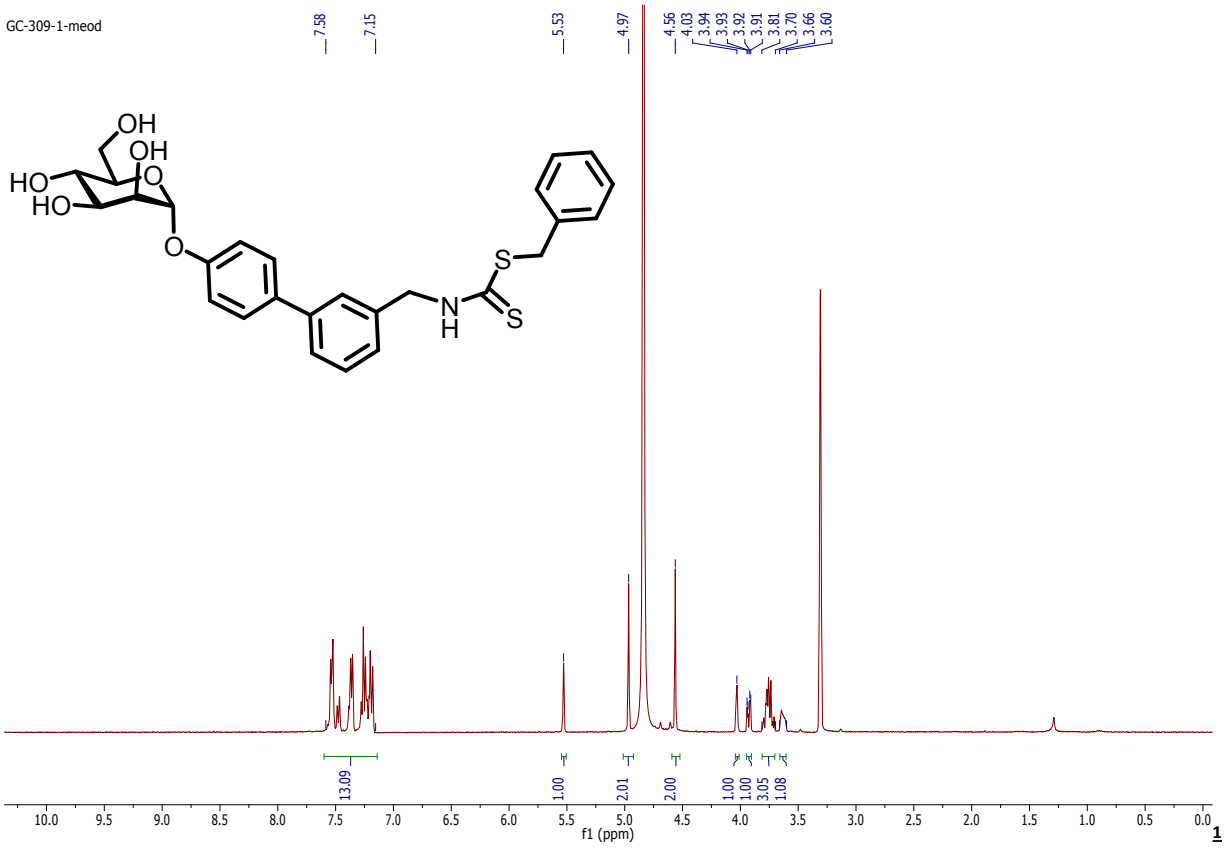


1

^{3}C NMR (100 MHz, CD_3OD):



_S_-Benzyl-_N_-(4'-(α-D-mannopyranosyloxybiphenyl))-3-methyldithiocarbamate 33: ^{1}H NMR (400 MHz, CD_3OD):



^{3}C NMR (100 MHz, CD_3OD):