# **Supporting Information**

# Synthesis of Trisaccharide Repeating Unit of Fucosylated

## **Chondroitin Sulfate**

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**Materials and methods.** All reagents and chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted. Dry tetrahydrofuran (THF) was distilled over sodium. Dichloromethane (DCM) was distilled over calcium hydride. Reactions were generally run under inert atmosphere (argon), by using standard techniques for manipulating air-sensitive compounds. Starting materials and reagents used in reactions were obtained commercially from Aladdin, Acros, Aldrich and were used without purification, unless otherwise indicated. Silica gel (200 - 300 mesh, Qingdao Marine Chemical Ltd., China), hexane and ethyl acetate were used for product purification by flash column chromatography. Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra were recorded on Bruker Avance 400 and 600 spectrometer at 400 and 600MHz. Data for <sup>1</sup>H are reported as follows: chemical shift ( $\delta$  ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m =multiplet), coupling constant in Hz, and integration.Carbon-13 nuclear magnetic resonance (<sup>13</sup>C-NMR) was recorded on BrukerAvance 400 and 600 spectrometer at 100 and 150MHz. HRMS determinations were recorded on a mass spectrometer (UPLC-IT-TOF) with ESI ionization.

**4-Methylphenyl 4,6-O- benzylidene-1-thio-\beta-D-glucopyranoside (14).** BF<sub>3</sub>·Et<sub>2</sub>O (2.5 ml, 20.8 mmol) was added to a mixture of  $\beta$ -D-Glucose pentaacetate **15** (1.79 g, 2.91 mmol) and 4-methoxybenzenethiol (2.4g, 19.5 mmol) in DCM (50 mL) under an argon atmosphere at 0 °C. The temperature was gradually raised to room temperature over 2 h, and the mixture was stirred for 10 h. Then it was quenched with saturated aqueous NaHCO<sub>3</sub>, extracted with DCM, and washed with brine. The organic phase was dried by Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The crude product was recrystallized with hexane/DCM to give 4-Methylphenyl 2,3,4,6-tetra-O-acetyl-1-thio- $\beta$ -D-glucopyranoside (6.5 g. 99%).

Tetra-O-acetyl compound (6.5g, 14.3 mmol) was dissolved in MeOH (43 mL) under argon atmosphere, and Na (66 mg, 2.9 mmol) was added at 0°C. After being warmed to room temperature, the mixture was stirred 2 h and DOWEX 50X8-200 added and stirring continued for a further 30 min. The DOWEX was removed by filtration and the solvent removed *in vacuo* to afford crude product (3.05 g, 98%) as a yellow solid. This compound was suitable for the next step without purification. To a solution the crude product (3.05 g, 10.7 mmol) in acetonitrile (30 mL) was added p-anisaldehyde dimethyl acetal (1.7 ml, 11.8 mmol), *DL*-10-camphorsulfonic acid (621 mg, 2.7 mmol) and the mixture stirred at room temperature overnight. The reaction mixture was quenched with Et<sub>3</sub>N and the solvent concentrated *in vacuo* to afford a yellow oil. Purification by flash chromatography (EtOAc/Petroleum ether =1/1) afforded **14** (3.07 g, 91%) as a white amorphous. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.50 – 7.38 (m, 4H), 7.38 – 7.31 (m, 3H), 7.12 (d,

J = 7.8 Hz, 2H), 5.46 (s, 1H), 4.50 (d, J = 9.7 Hz, 1H), 4.32 (dd, J = 10.5, 4.3 Hz, 1H), 3.79 - 3.64 (m, 2H), 3.49 - 3.32 (m, 4H), 3.16 (d, J = 2.9 Hz, 1H), 2.34 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  138.75, 136.91, 133.59, 129.89, 129.34, 128.39, 127.48, 126.35, 101.88, 88.63, 80.19, 77.29, 74.49, 72.53, 70.44, 68.56, 21.22. HRMS (ESI): m/z calcd for C<sub>20</sub>H<sub>22</sub>O<sub>5</sub>NaS ([M + Na]<sup>+</sup>): 397.1080, found: 397.1081.

**4-Methylphenyl 4,6-O-benzylidene-3-O-(p-methoxybenzyl)-1-thio-β-D-glucopyranoside (13).** To a solution of **14** (3 g, 8.01 mmol) in DCM (30 ml) was added Et<sub>3</sub>N (11.1 ml, 110 mmol), TMSCI (2.88 ml, 32 mmol) at 0°C under argon atmosphere. After being warmed to room temperature, the mixture was stirred 6 h and the solvent concentrated to afford a yellow oil. Purification by flash chromatography (EtOAc/Petroleum ether =1 /10) afforded 4-Methylphenyl 2,3-di-trimethylsily-4,6-O-benzylidene-1-thio-β-D-glucopyranoside (3.96 g, 96%) as a white amorphous.

To a solution of 4-Methylphenyl 2,3-di-trimethylsily-4,6-O-benzylidene-1-thio- $\beta$ -D-glucopyranoside (2.5 g, 4.83 mmol), Anisic aldehyde (0.7 ml, 5.8 mmol), Et<sub>3</sub>SiH (0.92 ml, 5.8 mmol) and freshly dried 3Å molecular sieves (2.5 g) in dichloromethane (43 mL) was added TMSOTf (86.8 µl, 0.48 mmol) at -80°C under argon atmosphere. The mixture was stirred at same temperature for 5 h, TBAF (1M in THF, 9.66 mmol) was added to the mixture, the reaction flask was gradually warmed up to room temperature, and the solution was kept stirring overnight. The whole mixture was filtered through a pad of celite and concentrated *in vacuo*. Purification by flash chromatography (EtOAc/Petroleum ether =1 /3) afforded 1**3** (2.25 g, 95%) as a white amorphous. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.52 – 7.45 (m, 2H), 7.45 – 7.33 (m, 5H), 7.30 – 7.25 (m, 2H), 7.12 (d, J = 7.8 Hz, 2H), 6.87 – 6.79 (m, 2H), 5.55 (s, 1H), 4.86 (d, J = 11.2 Hz, 1H), 4.71 (d, J = 11.2 Hz, 1H), 4.55 (d, J = 9.6 Hz, 1H), 4.37 (dd, J = 10.5, 4.9 Hz, 1H), 3.77 (s, 4H), 3.68 – 3.56 (m, 2H), 3.51 – 3.40 (m, 2H), 2.57 (d, J = 2.3 Hz, 1H), 2.33 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.39, 138.74, 137.25, 133.85, 130.29, 129.85, 129.83, 129.03, 128.29, 127.25, 126.03, 113.91, 101.23, 88.51, 81.23, 81.17, 74.49, 72.05, 70.74, 68.66, 55.28, 21.21. HRMS (ESI): m/z calcd for C<sub>35</sub>H<sub>34</sub>O<sub>7</sub>NaS ([M + Na]<sup>+</sup>): 517.1655, found: 517.1655.

4-Methylphenyl 4,6-O-Benzylidene-2-O-benzoyl-3-O-(p-methoxybenzyl)-1-thio-β-D-glucopyranoside (12). To a solution of compound 13 (2.3 g, 4.65 mmol), Benzoic anhydride (3.15 g, 13.96 mmol), DMAP (281 mg, 2.3 mmol) in DCM (30 ml) was added Et<sub>3</sub>N (2.35 ml, 23.3 mmol) at 0°C. After being warmed to room temperature, the mixture was stirred overnight. The reaction mixture was quenched with H<sub>2</sub>O, extracted with DCM, and washed with brine. The organic phase was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. Purification by flash chromatography (EtOAc/Petroleum ether =1 /5) afforded 12 (3.8 g, 94%) as a white amorphous. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.05 – 7.93 (m, 2H), 7.60 (d, J = 7.7 Hz, 1H), 7.54 – 7.29 (m, 9H), 7.05 (dd, J = 24.2, 8.2 Hz, 4H), 6.63 – 6.52 (m, 2H), 5.59 (s, 1H), 5.22 (dd, J = 10.0, 8.6 Hz, 1H), 4.74 (dd, J = 17.1, 10.5 Hz, 2H), 4.58 (d, J = 11.6 Hz, 1H), 4.41 (dd, J = 10.5, 5.0 Hz, 1H), 3.92 – 3.70 (m, 4H), 3.68 (s, 3H), 3.58 – 3.46 (m, 1H), 2.32 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.98, 159.08, 138.53, 137.21, 133.67, 133.17, 129.93, 129.87, 129.80, 129.66, 129.05, 128.36, 128.30, 128.18, 126.02, 113.54, 101.25, 87.18, 81.46, 78.78, 77.25, 73.86, 72.03, 70.60, 68.62, 55.10, 21.18. HRMS (ESI): m/z calcd for C<sub>35</sub>H<sub>34</sub>O<sub>7</sub>NaS ([M + Na]<sup>+</sup>): 621.1917, found: 621.1917. **4-Methylphenyl 2-O-Benzoyl-3-O-(p-methoxybenzyl)-1-thio-β-D-glucopyranoside (11).** To a solution of compound **12** (500mg, 0.83mmol) in MeOH/MeCN (10 ml/10 ml) was added *p*-Toluenesulfonic acid monohydrate (32 mg, 0.17 mmol). The mixture was stirred at 50°C for 4 h, then it was quenched with Et<sub>3</sub>N and the solvent concentrated *in vacuo*. Purification by flash chromatography (EtOAc/Petroleum ether =1 /4) afforded **11** (402mg, 79%) as a white amorphous. <sup>1</sup>H NMR (400 MHz, Methanol-d<sub>4</sub>) δ 7.95 (d, J = 7.7 Hz, 2H), 7.61 (d, J = 7.5 Hz, 1H), 7.33 (d, J = 7.7 Hz, 2H), 7.04 (dd, J = 19.5, 7.9 Hz, 4H), 6.57 (d, J = 8.1 Hz, 2H), 5.03 (t, J = 9.5 Hz, 1H), 4.83 (s, 1H), 4.73 (d, J = 11.1 Hz, 1H), 4.54 (d, J = 11.1 Hz, 1H), 3.92 (d, J = 12.2 Hz, 1H), 3.79 – 3.66 (m, 2H), 3.61 (d, J = 18.7 Hz, 4H), 3.49 – 3.38 (m, 1H), 2.27 (s, 3H). <sup>13</sup>C NMR (100 MHz, Methanol-d<sub>4</sub>) δ 165.43, 159.16, 137.66, 133.06, 132.18, 130.16, 129.88, 129.49, 129.39, 129.31, 129.20, 128.20, 113.05, 86.37, 83.43, 80.91, 74.28, 72.23, 70.41, 61.25, 54.09, 19.73. HRMS (ESI): m/z calcd for C<sub>28</sub>H<sub>30</sub>O<sub>7</sub>NaS ([M + Na]<sup>+</sup>): 533.1604, found: 533.1604.

Benzyl (p-Methylphenyl-2-O-Benzoyl-3-O-(p-methoxybenzyl) -1-thio-D -glucopyranoside)urinate (10). To a solution of 11 (800 mg, 1.57 mmol) in DCM/H<sub>2</sub>O (10 ml/5 ml) was added TEMPO (48 mg, 0.313 mmol), BAIB (1256 mg, 3.14 mmol). The mixture was stirred at room temperature for 30min, then it was quenched with saturated aqueous Na<sub>2</sub>SO<sub>3</sub>, extracted with DCM, and washed with brine. The organic phase was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated in vacuo to afford a yellow solid. This compound was suitable for the next step without purification. The crude acid was dissolved in acetone (10 mL) and treated with BnBr (372  $\mu$ L, 3.14 mmol), K<sub>2</sub>CO<sub>3</sub> (325mg, 2.36 mmol), and Et<sub>3</sub>N (361  $\mu$ l, 1.89 mmol) at 55 °C under argon atmosphere. After complete disappearance of the acid, the mixture was neutralized with 1 N HCl and extracted with DCM. The organic phase was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated in vacuo. Purification by flash chromatography (EtOAc/Petroleum ether =1 /3) afforded 10 (676mg, 68%) as a light yellow amorphous. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.06 – 7.89 (m, 2H), 7.59 (d, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 3H), 7.41 – 7.29 (m, 6H), 7.06 (d, J = 8.3 Hz, 2H), 6.96 (d, J = 7.8 Hz, 2H), 6.67 – 6.58 (m, 2H), 5.27 (s, 2H), 5.17 (t, J = 9.6 Hz, 1H), 4.71 (d, J = 10.1 Hz, 1H), 4.69 – 4.57 (m, 2H), 4.05 – 3.94 (m, 2H), 3.91 (s, 1H), 3.69 (s, 4H), 3.03 (d, J = 2.7 Hz, 1H), 2.29 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.72, 165.03, 159.20, 138.51, 134.96, 133.84, 133.24, 129.90, 129.82, 129.78, 129.76, 129.55, 128.70, 128.59, 128.42, 128.31, 128.07, 113.70, 87.08, 81.83, 77.75, 74.39, 71.98, 71.46, 67.56, 55.13, 21.18. HRMS (ESI): m/z calcd for C<sub>35</sub>H<sub>34</sub>O<sub>8</sub>NaS ([M + Na]<sup>+</sup>): 637.1867, found: 637.1869.

#### Benzyl (p-Methylphenyl-2-O-Benzoyl-3-O-(p-methoxybenzyl)-4-levulinyl-1-thio-D

glucopyranoside)urinate (7). To a solution of 10 (676 mg, 1.07 mmol) in DCM (7 ml) was added EDCI (1024 mg, 5.36 mmol), DMAP (13 mg, 0.11 mmol) and Levulinic acid (330  $\mu$ l, 3.21 mmol) at room temperature under argon atmosphere. The mixture was stirred for 10h, then H<sub>2</sub>O was added and extracted with DCM. The organic phase was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. Purification by flash chromatography (EtOAc/Petroleum ether =1 /3) afforded 7 (823 mg, 93%) as a white amorphous. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.06 – 7.96 (m, 2H), 7.59 (d, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 3H), 7.41 – 7.29 (m, 6H), 7.00 (t, J = 8.7 Hz, 4H), 6.67 – 6.59 (m, 2H), 5.30 – 5.12 (m, 4H), 4.72 (d, J = 9.9 Hz, 1H), 4.58

- 4.41 (m, 2H), 4.04 (d, J = 9.9 Hz, 1H), 3.87 (d, J = 9.1 Hz, 1H), 3.68 (s, 3H), 2.65 - 2.48 (m, 2H), 2.45 (dd, J = 8.3, 6.5 Hz, 1H), 2.39 (t, J = 6.8 Hz, 1H), 2.12 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 206.03, 171.18, 166.82, 164.72, 159.15, 138.76, 135.07, 134.35, 133.26, 129.87, 129.74, 129.70, 129.59, 129.49, 128.64, 128.60, 128.51, 128.41, 127.20, 113.57, 86.23, 79.96, 76.46, 73.87, 71.41, 71.19, 67.64, 55.09, 37.67, 29.78, 27.72, 21.19. HRMS (ESI): m/z calcd for  $C_{10}H_{40}O_{10}NaS$  ([M + Na]<sup>+</sup>): 735.2234, found: 735.2233.

**3,4,6-tri-O-acetyl-2-azido-2-deoxy-β-D-galactopyranosyl acetate Acetyl (20)**. To a solution of **21** (5 g, 23.25 mmol) in MeOH(100 ml) was added K<sub>2</sub>CO<sub>3</sub>(8 g, 58.13 mmol), CuSO<sub>4</sub>·5H<sub>2</sub>O (42 mg, 0.23 mmol) and imidazole-1-sulfonyl azide hydrochloride(6 g, 34.88 mmol) at room temperature under argon atmosphere. The mixture was stirred for 3h and the solvent was concentrated *in vacuo* to afford a yellow solid, then pyridine (40 ml), Ac<sub>2</sub>O(35 ml) was added. The mixture was stirred at room temperature overnight and the solvent was concentrated *in vacuo*. Purification by flash chromatography (EtOAc/Petroleum ether =1 /2) afforded **20** (6.96 g, 81%, α/β = 1/7) as a white amorphous. β-isomer-<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.55 (d, J = 8.6 Hz, 1H), 5.38 (dd, J = 3.4, 1.1 Hz, 1H), 4.90 (dd, J = 10.8, 3.4 Hz, 1H), 4.17 – 4.06 (m, 2H), 4.05 – 3.97 (m, 1H), 3.84 (dd, J = 10.8, 8.6 Hz, 1H), 2.21 (s, 3H), 2.17 (s, 3H), 2.06 (d, J = 11.2 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl3) δ 170.33, 169.94, 169.62, 168.57, 92.84, 71.70, 71.27, 66.15, 60.94, 59.64, 20.88, 20.63, 20.59, 20.56. HRMS (ESI): m/z calcd for C<sub>14</sub>H<sub>19</sub>N<sub>3</sub>O<sub>9</sub>Na ([M + Na]<sup>+</sup>): 396.1014, found: 396.1015.

**4-Methoxyphenyl 3,4,5-tri-O-acetyl-2-deoxy-2-azido-β-D-galactopyranoside (19)**. To a solution of compound **20** (4.48 g, 12 mmol), 4-Methoxyphenoll (2.98 g, 24 mmol) in DCM (60 ml) was add TfOH (0.21 ml, 2.4 mmol) at 0°C under Argon atmosphere. The temperature was gradually raised to room temperature over 1 h, and the mixture was stirred for 16h. Then it was quenched with Et<sub>3</sub>N and concentrated *in vacuo*. Purification by flash chromatography (EtOAc/Petroleum ether =1 /5) afforded **19** (2.3 g, 95%,  $\alpha/\beta$  = 1.1/1) as a light yellow liquid.  $\alpha/\beta$  = 1.1/1, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.09 – 6.98 (m, 4H), 6.88 – 6.79 (m, 4H), 5.61 – 5.55 (m, 1H), 5.53 (t, *J* = 4.1 Hz, 2H,α-H'-1, α-H'-4), 5.38 (d, *J* = 2.0 Hz, 1H, β-H'-4), 4.85 (dd, *J* = 10.9, 3.3 Hz, 1H), 4.81 (d, *J* = 8.1 Hz, 1H, β-H'-1), 4.44 – 4.36 (m, 1H), 4.26 – 4.16 (m, 1H), 4.17 – 4.04 (m, 5H), 4.03 – 3.90 (m, 2H), 3.79 (s, 3H), 3.78 (s, 4H), 2.18 (s, 3H), 2.17 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 1.99 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.33, 170.08, 170.02, 169.93, 169.84, 169.79, 169.61, 168.56, 155.91, 155.64, 150.80, 150.20, 118.71, 118.23, 114.69, 114.60, 101.90, 97.95, 92.84, 90.39, 71.70, 71.28, 70.93, 68.74, 68.65, 68.16, 67.50, 67.39, 66.83, 66.21, 66.15, 61.53, 61.29, 61.08, 60.94, 60.64, 59.64, 57.37, 56.81, 55.65, 20.92, 20.88, 20.68, 20.66, 20.63. HRMS (ESI): m/z calcd for C<sub>19</sub>H<sub>23</sub>N<sub>3</sub>O<sub>9</sub>Na ([M + Na]<sup>+</sup>): 460.1327, found: 460.1326.

**4-Methoxyphenyl 4,6-O-benzylidene-2-deoxy-2-azido-β-D-galactopyranoside (8).** Compound **19** (2.48 g, 5.45 mmol) was dissolved in MeOH (27 mL) under argon atmosphere, and Na (25 mg, 1.1 mmol) was added at 0 °C. After being warmed to room temperature, the mixture was stirred 1 h and DOWEX 50X8-200 added and stirring continued for a further 30 min. The DOWEX was removed by filtration and the solvent removed *in vacuo* to afford triol (1.27 g, 98%) as a yellow solid. This compound was suitable for

the next step without purification. Then a mixture of triol, p-anisaldehyde dimethyl acetal (1.6 ml, 10.9 mmol), *p*-toluenesulfonic acid (275 mg, 1.6 mmol) in acetonitrile (30 mL) was stirred at 50°C for 8h. The reaction mixture was quenched with Et<sub>3</sub>N and the solvent concentrated *in vacuo* to afford a yellow oil. Purification by flash chromatography (EtOAc/Petroleum ether =1/1) afforded **8** (831 mg, 45%, β-isomer), and α-isomer (923mg, 50%) as a white amorphous. β-isomer- <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.56 – 7.47 (m, 2H), 7.38 (dd, J = 5.1, 2.0 Hz, 3H), 7.07 (d, J = 9.0 Hz, 2H), 6.83 (d, J = 9.0 Hz, 2H), 5.57 (s, 1H), 4.74 (d, J = 8.0 Hz, 1H), 4.36 (dd, J = 12.5, 1.6 Hz, 1H), 4.19 (d, J = 3.7 Hz, 1H), 4.08 (dd, J = 12.5, 1.9 Hz, 1H), 3.87 (dd, J = 10.2, 8.0 Hz, 1H), 3.77 (s, 3H), 3.60 (dq, J = 7.4, 3.5 Hz, 1H), 3.53 – 3.47 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.70, 151.09, 137.25, 129.45, 128.35, 126.44, 118.92, 114.55, 101.82, 101.48, 74.36, 71.36, 68.95, 66.65, 63.76, 55.67. HRMS (ESI): m/z calcd for C<sub>20</sub>H<sub>21</sub>N<sub>3</sub>O<sub>6</sub>Na ([M + Na]<sup>+</sup>):422.1323, found: 422.1320.

**4-Methylphenyl 2,3,4-tri-O-acetyl-1-thio-β-L-fucopyranoside (23).** L-Fucose (1 g, 6.10 mmol) was dissolved in Ac<sub>2</sub>O/ pyridine (5 ml/10 ml). The mixture was stirred at room temperature for 8h, then concentrated *in vacuo* to afford a yellow liquid (2.02 g, 100%), which was used in the next step without further purification. To a solution of this crude product, 4-methoxybenzenethiol (1.5 g, 12.16 mmol) in DCM (30 ml) was add BF<sub>3</sub>·Et<sub>2</sub>O (1.57 ml, 12.16 mmol) at 0°C under argon atmosphere. The temperature was gradually raised to room temperature over 1 h, and the mixture was stirred overnight. Then it was quenched with saturated aqueous NaHCO<sub>3</sub>, extracted with DCM, and washed with brine. The organic phase was dried by Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. Purification by flash chromatography (EtOAc/Petroleum ether =1 /6) afforded **23** (2.3 g, 95%) as a white amorphous. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.47 – 7.35 (m, 2H), 7.13 (d, J = 7.8 Hz, 2H), 5.29 – 5.14 (m, 2H), 5.04 (dd, J = 9.9, 3.4 Hz, 1H), 4.64 (d, J = 9.9 Hz, 1H), 3.86 – 3.76 (m, 1H), 2.34 (s, 3H), 2.14 (s, 3H), 2.09 (s, 3H), 1.97 (s, 3H), 1.23 (d, J = 6.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.64, 170.16, 169.51, 138.22, 132.91, 129.73, 129.63, 129.07, 86.85, 73.11, 72.46, 70.35, 67.40, 21.16, 20.91, 20.68, 20.65, 16.48. HRMS (ESI): m/z calcd for C<sub>19</sub>H<sub>24</sub>O<sub>7</sub>NaS ([M + Na]<sup>+</sup>): 419.1135, found: 419.1132.

**4-Methylphenyl 3-O-benzyl-1-thio-β-L-fucopyranoside (22).** To a solution of **23** (2.1 g, 5.35 mmol) in MeOH (100 ml) was added Na (25 mg, 1.07 mmol) at 0 °C under argon atmosphere. After being warmed to room temperature, the mixture was stirred 2 h and DOWEX 50X8-200 added and stirring continued for a further 30 min. The DOWEX was removed by filtration and the solvent removed *in vacuo* to afford triol (1.45 g, 100%) as a yellow solid. This compound was suitable for the next step without purification. Then a solution of triol, Bu<sub>2</sub>SnO(1.84 g, 7.4 mmol), TBAB(2.5 g, 7.88 mmol), BnBr(0.94 ml, 7.88 mol) in toluene was reflux at 120°C overnight and the solvent was concentrated *in vacuo*. Purification by flash chromatography (EtOAc/Petroleum ether =1 /3) afforded **22** (1.28 g, 68%) as a light yellow amorphous. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.51 – 7.42 (m, 2H), 7.40 – 7.27 (m, 4H), 7.11 (d, J = 7.9 Hz, 2H), 4.73 (d, J = 2.4 Hz, 2H), 4.41 (d, J = 9.7 Hz, 1H), 3.79 (d, J = 3.2 Hz, 1H), 3.70 (td, J = 9.4, 1.9 Hz, 1H), 3.58 (q, J = 6.5 Hz, 1H), 3.44 (dd, J = 9.0, 3.3 Hz, 1H), 2.48 (d, J = 2.4 Hz, 1H), 2.33 (s, 3H), 2.22 (d, J = 3.3 Hz, 1H), 1.36 (d, J = 6.5 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 138.27, 137.69, 133.29, 129.74, 128.62, 128.16, 128.09, 127.95,

88.58, 81.73, 74.63, 72.04, 69.34, 68.59, 21.17, 16.77. HRMS (ESI): m/z calcd for C<sub>20</sub>H<sub>24</sub>O<sub>4</sub>NaS ([M + Na]<sup>+</sup>): 383.1288, found: 383.1286.

**4-Methylphenyl 2,4-di-O-Allyloxycarbonyl-3-O-benzyl-1-thio-β-L-fucopyranoside (9)**. To a solution of compound **22** (1.05 g, 2.92 mmol) in DCM (20 ml) was added Allyl chloroformate (1.25 ml, 11.7 mmol), DMAP (2.14 g, 17.5 mmol) at 0 °C under Ar. After being warmed to room temperature, the mixture was stirred 4 h and the solvent was concentrated *in vacuo*. Purification by flash chromatography (EtOAc/Petroleum ether =1 /5) afforded **9** (1.4 g, 86%) as a white amorphous. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41 (d, J = 8.1 Hz, 2H), 7.28 (dq, J = 6.7, 4.1, 2.8 Hz, 4H), 7.09 (d, J = 7.8 Hz, 2H), 6.05 – 5.79 (m, 2H), 5.43 – 5.31 (m, 2H), 5.26 (ddd, J = 15.4, 10.4, 1.5 Hz, 2H), 5.14 (d, J = 3.3 Hz, 1H), 4.97 (t, J = 9.7 Hz, 1H), 4.78 – 4.54 (m, 6H), 4.48 (d, J = 12.0 Hz, 1H), 3.72 – 3.56 (m, 2H), 2.32 (s, 3H), 1.29 (d, J = 6.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  155.11, 154.04, 138.09, 137.36, 133.14, 131.49, 131.36, 129.59, 129.15, 128.32, 127.79, 127.71, 118.88, 118.66, 86.72, 78.19, 77.25, 73.46, 73.18, 73.07, 71.50, 68.79, 68.73, 21.17, 16.58. HRMS (ESI): m/z calcd for C<sub>28</sub>H<sub>32</sub>O<sub>8</sub>NaS ([M + Na]<sup>+</sup>): 551.1710, found: 551.1712.

#### 4-Methoxyphenyl (Benzyl 2-O-Benzoyl-3-O-(p-methoxybenzyl)-4-O-levulinyl-

 $\beta$ -D-glucopyranosyluronate)-(1 $\rightarrow$ 3)-2-azido-4,6-O-benzylidene- $\beta$ -D-galactopyranoside (6). A mixture of the thioglycoside 7 (280 mg, 0.39 mmol) and acceptor 9 (130 mg, 0.33 mmol) in dry DCM (5 mL) was added to a reaction flask containing freshly dried 4 Å molecular sieves under argon atmosphere. The mixture was stirred at room temperature for 1 h, and the solution was cooled to -75 °C. NIS (176 mg, 0.78 mmol) and TfOH (7 µL, 0.078 mmol) were added to the reaction flask, and the mixture was gradually warmed up to -45 °C. The resulting solution was kept stirring for 0.5 h, and Et<sub>3</sub>N was added to quench the reaction. The whole mixture was filtered through Celite followed by washing with DCM, and the filtrate was sequentially washed with 10% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>(aq) and brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to get the yellow liquid. Purification of this liquid by flash chromatography (EtOAc/Petroleum ether =1/1) afforded 6 (241 mg, 75%) as a white amorphous. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.06 – 7.97 (m, 2H), 7.56 (d, J = 7.5 Hz, 1H), 7.52 - 7.28 (m, 13H), 7.11 - 7.04 (m, 2H), 7.02 - 6.94 (m, 2H), 6.84 - 6.75 (m, 2H), 6.70 - 6.60 (m, 2H), 5.47 -5.32 (m, 3H), 5.22 – 5.07 (m, 2H), 5.02 (d, J = 7.2 Hz, 1H), 4.69 (d, J = 8.1 Hz, 1H), 4.56 (q, J = 11.6 Hz, 2H), 4.33 – 4.20 (m, 2H), 4.11 (d, J = 10.0 Hz, 1H), 4.02 – 3.86 (m, 3H), 3.72 (d, J = 24.5 Hz, 7H), 3.55 (dd, J = 10.6, 3.4 Hz, 1H), 3.37 (s, 1H), 2.53 (dt, J = 16.0, 6.6 Hz, 2H), 2.41 – 2.25 (m, 2H), 2.12 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 206.09, 177.34, 171.34, 167.30, 164.83, 159.16, 155.53, 151.09, 137.58, 134.95, 133.22, 129.76, 129.60, 129.53, 128.81, 128.71, 128.67, 128.44, 128.00, 126.29, 118.73, 114.46, 113.61, 102.16, 101.65, 100.57, 78.44, 77.51, 77.37, 74.60, 73.09, 72.82, 72.64, 70.91, 68.67, 67.76, 66.72, 61.59, 55.63, 55.12, 37.62, 29.78, 27.71. HRMS (ESI): m/z calcd for  $C_{53}H_{53}N_3O_{16}Na$  ([M + Na]<sup>+</sup>): 1010.3318, found: 1010.3319

4-Methoxyphenyl (Benzyl 2-O-Benzoyl-4-O-levulinyl- $\beta$ -D-glucopyranosyluronate)- $(1\rightarrow 3)$ -

**2-azido-4,6-O-benzylidene-β-D-galactopyranoside (5).** To a solution of compound **6** (230 mg, 0.233 mmol) in DCM /H<sub>2</sub>O (5 ml/1.25 ml) was add DDQ (106 mg, 0.466 mmol) at room temperature. The mixture was stirred for 12h. Then it was quenched with saturated aqueous NaHCO<sub>3</sub>, extracted with CH<sub>2</sub>Cl<sub>2</sub>, and washed with brine. The organic phase was dried by Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. Purification by flash chromatography (EtOAc/Petroleum ether =1 /1) afforded **5** (172 mg, 85%) as a light yellow amorphous. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.13 – 8.03 (m, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.49 – 7.41 (m, 4H), 7.39 – 7.28 (m, 8H), 7.06 – 6.96 (m, 2H), 6.84 – 6.74 (m, 2H), 5.41 (s, 1H), 5.29 (t, J = 9.5 Hz, 1H), 5.24 – 5.13 (m, 3H), 5.04 (d, J = 7.2 Hz, 1H), 4.73 (d, J = 8.0 Hz, 1H), 4.32 – 4.21 (m, 2H), 4.12 (d, J = 10.1 Hz, 1H), 4.02 – 3.84 (m, 3H), 3.75 (s, 3H), 3.57 (dd, J = 10.6, 3.4 Hz, 1H), 3.44 (d, J = 5.7 Hz, 1H), 3.38 (s, 1H), 2.63 (dt, J = 9.6, 6.6 Hz, 2H), 2.51 – 2.41 (m, 1H), 2.36 – 2.25 (m, 1H), 2.12 (s, 3H), 1.81 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 206.94, 171.91, 167.19, 166.00, 155.59, 151.07, 137.54, 134.94, 133.44, 129.86, 129.32, 128.88, 128.86, 128.76, 128.71, 128.53, 128.08, 126.33, 118.76, 114.50, 102.15, 101.54, 100.74, 77.70, 77.26, 74.67, 74.14, 73.27, 72.28, 72.07, 68.69, 67.78, 66.67, 61.64, 55.64, 38.02, 29.75, 27.81. HRMS (ESI): m/z calcd for C<sub>45</sub>H<sub>45</sub>N<sub>3</sub>O<sub>15</sub>Na ([M + Na]<sup>+</sup>): 890.2743, found: 890.2744

## 4-Methoxyphenyl (2,4-di-O-Allyloxycarbonyl-3-O-benzyl-1-thio-α-L-fucopyranosyl)-(1→3)-(Benzyl 2-O-Benzoyl-4-O-levulinyl-β-D-glucopyranosyluronate)-(1→3)-2-azido-4,6-O-benzylidene-β-D-

galactopyranoside (4). A mixture of the thioglycoside 9 (194 mg, 0.37 mmol) and acceptor 5 (246 mg, 0.28 mmol) in dry DCM (5 mL) was added to a reaction flask containing freshly dried 4 Å molecular sieves under Argon atmosphere. The mixture was stirred at room temperature for 1 h, and the solution was cooled to -50 °C. NIS (165 mg, 0.74 mmol) and TfOH (6  $\mu$ L, 0.074 mmol) were added to the reaction flask, and the mixture was gradually warmed up to -20 °C. The resulting solution was kept stirring for 0.5 h, and  $Et_3N$  was added to quench the reaction. The whole mixture was filtered through Celite followed by washing with DCM, and the filtrate was sequentially washed with 10% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>(aq) and brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to get the yellow liquid. Purification of this liquid by flash chromatography (EtOAc/Petroleum ether =1/1) afforded **4** (298 mg, 83%) as a white amorphous. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.04 (d, J = 7.8 Hz, 2H), 7.66 - 7.16 (m, 16H), 6.99 (d, J = 8.6 Hz, 2H), 6.78 (d, J = 8.6 Hz, 2H), 5.81 (ddq, J = 27.4, 10.5, 5.5 Hz, 1H), 5.50 - 5.05 (m, 9H), 5.01 (d, J = 7.4 Hz, 1H), 4.80 (dd, J = 10.5, 3.7 Hz, 1H), 4.73 - 4.51 (m, 4H), 4.41 (t, J = 9.9 Hz, 3H), 4.26 (dd, J = 8.3, 4.6 Hz, 3H), 4.15 – 3.87 (m, 5H), 3.75 (s, 3H), 3.52 (dd, J = 10.6, 3.4 Hz, 1H), 3.37 (s, 1H), 2.62 (t, J = 7.4 Hz, 1H), 2.56 – 2.37 (m, 2H), 2.35 – 2.21 (m, 1H), 2.12 (s, 3H), 1.14 (d, J = 6.6 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 205.97, 171.53, 167.10, 164.92, 155.56, 155.09, 154.42, 151.08, 138.01, 137.59, 134.91, 133.10, 131.72, 131.43, 129.80, 129.61, 128.86, 128.75, 128.68, 128.37, 128.13, 128.01, 127.78, 127.46, 126.26, 118.72, 118.53, 114.46, 102.25, 101.33, 100.52, 97.09, 77.66, 75.23, 74.61, 73.60, 73.23, 72.78, 72.53, 72.41, 70.68, 68.61, 68.43, 67.86, 66.70, 65.67, 61.57, 55.63, 37.48, 29.79, 27.67, 15.71. HRMS (ESI): m/z calcd for  $C_{66}H_{69}N_3O_{23}Na$  ([M + Na]<sup>+</sup>): 1294.4214, found: 1298.4212

4-Methoxyphenyl (2,4-di-O-Allyloxycarbonyl-3-O-benzyl-1-thio- $\alpha$ -L-fucopyranosyl)-(1 $\rightarrow$ 3)-(Benzyl 2-O-Benzoyl-4-O-levulinyl- $\beta$ -D-glucopyranosyluronate)-(1 $\rightarrow$ 3)-2-acetylamino- $\beta$ -D-galactopyranoside (3).

To a solution of compound 4 (126 mg, 0.099 mmol) in Pyridine /H<sub>2</sub>O (2.4 ml/600  $\mu$ l) was add Et<sub>3</sub>N (137 μl, 0.99 mmol) and 1,3-Dimercaptopropane(149 μl, 1.487 mmol) at room temperature. The mixture was stirred for 1h and the solvent was concentrated in vacuo to afford the crude product. Then Ac<sub>2</sub>O (40  $\mu$ l), Et<sub>3</sub>N (200 μl) was add to a solution of this crude product in DCM (2 ml) at room temperature. The mixture was stirred for 3h and MeOH was added to quench the reaction. The solvent was concentrated *in vacuo* and AcOH(2 ml),  $H_2O(0.5 ml)$  was added, the mixture was stirred at 80° C for 3h. The solvent was concentrated under reduced pressure to get the yellow liquid. Purification of this liquid by flash chromatography (DCM/MeOH =60/1) afforded 3 (83 mg, 70%) as a yellow amorphous. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.03 (d, J = 7.7 Hz, 2H), 7.58 (d, J = 7.4 Hz, 1H), 7.51 – 7.33 (m, 7H), 7.30 – 7.15 (m, 5H), 6.90 - 6.81 (m, 2H), 6.79 - 6.68 (m, 2H), 5.84 (ddd, J = 16.7, 10.8, 5.5 Hz, 2H), 5.60 (d, J = 6.7 Hz, 1H), 5.49 (d, J = 8.3 Hz, 1H), 5.40 (t, J = 8.3 Hz, 1H), 5.34 - 5.06 (m, 8H), 4.84 - 4.77 (m, 2H), 4.72 - 4.49 (m, 4H), 4.41 - 4.22 (m, 3H), 4.22 - 4.03 (m, 3H), 4.01 - 3.85 (m, 2H), 3.73 (s, 4H), 3.62 (d, J = 5.9 Hz, 1H), 3.36 (dt, J = 10.3, 7.3 Hz, 1H), 3.02 (s, 1H), 2.75 – 2.59 (m, 1H), 2.45 (dt, J = 11.5, 7.1 Hz, 2H), 2.26 – 2.16 (m, 1H), 2.12 (s, 3H), 1.26 (d, J = 4.3 Hz, 3H), 1.18 (d, J = 6.5 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 206.04, 177.26, 171.50, 171.33, 166.84, 155.33, 155.08, 154.21, 151.08, 137.95, 134.66, 133.64, 131.62, 131.40, 129.89, 129.24, 128.75, 128.71, 128.68, 128.10, 127.73, 127.45, 118.72, 118.60, 114.50, 101.11, 98.11, 96.56, 78.21, 77.23, 75.91, 75.09, 73.99, 73.52, 73.03, 72.86, 72.14, 70.18, 68.62, 68.50, 68.44, 68.03, 65.63, 62.44, 60.42, 55.61, 54.59, 37.47, 27.64, 22.79, 21.07, 15.76, 14.21. HRMS (ESI): m/z calcd for C<sub>61</sub>H<sub>69</sub>NO<sub>24</sub>Na ([M + Na]<sup>+</sup>): 1222.4102, found: 1222.4106

#### 4-Methoxyphenyl (3-O-benzyl-1-thio- $\alpha$ -L-fucopyranosyl)-(1 $\rightarrow$ 3)-(Benzyl

#### -2-O-Benzoyl-4-O-levulinyl-β-D-glucopyranosyluronate)-(1→3)-2-acetylamino-β-D-galactopyranoside

(3). To a solution of compound 3 (60 mg, 0.05 mmol) in THF (1 ml) was add PPh<sub>3</sub> (8 mg, 0.03 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (7 mg, 0.005 mmol), Ammonium formate (12 mg,0.2 mmol) at room temperature under argon atmosphere. The mixture was stirred for 3h and the whole mixture was filtered through Celite and concentrated *in vacuo*. Purification of this liquid by flash chromatography (DCM/MeOH =50/1) afforded 2 (45 mg, 86%) as a light yellow amorphous. <sup>1</sup>H NMR (400 MHz, DMSO-d6)  $\delta$  7.95 (d, J = 7.8 Hz, 2H), 7.61 (d, J = 7.3 Hz, 1H), 7.51 (dt, J = 15.2, 8.4 Hz, 3H), 7.41 (d, J = 4.3 Hz, 5H), 7.33 – 7.18 (m, 5H), 6.91 – 6.74 (m, 4H), 5.23 – 5.11 (m, 2H), 5.12 – 4.95 (m, 3H), 4.76 (dd, J = 21.4, 5.7 Hz, 3H), 4.54 – 4.31 (m, 5H), 4.21 (dd, J = 8.1, 4.5 Hz, 2H), 4.04 – 3.85 (m, 2H), 3.82 (d, J = 6.5 Hz, 2H), 3.69 (d, J = 4.7 Hz, 4H), 3.60 – 3.43 (m, 5H), 2.64 – 2.53 (m, 2H), 2.43 – 2.29 (m, 1H), 2.28 – 2.16 (m, 1H), 2.08 (s, 3H), 1.20 (s, 3H), 1.03 (d, J = 6.5 Hz, 3H). <sup>13</sup>C NMR (100 MHz, DMSO)  $\delta$  206.81, 171.78, 169.32, 167.55, 164.58, 154.96, 152.10, 139.73, 135.60, 133.26, 130.52, 130.10, 128.98, 128.85, 128.66, 128.34, 127.84, 127.43, 118.43, 114.89, 101.34, 101.20, 100.82, 80.36, 78.11, 77.06, 75.73, 73.25, 71.72, 71.04, 68.91, 67.39, 60.98, 55.80, 50.70, 37.41, 30.07, 27.86, 22.61, 16.75. HRMS (ESI): m/z calcd for C<sub>53</sub>H<sub>60</sub>NO<sub>20</sub> ([M - H]-): 1030.3714, found: 1030.3718

### 4-Methoxyphenyl (3,6-di-O-sulfonato-α-L-fucopyranosyl)-(1→3)-(β-D-gluco-

**pyranosyluronate**)-(1→3)-4,6-di-O-sulfonato-2-acetylamino-β-D-galactopyranoside (1). A solution of compound 2 (13 mg, 0.013 mmol) and SO<sub>3</sub>•Me<sub>3</sub>N (70 mg, 0.504 mmol) in dry DMF (0.6 ml) were kept stirring at 55 °C under Argon atmosphere for 30h. It was quenched with MeOH, concentrated to afford a yellow solid. This compound was suitable for the next step without purification.

The crude product was dissolved in THF (1 ml) at 0 °C. To this were added 1 M aq. LiOH (160  $\mu$ l) and 30% H<sub>2</sub>O<sub>2</sub> (350  $\mu$ l). The reaction stirred at 0 °C for 1 h and at room temperature for 24 h. At this time, 4 M NaOH (300  $\mu$ l) and MeOH (600  $\mu$ l) were added and the reaction stirred for another 24 h. It was then neutralized with AcOH, filtered, and lyophilized to afford a yellow solid. This compound was suitable for the next step without purification.

A solution of crude sodium salt in H<sub>2</sub>O/MeOH (4.5 mL/0.5 mL) was hydrogenated in the presence of Pd/C 10% (28 mg) at room temperature. After 24 h, the suspension was filtered through Celite, concentrated. The product was purified by Sephadex G-25 (100% H<sub>2</sub>O) and lyophilized to afford **1** as a white amorphous (9mg, 69% over three steps). <sup>1</sup>H NMR (600 MHz, D<sub>2</sub>O)  $\delta$  7.10 (d, J = 9.1 Hz, 2H, ArH), 6.99 (d, J = 9.1 Hz, 2H, ArH), 5.59 (d, J = 3.8 Hz, 1H, H-1"), 5.05 (d, J = 8.5 Hz, 1H, H-1), 4.91 (d, J = 3.0 Hz, 1H, H-4"), 4.71 – 4.66 (m, 1H, H-5), 4.54 (dd, J = 12.9, 6.7 Hz, 2H, H-1',H-5"), 4.46 (dd, J = 10.6, 3.8 Hz, 1H, H-2"), 4.38 – 4.33 (m, 2H,H-5',H-6<sub>a</sub>), 4.33 – 4.29 (m, 1H,H-4), 4.25 (d, J = 7.4 Hz, 2H, H-6<sub>b</sub>,H-3'), 4.21 – 4.13 (m, 3H, H-3", H-4',H-5), 3.82 (d, J = 1.0 Hz, 3H, OMe), 3.70 (d, J = 2.9 Hz, 1H, H-2), 3.63 (t, J = 6.1 Hz, 2H, H-2',H-3), 2.06 – 2.02 (m, 3H, NHAc), 1.26 (d, J = 6.6 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (150 MHz, D<sub>2</sub>O)  $\delta$  175.69, 175.03, 154.80, 151.18, 118.40, 118.33, 115.03, 103.46, 100.65, 96.76, 81.61, 80.86, 76.91, 75.88, 75.16, 75.08, 73.01, 72.59, 70.07, 67.79, 66.41, 66.12, 55.77, 51.60, 22.24, 15.63. HRMS (ESI): m/z calcd for C<sub>27</sub>H<sub>34</sub>NO<sub>29</sub>Na<sub>7</sub>S<sub>4</sub> ([M + 2Na]<sup>2+</sup>): 562.4686, found: 562.4683.



<sup>13</sup>C NMR (100 MHz, CDCl3) of compound 14



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 13

#### (5) 5013



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 12



<sup>13</sup>C NMR (100 MHz, Methanol-d4) of compound 11





<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 10

# P. 100 Sector 10 Sector



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 7





<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 22



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 9



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 20



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 19



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 8

8.0034 8.0034 8.0015 8.



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 6



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 5



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 4

8 (202) 8 (202) 8 (202) 1 (382) 1 (



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 3



<sup>1</sup>H NMR(400MHz, CDCl<sub>3</sub>) of compound 2 (slightly soluble in CDCl<sub>3</sub>)

-53005 -5305 -5305 -5306 -530





<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of compound 2



<sup>13</sup>H NMR (150 MHz, D<sub>2</sub>O) of compound 1



DEPT (150 MHz, D<sub>2</sub>O) of compound 1



**COSY of compound 1** 



**HSQC of compound 1** 





HRMS (ESI) of compound 1