

# Supporting Information

## Total Syntheses of Resin Glycosides Murucoidin IV and V

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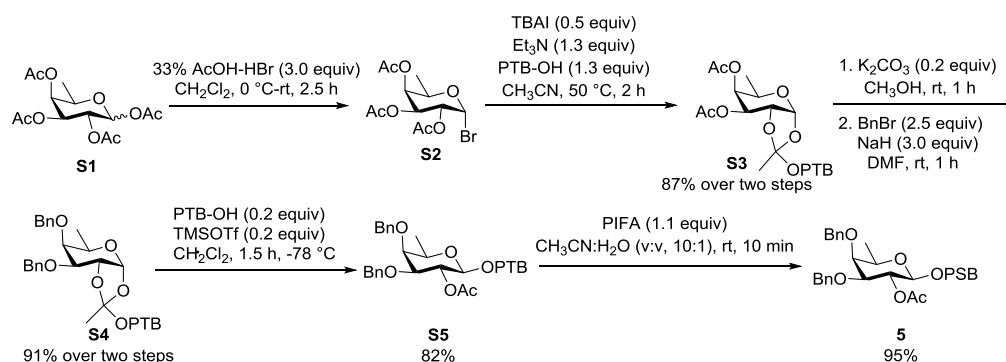
## 1. General Comments

All reactions were monitored by thin-layer chromatography over silica-gel-coated TLC plates (Yantai Chemical Industry Research Institute). The spots on TLC were visualized by warming 10% H<sub>2</sub>SO<sub>4</sub> (10% H<sub>2</sub>SO<sub>4</sub> in ethanol) sprayed plates on a hot plate. Column chromatography was performed using silica gel (Qingdao Marine Chemical Inc., China), and Sephadex LH-20 (GE Healthcare Bio-Sciences AB, Sweden). NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz) and Bruker Ascend TM-600 spectrometer (600 MHz), and the <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts were referenced to the solvent or solvent impurity peaks for CDCl<sub>3</sub> at  $\delta$  H 7.24 and  $\delta$  C 77.23. Optical rotations were measured at 20 °C with a Rudolph Autopol IV automatic polarimeter using a quartz cell with 2 mL capacity and a 1 dm path length. Concentrations (*c*) are given in g/100 mL. High resolution mass spectra were recorded on a Bruker micrOTOF II spectrometer using electrospray ionization (ESI).

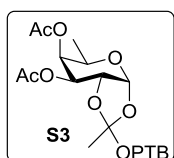
## 2. Materials

Prior to running the glycosylation reactions, all reagents except Tf<sub>2</sub>O and those with low boiling point (<180 °C) were dried by repeated azeotropic removal of water using toluene and a rotary evaporator at 27 °C. Solvents for reactions were dried on an Innovative Technologies Pure Solv400 solvent purifier. Molecular sieves (4 Å, powder < 50 µm) for reactions were flame dried immediately before use. Trifluoromethanesulfonic anhydride (Tf<sub>2</sub>O) was purchased from Acros. Bis(trifluoroacetoxy)iodobenzene (PIFA), 3-chloroperoxybenzoic acid (*m*-CPBA) and all other commercial available chemicals were purchased from Adamas and used without further purification.

## 3. Syntheses of 19-membered macrolactone 11, related to Scheme 2.



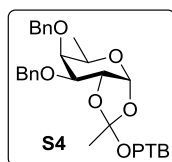
### 3,4-Di-*O*-acetyl-1,2-*O*-[1-(2-(2-propylthiol)benzyl)oxyethylidene]- $\beta$ -D-fucopyranoside (S3)



Compound **S1**<sup>1</sup> (8.6 g, 25.88 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (13.0 mL), and the solution was cooled to 0 °C. Acetic anhydride (2.4 mL) was added slowly followed by 33% HBr (12.8 mL, 77.64 mmol). The mixture was stirred at room temperature for 2.5 h. The residue was diluted with water and extracted with EtOAc. The organic layers were combined and washed with water, saturated aqueous NaHCO<sub>3</sub> and brine sequentially, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated *in vacuo* then could we get **S2** as yellow syrup. *R*<sub>f</sub> = 0.7 (petroleum ether-EtOAc 2:1). Compound **S2** (7.63 g, 21.60 mmol), PTB-OH<sup>2</sup> (5.14 g, 28.20 mmol) and freshly activated 4 Å molecular sieves in dry MeCN (36.0 mL) was cooled to 0 °C

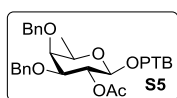
and stirred under nitrogen for 5 min. Then TBAI (3.99 g, 10.80 mmol) and TEA (3.89 mL, 28.08 mmol) was added. The resulting mixture was stirred under nitrogen for 3 h. Then quenched with Et<sub>3</sub>N and extracted with EtOAc. The organic layer was washed with H<sub>2</sub>O and brine, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography to give **S3** (8.23 g, 87%) as a colorless syrup.  $R_f = 0.3$  (petroleum-EtOAc 6:1).  $[\alpha]_D^{25} = 63.54$  ( $c$  1.50, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.43-7.20 (m, 4H, Ar-CH), 5.87 (d,  $J = 4.8$  Hz, 1H, H-1), 5.24 (dd,  $J = 3.2, 1.6$  Hz, 1H, H-4), 5.03 (dd,  $J = 7.2, 3.6$  Hz, 1H, H-3), 4.74 (d,  $J = 12.0$  Hz, 1H, PhCH<sub>2</sub>), 4.71 (d,  $J = 12.0$  Hz, 1H, PhCH<sub>2</sub>), 4.30 (d,  $J = 7.2, 5.2$  Hz, 1H, H-2), 4.26-4.21 (m, 1H, H-5), 3.38-3.28 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.12 (s, 3H, CH<sub>3</sub>), 2.04 (s, 3H, CH<sub>3</sub>), 1.74 (s, 3H, CH<sub>3</sub>), 1.26 (s, 3H, CH<sub>3</sub>), 1.25 (s, 3H, CH<sub>3</sub>), 1.18 (d,  $J = 6.4$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.5, 170.4, 139.4, 134.1, 132.5, 128.4, 128.0, 127.2, 120.7, 98.3, 73.1, 72.4, 69.0, 67.4, 63.3, 38.7, 23.9, 23.33, 23.29, 21.0, 20.8, 16.3. HRMS (ESI<sup>+</sup>): calc. for C<sub>22</sub>H<sub>30</sub>NaO<sub>8</sub>S [M+Na]<sup>+</sup>: 477.1559, found: 477.1585.

### 3,4-Di-*O*-benzyl-1,2-*O*-[1-(2-(2-propylthiol)benzyl)oxyethylidene]- $\beta$ -D-fucopyranoside (**S4**)



To a solution of compound **S3** (3.0 g, 6.60 mmol) in MeOH (16.5 mL) was added K<sub>2</sub>CO<sub>3</sub> (182.0 mg, 1.32 mmol), the mixture was stirred for 1 h at room temperature, then filtered off and evaporated to dryness to give the deacetylated compound as white syrup. This compound was dissolved in DMF (16.5 mL), and the solution was cooled to 0 °C. NaH (792.0 mg, 19.8 mmol) was added slowly followed by benzyl bromide (1.95 mL, 16.5 mmol). The reaction mixture was stirred at room temperature for 1 h and quenched with MeOH. The mixture was then concentrated under reduced pressure and purified by chromatography to give **S4** (3.1 g, 91%) as a colorless syrup.  $R_f = 0.42$  (petroleum ether-EtOAc 20:1).  $[\alpha]_D^{25} = 11.52$  ( $c$  4.60, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.49-7.20 (m, 14H, Ar-CH), 5.85 (d,  $J = 4.4$  Hz, 1H, H-1), 4.95 (d,  $J = 11.6$  Hz, 1H, PhCH<sub>2</sub>), 4.83 (d,  $J = 12.4$  Hz, 1H, PhCH<sub>2</sub>), 4.78 (d,  $J = 12.8$  Hz, 1H, PhCH<sub>2</sub>), 4.74 (d,  $J = 12.4$  Hz, 1H, PhCH<sub>2</sub>), 4.68 (d,  $J = 12.0$  Hz, 2H, PhCH<sub>2</sub>), 4.53 (dd,  $J = 6.0, 4.4$  Hz, 1H, H-2), 4.03-3.97 (m, 1H, H-5), 3.69 (t,  $J = 2.4$  Hz, 1H, H-4), 3.65 (d,  $J = 2.4, 6.0$  Hz, 1H, H-3), 3.38-3.28 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.68 (s, 3H, CH<sub>3</sub>), 1.27 (s, 3H, CH<sub>3</sub>), 1.25-1.23 (m, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  138.5, 138.4, 134.0, 132.8, 128.6, 128.51, 128.48, 128.3, 127.9, 127.83, 127.80, 127.3, 121.6, 98.0, 80.8, 78.9, 75.5, 74.6, 71.6, 70.5, 62.9, 38.8, 24.8, 23.4, 23.4, 16.8. HRMS (ESI<sup>+</sup>): calc. for C<sub>32</sub>H<sub>38</sub>NaO<sub>6</sub>S [M+Na]<sup>+</sup>: 573.2287, found: 573.2292.

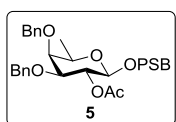
### 2-(2-Propylthiol)benzyl 2-*O*-acetyl-3,4-di-*O*-benzyl- $\beta$ -D-fucopyranoside (**S5**)



A mixture of **S4** (3.0 g, 5.45 mmol), PTB-OH<sup>2</sup> (199.0 mg, 1.09 mmol) and freshly activated 4 Å molecular sieves in dry CH<sub>2</sub>Cl<sub>2</sub> (18.0 mL) was cooled to -78 °C and stirred under nitrogen for 10 min. Then TMSOTf (197.0  $\mu$ L, 1.09 mmol) was added. The resulting mixture was stirred under nitrogen for 1.5 h and quenched with Et<sub>3</sub>N. The residue was diluted with EtOAc, washed with water, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. Column chromatography (petroleum-EtOAc 10:1) of the residue to give **S5** (2.5 g, 82% yield) as a white solid.  $R_f = 0.55$  (petroleum-EtOAc 5:1). mp 90-92 °C.  $[\alpha]_D^{25} = -21.17$  ( $c$  3.4, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.44-7.18 (m, 14H, Ar-CH), 5.43 (dd,  $J = 10.0, 8.0$  Hz, 1H, H-2), 4.98 (d,  $J = 12.0$  Hz, 1H, PhCH<sub>2</sub>), 4.95 (d,  $J = 13.2$  Hz, 1H, PhCH<sub>2</sub>), 4.77 (d,  $J = 12.8$  Hz, 1H, PhCH<sub>2</sub>), 4.67 (d,  $J = 12.0$  Hz, 1H, PhCH<sub>2</sub>), 4.66 (d,  $J = 12.4$  Hz, 1H, PhCH<sub>2</sub>), 4.53 (d,  $J =$

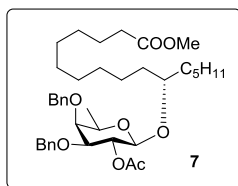
12.0 Hz, 1H, PhCH<sub>2</sub>), 4.37 (d, *J* = 8.0 Hz, 1H, H-1), 3.61 (d, *J* = 2.4 Hz, 1H, H-4), 3.50 (dd, *J* = 7.2, 2.8 Hz, 1H, H-5), 3.47 (t, *J* = 6.4 Hz, 1H, H-3), 3.35-3.25 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.00 (s, 3H, COCH<sub>3</sub>), 1.23 (d, *J* = 6.4 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 169.8, 139.5, 138.6, 138.2, 133.9, 132.5, 128.64, 128.62, 128.4, 128.4, 127.9, 127.8, 127.8, 127.7, 127.2, 100.5, 80.9, 75.4, 74.6, 72.3, 71.6, 70.9, 68.5, 38.7, 23.34, 23.31, 21.3, 17.1. HRMS (ESI<sup>+</sup>): calc. for C<sub>32</sub>H<sub>38</sub>NaO<sub>6</sub>S [M+Na]<sup>+</sup>: 573.2287, found: 573.2289.

## 2-(2-Propylsulfinyl)benzyl 2-acetyl-3,4-di-*O*-benzyl-β-D-fucopyranoside (5)



To a solution of **S5** (500.0 mg, 0.091 mmol) in wet CH<sub>3</sub>CN (9.1 mL, containing ca 5% water) was added PIFA (468.0 mg, 1.09 mmol). The reaction mixture was stirred at room temperature for 10 min, then diluted with water, extracted with EtOAc. The organic layer was washed with saturated NaHCO<sub>3</sub>, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and the filtrate was concentrated *in vacuo*. The residue was subjected to flash column chromatography to afford **5** as a colorless syrup (488.0 mg, 95%). *R*<sub>f</sub> = 0.50 (petroleum ether-EtOAc 1:2). A sulfoxide mixture (*R* and *S* 1:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86-7.26 (m, 28H, Ar-CH), 5.40 (dd, *J* = 10.0, 8.0 Hz, 1H, H-2), 5.32 (dd, *J* = 10.0, 8.0 Hz, 1H, H-2), 4.96 (d, *J* = 11.6 Hz, 1H, PhCH<sub>2</sub>), 4.95 (d, *J* = 12.0 Hz, 1H, PhCH<sub>2</sub>), 4.88 (d, *J* = 12.0 Hz, 1H, PhCH<sub>2</sub>), 4.86 (d, *J* = 12.4 Hz, 1H, PhCH<sub>2</sub>), 4.72 (d, *J* = 12.0 Hz, 1H, PhCH<sub>2</sub>), 4.68 (d, *J* = 13.6 Hz, 1H, PhCH<sub>2</sub>), 4.66 (d, *J* = 12.0 Hz, 1H, PhCH<sub>2</sub>), 4.65 (d, *J* = 12.0 Hz, 1H, PhCH<sub>2</sub>), 4.63 (d, *J* = 11.6 Hz, 2H, PhCH<sub>2</sub>), 4.52 (d, *J* = 12.4 Hz, 1H, PhCH<sub>2</sub>), 4.51 (d, *J* = 12.4 Hz, 1H, PhCH<sub>2</sub>), 4.42 (d, *J* = 8.0 Hz, 1H, H-1), 4.36 (d, *J* = 8.0 Hz, 1H, H-1), 3.61 (d, *J* = 2.8 Hz, 1H, H-4), 3.60 (d, *J* = 2.8 Hz, 1H, H-4), 3.53-3.44 (m, 4H, H-3, H-5, H-3, H-5), 2.97-2.93 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.92-2.87 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.03 (s, 3H, COCH<sub>3</sub>), 1.93 (s, 3H, COCH<sub>3</sub>), 1.25 (d, *J* = 7.2 Hz, 9H, CH<sub>3</sub>), 1.18 (d, *J* = 6.4 Hz, 3H, CH<sub>3</sub>), 1.07 (s, 3H, CH<sub>3</sub>), 1.05 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 169.8, 169.7, 141.14, 141.11, 138.5, 138.4, 138.08, 138.05, 135.5, 135.3, 131.0, 129.9, 129.4, 128.8, 128.72, 128.66, 128.6, 128.5, 128.42, 128.39, 128.03, 128.01, 127.9, 127.8, 127.7, 125.3, 125.1, 100.4, 100.2, 80.9, 80.8, 75.4, 75.2, 74.8, 74.7, 72.4, 71.3, 71.1, 66.2, 65.7, 54.0, 53.5, 21.3, 21.2, 17.5, 17.4, 17.1, 17.0, 13.2, 12.9. HRMS (ESI<sup>+</sup>): calc. for C<sub>32</sub>H<sub>38</sub>NaO<sub>7</sub>S [M+Na]<sup>+</sup>: 589.2236, found: 589.2246.

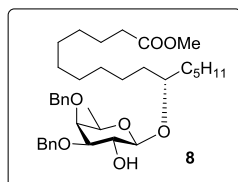
## 1-(Methoxycarbonyl)pentadec-10(*S*)-yl 2-acetyl-3,4-di-*O*-benzyl-β-D-fucopyranoside (7)



A solution of **5** (95.0 mg, 0.17 mmol) and DTBMP (43.0 mg, 0.21 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.23 mL) in the presence of 4 Å MS (100 wt%) was stirred for 15 min at -40 °C. After addition of Tf<sub>2</sub>O (28.2 μL, 0.17 mmol), the solution was stirred at -40 °C for 3 min, and then **6**<sup>3</sup> (40.0 mg, 0.14 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.23 mL) was added. The reaction mixture was stirred at -40 °C for 1 h and quenched with Et<sub>3</sub>N. The organic phase was washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>, concentrated, and purified by silica gel column chromatography to give compound **7** as a white solid. (77.7 mg, 85%). *R*<sub>f</sub> = 0.54 (toluene-EtOAc 13:1). mp 42-47 °C. [α]<sub>D</sub><sup>25</sup> = -4.02 (c, 0.62 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.29-7.15 (m, 10H, Ar-CH), 5.22 (dd, *J* = 7.6, 10.0 Hz, 1H, H-2), 4.89 (d, *J* = 12.0 Hz, 1H, PhCH<sub>2</sub>), 4.61-4.58 (m, 2H, PhCH<sub>2</sub>), 4.45 (d, *J* = 12.0 Hz, 1H, PhCH<sub>2</sub>), 4.22 (d, *J* = 8.0 Hz, 1H, H-1), 3.58 (s, 3H, OCH<sub>3</sub>), 3.51 (d, *J* = 2.4 Hz, 1H, H-4), 3.42 (dd, *J* = 2.8, 10.0 Hz, 1H, H-3), 3.38-3.34 (m, 2H, jia-11, H-5), 2.22 (t, *J* = 7.6 Hz, 1H, jia-2), 1.94 (s, 3H, COCH<sub>3</sub>), 1.55-1.51 (m, 3H, CH<sub>2</sub>), 1.38-1.17 (m, 21H, CH<sub>2</sub>), 1.12 (d, *J* = 6.4 Hz, 3H, CH<sub>3</sub>), 0.78 (t, *J* = 6.8 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ

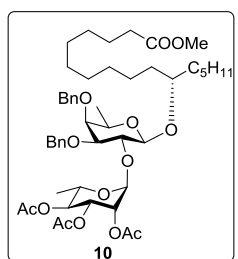
174.5, 169.6, 138.7, 138.3, 128.61, 128.60, 128.3, 127.9, 127.70, 127.66, 101.3, 81.2, 80.9, 75.4, 74.5, 72.2, 72.0, 70.6, 51.6, 34.9, 34.3, 34.2, 32.1, 30.1, 29.8, 29.7, 29.4, 29.3, 25.2, 25.1, 25.0, 22.8, 21.3, 17.2, 14.3. HRMS (ESI<sup>+</sup>): calc. for C<sub>39</sub>H<sub>58</sub>NaO<sub>8</sub> [M+Na]<sup>+</sup> 677.4024, found: 677.4004.

### 1-(Methoxycarbonyl)pentadec-10(*S*)-yl 3,4-di-*O*-benzyl- $\beta$ -D-fucopyranoside (**8**)



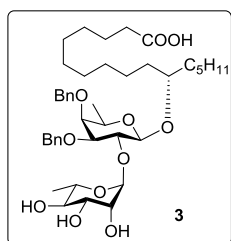
To a solution of compound **7** (500.0 mg, 0.76 mmol) in CH<sub>2</sub>Cl<sub>2</sub>–MeOH (1:7, v/v, 10.9 mL) was added DBU (798.0  $\mu$ L, 5.34 mmol) at 0 °C. The mixture was stirred for 1 days at 55 °C. Then the reaction was poured into ice water and extracted with EtOAc. The combined organic extracts were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residue was purified by column chromatography to afford **8** as a colorless syrup (430.5 mg, 92%). *R*<sub>f</sub> = 0.55 (toluene–EtOAc 13:1). [ $\alpha$ ]<sub>D</sub><sup>25</sup> = –13.40 (*c*, 1.00 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.38–7.22 (m, 10H, Ar-CH), 4.91 (d, *J* = 12.0 Hz, 1H, PhCH<sub>2</sub>), 4.75 (d, *J* = 12.0 Hz, 1H, PhCH<sub>2</sub>), 4.71 (d, *J* = 12.8 Hz, 1H, PhCH<sub>2</sub>), 4.68 (d, *J* = 12.0 Hz, 1H, PhCH<sub>2</sub>), 4.18 (d, *J* = 8.0 Hz, 1H, H-1), 3.88 (ddd, *J* = 1.2, 8.0, 9.6 Hz, 1H, H-2), 3.64 (s, 3H, OCH<sub>3</sub>), 3.59–3.54 (m, 2H, jia-11, H-4), 3.46–3.40 (m, 1H, H-5), 3.42 (dd, *J* = 3.2, 9.6 Hz, 1H, H-3), 2.30–2.26 (m, 3H, jia-2, OH), 1.61–1.56 (m, 4H), 1.54–1.42 (m, 3H), 1.35–1.20 (m, 17H), 1.16 (d, *J* = 6.8 Hz, 3H, CH<sub>3</sub>), 0.85 (t, *J* = 6.8 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  174.5, 138.8, 138.7, 128.64, 128.58, 128.3, 127.85, 127.79, 127.7, 102.8, 82.8, 80.1, 76.3, 74.8, 72.9, 71.8, 70.8, 51.6, 34.9, 34.3, 34.1, 32.1, 30.0, 29.7, 29.6, 29.4, 29.3, 25.4, 25.1, 25.0, 22.8, 17.2, 14.3. HRMS (ESI<sup>+</sup>): calc. for C<sub>37</sub>H<sub>56</sub>NaO<sub>7</sub> [M+Na]<sup>+</sup>: 635.3918, found: 635.3945.

### 1-(Methoxycarbonyl)pentadec-10(*S*)-yl 2-*O*-(2,3,4-tri-*O*-acetyl- $\alpha$ -L-rhamnopyranosyl)-3,4-di-*O*-benzyl- $\beta$ -D-fucopyranoside (**10**)



A solution of **8** (167.0 mg, 0.27 mmol), DTBMP (83.9 mg, 0.41 mmol) and **9**<sup>4</sup> (159.0 mg, 0.33 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5.4 mL) in the presence of 4 Å MS (100 wt%) was stirred for 15 min at –20 °C. After addition of Tf<sub>2</sub>O (55.0  $\mu$ L, 0.33 mmol), the solution was stirred at –20 °C for 1 h. The reaction mixture was quenched with Et<sub>3</sub>N, filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>, concentrated, and purified by silica gel flash column chromatography to give **10** (229.6 mg, 95%) as a colorless solid. *R*<sub>f</sub> = 0.29 (petroleum ether–EtOAc 5:1). [ $\alpha$ ]<sub>D</sub><sup>25</sup> = –37.28 (*c*, 1.8 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.31–7.23 (m, 10H, Ar-CH), 5.31 (dd, *J* = 1.2, 3.2 Hz, 1H, H-2'), 5.27 (s, 1H, H-1'), 5.19 (dd, *J* = 3.2, 9.6 Hz, 1H, H-3'), 5.00 (t, *J* = 10.0 Hz, 1H, H-4'), 4.86 (d, *J* = 12.0 Hz, 1H, PhCH<sub>2</sub>), 4.63 (d, *J* = 12.8 Hz, 2H, PhCH<sub>2</sub>), 4.50–4.40 (m, 2H, PhCH<sub>2</sub>, H-5'), 4.28 (d, *J* = 7.6 Hz, 1H, H-1), 3.96 (dd, *J* = 8.0, 9.6 Hz, 1H, H-2), 3.63 (s, 3H, OCH<sub>3</sub>), 3.62–3.53 (m, 3H, jia-11, H-3, H-4), 3.43–3.40 (m, 1H, H-5), 2.26 (t, *J* = 7.2 Hz, 2H, jia-2), 2.03 (s, 3H, COCH<sub>3</sub>), 1.99 (s, 3H, COCH<sub>3</sub>), 1.93 (s, 3H, COCH<sub>3</sub>), 1.16 (d, *J* = 6.4 Hz, 3H, CH<sub>3</sub>), 1.12 (d, *J* = 6.4 Hz, 3H, CH<sub>3</sub>), 0.84 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  174.5, 170.2, 170.13, 170.07, 138.7, 137.8, 128.7, 128.6, 128.4, 128.2, 128.0, 127.8, 100.4, 97.9, 84.8, 78.5, 75.7, 74.6, 73.4, 72.7, 71.5, 70.5, 69.8, 69.7, 66.1, 51.6, 34.8, 34.3, 33.6, 32.2, 30.1, 29.8, 29.7, 29.5, 29.4, 25.6, 25.2, 24.8, 22.9, 21.1, 21.0, 20.9, 17.3, 17.2, 14.3. HRMS (ESI<sup>+</sup>): calc. for C<sub>49</sub>H<sub>72</sub>NaO<sub>14</sub> [M+Na]<sup>+</sup> 907.4814, found: 907.4812.

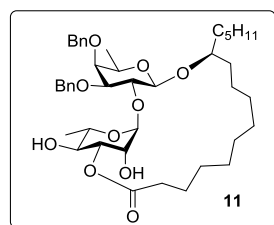
**1-(Hydroxycarbonyl)pentadec-10(*S*)-yl 2-*O*-( $\alpha$ -*L*-rhamnopyranosyl)-3,4-di-*O*-benzyl- $\beta$ -*D*-fucopyranoside (**3**)**



A mixture of **10** (222.0 mg, 0.25 mmol) and KOH (239.0 mg, 4.26 mmol) in THF–H<sub>2</sub>O (9:1, v/v, 12.5 mL) was stirred at 55 °C for 24 h. Then the reaction was quenched 1.0 M HCl and evaporated to remove THF under reduced pressure, then the residue was extracted with EtOAc. The combined organic extracts were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The resulting residue was purified by column chromatography to afford **3** as a white solid.

(174.0 mg, 93%).  $R_f$  = 0.48 (CH<sub>2</sub>Cl<sub>2</sub>–EtOAc 10:1). mp 64–76 °C;  $[\alpha]_D^{25}$  = –38.02 (*c*, 1.82 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36–7.22 (m, 10H, Ar-CH), 5.28 (s, 1H, H-1'), 4.87 (d,  $J$  = 12.0 Hz, 1H, PhCH<sub>2</sub>), 4.65 (d,  $J$  = 11.2 Hz, 1H, PhCH<sub>2</sub>), 4.64 (d,  $J$  = 11.6 Hz, 1H, PhCH<sub>2</sub>), 4.49 (d,  $J$  = 11.6 Hz, 1H, PhCH<sub>2</sub>), 4.23 (d,  $J$  = 8.0 Hz, 1H, H-1), 4.22–4.13 (m, 1H, H-5'), 3.96 (dd,  $J$  = 7.6, 9.6 Hz, 1H, H-2), 3.81 (d,  $J$  = 2.0 Hz, 1H, H-2'), 3.67 (dd,  $J$  = 3.2, 9.2 Hz, 1H, H-3'), 3.61–3.55 (m, 1H, jia-11), 3.54 (d,  $J$  = 2.0 Hz, 1H, H-4), 3.48 (dd,  $J$  = 2.4, 9.6 Hz, 1H, H-3), 3.42 (t,  $J$  = 9.2 Hz, 1H, H-4'), 3.40–3.37 (m, 1H, H-5), 2.29 (t,  $J$  = 6.8 Hz, 2H, jia-2), 1.63–1.56 (m, 2H, CH<sub>2</sub>), 1.50–1.42 (m, 4H, CH<sub>2</sub>), 1.36–1.18 (m, 21H, CH<sub>2</sub>, CH<sub>3</sub>), 1.15 (d,  $J$  = 6.0 Hz, 3H, CH<sub>3</sub>), 0.84 (t,  $J$  = 6.4 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  138.7, 138.1, 128.8, 128.6, 128.4, 128.1, 128.0, 127.8, 100.5, 100.3, 84.8, 78.3, 75.7, 74.6, 74.1, 73.7, 72.6, 72.3, 71.3, 70.4, 67.9, 35.0, 34.1, 33.7, 32.2, 30.1, 29.4, 29.2, 28.8, 28.7, 25.6, 25.0, 24.7, 22.8, 17.4, 17.2, 14.3. HRMS (ESI<sup>+</sup>): calc. for C<sub>42</sub>H<sub>64</sub>NaO<sub>11</sub> [M+Na]<sup>+</sup> 767.4346, found: 767.4344.

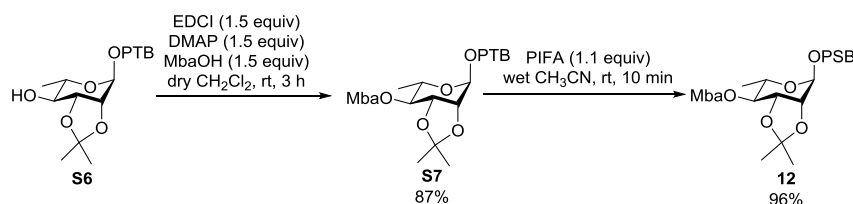
**11(*S*)-Hydroxyhexadecanoic acid 11-*O*- $\alpha$ -*L*-rhamnopyranosyl-(1 $\rightarrow$ 2)-3,4-di-*O*-benzyl- $\beta$ -*D*-fucopyranoside 1,3'-Lactone (**11**)**



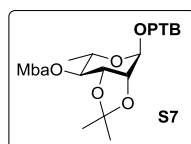
A solution of **3** (5.0 mg, 0.0067 mmol), (PyS)<sub>2</sub> (14.8 mg, 0.067 mmol), Ph<sub>3</sub>P (17.6 mg, 0.67 mmol) in deoxygenated anhydrous toluene (0.16 mL) was stirred at 25 °C for 5 h. The mixture was diluted with deoxygenated anhydrous toluene (0.45 mL) and then the resulting solution was added dropwise by a syringe pump to refluxing dry deoxygenated toluene (6.1 mL) over 2 h. The solution was refluxed under nitrogen for 1.5 days. After removal

of toluene under reduced pressure, the residue was purified by column chromatography to afford **11** (2.8 mg, 57%). Colorless syrup.  $R_f$  = 0.22 (petroleum ether–EtOAc 2:1).  $[\alpha]_D^{25}$  = –28.73 (*c*, 0.55 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35–7.25 (m, 10H, Ar-CH), 5.35 (d,  $J$  = 1.2 Hz, 1H, H-1'), 4.88 (d,  $J$  = 12.0 Hz, 1H, PhCH<sub>2</sub>), 4.77 (dd,  $J$  = 2.8, 10.0 Hz, 1H, H-3'), 4.67 (d,  $J$  = 12.0 Hz, 1H, PhCH<sub>2</sub>), 4.66 (d,  $J$  = 11.6 Hz, 1H, PhCH<sub>2</sub>), 4.46 (d,  $J$  = 11.6 Hz, 1H, PhCH<sub>2</sub>), 4.42 (m, 1H, H-5'), 4.26 (d,  $J$  = 7.6 Hz, 1H, H-1), 4.15 (s, 1H, H-2'), 4.02 (dd,  $J$  = 8.2, 9.8 Hz, 1H, H-2), 3.66 (t,  $J$  = 9.6 Hz, 1H, H-4'), 3.60–3.57 (m, 2H, H-3, H-4), 3.52–3.46 (m, 1H, jia-11), 3.44–3.39 (m, 1H, H-5), 2.39–2.36 (m, 2H, jia-2), 1.25 (d,  $J$  = 6.0 Hz, 3H, CH<sub>3</sub>), 1.16 (d,  $J$  = 6.4 Hz, 3H, CH<sub>3</sub>), 0.84 (t,  $J$  = 7.0 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  175.2, 138.7, 138.0, 128.79, 128.76, 128.4, 128.1, 127.8, 101.4, 99.2, 85.4, 80.3, 75.4, 74.6, 72.5, 71.7, 70.7, 70.6, 69.7, 68.1, 34.9, 34.7, 34.2, 32.2, 29.9, 29.7, 27.7, 27.3, 26.8, 26.5, 26.2, 24.3, 24.2, 22.9, 17.7, 17.2, 14.4. HRMS (ESI<sup>+</sup>): calc. for C<sub>42</sub>H<sub>62</sub>NaO<sub>10</sub> [M+Na]<sup>+</sup> 749.4235, found: 749.4247.

#### 4. Syntheses of OPSB glycosides **4**, related to Scheme 3

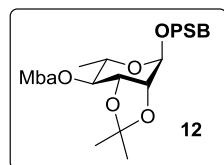


#### 2-(2-Propylthiol)benzyl 2,3-*O*-(1-methylethylidene)-4-*O*-(2*S*)-methylbutyryl- $\alpha$ -L-rhamnopyranoside (**S7**)



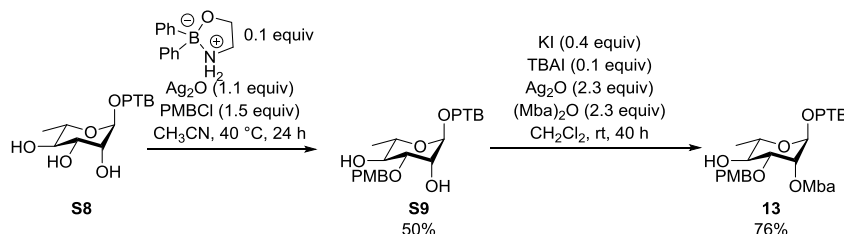
To a solution of 2-(2-propylthiol)benzyl 2,3-*O*-(1-methylethylidene)- $\alpha$ -L-rhamnopyranoside **S6**<sup>5</sup> (245.0 mg, 0.66 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (7.8 mL) was added (*S*)-(+)-2-methylbutyric acid (MbaOH, 109.0  $\mu$ L, 1.0 mmol), DMAP (122.0 mg, 1.0 mmol) and 3-(3-dimethylaminopropyl)-1-ethyl-carbodiimide hydrochloride (EDCI, 191 mg, 1.0 mmol) at 0 °C, the resulting solution was stirred at room temperature for 3 h, and then quenched with H<sub>2</sub>O. The reaction mixture was extracted with EtOAc. The combined organic layer was washed with H<sub>2</sub>O and brine, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography to give compound **S7** (263.0 mg, 87%) as a colorless syrup. *R*<sub>f</sub> = 0.73 (petroleum ether-EtOAc 6:1). [ $\alpha$ ]<sub>D</sub><sup>25</sup> = 15.40 (*c*, 3.65 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.45 (dd, *J* = 1.2, 7.2 Hz, 1H, Ar-CH), 7.39 (dd, *J* = 1.2, 7.2 Hz, 1H, Ar-CH), 7.28-7.24 (m, 1H, Ar-CH), 7.24-7.21 (m, 1H, Ar-CH), 5.11 (s, 1H, H-1), 4.91-4.86 (m, 2H, H-4, PhCH<sub>2</sub>), 4.62 (d, *J* = 12.0 Hz, 1H, PhCH<sub>2</sub>), 4.16-4.14 (m, 2H, H-2, H-3), 3.89-3.82 (m, 1H, H-5), 3.36 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.42-2.34 (m, 1H, COCH(CH<sub>3</sub>)), 1.73-1.63 (m, 1H, COCH(CH<sub>3</sub>)CH<sub>2</sub>), 1.54 (s, 3H, CH<sub>3</sub>), 1.51-1.42 (m, 1H, COCH(CH<sub>3</sub>)CH<sub>2</sub>), 1.31 (s, 3H, CH<sub>3</sub>), 1.28 (d, *J* = 2.4 Hz, 3H, CH<sub>3</sub>), 1.26 (d, *J* = 2.8 Hz, 3H, CH<sub>3</sub>), 1.14 (t, *J* = 6.8 Hz, 6H, CH<sub>3</sub>), 0.90 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  176.0, 138.6, 135.6, 132.7, 129.6, 128.6, 127.1, 109.9, 96.7, 76.3, 76.1, 74.3, 68.0, 64.5, 41.3, 38.9, 27.9, 26.9, 26.8, 23.4, 23.3, 17.2, 16.7, 11.7. HRMS (ESI<sup>+</sup>): calc. for C<sub>24</sub>H<sub>36</sub>NaO<sub>6</sub>S [M+Na]<sup>+</sup> 475.2125, found: 475.2121.

#### 2-(2-Propylsulfinyl)benzyl 2,3-*O*-(1-methylethylidene)-4-*O*-(2*S*)-methylbutyryl- $\alpha$ -L-rhamnopyranoside (**12**)

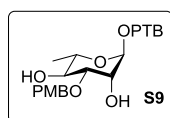


To a solution of compound **S7** (345.0 mg, 0.77 mmol) in wet CH<sub>3</sub>CN (7.7 mL, containing ca 5% water) was added PIFA (360.0 mg, 0.85 mmol). The reaction mixture was stirred at room temperature for 10 min, then diluted with water, extracted with EtOAc. The organic layer was washed with saturated NaHCO<sub>3</sub>, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and the filtrate was concentrated *in vacuo*. The residue was subjected to flash column chromatography to afford **12** as a colorless syrup (347.0 mg, 96%). *R*<sub>f</sub> = 0.24 (petroleum ether-EtOAc 3:1). A sulfoxide mixture (*R* and *S* 1:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.91 (d, *J* = 7.6 Hz, 2H, Ar-CH), 7.53 (t, *J* = 7.2 Hz, 2H, Ar-CH), 7.47 (t, *J* = 7.6 Hz, 2H, Ar-CH), 7.42 (d, *J* = 7.2 Hz, 2H, Ar-CH), 5.11 (s, 1H, H-1), 5.06 (s, 1H, H-1'), 4.90-4.84 (m, 2H, H-4, H-4'), 4.81 (d, *J* = 12.0 Hz, 1H, PhCH<sub>2</sub>), 4.80 (d, *J* = 12.0 Hz, 1H, PhCH<sub>2</sub>), 4.56 (dd, *J* = 11.6 Hz, 1H, PhCH<sub>2</sub>), 4.53 (dd, *J* = 11.6 Hz, 1H, PhCH<sub>2</sub>), 4.12-4.06 (m, 4H, H-2, H-3, H-2', H-3'), 3.81-3.75 (m, 1H, H-5), 3.75-3.70 (m, 1H, H-5'), 2.90 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>, CH(CH<sub>3</sub>)<sub>2</sub>), 2.43-2.32 (m, 2H, COCH(CH<sub>3</sub>), COCH(CH<sub>3</sub>)), 1.73-1.60 (m,

2H, COCH(CH<sub>3</sub>)CH<sub>2</sub>, COCH(CH<sub>3</sub>)CH<sub>2</sub>) 1.53 (s, 3H, CH<sub>3</sub>), 1.52 (s, 3H, CH<sub>3</sub>), 1.50-1.42 (m, 2H, COCH(CH<sub>3</sub>)CH<sub>2</sub>, COCH(CH<sub>3</sub>)CH<sub>2</sub>) 1.31-1.29 (m, 12H, CH<sub>3</sub>), 1.18-1.11 (m, 18H, CH<sub>3</sub>), 0.90 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>), 0.89(t, *J* = 7.2Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 176.0, 175.9, 134.9, 134.7, 131.3, 130.3, 129.9, 129.37, 129.35, 125.9, 125.7, 110.11, 110.08, 97.0, 96.8, 76.01, 75.97, 75.9, 73.9, 73.8, 65.9, 65.8, 65.0, 64.8, 54.1, 41.23, 41.20, 27.8, 26.90, 26.89, 26.7, 17.7, 17.6, 17.20, 17.15, 16.71, 16.69, 13.22, 13.20, 11.7, 11.6. HRMS (ESI<sup>+</sup>): calc. for C<sub>24</sub>H<sub>36</sub>NaO<sub>7</sub>S [M+Na]<sup>+</sup> 491.2074, found: 491.2080.

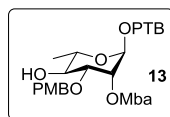


## 2-(2-Propylthiol)benzyl 3-*O*-*p*-methoxybenzyl- $\alpha$ -L-rhamnopyranoside (S9)



The compound **S8**<sup>5</sup> (2.0 g, 6.09 mmol), 2-aminoethyl diphenylborinate (137.0 mg, 0.61 mmol) and silver oxide (Ag<sub>2</sub>O, 1.55 g, 6.70 mmol) were weighed into a 50 mL round-bottomed flask, dry acetonitrile (61.0 mL) and 4-methoxybenzylchloride (1.24 mL, 9.13 mmol) was then added. The mixture was stirred at 40 °C for 24 h. The resulting mixture was diluted with EtOAc, filtered and concentrated to dryness. The residue was purified by silica gel column chromatography to give compound **S9** as a colorless syrup (1.36 g, 50%). *R<sub>f</sub>* = 0.48 (petroleum ether-EtOAc 1:1). [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -26.86 (*c*, 0.70 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.26 (dd, *J* = 1.2, 8.4 Hz, 1H, Ar-CH), 7.18 (dd, *J* = 2.0, 7.2 Hz, 1H, Ar-CH), 7.09-7.03 (m, 4H, Ar-CH), 6.69 (d, *J* = 8.4 Hz, 2H, Ar-CH), 4.75 (s, 1H, H-1), 4.64 (d, *J* = 12.0 Hz, 1H, PhCH<sub>2</sub>), 4.46 (d, *J* = 11.6 Hz, 1H, PhCH<sub>2</sub>), 4.43 (d, *J* = 10.4 Hz, 1H, PhCH<sub>2</sub>), 4.29 (d, *J* = 11.2 Hz, 1H, PhCH<sub>2</sub>), 3.86 (s, 1H, H-2), 3.60-3.55 (m, 4H, OCH<sub>3</sub>, H-5), 3.48 (dd, *J* = 3.2, 9.2 Hz, 1H, H-3), 3.35 (t, *J* = 9.2 Hz, 1H, H-4), 3.17 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.25 (s, 1H, OH), 2.05 (s, 1H, OH), 1.11 (d, *J* = 6.4 Hz, 3H, CH<sub>3</sub>), 1.08 (d, *J* = 6.8 Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.8, 139.0, 135.2, 132.6, 129.91, 129.87, 129.1, 128.4, 127.0, 114.3, 99.1, 79.7, 71.7, 71.5, 68.2, 68.0, 67.8, 55.5, 38.8, 23.3, 17.8. HRMS (ESI<sup>+</sup>): calc. for C<sub>24</sub>H<sub>32</sub>NaO<sub>6</sub>S [M+Na]<sup>+</sup> 471.1812, found: 471.1826.

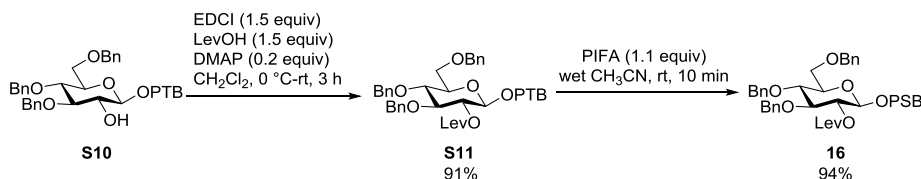
## 2-(2-Propylthiol)benzyl 2-*O*-(2*S*)-methylbutyryl-3-*O*-*p*-methoxybenzyl- $\alpha$ -L-rhamnopyranoside (13)



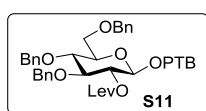
The compound **S9** (234.0 mg, 0.52 mmol), TBAI (19.0 mg, 0.052 mmol) and Ag<sub>2</sub>O (278.0 mg, 1.20 mmol) were weighed into a 50 mL round-bottomed flask, dry CH<sub>2</sub>Cl<sub>2</sub> (5.2 mL) was then added. The mixture was stirred at room temperature for 10 min, KI (35.0 mg, 0.21 mmol) and (*S*)-(+)-2-methylbutyric anhydride (232.0 mg, 1.25 mmol) was added, the mixture was stirred for 40 h at room temperature. The resulting mixture was diluted with EtOAc, filtered and concentrated to dryness. The residue was purified by silica gel column chromatography to give compound **13** as a colorless syrup (211.0 mg, 76%). *R<sub>f</sub>* = 0.65 (petroleum ether-EtOAc 3:1). [ $\alpha$ ]<sub>D</sub><sup>25</sup> = 1.40 (*c*, 0.5 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45-7.43 (m, 1H, Ar-CH), 7.39-7.37 (m, 1H, Ar-CH), 7.26-7.20 (m, 4H, Ar-CH), 6.84



(d,  $J = 8.4$  Hz, 2H, Ar-CH), 5.43 (brs, 1H, H-2), 4.87 (s, 1H, H-1), 4.86 (d,  $J = 11.6$  Hz, 1H, PhCH<sub>2</sub>), 4.64 (d,  $J = 12.0$  Hz, 1H, PhCH<sub>2</sub>), 4.63 (d,  $J = 10.4$  Hz, 1H, PhCH<sub>2</sub>), 4.31 (d,  $J = 10.8$  Hz, 1H, PhCH<sub>2</sub>), 3.82-3.77 (m, 4H, H-5, OCH<sub>3</sub>), 3.74 (dd,  $J = 3.2, 9.6$  Hz, 1H, H-3), 3.52 (t,  $J = 9.6$  Hz, 1H, H-4), 3.34 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.49-2.40 (m, 1H, COCH(CH<sub>3</sub>)), 2.28 (s, 1H, OH), 1.74-1.63 (m, 1H, COCH(CH<sub>3</sub>)CH<sub>2</sub>), 1.52-1.41 (m, 1H, COCH(CH<sub>3</sub>)CH<sub>2</sub>), 1.30 (d,  $J = 6.0$  Hz, 3H, CH<sub>3</sub>), 1.27 (d,  $J = 6.8$  Hz, 6H, CH<sub>3</sub>), 1.14 (d,  $J = 6.8$  Hz, 3H, CH<sub>3</sub>), 0.88 (t,  $J = 7.2$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  176.2, 159.6, 139.0, 134.9, 132.9, 130.1, 129.9, 128.9, 128.4, 127.2, 114.1, 98.1, 71.9, 71.1, 68.7, 67.9, 67.8, 55.5, 41.2, 38.9, 27.0, 23.3, 18.0, 16.7, 11.7. HRMS (ESI<sup>+</sup>): calc. for C<sub>29</sub>H<sub>40</sub>NaO<sub>7</sub>S [M+Na]<sup>+</sup> 555.2387, found: 555.2396.

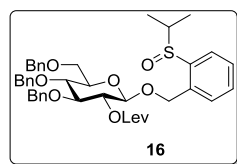


## 2-(2-Propylthiol)benzyl 2-O-levulinoyloxy-3,4,6-tri-O-benzyl- $\beta$ -D-glucopyranoside (S11)



To a solution of **S10**<sup>2</sup> (528.0 mg, 0.86 mmol) was added levulinic Acid (LevOH, 132.0  $\mu$ L, 1.29 mmol), DMAP (21.0 mg, 0.17 mmol) and EDCI (247.0 mg, 1.29 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (17.0 mL) at 0 °C, the resulting solution was stirred at room temperature for 3 h, and then quenched with H<sub>2</sub>O. The reaction mixture was extracted repeatedly with EtOAc. The combined organic layer was washed with H<sub>2</sub>O and brine. The organic layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to give compound **S11** (557.0 mg, 91%) as a white solid.  $R_f = 0.32$  (petroleum ether-EtOAc 5:1). mp 74-78 °C;  $[\alpha]_{\text{D}}^{25} = -17.06$  (c, 0.92 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37-7.34 (m, 2H, Ar-CH), 7.32-7.17 (m, 15H, Ar-CH), 7.13-7.11 (m, 2H, Ar-CH), 5.04 (t,  $J = 8.0$  Hz, 1H, H-2), 4.95 (d,  $J = 12.8$  Hz, 1H, PhCH<sub>2</sub>), 4.75 (d,  $J = 13.2$  Hz, 1H, PhCH<sub>2</sub>), 4.74 (d,  $J = 10.4$  Hz, 1H, PhCH<sub>2</sub>), 4.71 (d,  $J = 10.8$  Hz, 1H, PhCH<sub>2</sub>), 4.65 (d,  $J = 11.2$  Hz, 1H, PhCH<sub>2</sub>), 4.59 (d,  $J = 12.4$  Hz, 1H, PhCH<sub>2</sub>), 4.51 (d,  $J = 12.0$  Hz, 1H, PhCH<sub>2</sub>), 4.50 (d,  $J = 10.8$  Hz, 1H, PhCH<sub>2</sub>), 4.40 (d,  $J = 7.6$  Hz, 1H, H-1), 3.73 (dd,  $J = 1.8, 11.0$  Hz, 1H, H-6a), 3.70-3.65 (m, 2H, H-6b, H-3), 3.62 (t,  $J = 9.0$  Hz, 1H, H-4), 3.46-3.43 (m, 1H, H-5), 3.28 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.66-2.53 (m, 2H, CH<sub>2</sub>CO), 2.50-2.37 (m, 2H, CH<sub>2</sub>CO), 2.06 (s, 3H, CH<sub>3</sub>CO), 1.20 (d,  $J = 1.6$  Hz, 3H, CH<sub>3</sub>), 1.19 (d,  $J = 1.6$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  206.5, 171.7, 139.1, 138.4, 138.3, 138.1, 134.3, 132.4, 128.7, 128.55, 128.54, 128.4, 128.2, 128.1, 128.00, 127.97, 127.84, 127.78, 127.1, 100.1, 83.1, 78.1, 75.4, 75.18, 75.17, 73.8, 73.7, 68.9, 68.8, 38.7, 38.1, 30.0, 28.2, 23.32, 23.27. HRMS (ESI<sup>+</sup>): calc. for C<sub>42</sub>H<sub>48</sub>NaO<sub>8</sub>S [M+Na]<sup>+</sup> 735.2962, found: 735.2968.

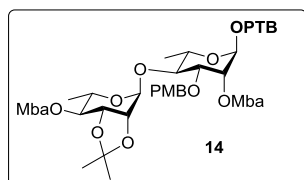
## 2-(2-Propylsulfanyl)benzyl 2-O-levulinoyloxy-3,4,6-tri-O-benzyl- $\beta$ -D-glucopyranoside (16)



To a solution of **S11** (695.0 mg, 0.98 mmol) in wet CH<sub>3</sub>CN (9.8 mL, containing ca 5% water) was added PIFA (462.0 mg, 1.07 mmol). The reaction mixture was stirred at room temperature for 10 min, then diluted with water, extracted with EtOAc. The organic layer was washed with saturated NaHCO<sub>3</sub>, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and the filtrate was concentrated *in vacuo*. The residue was subjected to flash column

chromatography to afford **16** as a colorless syrup (667.0 mg, 94%).  $R_f$  = 0.48 (petroleum ether-EtOAc 1:2). A sulfoxide mixture (*R* and *S* 1:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88-7.83 (m, 2H, Ar-CH), 7.52-7.42 (m, 6H, Ar-CH), 7.35-7.27 (m, 26H, Ar-CH), 7.17-7.15 (m, 4H, Ar-CH), 5.07-4.97 (m, 2H, H-2), 4.94-4.90 (m, 2H,  $\text{PhCH}_2$ ), 4.79-4.73 (m, 4H,  $\text{PhCH}_2$ ), 4.70-4.63 (m, 4H,  $\text{PhCH}_2$ ), 4.56-4.53 (m, 4H,  $\text{PhCH}_2$ ), 4.53-4.42 (m, 4H,  $\text{PhCH}_2$ , H-1), 3.79-3.63 (m, 8H, H-6a, H-6b, H-3, H-4), 3.51-3.45 (m, 2H, H-5), 2.90 (m, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 2.68-2.64 (m, 2H,  $\text{CH}_2\text{CO}$ ), 2.60-2.55 (m, 2H,  $\text{CH}_2\text{CO}$ ), 2.53-2.31 (m, 4H,  $\text{CH}_2\text{CO}$ ), 2.12-2.08 (m, 6H,  $\text{CH}_3\text{CO}$ ), 1.25 (t,  $J$  = 8.0 Hz, 6H,  $\text{CH}_3$ ), 1.07 (t,  $J$  = 7.4 Hz, 6H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  206.4, 206.3, 171.7, 171.6, 141.6, 141.0, 138.3, 138.2, 138.05, 138.01, 135.5, 134.9, 131.1, 131.0, 129.7, 129.6, 129.0, 128.8, 128.62, 128.61, 128.57, 128.2, 128.1, 128.1, 128.0, 127.92, 127.90, 125.3, 125.2, 100.3, 100.2, 83.04, 82.99, 78.0, 77.9, 75.4, 75.4, 75.25, 75.21, 75.19, 75.16, 73.74, 73.71, 73.6, 73.5, 68.8, 66.7, 66.5, 54.0, 53.8, 37.98, 38.96, 30.02, 29.98, 28.1, 17.42, 17.36, 13.4, 12.9. HRMS (ESI<sup>+</sup>): calc. for  $\text{C}_{42}\text{H}_{48}\text{NaO}_9\text{S}$   $[\text{M}+\text{Na}]^+$  751.2911, found: 751.2909.

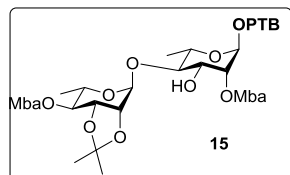
**2-(2-Propylthiol)benzyl 2-*O*-(2*S*)-methylbutyryl-3-*O*-*p*-methoxybenzyl-4-*O*-(2,3-*O*-(1-methylethylidene)-4-*O*-(2*S*)-methylbutyryl- $\alpha$ -L-rhamnopyranosyl)- $\alpha$ -L-rhamnopyranoside (**14**)**



A solution of **12** (96.6 mg, 0.21 mmol), DTBMP (53.0 mg, 0.26 mmol) and **13** (90.0 mg, 0.17 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.7 mL) in the presence of 4 Å MS (100 wt%) was stirred for 10 min at  $-40^\circ\text{C}$ . After addition of  $\text{Ti}_2\text{O}$  (35.0  $\mu\text{L}$ , 0.21 mmol), the solution was stirred at  $-40^\circ\text{C}$  for 1 h. The reaction mixture was quenched with  $\text{Et}_3\text{N}$ , filtered through Celite and extracted with EtOAc. The

organic phase was washed with brine, dried with  $\text{Na}_2\text{SO}_4$ , concentrated, and purified by silica gel flash column chromatography to give **14** (113.6 mg, 82%) as a colorless syrup.  $R_f$  = 0.60 (petroleum ether-EtOAc 5:1).  $[\alpha]_{\text{D}}^{25}$  = -12.42 (*c*, 0.95 in  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46-7.43 (m, 1H, Ar-CH), 7.40-7.37 (m, 1H, Ar-CH), 7.28-7.25 (m, 2H, Ar-CH), 7.21-7.19 (m, 2H, Ar-CH), 6.80-6.78 (m, 2H, Ar-CH), 5.46 (dd,  $J$  = 2.0, 2.8 Hz, 1H, H-2'), 5.45 (s, 1H, H-1), 4.87-4.82 (m, 2H,  $\text{PhCH}_2$ , H-4), 4.84 (s, 1H, H-1'), 4.63 (d,  $J$  = 12.0 Hz, 1H,  $\text{PhCH}_2$ ), 4.56 (d,  $J$  = 10.8 Hz, 1H,  $\text{PhCH}_2$ ), 4.31 (d,  $J$  = 10.8 Hz, 1H,  $\text{PhCH}_2$ ), 4.10 (d,  $J$  = 5.2 Hz, 1H, H-2), 4.06 (dd,  $J$  = 5.4, 8.0 Hz, 1H, H-3), 3.86 (dd,  $J$  = 2.8, 9.2 Hz, 1H, H-3'), 3.81-3.72 (m, H-5, 5H,  $\text{OCH}_3$ , H-5'), 3.64 (t,  $J$  = 9.4 Hz, 1H, H-4'), 3.34 (m, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 2.46-2.33 (m, 2H,  $\text{COCH}(\text{CH}_3)$ ,  $\text{COCH}(\text{CH}_3)$ ), 1.72-1.60 (m, 2H,  $\text{COCH}(\text{CH}_3)\text{CH}_2$ ,  $\text{COCH}(\text{CH}_3)\text{CH}_2$ ), 1.53 (s, 3H,  $\text{CH}_3$ ), 1.50-1.36 (m, 2H,  $\text{COCH}(\text{CH}_3)\text{CH}_2$ ,  $\text{COCH}(\text{CH}_3)\text{CH}_2$ ), 1.30-1.28 (m, 9H,  $\text{CH}_3$ ), 1.26 (d,  $J$  = 1.6 Hz, 3H,  $\text{CH}_3$ ), 1.14 (d,  $J$  = 6.8 Hz, 3H,  $\text{CH}_3$ ), 1.11-1.09 (d,  $J$  = 6.4 Hz, 6H,  $\text{CH}_3$ ), 0.90 (t,  $J$  = 7.6 Hz, 3H,  $\text{CH}_3$ ), 0.82 (d,  $J$  = 7.6 Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  176.2, 176.0, 159.4, 139.0, 134.9, 132.9, 130.2, 129.8, 128.8, 128.4, 127.2, 113.8, 109.6, 99.0, 97.8, 78.6, 76.6, 76.0, 74.1, 70.8, 67.9, 67.8, 67.5, 64.9, 55.4, 41.3, 41.2, 39.0, 27.9, 27.1, 26.9, 26.8, 23.4, 23.3, 18.3, 16.8, 16.74, 16.66, 11.7, 11.6. HRMS (ESI<sup>+</sup>): calc. for  $\text{C}_{43}\text{H}_{62}\text{NaO}_{12}\text{S}$   $[\text{M}+\text{Na}]^+$  825.3854, found: 825.3835.

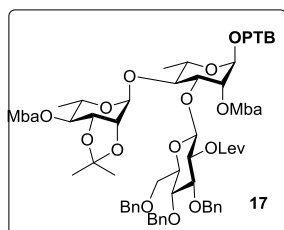
**2-(2-Propylthiol)benzyl 2-*O*-(2*S*)-methylbutyryl-4-*O*-(2,3-*O*-(1-methylethylidene)-4-*O*-(2*S*)-methylbutyryl- $\alpha$ -L-rhamnopyranosyl)- $\alpha$ -L-rhamnopyranoside (**15**)**



To a solution of **14** (105.0 mg, 0.13 mmol) in  $\text{CH}_2\text{Cl}_2$ - $\text{H}_2\text{O}$  (17:1, v/v, 13.0 mL) was added DDQ (59.0 mg, 0.26 mmol) at  $0^\circ\text{C}$ . The reaction mixture was stirred for 24 h during which time it was

gradually warmed to ambient temperature, and then was quenched with aqueous  $\text{NaHCO}_3$  and extracted with EtOAc. The combined organic extracts were washed with water, aqueous  $\text{NaHCO}_3$  and brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated. The obtained residue was purified by column chromatography to afford **15** as white solid (73.0 mg, 81%).  $R_f = 0.38$  (petroleum ether-EtOAc 5:1). mp 61-68 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44-7.42 (m, 1H, Ar-CH), 7.40-7.38 (m, 1H, Ar-CH), 7.28-7.25 (m, 1H, Ar-CH), 7.24-7.21 (m, 1H, Ar-CH), 5.46 (s, 1H, H-1), 5.12 (d,  $J = 2.0$  Hz, 1H, H-2'), 4.89-4.84 (m, 3H, H-4, H-1',  $\text{PhCH}_2$ ), 4.62 (d,  $J = 12.4$  Hz, 1H,  $\text{PhCH}_2$ ), 4.19 (d,  $J = 5.2$  Hz, 1H, H-2), 4.17-4.14 (m, 1H, H-3'), 4.10 (dd,  $J = 5.6, 7.6$  Hz, 1H, H-3), 3.83-3.77 (m, 2H, H-5, H-5'), 3.55 (t,  $J = 9.6$  Hz, 1H, H-4'), 3.34 (m, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 2.45 (m, 1H,  $\text{COCH}(\text{CH}_3)$ ), 2.39 (m, 1H,  $\text{COCH}(\text{CH}_3)$ ), 2.04 (d,  $J = 6.0$  Hz, 1H, OH), 1.74-1.63 (m, 2H,  $\text{COCH}(\text{CH}_3)\text{CH}_2$ ,  $\text{COCH}(\text{CH}_3)\text{CH}_2$ ), 1.58 (s, 3H,  $\text{CH}_3$ ), 1.49-1.44 (m, 2H,  $\text{COCH}(\text{CH}_3)\text{CH}_2$ ,  $\text{COCH}(\text{CH}_3)\text{CH}_2$ ), 1.32 (s, 3H,  $\text{CH}_3$ ), 1.30 (d,  $J = 6.8$  Hz, 3H,  $\text{CH}_3$ ), 1.26 (d,  $J = 6.8$  Hz, 6H,  $\text{CH}_3$ ), 1.14 (m, 9H,  $\text{CH}_3$ ), 0.94-0.89 (m, 6H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  177.0, 176.0, 138.8, 134.9, 132.8, 128.9, 128.5, 127.2, 109.8, 98.6, 97.4, 79.8, 76.5, 75.9, 73.9, 73.0, 71.4, 68.0, 67.0, 65.4, 41.2, 38.9, 27.9, 27.0, 26.9, 26.7, 23.3, 18.2, 16.9, 16.74, 16.69, 11.8, 11.7. HRMS ( $\text{ESI}^+$ ): calc. for  $\text{C}_{35}\text{H}_{54}\text{NaO}_{11}\text{S}$   $[\text{M}+\text{Na}]^+$  705.3279, found: 705.3264.

**2-(2-Propylthiol)benzyl 2-O-(2S)-methylbutyryl-3-O-(2-O-levulinoyloxy-3,4,6-tri-O-benzyl- $\beta$ -D-glucopyranosyl)-4-O-(2,3-O-(1-methylethylidene)-4-O-(2S)-methylbutyryl- $\alpha$ -L-rhamnopyranosyl)- $\alpha$ -L-rhamnopyranoside (17)**

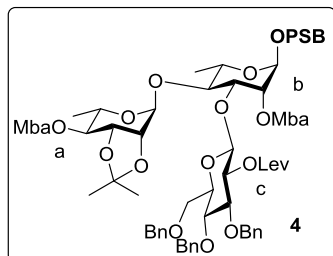


A solution of **16** (192.0 mg, 0.26 mmol) and DTBMP (67.6 mg, 0.33 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.1 mL) in the presence of 4 Å MS (100 wt%) was stirred for 15 min at -40 °C. After addition of  $\text{Tf}_2\text{O}$  (44.0  $\mu\text{L}$ , 0.26 mmol), the solution was stirred at -40 °C for 3 min, and then **15** (150.0 mg, 0.22 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.1 mL) was added. The reaction mixture was stirred at -40 °C for 1 h and quenched with saturated aqueous  $\text{NaHCO}_3$ . The organic phase

was washed with  $\text{H}_2\text{O}$ , brine, dried with  $\text{Na}_2\text{SO}_4$ , concentrated and purified by silica gel column chromatography to give compound **17** (221.0 mg, 83%) as a colorless syrup.  $R_f = 0.51$  (petroleum ether-EtOAc 5:1).  $[\alpha]_D^{25} = -15.07$  (c, 0.75 in  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J = 7.6$  Hz, 1H, Ar-CH), 7.34-7.11 (m, 18H, Ar-CH), 5.34 (s, 1H, rha'-1), 5.31 (dd,  $J = 1.6, 2.8$  Hz, 1H, rha'-2), 4.93 (dd,  $J = 8.0, 8.8$  Hz, 1H, glc-2), 4.87-4.81 (m, 3H,  $\text{PhCH}_2$ , rha'-1, rha'-4), 4.84 (s, 1H, rha'-1), 4.70 (d,  $J = 11.2$  Hz, 2H,  $\text{PhCH}_2$ ), 4.64-4.59 (m, 3H,  $\text{PhCH}_2$ ), 4.58 (d,  $J = 7.6$  Hz, 1H, glc-1), 4.54 (d,  $J = 12.4$  Hz, 1H,  $\text{PhCH}_2$ ), 4.50 (d,  $J = 12.8$  Hz, 1H,  $\text{PhCH}_2$ ), 4.19 (dd,  $J = 3.6, 8.8$  Hz, 1H, rha'-3), 4.11-4.04 (m, 2H, rha'-2, rha'-3), 3.80-3.66 (m, 5H, rha'-5, rha-5, glc-6a, glc-6b, rha-4), 3.65 (t,  $J = 9.2$  Hz, 1H, glc-4), 3.54 (t,  $J = 9.2$  Hz, 1H, glc-3), 3.48-3.44 (m, 1H, glc-5), 3.29 (m, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 2.78-2.70 (m, 1H,  $\text{COCH}(\text{CH}_3)$ ), 2.67-2.63 (m, 2H,  $\text{COCH}_2$ ), 2.48-2.36 (m, 3H,  $\text{COCH}_2$ ,  $\text{COCH}(\text{CH}_3)$ ), 2.11 (s, 3H,  $\text{COCH}_3$ ), 1.73-1.63 (m, 2H,  $\text{COCH}(\text{CH}_3)\text{CH}_2$ ,  $\text{COCH}(\text{CH}_3)\text{CH}_2$ ), 1.52-1.43 (m, 5H,  $\text{COCH}(\text{CH}_3)\text{CH}_2$ ,  $\text{COCH}(\text{CH}_3)\text{CH}_2$ ,  $\text{CH}_3$ ), 1.48 (s, 3H,  $\text{CH}_3$ ), 1.31 (s, 3H,  $\text{CH}_3$ ), 1.30 (d,  $J = 6.8$  Hz, 3H, rha'-6), 1.23 (d,  $J = 6.4$  Hz, 6H,  $\text{CH}_3$ ), 1.15-1.10 (m, 9H, rha-6,  $\text{CH}_3$ ), 0.91 (t,  $J = 7.6$  Hz, 6H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  206.4, 176.0, 176.0, 171.9, 139.2, 138.6, 138.3, 138.1, 134.5, 132.8, 128.6, 128.55, 128.49, 128.22, 128.17, 128.04, 127.98, 127.9, 127.8, 127.6, 127.2, 109.7, 101.3, 98.2, 97.4, 83.4, 78.6, 78.2, 76.6, 76.4, 76.0, 75.8, 75.3, 75.2, 73.91, 73.86, 73.5, 72.8, 69.0, 67.8, 67.3, 64.9, 41.3, 41.2, 38.9, 38.3, 30.0, 28.0, 27.8, 27.1, 26.9, 26.8, 23.34, 23.33, 18.5, 16.81, 16.75, 16.3, 11.8, 11.7. HRMS ( $\text{ESI}^+$ ): calc.

for  $C_{67}H_{88}NaO_{18}S$   $[M+Na]^+$  1235.5584, found: 1235.5589

**2-(2-Propylsulfinyl)benzyl 2-O-(2S)-methylbutyryl-3-O-(2-O-levulinoyloxy-3,4,6-tri-O-benzyl- $\beta$ -D-glucopyranosyl)-4-O-(2,3-O-(1-methylethylidene)-4-O-(2S)-methylbutyryl- $\alpha$ -L-rhamnopyranosyl)- $\alpha$ -L-rhamnopyranoside (4)**

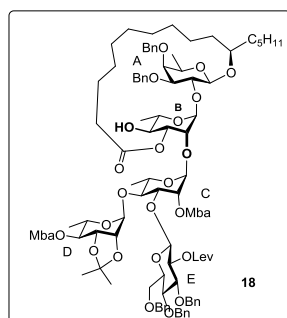


To a solution of **17** (245.0 mg, 0.20 mmol) in wet  $CH_3CN$  (4.0 mL, containing ca 5% water) was added PIFA (95.5 mg, 0.22 mmol). The reaction mixture was stirred at room temperature for 10 min, then diluted with water, extracted with EtOAc. The organic layer was washed with saturated  $NaHCO_3$ , dried with  $Na_2SO_4$ , filtered, and the filtrate was concentrated *in vacuo*. The residue was subjected to flash column chromatography to afford **4** as a colorless syrup (238.0 mg,

96%).  $R_f$  = 0.24 (petroleum ether-EtOAc 2:1). A sulfoxide mixture (*R* and *S* 1:1).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.88-7.85 (m, 2H, Ar-CH), 7.50-7.46 (m, 2H, Ar-CH), 7.40-7.21 (m, 30H, Ar-CH), 7.15-7.12 (m, 4H, Ar-CH), 5.36 (s, 1H), 5.33 (s, 1H), 5.26 (dd,  $J$  = 1.2, 2.8 Hz, 1H), 5.22 (dd,  $J$  = 1.2, 2.8 Hz, 1H), 4.92 (t,  $J$  = 8.4 Hz, 2H), 4.87-4.74 (m, 6H), 4.72-4.62 (m, 6H), 4.58-4.48 (m, 8H), 4.41 (d,  $J$  = 11.6 Hz, 1H), 4.37 (d,  $J$  = 12.0 Hz, 1H), 4.12-4.05 (m, 6H), 3.78-3.60 (m, 12H), 3.54 (t,  $J$  = 9.2 Hz, 2H), 3.47-3.43 (m, 2H), 2.88-2.71 (m, 4H), 2.67-2.63 (m, 4H), 2.47-2.36 (m, 6H), 2.11 (s, 3H,  $COCH_3$ ), 2.11 (s, 3H,  $COCH_3$ ), 1.72-1.62 (m, 4H), 1.54-1.43 (m, 4H), 1.50 (s, 3H,  $CH_3$ ), 1.48 (s, 3H,  $CH_3$ ), 1.33-1.22 (m, 18H,  $CH_3$ ), 1.16-1.09 (m, 24H,  $CH_3$ ), 0.93-0.88 (m, 12H,  $CH_3$ ).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  206.33, 206.31, 176.1, 176.04, 176.02, 175.98, 171.97, 171.87, 141.7, 141.0, 138.5, 138.4, 138.24, 138.22, 138.0, 137.9, 135.1, 134.7, 131.2, 131.1, 129.7, 129.2, 129.1, 129.0, 128.6, 128.53, 128.48, 128.18, 128.17, 128.1, 128.0, 127.93, 127.86, 127.85, 127.7, 127.6, 125.7, 125.2, 109.7, 109.6, 101.4, 101.3, 98.4, 98.3, 97.6, 97.2, 83.3, 78.6, 78.3, 78.13, 78.12, 76.8, 76.7, 76.54, 76.52, 75.9, 75.8, 75.7, 75.25, 75.22, 75.19, 73.8, 73.73, 73.67, 73.6, 73.4, 73.3, 72.5, 72.4, 69.0, 68.9, 67.7, 67.5, 66.1, 65.2, 65.02, 64.99, 54.3, 53.9, 41.2, 41.15, 41.09, 38.2, 30.0, 27.9, 27.8, 27.04, 27.01, 26.92, 26.90, 26.8, 26.7, 18.5, 18.4, 17.8, 17.2, 16.79, 16.78, 16.7, 16.3, 16.2, 13.6, 13.2, 11.74, 11.73, 11.7. HRMS (ESI $^+$ ): calc. for  $C_{67}H_{88}NaO_{19}S$   $[M+Na]^+$  1251.5533, found: 1251.5572.

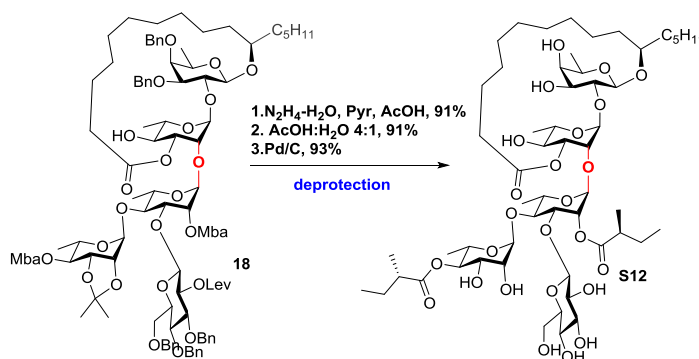
**5. Problematic site selectivity of [3+2] coupling, related to Scheme 4**

**11(S)-Hydroxyhexadecanoic acid 11-O-2-O-levulinoyloxy-3,-4,6-tri-O-benzyl- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 3)-O-[2,3-O-(1-methylethylidene)-4-O-(2S)-methylbutyryl- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 4)]-2-O-(2S)-methylbutyryl- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)-O- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)-3,4-di-O-benzyl- $\beta$ -D-fucopyranoside 1,3'-Lactone (18)**

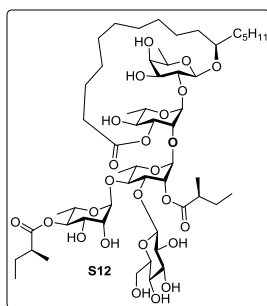


A solution of **11** (12.0 mg, 0.016 mmol), DTBMP (4.0 mg, 0.020 mmol) and **4** (20.3 mg, 0.016 mmol) in  $CH_2Cl_2$  (0.33 mL) in the presence of 4 Å MS (100 wt%) was stirred for 10 min at 0 °C. After addition of  $Tf_2O$  (2.8  $\mu$ L, 0.016 mmol), the solution was stirred at 0 °C for 1 h. The reaction mixture was quenched with  $Et_3N$ , filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried with  $Na_2SO_4$ , concentrated, and purified by silica gel flash column chromatography to give **18** (17.0 mg, 58%) as a colorless syrup.  $R_f$

= 0.51 (petroleum ether-EtOAc 3:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41-7.21 (m, 23H, Ar-CH), 7.17-7.15 (m, 2H, Ar-CH), 5.42 (s, 1H, H-1b), 5.27 (s, 1H, H-1d), 5.21 (s, 1H, H-2c), 4.94 (dd,  $J$  = 8.0, 8.8 Hz, 1H, H-2e), 4.85 (dd,  $J$  = 8.0, 10.0 Hz, 1H, H-4d), 4.82-4.79 (m, 2H,  $\text{PhCH}_2$ ), 4.78 (dd,  $J$  = 2.8, 10.0 Hz, 1H, H-3b), 4.72 (d,  $J$  = 11.2 Hz, 1H,  $\text{PhCH}_2$ ), 4.71 (d,  $J$  = 10.8 Hz, 1H,  $\text{PhCH}_2$ ), 4.69 (s, 1H, H-1c), 4.67-4.63 (m, 3H,  $\text{PhCH}_2$ ), 4.60-4.54 (m, 4H,  $\text{PhCH}_2$ ,  $\text{PhCH}_2$ ,  $\text{PhCH}_2$ , H-1e), 4.47-4.40 (m, 1H, H-5b), 4.26 (s, 1H, H-2b), 4.23 (d,  $J$  = 7.6 Hz, 1H, H-1a), 4.17 (dd,  $J$  = 3.2, 8.8 Hz, 1H, H-3c), 4.14-4.05 (m, 2H, H-2d, H-2a), 4.12 (dd,  $J$  = 5.2, 7.6 Hz, 1H, H-3d), 3.95 (dd,  $J$  = 3.2, 11.6 Hz, 1H, H-6e<sub>1</sub>), 3.76 (t,  $J$  = 9.2 Hz, 1H, H-4e), 3.71 (d,  $J$  = 11.6 Hz, 1H, H-6e<sub>2</sub>), 3.65-3.55 (m, 5H, H-5c, H-4b, H-5d, H-4c, H-3e), 3.54 (dd,  $J$  = 3.6, 9.6 Hz, 1H, H-3a), 3.48-3.45 (m, 3H, H-4a, H-5e, H-11), 3.38-3.31 (m, 1H, H-5a), 2.77-2.70 (m, 1H,  $\text{COCH}_2$ ), 2.64 (t,  $J$  = 6.4 Hz, 2H, H-2), 2.48-2.36 (m, 3H,  $\text{COCH}(\text{CH}_3)$ ,  $\text{COCH}_2$ ), 2.32-2.22 (m, 2H,  $\text{COCH}(\text{CH}_3)$ ,  $\text{COCH}_2$ ), 2.10 (s, 3H,  $\text{COCH}_3$ ), 1.88 (brs, 1H, 4b-OH), 1.78-1.67 (m, 2H), 1.67-1.59 (m, 4H), 1.56-1.39 (m, 7H), 1.50 (s, 3H,  $\text{CH}_3$ ), 1.35 (s, 3H,  $\text{CH}_3$ ), 1.28-1.18 (m, 26H), 1.27 (d,  $J$  = 6.0 Hz, 3H,  $\text{CH}_3$ ), 1.19 (d,  $J$  = 6.8 Hz, 3H,  $\text{CH}_3$ ), 1.11 (d,  $J$  = 6.4 Hz, 3H,  $\text{CH}_3$ ), 1.08 (d,  $J$  = 6.8 Hz, 3H,  $\text{CH}_3$ ), 1.05 (d,  $J$  = 6.0 Hz, 3H,  $\text{CH}_3$ ), 0.95 (t,  $J$  = 7.4 Hz, 3H,  $\text{CH}_3$ ), 0.88 (t,  $J$  = 6.8 Hz, 3H,  $\text{CH}_3$ ), 0.85 (t,  $J$  = 6.8 Hz, 3H,  $\text{CH}_3$ ), 0.79 (d,  $J$  = 5.2 Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  206.4, 176.0, 175.7, 175.6, 172.0, 138.9, 138.6, 138.3, 138.2, 138.1, 128.72, 128.70, 128.67, 128.6, 128.5, 128.3, 128.2, 128.0, 127.9, 127.85, 127.79, 127.5, 127.4, 127.1, 109.7, 101.3, 98.7, 98.5, 98.3, 84.4, 83.3, 80.3, 78.8, 77.9, 76.6, 76.3, 76.0, 75.82, 75.79, 75.6, 75.3, 75.2, 75.0, 74.4, 73.9, 73.4, 72.9, 71.3, 71.2, 70.7, 70.4, 69.4, 68.1, 67.5, 64.8, 41.3, 41.1, 38.3, 34.5, 34.4, 34.0, 32.2, 30.0, 29.9, 29.4, 28.0, 27.8, 27.4, 27.2, 27.1, 27.0, 26.8, 26.6, 26.4, 26.1, 24.2, 24.0, 22.9, 18.0, 17.9, 17.2, 16.8, 16.6, 16.3, 14.4, 11.7. HRMS (ESI<sup>+</sup>): calc. for  $\text{C}_{99}\text{H}_{136}\text{NaO}_{27}$   $[\text{M}+\text{Na}]^+$  1779.9161, found: 1779.9181.

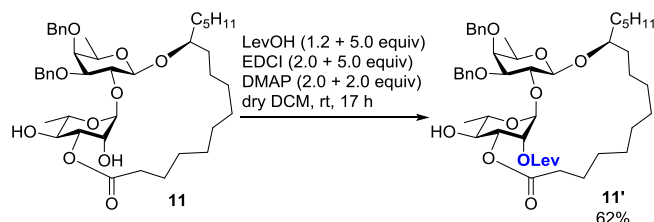


**11(*S*)-Hydroxyhexadecanoic acid 11-*O*- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 3)-*O*-[4-*O*-(2*S*)-methylbutyryl- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 4)]-2-*O*-(2*S*)-methylbutyryl- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)-*O*- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)- $\beta$ -D-fucopyranoside 1,3'-Lactone (S12)**

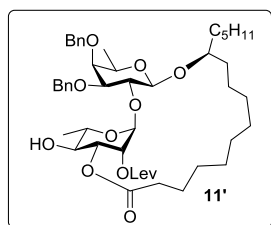


To a solution of **18** (23.7 mg, 0.013 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.27 mL) were added pyridine (32.6  $\mu\text{L}$ , 0.40 mmol), AcOH (23.0  $\mu\text{L}$ , 0.40 mmol) and hydrazine hydrate (3.3  $\mu\text{L}$ , 0.067 mmol). The reaction mixture was stirred at room temperature for 4 h. Then it was quenched with aqueous  $\text{NaHCO}_3$  and extracted with EtOAc. The combined organic extracts were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated. The residue was purified by column chromatography to afford the desired alcohol as a colorless syrup (20.3 mg, 91%). The obtained alcohol (20.3 mg,

0.012 mmol) was dissolved in AcOH–H<sub>2</sub>O (4:1, v/v, 2 mL), and the resulting mixture was warmed gradually to 65 °C. The mixture was stirred for 6 h at the same temperature, then the mixture was cooled and concentrated to give the residue. The residue was purified by column chromatography to afford the desired alcohol as a colorless syrup (18.0 mg, 91%). the obtained alcohol (18.0 mg, 0.011 mmol) was subjected to hydrogenation (H<sub>2</sub>) with catalytic 10% Pd-C in ethanol (5.0 mL) for 36 h. After being filtered and concentrated, the residue was purified by column chromatography to afford compound **S12** as a white solid (12.1 mg, 93%). *R*<sub>f</sub> = 0.43 (CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>OH 10:1). mp 123–133 °C; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = –29.14 (*c*, 0.70 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N)  $\delta$  6.34 (s, 1H, H-1b), 6.10 (s, 1H, H-1d), 6.04 (dd, *J* = 1.2, 3.2 Hz, 1H, H-2c), 5.72 (t, *J* = 9.2 Hz, 1H, H-4d), 5.47 (dd, *J* = 3.2, 10.0 Hz, 1H, H-3b), 5.19 (s, 1H, H-1c), 5.12 (s, 1H, H-2b), 5.03–4.96 (m, 1H, H-5b), 4.80 (brs, 1H, H-2d), 4.77 (d, *J* = 7.6 Hz, 1H, H-1e), 4.73 (d, *J* = 8.0 Hz, 1H, H-1a), 4.58–4.52 (m, 2H, H-3c, H-2a), 4.42–4.36 (m, 4H, H-3d, H-4b, H-5c, H-6e<sub>1</sub>), 4.24–4.16 (m, 3H, H-5d, H-4c, H-3a), 4.10 (m, *J* = 5.6, 12.0 Hz, 1H, H-6e<sub>2</sub>), 4.05–3.95 (m, 3H, H-3e, H-4e, H-4a), 3.88 (t, *J* = 8.0 Hz, 1H, H-2e), 3.84–3.79 (m, 2H, H-5a, H-11), 3.74–3.70 (m, 1H, H-5e), 2.68–2.61 (m, 1H, COCH(CH<sub>3</sub>)), 2.58–2.50 (m, 2H, H-11), 2.46–2.37 (m, 1H, COCH(CH<sub>3</sub>)), 1.58 (d, *J* = 6.0 Hz, 3H, CH<sub>3</sub>), 1.56 (d, *J* = 6.0 Hz, 3H, CH<sub>3</sub>), 1.53 (d, *J* = 6.0 Hz, 3H, CH<sub>3</sub>), 1.30 (d, *J* = 6.0 Hz, 3H, CH<sub>3</sub>), 1.21 (d, *J* = 7.2 Hz, 3H, CH<sub>3</sub>), 1.04 (d, *J* = 7.2 Hz, 3H, CH<sub>3</sub>), 0.95 (t, *J* = 7.6 Hz, 3H, CH<sub>3</sub>), 0.83 (t, *J* = 6.8 Hz, 3H, CH<sub>3</sub>), 0.80 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>5</sub>N)  $\delta$  177.3, 176.6, 176.0, 105.9, 103.6, 102.4, 100.8, 99.3, 80.7, 80.5, 78.8, 78.7, 78.2, 78.1, 77.4, 77.1, 75.44, 75.40, 74.0, 73.9, 73.5, 72.6, 72.0, 71.5, 70.5, 70.4, 69.2, 68.4, 68.3, 63.6, 41.9, 41.6, 35.7, 35.4, 35.2, 32.6, 30.6, 28.7, 28.1, 27.5, 27.4, 27.3, 27.1, 26.8, 25.2, 24.2, 23.3, 18.8, 18.7, 18.2, 17.6, 17.4, 17.0, 14.6, 12.1, 11.8. HRMS (ESI<sup>+</sup>): calc. for C<sub>56</sub>H<sub>96</sub>NaO<sub>25</sub> [M+Na]<sup>+</sup> 1191.6133, found: 1191.6131.

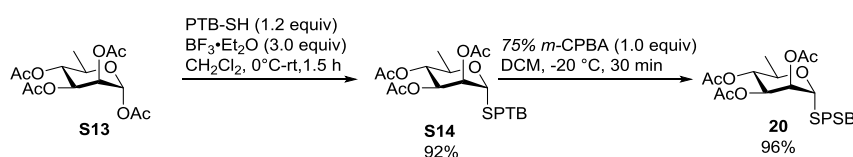


**11(S)-Hydroxyhexadecanoic acid 11-*O*-2-*O*-levulinoyloxy- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)-3,4-di-*O*-benzyl- $\beta$ -D-fucopyranosid 1,3'-Lactone (11')**

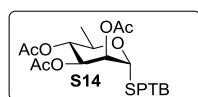


To a solution of **11** (15.0 mg, 0.21 mmol) was added levulinic Acid (LevOH, 2.5  $\mu$ L, 0.25 mmol), DMAP (5.0 mg, 0.41 mmol) and EDCI (7.9 mg, 0.41 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.2 mL) at 0 °C, the resulting solution was stirred at room temperature for 7 h, TLC indicated the reactant was remaining, and then additional levulinic acid (LevOH, 10.0  $\mu$ L, 0.10 mmol), DMAP (5.0 mg, 0.41 mmol) and EDCI (7.9 mg, 0.41 mmol) was added, the resulting solution continued to stir at room temperature for 10 h, TLC indicated no significant progress in the reaction. The mixture was quenched with H<sub>2</sub>O and extracted repeatedly with EtOAc. The combined organic layer was washed with brine, the organic layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to give compound **11'** (10.6 mg, 62%) as a white solid. *R*<sub>f</sub> = 0.59 (petroleum ether–EtOAc 2:1). [ $\alpha$ ]<sub>D</sub><sup>25</sup> = –23.40 (*c*, 0.50 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.32–7.24 (m, 10H, Ar-CH), 5.46

(dd,  $J = 1.8, 3.0$  Hz, 1H, H-2'), 5.35 (d,  $J = 0.6$  Hz, 1H, H-1'), 4.92 (dd,  $J = 3.0, 10.2$  Hz, 1H, H-3'), 4.88 (d,  $J = 12.0$  Hz, 1H, PhCH<sub>2</sub>), 4.65 (d,  $J = 12.0$  Hz, 1H, PhCH<sub>2</sub>), 4.61 (d,  $J = 11.4$  Hz, 1H, PhCH<sub>2</sub>), 4.51 (d,  $J = 11.4$  Hz, 1H, PhCH<sub>2</sub>), 4.47-4.43 (m, 1H, H-5'), 4.26 (d,  $J = 7.8$  Hz, 1H, H-1), 4.02 (dd,  $J = 7.8, 9.6$  Hz, 1H, H-2), 3.65 (t,  $J = 10.2$  Hz, 1H, H-4'), 3.57 (dd,  $J = 2.4, 9.6$  Hz, 1H, H-3), 3.54 (d,  $J = 1.8$  Hz, 1H, H-4), 3.51-3.47 (m, 1H, H-11), 3.42-3.39 (m, 1H, H-5), 2.74-2.68 (m, 1H, CH<sub>2</sub>CO), 2.63-2.57 (m, 2H, CH<sub>2</sub>CO), 2.51-2.47 (m, 1H, CH<sub>2</sub>CO), 2.34-2.24 (m, 2H, H-2), 2.15 (s, 3H, COCH<sub>3</sub>), 2.03 (s, 1H, OH), 1.28 (d,  $J = 6.6$  Hz, 3H, CH<sub>3</sub>), 1.13 (d,  $J = 6.0$  Hz, 3H, CH<sub>3</sub>), 0.84 (t,  $J = 7.2$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  206.4, 174.8, 171.7, 138.7, 138.0, 128.7, 128.6, 128.4, 128.3, 127.9, 127.8, 101.3, 97.0, 85.1, 80.5, 75.6, 74.6, 74.1, 72.6, 71.4, 70.8, 70.6, 70.5, 68.1, 38.1, 34.5, 34.4, 34.1, 32.2, 30.1, 29.7, 28.1, 27.8, 27.3, 26.8, 26.37, 26.35, 24.2, 23.8, 22.9, 17.7, 17.2, 14.4. HRMS (ESI<sup>+</sup>): calc. for C<sub>47</sub>H<sub>68</sub>NaO<sub>12</sub> [M+Na]<sup>+</sup> 847.4603, found: 847.4565.

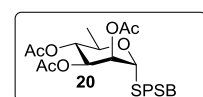


### S-2-(2-Propylthiol)benzyl 2,3,4-tri-O-acetyl-6-deoxy- $\alpha$ -D-mannopyranose (S14)



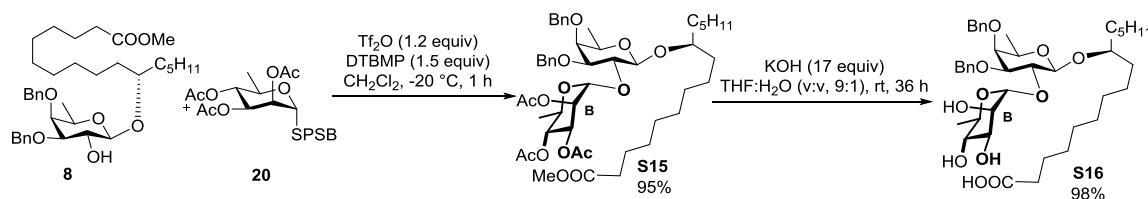
Compound **S13**<sup>6</sup> (200.0 mg, 0.60 mmol) and 4 Å MS (100 wt%) was added to a round-bottom flask under argon. a solution of PTB-SH (143.0 mg, 0.72 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) was added to the flask. After the addition of BF<sub>3</sub>·Et<sub>2</sub>O (474.0  $\mu$ L, 1.80 mmol) at 0  $^\circ$ C, the reaction mixture was stirred at room temperature for 1.5 h. The reaction mixture was quenched with Et<sub>3</sub>N, then filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated *in vacuo*, and purified by silica gel column chromatography to give **S14** (261.0 mg, 92%) as a colorless syrup.  $R_f = 0.29$  (petroleum ether-EtOAc 5:1).  $[\alpha]_D^{25} = 129.70$  (c, 1.02 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 (d,  $J = 7.2$  Hz, 1H, Ar-CH), 7.30 (d,  $J = 7.6$  Hz, 1H, Ar-CH), 7.19 (t,  $J = 7.2$  Hz, 1H, Ar-CH), 7.14 (t,  $J = 7.6$  Hz, 1H, Ar-CH), 5.23 (d,  $J = 3.2$  Hz, 1H, H-2), 5.19 (dd,  $J = 3.6, 10.0$  Hz, 1H, H-3), 5.11 (s, 1H, H-1), 5.06 (t,  $J = 10.0$  Hz, 1H, H-4), 4.23 (m, 1H, H-5), 4.02 (d,  $J = 12.4$  Hz, 1H, PhCH<sub>2</sub>), 3.92 (d,  $J = 12.4$  Hz, 1H, PhCH<sub>2</sub>), 3.78 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.16 (s, 3H, COCH<sub>3</sub>), 2.02 (s, 3H, COCH<sub>3</sub>), 1.93 (s, 3H, COCH<sub>3</sub>), 1.28 (t,  $J = 7.6$  Hz, 6H, CH<sub>3</sub>), 1.17 (d,  $J = 6.4$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.2, 170.1, 170.0, 138.8, 135.7, 132.9, 130.3, 128.1, 127.0, 81.9, 71.5, 71.3, 69.9, 67.2, 39.0, 33.7, 23.4, 23.3, 21.1, 21.0, 20.8, 17.5. HRMS (ESI) calc. for C<sub>22</sub>H<sub>30</sub>NaO<sub>7</sub>S<sub>2</sub> [M+Na]<sup>+</sup> 493.1325, found: 493.1342.

### S-2-(2-Propylsulfinyl)benzyl 2,3,4-tri-O-acetyl-6-deoxy- $\alpha$ -D-mannopyranose (20)

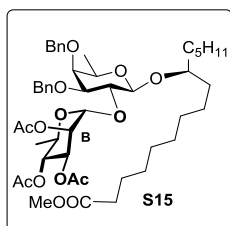


A solution of **S14** (1.24 g, 2.64 mmol) was stirred for 10 min at -20  $^\circ$ C. After addition of 3-chloroperbenzoic acid (*m*-CPBA, 606.3 mg, 2.64 mmol), the solution was stirred at -20  $^\circ$ C for 30 min. The reaction mixture was quenched with saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and extracted with EtOAc. The organic phase was washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>, concentrated, and purified by silica gel flash column chromatography to give **20** (1.23 g, 96%) as a colorless syrup.  $R_f = 0.18$  (petroleum ether-EtOAc 3:1). A sulfoxide mixture (*R* and *S* 1:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 (t,  $J = 7.2$  Hz, 2H, Ar-CH), 7.47-7.36 (m, 6H, Ar-CH), 5.27 (brs, 1H, H-2),

5.23 (brs, 1H, H-2), 5.19 (s, 1H, H-1), 5.17-5.12 (m, 2H, H-3, H-3), 5.06 (t,  $J = 9.6$  Hz, 1H, H-4), 5.05 (t,  $J = 9.6$  Hz, 1H, H-4), 5.03 (s, 1H, H-1), 4.20-4.09 (m, 2H, H-5, H-5), 3.94-3.84 (m, 4H, PhCH<sub>2</sub>), 3.04-2.90 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>, CH(CH<sub>3</sub>)<sub>2</sub>), 2.11 (s, 3H, COCH<sub>3</sub>), 2.08 (s, 3H, COCH<sub>3</sub>), 2.02 (s, 3H, COCH<sub>3</sub>), 2.01 (s, 3H, COCH<sub>3</sub>), 1.93 (s, 6H, COCH<sub>3</sub>), 1.29 (d,  $J = 6.8$  Hz, 3H, CH<sub>3</sub>), 1.26 (d,  $J = 7.2$  Hz, 3H, CH<sub>3</sub>), 1.21 (d,  $J = 6.0$  Hz, 3H, CH<sub>3</sub>), 1.16-1.13 (m, 9H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.14, 170.10, 170.07, 170.0, 141.5, 141.2, 135.3, 135.2, 131.3, 130.8, 130.7, 128.7, 128.6, 126.1, 125.9, 82.6, 81.2, 71.2, 71.0, 70.9, 69.7, 69.6, 67.6, 54.4, 54.1, 31.5, 30.5, 21.1, 21.0, 20.9, 20.8, 17.7, 17.6, 17.5, 17.3, 13.7, 13.3. HRMS (ESI) calc. for C<sub>22</sub>H<sub>30</sub>NaO<sub>8</sub>S<sub>2</sub> [M+Na]<sup>+</sup> 509.1274, found: 509.1282.

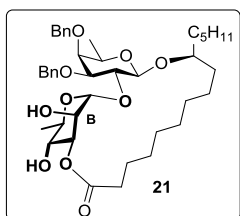


### 1-(Methoxycarbonyl)pentadec-10(*S*)-yl 2-*O*-(2,3,4-tri-*O*-acetyl-6-deoxy- $\alpha$ -D-mannopyranosyl)-3,4-di-*O*-benzyl- $\beta$ -D-fucopyranoside (**S15**)



A solution of **20** (54.0 mg, 0.11 mmol), DTBMP (28.5mg, 0.14 mmol) and **8** (56.7 mg, 0.092 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.8 mL) in the presence of 4 Å MS (100 wt%) was stirred for 10 min at -20 °C. After addition of Tf<sub>2</sub>O (18.7  $\mu$ L, 0.11 mmol), the solution was stirred at -20 °C for 1 h. The reaction mixture was quenched with Et<sub>3</sub>N, filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>, concentrated, and purified by silica gel flash column chromatography to give **S15** (77.5 mg, 95%) as a colorless syrup.  $R_f = 0.29$  (petroleum ether-EtOAc 5:1).  $[\alpha]_D^{25} = 25.50$  ( $c$ , 0.4 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36-7.24 (m, 10H, Ar-CH), 5.28 (s, 1H, H-2'), 5.23 (s, 1H, H-1'), 5.25 (dd,  $J = 3.2, 9.6$  Hz, 1H, H-3'), 4.95 (t,  $J = 10.0$  Hz, 1H, H-4'), 4.93 (d,  $J = 10.4$  Hz, 1H, PhCH<sub>2</sub>), 4.74 (d,  $J = 11.6$  Hz, 1H, PhCH<sub>2</sub>), 4.71 (d,  $J = 12.0$  Hz, 1H, PhCH<sub>2</sub>), 4.62 (d,  $J = 11.6$  Hz, 1H, PhCH<sub>2</sub>), 4.30 (d,  $J = 8.0$  Hz, 1H, H-1), 4.23 (m, 1H, H-5'), 4.01 (dd,  $J = 8.0, 10.0$  Hz, 1H, H-2), 3.64 (s, 3H, OCH<sub>3</sub>), 3.62 (d,  $J = 2.4$  Hz, 1H, H-4), 3.56 (m, 1H, H-11), 3.47 (dd,  $J = 2.8, 10.0$  Hz, 1H, H-3), 3.44 (m, 1H, H-5), 2.28 (t,  $J = 7.6$  Hz, 2H, CH<sub>2</sub>CO), 2.09 (s, 3H, COCH<sub>3</sub>), 1.95 (s, 3H, COCH<sub>3</sub>), 1.84 (s, 3H, COCH<sub>3</sub>), 1.65-1.55 (m, 4H), 1.48-1.36 (m, 4H), 1.29-1.20 (m, 18H), 1.18 (d,  $J = 6.4$  Hz, 3H, CH<sub>3</sub>), 0.94 (d,  $J = 6.4$  Hz, 3H, CH<sub>3</sub>), 0.83 (t,  $J = 7.0$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  174.6, 170.3, 170.2, 169.9, 138.9, 138.1, 128.5, 128.4, 128.3, 127.9, 127.7, 102.3, 97.1, 82.0, 79.1, 76.4, 75.0, 73.7, 72.9, 71.4, 70.5, 69.72, 69.69, 66.2, 51.6, 34.4, 34.3, 33.4, 32.2, 30.0, 29.71, 29.68, 29.5, 29.4, 25.5, 25.2, 24.5, 22.8, 21.1, 21.0, 17.3, 17.1, 14.3. HRMS (ESI<sup>+</sup>): calc. for C<sub>49</sub>H<sub>72</sub>NaO<sub>14</sub> [M+Na]<sup>+</sup> 907.4814, found: 907.4830.

### 11(*S*)-Hydroxyhexadecanoic acid 11-*O*-2-*O*-(6-deoxy- $\alpha$ -D-mannopyranosyl)-3,4-di-*O*-benzyl- $\beta$ -D-fucopyranoside 1,3'-Lactone (**21**)

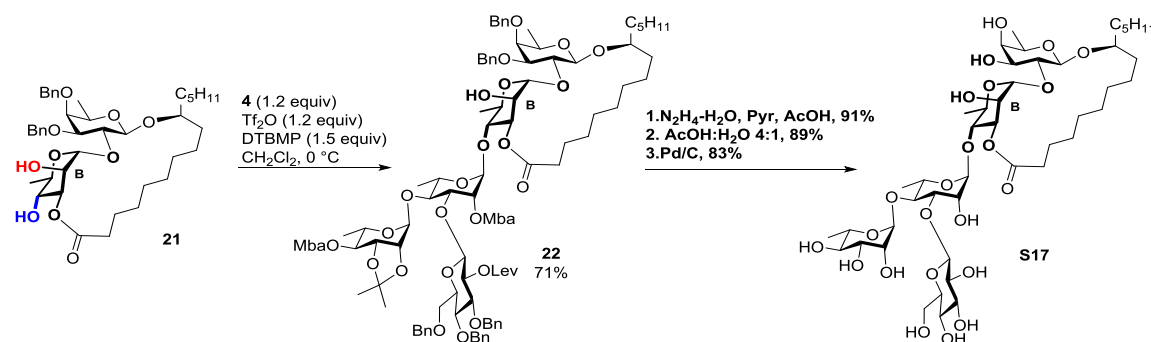


A mixture of **S15** (131.0 mg, 0.15 mmol) and KOH (141.0 mg, 2.51 mmol) in THF-H<sub>2</sub>O (9:1, v/v, 3 mL) was stirred at 55 °C for 34 h. Then the reaction was neutralized with acetic acid and extracted with EtOAc. The combined organic extracts were washed with brine, dried

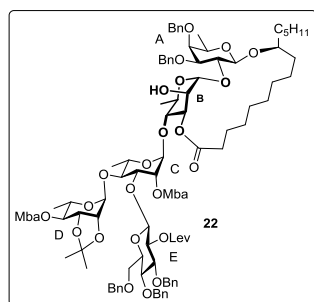
S16



over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated. The resulting residue was purified by column chromatography to afford **S16** (107.5 mg, 98%) as a white solid.  $R_f = 0.56$  ( $\text{CH}_2\text{Cl}_2$ -EtOAc 2:1). Compound **21** was synthesized as described procedure in compound **7**. HRMS ( $\text{ESI}^+$ ): calc. for  $\text{C}_{42}\text{H}_{64}\text{NaO}_{11} [\text{M}+\text{Na}]^+$  767.4341, found: 767.4342. mp 148-158 °C;  $[\alpha]_{\text{D}}^{25} = 28.54$  (c, 0.48 in  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39-7.24 (m, 10H, Ar-CH), 5.28 (s, 1H, H-1b), 5.03 (dd,  $J = 2.8, 10.0$  Hz, 1H, H-3b), 4.95 (d,  $J = 11.6$  Hz, 1H,  $\text{PhCH}_2$ ), 4.73 (d,  $J = 11.2$  Hz, 2H,  $\text{PhCH}_2$ ), 4.54 (d,  $J = 11.2$  Hz, 1H,  $\text{PhCH}_2$ ), 4.24 (d,  $J = 8.0$  Hz, 1H, H-1a), 3.99 (dd,  $J = 8.0, 8.8$  Hz, 1H, H-2a), 3.93 (m, 1H, H-5b), 3.87 (s, 1H, H-2b), 3.63 (t,  $J = 2.0$  Hz, 1H, H-4a), 3.49-3.41 (m, 4H, H-3a, H-4b, H-5a, H-11), 2.52-2.46 (m, 1H,  $\text{CH}_2\text{CO}$ ), 2.40-2.33 (m, 1H,  $\text{CH}_2\text{CO}$ ), 1.86 (brs, 1H, OH), 1.74-1.54 (m, 4H), 1.49-1.37 (m, 4H), 1.36-1.23 (m, 17H), 1.19 (d,  $J = 6.4$  Hz, 3H,  $\text{CH}_3$ ), 1.01 (d,  $J = 6.0$  Hz, 3H,  $\text{CH}_3$ ), 0.84 (t,  $J = 6.8$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.9, 138.9, 138.2, 128.7, 128.39, 128.37, 128.2, 128.1, 127.8, 103.8, 99.3, 82.3, 80.2, 76.3, 74.9, 74.8, 74.6, 72.8, 71.5, 70.6, 70.5, 68.7, 35.1, 35.0, 34.8, 32.0, 30.0, 28.1, 28.0, 27.6, 27.0, 26.0, 25.6, 24.9, 22.8, 17.3, 17.1, 14.3. HRMS ( $\text{ESI}^+$ ): calc. for  $\text{C}_{42}\text{H}_{62}\text{NaO}_{10} [\text{M}+\text{Na}]^+$  749.4235, found: 749.4258.



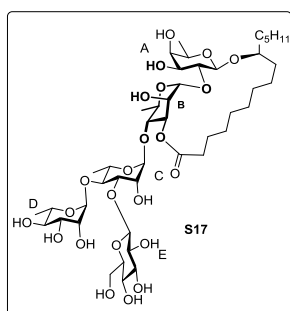
**11(S)-Hydroxyhexadecanoic acid 11-O-2-O-levulinoyloxy-3,4,6-tri-O-benzyl- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 3)-O-[2,3-O-(1-methylethylidene)-4-O-(2S)-methylbutyryl- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 4)]-2-O-(2S)-methylbutyryl- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-O-6-deoxy- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-3,4-di-O-benzyl- $\beta$ -D-fucopyranoside 1,3'-Lactone (**22**)**



A solution of **4** (33.8 mg, 0.033 mmol), DTBMP (8.5 mg, 0.041 mmol) and **21** (20.0 mg, 0.028 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.55 mL) in the presence of 4 Å MS (100 wt%) was stirred for 10 min at 0 °C. After addition of  $\text{Tf}_2\text{O}$  (5.5  $\mu\text{L}$ , 0.033 mmol), the solution was stirred at 0 °C for 1 h. The reaction mixture was quenched with  $\text{Et}_3\text{N}$ , filtered through Celite and extracted with ethyl acetate. The organic phase was washed with  $\text{H}_2\text{O}$ , brine, dried with  $\text{Na}_2\text{SO}_4$ , concentrated, and purified by silica gel flash column chromatography to give **22** (34.4 mg, 71%) as a colorless syrup.  $R_f = 0.28$  (petroleum ether-EtOAc 4:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36-7.10 (m, 25H, Ar-CH), 5.34-5.31 (m, 1H, H-3b), 5.34 (s, 2H, H-1b, H-1d), 5.07 (s, 1H, H-2c), 4.91 (d,  $J = 12.0$  Hz, 1H,  $\text{PhCH}_2$ ), 4.90 (t,  $J = 9.2$  Hz, 1H, H-2e), 4.83 (dd,  $J = 8.0, 10.0$  Hz, 1H, H-4d), 4.76 (s, 1H, H-1c), 4.71-4.48 (m, 8H,  $\text{PhCH}_2$ ), 4.44 (d,  $J = 7.6$  Hz, 1H, H-1e), 4.36 (d,  $J = 12.4$  Hz, 1H,  $\text{PhCH}_2$ ), 4.23-4.19 (m, 1H, H-5b), 4.20 (d,  $J = 7.6$  Hz, 1H, H-1a), 4.10 (d,  $J = 4.8$  Hz, 1H, H-2d), 4.04 (dd,  $J = 5.2, 7.6$  Hz, 1H, H-3d), 3.98 (dd,  $J = 8.0, 9.6$  Hz, 1H, H-2a), 3.88 (dd,  $J = 3.2, 9.2$  Hz, 1H, H-3c), 3.87 (s, 1H, H-2b), 3.73-3.63 (m, 6H, H-5d, H-5c, H-4b, H-4c, H-4e, H-6e<sub>1</sub>), 3.54 (d,  $J = 2.0$  Hz, 1H,

H-4a), 3.52-3.45 (m, 2H, jia-11, H-3e), 3.42-3.33 (m, 3H, H-5a, H-3a, H-6e<sub>2</sub>), 3.23 (d,  $J = 9.2$  Hz, 1H, H-5e), 2.79-2.71 (m, 1H), 2.65 (td,  $J = 2.0, 7.2$  Hz, 2H), 2.49-2.36 (m, 5H), 2.11 (s, 3H, COCH<sub>3</sub>), 2.06 (s, 1H, OH-2b), 1.49 (s, 3H, COCH<sub>3</sub>), 1.33 (s, 3H, CH<sub>3</sub>), 1.24 (d,  $J = 6.8$  Hz, 3H, CH<sub>3</sub>), 1.16 (d,  $J = 6.8$  Hz, 6H, CH<sub>3</sub>), 1.14 (d,  $J = 7.2$  Hz, 3H, CH<sub>3</sub>), 1.11 (d,  $J = 7.2$  Hz, 3H, CH<sub>3</sub>), 1.09 (d,  $J = 6.4$  Hz, 3H, CH<sub>3</sub>), 0.88 (t,  $J = 6.4$  Hz, 3H, CH<sub>3</sub>), 0.84 (t,  $J = 7.2$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  206.5, 176.0, 173.7, 171.9, 138.9, 138.5, 138.3, 138.24, 138.15, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 128.03, 127.99, 127.9, 127.8, 127.7, 127.6, 109.7, 103.4, 101.4, 99.0, 98.8, 98.0, 83.2, 80.9, 80.1, 79.0, 78.3, 77.8, 76.6, 76.2, 75.8, 75.6, 75.21, 75.15, 74.82, 74.76, 73.8, 73.7, 73.2, 72.8, 72.7, 72.1, 70.42, 70.40, 68.6, 67.6, 67.5, 64.9, 41.2, 41.0, 38.2, 35.2, 34.5, 34.4, 32.9, 32.1, 32.0, 30.0, 29.9, 29.7, 28.04, 27.97, 27.84, 27.79, 27.6, 27.5, 27.0, 26.9, 26.8, 25.7, 25.6, 24.8, 22.8, 18.6, 17.9, 17.1, 16.8, 16.7, 16.2, 14.3, 11.7, 11.6. HRMS (ESI<sup>+</sup>): calc. for C<sub>99</sub>H<sub>136</sub>NaO<sub>27</sub> [M+Na]<sup>+</sup> 1779.9161, found: 1779.9157.

**11(S)-Hydroxyhexadecanoic acid 11-O- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 3)-O-[4-O-(2S)-methylbutyryl- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 4)]-2-O-(2S)-methylbutyryl- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-O-6-deoxy- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 2)-O- $\beta$ -D-fucopyranoside 1,3'-Lactone (S17)**



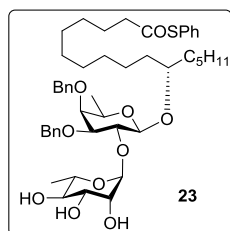
To a solution of **22** (19.0 mg, 0.011 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.22 mL) were added pyridine (26.1  $\mu$ L, 0.32 mmol), AcOH (18.6  $\mu$ L, 0.32 mmol) and hydrazine hydrate (2.6  $\mu$ L, 0.054 mmol). The reaction mixture was stirred at room temperature for 4 h. Then it was quenched with aqueous NaHCO<sub>3</sub> and extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residue was purified by column chromatography to afford the desired alcohol as a colorless syrup (16.3 mg, 91%). The obtained alcohol (16.3

mg, 0.0098 mmol) was dissolved in AcOH-H<sub>2</sub>O (4:1, v/v, 2 mL), and the resulting mixture was warmed gradually to 65 °C. The mixture was stirred for 7 h at the same temperature, then the mixture was cooled and concentrated to give the residue. The residue was purified by column chromatography to afford the desired alcohol as a colorless syrup (14.1 mg, 89%). the obtained alcohol (14.1 mg, 0.0086 mmol) was subjected to hydrogenation (H<sub>2</sub>) with catalytic 10% Pd-C in methanol (5.0 mL) for 18 h. After being filtered and concentrated, the residue was purified by column chromatography to afford compound **S17** as white solid (8.5 mg, 83%). mp 123-133 °C;  $[\alpha]_D^{25}$  -13.23 (c, 0.45 in MeOH).  $R_f$  = 0.15 (CH<sub>2</sub>Cl<sub>2</sub>-EtOAc 2:1). <sup>1</sup>H NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N)  $\delta$  6.18 (d, 1H,  $J = 1.2$  Hz, H-1d), 6.12 (dd,  $J = 2.8, 10.0$  Hz, 1H, H-3b), 5.90 (dd,  $J = 1.6, 3.0$  Hz, 1H, H-2c), 5.84 (s, 1H, H-1b), 5.79 (t,  $J = 9.4$  Hz, 1H, H-4d), 5.28 (d,  $J = 1.2$  Hz, 1H, H-1c), 5.17 (m, 1H, H-5b), 4.91 (dd,  $J = 1.8, 3.2$  Hz, 1H, H-2d), 4.80 (d,  $J = 8.0$  Hz, 1H, H-1e), 4.69 (d,  $J = 8.0$  Hz, 1H, H-1a), 4.59 (dd,  $J = 1.6, 2.0$  Hz, 1H, H-2b), 4.55 (dd,  $J = 3.4, 9.4$  Hz, 1H, H-3d), 4.49 (t,  $J = 9.8$  Hz, 1H, H-4d), 4.44-4.38 (m, 2H, H-5d, H-3c), 4.37-4.27 (m, 3H, H-5c, H-4e, H-2a), 4.22 (t,  $J = 9.2$  Hz, 1H, H-4c), 4.19 (dd,  $J = 4.4, 12.0$  Hz, 1H, H-6e<sub>1</sub>), 4.09 (t,  $J = 8.8$  Hz, 1H, H-3e), 4.06 (m, 1H, H-6e<sub>2</sub>), 4.00 (dd,  $J = 3.4, 9.4$  Hz, 1H, H-3a), 3.96 (d,  $J = 3.2$  Hz, 1H, H-4a), 3.90 (t,  $J = 8.0$  Hz, 1H, H-2e), 3.80-3.73 (m, 2H, H-5a, jia-11), 3.57 (m, 1H, H-5e), 2.69-2.59 (m, 2H), 2.55 (m, 1H), 2.40 (m, 1H), 1.85-1.72 (m, 3H), 1.70 (d,  $J = 6.0$  Hz, 3H, CH<sub>3</sub>), 1.66-1.56 (m, 6H), 1.54-1.35 (m, 23H), 1.29-1.15 (m, 9H), 1.02 (d,  $J = 6.8$  Hz, 3H, CH<sub>3</sub>), 0.96 (d,  $J = 7.4$  Hz, 3H, CH<sub>3</sub>), 0.83 (t,  $J = 7.0$  Hz, 3H, CH<sub>3</sub>), 0.78 (t,  $J = 7.6$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, C<sub>5</sub>D<sub>5</sub>N)  $\delta$  177.0, 176.7, 174.5, 106.0, 104.0, 103.6, 101.9, 100.5, 81.4, 80.0, 79.7, 79.1, 78.7, 78.6,

77.9, 75.5, 75.4, 73.83, 73.80, 73.62, 73.57, 72.8, 71.5, 71.2, 70.6, 69.0, 68.61, 68.57, 62.9, 41.9, 41.5, 35.7, 35.4, 35.3, 32.4, 30.3, 28.6, 28.3, 27.8, 27.5, 27.4, 27.3, 26.2, 25.8, 25.5, 23.2, 19.5, 18.7, 18.4, 17.5, 17.4, 16.9, 14.6, 12.2, 11.7. HRMS (ESI<sup>+</sup>): calc. for C<sub>56</sub>H<sub>96</sub>NaO<sub>25</sub> [M+Na]<sup>+</sup> 1191.6133, found: 1191.6134.

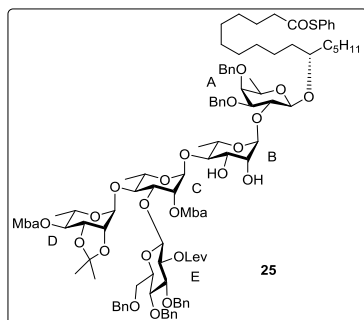
## 6. [3+2] IPRm glycosylation-macrolactonization assembly sequence to murucoidin V and IV, related to Scheme 5.

### 1-(*S*-phenylcarbonyl)pentadec-10(*S*)-yl $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)-3,4-di-*O*-benzyl- $\beta$ -D-fucopyranoside (**23**)



To a solution of **3** (234.0 mg, 0.31 mmol) in ethyl acetate (3.0 mL) at room temperature were added thiophenol (129.0  $\mu$ L, 1.26 mmol), 4-(dimethylamino)pyridine (7.7 mg, 0.063 mmol), and 1,3-dicyclohexylcarbodiimide (97.0 mg, 0.47 mmol). After 1.5 h, the additional thiophenol (129.0  $\mu$ L, 1.26 mmol), 4-(dimethylamino)pyridine (7.7 mg, 0.063 mmol), and 1,3-dicyclohexylcarbodiimide (97.0 mg, 0.47 mmol) were added into the reaction mixture, the mixture was stirred for an additional 3 h at room temperature. And then the reaction mixture was poured into saturated NaHCO<sub>3</sub> and the aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with 2 N H<sub>2</sub>SO<sub>4</sub> and dried with Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent at reduced pressure, the crude residue was chromatographed on silica gel to afford compound **23** (238.0 mg, 91%) as a white solid.  $R_f$  = 0.30 (petroleum ether-EtOAc 1:1).  $[\alpha]_D^{25}$  = -30.00 (c, 0.5 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.24-7.08 (m, 15H, Ar-CH), 5.13 (s, 1H, H-1'), 4.74 (d,  $J$  = 12.0 Hz, 1H, PhCH<sub>2</sub>), 4.53 (d,  $J$  = 11.6 Hz, 1H, PhCH<sub>2</sub>), 4.52 (d,  $J$  = 12.0 Hz, 1H, PhCH<sub>2</sub>), 4.34 (d,  $J$  = 11.6 Hz, 1H, PhCH<sub>2</sub>), 4.10 (d,  $J$  = 7.6 Hz, 1H, H-1), 4.05-3.98 (m, 1H, H-5'), 3.82 (dd,  $J$  = 8.0, 9.6 Hz, 1H, H-2), 3.61 (d,  $J$  = 2.0 Hz, 1H, H-2'), 3.47 (dd,  $J$  = 3.6, 9.6 Hz, 1H, H-3'), 3.46-3.42 (m, 2H, H-11, H-4), 3.35 (dd,  $J$  = 3.2, 9.6 Hz, 1H, H-3), 3.29-3.24 (m, 1H, H-5), 3.18 (t,  $J$  = 9.6 Hz, 1H, H-4'), 2.49 (t,  $J$  = 7.6 Hz, 2H, H-2), 1.58-1.50 (m, 2H, CH<sub>2</sub>), 1.36-1.31 (m, 4H, CH<sub>2</sub>), 1.18-1.06 (m, 21H, CH<sub>2</sub>, CH<sub>3</sub>), 1.07 (d,  $J$  = 6.4 Hz, 3H, CH<sub>3</sub>), 1.03 (d,  $J$  = 6.4 Hz, 3H, CH<sub>3</sub>), 0.71 (t,  $J$  = 6.4 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  198.1, 138.7, 138.2, 134.7, 129.5, 129.4, 128.8, 128.6, 128.4, 128.1, 127.9, 127.8, 100.6, 100.1, 84.9, 78.4, 75.6, 74.6, 74.1, 73.8, 72.6, 72.1, 71.2, 70.5, 67.7, 43.9, 34.9, 33.7, 32.2, 30.1, 29.7, 29.5, 29.4, 29.1, 25.8, 25.5, 24.9, 22.8, 17.5, 17.2, 14.3. HRMS (ESI<sup>+</sup>): calc. for C<sub>48</sub>H<sub>68</sub>NaO<sub>10</sub>S [M+Na]<sup>+</sup> 859.4425, found: 859.4461.

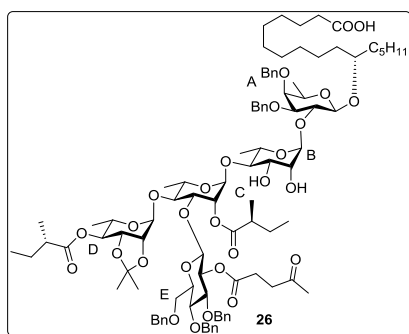
### 1-(*S*-phenylcarbonyl)pentadec-10(*S*)-yl 2-*O*-levulinoyloxy-3,4,6-tri-*O*-benzyl- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 3)-*O*-[2,3-*O*-(1-methylethylidene)-4-*O*-(2*S*)-methylbutyryl- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 4)]-2-*O*-(2*S*)-methylbutyryl- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-*O*- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)-3,4-di-*O*-benzyl- $\beta$ -D-fucopyranoside (**25**)



Compound **23** (51.0 mg, 0.061 mmol) and arylboronic acid (7.4 mmol, 0.061 mmol) were placed in a round-bottom flask equipped with a stir bar. Toluene (2.5 mL) was added to the flask, and the solution was stirred at 110 °C for overnight. The solution was then cooled to room temperature, and solvent was removed under reduced pressure to give the boronic ester **24**. Compound **4** (89.8 mg, 0.073 mmol) and DTBMP (18.8 mg, 0.091 mmol)

which was dissolved in  $\text{CH}_2\text{Cl}_2$  (0.6 mL) in the presence of 4 Å MS (100 wt%) was stirred for 15 min at  $-40\text{ }^\circ\text{C}$ . After addition of  $\text{TiF}_2\text{O}$  (12.3  $\mu\text{L}$ , 0.073 mmol), the solution was stirred at  $-40\text{ }^\circ\text{C}$  for 3 min, and then the boronic ester **24** in  $\text{CH}_2\text{Cl}_2$  (0.6 mL) was added. The reaction mixture was stirred at  $-40\text{ }^\circ\text{C}$  for 1 h and quenched with saturated aqueous  $\text{NaHCO}_3$ . The organic phase was washed with brine, dried with  $\text{Na}_2\text{SO}_4$ , concentrated, and purified by silica gel column chromatography to give compound **25** (73.0 mg, 64%) as a colorless syrup.  $R_f = 0.47$  (petroleum ether-EtOAc 2:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37-7.22 (m, 28H, Ar-CH), 7.06-7.04 (m, 2H, Ar-CH), 5.40 (brs, 1H, H-2c), 5.36 (s, 1H, H-1d), 5.27 (s, 1H, H-1b), 4.92 (t,  $J = 8.4$  Hz, 1H, H-2e), 4.90 (s, 1H, H-1c), 4.86 (d,  $J = 12.4$  Hz, 1H,  $\text{PhCH}_2$ ), 4.86 (t,  $J = 9.2$  Hz, 1H, H-4d), 4.70-4.60 (m, 5H,  $\text{PhCH}_2$ ), 4.60-4.56 (m, 2H,  $\text{PhCH}_2$ ), 4.57 (d,  $J = 9.2$  Hz, 1H, H-1e), 4.45 (d,  $J = 11.6$  Hz, 1H,  $\text{PhCH}_2$ ), 4.44 (d,  $J = 10.8$  Hz, 1H,  $\text{PhCH}_2$ ), 4.20 (d,  $J = 7.6$  Hz, 1H, H-1a), 4.20-4.14 (m, 1H, H-5b), 4.11 (dd,  $J = 3.2, 8.8$  Hz, 1H, H-3c), 4.08-4.02 (m, 2H, H-2d, H-3d), 3.95 (dd,  $J = 8.0, 9.6$  Hz, 1H, H-2a), 3.84-3.78 (m, 1H, H-5c), 3.75-3.67 (m, 4H, H-5d, H-3b, H-2b, H-4c), 3.64-3.58 (m, 3H, H-6e<sub>1</sub>, H-11, H-5e), 3.56-3.51 (m, 2H, H-4a, H-3e), 3.48-3.41 (m, 3H, H-4e, H-3a, H-6e<sub>2</sub>), 3.39-3.34 (m, 2H, H-5a, H-4b), 2.80-2.63 (m, 3H), 2.59 (t,  $J = 7.6$  Hz, 2H, H-2), 2.52-2.36 (m, 3H), 2.15 (brs, 1H, OH<sub>b-2</sub>), 2.12 (s, 3H,  $\text{COCH}_3$ ), 1.72-1.62 (m, 5H), 1.52-1.45 (m, 8H), 1.49 (s, 3H,  $\text{CH}_3$ ), 1.34 (s, 3H,  $\text{CH}_3$ ), 1.34-1.23 (m, 21H), 1.23 (d,  $J = 6.0$  Hz, 3H,  $\text{CH}_3$ ), 1.17-1.10 (m, 12H,  $\text{CH}_3$ ), 0.91 (t,  $J = 7.6$  Hz, 3H,  $\text{CH}_3$ ), 0.90 (t,  $J = 7.6$  Hz, 3H,  $\text{CH}_3$ ), 0.86 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  206.5, 197.6, 176.2, 176.0, 172.0, 138.7, 138.2, 138.0, 137.9, 134.6, 129.5, 129.4, 128.73, 128.68, 128.61, 128.57, 128.4, 128.2, 128.08, 128.05, 127.98, 127.96, 127.9, 127.8, 109.7, 101.3, 100.5, 99.6, 97.7, 84.5, 83.4, 83.0, 78.1, 77.8, 76.7, 75.8, 75.4, 75.2, 74.5, 73.8, 73.5, 73.3, 72.7, 72.4, 71.8, 71.0, 70.5, 69.3, 67.7, 66.8, 64.9, 43.9, 41.2, 41.1, 38.2, 34.8, 33.4, 32.3, 30.0, 29.9, 29.7, 29.6, 29.2, 28.0, 27.8, 27.1, 26.9, 26.8, 25.8, 25.3, 24.9, 22.9, 18.6, 17.8, 17.2, 16.8, 16.7, 16.3, 14.4, 11.75, 11.66. HRMS (ESI<sup>+</sup>): calc. for  $\text{C}_{105}\text{H}_{142}\text{NaO}_{27}\text{S}$   $[\text{M}+\text{Na}]^+$  1889.9302, found: 1889.9308.

**1-(Hydroxycarbonyl)pentadec-10(S)-yl 2-O-levulinoyloxy-3,4,6-tri-O-benzyl- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 3)-O-[2,3-O-(1-methylethylidene)-4-O-(2S)-methylbutyryl- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 4)]-2-O-(2S)-methylbutyryl- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-O- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)-3,4-di-O-benzyl- $\beta$ -D-fucopyranoside (**26**)**

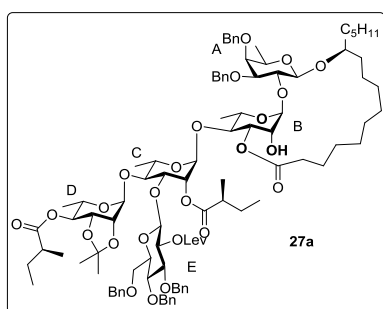


Silver trifluoroacetate (18.9 mg, 0.086 mmol) was added to a solution of compound **25** (40.0 mg, 0.021 mmol) in THF-H<sub>2</sub>O (4:1, v/v, 0.2 mL). The mixture was stirred at  $55\text{ }^\circ\text{C}$  for overnight. The precipitate was filtered off and washed with THF. Then the volatiles were removed from the filtrate under reduced pressure. Water was added to the residue, and this mixture was extracted with EtOAc. The solution was dried with  $\text{Na}_2\text{SO}_4$ , and purified by column chromatography to afford the desired acid **26** as a colorless syrup (35.7 mg,

94%).  $R_f = 0.14$  (petroleum ether-EtOAc 2:1).  $[\alpha]_D^{25} = -26.15$  (c, 0.26 in  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32-7.21 (m, 23H, Ar-CH), 7.05-7.03 (m, 2H, Ar-CH), 5.41 (brs, 1H, H-2c), 5.36 (s, 1H, H-1d), 5.26 (s, 1H, H-1b), 4.91 (t,  $J = 8.4$  Hz, 1H, H-2e), 4.87 (s, 1H, H-1c), 4.85 (d,  $J = 12.4$  Hz, 1H,  $\text{PhCH}_2$ ), 4.83 (dd,  $J = 8.4, 10.0$  Hz, 1H, H-4d), 4.71-4.56 (m, 7H,  $\text{PhCH}_2$ ), 4.57 (d,  $J = 8.0$  Hz, 1H, H-1e), 4.46 (d,  $J = 12.0$  Hz, 1H,  $\text{PhCH}_2$ ), 4.43 (d,  $J = 11.2$  Hz, 1H,  $\text{PhCH}_2$ ), 4.20 (d,  $J = 7.6$  Hz, 1H, H-1a), 4.19-4.16 (m, 1H, H-5b), 4.11 (dd,  $J = 3.2, 9.2$  Hz, 1H, H-3c), 4.08 (t,  $J = 5.2$  Hz, 1H, H-2d), 4.04 (dd,  $J$

= 5.2, 8.0 Hz, 1H, H-3d), 3.96 (dd,  $J$  = 8.0, 9.6 Hz, 1H, H-2a), 3.84-3.78 (m, 1H, H-5c), 3.76-3.66 (m, 4H, H-5d, H-3b, H-2b, H-4c), 3.61-3.57 (m, 4H, H-6e<sub>1</sub>, H-11, H-5e, H-3e), 3.54 (d,  $J$  = 2.0 Hz, 1H, H-4a), 3.48-3.44 (m, 2H, H-4e, H-3a), 3.43 (dd,  $J$  = 2.8, 10.0 Hz, 1H, H-6e<sub>2</sub>), 3.40-3.34 (m, 2H, H-5a, H-4b), 2.80-2.59 (m, 3H), 2.53-2.46 (m, 1H), 2.44-2.36 (m, 2H), 2.27 (t,  $J$  = 7.2 Hz, 2H, H-2), 2.12 (s, 3H, COCH<sub>3</sub>), 1.72-1.56 (m, 5H), 1.52-1.45 (m, 5H), 1.48 (s, 3H, CH<sub>3</sub>), 1.33-1.20 (m, 18H), 1.33 (s, 3H, CH<sub>3</sub>), 1.27 (d,  $J$  = 6.0 Hz, 3H, CH<sub>3</sub>), 1.23 (d,  $J$  = 6.4 Hz, 3H, CH<sub>3</sub>), 1.16-1.09 (m, 12H, CH<sub>3</sub>), 0.91 (t,  $J$  = 7.2 Hz, 3H, CH<sub>3</sub>), 0.90 (t,  $J$  = 7.2 Hz, 3H, CH<sub>3</sub>), 0.85 (t,  $J$  = 6.8 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  206.9, 179.2, 176.3, 176.1, 172.0, 138.7, 138.2, 138.1, 138.0, 137.6, 128.74, 128.69, 128.63, 128.57, 128.4, 128.3, 128.2, 128.1, 128.05, 127.99, 127.94, 127.90, 127.8, 110.9, 109.8, 100.5, 100.2, 99.7, 99.6, 97.4, 84.5, 83.3, 82.8, 78.0, 76.7, 75.8, 75.41, 75.37, 75.3, 75.1, 74.6, 73.8, 73.7, 73.5, 73.3, 72.6, 72.4, 71.8, 71.0, 70.8, 70.5, 70.0, 69.3, 67.7, 66.9, 64.9, 41.2, 41.1, 38.2, 34.9, 33.8, 32.3, 30.1, 29.7, 29.5, 29.2, 29.0, 28.0, 27.8, 27.0, 26.9, 26.8, 25.3, 24.9, 24.8, 22.9, 18.6, 17.7, 17.2, 16.8, 16.7, 16.3, 14.4, 11.8, 11.7. HRMS (ESI<sup>+</sup>): calc. for C<sub>99</sub>H<sub>138</sub>NaO<sub>28</sub> [M+Na]<sup>+</sup> 1797.9267, found: 1797.9296.

**11(S)-Hydroxyhexadecanoic acid 11-O-2-O-levulinoyloxy-3,4,6-tri-O-benzyl- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 3)-O-[2,3-O-(1-methylethylidene)-4-O-(2S)-methylbutyryl- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 4)]-2-O-(2S)-methylbutyryl- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-O- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)-3,4-di-O-benzyl- $\beta$ -D-fucopyranoside 1,3'-Lactone (27a)**

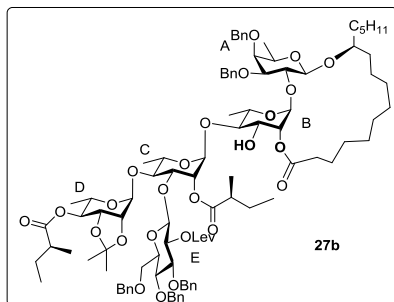


A solution of **26** (35.0 mg, 0.02 mmol), (PyS)<sub>2</sub> (43.4 mg, 0.2 mmol), Ph<sub>3</sub>P (51.7 mg, 0.2 mmol) in deoxygenated anhydrous toluene (0.2 mL) was stirred at 25 °C for 5 h. The mixture was diluted with deoxygenated anhydrous toluene (1.8 mL) and then the resulting solution was added dropwise by a syringe pump to refluxing dry deoxygenated toluene (17.7 mL) over 2 h. The solution was refluxed under nitrogen for 1.5 days. After removal of toluene under reduced pressure, the residue was

purified by column chromatography to afford **27a** (18.6 mg, 54%) and **27b** (14.5 mg, 42%) as a colorless syrup. **27a**:  $R_f$  = 0.28 (petroleum ether-EtOAc 3:1).  $[\alpha]_D^{25}$  = -26.50 (c, 0.2 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.34-7.23 (m, 23H, Ar-CH), 7.13-7.10 (m, 2H, Ar-CH), 5.34 (d,  $J$  = 1.8 Hz, 1H, H-1d), 5.29 (s, 2H, H-2c, H-1b), 5.04 (s, 1H, H-1c), 4.93 (dd,  $J$  = 2.4, 9.2 Hz, 1H, H-3d), 4.92-4.82 (m, 3H, PhCH<sub>2</sub>, H-2e, H-4d), 4.72-4.62 (m, 6H, PhCH<sub>2</sub>), 4.58 (d,  $J$  = 8.0 Hz, 1H, H-1e), 4.56-4.49 (m, 3H, PhCH<sub>2</sub>), 4.40-4.33 (m, 1H, H-5b), 4.29 (d,  $J$  = 8.0 Hz, 1H, H-1a), 4.28 (s, 1H, H-2b), 4.10 (d,  $J$  = 5.2 Hz, 1H, H-2d), 4.06-3.99 (m, 3H, H-3d, H-2a, H-3c), 3.86-3.69 (m, 7H, H-4b, H-4e, H-4c, H-5c, H-5d, H-6e<sub>1</sub>, H-6e<sub>2</sub>), 3.61-3.54 (m, 3H, H-3a, H-4a, H-3e), 3.52-3.48 (m, 1H, H-11), 3.44-3.40 (m, 2H, H-5a, H-5e), 2.71-2.60 (m, 3H), 2.50-2.28 (m, 5H), 2.10 (s, 3H, COCH<sub>3</sub>), 2.00 (brs, 1H, OH), 1.49 (s, 3H, CH<sub>3</sub>), 1.33 (s, 3H, CH<sub>3</sub>), 1.28 (d,  $J$  = 6.0 Hz, 6H, CH<sub>3</sub>), 1.16 (d,  $J$  = 5.2 Hz, 3H, CH<sub>3</sub>), 1.15 (d,  $J$  = 6.8 Hz, 3H, CH<sub>3</sub>), 1.12 (d,  $J$  = 6.0 Hz, 3H, CH<sub>3</sub>), 1.08 (d,  $J$  = 6.8 Hz, 3H, CH<sub>3</sub>), 0.91 (t,  $J$  = 7.6 Hz, 3H, CH<sub>3</sub>), 0.88 (t,  $J$  = 7.6 Hz, 3H, CH<sub>3</sub>), 0.85 (t,  $J$  = 7.2 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  206.2, 176.0, 175.1, 174.3, 171.8, 138.7, 138.6, 138.4, 138.3, 138.0, 128.8, 128.7, 128.6, 128.51, 128.45, 128.4, 128.1, 128.02, 127.98, 127.9, 127.84, 127.81, 127.7, 127.6, 109.7, 101.5, 100.3, 99.1, 98.0, 84.9, 83.1, 80.2, 78.1, 77.8, 76.5, 75.8, 75.7, 75.5, 75.1, 74.7, 74.6, 73.85, 73.80, 73.7, 72.5, 72.2, 70.9, 70.6, 70.1, 69.0, 67.8, 67.7, 65.0, 41.3, 41.1, 38.1, 35.2, 34.9, 34.2, 32.3, 30.00, 29.97, 29.9, 28.2, 28.0, 27.9, 27.4, 27.0, 26.9, 26.8, 26.7, 26.5, 26.4, 24.8,

23.5, 23.0, 18.9, 18.5, 17.2, 16.8, 16.7, 16.3, 14.4, 11.8, 11.7. HRMS (ESI<sup>+</sup>): calc. for C<sub>99</sub>H<sub>136</sub>NaO<sub>27</sub> [M+Na]<sup>+</sup> 1779.9161, found: 1779.9094.

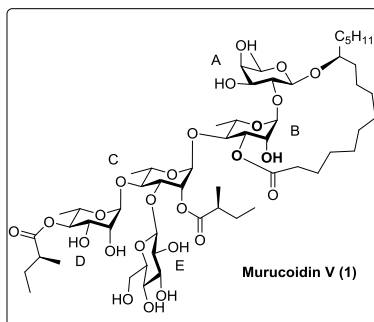
**11(*S*)-Hydroxyhexadecanoic acid 11-*O*-2-*O*-levulinoyloxy-3,4,6-tri-*O*-benzyl- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 3)-*O*-[2,3-*O*-(1-methylethylidene)-4-*O*-(2*S*)-methylbutyryl- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 4)]-2-*O*-(2*S*)-methylbutyryl- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-*O*- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)-3,4-di-*O*-benzyl- $\beta$ -D-fucopyranoside 1,2'-Lactone (**27b**)**



**27b:** Colorless syrup.  $R_f$  = 0.44 (petroleum ether-EtOAc 3:1).  $[\alpha]_D^{20}$  = -13.50 (*c*, 0.2 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37-7.20 (m, 23H, Ar-CH), 7.09-7.07 (m, 2H, Ar-CH), 5.35 (s, 1H, H-1d), 5.29 (s, 1H, H-2c), 5.12 (s, 1H, H-2b), 5.06 (s, 1H, H-1c), 4.94 (s, 1H, H-1b), 4.92 (t, *J* = 8.4 Hz, 1H, H-2e), 4.87-4.82 (m, 2H, PhCH<sub>2</sub>, H-4d), 4.70-4.57 (m, 5H, PhCH<sub>2</sub>), 4.58 (d, *J* = 7.2 Hz, 1H, H-1e), 4.54 (d, *J* = 12.8 Hz, 1H, PhCH<sub>2</sub>), 4.51 (d, *J* = 12.4 Hz, 1H, PhCH<sub>2</sub>), 4.44 (d, *J* = 11.6 Hz, 1H,

PhCH<sub>2</sub>), 4.41 (d, *J* = 12.0 Hz, 1H, PhCH<sub>2</sub>), 4.19 (d, *J* = 7.2 Hz, 1H, H-1a), 4.16-4.13 (m, 2H, H-3c, H-2d), 4.09 (dd, *J* = 5.2, 7.6 Hz, 1H, H-3d), 3.98-3.95 (m, 1H, H-3b), 3.84-3.77 (m, 5H, H-2a, H-5b, H-5c, H-5d, H-4c), 3.63-3.52 (m, 5H, H-4e, H-6e<sub>1</sub>, H-6e<sub>2</sub>, H-11, H-3e), 3.47-3.41 (m, 3H, H-4a, H-4b, H-5e), 3.34-3.29 (m, 1H, H-5a), 3.23 (dd, *J* = 2.4, 9.6 Hz, 1H, H-3a), 2.75-2.63 (m, 3H), 2.49-2.35 (m, 4H), 2.29-2.23 (m, 1H), 2.11 (s, 3H, COCH<sub>3</sub>), 1.94 (d, *J* = 4.4 Hz, 1H, OH), 1.50 (s, 3H, CH<sub>3</sub>), 1.32 (s, 3H, CH<sub>3</sub>), 1.30 (d, *J* = 6.0 Hz, 3H, CH<sub>3</sub>), 1.16-1.10 (m, 12H, CH<sub>3</sub>), 0.94-0.84 (m, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  206.4, 176.0, 175.9, 173.2, 171.9, 138.7, 138.4, 138.2, 137.9, 128.9, 128.68, 128.66, 128.6, 128.5, 128.3, 128.2, 128.15, 128.08, 128.0, 127.96, 127.94, 127.91, 127.8, 127.7, 109.7, 104.4, 100.9, 98.5, 98.4, 98.3, 83.6, 83.4, 81.8, 80.5, 78.4, 78.1, 76.6, 76.5, 75.8, 75.6, 75.23, 75.19, 74.4, 73.8, 73.6, 73.4, 72.7, 72.1, 70.0, 69.7, 69.1, 68.0, 67.8, 65.0, 41.2, 41.1, 38.2, 34.2, 33.9, 32.8, 32.4, 30.0, 29.9, 28.0, 27.8, 27.7, 27.5, 27.31, 27.25, 27.0, 26.9, 26.8, 25.2, 25.0, 22.9, 22.7, 18.7, 18.5, 17.4, 16.81, 16.76, 16.3, 14.3, 11.8, 11.7. HRMS (ESI<sup>+</sup>): calc. for C<sub>99</sub>H<sub>136</sub>NaO<sub>27</sub> [M+Na]<sup>+</sup> 1779.9161, found: 1779.9086.

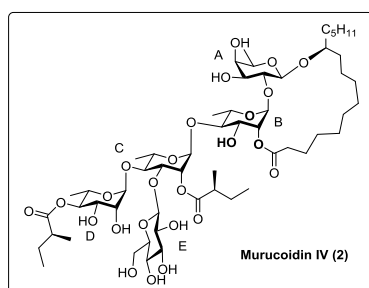
**Murucoidin V (1)**



To a solution of **27a** (20.0 mg, 0.011 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.6 mL) were added pyridine (27.5  $\mu$ L, 0.34 mmol), AcOH (19.5  $\mu$ L, 0.34 mmol) and hydrazine hydrate (2.8  $\mu$ L, 0.057 mmol). The reaction mixture was stirred at room temperature for 3 h. Then it was quenched with aqueous NaHCO<sub>3</sub> and extracted with EtOAc. The combined organic extracts were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residue was purified by column chromatography to afford the desired alcohol as a colorless syrup. (17.1 mg, 91%). The obtained alcohol (15.0 mg, 0.009 mmol) was dissolved in THF-H<sub>2</sub>O-TFA (2:1:2, v/v/v, 0.5 mL), the mixture was stirred for 2 h at the room temperature, then this mixture was extracted with EtOAc. The solution was dried with Na<sub>2</sub>SO<sub>4</sub>, and purified by column chromatography to afford the desired compound as a colorless syrup (12.8 mg, 88%). the obtained alcohol (27.3 mg, 0.017 mmol) was subjected to hydrogenation (H<sub>2</sub>) with catalytic 10% Pd-C in methanol (5.0 mL) for 22 h. After being filtered and concentrated, the residue was purified by

column chromatography to afford compound **1**<sup>7</sup> as white solid (16.9 mg, 86%).  $R_f = 0.36$  (dichloromethane-methanol 10:1). HRMS (ESI<sup>+</sup>): calc. for C<sub>56</sub>H<sub>96</sub>NaO<sub>25</sub> [M+Na]<sup>+</sup> 1191.6133, found: 1191.6091. mp 117-120 °C (lit.<sup>7</sup> mp 148-150 °C);  $[\alpha]_D^{24} = -44.91$  (c, 1.18 in CH<sub>3</sub>OH) (lit.<sup>7</sup>  $[\alpha]_D^{24} = -29$  (c, 0.14 in CH<sub>3</sub>OH)). <sup>1</sup>H NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N)  $\delta$  6.34 (d,  $J = 0.4$  Hz, 1H, H-1b), 6.16 (d,  $J = 2.4$  Hz, 1H, H-1d), 6.00 (v dd,  $J = 1.2, 2.8$  Hz, 1H, H-2c), 5.72 (t,  $J = 9.6$  Hz, 1H, H-4d), 5.62 (dd,  $J = 2.4, 10.0$  Hz, 1H, H-3b), 5.58 (s, 1H, H-1c), 5.23 (brs, 1H, H-2b), 5.05 (d,  $J = 7.6$  Hz, 1H, H-1e), 5.00-4.93 (m, 1H, H-5b), 4.86 (dd,  $J = 2.0, 2.4$  Hz, 1H, H-2d), 4.81 (d,  $J = 7.6$  Hz, 1H, H-1a), 4.67 (t,  $J = 10.0$  Hz, 1H, H-4b), 4.55 (dd,  $J = 3.6, 9.2$  Hz, 1H, H-3c), 4.51 (dd,  $J = 8.0, 9.6$  Hz, 1H, H-2a), 4.46-4.41 (m, 2H, H-3d, H-6e<sub>1</sub>), 4.35-4.28 (m, 3H, H-6e<sub>2</sub>, H-5c, H-5d), 4.22 (t,  $J = 9.2$  Hz, 1H, H-4c), 4.18 (dd,  $J = 2.8, 9.2$  Hz, 1H, H-3a), 4.13 (t,  $J = 9.2$  Hz, 1H, H-4e), 4.10 (t,  $J = 8.8$  Hz, 1H, H-3e), 3.92-3.78 (m, 5H, H-4a, H-5a, H-2e, H-5e, H-11), 2.56-2.36 (m, 3H, COCH(CH<sub>3</sub>), COCH(CH<sub>3</sub>), H-12), 2.20 (ddd,  $J = 2.8, 7.6, 14.4$  Hz, 1H, H-12), 1.58 (d,  $J = 6.0$  Hz, 3H, H-6b), 1.54 (d,  $J = 6.0$  Hz, 3H, H-6c), 1.49 (d,  $J = 6.4$  Hz, 3H, H-6a), 1.36 (d,  $J = 6.4$  Hz, 3H, H-6d), 1.16 (d,  $J = 6.8$  Hz, 3H, CH<sub>3</sub>), 1.07 (d,  $J = 6.8$  Hz, 3H, CH<sub>3</sub>), 0.89 (t,  $J = 7.6$  Hz, 3H, CH<sub>3</sub>), 0.87 (d,  $J = 7.6$  Hz, 3H, CH<sub>3</sub>), 0.79 (d,  $J = 7.6$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, C<sub>5</sub>D<sub>5</sub>N)  $\delta$  176.3, 176.1, 174.5, 105.1, 103.4, 101.5, 100.2, 99.1, 80.3, 79.4, 78.7, 78.3, 78.2, 77.8, 76.6, 75.6, 75.22, 75.19, 73.6, 73.5, 72.4, 72.2, 71.3, 70.7, 70.2, 69.9, 68.1, 68.0, 62.5, 41.5, 41.3, 35.5, 35.2, 34.3, 32.5, 30.4, 28.3, 27.7, 27.1, 27.0, 26.7, 26.5, 25.0, 23.5, 23.1, 19.2, 18.7, 18.0, 17.2, 17.0, 16.7, 14.5, 11.8, 11.6. HRMS (ESI<sup>+</sup>): calc. for C<sub>56</sub>H<sub>96</sub>NaO<sub>25</sub> [M+Na]<sup>+</sup> 1191.6133, found: 1191.6138.

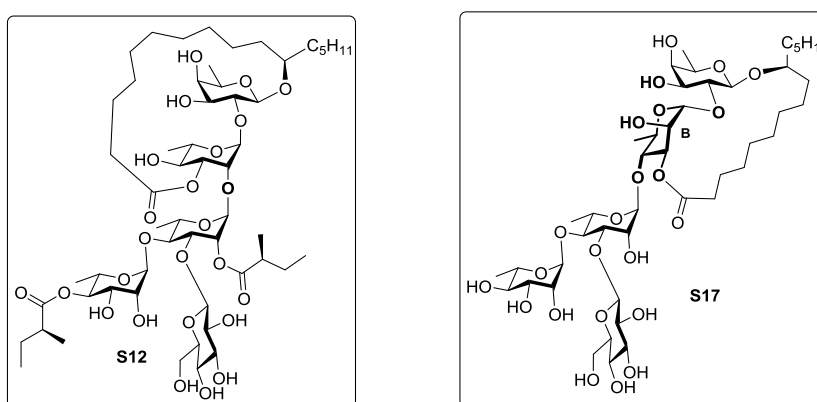
## Murucoidin IV (2)



To a solution of **27b** (18.3 mg, 0.10 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) were added pyridine (25.2  $\mu$ L, 0.31 mmol), AcOH (17.9  $\mu$ L, 0.31 mmol) and hydrazine hydrate (2.5  $\mu$ L, 0.052 mmol). The reaction mixture was stirred at room temperature for 3 h. Then it was quenched with aqueous NaHCO<sub>3</sub> and extracted with EtOAc. The combined organic extracts were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residue was purified by column chromatography to afford the desired alcohol as a colorless syrup (15.1 mg, 87%). The obtained alcohol (15.1 mg, 0.009 mmol) was dissolved in AcOH-H<sub>2</sub>O (4:1, v/v, 0.5 mL), and the resulting mixture was warmed gradually to 65 °C. The mixture was stirred for overnight at the same temperature, then the mixture was cooled and concentrated. The residue was purified by column chromatography to afford the desired alcohol as a colorless syrup (11.4 mg, 85%). The obtained alcohol (11.4 mg, 0.007 mmol) was subjected to hydrogenation (H<sub>2</sub>) with catalytic 15% Pd(OH)<sub>2</sub> in ethyl acetate (5.0 mL) for 22 h. After being filtered and concentrated, the residue was purified by column chromatography to afford compound **2** as white solid (6.1 mg, 74%).  $R_f = 0.1$  (CH<sub>2</sub>Cl<sub>2</sub>-methanol 10:1). mp 153-158 °C (lit.<sup>7</sup> mp 157-159 °C);  $[\alpha]_D^{24} = -16.57$  (c, 0.35 in CH<sub>3</sub>OH) (lit.<sup>7</sup>  $[\alpha]_D^{24} = -29$  (c, 0.15 in CH<sub>3</sub>OH)). <sup>1</sup>H NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N)  $\delta$  6.30 (dd,  $J = 1.6, 2.8$  Hz, 1H, H-2c), 6.20 (d,  $J = 1.2$  Hz, 1H, H-1d), 5.91 (dd,  $J = 2.4, 3.2$  Hz, 1H, H-2b), 5.83 (d,  $J = 0.8$  Hz, 1H, H-1c), 5.76 (t,  $J = 9.6$  Hz, 1H, H-4d), 5.48 (s, 1H, H-1b), 5.03 (d,  $J = 7.6$  Hz, 1H, H-1e), 4.99 (dd,  $J = 3.2, 9.6$  Hz, 1H, H-3b), 4.93 (dd,  $J = 2.0, 3.2$  Hz, 1H, H-2d), 4.71 (dd,  $J = 2.8, 9.2$  Hz, 1H, H-3c), 4.69 (d,  $J = 7.2$  Hz, 1H, H-1a), 4.52 (dd,  $J = 3.2, 9.2$  Hz, 1H, H-3d), 4.48-4.44 (m, 1H, H-5b), 4.40-4.34 (m, 3H, H-5c, H-5d, H-6e<sub>1</sub>), 4.28 (t,  $J = 9.6$  Hz, 1H, H-4c), 4.14 (t,  $J = 9.6$  Hz, 1H, H-4b), 4.14 (dd,  $J = 7.2, 10.0$  Hz, 1H, H-2a), 4.07-4.01 (m, 3H, H-6e<sub>2</sub>,

H-4e, H-3a), 3.95 (d,  $J = 3.2$  Hz, 1H, H-4a), 3.92 (t,  $J = 8.8$  Hz, 2H, H-2e, H-3e), 3.84-3.80 (m, 1H, jia-11), 3.76-3.69 (m, 2H, H-5a, H-5e), 2.54-2.49 (m, 1H, COCH(CH<sub>3</sub>)), 2.46-2.36 (m, 2H, COCH(CH<sub>3</sub>), jia-2), 2.28-2.22 (m, 1H, jia-2), 1.65 (d,  $J = 6.4$  Hz, 3H, H-6c), 1.62 (d,  $J = 6.4$  Hz, 3H, H-6b), 1.49 (d,  $J = 6.0$  Hz, 3H, H-6a), 1.40 (d,  $J = 6.0$  Hz, 3H, H-6d), 1.19 (d,  $J = 6.8$  Hz, 3H, CH<sub>3</sub>), 1.01 (d,  $J = 7.2$  Hz, 3H, CH<sub>3</sub>), 0.92 (t,  $J = 7.2$  Hz, 3H, CH<sub>3</sub>), 0.85 (d,  $J = 6.8$  Hz, 3H, CH<sub>3</sub>), 0.77 (d,  $J = 7.2$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>N)  $\delta$  176.30, 176.28, 173.1, 105.4, 104.3, 103.3, 100.0, 98.5, 82.3, 81.5, 80.1, 79.9, 78.8, 78.5, 78.0, 75.2, 73.6, 73.4, 73.0, 72.9, 72.4, 71.5, 70.8, 70.3, 69.4, 68.9, 68.4, 68.2, 62.9, 41.5, 41.2, 34.3, 34.2, 33.2, 32.4, 32.1, 30.0, 29.9, 29.6, 29.1, 28.2, 27.6, 27.22, 27.19, 27.1, 26.9, 25.0, 24.9, 23.4, 23.2, 22.9, 19.1, 18.9, 18.0, 17.3, 17.0, 16.6, 14.3, 11.8, 11.4. HRMS (ESI<sup>+</sup>): calc. for C<sub>56</sub>H<sub>96</sub>NaO<sub>25</sub> [M+Na]<sup>+</sup> 1191.6133, found: 1191.6173.

## 7. Comparison of <sup>1</sup>H and <sup>13</sup>C NMR spectra of synthetic and isolated resin glycosides

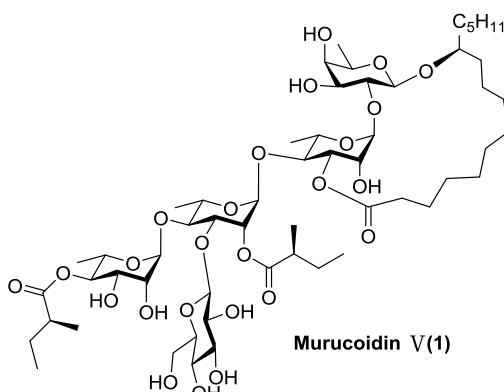


**Table S1. Comparison of the partial <sup>13</sup>C NMR data of compounds S12, S17 and naturally occurring murucoidin V (in C<sub>5</sub>D<sub>5</sub>N)**

No	S12(100MHz)		Murucoidin V <sup>7</sup> (isolated) (125 MHz)	S17(100MHz)	
	$\Delta\delta = \delta_{S12} - \delta_I$	data		data	$\Delta\delta = \delta_{S21} - \delta_I$
1	<b>+1.0</b>	177.3	176.3	176.2	<b>-0.1</b>
2	<b>+0.5</b>	176.6	176.1	174.7	<b>-1.4</b>
3	<b>+1.6</b>	176.0	174.4	173.9	<b>-0.5</b>
4	<b>+0.8</b>	105.9	105.1	104.4	<b>-0.7</b>
5	<b>+0.2</b>	103.6	103.4	103.2	<b>-0.2</b>
6	<b>+0.9</b>	102.4	101.5	102.0	<b>+0.5</b>
7	<b>-0.8</b>	99.3	100.1	101.3	<b>+1.2</b>
8	<b>+1.7</b>	100.8	99.1	99.1	/
9	<b>+0.5</b>	80.7	80.2	81.0	<b>+0.8</b>
10	<b>+1.0</b>	80.5	79.5	79.3	<b>-0.2</b>
11	/	78.8	78.8	78.9	<b>+0.1</b>
12	<b>+0.5</b>	78.7	78.3	78.6	<b>+0.3</b>
13	<b>+0.1</b>	78.2	78.1	77.9	<b>-0.3</b>
14	<b>+0.3</b>	78.1	77.8	77.2	<b>-0.6</b>
15	<b>+0.8</b>	77.4	76.6	76.5	<b>-0.1</b>
16	<b>+1.4</b>	77.1	75.7	75.5	<b>-0.2</b>



17	<b>+0.2</b>	75.4	75.2	74.8	<b>-0.4</b>
18	<b>+0.2</b>	75.4	75.2	74.6	<b>-0.8</b>
19	<b>+0.4</b>	74.0	73.6	74.3	<b>-0.7</b>
20	<b>+0.3</b>	73.9	73.6	73.9	<b>+0.3</b>
21	<b>+1.1</b>	73.5	72.4	72.9	<b>+0.5</b>
22	<b>+0.4</b>	72.6	72.2	72.3	<b>+0.1</b>
23	<b>+0.7</b>	72.0	71.3	71.4	<b>+0.1</b>
24	<b>+0.7</b>	71.5	70.8	70.8	/
25	<b>+0.3</b>	70.5	70.2	70.4	<b>+0.2</b>
26	<b>+0.4</b>	70.4	70.0	69.0	<b>+1.0</b>
27	<b>+1.1</b>	69.2	68.1	69.7	<b>+1.6</b>
28	<b>+0.3</b>	68.4	68.1	68.2	<b>+0.1</b>
29	<b>+0.3</b>	68.3	68.0	67.5	<b>-0.5</b>
30	<b>+1.0</b>	63.6	62.6	62.9	<b>+0.3</b>
31	<b>+0.4</b>	41.9	41.5	41.9	<b>+0.4</b>
32	<b>+0.3</b>	41.6	41.3	41.5	<b>+0.2</b>



**Table S2. Comparison of the  $^1\text{H}$  NMR data of synthetic and isolated murucoidin V (in  $\text{C}_5\text{D}_5\text{N}$ )**

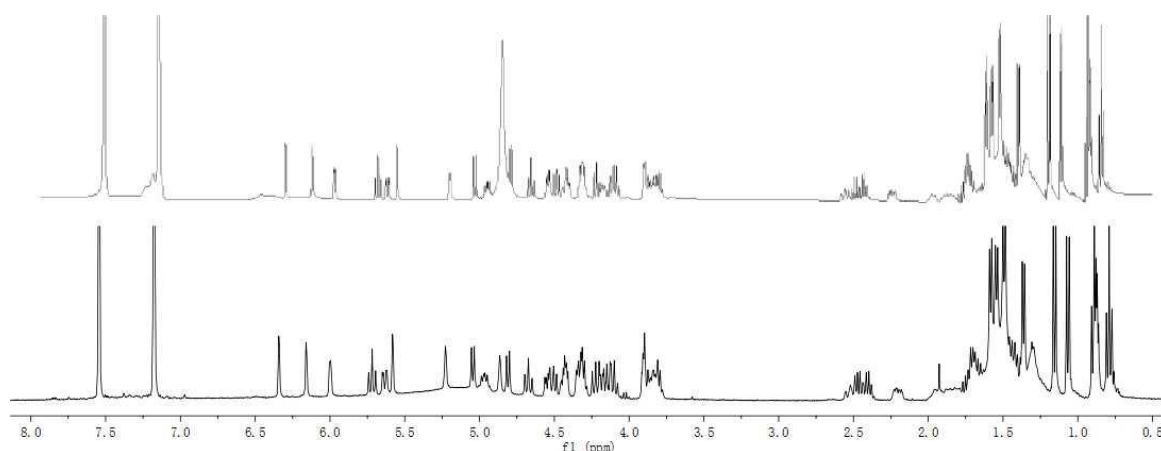
Position	Isolated <sup>7</sup> (500 MHz)	Synthetic (400 MHz)	$\Delta\delta = \delta_{\text{S}} - \delta_{\text{I}}$
Fuc-1	4.82 d (7.9)	4.81 d (7.6)	-0.01
2	4.50 dd (7.9, 9.4)	4.51 dd (8.0, 9.6)	+0.01
3	4.19 dd (2.9, 9.4)	4.18 dd (2.8, 9.2)	-0.01
4	3.90	3.92-3.78 m	/
5	3.82 dq (0.5, 6.3)	3.92-3.78 m	/
6	1.50 d (6.3)	1.49 d (6.4)	-0.01
Rha-1	6.34 d (1.3)	6.34 d (0.4)	
2	5.22 brs	5.23 brs	+0.01
3	5.64 dd (2.7, 9.8)	5.62 dd (2.4, 10.0)	-0.02
4	4.66 dd (9.7, 9.7)	4.67 t (10.0)	+0.01
5	4.88 brs	4.97 m	+0.09
6	1.60 d (6.1)	1.58 d (6.0)	-0.02
Rha'-1	5.58 d (1.3)	5.58 s	
2	6.00 dd (1.6, 3.3)	6.00 dd (1.2, 2.8)	
3	4.56 dd (3.4, 9.0)	4.55 dd (3.6, 9.2)	-0.01
4	4.23 dd (9.2, 9.2)	4.22 t (9.2)	-0.01

5	4.32 dq (6.2, 9.2)	4.35-4.28 m	/
6	1.56 d (6.2)	1.54 d (6.0)	-0.02
Rha''-1	6.16 d (1.7)	6.16 d (2.4)	
2	4.88 brs	4.86 dd (2.0, 2.4)	-0.02
3	4.43 dd (3.2, 9.5)	4.46-4.41 m	/
4	5.72 dd (9.3, 9.3)	5.72 t (9.6)	
5	4.32 dq (6.6, 9.0)	4.35-4.28 m	/
6	1.38 d (6.3)	1.36 d (6.4)	-0.02
Glc-1	5.05 d (7.6)	5.05 d (7.6)	
2	3.90*	3.92-3.78 m	/
3	4.12 dd (8.8, 8.9)	4.10 t (8.8)	-0.02
4	4.14 dd (8.8, 9.1)	4.13 t (9.2)	-0.02
5	3.84 ddd (3.4, 6.0, 9.0)	3.92-3.78 m	/
6	4.31 dd (6.1, 12.3)	4.35-4.28 m	/
	4.44 dd (3.0, 12.0)	4.46-4.41 m	/
Jia-2	2.23 ddd (2.8, 7.2, 14.6)	2.20 ddd (2.8, 7.6, 14.4)	-0.03
	2.55 dd (3.2, 14.6)	2.56-2.36 m	/
11	3.88 m	3.92-3.78 m	/
16	0.90 t (7.4)	0.87 d (7.6)	-0.03
Mba-2	2.44 tq (6.9, 7.0)	2.56-2.36 m	/
2-Me	1.10 d (6.9)	1.07 d (6.8)	-0.03
3-Me	0.83 t (7.4)	0.79 d (7.6)	-0.04
Mba'-2	2.48 tq (6.9, 7.0)	2.56-2.36 m	/
2-Me	1.18 d (7.0)	1.16 d (6.8)	-0.02
3-Me	0.92 t (7.4)	0.89 t (7.6)	-0.03

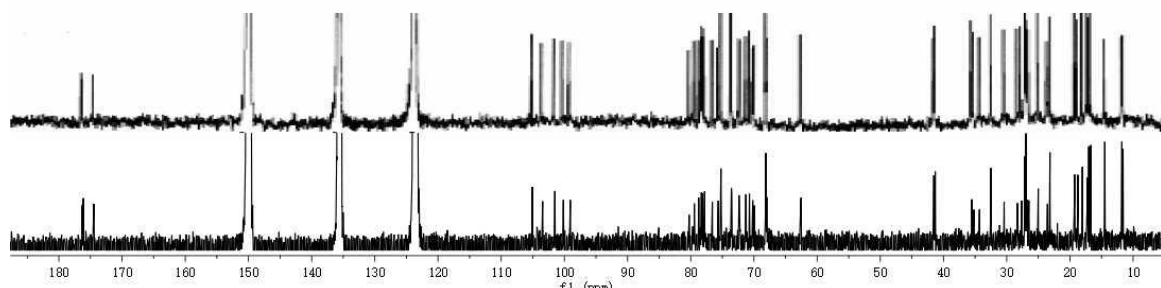
**Table S3. Comparison of the  $^{13}\text{C}$  NMR data of synthetic and isolated murucoidin V (in  $\text{C}_5\text{D}_5\text{N}$ )**

Position	Isolated <sup>7</sup> (125MHz)	Synthetic (100MHz)	$\Delta\delta$ $=\delta_{\text{S}}-\delta_{\text{I}}$	assignment	Isolated <sup>7</sup> (125MHz)	Synthetic (100MHz)	$\Delta\delta$ $=\delta_{\text{S}}-\delta_{\text{I}}$
Fuc-1	101.5	101.5		Rha''-1	103.4	103.4	
2	73.6	73.5	-0.1	2	72.4	72.4	
3	76.6	76.6		3	70.2	70.2	
4	73.6	73.6		4	75.2	75.2	
5	71.3	71.3		5	68.1	68.1	
6	17.2	17.2		6	18.0	18.0	
Rha-1	100.1	100.2	+0.1	Glc-1	105.1	105.1	
2	70.0	69.9	-0.1	2	75.2	75.2	
3	78.3	78.3		3	78.1	78.2	+0.1
4	75.7	75.6	-0.1	4	70.8	70.7	-0.1
5	68.0	68.0		5	77.8	77.8	
6	19.2	19.2		6	62.6	62.5	-0.1
Rha'-1	99.1	99.1		Jia-1	174.4	174.5	+0.1

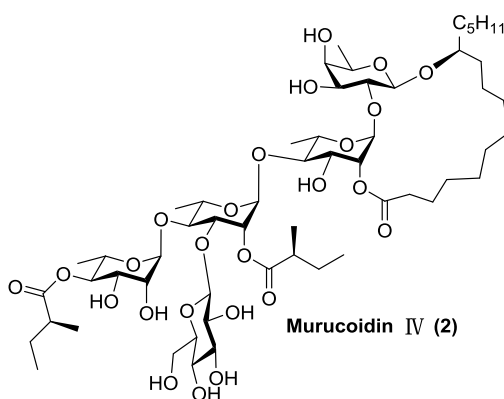
2	72.2	72.2		2	34.3	34.3	
3	80.2	80.3	+0.1	11	79.5	79.4	-0.1
4	78.8	78.7	-0.1	16	14.5	14.5	
5	68.1	68.1					
6	18.7	18.7					
Mba-1	176.1	176.1		Mba'-1	176.3	176.3	
Mba-2	41.3	41.3		Mba'-2	41.5	41.5	
2-Me	16.8	16.7	-0.1	2-Me	17.0	17.0	
3-Me	11.6	11.6		3-Me	11.7	11.8	+0.1



**Figure S1.** Comparison of  $^1\text{H}$  NMR Spectra of synthetic and isolated murucodine V (above is the spectrum of isolated murucodine V, below is the spectrum of synthetic one)



**Figure S2.** Comparison of  $^{13}\text{C}$  NMR Spectra of synthetic and isolated murucodine V (above is the spectrum of isolated murucodine V, below is the spectrum of synthetic one)

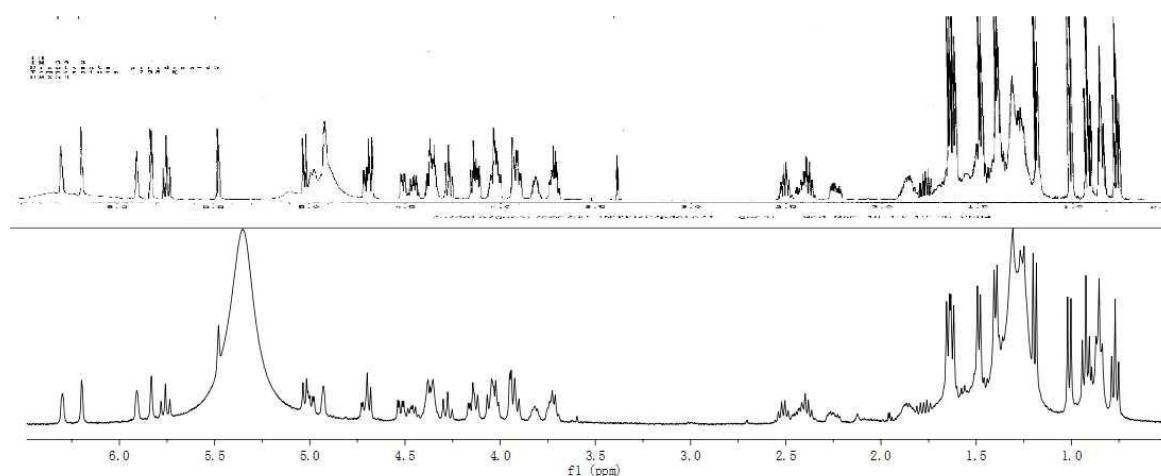


**Table S4. Comparison of the  $^1\text{H}$  NMR data of synthetic and isolated murucoidin IV (in  $\text{C}_5\text{D}_5\text{N}$ )**

Position	Isolated <sup>7</sup> (500 MHz)	Synthetic (400 MHz)	$\Delta\delta = \delta_{\text{S}} - \delta_{\text{I}}$
Fuc-1	4.68 d (7.5)	4.69 d (7.2),	+0.01
2	4.12 dd (7.5, 9.4)	4.14 dd (7.2, 10.0)	+0.02
3	4.00 dd (3.0, 9.4)	4.07-4.01 m	/
4	3.93 d (3.0)	3.95 d (3.2)	+0.02
5	3.72 dq (0.5, 6.3)	3.76-3.69 m	/
6	1.48 d (6.3)	1.49 d (6.0)	+0.01
Rha-1	5.48 brs	5.48 s	
2	5.90 dd (1.0, 2.5)	5.91 dd (2.4, 3.2)	+0.01
3	4.97 dd (2.5, 9.5)	4.99 dd (3.2, 9.6)	+0.02
4	4.14 dd (9.4, 9.5)	4.14 t (9.6 Hz)	
5	4.45 dq (6.0, 9.5)	4.46 m	+0.01
6	1.62 d (6.0)	1.62 d (6.4)	
Rha'-1	5.82 d (1.0)	5.83 d (0.8)	+0.01
2	6.30 dd (1.0, 3.0)	6.30 dd (1.6, 2.8)	
3	4.70 dd (3.0, 9.2)	4.71 dd (2.8, 9.2)	+0.01
4	4.27 dd (9.2, 9.4)	4.28 t (9.6)	+0.01
5	4.36 dq (6.1, 9.4)	4.40-4.34 m	/
6	1.64 d (6.1)	1.65 d (6.4)	+0.01
Rha''-1	6.18 d (1.3)	6.20 d (1.2)	+0.02
2	4.92 brs	4.93 dd (2.0, 3.2)	+0.01
3	4.52 dd (3.3, 9.2)	4.52 dd (3.2, 9.2)	
4	5.74 dd (9.3, 9.4)	5.76 t (9.6 Hz)	+0.02
5	4.36 dq (6.5, 9.4)	4.40-4.34 m	/
6	1.40 d (6.5)	1.40 d (6.0)	
Glc-1	5.02 d (7.7)	5.03 d (7.6)	+0.01
2	3.90 dd (8.0, 8.8)	3.92 t (8.8)	+0.02
3	4.00	3.92 t (8.8)	-0.08
4	4.00	4.07-4.01 m	/
5	3.73 ddd (2.4, 5.8, 8.4)	3.76-3.69 m	/
6	4.02 dd (5.9, 12.0)	4.07-4.01 m	/
	4.35 dd (2.4, 12.0)	4.40-4.34 m	/
Jia-2	2.25 ddd (3.8, 7.9, 14.6)	2.25 m	
	2.42 dd (3.9, 14.6)	2.46-2.36 m	/
11	3.81 m	3.82 m	0.01
16	0.85 t (7.0)	0.85 d (6.8)	
Mba-2	2.39 tq (6.9, 7.0)	2.46-2.36 m	/
2-Me	1.01 d (7.0)	1.01 d (7.2 Hz)	
3-Me	0.77 t (7.4)	0.77 d (7.2)	
Mba'-2	2.50 tq (6.9, 7.0)	2.51 m	+0.01
2-Me	1.19 d (7.0)	1.19 d (6.8)	
3-Me	0.92 t (7.4)	0.92 t (7.2)	

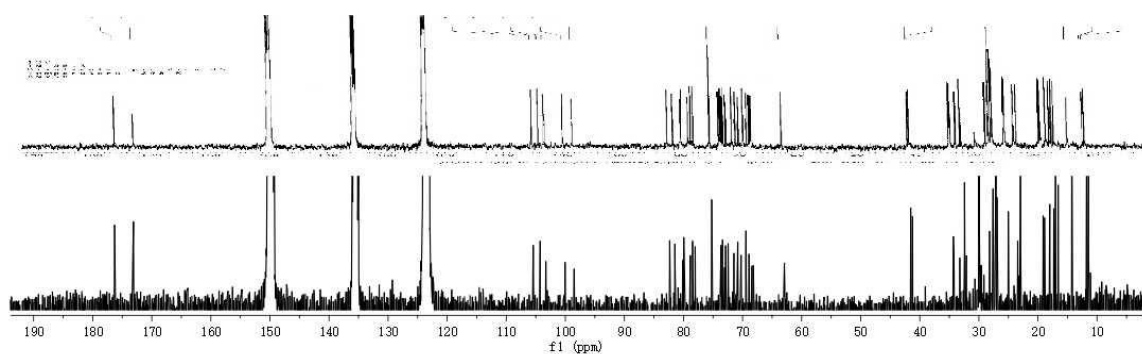
**Table S5. Comparison of the  $^{13}\text{C}$  NMR data of synthetic and isolated murucoidin IV (in  $\text{C}_5\text{D}_5\text{N}$ )**

Position	Isolated <sup>7</sup> (125MHz)	Synthetic (100MHz)	$\Delta\delta$ $=\delta_{\text{S}}-\delta_{\text{I}}$	assignment	Isolated <sup>7</sup> (125MHz)	Synthetic (100MHz)	$\Delta\delta$ $=\delta_{\text{S}}-\delta_{\text{I}}$
Fuc-1	104.3	104.3		Rha''-1	103.3	103.3	
2	80.0	79.9	-0.1	2	72.5	72.4	-0.1
3	73.4	73.4		3	70.3	70.3	
s4	72.9	72.9		4	75.2	75.2	
5	70.8	70.8		5	68.4	68.4	
6	17.3	17.3		6	18.0	18.0	
Rha-1	98.5	98.5		Glc-1	105.5	105.4	-0.1
2	73.6	73.6		2	75.2	75.2	
3	69.4	69.4		3	78.5	78.5	
4	81.4	81.5	+0.1	4	71.5	71.5	
5	68.9	68.9		5	78.0	78.0	
6	19.1	19.1		6	62.9	62.9	
Rha'-1	100.0	100.0		Jia-1	173.1	173.1	
2	73.0	73.0		2	34.2	34.2	
3	80.2	80.1	-0.1	11	82.3	82.3	
4	78.9	78.8	-0.1	16	14.3	14.3	
5	68.2	68.2					
6	18.9	18.9					
Mba-1	176.3	176.3		Mba'-1	176.3	176.3	
Mba-2	41.2	41.2		Mba'-2	41.5	41.5	
2-Me	16.6	16.6		2-Me	16.9	17.0	+0.1
3-Me	11.4	11.4		3-Me	11.7	11.8	+0.1



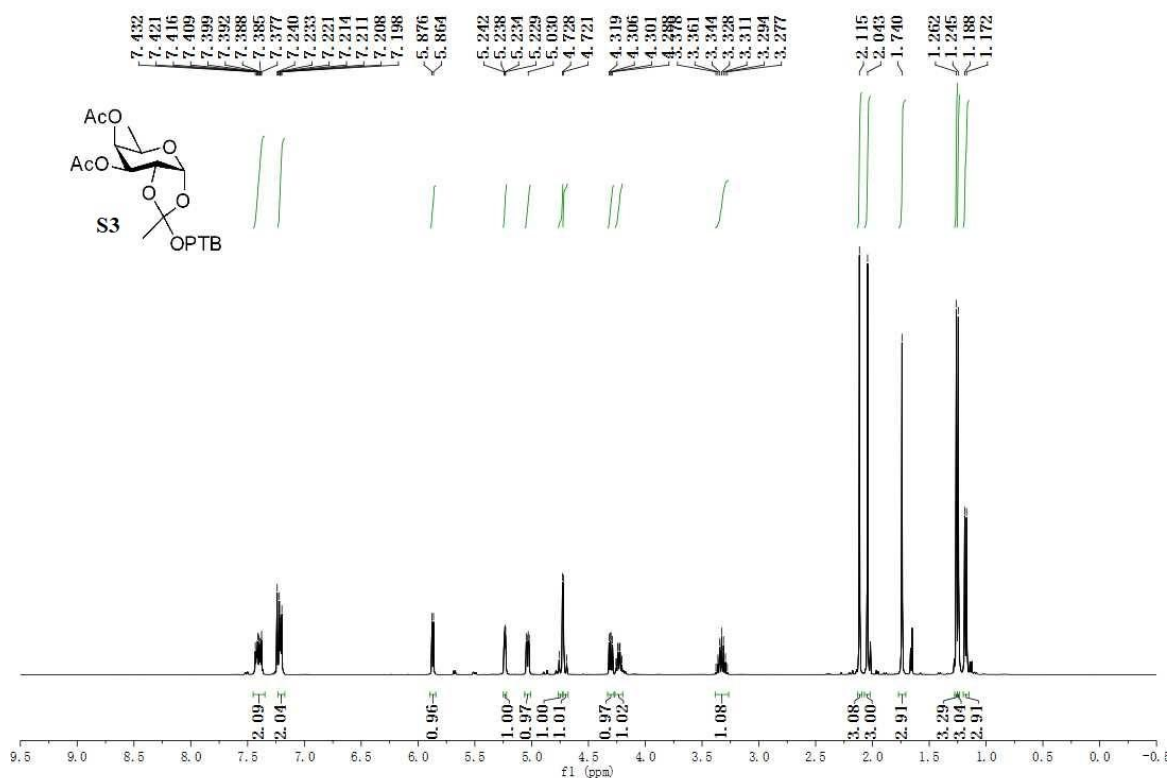
**Figure S3. Comparison of  $^1\text{H}$  NMR Spectra of synthetic and isolated murucoidin IV**

(above is the spectrum of isolated murucodin IV, below is the spectrum of synthetic one)

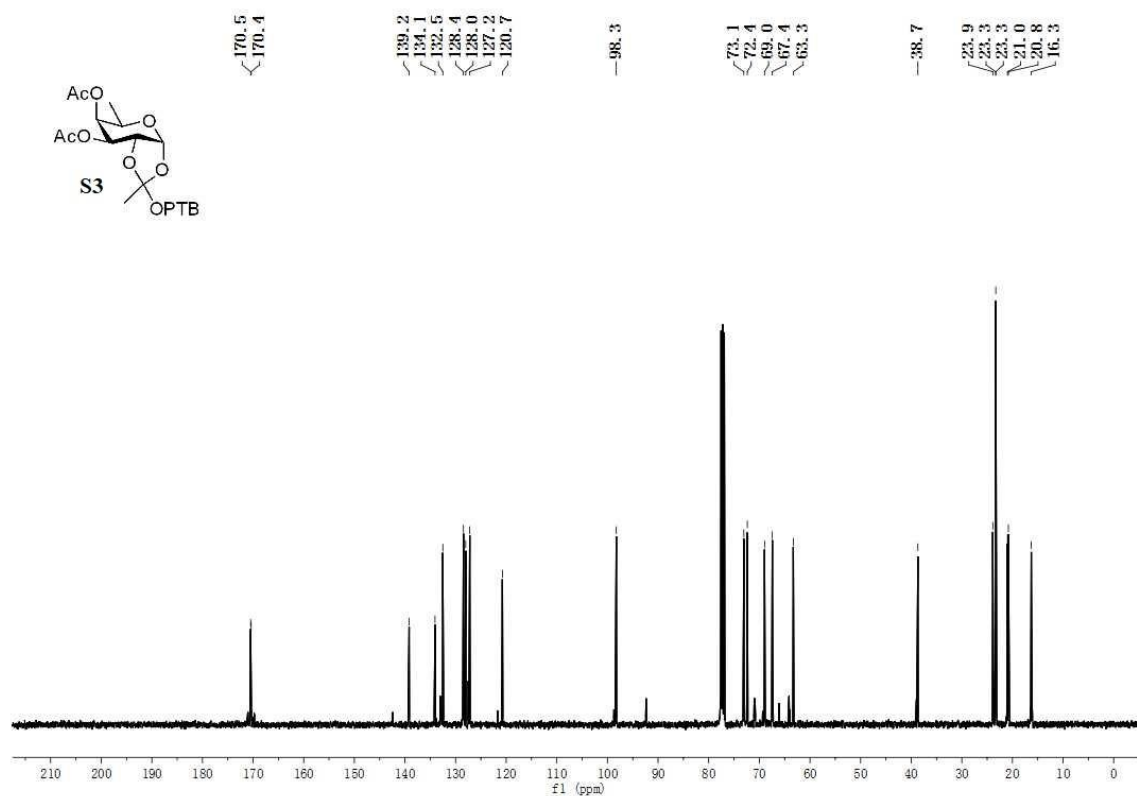


**Figure S4.** Comparison of  $^{13}\text{C}$  NMR Spectra of synthetic and isolated murucodin IV (above is the spectrum of isolated murucodin IV, below is the spectrum of synthetic one)

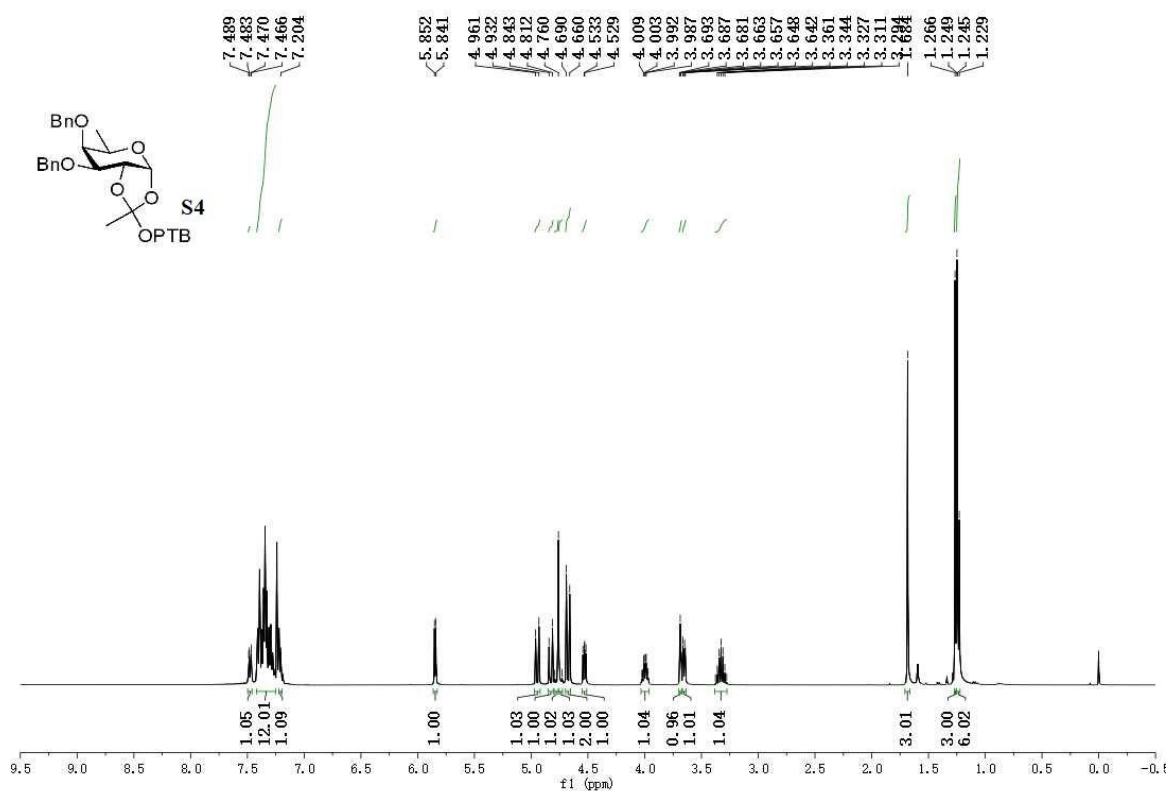
## Copies of NMR Spectra



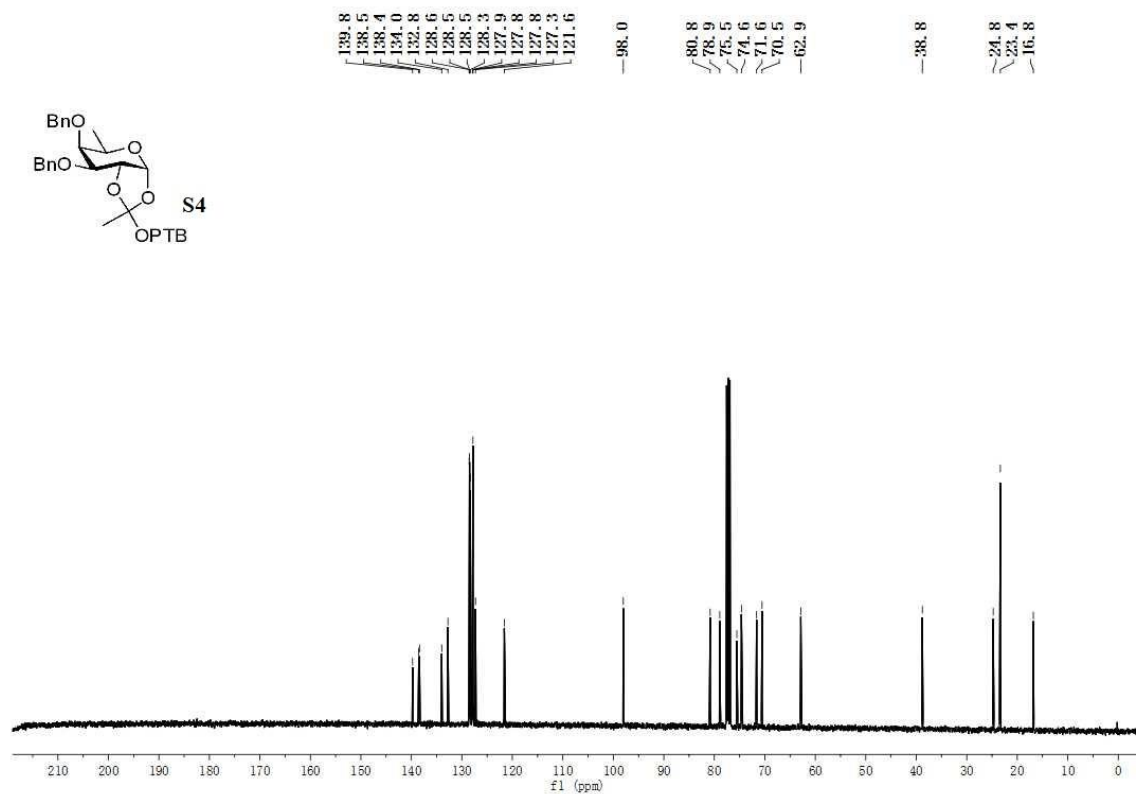
**Figure S5.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of S3



**Figure S6.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **S3**

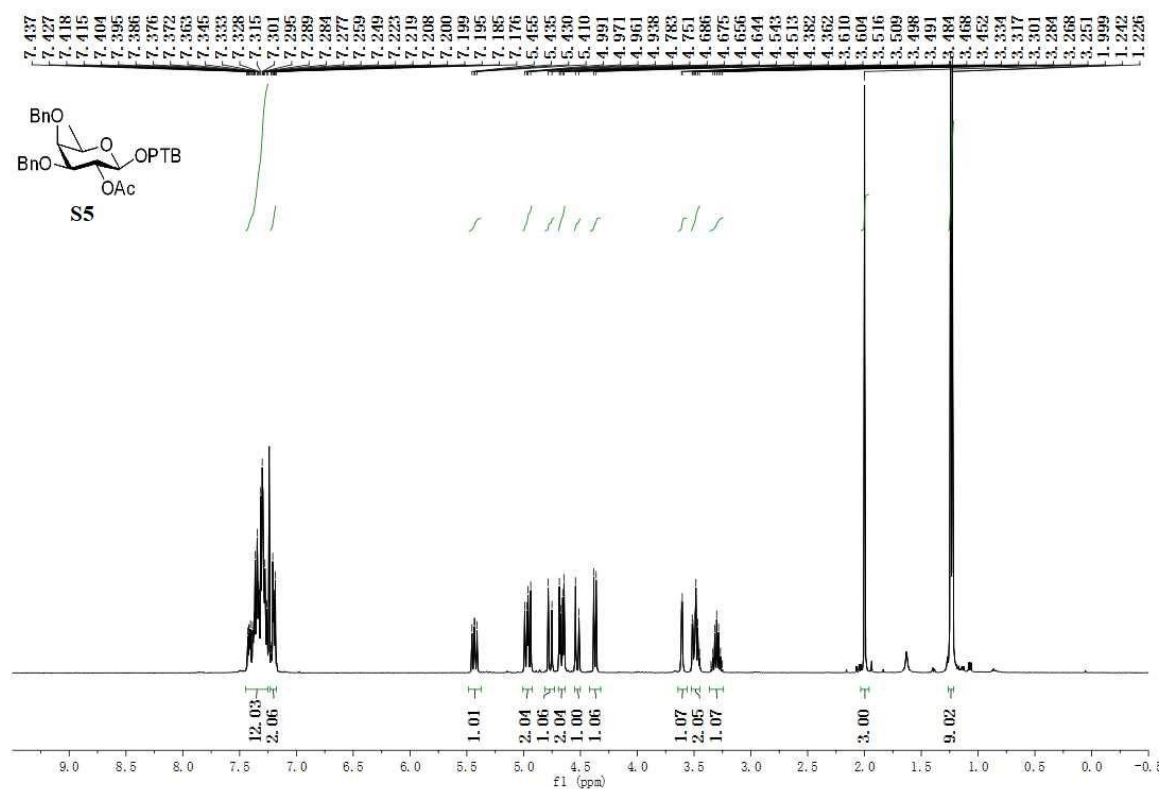


**Figure S7.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **S4**

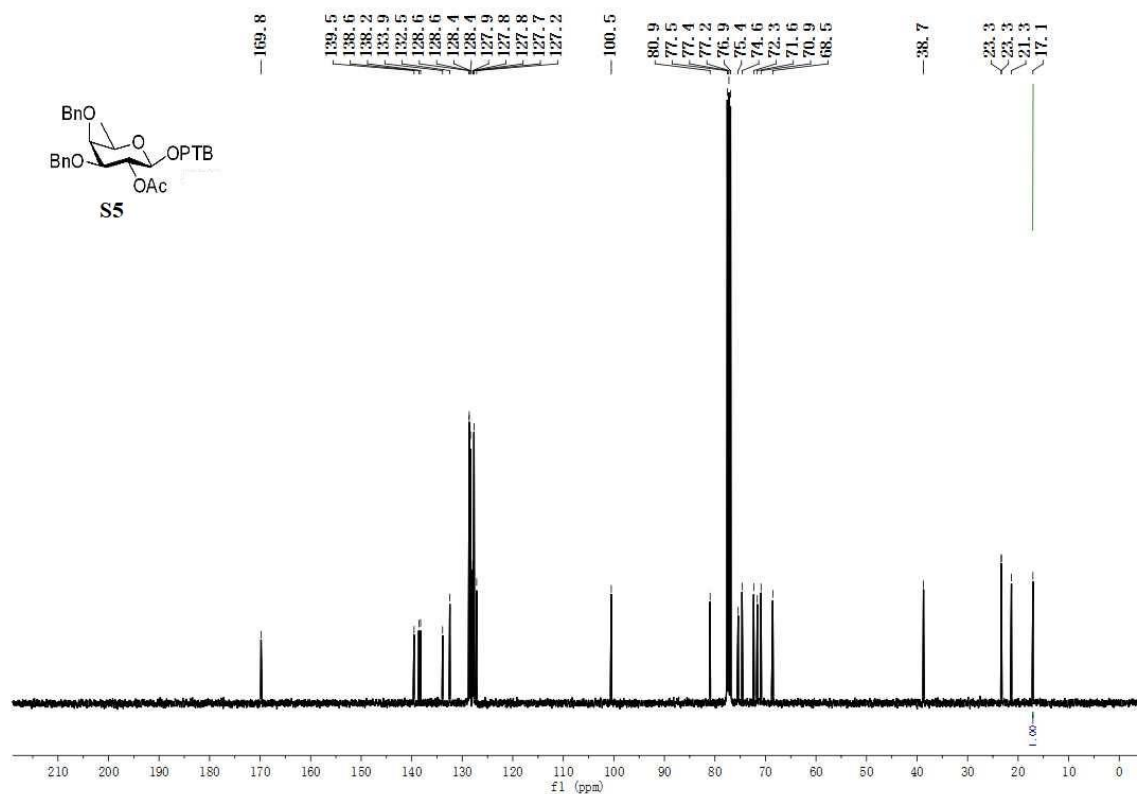


**Figure S8.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **S4**



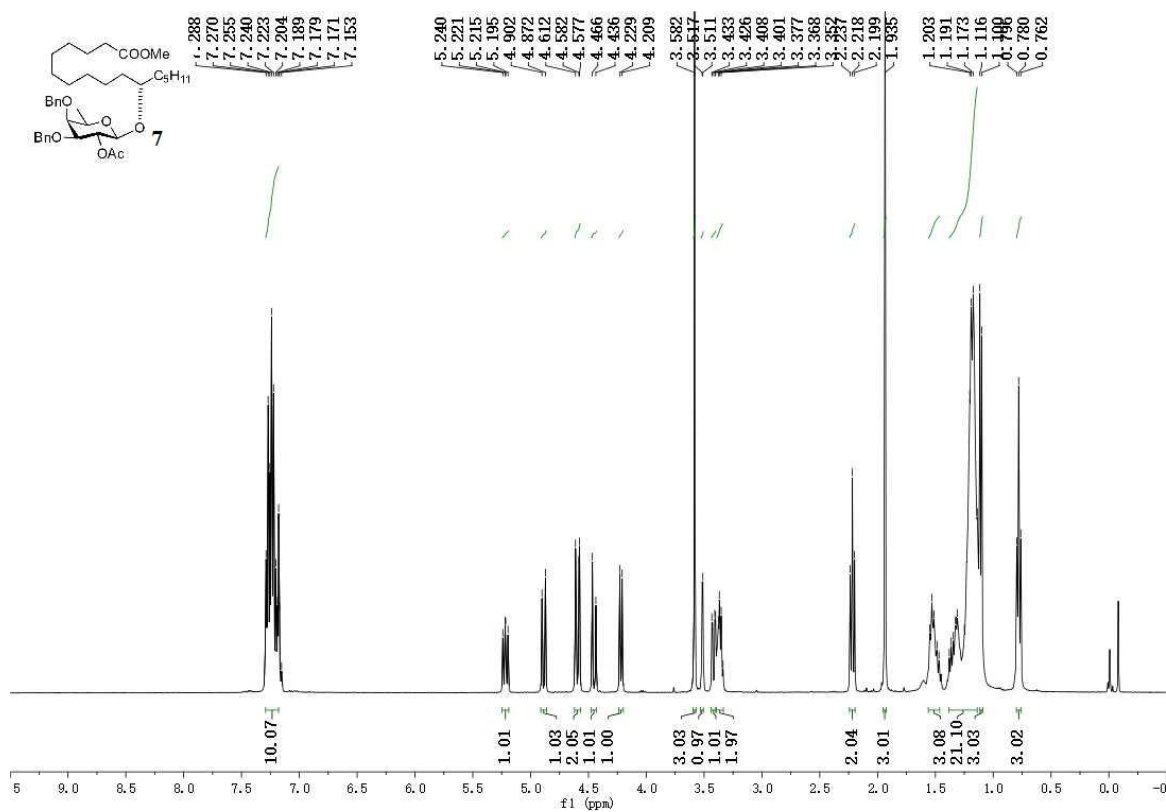


**Figure S9.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **S5**

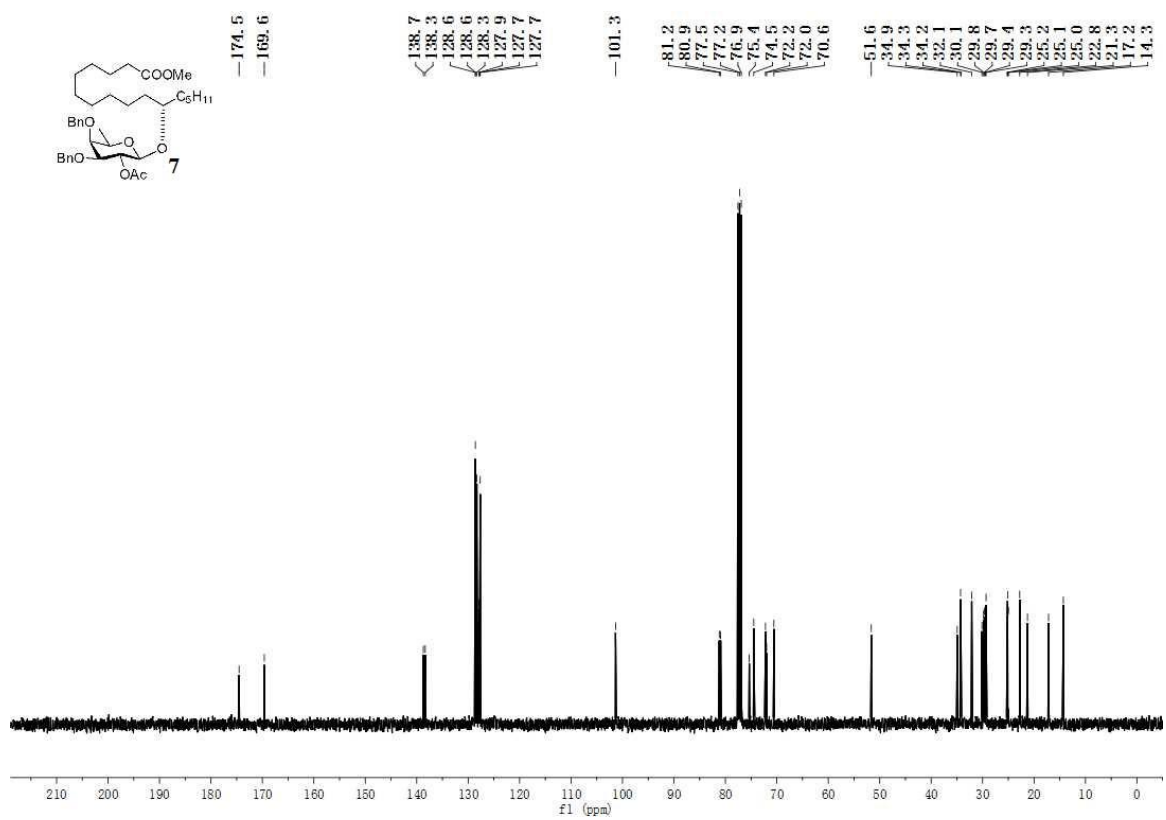


**Figure S10.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **S5**

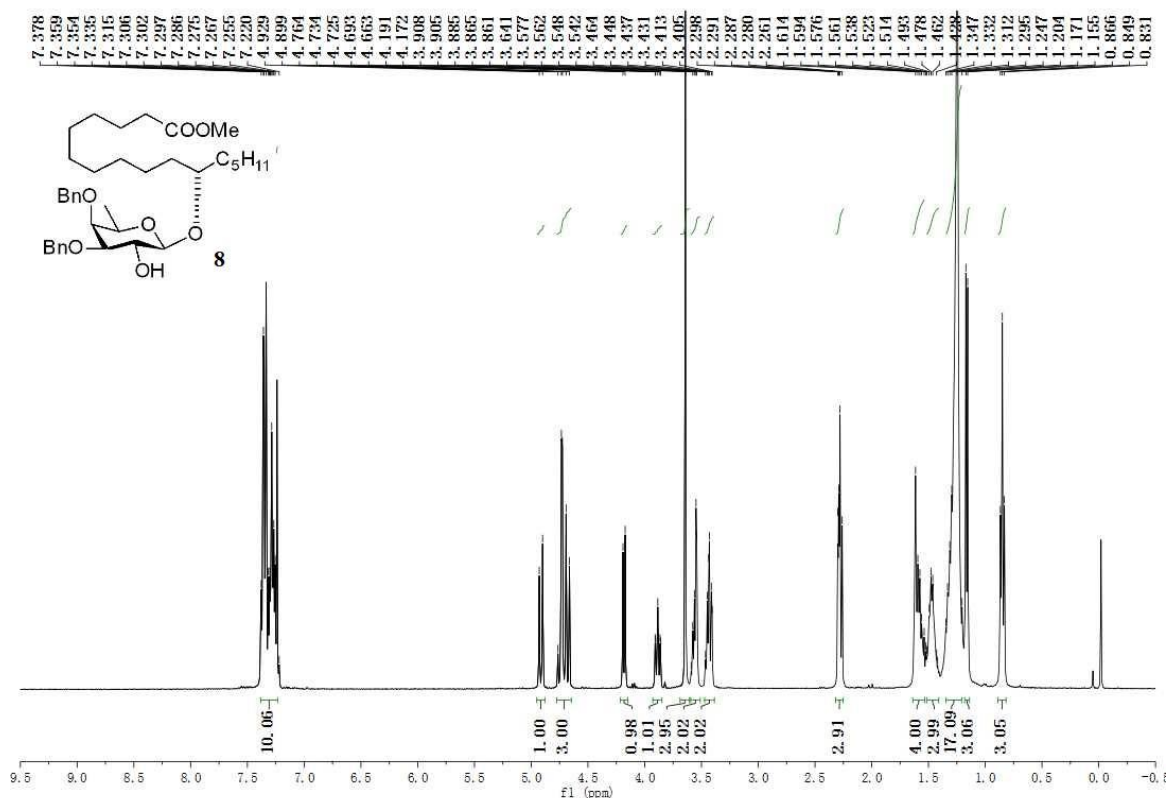




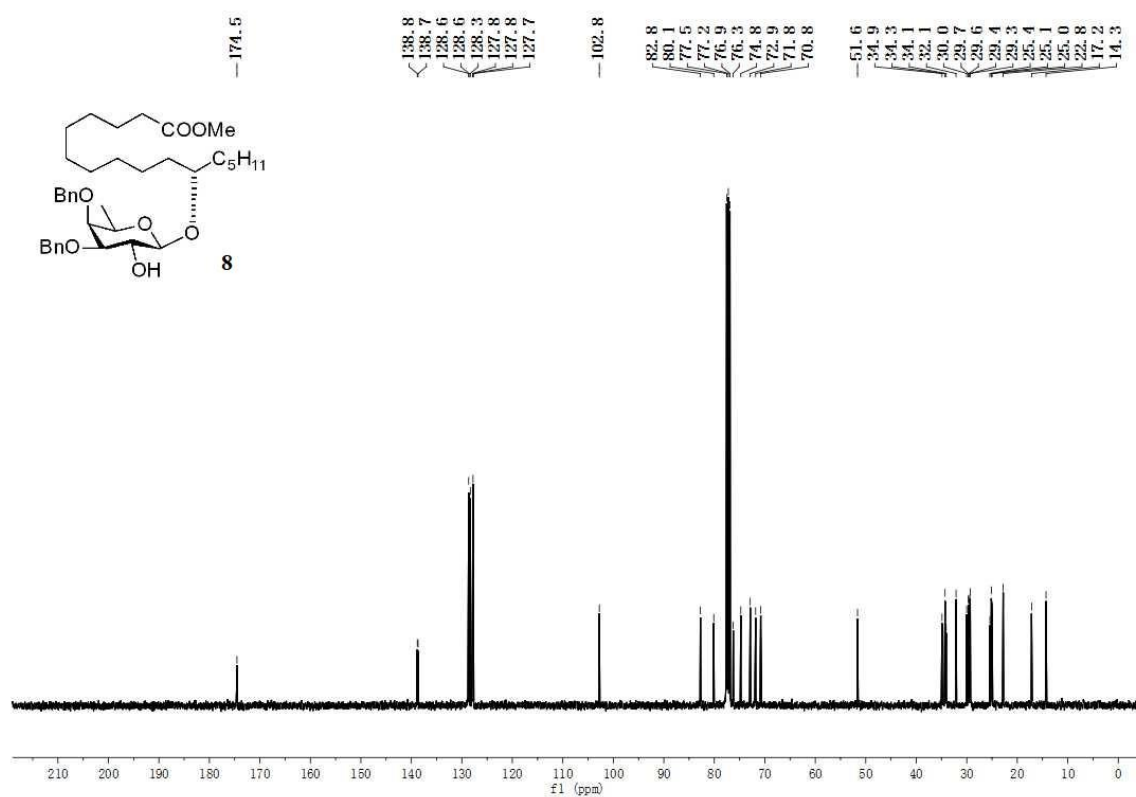
**Figure S13.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of 7**



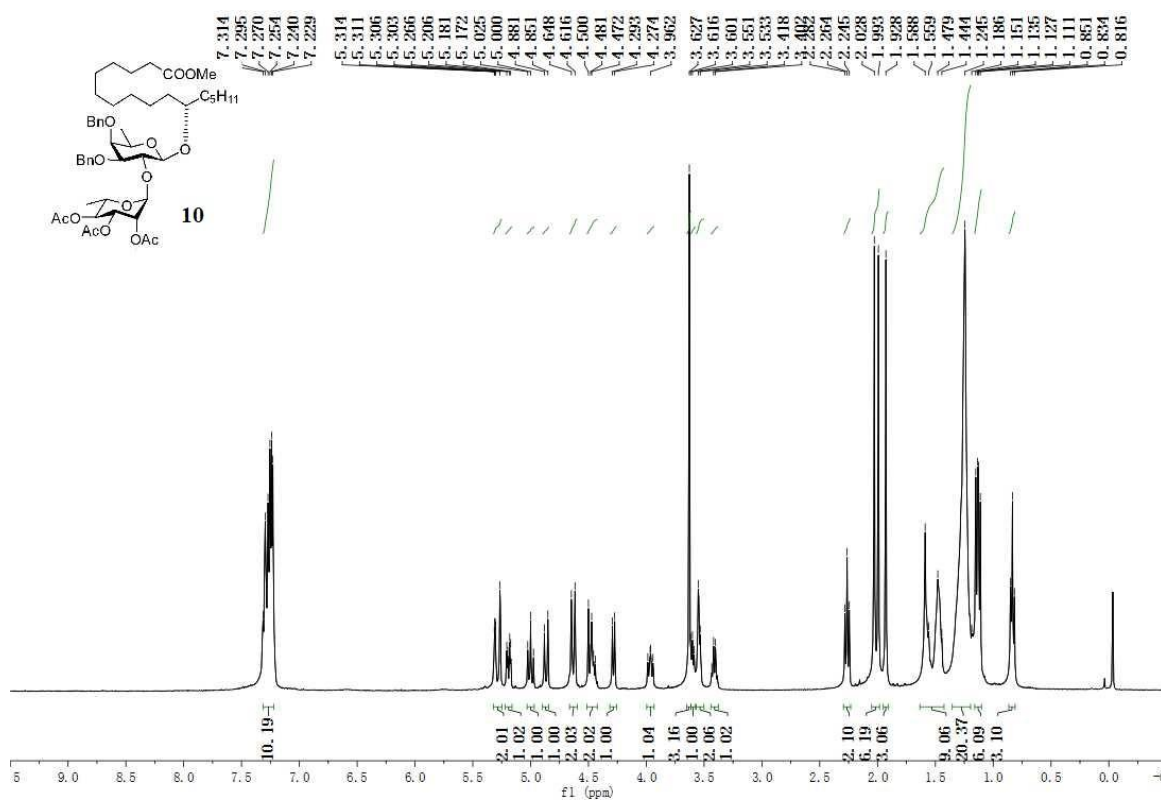
**Figure S14.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of 7**



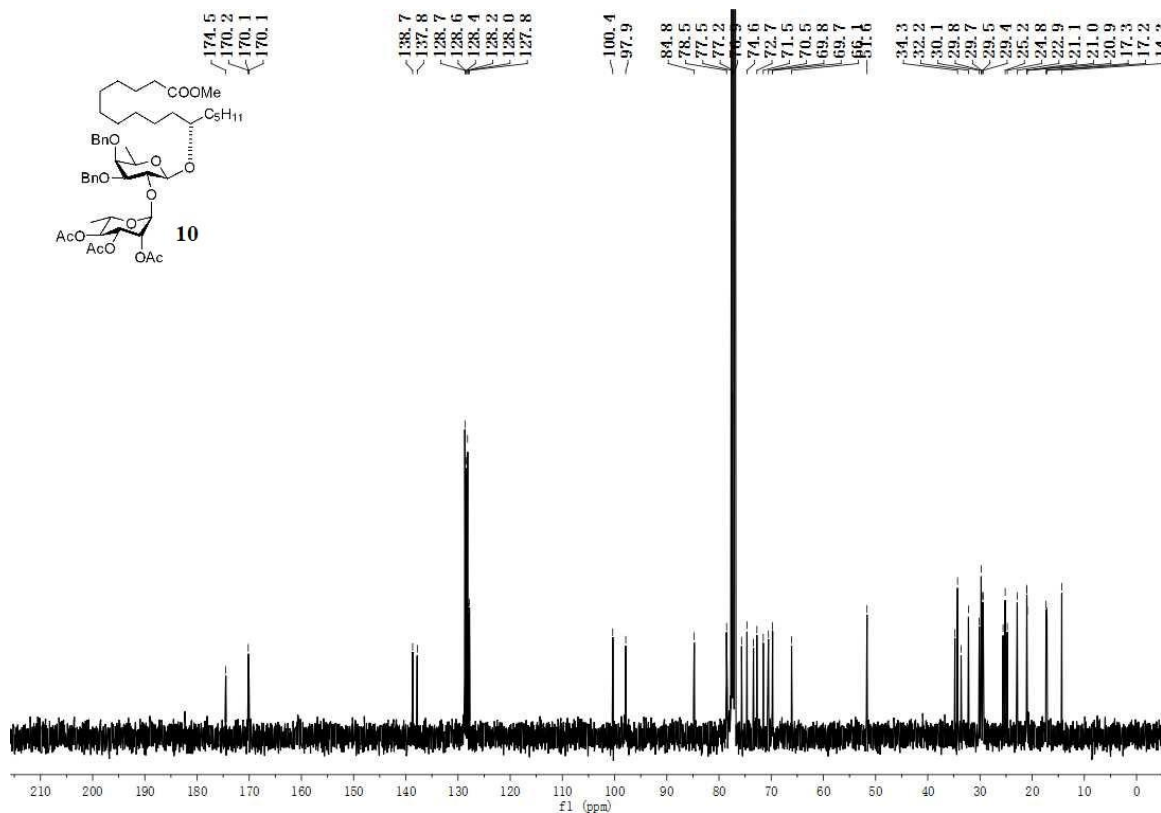
**Figure S15.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **8**



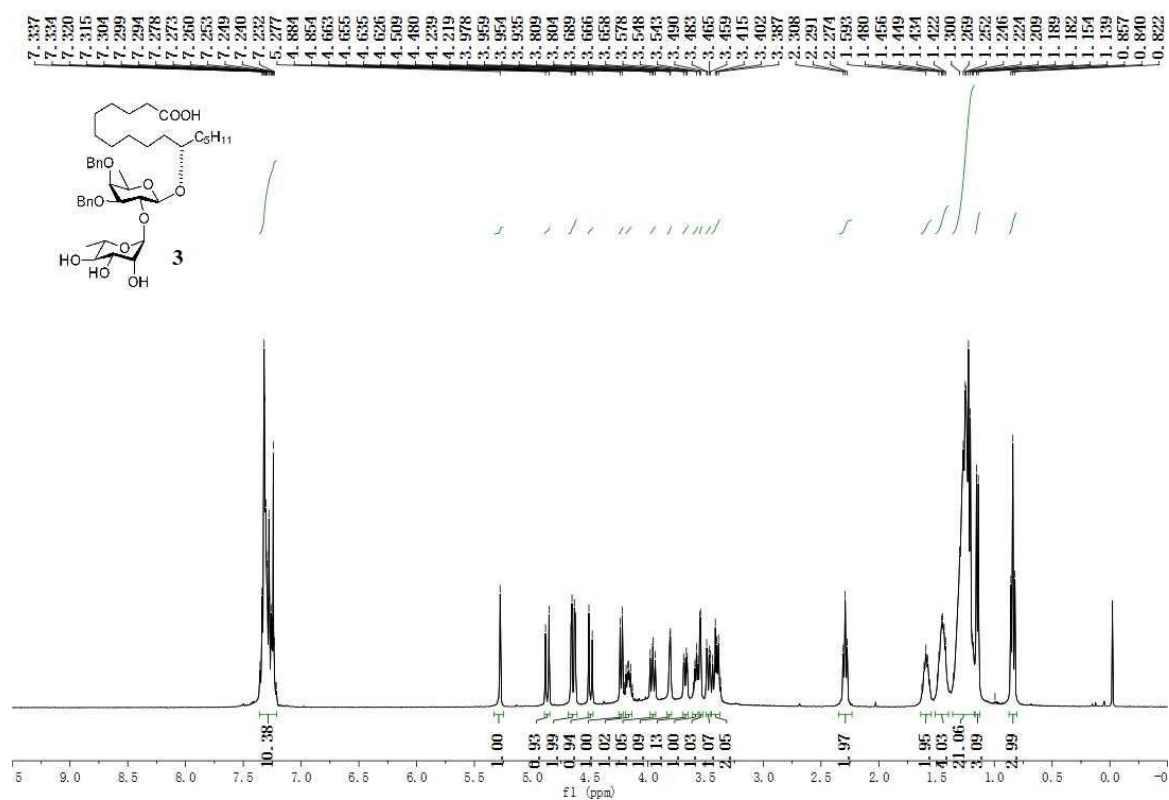
**Figure S16.** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **8**



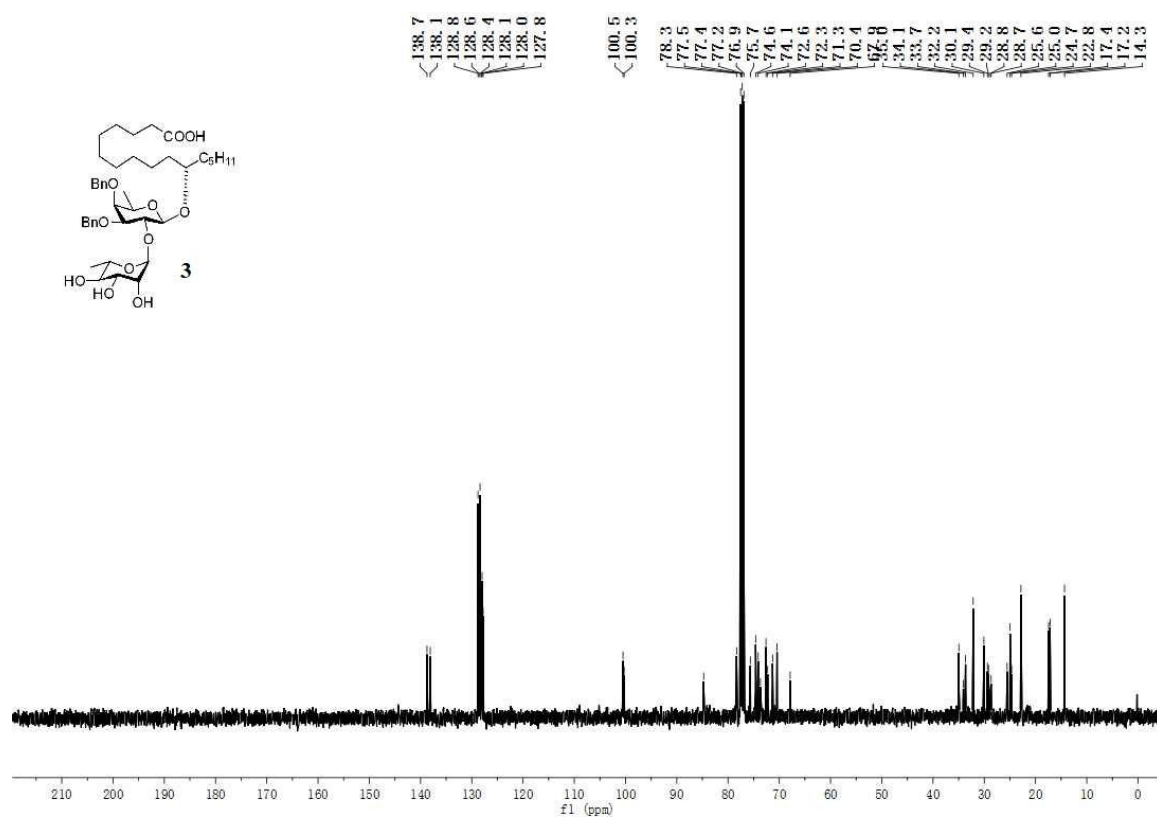
**Figure S17.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **10**



**Figure S18.** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **10**



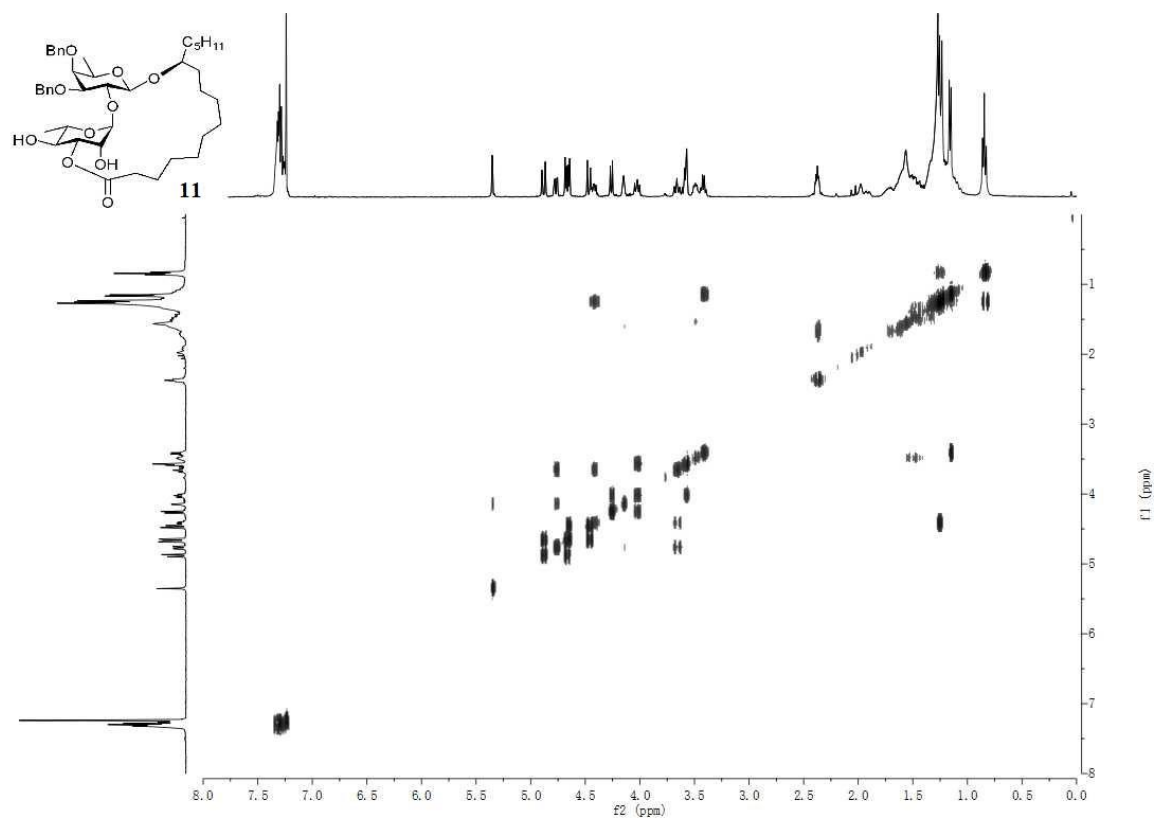
**Figure S19.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **3**



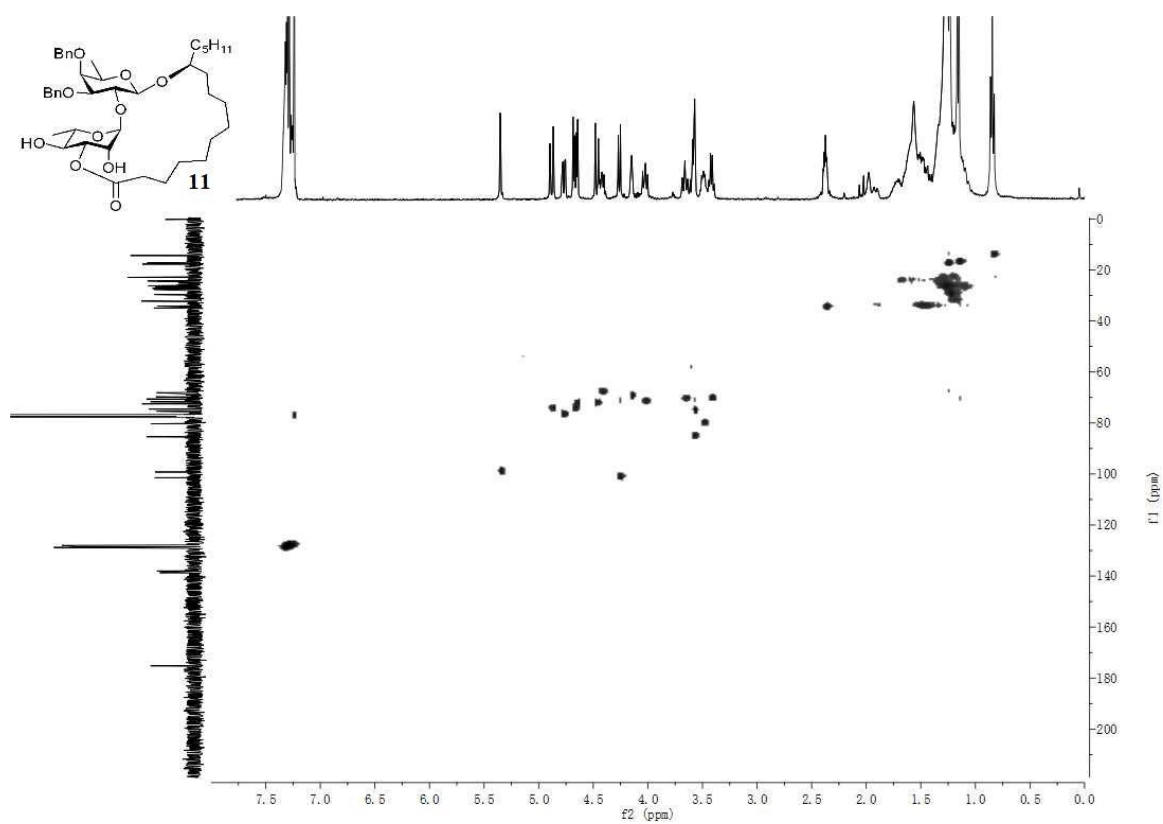
**Figure S20.** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **3**







**Figure S23.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **11**



**Figure S24.** HMBC spectrum of **11**



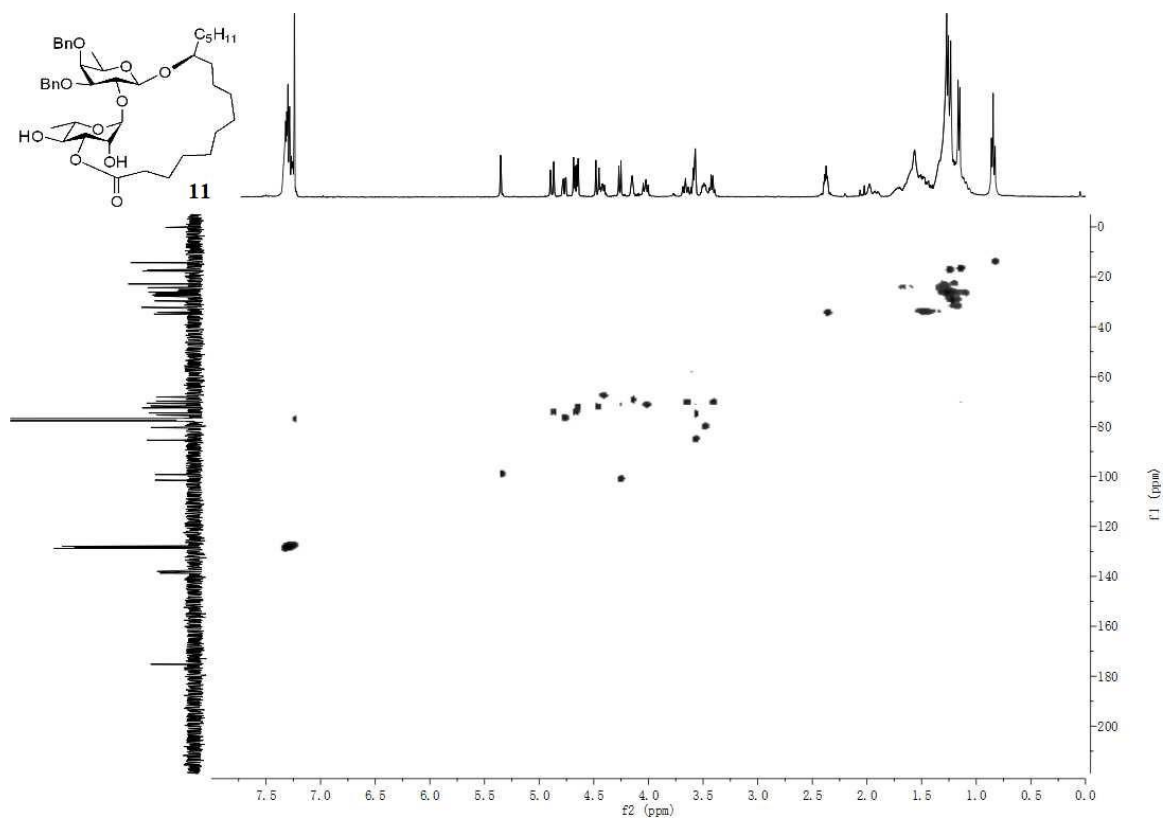


Figure S25. HSQC spectrum of **11**

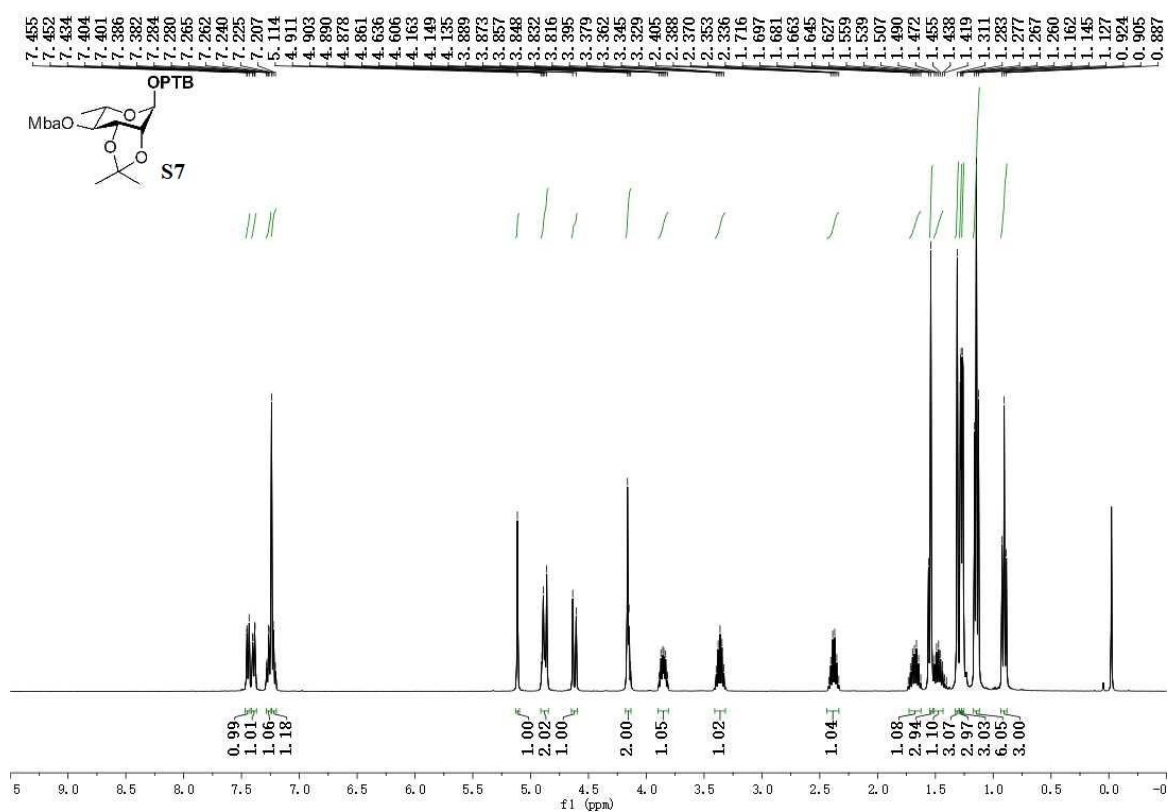
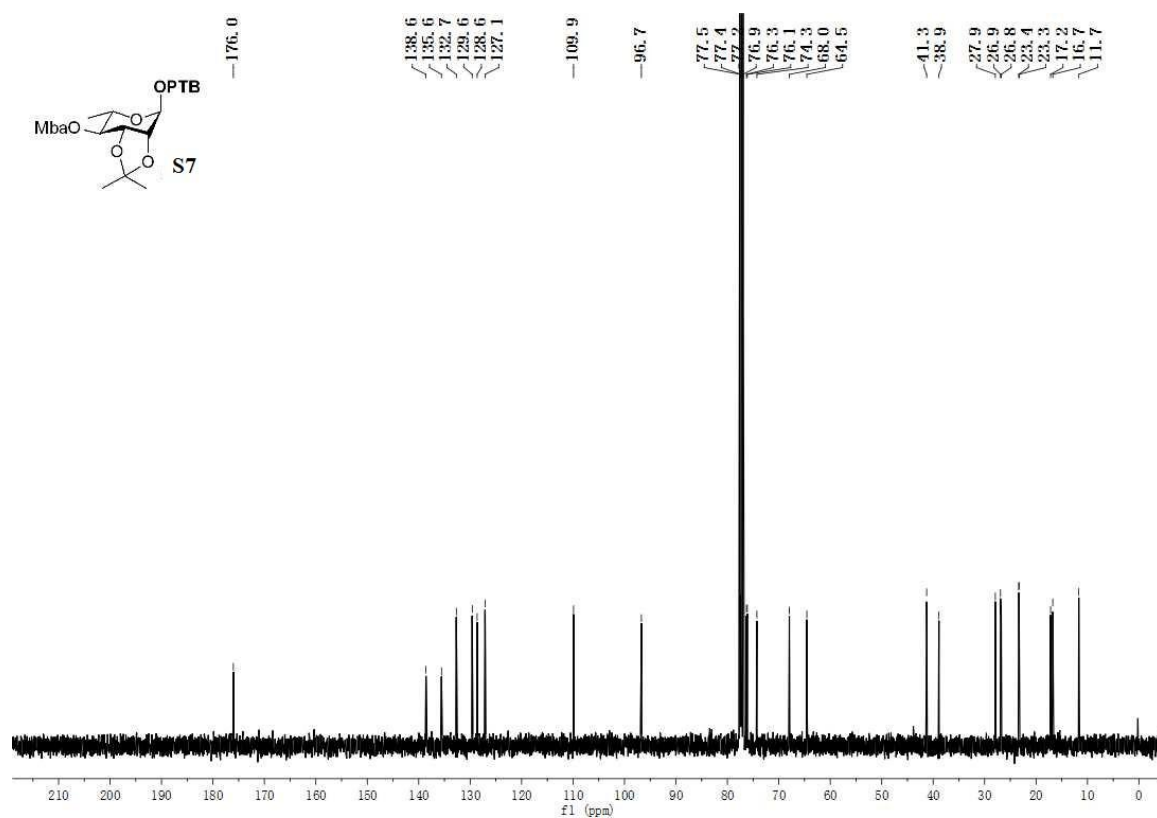
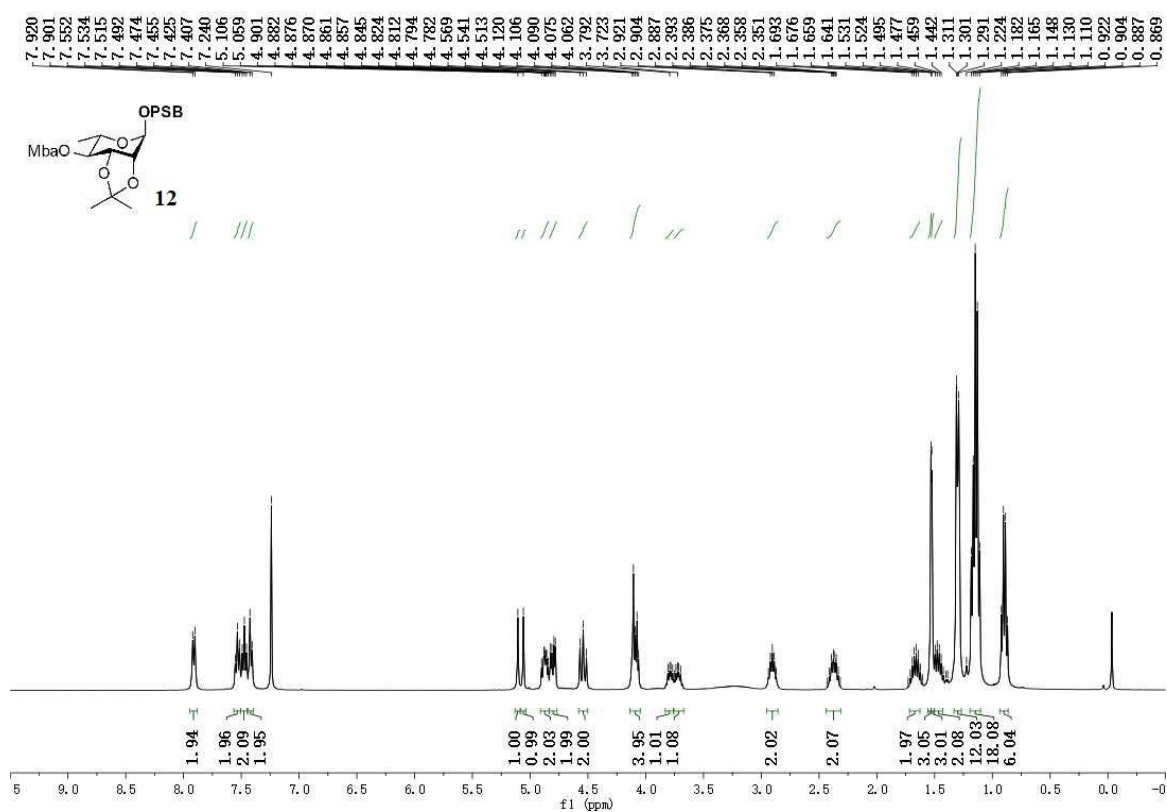


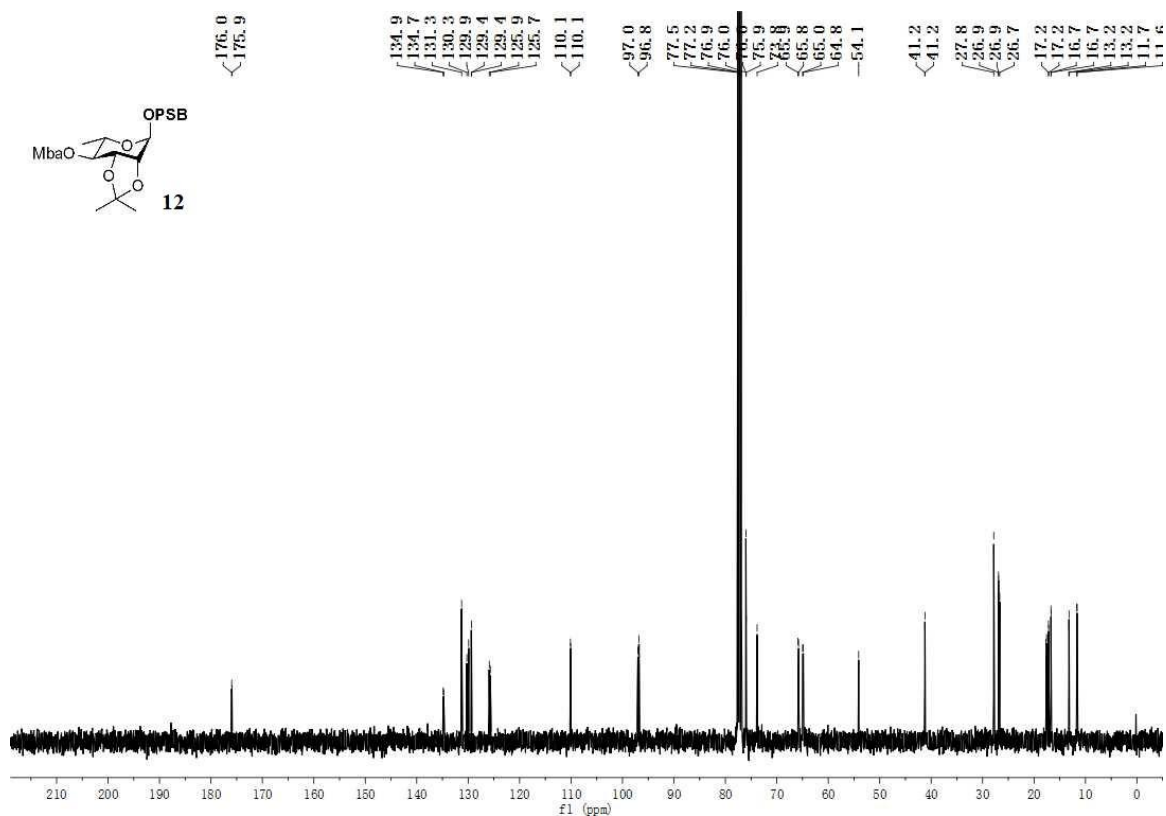
Figure S26.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **S7**



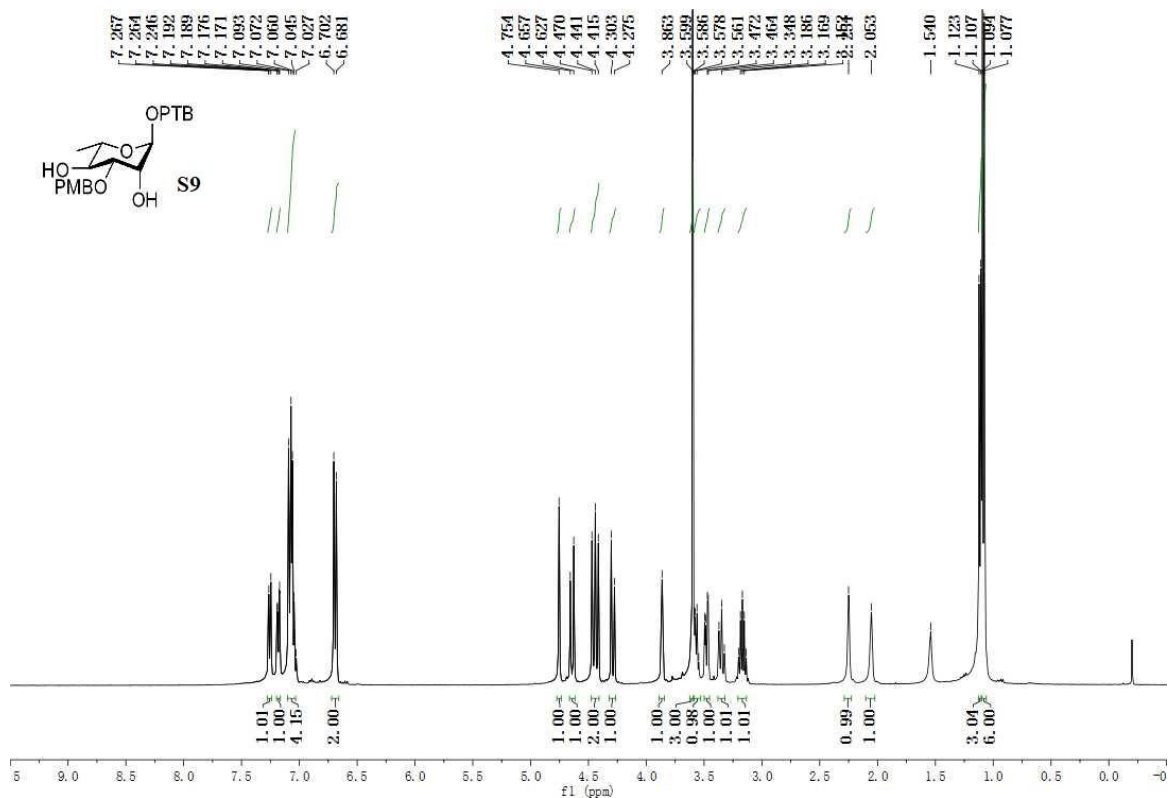
**Figure S27.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **S7**



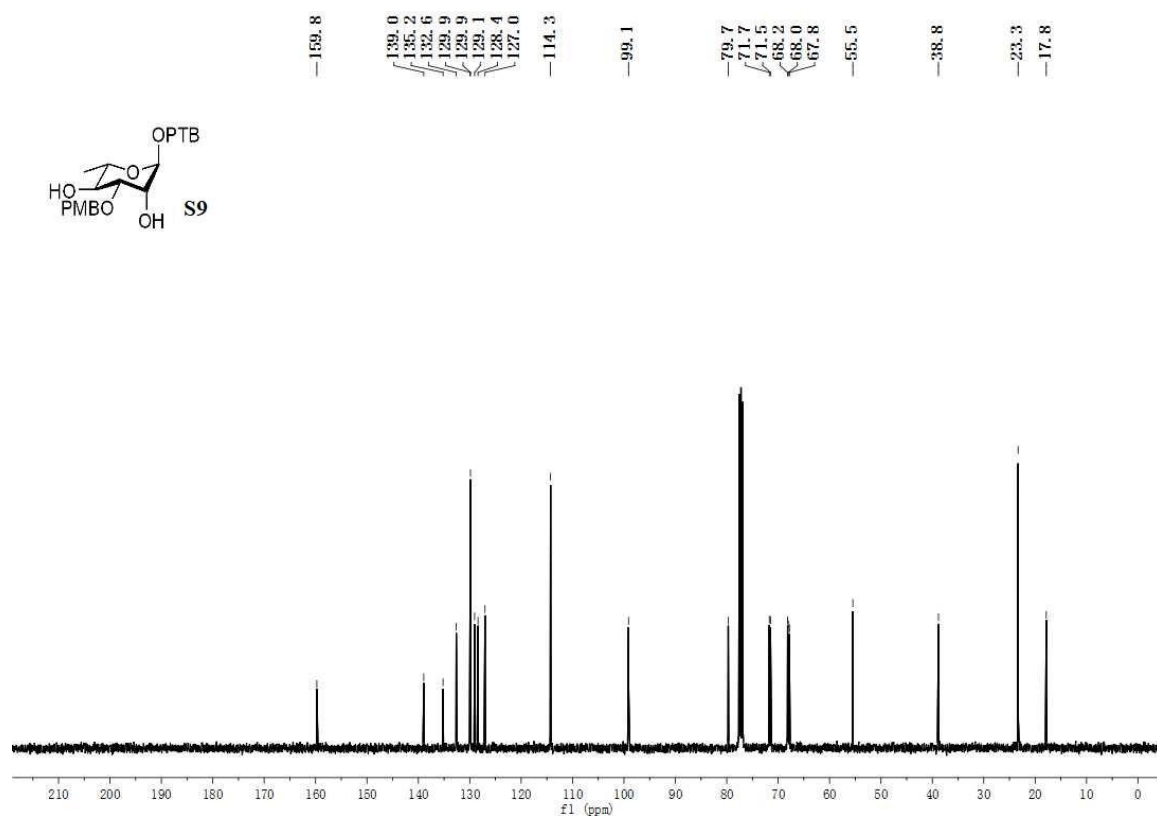
**Figure S28.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **12**



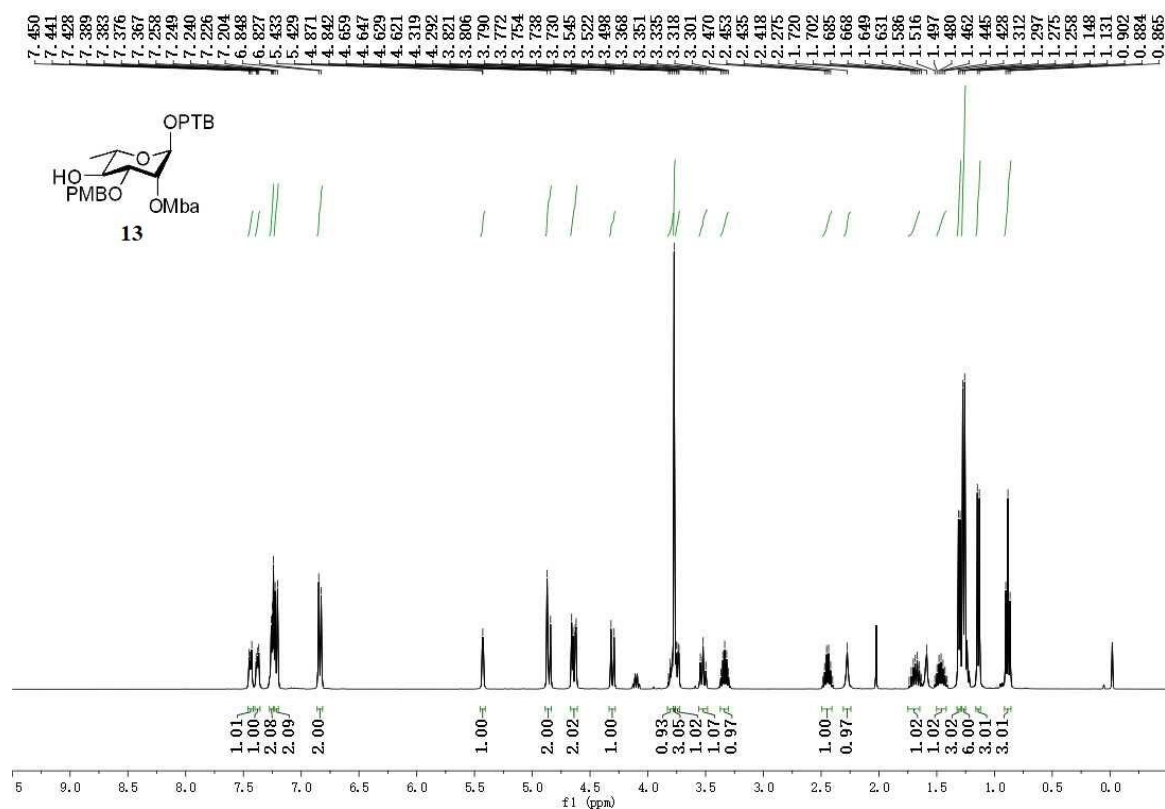
**Figure S29.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **12**



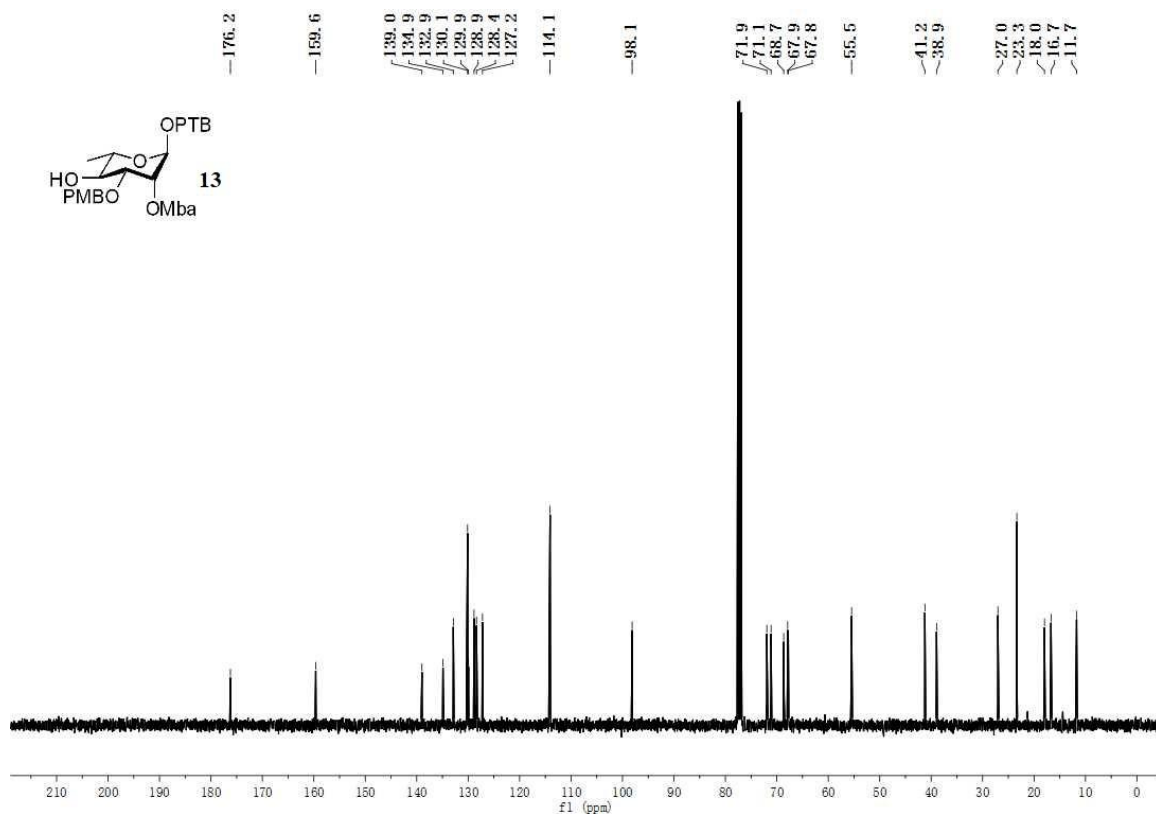
**Figure S30.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **S9**



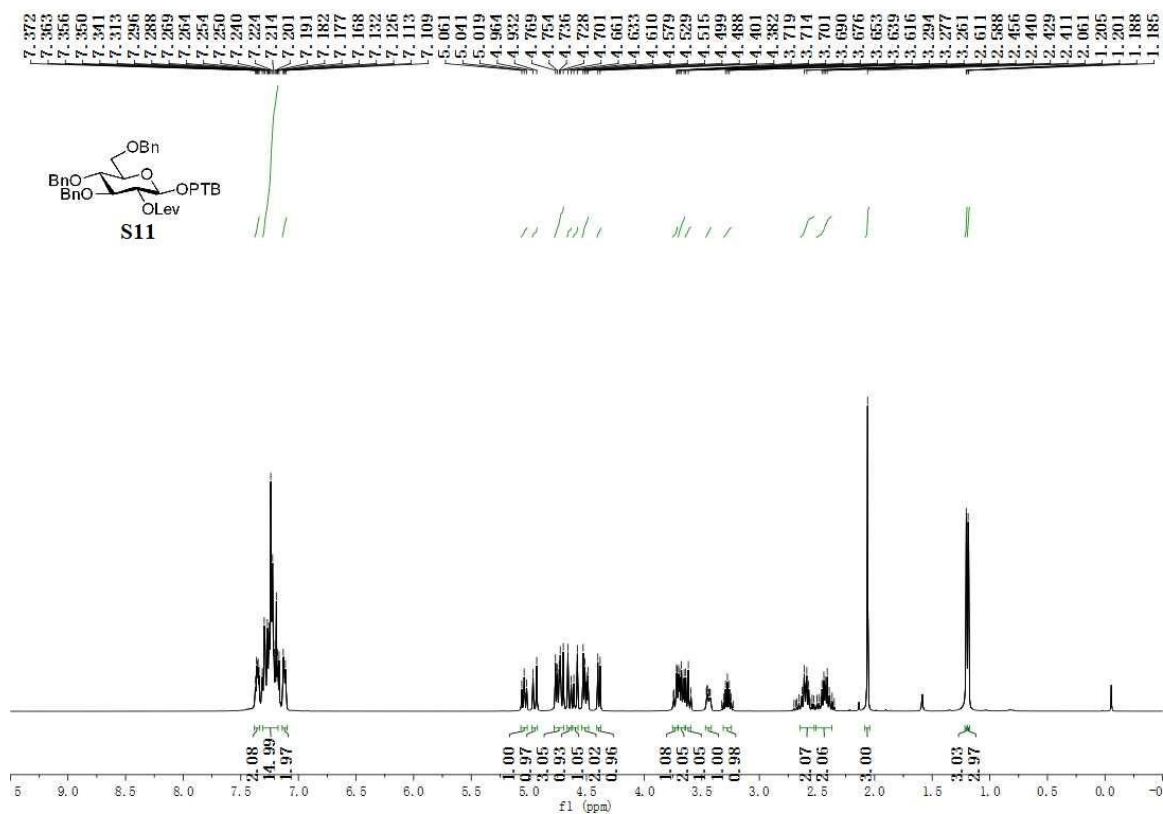
**Figure S31.** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of S9



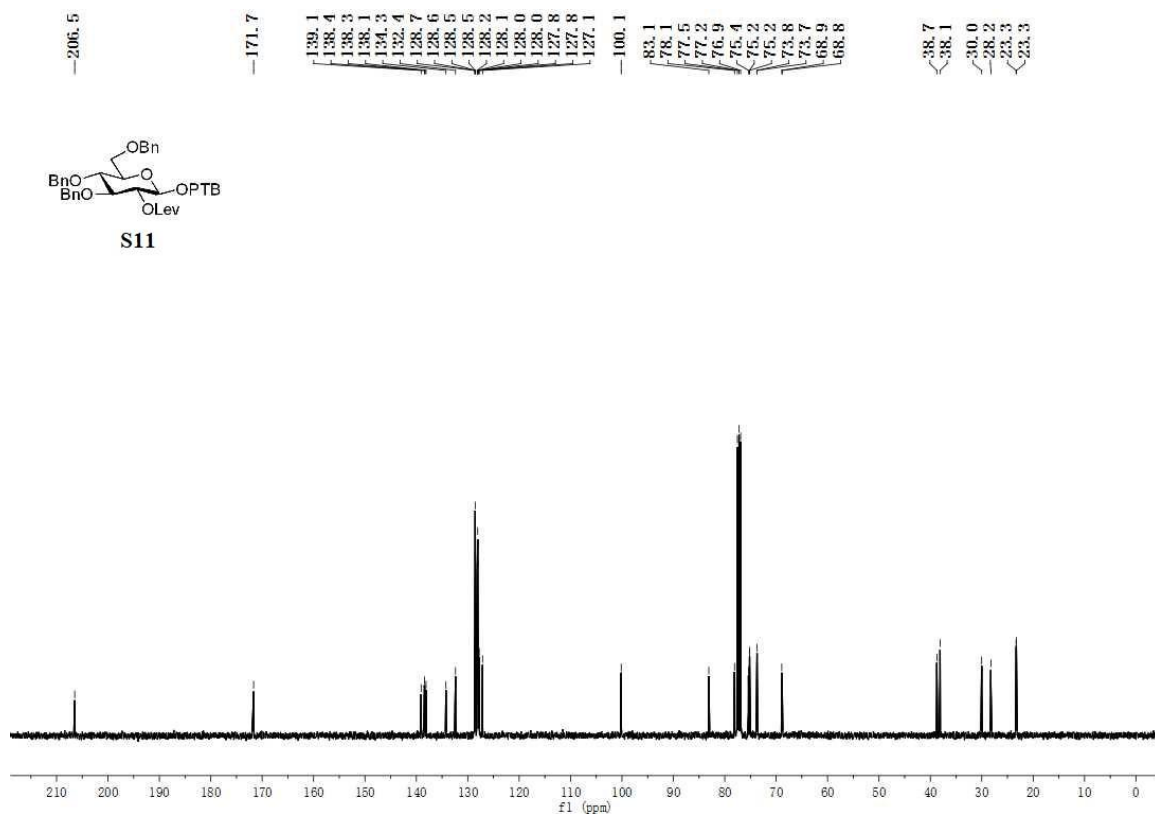
**Figure S32.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 13



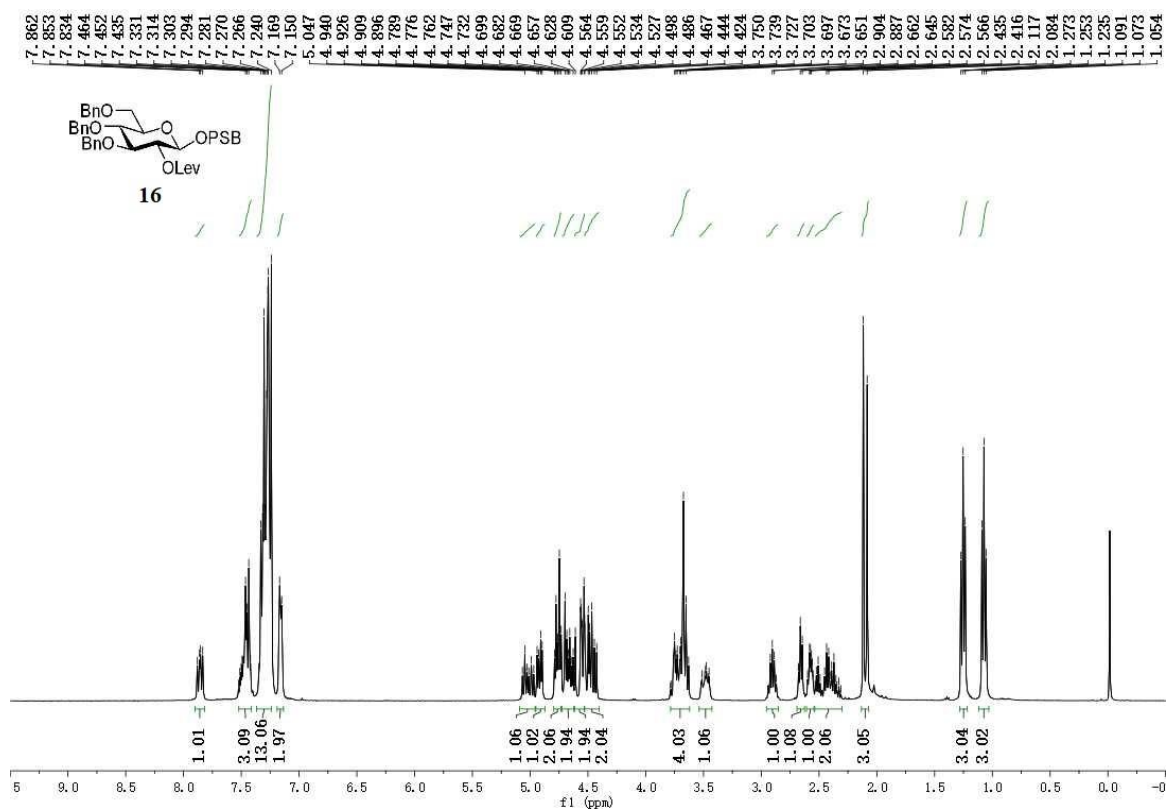
**Figure S33.** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **13**



**Figure S34.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **S11**



**Figure S35.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **S11**



**Figure S36.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **16**

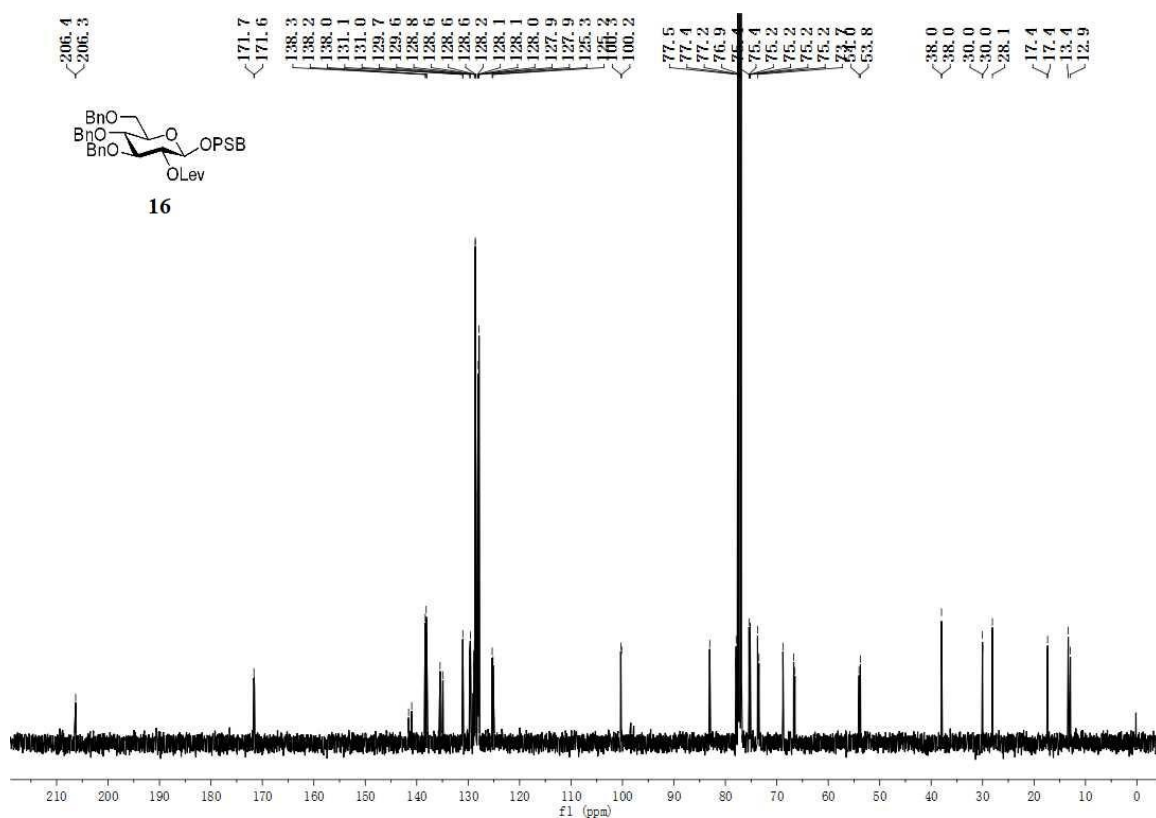


Figure S37. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **16**

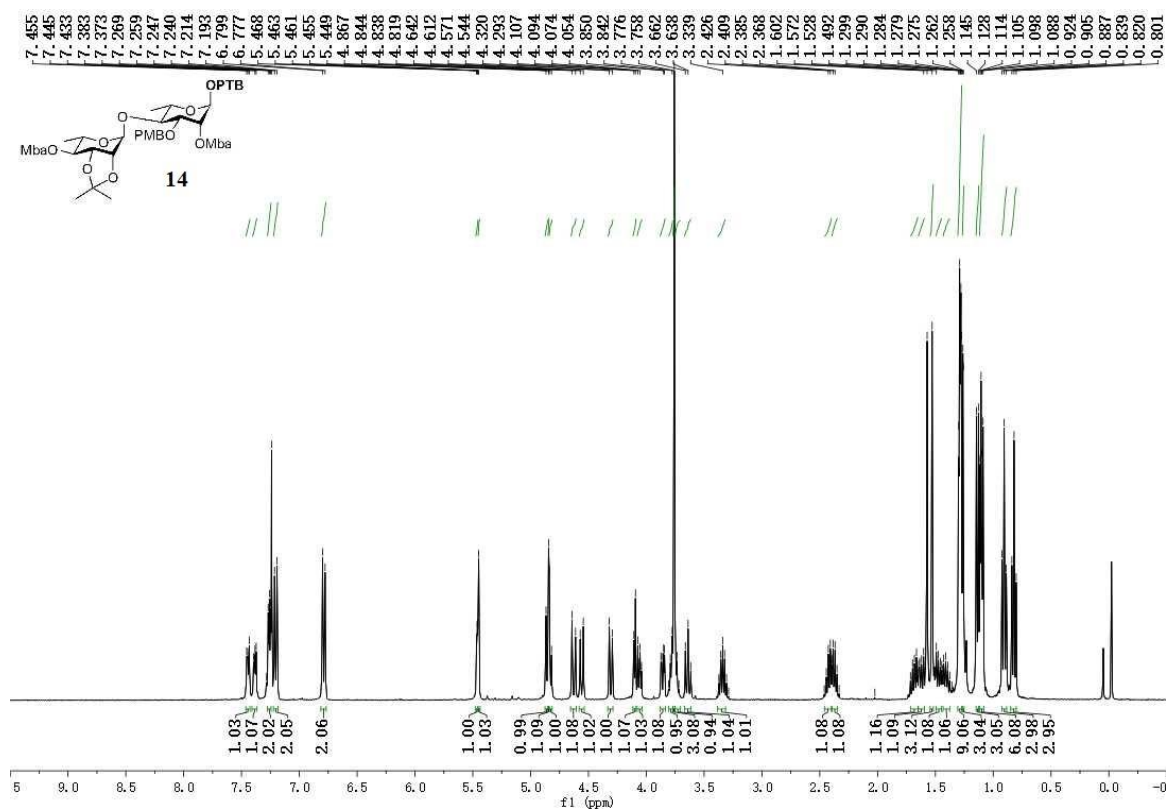
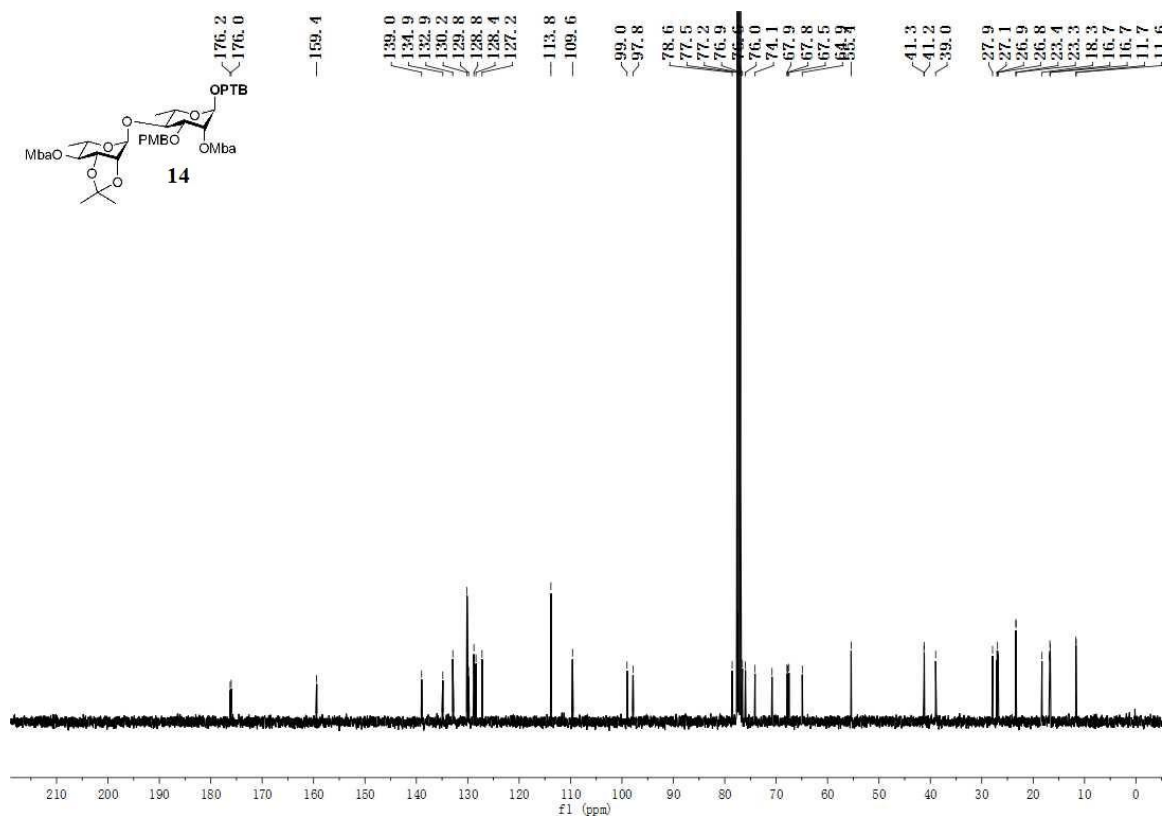
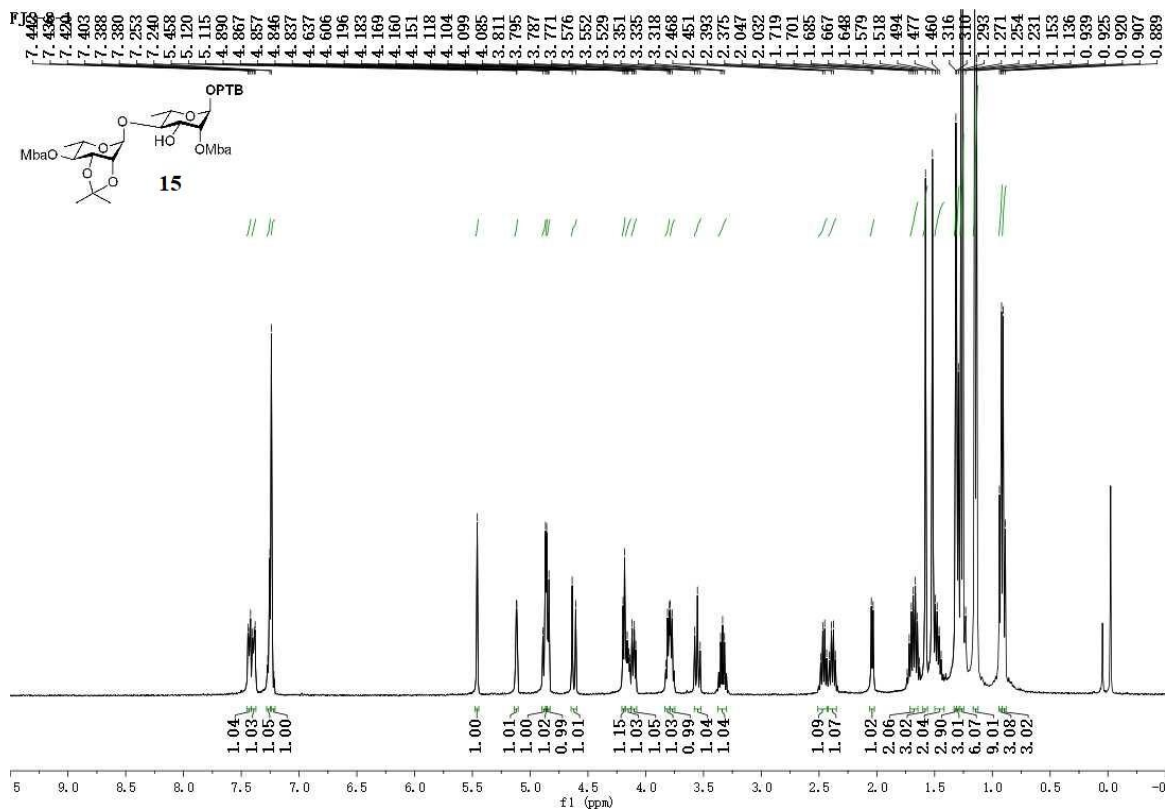


Figure S38. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **14**



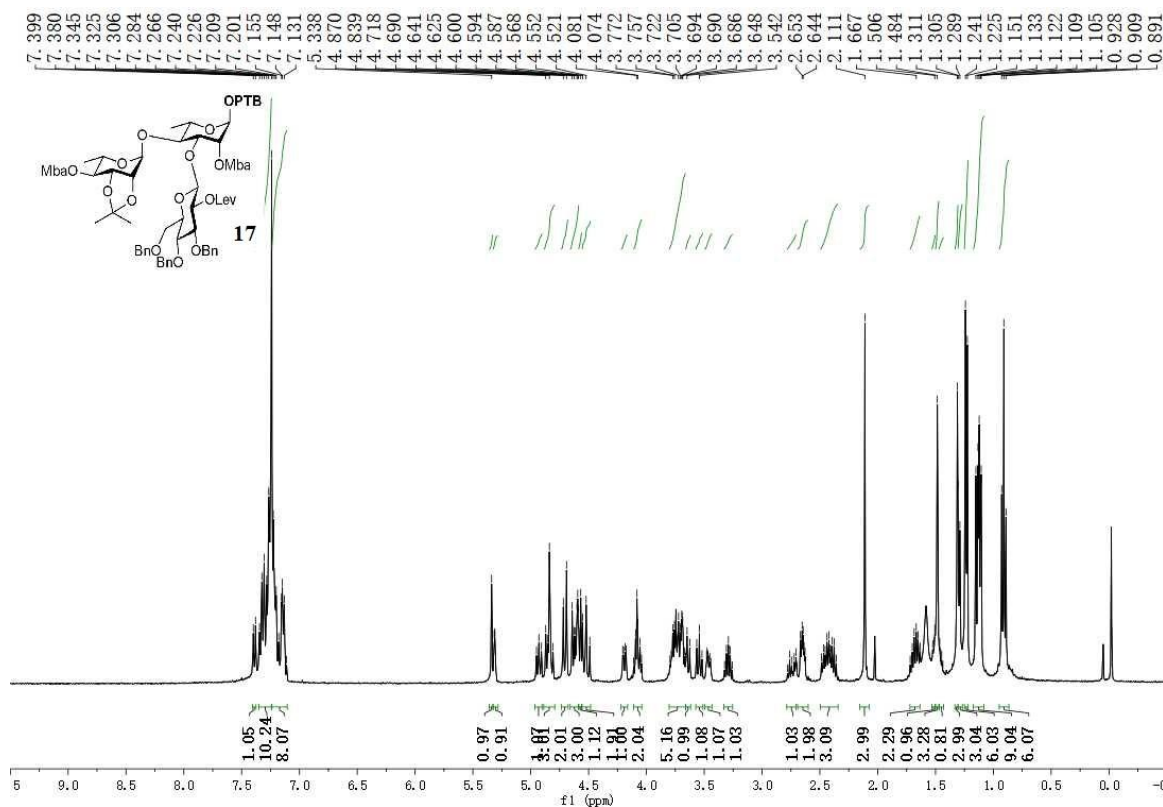
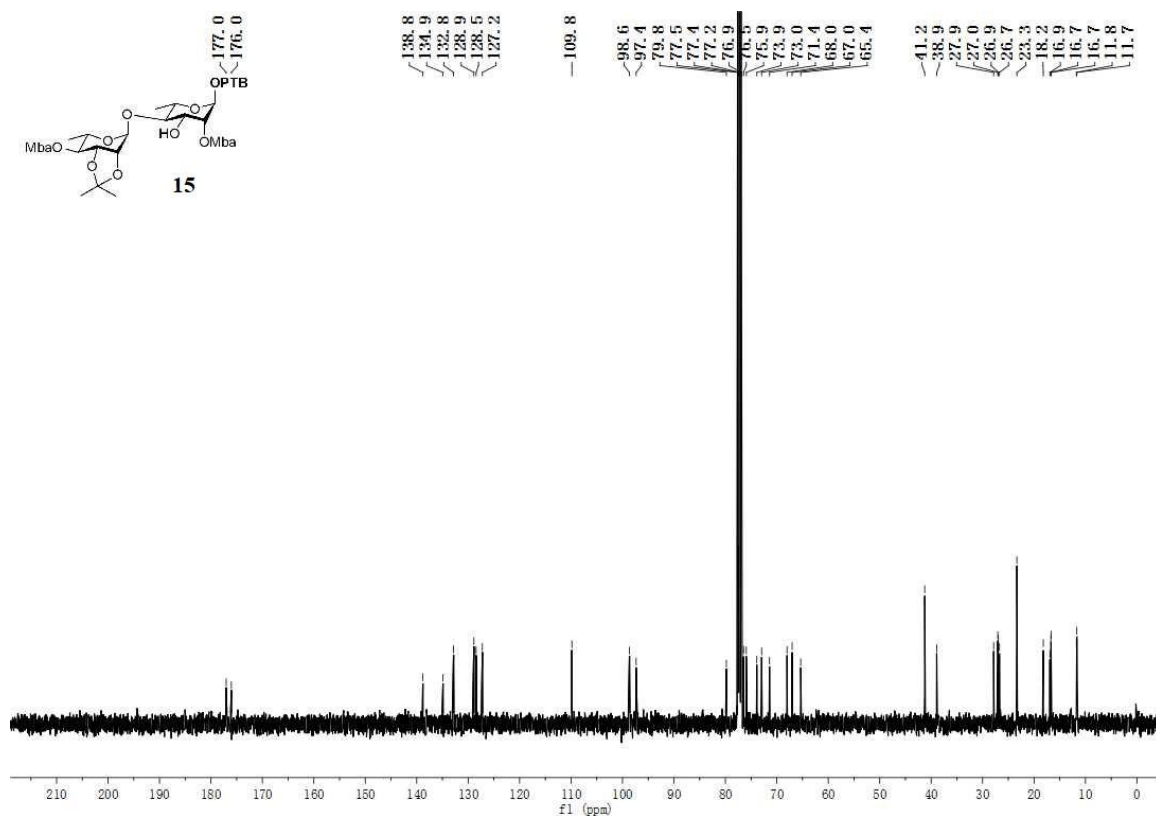


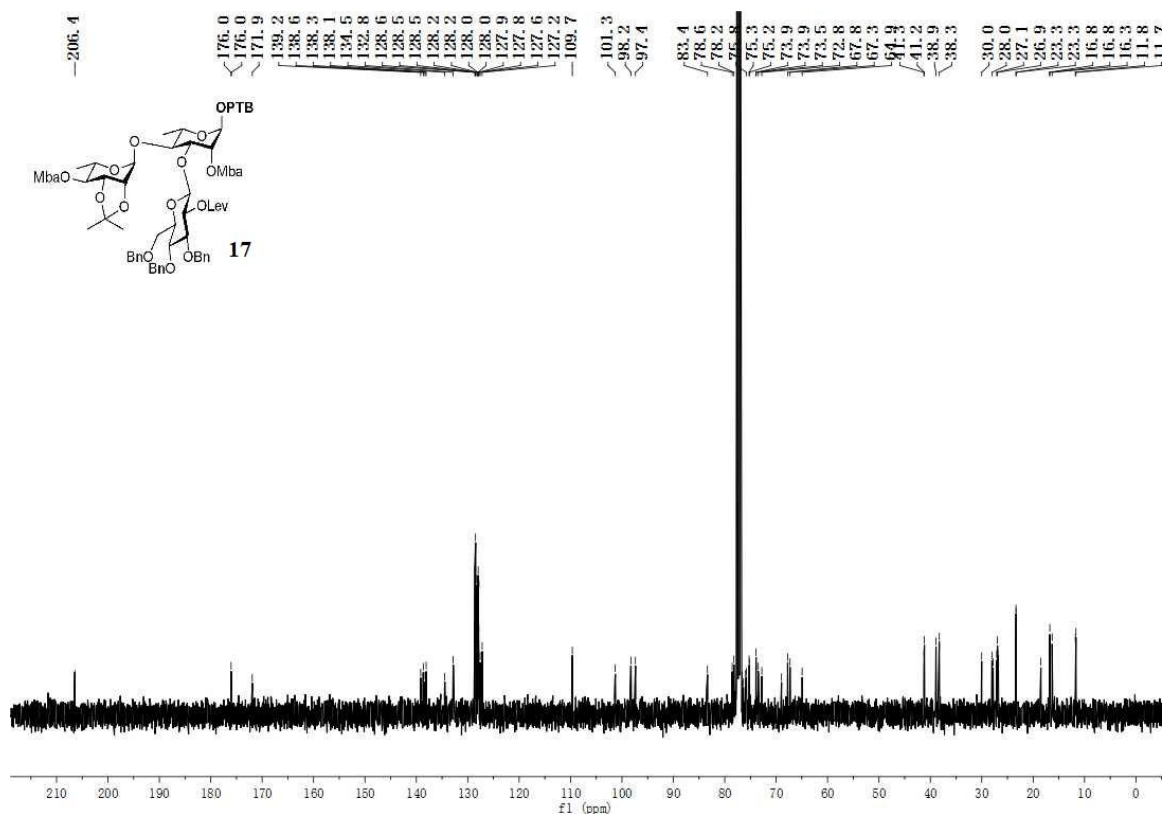
**Figure S39.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **14**



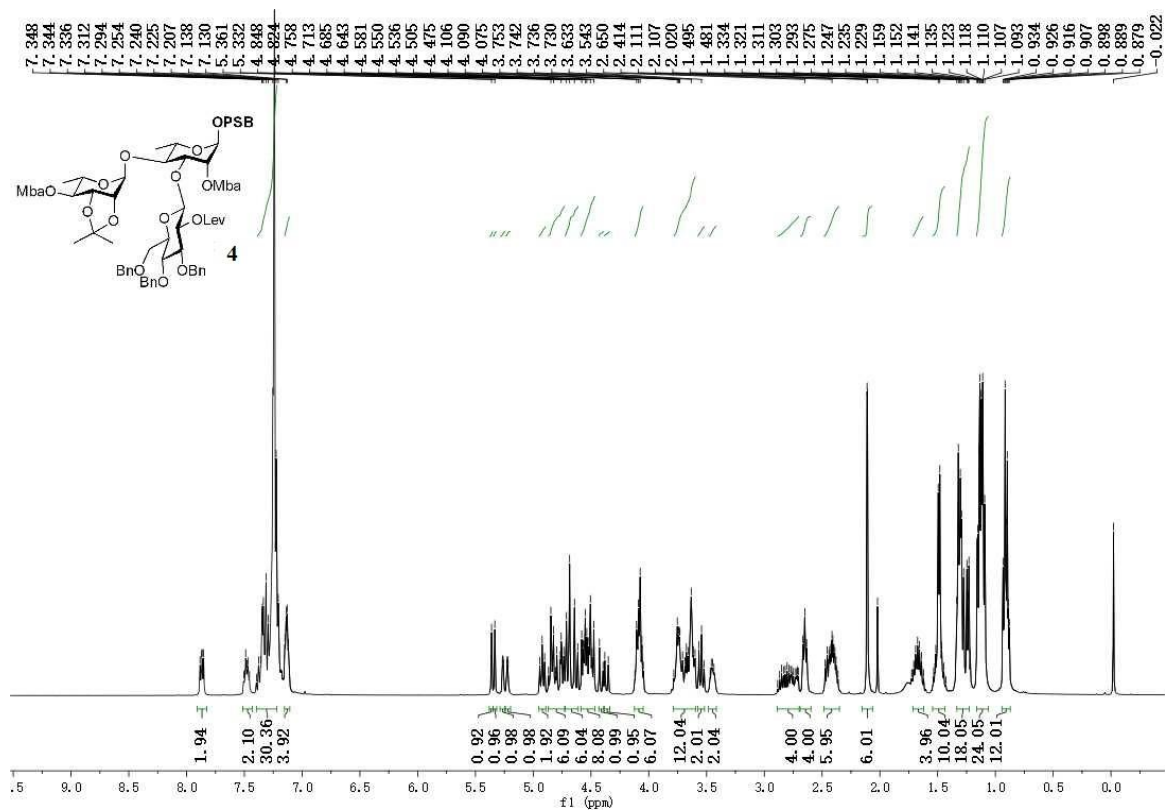
**Figure S40.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **15**



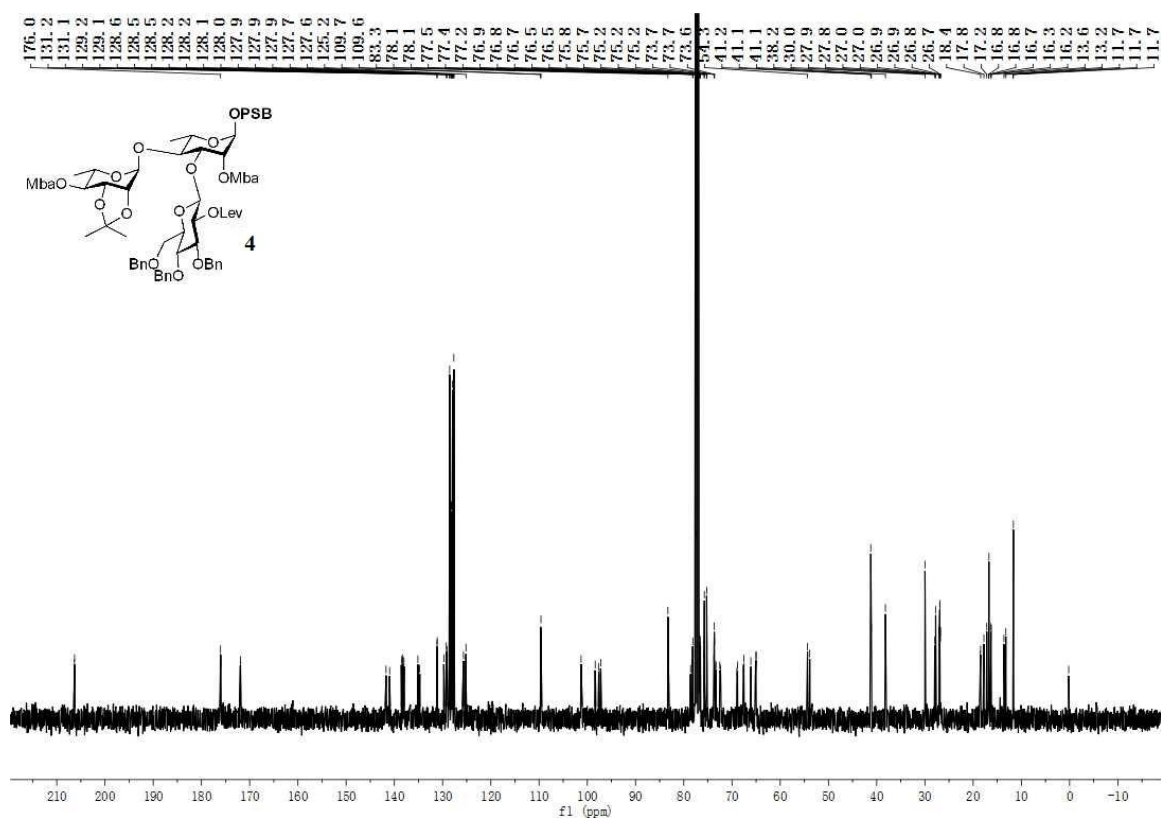




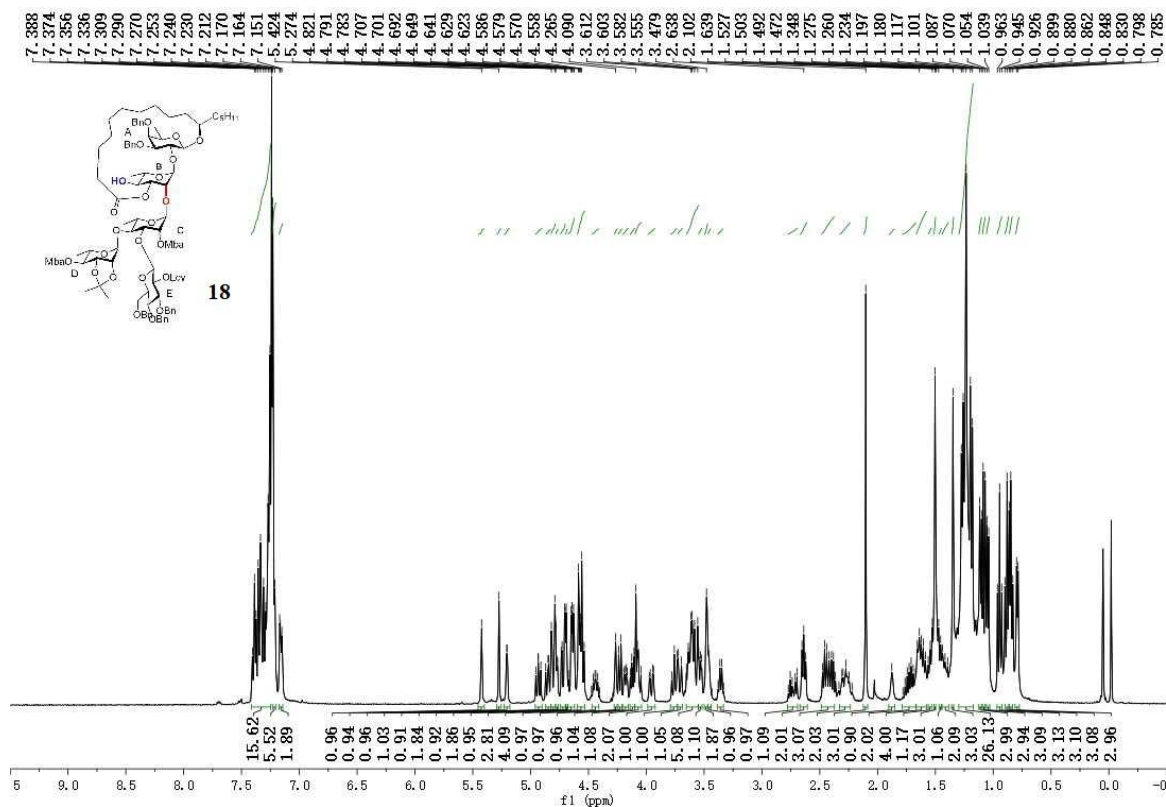
**Figure S43.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **17**



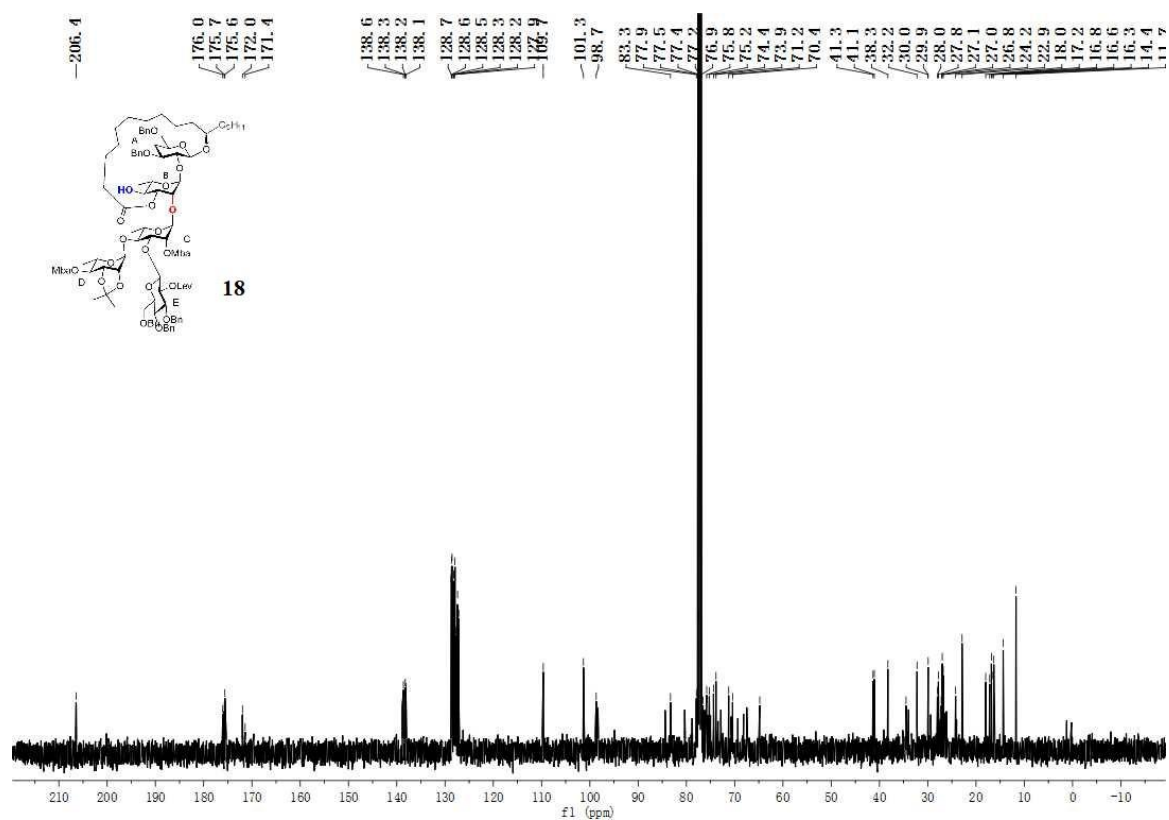
**Figure S44.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **4**



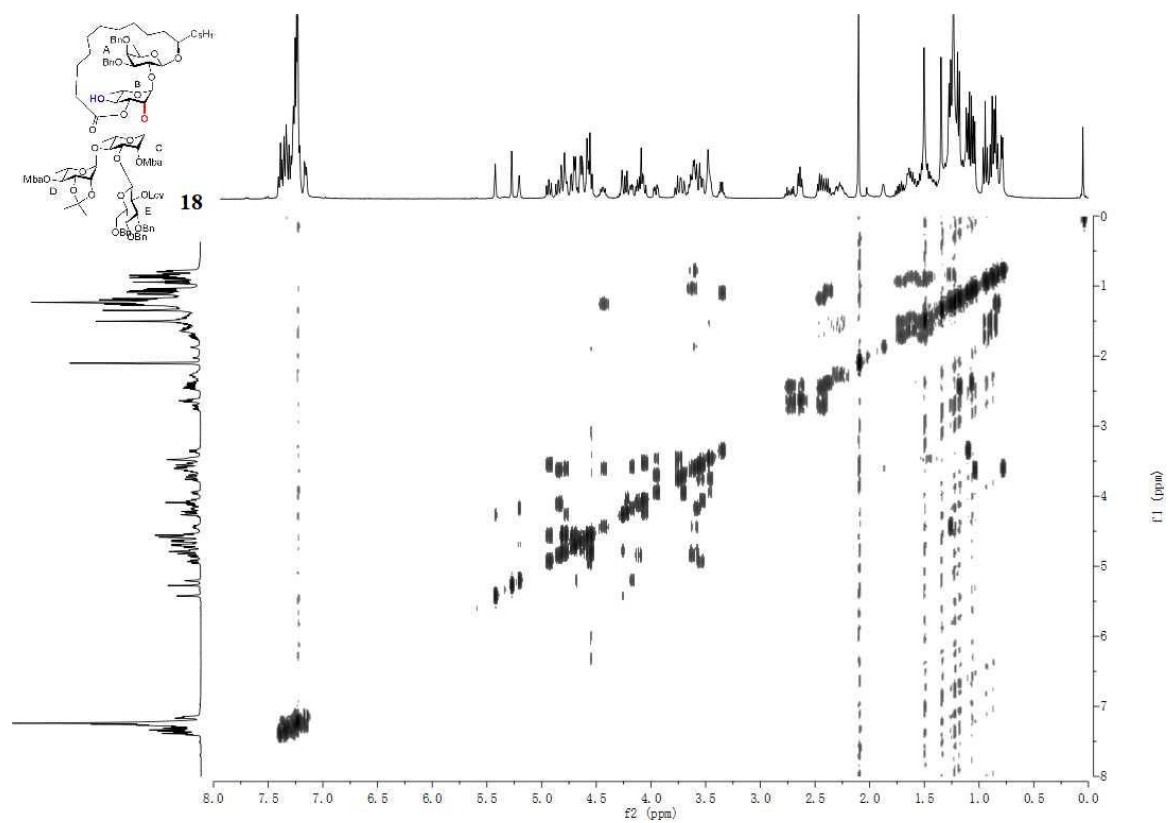
**Figure S45.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **4**



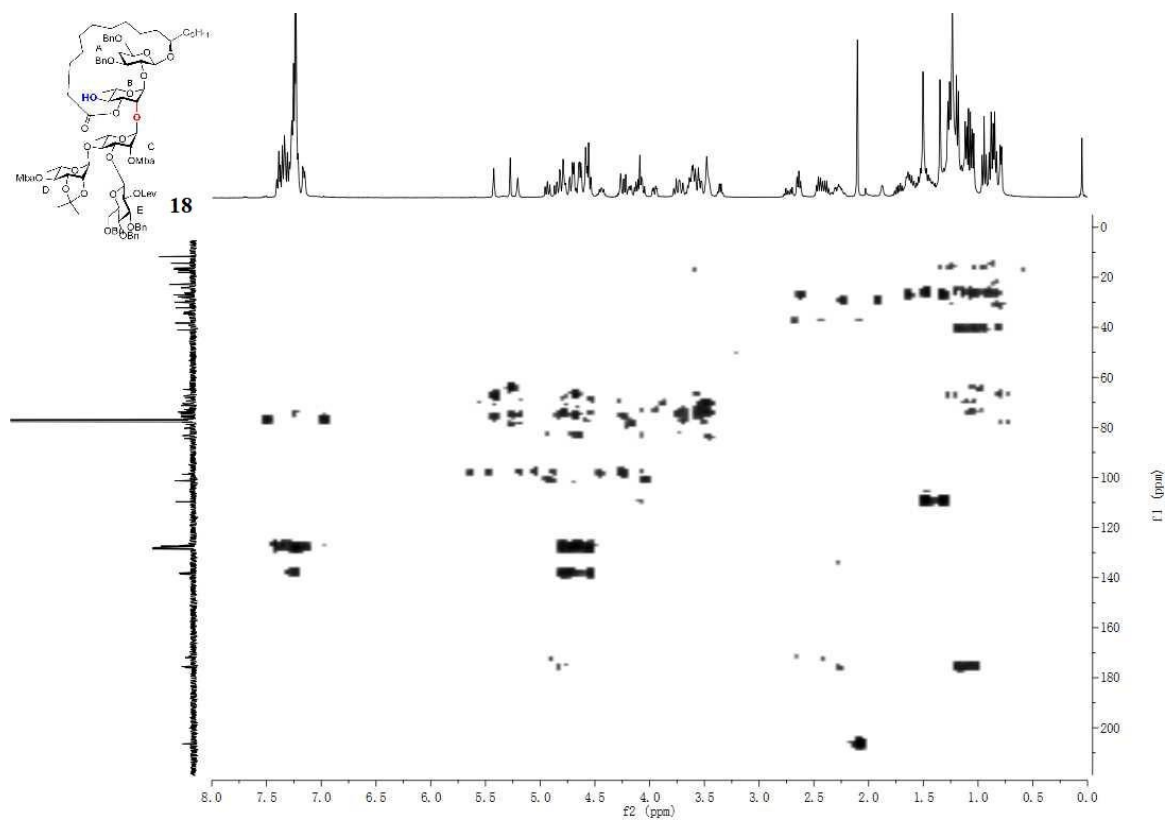
**Figure S46.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **18**



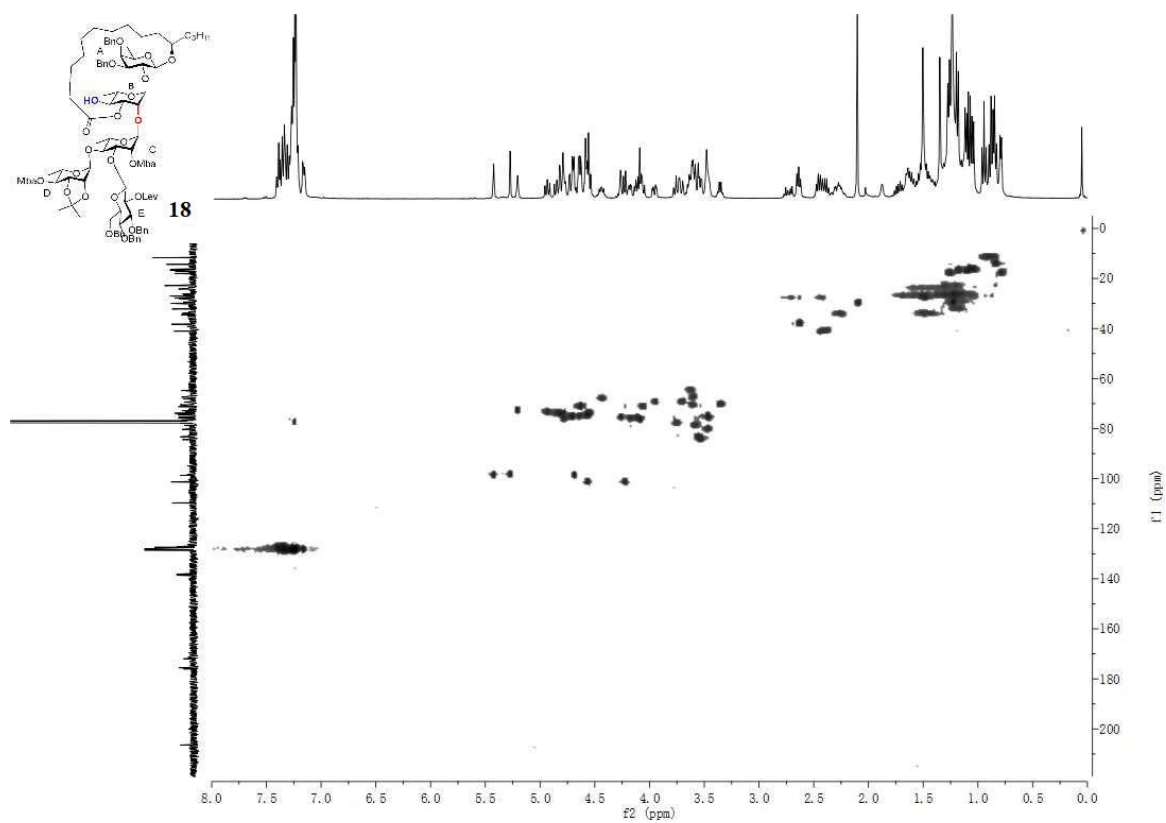
**Figure S47.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **18**



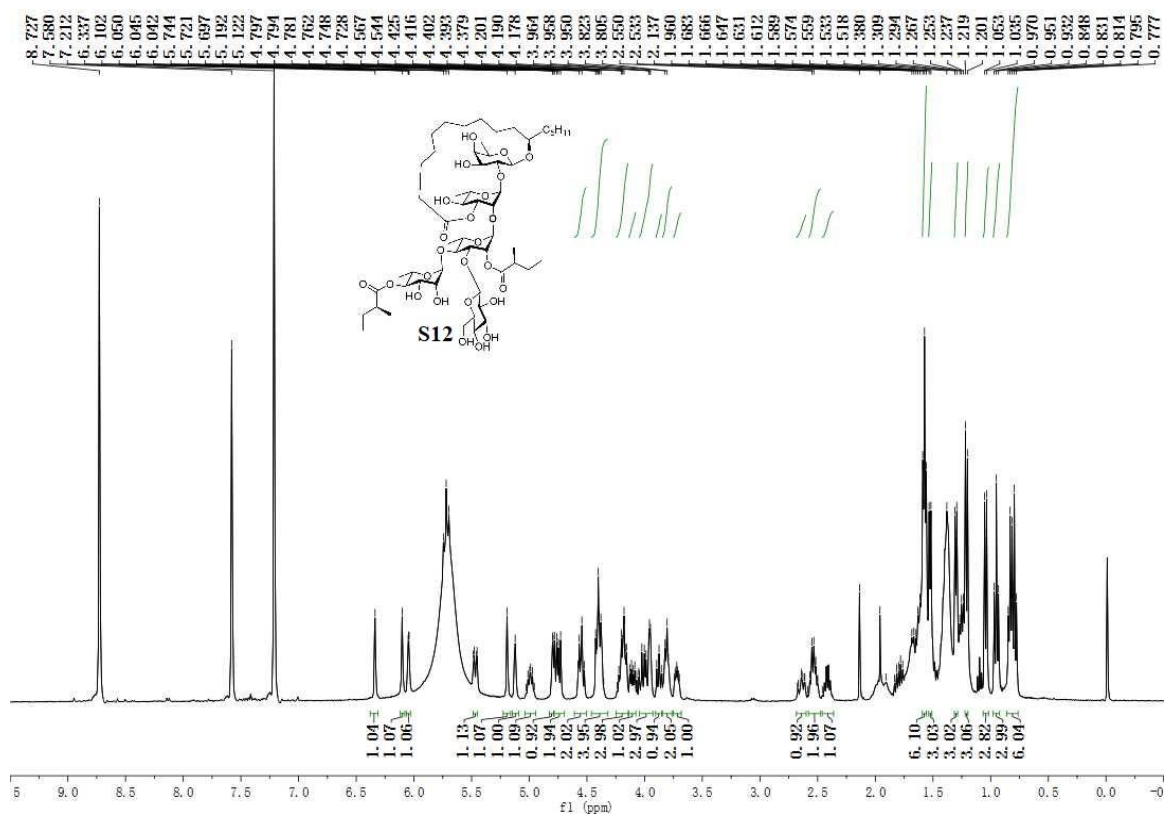
**Figure S48.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **18**



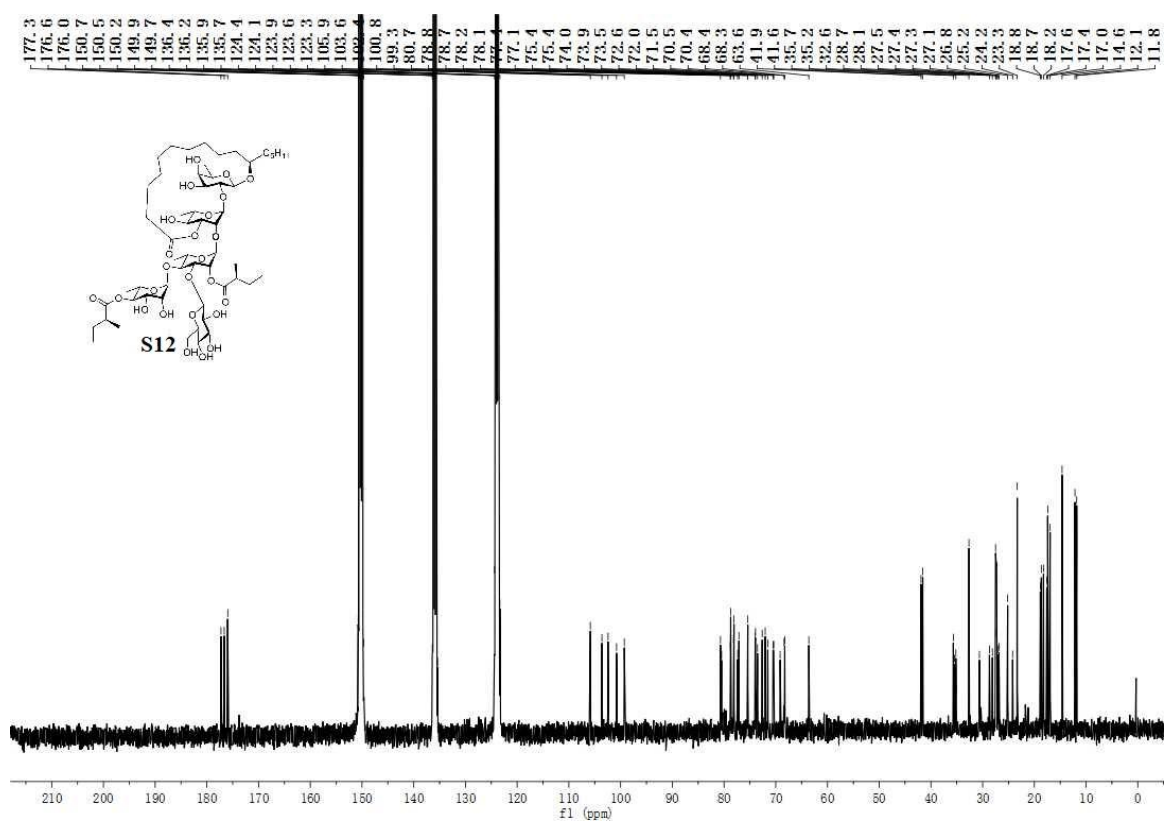
**Figure S49.** HMBC spectrum of **18**



**Figure S50.** HSQC spectrum of **18**

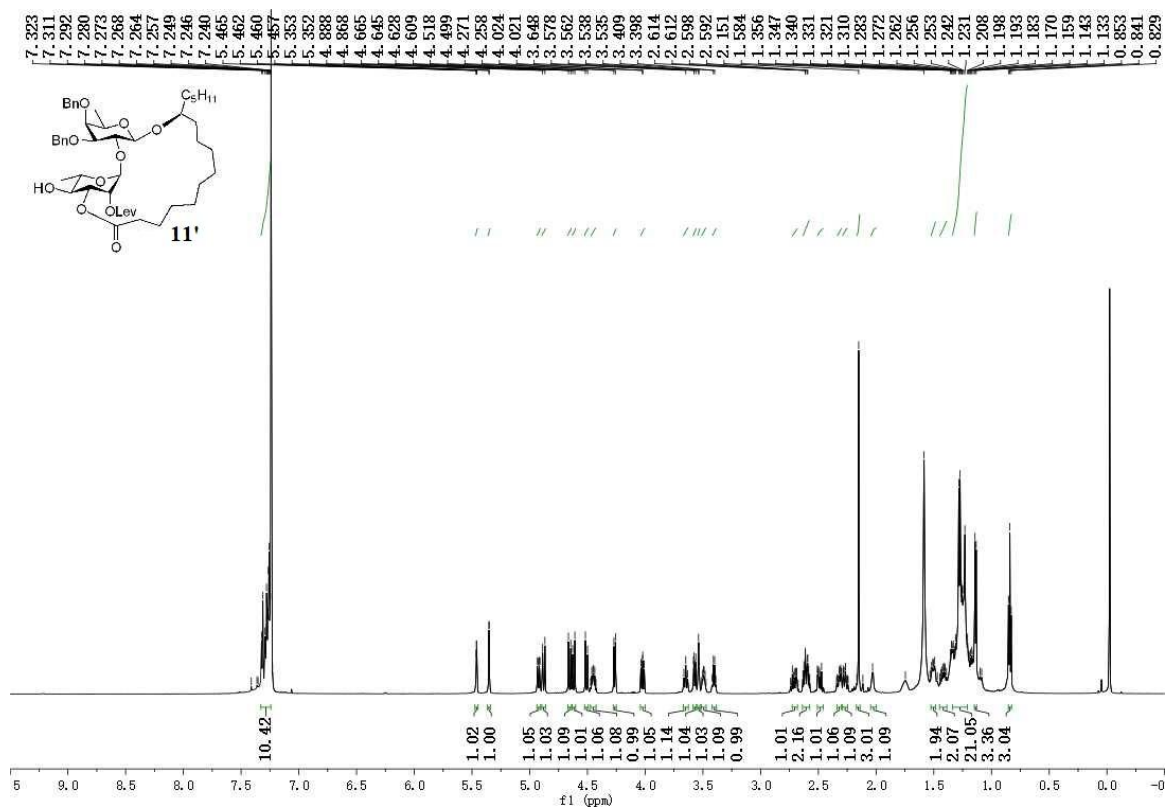


**Figure S51.**  $^1\text{H}$  NMR (400 MHz,  $\text{C}_5\text{D}_5\text{N}$ ) spectrum of **S12**

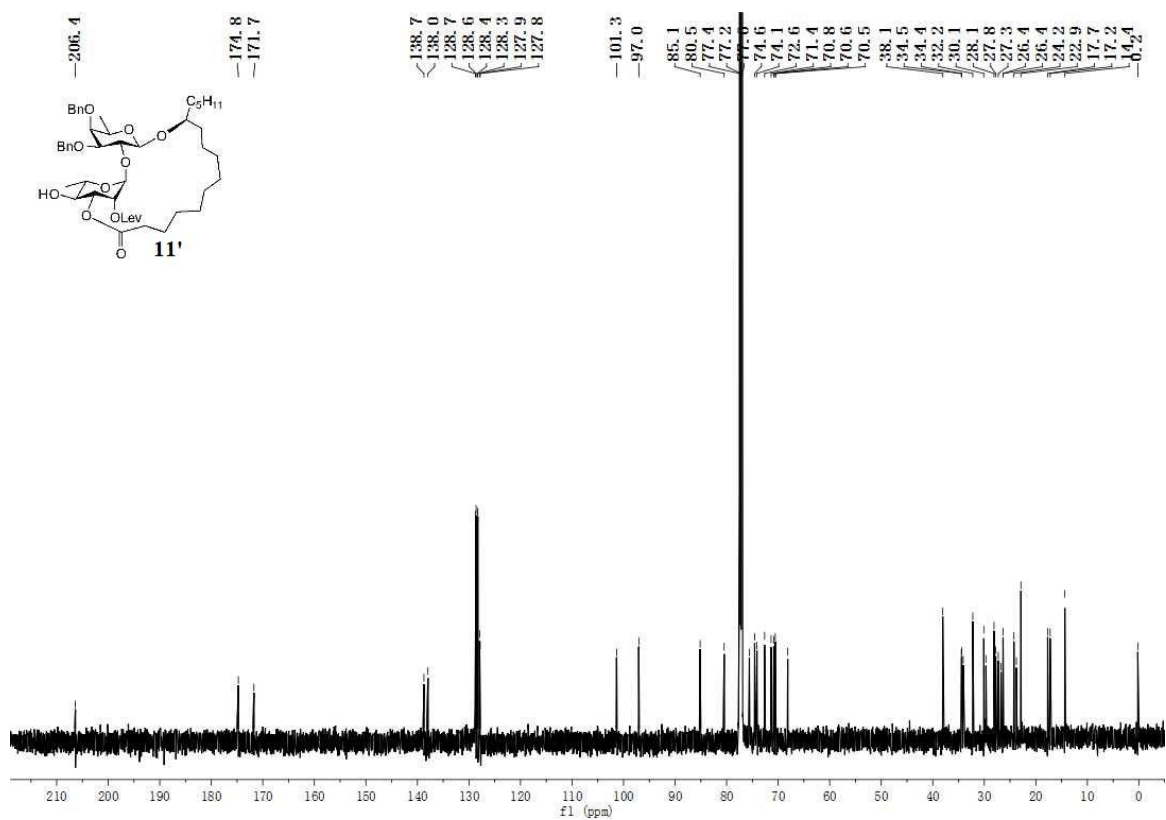


**Figure S52.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_5\text{D}_5\text{N}$ ) spectrum of **S12**

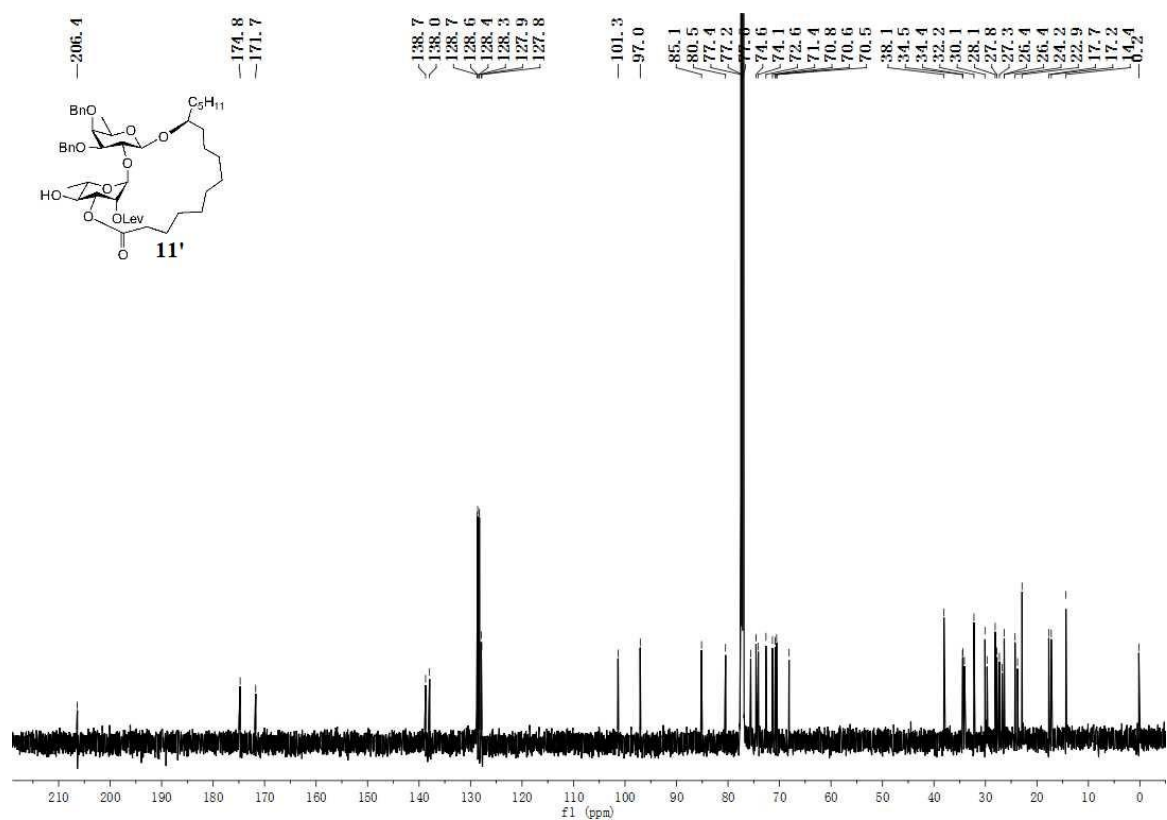




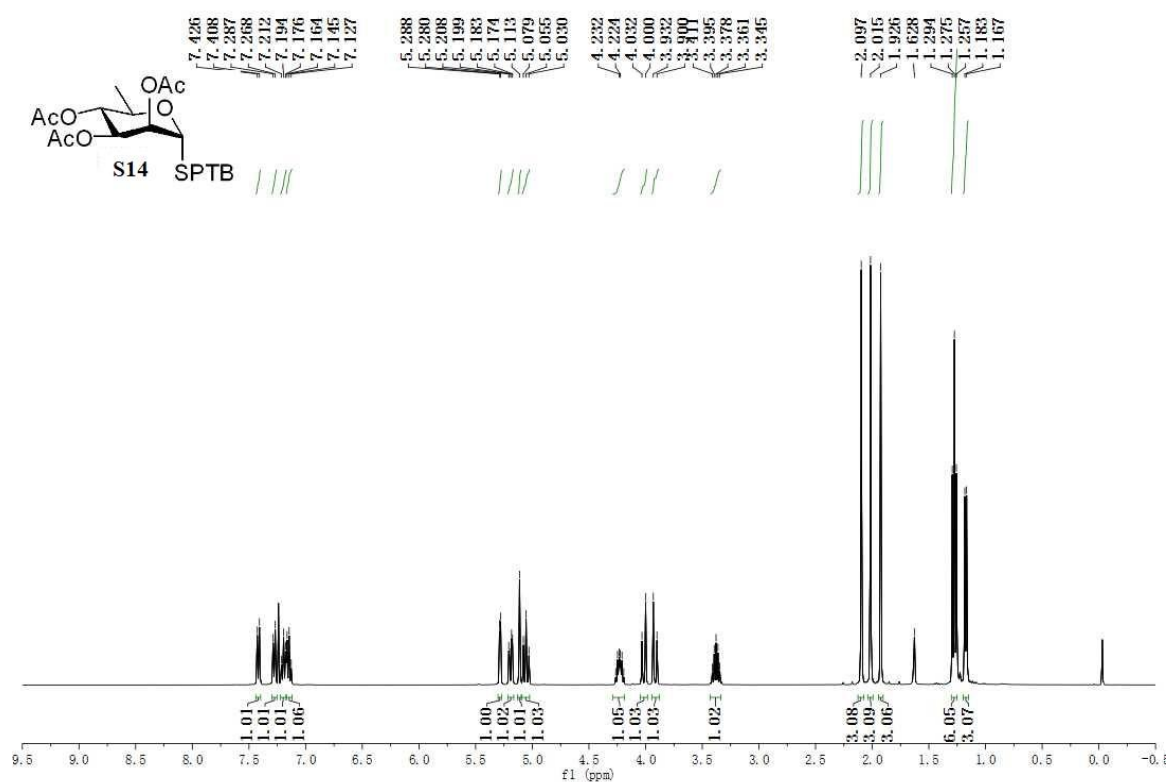
**Figure S53.** <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of **11'**



**Figure S54.** <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **11'**

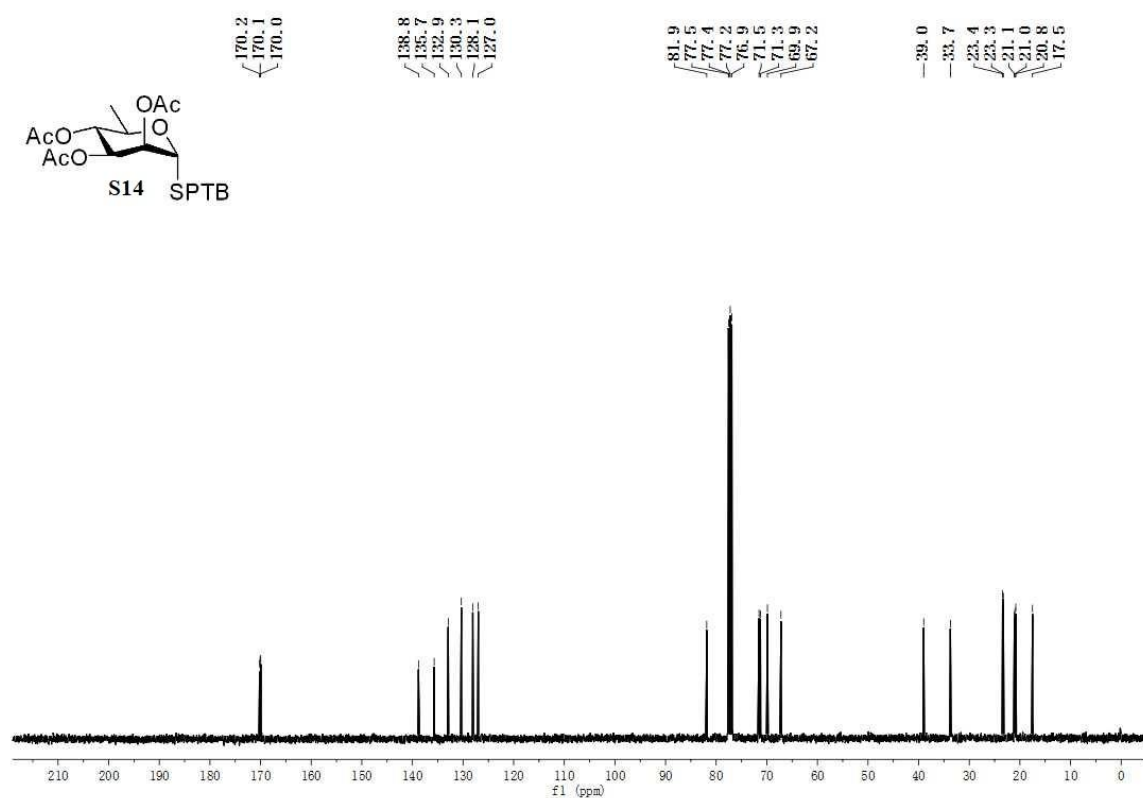


**Figure S55.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **11'**

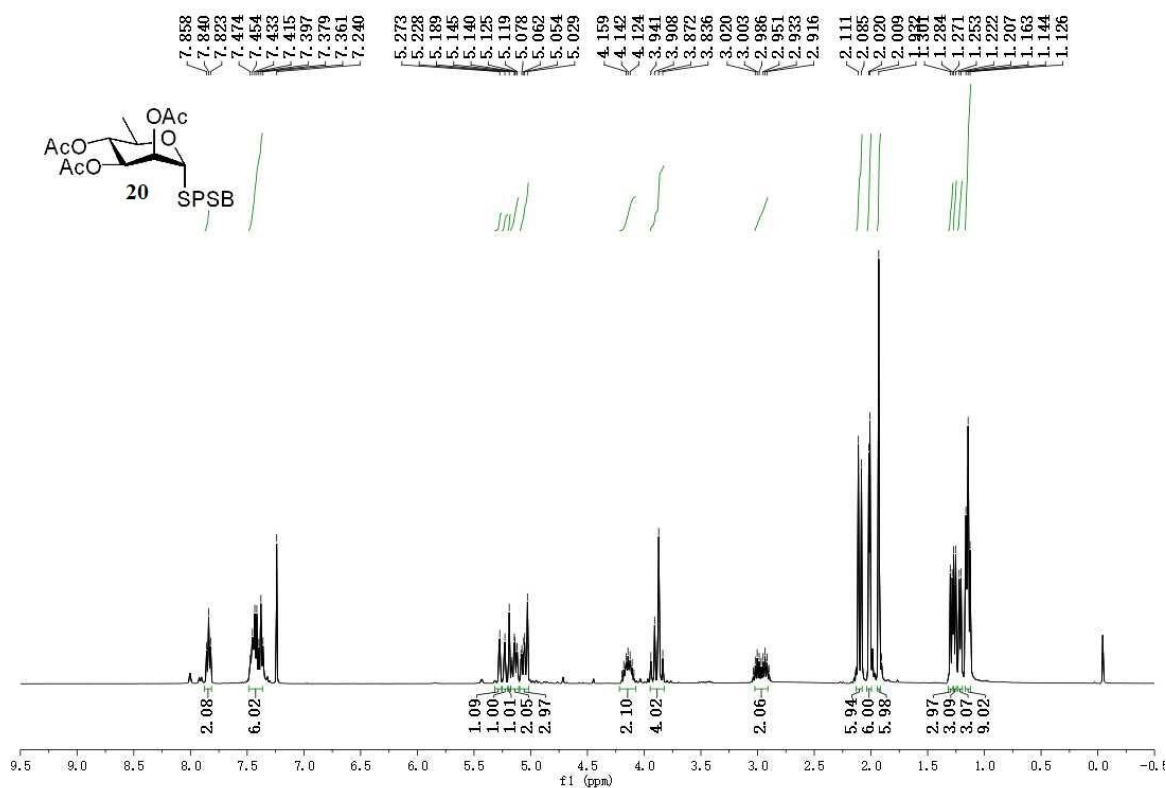


**Figure S56.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **S14**

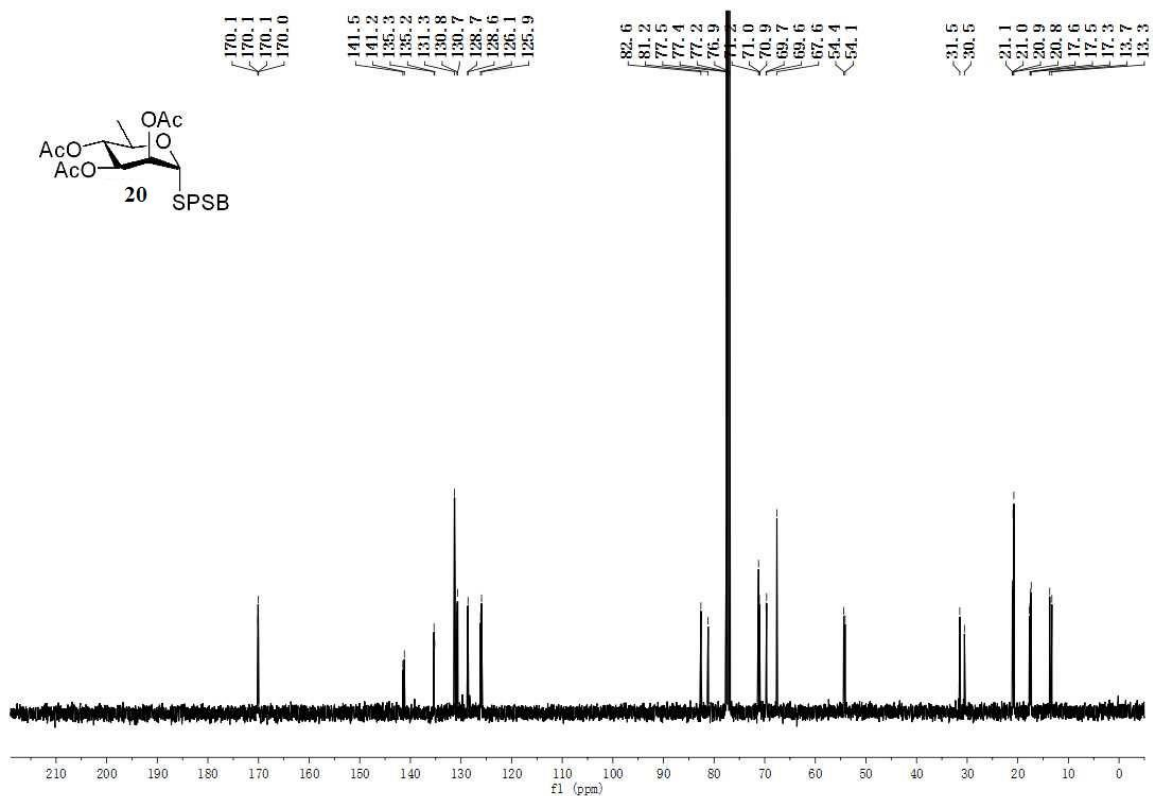




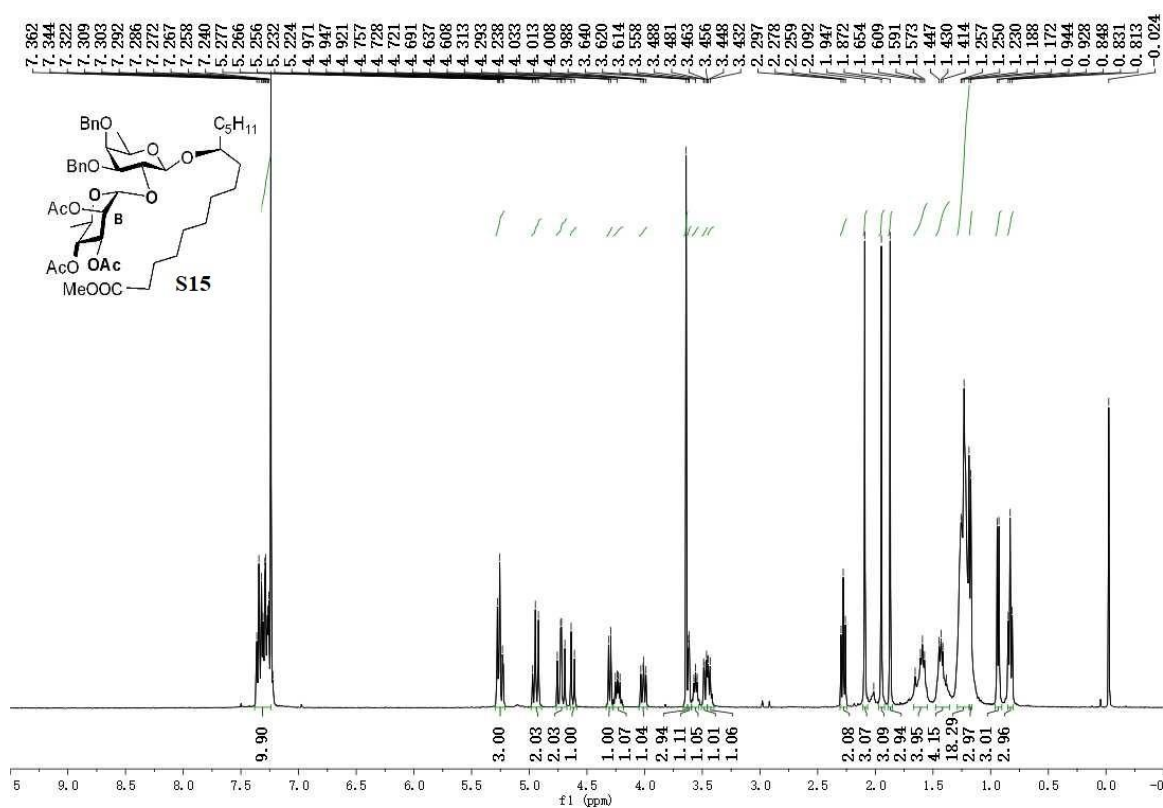
**Figure S57.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of S14



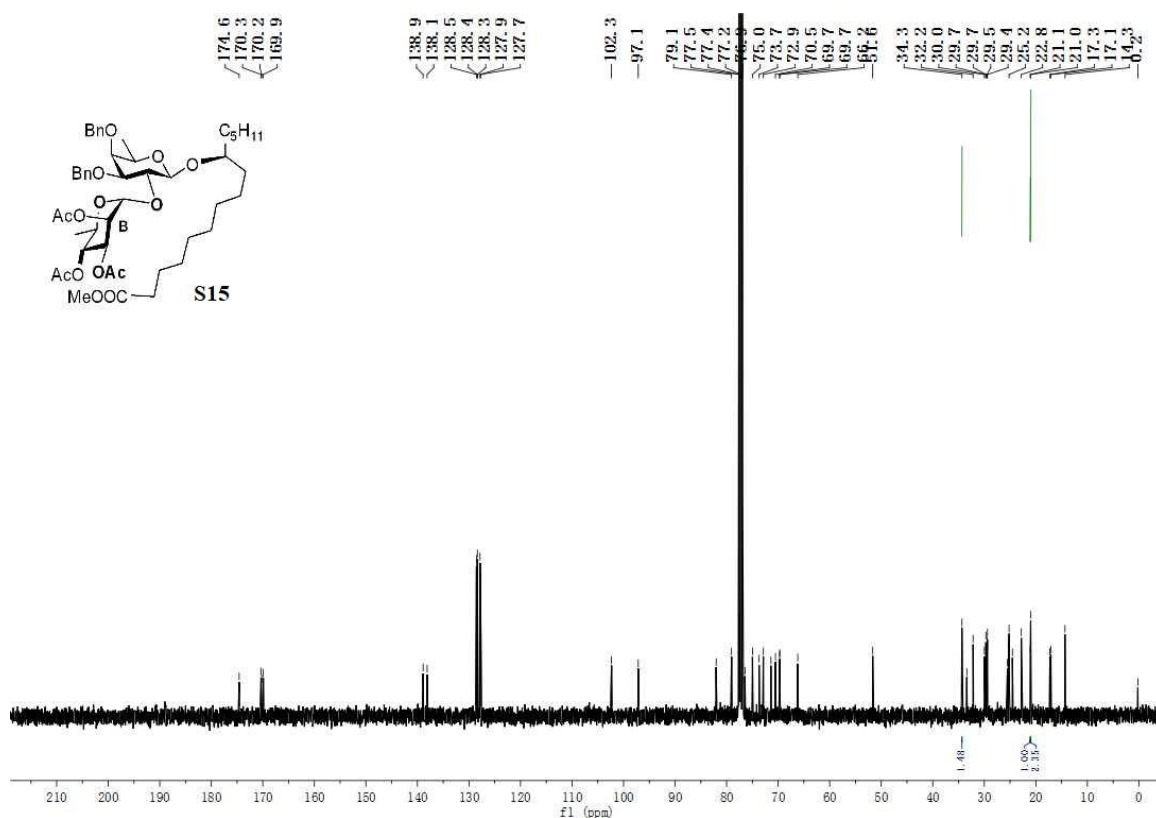
**Figure S58.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of 20



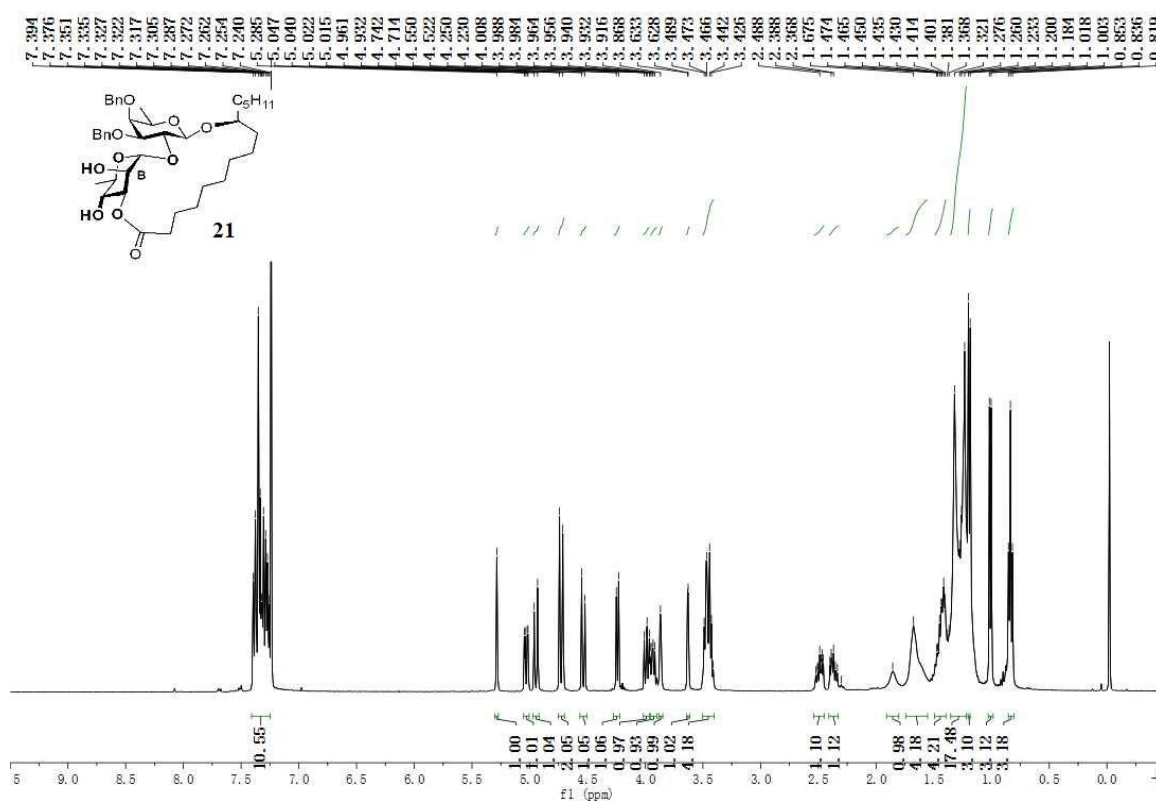
**Figure S59.** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **20**



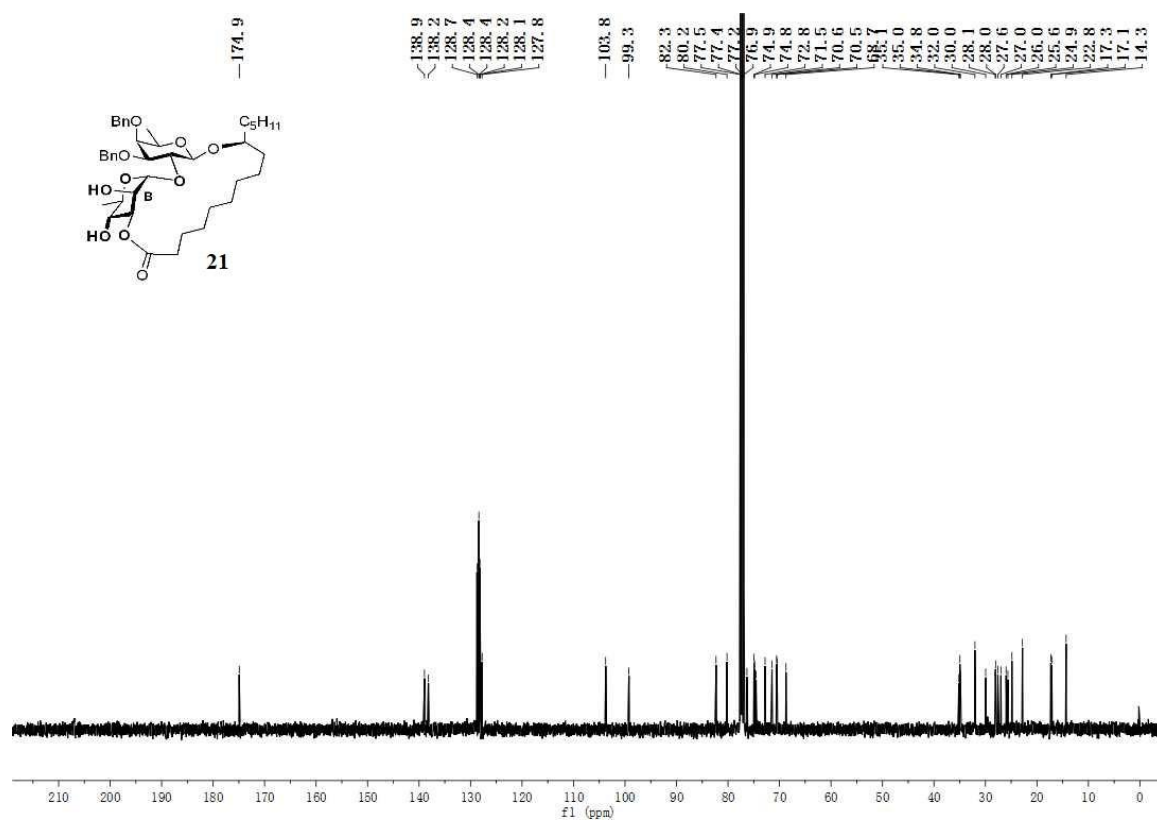
**Figure S60.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **S15**



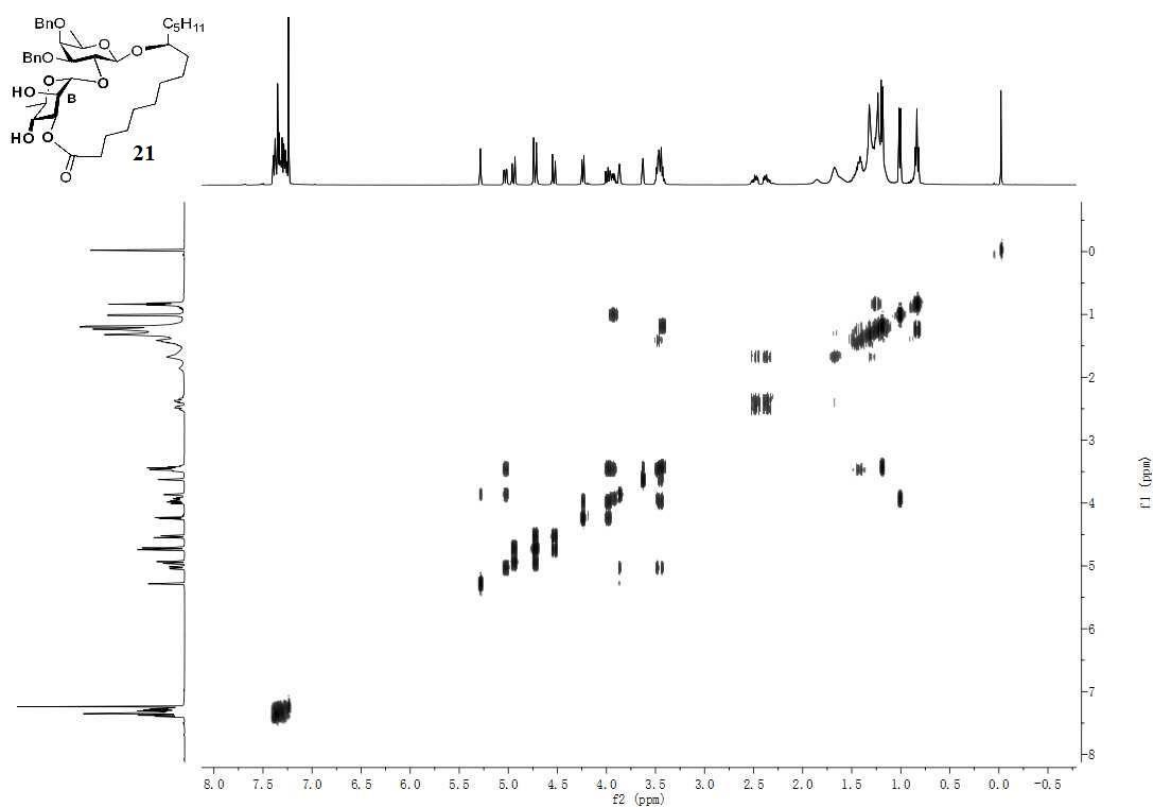
**Figure S61.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **S15**



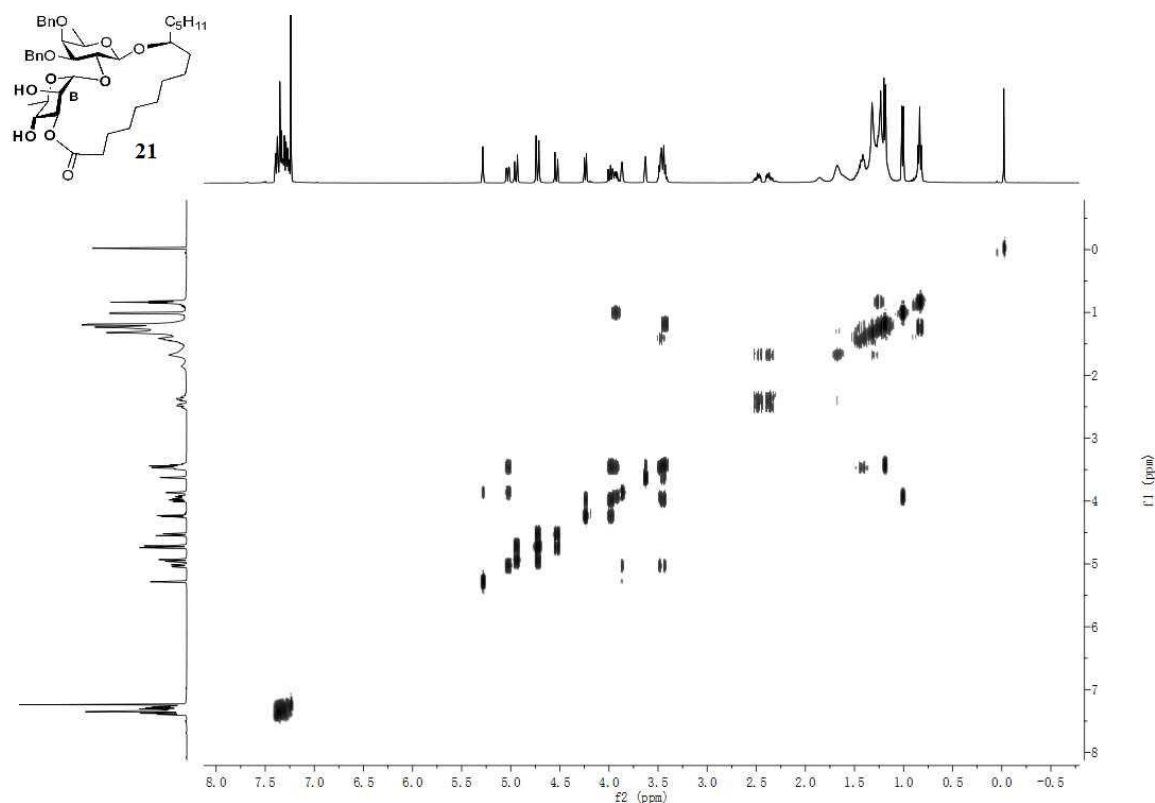
**Figure S62.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **21**



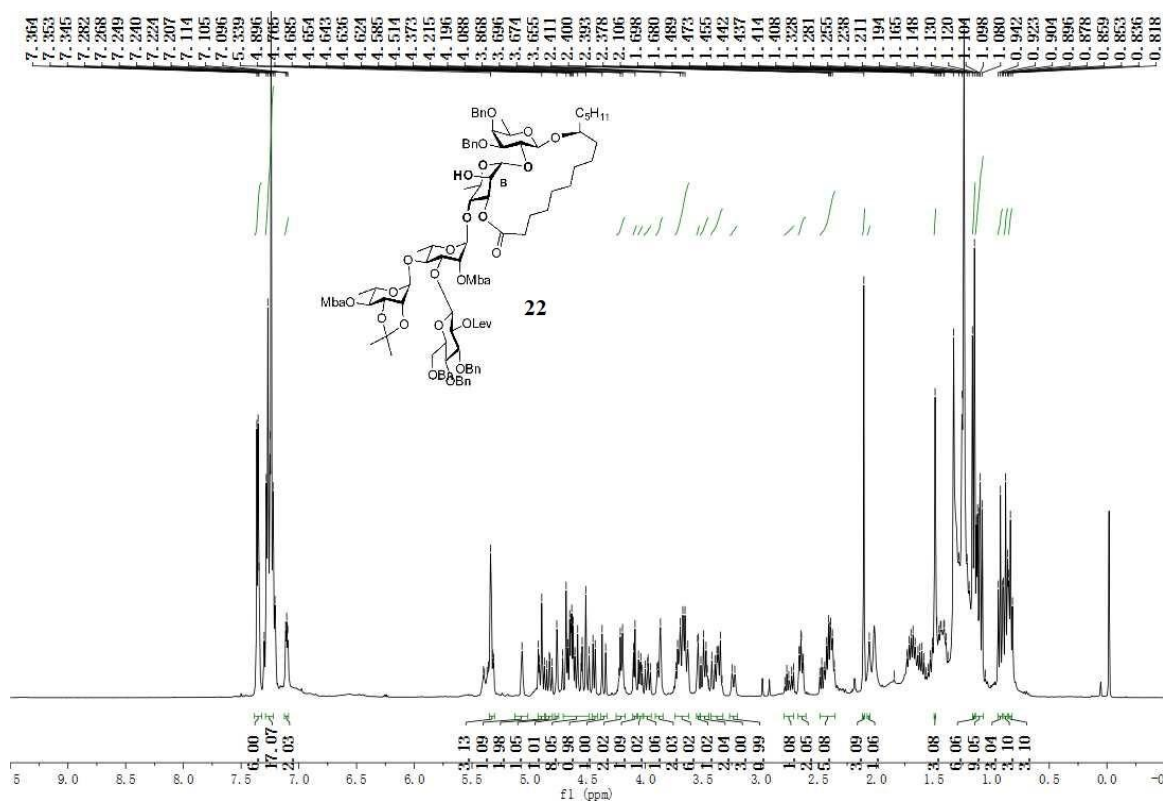
**Figure S63.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **21**



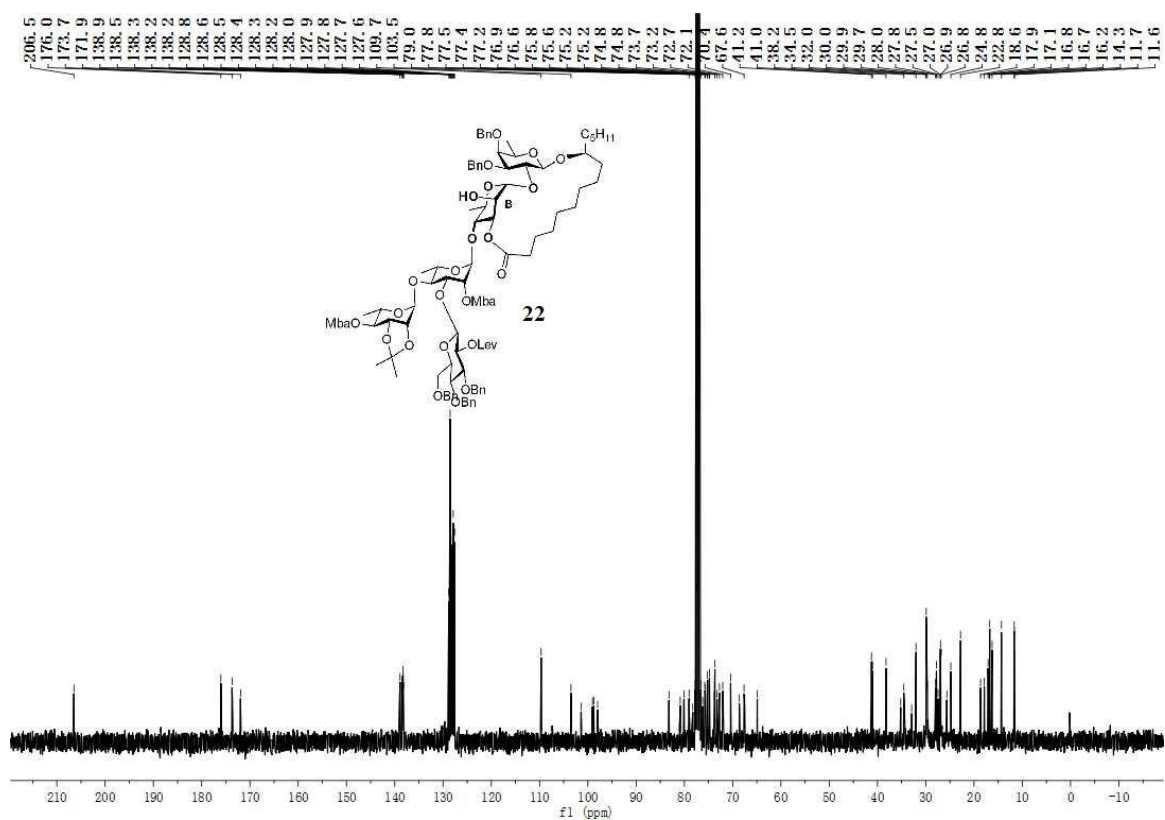
**Figure S64.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **21**



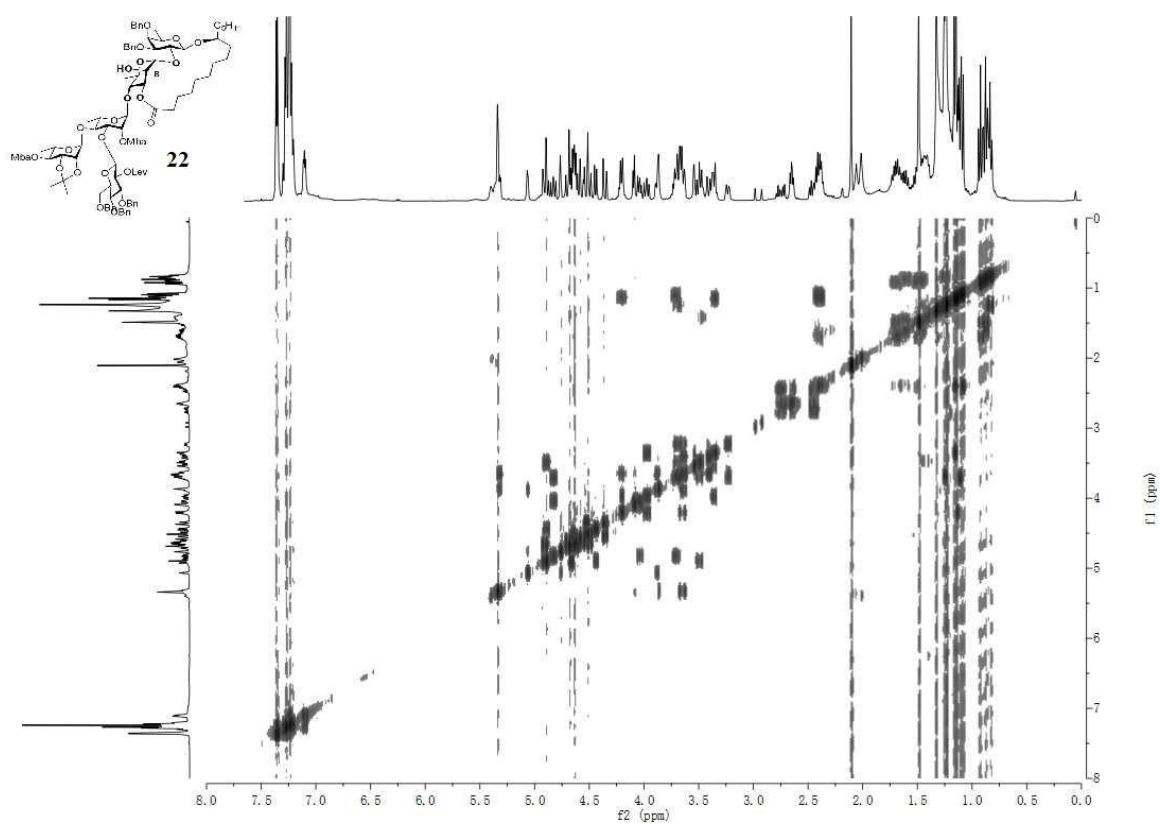
**Figure S65.** HSQC spectrum of **21**



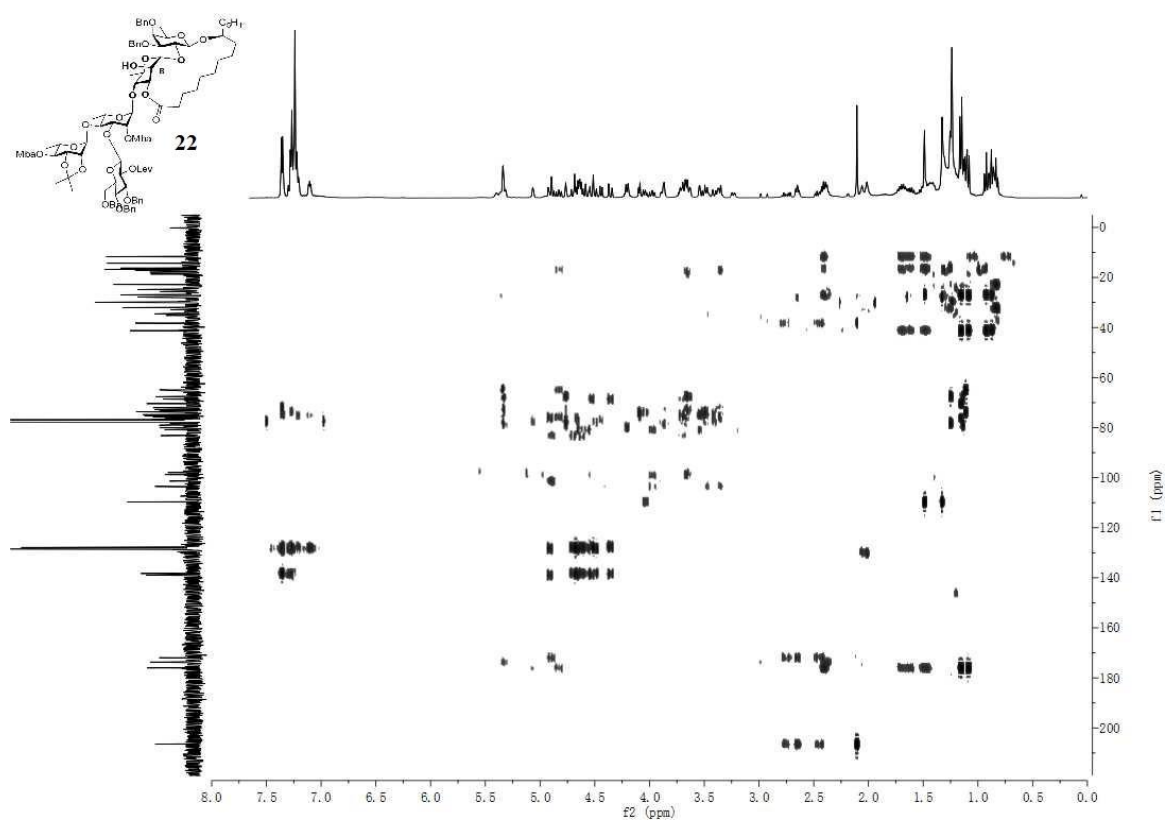
**Figure S66.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **22**



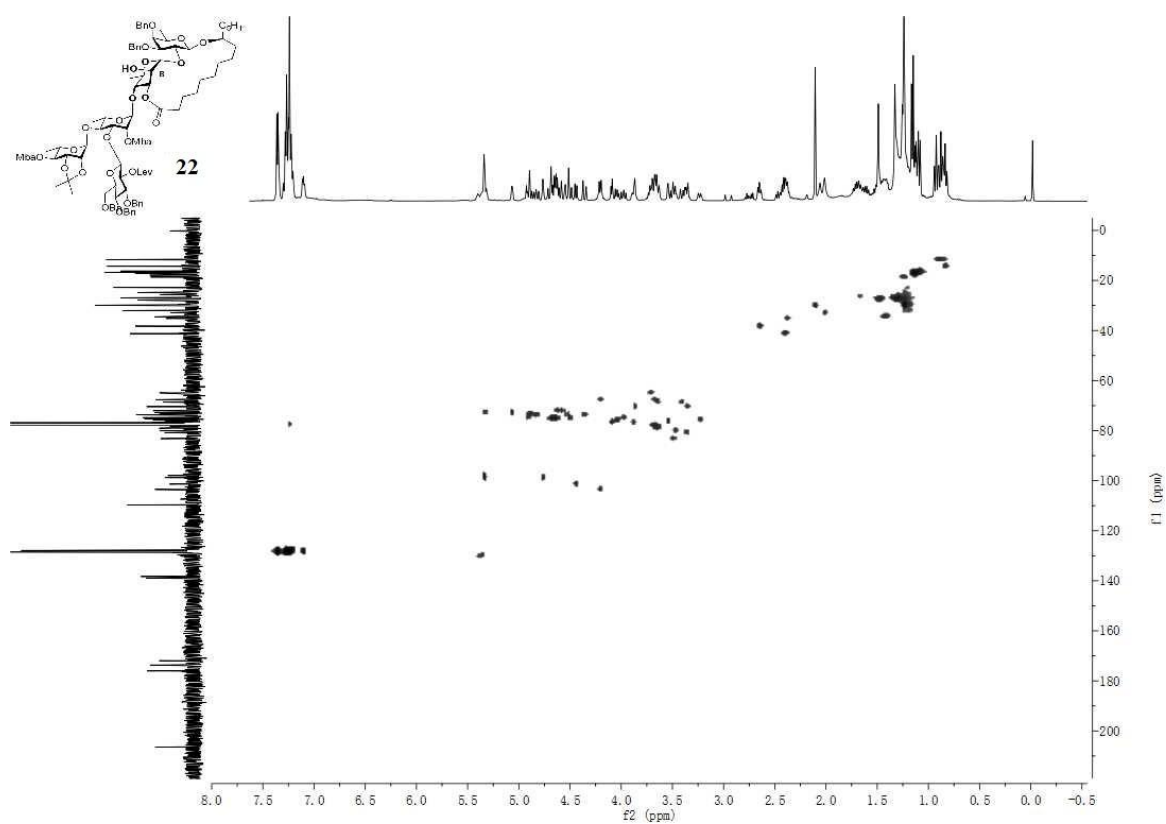
**Figure S67.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **22**



**Figure S68.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **22**

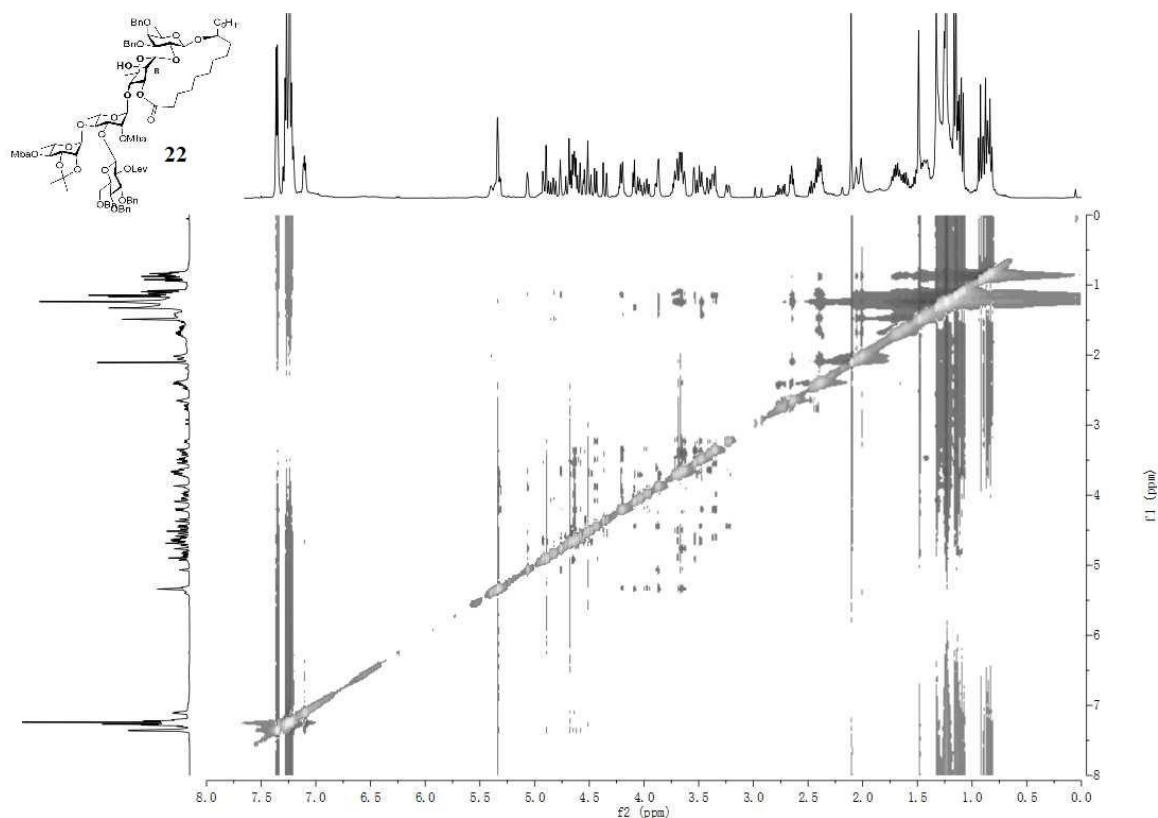


**Figure S69.** HMBC spectrum of **22**

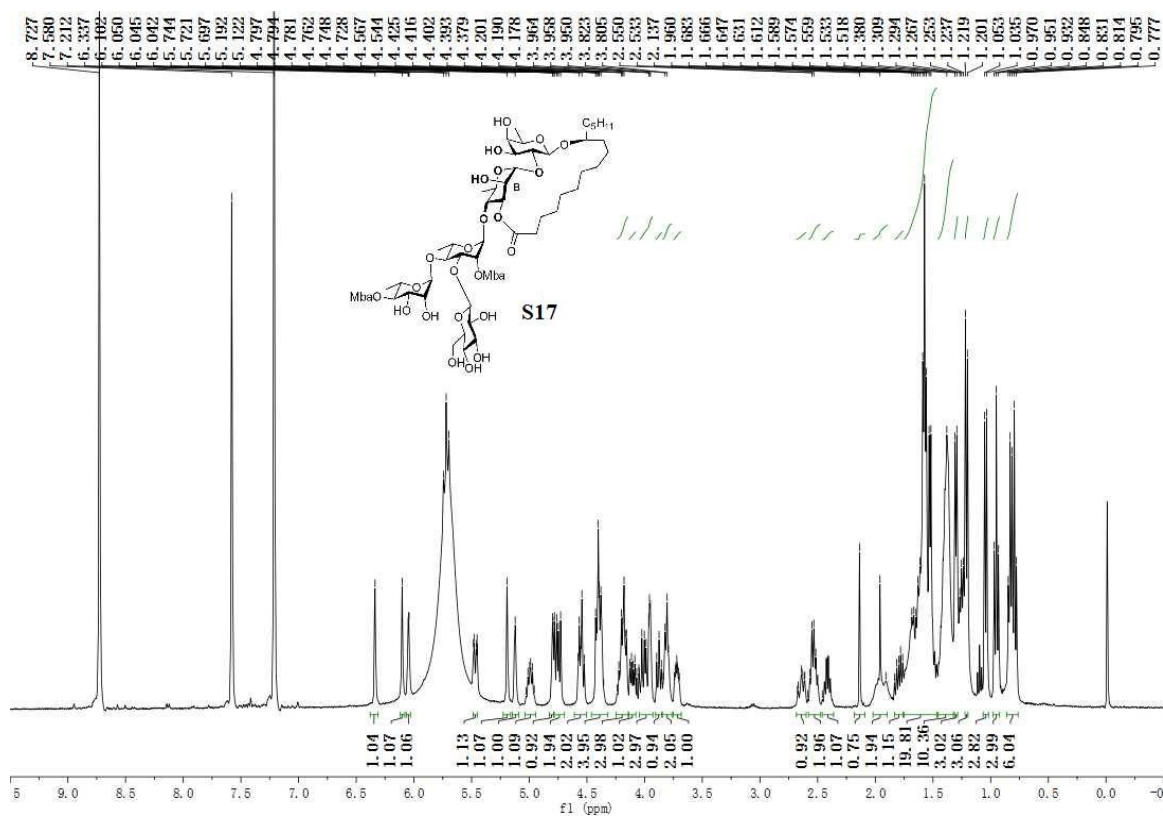


**Figure S70.** HSQC spectrum of **22**



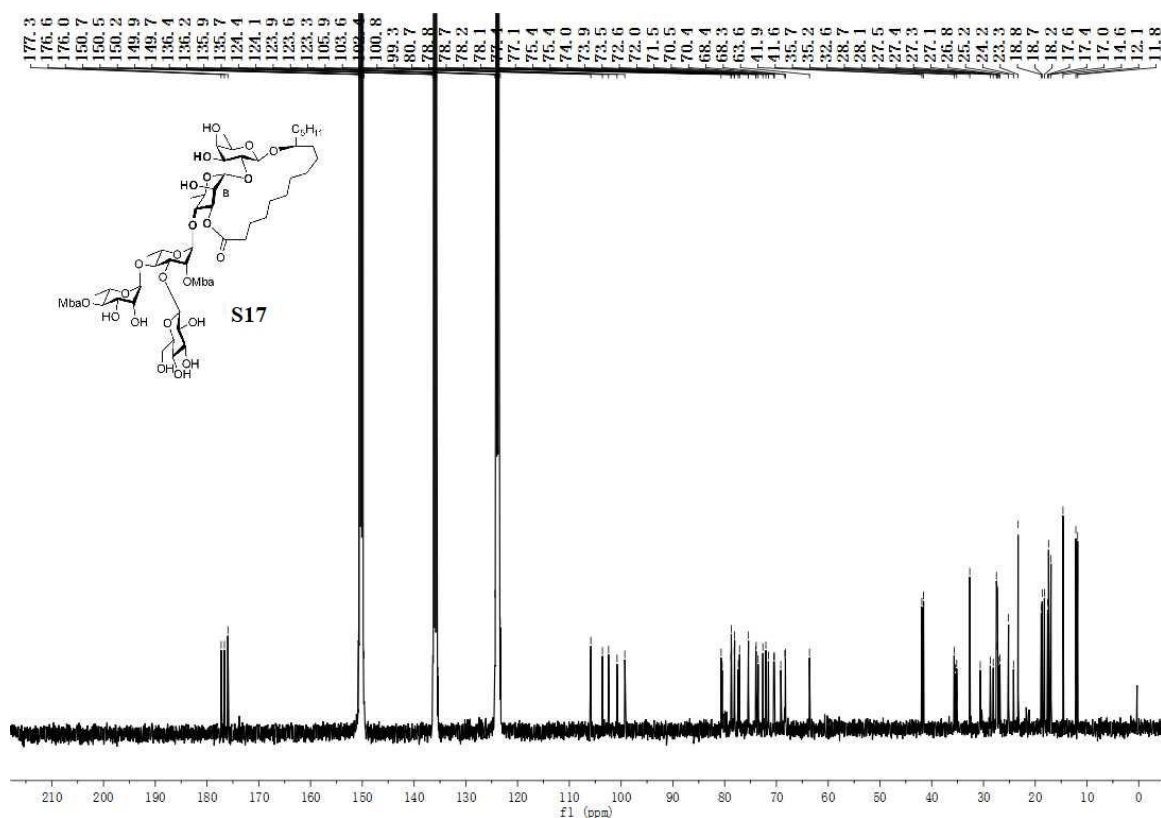


**Figure S71.** NOESY spectrum of **22**

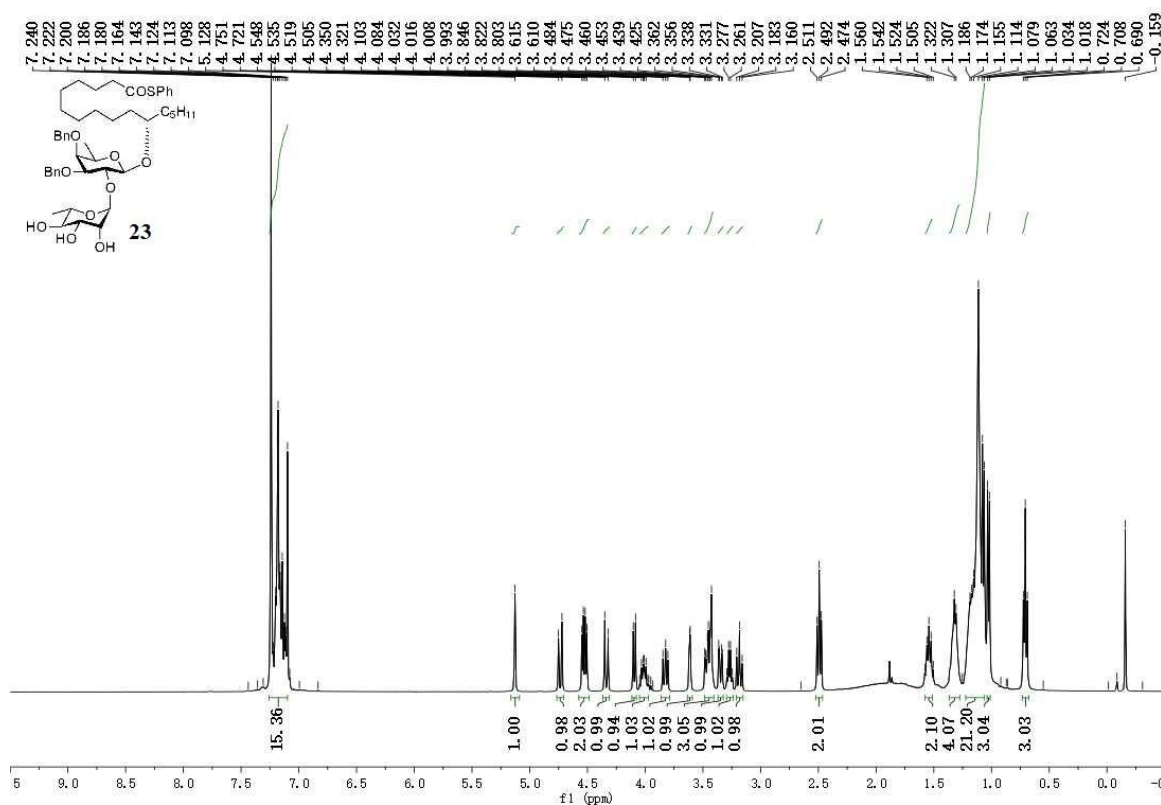


**Figure S72.**  $^1\text{H}$  NMR (400 MHz,  $\text{C}_5\text{D}_5\text{N}$ ) spectrum of **S17**

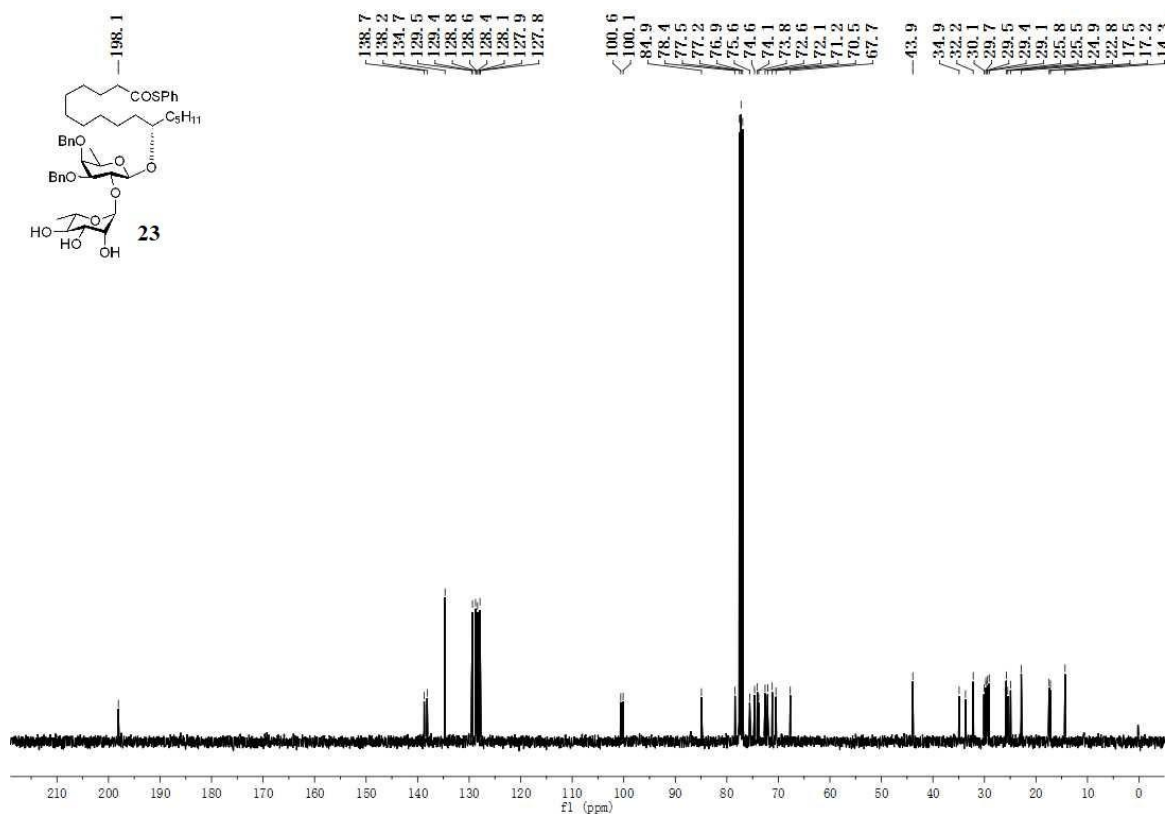




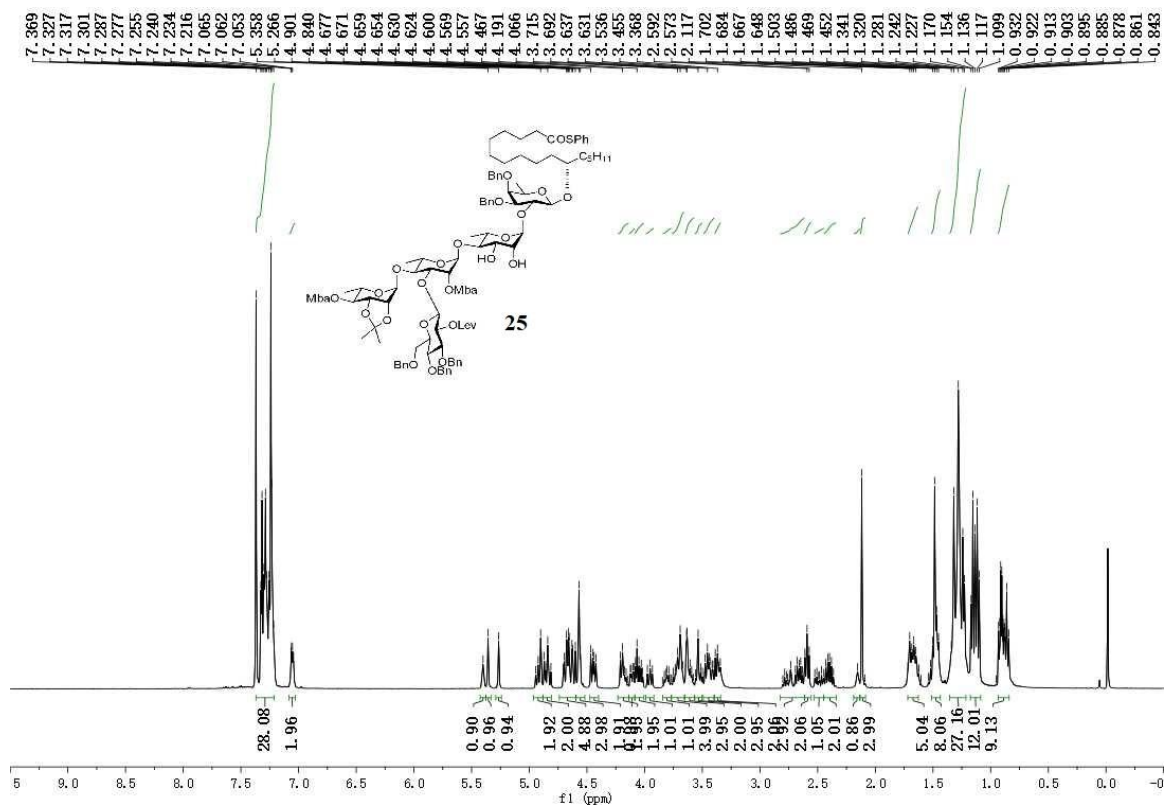
**Figure S73.** <sup>13</sup>C NMR (100 MHz, C<sub>5</sub>D<sub>5</sub>N) spectrum of **S17**



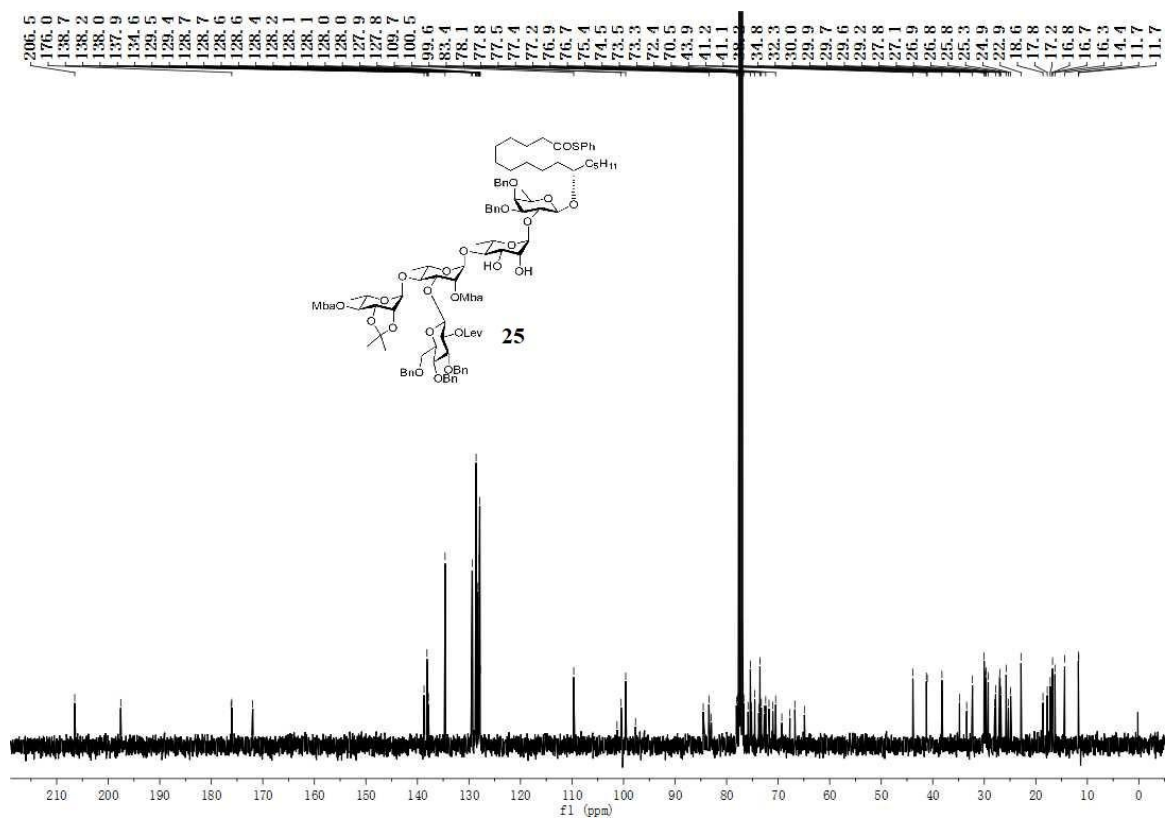
**Figure S74.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **23**



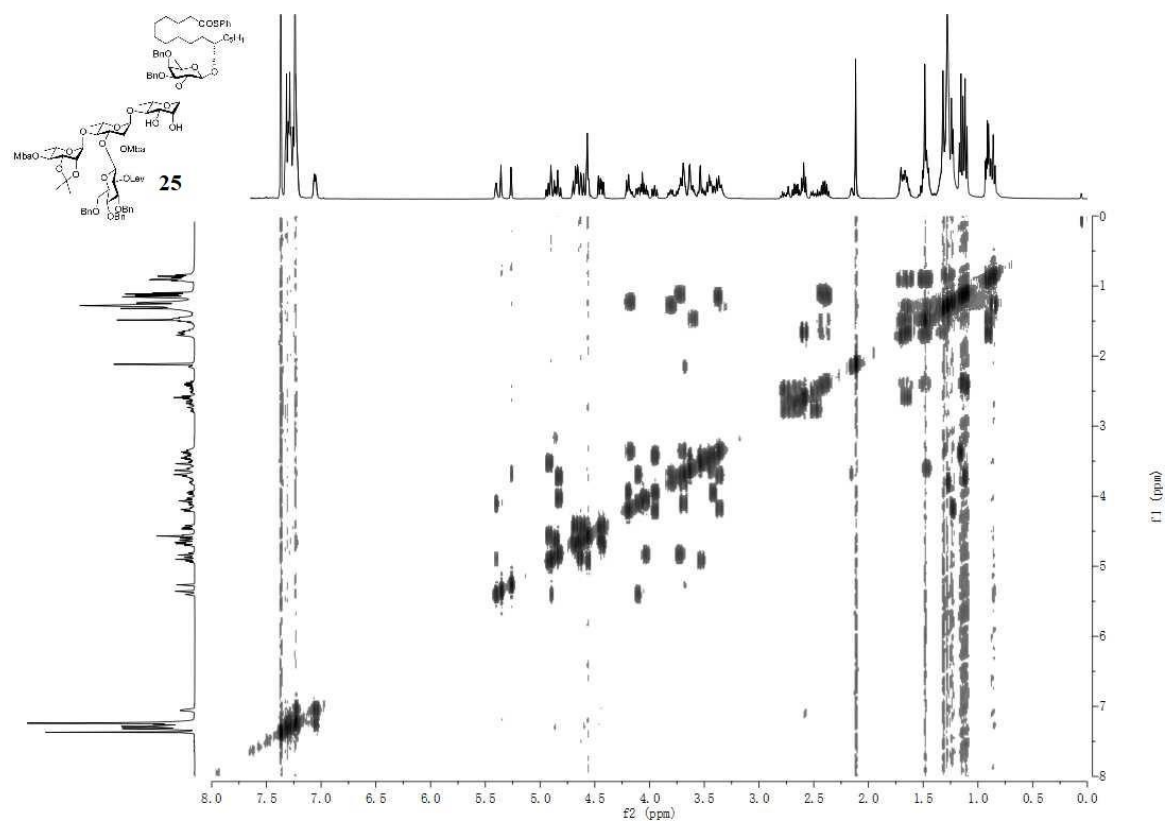
**Figure S75.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **23**



**Figure S76.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **25**



**Figure S77.** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **25**



**Figure S78.** <sup>1</sup>H-<sup>1</sup>H COSY spectrum of **25**



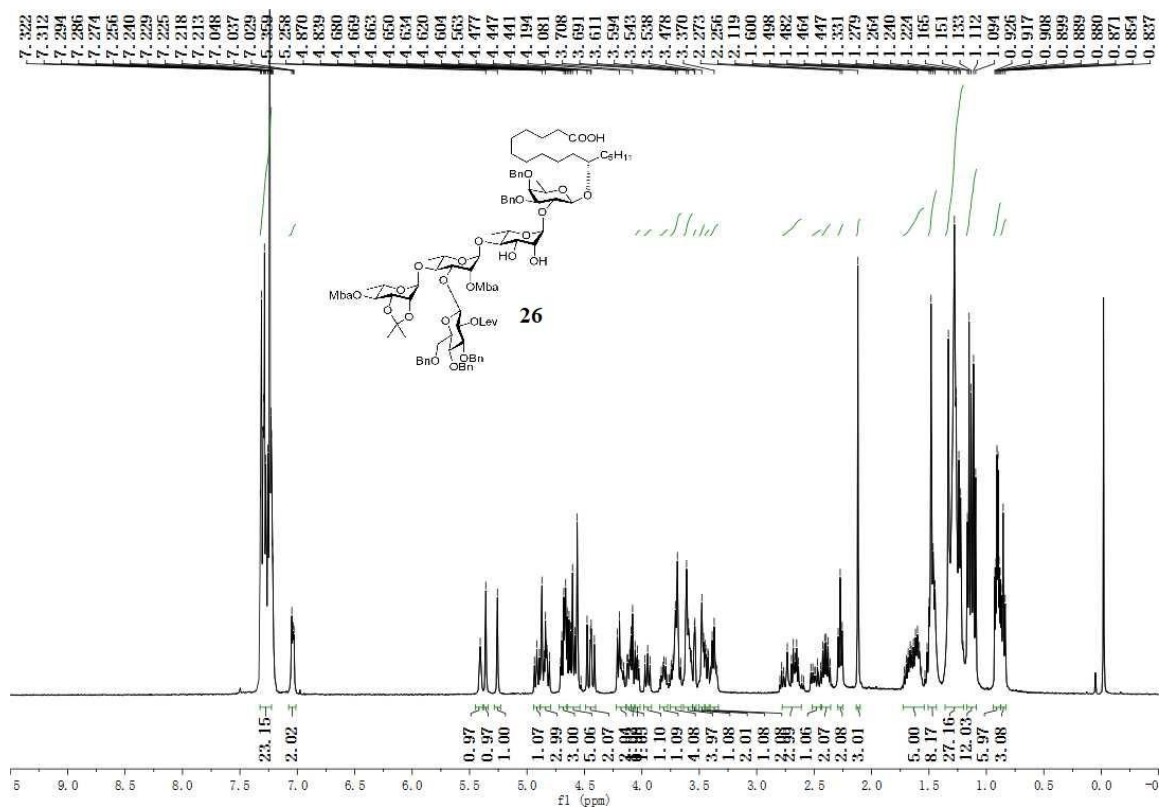


Figure S81 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 26

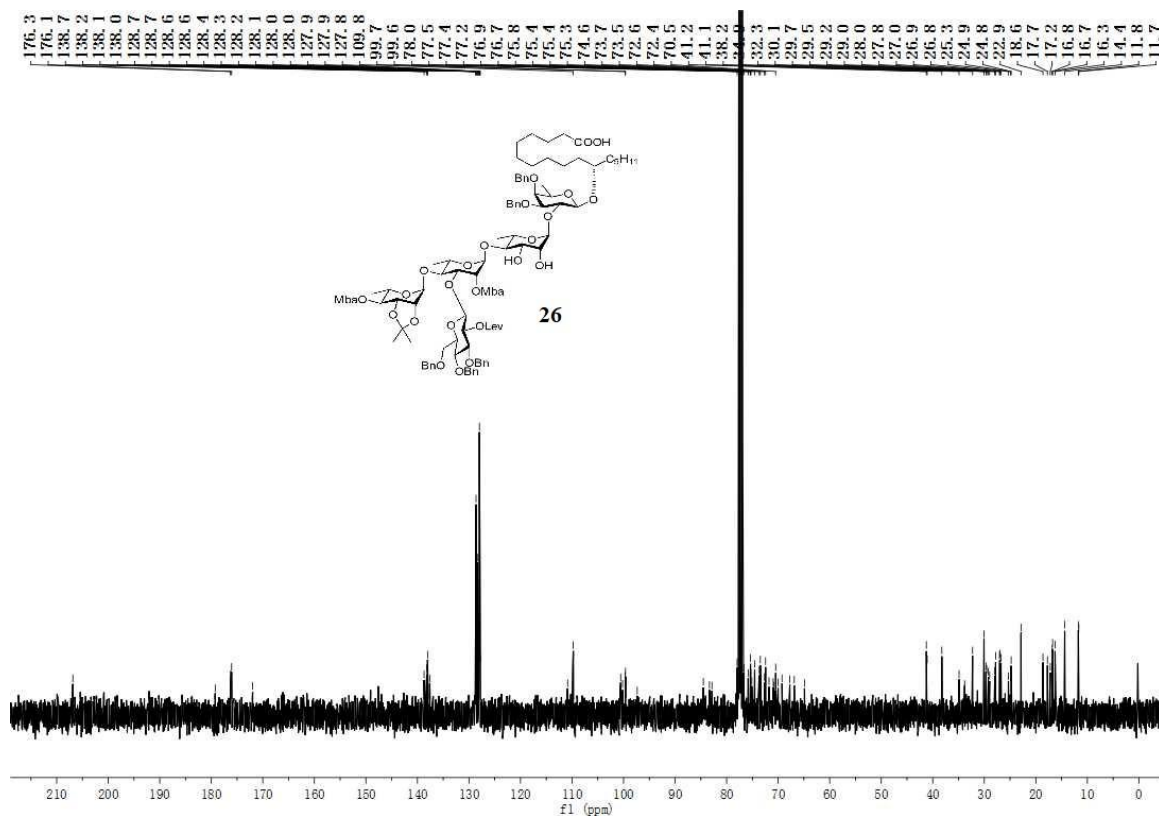
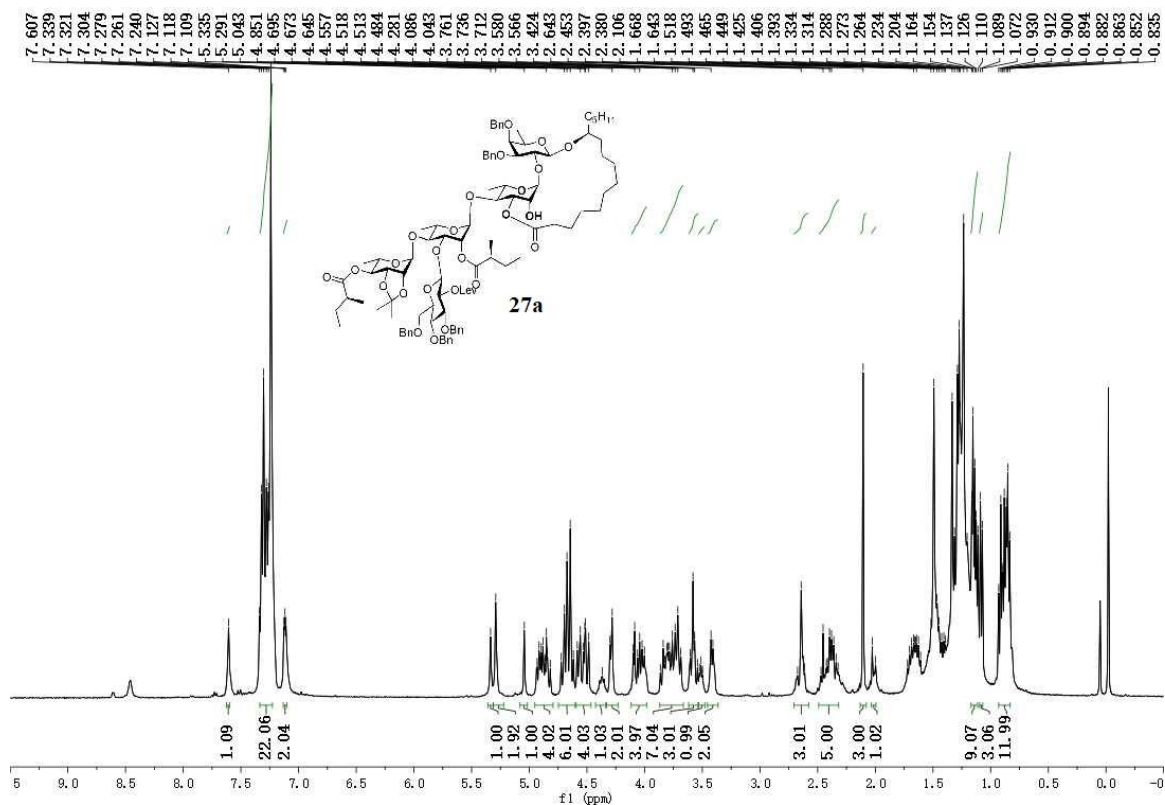
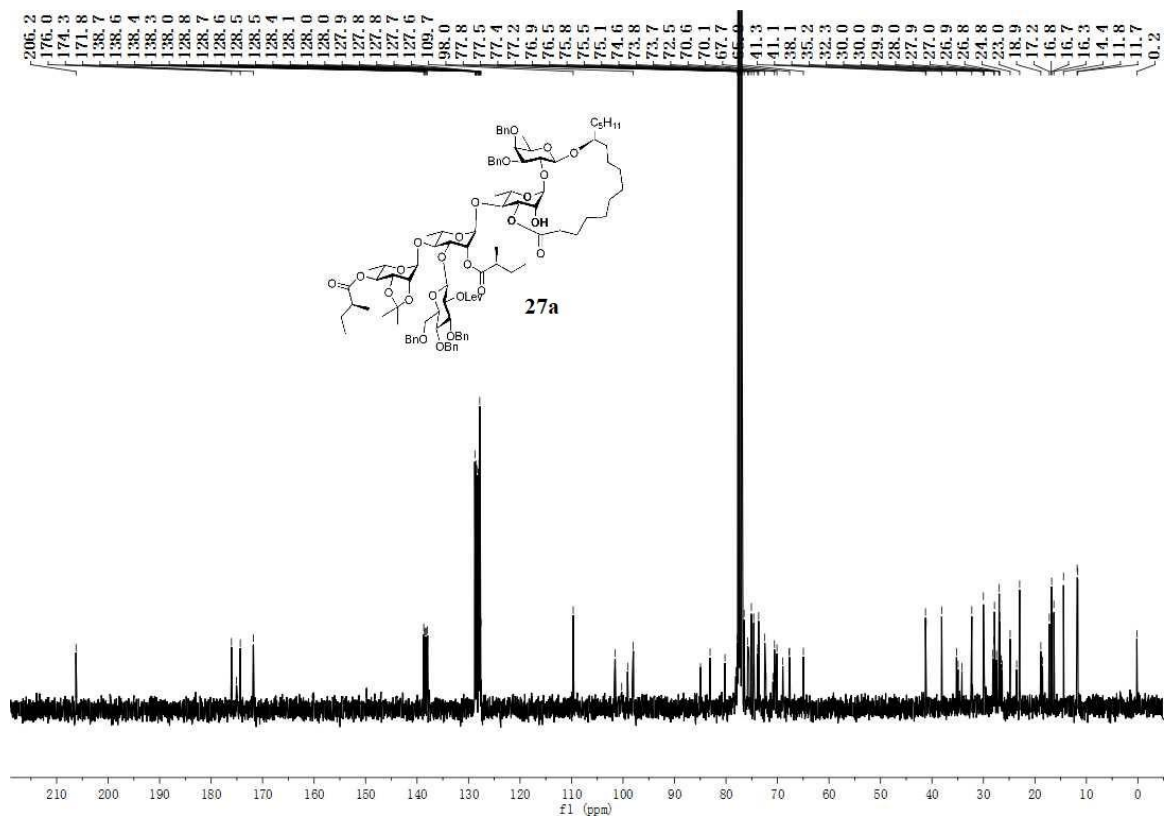


Figure S82. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 26

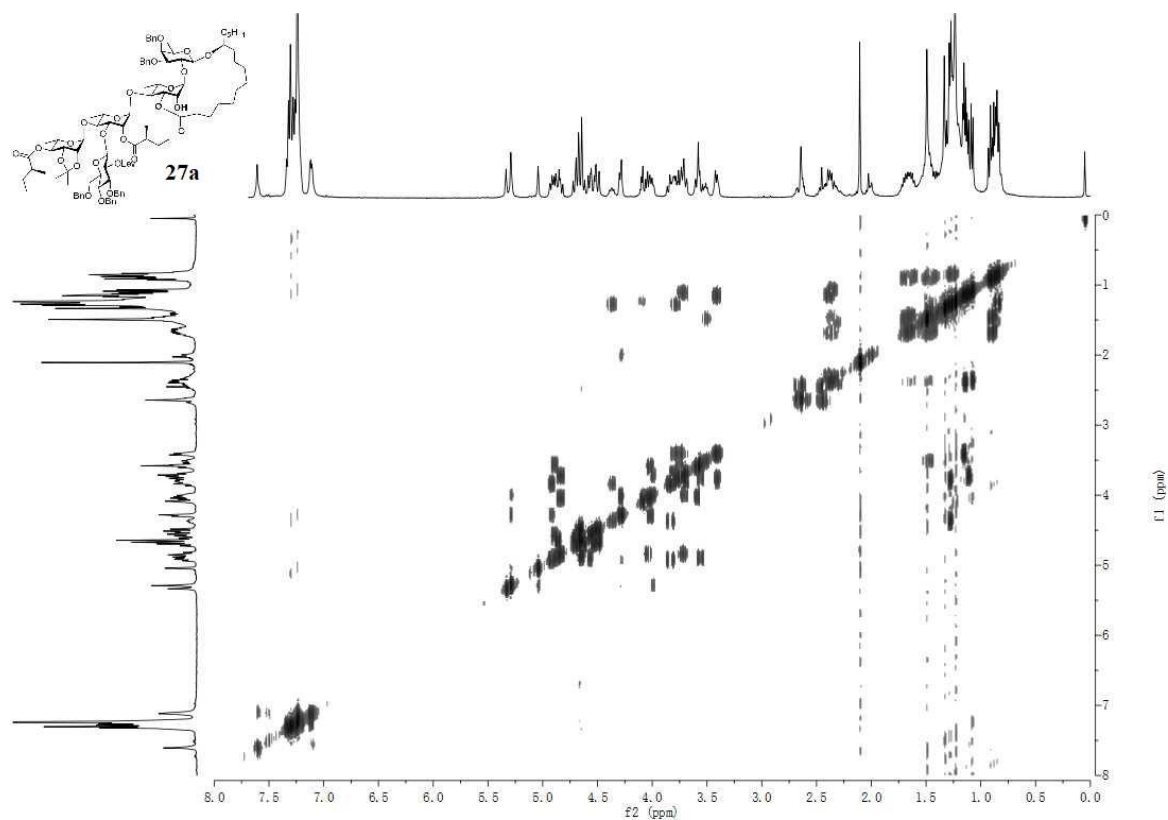


**Figure S83.**  $^1H$  NMR (400 MHz,  $CDCl_3$ ) spectrum of **27a**

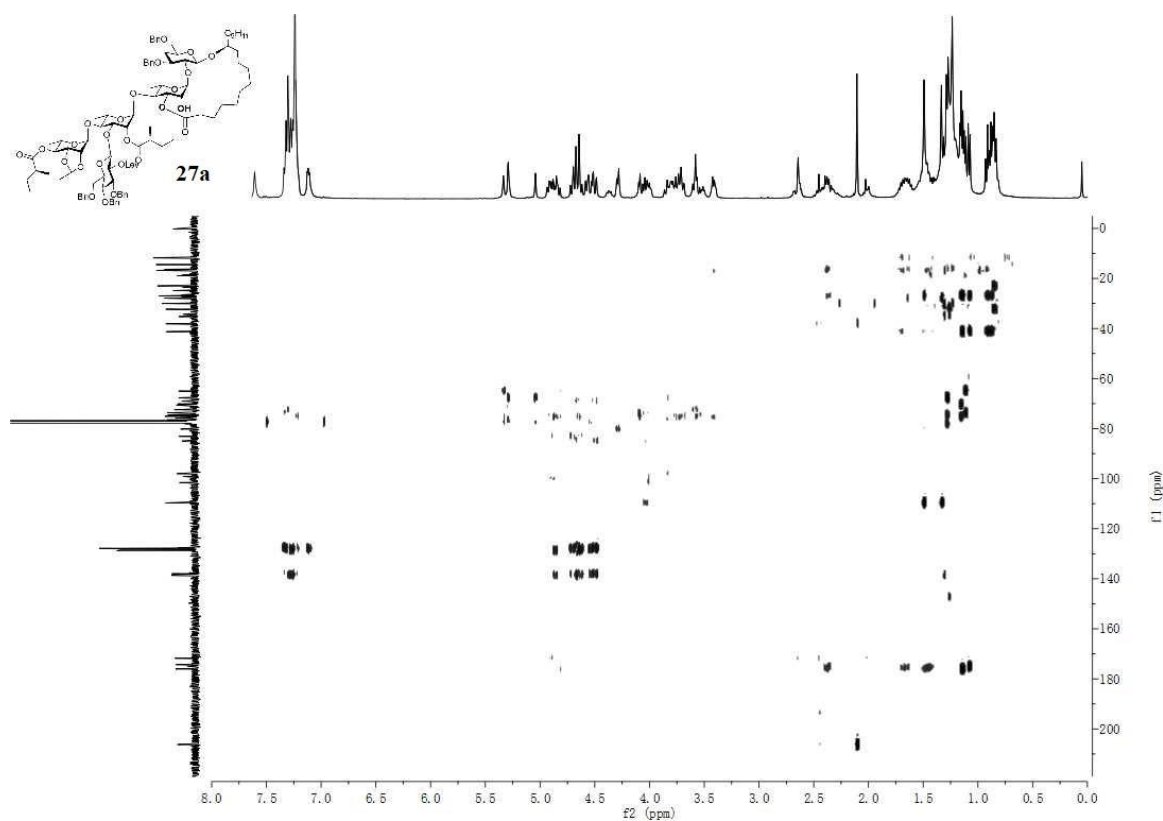


**Figure S84.**  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ) spectrum of **27a**

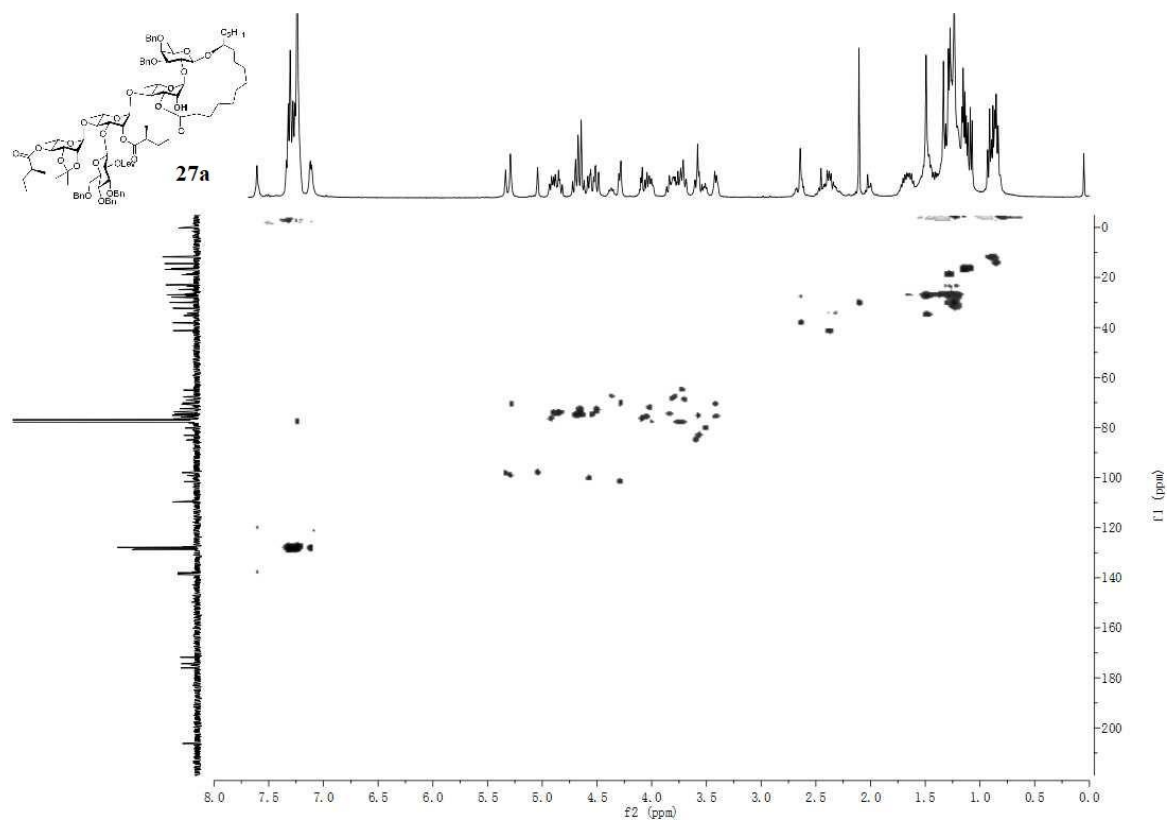




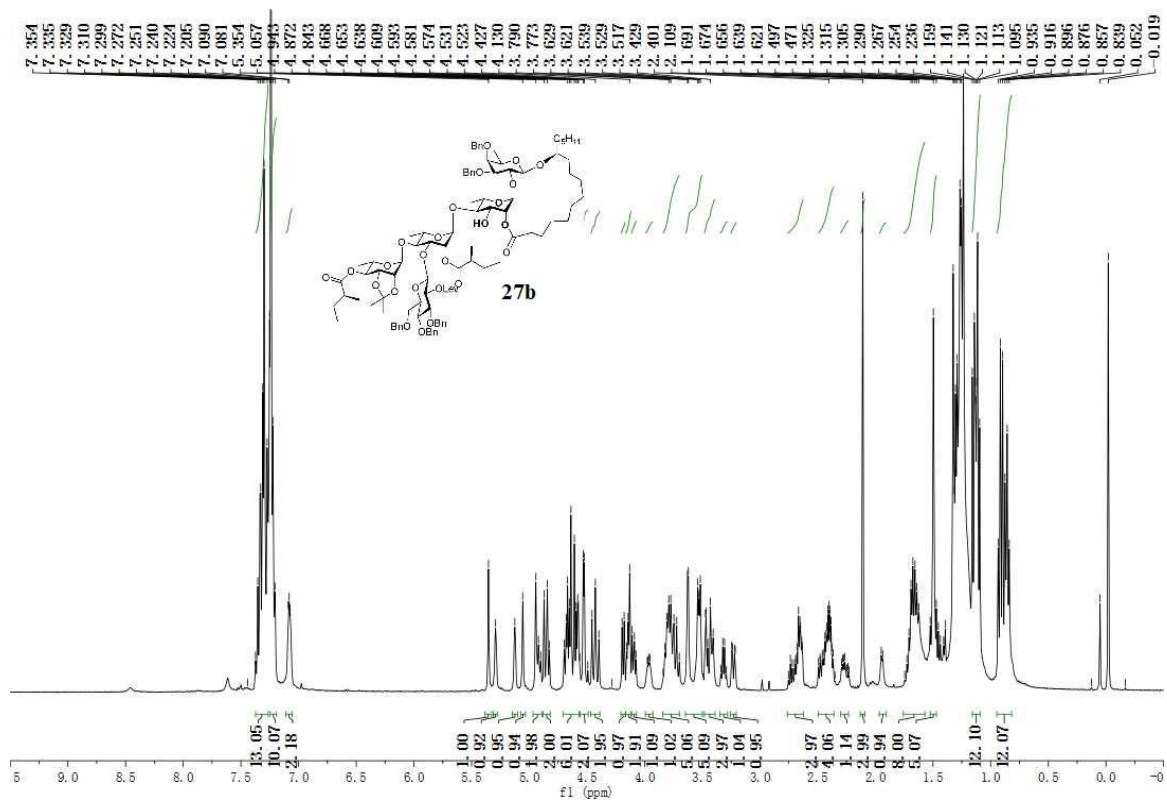
**Figure S85.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **27a**



**Figure S86.** HMBC spectrum of **27a**

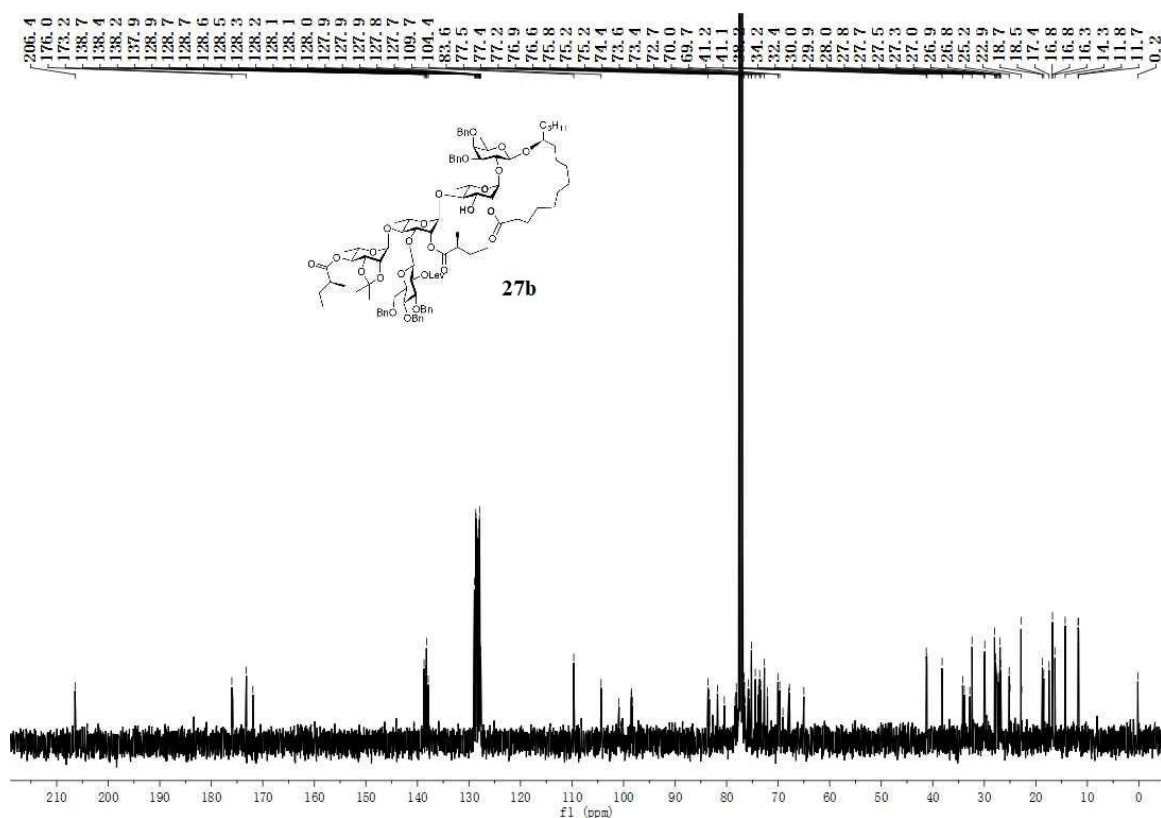


**Figure S87.** HSQC spectrum of **27a**

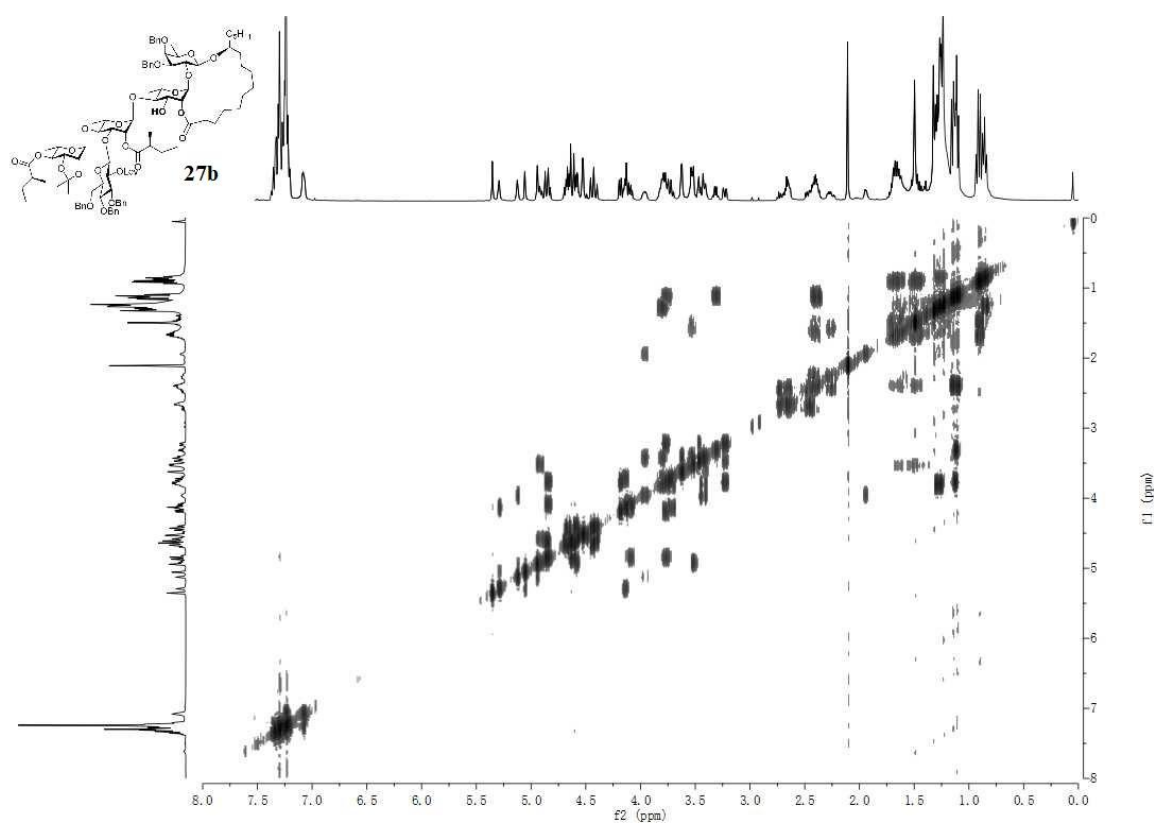


**Figure S88.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **27b**

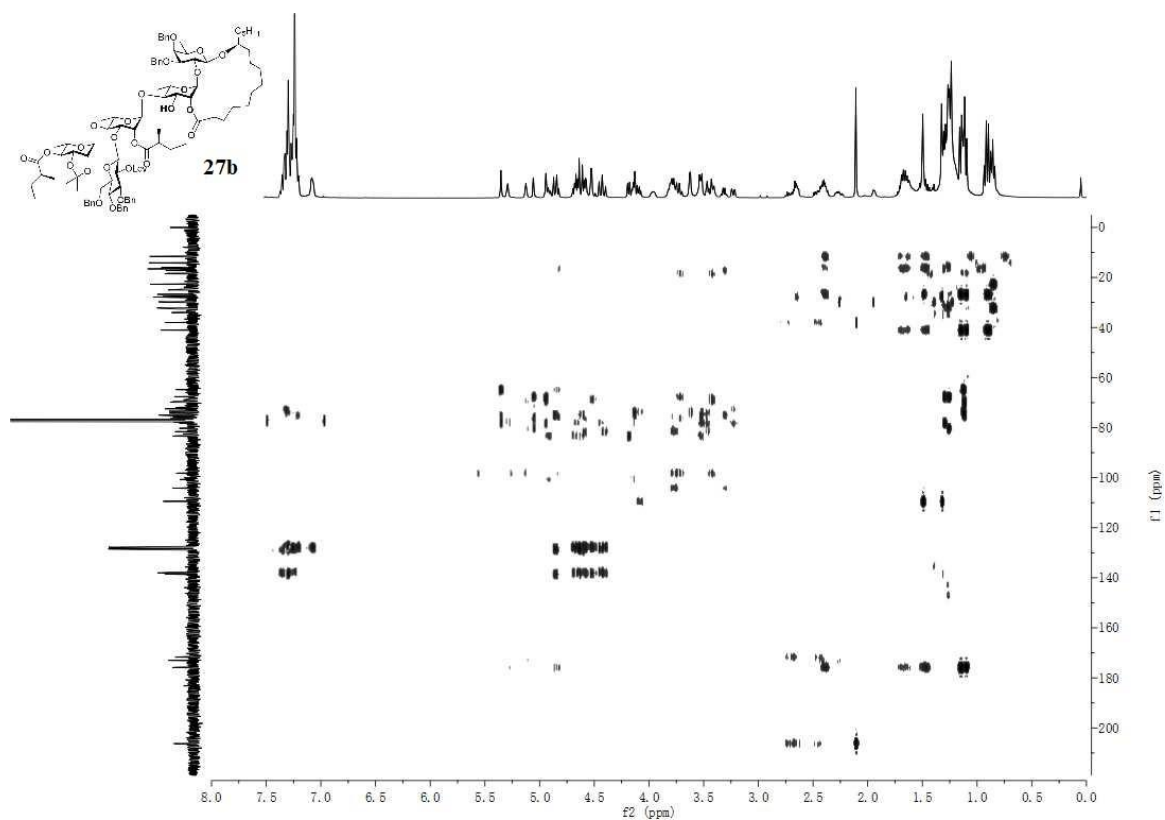




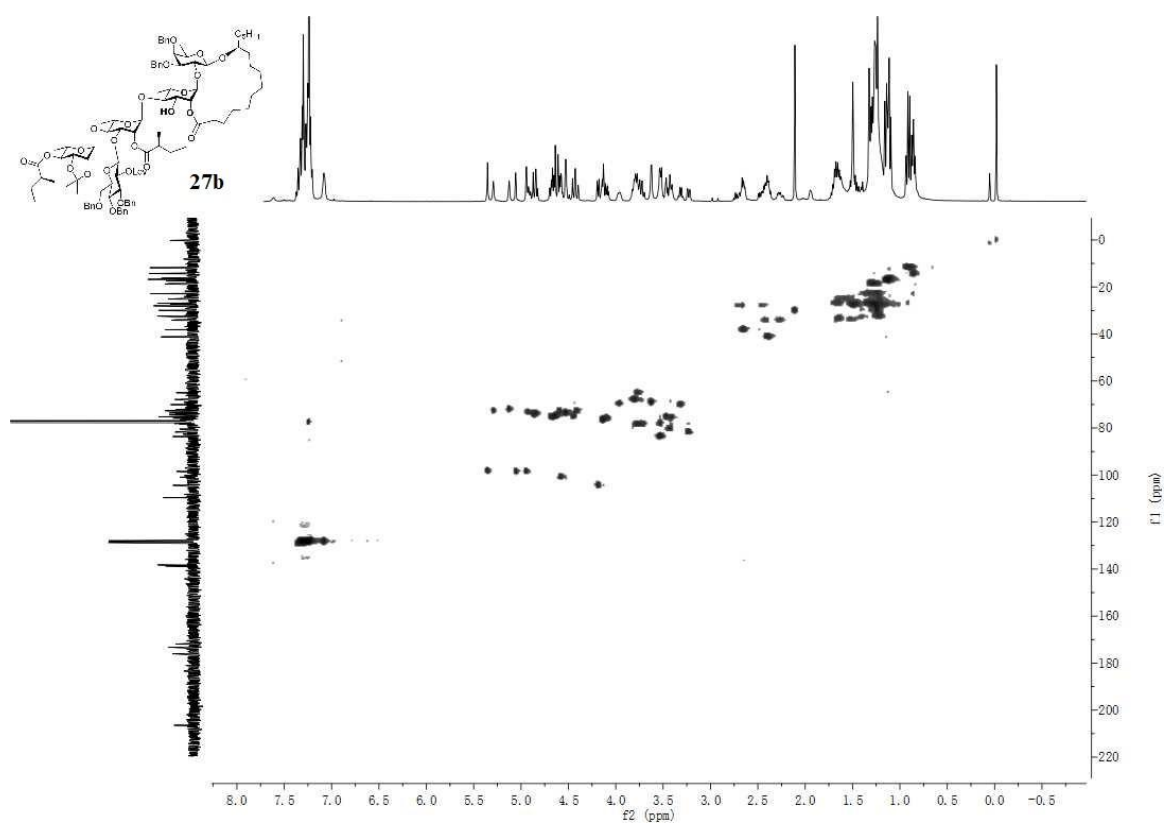
**Figure S89.** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **27b**



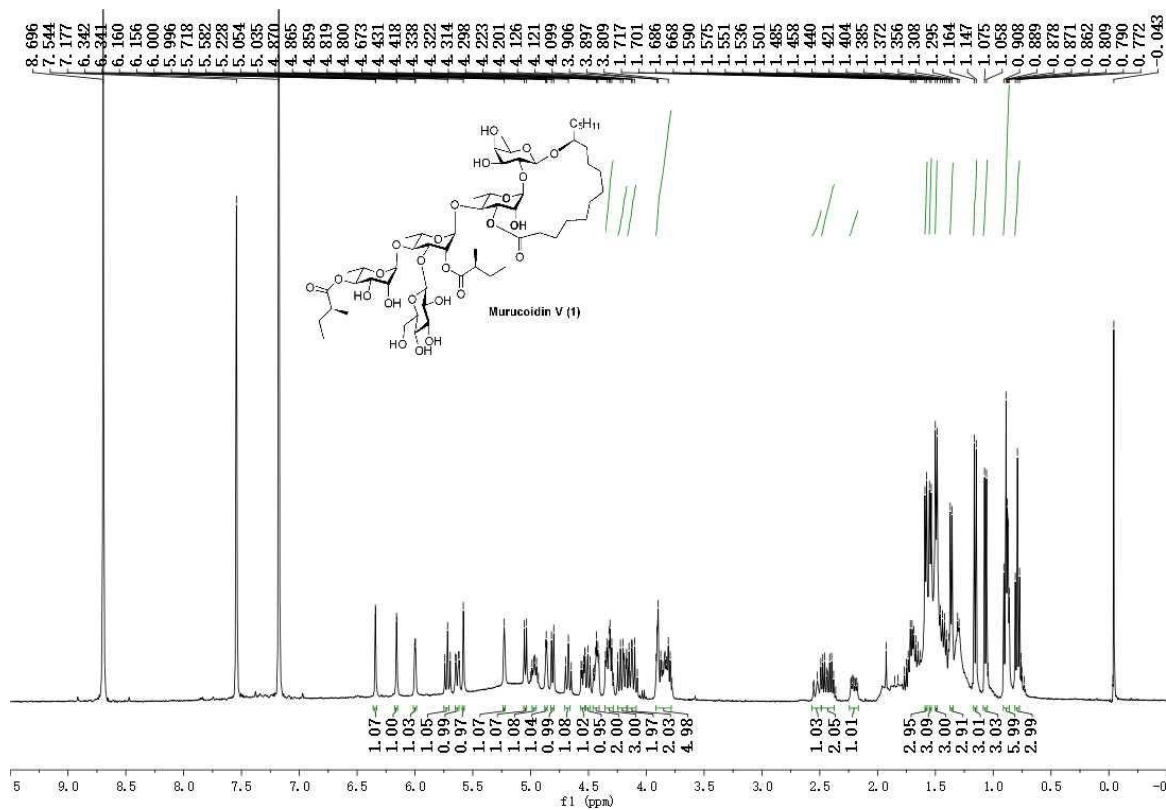
**Figure S90.** <sup>1</sup>H-<sup>1</sup>H COSY spectrum of **27b**



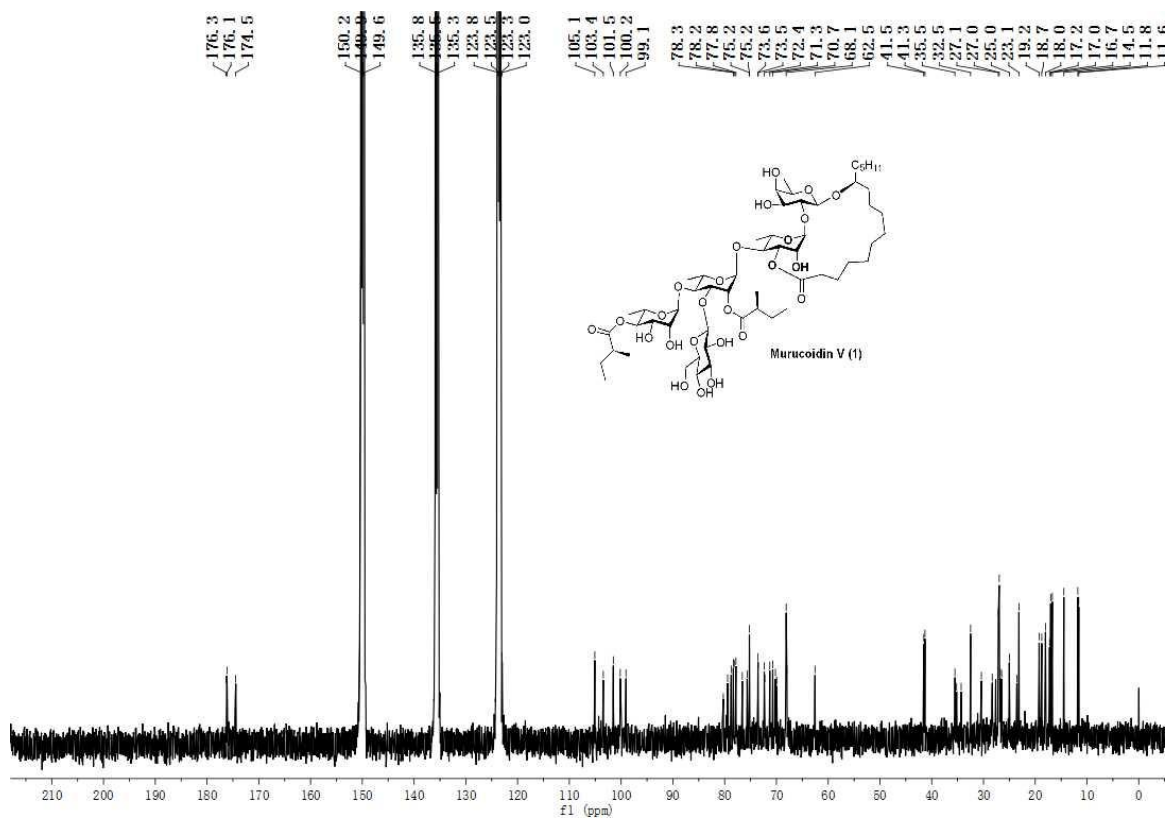
**Figure S91.** HMBC spectrum of **27b**



**Figure S92.** HSQC spectrum of **27b**



**Figure S93.**  $^1\text{H}$  NMR (400 MHz,  $\text{C}_5\text{D}_5\text{N}$ ) spectrum of **1**



**Figure S94.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_5\text{D}_5\text{N}$ ) spectrum of **1**



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