Supporting Information

Recyclable Fluorous-Tag Assisted Two Directional Oligosaccharide Synthesis Enabled by Interrupted Pummerer Reaction Mediated Glycosylation

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1. General Comments

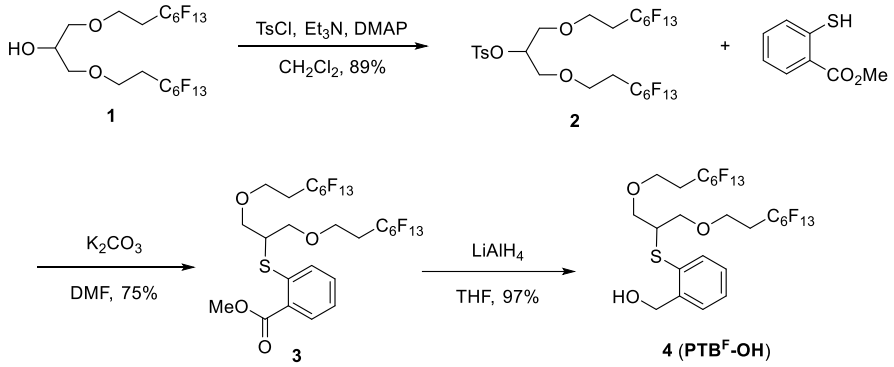
All reactions were monitored by thin-layer chromatography over silica-gel-coated TLC plates (Yantai Chemical Industry Research Institute). The spots on TLC were visualized by warming 10% H_2SO_4 (10% H_2SO_4 in ethanol) or 0.5% $KMnO_4$ (0.5% $KMnO_4$ in water) sprayed plates on a hot plate. Column chromategraphy was performed using silica gel (Qingdao Marine Chemical Inc., China). NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz), Bruker Ascend TM-600 spectrometer (600 MHz) and Bruker AVANCE NEO 600 (600 MHz) and the ^{1}H NMR and ^{13}C NMR chemical shifts were referenced to the solvent or solvent impurity peaks for $CDCl_3$ at δ_H 7.24 and δ_C 77.23. All reaction were heated by metal sand bath (WATTCAS, Z100500, http://www.xinweier.com/Product/Product_Info.aspx?ProductID=4140). The matrix-assisted laser desorption ionization time-of-flight mass spectra (MALDI-TOF MS) were obtained with an AB SCIEX 5800MALDI-TOF/TOF mass spectrometer in linear mode using 2,5-dihydroxybenzoic acid (DHB) as matrix. High resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF II spectrometer using electrospray ionization (ESI). Optical rotations were measured at 20 ℃ with a Rudolph Autopol IV automatic polarimeter using a quartz cell with 1 mL capacity and a 1 dm path length. Concentrations (*c*) are given in g/100 mL.

2. Materials

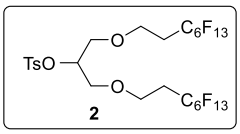
Prior to running the glycosylation reactions, all reagents except Tf_2O and those with low boiling point (<180 ℃) were dried by repeated azeotropic removal of water using toluene and a rotary evaporator at 30 ℃. Unless otherwise noted, all reactions were performed under argon atmosphere. Solvents for reactions were dried on an Innovative Technologies Pure Solv400 solvent purifier. Molecular sieves (4Å, powder < 50 μm) for reactions were flame dried immediately before use. Trifluoromethanesulfonic anhydride (Tf_2O) was purchased from TCI. 2,6-Di-*tert*-butyl-4-methylpyridine (DTBMP) was purchased from Acros. Polytetrafluoroethylene (PTFE) powder was purchased from Sigma (200 μm particle size, SKU: 737992-100G). [Bis(trifluoroacetoxy)iodo]benzene (PIFA) and all other chemicals were purchased from Adamas and used without further purification.

3. General Procedure A for PTFE assisted filtration: PTFE powder (200 μm particle size, roughly 5-10 times the mass of fluorous-tagged product) was added to the crude reaction residue followed by adding a solvent mixture of acetone/H_2O (6:4, v:v, roughly 2 mL/g PTFE). The resulting mixtures were stirred at room temperature for 10-20 min and filtrated through a sand core funnel, washed with additional acetone/H_2O (3-10 times) to thoroughly remove non-fluorous components that remained in solution. Finally, PTFE was washed with dichloromethane or ethyl acetate (3-5 times), the filtrate was dried over anhydrous Na_2SO_4, concentrated under reduced pressure to provide the fluorous-tagged products. PTFE was recovered and used for the next purification.

4. Preparation of fluorous-tag (Scheme 1)

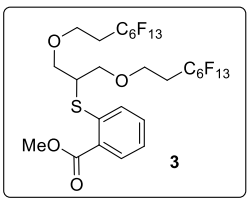


1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl 4-methyl-benzenesulfonate (2)



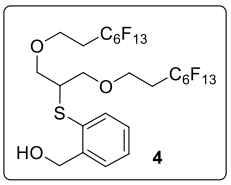
To a stirred solution of compound **1**[1] (6.2 g, 7.90 mmol, 1.0 equiv) and tosyl chloride (3.8 g, 19.8 mmol, 2.5 equiv) in anhydrous CH_2Cl_2 (10.0 mL) were added a solution of Et_3N (2.7 mL, 19.8 mmol, 2.5 equiv) and DMAP (193 mg, 1.58 mmol, 0.2 equiv) in CH_2Cl_2 (6.0 mL) at 0 ℃, the resulting mixture was stirred at room temperature overnight and extracted with EtOAc, the organic phase was washed with saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **2** (7.3 g, yield 89%) as white solid, R_f = 0.4 (petroleum ether-EtOAc 8:1). m.p. 58.3-59.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 2H, Ar-H), 7.30 (d, J = 8.0 Hz, 2H, Ar-H), 4.62 (dt, J = 4.8, 9.6 Hz, 1H), 3.67-3.55 (m, 8H), 2.41 (s, 3H, CH_3), 2.29-2.16 (m, 4H, C**H**$_2$C**H**$_2$C$_6$F$_{13}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 134.1, 129.9, 128.2, 79.0, 69.6, 63.5 (t, J = 4.0 Hz, **C**H_2CH_2C$_6$F$_{13}$), 31.5 (t, J = 21.0 Hz, CH_2**C**H_2C$_6$F$_{13}$). HRMS (ESI$^+$): calc. for $C_{26}H_{20}F_{26}O_5SNa^+$ $[M+Na]^+$: 961.0508, found: 961.0545.

Methyl 2-[(1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzoate (3)



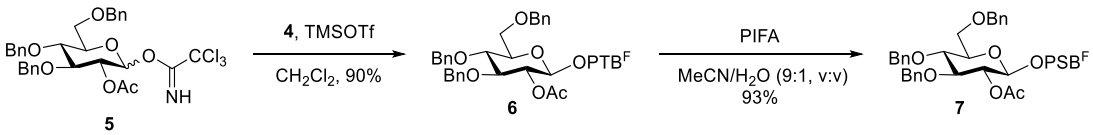
To a stirred solution of compound **2** (7.3 g, 7.77 mmol, 1.0 equiv) and K_2CO_3 (2.1 g, 15.54 mmol, 2.0 equiv) in DMF (25.9 mL) was added methyl thiosalicylate (1.6 mL, 11.66 mmol, 1.5 equiv) at 0 ℃. After stirring at 60 ℃ overnight, the reaction mixture was extracted with EtOAc, the organic phase was washed with H_2O and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **3** (5.5 g, yield 75%) as white solid, R_f = 0.66 (petroleum ether-EtOAc 5:1). m.p. 119.5-120.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.6 Hz, 1H, Ar-H),7.44-7.40 (m, 2H, Ar-H), 7.22-7.18 (m, 1H, Ar-H), 3.89 (s, 3H, OMe), 3.75-3.70 (m, 8H), 3.58-3.52 (m, J = 6.4 Hz, 1H, SCH), 2.44-2.31 (m, 4H, C**H$_2$**C**H$_2$**C$_6$F$_{13}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 138.8, 132.4, 131.3, 130.5, 128.3, 125.4, 70.4, 63.3 (t, J = 4.0 Hz, **C**H$_2$CH$_2$C$_6$F$_{13}$), 52.4, 46.1, 31.6 (t, J = 21.0 Hz, CH$_2$**C**H$_2$C$_6$F$_{13}$). HRMS (ESI$^+$): calc. for $C_{27}H_{20}F_{26}O_4SNa^+$ $[M+Na]^+$: 957.0559, found: 957.0560.

2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzenemethanol (4)

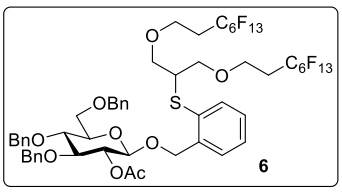


To a stirred suspension of $LiAlH_4$ (436 mg, 11.77 mmol, 2.0 equiv) in anhydrous THF (19.0 mL) was added a solution of compound **3** (5.5 g, 5.89 mmol, 1.0 equiv) in anhydrous THF (10.0 mL) slowly at 0 ℃. The resulting mixture was allowed to stir at room temperature overnight. H_2O (0.44 mL) was added to the reaction mixture slowly, followed by addition of 15% NaOH (0.44 mL) and H_2O (1.33 mL). Then, the mixture was filtered through a sand core funnel. The filtrate was diluted and extracted with EtOAc, the organic phase was washed with H_2O and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **4** (5.1 g, yield 97%) as colorless liquid, R_f = 0.27 (petroleum ether-EtOAc 6:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49-7.47 (m, 1H, Ar-H), 7.38 (dd, J = 1.2, 6.6 Hz, 1H, Ar-H), 7.29-7.25 (m, 2H, Ar-H), 4.77 (d, J = 6.6 Hz, 2H, PhCH$_2$), 3.70 (t, J = 6.6 Hz, 4H), 3.66-3.62 (m, 4H), 3.37-3.33 (m, J = 6.0 Hz, 1H, SCH), 2.94 (t, J = 6.6 Hz, 1H, OH), 2.40-2.32 (m, 4H, C**H$_2$**C**H$_2$**C$_6$F$_{13}$). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.6, 134.3, 133.1, 129.6, 128.7, 128.6, 70.6, 64.4, 63.3 (t, J = 4.0 Hz, **C**H$_2$CH$_2$C$_6$F$_{13}$), 49.4, 31.5 (t, J = 21.0 Hz, CH$_2$**C**H$_2$C$_6$F$_{13}$). HRMS (ESI$^+$): calc. for $C_{26}H_{20}F_{26}O_3SNa^+$ $[M+Na]^+$: 929.0610, found: 929.0612.

5. Preparation of fluorous-tagged glycosyl donor 7 (Scheme 2)

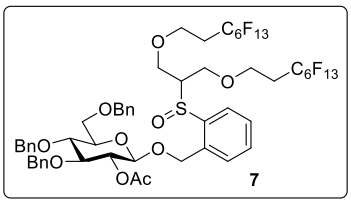


2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranoside (6)



A suspension of compound **4** (188 mg, 0.21 mmol, 1.0 euqiv) and compound **5**[2] (158.5 mg, 0.25 mmol, 1.2 equiv) containing activated 4Å MS (100 wt%) in anhydrous CH_2Cl_2 (2.0 mL) was stirred at room temperature for 5 min under argon. After cooling to −20 ℃, TMSOTf (19 μL, 0.10 mmol, 0.5 equiv) was added. The reaction mixture was stirred at −20 ℃ for 1 h and quenched by addition of Et_3N (0.5 mL). The suspension was diluted with EtOAc and filtered through Celite. The filtrate was concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **6** (258 mg, yield 90%) as colorless syrup, R_f = 0.2 (petroleum ether-EtOAc 5:1). $[\alpha]_D^{20}$ −4.3 (*c*, 1.14 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.15 (m, 19H, Ar-H), 5.06 (dd, *J* = 8.0, 9.2 Hz, 1H, H-2), 5.02 (d, *J* = 13.2 Hz, 1H, $PhCH_2$), 4.77 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.77 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.75 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.64 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.61 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.54 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.53 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.43 (d, *J* = 8.0 Hz, 1H, **H-1**), 3.77-3.57 (m, 12H), 3.48 (ddd, *J* = 2.4, 4.8, 9.6 Hz, 1H, H-5), 3.33-3.28 (m, 1H, SCH), 2.39-2.26 (m, 4H, C**H**$_2$C**H**$_2$C$_6$F$_{13}$), 1.92 (s, 3H, OAc). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.8, 139.4, 138.4, 138.3, 138.1, 133.3, 132.5, 128.9, 128.6, 128.6, 128.6, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.8, 100.4 (**C-1**), 83.2, 78.2, 75.5, 75.3, 75.3, 73.7, 73.4, 70.4, 70.4, 69.0, 68.9, 63.2 (t, *J* = 4.0 Hz, **C**H$_2$CH$_2$C$_6$F$_{13}$), 48.4, 31.5 (t, *J* = 21.0 Hz, CH$_2$**C**H$_2$C$_6$F$_{13}$), 21.1. HRMS (ESI$^+$): calc. for $C_{55}H_{50}F_{26}O_9SNa^+$ $[M+Na]^+$: 1403.2653, found: 1403.2640.

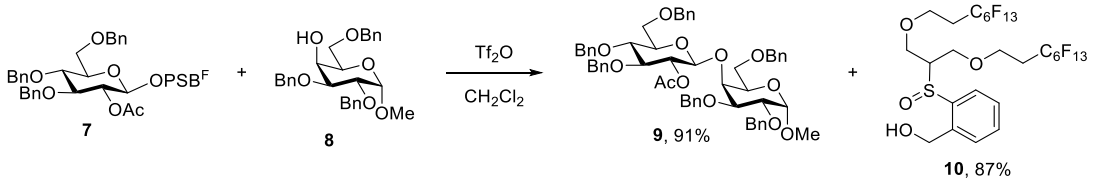
2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)sulfinyl]benzyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranoside (7)



To a stirred solution of compound **6** (258 mg, 0.19 mmol, 1.0 equiv) in MeCN/H_2O (9:1, v:v, 1.9 mL) was added PIFA (96.4 mg, 0.22 mmol, 1.2 equiv). The resulting mixture was stirred at room temperature for 30 min. The reaction mixture was extracted with EtOAc. The organic phase was washed with saturated $Na_2S_2O_3$, saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to give compound **7** (242.5 mg, yield 93%) as white foam, R_f = 0.33 (petroleum ether-EtOAc 2:1). A mixture of sulfoxide *R*/*S* (1:1) isomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.87 (m, 4H, Ar-H), 7.52-7.43 (m, 6H, Ar-H), 7.32-7.25 (m, 20H, Ar-H), 7.22-7.15 (m, 10H, Ar-H), 5.03 (dd, *J* = 8.0, 9.2 Hz, 1H), 5.01 (dd, *J* = 8.0, 9.2 Hz, 1H), 4.94 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.92 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.78-4.43 (m, 16H), 3.78-3.44 (m, 26H), 3.24-3.18 (m, 2H, SCH), 2.38-2.08 (m, 8H, C**H**$_2$C**H**$_2$C$_6$F$_{13}$), 1.93 (s, 3H, OAc), 1.87 (s, 3H, OAc). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 169.6, 141.3, 140.6, 138.3, 138.2, 138.2, 138.1, 135.6, 135.2, 131.3, 131.3, 130.0, 129.5, 129.1, 128.9, 128.6, 128.6, 128.1, 128.1, 128.0, 127.9, 127.9, 125.2, 125.1, 100.4 (**C-1**), 100.3 (**C-1**), 83.2, 83.1, 78.1, 78.0, 75.4, 75.4, 75.3, 75.3, 75.2, 73.7, 73.7, 73.1, 73.1, 68.8, 67.0, 66.5, 66.5, 64.3, 64.2, 63.4 (t, *J* = 4.0 Hz, **C**H$_2$CH$_2$C$_6$F$_{13}$), 63.0 (t, *J* = 4.0 Hz, **C**H$_2$CH$_2$C$_6$F$_{13}$),

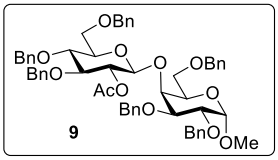
62.9, 31.4 (t, J = 21.0 Hz, $CH_2\underline{\mathbf{C}}H_2C_6F_{13}$), 31.3 (t, J = 21.0 Hz, $CH_2\underline{\mathbf{C}}H_2C_6F_{13}$), 20.9. HRMS ($ESI^+$): calc. for $C_{55}H_{50}F_{26}O_{10}SNa^+$ $[M+Na]^+$: 1419.2602, found: 1419.2589.

6. IPRm glycosylation of fluorous-tagged glycosyl donor 7 (Scheme 2)



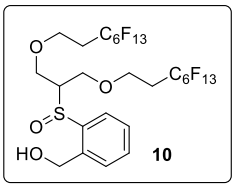
A solution of compound **7** (50 mg, 0.036 mmol, 1.2 equiv) and **8**[3] (13.9 mg, 0.030 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (0.60 mL) in the presence of 4Å MS (100 wt%) was stirred for 10 min at 0 ℃. After the addition of Tf_2O (6.0 μL, 0.036 mmol, 1.2 equiv), the solution was stirred at 0 ℃ for 30 min and quenched by addition of H_2O (1.0 mL). The mixture was filtered through Celite and extracted with EtOAc. The organic phase was washed with brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by flash column chromatography on silica gel to give compound **9** (25.6 mg, yield 91%) and compound **10** (28.7 mg, yield 87%).

Methyl 4-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-*α*-D-galactopyranoside (9)



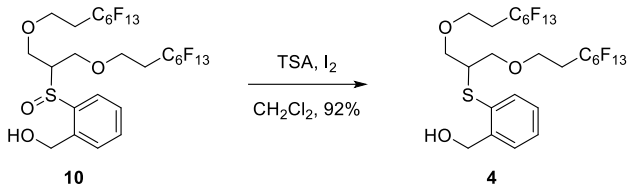
Colorless syrup, R_f = 0.63 (petroleum ether-EtOAc 2:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.25 (m, 28H, Ar-H), 7.18-7.16 (m, 2H, Ar-H), 4.99 (t, J = 8.4 Hz, 1H), 4.81-4.73 (m, 4H), 4.69-4.63 (m, 4H), 4.58 (d, J = 12.0 Hz, 1H, $PhCH_2$), 4.55 (d, J = 11.2 Hz, 1H, $PhCH_2$), 4.49-4.46 (m, 3H), 4.40 (d, J = 12.0 Hz, 1H, $PhCH_2$), 4.03 (d, J = 2.0 Hz, 1H), 3.89-3.83 (m, 2H), 3.81-3.77 (m, 2H), 3.71-3.60 (m, 5H), 3.39-3.36 (m, 1H), 3.35 (s, 3H, OMe), 1.74 (s, 3H, OAc). ^1H NMR data for **9** were the same as those reported in the literature.[4]

2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)sulfinyl]benzenemethanol (10)



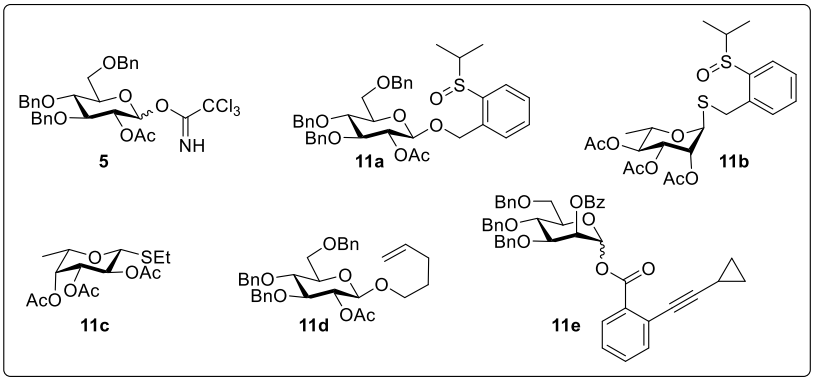
White solid, R_f = 0.22 (petroleum ether-EtOAc 2:1). m.p. 58.9-60.3 ℃. A mixture of sulfoxide *R*/*S* (1:1) isomers. ^1H NMR (400 MHz, $CDCl_3$) δ 7.82-7.79 (m, 1H, Ar-H), 7.49-7.43 (m, 3H, Ar-H), 4.85 (dd, J = 6.0, 12.8 Hz, 1H, $PhCH_2$), 4.69 (dd, J = 6.0, 12.8 Hz, 1H, $PhCH_2$), 3.79-3.52 (m, 8H), 3.44-3.38 (m, 1H, SCH), 2.98 (t, J = 6.0 Hz, 1H, OH), 2.38-2.14 (m, 4H, $C\underline{\mathbf{H}_2}C\underline{\mathbf{H}_2}C_6F_{13}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 139.6, 131.8, 130.2, 128.8, 126.0, 67.1, 64.5, 63.7, 63.5 (t, J = 4.0 Hz, $\underline{\mathbf{C}}H_2CH_2C_6F_{13}$), 62.4, 31.4 (t, J = 21.0 Hz, $CH_2\underline{\mathbf{C}}H_2C_6F_{13}$). HRMS ($ESI^+$): calc. for $C_{26}H_{20}F_{26}O_4SNa^+$ $[M+Na]^+$: 945.0559, found: 945.0558.

7. Regeneration of fluorous-tag (Scheme 2)

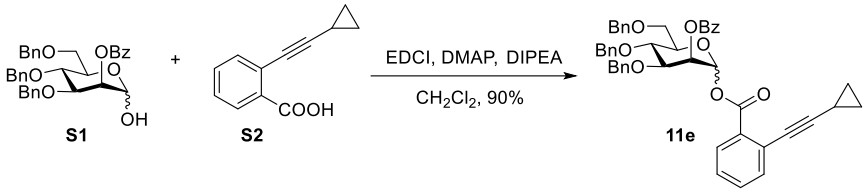


To a stirred solution of compound **10** (23.5 mg, 0.025 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (0.25 mL) was added thiosalicylic acid (11.8 mg, 0.076 mmol, 3.0 equiv) and I_2 (50 μL, 0.05 M in CH_2Cl_2, 2.55 μmol, 0.1 equiv). The resulting mixture was stirred at room temperature for 11 h and extracted with EtOAc. The organic phase was washed with saturated $Na_2S_2O_3$, saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **4** (21.2 mg, yield 92%) as colorless liquid. ^{1}H NMR data of regenerated **4** were exactly the same as shown on page S5.

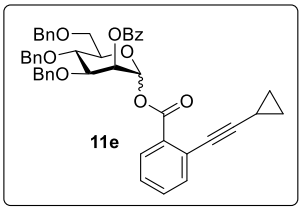
8. Preparation of donors



Compound **5**,[2] **11a**,[4] **11b**,[5] **11c**,[6] **11d**,[7] were synthesised according to the reported procedures.

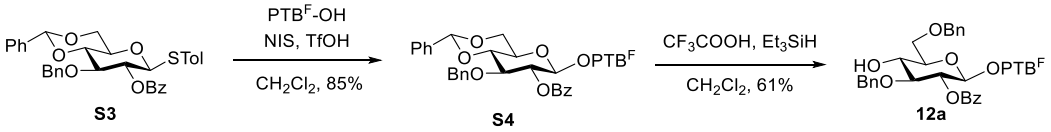


2-*O*-Benzoyl-3,4,5-tri-*O*-benzyl-*α*-D-mannopyranosyl *ortho*-cyclopropylethynylbenzoate (11e)

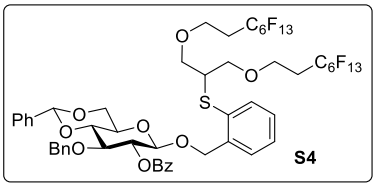


To a stirred solution of **S1**[8] (298 mg, 0.54 mmol, 1.0 equiv) and *ortho*-cyclopropylethynyl benzoic acid **S2** (120 mg, 0.64 mmol, 1.2 equiv) in anhydrous CH_2Cl_2 (5.4 mL) was added DMAP (65.9 mg, 0.54 mmol, 1.0 equiv), EDCI (154.5 mg, 0.80 mmol, 1.5 equiv) and DIPEA (0.16 mL, 0.97 mmol, 1.8 equiv). The resulting mixture was stirred at room temperature overnight. The mixture was extracted with EtOAc, washed with H_2O, saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by flash column chromatography on silica gel to give **11e** (351 mg, yield 90%, α/β 1.2:1). ***α* isomer:** Colorless syrup, R_f = 0.67 (petroleum ether-EtOAc 5:1). $[\alpha]_D^{20}$ +10.6 (*c*, 0.64 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 1.2, 8.4 Hz, 2H, Ar-H), 7.83 (dd, *J* = 0.8, 8.0 Hz, 1H, Ar-H), 7.55 (tt, *J* = 1.2, 7.6 Hz, 1H, Ar-H), 7.46 (dd, *J* = 1.2, 8.0 Hz, 1H, Ar-H), 7.43 (dd, *J* = 1.2, 6.8 Hz, 1H, Ar-H), 7.41-7.22 (m, 16H, Ar-H), 7.16-7.14 (m, 4H, Ar-H), 6.50 (d, *J* = 2.0 Hz, 1H, **H-1**), 5.76 (t, *J* = 2.8 Hz, 1H, H-2), 4.86 (d, *J* = 10.4 Hz, 1H, $PhCH_2$), 4.84 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.77 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.61 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.57 (d, *J* = 10.4 Hz, 1H, $PhCH_2$), 4.55 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.30 (dd, *J* = 3.2, 9.6 Hz, 1H, H-3), 4.25 (t, *J* = 9.6 Hz, 1H, H-4), 4.11 (ddd, *J* = 1.2, 3.2, 9.6 Hz, 1H, H-5), 3.95 (dd, *J* = 3.2, 11.2 Hz, 1H, H-6a), 3.79 (dd, *J* = 1.6, 11.2 Hz, 1H, H-6b), 1.58-1.51 (m, 1H), 0.81-0.69 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 164.2, 138.7, 138.5, 137.9, 134.8, 133.5, 132.4, 131.0, 130.7, 130.3, 129.8, 128.7, 128.6, 128.5, 128.4, 128.2, 127.9, 127.7, 127.7, 127.3, 125.1, 100.4 (**C-1**), 92.4, 78.1, 75.7, 74.9, 74.7, 74.0, 73.8, 72.1, 68.9, 68.3, 9.3, 0.9. HRMS (ESI^+): calc. for $C_{46}H_{42}O_8Na^+$ $[M+Na]^+$: 745.2772, found: 745.2765. ***β* isomer:** Colorless syrup, R_f = 0.65 (petroleum ether-EtOAc 5:1). $[\alpha]_D^{20}$ −12.9 (*c*, 0.45 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.70 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.56 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.42-7.25 (m, 17H, Ar-H), 7.22-7.20 (m, 2H, Ar-H), 7.08 (dt, *J* = 1.2, 8.0 Hz, 1H, Ar-H), 6.07 (s, 1H, **H-1**), 5.94 (d, *J* = 2.8 Hz, 1H, H-2), 4.89 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.83 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.74 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.58 (d, *J* = 11.2 Hz, 2H, $PhCH_2$), 4.54 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.16 (t, *J* = 9.6 Hz, 1H, H-4), 3.94-3.90 (m, 2H), 3.86 (dd, *J* = 1.6, 11.2 Hz, 1H), 3.73 (ddd, *J* = 1.6, 3.2, 9.6 Hz, 1H, H-5), 1.50-1.44 (m, 1H), 0.86-0.80 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 163.5, 138.6, 138.4, 137.6, 134.4, 133.4, 132.3, 130.9, 130.3, 130.1, 128.6, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.7, 127.7, 127.1, 125.8, 100.4 (**C-1**), 92.0, 80.2, 76.5, 75.5, 74.5, 74.0, 73.6, 71.7, 68.9, 68.5, 9.1, 9.1, 0.9. HRMS (ESI^+): calc. for $C_{46}H_{42}O_8Na^+$ $[M+Na]^+$: 745.2772, found: 745.2777.

9. Preparation of fluorous-tagged acceptors 12

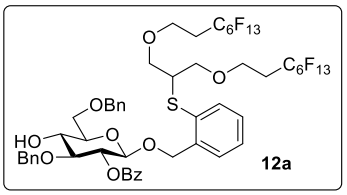


2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-glucopyranoside (S4)



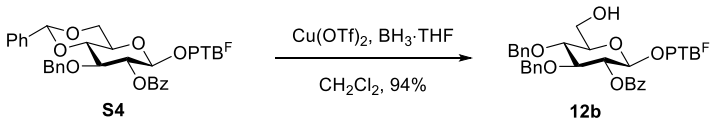
A suspension of PTB^{F}-OH (500 mg, 0.55 mmol, 1.0 equiv), **S3**[9] (376 mg, 0.66 mmol, 1.2 equiv) containing activated 4Å MS (100 wt%) in anhydrous CH_2Cl_2 (6.6 mL) was stirred at 0 ℃ for 10 min under argon. Then, *N*-iodosuccinimide (186 mg, 0.83 mmol, 1.5 equiv) and TfOH (10 μL, 0.11 mmol, 0.2 equiv) were added. After stirring at 0 ℃ for 1 h, the reaction was quenched by addition of Et_3N (0.3 mL). The suspension was filtered through Celite and concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **S4** (640 mg, yield 85%) as yellow foam, R_f = 0.20 (petroleum ether-EtOAc 8:1). $[\alpha]_D^{20}$ +4.4 (*c*, 1.08 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.92 (m, 2H, Ar-H), 7.57 (t, *J* =7.6 Hz, 1H, Ar-H), 7.50-7.48 (m, 2H, Ar-H), 7.44-7.36 (m, 5H, Ar-H), 7.33 (d, *J* =7.6 Hz, 1H, Ar-H), 7.28 (t, *J* =7.2 Hz, 1H, Ar-H), 7.16-7.10 (m, 4H, Ar-H), 7.07-6.99 (m, 3H, Ar-H), 5.60 (s, 1H), 5.35 (t, *J* =8.4 Hz, 1H), 4.98 (d, *J* = 12.8 Hz, 1H, $PhCH_2$), 4.80 (d, *J* = 12.4 Hz, 2H, $PhCH_2$), 4.67 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.66 (d, *J* = 8.0 Hz, 1H, **H-1**), 4.40 (dd, *J* = 4.8, 10.4 Hz, 1H), 3.89-3.81 (m, 3H), 3.66-3.61 (m, 4H), 3.54-3.47 (m, 5H), 3.23-3.17 (m, *J* = 6.0 Hz, 1H, SCH), 2.38-2.25 (m, 4H, C**H**$_2$C**H**$_2$C$_6$F$_{13}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 138.9, 138.1, 137.5, 133.2, 132.5, 130.2, 130.1, 129.3, 128.9, 128.5, 128.5, 128.4, 128.4, 128.2, 127.8, 127.7, 126.2, 101.6, 100.9 (**C-1**), 81.9, 78.2, 74.2, 73.6, 70.3, 70.3, 69.1, 69.0, 66.6, 63.2 (t, *J* = 4.0 Hz, **C**H$_2$CH$_2$C$_6$F$_{13}$), 48.3, 31.5 (t, *J* = 21.0 Hz, CH$_2$**C**H$_2$C$_6$F$_{13}$). HRMS (ESI$^+$): calc. for $C_{53}H_{44}F_{26}O_9SNa^+$ $[M+Na]^+$: 1373.2183, found: 1373.2157.

2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-*β*-D-glucopyranoside (12a)

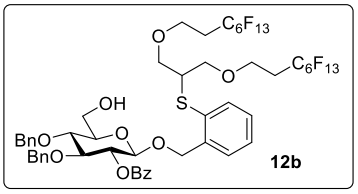


A suspension of **S4** (300 mg, 0.22 mmol, 1.0 equiv) and 4Å MS (100 wt%) in anhydrous CH_2Cl_2 (1.1 mL) was stirred at 0 ℃ for 10 min under argon. Then, Et_3SiH (0.18 mL, 1.11 mmol, 5.0 equiv) and CF_3COOH (83 μL, 1.11 mmol, 5.0 equiv) were added at 0 ℃. The mixture was warmed up to room temperature and stirred for 4 h. The suspension was filtered through Celite and extracted with EtOAc. The organic phase was washed with saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by flash column chromatography on silica gel to give **12a** (183.6 mg, yield 61%) as colorless syrup (the General Procedure A wasn't used due to the existence of a small amount of fluorous by-products, which were difficult to be separated by fluorous based purification). R_f = 0.20 (petroleum ether-EtOAc 5:1). $[\alpha]_D^{20}$ −5.5 (*c*, 1.26 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.05 (m, 2H, Ar-H), 7.64 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.49 (t, *J* = 7.6 Hz, 2H, Ar-H), 7.42-7.32 (m, 9H, Ar-H), 7.22-7.20 (m, 4H, Ar-H), 7.10 (dt, *J* = 0.8, 7.6 Hz, 1H, Ar-H), 5.40 (dd, *J* = 8.0, 9.6 Hz, 1H, H-2), 5.06 (d, *J* = 12.8 Hz, 1H, $PhCH_2$), 4.88 (d, *J* = 13.2 Hz, 1H, $PhCH_2$), 4.79 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.73 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.71 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.67 (d, *J* = 8.0 Hz, 1H, **H-1**), 4.65 (d, *J* = 11.6, 1H, $PhCH_2$), 3.91 (dd, *J* = 2.4, 9.2 Hz, 1H, H-

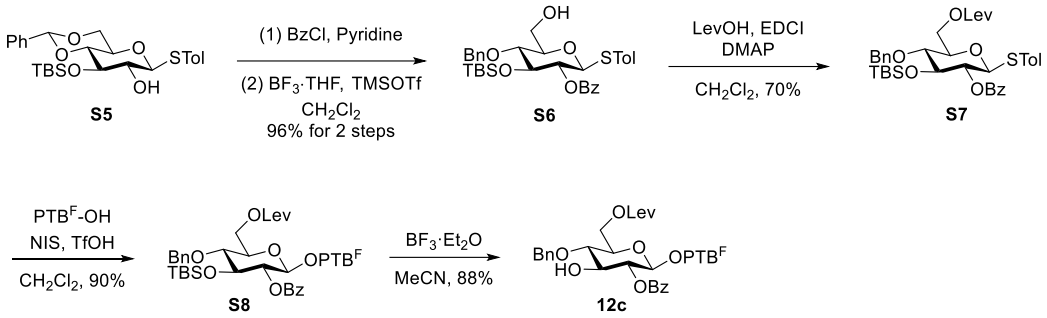
6a), 3.88 (d, *J* = 4.4 Hz, 2H), 3.75-3.67 (m, 5H), 3.62 (dd, *J* = 4.4, 9.6 Hz, 1H, H-6b), 3.59-3.53 (m, 4H), 3.30-3.25 (m, *J* = 6.0 Hz, 1H, SCH), 2.80 (d, *J* = 2.4 Hz, 1H, OH), 2.45-2.32 (m, 4H, C**H**$_2$C**H**$_2$C$_6$F$_{13}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 139.2, 138.2, 133.3, 133.1, 132.4, 130.2, 130.1, 128.8, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 128.0, 127.7, 100.4 (**C-1**), 82.4, 74.7, 74.3, 74.0, 73.6, 72.5, 70.5, 70.3, 70.2, 68.8, 63.2 (t, *J* = 4.0 Hz, **C**H$_2$CH$_2$C$_6$F$_{13}$), 48.2, 31.4 (t, *J* = 21.0 Hz, CH$_2$**C**H$_2$C$_6$F$_{13}$). HRMS (ESI$^+$): calc. for $C_{53}H_{46}F_{26}O_9SNa^+$ [M+Na]$^+$: 1375.2340, found: 1375.2341.



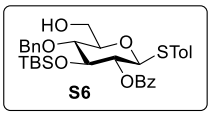
2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 2-*O*-benzoyl-3,4-di-*O*-benzyl-*β*-D-glucopyranoside (12b)



A suspension of **S4** (300 mg, 0.22 mmol, 1.0 equiv) and 4Å MS (100 wt%) in anhydrous CH_2Cl_2 (2.2 mL) was stirred at 0 ℃ for 10 min under argon. Then, BH_3·THF (1.1 mL, 1 M in THF, 1.1 mmol, 5.0 equiv) and $Cu(OTf)_2$ (12.0 mg, 0.03 mmol, 0.15 equiv) were added at 0 ℃. The mixture was warmed up to room temperature and stirred for 2.5 h and quenched by addition of MeOH (0.5 mL). The suspension was filtered through Celite and concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give **12b** (280.9 mg, yield 94%) as white solid, R_f = 0.37 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{20}$ +8.1 (*c*, 3.81 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.55 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.43-7.27 (m, 9H, Ar-H), 7.18-7.02 (m, 7H, Ar-H), 5.30 (t, *J* = 8.8 Hz, 1H, H-2), 4.95 (d, *J* = 12.4 Hz, 1H, PhCH$_2$), 4.85 (d, *J* = 11.2 Hz, 1H, PhCH$_2$), 4.83 (d, *J* = 12.8 Hz, 1H, PhCH$_2$), 4.72 (d, *J* = 11.2 Hz, 1H, PhCH$_2$), 4.66 (d, *J* = 10.8 Hz, 1H, PhCH$_2$), 4.64 (d, *J* = 10.0 Hz, 1H, PhCH$_2$), 4.62 (d, *J* = 7.6 Hz, 1H, **H-1**), 3.88 (ddd, *J* = 2.4, 5.6, 11.6 Hz, 1H), 3.81 (t, *J* = 9.2 Hz, 1H, H-3), 3.75-3.63 (m, 6H), 3.57-3.49 (m, 4H), 3.44 (ddd, *J* = 2.4, 4.4, 9.6 Hz, 1H, H-5), 3.28-3.22 (m, *J* = 6.0 Hz, 1H, SCH), 2.38-2.28 (m, 4H, C**H**$_2$C**H**$_2$C$_6$F$_{13}$), 2.00 (t, *J* = 6.0 Hz, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 139.1, 138.0, 137.9, 133.3, 133.3, 132.6, 130.2, 130.0, 129.1, 128.7, 128.5, 128.5, 128.3, 128.2, 127.9, 127.8, 100.3 (**C-1**), 82.8, 77.9, 75.7, 75.3, 73.9, 70.3, 70.3, 69.0, 63.2 (t, *J* = 4.0 Hz, **C**H$_2$CH$_2$C$_6$F$_{13}$), 48.2, 31.4 (t, *J* = 21.0 Hz, CH$_2$**C**H$_2$C$_6$F$_{13}$). HRMS (ESI$^+$): calc. for $C_{53}H_{46}F_{26}O_9SNa^+$ [M+Na]$^+$: 1975.2340, found: 1975.2369.

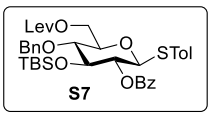


4-Methylphenyl 2-*O*-benzoyl-3-*O*-(*tert*-butyldimethylsilyl)-4-*O*-benzyl-1-thio-*β*-D-glucopyranoside (S6)



To a stirred soltuion of **S5**[10] (980 mg, 2.01 mmol, 1.0 equiv) in pyridine (10.0 mL) was added benzoyl chloride (1.2 mL, 10.03 mmol, 5.0 equiv). The mixture was warmed up to 80 ℃, stirred overnight and extracted with EtOAc. The organic phase was washed with 1 M HCl, saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* to give crude product. A suspension of the above crude product and 4Å MS (100 wt%) in anhydrous CH_2Cl_2 (10.0 mL) was stirred at 0 ℃ for 10 min under argon. Then, BH_3·THF (10.0 mL, 1 M in THF, 10.0 mmol, 5.0 equiv) and TMSOTf (54 μL, 0.30 mmol, 0.15 equiv) were added at 0 ℃. The mixture was warmed up to room temperature and stirred for 4 h and quenched by addition of Et_3N (0.5 mL). The suspension was filtered through Celite and extracted with EtOAc, washed with H_2O and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by flash column chromatography on silica gel to give **S6** (1.15 g, 96% yield for two steps) as colorless syrup, R_f = 0.47 (petroleum ether-EtOAc 6:1). $[\alpha]_D^{20}$ +16.6 (*c*, 1.00 in $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06-8.05 (m, 2H, Ar-H), 7.58 (t, *J* = 7.8 Hz, 1H, Ar-H), 7.45 (t, *J* =7.8 Hz, 2H, Ar-H), 7.34-7.26 (m, 7H, Ar-H), 7.06 (d, *J* = 7.8 Hz, 2H, Ar-H), 5.16 (t, *J* = 9.6 Hz, 1H), 4.83 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.71 (d, *J* = 10.2 Hz, 1H, **H-1**), 4.61 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 3.93 (t, *J* = 9.0 Hz, 1H), 3.85 (d, *J* = 10.8 Hz, 1H), 3.65 (dd, *J* = 3.6, 12.0 Hz, 1H), 3.53 (t, *J* = 9.6 Hz, 1H), 3.44 (ddd, *J* = 2.4, 4.2, 9.6 Hz, 1H), 2.30 (s, 3H, CH_3), 1.92 (brs, 1H, OH), 0.76 (s, 9H, $C(CH_3)_3$), −0.01 (s, 3H, CH_3), −0.18 (s, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.6, 138.4, 138.1, 133.3, 133.2, 130.4, 130.1, 129.9, 129.3, 128.6, 128.6, 127.9, 127.8, 87.1 (**C-1**), 79.8, 78.5, 76.8, 75.3, 73.5, 62.2, 25.9, 21.3, 18.0, −3.8, −4.1. HRMS (ESI^+): calc. for $C_{33}H_{42}O_6SSiNa^+$ $[M+Na]^+$: 617.2363, found: 617.2362.

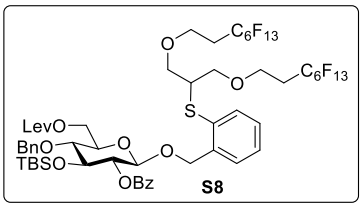
4-Methylphenyl 2-*O*-benzoyl-3-*O*-(*tert*-butyldimethylsilyl)-4-*O*-benzyl-6-*O*-levulinyl-1-thio-*β*-D-glucopyranoside (S7)



To a stirred solution of **S6** (500 mg, 0.84 mmol, 1.0 equiv), EDCI (322 mg, 1.68 mmol, 2.0 equiv) and DMAP (21 mg, 0.17 mmol, 0.2 equiv) in anhydrous CH_2Cl_2 (8.4 mL) was added levulinic acid (0.17 mL, 1.68 mmol, 2.0 equiv) at 0 ℃. The resulting mixture was warmed up to room temperature, stirred overnight and extracted with EtOAc. The organic phase was washed with saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, concentrated

in vacuo and purified by flash column chromatography on silica gel to give **S7** (410 mg, yield 70%) as colorless syrup, R_f = 0.26 (petroleum ether-EtOAc 5:1). $[\alpha]_D^{20}$ +21.1 (*c*, 1.00 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.03 (m, 2H, Ar-H), 7.57 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.44 (t, *J* =7.6 Hz, 2H, Ar-H), 7.34-7.26 (m, 7H, Ar-H), 7.04 (d, *J* = 8.0 Hz, 2H, Ar-H), 5.14 (t, *J* = 9.6 Hz, 1H), 4.84 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.66 (d, *J* = 10.0 Hz, 1H, **H-1**), 4.53 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.41 (dd, *J* = 2.0, 12.0 Hz, 1H, H-6a), 4.10 (dd, *J* = 5.2, 12.0 Hz, 1H, H-6b), 3.92 (t, *J* = 8.8 Hz, 1H), 3.58 (ddd, *J* =2.0, 5.2, 9.6 Hz, 1H, H-5), 3.48 (t, *J* = 9.6 Hz, 1H), 2.73 (t, *J* = 6.8 Hz, 2H), 2.59-2.56 (m, 2H), 2.29 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 0.76 (s, 9H, $C(CH_3)_3$), 0.02 (s, 6H, CH_3 ×2). ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.6, 172.5, 165.6, 138.2, 137.8, 133.3, 133.2, 130.5, 130.1, 129.7, 129.5, 128.6, 128.6, 128.0, 127.9, 87.1 (**C-1**), 78.7, 77.3, 77.0, 75.4, 73.2, 63.5, 38.1, 30.1, 28.1, 25.9, 21.3, 18.0, −3.8, −4.0. HRMS (ESI^+): calc. for $C_{38}H_{38}O_8SSiNa^+$ $[M+Na]^+$: 715.2731, found: 715.2721.

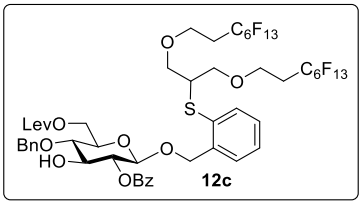
2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 2-*O*-benzoyl-3-*O*-(*tert*-butyldimethylsilyl)-4-*O*-benzyl-6-*O*-levulinyl-*β*-D-glucopyranoside (S8)



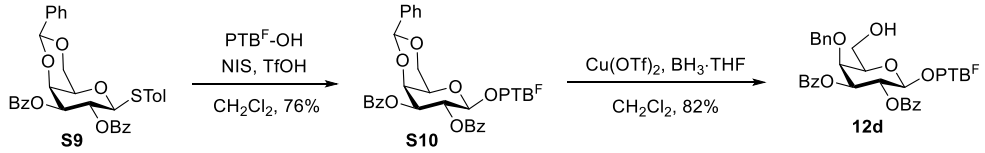
S8

A suspension of **S7** (358 mg, 0.52 mmol, 1.2 equiv), PTB^F-OH (395 mg, 0.44 mmol, 1.0 equiv) and 4Å MS (100 wt%) in anhydrous CH_2Cl_2 (2.9 mL) was stirred at 0 ℃ for 10 min. Then, *N*-iodosuccinimide (147 mg, 0.65mmol, 1.5 equiv) and TfOH (3.9 μL, 0.06 mmol, 0.1 equiv) were added at 0 ℃. The reaction mixture was stirred at 0 ℃ for 1 h and then quenched by addition of Et_3N (0.2 mL). The suspension was filtered through Celite and concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **S8** (579 mg, yield 90%) as colorless syrup, R_f = 0.25 (petroleum ether-EtOAc 5:1). $[\alpha]_D^{20}$ +4.1 (*c*, 1.00 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 1.6, 8.4 Hz, 2H, Ar-H), 7.54 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.40 (t, *J* = 7.6 Hz, 2H, Ar-H), 7.35-7.25 (m, 7H, Ar-H), 7.13 (dt, *J* = 1.6, 7.6 Hz, 1H, Ar-H), 6.99 (dt, *J* = 1.2, 7.6 Hz, 1H, Ar-H), 5.22 (dd, *J* = 8.0, 9.2 Hz, 1H, Ar-H), 4.93 (d, *J* = 12.8 Hz, 1H, $PhCH_2$), 4.86 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.78 (d, *J* = 13.2 Hz, 1H, $PhCH_2$), 4.55 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.52 (d, *J* = 8.0 Hz, 1H, **H-1**), 4.41 (d, *J* = 11.2 Hz, 1H), 4.16 (dd, *J* = 4.0, 12.0 Hz, 1H, H-6a), 3.93-3.89 (m, 1H), 3.63 (q, *J* = 6.8 Hz, 4H), 3.57-3.47 (m, 6H), 3.21-3.16 (m, *J* = 5.6 Hz, 1H, SCH), 2.75-2.70 (m, 2H), 2.60-2.57 (m, 2H), 2.39-2.26 (m, 4H, $C\underline{\mathbf{H_2}}C\underline{\mathbf{H_2}}C_6F_{13}$), 2.16 (s, 3H, CH_3), 0.77 (s, 9H, $C(CH_3)_3$), −0.01 (s, 3H, CH_3), −0.02 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.6, 172.6, 165.4, 139.2, 137.9, 133.2, 133.2, 132.4, 130.5, 130.2, 128.9, 128.6, 128.4, 128.3, 128.0, 127.9, 127.7, 100.1 (**C-1**), 78.9, 75.5, 75.3, 74.5, 73.3, 70.3, 70.2, 68.7, 63.2 (t, *J* = 4.0 Hz, $\underline{\mathbf{C}}H_2CH_2C_6F_{13}$), 48.2, 38.1, 31.4 (t, *J* = 21.0 Hz, $CH_2\underline{\mathbf{C}}H_2C_6F_{13}$), 30.0, 28.1, 25.9, 18.0, −3.9, −4.1. HRMS (ESI^+): calc. for $C_{57}H_{60}F_{26}O_{11}SSiNa^+$ $[M+Na]^+$: 1497.3103, found: 1497.3124.

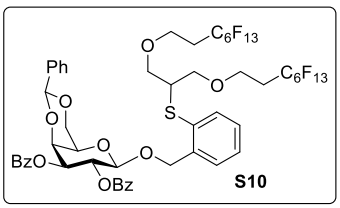
2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 2-*O*-benzoyl-4-*O*-benzyl-6-*O*-levulinyl-*β*-D-glucopyranoside (12c)



To a stirred solution of **S8** (320 mg, 0.22 mmol, 1.0 equiv) in MeCN (2.2 mL) was added $BF_3·Et_2O$ (30 μL, 0.24 mmol, 1.1 equiv) at 0 ℃, the resulting mixture was stirred for 0.5 h and extracted with EtOAc. The organic phase was washed with saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **12c** (259 mg, yield 88%) as colorless syrup, R_f = 0.30 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{20}$ −8.0 (*c*, 2.70 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 1.2, 8.4 Hz, 2H, Ar-H), 7.55 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.43-7.31 (m, 9H, Ar-H), 7.18 (dt, *J* = 1.6, 7.6 Hz, 1H, Ar-H), 7.09 (dt, *J* = 1.2, 7.6 Hz, 1H, Ar-H), 5.09 (dd, *J* = 8.0, 9.6 Hz, 1H), 4.98 (d, *J* = 12.8 Hz, 1H, $PhCH_2$), 4.86 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.83 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.70 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.63 (d, *J* = 7.6 Hz, 1H, **H-1**), 4.41 (dd, *J* = 2.0, 12.4 Hz, 1H, H-6a), 4.32 (dd, *J* = 4.4, 12.0 Hz, 1H, H-6b), 3.91-3.88 (dt, *J* = 4.0, 8.8 Hz, 1H), 3.66-3.58 (m, 6H), 3.55-3.49 (m, 4H), 3.25-3.20 (m, *J* = 6.0 Hz, 1H, SCH), 2.76-2.72 (m, 3H), 2.60 (t, *J* = 6.4 Hz, 2H), 2.37-2.24 (m, 4H, C**H**$_2$C**H**$_2$C$_6$F$_{13}$), 2.17 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.6, 172.7, 166.6, 138.9, 138.0, 133.6, 133.5, 132.4, 130.2, 129.8, 129.2, 128.8, 128.5, 128.5, 128.5, 128.4, 128.3, 127.7, 99.8 (**C-1**), 78.1, 76.5, 75.1, 75.1, 73.2, 70.3, 70.3, 69.0, 63.2 (t, *J* = 4.0 Hz, **C**H$_2$CH$_2$C$_6$F$_{13}$), 48.3, 38.1, 31.4 (t, *J* = 21.0 Hz, CH$_2$**C**H$_2$C$_6$F$_{13}$), 30.0, 28.1. HRMS (ESI$^+$): calc. for $C_{51}H_{46}F_{26}O_{11}SNa^+$ [M+Na]$^+$: 1383.2238, found: 1383.2233.



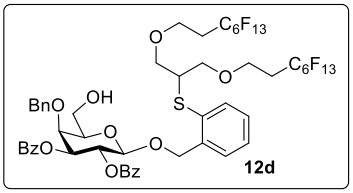
2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-*β*-D-galactopyranoside (S10)



A suspension of **S9**[11] (110 mg, 0.19 mmol, 1.2 equiv), PTB^F-OH (143 mg, 0.16 mmol, 1.0 equiv) and 4Å MS (100 wt%) in anhydrous CH_2Cl_2 (1.9 mL) was stirred at 0 ℃ for 10 min. Then, *N*-iodosuccinimide (54.4 mg, 0.24 mmol, 1.5 equiv) and TfOH (2.3 μL, 0.03 mmol, 0.2 equiv) were added at 0 ℃. The reaction mixture was stirred at 0 ℃ for 2 h and then quenched by addition of Et_3N (0.2 mL). The suspension was filtered through Celite and concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **S10** (197 mg, yield 76%) as white foam, R_f = 0.50 (petroleum ether-EtOAc 4:1). $[\alpha]_D^{20}$ +45.3 (*c*, 2.97 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.92 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.52-7.45 (m, 4H, Ar-H), 7.39-7.32 (m, 9H, Ar-H), 7.16 (dt, *J* = 0.8, 7.6 Hz, 1H, Ar-H), 7.05 (t, *J* = 7.6 Hz, 1H, Ar-H), 5.92 (dd, *J* = 8.0, 10.0 Hz, 1H, H-2), 5.55 (s, 1H, PhCH), 5.33 (dd, *J* = 3.6, 10.4 Hz, 1H, H-3), 5.11 (d, *J* = 12.8 Hz, 1H, $PhCH_2$), 4.89 (d, *J* = 13.2 Hz, 1H, $PhCH_2$), 4.81 (d, *J* = 8.0 Hz, 1H, **H-1**), 4.58 (d, *J* = 3.6 Hz, 1H, H-4), 4.43

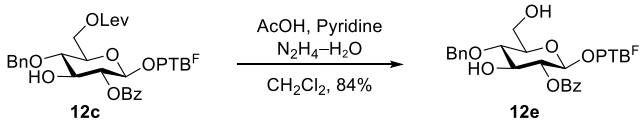
(d, *J* = 12.8 Hz, 1H, H-6a), 4.14 (dd, *J* = 1.2, 12.4 Hz, 1H, H-6b), 3.67-3.62 (m, 5H), 3.58-3.50 (m, 4H), 3.25-3.20 (m, *J* = 5.6 Hz, 1H, SCH), 2.38-2.23 (m, 4H, C**H**$_2$C**H**$_2$C$_6$F$_{13}$). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.4, 165.4, 139.3, 137.7, 133.6, 133.3, 133.2, 132.8, 130.2, 130.0, 130.0, 129.3, 129.2, 129.1, 128.6, 128.5, 128.4, 128.3, 127.9, 126.5, 101.1, 100.4 (**C-1**), 73.8, 73.0, 70.3, 70.2, 69.4, 69.1, 68.8, 66.8, 63.2 (brs, **C**H$_2$CH$_2$C$_6$F$_{13}$), 48.4, 31.4 (t, *J* = 21.0 Hz, CH$_2$**C**H$_2$C$_6$F$_{13}$). HRMS (ESI$^+$): calc. for $C_{53}H_{42}F_{26}O_{10}SNa^+$ $[M+Na]^+$: 1387.1976, found: 1387.1976.

2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 2,3-di-*O*-benzoyl-4-*O*-benzyl-*β*-D-galactopyranoside (12d)

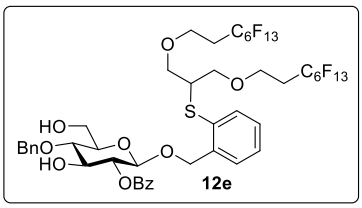


12d

A suspension of **S10** (267 mg, 0.20 mmol, 1.0 equiv) and 4Å MS (100 wt%) in anhydrous CH_2Cl_2 (1.9 mL) was stirred at 0 ℃ for 10 min under argon. Then, BH_3·THF (1.0 mL, 1 M in THF, 1.0 mmol, 5.0 equiv) and $Cu(OTf)_2$ (10.7 mg, 0.03 mmol, 0.15 equiv) were added at 0 ℃. The mixture was warmed up to room temperature, stirred for 2 h and quenched by addition of Et_3N (0.3 mL). The suspension was filtered through Celite and concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **12d** (219 mg, yield 82%) as colorless syrup, R_f = 0.50 (petroleum ether-EtOAc 4:1). $[\alpha]_D^{20}$ +19.2 (*c*, 2.50 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 1.6, 8.4 Hz, 2H, Ar-H), 7.90 (dd, *J* = 1.2, 8.4 Hz, 2H, Ar-H), 7.52-7.46 (m, 2H, Ar-H), 7.39-7.31 (m, 6H, Ar-H), 7.26-7.21 (m, 5H, Ar-H), 7.17 (dt, *J* = 1.2, 7.6 Hz, 1H, Ar-H), 7.06 (dt, *J* = 1.2, 7.6 Hz, 1H, Ar-H), 5.89 (dd, *J* = 8.0, 10.4 Hz, 1H), 5.29 (dd, *J* = 3.2, 4.4 Hz, 1H, Ar-H), 5.00 (d, *J* = 12.8 Hz, 1H, PhCH$_2$), 4.92 (d, *J* = 12.8 Hz, 1H, PhCH$_2$), 4.77 (d, *J* = 11.6 Hz, 1H, PhCH$_2$), 4.72 (d, *J* = 8.0 Hz, 1H, **H-1**), 4.47 (d, *J* = 12.0 Hz, 1H, PhCH$_2$), 4.12 (d, *J* = 2.8 Hz, 1H), 3.88 (dd, *J* = 7.2, 11.2 Hz, 1H), 3.70 (t, *J* = 6.0 Hz, 1H), 3.67-3.67 (dt, *J* = 1.6, 6.4 Hz, 1H), 3.57-3.49 (m, 4H), 3.26-3.20 (m, *J* = 6.4 Hz, 1H, SCH), 2.39-2.26 (m, 4H, C**H**$_2$C**H**$_2$C$_6$F$_{13}$), 1.73 (d, *J* = 3.6 Hz, 1H, OH). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.2, 165.5, 139.0, 137.5, 133.7, 133.5, 133.2, 132.6, 130.1, 130.0, 129.9, 129.3, 129.2, 128.8, 128.7, 128.7, 128.5, 128.4, 127.8, 100.4 (**C-1**), 75.4, 75.0, 75.0, 73.5, 70.3, 70.3, 68.7, 63.2 (brs, **C**H$_2$CH$_2$C$_6$F$_{13}$), 62.0, 48.4, 31.4 (t, *J* = 21.0 Hz, CH$_2$**C**H$_2$C$_6$F$_{13}$). HRMS (ESI$^+$): calc. for $C_{53}H_{44}F_{26}O_{10}SNa^+$ $[M+Na]^+$: 1389.2132, found: 1389.2150.

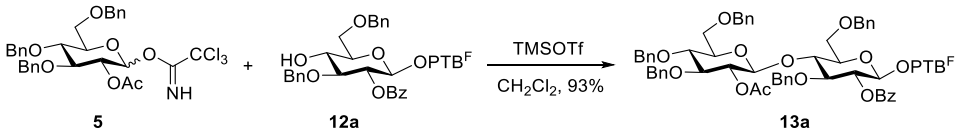


2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 2-*O*-benzoyl-4-*O*-benzyl-*β*-D-glucopyranoside (12e)

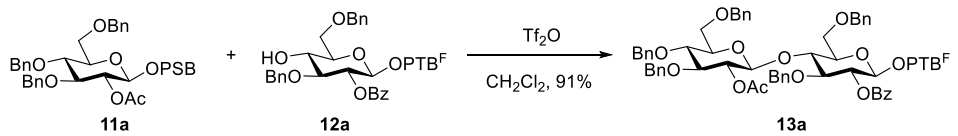


To a stirred solution of **12c** (230 mg, 0.17 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (1.7 mL) was successively added AcOH (0.29 mL, 5.07 mmol, 30.0 equiv), pyridine (0.41 mL, 5.07 mmol, 30.0 equiv) and N_2H_4-H_2O (16.4 μL, 0.34 mmol, 2.0 equiv) at 0 ℃. The resulting mixture was warmed up to room temperature and stirred for 30 min. The mixture was extracted with EtOAc, the organic phase was washed with 1 M HCl, saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **12e** (180 mg, yield 84%) as colorless syrup, R_f = 0.25 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{20}$ −7.0 (*c*, 0.43 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.56 (t, *J* = 7.2 Hz, 1H, Ar-H), 7.44-7.28 (m, 9H, Ar-H), 7.19 (dt, *J* = 0.8, 7.2 Hz, 1H, Ar-H), 7.09 (dt, *J* = 0.8, 7.2 Hz, 1H, Ar-H), 5.08 (dd, *J* = 8.0, 9.2 Hz, 1H, H-2), 4.98 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.85 (d, *J* = 12.8 Hz, 1H, $PhCH_2$), 4.84 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.74 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.67 (d, *J* = 8.0 Hz, 1H, **H-1**), 3.93-3.88 (m, 2H), 3.75 (ddd, *J* = 4.4, 7.2, 12.0 Hz, 1H), 3.68-3.61 (m, 5H), 3.57-3.50 (m, 4H), 3.43 (ddd, *J* = 2.8, 4.4, 9.6 Hz, 1H, H-5), 3.30-3.24 (m, *J* = 5.6 Hz, 1H, SCH), 2.60 (d, *J* = 4.0 Hz, 1H, OH), 2.40-2.26 (m, 4H, $C\underline{\mathbf{H}_2}C\underline{\mathbf{H}_2}C_6F_{13}$), 2.04 (t, *J* = 6.4 Hz, 1H, OH). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5, 139.0, 138.1, 133.6, 133.5, 132.6, 130.2, 129.8, 129.3, 128.8, 128.6, 128.6, 128.4, 128.3, 127.8, 100.0 (**C-1**), 78.1, 76.2, 75.5, 75.1, 75.1, 70.3, 70.3, 69.2, 63.2 (t, *J* = 4.0 Hz, $\underline{\mathbf{C}}H_2CH_2C_6F_{13}$), 62.1, 48.3, 31.4 (t, *J* = 21.0 Hz, $CH_2\underline{\mathbf{C}}H_2C_6F_{13}$). HRMS ($ESI^+$): calc. for $C_{46}H_{40}F_{26}O_9SNa^+$ $[M+Na]^+$: 1285.1870, found:1285.1884.

10. Orthogonal glycosylations of fluorous-tagged acceptors (Table 1)

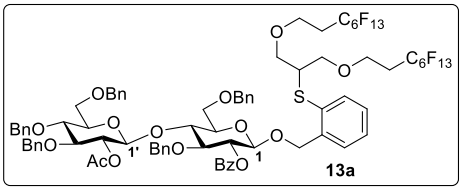


A solution of glycosyl donor **5** (19.8 mg, 0.031 mmol, 1.5 equiv), fluorous acceptor **12a** (35 mg, 0.026 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (0.52 mL) in the presence of 4Å MS (100 wt%) was stirred at 0 ℃ for 10 min. After addition of TMSOTf (1.4 μL, 0.008 mmol, 0.3 equiv), the solution was stirred at 0 ℃ for 2 h and quenched by addition of Et_3N (0.2 mL). The mixture was filtered through Celite and concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **13a** (44.1 mg, yield 93%) as colorless syrup.

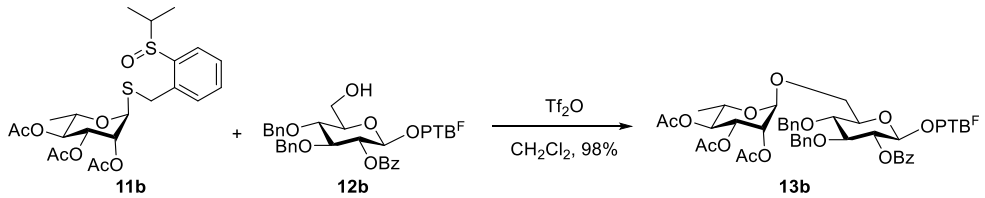


A solution of glycosyl donor **11a** (17.9 mg, 0.027 mmol, 1.2 equiv), fluorous acceptor **12a** (30 mg, 0.022 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (0.44 mL) in the presence of 4Å MS (100 wt%) was stirred at 0 ℃ for 10 min. After addition of Tf_2O (4.5 μL, 0.027 mmol, 1.2 equiv), the solution was stirred at 0 ℃ for 30 min and quenched by addition of saturated aqueous $NaHCO_3$ (0.2 mL). The mixture was filtered through Celite and concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **13a** (36.9 mg, yield 91%) as colorless syrup.

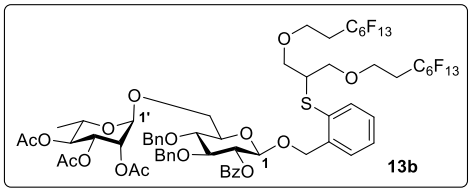
2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 4-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranosyl)-2-*O*-benzoyl-3,6-di-*O*-benzyl-*β*-D-glucopyranoside (13a)



Colorless syrup. R_f = 0.50 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{20}$ +10.7 (*c*, 2.99 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.53 (t, *J* = 7.2 Hz, 1H, Ar-H), 7.39-7.25 (m, 18H, Ar-H), 7.23-7.08 (m, 9H, Ar-H), 7.03-6.93 (m, 4H, Ar-H), 5.31 (dd, *J* = 8.0, 9.2 Hz, 1H), 4.98 (dd, *J* = 8.0, 9.2 Hz, 1H), 4.98 (d, *J* = 13.2 Hz, 1H, $PhCH_2$), 4.89 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.80-4.70 (m, 4H, $PhCH_2$), 4.64 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.61 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.56 (d, *J* = 7.6 Hz, 1H, **H-1**), 4.54 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.53 (d, *J* = 7.6 Hz, 1H, **H-1'**), 4.51 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.39 (t, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.10 (t, 1H, *J* = 9.2 Hz), 3.76-3.57 (m, 10H), 3.55-3.47 (m, 5H), 3.42 (dt, *J* = 2.4, 9.6 Hz, 1H), 3.32-3.29 (m, 1H), 3.22-3.16 (m, *J* = 6.0 Hz, 1H, SCH), 2.36-2.23 (m, 4H, C**H**$_2$C**H**$_2$C$_6$F$_{13}$), 1.89 (s, 3H, OAc). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 165.3, 139.3, 138.7, 138.5, 138.4, 138.2, 138.2, 133.0, 133.0, 132.4, 130.4, 130.1, 128.8, 128.7, 128.6, 128.6, 128.5, 128.4, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 127.3, 100.5 (**C-1**), 100.4 (**C-1'**), 83.2, 80.4, 78.2, 75.6, 75.4, 75.3, 75.1, 74.5, 73.9, 73.9, 73.6, 73.3, 70.3, 70.2, 68.8, 68.7, 68.0, 63.1 (t, *J* = 4.0 Hz, **C**H$_2$CH$_2$C$_6$F$_{13}$), 48.2, 31.5 (t, *J* = 21.0 Hz, CH$_2$**C**H$_2$C$_6$F$_{13}$), 21.1. HRMS (ESI$^+$): calc. for $C_{82}H_{76}F_{26}O_{15}SNa^+$ $[M+Na]^+$: 1849.4382, found: 1849.4357.

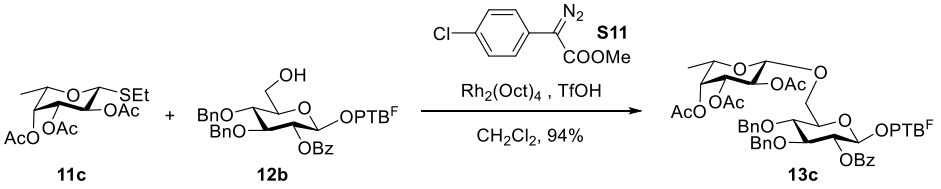


2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 6-*O*-(2,3,4-tri-*O*-acetyl-*α*-L-rhamnopyranosyl)-2-*O*-benzoyl-3,4-di-*O*-benzyl-*β*-D-glucopyranoside (13b)

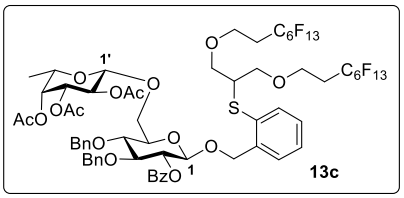


A solution of glycosyl donor **11b** (21.6 mg, 0.044 mmol, 1.2 equiv), fluorous acceptor **12b** (50 mg, 0.037 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (0.74 mL) in the presence of 4Å MS

(100 wt%) was stirred at 0 ℃ for 10 min, then Tf_2O (7.5 μL, 0.044 mmol, 1.2 equiv) was added. The reaction mixture was stirred at 0 ℃ for 30 min and quenched by addition of Et_3N (0.2 mL). The mixture was filtered through Celite and concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **13b** (58.9 mg, yield 98%) as yellow syrup, R_f = 0.50 (petroleum ether-EtOAc 4:1). $[\alpha]_D^{20}$ −6.7 (*c*, 1.40 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.54 (t, *J* = 7.2 Hz, 1H, Ar-H), 7.40 (t, *J* = 7.2 Hz, 2H, Ar-H), 7.33-7.27 (m, 6H, Ar-H), 7.17-7.03 (m, 8H, Ar-H), 5.33-5.26 (m, 3H, **H-1'**), 5.05 (t, *J* = 10.0 Hz, 1H), 4.93 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.89 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.77 (d, *J* = 14.4 Hz, 2H, $PhCH_2$), 4.71 (d, *J* = 10.8 Hz, 1H), 4.63 (d, *J* = 11.2 Hz, 2H, $PhCH_2$), 4.56 (d, *J* = 8.0 Hz, 1H, **H-1**), 4.00-3.91 (m, 2H), 3.79 (t, *J* = 8.8 Hz, 1H), 3.72-3.65 (m, 2H), 3.61 (q, *J* = 6.8 Hz, 4H), 3.54-3.44 (m, 5H), 3.22-3.16 (m, *J* = 6.0 Hz, 1H, SCH), 2.36-2.25 (m, 4H, C**H**$_2$C**H**$_2$$C_6F_{13}$), 2.11 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.96 (s, 3H, OAc), 1.16 (d, *J* = 6.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 170.2, 170.1, 165.3, 138.8, 138.1, 137.8, 133.8, 133.2, 132.1, 130.3, 130.1, 129.3, 128.7, 128.5, 128.2, 128.2, 128.1, 127.9, 127.5, 100.0 (**C-1**), 97.9 (**C-1'**), 83.1, 78.1, 75.4, 75.3, 74.9, 73.9, 71.1, 70.3, 70.2, 69.9, 69.4, 68.9, 66.8, 66.7, 63.1 (t, *J* = 4.0 Hz, **C**$H_2CH_2C_6F_{13}$), 48.1, 31.4 (t, *J* = 21.0 Hz, CH_2**C**$H_2C_6F_{13}$), 21.1, 20.9, 17.5. HRMS (ESI^+): calc. for $C_{65}H_{62}F_{26}O_{16}SNa^+$ $[M+Na]^+$: 1647.3236, found: 1647.3240.

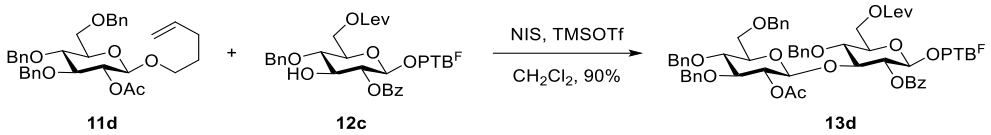


2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 6-*O*-(2,3,4-tri-*O*-acetyl-6-deoxy-*β*-L-galactopyranosyl)-2-*O*-benzoyl-3,4-di-*O*-benzyl-*β*-D-glucopyranoside (13c)

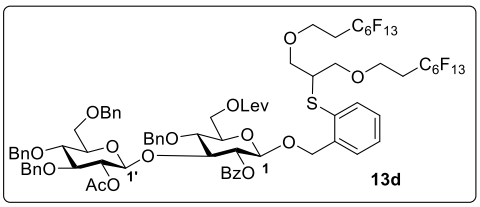


To a stirred mixture of donor **11c** (11.1 mg, 0.033 mmol, 1.5 equiv), fluorous acceptor **12b** (30 mg, 0.022 mmol, 1.0 equiv), diazo compound **S11** (8.4 mg, 0.040 mmol, 1.8 equiv) in anhydrous CH_2Cl_2 (0.74 mL) in the presence of 4Å MS (100 wt%) was added $Rh_2(oct)_4$ (17.2 μL, 5 mg/mL in CH_2Cl_2, 0.5 mol%). The resulting mixture was stirred at 0 ℃ for 30 min until the yellow color disappeared. Then, TfOH (0.4 μL, 0.004 mmol, 0.2 equiv) was added and the resulting mixture was stirred at 0 ℃ for 1 h, quenched by addition of saturated aqueous $NaHCO_3$ (0.2 mL). The mixture was filtered through Celite and concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **13c** (33.5 mg, yield 94%) as colorless syrup, R_f = 0.30 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{20}$ +7.9 (*c*, 2.10 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.54 (t, *J* = 7.2 Hz, 1H, Ar-H), 7.40 (t, *J* = 7.6 Hz, 2H, Ar-H), 7.34 (dd, *J* = 0.8, 8.0 Hz, 2H, Ar-H), 7.30-7.26 (m, 5H, Ar-H), 7.17 (dt, *J* = 1.2, 7.2 Hz, 1H, Ar-H), 7.11-7.06 (m, 6H, Ar-H), 5.28-5.21 (m, 3H), 5.00 (dd,

J = 3.2, 10.4 Hz, 1H), 4.93 (d, *J* = 13.2 Hz, 1H, $PhCH_2$), 4.80 (d, *J* = 13.2 Hz, 1H, $PhCH_2$), 4.79 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.72 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.70 (d, *J* = 10.4 Hz, 1H, $PhCH_2$), 4.63 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.61 (d, *J* = 8.0 Hz, 1H, **H-1**), 4.55 (d, *J* = 8.0 Hz, 1H, **H-1′**), 4.17 (dd, *J* = 2.8, 12.4 Hz, 1H, H-6a), 3.87 (dd, *J* = 0.8, 12.0 Hz, 1H, H-6b), 3.78-3.70 (m, 3H), 3.67-3.61 (m, 4H), 3.53-3.51 (m, 4H), 3.43 (d, *J* = 8.0 Hz, 1H), 3.26-3.20 (m, *J* = 6.0 Hz, 1H, SCH), 2.37-2.26 (m, 4H, $C\underline{\mathbf{H}_2}C\underline{\mathbf{H}_2}C_6F_{13}$), 2.16 (s, 3H, OAc), 2.14 (s, 3H, OAc), 1.98 (s, 3H, OAc), 1.20 (d, *J* = 6.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 170.4, 170.1, 165.4, 139.2, 138.3, 138.1, 133.2, 133.1, 131.9, 130.2, 130.0, 128.8, 128.6, 128.5, 128.4, 128.4, 128.3, 128.1, 128.0, 127.8, 127.6, 101.7 (**C-1**), 100.6 (**C-1′**), 82.4, 75.4, 75.3, 75.1, 73.8, 71.6, 70.5, 70.3, 70.2, 69.4, 69.2, 68.9, 67.1, 63.2 (brs, $\underline{\mathbf{C}}H_2CH_2C_6F_{13}$), 48.1, 31.4 (t, *J* = 21.0 Hz, $CH_2\underline{\mathbf{C}}H_2C_6F_{13}$), 21.3, 20.9, 20.8, 16.3. HRMS (ESI$^+$): calc. for $C_{65}H_{62}F_{26}O_{16}SNa^+$ $[M+Na]^+$: 1647.3236, found: 1647.3230.

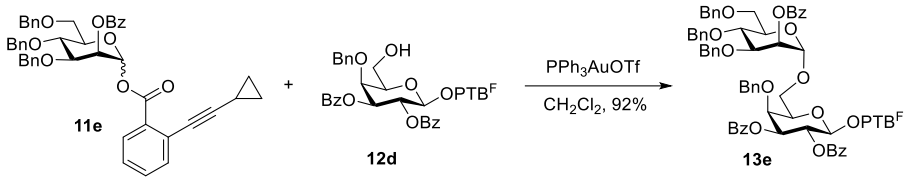


2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 3-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranosyl)-2-*O*-benzoyl-4-*O*-benzyl-6-*O*-levulinyl-*β*-D-glucopyranoside (13d)

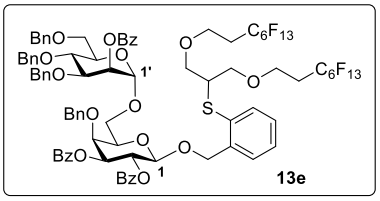


A stirred mixture of donor **11d** (30.9 mg, 0.055 mmol, 2.5 equiv), fluorous acceptor **12c** (30 mg, 0.022 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (0.44 mL) in the presence of 4Å MS (100 wt%) was stirred at 0 ℃ for 10 min, then *N*-iodosuccinimide (14.9 mg, 0.066 mmol, 3.0 equiv) and TMSOTf (2.4 μL, 0.013 mmol, 0.6 equiv) was added. After stirring at 0 ℃ for 1 h, the reaction mixture was quenched by addition of Et_3N (0.2 mL). The mixture was filtered through Celite and concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **13d** (36.4 mg, yield 90%) as colorless syrup, R_f = 0.41 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{20}$ +4.1 (*c*, 2.2 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.96 (m, 2H, Ar-H), 7.60 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.46 (t, *J* = 7.6 Hz, 2H, Ar-H), 7.33 (dd, *J* = 1.2, 7.6 Hz, 3H, Ar-H), 7.28-7.22 (m, 15H, Ar-H), 7.14 (dt, *J* = 1.2, 7.6 Hz, 1H, Ar-H), 7.11-7.09 (m, 4H, Ar-H), 7.03 (dt, *J* = 0.8, 7.6 Hz, 1H, Ar-H), 5.24 (dd, *J* = 8.0, 9.6 Hz, 1H), 5.03 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.95 (t, *J* = 8.0 Hz, 1H), 4.93 (d, *J* = 12.8 Hz, 1H, $PhCH_2$), 4.75 (d, *J* = 12.8 Hz, 1H, $PhCH_2$), 4.68 (d, *J* = 10.4 Hz, 1H, $PhCH_2$), 4.59 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.58 (d, *J* = 8.0 Hz, 1H, **H-1'**), 4.54 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.46 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.45 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.44 (d, *J* = 8.0 Hz, 1H, **H-1**), 4.43 (d, *J* = 10.4 Hz, 1H), 4.39-4.35 (m, 2H), 4.23 (dd, *J* = 4.4, 11.6 Hz, 1H), 4.12 (t, *J* = 9.2 Hz, 1H), 3.74 (dd, *J* = 1.2, 10.8 Hz, 1H), 3.65-3.48 (m, 12H), 3.38 (ddd, *J* = 1.2, 5.2, 10.0 Hz, 1H), 3.25-3.17 (m, 2H), 2.70 (t, *J* = 6.8 Hz, 1H), 2.62-2.47 (m, 2H), 2.38-2.24 (m, 4H, $C\underline{\mathbf{H}_2}C\underline{\mathbf{H}_2}C_6F_{13}$), 2.16 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5,

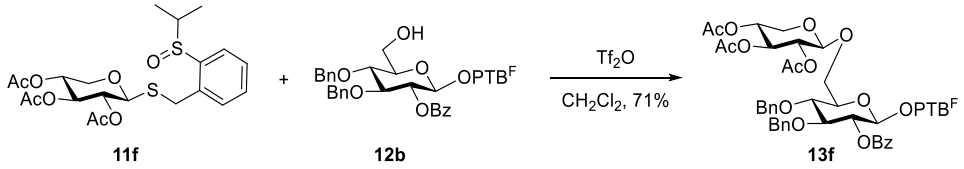
172.7, 170.3, 164.9, 138.8, 138.4, 138.3, 138.1, 137.8, 133.4, 133.4, 132.1, 130.2, 129.8, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.2, 127.9, 127.7, 127.7, 127.6, 101.1 (**C-1′**), 99.6 (**C-1**), 83.2, 80.7, 78.2, 75.7, 75.4, 75.3, 75.2, 75.0, 74.1, 73.7, 73.3, 72.9, 70.3, 70.2, 69.4, 68.8, 63.2 (t, *J* = 4.0 Hz, $\underline{\mathbf{C}}H_2CH_2C_6F_{13}$), 48.1, 38.1, 31.4 (t, *J* = 21.0 Hz, $CH_2\underline{\mathbf{C}}H_2C_6F_{13}$), 30.0, 28.1, 20.8. HRMS (ESI$^+$): calc. for $C_{80}H_{76}F_{26}O_{17}SNa^+$ $[M+Na]^+$: 1857.4280, found: 1857.4281.



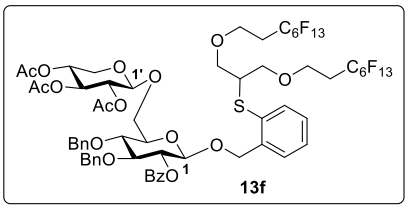
2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 6-*O*-(2-*O*-benzoyl-3,4,5-tri-*O*-benzyl-*α*-D-mannopyranosyl)-2,3-di-*O*-benzoyl-4-*O*-benzyl-*β*-D-galactopyranoside (13e)



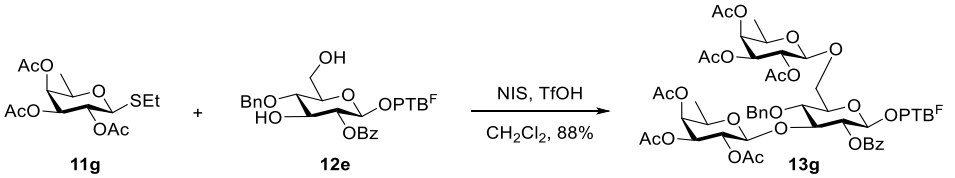
To a stirred mixture of donor **11e** (23.7 mg, 0.033 mmol, 1.2 equiv), fluorous acceptor **12d** (37.0 mg, 0.027 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (0.55 mL) in the presence of 4Å MS (100 wt%) was added freashly prepared PPh_3AuOTf (0.27 mL, 0.02 M in CH_2Cl_2, 0.006 mmol, 0.2 equiv) at room temperature. After stirring for 4 h, the mixture was filtered through Celite and concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **13e** (48.1 mg, yield 92%) as colorless syrup, R_f = 0.49 (petroleum ether-EtOAc 5:1). $[\alpha]_D^{20}$ −0.9 (*c*, 2.3 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.98 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.90 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.57-7.45 (m, 5H, Ar-H), 7.39-7.25 (m, 18H, Ar-H), 7.23-7.11 (m, 9H, Ar-H), 7.03 (t, *J* = 7.6 Hz, 1H, Ar-H), 5.89 (dd, *J* = 8.0, 10.0 Hz, 1H), 5.47 (brs, 1H), 5.34 (dd, *J* = 2.8, 10.4 Hz, 1H), 5.01 (d, *J* = 13.2 Hz, 1H, $PhCH_2$), 4.86 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.80 (d, *J* = 11.2 Hz, 2H, $PhCH_2$), 4.79 (d, *J* = 12.8 Hz, 1H, $PhCH_2$), 4.73 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.72 (d, *J* = 2.4 Hz, 1H, **H-1′**), 4.72 (d, *J* = 7.2 Hz, 1H, **H-1**), 4.59 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.53 (d, *J* = 11.2 Hz, 2H, $PhCH_2$), 4.47 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.14 (d, *J* = 2.4 Hz, 1H), 4.09 (t, *J* = 9.2 Hz, 1H), 4.04 (dd, *J* = 2.8, 9.2 Hz, 1H), 3.91-3.80 (m, 5H), 3.49-3.42 (m, 4H), 3.21-3.16 (m, *J* = 6.0 Hz, 1H, SCH), 2.34-2.22 (m, 4H, $C\underline{\mathbf{H}_2}C\underline{\mathbf{H}_2}C_6F_{13}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.8, 165.5, 138.8, 138.6, 138.1, 137.6, 134.4, 134.3, 133.8, 133.7, 133.4, 133.1, 132.2, 132.2, 132.2, 130.2, 130.1, 130.0, 130.0, 130.0, 129.5, 129.4, 129.3, 128.7, 128.6, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.8, 127.7, 127.5, 100.6 (**C-1**), 98.3 (**C-1′**), 78.2, 75.5, 75.3, 75.0, 74.3, 73.7, 73.6, 73.1, 72.2, 72.0, 70.3, 70.2, 69.2, 69.2, 69.1, 65.7, 63.1 (brs, $\underline{\mathbf{C}}H_2CH_2C_6F_{13}$), 48.1, 31.4 (t, *J* = 21.0 Hz, $CH_2\underline{\mathbf{C}}H_2C_6F_{13}$). HRMS (ESI$^+$): calc. for $C_{87}H_{76}F_{26}O_{16}SNa^+$ $[M+Na]^+$: 1925.4331, found: 1925.4333.



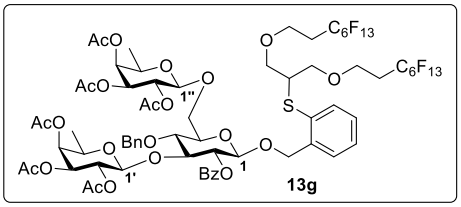
2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 6-*O*-(2,3,4-tri-*O*-acetyl-*β*-D-xylopyranosyl)-2-*O*-benzoyl-3,4-di-*O*-benzyl-*β*-D-glucopyranoside (13f)



A solution of glycosyl donor **11f**[5] (41.9 mg, 0.089 mmol, 1.2 equiv), fluorous acceptor **12b** (100 mg, 0.074 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (0.74 mL) in the presence of 4Å MS (100 wt%) was stirred at 0 ℃ for 10 min, then Tf_2O (14.9 μL, 0.089 mmol, 1.2 equiv) was added. The reaction mixture was stirred at 0 ℃ for 30 min and quenched by addition of Et_3N (0.2 mL). The mixture was filtered through Celite and concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **13f** (84.6 mg, yield 71%) as colorless syrup, R_f = 0.53 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{20}$ −12.3 (*c*, 0.75 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.54 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.39 (t, *J* = 7.6 Hz, 2H, Ar-H),7.35-7.24 (m, 8H, Ar-H), 7.15 (dt, *J* = 1.2, 7.6 Hz, 1H, Ar-H), 7.10-7.08 (m, 4H, Ar-H), 7.05 (dt, *J* = 0.8, 7.6 Hz, 1H, Ar-H), 5.27 (dd, *J* = 8.0, 9.2 Hz, 1H), 5.10 (t, *J* = 8.0 Hz, 1H), 4.97-4.88 (m, 3H), 4.83 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.77 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.69 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.62 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.59 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.56 (d, *J* = 8.0 Hz, 1H, **H-1**), 4.55 (d, *J* = 6.0 Hz, 1H, **H-1′**), 4.14 (dd, *J* = 4.4, 11.6 Hz, 1H), 4.04 (dd, *J* = 1.2, 10.4 Hz, 1H), 3.78 (t, *J* = 8.8 Hz, 1H), 3.73-3.60 (m, 6H), 3.56-3.45 (m, 5H), 3.33 (dd, *J* = 8.0, 12.0 Hz, 1H), 3.24-3.18 (m, *J* = 5.6 Hz, 1H, SCH), 2.38-2.24 (m, 4H, C**H**$_2$C**H**$_2$C$_6$F$_{13}$), 2.04 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.99 (s, 3H, OAc). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.2, 170.0, 169.5, 165.3, 138.9, 138.0, 137.9, 133.6, 133.2, 132.1, 130.2, 130.0, 129.1, 128.7, 128.5, 128.5, 128.4, 128.2, 128.1, 127.9, 127.5, 100.4 (**C-1**), 100.1 (**C-1′**), 82.9, 78.0, 75.3, 75.1, 74.9, 73.9, 71.2, 70.6, 70.3, 70.2, 68.9, 68.9, 67.7, 63.1 (t, *J* = 4.0 Hz, **C**H$_2$CH$_2$C$_6$F$_{13}$), 61.8, 48.1, 31.4 (t, *J* = 21.0 Hz, CH$_2$**C**H$_2$C$_6$F$_{13}$), 20.9, 20.9. HRMS (ESI$^+$): calc. for $C_{64}H_{60}F_{26}O_{16}SNa^+$ $[M+Na]^+$: 1633.3079, found: 1633.3066.

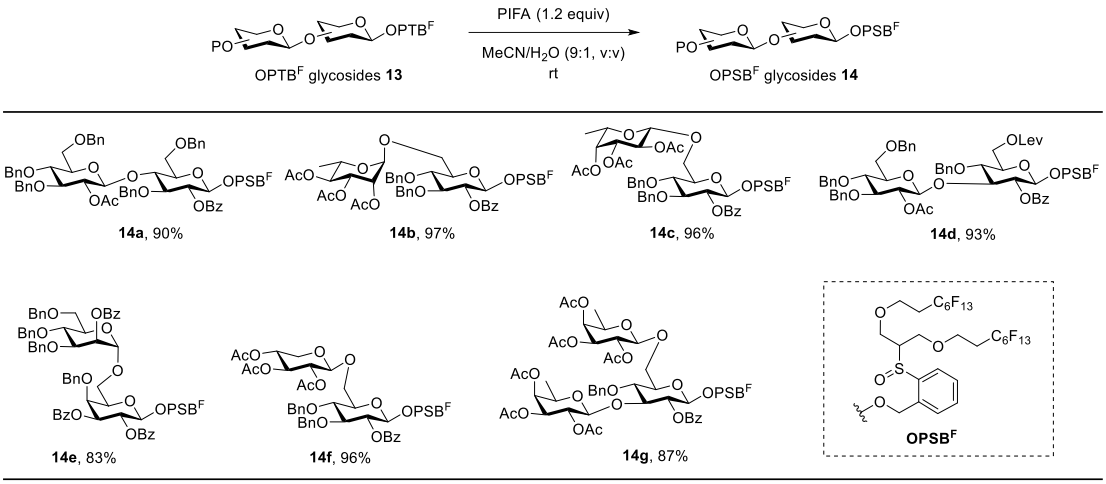


2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 3,6-di-*O*-(2,3,4-tri-*O*-acetyl-6-deoxy-*β*-D-galactopyranosyl)-2-*O*-benzoyl-4-*O*-benzyl-*β*-D-glucopyranoside (13g)



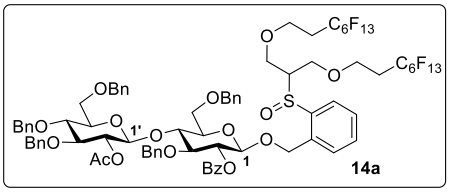
A suspension of **11g**[12] (23.8 mg, 0.071 mmol, 3.0 equiv), fluorous acceptor **12e** (30 mg, 0.024 mmol, 1.0 equiv) and 4Å MS (100 wt%) in anhydrous CH_2Cl_2 (0.48 mL) was stirred at 0 ℃ for 10 min. Then, *N*-iodosuccinimide (21.4 mg, 0.095 mmol, 4.0 equiv) and TfOH (0.63 μL, 0.007 mmol, 0.3 equiv) were added at 0 ℃. The reaction mixture was stirred at 0 ℃ for 1 h and then quenched by addition of Et_3N (0.2 mL). The mixture was filtered through Celite and concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **13g** (37.9 mg, yield 88%) as colorless syrup, R_f = 0.39 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{20}$ −5.0 (*c*, 2.52 in $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.59 (t, *J* = 7.2 Hz, 1H, Ar-H), 7.45 (t, *J* = 7.8 Hz, 2H, Ar-H), 7.39 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.33-7.26 (m, 5H, Ar-H), 7.14 (dt, *J* = 1.2, 7.8 Hz, 1H, Ar-H), 7.04 (t, *J* = 7.8 Hz, 1H, Ar-H), 5.25 (dd, *J* = 8.4, 9.0 Hz, 1H), 5.22 (dd, *J* = 7.8, 10.8 Hz, 1H), 5.19 (d, *J* = 3.6 Hz, 1H), 5.12 (d, *J* = 8.4 Hz, 1H), 5.11 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 5.09 (dd, *J* = 2.4, 10.2 Hz, 1H), 4.95 (d, *J* = 12.6 Hz, 1H, $PhCH_2$), 4.93 (dd, *J* = 3.6, 10.8 Hz, 1H), 4.74 (d, *J* = 12.6 Hz, 1H, $PhCH_2$), 4.61 (d, *J* = 8.4 Hz, 1H, **H-1′′**), 4.59 (dd, *J* = 2.4, 11.4 Hz, 1H), 4.51 (d, *J* = 10.2 Hz, 1H, $PhCH_2$), 4.50 (d, *J* = 7.8 Hz, 1H, **H-1**), 4.48 (d, *J* = 7.8 Hz, 1H, **H-1′**), 4.18-4.14 (m, 2H), 3.76 (dd, *J* = 4.8, 10.8 Hz, 1H), 3.68 (q, *J* = 6.6 Hz, 1H), 3.64-3.56 (m, 7H), 3.50-3.44 (m, 4H), 3.22-3.18 (m, *J* = 6.0 Hz, 1H, SCH), 2.36-2.25 (m, 4H, $C\underline{\mathbf{H}}_2C\underline{\mathbf{H}}_2C_6F_{13}$), 2.14 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.97 (s, 3H, OAc), 1.95 (s, 3H, OAc), 1.86 (s, 3H, OAc), 1.19 (d, *J* = 6.6 Hz, 3H, CH_3), 1.09 (d, *J* = 6.6 Hz, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.9, 170.8, 170.4, 170.4, 170.2, 169.6, 165.0, 138.8, 138.5, 133.6, 133.5, 132.0, 130.1, 129.8, 129.0, 128.8, 128.5, 128.4, 128.4, 128.0, 127.4, 101.5 (**C-1′**), 100.8 (**C-1′′**), 99.7 (**C-1**), 80.0, 76.0, 75.2, 75.0, 74.0, 71.7, 71.6, 70.5, 70.3, 70.3, 70.2, 69.4, 69.3, 69.1, 68.9, 68.4, 63.1 (t, *J* = 4.0 Hz, $\underline{\mathbf{C}}H_2CH_2C_6F_{13}$), 48.0, 31.4 (t, *J* = 21.0 Hz, $CH_2\underline{\mathbf{C}}H_2C_6F_{13}$), 21.1, 20.8, 20.8, 20.8, 20.7, 20.7, 16.2, 16.1. HRMS (ESI^+): calc. for $C_{70}H_{72}F_{26}O_{23}SNa^+$ $[M+Na]^+$: 1829.3662, found: 1829.3666.

11. Table S1. Preparation of OPSB^F glycosyl donors 14



General procedure B for preparing OPSB^F glycosyl donors **14a**-**14g**: PIFA (1.2 equiv. to OPTB^F glycosides) was added to the mixture of donor **13** in MeCN/H_2O (9:1, v:v, 0.1 M) at room temperature, the resulting mixture was allowed to stirred for an appropriate time until the starting material completely consumed. The mixture was extacted with EtOAc. The organic phase was washed with saturated $Na_2S_2O_3$, saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo*. Most of the compounds colud be directly used for subsequent glycosylation reactions. For obtaining higher purity, these products such as **14a**, **14d**, **14e** and **14g** could be further purified by flash column chromatography on silica gel due to the existence of a small amount of fluorous sulfone by-products resulted from overoxidation. These by-products were difficult to be separated by fluorous based purification.

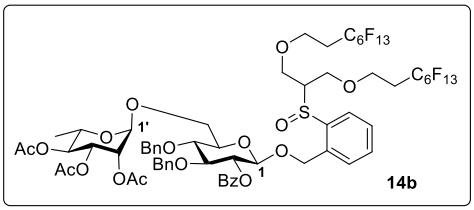
2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)sulfinyl]benzyl 4-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranosyl)-2-*O*-benzoyl-3,6-di-*O*-benzyl-*β*-D-glucopyranoside (14a)



Prepared according to the General Procedure B (45.4 mg, yield 90%). Colorless syrup, R_f = 0.16 (petroleum ether-EtOAc 3:1). A mixture of sulfoxide *R*/*S* (1:1) isomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.4 Hz, 2H, Ar-H), 7.80 (d, J = 7.6 Hz, 1H, Ar-H), 7.54 (t, J = 7.6 Hz, 1H, Ar-H), 7.42-7.25 (m, 18H, Ar-H), 7.23-7.14 (m, 7H, Ar-H), 7.06 (d, J = 8.0 Hz, 2H, Ar-H), 7.02-6.92 (m, 3H, Ar-H), 5.26 (dd, J = 8.0, 9.2 Hz, 1H), 4.98 (dd, J = 8.0, 9.2 Hz, 1H), 4.92 (d, J = 12.4 Hz, 1H, $PhCH_2$), 4.88 (d, J = 12.0 Hz, 1H, $PhCH_2$), 4.77 (d, J = 11.2 Hz, 1H, $PhCH_2$), 4.73 (d, J = 10.8 Hz, 1H, $PhCH_2$), 4.65-4.59 (m, 5H, $PhCH_2$, **H-1**), 4.54 (d, J = 8.4 Hz, 1H, **H-1′**), 4.53 (d, J = 10.8 Hz, 1H, $PhCH_2$), 4.44 (d, J = 12.0 Hz, 1H, $PhCH_2$), 4.37 (s, 2H), 4.07 (t, J = 9.2 Hz, 1H), 3.76-3.63 (m, 5H), 3.59-3.35 (m, 11H), 3.32-3.28 (m, 1H), 3.14-3.08 (m, 1H, SCH), 2.27-2.04 (m, 4H, C**H**$_2$C**H**$_2$C$_6$F$_{13}$), 1.88 (s, 3H, OAc). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 165.2, 140.5, 138.6, 138.4, 138.4, 138.2, 138.1, 135.7, 133.3, 131.2, 130.1, 130.1, 130.0, 128.8, 128.7, 128.7, 128.6, 128.5, 128.5, 128.1, 128.1, 128.1,

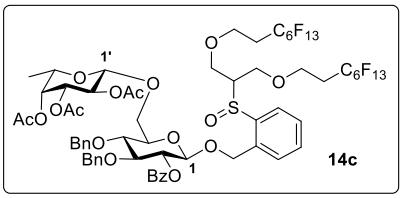
128.1, 128.0, 128.0, 127.9, 127.9, 127.7, 127.6, 127.3, 125.1, 100.9 (**C-1′**), 100.5 (**C-1**), 83.2, 80.4, 78.2, 76.7, 75.5, 75.4, 75.3, 75.1, 74.5, 73.9, 73.9, 73.5, 73.2, 68.8, 68.0, 66.8, 66.4, 64.2, 63.3 (brs, $\underline{\mathbf{C}}H_2CH_2C_6F_{13}$), 63.1 (brs, $\underline{\mathbf{C}}H_2CH_2C_6F_{13}$), 31.4 (t, J = 21.0 Hz, $CH_2\underline{\mathbf{C}}H_2C_6F_{13}$), 31.3 (t, J = 21.0 Hz, $CH_2\underline{\mathbf{C}}H_2C_6F_{13}$), 21.0. HRMS ($ESI^+$): calc. for $C_{82}H_{76}F_{26}O_{16}SNa^+$ $[M+Na]^+$: 1865.4331, found: 1865.4334.

2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)sulfinyl]benzyl 6-*O*-(2,3,4-tri-*O*-acetyl-*α*-L-rhamnopyranosyl)-2-*O*-benzoyl-3,4-di-*O*-benzyl-*β*-D-glucopyranoside (14b)



Prepared according to the General Procedure B (117.8 mg, yield 97%). Colorless syrup, R_f = 0.25 (petroleum ether-EtOAc 2:1). A mixture of sulfoxide *R*/*S* (1:1) isomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.2 Hz, 2H, Ar-H), 7.91 (d, J = 7.2 Hz, 2H, Ar-H), 7.85 (d, J = 7.6 Hz, 1H, Ar-H), 7.81 (d, J = 8.0 Hz, 1H, Ar-H), 7.58-7.53 (m, 2H, Ar-H), 7.45-7.25 (m, 22H, Ar-H), 7.12-7.05 (m, 8H, Ar-H), 5.30-5.24 (m, 6H, **H-1**), 5.06 (t, J = 9.6 Hz, 1H), 5.06 (t, J = 9.6 Hz, 1H), 4.89-4.83 (m, 4H), 4.77-4.53 (m, 12H, **H-1′**), 3.96-3.87 (m, 4H), 3.79 (t, J = 9.2 Hz, 1H), 3.77 (t, J = 8.8 Hz, 1H), 3.68-3.52 (m, 14H), 3.47-3.34 (m, 8H), 3.23-3.17 (m, 1H, SCH), 3.14-3.08 (m, 1H, SCH), 2.39-2.20 (m, 4H, $C\underline{\mathbf{H}}_2C\underline{\mathbf{H}}_2C_6F_{13}$), 2.13-2.00 (m, 16H), 1.96 (s, 3H, OAc), 1.96 (s, 3H, OAc), 1.17 (d, J = 6.0 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 170.3, 170.3, 170.3, 170.1, 170.1, 165.2, 141.6, 140.8, 137.9, 137.7, 134.9, 134.5, 133.5, 133.4, 131.2, 131.1, 130.5, 130.1, 129.9, 129.9, 129.0, 129.0, 128.7, 128.6, 128.6, 128.5, 128.2, 128.2, 128.1, 128.1, 128.0, 127.9, 125.1, 125.0, 100.3 (**C-1**), 99.5 (**C-1**), 98.1 (**C-1′**), 97.9 (**C-1′**), 83.1, 83.0, 78.2, 78.0, 75.5, 75.5, 75.3, 75.1, 74.9, 73.8, 73. 7, 71.1, 69. 9, 69.8, 69.3, 67.0, 66.9, 66.8, 66.8, 66.7, 66.7, 66.5, 66.0, 64.0, 63.3 (t, J = 4.0 Hz, $\underline{\mathbf{C}}H_2CH_2C_6F_{13}$), 62.8 (t, J = 4.0 Hz, $\underline{\mathbf{C}}H_2CH_2C_6F_{13}$), 31.3 (t, J = 21.0 Hz, $CH_2\underline{\mathbf{C}}H_2C_6F_{13}$), 31.2 (t, J = 21.0 Hz, $CH_2\underline{\mathbf{C}}H_2C_6F_{13}$), 21.0, 21.0, 20.9, 20.9, 17.6, 17.5. HRMS (ESI^+): calc. for $C_{65}H_{62}F_{26}O_{17}SNa^+$ $[M+Na]^+$: 1663.3185, found: 1663.3209.

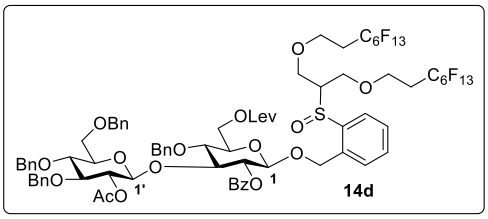
2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)sulfinyl]benzyl 6-*O*-(2,3,4-tri-*O*-acetyl-6-deoxy-*β*-L-galactopyranosyl)-2-*O*-benzoyl-3,4-di-*O*-benzyl-*β*-D-glucopyranoside (14c)



Prepared according to the General Procedure B (110 mg, yield 96%). Colorless syrup, R_f = 0.23 (petroleum ether-EtOAc 2:1). A mixture of sulfoxide *R*/*S* (1.3:1) isomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 2.6H, Ar-H), 7.90 (t, J = 8.4 Hz, 2H, Ar-H), 7.83 (dt, J = 1.2, 7.2 Hz, 2.3H, Ar-H), 7.57-7.53 (m, 2.3H, Ar-H), 7.50-7.45 (m, 2.6H, Ar-H), 7.45-7.33 (m, 8.5H, Ar-H), 7.33-7.25 (m, 12.6H, Ar-H), 7.11-7.05 (m, 11H, Ar-H), 5.25-5.18 (m, 7H), 5.03 (dd, J = 3.0, 10.2 Hz, 1H), 4.99 (dd, J = 3.6, 10.2 Hz, 1.3H), 4.91 (d, J = 12.6 Hz, 1.3H, $PhCH_2$), 4.85 (d, J = 13.2 Hz, 1H, $PhCH_2$), 4.80 (d, J = 13.8 Hz, 1H, $PhCH_2$), 4.80 (d, J = 10.8 Hz, 1H,

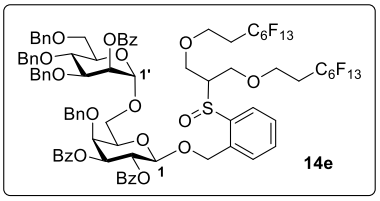
$PhCH_2$), 4.78 (d, J = 10.8 Hz, 1.3H, $PhCH_2$), 4.73-4.68 (m, 4.6H), 4.66 (d, J = 12.6 Hz, 1.3H, $PhCH_2$), 4.62 (d, J = 7.8 Hz, 2.6H, **H-1**), 4.60 (d, J = 8.4 Hz, 1H, **H-1′**), 4.58 (d, J = 8.4 Hz, 1H, **H-1′**), 4.49 (t, J = 7.8 Hz, 2.3H), 4.16 (ddd, J = 3.0, 5.4, 12.0 Hz, 2.3H), 3.84-3.81 (m, 2.3H), 3.78-3.67 (m, 8.6H), 3.64-3.39 (m, 21H), 3.18-3.14 (m, J = 5.4 Hz, 1H, SCH), 3.11-3.07 (m, J = 5.4 Hz, 1.3H, SCH), 2.35-2.19 (m, 5H, C**H**$_2$C**H**$_2$$C_6F_{13}$), 2.16-2.07 (m, 18H), 1.98 (s, 3H, OAc), 1.97 (s, 3.9H, OAc), 1.21-1.18 (m, 6.9H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.9, 170.9, 170.4, 169.9, 165.2, 165.2, 138.3, 138.2, 138.0, 137.9, 135.8, 135.3, 133.4, 131.4, 131.3, 130.2, 130.0, 129.9, 129.9, 129.7, 128.9, 128.9, 128.6, 128.4, 128.2, 128.1, 128.0, 128.0, 127.8, 125.2, 124.9, 101.9 (**C-1**), 101.7 (**C-1**), 100.8 (**C-1′**), 99.7 (**C-1′**), 82.5, 82.4, 77.7, 75.4, 75.3, 75.2, 75.2, 73.7, 71.5, 71.5, 70.5, 69.4, 69.4, 69.3, 69.3, 67.4, 67.3, 66.8, 66.8, 66.2, 65.6, 64.2, 64.1, 63.4 (t, J = 4.0 Hz, **C**$H_2CH_2C_6F_{13}$), 63.0 (t, J = 4.0 Hz, **C**$H_2CH_2C_6F_{13}$), 31.3 (t, J = 21.0 Hz, CH_2**C**$H_2C_6F_{13}$), 31.2 (t, J = 21.0 Hz, CH_2**C**$H_2C_6F_{13}$), 21.2, 21.1, 20.9, 20.8, 20.8, 16.2, 16.2. HRMS (ESI^+): calc. for $C_{65}H_{62}F_{26}O_{17}SNa^+$ $[M+Na]^+$: 1663.3185, found: 1663.3186.

2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)sulfinyl]benzyl 3-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranosyl)-2-*O*-benzoyl-4-*O*-benzyl-6-*O*-levulinyl-*β*-D-glucopyranoside (14d)



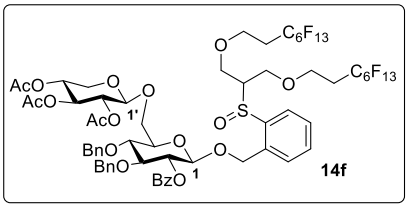
Prepared according to the General Procedure B (62.9 mg, yield 93%). Colorless syrup, R_f = 0.18 (petroleum ether-EtOAc 2:1). A mixture of sulfoxide *R*/*S* (1.3:1) isomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.2 Hz, 2.6H, Ar-H), 7.95 (d, J = 6.8 Hz, 2H, Ar-H), 7.83 (d, J = 8.0 Hz, 1H, Ar-H), 7.78 (d, J = 8.0 Hz, 1.3H, Ar-H), 7.63 (t, J = 7.6 Hz, 2.3H, Ar-H), 7.50-7.31 (m, 15H, Ar-H), 7.25-7.21 (m, 33.6H, Ar-H), 7.10-7.07 (m, 9H, Ar-H), 5.20 (t, J = 8.8 Hz, 2.3H), 5.02 (d, J = 10.8 Hz, 2.3H, $PhCH_2$), 4.95-4.87 (m, 4H), 4.78 (d, J = 13.2 Hz, 1H, $PhCH_2$), 4.74 (d, J = 13.2 Hz, 1H, $PhCH_2$), 4.69-4.32 (m, 24H, $PhCH_2$, **H-1**, **H-1′**), 4.19 (dt, J = 4.4, 12.0 Hz, 2.3H), 4.14-4.07 (m, 2.6H), 3.73 (d, J = 10.8 Hz, 2.3H, $PhCH_2$), 3.68-3.35 (m, 28.5H), 3.19 (q, J = 9.2 Hz, 2.3H), 3.12-3.06 (m, 2.3H, SCH), 2.71-2.68 (m, 4.6H), 2.61-2.46 (m, 4.6H), 2.35-2.21 (m, 4.6H, C**H**$_2$C**H**$_2$$C_6F_{13}$), 2.15 (s, 6.9H), 2.11-2.00 (m, 4.6H, C**H**$_2$C**H**$_2$$C_6F_{13}$), 1.87 (s, 3H), 1.86 (s, 3.9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.5, 172.6, 170.2, 164.9, 164.8, 141.1, 140.5, 138.4, 138.4, 138.2, 138.2, 138.1, 137.8, 135.1, 135.0, 133.7, 133.7, 131.2, 130.4, 129.9, 129.9, 129.7, 129.4, 129.0, 128.9, 128.8, 128.8, 128.7, 128.6, 128.6, 128.5, 128.4, 128.2, 127.9, 127.9, 127.7, 127.7, 127.6, 125.1, 124.9, 101.2 (**C-1′**), 101.2 (**C-1′**), 99.9 (**C-1**), 99.3 (**C-1**), 83.2, 80.6, 80.6, 78.1, 75.7, 75.4, 75.3, 75.1, 75.1, 74.9, 74.9, 74.0, 73.7, 73.5, 73.4, 72.9, 72.9, 69.2, 66.9, 66.7, 66.2, 65.5, 64.2, 64.0, 63.7, 63.3 (t, J = 4.0 Hz, **C**$H_2CH_2C_6F_{13}$), 63.0 (t, J = 4.0 Hz, **C**$H_2CH_2C_6F_{13}$), 38.0, 38.0, 31.3 (t, J = 21.0 Hz, CH_2**C**$H_2C_6F_{13}$), 31.2 (t, J = 21.0 Hz, CH_2**C**$H_2C_6F_{13}$), 30.0, 30.0, 28.0, 27.9, 20.7, 20.7. HRMS (ESI^+): calc. for $C_{80}H_{76}F_{26}O_{18}SNa^+$ $[M+Na]^+$: 1873.4229, found: 1873.4223.

2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)sulfinyl]benzyl 6-*O*-(2-*O*-benzoyl-3,4,5-tri-*O*-benzyl-*α*-D-mannopyranosyl)-2,3-di-*O*-benzoyl-4-*O*-benzyl-*β*-D-galactopyranoside (14e)



Prepared according to the General Procedure B (41.8 mg, yield 83%). Colorless syrup, R_f = 0.29 (petroleum ether-EtOAc 3:1). A mixture of sulfoxide *R*/*S* (1:1) isomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 4H, Ar-H), 7.97-7.91 (m, 6H, Ar-H), 7.86 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.79 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.57-7.46 (m, 7H, Ar-H), 7.43-7.24 (m, 38H, Ar-H), 7.23-7.12 (m, 20H, Ar-H), 5.83 (dd, *J* = 2.4, 7.6 Hz, 1H), 5.81 (dd, *J* = 2.4, 7.6 Hz, 1H), 5.47 (brs, 2H), 5.36-5.32 (m, 2H), 4.91-4.82 (m, 4H), 4.79-4.67 (m, 12H, $PhCH_2$, **H-1**, **H-1′**), 4.57 (d, *J* = 10.8 Hz, 2H, $PhCH_2$), 4.54-4.51 (m, 4H), 4.46 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.44 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.13 (dd, *J* = 2.4, 8.0 Hz, 2H), 4.10-4.00 (m, 4H), 3.91-3.78 (m, 10H), 3.67 (dd, *J* = 5.6, 10.0 Hz, 1H), 3.62-3.46 (m, 11H), 3.44-3.34 (m, 6H), 3.18-3.11 (m, 2H, SCH), 2.32-2.16 (m, 4H, C**H**$_2$C**H**$_2$C$_6$F$_{13}$), 2.14-1.97 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.1, 166.1, 165.8, 165.4, 165.4, 141.8, 140.9, 138.6, 138.5, 138.5, 138.1, 138.0, 137.5, 137.5, 135.0, 134.7, 133.7, 133.4, 133.4, 131.2, 131.1, 130.7, 130.2, 130.0, 130.0, 129.9, 129.9, 129.7, 129.6, 129.1, 129.1, 129.0, 128.8, 128.7, 128.6, 128.6, 128.5, 128.5, 128.3, 128.3, 128.3, 128.2, 128.1, 127.9, 127.8, 127.8, 127.8, 127.7, 125.2, 125.2, 101.0 (**C-1**), 100.3 (**C-1**), 98.3 (**C-1′**), 78.1, 78.0, 77.4, 75.5, 75.5, 75.4, 75.3, 74.8, 74.7, 74.3, 74.3, 73.7, 73.7, 73.7, 73.6, 73.3, 72.3, 72.2, 71.9, 71.9, 70.2, 70.1, 69.2, 69.1, 69.1, 67.0, 67.0, 66.8, 66.3, 65.9, 65.7, 64.2, 64.1, 63.3 (t, *J* = 4.0 Hz, **C**H$_2$CH$_2$C$_6$F$_{13}$), 62.8 (t, *J* = 4.0 Hz, **C**H$_2$CH$_2$C$_6$F$_{13}$), 31.3 (t, *J* = 21.0 Hz, CH$_2$**C**H$_2$C$_6$F$_{13}$), 31.2 (t, *J* = 21.0 Hz, CH$_2$**C**H$_2$C$_6$F$_{13}$). HRMS (ESI$^+$): calc. for $C_{87}H_{76}F_{26}O_{17}SNa^+$ $[M+Na]^+$: 1941.4280, found: 1941.4285.

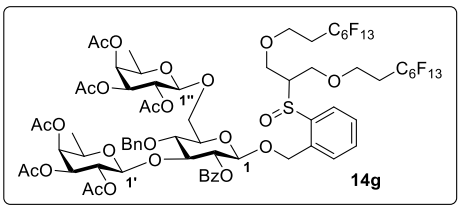
2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)sulfinyl]benzyl 6-*O*-(2,3,4-tri-*O*-acetyl-*β*-D-xylopyranosyl)-2-*O*-benzoyl-3,4-di-*O*-benzyl-*β*-D-glucopyranoside (14f)



Prepared according to the General Procedure B (60.0 mg, yield 96%). Colorless syrup, R_f = 0.18 (petroleum ether-EtOAc 2:1). A mixture of sulfoxide *R*/*S* (1:1) isomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 1.2, 8.0 Hz, 2H, Ar-H), 7.90 (dd, *J* = 1.2, 8.4 Hz, 2H, Ar-H), 7.85 (dd, *J* = 1.2, 8.0 Hz, 1H, Ar-H), 7.81 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.57-7.53 (m, 2H, Ar-H), 7.47-7.26 (m, 20H, Ar-H), 7.11-7.05 (m, 10H), 5.25 (d, *J* = 8.0 Hz, 1H, **H-1**), 5.23 (d, *J* = 7.6 Hz, 1H, **H-1′**), 5.12 (t, *J* = 8.0 Hz, 1H), 5.11 (t, *J* = 8.0 Hz, 1H), 4.95-4.90 (m, 4H), 4.85-4.73 (m, 4H), 4.70-4.56 (m, 8H), 4.53-4.49 (m, 2H), 4.13 (dd, *J* = 5.2, 10.8 Hz, 1H), 4.12 (dd, *J* = 5.2, 10.8 Hz, 1H), 4.06 (dd, *J* = 1.2, 11.2 Hz, 1H), 4.00 (dd, *J* = 1.2, 11.2 Hz, 1H), 3.77 (t, *J* = 8.8 Hz, 2H), 3.73-3.53 (m, 16H), 3.50-3.29 (m, 10H), 3.18-3.11 (m, 2H, SCH), 2.38-2.25 (m, 4H, C**H**$_2$C**H**$_2$C$_6$F$_{13}$), 2.16-2.01 (m, 16H), 1.96 (s, 3H, OAc), 1.95 (s, 3H, OAc). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.3, 170.3, 170.1, 169.5, 165.2, 165.2,

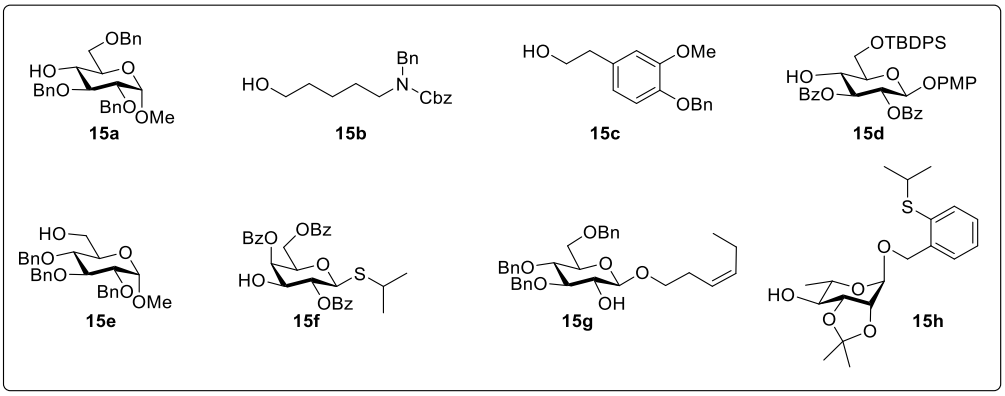
141.4, 140.6, 138.0, 137.8, 137.8, 135.2, 134.7, 133.5, 133.5, 131.2, 131.2, 130.4, 130.0, 129.9, 129.9, 129.0, 129.0, 128.7, 128.6, 128.6, 128.5, 128.2, 128.1, 128.1, 128.1, 128.0, 127.9, 125.1, 125.0, 100.7 (**C-1**), 100.5 (**C-1**), 100.3 (**C-1′**), 99.4 (**C-1′**), 82.9, 78.0, 77.8, 75.3, 75.3, 75.1, 74.9, 74.8, 73.7, 71.5, 71.2, 70.8, 70.6, 68.9, 68.9, 67.8, 67.6, 66.9, 66.9, 66.4, 65.6, 64.1, 64.0, 63.3 (t, J = 4.0 Hz, $\underline{\mathbf{C}}H_2CH_2C_6F_{13}$), 62.0 (t, J = 4.0 Hz, $\underline{\mathbf{C}}H_2CH_2C_6F_{13}$), 31.3 (t, J = 21.0 Hz, $CH_2\underline{\mathbf{C}}H_2C_6F_{13}$), 31.2 (t, J = 21.0 Hz, $CH_2\underline{\mathbf{C}}H_2C_6F_{13}$), 21.0, 20.9, 20.9, 20.9. HRMS (ESI^+): calc. for $C_{64}H_{60}F_{26}O_{17}SNa^+$ $[M+Na]^+$: 1649.3028, found: 1649.3034.

2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)sulfinyl]benzyl 3,6-di-*O*-(2,3,4-tri-*O*-acetyl-6-deoxy-*β*-D-galactopyranosyl)-2-*O*-benzoyl-4-*O*-benzyl-*β*-D-glucopyranoside (14g)

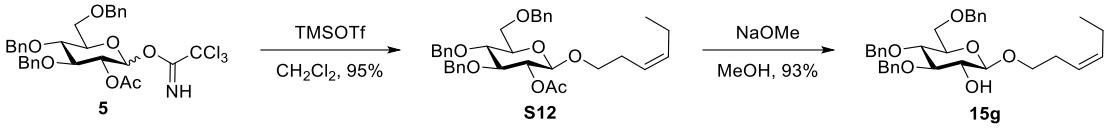


Prepared according to the General Procedure B (26.3 mg, yield 87%). Colorless syrup, R_f = 0.56 (petroleum ether-EtOAc 1:1). A mixture of sulfoxide *R*/*S* (1:1) isomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00-7.98 (m, 2H, Ar-H), 7.95-7.93 (m, 2H, Ar-H), 7.83 (dd, J = 1.2, 8.4 Hz, 1H, Ar-H), 7.79-7.78 (m, 1H, Ar-H), 7.63-7.60 (m, 2H, Ar-H), 7.48-7.35 (m, 12H, Ar-H), 7.32-7.26 (m, 7H, Ar-H), 7.21 (dt, J = 1.2, 7.2 Hz, 1H, Ar-H), 5.23-5.19 (m, 6H), 5.14 (d, J = 10.8 Hz, 1H, $PhCH_2$), 5.12-5.10 (m, 3H), 5.08 (d, J = 10.8 Hz, 1H, $PhCH_2$), 5.07 (d, J = 10.8 Hz, 1H, $PhCH_2$), 4.97-4.92 (m, 3H), 4.82 (d, J = 12.6 Hz, 1H, $PhCH_2$), 4.72 (d, J = 12.6 Hz, 1H, $PhCH_2$), 4.64 (d, J = 12.6 Hz, 1H, $PhCH_2$), 4.59 (d, J = 7.8 Hz, 1H, **H-1**), 4.58 (d, J = 7.8 Hz, 1H, **H-1**), 4.57 (dd, J = 3.6, 5.4 Hz, 1H), 4.56 (dd, J = 3.6, 5.4 Hz, 1H), 4.53 (d, J = 7.8 Hz, 1H, **H-1′**), 4.50 (d, J = 10.2 Hz, 2H), 4.47 (d, J = 8.4 Hz, 1H, **H-1′**), 4.42 (d, J = 7.8 Hz, 1H, **H-1′′**), 4.41 (d, J = 7.8 Hz, 1H, **H-1′′**), 4.18-4.10 (m, 4H), 3.75-3.73 (m, 2H), 3.71-3.56 (m, 14H), 3.54-3.38 (m, 10H), 3.16-3.13 (m, J = 5.4 Hz, 1H, SCH), 3.11-3.07 (m, J = 5.4 Hz, 1H, SCH), 2.37-2.18 (m, 4H, $C\underline{\mathbf{H}}_2C\underline{\mathbf{H}}_2C_6F_{13}$), 2.13 (s, 3H, OAc), 2.13 (s, 3H, OAc), 2.12-2.02 (m, 4H, $C\underline{\mathbf{H}}_2C\underline{\mathbf{H}}_2C_6F_{13}$), 2.05 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.01 (s, 3H, OAc), 2.00 (s, 3H, OAc), 1.95 (s, 3H, OAc), 1.95 (s, 3H, OAc), 1.94 (s, 3H, OAc), 1.94 (s, 3H, OAc), 1.86 (s, 3H, OAc), 1.85 (s, 3H, OAc). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.9, 170.7, 170.4, 170.4, 170.3, 170.1, 169.6, 169.6, 164.9, 164.8, 141.2, 140.5, 138.6, 138.5, 135.1, 134.8, 133.9, 131.3, 131.2, 130.4, 129.8, 129.7, 129.7, 129.0, 128.9, 128.9, 128.5, 128.4, 128.4, 128.0, 128.0, 125.1, 125.0, 101.7 (**C-1′′**), 101.6 (**C-1′′**), 100.8 (**C-1**), 100.8 (**C-1**), 99.8 (**C-1′**), 99.3 (**C-1′**), 80.0, 80.0, 77.4, 77.0, 75.9, 75.8, 75.0, 74.9, 74.9, 73.9, 71.7, 71.5, 70.5, 70.5, 69.4, 69.4, 69.3, 69.1, 68.9, 68.5, 68.3, 66.9, 66.8, 66.2, 65.6, 64.1, 64.0, 63.6, 63.4 (t, J = 4.0 Hz, $\underline{\mathbf{C}}H_2CH_2C_6F_{13}$), 63.3 (t, J = 4.0 Hz, $\underline{\mathbf{C}}H_2CH_2C_6F_{13}$), 62.9, 62.9, 62.8, 31.3 (t, J = 21.0 Hz, $CH_2\underline{\mathbf{C}}H_2C_6F_{13}$), 31.2 (t, J = 21.0 Hz, $CH_2\underline{\mathbf{C}}H_2C_6F_{13}$), 21.0, 20.8, 20.8, 20.7, 20.6, 16.2, 16.1, 16.1. HRMS (ESI^+): calc. for $C_{70}H_{72}F_{26}O_{24}SNa^+$ $[M+Na]^+$: 1845.3611, found: 1845.3614.

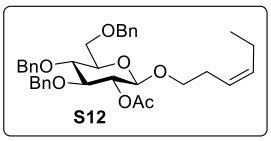
12. Table S2. Preparation of acceptors 15



Compound **15a**,[13] **15b**,[14] **15c**,[4] **15d**,[15] **15e**,[16] **15f**,[17] **15h**,[18] were synthesized according to the reported procedures.

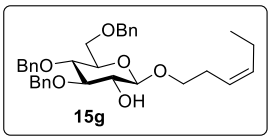


(*Z*)-3-Hexenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranoside (S12)



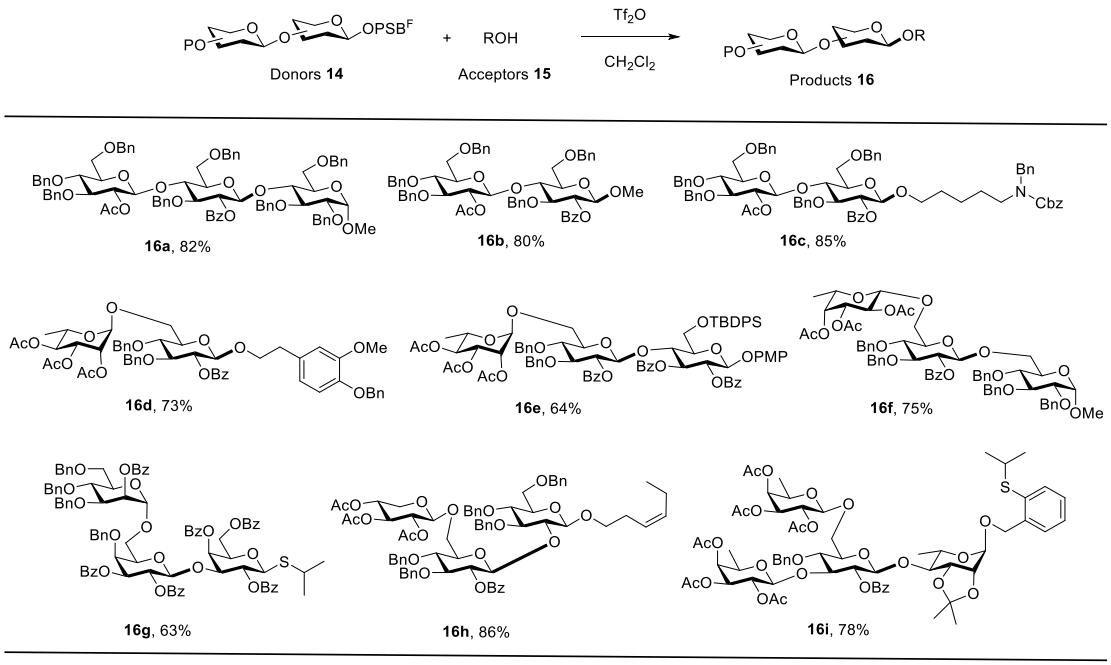
A suspension of (*Z*)-3-Hexen-1-ol (81.8 μL, 0.70 mmol, 1.0 euqiv) and compound **5**[2] (531.3 mg, 0.83 mmol, 1.2 equiv) containing activated 4Å MS (100 wt%) in anhydrous CH_2Cl_2 (4.7 mL) was stirred at room temperature for 10 min under argon. After cooling to −20 ℃, TMSOTf (37.4 μL, 0.21 mmol, 0.3 equiv) was added. The reaction mixture was stirred at −20 ℃ for 1 h and quenched by addition of Et_3N (0.3 mL). The mixture was filtered through Celite and extracted with EtOAc, washed with saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by flash column chromatography on silica gel to give **S12** (380 mg, yield 95%) as white solid, R_f = 0.42 (petroleum ether-EtOAc 5:1). m.p. 59.2-60.7 ℃. $[\alpha]_D^{20}$ +2.0 (*c*, 1.50 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.25 (m, 13H, Ar-H), 7.17-7.15 (m, 2H, Ar-H), 5.46-5.39 (m, 1H, CH=CH), 5.31-5.24 (m, 1H, CH=CH), 5.00-4.95 (m, 1H), 4.77 (d, *J* = 10.8 Hz, 2H, $PhCH_2$), 4.65 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.61 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.54 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.54 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.35 (d, *J* = 8.0 Hz, 1H, **H-1**), 3.85 (dt, *J* = 6.8, 9.6 Hz, 1H), 3.73 (dd, *J* = 2.0, 10.8 Hz, 1H), 3.72-3.61 (m, 3H), 3.49-3.40 (m, 2H), 2.30 (q, *J* = 6.8 Hz, 2H), 2.05-1.98 (m, 2H), 1.95 (s, 3H, OAc), 0.93 (t, *J* = 7.6 Hz, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.7, 138.4, 138.3, 138.1, 134.0, 128.6, 128.6, 128.6, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 124.7, 101.2 (**C-1**), 83.2, 78.2, 75.4, 75.2, 75.2, 73.7, 73.3, 69.5, 69.0, 27.9, 21.1, 20.8, 14.4. HRMS (ESI^+): calc. for $C_{35}H_{42}O_7Na^+$ $[M+Na]^+$: 597.2823, found: 597.2841.

(*Z*)-3-Hexenyl 3,4,6-tri-*O*-benzyl-*β*-D-glucopyranoside (15g)



To a stirred mixture of compound **S11** (420 mg, 0.73 mmol, 1.0 equiv) in MeOH (3.7 mL) was added NaOMe (11.8 mg, 0.22 mmol, 0.3 equiv). The mixture was stirred at 40 ℃ for 3 h, then Amberlyst (*R*)15 ion-exchange resin was added to neutralize the mixture. Following removal of the resin, the filtrate was evaporated under reduced pressure and purified by flash column chromatography on silica gel to give **15g** (362 mg, yield 93%) as white solid, R_f = 0.38 (petroleum ether-EtOAc 5:1). m.p. 66.3-68.5 ℃. $[\alpha]_D^{20}$ −7.5 (*c*, 1.70 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.25 (m, 13H, Ar-H), 7.16-7.14 (m, 2H, Ar-H), 5.51-5.45 (m, 1H, CH=CH), 5.36-5.29 (m, 1H, CH=CH), 4.93 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.82 (d, *J* = 11.6 Hz, 2H, $PhCH_2$), 4.60 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.53 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.52 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.24 (d, *J* = 7.2 Hz, 1H, **H-1**), 3.93 (ddd, *J* = 6.0, 7.2, 9.2 Hz, 1H), 3.73 (dd, *J* = 2.0, 10.8 Hz, 1H, H-6a), 3.67 (dd, *J* = 4.4, 10.4 Hz, 1H, H-6b), 3.59-3.45 (m, 5H), 2.44-2.33 (m, 3H), 2.08-2.01 (m, 2H), 0.95 (t, *J* = 7.6 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 138.3, 138.3, 134.4, 128.6, 128.6, 128.5, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 124.6, 103.0 (**C-1**), 84.7, 77.7, 75.4, 75.3, 75.2, 75.0, 73.7, 69.8, 69.1, 28.0, 20.8, 14.4. HRMS (ESI^+): calc. for $C_{33}H_{40}O_6Na^+$ $[M+Na]^+$: 555.2717, found: 555.2717.

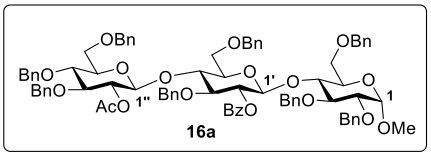
13. IPRm glycosylations of OPSB^F glycosyl donors (Scheme 3)



General Procedure C for preparing compounds **16a-16i**: A solution of OPSB^F donor **14** (1.0 equiv) in anhydrous CH_2Cl_2 (0.05 M) in the presence of 4Å MS (100 wt%) was stirred for 15 min at −40 ℃. After addition of Tf_2O (1.0 equiv), the solution was stirred at −40 ℃ for 3 min, then acceptors **15** (1.2 equiv) in anhydrous CH_2Cl_2 (0.3 mL) was added. The reaction mixture was stirred at −40 ℃ for 0.5 h to 1 h and quenched by

addition of H_2O (1.0 mL). The mixture was filtered through Celite and extracted with EtOAc, the organic phase was washed with brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography on silica gel to give compounds **16a-16i**.

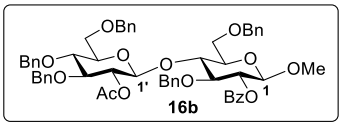
Methyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-benzyl-*β*-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-*α*-D-glucopyranoside (16a)



16a

Prepared according to the General Procedure C (18.4 mg, yield 82%). Colorless syrup, R_f = 0.65 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{20}$ +15.3 (*c*, 1.55 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.82 (m, 2H, Ar-H), 7.53 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.38 (t, *J* = 7.6 Hz, 2H, Ar-H), 7.34-7.25 (m, 17H, Ar-H), 7.23-7.15 (m, 18H, Ar-H), 7.06-7.04 (m, 2H, Ar-H), 7.01-6.98 (m, 1H, Ar-H), 6.94-6.90 (m, 2H, Ar-H), 5.13 (dd, *J* = 8.0, 9.6 Hz, 1H), 5.05 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.99 (dd, *J* = 8.4, 9.6 Hz, 1H), 4.90 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.78-4.72 (m, 3H), 4.70 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.62-4.52 (m, 5H), 4.49 (d, *J* = 3.6 Hz, 1H, **H-1**), 4.46 (d, *J* = 8.4 Hz, 1H, **H-1′′**), 4.45 (d, *J* = 8.0 Hz, 1H, **H-1′**), 4.43 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.35 (s, 2H), 4.28 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.18 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.00 (t, *J* = 9.2 Hz, 1H), 3.85-3.76 (m, 2H), 3.71 (t, *J* = 9.2 Hz, 1H), 3.66 (dd, *J* = 0.8, 10.4 Hz, 1H), 3.58-3.51 (m, 3H), 3.50-3.38 (m, 5H), 3.33 (dd, *J* = 1.2, 10.8 Hz, 1H), 3.28-3.23 (m, 4H), 3.10 (dd, *J* = 2.0, 9.6 Hz, 1H), 1.88 (s, 3H, OAc). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 165.0, 139.9, 138.9, 138.5, 138.5, 138.4, 138.4, 138.2, 138.0, 133.1, 130.1, 130.0, 128.8, 128.6, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6, 127.2, 127.1, 100.7 (**C-1′′**), 100.4 (**C-1′**), 98.5 (**C-1**), 83.1, 80.6, 80.4, 79.1, 78.2, 75.5, 75.3, 75.3, 75.1, 74.6, 73.9, 73.7, 73.7, 73.6, 73.5, 69.7, 68.8, 68.0, 67.8, 55.4, 21.1. HRMS (ESI^+): calc. for $C_{84}H_{88}O_{18}Na^+$ $[M+Na]^+$: 1407.5863, found: 1407.5855.

Methyl 4-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranosyl)-2-*O*-benzoyl-3,6-di-*O*-benzyl-*β*-D-glucopyranoside (16b)

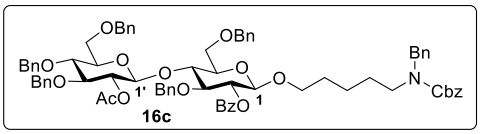


16b

Prepared according to the General Procedure C with small modifications, 50.0 equiv. of MeOH was used as acceptor. (15.3 mg, yield 80%). Colorless syrup, R_f = 0.63 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{20}$ +26.1 (*c*, 1.50 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.53 (tt, *J* = 1.2, 7.6 Hz, 1H, Ar-H), 7.39 (t, *J* = 7.6 Hz, 2H, Ar-H), 7.34-7.25 (m, 14H, Ar-H), 7.23-7.15 (m, 6H, Ar-H), 7.10-7.08 (m, 2H, Ar-H), 7.01-6.94 (m, 3H, Ar-H), 5.21 (dd, *J* = 8.0, 9.2 Hz, 1H), 4.98 (dd, *J* = 8.0, 9.6 Hz, 1H), 4.90 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.78 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.74 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.71 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.63 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.61 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.55 (d, *J* = 8.0 Hz, 1H, **H-1′**), 4.54 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.51 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.38 (d, *J* = 8.0 Hz, 1H, **H-1**), 4.37 (brs, 2H), 4.06 (t, *J* = 9.2 Hz, 1H), 3.76-3.69 (m, 4H), 3.66 (dd, *J* = 1.6, 10.8 Hz, 1H), 3.54 (dd, *J* = 4.0, 10.8 Hz, 1H), 3.51 (t,

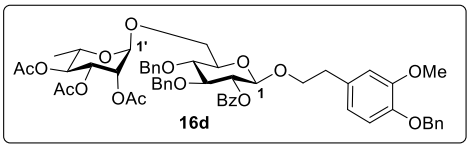
J = 9.2 Hz, 1H), 3.45-3.41 (m, 4H), 3.30 (ddd, *J* = 1.6, 4.0, 10.0 Hz, 1H), 1.89 (s, 3H, OAc). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 165.4, 138.7, 138.4, 138.4, 138.2, 133.1, 130.2, 130.0, 128.7, 128.6, 128.6, 128.5, 128.4, 128.1, 128.0, 128.0, 127.9, 127.9, 127.7, 127.6, 127.2, 102.2 (**C-1**), 100.5 (**C-1′**), 83.2, 80.5, 78.2, 75.5, 75.4, 75.3, 75.1, 74.5, 73.9, 73.8, 73.5, 73.2, 68.8, 68.0, 56.8, 21.1. HRMS (ESI$^+$): calc. for $C_{57}H_{60}O_{13}Na^+$ $[M+Na]^+$: 975.3926, found: 975.3940.

_N_-Benzyl-_N_-benzyloxycarbonyl-5-pentyl 4-_O_-(2-_O_-acetyl-3,4,6-tri-_O_-benzyl-_β_-D-glucopyranosyl)-2-_O_-benzoyl-3,6-di-_O_-benzyl-_β_-D-glucopyranoside (16c)



Prepared according to the General Procedure C (29.9 mg, yield 85%). Colorless syrup, R_f = 0.31 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{20}$ +18.8 (*c*, 1.77 in $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.44 (t, *J* = 7.2 Hz, 1H, Ar-H), 7.33-7.24 (m, 21H, Ar-H), 7.23-6.95 (m, 16H, Ar-H), 5.18 (t, *J* = 9.0 Hz, 1H), 5.11 (d, *J* = 6.0 Hz, 2H), 4.98 (dd, *J* = 8.4, 9.6 Hz, 1H), 4.88 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.77 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.74 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.70 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.63 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.61 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.55 (d, *J* = 7.8 Hz, 1H, **H-1′**), 4.54 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.49 (d, *J* = 12.6 Hz, 1H, $PhCH_2$), 4.41-4.32 (m, 5H, **H-1**), 4.04 (t, *J* = 9.0 Hz, 1H), 3.79-3.68 (m, 5H), 3.67 (dd, *J* = 1.8, 10.8 Hz, 1H), 3.55 (dd, *J* = 4.2, 10.8 Hz, 1H), 3.50 (t, *J* = 9.6 Hz, 1H), 3.40 (brd, *J* = 7.8 Hz, 1H), 3.35-3.29 (m, 2H), 3.02-2.91 (m, 2H), 1.89 (s, 3H, OAc), 1.46-1.29 (m, 4H), 1.15-1.03 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 165.3, 138.8, 138.4, 138.4, 138.2, 133.1, 130.3, 129.9, 128.7, 128.6, 128.6, 128.5, 128.4, 128.1, 128.1, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.6, 127.2, 101.4 (**C-1**), 100.5 (**C-1′**), 83.2, 80.4, 78.2, 77.0, 75.5, 75.3, 75.3, 75.1, 74.4, 73.9, 73.8, 73.5, 73.3, 68.8, 68.1, 67.3, 29.2, 29.2, 23.2, 21.1. HRMS (ESI$^+$): calc. for $C_{76}H_{81}NO_{15}Na^+$ $[M+Na]^+$: 1270.5498, found: 1270.5499.

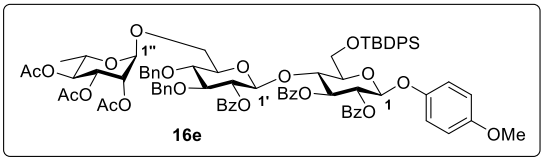
2-(4-(Benzyloxy)-3-methoxyphenyl)ethyl 6-_O_-(2,3,4-tri-_O_-acetyl-_α_-L-rhamnopyranosyl)-2-_O_-benzoyl-3,4-di-_O_-benzyl-_β_-D-glucopyranoside (16d)



Prepared according to the General Procedure C (19.6 mg, yield 73%). Colorless syrup, R_f = 0.49 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{20}$ −2.8 (*c*, 1.00 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.93 (m, 2H, Ar-H), 7.54 (tt, *J* = 1.2, 7.6 Hz, 1H, Ar-H), 7.42-7.26 (m, 12H, Ar-H), 7.13-7.09 (m, 5H, Ar-H), 6.63 (d, *J* = 2.0 Hz, 1H, Ar-H), 6.50 (dd, *J* = 2.0, 8.0 Hz, 1H, Ar-H), 6.43 (d, *J* = 8.0 Hz, 1H, Ar-H), 5.28-5.22 (m, 3H), 5.04 (t, *J* = 9.6 Hz, 1H), 4.93 (m, 2H), 4.88 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.74 (d, *J* = 1.2 Hz, 1H, **H-1′**), 4.71 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.63 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.60 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.49 (d, *J* = 7.6 Hz, 1H, **H-1**), 4.04-3.99 (m, 1H), 3.96-3.87 (m, 2H), 3.79 (t, *J* = 8.8 Hz, 1H), 3.77 (s, 3H, OMe), 3.64 (dd, *J* = 5.6, 11.2 Hz, 1H), 3.62-3.50 (m, 3H), 2.70 (dt, *J* = 2.0, 6.8 Hz, 2H), 2.08 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.96 (s, 3H, OAc), 1.15 (d, *J* = 6.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 170.2,

170.1, 165.4, 149.5, 146.7, 138.0, 137.8, 137.6, 133.2, 132.0, 130.2, 129.9, 128.7, 128.7, 128.6, 128.5, 128.3, 128.2, 128.2, 127.9, 127.9, 127.4, 120.9, 114.0, 113.0, 101.2 (**C-1**), 98.0 (**C-1′**), 83.0, 78.2, 75.4, 75.3, 75.0, 73.9, 71.2, 71.1, 70.7, 69.9, 69.4, 67.0, 66.6, 56.1, 35.8, 21.1, 21.0, 20.9, 17.5. HRMS (ESI$^+$): calc. for $C_{55}H_{60}O_{16}Na^+$ $[M+Na]^+$: 999.3774, found: 999.3797.

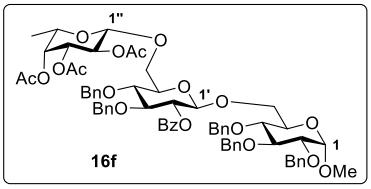
_p_-Methoxyphenyl 2,3,4-tri-*O*-acetyl-*α*-L-rhamnopyranosyl-(1→6)-2-*O*-benzoyl-3,4-di-*O*-benzyl-*β*-D-glucopyranosyl-(1→4)-2,3-di-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-*β*-D-glucopyranoside (16e)



16e

Prepared according to the General Procedure C (31.2 mg, yield 64%). Colorless syrup, R_f = 0.42 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{20}$ +16.2 (*c*, 1.70 in $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.92 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.77 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.72 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.69 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.48-7.42 (m, 4H, Ar-H), 7.41-7.27 (m, 10H, Ar-H), 7.22-7.18 (m, 6H, Ar-H), 7.12-7.06 (m, 5H, Ar-H), 5.72 (dd, *J* = 7.8, 9.6 Hz, 1H), 5.66 (t, *J* = 9.0 Hz, 1H), 5.32 (dd, *J* = 3.6, 9.6 Hz, 1H), 5.27 (dd, *J* = 1.8, 3.6 Hz, 1H), 5.14 (dd, *J* = 7.8, 9.6 Hz, 1H), 5.06 (t, *J* = 9.6 Hz, 1H), 5.01 (d, *J* = 7.8 Hz, 1H, **H-1**), 4.91 (d, *J* = 7.8 Hz, 1H, **H-1′**), 4.76 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.67 (s, 1H, **H-1′′**), 4.66 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.57 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.47-4.42 (m, 2H), 3.88 (dd, *J* = 0.6, 11.4 Hz, 1H), 3.82 (dd, *J* = 3.0, 11.4 Hz, 1H), 3.76 (dq, *J* = 6.0, 10.2 Hz, 1H), 3.70 (s, 3H, OMe), 3.65 (t, *J* = 9.0 Hz, 1H), 3.56 (dd, *J* = 1.2, 10.8 Hz, 1H), 3.46-3.41 (m, 2H), 3.19 (t, *J* = 9.0 Hz, 1H), 2.83 (dd, *J* = 1.2, 11.4 Hz, 1H), 2.24 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.97 (s, 3H, OAc), 1.15 (d, *J* = 6.0 Hz, 3H, CH_3), 1.08 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.3, 170.2, 169.8, 165.8, 165.2, 164.8, 155.6, 151.6, 137.8, 137.7, 136.2, 135.8, 134.0, 133.2, 130.4, 130.1, 130.0, 129.9, 129.9, 129.8, 129.6, 128.7, 128.6, 128.5, 128.5, 128.5, 128.2, 128.2, 128.1, 128.1, 127.9, 127.9, 119.1, 114.6, 101.1 (**C-1**), 99.6 (**C-1′**), 97.7 (**C-1′′**), 83.1, 78.4, 75.9, 75.5, 75.3, 75.2, 74.1, 73.7, 73.3, 72.2, 71.6, 70.2, 69.0, 66.6, 66.6, 61.4, 55.8, 27.0, 21.2, 21.1, 20.9, 19.4, 17.7. HRMS (ESI$^+$): calc. for $C_{82}H_{86}O_{22}SiNa^+$ $[M+Na]^+$: 1473.5272, found: 1473.5252.

Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-*β*-L-galactopyranosyl-(1→6)-2-*O*-benzoyl-3,4-di-*O*-benzyl-*β*-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (16f)

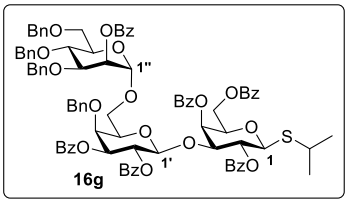


16f

Prepared according to the General Procedure C (38.1 mg, yield 75%). Colorless syrup, R_f = 0.47 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{20}$ +28.5 (*c*, 2.45 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.45 (t, *J* = 7.2 Hz, 1H, Ar-H), 7.31-7.22 (m, 20H, Ar-H), 7.10-7.08 (m, 7H, Ar-H), 5.23 (t, *J* = 8.4 Hz, 1H), 5.22 (dd, *J* = 8.0, 10.4 Hz, 1H), 5.15 (d, *J* = 3.2 Hz, 1H), 5.01 (dd, *J* = 3.6, 10.4 Hz, 1H), 4.85 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.79 (d, *J* = 10.4 Hz, 1H, $PhCH_2$), 4.73 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.72 (d,

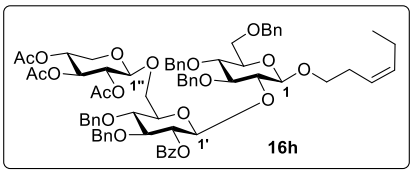
J = 12.4 Hz, 1H, $PhCH_2$), 4.70-4.64 (m, 4H, $PhCH_2$, **H-1′**), 4.57 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.56 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.44 (d, *J* = 8.0 Hz, 1H, **H-1″**), 4.41 (d, *J* = 3.6 Hz, 1H, **H-1**), 4.35 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.13 (dd, *J* = 3.2, 12.0 Hz, 1H), 4.03 (d, *J* = 9.6 Hz, 1H), 3.89-3.83 (m, 2H), 3.78-3.73 (m, 2H), 3.71-3.61 (m, 3H), 3.40-3.35 (m, 3H), 3.18 (s, 3H, OMe), 2.13 (s, 3H, OAc), 2.12 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.14 (d, *J* = 6.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 170.9, 170.2, 170.0, 165.2, 138.9, 138.5, 138.3, 138.2, 138.0, 133.2, 130.0, 129.9, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 127.7, 127.7, 127.6, 101.6 (**C-1″**), 101.5 (**C-1′**), 98.1 (**C-1**), 82.3, 82.1, 80.0, 77.7, 77.6, 75.8, 75.4, 75.3, 75.0, 74.8, 73.8, 73.5, 71.5, 70.4, 69.9, 69.3, 69.1, 68.5, 67.0, 55.1, 21.2, 20.8, 20.8, 16.2. HRMS (ESI^+): calc. for $C_{67}H_{74}O_{19}Na^+$ $[M+Na]^+$: 1205.4717, found: 1205.4721.

Isopropyl 2-*O*-benzoyl-3,4,5-tri-*O*-benzyl-*α*-D-mannopyranosyl-(1→6)-2,3-di-*O*-benzoyl-4-*O*-benzyl-*β*-D-galactopyranosyl-(1→3)-2,4,6-tri-*O*-benzoyl-1-thio-*β*-D-galactopyranoside (16g)



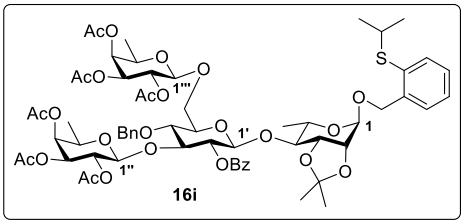
Prepared according to the General Procedure C (21.7 mg, yield 63%). Colorless syrup, R_f = 0.32 (petroleum ether-EtOAc 3:1). $[\alpha]_D$ ^{20} +22.0 (*c*, 0.80 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.05 (dd, *J* = 1.2, 8.0 Hz, 2H, Ar-H), 8.01-7.97 (m, 4H, Ar-H), 7.84-7.81 (m, 4H, Ar-H), 7.57-7.41 (m, 8H, Ar-H), 7.40-7.25 (m, 19H, Ar-H), 7.23-7.08 (m, 13H, Ar-H), 5.80 (d, *J* = 3.2 Hz, 1H), 5.59 (dd, *J* = 8.0, 10.4 Hz, 1H), 5.58 (t, *J* = 9.6 Hz, 1H), 5.46 (dd, *J* = 2.4, 3.2 Hz, 1H), 5.03 (dd, *J* = 2.8, 10.4 Hz, 1H), 4.86 (d, *J* = 10.8 Hz, 1H), 4.79 (d, *J* = 8.0 Hz, 1H, **H-1′**), 4.76 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.74 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.71 (d, *J* = 10.0 Hz, 1H, **H-1**), 4.66 (d, *J* = 2.4 Hz, 1H, **H-1″**), 4.64 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.56 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.54 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.54 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.44 (dd, *J* = 4.8, 11.6 Hz, 1H), 4.37 (dd, *J* = 3.6, 9.6 Hz, 1H), 4.33 (dd, *J* = 8.0, 12.0 Hz, 1H), 4.30 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.14-4.09 (m, 2H), 4.04 (dd, *J* = 3.2, 9.6 Hz, 1H), 3.97 (d, *J* = 2.8 Hz, 1H), 3.93 (dd, *J* = 3.6, 10.8 Hz, 1H), 3.87-3.79 (m, 3H), 3.66 (t, *J* = 6.8 Hz, 1H), 3.39 (dd, *J* = 7.6, 9.6 Hz, 1H), 3.09-3.02 (m, *J* = 6.8 Hz, 1H, SCH), 1.14 (d, *J* = 6.8 Hz, 3H, CH_3), 1.12 (d, *J* = 6.8 Hz, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) *δ* 166.3, 166.1, 166.0, 165.8, 165.0, 164.9, 138.7, 138.5, 138.1, 137.6, 133.6, 133.4, 133.4, 133.3, 133.1, 132.7, 130.3, 130.2, 130.0, 129.9, 129.8, 129.7, 129.7, 129.5, 129.0, 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 128.5, 128.3, 128.2, 128.2, 128.0, 127.9, 127.8, 127.8, 127.7, 100.8 (**C-1′**), 97.8 (**C-1″**), 83.9 (**C-1**), 78.4, 77.4, 76.6, 75.8, 75.5, 75.0, 74.7, 74.3, 73.7, 73.3, 73.1, 72.2, 71.9, 70.9, 70.5, 70.1, 69.2, 69.1, 65.4, 63.6, 35.7, 24.1, 23.9. HRMS (ESI^+): calc. for $C_{91}H_{86}O_{21}SNa^+$ $[M+Na]^+$: 1569.5275, found: 1569.5274.

(*Z*)-3-Hexenyl 2,3,4-tri-*O*-acetyl-*β*-D-xylopyranosyl-(1→6)-2-*O*-benzoyl-3,4-di-*O*-benzyl-*β*-D-glucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranoside (16h)



Prepared according to the General Procedure C (31.5 mg, yield 86%). Colorless syrup, R_f = 0.71 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{20}$ −5.7 (*c*, 2.35 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.46 (t, *J* = 7.2 Hz, 1H, Ar-H), 7.36-7.24 (m, 12H, Ar-H), 7.24-7.18 (m, 6H, Ar-H), 7.13-7.07 (m, 7H, Ar-H), 7.03-7.01 (m, 2H, Ar-H), 5.51-5.39 (m, 2H), 5.26 (dd, *J* = 8.0, 9.2 Hz, 1H), 5.20-5.15 (m, *J* = 4.4 Hz, 1H), 5.04 (d, *J* = 7.6 Hz, 1H, **H-1′**), 4.94 (dd, *J* = 4.8, 8.8 Hz, 1H), 4.91 (d, *J* = 5.2 Hz, 1H, **H-1′′**), 4.91 (d, *J* = 4.0 Hz, 1H), 4.81 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.69 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.64 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.61-4.54 (m, 6H), 4.43 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.36 (d, *J* = 7.6 Hz, 1H, **H-1**), 4.09 (dd, *J* = 5.2, 11.6 Hz, 1H), 4.01 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 3.85 (dt, *J* = 7.6, 9.6 Hz, 1H), 3.80-3.71 (m, 4H), 3.66 (dd, *J* = 5.2, 11.2 Hz, 1H), 3.61-3.49 (m, 5H), 3.44-3.37 (m, 2H), 2.38 (q, *J* = 6.8 Hz, 2H), 2.11-2.04 (m, 2H), 2.00 (s, 3H, OAc), 1.97 (s, 3H, OAc), 1.96 (s, 3H, OAc), 0.98 (t, *J* = 7.6 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 169.7, 165.3, 138.7, 138.5, 138.2, 137.8, 137.7, 133.8, 133.2, 129.9, 129.8, 128.8, 128.5, 128.5, 128.4, 128.4, 128.2, 128.2, 128.0, 127.9, 127.8, 127.7, 127.5, 127.4, 125.0, 102.2 (**C-1**), 100.3 (**C-1′**), 100.3 (**C-1′′**), 85.2, 83.2, 79.5, 78.5, 78.3, 75.8, 75.4, 75.3, 75.2, 74.9, 74.3, 73.7, 72.0, 71.4, 70.1, 69.5, 69.2, 67.6, 62.0, 28.2, 21.0, 20.9, 14.5. HRMS (ESI^+): calc. for $C_{71}H_{80}O_{19}Na^+$ $[M+Na]^+$: 1259.5186, found: 1259.5184.

2-Isopropylmercaptobenzyl 2-*O*-benzoyl-4-*O*-benzyl-3,6-di-*O*-(2,3,4-tri-*O*-acetyl-6-deoxy-*β*-D-galactopyranosyl)-*β*-D-glucopyranosyl-(1→4)-2,3-*O*-isopropylidene-*α*-L-rhamnopyranoside (16i)

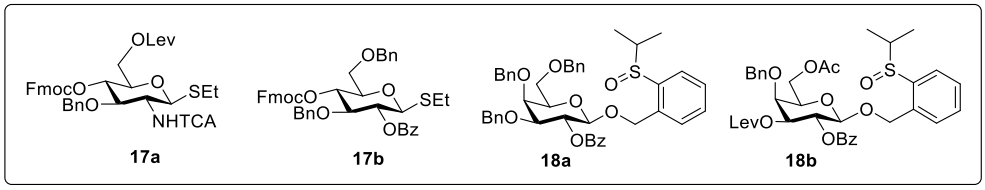


Prepared according to the General Procedure C (24.8 mg, yield 78%). Colorless syrup, R_f = 0.19 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{20}$ −22.4 (*c*, 2.28 in $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05-8.04 (m, 2H, Ar-H), 7.58 (t, *J* = 7.2 Hz, 1H, Ar-H), 7.44 (t, *J* = 7.2 Hz, 2H, Ar-H), 7.40-7.38 (m, 3H, Ar-H), 7.30-7.25 (m, 4H, Ar-H), 7.21 (dt, *J* = 1.2, 7.8 Hz, 1H, Ar-H), 7.15 (dt, *J* = 1.2, 7.8 Hz, 1H, Ar-H), 5.21-5.18 (m, 2H), 5.14-5.07 (m, 4H), 4.97 (s, 1H, **H-1**), 4.95 (dd, *J* = 3.0, 10.2 Hz, 1H), 4.92 (d, *J* = 8.4 Hz, 1H, **H-1′**), 4.74 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.61 (dd, *J* = 2.4, 10.8 Hz, 1H), 4.60 (d, *J* = 7.8 Hz, 1H, **H-1′′′**), 4.53 (t, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.48 (d, *J* = 8.4 Hz, 1H, **H-1′′**), 4.20 (dd, *J* = 8.4, 9.0 Hz, 1H), 4.09 (dd, *J* = 1.2, 11.4 Hz, 1H), 3.95 (d, *J* = 6.0 Hz, 1H), 3.86 (dd, *J* = 6.0, 7.2 Hz, 1H), 3.76 (dd, *J* = 5.4, 11.4 Hz, 1H), 3.70 (dd, *J* = 6.6, 13.8 Hz, 1H), 3.66-3.61 (m, 2H), 3.58-3.52 (m, 2H), 3.46 (dd, *J* = 7.2, 10.2 Hz, 1H), 3.32-3.25 (m, 1H, *J* = 6.6 Hz, SCH), 2.17 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.96 (s, 3H, OAc), 1.87 (s, 3H, OAc), 1.44 (s, 3H, CH_3), 1.26 (d, *J* = 6.0 Hz, 3H, CH_3), 1.21-1.19 (m, 12H, CH_3 ×4), 1.08 (d, *J* = 6.0 Hz, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.0, 170.8, 170.5, 170.4, 170.2, 169.7, 165.3, 138.7, 138.5, 135.5, 133.5, 132.6, 130.1, 129.9, 129.6, 128.8, 128.5, 128.5, 128.3, 127.9, 127.0, 109.2, 101.4 (**C-1′′**), 100.7 (**C-1′′′**), 100.1 (**C-1′**), 96.5 (**C-1**), 80.1, 80.0, 78.4, 76.3, 76.1, 75.0, 74.9, 74.2, 71.9, 71.6,

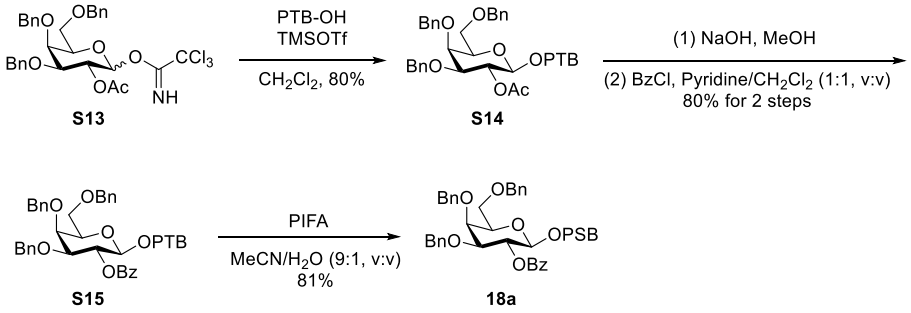
70.6, 70.3, 69.4, 69.2, 68.9, 68.5, 67.7, 64.5, 38.8, 28.1, 26.4, 23.3, 23.3, 21.1, 20.9, 20.8, 20.8, 20.8, 17.7, 16.2, 16.2. HRMS (ESI$^+$): calc. for $C_{63}H_{80}O_{25}SNa^+$ $[M+Na]^+$: 1291.4602, found: 1291.4600.

14. Fluorous-tag assisted two-directional syntheses of ST14 repeating units (Scheme 4)

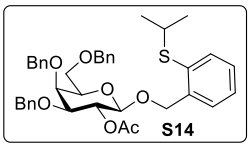
Preparation of donors 17a, 17b, 18a, 18b



Compound **17a**,[19] **17b**,[20] were synthesized according to the reported procedures.



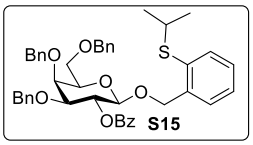
2-Isopropylmercaptobenzyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranoside (S14)



To a mixture of PTB-OH[4] (544 mg, 2.99 mmol, 1.0 equiv), **S13**[21] (2.28 g, 3.59 mmol, 1.2 equiv) and 4Å MS (100 wt%) in anhydrous CH_2Cl_2 (15.0 mL) was added TMSOTf (108 μL, 0.6 mmol, 0.2 equiv) at −20 ℃, The mixture was stirred for 1 h and quenched by addition of Et_3N (0.3 mL). The mixture was filtered through Celite and extracted with EtOAc. The organic phase was washed with saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by flash column chromatography on silica gel to give **S14** (1.88 g, yield 80%) as white foam, R_f = 0.16 (petroleum ether-EtOAc 8:1). $[\alpha]_D^{20}$ −10.3 (*c*, 0.95 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.17 (m, 4H, Ar-H), 5.43 (dd, *J* = 8.0, 10.0 Hz, 1H, H-2), 4.96 (d, *J* = 13.2 Hz, 1H, $PhCH_2$), 4.93 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.76 (d, *J* = 13.2 Hz, 1H, $PhCH_2$), 4.65 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.59 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.49 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.45-4.41 (m, 2H), 4.40 (d, *J* = 7.6 Hz, 1H, **H-1**), 3.95 (d, *J* = 2.4 Hz, 1H, H-4), 3.65 (d, *J* = 6.4 Hz, 2H), 3.56 (t, *J* = 6.4 Hz, 1H), 3.49 (dd, *J* =

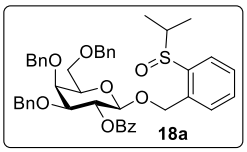
2.4, 10.0 Hz, 1H, H-6a), 3.33-3.26 (m, *J* = 6.4 Hz, 1H, SCH), 1.99 (s, 3H, OAc), 1.22 (d, *J* = 6.4 Hz, 6H, CH_3 ×2). ^{13}C NMR (150 MHz, $CDCl_3$) *δ* 169.8, 139.3, 138.7, 138.2, 138.1, 134.0, 132.5, 128.7, 128.6, 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.15, 100.7 (**C-1**), 80.6, 74.7, 73.9, 73.8, 72.8, 72.2, 71.7, 68.8, 68.8, 38.7, 23.3, 23.3, 21.3. HRMS (ESI$^+$): calc. for $C_{39}H_{44}O_7SNa^+$ [M+Na]$^+$: 679.2700, found: 679.2708.

2-Isopropylmercaptobenzyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranoside (S15)



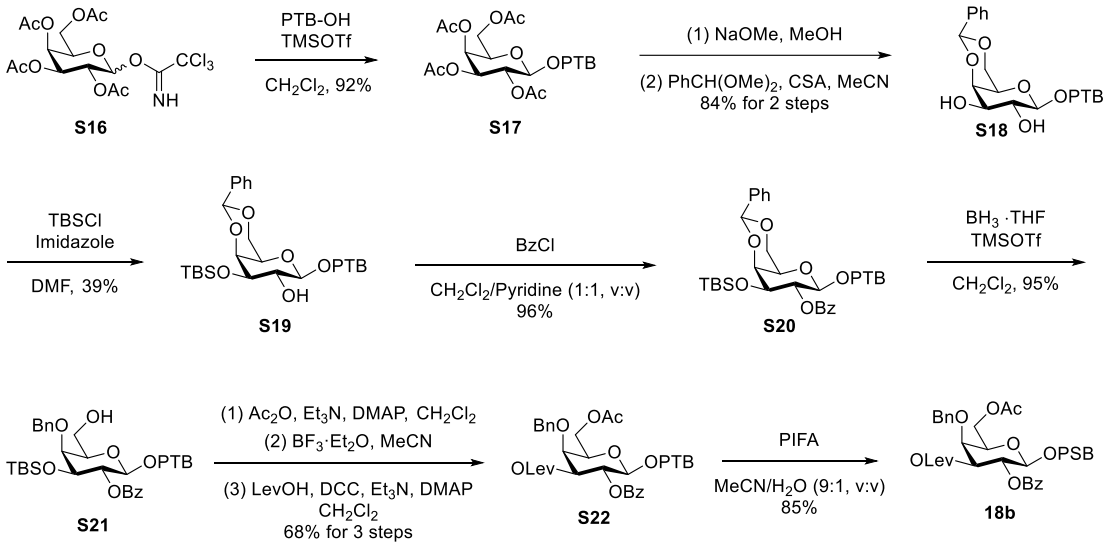
To a stirred mixture of compound **S14** (788 mg, 1.20 mmol, 1.0 equiv) in MeOH (6.0 mL) was added NaOMe (19.4 mg, 0.36 mmol, 0.3 equiv). The mixture was stirred at 40 ℃ overnight, then Amberlyst (*R*) 15 ion-exchange resin was added to neutralize the mixture. Following removal of the resin, the filtrate was evaporated under reduced pressure. To a stirred solution of the above crude product in pyridine/CH_2Cl_2 (1:1, v:v, 12.0 mL) was added benzoyl chloride (0.49 mL, 4.20 mmol, 3.5 equiv) at 0 ℃, then warmed up to 40 ℃ and stirred overnight. The reaction mixture was extracted with EtOAc. The organic phase was washed with 1 M HCl, saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by flash column chromatography on silica gel to give **S15** (690 mg, 80% yield for two steps) as white foam, R_f = 0.25 (petroleum ether-EtOAc 7:1). $[\alpha]_D^{20}$ +3.1 (*c*, 0.97 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.98 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.55 (t, *J* = 7.2 Hz, 1H, Ar-H), 7.34 (t, *J* = 7.2 Hz, 1H, Ar-H), 7.37-7.26 (12H, m, Ar-H), 7.19-7.07 (6H, m, Ar-H), 6.95 (t, *J* = 7.6 Hz, 1H, Ar-H), 5.72 (dd, *J* = 8.0, 10.0 Hz, 1H), 4.99 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.92 (d, *J* = 13.6 Hz, 1H, $PhCH_2$), 4.83 (d, *J* = 13.2 Hz, 1H, $PhCH_2$), 4.64 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.62 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.52 (d, *J* = 8.0 Hz, 1H, **H-1**), 4.50-4.42 (m, 3H), 4.01 (d, *J* = 2.4 Hz, 1H, H-4), 3.72-3.65 (m, 2H), 3.63-3.58 (m, 2H), 3.22-3.12 (m, *J* = 6.8 Hz, 1H, SCH), 1.11 (d, *J* = 6.8 Hz, 3H, CH_3), 1.11 (d, *J* = 6.8 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 165.5, 139.2, 138.6, 138.1, 137.9, 134.0, 133.0, 132.4, 130.5, 130.1, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.2, 128.1, 127.9, 127.8, 127.8, 127.1, 100.5 (**C-1**), 80.1, 74.7, 73.9, 73.8, 72.6, 72.2, 71.9, 68.8, 68.4, 38.6, 23.2, 23.2. HRMS (ESI$^+$): calc. for $C_{44}H_{46}O_7SNa^+$ [M+Na]$^+$: 741.2856, found: 741.2858.

2-Isopropylsulfinylbenzyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranoside (18a)

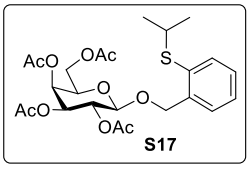


To a stirred solution of **S15** (690 mg, 0.96 mmol, 1.0 equiv) in MeCN/H_2O (9:1, v:v, 10.0 mL) was added PIFA (454 mg, 1.06 mmol, 1.1 equiv), the mixture was stirred at room temperature for 1 h. The reaction mixture was extracted with EtOAc, washed successively with saturated $Na_2S_2O_3$, saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by flash column chromatography on silica gel to give **18a** (569 mg, yield 81%) as white foam, R_f = 0.25 (petroleum ether-EtOAc 7:1). A mixture of sulfoxide *R*/*S* (1.3:1) isomers. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.99 (d, *J* = 7.2 Hz, 2.6H, Ar-H), 7.89 (d, *J* = 7.6 Hz, 2H, Ar-H),

7.78 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.75 (d, *J* = 8.0 Hz, 1.3H, Ar-H), 7.60-7.54 (m, 2.6H, Ar-H), 7.46-7.25 (m, 34.6H, Ar-H), 7.18-7.11 (m, 11H, Ar-H), 5.67 (dd, *J* = 8.0, 9.6 Hz, 1.3H), 5.63 (dd, *J* = 8.0, 9.6 Hz, 1H), 4.97 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.96 (d, *J* = 11.6 Hz, 1.3H, $PhCH_2$), 4.89 (d, *J* = 12.0 Hz, 1.3H, $PhCH_2$), 4.84 (d, *J* = 12.8 Hz, 1H, $PhCH_2$), 4.71-4.58 (m, 8.3H), 4.48-4.43 (m, 7.6H), 4.00 (d, *J* = 2.4 Hz, 2.3H), 3.69-3.57 (m, 9.3H), 2.83-2.73 (m, 2.3H, SCH), 1.13 (d, *J* = 6.8 Hz, 3H, CH_3), 1.03 (d, *J* = 6.8 Hz, 3.9H, CH_3), 0.90 (d, *J* = 6.4 Hz, 3H, CH_3), 0.85 (d, *J* = 6.8 Hz, 3.9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 138.6, 138.5, 138.0, 137.9, 137.7, 135.2, 133.4, 133.3, 130.9, 130.8, 130.2, 130.1, 130.1, 130.0, 129.8, 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 128.5, 128.5, 128.2, 128.1, 128.0, 127.9, 127.9, 125.2, 125.2, 100.9 (**C-1**), 99.9 (**C-1**), 80.0, 80.0, 74.8, 74.8, 74.1, 74.0, 73.9, 73.8, 72.5, 72.5, 72.0, 71.9, 71.8, 68.8, 66.4, 65.5, 17.4, 17.3, 12.9, 12.6. HRMS (ESI^+): calc. for $C_{44}H_{46}O_8SNa^+$ $[M+Na]^+$: 757.2806, found: 757.2798.



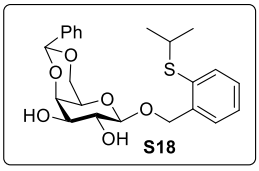
2-Isopropylmercaptobenzyl 2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranoside (S17)



A suspension of PTB-OH (2.2 g, 12.20 mmol, 2.0 equiv) and **S16**[22] (3.0 g, 6.09 mmol, 1.0 equiv) containing activated 4Å MS (100 wt%) in anhydrous CH_2Cl_2 (12.0 mL) was stirred at room temperature for 10 min under argon. After cooling to −20 ℃, TMSOTf (0.44 mL, 2.44 mmol, 0.4 equiv) was added. The reaction mixture was stirred at −20 ℃ for 1 h and quenched by addition of Et_3N (1.0 mL). The mixture was filtered through Celite and extracted with EtOAc, washed with saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by flash column chromatography on silica gel to give **S17** (2.86 g, yield 92%) as colorless syrup, R_f = 0.22 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{20}$ −22.4 (*c*, 2.8 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 2.0, 7.6 Hz, 1H, Ar-H), 7.37 (dd, *J* = 2.4, 7.6 Hz, 1H, Ar-H), 7.26-7.20 (m, 2H), 5.37 (dd, *J* = 0.8, 3.6 Hz, 1H, H-4), 5.26 (dd, *J* = 8.0, 10.4 Hz, 1H, H-2), 5.01-4.95 (m, 2H), 4.82 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.52 (d, *J* = 8.0 Hz, 1H, **H-1**), 4.21 (dd, *J* = 6.4, 11.2 Hz, 1H, H-6a), 4.13 (dd, *J* = 7.2, 11.2 Hz, 1H, H-6b), 3.89 (dt, *J* = 0.8, 6.8 Hz, 1H, H-5), 3.38-3.28 (m, *J* = 6.8 Hz, 1H,

SCH), 2.13 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.00 (s, 3H, OAc), 1.95 (s, 3H, OAc), 1.25 (d, J = 6.8 Hz, 6H, CH_3 ×2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.5, 170.4, 169.7, 138.3, 134.7, 132.4, 128.8, 128.4, 127.1, 100.3 (**C-1**), 71.1, 70.9, 69.3, 69.0, 67.3, 61.5, 38.7, 23.3, 23.3, 21.1, 20.9, 20.9, 20.8. HRMS (ESI$^+$): calc. for $C_{24}H_{32}O_{10}SNa^+$ $[M+Na]^+$: 535.1608, found: 535.1597.

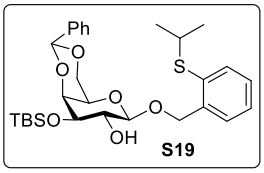
2-Isopropylmercaptobenzyl 4,6-*O*-benzylidene-*β*-D-galactopyranoside (S18)



S18

To a stirred mixture of **S17** (2.56 g, 4.99 mmol, 1.0 equiv) in MeOH (16.6 mL) was added NaOMe (80.9 mg, 1.50 mmol, 0.3 equiv). The mixture was stirred at room temperature for 1 h, then Amberlyst (*R*) 15 ion-exchange resin was added to neutralize the mixture. After removal of the resin, the filtrate was evaporated under reduced pressure. To a stirred solution of the above crude product in MeCN (4.9 mL) was added CSA (232 mg, 1.00 mmol, 0.2 equiv) and $PhCH(OMe)_2$ (1.1 mL, 7.50 mmol, 1.5 equiv). The mixture was stirred at room temperature overnight and quenched by addition of Et_3N (0.5 mL). The mixture was extracted with EtOAc, washed with H_2O, saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and recrystallized with petroleum ether/CH_2Cl_2 to give **S18** (1.82 g, 84% yield for two steps) as white solid, R_f = 0.42 (petroleum ether-EtOAc 4:1). m.p. 89.8-90.5 ℃. $[\alpha]_D^{20}$ −29.4 (*c*, 1.90 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.47 (m, 2H, Ar-H), 7.45 (dd, J = 1.2, 7.6 Hz, 1H, Ar-H), 7.40 (dd, J = 1.2, 7.6 Hz, 1H, Ar-H), 7.35-7.33 (m, 3H, Ar-H), 7.27 (dd, J = 1.6, 7.2 Hz, 1H, Ar-H), 7.40 (dd, J = 1.6, 7.2 Hz, 1H, Ar-H), 5.54 (s, 1H, PhCH), 5.03 (d, J = 12.0 Hz, 1H, $PhCH_2$), 4.83 (d, J = 12.0 Hz, 1H, $PhCH_2$), 4.37 (d, J = 7.6 Hz, 1H, **H-1**), 4.35 (dd, J = 1.2, 11.2 Hz, 1H, H-6a), 4.18 (d, J = 3.6 Hz, 1H, H-4), 4.07 (dd, J = 1.6, 12.4 Hz, 1H, H-6b), 3.80 (dd, J = 7.6, 9.6 Hz, 1H, H-2), 3.68 (dd, J = 4.0, 9.6 Hz, 1H, H-3), 3.46 (brd, J = 0.8 Hz, 1H, H-5), 3.44-3.37 (m, J = 6.8 Hz, 1H, SCH), 2.54 (brs, 2H, OH ×2), 1.28 (d, J = 6.8 Hz, 6H, CH_3 ×2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 137.7, 135.4, 131.4, 129.7, 129.4, 128.7, 128.4, 126.8, 126.6, 102.0, 101.6 (**C-1**), 75.5, 72.8, 71.9, 69.7, 69.3, 66.9, 38.1, 23.3, 23.2. HRMS (ESI$^+$): calc. for $C_{23}H_{28}O_6SNa^+$ $[M+Na]^+$: 455.1499, found: 455.1511.

2-Isopropylmercaptobenzyl 3-*O*-*tert*-butyldimethylsilyl-4,6-*O*-benzylidene-*β*-D-galactopyranoside (S19)

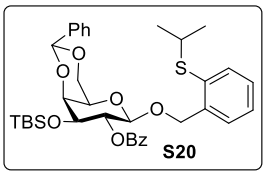


S19

To a stirred solution of compound **S18** (1.77 g, 4.10 mmol, 1.0 equiv) in DMF (8.2 mL) was added imidazole (1.23 g, 8.18 mmol, 3.0 equiv) and *tert*-butyldimethylsilyl chloride (835.6 mg, 12.30 mmol, 3.0 equiv) at 0 ℃. The mixture was stirred at room temperature overnight and extracted with EtOAc, washed with 1 M HCl, saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by flash column chromatography on silica gel to give **S19** (848 mg, yield 39%) as colorless syrup, R_f = 0.25 (petroleum ether-EtOAc 4:1). $[\alpha]_D^{20}$ −2.2 (*c*, 1.08 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.48 (m, 3H, Ar-H), 7.42-7.38 (m, 4H, Ar-H), 7.35-7.29 (m, 3H, Ar-H), 7.24-7.20 (m, 2H, Ar-H), 5.51 (s, 1H, PhCH), 5.04 (d, J = 12.4 Hz, 1H, $PhCH_2$), 4.86 (d, J = 12.4 Hz, 1H, $PhCH_2$), 4.37 (d, J = 7.6

Hz, 1H, **H-1**), 4.36 (dd, *J* = 1.2, 12.0 Hz, 1H), 4.06 (dd, *J* = 1.6, 12.4 Hz, 1H), 4.01 (d, *J* = 3.2 Hz, 1H), 3.88 (t, *J* = 8.0 Hz, 1H), 3.70 (dd, *J* = 4.0, 9.6 Hz, 1H), 3.41 (brs, 1H), 3.40-3.32 (m, *J* = 6.4 Hz, 1H, SCH), 2.38 (brs, 1H), 1.27 (d, *J* = 6.8 Hz, 3H, CH_3), 1.26 (d, *J* = 6.4 Hz, 3H, CH_3), 0.89 (s, 9H, $C(CH_3)_3$), 0.10 (s, 3H, CH_3), 0.09 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 138.2, 134.8, 132.2, 129.2, 128.9, 128.3, 128.2, 127.0, 126.4, 102.3, 101.1 (**C-1**), 76.8, 74.3, 71.2, 69.5, 69.1, 67.0, 38.5, 26.0, 23.3, 23.3, 18.5, −4.1, −4.5. HRMS (ESI$^+$): calc. for $C_{29}H_{42}O_6SSiNa^+$ $[M+Na]^+$: 569.2364, found: 569.2364.

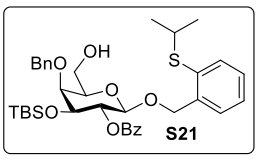
2-Isopropylmercaptobenzyl 2-*O*-benzoyl-3-*O*-*tert*-butyldimethylsilyl-4,6-*O*-benzylidene-*β*-D-galactopyranoside (S20)



S20

To a stirred soltuion of compound **S19** (848 mg, 1.55 mmol, 1.0 equiv) in CH_2Cl_2/pyridine (1:1, v:v, 7.8 mL) was added benzoyl chloride (0.9 mL, 7.75 mmol, 5.0 equiv) at 0 ℃. The mixture was warmed up to 80 ℃, stirred overnight and extracted with EtOAc, washed with 1 M HCl, saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by flash column chromatography on silica gel to give **S20** (962 mg, yield 96%) as yellow solid, R_f = 0.20 (petroleum ether-EtOAc 6:1). m.p. 109.6-110.5 ℃. $[\alpha]_D^{20}$ +26.7 (*c*, 1.73 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 0.8, 8.0 Hz, 2H, Ar-H), 7.58-7.51 (m, 3H, Ar-H), 7.42-7.30 (m, 7H, Ar-H), 7.11 (dt, *J* = 0.8, 7.6 Hz, 1H, Ar-H), 6.96 (dt, *J* = 0.8, 7.2 Hz, 1H, Ar-H), 5.59 (dd, *J* = 8.4, 9.2 Hz, 1H, H-2), 5.55 (s, 1H, PhCH), 4.97 (d, *J* = 13.6 Hz, 1H, $PhCH_2$), 4.92 (d, *J* = 13.6 Hz, 1H, $PhCH_2$), 4.60 (d, *J* = 8.0 Hz, 1H, **H-1**), 4.42 (dd, *J* = 0.8, 12.4 Hz, 1H, H-6a), 4.11 (d, *J* = 12.4 Hz, 1H, H-6b), 4.09 (d, *J* = 3.6 Hz, 1H, H-4), 3.98 (dd, *J* = 3.6, 9.6 Hz, 1H, H-3), 3.47 (s, 1H, H-5), 3.24-3.14 (m, *J* = 6.8 Hz, 1H, SCH), 1.14 (d, *J* = 6.4 Hz, 6H, CH_3 × 2), 0.74 (s, 9H, $C(CH_3)_3$), 0.02 (s, 3H, CH_3), −0.14 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 139.4, 138.0, 134.0, 132.9, 132.6, 130.7, 130.4, 130.0, 129.0, 128.7, 128.5, 128.4, 128.3, 127.8, 127.2, 126.5, 101.1, 100.3 (**C-1**), 76.8, 72.6, 72.4, 69.3, 68.2, 67.0, 38.7, 25.6, 23.3, 23.2, 18.1, −4.4, −4.5. HRMS (ESI$^+$): calc. for $C_{36}H_{46}O_7SSiNa^+$ $[M+Na]^+$: 673.2626, found: 673.2625.

2-Isopropylmercaptobenzyl 2-*O*-benzoyl-3-*O*-*tert*-butyldimethylsilyl-4-*O*-benzyl-*β*-D-galactopyranoside (S21)

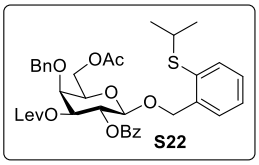


S21

To a stirred suspention of **S20** (914.6 mg, 1.41 mmol, 1.0 equiv) and 4Å MS (100 wt%) in CH_2Cl_2 (14.0 mL) was added BH_3·THF (7.0 mL, 1 M in THF, 7.03 mmol, 5.0 equiv) and TMSOTf (0.13 mL, 0.70 mmol, 0.5 equiv) at 0 ℃. The mixture was stirred at room temperature for 3 h and quenched by addition of Et_3N (0.2 mL). The reaction mixture was extracted with EtOAc, washed with saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* to afford **S21** (871 mg, yield 95%) as white foam, R_f = 0.39 (petroleum ether-EtOAc 3:1). $[\alpha]_D^{20}$ −6.5 (*c*, 1.92 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 1.6, 8.4 Hz, 2H, Ar-H), 7.54 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.43-7.27 (m, 9H, Ar-H), 7.12 (dt, *J* = 1.2, 7.6 Hz, 1H, Ar-H),

6.95 (dt, *J* = 1.2, 7.6 Hz, 1H, Ar-H), 5.66 (dd, *J* = 8.0, 9.6 Hz, 1H, H-2), 5.08 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.92 (d, *J* = 13.6 Hz, 1H, $PhCH_2$), 4.88 (d, *J* = 13.6 Hz, 1H, $PhCH_2$), 4.60 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.52 (d, *J* = 8.0 Hz, 1H, **H-1**), 3.91 (dd, *J* = 2.4, 9.6 Hz, 1H, H-3), 3.86 (dd, *J* = 6.8, 10.8 Hz, 1H, H-6a), 3.72 (d, *J* = 2.4 Hz, 1H, H-4), 3.61-3.51 (m, 2H, H-5, H-6b), 3.24-3.14 (m, *J* = 6.8 Hz, 1H, SCH), 1.65 (s, 1H, OH), 1.15 (d, *J* = 6.8 Hz, 6H, CH_3 ×2), 0.78 (s, 9H, $C(CH_3)_3$), 0.09 (s, 3H, CH_3), −0.11 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 165.4, 139.0, 138.6, 134.2, 133.0, 132.4, 130.6, 130.1, 128.7, 128.7, 128.5, 128.4, 128.1, 127.9, 127.1, 100.4 (**C-1**), 76.6, 75.1, 75.0, 74.7, 73.0, 68.2, 62.3, 38.7, 25.8, 23.2, 23.1, 18.0, −3.9, −4.8. HRMS (ESI^+): calc. for $C_{36}H_{48}O_7SSiNa^+$ $[M+Na]^+$: 675.2782, found: 675.2780.

2-Isopropylmercaptobenzyl 2-*O*-benzoyl-3-*O*-levulinyl-4-*O*-benzyl-6-*O*-acetyl-*β*-D-galactopyranoside (S22)

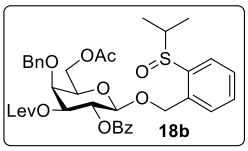


S22

To a stirred solution of **S21** (500 mg, 0.77 mmol, 1.0 equiv) and DMAP (18.7 mg, 0.15 mmol, 0.2 equiv) in anhydrous CH_2Cl_2 (3.0 mL) were successively added Et_3N (0.2 mL, 1.53 mmol, 2.0 equiv) and acetic anhydride (75.2 μL, 1.53 mmol, 2.0 equiv) at 0 ℃. The mixture was warmed up to room temperature, stirred for 0.5 h and extracted with EtOAc, washed with saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* to give crude product. To a stirred solution of the above crude product in MeCN (3.0 mL) was added BF_3 Et_2O (0.12 mL, 0.92 mmol, 1.2 equiv) at 0 ℃. The mixture was stirred at 0 ℃ for 0.5 h, quenched by addition of saturated $NaHCO_3$ (0.5 mL) and extracted with EtOAc, washed with saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* to give crude product. To a stirred solution of the above crude product, DCC (316 mg, 1.53 mmol, 2.0 equiv) and DMAP (46.8 mg, 0.38 mmol, 0.5 equiv) in CH_2Cl_2 (3.0 mL) were successively added Et_3N (0.2 mL, 1.53 mmol, 2.0 equiv) and levulinic acid (0.16 mL, 1.53 mmol, 2.0 equiv) at 0 ℃. The resulting mixture was warmed up to room temperature, stirred overnight and filtered through Celite and washed with CH_2Cl_2. The organic phase was concentrated *in vacuo* and purified by flash column chromatography on silica gel to give **S22** (353 mg, 68% yield for three steps) as white solid, R_f = 0.25 (petroleum ether-EtOAc 3:1). m.p. 105.2-106.4 ℃. $[\alpha]_D^{20}$ −6.5 (*c*, 1.92 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.96 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.55 (t, *J* = 7.2 Hz, 1H, Ar-H), 7.43-7.26 (m, 9H, Ar-H), 7.13 (t, *J* = 7.6 Hz, 1H, Ar-H), 6.98 (t, *J* = 7.6 Hz, 1H, Ar-H), 5.71 (dd, *J* = 8.0, 10.4 Hz, 1H, H-2), 5.13 (dd, *J* = 2.8, 10.4 Hz, 1H, H-3), 4.93 (d, *J* = 13.2 Hz, 1H, $PhCH_2$), 4.87 (d, *J* = 13.2 Hz, 1H, $PhCH_2$), 4.85 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.61 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.60 (d, *J* = 8.4 Hz, 1H, **H-1**), 4.32 (dd, *J* = 6.4, 11.2 Hz, 1H, H-6a), 4.08 (dd, *J* = 6.8, 11.2 Hz, 1H, H-6b), 3.96 (d, *J* = 2.8 Hz, 1H, H-4), 3.74 (t, *J* = 6.4 Hz, 1H, H-5), 3.23-3.13 (m, *J* = 6.8 Hz, 1H, SCH), 2.67-2.57 (m, 1H), 2.54-2.49 (m, 1H), 2.48-2.43 (m, 1H), 2.36-2.27 (m, 1H), 2.00 (s, 3H), 1.99 (s, 3H), 1.12 (d, *J* = 6.8 Hz, 3H, CH_3), 1.12 (d, *J* = 6.8 Hz, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) *δ* 206.2, 172.4, 170.6, 165.4, 138.6, 137.8, 134.4, 133.3, 132.4, 130.1, 129.9, 128.7, 128.6, 128.5, 128.5, 128.1, 128.0, 127.0, 100.1 (**C-1**), 75.1, 74.3, 73.7,

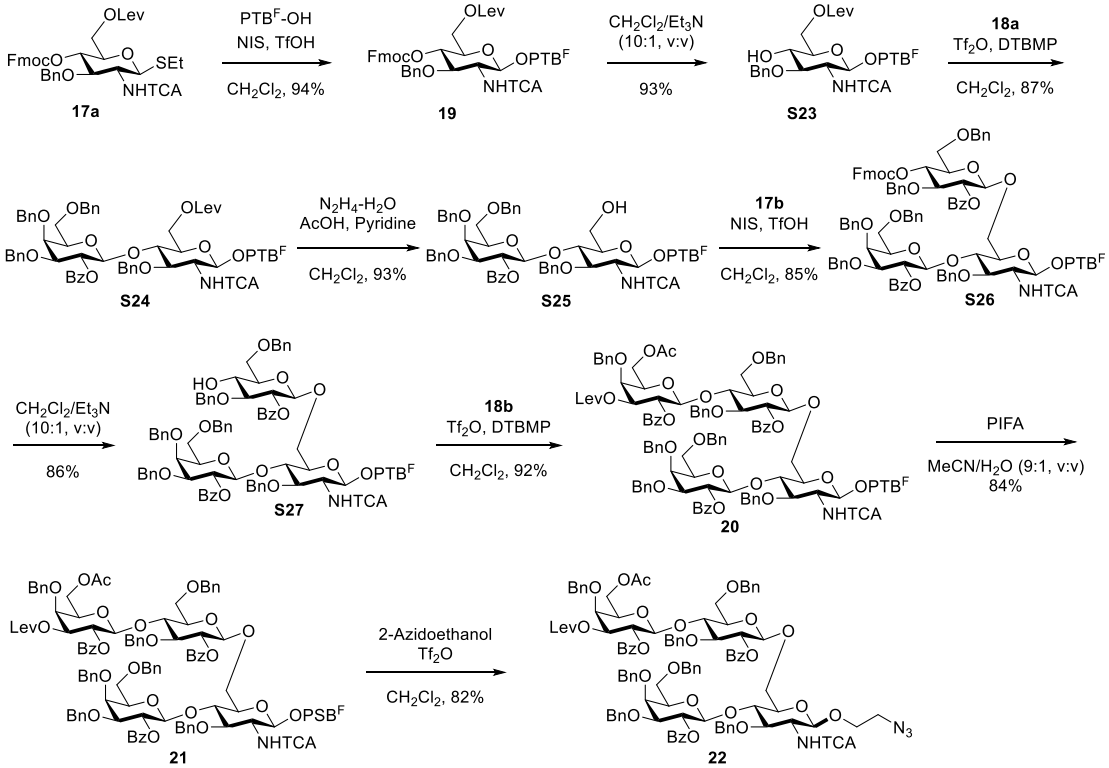
72.3, 70.3, 68.6, 62.4, 38.6, 37.8, 29.7, 28.1, 23.2, 23.1, 21.0. HRMS (ESI^+): calc. for $C_{37}H_{42}O_{10}SNa^+$ $[M+Na]^+$: 701.2391, found: 701.2391.

2-Isopropylsulfinylbenzyl 2-*O*-benzoyl-3-*O*-levulinyl-4-*O*-benzyl-6-*O*-acetyl-*β*-D-galactopyranoside (18b)

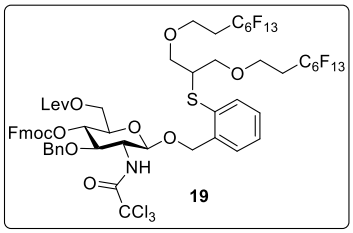


To a stirred solution of **S22** (333 mg, 0.49 mmol, 1.0 equiv) in MeCN/H_2O (9:1, v:v, 6.0 mL) was added PIFA (232 mg, 0.54 mmol, 1.1 equiv), the mixture was stirred for 1 h and extracted with EtOAc, washed with saturated $Na_2S_2O_3$, saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by flash column chromatography on silica gel to give **18b** (290 mg, yield 85%) as colorless syrup, R_f = 0.3 (petroleum ether-EtOAc 1:1). A mixture of sulfoxide *R*/*S* (1.4:1) isomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.97 (m, 2.8H, Ar-H), 7.91-7.89 (m, 2H, Ar-H), 7.80 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.76 (d, *J* = 7.6 Hz, 1.4H, Ar-H), 7.59-7.54 (m, 2.4H, Ar-H), 7.46-7.20 (m, 24H, Ar-H), 5.70-5.63 (m, 2.4H), 5.17 (dd, *J* = 2.8, 10.4 Hz, 1.4H), 5.11 (dd, *J* = 2.8, 10.4 Hz, 1H), 4.92-4.83 (m, 4.8H), 4.76-4.69 (m, 4H), 4.61-4.56 (m, 3.4H), 4.31 (dd, *J* = 6.4, 11.2 Hz, 1H), 4.24 (dd, *J* = 6.4, 11.2 Hz, 1.4H), 4.10 (dd, *J* = 6.4, 11.2 Hz, 1H), 4.04 (dd, *J* = 6.8, 11.2 Hz, 1.4H), 3.97 (t, *J* = 2.4 Hz, 2.4H), 3.76 (t, *J* = 6.8 Hz, 2.4H), 2.84-2.75 (m, 2.4H), 2.64-2.58 (m, 2.4H), 2.53-2.44 (m, 4.8H), 2.34-2.26 (m, 2.4H), 2.02-1.99 (m, 14.4H), 1.15 (d, *J* = 7.2 Hz, 3H), 1.06 (d, *J* = 7.2 Hz, 4.2H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 7.2 Hz, 4.2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 172.4, 172.4, 170.7, 170.6, 165.3, 137.7, 137.7, 134.8, 134.3, 133.6, 133.6, 131.0, 130.8, 130.2, 130.0, 130.0, 129.7, 129.6, 129.6, 129.0, 128.9, 128.7, 128.7, 128.7, 128.6, 128.5, 128.2, 128.2, 125.3, 125.3, 100.8 (**C-1**), 99.6 (**C-1**), 75.2, 74.1, 73.7, 73.6, 72.7, 72.6, 70.1, 70.0, 66.8, 65.6, 62.5, 62.3, 53.9, 53.6, 37.8, 29.7, 28.1, 21.0, 17.3, 12.8, 12.6. HRMS (ESI^+): calc. for $C_{37}H_{42}O_{11}SNa^+$ $[M+Na]^+$: 717.2340, found: 717.2321.

Synthesis of ST14 tetrasaccharide 22



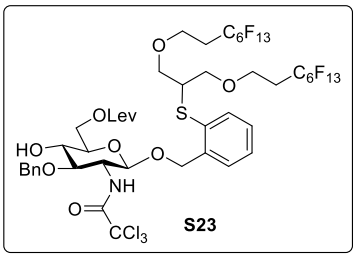
2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 3-*O*-benzyl-4-*O*-fluorenylmethoxycarbonyl-6-*O*-levulinyl-2-deoxy-2-trichloroacetamino-*β*-D-glucopyranoside (19)



A solution of **17a**[19] (1.50 g, 1.93 mmol, 1.2 equiv), PTB^F-OH (1.45 g, 1.60 mmol, 1.0 equiv) and 4Å MS (100 wt%) in anhydrous CH_2Cl_2 (16.0 mL) was stirred at −20 ℃ for 10 min, then *N*-iodosuccinimide (541.3 mg, 2.40 mmol, 1.5 equiv) and TfOH (28.4 μL, 0.32 mmol, 0.2 equiv) were added. The reaction mixture was stirred at −20 ℃ for 1 h and quenched by addition of Et_3N (0.5 mL). The suspension was filtered through Celite and concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **19** (2.45 g, yield 94%) as white solid, R_f = 0.33 (petroleum ether-EtOAc 3:1). m.p. 88.5-90.8 ℃. $[\alpha]_D^{20}$ +9.6 (*c*, 0.51 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 3.2, 7.2 Hz, 2H, Ar-H), 7.58 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.54 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.46-7.35 (m, 4H, Ar-H), 7.32-7.14 (m, 9H, Ar-H), 6.96 (d, *J* = 7.6 Hz, 1H, NH), 5.03 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 5.01 (d, *J* = 7.6 Hz, 1H, **H-1**), 4.93 (t, *J* = 9.2 Hz, 1H), 4.80 (d, *J* =12.0 Hz, 1H, $PhCH_2$), 4.60 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.57 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.47 (dd, *J* = 6.8, 10.4 Hz, 1H), 4.36-4.22 (m, 4H), 4.17 (t, *J* = 7.2 Hz, 1H, H-2), 3.79-3.74 (m, 1H), 3.70 (t, *J* =6.8 Hz, 4H), 3.67-3.57 (m, 5H), 3.34-3.28 (m, *J* = 5.6 Hz, 1H, SCH), 2.74-2.69 (m, 2H), 2.62-2.57 (m, 2H), 2.42-2.29 (m, 4H, C**H**$_2$C**H**$_2$C$_6$F$_{13}$), 2.13 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.6, 172.6, 162.1, 154.4, 143.5, 143.2, 141.5, 141.5, 138.7, 137.4, 133.9, 132.7, 129.5, 128.9, 128.6, 128.2, 128.2, 128.1, 128.1, 128.0, 127.9, 127.4, 125.3, 125.1,

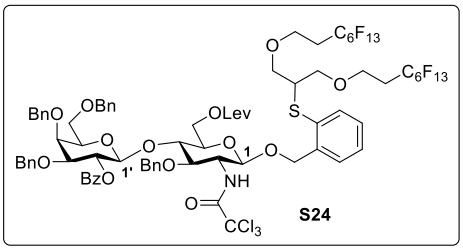
120.3, 120.3, 98.5 (**C-1**), 92.5, 77.1, 75.3, 74.8, 71.9, 70.5, 70.4, 69.5, 63.3 (t, *J* = 4.0 Hz, **C**$H_2CH_2C_6F_{13}$), 62.7, 58.4, 48.6, 46.9, 38.0, 31.5 (t, *J* = 21.0 Hz, CH_2**C**$H_2C_6F_{13}$), 30.0, 28.1. HRMS (ESI^+): calc. for $C_{61}H_{52}Cl_3F_{26}NO_{12}SNa^+$ $[M+Na]^+$: 1644.1753, found: 1644.1760.

2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 3-*O*-benzyl-6-*O*-levulinyl-2-deoxy-2-trichloroacetamino-*β*-D-glucopyranoside (S23)



To a stirred solution of **19** (1.1 g, 0.68 mmol) in CH_2Cl_2 (13.0 mL) was added Et_3N (1.3 mL). The resulting mixture was stirred at room temperature for 3 h and concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **S23** (885 mg, yield 93%) as white solid. R_f = 0.26 (petroleum ether-EtOAc 2:1). m.p. 82.5-83.3 ℃. $[\alpha]_D^{20}$ −14.1 (*c*, 2.14 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.44-7.40 (m, 2H, Ar-H), 7.31-7.26 (m, 5H, Ar-H), 7.23-7.20 (m, 2H, Ar-H), 6.89 (d, *J* = 8.0 Hz, 1H, NH), 5.02 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.87 (d, *J* = 8.4 Hz, 1H, **H-1**), 4.80-4.73 (m, 3H), 4.61 (dd, *J* = 3.6, 12.0 Hz, 1H, H-6a), 4.24 (dd, *J* = 2.4, 12.0 Hz, 1H, H-6b), 3.94 (dd, *J* = 8.8, 10.0 Hz, 1H, H-2), 3.70 (t, *J* = 6.8 Hz, 4H), 3.66-3.57 (m, 6H), 3.49 (ddd, *J* = 2.4, 3.6, 9.6 Hz, 1H, H-5), 3.33-3.28 (m, *J* = 6.0 Hz, 1H, SCH), 3.03 (d, *J* = 4.0 Hz, 1H, OH), 2.79-2.75 (m, 2H), 2.62-3.58 (m, 2H), 2.41-2.29 (m, 4H, C**H**$_2$C**H**$_2C_6F_{13}$), 2.17 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ* 207.1, 173.7, 162.0, 138.9, 138.1, 133.6, 132.5, 129.3, 128.8, 128.7, 128.3, 128.2, 127.9, 99.1 (**C-1**), 92.7, 79.5, 74.9, 74.2, 71.1, 70.3, 69.3, 63.3 (t, *J* = 4.0 Hz, **C**$H_2CH_2C_6F_{13}$), 58.3, 48.5, 38.2, 31.5 (t, *J* = 21.0 Hz, CH_2**C**$H_2C_6F_{13}$), 30.0, 28.1. HRMS (ESI^+): calc. for $C_{46}H_{42}Cl_3F_{26}NO_{10}SNa^+$ $[M+Na]^+$: 1422.1072, found: 1422.1090.

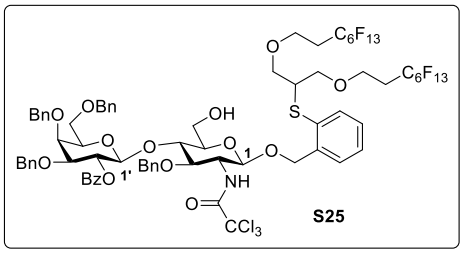
2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl-(1→4)-3-*O*-benzyl-6-*O*-levulinyl-2-deoxy-2-trichloroacetamino-*β*-D-glucopyranoside (S24)



A solution of **18a** (220.3 mg, 0.30 mmol, 1.2 equiv) and DTBMP (76.9 mg, 0.37 mmol, 1.5 equiv) in CH_2Cl_2 (3.3 mL) in the presence of 4Å MS (100 wt%) was stirred for 15 min at −40 ℃. After addition of Tf_2O (50.3 μL, 0.30 mmol, 1.2 equiv), the solution was stirred at −40 ℃ for 3 min, and then **S23** (350 mg, 0.25 mmol, 1.0 equiv) in CH_2Cl_2 (1.7 mL) was added. The reaction mixture was stirred at −40 ℃ for 30 min, quenched by addition of Et_3N (0.2 mL) and extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **S24** (421 mg, yield 87%) as colorless syrup, R_f = 0.47 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{20}$ −2.1 (*c*, 2.32 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.04-8.02 (m, 2H, Ar-H), 7.56 (t, *J* = 7.2 Hz,

1H, Ar-H), 7.45-7.38 (m, 3H, Ar-H), 7.36-7.25 (m, 10H, Ar-H), 7.22-7.11 (m, 13H, Ar-H), 6.99 (d, *J* = 8.4 Hz, 1H, NH), 5.64 (dd, *J* = 8.0, 10.0 Hz, 1H), 4.99 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.92 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.90 (d, *J* = 12.8 Hz, 1H, $PhCH_2$), 4.72 (d, *J* = 7.2 Hz, 1H, **H-1**), 4.64 (d, *J* = 7.6 Hz, 1H, **H-1′**), 4.63 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.62 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.56 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.54 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.50 (d, *J* = 12.8 Hz, 1H, $PhCH_2$), 4.34 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.29 (dd, *J* = 4.0, 11.6 Hz, 1H), 4.25 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.17 (dd, *J* = 3.6, 11.6 Hz, 1H), 4.00 (d, *J* = 2.4 Hz, 1H), 3.93-3.77 (m, 4H), 3.72 (dd, *J* = 6.0, 7.2 Hz, 1H), 3.68-3.63 (m, 4H), 3.61-3.54 (m, 4H), 3.53-3.47 (m, 2H), 3.37 (dd, *J* = 5.2, 9.2 Hz, 1H), 3.28-3.22 (m, *J* = 6.0 Hz, 1H, SCH), 2.77 (ddd, *J* = 4.4, 8.4, 18.0 Hz, 1H), 2.60-2.48 (m, 2H), 2.42-2.27 (m, 5H, $C\underline{\mathbf{H}_2}C\underline{\mathbf{H}_2}C_6F_{13}$), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5, 172.6, 165.6, 162.0, 139.0, 138.9, 138.3, 138.1, 138.0, 133.4, 133.2, 132.5, 130.2, 129.9, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 101.2 (**C-1′**), 99.2 (**C-1**), 92.6, 80.0, 77.9, 76.3, 74.9, 74.5, 73.8, 73.7, 73.5, 73.2, 72.6, 72.1, 70.3, 69.1, 68.4, 63.2 (t, *J* = 4.0 Hz, $\underline{\mathbf{C}}H_2CH_2C_6F_{13}$), 56.4, 48.4, 38.0, 31.4 (t, *J* = 21.0 Hz, $CH_2\underline{\mathbf{C}}H_2C_6F_{13}$), 30.0, 28.0. HRMS ($ESI^+$): calc. for $C_{80}H_{74}Cl_3F_{26}NO_{16}SNa^+$ $[M+Na]^+$: 1958.3271, found: 1958.3266.

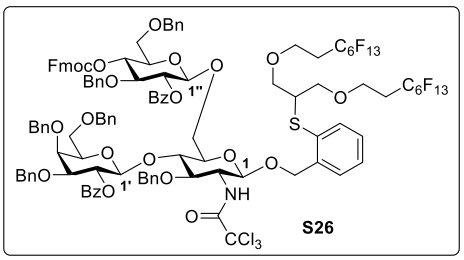
2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl-(1→4)-3-*O*-benzyl-2-deoxy-2-trichloroacetamino-*β*-D-glucopyranoside (S25)



To a solution of **S24** (421 mg, 0.22 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (2.2 mL) was successively added AcOH (0.37 mL, 6.52 mmol, 30.0 equiv), pyridine (0.53 mL, 6.52 mmol, 30.0 equiv) and N_2H_4-H_2O (21.1 μL, 0.44 mmol, 2.0 equiv) at 0 ℃. The resulting mixture was warmed up to room temperature, stirred for 1 h and extracted with EtOAc, washed with 1 M HCl, saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **S25** (371.7 mg, yield 93%) as white foam, R_f = 0.32 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{20}$ −0.2 (*c*, 1.65 in $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 1.2, 7.8 Hz, 2H, Ar-H), 7.58 (tt, *J* = 1.2, 7.8 Hz, 1H, Ar-H), 7.44 (t, *J* = 7.8 Hz, 2H, Ar-H), 7.41-7.40 (m, 1H, Ar-H), 7.35-7.34 (m, 1H, Ar-H), 7.33-7.25 (m, 10H, Ar-H), 7.21-7.10 (m, 12H, Ar-H), 6.86 (d, *J* = 7.8 Hz, 1H, NH), 5.64 (dd, *J* = 7.8, 10.2 Hz, 1H), 4.99 (t, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.92 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.79 (d, *J* = 7.8 Hz, 1H, **H-1**), 4.64 (d, *J* = 8.4 Hz, 1H, **H-1′**), 4.63 (d, *J* = 12.8 Hz, 1H, $PhCH_2$), 4.61 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.58 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.54 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.46 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.32 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.24 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.01 (d, *J* = 2.4 Hz, 1H), 3.91-3.87 (m, 2H), 3.69-3.55 (m, 14H), 3.51 (t, *J* = 9.0 Hz, 1H), 3.34 (dd, *J* = 4.8, 9.0 Hz, 1H), 3.31-3.27 (m, *J* = 6.0 Hz, 1H, SCH), 3.26-3.24 (m, 1H, OH), 2.37-2.28 (m, 4H, $C\underline{\mathbf{H}_2}C\underline{\mathbf{H}_2}C_6F_{13}$). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.4, 161.9, 139.0, 138.8, 138.3, 138.1, 137.8, 133.4, 133.3, 132.7, 130.0, 129.2, 128.7, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 128.0,

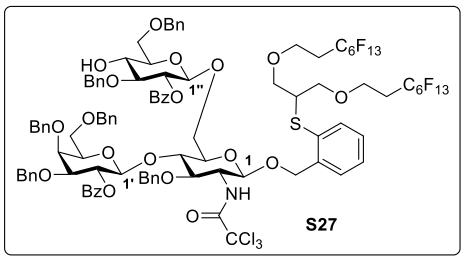
127.9, 127.9, 127.8, 127.6, 101.2 (**C-1′**), 99.4 (**C-1**), 92.7, 79.8, 78.0, 76.2, 75.9, 75.0, 74.9, 73.8, 73.7, 72.9, 72.6, 71.8, 70.3, 70.2, 69.4, 68.2, 63.3 (t, *J* = 4.0 Hz, **C**$H_2CH_2C_6F_{13}$), 61.1, 57.6, 48.3, 31.4 (t, *J* = 21.0 Hz, CH_2**C**$H_2C_6F_{13}$). HRMS (ESI^+): calc. for $C_{75}H_{68}Cl_3F_{26}NO_{14}SNa^+$ $[M+Na]^+$: 1860.2903, found: 1860.2906.

2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-4-*O*-fluorenylmethoxycarbonyl-*β*-D-glucopyranosyl-(1→6)-4-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-3-*O*-benzyl-2-deoxy-2-trichloroacetamino-*β*-D-glucopyranoside (S26)



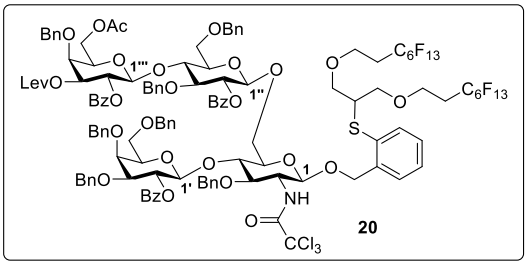
A solution of **17b**[20] (156.1 mg, 0.21 mmol, 1.5 equiv), **S25** (262 mg, 0.14 mmol, 1.0 equiv) containing 4Å MS (100 wt%) in anhydrous CH_2Cl_2 (16.0 mL) was stirred at −20 ℃ for 10 min, then *N*-iodosuccinimide (64.1 mg, 0.28 mmol, 2.0 equiv) and TfOH (2.5 μL, 0.03 mmol, 0.2 equiv) were added. The reaction mixture was stirred at −20 ℃ for 1 h and quenched by addition of Et_3N (0.2 mL). The suspension was filtered through Celite and concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **S26** (303.7 mg, yield 85%) as colorless syrup, R_f = 0.33 (petroleum ether-EtOAc 4:1). $[\alpha]_D^{20}$ +6.2 (*c*, 2.20 in $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.96 (dd, *J* = 1.2, 7.8 Hz, 2H, Ar-H), 7.77-7.73 (m, 4H, Ar-H), 7.57 (dd, *J* = 0.6, 7.8 Hz, 1H, Ar-H), 7.55-7.52 (m, 2H, Ar-H), 7.43 (tt, *J* = 1.2, 7.2 Hz, 1H, Ar-H), 7.40-7.35 (m, 5H, Ar-H), 7.32-7.25 (m, 13H, Ar-H), 7.24-7.14 (m, 19H, Ar-H), 7.09-7.02 (m, 6H, Ar-H, NH), 5.11 (dd, *J* = 7.8, 10.2 Hz, 1H), 5.24 (dd, *J* = 7.8, 9.6 Hz, 1H), 4.99 (t, *J* = 9.6 Hz, 1H), 4.92 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.70 (d, *J* = 12.6 Hz, 1H, $PhCH_2$), 4.68 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.62 (d, *J* = 12.6 Hz, 1H, $PhCH_2$), 4.57 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.56 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.54 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.51 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.50 (d, *J* = 7.8 Hz, 1H, **H-1′′**), 4.48 (d, *J* = 12.6 Hz, 1H, $PhCH_2$), 4.42 (d, *J* = 6.6 Hz, 1H, **H-1**), 4.41 (d, *J* = 12.6 Hz, 1H, $PhCH_2$), 4.40 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.37 (d, *J* = 7.8 Hz, 1H, **H-1′**), 4.35-4.32 (m, 3H), 4.30 (dd, *J* = 7.8, 10.8 Hz, 1H), 4.24 (d, *J* = 13.2 Hz, 1H, $PhCH_2$), 4.12 (t, *J* = 7.2 Hz, 1H), 4.01 (d, *J* = 2.4 Hz, 1H), 3.97-3.92 (m, 3H), 3.78 (t, *J* = 9.6 Hz, 1H), 3.71-3.68 (m, 2H), 3.67-3.50 (m, 14H), 3.46 (q, *J* = 6.0 Hz, 1H), 3.41 (dd, *J* = 4.8, 9.0 Hz, 1H), 3.27-3.24 (m, 1H, SCH), 2.36-2.25 (m, 4H, C**H**$_2$C**H**$_2$$C_6F_{13}$). ^{13}C NMR (150 MHz, $CDCl_3$) *δ* 165.7, 165.0, 162.0, 154.4, 143.5, 143.3, 141.5, 141.5, 139.5, 138.8, 138.4, 138.2, 138.1, 138.1, 137.6, 133.5, 133.4, 132.8, 132.4, 130.0, 130.0, 129.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 127.4, 125.3, 125.2, 120.3, 101.4 (**C-1′**), 100.4 (**C-1′′**), 99.8 (**C-1**), 92.7, 80.2, 79.6, 78.6, 75.9, 75.8, 74.9, 74.9, 74.2, 73.6, 73.6, 73.4, 73.1, 73.0, 72.8, 72.1, 70.3, 70.2, 70.2, 69.8, 69.0, 68.9, 68.1, 63.1 (t, *J* = 4.0 Hz, **C**$H_2CH_2C_6F_{13}$), 55.3, 48.3, 46.9, 31.4 (t, *J* = 21.0 Hz, CH_2**C**$H_2C_6F_{13}$). HRMS (ESI^+): calc. for $C_{117}H_{104}Cl_3F_{26}NO_{22}SNa^+$ $[M+Na]^+$: 2528.5313, found: 2528.5314.

2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-*β*-D-glucopyranosyl-(1→6)-4-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-3-*O*-benzyl-2-deoxy-2-trichloroacetamino-*β*-D-glucopyranoside (S27)



To a stirred solution of **S26** (303.7 mg, 0.12 mmol) in CH_2Cl_2 (2.4 mL) was added Et_3N (0.24 mL). The resulting mixture was stirred at room temperature for 3 h and concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **S27** (237 mg, yield 86%) as white foam, R_f = 0.32 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{20}$ +0.3 (*c*, 3.37 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.98 (m, 2H, Ar-H), 7.75 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.54 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.45-7.13 (m, 40H, Ar-H, NH), 5.51 (dd, *J* = 8.0, 10.0 Hz, 1H), 5.18 (dd, *J* = 7.6, 9.2 Hz, 1H), 4.93 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.73-4.61 (m, 6H), 4.58 (d, *J* = 10.4 Hz, 1H, $PhCH_2$), 4.54 (d, *J* = 1.2 Hz, 1H), 4.51 (d, *J* = 8.0 Hz, 1H, **H-1″**), 4.50 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.43 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.43 (d, *J* = 7.8 Hz, 1H, **H-1**), 4.41 (d, *J* = 9.0 Hz, 1H, **H-1′**), 4.40 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.33 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.16 (d, *J* = 13.2 Hz, 1H, $PhCH_2$), 4.00-3.97 (m, 3H), 3.93 (dd, *J* = 6.8, 10.0 Hz, 1H), 3.80 (dd, *J* = 1.6, 10.0 Hz, 1H), 3.77-3.51 (m, 16H), 3.47-3.37 (m, 3H), 3.27-3.22 (m, *J* = 6.0 Hz, 1H, SCH), 2.91 (d, *J* = 2.0 Hz, 1H, OH), 2.39-2.23 (m, 4H, C**H**$_2$C**H**$_2$C$_6$F$_{13}$). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.7, 165.3, 162.1, 139.6, 138.8, 138.4, 138.2, 138.2, 138.1, 137.8, 133.4, 133.4, 132.7, 132.6, 130.1, 129.9, 129.8, 128.7, 128.7, 128.6, 128.6, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 127.9, 127.9, 127.9, 127.8, 127.7, 127.6, 127.5, 101.4 (**C-1′**), 100.3 (**C-1″**), 99.9 (**C-1**), 92.7, 82.1, 80.2, 78.5, 76.1, 74.9, 74.6, 73.9, 73.8, 73.7, 73.6, 73.4, 73.1, 72.9, 72.8, 72.2, 70.9, 70.3, 70.2, 69.0, 68.6, 68.3, 63.1 (brs, **C**H$_2$CH$_2$C$_6$F$_{13}$), 55.1, 48.4, 31.4 (t, *J* = 21.0 Hz, CH$_2$**C**H$_2$C$_6$F$_{13}$). HRMS (ESI$^+$): calc. for $C_{102}H_{94}Cl_3F_{26}NO_{20}SNa^+$ $[M+Na]^+$: 2306.4633, found: 2306.4682.

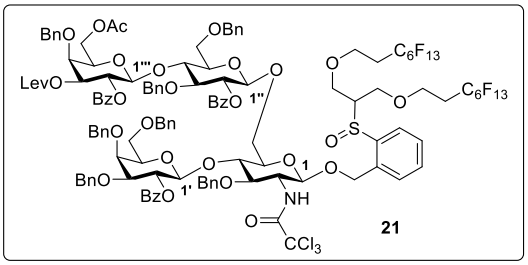
2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 2-*O*-benzoyl-3-*O*-levulinyl-4-*O*-benzyl-6-*O*-acetyl-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-benzyl-*β*-D-glucopyranosyl-(1→6)-4-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-3-*O*-benzyl-2-deoxy-2-trichloroacetamino-*β*-D-glucopyranoside (20)



A solution of **18b** (79.0 mg, 0.114 mmol, 2.5 equiv) and DTBMP (23.4 mg, 0.114 mmol, 2.5 equiv) in anhydrous CH_2Cl_2 (1.1 mL) in the presence of 4Å MS (100 wt%) was stirred for 15 min at −40 ℃. After addition of Tf_2O (19.1 μL, 0.114 mmol, 2.5 equiv), the solution was stirred at −40 ℃ for 3 min, and then **S27** (104 mg, 0.046 mmol, 1.0 equiv) in CH_2Cl_2 (0.4 mL) was added.

The reaction mixture was stirred at −40 ℃ for 1 h, quenched by addition of Et_3N (0.2 mL). The suspension was filtered through Celite and concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **20** (162 mg, yield 92%) as white foam, R_f = 0.23 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{20}$ −0.2 (*c*, 1.20 in $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 4H, Ar-H), 7.67-7.65 (m, 2H, Ar-H), 7.56 (t, *J* = 7.8 Hz, 1H, Ar-H), 7.50 (t, *J* = 7.8 Hz, 1H, Ar-H), 7.43 (t, *J* = 7.8 Hz, 2H, Ar-H), 7.39-7.25 (m, 23H, Ar-H), 7.23-7.05 (m, 20H, Ar-H), 7.00 (t, *J* = 7.8 Hz, 2H, Ar-H, NH), 5.62 (dd, *J* = 7.8, 10.2 Hz, 1H), 5.45 (dd, *J* = 7.8, 10.2 Hz, 1H), 5.14 (dd, *J* = 7.8, 9.6 Hz, 1H), 5.00 (dd, *J* = 3.0, 10.8 Hz, 1H), 4.88 (t, *J* = 11.4 Hz, 2H, $PhCH_2$), 4.82 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.67 (d, *J* = 7.8 Hz, 1H, **H-1′′**), 4.66 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.62 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.60 (d, *J* = 12.6 Hz, 1H, $PhCH_2$), 4.59 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.55 (d, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.53 (d, *J* = 12.6 Hz, 1H, $PhCH_2$), 4.52 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.46 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.41 (d, *J* = 8.4 Hz, 1H, **H-1**), 4.41 (d, *J* = 6.0 Hz, 1H, **H-1′′′**), 4.38 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.29 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.19 (d, *J* = 14.4 Hz, 1H, $PhCH_2$), 4.17 (d, *J* = 12.6 Hz, 1H, $PhCH_2$), 4.14 (d, *J* = 7.8 Hz, 1H, **H-1′**), 4.07 (t, *J* = 9.6 Hz, 1H), 4.01-3.98 (m, 2H), 3.96-3.86 (m, 5H), 3.67-3.47 (m, 16H), 3.41 (dd, *J* = 6.0, 10.8 Hz, 1H), 3.38 (dd, *J* = 1.2, 10.8 Hz, 1H), 3.35 (dd, *J* = 5.4, 9.0 Hz, 1H), 3.24-3.20 (m, 1H, SCH), 3.00 (ddd, *J* = 1.8, 3.0, 9.6 Hz, 1H), 2.62 (ddd, *J* = 4.8, 8.4, 18.6 Hz, 1H), 2.53-2.45 (m, 2H), 2.35-2.23 (m, 5H, $C\underline{\mathbf{H}}_2C\underline{\mathbf{H}}_2C_6F_{13}$), 2.00 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.1, 172.3, 170.4, 165.7, 165.3, 165.1, 162.0, 139.5, 138.8, 138.6, 138.4, 138.2, 138.2, 138.1, 138.1, 133.7, 133.4, 133.3, 132.8, 132.5, 130.3, 129.9, 129.9, 129.7, 129.5, 128.8, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 128.1, 128.1, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 127.4, 127.4, 101.4 (**C-1′**), 100.5 (**C-1′′**, **C-1′′′**), 99.8 (**C-1**), 92.7, 80.3, 80.1, 78.4, 76.4, 76.0, 75.2, 74.9, 74.8, 74.7, 74.7, 74.2, 74.0, 73.6, 73.6, 73.6, 73.2, 73.0, 72.9, 72.2, 72.2, 70.8, 70.2, 70.2, 69.0, 68.7, 68.0, 67.9, 63.1 (t, *J* = 4.0 Hz, $\underline{\mathbf{C}}H_2CH_2C_6F_{13}$), 62.0, 55.2, 48.3, 37.9, 31.4 (t, *J* = 21.0 Hz, $CH_2\underline{\mathbf{C}}H_2C_6F_{13}$), 29.7, 28.2, 20.9. HRMS (ESI^+): calc. for $C_{129}H_{122}Cl_3F_{26}NO_{29}SNa^+$ $[M+Na]^+$: 2802.6366, found: 2802.6369.

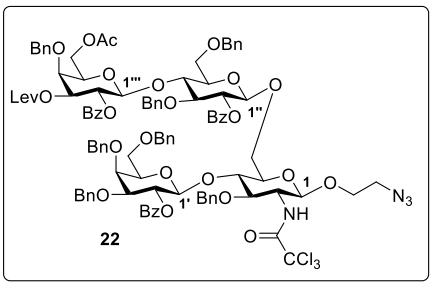
2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)sulfinyl]benzyl 2-*O*-benzoyl-3-*O*-levulinyl-4-*O*-benzyl-6-*O*-acetyl-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-benzyl-*β*-D-glucopyranosyl-(1→6)-4-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-3-*O*-benzyl-2-deoxy-2-trichloroacetamino-*β*-D-glucopyranoside (21)



To a stirred solution of **20** (130 mg, 0.047 mmol, 1.0 equiv) in MeCN/H_2O (9:1, v:v, 0.93 mL) was added PIFA (22.1 mg, 0.051 mmol, 1.1 equiv), the mixture was stirred at room temperature for 20 min. The reaction mixture was extracted with EtOAc, washed with saturated $Na_2S_2O_3$, saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by flash column chromatography on silica gel to give compound **21** (110 mg, yield 84%) as

white foam, R_f = 0.59 (petroleum ether-EtOAc 1:1). A mixture of sulfoxide *R*/*S* (1:1) isomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96-7.92 (m, 8H, Ar-H), 7.85 (dd, *J* = 1.2, 7.8 Hz, 1H, Ar-H), 7.79 (dd, *J* = 0.6, 7.8 Hz, 1H, Ar-H), 7.76 (dd, *J* = 1.2, 7.8 Hz, 2H, Ar-H), 7.69 (dd, *J* = 1.2, 8.4 Hz, 2H, Ar-H), 7.57 (tt, *J* = 1.2, 7.8 Hz, 1H, Ar-H), 7.54-7.49 (m, 3H, Ar-H), 7.46-7.40 (m, 8H, Ar-H), 7.38-7.25 (m, 40H, Ar-H), 7.23-7.06 (m, 39H, Ar-H), 7.02-6.99 (m, 4H, Ar-H), 6.93 (d, *J* = 9.0 Hz, 1H, NH), 5.65 (dd, *J* = 7.8, 10.8 Hz, 1H), 5.64 (dd, *J* = 7.8, 10.2 Hz, 1H), 5.48 (dd, *J* = 7.8, 10.2 Hz, 1H), 5.47 (dd, *J* = 7.8, 10.2 Hz, 1H), 5.12 (dd, *J* = 7.8, 9.6 Hz, 1H), 5.10 (dd, *J* = 7.8, 9.6 Hz, 1H), 5.04 (dd, *J* = 3.0, 10.2 Hz, 1H), 5.01 (dd, *J* = 3.0, 10.8 Hz, 1H), 4.92-4.87 (m, 4H), 4.84 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.83 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.67 (d, *J* = 7.8 Hz, 2H, **H-1″**, **H-1″**), 4.63-4.41 (m, 19H, **H-1**), 4.38-4.35 (m, 4H, **H-1‴**, **H-1‴**), 4.28 (d, *J* = 11.4 Hz, 2H, $PhCH_2$), 4.25 (d, *J* = 7.2 Hz, 1H, **H-1**), 4.23 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.17 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.07-3.94 (m, 12H, **H-1′**, **H-1′**), 3.91 (dd, *J* = 2.4, 9.0 Hz, 2H), 3.87-3.80 (m, 6H), 3.70-3.42 (m, 33H), 3.40-3.31 (m, 5H), 3.17-3.13 (m, *J* = 6.0 Hz, 1H, SCH), 3.08-3.05 (m, *J* = 6.0 Hz, 1H, SCH), 2.95-2.91 (m, 2H), 2.66-2.60 (m, 2H), 2.54-2.46 (m, 4H), 2.35-2.30 (m, 2H), 2.28-2.08 (m, 8H, $C\underline{H_2}C\underline{H_2}C_6F_{13}$), 2.01 (s, 6H), 1.93 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.1, 172.3, 170.4, 170.3, 165.6, 165.6, 165.3, 165.3, 165.1, 165.0, 162.1, 162.0, 140.7, 140.7, 138.8, 138.7, 138.5, 138.2, 138.2, 138.1, 138.1, 138.1, 138.0, 138.0, 135.6, 135.5, 133.7, 133.7, 133.6, 133.3, 131.3, 131.3, 130.3, 130.2, 130.2, 130.0, 129.9, 129.9, 129.8, 129.8, 129.8, 129.5, 128.9, 128.8, 128.6, 128.6, 128.6, 128.4, 128.3, 128.3, 128.2, 128.2, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 128.0, 127.9, 127.7, 127.7, 127.6, 127.5, 127.5, 127.4, 125.2, 124.9, 101.7 (**C-1′**), 101.5 (**C-1′**), 100.6 (**C-1″**), 100.6 (**C-1″**), 100.5 (**C-1‴**), 100.2 (**C-1‴**), 99.9 (**C-1**), 99.8 (**C-1**), 92.6, 92.6, 80.2, 80.2, 80.0, 79.9, 78.9, 78.2, 77.0, 76.7, 76.4, 75.9, 75.8, 75.2, 74.9, 74.9, 74.8, 74.7, 74.6, 74.5, 74.2, 74.1, 74.0, 74.0, 73.6, 73.5, 73.5, 73.5, 73.3, 73.1, 73.0, 72.9, 72.9, 72.7, 72.7, 72.2, 72.2, 72.1, 72.1, 70.8, 70.8, 69.2, 69.0, 68.1, 68.0, 67.2, 66.7, 66.6, 66.5, 64.3, 63.8, 63.3 (brs, $\underline{C}H_2CH_2C_6F_{13}$), 63.0 (brs, $\underline{C}H_2CH_2C_6F_{13}$), 62.0, 61.9, 55.2, 54.8, 37.9, 31.2 (t, *J* = 21.0 Hz, $CH_2\underline{C}H_2C_6F_{13}$), 29.7, 28.1, 20.9. HRMS (ESI^+): calc. for $C_{129}H_{122}Cl_3F_{26}NO_{30}SNa^+$ $[M+Na]^+$: 2818.6315, found: 2818.6366.

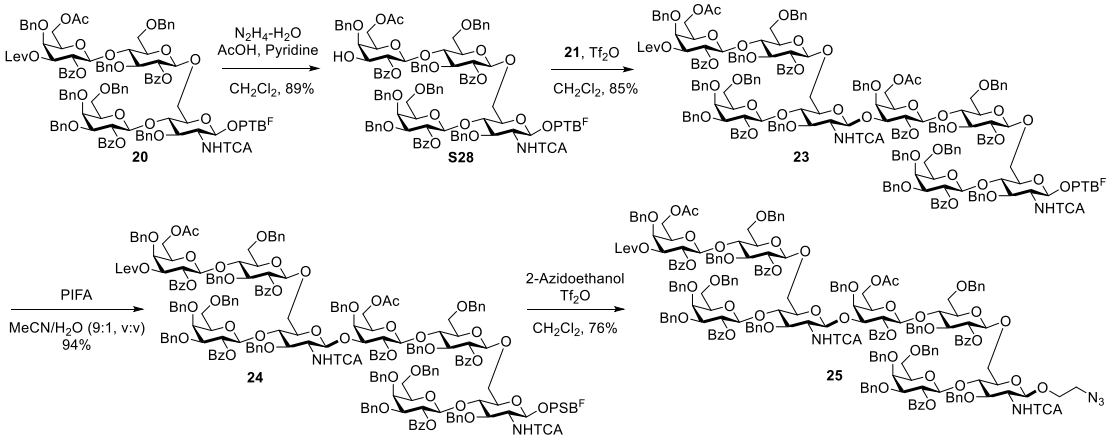
2-Azidoethyl 2-*O*-benzoyl-3-*O*-levulinyl-4-*O*-benzyl-6-*O*-acetyl-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-benzyl-*β*-D-glucopyranosyl-(1→6)-4-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-3-*O*-benzyl-2-deoxy-2-trichloroacetamino-*β*-D-glucopyranoside (22)



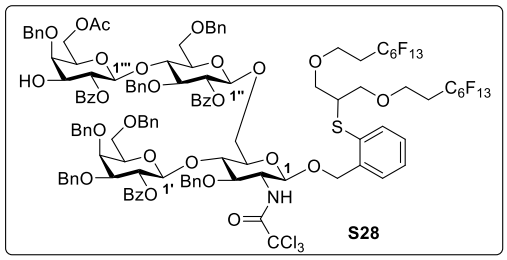
A solution of glycosyl donor **21** (30 mg, 0.011 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (0.36 mL) in the presence of 4Å MS (100 wt%) was stirred at −40 ℃ for 20 min. Tf_2O (3.6 μL, 0.021 mmol, 2.0 equiv) and 2-azidoethanol (40.6 μL, 0.536 mmol, 50.0 equiv) were successively added. The resulting mixture was stirred at −40 ℃ for 1 h and quenched by addition of H_2O (0.5 mL). The mixture was filtered through Celite and extracted with EtOAc, washed with brine, dried over

anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography on silica gel to give compound **22** (17.3 mg, yield 82%) as colorless syrup, R_f = 0.31 (petroleum ether-EtOAc 3:2). $[\alpha]_D^{20}$ +3.6 (*c*, 1.70 in $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96-7.92 (m, 4H, Ar-H), 7.78 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.58 (t, *J* = 7.8 Hz, 1H, Ar-H), 7.53 (t, *J* = 7.2 Hz, 1H, Ar-H), 7.46-7.43 (m, 3H, Ar-H), 7.37-7.25 (m, 20H, Ar-H), 7.23-6.99 (m, 20H, Ar-H, NH), 5.63 (dd, *J* = 7.8, 10.2 Hz, 1H), 5.48 (dd, *J* = 7.8, 10.2 Hz, 1H), 5.11 (dd, *J* = 7.8, 9.0 Hz, 1H), 5.01 (dd, *J* = 3.0, 10.8 Hz, 1H), 5.91 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.87 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.82 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.68 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.67 (d, *J* = 8.4 Hz, 1H, **H-1′′**), 4.60 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.59 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.58-4.54 (m, 3H), 4.51 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.43 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.42 (d, *J* = 7.8 Hz, 1H, **H-1′′′**), 4.40 (d, *J* = 6.6 Hz, 1H, **H-1**), 4.35 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.27 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.23 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.14 (d, *J* = 7.8 Hz, 1H, **H-1′**), 4.07 (t, *J* = 9.0 Hz, 1H), 4.00 (dd, *J* = 5.4, 10.8 Hz, 1H), 3.96 (d, *J* = 2.4 Hz, 1H), 3.94 (dd, *J* = 7.8, 10.8 Hz, 1H), 3.90 (d, *J* = 2.4 Hz, 1H), 3.82 (dd, *J* = 4.8, 9.6 Hz, 1H), 3.78 (t, *J* = 5.4 Hz, 1H), 3.72-3.68 (m, 2H), 3.61-3.53 (m, 5H), 3.50-3.41 (m, 5H), 3.32 (dd, *J* = 5.4, 9.0 Hz, 1H), 3.10-3.00 (m, 3H), 2.96-2.93 (m, 1H), 2.65-2.60 (m, 1H), 2.53-2.45 (m, 2H), 2.34-2.29 (m, 1H), 2.01 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.1, 172.3, 170.4, 165.6, 165.3, 165.1, 162.0, 138.7, 138.5, 138.4, 138.2, 138.0, 138.0, 133.7, 133.5, 133.3, 130.3, 129.9, 129.9, 129.9, 129.8, 129.5, 128.9, 128.8, 128.6, 128.6, 128.6, 128.5, 128.4, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 101.5 (**C-1′**), 100.5 (**C-1′′**), 100.5 (**C-1′′′**), 99.7 (**C-1**), 92.6, 80.3, 80.1, 78.2, 76.4, 75.6, 75.5, 75.2, 74.9, 74.7, 74.6, 74.2, 73.9, 73.6, 73.6, 73.5, 73.5, 73.3, 72.9, 72.7, 72.2, 72.0, 70.8, 68.9, 68.1, 68.0, 62.0, 55.8, 50.5, 37.9, 29.7, 28.1, 21.0. HRMS (ESI^+): calc. for $C_{105}H_{107}Cl_3N_4O_{27}Na^+$ $[M+Na]^+$: 1983.6080, found: 1983.6060.

Synthesis of ST14 octasaccharide 25

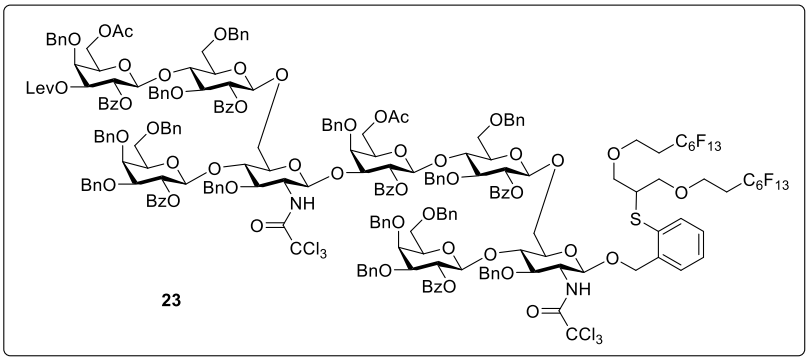


2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl 2-*O*-benzoyl-4-*O*-benzyl-6-*O*-acetyl-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-benzyl-*β*-D-glucopyranosyl-(1→6)-4-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-3-*O*-benzyl-2-deoxy-2-trichloroacetamino-*β*-D-glucopyranoside (S28)



To a stirred solution of **20** (100 mg, 0.036 mmol, 1.0 equiv) in CH_2Cl_2 (0.72 mL) was successively added AcOH (61.7 μL, 1.078 mmol, 30.0 equiv), pyridine (87.2 μL, 1.078 mmol, 30.0 equiv) and N_2H_4-H_2O (3.5 μL, 0.072 mmol, 2.0 equiv) at 0 ℃. The resulting mixture was warmed up to room temperature, stirred for 1 h and extracted with EtOAc, washed with 1 M HCl, saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by flash column chromatography on silica gel to give compound **S28** (86 mg, yield 89%) as white foam, R_f = 0.35 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{20}$ −2.2 (*c*, 1.00 in $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96-7.92 (m, 4H, Ar-H), 7.67 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.55 (t, *J* = 7.8 Hz, 1H, Ar-H), 7.50 (t, *J* = 7.8 Hz, 1H, Ar-H), 7.41 (t, *J* = 7.8 Hz, 2H, Ar-H), 7.38-7.25 (m, 24H, Ar-H), 7.20-7.08 (m, 18H, Ar-H), 7.07 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.02 (t, *J* = 7.8 Hz, 2H, Ar-H, NH), 5.46 (dd, *J* = 7.8, 9.6 Hz, 1H), 5.25 (dd, *J* = 7.8, 10.2 Hz, 1H), 5.15 (dd, *J* = 7.8, 9.0 Hz, 1H), 4.88 (t, *J* = 11.4 Hz, 2H, $PhCH_2$), 4.74 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.70 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.68 (d, *J* = 13.2 Hz, 1H, $PhCH_2$), 4.65 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.63 (d, *J* = 7.8 Hz, 1H, **H-1″**), 4.60 (d, *J* = 12.6 Hz, 1H, $PhCH_2$), 4.59 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.58 (d, *J* = 12.6 Hz, 1H, $PhCH_2$), 4.56 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.51 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.45 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.43 (d, *J* = 6.6 Hz, 1H, **H-1**), 4.43 (d, *J* = 8.4 Hz, 1H, **H-1‴**), 4.38 (d, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.29 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.24 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.21 (d, *J* = 13.2 Hz, 1H, $PhCH_2$), 4.17 (d, *J* = 7.8 Hz, 1H, **H-1′**), 4.11-4.08 (m, 2H), 4.00 (dd, *J* = 7.8, 10.8 Hz, 1H), 3.98 (d, *J* = 2.4 Hz, 1H), 3.93-3.86 (m, 3H), 3.80-3.77 (m, 2H), 3.69-3.48 (m, 17H), 3.42 (dd, *J* = 6.0, 10.8 Hz, 1H), 3.34 (dd, *J* = 4.8, 9.0 Hz, 1H), 3.24-3.20 (m, 1H, SCH), 3.06 (ddd, *J* = 2.4, 3.0, 10.2 Hz, 1H), 2.34-2.23 (m, 5H, C**H**$_2$C**H**$_2$$C_6F_{13}$, OH), 1.98 (s, 3H, OAc). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.5, 166.7, 165.7, 165.1, 162.0, 139.5, 138.8, 138.6, 138.4, 138.3, 138.2, 138.1, 137.9, 133.7, 133.4, 133.3, 132.8, 132.5, 131.8, 130.2, 130.0, 129.9, 129.9, 129.8, 129.7, 128.8, 128.8, 128.8, 128.7, 128.7, 128.7, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 127.4, 127.4, 101.4 (**C-1′**), 100.5 (**C-1‴**), 100.2 (**C-1″**), 99.8 (**C-1**), 92.7, 80.4, 80.2, 78.4, 76.7, 76.3, 76.0, 75.9, 75.0, 74.9, 74.8, 74.5, 74.5, 73.7, 73.6, 73.6, 73.4, 73.2, 73.0, 72.8, 72.3, 72.2, 70.2, 70.2, 69.1, 68.6, 68.1, 68.0, 67.0, 64.5, 63.7, 63.1 (t, *J* = 4.0 Hz, **C**$H_2CH_2C_6F_{13}$), 62.3, 55.3, 48.3, 31.4 (t, *J* = 21.0 Hz, CH_2**C**$H_2C_6F_{13}$), 21.0. HRMS (ESI^+): calc. for $C_{124}H_{116}Cl_3F_{26}NO_{27}SNa^+$ $[M+Na]^+$: 2704.5998, found: 2704.5993.

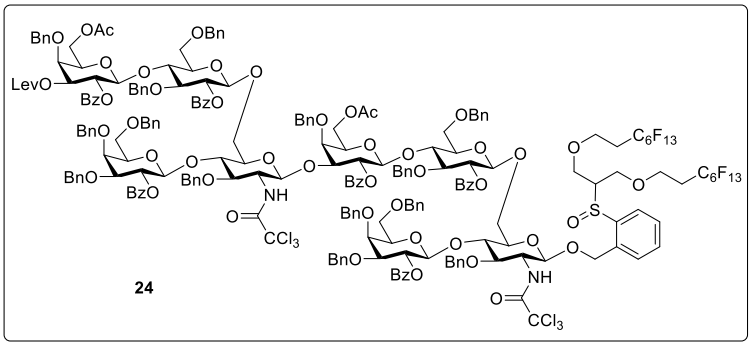
2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)thio]benzyl [2-*O*-benzoyl-3-*O*-levulinyl-4-*O*-benzyl-6-*O*-acetyl-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-benzyl-*β*-D-glucopyranosyl-(1→6)-4-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-3-*O*-benzyl-2-deoxy-2-trichloroacetamino]-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-6-*O*-acetyl-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-benzyl-*β*-D-glucopyranosyl-(1→6)-4-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-3-*O*-benzyl-2-deoxy-2-trichloroacetamino-*β*-D-glucopyranoside (23)



A solution of glycosyl donor **21** (62.6 mg, 0.022 mmol, 2.0 equiv), fluorous acceptor **S28** (30 mg, 0.011 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (0.37 mL) in the presence of 4Å MS (100 wt%) was stirred at −40 ℃ for 20 min. After addition of Tf_2O (3.8 μL, 0.022 mmol, 2.0 equiv), the solution was stirred at −40 ℃ for 3 h and quenched by addition of H_2O (0.5 mL). The mixture was filtered through Celite and concentrated *in vacuo*. Then, the crude product was purified by the General Procedure A to give compound **23** (43.6 mg, yield 85%) as white foam, R_f = 0.23 (petroleum ether-EtOAc 2:1). $[\alpha]_D^{20}$ +2.4 (*c*, 2.14 in $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.93 (d, *J* = 5.4 Hz, 6H, Ar-H), 7.73 (brs, 2H, Ar-H), 7.66 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.58 (t, *J* = 7.8 Hz, 1H, Ar-H), 7.53-7.26 (m, 35H, Ar-H), 7.23-6.99 (m, 55H, Ar-H), 6.94 (t, *J* = 7.2 Hz, 2H, Ar-H, NH), 6.83 (d, *J* = 8.4 Hz, 1H, NH), 5.62 (t, *J* = 9.6 Hz, 1H), 5.51 (t, *J* = 9.0 Hz, 1H), 5.44 (t, *J* = 9.0 Hz, 1H), 5.38 (t, *J* = 9.0 Hz, 1H), 5.14 (t, *J* = 9.0 Hz, 1H), 5.10 (t, *J* = 8.4 Hz, 1H), 4.99 (d, *J* = 10.8 Hz, 1H), 4.89-4.81 (m, 6H), 4.66-4.48 (m, 18H), 4.44-4.33 (m, 7H), 4.29-4.14 (m, 6H), 4.08-3.81 (m, 16H), 3.69 (d, *J* = 10.2 Hz, 1H), 3.65-3.51 (m, 19H), 3.47-3.44 (m, 3H), 3.40-3.34 (m, 4H), 3.32-3.20 (m, 6H), 2.99 (d, *J* = 9.6 Hz, 1H), 2.93 (d, *J* = 9.6 Hz, 1H), 2.65-2.60 (m, 1H), 2.53-2.45 (m, 2H), 2.34-2.24 (m, 5H, C**H**$_2$C**H**$_2$C$_6$F$_{13}$), 2.01 (s, 3H), 1.91 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.1, 172.3, 170.7, 170.4, 165.7, 165.6, 165.3, 165.2, 165.0, 165.0, 162.0, 139.6, 138.8, 138.8, 138.8, 138.7, 138.5, 138.5, 138.4, 138.3, 138.2, 138.1, 138.1, 138.1, 138.0, 138.0, 133.8, 133.7, 133.5, 133.5, 133.4, 133.2, 132.8, 132.6, 130.3, 130.2, 130.1, 130.0, 129.9, 129.9, 129.7, 129.5, 129.0, 128.9, 128.8, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 127.6, 127.6, 127.4, 127.4, 127.4, 127.3, 127.3, 127.2, 101.8, 101.4, 100.6, 100.5, 100.4, 99.8, 92.7, 92.1, 80.6, 80.2, 80.2, 80.1, 80.1, 78.5, 78.4, 76.8, 76.2, 76.0, 75.9, 75.9, 75.2, 74.9, 74.8, 74.8, 74.6, 74.5, 74.1, 73.9, 73.7, 73.7, 73.6, 73.5, 73.5, 73.1, 73.0, 73.0, 72.9, 72.9, 72.7, 72.3, 72.3, 72.2, 72.2, 72.1, 72.0, 70.8, 70.2, 70.2, 69.1, 68.6, 68.4, 68.0, 67.8, 67.8, 63.5, 63.1 (t, *J* = 4.0 Hz, **C**H$_2$CH$_2$C$_6$F$_{13}$), 62.0, 55.5, 55.2, 48.3, 37.9, 31.4 (t, *J* = 21.0 Hz, CH$_2$**C**H$_2$C$_6$F$_{13}$), 29.7,

28.1, 20.9. MALDI-TOF MS: calc. for $C_{227}H_{218}Cl_6F_{26}N_2O_{53}SNa^+$ $[M+Na]^+$: 4578.1754, found: 4578.8472.

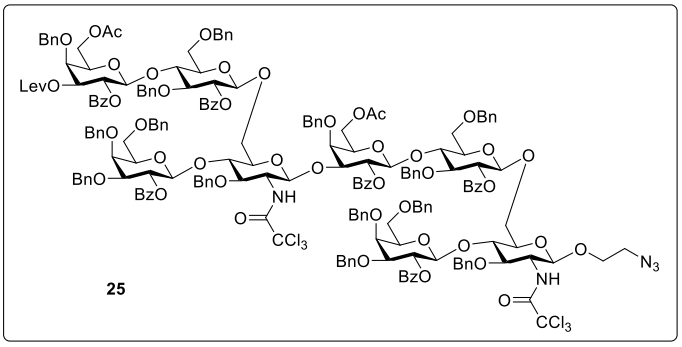
2-[(1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)propan-2-yl)sulfinyl]benzyl [2-*O*-benzoyl-3-*O*-levulinyl-4-*O*-benzyl-6-*O*-acetyl-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-benzyl-*β*-D-glucopyranosyl-(1→6)-4-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-3-*O*-benzyl-2-deoxy-2-trichloroacetamino]-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-6-*O*-acetyl-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-benzyl-*β*-D-glucopyranosyl-(1→6)-4-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-3-*O*-benzyl-2-deoxy-2-trichloroacetamino-*β*-D-glucopyranoside (24)



To a stirred solution of **23** (50 mg, 0.011 mmol, 1.0 equiv) in MeCN/H_2O (9:1, v:v, 0.4 mL) was added PIFA (5.2 mg, 0.012 mmol, 1.1 equiv), the mixture was stirred at room temperature for 10 min. The reaction mixture was extracted with EtOAc, washed with saturated $Na_2S_2O_3$, saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to give compound **24** (47.4 mg, yield 94%) as white foam, R_f = 0.28 (petroleum ether-EtOAc 3:2). A mixture of sulfoxide *R*/*S* (1:1) isomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10-8.09 (m, 3H, Ar-H), 7.96-7.94 (m, 11H, Ar-H), 7.86 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.81-7.73 (m, 9H, Ar-H), 7.60 (t, *J* = 7.2 Hz, 2H, Ar-H), 7.55-7.25 (m, 95H, Ar-H), 7.23-6.97 (m, 87H, Ar-H), 6.86 (brd, *J* = 7.2 Hz, 2H, NH), 5.67-5.64 (m, 2H), 5.58-5.55 (m, 2H), 5.52-5.48 (m, 2H), 5.43-5.40 (m, 2H), 5.19-5.15 (m, 2H), 5.12-5.07 (m, 2H), 5.03-5.01 (m, 2H), 4.95-4.85 (m, 12H), 4.69-4.25 (m, 56H), 4.20-4.08 (m, 8H), 4.01-3.90 (m, 24H), 3.84-3.29 (m, 70H), 3.19-3.17 (m, *J* = 5.4 Hz, 1H, SCH), 3.10-3.09 (m, *J* = 5.4 Hz, 1H, SCH), 3.01 (brs, 2H), 2.89 (brs, 1H), 2.84 (brs, 1H), 2.67-2.62 (m, 2H), 2.55-2.48 (m, 4H), 2.37-2.32 (m, 2H), 2.31-2.09 (m, 8H, C**H**$_2$C**H**$_2$$C_6F_{13}$), 2.02 (s, 6H), 1.94 (s, 3H), 1.93 (s, 3H), 1.83 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.1, 172.3, 170.6, 170.3, 165.7, 165.6, 165.5, 165.5, 165.2, 165.1, 165.0, 165.0, 162.0, 161.9, 161.9, 140.7, 140.6, 138.8, 138.8, 138.7, 138.7, 138.6, 138.4, 138.4, 138.3, 138.2, 138.1, 138.1, 138.0, 138.0, 137.9, 135.6, 135.5, 133.8, 133.7, 133.7, 133.6, 133.6, 133.5, 133.4, 133.2, 131.3, 130.4, 130.2, 130.0, 130.0, 130.0, 129.9, 129.8, 129.8, 129.7, 129.5, 128.9, 128.8, 128.8, 128.7, 128.6, 128.5, 128.5, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 128.1, 128.0, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 127.5, 127.4, 127.4, 127.3, 125.2, 124.8, 101.7, 101.6, 101.5, 101.3, 100.8, 100.6, 100.6, 100.5, 100.4, 100.4, 99.8, 92.6, 92.6, 92.0, 80.5, 80.1, 80.1, 80.1, 79.9, 79.8, 79.8, 79.0, 78.4, 78.1, 76.7, 76.5, 76.2, 76.0, 75.9, 75.5, 75.2, 74.9, 74.9, 74.8, 74.8, 74.7, 74.7, 74.6, 74.5, 74.1, 73.9, 73.7, 73.5, 73.5, 73.4, 73.3, 73.2, 73.2, 73.1, 73.0, 72.9, 72.8, 72.7, 72.7, 72.3, 72.2, 72.1, 72.0, 72.0, 70.8, 68.9, 68.4, 68.1, 67.9, 67.8, 67.3, 66.6, 66.6, 64.3, 64.3,

63.9, 63.4, 63.3 (t, J = 4.0 Hz, **C**$H_2CH_2C_6F_{13}$), 63.0 (t, J = 4.0 Hz, **C**$H_2CH_2C_6F_{13}$), 61.9, 55.6, 54.9, 37.8, 31.1 (t, J = 21.0 Hz, CH_2**C**$H_2C_6F_{13}$), 29.6, 28.1, 20.9. MALDI-TOF MS: calc. for $C_{227}H_{218}Cl_6F_{26}N_2O_{54}SNa^+$ $[M+Na]^+$: 4594.1703, found: 4594.8735.

2-Azidoethyl [2-*O*-benzoyl-3-*O*-levulinyl-4-*O*-benzyl-6-*O*-acetyl-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-benzyl-*β*-D-glucopyranosyl-(1→6)-4-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-3-*O*-benzyl-2-deoxy-2-trichloroacetamino]-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-6-*O*-acetyl-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-benzyl-*β*-D-glucopyranosyl-(1→6)-4-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-3-*O*-benzyl-2-deoxy-2-trichloroacetamino-*β*-D-glucopyranoside (25)



A solution of glycosyl donor **24** (26 mg, 0.006 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (0.19 mL) in the presence of 4Å MS (100 wt%) was stirred at −40 ℃ for 20 min. Tf_2O (1.9 μL, 0.011 mmol, 2.0 equiv) and 2-azidoethanol (21.5 μL, 0.284 mmol, 50.0 equiv) were successively added. The resulting mixture was stirred at −40 ℃ for 1 h and quenched by addition of H_2O (0.5 mL). The mixture was filtered through Celite and extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography on silica gel to give compound **25** (16.1 mg, yield 76%) as white foam, R_f = 0.25 (petroleum ether-EtOAc 3:2). $[\alpha]_D^{20}$ +4.0 (*c*, 1.05 in $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, J = 8.4 Hz, 2H, Ar-H), 7.93-7.91 (m, 6H, Ar-H), 7.76-7.72 (m, 4H, Ar-H), 7.58 (t, J = 7.2 Hz, 1H, Ar-H), 7.53-7.48 (m, 3H, Ar-H), 7.45-7.40 (m, 5H, Ar-H), 7.36-7.26 (m, 28H, Ar-H), 7.23-6.98 (m, 49H, Ar-H), 6.95 (t, J = 7.2 Hz, 3H, Ar-H, NH), 6.82 (d, J = 9.0 Hz, 1H, NH), 5.62 (dd, J = 7.8, 10.2 Hz, 1H), 5.51 (dd, J = 8.4, 10.2 Hz, 1H), 5.47 (dd, J = 7.8, 10.2 Hz, 1H), 5.38 (dd, J = 7.8, 10.2 Hz, 1H), 5.13 (dd, J = 7.8, 9.6 Hz, 1H), 5.06 (dd, J = 7.8, 9.0 Hz, 1H), 4.99 (dd, J = 3.0, 10.8 Hz, 1H), 4.90 (d, J = 11.4 Hz, 1H, $PhCH_2$), 4.88-4.81 (m, 5H), 4.69 (d, J = 11.4 Hz, 1H, $PhCH_2$), 4.64 (d, J = 7.8 Hz, 1H), 4.63 (d, J = 12.0 Hz, 1H, $PhCH_2$), 4.59-4.52 (m, 8H), 4.50-4.47 (m, 6H), 4.41-4.35 (m, 5H), 4.32 (d, J = 8.4 Hz, 1H), 4.29 (d, J = 9.0 Hz, 1H), 4.27 (d, J = 12.0 Hz, 1H, $PhCH_2$), 4.22 (d, J = 11.4 Hz, 1H, $PhCH_2$), 4.22 (d, J = 12.0 Hz, 1H, $PhCH_2$), 4.15 (d, J = 12.0 Hz, 1H, $PhCH_2$), 4.13 (d, J = 7.8 Hz, 1H), 4.06 (t, J = 9.6 Hz, 1H), 4.01-3.94 (m, 5H), 3.92-3.87 (m, 7H), 3.75 (dd, J = 3.6, 9.6 Hz, 1H), 3.71-3.58 (m, 8H), 3.56-3.39 (m, 13H), 3.35 (d, J = 10.2 Hz, 1H), 3.31-3.24 (m, 5H), 3.09-3.04 (m, 2H), 2.98 (brd, J = 9.6 Hz, 1H), 2.94-2.89 (m, 2H), 2.65-2.60 (m, 1H), 2.53-2.45 (m, 2H), 2.34-2.29 (m, 1H), 2.00 (s, 3H), 1.91 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.1, 172.3, 170.7, 170.4, 165.7, 165.5, 165.3, 165.1, 165.0, 165.0, 162.0, 162.0, 138.8, 138.8, 138.7, 138.5, 138.4, 138.3, 138.2, 138.1, 138.1, 138.0, 138.0, 133.8, 133.7, 133.6, 133.4, 133.3, 130.3, 130.2, 130.1, 130.0, 129.9, 129.9, 129.8, 129.7, 129.5, 129.0, 128.9, 128.8, 128.7, 128.7, 128.6, 128.6,

128.5, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.6, 127.4, 127.4, 127.3, 127.2, 101.8, 101.5, 101.4, 100.7, 100.6, 100.5, 100.4, 99.6, 92.6, 92.1, 80.6, 80.2, 80.1, 80.0, 78.5, 78.3, 76.8, 76.3, 76.0, 76.0, 75.9, 75.4, 75.2, 75.2, 74.9, 74.8, 74.8, 74.8, 74.6, 74.5, 74.1, 73.9, 73.7, 73.7, 73.6, 73.5, 73.5, 73.5, 73.3, 73.0, 72.9, 72.9, 72.8, 72.7, 72.3, 72.3, 72.2, 72.0, 72.0, 70.8, 68.9, 68.5, 68.1, 68.0, 68.0, 67.8, 67.8, 63.5, 62.0, 56.1, 55.6, 50.5, 37.9, 29.7, 28.1, 21.0, 20.9. MALDI-TOF MS: calc. for $C_{203}H_{203}Cl_6N_5O_{51}Na^+$ $[M+Na]^+$: 3759.1468, found: 3759.0154.

15. References

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16. NMR Spectra

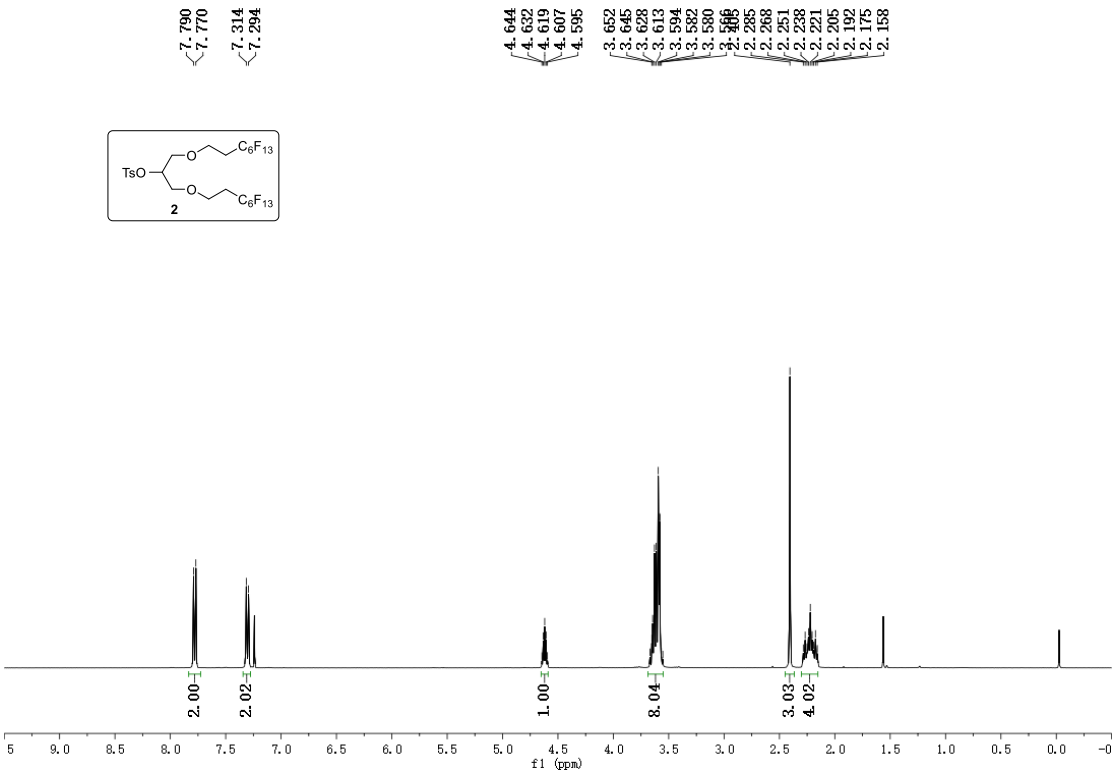

Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2**

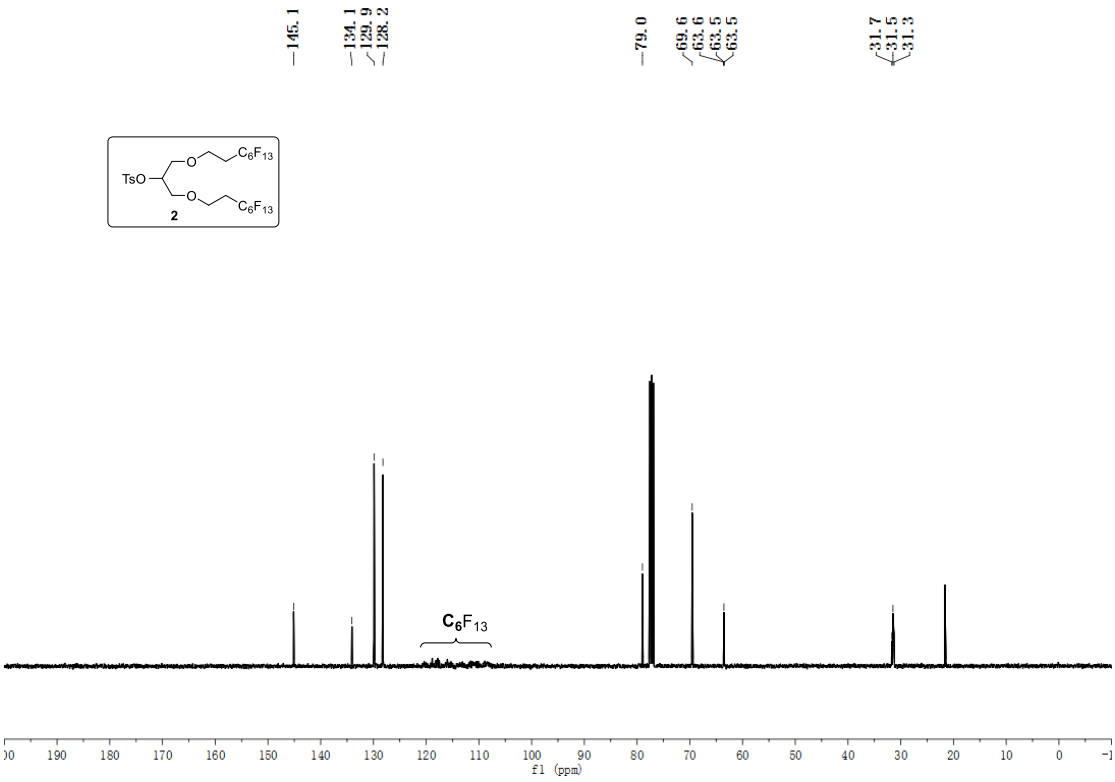

Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2**

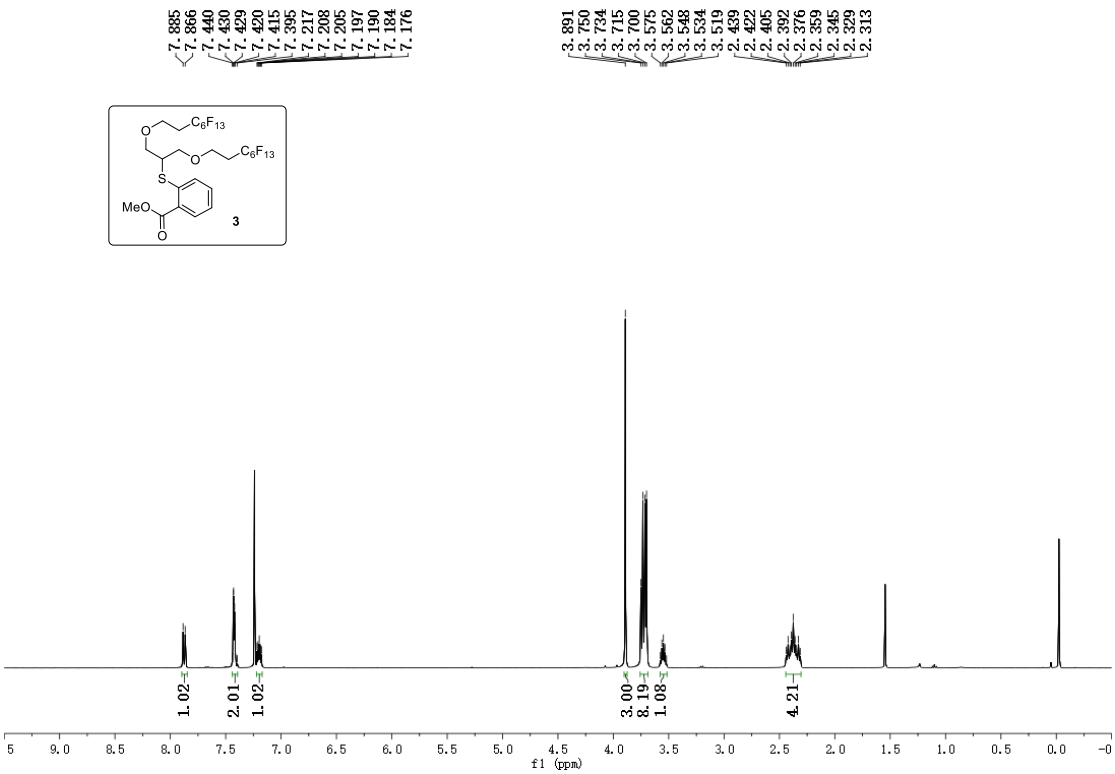

Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3**

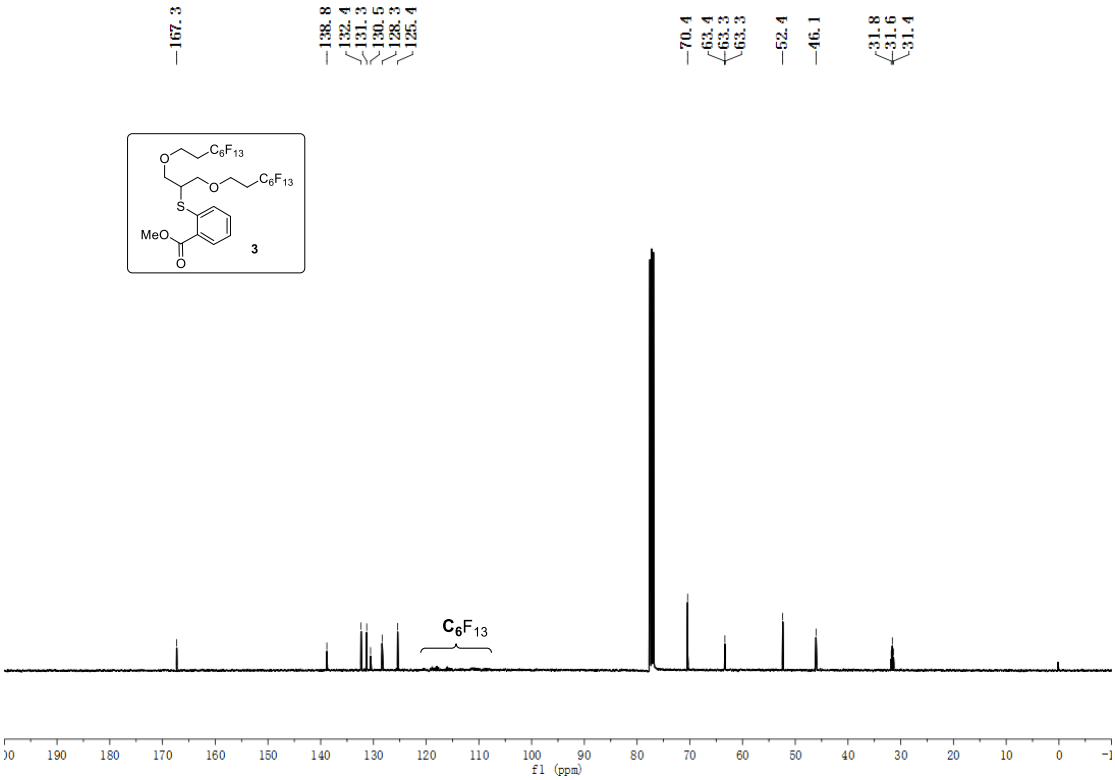

Figure S4. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3**

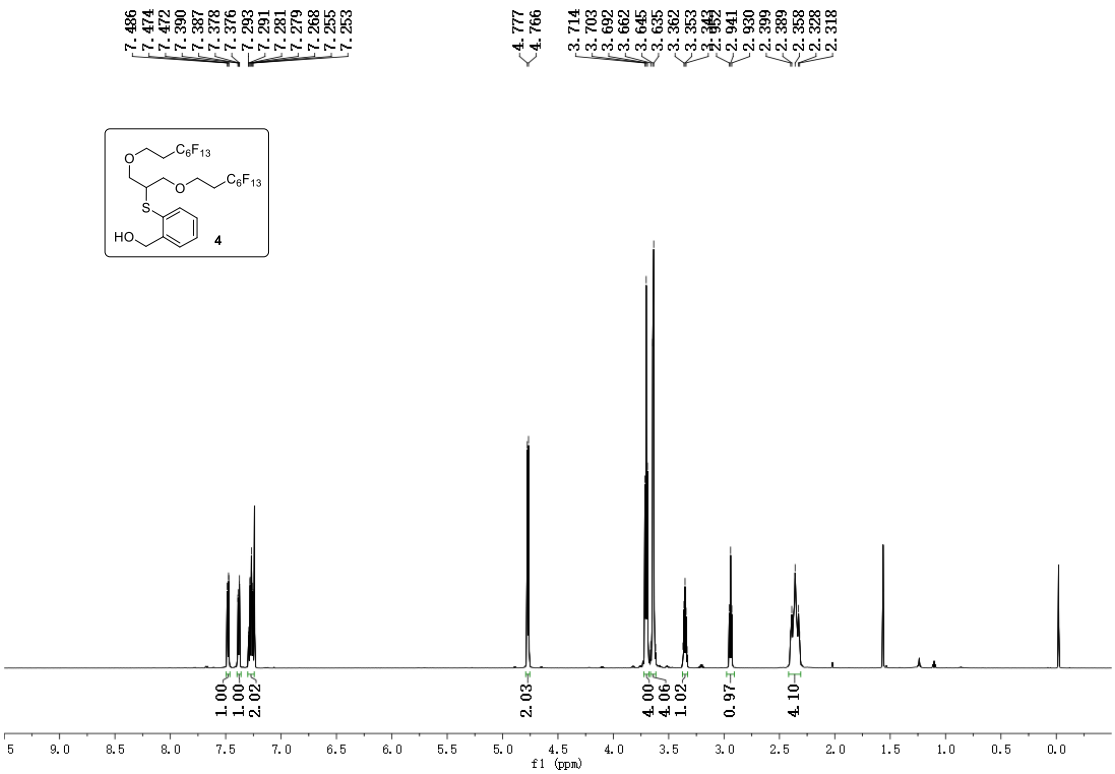

Figure S5. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4**

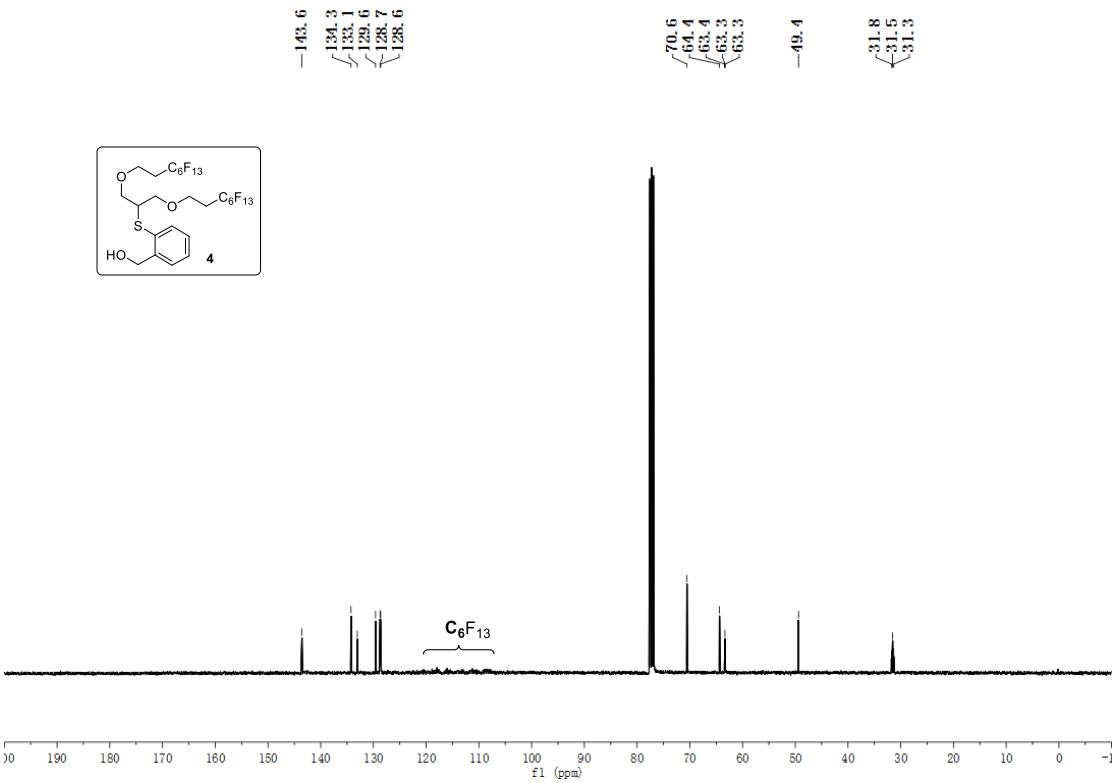

Figure S6. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **4**

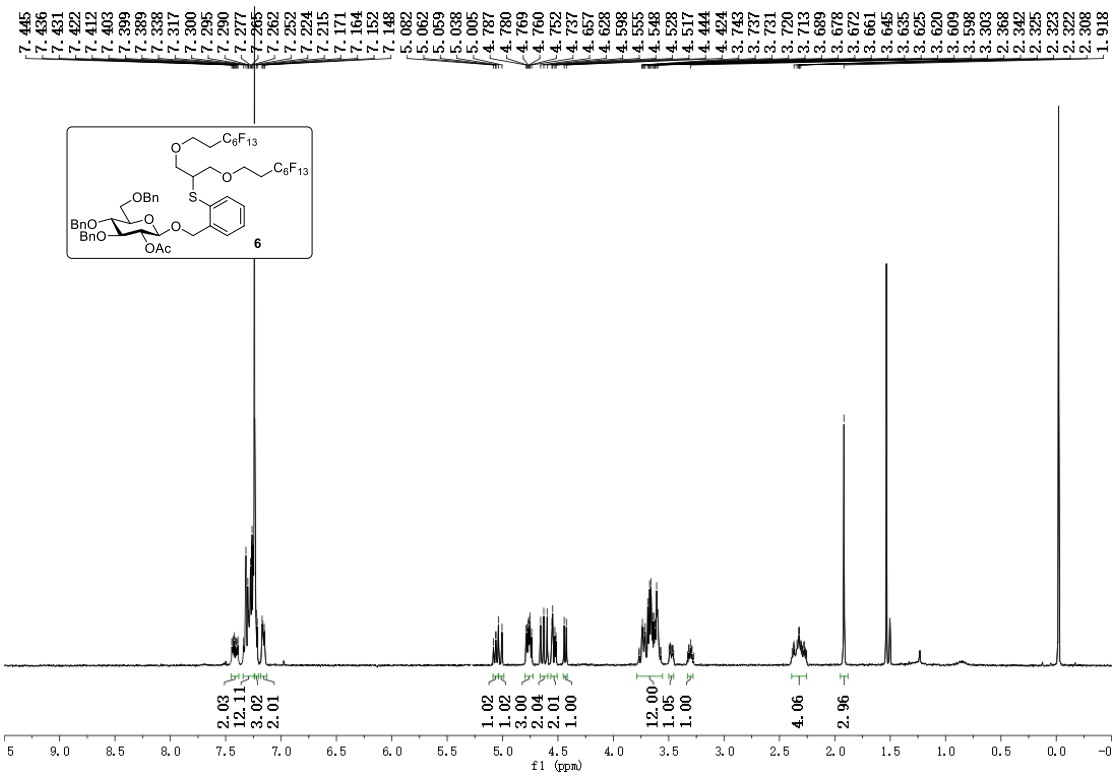

Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6**

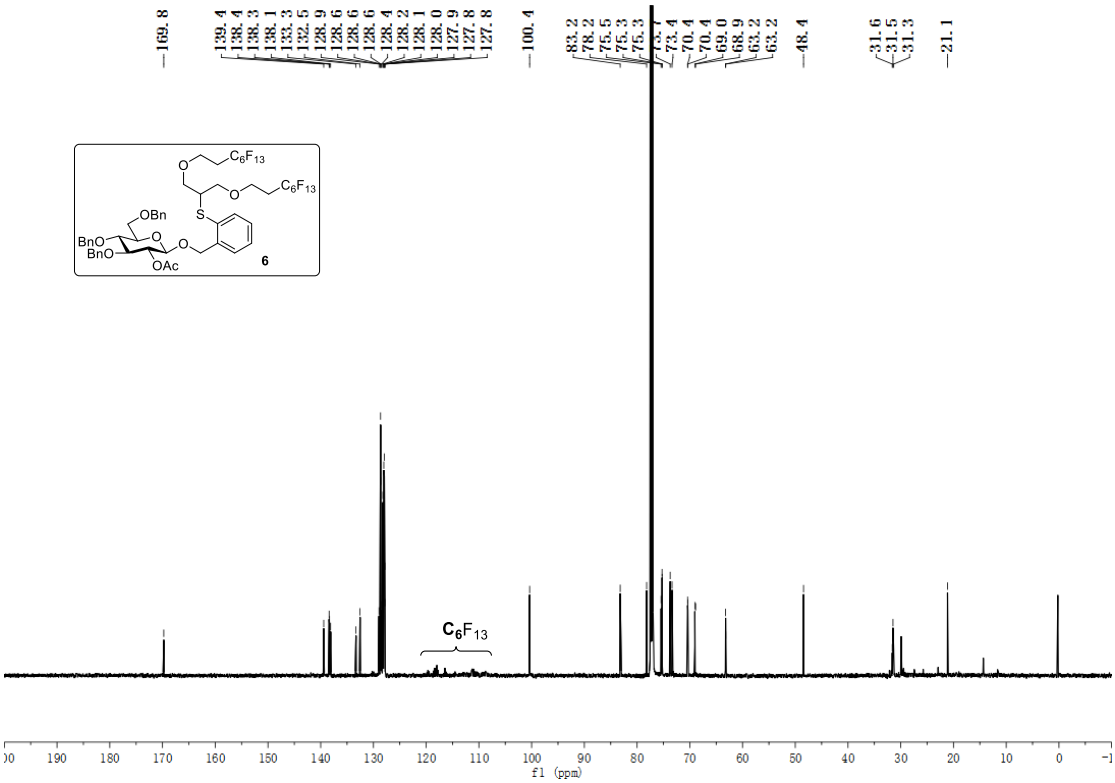

Figure S8. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **6**

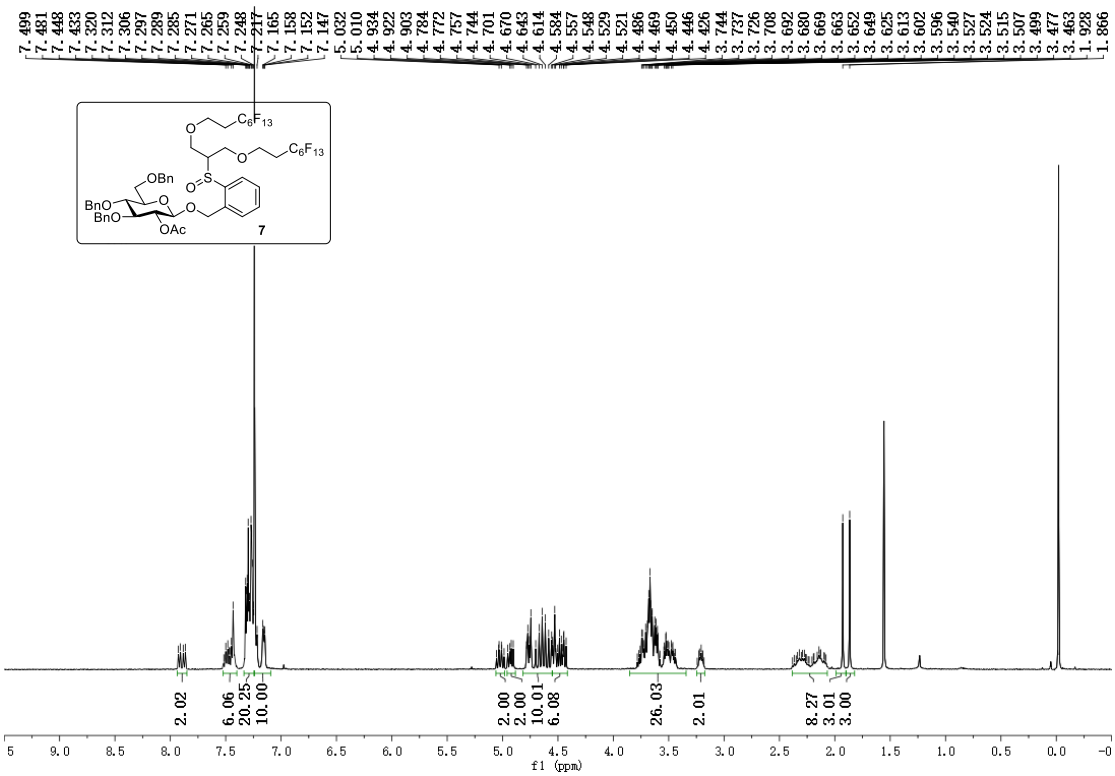

Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7**

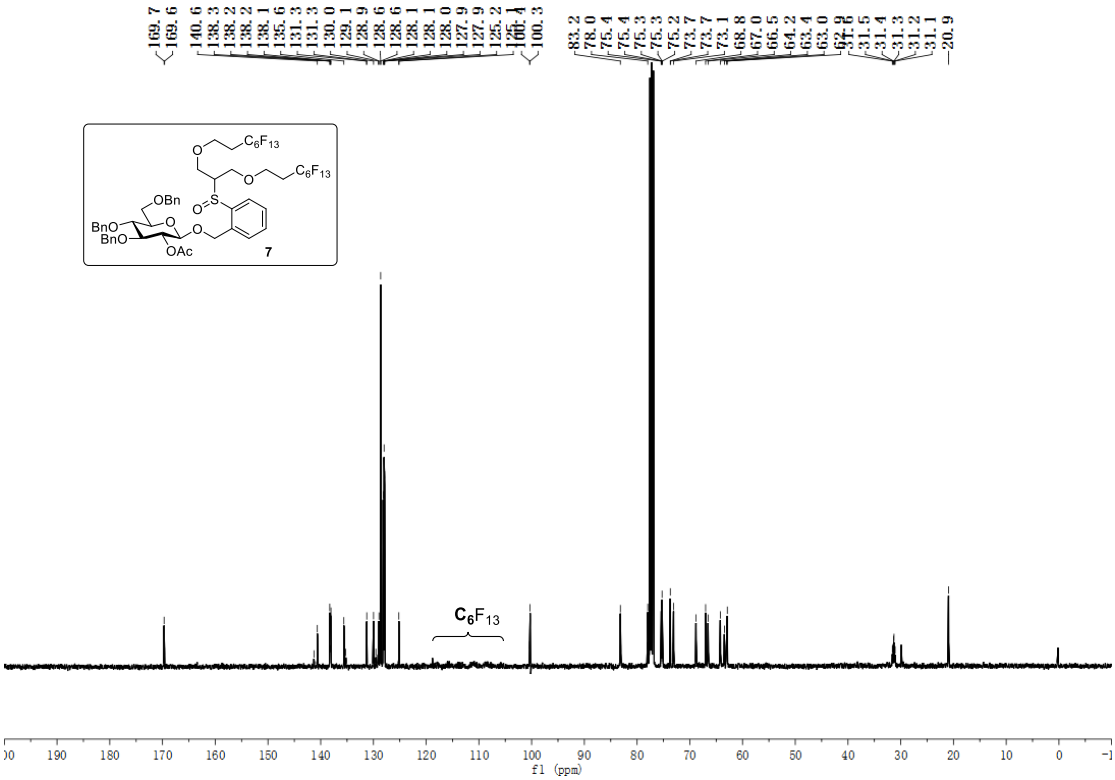

Figure S10. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **7**

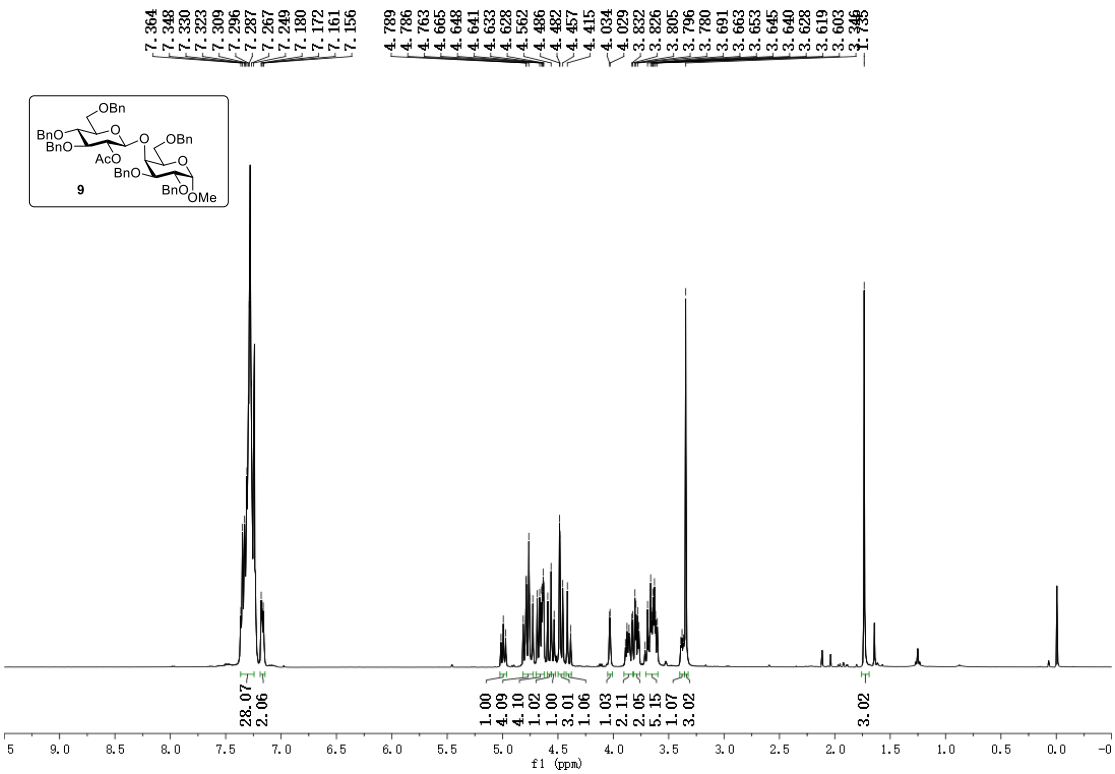

Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **9**

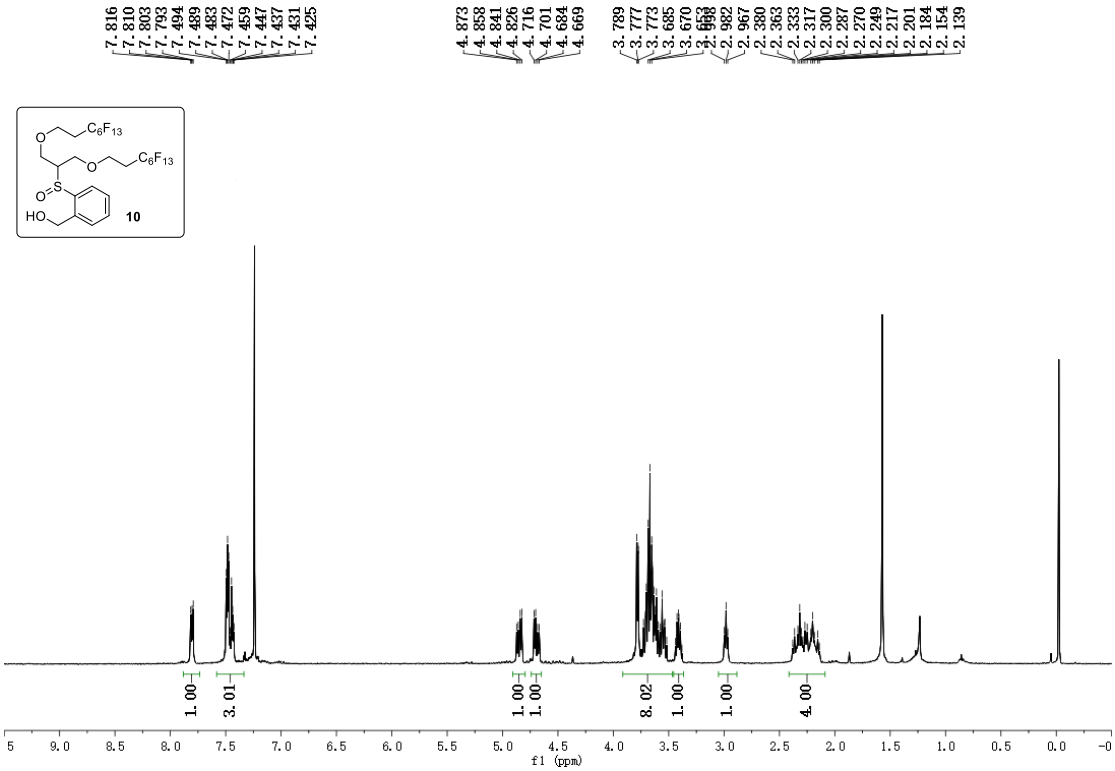

Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10**

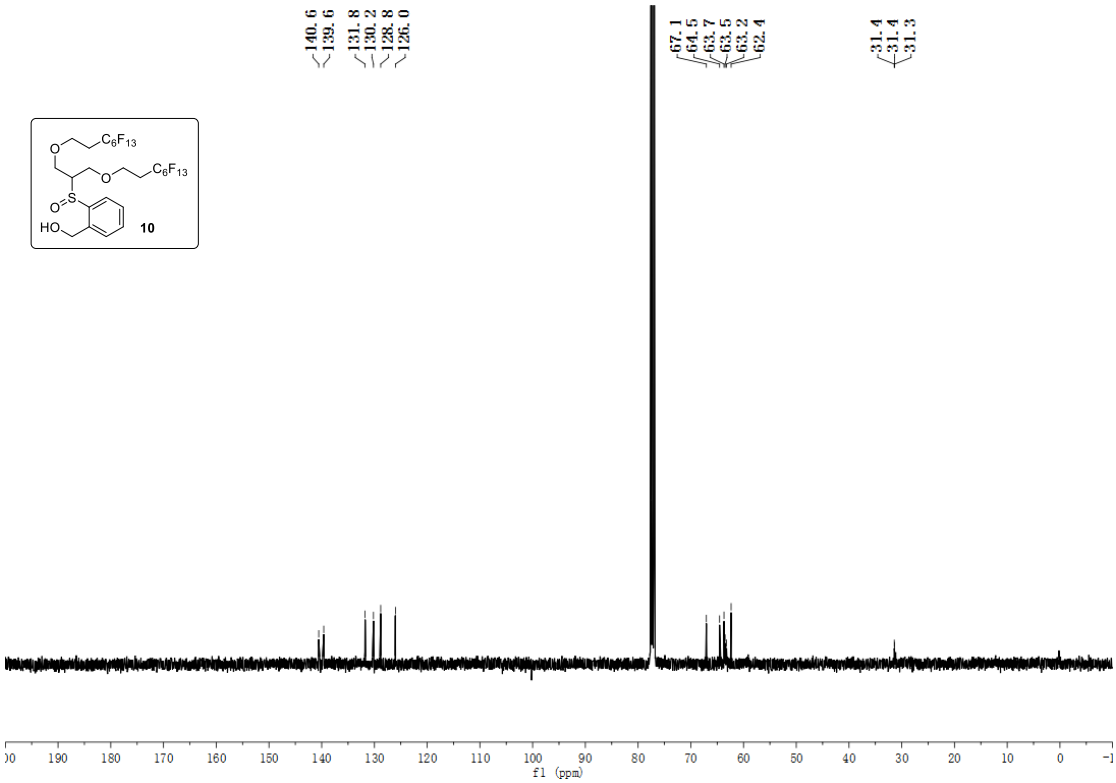

Figure S13. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10**

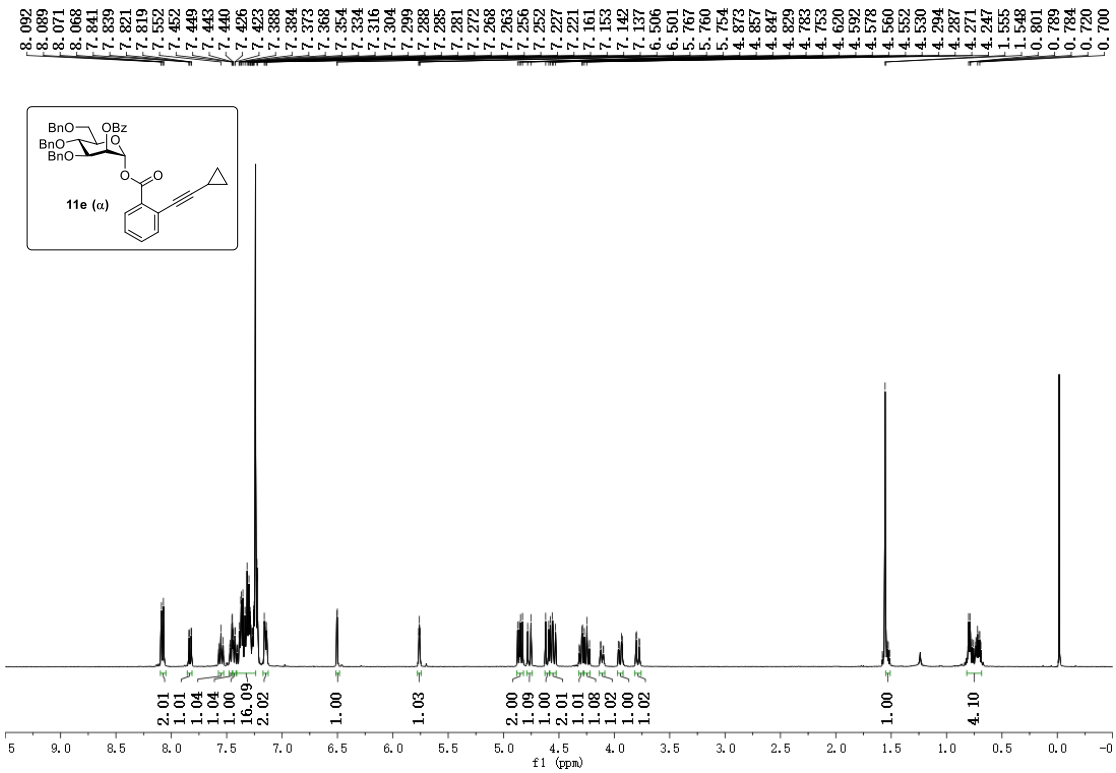

Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11e (α)**

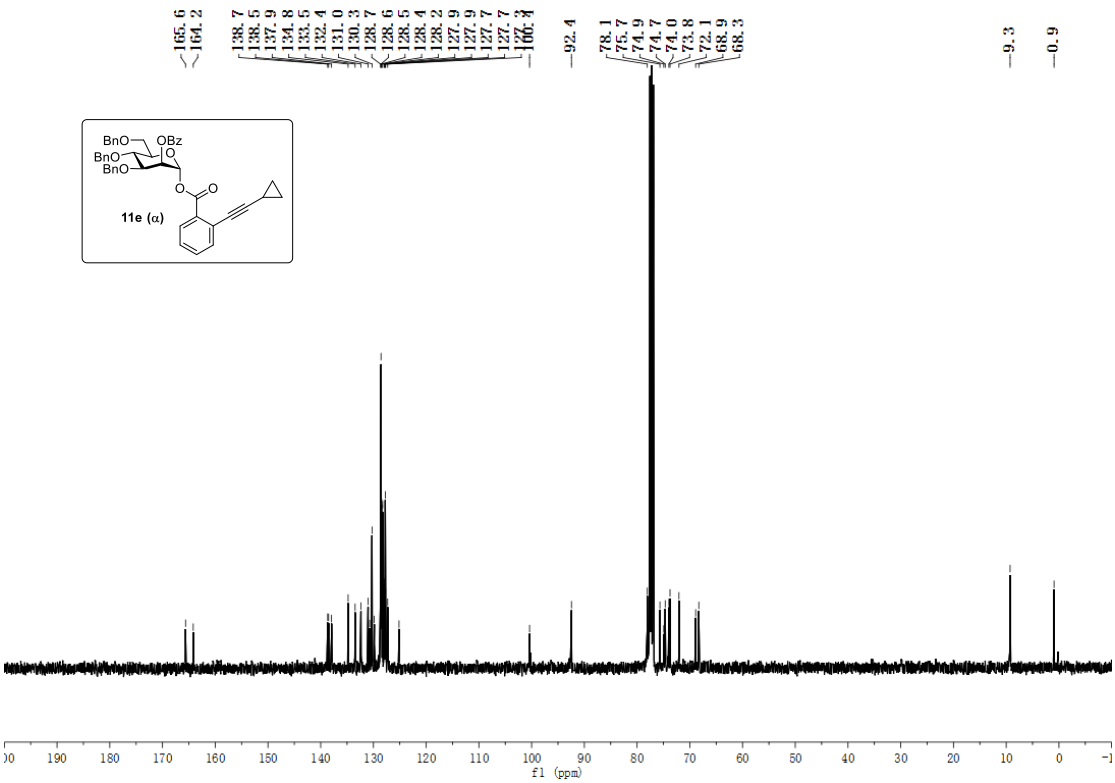

Figure S15. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **11e (α)**

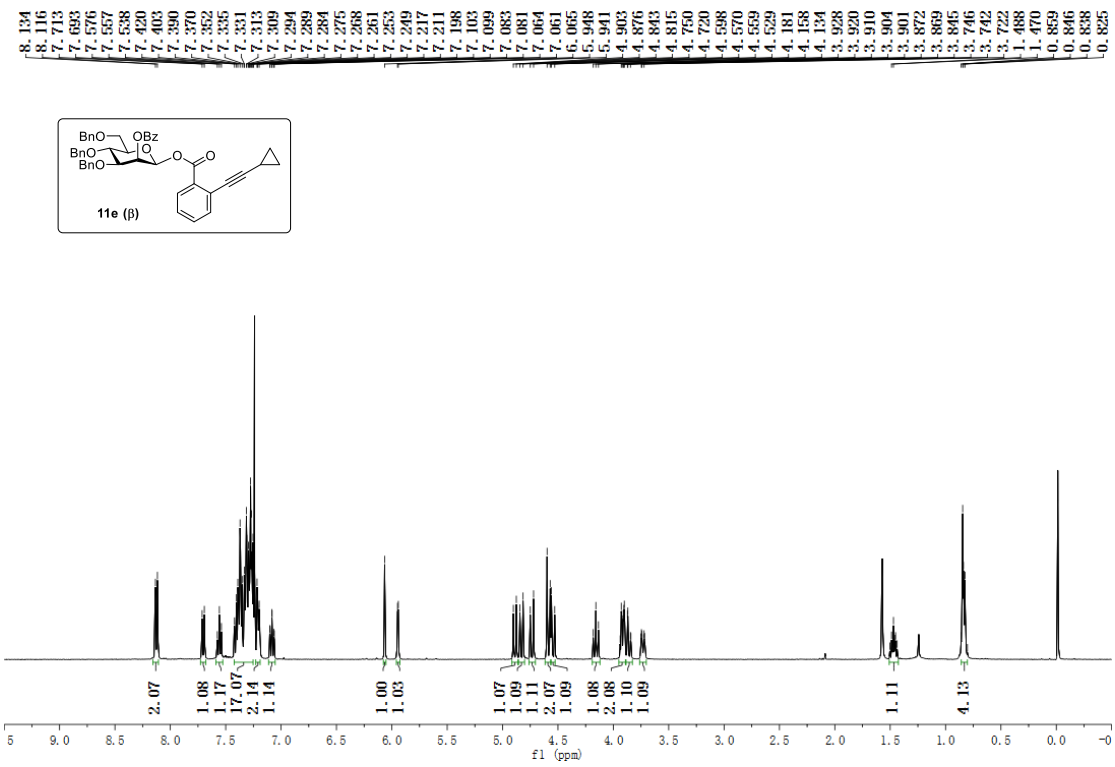

Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11e (β)**

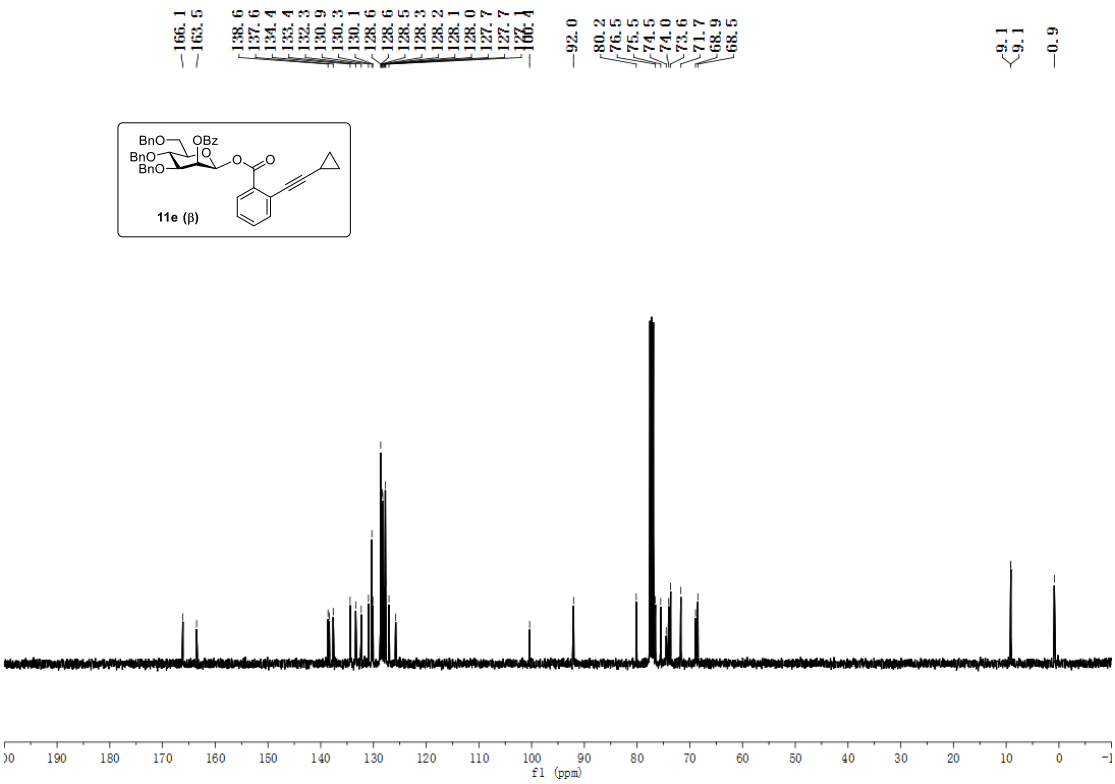

Figure S17. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **11e (β)**

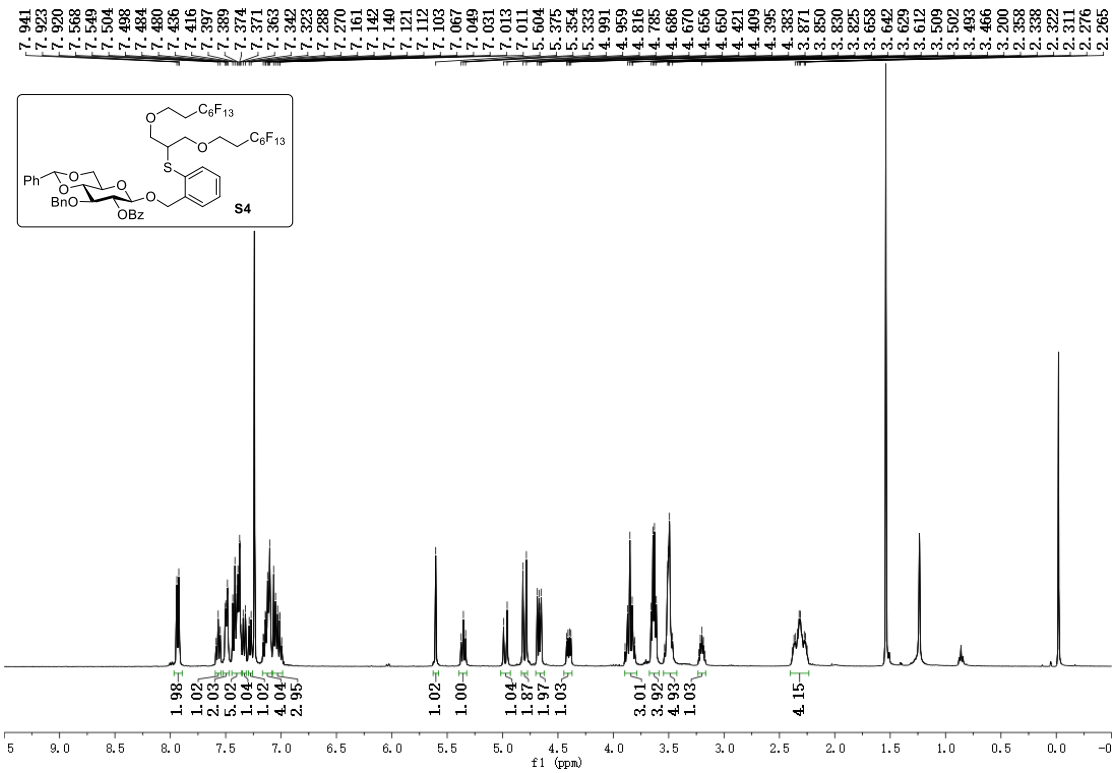

Figure S18. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S4**

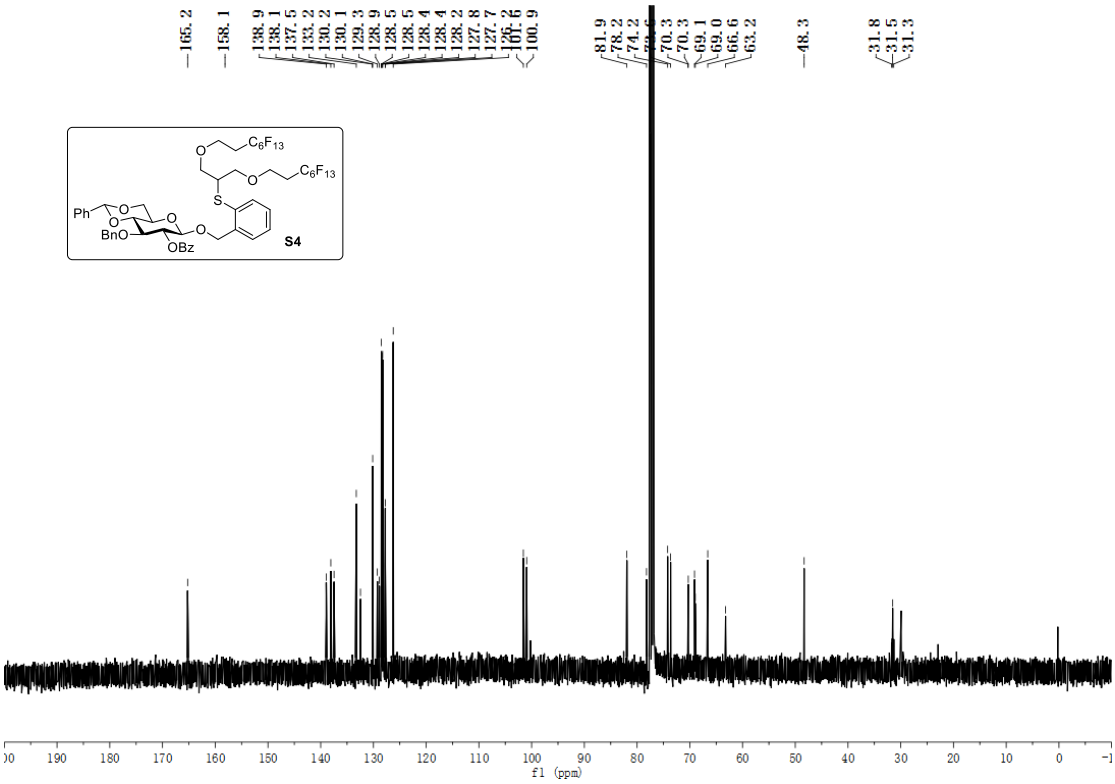

Figure S19. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **S4**

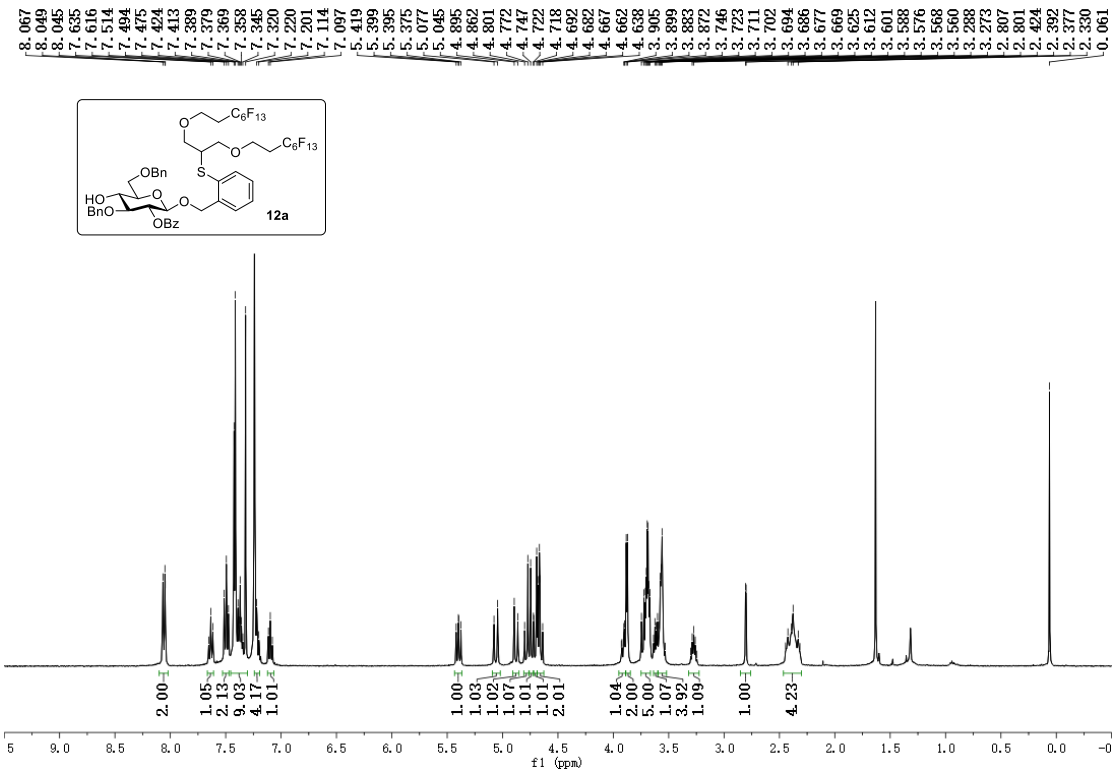

Figure S20. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12a**

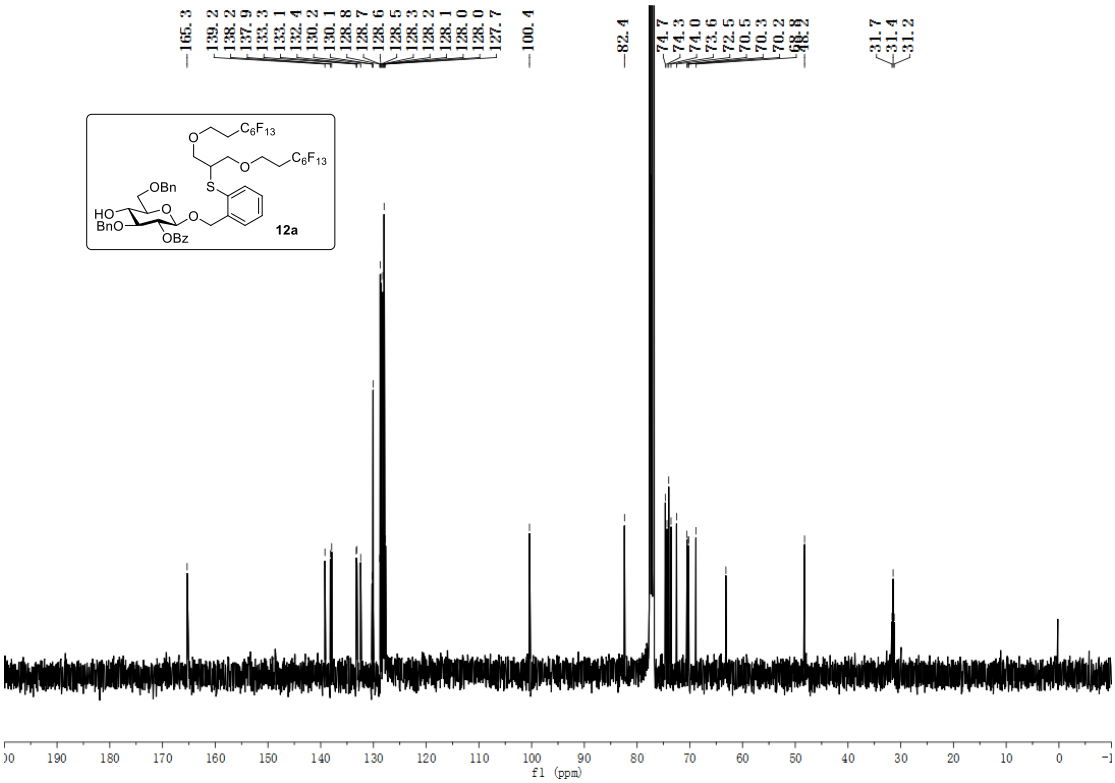

Figure S21. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **12a**

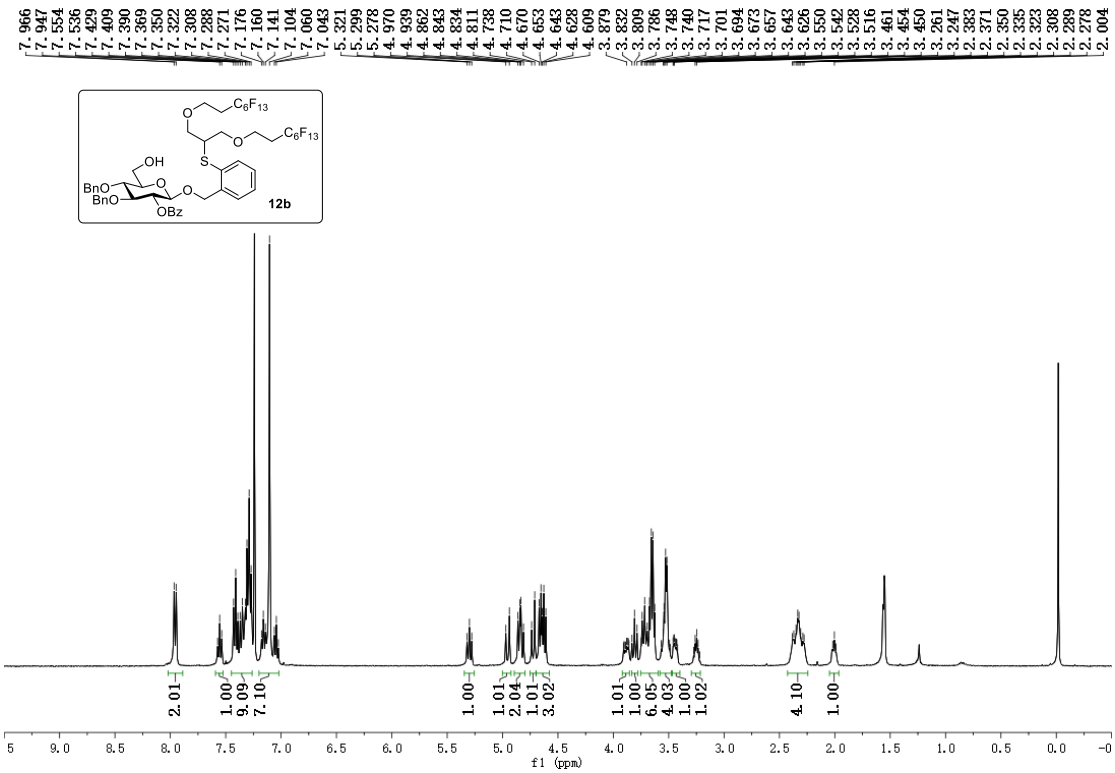

Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12b**

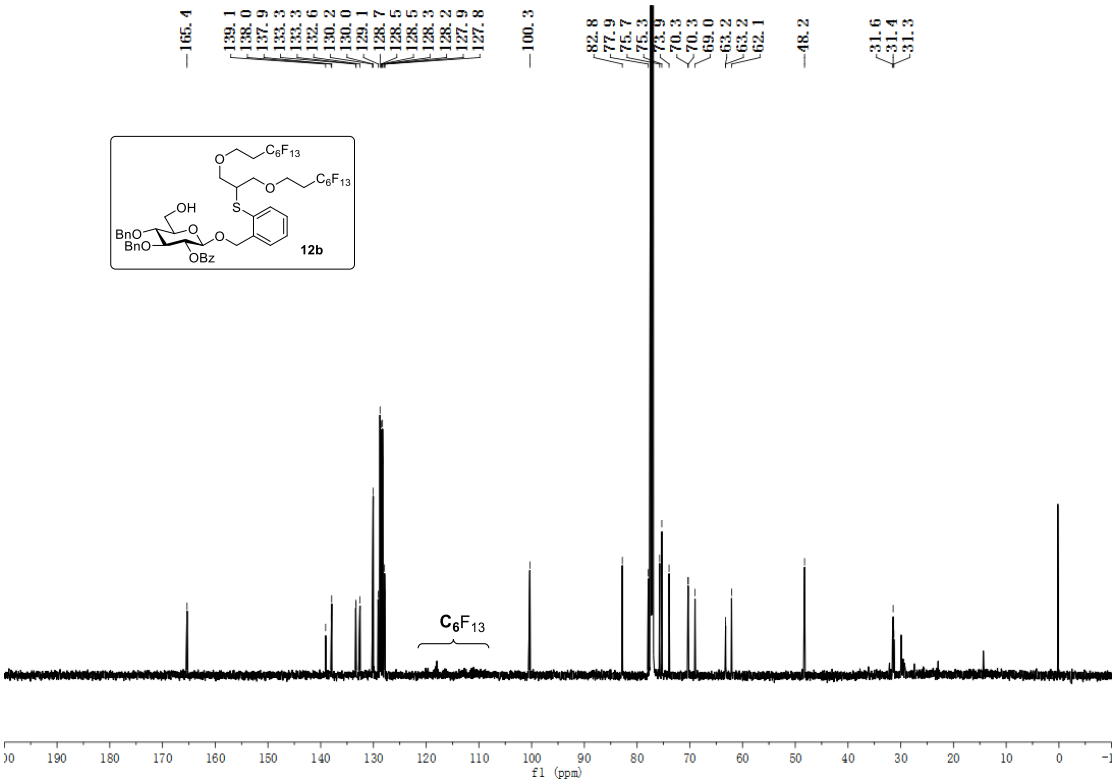

Figure S23. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **12b**

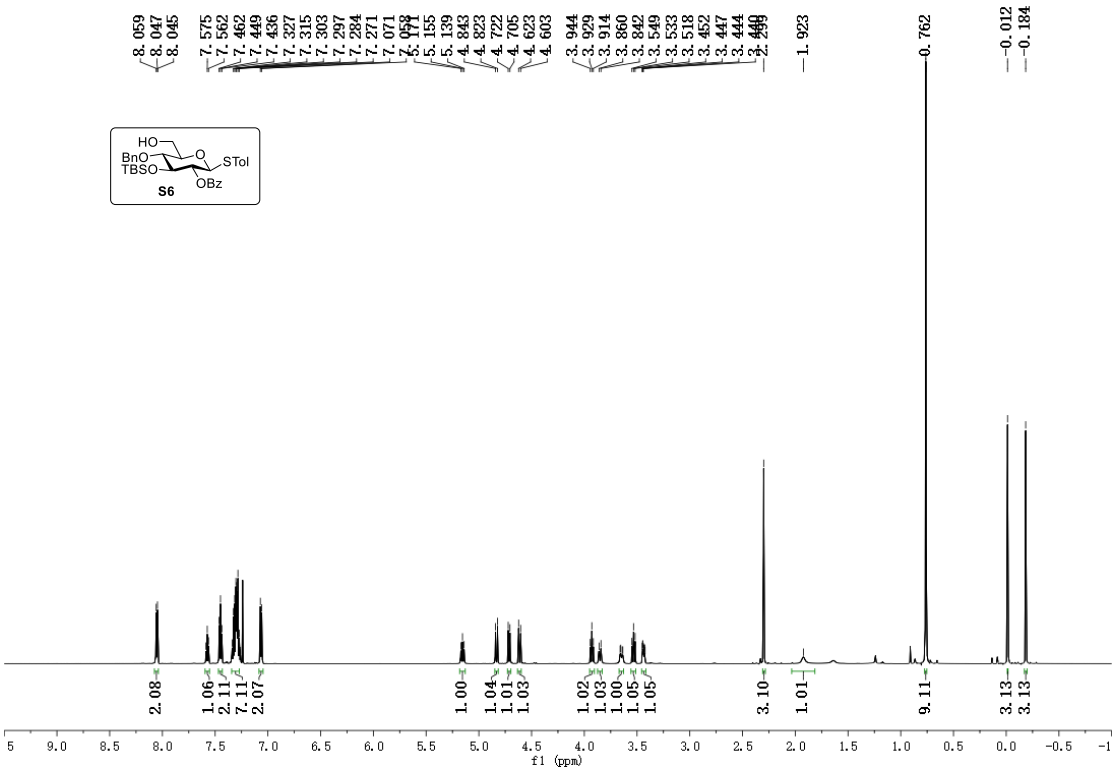

Figure S24. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **S6**

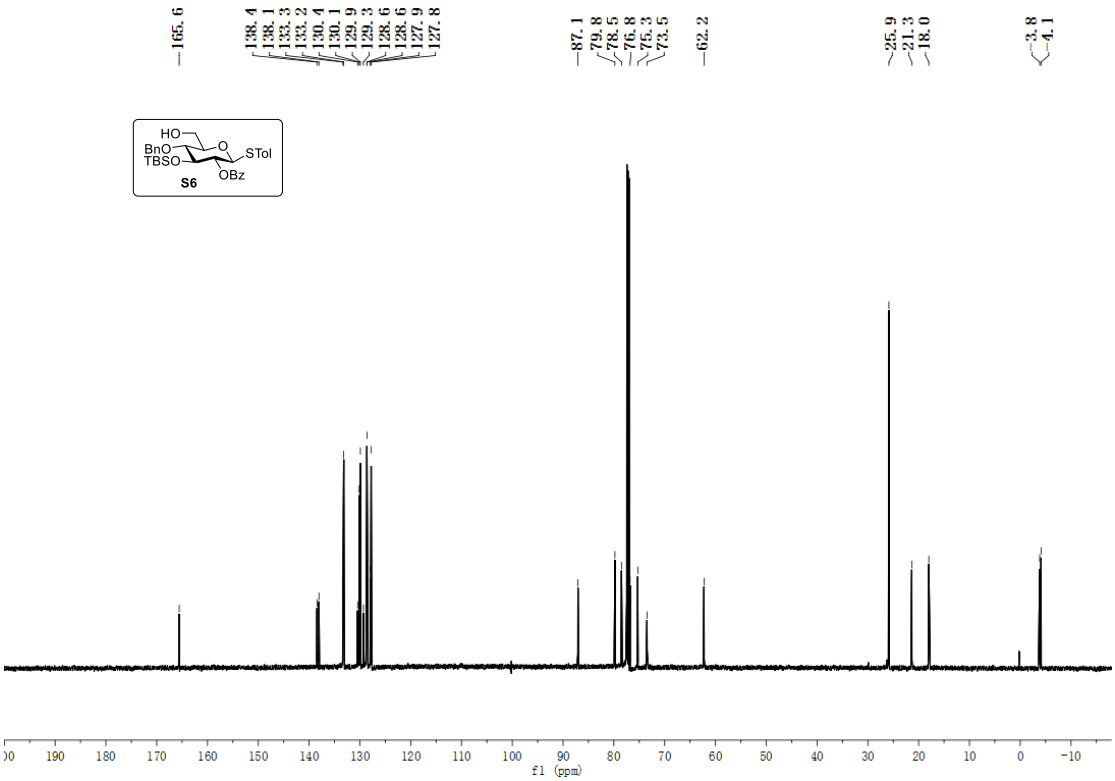

Figure S25. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **S6**

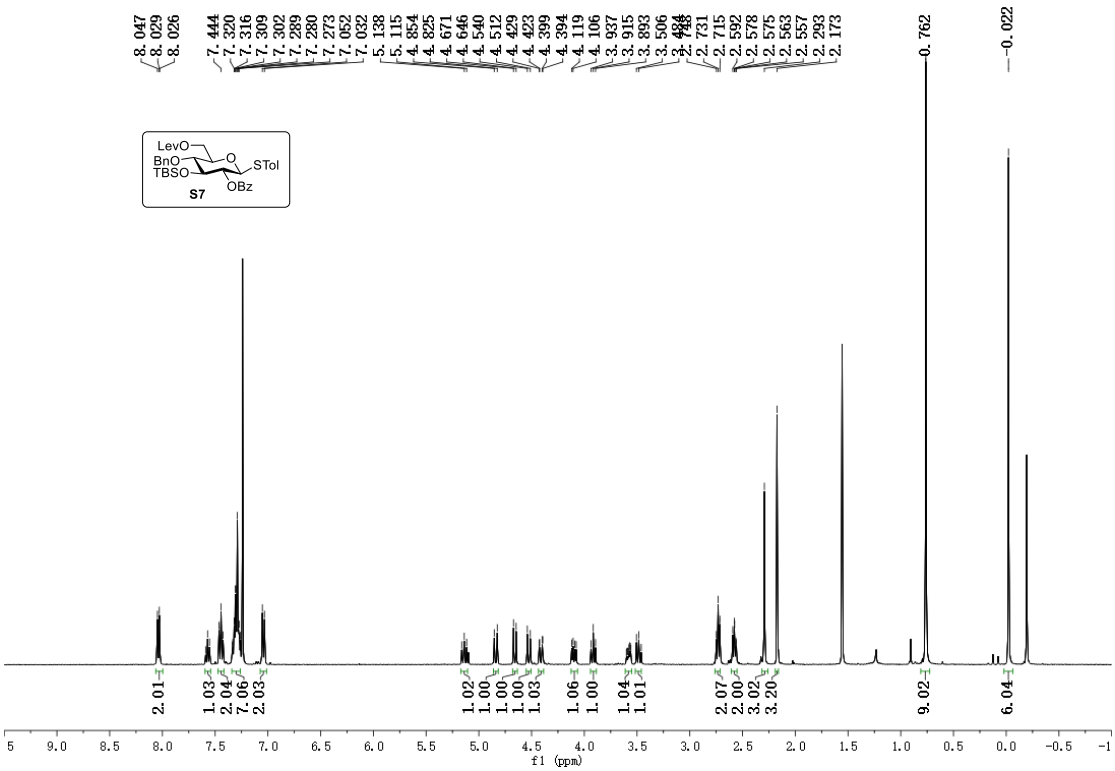

Figure S26. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S7**

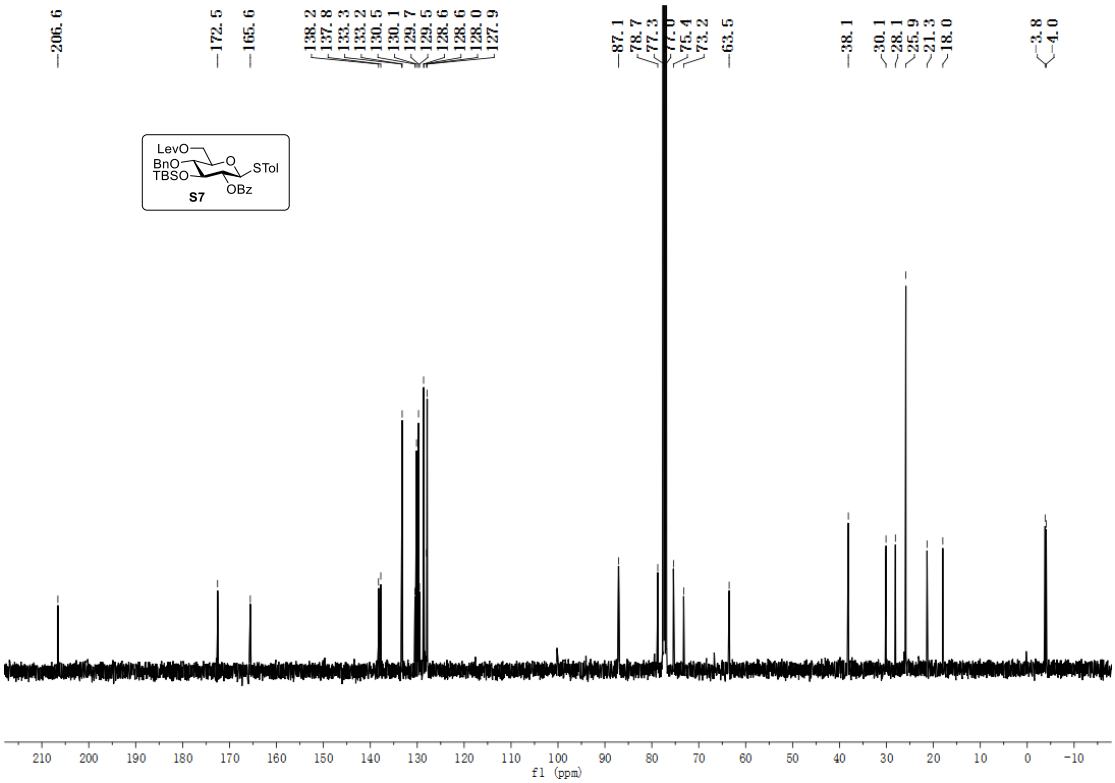

Figure S27. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **S7**

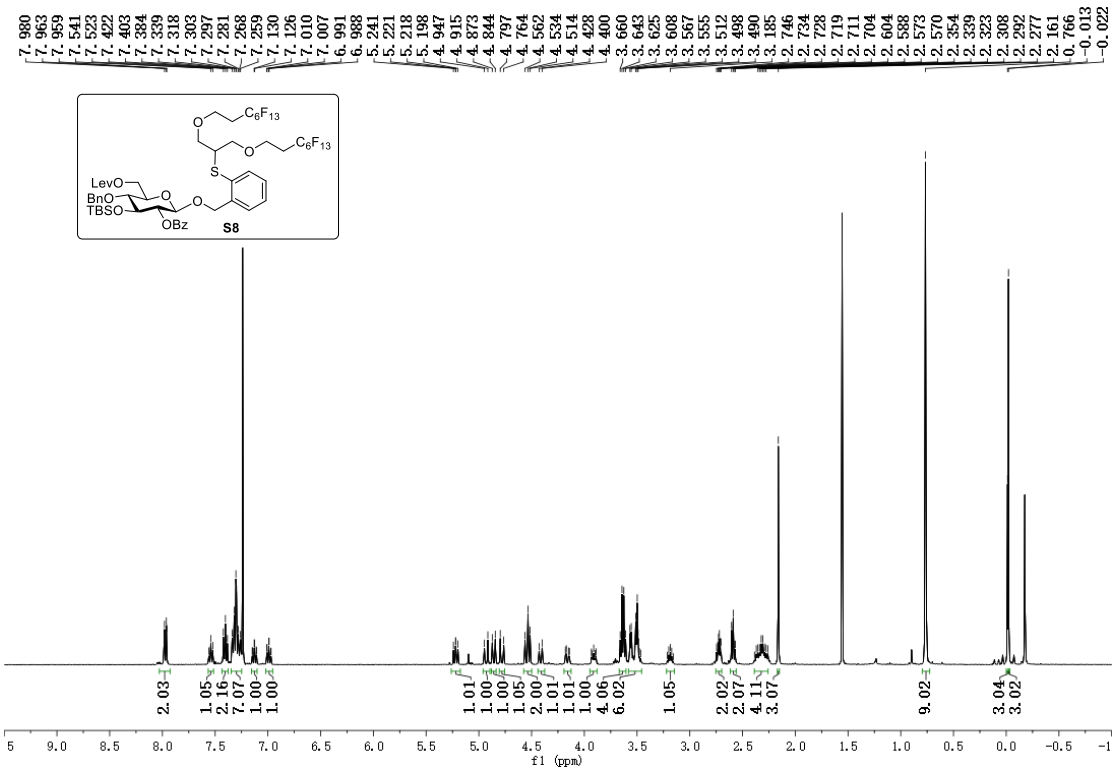

Figure S28. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S8**

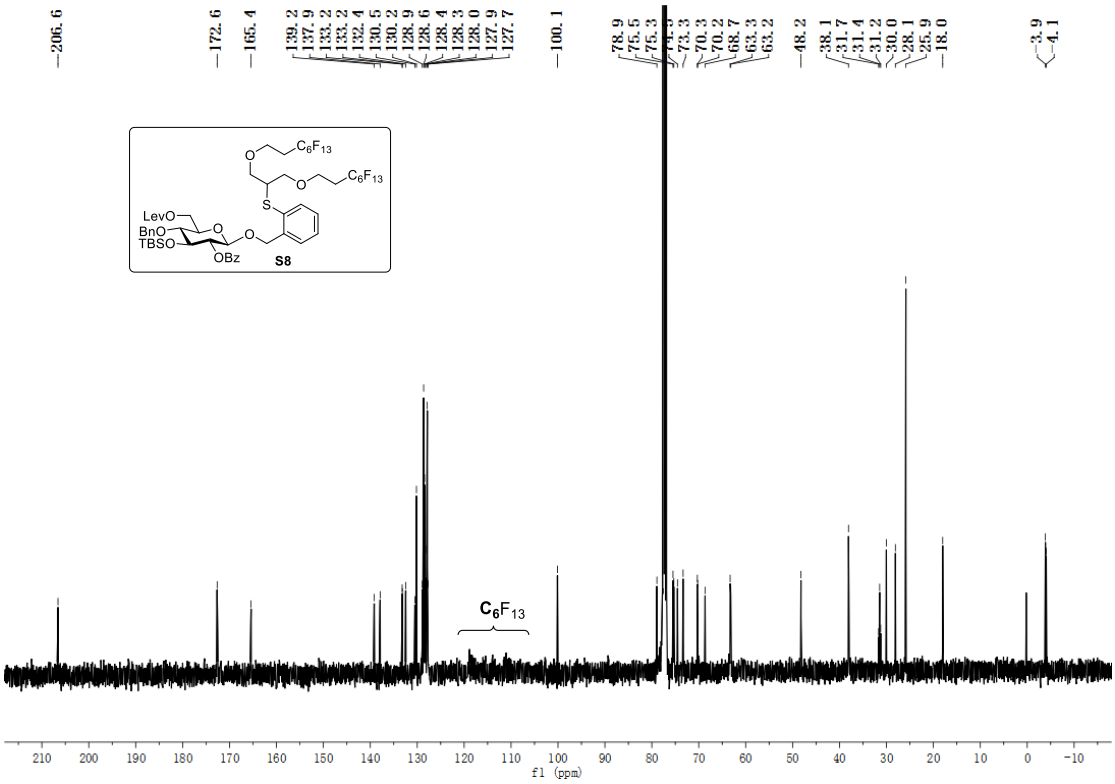

Figure S29. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **S8**

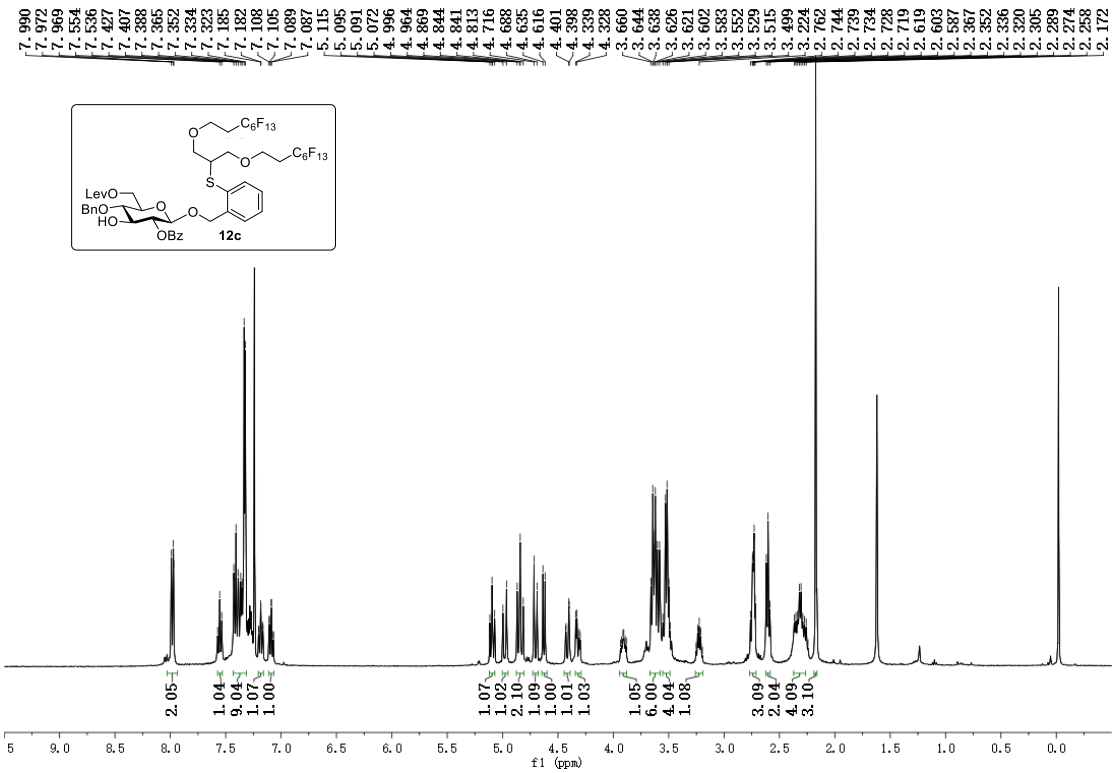

Figure S30. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12c**

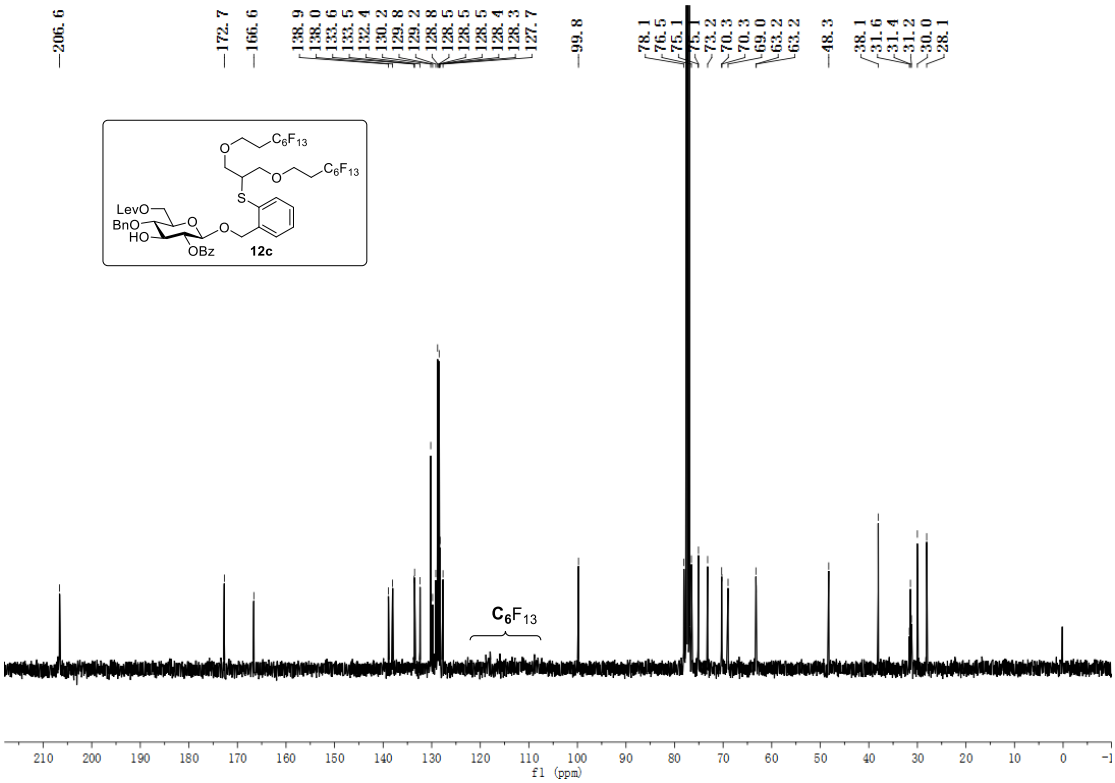

Figure S31. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **12c**

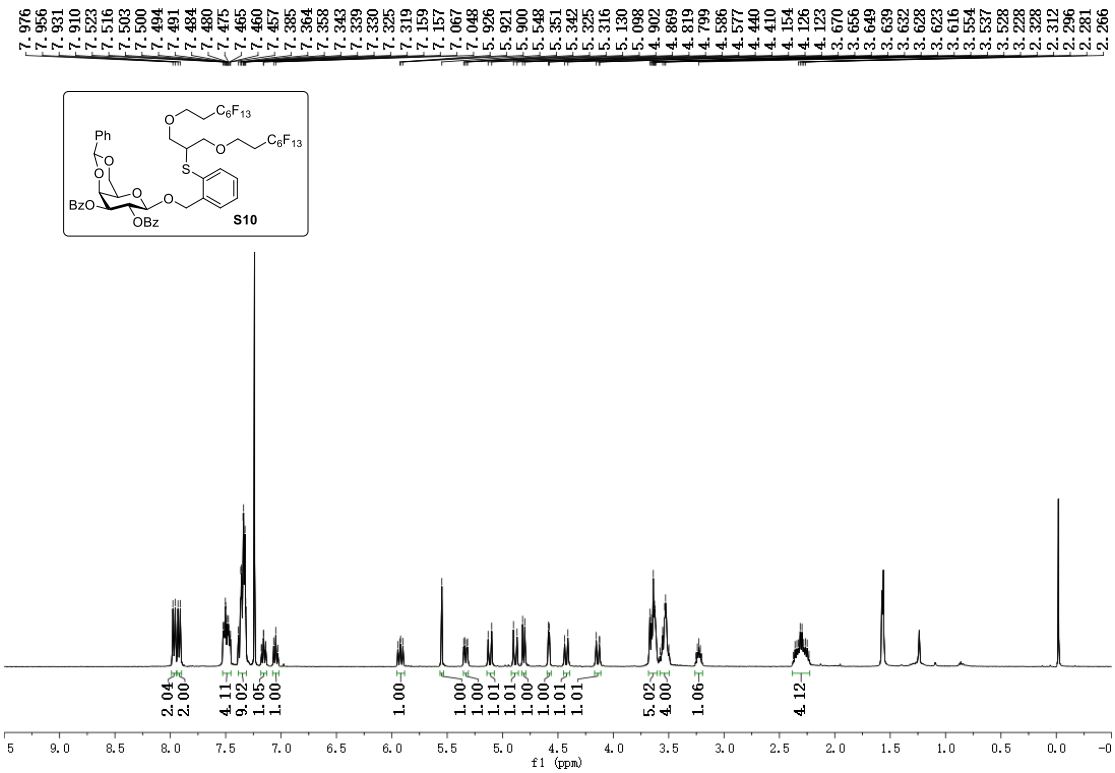

Figure S32. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S10**

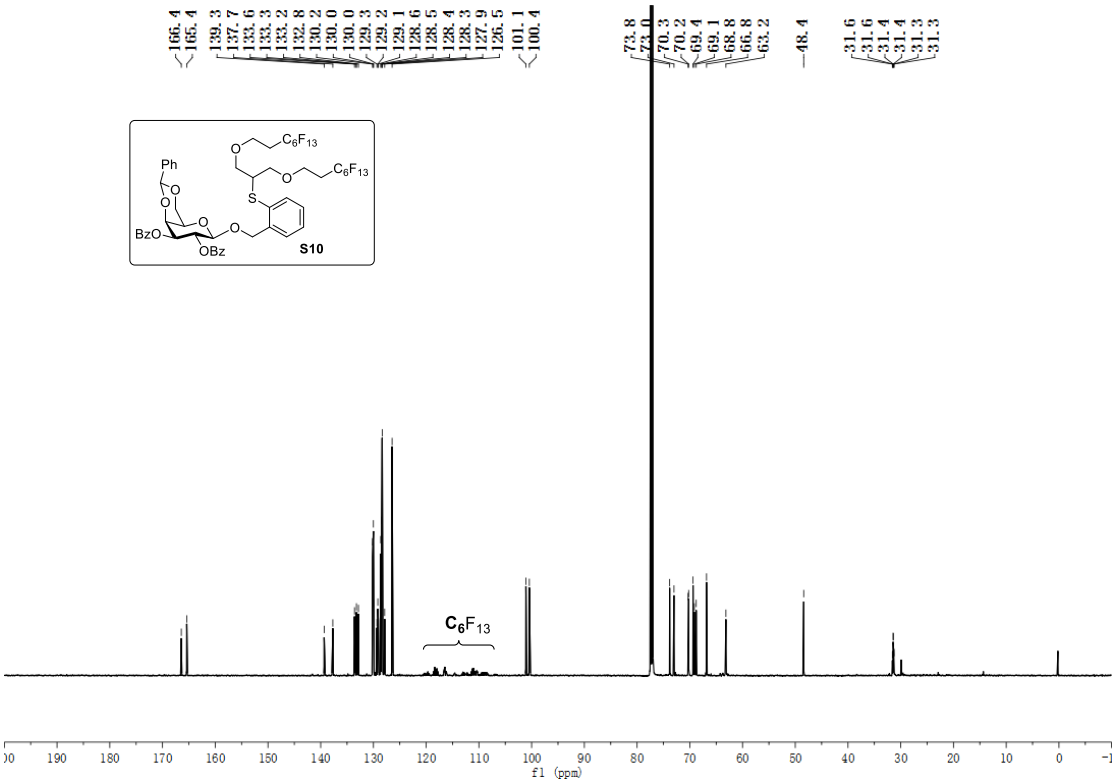

Figure S33. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **S10**

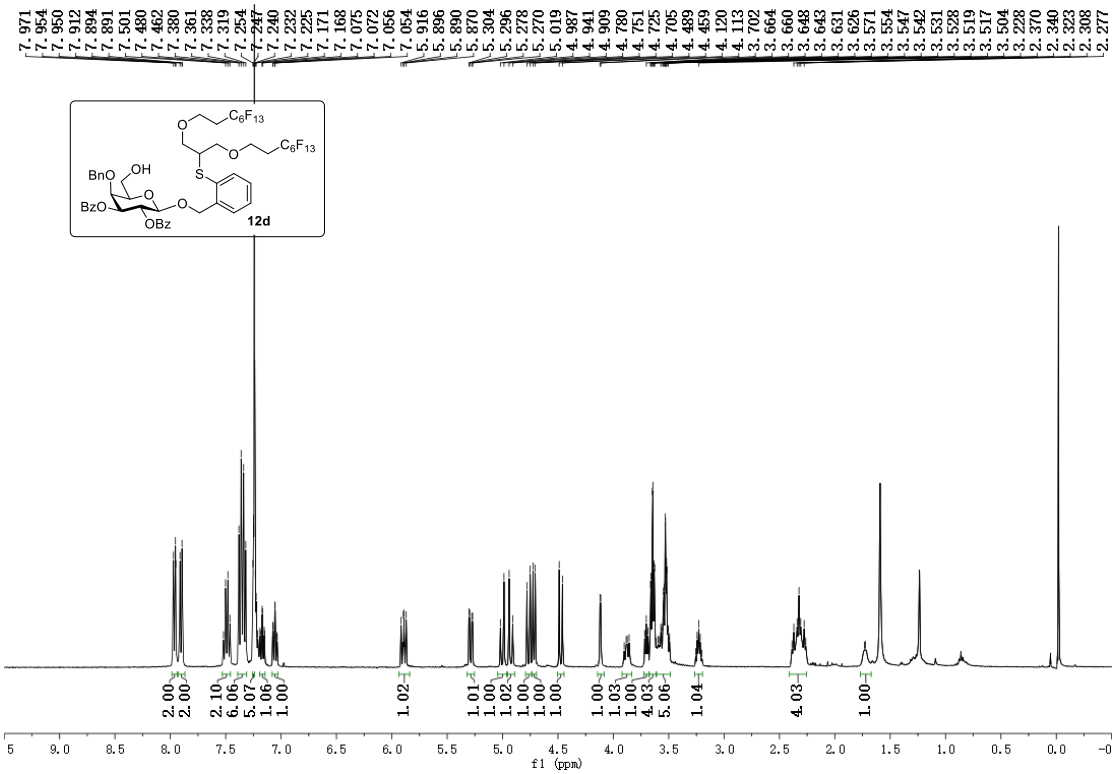

Figure S34. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12d**

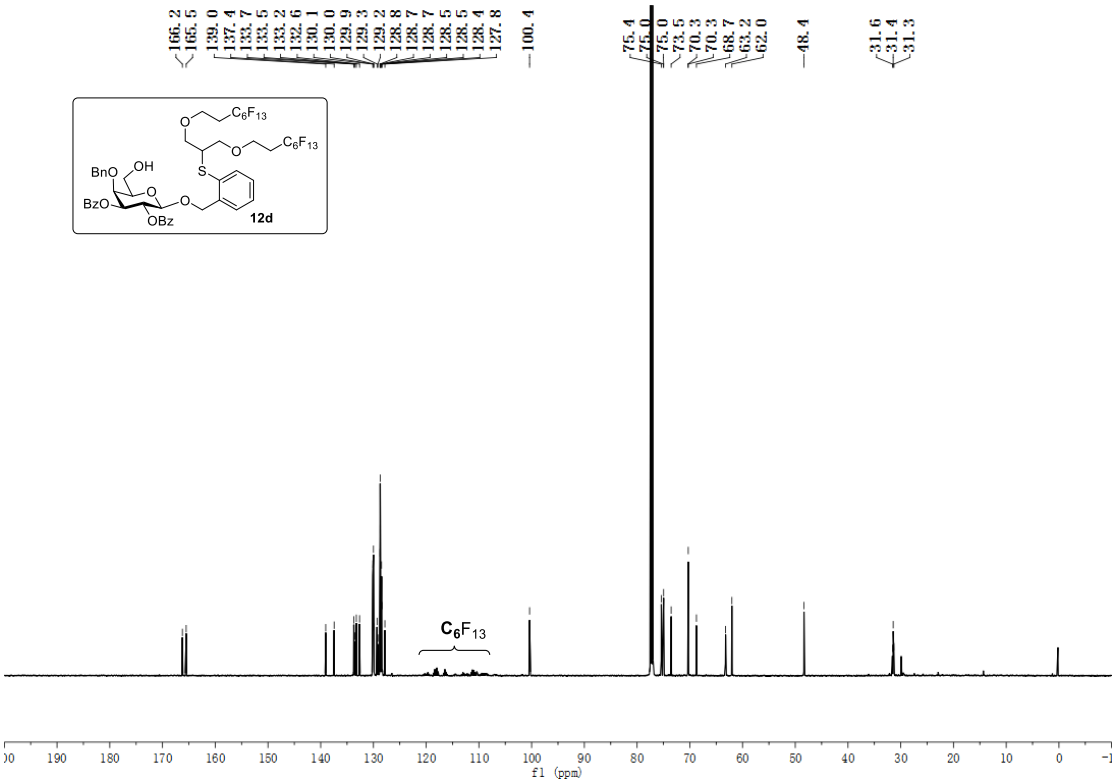

Figure S35. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **12d**

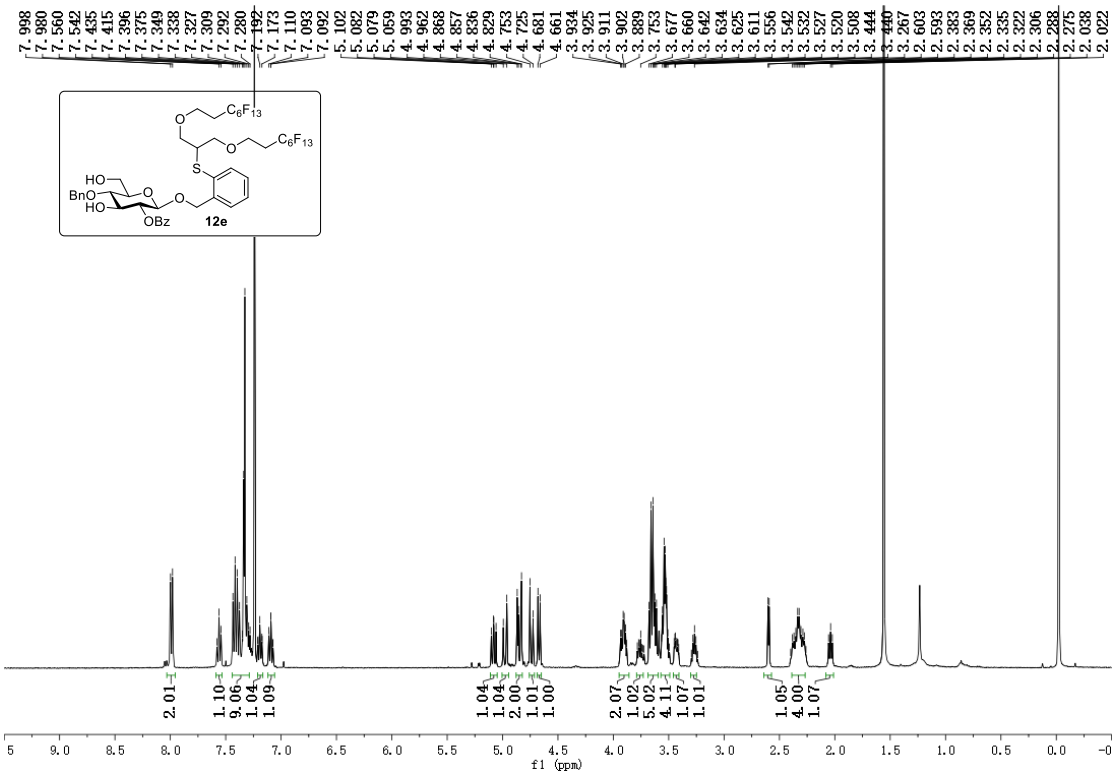

Figure S36. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12e**

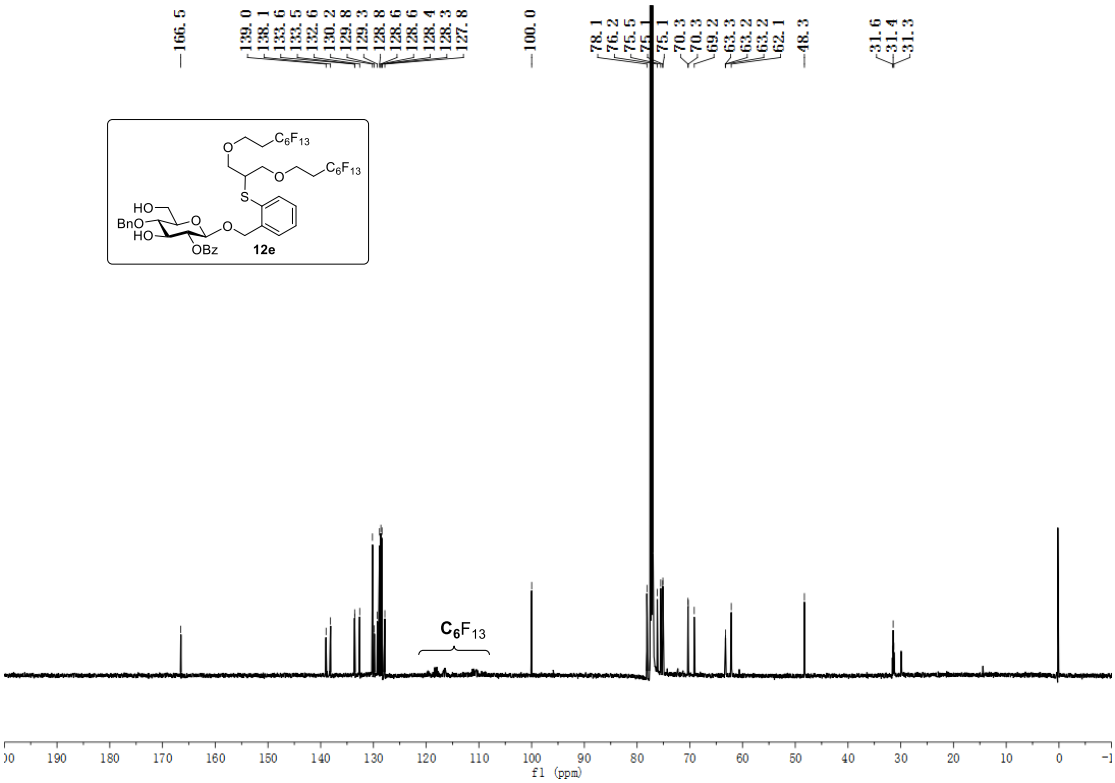

Figure S37. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **12e**

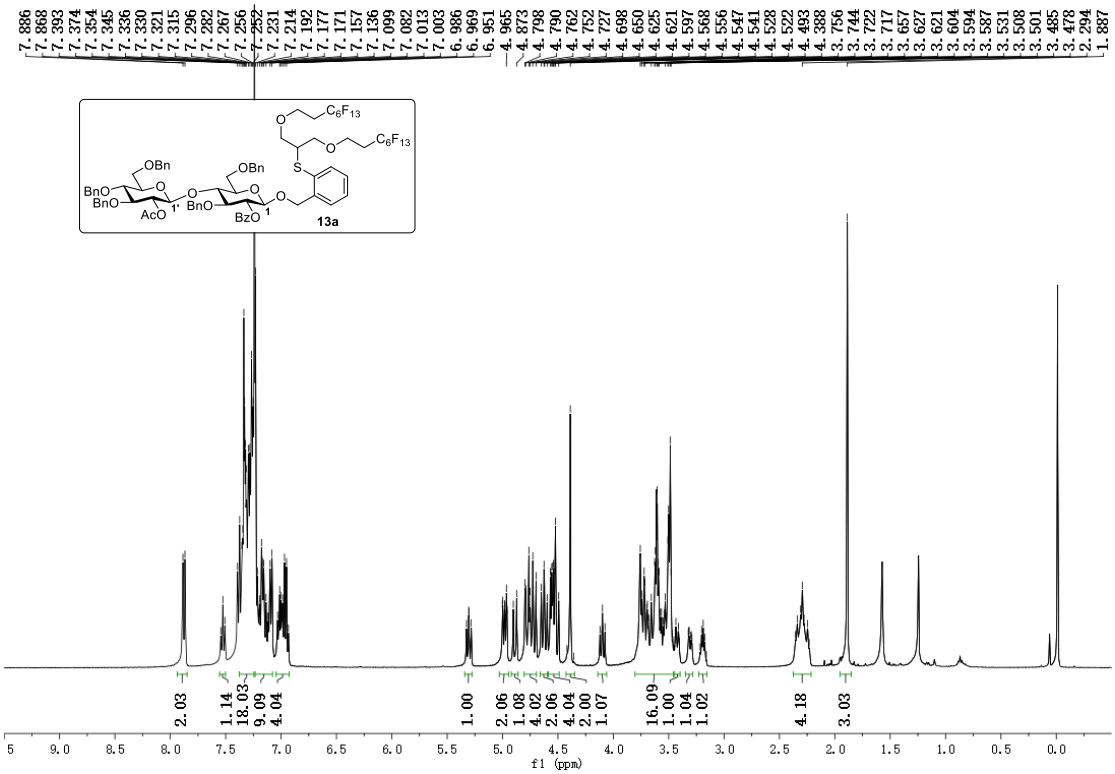

Figure S38. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **13a**

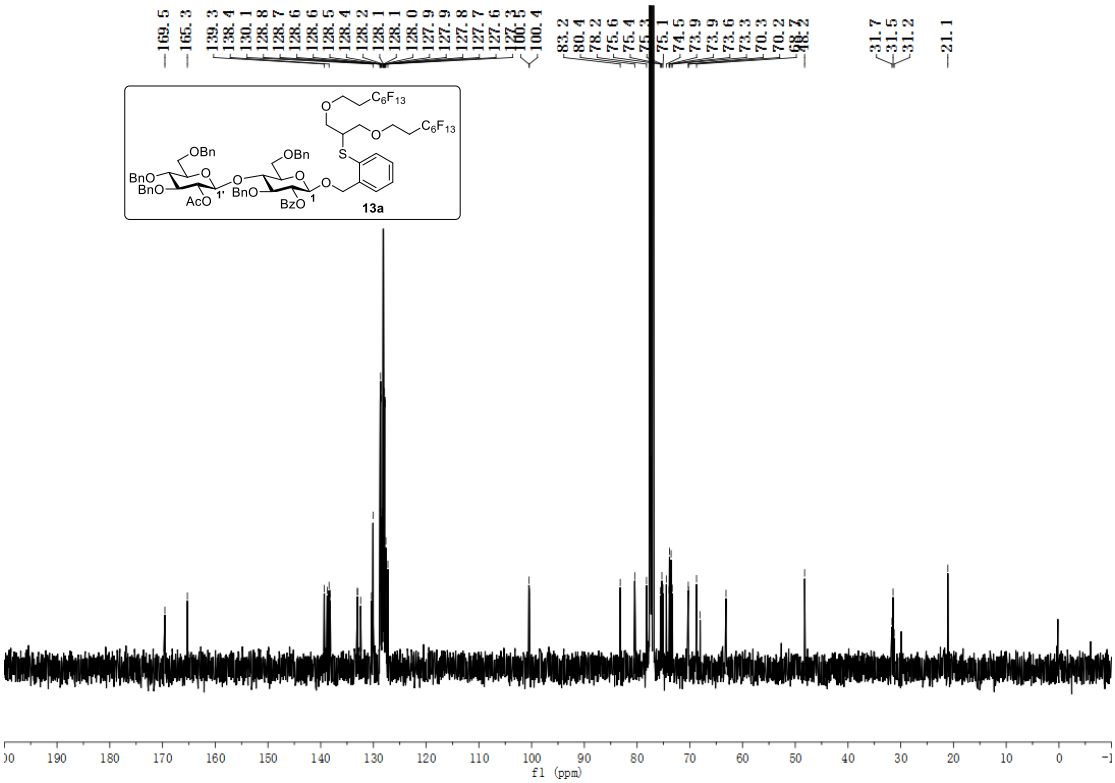

Figure S39. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **13a**

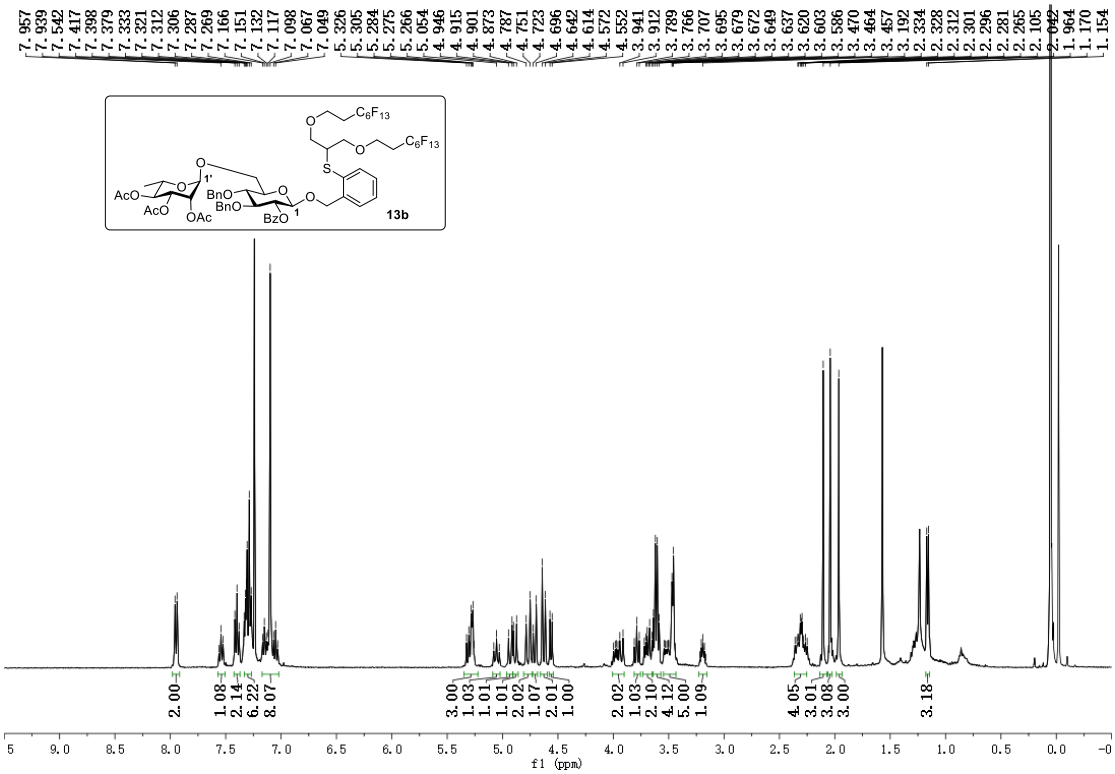

Figure S40. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **13b**

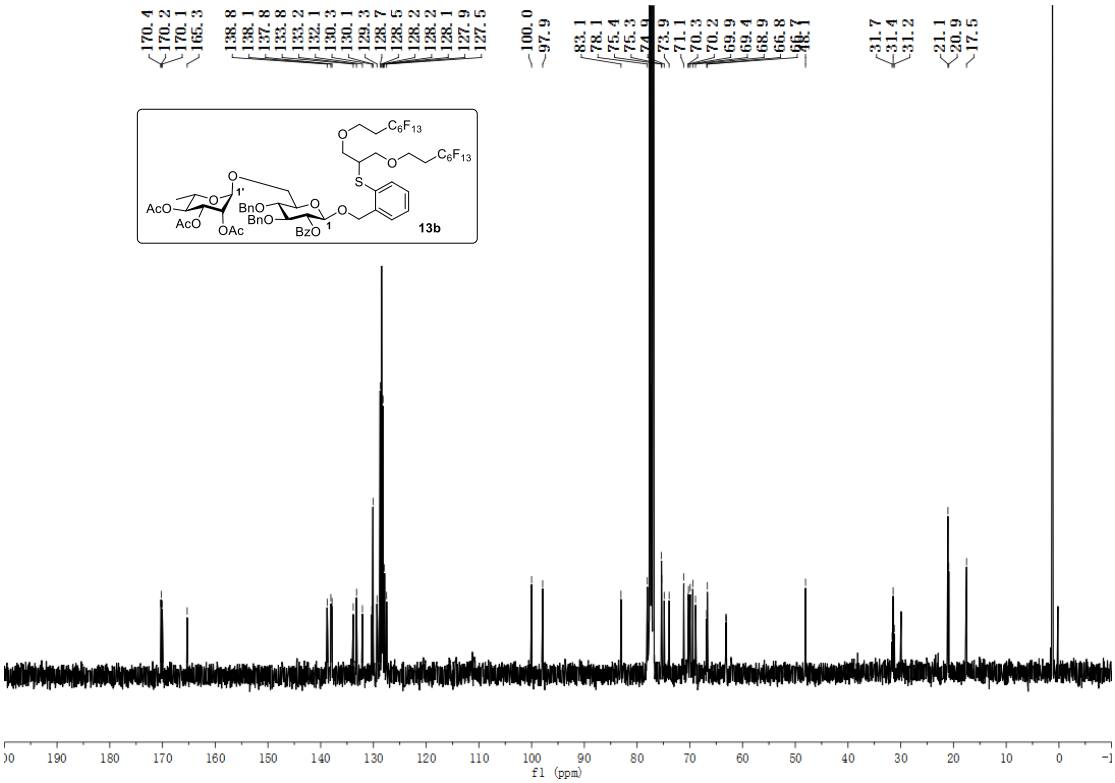

Figure S41. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **13b**

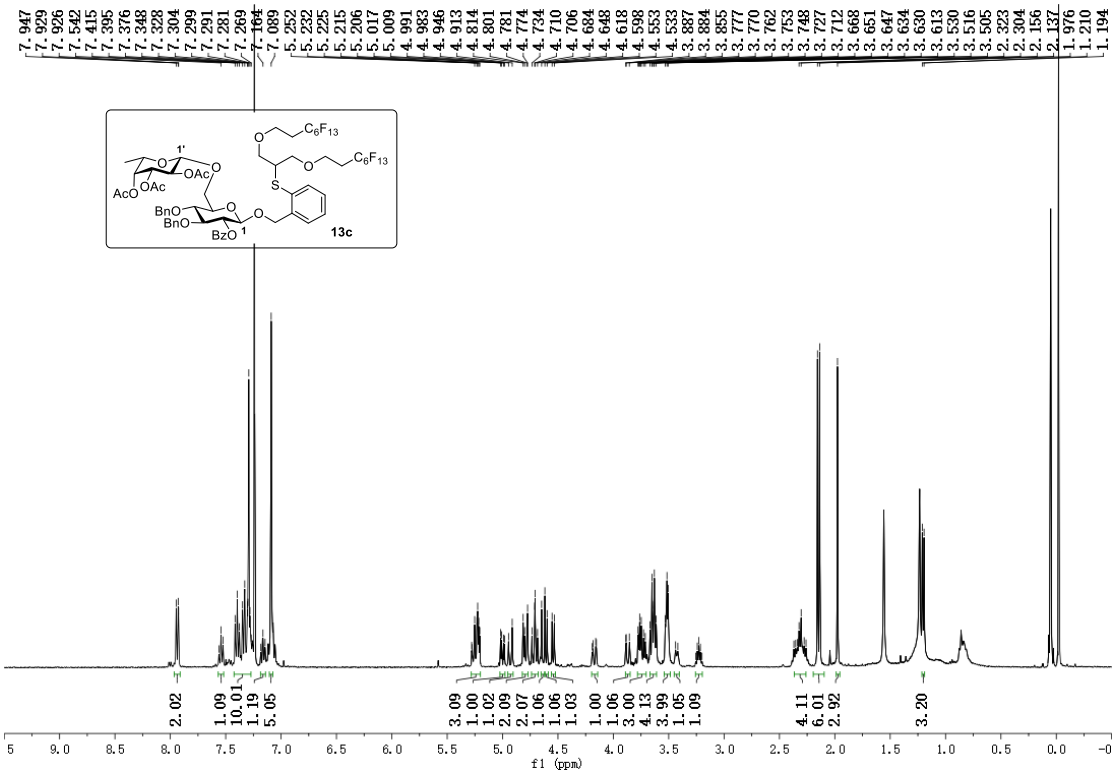

Figure S42. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **13c**

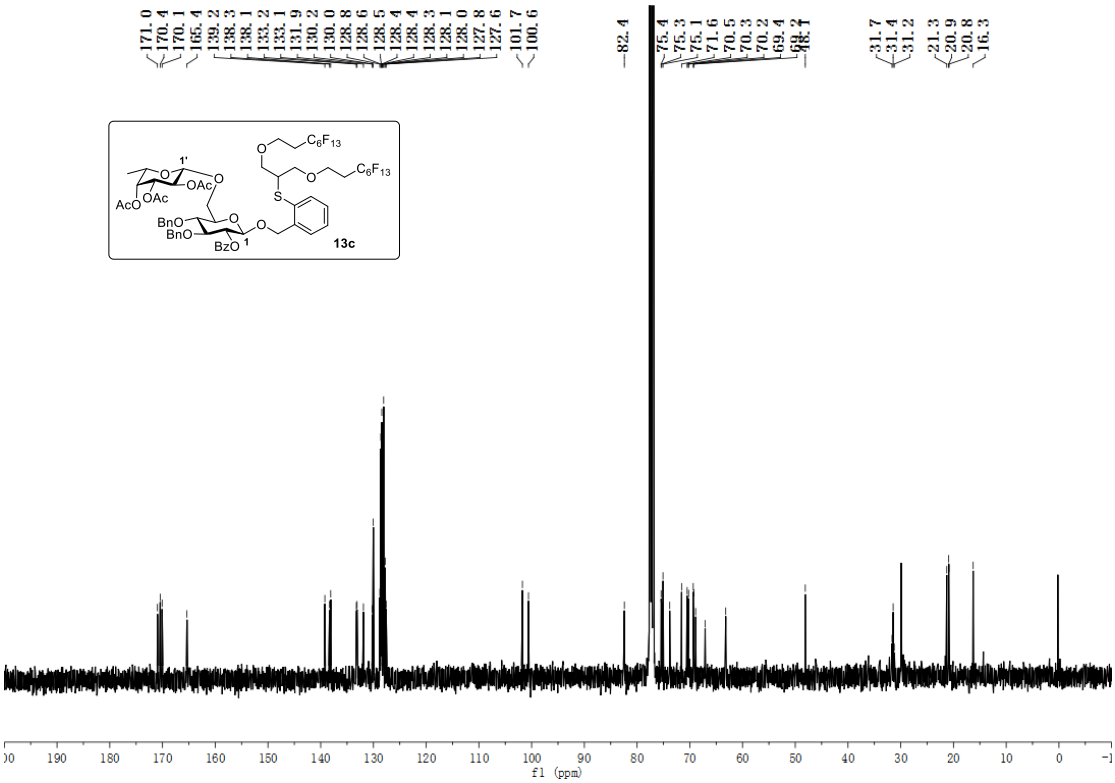

Figure S43. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **13c**

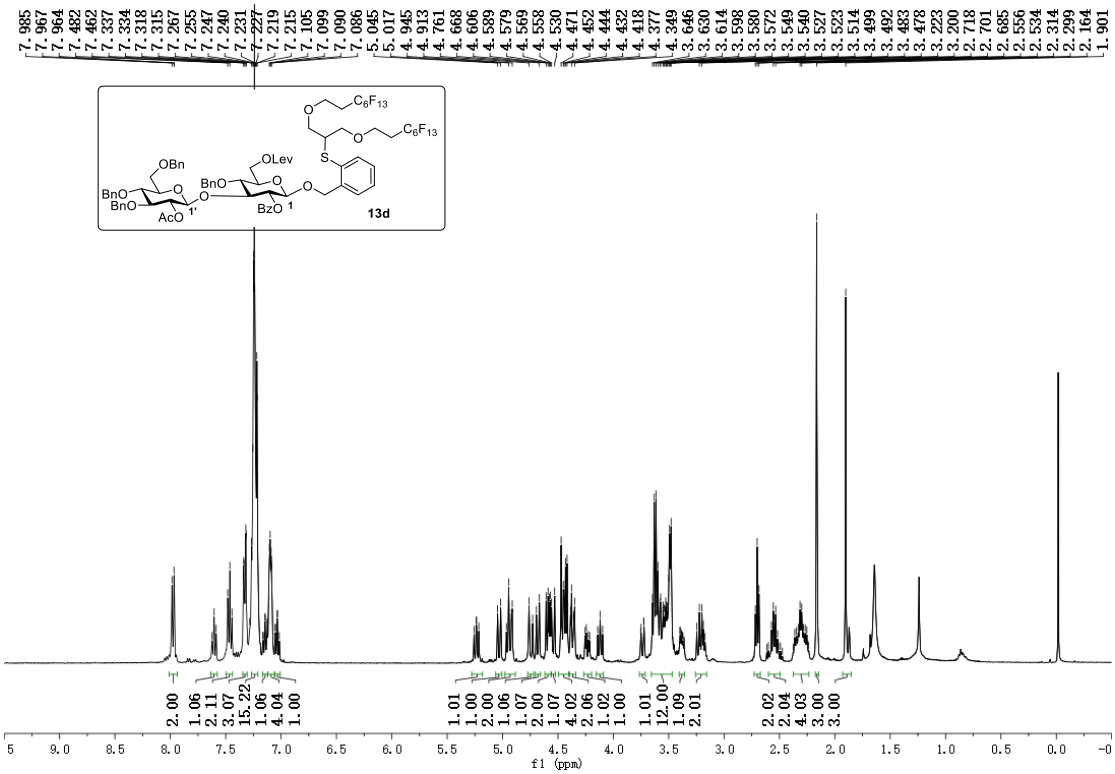

Figure S44. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **13d**

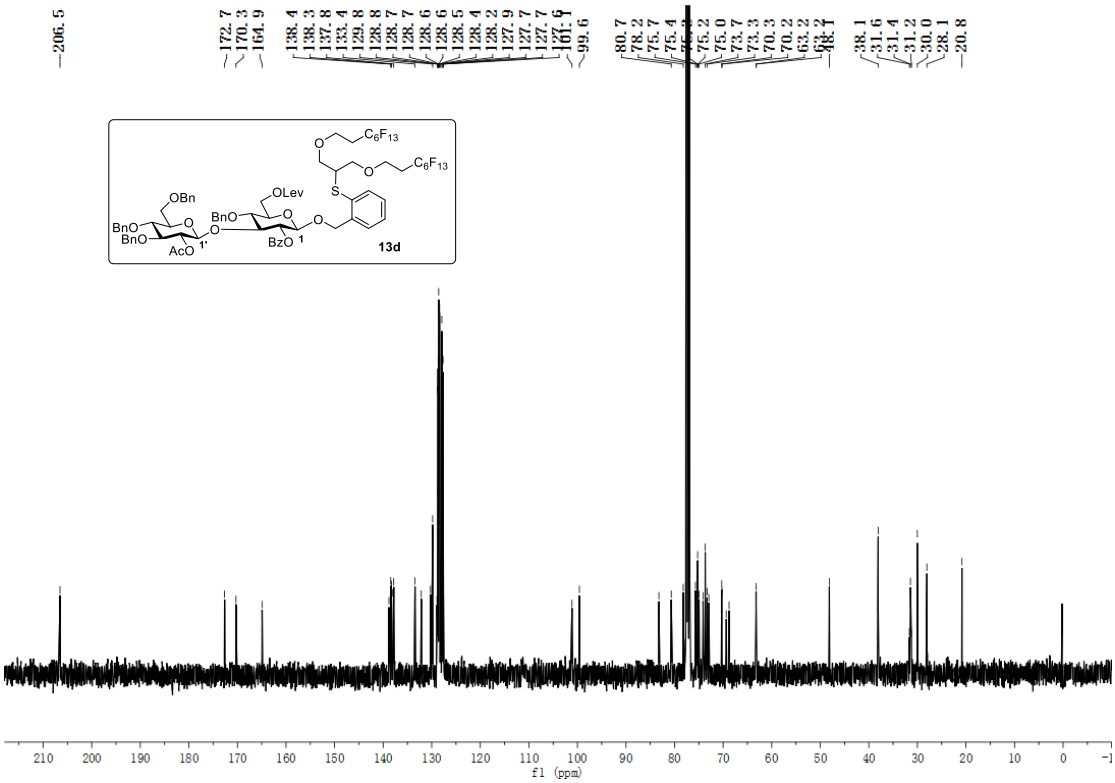

Figure S45. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **13d**

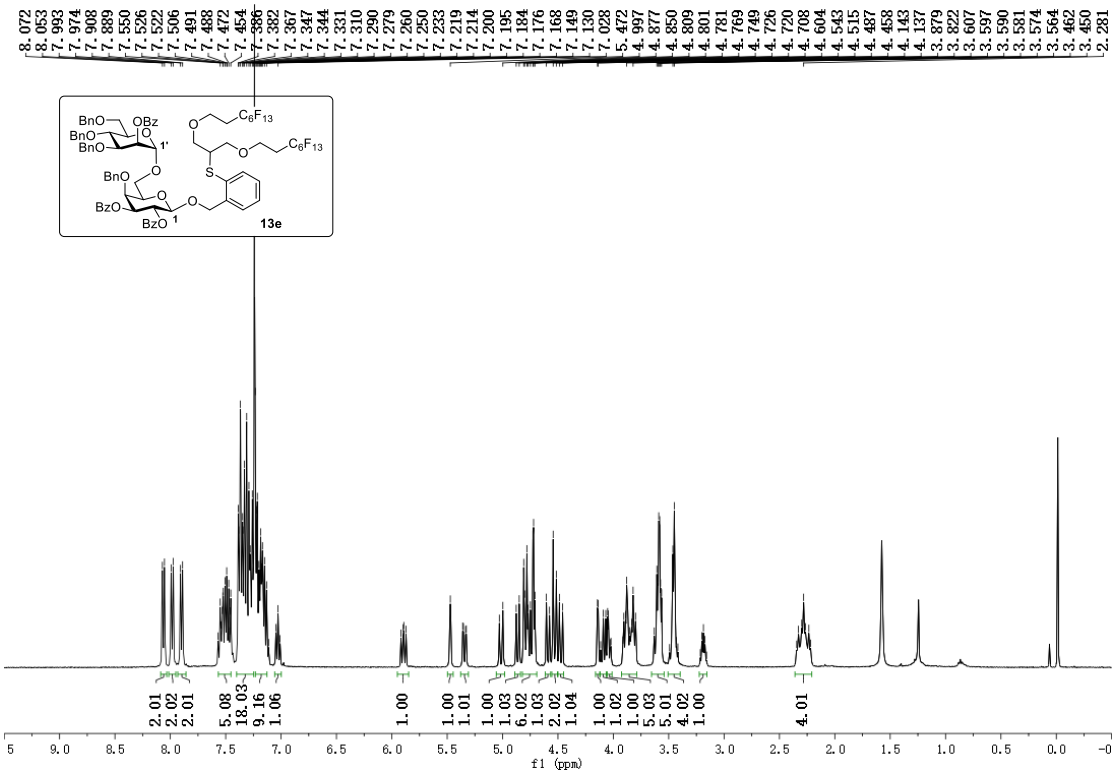

Figure S46. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **13e**

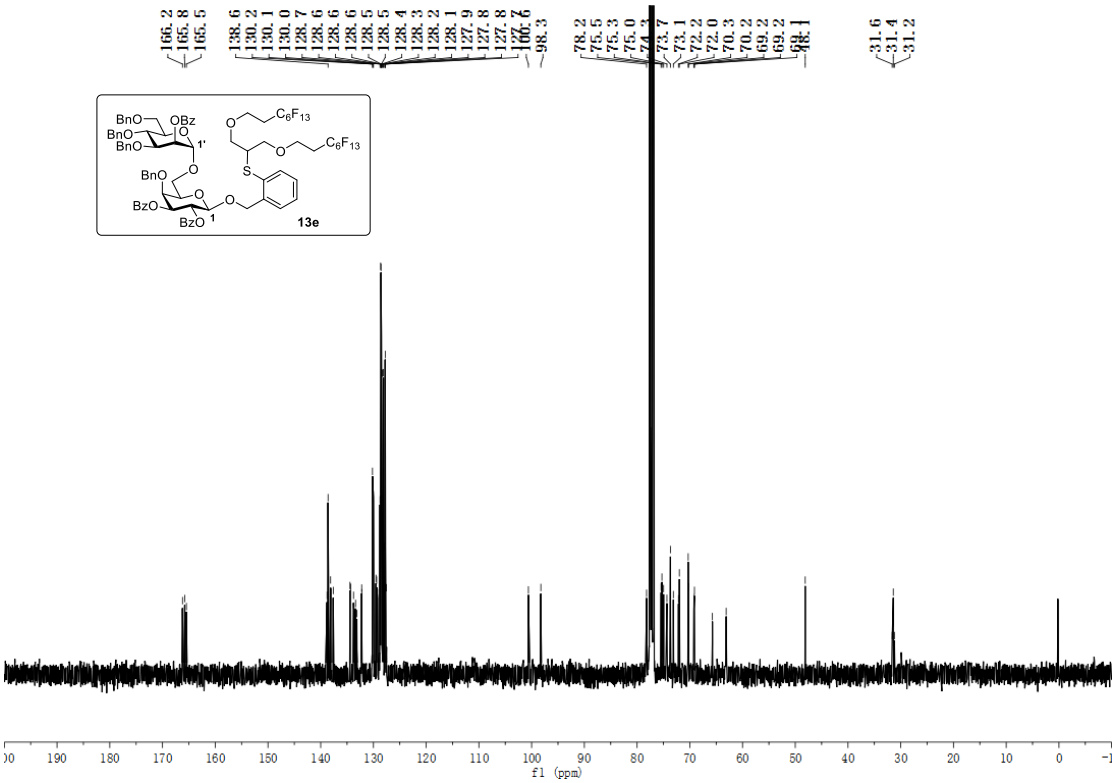

Figure S47. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **13e**

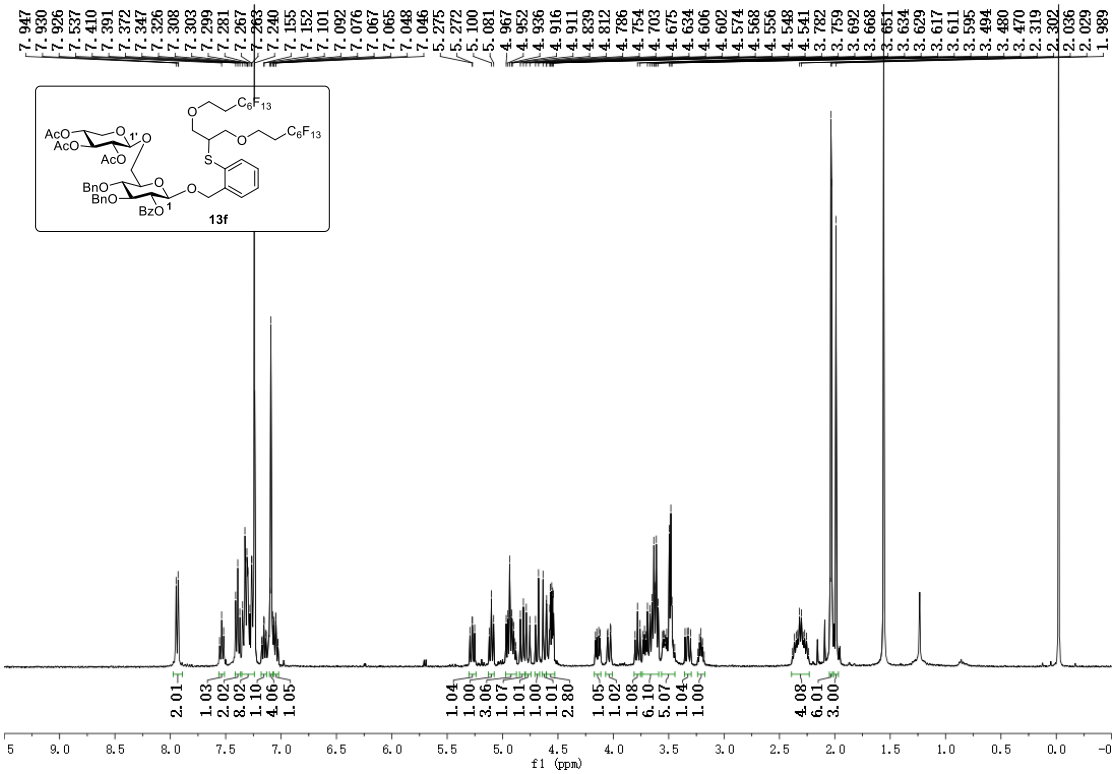

Figure S48. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **13f**

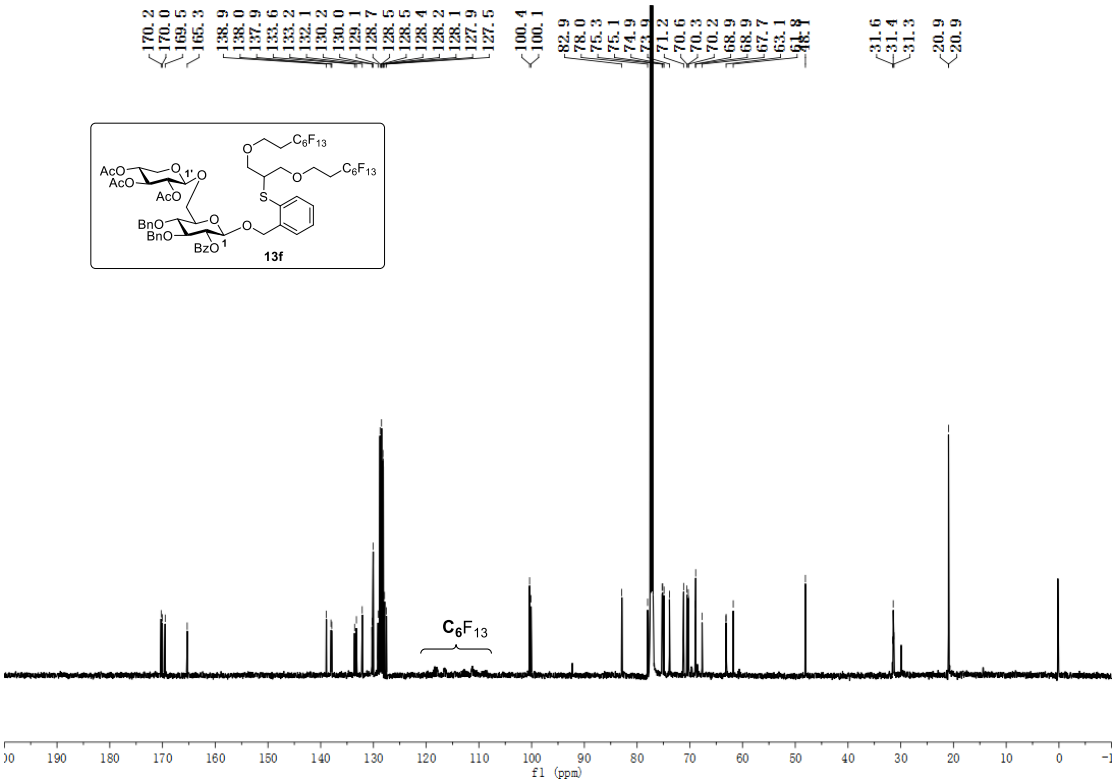

Figure S49. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **13f**

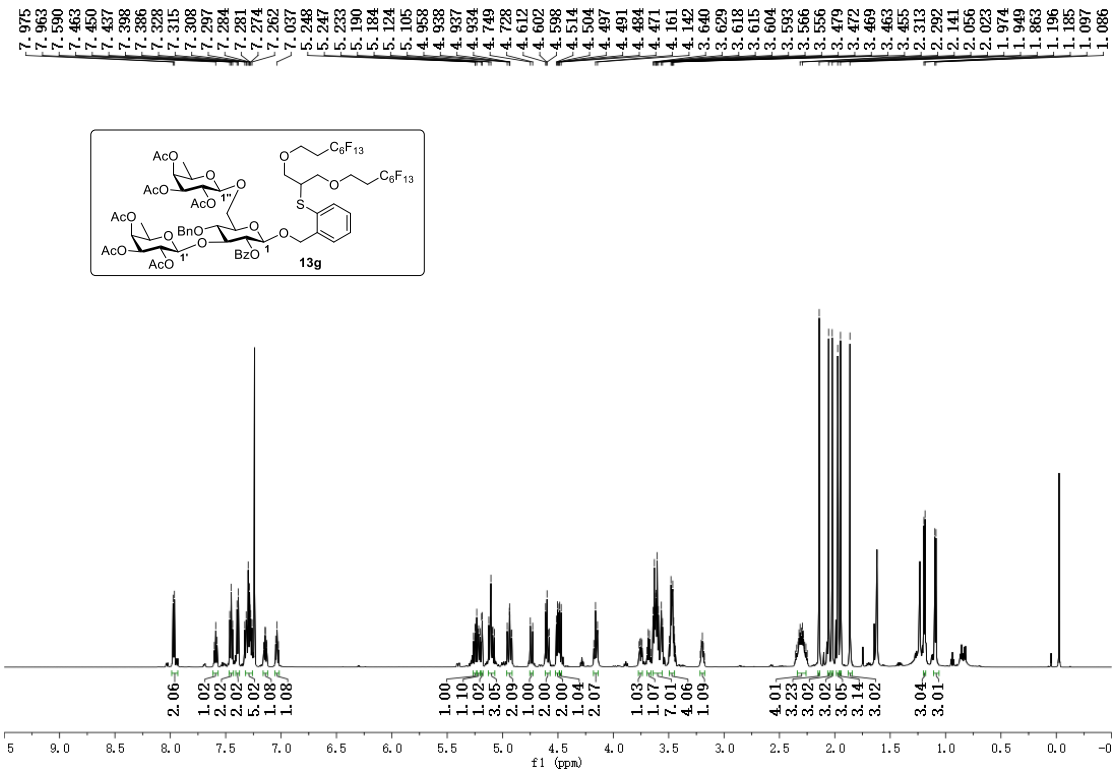

Figure S50. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **13g**

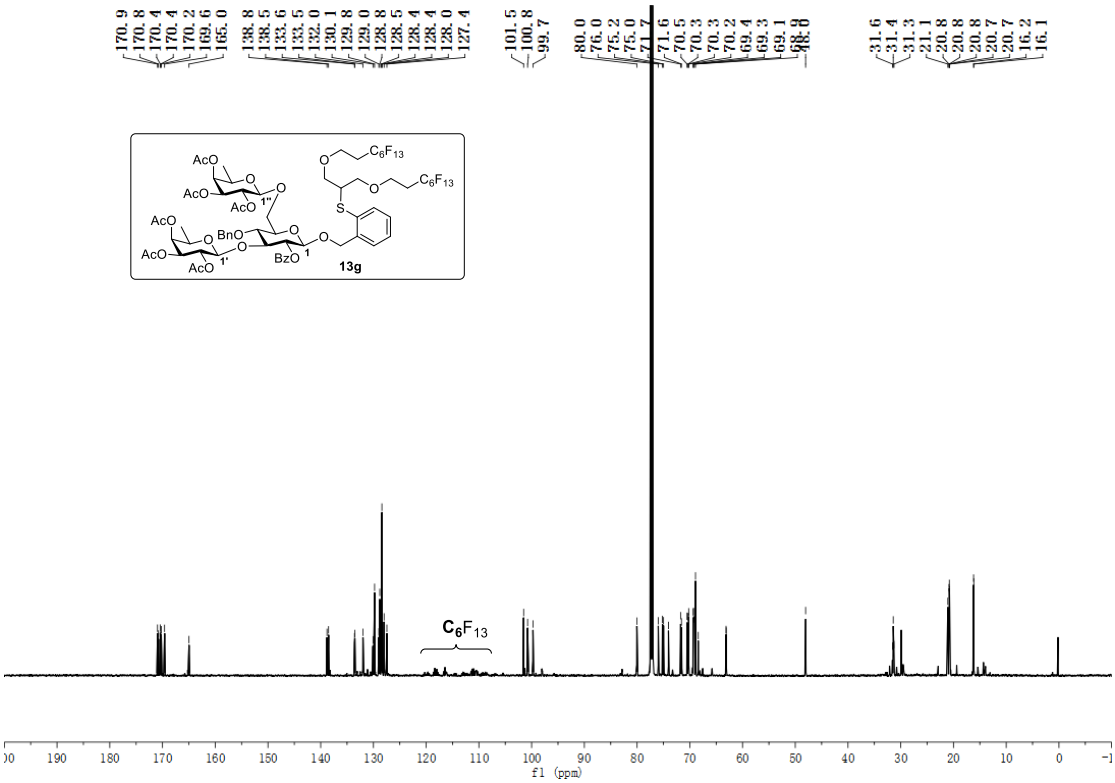

Figure S51. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **13g**

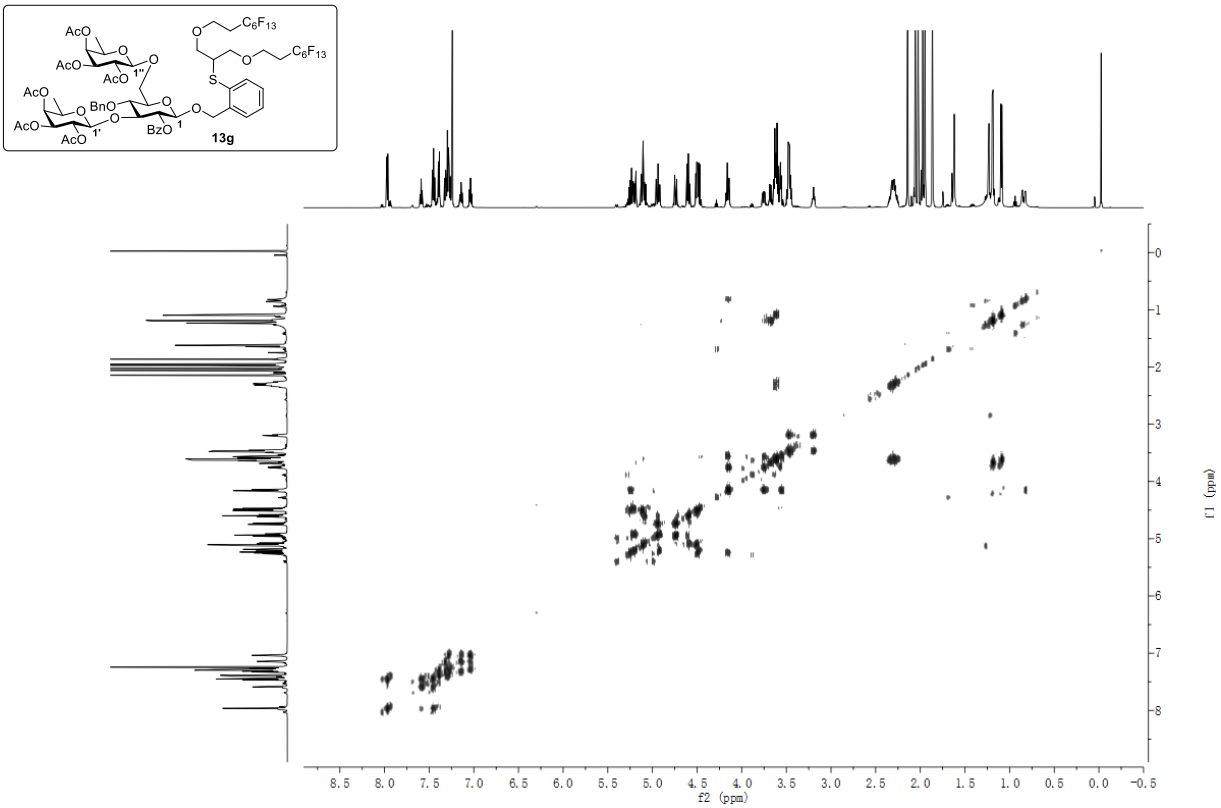

Figure S52. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **13g**

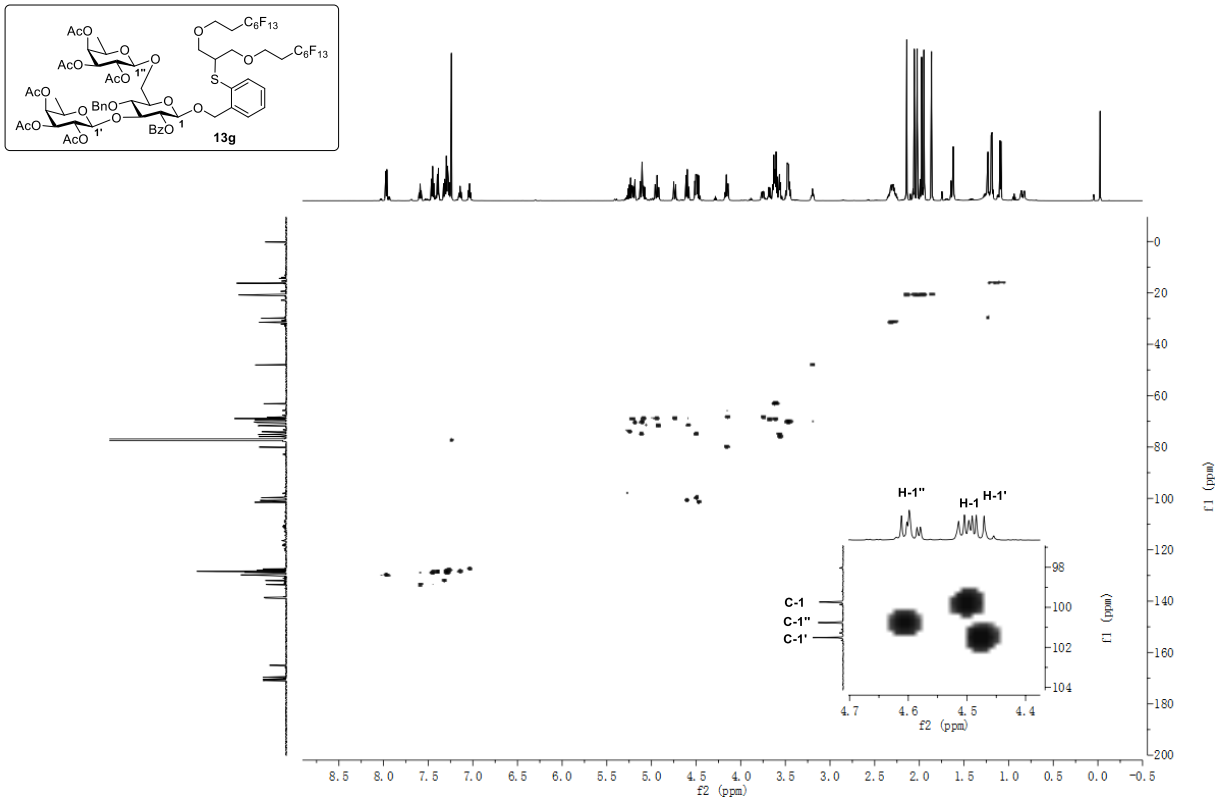

Figure S53. HSQC spectrum of **13g**

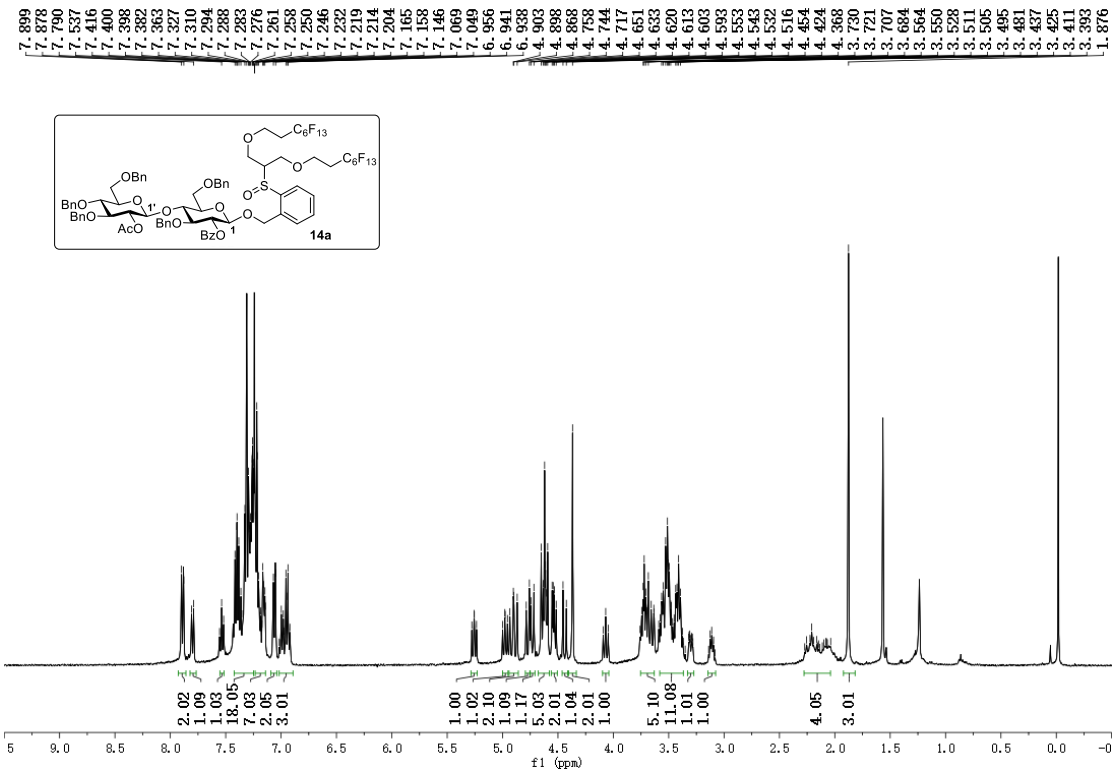

Figure S54. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **14a**

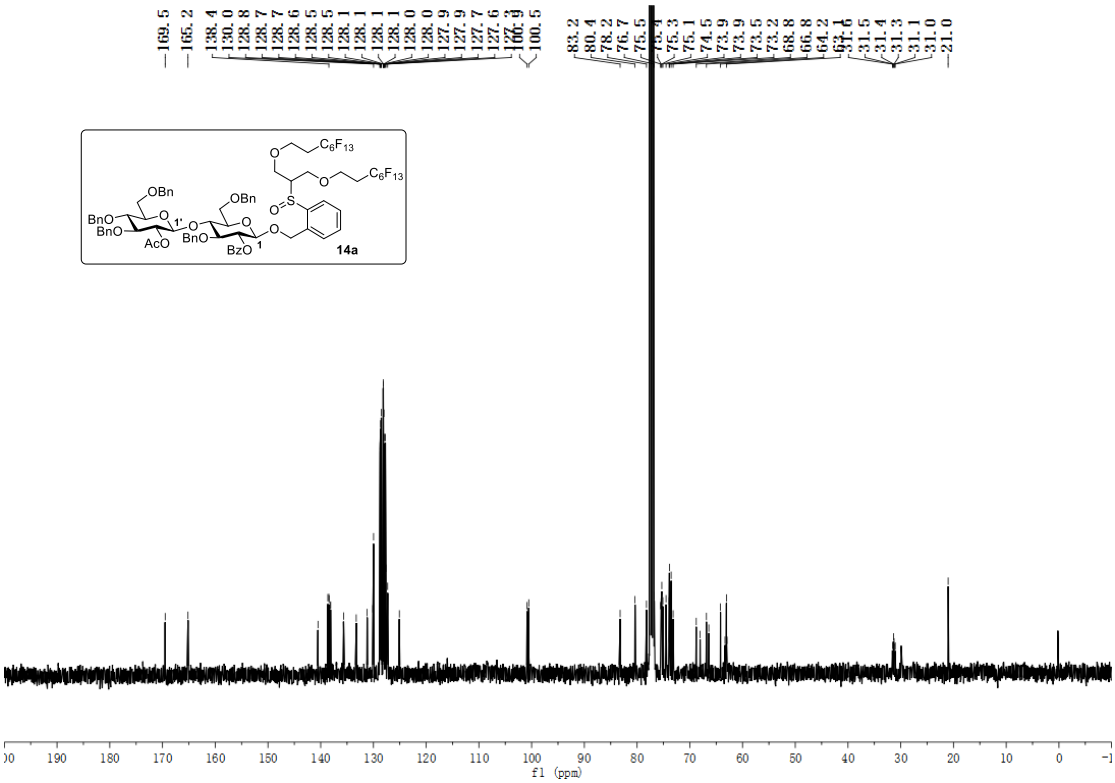

Figure S55. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **14a**

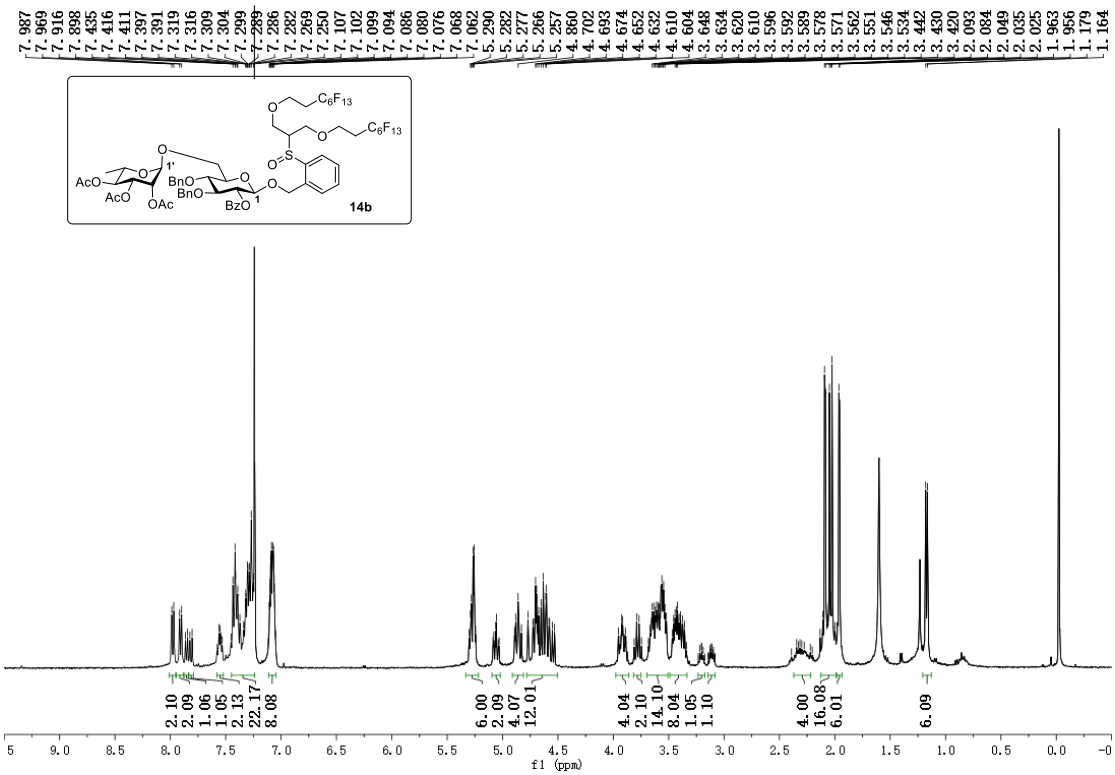

Figure S56. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **14b**

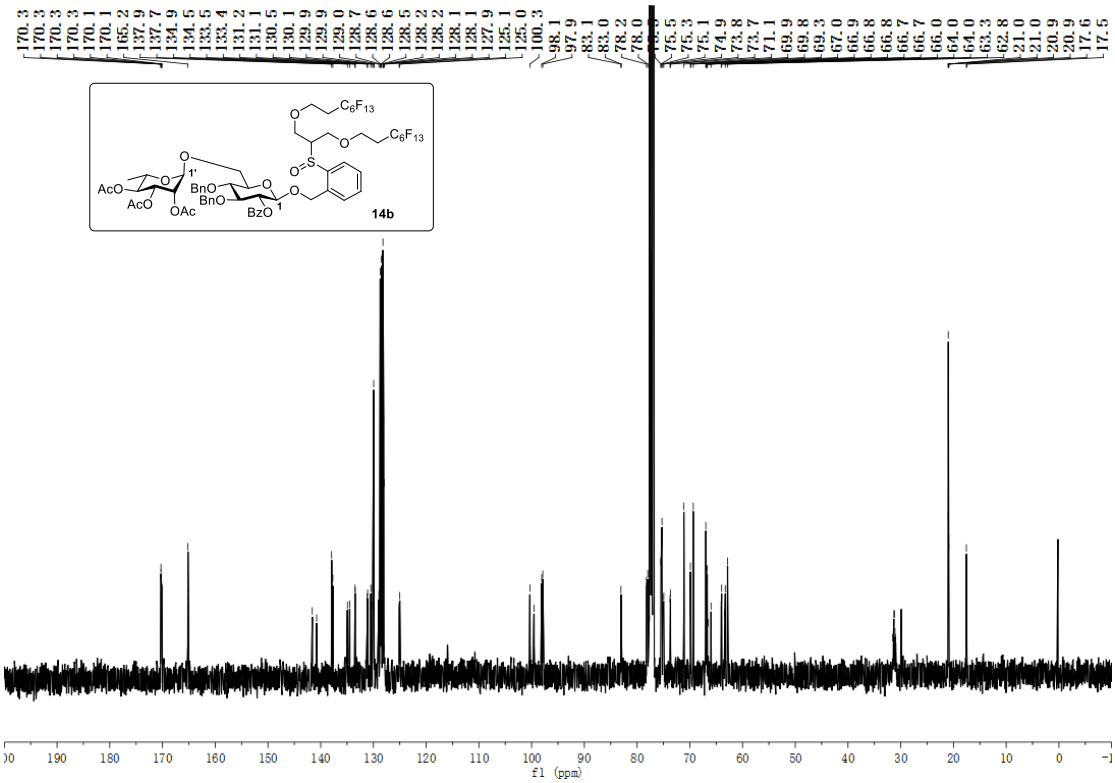

Figure S57. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **14b**

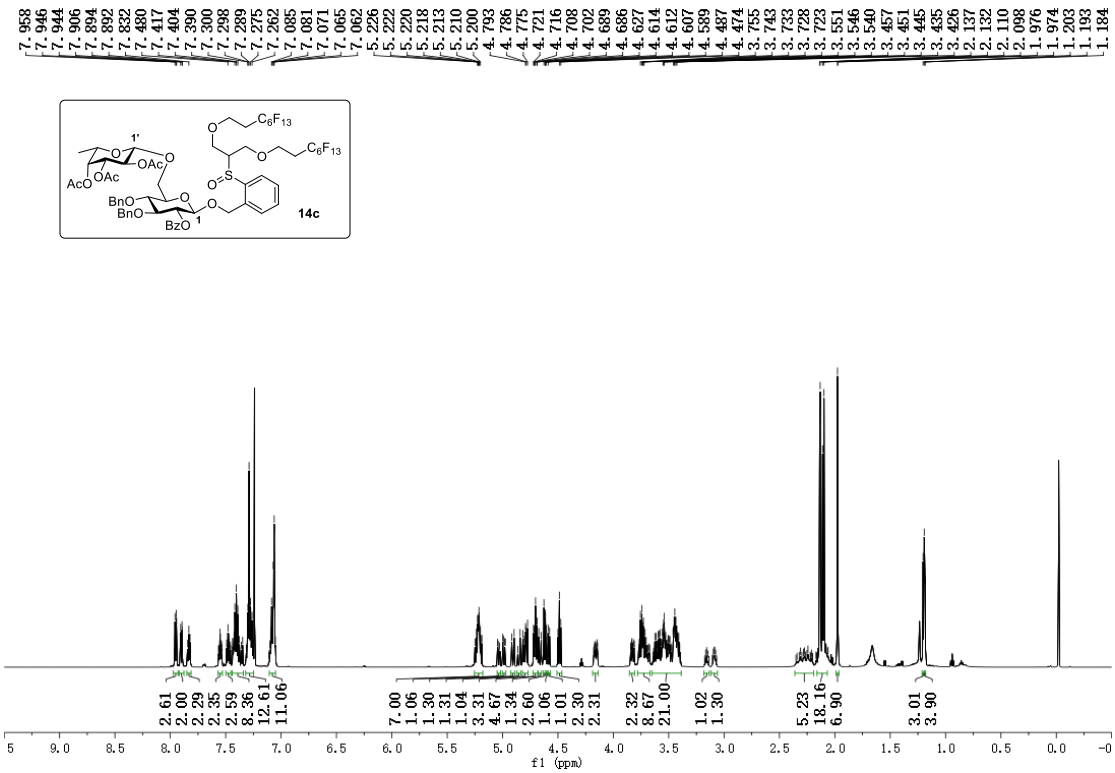

Figure S58. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **14c**

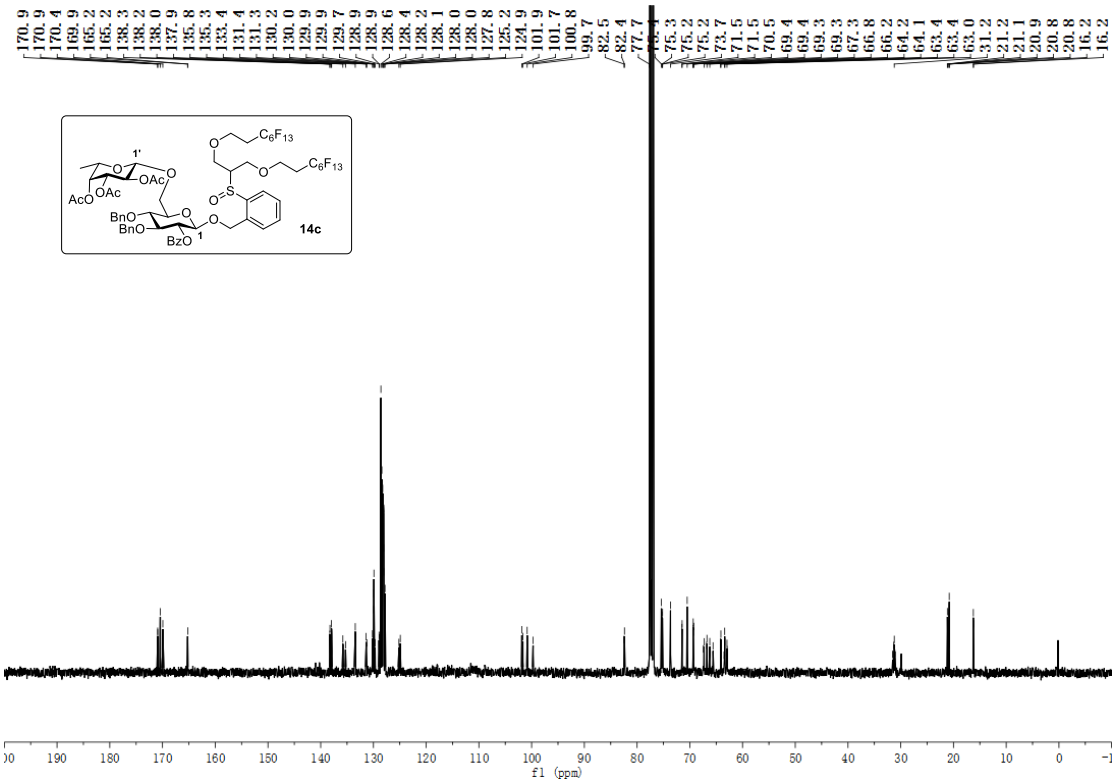

Figure S59. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **14c**

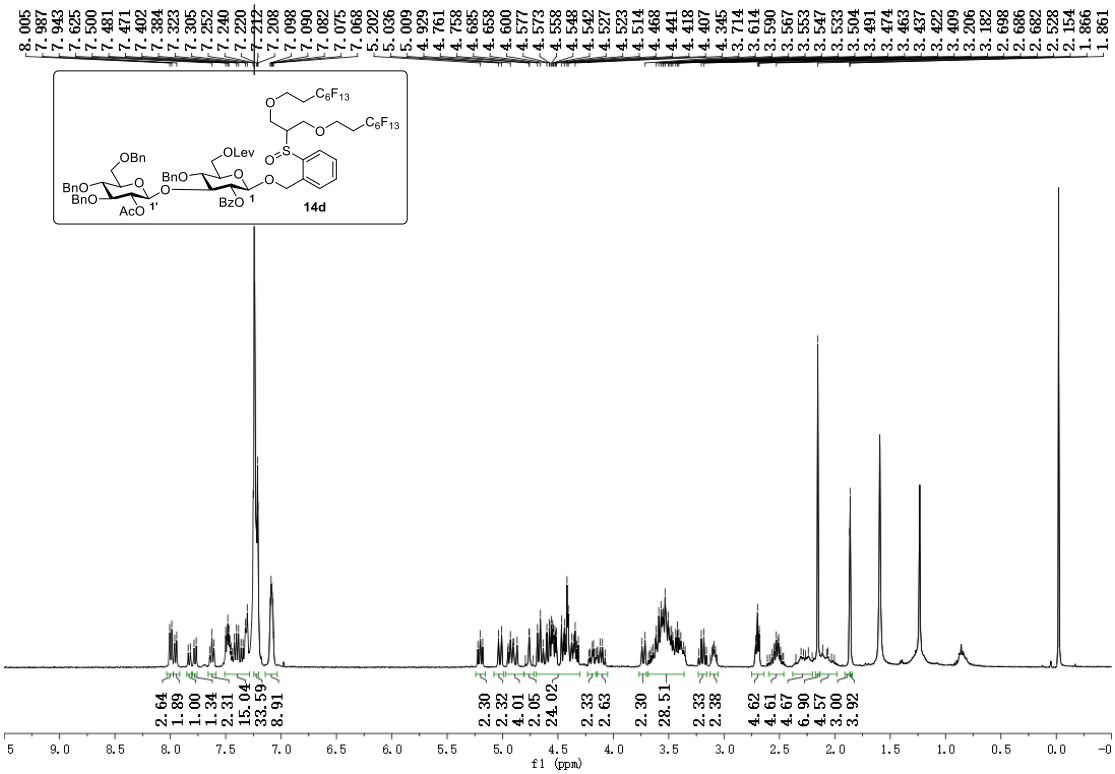

Figure S60. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **14d**

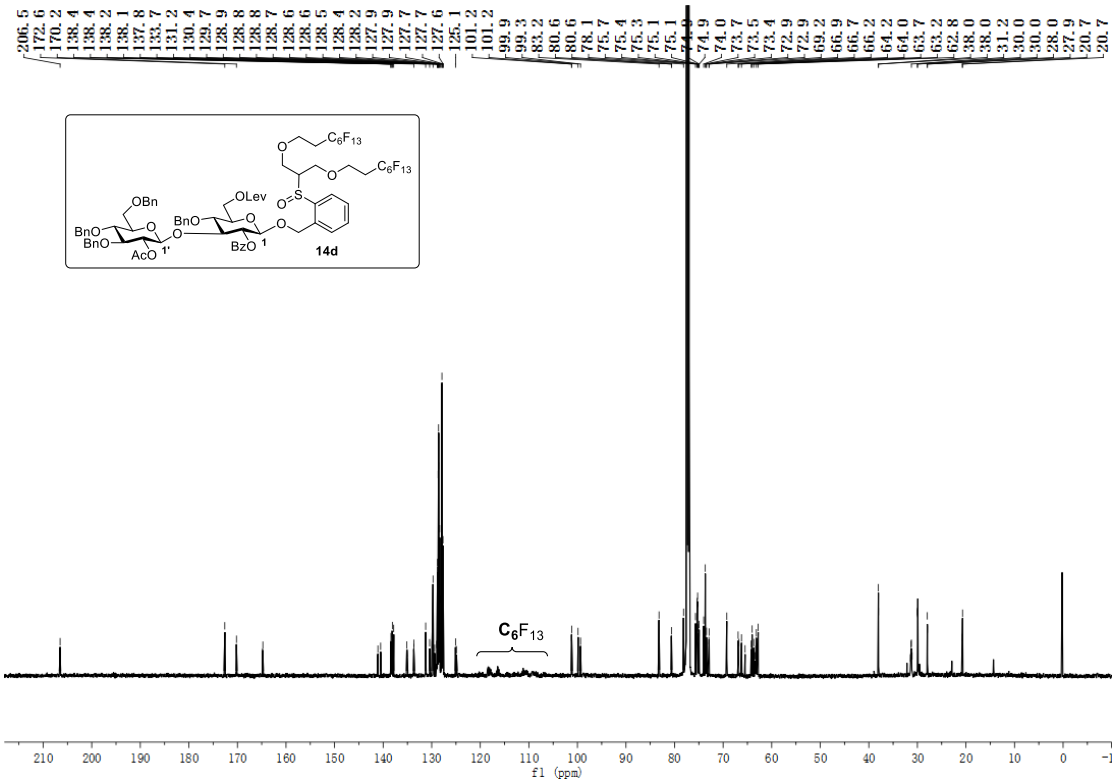

Figure S61. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **14d**

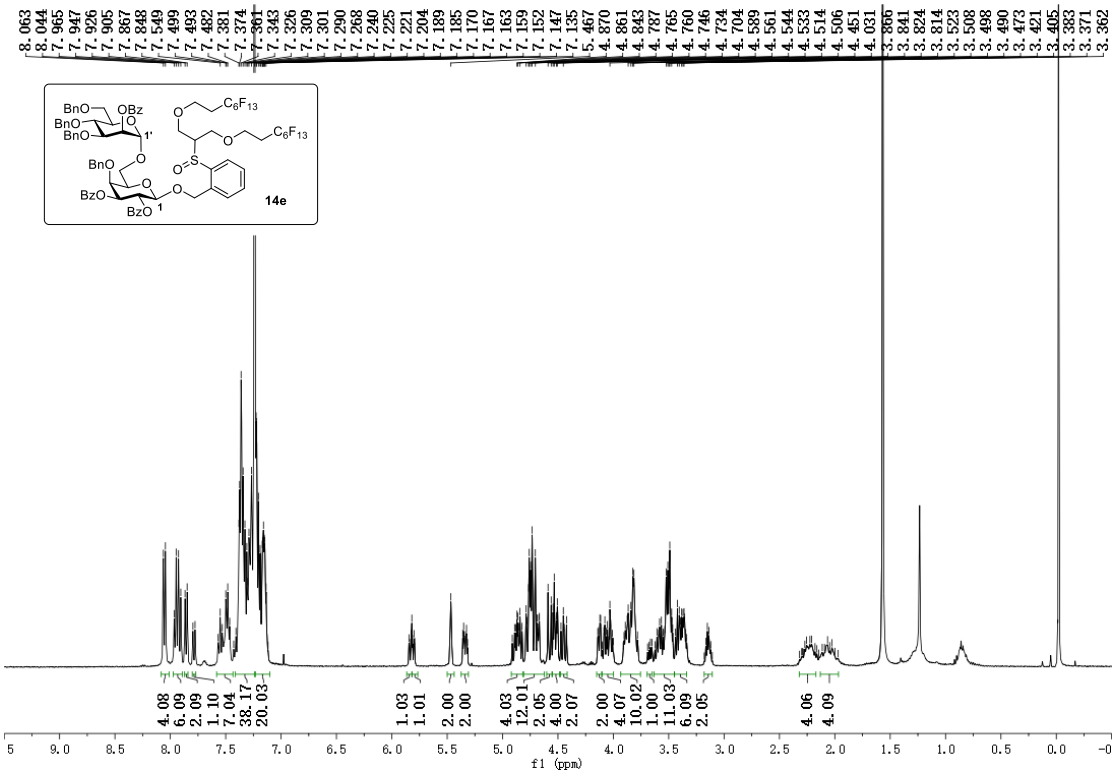

Figure S62. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **14e**

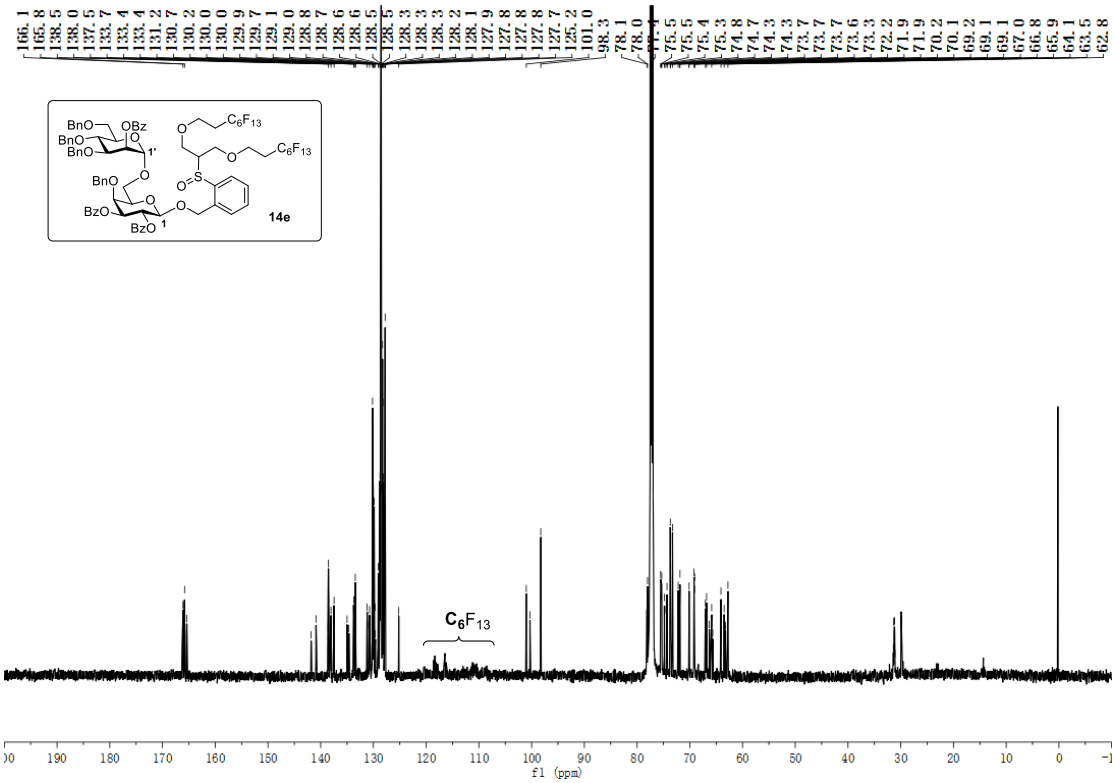

Figure S63. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **14e**

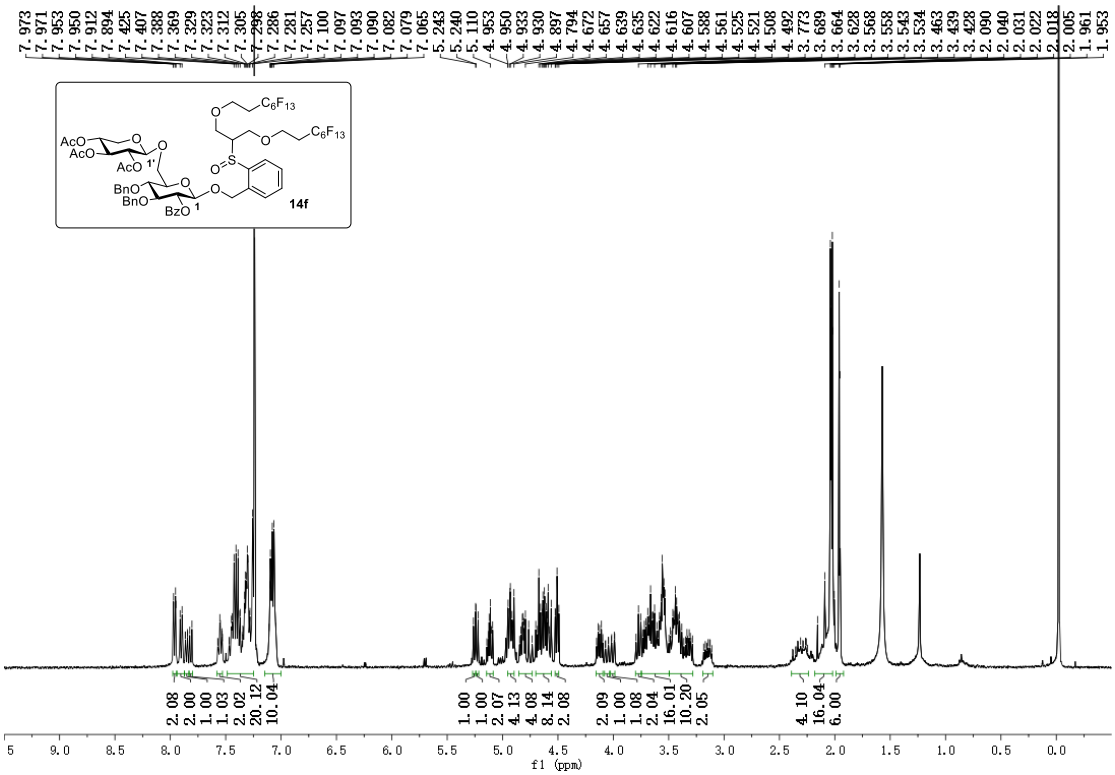

Figure S64. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **14f**

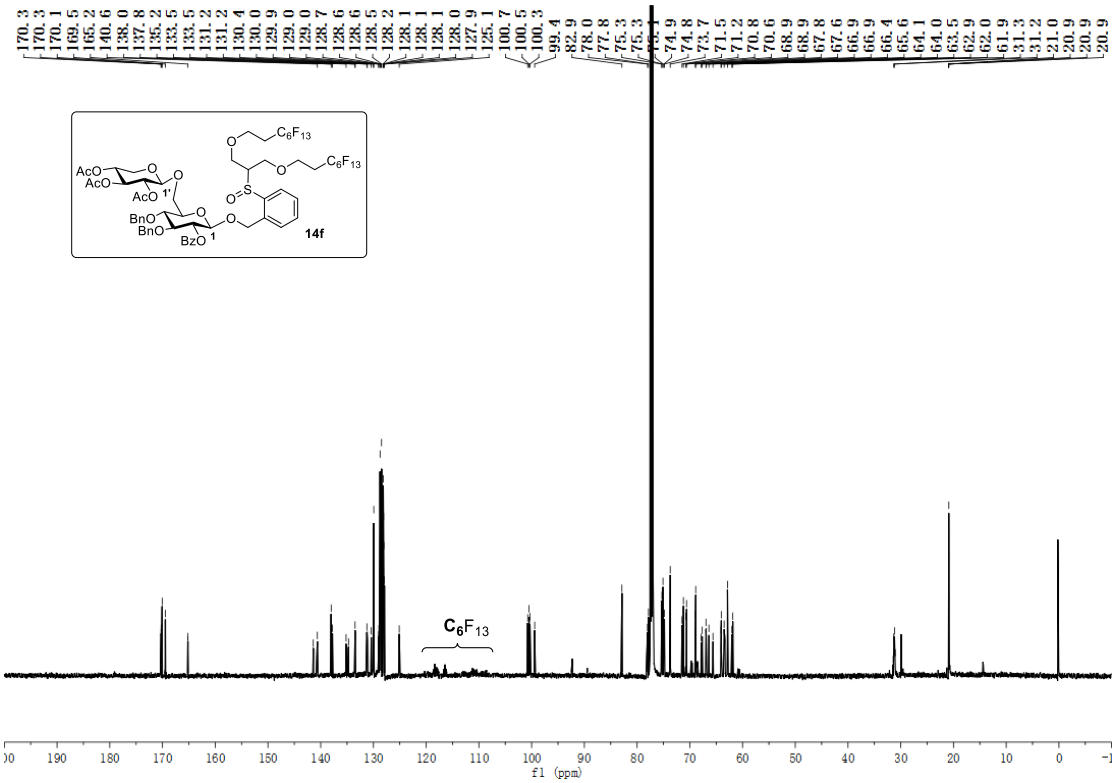

Figure S65. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **14f**

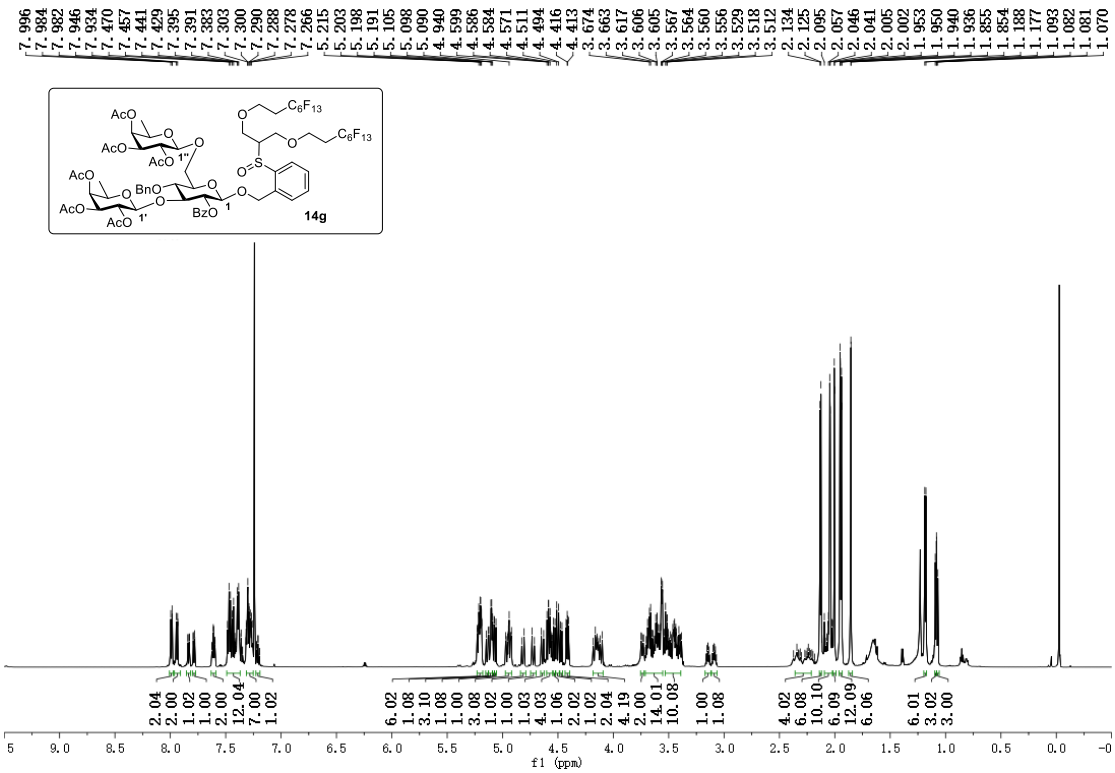

Figure S66. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **14g**

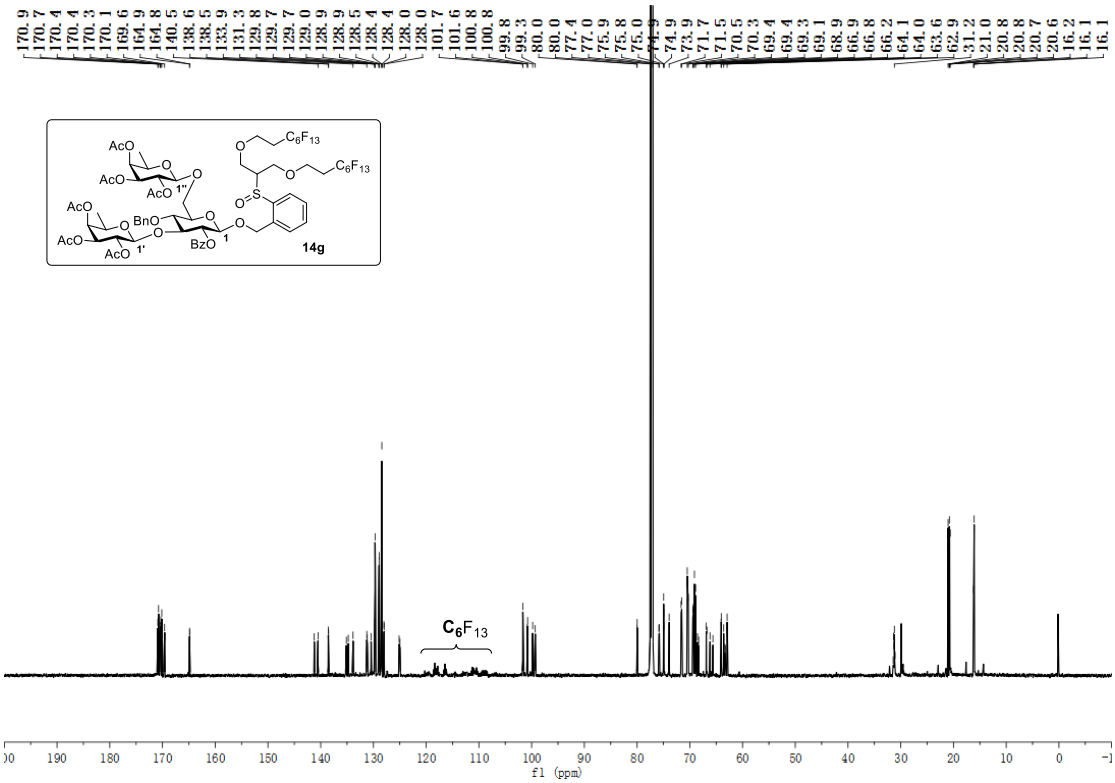

Figure S67. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **14g**

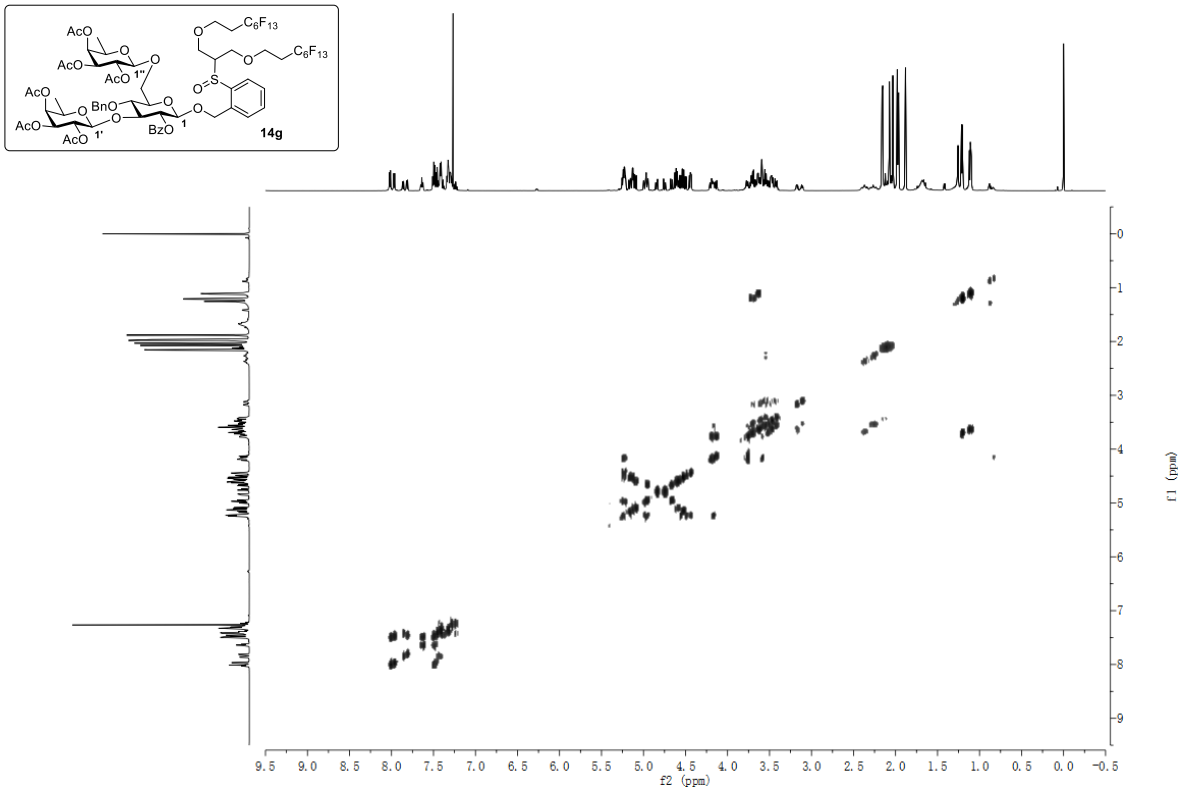

Figure S68. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **14g**

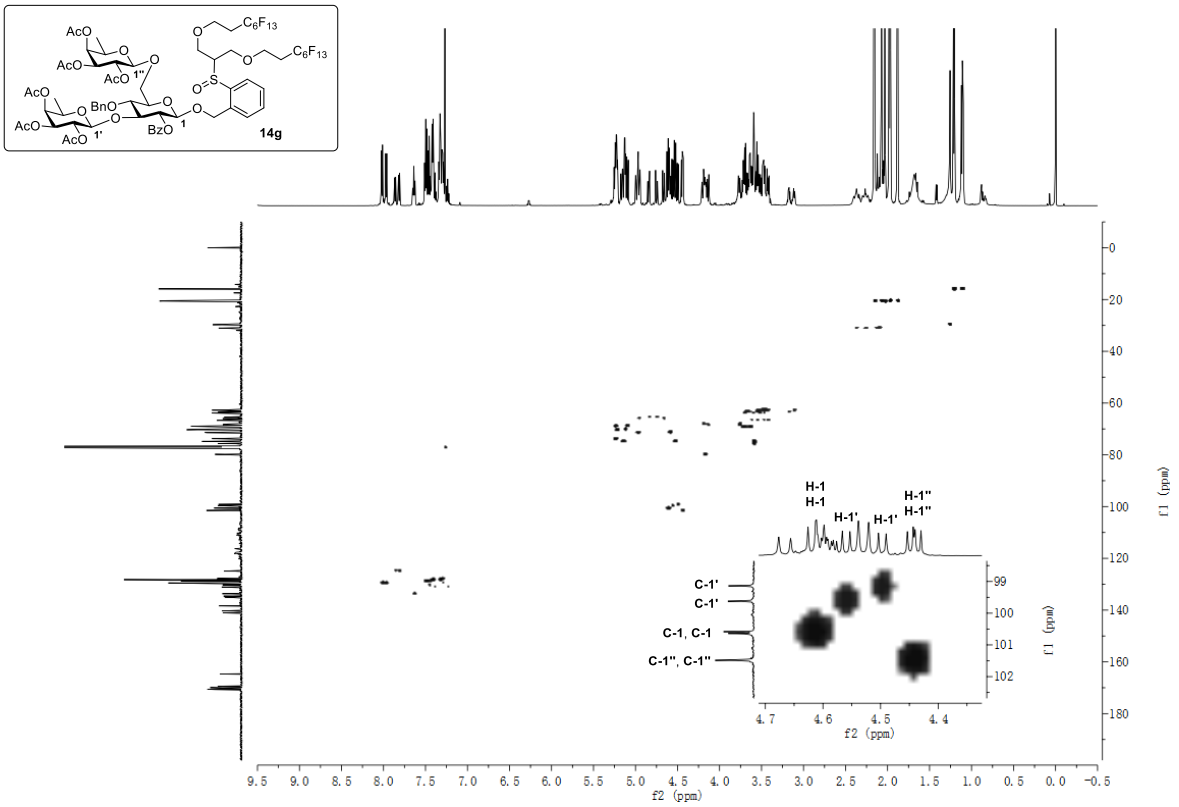

Figure S69. HSQC spectrum of **14g**

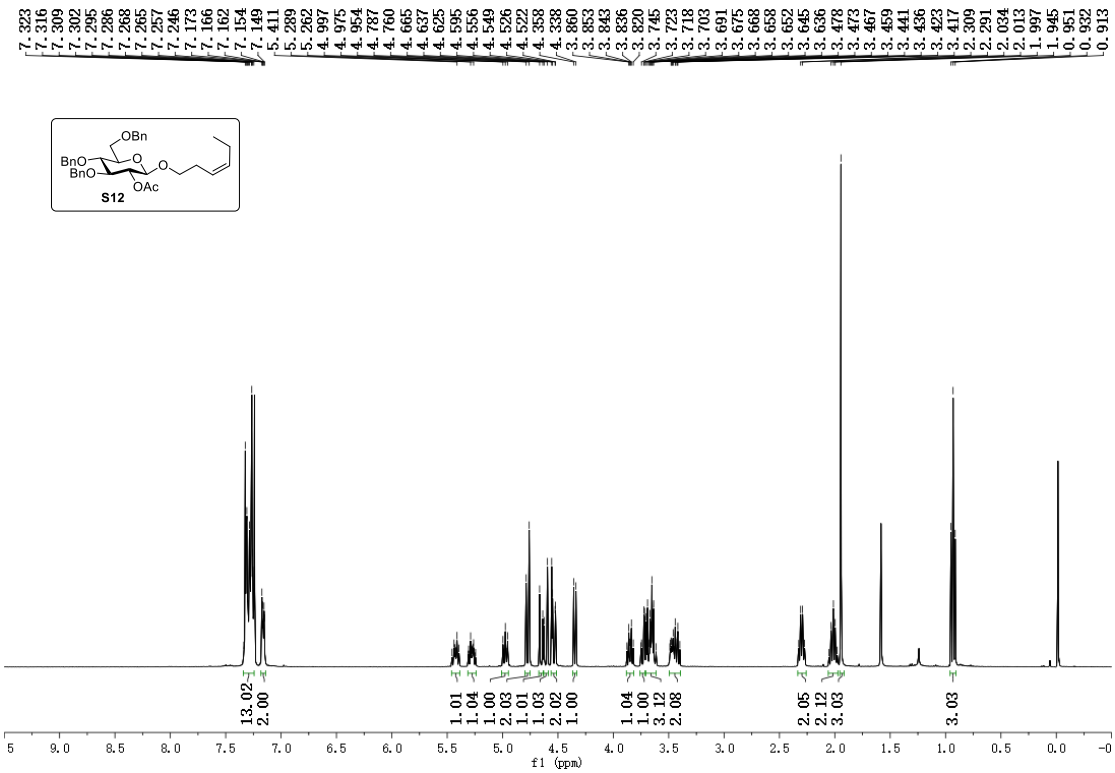

Figure S70. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S12**

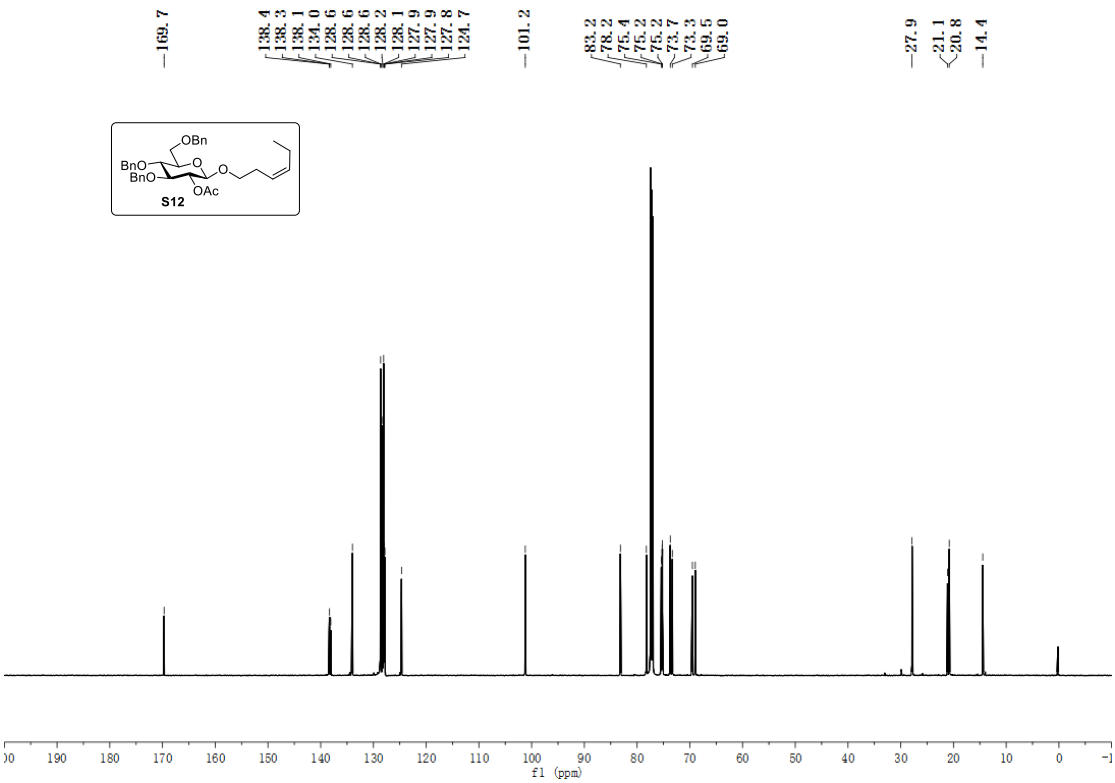

Figure S71. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **S12**

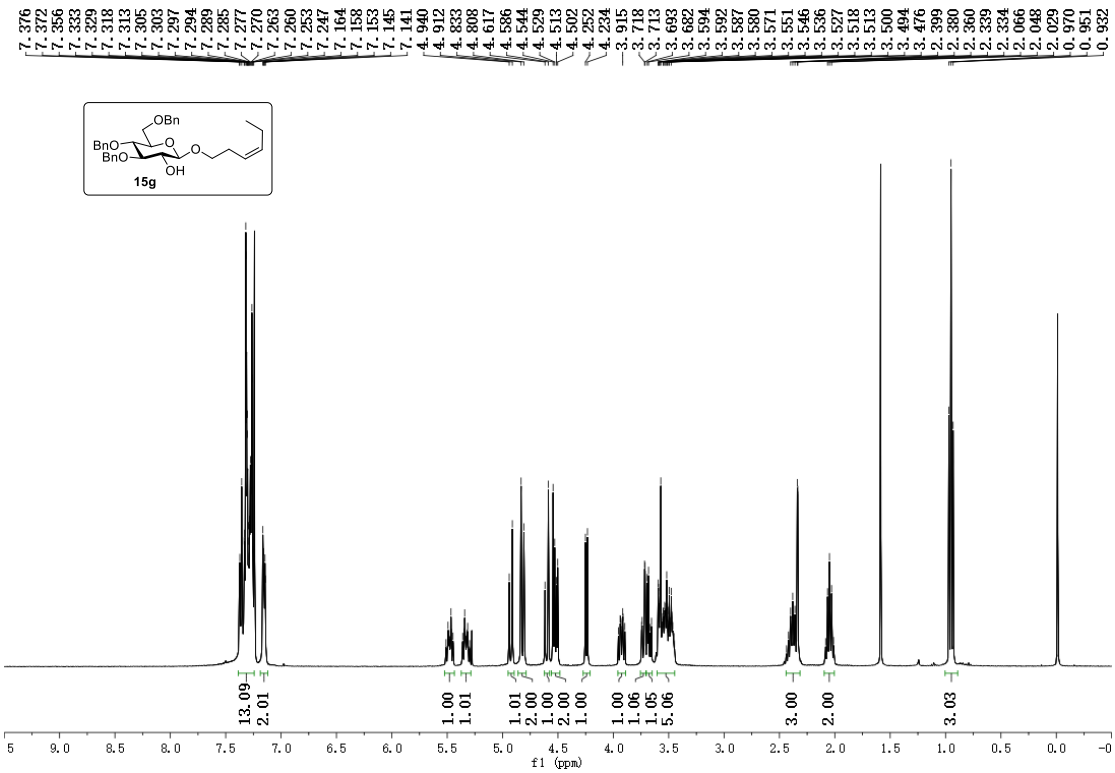

Figure S72. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **15g**

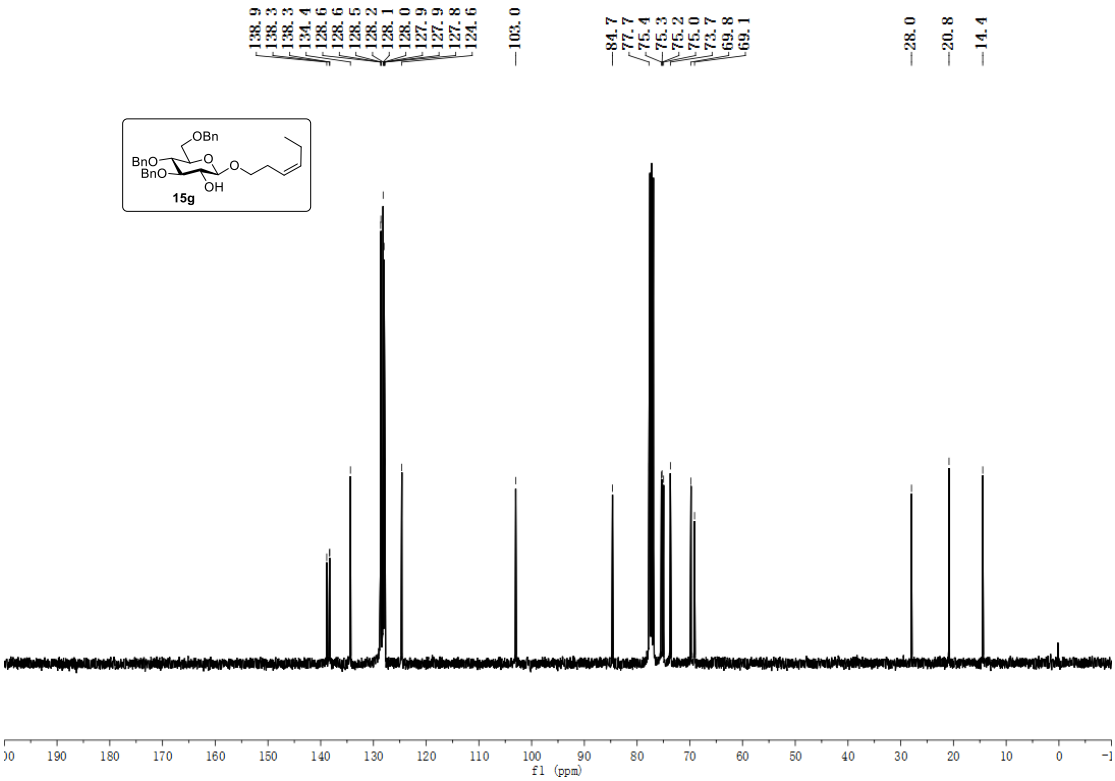

Figure S73. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **15g**

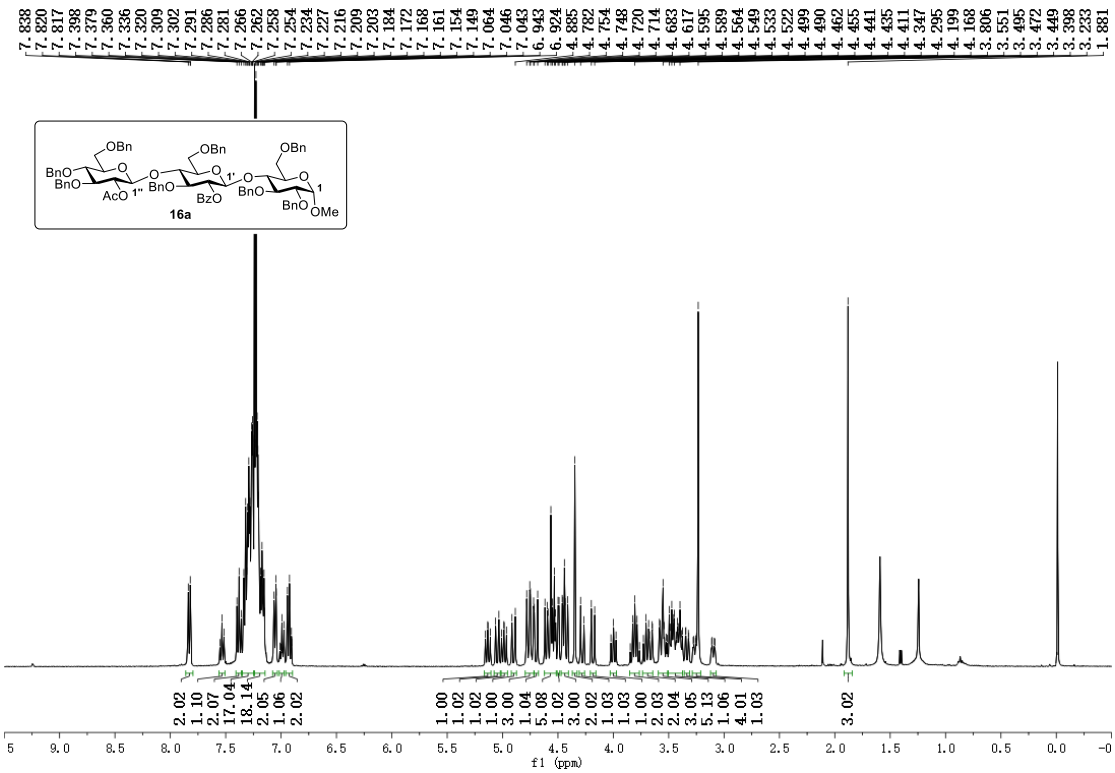

Figure S74. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **16a**

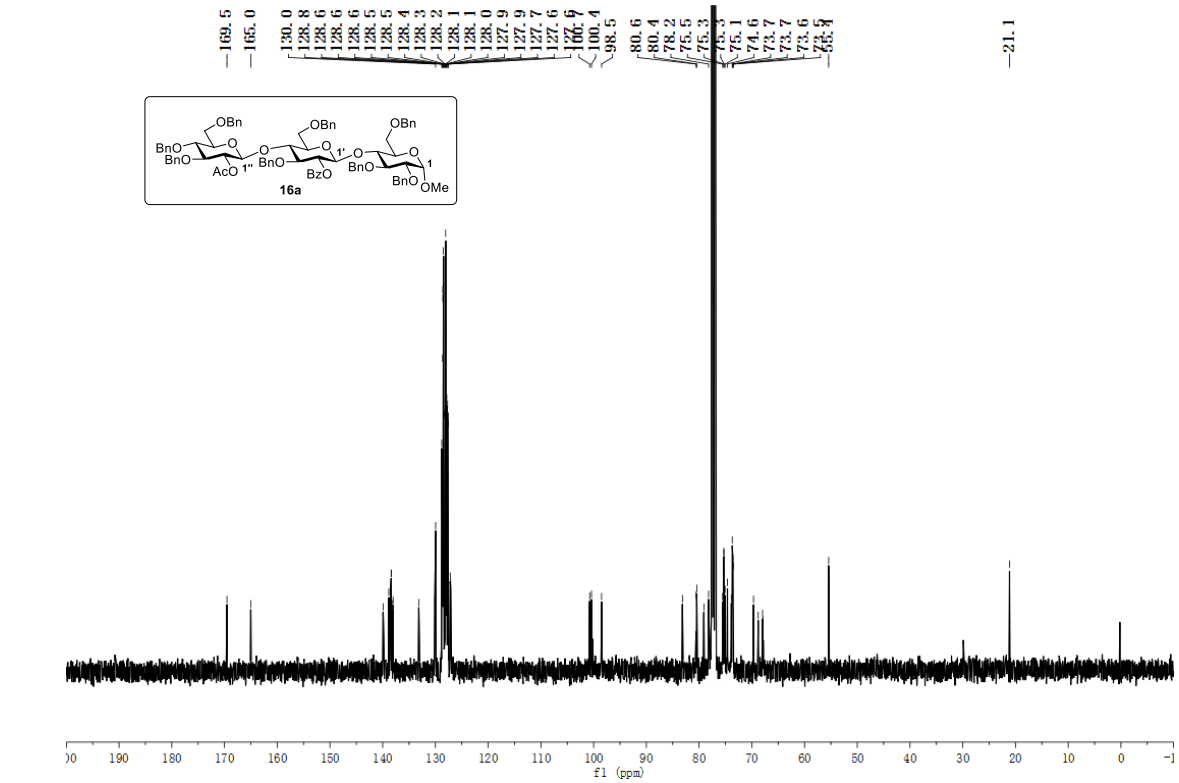

Figure S75. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **16a**

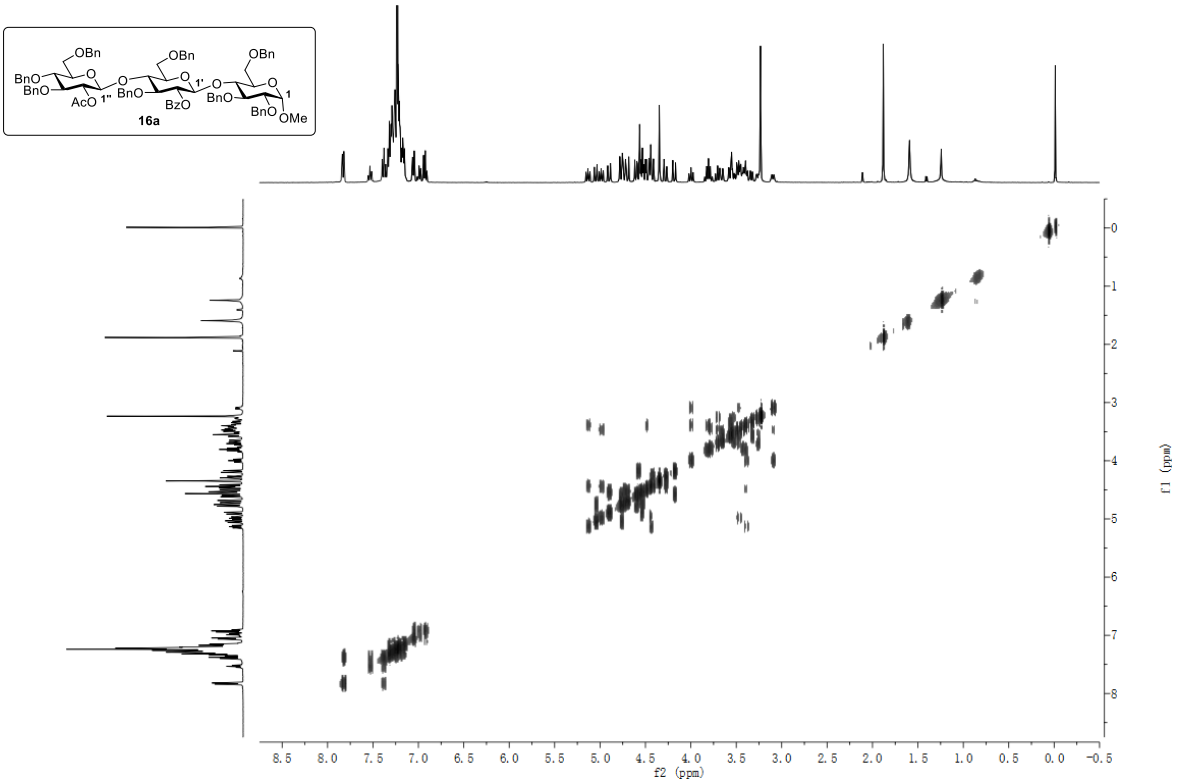

Figure S76. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **16a**

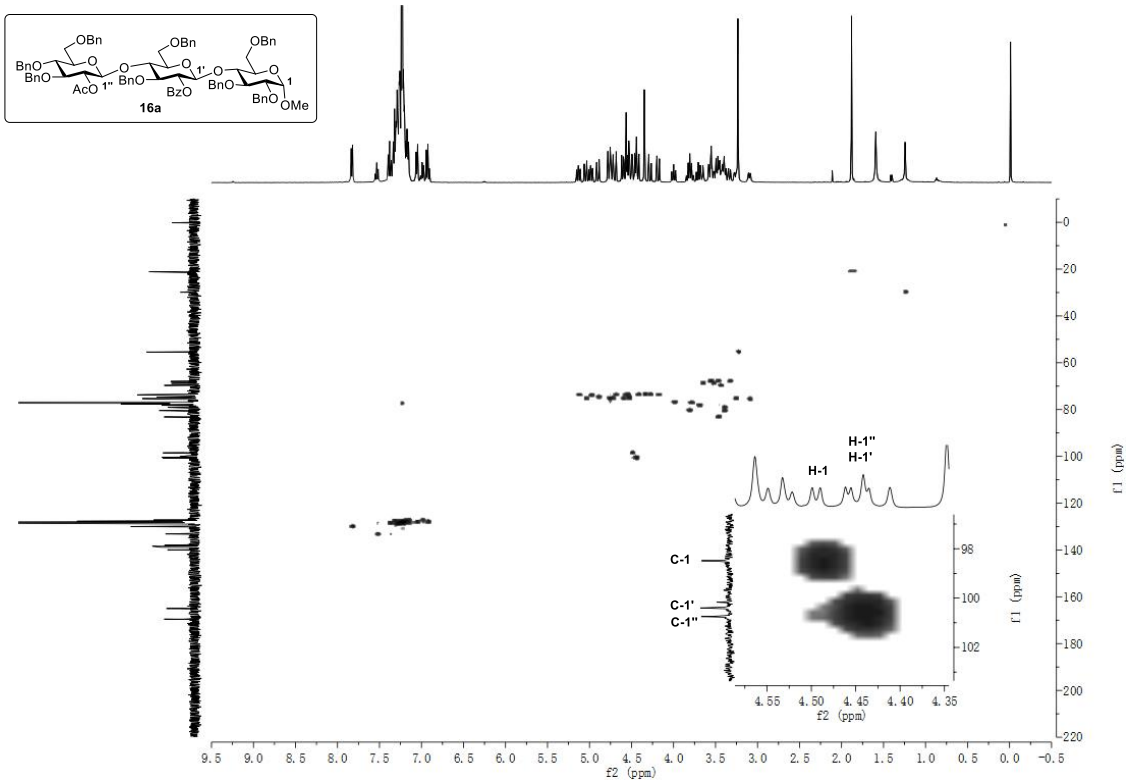

Figure S77. HSQC spectrum of **16a**

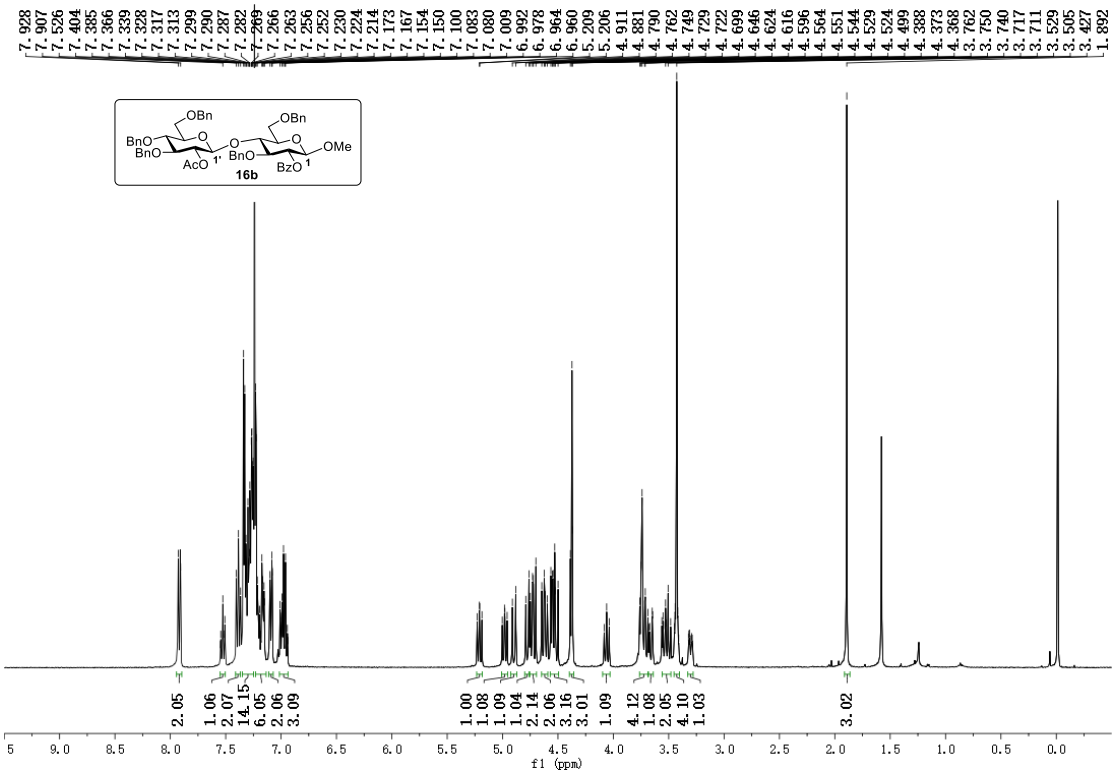

Figure S78. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **16b**

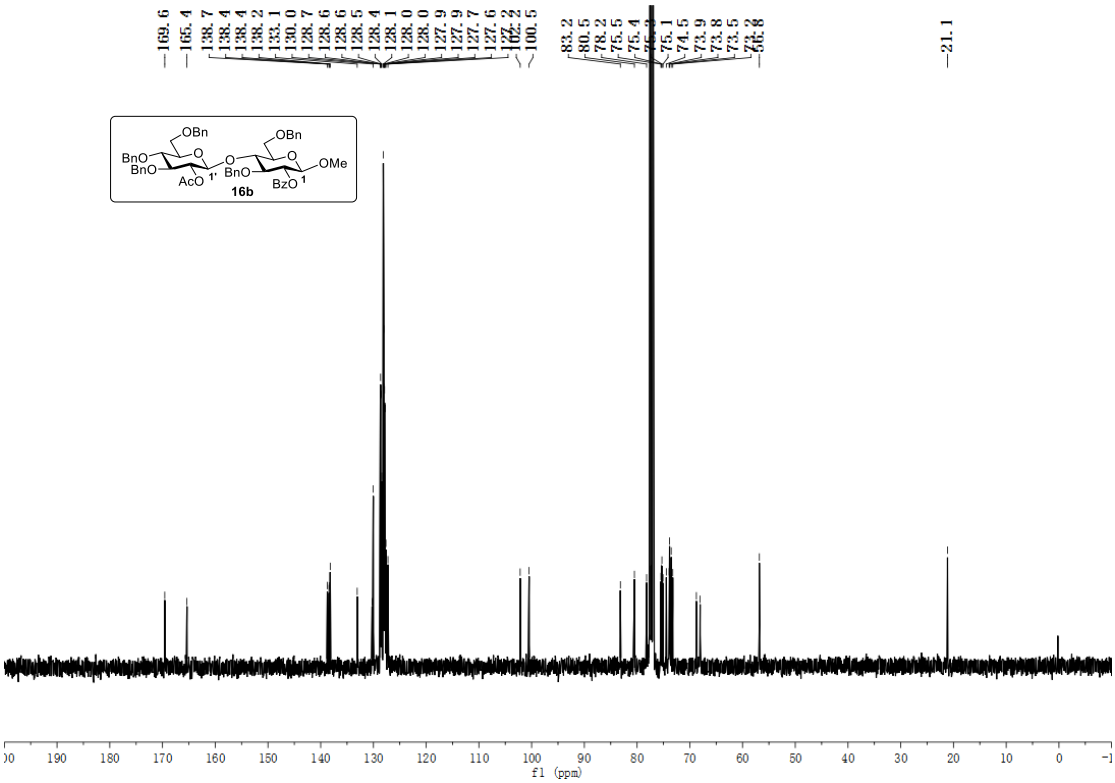

Figure S79. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **16b**

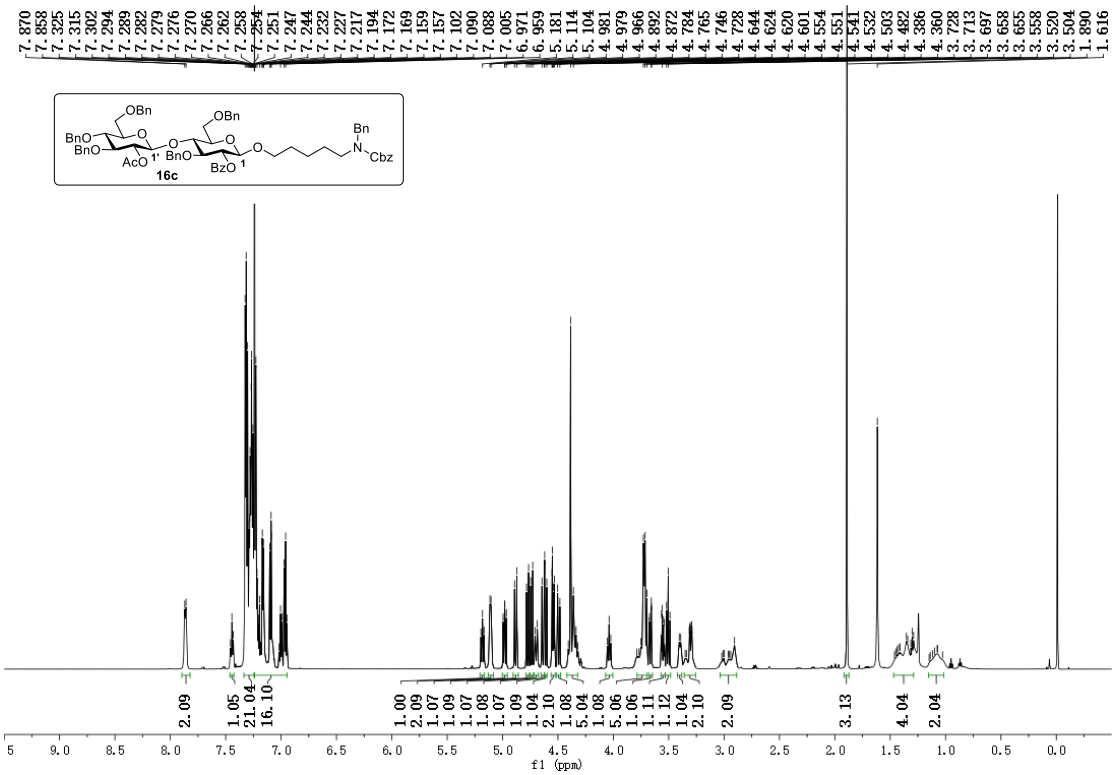

Figure S80. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **16c**

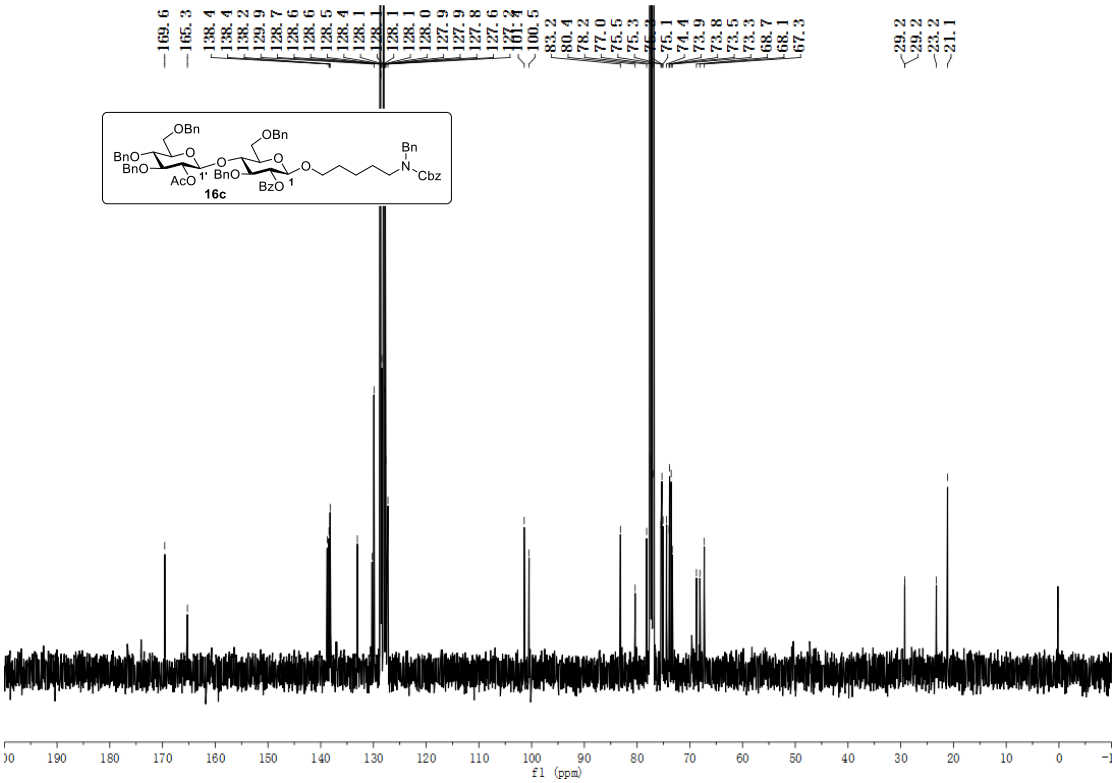

Figure S81. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **16c**

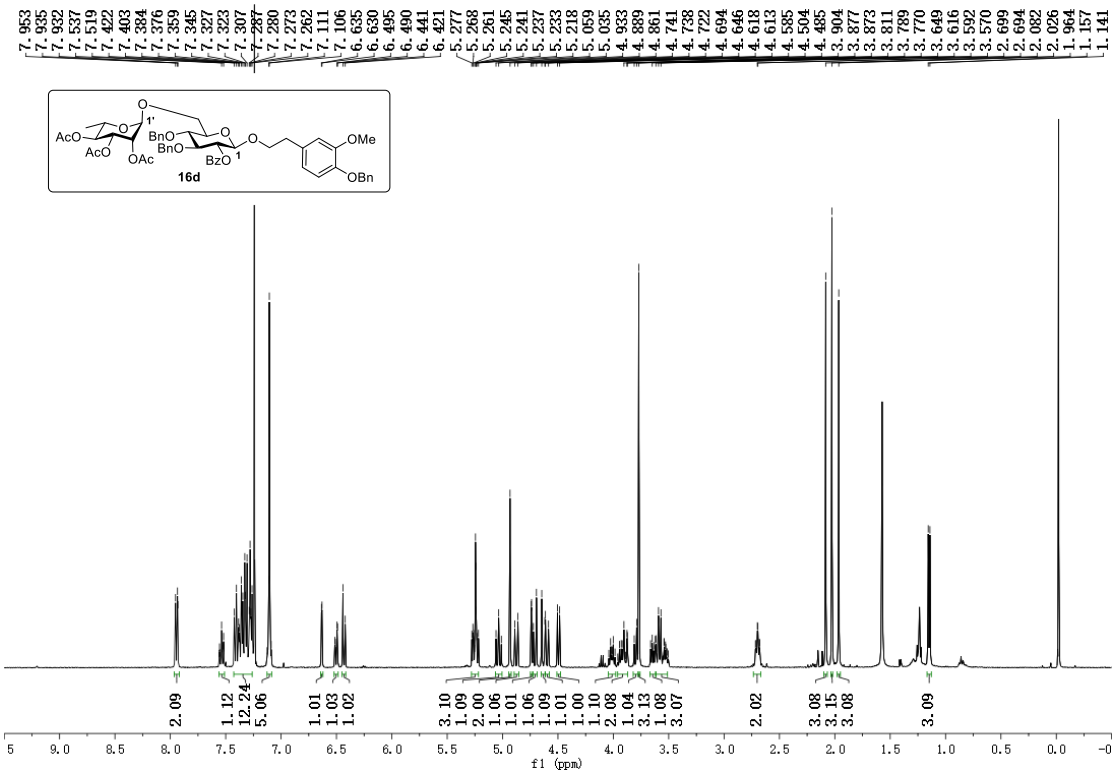

Figure S82. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **16d**

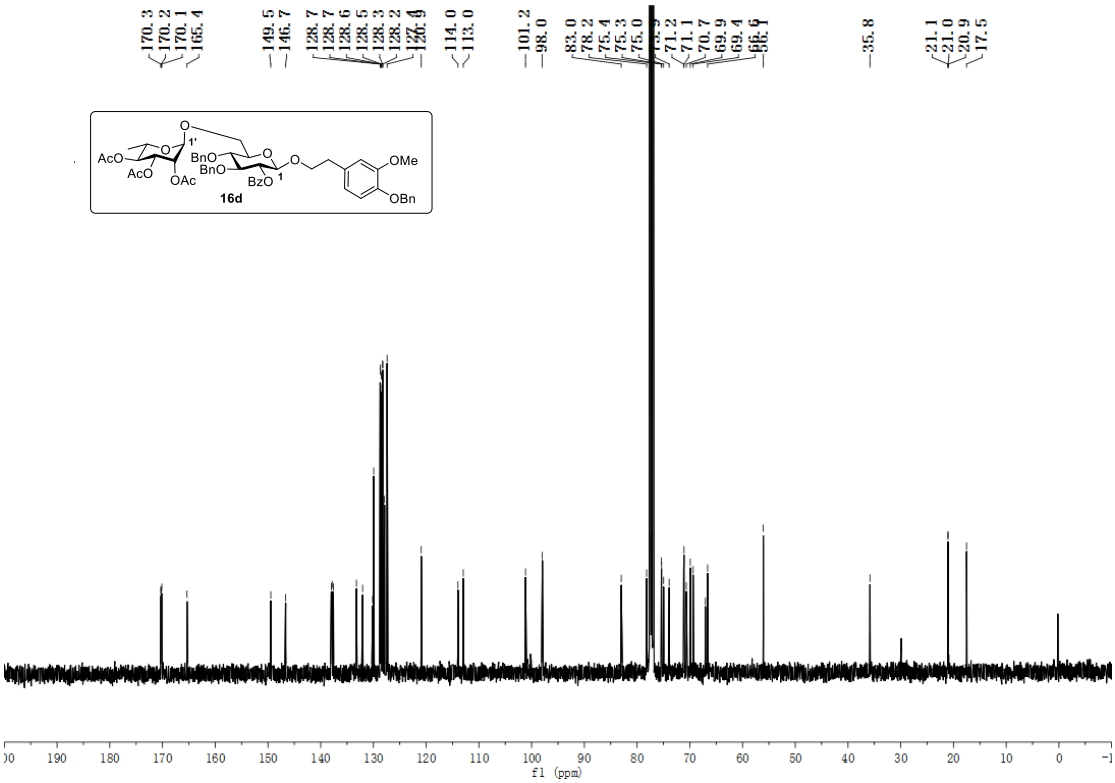

Figure S83. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **16d**

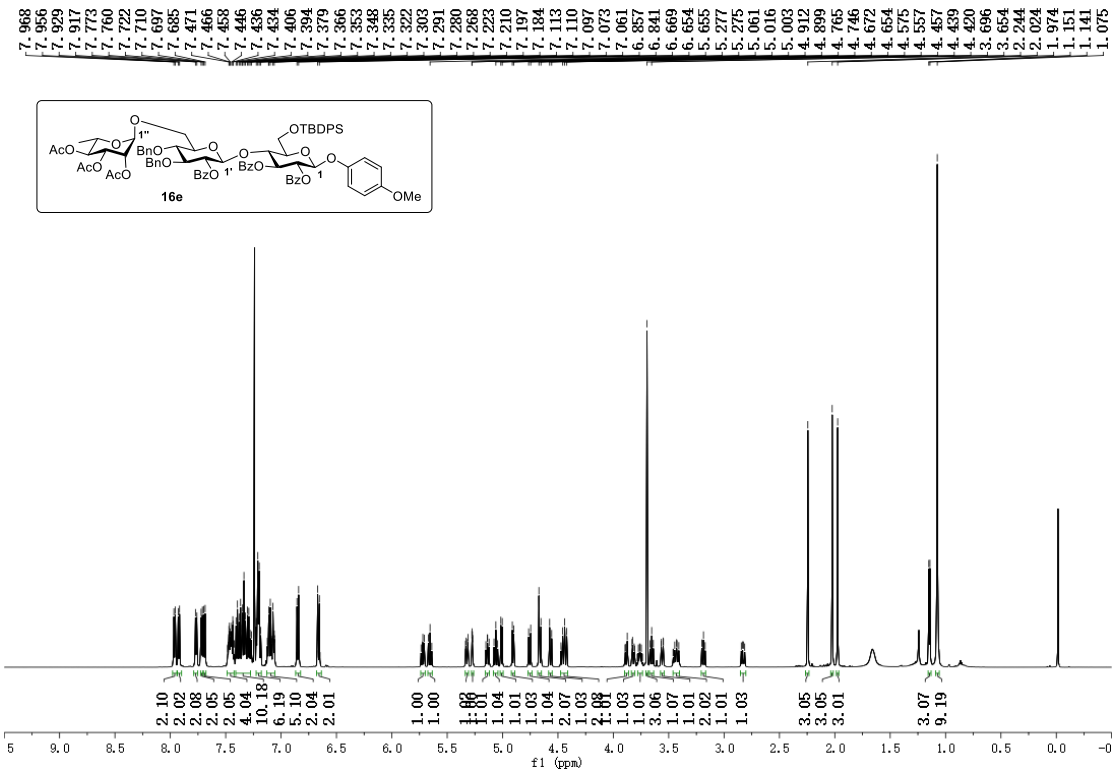

Figure S84. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **16e**

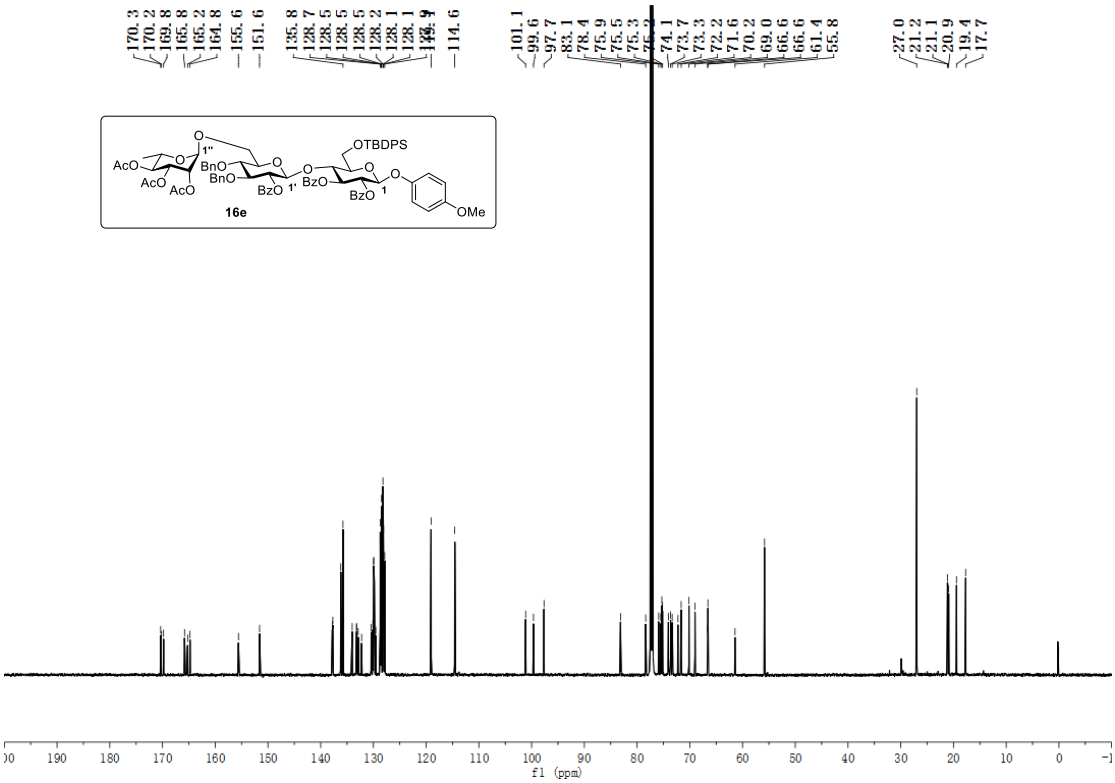

Figure S85. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **16e**

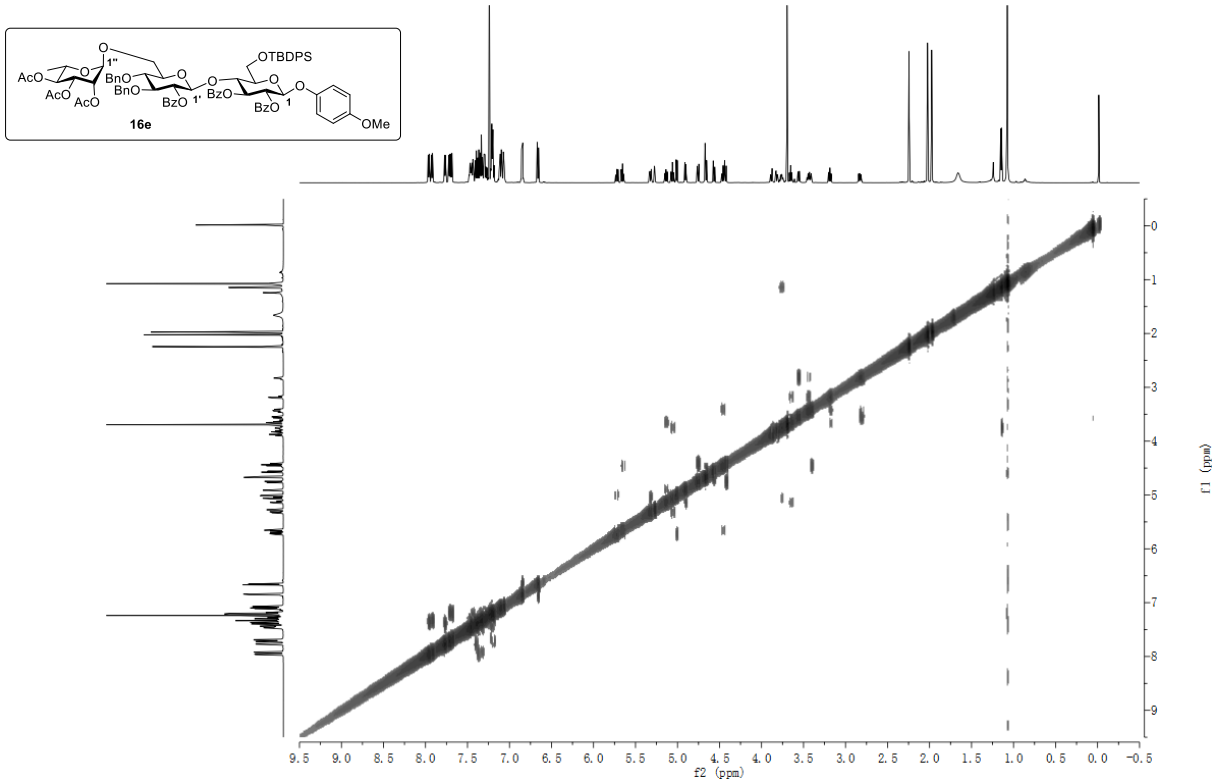

Figure S86. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **16e**

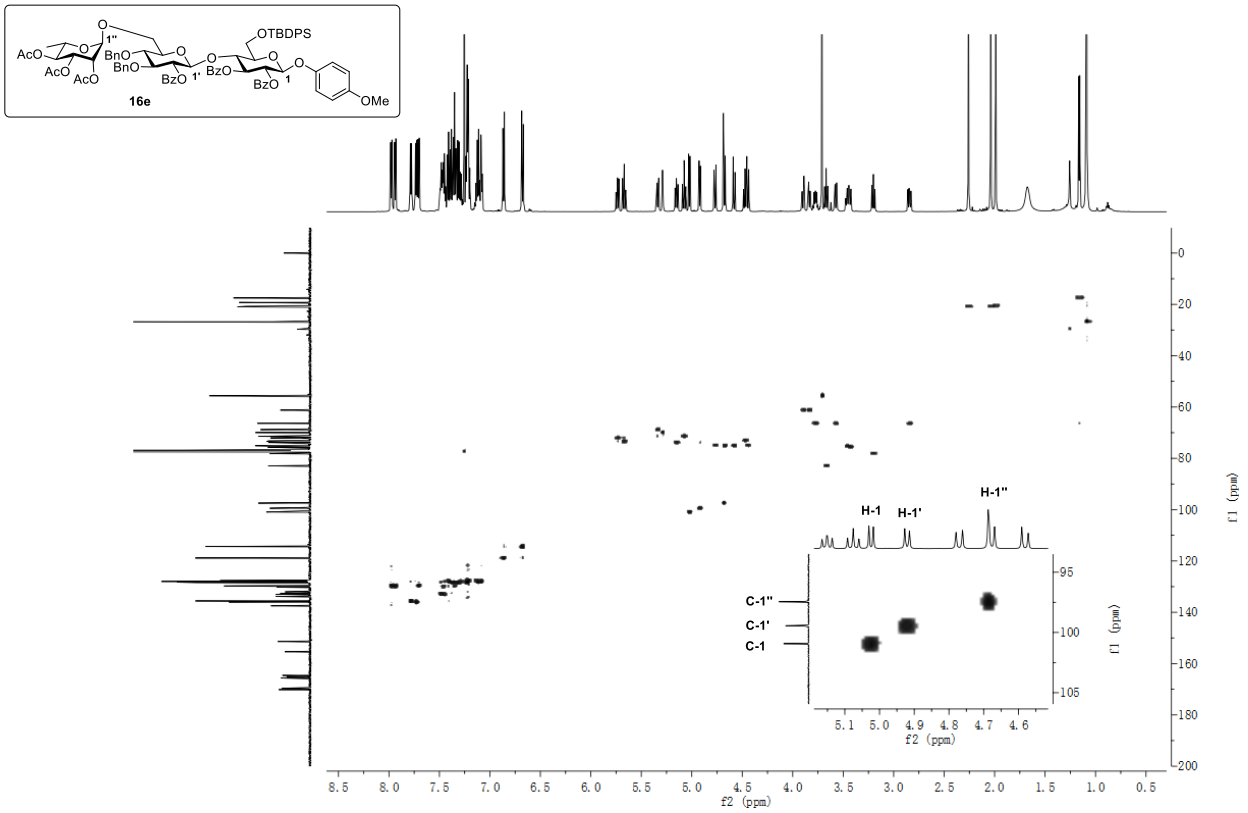

Figure S87. HSQC spectrum of **16e**

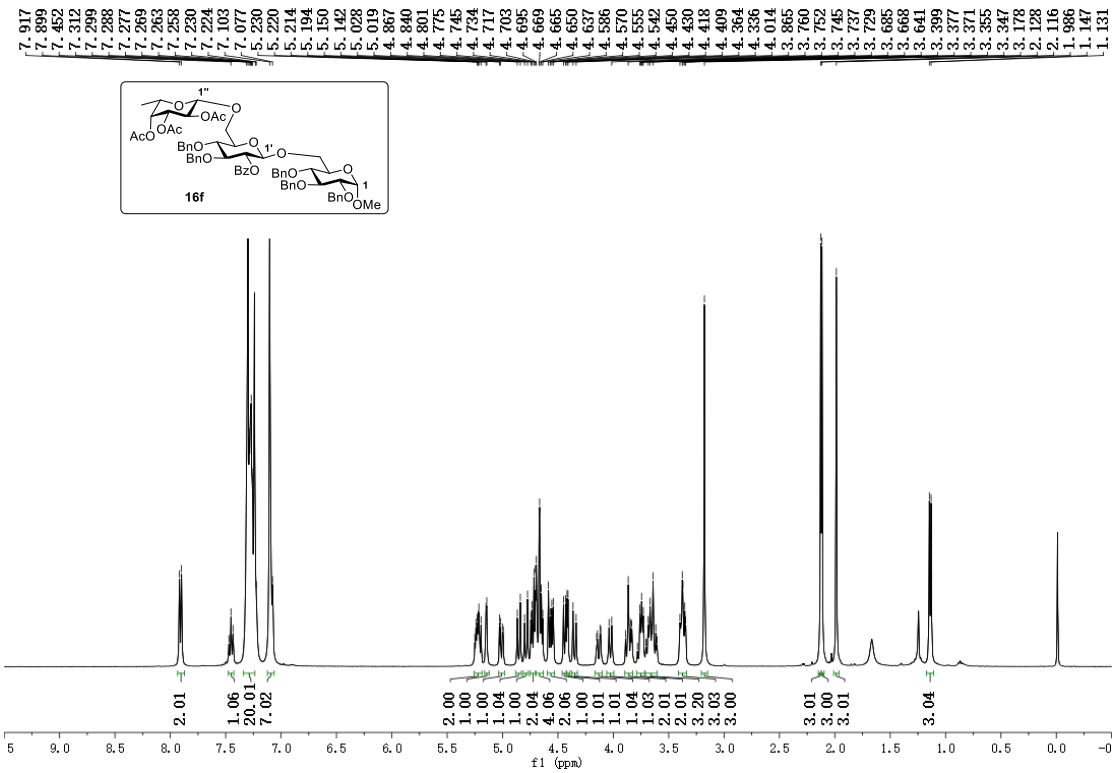

Figure S88. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **16f**

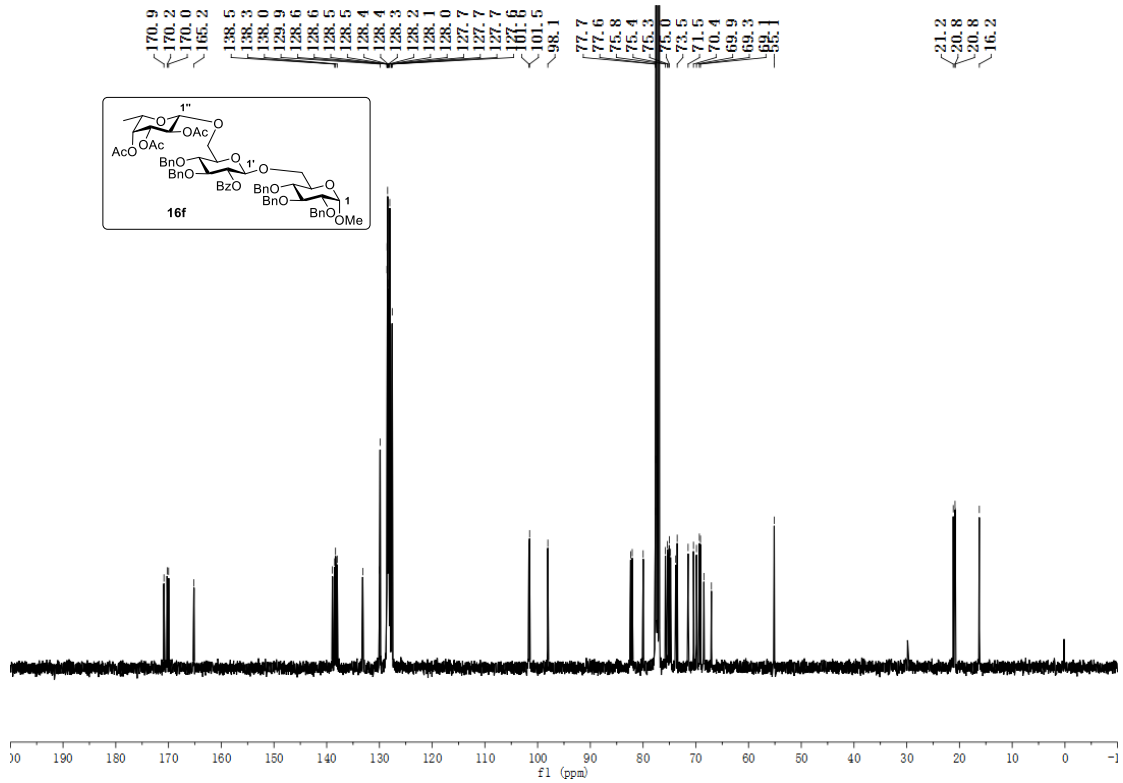

Figure S89. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **16f**

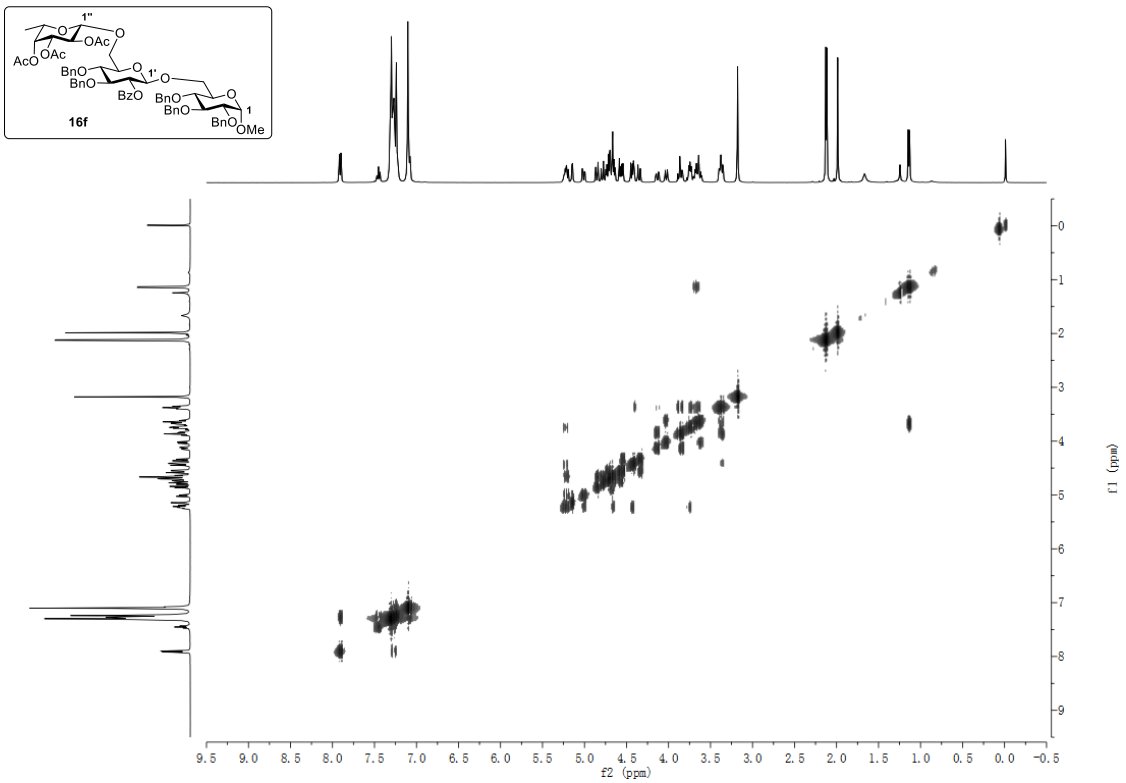

Figure S90. ^{1}H-^{1}H COSY (400 MHz, $CDCl_3$) spectrum of **16f**

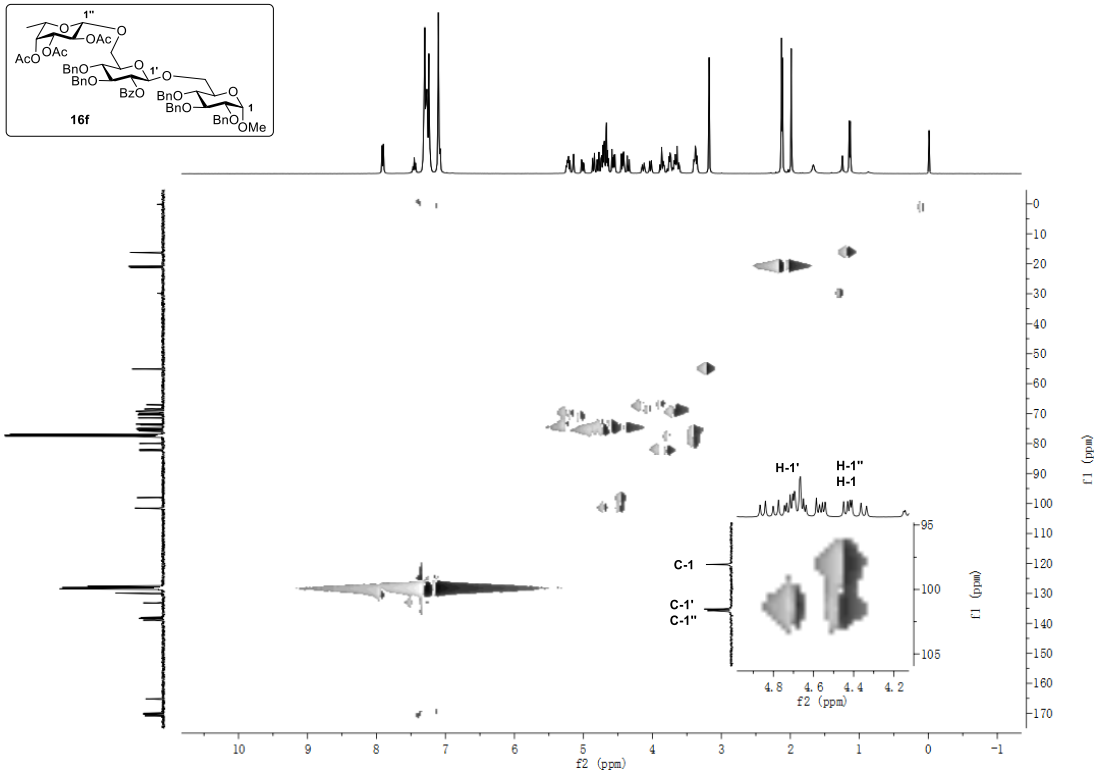

Figure S91. HSQC spectrum of **16f**

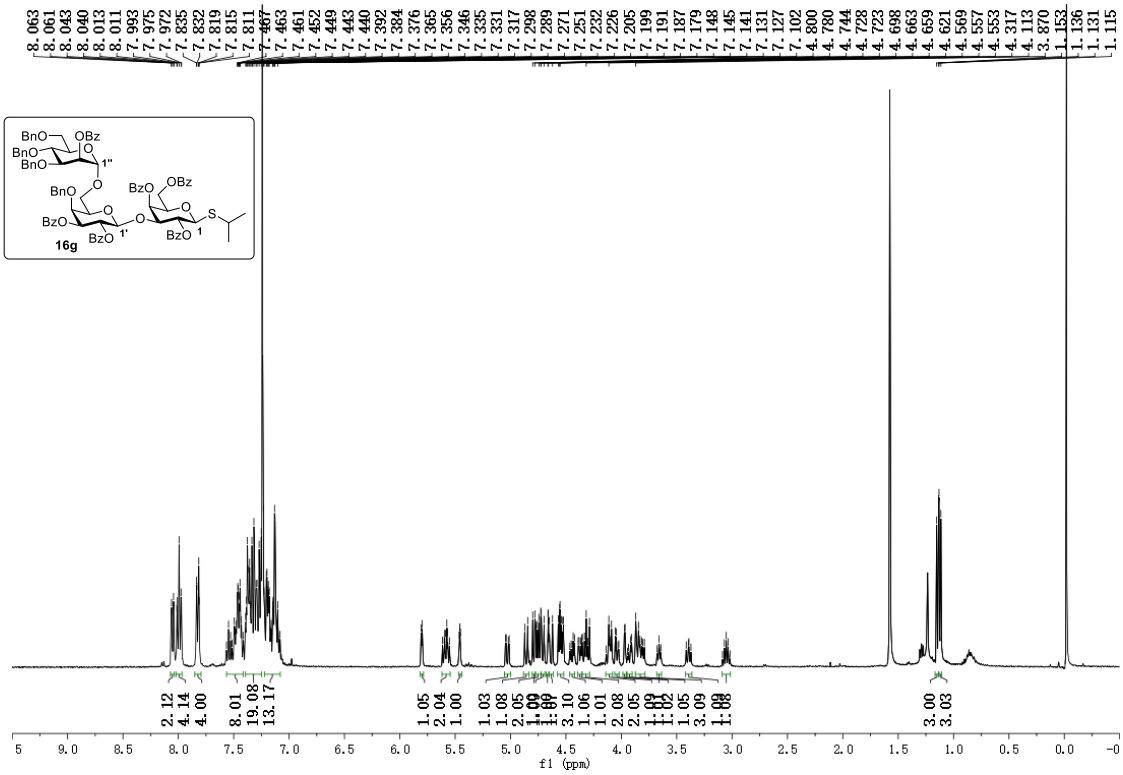

Figure S92. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **16g**

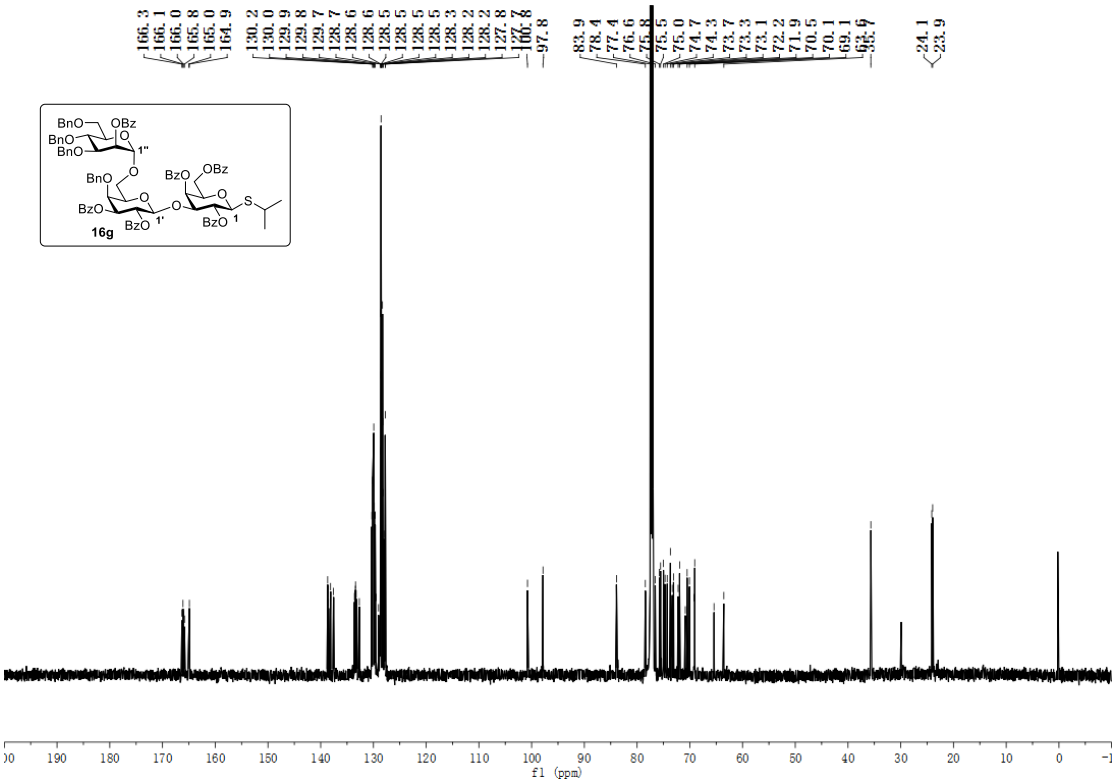

Figure S93. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **16g**

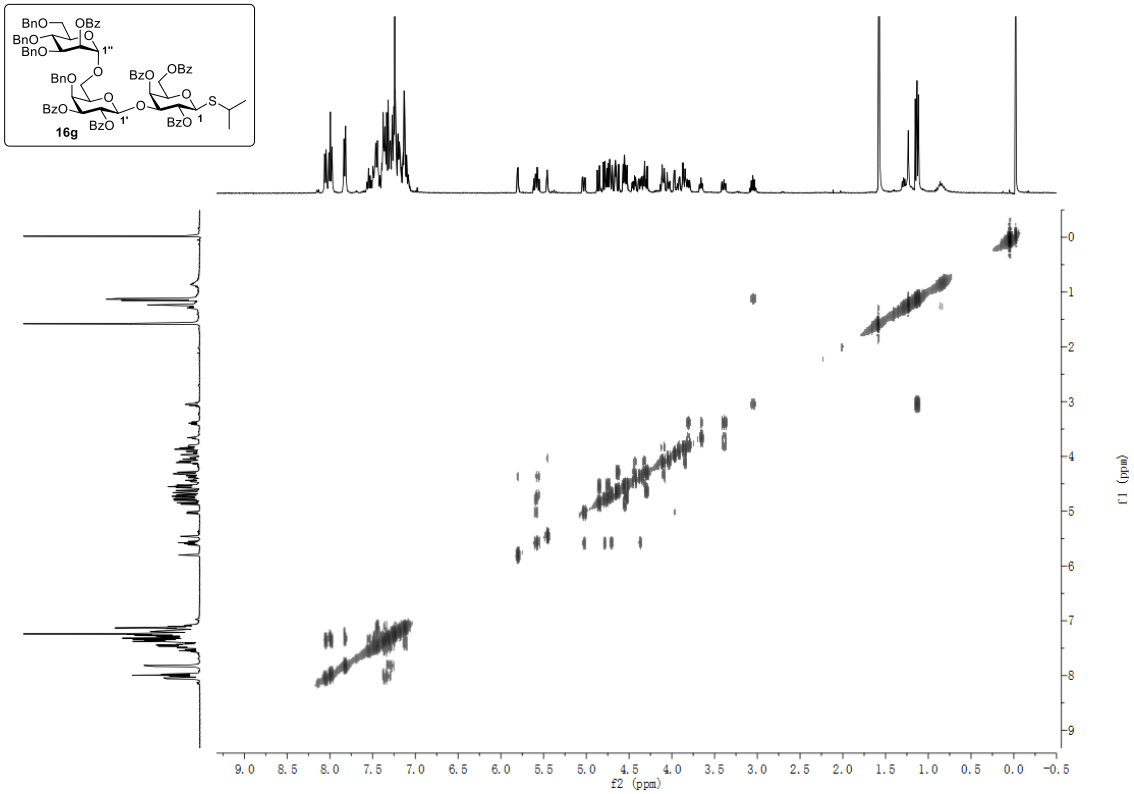

Figure S94. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **16g**

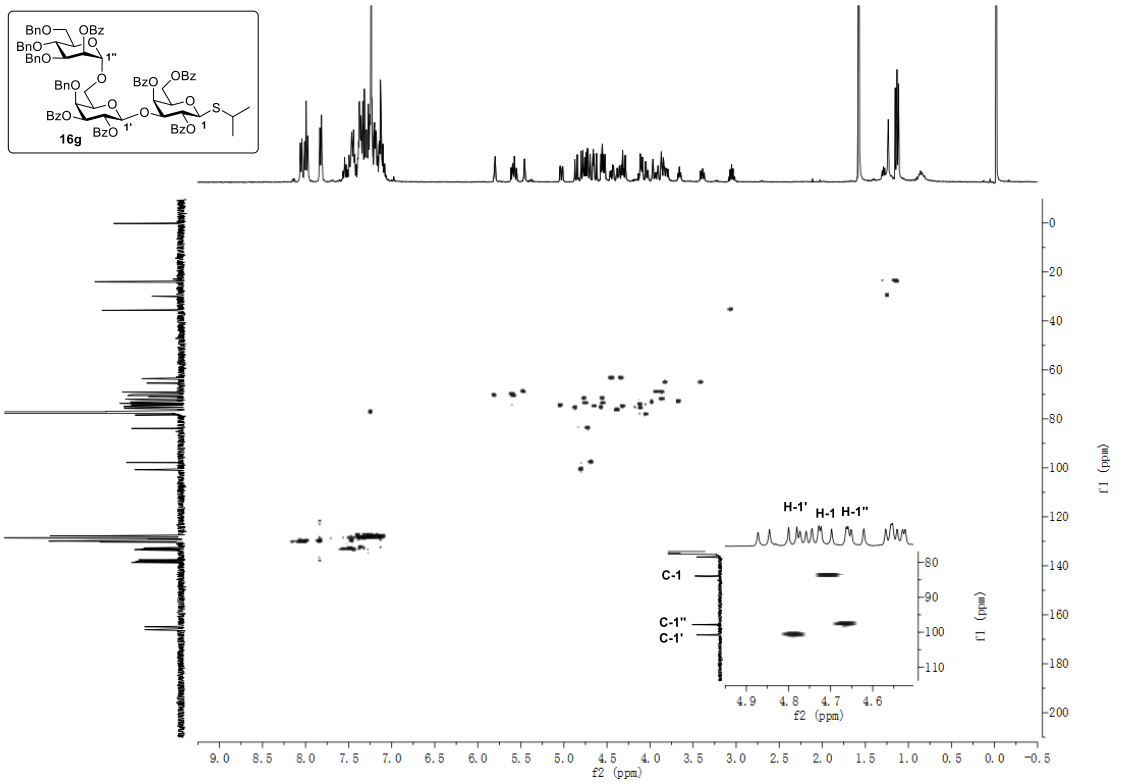

Figure S95. HSQC spectrum of **16g**

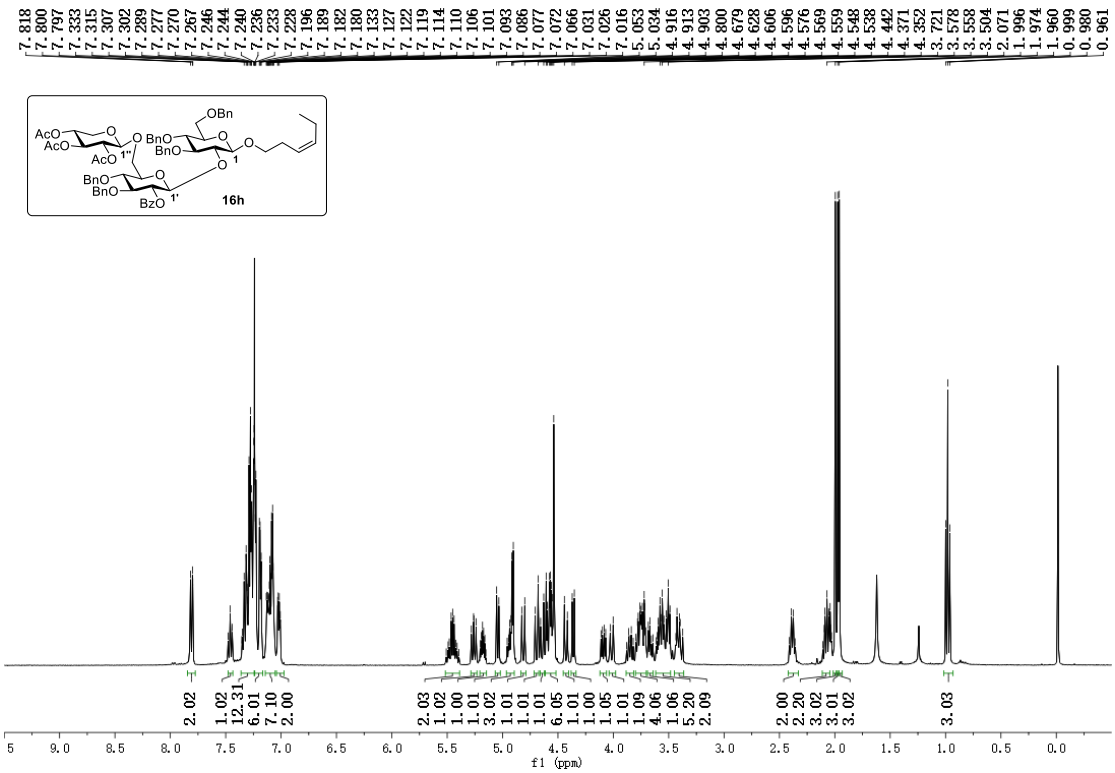

Figure S96. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **16h**

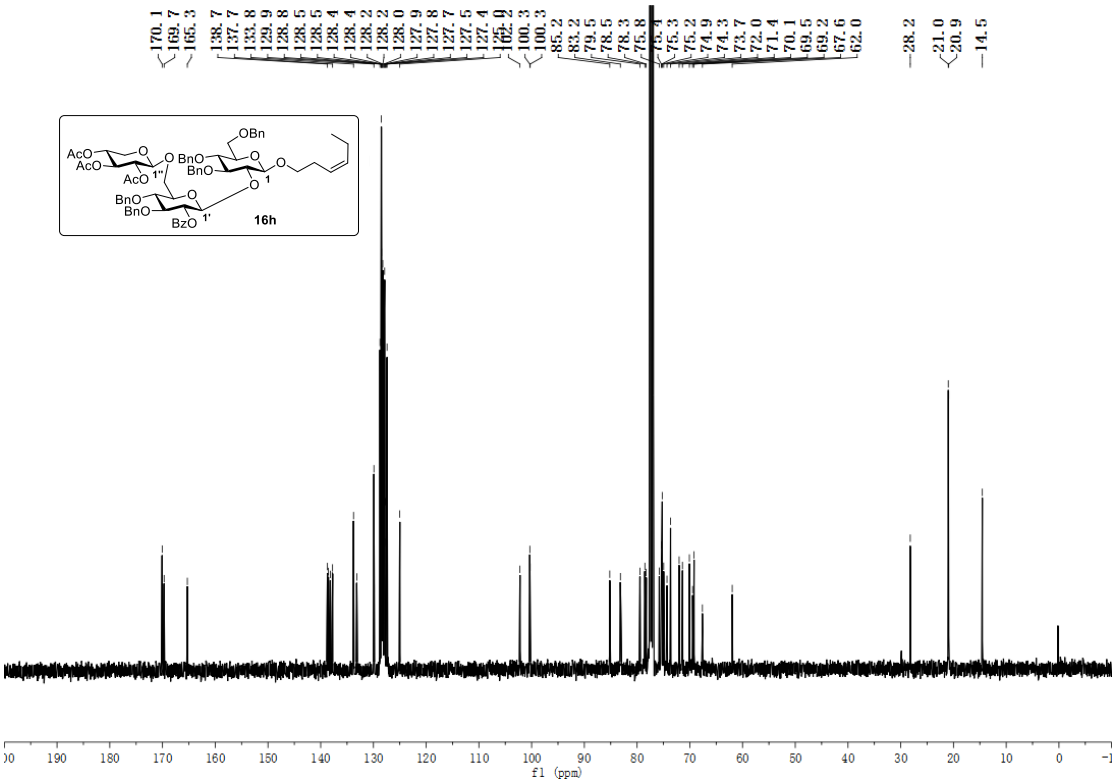

Figure S97. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **16h**

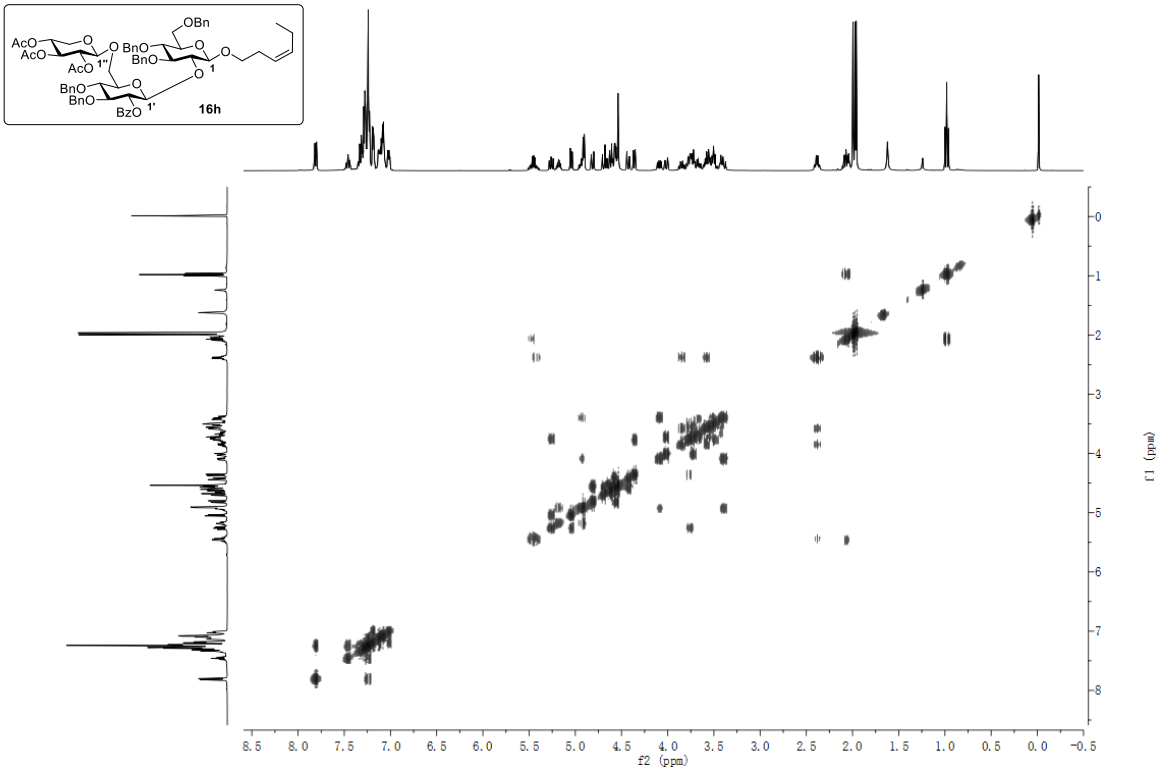

Figure S98. ^{1}H-^{1}H COSY (400 MHz, $CDCl_3$) spectrum of **16h**

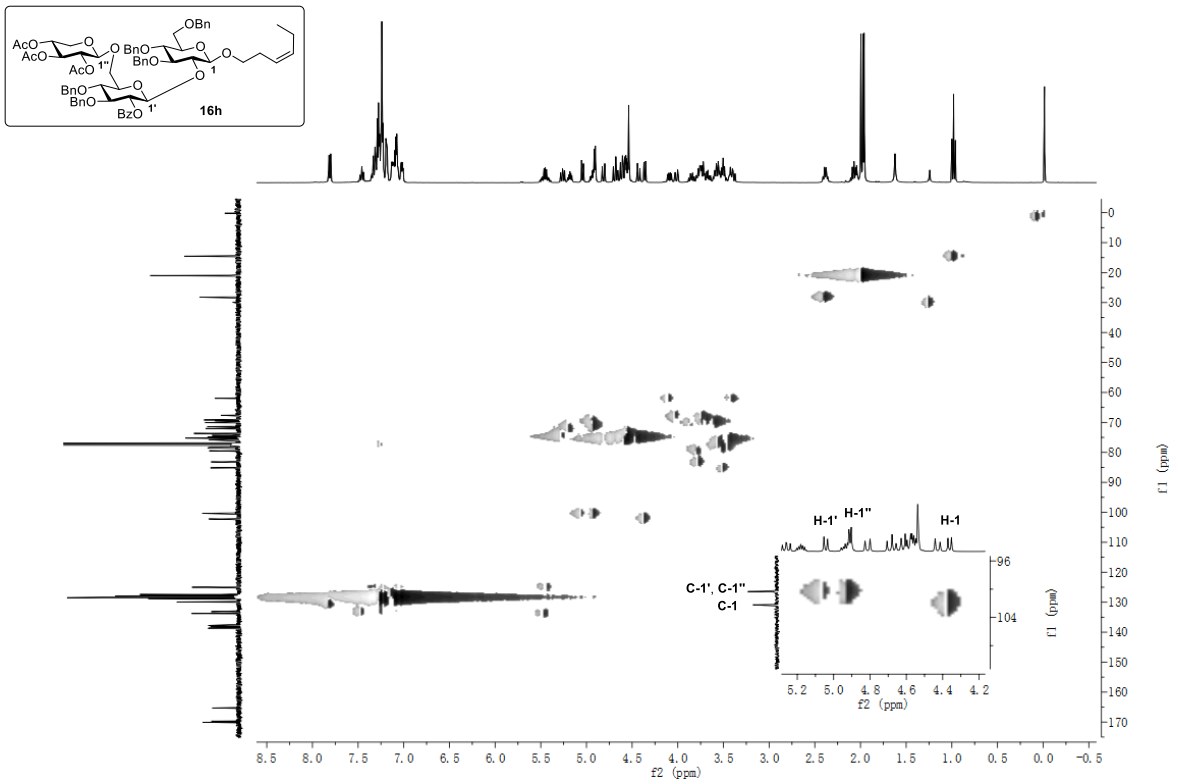

Figure S99. HSQC spectrum of **16h**

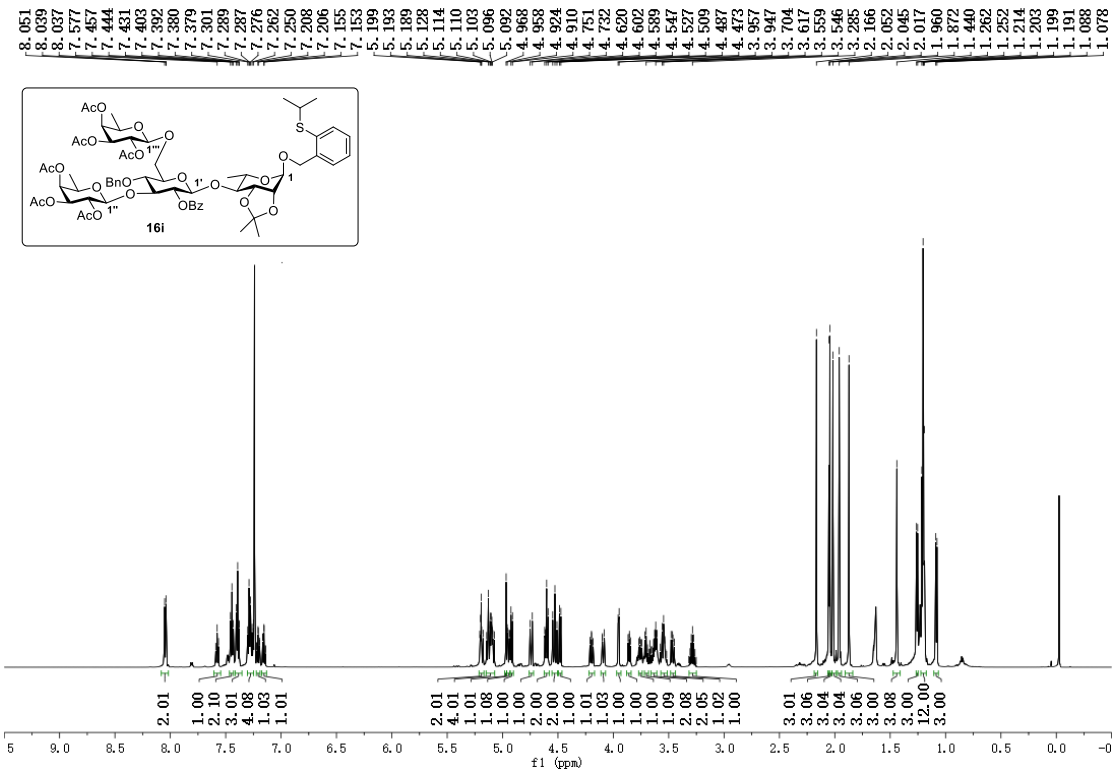

Figure S100. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **16i**

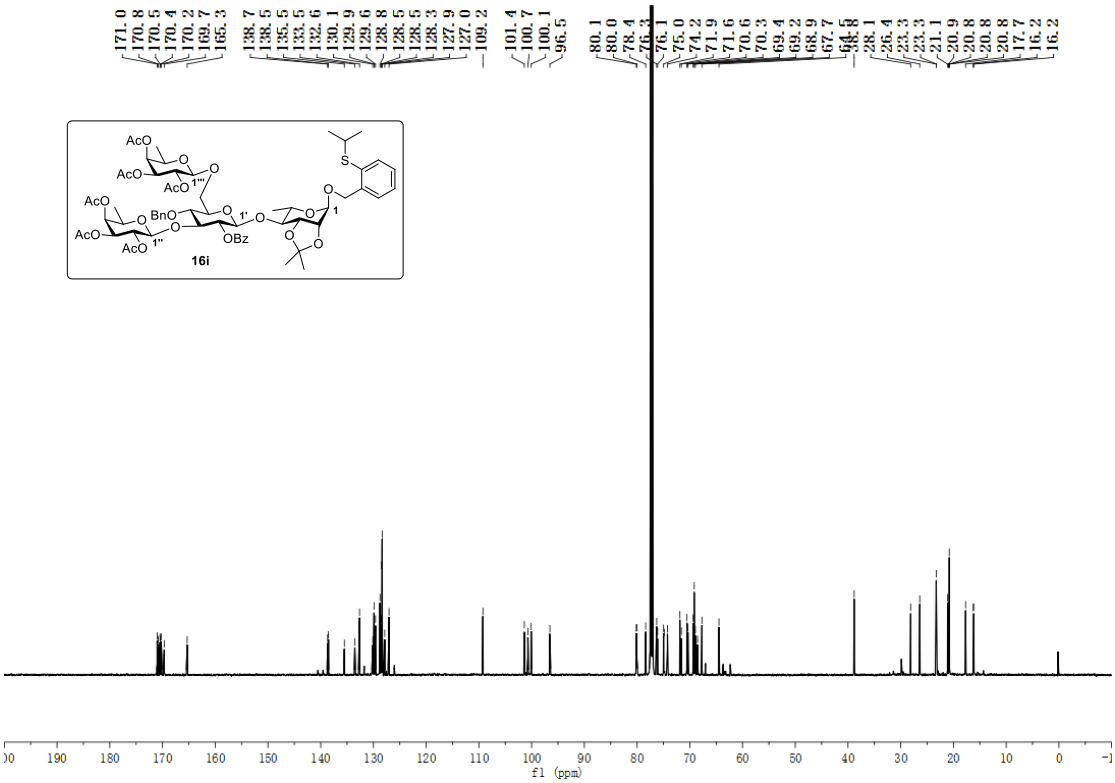

Figure S101. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **16i**

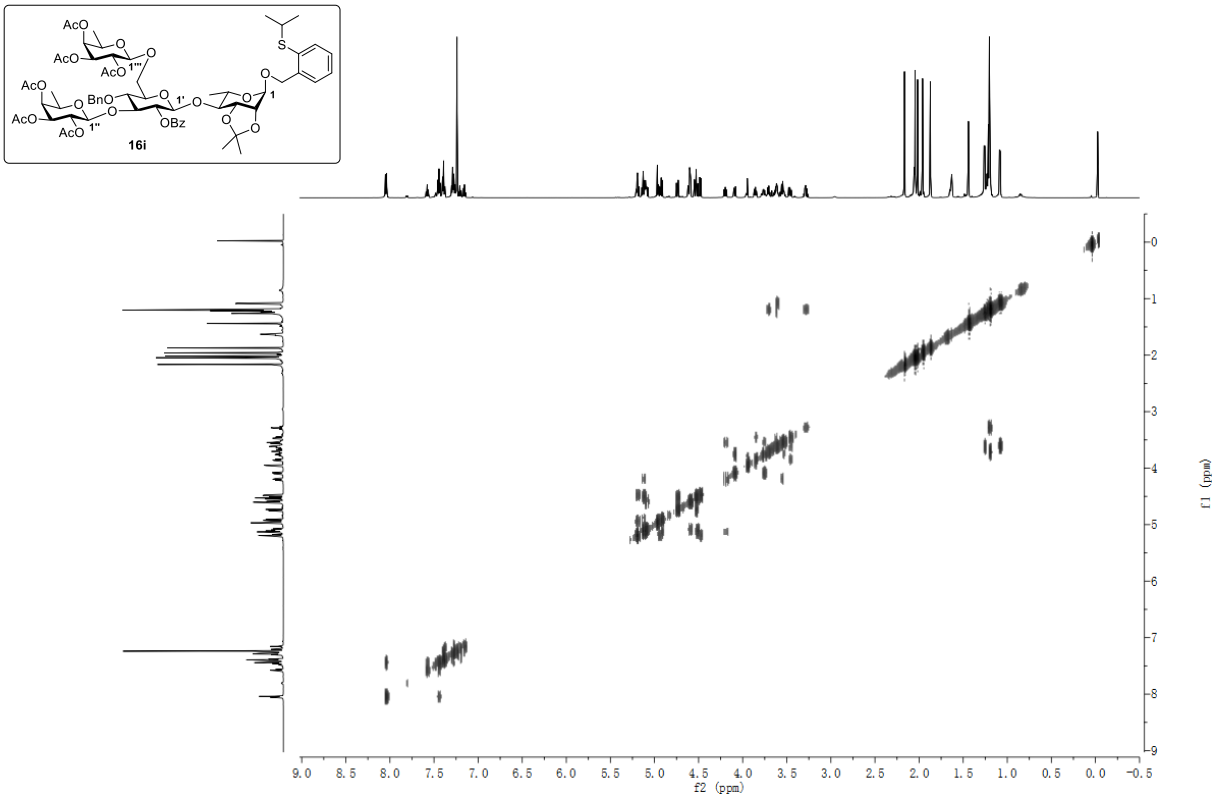

Figure S102. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **16i**

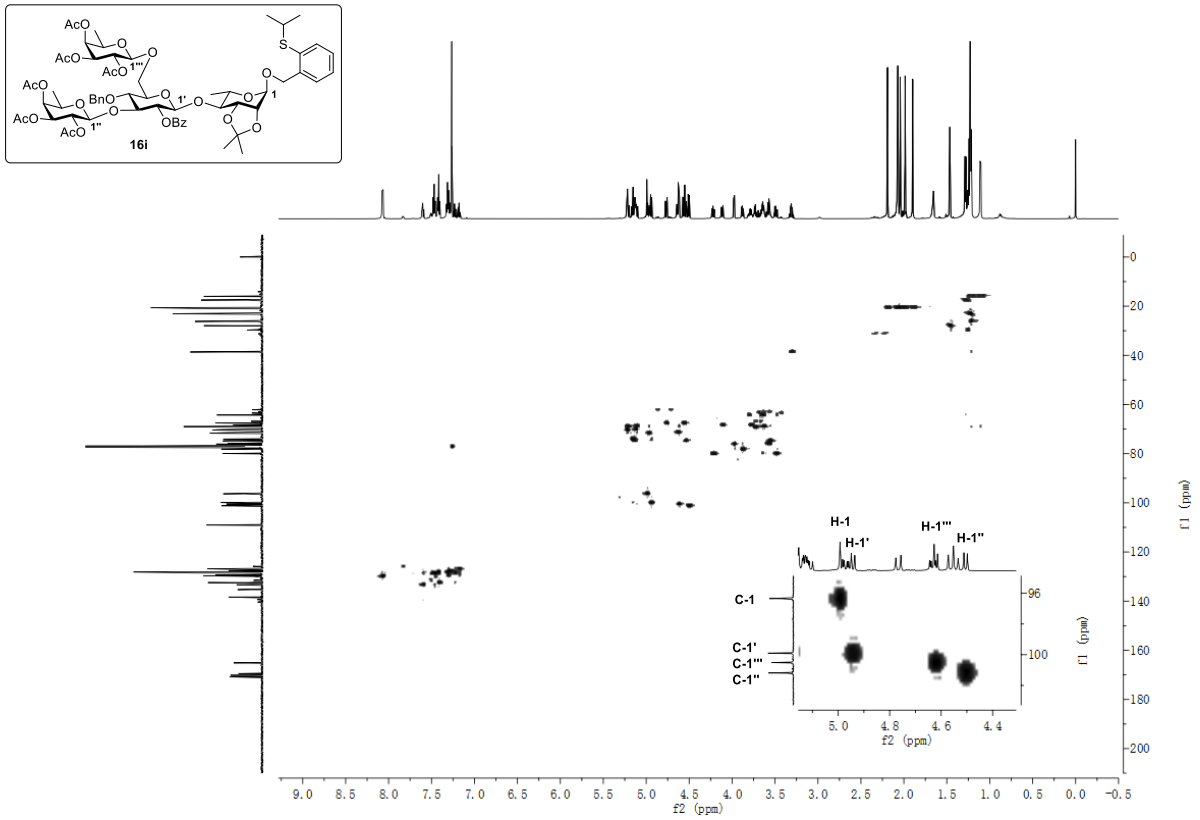

Figure S103. HSQC spectrum of **16i**

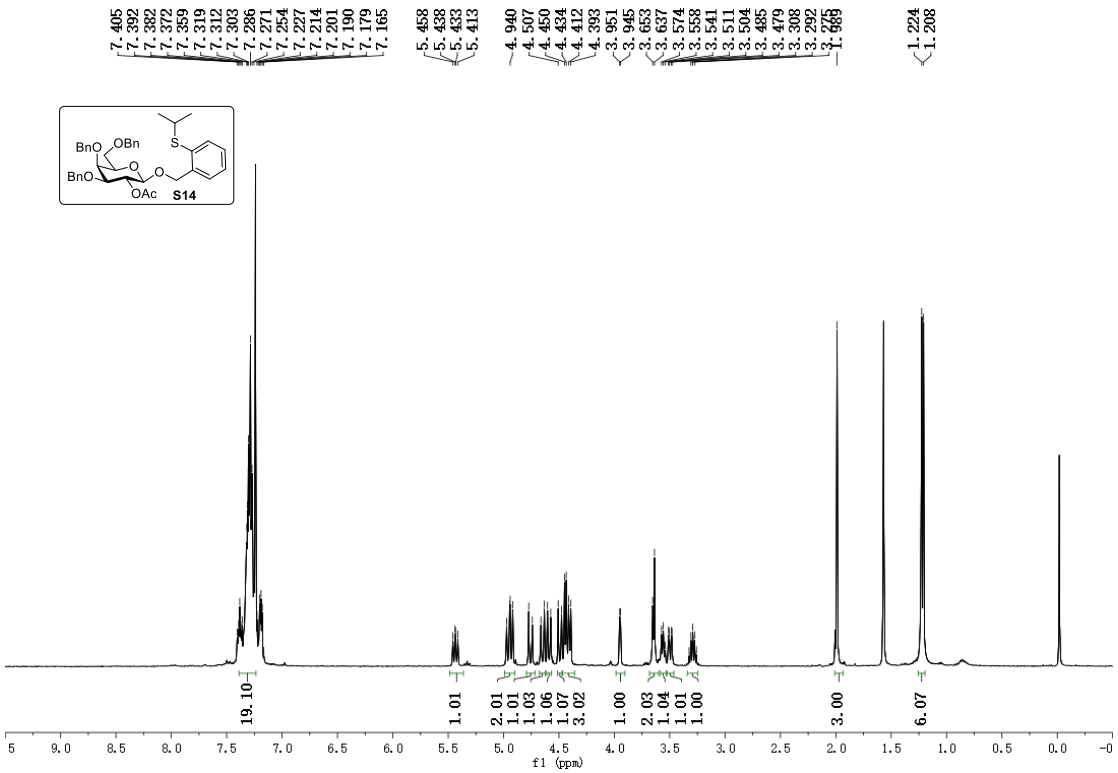

Figure S104. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S14**

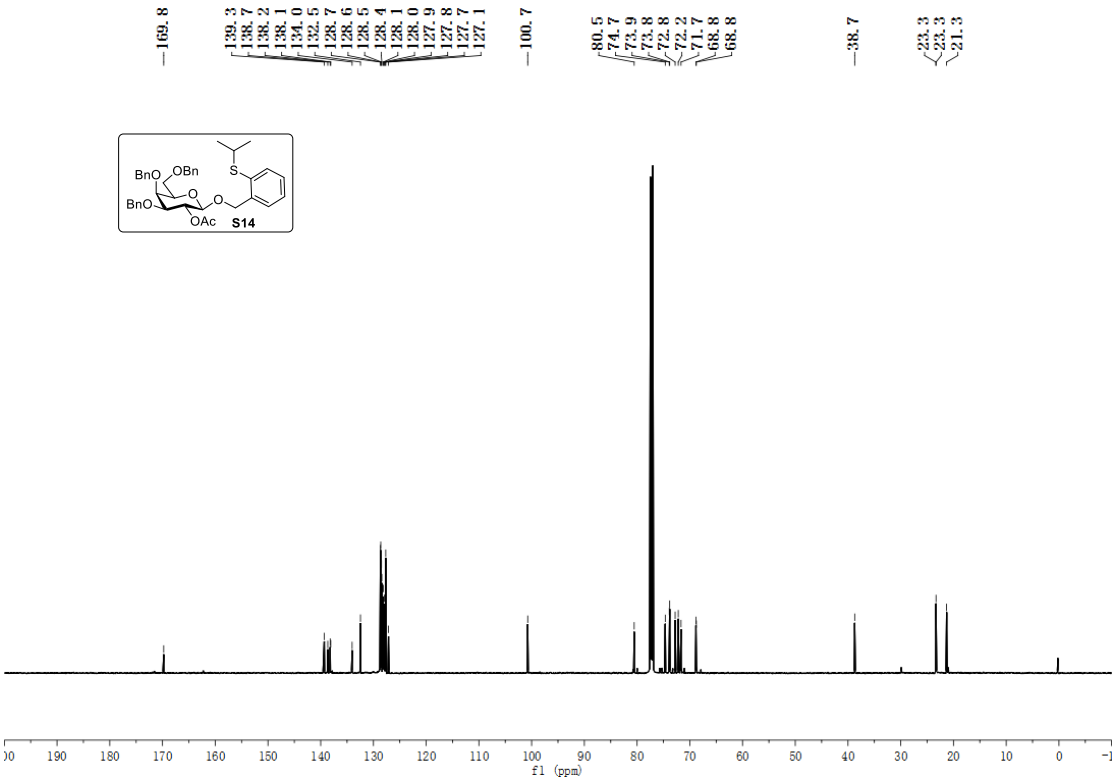

Figure S105. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **S14**

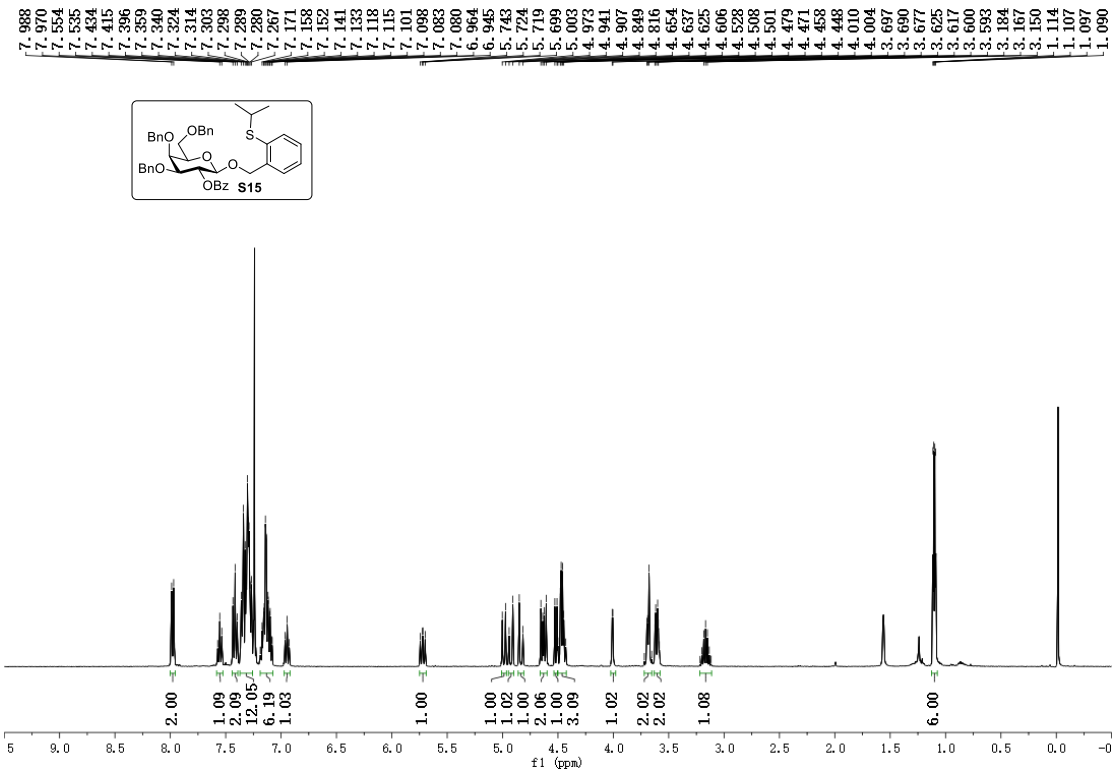

Figure S106. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S15**

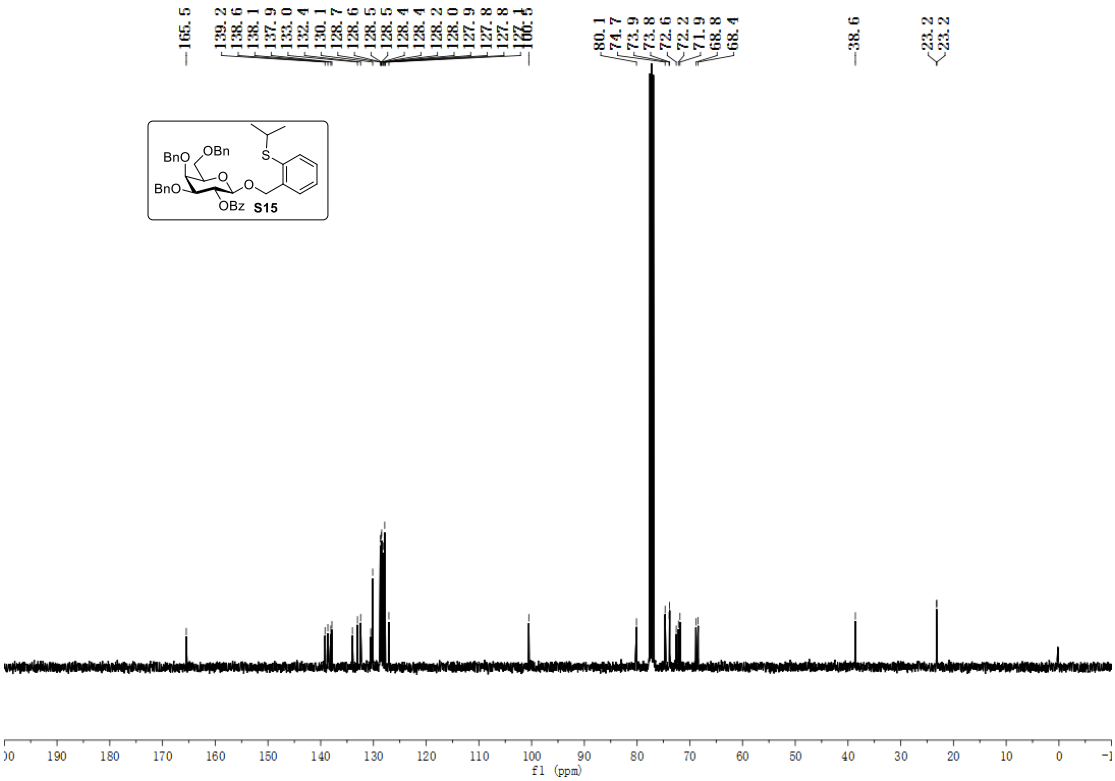

Figure S107. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **S15**

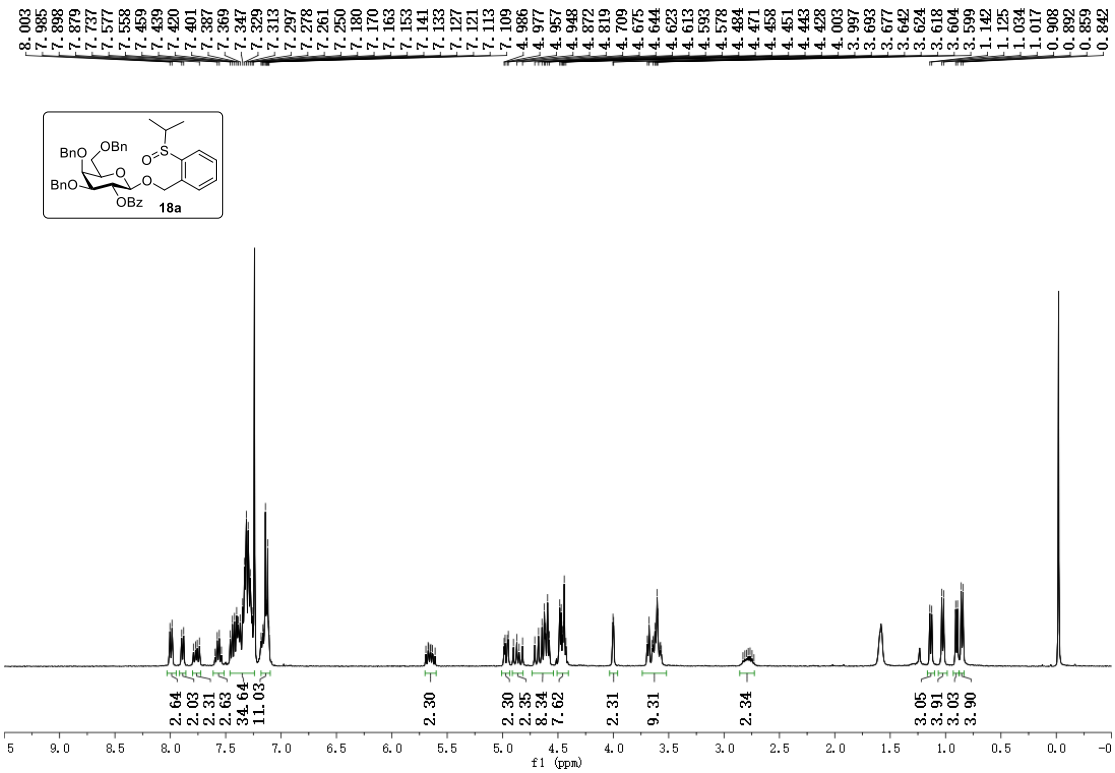

Figure S108. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **18a**

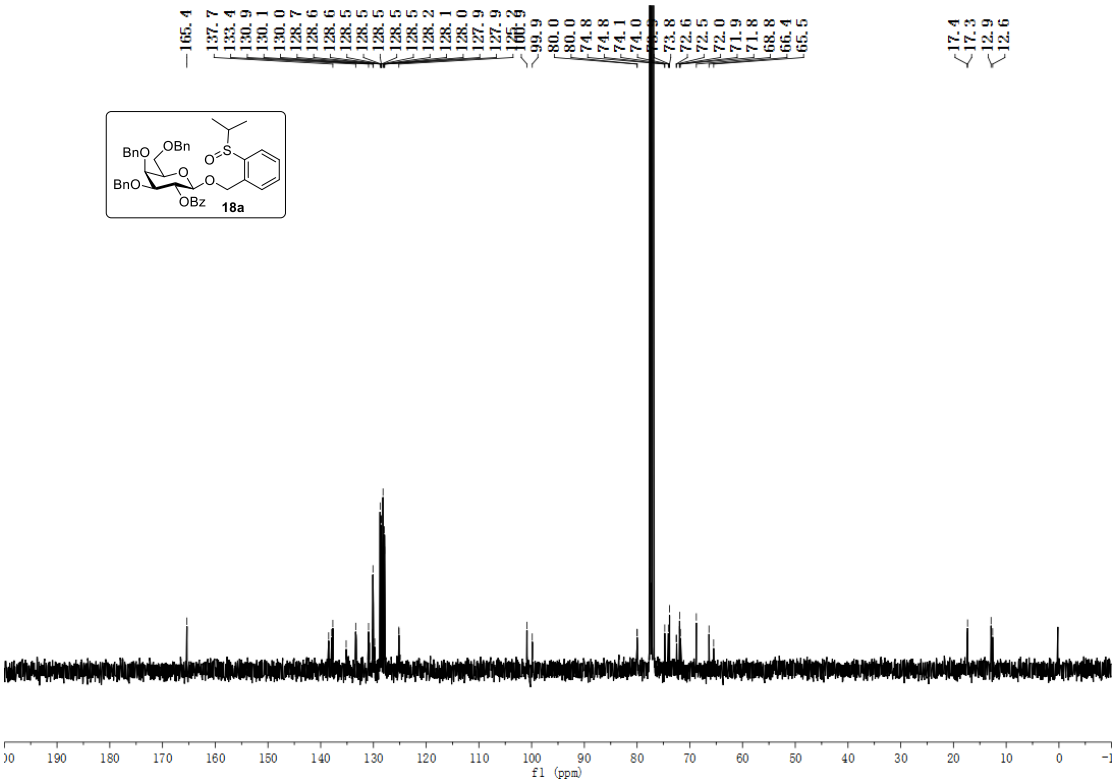

Figure S109. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **18a**

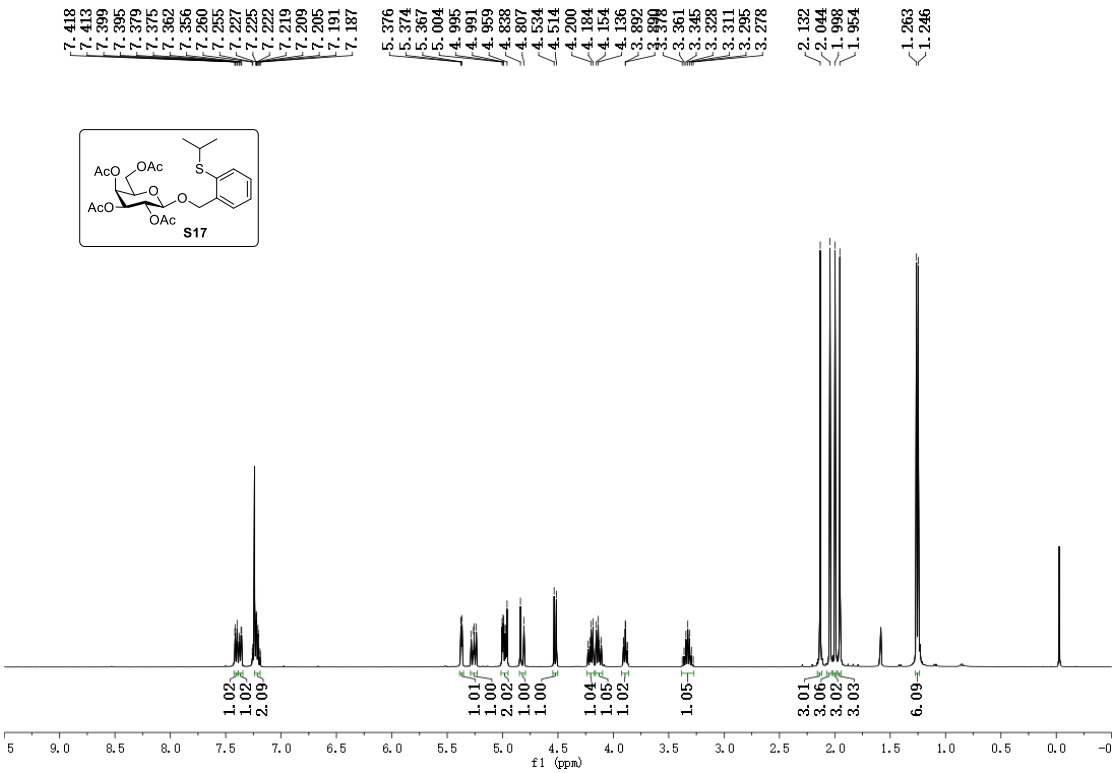

Figure S110. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S17**

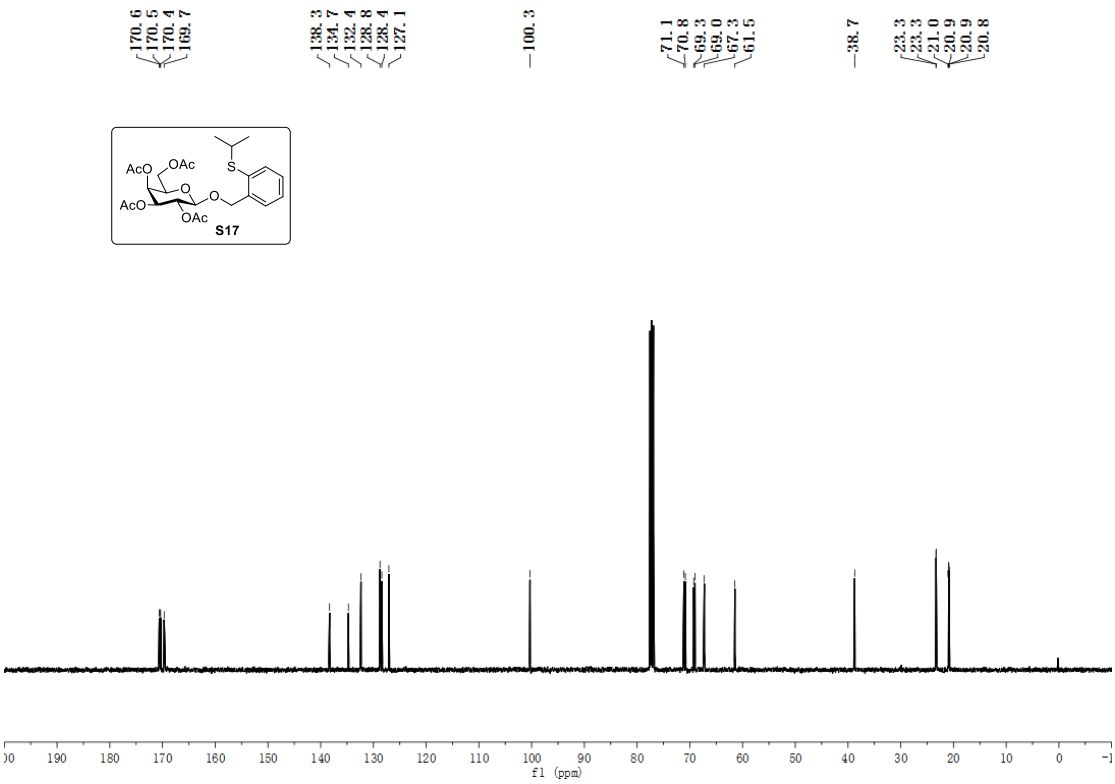

Figure S111. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **S17**

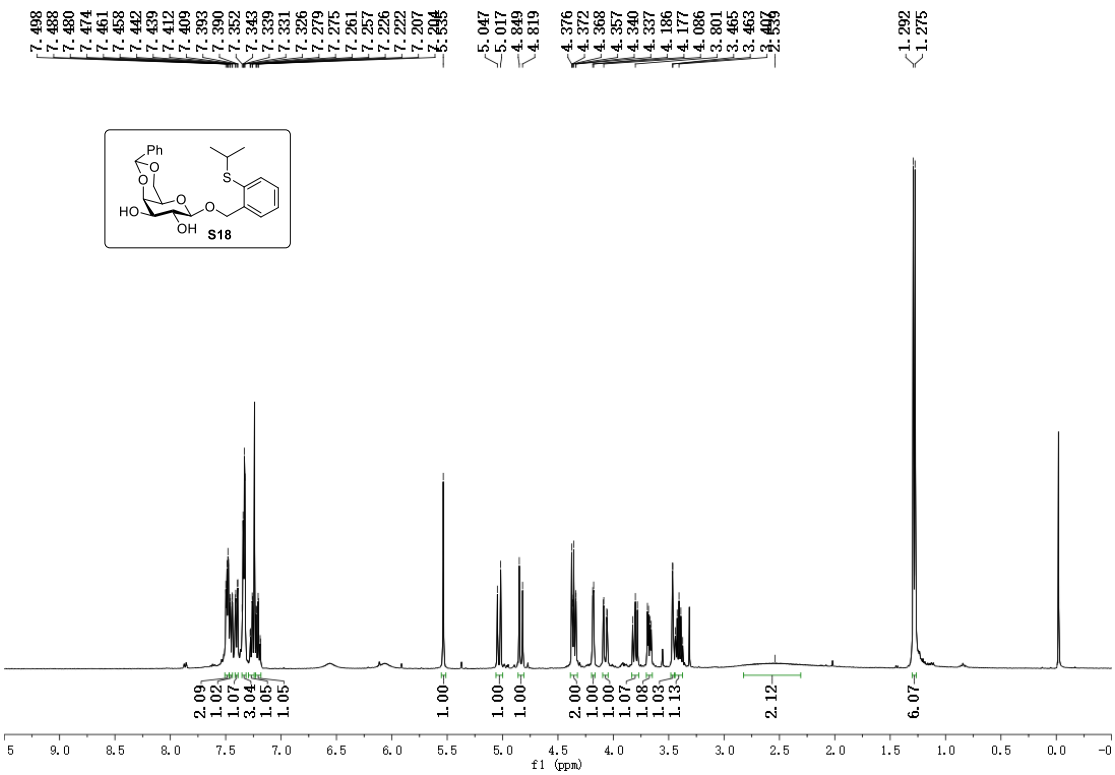

Figure S112. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S18**

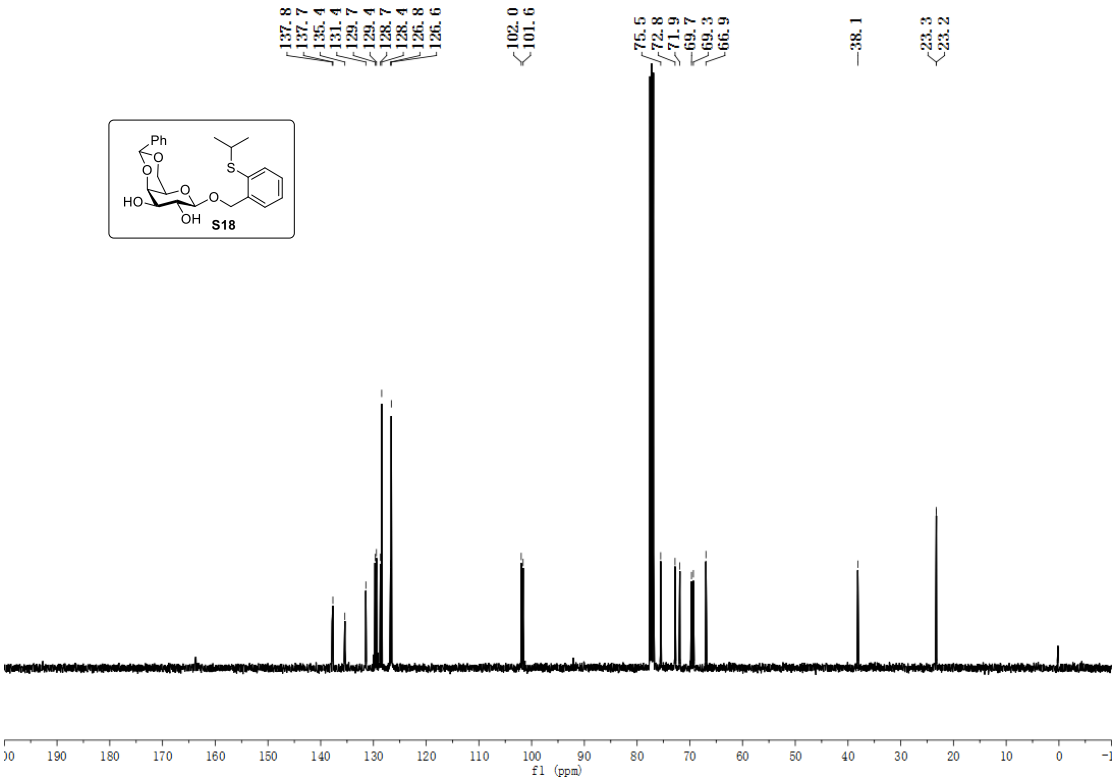

Figure S113. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **S18**

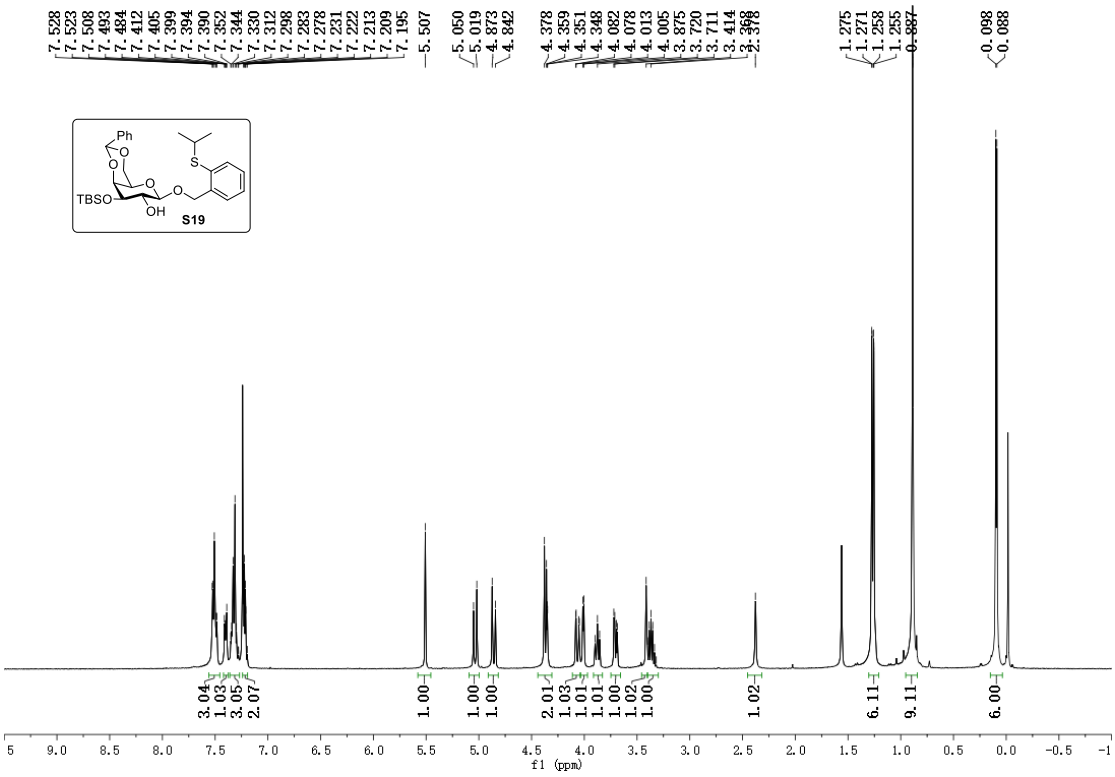

Figure S114. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S19**

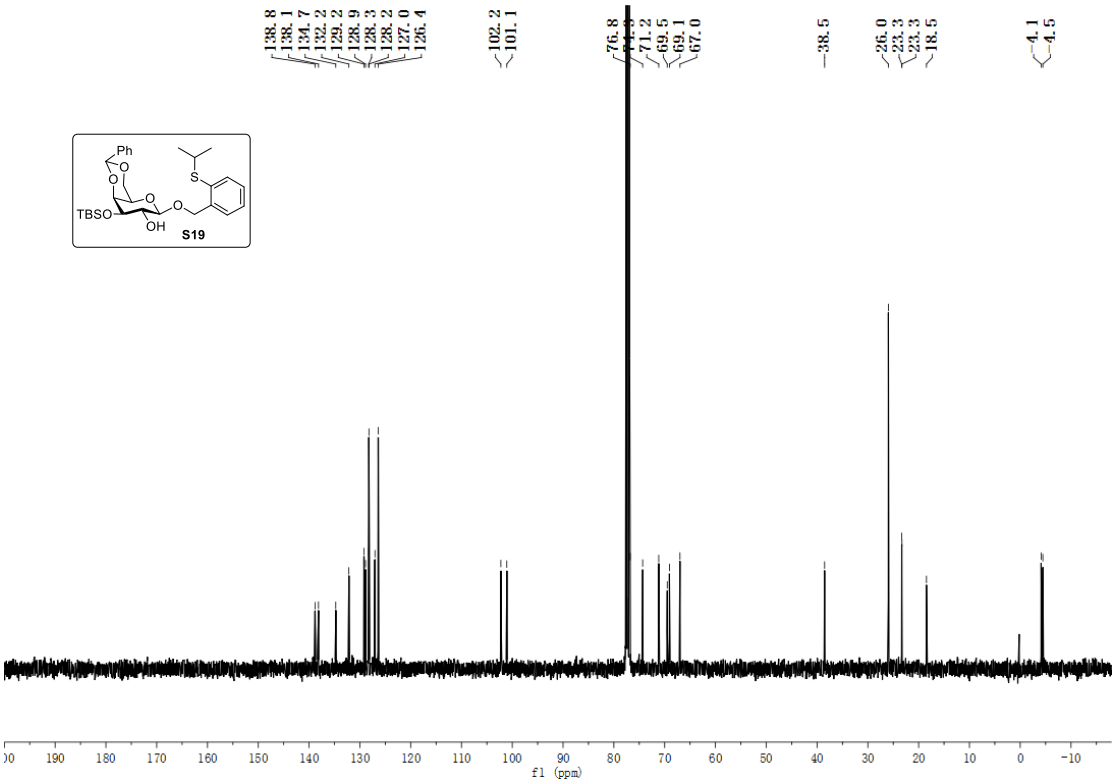

Figure S115. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **S19**

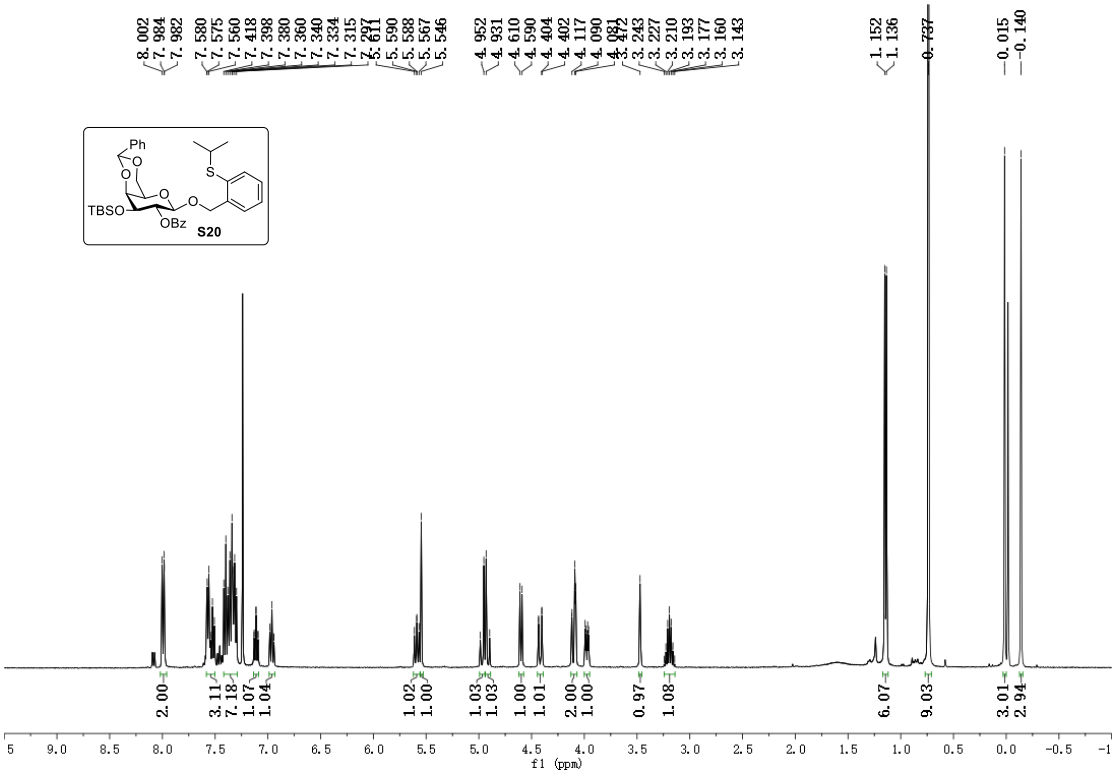

Figure S116. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S20**

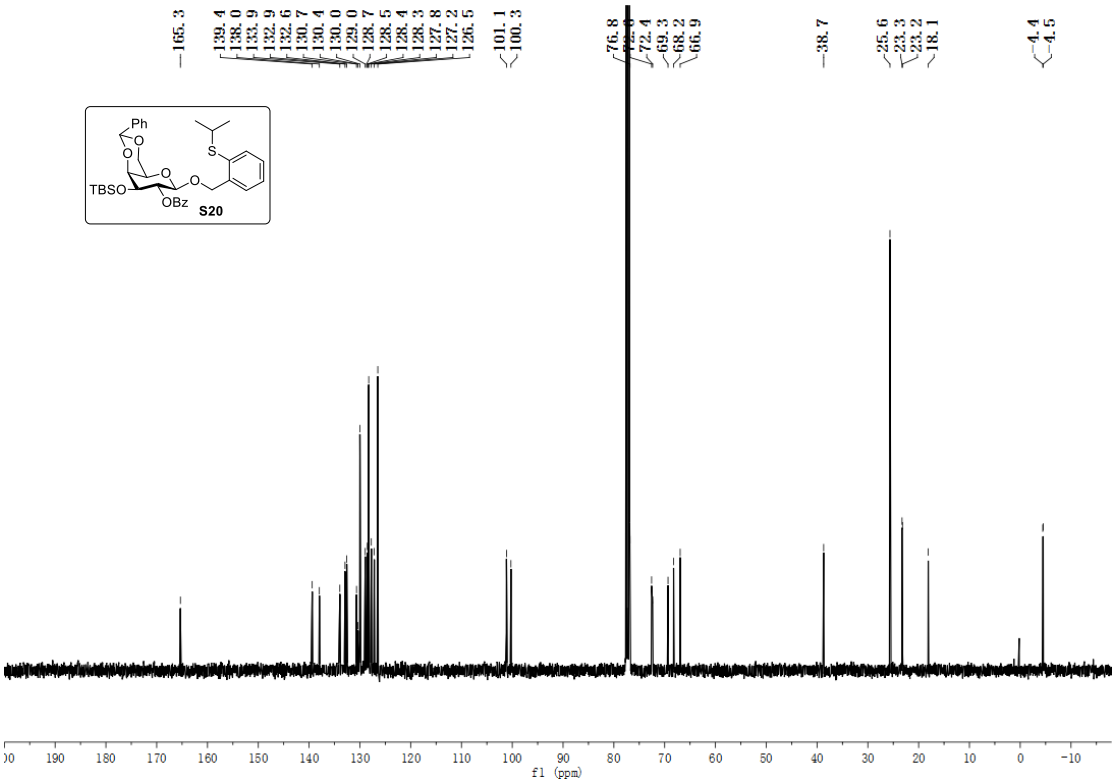

Figure S117. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **S20**

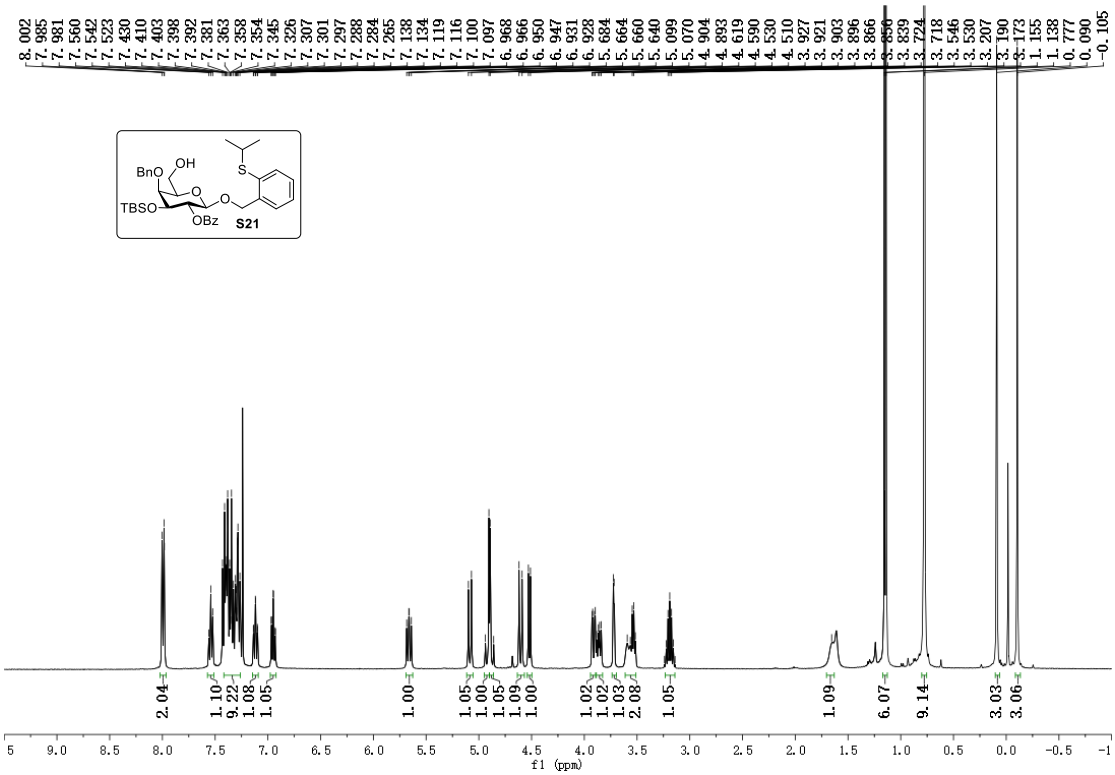

Figure S118. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S21**

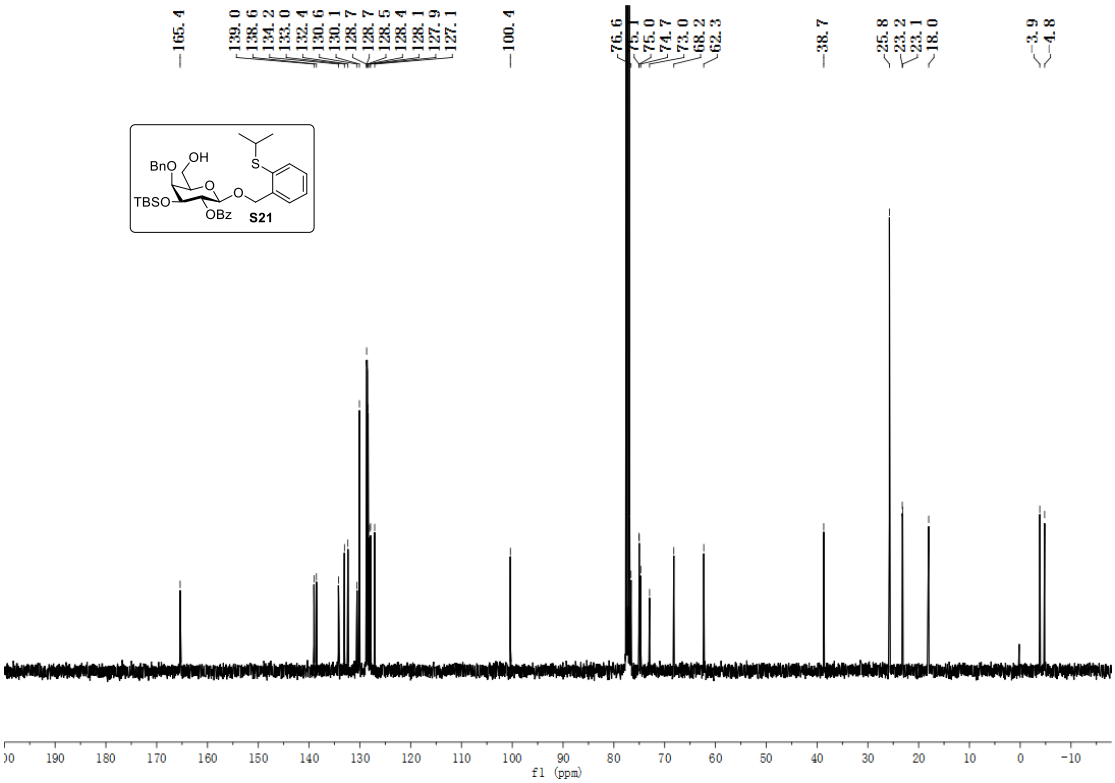

Figure S119. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **S21**

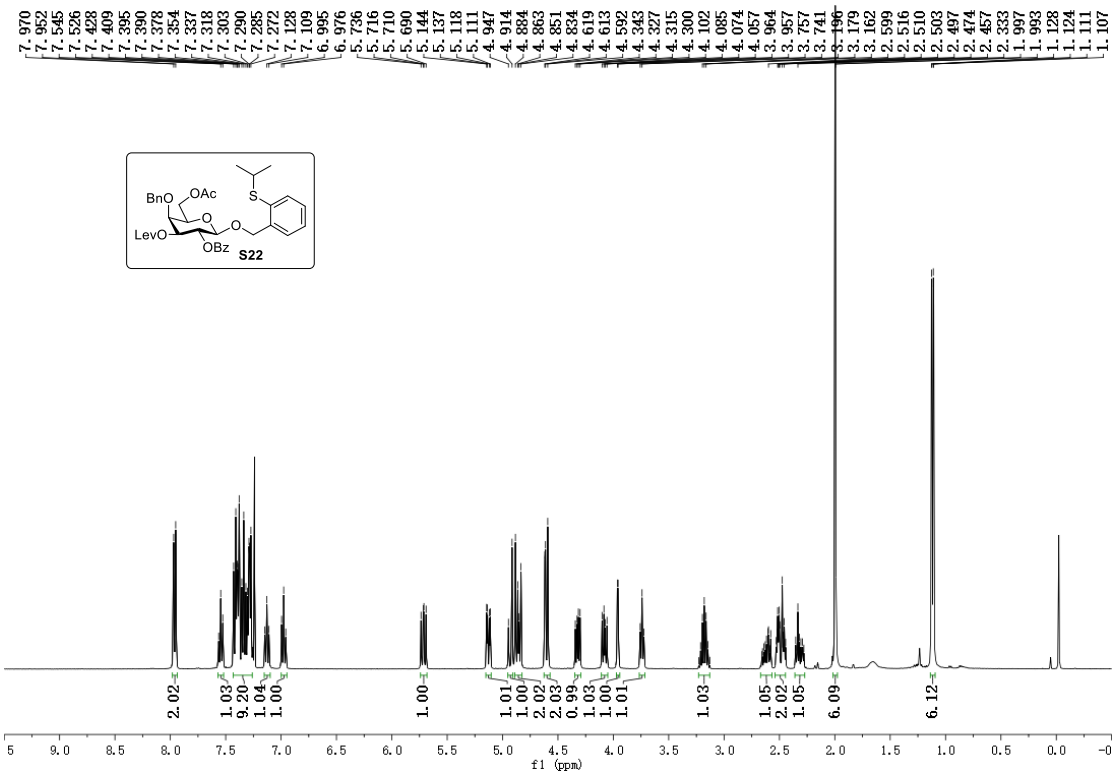

Figure S120. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S22**

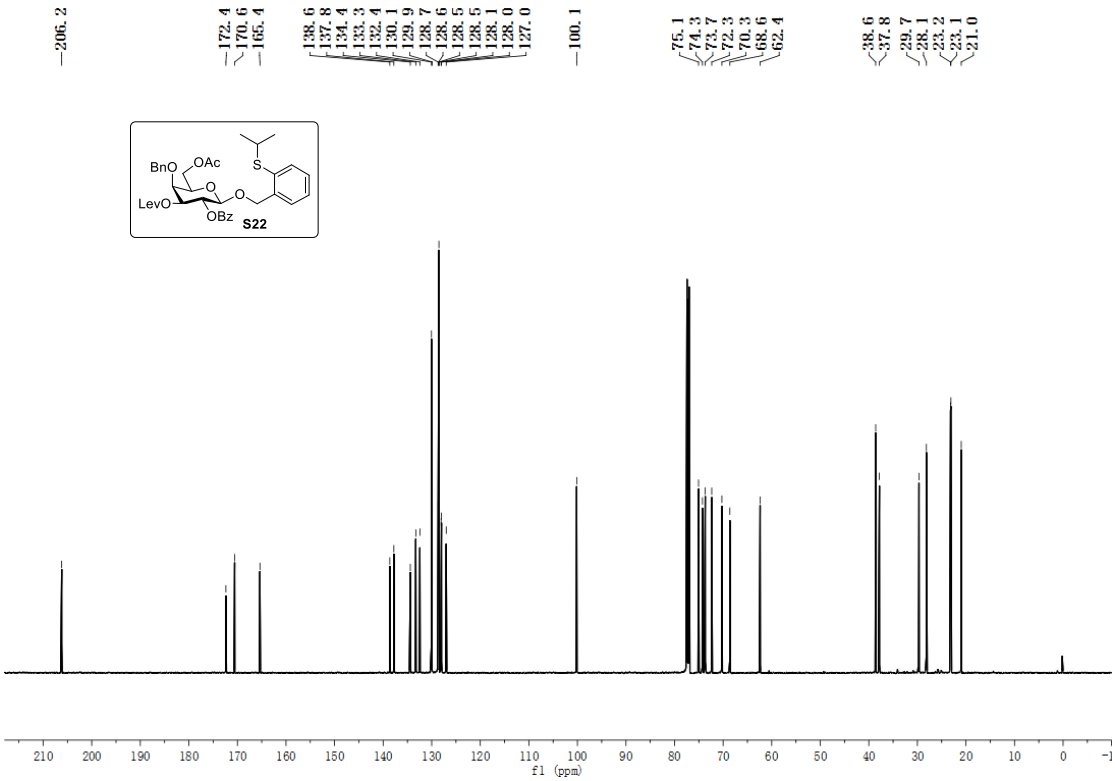

Figure S121. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **S22**

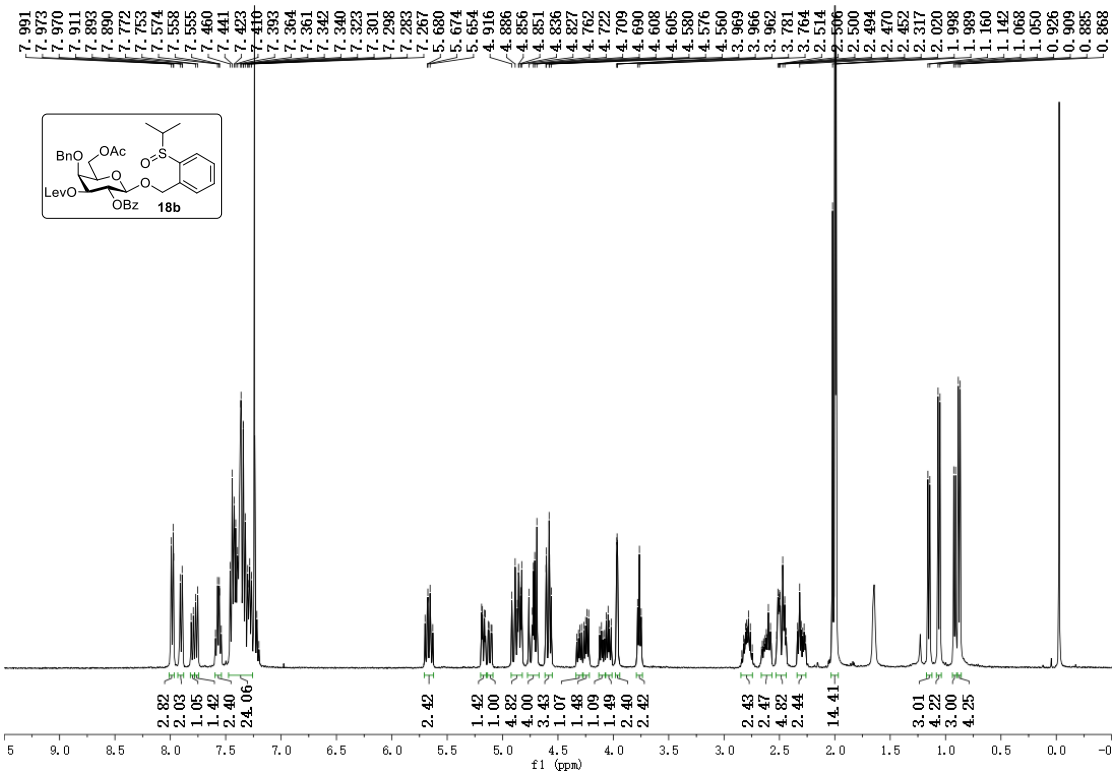

Figure S122. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **18b**

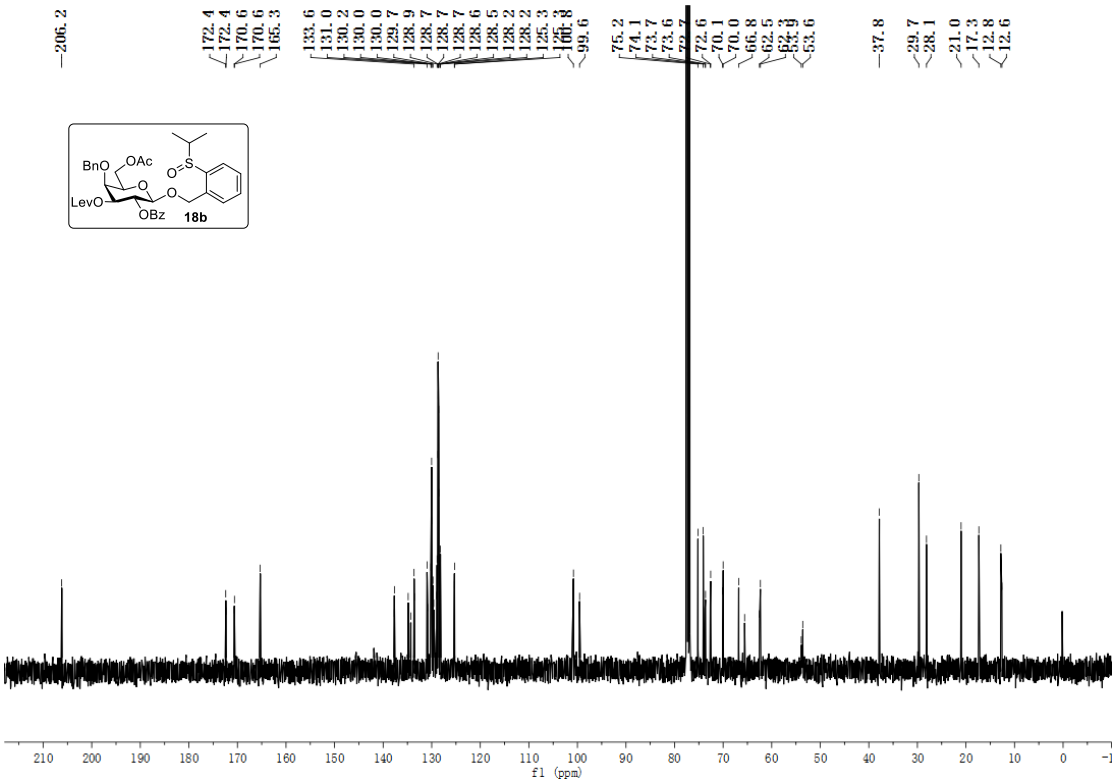

Figure S123. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **18b**

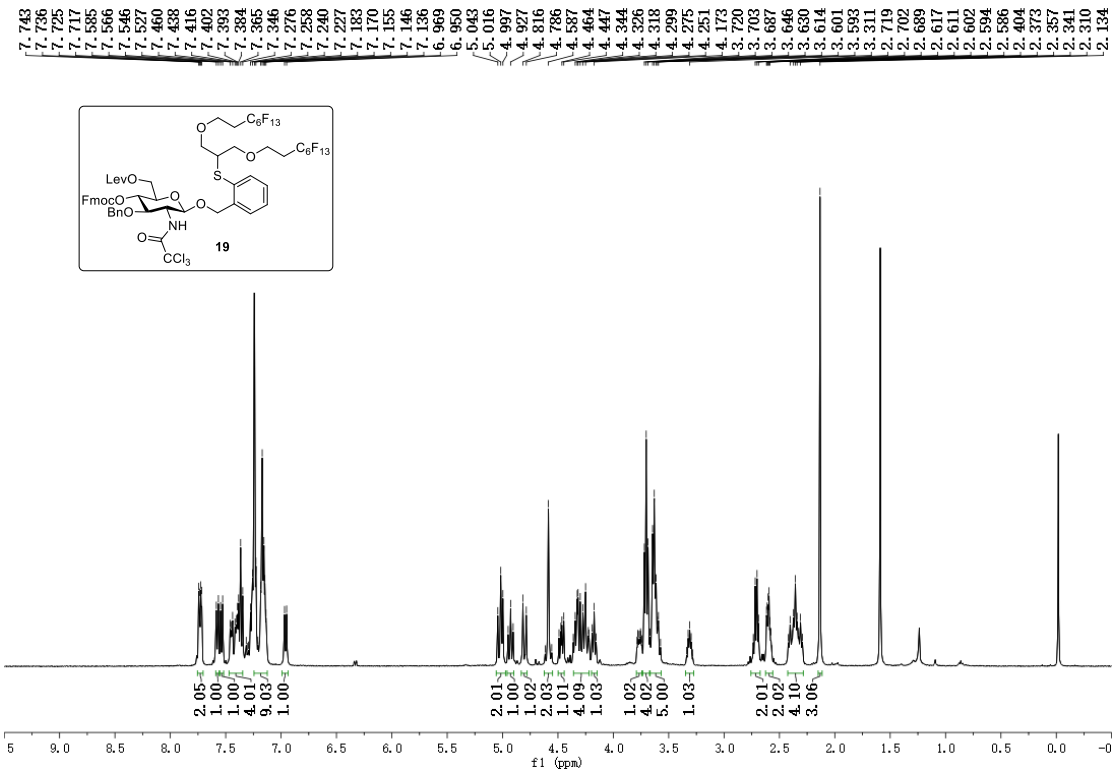

Figure S124. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **19**

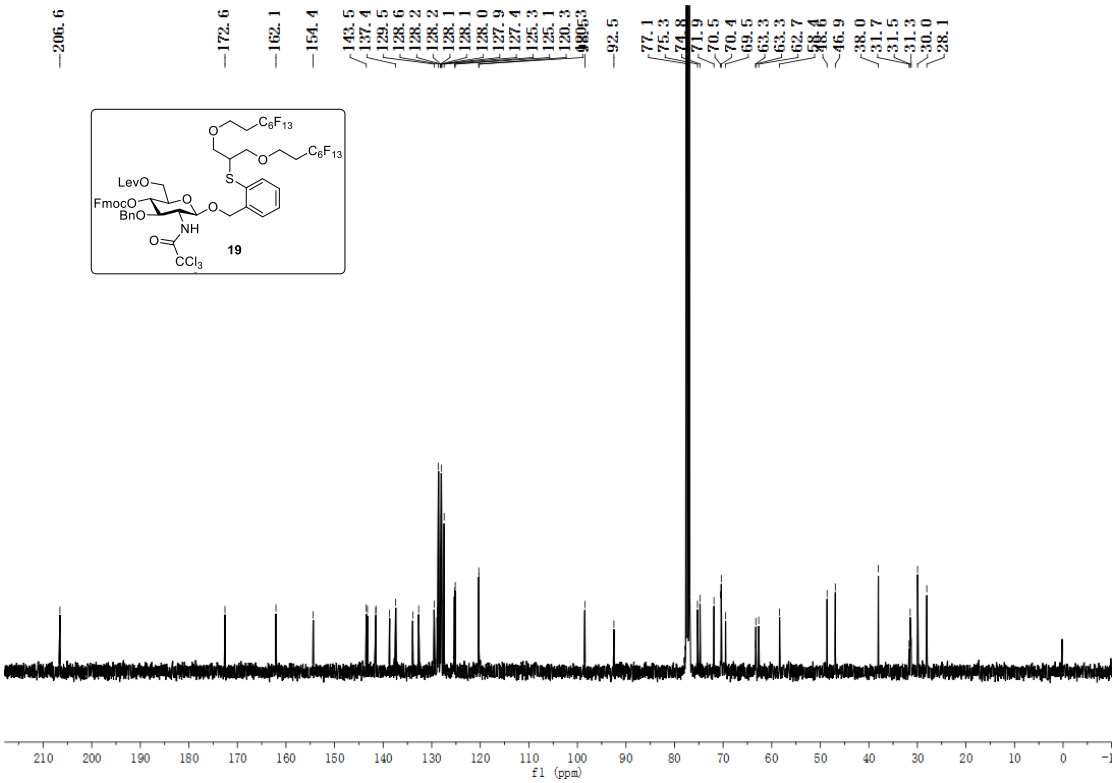

Figure S125. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **19**

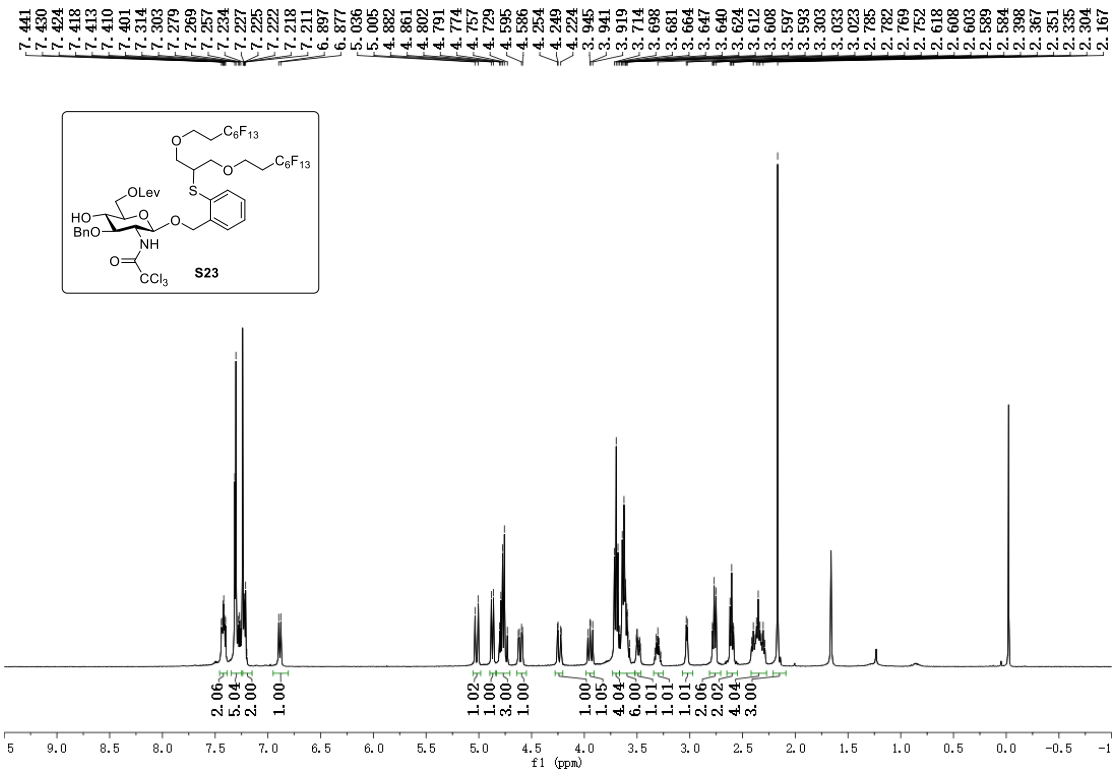

Figure S126. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S23**

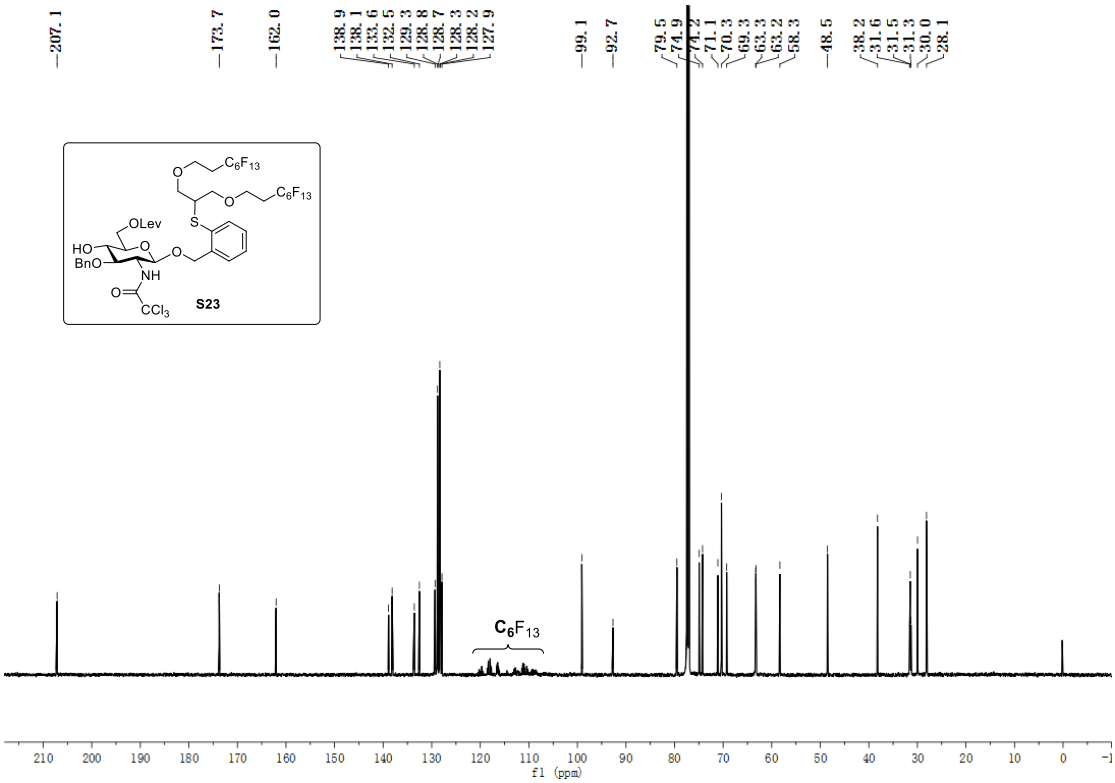

Figure S127. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **S23**

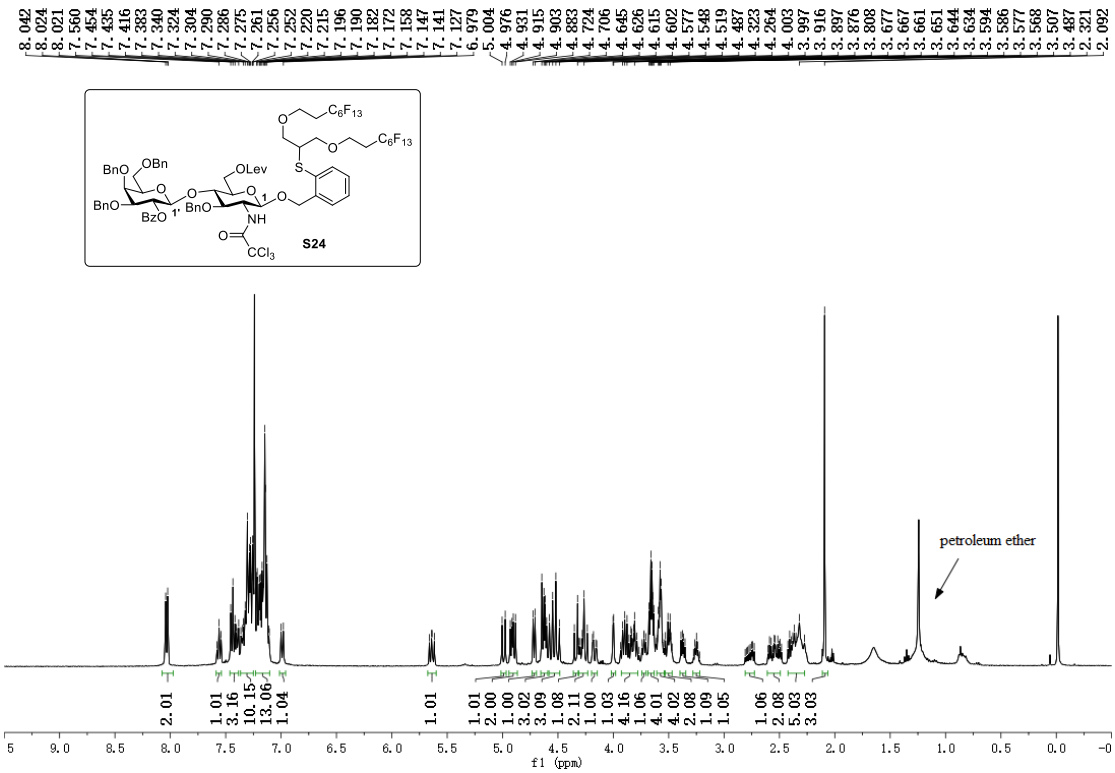

Figure S128. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S24**

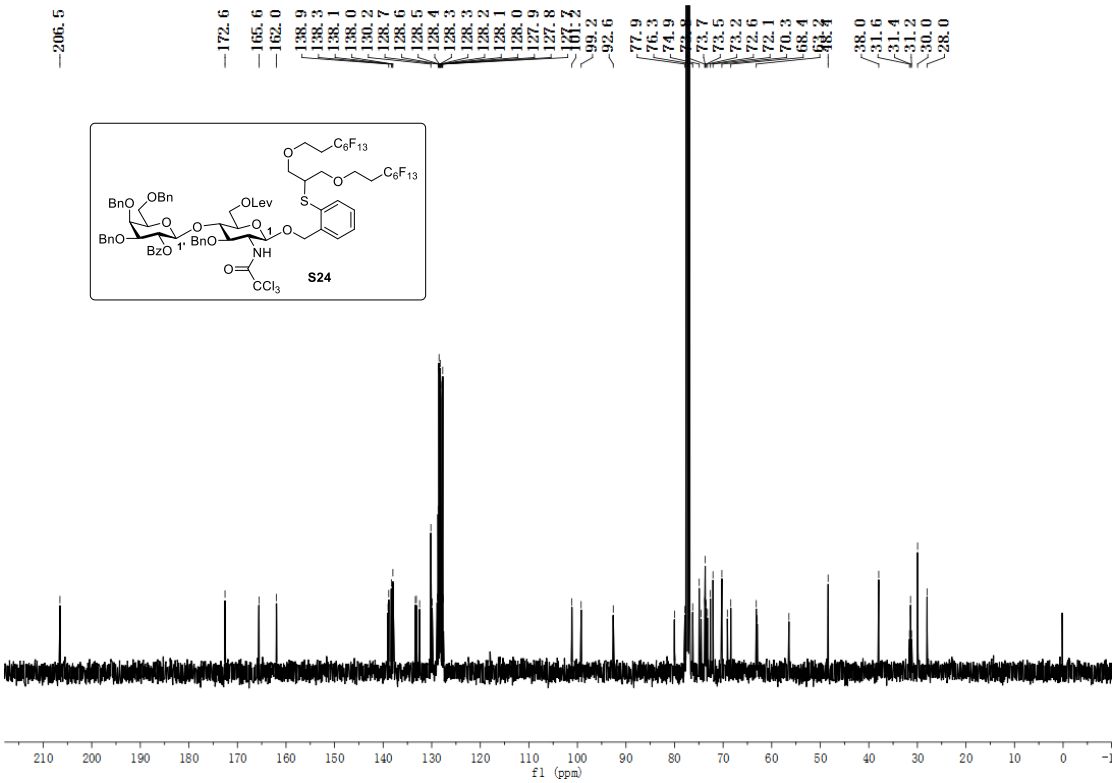

Figure S129. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **S24**

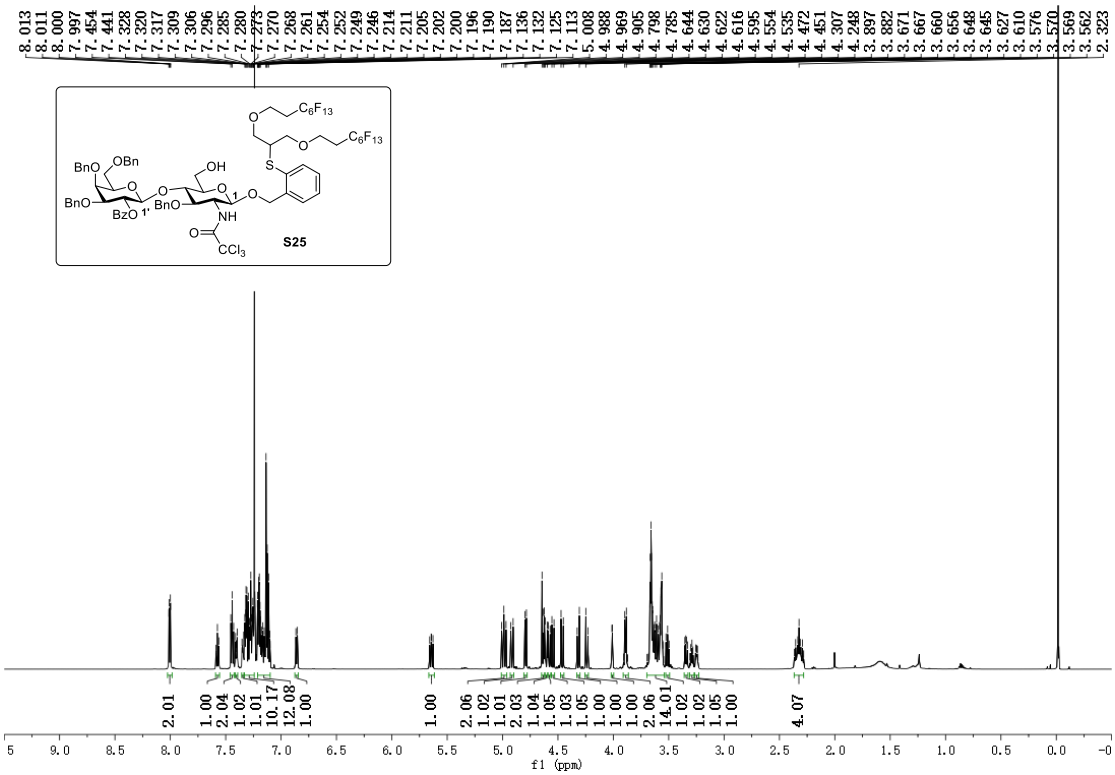

Figure S130. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **S25**

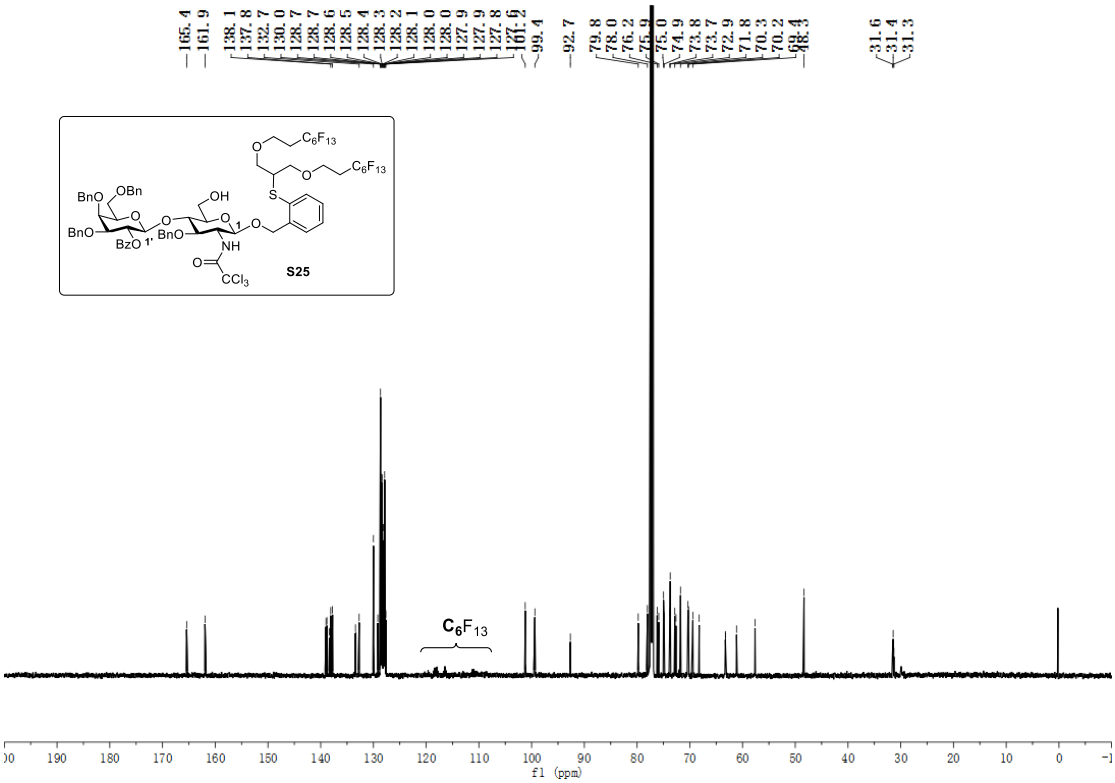

Figure S131. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **S25**

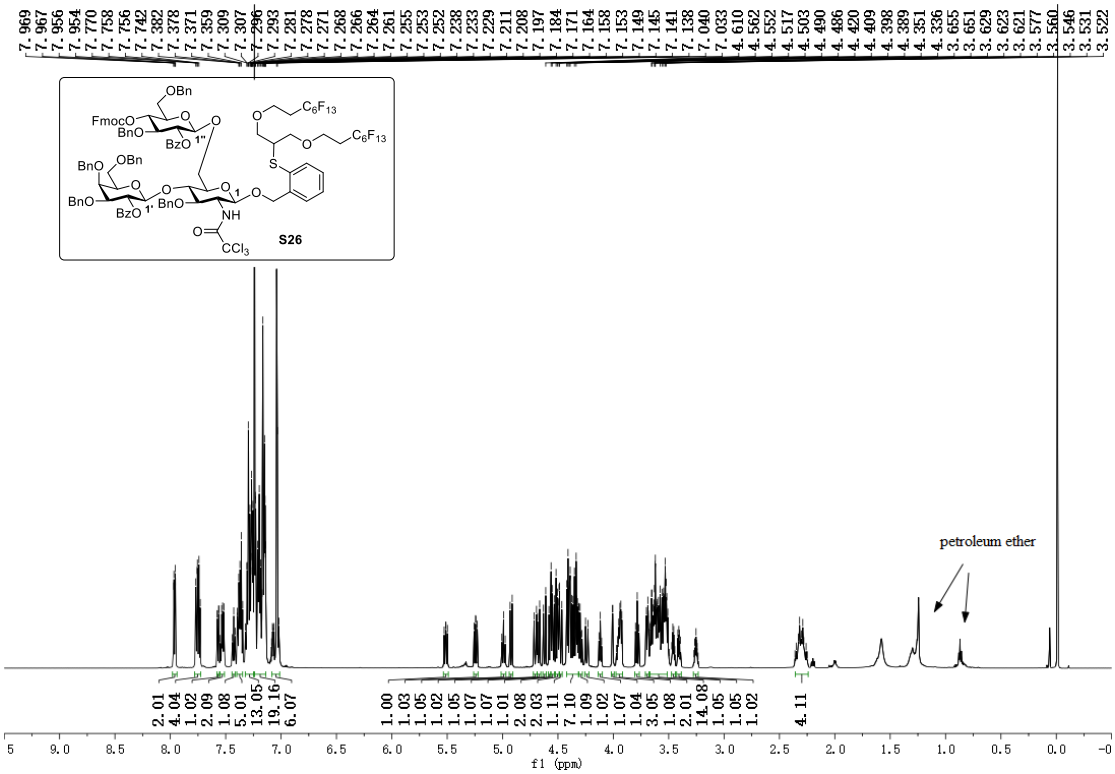

Figure S132. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **S26**

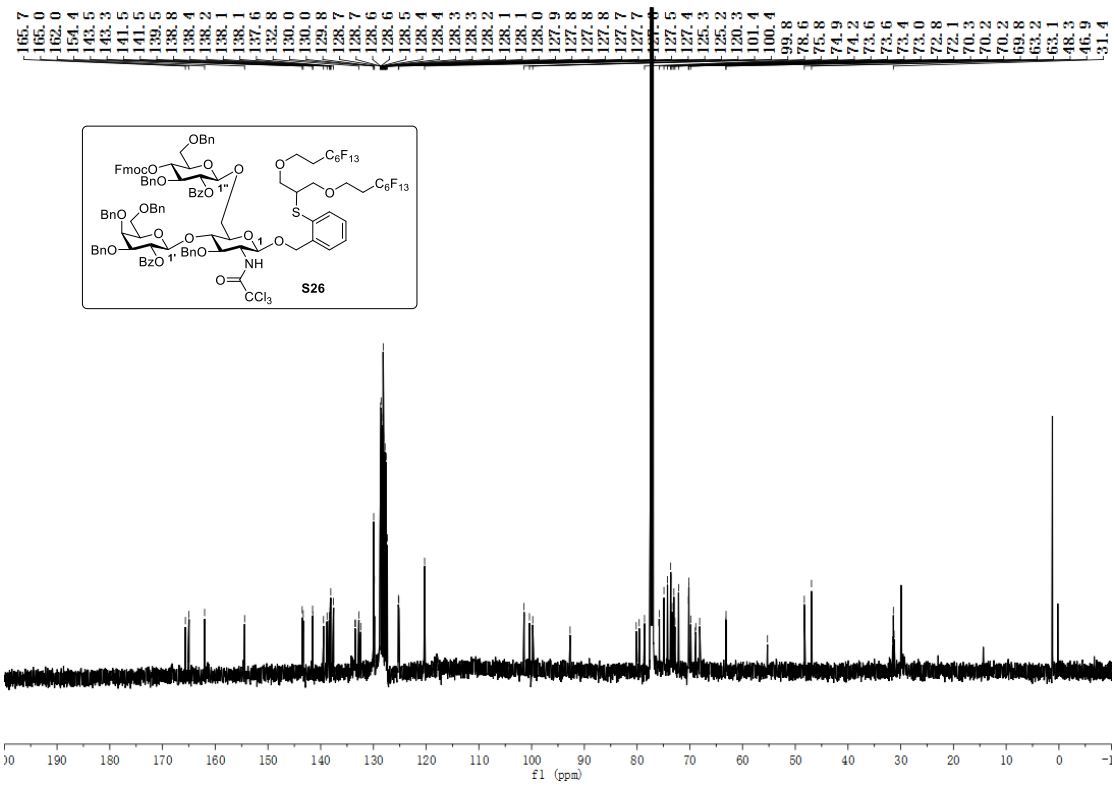

Figure S133. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **S26**

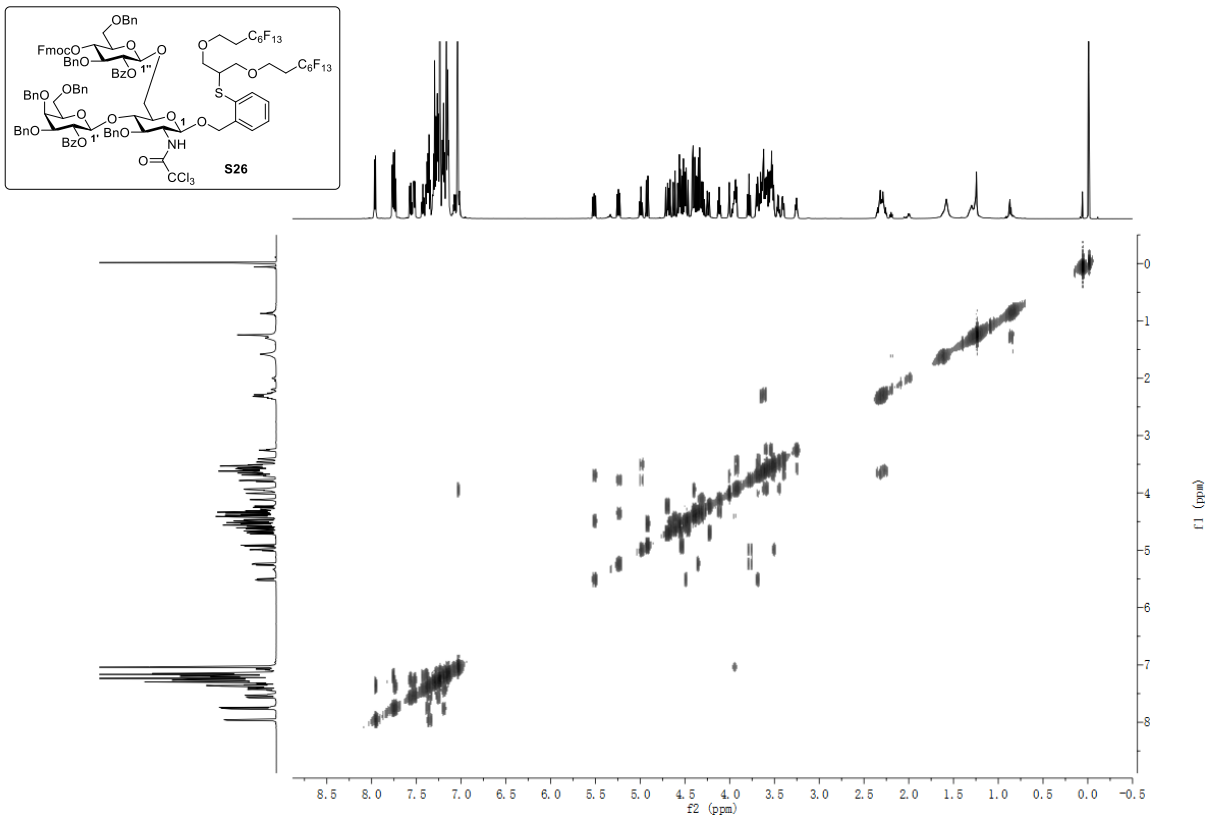

Figure S134. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **S26**

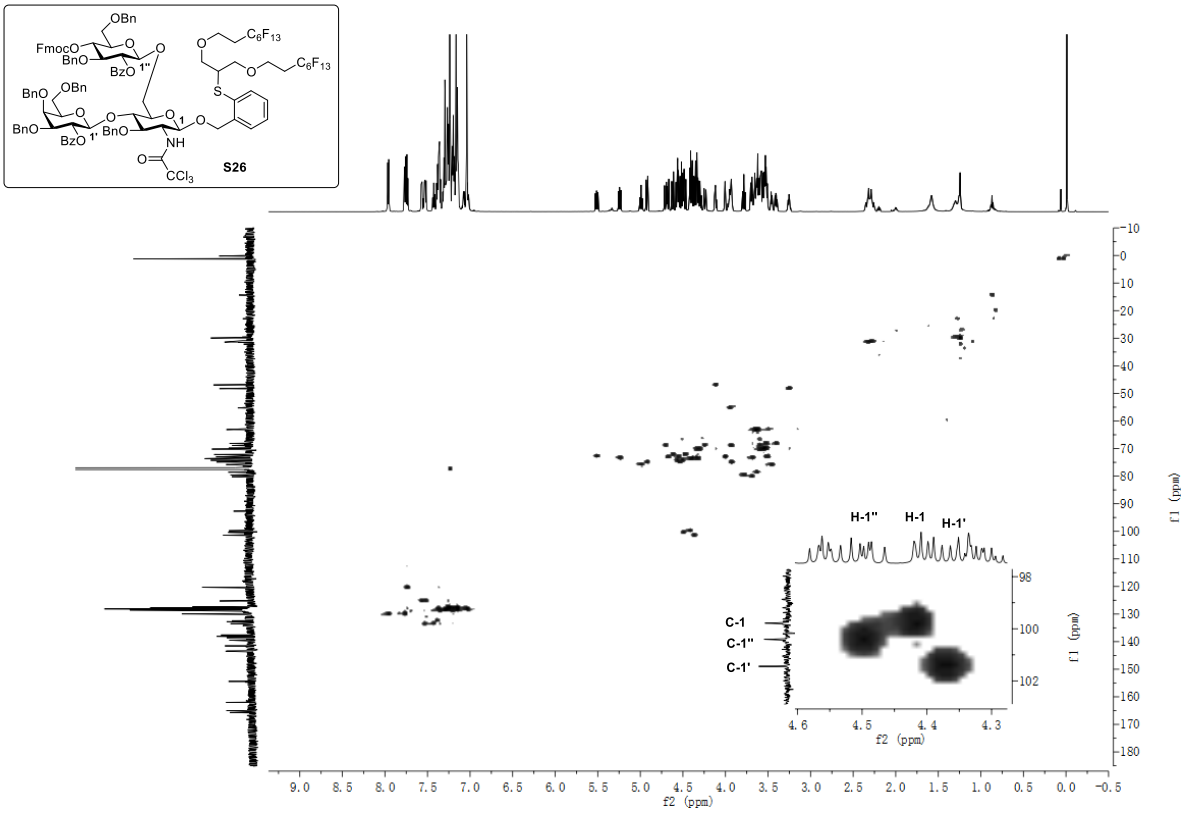

Figure S135. HSQC spectrum of **S26**

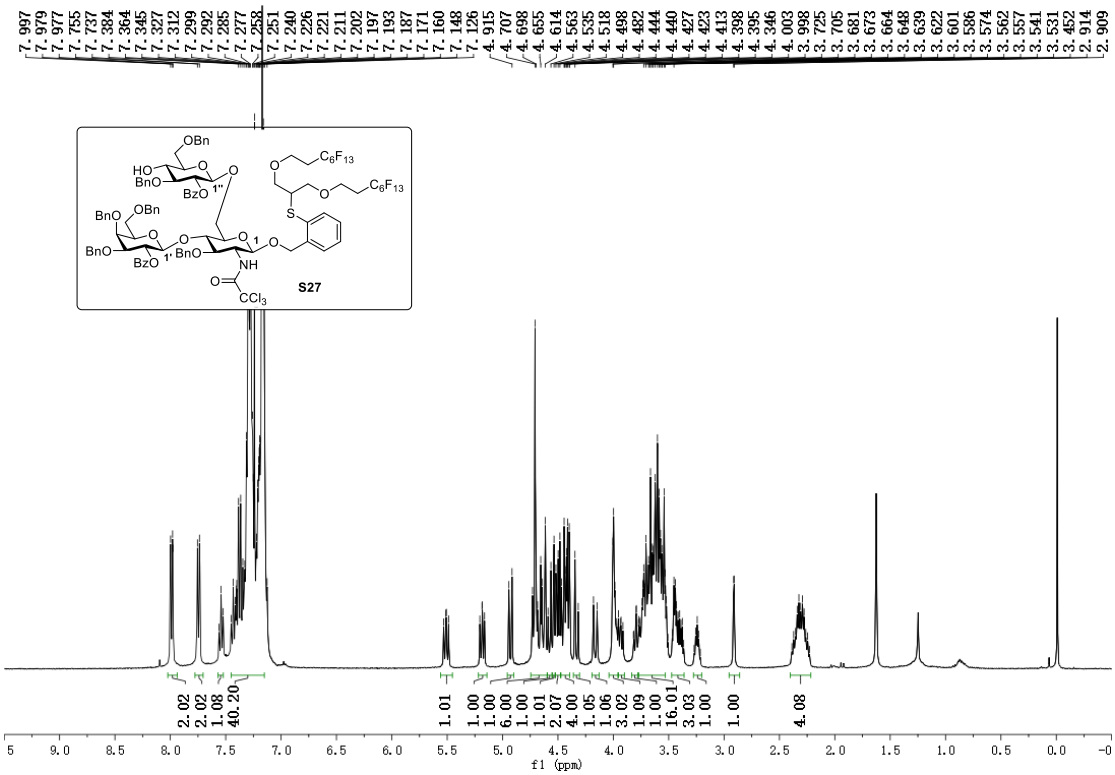

Figure S136. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S27**

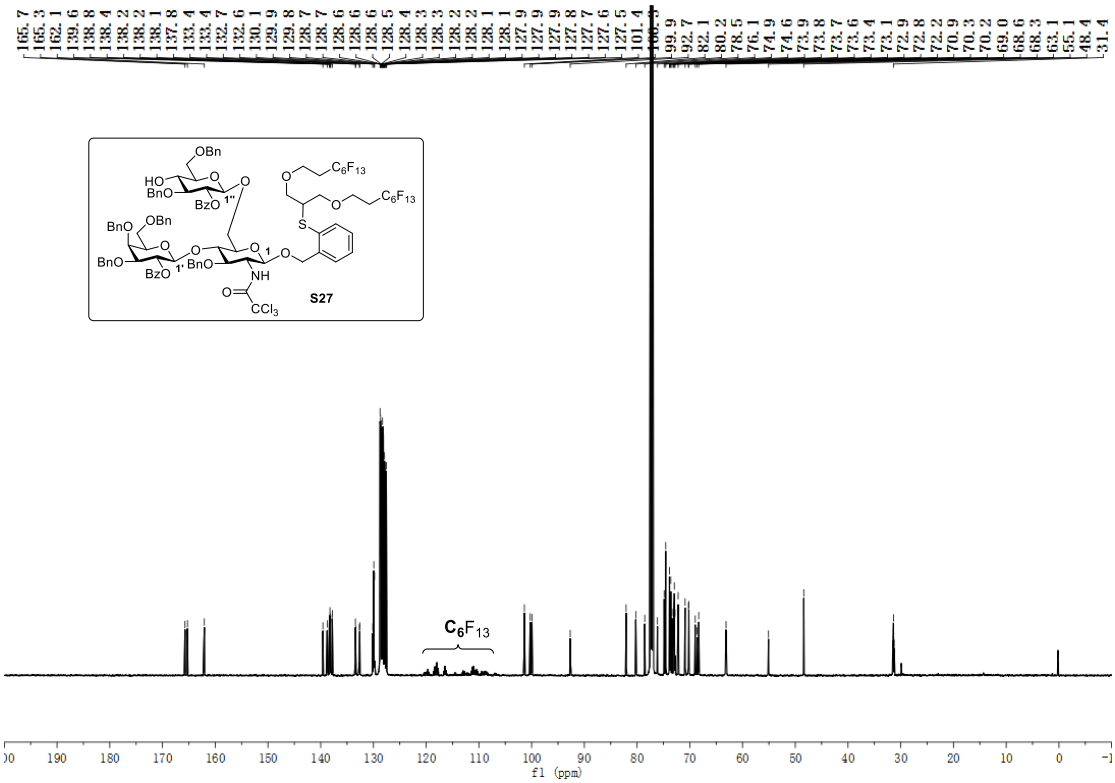

Figure S137. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **S27**

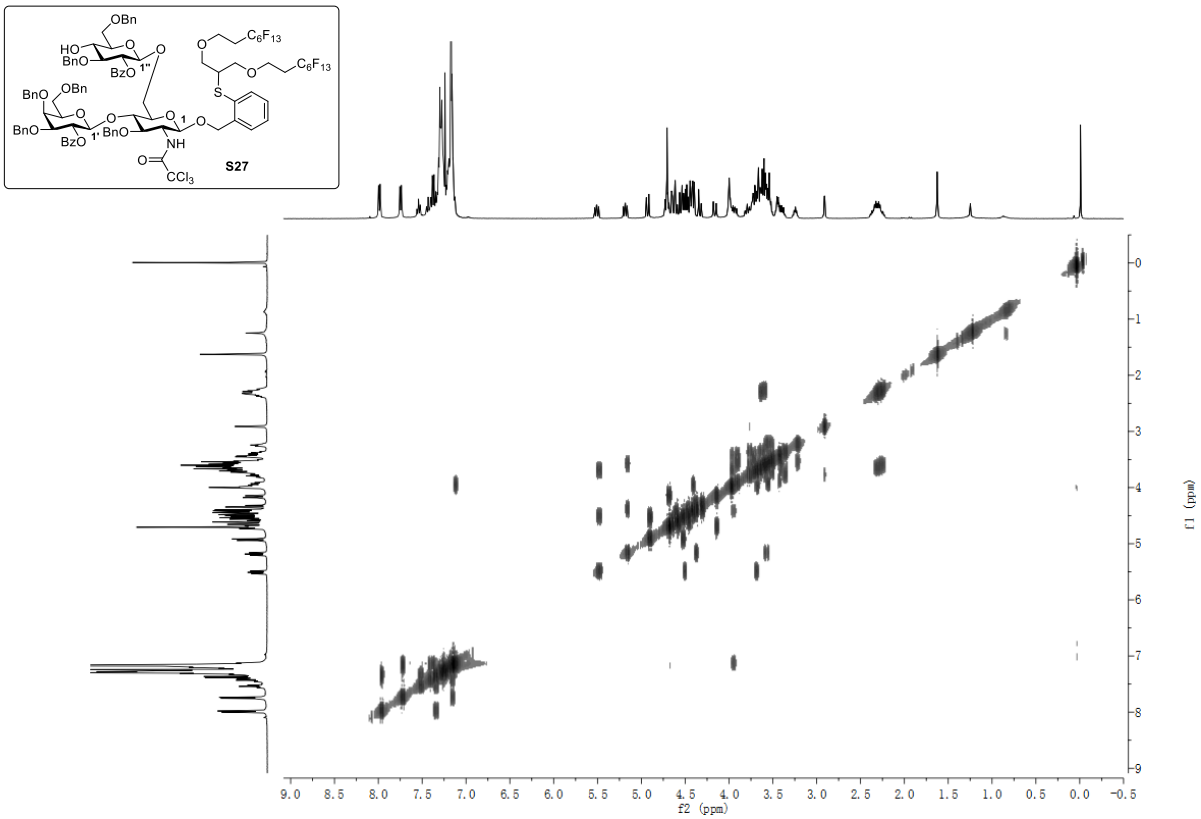

Figure S138. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **S27**

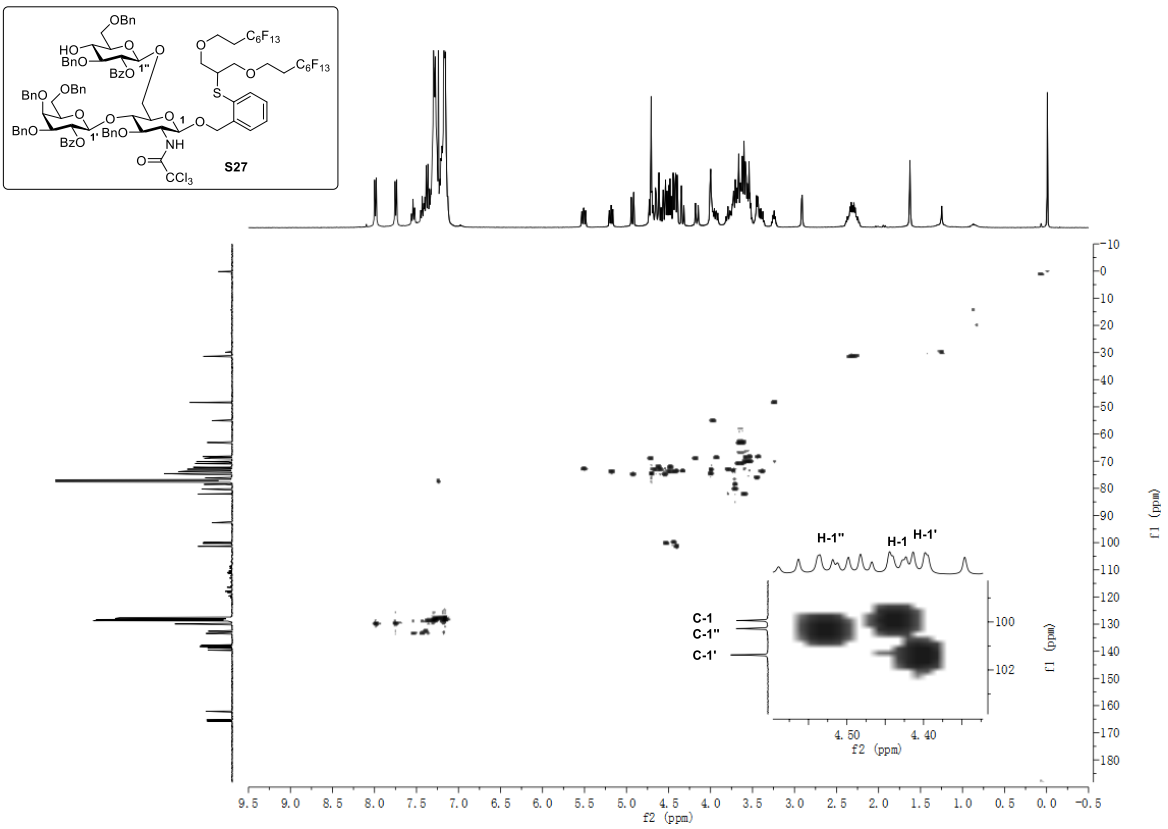

Figure S139. HSQC spectrum of **S27**

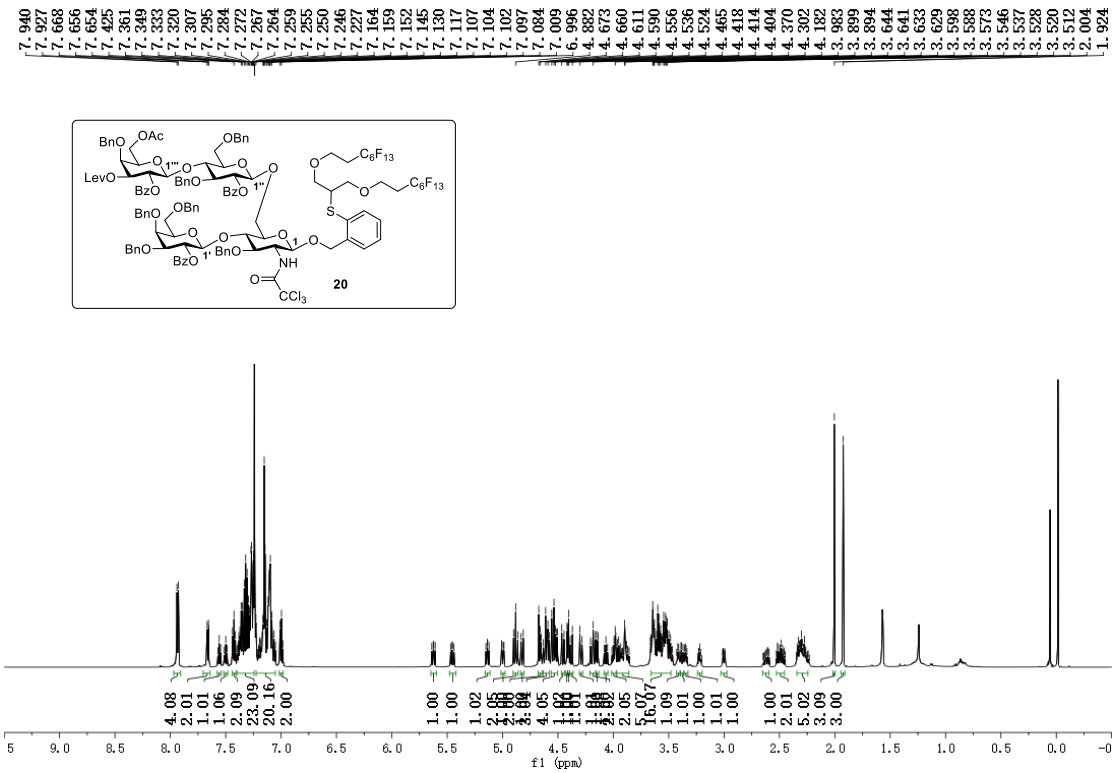

Figure S140. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **20**

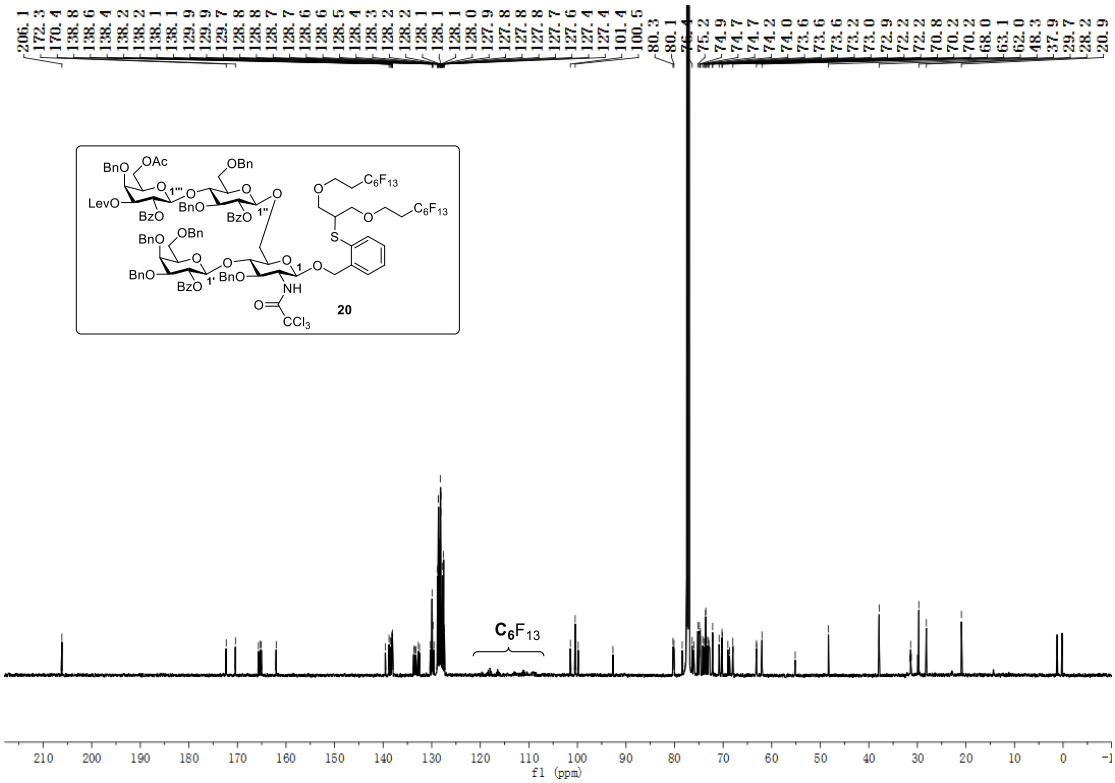

Figure S141. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **20**

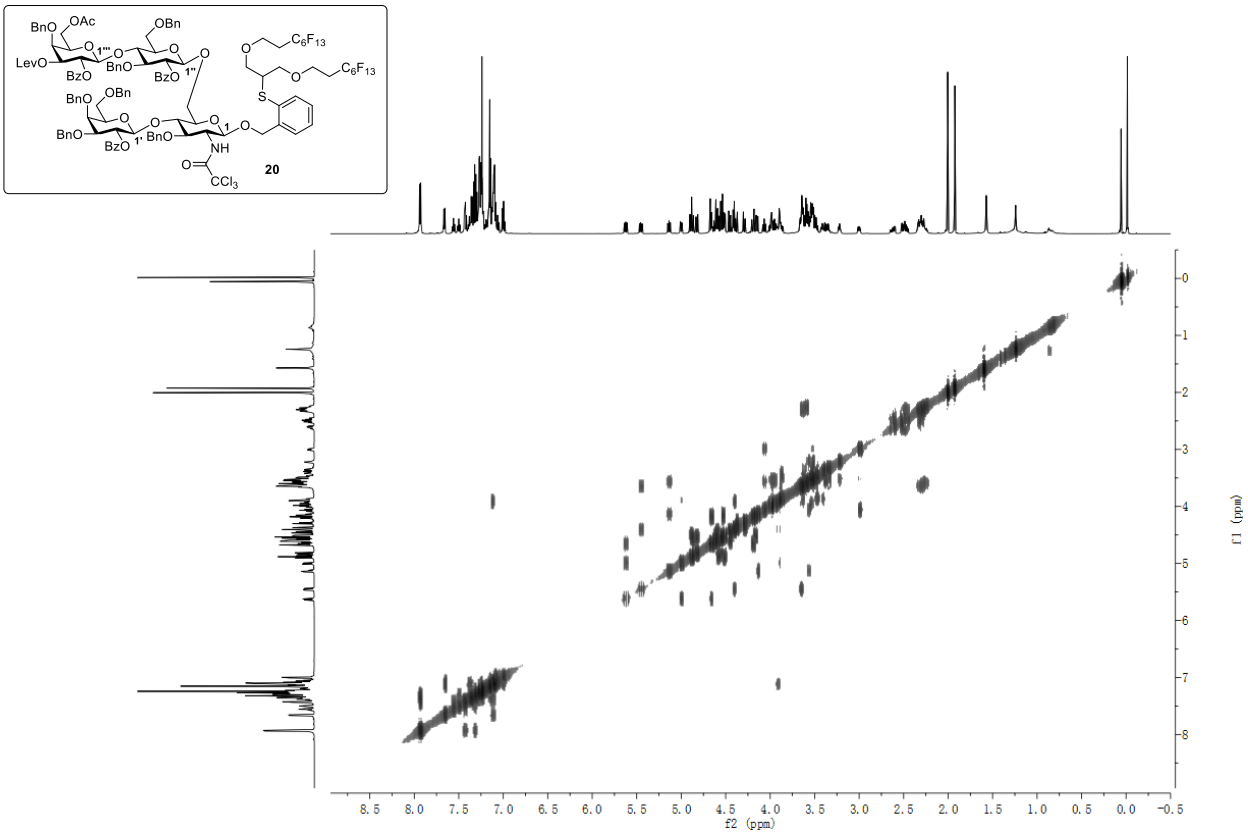

Figure S142. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **20**

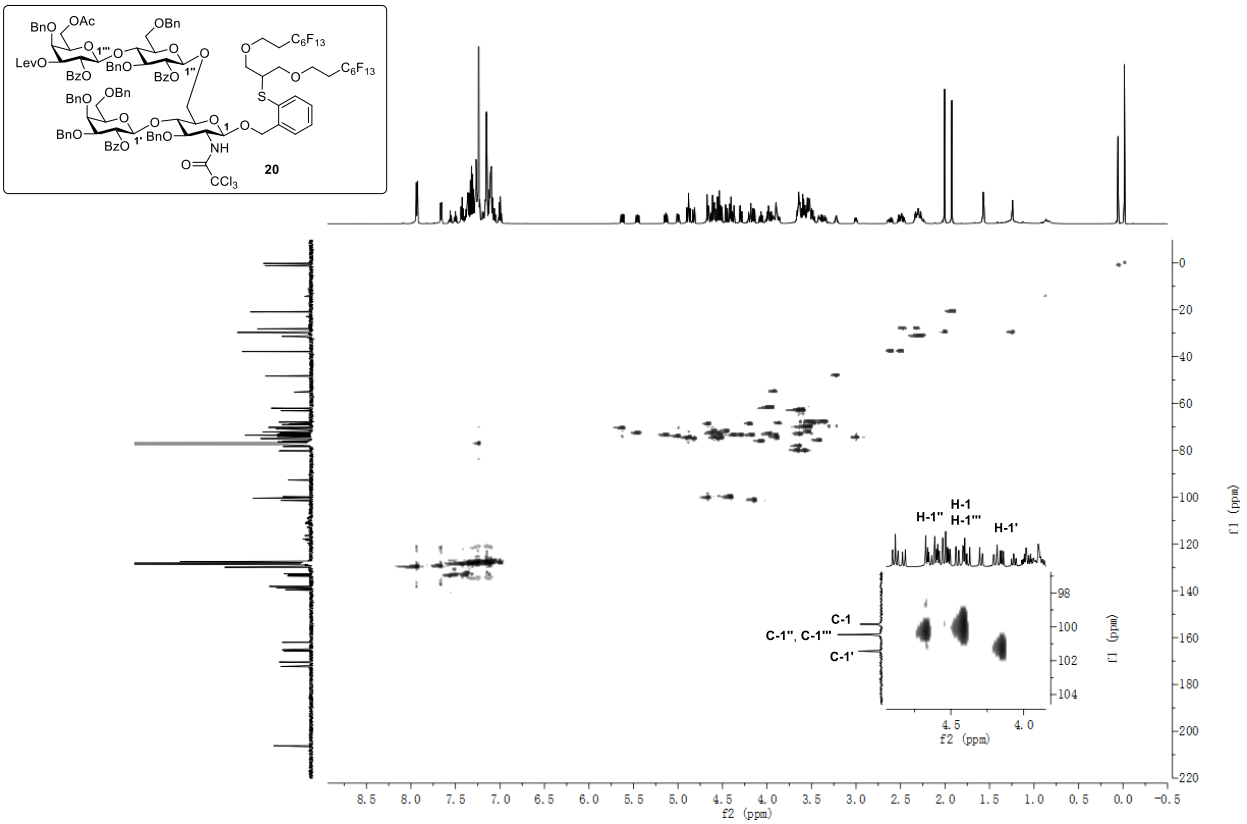

Figure S143. HSQC spectrum of **20**

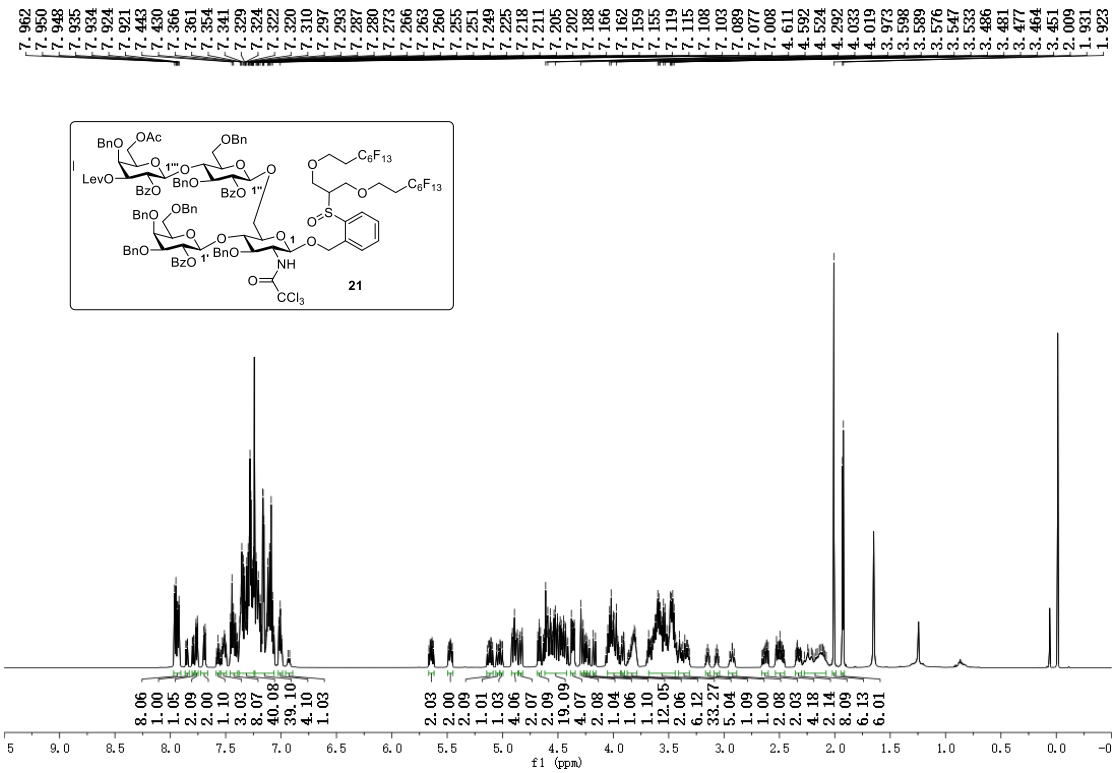

Figure S144. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **21**

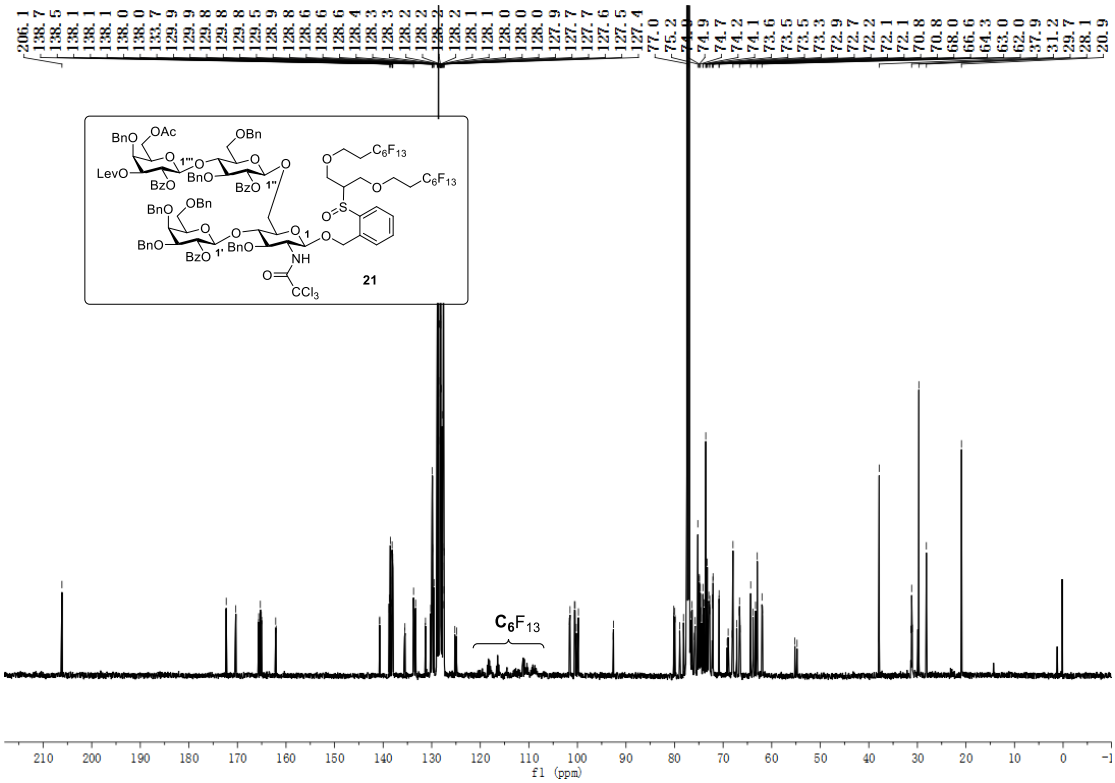

Figure S145. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **21**

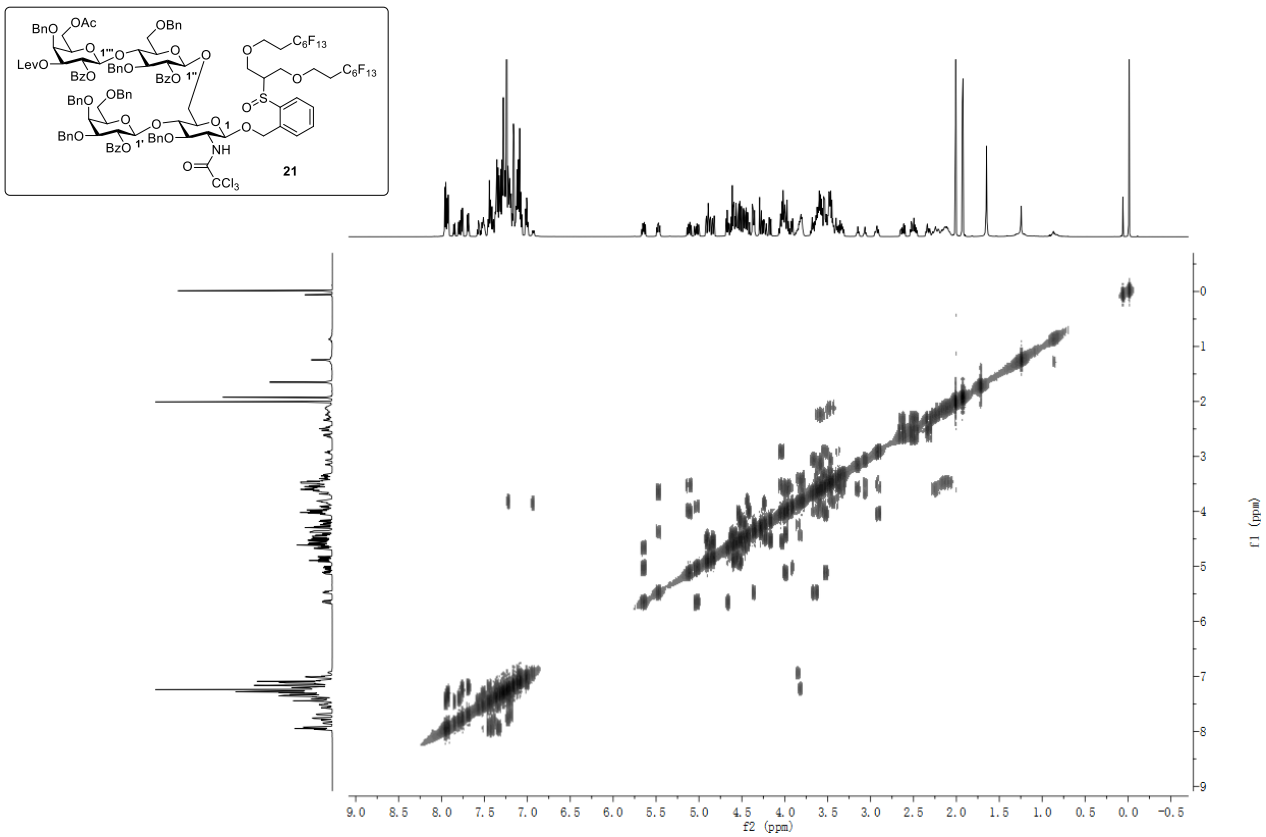

Figure S146. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **21**

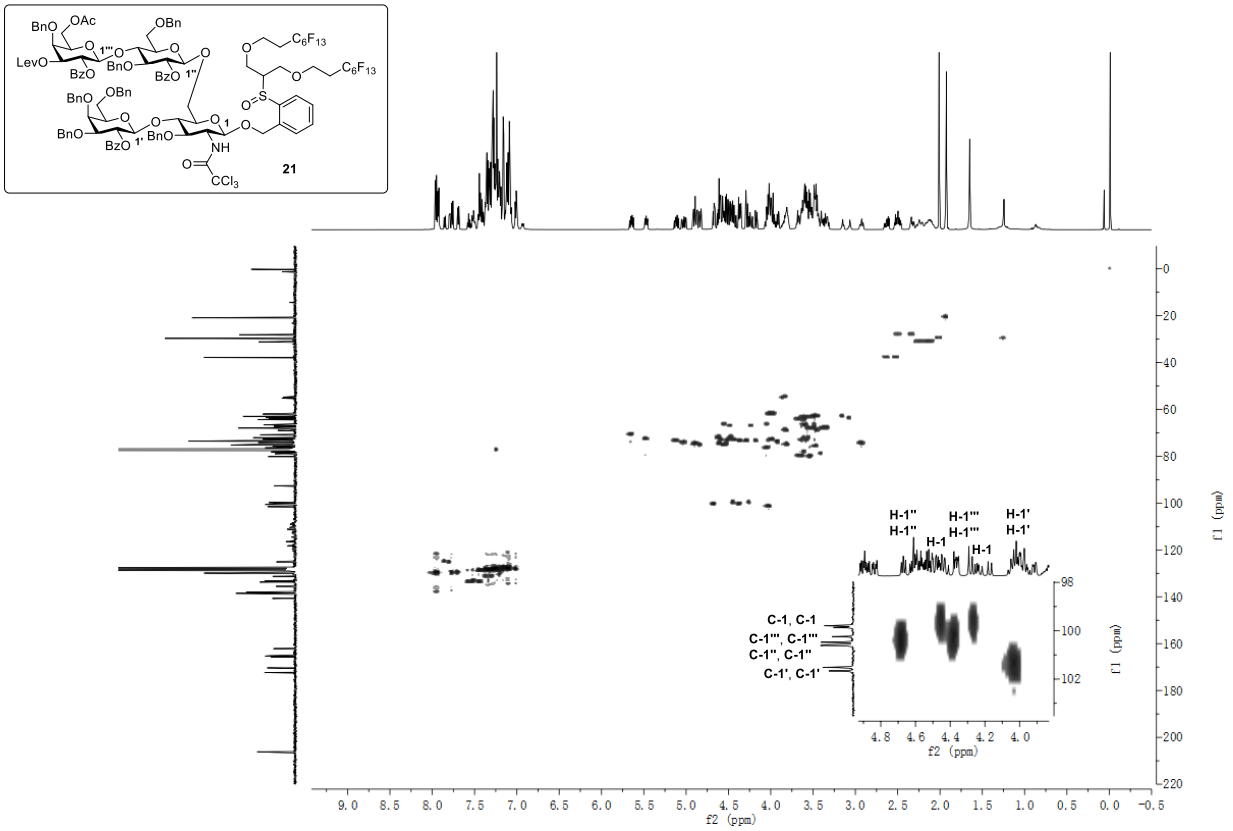

Figure S147. HSQC spectrum of **21**

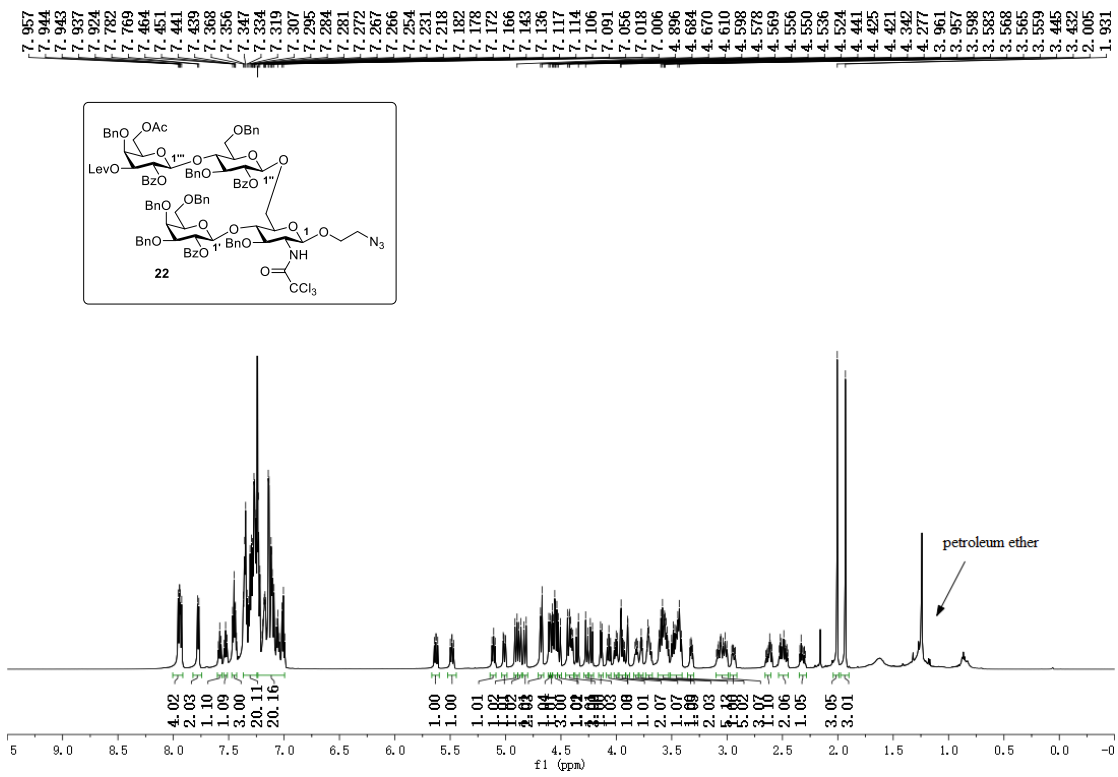

Figure S148. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **22**

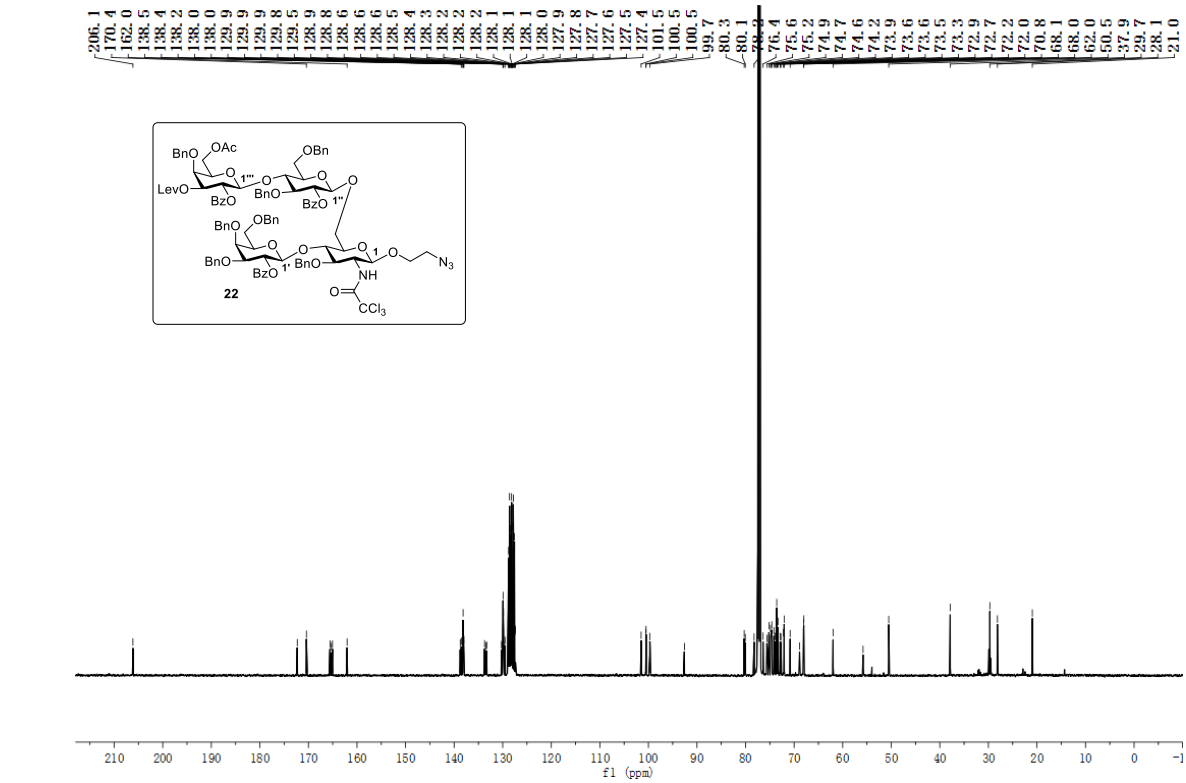

Figure S149. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **22**

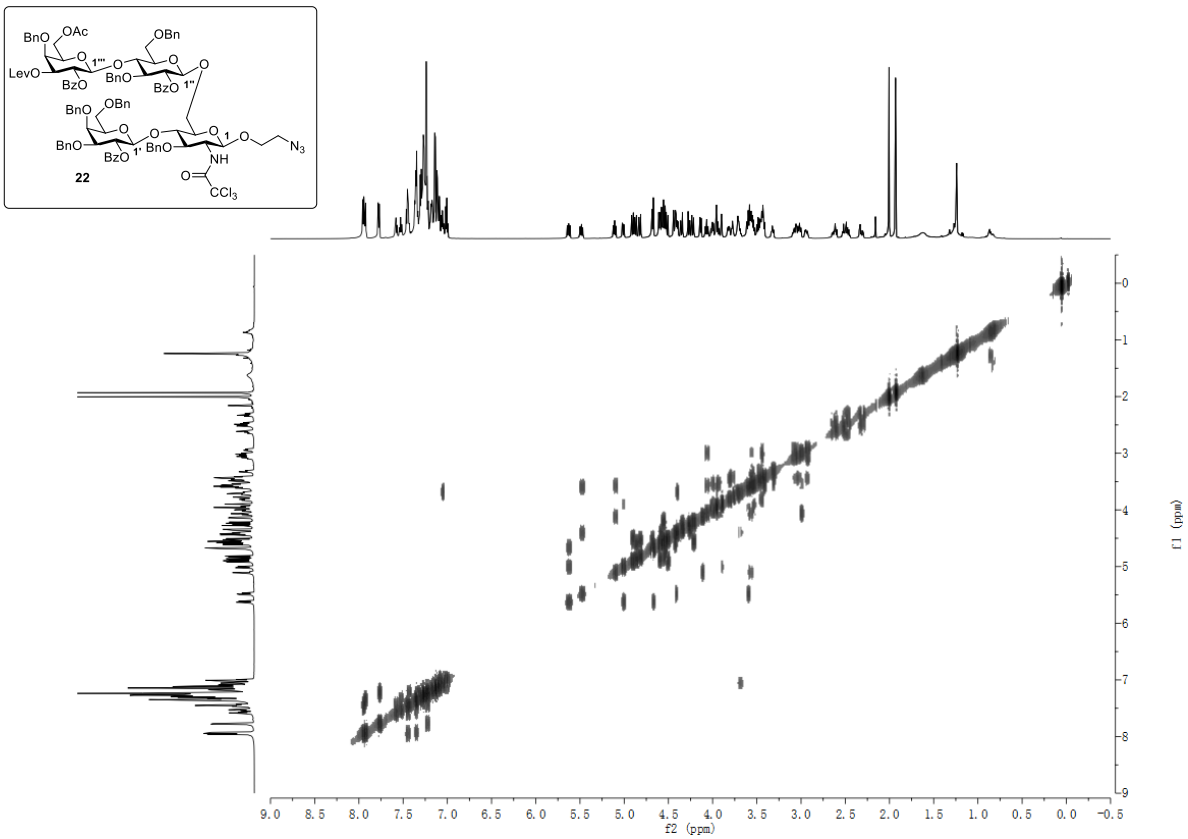

Figure S150. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **22**

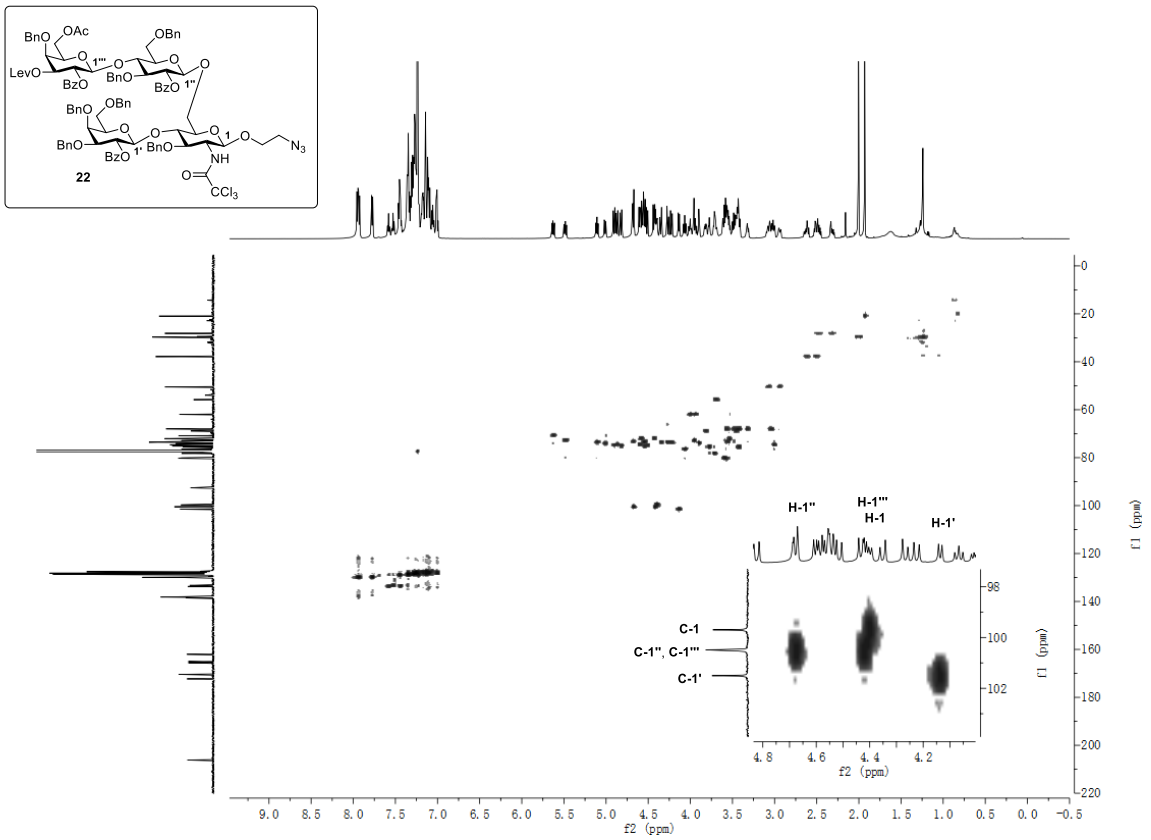

Figure S151. HSQC spectrum of **22**

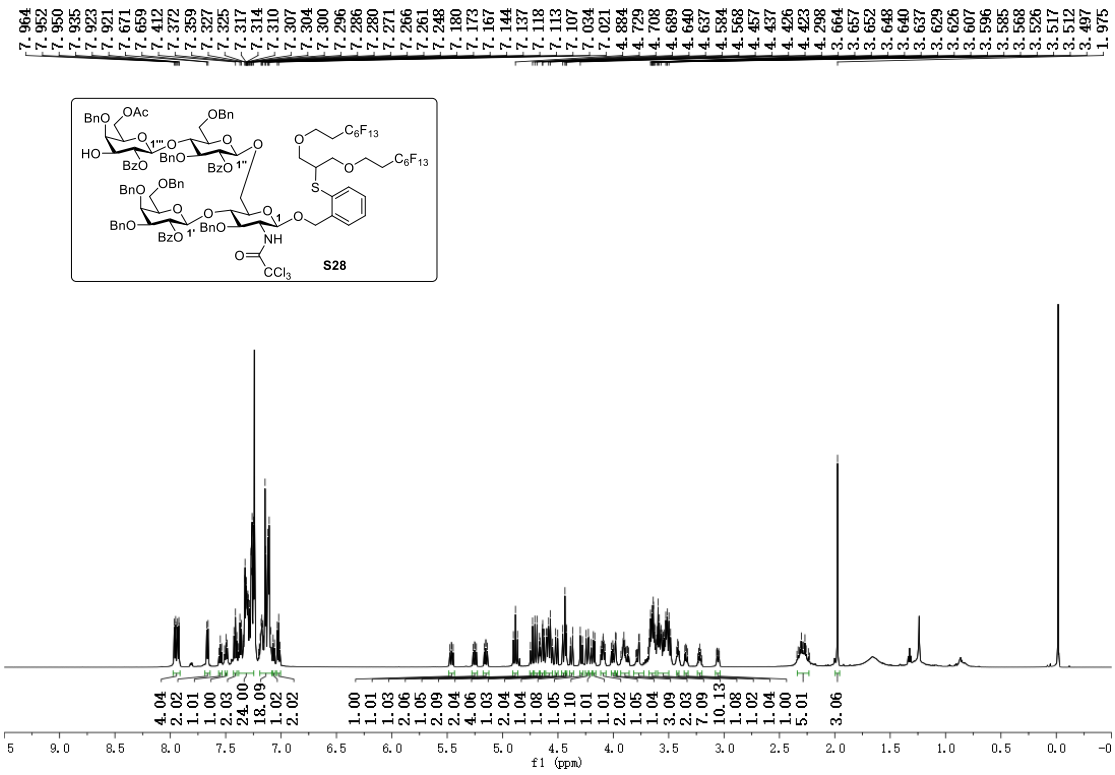

Figure S152. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **S28**

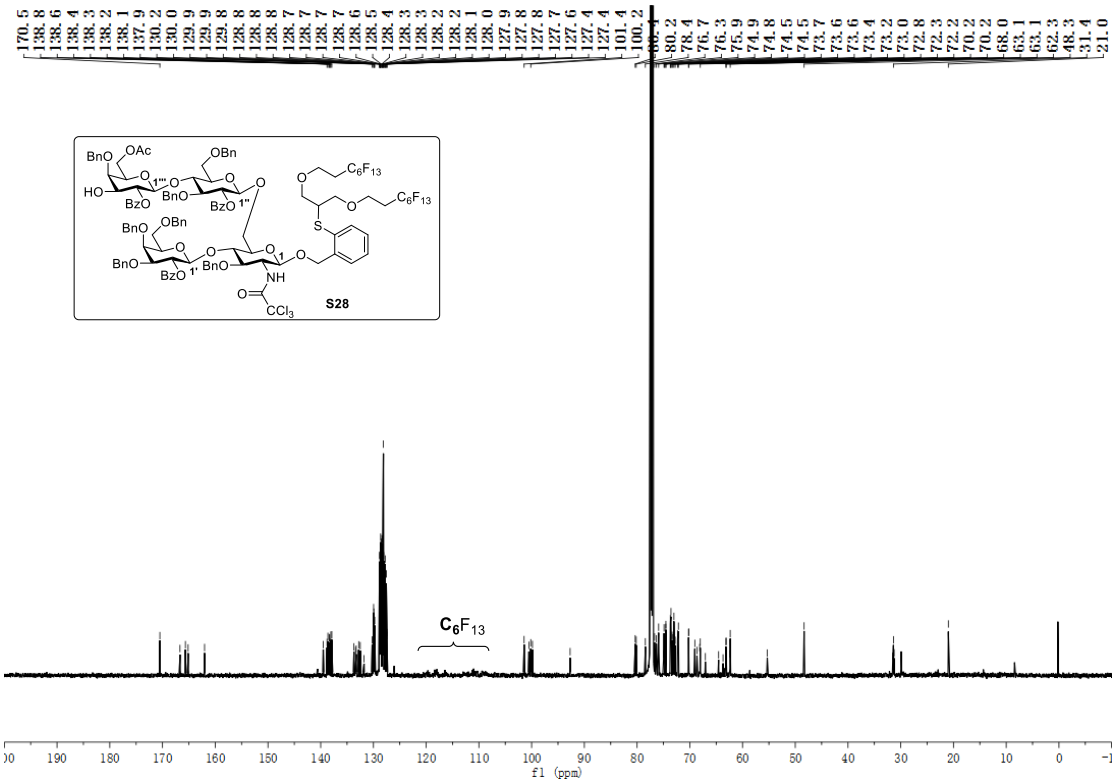

Figure S153. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **S28**

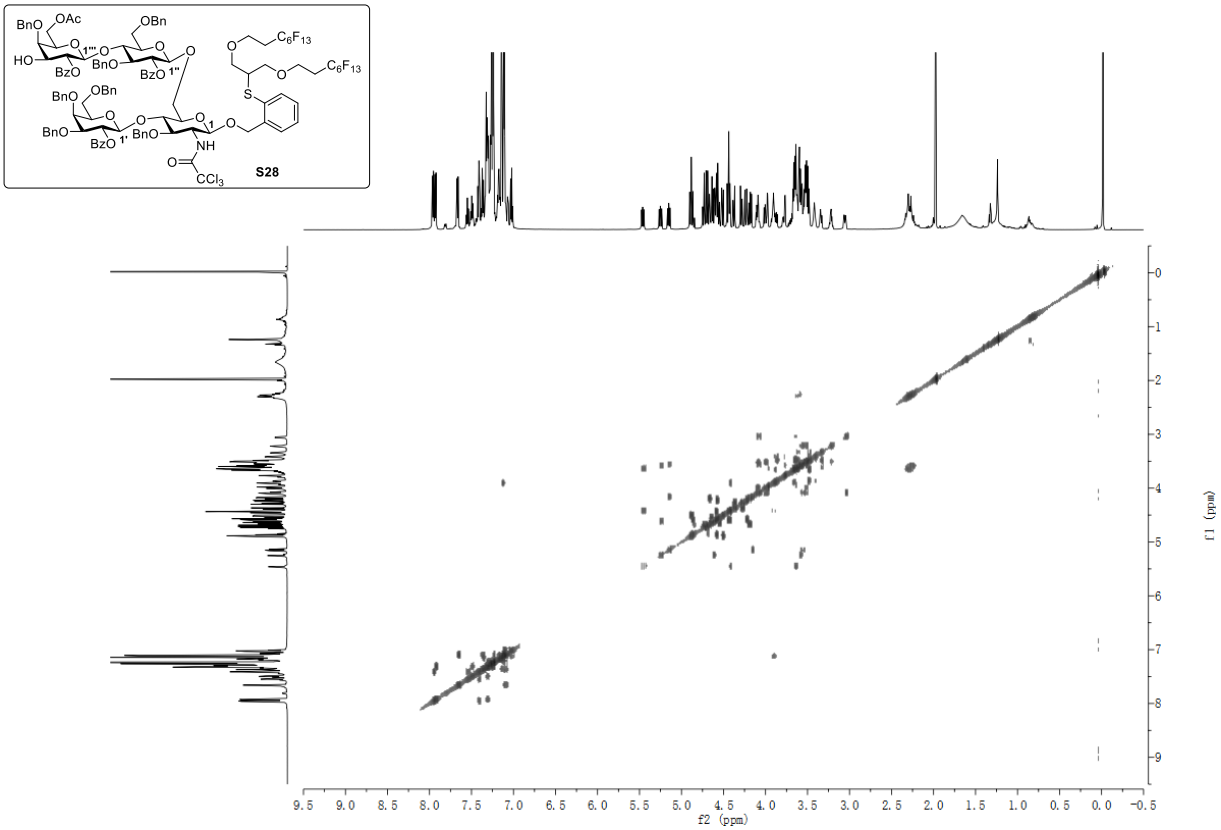

Figure S154. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **S28**

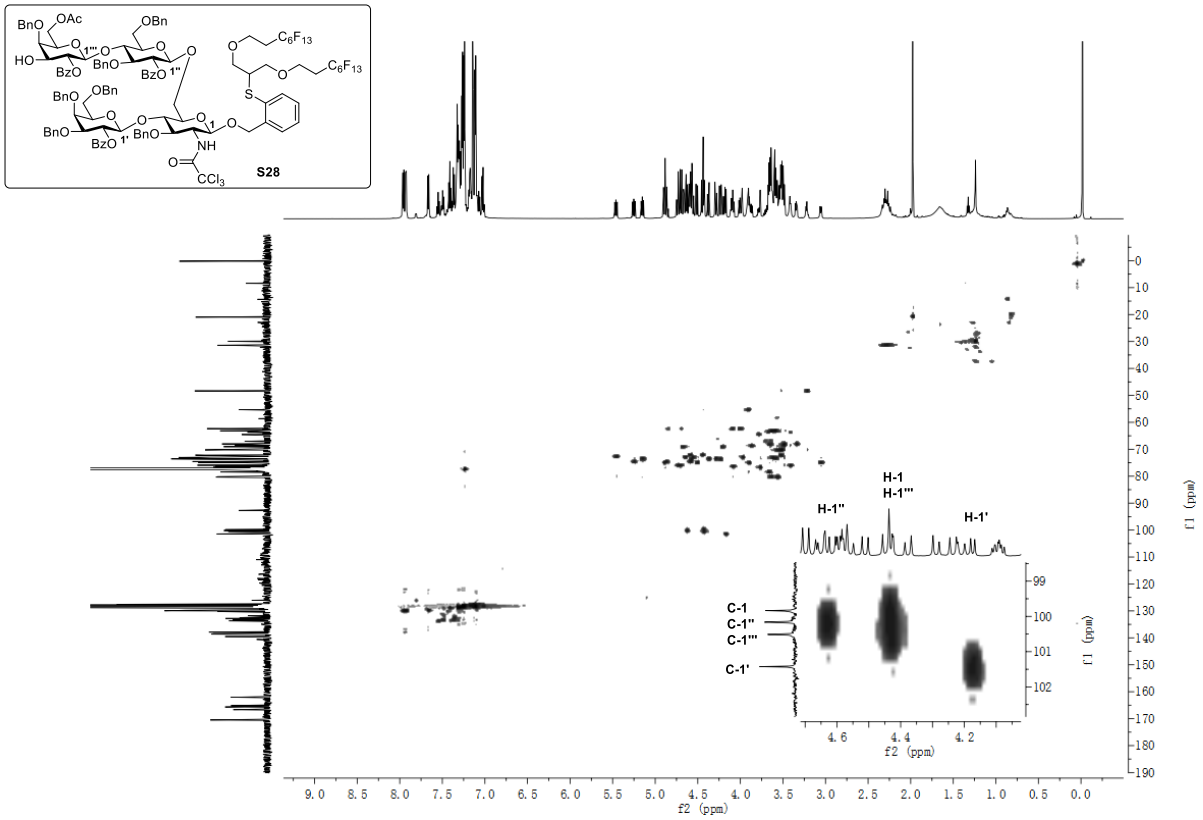

Figure S155. HSQC spectrum of **S28**

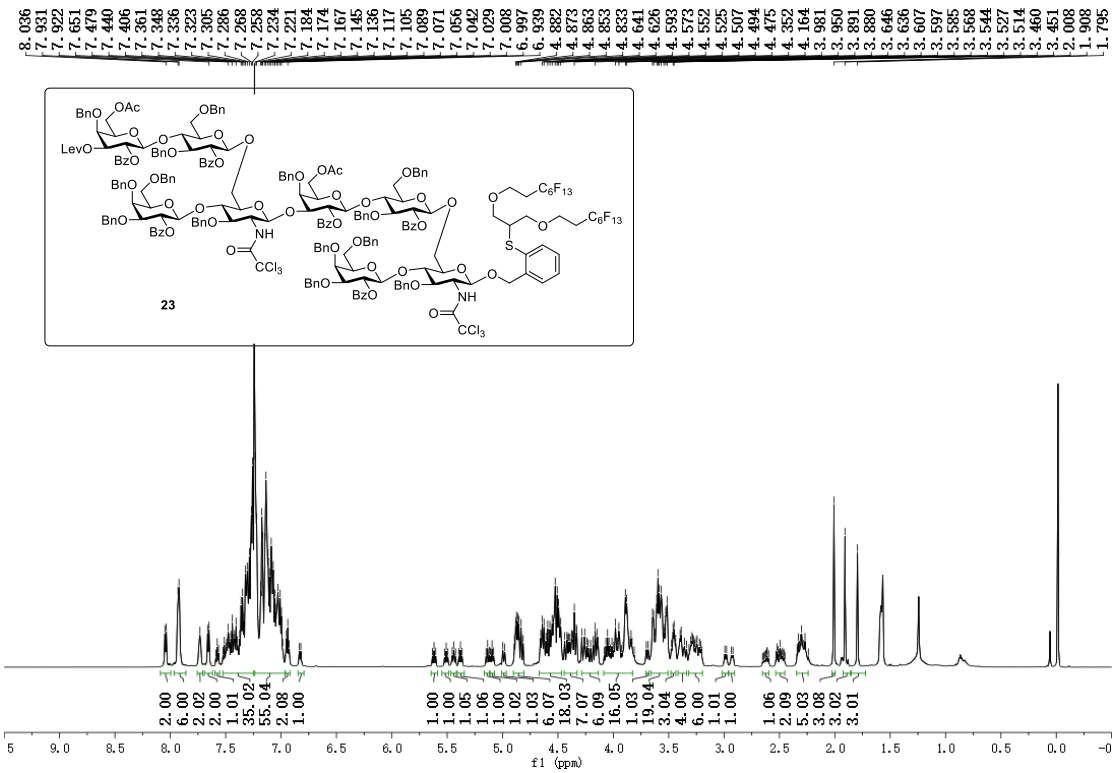

Figure S156. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **23**

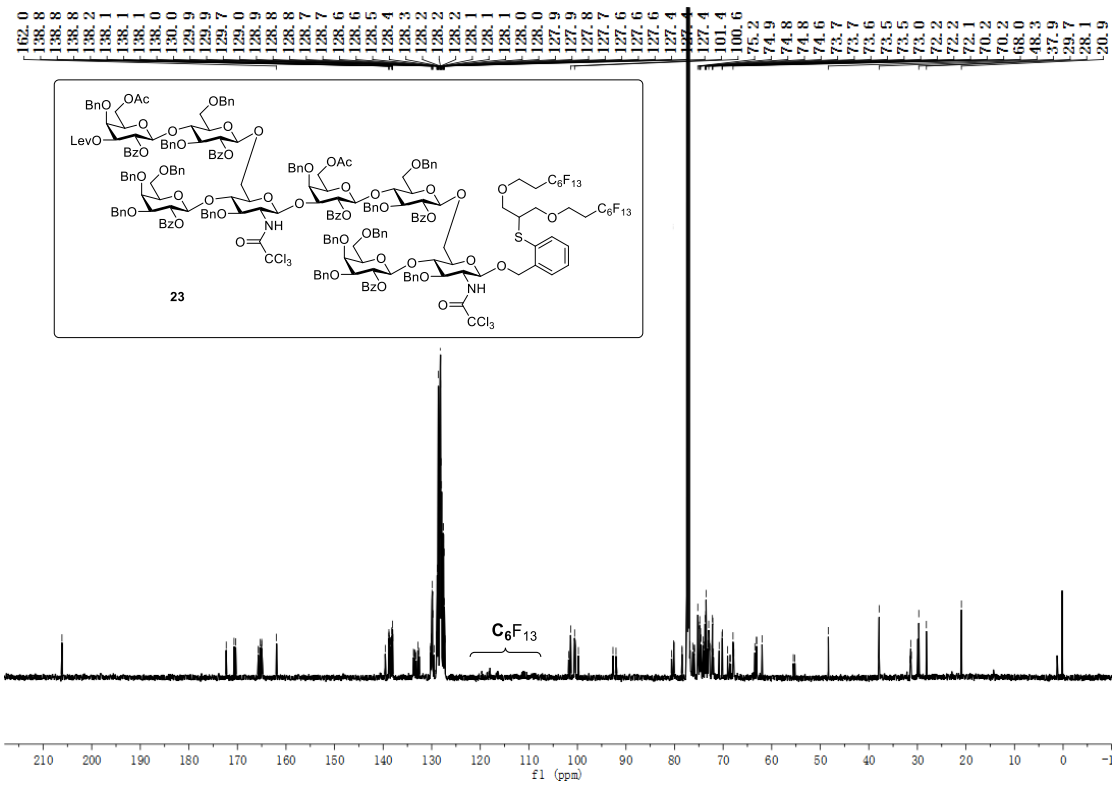

Figure S157. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **23**

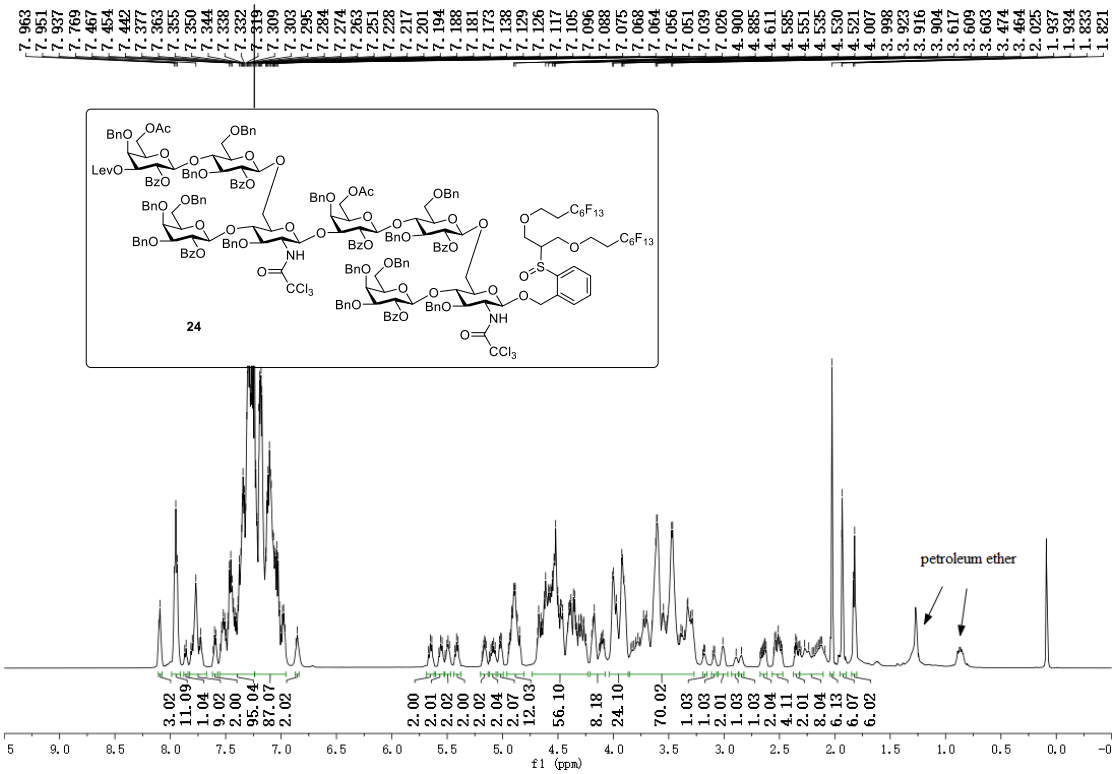

Figure S158. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **24**

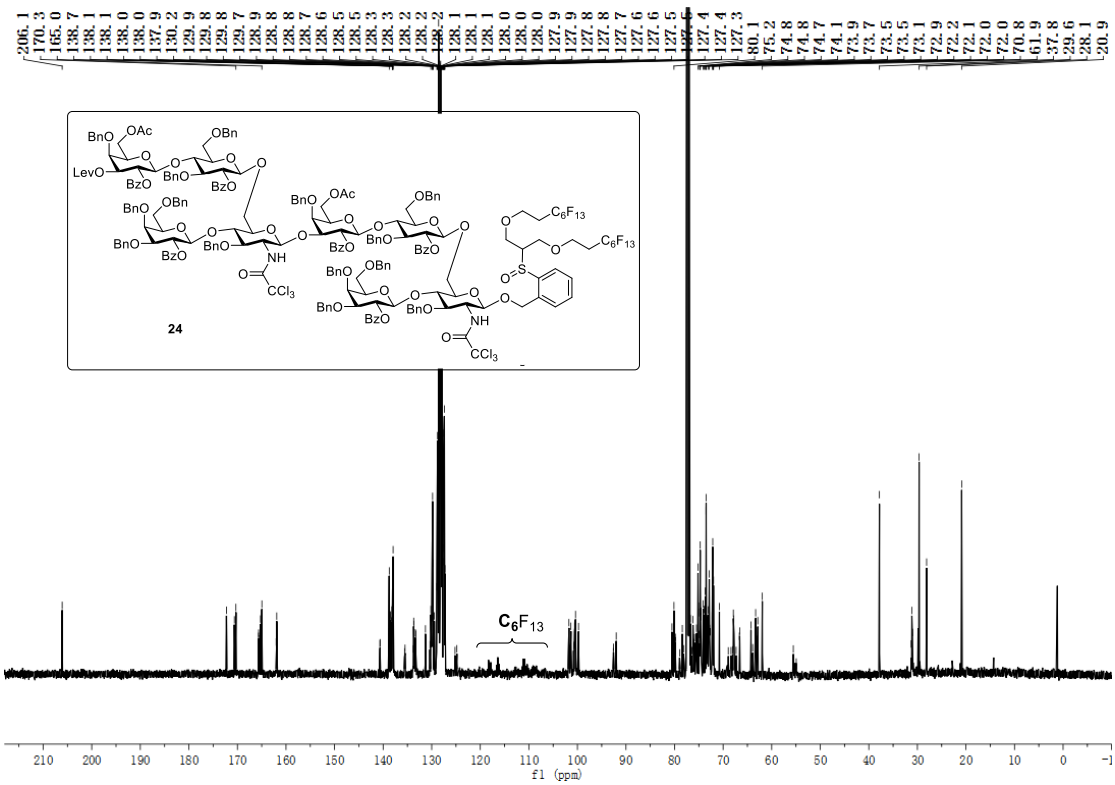

Figure S159. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **24**

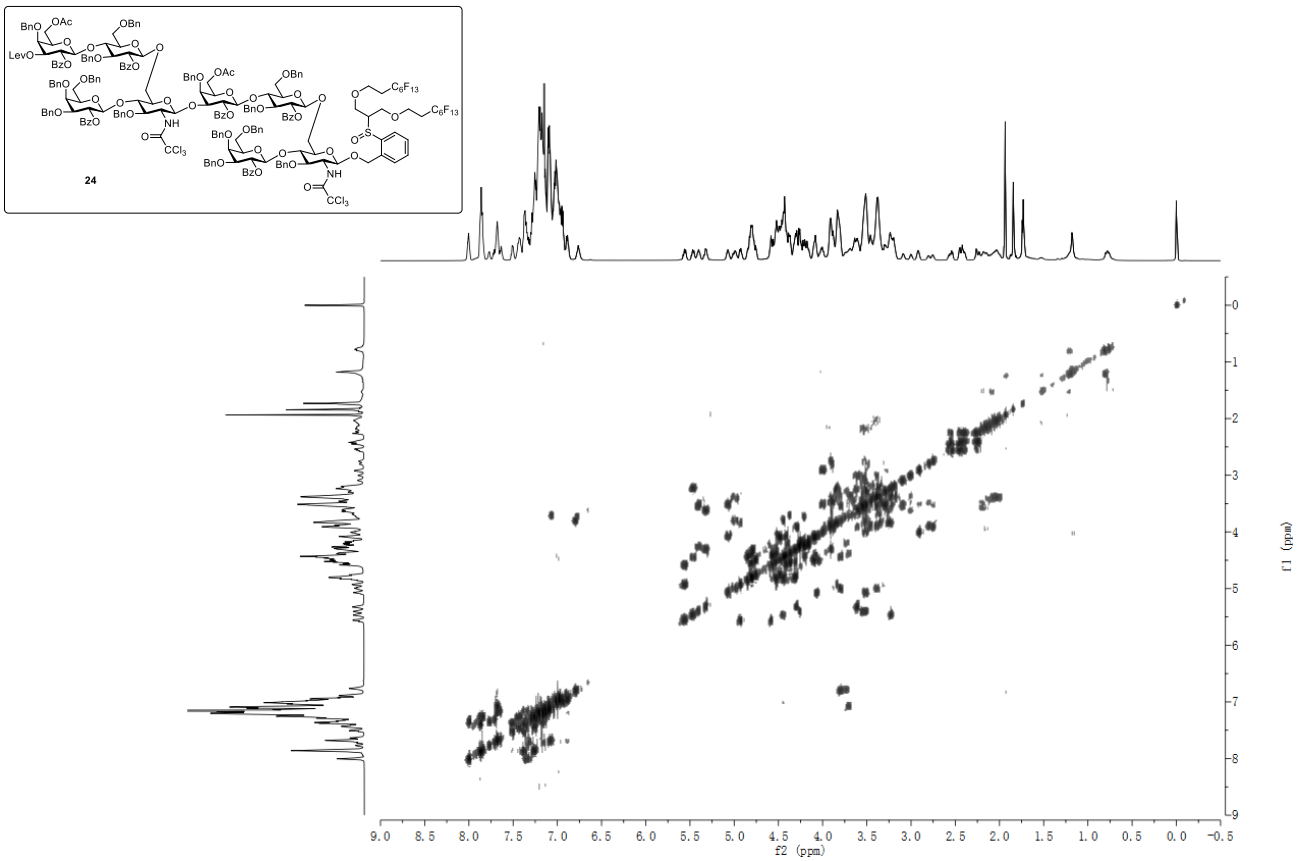

Figure S160. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **24**

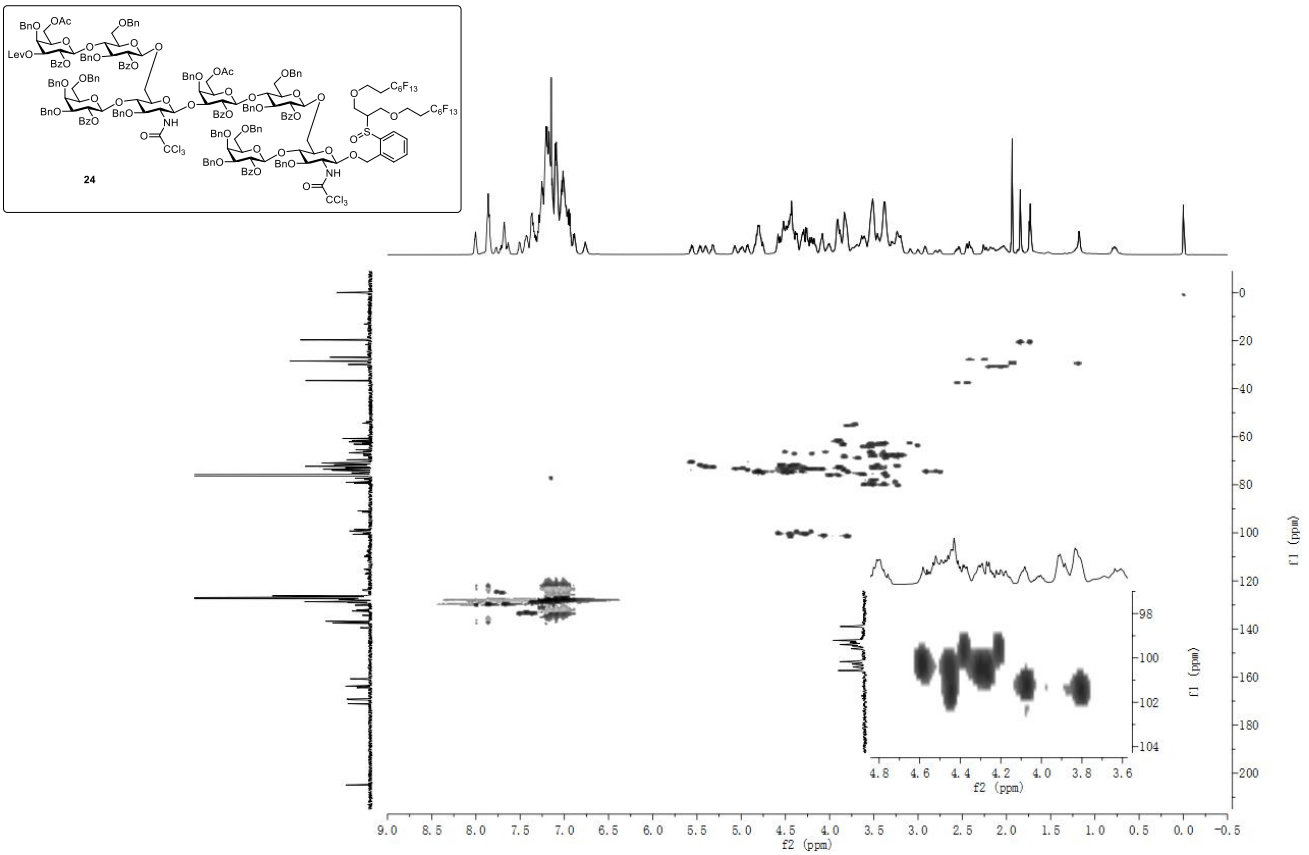

Figure S161. HSQC spectrum of **24**

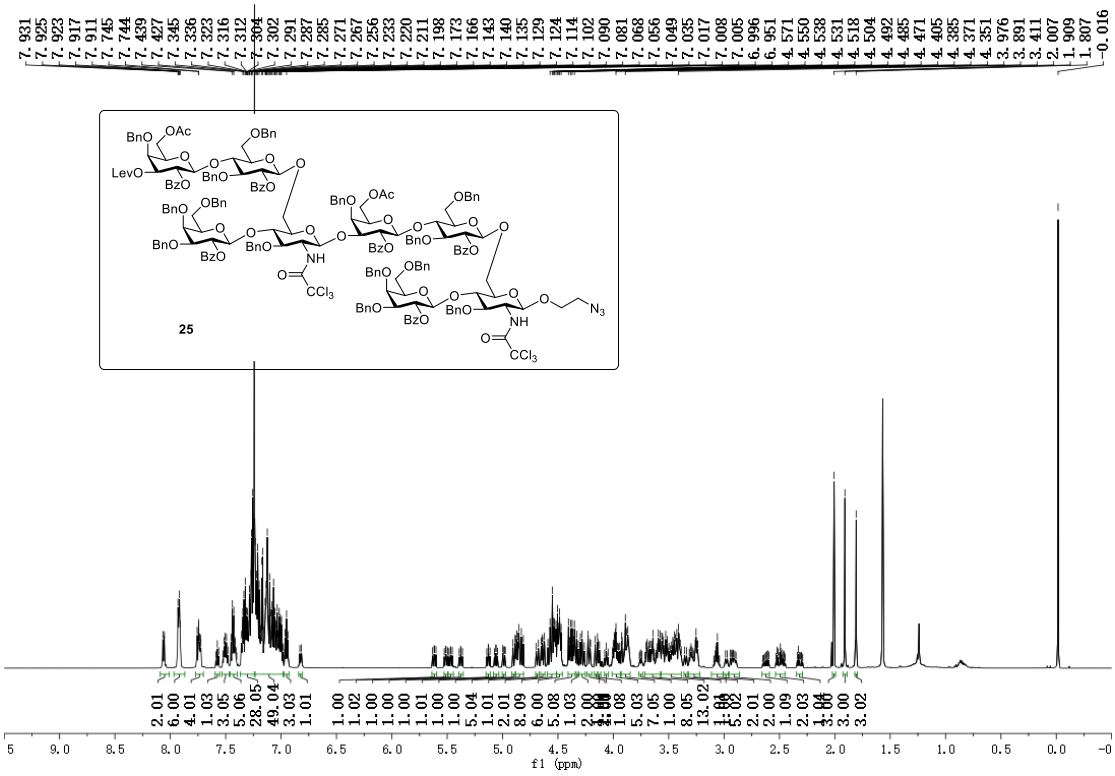

Figure S162. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **25**

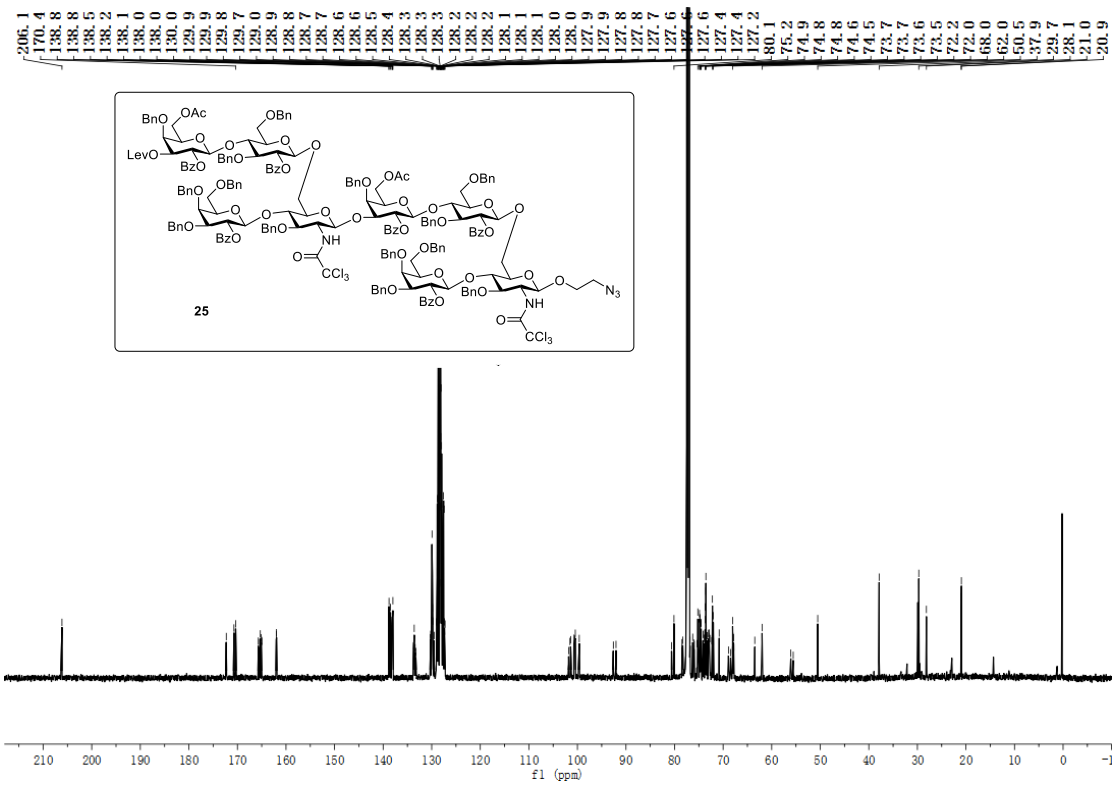

Figure S163. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **25**

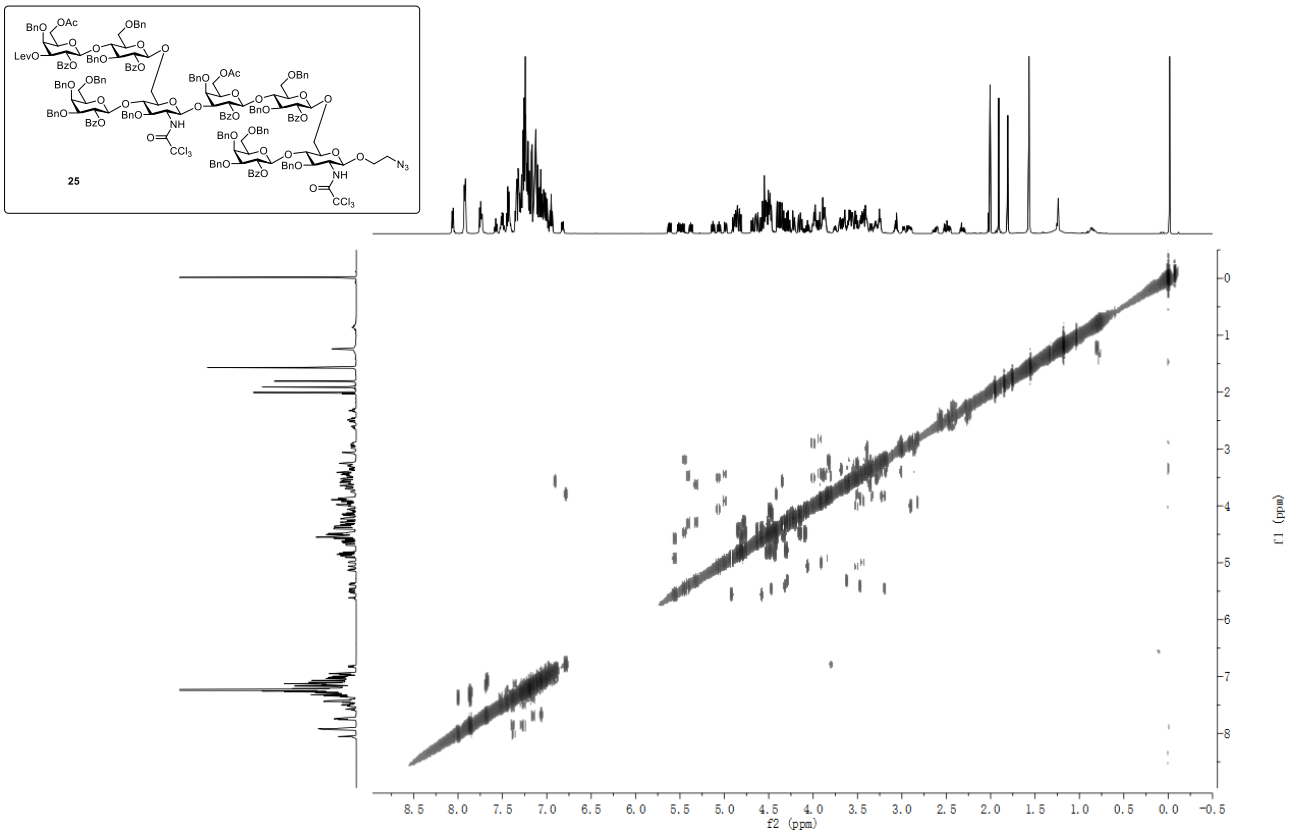

Figure S164. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **25**

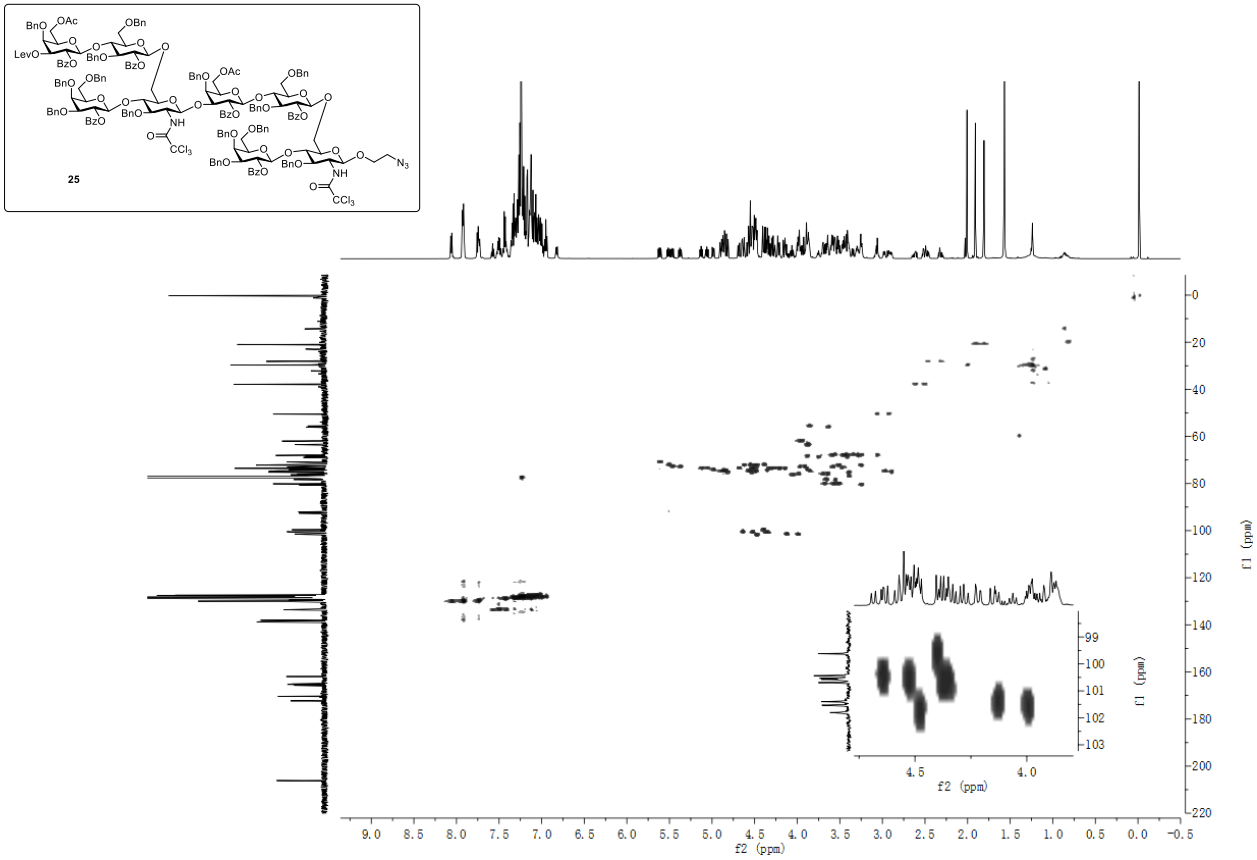

Figure S165. HSQC spectrum of **25**