

Total Synthesis of a Densely Functionalized *Plesiomonas shigelloides* Serotype 51 Aminoglycoside Trisaccharide Antigen

Chunjun Qin,^{†,‡} Benjamin Schumann,^{‡,§} Xiaopeng Zou,^{†,‡} Claney L. Pereira,^{‡,||} Guangzong Tian,^{†,‡} Jing Hu,[†]

Peter H. Seeberger,^{*,‡} and Jian Yin^{*,†}

[†]Key Laboratory of Carbohydrate Chemistry and Biotechnology, Ministry of Education, School of Biotechnology,

Jiangnan University, Wuxi, Jiangsu Province 214122, P.R. China

[‡]Department of Biomolecular Systems, Max Planck Institute of Colloids and Interfaces, Am Mühlenberg 1,

14476 Potsdam, Germany

* jianyin@jiangnan.edu.cn (J.Y.)

* peter.seeberger@mpikg.mpg.de (P.H.S.)

[§]Present address: Department of Chemistry, Stanford University, 380 Roth Way, Stanford, CA 94305, USA.

^{||}Present address: Vaxxilon Deutschland GmbH, Magnusstraße 11, 12489 Berlin, Germany.

Content

List of NMR spectra for new compounds	S3-S5
General information	S6
Part 1. Synthesis of diamino-D-glucuronate 6 .	S7-S17
Part 2. Synthesis of L-fucosamine 8 and 8' .	S17-S19
Part 3. Model introduction of an acetamidino group to 23 .	S19-S21
Part 4. Synthesis of D-quinovosamine 9 .	S21-S30
Part 5. Attempt of fully protected trisaccharide 37 .	S30-S33
Part 6. Assembly toward fully protected trisaccharide 51 .	S33-S45
Part 7. Synthesis of target trisaccharides 2 and 3 .	S46-S55
References	S56

List of NMR spectra for new compounds

¹ H & ¹³ C NMR of compound S1	S57
¹ H & ¹³ C NMR of compound 10	S58
¹ H & ¹³ C NMR of compound 11	S59
¹ H & ¹³ C NMR of compound S2	S60
¹ H & ¹³ C & 2D NMR of compound 12	S61
¹ H & ¹³ C NMR of compound S3	S63
¹ H & ¹³ C & 2D NMR of compound 13	S64
¹ H & ¹³ C NMR of compound S4	S66
¹ H & ¹³ C NMR of compound 14	S67
¹ H & ¹³ C NMR of compound 15	S68
¹ H & ¹³ C NMR of compound 16	S69
¹ H & ¹³ C NMR of compound 17	S70
¹ H & ¹³ C NMR of compound 18	S71
¹ H & ¹³ C NMR of compound 20	S72
¹ H & ¹³ C NMR of compound 21	S73
¹ H NMR of compound 8	S74
¹ H & ¹³ C NMR of compound 8'	S75
¹ H & ¹³ C NMR of compound 22	S76
¹ H & ¹³ C NMR of compound 23	S77
¹ H & ¹³ C & 2D NMR of compound 24	S78
¹ H & ¹³ C NMR of compound 25	S80

¹ H & ¹³ C NMR of compound 26	S81
¹ H & ¹³ C NMR of compound 27	S82
¹ H & ¹³ C NMR of compound 28	S83
¹ H & ¹³ C NMR of compound 29	S84
¹ H & ¹³ C NMR of compound 30	S85
¹ H & ¹³ C NMR of compound 31	S86
¹ H & ¹³ C NMR of compound S5	S87
¹ H & ¹³ C NMR of compound 32	S88
¹ H & ¹³ C NMR of compound S6	S89
¹ H NMR of compound S7	S90
¹ H & ¹³ C & 2D NMR of compound 34	S91
¹ H & ¹³ C NMR of compound 35	S93
¹ H & ¹³ C NMR of compound 9	S94
¹ H & ¹³ C & 2D NMR of compound 36	S95
¹ H & ¹³ C & 2D NMR of compound 7	S97
¹ H & 2D NMR of compound 38	S100
¹ H & ¹³ C NMR of compound S8	S102
¹ H & ¹³ C NMR of compound 39	S103
¹ H & ¹³ C & 2D NMR of compound 40	S104
¹ H & ¹³ C NMR of compound 41	S106
¹ H & ¹³ C & 2D NMR of compound 42	S107
¹ H & ¹³ C & 2D NMR of compound 43	S109

¹ H & ¹³ C & 2D NMR of compound 44	S111
¹ H & ¹³ C & 2D NMR of compound 45	S113
¹ H & ¹³ C & 2D NMR of compound 46	S115
¹ H & ¹³ C & 2D NMR of compound 47	S117
¹ H & ¹³ C & 2D NMR of compound 48	S119
¹ H & ¹³ C & 2D NMR of compound 49	S121
¹ H & ¹³ C & 2D NMR of compound 50	S125
¹ H & ¹³ C & 2D NMR of compound 51	S127
¹ H & ¹³ C & 2D NMR of compound 52	S129
¹ H & ¹³ C & 2D NMR of compound 53	S131
¹ H & ¹³ C & 2D NMR of compound 54	S133
¹ H & ¹³ C & 2D NMR of compound 55	S135
¹ H & ¹³ C & 2D NMR of compound 4	S137
¹ H & ¹³ C & 2D NMR of compound 5	S139
¹ H & ¹³ C & 2D NMR of compound 2	S141
¹ H & ¹³ C & 2D NMR of compound 3	S143

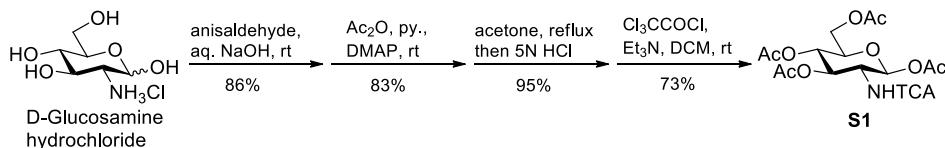
General information

Commercially available reagents were used without further purification, unless otherwise stated. The anhydrous solvents used in the reactions were obtained from an MBraun MB-SPS 800 Dry Solvent System. Solvents for chromatography were of analytical grade and distilled under reduced pressure prior to use. Analytical TLC was performed on silica gel 60-F254 precoated on glass plate or aluminum plate. Spots were visualized with sugar stain (0.1% (v/v) 3-methoxyphenol, 2.5% (v/v) sulfuric acid in EtOH), CAM stain (5% (w/v) ammonium molybdate, 1% (w/v) cerium(II) sulfate and 10% (v/v) sulfuric acid in water) or ninhydrin stain (1.5% (w/v) ninhydrin and 3% (v/v) acetic acid in *n*-butanol) dipping solutions. The normal phase column chromatography was performed on silica gel (200-300 mesh). Size exclusion chromatography (SEC) was performed using Sephadex ® LH-20 (GE Healthcare).

¹H, ¹³C and two-dimensional NMR spectra were recorded on a Bruker Ascend 400 MHz spectrometer, Bruker Ultrashield Plus 400 MHz spectrometer or Bruker AVIII 700 (700 MHz) spectrometer at 25 °C. High-resolution mass spectrometry was performed on an Agilent 6220 ESI-TOF mass spectrometer. Optical rotations (OR) were measured with a Schmidt & Haensch UniPol L 1000 at 589 nm and a concentration (c) expressed in g/100 ml. IR spectra were recorded on Thermo Fisher Scientific Nicolet iS5 spectrometer. Analytical HPLC was performed on an Agilent 1200 series coupled to a quadrupole ESI LC/MS 6130 using a Thermo Scientific Hypercarb column (150 × 4.6 mm). Preparative HPLC was performed on an Agilent 1200 series using a semi-preparative Thermo Scientific Hypercarb column (150 × 10 mm).

Part 1. Synthesis of diamino-D-glucuronate 6.

1,3,4,6-Tetra-O-acetyl-2-deoxy-2-trichloracetamido- β -D-glucopyranoside (S1)



D-Glucosamine hydrochloride (100 g, 0.464 mol) was dissolved in 480 mL of 1 M aqueous sodium hydroxide, forming a colorless solution. Anisaldehyde (57 mL, 0.469 mol) was added using a syringe while stirring the mixture vigorously, and a turbid solution formed. After several minutes of agitation, a white precipitate was formed. The reaction mixture was kept in an ice bath for 1 h to ensure complete precipitation. The solid was then collected by filtration and washed with water (4×200 mL) and a 1:1 mixture of MeOH and Et_2O (4×200 mL). The precipitate was dried overnight under vacuum, affording 2-p-methoxybenzylideneamino-D-glucopyranose as white solid (119 g, 0.400 mol, 86%).

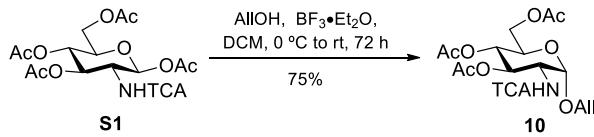
The 2-p-methoxybenzylideneamino-D-glucopyranose (92 g, 0.309 mol) was treated with Ac_2O (380 mL), pyridine (395 mL) and DMAP (1.14 g) at 0 °C under nitrogen. The solid slowly went into solution and the reaction mixture was left at room temperature overnight. The reaction mixture was poured into 1800 g ice, forming a white crystalline solid. The crystals were collected by filtration, washed with water (2×100 mL) and Et_2O (2×100 mL) and dried under vacuum to afford 2-deoxy-2-p-methoxybenzylidene-amino-1,3,4,6-tetra-O-acetyl- β -D-glucopyranoside (118.5 g, 0.255 mol, 83%).

The 2-deoxy-2-p-methoxybenzylidene-amino-1,3,4,6-tetra-O-acetyl- β -D-glucopyranoside (76.5 g, 0.164 mol) was dissolved in 380 mL of refluxing acetone and to this solution 38 mL of 5 N HCl were added dropwise. The reaction mixture was cooled to room temperature. The precipitate was filtered and washed with acetone (90 mL) and Et_2O (4×90 mL). The crude product was dried under vacuum overnight, yielding 2-amino-1,3,4,6-tetra-O-acetyl-2-deoxy- β -D-glucopyranosyl hydrochloride as white solid (54 g, 0.155 mol, 95%).

The 2-amino-1,3,4,6-tetra-O-acetyl-2-deoxy- β -D-glucopyranosyl hydrochloride (85.6 g, 0.246 mol) was dispersed in anhydrous DCM (750 mL) under nitrogen. Et_3N (61 mL, 0.440 mol) and trichloroacetyl chloride (33 mL, 0.295 mol) were added

successively at 0 °C. The mixture was stirred for 30 min at room temperature, and diluted with DCM (700 mL), washed with water (350 mL), satd. aq. NaHCO₃ (350 mL) and water (2 × 350 mL), dried over Na₂SO₄, and concentrated under vacuum. The crude product was recrystallized in *n*-hexane : ethyl acetate (1 : 1 v/v) and afforded **S1** (88.9 g, 0.180 mol, 73%) as white solid. [α]_D²⁰ = + 4.7° (c = 1.00, CHCl₃); IR ν_{max} (film) 3341, 1753, 1724, 1531, 1369, 1215, 1079, 1040, 904, 822, 761 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.18 (d, *J* = 9.5 Hz, 1H, NH), 5.81 (d, *J* = 8.7 Hz, 1H, 1-H), 5.37 (dd, *J* = 10.7, 9.5 Hz, 1H, 3-H), 5.17 (dd, *J* = 9.7, 9.7 Hz, 1H, 4-H), 4.35-4.30 (m, 1H, 6-H_a), 4.30-4.26 (m, 1H, 2-H), 4.20-4.15 (m, 1H, 6-H_b), 3.89 (ddd, *J* = 9.9, 4.8, 2.2 Hz, 1H, 5-H), 2.12 (s, 3H, CH₃CO), 2.11 (s, 3H, CH₃CO), 2.08 (s, 3H, CH₃CO), 2.06 (s, 3H, CH₃CO); ¹³C NMR (100 MHz, CDCl₃) δ = 171.4, 170.6, 169.3, 169.2, 162.2, 92.0, 73.1, 71.8, 67.8, 61.6, 54.5, 20.71, 20.70, 20.53, 20.51; HR-ESI-MS (m/z): calcd for C₁₆H₂₀Cl₃NO₁₀Na⁺ (M + Na⁺): 514.0050, found: 514.0044.

Allyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-trichloracetamido- α -D-glucopyranoside (**10**)

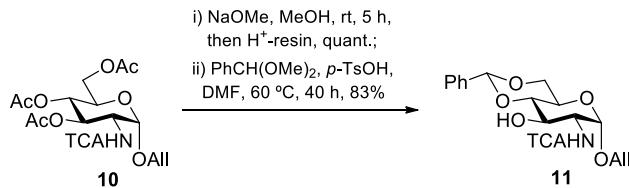


Under an argon atmosphere, **S1** (27 g, 0.055 mol) was dissolved in anhydrous DCM (130 mL), 4 Å molecular sieves (flame dried) and allyl alcohol (18.6 mL, 0.273 mol) was added, then cooled to -5 °C. Boron trifluoride diethyl ether complex (69 mL, 0.547 mol) was added dropwise. The reaction solution was stirred for 30 min at 0 °C, then stirred for 71 h at room temperature. After the reaction, the solution was poured onto ice (200 g), filtered through celite, washed with water (4 × 200 mL), satd. aq. NaHCO₃ (2 × 200 mL), brine (200 mL), and dried over Na₂SO₄ and concentrated. The residue was purified by silica gel column chromatography using petroleum ether : ethyl acetate (5 : 1 v/v) as eluent to yield pure **10** as yellow syrup (19.9 g, 0.041 mol, 75%). [α]_D²⁰ = + 87.8° (c = 1.20, CHCl₃); IR ν_{max} (film) 3429, 2960, 1749, 1722, 1517, 1368, 1229, 1048, 822, 682 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 6.93 (d, *J* = 9.1 Hz, 1H, NH), 5.88 (dd, *J* = 17.0, 10.3, 6.5, 5.4 Hz, 1H, CH=C), 5.41-5.23 (m, 3H, 4-H, C=CH₂), 5.16 (dd, *J* = 9.8, 9.8 Hz, 1H, 3-H), 5.01 (d, *J* = 3.7 Hz, 1H, 1-H), 4.34-4.19 (m, 3H, 6-CH₂, OCH_a), 4.11 (dd, *J* = 12.4, 2.4 Hz, 1H, OCH_b), 4.09-3.98 (m, 2H, 2-H, 5-H), 2.11 (s, 3H, CH₃CO), 2.05 (s, 3H, CH₃CO), 2.02 (s, 3H, CH₃CO); ¹³C NMR (100 MHz, CDCl₃) δ = 171.4, 170.6, 169.3, 169.2, 162.2, 92.0, 73.1, 71.8, 67.8, 61.6, 54.5, 20.71, 20.70, 20.53, 20.51.

MHz, CDCl₃) δ = 171.1, 170.6, 169.3, 161.9, 132.6, 119.1, 95.5, 92.1, 77.3, 70.7, 69.0, 68.1, 67.8, 61.8, 53.9, 20.7, 20.63, 20.59;

HR-ESI-MS (m/z): calcd for C₁₇H₂₂Cl₃NO₉Na⁺ (M + Na⁺): 512.0258, found: 512.0254.

Allyl 4,6-O-benzylidene-2-deoxy-2-trichloracetamido- α -D-glucopyranoside (**11**)

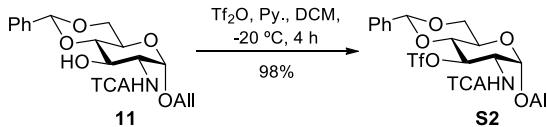


Compound **10** (50 g, 0.102 mol) was dissolved in MeOH (800 mL). NaOMe (2.8 g, 0.052 mol) was added and the solution was stirred at room temperature for 5 h. The solution was neutralized with Amberlite IR 120 (H⁺) ion exchange resin and filtered. The filtrate was evaporated to afford allyl 2-deoxy-2-trichloracetamido- α -D-glucopyranoside as white solid (37.1 g, 0.102 mol, quant.).

The allyl 2-deoxy-2-trichloracetamido- α -D-glucopyranoside (71.5 g, 0.196 mol) was then dissolved in 390 mL anhydrous DMF under nitrogen, followed by the addition of benzaldehyde dimethyl acetal (35 mL, 0.233 mol) and *p*-TsOH (4.38 g, 0.023 mol) at room temperature. The reaction mixture was stirred at 60 °C for 24 h, and concentrated on a rotary evaporator to remove the MeOH formed. When TLC showed that the starting materials were completely consumed, DMF was removed under reduced pressure. The residue was diluted with ethyl acetate (350 mL) and washed with satd. aq. NaHCO₃ (3 × 200 mL). The aqueous phase was extracted with ethyl acetate (3 × 80 mL), and the combined organic phase was washed with water (3 × 80 mL) and brine (2 × 80 mL) and dried over Na₂SO₄. The crude residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate 10 : 1 v/v) to yield **11** (73.6 g, 0.163 mol, 83%) as a white solid. [α]_D²⁰ = + 68.6° (c = 1.00, CHCl₃); IR ν_{max} (film) 3339, 2919, 1695, 1530, 1451, 1372, 1085, 1027, 989, 748, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.55–7.34 (m, 5H, Ph), 6.96 (d, *J* = 8.8 Hz, 1H, NH), 5.86 (dd, *J* = 16.9, 10.3, 6.4, 5.3 Hz, 1H, CH=C), 5.53 (s, 1H, PhCH), 5.35–5.20 (m, 2H, C=CH₂), 4.97 (d, *J* = 3.8 Hz, 1H, 1-H), 4.27 (dd, *J* = 10.2, 4.8 Hz, 1H, 4-H), 4.24–4.11 (m, 2H, 2-H, OCH_a), 4.06–3.94 (m, 2H, OCH_b, 5-H), 3.86 (ddd, *J* = 9.9, 9.8, 4.7 Hz, 1H, 6-CH_a), 3.74 (t, *J* = 10.3 Hz, 1H, 6-CH_b), 3.56 (t, *J* = 9.3 Hz, 1H, 3-H), 2.78 (br, 1H, 3-OH); ¹³C NMR (100 MHz, CDCl₃) δ = 162.3, 137.0, 132.9, 129.3, 128.3, 126.3, 118.7, 101.9, 96.3, 92.4, 81.5, 69.7, 68.8, 68.6, 62.8, 55.4; HR-ESI-MS

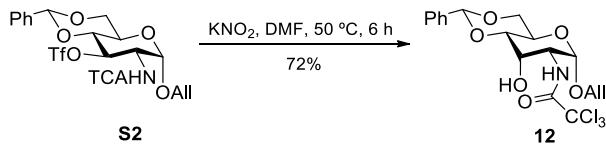
(m/z): calcd for $C_{18}H_{20}Cl_3NO_6Na^+$ ($M + Na^+$): 474.0254, found: 474.0245.

Allyl 4,6-O-benzylidene-2-deoxy-3-O-trifluoromethanesulfonyl-2-trichloracetamido- α -D-glucopyranoside (S2)



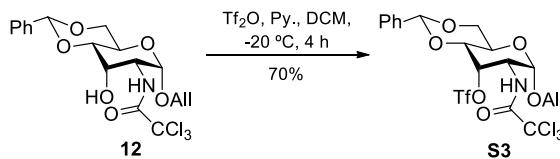
To a solution of **11** (53.1 g, 0.117 mol) in anhydrous DCM (580 mL), pyridine (81 mL) was added at -20 °C under nitrogen. Tf₂O (40 mL, 0.237 mol) in anhydrous DCM (150 mL) was added dropwise, and the mixture was stirred while allowing to warm from -20 °C to 10 °C over 2 h. The resulting mixture was subsequently diluted with DCM (400 mL) and washed with 1 M HCl (3 × 250 mL), satd. aq. NaHCO₃ (3 × 250 mL), water (2 × 250 mL) and brine (250 mL). The organic phase was dried over Na₂SO₄ and concentrated under vacuum at 30 °C. The residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate 5 : 1 to 2 : 1 v/v) to afford product **S2** as yellow syrup (66.8 g, 0.115 mol, 98%). $[\alpha]_D^{20} = +35.3^\circ$ ($c = 1.00, CHCl_3$); IR ν_{max} (film) 3348, 1698, 1529, 1414, 1373, 1203, 1146, 1122, 959, 836, 753, 628 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.52-7.33 (m, 5H, Ph), 7.06 (d, $J = 9.6$ Hz, 1H, NH), 5.87 (dd, $J = 17.0, 10.2$, 6.8, 5.4 Hz, 1H, CH=C), 5.62 (s, 1H, PhCH), 5.37-5.27 (m, 2H, C=CH₂), 5.13 (dd, $J = 10.3, 9.1$ Hz, 1H, 3-H), 5.03 (d, $J = 3.7$ Hz, 1H, 1-H), 4.50 (ddd, $J = 10.0, 10.0, 3.8$ Hz, 1H, 2-H), 4.36 (dd, $J = 10.4, 4.5$ Hz, 1H, 6-CH_a), 4.25 (ddt, $J = 12.7, 5.5, 1.3$ Hz, 1H, OCH_a), 4.06 (ddt, $J = 12.7, 6.8, 1.2$ Hz, 1H, OCH_b), 3.98 (td, $J = 9.6, 4.6$ Hz, 1H, 5-H), 3.92 (dd, $J = 9.2$ Hz, 1H, 6-CH_b), 3.84 (dd, $J = 10.1, 10.1$ Hz, 1H, 4-H); ¹³C NMR (100 MHz, CDCl₃) δ = 162.2, 136.2, 132.2, 129.2, 128.2, 125.9, 119.9, 116.8, 101.6, 96.4, 91.8, 83.1, 78.2, 69.3, 68.4, 63.3, 53.8; HR-ESI-MS (m/z): calcd for $C_{19}H_{19}Cl_3F_3NO_8SNa^+$ ($M + Na^+$): 605.9747, found: 605.9760.

Allyl 4,6-O-benzylidene-2-deoxy-2-trichloracetamido- α -D-allopyranoside (12)



KNO_2 (364 mg, 4.277 mmol) was added to a solution of triflate **S2** (0.5 g, 0.858 mmol) in anhydrous DMF (10 mL) under nitrogen. After stirring at 50 °C for 6 h, the mixture was diluted with DCM (50 mL) and washed with brine (3×30 mL). The organic phase was dried over Na_2SO_4 and concentrated under vacuum. Purification of the residue by silica gel column chromatography (petroleum ether : ethyl acetate 8 : 1 v/v) afforded the inversion product **12** as white solid (278 mg, 0.614 mmol, 72%). $[\alpha]_D^{20} = + 74.0^\circ$ ($c = 1.00, \text{CHCl}_3$); IR ν_{max} (film) 3419, 1711, 1507, 1378, 1218, 1102, 1065, 1023, 820, 756, 699 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.57-7.33 (m, 6H, NH, Ph), 5.88 (dd, $J = 16.9, 10.3, 6.4, 5.2$ Hz, 1H, $\text{CH}=\text{C}$), 5.63 (s, 1H, PhCH), 5.37-5.20 (m, 2H, $\text{C}=\text{CH}_2$), 5.00 (d, $J = 4.2$ Hz, 1H, 1-H), 4.38 (dd, $J = 10.3, 5.1$ Hz, 1H, 6- CH_b), 4.27 (m, 2H, 3-H, OCH_a), 4.24-4.16 (m, 2H, 2-H, 5-H), 4.05 (ddt, $J = 13.0, 6.5, 1.3$ Hz, 1H, OCH_b), 3.80 (t, $J = 10.3$ Hz, 1H, 6- CH_a), 3.67 (dd, $J = 9.7, 2.8$ Hz, 1H, 4-H), 2.66 (br, 1H, 3-OH); ^{13}C NMR (100 MHz, CDCl_3) δ = 161.7, 136.9, 132.9, 129.3, 128.4, 126.2, 118.8, 101.9, 96.0, 92.3, 78.1, 77.2, 69.5, 69.0, 67.3, 57.6, 51.2; HR-ESI-MS (m/z): calcd for $\text{C}_{18}\text{H}_{20}\text{Cl}_3\text{NO}_6\text{Na}^+$ ($\text{M} + \text{Na}^+$): 474.0254, found: 474.0245.

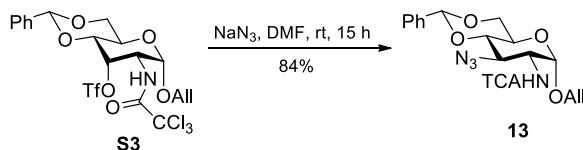
Allyl 4,6-*O*-benzylidene-2-deoxy-3-*O*-trifluoromethanesulfonyl-2-trichloracetamido- α -D-allopyranoside (**S3**)



To a solution of **12** (178 mg, 0.393 mmol) in anhydrous DCM (3.93 mL) was added pyridine (273 μL , 3.382 mmol) at -20 °C under nitrogen. Tf_2O (133 μL , 0.787 mmol) was added dropwise, and the mixture was stirred while allowing to warm from -20 °C to 10 °C over 2 h. The resulting mixture was subsequently diluted with DCM (10 mL) and washed with 1 M HCl (3×10 mL), satd. aq. NaHCO_3 (2×10 mL), water (2×10 mL) and brine (10 mL). The organic phase was dried over Na_2SO_4 and concentrated under vacuum at 30 °C. The residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate 10 : 1 to 5 : 1 to 2 : 1 v/v) to afford triflate **S3** as yellow syrup (160 mg, 0.274 mmol, 70%). $[\alpha]_D^{20} = + 40.4^\circ$ ($c = 1.00, \text{CHCl}_3$); IR ν_{max} (film) 2923, 2853, 1750, 1497, 1416, 1211, 1028, 821, 617 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.53-7.35 (m, 5H, Ph), 7.33 (d, $J = 8.5$ Hz, 1H,

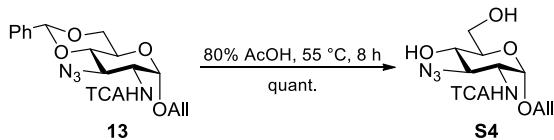
NH), 5.89 (dddd, $J = 16.8, 10.6, 6.0, 4.7$ Hz, 1H, CH=C), 5.61 (s, 1H, PhCH), 5.44 (t, $J = 2.9$ Hz, 1H, 3-H), 5.37 (dq, $J = 17.3, 1.6$ Hz, 1H, C=CH_a), 5.28 (dq, $J = 10.5, 1.4$ Hz, 1H, C=CH_b), 4.96 (d, $J = 4.3$ Hz, 1H, 1-H), 4.44 (ddd, $J = 8.0, 4.3, 3.2$ Hz, 1H, 2-H), 4.41-4.31 (m, 2H, 6-H_a, OCH_a), 4.26 (td, $J = 9.9, 5.2$ Hz, 1H, 5-H), 4.05 (ddt, $J = 13.3, 6.0, 1.4$ Hz, 1H, OCH_b), 3.87 (dd, $J = 9.7, 2.5$ Hz, 1H, 4-H), 3.78 (t, $J = 10.4$ Hz, 1H, 6-H_b); ¹³C NMR (100 MHz, CDCl₃) δ = 162.0, 136.3, 132.4, 129.4, 128.3, 126.2, 118.1, 102.4, 94.9, 91.5, 80.7, 74.9, 69.0, 68.8, 58.1, 50.2; HR-ESI-MS (m/z): calcd for C₁₉H₁₉Cl₃F₃NO₈SNa⁺ (M + Na⁺): 605.9747, found: 605.9753.

Allyl 3-azido-4,6-O-benzylidene-2,3-dideoxy-2-trichloracetamido- α -D-glucopyranoside (13)



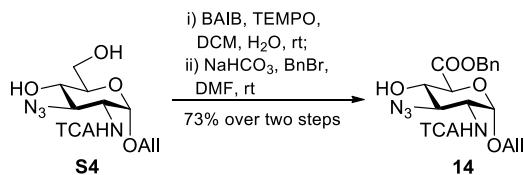
Triflate **S3** (65 mg, 0.111 mmol) was dissolved in anhydrous DMF (1.4 mL) under nitrogen, NaN₃ (36 mg, 0.554 mmol) was added, and the resulting mixture was stirred at room temperature overnight. The reaction progress was monitored by TLC analysis. The mixture was diluted with ethyl acetate (15 mL), washed thoroughly with water (3 × 15 mL), brine (10 mL), dried with Na₂SO₄ and concentrated. The residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate 20 : 1 to 8 : 1 v/v) to give product **13** as white solid (44.2 mg, 0.093 mmol, 84%). $[\alpha]_D^{20} = +39.7^\circ$ (c = 1.00, CHCl₃); IR ν_{max} (film) 3120, 2917, 2849, 2110, 1692, 1528, 1372, 1258, 1124, 1080, 1055, 1016, 836, 750, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.55-7.33 (m, 5H, Ph), 6.88 (d, $J = 9.5$ Hz, 1H, NH), 5.94-5.80 (m, 1H, CH=C), 5.63 (s, 1H, PhCH), 5.36-5.23 (m, 2H, C=CH₂), 4.92 (d, $J = 3.6$ Hz, 1H, 1-H), 4.32 (dd, $J = 10.4, 4.9$ Hz, 1H, 6-CH_a), 4.24 (ddt, $J = 12.7, 5.5, 1.4$ Hz, 1H, OCH_a), 4.13 (ddd, $J = 11.2, 9.7, 3.7$ Hz, 1H, 2-H), 4.05 (ddt, $J = 12.8, 6.6, 1.4$ Hz, 1H, OCH_b), 3.99-3.88 (m, 2H, 3-H, 5-H), 3.79 (t, $J = 10.3$ Hz, 1H, 6-CH_b), 3.70 (t, $J = 9.6$ Hz, 1H, 4-H); ¹³C NMR (100 MHz, CDCl₃) δ = 161.9, 136.7, 132.6, 129.1, 128.3, 125.9, 119.2, 101.5, 95.9, 92.3, 80.3, 77.2, 68.9, 68.7, 63.3, 61.2, 53.5; HR-ESI-MS (m/z): calcd for C₁₈H₁₉Cl₃N₄O₅Na⁺ (M + Na⁺): 499.0319, found: 499.0311.

Allyl 3-azido-2,3-dideoxy-2-trichloracetamido- α -D-glucopyranoside (S4)



A suspension of **13** (20 mg, 0.042 mmol) in 80% HOAc (0.9 mL) was heated to 55 °C with stirring until all starting material was consumed. After evaporation under reduced pressure to remove most solvent, the residue was purified by silica gel column chromatography (DCM : MeOH 60 : 1 to 40 : 1 to 30 : 1 v/v) to afford product **S4** as white solid (16.3 mg, 0.042 mmol, quant.). $[\alpha]_D^{20} = +16.9^\circ$ ($c = 0.35$, CHCl₃); IR ν_{max} (film) 3411, 2924, 2108, 1712, 1517, 1262, 1049, 822, 680 cm⁻¹; ¹H NMR (400 MHz, CD₃OD) δ = 5.98 (dd, $J = 17.0, 10.4, 6.4, 5.1$ Hz, 1H, CH=C), 5.38 (dq, $J = 17.3, 1.7$ Hz, 1H, C=CH_a), 5.24 (dq, $J = 10.4, 1.4$ Hz, 1H, C=CH_b), 4.94 (d, $J = 3.6$ Hz, 1H, 1-H), 4.29 (ddt, $J = 13.2, 5.2, 1.5$ Hz, 1H, OCH_a), 4.10 (ddt, $J = 13.1, 6.4, 1.4$ Hz, 1H, OCH_b), 3.99 (dd, $J = 11.5, 9.2$ Hz, 1H, 3-H), 3.93-3.81 (m, 2H, 2-H, 6-H_a), 3.81-3.68 (m, 2H, 5-H, 6-H_b), 3.52 (t, $J = 9.3$ Hz, 1H, 4-H); ¹³C NMR (100 MHz, CD₃OD) δ = 166.7, 137.6, 120.8, 98.9, 76.5, 73.7, 72.0, 67.5, 64.8, 58.1; HR-ESI-MS (m/z): calcd for C₁₁H₁₅Cl₃N₄O₅Na⁺ (M + Na⁺): 411.0006, found: 411.0001.

Benzyl (allyl 3-azido-2,3-dideoxy-2-trichloroacetamido- α -D-glucopyranosid) uronate (**14**)

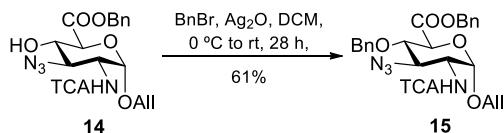


Water (1.4 L), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) (4.4 g, 0.028 mol) and (diacetoxyiodo) benzene (BAIB) (45.4 g, 0.141 mol) were added to a solution of **S4** (22 g, 0.056 mol) in DCM (2.8 L) at 0 °C under nitrogen. The resulting mixture was stirred for 4 h at room temperature. After that, the reaction mixture was passed through a pad of silica gel, concentrated and dried under high vacuum. The crude acid was used in the next step without further purification.

The crude acid was dissolved in anhydrous DMF (2.8 L) under nitrogen. To this solution, sodium hydrogencarbonate (21.4 g, 0.255 mol) was added followed by BnBr (50.4 mL, 0.424 mol) at room temperature. When TLC showed that the starting materials were completely consumed, the solvent was removed under high vacuum. The residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate 10 : 1 v/v) to afford benzylglucuronate **14** as yellow syrup (20.4 g, 0.041 mol, 73%

over two steps). $[\alpha]_D^{20} = +54.5^\circ$ ($c = 1.00$, CHCl_3); IR ν_{max} (film) 3412, 2930, 2110, 1717, 1514, 1264, 1057, 909, 820, 733, 698
 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) $\delta = 7.43\text{-}7.33$ (m, 5H, Ph), 6.79 (d, $J = 9.4$ Hz, 1H, NH), 5.86 (dd, $J = 17.0, 10.3$, 1H, $\text{CH}=\text{C}$), 5.37-5.20 (m, 4H, PhCH_2 , $\text{C}=\text{CH}_2$), 4.97 (d, $J = 3.6$ Hz, 1H, 1-H), 4.31-4.20 (m, 2H, 5-H, OCH_a), 4.13-4.00 (m, 2H, 2-H, OCH_b), 3.91 (t, $J = 9.5$ Hz, 1H, 4-H), 3.75 (dd, $J = 11.1, 9.3$ Hz, 1H, 3-H), 3.31 (br, 1H, 4-OH); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 169.5, 161.9, 134.8, 132.4, 128.77, 128.75, 128.3, 119.4, 95.6, 92.2, 77.2, 71.2, 70.5, 69.3, 67.8, 63.6, 52.7$; HR-ESI-MS (m/z): calcd for $\text{C}_{18}\text{H}_{19}\text{Cl}_3\text{N}_4\text{O}_6\text{Na}^+$ ($M + \text{Na}^+$): 515.0268, found: 515.0264.

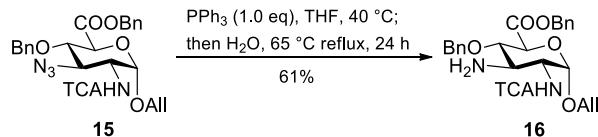
Benzyl (allyl 3-azido-4-O-benzyl-2,3-dideoxy-2-trichloroacetamido- α -D-glucopyranosid) uronate (15)



Benzylglucuronate **14** (20.3 g, 0.041 mol) was dissolved in anhydrous DCM (400 mL) under nitrogen and at 0 °C, BnBr (49 mL, 0.413 mol) and Ag₂O (28.5 g, 0.123 mol) were added. The reaction mixture was stirred at 0 °C for 5 h and then at room temperature for 28 h. After filtration through celite and concentration, the residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate 40 : 1 to 10 : 1 v/v) to afford product **15** as white solid (14.7 g, 0.025 mol, 61%). $[\alpha]_D^{20} = +66.3^\circ$ (c = 1.00, CHCl₃); IR ν_{max} (film) 3357, 2935, 2108, 1743, 1713, 1514, 1253, 1185, 1111, 1063, 1028, 820, 750, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.43-7.10 (m, 10H, 2Ph), 6.81 (d, *J* = 9.6 Hz, 1H, NH), 5.84 (dddd, *J* = 17.0, 10.3, 6.6, 5.4 Hz, 1H, CH=C), 5.32-5.22 (m, 2H, C=CH₂), 5.21 (s, 2H, COOCH₂Ph), 4.95 (d, *J* = 3.5 Hz, 1H, 1-H), 4.69 (d, *J* = 10.5 Hz, 1H, PhCH₂), 4.49 (d, *J* = 10.5 Hz, 1H, PhCH₂), 4.35-4.27 (m, 1H, 5-H), 4.24 (ddt, *J* = 12.8, 5.4, 1.4 Hz, 1H, OCH_a), 4.17-4.08 (m, 1H, 2-H), 4.04 (ddt, *J* = 12.8, 6.6, 1.2 Hz, 1H, OCH_b), 3.83-3.74 (m, 2H, 3-H, 4-H); ¹³C NMR (100 MHz, CDCl₃) δ = 168.4, 161.8, 136.9, 134.9, 132.4, 128.7, 128.59, 128.56, 128.5, 128.4, 128.24, 128.21, 128.14, 128.12, 119.44, 119.39, 95.5, 92.3, 78.2, 75.1, 71.0, 69.1, 67.6, 64.3,

53.0; HR-ESI-MS (m/z): calcd for $C_{25}H_{25}Cl_3N_4O_6Na^+$ ($M + Na^+$): 605.0737, found: 605.0731.

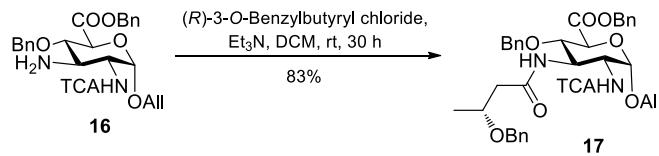
Benzyl (allyl 3-amino-4-O-benzyl-2,3-dideoxy-2-trichloroacetamido- α -D-glucopyranosid) uronate (16)



Compound **15** (90.5 mg, 0.155 mmol) was dissolved in THF (2.6 mL), PPh_3 (40.7 mg, 0.155 mmol) was added under nitrogen.

The mixture was stirred at 40 °C for 4 h. After the starting material was completely consumed, water (0.5 mL) was added. The mixture was refluxed at 65 °C overnight. When TLC showed the reaction was completed, the mixture was concentrated to give the crude product. The residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate 6 : 1 v/v) to furnish product **16** as colorless syrup (52.7 mg, 0.094 mmol, 61%). $[\alpha]_D^{20} = +43.1^\circ$ ($c = 1.00, CHCl_3$); IR ν_{max} (film) 2928, 1744, 1712, 1515, 1455, 1272, 1177, 1056, 821, 748, 697 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ = 7.43-7.06 (m, 10H, 2Ph), 6.93 (d, J = 8.6 Hz, 1H, NH), 5.84 (dd, J = 17.0, 10.4, 6.4, 5.2 Hz, 1H, $CH=C$), 5.34-5.16 (m, 4H, $C=CH_2$, $PhCH_2$), 5.03 (d, J = 3.6 Hz, 1H, 1-H), 4.49 (d, J = 1.3 Hz, 2H, $PhCH_2$), 4.31 (d, J = 9.4 Hz, 1H, 5-H), 4.24 (ddt, J = 12.9, 5.3, 1.5 Hz, 1H, OCH_a), 4.10-3.89 (m, 2H, OCH_b , 2-H), 3.56 (t, J = 9.3 Hz, 1H, 4-H), 3.14 (dd, J = 10.9, 9.2 Hz, 1H, 3-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.4, 162.3, 137.5, 135.0, 132.9, 128.7, 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 118.7, 95.4, 92.4, 80.9, 77.2, 74.7, 71.3, 69.0, 67.5, 54.9, 54.1; HR-ESI-MS (m/z): calcd for $C_{25}H_{28}Cl_3N_2O_6^+$ ($M + H^+$): 557.1013, found: 557.1005.

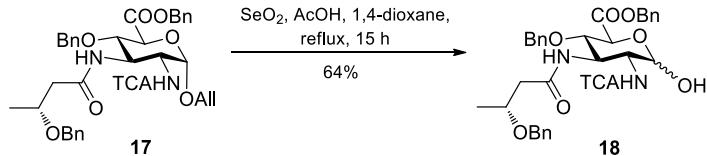
Benzyl (allyl 4-O-benzyl-3-N-(R)-3-O-benzylbutyryl-2,3-dideoxy-2-trichloroacetamido- α -D-glucopyranosid) uronate (17)



(R)-3-O-Benzylbutyric acid¹ (7.0 mg, 0.036 mmol) was dissolved in anhydrous DCM (0.7 mL) under nitrogen and cooled to 0 °C. Oxalyl chloride (24 μ L, 0.280 mmol) was added to the mixture. The reaction was stirred at room temperature for 4h. After evaporation of the solvent and excess reagent, the product was dried under vacuum to give (R)-3-O-benzylbutyryl chloride. Amine **16** (10 mg, 0.018 mmol) was dissolved in anhydrous DCM (1.1 mL) under nitrogen, and Et_3N (5 μ L, 0.036 mmol) and a solution of

(*R*)-3-*O*-benzylbutyryl chloride in anhydrous DCM (1.1 mL) were added. The reaction mixture was stirred at room temperature overnight. After concentration, the residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate 10 : 1 v/v) to give product **17** as yellow syrup (11.3 mg, 0.015 mmol, 83%). $[\alpha]_D^{20} = +30.8^\circ$ ($c = 0.30$, CHCl_3); IR ν_{max} (film) 2924, 2853, 1747, 1714, 1519, 1456, 1262, 1066, 1028, 820, 752, 697 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) $\delta = 7.48$ (d, $J = 7.7$ Hz, 1H, 2-NH), 7.40-7.22 (m, 13H, Ar-13H), 7.12-7.02 (m, 2H, Ar-2H), 6.29 (d, $J = 8.7$ Hz, 1H, 3-NH), 5.93-5.75 (m, 1H, $\text{CH}=\text{C}$), 5.32-5.16 (m, 4H, $\text{C}=\text{CH}_2$, PhCH_2), 5.05 (d, $J = 3.1$ Hz, 1H, 1-H), 4.57 (m, 2H, 3-H, PhCH_a), 4.37 (d, $J = 9.5$ Hz, 1H, 5-H), 4.33-4.16 (m, 4H, OCH_a , PhCH_b , PhCH_2), 4.03 (dd, $J = 12.8$, 6.5 Hz, 1H, OCH_b), 3.89 (td, $J = 8.1$, 4.1 Hz, 1H, 2-H), 3.80 (t, $J = 5.9$ Hz, 1H, butyryl-CH), 3.49 (t, $J = 9.8$ Hz, 1H, 4-H), 2.31 (d, $J = 5.4$ Hz, 2H, butyryl- CH_2), 1.20 (d, $J = 6.1$ Hz, 3H, butyryl- CH_3); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 172.6$, 169.1, 162.4, 137.9, 137.3, 134.9, 132.8, 128.7, 128.6, 128.5, 128.4, 128.0, 127.95, 127.9, 127.7, 118.9, 95.1, 92.1, 73.5, 71.7, 71.1, 70.5, 69.1, 67.5, 55.6, 50.0, 43.5, 29.7, 19.2; HR-ESI-MS (m/z): calcd for $\text{C}_{36}\text{H}_{39}\text{Cl}_3\text{N}_2\text{O}_8\text{Na}^+$ (M + Na^+): 755.1670, found: 755.1649.

Benzyl (4-*O*-benzyl-3-*N*-(*R*)-3-*O*-benzylbutyryl-2,3-dideoxy-2-trichloroacetamido-D-glucopyranosid) uronate (**18**)

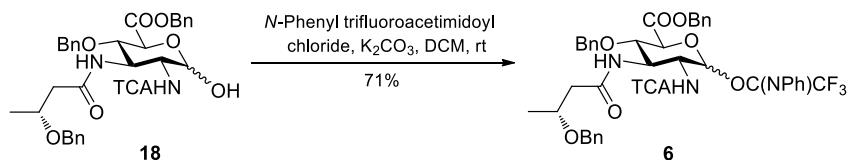


SeO_2 (31 mg, 0.279 mmol) was added to a solution of compound **17** (41.1 mg, 0.056 mmol) and AcOH (9.6 μL , 0.168 mmol) in 1,4-dioxane (5.6 mL) under nitrogen and the resulting suspension was refluxed for 15 h. After cooling to room temperature, the mixture was neutralized with Et_3N (0.5 mL) and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate 4 : 1 v/v) to give the hemiacetal **18** as white solid (24.8 mg, 0.036 mmol, 64%). $[\alpha]_D^{20} = +3.2^\circ$ ($c = 0.26$, CHCl_3); IR ν_{max} (film) 3299, 2923, 2851, 1734, 1698, 1648, 1547, 1357, 1220, 1067, 825, 694, 585 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) $\delta = 7.57$ (d, $J = 7.9$ Hz, 1H, NH), 7.39-7.27 (m, 13H, Ar-13H), 7.11-7.04 (m, 2H, Ar-2H), 6.30 (d, $J = 8.8$ Hz, 1H, NH), 5.42 (t, $J = 3.7$ Hz, 1H, 1-H), 5.20 (d, $J = 12.1$ Hz, 1H, PhCH_2), 5.16 (d, $J = 12.2$ Hz, 1H, PhCH_2),

4.70-4.53 (m, 3H, PhCH₂-1H, 3-H, 5-H), 4.33-4.18 (m, 3H, PhCH₂-1H, PhCH₂), 3.88 (ddd, *J* = 11.8, 7.9, 3.3 Hz, 1H, 2-H), 3.80 (h, *J* = 6.1 Hz, 1H, CHOBn), 3.49 (t, *J* = 9.8 Hz, 1H, 4-H), 3.29 (d, *J* = 3.2 Hz, 1H, 1-OH), 2.37-2.23 (m, 2H, CH₂CO), 1.20 (d, *J* = 6.2 Hz, 3H, CH₃).; ¹³C NMR (100 MHz, CDCl₃) δ = 172.8, 169.3, 162.6, 137.9, 137.4, 134.9, 128.7, 128.6, 128.55, 128.4, 128.0, 127.9, 127.78, 127.76, 92.1, 90.7, 73.4, 71.6, 70.8, 70.4, 67.5, 55.5, 49.8, 43.5, 29.7, 19.3; HR-ESI-MS (m/z): calcd for C₃₃H₃₅Cl₃N₂O₈Na⁺ (M + Na⁺): 715.1357, found: 715.1347.

Benzyl (4-*O*-benzyl-3-*N*-(*R*)-3-*O*-benzylbutyryl-2,3-dideoxy-2-trichloroacetamido-D-glucopyranosyl

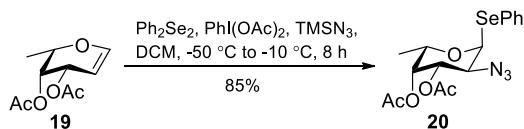
1-(*N*-phenyl)-2,2,2-trifluoroacetimidate) uronate (**6**)



A suspension of 1-OH compound **18** (35.7 mg, 0.051 mmol), K₂CO₃ (14.1 mg, 0.102 mmol) and *N*-phenyl trifluoroacetimidoyl chloride (15 μL, 0.100 mmol) in anhydrous DCM (0.5 mL) under nitrogen was stirred at room temperature overnight. The mixture was filtered with washing with DCM (4 × 2 mL). The filtrates were concentrated under vacuum to give a residue, which was purified by silica gel column chromatography (*n*-hexane : ethyl acetate 5 : 1 v/v) to afford product **6** as colorless syrup (31.1 mg, 0.036 mmol, 71%). HR-ESI-MS (m/z): calcd for C₄₁H₃₉Cl₃F₃N₃O₈Na⁺ (M + Na⁺): 886.1653, found: 886.1614.

Part 2. Synthesis of L-fucosamine **8** and **8'**.

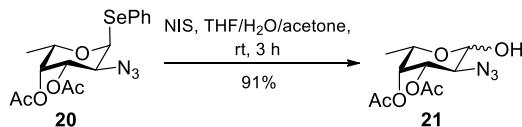
Phenyl 2-azido-3,4-di-*O*-acetyl-2-deoxy-1-seleno- α -L-fucopyranoside (**20**)



To a solution of known fucal **19**² (3.6 g, 16.8 mmol) and diphenyl diselenide (5.3 g, 17.0 mmol) in anhydrous DCM (85 mL) at -50 °C was added (diacetoxyiodo) benzene (BAIB) (5.4 g, 16.8 mmol) followed by trimethylsilyl azide (4.5 mL, 34.0 mmol) under nitrogen. The reaction mixture was warmed to -10 °C over a period of 1.5 h by which time no starting material was observed by

TLC. The solvent was removed under vacuum to obtain the crude product as reddish brown oil. The residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate 20 : 1 v/v) to afford the compound **20** as a clear oil (5.9 g, 14.3 mmol, 85%). $[\alpha]_D^{20} = -178.7^\circ$ (c = 1.00, CHCl₃); IR ν_{max} (film) 2110, 1747, 1368, 1231, 1084, 1020, 908, 740, 692, 546 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.62-7.53 (m, 2H, Ph-2H), 7.33-7.23 (m, 3H, Ph-3H), 5.95 (d, *J* = 5.4 Hz, 1H, 1-H), 5.32 (dd, *J* = 3.3, 1.2 Hz, 1H, 4-H), 5.13 (dd, *J* = 10.8, 3.2 Hz, 1H, 3-H), 4.53-4.46 (m, 1H, 5-H), 4.23 (dd, *J* = 10.9, 5.4 Hz, 1H, 2-H), 2.17 (s, 3H, CH₃CO), 2.06 (s, 3H, CH₃CO), 1.09 (d, *J* = 6.5 Hz, 3H, 6-CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 170.4, 169.8, 134.8, 129.3, 128.2, 128.1, 84.6, 71.8, 70.2, 67.6, 58.9, 20.8, 20.7, 15.9; HR-ESI-MS (m/z): calcd for C₁₆H₁₉N₃O₅SeNa⁺ (M + Na⁺): 436.0388, found: 436.0378.

2-Azido-3,4-di-O-acetyl-2-deoxy-L-fucopyranose (21)

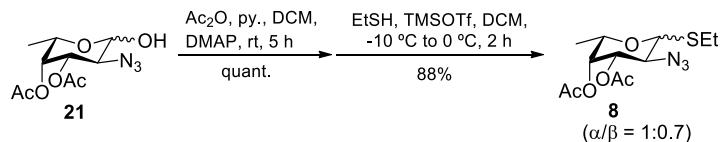


A solution of azidoselenide **20** (50 mg, 0.121 mmol) in a mixture of THF, water and acetone (1 : 1 : 0.5; 0.3 mL : 0.3 mL : 0.15 mL) was cooled to 0 °C under nitrogen. *N*-iodosuccinimide (55 mg, 0.244 mmol) was added and the reaction mixture stirred at room temperature for 3 h. The reaction was diluted with ethyl acetate (2 mL) and the organic layer washed with sat. aq. Na₂S₂O₃ (3 × 2 mL) and brine (2 mL) respectively. The organic layer was dried over Na₂SO₄, filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate 5 : 1 v/v) to afford hemiacetal **21** as yellow syrup (30 mg, 0.110 mmol, 91%). $[\alpha]_D^{20} = -110.4^\circ$ (c = 0.50, CHCl₃); IR ν_{max} (film) 3426, 2920, 2114, 1750, 1371, 1240, 1081, 910, 824 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 5.42-5.36 (m, 2H, 1 α -H, 3 α -H), 5.31 (dd, *J* = 3.3, 1.3 Hz, 1H, 4 α -H), 5.19 (dd, *J* = 3.3, 0.8 Hz, 1H, 4 β -H), 4.82 (dd, *J* = 10.8, 3.3 Hz, 1H, 3 β -H), 4.67 (dd, *J* = 7.9, 5.4 Hz, 1H, 1 β -H), 4.44-4.35 (m, 1H, 5 α -H), 3.81 (qd, *J* = 6.4, 1.0 Hz, 1H, 5 β -H), 3.74 (ddd, *J* = 11.1, 3.7, 0.7 Hz, 1H, 2 α -H), 3.63 (dd, *J* = 10.9, 7.9 Hz, 1H, 2 β -H), 3.49 (d, *J* = 5.4 Hz, 1H, 1 β -OH), 2.94 (dd, *J* = 3.3, 1.1 Hz, 1H, 1 α -OH), 2.19 (s, 3H, β -CH₃CO), 2.18 (s, 3H, α -CH₃CO), 2.06 (s, 3H, α -CH₃CO), 2.06 (s, 3H, β -CH₃CO), 1.22 (d, *J* = 6.4 Hz, 3H, 6 β -CH₃), 1.15 (d, *J* = 6.6 Hz, 3H, 6 α -CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 170.51, 170.49,

170.0, 96.3, 92.4, 71.6, 70.7, 69.5, 69.4, 68.8, 64.9, 62.0, 58.0, 29.7, 20.8, 20.69, 20.68, 16.2, 16.0; HR-ESI-MS (m/z): calcd for

$\text{C}_{10}\text{H}_{15}\text{N}_3\text{O}_6\text{Na}^+$ ($\text{M} + \text{Na}^+$): 296.0859, found: 296.0852.

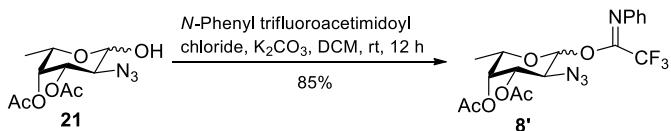
Ethyl 2-azido-3,4-di-O-acetyl-2-deoxy-1-thio-L-fucopyranoside (8)



To a solution of hemiacetal **21** (44.4 mg, 0.16 mmol) in 4:1 (v/v) anhydrous DCM-pyridine (1.6 mL) under nitrogen, Ac₂O (150 µL, 1.59 mmol) was added dropwise at 0 °C. After addition of DMAP (cat.), the solution was stirred at room temperature. The progress was monitored by TLC analysis. The mixture was partitioned with satd. aq. NaHCO₃ (4 mL), and the combined organic layers were dried (Na₂SO₄), filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate 10 : 1 v/v) to give 1-OAc fucoside (50.5 mg, 0.16 mmol, quant.).

The 1-OAc fucoside (50.5 mg, 0.16 mmol) and ethanethiol (18 μ L, 0.25 mmol) were dissolved in anhydrous DCM (1.6 mL), and 4 Å molecular sieves (flame dried) were added under nitrogen. The mixture was cooled to -10 °C and then TMSOTf (35 μ L, 0.19 mmol) was added. The reaction mixture was stirred at 0 °C for 2 h. After starting material had been completely consumed, the reaction was quenched with Et₃N (0.1 mL). The solvent was evaporated, and the residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate 10 : 1 v/v) to give product **8** (44.0 mg, 0.14 mmol, 88%, $\alpha/\beta = 1:0.7$). ¹H NMR (400 MHz, CDCl₃) δ = 5.45 (d, J = 5.6 Hz, 1H, 1 α -H), 5.28 (dd, J = 3.4, 1.2 Hz, 1H, 4 α -H), 5.26-5.21 (m, 1H, 4 β -H), 5.13 (dd, J = 11.0, 3.3 Hz, 1H, 3 α -H), 4.88 (dd, J = 10.2, 3.3 Hz, 1H, 3 β -H), 4.49 (qd, J = 6.5, 1.3 Hz, 1H, 5 α -H), 4.37 (d, J = 10.2 Hz, 1H, 1 β -H), 4.22 (dd, J = 11.0, 5.5 Hz, 1H, 2 α -H), 3.82-3.72 (m, 1H, 5 β -H), 3.67 (t, J = 10.2 Hz, 1H, 2 β -H), 2.87-2.71 (m, 2H, β -SCH₂CH₃), 2.61 (dddd, J = 20.3, 12.9, 7.4, 5.4 Hz, 2H, α -SCH₂CH₃), 2.18 (s, 5H, 2CH₃CO), 2.05 (s, 6H, 2CH₃CO), 1.34 (t, J = 7.4 Hz, 2H, β -SCH₂CH₃), 1.31 (t, J = 6.4 Hz, 3H, α -SCH₂CH₃), 1.21 (d, J = 6.5 Hz, 2H, 6 β -CH₃), 1.16 (d, J = 6.5 Hz, 3H, 6 α -CH₃).

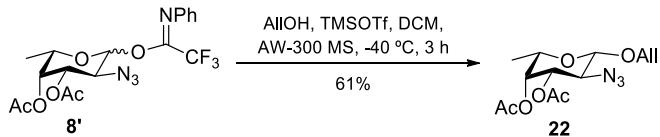
2-Azido-3,4-di-O-acetyl-2-deoxy-L-fucopyranosyl 1-(*N*-phenyl)-2,2,2-trifluoroacetimidate (8')



A suspension of hemiacetal **21** (70 mg, 0.256 mmol), K₂CO₃ (71 mg, 0.514 mmol) and *N*-phenyl trifluoroacetimidoyl chloride (77 µL, 0.516 mmol) in anhydrous DCM (2.6 mL) under nitrogen was stirred at room temperature overnight. The mixture was diluted with DCM (4 × 3 mL) and filtered. The filtrate was concentrated under vacuum to give a residue, which was purified by silica gel column chromatography (*n*-hexane : ethyl acetate 10 : 1 *v/v*) to afford imidate **8'** (96.7 mg, 0.218 mmol, 85%). ¹H NMR (400 MHz, CDCl₃) δ = 7.40-6.75 (m, 5H, Ph), 5.58 (m, 1H, 1-H), 5.20 (m, 1H, 4-H), 4.84 (m, 1H, 3-H), 3.90 (t, *J* = 9.3 Hz, 1H, 2-H), 3.74 (m, 1H, 5-H), 2.20 (s, 3H, CH₃CO), 2.07 (s, 3H, CH₃CO), 1.21 (d, *J* = 6.4 Hz, 3H, 6-CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 170.3, 169.7, 143.0, 128.8, 124.6, 119.2, 95.7, 71.5, 70.4, 69.1, 59.9, 20.6, 15.9.

Part 3. Model introduction of an acetamidino group to 23.

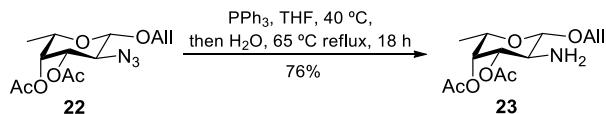
Allyl 2-azido-3,4-di-O-acetyl-2-deoxy- β -L-fucopyranoside (22)



Trifluoroacetimidate donor **8'** (56 mg, 0.126 mmol) and allyl alcohol (17 μ L, 0.250 mmol) were dissolved in anhydrous DCM (4 mL) and flame-dried molecular sieves (AW-300) were added under nitrogen. The mixture was stirred at room temperature for 30 min. After cooling to -40 °C, TMSOTf (2.4 μ L, 0.013 mmol) was added. The reaction mixture was allowed to warm gradually and stirred for 3 h. When TLC showed the reaction was complete, Et₃N (5 drops) was added to neutralize the reaction under 0 °C, and filtered (celite). The reaction mixture was washed with satd. aq. NaHCO₃ (5 mL), extracted with DCM (4 \times 5 mL), and the combined organic solvent was removed under vacuum. The residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate 10 : 1 v/v) to give product **22** as yellow syrup (24 mg, 0.077 mmol, 61%). $[\alpha]_D^{20} = +28.1^\circ$ (c = 0.60, CHCl₃);

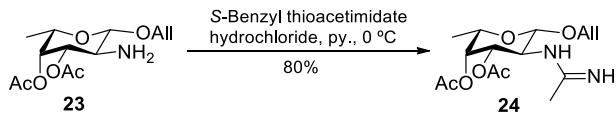
5.2 Hz, 1H, CH=C), 5.36 (dq, J = 17.2, 1.6 Hz, 1H, C=CH_a), 5.25 (dq, J = 10.4, 1.4 Hz, 1H, C=CH_b), 5.18 (dd, J = 3.4, 1.1 Hz, 1H, 4-H), 4.78 (dd, J = 10.9, 3.4 Hz, 1H, 3-H), 4.44 (ddt, J = 12.8, 5.2, 1.5 Hz, 1H, OCH_a), 4.39 (d, J = 8.0 Hz, 1H, 1-H), 4.16 (ddt, J = 12.8, 6.2, 1.4 Hz, 1H, OCH_b), 3.74 (qd, J = 6.4, 1.1 Hz, 1H, 5-H), 3.69 (dd, J = 10.9, 8.0 Hz, 1H, 2-H), 2.17 (s, 3H, CH₃CO), 2.05 (s, 3H, CH₃CO), 1.22 (d, J = 6.4 Hz, 3H, 6-CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 170.5, 169.9, 133.2, 118.1, 100.9, 71.5, 70.5, 69.6, 69.1, 60.8, 20.7, 16.1; HR-ESI-MS (m/z): calcd for C₁₃H₁₉N₃O₆Na⁺ (M + Na⁺): 336.1172, found 336.1168.

Allyl 2-amino-3,4-di-O-acetyl-2-deoxy-β-L-fucopyranoside (23)



Compound **22** (12 mg, 0.038 mmol) was dissolved in THF (0.5 mL) under nitrogen, and PPh₃ (13 mg, 0.050 mmol) was added. The mixture was stirred at 40 °C for 2 h. After the starting material had been completely consumed, water (10 µL) was added. The mixture was refluxed at 65 °C for 18 h. When TLC showed the reaction was completed, the mixture was concentrated to give crude amine. The residue was purified by silica gel column chromatography (DCM : MeOH 80 : 1 v/v) to furnish product **23** as white solid (8.2 mg, 0.029 mmol, 76%). $[\alpha]_D^{20} = +1.1^\circ$ (c = 0.40, CHCl₃); IR ν_{max} (film) 2985, 1743, 1370, 1245, 1173, 1073, 931 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 5.95 (ddddd, J = 17.0, 10.2, 6.5, 5.3, 1.3 Hz, 1H, CH=C), 5.37-5.20 (m, 2H, C=CH₂), 5.20-5.17 (m, 1H, 4-H), 4.81 (dd, J = 10.8, 3.3 Hz, 1H, 3-H), 4.47-4.37 (m, 1H, OCH_a), 4.32 (d, J = 7.9 Hz, 1H, 1-H), 4.12 (ddq, J = 12.6, 6.4, 1.4 Hz, 1H, OCH_b), 3.88-3.74 (m, 1H, 5-H), 3.27-3.09 (m, 1H, 2-H), 2.14 (s, 3H, CH₃CO), 2.04 (s, 3H, CH₃CO), 2.00-1.81 (br, 2H, NH₂), 1.22 (d, J = 6.4 Hz, 3H, 6-CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 170.7, 170.4, 133.7, 118.0, 102.7, 77.2, 74.0, 70.4, 69.6, 69.1, 51.4, 20.9, 20.7, 16.3; HR-ESI-MS (m/z): calcd for C₁₃H₂₁NO₆Na⁺ (M + Na⁺): 310.1267, found: 310.1244.

Allyl 2-acetamidino-3,4-di-O-acetyl-2-deoxy-β-L-fucopyranoside (24)

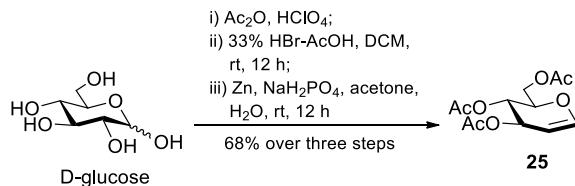


A solution of aminosugar **23** (8.0 mg, 27.8 µmol) in anhydrous pyridine (0.3 mL) was cooled to 0 °C. S-Benzyl thioacetimidate hydrochloride (5.7 mg, 28.3 µmol) was added to the solution. The mixture was stirred at 0 °C for 5 h under argon,

and the solvent was evaporated. The residue was purified by silica gel column chromatography (DCM : MeOH 10 : 1 v/v) to give product **24** as colorless syrup (7.3 mg, 22.2 μ mol, 80%). $[\alpha]_D^{20} = -20.6^\circ$ ($c = 0.50$, CHCl₃); IR ν_{max} (film) 3021, 1745, 1683, 1638, 1367, 1239, 1170, 1070, 751 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 10.75-9.48 (m, 2H, 2NH), 5.87 (dtd, $J = 17.5, 9.8, 8.5, 5.9$ Hz, 1H, CH=C), 5.53-5.12 (m, 4H, C=CH₂, 3-H, 4-H), 4.73-4.65 (d, $J = 8.2$ Hz, 1H, 1-H), 4.38 (dd, $J = 12.5, 5.1$ Hz, 1H, OCH_a), 4.13 (td, $J = 12.3, 11.2, 6.3$ Hz, 1H, OCH_b), 3.98 (dq, $J = 19.0, 6.4$ Hz, 1H, 5-H), 3.72-3.57 (m, 1H, 2-H), 2.47 (s, 3H, Am-CH₃), 2.19 (s, 3H, CH₃CO), 2.00 (s, 3H, CH₃CO), 1.24 (d, $J = 6.4$ Hz, 3H, 6-CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 170.53, 170.49, 169.9, 169.8, 169.7, 167.8, 133.1, 132.8, 119.1, 118.5, 100.2, 100.0, 70.78, 70.76, 70.6, 70.4, 69.4, 69.2, 69.0, 68.9, 54.8, 54.6, 21.0, 20.8, 20.7, 19.2, 17.1, 16.1; HR-ESI-MS (m/z): calcd for C₁₅H₂₅N₂O₆⁺ (M + H⁺): 329.1713, found: 329.1714.

Part 4. Synthesis of D-quinovosamine **9**.

3,4,6-Tri-O-acetyl-D-glucal (**25**)



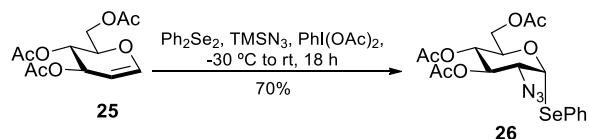
To a solution of D-glucose (20 g, 0.111 mol) in Ac₂O (80 mL, 0.846 mol) under nitrogen, HClO₄ (0.2 mL, 3.5 mmol) was added at 0 °C. After stirring for 30 min at room temperature, the mixture was poured into 0.5 L ice water and extracted with DCM (3 × 150 mL). The combined organic phase was washed with satd. aq. NaHCO₃ (3 × 400 mL), brine (400 mL) and dried over Na₂SO₄. The organic layer was concentrated to 200 mL and directly used in next step.

To a solution of peracetylglucose in anhydrous DCM (200 mL) under nitrogen, HBr-AcOH (33% w/w, 80 mL, 0.463 mol) was added dropwise during 30 min at 0 °C. After stirring for 12 h at room temperature, the reaction mixture was diluted with 200 mL DCM, washed with ice water (3 × 400 mL), satd. aq. NaHCO₃ (3 × 400 mL), brine (400 mL), and dried over Na₂SO₄. After concentration under high vacuum, the crude bromide was used directly in the next step without further purification.

To a solution of the crude bromide in acetone (200 mL), 250 mL satd. aq. NaH₂PO₄ was added under nitrogen. After

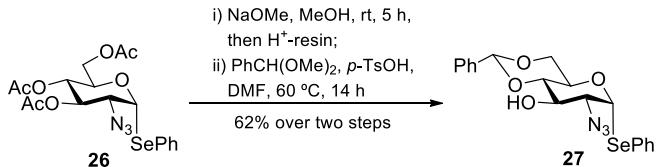
portion-wisely addition of zinc powder (80 g, 1.223 mol) during 30 min, the reaction mixture was stirred for 12 h. When TLC showed that the reaction was complete, the solution was filtered through a celite bed and the filtrate was extracted with ethyl acetate (3 × 200 mL). The combined organic layer was washed with satd. aq. NaHCO₃ (3 × 200 mL), dried over Na₂SO₄ and concentrated. The residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate 5 : 1 v/v) to give product **25** as slightly yellow syrup (20.4 g, 0.075 mol, 68% over three steps). [α]_D²⁰ = -20.5° (c = 1.00, CHCl₃); IR ν_{max} (film) 2918, 1736, 1648, 1368, 1217, 1031, 602 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 6.47 (dd, *J* = 6.1, 1.3 Hz, 1H, 1-H), 5.35 (ddd, *J* = 5.5, 3.1, 1.1 Hz, 1H, 3-H), 5.23 (dd, *J* = 7.6, 5.7 Hz, 1H, 4-H), 4.85 (dd, *J* = 6.2, 3.3 Hz, 1H, 2-H), 4.41 (dd, *J* = 12.0, 5.7 Hz, 1H, 6-CH_a), 4.26 (ddd, *J* = 8.1, 5.6, 3.1 Hz, 1H, 5-H), 4.20 (dd, *J* = 12.0, 3.1 Hz, 1H, 6-CH_b), 2.10 (s, 3H, CH₃CO), 2.08 (s, 3H, CH₃CO), 2.05 (s, 3H, CH₃CO); ¹³C NMR (100 MHz, CDCl₃) δ = 170.6, 170.4, 169.6, 145.6, 99.0, 74.0, 67.5, 67.2, 61.4, 21.0, 20.8, 20.7; HR-ESI-MS (m/z): calcd for C₁₂H₁₆O₇Na⁺ (M + Na⁺): 295.0794, found: 295.0785.

Phenyl 2-azido-3,4,6-tri-O-acetyl-2-deoxy-1-seleno- α -D-glucopyranoside (26)



Glucal **25** (29.4 g, 108 mmol) was dissolved in anhydrous DCM (500 mL) and diphenyl diselenide (33.7 g, 108 mmol) was added. The solution was cooled to -30 °C under argon and (diacetoxymethyl) benzene (BAIB) (34.8 g, 108 mmol) and trimethylsilyl azide (28.6 mL, 216 mmol) were added. The solution was stirred overnight and allowed to warm to room temperature. After complete conversion of the starting material, the solution was extracted with satd. aq. NaHCO₃ (3 × 250 mL), dried over Na₂SO₄ and the solvent was removed under vacuum. The residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate 5 : 1 v/v) to give product **26** as slightly yellow syrup (35.6 g, 76 mmol, 70%). $[\alpha]_D^{20} = +204.2^\circ$ (c = 1.00, CHCl₃); IR ν_{max} (film) 2110, 1748, 1367, 1228, 1054, 740, 692 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.61-7.55 (m, 2H, Ph-2H), 7.35-7.27 (m, 3H, Ph-3H), 5.93 (d, *J* = 5.5 Hz, 1H, 1-H), 5.28 (dd, *J* = 10.3, 9.2 Hz, 1H, 4-H), 5.05 (dd, *J* = 10.2, 9.3 Hz, 1H, 3-H), 4.50 (ddd, *J* = 10.2, 4.9, 2.2 Hz, 1H, 5-H), 4.28 (dd, *J* = 12.4, 4.9 Hz, 1H, 6-CH₃), 4.06 (dd, *J* = 10.2, 5.5 Hz, 1H, 2-H), 3.95 (dd, *J* = 12.4, 2.2 Hz, 1H,

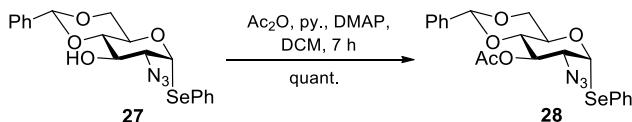
Phenyl 2-azido-4,6-O-benzylidene-2-deoxy-1-seleno- α -D-glucopyranoside (27)



Triacetylglucoside **26** (65.6 g, 139 mmol) was dissolved in MeOH (280 mL), NaOMe (3.8 g, 70 mmol) was added and the solution was stirred at room temperature for 5 h. The solution was neutralized with Amberlite IR 120 (H^+) ion exchange resin and filtered through a cotton plug. The filtrate was evaporated and used directly in next step.

The crude trihydroxyglucose was dissolved in 250 mL anhydrous DMF under nitrogen, followed by the addition of benzaldehyde dimethyl acetyl (25.1 mL, 167 mmol) and *p*-TsOH (3.18 g, 16.7 mmol) at room temperature. The reaction mixture was stirred at 60 °C for 7-10 h, and was concentrated on a rotary evaporator to remove the MeOH formed. The reaction was monitored by TLC. These steps were repeated until TLC showed all starting material consumed. DMF was then removed under reduced pressure, and the residue was diluted with ethyl acetate (300 mL) and washed with satd. aq. NaHCO₃ (3 × 150 mL). The aqueous phase was extracted with ethyl acetate (3 × 100 mL), and the combined organic phase was washed with water (3 × 100 mL) and brine (150 mL) and dried over Na₂SO₄. After evaporation and recrystallization (petroleum ether : ethyl acetate), pure product **27** (37.2 g, 86.0 mmol, 62% over two steps) was obtained in the form of white solid. $[\alpha]_D^{20} = + 252.7^\circ$ ($c = 0.80$, CHCl₃); IR ν_{max} (film) 3445, 2108, 1476, 1264, 1088, 1068, 966, 736, 699, 588 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.68-7.27 (m, 10H, 2Ph), 5.86 (d, $J = 5.4$ Hz, 1H, 1-H), 5.55 (s, 1H, PhCH), 4.30 (td, $J = 9.9, 5.0$ Hz, 1H, 5-H), 4.16 (dd, $J = 10.4, 5.0$ Hz, 1H, 6-CH_a), 4.03 (td, $J = 9.4, 2.7$ Hz, 1H, 3-H), 3.89 (dd, $J = 9.7, 5.4$ Hz, 1H, 2-H), 3.74 (t, $J = 10.3$ Hz, 1H, 6-CH_b), 3.59 (t, $J = 9.4$ Hz, 1H, 4-H), 2.79 (d, $J = 2.7$ Hz, 1H, 3-OH); ¹³C NMR (100 MHz, CDCl₃) δ = 136.8, 134.9, 129.5, 129.3, 128.4, 128.2, 128.0, 126.3, 102.2, 84.9, 81.3, 71.7, 68.3, 64.9, 64.6; HR-ESI-MS (m/z): calcd for C₁₉H₁₀N₃O₄SeNa⁺ (M + Na⁺): 456.0438, found: 456.0422.

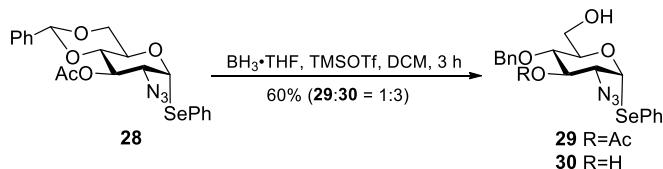
Phenyl 2-azido-3-O-acetyl-4,6-O-benzylidene-2-deoxy-1-seleno- α -D-glucopyranoside (28)



To a solution of compound **27** (29 g, 67.1 mmol) and DMAP (180 mg, 1.5 mmol) in 4:1 (v/v) anhydrous DCM-Pyridine (336 mL) under nitrogen, Ac₂O (12.7 mL, 134.4 mmol) was added dropwise at 0 °C. After stirring for 7 h at room temperature, the mixture was partitioned with satd. aq. NaHCO₃ (2 × 300 mL). The organic phase was washed with water (2 × 300 mL) and dried over Na₂SO₄. After removal of solvent, the residue was co-evaporated with toluene to give product **28** as white solid (31.8 g, 67.0 mmol, quant.). [α]_D²⁰ = + 176.0° (c = 1.00, CHCl₃); IR ν_{max} (film) 2106, 1748, 1368, 1227, 1210, 1094, 1036, 972, 738, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.68-7.23 (m, 10H, 2Ph), 5.92 (d, J = 5.5 Hz, 1H, 1-H), 5.51 (s, 1H, PhCH), 5.48 (dd, J = 9.8 Hz, 1H, 3-H), 4.39 (td, J = 9.8, 4.9 Hz, 1H, 5-H), 4.16 (dd, J = 10.4, 4.9 Hz, 1H, 6-CH_a), 4.05 (dd, J = 10.0, 5.5 Hz, 1H, 2-H), 3.76 (t, J = 10.3 Hz, 1H, 6-CH_b), 3.69 (t, J = 9.6 Hz, 1H, 4-H), 2.16 (s, 3H, CH₃CO); ¹³C NMR (100 MHz, CDCl₃) δ = 169.5, 136.7, 135.1, 129.3, 129.2, 128.32, 128.26, 127.6, 126.1, 101.6, 84.3, 79.1, 71.3, 68.2, 65.3, 63.0, 20.8; HR-ESI-MS (m/z): calcd for C₂₁H₂₁N₃O₅SeNa⁺ (M + Na⁺): 498.0544, found: 498.0537.

Phenyl 2-azido-3-O-acetyl-4-O-benzyl-2-deoxy-1-seleno- α -D-glucopyranoside (29)

Phenyl 2-azido-4-O-benzyl-2-deoxy-1-seleno- α -D-glucopyranoside (30)



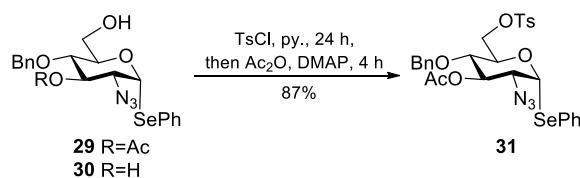
Compound **28** (1 g, 2.108 mmol) was co-evaporated with toluene and dissolved under argon in anhydrous DCM (18 mL). A 1 M solution of BH₃·THF (12.4 mL, 12.4 mmol) was added and the solution was cooled to 0 °C. After 10 min, TMSOTf (190 μL, 1.050 mmol) was added dropwise, the reaction mixture was stirred and allowed to warm to room temperature. After complete conversion of the starting material (TLC), the solution was diluted with DCM (60 mL) and extracted with satd. aq. NaHCO₃ (3 × 80 mL). The organic phase was dried over Na₂SO₄ and the solvent was removed under vacuum. The residue was purified by silica gel

column chromatography (*n*-hexane : ethyl acetate 4 : 1 *v/v*) to give a mixture of **29** as slightly yellow syrup (149 mg, 0.313 mmol, 15%) and **30** as slightly yellow syrup (408 mg, 0.939 mmol, 45%).

29: $[\alpha]_D^{20} = +159.5^\circ$ ($c = 1.00$, CHCl_3); IR ν_{max} (film) 3459, 2924, 2106, 1748, 1364, 1228, 1088, 737, 694 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) $\delta = 7.70\text{-}7.14$ (m, 10H, 2Ph), 5.87 (d, $J = 5.4$ Hz, 1H, 1-H), 5.38 (t, $J = 9.8$ Hz, 1H, 3-H), 4.74-4.54 (m, 2H, PhCH_2), 4.19 (dt, $J = 9.9, 2.9$ Hz, 1H, 6- CH_a), 3.90 (dd, $J = 10.3, 5.4$ Hz, 1H, 2-H), 3.72 (m, 3H, 4-H, 5-H, 6- CH_b), 2.04 (s, 3H, CH_3CO), 1.64 (dd, $J = 7.7, 5.2$ Hz, 1H, 6-OH); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 169.7, 137.4, 134.9, 129.2, 128.6, 128.2, 128.1, 128.0, 127.9, 84.0, 75.4, 74.7, 74.2, 73.8, 63.0, 61.1, 20.9$; HR-ESI-MS (m/z): calcd for $\text{C}_{21}\text{H}_{23}\text{N}_3\text{O}_5\text{SeNa}^+$ ($M + \text{Na}^+$): 500.0701, found: 500.0682.

30: $[\alpha]_D^{20} = +220.6^\circ$ ($c = 1.00$, CHCl_3); IR ν_{max} (film) 3384, 2920, 2107, 1260, 1066, 982, 734, 692, 572 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) $\delta = 7.61\text{-}7.27$ (m, 10H, 2Ph), 5.82 (d, $J = 5.3$ Hz, 1H, 1-H), 4.77 (s, 2H, PhCH_2), 4.11 (dt, $J = 9.9, 3.2$ Hz, 1H, 5-H), 3.88 (ddd, $J = 10.2, 9.8, 2.5$ Hz, 1H, 3-H), 3.78-3.69 (m, 3H, 2-H, 6- CH_2), 3.55 (dd, $J = 9.9, 8.8$ Hz, 1H, 4-H), 2.33 (d, $J = 3.4$ Hz, 1H, 3-OH), 1.81 (s, 1H, 6-OH); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 137.8, 134.9, 129.3, 128.8, 128.3, 128.2, 128.1, 84.6, 77.5, 77.4, 77.3, 77.1, 76.8, 75.1, 74.8, 73.6, 64.6, 61.4$; HR-ESI-MS (m/z): calcd for $\text{C}_{19}\text{H}_{21}\text{N}_3\text{O}_4\text{SeNa}^+$ ($M + \text{Na}^+$): 458.0595, found: 458.0579.

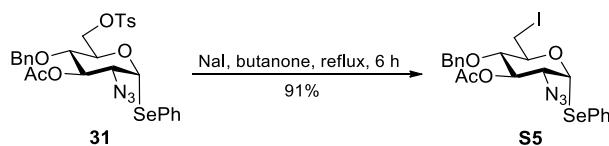
Phenyl 2-azido-3-*O*-acetyl-4-*O*-benzyl-2-deoxy-6-*O*-(*p*-toluenesulfonyl)-1-seleno- α -D-glucopyranoside (**31**)



To a solution of 6-hydroxyglucopyranoside **29** (1.44 g, 3.02 mmol) and 3,6-dihydroxyglucopyranoside **30** (5.9 g, 13.58 mmol) in anhydrous pyridine (110 mL), *p*-toluene-sulfonyl chloride (8.0 g, 41.96 mmol) was added under nitrogen. The reaction mixture was stirred at room temperature overnight, when TLC showed that the starting materials were completely consumed. Ac_2O (13 mL, 0.138 mol) and DMAP (cat.) were added at 0 °C. The reaction mixture was stirred at room temperature for 5 h. The mixture was concentrated, diluted with DCM (150 mL), washed with satd. aq. NaHCO_3 (3×80 mL) and water (3×80 mL), then dried (Na_2SO_4), filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate 5 : 1 *v/v*)

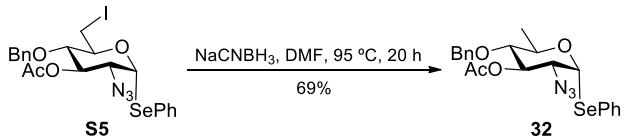
to give product **31** as yellow syrup (9.06 g, 14.37 mmol, 87%). $[\alpha]_D^{20} = +123.2^\circ$ ($c = 1.00$, CHCl_3); IR ν_{max} (film) 2107, 1749, 1363, 1214, 1176, 1094, 977, 939, 815, 738, 681 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.83–7.14 (m, 14H, 3Ph), 5.76 (d, $J = 5.4$ Hz, 1H, 1-H), 5.38–5.22 (m, 1H, 3-H), 4.53 (s, 2H, PhCH_2), 4.38–4.21 (m, 2H, 5-H, 6- CH_a), 4.09–3.97 (m, 1H, 6- CH_b), 3.85 (dd, $J = 10.3$, 5.4 Hz, 1H, 2-H), 3.65 (t, $J = 9.1$ Hz, 1H, 4-H), 2.42 (s, 3H, PhCH_3), 2.05 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, CDCl_3) δ = 169.5, 145.0, 137.0, 134.5, 132.6, 129.8, 129.2, 128.6, 128.2, 128.12, 128.05, 128.0, 127.9, 84.1, 75.3, 74.9, 74.1, 71.3, 67.8, 62.7, 21.7, 20.8; HR-ESI-MS (m/z): calcd for $\text{C}_{28}\text{H}_{29}\text{N}_3\text{O}_7\text{SSeNa}^+$ ($M + \text{Na}^+$): 654.0789, found: 654.0795.

Phenyl 2-azido-3-O-acetyl-4-O-benzyl-2,6-dideoxy-6-iodo-1-seleno- α -D-glucopyranoside (S5)



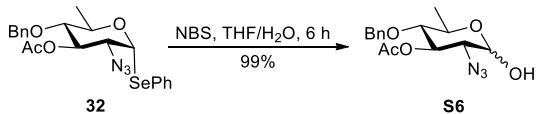
Tosylate compound **31** (401 mg, 0.64 mmol) was refluxed for 6 h in butanone (8 mL) together with NaI (480 mg, 3.20 mmol) under nitrogen. After cooling to room temperature, ethyl acetate (20 mL) was added and the mixture was washed with aq. 1 M $\text{Na}_2\text{S}_2\text{O}_3$ solution (2×15 mL) and water (2×15 mL). The organic phase was dried (Na_2SO_4), filtered, and concentrated. The residue was purified by silica gel column chromatography (*n*-hexane : ethyl acetate 10 : 1 v/v) to give product **S5** as yellow syrup (340 mg, 0.58 mmol, 91%). $[\alpha]_D^{20} = +170.3^\circ$ ($c = 1.20$, CHCl_3); IR ν_{max} (film) 2928, 2108, 1746, 1367, 1226, 1091, 1044, 739, 694 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.63–7.55 (m, 2H, Ar-2H), 7.41–7.23 (m, 8H, Ar-8H), 5.89 (d, $J = 5.3$ Hz, 1H, 1-H), 5.41 (t, $J = 9.7$ Hz, 1H, 3-H), 4.71 (q, $J = 11.0$ Hz, 2H, PhCH_2), 3.94 (dd, $J = 10.3, 5.4$ Hz, 1H, 2-H), 3.87 (dt, $J = 9.1, 3.2$ Hz, 1H, 5-H), 3.59 (t, $J = 9.2$ Hz, 1H, 4-H), 3.48 (dd, $J = 11.1, 3.9$ Hz, 1H, 6- CH_a), 3.32 (dd, $J = 11.1, 2.8$ Hz, 1H, 6- CH_b), 2.06 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, CDCl_3) δ = 169.6, 137.2, 134.6, 129.3, 128.7, 128.2, 128.1, 128.0, 127.9, 84.0, 79.9, 75.1, 73.8, 71.3, 62.9, 20.9, 7.3; HR-ESI-MS (m/z): calcd for $\text{C}_{21}\text{H}_{22}\text{IN}_3\text{O}_4\text{SeNa}^+$ ($M + \text{Na}^+$): 609.9718, found: 609.9698

Phenyl 2-azido-3-O-acetyl-4-O-benzyl-2-deoxy-1-seleno- α -D-quinovopyranoside (32)



To a solution of compound **S5** (150 mg, 0.26 mmol) in anhydrous DMF (3.5mL) under nitrogen, sodium cyanoborohydride (82 mg, 1.30 mmol) was added and the reaction mixture stirred overnight at 95 °C. The mixture was poured into water and extracted twice with ethyl acetate. The organic phase was washed with water, dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography (toluene) to give product **32** as white solid (84 mg, 0.18 mmol, 69%). $[\alpha]_D^{20} = +201.3^\circ$ ($c = 1.00, \text{CHCl}_3$); IR ν_{max} (film) 2925, 2108, 1752, 1367, 1223, 1083, 735, 692 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) $\delta = 7.63\text{-}7.52$ (m, 2H, Ar-2H), 7.40-7.22 (m, 8H, Ar-8H), 5.81 (d, $J = 5.4$ Hz, 1H, 1-H), 5.34 (dd, $J = 10.3, 9.1$ Hz, 1H, 3-H), 4.71-4.51 (m, 2H, PhCH_2), 4.26 (dq, $J = 9.6, 6.2$ Hz, 1H, 5-H), 3.91 (dd, $J = 10.3, 5.4$ Hz, 1H, 2-H), 3.26 (t, $J = 9.4$ Hz, 1H, 4-H), 2.04 (s, 3H, CH_3CO), 1.26 (d, $J = 6.2$ Hz, 3H, 6-CH₃); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 169.6, 137.5, 134.7, 129.1, 128.5, 128.4, 128.03, 127.97, 127.9, 84.1, 81.8, 74.8, 74.1, 69.9, 63.3, 20.9, 17.6$; HR-ESI-MS (m/z): calcd for $\text{C}_{21}\text{H}_{23}\text{N}_3\text{O}_4\text{SeNa}^+$ ($M + \text{Na}^+$): 484.0751, found: 484.0755

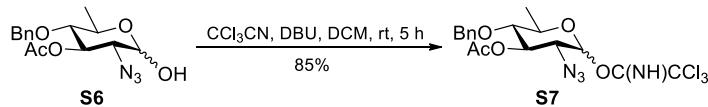
2-Azido-3-O-acetyl-4-O-benzyl-2-deoxy-D-quinovopyranose (**S6**)



A solution of **32** (4.81 g, 10.4 mmol) in 1:1 v/v THF/water (25 mL) was treated with *N*-bromosuccinimide (4.45 g, 25.0 mmol) under nitrogen. After complete conversion of the starting material, the solution was diluted with DCM (300 mL) and washed with 1:1 v/v 10% $\text{Na}_2\text{S}_2\text{O}_3$ /1 M NaHCO_3 (400 mL), filtered and concentrated. The residue was purified by silica gel column chromatography (*n*-hexane : ethyl acetate 5 : 1 v/v) to afford product **S6** as colorless syrup (3.31 g, 10.3 mmol, 99%). $[\alpha]_D^{20} = +33.9^\circ$ ($c = 1.00, \text{CHCl}_3$); IR ν_{max} (film) 3402, 2934, 2111, 1751, 1363, 1227, 1077, 752, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) $\delta = 7.40\text{-}7.18$ (m, 10H, Ph), 5.57 (dd, $J = 10.3, 9.4$ Hz, 1H, 3-H), 5.30 (d, $J = 3.3$ Hz, 1H, 1-H), 5.06 (dd, $J = 10.2, 9.4$ Hz, 1H, 3-H), 4.69 (d, $J = 8.0$ Hz, 1H, 1-H), 4.66-4.54 (m, 4H, PhCH_2), 4.13 (dq, $J = 12.5, 6.2$ Hz, 1H, 5'-H), 3.76 (s, 1H, 1-OH), 3.52 (dq, $J = 12.4, 6.2$ Hz, 1H, 5-H), 3.35 (dd, $J = 10.3, 8.0$ Hz, 1H, 2-H), 3.30-3.05 (m, 4H, 2-H, 4-H, 4'-H, 1-OH), 2.05 (s, 6H, CH_3CO), 1.34

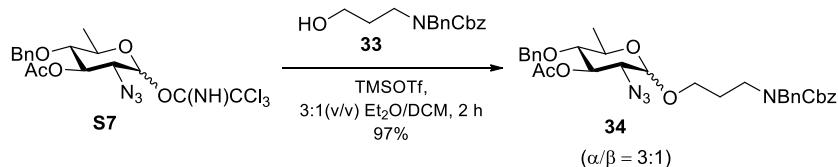
(d, $J = 6.2$ Hz, 3H, 6-CH₃), 1.29 (d, $J = 6.3$ Hz, 3H, 6'-CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 170.01, 169.95, 137.6, 137.4, 128.52, 128.49, 128.0, 127.93, 127.88, 127.8, 95.8, 92.2, 82.1, 81.4, 75.0, 74.8, 73.9, 71.8, 71.6, 66.9, 65.6, 62.3, 20.9, 17.8; HR-ESI-MS (m/z): calcd for C₁₅H₁₉N₃O₅Na⁺ (M + Na⁺): 344.1222, found: 344.1224.

2-Azido-3-O-acetyl-4-O-benzyl-2-deoxy-D-quinovopyranosyl trichloroacetimidate (S7)



To a solution of **S6** (11 mg, 0.034 mmol) in anhydrous DCM (0.4 mL), trichloroacetonitrile (34 μ L, 0.339 mmol) and DBU (0.6 μ L, 0.004 mmol) were added under nitrogen. The mixture was stirred at room temperature for 5 h, when TLC showed complete conversion. The solvent was then evaporated, and the residue was purified by silica gel column chromatography (*n*-hexane : ethyl acetate 7 : 3 *v/v*, containing 0.5% Et₃N) to give product **S7** (13.6 mg, 0.029 mmol, 85%) as a clear oil. ¹H NMR (400 MHz, CDCl₃) δ = 9.49 (s, 1H, NH), 7.46-7.23 (m, 5H, Ph), 6.48 (d, $J = 3.5$ Hz, 1H, 1-H), 5.62-5.42 (m, 1H, 3-H), 4.72 (s, 2H, PhCH₂), 4.04 (dq, $J = 12.5, 6.2$ Hz, 1H, 5-H), 3.93 (dd, $J = 10.7, 3.5$ Hz, 1H, 2-H), 3.49 (t, $J = 9.5$ Hz, 1H, 4-H), 2.08 (s, 3H, CH₃CO), 1.29 (d, $J = 6.2$ Hz, 3H, 6-CH₃).

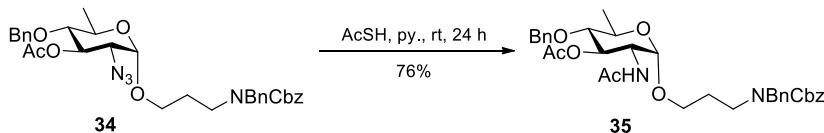
N-Benzyl-N-benzyloxycarbonyl-3-aminopropyl 2-azido-3-O-acetyl-4-O-benzyl-2-deoxy-D-quinovopyranoside (34)



Trichloroacedimidate donor **S7** (2.48 g, 5.325 mmol) and *N*-Bn-*N*-Cbz-3-aminopropan-1-ol³ (1.91 g, 6.380 mmol) were dissolved in 3:1 (*v/v*) anhydrous Et₂O/ anhydrous DCM (130 mL) under nitrogen. This solution was treated with flame-dried molecular sieves (AW-300) and was stirred for 30 min. The mixture was cooled to -40 °C and TMSOTf (1.16 mL, 6.409 mmol) was slowly added. The mixture was stirred under -40 °C for 2 h. When TLC showed the reaction was complete, the mixture was neutralized with Et₃N (20 mL) under -40 °C and filtered through a pad of celite. The filtrate was washed with satd. aq. NaHCO₃ (3 \times 50 mL), dried over Na₂SO₄ and concentrated. The residue was purified by silica gel column chromatography (petroleum ether :

ethyl acetate 15 : 1 v/v) to give product **34** (3.10 g, 5.144 mmol, 97%, $\alpha/\beta = 3:1$). IR ν_{max} (film) 2919, 2107, 1749, 1696, 1454, 1421, 1361, 1222, 1044, 735, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.44-7.13 (m, 20H, α -3Ph, β -3Ph), 5.49 (dd, J = 10.6, 9.0 Hz, 1H, α 3-H), 5.18 (d, J = 8.7 Hz, 2.6H, α -PhCH₂, β -PhCH₂), 4.98 (s, 0.3H, β 3-H), 4.82 (s, 1H, α 1-H), 4.61 (m, 2.6H, α -PhCH₂, β -PhCH₂), 4.57-4.43 (m, 2.6H, α -PhCH₂, β -PhCH₂), 4.29 (d, J = 8.2 Hz, 0.3H, β 1-H), 3.98-3.52 (m, 2.4H, linker-OCH_a, α 5-H), 3.50-3.26 (m, 4.7H, linker-NCH₂, linker-OCH_b, β 5-H, β 2-H), 3.20 (t, J = 9.3 Hz, 1.3H, α 4-H, β 4-H), 3.06 (d, J = 10.4 Hz, 1H, α 2-H), 2.05 (s, 3H, α -CH₃CO), 2.04 (s, 1H, β -CH₃CO), 1.86 (d, J = 27.9 Hz, 2.7H, linker-CH₂), 1.30 (d, J = 6.2 Hz, 1H, β 6-CH₃), 1.26 (d, J = 6.1 Hz, 3H, α 6-CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 169.9, 169.8, 163.5, 156.7, 156.2, 137.9, 137.8, 137.7, 137.5, 136.8, 128.6, 128.54, 128.52, 128.49, 128.0, 127.93, 127.9, 127.8, 127.4, 101.6 (β anomeric), 97.9 (α anomeric), 91.9, 82.3, 81.6, 77.2, 74.9, 73.9, 72.0, 71.4, 67.3, 66.9, 66.0, 65.8, 64.6, 61.6, 50.8, 44.8, 43.9, 28.3, 27.9, 20.9, 17.8; HR-ESI-MS (m/z): calcd for C₃₃H₃₈N₄O₇Na⁺ (M + Na⁺): 625.2638, found: 625.2629.

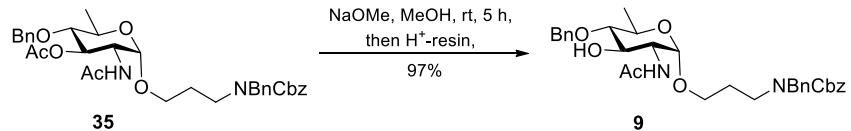
N-Benzyl-N-benzyloxycarbonyl-3-aminopropyl 2-acetamido-3-O-acetyl-4-O-benzyl-2-deoxy- α -D-quinovopyranoside (35 α)



To a stirred solution of azidoglucopyranoside **34** (15.0 mg, 0.025 mmol) in anhydrous pyridine (0.42 mL) was added thioacetic acid (0.42 mL) at 0 °C under nitrogen. The mixture was warmed to room temperature, and stirred for 24 h at that temperature. The solution was co-evaporated with toluene and the residue was purified by silica gel column chromatography (petroleum ether : acetone 6 : 1 v/v) to give product **35** as colorless syrup (11.8 mg, 0.019 mmol, 76%). $[\alpha]_D^{20} = +53.1^\circ$ (c = 1.00, CHCl₃); IR ν_{max} (film) 3343, 2936, 1745, 1696, 1455, 1423, 1366, 1233, 1120, 1048, 737, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.48-7.01 (m, 15H, 3Ph), 6.51 (d, J = 8.9 Hz, 1H, NH), 5.37-5.01 (m, 3H, 3-H, PhCH₂), 4.80-4.31 (m, 5H, 1-H, 2PhCH₂), 4.24 (m, 1H, 2-H), 3.85-3.51 (m, 3H, 5-H, linker-2H), 3.43-3.13 (m, 3H, 4-H, linker-2H), 1.99 (s, 3H, CH₃CO), 1.96 (s, 3H, CH₃CO), 1.75 (m, 2H, linker-CH₂), 1.27 (d, J = 6.2 Hz, 3H, 6-CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 171.1, 156.3, 137.9, 137.6, 136.6, 128.7, 128.5, 128.1, 127.9, 127.8, 127.5, 127.3, 97.2 (anomeric), 81.9, 75.1, 74.0, 67.4, 67.1, 64.1, 52.3, 49.9, 43.2, 27.3, 23.1, 21.0, 17.9;

HR-ESI-MS (*m/z*): calcd for C₃₅H₄₂N₂O₈Na⁺ (M + Na⁺): 641.2839, found: 641.2828.

N-Benzyl-N-benzyloxycarbonyl-3-aminopropyl 2-acetamido-4-O-benzyl-2-deoxy- α -D-quinovopyranoside (9)

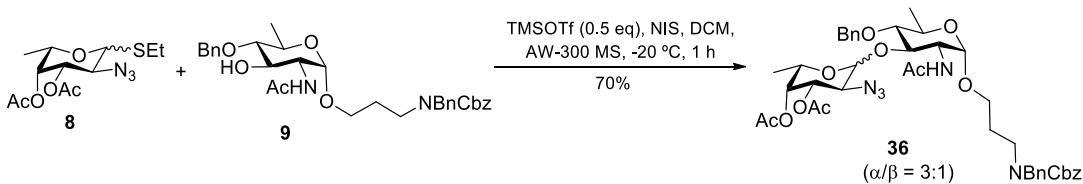


To a solution of **35** (7.4 mg, 12.0 μmol) in MeOH (0.5 mL), NaOMe (0.3 mg, 5.6 μmol) was added and the solution was stirred at room temperature for 5 h. The reaction solution was neutralized with Amberlite IR 120 (H^+) ion exchange resin and filtered through a cotton plug. The crude mixture was purified by silica gel column chromatography (petroleum ether : acetone 4 : 1 v/v) to give product **9** as colorless syrup (6.7 mg, 11.6 μmol , 97%). $[\alpha]_D^{20} = +27.9^\circ$ ($c = 1.10$, CHCl_3); IR ν_{max} (film) 3325, 2938, 1695, 1544, 1424, 1369, 1235, 1120, 1070, 736, 699 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.51 (d, $J = 6.9$ Hz, 1H, NH), 7.44-7.12 (m, 15H, 3Ph), 5.22-5.10 (m, 2H, PhCH_2), 5.02 (d, $J = 11.0$ Hz, 1H, $\text{PhCH}_{\text{a}1}$), 4.78-4.63 (m, 2H, $\text{PhCH}_{\text{b}1}$, $\text{PhCH}_{\text{a}2}$), 4.50 (d, $J = 3.6$ Hz, 1H, 1-H), 4.26 (d, $J = 15.9$ Hz, 1H, $\text{PhCH}_{\text{b}2}$), 4.21 (s, 1H, 3-OH), 4.00 (m, 2H, 2-H, linker-1H), 3.91 (t, $J = 9.4$ Hz, 1H, 3-H), 3.67 (m, 2H, 5-H, linker-1H), 3.21-3.07 (m, 2H, 4-H, linker-1H), 3.00 (dt, $J = 14.2, 4.5$ Hz, 1H, linker-1H), 2.12 (s, 3H, CH_3CO), 1.70 (dq, $J = 9.6, 5.4$ Hz, 2H, linker- CH_2), 1.25 (d, $J = 6.2$ Hz, 3H, 6- CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ = 174.1, 156.7, 138.7, 137.3, 136.5, 128.7, 128.5, 128.4, 128.3, 128.2, 127.7, 127.6, 127.3, 96.9, 84.7, 77.3, 76.0, 75.1, 67.5, 66.5, 62.9, 55.3, 49.4, 42.3, 26.9, 22.6, 17.9; HR-ESI-MS (m/z): calcd for $\text{C}_{33}\text{H}_{40}\text{N}_2\text{O}_7\text{Na}^+$ ($M + \text{Na}^+$): 599.2733, found: 599.2750.

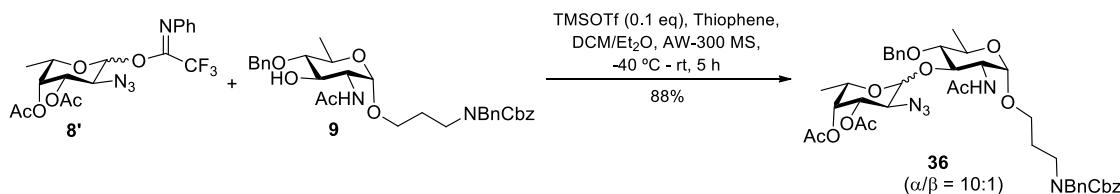
Part 5. Attempt of fully protected trisaccharide 37.

N-Benzyl-N-benzyloxycarbonyl-3-aminopropyl

4-O-benzyl-2-acetamido-3-O-(3,4-di-O-acetyl-2-azido-2-deoxy-L-fucopyranosyl)-2-deoxy- α -D-quinoxopyranoside (36)



To a solution of **9** (118 mg, 0.205 mmol) and glycosyl donor **8** (32.3 mg, 0.102 mmol) in anhydrous DCM (2 mL) were added flame-dried molecular sieve (AW-300) and the reaction mixture was stirred at room temperature under argon for 1 h. The mixture was cooled to -20 °C and *N*-iodosuccinimide (28 mg, 0.124 mmol) and TMSOTf (9 µL, 0.050 mmol) were added. After stirring at the same temperature for 1 h, the mixture was filtered through a pad of celite and washed with DCM. The organic layer was successively washed with 5% (w/v) Na₂S₂O₃ (3 × 10 mL), satd. aq. NaHCO₃ (2 × 10 mL), and water (2 × 10 mL), then dried (Na₂SO₄) and evaporated to dryness. The residue was purified by silica gel column chromatography (petroleum ether : acetone 6 : 1 to 3 : 1 v/v) to give disaccharide **36** (59 mg, 0.071 mmol, 70%, $\alpha/\beta = 3:1$).

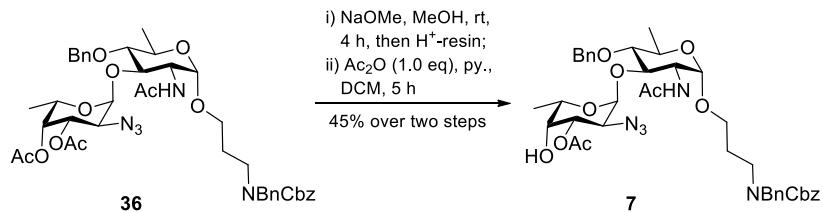


Trifluoroacetimidate donor **8'** (159 mg, 0.358 mmol) and acceptor **9** (207 mg, 0.359 mmol) were dissolved in anhydrous DCM / anhydrous Et₂O (v/v, 1/3, 12 mL) under argon, thiophene (344 µL, 4.297 mmol) and flame-dried molecular sieves (AW-300) were added. The mixture was stirred at room temperature for 30 min. After cooling to -40 °C, TMSOTf (6.5 µL, 0.036 mmol) was added. The reaction mixture was allowed to warm to room temperature and stirred for 5 h. Et₃N (5 drops) was added to neutralize the reaction under 0 °C, and filtered through a pad of celite. The reaction mixture was washed with satd. aq. NaHCO₃ (2 × 15 mL), extracted with DCM (4 × 15 mL) and the combined organic solvent was removed under vacuum. The residue was purified by silica gel column chromatography (petroleum ether : acetone 6 : 1 to 3 : 1 v/v) to afford disaccharide **36** (262 mg, 0.315 mmol, 88%, $\alpha/\beta = 10:1$). $[\alpha]_D^{20} = -178.6^\circ$ (c = 0.90, CHCl₃); IR ν_{max} (film) 3337, 2936, 2112, 1749, 1680, 1371, 1233, 1044, 975, 751, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.48–7.08 (m, 15H, 3Ph), 6.79 (d, *J* = 9.3 Hz, 1H, NH), 5.40–5.30 (m, 2H, 1'-H, 3'-H), 5.14 (s, 2H, PhCH₂), 5.01 (s, 1H, 4'-H), 4.80–4.69 (m, 2H, PhCH₂), 4.60 (m, 2H, 1-H, NCH_aPh), 4.40 (m, 2H, NCH_bPh, 2-H), 4.30–4.18 (m, 1H,

5'-H), 3.96 (dd, $J = 19.8, 9.9$ Hz, 1H, 3-H), 3.80 (dd, $J = 9.1, 6.3$ Hz, 1H, 5-H), 3.70-3.62 (m, 2H, OCH_aCCH_aN), 3.58 (dd, $J = 11.4, 2.9$ Hz, 1H, 2'-H), 3.29 (dd, $J = 10.3, 4.7$ Hz, 2H, OCH_bCCH_bN), 3.21 (t, $J = 9.3$ Hz, 1H, 4-H), 2.11 (s, 3H, CH_3CO), 2.06 (s, 3H, CH_3CO), 2.03 (s, 3H, CH_3CO), 1.74 (s, 2H, $OCCH_2CN$), 1.34 (d, $J = 6.2$ Hz, 3H, 6- CH_3), 0.71 (d, $J = 6.4$ Hz, 3H, 6'- CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 170.4, 169.8, 156.4, 137.7, 137.5, 136.5, 128.7, 128.6, 128.5, 128.1, 128.0, 127.8, 127.7, 127.5, 127.2, 97.8$ (1'-C), 97.5 (1-C), 83.6, 75.7, 75.5, 70.7, 68.4, 67.6, 67.4, 64.9, 63.9, 57.8, 53.4, 49.8, 43.0, 27.3, 23.1, 20.8, 20.7, 18.2, 15.5; HR-ESI-MS (m/z): calcd for $C_{43}H_{53}N_5O_{12}Na^+$ ($M + Na^+$): 854.3588, found: 854.3582.

N-Benzyl-N-benzyloxycarbonyl-3-aminopropyl

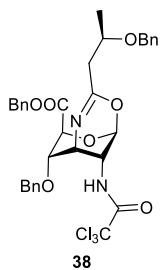
2-acetamido-4-O-benzyl-3-O-(2-azido-3-O-acetyl-2-deoxy- α -L-fucopyranosyl)-2-deoxy- α -D-quinovopyranoside (7)



To a solution of **36** (31.0 mg, 37.3 μ mol) in MeOH (1.2 mL), NaOMe (1.0 mg, 18.5 μ mol) was added and the solution was stirred at room temperature for 4 h. The reaction solution was neutralized with Amberlite IR 120 (H^+) ion exchange resin and filtered through a cotton plug. The crude mixture was purified by silica gel column chromatography (petroleum ether : acetone 3 : 2 v/v) to give the intermediate diol sugar (27.8 mg, 37.2 μ mol, quant.).

To a solution of the intermediate diol sugar (34.2 mg, 45.7 μ mol) in 4:1 (v/v) anhydrous DCM-pyridine (1.25 mL) under nitrogen, Ac_2O (4.3 μ L, 45.5 μ mol) was added at 0 °C. The solution was stirred at room temperature for 5 h. The mixture was partitioned with satd. aq. $NaHCO_3$ (3×5 mL), and combined organic layers were dried (Na_2SO_4), filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether : acetone 5 : 1 v/v) to give product **7** (16.2 mg, 20.5 μ mol, 45%). IR ν_{max} (film) 3339, 2925, 2112, 1744, 1690, 1454, 1234, 1070, 1043, 736, 699, 593 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) $\delta = 7.57$ -7.06 (m, 15H, 3Ph), 6.71 (d, $J = 8.78$ Hz, 1H, NH), 5.34 (s, 1H, 1'-H), 5.26 (dd, $J = 11.0, 2.9$ Hz, 1H, 3'-H), 5.19 (m, 2H,

PhCH_2), 4.75 (q, $J = 10.5$ Hz, 2H, PhCH_2), 4.71-4.49 (m, 2H, 1-H, NCH_aPh), 4.54-4.33 (m, 2H, NCH_bPh , 2-H), 4.18 (d, $J = 6.8$ Hz, 1H, 5'-H), 3.95 (q, $J = 13.9$, 11.9 Hz, 1H, 3-H), 3.78 (m, 1H, 5-H), 3.64 (m, 4H, 4'-H, 2'-H, linker-2H), 3.39-3.24 (m, 2H, linker-2H), 3.20 (t, $J = 9.3$ Hz, 1H, 4-H), 2.17 (s, 3H, CH_3CO), 2.01 (s, 3H, CH_3CO), 1.75 (m, 2H, linker- CH_2), 1.33 (d, $J = 6.2$ Hz, 3H, 6- CH_3), 0.91 (d, $J = 6.7$ Hz, 3H, 6'- CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ = 169.7, 137.9, 137.6, 136.6, 128.7, 128.62, 128.57, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.5, 127.3, 97.8, 97.5, 83.9, 75.7, 75.5, 71.2, 70.1, 67.6, 67.4, 66.0, 64.2, 53.5, 23.1, 21.0, 18.1, 15.7; HR-ESI-MS (m/z): calcd for $\text{C}_{41}\text{H}_{51}\text{N}_5\text{O}_{11}\text{Na}^+$ ($M + \text{Na}^+$): 812.3483, found: 812.3473.



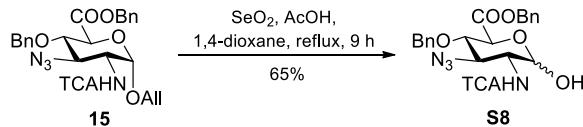
2-(R)-2-O-benzylpropyl (benzyl

4-O-benzyl-2-trichloroacetamido-2,3-dideoxy- α -D-glucopyranuronate)-5,6-dihydro-4H-1,3-oxazine (38)

The compound **38** (15.3 mg, 0.023 mmol) was isolated in 64% yield from the attempted TMSOTf-induced glycosylation reaction of imidate **6** (31 mg, 0.036 mmol) with disaccharide **7** (14 mg, 0.018 mmol) as described above for the preparation of disaccharide **36**. $[\alpha]_D^{20} = +43.4^\circ$ ($c = 1.00$, CHCl_3); IR ν_{max} (film) 3334, 2926, 1756, 1715, 1666, 1514, 1194, 1089, 822, 737, 697 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 8.67 (d, $J = 7.5$ Hz, 1H, NH), 7.46-7.20 (m, 15H, 3Ph), 5.52 (dd, $J = 2.2$ Hz, 1H, 1-H), 5.11 (m, 2H, PhCH_2), 4.73 (s, 1H, 5-H), 4.70 (d, $J = 11.1$ Hz, 1H, PhCH_2), 4.62 (d, $J = 11.1$ Hz, 1H, PhCH_2), 4.54 (d, $J = 11.7$ Hz, 1H, PhCH_2), 4.43 (d, $J = 3.3$ Hz, 1H, 4-H), 4.42 (d, $J = 11.8$ Hz, 1H, PhCH_2), 4.01 (ddd, $J = 6.9, 2.9, 2.9$ Hz, 1H, 2-H), 3.92 (ddd, $J = 3.3$ Hz, 1H, 3-H), 3.83 (dp, $J = 8.2, 6.0$ Hz, 1H, propyl-CH), 2.21 (dd, $J = 14.8, 8.0$ Hz, 1H, propyl- CH_2), 2.08 (dd, $J = 14.8, 5.2$ Hz, 1H, propyl- CH_2), 1.18 (d, $J = 6.1$ Hz, 3H, propyl- CH_3); HR-ESI-MS (m/z): calcd for $\text{C}_{33}\text{H}_{33}\text{Cl}_3\text{N}_2\text{O}_7\text{Na}^+$ ($M + \text{Na}^+$): 697.1251, found: 697.1258.

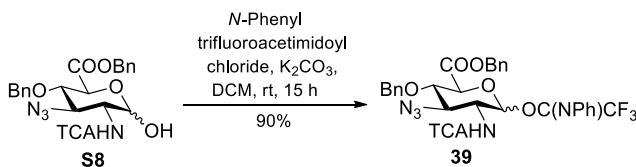
Part 6. Assembly toward fully protected trisaccharide **51**.

Benzyl 3-azido-4-O-benzyl-2,3-dideoxy-2-trichloroacetamido-D-glucopyranosyl uronate (S8)



SeO_2 (91 mg, 0.820 mmol) was added to a solution of compound **15** (95.8 mg, 0.164 mmol) and AcOH (28 μL , 0.490 mmol) in 1,4-dioxane (2 mL) under nitrogen and the resulting suspension was stirred at reflux temperature for 9 h. After cooling to room temperature, the mixture was neutralized with Et_3N (0.5 mL) and concentrated. The residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate 8 : 1 to 4 : 1 v/v) to give the desired hemiacetal **S8** as slightly yellow solid (58.0 mg, 0.107 mmol, 65%). $[\alpha]_D^{20} = +33.2^\circ$ ($c = 1.00, \text{CHCl}_3$); IR ν_{max} (film) 3410, 2944, 2113, 1712, 1518, 1457, 1357, 1264, 1187, 1113, 1068, 822, 752, 698 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.37-7.27 (m, 8H, Ar-8H), 7.23-7.16 (m, 2H, Ar-2H), 6.92 (d, J = 9.5 Hz, 1H, NH), 5.29 (t, J = 3.5 Hz, 1H, 1-H), 5.21 (d, J = 12.1 Hz, 1H, $\text{PhCH}_{\text{a}1}$), 5.17 (d, J = 12.1 Hz, 1H, $\text{PhCH}_{\text{a}2}$), 4.70 (d, J = 10.5 Hz, 1H, $\text{PhCH}_{\text{b}1}$), 4.56-4.44 (m, 2H, $\text{PhCH}_{\text{b}2}$, 5-H), 4.11 (td, J = 9.7, 3.4 Hz, 1H, 2-H), 3.81 (m, 2H, 3-H, 4-H), 3.57 (d, J = 3.7 Hz, 1H, 1-OH); ^{13}C NMR (100 MHz, CDCl_3) δ = 168.6, 162.1, 136.8, 134.7, 128.8, 128.7, 128.5, 128.3, 128.2, 92.2, 90.9, 78.0, 75.0, 70.8, 67.8, 63.7, 53.1; HR-ESI-MS (m/z): calcd for $\text{C}_{22}\text{H}_{21}\text{Cl}_3\text{N}_4\text{O}_6\text{Na}^+$ ($M + \text{Na}^+$): 567.0395, found: 567.0414.

Benzyl (3-azido-4-O-benzyl-2,3-dideoxy-2-trichloroacetamido-D-glucopyranosyl 1-(*N*-phenyl)-2,2,2-trifluoroacetimidate) uronate (39)

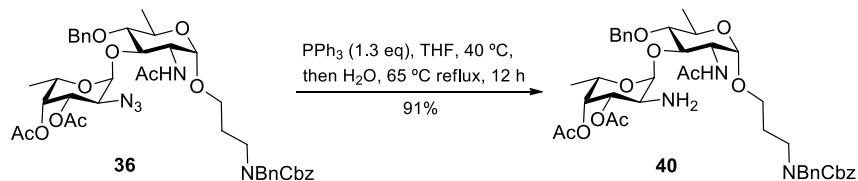


A suspension of 1-OH compound **S8** (22.7 mg, 0.042 mmol), K_2CO_3 (12 mg, 0.087 mmol) and *N*-phenyl trifluoroacetimidoyl chloride (13 μL , 0.087 mmol) in anhydrous DCM (0.4 mL) under nitrogen was stirred at room temperature overnight. The mixture was diluted with DCM (3 mL) and filtered. The filtrate was concentrated under vacuum to give a residue, which was purified by silica gel column chromatography (*n*-hexane : ethyl acetate 18 : 1 v/v) to afford product **39** as colorless syrup (27.4 mg, 0.038 mmol, 90%). IR ν_{max} (film) 3346, 2112, 1723, 1524, 1317, 1213, 1166, 1090, 823, 752, 697 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.44 (s,

1H), 7.35-7.11 (m, 20H), 7.03 (q, $J = 7.5$ Hz, 2H), 6.80 (d, $J = 8.8$ Hz, 1H), 6.73 (d, $J = 7.8$ Hz, 2H), 6.68 (d, $J = 7.8$ Hz, 2H), 6.38 (s, 1H), 6.12 (s, 1H), 5.30-5.02 (m, 3H), 4.61 (d, $J = 10.5$ Hz, 1H), 4.56 (d, $J = 10.6$ Hz, 1H), 4.52-4.44 (m, 2H), 4.37 (d, $J = 7.6$ Hz, 1H), 4.24 (s, 1H), 4.07 (dt, $J = 14.0, 7.2$ Hz, 1H), 3.92 (s, 1H), 3.85 (dd, $J = 13.4, 7.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ = 167.4, 167.2, 162.0, 142.5, 136.2, 136.1, 134.7, 134.5, 128.83, 128.77, 128.69, 128.67, 128.64, 128.58, 128.56, 128.5, 128.41, 128.37, 124.8, 124.5, 119.3, 119.1, 75.0, 74.3, 73.8, 72.7, 67.9, 67.8, 62.5, 51.7; HR-ESI-MS (m/z): calcd for $\text{C}_{30}\text{H}_{25}\text{Cl}_3\text{F}_3\text{N}_5\text{O}_6\text{Na}^+$ ($\text{M} + \text{Na}^+$): 738.0691, found: 738.0722.

N-Benzyl-*N*-benzyloxycarbonyl-3-aminopropyl

2-acetamido-4-*O*-benzyl-3-*O*-(2-amino-3,4-di-*O*-acetyl-2-deoxy- α -L-fucopyranosyl)-2-deoxy- α -D-quinovopyranoside (40)

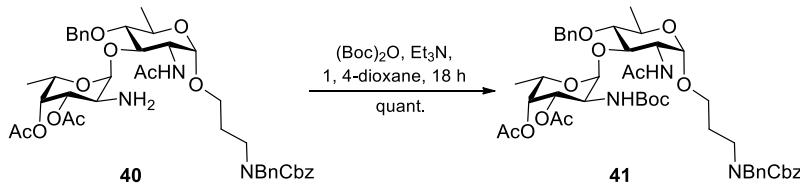


Compound **36** (253 mg, 0.304 mmol) was dissolved in THF (5 mL), and PPh_3 (104 mg, 0.397 mmol) was added under nitrogen. The mixture was stirred at 40 °C for 4 h. After starting material completely consumed, water (66 μL , 3.667 mmol) was added. The mixture was refluxed at 65 °C for 12 h, the mixture was concentrated. The residue was purified by silica gel column chromatography (DCM : MeOH 40 : 1 v/v) to give product **40** as colorless syrup (224 mg, 0.278 mmol, 91%). $[\alpha]_D^{20} = -55.0^\circ$ ($c = 1.10, \text{CHCl}_3$); IR ν_{max} (film) 3332, 2937, 1744, 1676, 1424, 1369, 1225, 1132, 1072, 1029, 972, 750, 699 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.49-7.12 (m, 15H, 3Ph), 7.08 (d, $J = 9.1$ Hz, 1H, NH), 5.25-5.07 (m, 3H, 1'-H, PhCH_2), 4.99 (dd, $J = 11.0, 3.0$ Hz, 1H, 3'-H), 4.93 (s, 1H, 4'-H), 4.83-4.66 (m, 2H, PhCH_2), 4.60 (d, $J = 15.8$ Hz, 1H, NCH_aPh), 4.53 (d, $J = 2.9$ Hz, 1H, 1-H), 4.49-4.28 (m, 2H, NCH_bPh , 2-H), 4.27-4.10 (m, 1H, 5'-H), 4.00 (t, $J = 9.7$ Hz, 1H, 3-H), 3.82 (dd, $J = 9.0, 6.3$ Hz, 1H, 5-H), 3.68 (ddd, $J = 15.0, 12.0, 6.1$ Hz, 2H, $\text{OCH}_a\text{CCH}_a\text{N}$), 3.30 (d, $J = 7.7$ Hz, 2H, $\text{OCH}_b\text{CCH}_b\text{N}$), 3.23-3.09 (m, 2H, 4-H, 2'-H), 2.07 (s, 3H, CH_3CO), 2.03 (s, 6H, 2 CH_3CO), 1.74 (s, 2H, OCCH_2CN), 1.59 (s, 2H, NH₂), 1.35 (d, $J = 6.1$ Hz, 3H, 6-CH₃), 0.61 (d, $J = 6.3$ Hz, 3H,

$6'-\text{CH}_3$; ^{13}C NMR (100 MHz, CDCl_3) δ = 170.5, 137.7, 137.4, 128.6, 128.5, 128.0, 127.8, 127.7, 127.5, 127.2, 99.6, 97.6, 83.3, 77.2, 75.6, 75.0, 71.8, 70.7, 67.7, 67.4, 64.8, 63.6, 53.7, 49.7, 49.2, 42.9, 27.2, 23.3, 20.9, 20.6, 18.2, 15.6; HR-ESI-MS (m/z): calcd for $\text{C}_{43}\text{H}_{55}\text{N}_3\text{O}_{12}\text{Na}^+$ ($M + \text{Na}^+$): 828.3683, found: 828.3733.

N-Benzyl-N-benzyloxycarbonyl-3-aminopropyl 2-acetamido-4-O-benzyl-3-O-(3, 4-di-O-acetyl-2-(tert-butoxycarbonyl)

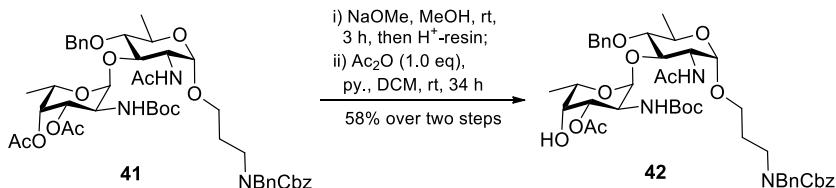
amino-2-deoxy- α -L-fucopyranosyl)-2-deoxy- α -D-quinovopyranoside (41)



To a solution of compound **40** (21.8 mg, 0.027 mmol) and Boc_2O (9 mg, 0.041 mmol) in anhydrous 1,4-dioxane (0.3 mL), Et_3N (11 μL , 0.079 mmol) was added dropwise under argon. After 18 h of stirring at room temperature, the solution was concentrated. The resulting residue was dissolved in DCM (5 mL), washed with satd. aq. NaHCO_3 (3×5 mL), and water (2×5 mL). The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography (petroleum ether : acetone 4 : 1 v/v) to furnish product **41** as colorless syrup (24.5 mg, 0.027 mmol, quant.). ^1H NMR (400 MHz, CDCl_3) δ = 7.31 (ddd, J = 16.6, 8.5, 3.1 Hz, 15H, 3Ph), 7.17 (d, J = 6.7 Hz, 1H, NH), 5.14 (m, 3H, PhCH_2 , 1'-H), 5.08 (dd, J = 11.4, 1.8 Hz, 1H, 3'-H), 4.99 (d, J = 9.9 Hz, 1H, N'H), 4.85 (s, 1H, 4'-H), 4.80 (d, J = 10.9 Hz, 1H, PhCH_a), 4.64 (d, J = 11.0 Hz, 1H, PhCH_b), 4.60 (d, J = 16.0 Hz, 1H, NCH_aPh), 4.49 (d, J = 2.36 Hz, 1H, 1-H), 4.46-4.30 (m, 2H, NCH_bPh , 2-H), 4.16 (m, 2H, 2'-H, 5'-H), 3.95 (t, J = 9.5 Hz, 1H, 3-H), 3.81 (d, J = 6.3 Hz, 1H, 5-H), 3.77-3.58 (m, 2H, $\text{OCH}_a\text{CCH}_a\text{N}$), 3.39-3.21 (m, 2H, $\text{OCH}_b\text{CCH}_b\text{N}$), 3.17 (t, J = 9.4 Hz, 1H, 4-H), 2.10 (s, 3H, CH_3CO), 1.99 (s, 6H, 2 CH_3CO), 1.73 (s, 2H, OCCH_2CN), 1.47 (s, 9H, $\text{Boc}-3\text{CH}_3$), 1.35 (d, J = 6.1 Hz, 3H, 6- CH_3), 0.58 (d, J = 6.3 Hz, 3H, 6'- CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ = 170.6, 170.5, 156.4, 155.7, 137.7, 137.5, 136.5, 130.4, 129.5, 128.7, 128.5, 128.1, 127.9, 127.8, 127.5, 127.2, 126.9, 126.4, 98.2, 97.8, 83.4, 79.2, 77.2, 75.7, 74.7, 70.8, 69.6, 68.0, 67.5, 65.0, 63.8, 53.4, 49.8, 48.4, 43.0, 28.3, 27.3, 23.0, 20.8, 18.2, 15.5.

N-Benzyl-N-benzyloxycarbonyl-3-aminopropyl 2-acetamido-4-O-benzyl-3-O-(3-O-acetyl-2-(tert-butoxycarbonyl)

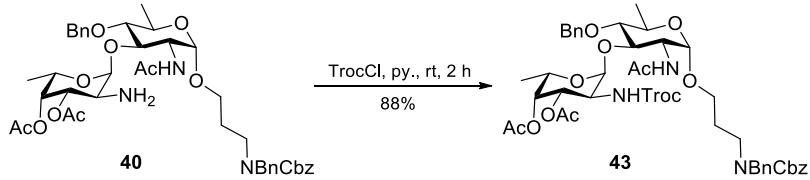
amino-2-deoxy- α -L-fucopyranosyl)-2-deoxy- α -D-quinovopyranoside (42)



Compound **41** (24.5 mg, 0.027 mmol) was dissolved in MeOH (0.9 mL), NaOMe (5 M in MeOH, 2.8 μ L, 0.014 mmol) was added and the solution was stirred at room temperature for 3 h. The reaction solution was neutralized with Amberlite IR 120 (H^+) ion exchange resin and filtered through a cotton plug. The filtrate was purified by silica gel column chromatography (petroleum ether : acetone 2 : 1 v/v) to afford the intermediate diol sugar (21.0 mg, 0.026 mmol, 96%).

To a solution of the intermediate diol sugar (16.5 mg, 0.020 mmol) in 4:1 (v/v) anhydrous DCM-pyridine (0.65 mL) under nitrogen, Ac₂O (2 μ L, 0.021 mmol) was added at 0 °C. After stirring overnight at room temperature, the reaction was monitored by TLC. Ac₂O (1 μ L, 0.011 mmol) was added until TLC showed that the reaction was complete. The mixture was partitioned with satd. aq. NaHCO₃ (2 \times 3 mL), and combined organic layers were dried (Na₂SO₄), filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether : acetone 7 : 1 v/v) to give product **42** (10.6 mg, 0.012 mmol, 60%). ¹H NMR (400 MHz, CDCl₃) δ = 7.51-7.24 (m, 15H, 3Ph), 7.20 (d, J = 6.8 Hz, 1H, NH), 5.29-4.96 (m, 5H, PhCH₂, 1'-H, 3'-H, N'H), 4.81 (d, J = 11.0 Hz, 1H, PhCH_{a1}), 4.69 (d, J = 11.0 Hz, 1H, PhCH_{a2}), 4.66-4.57 (m, 1H, NCH_aPh), 4.51 (d, J = 2.51 Hz, 1H, 1-H), 4.41 (m, 2H, NCH_bPh, 2-H), 4.22 (ddd, J = 10.7, 10.7, 3.2 Hz, 1H, 2'-H), 4.12 (d, J = 6.2 Hz, 1H, 5'-H), 3.98 (t, J = 9.6 Hz, 1H, 3-H), 3.83 (m, 1H, 5-H), 3.77-3.56 (m, 2H, OCH_aCCH_aN), 3.46 (s, 1H, 4'-H), 3.31 (m, 2H, OCH_bCCH_bN), 3.19 (t, J = 9.4 Hz, 1H, 4-H), 2.12 (s, 3H, CH₃CO), 2.00 (s, 3H, CH₃CO), 1.80 (m, 2H, OCCH₂CN), 1.48 (s, 9H, Boc-3CH₃), 1.36 (d, J = 6.1 Hz, 3H, 6-CH₃), 0.80 (d, J = 6.4 Hz, 3H, 6'-CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 170.9, 170.4, 156.4, 155.8, 137.9, 137.5, 136.5, 128.7, 128.5, 128.4, 128.1, 127.8, 127.7, 127.5, 127.4, 127.2, 98.2, 97.8, 83.5, 79.2, 77.2, 75.5, 74.7, 72.3, 70.1, 67.9, 67.5, 66.1, 63.8, 53.4, 49.8, 48.0, 43.0, 29.7, 28.3, 27.3, 23.1, 21.0, 18.2, 15.6.

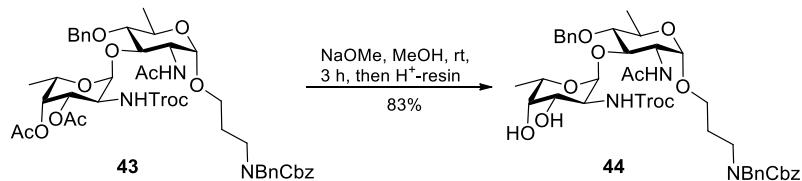
N-Benzyl-N-benzyloxycarbonyl-3-aminopropyl 2-acetamido-4-O-benzyl-3-O-(3,4-di-O-acetyl-2-(2,2,2-trichloroethoxycarbonyl) amino-2-deoxy- α -L-fucopyranosyl)-2-deoxy- α -D-quinoxopyranoside (43)



Compound **40** (224 mg, 0.278 mmol) was dissolved in anhydrous pyridine (7 mL) under nitrogen and cooled to 0 °C. To this was added TrocCl (96 µL, 0.697 mmol) dropwise over a period of 30-45 min. The reaction was allowed to stir at room temperature for 1 h. The reaction was neutralized by adding MeOH (3.5 mL). The solvents were removed under reduced pressure. The residue was dissolved in DCM (15 mL) and washed with water (3 × 15 mL), dried (Na₂SO₄), and concentrated. The residue was purified by silica gel column chromatography (petroleum ether : acetone 7 : 1 v/v) to afford product **43** as colorless syrup (239 mg, 0.244 mmol, 88%). [α]_D²⁰ = -34.1° (c = 1.00, CHCl₃); IR ν_{max} (film) 3322, 2938, 1744, 1679, 1522, 1425, 1369, 1225, 1077, 1045, 740, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.48-7.07 (m, 15H, 3Ph), 6.89 (d, *J* = 8.9 Hz, 1H, NH), 5.45 (d, *J* = 9.2 Hz, 1H, N'H), 5.21 (d, *J* = 2.8 Hz, 1H, 1'-H), 5.13 (m, 3H, 3'-H, PhCH₂), 5.00 (d, *J* = 11.9 Hz, 1H, Troc-CH_a), 4.81 (m, 2H, 4'-H, PhCH_a), 4.59 (m, 3H, PhCH_a, PhCH_b, Troc-CH_b), 4.45 (s, 1H, 1-H), 4.43-4.28 (m, 2H, 2-H, PhCH_b), 4.27-4.07 (m, 2H, 2'-H, 5'-H), 3.96 (t, *J* = 9.5 Hz, 1H, 3-H), 3.87-3.68 (m, 2H, 5-H, OCCCH_aN), 3.69-3.54 (m, 1H, OCH_aCCN), 3.19 (m, 3H, OCH_bCCH_bN, 4-H), 2.09 (s, 3H, CH₃CO), 1.96 (s, 6H, 2CH₃CO), 1.72 (m, 2H, OCCH₂CN), 1.35 (d, *J* = 6.1 Hz, 3H, 6-CH₃), 0.58 (d, *J* = 6.3 Hz, 3H, 6'-CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 171.0, 170.5, 156.4, 154.9, 137.5, 137.4, 136.4, 128.7, 128.53, 128.46, 128.1, 128.0, 127.7, 127.4, 127.2, 97.7, 97.2, 83.3, 77.2, 75.8, 74.7, 74.5, 70.5, 68.9, 67.8, 67.4, 64.9, 63.5, 53.3, 49.7, 49.4, 42.8, 27.1, 23.0, 20.73, 20.65, 18.2, 15.4; HR-ESI-MS (m/z): calcd for C₄₆H₅₆Cl₃N₃O₁₄Na⁺ (M + Na⁺): 1002.2726, found: 1002.2787

N-Benzyl-*N*-benzyloxycarbonyl-3-aminopropyl 2-acetamido-4-*O*-benzyl-3-*O*-(2-(2,2,2-trichloroethoxycarbonyl)

amino-2-deoxy- α -L-fucopyranosyl)-2-deoxy- α -D-quinovopyranoside (44)

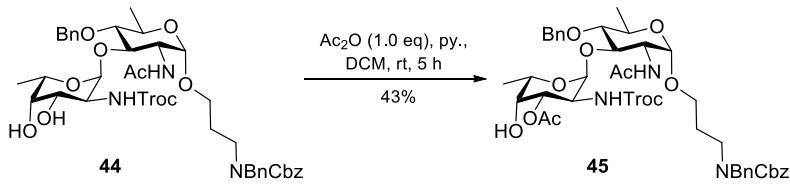


Compound **43** (239 mg, 0.244 mmol) was dissolved in MeOH (8 mL), NaOMe (6.6 mg, 0.122 mmol) was added and the

solution was stirred at room temperature for 3 h. The reaction solution was neutralized with Amberlite IR 120 (H^+) ion exchange resin, filtered through a cotton plug and concentrated. The residue was purified by silica gel column chromatography (petroleum ether : acetone 4 : 1 v/v) to afford product **44** as white solid (181 mg, 0.202 mmol, 83%). $[\alpha]_D^{20} = +6.4^\circ$ ($c = 1.00, \text{CHCl}_3$); IR ν_{max} (film) 3331, 2934, 1679, 1533, 1456, 1225, 1042, 818, 737, 699 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.40-7.14 (m, 15H, 3Ph), 7.12 (d, $J = 9.1$ Hz, 1H, NH), 6.19 (d, $J = 6.7$ Hz, 1H, N'H), 5.13 (m, 3H, 1'-H, PhCH_2), 4.77 (m, 3H, Troc- CH_2 , PhCH_a), 4.60 (m, 2H, PhCH_a , PhCH_b), 4.44 (s, 1H, 1-H), 4.35 (m, 2H, 2-H, PhCH_b), 4.15-4.01 (m, 2H, 5'-H, 3'-OH), 3.96 (m, 2H, 3-H, 2'-H), 3.83 (m, 3H, OCCCH_aN , 5-H, 3'-H), 3.69-3.55 (m, 1H, OCH_aCCN), 3.36 (s, 1H, 4'-H), 3.33-3.05 (m, 3H, $\text{OCH}_b\text{CCH}_b\text{N}$, 4-H), 2.60 (s, 1H, 4'-OH), 2.00 (s, 3H, CH_3CO), 1.72 (m, 2H, OCCH_2CN), 1.32 (d, $J = 6.1$ Hz, 3H, 6- CH_3), 0.82 (d, $J = 6.4$ Hz, 3H, 6'- CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ = 172.0, 157.5, 156.5, 137.7, 137.3, 136.4, 128.7, 128.5, 128.4, 128.1, 127.8, 127.7, 127.5, 127.2, 127.1, 97.7, 96.9, 95.5, 83.2, 77.2, 75.4, 74.8, 74.7, 71.5, 71.0, 67.8, 67.4, 65.6, 63.3, 53.6, 51.8, 49.6, 42.6, 27.0, 23.0, 18.1, 15.7; HR-ESI-MS (m/z): calcd for $\text{C}_{42}\text{H}_{52}\text{Cl}_3\text{N}_3\text{O}_{12}\text{Na}^+$ ($\text{M} + \text{Na}^+$): 918.2514, found: 918.2558

N-Benzyl-N-benzyloxycarbonyl-3-aminopropyl 2-acetamido-4-O-benzyl-3-O-(3-O-acetyl-2-(2,2,2-trichloroethoxycarbonyl)

amino-2-deoxy- α -L-fucopyranosyl)-2-deoxy- α -D-quinovopyranoside (45)

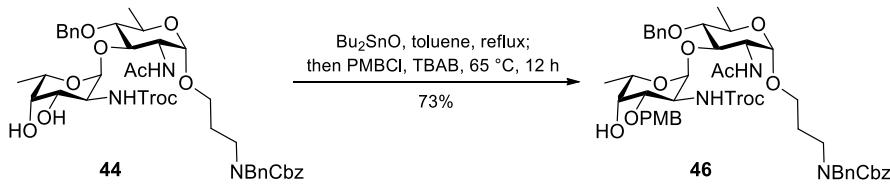


To a solution of diol **44** (95 mg, 0.106 mmol) in 4:1 (*v/v*) anhydrous DCM-pyridine (1.5 mL) under nitrogen, Ac₂O (10 µL, 0.106 mmol) was added at 0 °C. The reaction mixture was stirred at room temperature for 5 h. The mixture was partitioned with satd. aq. NaHCO₃ (5 mL), and combined organic layers were dried (Na₂SO₄), filtered and concentrated. The residue was purified by silica gel column chromatography (*n*-hexane : acetone 7 : 1 *v/v*) to give product **45** (43 mg, 0.046 mmol, 43%). ¹H NMR (400 MHz,

5.09 (m, 3H, PhCH₂, 3'-H), 5.00 (d, *J* = 12.2 Hz, 1H, Troc-CH_a), 4.79 (d, *J* = 11.0 Hz, 1H, PhCH_a), 4.66 (d, *J* = 10.9 Hz, 1H, PhCH_a), 4.58 (d, *J* = 15.7 Hz, 1H, PhCH_b), 4.53 (d, *J* = 12.1 Hz, 1H, Troc-CH_b), 4.45 (s, 1H, 1-H), 4.37 (m, 2H, 2-H, PhCH_b), 4.21 (t, *J* = 10.2 Hz, 1H, 2'-H), 4.11 (d, *J* = 6.2 Hz, 1H, 5'-H), 3.96 (t, *J* = 9.2 Hz, 1H, 3-H), 3.79 (m, 1H, 5-H), 3.71 (m, 1H, OCCCH_aN), 3.63 (m, 1H, OCH_aCCN), 3.41 (s, 1H, 4'-H), 3.20 (m, 3H, OCH_bCCH_bN, 4-H), 2.06 (s, 3H, CH₃CO), 1.96 (s, 3H, CH₃CO), 1.72 (m, 2H, OCCH₂CN), 1.33 (d, *J* = 5.9 Hz, 3H, 6-CH₃), 0.78 (d, *J* = 6.3 Hz, 3H, 6'-CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 171.0, 170.4, 156.4, 154.8, 137.8, 137.4, 136.4, 128.7, 128.5, 128.4, 128.0, 127.7, 127.5, 127.3, 127.2, 97.7, 97.2, 95.7, 83.4, 77.2, 75.6, 74.7, 74.5, 71.5, 69.9, 67.8, 67.4, 65.9, 63.6, 53.4, 49.7, 49.1, 42.9, 27.1, 23.0, 21.0, 18.2, 15.5; HR-ESI-MS (m/z): calcd for C₄₄H₅₄Cl₃N₃O₁₃Na⁺ (M + Na⁺): 960.2620, found: 960.2665.

***N*-Benzyl-*N*-benzyloxycarbonyl-3-aminopropyl 2-acetamido-4-*O*-benzyl-3-*O*-(3-*O*-4-methoxybenzyl-2-(2,2,**

2-trichloroethoxycarbonyl) amino-2-deoxy- α -L-fucopyranosyl)-2-deoxy- α -D-quinovopyranoside (46)



The diol **44** (9.5 mg, 0.011 mmol) was co-evaporated with anhydrous toluene and dried under high vacuum for 30 min. Then, anhydrous toluene (0.8 mL) was added under nitrogen, followed by Bu₂SnO (4 mg, 0.016 mmol) and 4 Å molecular sieves (flame dried). The reaction was stirred for 1 h under reflux. The reaction was cooled to room temperature, PMBCl (4.3 µL, 0.032 mmol) and TBAB (5 mg, 0.016 mmol) were added and stirred overnight at 65 °C. The reaction was filtered and the solvent was evaporated. The residue was purified by silica gel column chromatography (petroleum ether : acetone 7 : 1 v/v) to afford **46** as colorless syrup (8.2 mg, 0.008 mmol, 73%). [α]_D²⁰ = -13.8° (c = 0.50, CHCl₃); IR ν_{max} (film) 3330, 2934, 1735, 1675, 1513, 1454, 1422, 1303, 1265, 1245, 1091, 1051, 965, 823, 734, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.41-7.27 (m, 11H, Ar-1H), 7.25-7.12 (m, 6H, Ar-6H), 6.94-6.81 (m, 3H, 2-NH, Ph-2H), 5.35 (d, *J* = 9.8 Hz, 1H, 2'-NH), 5.26-5.09 (m, 3H, 1'-H, CH₂), 5.05 (d, *J* = 12.0 Hz, 1H, CH_{a1}), 4.70-4.42 (m, 7H, 1-H, CH_{a2}, 2CH₂, CH_{b1}), 4.35 (m, 2H, 2-H, CH_{b2}), 4.14 (ddd, *J* = 10.3, 10.1, 3.3 Hz, 1H, 2'-H), 4.05-3.86 (m, 2H, 5'-H, 3-H), 3.86-3.68 (m, 5H, 5-H, OCH₃, linker-1H), 3.63 (dd, *J* = 10.7, 5.9 Hz, 1H, linker-1H), 3.49 (d, *J* = 11.3 Hz, 1H,

3'-H), 3.42 (s, 1H, 4'-H), 3.39-3.12 (m, 2H, linker-2H), 3.09 (t, J = 9.3 Hz, 1H, 4-H), 1.98 (s, 3H, CH_3CO), 1.79-1.61 (m, 2H, linker- CH_2), 1.29 (d, J = 6.3 Hz, 3H, 6- CH_3), 0.88 (d, J = 6.5 Hz, 3H, 6'- CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ = 171.2, 159.5, 156.4, 154.9, 137.7, 137.4, 136.4, 129.6, 129.4, 128.7, 128.5, 128.4, 128.1, 127.83, 127.76, 127.5, 127.2, 114.0, 97.8, 95.9, 83.4, 75.6, 75.3, 74.9, 74.6, 71.2, 68.6, 67.7, 67.5, 65.7, 63.6, 55.3, 53.4, 50.0, 49.8, 42.8, 29.7, 27.2, 23.1, 18.1, 15.8; HR-ESI-MS (m/z): calcd for $\text{C}_{50}\text{H}_{60}\text{Cl}_3\text{N}_3\text{O}_{13}\text{Na}^+$ ($M + \text{Na}^+$): 1038.3089, found: 1038.3052.

N-Benzyl-N-benzyloxycarbonyl-3-aminopropyl 2-acetamido-4-O-benzyl-3-O-(4-O-[benzyl

3-azido-4-O-benzyl-2,3-dideoxy-2-trichloroacetamido- β -D-glucopyranosyl uronate]-2-(2,2,2-trichloroethoxycarbonyl) amino-2-deoxy- α -L-fucopyranosyl)-2-deoxy- α -D-quinovopyranoside (47);

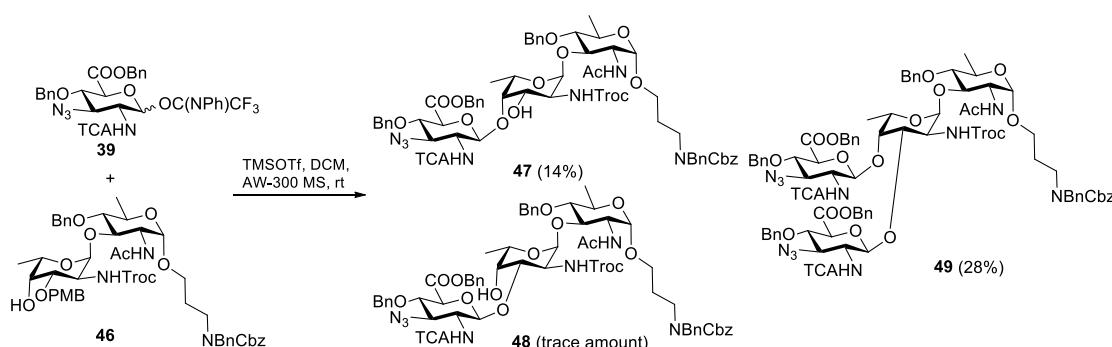
N-Benzyl-N-benzyloxycarbonyl-3-aminopropyl 2-acetamido-4-O-benzyl-3-O-(3-O-[benzyl

3-azido-4-O-benzyl-2,3-dideoxy-2-trichloroacetamido- β -D-glucopyranosyl uronate]-2-(2,2,2-trichloroethoxycarbonyl) amino-2-deoxy- α -L-fucopyranosyl)-2-deoxy- α -D-quinovopyranoside (48);

N-Benzyl-N-benzyloxycarbonyl-3-aminopropyl 2-acetamido-4-O-benzyl-3-O-(4-O-[benzyl

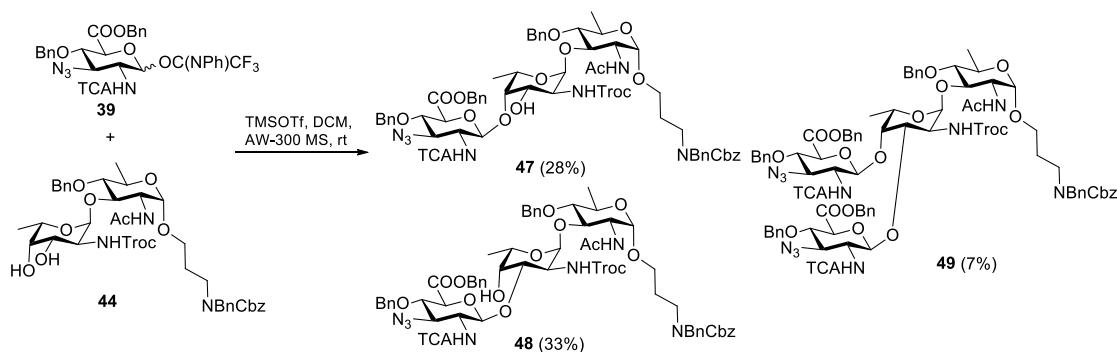
3-azido-4-O-benzyl-2,3-dideoxy-2-trichloroacetamido- β -D-glucopyranosyl uronate]-3-O-[benzyl

3-azido-4-O-benzyl-2,3-dideoxy-2-trichloroacetamido- β -D-glucopyranosyl uronate]-2-(2,2,2-trichloroethoxycarbonyl) amino-2-deoxy- α -L-fucopyranosyl)-2-deoxy- α -D-quinovopyranoside (49)

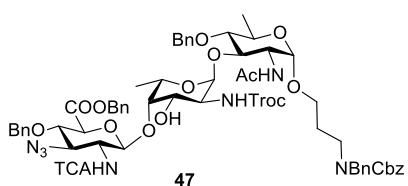


Trifluoroacetimidate donor **39** (32.9 mg, 46.02 μmol) and disaccharide acceptor **46** (12.2 mg, 11.99 μmol) were dissolved in anhydrous DCM (1.5 mL) under nitrogen, flame-dried molecular sieves (AW-300) were added. The mixture was stirred at room

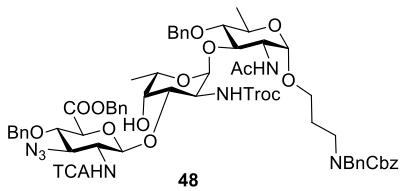
temperature for 30 min. TMSOTf (0.8 μ L, 4.42 μ mol) was added at room temperature. The reaction mixture was stirred at room temperature for 7 h. Pyridine (2 drops) was added to neutralize the reaction under 0 °C, and filtered through celite. The reaction mixture was washed with satd. aq. NaHCO₃ (3 × 5 mL), extracted with DCM (3 × 5 mL), the combined organic solvent was removed under vacuum. The residue was purified by silica gel column chromatography (petroleum ether : acetone 7 : 1 to 2 : 1 v/v) to afford trisaccharide **47** as white solid (2.4 mg, 1.69 μ mol, 14%, β -only), trisaccharide **48** (trace amount) and tetrasaccharide **49** as white solid (6.6 mg, 3.39 μ mol, 28%, β -only). Disaccharide **46** (40%) and diol disaccharide **44** (14%) were recovered.



Trifluoroacetimidate donor **39** (31.5 mg, 44.06 μ mol) and disaccharide acceptor **44** (21.4 mg, 23.85 μ mol) were dissolved in anhydrous DCM (1.5 mL) under nitrogen, flame-dried molecular sieves (AW-300) were added. The mixture was stirred at room temperature for 30 min. TMSOTf (0.8 μ L, 4.42 μ mol) was added at room temperature. The reaction mixture was stirred at room temperature for 4 h. Pyridine (2 drops) was added to neutralize the reaction under 0 °C, and filtered through celite. The reaction mixture was washed with satd. aq. NaHCO₃ (3 × 5 mL), extracted with DCM (3 × 5 mL), the combined organic solvent was removed under vacuum. The residue obtained was purified by silica gel column chromatography (*n*-hexane : acetone 6 : 1 to 2 : 1 v/v) to afford trisaccharide **47** as white solid (9.4 mg, 6.61 μ mol, 28%, β -only), trisaccharide **48** as white solid (11.2 mg, 7.87 μ mol, 33%, β -only) and tetrasaccharide **49** as white solid (3.4 mg, 1.74 μ mol, 7%, β -only).

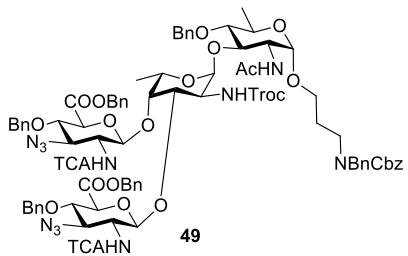


47: $[\alpha]_D^{20} = -6.5^\circ$ ($c = 1.00$, CHCl_3); IR ν_{max} (film) 3317, 2934, 2107, 1704, 1517, 1216, 1039, 826, 751, 697 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) $\delta = 7.44\text{-}7.12$ (m, 26H, 5Ph, 2''-NH), 6.90 (d, $J = 9.4$ Hz, 1H, 2-NH), 5.69 (d, $J = 8.6$ Hz, 1H, 2'-NH), 5.23 (q, $J = 12.2$ Hz, 2H, CH_2), 5.18-5.03 (m, 4H, CH_2 , 1'-H, 1''-H), 4.80-4.65 (m, 3H, CH_2 , $\text{CH}_{\text{a}1}$), 4.67-4.50 (m, 4H, CH_2 , $\text{CH}_{\text{a}2}$, $\text{CH}_{\text{b}1}$), 4.46 (d, $J = 3.5$ Hz, 1H, 1-H), 4.41-4.29 (m, 3H, $\text{CH}_{\text{b}2}$, 3''-H, 2-H), 4.09 (d, $J = 9.6$ Hz, 1H, 5''-H), 4.06 (d, $J = 6.8$ Hz, 1H, 5'-H), 4.01-3.84 (m, 2H, 2'-H, 3-H), 3.83-3.57 (m, 5H, 5-H, 3'-H, linker-2H, 4''-H), 3.47 (s, 1H, 3'-OH), 3.41 (s, 1H, 4'-H), 3.23 (m, 3H, linker-2H, 2''-H), 3.12 (t, $J = 9.3$ Hz, 1H, 4-H), 2.00 (s, 3H, CH_3CO), 1.73 (s, 2H, linker- CH_2), 1.31 (d, $J = 6.2$ Hz, 3H, 6- CH_3), 0.70 (d, $J = 6.4$ Hz, 3H, 6'- CH_3); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 171.5, 167.1, 162.0, 156.4, 155.8, 137.7, 137.4, 136.9, 136.4, 134.8, 128.71, 128.67, 128.6, 128.53, 128.47, 128.4, 128.2, 128.1, 127.9, 127.8, 127.5, 127.2, 127.1, 99.6$ (1''-C), 97.7 (1-C, 1'-C), 95.7, 91.8, 83.4, 83.0, 78.5, 77.3, 75.4, 75.1, 74.9, 74.7, 74.6, 69.4, 67.9, 67.5, 66.5, 63.6, 62.7, 58.1, 53.4, 52.2, 49.7, 42.8, 27.1, 23.1, 18.2, 16.1; HR-ESI-MS (m/z): calcd for $\text{C}_{64}\text{H}_{71}\text{Cl}_6\text{N}_7\text{O}_{17}\text{Na}^+$ ($\text{M} + \text{Na}^+$): 1444.2906, found: 1444.2916.



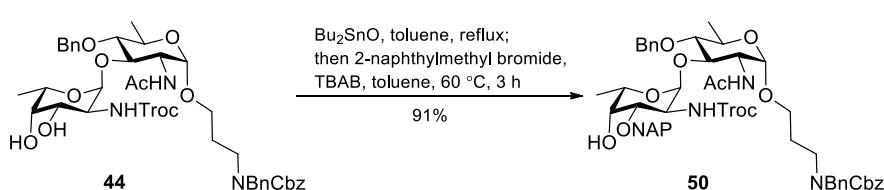
48: $[\alpha]_D^{20} = -14.4^\circ$ ($c = 1.00$, CHCl_3); IR ν_{max} (film) 3323, 2932, 2108, 1722, 1524, 1456, 1220, 1074, 824, 738, 699 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) $\delta = 7.80$ (d, $J = 6.9$ Hz, 1H, 2''-NH), 7.51-7.11 (m, 25H, 5Ph), 6.73 (d, $J = 9.5$ Hz, 1H, 2-NH), 5.48-5.35 (m, 2H, PhCH_2 -1H, 2'-NH), 5.30-5.09 (m, 4H, 1'-H, PhCH_2), 5.06 (d, $J = 8.0$ Hz, 1H, 1''-H), 4.92 (d, $J = 12.2$ Hz, 1H, PhCH_2), 4.79 (d, $J = 12.2$ Hz, 1H, PhCH_2), 4.76 (d, $J = 10.5$ Hz, 1H, PhCH_2), 4.70-4.55 (m, 3H, Troc- CH_2 , PhCH_2), 4.49-4.26 (m, 5H, 1-H, PhCH_2 , 3''-H, 2-H), 4.05 (m, 2H, 5''-H, 2'-H), 4.00-3.84 (m, 2H, 5'-H, 3-H), 3.83-3.53 (m, 5H, 5-H, linker-2H, 4''-H, 3'-H), 3.36-3.11 (m, 4H, linker-2H, 4'-H, 2''-H), 2.94 (q, $J = 12.5, 10.9$ Hz, 1H, 4-H), 2.45 (d, $J = 26.8$ Hz, 1H, 4'-OH), 1.99 (s, 3H, CH_3CO), 1.74 (q, $J = 6.4$ Hz, 2H, linker- CH_2), 1.32 (d, $J = 6.3$ Hz, 3H, 6- CH_3), 0.85 (d, $J = 6.4$ Hz, 3H, 6'- CH_3); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 171.1, 167.5, 162.6, 156.4, 155.4, 137.8, 137.5, 137.1, 136.5, 135.1, 129.0, 128.7, 128.6, 128.5, 128.2, 128.1, 127.8, 127.5, 127.2, 127.0, 97.7$ (1-C), 97.0 (1'-C), 96.0 (1''-C), 92.1, 83.2, 78.4, 77.7, 75.2, 75.0, 74.8, 74.7, 74.2, 68.9, 67.8, 67.7, 67.5, 65.9, 63.8, 62.5, 57.6,

53.4, 49.8, 49.4, 43.0, 27.3, 23.2, 18.2, 15.8; HR-ESI-MS (m/z): calcd for $C_{64}H_{71}Cl_6N_7O_{17}Na^+$ ($M + Na^+$): 1444.2906, found: 1444.2998.



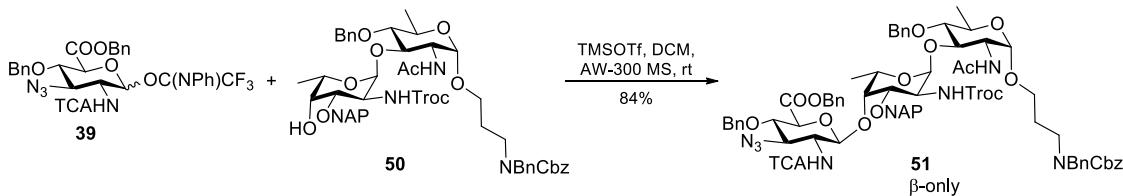
49: $[\alpha]_D^{20} = -31.1^\circ$ ($c = 1.00$, CHCl_3); IR ν_{max} (film) 3324, 2938, 2104, 1720, 1661, 1532, 1456, 1237, 1079, 823, 749, 698 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) $\delta = 7.79$ (d, $J = 9.7$ Hz, 1H, 2"-NH), 7.42-7.02 (m, 36H, 7Ph, 2""-NH), 6.65 (d, $J = 9.6$ Hz, 1H, 2-NH), 5.27 (m, 2H, CH_2 -1H, 2'-NH), 5.21 (d, $J = 12.1$ Hz, 1H, CH_2 -1H), 5.11 (m, 3H, CH_2 -1H, CH_2), 5.05 (s, 1H, 1'-H), 4.97 (m, 3H, 1'''-H, CH_2 -1H, CH_2 -1H), 4.81-4.70 (m, 3H, CH_2 -1H, 1"-H, CH_2 -1H), 4.64 (d, $J = 11.0$ Hz, 1H, CH_2 -1H), 4.59 (d, $J = 15.7$ Hz, 1H, NCH_aPh), 4.49 (m, 3H, 3'''-H, CH_2), 4.42-4.23 (m, 5H, 1-H, CH_2 , NCH_bPh , 2-H), 4.11 (m, 2H, 2'-H, 4'-H), 4.00 (m, 2H, 5"-H, 2"-H), 3.85 (q, $J = 7.7, 6.9$ Hz, 1H, 5'-H), 3.81-3.64 (m, 6H, 3"-H, 3-H, 5-H, linker-1H, 4""-H, 5""-H), 3.64-3.45 (m, 3H, linker-1H, 3'-H, 4"-H), 3.19 (dt, $J = 38.4, 7.6$ Hz, 2H, linker-2H), 3.03 (dd, $J = 11.1, 7.0$ Hz, 1H, 2'''-H), 2.95 (t, $J = 9.3$ Hz, 1H, 4-H), 1.98 (s, 3H, CH_3CO), 1.70 (m, 2H, linker- CH_2), 1.23 (d, $J = 6.1$ Hz, 3H, 6- CH_3), 0.65 (d, $J = 7.5$ Hz, 3H, 6'- CH_3); ^{13}C NMR (100 MHz, CDCl_3) $\delta = 170.1, 169.3, 166.3, 161.3, 160.8, 155.3, 153.9, 136.9, 136.3, 136.1, 135.4, 133.8, 132.8, 128.1, 128.0, 127.95, 127.7, 127.65, 127.54, 127.48, 127.4, 127.34, 127.29, 127.1, 126.9, 126.8, 126.5, 126.2, 97.0 (1'-C, 1'''-C), 96.6 (1-C), 93.8 (1"-C), 92.1, 90.7, 82.3, 78.0, 77.3, 76.2, 74.5, 74.2, 73.82, 73.78, 73.0, 67.6, 66.6, 66.4, 65.3, 65.0, 62.7, 61.0, 57.4, 54.4, 52.0, 48.7, 48.6, 41.9, 26.1, 22.1, 17.0, 15.5; HR-ESI-MS (m/z): calcd for $\text{C}_{86}\text{H}_{90}\text{Cl}_9\text{N}_{11}\text{O}_{22}\text{Na}^+$ ($M + \text{Na}^+$): 1970.3297, found: 1970.3309.$

N-Benzyl-N-benzyloxycarbonyl-3-aminopropyl 2-acetamido-4-O-benzyl-3-O-(3-O-(2-naphthyl)methyl-2-(2,2,2-trichloroethoxycarbonyl) amino-2-deoxy- α -L-fucopyranosyl)-2-deoxy- α -D-quinovopyranoside (50)



The diol **44** (200 mg, 0.223 mmol) was co-evaporated with anhydrous toluene and dried under high vacuum for 30 min. Then, anhydrous toluene (3.2 mL) was added under nitrogen, followed by Bu₂SnO (83 mg, 0.333 mmol) and 4 Å molecular sieves (flame dried). The reaction was stirred for 1 h under reflux. The reaction was cooled to room temperature, NapCH₂Br (148 mg, 0.669 mmol) and TBAB (108 mg, 0.335 mmol) were added and left stir for 3 h at 60 °C. The reaction was filtered and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether : acetone 7 : 1 v/v) to give product **50** as white solid (212 mg, 0.204 mmol, 91%). $[\alpha]_D^{20} = -14.2^\circ$ (c = 1.00, CHCl₃); IR ν_{max} (film) 3013, 2932, 1735, 1670, 1515, 1454, 1215, 1091, 1053 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.93-6.95 (m, 22H, Ar-22H), 6.88 (d, *J* = 9.5 Hz, 1H, 2-NH), 5.43 (d, *J* = 9.7 Hz, 1H, 2'-NH), 5.27-5.09 (m, 3H, 1'-H, CH₂), 5.05 (d, *J* = 12.1 Hz, 1H, CH₂-1H), 4.86-4.69 (m, 2H, CH₂), 4.65-4.51 (m, 3H, NCH_aPh, CH₂), 4.45 (d, *J* = 3.5 Hz, 1H, 1-H), 4.34 (m, 3H, NCH_bPh, CH₂-1H, 2-H), 4.20 (ddd, *J* = 10.2, 10.2, 3.6 Hz, 1H, 2'-H), 4.01-3.84 (m, 2H, 5'-H, 3-H), 3.83-3.70 (m, 2H, 5-H, linker-1H), 3.69-3.60 (m, 1H, linker-1H), 3.57 (dd, *J* = 10.7, 3.0 Hz, 1H, 3'-H), 3.43 (s, 1H, 4'-H), 3.26 (d, *J* = 9.1 Hz, 1H, linker-1H), 3.20-3.10 (m, 1H, linker-1H), 3.04 (t, *J* = 9.2 Hz, 1H, 4-H), 2.38 (s, 1H, 4'-OH), 1.91 (s, 3H, CH₃CO), 1.71 (t, *J* = 6.2 Hz, 2H, linker-CH₂), 1.27 (d, *J* = 6.9 Hz, 3H, 6-CH₃), 0.85 (d, *J* = 6.5 Hz, 3H, 6'-CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 171.2, 156.4, 155.0, 137.6, 137.4, 136.4, 135.1, 133.1, 128.7, 128.5, 128.3, 128.1, 127.9, 127.8, 127.7, 127.5, 127.2, 127.0, 126.7, 126.4, 126.2, 125.7, 97.9, 97.7, 95.8, 83.4, 77.2, 76.1, 75.2, 75.0, 74.6, 71.8, 68.8, 67.7, 67.4, 65.7, 63.5, 53.4, 50.1, 49.7, 42.7, 27.1, 23.1, 18.1, 15.8; HR-ESI-MS (m/z): calcd for C₅₃H₆₀Cl₃N₃O₁₂Na⁺ (M + Na⁺): 1058.3140, found: 1058.3133.

N-Benzyl-N-benzyloxycarbonyl-3-aminopropyl 2-acetamido-4-O-benzyl-3-O-(4-O-[benzyl 3-azido-4-O-benzyl-2,3-dideoxy-2-trichloroacetamido-β-D-glucopyranosyl uronate]-3-O-(2-naphthyl)methyl-2-(2,2,2-trichloroethoxycarbonyl) amino-2-deoxy-α-L-fucopyranosyl)-2-deoxy-α-D-quinoxopyranoside (51)



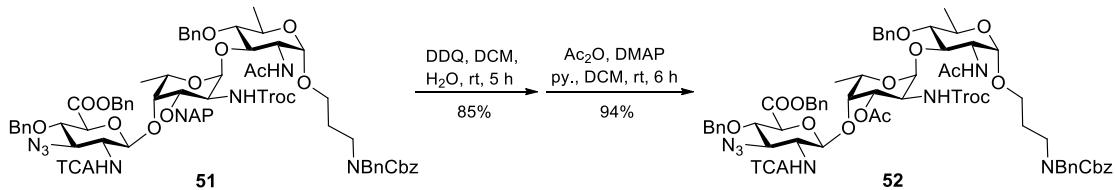
Trifluoroacetimidate donor **39** (69 mg, 0.097 mmol) and disaccharide acceptor **50** (20 mg, 0.019 mmol) were dissolved in anhydrous DCM (3.2 mL) under nitrogen, flame-dried molecular sieves (AW-300) were added. The mixture was stirred at room temperature for 30 min. TMSOTf (1.8 μ L, 0.010 mmol) was added at room temperature. The reaction mixture was stirred at room temperature for 4 h. Pyridine (4 drops) was added to neutralize the reaction under 0 °C, and filtered. The reaction mixture was washed with satd. aq. NaHCO₃ (3 \times 10 mL), extracted with DCM (3 \times 10 mL), the combined organic solvent was removed under vacuum. The residue was purified by silica gel column chromatography (petroleum ether : acetone 6 : 1 v/v) to afford trisaccharide **51** as white solid (24.6 mg, 0.016 mmol, 84%, β -only). $[\alpha]_D^{20} = -22.9^\circ$ (c = 1.00, CHCl₃); IR ν_{max} (film) 3016, 2107, 1743, 1676, 1516, 1454, 1265, 1216, 1092, 1047, 752, 699 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.91-7.69 (m, 4H, Ar-4H), 7.55-7.43 (m, 4H, 2''-NH, Ar-3H), 7.40-7.27 (m, 16H, Ar-16H), 7.26-7.07 (m, 9H, Ar-9H), 6.81 (d, *J* = 9.4 Hz, 1H, 2-NH), 5.37 (d, *J* = 9.9 Hz, 1H, 2'-NH), 5.22-5.05 (m, 6H, 2CH₂, 1'-H, 1''-H), 5.01 (d, *J* = 12.0 Hz, 1H, CH₂-1H), 4.78 (d, *J* = 11.2 Hz, 1H, CH₂-1H), 4.70-4.52 (m, 6H, 5CH₂-1H, 3''-H), 4.51-4.40 (m, 3H, 2CH₂-1H, 1-H), 4.40-4.26 (m, 2H, CH₂-1H, 2-H), 4.20 (ddd, *J* = 10.9, 10.6, 3.5 Hz, 1H, 2'-H), 4.04 (d, *J* = 9.7 Hz, 1H, 5''-H), 3.97 (t, *J* = 6.2 Hz, 1H, 5'-H), 3.88 (t, *J* = 9.7 Hz, 1H, 3-H), 3.80 (s, 1H, 4'-H), 3.78-3.67 (m, 2H, linker-1H, 5-H), 3.66-3.54 (m, 2H, linker-1H, 3'-H), 3.50 (t, *J* = 9.4 Hz, 1H, 4''-H), 3.34-3.11 (m, 3H, linker-2H, 2''-H), 3.06 (t, *J* = 9.3 Hz, 1H, 4-H), 1.98 (s, 3H, CH₃CO), 1.74 (s, 2H, linker-CH₂), 1.30-1.18 (d, *J* = 5.3 Hz, 3H, 6-CH₃), 0.80 (d, *J* = 6.6 Hz, 3H, 6'-CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 171.2, 167.7, 162.4, 156.4, 154.6, 137.7, 137.4, 137.2, 136.4, 134.8, 134.3, 133.3, 133.2, 128.8, 128.7, 128.64, 128.62, 128.5, 128.47, 128.4, 128.1, 128.0, 127.8, 127.51, 127.46, 127.3, 127.2, 126.32, 126.27, 126.2, 100.0, 97.8 (anomeric), 97.6 (1-C), 97.0 (anomeric), 95.9, 91.9, 83.7, 78.7, 77.2, 75.6, 75.2, 74.7, 74.6, 73.1, 72.5, 67.6, 67.49, 67.45, 66.8, 63.6, 61.9, 57.8, 53.3, 50.9, 49.8, 42.9, 27.2, 23.2, 18.2, 16.6; HR-ESI-MS (m/z): calcd for C₇₅H₇₉Cl₆N₇O₁₇Na⁺ (M + Na⁺): 1584.3532, found: 1584.3595.

Part 7. Synthesis of target trisaccharides **2** and **3**.

N-Benzyl-N-benzyloxycarbonyl-3-aminopropyl 2-acetamido-4-O-benzyl-3-O-(4-O-[benzyl

3-azido-4-O-benzyl-2,3-dideoxy-2-trichloroacetamido- β -D-glucopyranosyl uronate]-3-O-acetyl-2-(2,2,

2-trichloroethoxycarbonyl) amino-2-deoxy- α -L-fucopyranosyl)-2-deoxy- α -D-quinovopyranoside (52)



To a solution of sugar **51** (1.148 g, 0.734 mmol) in a mixture of DCM (6.6 mL) and water (2.6 mL), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (246 mg, 1.103 mmol) was added under nitrogen. The reaction mixture was stirred at room temperature for 5 h. Separation of the organic phase followed by washing (5% $\text{Na}_2\text{S}_2\text{O}_3$, 3 × 10 mL) and concentration gave a residue which was purified by silica gel column chromatography (petroleum ether : acetone 7 : 1 to 6 : 1 v/v) to give product **47** (0.890 g, 0.625 mmol, 85%).

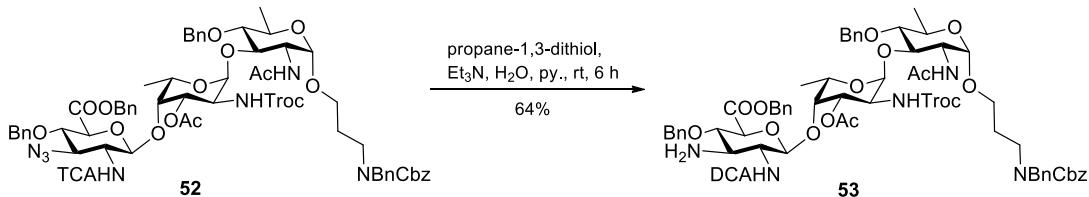
To a solution of sugar **47** (828 mg, 0.582 mmol) in 4:1 (v/v) anhydrous DCM-pyridine (30 mL) under nitrogen, Ac_2O (550 μL , 5.818 mmol) was added dropwise at 0 °C. After addition of DMAP (1.4 mg, 0.012 mmol), the solution was stirred at room temperature for 6 h. The mixture was partitioned with satd. aq. NaHCO_3 (3 × 15 mL), and combined organic layers were dried (Na_2SO_4), filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether : acetone 6 : 1 v/v) to give product **52** as white solid (798 mg, 0.545 mmol, 94%). $[\alpha]_D^{20} = -37.0^\circ$ ($c = 1.00, \text{CHCl}_3$); IR ν_{max} (film) 3337, 2964, 2108, 1744, 1521, 1456, 1367, 1260, 1074, 1021, 800, 752, 697 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.42-7.27 (m, 18H, Ar-18H), 7.25-7.11 (m, 8H, Ar-7H, 2"-NH), 6.78 (d, $J = 9.5$ Hz, 1H, 2-NH), 5.43 (d, $J = 9.9$ Hz, 1H, 2'-NH), 5.23-5.07 (m, 5H, 1'-H, PhCH_2 -4H), 5.01 (d, $J = 12.0$ Hz, 1H, CH_2 -1H), 4.94 (dd, $J = 11.8, 2.7$ Hz, 1H, 3'-H), 4.89 (d, $J = 8.1$ Hz, 1H, 1"-H), 4.78 (d, $J = 10.8$ Hz, 1H, PhCH_2), 4.68 (d, $J = 10.7$ Hz, 1H, CH_2 -1H), 4.64-4.48 (m, 4H, CH₂-4H), 4.47-4.42 (m, 2H, 1-H, 3"-H), 4.37 (m, 2H, 2-H, NCH_2Ph), 4.21 (ddd, $J = 11.4, 9.8, 3.5$ Hz, 1H, 2'-H), 4.04 (t, $J = 6.5$ Hz, 1H, 5'-H), 3.92 (m, 2H, 3-H, 5"-H), 3.83-3.54 (m, 5H, 5-H, 4"-H, 4'-H, linker-2H), 3.34-3.08 (m, 4H, 4-H, 2"-H, linker-2H), 1.97 (s, 3H, CH_3CO), 1.96 (s, 3H, CH_3CO), 1.73 (m, 2H, linker-2H), 1.33 (d, $J = 6.2$ Hz, 3H, 6- CH_3), 0.61 (d, $J = 6.7$ Hz, 3H, 6'- CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ = 170.9, 167.6, 162.0, 158.0, 156.0, 154.0, 152.0, 149.0, 147.0, 145.0, 143.0, 141.0, 139.0, 137.0, 135.0, 133.0, 131.0, 129.0, 127.0, 125.0, 123.0, 121.0, 119.0, 117.0, 115.0, 113.0, 111.0, 109.0, 107.0, 105.0, 103.0, 101.0, 99.0, 97.0, 95.0, 93.0, 91.0, 89.0, 87.0, 85.0, 83.0, 81.0, 79.0, 77.0, 75.0, 73.0, 71.0, 69.0, 67.0, 65.0, 63.0, 61.0, 59.0, 57.0, 55.0, 53.0, 51.0, 49.0, 47.0, 45.0, 43.0, 41.0, 39.0, 37.0, 35.0, 33.0, 31.0, 29.0, 27.0, 25.0, 23.0, 21.0, 19.0, 17.0, 15.0, 13.0, 11.0, 9.0, 7.0, 5.0, 3.0, 1.0, -1.0, -3.0, -5.0, -7.0, -9.0, -11.0, -13.0, -15.0, -17.0, -19.0, -21.0, -23.0, -25.0, -27.0, -29.0, -31.0, -33.0, -35.0, -37.0, -39.0, -41.0, -43.0, -45.0, -47.0, -49.0, -51.0, -53.0, -55.0, -57.0, -59.0, -61.0, -63.0, -65.0, -67.0, -69.0, -71.0, -73.0, -75.0, -77.0, -79.0, -81.0, -83.0, -85.0, -87.0, -89.0, -91.0, -93.0, -95.0, -97.0, -99.0, -101.0, -103.0, -105.0, -107.0, -109.0, -111.0, -113.0, -115.0, -117.0, -119.0, -121.0, -123.0, -125.0, -127.0, -129.0, -131.0, -133.0, -135.0, -137.0, -139.0, -141.0, -143.0, -145.0, -147.0, -149.0, -151.0, -153.0, -155.0, -157.0, -159.0, -161.0, -163.0, -165.0, -167.0, -169.0, -171.0, -173.0, -175.0, -177.0, -179.0, -181.0, -183.0, -185.0, -187.0, -189.0, -191.0, -193.0, -195.0, -197.0, -199.0, -201.0, -203.0, -205.0, -207.0, -209.0, -211.0, -213.0, -215.0, -217.0, -219.0, -221.0, -223.0, -225.0, -227.0, -229.0, -231.0, -233.0, -235.0, -237.0, -239.0, -241.0, -243.0, -245.0, -247.0, -249.0, -251.0, -253.0, -255.0, -257.0, -259.0, -261.0, -263.0, -265.0, -267.0, -269.0, -271.0, -273.0, -275.0, -277.0, -279.0, -281.0, -283.0, -285.0, -287.0, -289.0, -291.0, -293.0, -295.0, -297.0, -299.0, -301.0, -303.0, -305.0, -307.0, -309.0, -311.0, -313.0, -315.0, -317.0, -319.0, -321.0, -323.0, -325.0, -327.0, -329.0, -331.0, -333.0, -335.0, -337.0, -339.0, -341.0, -343.0, -345.0, -347.0, -349.0, -351.0, -353.0, -355.0, -357.0, -359.0, -361.0, -363.0, -365.0, -367.0, -369.0, -371.0, -373.0, -375.0, -377.0, -379.0, -381.0, -383.0, -385.0, -387.0, -389.0, -391.0, -393.0, -395.0, -397.0, -399.0, -401.0, -403.0, -405.0, -407.0, -409.0, -411.0, -413.0, -415.0, -417.0, -419.0, -421.0, -423.0, -425.0, -427.0, -429.0, -431.0, -433.0, -435.0, -437.0, -439.0, -441.0, -443.0, -445.0, -447.0, -449.0, -451.0, -453.0, -455.0, -457.0, -459.0, -461.0, -463.0, -465.0, -467.0, -469.0, -471.0, -473.0, -475.0, -477.0, -479.0, -481.0, -483.0, -485.0, -487.0, -489.0, -491.0, -493.0, -495.0, -497.0, -499.0, -501.0, -503.0, -505.0, -507.0, -509.0, -511.0, -513.0, -515.0, -517.0, -519.0, -521.0, -523.0, -525.0, -527.0, -529.0, -531.0, -533.0, -535.0, -537.0, -539.0, -541.0, -543.0, -545.0, -547.0, -549.0, -551.0, -553.0, -555.0, -557.0, -559.0, -561.0, -563.0, -565.0, -567.0, -569.0, -571.0, -573.0, -575.0, -577.0, -579.0, -581.0, -583.0, -585.0, -587.0, -589.0, -591.0, -593.0, -595.0, -597.0, -599.0, -601.0, -603.0, -605.0, -607.0, -609.0, -611.0, -613.0, -615.0, -617.0, -619.0, -621.0, -623.0, -625.0, -627.0, -629.0, -631.0, -633.0, -635.0, -637.0, -639.0, -641.0, -643.0, -645.0, -647.0, -649.0, -651.0, -653.0, -655.0, -657.0, -659.0, -661.0, -663.0, -665.0, -667.0, -669.0, -671.0, -673.0, -675.0, -677.0, -679.0, -681.0, -683.0, -685.0, -687.0, -689.0, -691.0, -693.0, -695.0, -697.0, -699.0, -701.0, -703.0, -705.0, -707.0, -709.0, -711.0, -713.0, -715.0, -717.0, -719.0, -721.0, -723.0, -725.0, -727.0, -729.0, -731.0, -733.0, -735.0, -737.0, -739.0, -741.0, -743.0, -745.0, -747.0, -749.0, -751.0, -753.0, -755.0, -757.0, -759.0, -761.0, -763.0, -765.0, -767.0, -769.0, -771.0, -773.0, -775.0, -777.0, -779.0, -781.0, -783.0, -785.0, -787.0, -789.0, -791.0, -793.0, -795.0, -797.0, -799.0, -801.0, -803.0, -805.0, -807.0, -809.0, -811.0, -813.0, -815.0, -817.0, -819.0, -821.0, -823.0, -825.0, -827.0, -829.0, -831.0, -833.0, -835.0, -837.0, -839.0, -841.0, -843.0, -845.0, -847.0, -849.0, -851.0, -853.0, -855.0, -857.0, -859.0, -861.0, -863.0, -865.0, -867.0, -869.0, -871.0, -873.0, -875.0, -877.0, -879.0, -881.0, -883.0, -885.0, -887.0, -889.0, -891.0, -893.0, -895.0, -897.0, -899.0, -901.0, -903.0, -905.0, -907.0, -909.0, -911.0, -913.0, -915.0, -917.0, -919.0, -921.0, -923.0, -925.0, -927.0, -929.0, -931.0, -933.0, -935.0, -937.0, -939.0, -941.0, -943.0, -945.0, -947.0, -949.0, -951.0, -953.0, -955.0, -957.0, -959.0, -961.0, -963.0, -965.0, -967.0, -969.0, -971.0, -973.0, -975.0, -977.0, -979.0, -981.0, -983.0, -985.0, -987.0, -989.0, -991.0, -993.0, -995.0, -997.0, -999.0, -1001.0, -1003.0, -1005.0, -1007.0, -1009.0, -1011.0, -1013.0, -1015.0, -1017.0, -1019.0, -1021.0, -1023.0, -1025.0, -1027.0, -1029.0, -1031.0, -1033.0, -1035.0, -1037.0, -1039.0, -1041.0, -1043.0, -1045.0, -1047.0, -1049.0, -1051.0, -1053.0, -1055.0, -1057.0, -1059.0, -1061.0, -1063.0, -1065.0, -1067.0, -1069.0, -1071.0, -1073.0, -1075.0, -1077.0, -1079.0, -1081.0, -1083.0, -1085.0, -1087.0, -1089.0, -1091.0, -1093.0, -1095.0, -1097.0, -1099.0, -1101.0, -1103.0, -1105.0, -1107.0, -1109.0, -1111.0, -1113.0, -1115.0, -1117.0, -1119.0, -1121.0, -1123.0, -1125.0, -1127.0, -1129.0, -1131.0, -1133.0, -1135.0, -1137.0, -1139.0, -1141.0, -1143.0, -1145.0, -1147.0, -1149.0, -1151.0, -1153.0, -1155.0, -1157.0, -1159.0, -1161.0, -1163.0, -1165.0, -1167.0, -1169.0, -1171.0, -1173.0, -1175.0, -1177.0, -1179.0, -1181.0, -1183.0, -1185.0, -1187.0, -1189.0, -1191.0, -1193.0, -1195.0, -1197.0, -1199.0, -1201.0, -1203.0, -1205.0, -1207.0, -1209.0, -1211.0, -1213.0, -1215.0, -1217.0, -1219.0, -1221.0, -1223.0, -1225.0, -1227.0, -1229.0, -1231.0, -1233.0, -1235.0, -1237.0, -1239.0, -1241.0, -1243.0, -1245.0, -1247.0, -1249.0, -1251.0, -1253.0, -1255.0, -1257.0, -1259.0, -1261.0, -1263.0, -1265.0, -1267.0, -1269.0, -1271.0, -1273.0, -1275.0, -1277.0, -1279.0, -1281.0, -1283.0, -1285.0, -1287.0, -1289.0, -1291.0, -1293.0, -1295.0, -1297.0, -1299.0, -1301.0, -1303.0, -1305.0, -1307.0, -1309.0, -1311.0, -1313.0, -1315.0, -1317.0, -1319.0, -1321.0, -1323.0, -1325.0, -1327.0, -1329.0, -1331.0, -1333.0, -1335.0, -1337.0, -1339.0, -1341.0, -1343.0, -1345.0, -1347.0, -1349.0, -1351.0, -1353.0, -1355.0, -1357.0, -1359.0, -1361.0, -1363.0, -1365.0, -1367.0, -1369.0, -1371.0, -1373.0, -1375.0, -1377.0, -1379.0, -1381.0, -1383.0, -1385.0, -1387.0, -1389.0, -1391.0, -1393.0, -1395.0, -1397.0, -1399.0, -1401.0, -1403.0, -1405.0, -1407.0, -1409.0, -1411.0, -1413.0, -1415.0, -1417.0, -1419.0, -1421.0, -1423.0, -1425.0, -1427.0, -1429.0, -1431.0, -1433.0, -1435.0, -1437.0, -1439.0, -1441.0, -1443.0, -1445.0, -1447.0, -1449.0, -1451.0, -1453.0, -1455.0, -1457.0, -1459.0, -1461.0, -1463.0, -1465.0, -1467.0, -1469.0, -1471.0, -1473.0, -1475.0, -1477.0, -1479.0, -1481.0, -1483.0, -1485.0, -1487.0, -1489.0, -1491.0, -1493.0, -1495.0, -1497.0, -1499.0, -1501.0, -1503.0, -1505.0, -1507.0, -1509.0, -1511.0, -1513.0, -1515.0, -1517.0, -1519.0, -1521.0, -1523.0, -1525.0, -1527.0, -1529.0, -1531.0, -1533.0, -1535.0, -1537.0, -1539.0, -1541.0, -1543.0, -1545.0, -1547.0, -1549.0, -1551.0, -1553.0, -1555.0, -1557.0, -1559.0, -1561.0, -1563.0, -1565.0, -1567.0, -1569.0, -1571.0, -1573.0, -1575.0, -1577.0, -1579.0, -1581.0, -1583.0, -1585.0, -1587.0, -1589.0, -1591.0, -1593.0, -1595.0, -1597.0, -1599.0, -1601.0, -1603.0, -1605.0, -1607.0, -1609.0, -1611.0, -1613.0, -1615.0, -1617.0, -1619.0, -1621.0, -1623.0, -1625.0, -1627.0, -1629.0, -1631.0, -1633.0, -1635.0, -1637.0, -1639.0, -1641.0, -1643.0, -1645.0, -1647.0, -1649.0, -1651.0, -1653.0, -1655.0, -1657.0, -1659.0, -1661.0, -1663.0, -1665.0, -1667.0, -1669.0, -1671.0, -1673.0, -1675.0, -1677.0, -1679.0, -1681.0, -1683.0, -1685.0, -1687.0, -1689.0, -1691.0, -1693.0, -1695.0, -1697.0, -1699.0, -1701.0, -1703.0, -1705.0, -1707.0, -1709.0, -1711.0, -1713.0, -1715.0, -1717.0, -1719.0, -1721.0, -1723.0, -1725.0, -1727.0, -1729.0, -1731.0, -1733.0, -1735.0, -1737.0, -1739.0, -1741.0, -1743.0, -1745.0, -1747.0, -1749.0, -1751.0, -1753.0, -1755.0, -1757.0, -1759.0, -1761.0, -1763.0, -1765.0, -1767.0, -1769.0, -1771.0, -1773.0, -1775.0, -1777.0, -1779.0, -1781.0, -1783.0, -1785.0, -1787.0, -1789.0, -1791.0, -1793.0, -1795.0, -1797.0, -1799.0, -1801.0, -1803.0, -1805.0, -1807.0, -1809.0, -1811.0, -1813.0, -1815.0, -1817.0, -1819.0, -1821.0, -1823.0, -1825.0, -1827.0, -1829.0, -1831.0, -1833.0, -1835.0, -1837.0, -1839.0, -1841.0, -1843.0, -1845.0, -1847.0, -1849.0, -1851.0, -1853.0, -1855.0, -1857.0, -1859.0, -1861.0, -1863.0, -1865.0, -1867.0, -1869.0, -1871.0, -1873.0, -1875.0, -1877.0, -1879.0, -1881.0, -1883.0, -1885.0, -1887.0, -1889.0, -1891.0, -1893.0, -1895.0, -1897.0, -1899.0, -1901.0, -1903.0, -1905.0, -1907.0, -1909.0, -1911.0, -1913.0, -1915.0, -1917.0, -1919.0, -1921.0, -1923.0, -1925.0, -1927.0, -1929.0, -1931.0, -1933.0, -1935.0, -1937.0, -1939.0, -1941.0, -1943.0, -1945.0, -1947.0, -1949.0, -1951.0, -1953.0, -1955.0, -1957.0, -1959.0, -1961.0, -1963.0, -1965.0, -1967.0, -1969.0, -1971.0, -1973.0, -1975.0, -1977.0, -1979.0, -1981.0, -1983.0, -1985.0, -1987.0, -1989.0, -1991.0, -1993.0, -1995.0, -1997.0, -1999.0, -2001.0, -2003.0, -2005.0, -2007.0, -2009.0, -2011.0, -2013.0, -2015.0, -2017.0, -2019.0, -2021.0, -2023.0, -2025.0, -2027.0, -2029.0, -2031.0, -2033.0, -2035.0, -2037.0, -2039.0, -2041.0, -2043.0, -2045.0, -2047.0, -2049.0, -2051.0, -2053.0, -2055.0, -2057.0, -2059.0, -2061.0, -2063.0, -2065.0, -2067.0, -2069.0, -2071.0, -2073.0, -2075.0, -2077.0, -2079.0, -2081.0, -2083.0, -2085.0, -2087.0, -2089.0, -2091.0, -2093.0, -2095.0, -2097.0, -2099.0, -2101.0, -2103.0, -2105.0, -2107.0, -2109.0, -2111.0, -2113.0, -2115.0, -2117.0, -2119.0, -2121.0, -2123.0, -2125.0, -2127.0, -2129.0, -2131.0, -2133.0, -2135.0, -2137.0, -2139.0, -2141.0, -2143.0, -2145.0, -2147.0, -2149.0, -2151.0, -2153.0, -2155.0, -2157.0, -2159.0, -2161.0, -2163.0, -2165.0, -2167.0, -2169.0, -2171.0, -2173.0, -2175.0, -2177.0, -2179.0, -2181.0, -2183.0, -2185.0, -2187.0, -2189.0, -2191.0, -2193.0, -2195.0, -2197.0, -2199.0, -2201.0, -2203.0, -2205.0, -2207.0, -2209.0, -2211.0, -2213.0, -2215.0, -2217.0, -2219.0, -2221.0, -2223.0, -2225.0, -2227.0, -2229.0, -2231.0, -2233.0, -2235.0, -2237.0, -2239.0, -2241.0, -2243.0, -2245.0, -2247.0, -2249.0, -2251.0, -2253.0, -2255.0, -2257.0, -2259.0, -2261.0, -2263.0, -2265.0, -2267.0, -2269.0, -2271.0, -2273.0, -2275.0, -2277.0, -2279.0, -2281.0, -2283.0, -2285.0, -2287.0, -2289.0, -2291.0, -2293.0, -2295.0, -2297.0, -2299.0, -2301.0, -2303.0, -2305.0, -2307.0, -2309.0, -2311.0, -2313.0, -2315.0, -2317.0, -2319.0, -2321.0, -2323.0, -2325.0, -2327.0, -2329.0, -2331.0, -2333.0, -2335.0, -2337.0, -2339.0, -2341.0, -2343.0, -2345.0, -2347.0, -2349.0, -2351.0, -2353.0, -2355.0, -2357.0, -2359.0, -2361.0, -2363.0, -2365.0, -2367

156.4, 154.8, 137.7, 137.4, 137.0, 136.4, 134.7, 128.8, 128.7, 128.53, 128.46, 128.4, 128.0, 127.9, 127.8, 127.5, 127.3, 98.7, 97.6, 97.4, 95.8, 91.9, 83.4, 79.0, 77.2, 75.6, 75.0, 74.9, 74.5, 67.8, 67.76, 67.5, 65.7, 62.3, 58.4, 53.4, 49.8, 49.2, 42.9, 27.1, 23.1, 20.9, 18.2, 15.8; HR-ESI-MS (m/z): calcd for $C_{66}H_{74}Cl_6N_7O_{18}^+$ ($M + H^+$): 1464.3192, found: 1464.3281.

N-Benzyl-N-benzyloxycarbonyl-3-aminopropyl 2-acetamido-4-O-benzyl-3-O-(4-O-[benzyl

3-amino-4-O-benzyl-2-dichloroacetamido-2,3-dideoxy- β -D-glucopyranosyl uronate]-3-O-acetyl-2-(2,2,

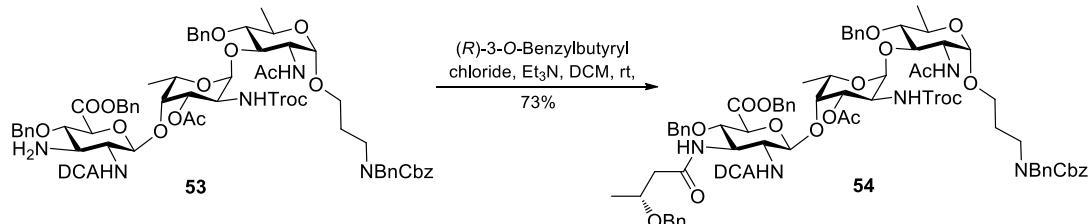
2-trichloroethoxycarbonyl) amino-2-deoxy- α -L-fucopyranosyl)-2-deoxy- α -D-quinoxopyranoside (53)



Water (4.76 mL, 264 mmol), Et₃N (1.06 mL, 7.647 mmol) and 1,3-propanedithiol (1 mL, 9.961 mmol) were added to a solution of azide **52** (745 mg, 0.509 mmol) in pyridine (51 mL) under nitrogen and the resulting mixture was stirred for 6 h at room temperature. After that, the reaction mixture was concentrated and the residue was purified by silica gel column chromatography (petroleum ether : acetone 5 : 1 to 3 : 1 v/v) to afford product **53** as colorless syrup (460 mg, 0.327 mmol, 64%). $[\alpha]_D^{20} = -63.1^\circ$ ($c = 1.00, \text{CHCl}_3$); IR ν_{max} (film) 3322, 2940, 1746, 1682, 1526, 1454, 1363, 1242, 1074, 738, 699 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.51-7.27 (m, 18H, Ar-18H), 7.25-7.09 (m, 7H, Ar-7H), 6.81 (d, $J = 9.3$ Hz, 1H, 2'-NH), 5.90 (s, 1H, CHCl₂), 5.47 (s, 1H, 2''-NH), 5.30-5.05 (m, 5H, 2CH₂, 1'-H), 4.98 (m, 2H, 3'-H, CH₂-1H), 4.77 (d, $J = 10.9$ Hz, 1H, CH₂-1H), 4.71 (s, 1H, 1''-H), 4.67-4.49 (m, 5H, NCH_aPh, CH₂, 2CH₂-1H), 4.45 (d, $J = 4.0$ Hz, 1H, 1-H), 4.41-4.30 (m, 2H, NCH_bPh, 2-H), 4.29-4.16 (m, 1H, 2'-H), 4.14-3.98 (m, 1H, 5'-H), 3.91 (m, 2H, 5''-H, 3-H), 3.78 (q, $J = 7.5, 7.0$ Hz, 1H, 5-H), 3.83-3.56 (m, 4H, 4'-H, 4''-H, linker-2H), 3.47 (s, 1H, 2''-H), 3.36-3.06 (m, 4H, linker-2H, 4-H, 3''-H), 1.96 (s, 6H, 2CH₃CO), 1.73 (m, 2H, linker-CH₂), 1.33 (d, $J = 6.1$ Hz, 3H, 6-CH₃), 0.63 (d, $J = 6.5$ Hz, 3H, 6'-CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 171.1, 168.3, 156.4, 137.9, 137.5, 137.4, 136.5, 134.8, 128.74, 128.68, 128.5, 128.4, 128.1, 127.9, 127.8, 127.5, 127.3, 100.2, 97.6, 95.8, 83.3, 77.2, 75.6, 74.5, 74.4, 69.9, 67.8, 67.6, 67.5, 66.5, 66.0, 63.7, 54.2, 53.4, 49.8, 49.1, 27.2, 23.1, 20.9, 18.2, 15.9; HR-ESI-MS (m/z): calcd for $C_{66}H_{77}Cl_5N_5O_{18}^+$ ($M + H^+$): 1404.3677, found: 1404.3643.

N-Benzyl-*N*-benzyloxycarbonyl-3-aminopropyl 2-acetamido-4-*O*-benzyl-3-*O*-(4-*O*-[benzyl
4-*O*-benzyl-3-*N*-(R)-3-*O*-benzylbutyryl-2-dichloroacetamido-2,3-dideoxy- β -D-glucopyranosyl
uronate]-3-*O*-acetyl-2-(2,2,2-trichloroethoxycarbonyl) amino-2-deoxy- α -L-fucopyranosyl)-2-deoxy- α -D-quinovopyranoside

(54)



(*R*)-3-*O*-Benzylbutyric acid¹ (234 mg, 1.205 mmol) was dissolved in anhydrous DCM (23 mL) under nitrogen and cooled to 0 °C. Oxalyl chloride (0.8 mL, 9.322 mmol) was added to the mixture. The reaction mixture was stirred at room temperature for 4 h. After evaporation of the solvent and excess reagent, the product was dried under vacuum to give (*R*)-3-*O*-benzylbutyryl chloride.

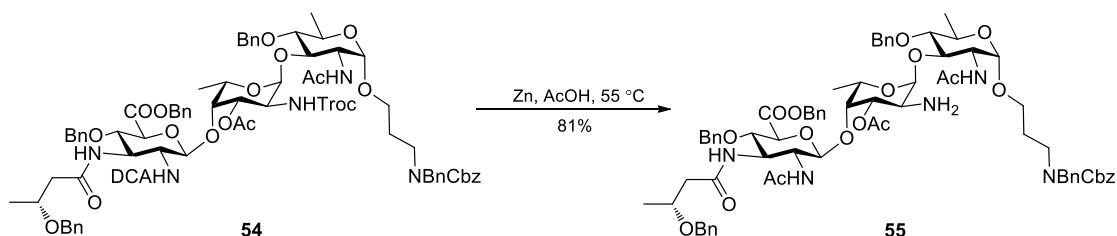
Amine **53** (113 mg, 0.080 mmol) was dissolved in anhydrous DCM (4 mL) under nitrogen, and Et₃N (167 µL, 1.205 mmol) and a solution of (*R*)-3-*O*-benzylbutyryl chloride in anhydrous DCM (4 mL) were added. The reaction mixture was stirred at room temperature overnight. After that, the reaction mixture was quenched with MeOH (0.3 mL) at 0 °C and concentrated. The residue was purified by silica gel column chromatography (petroleum ether : acetone 5 : 1 v/v) to give product **54** as colorless syrup (92 mg, 0.058 mmol, 73%). [α]_D²⁰ = - 47.1° (c = 1.00, CHCl₃); IR ν_{max} (film) 3281, 2935, 1744, 1661, 1532, 1454, 1246, 1045, 737, 698 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.54 (d, *J* = 5.1 Hz, 1H, 2-NH), 7.46-7.27 (m, 20H, Ar-20H), 7.25-7.10 (m, 8H, Ar-8H), 7.09-6.88 (m, 2H, Ar-2H), 6.76 (d, *J* = 9.6 Hz, 1H, 2"-NH), 6.64 (d, *J* = 9.1 Hz, 1H, 3"-NH), 5.78 (s, 1H, DCA-1H), 5.40 (d, *J* = 9.9 Hz, 1H, 2'-NH), 5.29-4.94 (m, 6H, 2CH₂, CH₂-1H, 1'-H), 4.88 (d, *J* = 11.1 Hz, 1H, 3'-H), 4.70 (s, 2H, CH₂), 4.65-4.50 (m, 3H, CH₂-3H), 4.50-4.45 (m, 1H, 1"-H), 4.44-4.27 (m, 5H, 1-H, 2"-H, 3"-H, CH₂), 4.26-4.04 (m, 3H, 2'-H, CH₂), 4.02-3.85 (m, 4H, 5"-H, 5'-H, 3-H, 2-H), 3.79 (m, 2H, butyryl-CH, 5-H), 3.66 (m, 2H, linker-2H), 3.53 (t, *J* = 8.6 Hz, 1H, 4"-H), 3.40 (s, 1H, 4'-H), 3.26 (s, 2H, linker-2H), 3.14 (t, *J* = 9.2 Hz, 1H, 4-H), 2.40-2.12 (m, 2H, butyryl-CH₂), 1.96 (s, 6H, 2CH₃CO), 1.72 (s, 2H, linker-2H), 1.28 (d, *J* = 6.3 Hz, 3H, 6-CH₃), 1.19 (d, *J* = 6.2 Hz, 3H, butyryl-CH₃), 0.65 (d, *J* = 6.4 Hz, 3H, 6'-CH₃); ¹³C NMR (100

MHz, CDCl₃) δ = 171.9, 171.2, 171.0, 168.0, 164.4, 156.4, 154.5, 137.9, 137.44, 137.35, 136.5, 134.9, 128.8, 128.71, 128.65, 128.6, 128.5, 128.42, 128.38, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.4, 127.3, 102.0 (1-C), 97.6 (1'-C, 1''-C), 95.9, 83.3, 77.3, 75.6, 75.3, 74.5, 74.0, 71.5, 70.4, 69.8, 67.7, 67.5, 66.3, 66.0, 63.7, 54.6, 53.4, 52.5, 49.8, 49.1, 43.6, 43.0, 27.2, 23.2, 20.9, 19.4, 18.2, 15.9; HR-ESI-MS (m/z): calcd for C₇₇H₈₈Cl₅N₅O₂₀Na⁺ (M + Na⁺): 1602.4333, found: 1602.4312.

N-Benzyl-N-benzyloxycarbonyl-3-aminopropyl 2-acetamido-4-O-benzyl-3-O-(4-O-[benzyl

2-acetamido-4-O-benzyl-3-N-(R)-3-O-benzylbutyryl-2,3-dideoxy- β -D-glucopyranosyl

uronate]-2-amino-3-O-acetyl-2-deoxy- α -L-fucopyranosyl)-2-deoxy- α -D-quinovopyranoside (55)

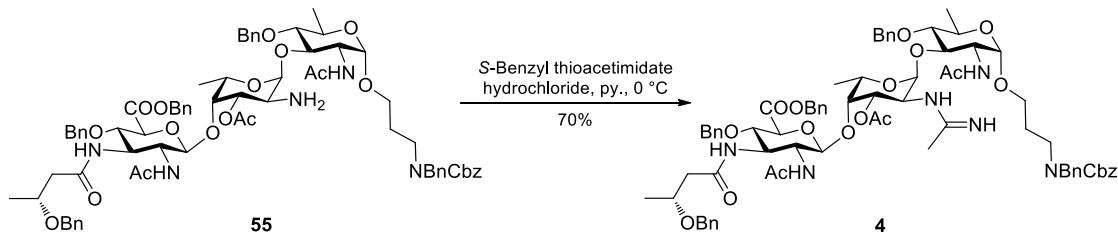


To a solution of trisaccharide **54** (48.3 mg, 0.031 mmol) in AcOH (10 mL) under nitrogen was added zinc powder (excess) at 55 °C. After 4 h at 55 °C, the reaction mixture was filtered (celite) and concentrated. The residue was purified by silica gel column chromatography (DCM : MeOH 20 : 1 v/v) to give trisaccharide **55** (33.4 mg, 0.025 mmol, 81%). $[\alpha]_D^{20} = -73.4^\circ$ ($c = 0.50$, CHCl_3); IR ν_{max} (film) 3289, 2924, 1748, 1656, 1546, 1367, 1238, 1073, 739, 698 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.45-6.99 (m, 30H, 6Ph), 5.13 (m, 5H, 2 PhCH_2 , 1'-H), 4.93 (m, 1H, 3'-H), 4.72 (s, 2H, PhCH_2), 4.68-4.44 (m, 4H, NCH_aPh , PhCH_2 -1H, 1-H, 3''-H), 4.42-4.28 (m, 4H, PhCH_2 , PhCH_2 -1H, NCH_bPh), 4.27-4.07 (m, 2H, 2-H, 1''-H), 4.01 (d, $J = 6.6$ Hz, 1H, 5'-H), 3.90 (m, 4H, butyryl-CH, 2''-H, 3-H, 5''-H), 3.71 (m, 5H, 5-H, 4'-H, linker-2H, 4''-H), 3.50-3.03 (m, 4H, 2'-H, linker-2H, 4-H), 2.34 (d, $J = 31.3$ Hz, 2H, butyryl- CH_2), 2.16-1.86 (m, 6H, 2 CH_3CO), 1.82 (s, 3H, CH_3CO), 1.77-1.62 (m, 2H, linker- CH_2), 1.30 (d, $J = 6.2$ Hz, 3H, 6- CH_3), 1.19 (d, $J = 6.1$ Hz, 3H, butyryl- CH_3), 0.80-0.48 (d, $J = 5.6$ Hz, 3H, 6'- CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ = 172.3, 171.0, 168.2, 156.4, 138.3, 138.0, 137.5, 136.5, 134.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 127.7, 127.5, 127.2, 102.7 (1''-C), 97.4 (1-C, 1'-C), 77.2, 75.7, 75.3, 74.1, 71.8, 70.4, 67.5, 67.4, 66.0, 54.2, 53.2, 49.8, 48.7, 43.5, 43.1, 29.7, 27.2, 23.3, 21.3, 19.2, 18.1, 15.9; HR-ESI-MS (m/z): calcd for $\text{C}_{74}\text{H}_{90}\text{N}_5\text{O}_{18}^+ (\text{M} + \text{H}^+)$: 1336.6281, found: 1336.6243.

N-Benzyl-*N*-benzyloxycarbonyl-3-aminopropyl 2-acetamido-4-*O*-benzyl-3-*O*-(4-*O*-[benzyl 2-acetamido-4-*O*-benzyl-3-*N*-

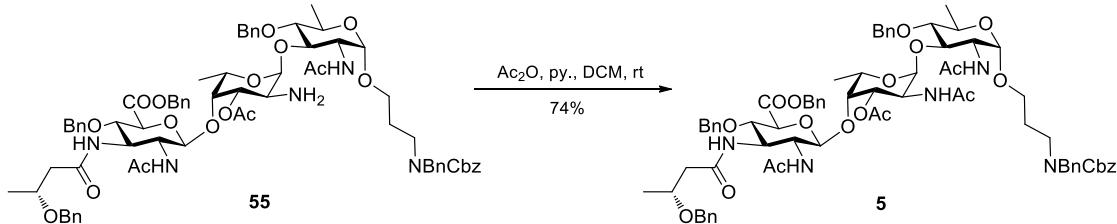
(R)-3-O-benzylbutyryl-2,3-dideoxy- β -D-glucopyranosyl

uronate]-2-acetamidino-3-O-acetyl-2-deoxy- α -L-fucopyranosyl)-2-deoxy- α -D-quinovopyranoside (4)



A solution of aminosugar **55** (12.5 mg, 9.35 μmol) in anhydrous pyridine (2 mL) under argon was cooled to 0 °C. *S*-Benzyl thioacetimidate hydrochloride (3.8 mg, 18.84 μmol) was added to the solution. The mixture was stirred at 0 °C for 5 h. The reaction mixture was concentrated, and the residue was purified by silica gel column chromatography (DCM : MeOH 20 : 1 v/v) to give product **4** as colorless syrup (9.0 mg, 6.53 μmol , 70%). $[\alpha]_D^{20} = -72.7^\circ$ ($c = 0.50$, CHCl_3); IR ν_{max} (film) 3292, 1749, 1657, 1564, 1373, 1232, 1074, 1047, 739, 698 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.49 (d, $J = 8.7$ Hz, 2H, 2-NH, 3"-NH), 7.44-7.15 (m, 30H, 6Ph), 6.96 (s, 1H, 2'-NH), 5.28-5.07 (m, 4H, 2Ph CH_2), 4.99 (m, 2H, 1'-H, 3'-H), 4.83 (d, $J = 10.8$ Hz, 1H, Ph CH_2 -1H), 4.67 (d, $J = 15.7$ Hz, 1H, Ph CH_2 -1H), 4.61-4.37 (m, 6H, 2Ph CH_2 , Ph CH_2 -1H, 1-H), 4.35-4.11 (m, 5H, Ph CH_2 -1H, 1"-H, 2'-H, 2-H, 3"-H), 4.06 (d, $J = 6.6$ Hz, 1H, 5'-H), 3.92 (m, 6H, linker-1H, butyryl-CH, 3-H, 2"-H, 4"-H, 5"-H), 3.86-3.77 (m, 1H, 5-H), 3.67 (m, 2H, linker-1H, 4'-H), 3.17 (m, 2H, linker-1H, 4-H), 3.06 (d, $J = 14.2$ Hz, 1H, linker-1H), 2.59 (s, 3H, Am- CH_3), 2.39 (m, 2H, butyryl- CH_2), 2.09 (s, 3H, CH_3CO), 2.02 (s, 3H, CH_3CO), 1.81 (s, 3H, CH_3CO), 1.73 (m, 2H, linker- CH_2), 1.36 (d, $J = 6.4$ Hz, 3H, 6- CH_3), 1.17 (d, $J = 5.8$ Hz, 3H, butyryl- CH_3), 0.50 (d, $J = 6.3$ Hz, 3H, 6'- CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ = 172.9, 170.6, 168.2, 166.8, 156.6, 138.5, 137.7, 137.4, 136.3, 134.8, 128.8, 128.7, 128.65, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.71, 127.65, 127.6, 127.5, 127.3, 102.3 (1"-C), 97.6 (1-C), 96.4 (1'-C), 83.2, 77.2, 76.0, 75.8, 75.1, 74.3, 71.9, 70.8, 70.4, 68.0, 67.7, 67.5, 66.2, 63.3, 54.0, 53.0, 50.1, 49.7, 43.5, 42.6, 27.0, 23.3, 21.2, 19.8, 19.5, 18.2, 15.4; HR-ESI-MS (m/z): calcd for $\text{C}_{76}\text{H}_{93}\text{N}_6\text{O}_{18}^+ (\text{M} + \text{H}^+)$: 1377.6546, found: 1377.6526.

N-Benzyl-N-benzyloxycarbonyl-3-aminopropyl 2-acetamido-4-O-benzyl-3-O-(4-O-[benzyl 2-acetamido-4-O-benzyl-3-N-(R)-3-O-benzylbutyryl-2,3-dideoxy- β -D-glucopyranosyl uronate]-2-acetamido-3-O-acetyl-2-deoxy- α -L-fucopyranosyl)-2-deoxy- α -D-quinovopyranoside (5)

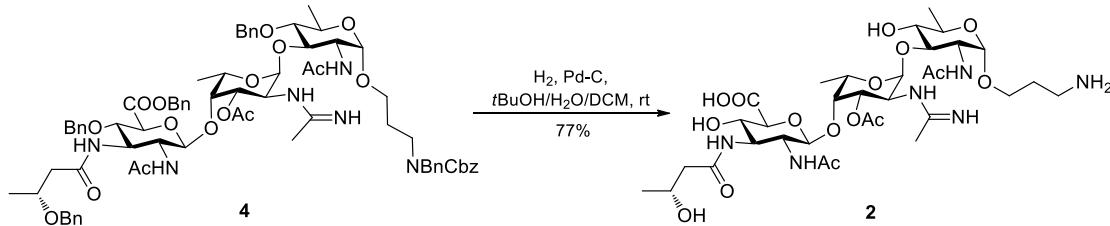


To a solution of sugar **55** (15.5 mg, 11.6 μ mol) in 4:1 (*v/v*) anhydrous DCM-pyridine (0.6 mL) under argon, Ac_2O (5.5 μ L, 58.2 μ mol) was added at 0 °C. The solution was stirred at room temperature overnight. The progress was monitored by TLC analysis. The mixture was partitioned with satd. aq. NaHCO_3 (5 mL), and combined organic layers were dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography (DCM : MeOH 30 : 1 *v/v*) to give product **5** as colorless syrup (11.8 mg, 8.6 μ mol, 74%). $[\alpha]_D^{20} = -70.1^\circ$ ($c = 0.50$, CHCl_3); IR ν_{max} (film) 3340, 1748, 1688, 1667, 1558, 1456, 1374, 1247, 1078, 1049, 751, 699 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ = 7.44-7.27 (m, 20H, Ar-20H), 7.25-7.02 (m, 10H, Ar-10H), 6.91 (d, $J = 9.7$ Hz, 1H, 2'-NH), 6.60 (s, 1H, 3''-NH), 6.01 (s, 1H, 2''-NH), 5.86 (d, $J = 9.6$ Hz, 1H, 2'-NH), 5.13 (m, 4H, PhCH_2 -4H), 5.03 (d, $J = 3.6$ Hz, 1H, 1'-H), 4.93 (dd, $J = 11.5, 2.4$ Hz, 1H, 3'-H), 4.80 (d, $J = 11.0$ Hz, 1H, PhCH_2 -1H), 4.66-4.50 (m, 4H, PhCH_2 -2H, NCH_2Ph , 2'-H), 4.49-4.41 (m, 3H, PhCH_2 -1H, 1-H, 1''-H), 4.40-4.19 (m, 5H, PhCH_2 -2H, NCH_2Ph , 2-H, 3''-H), 4.02 (d, $J = 6.7$ Hz, 1H, 5'-H), 3.98-3.85 (m, 4H, butyryl-CH, 3-H, 2''-H, 5''-H), 3.85-3.70 (m, 3H, linker-1H, 5-H, 4''-H), 3.70-3.60 (m, 1H, linker-1H), 3.56 (s, 1H, 4'-H), 3.38-3.08 (m, 3H, linker-2H, 4-H), 2.34 (qd, $J = 15.0, 6.0$ Hz, 2H, butyryl- CH_2), 2.08 (s, 3H, CH_3CO), 1.97 (s, 3H, CH_3CO), 1.96 (s, 3H, CH_3CO), 1.80 (s, 3H, CH_3CO), 1.73 (m, 2H, linker- CH_2), 1.34 (d, $J = 6.2$ Hz, 3H, 6- CH_3), 1.20 (d, $J = 6.1$ Hz, 3H, butyryl- CH_3), 0.60 (d, $J = 6.4$ Hz, 3H, 6'- CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ = 171.7, 171.4, 170.5, 170.1, 168.2, 156.4, 138.3, 137.7, 137.6, 137.4, 136.5, 135.0, 128.7, 128.63, 128.56, 128.5, 128.44, 128.36, 128.1, 127.84, 127.8, 127.5, 127.4, 127.2, 102.1 (anomeric), 98.0 (1'-C), 97.8 (anomeric), 83.4, 77.2, 75.7, 75.4, 75.2, 74.3, 73.6, 72.0, 70.7, 69.9,

68.1, 67.5, 67.4, 65.9, 63.5, 54.3, 53.5, 52.3, 49.7, 46.4, 43.9, 42.8, 27.1, 23.5, 23.3, 23.0, 21.0, 19.3, 18.2, 15.7; HR-ESI-MS (m/z):

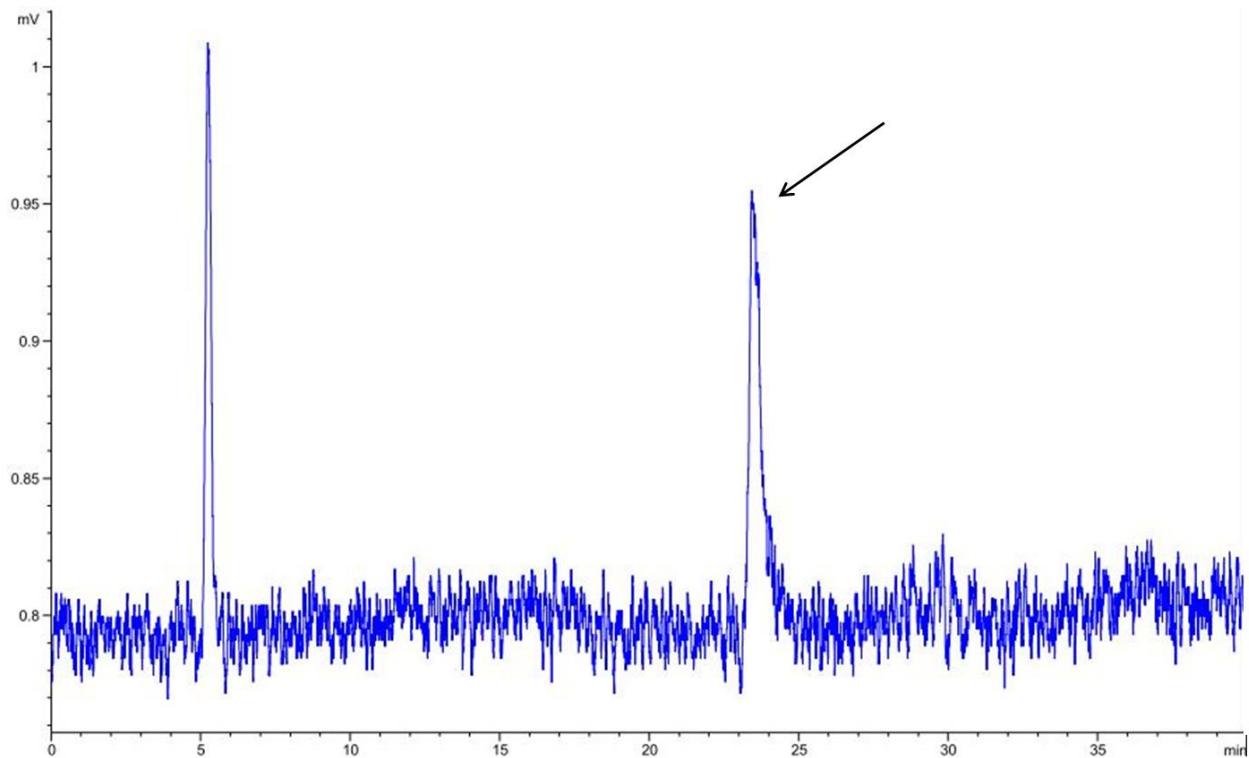
calcd for C₇₆H₉₁N₅O₁₉Na⁺ (M + Na⁺): 1400.6206, found: 1400.6175.

3-Aminopropyl 2-acetamido-3-O-[4-O-[2-acetamido-2,3-dideoxy-3-N-(R)-3-hydroxybutyryl-β-D-glucopyranosylurionate]-2-acetamidino-3-O-acetyl-2-deoxy-α-L-fucopyranosyl]-2-deoxy-α-D-quinovopyranoside (2)



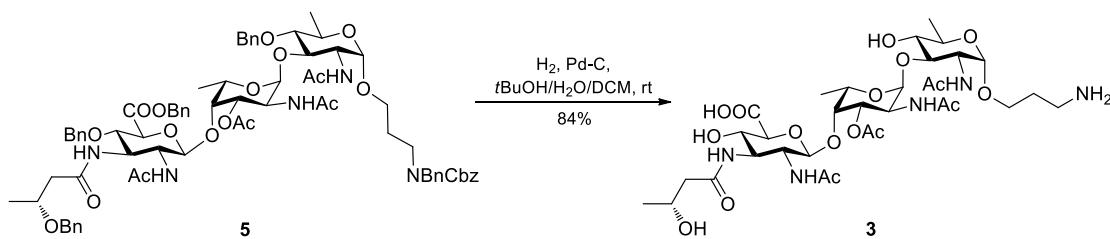
Trisaccharide **4** (4.3 mg, 3.1 μmol) was dissolved in a mixture of *t*BuOH/water/DCM (5 : 2 : 1 v/v/v, 3 mL). The solution was purged with nitrogen, 10% Pd/C was added and the solution was purged with H₂ for 5 min, then stirred under an H₂ atmosphere for 24 h, filtered (celite) and concentrated. The residue was purified with a Sep-Pak cartridge C18 (Macherey-Nagel, Düren, Germany) using water and methanol as eluents. The crude product was further purified by reversed phase HPLC using a semi-preparative Thermo Scientific Hypercarb column affording trisaccharide **2** as white solid (1.9 mg, 2.4 μmol , 77%). $[\alpha]_D^{20} = -66.26^\circ$ ($c = 0.10$, H₂O); ¹H NMR (700 MHz, D₂O) δ = 5.18 (d, *J* = 3.9 Hz, 1H, 1'-H), 5.10 (dd, *J* = 11.3, 2.7 Hz, 1H, 3'-H), 4.74 (d, *J* = 3.6 Hz, 1H, 1-H), 4.61 (d, *J* = 8.3 Hz, 1H, 1"-H), 4.53 (q, *J* = 6.7 Hz, 1H, 5'-H), 4.26 (dd, *J* = 11.1, 3.9 Hz, 1H, 2'-H), 4.21-4.12 (m, 3H, butyryl-CH, 4'-H, 2-H), 4.05-3.99 (m, 1H, 3"-H), 3.92-3.84 (m, 1H, 2"-H), 3.83-3.75 (m, 3H, 5-H, 3-H, linker-CH₃), 3.73 (d, *J* = 9.7 Hz, 1H, 5"-H), 3.71-3.62 (m, 1H, 4"-H), 3.55 (ddd, *J* = 21.7, 11.5, 6.1 Hz, 1H, linker-CH₃b), 3.34 (t, *J* = 9.3 Hz, 1H, 4-H), 3.13-3.03 (m, 2H, linker-CH₂), 2.49 (dd, *J* = 14.1, 7.4 Hz, 1H, butyryl-CH₂), 2.42-2.36 (m, 1H, butyryl-CH₂), 2.26 (s, 3H, Am-CH₃), 2.10 (s, 3H, CH₃CO), 2.01 (s, 3H, CH₃CO), 2.00-1.91 (m, 5H, linker-CH₂, CH₃CO), 1.31 (d, *J* = 6.2 Hz, 3H, 6-CH₃), 1.20 (d, *J* = 6.4 Hz, 6H, 6'-CH₃, butyryl-CH₃); ¹³C NMR (176 MHz, D₂O) δ = 175.1, 174.8, 174.4, 173.6, 173.1, 166.1, 102.7 (1"-C), 96.9 (1-C), 95.8 (1'-C), 78.9, 77.4, 75.9, 73.5, 70.4, 70.2, 67.8, 66.7, 65.0, 64.9, 54.3, 53.9, 53.4, 50.3, 45.1, 37.2, 27.1, 22.2, 21.8, 21.6, 20.3, 18.8, 16.7, 15.0; HR-ESI-MS (m/z): calcd for C₃₃H₅₇N₆O₁₆⁺ (M + H⁺): 793.3831, found: 793.3812.

Crude RP-HPLC of trisaccharide **2** (ELSD trace):



HPLC was performed using a Hypercarb column and a isocratic elution with 100% H₂O (5 min, containing 0.1% of formic acid, flow rate 1.3 mL/min), then a linear gradient from 100% to 70% H₂O (containing 0.1% of formic acid) in MeCN (30 min, flow rate 1.3 mL/min), then a linear gradient from 70% to 0% H₂O (containing 0.1% of formic acid) in MeCN (5 min, flow rate 1.3 mL/min).

3-Aminopropyl 2-acetamido-3-O-(4-O-[2-acetamido-2,3-dideoxy-3-N-(R)-3-hydroxybutyryl-β-D-glucopyranosyl uronate]-2-acetamido-3-O-acetyl-2-deoxy-α-L-fucopyranosyl)-2-deoxy-α-D-quinovopyranoside (3)



Trisaccharide **5** (9.7 mg, 7.0 μmol) was dissolved in a mixture of *t*BuOH/water/DCM (5 : 2 : 1 v/v/v, 5 mL). The solution was purged with nitrogen, 10% Pd/C was added and the solution was purged with H₂ for 5 min, then stirred under an H₂ atmosphere for

24 h, filtered (celite) and concentrated. The residue was purified on Sephadex LH20 (H₂O) to give trisaccharide **3** as white solid

(4.7 mg, 5.9 μmol, 84%). [α]_D²⁰ = -74.67° (c = 0.10, H₂O); ¹H NMR (400 MHz, D₂O) δ = 5.04 (d, *J* = 4.0 Hz, 1H, 1'-H), 5.00 (dd, *J* = 11.6, 2.8 Hz, 1H, 3'-H), 4.75 (d, *J* = 3.3 Hz, 1H, 1-H), 4.62 (d, *J* = 8.2 Hz, 1H, 1''-H), 4.52 (q, *J* = 6.5 Hz, 1H, 5'-H), 4.36 (dd, *J*

= 11.6, 3.9 Hz, 1H, 2'-H), 4.19 (m, 2H, butyryl-CH, 4'-H), 4.11 (dd, J = 10.3, 3.3 Hz, 1H, 2-H), 4.09-4.01 (m, 1H, 3''-H), 3.94-3.86 (m, 1H, 2''-H), 3.86-3.73 (m, 3H, linker-OCH_a, 3-H, 5-H), 3.73-3.63 (m, 2H, 4''-H, 5''-H), 3.54 (dt, J = 11.1, 5.9 Hz, 1H, linker-OCH_b), 3.33 (t, J = 9.7 Hz, 1H, 4-H), 3.14 (t, J = 7.6 Hz, 2H, linker-NCH₂), 2.55-2.36 (m, 2H, butyryl-CH₂), 2.19-1.89 (m, 14H, 4CH₃CO, linker-CH₂), 1.32 (d, J = 6.5 Hz, 3H, 6-CH₃), 1.22 (d, J = 6.3 Hz, 6H, 6'-CH₃, butyryl-CH₃); ¹³C NMR (100 MHz, D₂O) δ = 174.7, 174.33, 174.25, 174.14, 174.11, 173.7, 102.6 (1''-C), 97.3 (1'-C), 96.9 (1-C), 78.94, 77.0, 75.8, 73.7, 70.1, 69.91, 67.88, 66.5, 65.0, 64.8, 54.3, 54.0, 53.6, 47.2, 45.1, 37.2, 26.8, 22.2, 22.0, 21.8, 21.6, 20.3, 16.7, 15.2; HR-ESI-MS (m/z): calcd for C₃₃H₅₅N₅O₁₇Na⁺ (M + Na⁺): 816.3491, found: 816.3511.

Table s1. Comparison of ^1H and ^{13}C NMR Chemical Shifts (ppm) between isolated polysaccharide and synthetic 2

Residue		Chemical shifts (ppm)							
		H1/C1	H2/C2 (H2a, H2b/C2)	H3/C3	H4/C4	H5/C5	H6/C6	NAc (OAc) [Am ^b]	C=O [C=N]
$\rightarrow 3)$ - α -D-Quip	isolated ^a	5.08 96.5	4.03 54.0	3.69 76.5	3.22 74.2	3.78 68.8	1.24 17.4	1.96/22.9	174.2
	synthetic	4.74 96.9	4.16 53.4	3.79 75.9	3.34 73.5	3.79 67.8	1.31 16.7	1.99/21.8	174.4
$\rightarrow 4)$ - α -L-Fucp	isolated ^a	5.11 96.4	4.22 51.1	5.05 71.2	4.14 78.0	4.50 67.4	1.17 15.9	(2.08/21.0) [2.24/19.7]	173.9 [166.8]
	synthetic	5.18 95.8	4.26 50.3	5.10 70.4	4.20 77.4	4.53 66.7	1.20 15.0	(2.10/20.3) [2.26/18.8]	173.6 [166.1]
$\rightarrow 4)$ - β -D-Glcp	isolated ^a	4.60 103.2	3.84 55.0	4.24 54.8	3.98 73.1	3.76 79.2	- 175.0	1.98/23.0	175.2
	synthetic	4.61 102.7	3.88 53.9	4.02 54.3	3.67 70.2	3.73 78.9	- 174.8	2.01/22.2	175.1
D-3-Hydroxy butyric acid	isolated ^a	- 174.0	(2.27, 2.29) 45.8	4.06 65.7	1.15 22.8				
	synthetic	- 174.4	(2.39, 2.49) 45.1	4.20 65.0	1.20 21.6				

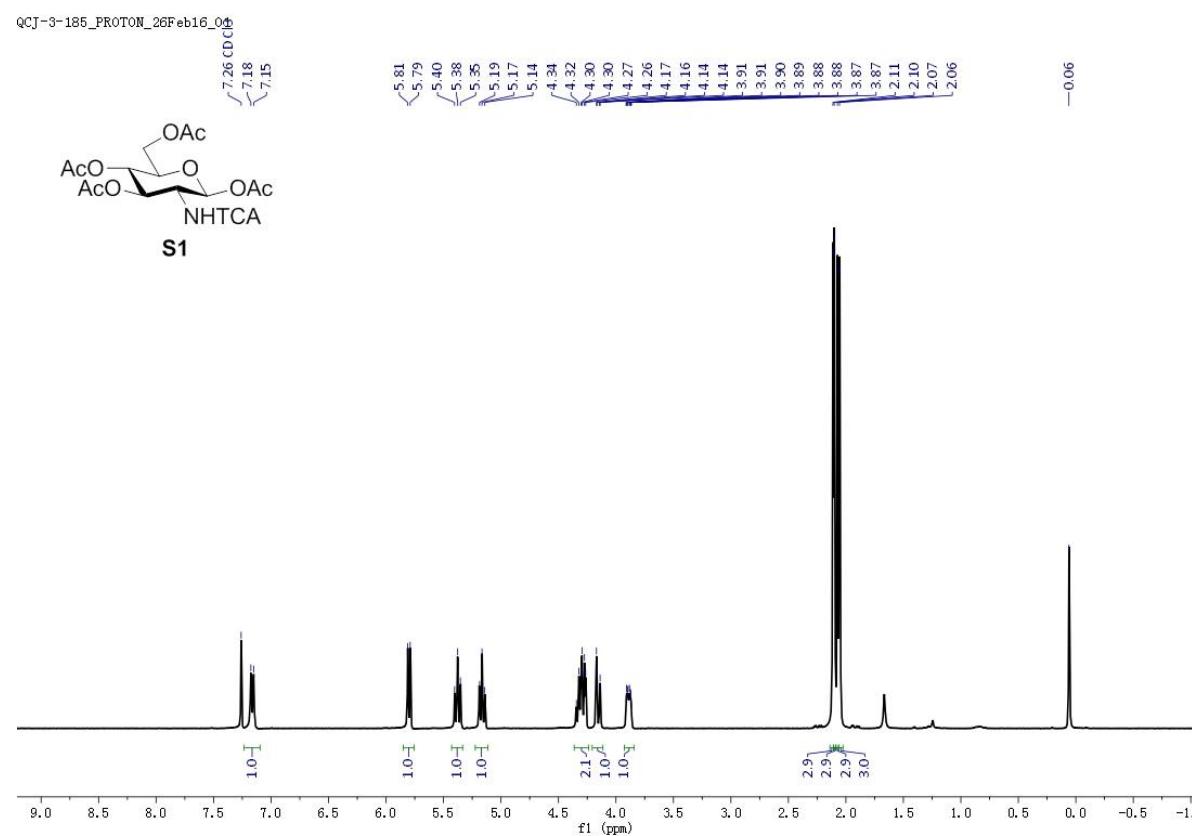
^a The data collected from ref 4.

^b Am: acetamidino group.

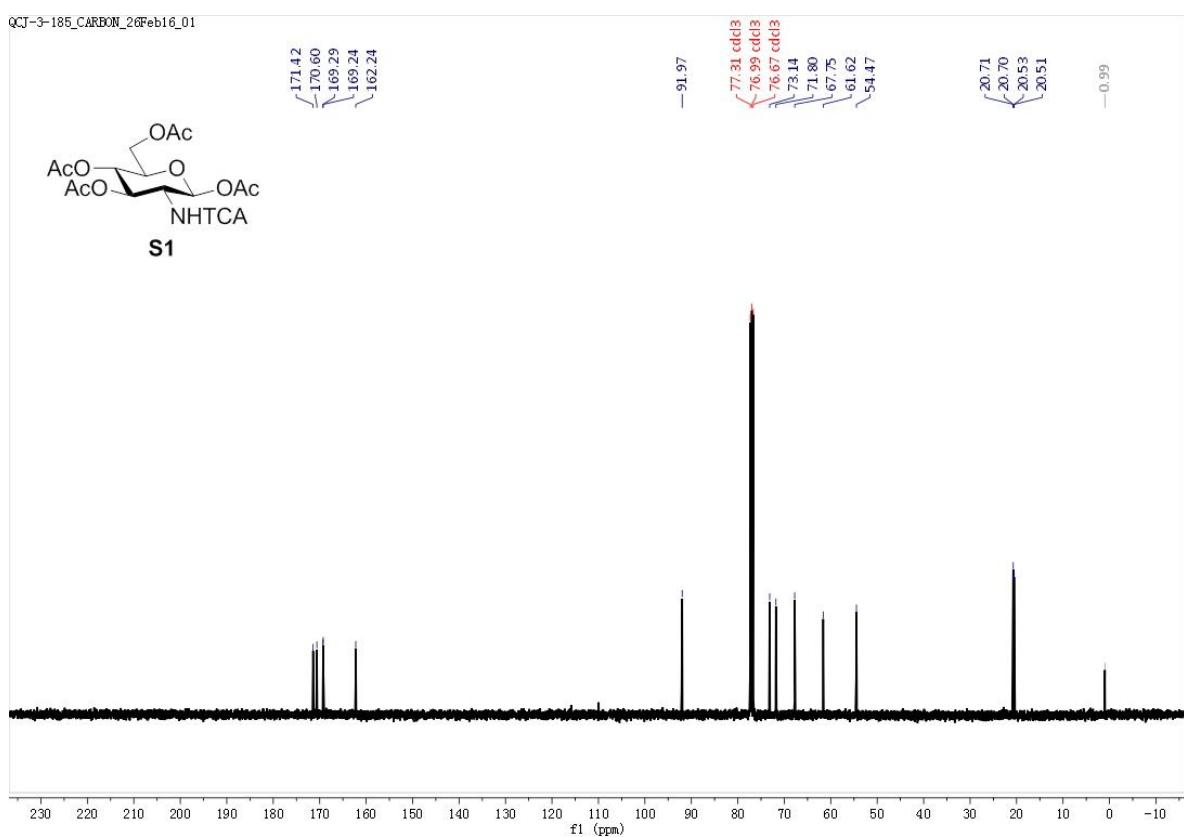
REFERENCES

- (1) Seebach, D.; Brandli, U.; Schnurrenberger, P. *Helv. Chim. Acta* **1988**, *71*, 155-167.
- (2) Pereira, C. L.; Geissner, A.; Anish, C.; Seeberger, P. H. *Angew. Chem., Int. Ed.* **2015**, *54*, 10016-10019.
- (3) Ishida, H.; Kimura, S.; Kogure, N.; Kitajima, M.; Takayama, H. *Org. Biomol. Chem.* **2015**, *13*, 7762-7771.
- (4) Maciejewska, A.; Lukasiewicz, J.; Niedziela, T.; Szewczuk, Z.; Lugowski, C. *Carbohydr. Res.* **2009**, *344*, 894-900.

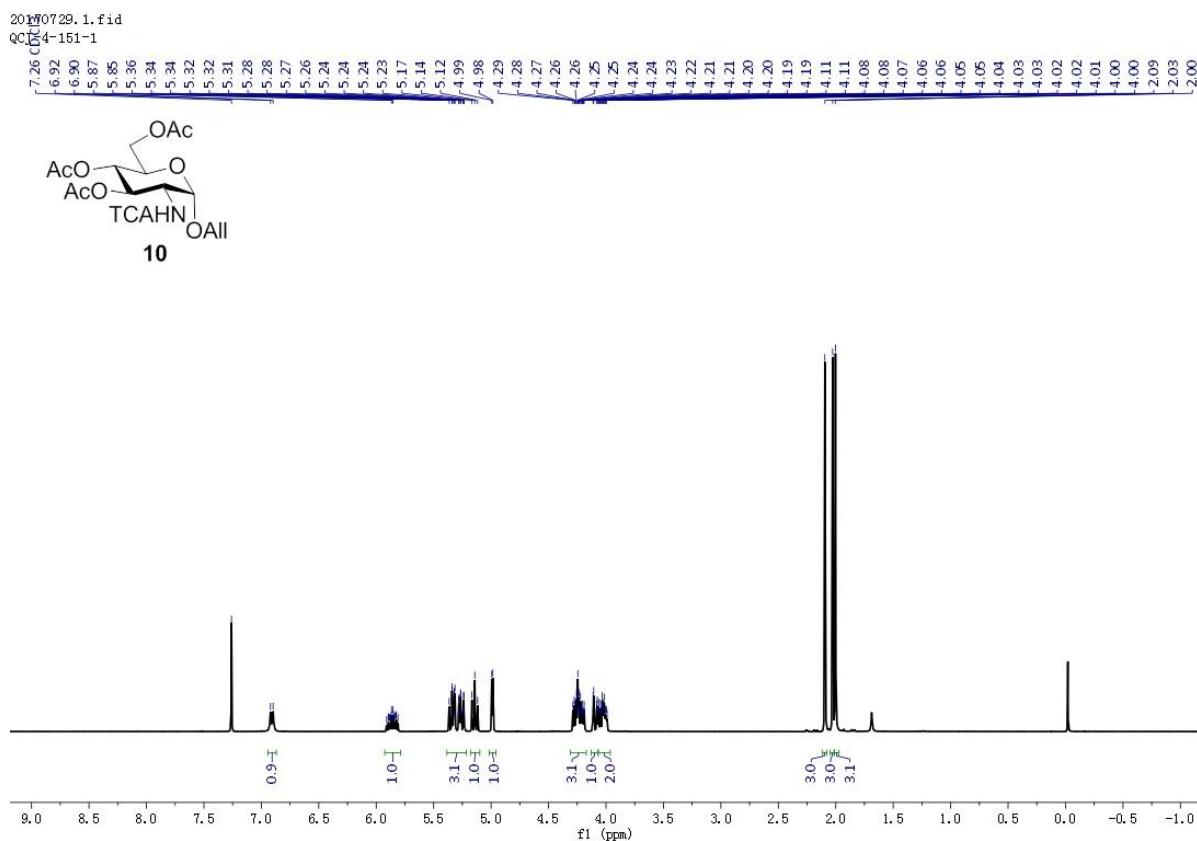
¹H NMR (CDCl₃, 400 MHz) of compound S1



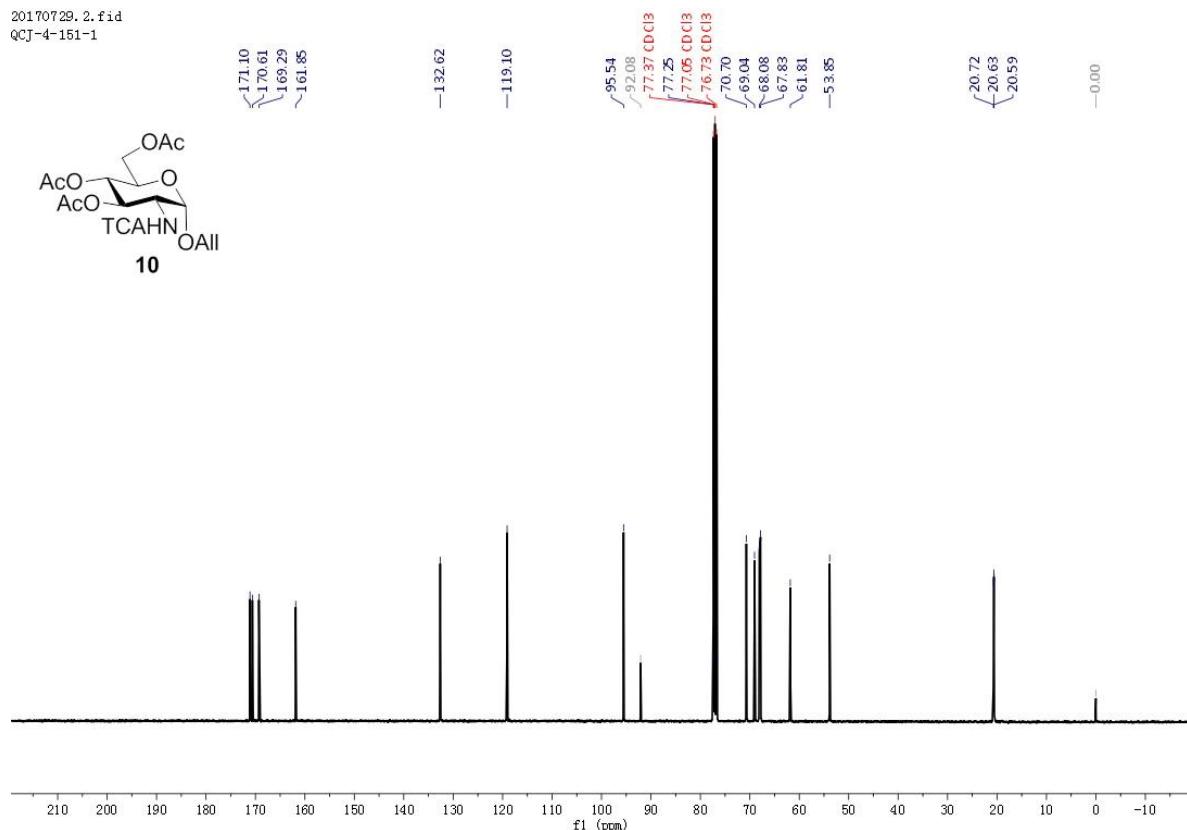
¹³C NMR (CDCl₃, 100 MHz) of compound S1



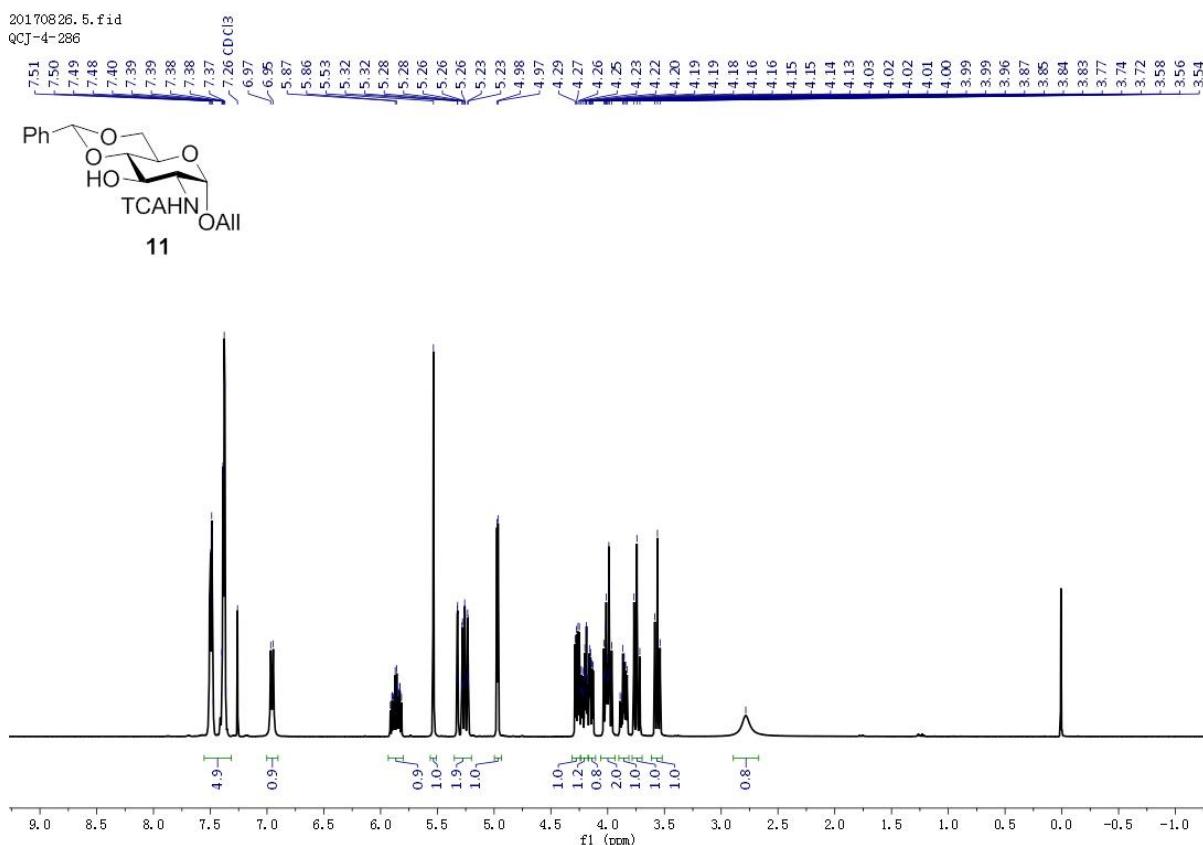
¹H NMR (CDCl₃, 400 MHz) of compound 10



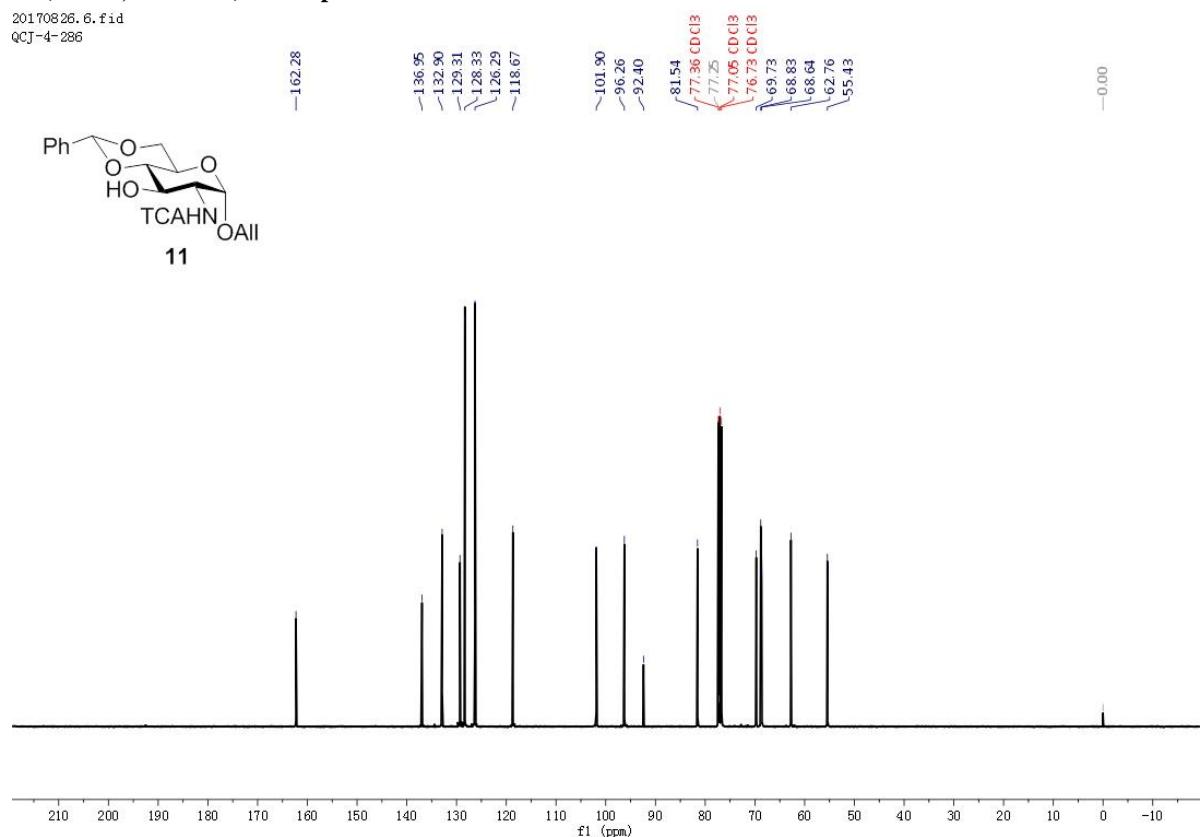
¹³C NMR (CDCl₃, 100 MHz) of compound 10



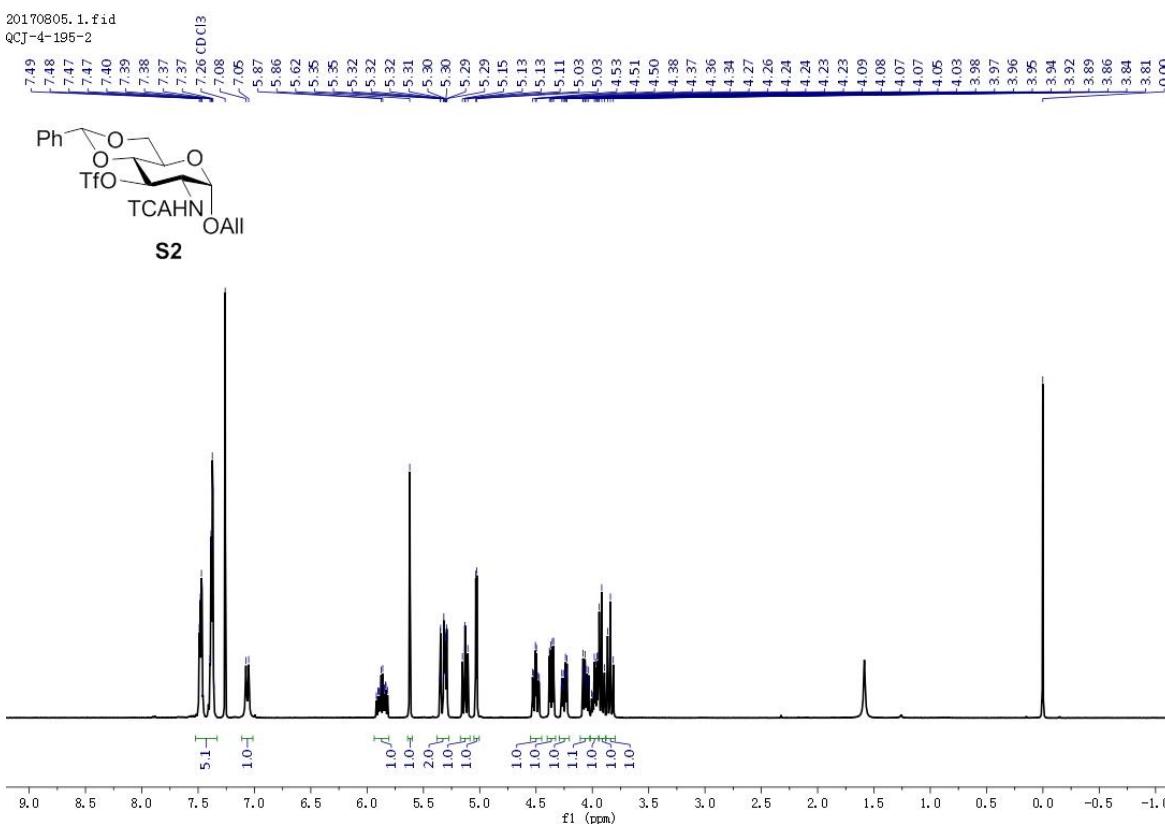
¹H NMR (CDCl₃, 400 MHz) of compound 11



¹³C NMR (CDCl₃, 100 MHz) of compound 11

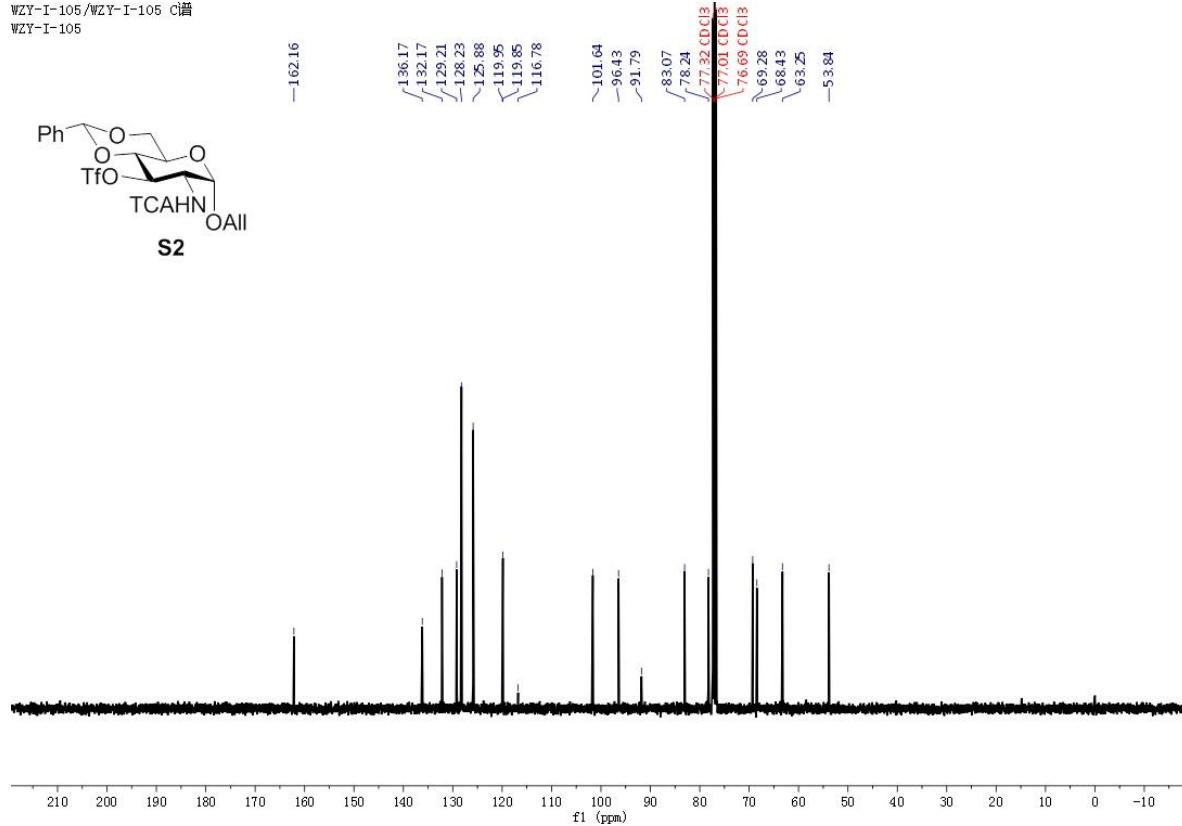
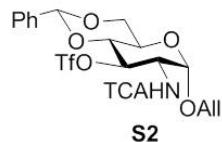


¹H NMR (CDCl₃, 400 MHz) of compound S2

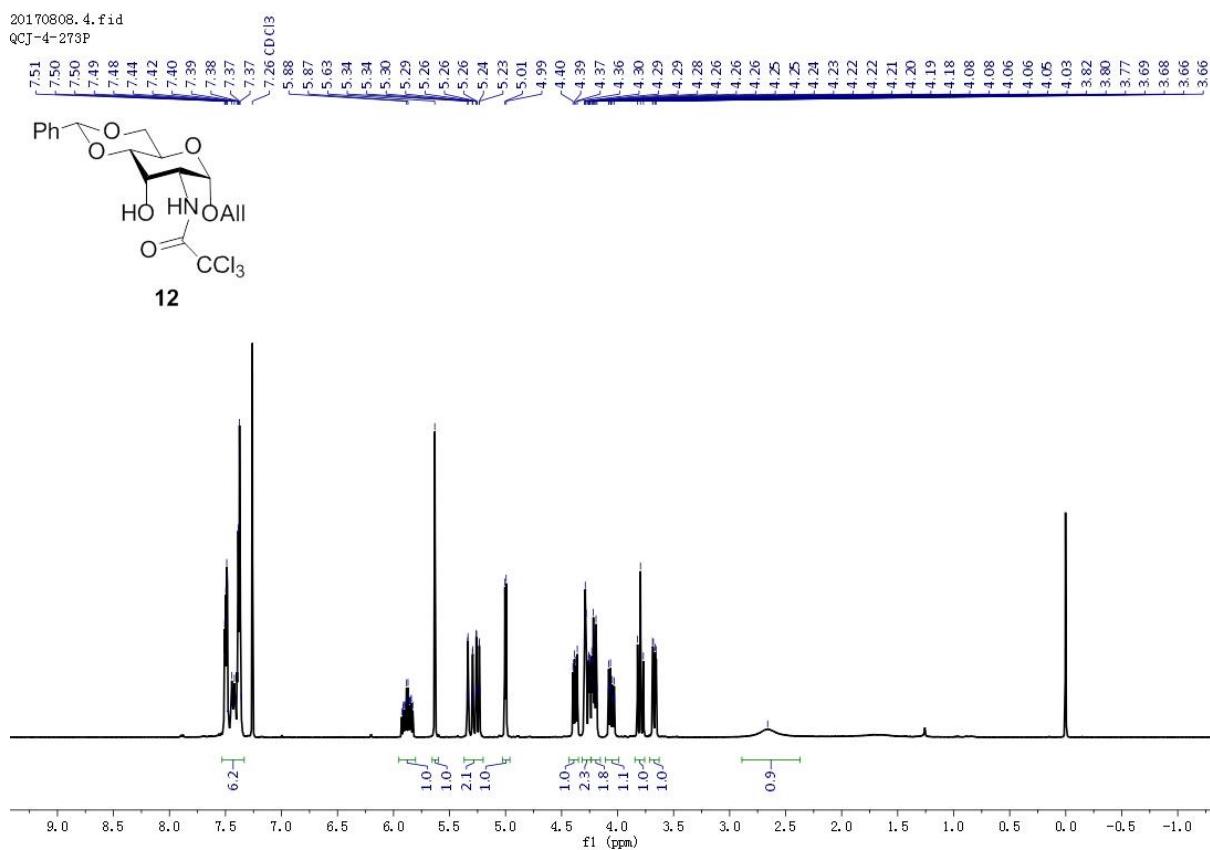


¹³C NMR (CDCl₃, 100 MHz) of compound S2

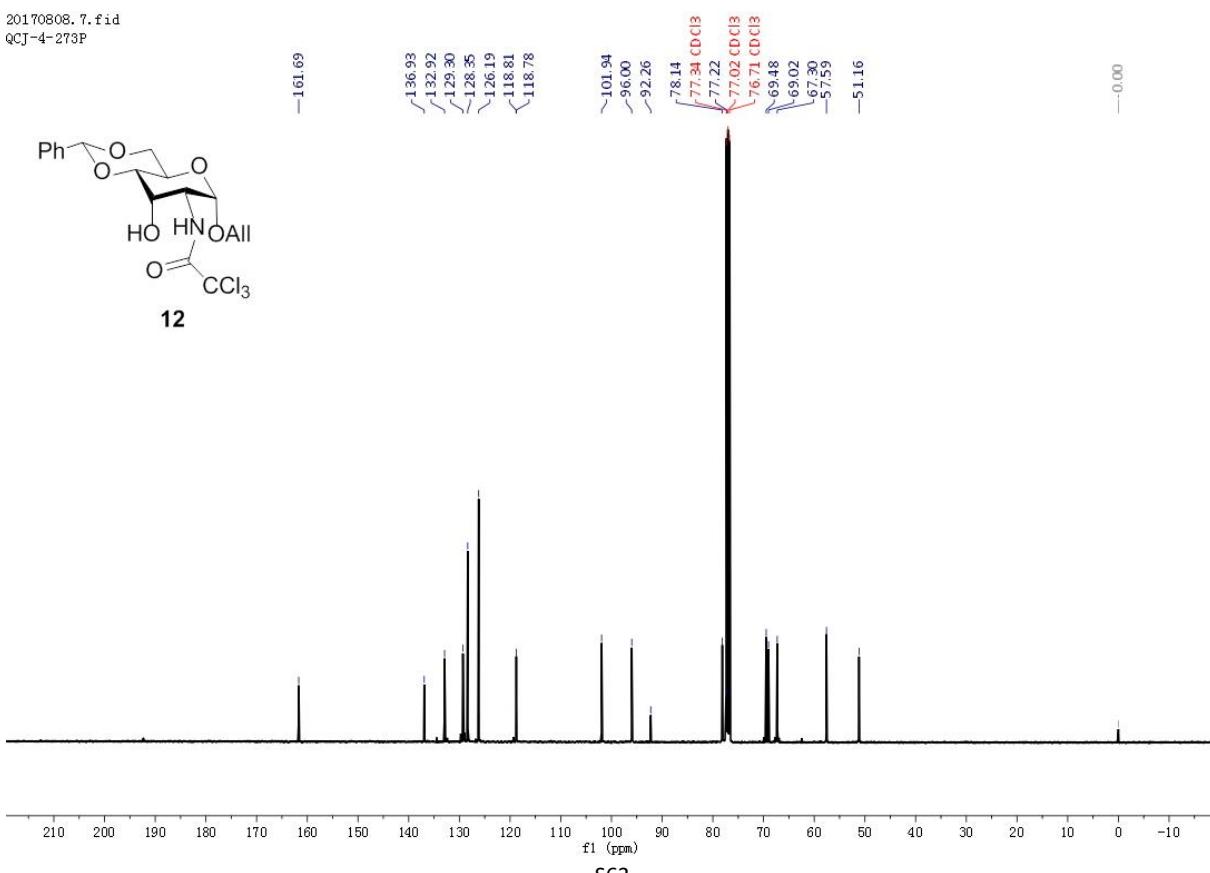
WZY-I-105/WZY-I-105 C譜
WZY-I-105



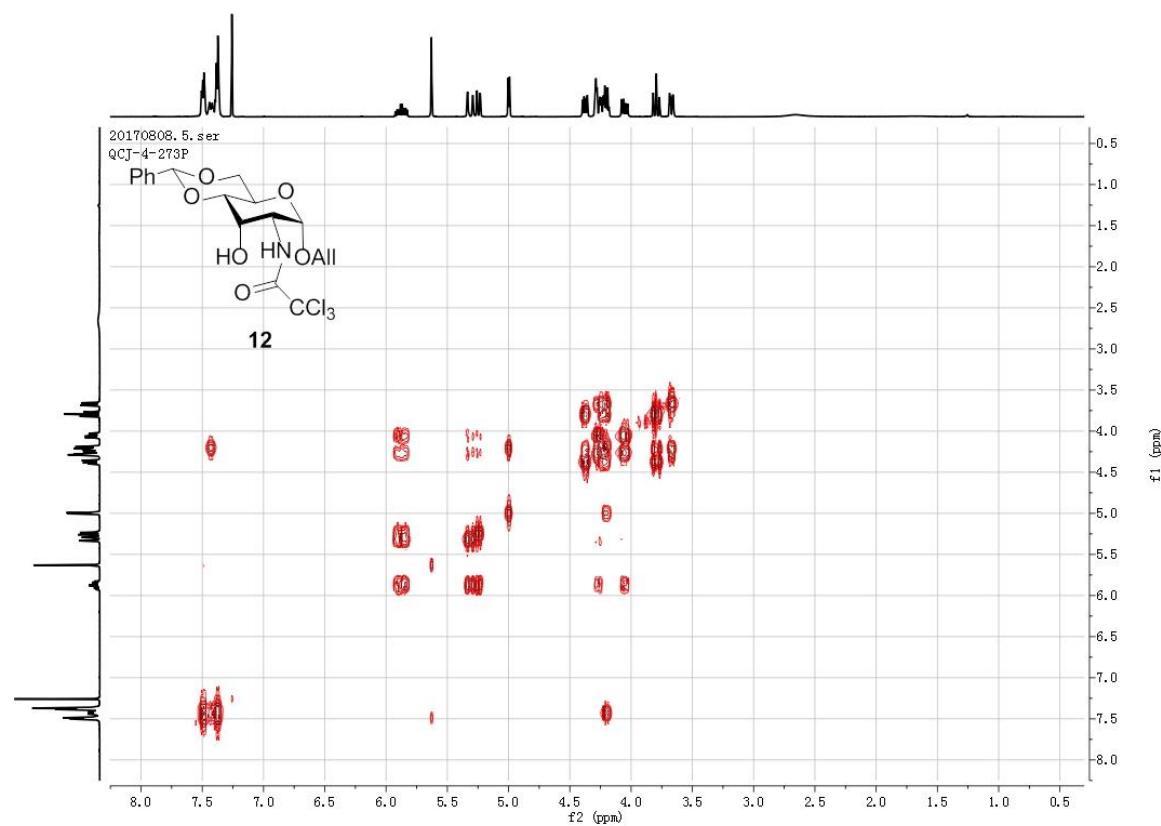
¹H NMR (CDCl₃, 400 MHz) of compound 12



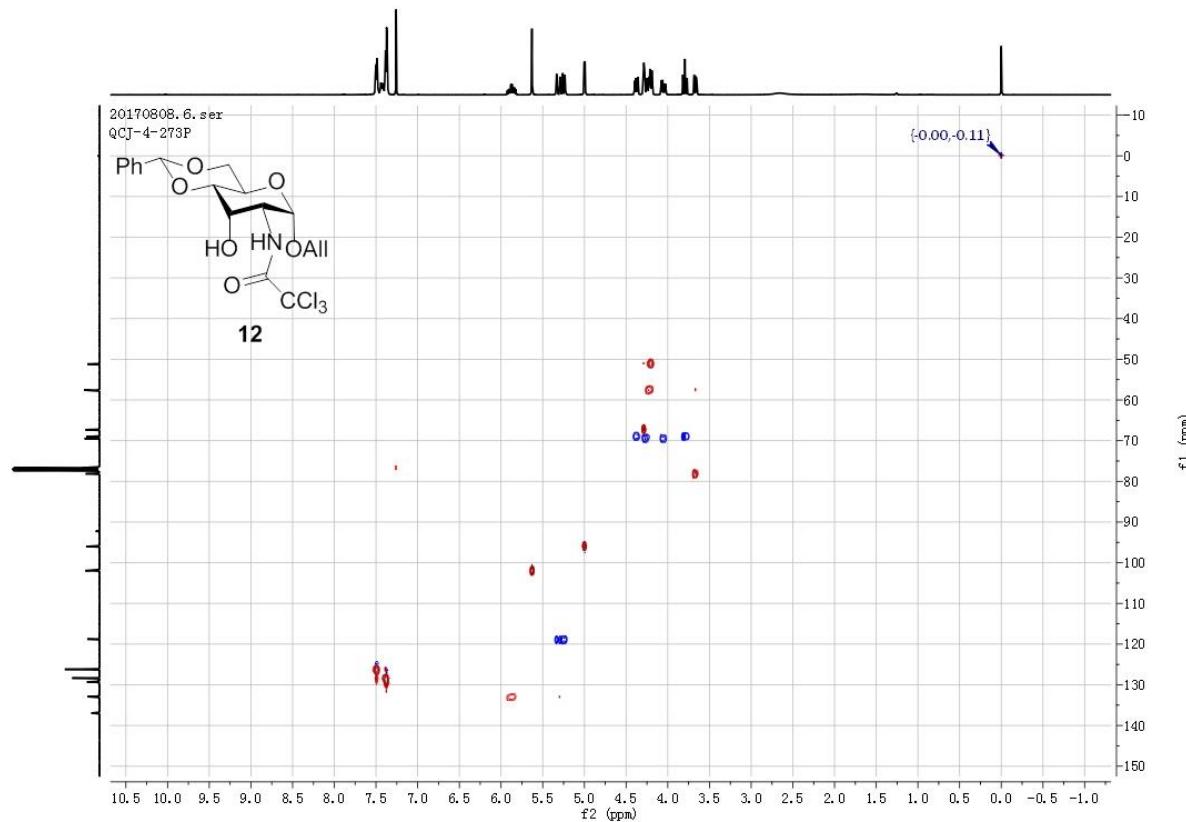
¹³C NMR (CDCl₃, 100 MHz) of compound 12



¹H-¹H COSY (CDCl₃, 400 MHz) of compound 12

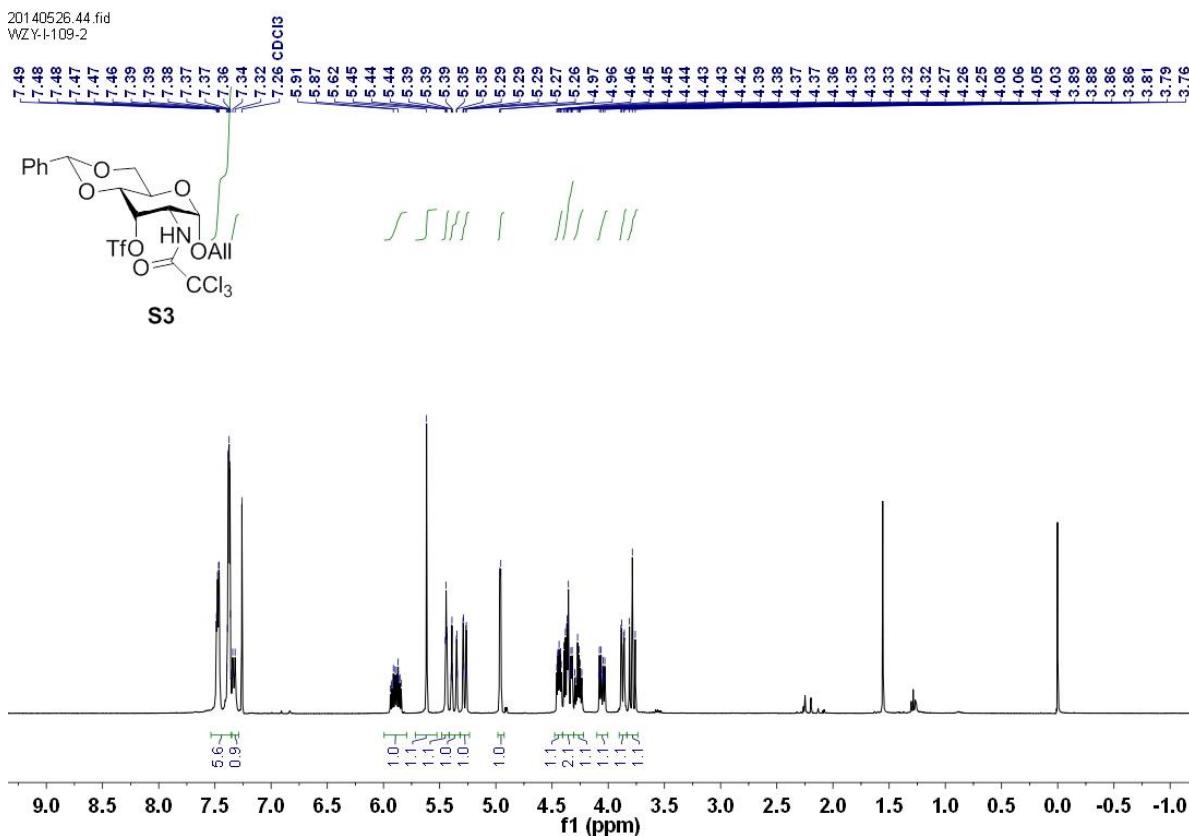


¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 12



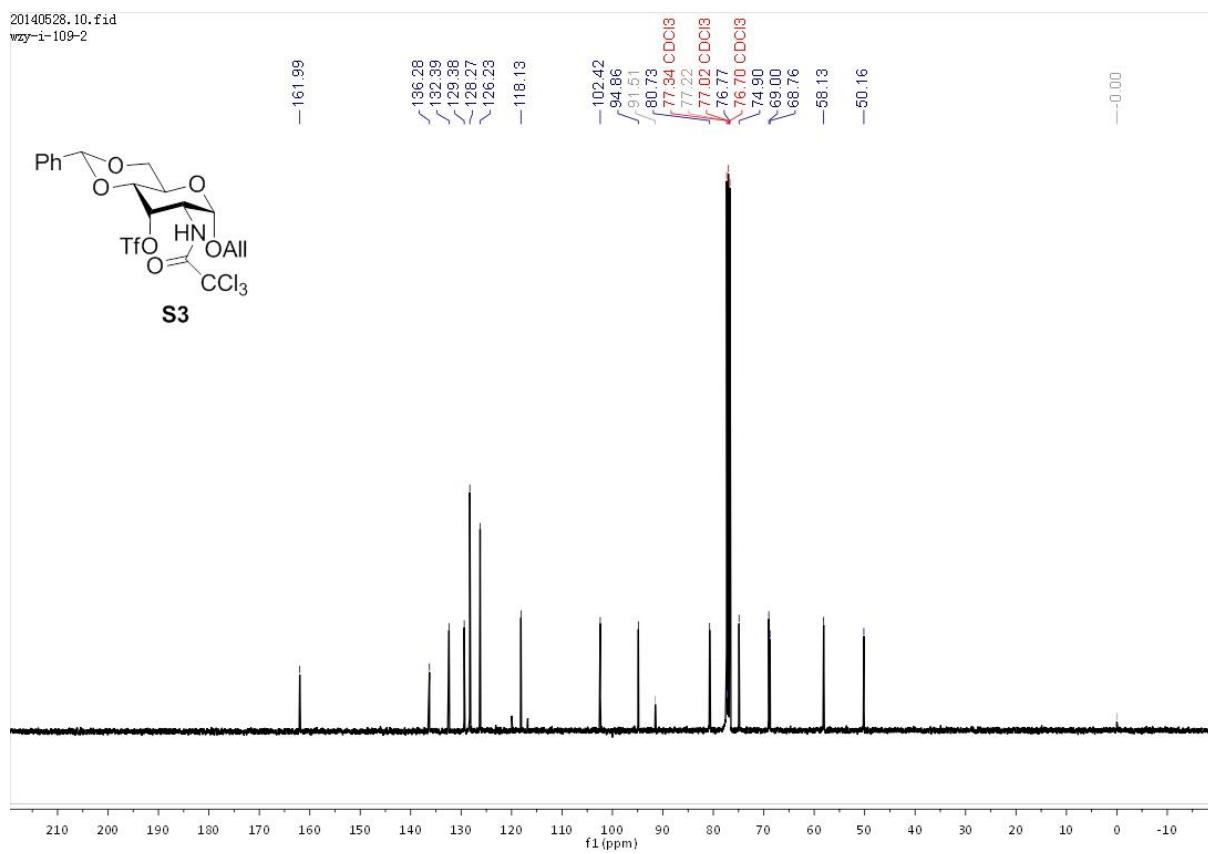
¹H NMR (CDCl₃, 400 MHz) of compound S3

20140526.44.fid
WZ Y-I-109-2

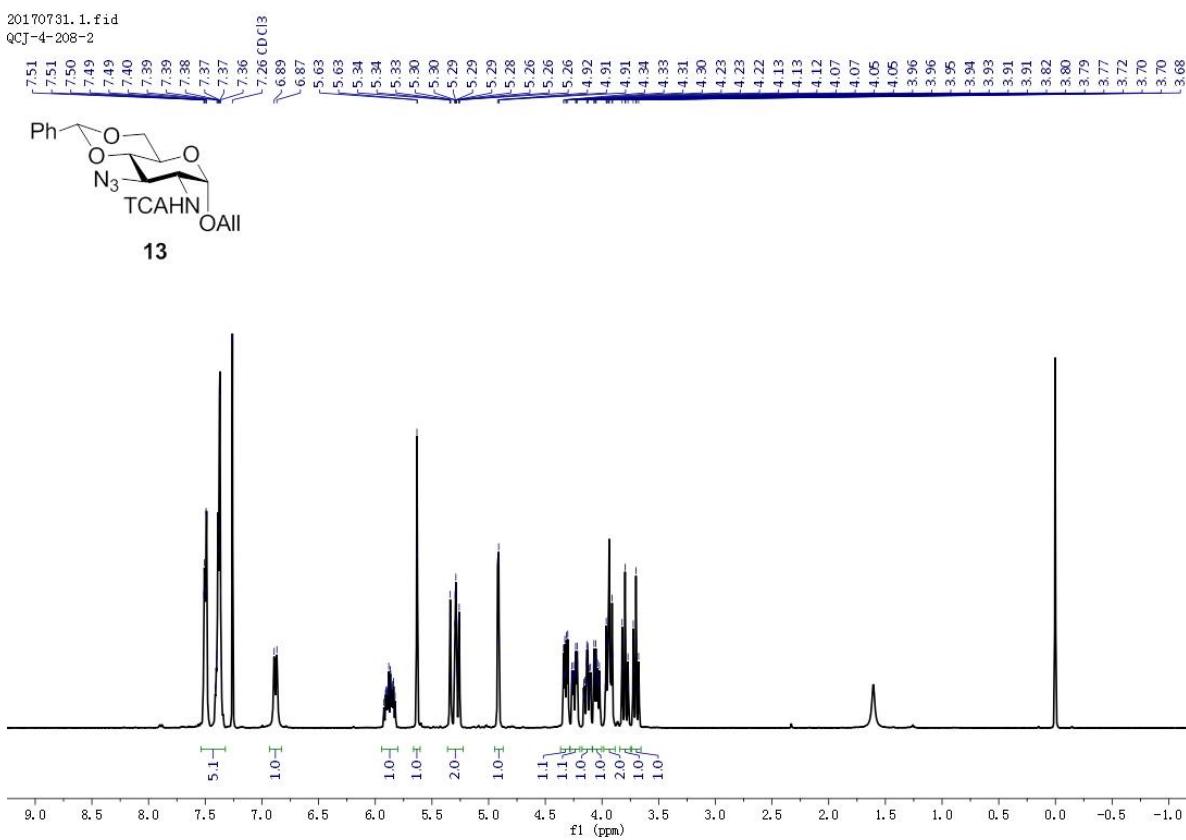


¹³C NMR (CDCl₃, 100 MHz) of compound S3

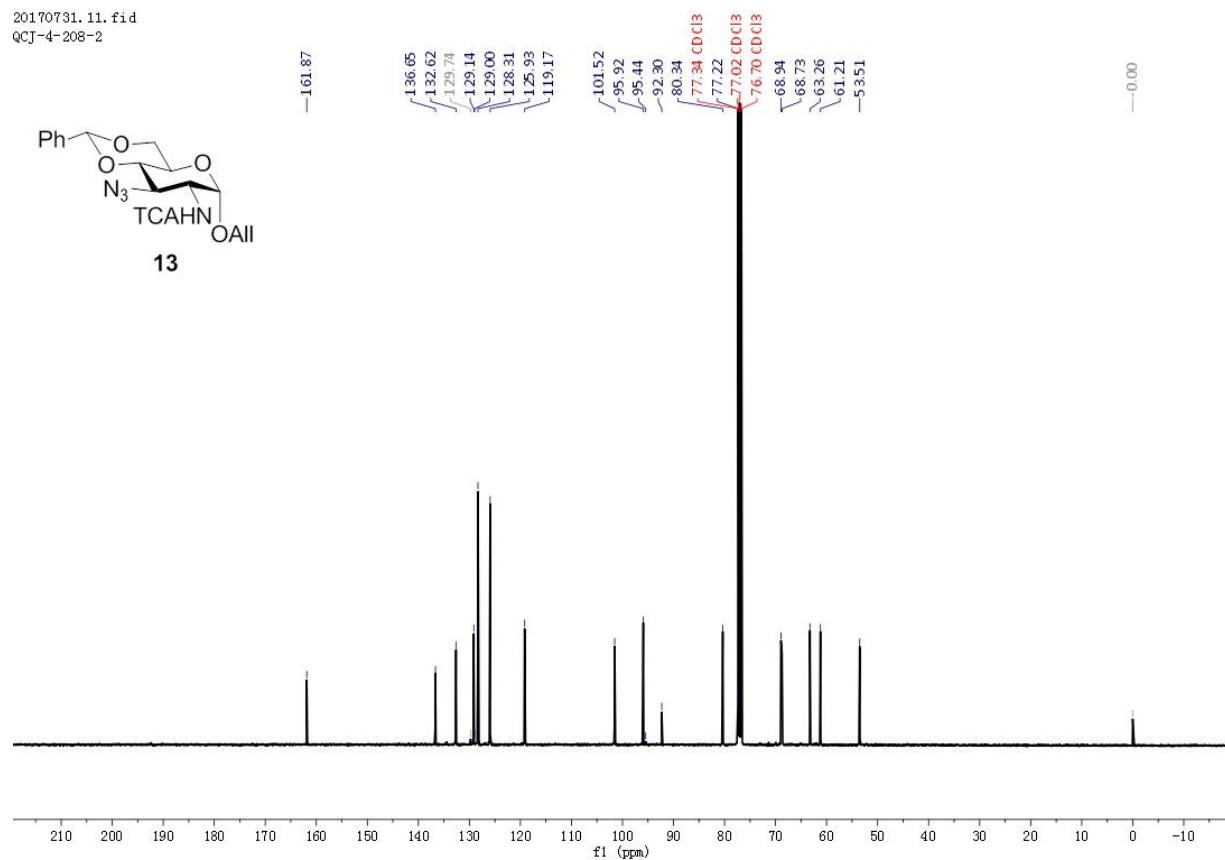
20140528.10.fid
wzy-i-109-2



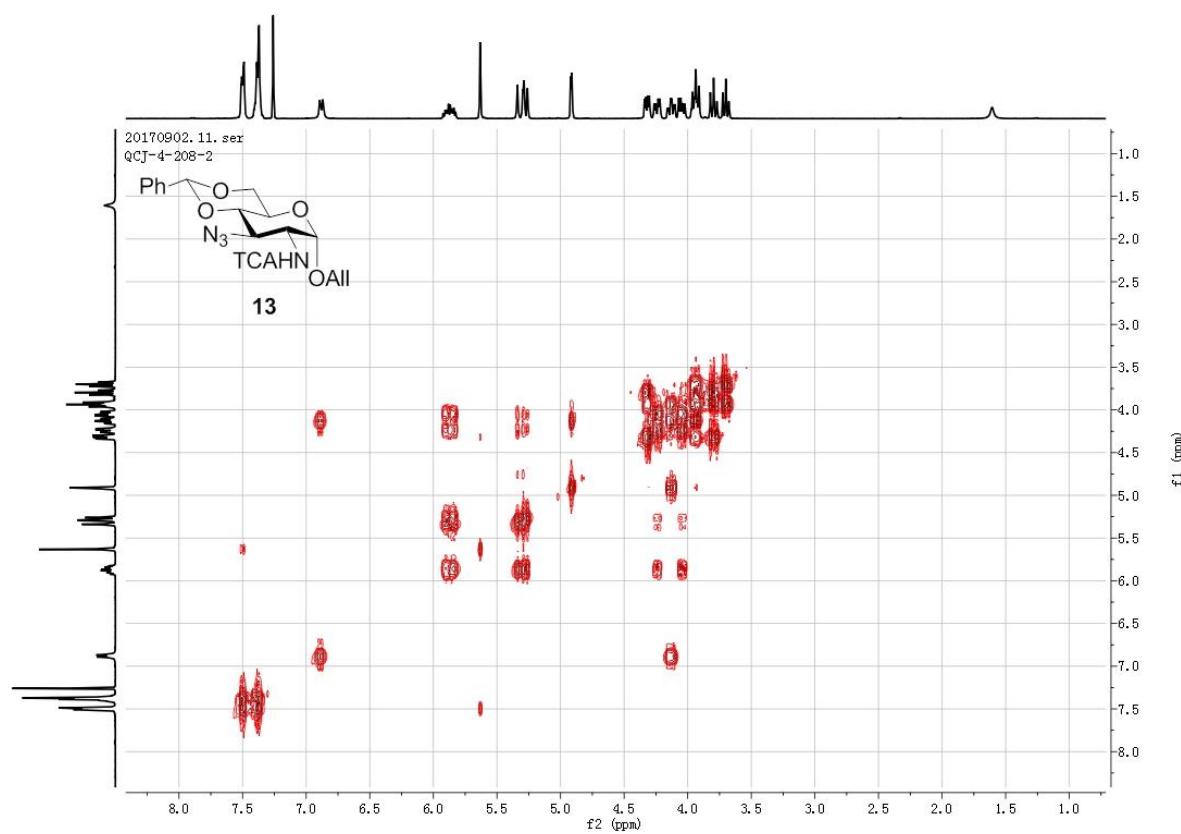
¹H NMR (CDCl₃, 400 MHz) of compound 13



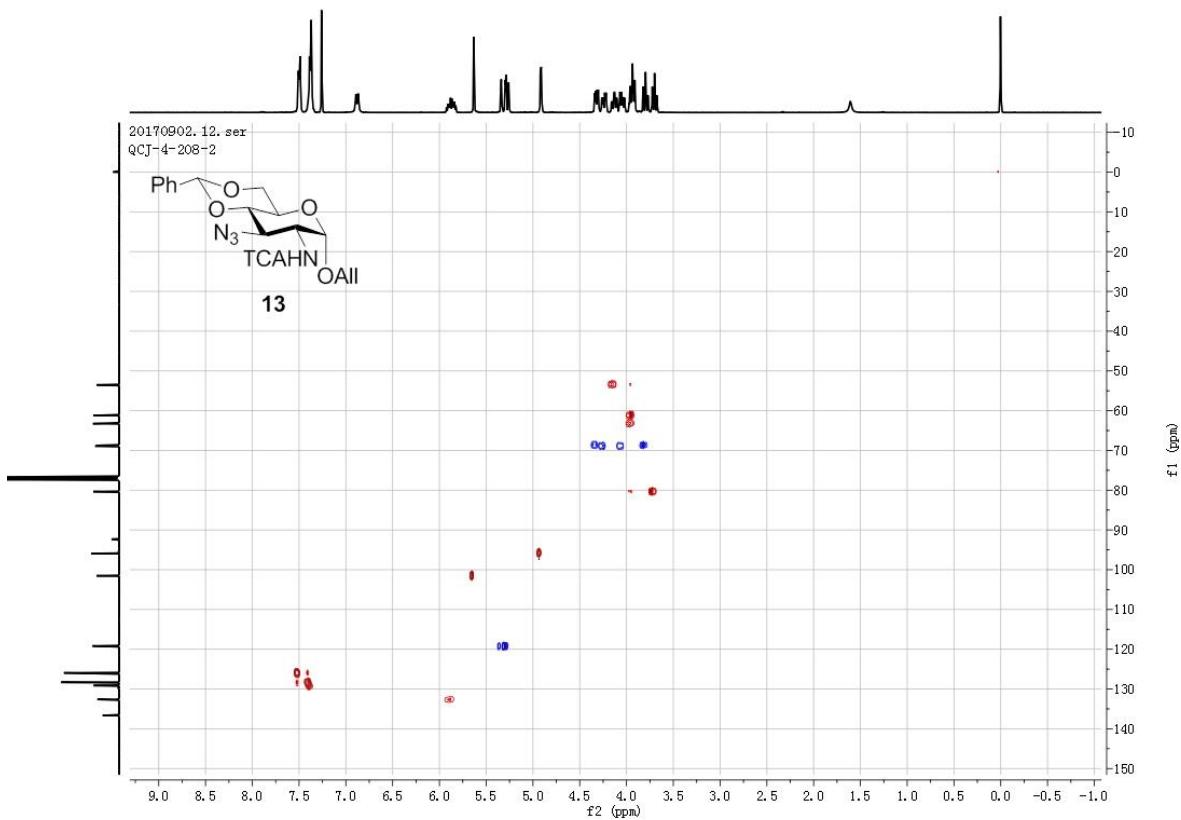
¹³C NMR (CDCl₃, 100 MHz) of compound 13



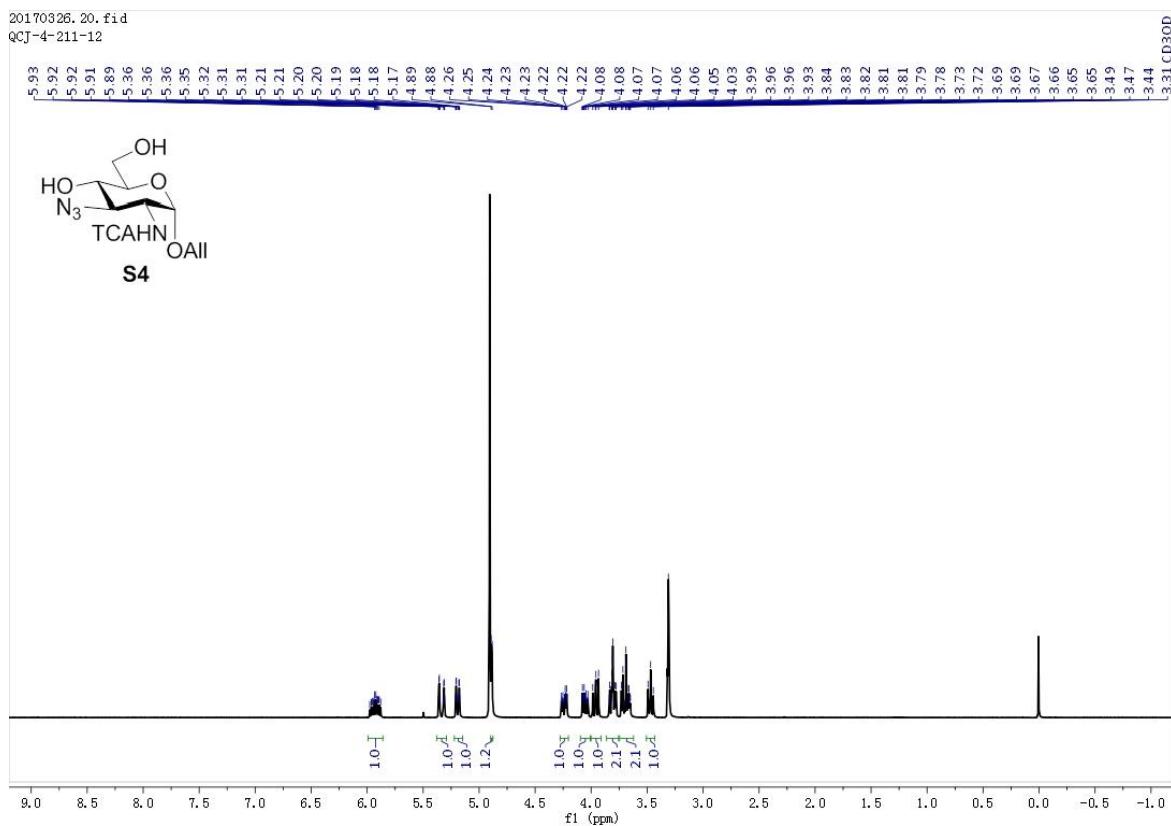
¹H-¹H COSY (CDCl₃, 400 MHz) of compound 13



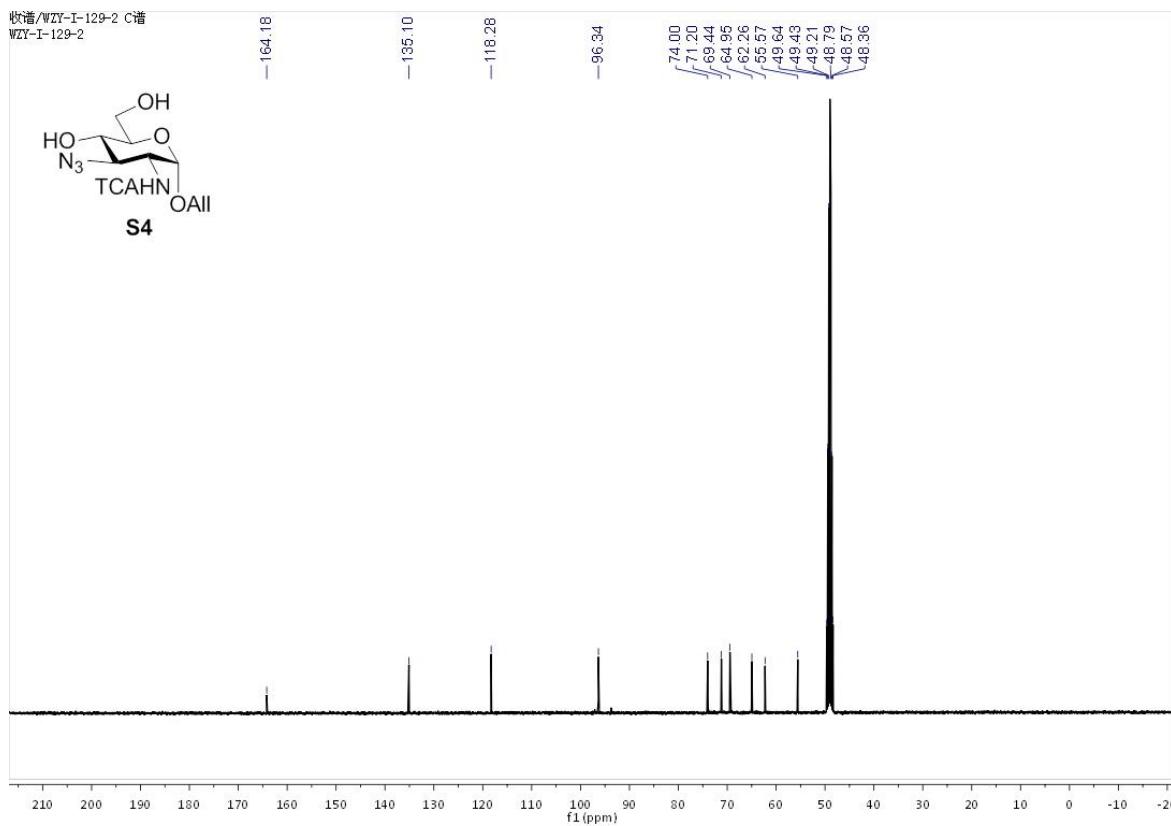
¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 13



¹HNMR (CD₃OD, 400 MHz) of compound S4

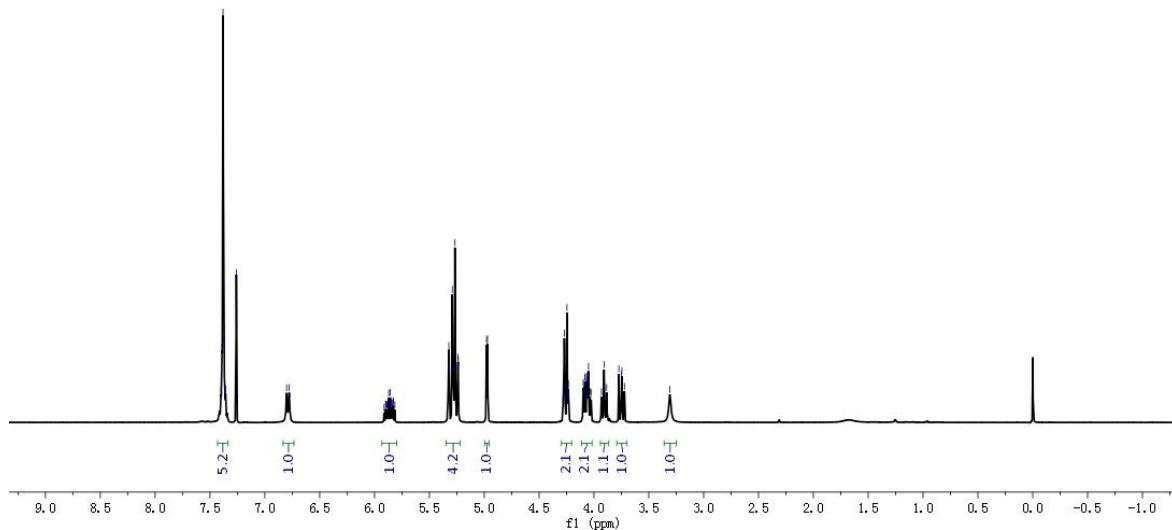
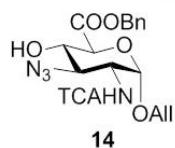


¹³CNMR (CD₃OD, 100 MHz) of compound S4



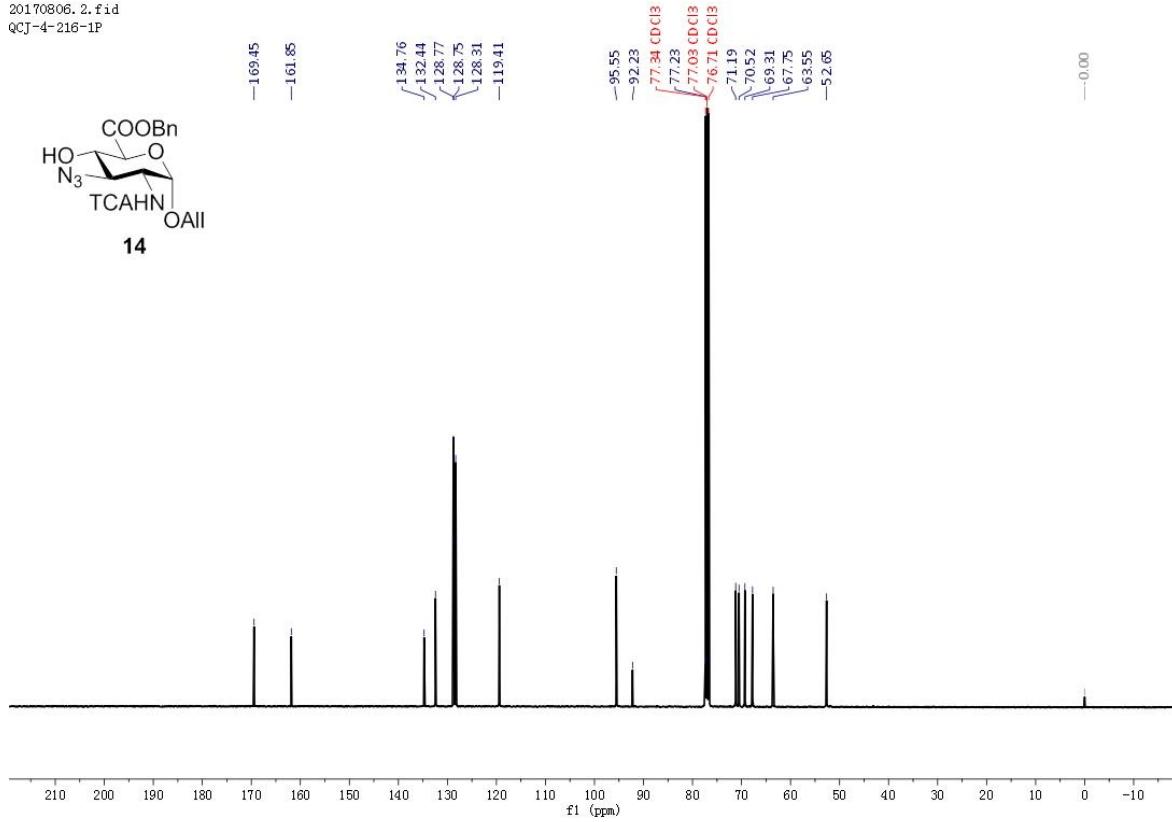
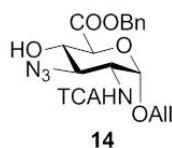
¹H NMR (CDCl₃, 400 MHz) of compound 14

20170806.1.fid
QCT-4-216-1P

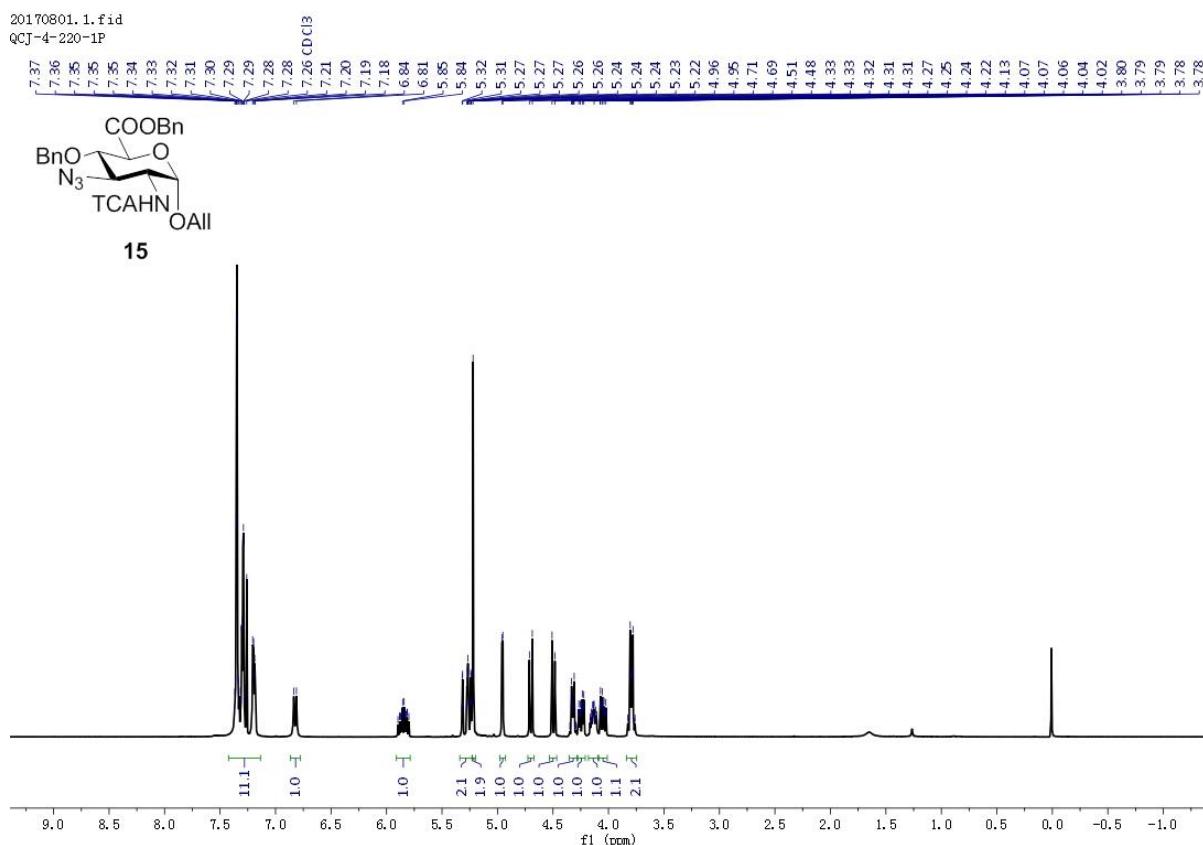


¹³C NMR (CDCl₃, 100 MHz) of compound 14

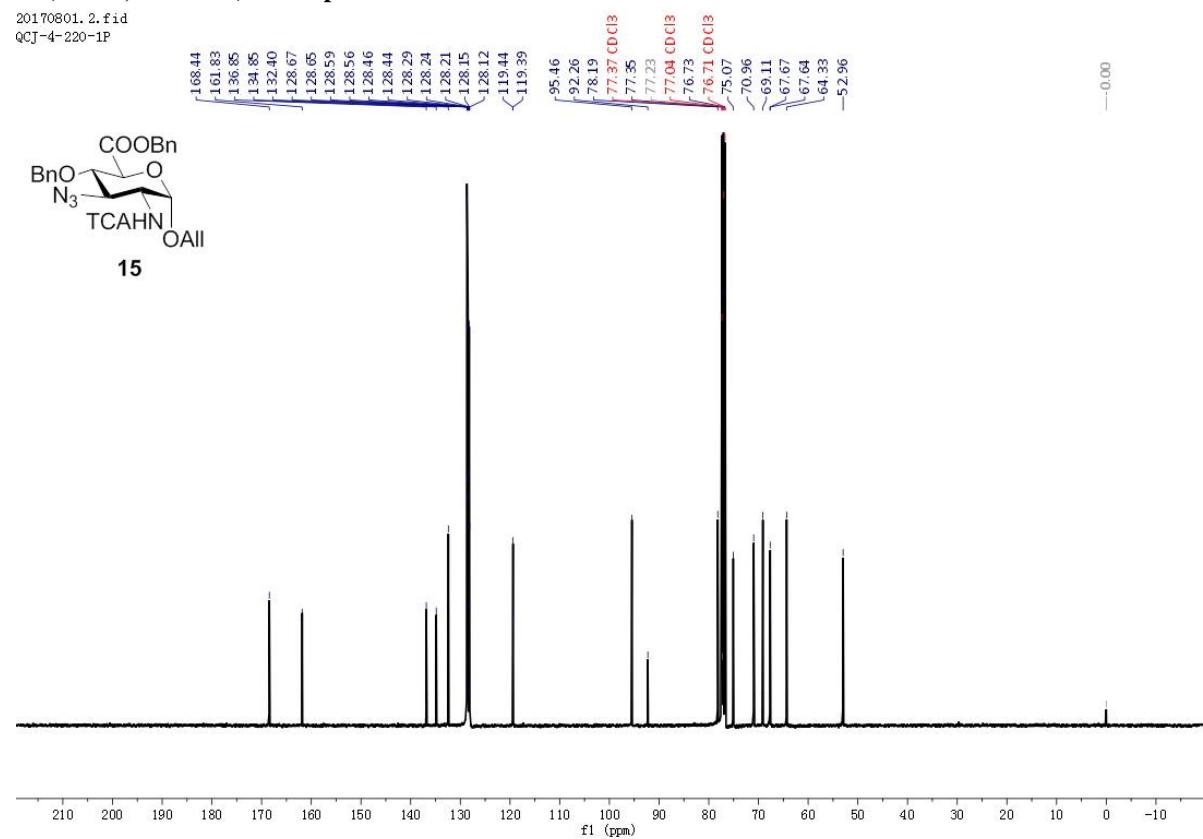
20170806.2.fid
QCJ-4-216-1P



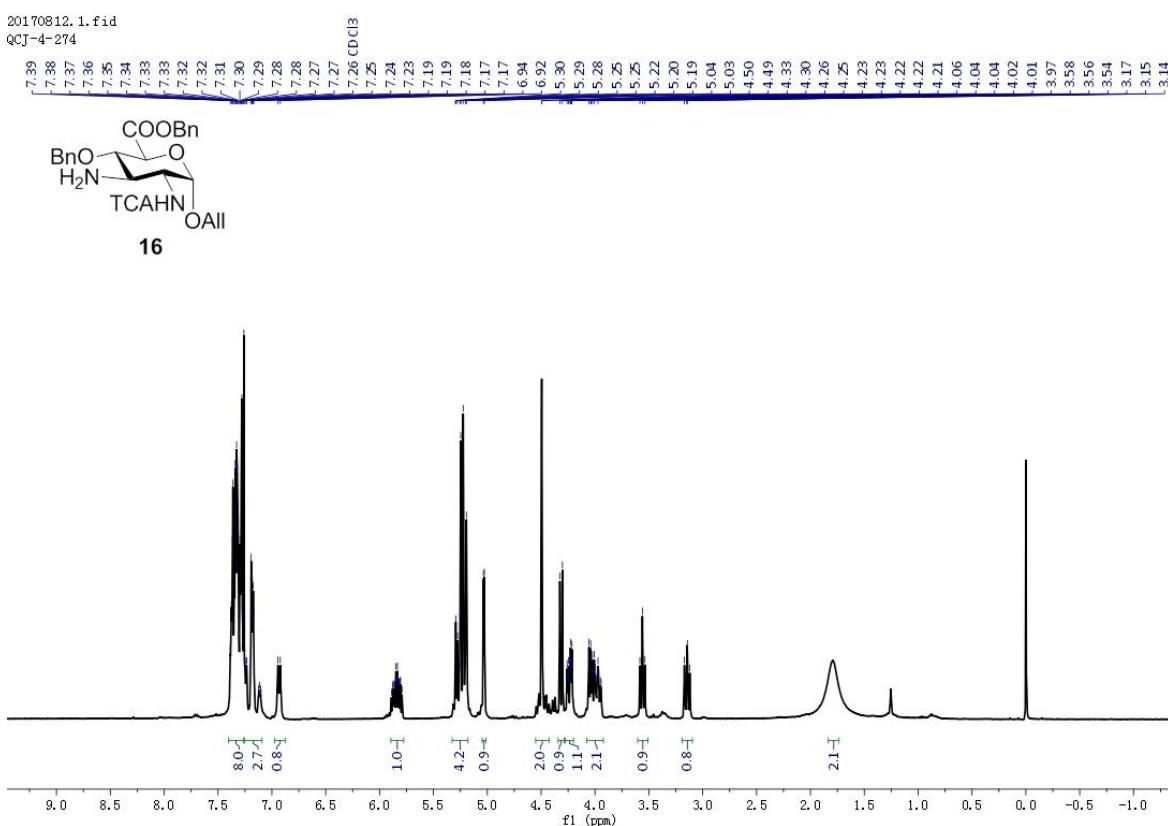
¹H NMR (CDCl₃, 400 MHz) of compound 15



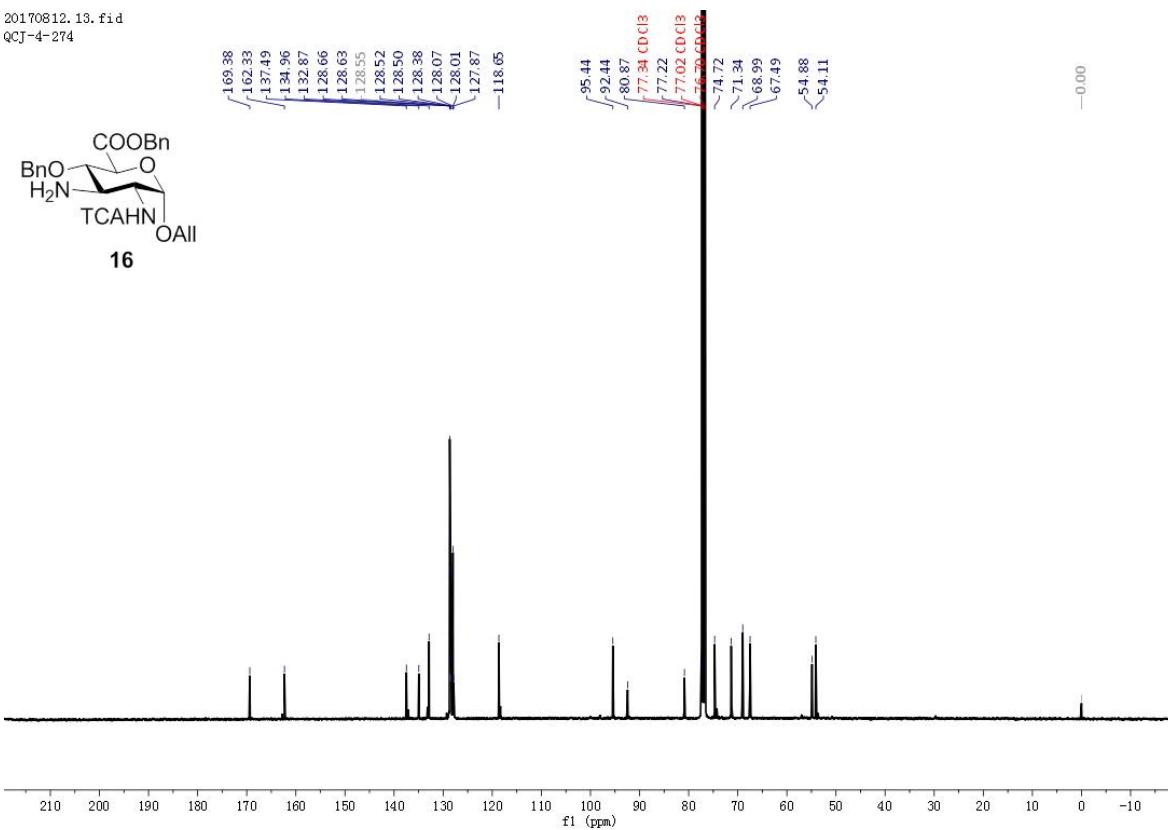
¹³C NMR (CDCl₃, 100 MHz) of compound 15



¹H NMR (CDCl₃, 400 MHz) of compound 16

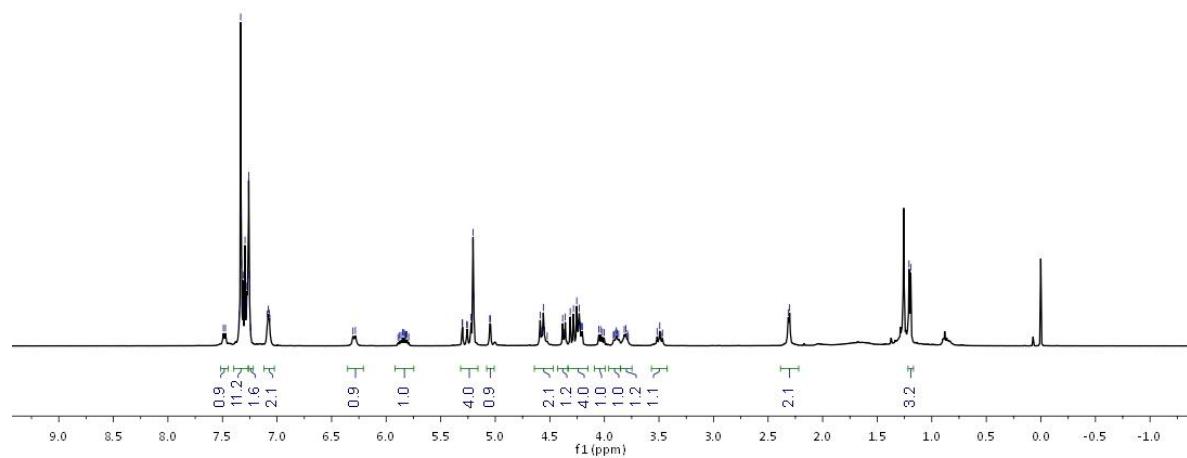
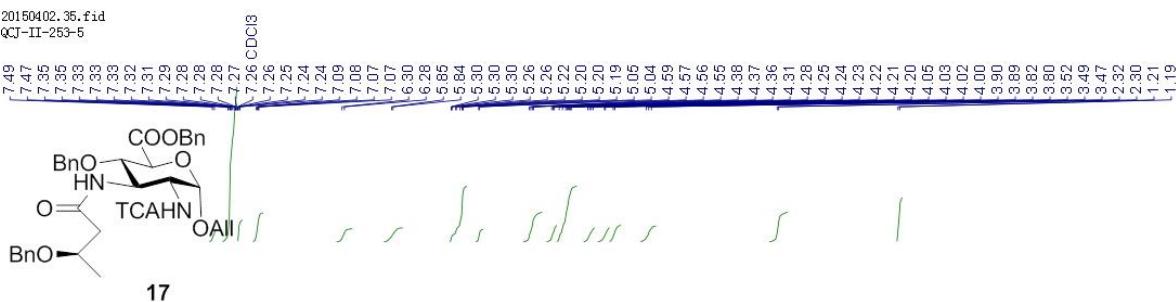


¹³C NMR (CDCl₃, 100 MHz) of compound 16

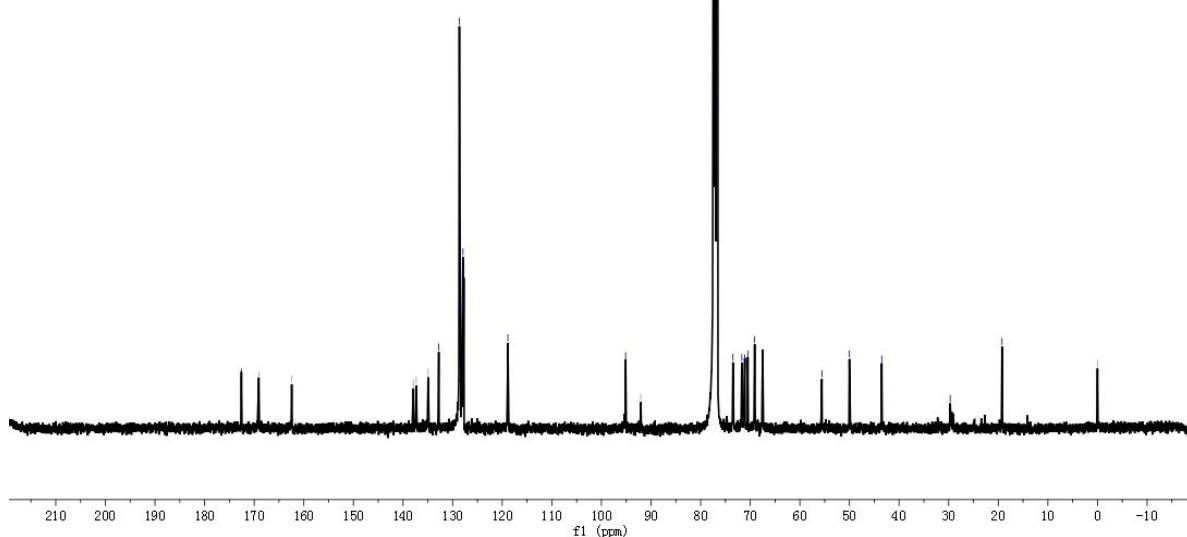


¹H NMR (CDCl₃, 400 MHz) of compound 17

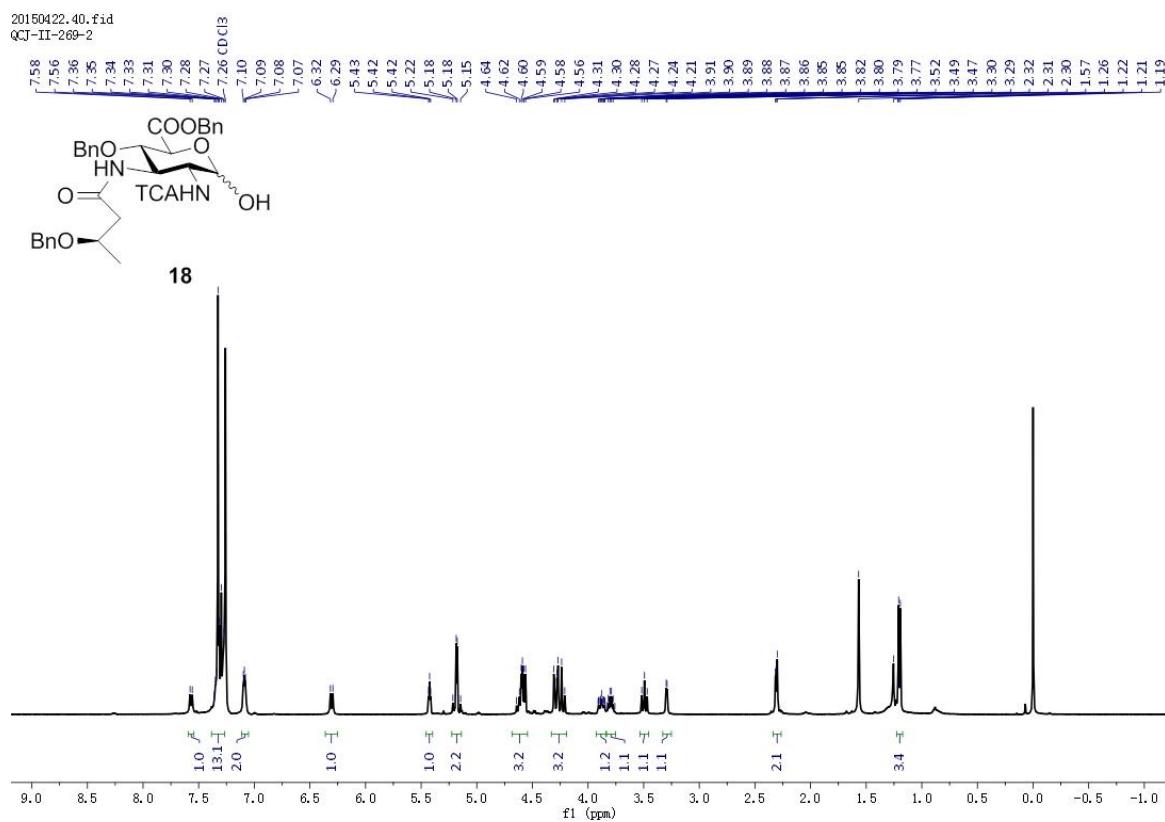
20150402.35.fid
QJ-II-253-5



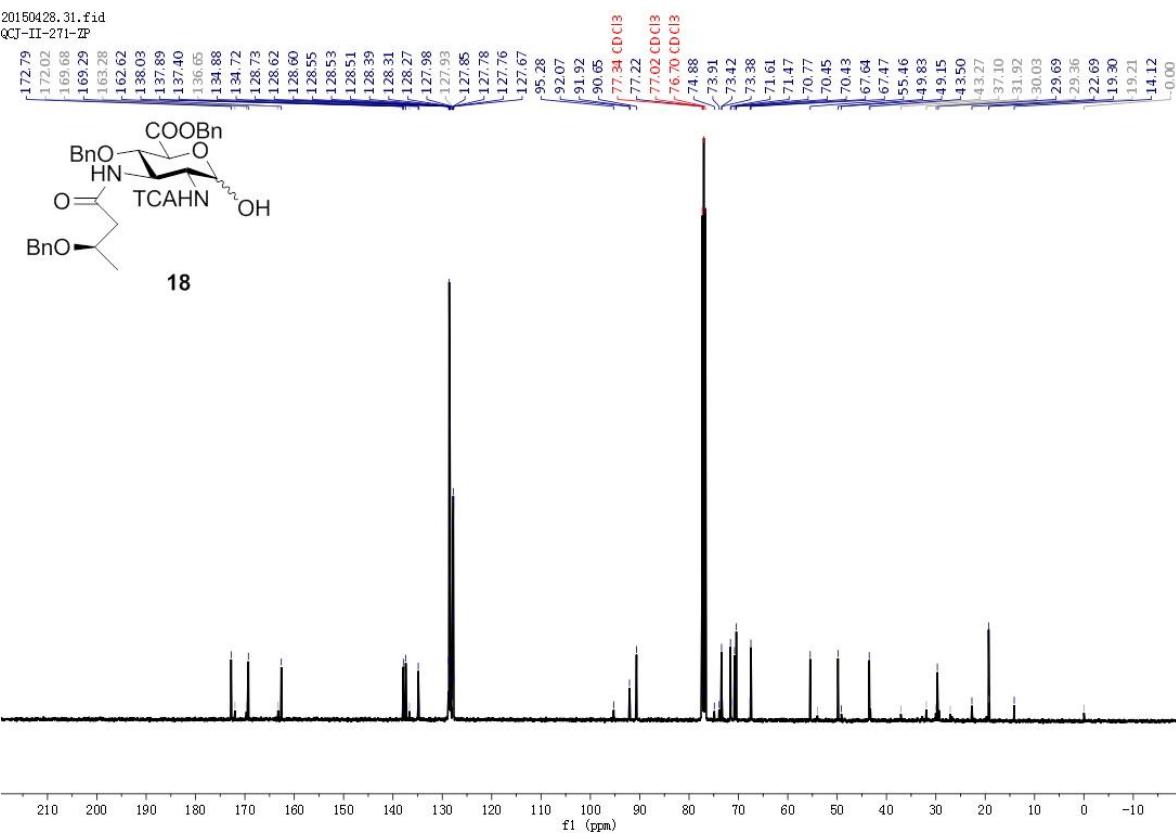
¹³C NMR (CDCl₃, 100 MHz) of compound 17



¹H NMR (CDCl₃, 400 MHz) of compound 18

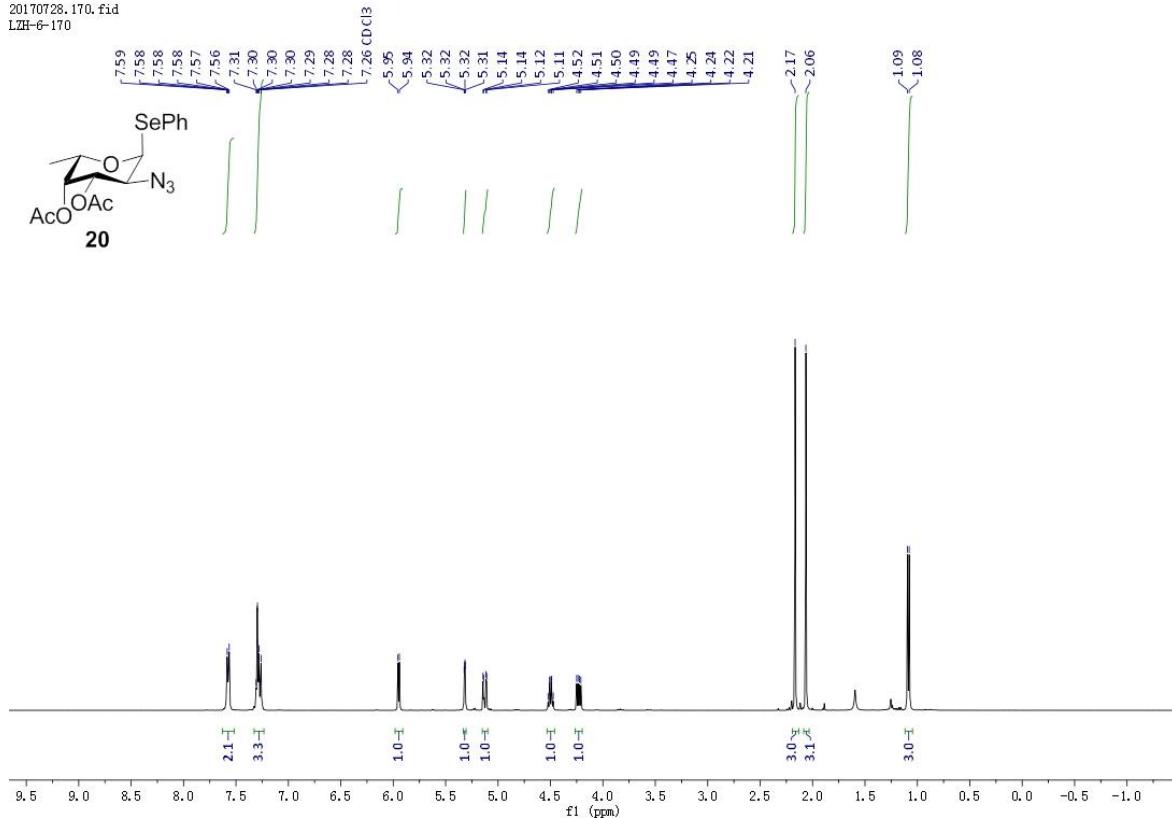
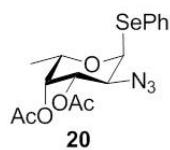


¹³C NMR (CDCl₃, 100 MHz) of compound 18



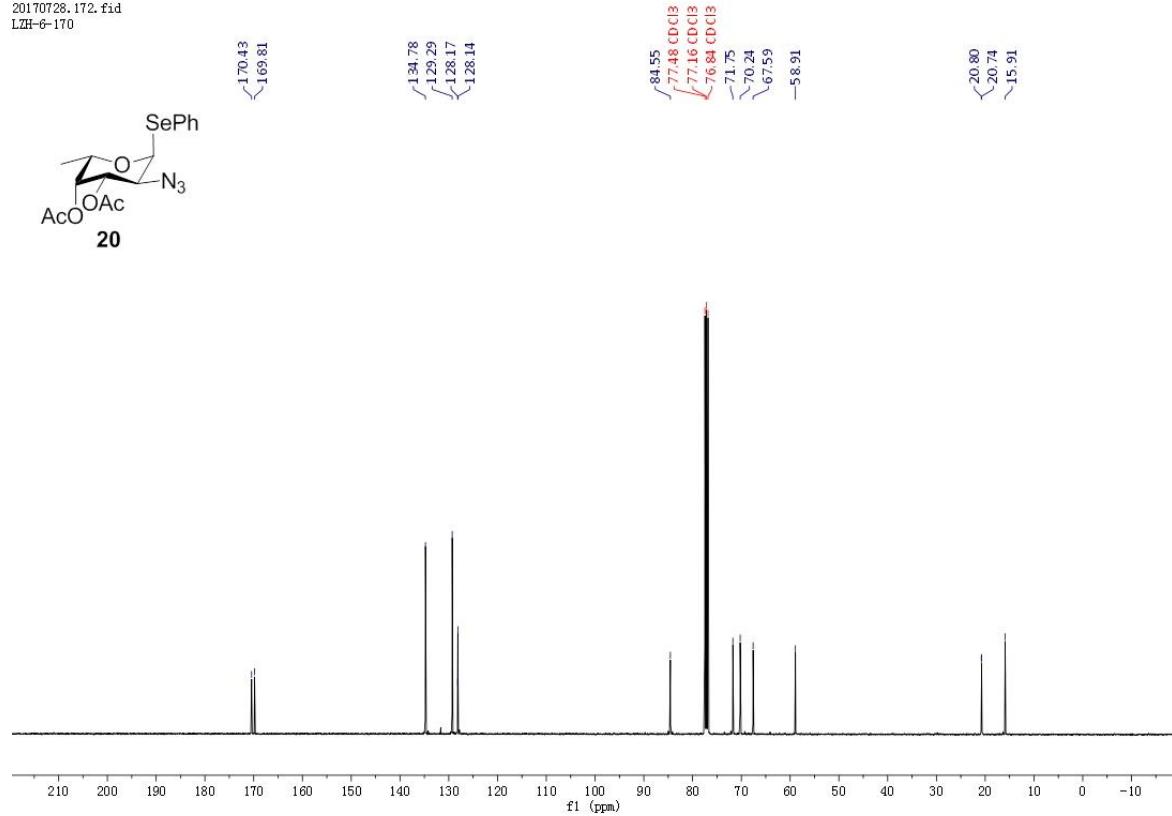
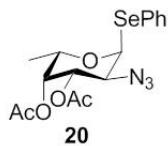
¹H NMR (CDCl₃, 400 MHz) of compound 20

20170728.170.fid
LZH-6-170



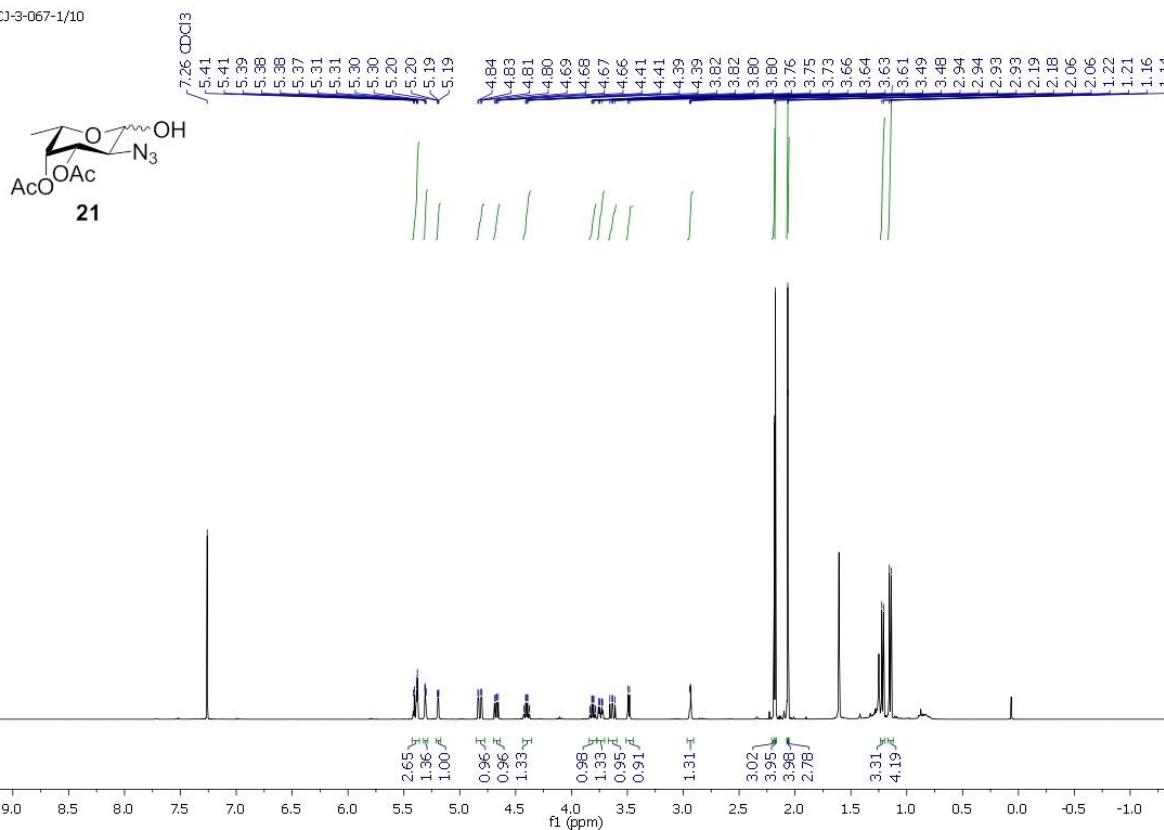
¹³C NMR (CDCl₃, 100 MHz) of compound 20

20170728.172.fid
LZH-6-170



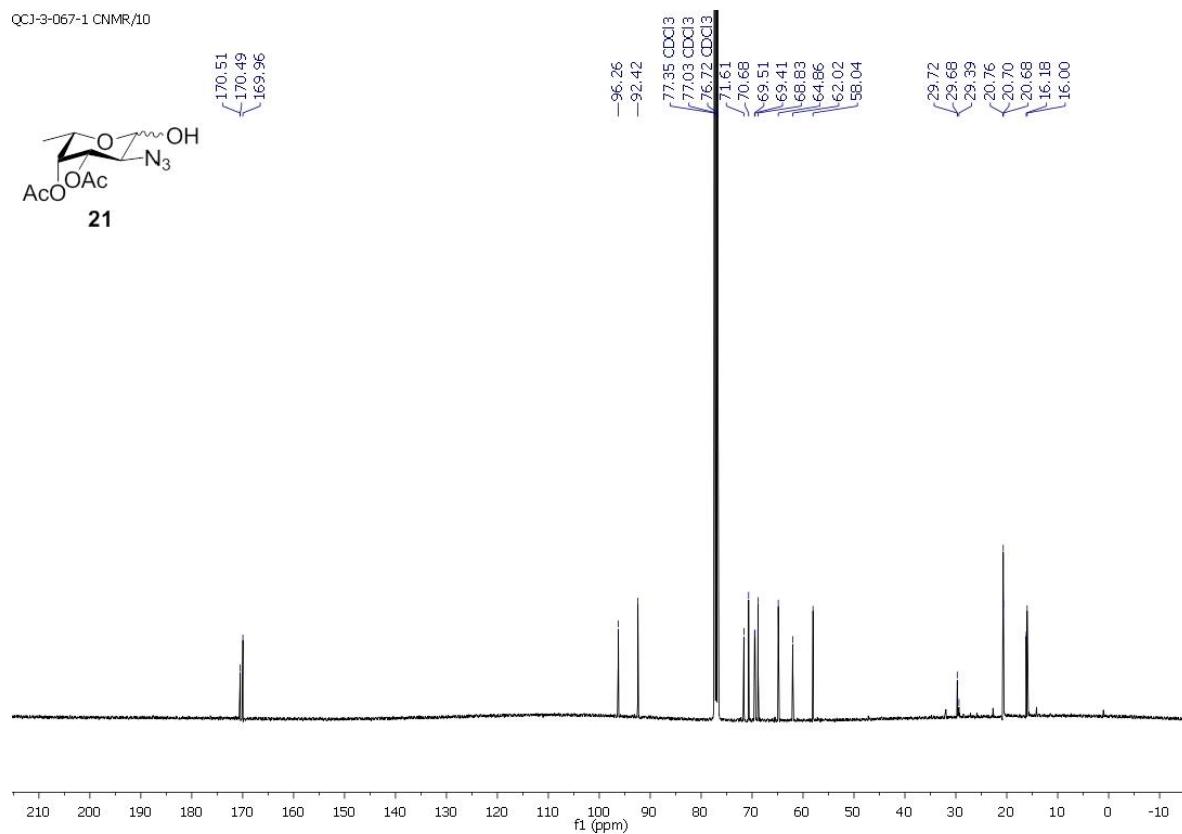
¹H NMR (CDCl₃, 400 MHz) of compound 21

OCJ-3-067-1/10

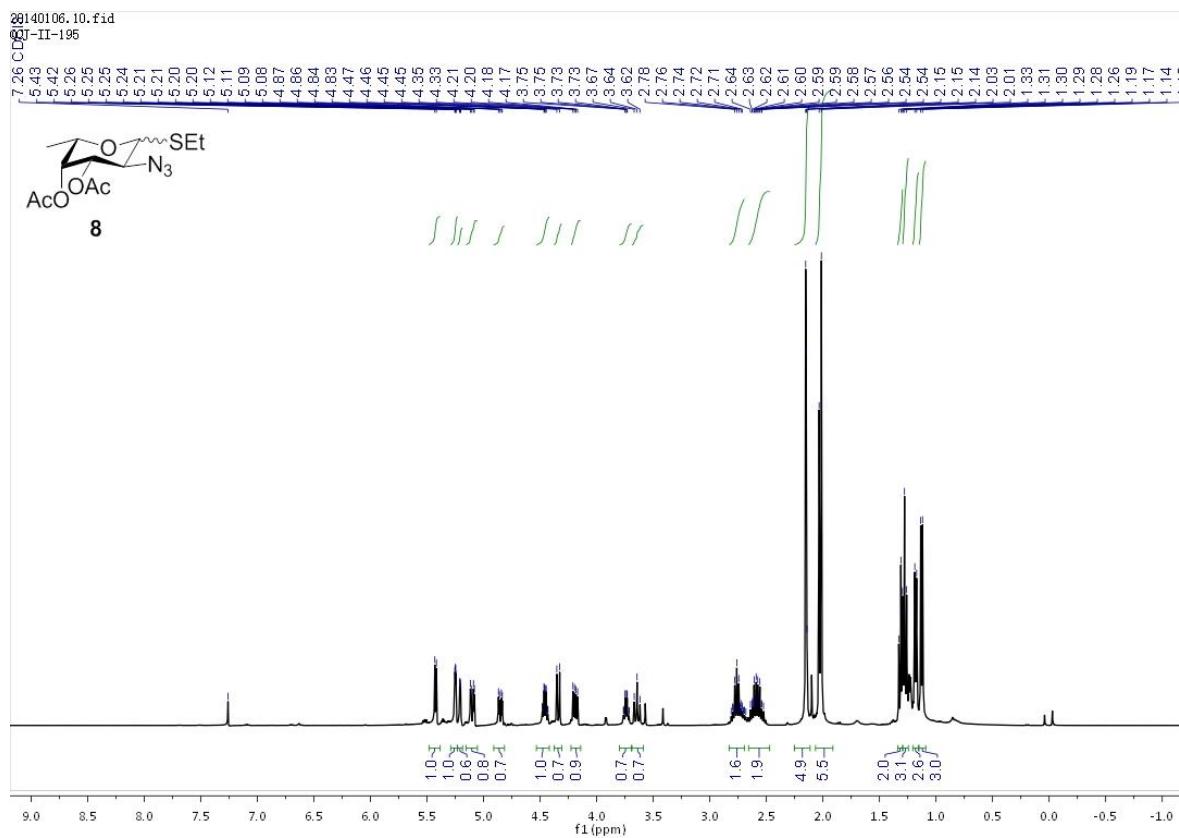


¹³C NMR (CDCl₃, 100 MHz) of compound 21

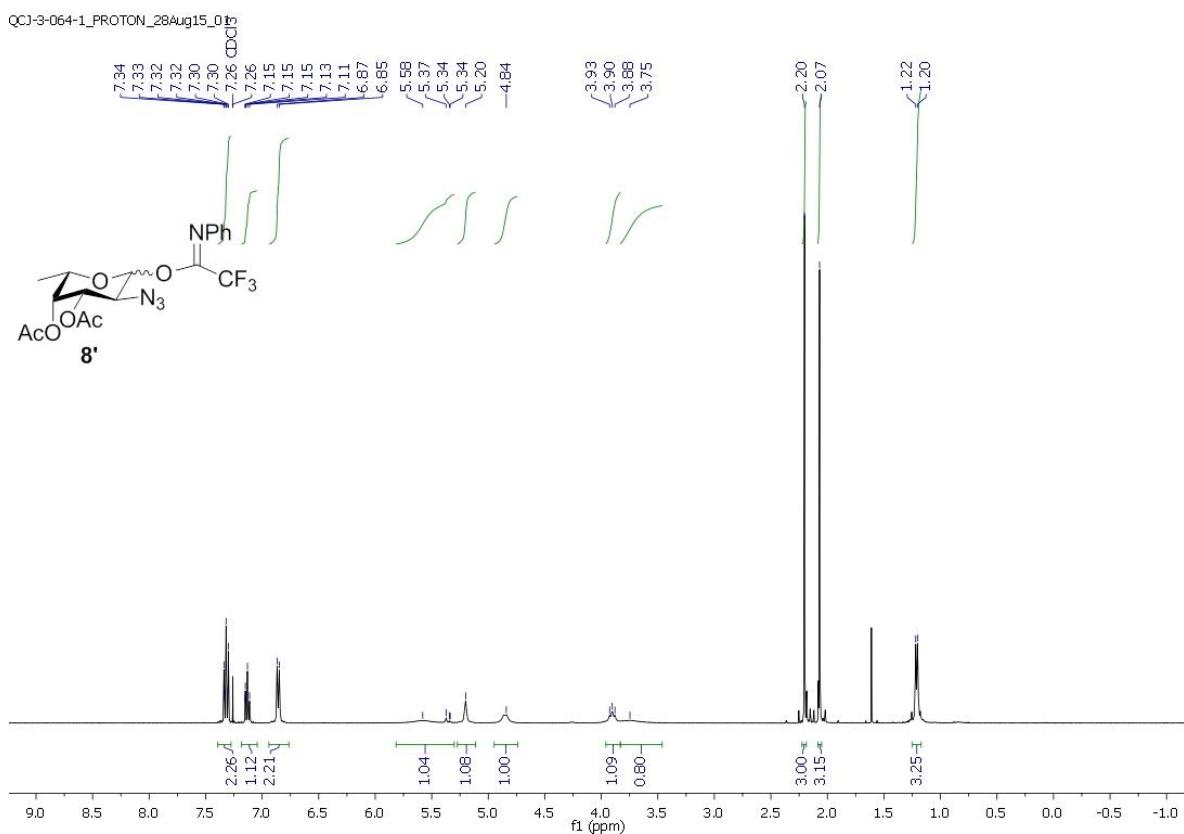
OC1-3-067-1 CNMR/10



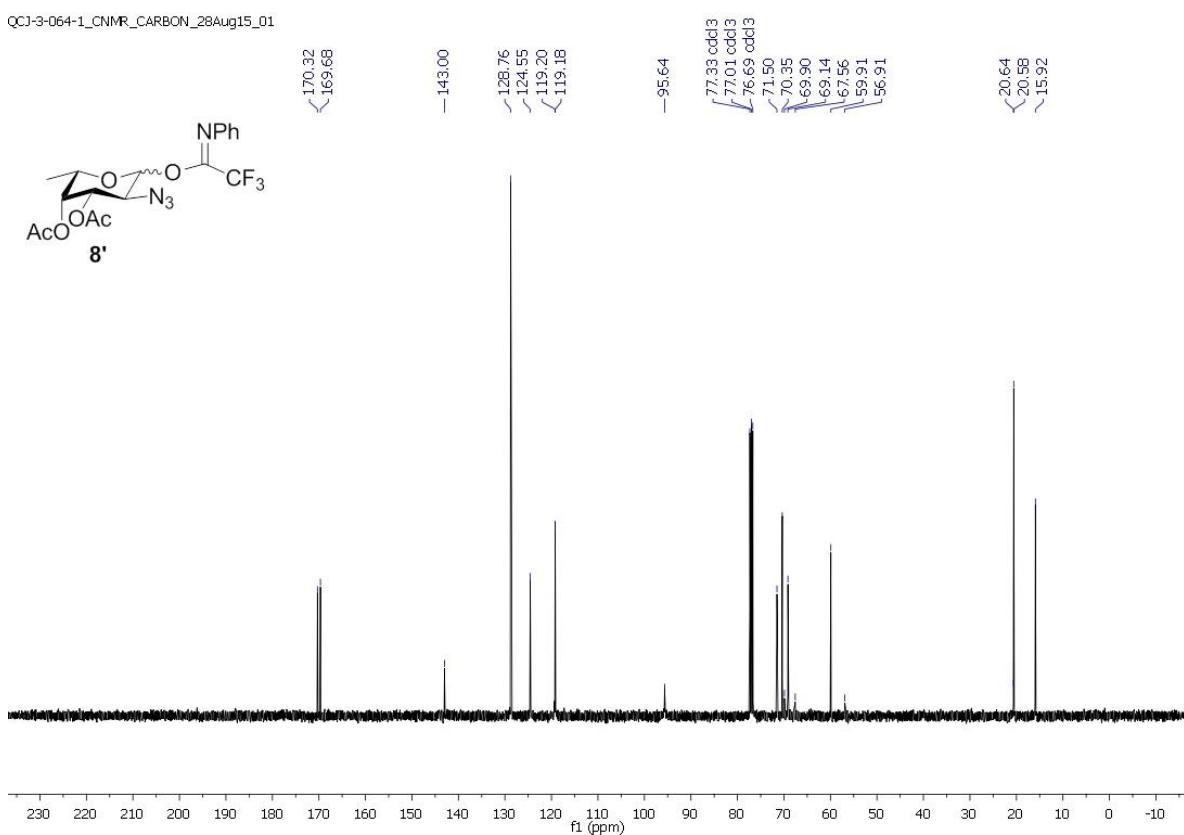
¹H NMR (CDCl₃, 400 MHz) of compound 8



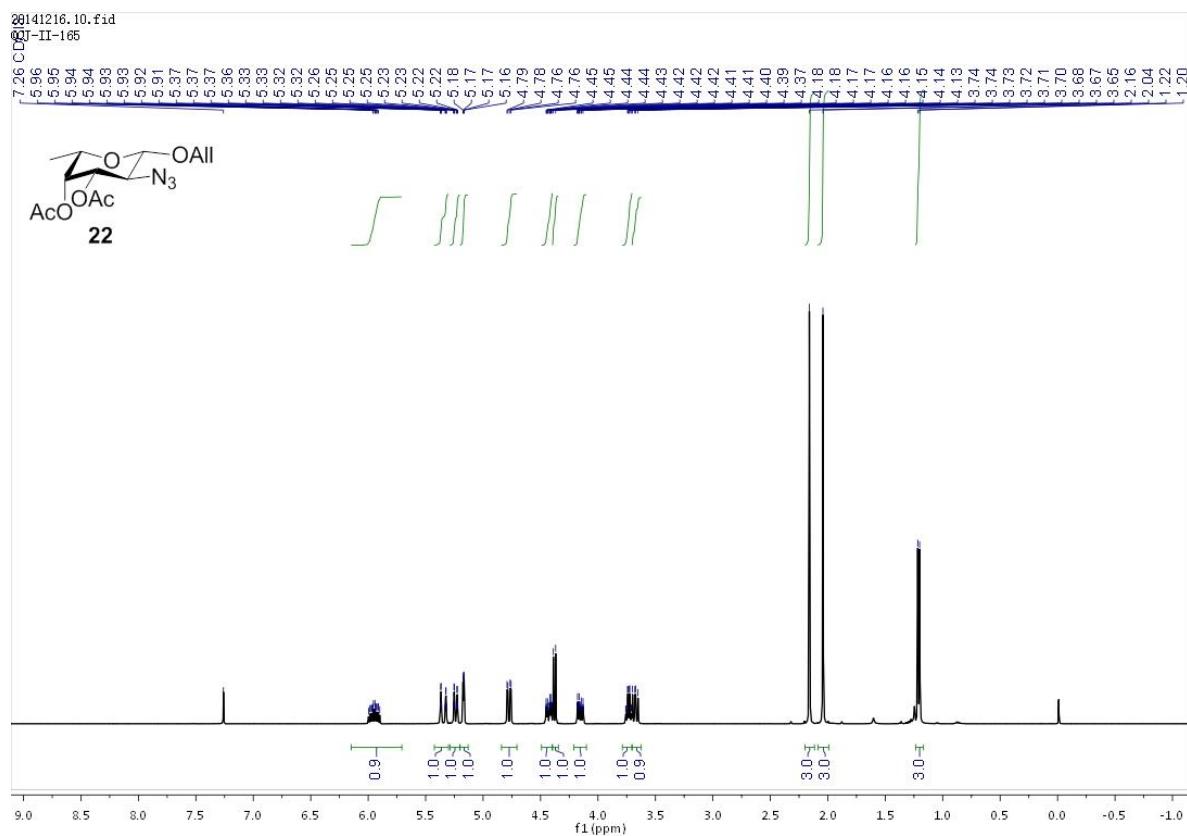
¹H NMR (CDCl₃, 400 MHz) of compound 8'



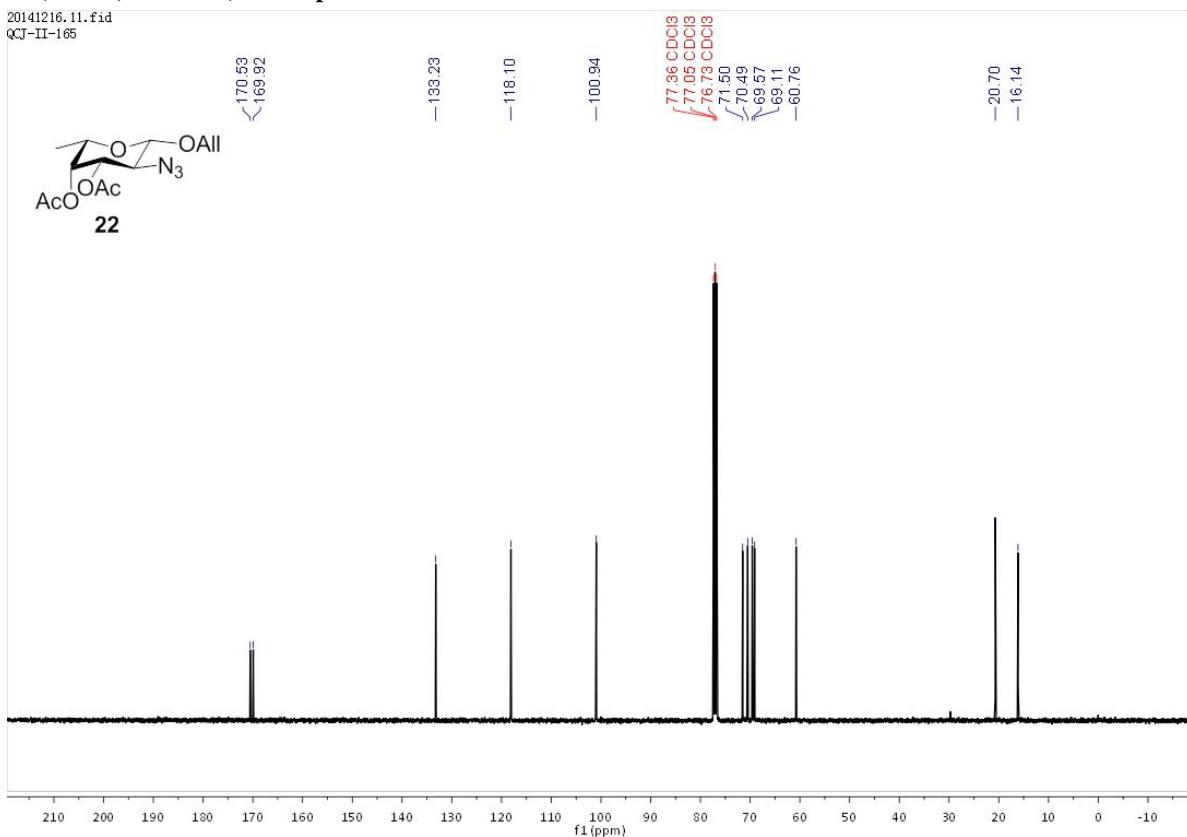
¹³C NMR (CDCl₃, 100 MHz) of compound 8'



¹H NMR (CDCl₃, 400 MHz) of compound 22

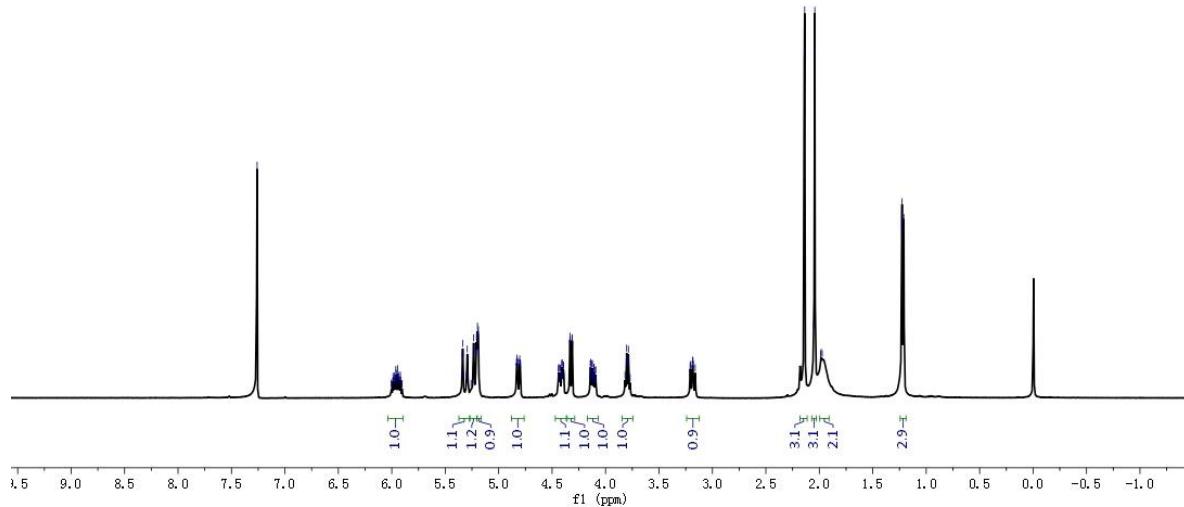
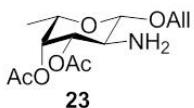


¹³C NMR (CDCl₃, 100 MHz) of compound 22



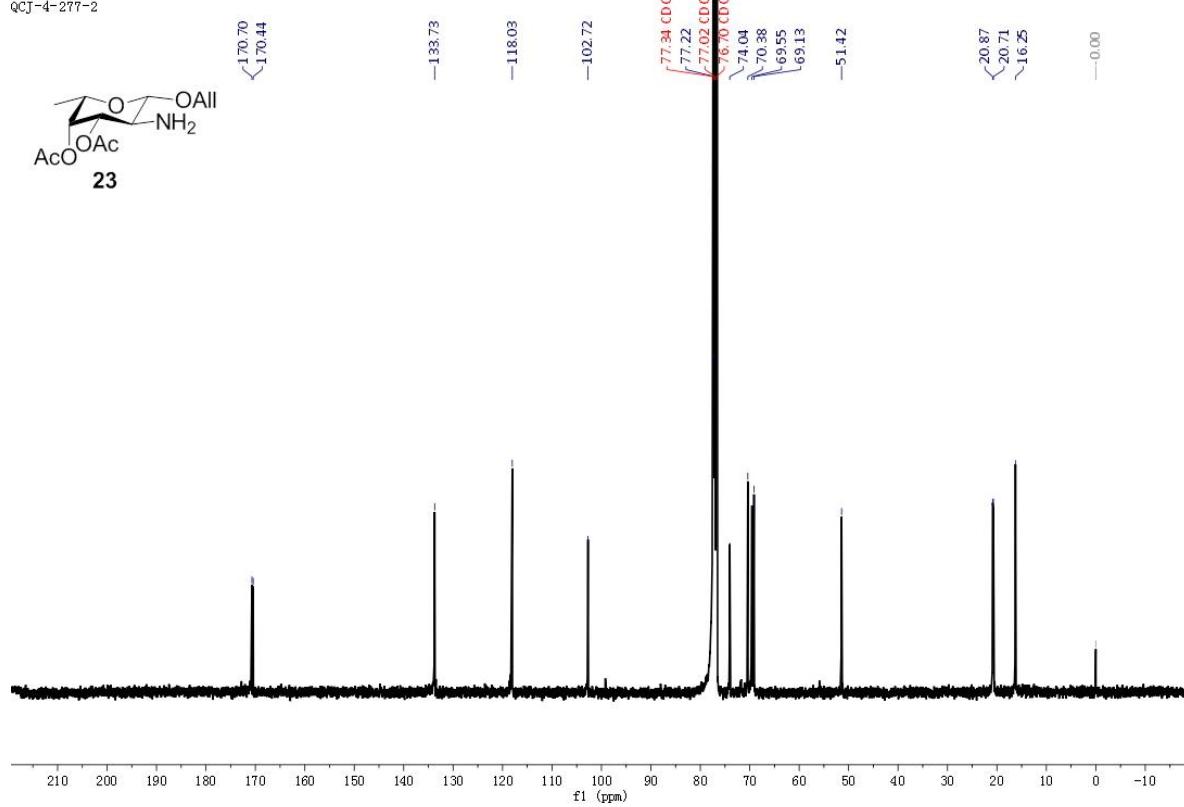
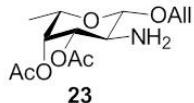
¹H NMR (CDCl₃, 400 MHz) of compound 23

20170814.1.fid
QCJG-4-277-2

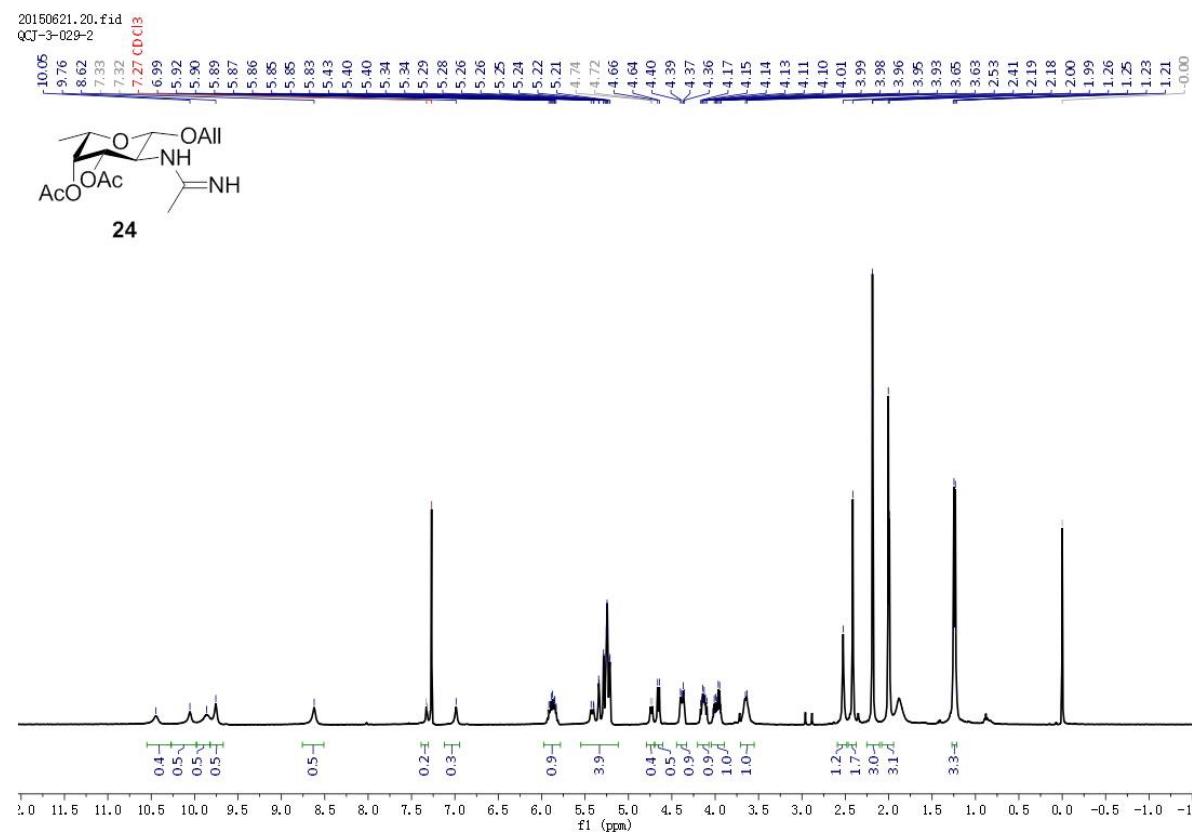


¹³C NMR (CDCl₃, 100 MHz) of compound 23

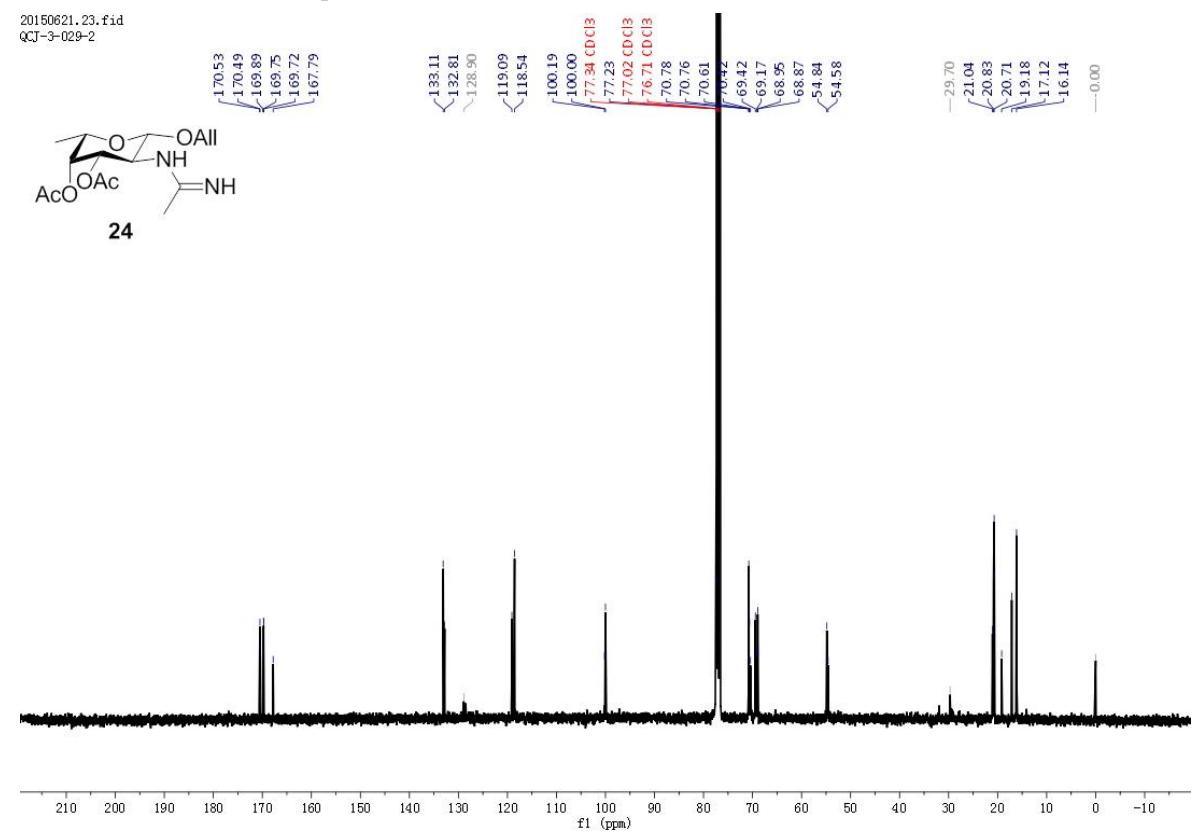
20170816.280.fid
QCJ-4-277-2



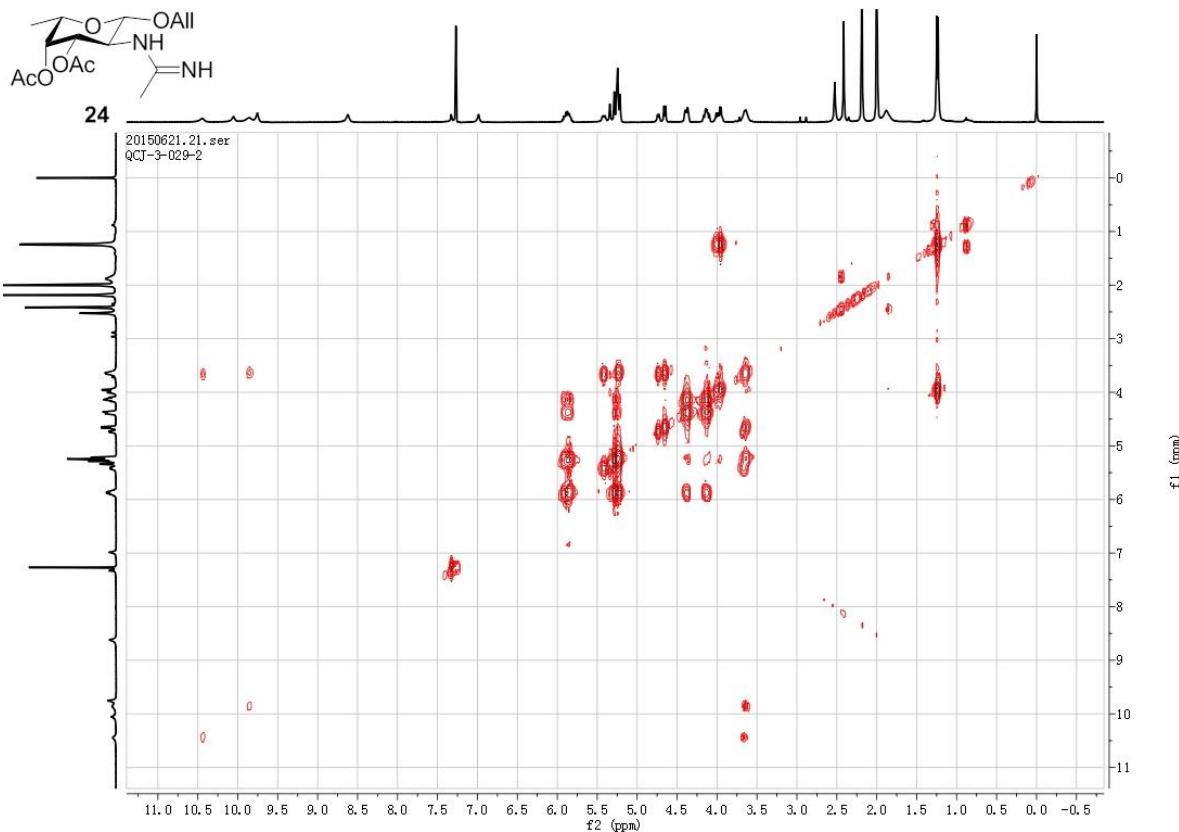
¹H NMR (CDCl₃, 400 MHz) of compound 24



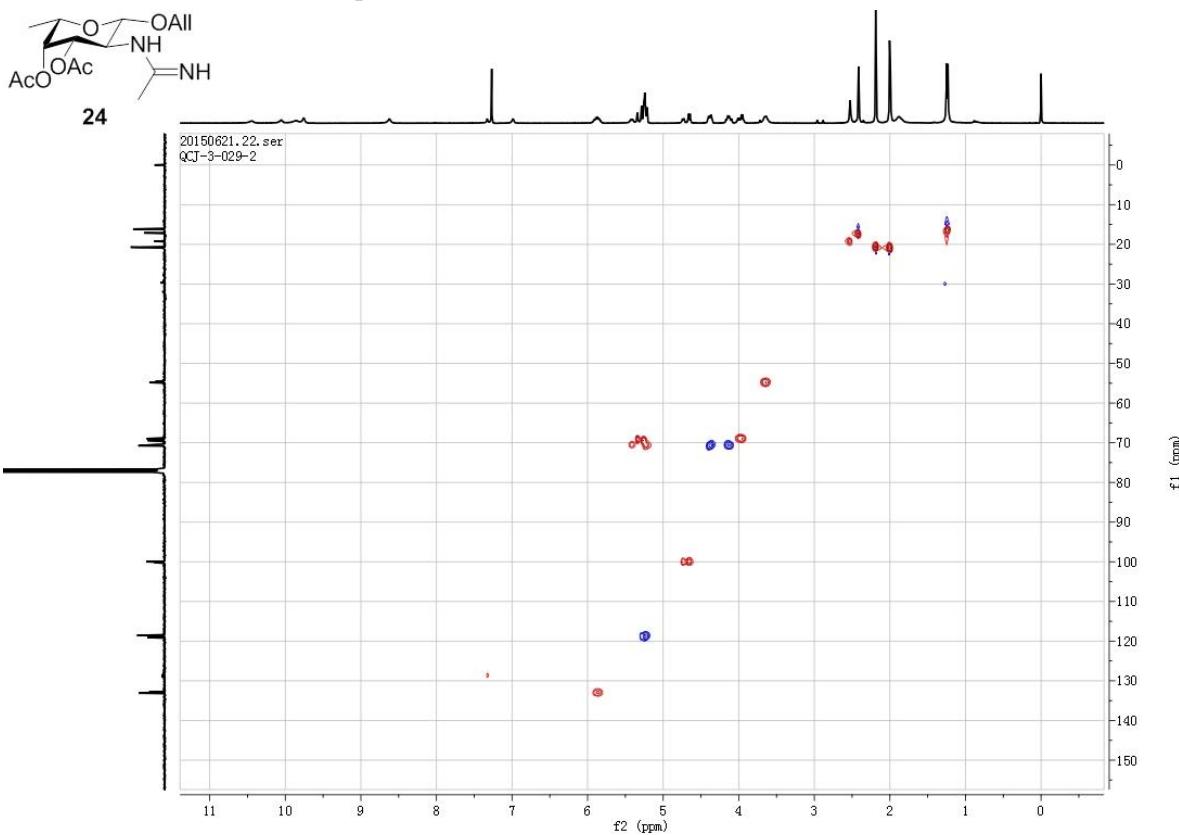
¹³C NMR (CDCl₃, 100 MHz) of compound 24



¹H-¹H COSY (CDCl₃, 400 MHz) of compound 24

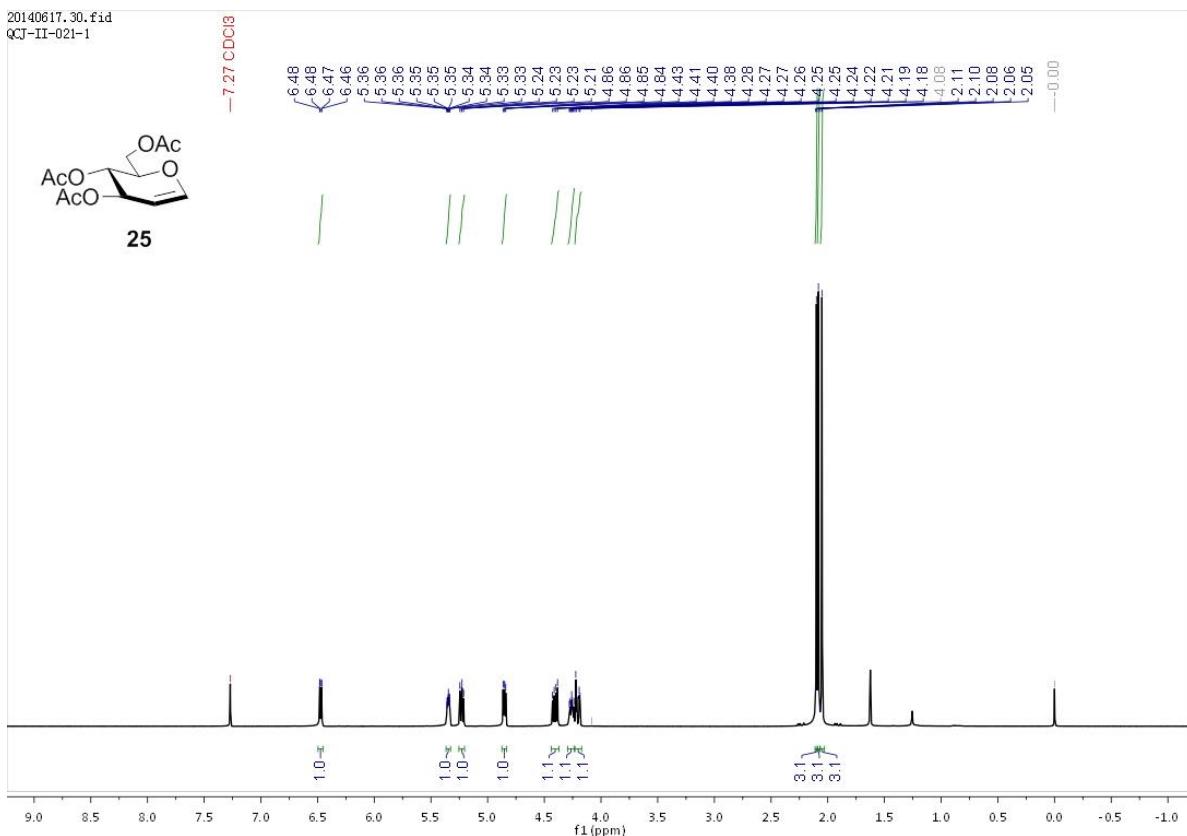
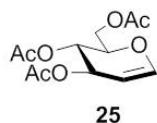


¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 24



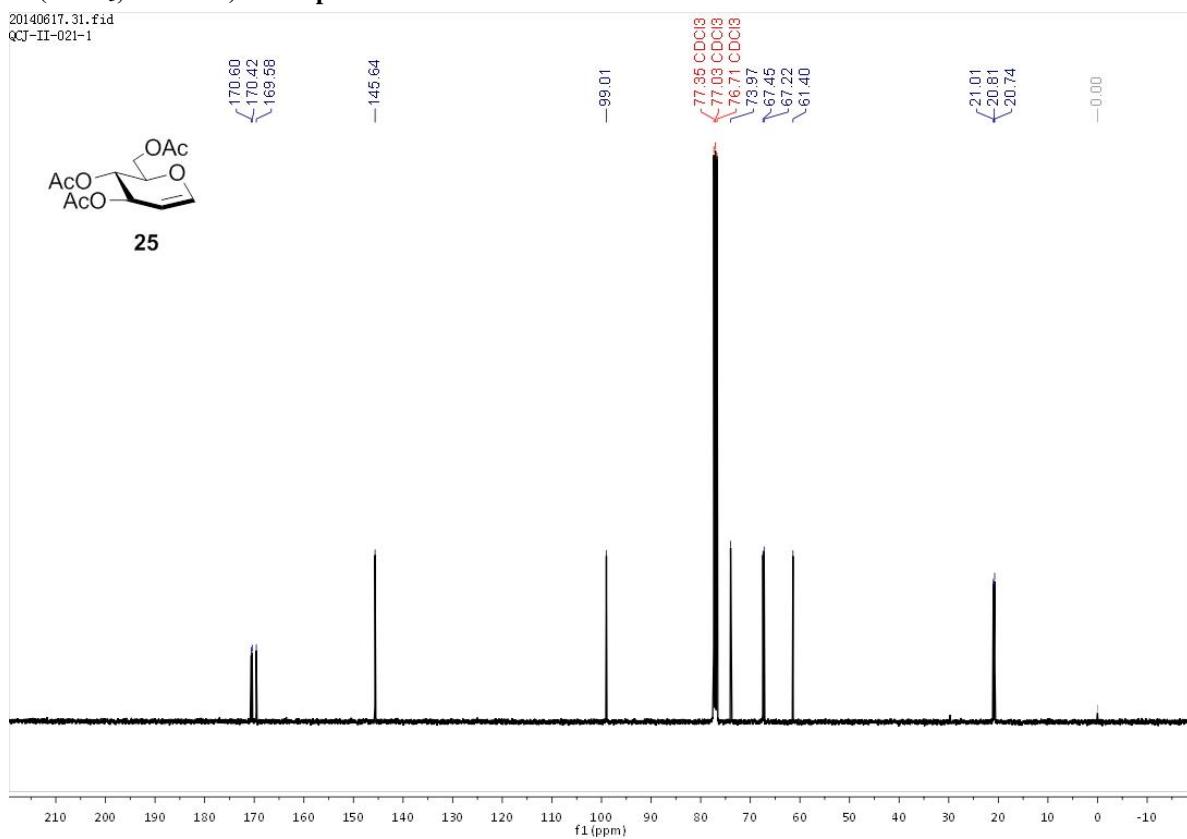
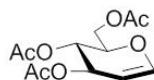
¹H NMR (CDCl₃, 400 MHz) of compound 25

20140617.30.fid
QCJ-II-021-1



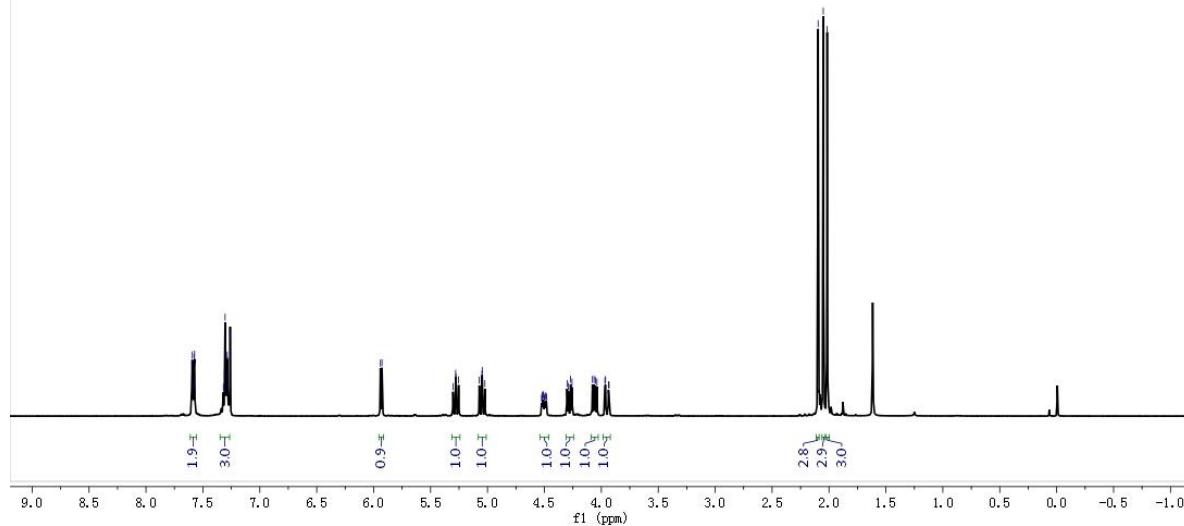
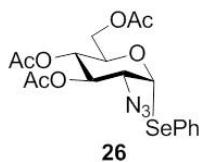
¹³C NMR (CDCl₃, 100 MHz) of compound 25

20140617.31.fid
OCT-II-021-1



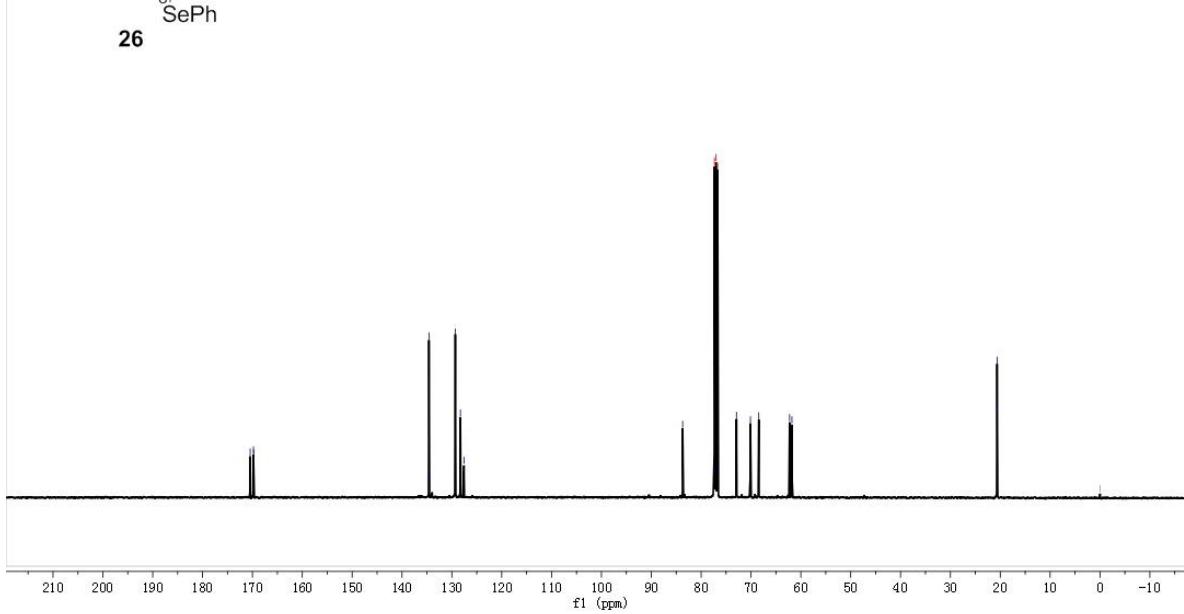
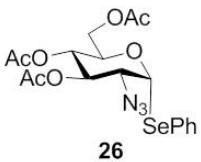
¹H NMR (CDCl₃, 400 MHz) of compound 26

20160717.20.fid
ZXP-I-081-1-2

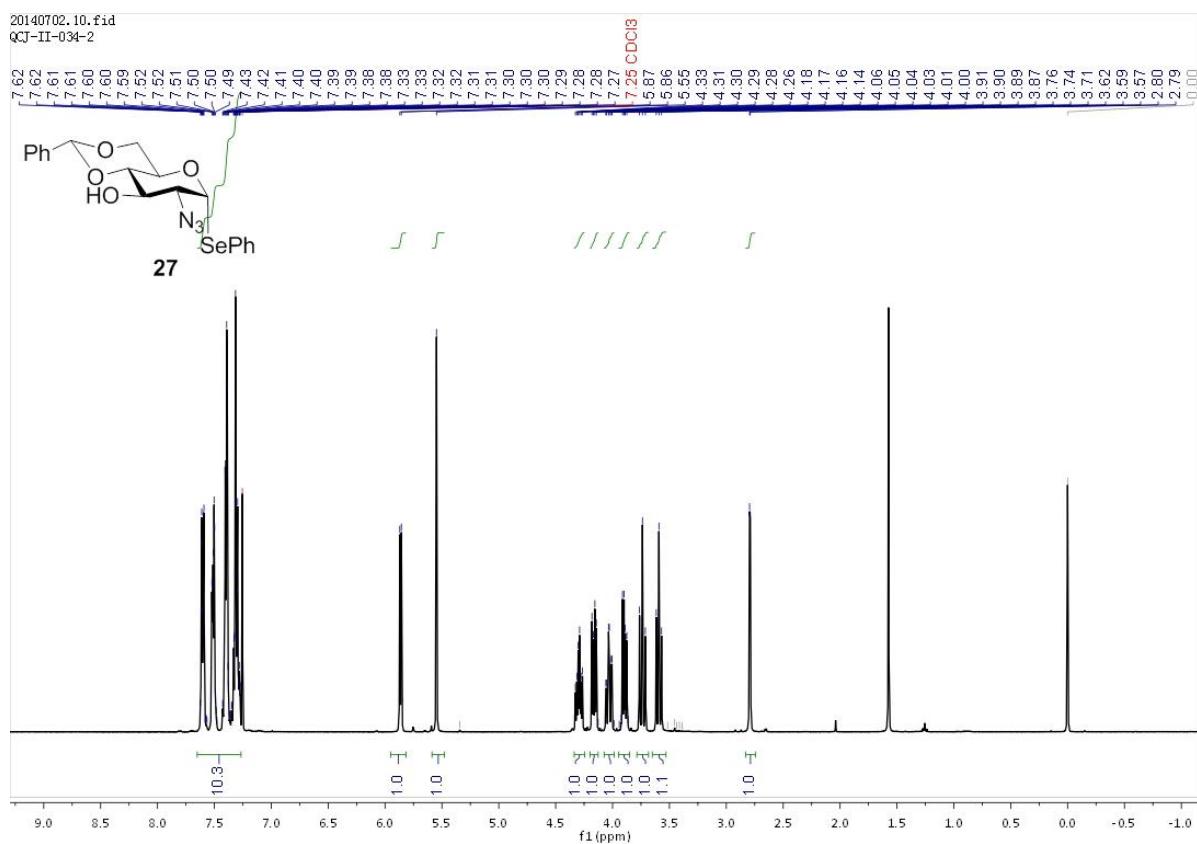


¹³C NMR (CDCl₃, 100 MHz) of compound 26

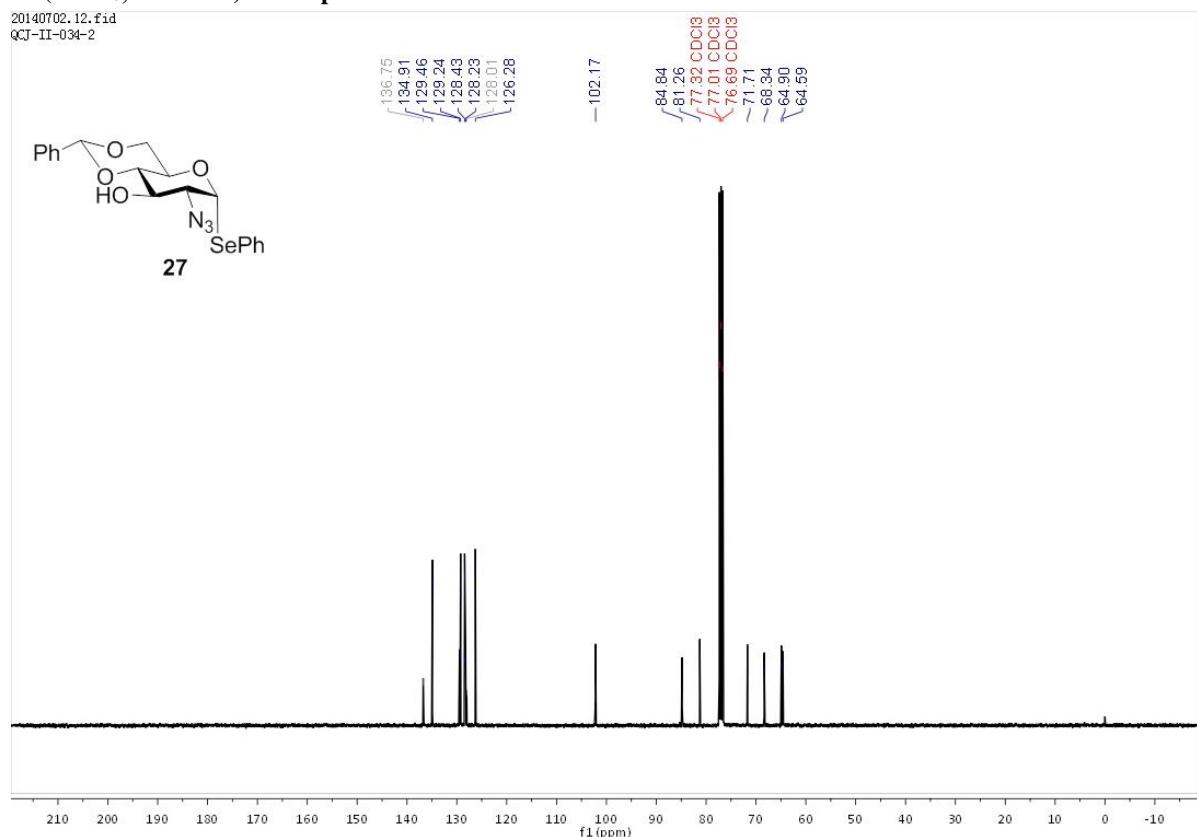
20160717.21.fid
TYP-I-081-1-2



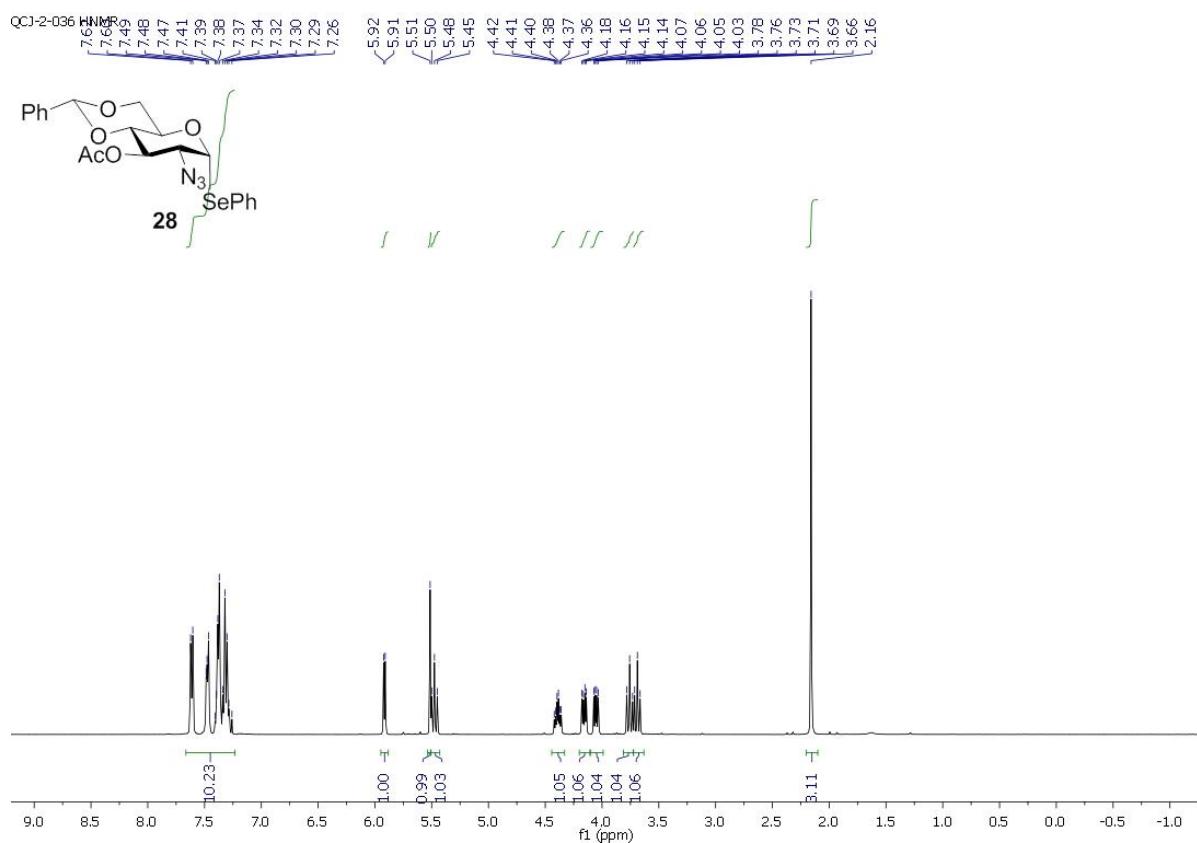
¹H NMR (CDCl₃, 400 MHz) of compound 27



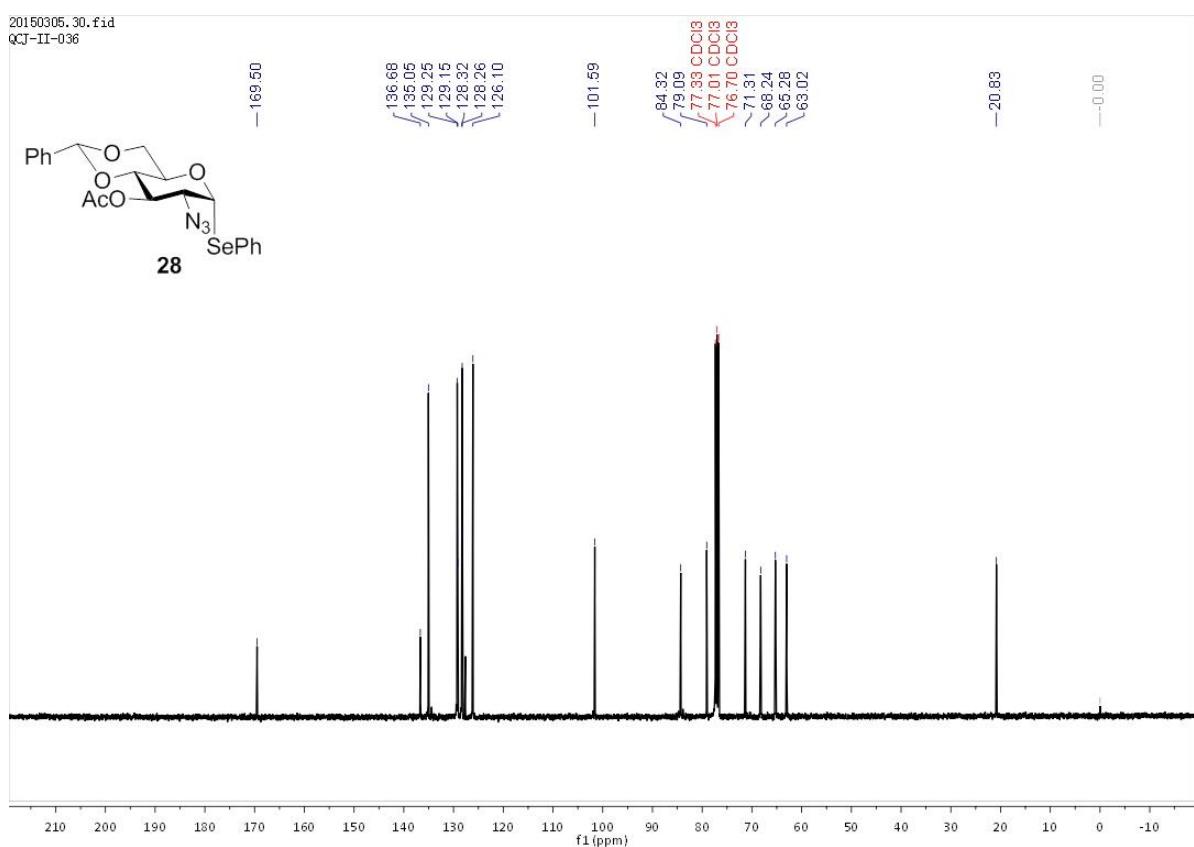
¹³C NMR (CDCl₃, 100 MHz) of compound 27



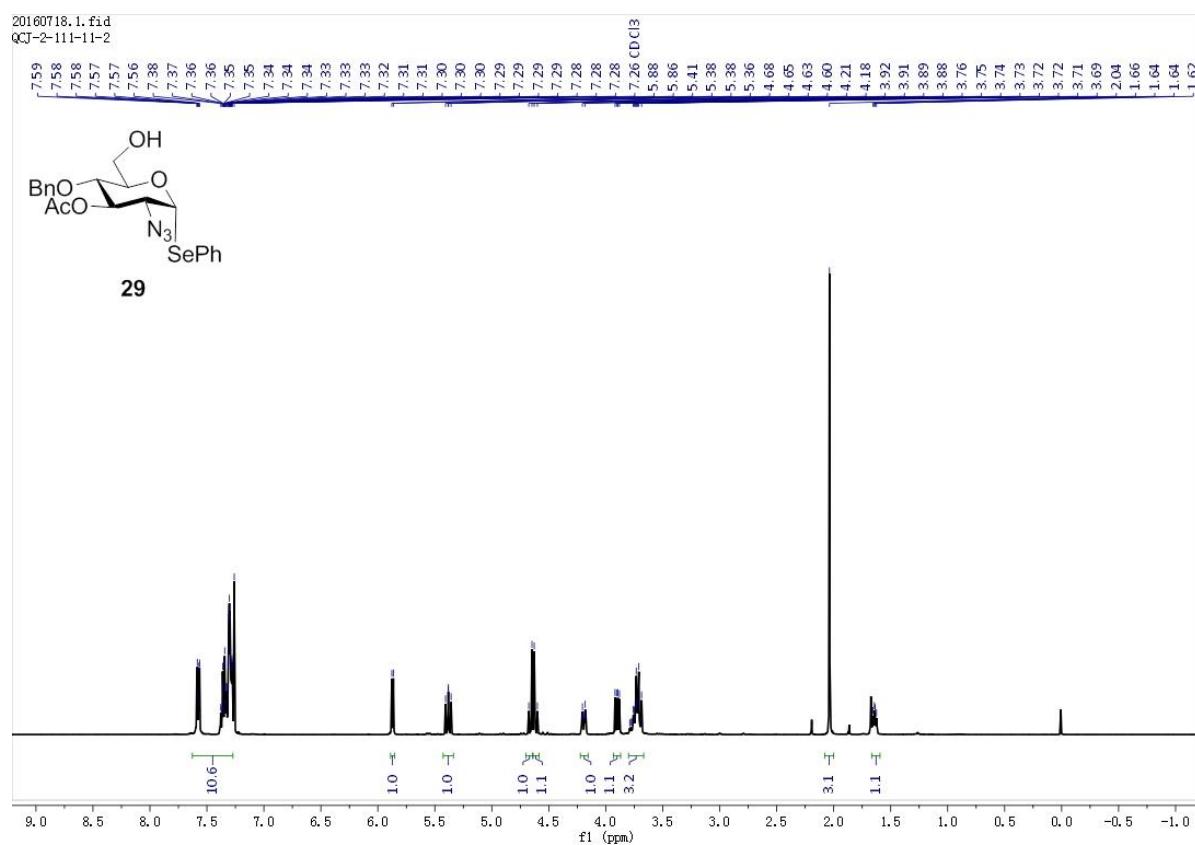
¹H NMR (CDCl₃, 400 MHz) of compound 28



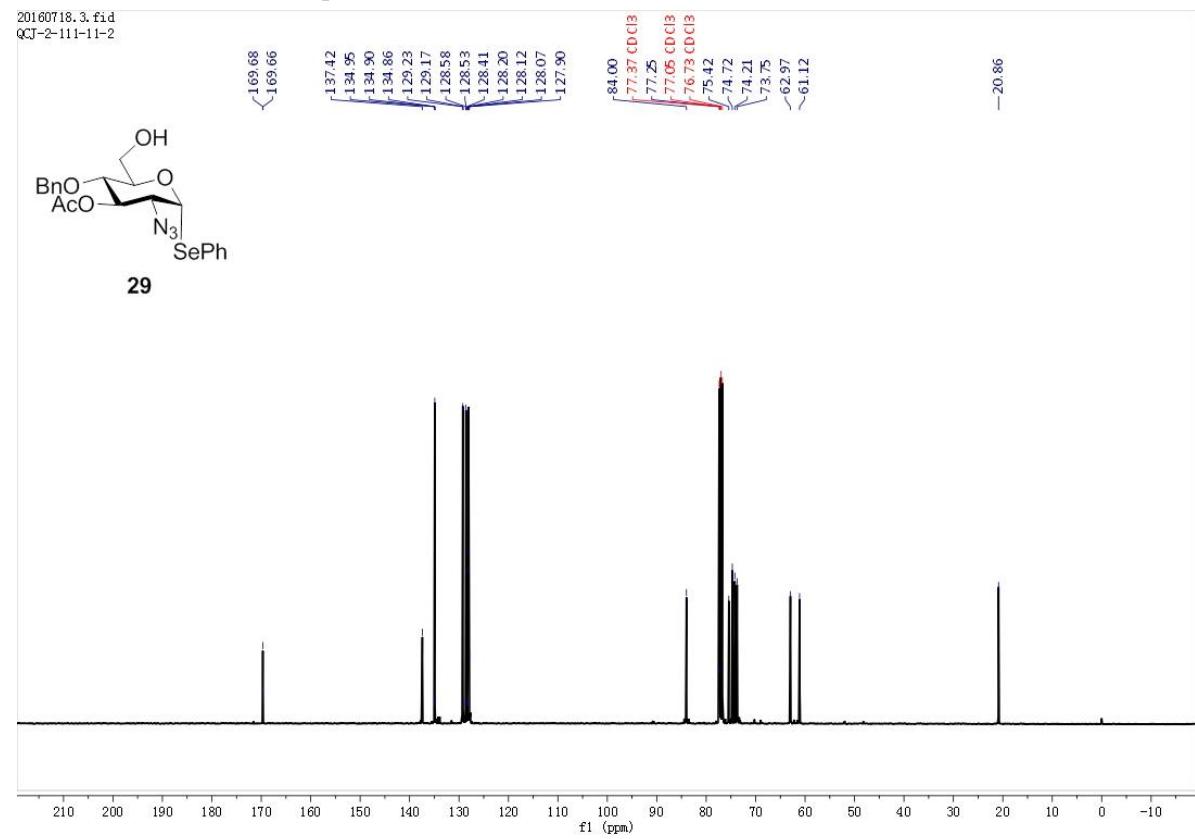
¹³C NMR (CDCl₃, 100 MHz) of compound 28



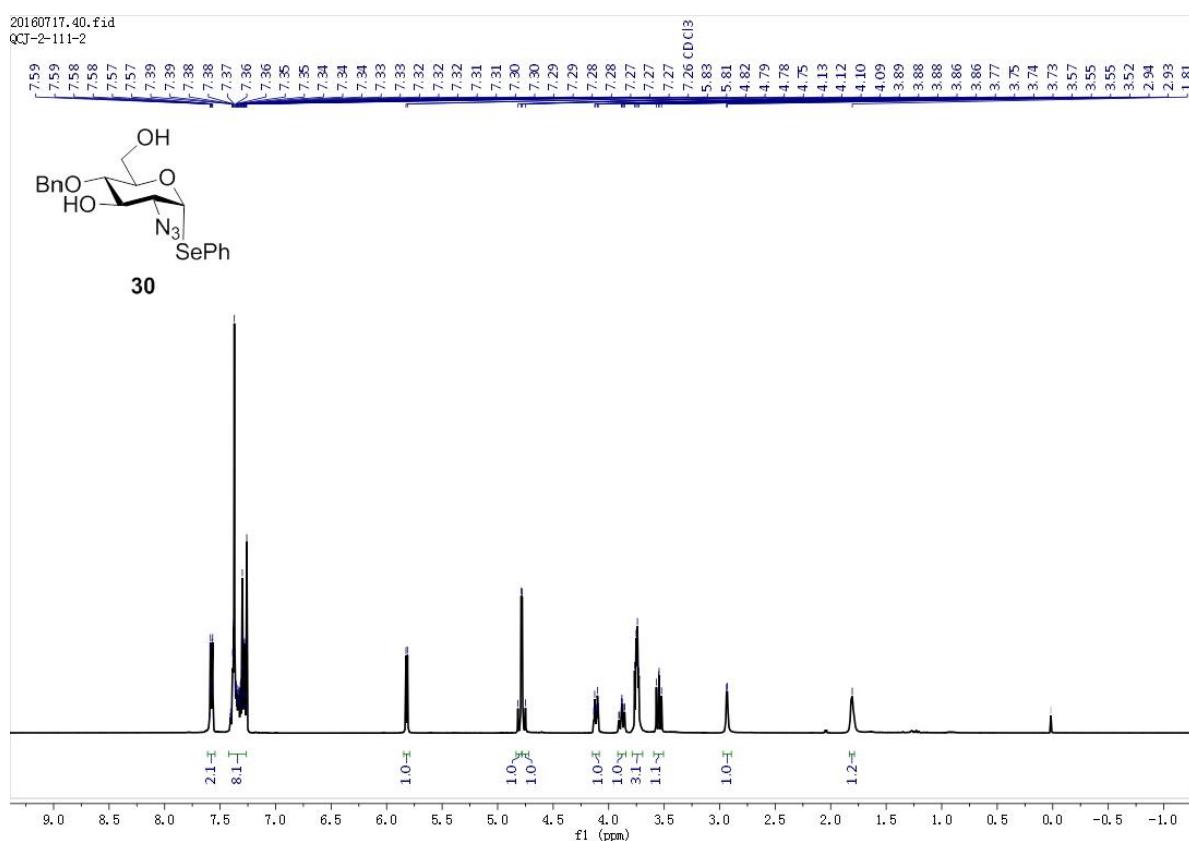
¹H NMR (CDCl₃, 400 MHz) of compound 29



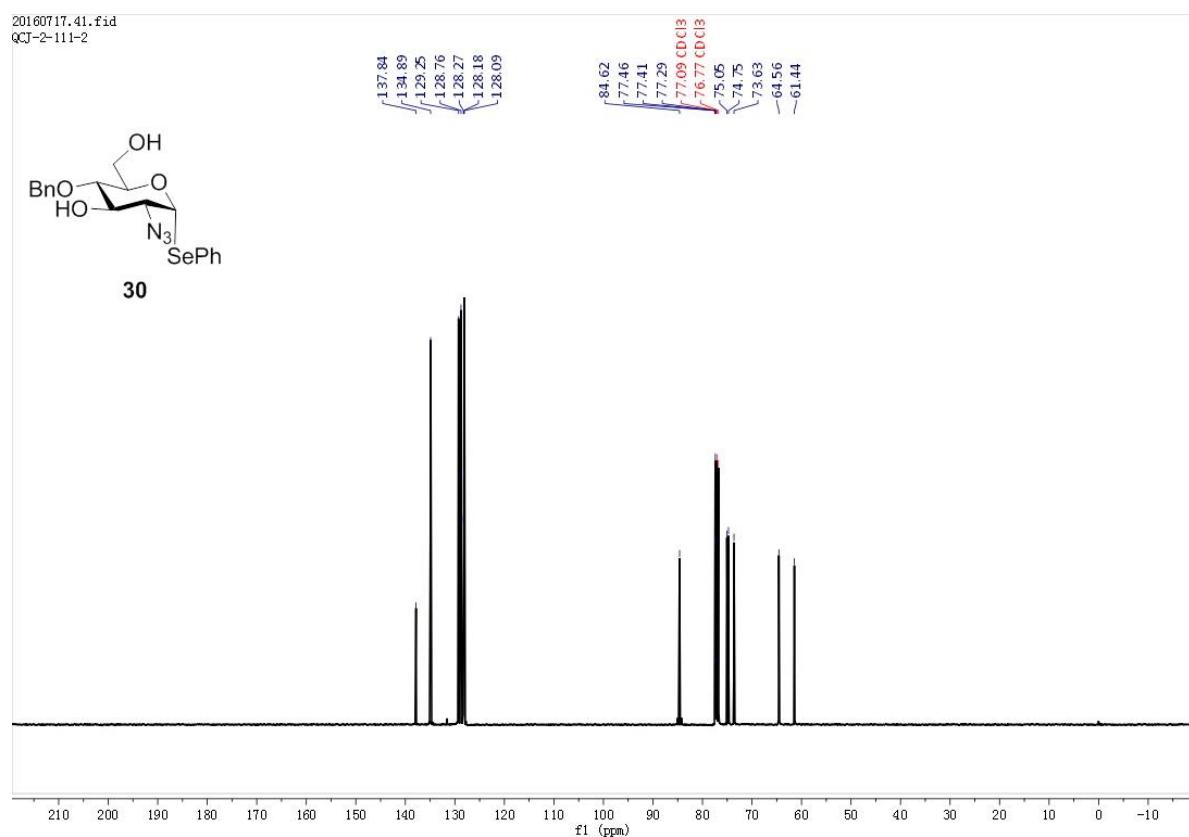
¹³C NMR (CDCl₃, 100 MHz) of compound 29



¹H NMR (CDCl₃, 400 MHz) of compound 30

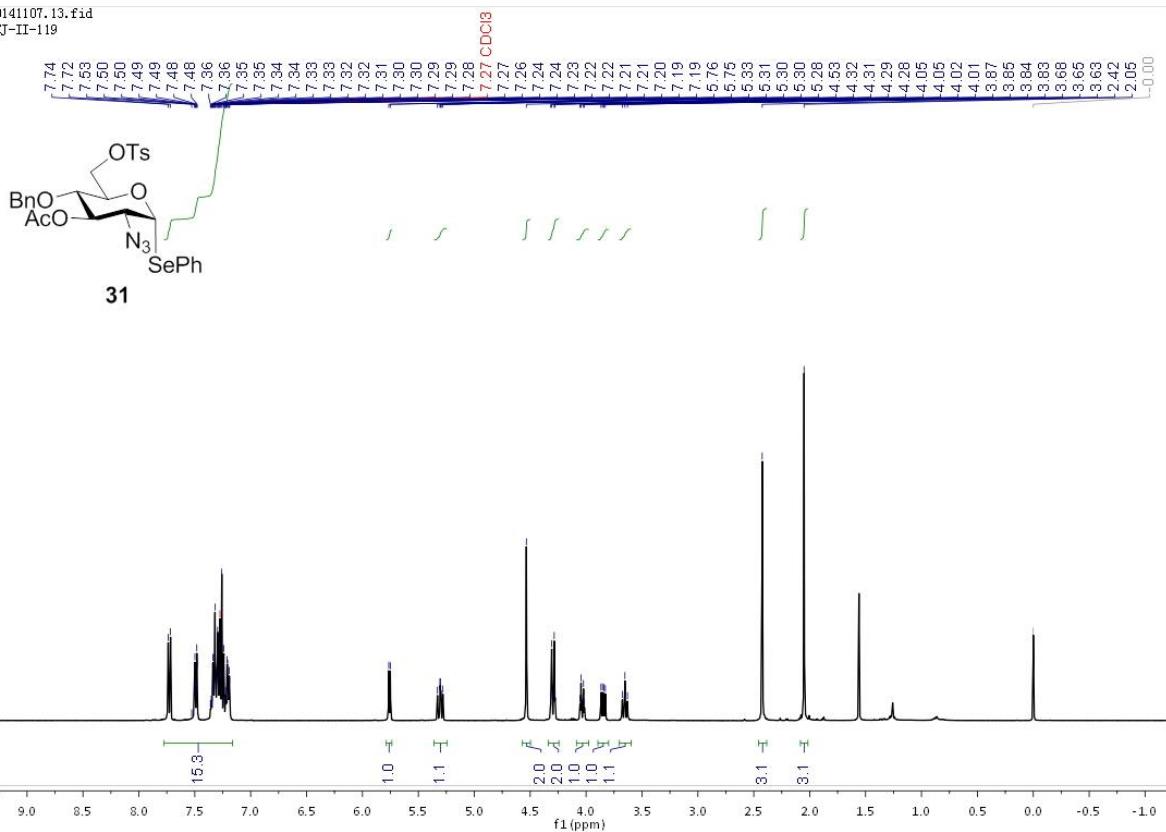


¹³C NMR (CDCl₃, 100 MHz) of compound 30



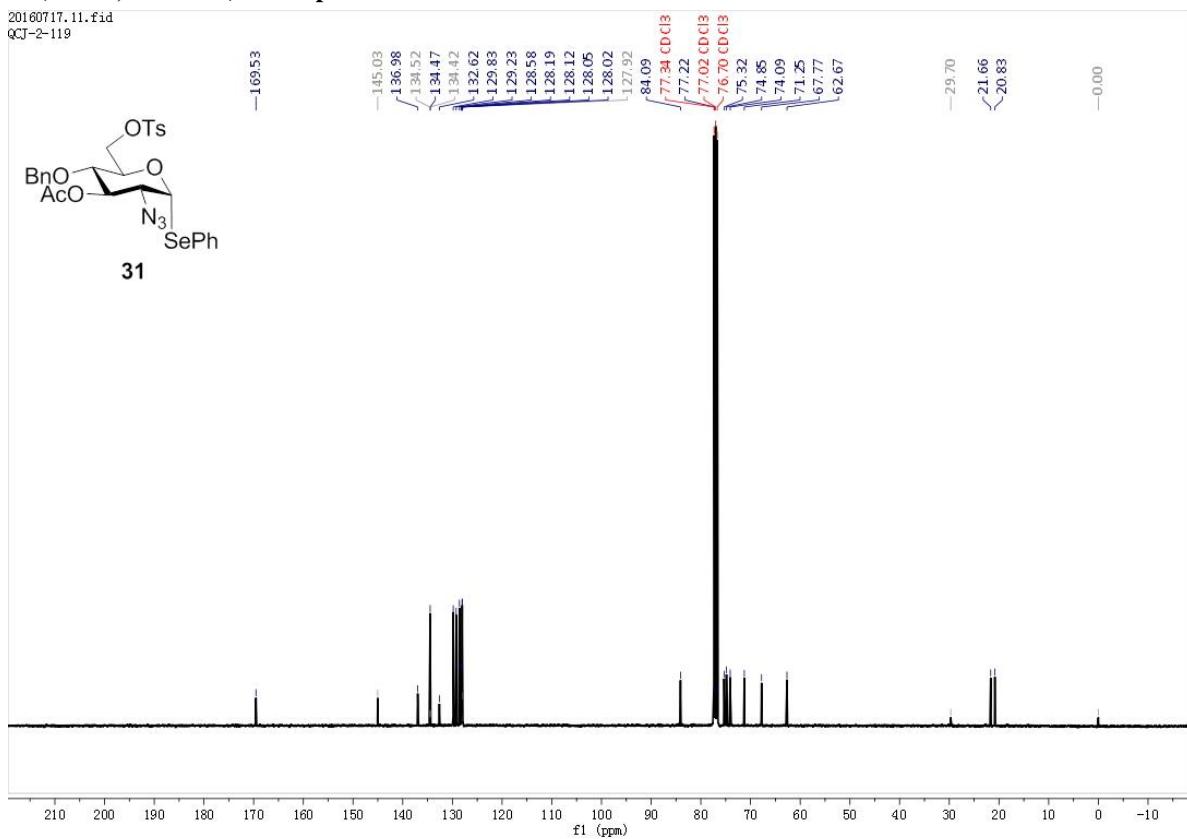
¹H NMR (CDCl₃, 400 MHz) of compound 31

20141107.13.fid
QCT-II-119



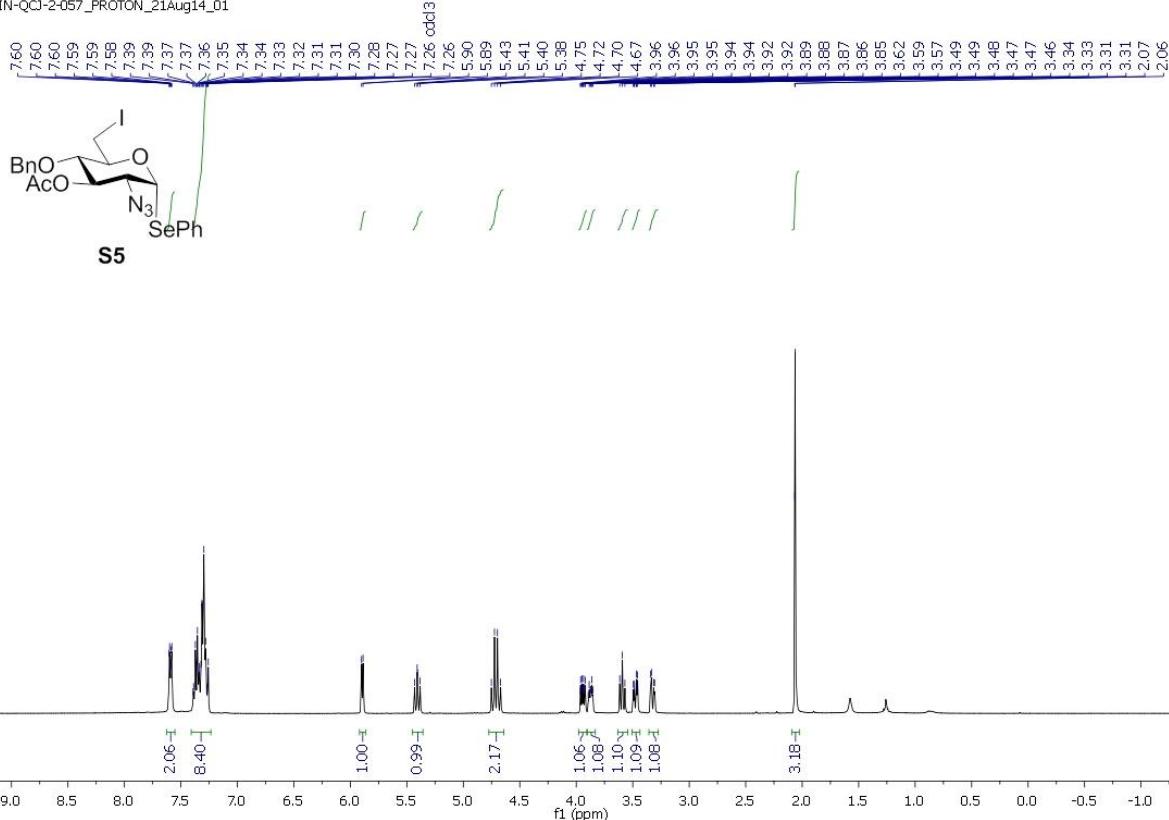
¹³C NMR (CDCl₃, 100 MHz) of compound 31

20160717.11.fid
QCT-2-119



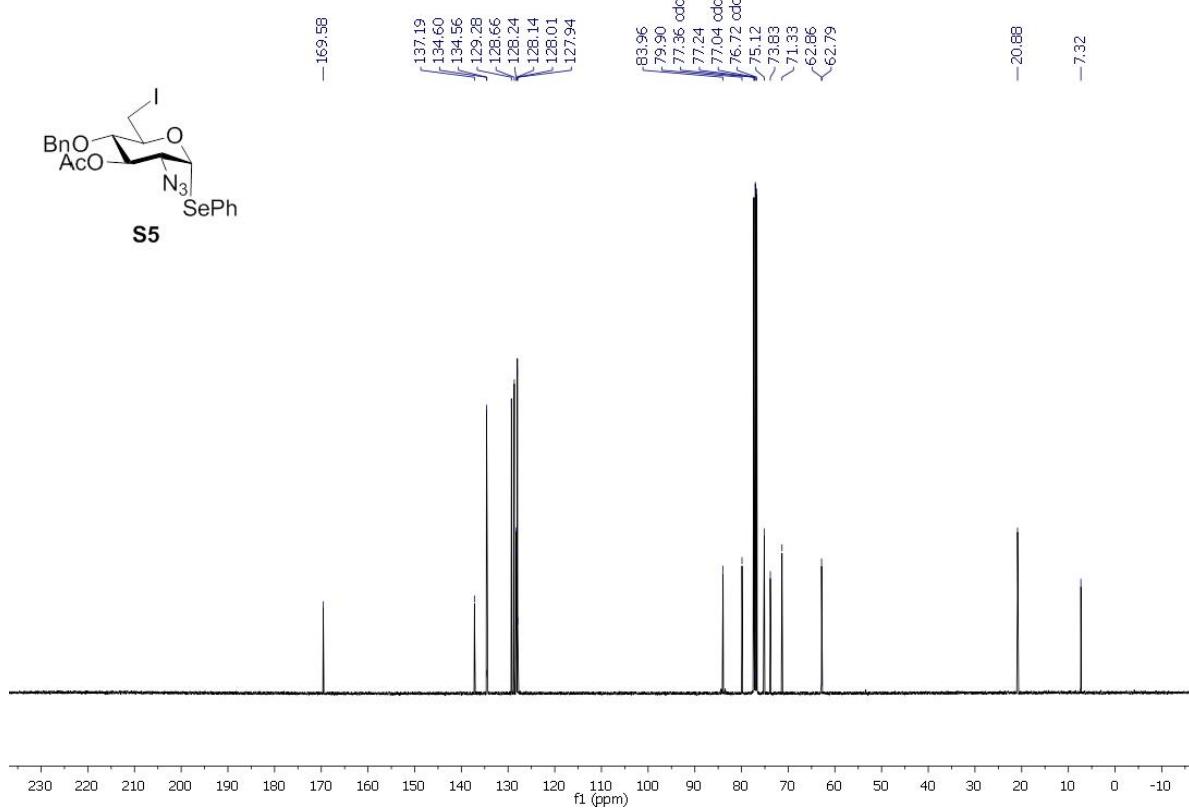
¹H NMR (CDCl₃, 400 MHz) of compound S5

QIN-QCJ-2-057 PROTON 21Aug14 01

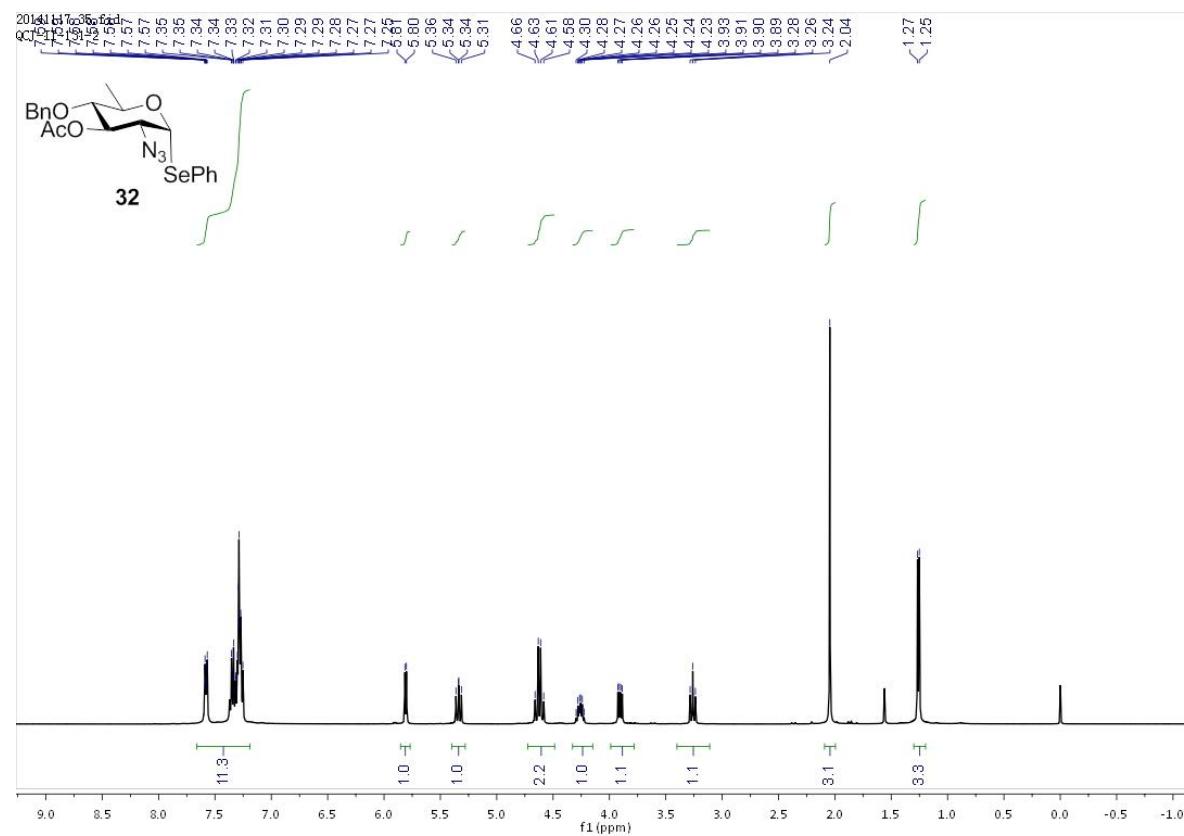


¹³C NMR (CDCl₃, 100 MHz) of compound S5

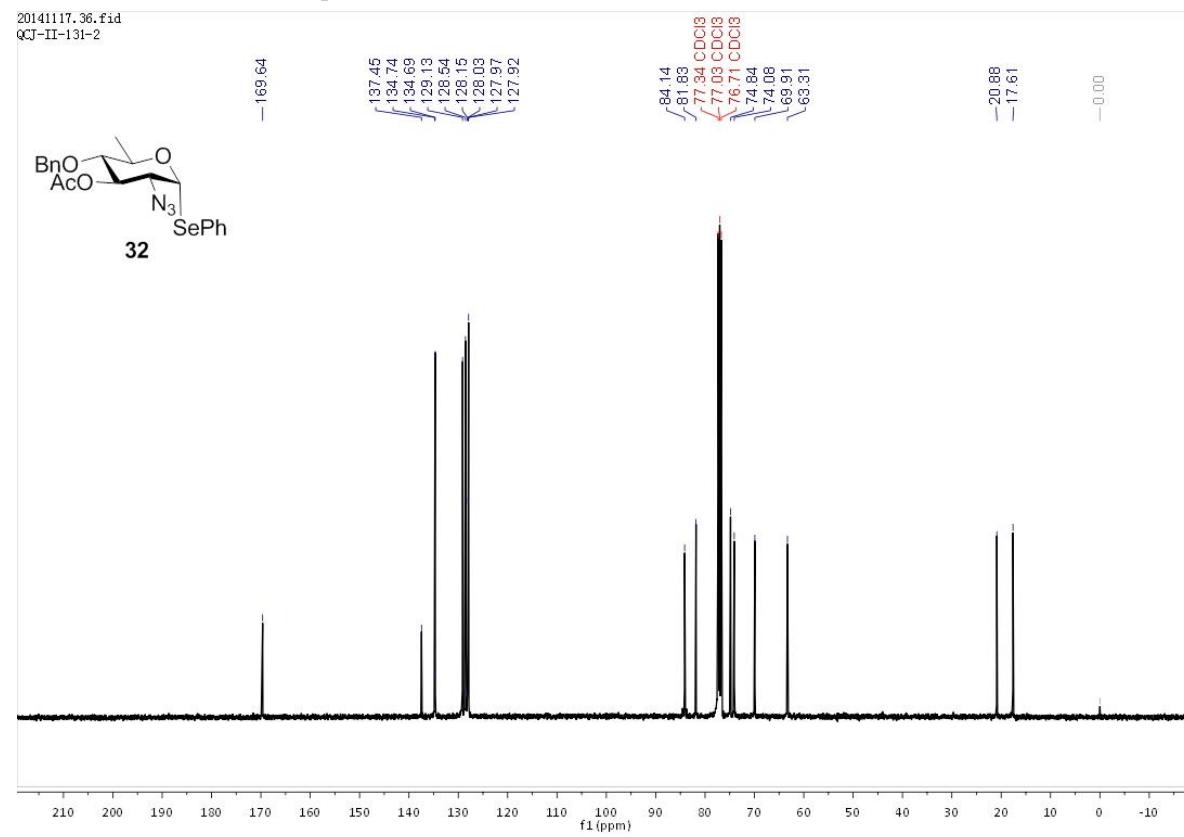
QIN-QCJ-2-059-1_OVERNIGHT_CARBON_27Aug14_01



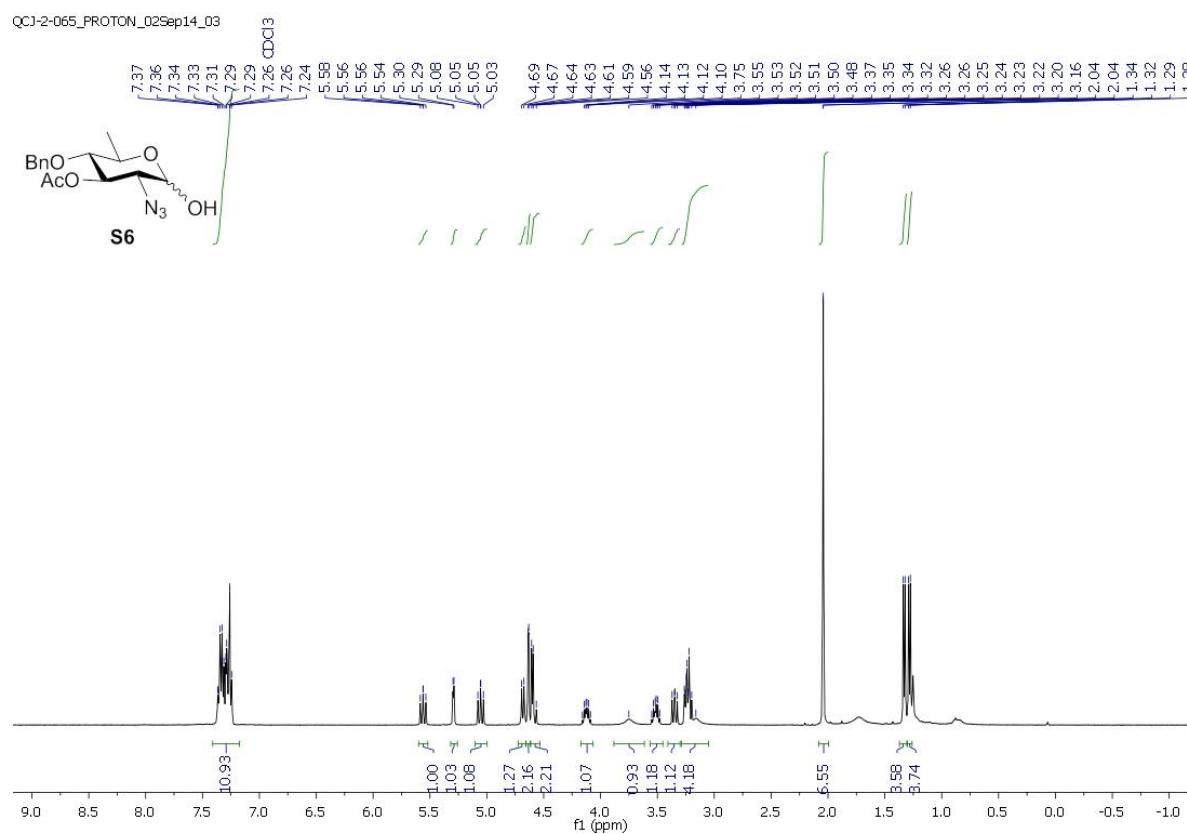
¹H NMR (CDCl₃, 400 MHz) of compound 32



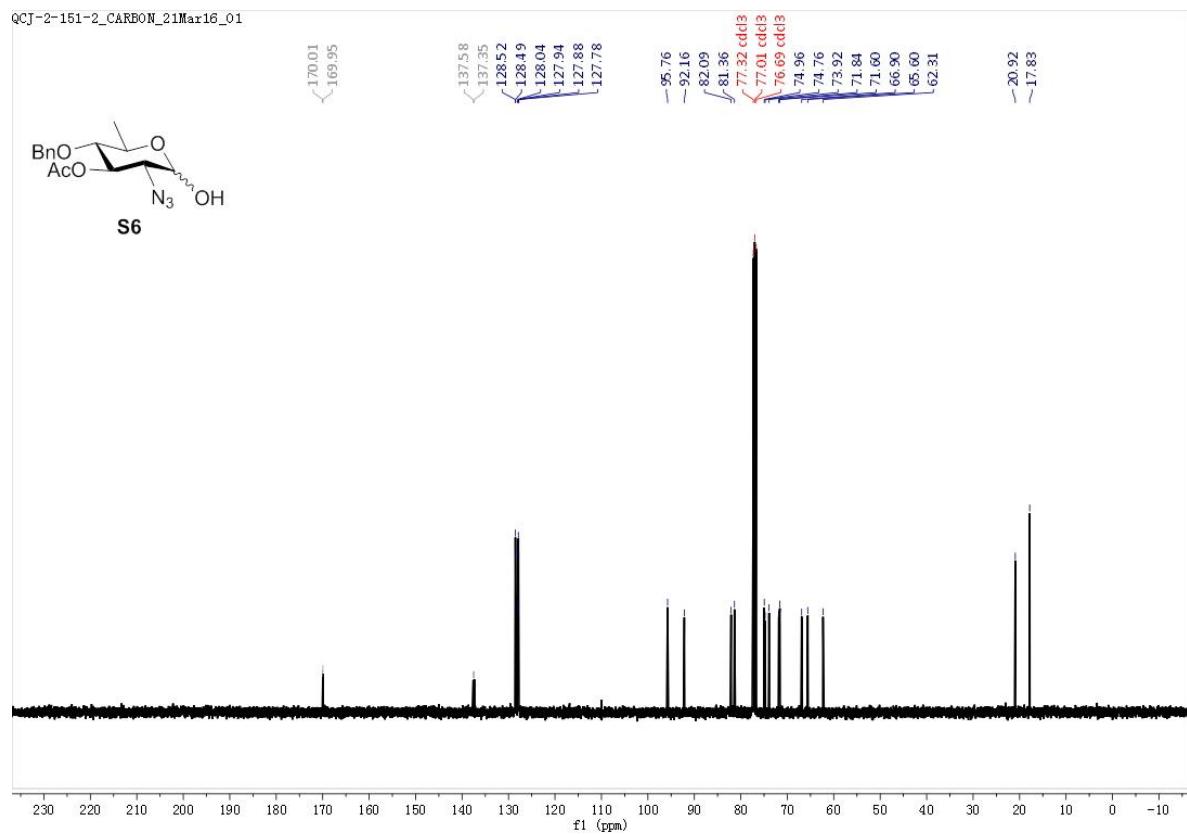
¹³C NMR (CDCl₃, 100 MHz) of compound 32



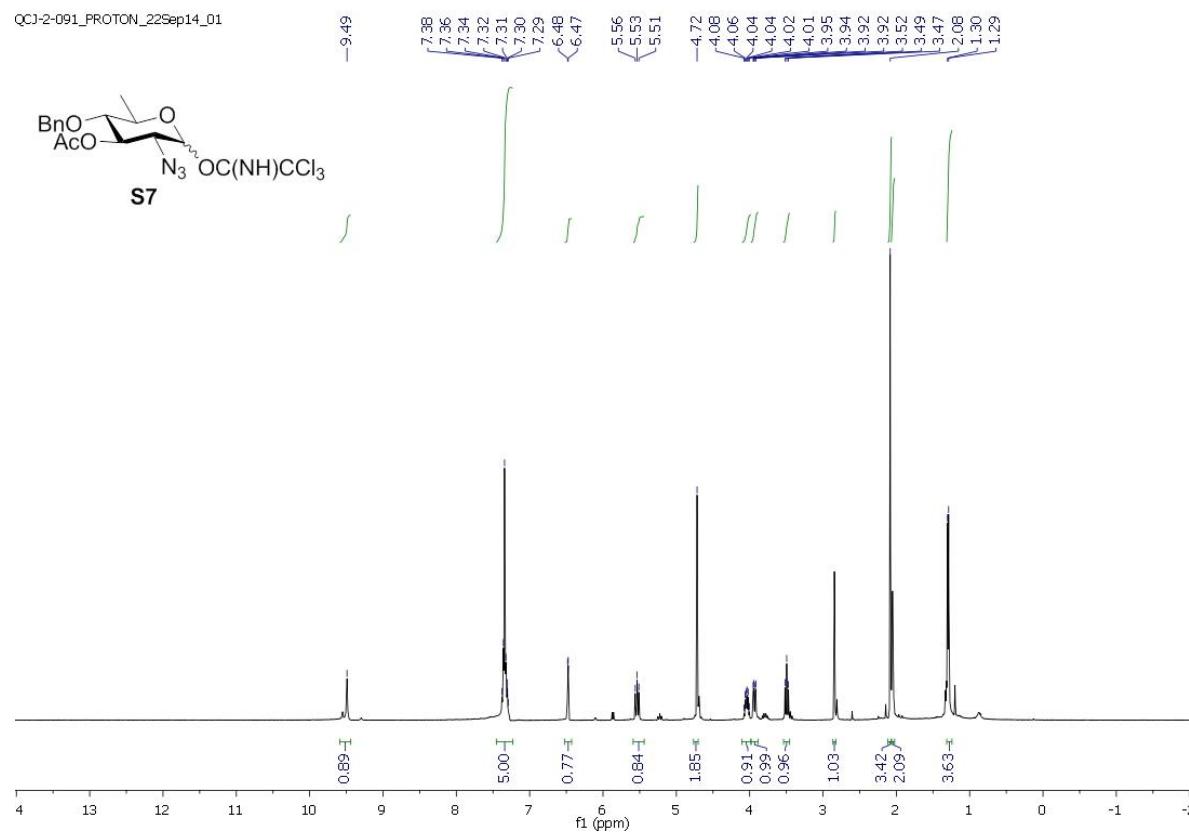
¹H NMR (CDCl₃, 400 MHz) of compound S6



¹³C NMR (CDCl₃, 100 MHz) of compound S6

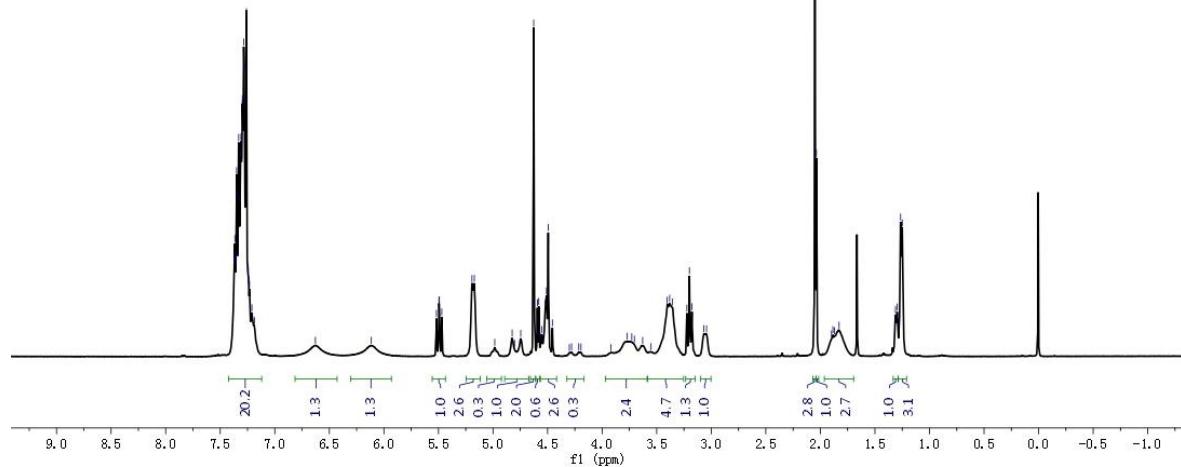
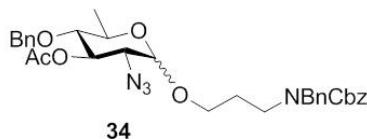


¹H NMR (CDCl₃, 400 MHz) of compound S7



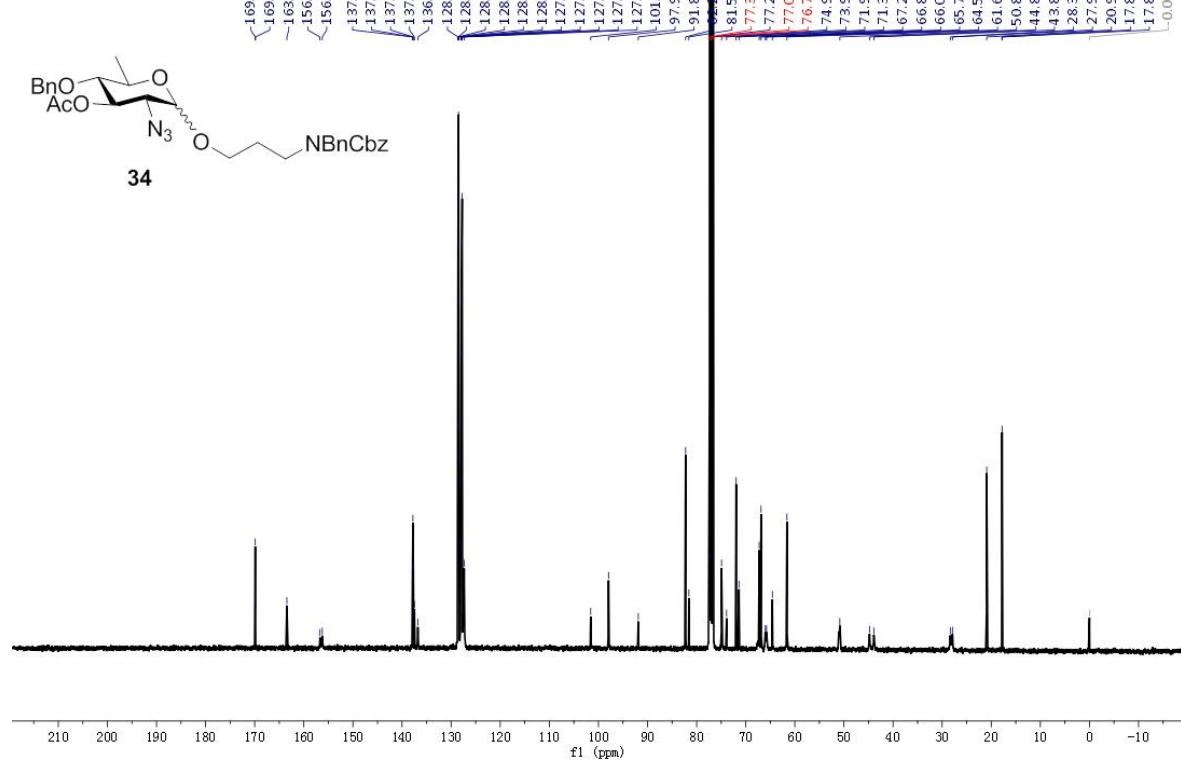
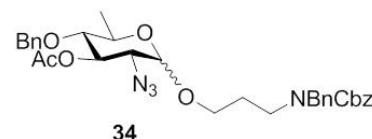
¹H NMR (CDCl₃, 400 MHz) of compound 34

20170802.3.fid
QCJ-4-133-3

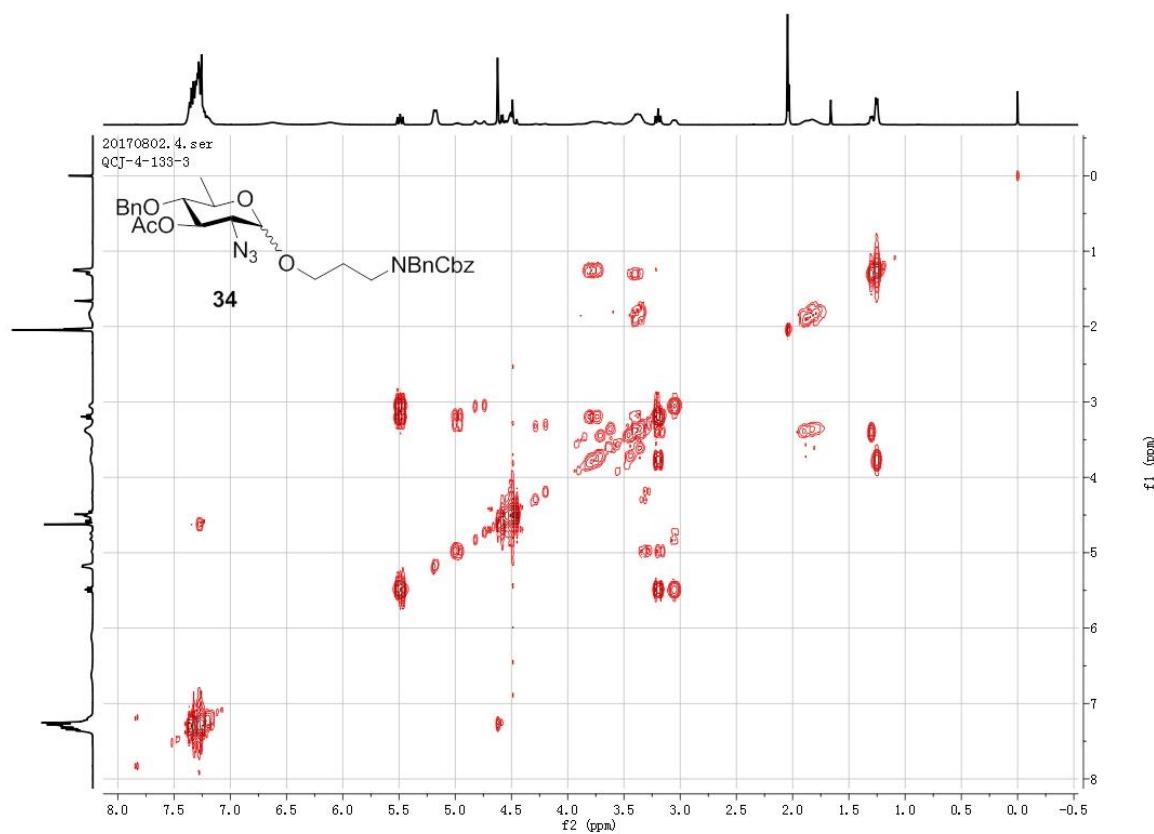


¹³C NMR (CDCl₃, 100 MHz) of compound 34

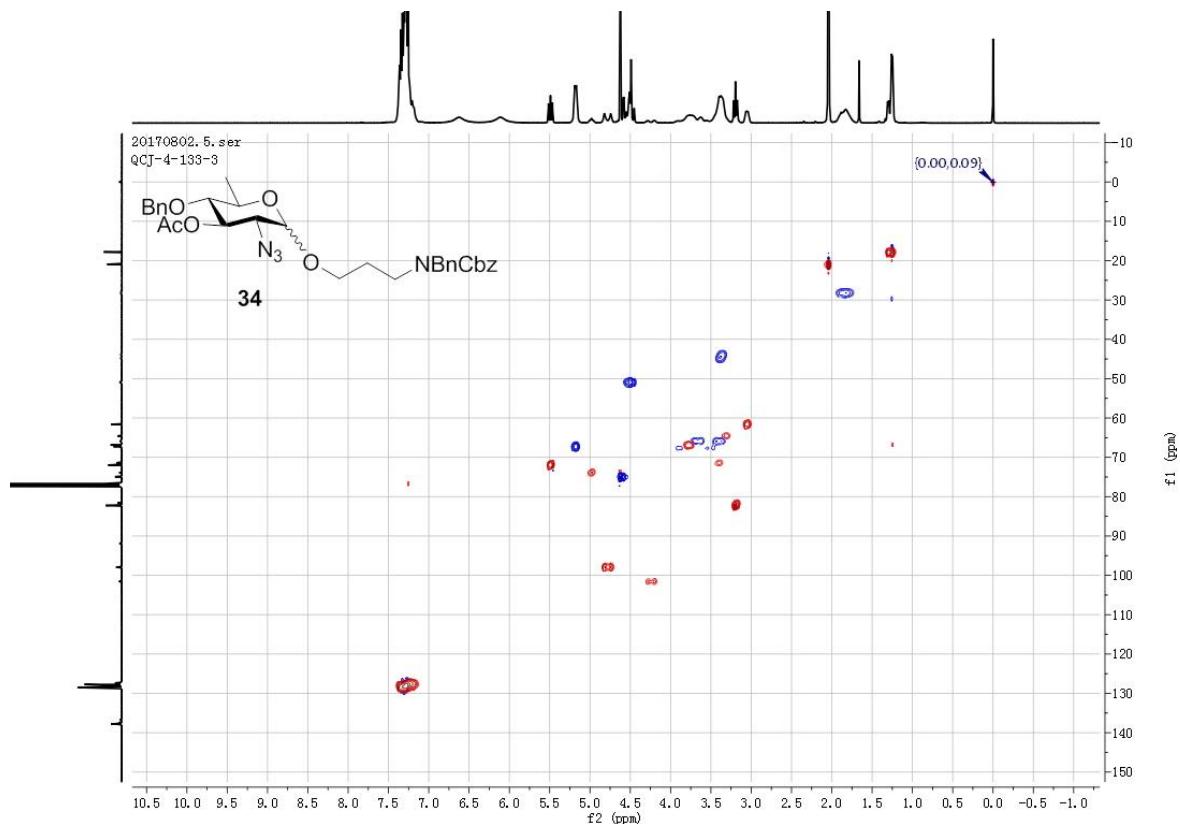
20170802.6.fid
QCJ-4-133-3



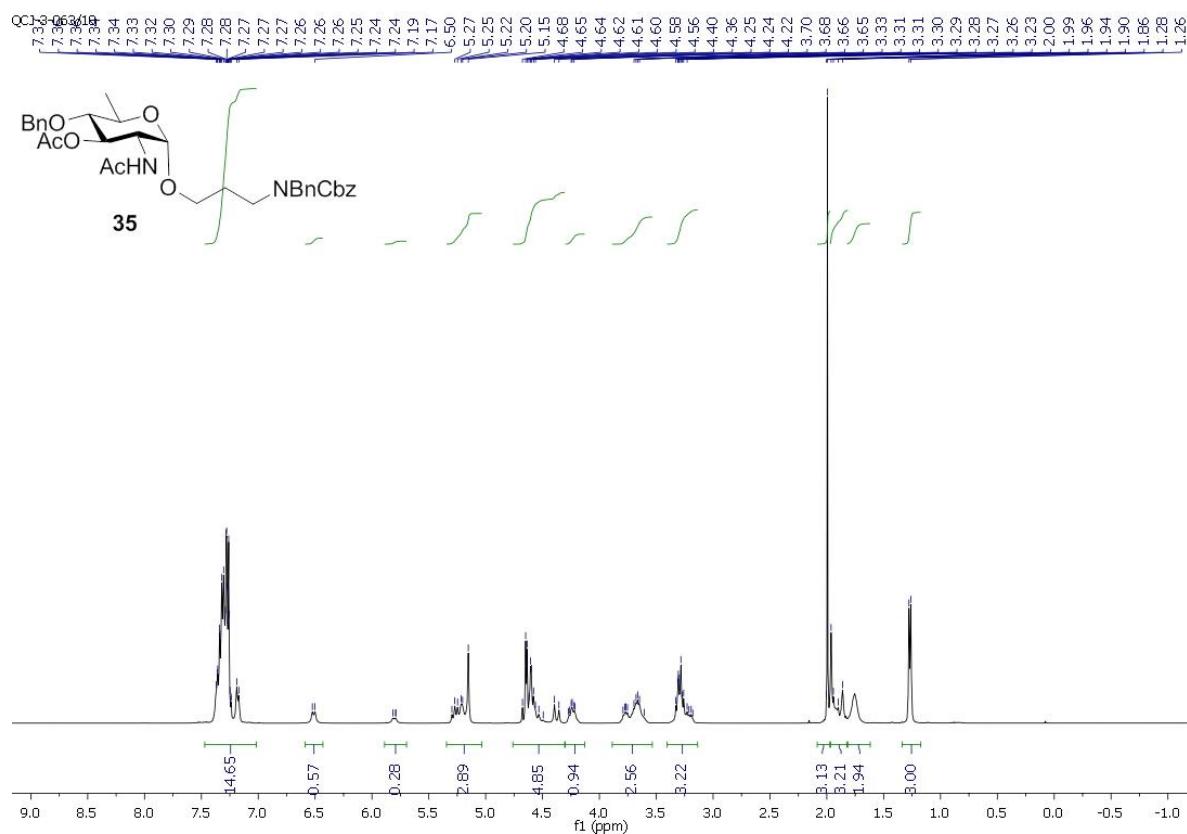
¹H-¹H COSY (CDCl₃, 400 MHz) of compound 34



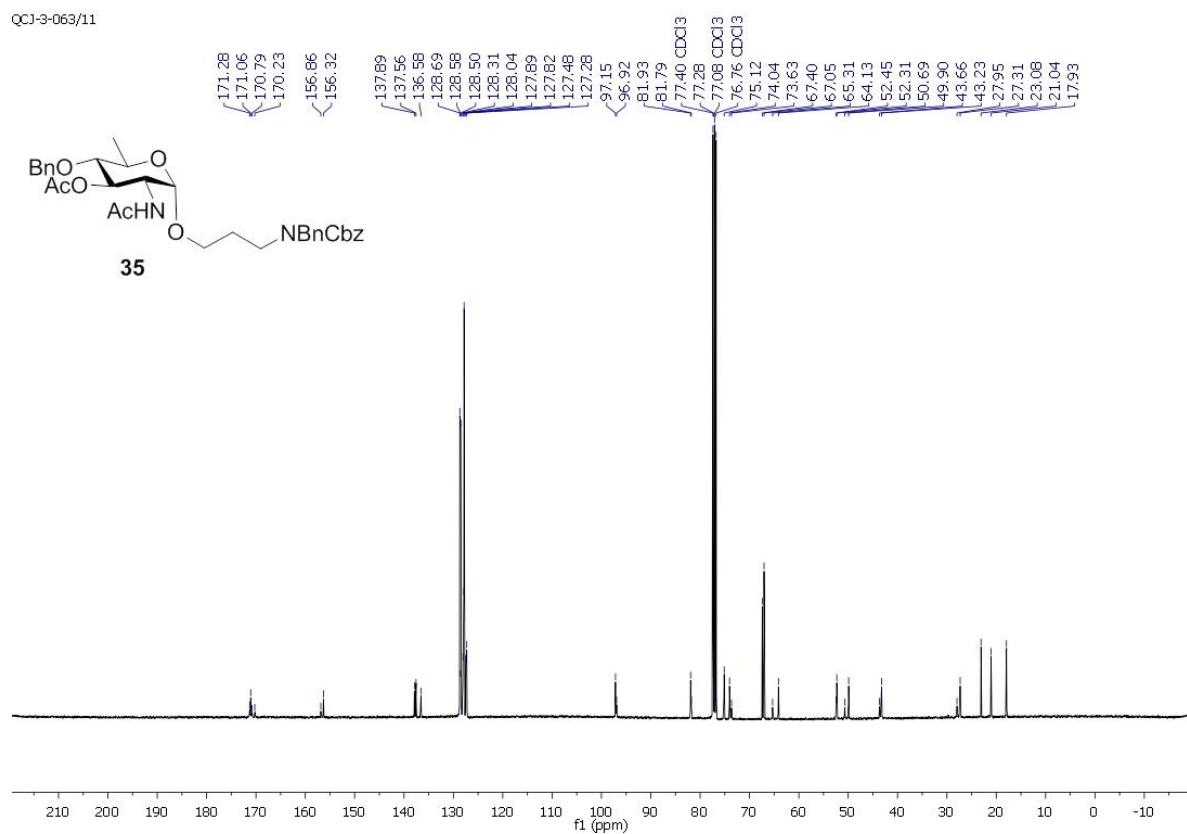
¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 34



¹H NMR (CDCl₃, 400 MHz) of compound 35

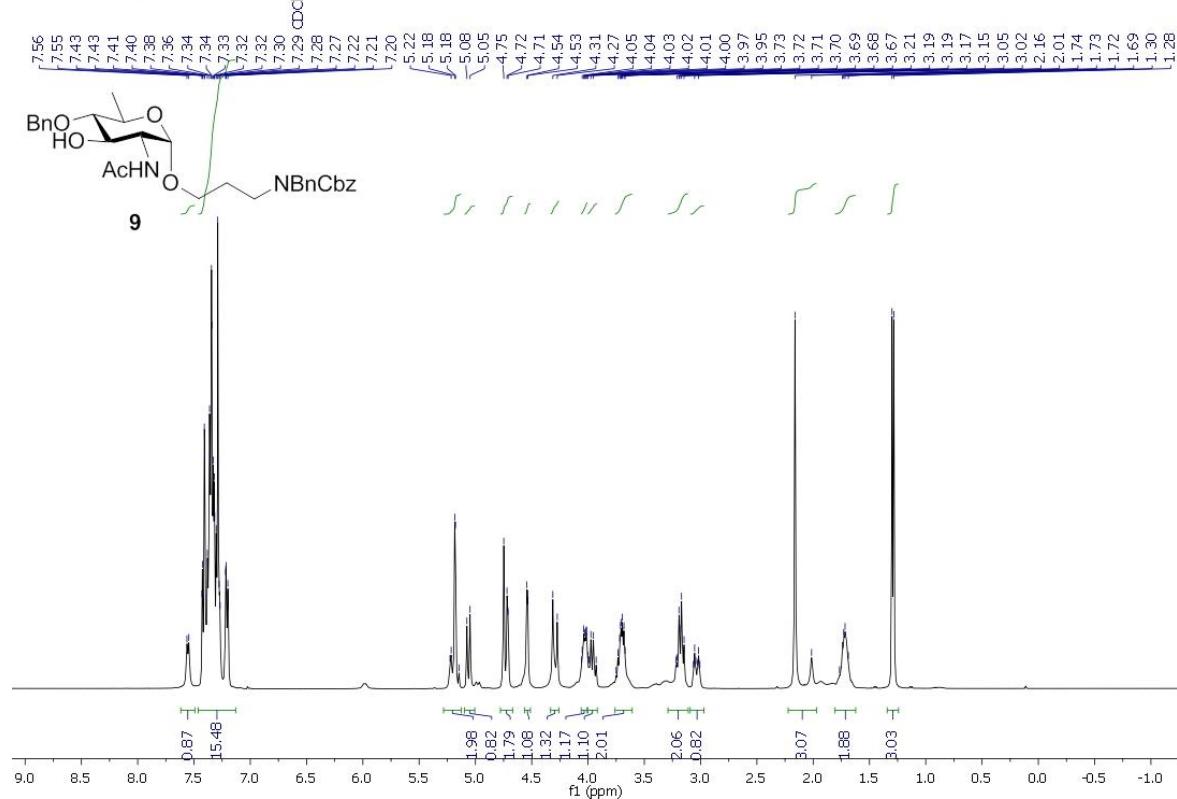


¹³C NMR (CDCl₃, 100 MHz) of compound 35



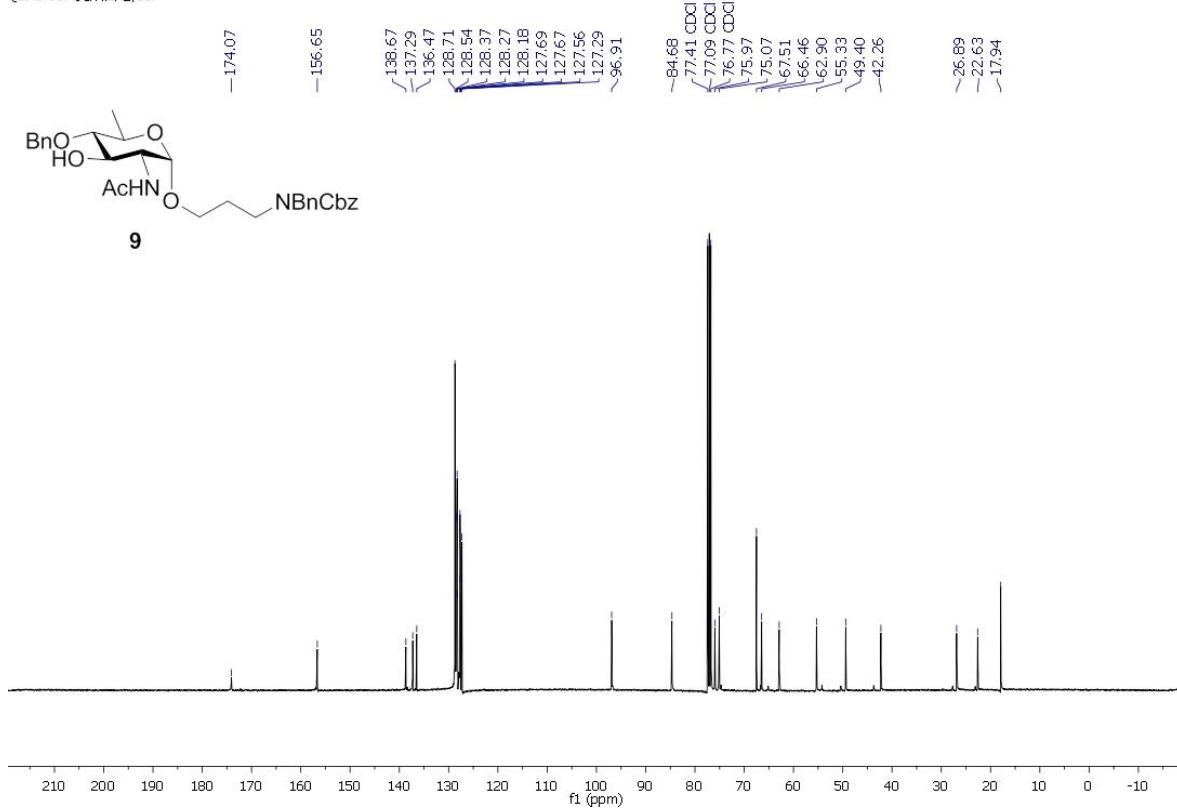
¹H NMR (CDCl₃, 400 MHz) of compound 9

QCJ-3-057 完成四谱/11

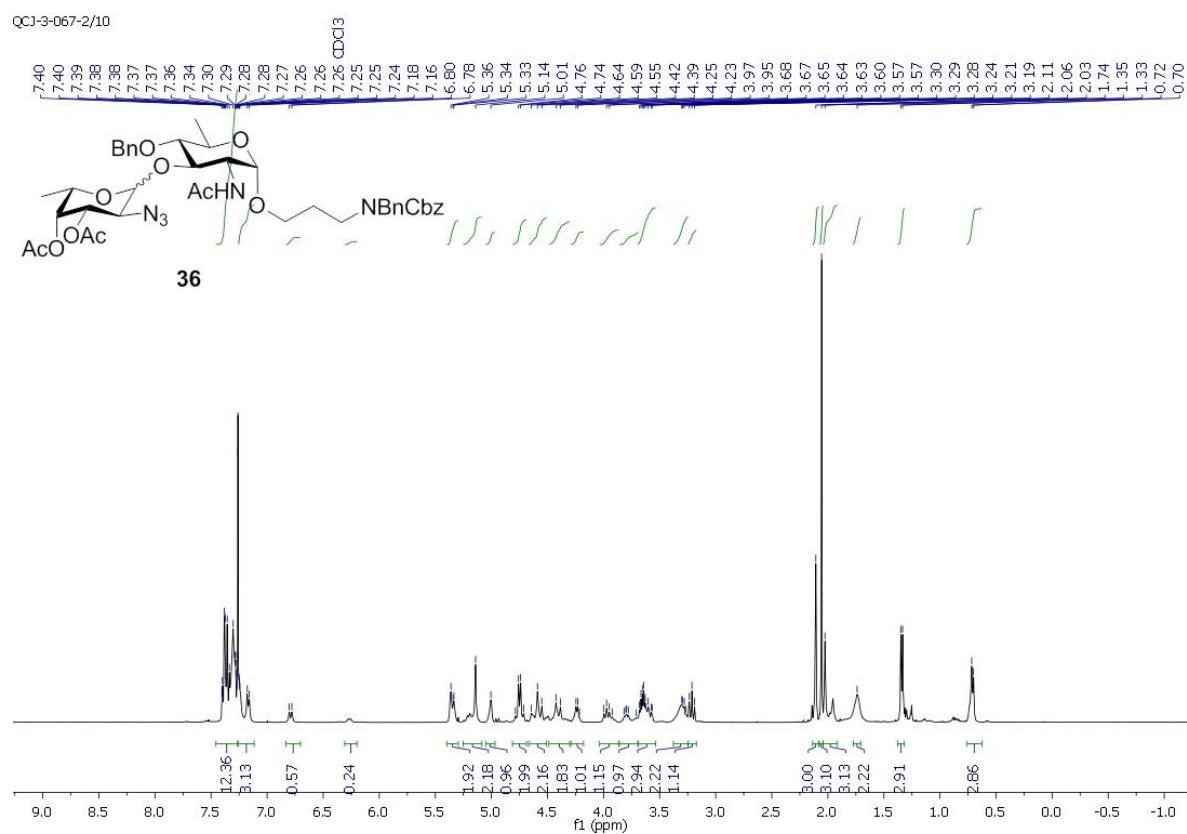


¹³C NMR (CDCl₃, 100 MHz) of compound 9

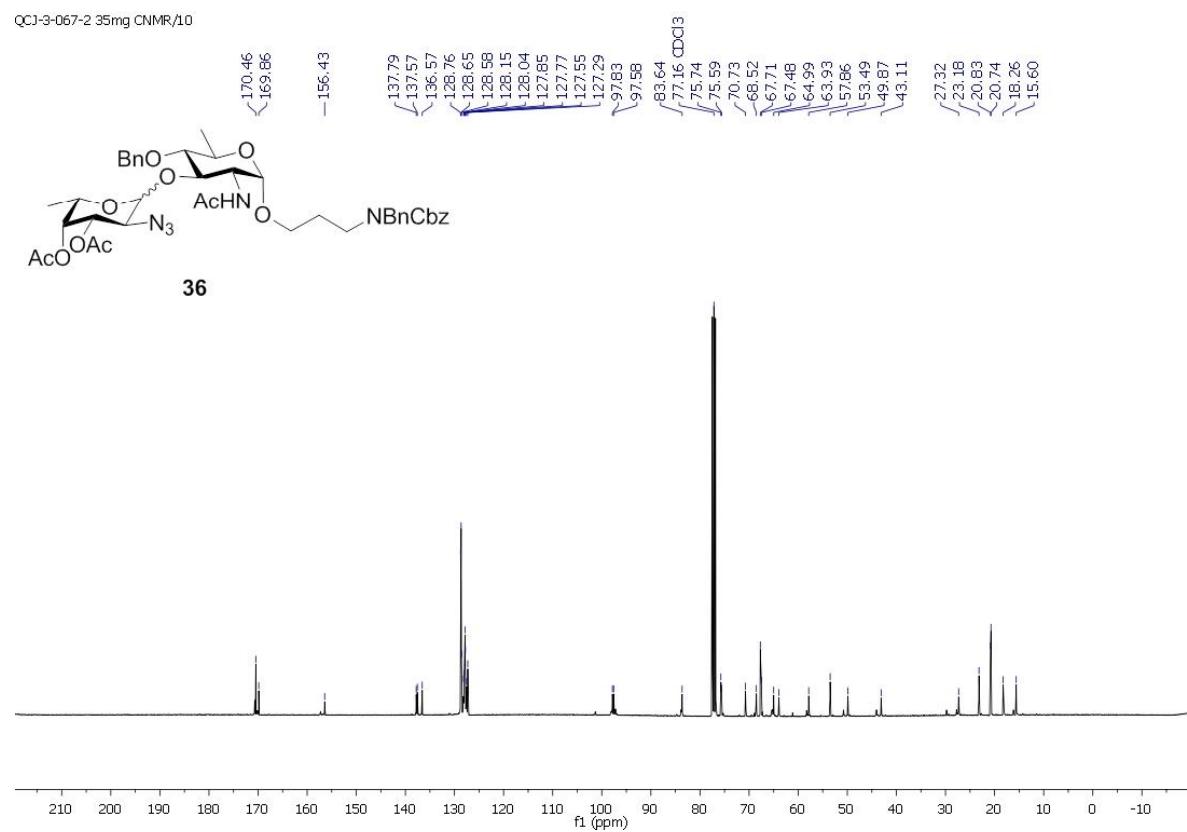
QCJ-3-057 完成四谱/10



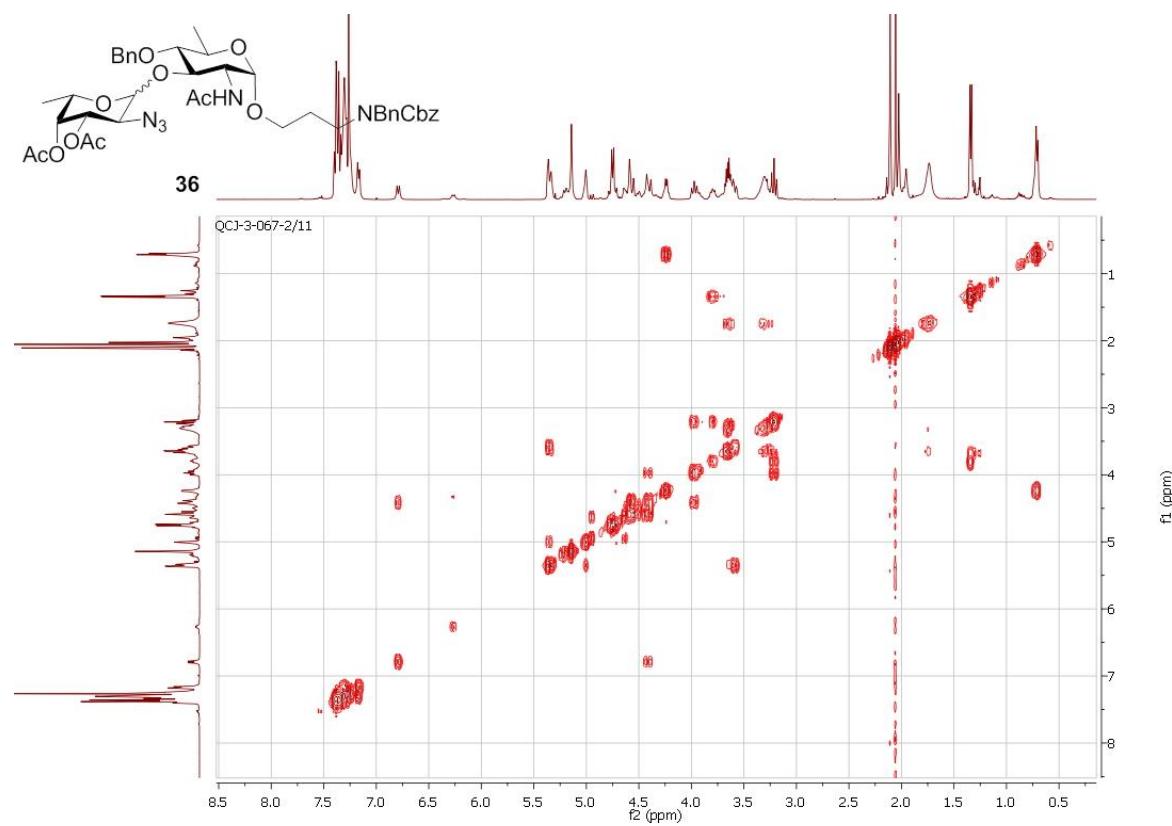
¹H NMR (CDCl₃, 400 MHz) of compound 36



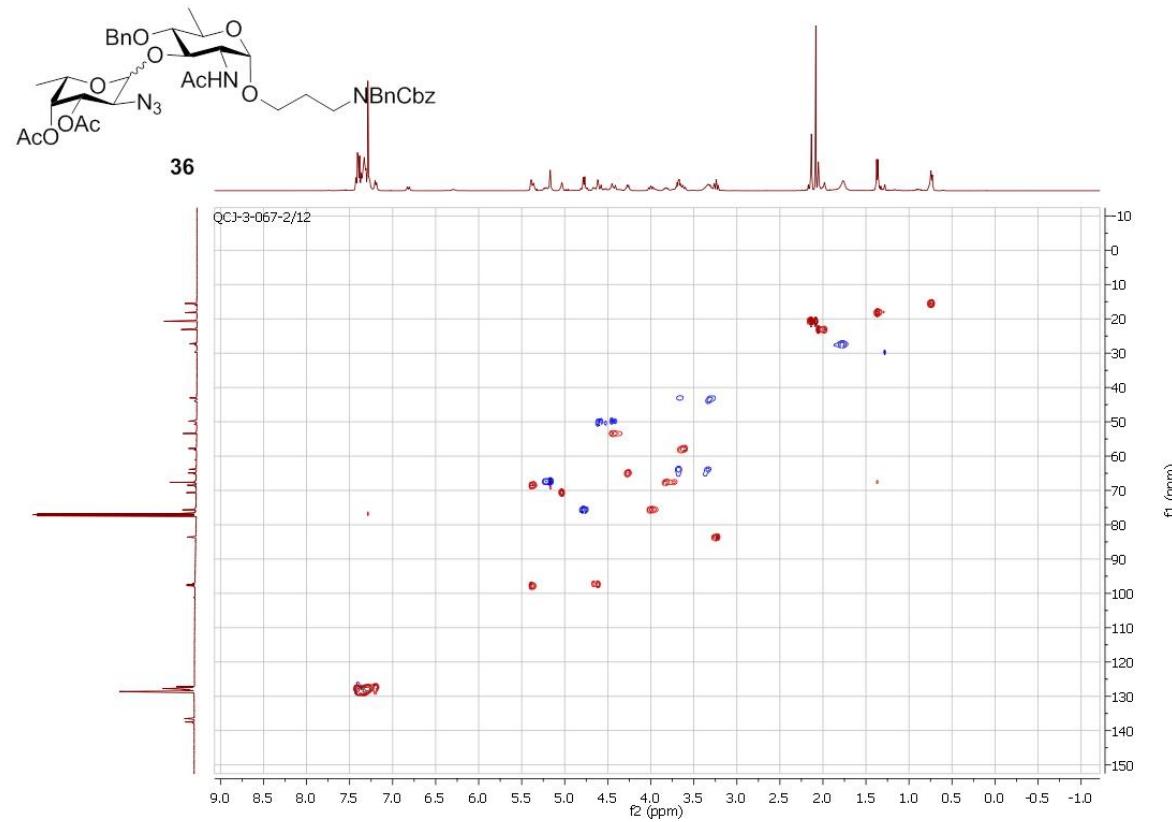
¹³C NMR (CDCl₃, 100 MHz) of compound 36



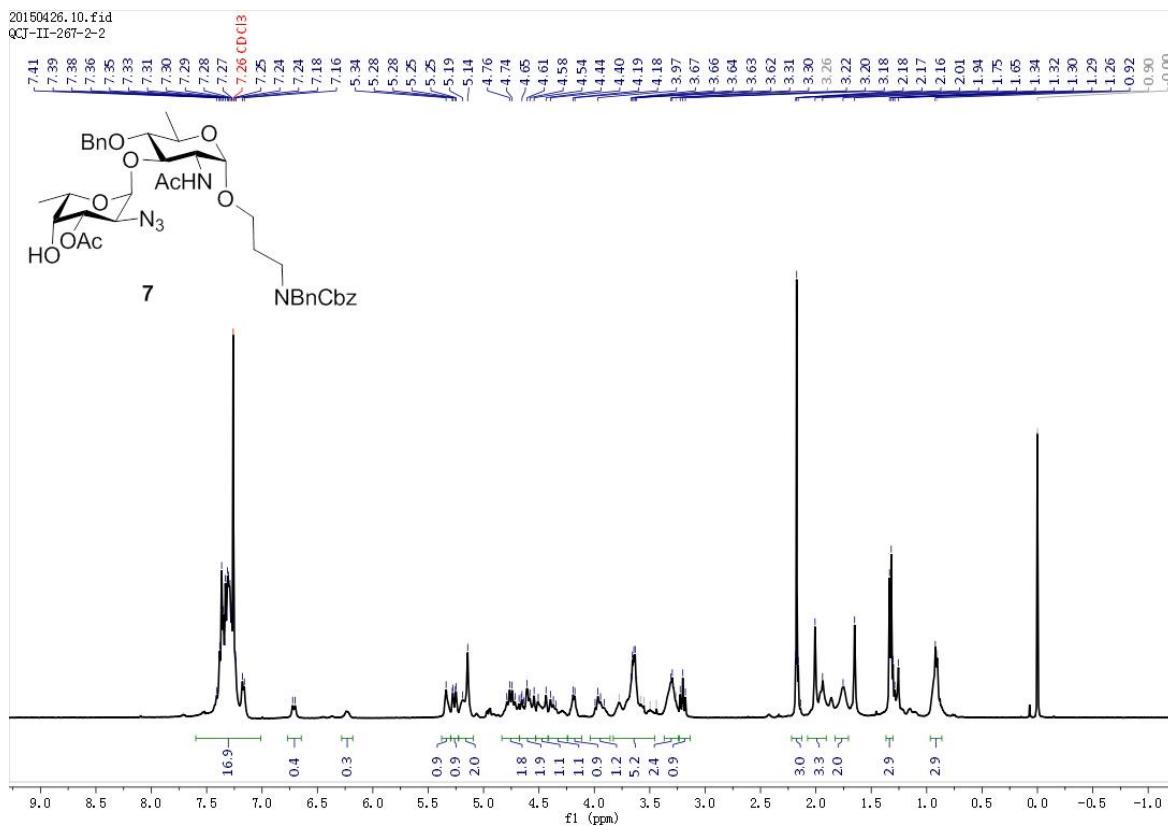
¹H-¹H COSY (CDCl₃, 400 MHz) of compound 36



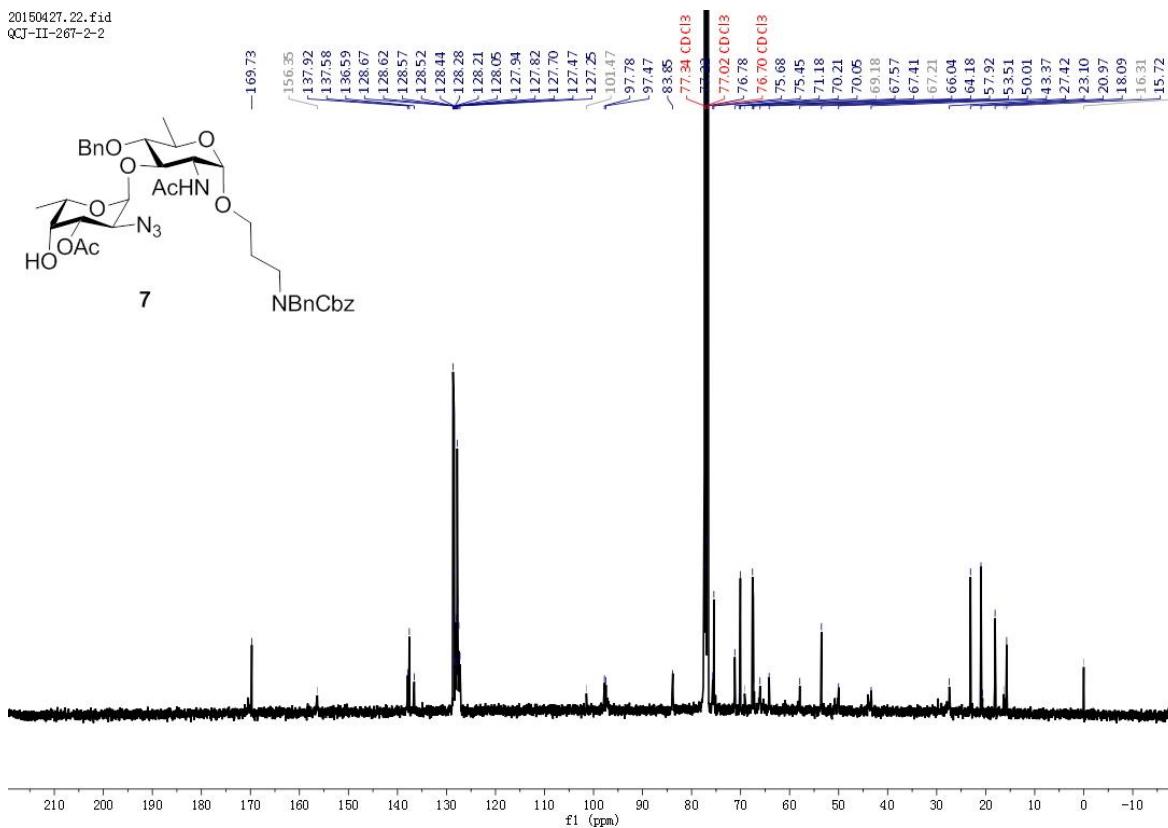
¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 36



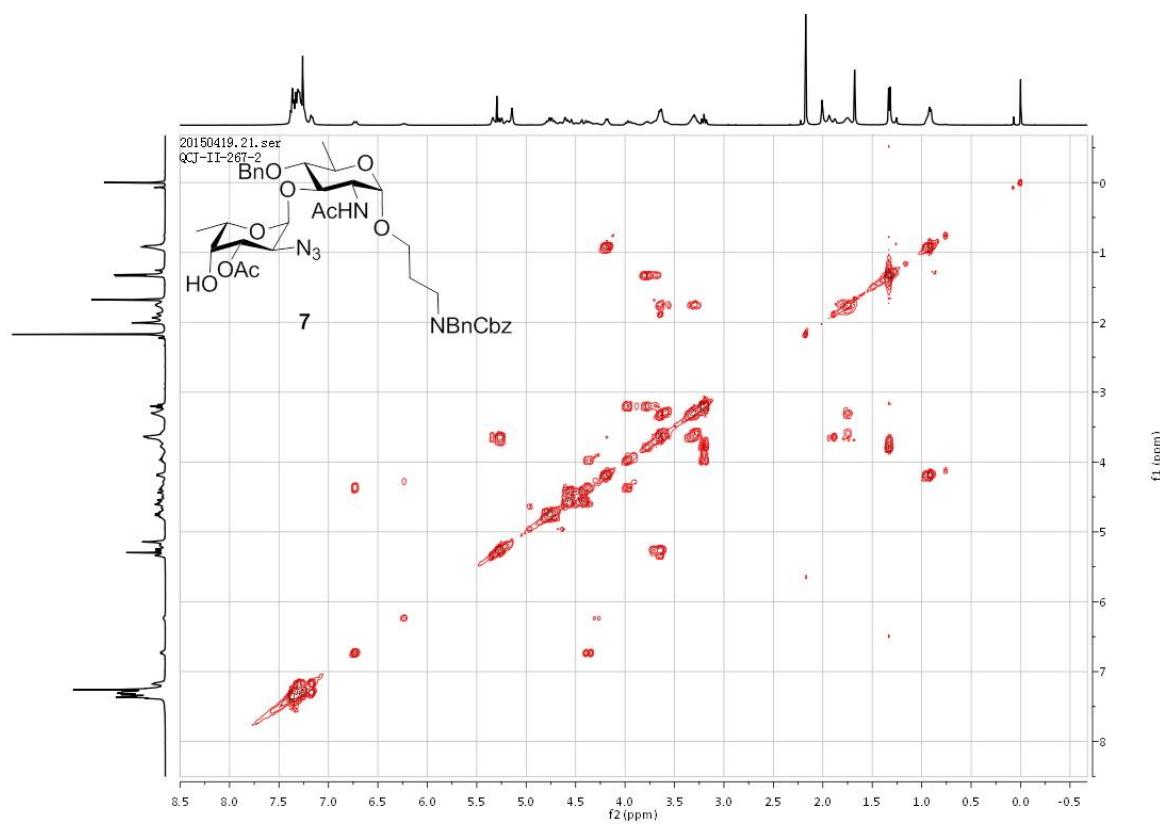
¹H NMR (CDCl₃, 400 MHz) of compound 7



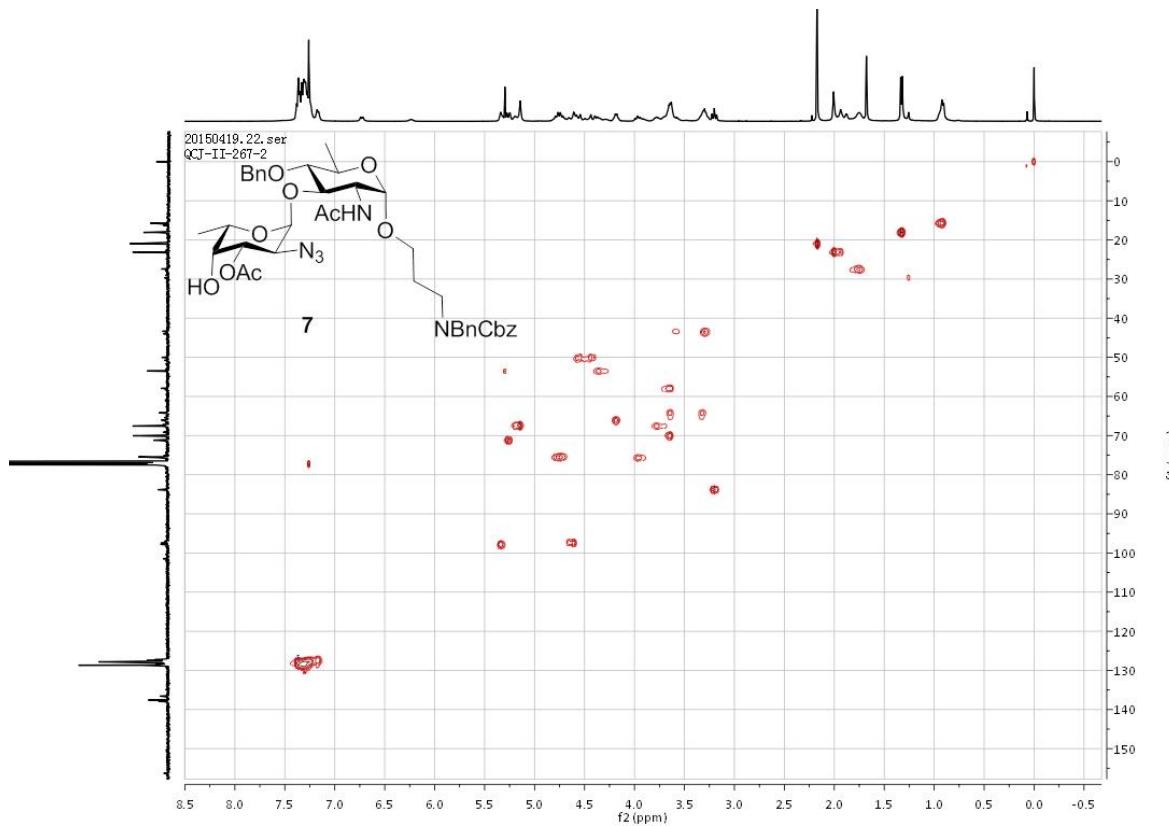
¹³C NMR (CDCl_3 , 100 MHz) of compound 7



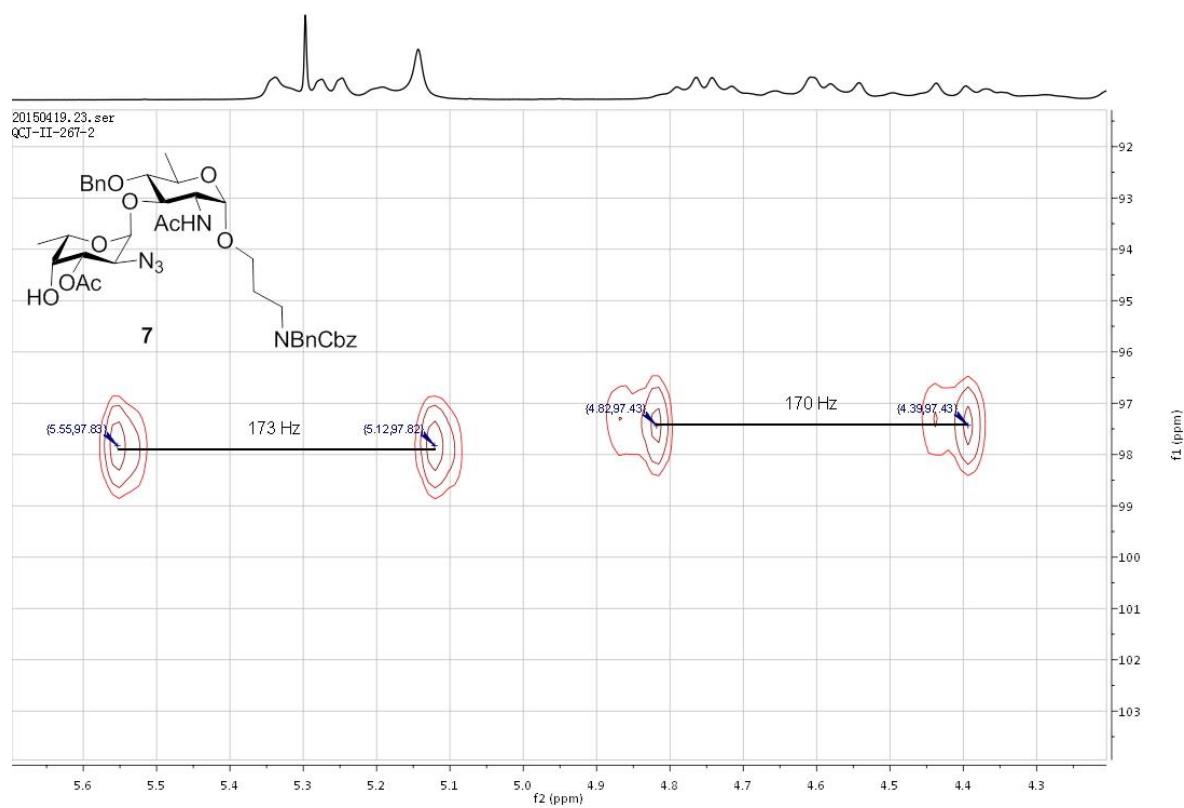
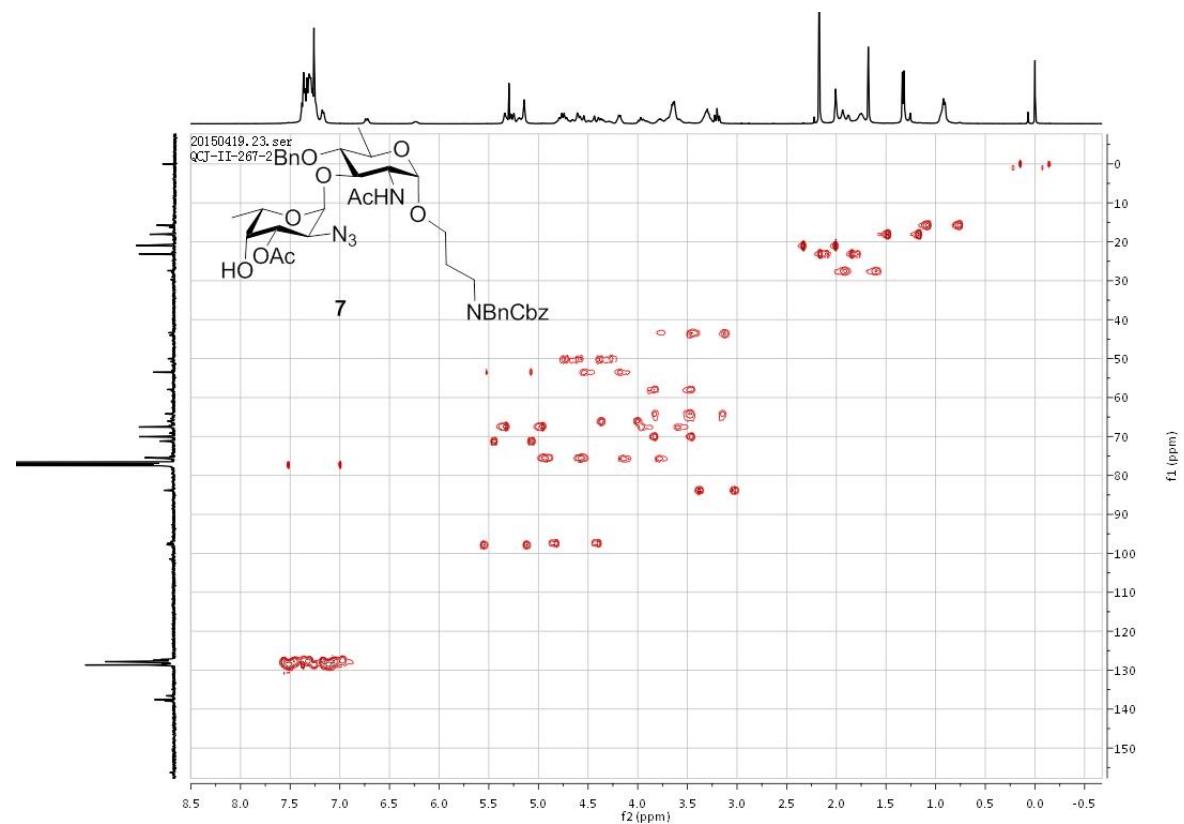
¹H-¹H COSY (CDCl₃, 400 MHz) of compound 7



¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 7

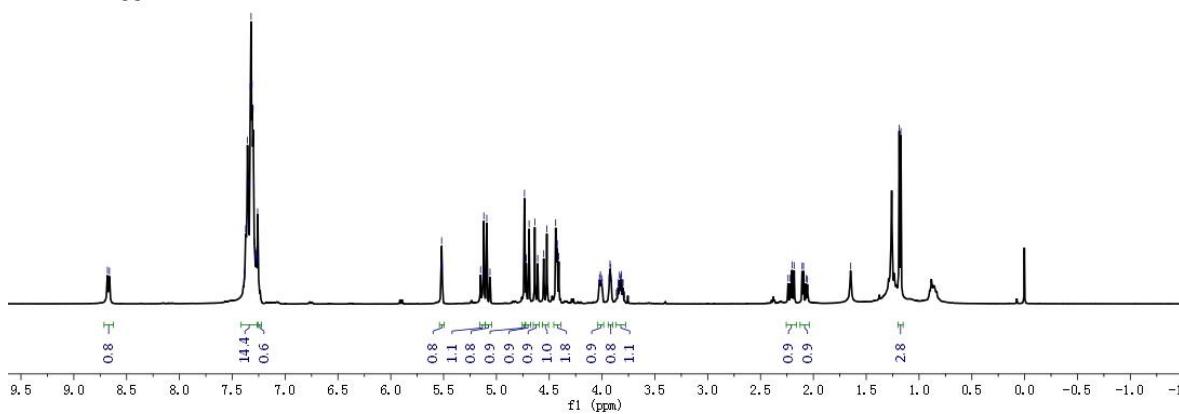
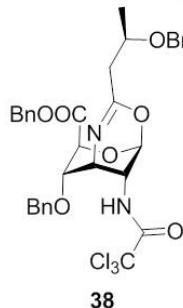


Coupled-HSQC (CDCl_3 , 400 MHz) of compound 7

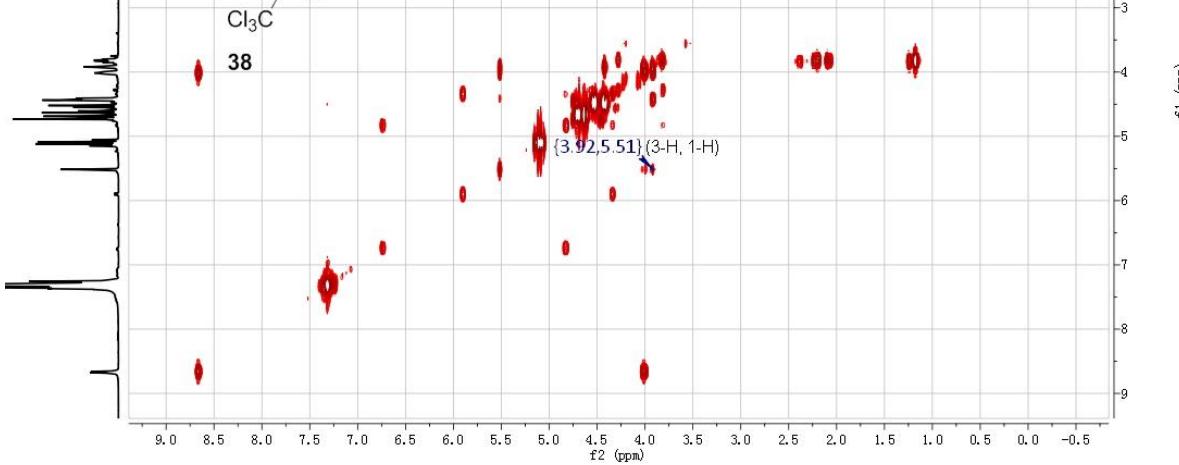
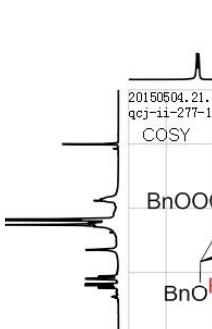


¹H NMR (CDCl₃, 400 MHz) of compound 38

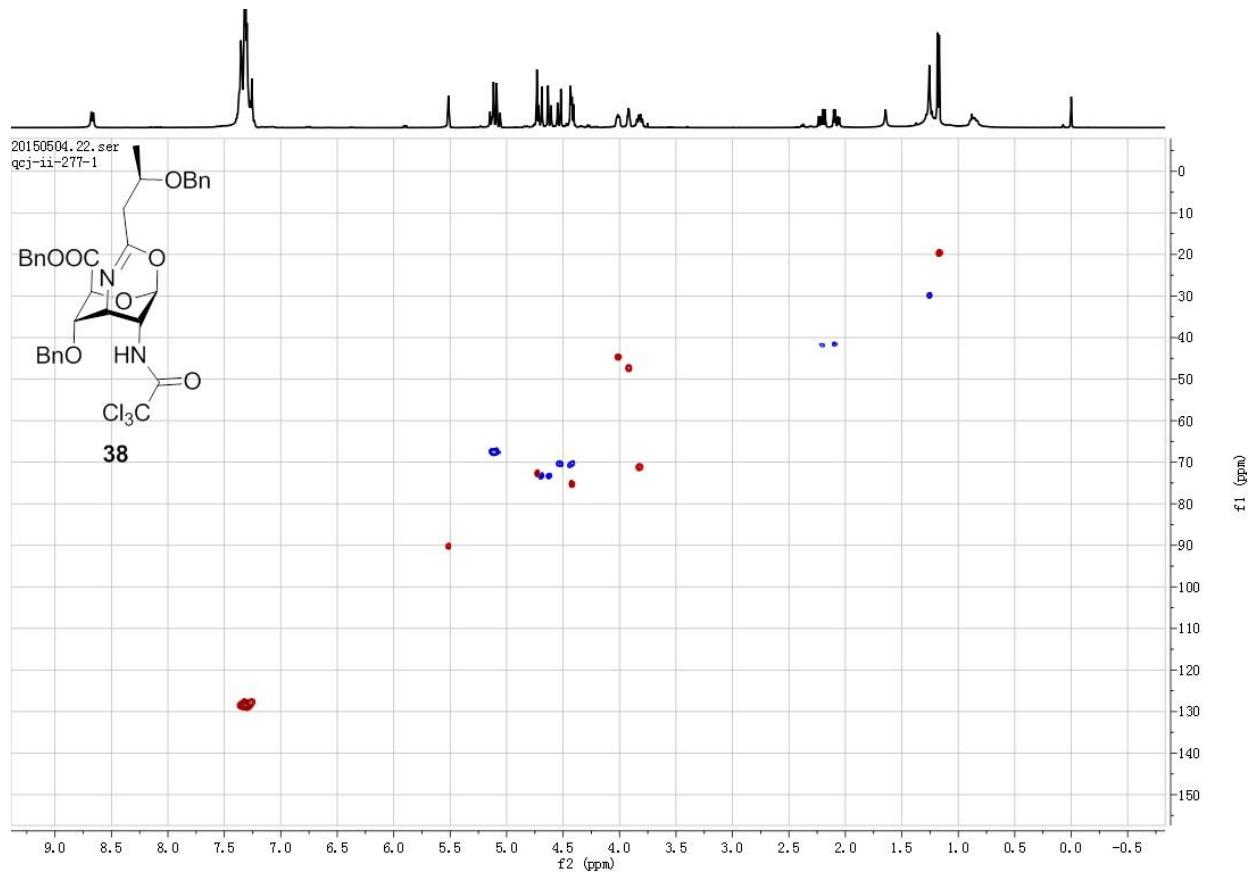
20150503.10.fid
QCJ-II-277-1



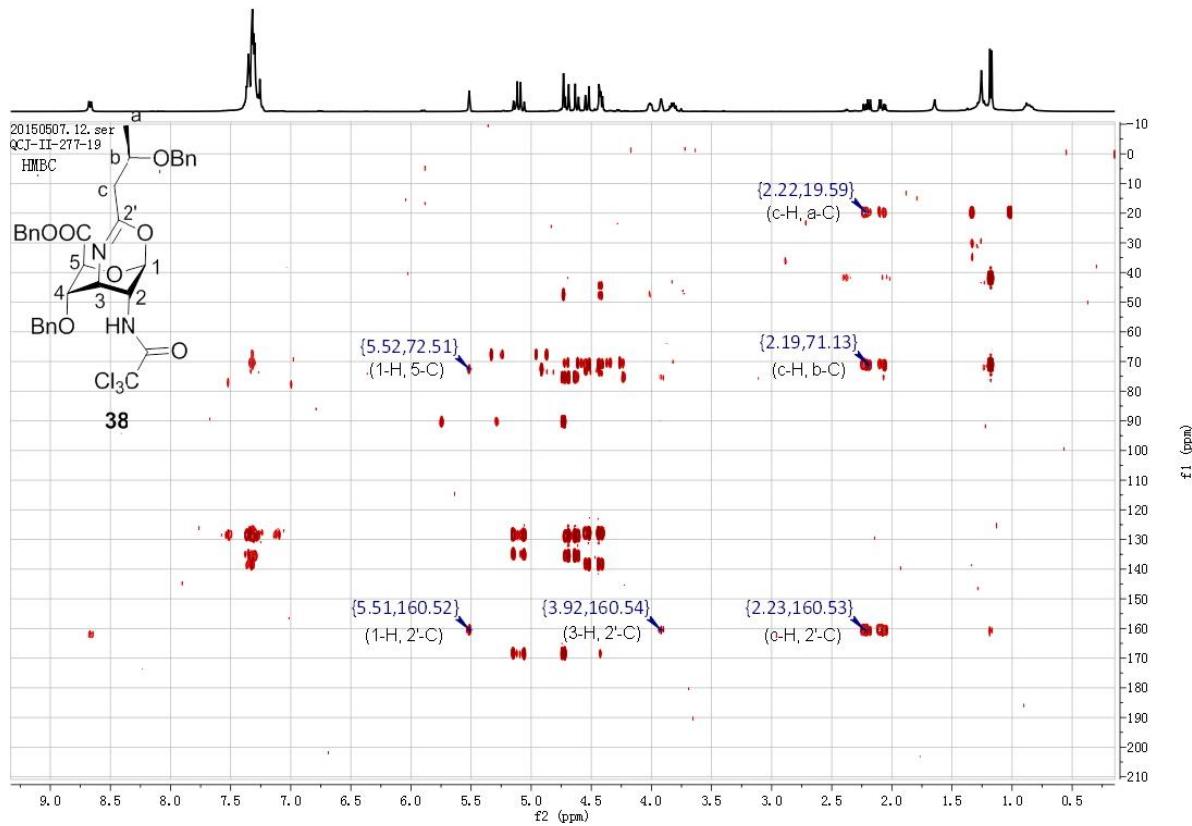
¹H-¹H COSY (CDCl₃, 400 MHz) of compound 38



¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 38

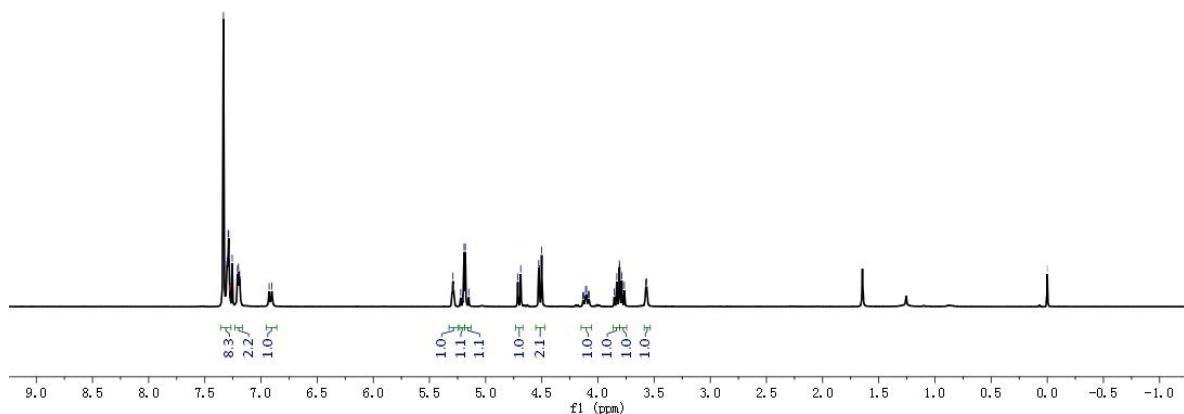
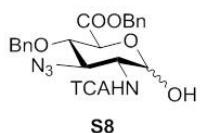


¹H-¹³C HMBC (CDCl₃, 400 MHz) of compound 38



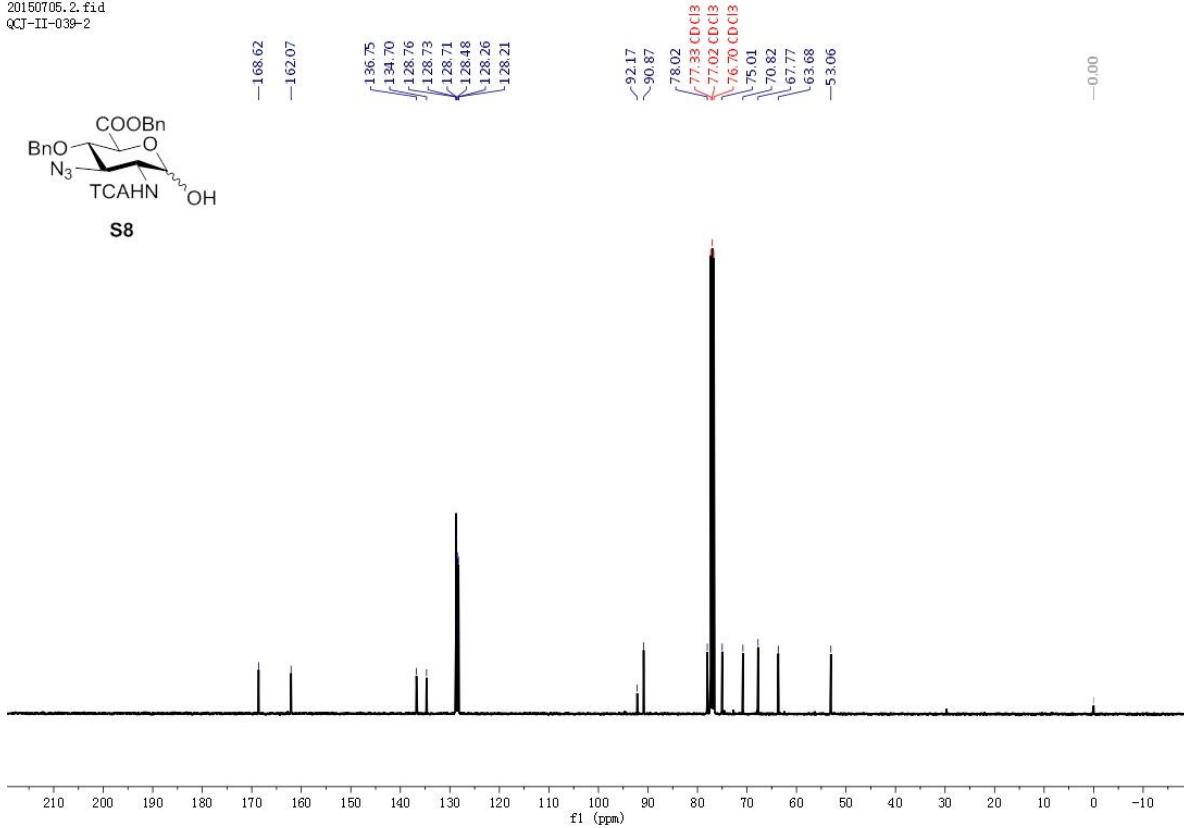
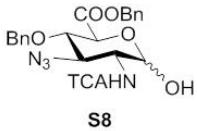
¹H NMR (CDCl₃, 400 MHz) of compound S8

20150705.1.fid
QCJ-II-039-2

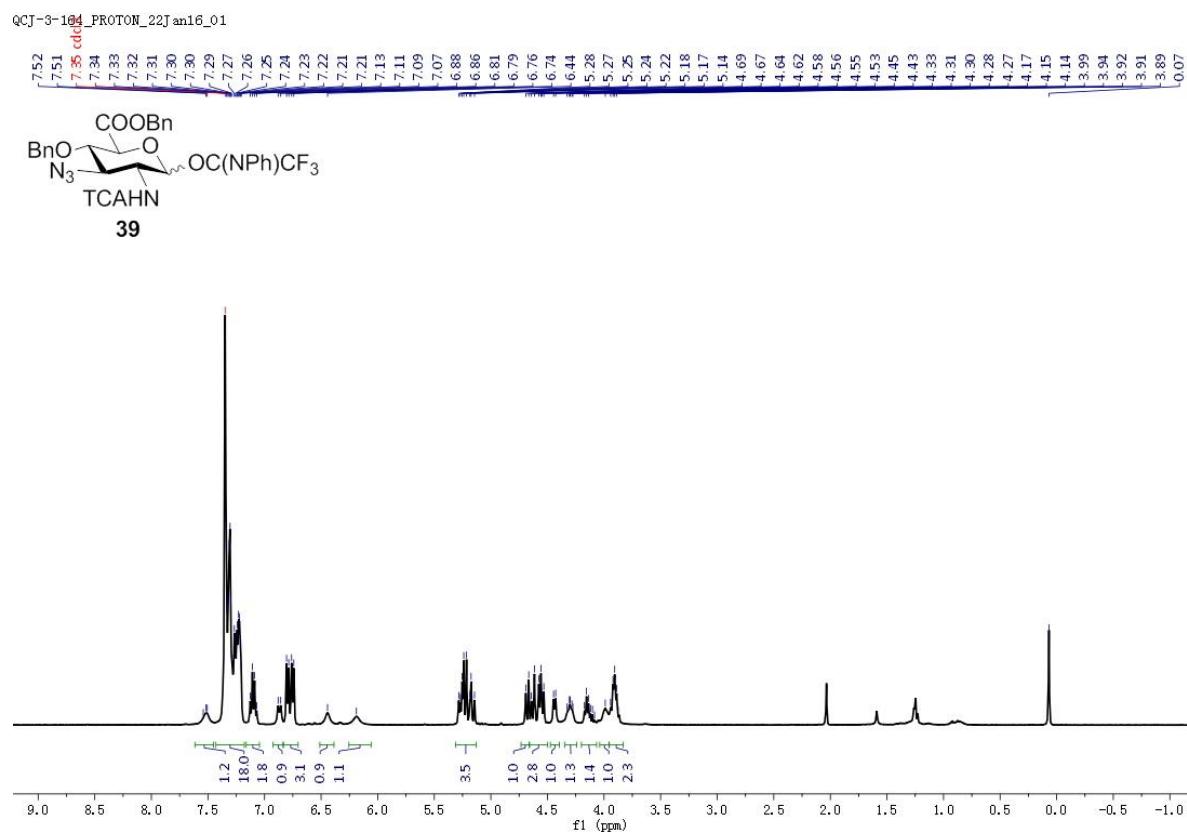


¹³C NMR (CDCl₃, 100 MHz) of compound S8

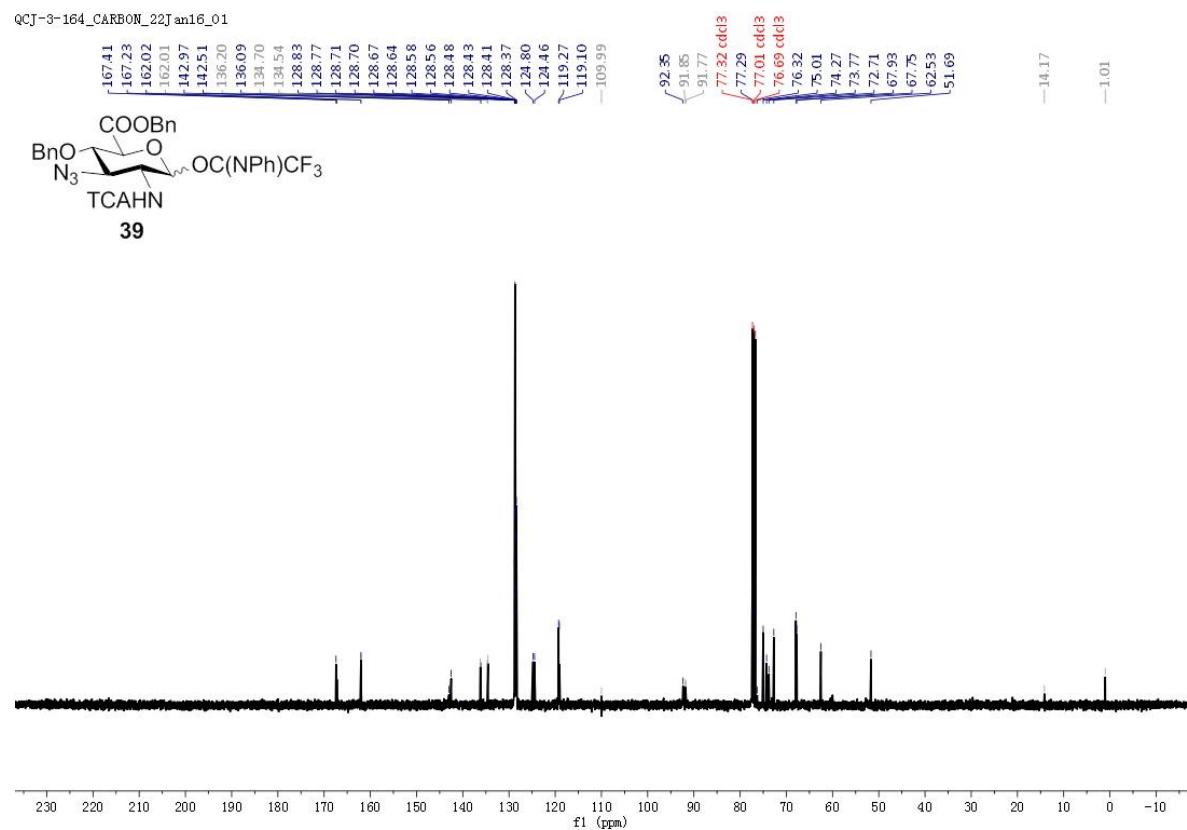
20150705.2.fid
QCT-II-039-2



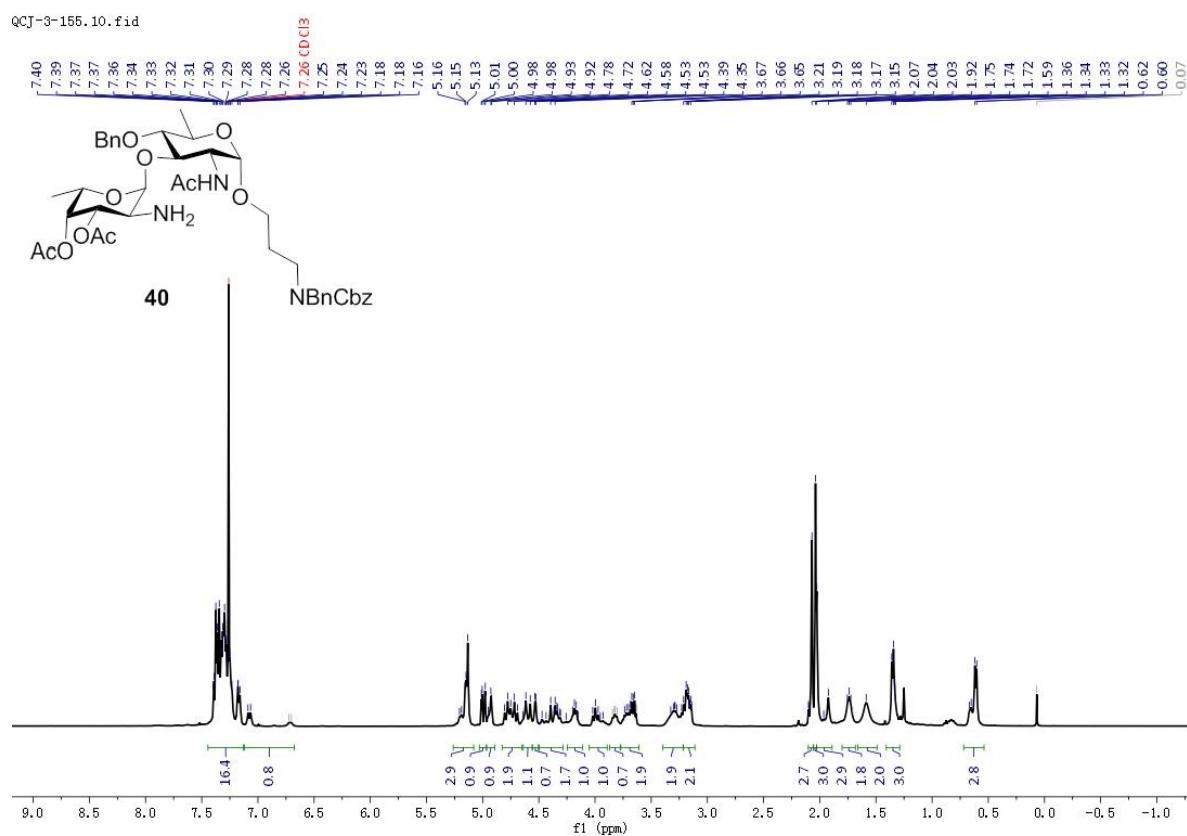
¹H NMR (CDCl₃, 400 MHz) of compound 39



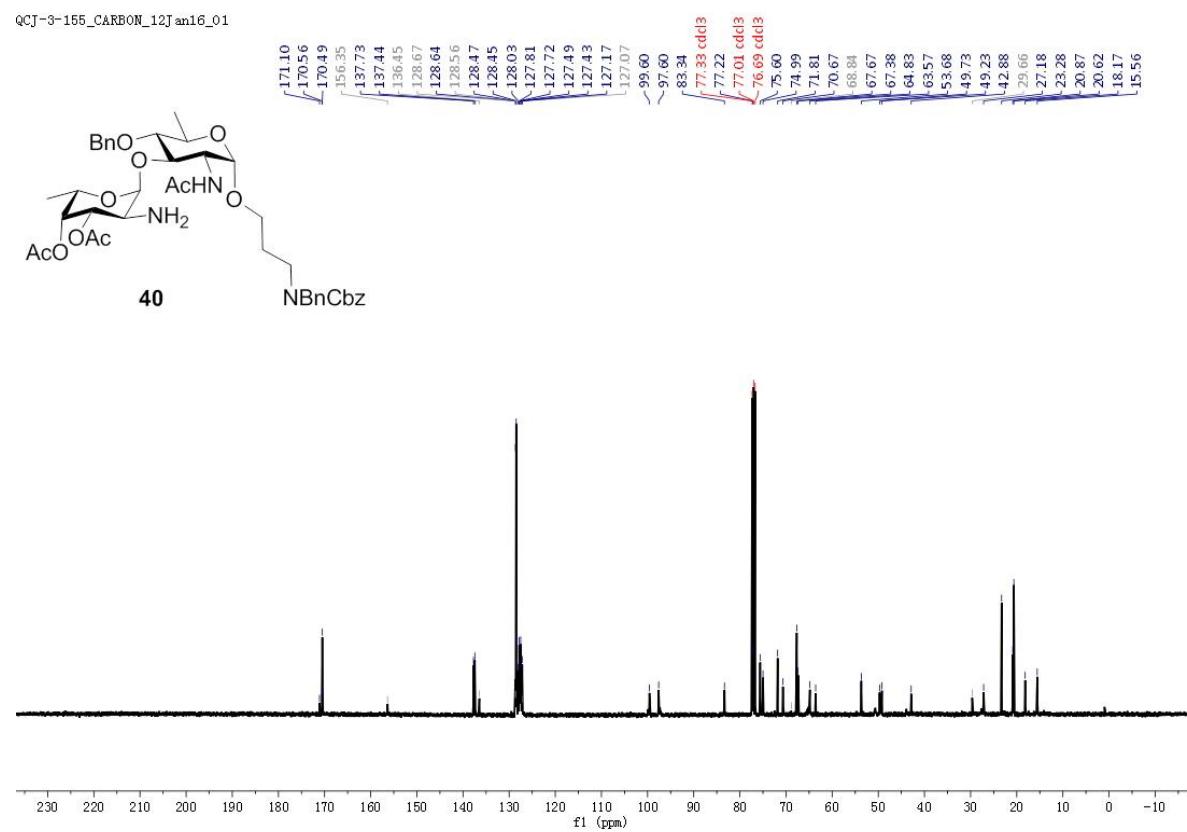
¹³C NMR (CDCl₃, 100 MHz) of compound 39



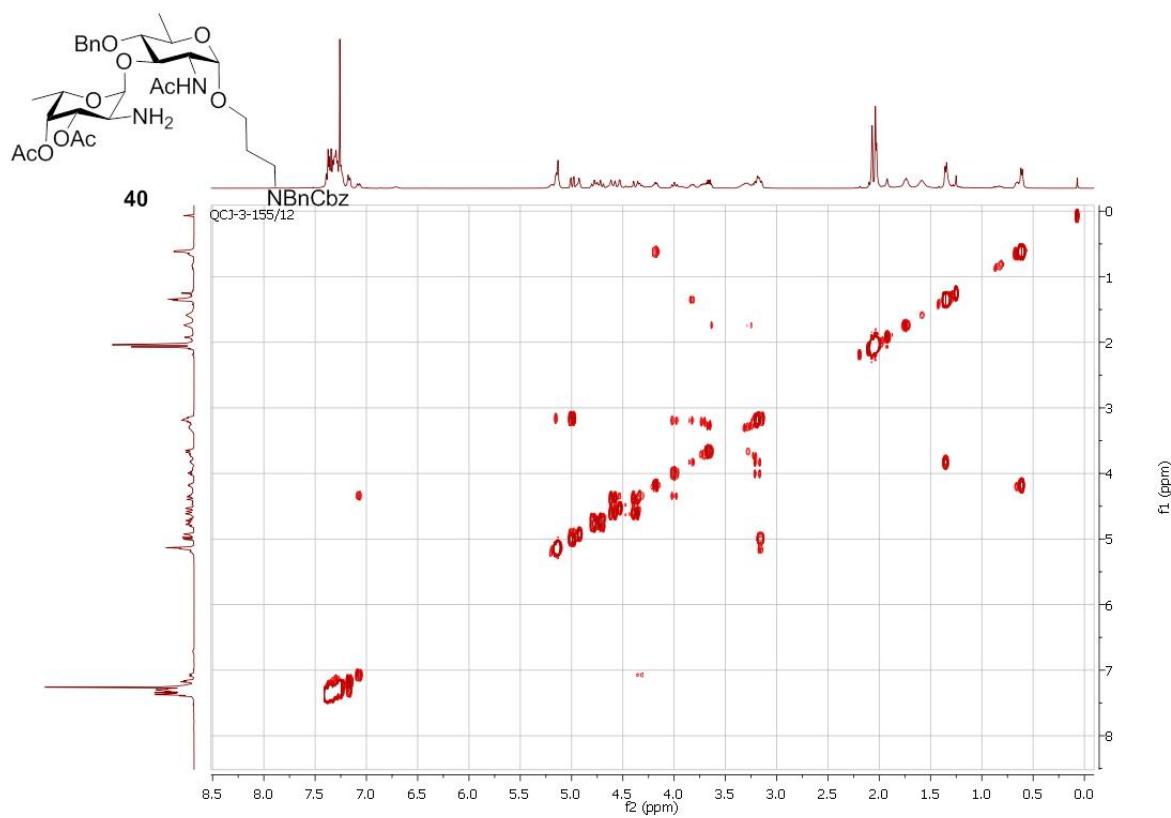
¹H NMR (CDCl₃, 400 MHz) of compound 40



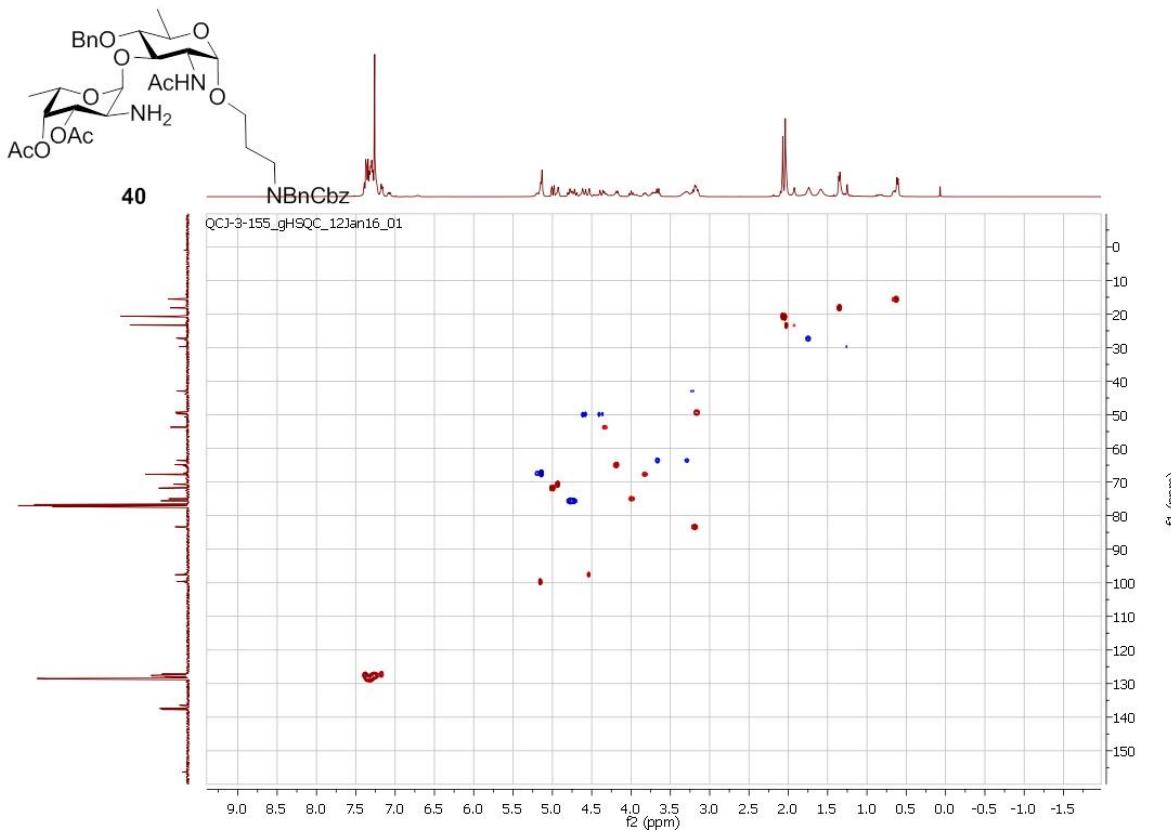
¹³C NMR (CDCl₃, 100 MHz) of compound 40



¹H-¹H COSY (CDCl₃, 400 MHz) of compound 40

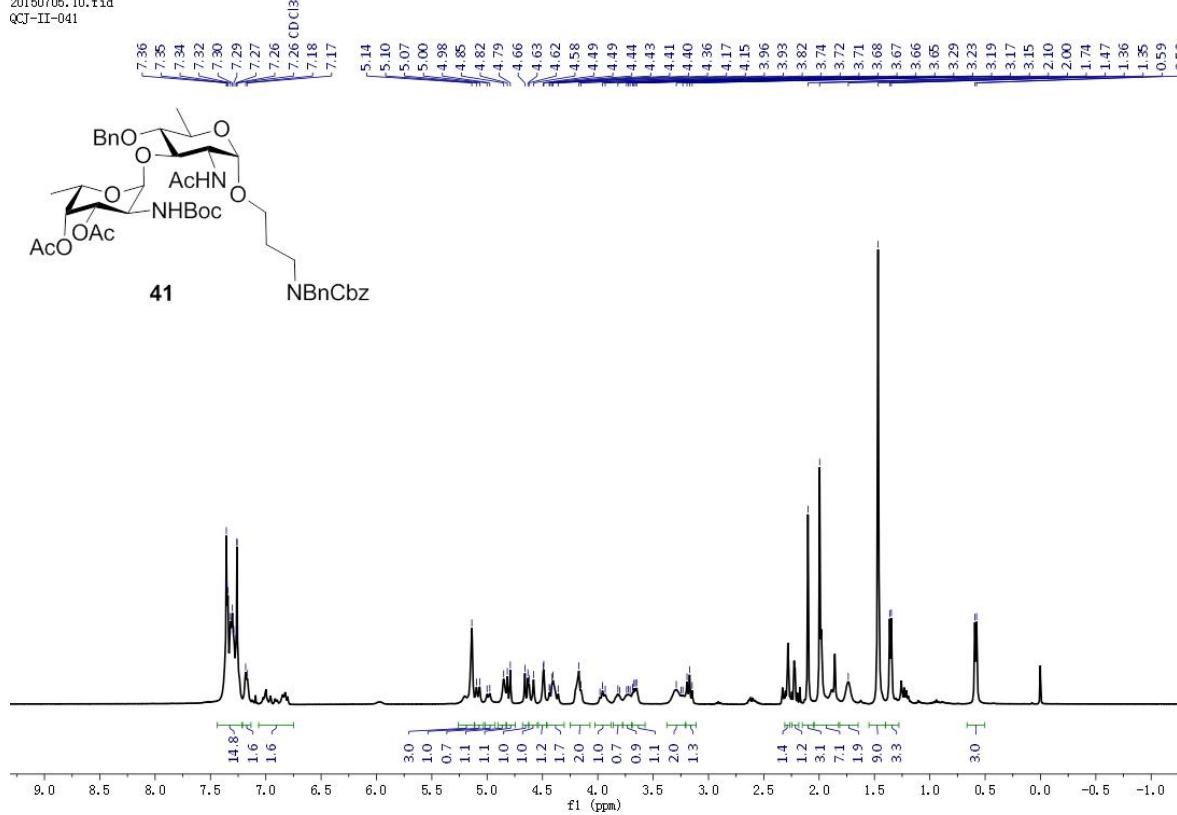
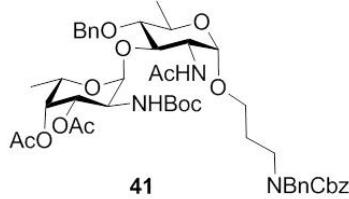


¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 40



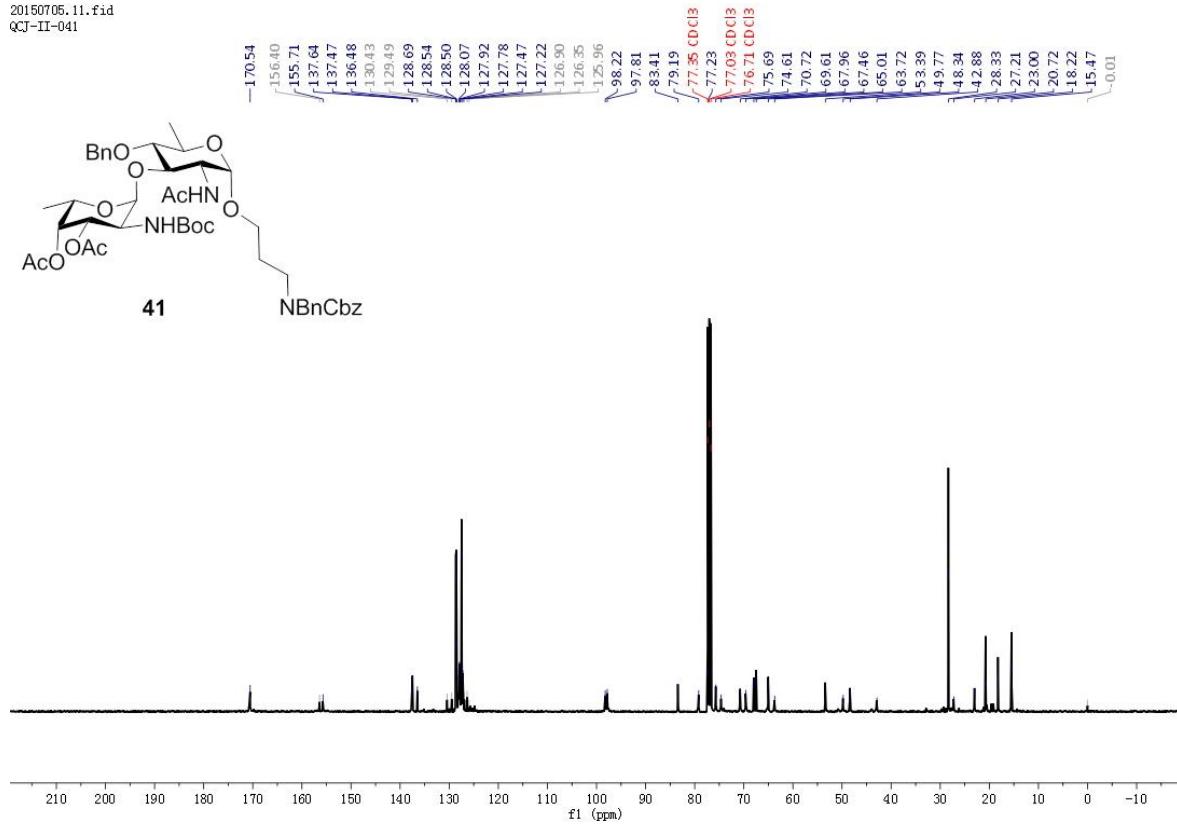
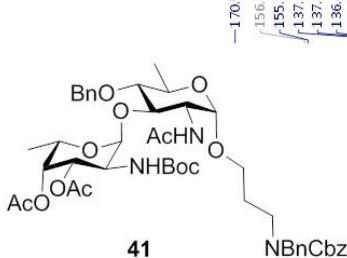
¹H NMR (CDCl₃, 400 MHz) of compound 41

20150705.10.fid
QCJ-II-041

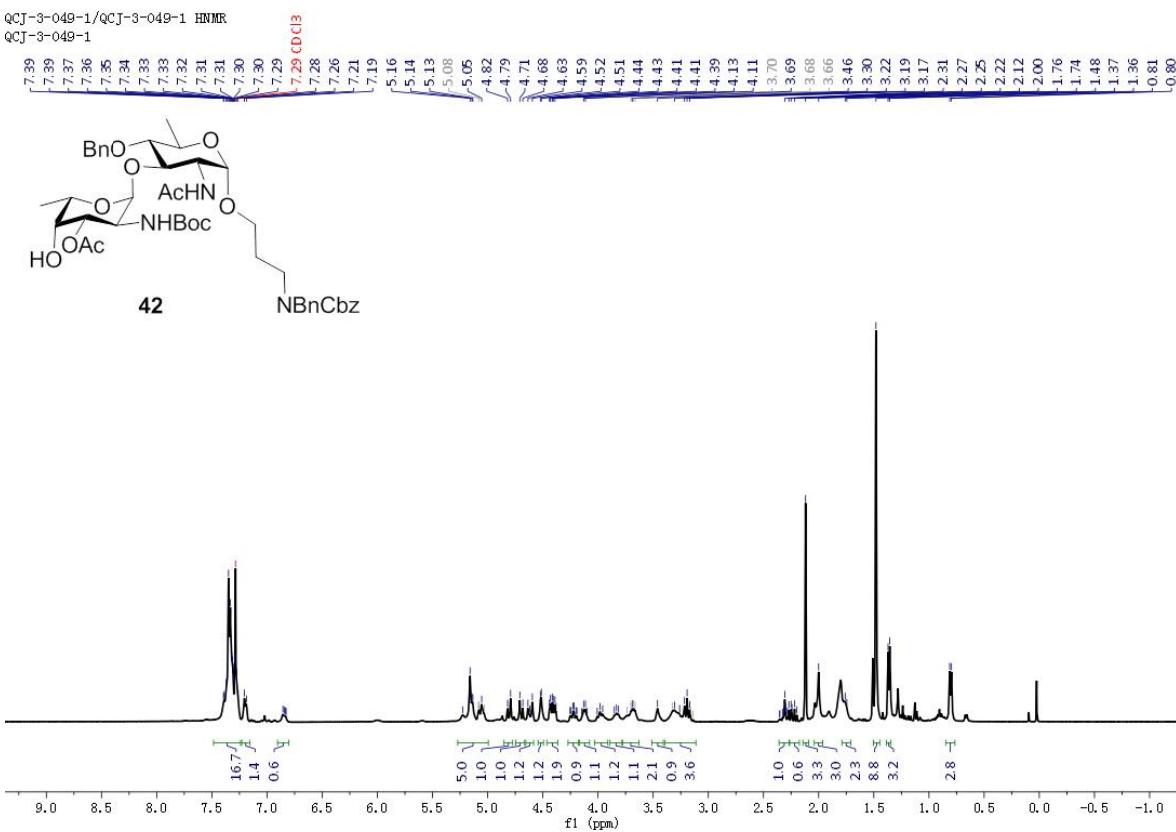


¹³C NMR (CDCl₃, 100 MHz) of compound 41

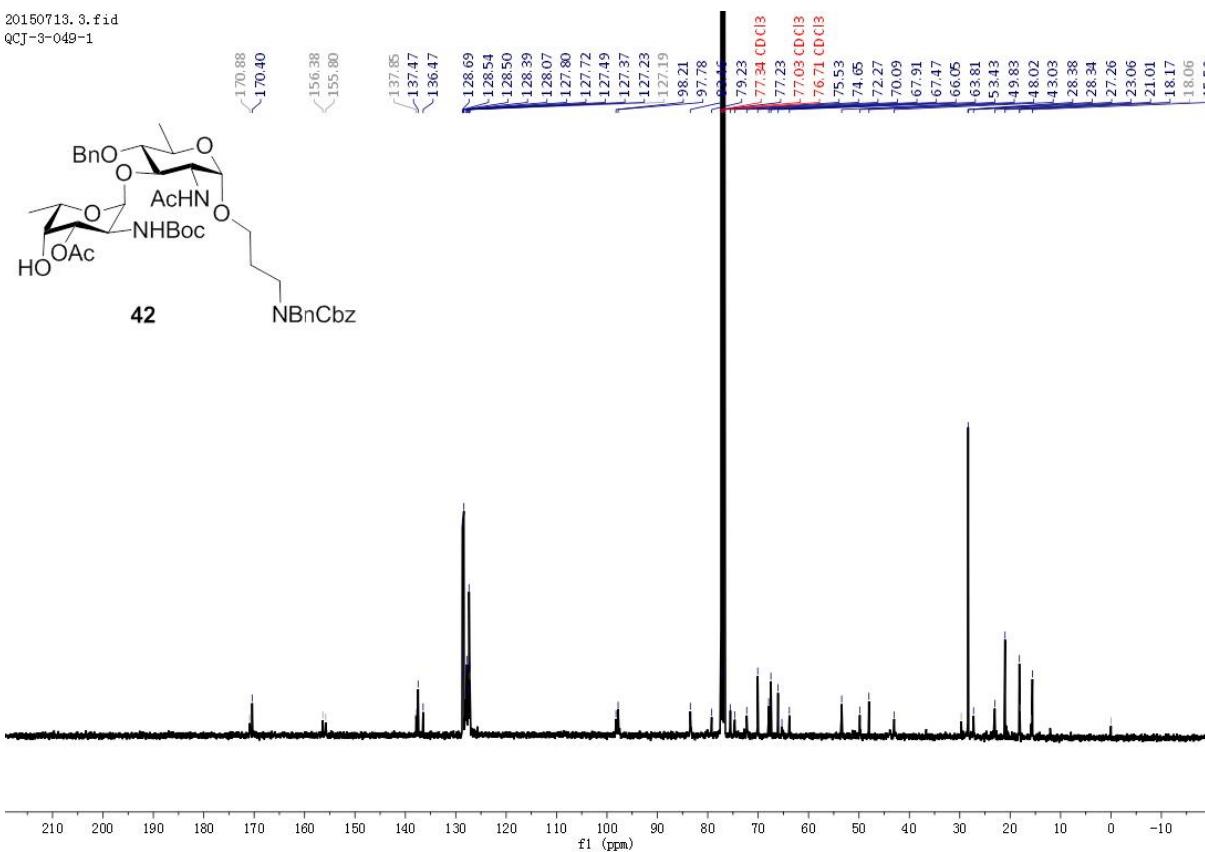
20150705.11.fid
QCJ-II-041



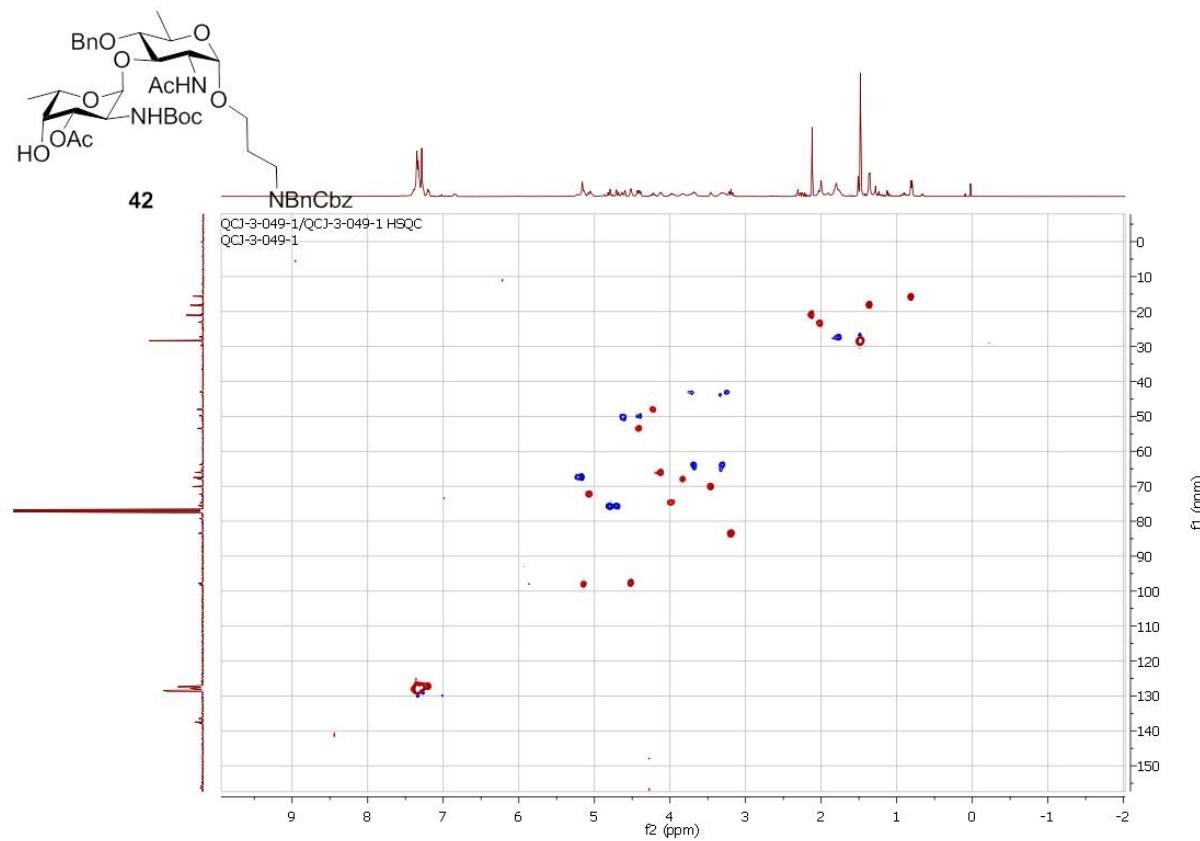
¹H NMR (CDCl₃, 400 MHz) of compound 42



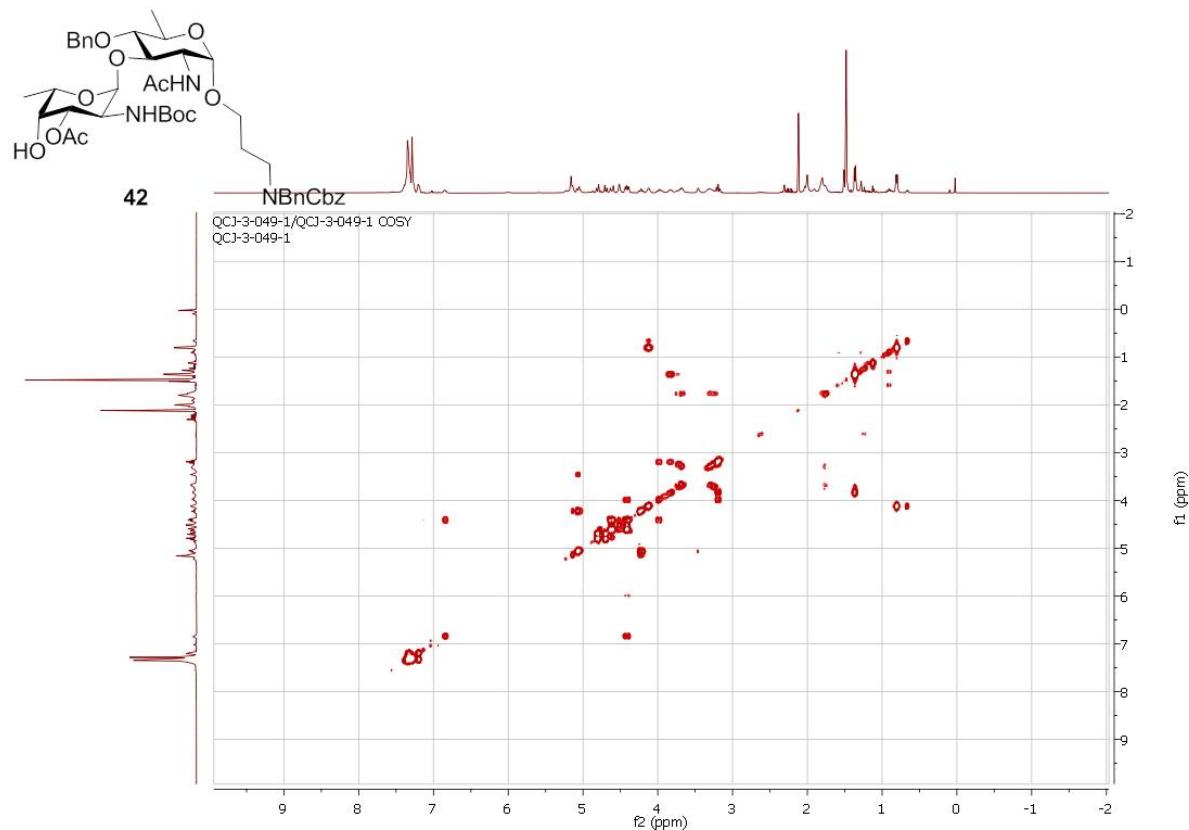
¹³C NMR (CDCl₃, 100 MHz) of compound 42



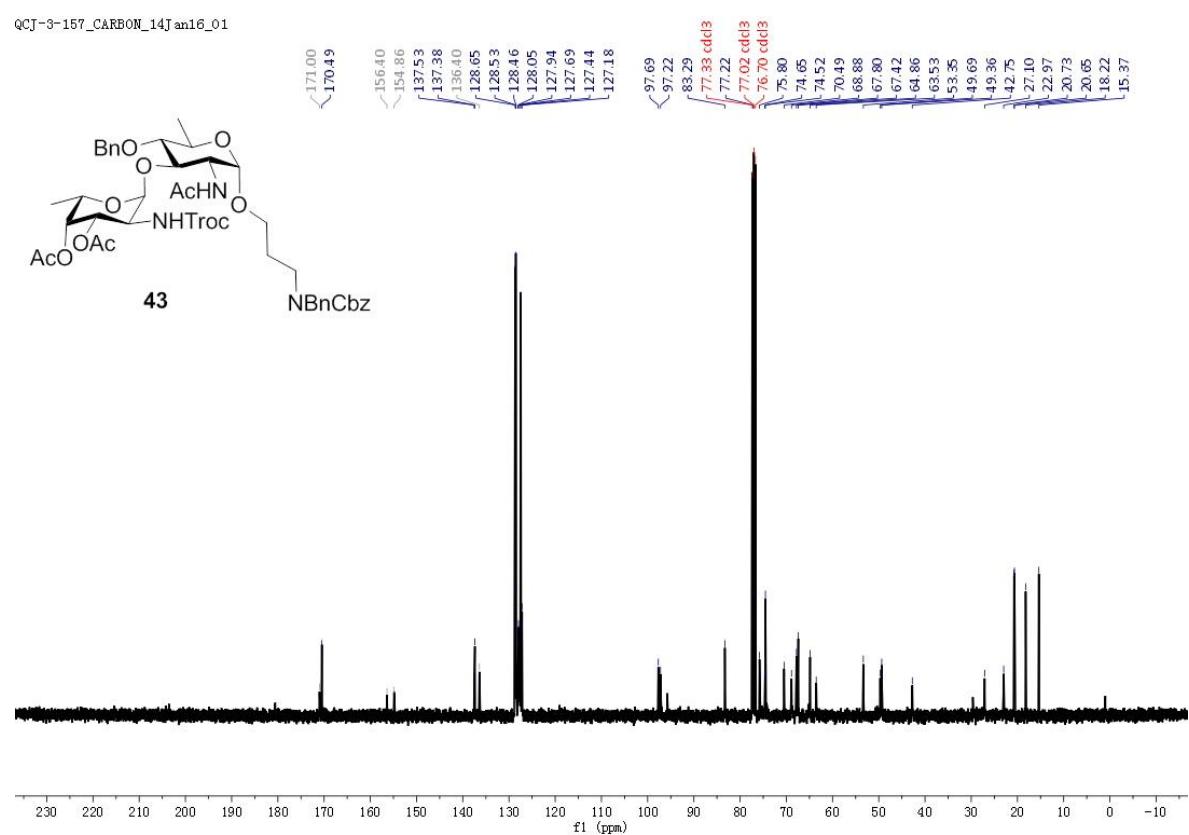
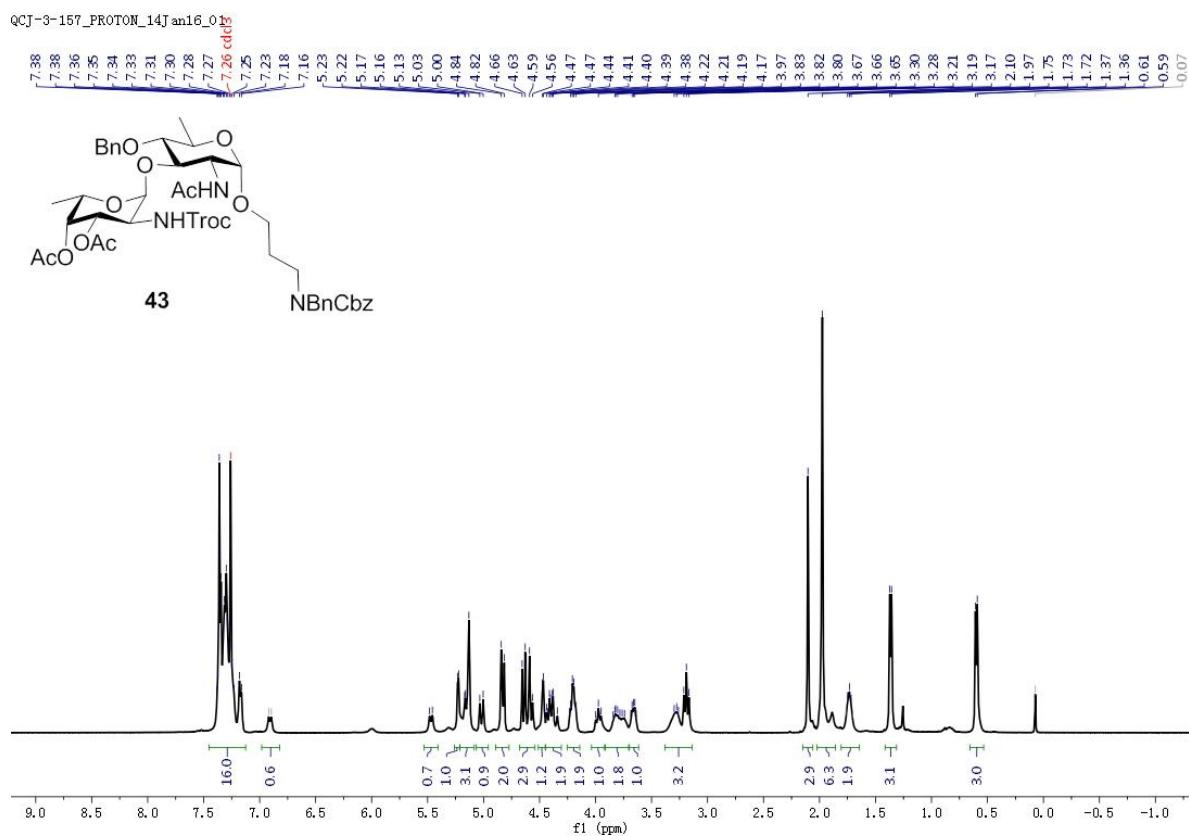
¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 42



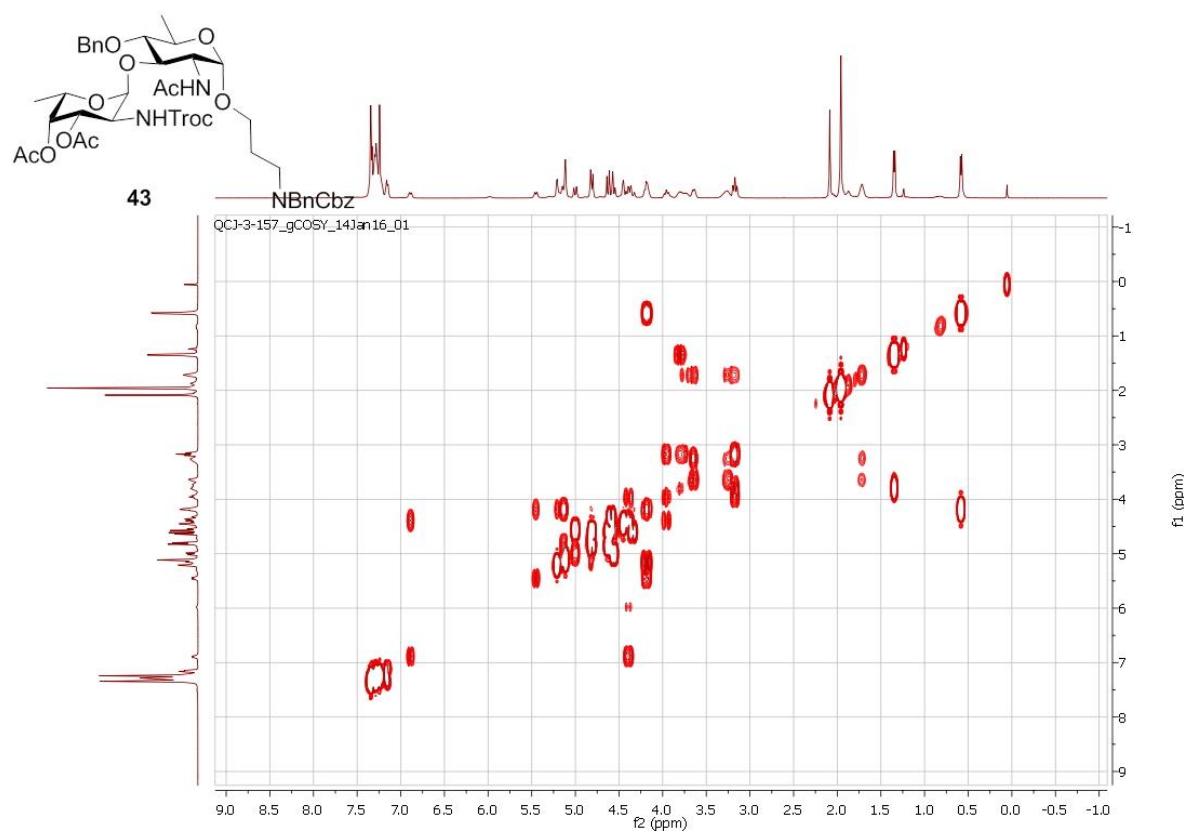
¹H-¹H COSY (CDCl₃, 400 MHz) of compound 42



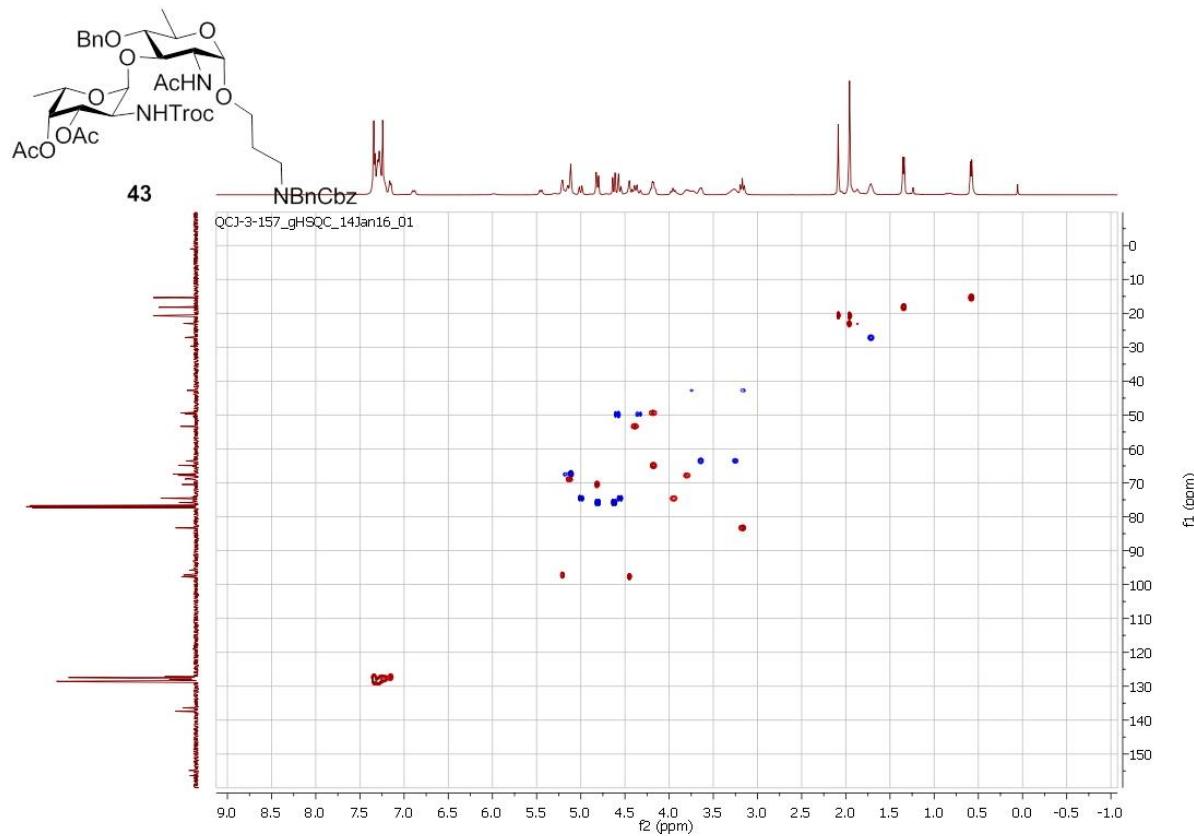
¹H NMR (CDCl₃, 400 MHz) of compound 43



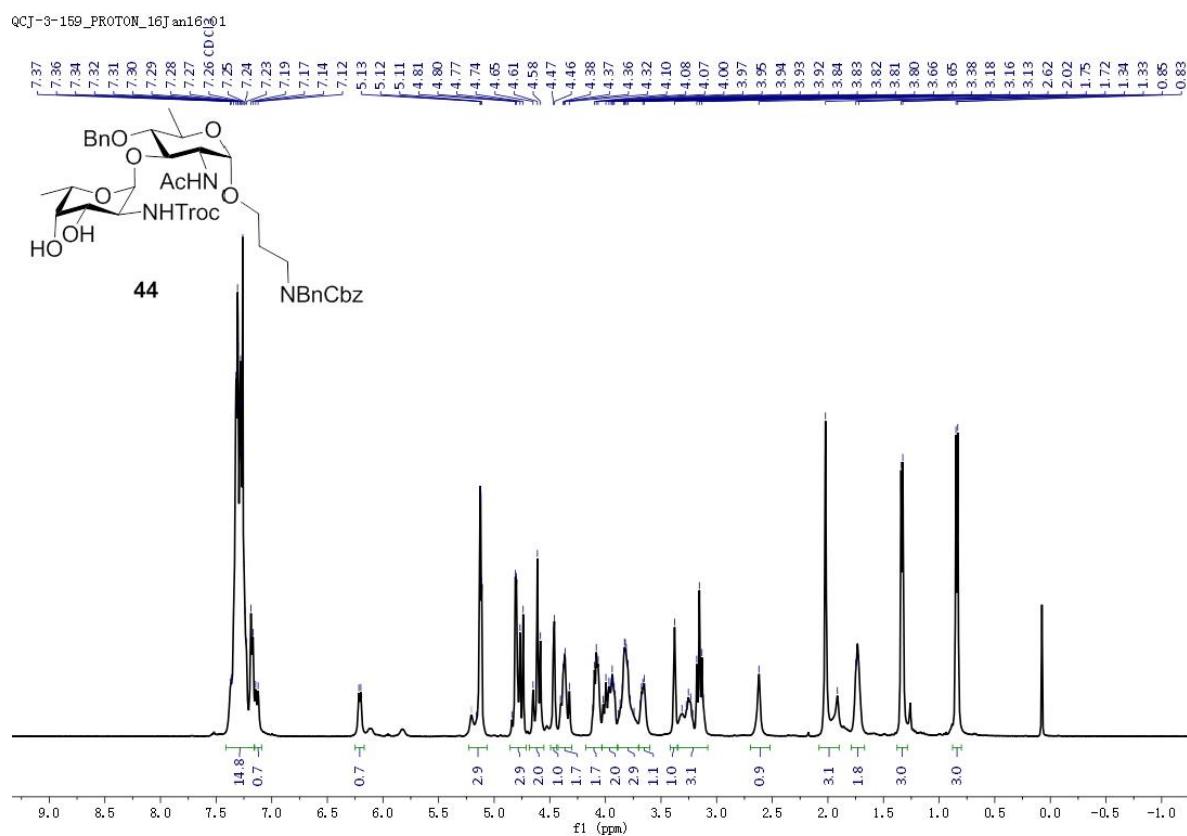
¹H-¹H COSY (CDCl₃, 400 MHz) of compound 43



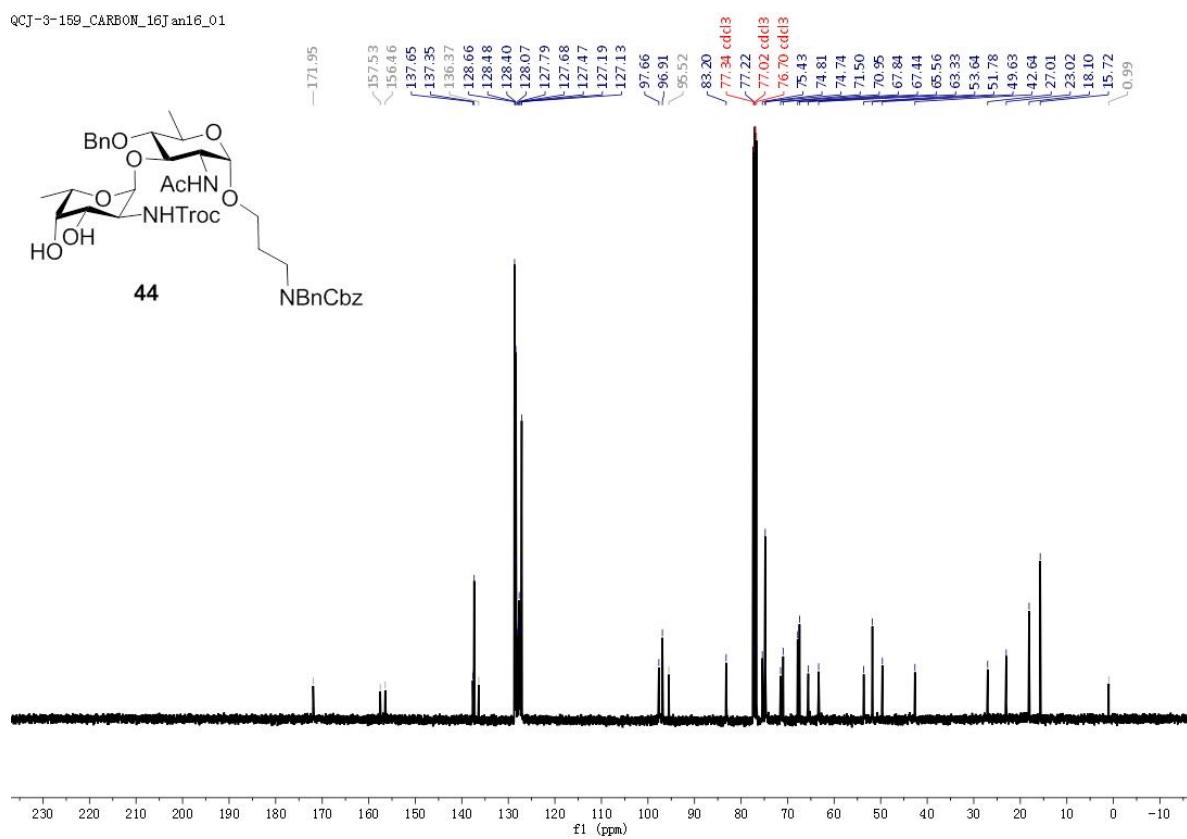
¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 43



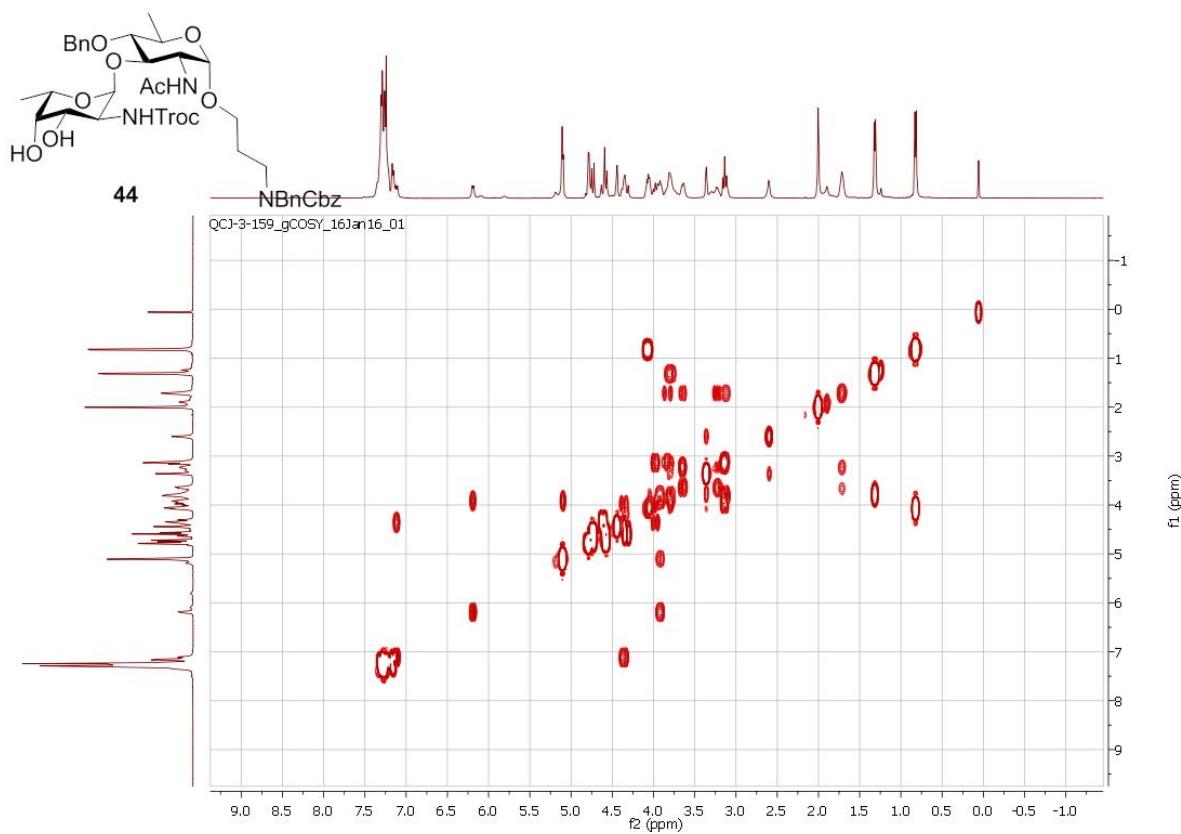
¹H NMR (CDCl₃, 400 MHz) of compound 44



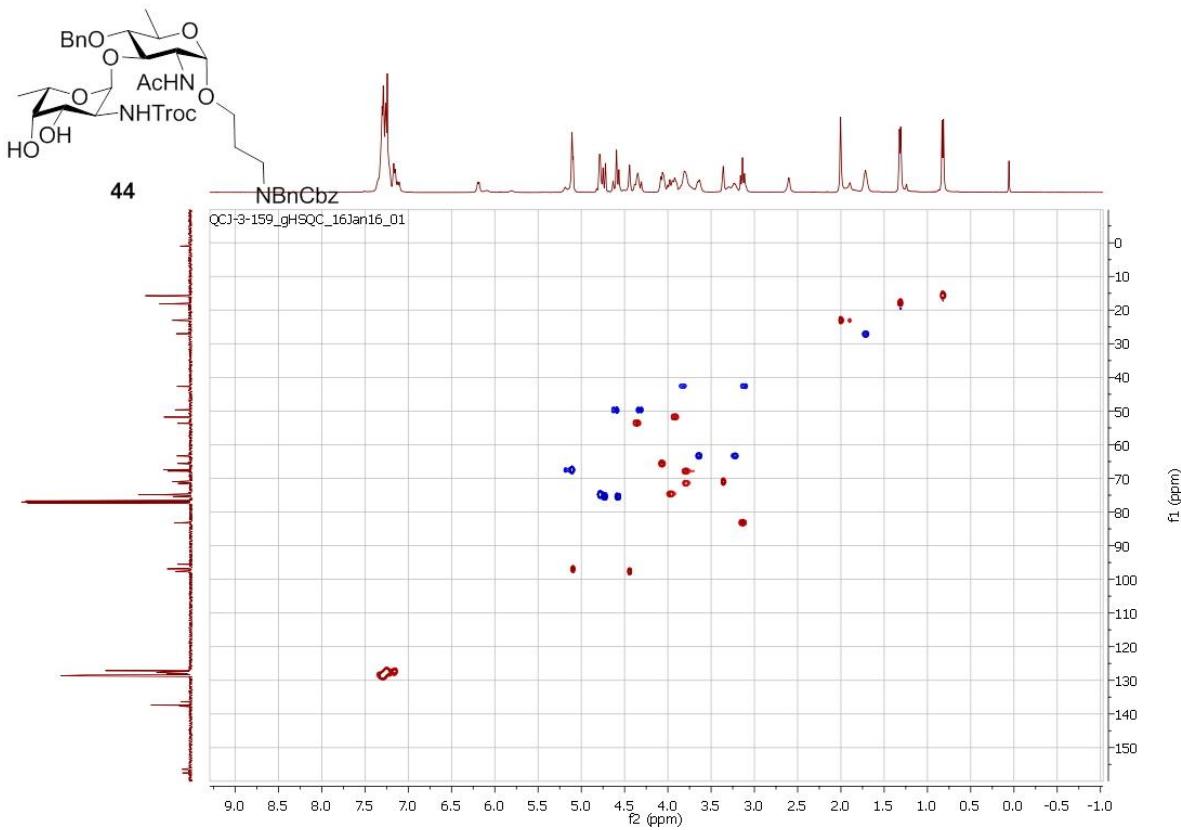
¹³C NMR (CDCl₃, 100 MHz) of compound 44



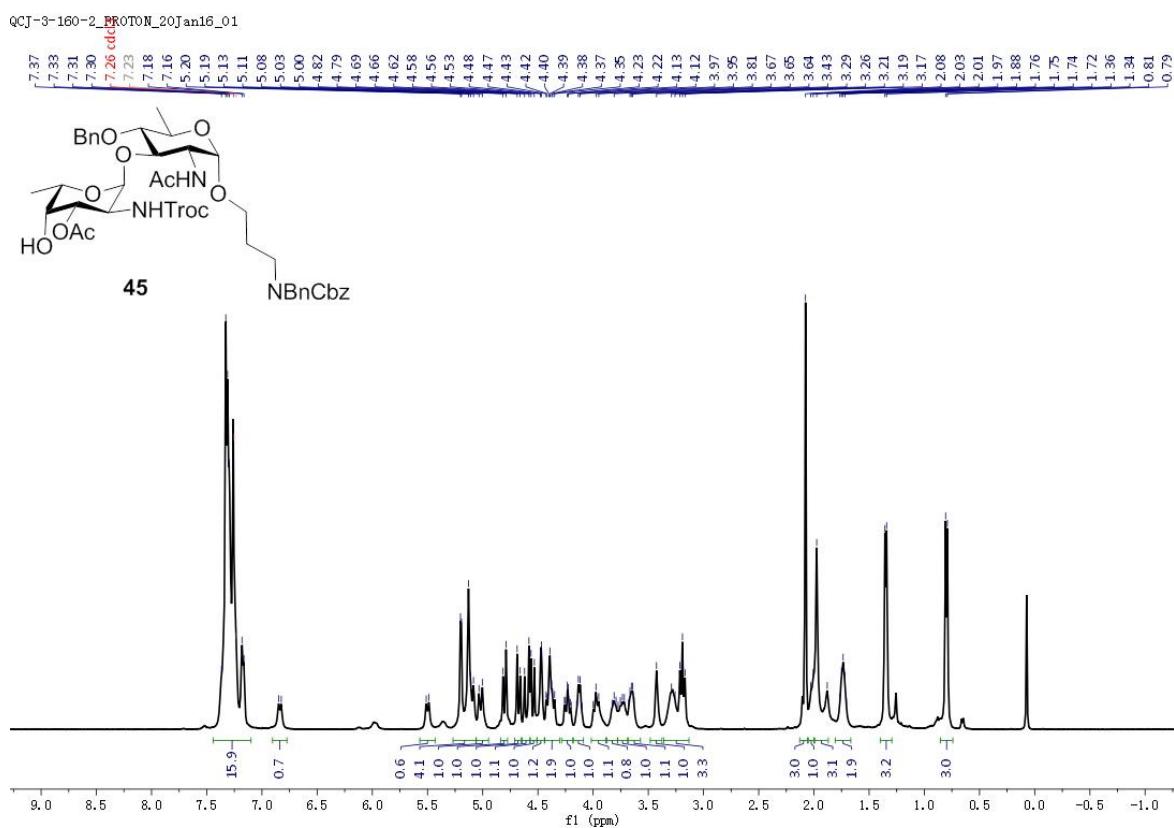
¹H-¹H COSY (CDCl₃, 400 MHz) of compound 44



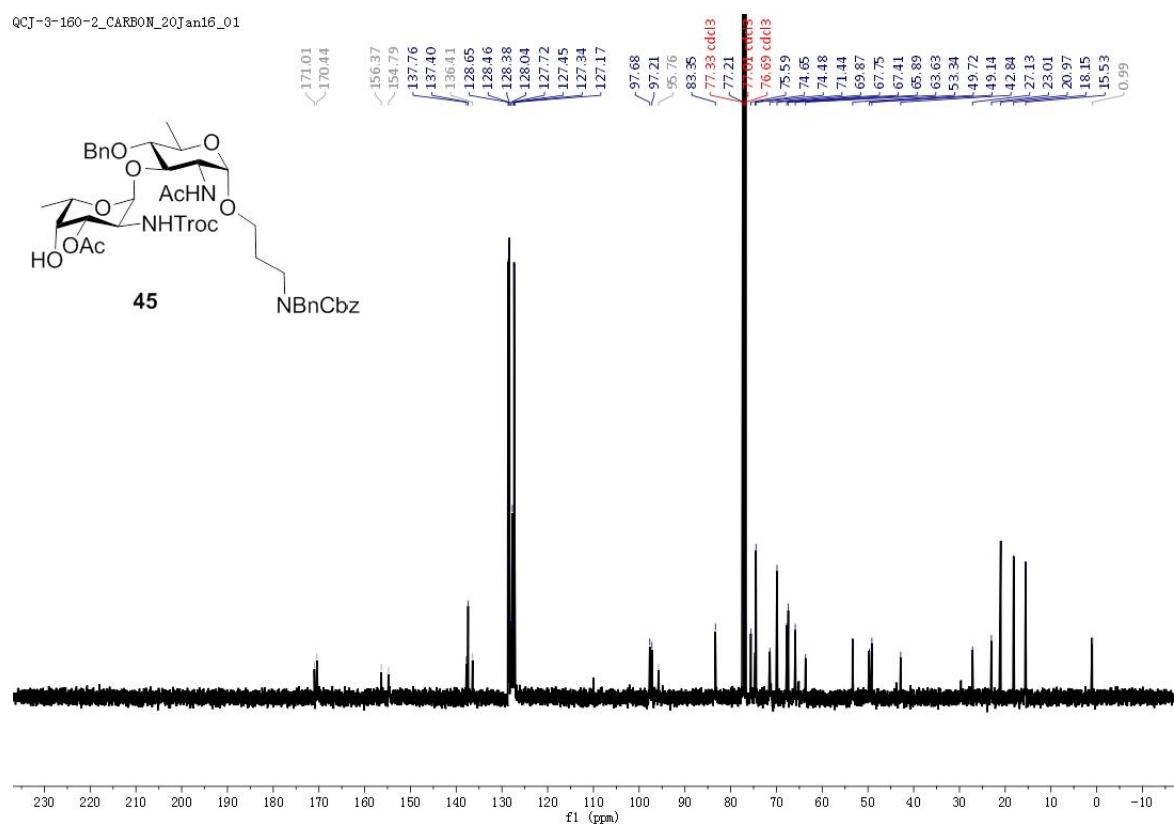
¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 44



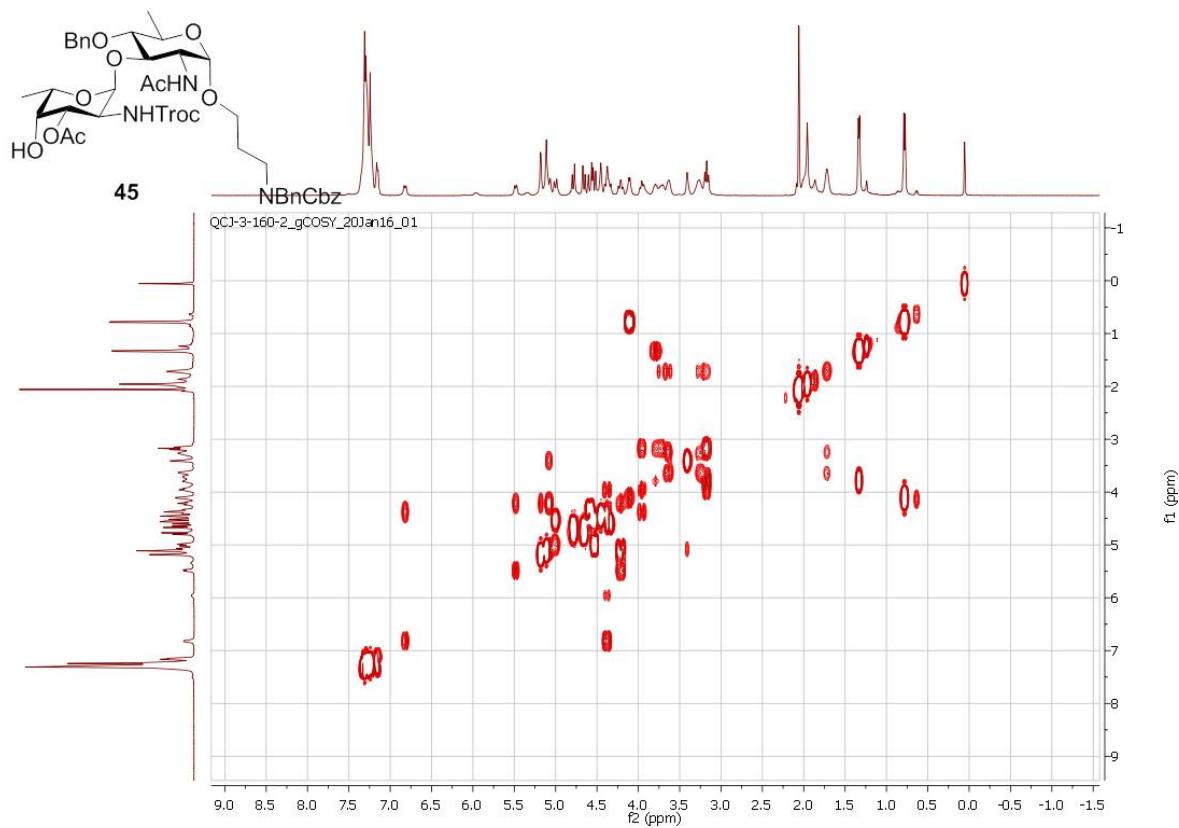
¹H NMR (CDCl₃, 400 MHz) of compound 45



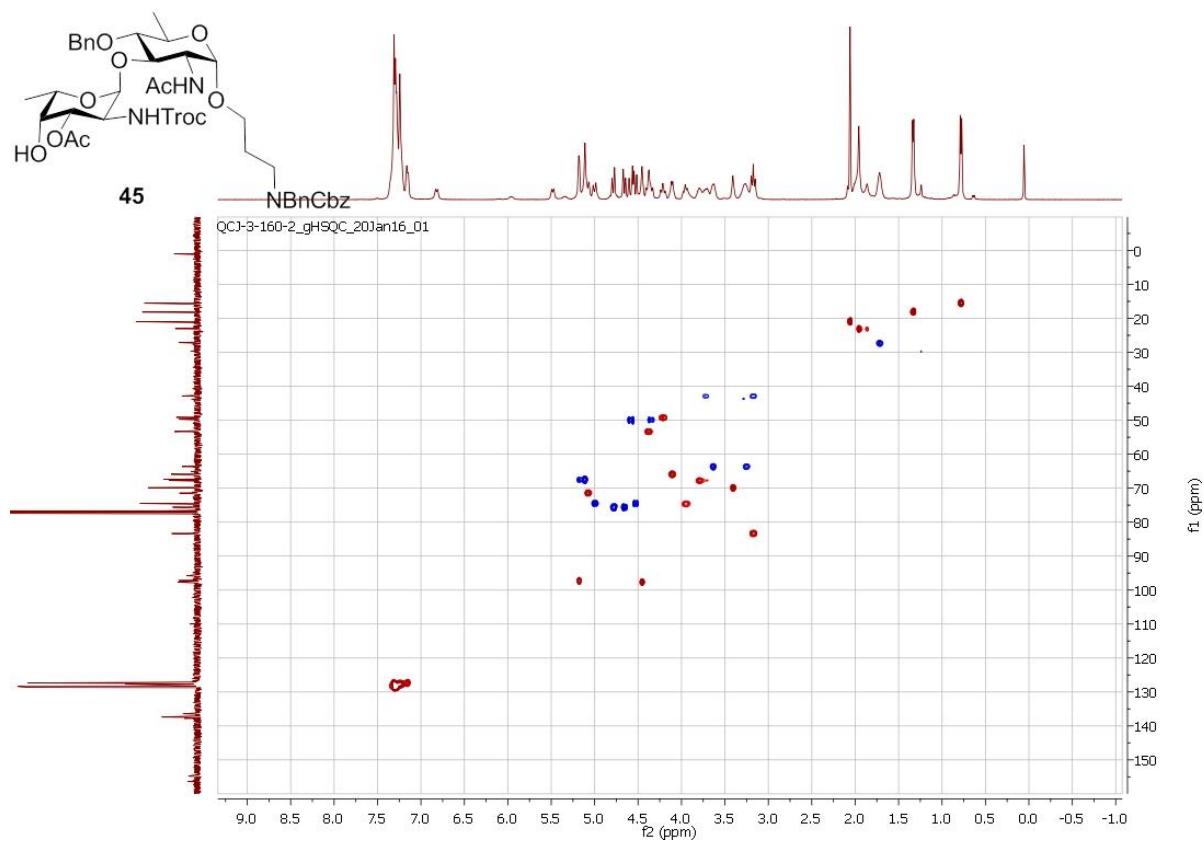
¹³C NMR (CDCl₃, 100 MHz) of compound 45



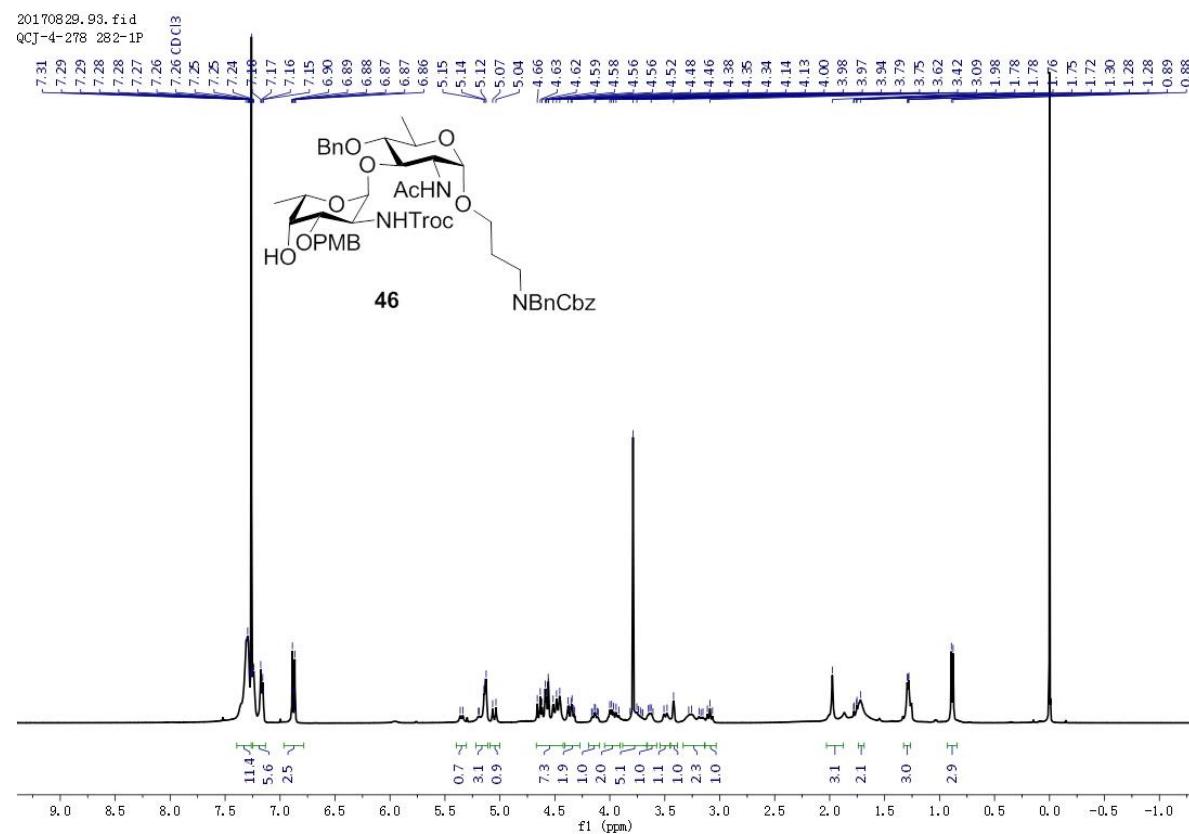
¹H-¹H COSY (CDCl₃, 400 MHz) of compound 45



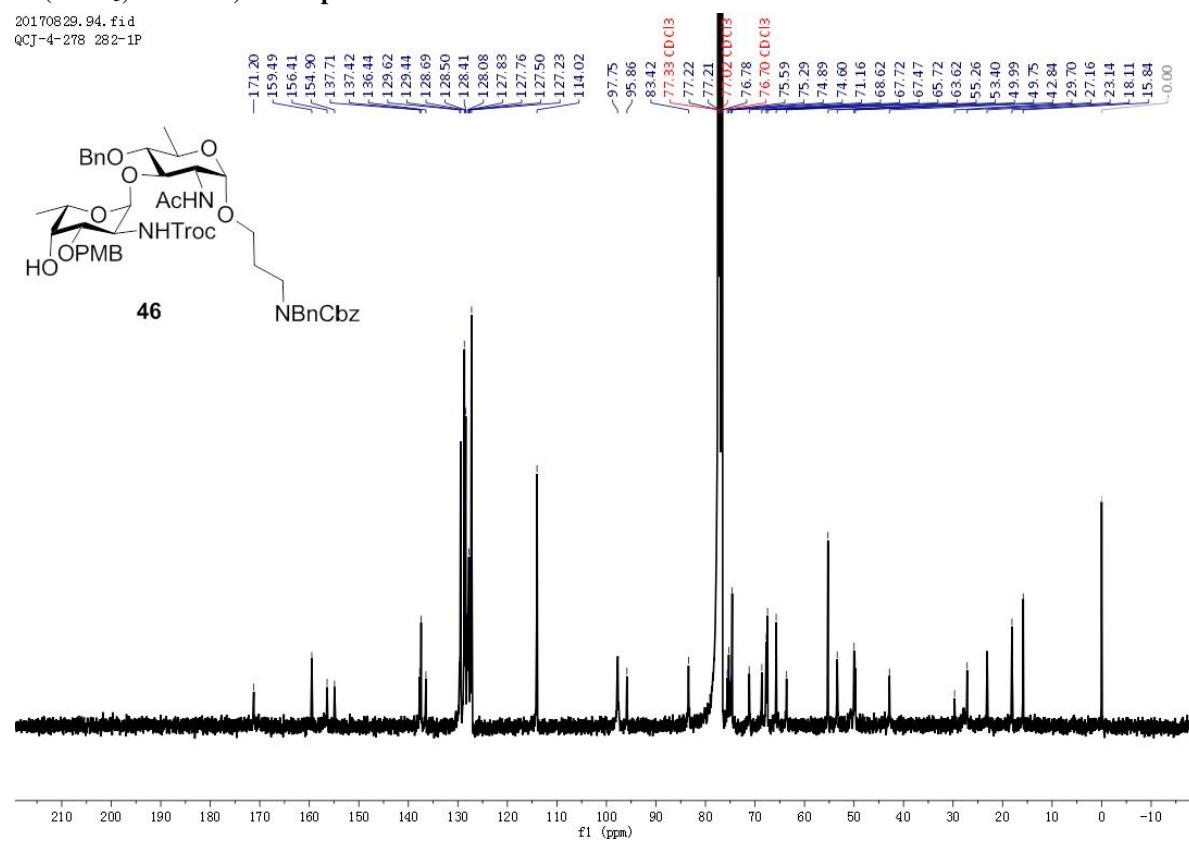
¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 45



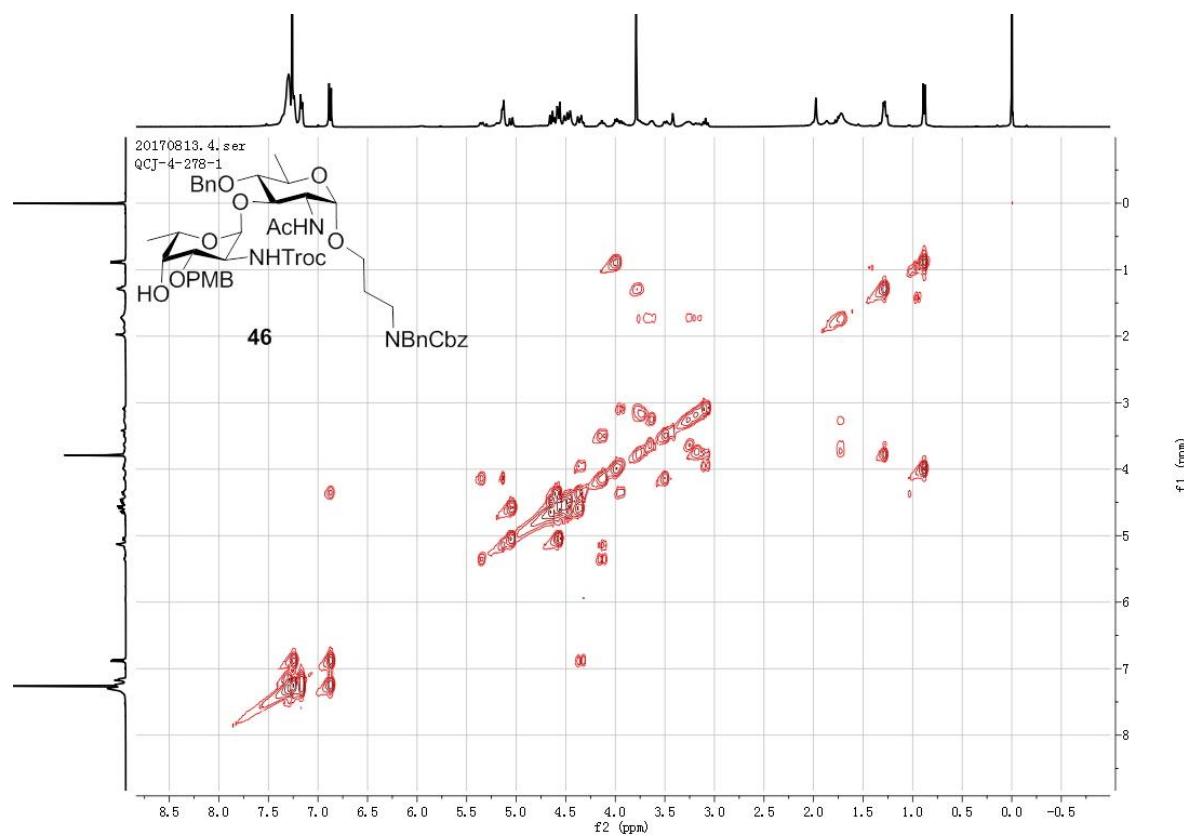
¹H NMR (CDCl₃, 400 MHz) of compound 46



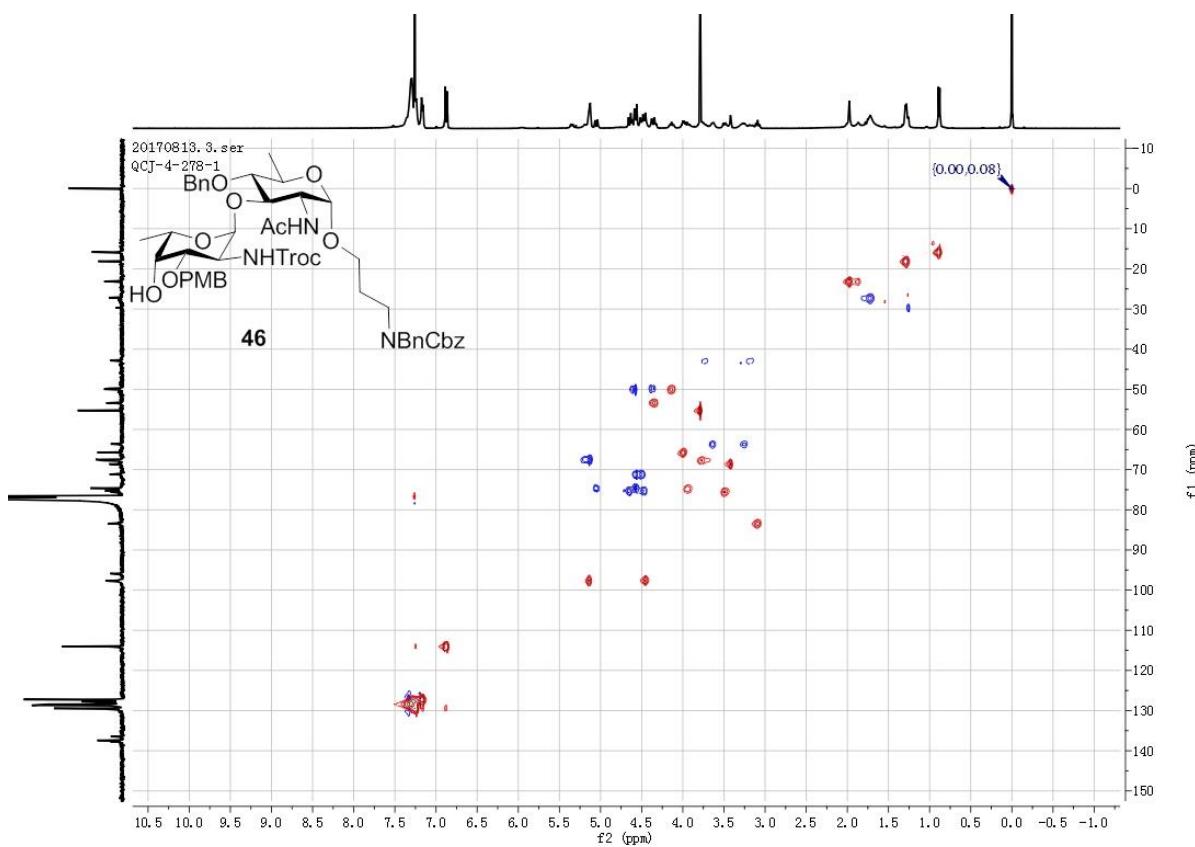
¹³C NMR (CDCl₃, 100 MHz) of compound 46



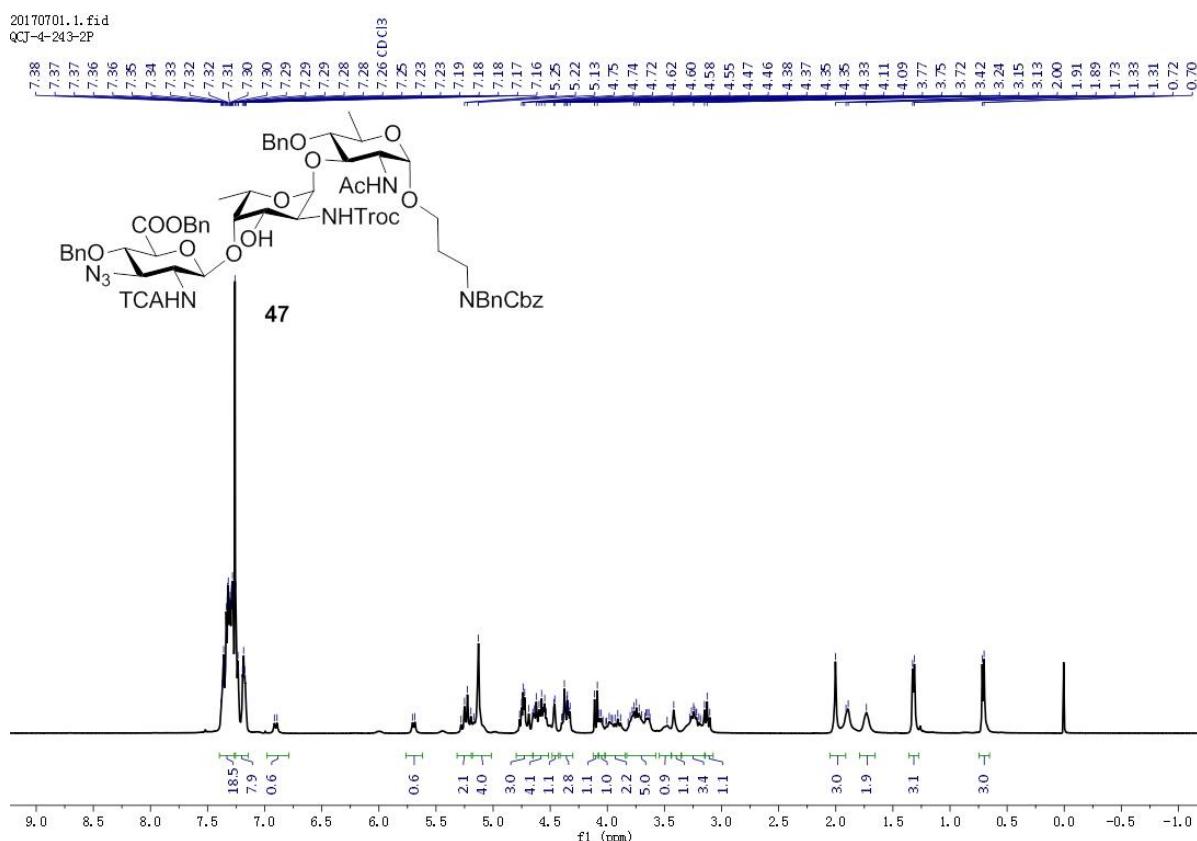
¹H-¹H COSY (CDCl₃, 400 MHz) of compound 46



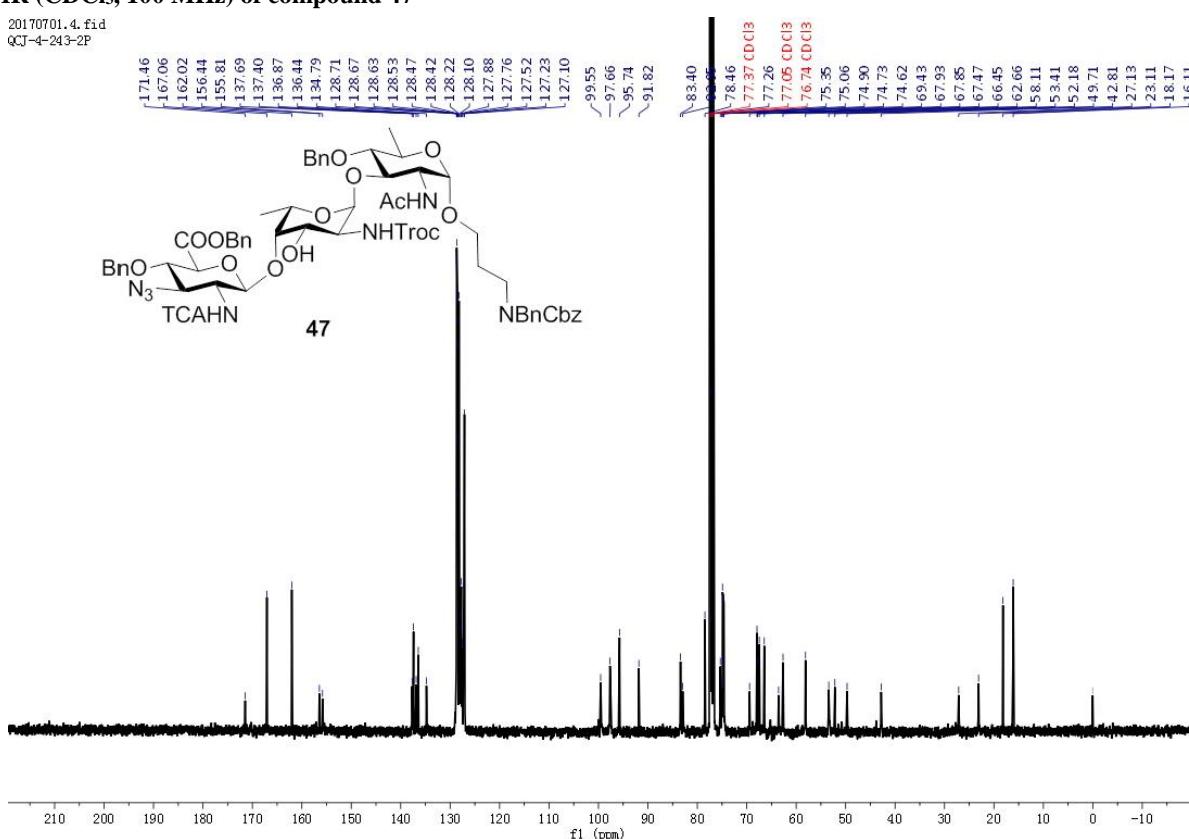
¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 46



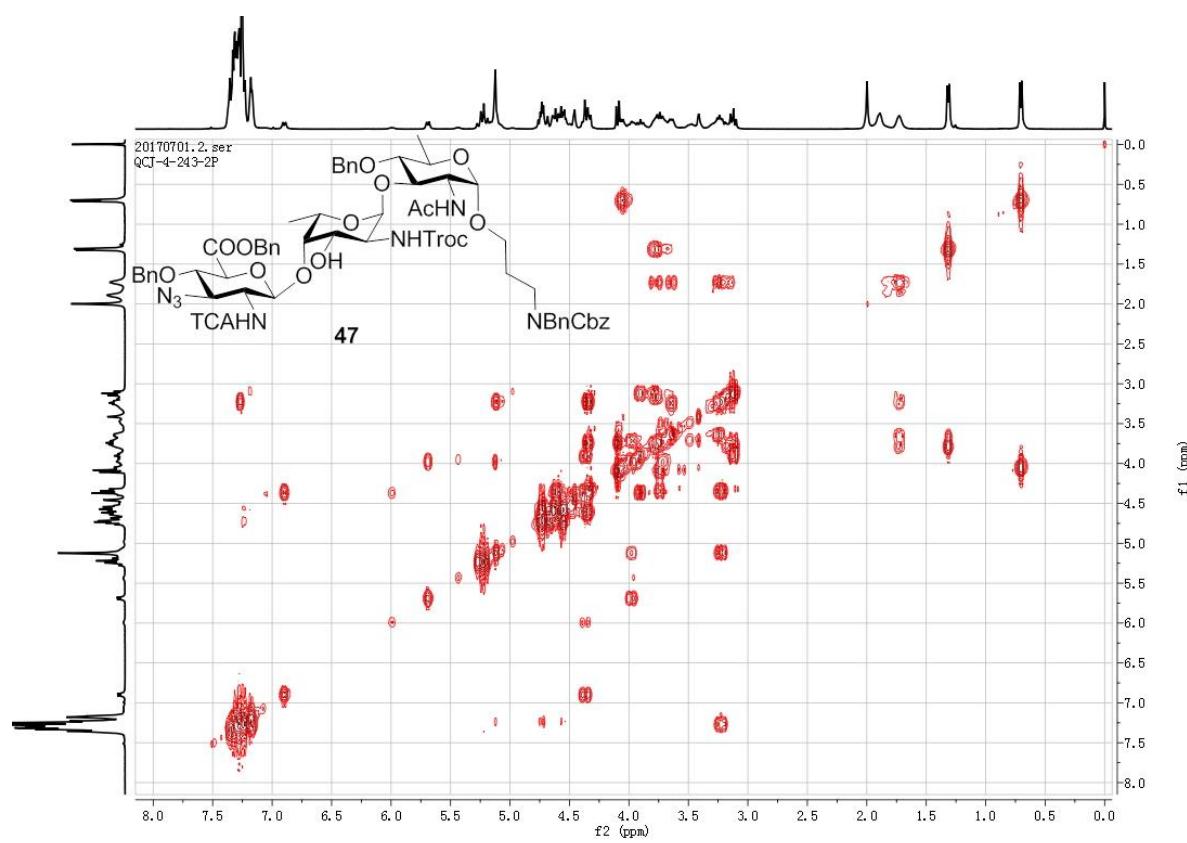
¹H NMR (CDCl₃, 400 MHz) of compound 47



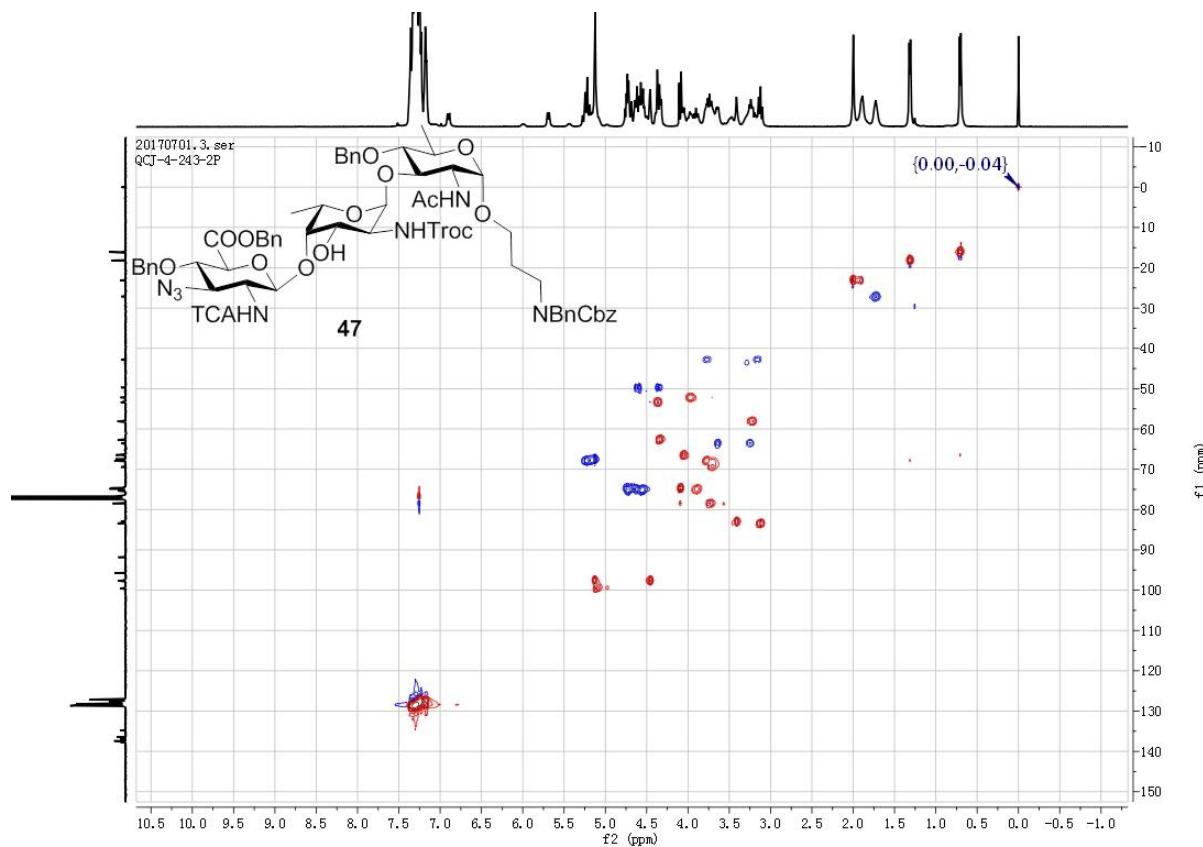
¹³C NMR (CDCl₃, 100 MHz) of compound 47



¹H-¹H COSY (CDCl₃, 400 MHz) of compound 47

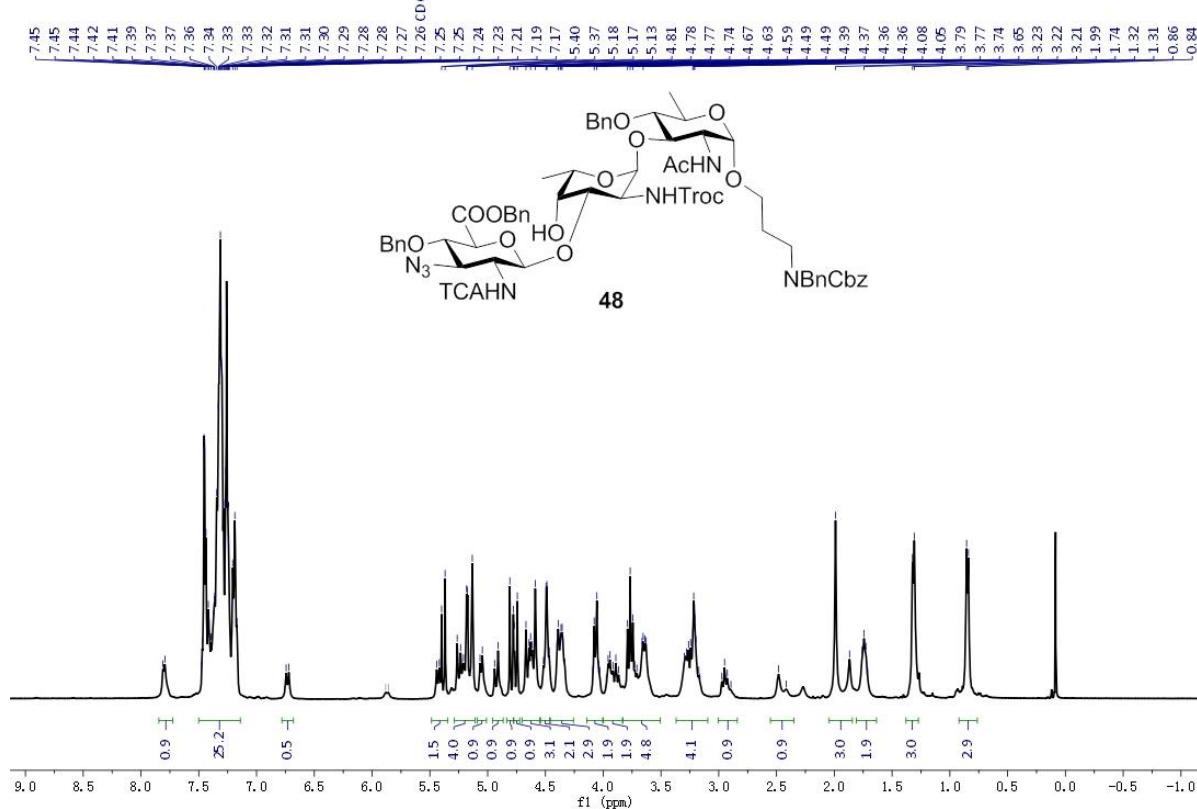


¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 47



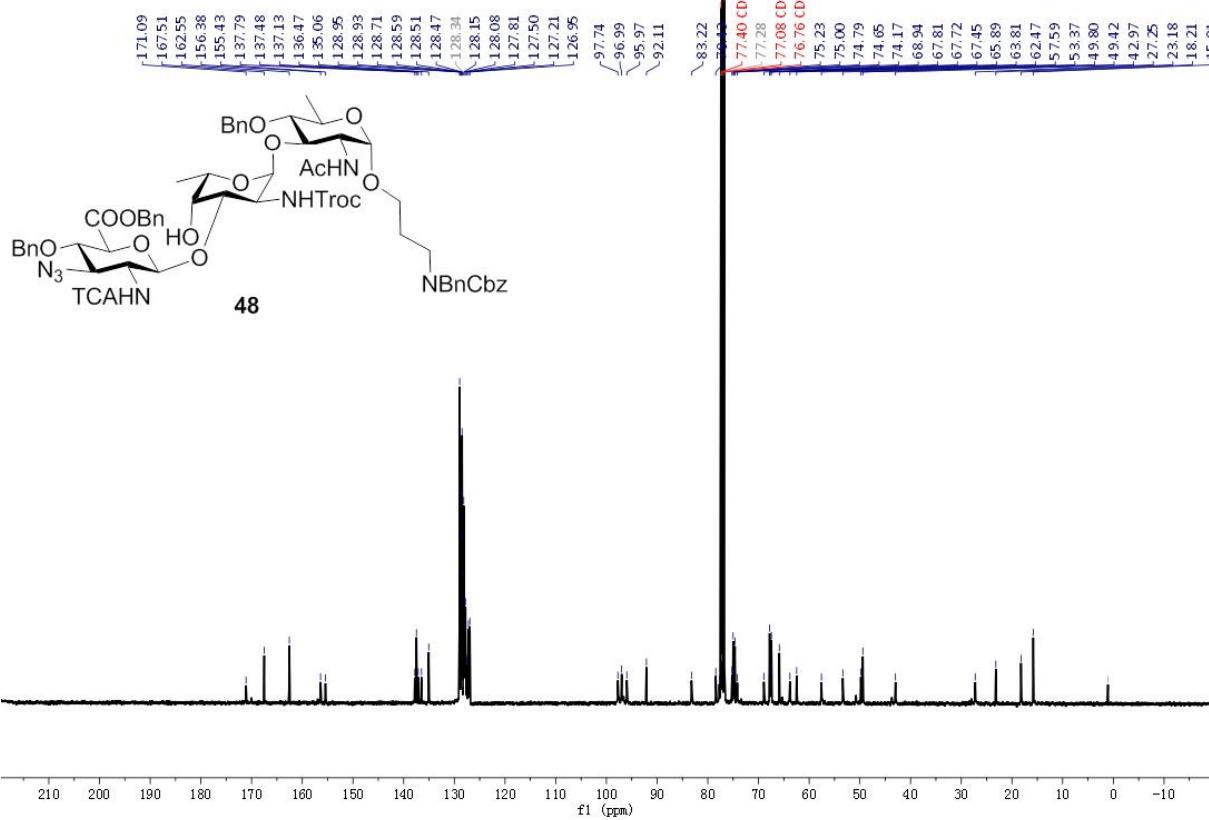
¹H NMR (CDCl₃, 400 MHz) of compound 48

QCT-3-212-3, 10, fid

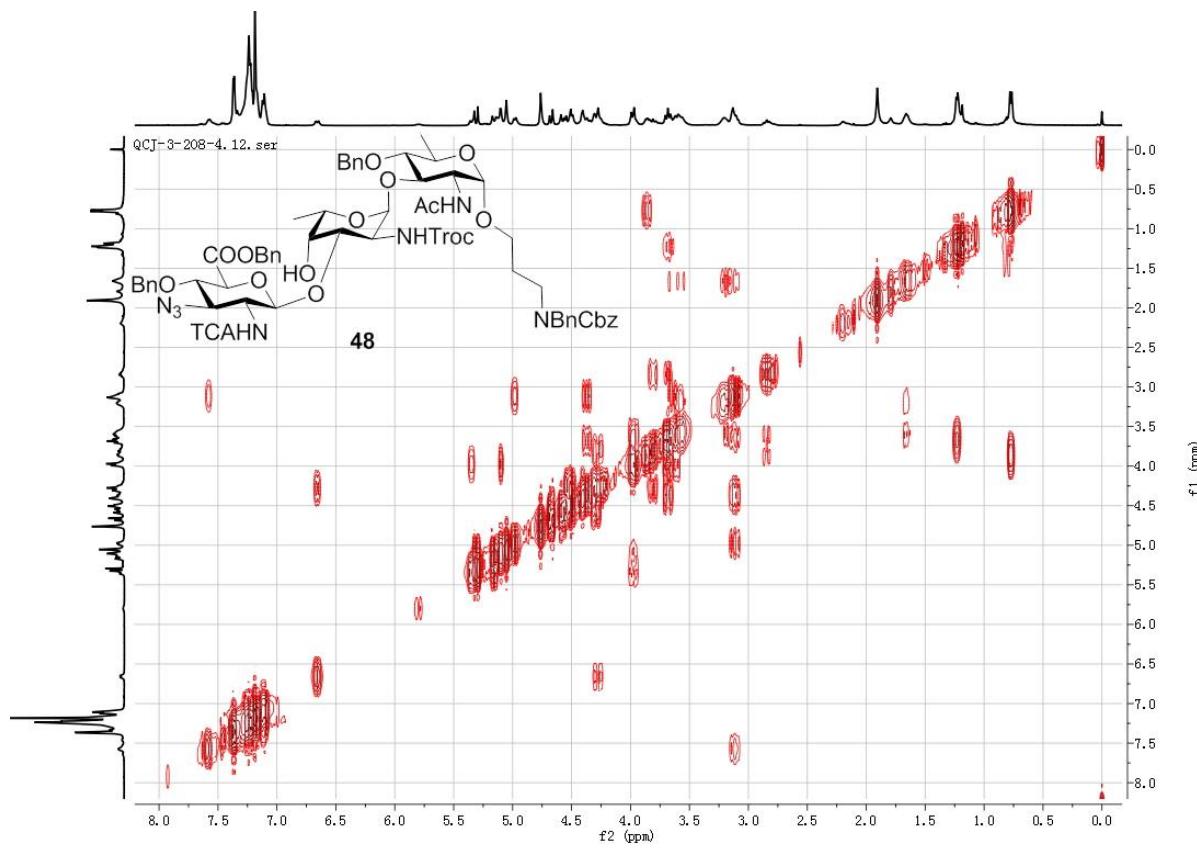


¹³C NMR (CDCl₃, 100 MHz) of compound 48

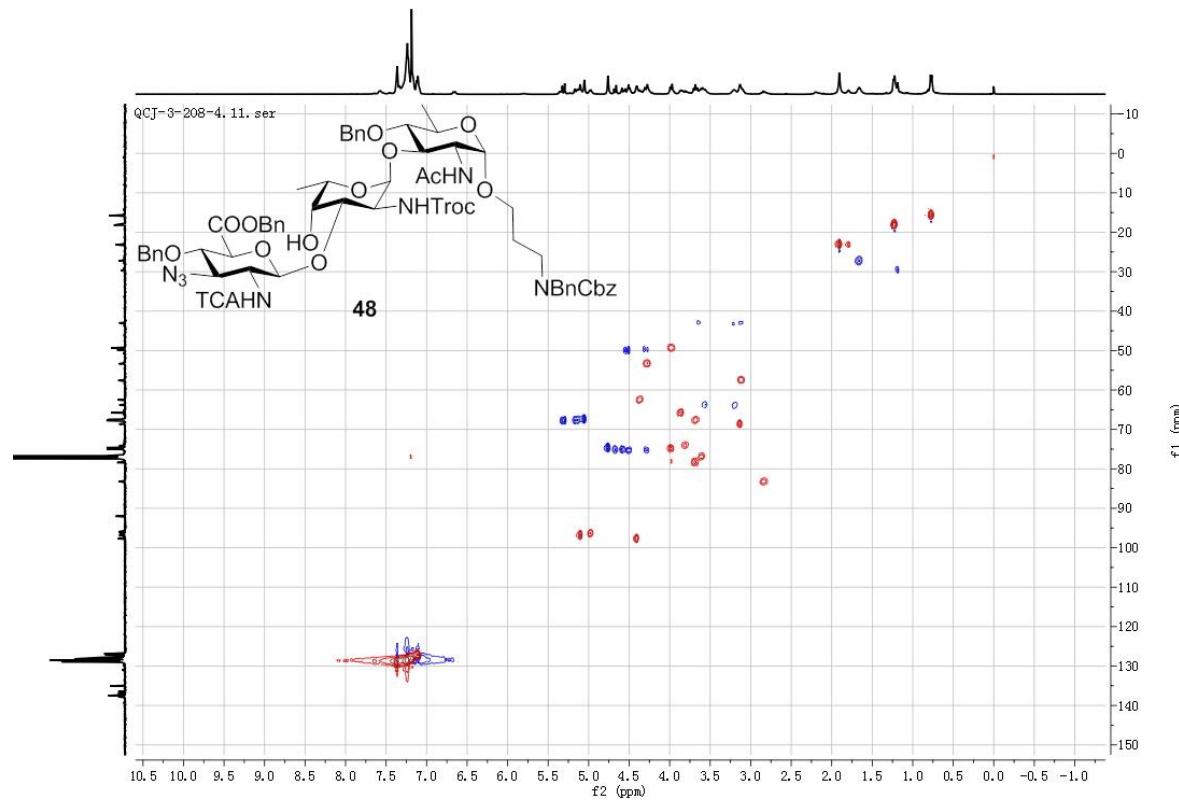
QCJ-3-212-3.11.fid



¹H-¹H COSY (CDCl₃, 400 MHz) of compound 48

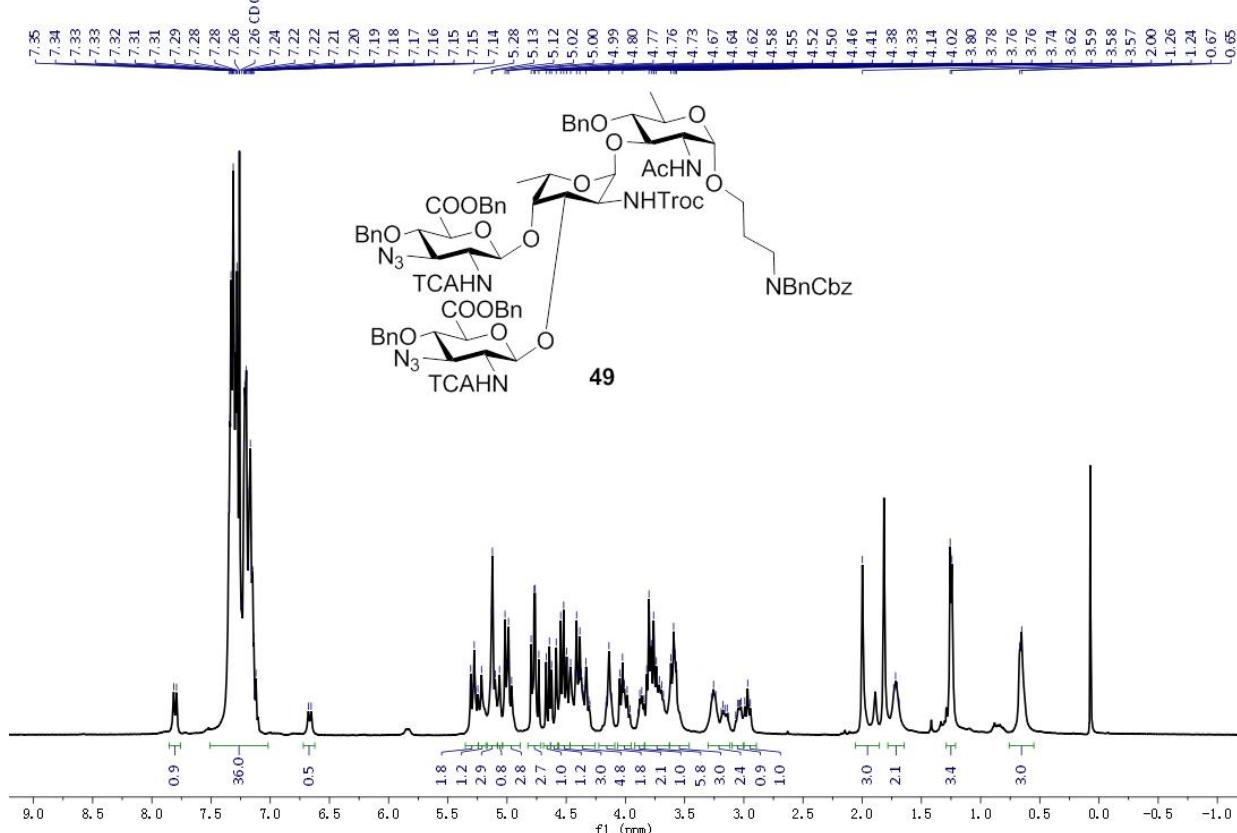


¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 48



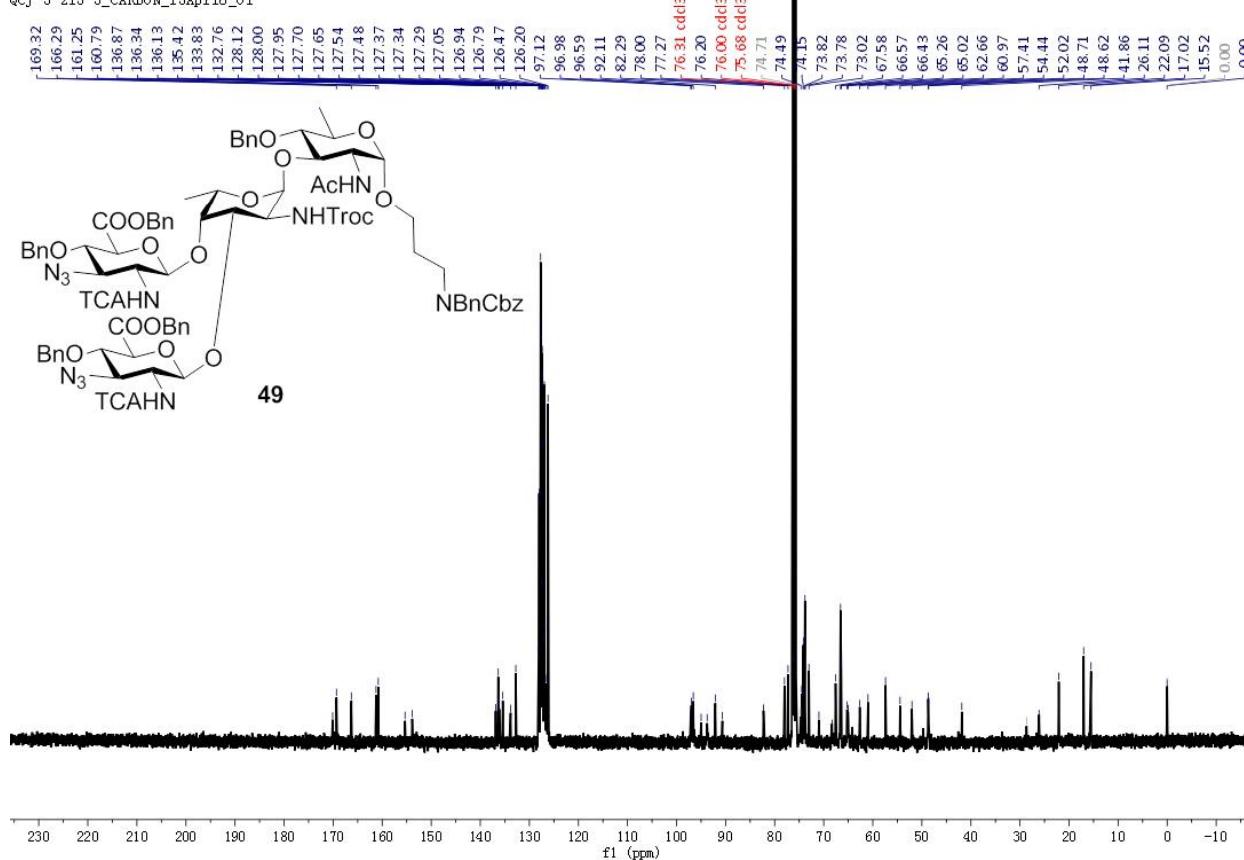
¹H NMR (CDCl₃, 400 MHz) of compound 49

QCJ-3-215-3_PROTON_13Apr16_01m

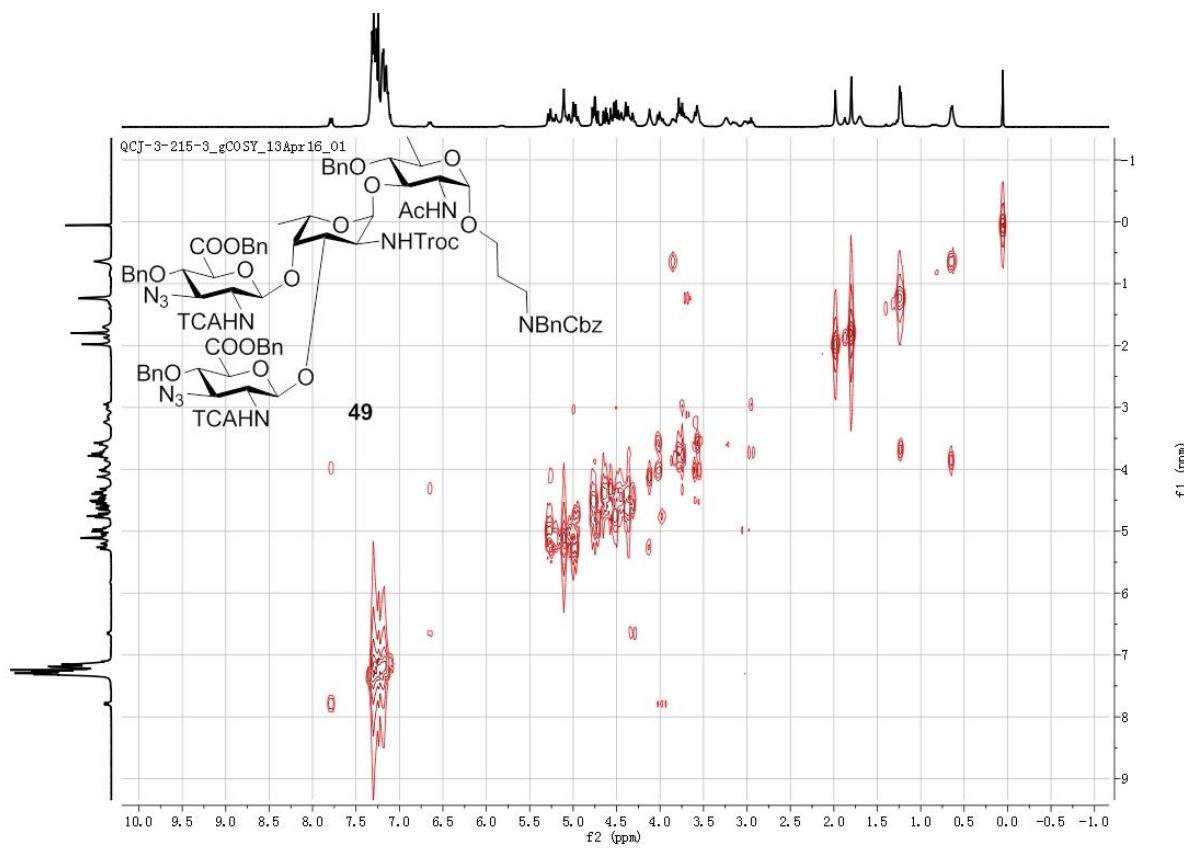


¹³C NMR (CDCl₃, 100 MHz) of compound 49

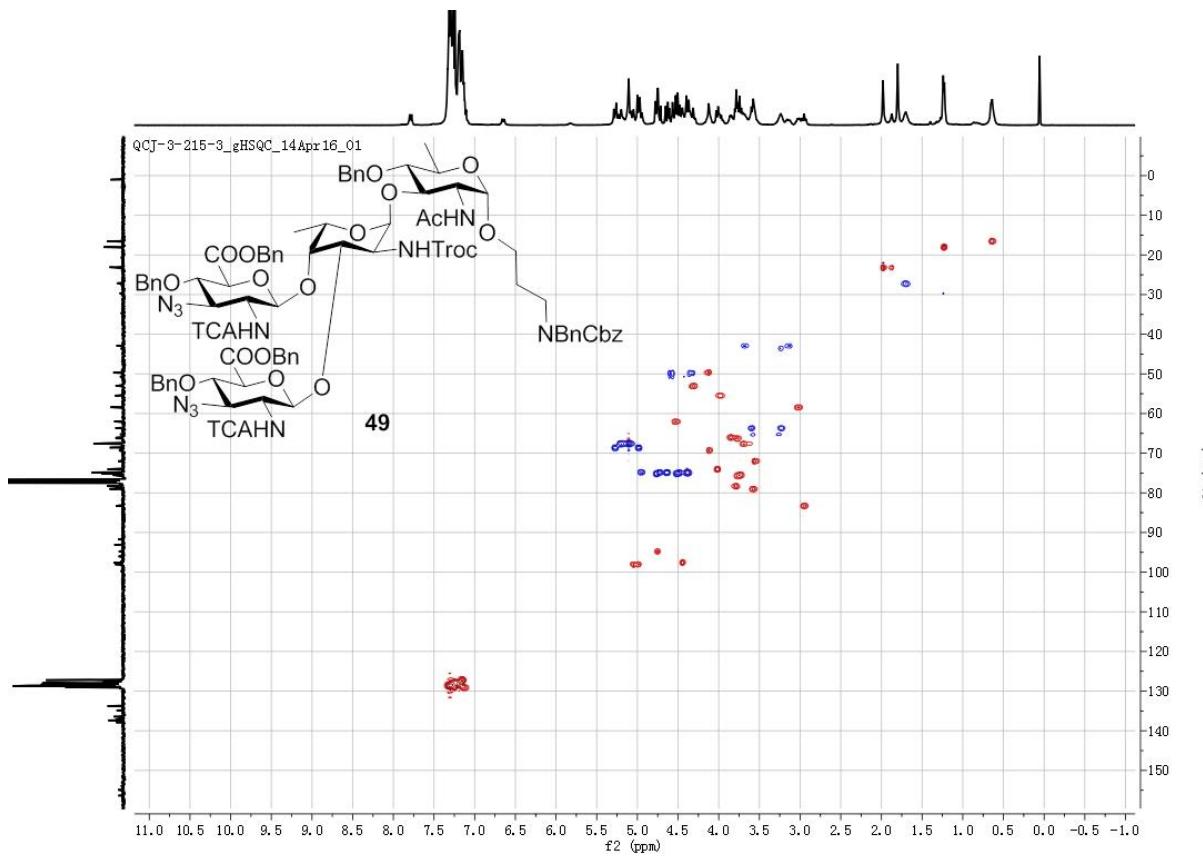
QCT-3-215-3 CARBON 15Apr16 01

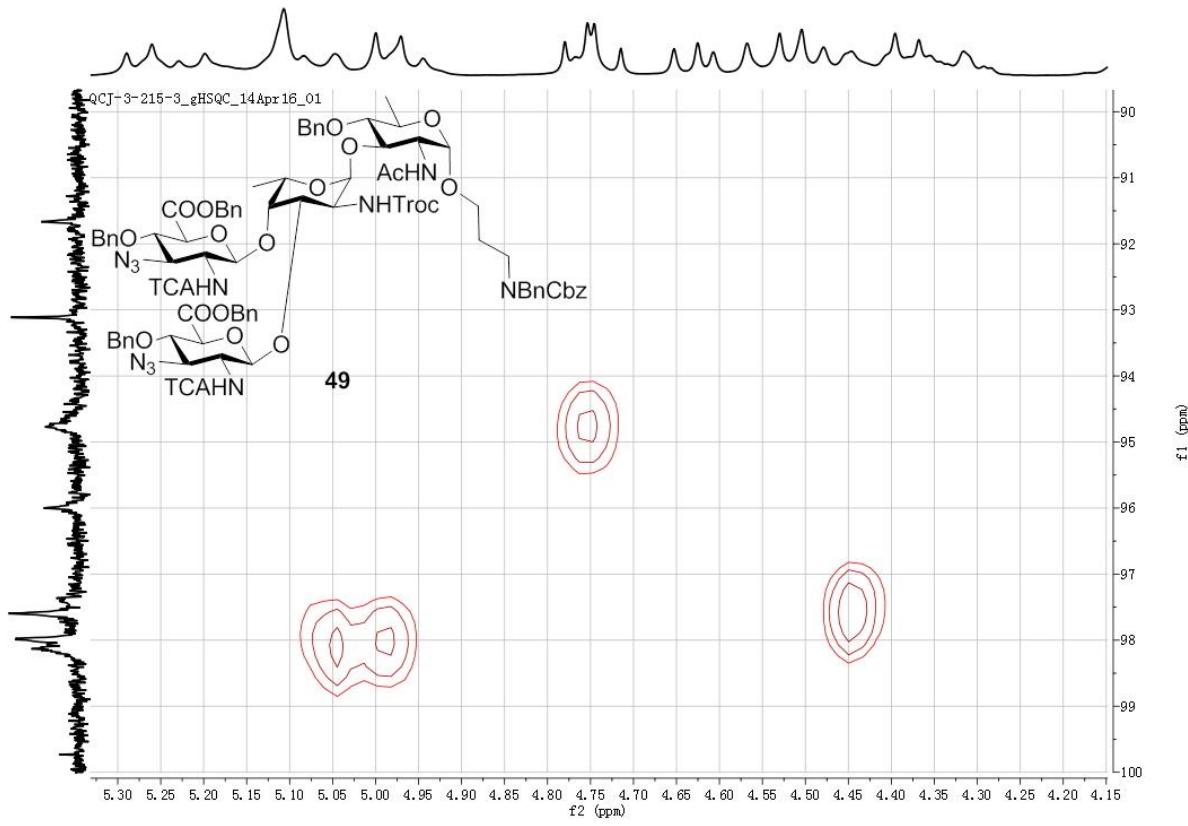


¹H-¹H COSY (CDCl₃, 400 MHz) of compound 49

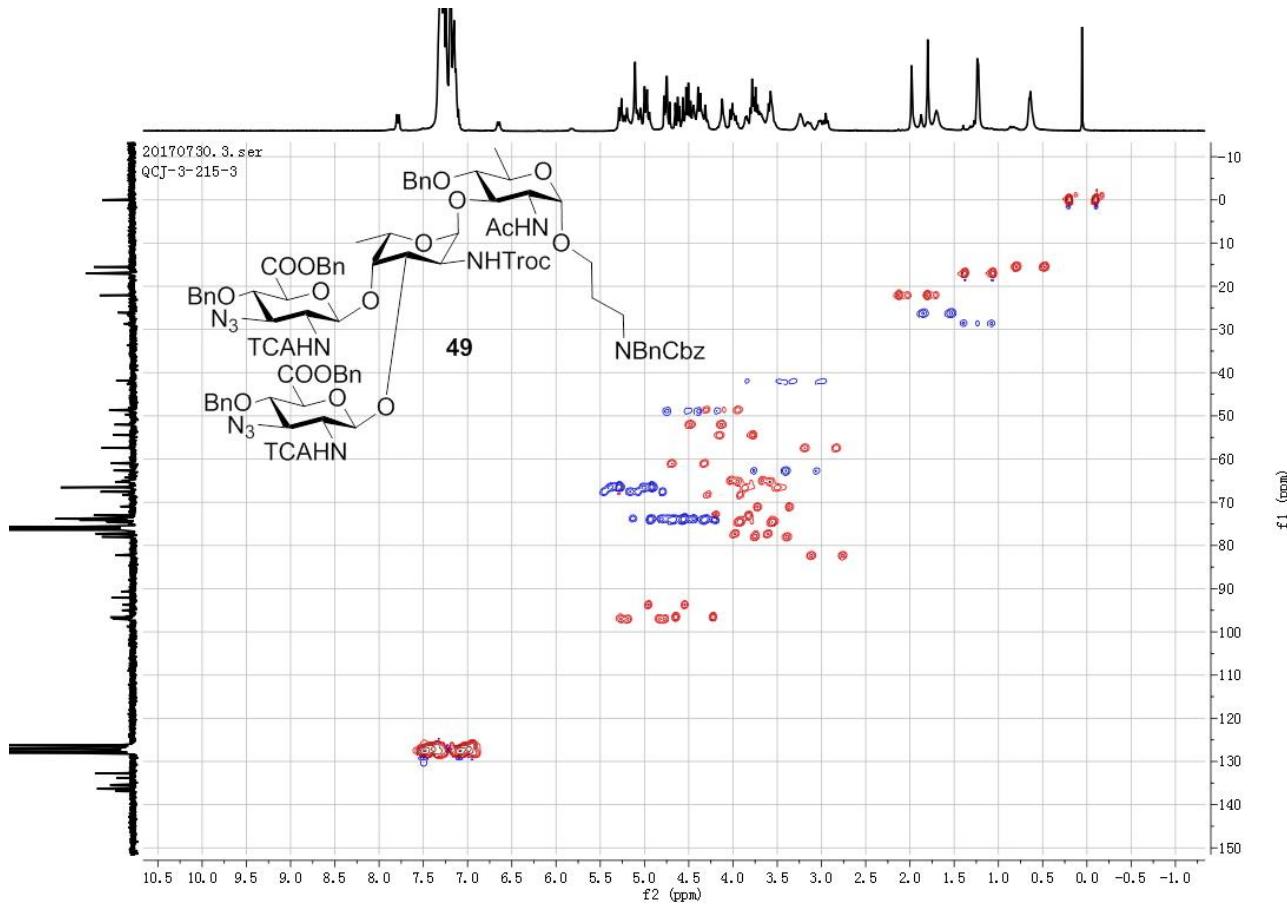


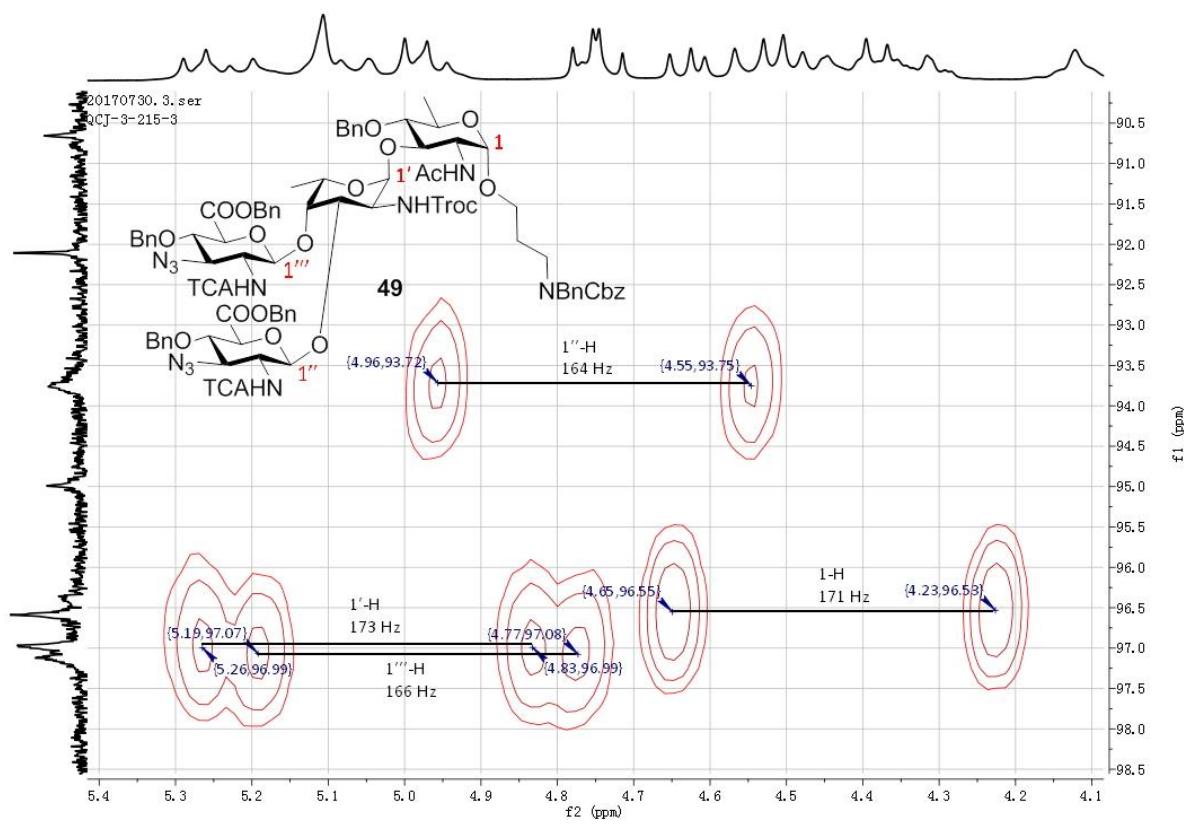
¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 49





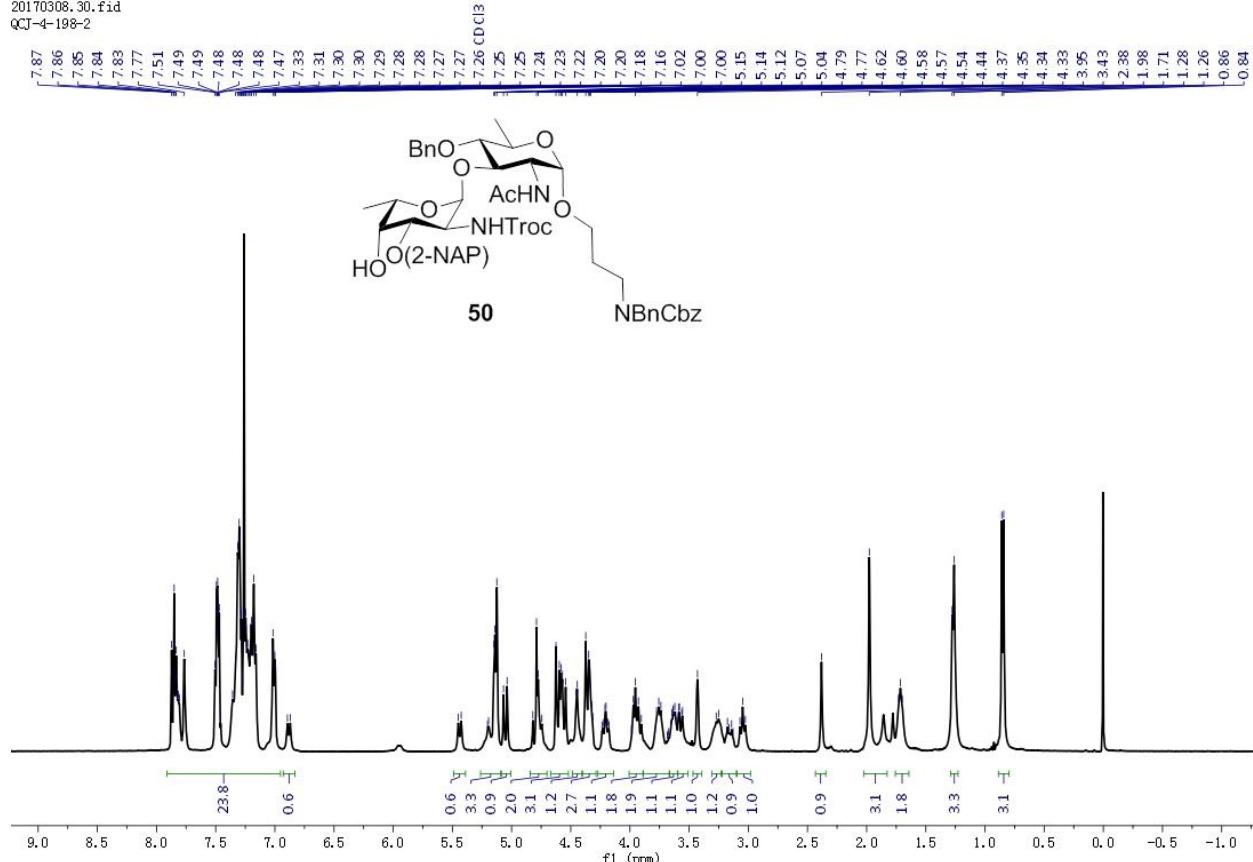
Coupled HSQC (CDCl_3 , 400 MHz) of compound 49





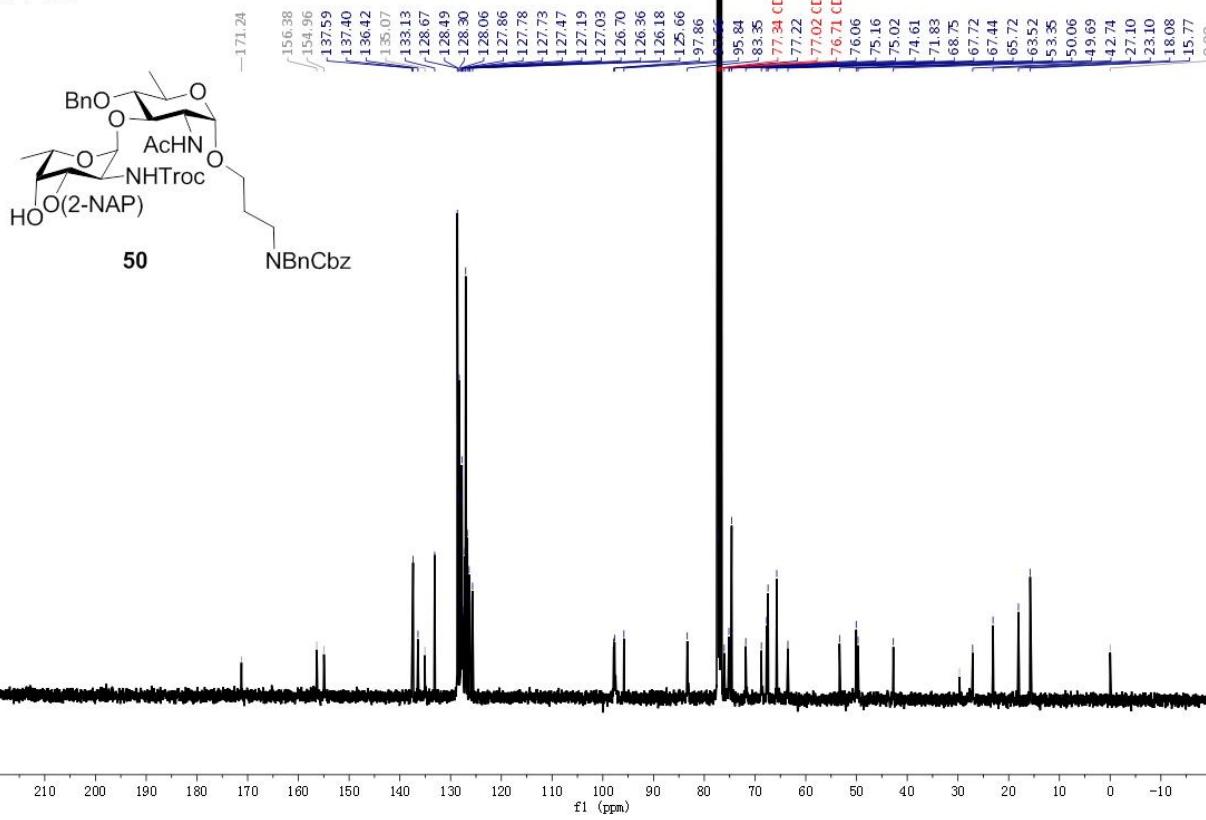
¹H NMR (CDCl₃, 400 MHz) of compound 50

20170308.30.fid
QCT-4-198-2

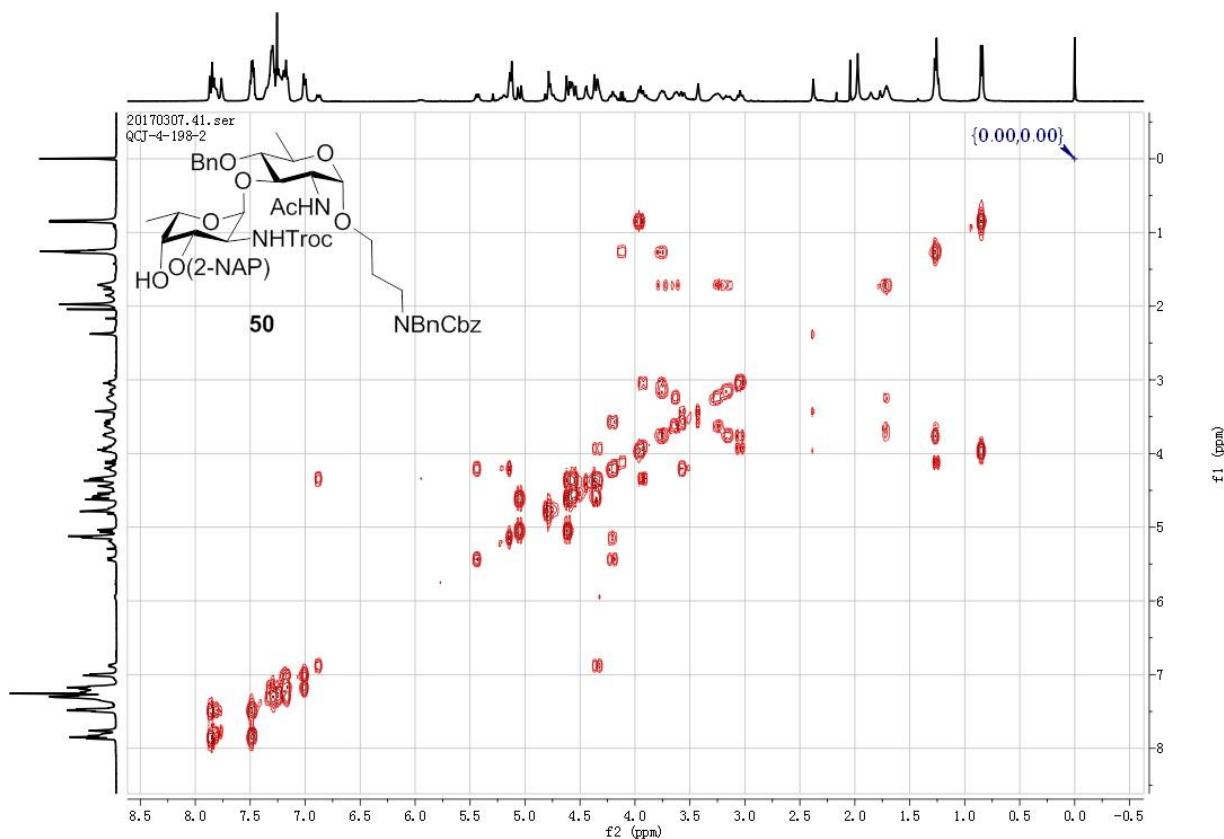


¹³C NMR (CDCl₃, 100 MHz) of compound 50

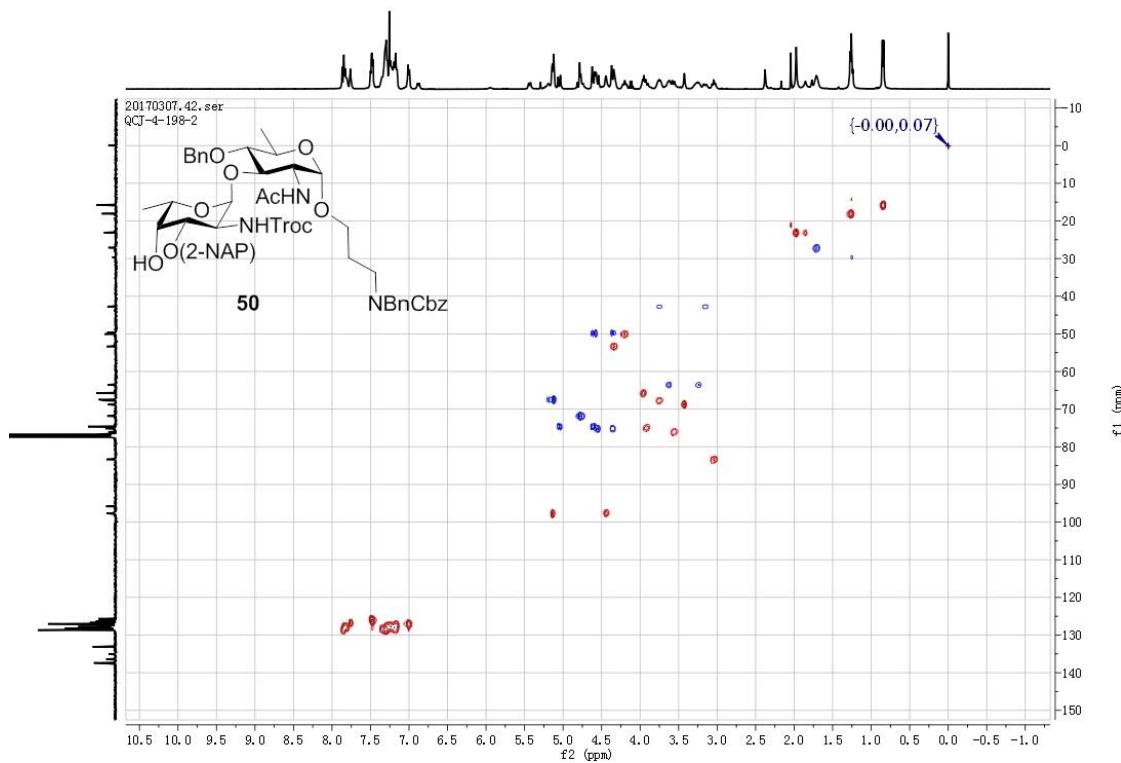
20170308.31.fid
QCT-4-198-2



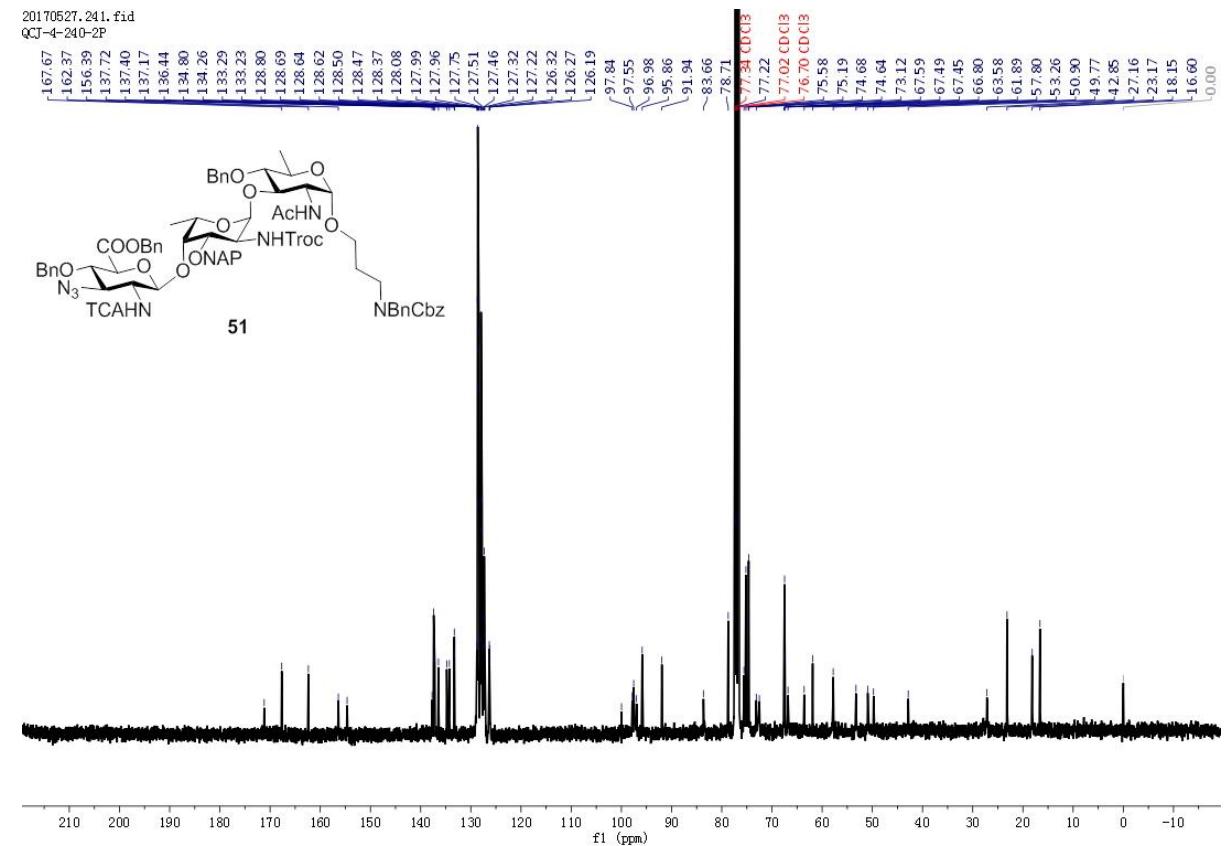
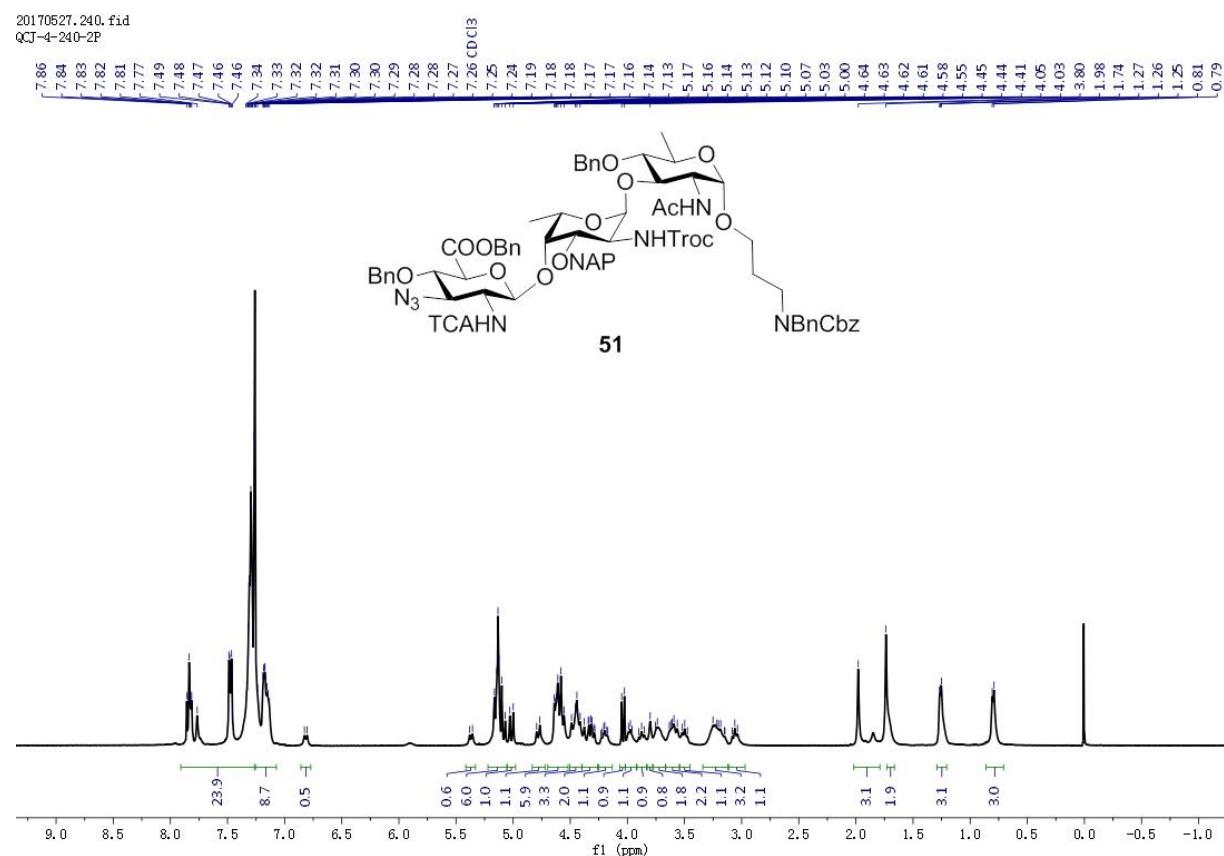
¹H-¹H COSY (CDCl₃, 400 MHz) of compound 50



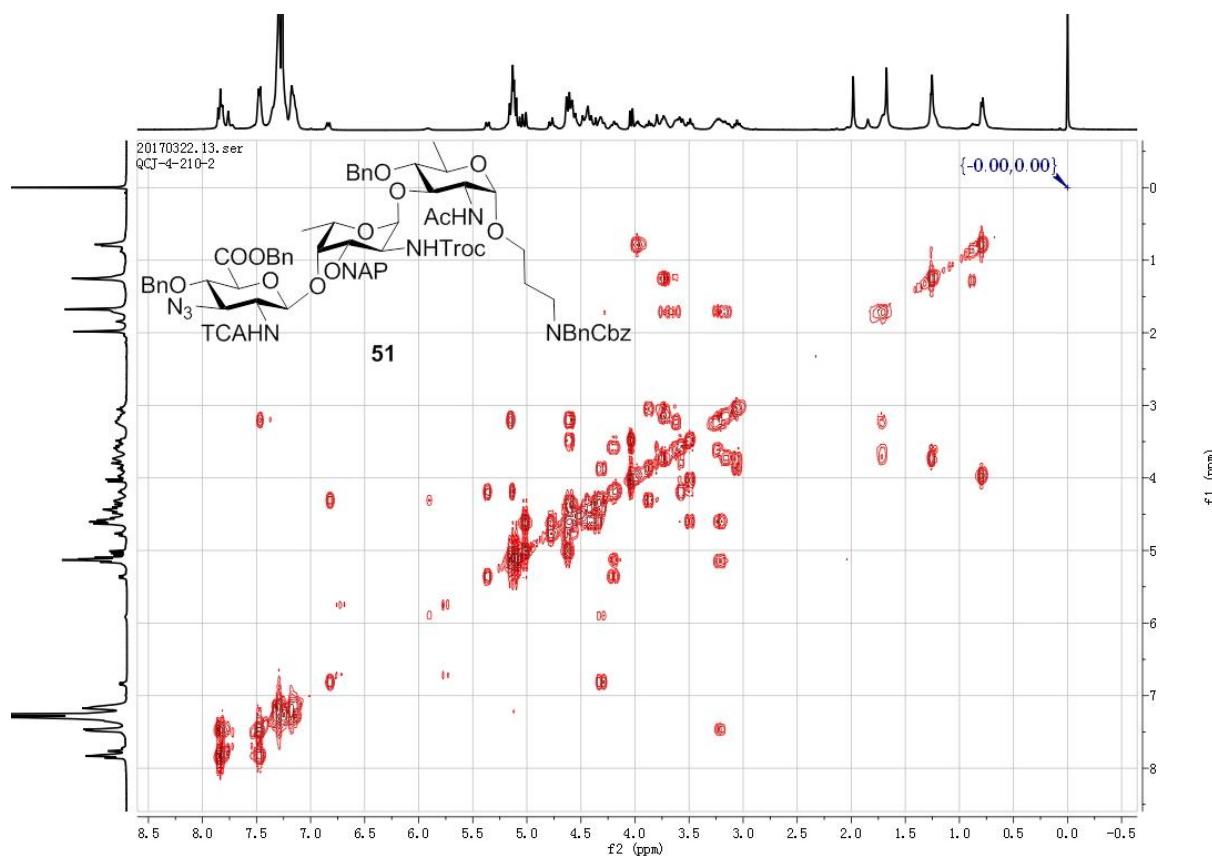
¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 50



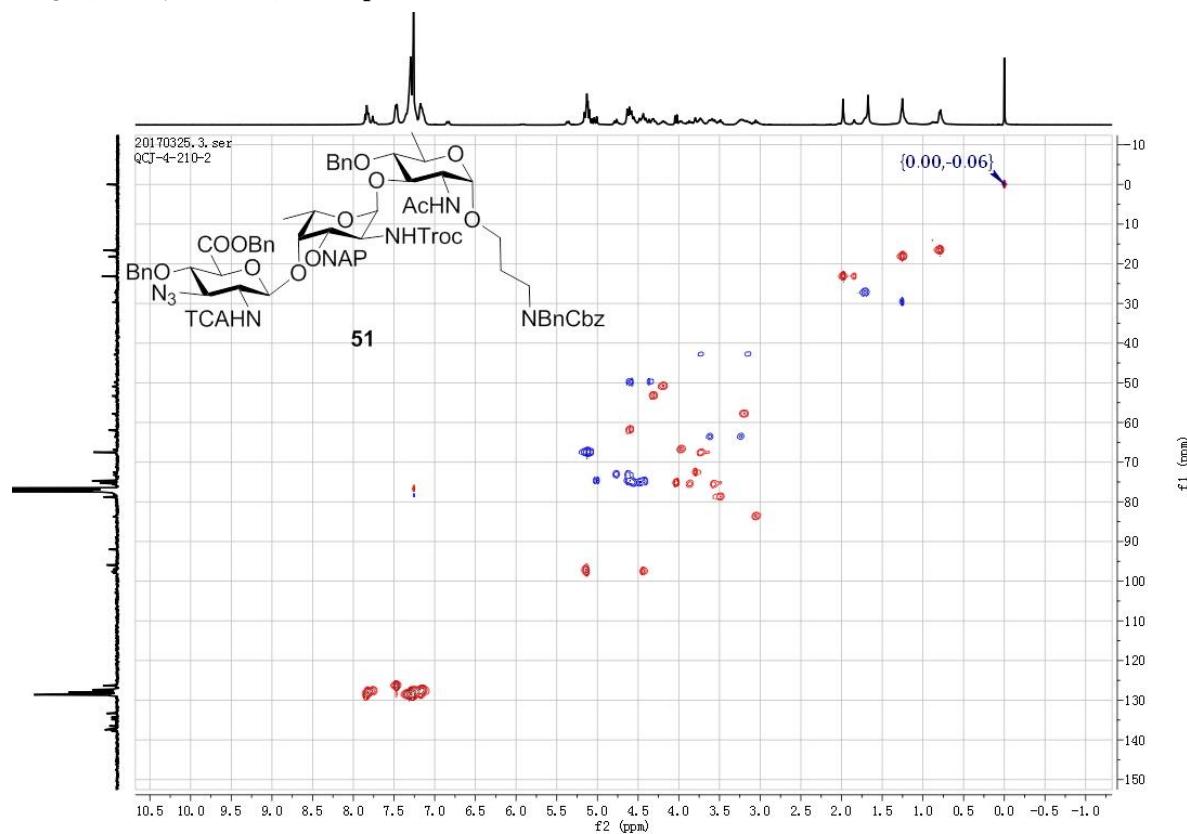
¹H NMR (CDCl₃, 400 MHz) of compound 51



¹H-¹H COSY (CDCl₃, 400 MHz) of compound 51

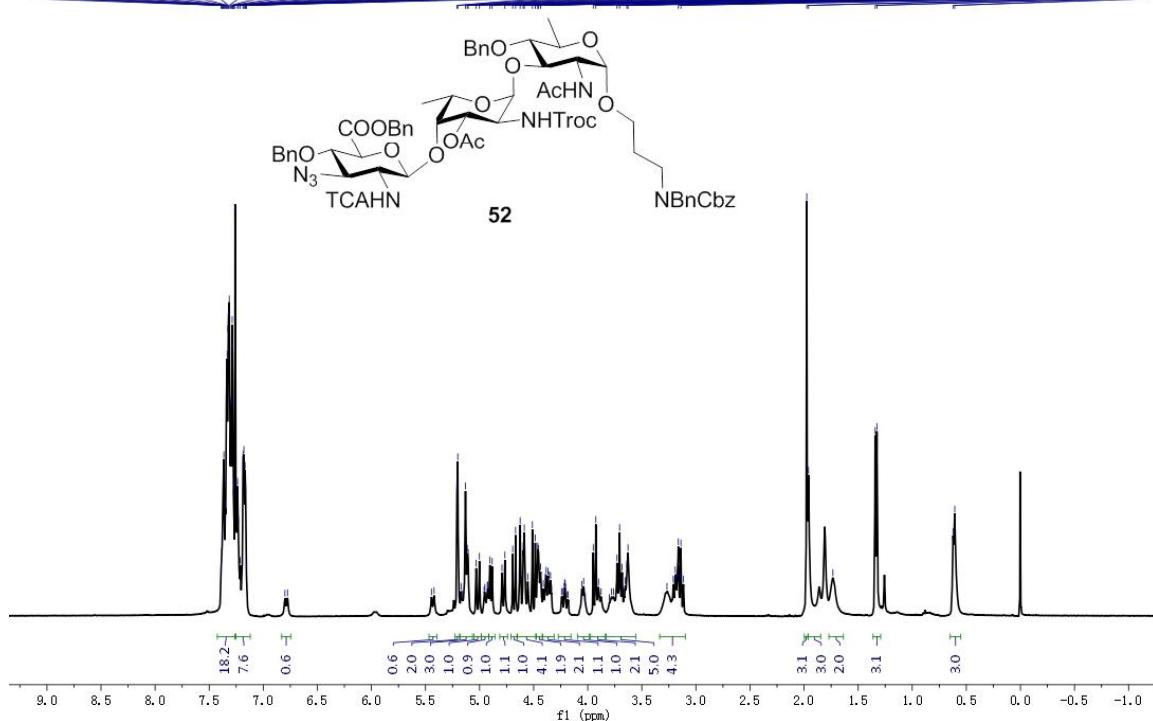


¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 51



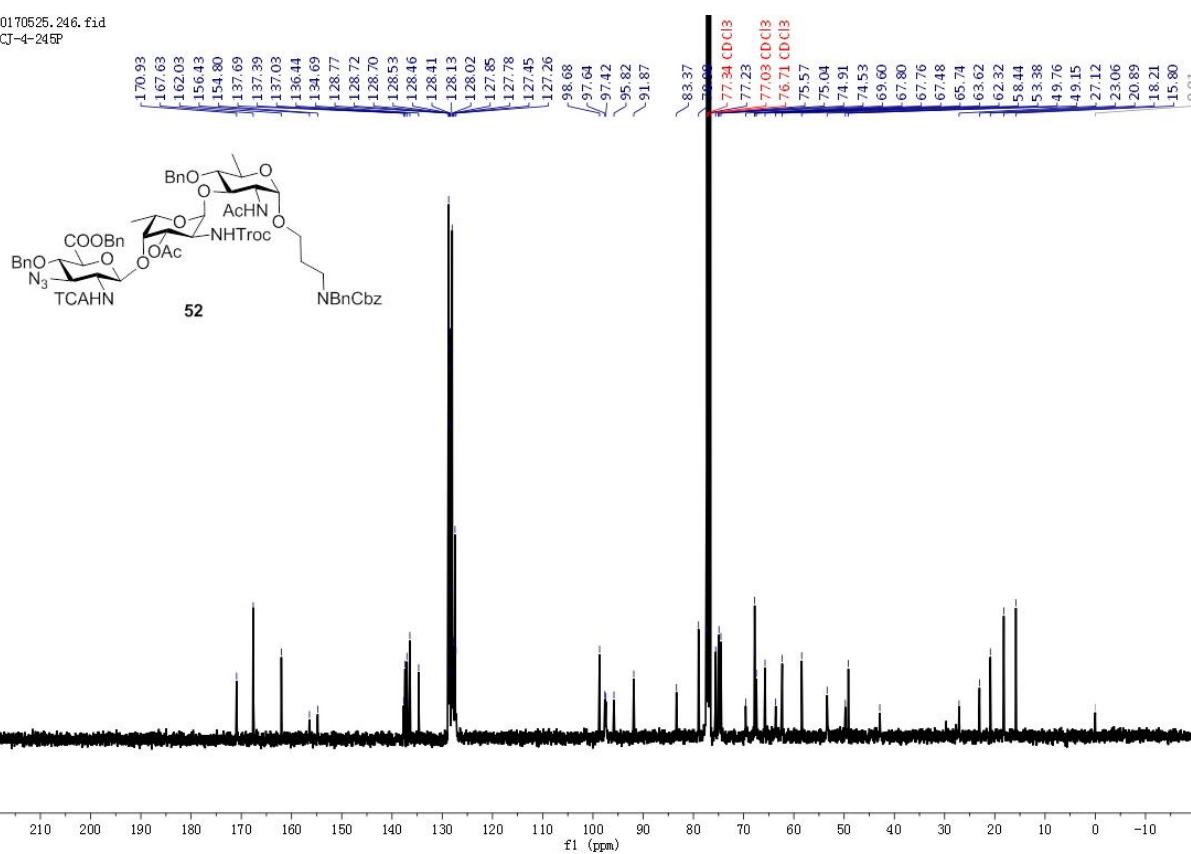
¹H NMR (CDCl₃, 400 MHz) of compound 52

20170525.245.fid
QCT-4-245P

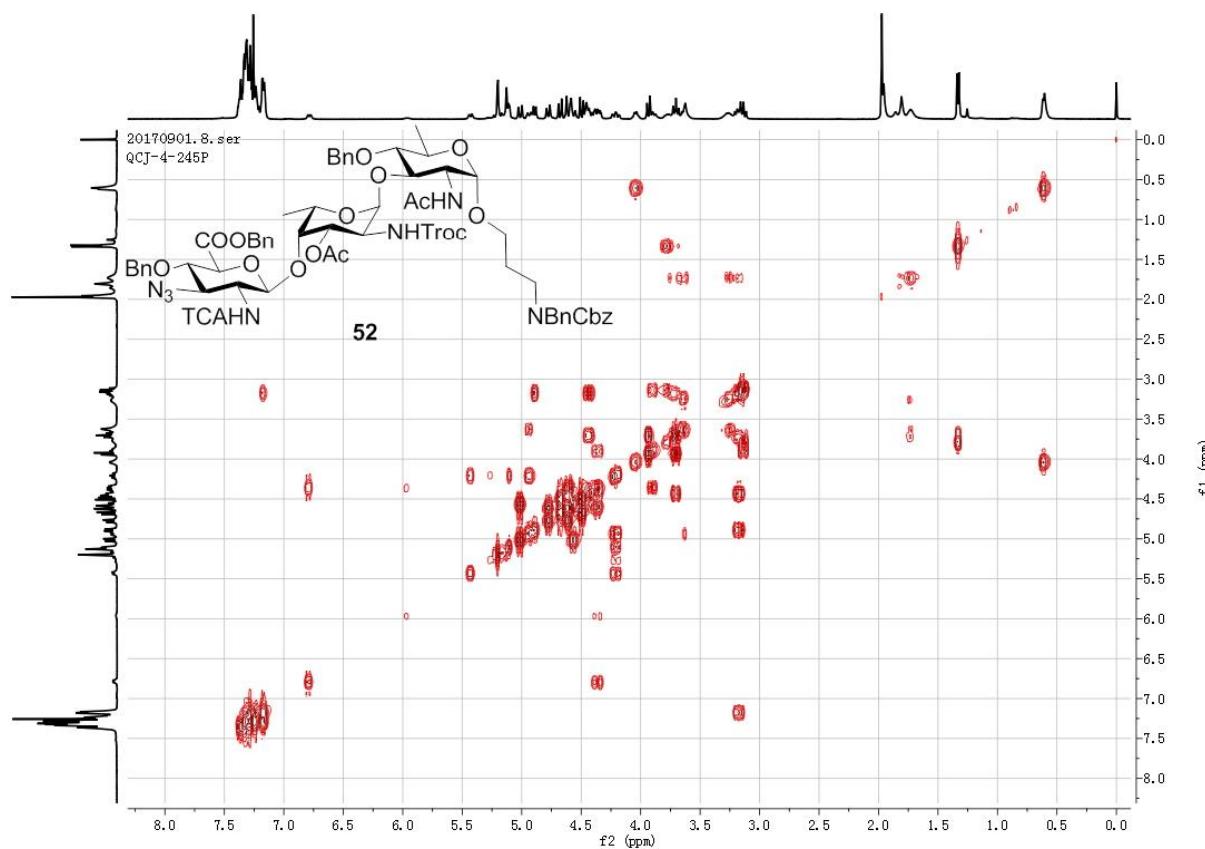


¹³C NMR (CDCl₃, 100 MHz) of compound 52

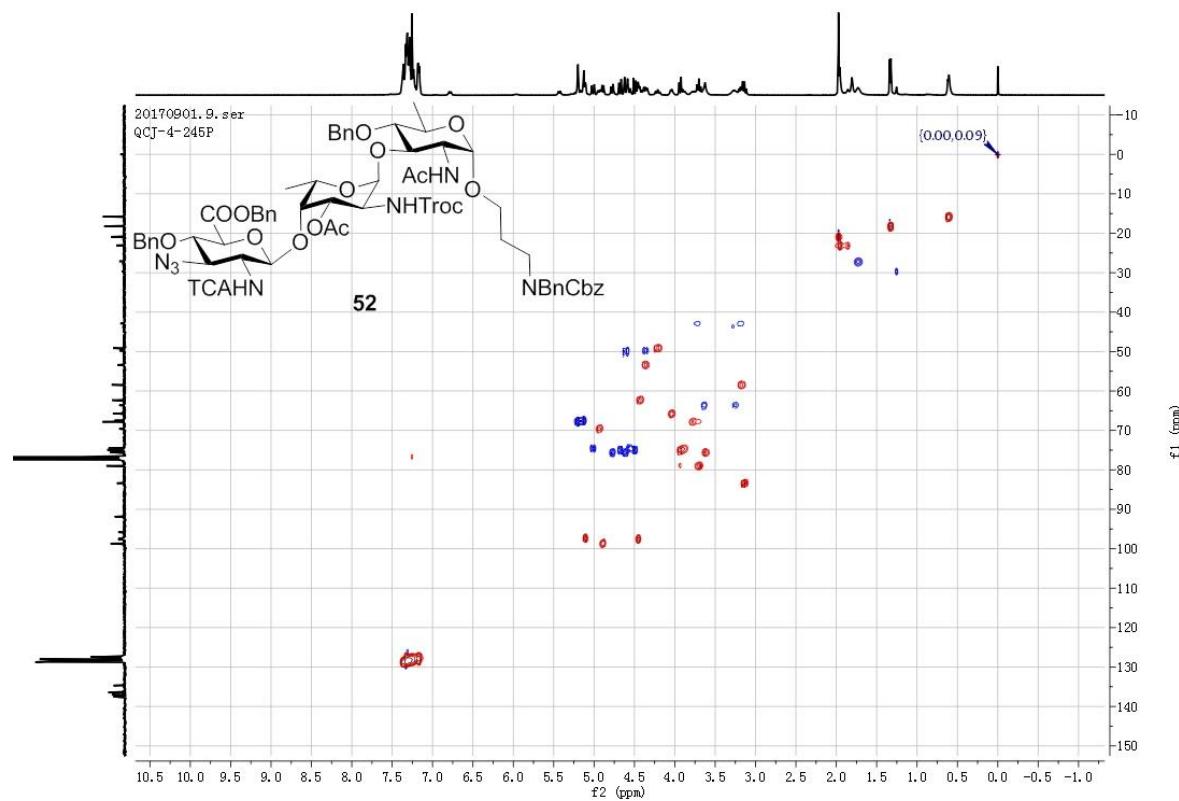
20170525.246.fid
OCT-4-245P



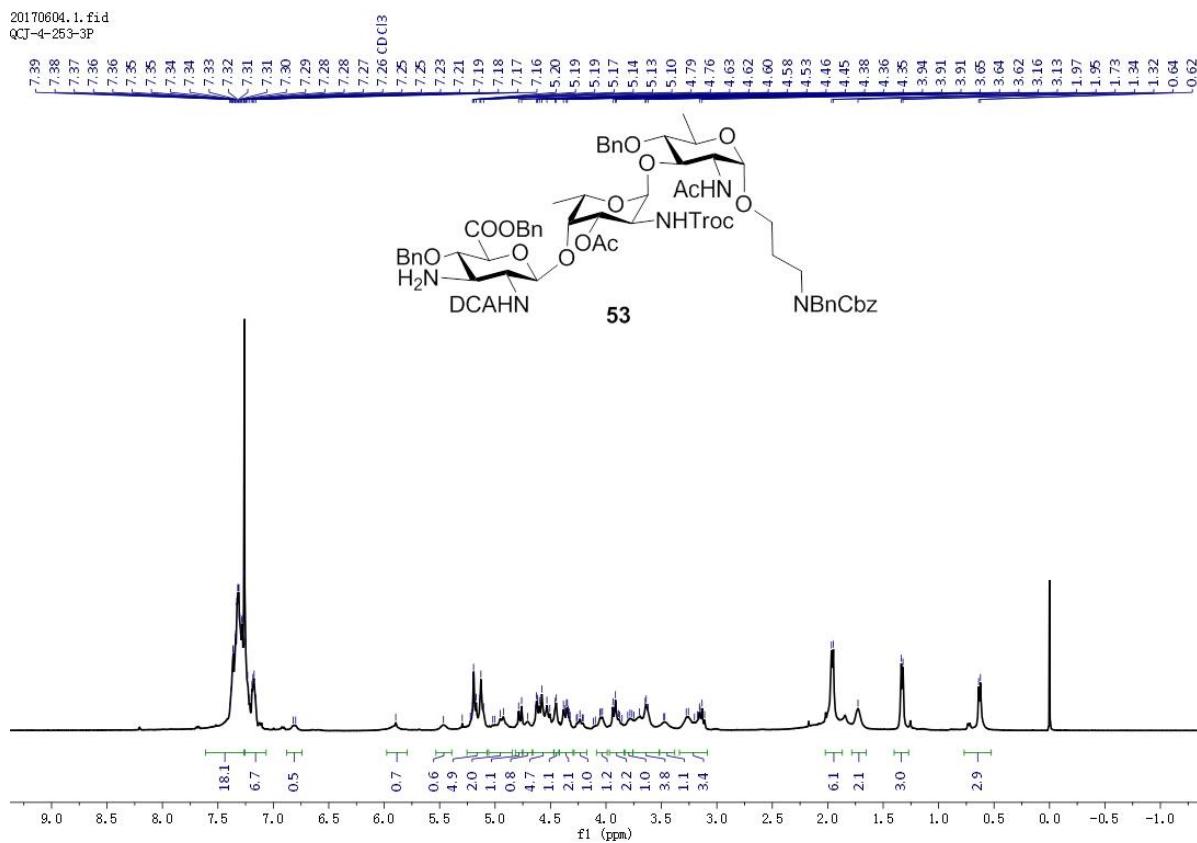
¹H-¹H COSY (CDCl₃, 400 MHz) of compound 52



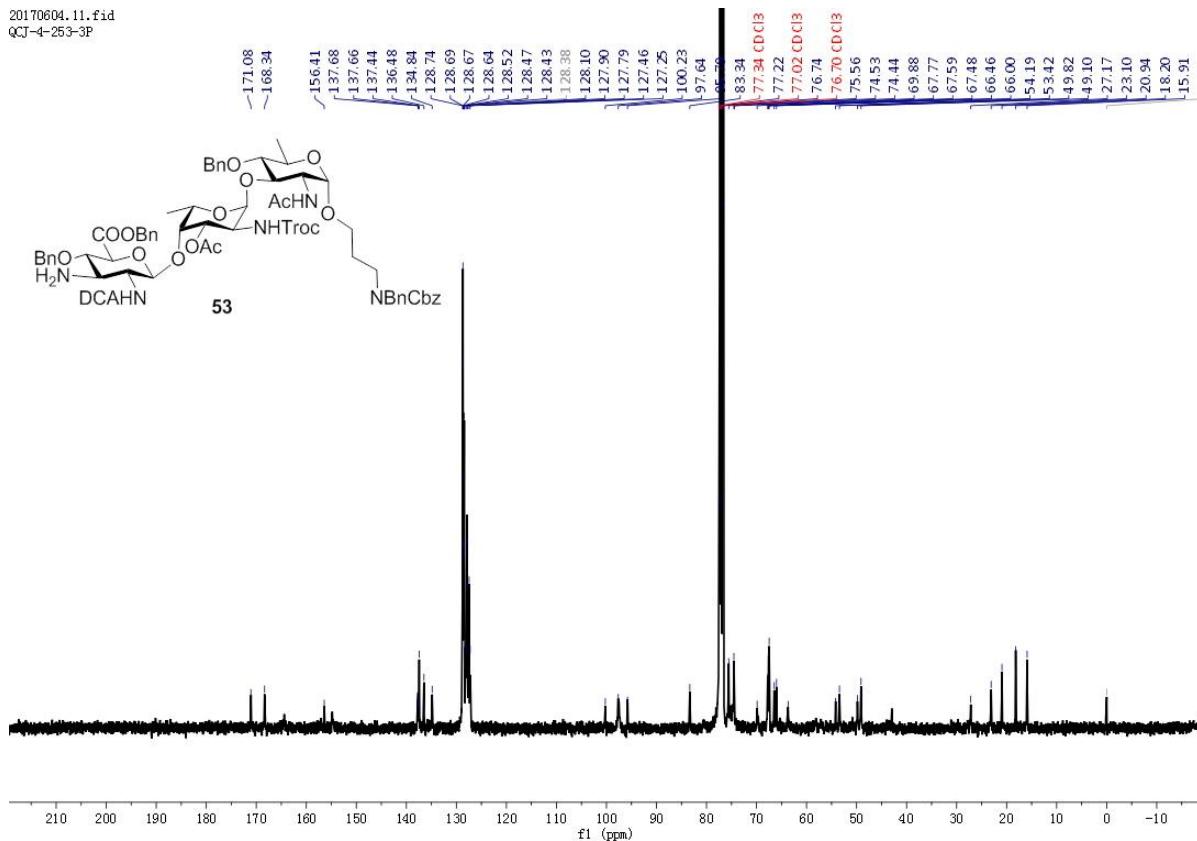
¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 52



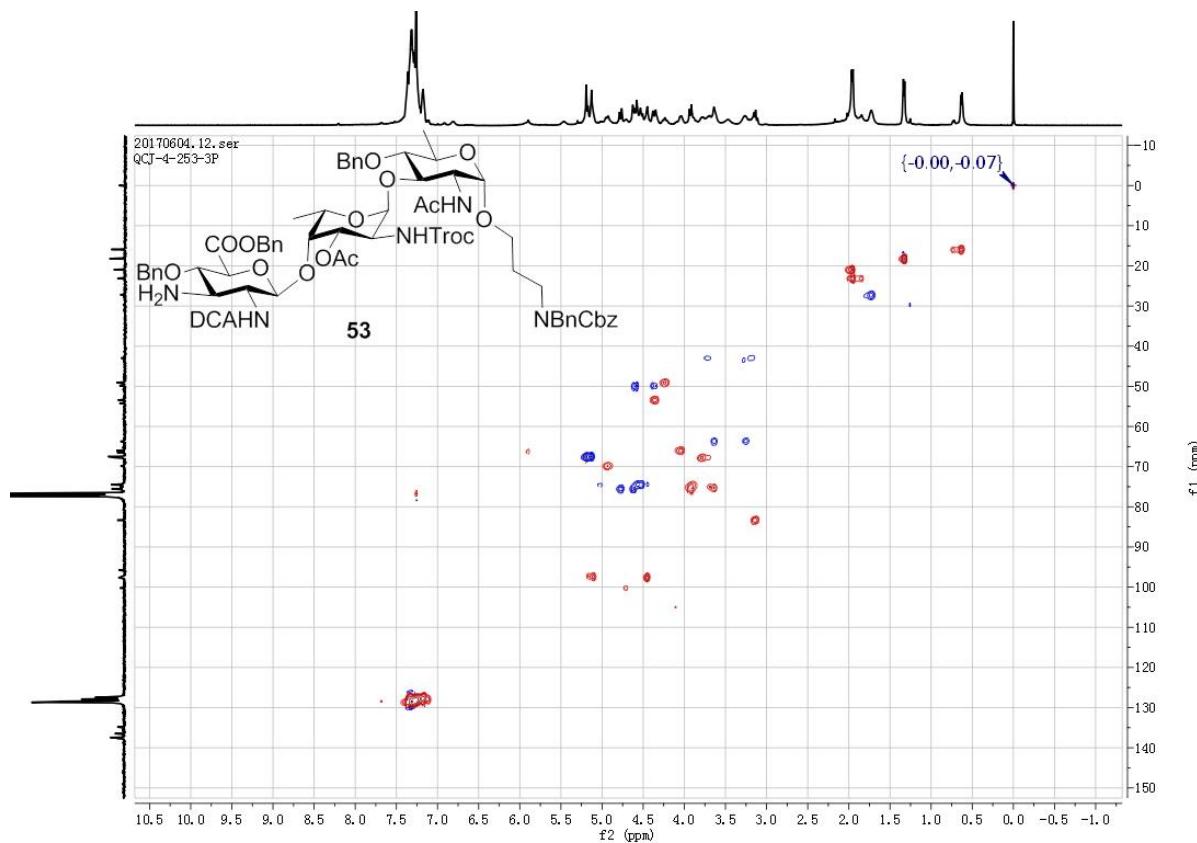
¹H NMR (CDCl₃, 400 MHz) of compound 53



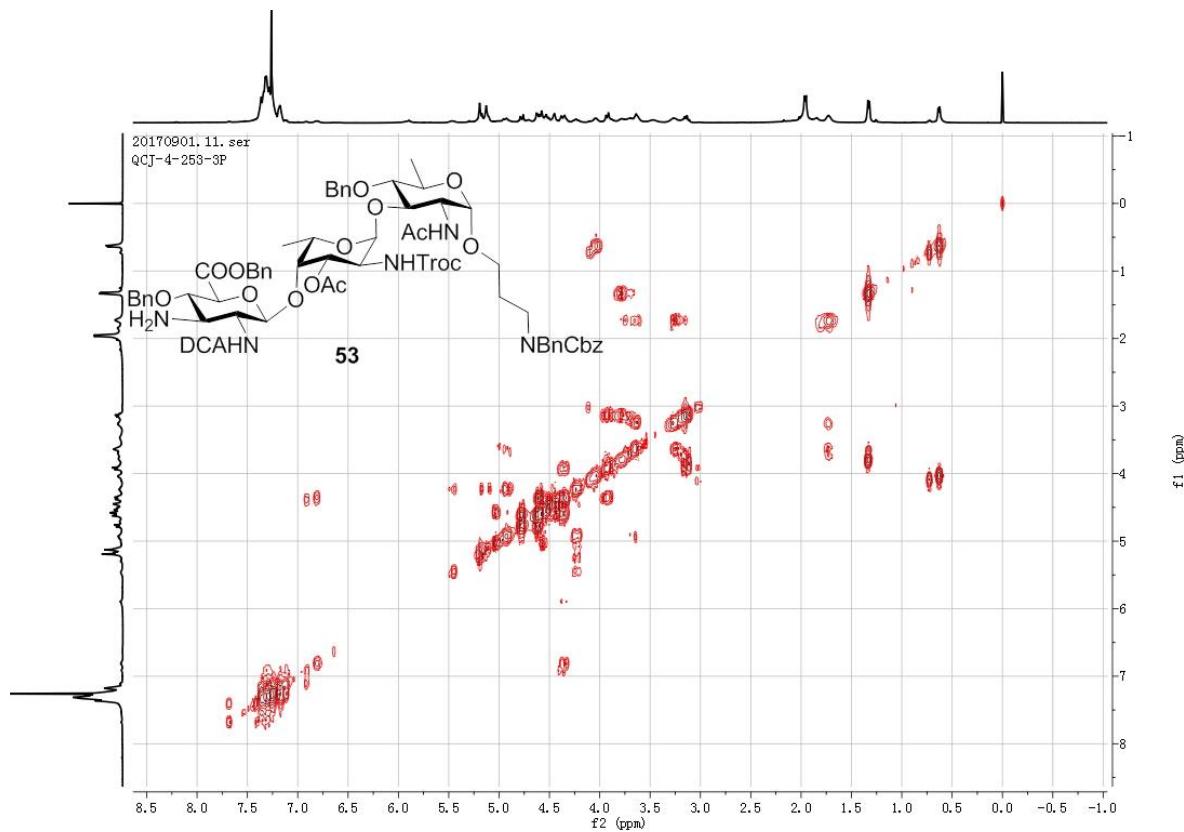
¹³C NMR (CDCl₃, 100 MHz) of compound 53



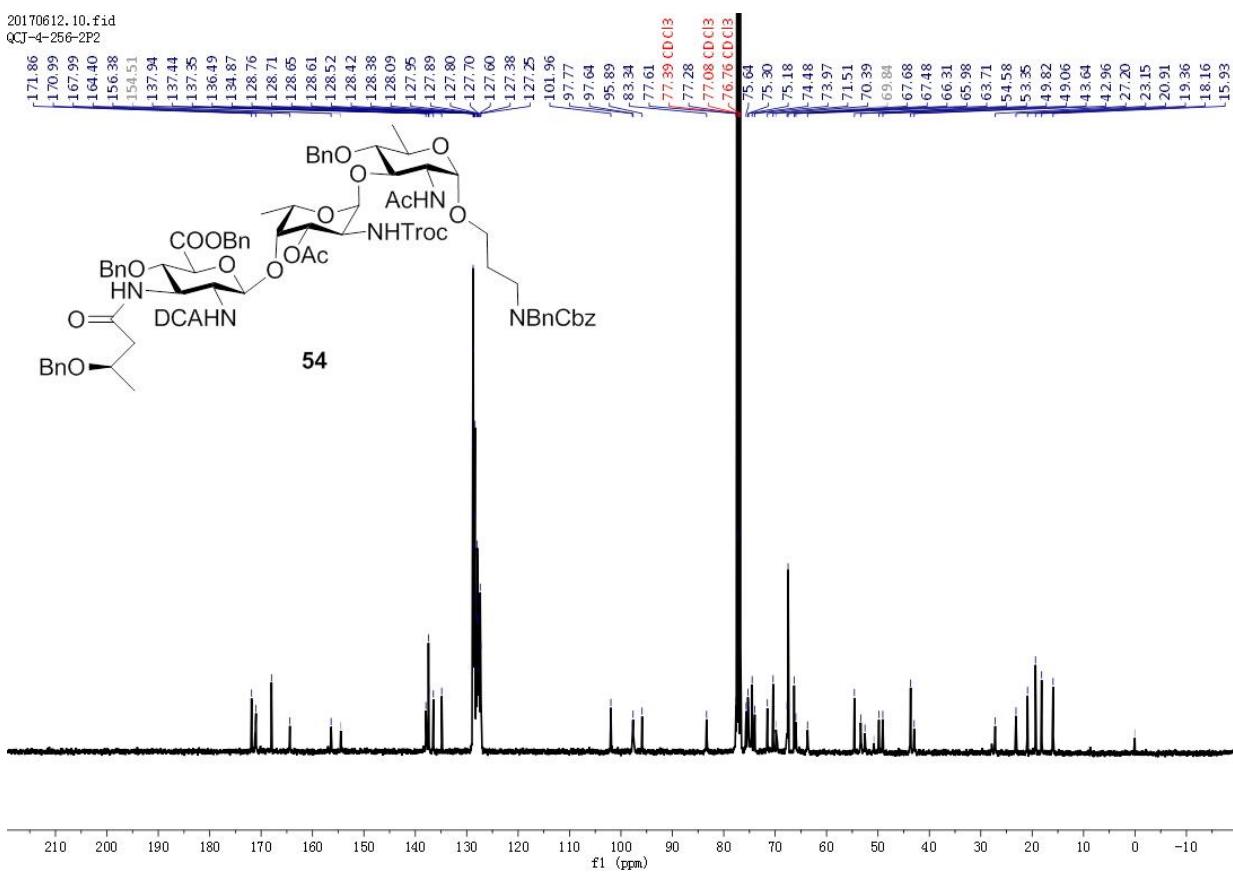
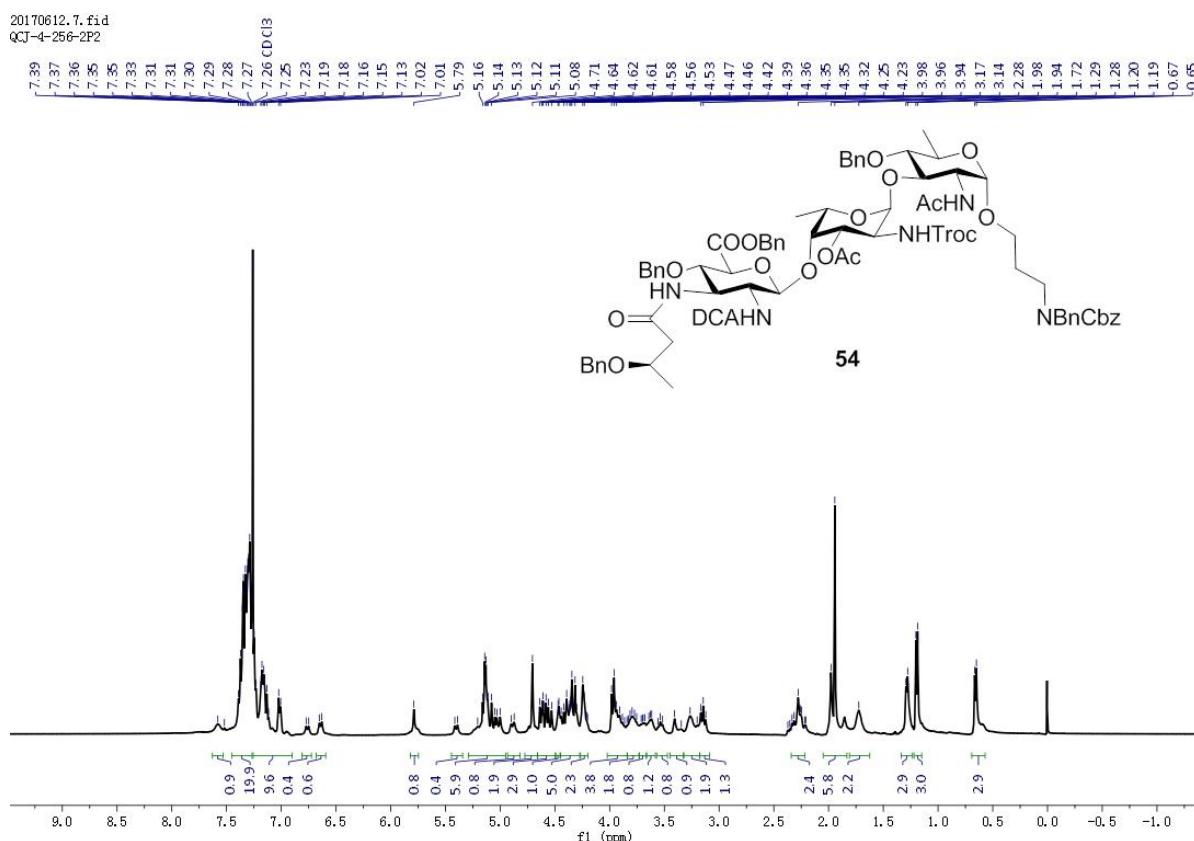
¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 53



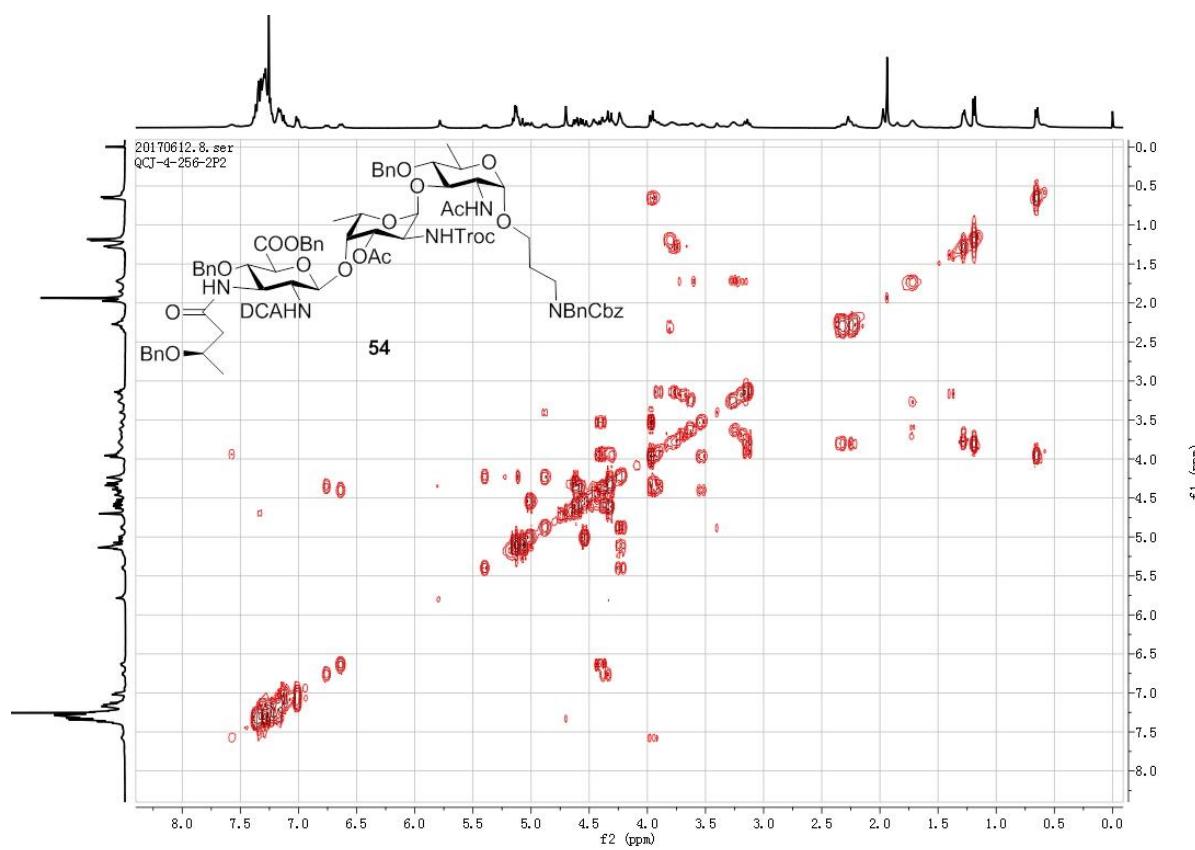
¹H-¹H COSY (CDCl₃, 400 MHz) of compound 53



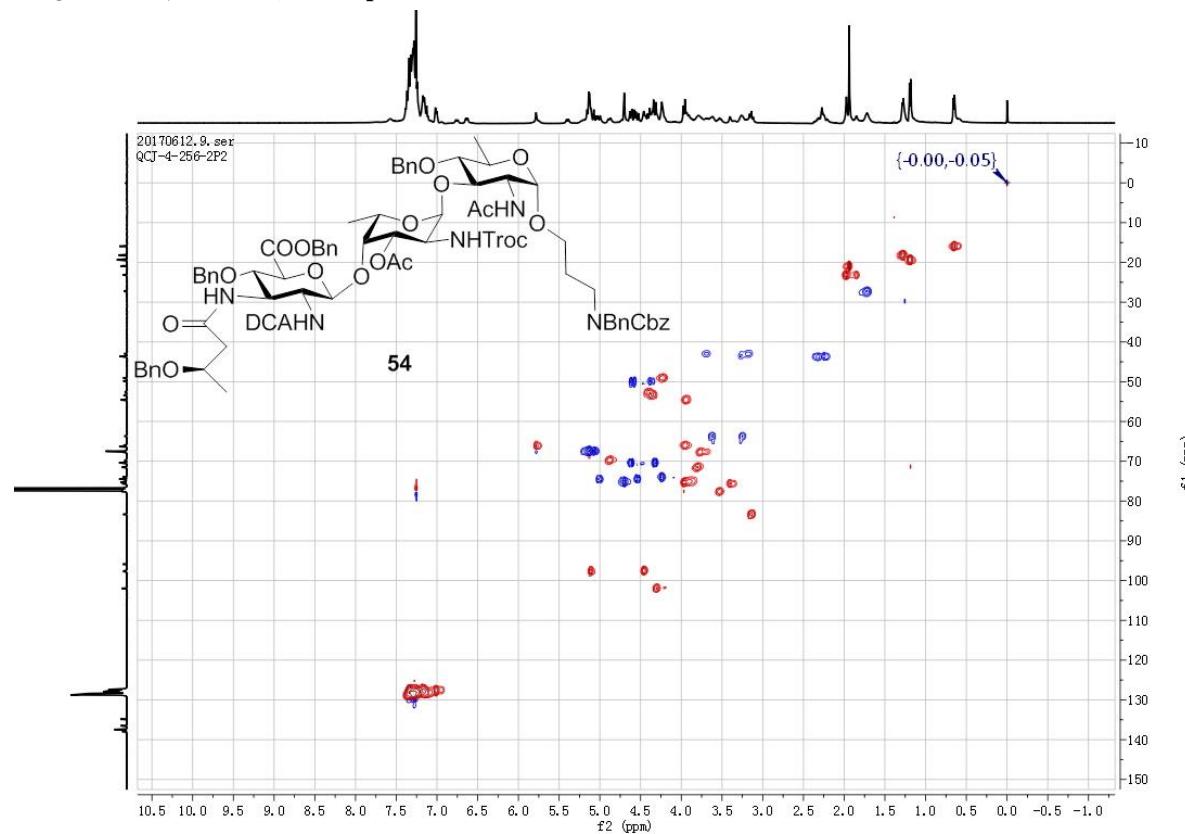
¹H NMR (CDCl₃, 400 MHz) of compound 54



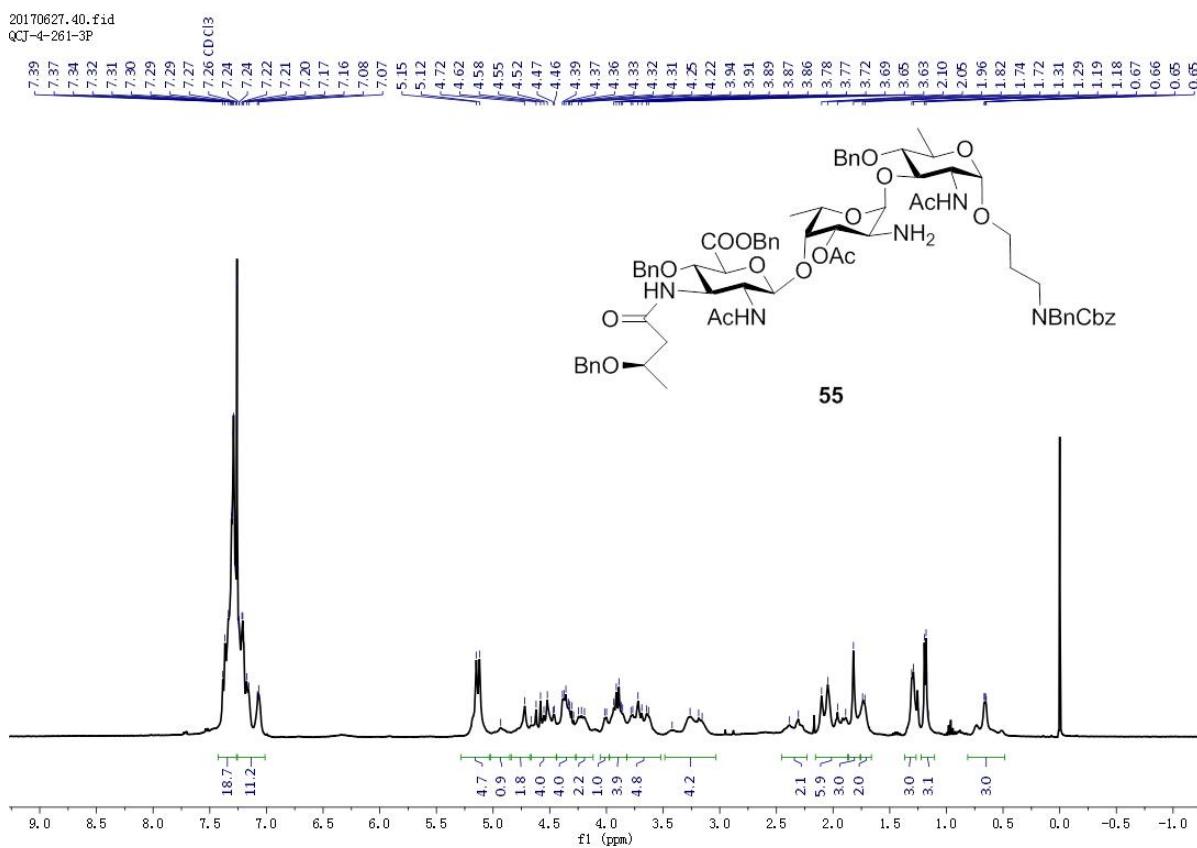
¹H-¹H COSY (CDCl₃, 400 MHz) of compound 54



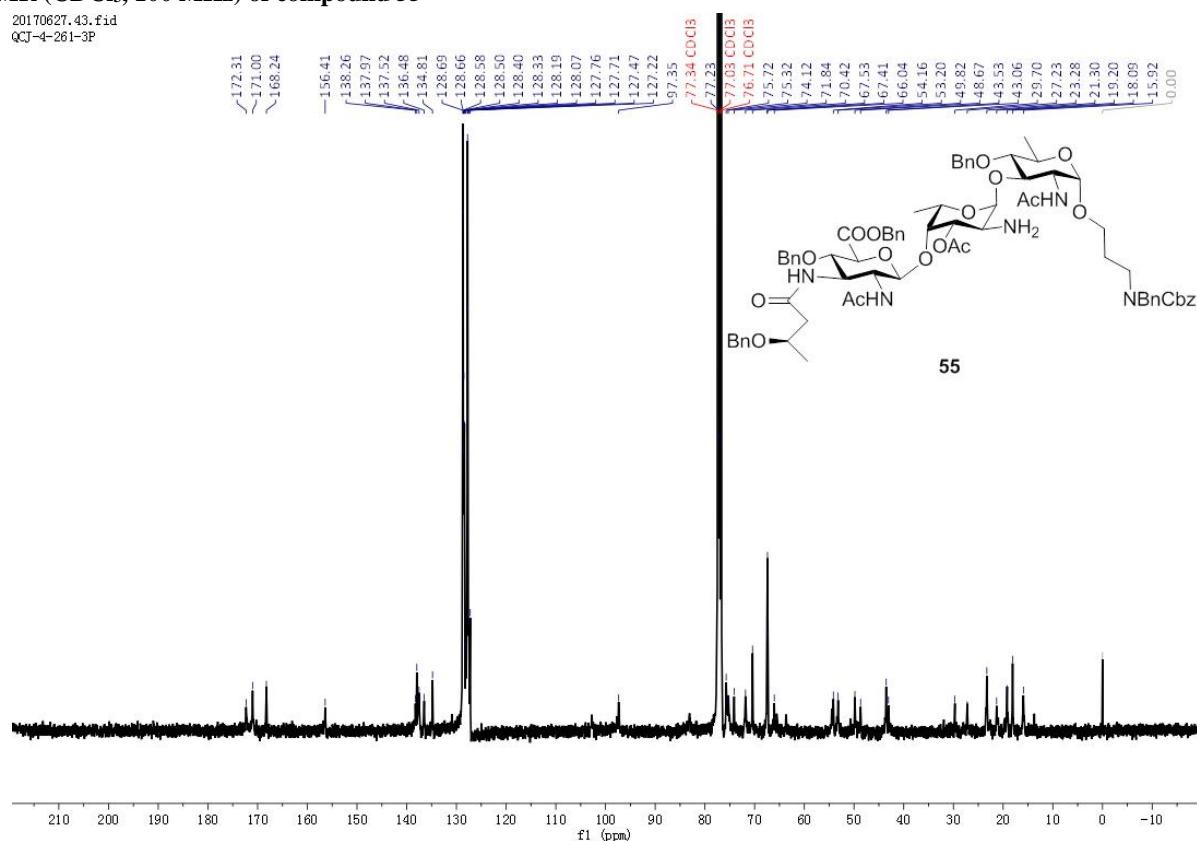
¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 54



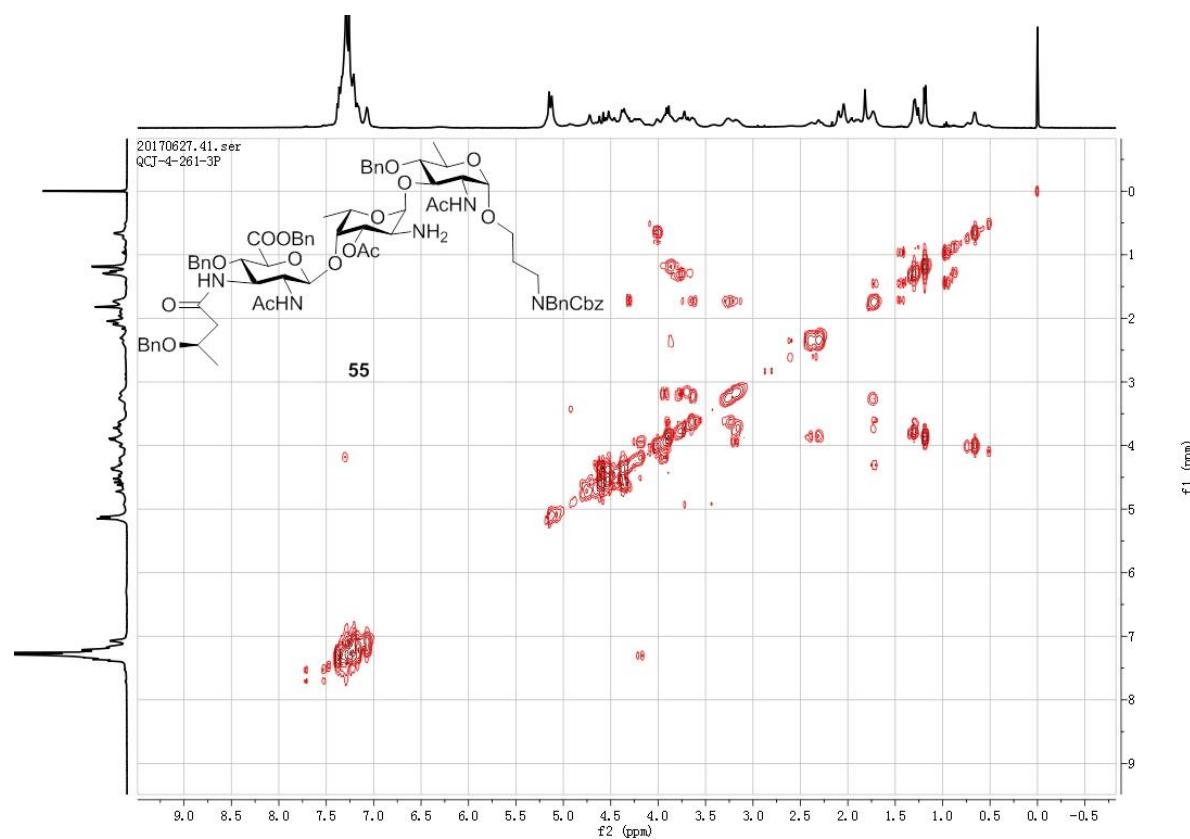
¹H NMR (CDCl₃, 400 MHz) of compound 55



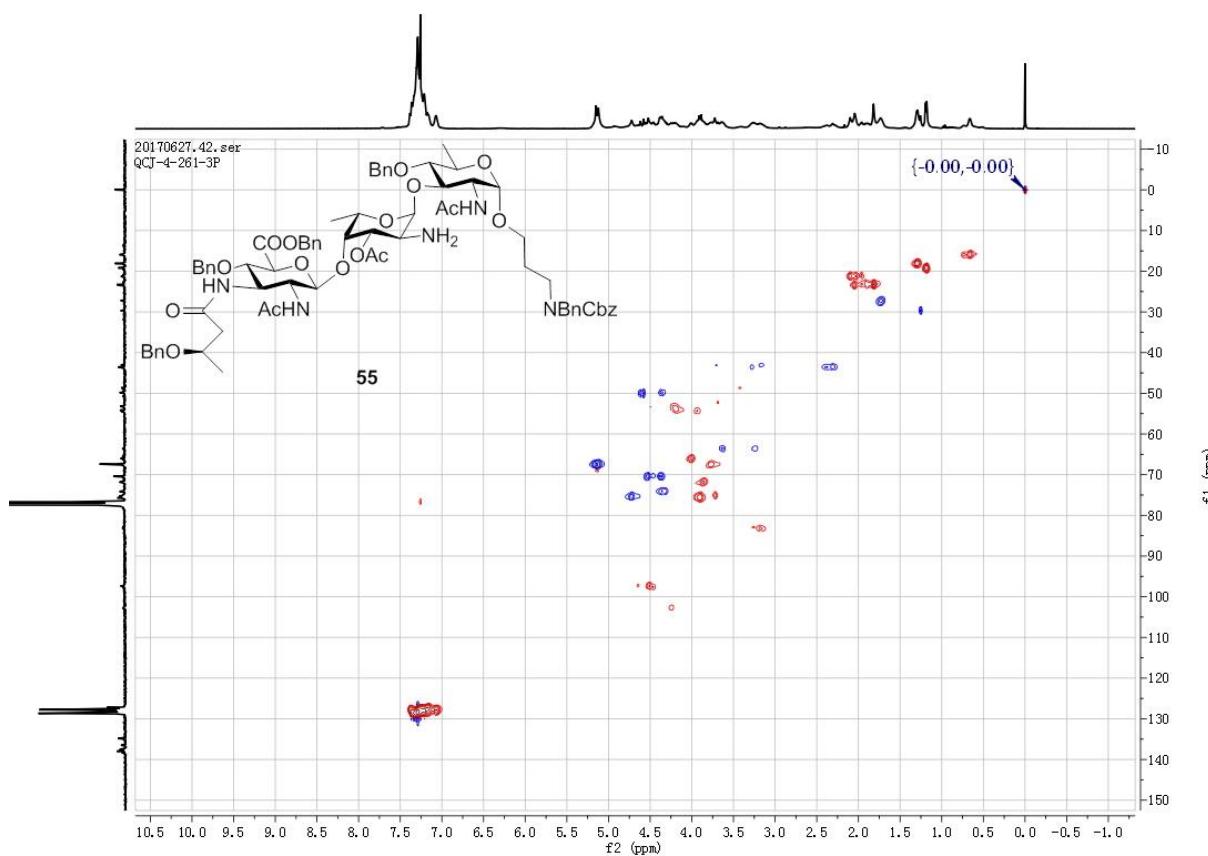
¹³C NMR (CDCl₃, 100 MHz) of compound 55



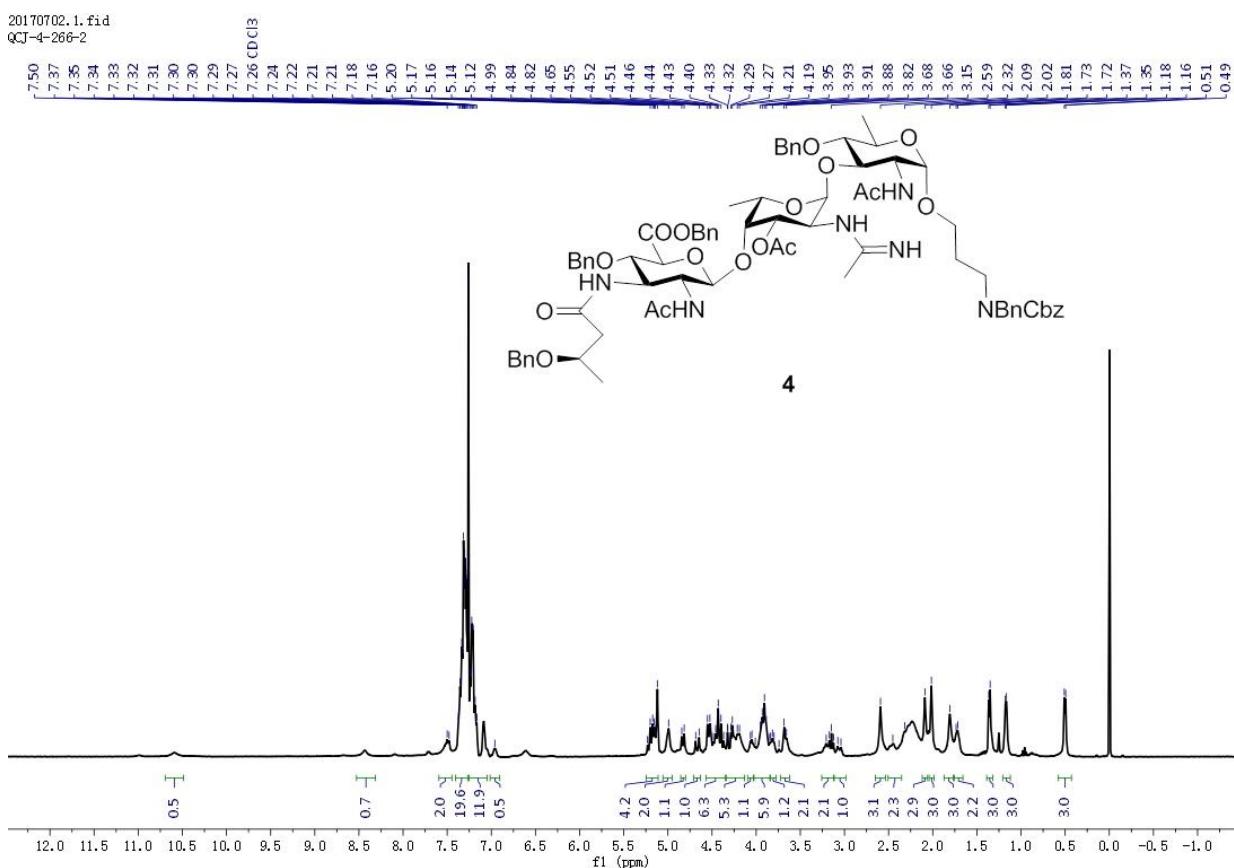
¹H-¹H COSY (CDCl₃, 400 MHz) of compound 55



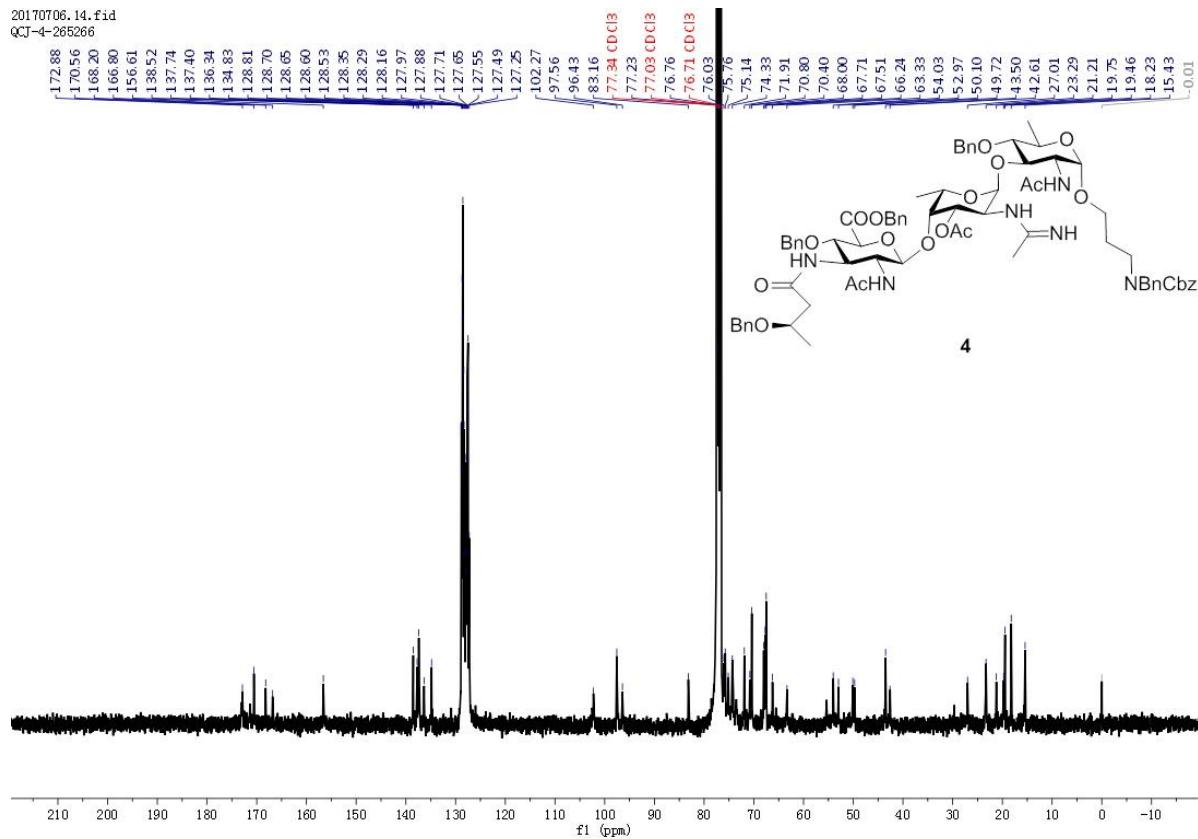
¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 55



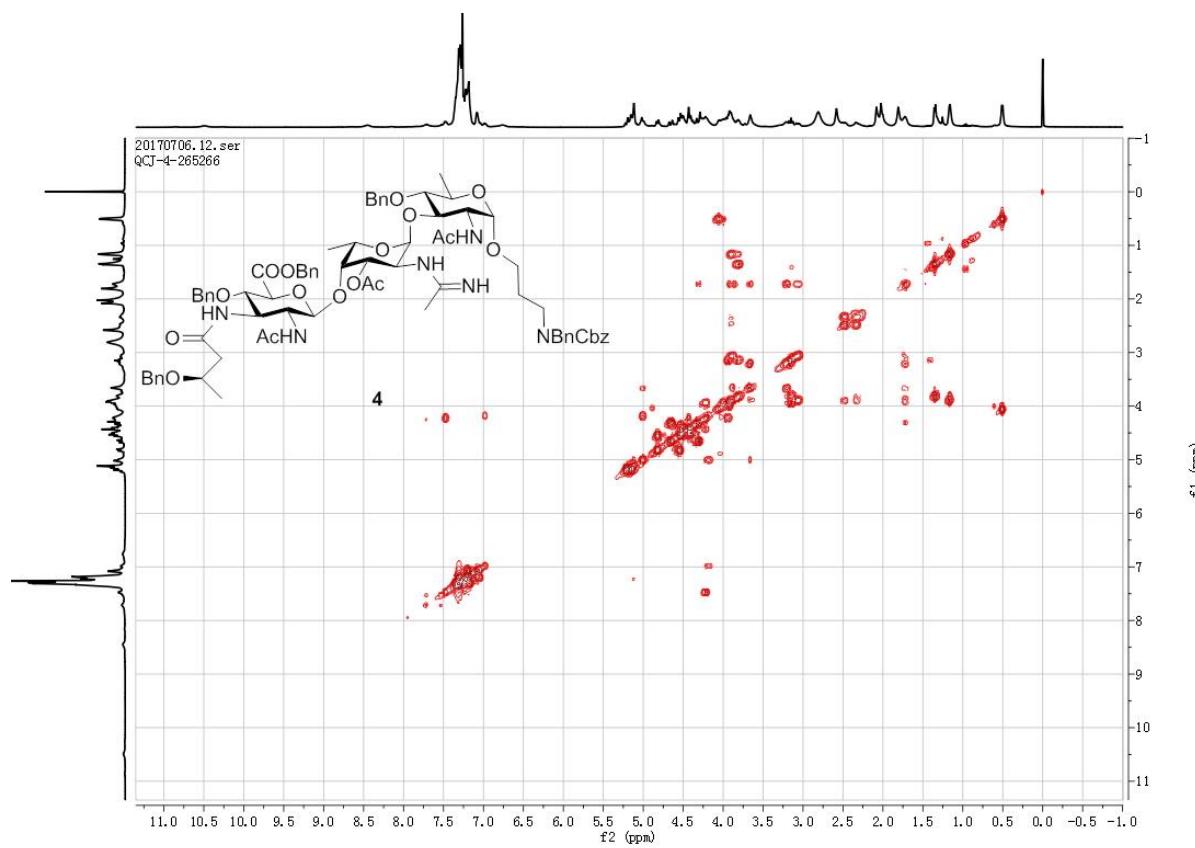
¹H NMR (CDCl₃, 400 MHz) of compound 4



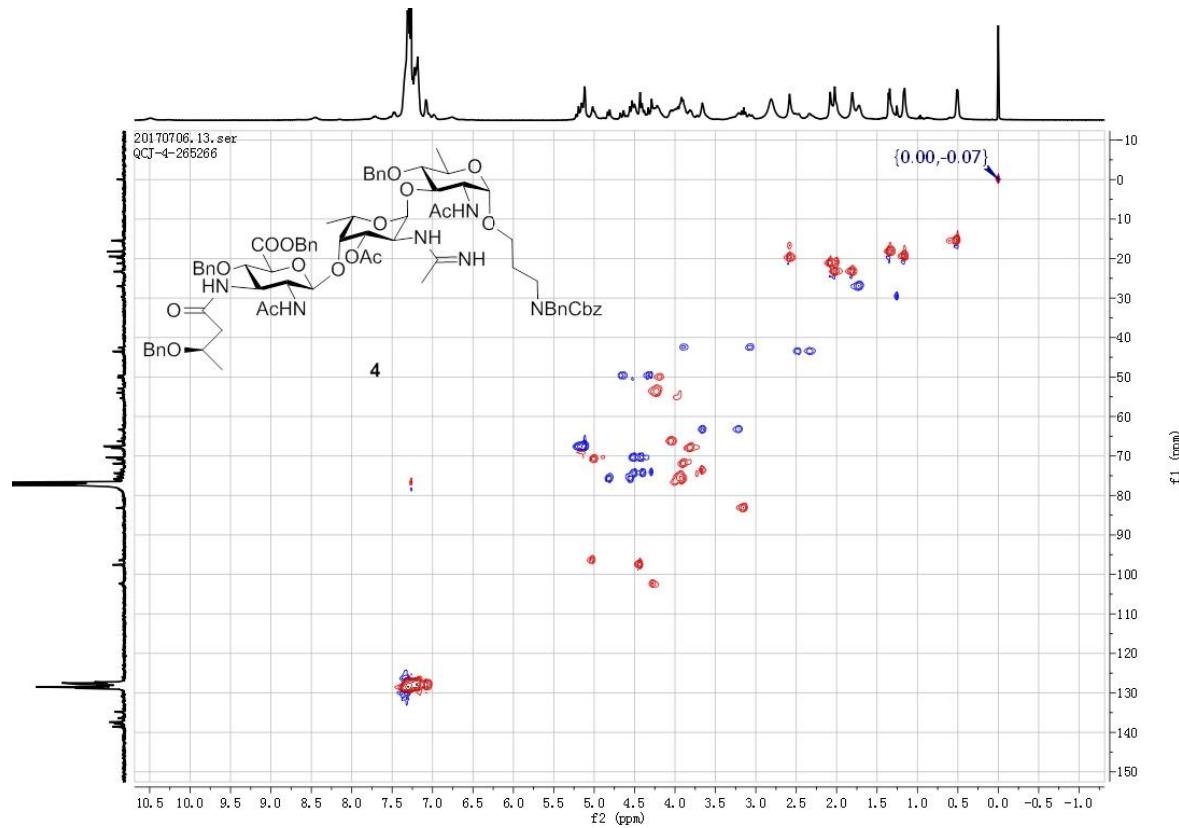
¹³C NMR (CDCl₃, 100 MHz) of compound 4



¹H-¹H COSY (CDCl₃, 400 MHz) of compound 4

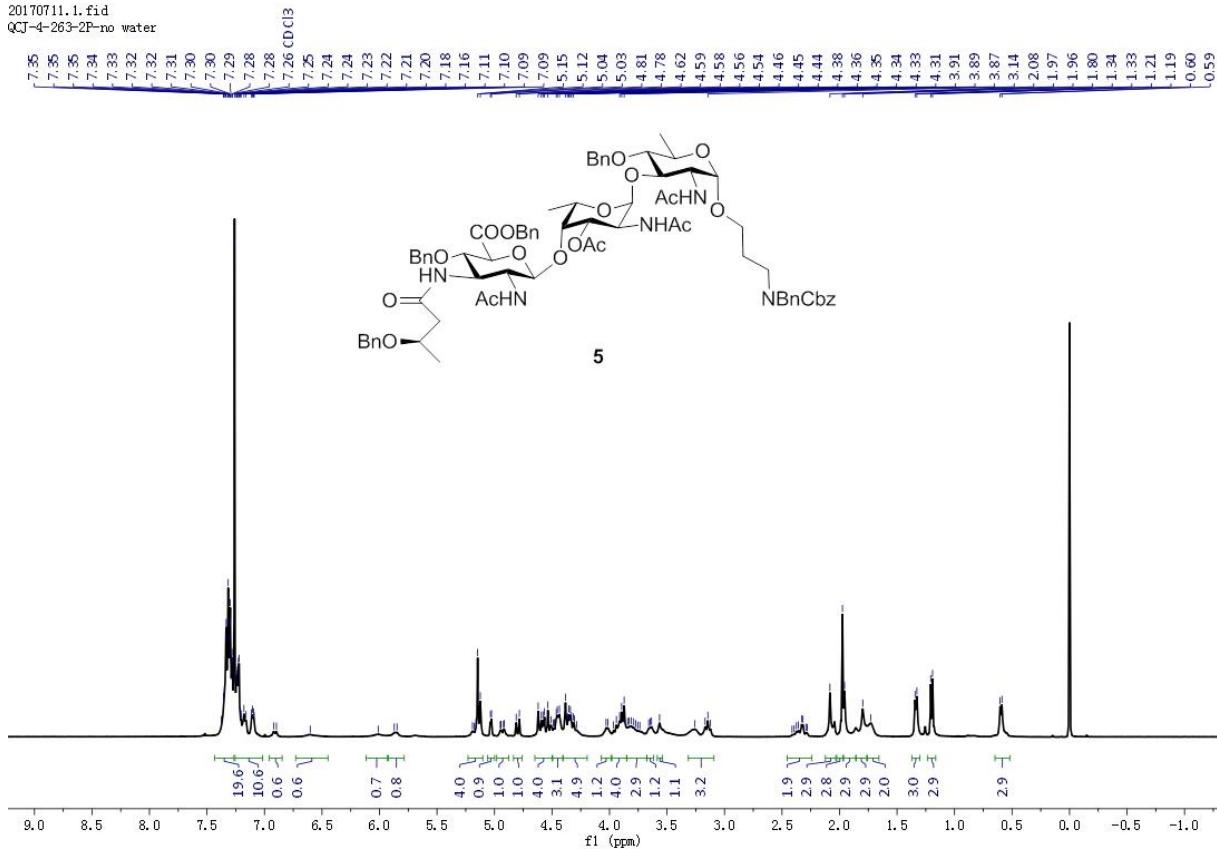


¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 4



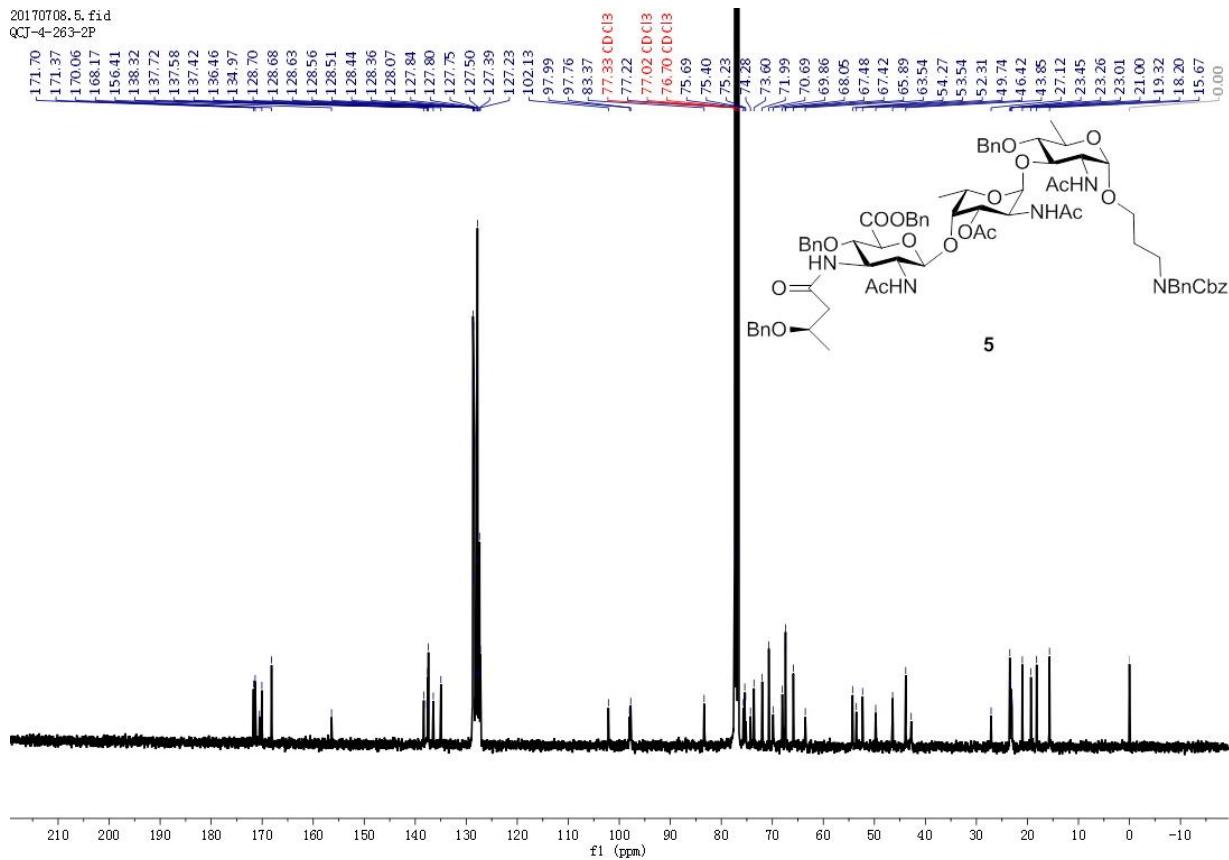
¹H NMR (CDCl₃, 400 MHz) of compound 5

20170711.1.fid
QCJ-4-263-2P-no water

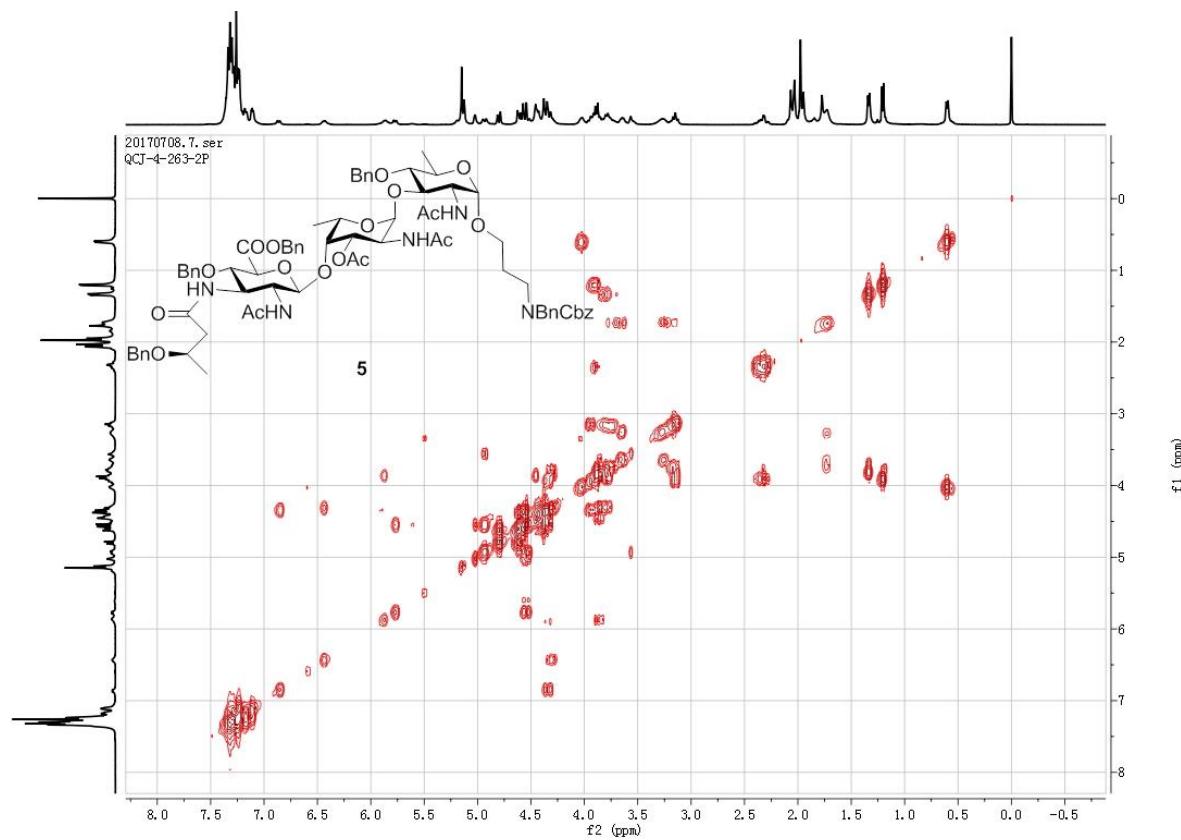


¹³C NMR (CDCl₃, 100 MHz) of compound 5

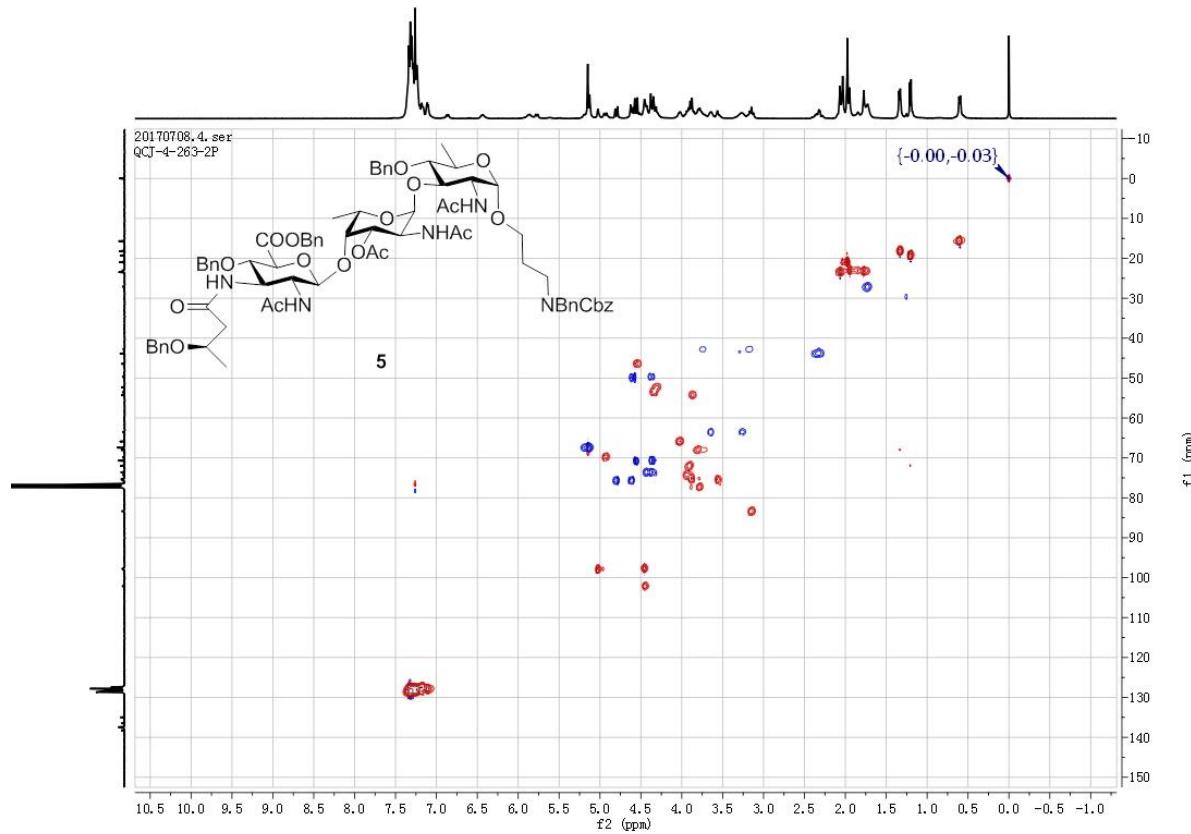
20170708.5.fid
QCJ-4-263-2P



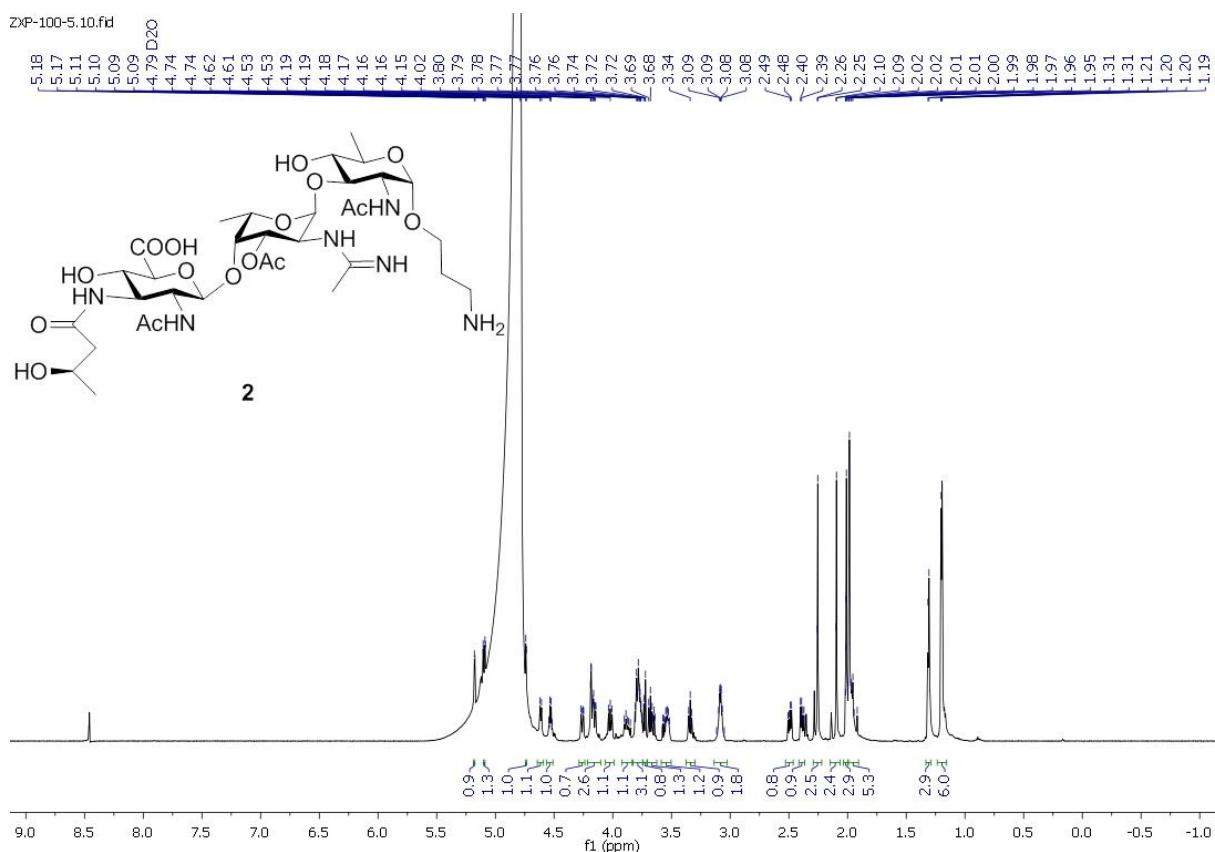
¹H-¹H COSY (CDCl₃, 400 MHz) of compound 5



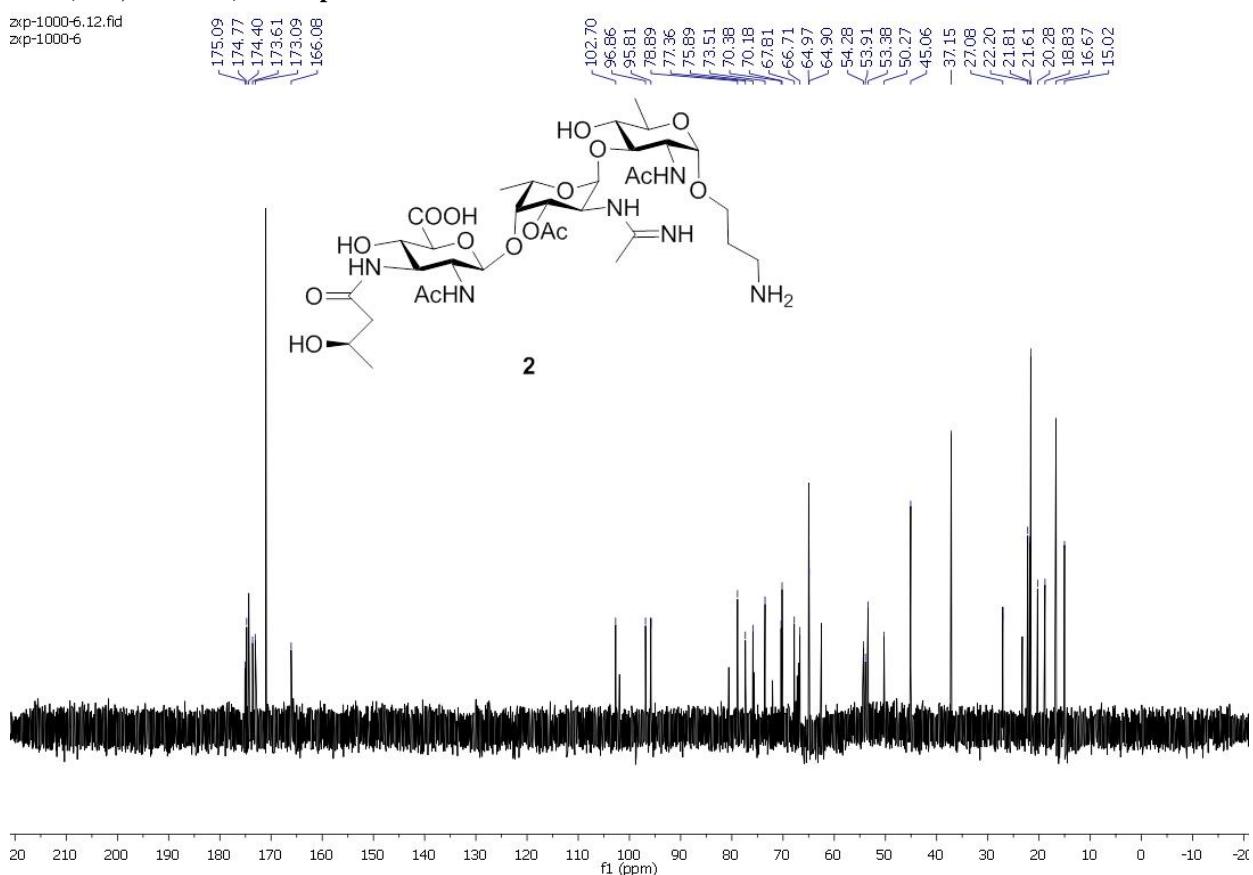
¹H-¹³C HSQC (CDCl₃, 400 MHz) of compound 5



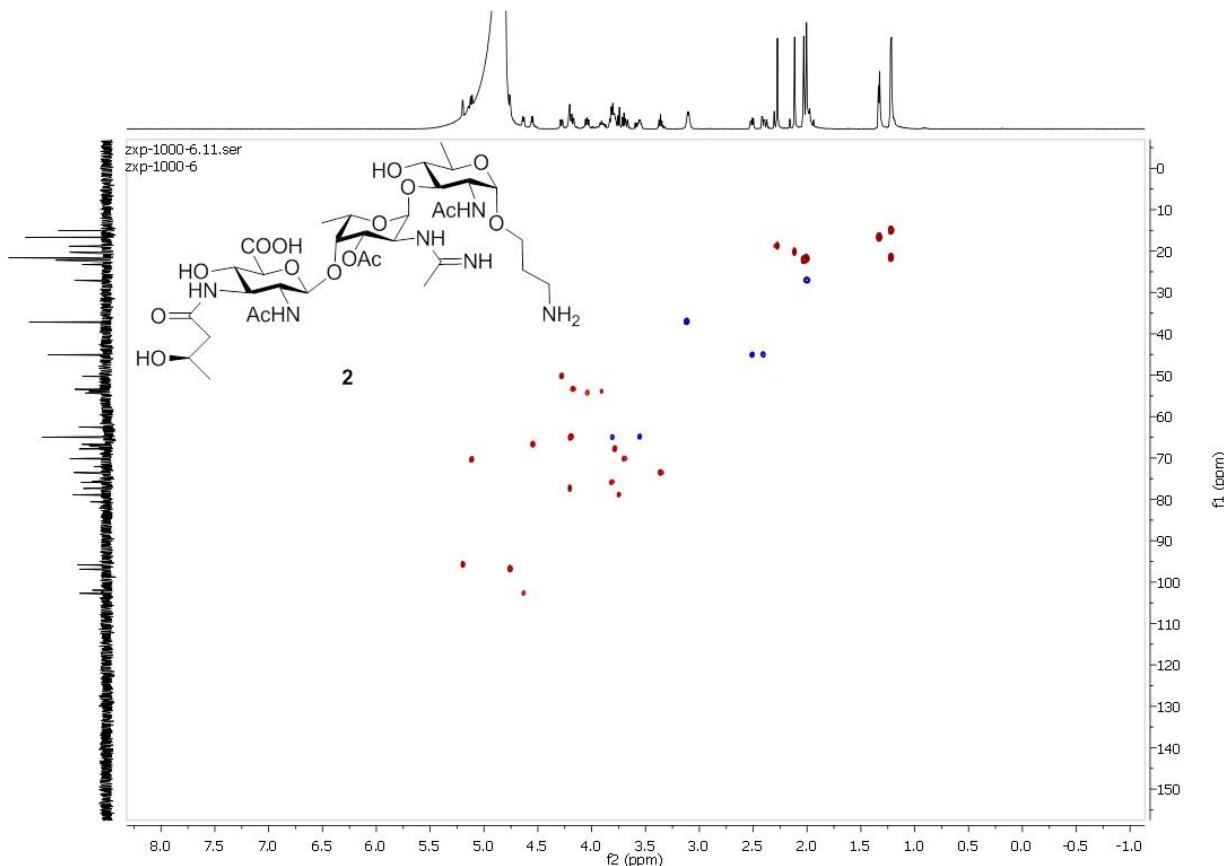
¹H NMR (D₂O, 700 MHz) of compound 2



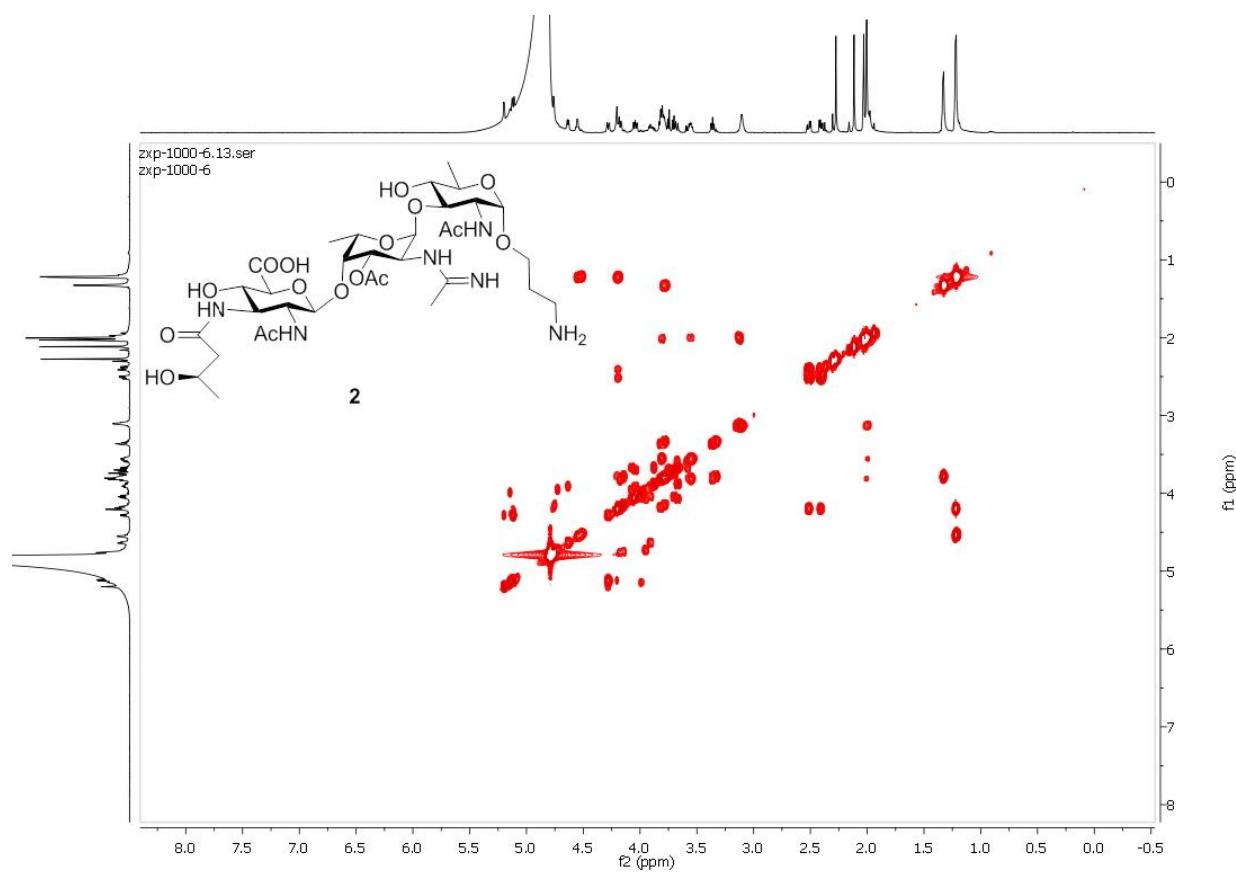
¹³C NMR (D₂O, 176 MHz) of compound 2



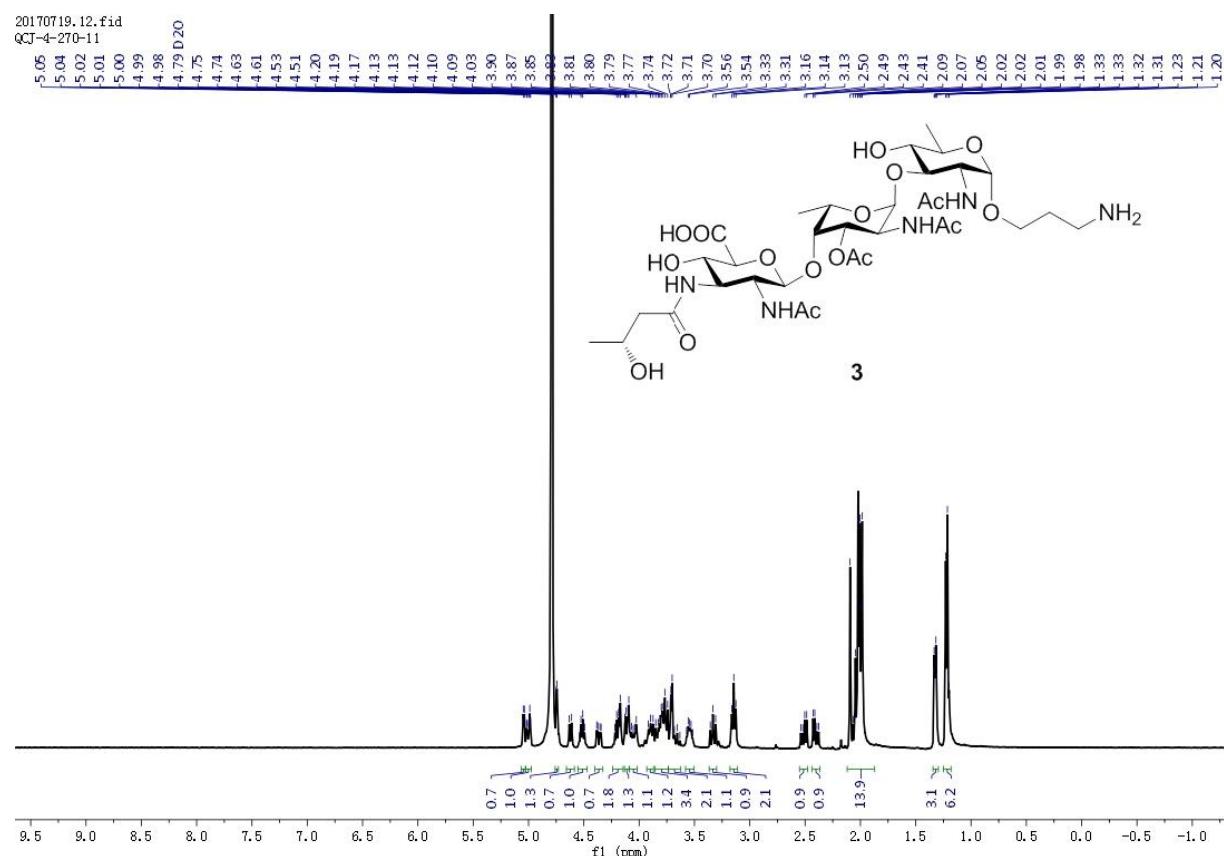
¹H-¹³C HSQC (D₂O, 700 MHz) of compound 2



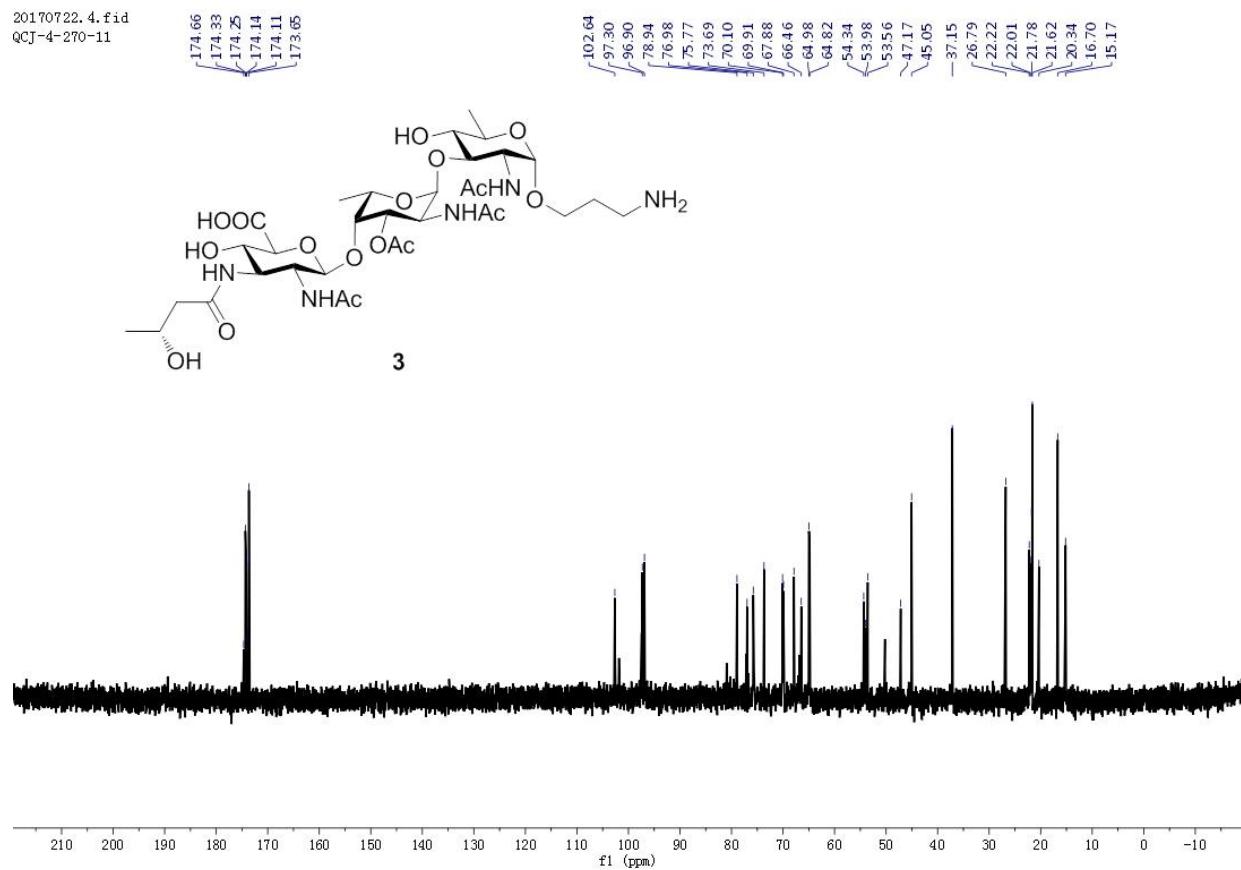
¹H-¹H COSY (D₂O, 700 MHz) of compound 2



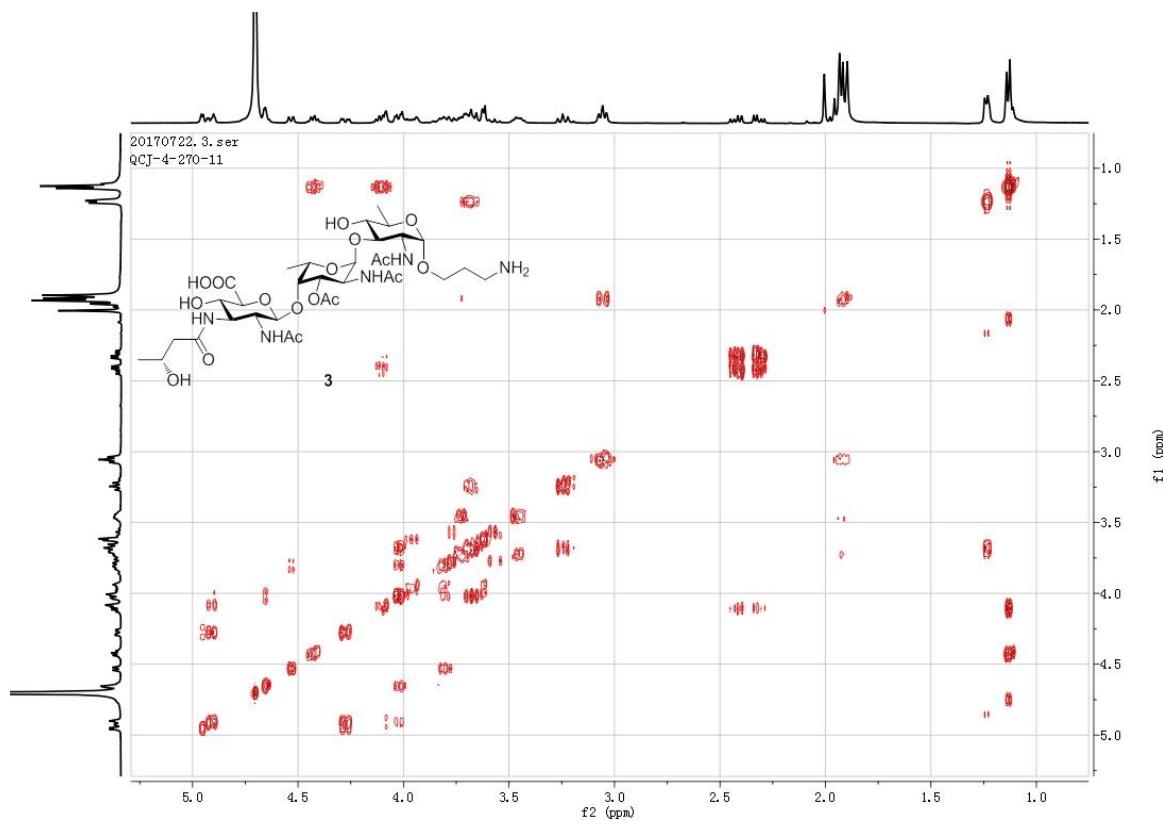
¹H NMR (D₂O, 400 MHz) of compound 3



¹³C NMR (D₂O, 100 MHz) of compound 3



¹H-¹H COSY (D_2O , 400 MHz) of compound 3



¹H-¹³C HSQC (D_2O , 400 MHz) of compound 3

