Total Synthesis of *Pseudomonas aeruginosa* 1244 Pilin Glycan via *de novo* Synthesis of Pseudaminic Acid

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Content

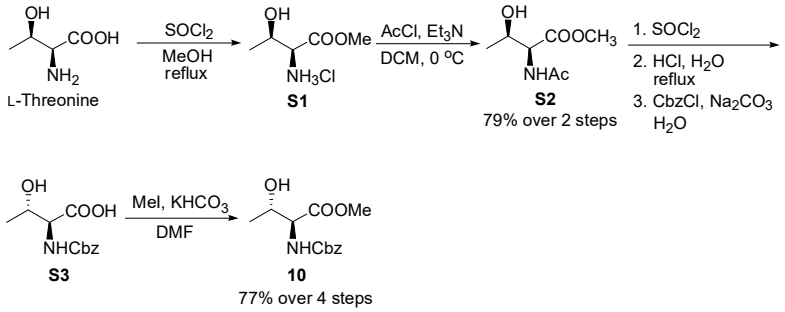
List of NMR spectra for new compounds

General Remarks

Commercially available reagents were used without further purification, unless otherwise stated. The anhydrous solvents were either prepared from AR grade solvents via standard methods (DCM, THF, MeCN, etc.), or purchased in anhydrous form (DMF, pyridine, etc.). The analytical TLC was performed on silica gel 60-F254 precoated on glass plate (E. Merck), with detection by fluorescence and/or or by staining with acidic ceric ammonium molybdate. The normal phase column chromatography was performed on silica gel (230-400 mesh, Merck), while the reverse phase chromatography was performed on C18 silica gel (Davisil 633NC18E, Grace Materials Technologies).

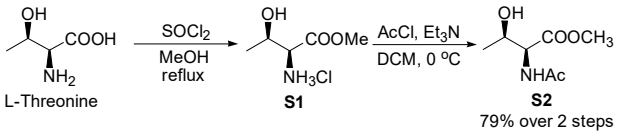
The ^{1}H and ^{13}C NMR spectra were recorded on Advance DRX Bruker 400, 500 and 600 MHz spectrometers at 25 ^{o}C. The 2D NMR spectra were recorded on Advance DRX Bruker 500 and 600 MHz spectrometers at 25 ^{o}C. The high-resolution mass spectrometry was performed on a Waters Micromass Q-Tof Premier Mass Spectrometer. The IR spectra were recorded on Shimadzu IRAffinity-1 spectrometer. The specific rotations were measured with an Bellingham & Stanley ADP440+ polarimeter with a path length of 5 cm.

Part 1. Synthesis of L-*allo*-threonine derivatives.



Scheme S1. Synthesis of L-allo-threonine derivatives from L-threonine.

Methyl (2*S*,3*R*)-2-acetamido-3-hydroxybutyrate (S2):



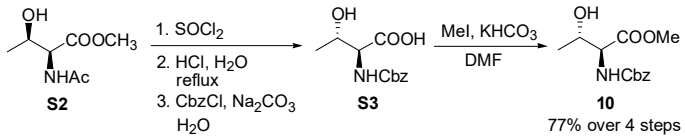
To a 1000 mL round bottom flask, MeOH (500 mL) was added. After being cooled to 0 °C, $SOCl_2$ (50 mL) was added dropwise to generate the HCl solution in MeOH. After 10 min, L-threonine (50.0 g, 419 mmol, 1.0 equiv) was added in one portion. The mixture was refluxed for 2 h, then the solvent was removed under vacuum. The residue was co-evaporated with DCM for two times to thoroughly remove MeOH. The product **S1** was obtained as a syrup and was directly used in the next step without further purification.

To the 1000 mL flask containing syrup **S1**, anhydrous DCM (600 mL) was added, followed by Et_3N (117 mL, 839 mmol, 2.0 equiv). The mixture was sonicated to give a suspension. After being cooled to 0 °C, acetyl chloride (30.0 mL, 419 mmol, 1.0 equiv) was added dropwise during 30 min, then the mixture was further stirred at 0 °C for 2 h. The mixture was filtered through celite to remove $Et_3N{\cdot}HCl$, and the filtrate was concentrated. The residue was purified by silica gel flash chromatography using ethyl acetate as eluent. The product **S2** was obtained as white solid (58.2 g, 79% over 2 steps). [1]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21 (d, J = 6.4 Hz, 3H), 2.08 (s, 3H), 3.45 (d, J = 5.2 Hz, 1H), 3.76 (s, 3H), 4.31–4.35 (m, 1H), 4.56 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 6.74 (d, J = 8.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.0, 23.0, 52.6, 57.6, 67.8, 171.3, 171.7.

Methyl (2*S*,3*S*)-2-benzyloxycarbonylamino-3-hydroxybutyrate (10):



To a 500 mL round bottom flask, **S2** (46.0 g, 263 mmol, 1.0 equiv) was added, followed by $SOCl_2$ (130 mL). The mixture was stirred at r.t. for 12 h, then the excess amount of $SOCl_2$ was removed under vacuum. The residue was co-evaporated with hexane for three times to remove the $SOCl_2$ thoroughly, and the crude oxazoline HCl salt intermediate was obtained as a syrup. To this residue, 10% HCl (aq, 120 mL) was added, and the mixture was refluxed for 7 h to hydrolyze the oxazoline. The HCl solution was removed under vacuum to give the crude HCl salt of L-*allo*-threonine as a residue. To this residue, water (120 mL) and Na_2CO_3 (83.6 g, 789 mmol, 3.0 equiv) was added, followed by CbzCl (45.1 mL, 316 mmol, 1.2 equiv). After being stirred at r.t. for 12 h, the mixture was diluted with water (300 mL), and was extracted with Et_2O (3 × 200 mL) to remove excess amount of CbzCl. Then the water phase was acidified with conc. HCl (aq), and was extrated with ethyl acetate (4 × 200 mL). The organic phase was dried over anhydrous Na_2SO_4, and was concentrated under vacuum to give crude acid product **S3** as a syrup, which was directly used in the next step without further purification.

The crude **S3** was dissolved in DMF (150 mL), then $KHCO_3$ (52.6 g, 526 mmol, 2.0 equiv) and MeI (24.5 mL, 394 mmol, 1.5 equiv) were added sequentially. After being stirred at r.t. for 12 h, the mixture was diluted with ethyl acetate (700 mL) and thoroughly washed with water (5 × 200 mL) and brine (200 mL). The organic phase was dried over anhydrous Na_2SO_4, concentrated under vacuum, and purified by silica gel flash chromatography using *n*-hexane : ethyl acetate 1 : 1 *v*/*v* as eluent. The product **10** was obtained as white solid (54.4 g, 77% over 4 steps).[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20 (d, J = 6.4 Hz, 3H), 3.08 (d, J = 4.8 Hz, 1H), 3.74 (s, 3H), 4.10–4.15 (m, 1H), 4.42 (dd, J_1 = 7.2 Hz, J_2 = 2.8 Hz, 1H), 5.10 (s, 2H), 5.83 (d, J = 7.2 Hz, 1H), 7.30–7.34 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.0, 52.6, 59.5, 67.4, 68.8, 128.2, 128.3, 128.6, 136.1, 156.6, 170.9.

Part 2. Diastereoselective synthesis of thioesters via aldol-type addition of glycine thioester isonitrile to the chiral aldehydes.

Methyl (2*S*,3*S*)-2-benzyloxycarbonylamino-3-(*tert*-butyldiphenylsiloxy)butyrate (11):

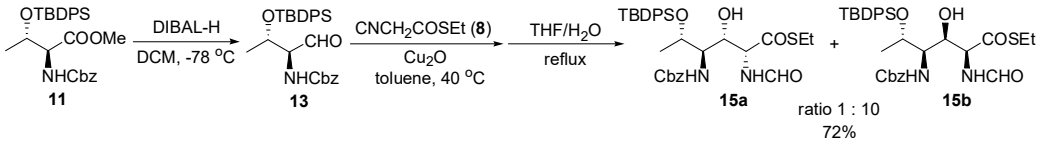
To a stirred solution of **10** (11.1 g, 41.5 mmol, 1.0 equiv) in anhydrous DMF (50 mL), imidazole (6.23 g, 91.4 mmol) and TBDPSCl (11.9 mL, 45.7 mmol, 1.1 equiv) were added sequentially. The mixture was stirred at r.t. for 36 h, then was diluted by ethyl acetate (400 mL). The organic phase was thoroughly washed with water (5 × 200 mL), dried over anhydrous Na_2SO_4, concentrated under vacuum, and purified by silica gel flash chromatography using *n*-hexane : ethyl acetate 20 : 1 to 10 : 1 *v*/*v* as eluent. The product **11** was obtained as colorless oil (19.9 g, 95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (s, 9H), 1.12 (d, J = 6.4 Hz, 3H), 3.75 (s, 3H), 4.11–4.17 (m, 1H), 4.34 (dd, J_1 = 8.4 Hz, J_2 = 3.2 Hz, 1H), 5.04 (d, J = 12.4 Hz, 1H), 5.08 (d, J = 12.4 Hz, 1H), 5.51 (d, J = 8.8 Hz, 1H), 7.31–7.43 (m, 11H), 7.62–7.67 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.3, 20.3, 26.9, 52.3, 60.2, 66.9, 71.0, 127.7, 127.9, 128.0, 128.2, 128.6, 129.9, 130.0, 133.2, 133.8, 135.91, 135.93, 136.5, 155.7, 170.5.

HR-ESI-MS (m/z): calcd for $C_{29}H_{35}NO_5SiNa^+$ (M + Na^+): 528.2177, found: 528.2193.

***S*-Ethyl (2*R*,3*S*,4*S*,5*S*)/(2*S*,3*R*,4*S*,5*S*)- 3-benzyloxycarbonylamino-4-(*tert*-butyldiphenylsiloxy) -2-formylamino-3-hydroxybutanethioate (15a/15b):**



The ester **11** (4.70 g, 9.3 mmol, 1.0 equiv) was dissolved in anhydrous DCM (100 mL), then the mixture was cooled to −78 °C. To this solution, DIBAL-H (1.0 M solution in hexane, 28.0 mL, 28.0 mmol, 3.0 equiv) was added dropwise within 20 min. After addition, the mixture was stirred at −78 °C for another 2 h, and was quenched by MeOH (5 mL) at the same temperature. The mixture was washed with 1 M HCl (aq) (2 × 50 mL), water (100 mL), and brine (100 mL). The

organic phase was dried over anhydrous Na_2SO_4, concentrated under vacuum, and purified by silica gel flash chromatography using *n*-hexane : ethyl acetate 5 : 1 *v*/*v* as eluent. The product **13** was obtained as colorless oil (3.85 g, 87%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02 (s, 9H), 1.31 (d, *J* = 6.4 Hz, 3H), 4.19–4.25 (m, 2H), 5.04 (s, 2H), 5.57 (d, *J* = 6.4 Hz, 1H), 7.33–7.44 (m, 11H), 7.61 (d, *J* = 6.8 Hz, 4H), 9.85 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.3, 20.9, 27.0, 65.7, 67.0, 71.1, 127.8, 127.9, 128.1, 128.2, 128.6, 130.0, 130.1, 132.8, 133.4, 135.86, 135.90, 136.4, 156.0, 198.4.

HR-ESI-MS (m/z): calcd for $C_{28}H_{33}NO_4SiNa^+$ (M + Na^+): 498.2071, found: 498.2051.

The aldehyde **13** (3.85 g, 8.1 mmol, 1.0 equiv) was dissolved in anhydrous toluene (30 mL), then isonitrile **8**[3] (1.25 g, 9.7 mmol, 1.2 equiv) was added, followed by Cu_2O (116 mg, 0.81 mmol, 0.10 equiv). The mixture was then stirred at 40 ^{o}C for 2 h. After full conversion of **13**, the mixture was filtered to remove Cu_2O, and the filtrate was concentrated under vacuum. The residue was dissolved in THF (40 mL) and water (20 mL), and the mixture was refluxed overnight. The THF was removed under vacuum, and the water phase was extracted with ethyl acetate (200 mL). The organic phase was washed with brine (100 mL), dried over anhydrous Na_2SO_4, and concentrated under vacuum. The ^{1}H NMR of the crude product indicated a 1 : 10 mixture of **15a** and **15b** was formed. The mixture of diastereomers **15a/15b** was purified by silica gel chromatography using *n*-hexane : ethyl acetate 3 : 1 to 2 : 1 *v*/*v* as eluent and was obtained as white solid (3.61 g, 72%). The pure major diastereomer **15b** was obtained as white solid via recrystallization from *n*-hexane/ethyl acetate. The minor diastereomer **15a** was collected from the mother solution and further purified by preparative TLC. Both **15a** and **15b** were mixture of rotamers caused by *cis*/*trans* tautomerization of formamide group.

For diastereomer **15a**:

^{1}H NMR (500 MHz, CD_3CN, selected peaks of major rotamer): δ = 0.92 (d, *J* = 6.5 Hz, 3H), 1.02 (s, 9H), 1.19 (t, *J* = 7.5 Hz, 3H), 2.81–2.86 (m, 2H), 3.74–3.79 (m, 2H), 3.93–3.98 (m, 1H), 4.49–4.51 (m, 1H), 4.55–4.57 (m, 1H), 5.02 (d, *J* = 12.5 Hz, 1H), 5.07 (d, *J* = 12.5 Hz, 1H), 5.61 (br, 1H), 7.18 (br, 1H), 7.30–7.48 (m, 11H), 7.68–7.71 (m, 4H), 8.03 (s, 1H).

^{13}C NMR (125 MHz, CD_3CN, selected peaks of major rotamer): δ = 14.8, 19.7, 19.8, 24.0, 27.4, 60.1, 61.4, 67.1, 69.4, 70.5, 128.60, 128.64, 128.7, 128.8, 129.4, 130.8, 130.9, 136.7, 136.8, 157.6, 162.4, 200.5.

HR-ESI-MS (m/z): calcd for $C_{33}H_{42}N_2O_6SSiNa^+$ (M + Na^+): 645.2425, found: 645.2420.

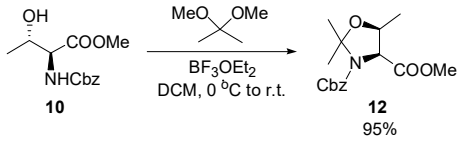
For diastereomer **15b**:

^{1}H NMR (400 MHz, CD_3CN, selected peaks of major rotamer): δ = 0.91 (d, *J* = 6.4 Hz, 3H), 1.01 (s, 9H), 1.19 (t, *J* = 7.2 Hz, 3H), 2.80–2.86 (m, 2H), 3.71–3.76 (m, 2H), 3.91–3.97 (m, 1H), 4.47 (q, *J* = 4.4 Hz, 1H), 4.53 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 5.01 (d, *J* = 12.4 Hz, 1H), 5.06 (d, *J* = 12.4 Hz, 1H), 5.59 (d, *J* = 9.6 Hz, 1H), 7.16 (d, *J* = 8.8 Hz, 1H), 7.34–7.47 (m, 11), 7.67–7.71 (m, 4H), 8.02 (s, 1H).

^{13}C NMR (100 MHz, CD_3CN, selected peaks of major rotamer): δ = 14.8, 19.6, 19.7, 24.0, 27.3, 60.0, 61.3, 67.1, 69.4, 70.4, 128.59, 128.63, 128.7, 128.8, 129.4, 130.8, 130.9, 134.4, 135.1, 136.7, 136.8, 157.6, 162.4, 200.5.

HR-ESI-MS (m/z): calcd for $C_{33}H_{42}N_2O_6SSiNa^+$ (M + Na^+): 645.2425, found: 645.2416.

Benzyl (4*S*,5*S*)-4-methoxycarbonyl-2,2,5-trimethyl-1,3-oxazolidine-3-carboxylate (12):



To a stirred solution of **10** (10.3 g, 38.5 mmol, 1.0 equiv) in anhydrous DCM (100 mL), 2,2-dimethoxypropane (23.7 mL, 193 mmol, 5.0 equiv) was added. The mixture was cooled to 0 °C, then $BF_3{\cdot}OEt_2$ (0.48 mL, 3.85 mmol, 0.10 equiv) was added dropwise. The mixture was gradually warmed to r.t. and stirred overnight. The reaction was quenched by Et_3N (2 mL), then the mixture was washed with $NaHCO_3$ (sat. aq, 2 × 50 mL) and brine (50 mL). The organic phase was dried over anhydrous Na_2SO_4, concentrated under vacuum, and purified by silica gel flash chromatography using *n*-hexane : ethyl acetate 15 : 1 *v*/*v* as eluent. The product **12** was obtained as colorless oil (11.3 g, 95%).

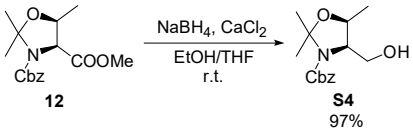
^{1}H NMR (400 MHz, $CDCl_3$, 2 : 1 mixture of two rotamers): δ = 1.25 (d, *J* = 5.6 Hz, 2H, major), 1.26 (d, *J* = 5.6 Hz, 1H, minor), 1.50 (s, 1H, minor), 1.56 (s, 2H, major), 1.70 (s, 1H, minor), 1.77 (s, 2H, major), 3.64 (s, 2H, major), 3.76 (s, 1H, minor), 4.38–4.45 (m, 2H, major & minor), 5.03 (d, *J* = 12.4 Hz, 0.67H, major), 5.14 (d, *J* = 12.4 Hz, 0.33H, minor), 5.16 (d, *J* = 12.4 Hz, 0.67H, major), 5.20 (d, *J* = 12.4 Hz, 0.33H, minor), 7.30–7.37 (m, 5H, major & minor).

^{13}C NMR (100 MHz, $CDCl_3$, 2 : 1 mixture of two rotamers): δ = 15.6 (major & minor), 24.3

(major), 25.4 (minor), 25.5 (major), 26.7 (minor), 52.0 (major), 52.1 (minor), 63.2 (major), 63.8 (minor), 66.8 (major), 67.7 (minor), 71.6 (minor), 72.0 (major), 127.7 (major), 128.07 (major), 128.13 (minor), 128.3 (minor), 128.5 (major), 128.7 (minor), 136.2 (minor), 136.5 (major), 151.7 (major), 153.0 (minor), 170.2 (minor), 170.3 (major).

HR-ESI-MS (m/z): calcd for $C_{16}H_{21}NO_5Na^+$ ($M + Na^+$): 330.1312, found: 330.1296.

Benzyl (4*S*,5*S*)-4-hydorxymethyl-2,2,5-trimethyl-1,3-oxazolidine-3-carboxylate (S4):



To a 250 mL round bottom flask, $CaCl_2$ (10.6 g, 95.9 mmol, 1.5 equiv) was added, followed by EtOH (120 mL). The mixture was sonicated to give a clear solution. To this solution, $NaBH_4$ (7.26 g, 192 mmol, 3.0 equiv) was added, followed by the solution of **12** (19.6 g, 63.9 mmol, 1.0 equiv) in anhydrous THF (60 mL). The mixture was stirred at r.t. for 24 h. The excess amount of hydride species was quenched by 1 M HCl (aq), then the mixture was diluted with ethyl acetate (400 mL) and water (200 mL). The organic phase was separated, and the water phase was extracted with ethyl acetate (2 × 150 mL). The combined organic phase was washed with brine (100 mL), dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by silica gel flash chromatography using *n*-hexane : ethyl acetate 2 : 1 *v*/*v* as eluent. The product **S4** was obtained as colorless oil (17.3 g, 95%).

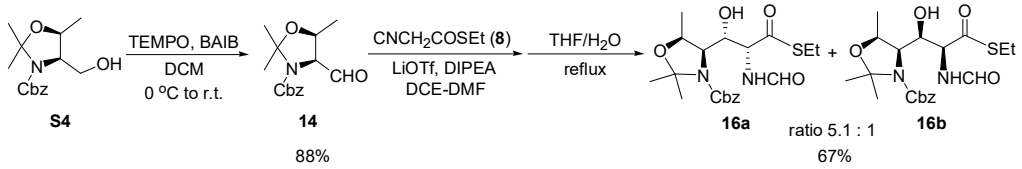
^{1}H NMR (400 MHz, $CDCl_3$, 1.3 : 1 mixture of two rotamers): δ = 1.31 (d, *J* = 6.4 Hz, 1.68H, major), 1.36 (d, *J* = 6.4 Hz, 1.32H, minor), 1.50 (s, 1.68H, major), 1.55 (s, 1.68H, major), 1.57 (s, 1.32H, minor), 1.62 (s, 1.32H, minor), 2.22 (br, 0.44H, minor), 3.38 (br, 0.56H, major), 3.62–3.70 (m, 1H, major & minor), 3.80–3.88 (m, 1.44H, major & minor), 4.02 (q, *J* = 5.6 Hz, 0.56H, major), 4.25–4.31 (m, 1H, major & minor), 5.12 (s, 0.88H, minor), 5.16 (s, 1.12H, major), 7.32–7.38 (m, 5H, major & minor).

^{13}C NMR (100 MHz, $CDCl_3$, 1.3 : 1 mixture of two rotamers): δ = 14.4 (major & minor), 23.4 (minor), 24.7 (major), 26.6 (minor), 27.8 (major), 60.7 (major & minor), 61.97 (minor), 62.03 (major), 66.8 (minor), 67.7 (major), 71.6 (major), 72.2 (minor), 93.1 (major), 93.3 (minor), 128.0 (major), 128.1 (major), 128.2 (minor), 128.3 (minor), 128.6 (major & minor), 136.0 (major), 136.5

(minor), 152.3 (minor), 154.6 (major).

HR-ESI-MS (m/z): calcd for $C_{15}H_{21}NO_4Na^+$ (M + Na^+): 302.1363, found: 302.1347.

Benzyl (4*S*,5*S*)-4-[(1*S*,2*R*)/(1*R*,2*S*)-3-ethylthio-2-formylamino-1-hydroxy-3-oxopropyl]-2,2,5-trimethyl-1,3-oxazolidine-3-carboxylate (16a/16b):



To a stirred solution of **S4** (5.34 g, 19.1 mmol, 1.0 equiv) in anhydrous DCM (110 mL), BAIB (8.01 g, 24.9 mmol, 1.3 equiv) was added at 0 °C, followed by TEMPO (597 mg, 3.8 mmol, 0.20 equiv). The mixture was gradually warmed to r.t. and was stirred overnight at the same temperature. After full conversion of **S4**, the mixture was diluted with DCM (100 mL) and thoroughly washed with $NaHCO_3$ (sat. aq, 2 × 100 mL). The organic phase was dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by silica gel flash chromatography using *n*-hexane : ethyl acetate 10 : 1 to 6 : 1 *v*/*v* as eluent. The product **14** was obtained as colorless oil (4.65 g, 88%).

^{1}H NMR (500 MHz, $CDCl_3$, 2 : 1 mixture of two rotamers): δ = 1.31–1.33 (m, 3H, major & minor), 1.53 (s, 1H, minor), 1.60 (s, 2H, major), 1.67 (s, 1H, minor), 1.75 (s, 2H, major), 4.18–4.20 (m, 0.66H, major), 4.29–4.31 (m, 0.34H, minor), 4.40–4.45 (m, 1H, major & minor), 5.06 (d, *J* = 12.5 Hz, 0.66H, major), 5.10 (d, *J* = 12.5 Hz, 0.66H, major), 5.16 (d, *J* = 12.5 Hz, 0.34H, minor), 5.20 (d, *J* = 12.5 Hz, 0.34H, minor), 7.25–7.36 (m, 5H, major & minor), 9.55 (s, 0.66H, major), 9.61 (s, 0.34H, minor).

^{13}C NMR (125 MHz, $CDCl_3$, 2 : 1 mixture of two rotamers): δ = 15.1 (major), 15.2 (minor), 23.8 (major), 25.0 (minor), 26.5 (major), 27.5 (minor), 67.0 (major), 67.6 (major), 67.8 (minor), 68.2 (minor), 72.1 (minor), 72.6 (major), 94.2 (minor), 94.9 (major), 127.8 (major), 128.2 (major), 128.4 (minor), 128.6 (major), 128.7 (minor), 135.9 (minor), 136.1 (major), 152.0 (major), 153.2 (minor), 199.8 (minor), 200.0 (major).

HR-ESI-MS (m/z): calcd for $C_{15}H_{19}NO_4Na^+$ (M + Na^+): 300.1206, found: 300.1200.

To the solution of freshly prepared **14** (4.65 g, 16.8 mmol, 1.0 equiv) in DCE (68 mL), isonitrile **8** (2.60 g, 20.1 mmol, 1.2 equiv) was added, followed by the solution of LiOTf (3.14 g,

20.1 mmol, 1.2 equiv) in anhydrous DMF (16.8 mL). The final concentration of **14** was controlled at 0.20 M. To this mixture, DIPEA (0.59 mL, 3.4 mmol, 0.20 equiv) was added to initiate the reaction. The mixture was stirred at r.t. for 2 h, then was diluted with DCM (200 mL) and thoroughly washed with water and brine. The organic phase was concentrated under vacuum, and the residue was dissolved in THF (60 mL) and water (30 mL). The mixture was refluxed overnight, then the THF was removed under vacuum. The water phase was extracted with ethyl acetate (200 mL), then the organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The ^{1}H NMR of the crude product indicated a 5.1 : 1 mixture of **16a** and **16b** was formed. The residue was purified by silica gel column chromatography. The minor diastereomer **16b** was eluted by *n*-hexane : ethyl acetate 3 : 1 *v*/*v* and obtained as colorless syrup (0.79 g, 11%), while the major diastereomer **16a** was eluted by *n*-hexane : ethyl acetate 2 : 1 *v*/*v* and obtained as white solid (4.01 g, 56%).

For diastereomer **16a**:

^{1}H NMR (400 MHz, CD_3CN, mixture of rotamers): δ = 1.20 (t, *J* = 7.6 Hz, 3H), 1.28–1.34 (m, 3H), 1.44–1.56 (m, 6H), 2.84 (q, *J* = 7.6 Hz, 2H), 3.76–3.79 (m, 0.44 H), 3.85–3.87 (m, 0.56H), 4.01 (br, 0.56H), 4.22–4.42 (m, 3H), 4.66 (d, *J* = 12.8 Hz, 0.44H), 4.78 (d, *J* = 6.8 Hz, 0.44H), 5.07 (d, *J* = 12.0 Hz, 0.56H), 5.16 (d, *J* = 12.0 Hz, 0.56H), 5.26 (d, *J* = 12.8 Hz, 0.44H), 7.16–7.24 (m, 1H), 7.33–7.42 (m, 5H), 7.91 (s, 0.56H), 8.03 (s, 0.44H).

^{13}C NMR (100 MHz, CD_3CN, mixture of rotamers): δ = 14.7, 15.0, 15.1, 23.7, 24.0, 24.6, 27.6, 60.0, 60.4, 61.2, 63.3, 63.4, 67.4, 68.4, 70.1, 70.2, 71.4, 73.0, 74.1, 94.0, 128.2, 128.6, 129.2, 129.3, 129.4, 129.5, 137.3, 137.9, 153.4, 155.8, 162.8, 202.4, 202.6.

HR-ESI-MS (m/z): calcd for $C_{20}H_{28}N_2O_6SNa^+$ ($M + Na^+$): 447.1560, found: 447.1562.

For diastereomer **16b**:

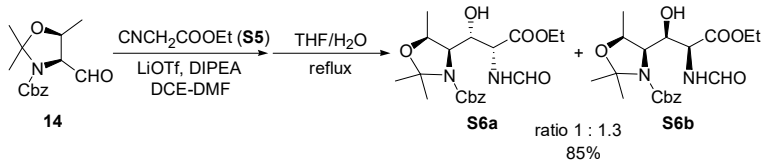
^{1}H NMR (400 MHz, CD_3CN, mixture of rotamers): δ = 1.21 (t, *J* = 7.2 Hz, 3H), 1.26–1.32 (m, 3H), 1.49–1.54 (m, 6H), 3.52–3.56 (m, 0.59H), 3.77–3.82 (m, 1H), 3.88–3.93 (m, 0.41H), 4.16–4.29 (m, 2H), 4.49 (d, *J* = 8.4 Hz, 0.59H), 4.72 (d, *J* = 6.8 Hz, 0.41H), 4.96 (d, *J* = 12.0 Hz, 0.59H), 5.06 (d, *J* = 12.0 Hz, 0.59H), 5.10–5.19 (m, 0.82H), 6.70 (br, 0.59H), 7.76–7.83 (m, 5.41H), 7.78 (s, 0.59H), 8.28 (s, 0.41H).

^{13}C NMR (100 MHz, CD_3CN, mixture of rotamers): δ = 14.5, 14.7, 14.9, 23.8, 24.0, 25.1, 26.9, 27.7, 60.0, 61.1, 67.4, 68.1, 68.5, 70.8, 72.6, 73.1, 93.8, 128.8, 129.0, 129.2, 129.5, 137.6, 138.1,

153.7, 156.1, 162.6, 162.9, 200.3.

HR-ESI-MS (m/z): calcd for $C_{20}H_{28}N_2O_6SNa^+$ ($M + Na^+$): 447.1560, found: 447.1559.

Benzyl (4*S*,5*S*)-4-[(1*S*,2*R*)/(1*R*,2*S*)-2-ethoxycarbonyl-2-formylamino-1-hydroxyethyl]-2,2,5-trimethyl-1,3-oxazolidine-3-carboxylate (S6a/S6b):



To the solution of freshly prepared **14** (68 mg, 0.24 mmol, 1.0 equiv) in DCE (1.6 mL), glycine *O*-ester derived isonitrile **S5** (33 mg, 0.29 mmol, 1.2 equiv) was added, followed by the solution of LiOTf (46 mg, 0.29 mmol, 1.2 equiv) in anhydrous DMF (0.4 mL). The final concentration of **14** was controlled at 0.12 M. To this mixture, DIPEA (8.5 μL, 0.48 mmol, 0.20 equiv) was added to initiate the reaction. The mixture was stirred at r.t. for 48 h to achieve full conversion of the aldehyde, then was diluted with ethyl acetate (20 mL) and thoroughly washed with water and brine. The organic phase was concentrated under vacuum, and the residue was dissolved in THF (4 mL) and water (2 mL). The mixture was refluxed overnight, then the THF was removed under vacuum. The water phase was extracted with ethyl acetate (20 mL), then the organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The ^{1}H NMR of the crude product indicated a 1 : 1.3 mixture of **S6a** and **S6b** was formed. The residue was purified by silica gel column chromatography. The major diastereomer **S6a** was eluted by *n*-hexane : ethyl acetate 1.5 : 1 *v*/*v* and obtained as colorless oil (47 mg, 48%), while the minor diastereomer **S6b** was eluted by *n*-hexane : ethyl acetate 1 : 1 *v*/*v* and obtained as white solid (36 mg, 37%).

For the same reaction, when the LiOTf in the above condition was changed to $LiBF_4$, almost no conversion (< 5%) was observed. When Cu_2O (20 mol%) was used as catalyst in toluene at 40 ^{o}C, 90% yield (**S6a** : **S6b** = 1 : 1.4) was obtained. These results demonstrate the much lower reactivity of the *O*-ester isonitrile **S5** than *S*-ester isonitrile **8**. It is due to the stronger capability of the thioester group for the stabilization of neibouring anion in the nucleophile than the corresponding ester group.

For diastereomer **S6a**:

^{1}H NMR (400 MHz, CD_3CN, mixture of rotamers): δ = 1.24 (t, *J* = 7.2 Hz, 3H), 1.30–1.38 (m,

3H), 1.50–1.55 (m, 6H), 3.41 (d, *J* = 6.4 Hz, 0.55H), 3.78–3.86 (m, 1H), 3.93–3.97 (m, 0.45H), 4.10–4.19 (m, 3H), 4.23–4.28 (m, 1H), 4.50 (d, *J* = 8.4 Hz, 0.55H), 4.72 (d, *J* = 7.6 Hz, 0.45H), 4.97 (d, *J* = 11.6 Hz, 0.55H), 5.08–5.16 (m, 1.45H), 6.59 (br, 0.55H), 7.19 (br, 0.45H), 7.34–7.42 (m, 5H), 7.79 (s, 0.55H), 8.24 (s, 0.45H).

^{13}C NMR (100 MHz, CD_3CN, mixture of rotamers): δ = 14.4, 14.9, 23.9, 25.1, 27.0, 27.8, 54.5, 60.0, 61.0, 62.4, 67.4, 68.2, 69.0, 71.5, 72.6, 73.2, 93.6, 93.7, 128.9, 129.1, 129.2, 129.5, 137.6, 138.1, 153.7, 156.4, 162.4, 162.7, 170.8.

HR-ESI-MS (m/z): calcd for $C_{20}H_{28}N_2O_7Na^+$ ($M + Na^+$): 431.1789, found: 431.1777.

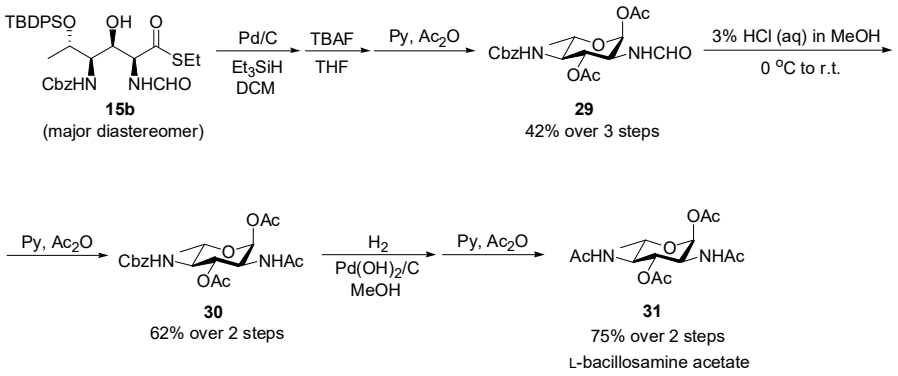
For diastereomer **S6b**:

^{1}H NMR (500 MHz, CD_3CN, mixture of rotamers): δ = 1.23 (t, *J* = 7.0 Hz, 3H), 1.30–1.37 (m, 3H), 1.42–1.48 (m, 3H), 1.51–1.55 (m, 3H), 3.66 (br, 0.45H), 3.84–3.88 (m, 0.45H), 4.03 (br, 0.55H), 4.12–4.24 (m, 3H), 4.26–4.40 (m, 2H), 4.69 (d, *J* = 12.5 Hz, 0.45H), 4.87 (d, *J* = 5.0 Hz, 0.55H), 5.09 (d, *J* = 12.0 Hz, 0.55H), 5.19 (d, *J* = 12.0 Hz, 0.55H), 5.26 (d, *J* = 12.5 Hz, 0.45H), 6.88–6.92 (m, 1H), 7.35–7.41 (m, 5H), 7.89 (s, 0.45H), 7.96 (s, 0.55H).

^{13}C NMR (125 MHz, CD_3CN, mixture of rotamers): δ = 14.4, 15.1, 15.3, 23.8, 24.7, 27.4, 53.4, 53.9, 61.4, 62.3, 63.8, 67.4, 68.5, 69.8, 71.0, 73.0, 74.1, 94.1, 128.4, 128.7, 129.3, 129.4, 129.5, 137.4, 138.0, 153.6, 156.2, 162.6, 172.0.

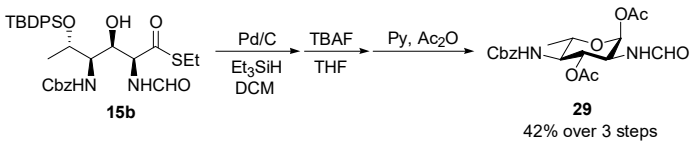
HR-ESI-MS (m/z): calcd for $C_{20}H_{28}N_2O_7Na^+$ ($M + Na^+$): 431.1789, found: 431.1776.

Part 3. Elucidation of the stereochemistry of 15b via derivatization.



Scheme S2. Elucidation of the stereochemistry of 15b via derivatization.

4-Benzyloxycarbonylamino-1,3-di-*O*-acetyl-2-formylamino-2,4,6-trideoxy-β-L-glucopyranose (29):



To a 50 mL round bottom flask, thioester **15b** (623 mg, 1.00 mmol, 1.0 equiv) and Pd/C (10% Pd on activated carbon, 100 mg, 0.10 equiv base on Pd) were added. After argon protection of the flask, anhydrous DCM (10 mL) was added, and the mixture was stirred mildly. Et_3SiH (0.60 mL, 3.80 mmol, 3.8 eq.) was added dropwise during 20 min, then the mixture was mildly stirred at r.t. for 2 h. When full conversion of 15**b** was achieved as indicate by TLC, the mixture was filtered through celite, and the filtrate was concentrated under vacuum to give the crude aldehyde, which was used directly in the next reaction without storage.

To the flask containing crude aldehyde, THF (18 mL) was added, followed by TBAF (1.0 M solution in THF, 2.0 mL, 2.00 mmol, 2.0 equiv). The mixture was stirred at r.t. for 12 h. When full deprotection of TBDPS group was achieved as indicated by TLC, the solution was concentrated under vacuum, and the residue was re-dissolved in pyridine (4.0 mL). To this mixture, Ac_2O (2.0 mL) was added. After being stirred at r.t. for 2 h, the mixture was concentrated under vacuum, and the residue was diluted with ethyl acetate (30 mL). The solution was sequentially washed with 1 M HCl (aq), sat. $NaHCO_3$ (aq), and brine. The organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum. The residue was purified by silica gel flash chromatography using *n*-hexane : ethyl acetate 1 : 2 as eluent. The product **29** was obtained as colorless syrup (170 mg, 42% over 3 steps). In NMR, **29** was the mixture of rotamers caused by

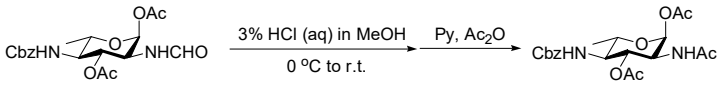
cis/*trans* isomerization of formamide group.

^{1}H NMR (400 MHz, $CDCl_3$, selected peaks of major rotamer): δ = 1.27 (d, *J* = 6.0 Hz, 3H, H-6), 1.95 (s, 3H, C*H*$_3$CO), 2.15 (s, 3H, C*H*$_3$CO), 3.65 (q, *J* = 10.0 Hz, 1H, H-4), 3.79–3.87 (m, 1H, H-5), 4.50 (td, J_1 = 10.4 Hz, J_2 = 3.6 Hz, 1H, H-2), 4.80 (d, *J* = 9.6 Hz, 1H, NH), 5.03–5.17 (m, 3H, H-3 & 2 × PhC*H*$_2$), 5.77 (d, *J* = 9.2 Hz, 1H, NH), 6.15 (d, *J* = 3.6 Hz, 1H, H-1), 7.33–7.37 (m, 5H, ArH), 8.12 (s, NHC*H*O).

^{13}C NMR (100 MHz, $CDCl_3$, selected peaks of major rotamer): δ = 17.9, 20.8, 21.1, 50.1, 56.8, 67.2, 69.4, 69.8, 70.4, 90.8, 128.2, 128.4, 128.7, 136.4, 156.0, 161.0, 169.1, 172.3.

HR-ESI-MS (m/z): calcd for $C_{19}H_{24}N_2O_8Na^+$ (M + Na^+): 431.1419, found: 431.1406.

2-Acetamido-1,3-di-*O*-acetyl-4-benzyloxycarbonylamino-2,4,6-trideoxy-β-L-glucopyranose (30):



29 **30**

62% over 2 steps

To a 50 mL round bottom flask, a solution of HCl (aq) in MeOH (3%, 6 mL, prepared from conc. HCl 0.5 mL and MeOH 5.5 mL) was added. The mixture was cooled to 0 °C, then **29** (170 mg, 0.42 mmol, 1.0 equiv) was added. The mixtrue was stirred at 0 °C to r.t. for 8 h. The solvent was removed under vacuum without heating, and the residue was co-evaporated with MeCN for two times to remove water and HCl thoroughly. The crude intermediate with formyl group removed was obtained as colorless foam. This foam was dissolved in pyridine (2.0 mL), then Ac_2O (1.0 mL) and DMAP (5 mg, 0.042 mmol, 0.10 equiv) were added. The mixture was stirred at r.t. for 1 h, then was concentrated under vacuum. The residue was co-evaporated with toluene for three times to thoroughly remove pyridine and Ac_2O, then was purified by silica gel flash chromatography using DCM : MeOH 30 : 1 as eluent. The product **30** was obtained as white solid (108 mg, 62%).

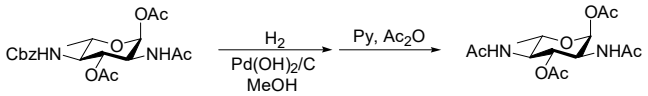
^{1}H NMR (400 MHz, $CDCl_3$, selected peaks of α anomer): δ = 1.26 (d, *J* = 6.0 Hz, 3H, H-6), 1.90 (s, 3H, C*H*$_3$CO), 1.94 (s, 3H, C*H*$_3$CO), 2.15 (s, 3H, C*H*$_3$CO), 3.64 (q, *J* = 10.0 Hz, 1H, H-4), 3.83–3.87 (m, 1H, H-5), 4.40 (ddd, J_1 = 10.8 Hz, J_2 = 9.2 Hz, J_3 = 3.2 Hz, 1H, H-2), 5.00–5.16 (m, 4H, H-3, NH & 2 × PhC*H*$_2$), 5.76 (d, *J* = 8.8 Hz, 1H, NH), 6.13 (d, *J* = 3.2 Hz, 1H, H-1),

7.31−7.35 (m, 5H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$, selected peaks of α anomer): δ = 17.9, 20.8, 21.1, 23.1, 51.7, 56.8, 67.1, 69.3, 70.6, 91.1, 128.2, 128.4, 128.7, 136.4, 156.0, 169.4, 170.4, 172.3.

HR-ESI-MS (m/z): calcd for $C_{20}H_{26}N_2O_8Na^+$ (M + Na^+): 445.1581, found: 445.1561.

2,4-Diacetamido-1,3-di-*O*-acetyl-2,4,6-trideoxy-β-L-glucopyranose (31):



To a 25 mL round bottom flask, **30** (94 mg, 0.22 mmol, 1.0 equiv) was added, followed by $Pd(OH)_2$/C (20% $Pd(OH)_2$ on activate carbon, 20 mg) and MeOH (5 mL). The mixture was stirred under 1 atm H_2 atmosphere for 2 h, then was filtered through celite to remove the catalyst. The filtrate was concentrated under vacuum, and the residue was dissolved in pyridine (2.0 mL). Ac_2O (1.0 mL) and DMAP (3 mg, 0.022 mmol, 0.10 equiv) were added, then the mixture was stirred at r.t. for 1 h. The mixture was concentrated under vacuum, then the residue was co-evaporated with toluene for three times to thoroughly remove pyridine and Ac_2O. The residue was purified by silica gel flash chromatography using DCM : MeOH 7 : 1 as eluent. The product **31** was obtained as white solid (55 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (d, *J* = 6.0 Hz, 3H, H-6), 1.95 (s, 3H, C*H*$_3$CO), 2.00 (s, 3H, C*H*$_3$CO), 2.06 (s, 3H, C*H*$_3$CO), 2.17 (s, 3H, C*H*$_3$CO), 3.82–3.89 (m, 1H, H-5), 3.99 (q, *J* = 10.0 Hz, 1H, H-4), 4.30 (ddd, J_1 = 10.8 Hz, J_2 = 9.2 Hz, J_3 = 3.6 Hz, 1H, H-2), 5.10 (t, *J* = 10.4 Hz, 1H H-3), 5.94 (d, *J* = 9.2 Hz, 1H, NH), 6.03 (d, *J* = 9.2 Hz, 1H, NH), 6.14 (d, *J* = 3.6 Hz, 1H, H-1).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.9, 20.9, 21.1, 23.1, 23.2, 51.6, 55.0, 69.2, 70.4, 91.0, 169.5, 171.0, 171.1, 172.4.

HR-ESI-MS (m/z): calcd for $C_{14}H_{22}N_2O_7Na^+$ (M + Na^+): 353.1314, found: 353.1303.

This compound **31** shows exactly the same ^{1}H and ^{13}C NMR to the 2,4-diacetamido-1,3-di-*O*-acetyl-2,4,6-trideoxy-α-D-glucopyranose, which was reported by Ito et al.[4]

Part 4. Analysis of distereoselectivity model for isonitrile addition.

Felkin-Anh model and Cram model are two diastereoselectivity models widely used in literatures. As shown in the figure, for bulky TBDPS group protected aldehyde **13**, Felkin-Anh model (stereoelectronic effect dominates) predict the formation of the desired product, while the Cram model (steric effect dominates) predict the undesired one. To inverse this diastereoselectivity, the size of the protecting group on the hydroxyl group should be minimized. Thus, we chose the acetonide protected Garner-type aldehyde **14**. To further weaken the effect of steric repulsion, lithium cation is involved to chelate the oxygen atoms from aldehyde group and protected hydroxyl group.

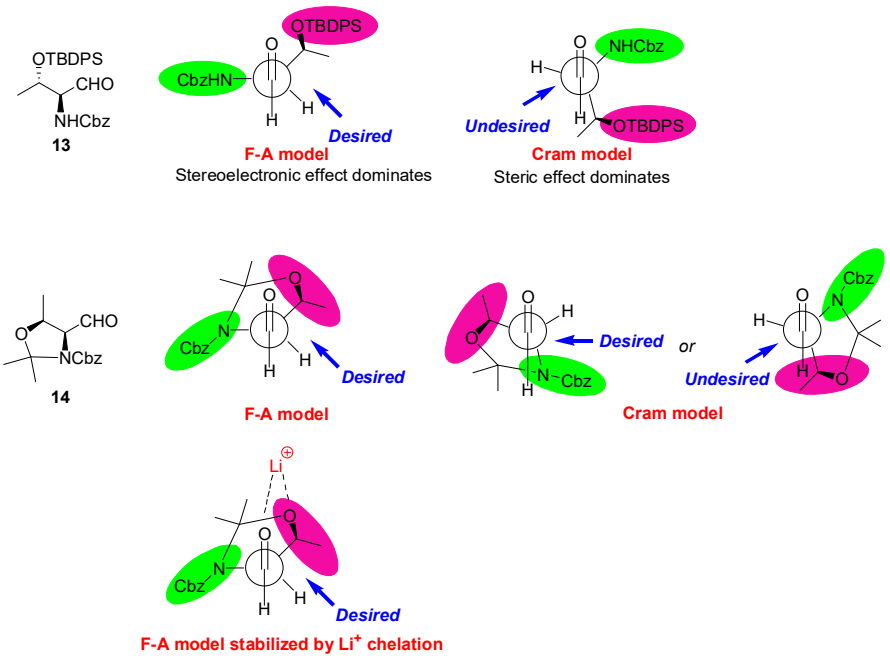
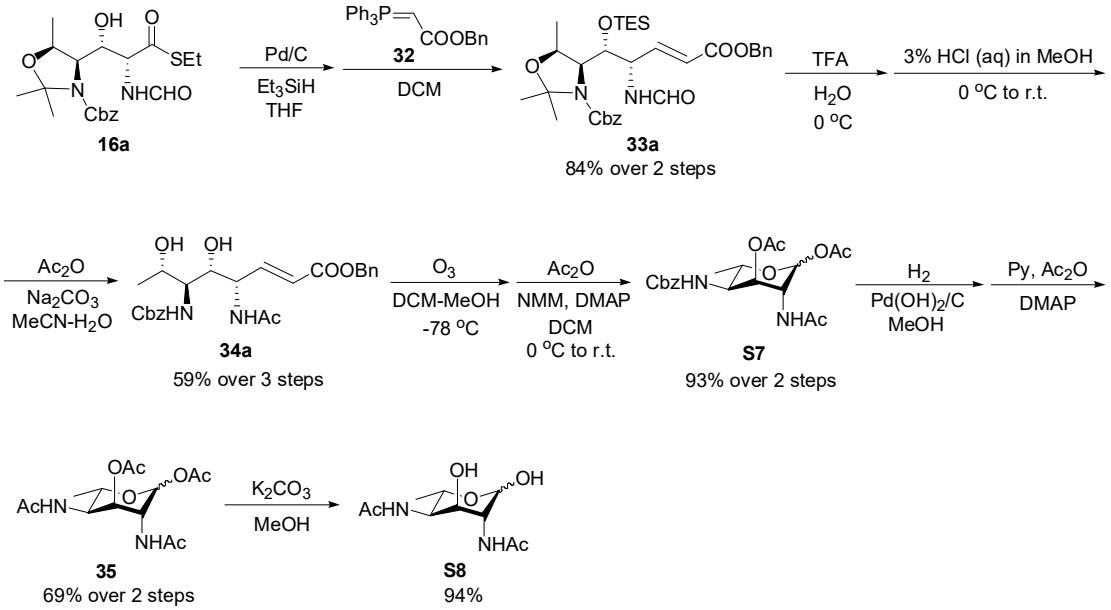


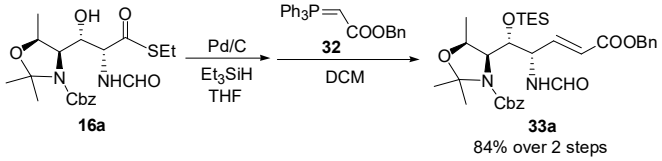
Figure S1. Analysis of the diastereoselectivity model of the aldol-type addition.

Part 5. Elucidation of the stereochemistry of 16 via derivatization.



Scheme S3. Elucidation of the stereochemistry of 16a via derivatization.

Benzyl (4*S*,5*S*)-4-[(1*R*,2*S*)-4-benzyloxycarbonyl-2-formylamino-1-triethylsiloxy-3-buten-1-yl]-2,2,5-trimethyl-1,3-oxazolidine-3-carboxylate (33a)



To a 50 mL round bottom flask, thioester **16a** (424 mg, 1.00 mmol, 1.0 equiv) and Pd/C (10% Pd on activated carbon, 100 mg, 0.10 equiv base on Pd) were added. After argon protection of the flask, anhydrous THF (5 mL) was added, and the mixture was stirred mildly. Et_3SiH (0.60 mL, 3.80 mmol, 3.8 eq.) was added dropwise during 20 min, then the mixture was mildly stirred at r.t. for 2 h. When full conversion of **16a** was achieved as indicate by TLC, the mixture was filtered through celite, and the filtrate was concentrated under vacuum. The residue was dilute with DCM (10 mL), and was sitrred with 1 M HCl (aq, 0.10 mL) for 40 min. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude aldehyde was obtained in crude form and directly used in the next step.

To the solution of crude aldehyde in DCM (10 mL), ylide **32** (615 mg, 1.50 mmol, 1.5 equiv) was added in one portion. The mixture was stirred at r.t. for 45 min, then the solvent was removed

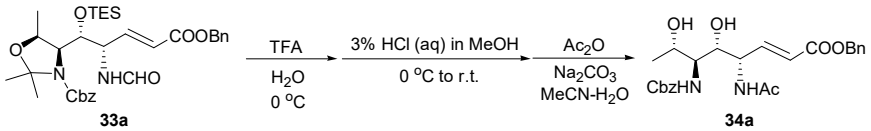
under vacuum. The residue was purified by silica gel flash chromatography using *n*-hexane : ethyl acetate 3 : 1 as eluent. The product **33a** was obtained as colorless syrup (511 mg, 84% over 2 steps).

^{1}H NMR (400 MHz, CD_3CN, selected peaks of major rotamer): δ = 0.55–0.60 (m, 6H), 0.90 (*t*, J = 7.6 Hz, 9H), 1.34 (d, *J* = 6.4 Hz, 3H), 1.45 (s, 3H), 1.50 (s, 3H), 3.96 (dd, J_1 = 6.0 Hz, J_2 = 2.4 Hz, 1H), 4.12 (br, 1H), 4.29–4.36 (m, 1H), 4.51 (br, 1H), 5.05 (d, *J* = 12.4 Hz, 1H), 5.13 (d, *J* = 12.4 Hz, 1H), 5.14 (d, *J* = 12.4 Hz, 1H), 5.18 (d, *J* = 12.4 Hz, 1H), 5.87 (d, *J* = 14.8 Hz, 1H), 6.54 (br, 1H), 6.87 (d, *J* = 14.8 Hz, 1H), 7.33–7.41 (m, 10H), 7.78–7.93 (m, 1H).

^{13}C NMR (100 MHz, CD_3CN, selected peaks of major rotamer): δ = 5.9, 7.3, 16.2, 23.3, 26.9, 53.0, 64.1, 66.9, 67.3, 73.2, 74.0, 94.1, 122.6, 129.07, 129.10, 129.2, 129.49, 129.52, 137.4, 138.0, 147.6, 154.1, 161.5, 166.4.

HR-ESI-MS (m/z): calcd for $C_{33}H_{46}N_2O_7SiNa^+$ (M + Na^+): 633.2966, found: 633.2952.

Benzyl *trans*-(4*S*,5*R*,6*S*,7*S*)-4-acetamido-6-benzyloxycarbonylamino-5,7-dihydroxy-2-octenoate (34a):



To a 25 mL round bottom flask, TFA (4.5 mL) and H_2O (0.5 mL) were added. The mixture was cooled to 0 °C , then **33a** (178 mg, 0.29 mmol, 1.0 equiv) was added. The mixture was stirred at 0 °C for 30 min, then was concentrated under vacuum without heating. The residue was co-evaporated with *n*-hexane for two times to remove TFA thoroughly.

To the flask containg the residue, a cold solution of HCl (aq) in MeOH (3%, 6 mL, prepared from conc. HCl 0.5 mL and MeOH 5.5 mL) was added. The mixture was stirred at 0 °C to r.t. for 8 h, then the solvent was removed under vacuum without heating, and the residue was co-evaporated with MeCN for two times to remove water and HCl thoroughly. The crude intermediate with formyl group removed was obtained as colorless foam.

To the solution the of crude intermediate in MeCN (4 mL), Ac_2O (0.11 mL, 1.16 mmol, 4.0 equiv) was added, followed by 0.5 M Na_2CO_3 (aq) (2 mL). The mixture was stirred at r.t. for 2 h,

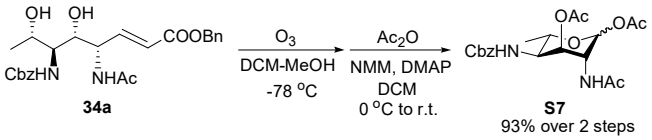
then was concentrated under vacuum. The residue was purified by silica gel flash chromatography using DCM : MeOH 30 : 1 as eluent. The product **34a** was obtained as white solid (82 mg, 59% over 3 steps).

^{1}H NMR (600 MHz, CD_3CN): δ = 1.10 (d, *J* = 6.3 Hz, 3H), 1.91 (s, 3H), 3.49–3.52 (m, 1H), 3.57 (d, *J* = 4.6 Hz, 1H), 3.88 (d, *J* = 9.0 Hz, 1H), 3.92–3.95 (m, 1H), 4.37 (d, *J* = 3.9 Hz, 1H), 4.71–4.73 (m, 1H), 4.97 (d, *J* = 12.5 Hz, 1H), 5.03 (d, *J* = 12.5 Hz, 1H), 5.14 (s, 2H), 5.59 (d, *J* = 10.0 Hz, 1H), 5.93 (dd, J_1 = 15.7 Hz, J_2 = 1.8 Hz, 1H), 6.61 (d, *J* = 8.6 Hz, 1H), 6.93 (dd, J_1 = 15.7 Hz, J_2 = 4.6 Hz, 1H), 7.29–7.38 (m, 10H).

^{13}C NMR (150 MHz, CD_3CN): δ = 20.0, 23.1, 52.8, 57.7, 66.9, 67.0, 70.2, 74.7, 122.0, 128.6, 128.8, 129.10, 129.12, 129.4, 129.5, 137.5, 138.3, 149.3, 157.3, 166.7, 171.1.

HR-ESI-MS (m/z): calcd for $C_{25}H_{30}N_2O_7Na^+$ (M + Na^+): 493.1940, found: 493.1920.

2-Acetamido-1,3-di-*O*-acetyl-4-benzyloxycarbonylamino-2,4,6-trideoxy-L-altropyranose (S7):



The solution of **34a** (101 mg, 0.22 mmol, 1.0 equiv) in DCM (10 mL) and MeOH (1 mL) was cooled to -78 °C. The O_3 (generated from O_2 and carried by the flow of O_2) was bubbled though this solution for 30 min. The colour of the solution turn purple, which indicated the saturation of O_3 in DCM. The excess amount of O_3 was blown off by the flow of O_2 and the purple colour disappeared. To this solution, Me_2S (0.50 mL, excess) was added to reduce the peroxide intermediate. After 1 h reduction at r.t., the solution was concentrated, and the residue was purified by silica gel flash chromatography using DCM : MeOH 20 : 1 as eluent. The intermediate was directly used in the next step.

The intermediate was dissolved in anhydrous DCM (10 mL) and the solution was cooled to 0 °C. To this solution, Ac_2O (0.12 mL, 1.25 mmol, 6.0 equiv), *N*-methylmorpholine (0.14 mL, 1.25 mmol, 6.0 equiv), and DMAP (2.5 mg, 0.022 mmol, 0.10 equiv) were added sequentially. The mixture was stirred at 0 °C to r.t. for 2 h, then was diluted with DCM (50 mL). The solution was washed with 1 M HCl (aq) and brine. The organic phase was dried over anhydrous Na_2SO_4, and

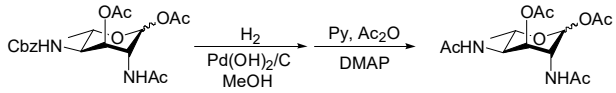
concentrated under vacuum. The residue was purified by silica gel flash chromatography using DCM : MeOH 40 : 1 as eluent. The product **S7** was obtained as colorless syrup (86 mg, 93% over 2 steps).

^{1}H NMR (500 MHz, $CDCl_3$, selected peaks of major anomer): δ = 1.32 (d, *J* = 5.5 Hz, 3H, H-6), 2.078 (s, 3H, C*H*$_3$CO), 2.10 (s, 3H, C*H*$_3$CO), 2.13 (s, 3H, C*H*$_3$CO), 3.87–3.88 (m, 2H, H-4 & H-5), 4.39 (ddd, J_1 = 8.5 Hz, J_2 = 4.0 Hz, J_3 = 2.0 Hz, 1H, H-2), 4.80 (d, *J* = 8.5 Hz, 1H, NH), 5.07 (d, *J* = 12.0 Hz, 1H, PhC*H*$_2$), 5.12 (d, *J* = 12.0 Hz, 1H, PhC*H*$_2$), 5.21 (dd, J_1 = 4.0 Hz, J_2 = 2.5 Hz, 1H, H-3), 5.86 (d, *J* = 8.5 Hz, 1H, NH), 5.98 (d, *J* = 2.0 Hz, 1H, H-1), 7.33–7.39 (m, 5H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$, selected peaks of major anomer): δ = 18.4, 21.1, 23.5, 49.3, 50.9, 67.7, 70.7, 72.7, 90.2, 128.4, 128.6, 128.8, 136.0, 156.0, 169.0, 169.4, 170.2.

HR-ESI-MS (m/z): calcd for $C_{20}H_{26}N_2O_8Na^+$ (M + Na^+): 445.1581, found: 445.1557.

2,4-Diacetamido-1,3-di-*O*-acetyl-2,4,6-trideoxy-L-altropyranose (35):



To a 25 mL round bottom flask, **S7** (86 mg, 0.20 mmol, 1.0 equiv) was added, followed by $Pd(OH)_2$/C (20% $Pd(OH)_2$ on activate carbon, 20 mg) and MeOH (5 mL). The mixture was stirred under 1 atm H_2 atmosphere for 2 h, then was filtered through celite to remove the catalyst. The filtrate was concentrated under vacuum, and the residue was dissolved in pyridine (2.0 mL). Ac_2O (1.0 mL) and DMAP (2.5 mg, 0.020 mmol, 0.10 equiv) were added, then the mixture was stirred at r.t. for 1 h. The mixture was concentrated under vacuum, then the residue was co-evaporated with toluene for three times to thoroughly remove pyridine and Ac_2O. The residue was purified by silica gel flash chromatography using DCM : MeOH 20 : 1 as eluent. The product **35** was obtained as colorless syrup (46 mg, 69% over 2 steps).

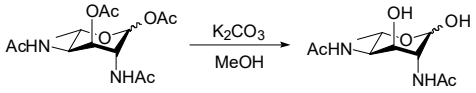
^{1}H NMR (500 MHz, $CDCl_3$, 1 : 0.9 mixture of α and β anomers): δ = 1.24 (d, *J* = 6.4 Hz, 2.7H, H-6, β), 1.29 (d, *J* = 6.4 Hz, 3H, H-6, α), 2.00 (s, 3H, C*H*$_3$CO, α), 2.01 (s, 2.7H, C*H*$_3$CO, β), 2.03 (s, 2.7H, C*H*$_3$CO, β), 2.06 (s, 3H, C*H*$_3$CO, α), 2.097 (s, 2.7H, C*H*$_3$CO, β), 2.102 (s, 3H, C*H*$_3$CO, α), 2.14 (s, 2.7H, C*H*$_3$CO, β), 2.15 (s, 3H, C*H*$_3$CO, α), 3.90–3.93 (m, 1H, H-5, α), 4.05–4.08 (m, 0.9H, H-5, β), 4.26 (td, J_1 = 9.2 Hz, J_2 = 3.3 Hz, 1H, H-4, α), 4.30 (td, J_1 = 9.4 Hz, J_2 = 3.4 Hz,

0.9H, H-4, β), 4.40–4.45 (m, 1.9H, H-2, α & β), 4.94 (t, J = 3.4 Hz, 0.9 H, H-3, β), 5.17 (dd, J_1 = 4.8 Hz, J_2 = 3.4 Hz, 1H, H-3, α), 5.75 (d, J = 9.5 Hz, 0.9H, NH, β), 5.79 (d, J = 9.5 Hz, 1H, NH, α), 5.88 (d, J = 1.6 Hz, 0.9H, H-1, β), 6.01 (d, J = 2.2 Hz, 1H, H-1, α), 6.16 (d, J = 8.6 Hz, 1H, NH, α), 6.54 (d, J = 9.0 Hz, 0.9H, NH, β).

^{13}C NMR (125 MHz, $CDCl_3$, 1 : 0.9 mixture of α and β anomers): δ = 17.6 (α), 18.4 (β), 20.9 (α), 20.96 (β), 20.99 (α & β), 23.1 (b), 23.2 (α), 23.30 (α), 23.34 (β), 48.05 (β), 48.12 (α), 48.7 (α), 48.9 (β), 66.5 (β), 69.8 (α), 70.3 (β), 72.6 (α), 90.3 (α), 91.4 (β), 168.8 (β), 169.0 (α), 169.59 (α or β), 169.60 (α or β), 169.7 (β), 169.9 (β), 170.0 (α), 170.2 (α).

HR-ESI-MS (m/z): calcd for $C_{14}H_{22}N_2O_7Na^+$ ($M + Na^+$): 353.1314, found: 353.1303.

2,4-Diacetamido -2,4,6-trideoxy-L-altropyranose (S8):



35 **S8** 94%

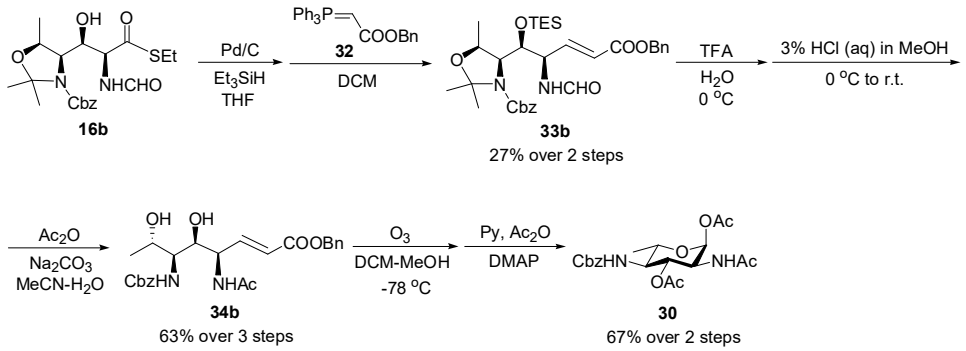
To a stirred solution of **35** (21 mg, 0.063 mmol) in MeOH (4.0 mL), K_2CO_3 (1.8 mg, 0.013 mmol, 0.20 equiv) was added. The solution was stirred at r.t. for 1 h, and the K_2CO_3 dissolved gradually. The pH of the system was around 9. After full conversion of the material, the reaction was quenched with DOWEX-50(H) resin. After filtration, the solvent was removed under vacuum, and the crude product was obtained as colorless solid. After further purification by BioGel column using H_2O as eluent, **S8** was obtained as white powder (15 mg, 94%).

^{1}H NMR (500 MHz, D_2O, 0.3 : 1 mixture of α and β anomers): δ = 1.21 (d, J = 6.1 Hz, 2.3H, H-6β), 1.24 (d, J = 6.4 Hz, 0.7 H, H-6α), 2.03 (s, 2.3H, CH_3COβ), 2.04 (s, 0.7H, CH_3COα), 2.05 (s, 0.7H, CH_3COα), 2.09 (s, 2.3H, CH_3COβ), 3.82 (dd, J_1 = 10.4 Hz, J_2 = 3.0 Hz, 0.77H, H-4β), 3.91–3.97 (m, 2H, H-3α, H-3β, H-4α & H-5β), 4.51 (dd, J_1 = 4.4 Hz, J_2 = 2.7 Hz, 0.23H, H-2α), 4.10 (dd, J_1 = 3.2 Hz, J_2 = 1.8 Hz, 0.77H, H-2β), 4.24 (dt, J_1 = 8.6 Hz, J_2 = 6.5 Hz, 0.23H, H-5α), 5.05 (d, J = 2.5 Hz, 0.23H, H-1α), 5.28 (d, J = 1.8 Hz, 0.77H, H-1β).

^{13}C NMR (125 MHz, D_2O, 0.3 : 1 mixture of α and β anomers): δ = 16.7 (α), 17.2 (β), 20.9 (α), 21.89 (α), 21.92 (β), 21.95 (β), 50.7 (β), 51.0 (α), 52.3 (α), 53.5 (β), 64.3 (α), 67.2 (α), 68.1 (β), 69.4 (β), 90.6 (β), 92.2 (α), 174.06 (β), 174.11 (α), 174.8 (α and β).

This compound **S8** shows exactly the same ^{1}H and ^{13}C NMR to the

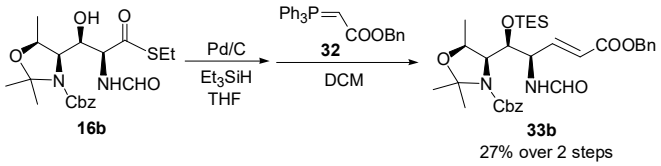
2,4-diacetamido-2,4,6-trideoxy-α/β-D-altropyranose, which was reported by Ito et al.[5]



Scheme S4. Elucidation of the stereochemistry of 16b via derivatization.

Benzyl

(4*S*,5*S*)-4-[(1*S*,2*R*)-4-benzyloxycarbonyl-2-formylamino-1-triethylsiloxy-3-buten-1-yl]-2,2,5-trimethyl-1,3-oxazolidine-3-carboxylate (33b)



To a 50 mL round bottom flask, thioester **16b** (212 mg, 0.50 mmol, 1.0 equiv) and Pd/C (10% Pd on activated carbon, 50 mg, 0.10 equiv base on Pd) were added. After argon protection of the flask, anhydrous THF (2.5 mL) was added, and the mixture was stirred mildly. Et_3SiH (0.30 mL, 1.90 mmol, 3.8 eq.) was added dropwise during 20 min, then the mixture was mildly stirred at r.t. for 2 h. When full conversion of **16b** was achieved as indicate by TLC, the mixture was filtered through celite, and the filtrate was concentrated under vacuum. The residue was dilute with DCM (5 mL), and was sitrred with 1 M HCl (aq, 0.050 mL) for 40 min. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude aldehyde was obtained in crude form and directly used in the next step.

To the solution of crude aldehyde in DCM (5 mL), ylide **32** (308 mg, 0.75 mmol, 1.5 equiv) was added in one portion. The mixture was stirred at r.t. for 45 min, then the solvent was removed under vacuum. The residue was purified by silica gel flash chromatography using *n*-hexane : ethyl acetate 3 : 1 as eluent. The product **33b** was obtained as colorless syrup (82 mg, 27% over 2 steps).

^{1}H NMR (500 MHz, $CDCl_3$, 1.5 : 1 mixture of rotamers): δ = 0.56–0.64 (m, 2.4H, minor), 0.65–0.74 (m, 3.6H, major), 0.92 (t, J = 8.0 Hz, 3.6H, minor), 0.99 (t, J = 8.0 Hz, 5.4H, major), 1.29 (d, J = 6.6 Hz, 1.2H, minor), 1.37 (d, J = 6.6 Hz, 1.8H, major), 1.45 (s, 1.8H, major), 1.56 (s, 1.8H, major), 1.58 (s, 1.2H, minor), 1.66 (s, 1.2H, minor), 3.72 (dd, J_1 = 8.4 Hz, J_2 = 5.2 Hz, 0.4H, minor), 3.93–3.96 (m, 1H, major & minor), 4.07 (dd, J_1 = 5.0 Hz, J_2 = 3.4 Hz, 0.6H, major), 4.18–4.21 (m, 0.6H, major), 4.23–4.26 (m, 0.4H, minor), 4.36 (br, 0.4H, minor), 4.74 (d, J = 12.2 Hz, 0.6H, major), 4.93 (d, J = 11.3 Hz, 0.4H, minor), 4.98 (br, 0.6H, major), 5.01 (d, J = 11.3 Hz, 0.4H, minor), 5.05 (s, 1.2H, major), 5.07 (d, J = 12.2 Hz, 0.6H, major), 5.18 (s, 0.8H, minor), 5.70 (d, J = 7.2 Hz, 0.4H, minor), 5.86 (dd, J_1 = 15.6 Hz, J_2 = 1.8 Hz, 0.4H, minor), 5.96 (dd, J_1 = 16.0 Hz, J_2 = 2.4 Hz, 0.6H, major), 6.82 (dd, J_1 = 15.6 Hz, J_2 = 4.6 Hz, 0.4H, minor), 7.24–7.46 (m, 11.2 H, major & minor), 8.33 (s, 1H, major & minor).

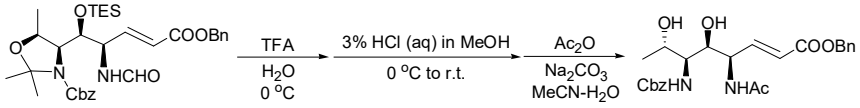
^{13}C NMR (125 MHz, $CDCl_3$, selected peaks of major rotamer): δ = 5.5, 6.9, 14.2, 25.3, 26.9, 50.8, 59.6, 66.2, 68.0, 72.0, 72.1, 94.1, 122.6, 128.1, 128.3, 128.4, 128.6, 129.0, 129.4, 135.6, 135.9, 144.8, 154.9, 161.0, 165.6.

HR-ESI-MS (m/z): calcd for $C_{33}H_{46}N_2O_7SiNa^+$ ($M + Na^+$): 633.2966, found: 633.2962.

Benzyl

***trans*-(4*R*,5*S*,6*S*,7*S*)-4-acetamido-6-benzyloxycarbonylamino-5,7-dihydroxy-2-octenoate**

(34b):



To a 25 mL round bottom flask, TFA (4.5 mL) and H_2O (0.5 mL) were added. The mixture was cooled to 0 °C , then **33b** (82 mg, 0.13 mmol, 1.0 equiv) was added. The mixture was stirred at 0 °C for 30 min, then was concentrated under vacuum without heating. The residue was co-evaporated with *n*-hexane for two times to remove TFA thoroughly.

To the flask containg the residue, a cold solution of HCl (aq) in MeOH (3%, 6 mL, prepared from conc. HCl 0.5 mL and MeOH 5.5 mL) was added. The mixture was stirred at 0 °C to r.t. for 8 h, then the solvent was removed under vacuum without heating, and the residue was co-evaporated with MeCN for two times to remove water and HCl thoroughly. The crude intermediate with

formyl group removed was obtained as colorless foam.

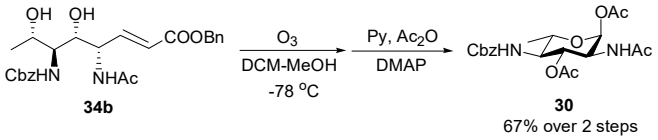
To the solution the of crude intermediate in MeCN (2 mL), Ac_2O (0.49 mL, 0.52 mmol, 4.0 equiv) was added, followed by 0.5 M Na_2CO_3 (aq) (1 mL). The mixture was stirred at r.t. for 2 h, then was concentrated under vacuum. The residue was purified by silica gel flash chromatography using DCM : MeOH 30 : 1 as eluent. The product **34b** was obtained as white solid (40 mg, 63% over 3 steps).

^{1}H NMR (400 MHz, CD_3CN): δ = 1.12 (d, J = 6.0 Hz, 3H), 1.90 (s, 3H), 3.42–3.47 (m, 1H), 3.70–3.76 (m, 1H), 4.05 (dd, J_1 = 6.4 Hz, J_2 = 2.0 Hz, 1H), 4.56–4.62 (m, 1H), 4.94 (d, J = 12.4 Hz, 1H), 5.08 (d, J = 12.4 Hz, 1H), 5.13 (s, 2H), 5.67 (d, J = 10.0 Hz, 1H), 5.93 (dd, J_1 = 15.6 Hz, J_2 = 2.0 Hz, 1H), 6.63 (d, J = 8.4 Hz, 1H), 7.02 (dd, J_1 = 15.6 Hz, J_2 = 5.2 Hz, 1H), 7.30–7.38 (m, 10H).

^{13}C NMR (100 MHz, CD_3CN): δ = 20.6 23.2, 54.3, 58.2, 66.9, 67.1, 68.4, 70.7, 121.8, 128.5, 128.8, 129.1, 129.4, 129.5, 147.1, 157.5, 166.7, 170.8.

HR-ESI-MS (m/z): calcd for $C_{25}H_{30}N_2O_7Na^+$ ($M + Na^+$): 493.1940, found: 493.1922.

2-Acetamido-1,3-di-*O*-acetyl-4-benzyloxycarbonylamino-2,4,6-trideoxy-L-glucopyranose (30):



The solution of **34b** (40 mg, 0.085 mmol, 1.0 equiv) in DCM (5 mL) and MeOH (0.5 mL) was cooled to -78 °C. The O_3 (generated from O_2 and carried by the flow of O_2) was bubbled though this solution for 15 min. The colour of the solution turn purple, which indicated the saturation of O_3 in DCM. The excess amount of O_3 was blown off by the flow of O_2 and the purple colour disappeared. To this solution, Me_2S (0.20 mL, excess) was added to reduce the peroxide intermediate. After 1 h reduction at r.t., the solution was concentrated, and the residue was purified by silica gel flash chromatography using DCM : MeOH 20 : 1 as eluent. The intermediate was directly used in the next step.

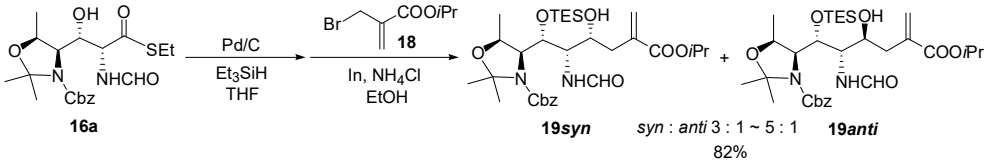
The residue was dissolved in pyridine (2.0 mL). Ac_2O (1.0 mL) and DMAP (1.0 mg, 0.008 mmol, 0.10 equiv) were added, then the mixture was stirred at r.t. for 1 h. The mixture was

concentrated under vacuum, then the residue was co-evaporated with toluene for three times to thoroughly remove pyridine and Ac_2O. The residue was purified by silica gel flash chromatography using DCM : MeOH 40 : 1 as eluent. The product **30** was obtained as white solid (24 mg, 67% over 2 steps).

This compound **30** shows exactly the same ^{1}H and ^{13}C NMR to the product **30** prepared from **29** (Part 3).

Part 6. Chain elongation through Fukuyama reduction and Barbier allylation.

Benzyl (4*S*,5*S*)-4-[(1*S*,2*S*,3*R*)/(1*S*,2*S*,3*S*)-2-formylamino-3-hydroxy-5-isopropyl-oxycarbonyl-1-(triethylsiloxy)hex-5-en-1-yl]-2,2,5-trimethyl-1,3-oxazolidine-3-carboxylate (19*syn*/19*anti*):



To a 250 mL round bottom flask, thioester **16a** (4.24 g, 10.0 mmol, 1.0 equiv) and Pd/C (10% Pd on activated carbon, 1.00g, 100 mg/mmol substrate, 0.10 equiv base on Pd) were added. After argon protection of the flask, anhydrous THF (40 mL) was added, and the mixture was stirred mildly. Et_3SiH (6.00 mL, 38 mmol, 0.60 mL/mmol substrate, 3.8 eq.) was added dropwise during 20 min, then the mixture was mildly stirred at r.t. for 2 h. When full conversion of **16a** was achieved as indicate by TLC, the mixture was filtered through celite, and the filtrate was concentrated under vacuum to give the crude aldehyde **17**, which was used directly in the Barbier reaction without storage.

To a 50 mL round bottom flask, indium powder (3.44 g, 30.0 mmol, 3.0 equiv) was added, followed by EtOH (40 mL), isopropyl bromomethylacrylate **18** (6.66 mL, 45.0 mmol, 4.5 equiv), and saturated NH_4Cl solution (6.0 mL). The mixture was sonicated for 20 min at 50 ^oC to generate the corresponding indium reagent. This so-obtained solution of indium reagent was added into the solution of crude aldehyde (freshly generated via Fukuyama reduction as described before) in EtOH (20 mL) in one portion, and the mixture was stirred at r.t. for 2 h. The reaction was quenched by $NaHCO_3$ (sat. aq, 50 mL), then the mixture was diluted with water (200 mL) and extracted with ethyl acetate (3 × 200 mL). The water phase was acidified by 1 M HCl solution, and was further extracted with ethyl acetate (2 × 150 mL). The organic phase was combined, sequentially washed with 1 M HCl (200 mL), $NaHCO_3$ (sat. aq, 200 mL), and brine, and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 3 : 1 *v*/*v* as eluent. The mixture of two diastereomers **19*syn*/*anti*** was obtained as colorless syrup (4.89 g, 82%).

For characterization, **19*syn*** and **19*anti*** were carefully separated by multiple silica gel column chromatography in small scale, and the ratio was calculated to be 3 : 1 ~ 5 : 1 (varied from batch

to batch) base on the weight of the purified **19*syn*** and **19*anti***. The configuration of the newly formed chiral center was not determined at this stage, due to the complex NMR spectra caused by the existence of multiple rotamers (from acetonide and formamide). In the following steps, the TES group and acetonide group on **19*syn*/*anti*** were removed to simplify the spectra, and the configuration was determined via comparison of the spectra with reported similar structures (*vide infra*).

For diastereomer **19*syn***:

^{1}H NMR (400 MHz, CD_3CN, complex mixture of rotamers): δ = 0.59–0.65 (m, 6H), 0.93 (t, *J* = 8.0 Hz, 9H), 1.23–1.26 (m, 6H), 1.42–1.44 (m, 3H), 1.46–1.49 (m, 3H), 1.59–1.61 (m, 3H), 2.34–2.45 (m, 2H), 3.89–4.05 (m, 3H), 4.28–4.36 (m, 2H), 4.97–5.04 (m, 1H), 5.06–5.18 (m, 2H), 5.62 (br, 1H), 6.15–6.18 (m, 1H), 6.35–6.54 (m, 1H), 7.32–7.39 (m, 5H), 7.90–8.13 (m, 1H).

^{13}C NMR (100 MHz, CD_3CN, complex mixture of rotamers): δ = 5.9, 6.2, 7.4, 7.5, 16.0, 22.0, 22.9, 24.3, 26.8, 27.7, 37.7, 38.0, 54.5, 62.2, 62.6, 62.8, 67.2, 67.7, 69.1, 69.2, 70.0, 72.8, 73.3, 73.6, 93.6, 127.9, 128.2, 129.0, 129.4, 137.8, 138.1, 138.8, 154.0, 154.8, 162.3, 162.6, 165.7, 167.5.

HR-ESI-MS (m/z): calcd for $C_{31}H_{50}N_2O_8SiNa^+$ ($M + Na^+$): 629.3229, found: 629.3210.

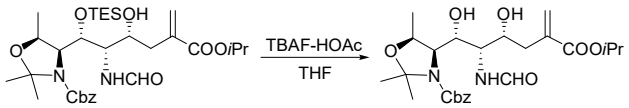
For diastereomer **19*anti***:

^{1}H NMR (400 MHz, CD_3CN, complex mixture of rotamers): δ = 0.66 (q, *J* = 8.0 Hz, 6H), 0.97 (t, *J* = 8.0 Hz, 9H), 1.23–1.26 (m, 6H), 1.35 (d, *J* = 6.8 Hz, 3H), 1.44 (s, 3H), 1.55 (s, 3H), 2.09–2.16 (m, 1H), 2.58–2.63 (m, 1H), 3.23 (br, 1H), 3.49 (br, 1H), 3.67 (br, 1H), 3.98 (d, *J* = 5.6 Hz, 1H), 4.31–4.38 (m, 1H), 4.59 (br, 1H), 4.94–5.00 (m, 1H), 5.09 (br, 2H), 5.62 (s, 1H), 6.12–6.14 (m, 1H), 6.31–6.54 (m, 1H), 7.32–7.44 (m, 5H), 7.85–7.97 (m, 1H).

^{13}C NMR (100 MHz, CD_3CN, complex mixture of rotamers): δ = 5.9, 7.4, 15.9, 21.99, 22.02, 23.2, 27.0, 38.0, 56.0, 65.3, 67.2, 67.8, 69.0, 70.3, 71.9, 73.4, 94.2, 127.7, 128.4, 129.0, 129.1, 129.5, 138.3, 139.3, 154.5, 161.6, 167.6.

HR-ESI-MS (m/z): calcd for $C_{31}H_{50}N_2O_8SiNa^+$ ($M + Na^+$): 629.3229, found: 629.3210.

Synthesis of benzyl (4*S*,5*S*)-4-[(1*S*,2*S*,3*R*)-2-formylamino-1,3-dihydroxy-5-(isopropyloxy-carbonyl)hex-5-en-1-yl]-2,2,5-trimethyl-1,3-oxazolidine-3-carboxylate (21*syn*):



19*syn* **21*syn*** 65%

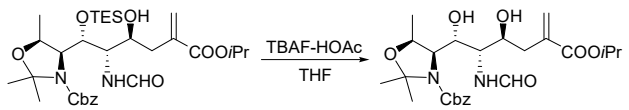
To an Eppendorf tube, TBAF (1 M solution in THF, 0.88 mL, 0.88 mmol, 2.0 equiv) and HOAc (0.061 mL, 1.06 mmol, 2.4 equiv) were added. The mixture was then added to a sitrred solution of **19*syn*** (270 mg, 0.44 mmol) in THF (8.0 mL). After being stirred at r.t. for 2 h, the mixture was diluted with ethyl acetate (50 mL) and washed with sat. $NaHCO_3$ (aq) and brine. The organic phase was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified silica gel flash chromatography using DCM : ethyl acetate 1 : 1 *v*/*v* as eluent. The product **21*syn*** was obtained as colorless syrup (143 mg, 65%). In NMR, **21*syn*** was a complex mixture of multiple rotamers, caused by acetonide and formamide.

^{1}H NMR (400 MHz, CD_3CN, selected peaks from complex mixture of multiple rotamers): δ = 1.22–1.25 (m, 6H), 1.34 (d, J = 6.8 Hz, 3H), 1.46 (s, 3H), 1.50 (s, 3H), 2.28–2.33 (m, 1H), 2.51 (dd, J_1 = 14.0 Hz, J_2 = 2.8 Hz, 1H), 3.53–3.56 (m, 1H), 3.76 (d, J = 7.6 Hz, 0.6H), 3.87–3.98 (m, 2.4H), 4.06–4.12 (m, 1.4H), 4.26–4.35 (m, 1H), 4.48 (d, J = 5.2 Hz, 0.6H), 4.82 (d, J = 12.8 Hz, 0.4H), 4.96–5.02 (m, 1H), 5.10 (d, J = 12.0 Hz, 0.6H), 5.18 (d, J = 12.0 Hz, 0.6H), 5.23 (d, J = 12.8 Hz, 0.4H), 5.64 (s, 1H), 6.13 (s, 1H), 6.70 (d, J = 7.2 Hz, 0.4H), 6.90 (d, J = 7.2 Hz, 0.6H), 7.36–7.40 (m, 5H), 7.95–7.99 (m, 1H).

^{13}C NMR (100 MHz, CD_3CN, selected peaks from complex mixture of multiple rotamers): δ = 15.3, 15.5, 22.0, 23.7, 24.8, 27.4, 27.5, 37.4, 37.7, 52.3, 54.4, 61.6, 63.7, 67.4, 68.4, 69.0, 69.1, 71.1, 71.2, 71.6, 72.5, 73.2, 73.4, 73.6, 74.1, 93.8, 127.6, 128.0, 128.5, 128.7, 129.2, 129.3, 129.4, 129.5, 137.5, 138.2, 139.0, 139.3, 153.5, 156.0, 162.7, 166.5, 167.5.

HR-ESI-MS (m/z): calcd for $C_{25}H_{36}N_2O_8Na^+$ ($M + Na^+$): 515.2364, found: 515.2368.

Synthesis of benzyl (4*S*,5*S*)-4-[(1*S*,2*S*,3*S*)-2-formylamino-1,3-dihydroxy-5-(isopropyloxy-carbonyl)hex-5- en-1-yl]-2,2,5-trimethyl-1,3-oxazolidine-3-carboxylate (21*anti*):



19*anti* **21*anti*** 81%

To an Eppendorf tube, TBAF (1 M solution in THF, 0.36 mL, 0.36 mmol, 2.0 equiv) and

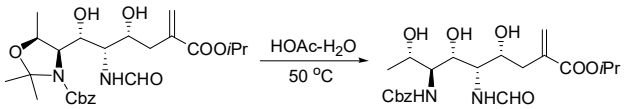
HOAc (0.025 mL, 0.43 mmol, 2.4 equiv) were added. The mixture was then added to a sitrred solution of **19*anti*** (108 mg, 0.18 mmol) in THF (4.0 mL). After being stirred at r.t. for 2 h, the mixture was diluted with ethyl acetate (30 mL) and washed with sat. $NaHCO_3$ (aq) and brine. The organic phase was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified silica gel flash chromatography using DCM : ethyl acetate 1 : 1 *v*/*v* as eluent. The product **21*anti*** was obtained as colorless syrup (71 mg, 81%). In NMR, **21*anti*** was a complex mixture of multiple rotamers, caused by acetonide and formamide.

^{1}H NMR (400 MHz, CD_3CN, selected peaks from complex mixture of multiple rotamers): δ = 1.23–1.25 (m, 6H), 1.32 (d, *J* = 6.4 Hz, 3H), 1.45–1.52 (m, 6H), 2.25–2.33 (m, 1H), 2.54–2.68 (m, 1H), 3.54–3.57 (m, 0.6H), 3.65–3.96 (m, 4H), 4.12–4.33 (m, 2H), 4.55 (d, *J* = 4.4 Hz, 0.4H), 4.73 (d, *J* = 12.8 Hz, 0.4H), 4.96–5.02 (m, 1H), 5.07–5.17 (m, 1.2H), 5.28 (d, *J* = 12.8 Hz, 0.4H), 5.65 (s, 1H), 6.14 (s, 1H), 6.85–6.89 (m, 1H), 7.34–7.40 (m, 5H), 7.85–7.96 (m, 1H).

^{13}C NMR (100 MHz, CD_3CN, selected peaks from complex mixture of multiple rotamers): δ = 15.5, 15.8, 22.0, 23.8, 24.9, 27.8, 37.2, 37.6, 53.4, 55.2, 61.2, 63.3, 67.3, 67.8, 68.3, 69.0, 69.1, 72.6, 73.3, 74.3, 93.8, 127.4, 127.5, 127.9, 128.3, 128.6, 129.0, 129.4, 129.5, 137.5, 138.2, 139.0, 139.3, 153.7, 155.8, 162.6, 163.2, 166.3, 167.5.

HR-ESI-MS (m/z): calcd for $C_{25}H_{36}N_2O_8Na^+$ (M + Na^+): 515.2364, found: 515.2366.

Synthesis of isopropyl (4*R*,5*S*,6*S*,7*S*,8*S*)-7-(benzyloxycarbonylamino)-5-formylamino-2-methylene-4,6,8- trihydroxynonanoate (22*syn*):



21*syn* **22*syn***
55%

To a 25 mL round bottom flask containing **21*syn*** (89 mg, 0.18 mmol), HOAc (3.0 mL) and H_2O (2.0 mL) were added. The mixture was stirred at 50 °C for 20 h. Then the mixture was concentrated under vacuum, and the residue was purified by silica gel flash chromatography using DCM : MeOH 30 : 1 to 15 : 1 *v*/*v* as eluent. The product **22*syn*** was obtained as colorless foam (45 mg, 55%). In NMR **22*syn*** was a mixture of rotamers caused by formamide *cis*/*trans* conformations.

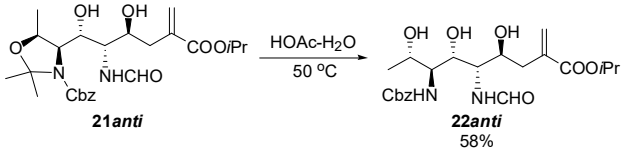
^{1}H NMR (400 MHz, CD_3CN, selected peaks from major rotamer): δ = 1.11 (d, *J* = 6.4 Hz, 3H),

1.24 (d, J = 6.0 Hz, 6H), 2.33 (dd, J_1 = 14.0 Hz, J_2 = 8.4 Hz, 1H), 2.46 (dd, J_1 = 14.0 Hz, J_2 = 4.0 Hz, 1H), 3.43 (q, J = 8.4 Hz, 1H), 3.62 (d, J = 4.0 Hz, 1H), 3.74 (br, 1H), 3.95–4.03 (m, 3H), 4.07–4.11 (m, 1H), 4.61 (br, 1H), 4.97–5.07 (m, 3H), 5.67 (d, J = 0.8 Hz, 1H), 5.70 (d, J = 9.6 Hz, 1H), 6.14 (d, J = 1.6 Hz, 1H), 6.81 (d, J = 9.2 Hz, 1H), 7.31–7.37 (m, 5H), 8.20 (s, 1H).

^{13}C NMR (100 MHz, CD_3CN, selected peaks from major rotamer): δ = 20.0, 22.0, 37.8, 51.6, 58.0, 67.0, 69.1, 70.0, 73.5, 75.7, 127.9, 128.6, 128.8, 129.4, 138.3, 138.7, 157.4, 162.9, 167.6.

HR-ESI-MS (m/z): calcd for $C_{22}H_{32}N_2O_8Na^+$ (M + Na^+): 475.2051, found: 475.2032.

Synthesis of isopropyl (4*S*,5*S*,6*S*,7*S*,8*S*)-7-(benzyloxycarbonylamino)-5-formylamino-2-methylene-4,6,8- trihydroxynonanoate (22*anti*):



21*anti* **22*anti***
58%

To a 25 mL round bottom flask containing **21*anti*** (70 mg, 0.14 mmol), HOAc (3.0 mL) and H_2O (2.0 mL) were added. The mixture was stirred at 50 °C for 20 h. Then the mixture was concentrated under vacuum, and the residue was purified by silica gel flash chromatography using DCM : MeOH 30 : 1 to 15 : 1 *v*/*v* as eluent. The product **22*anti*** was obtained as colorless foam (37 mg, 58%). In NMR **22*anti*** was a mixture of rotamers caused by formamide *cis*/*trans* conformations.

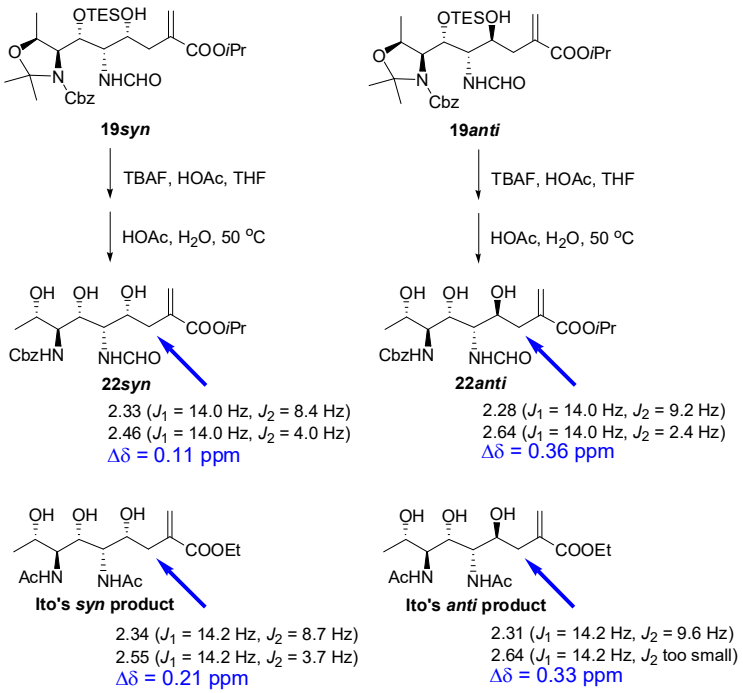
^{1}H NMR (400 MHz, CD_3CN, selected peaks from major rotamer): δ = 1.11 (d, J = 6.4 Hz, 3H), 1.24 (d, J = 6.4 Hz, 6H), 2.28 (dd, J_1 = 14.0 Hz, J_2 = 9.2 Hz, 1H), 2.64 (dd, J_1 = 14.0 Hz, J_2 = 2.4 Hz, 1H), 3.42–3.48 (m, 2H), 3.64 (br, 1H), 3.77–3.82 (m, 1H), 3.90–4.02 (m, 2H), 4.20 (d, J = 9.6 Hz, 1H), 4.50 (br, 1H), 4.97–5.07 (m, 3H), 5.64–5.67 (m, 2H), 6.14 (d, J = 1.6 Hz, 1H), 6.81 (d, J = 9.2 Hz, 1H), 7.31–7.37 (m, 5H), 8.12 (s, 1H).

^{13}C NMR (100 MHz, CD_3CN, selected peaks from major rotamer): δ = 19.9, 22.0, 37.9, 53.1, 57.7, 67.0, 69.1, 70.4, 71.6, 71.8, 127.7, 128.6, 128.8, 129.4, 138.3, 139.3, 157.4, 162.6, 167.6.

HR-ESI-MS (m/z): calcd for $C_{22}H_{32}N_2O_8Na^+$ (M + Na^+): 475.2051, found: 475.2032.

Comparison of the NMR spectra of 22*syn* and 22*anti* with the reported spectra of similar structures:

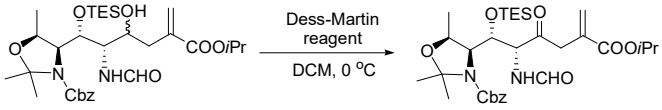
The configuration of the newly formed chiral center was determined via comparison the NMR spectra of **22** with Ito's product, which has similar structure.[5] As shown in the Figure S2, the differences betweeen δH-3a and δH-3b are smaller (0.11 ppm in **22*syn*** and 0.21 ppm in Ito's *syn* product) in *syn* diastereomers, while the differences are much larger (0.36 ppm in **22*anti*** and 0.33 ppm in Ito's *anti* product) in *anti* diastereomers. The coupling constants in **22*syn*** and **22*anti*** also show good accordance with Ito's *syn* and *anti* products, respectively.



Scheme S5. Comparison of adducts 21*syn*/*anti* with Ito's products.

Part 7. Synthesis of Pse glycosyl donors from chain elongation product.

Benzyl (4*S*,5*S*)-4-[(1*S*,2*R*)-2-formylamino-5-isopropyloxycarbonyl-3-oxo-1-(triethylsiloxy) -hex-5-en-1-yl]-2,2,5-trimethyl-1,3-oxazolidine-3-carboxylate (20):



19*syn* & 19*anti* **20** 98%

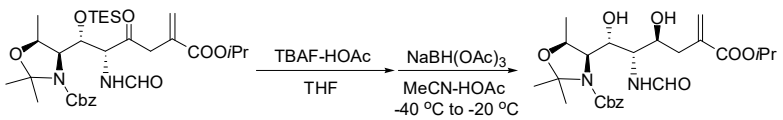
To a stirred solution of **19*syn*** and **19*anti*** mixture (2.56 g, 4.21 mmol, 1.0 equiv) in anhydrous DCM (35 mL), Dess-Martin reagent (2.68 g, 6.32 mmol, 1.5 equiv) was added at 0 °C. The mixture was sitrred at 0 °C for 2 h to achieve full conversion, as indicated by TLC. The mixture was then diluted with DCM (100 mL), filtered through celite, and washed with sat. $NaHCO_3$ (aq) and brine. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by silica gel flash chromatography using *n*-hexane : ethyl acetate 2 : 1 *v*/*v* as eluent to give **20** as colorless foam (2.50 g, 98%).

^{1}H NMR (400 MHz, CD_3CN, selected peaks from major rotamer): δ = 0.60 (q, *J* = 7.6 Hz, 6H), 0.94 (t, *J* = 7.6 Hz, 9H), 1.21 (d, *J* = 6.4 Hz, 3H), 1.22 (d, *J* = 6.4 Hz, 3H), 1.37 (d, *J* = 6.4 Hz, 3H), 1.45 (s, 3H), 1.48 (s, 3H), 3.44 (d, *J* = 18.0 Hz, 1H), 3.64 (d, *J* = 18.0 Hz, 1H), 3.97–3.99 (m, 1H), 4.30 (d, *J* = 6.8 Hz, 1H), 4.33–4.40 (m, 1H), 4.63 (s, 1H), 4.92–4.98 (m, 1H), 5.07 (d, *J* = 12.4 Hz, 1H), 5.17 (d, *J* = 12.4 Hz, 1H), 5.54 (s, 1H), 6.20 (s, 1H), 6.77 (br, 1H), 7.33–7.44 (m, 5H), 7.77 (br, 1H).

^{13}C NMR (100 MHz, CD_3CN, selected peaks from major rotamer): δ = 5.7, 7.3, 14.9, 15.8, 15.9, 21.87, 21.91, 44.0, 60.9, 62.6, 64.9, 65.1, 67.4, 69.2, 70.2, 71.0, 73.3, 94.3, 128.2, 129.1, 129.4, 129.5, 136.1, 162.2, 166.5, 167.4, 207.3.

HR-ESI-MS (m/z): calcd for $C_{31}H_{48}N_2O_8SiNa^+$ (M + Na^+): 627.3072, found: 627.3062.

Benzyl (4*S*,5*S*)-4-[(1*S*,2*S*,3*S*)-2-formylamino-1,3-dihydroxy-5-(isopropyloxycarbonyl)hex-5-en-1-yl]-2,2,5-trimethyl-1,3-oxazolidine-3-carboxylate (21*anti*):



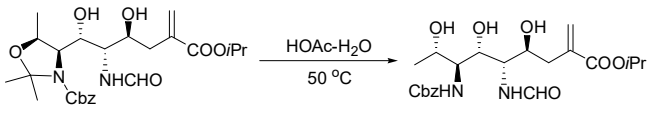
20 **21*anti***

To a plastic tube, TBAF (1 M in THF, 8.28 mL, 8.28 mmol, 2.0 equiv) and HOAc (0.57 mL,

9.94 mmol, 2.4 equiv) were added. This mixture was then added to the solution of **20** (2.50 g, 4.14 mmol, 1.0 equiv) in THF (50 mL). The mixture was stirred at r.t. for 2 h, then around half amount of the solvent was removed under vacuum. The residue was diluted with ethyl acetate (200 mL), and the organic phase was thoroughly washed with sat. $NaHCO_3$ (aq), water, and brine. The organic phase was dired over anhydrous Na_2SO_4 and concentrated under vacuum. The crude β-hydroxyketone intermediate was obtained as colorless syrup quantitatively and was directly used in the next step.

The β-hydroxyl group directed diastereoselective reduction was conducted following reported procedure.[6] To a 250 mL round bottom flask, $NaBH(OAc)_3$ (4.39 g, 20.7 mmol, 5.0 equiv), anhydrous MeCN (66 mL), and HOAc (6.6 mL) were added under argon sequentially. The mixture was stirred at –40 °C, then a solution of freshly prepared β-hydroxyketone in anhydrous MeCN (17 mL) was added dropwise. After addition, the mixtrue was stirred at –40 °C for 1 h, and was sitrred at –20 °C overnight. When full conversion was achieved as indicated by TLC, around 3/4 amount of the solvent was removed under vacuum, and the residue was diluted with ethyl acetate (200 mL). The organic phase was thoroughly washed with water, sat. $NaHCO_3$ (aq), and brine. After being dried over anhydrous Na_2SO_4, the solvent was removed under vacuum, and the residue was purified by silica gel flash chromatography using *n*-hexane : ethyl acetate 1 : 1.5 *v*/*v* as eluent. The product **21*anti*** was obtained as colorless foam (1.88 g, 92% over 2 steps). This product show exactly identical NMR spectra to the product obtained from **21*anti*** via deprotection of TES.

Isopropyl (4*S*,5*S*,6*S*,7*S*,8*S*)-7-(benzyloxycarbonylamino)-5-formylamino-2-methylene-4,6,8-trihydroxynonanoate (22*anti*):



21*anti* **22*anti***

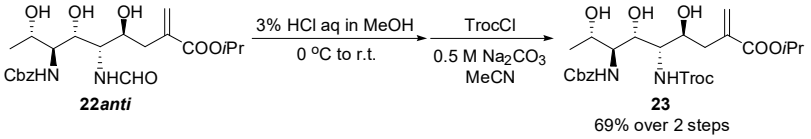
72% after 2 rounds conversion

To a 25 mL round bottom flask containing **21*anti*** (2.66 g, 5.40 mmol, 1.0 equiv), HOAc (12 mL) and H_2O (8 mL) were added. The mixture was stirred at 50 °C for 20 h. Then the mixture was concentrated under vacuum. The residue was purified by silica gel flash chromatography using DCM : MeOH 30 : 1 *v*/*v* as eluent to recover the unconverted material (1.40 g, 53%), and using

DCM : MeOH 15 : 1 *v*/*v* to elute the product (1.12 g, 46%).

The recovered material (1.40 g, 2.85 mmol) was redissolved in HOAc (9 mL) and H_2O (6 mL). The mixture was stirred at 50 °C for 20 h. After concentration, the residue was purified as described above. The product **22*anti*** (combined from two rounds) was obtained as colorless foam (1.77 g, 72%). This product show exactly identical NMR spectra to the sample synthesized in small scale.

Synthesis of isopropyl (4*S*,5*S*,6*S*,7*S*,8*S*)-7-(benzyloxycarbonylamino)-2-methylene-5-(2,2,2-trichloroethoxycarbonylamino)-4,6,8-trihydroxynonanoate (23):



To a 100 mL round bottom flask, a solution of HCl (aq) in MeOH (3%, 18 mL, prepared from conc. HCl 1.5 mL and MeOH 16.5 mL) was added. The mixture was cooled to 0 °C, then **22*anti*** (1.77 g, 3.92 mmol, 1.0 equiv) was added. The mixtrue was stirred at 0 °C to r.t. for 8 h. The solvent was removed under vacuum without heating, and the residue was co-evaporated with MeCN for two times to remove water and HCl thoroughly. The crude intermediate with formyl group removed was obtained as colorless foam, which was directly used in the next step.

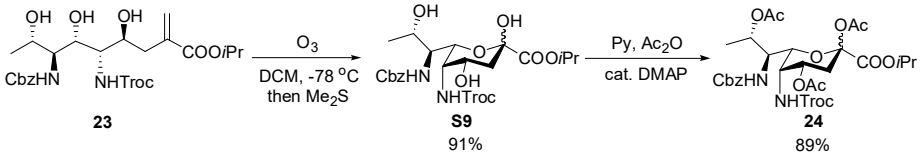
The intermediate was dissolved in MeCN 30 mL, then TrocCl (1.62 mL, 11.8 mmol, 3.0 equiv) was added, followed by Na_2CO_3 (aq, 0.5 M, 15 mL). The mixture was stirred at r.t. for 2 h, then the solvent was removed under vacuum. The residue was dissolved in ethyl acetate (100 mL), washed with brine, and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 1 : 1.5 to 1 : 2 as eluent. The product **23** was obtained as colorless foam (1.63 g, 69% over 2 steps).

^{1}H NMR (400 MHz, CD_3CN): δ = 1.12 (d, *J* = 6.4 Hz, 3H), 1.235 (*J* = 6.4 Hz, 3H), 1.242 (d, *J* = 6.4 Hz, 3H), 2.28 (dd, J_1 = 14.0 Hz, J_2 = 9.6 Hz, 1H), 2.66 (dd, J_1 = 14.0 Hz, J_2 = 2.4 Hz, 1H), 3.51 (dt, J_1 = 9.6 Hz, J_2 = 6.8 Hz, 1H), 3.64 (t, *J* = 8.4 Hz, 1H), 3.79–3.84 (m, 1H), 3.93–4.00 (m, 1H), 4.18 (d, *J* = 9.6 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.88 (d, *J* = 12.0 Hz, 1H), 4.96–5.05 (m, 1H), 5.02 (s, 2H), 5.57 (d, *J* = 10.0 Hz, 1H), 5.65 (s, 1H), 5.98 (d, *J* = 9.6 Hz, 1H), 6.14 (d, *J* = 1.6 Hz, 1H), 7.30–7.40 (m, 5H).

^{13}C NMR (100 MHz, CD_3CN): δ = 19.9, 21.97, 22.01, 37.9, 56.5, 57.6, 67.0, 69.1, 70.4, 71.5, 71.8, 75.1, 96.9, 127.7, 128.7, 128.8, 129.4, 138.3, 139.2, 155.7, 157.4, 167.5.

HR-ESI-MS (m/z): calcd for $C_{24}H_{33}Cl_3N_2O_9Na^+$ ($M + Na^+$): 621.1144, found: 621.1134.

Synthesis of isopropyl 7-(benzyloxycarbonylamino)-2,4,8-tri-*O*-acetyl-5-(2,2,2-trichloro-ethoxycarbonylamino)-3,5,7,9-tetradeoxy-L-*glycero*-L-*manno*-2-nonulopyranosonate (24):



The solution of **23** (1.17 g, 1.95 mmol, 1.0 equiv) in DCM (30 mL) was cooled to −78 °C. The O_3 (generated from O_2 and carried by the flow of O_2) was bubbled though this solution for 30 min. The colour of the solution turn purple, which indicated the saturation of O_3 in DCM. The excess amount of O_3 was blown off by the flow of O_2 and the purple colour disappeared. To this solution, Me_2S (0.50 mL, excess) was added to reduce the peroxide intermediate. After 1 h reduction at r.t., the solution was concentrated, and the residue was purified by silica gel flash chromatography using DCM : MeOH 30 : 1 to 20 : 1 as eluent. The intermediate **S9** was obtained as colorless foam (1.06 g, 91%), which was the mixture of linear and cyclic tautomers.

To the solution of the intermediate **S9** (1.06 g, 1.76 mmol, 1.0 equiv) in pyridine (8 mL), Ac_2O (4 mL) and DMAP (5 mg, 0.044 mmol, 0.025 equiv) were added sequentially. The mixture was stirred at r.t. for 2 h. The mixture was concentrated under vacuum, and the residue was dissolved in ethyl acetate (150 mL). The solution was washed with 1 M HCl (aq) and sat. $NaHCO_3$ (aq), dired over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by silica gel flash chromatography. The anomer **24β** was eluted by *n*-hexane : ethyl acetate 3 : 1 and was obtained as colorless solid (0.893 g, 69%), while the anomer **24α** was eluted by *n*-hexane : ethyl acetate 2 : 1 and was obtained as colorless solid (0.254 g, 20%). The configurations of both anomers were determined by HMBC spectra (correlation between H-3a and C-1).

For anomer **24α**:

$[\alpha]^{25}_D$ −73.9 ° (*c* = 0.49, DCM).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.22 (d, *J* = 6.6 Hz, 3H, H-9), 1.25−1.28 (m, 6H, $(CH_3)_2CH$),

1.98 (s, 3H, CH_3CO), 1.99 (s, 3H, CH_3CO), 2.05 (dd, J_1 = 13.7 Hz, J_2 = 8.0 Hz, 1H, H-3a), 2.11 (s, 3H, CH_3CO), 2.28 (dd, J_1 = 13.7 Hz, J_2 = 4.8 Hz, 1H, H-3e), 4.04 (d, J = 10.1 Hz, 1H, H-6), 4.28 (t, J = 10.3 Hz, 1H, H-7), 4.41–4.46 (m, 1H, H-5), 4.45 (d, J = 12.2 Hz, 1H, CCl_3CH_2), 4.88 (d, J = 10.2 Hz, 1H, NH), 4.97 (d, J = 12.2 Hz, 1H, PhCH_2), 5.00 (d, J = 12.2 Hz, 1H, CCl_3CH_2), 5.07–5.14 (m, 3H, PhCH_2, $(CH_3)_2CH$ & H-8), 5.19–5.23 (m, 1H, H-4), 5.87 (t, J = 10.0 Hz, 1H, NH), 7.30–7.37 (m, 5H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.1, 20.7, 20.9, 21.1, 21.4, 21.5, 30.8, 47.9, 52.1, 66.9, 67.2, 70.6, 71.4, 71.7, 74.5, 95.7, 97.3, 128.16, 128.18, 128.5, 136.1, 155.0, 155.7, 165.5, 167.9, 170.2, 170.4.

HR-ESI-MS (m/z): calcd for $C_{29}H_{37}Cl_3N_2O_{13}Na^+$ ($M + Na^+$): 749.1253, found: 749.1252.

For anomer **24β**:

$[\alpha]^{25}_D$ −52.5 ^{o} (c = 0.69, DCM).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.24–1.29 (m, 9H, H-9 & $(CH_3)_2CH$), 1.95 (s, 3H, CH_3CO), 1.98 (s, 3H, CH_3CO), 2.08 (t, J = 13.5 Hz, 1H, H-3a), 2.12 (s, 3H, CH_3CO), 2.44 (dd, J_1 = 13.5 Hz, J_2 = 4.8 Hz, 1H, H-3e), 4.28 (td, J_1 = 10.4 Hz, J_2 = 4.3 Hz, 1H, H-7), 4.39–4.45 (m, 2H, H-6 & H-5), 4.43 (d, J = 12.3 Hz, 1H, CCl_3CH_2), 4.78 (d, J = 10.7 Hz, 1H, NH), 4.96 (d, J = 12.2 Hz, 1H, PhCH_2), 5.03 (d, J = 12.3 Hz, 1H, CCl_3CH_2), 5.04–5.06 (m, 1H, H-4), 5.07–5.10 (m, 1H, $(CH_3)_2CH$), 5.10 (d, J = 12.2 Hz, 1H, PhCH_2), 5.14–5.18 (m, 1H, H-8), 5.55 (d, J = 9.7 Hz, 1H, NH), 7.29-7.37 (m, 5H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8, 20.8, 20.9, 21.1, 21.5, 21.6, 31.6, 47.7, 52.1, 67.1, 67.2, 69.9, 70.5, 73.4, 74.6, 95.7, 96.5, 128.9, 128.13, 128.5, 136.3, 154.8, 155.8, 167.0, 168.2, 170.1, 170.3.

HR-ESI-MS (m/z): calcd for $C_{29}H_{37}Cl_3N_2O_{13}Na^+$ ($M + Na^+$): 749.1253, found: 749.1251.

4-Methylphenyl 7-*N*-benzyloxycarbonyl-4,8-di-*O*-acetyl-1-isopropyl-5-*N*-(2,2,2-trichloro-ethoxycarbonyl)-α-thiopseudaminoside (25):

To a 50 mL round bottom flask, **24** (623 mg, 0.856 mmol, 1.0 equiv) and 4-toluenethiol (638

mg, 5.13 mmol, 6.0 equive) were added. Anhydrous DCM (17 mL) was added under argon, and the concentration of **24** was controlled at 50 mM. The mixture was cooled to 0 °C, then $BF_3{\cdot}OEt_2$ (211 μL, 1.71 mmol, 2.0 equiv) was added dropwise. The mixture was then stirred at 0 °C to r.t. for 20 h. The reaction was quenched by sat. $NaHCO_3$ (aq), and the organic phase was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by silica gel flash chromatography using *n*-hexane : ethyl acetate 4 : 1 to 3 : 1 as eluent. The thioglycoside donor **25** was obtained as single α anomer ($J_{C1\text{-}H3a}$ = 0 Hz, measured on Advance DRX Bruker 500 MHz NMR spectrometer by non-decoupled ^{13}C spectrum) colorless foam (544 mg, 80%).

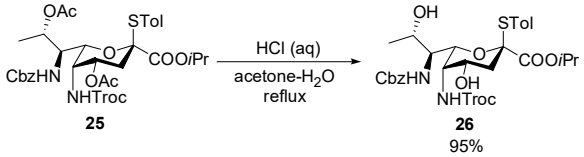
$[\alpha]^{25}_D$ –117 ° (*c* = 0.66, DCM).

^1H NMR (400 MHz, $CDCl_3$): δ = 1.12 (d, *J* = 6.0 Hz, 3H, $(CH_3)_2CH$), 1.15 (d, *J* = 6.0 Hz, 3H, $(CH_3)_2CH$), 1.24 (d, *J* = 6.8 Hz, 3H, H-9), 1.97 (s, 3H, CH_3CO), 2.03 (s, 3H, CH_3CO), 2.08 (t, *J* = 13.6 Hz, 1H, H-3a), 2.32 (s, 3H, $CH_3C_6H_4$), 2.36 (dd, J_1 = 13.6 Hz, J_2 = 4.4 Hz, 1H, H-3e), 4.30 (td, J_1 = 10.4 Hz, J_2 = 1.6 Hz, 1H, H-7), 4.41–4.44 (m, 1H, H-5), 4.43 (d, *J* = 12.0 Hz, 1H, CCl_3CH_2), 4.57 (d, *J* = 10.0 Hz, 1H, H-6), 4.83–4.89 (m, 1H, $(CH_3)_2CH$), 4.98 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 5.00 (d, *J* = 12.0 Hz, 1H, CCl_3CH_2), 5.10 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 5.12 (d, *J* = 10.0 Hz, 1H, NH), 5.14–5.18 (m, 1H, H-8), 5.31 (dt, J_1 = 12.4 Hz, J_2 = 4.0 Hz, 1H, H-4), 5.52 (d, *J* = 9.6 Hz, 1H, NH), 7.10 (d, *J* = 8.0 Hz, 2H, ArH), 7.29–7.38 (m, 7H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.5, 21.0, 21.3, 21.5, 21.6, 32.6, 48.4, 52.9, 67.2, 67.6, 70.4, 71.4, 71.7, 74.6, 89.2, 95.8, 126.5, 128.2, 128.6, 129.9, 134.8, 136.4, 139.7, 154.9, 155.8, 167.4, 170.4, 170.6.

HR-ESI-MS (m/z): calcd for $C_{34}H_{41}Cl_3N_2O_{11}SNa^+$ ($M + Na^+$): 813.1389, found: 813.1385.

4-Methylphenyl 7-*N*-benzyloxycarbonyl-1-isopropyl-5-*N*-(2,2,2-trichloroethoxycarbonyl) -α-thiopseudaminoside (26):



To a stirred solution of **25** (487 mg, 0.615 mmol, 1.0 equiv) in acetone (27 mL), a HCl (aq) solution (prepared from conc. HCl 2.7 mL and water 10.7 mL) was added. The mixture was

refluxed for 1 h, then more water (8.9 mL) was added. The mixture was further refluxed for 16 h. After being cooled to r.t., the acetone was removed under vacuum, then the water phase was extracted with ethyl acetate (2 × 50 mL). The organic phase was washed with sat. $NaHCO_3$ (aq) and brine, and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by silica gel flash chromatography using *n*-hexane : ethyl acetate 2 : 1 to 1.5 : 1 as eluent. The diol **26** was obtained as colorless solid (416 mg, 95%).

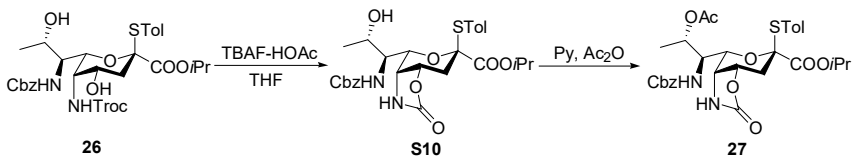
$[\alpha]^{25}_{D}$ −157 ^{o} (*c* = 0.69, DCM).

^{1}H NMR (400 MHz, CD_3CN): δ = 1.04 (d, *J* = 6.4 Hz, 3H, H-9), 1.07 (d, *J* = 6.4 Hz, 3H, $(CH_3)_2CH$), 1.22 (d, *J* = 6.4 Hz, 3H, $(CH_3)_2CH$), 1.96 (dd, J_1 = 14.4 Hz, J_2 = 12.0 Hz, 1H, H-3a), 2.23 (dd, J_1 = 14.4 Hz, J_2 = 4.0 Hz, 1H, H-3e), 2.35 (s, 3H, $CH_3C_6H_4$), 3.57 (td, J_1 = 9.6 Hz, J_2 = 7.2 Hz, 1H, H-7), 3.87–3.94 (m, 1H, H-8), 4.16–4.21 (m, 2H, H-4 & H-5), 4.60 (d, *J* = 10.0 Hz, 1H, H-6), 4.70 (d, *J* = 12.4 Hz, 1H, CCl_3CH_2), 4.76 (d, *J* = 12.4 Hz, 1H, CCl_3CH_2), 4.81–4.87 (m, 1H, $(CH_3)_2CH$), 5.03 (d, *J* = 12.8 Hz, 1H, $PhCH_2$), 5.07 (d, *J* = 12.8 Hz, 1H, $PhCH_2$), 5.63 (d, *J* = 9.6 Hz, 1H, NH), 6.16 (d, *J* = 10.4 Hz, 1H, NH), 7.20 (d, *J* = 8.0 Hz, 2H, ArH), 7.24–7.40 (m, 7H, ArH).

^{13}C NMR (100 MHz, CD_3CN): δ = 19.5, 21.3, 21.7, 21.9, 35.9, 52.3, 56.7, 65.9, 67.1, 69.9, 70.8, 74.9, 75.4, 90.0, 96.7, 126.9, 128.8, 128.9, 129.4, 130.7, 137.1, 138.3, 141.3, 156.5, 157.1, 168.4.

HR-ESI-MS (m/z): calcd for $C_{30}H_{37}Cl_3N_2O_9SNa^+$ (M + Na^+): 729.1178, found: 729.1141.

4-Methylphenyl 7-*N*-benzyloxycarbonyl-5-*N*,4-*O*-carbonyl-1-isopropyl-5-*N*-(2,2,2-trichloro-ethoxycarbonyl)-α-thiopseudaminoside (27):



26 **S10** **27**

87% over 2 steps

To a 1.5 mL Eppendorf tube, TBAF (1.0 M solution in THF, 0.40 mL, 0.40 mmol, 4.0 equiv) and HOAc (0.011 mL, 0.20 mmol, 2.0 equiv) were added. This mixture was then added to the solution of **26** (71 mg, 0.10 mmol, 1.0 equiv) in THF (0.80 mL). The mixture was stirred at r.t. for 12 h, then was diluted with ethyl acetate (30 mL) and washed with sat. $NaHCO_3$ (aq). The organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum to give

intermediate **S10** in crude form, which was used in the next step without purification.

To the solution of crude **S10** in pyridine (3.0 mL), Ac_2O (1.0 mL, large excess amount) was added. The mixture was stirred at r.t. overnight. After concentration, the residue was diluted with ethyl acetate (30 mL). The solution was washed with 1 M HCl (aq), sat. $NaHCO_3$ (aq), and brine. The organic phase was dried over anhydrous Na_2SO_4, then the solvent was removed under vacuum. The residue was purified by silica gel flash chromatography using *n*-hexane : ethyl acetate 1 : 1.5 as eluent. The product **27** was obtained as colorless solid (52 mg, 87% over 2 steps).

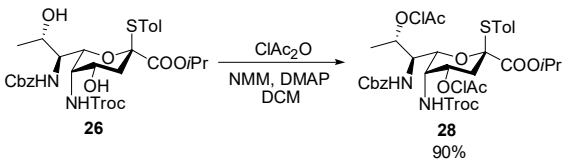
$[\alpha]^{25}_D$ −135 ^{o} (*c* = 0.83, DCM).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.80 (d, *J* = 6.0 Hz, 3H, $(CH_3)_2CH$), 1.14 (d, *J* = 6.0 Hz, 3H, $(CH_3)_2CH$), 1.47 (d, *J* = 6.5 Hz, 3H, H-9), 2.01 (dd, J_1 = 16.0 Hz, J_2 = 2.5 Hz, 1H, H-3a), 2.11 (s, 3H, CH_3CO), 2.32 (s, 3H, $CH_3C_6H_4$), 3.17 (dd, J_1 = 16.0 Hz, J_2 = 3.5 Hz, 1H, H-3e), 3.76 (dd, J_1 = 10.0 Hz, J_2 = 2.0 Hz, 1H, H-6), 3.80 (d, *J* = 9.5 Hz, 1H, H-5), 4.11 (td, J_1 = 9.5 Hz, J_2 = 2.0 Hz, 1H, H-7), 4.65–4.70 (m, 1H, $(CH_3)_2CH$), 4.86–4.88 (m, 1H, H-4), 5.11 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 5.15 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 5.32 (qd, J_1 = 6.5 Hz, J_2 = 2.5 Hz, 1H, H-8), 5.50 (d, *J* = 9.5 Hz, 1H, NH), 6.47 (s, 1H, NH), 7.12 (d, *J* = 8.0 Hz, 2H, ArH), 7.34-7.40 (m, 5H, ArH), 7.45 (d, *J* = 8.0 Hz, 2H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.9, 21.0, 21.3, 21.4, 21.5, 32.9, 51.3, 53.5, 67.8, 70.0, 70.4, 71.2, 71.8, 89.2, 126.4, 128.5, 128.6, 128.8, 129.7, 135.7, 136.0, 140.0, 157.2, 157.3, 167.8, 171.4.

HR-ESI-MS (m/z): calcd for $C_{30}H_{36}N_2O_9SNa^+$ ($M + Na^+$): 623.2034, found: 623.2015.

4-Methylphenyl 7-*N*-benzyloxycarbonyl-4,8-di-*O*-chloroacetyl-1-isopropyl-5-*N*-(2,2,2-trichloroethoxycarbonyl)-α-thiopseudaminoside (28):



To a stirred solution of **26** (274 mg, 0.388 mmol, 1.0 equiv) in anhydrous DCM (15 mL), *N*-methylmorpholine (213 μL, 1.94 mmol, 5.0 equiv) and chloroacetic anhydride (332 mg, 1.94 mmol, 5.0 equiv) were added sequentially. To this solution, DMAP (2.4 mg, 0.019 mmol, 0.05 equiv) was added. The mixture was stirred at r.t. for 2 h. After full conversion of **26**, the mixture

was sequentially washed with 1 M HCl (aq), sat. $NaHCO_3$ (aq), and brine. The organic phase was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by silica gel flash chromatography using *n*-hexane : ethyl acetate 4 : 1 as eluent. The product **28** was obtained as colorless solid (300 mg, 90%).

$[\alpha]^{25}_{D}$ –94.9 ^{o} (*c* = 0.94, DCM).

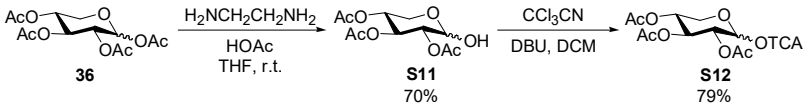
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.166 (d, *J* = 6.5 Hz, 3H, $(CH_3)_2CH$), 1.172 (d, *J* = 6.5 Hz, 3H, $(CH_3)_2CH$), 1.23 (d, *J* = 6.5 Hz, 3H, H-9), 2.13 (t, *J* = 13.5 Hz, 1H, H-3a), 2.33 (s, 3H, $CH_3C_6H_4$), 2.39 (dd, J_1 = 13.5 Hz, J_2 = 4.0 Hz, 1H, H-3e), 3.93–4.04 (m, 4H, 2 × $ClCH_2$), 4.35 (td, J_1 = 10.0 Hz, J_2 = 3.0 Hz, 1H, H-7), 4.43–4.46 (m, 1H, H-5), 4.45 (d, *J* = 12.0 Hz, 1H, CCl_3CH_2), 4.52 (d, *J* = 10.0 Hz, 1H, H-6), 4.87–4.92 (m, 1H, $(CH_3)_2CH$), 4.95 (d, *J* = 12.0 Hz, 1H, CCl_3CH_2), 4.98 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 5.01 (d, *J* = 10.5 Hz, 1H, NH), 5.09 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 5.21–5.25 (m, 1H, H-8), 5.40 (dt, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H, H-4), 5.56 (d, *J* = 9.5 Hz, 1H, NH), 7.13 (d, *J* = 8.0 Hz, 2H, ArH), 7.30–7.38 (m, 7H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.8, 21.3, 21.60, 21.63, 32.2, 40.8, 41.1, 48.2, 52.6, 67.4, 69.7, 70.7, 71.4, 73.0, 74.8, 88.8, 95.6, 126.3, 128.2, 128.4, 128.7, 130.1, 134.5, 136.3, 139.9, 155.1, 155.9, 166.77, 166.84, 167.3.

HR-ESI-MS (m/z): calcd for $C_{34}H_{39}Cl_5N_2O_{11}SNa^+$ ($M + Na^+$): 881.0609, found: 881.0557.

Part 8. Synthesis of xyloside building block, fucosamine building block, and disaccharide acceptor.

2,3,4-Tri-*O*-acetyl-α/β-D-xylopyranosyl trichloroacetimidate (S12):



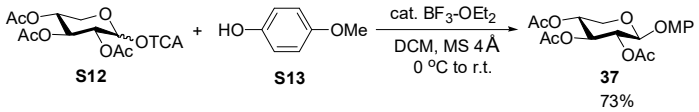
To a stirred solution of ethylenediamine (2.41 mL, 36.0 mmol, 1.2 equiv) in THF (200 mL), acetic acid (2.40 mL, 42.0 mmol, 1.4 equiv) was added. A white slurry was formed immediately. To this mixture, a solution of **36** (9.55 g, 30.0 mmol, 1.0 equiv) in THF (100 mL) was added in one portion. The mixture was stirred at r.t. for 16 h, till the full conversion was achieved (monitored by TLC). The THF was removed under vacuum, and the residue was diluted with ethyl acetate (300 mL), washed thoroughly with water, and dried over anhydrous Na_2SO_4. After concentration, the product 2,3,4-tri-*O*-acetyl-α/β-D-xylopyranose **S11** was obtained as white solid (5.77 g, 70%). The product was pure enough and used in the next step without further purification.

To a stirred solution of **S11** (2.76 g, 10.0 mmol, 1.0 equiv) in anhydrous DCM (15 mL), trichloroacetonitrile (3.00 mL, 30.0 mmol, 3.0 equiv) was added, followed by DBU (0.15 mL, 1.00 mmol, 0.10 equiv). The colour of the mixture became dark brown gradually. After being stirred at r.t. for 12 h, the solvent was removed under vacuum, and the residue was purified by silica gel column chromatography (buffered with Et_3N) using *n*-hexane : ethyl acetate 4 : 1 to 3 : 1 *v*/*v* as eluent. The product **S12** was obtained as white solid (3.31 g, 79%).[7]

^{1}H NMR (400 MHz, $CDCl_3$, α anomer): δ = 2.03 (s, 3H, CH_3CO), 2.06 (s, 3H, CH_3CO), 2.07 (s, 3H, CH_3CO), 3.82 (t, J = 11.0 Hz, 1H, H-5a), 3.99 (dd, J_1 = 11.2 Hz, J_2 = 5.9 Hz, 1H, H-5e), 5.07 (dd, J_1 = 10.1 Hz, J_2 = 3.7 Hz, 1H, H-2), 5.07–5.12 (m, 1H, H-4), 5.57 (t, J = 9.9 Hz, 1H, H-3), 6.49 (d, J = 3.6 Hz, 1H, H-1), 8.72 (s, 1H, C=NH).

^{13}C NMR (100 MHz, $CDCl_3$, α anomer): δ = 20.4, 20.6, 20.7, 60.7, 68.5, 69.3, 69.9, 90.7, 93.1, 160.8, 169.78, 169.83, 169.85.

4-Methoxyphenyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside (37):



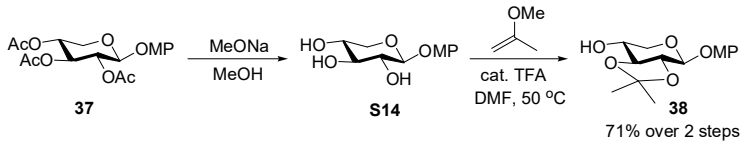
To a flame dried Schlenk flask, molecular sieves 4 Å (3.00 g, flame dried), 4-methoxyphenol

S13 (1.08 g, 8.66 mmol, 1.1 equiv), anhydrous DCM (30 mL), and **S12** (3.31 g, 7.87 mmol, 1.0 equiv) were added sequentially. The mixture was stirred at r.t. for 30 min, then was cooled to 0 °C. $BF_3 \cdot OEt_2$ (97 μL, 0.79 mmol, 0.10 equiv) was added, and the mixture was stirred at 0 °C to r.t. for 8 h. The reaction was quenched by Et_3N and filtered through celite. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 2 : 1 *v/v* as eluent. The product **37** was obtained as white solid (2.21 g, 73%).[8]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.07 (s, 3H, CH_3CO), 2.08 (s, 3H, CH_3CO), 2.09 (s, 3H, CH_3CO), 3.47 (dd, J_1 = 12.0 Hz, J_2 = 8.1 Hz, 1H, H-5a), 3.77 (s, 3H, CH_3O), 4.21 (dd, J_1 = 12.0 Hz, J_2 = 4.9 Hz, 1H, H-5e), 4.99–5.04 (m, 1H, H-4), 5.03 (d, J = 6.3 Hz, 1H, H-1), 5.15 (dd, J_1 = 8.3 Hz, J_2 = 6.3 Hz, 1H, H-2), 5.23 (t, J = 8.0 Hz, 1H, H-3), 6.82 (d, J = 9.1 Hz, 2H, ArH), 6.95 (d, J = 9.1 Hz, 2H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 55.8, 62.1, 68.7, 70.5, 71.1, 99.9, 114.7, 118.6, 150.7, 155.7, 169.5, 170.0, 170.1.

4-Methoxyphenyl 2,3-*O*-isopropylidene-β-D-xylopyranoside (38):



37 **S14** **38**

71% over 2 steps

To a stirred solution of **37** (8.44 g, 22.0 mmol, 1.0 equiv) in MeOH (50 mL), catalytic amount of MeONa (1.0 mL, 25% solution in MeOH) was added. The mixture was stirred at r.t. for 2 h, and neutralized by DOWEX 50W X8(H) cationic exchange resin. The resin was removed via filtration, and the solvent was removed under vacuum. The product **S14** was obtained as white solid, which was directly used in the next step without further purification.

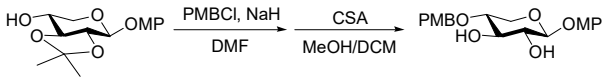
The **S14** was dissolved in anhydrous DMF, and 2-methoxypropene (7.20 mL, 75.0 mmol, 3.4 equiv) was added. The mixture was heated to 50 °C, then TFA (17 μL, 0.22 mmol, 0.01 equiv) was added. After being stirred at 50 °C for 12 h, another batch of 2-methoxypropene (3.60 mL, 37.5 mmol, 1.7 equiv) and TFA (8.5 μL, 0.11 mmol, 0.005 equiv) were added. The mixture was stirred at 50 °C for another 20 h, then was quenched with Et_3N. The mixture was diluted with ethyl acetate (200 mL), thoroughly washed with water and brine, and concentrated under vacuum. The residue (mainly contains over protected product) was redissolved in MeOH (50 mL) and cooled to

0 °C, then PPTS (200 mg) was added. The mixture was stirred at 0 °C for 15 min (full conversion of over protected product to product as indicated by TLC), and quenched with Et_3N. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography (buffered with Et_3N) using *n*-hexane : ethyl acetate 2 : 1 to 1.5 : 1 *v*/*v* as eluent. The product **38** was obtained as white solid (4.64 g, 71%).[9]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.49 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 2.80 (br, 1H, OH), 3.37 (dd, J_1 = 11.4 Hz, J_2 = 7.1 Hz, 1H, H-5a), 3.58–3.65 (m, 2H, H-2 & H-3), 3.77 (s, 3H, CH_3O), 4.09–4.16 (m, 2H, H-4 & H-5e), 5.17 (d, *J* = 7.0 Hz, 1H, H-1), 6.82 (d, *J* = 9.1 Hz, 2H, ArH), 7.03 (d, *J* = 9.1 Hz, 2H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.7, 26.9, 55.7, 67.6, 69.3, 76.4, 81.0, 100.7, 112.1, 114.6, 118.6, 150.5, 155.5.

4-Methoxyphenyl 4-*O*-(4-methoxybenzyl)-β-D-xylopyranoside (S15):



38 **S15** 89%

To a stirred solution of **38** (4.47 g, 15.0 mmol, 1.0 equiv) in anhydrous DMF (25 mL), NaH (60%, dispersed on mineral oil, 1.20 g, 30.0 mmol, 2.0 equiv) was added at 0 °C. After 15 min, 4-methoxybenzyl chloride (PMBCl, 3.05 mL, 22.5 mmol, 1.5 equiv) was added dropwise. The mixture was stirred at 0 °C to r.t. overnight, then was quenched by water. The mixture was extracted with ethyl acetate (200 mL) and washed thoroughly with water and brine. After being dried over anhydrous Na_2SO_4, the solvent was removed under vacuum, and the residue was redissolved in the mixture of MeOH (30 mL) and DCM (35 mL). To this solution, camphor-10-sulfonic acid (CSA, 348 mg, 1.50 mmol, 0.10 equiv) was added. After being stirred at r.t. for 30 min, the reaction was quenched by Et_3N, and the solvent was removed under vacuum. The residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate : DCM 1 : 1.3 : 1 *v*/*v* as eluent. The product **S15** was obtained as white solid (5.05 g, 89%).

$[\alpha]^{25}_D$ −85.6 ° (*c* = 1.2, DCM).

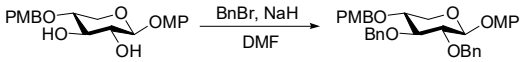
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.26 (t, *J* = 11.2 Hz, 1H, H-5a), 3.42 (dd, J_1 = 8.8 Hz, J_2 = 7.4 Hz, 1H, H-2), 3.48 (dd, J_1 = 9.8 Hz, J_2 = 5.1 Hz, 1H, H-4), 3.54 (t, *J* = 8.8 Hz, 1H, H-3), 3.73 (s, 3H, CH_3O), 3.77 (s, 3H, CH_3O), 3.92 (dd, J_1 = 11.5 Hz, J_2 = 5.1 Hz, 1H, H-5e), 4.57 (d, *J* = 11.3

Hz, 1H, $CH_3OC_6H_4CH_2$), 4.68 (d, J = 11.3 Hz, 1H, $CH_3OC_6H_4CH_2$), 4.70 (d, J = 7.4 Hz, 1H, H-1), 6.81 (d, J = 9.0 Hz, 2H, ArH), 6.89 (d, J = 8.4 Hz, 2H, ArH), 6.98 (d, J = 9.0 Hz, 2H, ArH), 7.30 (d, J = 8.4 Hz, 2H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.6, 56.0, 64.8, 73.8, 74.8, 77.0, 78.6, 103.9, 114.7, 115.4, 119.3, 130.7, 131.8, 152.9, 156.7, 160.9.

HR-ESI-MS (m/z): calcd for $C_{20}H_{24}O_7Na^+$ ($M + Na^+$): 399.1414, found: 399.1415.

4-Methoxyphenyl 2,3-di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-β-D-xylopyranoside (S16):



S15 → **S16** 94%

To a stirred solution of **S15** (4.86 g, 12.9 mmol, 1.0 equiv) in anhydrous DMF (25 mL), NaH (60%, dispersed on mineral oil, 1.56 g, 38.7 mmol, 3.0 equiv) was added at 0 °C. After 15 min, BnBr (4.63 mL, 38.7 mmol, 3.0 equiv) was added dropwise. The mixture was stirred at 0 °C to r.t. overnight, then was quenched by water. The mixture was extracted with ethyl acetate (200 mL) and washed thoroughly with water and brine. After being dried over anhydrous Na_2SO_4, the solvent was removed under vacuum, and the residue was purified by silica gel column chromatography using DCM : ethyl acetate 30 : 1 *v*/*v* as eluent. The product **S16** was obtained as white solid (6.77 g, 94%).

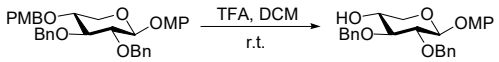
$[\alpha]^{25}_D$ −3.9 ° (*c* = 0.53, DCM).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.26 (dd, J_1 = 11.6 Hz, J_2 = 9.4 Hz, 1H, H-5a), 3.60–3.70 (m, 3H, H-2, H-3 & H-4), 3.77 (s, 3H, CH_3O), 3.79 (s, 3H, CH_3O), 3.92 (dd, J_1 = 11.6 Hz, J_2 = 4.6 Hz, 1H, H-5e), 4.56 (d, J = 11.3 Hz, 1H, PhCH_2), 4.67 (d, J = 11.3 Hz, 1H, PhCH_2), 4.83 (d, J = 11.0 Hz, 1H, PhCH_2), 4.85 (d, J = 7.0 Hz, 1H, H-1), 4.88 (s, 2H, $CH_3OC_6H_4CH_2$), 4.99 (d, J = 11.0 Hz, 1H, PhCH_2), 6.82 (d, J = 9.0 Hz, 2H, ArH), 6.85 (d, J = 8.6 Hz, 2H, ArH), 6.98 (d, J = 9.1 Hz, 2H, ArH), 7.24 (d, J = 8.6 Hz, 2H, ArH), 7.28–7.36 (m, 10H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4, 55.8, 64.1, 73.2, 75.3, 75.8, 77.5, 81.8, 83.8, 103.4, 114.0, 114.7, 118.6, 127.8, 127.9, 128.1, 128.3, 128.5, 129.7, 130.3, 138.5, 138.8, 151.4, 155.5, 159.5.

HR-ESI-MS (m/z): calcd for $C_{34}H_{36}O_7Na^+$ ($M + Na^+$): 579.2353, found: 579.2353.

4-Methoxyphenyl 2,3-di-*O*-benzyl-β-D-xylopyranoside (39):



S16 **39**

88%

To a stirred solution of **S16** (3.34 g, 6.00 mmol, 1.0 equiv) in DCM (150 mL), TFA (15 mL) was added in one portion. The colour of the mixture turned wine red immediately. After being stirred at r.t. for 15 min, $NaHCO_3$ solid (25.0 g) was added to neutralize the TFA, and the mixture was stirred until the red colour disappeared. Water was added, and the organic phase was separated. After being dried over anhydrous Na_2SO_4, the solvent was removed under vacuum, and the residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 4 : 1 to 3 : 1 *v*/*v* as eluent. The product **39** was obtained as white solid (2.32 g, 88%).

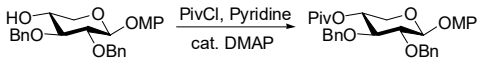
$[\alpha]^{25}_{D}$ −32.0 ^{o} (*c* = 1.2, DCM).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.62 (br, 1H, OH), 3.32 (dd, J_1 = 11.6 Hz, J_2 = 8.7 Hz, 1H, H-5a), 3.51 (t, *J* = 7.8 Hz, 1H, H-3), 3.67 (dd, J_1 = 7.8 Hz, J_2 = 6.5 Hz, 1H, H-2), 3.71–3.77 (m, 1H, H-4), 3.75 (s, 3H, CH_3O), 4.03 (dd, J_1 = 11.6 Hz, J_2 = 4.7 Hz, 1H, H-5e), 4.68 (d, *J* = 11.6 Hz, 1H, PhCH_2), 4.76 (d, *J* = 11.1 Hz, 1H, PhCH_2), 4.91 (d, *J* = 11.6 Hz, 1H, PhCH_2), 4.95 (d, *J* = 11.1 Hz, 1H, PhCH_2), 4.98 (d, *J* = 6.5 Hz, 1H, H-1), 6.83 (d, *J* = 9.1 Hz, 2H, ArH), 7.00 (d, *J* = 9.1 Hz, 2H, ArH), 7.29–7.36 (m, 10H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.7, 64.6, 69.0,74.5, 74.6, 80.0, 82.0, 102.3, 114.7, 118.4, 127.95, 128.00, 128.2, 128.6, 128.7, 138.0, 138.4, 151.2, 155.4.

HR-ESI-MS (m/z): calcd for $C_{26}H_{28}O_6Na^+$ (M + Na^+): 459.1778, found: 459.1778.

4-Methoxyphenyl 2,3-di-*O*-benzyl-4-*O*-pivaloyl-β-D-xylopyranoside (S17):



39 **S17**

95%

To a stirred solution of **39** (2.07 g, 4.75 mmol, 1.0 equiv) in pyridine (18 mL), pivaloyl chloride (PivCl, 1.17 mL, 9.50 mmol, 2.0 equiv) was added, followed by DMAP (29 mg, 0.24 mmol, 0.05 equiv). The mixture was stirred at 60 ^{o}C for 2 h, then the solvent was removed under vacuum. The residue was diluted with ethyl acetate (150 mL) and washed thoroughly with 1 M HCl (aq) and brine. After being dried over anhydrous Na_2SO_4 and concentration, the residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 5 : 1 *v*/*v* as eluent. The product **S17** was obtained as colorless syrup (2.34 g, 95%).

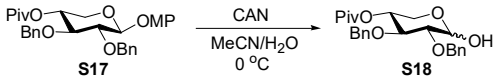
$[\alpha]^{25}_{D}$ −17.1 ^{o} (*c* = 1.1, DCM).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (s, 9H, $(CH_3)_3C$), 3.29 (dd, J_1 = 11.6 Hz, J_2 = 8.8 Hz, 1H, H-5a), 3.70–3.78 (m, 2H, H-2 & H-3), 3.74 (s, 3H, CH_3O), 4.13 (dd, J_1 = 11.6 Hz, J_2 = 5.3 Hz, 1H, H-5e), 4.73 (d, *J* = 11.1 Hz, 1H, PhCH_2), 4.78 (d, *J* = 11.0 Hz, 1H, PhCH_2), 4.83 (d, *J* = 11.1 Hz, 1H, PhCH_2), 4.964 (d, *J* = 6.7 Hz, 1H, H-1), 4.965 (d, *J* = 11.0 Hz, 1H, PhCH_2), 4.99–5.03 (m, 1H, H-4), 6.82 (d, *J* = 9.1 Hz, 2H, ArH), 7.00 (d, *J* = 9.1 Hz, 2H, ArH), 7.25–7.34 (m, 10H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.2, 38.8, 55.7, 62.7, 71.4, 74.96, 75.04, 80.8, 81.0, 103.0, 114.7, 118.5, 127.6, 127.7, 127.8, 128.2, 128.41, 128.44, 138.2, 138.3, 151.2, 155.5, 177.7.

HR-ESI-MS (m/z): calcd for $C_{31}H_{36}O_7Na^+$ ($M + Na^+$): 543.2353, found: 543.2353.

2,3-Di-*O*-benzyl-4-*O*-pivaloyl-α/β-D-xylopyranose (S18):



S17 **S18** 70%

To a stirred solution of **S17** (1.66 g, 3.20 mmol, 1.0 equiv) in MeCN (40 mL) and water (10 mL), ammonium cerium(IV) nitrate (CAN, 2.63 g, 4.80 mmol, 1.5 equiv) was added at 0 ^{o}C. The mixture was stirred at 0 ^{o}C for 30 min, then the other batch of ammonium cerium(IV) nitrate (0.88 g, 1.60 mmol, 0.5 equiv) was added. After being stirred at 0 ^{o}C for another 30 min, the reaction was quenched by $Na_2S_2O_3$ (aq). The mixture was extracted with ethyl acetate (150 mL), washed with water and brine, and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 3 : 1 *v*/*v* as eluent. The product **S18** was obtained as white solid (927 mg, 70%).

$[\alpha]^{25}_{D}$ +5.4 ^{o} (*c* = 1.0, DCM).

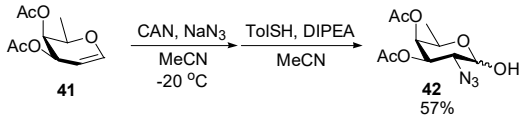
^{1}H NMR (400 MHz, $CDCl_3$, mixture of anomers): δ = 1.19 (s, 9H, $(CH_3)_3C\alpha$ & $(CH_3)_3C\beta$), 3.15 (d, *J* = 3.8 Hz, 0.6H, OHα), 3.31 (dd, J_1 = 11.8 Hz, J_2 = 8.2 Hz, 0.4H, H-5eβ), 3.40 (dd, J_1 = 7.8 Hz, J_2 = 6.4 Hz, 0.4H, H-2β), 3.54 (dd, J_1 = 8.4 Hz, J_2 = 3.3 Hz, 0.6H, H-2α), 3.60 (d, *J* = 6.6 Hz, 0.4H, OHβ), 3.70–3.81 (m, 1.6H, H-5aα, H-5eα, H-3β), 3.95 (t, *J* = 8.4 Hz, 0.6H, H-3α), 4.11 (dd, J_1 = 11.8 Hz, J_2 = 4.9 Hz, 0.4H, H-5aβ), 4.62 (d, *J* = 11.8 Hz, 0.6H, PhC$H_2\alpha$), 4.69–4.83 (m, 3.8H, H-1 β, PhC$H_2\alpha$ & PhC$H_2\beta$), 4.84–4.94 (m, 1H, H-4α & H-4β), 5.12 (t, *J* =3.5 Hz, 0.6H, H-1α), 7.25–7.33 (m, 10H, ArHα & ArHβ).

^{13}C NMR (100 MHz, $CDCl_3$, mixture of anomers): δ = 27.19, 27,21, 38.9, 59.4, 61.9, 70.6, 70.8,

73.5, 74.5, 74.9, 75.1, 77.9, 79.0, 79.9, 81.0, 91.5, 97.1, 127.7, 127.8, 127.9, 128.1, 128.5, 128.6, 137.7, 138.0. 138.2, 138.3, 177.9.

HR-ESI-MS (m/z): calcd for $C_{24}H_{30}O_6Na^+$ ($M + Na^+$): 437.1935, found: 437.1933.

2-Azido-2-deoxy-3,4-di-*O*-acetyl-α/β-D-fucopyranose (42):

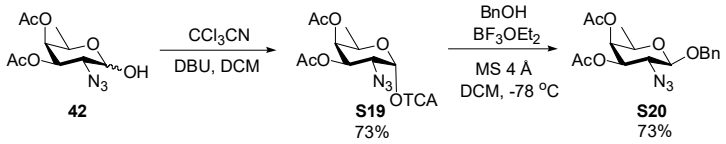


To a stirred solution of **41** (1.46 g, 6.80 mmol, 1.0 equiv) in anhydrous MeCN (35 mL), NaN_3 (663 mg, 10.2 mmol, 1.5 equiv) was added. The mixture was cooled to –20 °C, then ammonium cerium(IV) nitrate (CAN, 11.2 g, 20.4 mmol, 3.0 equiv) was added. The mixture was stirred at –20 °C for 5 h, then was diluted with Et_2O (200 mL) and washed with water. The organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum. The residue was redissolved in MeCN (13 mL), then *p*-thiocresol (1.27 g, 10.2 mmol, 1.5 equiv) and DIPEA (2.37 mL, 13.6 mmol, 2.0 equiv) were added sequentially. The mixture was stirred at r.t. for 10 min, then was diluted with DCM (150 mL) and washed with 1 M HCl (aq). After being dried over danhydrous Na_2SO_4, the solvent was removed under vacuum, and the residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 3 : 1 to 2 : 1 *v*/*v* as eluent. The product **42** was obtained as yellow syrup (1.06 g, 57%). [10]

^{1}H NMR (400 MHz, $CDCl_3$, mixture of anomers): δ = 1.15 (d, *J* = 6.6 Hz, 3H, H-6β), 1.22 (d, *J* = 6.4 Hz, 3H, H-6α), 2.068 (s, 3H, C*H*$_3$COα or C*H*$_3$COβ), 2.072 (s, 3H, C*H*$_3$COα or C*H*$_3$COβ), 2.18 (s, 3H, C*H*$_3$COα or C*H*$_3$COβ), 2.19 (s, 3H, C*H*$_3$COα or C*H*$_3$COβ), 3.65 (dd, J_1 = 10.8 Hz, J_2 = 7.7 Hz, 1H, H-2β), 3.73 (dd, J_1 = 11.0 Hz, J_2 = 3.4 Hz, 1H, H-2α), 3.83 (q, *J* = 6.6 Hz, 1H, H-5β), 4.03 (d, *J* = 3.0 Hz, 1H, OHα), 4.42 (q, *J* = 6.6 Hz, 1H, H-5α), 4.68 (dd, J_1 = 7.7 Hz, J_2 = 5.4 Hz, 1H, H-1β), 4.75 (d, *J* = 5.6 Hz, 1H, OHβ), 4.82 (dd, J_1 = 10.9 Hz, J_2 = 3.4 Hz, 1H, H-3β), 5.19 (d, *J* = 2.8 Hz, 1H, H-4β), 5.30 (d, *J* = 2.3 Hz, 1H, H-4α), 5.37–5.42 (m, 2H, H-1α & H-3α).

^{13}C NMR (100 MHz, $CDCl_3$, mixture of anomers): δ = 16.0, 16.2, 20.66, 20.71, 20.8, 58.1, 62.0, 64.7, 68.9, 69.4, 69.7, 70.9, 71.7, 92.3, 96.2, 170.3, 170.8.

Benzyl 2-azido-2-deoxy-3,4-di-*O*-acetyl-β-D-fucopyranoside (S20):



To a stirred solution of **42** (825 mg, 3.02 mmol, 1.0 equiv) in anhydrous DCM (10 mL), DBU (45 μL, 0.30 mmol, 0.10 equiv) was added. The mixture was sitrred at r.t. overnight, then the solvent was removed under vacuum. The residue was purified by silica gel column chromatography (buffered with Et_3N) using *n*-hexane : ethyl acetate 5 : 1 *v*/*v* as eluent. The major α anomer **S19** was obtained as white solid (919 mg, 73%). The α-configuration of the C-1 was confirmed by ^1H & ^{13}C NMR. The unstable intermediate was directly used in the next step without storage.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.18 (d, *J* = 6.5 Hz, 3H, H-6), 2.08 (s, 3H, CH_3CO), 2.20 (s, 3H, CH_3CO), 4.02 (dd, J_1 = 10.7 Hz, J_2 = 3.6 Hz, 1H, H-2), 4.35 (q, *J* = 6.5 Hz, 1H, H-5), 5.37–5.41 (m, 2H, H-3 & H-4), 6.46 (d, *J* = 3.6 Hz, 1H, H-1), 8.75 (s, 1H, C=NH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.1, 20.7, 20.8, 57.1, 67.7, 69.2, 70.1, 90.9, 85.0, 160.9, 169.9, 170.4.

To a flame dried Schlenk tube, 4 Å molecular sieves (2.00 g, flame dried) was added, followed by **S19** (880 mg, 2.11 mmol, 1.0 equiv), anhydrous DCM (20 mL), and benzyl alcohol (263 μL, 2.53 mmol, 1.2 equiv). The mixture was stirred at r.t. for 30 min, then was cooled to −78 °C. $BF_3{\cdot}OEt_2$ (26 μL, 0.21 mmol, 0.10 equiv) was added, and the mixture was stirred at −78 °C for 3 h. The reaction was quenched by Et_3N, and the mixture was filtered. After concentration, the residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 5 : 1 *v*/*v* as eluent. The product **S20** was obtained as colourless oil (560 mg, 73%).

$[\alpha]^{25}_D$ −20.8 ° (*c* = 1.2, DCM).

^1H NMR (400 MHz, $CDCl_3$): δ = 1.24 (d, *J* = 6.4 Hz, 3H, H-6), 2.04 (s, 3H, CH_3CO), 2.17 (s, 3H, CH_3CO), 3.70–3.76 (m, 2H, H-2 & H-5), 4.40 (d, *J* = 8.0 Hz, 1H, H-1), 4.70 (d, *J* = 11.9 Hz, 1H, PhCH_2), 4.76 (dd, J_1 = 10.9 Hz, J_2 = 3.3 Hz, 1H, H-3), 4.97 (d, *J* = 11.9 Hz, 1H, PhCH_2), 5.18 (dd, J_1 = 3.3 Hz, J_2 = 0.8 Hz, 1H, H-4), 7.30–7.41 (m, 5H, ArH).

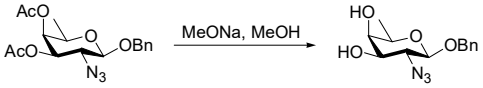
^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.2, 20.8, 60.9, 69.3, 69.7, 71.2, 71.6, 100.6, 128.1, 128.2, 128.6, 136.6, 170.0, 170.6.

IR (film) ν = 3039, 2991, 2942, 2878, 2112 (N_3), 1739, 1645, 1512, 1456, 1366, 1239, 1219, 1169,

1071, 1019, 930, 904, 735, 698 cm^{-1}.

HR-ESI-MS (m/z): calcd for $C_{17}H_{21}N_3O_6Na^+$ ($M + Na^+$): 386.1323, found: 386.1252.

Benzyl 2-azido-2-deoxy-β-D-fucopyranoside (43):



To a stirred solution of **S20** (560 mg, 1.54 mmol, 1.0 equiv) in MeOH (10 mL), MeONa (100 μL, 25% solution in MeOH) was added. The mixture was stirred at r.t. for 2 h, and the reaction was neutralized by DOWEX 50W X8(H) cationic exchange resin. The mixture was filter, and the solvent was removed under vacuum. The residue was purified by silica gel column chromatography using DCM : ethyl acetate 3 : 1 *v*/*v* as eluent. The product **43** was obtained as white solid (401 mg, 93%).

$[\alpha]^{25}_D$ +37.3 ^{o} (*c* = 1.0, DCM).

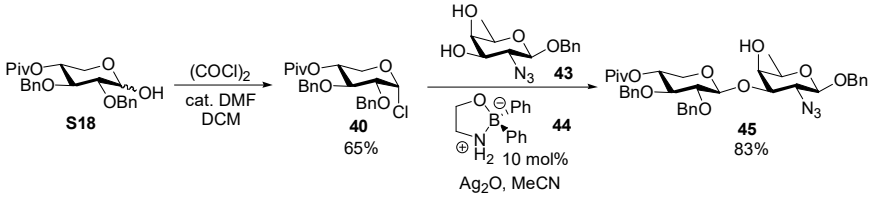
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (d, *J* = 6.5 Hz, 3H, H-6), 2.89 (br, 1H, OH), 3.18 (br, 1H, OH), 3.40 (dd, J_1 = 10.2 Hz, J_2 = 3.2 Hz, 1H, H-3), 3.52 (q, *J* = 6.5 Hz, 1H, H-5), 3.57 (dd, J_1 = 10.1 Hz, J_2 = 8.0 Hz, 1H, H-2), 3.66 (d, *J* = 2.9 Hz, 1H, H-4), 4.29 (d, *J* = 8.0 Hz, 1H, H-1), 4.66 (d, *J* = 11.9 Hz, 1H, PhCH_2), 4.92 (d, *J* = 11.9 Hz, 1H, PhCH_2), 7.28–7.39 (m, 5H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.4, 64.1, 70.7, 71.00, 71.04, 72.7, 100.8, 128.1, 128.6, 136.8.

IR (film) ν = 3037, 2983, 2939, 2919, 2862, 2109 (N_3), 1653, 1539, 1498, 1456, 1367, 1361, 1312, 1277, 1069, 996, 906, 735, 696 cm^{-1}.

HR-ESI-MS (m/z): calcd for $C_{13}H_{17}N_3O_4Na^+$ ($M + Na^+$): 302.1111, found: 302.1132.

Benzyl 2,3-di-*O*-benzyl-4-*O*-pivaloyl-β-D-xylopyranosyl-(1→3)-2-azido-2-deoxy-β-D-fuco-pyranoside (45):



To a stirred solution of **S18** (888 mg, 2.14 mmol, 1.0 equiv) in anhydrous DCM (16 mL), anhydrous DMF (50 μL, 0.64 mmol, 0.30 equiv) was added under argon, followed by $(COCl)_2$

(478 μL, 5.57 mmol, 2.6 equiv). After being stirred at r.t. for 2 h, the mixture was directly loaded onto a short silica gel column and eluted rapidly by *n*-hexane : ethyl acetate 10 : 1. The unstable glycosyl chloride donor **40** was obtained as colorless oil (602 mg, 65%) and was used directly in the next step without storage. The α-configuration of the C-1 position was confirmed by ^{1}H and ^{13}C NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (s, 9H, $(CH_3)_3C$), 3.71 (dd, J_1 = 9.6 Hz, J_2 = 3.6 Hz, 1H, H-2), 3.76 (t, J = 10.8 Hz, 1H, H-5a), 3.93 (dd, J_1 = 10.8 Hz, J_2= 5.6 Hz, 1H, H-5e), 4.00 (t, J = 9.2 Hz, 1H, H-3), 4.69 (d, J = 12.0 Hz, 1H, PhCH_2), 4.732 (d, J = 10.8 Hz, 1H, PhCH_2), 4.734 (d, J = 12.0 Hz, 1H, PhCH_2), 4.88 (d, J = 10.8 Hz, 1H, PhCH_2), 4.92 (ddd, J_1 = 10.8 Hz, J_2 = 9.2 Hz, J_3 = 5.6 Hz, 1H, H-4), 6.00 (d, J = 3.6 Hz, 1H, H-1), 7.28–7.36 (m, 10H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.3, 39.0, 61.3, 70.2, 73.3, 75.8, 78.3, 79.6, 93.8, 127.8, 127.9, 128.2, 128.3, 128.5, 128.7, 137.4, 138.3, 177.7.

To a flame dried Schlenk flask, Ag_2O (483 mg, 2.09 mmol, 1.5 equiv, dried under vacuum at 80 °C for 3 h before use) was added under argon, followed by **43** (388 mg, 1.39 mmol, 1.0 equiv), 2-aminoethyl diphenylborinate **44** (32 mg, 0.14 mmol, 0.10 equiv), and anhydrous MeCN (10 mL). To this stirred mixture, a solution of freshly prepared **40** (602 mg, 1.39 mmol, 1.0 equiv) in anhydrous MeCN (3.9 mL) was added in one portion. The concentration of donor and acceptor was 0.10 M. After being stirred at r.t. for 16 h, the mixture was filtered through celite, and the solvent was removed under vacuum. The residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 3 : 1 *v*/*v* as eluent. The product **45** was obtained as white solid (776 mg, 83%).

$[\alpha]^{25}_{D}$ −5.6 ° (*c* = 0.81, DCM).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (s, 9H, $(CH_3)_3C$), 1.39 (d, J = 6.4 Hz, 3H, H-6), 2.53 (s, 1H, OH), 3.17 (dd, J_1 = 11.5 Hz, J_2 = 9.4 Hz, 1H, H-5a'), 3.42 (dd, J_1 = 10.1 Hz, J_2 = 3.2 Hz, 1H, H-3), 3.51–3.55 (m, 2H, H-2' & H-5), 3.67 (t, J = 8.8 Hz, 1H, H-3'), 3.71 (dd, J_1 = 10.1 Hz, J_2 = 8.0 Hz, 1H, H-2), 3.74 (s, 1H, H-4), 4.04 (dd, J_1 = 11.5 Hz, J_2 = 5.3 Hz, 1H, H-5e'), 4.34 (d, J = 8.0 Hz, 1H, H-1), 4.63 (d, J = 7.1 Hz, 1H, H-1'), 4.67–4.71 (m, 2H, PhCH_2), 4.73 (d, J = 11.0 Hz, 1H, PhCH_2), 4.81 (d, J = 11.0 Hz, 1H, PhCH_2), 4.81–4.91 (m, 1H, H-4'), 4.96 (d, J = 10.2 Hz, 1H, PhCH_2), 4.98 (d, J = 10.2 Hz, 1H, PhCH_2), 7.26–7.40 (m, 15H, ArH).

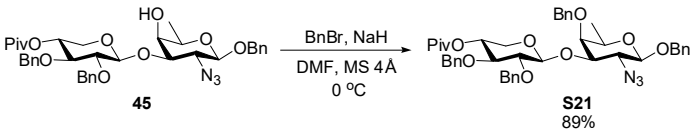
^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.5, 27.2, 38.9, 62.5, 62.7, 70.2, 70.4, 70.7, 71.1, 75.0, 75.2,

80.7, 80.89, 80.94, 100.8, 104.4, 127.7, 127.8, 127.9, 128.0, 128.1, 128.3, 128.47, 128.52, 137.0, 138.18, 138.23, 177.7.

IR (film) ν = 3066, 3033, 2977, 2873, 2113 (N_3), 1733, 1650, 1454, 1363, 1279, 1143, 1070, 735, 698 cm^{-1}.

HR-ESI-MS (m/z): calcd for $C_{37}H_{45}N_3O_9Na^+$ ($M + Na^+$): 698.3048, found: 698.3048.

Benzyl 2,3-di-*O*-benzyl-4-*O*-pivaloyl-β-D-xylopyranosyl-(1→3)-2-azido-2-deoxy-4-*O*-benzyl-β-D-fucopyranoside (S21):



To a flame dried Schlenk flask, 4 Å molecular sieves (1.60 g, flame dried), **45** (776 mg, 1.15 mmol, 1.0 equiv), anhydrous DMF (16 mL) were, and benzyl bromide (546 uL, 4.60 mmol, 4.0 equiv) were added under argon. After being stirred at r.t. for 0.5 h , the mixture was cooled to 0 °C, and the first portion of NaH (60%, dispersed on mineral oil, 92 mg, 2.30 mmol, 2.0 equiv) was added. After being stirred at 0 °C for 1 h, the second portion of NaH (92 mg, 2.30 mmol, 2.0 equiv) was added. After being stirred for another 3 h, the third portion of NaH (46 mg, 1.15 mmol, 1.0 equiv) was added. After another 1 h stirring, the reaction was quenched by HOAc and filtered through celite. The filtrate was diluted by ethyl acetate (150 mL) and washed thoroughly with water and brine. The organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum. The residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 5 : 1 to 4 : 1 *v*/*v* as eluent. The product **S21** was obtained as colourless syrup (780 mg, 89%).

$[\alpha]^{25}_D$ +3.4 ° (*c* = 0.87, DCM).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (s, 9H, $(CH_3)_3C$), 1.21 (d, *J* = 6.4 Hz, 3H, H-6), 3.14 (dd, J_1 = 11.2 Hz, J_2 = 9.6 Hz, 1H, H-5a'), 3.43–3.50 (m, 3H, H-2', H-3 & H-5), 3.59 (d, *J* = 2.4 Hz, 1H, H-4), 3.68 (t, *J* = 8.8 Hz, 1H, H-3'), 3.87 (dd, J_1 = 10.4 Hz, J_2 = 8.0 Hz, 1H, H-2), 4.00 (dd, J_1 = 11.2 Hz, J_2 = 5.2 Hz, 1H, H-5e'), 4.32 (d, *J* = 8.0 Hz, 1H, H-1), 4.64–4.71 (m, 5H, H-1' & $PhCH_2$), 4.82 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.87–4.97 (m, 4H, H-4' & $PhCH_2$), 7.24–7.40 (m, 20H, ArH).

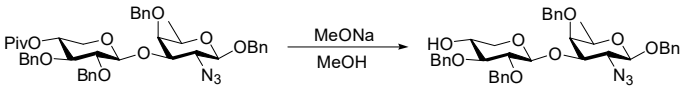
^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.7, 27.3, 38.9, 62.6, 63.5, 70.7, 70.8, 71.5, 75.0, 75.1, 75.4,

78.1, 79.8, 81.1, 81.6, 101.1, 105.1, 127.67, 127.71, 127.74, 127.8, 127.9, 128.1, 128.25, 128.31, 128.45, 128.50, 137.2, 138.2, 138.4, 138.5, 177.9.

IR (film) ν = 3065, 3032, 2977, 2935, 2112 (N_3), 1733, 1648, 1454, 1363, 1280, 1144, 1070, 736, 698 cm^{-1}.

HR-ESI-MS (m/z): calcd for $C_{44}H_{51}N_3O_9Na^+$ ($M + Na^+$): 788.3518, found: 788.3495.

Benzyl 2,3-di-*O*-benzyl-β-D-xylopyranosyl-(1→3)-2-azido-2-deoxy-4-*O*-benzyl-β-D-fuco-pyranoside (46):



S21 **46**
98%

To a stirred solution of **S21** (733 mg, 0.96 mmol, 1.0 equiv) in MeOH (20 mL) and DCM (5 mL), MeONa (0.50 mL, 25% solution in MeOH) was added. The mixture was stirred at r.t. for 4 h, then was neutralized by DOWEX 50W X8(H) cationic exchange resin. The mixture was filter, and the solvent was removed under vacuum. The residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 3 : 1 to 2 : 1 *v/v* as eluent. The product **46** was obtained as white solid (639 mg, 98%).

$[\alpha]^{25}_D$ −18.4 ° (*c* = 1.3, DCM).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.20 (d, *J* = 6.4 Hz, 3H, H-6), 2.44 (d, *J* = 4.3 Hz, 1H, OH), 3.26 (dd, J_1 = 11.5 Hz, J_2 = 8.8 Hz, 1H, H-5a'), 3.43–3.49 (m, 4H, H-2', H-3', H-3 & H-5), 3.60 (d, *J* = 2.6 Hz, 1H, H-4), 3.65–3.67 (m, 1H, H-4'), 3.87 (dd, J_1 = 10.6 Hz, J_2 = 7.9 Hz, 1H, H-2), 3.99 (dd, J_1 = 11.5 Hz, J_2 = 4.6 Hz, 1H, H-5e'), 4.32 (d, *J* = 7.9 Hz, 1H, H-1), 4.61 (d, *J* = 11.6 Hz, 1H, PhCH_2), 4.64–4.70 (m, 3H, PhCH_2), 4.72 (d, *J* = 6.0 Hz, 1H, H-1'), 4.87 (d, *J* = 11.6 Hz, 1H, PhCH_2), 4.92–4.96 (m, 3H, PhCH_2), 7.23–7.39 (m, 20H, ArH).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 16.6, 63.4, 64.3, 69.1, 70.57, 70.61, 74.2, 74.6, 74.7, 77.9, 79.8, 80.0, 81.7, 100.9, 104.3, 127.5, 127.79, 127.82, 128.0, 128.1, 128.3, 128.4, 128.5, 128.6, 137.0, 137.8, 138.3, 138.5.

IR (film) ν = 3037, 2938, 2112 (N_3), 1645, 1498, 1454, 1360, 1209, 1161, 1067, 984, 733, 697 cm^{-1}.

HR-ESI-MS (m/z): calcd for $C_{39}H_{43}N_3O_8Na^+$ ($M + Na^+$): 704.2942, found: 704.2950.

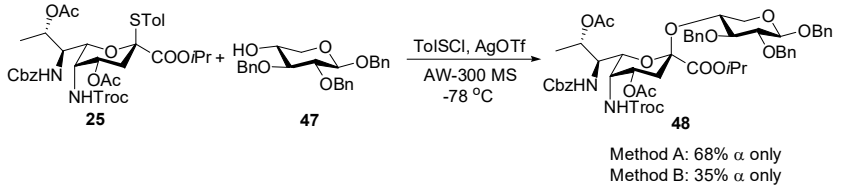
Part 9. Glycosylation research.

General procedure of glycosylation of Pse donors:

Method A: To a Schlenk tube, flame-dried AW-300 molecular sieves (100 mg/mL solvent) was added under argon, followed by Pse donor (1.0 equiv), acceptor (2.0 equiv), and freshly distilled anhydrous DCM (2.0 mL/0.10 mmol donor, 50 mM). After being stirred at r.t. for 1 h, the mixture was cooled to −78 °C, and AgOTf (3.0 equiv) was added. Finally, TolSCl (3.0 equiv) was added dropwise, and the mixture was stirred at −78 °C for 2 h. The reaction was quenched by addition of Et_3N. The mixture was filtered through celite, washed with sat. $NaHCO_3$ (aq), and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography to give the product. The α and β anomers (if formed) were separated and characterized respectively by NMR and HR-MS.

Method B: To a Schlenk tube, flame-dried AW-300 molecular sieves (100 mg/mL solvent) was added under argon, followed by Pse donor (1.0 equiv), acceptor (2.0 equiv), and freshly distilled anhydrous DCM-MeCN (3 : 1 *v*/*v*, 2.0 mL/0.10 mmol donor, 50 mM). After being stirred at r.t. for 1 h, the mixture was cooled to −78 °C, and AgOTf (3.0 equiv) was added. Finally, TolSCl (3.0 equiv) was added dropwise, and the mixture was stirred at −78 °C for 2 h. The reaction was quenched by addition of Et_3N. The mixture was filtered through celite, washed with sat. $NaHCO_3$ (aq), and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography to give the product. The α and β anomers (if formed) were separated and characterized respectively by NMR and HR-MS.

Benzyl 7-*N*-benzyloxycarbonyl-4,8-di-*O*-acetyl-1-isopropyl-5-*N*-(2,2,2-trichloroethoxy-carbonyl)-α-pseudaminosyl-(2→4)-2,3-di-*O*-benzyl-β-D-xylopyranoside (48):



Following **Method A**, the product was synthesized from donor **25** and xyloside acceptor **47** in 0.050 mmol scale. The product was purified by silica gel column chromatography using

n-hexane : ethyl acetate 4 : 1 *v*/*v* as eluent. Only the α anomer **48** was obtained ($J_{C1\text{-}H3a}$ = 0 Hz, measured on Advance DRX Bruker 500 MHz NMR spectrometer by non-decoupled ^{13}C spectrum) as colorless solid (36 mg, 67%).

Following **Method B**, the product was synthesized from donor **25** and xyloside acceptor **47** in 0.050 mmol scale. The product was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 4 : 1 *v*/*v* as eluent. Only the α anomer **48** was obtained as colorless solid (19 mg, 35%).

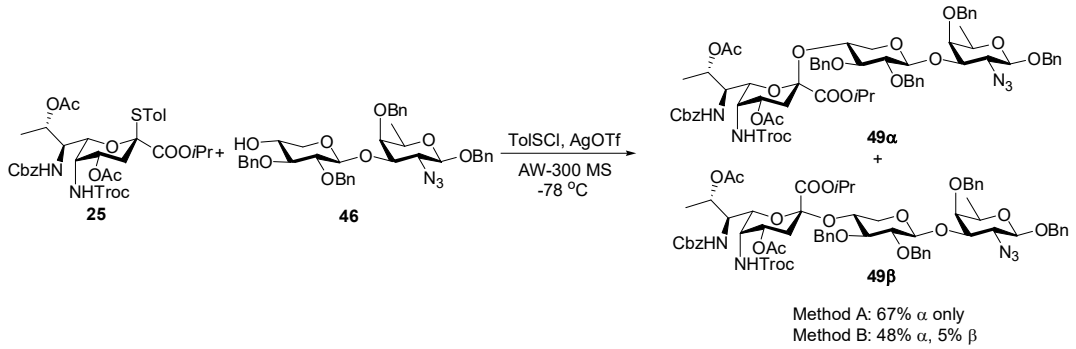
$[\alpha]^{25}_{D}$ −61.1 ^{o} (*c* = 0.45, DCM).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.97 (d, *J* = 6.5 Hz, 3H, H-9'), 1.33 (d, *J* = 6.5 Hz, 3H, $(CH_3)_2CH$), 1.34 (d, *J* = 6.5 Hz, 3H, $(CH_3)_2CH$), 1.76 (t, *J* = 13.0 Hz, 1H, H-3a'), 1.95 (s, 3H, CH_3CO), 2.03 (s, 3H, CH_3CO), 2.27 (dd, J_1 = 13.0 Hz, J_2 = 4.0 Hz, 1H, H-3e'), 2.89 (d, J = 10.0 Hz, 1H, NH), 3.13 (dd, J_1 = 13.0 Hz, J_2 = 11.0 Hz, 1H, H-5a), 3.45–3.53 (m, 2H, H-2 & H-3), 3.78–3.82 (m, 2H, H-4 & H-5e), 3.87–3.90 (m, 1H, H-5'), 4.02 (td, J_1 = 11.0 Hz, J_2 = 3.0 Hz, 1H, H-7'), 4.05–4.07 (m, 1H, H-6'), 4.35 (d, *J* = 12.0 Hz, 1H, CCl_3CH_2), 4.45 (d, *J* = 9.5 Hz, 1H, $PhCH_2$), 4.47 (d, *J* = 7.5 Hz, 1H, H-1), 4.63 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.80 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.88–4.99 (m, 4H, 4 × $PhCH_2$), 5.02 (d, *J* = 12.0 Hz, 1H, CCl_3CH_2), 5.04–5.08 (m, 1H, $(CH_3)_2CH$), 5.12 (d, *J* = 9.5 Hz, 1H, $PhCH_2$), 5.12–5.15 (m, 1H, H-8'), 5.24–5.28 (m, 1H, H-4'), 5.45 (d, *J* = 10.0 Hz, 1H, NH), 7.04 (t, *J* = 7.5 Hz, 1H, ArH), 7.28–7.44 (m, 19H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 21.1, 21.4, 21.75, 21.80, 32.6, 47.7, 52.2, 63.8, 67.0, 67.1, 69.4, 69.6, 70.3, 70.8, 71.3, 74.6, 74.8, 82.5, 82.6, 95.9, 97.2, 103.3, 128.0, 128.1, 128.2, 128.3, 128.5, 128.6, 128.65, 128.67, 128.8, 129.47, 129.54, 136.8, 137.3, 137.6, 138.1, 155.0, 155.8, 167.4, 170.37, 170.42.

HR-ESI-MS (m/z): calcd for $C_{53}H_{62}Cl_3N_2O_{16}^+$ ($M + H^+$): 1087.3159, found: 1087.3040.

Benzyl 7-*N*-benzyloxycarbonyl-4,8-di-*O*-acetyl-1-isopropyl-5-*N*-(2,2,2-trichloroethoxy-carbonyl)-α/β-pseudaminosyl-(2→4)-2,3-di-*O*-benzyl-β-D-xylopyranosyl-(1→3)-2-azido-4-*O*-benzyl-2-deoxy-β-D-fucopyranoside (49α/β):



Following **Method A**, the product was synthesized from donor **25** and disaccharide acceptor **46** in 0.10 mmol scale. The product was purified by multiple silica gel column chromatography using *n*-hexane : ethyl acetate 3 : 1 *v*/*v* as eluent. Only the α anomer **49α** was obtained ($J_{C1\text{-}H3a}$ = 0 Hz, measured on Advance DRX Bruker 500 MHz NMR spectrometer by non-decoupled ^{13}C spectrum) as colorless solid (91 mg, 67%).

Following **Method B**, the product was synthesized from donor **25** and disaccharide acceptor **46** in 0.142 mmol scale. The product was purified by multiple silica gel column chromatography using *n*-hexane : ethyl acetate 3 : 1 *v*/*v* and toluene : ethyl acetate 8 : 1 *v*/*v* as eluents to give **49α** (209 mg, 48%) and **49β** (21 mg, 5%) ($J_{C1\text{-}H3a}$ = 6.7 Hz, measured on Advance DRX Bruker 500 MHz NMR spectrometer by non-decoupled ^{13}C spectrum) as colorless solid.

For anomer **49α:**

$[\alpha]^{25}_{D}$ –25.2 ^{o} (*c* = 0.29, DCM).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.94 (d, *J* = 6.5 Hz, 3H, H-9''), 1.22 (d, *J* = 6.3 H, 3H, H-6), 1.32 (d, *J* = 6.2 Hz, 6H, $(CH_3)_2CH$), 1.75 (t, *J* = 13.0 Hz, 1H, H-3a''), 1.93 (s, 3H, CH_3CO), 2.03 (s, 3H, CH_3CO), 2.26 (dd, J_1 = 13.4 Hz, J_2 = 4.8 Hz, 1H, H-3e''), 2.85 (d, *J* = 10.7 Hz, 1H, NH), 3.06 (t, *J* = 11.2 Hz, 1H, H-5a'), 3.38 (dd, J_1 = 9.2 Hz, *J2* = 7.6 Hz, 1H, H-2'), 3.44–3.51 (m, 3H, H-3, H-5 & H-3'), 3.60 (d, *J* = 2.8 Hz, 1H, H-4), 3.69 (dd, J_1 = 11.5 Hz, J_2 = 5.1 Hz, 1H, H-5e'), 3.73–3.77 (m, 1H, H-4'), 3.86–3.88 (m, 1H, H-5''), 3.88 (dd, J_1 = 10.6 Hz, J_2 = 8.0 Hz, 1H, H-2), 4.01 (td, J_1 = 10.7 Hz, J_2 = 3.4 Hz, 1H, H-7''), 4.06 (dd, J_1 = 10.8 Hz, J_2 = 1.8 Hz, 1H, H-6''), 4.32 (d, *J* = 7.9 Hz, 1H, H-1), 4.35 (d, *J* = 12.1 Hz, 1H, CCl_3CH_2), 4.43 (d, *J* = 9.5 Hz, 1H, $PhCH_2$), 4.60 (d, *J* = 7.6 Hz, 1H, H-1'), 4.66 (d, *J* = 11.8 Hz, 1H, $PhCH_2$), 4.74 (d, *J* = 11.8 Hz, 1H, $PhCH_2$), 4.79 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.92–5.00 (m, 6H, CCl_3CH_2 & 5 × $PhCH_2$), 5.01–5.07 (m, 1H, $(CH_3)_2CH$), 5.13 (d, *J* = 9.4 Hz, 1H, $PhCH_2$), 5.13–5.15 (m, 1H, H-8''), 5.24 (dt, J_1 = 12.1 Hz, J_2 = 4.3 Hz, 1H, H-4''), 5.37 (br, 1H, NH), 7.04 (t, *J* = 7.4 Hz, 1H, ArH), 7.27–7.44 (m, 24H, ArH).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.2, 16.5, 21.0, 21.3, 21.6, 21.7, 32.4, 47.4, 52.0, 63.3, 63.4, 66.87, 66.92, 69.3, 69.7, 70.0, 70.4, 70.58, 70.62, 74.4, 74.6, 75.1, 78.1, 79.8, 82.1, 82.2, 95.7, 96.9, 100.9, 105.2, 127.5, 127.8, 127.9, 128.0, 128.09, 128.13, 128.2, 128.3, 128.4, 128.45, 128.49, 128.6, 128.7, 129.3, 129.4, 136.5, 137.0, 137.4, 137.8, 138.6, 154.8, 155.7, 167.2, 170.2, 170.3.

IR (film) ν = 3037, 2925, 2112 (N_3), 1646, 1456, 1374, 1363, 1272, 1236, 1218, 1099, 1069, 1028 cm^{-1}.

HR-ESI-MS (m/z): calcd for $C_{66}H_{76}Cl_3N_5O_{19}Na^+$ ($M + Na^+$): 1370.4092, found: 1370.4104.

For anomer **49β:**

$[\alpha]^{25}_D$ −25.0 ° (*c* = 0.98, DCM).

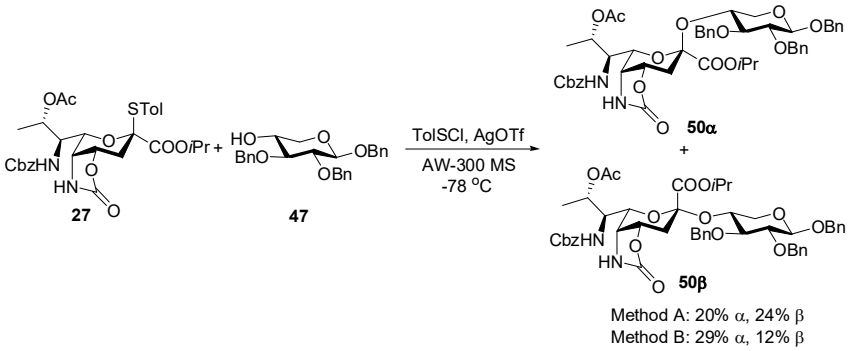
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.10 (d, *J* = 6.5 Hz, 3H, $(CH_3)_2CH$), 1.21 (d, *J* = 6.5 Hz, 3H, $(CH_3)_2CH$), 1.22 (d, *J* = 6.5 Hz, 3H, H-6), 1.31 (d, *J* = 6.5 Hz, 3H, H-9''), 1.86 (t, *J* = 13.0 Hz, 1H, H-3a''), 1.93 (s, 3H, CH_3CO), 1.99 (s, 3H, CH_3CO), 2.63 (dd, J_1 = 13.0 Hz, J_2 = 4.5 Hz, 1H, H-3e''), 3.25–3.31 (m, 2H, H-2' & H-5a'), 3.45–3.49 (m, 2H, H-3 & H-3'), 5.53 (q, *J* = 6.5 Hz, 1H, H-5), 3.62 (d, *J* = 10.0 Hz, 1H, H-6''), 3.68 (d, *J* = 2.0 Hz, 1H, H-4), 3.84 (dd, J_1 = 10.5 Hz, J_2 = 8.0 Hz, 1H, H-2), 3.85–3.89 (m, 1H, H-4'), 4.21 (dd, J_1 = 12.0 Hz, J_2 = 5.5 Hz, 1H, H-5e'), 4.27–4.33 (m, 2H, H-5'' & H-7''), 4.35 (d, *J* = 8.0 Hz, 1H, H-1), 4.40 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.60 (d, *J* = 7.0 Hz, 1H, H-1'), 4.63–4.69 (m, 4H, NH, CCl_3CH_2 & 2 × $PhCH_2$), 4.75 (d, *J* = 11.5 Hz, 1H, $PhCH_2$), 4.74–4.78 (m, 1H, H-4''), 4.78 (d, *J* = 11.5 Hz, 1H, $PhCH_2$), 4.90–4.97 (m, 5H, $(CH_3)_2CH$, CCl_3CH_2 & 3 × $PhCH_2$), 5.02 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 5.10 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 5.26–5.30 (m, 1H, H-8''), 5.32 (d, *J* = 10.0 Hz, 1H, NH), 7.23–7.39 (m, 25H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.4, 16.7, 21.0, 21.2, 21.6, 21.8, 33.6, 47.7, 52.6, 63.4, 65.2, 67.3, 67.8, 69.1, 70.78, 70.82, 71.5, 72.8, 74.7, 74.8, 75.2, 75.4, 78.7, 79.9, 81.7, 82.1, 95.8, 100.9, 101.2, 105.1, 127.51, 127.53, 127.7, 127.91, 127.94, 128.1, 128.18, 128.19, 128.22, 128.3, 128.39, 128.43, 128.5, 128.6, 136.4, 137.2, 138.4, 138.9, 139.1, 154.9, 156.0, 166.2, 170.3, 170.4.

IR (film) ν = 3038, 2994, 2112 (N_3), 1645, 1456, 1363, 1308, 1238, 1211, 1169, 1138, 1109, 1071, 1027 cm^{-1}.

HR-ESI-MS (m/z): calcd for $C_{66}H_{76}Cl_3N_5O_{19}Na^+$ ($M + Na^+$): 1370.4092, found: 1370.4080.

Benzyl 8-*O*-acetyl-7-*N*-benzyloxycarbonyl-5-*N*,4-*O*-carbonyl-1-isopropyl-α/β-pseudaminosyl-(2→4)-2,3-di-*O*-benzyl-β-D-xylopyranoside (50α/β):



Following **Method A**, the product was synthesized from donor **27** and xyloside acceptor **47** in 0.050 mmol scale. The product was purified by multiple silica gel column chromatography using *n*-hexane : ethyl acetate 2 : 1 to 1 : 1 *v*/*v* as eluent to give **50α** (9.0 mg, 20%) and **50β** (11 mg, 24%) as colorless solid.

Following **Method B**, the product was synthesized from donor **27** and xyloside acceptor **47** in 0.050 mmol scale. The product was purified by multiple silica gel column chromatography using *n*-hexane : ethyl acetate 2 : 1 to 1 : 1 *v*/*v* as eluent to give **50α** (13 mg, 29%) and **50β** (5.5 mg, 12%) as colorless solid.

The configuration of **50α** was determined through derivatization of **48** (vide infra).

For anomer **50α**:

$[\alpha]^{25}_{D}$ +3.9 ^{o} (*c* = 0.23, DCM).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.23 (d, *J* = 6.5 Hz, 3H, H-9'), 1.30 (d, *J* = 6.5 Hz, 6H, $(CH_3)_2CH$), 2.03 (s, 3H, CH_3CO), 2.04 (dd, J_1 = 15.0 Hz, J_2 = 5.0 Hz, 1H, H-3a'), 2.19 (dd, J_1 = 15.0 Hz, J_2 = 7.5 Hz, 1H, H-3e'), 3.12 (t, *J* = 11.0 Hz, 1H, H-5a), 3.18 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H, H-5'), 3.42–3.50 (m, 2H, H-2 & H-3), 3.68 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H, H-6'), 3.77 (dd, J_1 = 11.5 Hz, J_2 = 5.0 Hz, H-5e), 3.86 (td, J_1 = 9.5 Hz, J_2 = 5.0 Hz, H-4), 3.91–3.95 (m, 1H, H-7'), 4.44 (d, *J* = 7.0 Hz, 1H, H-1), 4.45 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.61–4.70 (m, 4H, H-4', NH & 2 × $PhCH_2$), 4.89–4.92 (m, 2H, 2 × $PhCH_2$), 4.99 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 5.00–5.04 (m, 1H, $(CH_3)_2CH$), 5.06 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 5.16–5.18 (m, 1H, H-8'), 5.17 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 6.38 (s, 1H, NH), 7.08–7.15 (m, 3H, ArH), 7.20–7.40 (m, 17H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.3, 21.4, 21.6, 21.8, 33.0, 51.5, 54.2, 63.7, 67.7, 68.7, 70.0, 70.77, 70.81, 71.1, 71.4, 74.7, 76.4, 82.4, 83.0, 96.4, 103.2, 128.0, 128.1, 128.2, 128.4, 128.5, 128.59, 128.61, 128.64, 128.7, 128.76, 128.82, 136.1, 137.2, 138.1, 138.2, 156.8, 158.2, 167.9, 171.3.

HR-ESI-MS (m/z): calcd for $C_{49}H_{56}N_2O_{14}Na^+$ (M + Na^+): 919.3624, found: 919.3582.

For anomer **50β:**

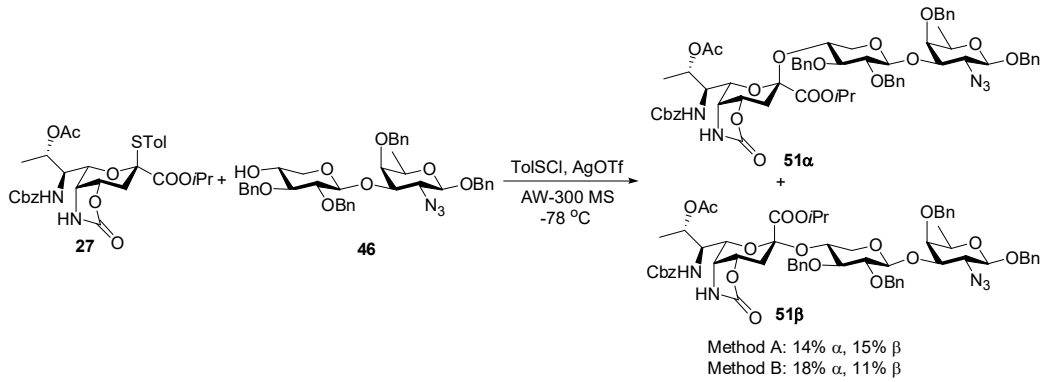
$[\alpha]^{25}_D$ +9.2 ^{o} (*c* = 0.38, DCM).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.152 (d, *J* = 6.5 Hz, 3H, $(CH_3)_2CH$), 1.154 (d, *J* = 6.5 Hz, 3H, $(CH_3)_2CH$), 1.38 (d, *J* = 6.5 Hz, 3H, H-9'), 2.02 (s, 3H, CH_3CO), 2.12 (dd, J_1 = 16.0 Hz, J_2 = 4.5 Hz, 1H, H-3a'), 2.48 (dd, J_1 = 16.0 Hz, J_2 = 3.0 Hz, 1H, H-3e'), 3.01 (t, *J* = 11.0 Hz, 1H, H-5a), 3.35 (dd, J_1 = 9.0 Hz, J_2 = 7.5 Hz, 1H, H-2), 3.41 (d, *J* = 10.0 Hz, 1H, H-6'), 3.51 (t, *J* = 9.0 Hz, 1H, H-3), 3.89 (d, *J* = 10.0 Hz, 1H, H-5'), 4.00–4.06 (m, 2H, H-4 & H-7'), 4.29 (dd, J_1 = 12.0 Hz, J_2 = 5.5 Hz, 1H, H-5e), 4.44 (d, *J* = 7.5 Hz, 1H, H-1), 4.61 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.67 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.73 (d, *J* = 11.5 Hz, 1H, $PhCH_2$), 4.83 (d, *J* = 11.5 Hz, 1H, $PhCH_2$), 4.86–4.91 (m, 2H, H-4' & $(CH_3)_2CH$), 4.87 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.91 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 5.08 (d, *J* = 9.5 Hz, 1H, NH), 5.12 (s, 2H, 2 × $PhCH_2$), 5.31–5.34 (m, 1H, H-8'), 6.27 (s, 1H, NH), 7.20–7.40 (m, 20H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.2, 21.2, 21.7, 21.8, 32.8, 50.8, 54.2, 65.5, 68.0, 70.3, 70.58, 70.61, 71.4, 71.5, 74.7, 74.9, 75.8, 82.2, 82.7, 99.2, 103.2, 127.3, 127.5, 127.8, 128.06, 128.11, 128.2, 128.3, 128.5, 128.6, 128.78, 128.83, 135.8, 137.7, 138.8, 139.3, 157.3, 158.0, 167.7, 170.6.

HR-ESI-MS (m/z): calcd for $C_{49}H_{56}N_2O_{14}Na^+$ (M + Na^+): 919.3624, found: 919.3584.

Benzyl 8-*O*-acetyl-7-*N*-benzyloxycarbonyl-5-*N*,4-*O*-carbonyl-1-isopropyl-α/β-pseudaminosyl-(2→4)-2,3-di-*O*-benzyl-β-D-xylopyranosyl-(1→3)-2-azido-4-*O*-benzyl-2-deoxy-β-D-fucopyranoside (51α/β):



Following **Method A**, the product was synthesized from donor **27** and disaccharide acceptor **46** in 0.050 mmol scale. The product was purified by multiple silica gel column chromatography using *n*-hexane : ethyl acetate 2 : 1 to 1 : 1 *v/v* as eluent to give **51α** (8.1 mg, 14%) and **51β** (8.7

mg, 15%) as colorless solid.

Following **Method B**, the product was synthesized from donor **27** and disaccharide acceptor **46** in 0.050 mmol scale. The product was purified by multiple silica gel column chromatography using *n*-hexane : ethyl acetate 2 : 1 to 1 : 1 *v/v* as eluent to give **51α** (10 mg, 18%) and **51β** (6.4 mg, 11%) as colorless solid.

The configuration of **51α** was determined through derivatization of **49α** (vide infra).

For anomer **51α:**

$[\alpha]^{25}_{D}$ +12.9 ^{o} (*c* = 1.3, DCM).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.17 (d, *J* = 6.5 Hz, 3H, H-9''), 1.20 (d, *J* = 6.0 Hz, 3H, H-6), 1.28 (d, *J* = 6.5 Hz, 3H, $(CH_3)_2CH$), 1.29 (d, *J* = 6.5 Hz, 3H, $(CH_3)_2CH$), 1.96 (s, 3H, CH_3CO), 2.05 (dd, J_1 = 14.5 Hz, J_2 = 4.5 Hz, 1H, H-3a''), 2.22 (dd, J_1 = 14.5 Hz, J_2 = 7.5 Hz, 1H, H-3e''), 3.06 (t, *J* = 10.5 Hz, 1H, H-5a'), 3.16 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H, H-5''), 3.36 (dd, J_1 = 9.0 Hz, J_2 = 7.5 Hz, 1H, H-2'), 3.43 (dd, J_1 = 10.5 Hz, J_2 = 3.0 Hz, 1H, H-3), 3.44–3.50 (m, 2H, H-5 & H-3'), 3.59 (d, *J* = 3.0 Hz, 1H, H-4), 3.64 (dd, J_1 = 8.5 Hz, J_2 = 2.5 Hz, 1H, H-6''), 3.68 (dd, J_1 = 11.5 Hz, J_2 = 5.0 Hz, 1H, H-5e'), 3.80–3.84 (m, 1H, H-4'), 3.86 (dd, J_1 = 10.5 Hz, J_2 = 8.0 Hz, 1H, H-2), 3.89–3.93 (m, 1H, H-7''), 4.32 (d, *J* = 8.0 Hz, 1H, H-1), 4.37 (d, *J* = 10.0 Hz, 1H, NH), 4.43 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.57 (d, *J* = 7.5 Hz, 1H, H-1'), 4.66 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.65–4.69 (m, 1H, H-4''), 4.72 (d, *J* = 11.5 Hz, 2H, 2 × $PhCH_2$), 4.94–5.06 (m, 6H, $(CH_3)_2CH$ & 5 × $PhCH_2$), 5.16 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 5.18–5.21 (m, 1H, H-8''), 6.28 (s, 1H, NH), 7.08–7.13 (m, 3H, ArH), 7.20–7.41 (m, 22H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.3, 16.7, 21.4, 21.6, 21.8, 33.0, 51.3, 54.1, 63.48, 63.53, 67.7, 68.7, 69.8, 70.4, 70.6, 70.7, 71.0, 74.6, 75.1, 76.5, 78.2, 80.1, 82.0, 82.9, 96.3, 101.0, 105.4, 127.7, 128.0, 128.1, 128.3, 128.4, 128.46, 128.52, 128.56, 128.58, 128.62, 128.7, 128.77, 128.82, 136.1, 137.1, 138.0, 138.2, 138.7, 156.8, 158.2, 167.7, 171.0.

IR (film) ν =3033, 2985, 2113 (N_3), 1646, 1308, 1239, 1215, 1163, 1100, 1066, 1048, 731, 696 cm^{-1}.

HR-ESI-MS (m/z): calcd for $C_{62}H_{71}N_5O_{17}Na^+$ ($M + Na^+$): 1180.4737, found: 1180.4608.

For anomer **51β:**

$[\alpha]^{25}_{D}$ +30.9 ^{o} (*c* = 0.21, DCM).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.11 (d, *J* = 6.5 Hz, 3H, $(CH_3)_2CH$), 1.14 (d, *J* = 6.5 Hz, 3H,

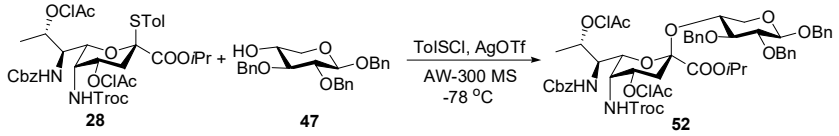
(CH_3)$_2$CH), 1.22 (d, J = 6.5 Hz, 3H, H-6), 1.35 (d, J = 6.5 Hz, 3H, H-9''), 1.96 (s, 3H, CH_3CO), 2.10 (dd, J_1 = 15.5 Hz, J_2 = 3.5 Hz, 1H, H-3a''), 2.50 (dd, J_1 = 15.5 Hz, J_2 = 2.5 Hz, 1H, H-3e''), 3.23–3.27 (m, 2H, H-2' & H-5a'), 3.40 (d, J = 10.0 Hz, 1H, H-6''), 3.45 (dd, J_1 = 10.5 Hz, J_2 = 2.0 Hz, 1H, H-3), 3.50–3.54 (m, 2H, H-5 & H-3'), 3.72 (d, J = 2.0 Hz, 1H, H-4), 3.82 (dd, J_1 = 10.5 Hz, J_2 = 8.0 Hz, 1H, H-2), 3.89 (d, J = 9.5 Hz, 1H, H-5''), 3.94–3.99 (m, 1H, H-4'), 4.04 (td, J_1 = 10.0 Hz, J_2 = 2.0 Hz, 1H, H-7''), 4.20 (dd, J_1 = 12.0 Hz, J_2 = 5.5 Hz, 1H, H-5e'), 4.34 (d, J = 8.0 Hz, 1H, H-1), 4.55 (d, J = 8.0 Hz, 1H, H-1'), 4.63–4.70 (m, 3H, 3 × PhCH_2), 4.75 (d, J = 11.0 Hz, 1H, PhCH_2), 4.82 (d, J = 12.0 Hz, 1H, PhCH_2), 4.82–4.85 (m, 1H, (CH_3)$_2$CH), 4.91–4.99 (m, 4H, H-4'' & 3 × PhCH_2), 5.05 (d, J = 9.5 Hz, 1H, NH), 5.13 (s, 2H, 2 × PhCH_2), 5.35–5.38 (m, 1H, H-8''), 6.27 (s, 1H, NH), 7.21–7.39 (m, 25H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.0, 16.6, 21.2, 21.7, 21.8, 32.6, 50.8, 54.2, 63.3, 65.4, 68.1, 69.9, 70.6, 70.8, 70.9, 71.5, 74.6, 74.8, 75.1, 75.7, 78.6, 80.5, 82.2, 82.4, 99.0, 101.4, 105.4, 127.3, 127.5, 127.9, 128.0, 128.1, 128.2, 128.3, 128.48, 128.54, 128.81, 128.85, 135.7, 137.3, 138.6, 139.2, 139.3, 157.3, 158.0, 167.7, 170.4.

IR (film) ν =3032, 2984, 2111 (N_3), 1646, 1456, 1244, 1165, 1099, 1067, 1028, 732, 695 cm^{-1}.

HR-ESI-MS (m/z): calcd for $C_{62}H_{71}N_5O_{17}Na^+$ (M + Na^+): 1180.4737, found: 1180.4604.

Benzyl 7-*N*-benzyloxycarbonyl-4,8-di-*O*-chloroacetyl-1-isopropyl-5-*N*-(2,2,2-trichloroethoxy-carbonyl)-α-pseudaminosyl-(2→4)-2,3-di-*O*-benzyl-β-D-xylopyranoside (52):



Method A: 68% α only
Method B: 32% α only

Following **Method A**, the product was synthesized from donor **28** and xyloside acceptor **47** in 0.050 mmol scale. The product was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 5 : 1 *v/v* as eluent. Only the α anomer **52** was obtained ($J_{C1\text{-}H3a}$ = 0 Hz, measured on Advance DRX Bruker 500 MHz NMR spectrometer by non-decoupled ^{13}C spectrum) as colorless solid (39 mg, 68%).

Following **Method B**, the product was synthesized from donor **28** and xyloside acceptor **47** in 0.10 mmol scale. The product was purified by silica gel column chromatography using

n-hexane : ethyl acetate 5 : 1 *v/v* as eluent. Only the α anomer **52** was obtained as colorless solid (37 mg, 32%).

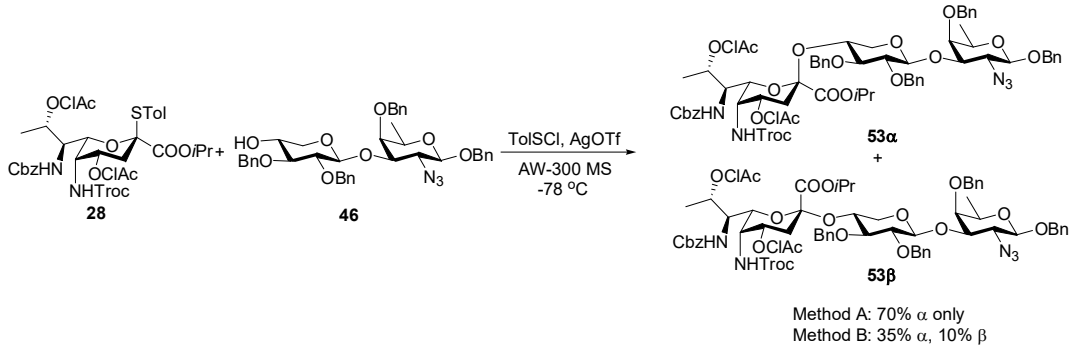
$[\alpha]^{25}_{D}$ −75.4 ^{o} (*c* = 0.75, DCM).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.01 (d, *J* = 6.5 Hz, 3H, H-9'), 1.34 (d, *J* = 6.5 Hz, 6H, $(CH_3)_2CH$), 1.83 (t, *J* = 13.0 Hz, 1H, H-3a'), 2.31 (dd, J_1 = 13.0 Hz, J_2 = 4.5 Hz, 1H, H-3e'), 2.83 (d, *J* = 10.5 Hz, 1H, NH), 3.13 (t, *J* = 12.0 Hz, 1H, H-5a), 3.45–3.50 (m, 2H, H-2 & H-3), 3.76–3.82 (m, 2H, H-4 & H-5e), 3.88–4.08 (m, 7H, H-5', H-6', H-7' & 4 × $ClCH_2CO$), 4.36 (d, *J* = 12.0 Hz, 1H, CCl_3CH_2), 4.42 (d, *J* = 9.5 Hz, 1H, $PhCH_2$), 4.48 (d, *J* = 6.5 Hz, 1H, H-1), 4.63 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.79 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.91–4.98 (m, 5H, CCl_3CH_2 & 4 × $PhCH_2$), 5.04–5.08 (m, 1H, $(CH_3)_2CH$), 5.12 (d, *J* = 9.5 Hz, 1H, $PhCH_2$), 5.18–5.21 (m, 1H, H-8'), 5.33 (dt, J_1 = 12.5 Hz, J_2 = 4.0 Hz, 1H, H-4'), 5.53 (d, *J* = 9.5 Hz, 1H, NH), 7.06 (t, *J* = 7.0 Hz, 1H, ArH), 7.31–7.45 (m, 19H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0, 21.7, 21.8, 32.3, 40.9, 41.2, 47.4, 51.9, 63.7, 67.2, 69.2, 69.4, 70.4, 71.0, 71.3, 71.5, 74.7, 74.8, 77.0, 82.4, 82.5, 95.7, 97.2, 103.2, 128.07, 128.12, 128.19, 128.24, 128.3, 128.5, 128.65, 128.69, 128.9, 129.5, 129.7, 136.6, 137.2, 137.5, 138.0, 155.1, 155.8, 166.7, 166.9, 167.1.

HR-ESI-MS (m/z): calcd for $C_{53}H_{59}Cl_5N_2O_{16}Na^+$ ($M + Na^+$): 1177.2199, found: 1177.2048.

Benzyl 7-*N*-benzyloxycarbonyl-4,8-di-*O*-chloroacetyl-1-isopropyl-5-*N*-(2,2,2-trichloroethoxy-carbonyl)-α/β-pseudaminosyl-(2→4)-2,3-di-*O*-benzyl-β-D-xylopyranosyl-(1→3)-2-azido-4-*O*-benzyl-2-deoxy-β-D-fucopyranoside (53α/β):



Following **Method A**, the product was synthesized from donor **28** and disaccharide acceptor **46** in 0.050 mmol scale. The product was purified by multiple silica gel column chromatography using *n*-hexane : ethyl acetate 3 : 1 *v/v* as eluent. Only the α anomer **53α** was obtained ($J_{C1\text{-}H3a}$ = 0

Hz, measured on Advance DRX Bruker 500 MHz NMR spectrometer by non-decoupled ^{13}C spectrum) as colorless solid (50 mg, 70%).

Following **Method B**, the product was synthesized from donor **28** and disaccharide acceptor **46** in 0.255 mmol scale. The product was purified by multiple silica gel column chromatography using *n*-hexane : ethyl acetate 4 : 1 *v*/*v* and toluene : ethyl acetate 10 : 1 *v*/*v* as eluents to give **53α** (128 mg, 35%) and **53β** (37 mg, 10%) ($J_{C1\text{-}H3a}$ = 6.6 Hz, measured on Advance DRX Bruker 500 MHz NMR spectrometer by non-decoupled ^{13}C spectrum) as colorless solid.

For anomer **53α:**

$[\alpha]^{25}_{D}$ –43.2 ^{o} (*c* = 0.82, DCM).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.98 (d, *J* = 6.6 Hz, 3H, H-9''), 1.22 (d, *J* = 6.3 Hz, 3H, H-6), 1.33 (d, *J* = 6.2 Hz, 6H, $(CH_3)_2CH$), 1.82 (t, *J* = 13.0 Hz, 1H, H-3a''), 2.31 (dd, J_1 = 13.4 Hz, J_2 = 4.6 Hz, 1H, H-3e''), 2.80 (d, *J* = 10.7 Hz, 1H, NH), 3.07 (t, *J* = 10.9 Hz, 1H, H-5a'), 3.39 (dd, J_1 = 9.0 Hz, J_2 = 7.6 Hz, 1H, H-2'), 3.45–3.51 (m, 3H, H-3, H-5 & H-3'), 3.60 (d, *J* = 2.6 Hz, 1H, H-4), 3.66–3.75 (m, 2H, H-4' & H-5e'), 3.86–3.90 (m, 2H, H-2 & H-5''), 3.91–4.08 (m, 6H, H-6'', H-7'' & 4 × $ClCH_2CO$), 4.32 (d, *J* = 8.0 Hz, 1H, H-1), 4.36 (d, *J* = 12.0 Hz, 1H, CCl_3CH_2), 4.40 (d, *J* = 9.6 Hz, 1H, $PhCH_2$), 4.61 (d, *J* = 7.5 Hz, 1H, H-1'), 4.92–5.03 (m, 6H, CCl_3CH_2 & 5 × $PhCH_2$), 5.04–5.08 (m, 1H, $(CH_3)_2CH$), 5.13 (d, *J* = 9.5 Hz, 1H, $PhCH_2$), 5.17–5.22 (m, 1H, H-8''), 5.30 (ddd, J_1 = 12.3 Hz, J_2 = 4.4 Hz, J_3 = 3.8 Hz, 1H, H-4''), 5.52 (d, *J* = 9.7 Hz, 1H, NH), 7.06 (t, *J* = 7.4 Hz, 1H, ArH), 7.27–7.45 (m, 24H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2, 16.5, 21.6, 21.7, 32.1, 40.8, 41.1, 47.2, 51.6, 63.3, 67.0, 69.0, 69.6, 70.1, 70.59, 70.62, 70.7, 71.5, 74.5, 74.6, 75.2, 76.9, 78.2, 79.7, 82.1, 82.2, 95.6, 96.9, 100.9, 105.2, 127.5, 127.8, 127.9, 128.0, 128.1, 128.18, 128.19, 128.4, 128.5, 128.6, 128.8, 129.3, 129.5, 136.4, 136.9, 137.4, 137.7, 138.6, 155.0, 155.7, 166.67, 166.71, 166.9.

IR (film) ν = 3033, 2959, 2929, 2856, 2113 (N_3), 1729, 1645, 1516, 1456, 1311, 1278, 1219, 1164, 1101, 1070, 1028, 698 cm^{-1}.

HR-ESI-MS (m/z): calcd for $C_{66}H_{74}Cl_5N_5O_{19}Na^+$ ($M + Na^+$): 1438.3313, found: 1438.3147.

For anomer **53β:**

$[\alpha]^{25}_{D}$ –33.6 ^{o} (*c* = 1.3, DCM).

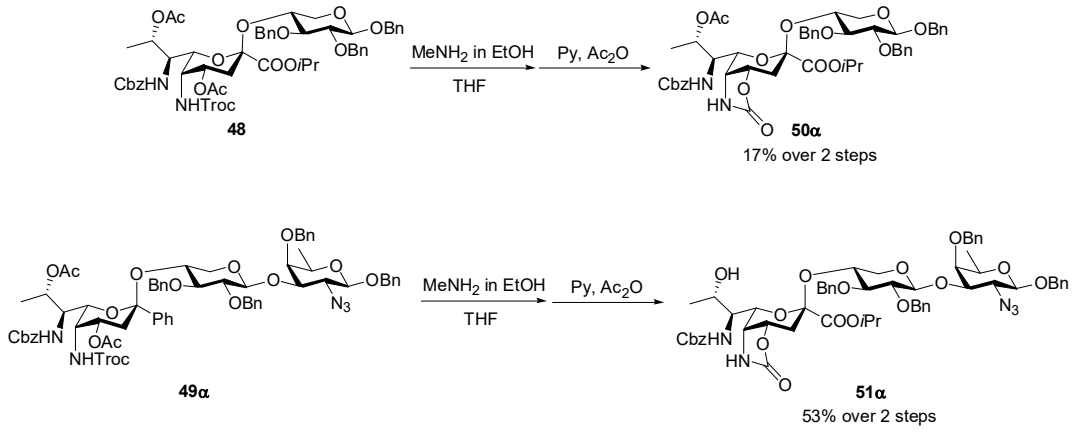
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.09 (d, *J* = 6.2 Hz, 3H, $(CH_3)_2CH$), 1.22 (d, *J* = 6.2 Hz, 3H, $(CH_3)_2CH$), 1.25 (d, *J* = 6.3 Hz, 3H, H-6), 1.35 (d, *J* = 6.5 Hz, 3H, H-9''), 1.92 (t, *J* = 13.1 Hz, 1H,

H-3a''), 2.66 (dd, J_1 = 13.1 Hz, J_2 = 4.4 Hz, 1H, H-3e''), 3.25–3.30 (m, 2H, H-2' & H-5a'), 3.45–3.49 (m, 2H, H-3 & H-3'), 3.55 (q, J = 6.3 Hz, 1H, H-5), 3.60 (d, J = 10.1 Hz, 1H, H-6''), 3.69 (s, 1H, H-4), 3.84 (dd, J_1 = 10.4 Hz, J_2 = 8.0 Hz, 1H, H-2), 3.85–3.88 (m, 3H, H-4' & 2 × ClCH_2CO), 3.98 (d, J = 15.2 Hz, 1H, ClCH_2CO), 4.02 (d, J = 15.2 Hz, 1H, ClCH_2CO), 4.18 (dd, J_1 = 11.7 Hz, J_2 = 5.2 Hz, 1H, H-5e'), 4.31–4.35 (m, 2H, H-5'' & H-7''), 4.36 (d, J = 7.9 Hz, 1H, H-1), 4.42 (d, J = 12.0 Hz, 1H, PhCH_2), 4.59 (d, J = 7.4 Hz, 1H, H-1'), 4.63–4.70 (m, 4H, NH, CCl_3CH_2 & 2 × PhCH_2), 4.76 (s, 2H, 2 × PhCH_2), 4.84 (dt, J_1 = 12.9 Hz, *J2* = 3.9 Hz, 1H, H-4''), 4.90–4.98 (m, 6H, $(CH_3)_2CH$, CCl_3CH_2 & 4 × PhCH_2), 5.08 (d, J = 12.2 Hz, 1H, PhCH_2), 5.34 (d, J = 9.7 Hz, 1H, NH), 5.35–5.38 (m, 1H, H-8''), 7.24–7.40 (m, 25H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.8, 16.5, 21.4, 21.7, 33.2, 40.7, 40.9, 47.2, 52.0, 63.2, 65.0, 67.3, 69.5, 70.7, 70.9, 71.7, 72.3, 74.6, 74.7, 75.1, 75.18, 75.25, 78.7, 79.8, 81.4, 81.9, 95.4, 100.7, 101.0, 105.0, 127.6, 127.68, 127.74, 127.8, 127.9, 128.0, 128.1, 128.2, 128.27, 128.31, 128.35, 128.5, 136.1, 137.0, 138.2, 138.7, 138.9, 154.9, 155.9, 165.9, 166.6, 166.7.

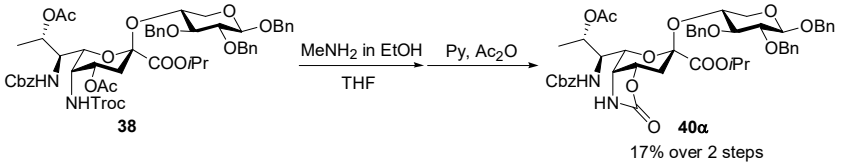
IR (film) ν = 3037, 2957, 2935, 2858, 2112 (N_3), 1645, 1456, 1358, 1310, 1209, 1167, 1109, 1071, 1026, 735, 698 cm^{-1}.

HR-ESI-MS (m/z): calcd for $C_{66}H_{74}Cl_5N_5O_{19}Na^+$ (M + Na^+): 1438.3313, found: 1438.3142.



Scheme S6. Elucidation of the glycosidic linkage configurations in 50α and 51α via derivatization of 48 and 49α.

Benzyl 8-*O*-acetyl-7-*N*-benzyloxycarbonyl-5-*N*,4-*O*-carbonyl-1-isopropyl-α-pseudaminosyl-(2→4)-2,3-di-*O*-benzyl-β-D-xylopyranoside (50α):

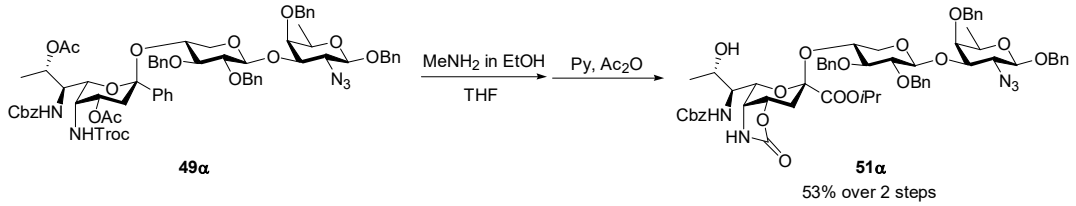


To a stirred solution of **48** (29 mg, 0.027 mmol, 1.0 equiv) in THF (0.5 mL), $MeNH_2$ (8 M solution in EtOH, 1.0 mL) was added in one portion. The mixture was stirred at r.t. for 24 h, then was diluted with ethyl acetate (20 mL). The solution was washed with 1 M HCl (aq) and water, and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by silica gel preparative TLC using *n*-hexane : ethyl acetate 1 : 1.5 *v*/*v* as eluent. The intermediate with cyclic carbamate structure was obtained as colorless solid (4.7 mg, 20%).

The intermediate was dissolved in pyridine (1.0 mL), then Ac_2O (0.10 mL, large excess amount) was added. The mixture was stirred at r.t. overnight, then was concentrated under vacuum. The residue was diluted with ethyl acetate (20 mL), and was thoroughly washed with 1 M HCl (aq), sat. $NaHCO_3$ (aq) and water. The organic phase was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by silica gel preparative TLC using *n*-hexane : ethyl acetate 1 : 1 *v*/*v* as eluent. The product **50α** was obtained as colorless solid (4.0 mg, 82%).

The product shows exactly the same ^{1}H and ^{13}C NMR spectra as the disaccharide **50α** obtained via glycosylation of donor **27** and acceptor **47**. This transformation provides unambiguous evidence for the α configuration of **50α**.

Benzyl 8-*O*-acetyl-7-*N*-benzyloxycarbonyl-5-*N*,4-*O*-carbonyl-1-isopropyl-α-pseudaminosyl-(2→4)-2,3-di-*O*-benzyl-β-D-xylopyranosyl-(1→3)-2-azido-4-*O*-benzyl-2-deoxy-β-D-fucopyranoside (51α):



To a stirred solution of **49α** (112 mg, 0.083 mmol, 1.0 equiv) in THF (1.5 mL), $MeNH_2$ (8 M solution in EtOH, 3.0 mL) was added in one portion. The mixture was stirred at r.t. for 24 h, then was diluted with ethyl acetate (30 mL). The solution was washed with 1 M HCl (aq) and water, and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was

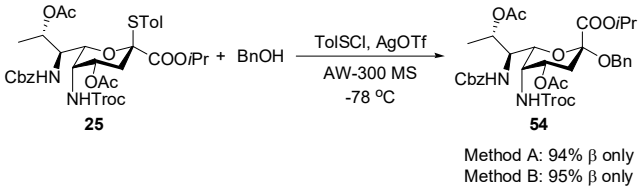
purified by silica gel column chromatography using *n*-hexane : ethyl acetate 1 : 1 to 1 : 1.5 *v*/*v* as eluent. The intermediate with cyclic carbamate structure was obtained as colorless solid (54 mg, 58%).

To a stirred solution of the intermediate (20 mg, 0.018 mmol, 1.0 equiv) in pyridine (2.0 mL), Ac_2O (0.20 mL, large excess amount) was added. The mixture was stirred at r.t. overnight, then was concentrated under vacuum. The residue was diluted with ethyl acetate (20 mL), and was thoroughly washed with 1 M HCl (aq), sat. $NaHCO_3$ (aq) and water. The organic phase was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 1 : 1 *v*/*v* as eluent. The product **51α** was obtained as colorless solid (19 mg, 92%).

The product shows exactly the same ^{1}H and ^{13}C NMR spectra as the trisaccharide **51α** obtained via glycosylation of donor **27** and acceptor **46**. This transformation provides unambiguous evidence for the α configuration of **51α**.

Part 10. Total synthesis of pseudaminic acid 1.

Benzyl 7-*N*-benzyloxycarbonyl-4,8-di-*O*-acetyl-1-isopropyl-5-*N*-(2,2,2-trichloroethoxy-carbonyl)-β-pseudaminoside (54):



Following **Method A** (Part 9), the product was synthesized from donor **25** and benzyl alcohol acceptor (4.0 equiv was used) in 0.10 mmol scale. The product was purified by silica gel column chromatography using toluene : ethyl acetate 10 : 1 *v*/*v* as eluent. Only the β anomer **54** was obtained ($J_{C1\text{-}H3a}$ = 6.6 Hz, measured on Advance DRX Bruker 500 MHz NMR spectrometer by non-decoupled ^{13}C spectrum) as colorless syrup (73 mg, 94%).

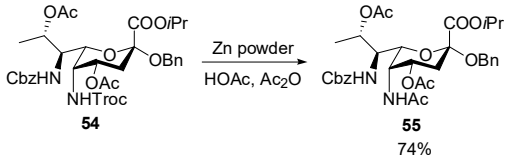
$[\alpha]^{25}_{D}$ –49.7 ° (*c* = 0.85, DCM).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (d, *J* = 6.5 Hz, 3H, $(CH_3)_2CH$), 1.32 (d, *J* = 6.5 Hz, 3H, $(CH_3)_2CH$), 1.38 (d, *J* = 6.5 Hz, 3H, H-9), 1.96 (t, *J* = 13.0 Hz, 1H, H-3a), 1.98 (s, 6H, 2 × CH_3CO), 2.55 (dd, J_1 = 13.0 Hz, J_2 = 4.0 Hz, 1H, H-3e), 3.97 (d, *J* = 9.5 Hz, 1H, H-6), 4.32–4.36 (m, 2H, H-5 & H-7), 4.40–4.43 (m, 2H, CCl_3CH_2 & $PhCH_2$), 4.71 (d, *J* = 11.0 Hz, 1H, NH), 4.80–4.84 (m, 2H, H-4 & CCl_3CH_2), 4.97 (d, *J* = 12.5 Hz, 1H, $PhCH_2$), 5.02 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 5.06–5.13 (m, 2H, $(CH_3)_2CH$ & $PhCH_2$), 5.35–5.38 (m, 1H, H-8), 5.43 (d, *J* = 10.0 Hz, 1H, NH), 7.29–7,37 (m, 10H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8, 21.0, 21.3, 21.8, 21.9, 33.3, 48.0, 52.9, 67.2, 67.3, 67.9, 69.6, 70.7, 72.9, 74.7, 95.8, 99.5, 128.27, 128.32, 128.6, 136.4, 136.7, 155.0, 156.0, 167.5, 170.41, 170.45.

HR-ESI-MS (m/z): calcd for $C_{34}H_{41}Cl_3N_2O_{12}Na^+$ ($M + Na^+$): 797.1617, found: 797.1596.

Benzyl 5-*N*-acetyl-7-*N*-benzyloxycarbonyl-4,8-di-*O*-acetyl-1-isopropyl-β-pseudaminoside (55):



To a stirred solution of **54** (73 mg, 0.94 mmol, 1.0 equiv) in HOAc (2.0 mL), Ac_2O (0.44 mL,

4.7 mmol, 5.0 equiv) and Zn powder (611 mg, 9.4 mmol, 10 equiv) were added. The mixture was stirred at 40 °C for 3 h. When full conversion was achieved, the mixture was diluted with ethyl acetate (30 mL) and filtered through celite. The filtrate was washed with sat. $NaHCO_3$ (aq) and brine, and the organic phase was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 1 : 1 as eluent. The product **55** was obtained as white foam (45 mg, 74%).

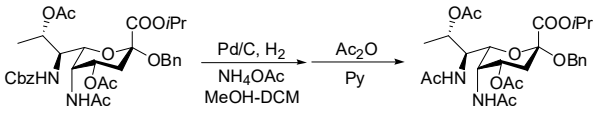
$[\alpha]^{25}_D$ −67.1 ° (*c* = 0.13, DCM).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (d, *J* = 6.5 Hz, 3H, $(CH_3)_2CH$), 1.32 (d, *J* = 6.5 Hz, 3H, $(CH_3)_2CH$), 1.36 (d, *J* = 7.0 Hz, 3H, H-9), 1.90 (t, *J* = 13.0 Hz, 1H, H-3a), 1.98 (s, 3H, CH_3CO), 2.01 (s, 3H, CH_3CO), 2.03 (s, 3H, CH_3CO), 2.53 (dd, J_1 = 13.0 Hz, J_2 = 4.0 Hz, 1H, H-3e), 3.98 (d, *J* = 10.0 Hz, 1H, NH), 4.31 (td, J_1 = 11.0 Hz, J_2 = 3.0 Hz, 1H, H-7), 4.42 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.59 (d, *J* = 9.0 Hz, 1H, H-5), 4.71 (d, *J* = 11.0 Hz, 1H, H-6), 4.81 (dt, J_1 = 13.0 Hz, J_2 = 4.0 Hz, 1H, H-4), 4.84 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.94 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 5.07–5.12 (m, 1H, $(CH_3)_2CH$), 5.15 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 5.35–5.37 (m, 1H, H-8), 5.86 (d, *J* = 9.5 Hz, 1H, NH), 7.30–7.36 (m, 10H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.6, 21.1, 21.3, 21.86, 21.91, 23.5, 33.5, 45.5, 52.8, 67.1, 67.3, 67.8, 69.6, 70.7, 73.0, 99.6, 128.21, 128.25, 128.27, 128.32, 128.62, 128.65, 136.5, 136.8, 156.2, 167.5, 170.5, 170.6, 170.9.

HR-ESI-MS (m/z): calcd for $C_{33}H_{43}N_2O_{11}^+$ ($M + H^+$): 643.2861, found: 643.2835.

Benzyl 5,7-di-*N*-acetyl-4,8-di-*O*-acetyl-1-isopropyl-β-pseudaminoside (56):



To a 25 mL round bottom flask containing **55** (45 mg, 0.070 mmol, 1.0 equiv), Pd/C (10% Pd on activated carbon, 30 mg) and NH_4OAc (11 mg, 0.14 mmol, 2.0 equiv), DCM (2.0 mL) and MeOH (2.0 mL) were added. The mixture was stirred under 1 atm H_2 atmosphere for 1 h, then was filtered through celite to remove catalyst. The filtrate was concentrated under vacuum, and the residue was dissolved in pyridine (2.0 mL). To this mixture, Ac_2O (1.0 mL, excess amount) was added. After being stirred at r.t. for 1 h, the mixture was concentrated under vacuum. The residue

was dissolved in ethyl acetate (30 mL), and the solution was sequentially washed with 1 M HCl (aq) and sat. $NaHCO_3$ (aq). The organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum. The residue was purified by silica gel column chromatography using DCM : MeOH 30 : 1 as eluent. The product **56** was obtained as colorless solid (36 mg, 93%).

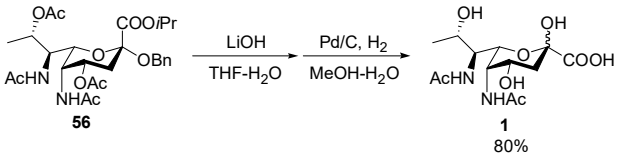
$[\alpha]^{25}_D$ −48.6 ^{o} (*c* = 0.21, DCM).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.29 (d, *J* = 6.5 Hz, 3H, $(CH_3)_2CH$), 1.32 (d, *J* = 6.5 Hz, 3H, $(CH_3)_2CH$), 1.39 (d, *J* = 6.5 Hz, 3H, H-9), 1.88 (t, *J* = 13.0 Hz, 1H, H-3a), 1.95 (s, 3H, CH_3CO), 1.995 (s, 3H, CH_3CO), 2.005 (s, 3H, CH_3CO), 2.04 (s, 3H, CH_3CO), 2.52 (dd, J_1 = 13.0 Hz, J_2 = 4.0 Hz, 1H, H-3e), 4.09 (dd, J_1 = 10.0 Hz, J_2 = 1.5 Hz, 1H, H-6), 4.42 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.51 (d, *J* = 10.0 Hz, 1H, H-5), 4.56 (td, J_1 = 10.5 Hz, J_2 = 3.0 Hz, 1H, H-7), 4.80 (dt, J_1 = 13.0 Hz, J_2 = 4.5 Hz, 1H, H-4), 4.84 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 5.08–5.13 (m, 1H, $(CH_3)_2CH$), 5.32 (qd, J_1 = 6.5 Hz, J_2 = 3.0 Hz, 1H, H-8), 5.60 (d, *J* = 10.5 Hz, 1H, NH), 5.94 (d, *J* = 9.0 Hz, 1H, NH), 7.29–7.38 (m, 5H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3, 21.1, 21.4, 21.88, 21.91, 23.35, 23.39, 33.4, 45.6, 50.8, 67.1, 67.8, 70.2, 70.6, 72.6, 99.5, 128.3, 128.4, 128.6, 136.8, 167.5, 170.4, 170.72, 170.74, 171.6.

HR-ESI-MS (m/z): calcd for $C_{27}H_{38}N_2O_{10}Na^+$ ($M + Na^+$): 573.2419, found: 573.2395.

5,7-Diacetamido-3,5,7,9-tetradeoxy-L-*glycero*-L-*manno*-2-nonulopyranosonic acid (1):



To a stirred solution of **56** (30 mg, 0.055 mmol, 1.0 equiv) in MeOH (2.2 mL) and THF (0.55 mL), the solution of LiOH (aq) (1 M solution, 0.55 mL, 0.55 mmol, 10 equiv) was added dropwise. The mixture was stirred at r.t. for 24 h. When full conversion was achieved, the mixture was neutralized by DOWEX 50(H) resin. After filtration, the solvent was removed under vacuum, and the residue was used in the next step without purification.

To a 25 mL round bottom flask containing the saponification product, Pd/C (10% Pd on activated carbon, 30 mg) was added, followed by MeOH (4.0 mL) and H_2O (1.0 mL). The mixture was stirred under 1 atm H_2 atmosphere for 12 h. After filtration, the solvent was removed under vacuum, and the residue was further purified by BioGel column using H_2O as eluent. The product

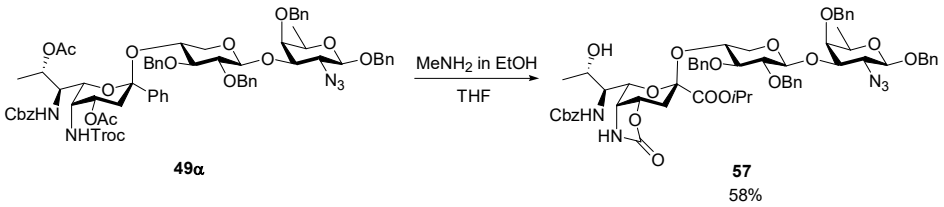
1 was obtained after lyophilization as white solid (15 mg, 80%). The product shows the same NMR spectra as the literature report.[11]

^{1}H NMR (400 MHz, D_2O): δ = 1.08 (d, *J* = 6.4 Hz, 3H, H-9), 1.76 (t, *J* = 12.8 Hz, 1H, H-3a), 1.91 (dd, J_1 = 13.6 Hz, J_2 = 4.8 Hz, 1H, H-3e), 1.95 (s, 3H, CH_3CO), 1.99 (s, 3H, CH_3CO), 4.00 (d, *J* = 10.4 Hz, 1H, H-6), 4.07-4.17 (m, 3H, H-5, H-7 & H-8), 4.22 (br, 1H, H-4).

^{13}C NMR (100 MHz, D_2O): δ = 15.2, 21.8, 22.0, 34.8, 48.8, 52.9, 65.1, 66.7, 69.9, 96.4, 173.7, 174.6, 176.4.

Part 11. Attempts for trisaccharide side chain manipulation.

Benzyl 7-*N*-benzyloxycarbonyl-5-*N*,4-*O*-carbonyl-1-isopropyl-α/β-pseudaminosyl-(2→4)-2,3-di-*O*-benzyl-β-D-xylopyranosyl-(1→3)-2-azido-4-*O*-benzyl-2-deoxy-β-D-fucopyranoside (57):



49α **57**
58%

To a stirred solution of **49α** (112 mg, 0.083 mmol, 1.0 equiv) in THF (1.5 mL), $MeNH_2$ (8 M solution in EtOH, 3.0 mL) was added in one portion. The mixture was stirred at r.t. for 24 h, then was diluted with ethyl acetate (30 mL). The solution was washed with 1 M HCl (aq) and water, and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 1 : 1 to 1 : 1.5 *v*/*v* as eluent. Only the product **57** with Troc group destroyed was obtained as colorless solid (54 mg, 58%).

$[\alpha]^{25}_{D}$ +34.6 ^{o} (*c* = 0.37, DCM).

^{1}H NMR (500 MHz, CD_3CN): δ = 1.02 (d, *J* = 6.5 Hz, 3H, H-9''), 1.20 (d, *J* = 6.5 Hz, 3H, H-6), 1.237 (d, *J* = 6.0 Hz, 3H, $(CH_3)_2CH$), 1.242 (d, *J* = 6.0 Hz, 3H, $(CH_3)_2CH$), 2.10 (dd, J_1 = 15.5 Hz, J_2 = 3.5 Hz, 1H, H-3a''), 2.54 (dd, J_1 = 15.5 Hz, J_2 = 5.0 Hz, 1H, H-3e''), 3.16 (dd, J_1 = 11.5 Hz, J_2 = 10.0 Hz, 1H, H-5a'), 3.33 (dd, J_1 = 9.0 Hz, J_2 = 7.5 Hz, 1H, H-2'), 3.36 (d, *J* = 4.5 Hz, 1H, OH), 3.50 (t, *J* = 9.0 Hz, 1H, H-3'), 3.54 (dd, J_1 = 10.5 Hz, J_2 = 3.0 Hz, 1H, H-3), 3.55–3.60 (m, 3H, H-5, H-5'' & H-7''), 3.65 (dd, J_1 = 11.5 Hz, J_2 = 5.0 Hz, 1H, H-5e'), 3.66 (d, *J* = 3.0 Hz, 1H, H-4), 3.71 (dd, J_1 = 10.5 Hz, J_2 = 8.0 Hz, 1H, H-2), 3.72 (dd, J_1 = 10.0 Hz, J_2 = 2.5 Hz, 1H, H-6''), 3.88 (dt, J_1 = 10.0 Hz, J_2 = 5.0 Hz, 1H, H-4'), 4.01–4.06 (m, 1H, H-8''), 4.42 (d, *J* = 8.0 Hz, 1H, H-1), 4.59 (d, *J* = 7.5 Hz, 1H, H-1'), 4.62–4.67 (m, 3H, 3 × $PhCH_2$), 4.70 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.74 (d, *J* = 10.5 Hz, 1H, NH), 4.78–4.82 (m, 1H, H-4''), 4.86 (d, *J* = 11.5 Hz, 1H, $PhCH_2$), 4.87 (d, *J* = 11.5 Hz, 1H, $PhCH_2$), 4.94 (d, *J* = 11.5 Hz, 1H, $PhCH_2$), 4.95–4.99 (m, 1H, $(CH_3)_2CH$), 4.97 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 5.07 (d, *J* = 12.5 Hz, 1H, $PhCH_2$), 5.12 (d, J = 12.5 Hz, 1H, $PhCH_2$), 6.07 (s, 1H, NH), 7.20–7.42 (m, 25H).

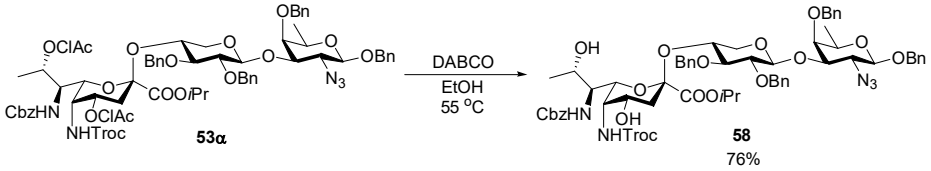
^{13}C NMR (125 MHz, CD_3CN): δ = 16.9, 18.8, 21.7, 21.8, 33.4, 51.6, 57.2, 63.9, 64.4, 67.6, 67.8,

71.2, 71.3, 71.5, 72.1, 75.2, 75.9, 76.6, 79.9, 80.9, 82.9, 83.1, 97.1, 102.1, 106.0, 128.46, 128.49, 128.78, 128.82, 129.0, 129.07, 129.10, 129.13, 129.20, 129.24, 129.3, 129.37, 129.39, 129.6, 137.8, 138.6, 139.6, 139.7, 140.2, 158.4, 158.5, 169.2.

IR (film) ν = 3033, 2975, 2857, 2112 (N_3), 1645, 1516, 1456, 1361, 1216, 1166, 1099, 1070, 735, 698 cm^{-1}.

HR-ESI-MS (m/z): calcd for $C_{60}H_{69}N_5O_{16}Na^+$ ($M + Na^+$): 1138.4632, found: 1138.4623.

Benzyl 7-*N*-benzyloxycarbonyl-1-isopropyl-5-*N*-(2,2,2-trichloroethoxycarbonyl)-α/β-pseudaminosyl-(2→4)-2,3-di-*O*-benzyl-β-D-xylopyranosyl-(1→3)-2-azido-4-*O*-benzyl-2-deoxy-β-D-fucopyranoside (58):



To a 10 mL round bottom flask containing **53α** (84 mg, 0.059 mmol, 1.0 equiv), DABCO (99 mg, 0.883 mmol, 15 equiv) and EtOH (3.0 mL) were added. The mixture was stirred at 55 °C for 2 h, then was diluted with ethyl acetate (30 mL). The solution was washed with 1 M HCl (aq) and water, and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 2 : 1 *v*/*v* as eluent. The product **58** was obtained as colorless solid (56 mg, 76%).

$[\alpha]^{25}_D$ −5.2 ° (*c* = 0.77, DCM).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.06 (d, *J* = 6.0 Hz, 3H, H-9''), 1.24 (d, *J* = 6.5 Hz, 3H, H-6), 1.31 (d, *J* = 6.0 Hz, 3H, $(CH_3)_2CH$), 1.32 (d, *J* = 6.0 Hz, 3H, $(CH_3)_2CH$), 1.54 (t, J = 13.0 Hz, 1H, H-3a''), 1.83 (br, 1H, OH), 2.32 (dd, J_1 = 13.5 Hz, J_2 = 4.5 Hz, 1H, H-3e''), 2.52 (br, 1H, OH), 2.96 (d, *J* = 11.0 Hz, 1H, NH), 3.08 (t, *J* = 11.0, 1H, H-5a'), 3.36 (dd, J_1 = 9.5 Hz, J_2 = 8.0 Hz, 1H, H-2'), 3.45 (dd, J_1 = 7.5 Hz, J_2 = 3.0 Hz, 1H, H-3), 3.46–3.51 (m, H-5 & H-3'), 3.57 (d, *J* = 3.0 Hz, 1H, H-4), 3.60–3.66 (m, 3H, H-4', H-5'' & H-7''), 3.79 (dd, J_1 = 10.0 Hz, J_2 = 5.5 Hz, 1H, H-5e'), 3.83 (q, *J* = 7.0 Hz, 1H, H-8''), 3.87 (dd, J_1 = 10.5 Hz, J_2 = 7.5 Hz, 1H, H-2), 4.04–4.08 (m, 1H, H-4''), 4.10 (dd, J_1 = 10.5 Hz, J_2 = 1.5 Hz, 1H, H-6''), 4.32 (d, *J* = 8.0 Hz, 1H, H-1), 4.41 (d, *J* = 10.5 Hz, 1H, $PhCH_2$), 4.46 (d, *J* = 12.0 Hz, 1H, CCl_3CH_2), 4.61 (d, *J* = 7.5 Hz, 1H, H-1'), 4.66 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.71 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.73 (d, *J* = 11.5 Hz, 1H, $PhCH_2$),

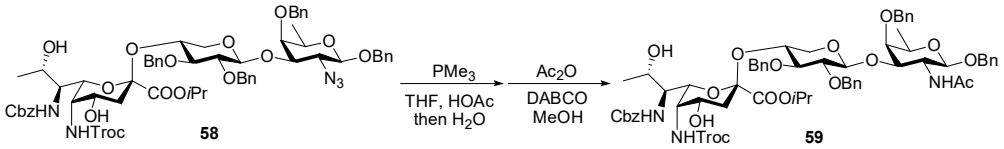
4.85 (d, J = 12.0 Hz, 1H, CCl_3CH_2), 4.92–5.01 (m, 5H, 5 × $PhCH_2$), 5.03–5.08 (m, 1H, $(CH_3)_2CH$), 5.12 (d, J = 10.5 Hz, 1H, $PhCH_2$), 5.33 (d, J = 9.5 Hz, 1H, NH), 7.04 (t, J = 7.0 Hz, 1H, ArH), 7.22-7.44 (m, 24H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.6, 19.0, 21.7, 21.8, 35.2, 50.8, 54.4, 63.4, 63.5, 66.0, 67.1, 69.6, 70.5, 70.7, 70.8, 71.0, 72.6, 74.8, 75.0, 75.4, 76.6, 78.5, 79.6, 82.4, 82.5, 95.4, 97.3, 101.0, 105.1, 127.7, 127.95, 127.98, 128.1, 128.2, 128.30, 128.33, 128.4, 128.5, 128.61, 128.65, 128.9, 129.4, 136.6, 137.1, 137.8, 138.6, 155.9, 156.3, 167.6.

IR (film) ν = 3032, 2987, 2933, 2857, 2112 (N_3), 1641, 1516, 1456, 1358, 1217, 1164, 1100, 1069, 1040, 1028 cm^{-1}.

HR-ESI-MS (m/z): calcd for $C_{62}H_{73}Cl_3N_5O_{17}^+$ ($M + H^+$): 1264.4062, found: 1264.3921.

Benzyl 7-*N*-benzyloxycarbonyl-1-isopropyl-5-*N*-(2,2,2-trichloroethoxycarbonyl)-α/β-pseudaminosyl-(2→4)-2,3-di-*O*-benzyl-β-D-xylopyranosyl-(1→3)-2-acetamido-4-*O*-benzyl-2-deoxy-β-D-fucopyranoside (59):



To a stirred solution of **58** (39 mg, 0.031 mmol, 1.0 equiv) in THF (2.0 mL) under argon atmosphere, HOAc (9.0 μL, 0.016 mmol, 5.0 equiv) was added, followed by PMe_3 (1.0 M solution in THF, 0.31 mL, 0.31 mmol, 10 equiv). The mixture was stirred at r.t. for 10 h, then H_2O (0.20 mL) was added. After being stirred for further 12 h, the mixture was concentrated under vacuum, and the residue was dissolved in ethyl acetate (20 mL). The solution was washed with water, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was dissolved in MeOH (2.0 mL), then DABCO (17 mg, 0.155 mmol, 5.0 equiv) and Ac_2O (0.30 mL, large excess amount) were added. The mixture was stirred at r.t. for 2 h, then was diluted with ethyl acetate (20 mL). The solution was sequentially washed with 1 M HCl (aq), sat. $NaHCO_3$ (aq) and water. The organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum. The residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 1 : 1.2 *v*/*v* as eluent. The product **59** was obtained as colorless solid (22 mg, 56%).

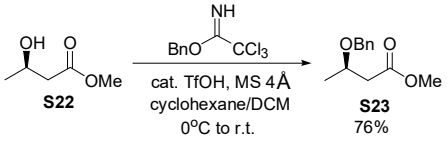
$[\alpha]^{25}_D$ −18.3 ^{o} (*c* = 0.88, DCM).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.07 (d, *J* = 6.0 Hz, 3H, H-9''), 1.23 (d, *J* = 6.5 Hz, 3H, H-6), 1.32 (d, *J* = 6.0 Hz, 3H, $(CH_3)_2CH$), 1.34 (d, *J* = 6.0 Hz, 3H, $(CH_3)_2CH$), 1.52 (s, 3H, CH_3CO), 1.55 (t, *J* = 13.0, 1H, H-3a''), 2.33 (dd, J_1 = 13.5 Hz, J_2 = 4.5 Hz, 1H, H-3e''), 2.46 (d, *J* = 4.0 Hz, 1H, OH), 2.98 (d, *J* = 10.5 Hz, 1H, NH), 3.10 (t, *J* = 11.0 Hz, 1H, H-5a'), 3.27–3.32 (m, 2H, H-2 & H-2'), 3.44 (t, *J* = 9.5 Hz, 1H, H-3'), 3.58 (br, 1H, OH), 3.61–3.67 (m, 5H, H-4, H-5, H-5e', H-5'' & H-7''), 3.78–3.85 (m, 2H, H-4' & H-8''), 4.06–4.09 (m, 1H, H-4''), 4.12 (d, *J* = 11.0 Hz, 1H, H-6''), 4.32 (d, *J* = 8.0 Hz, 1H, H-1'), 4.47 (d, *J* = 12.0 Hz, 1H, CCl_3CH_2), 4.48 (d, *J* = 10.0 Hz, 1H, $PhCH_2$), 4.50 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.65 (dd, J_1 = 11.0 Hz, J_2 = 3.0 Hz, 1H, H-3), 4.77 (d, *J* = 12.0 Hz, 1H, CCl_3CH_2), 4.79 (s, 2H, 2 × $PhCH_2$), 4.86 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.87 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.93 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.95 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 5.00 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 5.03 (d, *J* = 8.5 Hz, 1H, H-1), 5.05–5.10 (m, 1H, $(CH_3)_2CH$), 5.13 (d, *J* = 10.5 Hz, 1H, $PhCH_2$), 5.19 (d, *J* = 6.5 Hz, 1H, NH), 5.31 (d, *J* = 9.0 Hz, 1H, NH), 7.05 (t, *J* = 7.0 Hz, 1H, ArH), 7.25–7.45 (m, 24H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.8, 19.2, 21.8, 23.5, 35.3, 50.9, 54.4, 56.1, 63.4, 66.2, 67.1, 69.7, 70.4, 70.6, 71.0, 71.2, 72.6, 74.6, 75.1, 75.2, 76.6, 77.6, 79.5, 82.9, 95.4, 97.4, 98.3, 105.1, 127.4, 127.5, 127.9, 128.0, 128.17, 128.22, 128.27, 128.33, 128.4, 128.6, 128.8, 129.0, 129.5, 136.6, 137.78, 137.83, 138.5, 139.3, 155.9, 156.3, 167.5, 171.4.

HR-ESI-MS (m/z): calcd for $C_{64}H_{77}Cl_3N_3O_{18}^+$ ($M + H^+$): 1280.4262, found: 1280.4117.

Methyl (*R*)-3-benzyloxybutanoate (S23):



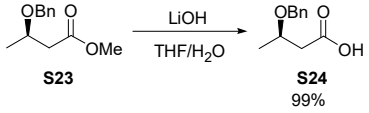
Methyl (*R*)-3-hydroxybutanoate **S22** (1.49 mL, 13.3 mmol, 1.0 equiv), *O*-benzyl trichloroacetimidate (4.03 g, 15.9 mmol, 1.2 equiv), and 4 Å molecular sieves (2.00 g, flame dried) were added to the mixture of cyclohexane (20 mL) and DCM (10 mL). The mixture was stirred at r.t. for 30 min and cooled to 0 °C. Triflic acid (199 μL, 2.25 mmol, 0.17 equiv) was added dropwise at 0 °C, then the mixture was stirred at r.t. for 16 h. The reaction was quenched with Et_3N, filtered through a pad of celite, and concentrated. The residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 30 : 1 *v*/*v* as eluent. The methyl

(*R*)-benzyloxybutanoate **S23** was obtained as colourless liquid (2.09 g, 76%).[12]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (d, *J* = 6.2 Hz, 3H), 2.44 (dd, J_1 = 15.1 Hz, J_2 = 5.7 Hz, 1H), 2.66 (dd, J_1 = 15.1 Hz, J_2 = 7.3 Hz, 1H), 3.68 (s, 3H), 3.97–4.05 (m, 1H), 4.50 (d, *J* = 11.6 Hz, 1H), 4.53 (d, *J* = 11.6 Hz, 1H), 7.28–7.35 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.0, 42.0, 51.7, 71.0, 72.1, 127.7, 127.8, 128.5, 138.6, 172.1.

(*R*)-3-Benzyloxybutanoic acid (S24):



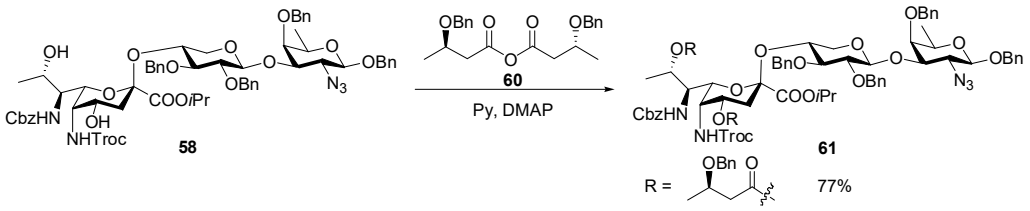
S23 **S24**
99%

Methyl (*R*)-benzyloxybutanoate **S23** (2.09 g, 10.1 mmol, 1 equiv) was dissolved in THF (40 mL), and a solution of LiOH·H_2O (847 mg, 20.2 mmol, 2 equiv) in H_2O (10 mL) was added dropwise. The mixture was stirred at r.t. for 12 h. After acidification with 1 M HCl (aq), the mixture was extracted with ethyl acetate (150 mL) and dired over anhydrous Na_2SO_4. After concentration, the product (*R*)-3-benzyloxybutanoic acid **S24** was obtained as colourless oil (1.93 g, 99%). The product was pure enough for characterization and further application.[12]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (d, *J* = 6.2 Hz, 3H), 2.47 (dd, J_1 = 15.3 Hz, J_2 = 5.6 Hz, 1H), 2.64 (dd, J_1 = 15.3 Hz, J_2 = 7.1 Hz, 1H), 3.94–4.02 (m, 1H), 4.50 (d, *J* = 11.6 Hz, 1H), 4.57 (d, *J* = 11.6 Hz, 1H), 7.23–7.37 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.7, 42.1, 70.9, 71.9, 127.81, 127.84, 128.5, 138.3, 176.9.

7-*N*-benzyloxycarbonyl-4,8-di-*O*-[(*R*)-3-benzyloxybutyryl]-1-isopropyl-5-*N*-(2,2,2-trichloroethoxycarbonyl)-α-pseudaminosyl-(2→4)-2,3-di-*O*-benzyl-β-D-xylopyranosyl-(1→3)-2-azido-4-*O*-benzyl-2-deoxy-β-D-fucopyranoside (61):



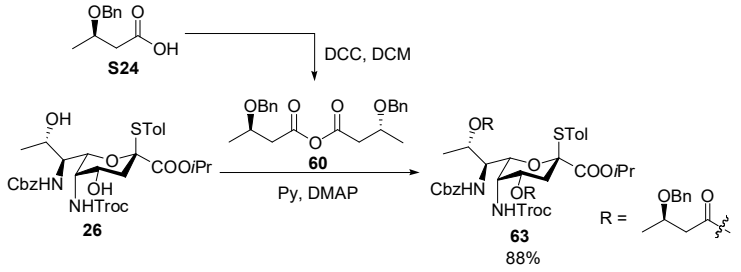
To a stirred solution of anhydride **60** (freshly prepared from the corresponding acid **S24** via DCC coupling, 37 mg, 0.10 mmol, 10 equiv, see Part 11) in anhydrous pyridine (0.30 mL), diol **58** (13 mg, 0.010 mmol, 1.0 equiv) was added, followed by DMAP (0.6 mg, 0.005 mmol, 0.5 equiv).

The mixture was stirred at r.t. for 16 h, then was diluted with ethyl acetate (20 mL). The solution was thoroughly washed with 1 M HCl (aq), sat. $NaHCO_3$ (aq) and water. The organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum. The residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 3 : 1 *v*/*v* as eluent. The product **61** was obtained as colorless solid (13 mg, 77%).

The product shows exactly the same ^{1}H and ^{13}C NMR spectra as the trisaccharide **61α** obtained via glycosylation of donor **63** and acceptor **46** (see Part 12).

Part 12. Final steps toward total synthesis of *P. aeruginosa* 1244 pilin glycan 3.

4-Methylphenyl 7-*N*-benzyloxycarbonyl-4,8-di-*O*-[(*R*)-3-benzyloxybutyryl]-1-isopropyl-5-*N*-(2,2,2-trichloroethoxycarbonyl)-α-thiopseudaminoside (63):



To a stirred solution of acid **S24** (1.74 g, 9.0 mmol, 2.0 equiv) in anhydrous DCM, DCC (925 mg, 4.5 mmol, 1.0 equiv) was added at 0 °C. The mixture was stirred at 0 °C for 3 h, then the solvent was removed under vacuum. The residue was dissolved in anhydrous *n*-hexane (10 mL), and was filtered through celite to remove DCU. After concentration, the desired anhydride **60** was obtained in crude form (1.56 g, < 4.0 mmol), which was directly used in the acylation of diol **26**.

To a stirred solution of anhydride **60** (1.56 g, < 4.0 mmol, ~ 6.0 equiv) in anhydrous pyridine (7.0 mL), diol **26** (415 mg, 0.586 mmol, 1.0 equiv) was added in one portion, followed by DMAP (3.6 mg, 0.029 mmol, 0.05 equiv). The mixture was stirred at r.t. overnight. After concentration, the residue was diluted with ethyl acetate (80 mL). The solution was thoroughly washed with 1 M HCl (aq), sat. $NaHCO_3$ (aq), and brine. The organic phase was dried over anhydrous Na_2SO_4, then the solvent was removed under vacuum. The residue was purified by silica gel flash chromatography using *n*-hexane : ethyl acetate 4 : 1 as eluent. The product **63** was obtained as colorless solid (550 mg, 88%).

$[\alpha]^{25}_D$ –91.6 ° (*c* = 0.81, DCM).

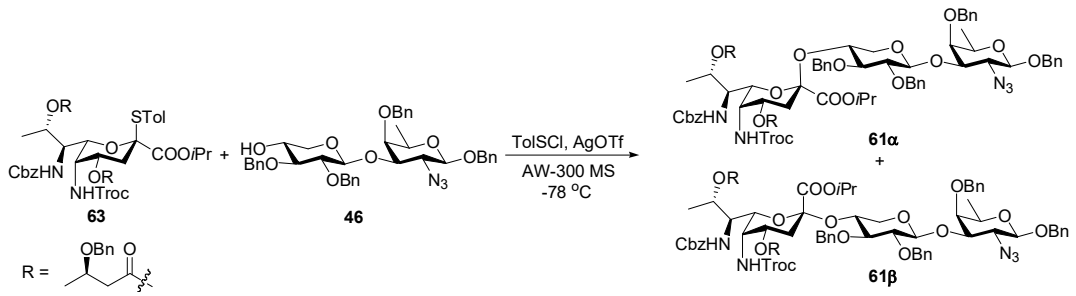
^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.11 (d, *J* = 6.2 Hz, 3H, $(CH_3)_2CH$), 1.15 (d, *J* = 6.2 Hz, 3H, $(CH_3)_2CH$), 1.22–1.26 (m, 9H, H-9& 2 × CH_3CHOBn), 2.01 (t, J = 13.3 Hz, 1H, H-3a), 2.27 (s, 3H, $CH_3C_6H_4$), 2.37–2.40 (m, 1H, H-3e), 2.39 (dd, J_1 = 15.8 Hz, J_2 = 4.8 Hz, 1H, CH_2CO), 2.50 (dd, J_1 = 15.1 Hz, J_2 = 5.2 Hz, 1H, CH_2CO), 2.51–2.55 (m, 1H, CH_2CO), 2.56 (dd, J_1 = 14.7 Hz, J_2 = 6.8 Hz, 1H, CH_2CO), 4.00–4.03 (m, 2H, 2 × CH_3CHOBn), 4.24–4.27 (m, 2H, H-5 & H-7), 4.42 (d, *J* = 12.1 Hz, 1H, CCl_3CH_2), 4.49–4.57 (m, 5H, 4 × $PhCH_2OCH$ & H-6), 4.83–4.85 (m, 1H, $(CH_3)_2CH$), 4.95 (d, *J* = 12.1 Hz, 1H, CCl_3CH_2), 4.98 (d, *J* = 12.2 Hz, 1H, $PhCH_2$), 5.02 (d, *J* = 10.7 Hz, 1H, NH), 5.06 (d, *J* = 12.2 Hz, 1H, $PhCH_2$), 5.19–5.21 (m, 1H, H-8), 5.27 (dt, J_1 = 12.5

Hz, J_2 = 4.3 Hz, 1H, H-4), 5.37 (d, J = 9.9 Hz, 1H, NH), 7.09 (d, J = 8.0 Hz, 2H, ArH), 7.22–7.36 (m, 15H, ArH), 7.40 (d, J = 8.0 Hz, 2H, ArH).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 15.7, 19.6, 19.9, 21.2, 21.4, 21.6, 32.5, 41.80, 41.85, 48.3, 52.8, 67.1, 67.7, 70.3, 70.8, 71.0, 71.4, 71.88, 71.92, 72.0, 74.6, 89.2, 95.6, 126.3, 127.5, 127.6, 127.7, 128.1, 128.36, 128.40, 128.45, 129.8, 135.0, 136.3, 138.4, 138.6, 139.7, 154.6, 155.6, 167.1, 170.6, 170.7.

HR-ESI-MS (m/z): calcd for $C_{52}H_{61}Cl_3N_2O_{13}SNa^+$ ($M + Na^+$): 1081.2852, found: 1081.2805.

Benzyl 7-*N*-benzyloxycarbonyl-4,8-di-*O*-[(*R*)-3-benzyloxybutyryl]-1-isopropyl-5-*N*-(2,2,2-trichloroethoxycarbonyl)-α/β-pseudaminosyl-(2→4)-2,3-di-*O*-benzyl-β-D-xylopyranosyl-(1→3)-2-azido-4-*O*-benzyl-2-deoxy-β-D-fucopyranoside (61α/β):



Following **Method A** (Part 9), the product was synthesized from donor **63** and disaccharide acceptor **46** in 0.050 mmol scale. The product was purified by multiple silica gel column chromatography using *n*-hexane : ethyl acetate 3 : 1 *v*/*v* as eluent. Only the α anomer **61α** was obtained ($J_{C1\text{-}H3a}$ = 0 Hz, measured on Advance DRX Bruker 500 MHz NMR spectrometer by non-decoupled ^{13}C spectrum) as colorless solid (108 mg, 67%).

Following **Method B** (Part 9), the product was synthesized from donor **63** and disaccharide acceptor **46** in 0.30 mmol scale. The product was purified by multiple silica gel column chromatography using *n*-hexane : ethyl acetate 3 : 1 *v*/*v* and toluene : ethyl acetate 10 : 1 *v*/*v* as eluents to give **61α** (236 mg, 49%) and **61β** (41 mg, 9%) ($J_{C1\text{-}H3a}$ = 6.6 Hz, measured on Advance DRX Bruker 500 MHz NMR spectrometer by non-decoupled ^{13}C spectrum) as colorless solid.

For anomer **61α:**

$[\alpha]^{25}_D$ –34.7 ^{o} (*c* = 1.4, DCM).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.93 (d, J = 6.5 Hz, 3H, H-9"), 1.15 (d, J = 6.2 Hz, 3H,

CH_3CHOBn), 1.22 (d, J = 6.4 Hz, 3H, H-6), 1.28 (d, J = 6.2 Hz, 3H, CH_3CHOBn), 1.30–1.32 (m, 6H, $(CH_3)_2$CH), 1.73 (t, J = 13.0 Hz, 1H, H-3a"), 2.25 (dd, J_1 = 13.4 Hz, J_2 = 4.4 Hz, 1H, H-3e"), 2.32 (dd, J_1 = 15.5 Hz, J_2 = 5.4 Hz, 1H, CH_2CO), 2.42 (dd, J_1 = 15.5 Hz, J_2 = 5.4 Hz, 1H, CH_2CO), 2.53 (dd, J_1 = 15.5 Hz, J_2 = 7.4 Hz, 1H, CH_2CO), 2.57 (dd, J_1 = 15.5 Hz, J_2 = 7.4 Hz, 1H, CH_2CO), 2.86 (d, J = 9.7 Hz, 1H, NH), 3.08 (t, J = 10.4 Hz, 1H, H-5a'), 3.37 (t, J = 8.4 Hz, 1H, H-2'), 3.45–3.51 (m, 3H, H-3, H-5 & H-3'), 3.60 (d, J = 1.8 Hz, 1H, H-4), 3.70 (dd, J_1 = 11.4 Hz, J_2 = 4.8 Hz, 1H, H-5e'), 3.73–3.78 (m, 1H, H-4'), 3.83–3.85 (m, 1H, H-5"), 3.88 (dd, J_1 = 10.3 Hz, J_2 = 8.1 Hz, 1H, H-2), 3.90–3.93 (m, 1H, CH_3CHOBn), 3.97–4.01 (m, 2H, H-7" & H-6"), 4.04–4.09 (m, 1H, CH_3CHOBn), 4.32 (d, J = 7.7 Hz, 1H, H-1), 4.33 (d, J = 12.3 Hz, 1H, CCl_3CH_2), 4.44 (d, J = 9.5 Hz, 1H, PhCH_2), 4.46 (s, 2H, 2 × PhCH_2), 4.54 (d, J = 11.6 Hz, 1H, PhCH_2), 4.59 (d, J = 11.3 Hz, 1H, PhCH_2), 4.61 (d, J = 7.4 Hz, 1H, H-1'), 4.67 (d, J = 12.0, 1H, PhCH_2), 4.73 (d, J = 11.7 Hz, 1H, PhCH_2), 4.78 (d, J = 11.2 Hz, 1H, PhCH_2), 4.93–4.95 (m, 4H, 3 × PhCH_2 & CCl_3CH_2), 4.97–5.01 (m, 2H, 2 × PhCH_2), 5.03–5.07 (m, 1H, $(CH_3)_2$CH), 5.13 (d, J = 9.5 Hz, 1H, PhCH_2), 5.17–5.20 (m, 1H, H-8"), 5.27 (dt, J_1 = 12.2 Hz, J_2 = 4.1 Hz, 1H, H-4"), 5.33 (d, J = 10.0 Hz, 1H, NH), 7.01 (t, J = 7.3 Hz, 1H, ArH), 7.21–7.42 (m, 34H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8, 16.5, 19.88, 19.90, 21.6, 21.7, 32.4, 41.8, 42.0, 47.5, 52.0, 63.37, 63.45, 66.8, 69.2, 69.5, 70.0, 70.4, 70.59, 70.63, 70.8, 70.9, 71.9, 72.1, 74.5, 74.6, 75.2, 76.9, 78.2,79.7, 82.0, 82.3, 95.7, 96.9, 100.9, 105.2, 127.3, 127.5, 127.56, 127.65, 127.8, 127.9, 128.0, 128.05, 128.11, 128.18, 128.21, 128.24, 128.3, 128.39, 128.43, 128.46, 128.57, 128.63, 129.3, 129.4, 136.6, 137.0, 137.4, 137.8, 138.5, 138.6, 138.8, 154.7, 155.6, 167.1, 170.6, 170.8.

IR (film) ν = 3067, 3033, 2981, 2933, 2858, 2112 (N_3), 1739, 1643, 1516, 1454, 1377, 1362, 1308, 1276, 1218, 1177, 1139, 1097, 1071, 1028, 814, 735, 698 cm^{-1}.

HR-ESI-MS (m/z): calcd for $C_{84}H_{96}Cl_3N_5O_{21}Na^+$ (M + Na^+): 1638.5556, found: 1638.5369.

For anomer **61β:**

$[\alpha]^{25}_D$ –23.5 ^{o} (c = 0.91, DCM).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.11 (d, J = 6.2 Hz, 3H, $(CH_3)_2$CH), 1.16 (d, J = 6.3 Hz, 3H, H-6), 1.19 (d, J = 6.2 Hz, 3H, CH_3CHOBn), 1.22 (d, J = 6.2 Hz, 3H, $(CH_3)_2$CH), 1.24 (d, J = 6.2 Hz, 3H, CH_3CHOBn), 1.32 (d, J =6.6 Hz, 3H, H-9"), 1.83 (t, J = 13.2 Hz, 1H, H-3a"), 2.32–2.35 (m, 1H, CH_2CO), 2.38 (dd, J_1 = 15.5 Hz, J_2 = 5.2 Hz, 1H, CH_2CO), 2.49 (dd, J_1 = 15.4 Hz, J_2 = 7.2 Hz, 1H, CH_2CO), 2.55 (dd, J_1 = 15.8 Hz, J_2 = 7.7 Hz, 1H, CH_2CO), 2.65 (dd, J_1 = 13.0 Hz, J_2

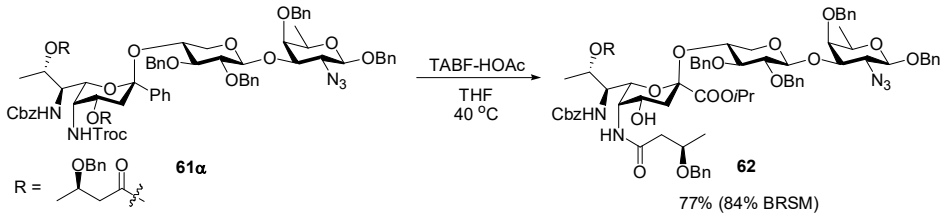
= 4.3 Hz, 1H, H-3e"), 3.24–3.29 (m, 2H, H-2' & H-5a'), 3.36 (q, J = 6.3 Hz, 1H, H-5), 3.43–3.49 (m, 2H, H-3 & H-3'), 3.59 (s, 1H, H-4), 3.62 (d, J = 10.2 Hz, 1H, H-6"), 3.82 (dd, J_1 = 10.4 Hz, J_2 = 7.9 Hz, 1H, H-2), 3.85–3.87 (m, 1H, H-4'), 3.92–3.96 (m, 1H, CH_3CHOBn), 3.98–4.02 (m, 1H, CH_3CHOBn), 4.18 (dd, J_1 = 12.0 Hz, J_2 = 5.2 Hz, 1H, H-5e'), 4.20–4.22 (m, 1H, H-5"), 4.25–4.29 (m, 1H, H-7"), 4.27 (d, J = 7.8 Hz, 1H, H-1), 4.39 (d, J = 12.0 Hz, 1H, CCl_3CH_2), 4.47 (d, J = 11.6 Hz, 1H, PhCH_2), 4.49 (d, J = 11.5 Hz, 1H, PhCH_2), 4.50 (d, J = 11.5 Hz, 1H, PhCH_2), 4.56 (d, J = 11.5 Hz, 1H, PhCH_2), 4.60 (d, J = 7.4 Hz, 1H, H-1'), 4.61–4.65 (m, 3H, 3 × PhCH_2), 4.70–4.75 (m, 2H, H-4" & NH), 4.74 (d, J = 11.5 Hz, 1H, PhCH_2), 4.79 (d, J = 11.5 Hz, 1H, PhCH_2), 4.92–5.00 (m, 6H, $(CH_3)_2CH$, CCl_3CH_2 & 4 x PhCH_2), 5.05 (d, J = 12.2 Hz, 1H, PhCH_2), 5.30–5.32 (m, 1H, H-8"), 5.31 (d, J = 9.6 Hz, 1H, NH), 7.21–7.39 (m, 35H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.4, 16.5, 19.7, 19.8, 21.4, 21.6, 33.6, 41.8, 41.9, 47.6, 52.5, 63.3, 65.0, 67.1, 67.8, 69.2, 70.5, 70.6, 70.7, 71.0, 71.3, 71.76, 71.84, 72.7, 74.6, 74.8, 75.1, 75.2, 75.3, 78.5, 79.5, 81.6, 81.9, 95.6, 100.9, 101.0, 104.9, 127.38, 127.41, 127.49, 127.55, 127.59, 127.62, 127.7, 127.77, 127.79, 127.9, 128.0, 128.09, 128.14, 128.2, 128.3, 128.36, 128.37, 128.5, 136.3, 137.0, 138.2, 138.5, 138.6, 138.7, 138.8, 154.6, 155.7, 166.0, 170.57, 170.62.

IR (film) ν = 3066, 3033, 2982, 2933, 2112 (N_3), 1738, 1643, 1454, 1376, 1360, 1303, 1209, 1176, 1135, 1070, 1027, 735, 697 cm^{-1}.

HR-ESI-MS (m/z): calcd for $C_{84}H_{96}Cl_3N_5O_{21}Na^+$ (M + Na^+): 1638.5556, found: 1638.5374.

Benzyl 5-*N*-[(*R*)-3-benzyloxybutyryl]-8-*O*-[(*R*)-3-benzyloxybutyryl]-7-*N*-benzyloxycarbonyl-1-isopropyl-α-pseudaminosyl-(2→4)-2,3-di-*O*-benzyl-β-D-xylopyranosyl-(1→3)-2-azido-4-*O*-benzyl-2-deoxy-β-D-fucopyranoside (62):



In a 1.5 mL Eppendorf tube, TBAF (1.0 M solution in THF, 1.14 mL, 1.14 mmol, 10 equiv) and HOAc (0.032 mL, 0.507 mmol, 5.0 equiv) were added. This mixture was then added to the solution of **61α** (184 mg, 0.114 mmol, 1.0 equiv) in THF (2.28 mL). The final concentration of the TBAF was controlled at 0.33 M. After being heated at 40 °C for 48 h, the mixture was diluted with

ethyl acetate (30 mL), washed with sat. $NaHCO_3$ (aq) and water, and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 1 : 1 *v*/*v* as eluent. The product **62** was obtained as colorless solid (126 mg, 77%), together with recovered **61α** (17 mg, 9%).

$[\alpha]^{25}_{D}$ +9.6 ^{o} (*c* = 1.3, DCM).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.98 (d, *J* = 6.5 Hz, 3H, H-9''), 1.16 (d, *J* = 6.2 Hz, 3H, CH_3CHOBn), 1.19 (d, *J* = 6.2 Hz, 3H, CH_3CHOBn), 1.22 (d, *J* = 6.3 Hz, 6H, H-6 & (CH_3)$_2$CH), 1.27 (d, *J* = 6.3 Hz, 3H, (CH_3)$_2$CH), 1.30 (t, *J* = 13.2 Hz, 1H, H-3a''), 2.16 (dd, J_1 = 13.5 Hz, J_2 = 4.3 Hz, 1H, H-3e''), 2.25 (dd, J_1 = 14.6 Hz, J_2 = 4.1 Hz, 1H, CH_2CO), 2.27–2.31 (m, 1H, CH_2CO), 2.33 (dd, J_1 = 15.5 Hz, J_2 = 5.3 Hz, 1H, CH_2CO), 2.52 (dd, J_1 = 15.5 Hz, J_2 = 7.6 Hz, 1H, CH_2CO), 3.06 (t, *J* = 10.7 Hz, 1H, H-5a'), 3.12 (d, *J* = 10.8 Hz, 1H, NH), 3.32 (dd, J_1 = 9.0 Hz, J_2 = 7.8 Hz, 1H, H-2'), 3.40–3.44 (m, 2H, OH & H-3'), 3.46 (dd, J_1 = 10.6 Hz, J_2 = 3.0 Hz, 1H, H-3), 3.50 (q, *J* = 6.3 Hz, 1H, H-5), 3.59 (d, *J* = 2.4 Hz, 1H, H-4), 3.65–3.72 (m, 3H, H-4', H-5e' & H-5''), 3.86–3.89 (m, 2H, H-2 & H-6''), 3.91–3.97 (m, 2H, 2 × CH_3CHOBn), 3.99 (td, J_1 = 10.9 Hz, J_2 = 2.9 Hz, 1H, H-7''), 4.05–4.07 (m, 1H, H-4''), 4.32 (d, *J* = 8.0 Hz, 1H, H-1), 4.34 (d, *J* = 9.8 Hz, 1H, PhCH_2), 4.42 (d, *J* = 11.2 Hz, 1H, PhCH_2), 4.47 (s, 2H, 2 × PhCH_2), 4.50 (d, *J* = 11.2 Hz, 1H, PhCH_2), 4.59 (d, *J* = 7.6 Hz, 1H, H-1'), 4.66 (d, *J* = 12.0 Hz, 1H, PhCH_2), 4.73 (d, *J* = 12.2 Hz, 1H, PhCH_2), 4.75 (d, *J* = 11.9 Hz, 1H, PhCH_2), 4.92–5.01 (m, 6H, (CH$_3$)$_2$CH & 5 × PhCH_2), 5.10 (d, *J* = 9.8 Hz, 1H, PhCH_2), 5.19–5.23 (m, 1H, H-8''), 6.17 (d, *J* = 8.2 Hz, 1H, NH), 7.03 (t, *J* = 7.4 Hz, 1H, ArH), 7.18–7.44 (m, 34H, ArH).

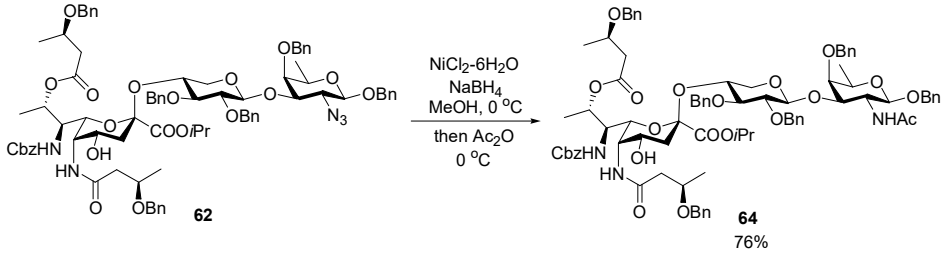
^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.7, 16.5, 19.8, 19.9, 21.55, 21.60, 35.5, 42.1, 44.3, 48.7, 52.1, 63.4, 63.5, 66.7, 66.9, 69.1, 69.4, 69.6, 70.1, 70.58, 70.61, 70.8, 70.9, 72.0, 72.5, 74.5, 75.1, 76.8, 78.2, 79.7, 81.8, 82.5, 97.4, 100.9, 105.2, 127.4, 127.50, 127.54, 127.8, 127.86, 127.95, 128.00, 128.03, 128.1, 128.2, 128.27, 128.29, 128.33, 128.35, 128.38, 128.50, 128.54, 128.59, 128.60, 129.3, 136.5, 137.0, 137.67, 137.73, 138.4, 138.5, 138.8, 155.6, 167.7, 170.7, 174.4.

IR (film) ν = 3033, 2985, 2935, 2112 (N_3), 1724, 1646, 1518, 1497, 1454, 1376, 1359, 1267, 1217, 1099, 1070, 735, 698 cm^{-1}.

HR-ESI-MS (m/z): calcd for $C_{81}H_{96}N_5O_{19}^{+}$ (M + H^{+}): 1442.6700, found: 1442.6659.

Benzyl 5-*N*-[(*R*)-3-benzyloxybutyryl]-8-*O*-[(*R*)-3-benzyloxybutyryl]-7-*N*-benzyloxycarbonyl-

1-isopropyl-α-pseudaminosyl-(2→4)-2,3-di-*O*-benzyl-β-D-xylopyranosyl-(1→3)-2-acetamido-4-*O*-benzyl-2-deoxy-β-D-fucopyranoside (64):



To a stirred solution of **62** (126 mg, 0.087 mmol, 1.0 equiv) in MeOH (10 mL), $NiCl_2 \cdot 6H_2O$ (104 mg, 0.437 mmol, 5.0 equiv) was added. The solution was cooled to 0 °C, then $NaBH_4$ (33 mg, 0.874 mmol, 10 equiv) was added carefully. The black suspension of reactive nickel boride species was immediately generated. The mixture was stirred at 0 °C for 1 h to achieve full conversion, then Ac_2O (0.33 mL, 3.50 mmol, 40 equiv) was added. After being stirred at 0 °C for another 1 h, the mixture was diluted with ethyl acetate (50 mL), washed with sat. $NaHCO_3$ (aq) and water, and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate 1 : 1.5 to 1 : 2 *v*/*v* as eluent. The product **64** was obtained as colorless solid (97 mg, 76%).

$[\alpha]^{25}_{D}$ −6.1 ° (*c* = 1.3, DCM).

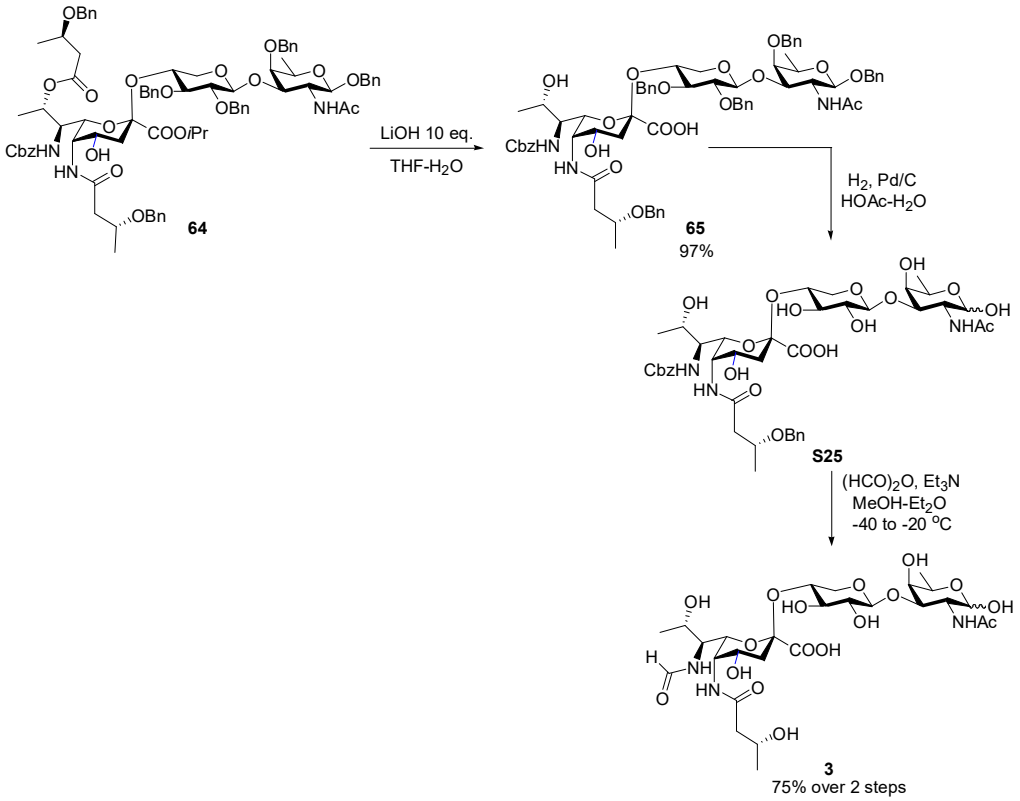
^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.99 (d, *J* = 6.5 Hz, 3H, H-9''), 1.15 (d, *J* = 6.2 Hz, 3H, C*H*$_3$CHOBn), 1.20 (d, *J* = 6.2 Hz, 3H, C*H*$_3$CHOBn), 1.22 (d, *J* = 6.3 Hz, 3H, H-6), 1.23 (d, *J* = 6.3 Hz, 3H, (C*H*$_3$)$_2$CH), 1.30 (d, *J* = 6.3 Hz, 3H, (C*H*$_3$)$_2$CH), 1.42 (t, *J* = 13.0 Hz, 1H, H-3a''), 1.57 (s, 3H, C*H*$_3$CO), 2.17 (dd, J_1 = 13.5 Hz, J_2 = 4.2 Hz, 1H, H-3e''), 2.27 (dd, J_1 = 14.6 Hz, J_2 = 4.0 Hz, 1H, C*H*$_2$CO), 2.31–2.37 (m, 2H, 2 × C*H*$_2$CO), 2.52 (dd, J_1 = 15.6 Hz, J_2 = 7.6 Hz, 1H, C*H*$_2$CO), 3.06–3.12 (m, 2H, H-5a' & NH), 3.25 (dd, J_1 = 9.0 Hz, J_2 = 8.0 Hz, 1H, H-2'), 3.30–3.35 (m, 1H, H-2), 3.39 (t, *J* = 9.0 Hz, 1H, H-3'), 3.49 (br, 1H, OH), 3.63 (q, *J* = 6.3 Hz, 1H, H-5), 3.66–3.70 (m, 3H, H-4, H-4' & H-5e'), 3.73–3.75 (m, 1H H-5''), 3.89 (d, *J* = 9.6 Hz, 1H, H-6''), 3.91–3.99 (m, 2H, 2 × CH$_3$C*H*OBn), 4.00–4.05 (m, 1H, H-7''), 4.07–4.09 (m, 1H, H-4''), 4.32 (d, *J* = 7.8 Hz, 1H, H-1'), 4.42 (d, *J* = 9.8 Hz, 1H, PhC*H*$_2$), 4.43 (d, *J* = 11.2 Hz, PhC*H*$_2$), 4.46 (s, 2H, 2 × PhC*H*$_2$), 4.49 (d, *J* = 11.8 Hz, 1H, PhC*H*$_2$), 4.52 (d, *J* = 11.3 H, 1H, PhC*H*$_2$), 4.64 (dd, J_1 = 11.0 Hz, J_2 = 2.8 Hz, 1H, H-3), 4.75–4.82 (m, 3H, 3 × PhC*H*$_2$), 4.87 (d, *J* = 11.8 Hz, 1H, PhC*H*$_2$), 4.92–5.00 (m, 4H, (CH$_3$)$_2$C*H* & 3 × PhC*H*$_2$), 5.04 (d, *J* = 8.3 Hz, 1H, H-1), 5.11 (d, *J* = 9.8 Hz, 1H, PhC*H*$_2$), 5.20–5.23 (m, 1H, H-8''), 5.23 (d, *J* = 7.0 Hz, 1H, NH), 6.36–6.41 (m, 1H, NH), 7.03 (t, *J*

= 7.3 Hz, 1H, ArH), 7.19–7.44 (m, 34H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.7, 16.7, 19.78, 19.84, 21.57, 21.59, 23.4, 35.6, 42.0, 44.2, 48.8, 52.0, 55.9, 63.4, 66.8, 66.9, 69.2, 69.6, 69.7, 70.3, 70.8, 70.9, 71.1, 72.0, 72.5, 74.3, 75.0, 76.7, 77.6, 79.1, 82.3, 82.7, 97.3, 98.2, 105.1, 127.3, 127.4, 127.48, 127.51, 127.55, 127.7, 127.86, 127.95, 128.03 128.05, 128.08, 128.14, 128.19, 128.21, 128.26, 128.30, 128.49, 128.52, 128.6, 128.7, 129.4, 136.5, 137.6, 137.7, 138.3, 138.4, 138.8, 139.1, 155.6, 167.8, 170.8, 171.2, 174.5.

HR-ESI-MS (m/z): calcd for $C_{83}H_{100}N_3O_{20}^+$ ($M + H^+$): 1458.6895, found: 1458.6849.

7-*N*-Formylamino-5-*N*-[(*R*)-3-hydroxybutyryl]-α-pseudaminosyl-(2→4)-β-D-xylopyranosyl-(1→3)-2-acetamido-2-deoxy-α/β-D-fucopyranose (3):



To a stirred solution of **64** (42 mg, 0.029 mmol) in THF (5.8 mL), the solution of LiOH (12 mg, 0.29 mmol, 10 equiv) in H_2O (0.58 mL) was added. The concentration of **64** was controlled at 5 mM. The mixture was stirred at r.t. for 24 h. When full conversion was achieved, the mixture was neutralized by $NaHSO_4$ (0.1 M solution in H_2O), and was extracted by ethyl acetate (50 mL). The organic phase was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by silica gel flash chromatography using

DCM : MeOH 10 : 1 to 5 : 1 as eluent. The product **65** was obtained as colorless solid (35 mg, 97%).

To a 10 mL round bottom flask containing **65** (20 mg, 0.016 mmol, 1.0 equiv) and Pd/C (10% Pd on activated carbon, 30 mg), HOAc (2.0 mL) and H_2O (0.5 mL) were added. The mixture was stirred under 1 atm H_2 atmosphere for 48 h. After filtration, the filtrate was diluted with H_2O and lyophilized to give the global deprotected intermediate **S25**, which was used in the next formylation step without purification.

To a flask containing **S25**, anhydrous MeOH (2.0 mL) was added, followed by Et_3N (0.20 mL). The mixture was cooled to -40 ^oC, then a solution of formic anhydride (~0.8 mol/L in Et_2O, freshly prepared from HCOOH and DCC following reported procedure, 1.0 mL) was added. The mixture was stirred at -40 ^oC for 1 h, then was stirred at -20 ^oC for 5 h. The reaction was quenched by H_2O dilution, and the MeOH and Et_2O was removed under vacuum. The suspension was filtered to remove DCU (from formic anhydride preparation step), and the filtrate was lyophilized to give the crude product with good purity (as indicated by ^1H NMR). The crude product was further purified by C18 silica gel column using H_2O as eluent. The product **3** was obtained as white powder (8.2 mg, 75% over 2 steps) after lyophilization.

$[\alpha]^{25}_D$ –32.9 ^{o} (*c* = 0.55, H_2O).

^1H NMR (600 MHz, D_2O, mixture of α and β anomers at the reducing end): δ = 1.07 (d, *J* = 6.6 Hz, 1.5H, H-9"α or β), 1.10–1.12 (m, 7.5H, C*H*$_3$CHOHαβ, H-6αβ & H-9"α or β), 1.42 (t, *J* = 13.0 Hz, 1H, H-3a"αβ), 1.90 (s, 3H, C*H*$_3$COαβ), 2.01 (dd, J_1 = 13.5 Hz, J_2 = 4.6 Hz, 1H, H-3e"αβ), 2.26 (dd, J_1 = 14.7 Hz, J_2 = 4.3 Hz, 1H, C*H*$_2$COαβ), 2.34 (dd, J_1 = 14.7 Hz, J_2 = 8.6 Hz, 1H, C*H*$_2$COαβ), 3.12–3.18 (m, 2H, H-2'αβ & H-5a'αβ), 3.42–3.44 (m, 2H, H-3'αβ & H-4'αβ), 3.64 (t, *J* = 6.7 Hz, 0.5H, H-5α or β), 3.67 (dd, J_1 = 11.0 Hz, J_2 = 3.0 Hz, 0.5H, H-3β), 3.77 (d, *J* = 3.0 Hz, 0.5H, H-4β), 3.80–3.84 (m, 2H, H-2β, H-4α & H-5e'αβ), 3.87 (dd, J_1 = 11.0 Hz, J_2 = 3.0 Hz, 0.5H, H-3α), 4.06–4.18 (m, 7H, H-2α, H-5α or β, H-4"αβ, H-5"αβ, H-6"αβ, H-7"αβ, H-8"αβ & CH$_3$C*H*OHαβ), 4.26 (d, *J* = 7.7 Hz, 0.5H, H-1'α or β), 4.32 (d, *J* = 7.7 Hz, 0.5H, H-1'α or β), 4.51 (d, *J* = 8.5 Hz, 0.5H, H-1β), 5.01 (d, *J* = 3.7 Hz, 0.5H, H-1α), 7.93 (s, 1H, C*H*Oαβ).

^{13}C NMR (600 MHz, D_2O, mixture of α and β anomers at the reducing end): δ = 15.5, 16.1, 21.98, 22.02, 22.2, 35.4, 44.8, 48.6, 48.7, 52.1, 52.6, 62.8, 64.8, 65.0, 66.1, 66.8, 70.3, 70.6, 71.2, 72.7, 72.8, 73.6, 73.7, 76.8, 79.9, 91.0 (C-1α), 94.9 (C-1β), 98.2 (C-2"), 104.7 (C-1'α or β), 104.9 (C-1'α

or β), 163.8, 174.6, 174.7, 174.9, 176.3.

HR-ESI-MS (m/z): calcd for $C_{27}H_{46}N_3O_{17}^+$ ($M + H^+$): 684.2822, found: 684.2005.

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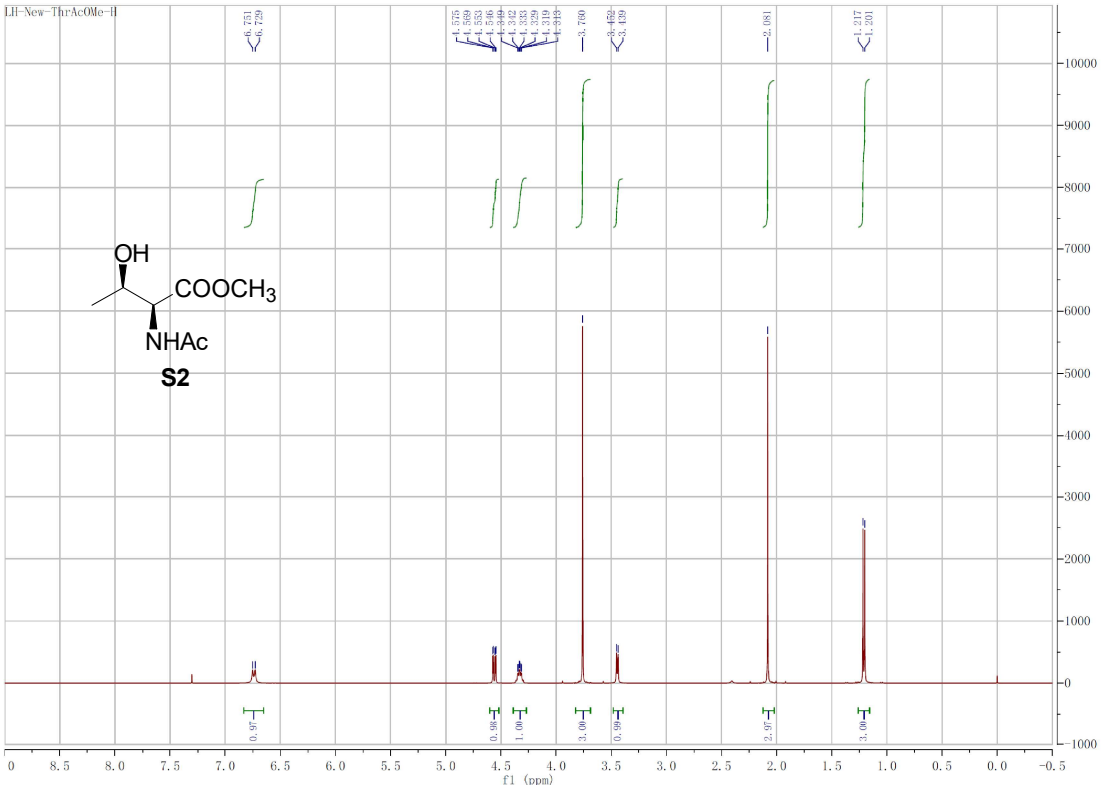
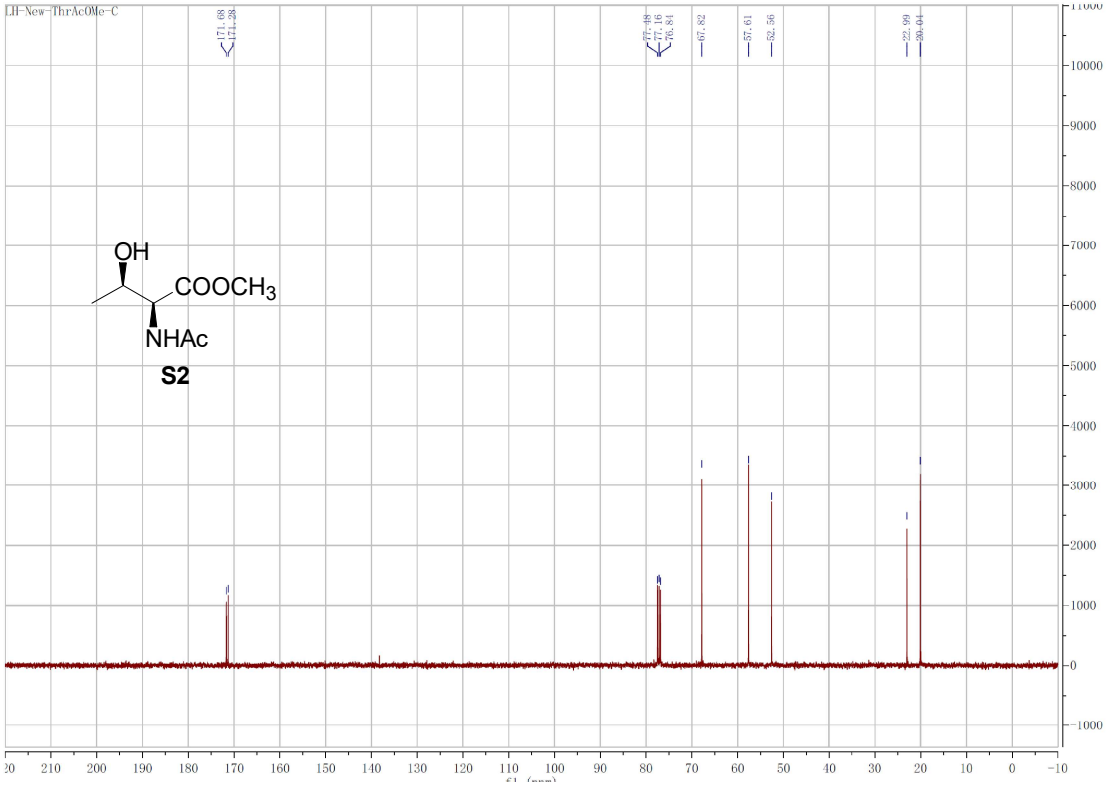
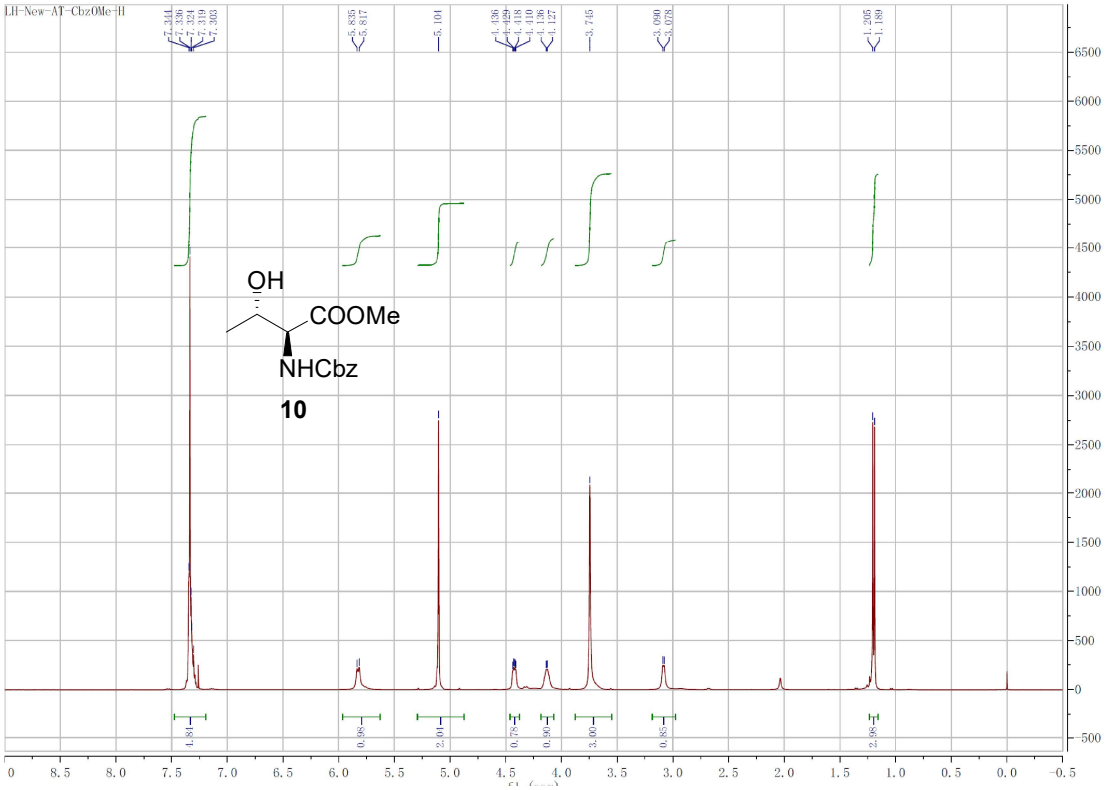
^{1}H NMR of compound S2



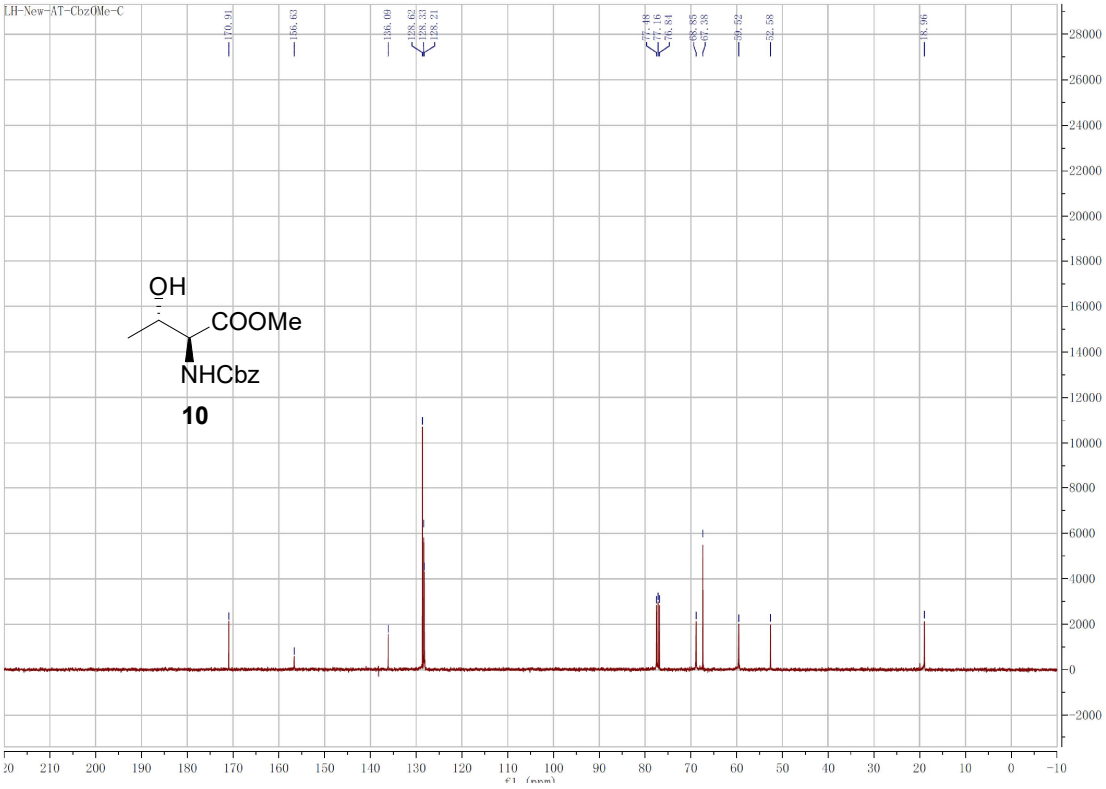
^{13}C NMR of compound S2



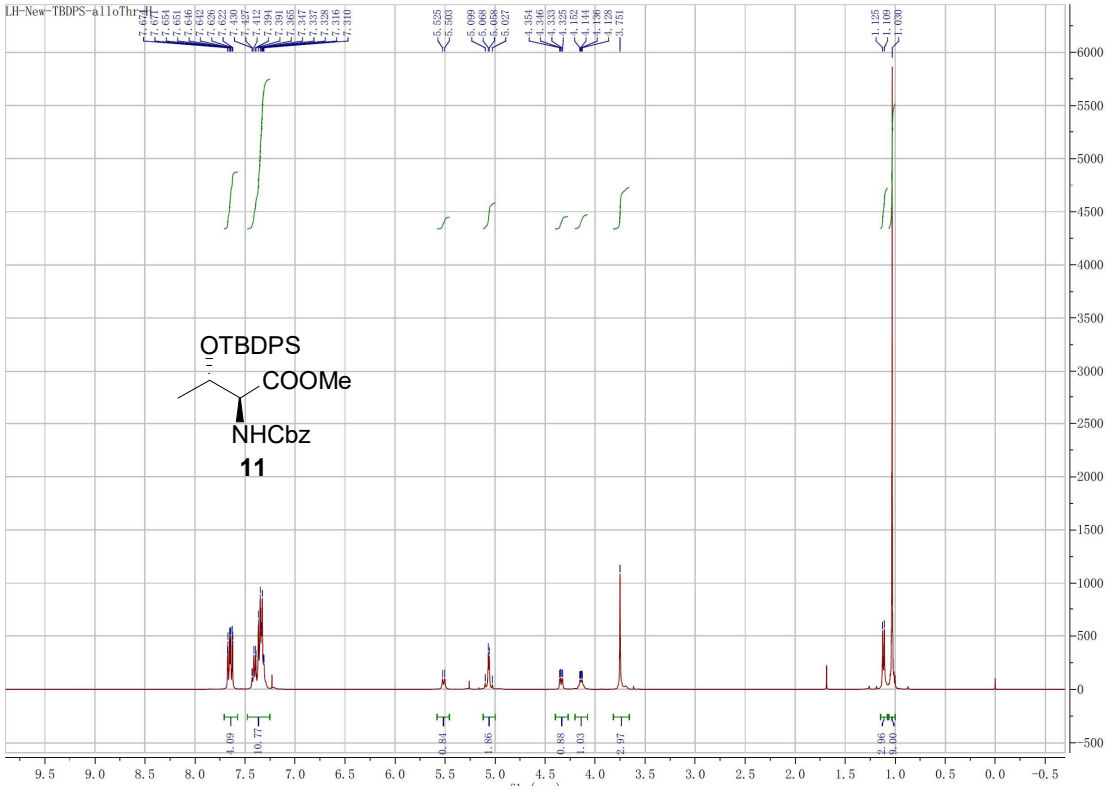
^{1}H NMR of compound 10



^{13}C NMR of compound 10



[1]H NMR of compound 11



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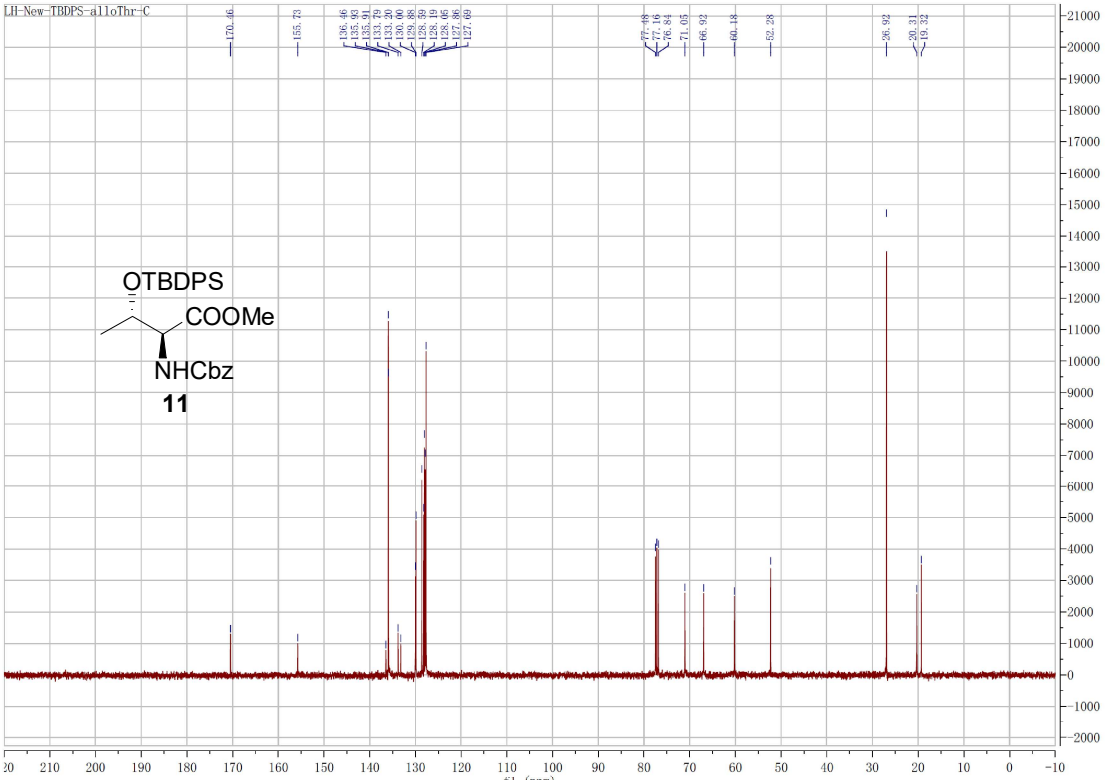
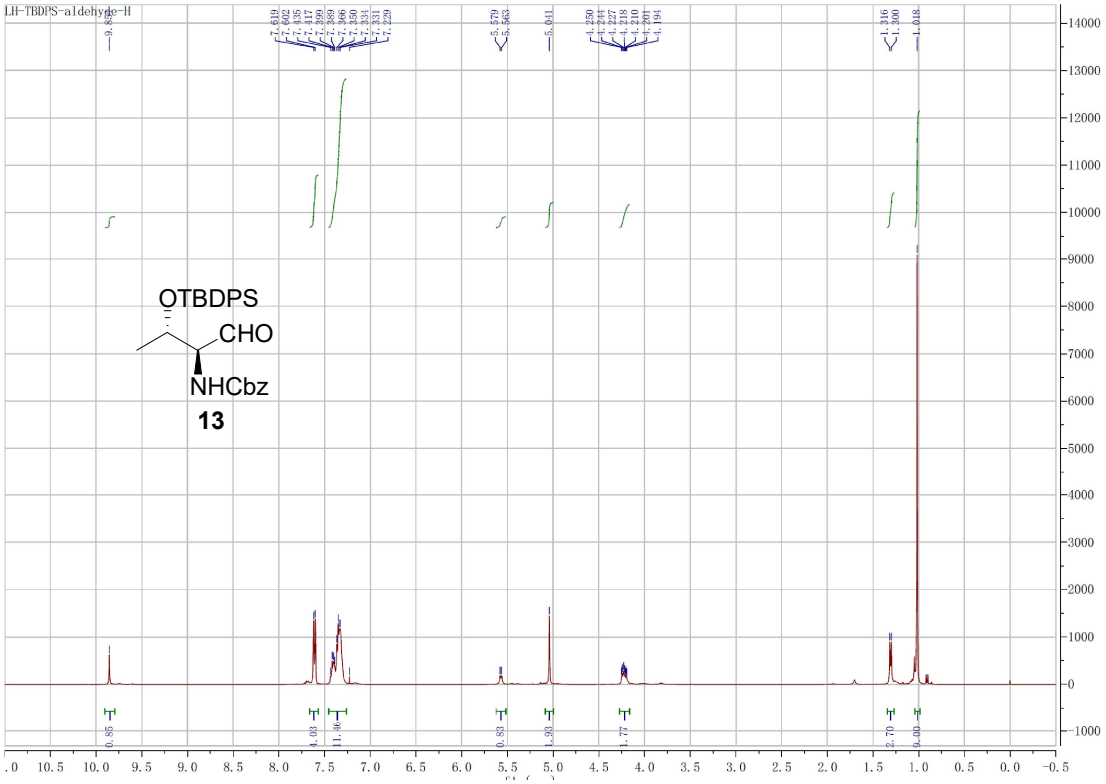
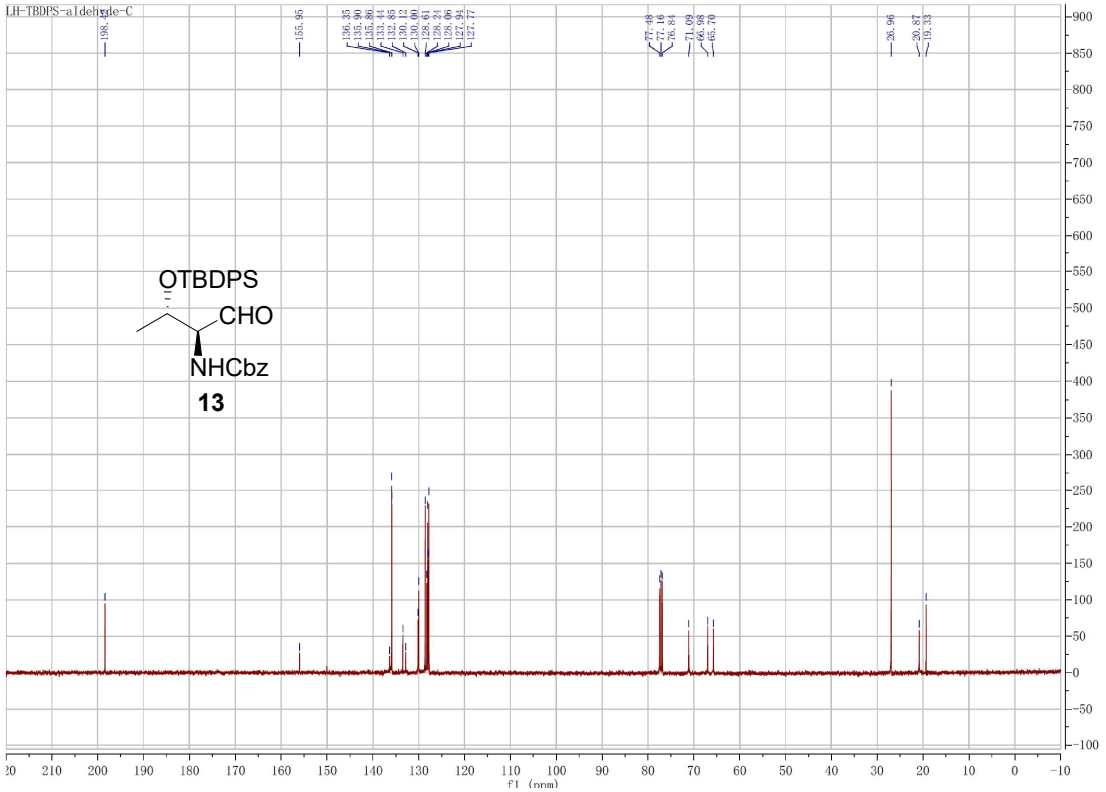


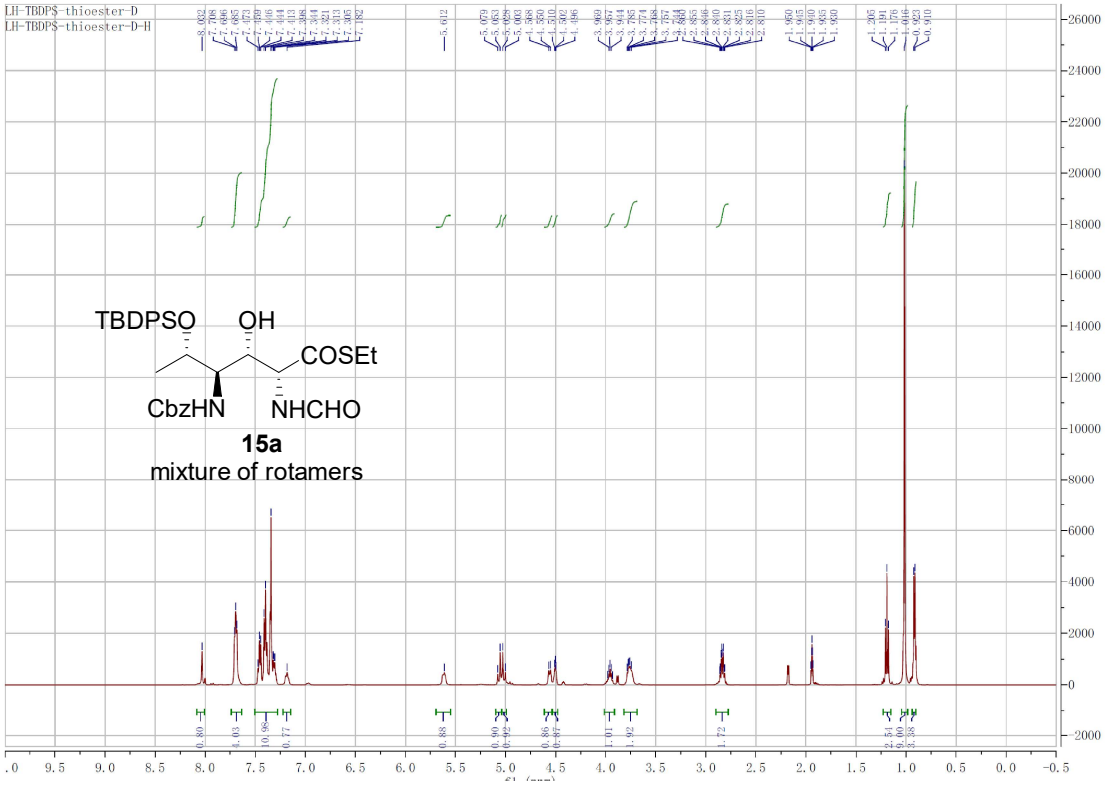
^{1}H NMR of compound 13



^{13}C NMR of compound 13



^{1}H NMR of compound 15a



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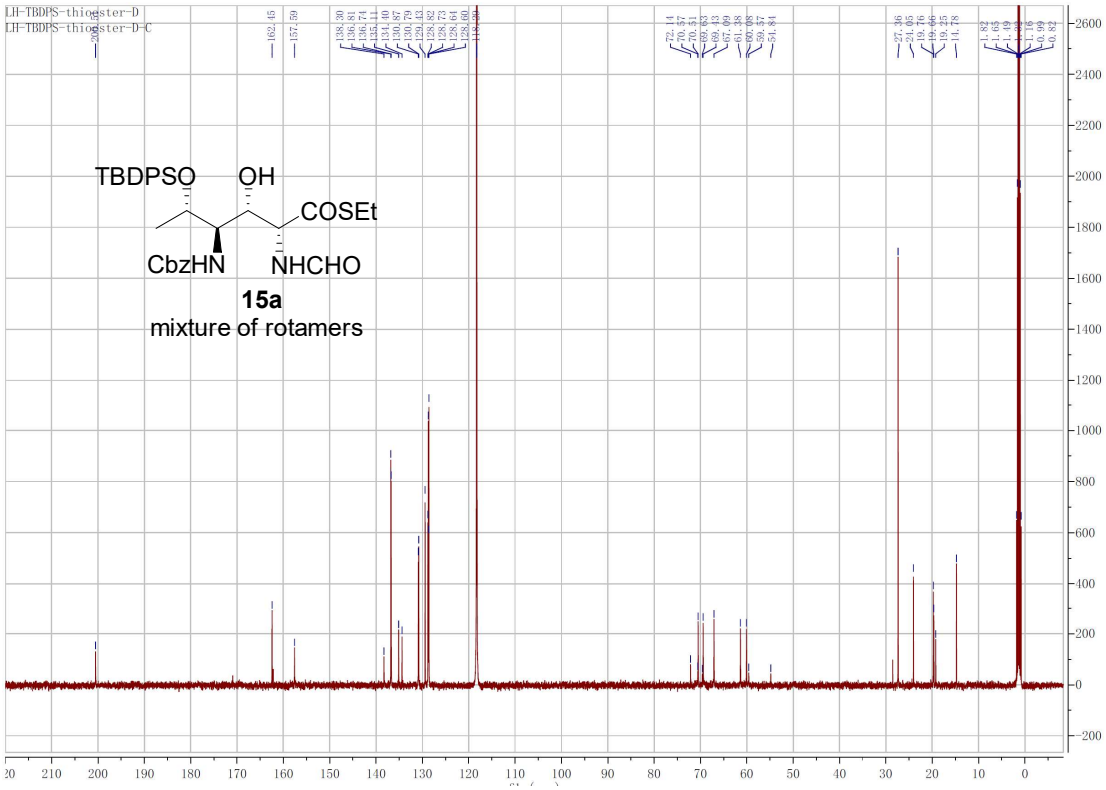

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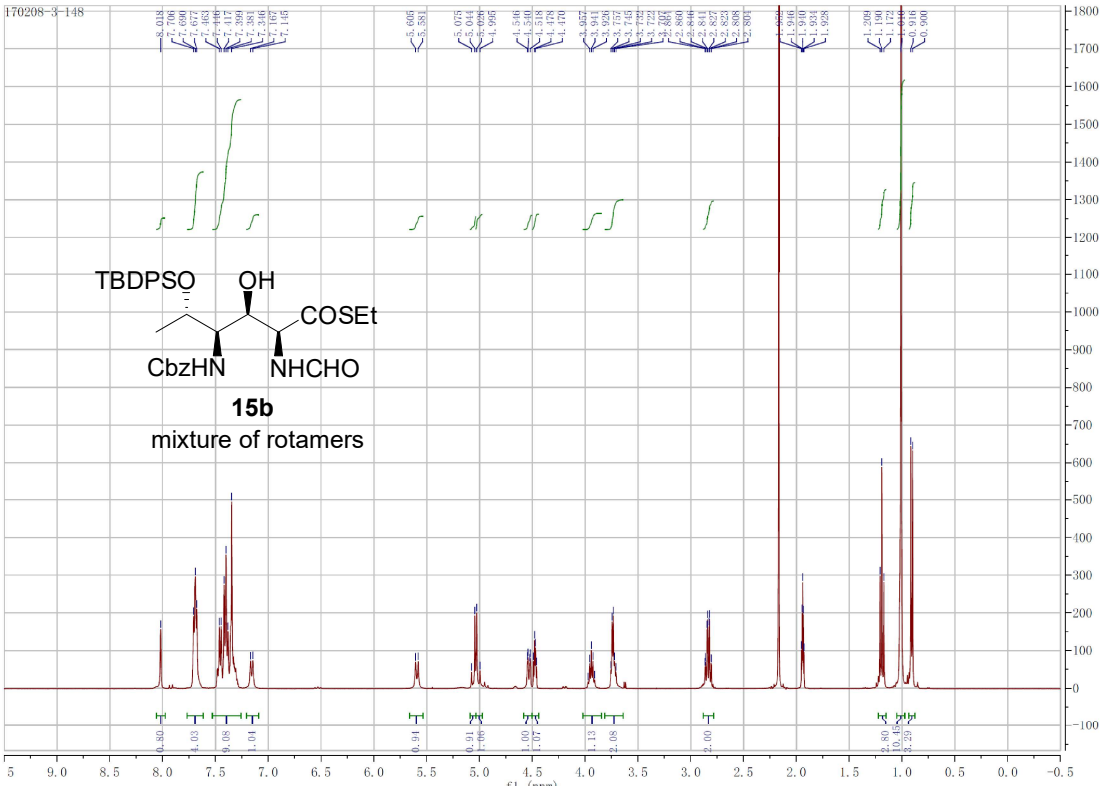

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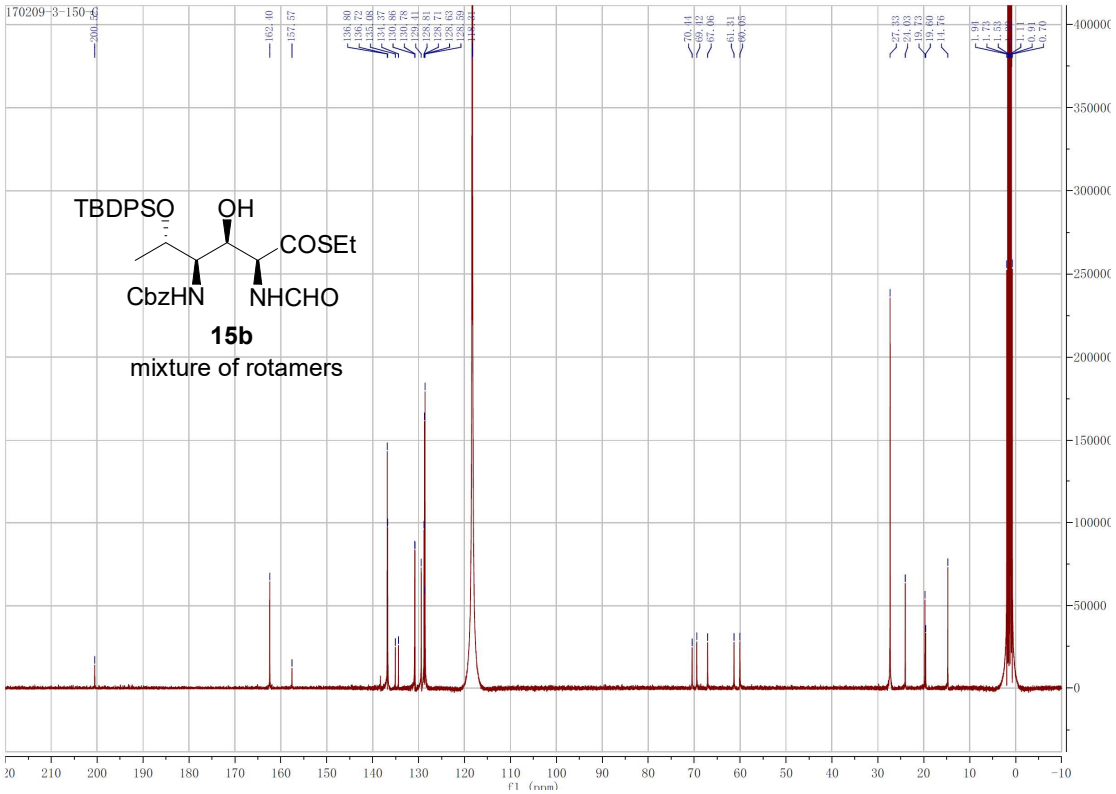

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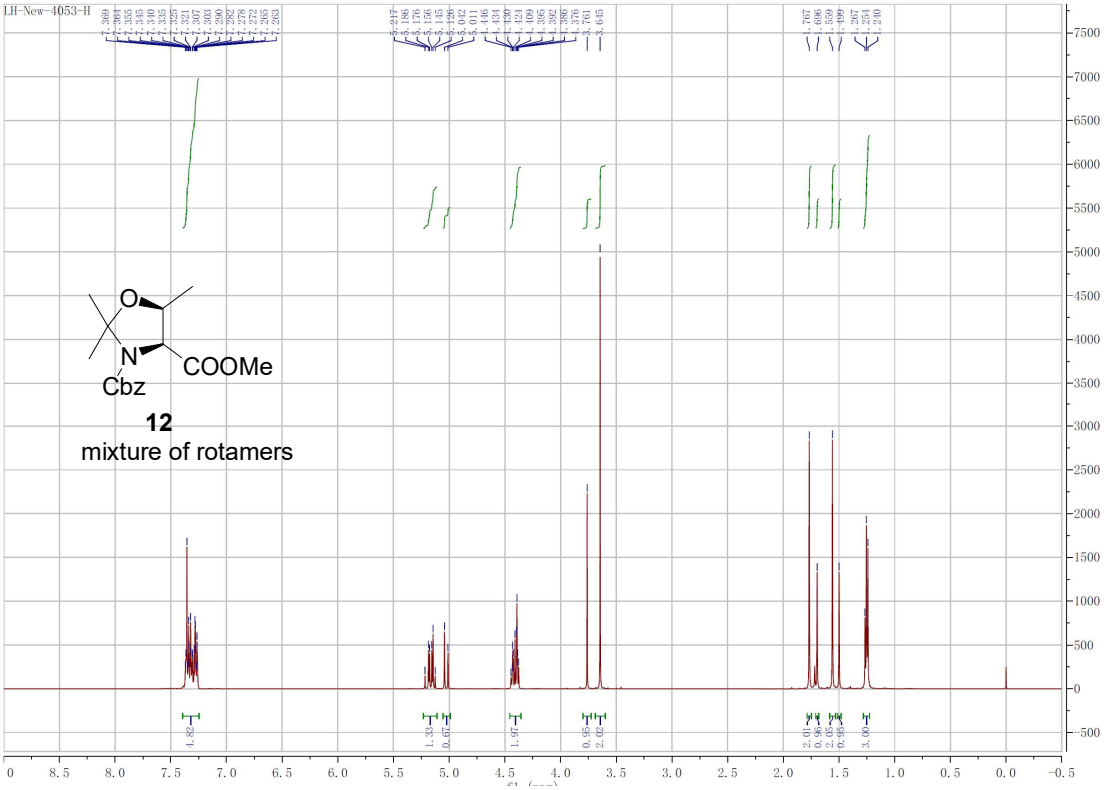
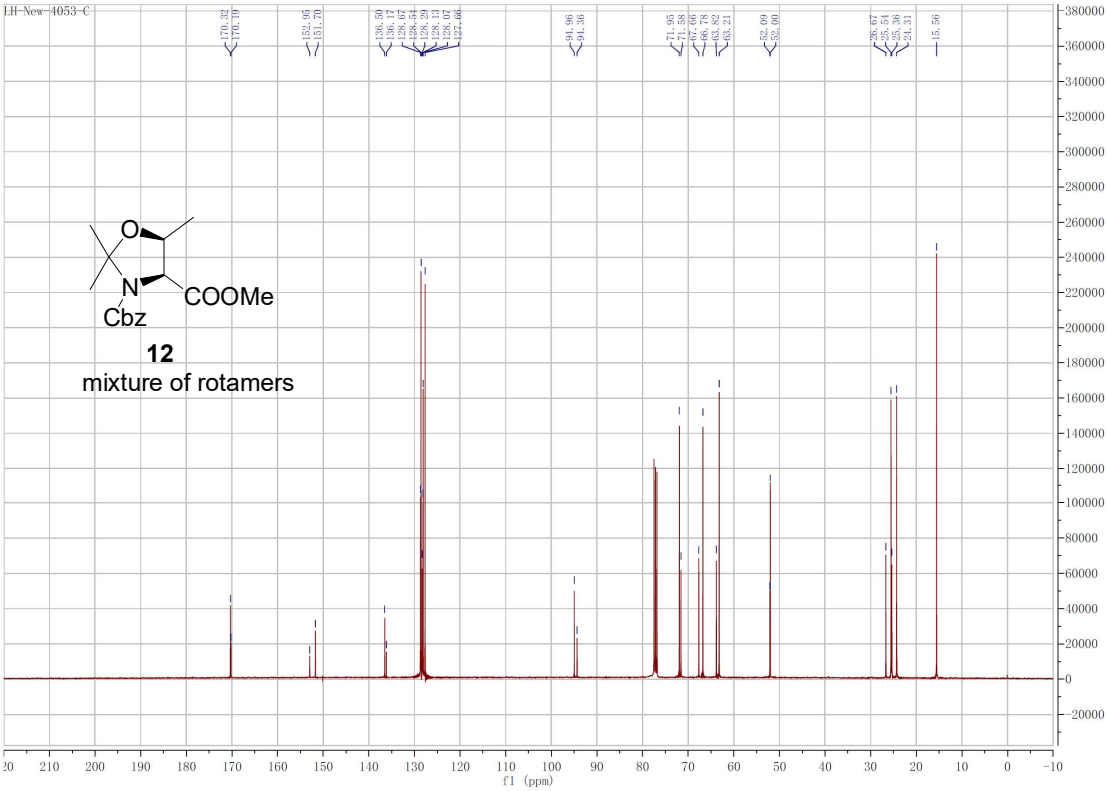
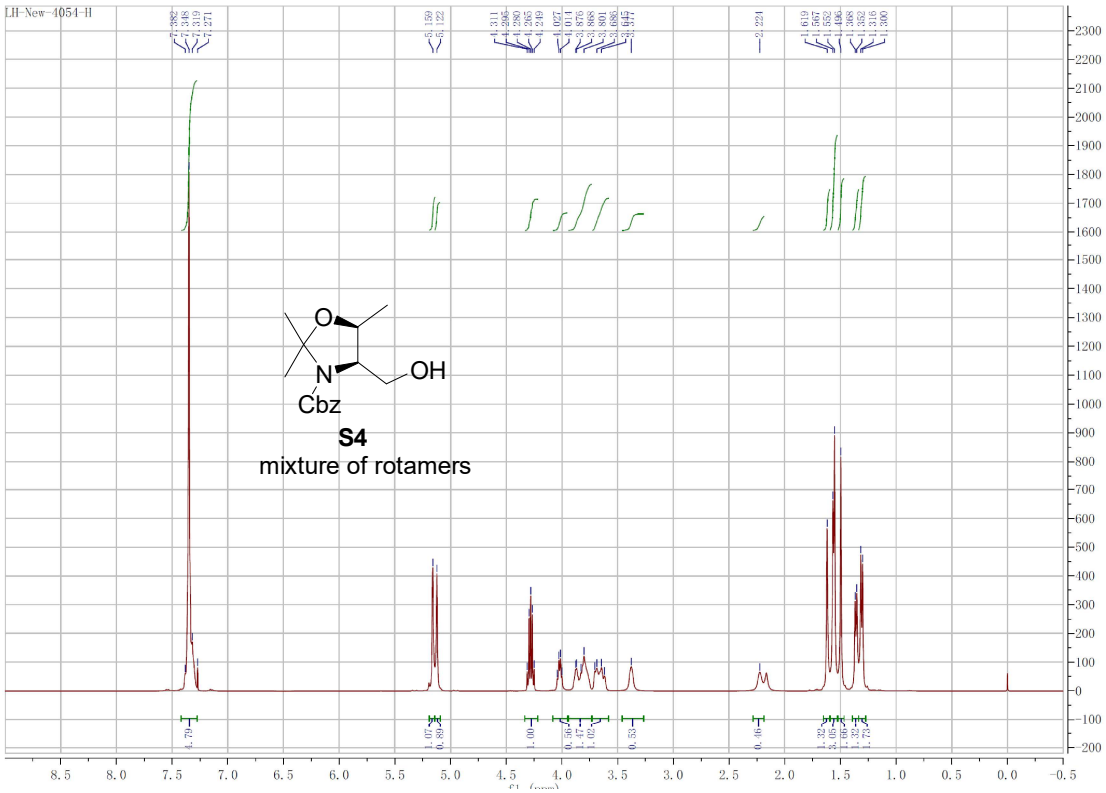


^{13}C NMR of compound 12



^{1}H NMR of compound S4



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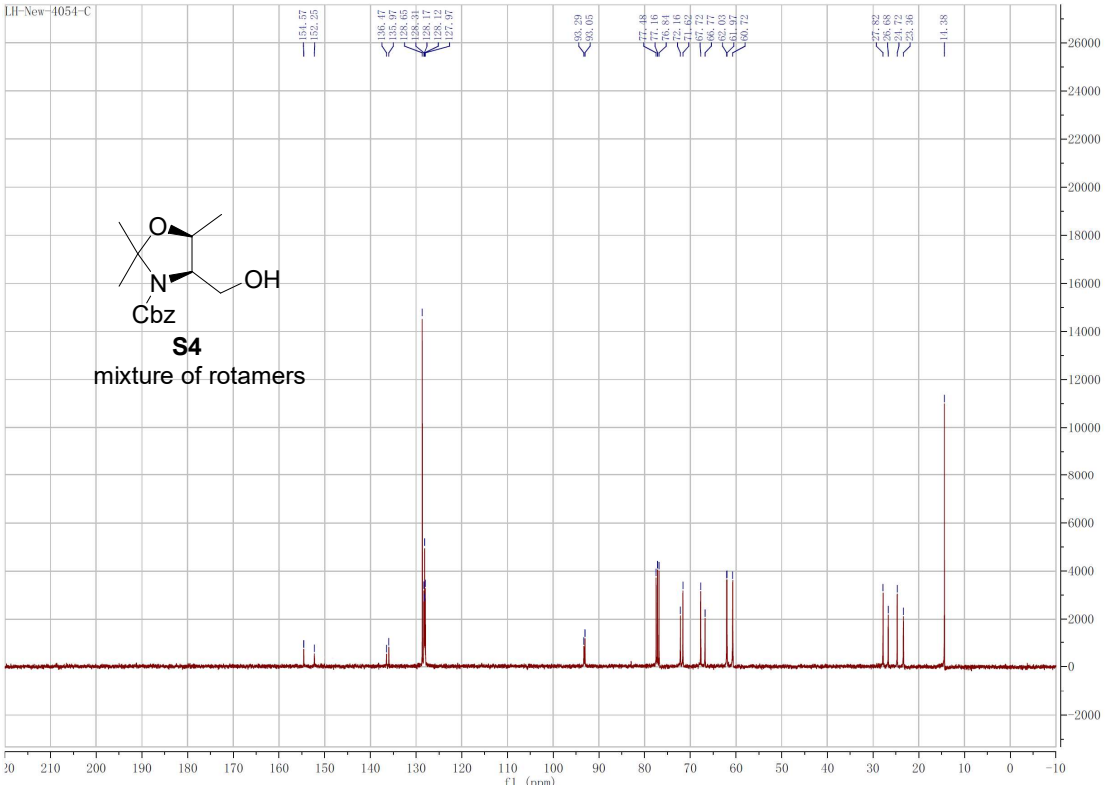
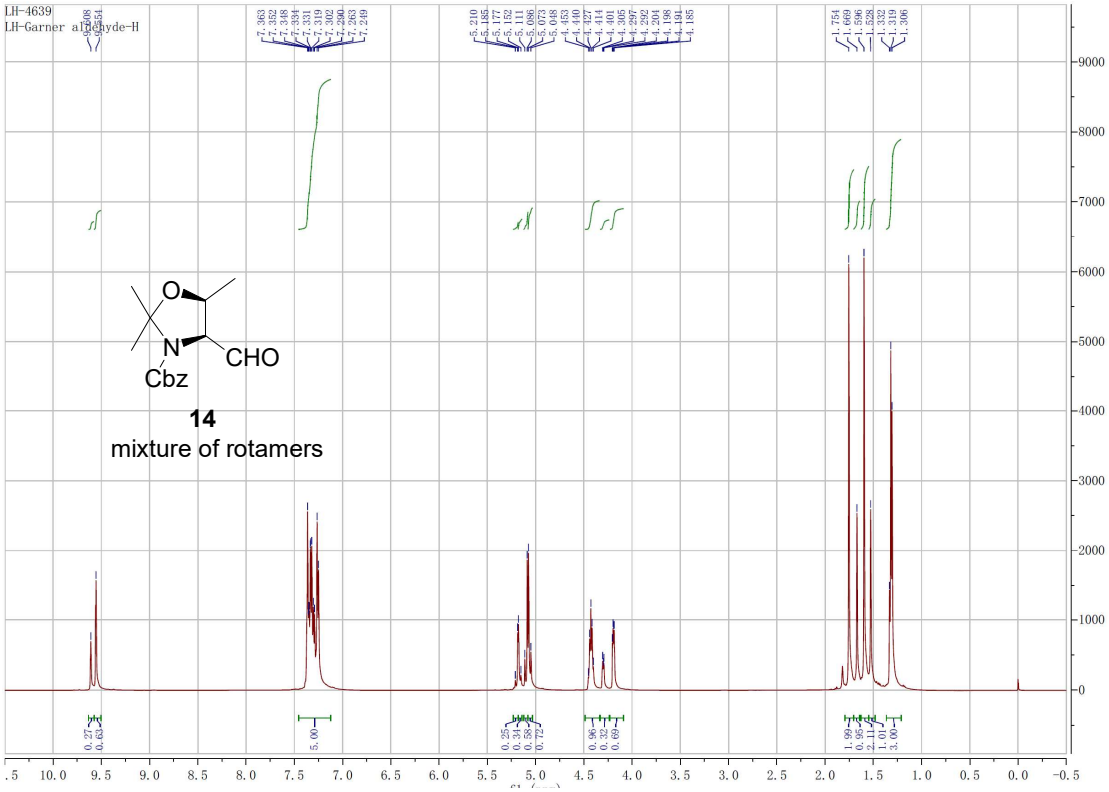
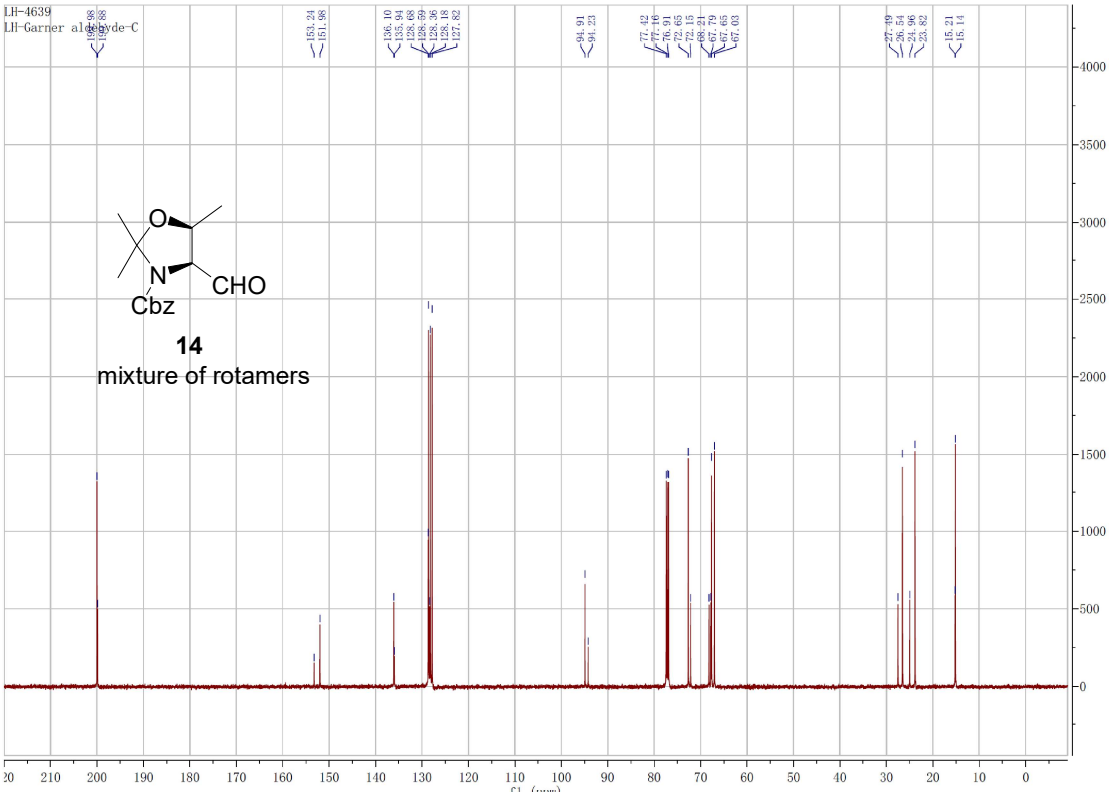


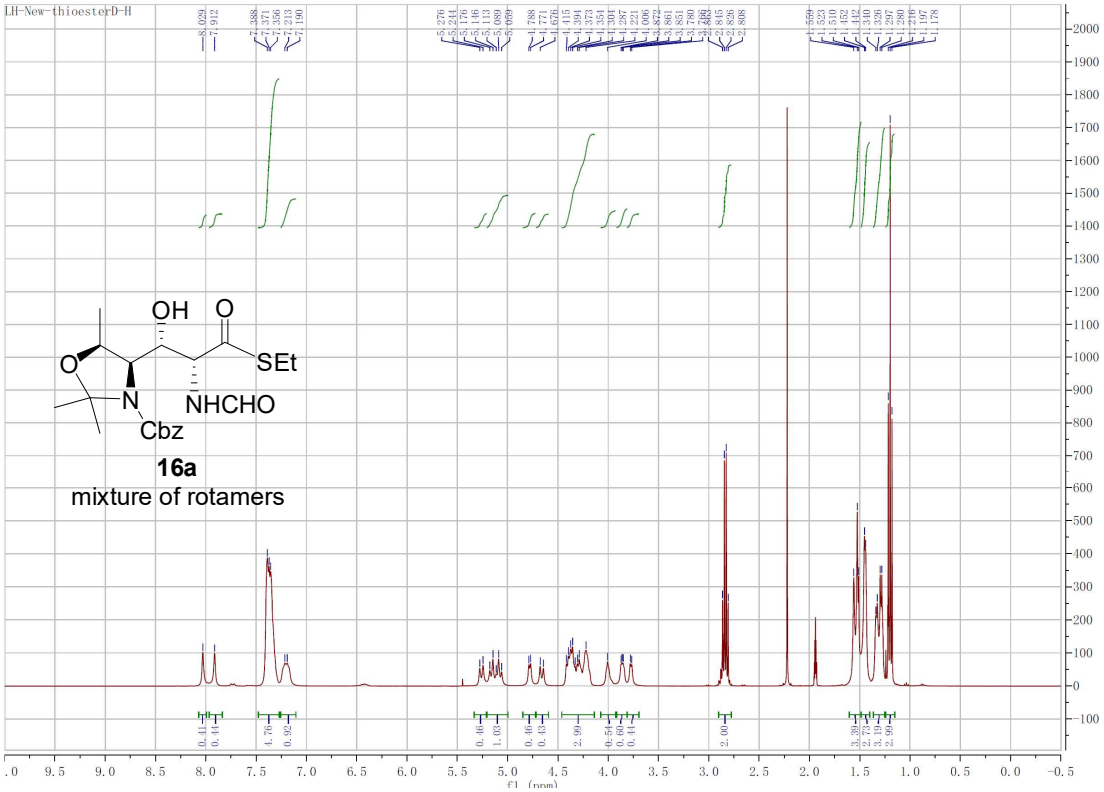
^{1}H NMR of compound 14



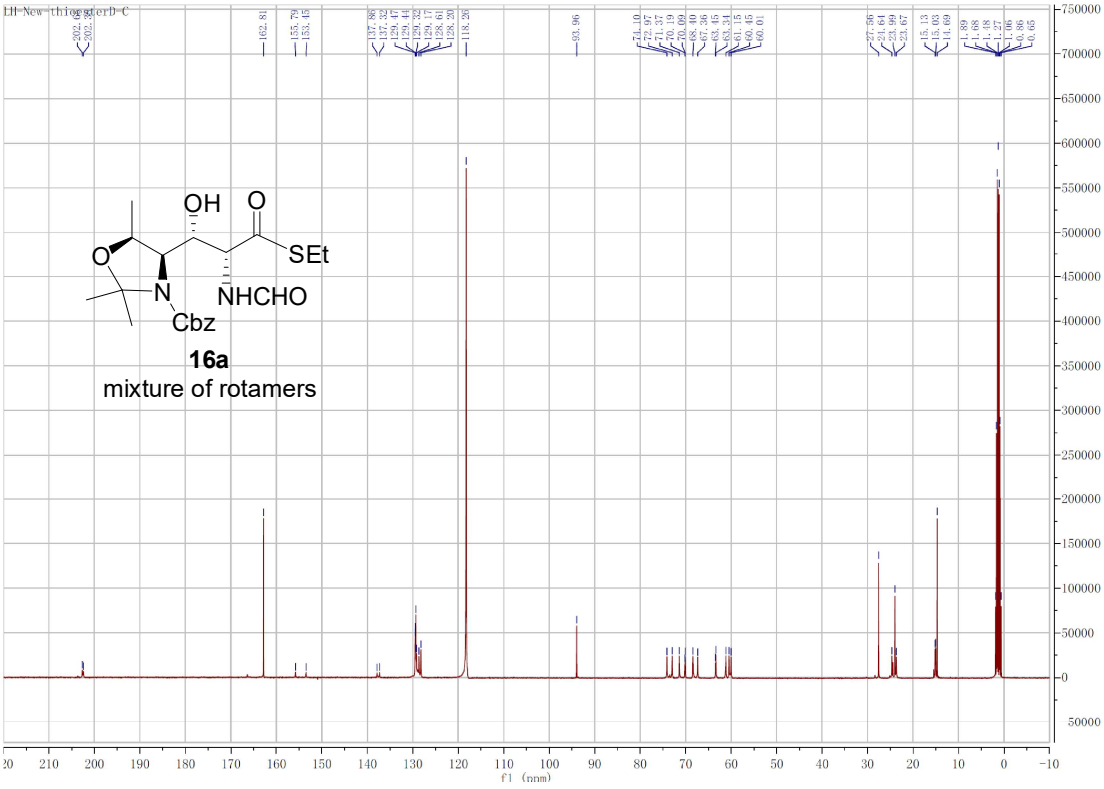
^{13}C NMR of compound 14



^{1}H NMR of compound 16a



^{13}C NMR of compound 16a



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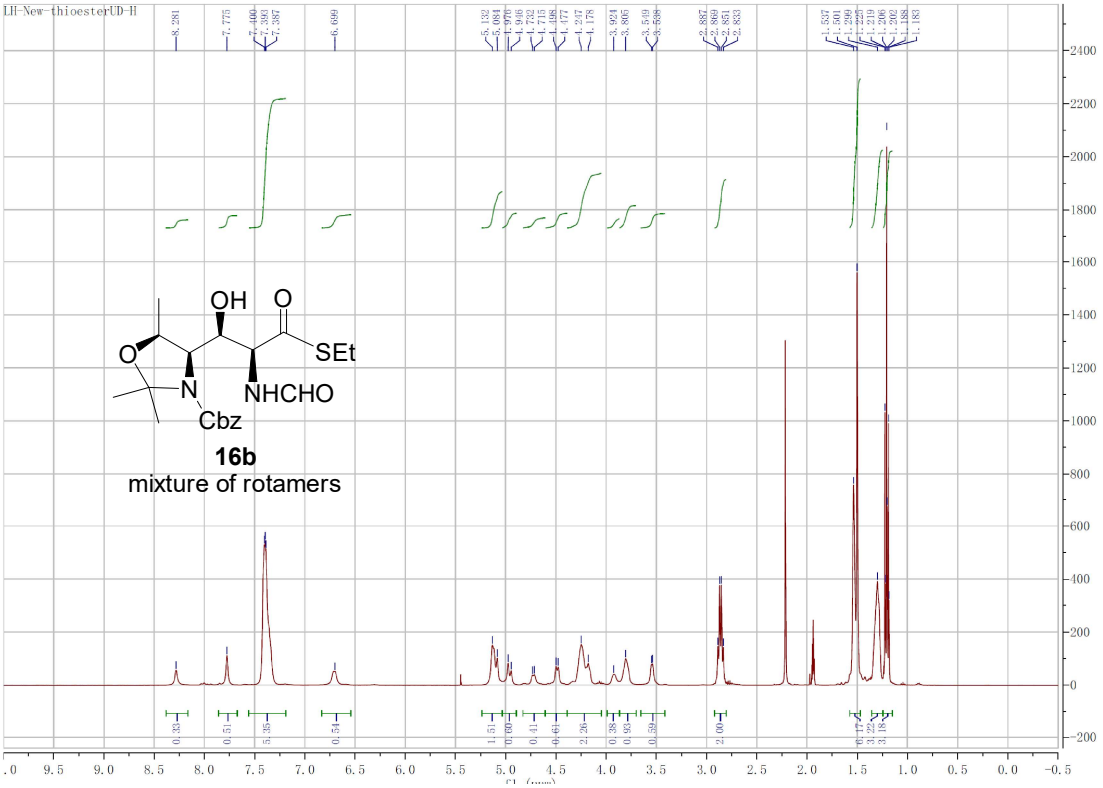
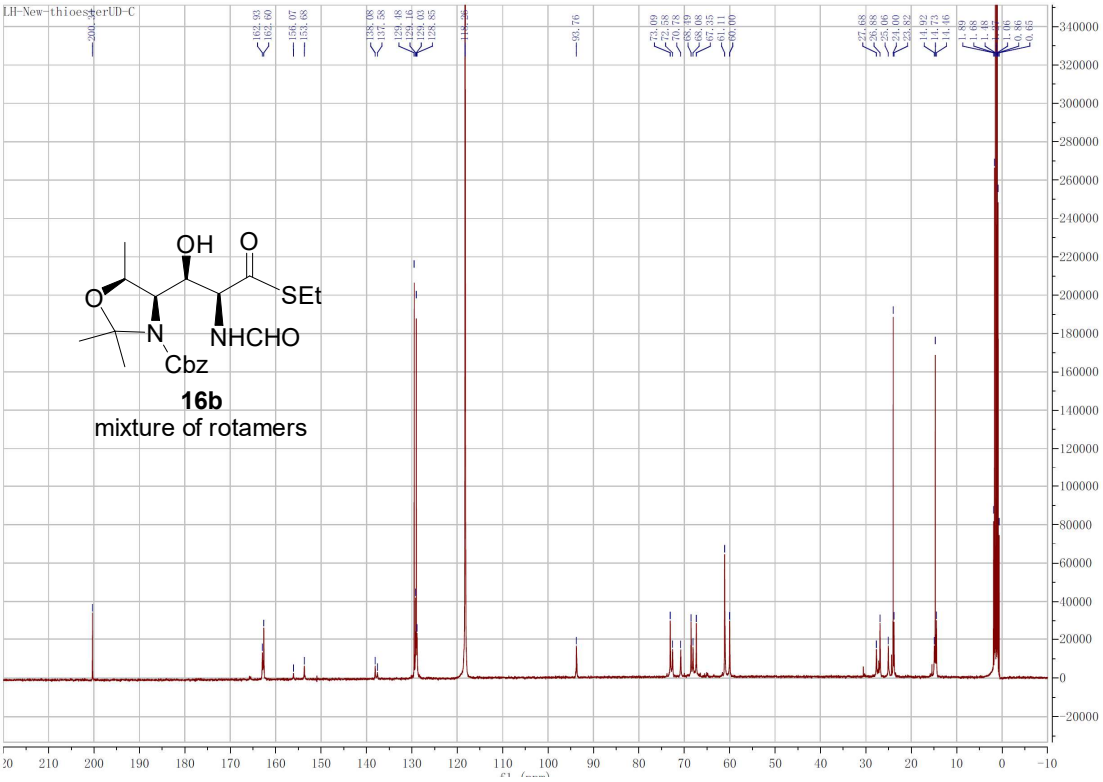
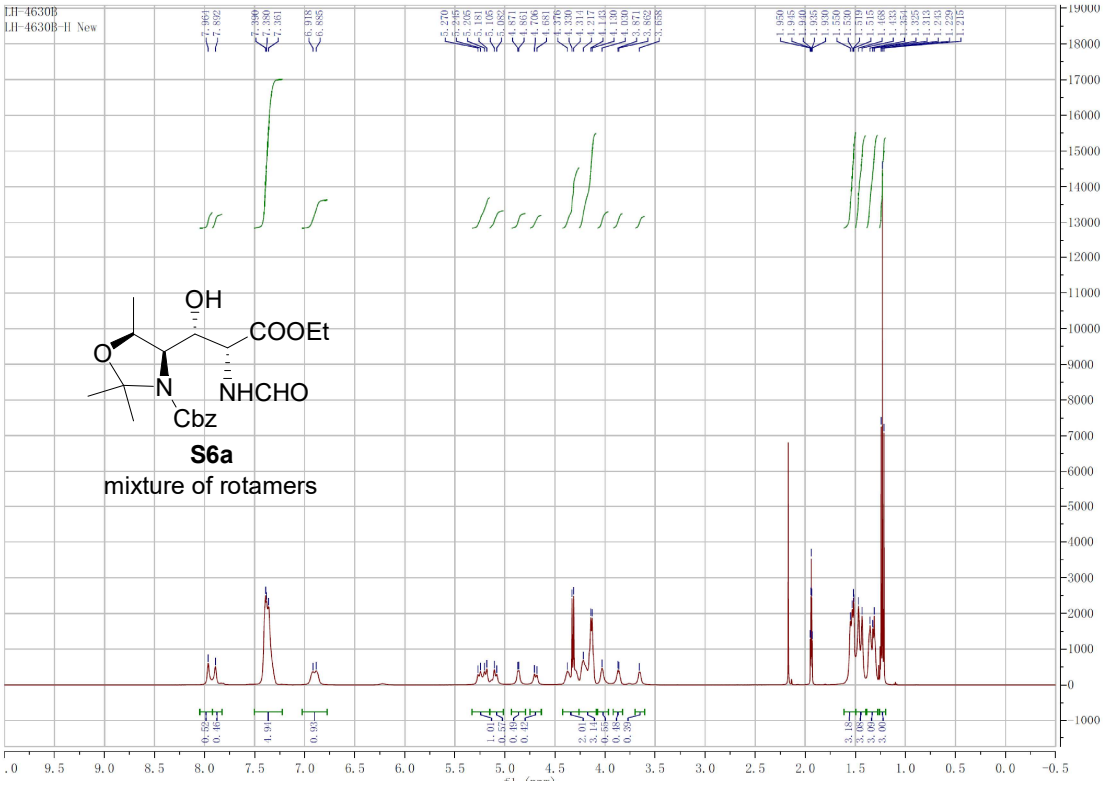


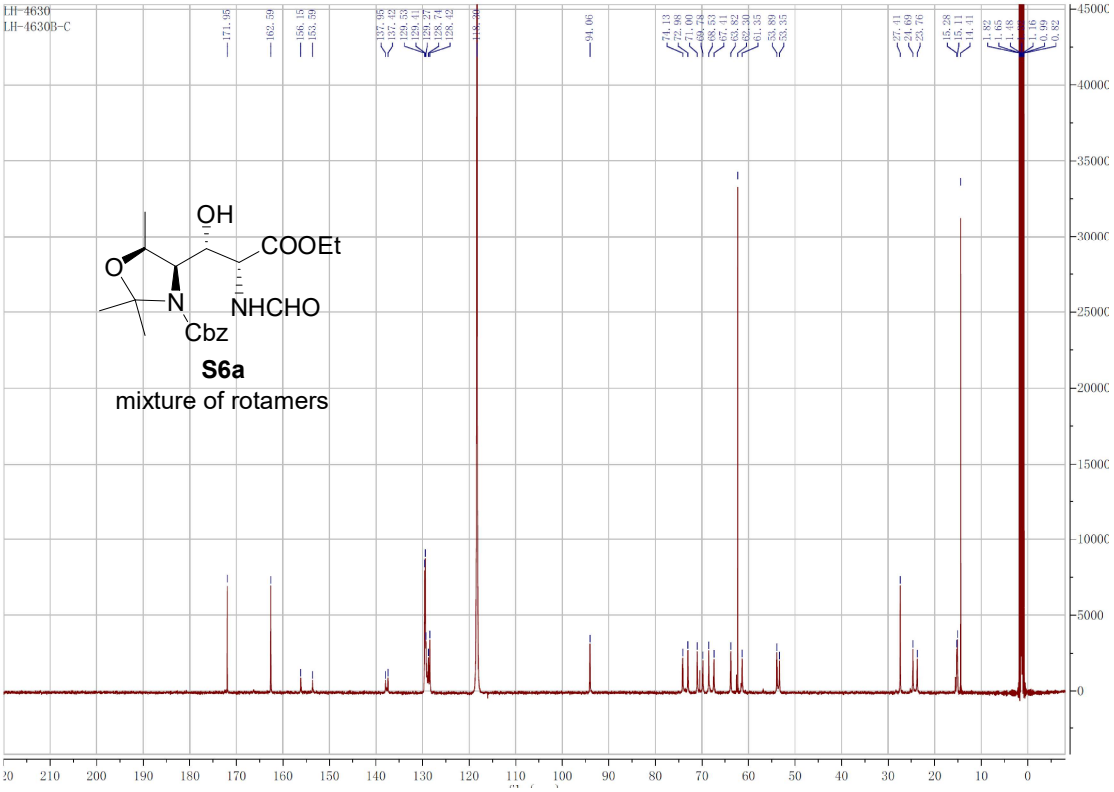
^{13}C NMR of compound 16b



^{1}H NMR of compound S6a



^{13}C NMR of compound S6a



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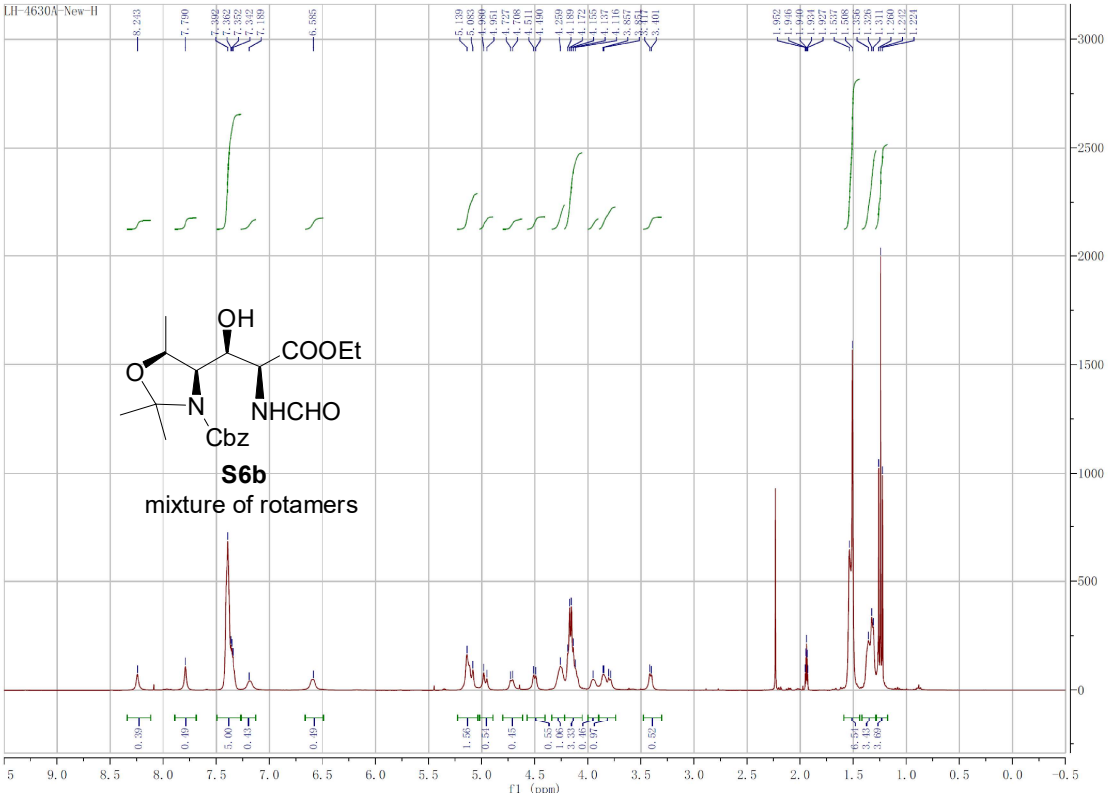

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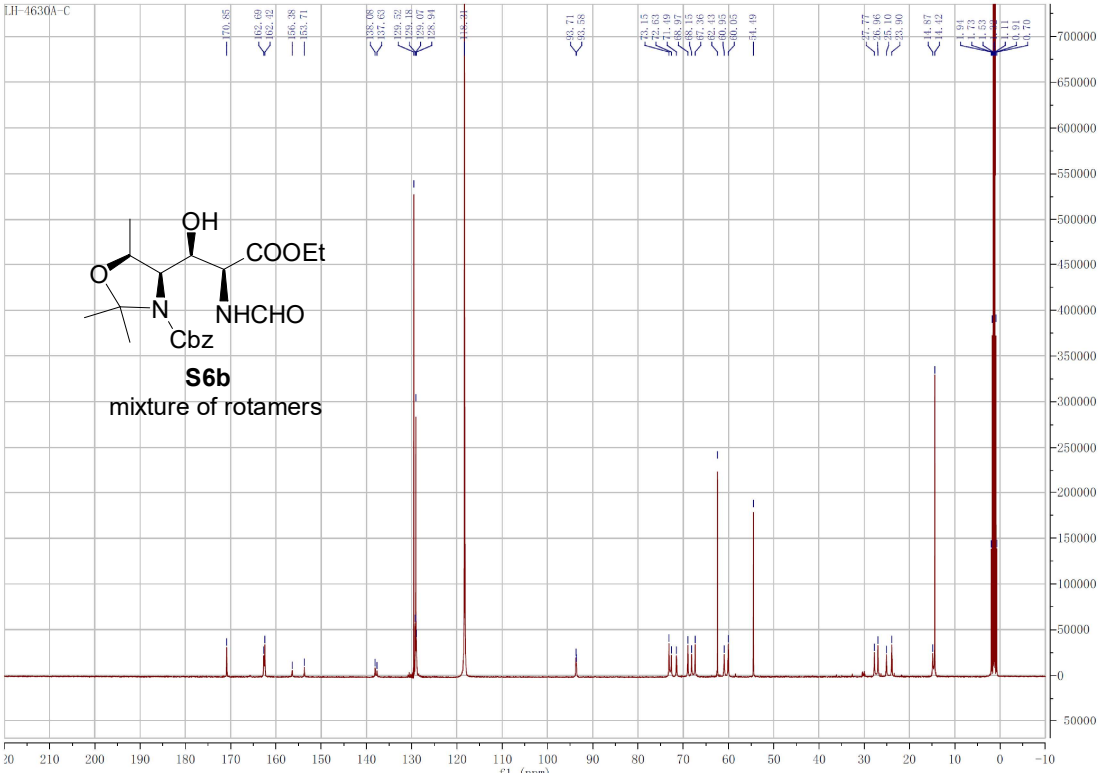
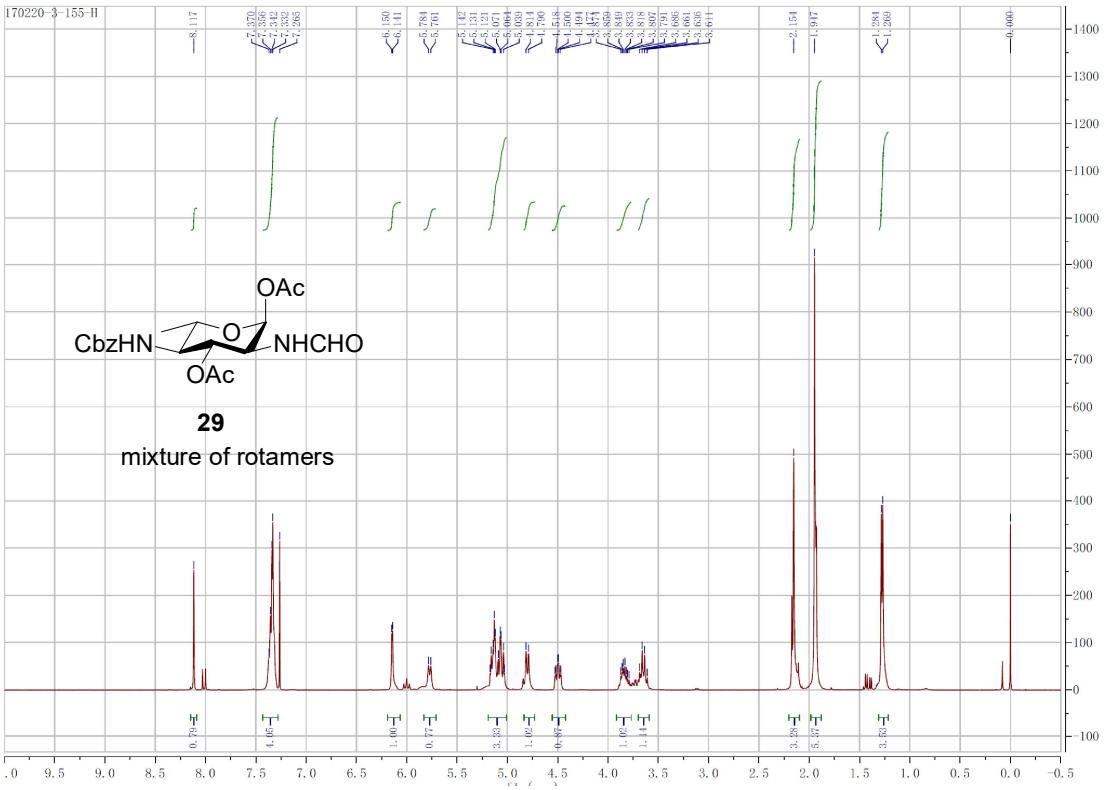
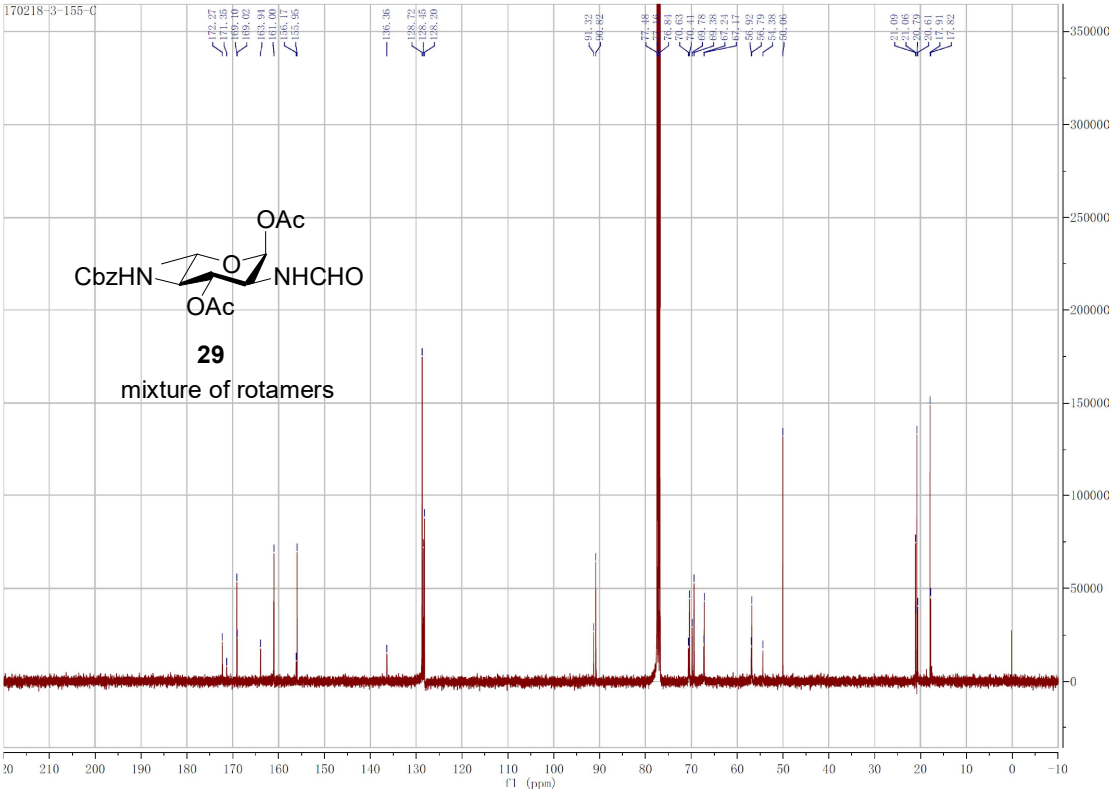


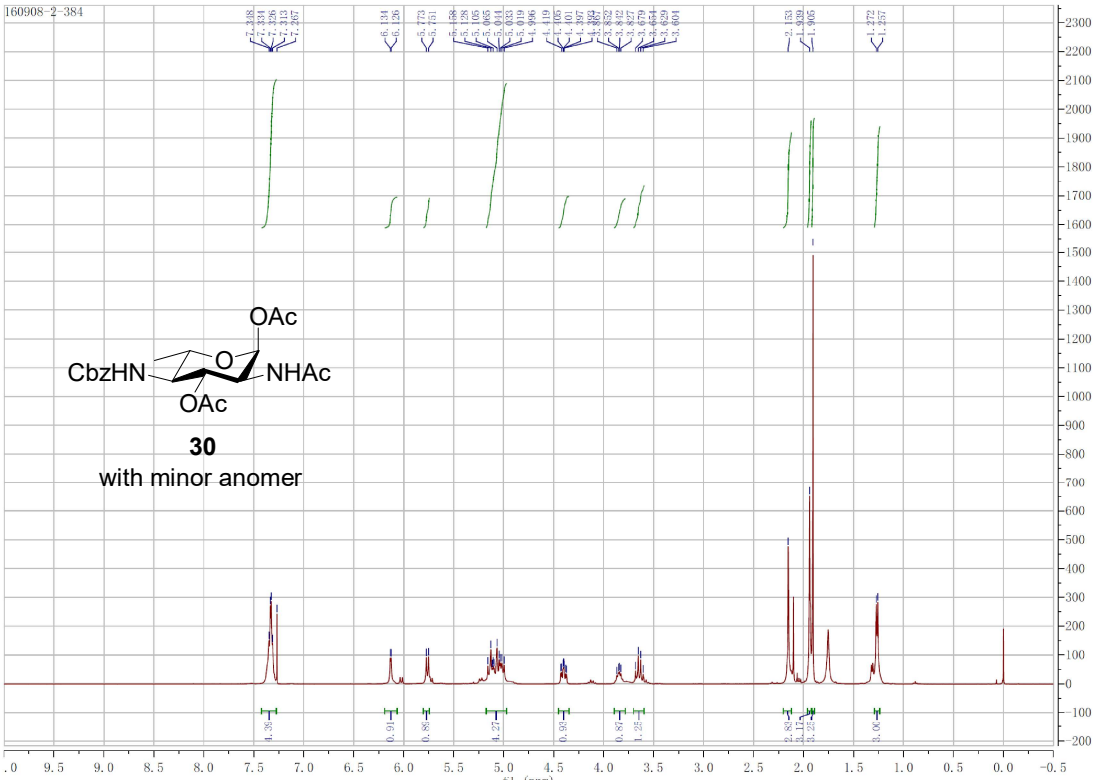
^{1}H NMR of compound 29



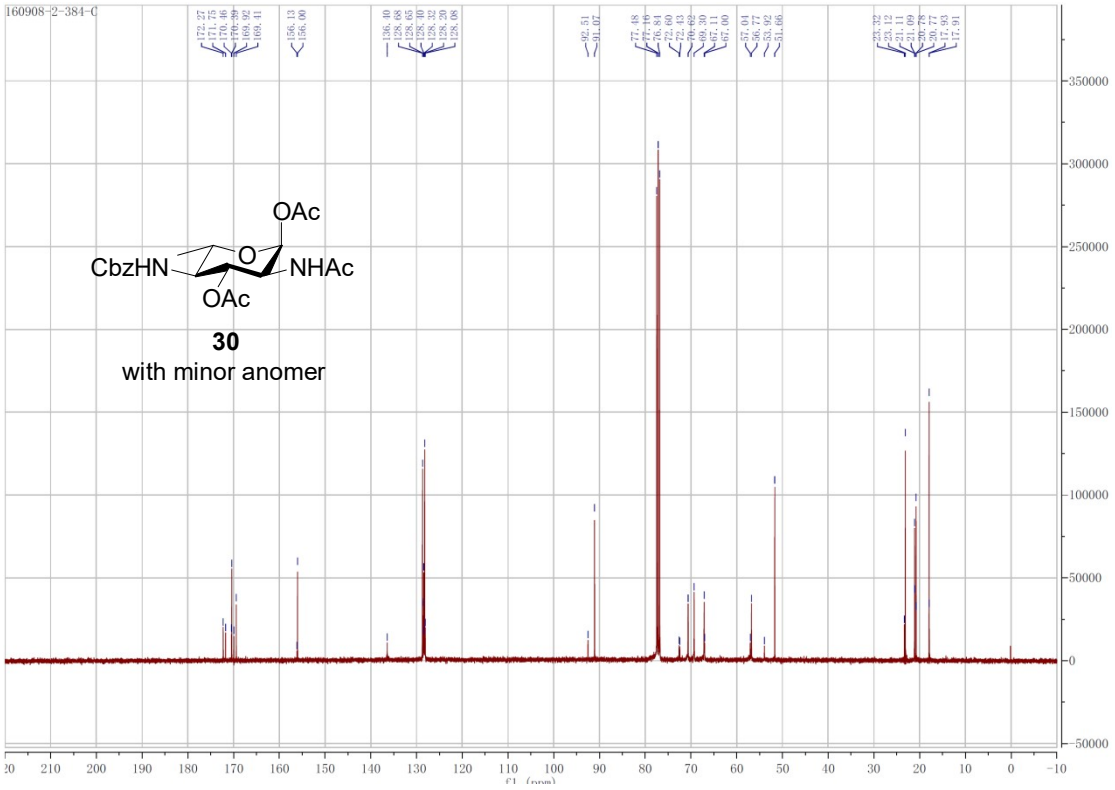
^{13}C NMR of compound 29



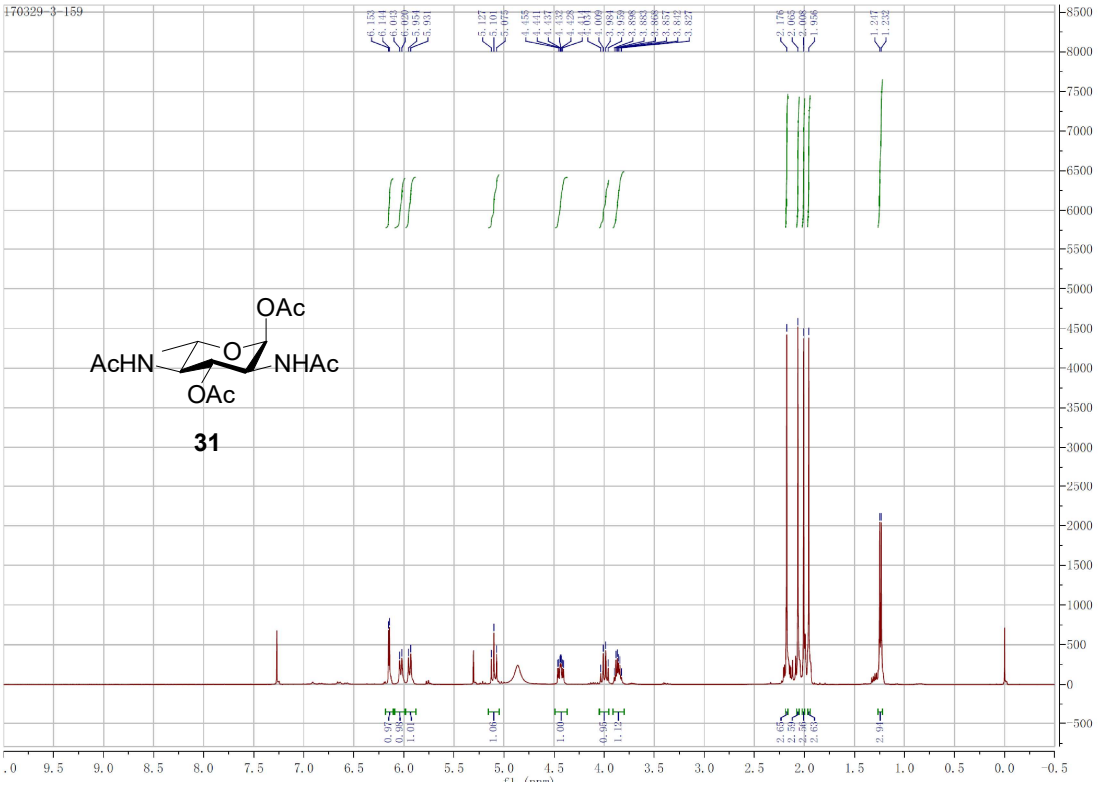
^{1}H NMR of compound 30



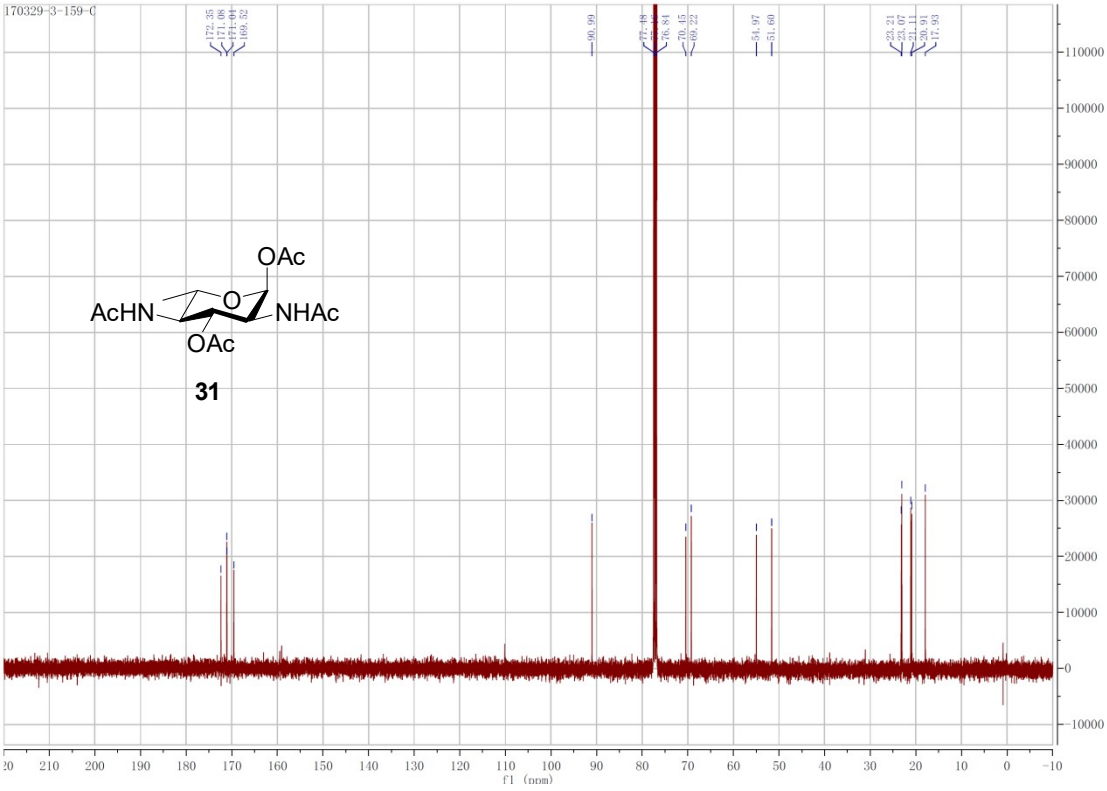
^{13}C NMR of compound 30



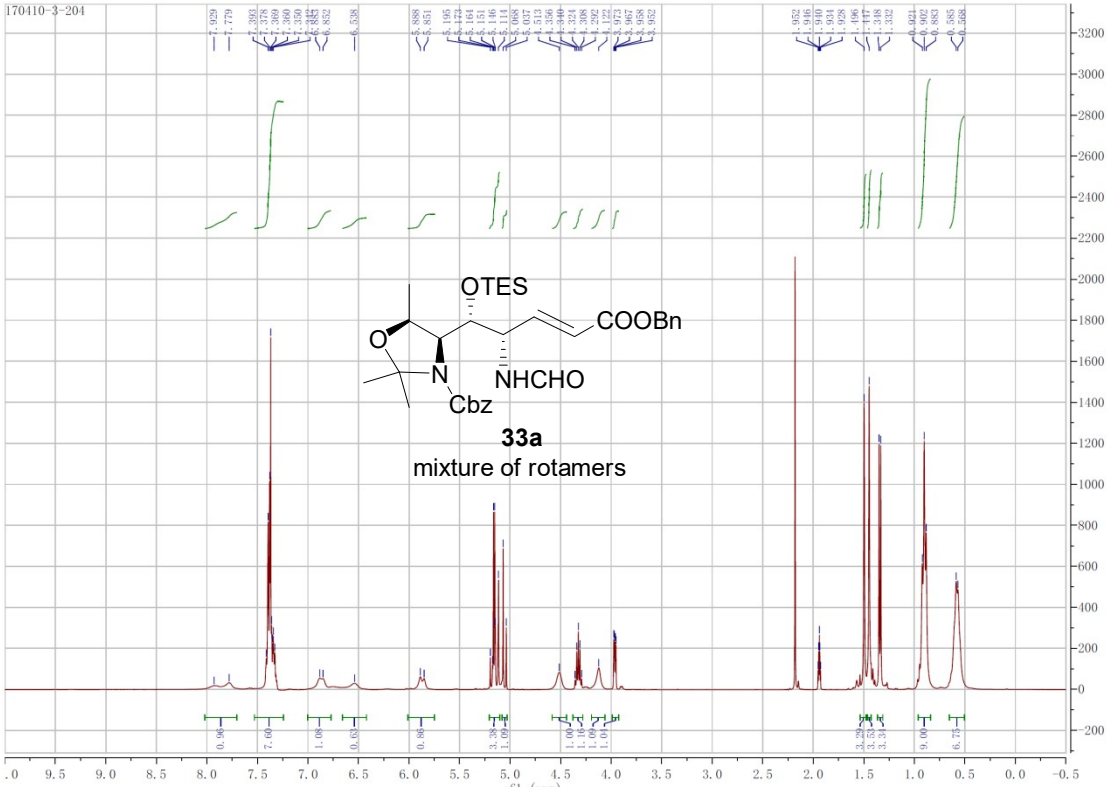
^{1}H NMR of compound 31



^{13}C NMR of compound 31



^{1}H NMR of compound 33a



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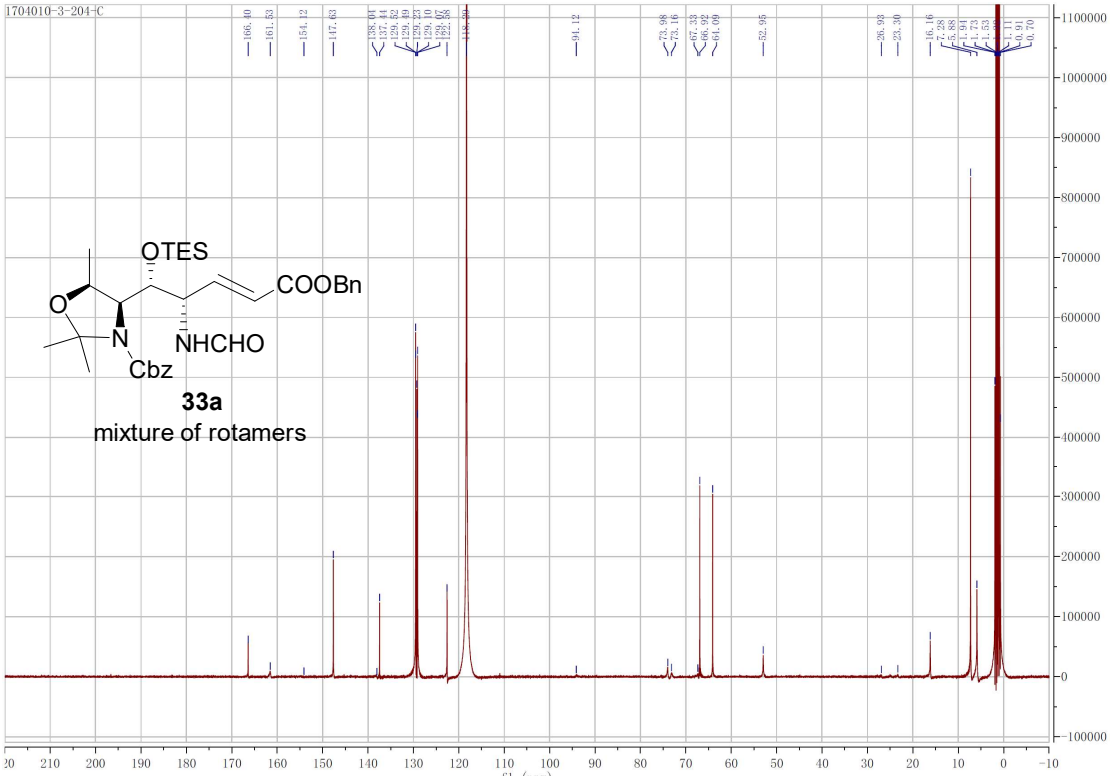

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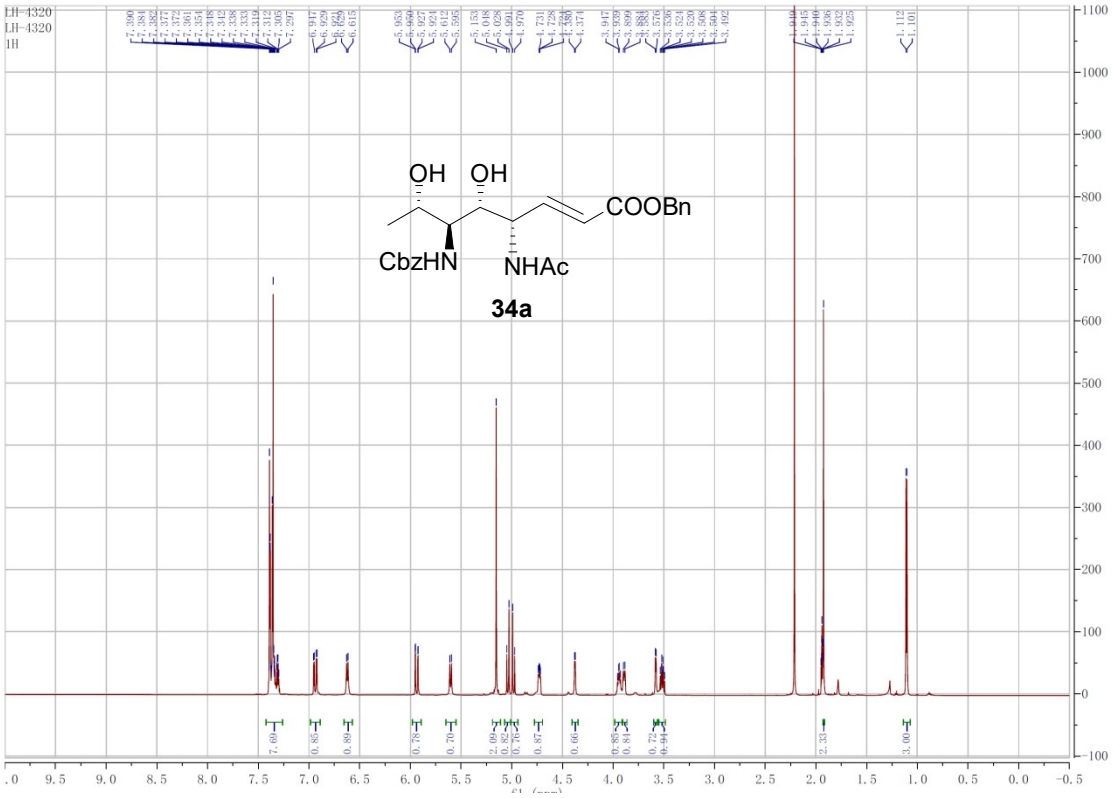

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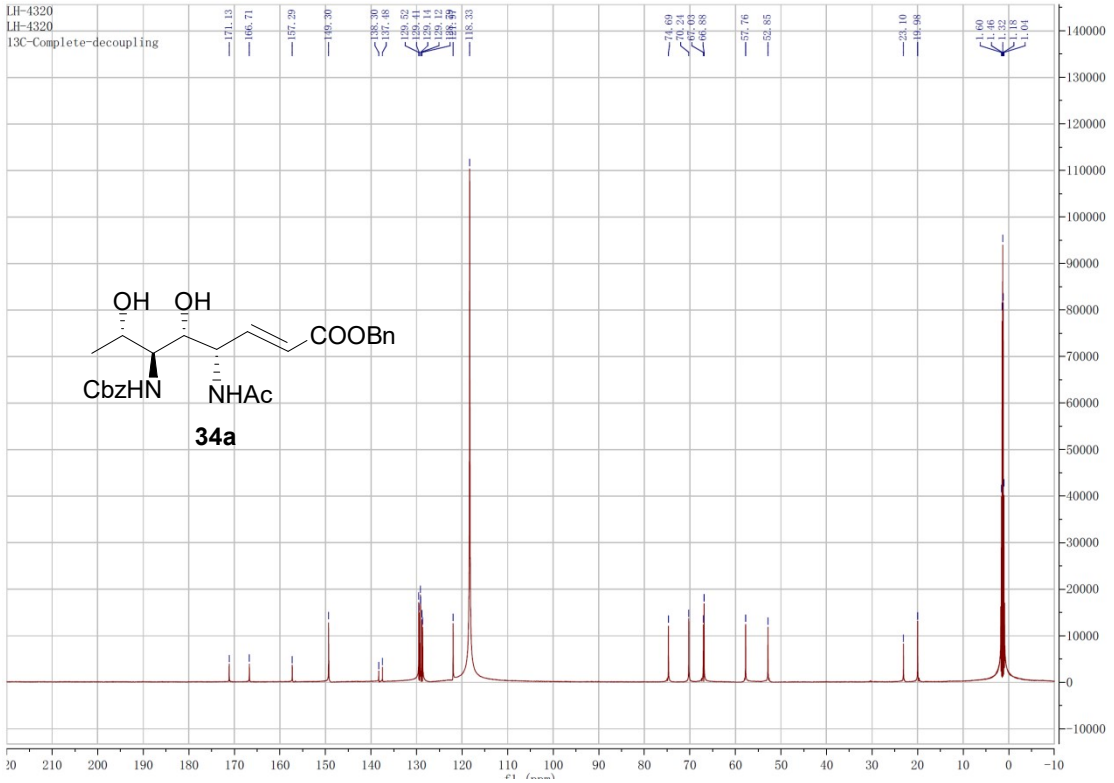
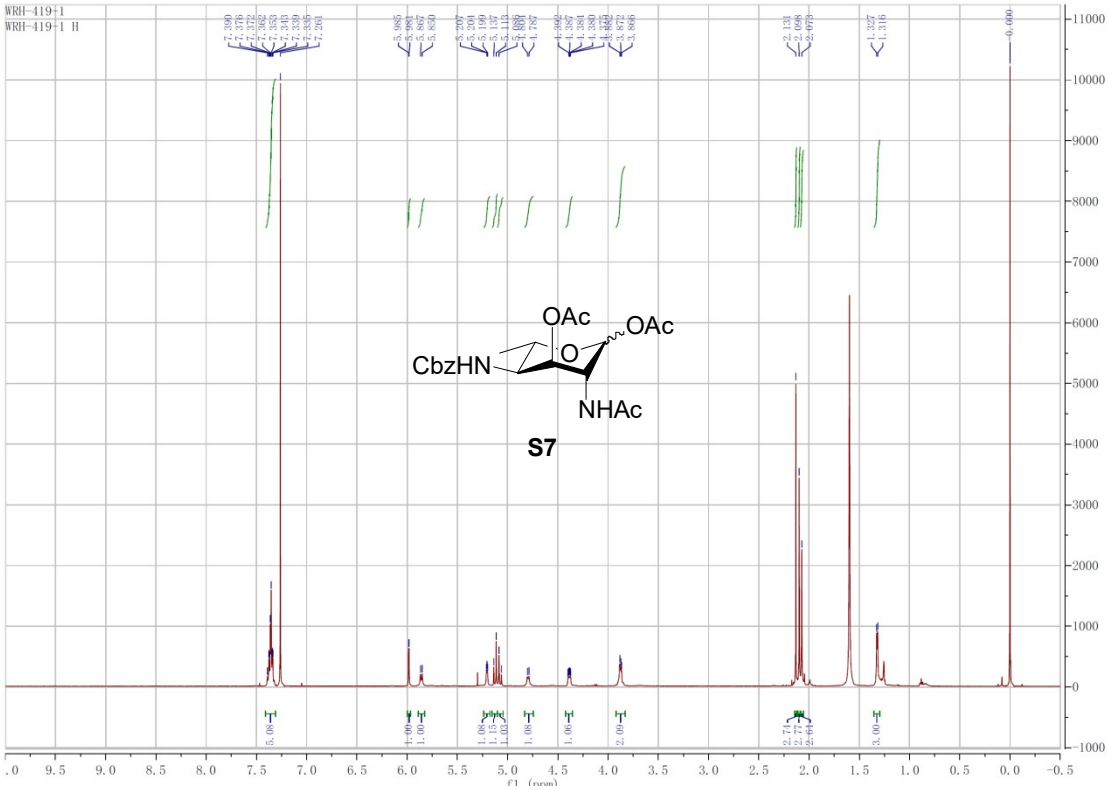
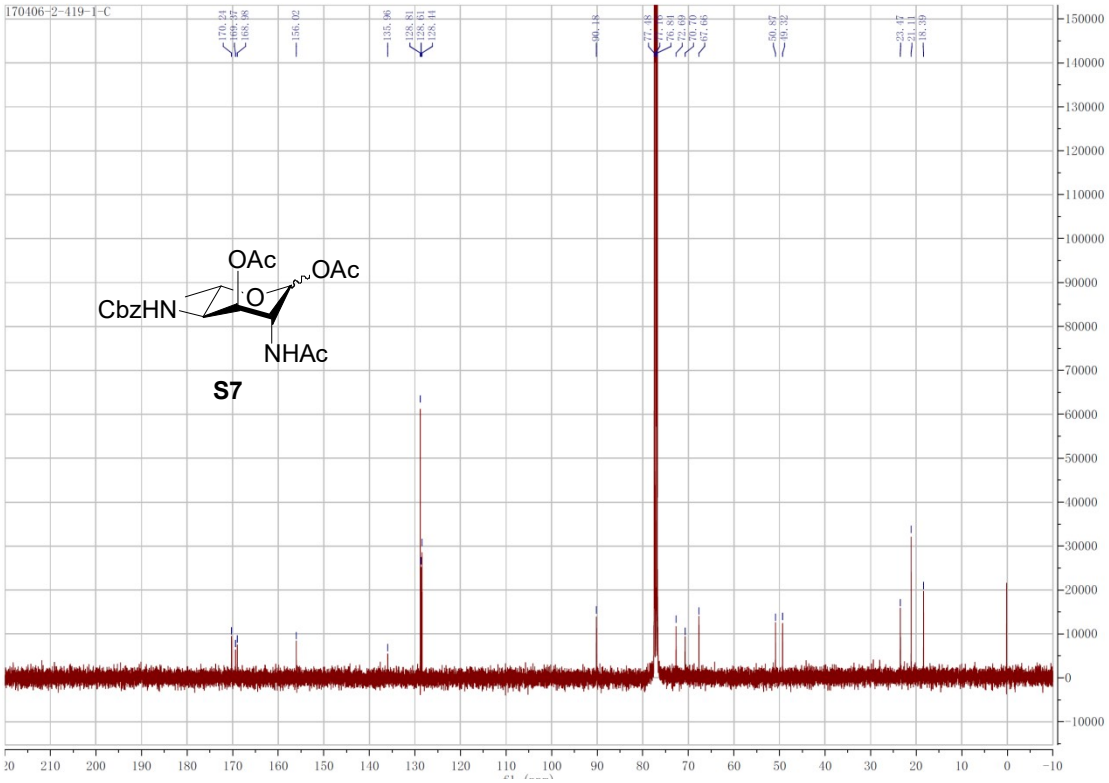


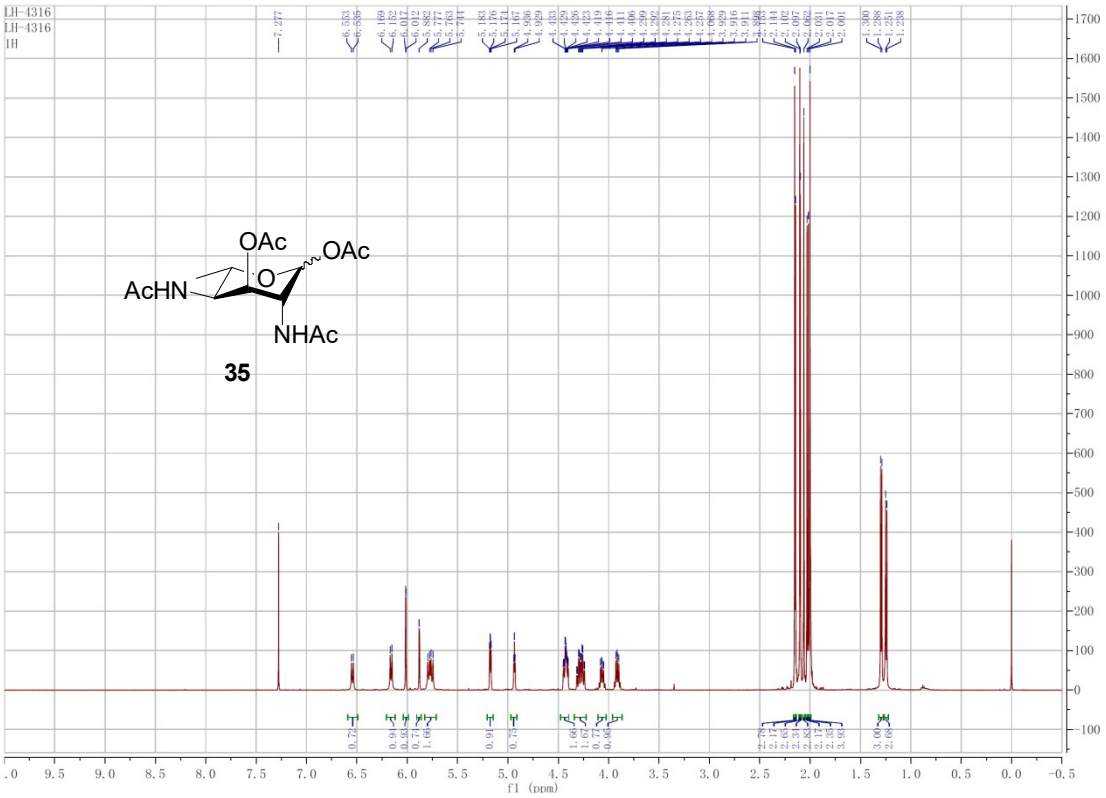
^{1}H NMR of compound S7



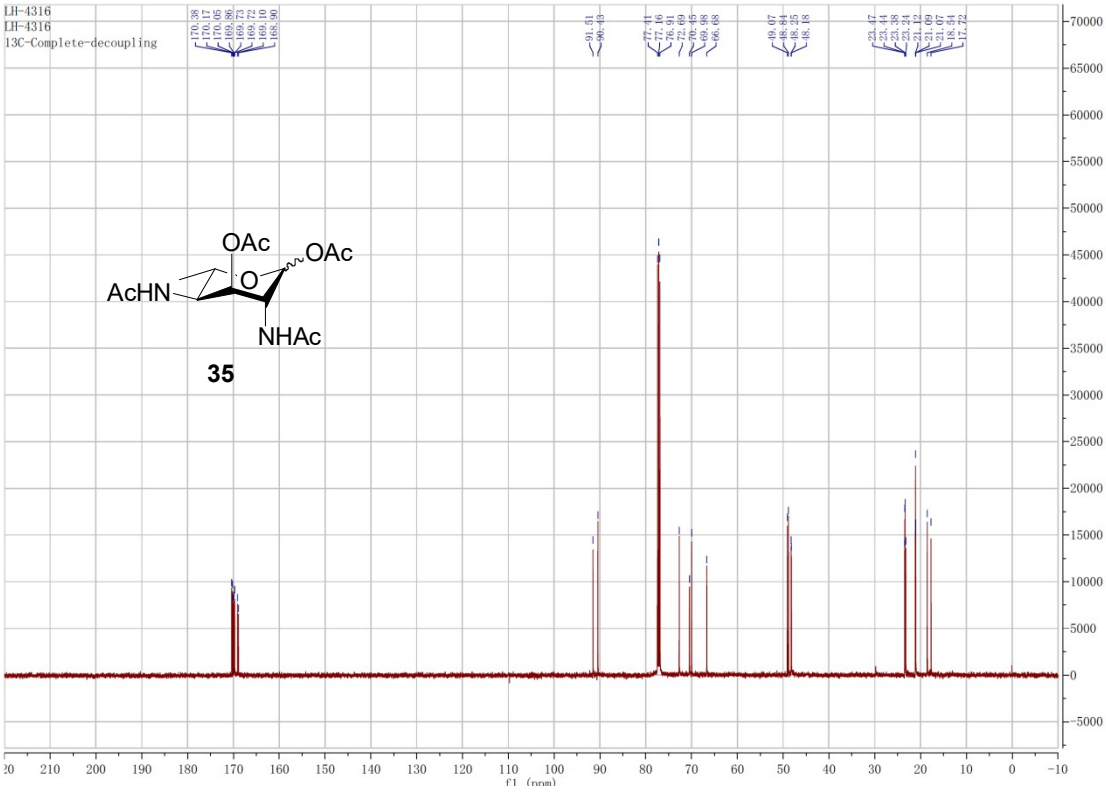
^{13}C NMR of compound S7



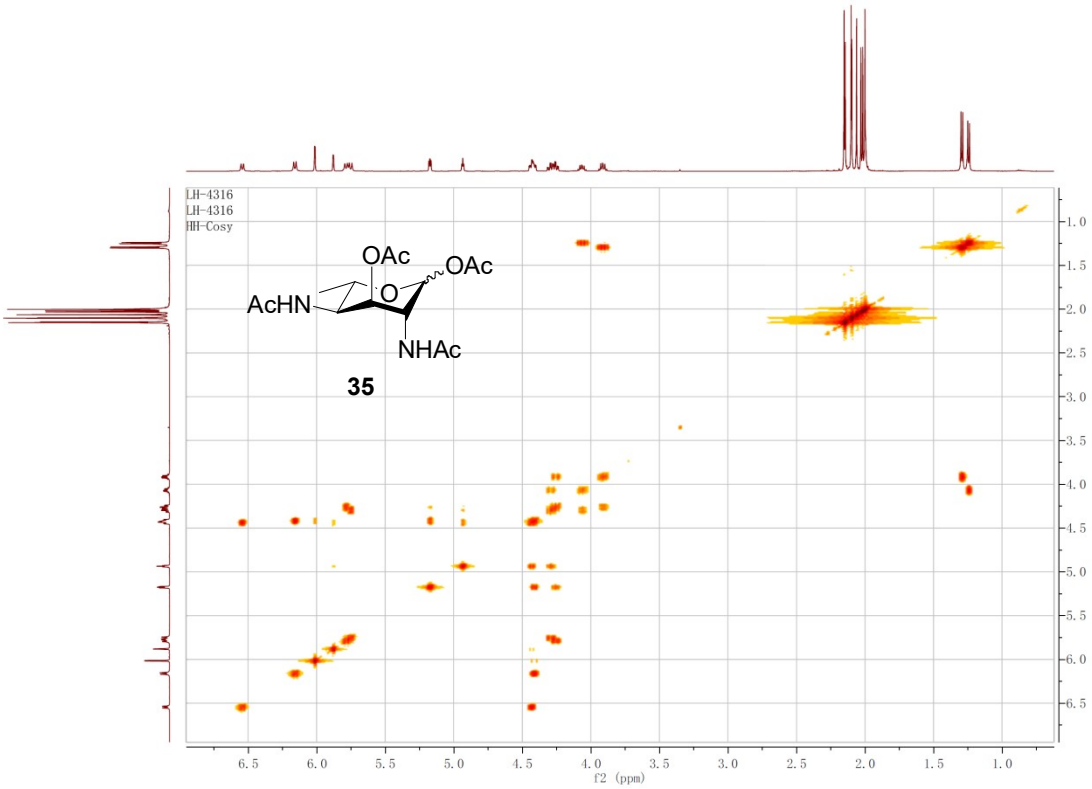
^{1}H NMR of compound 35



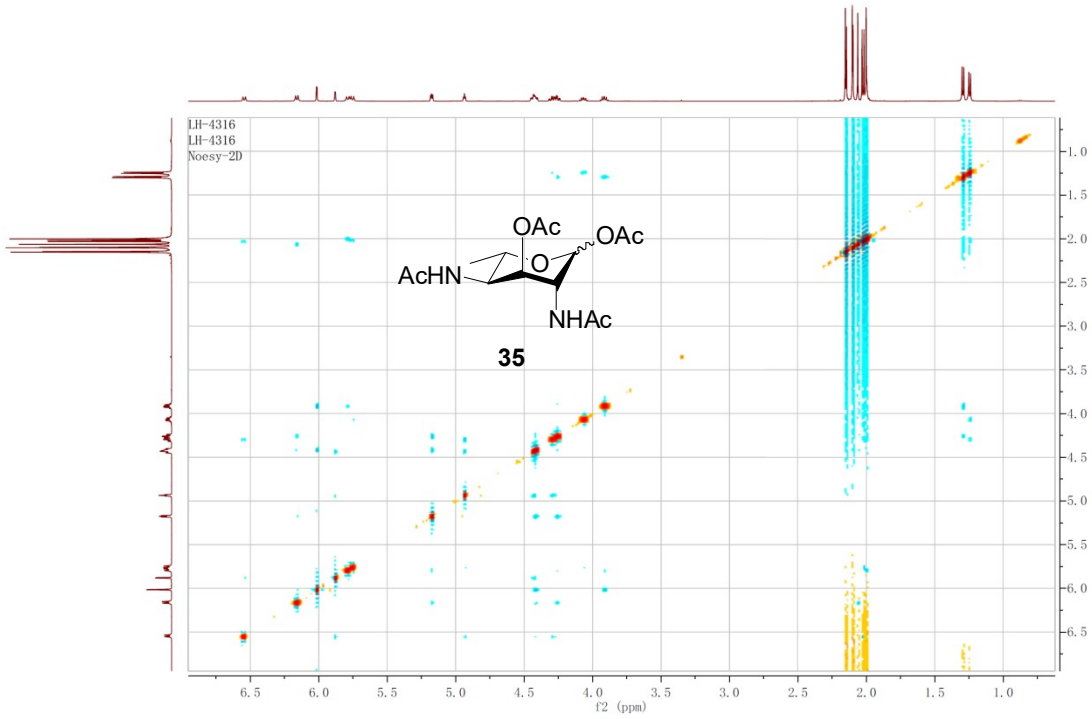
^{13}C NMR of compound 35



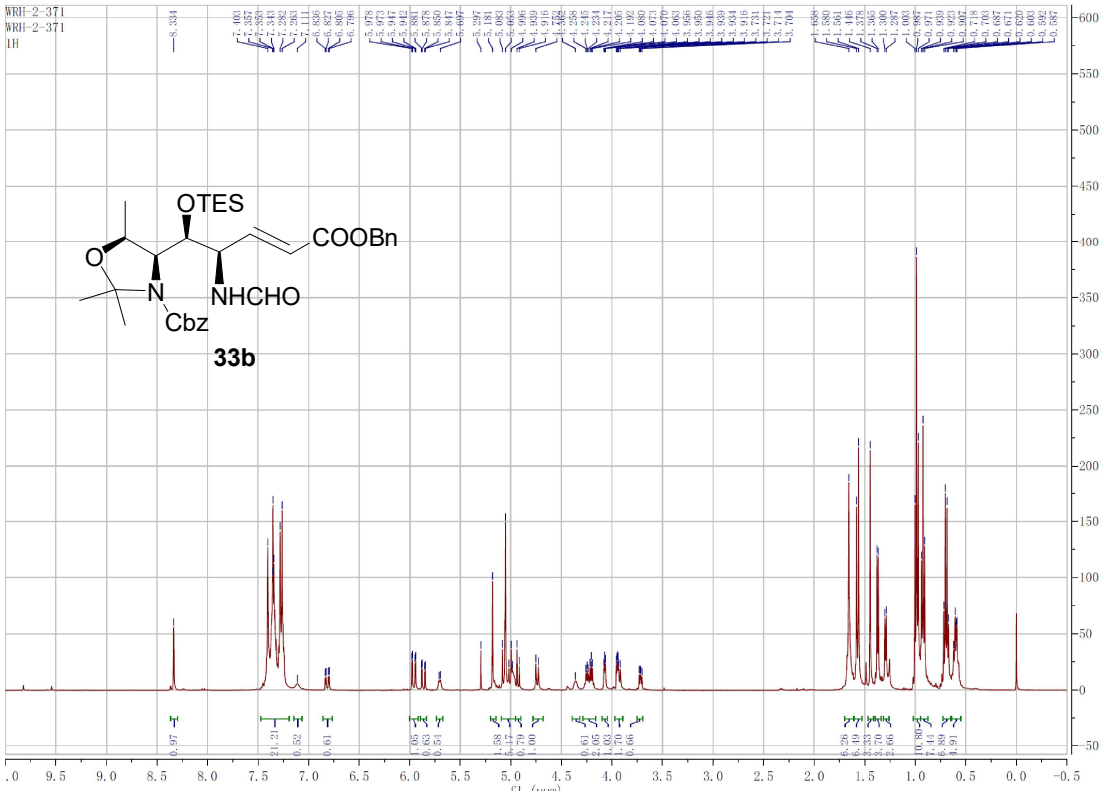
^{1}H-^{1}H COSY of compound 35



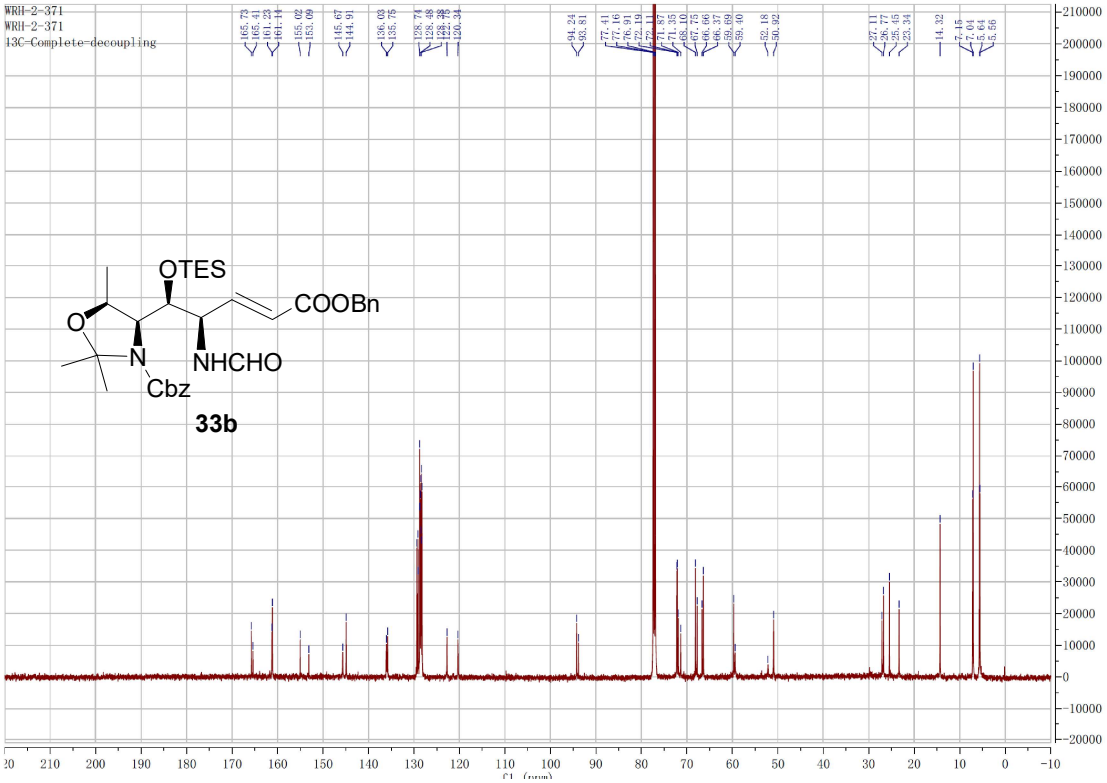
2D NOESY of compound 35



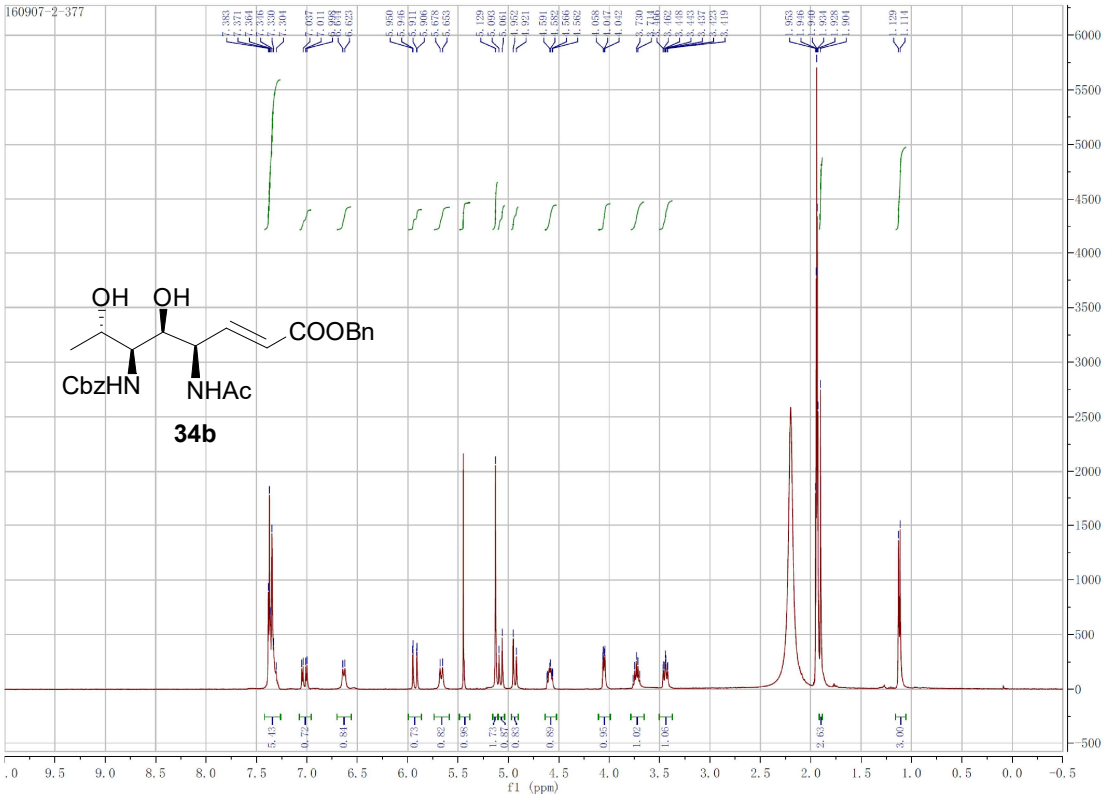
^{1}H NMR of compound 33b



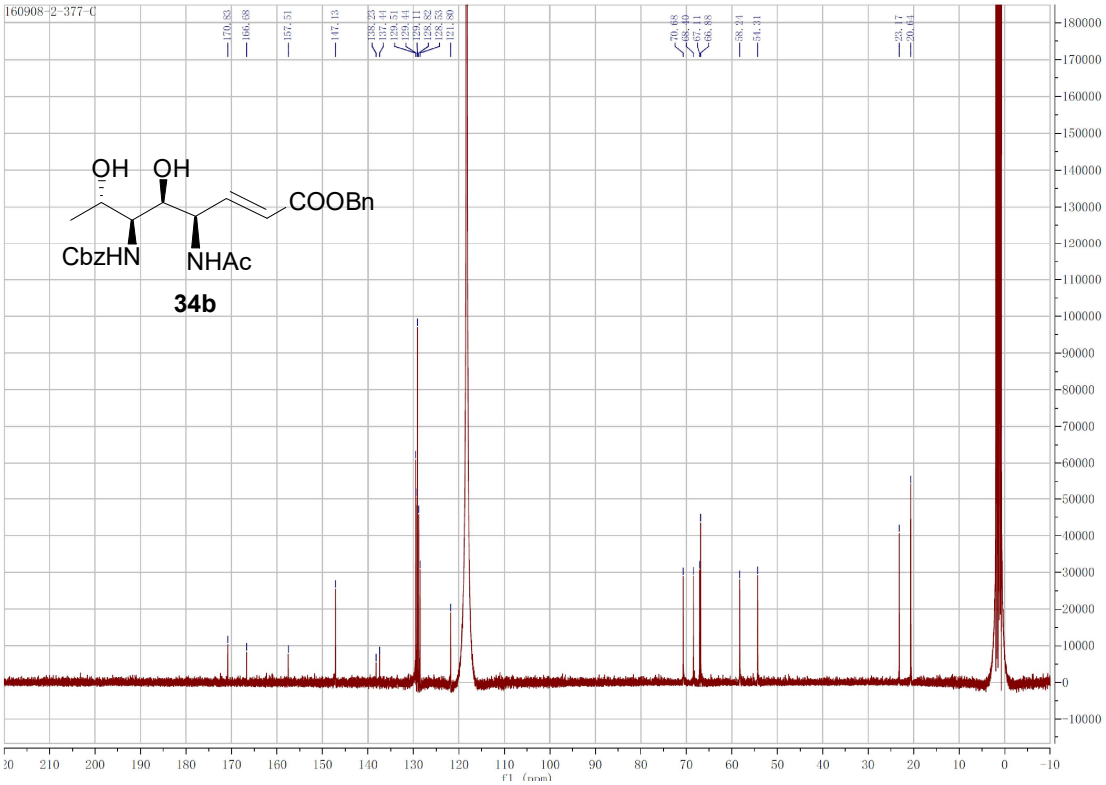
^{13}C NMR of compound 33b



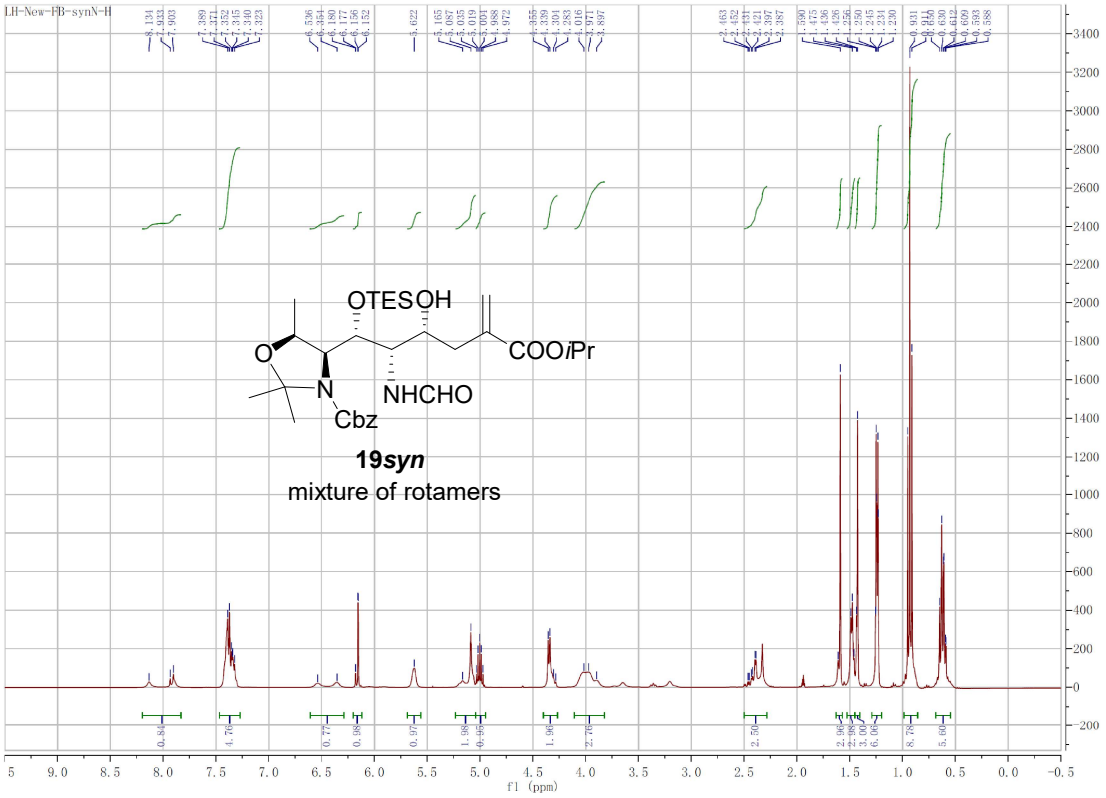
^{1}H NMR of compound 34b



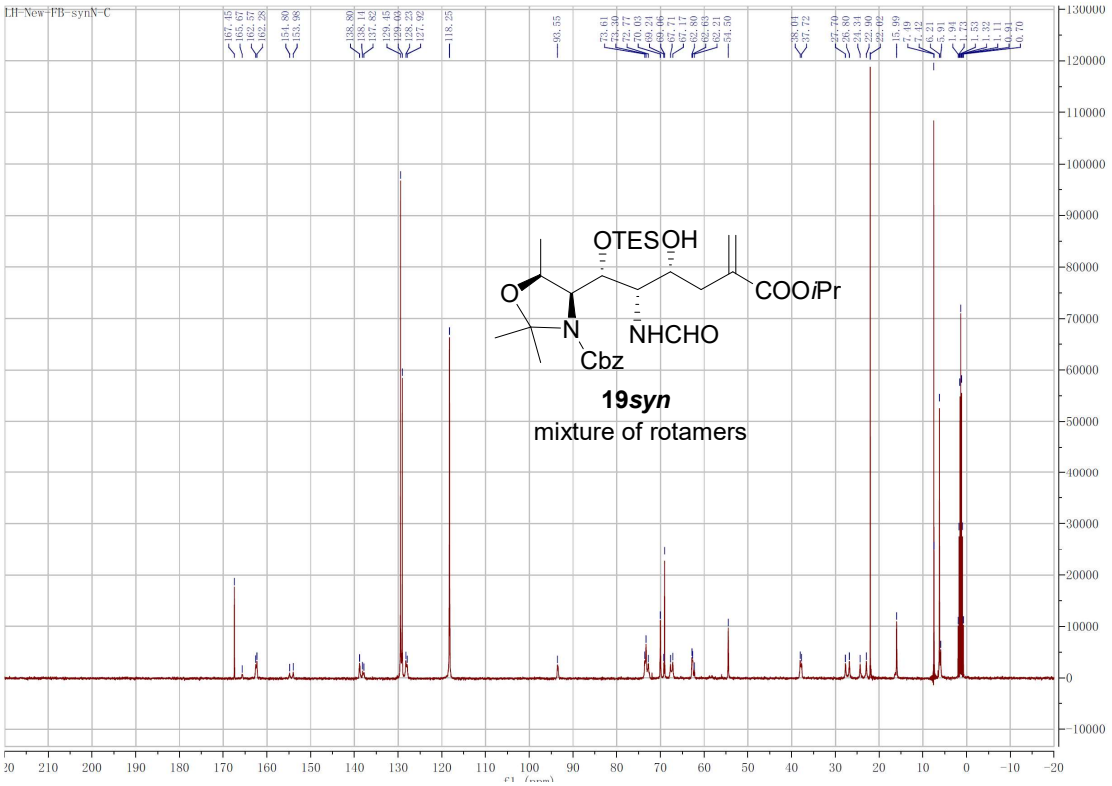
^{13}C NMR of compound 34b



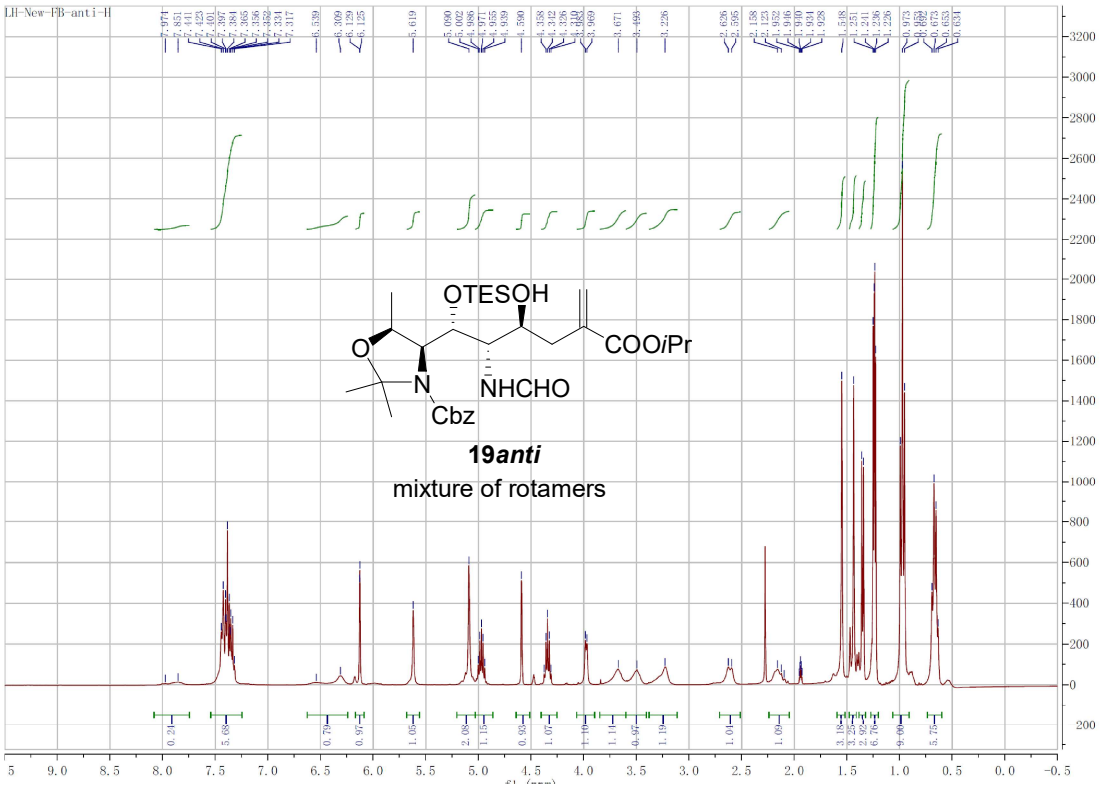
^{1}H NMR of compound 19*syn*



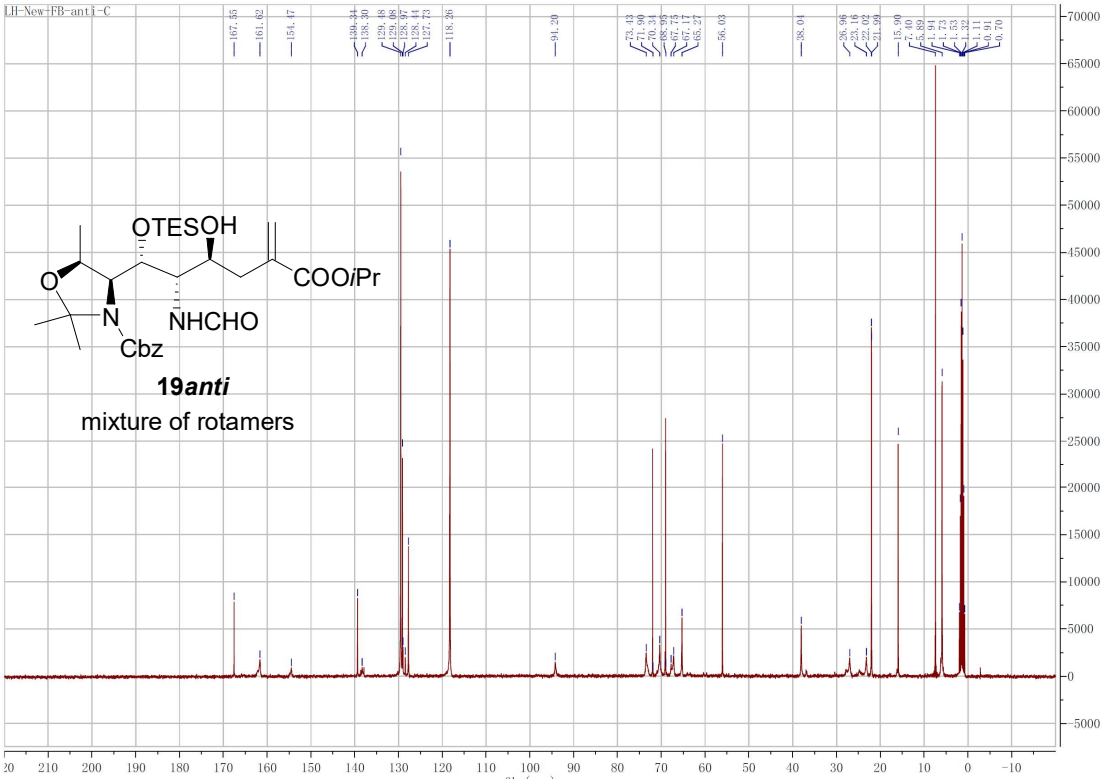
^{13}C NMR of compound 19*syn*



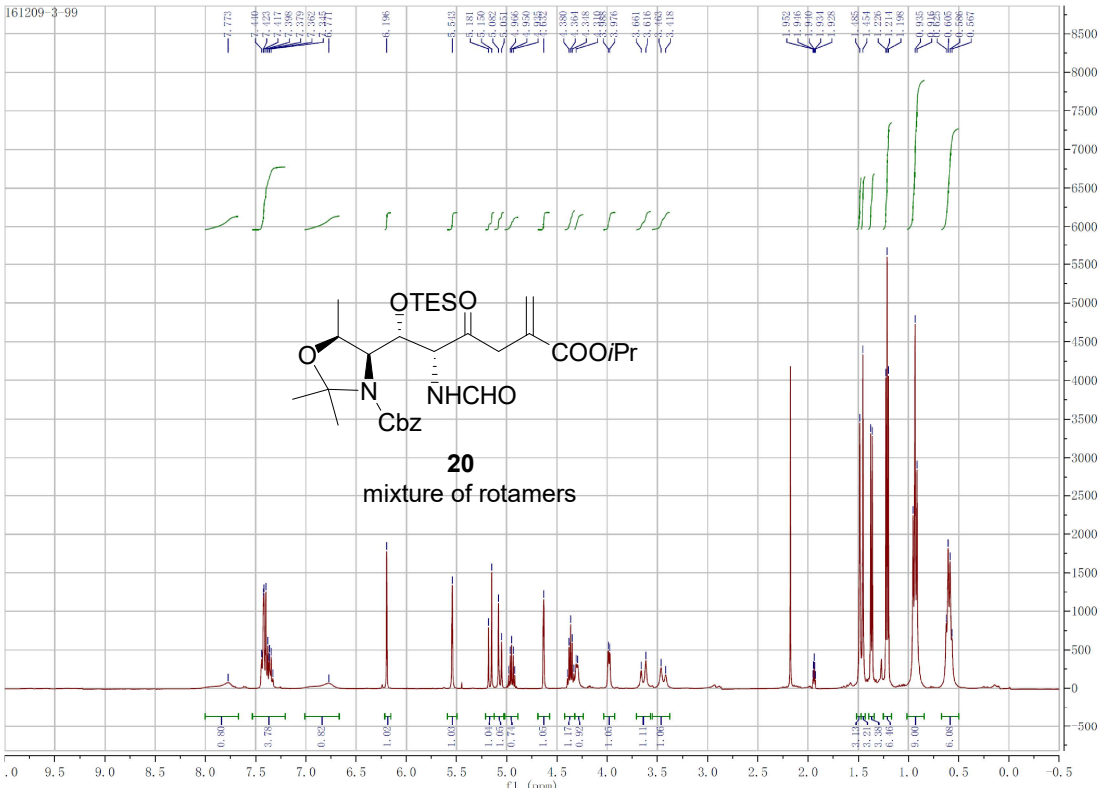
^{1}H NMR of compound 19*anti*



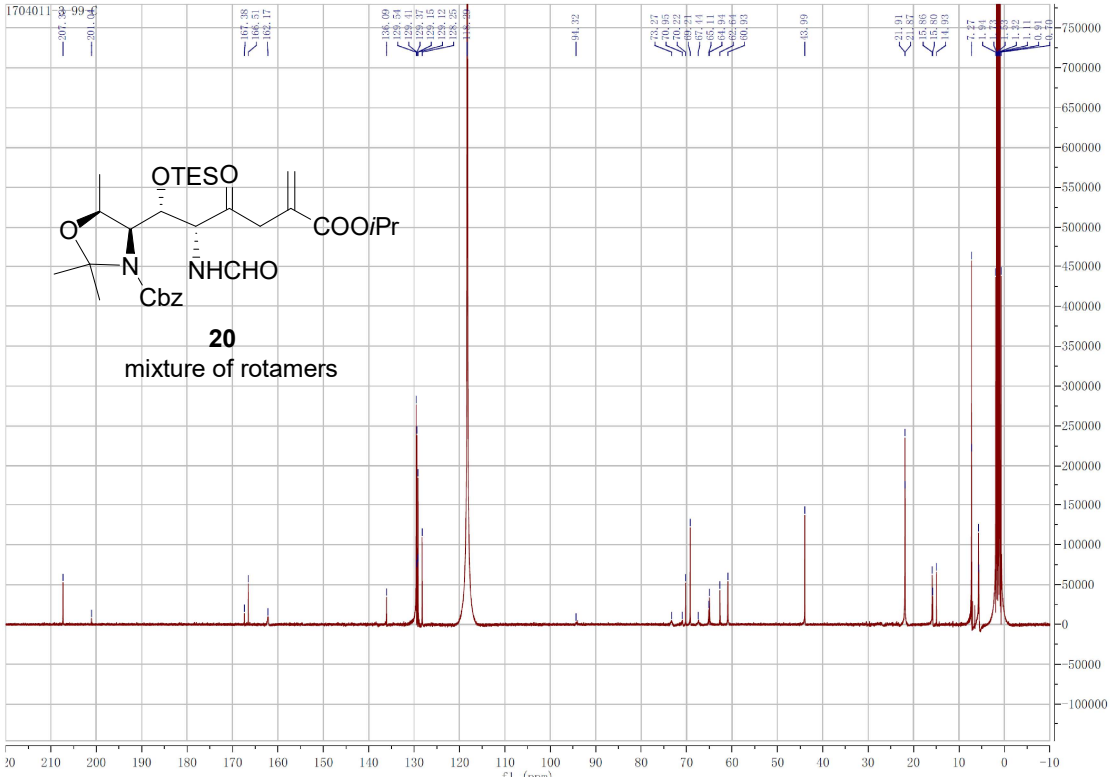
^{13}C NMR of compound 19*anti*



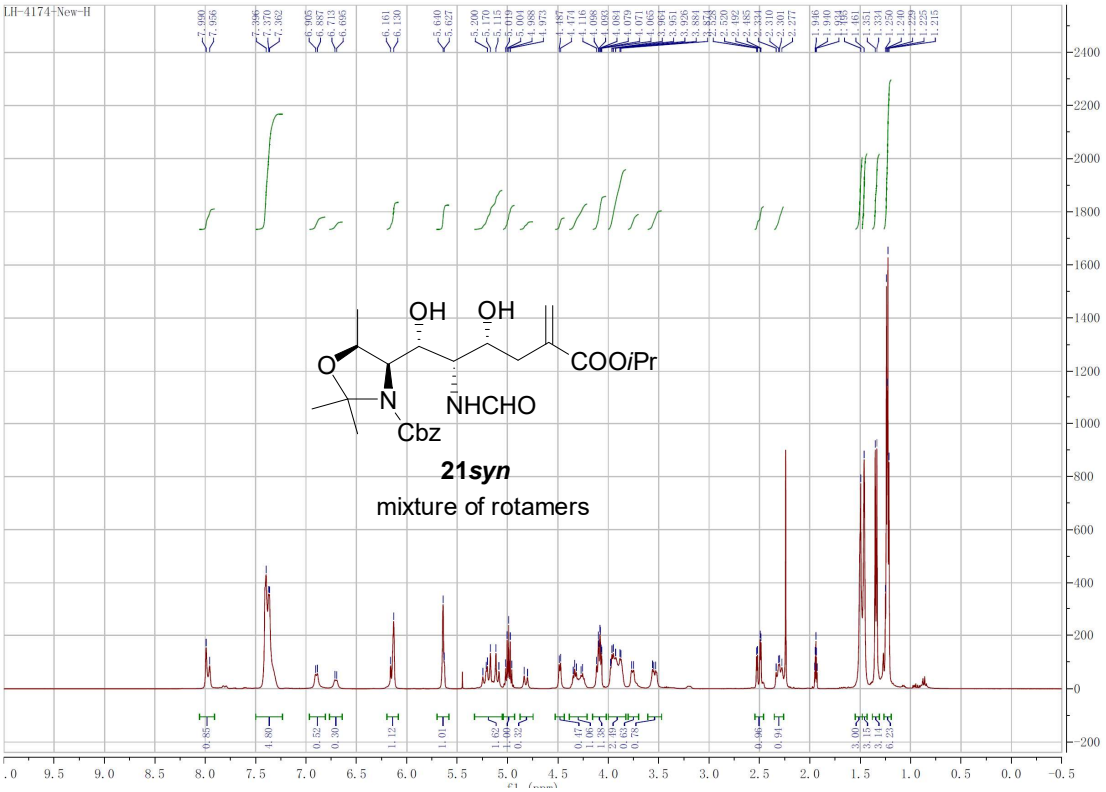
^{1}H NMR of compound 20



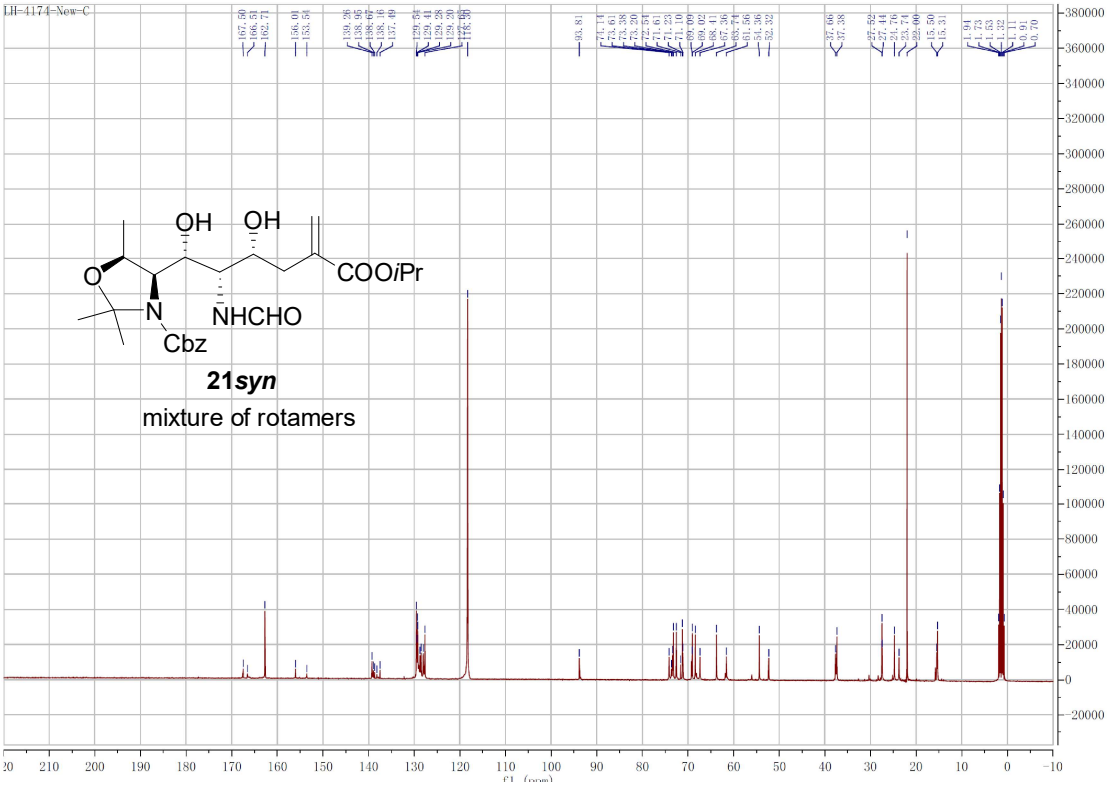
^{13}C NMR of compound 20



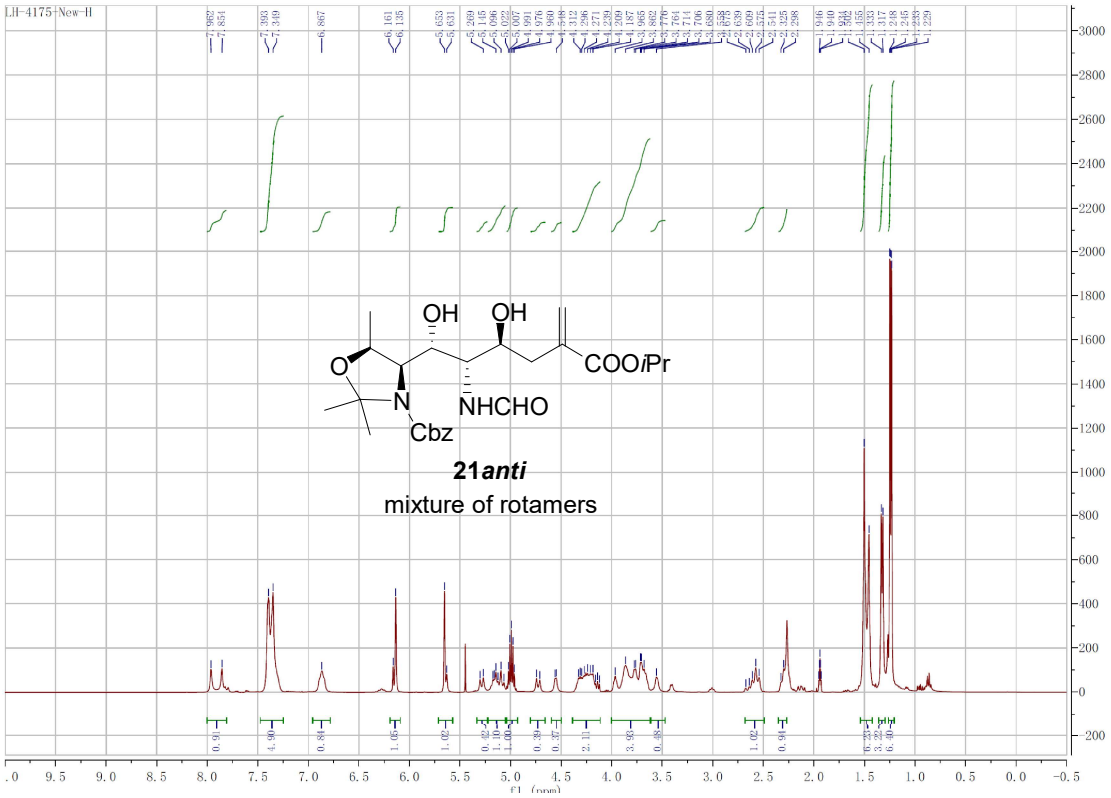
^{1}H NMR of compound 21*syn*



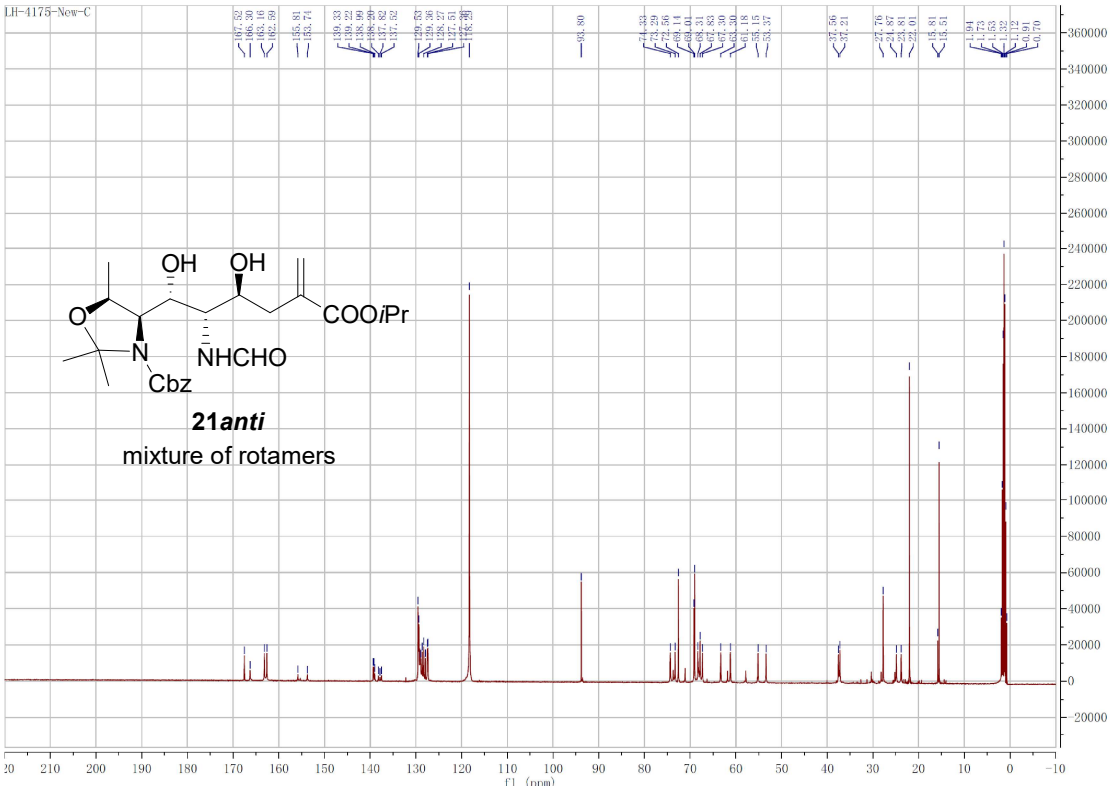
^{13}C NMR of compound 21*syn*



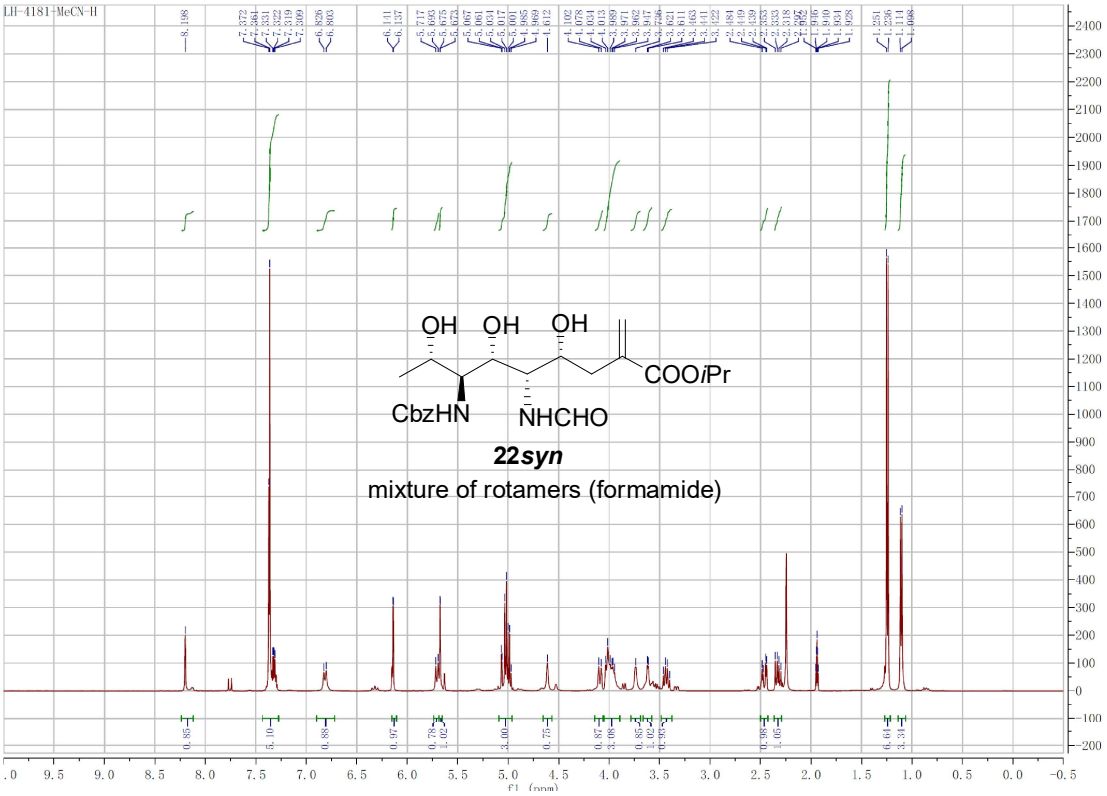
^{1}H NMR of compound 21*anti*



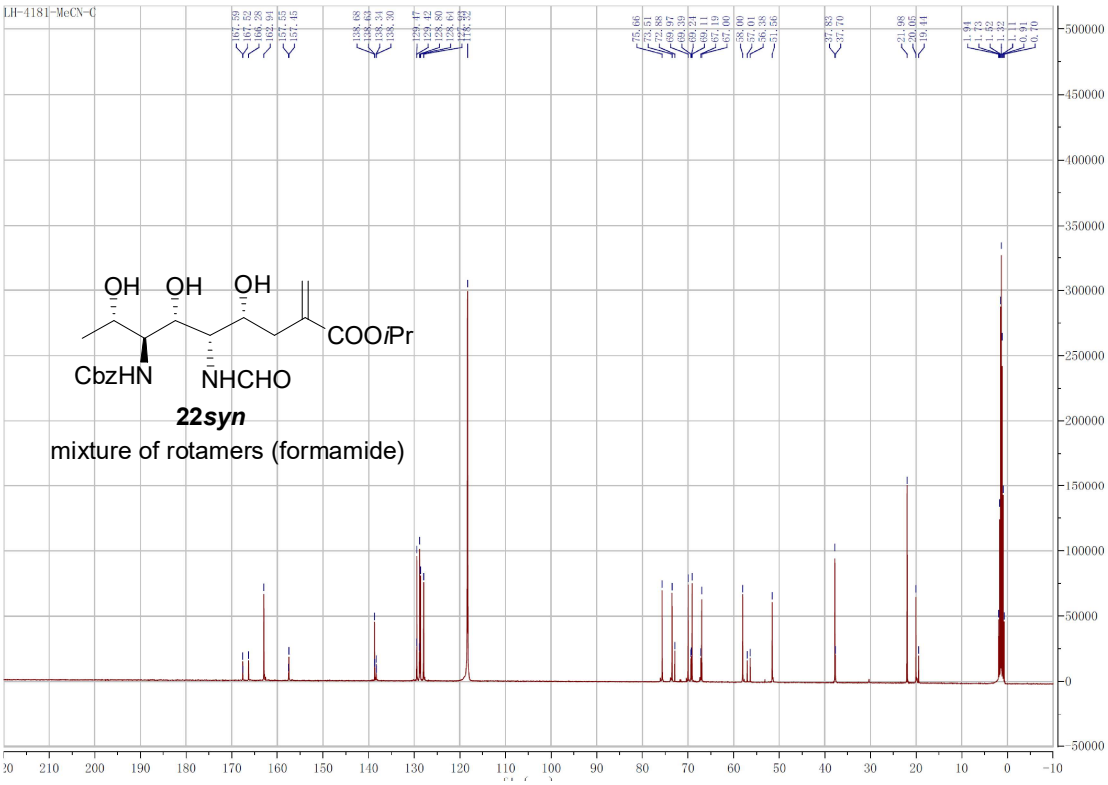
^{13}C NMR of compound 21*anti*



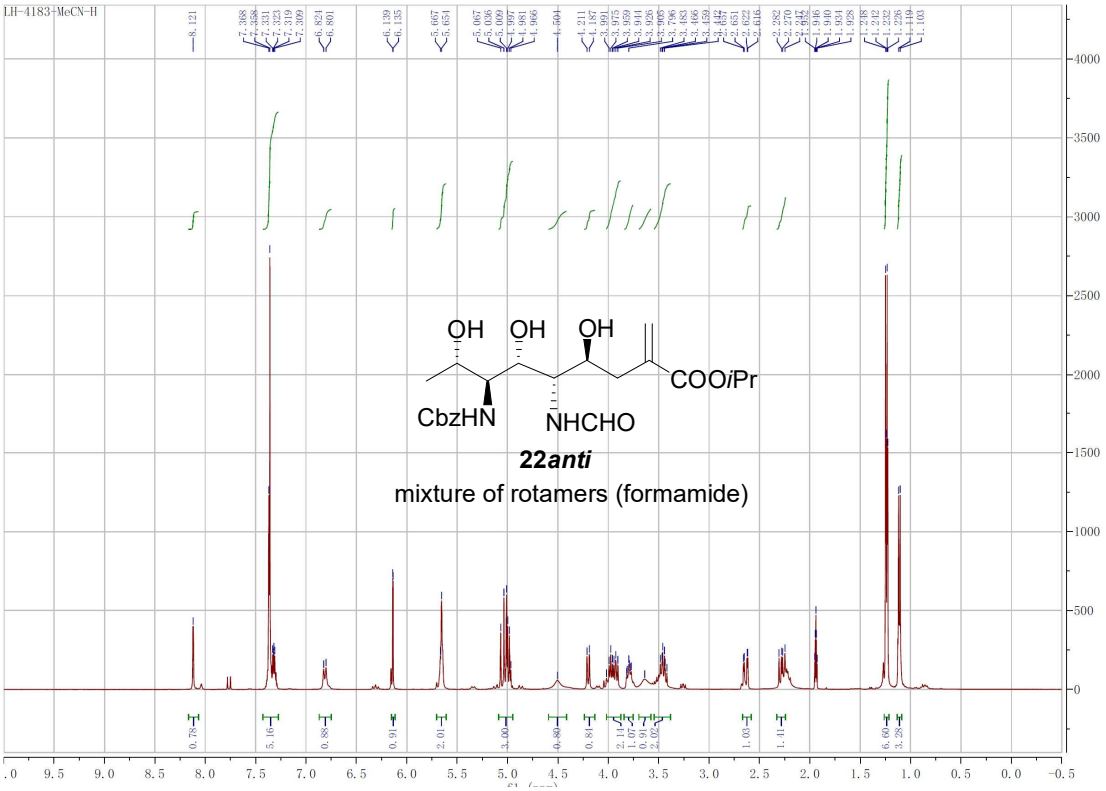
^{1}H NMR of compound 22*syn*



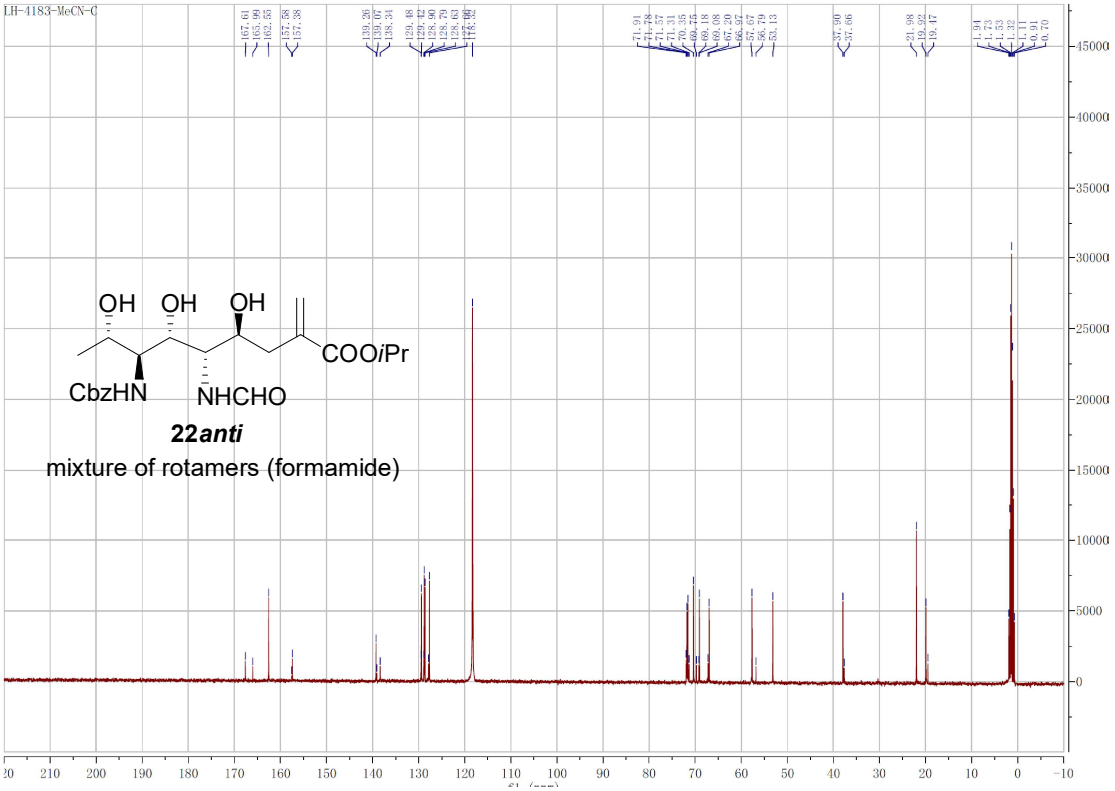
^{13}C NMR of compound 22*syn*



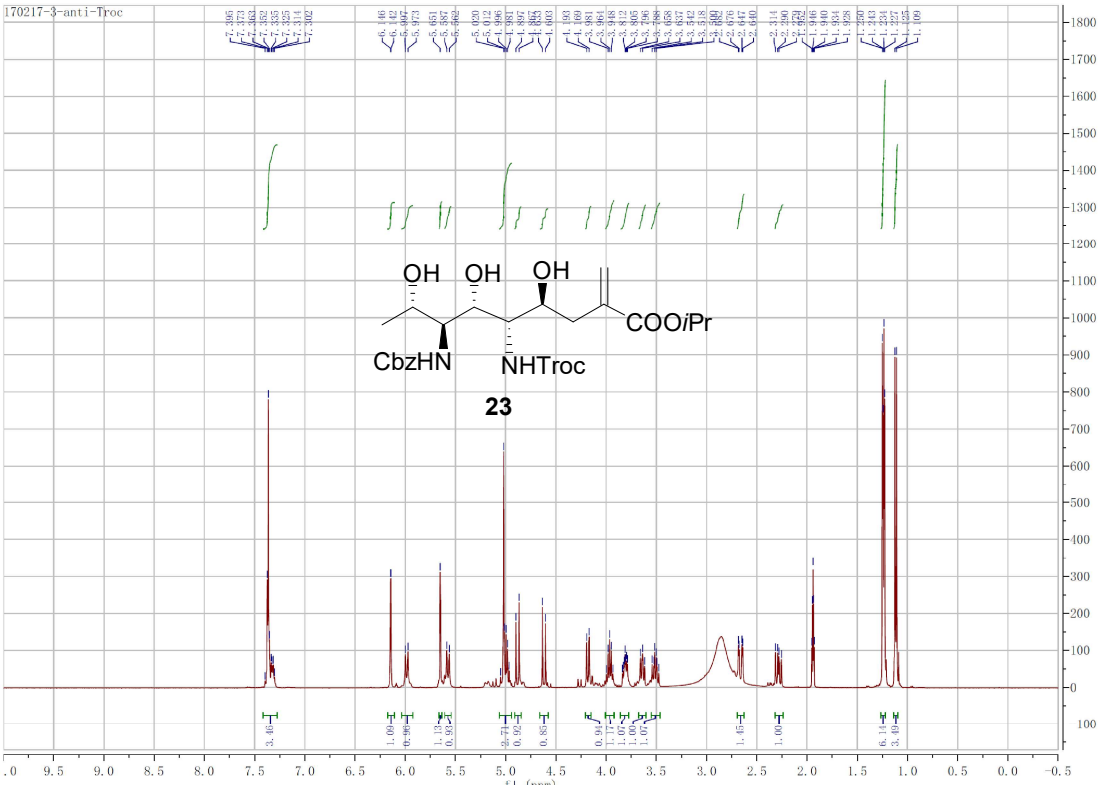
^{1}H NMR of compound 22*anti*



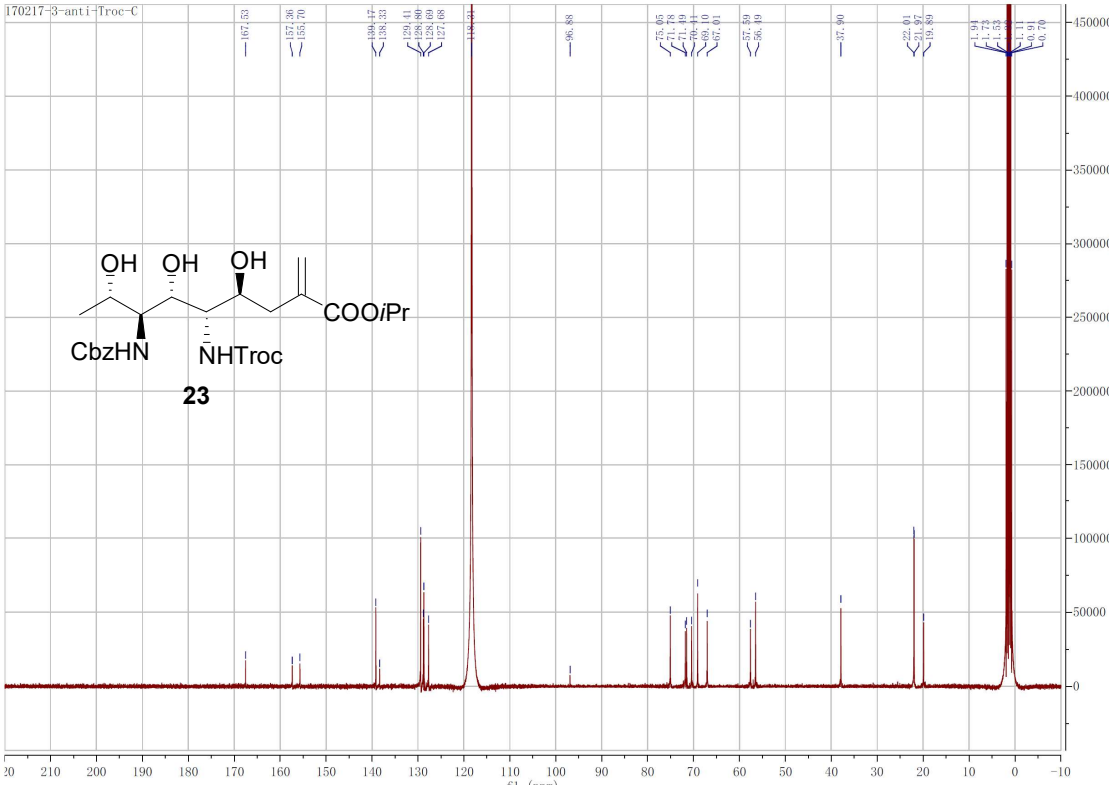
^{13}C NMR of compound 22*anti*



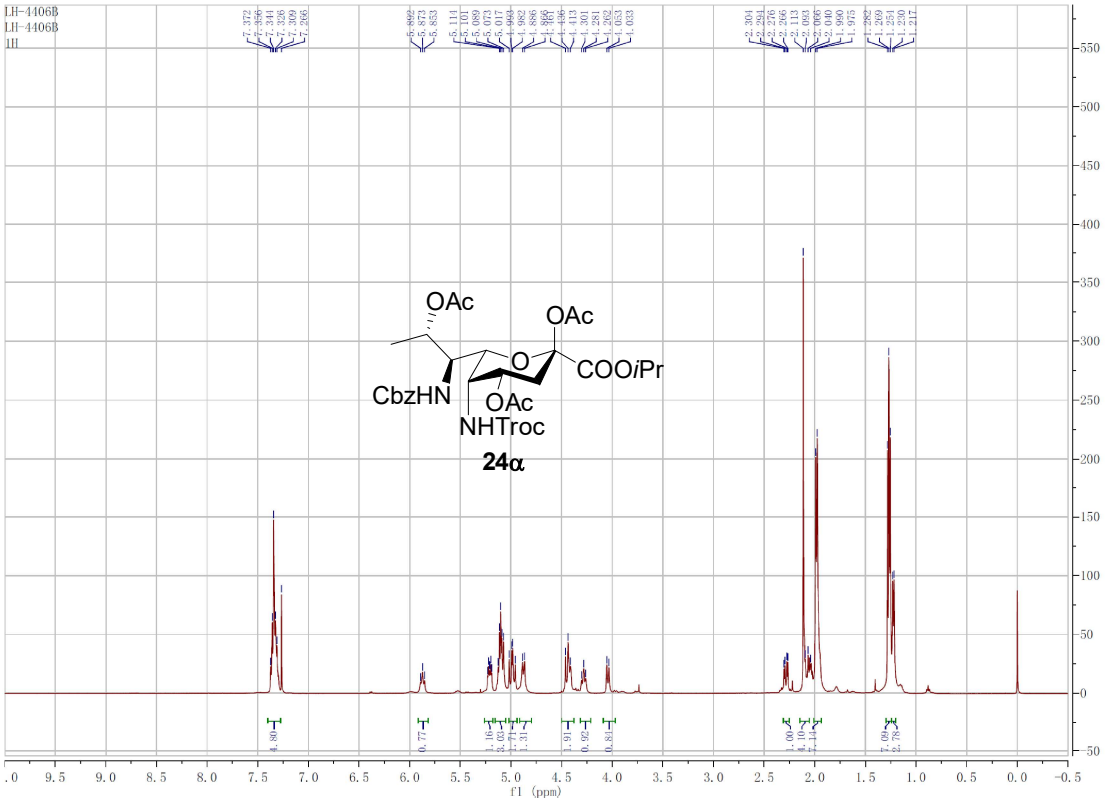
^{1}H NMR of compound 23



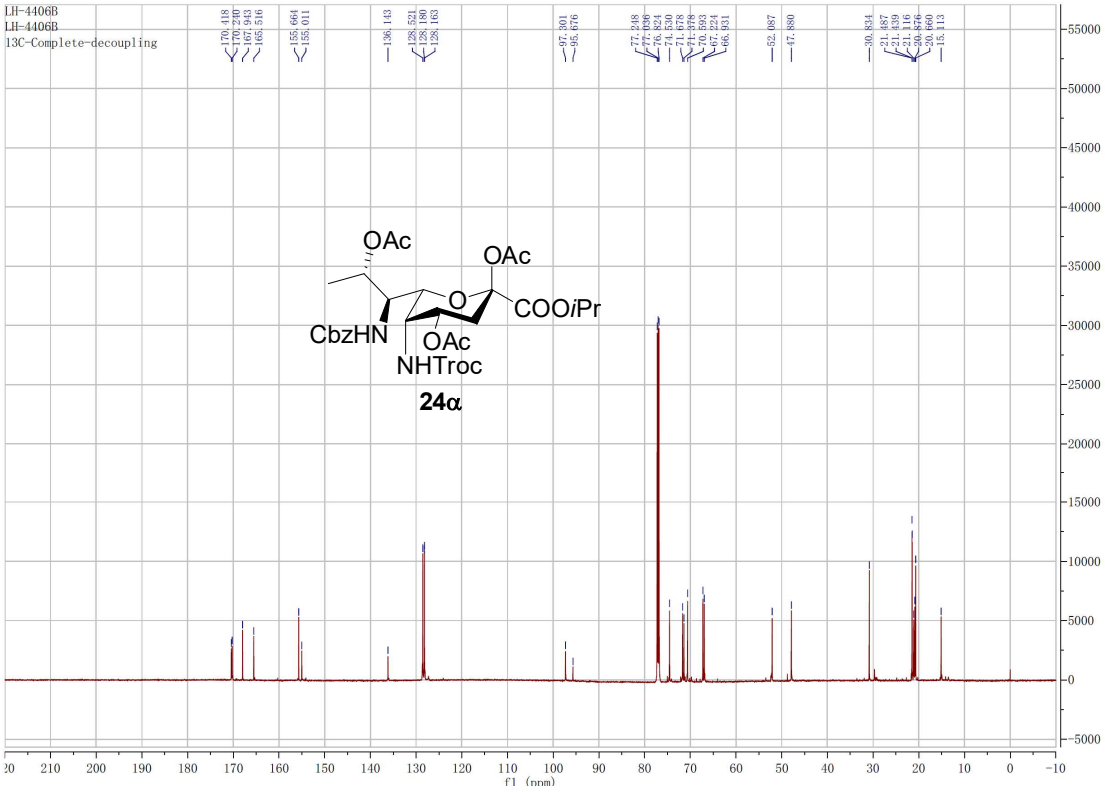
^{13}C NMR of compound 23



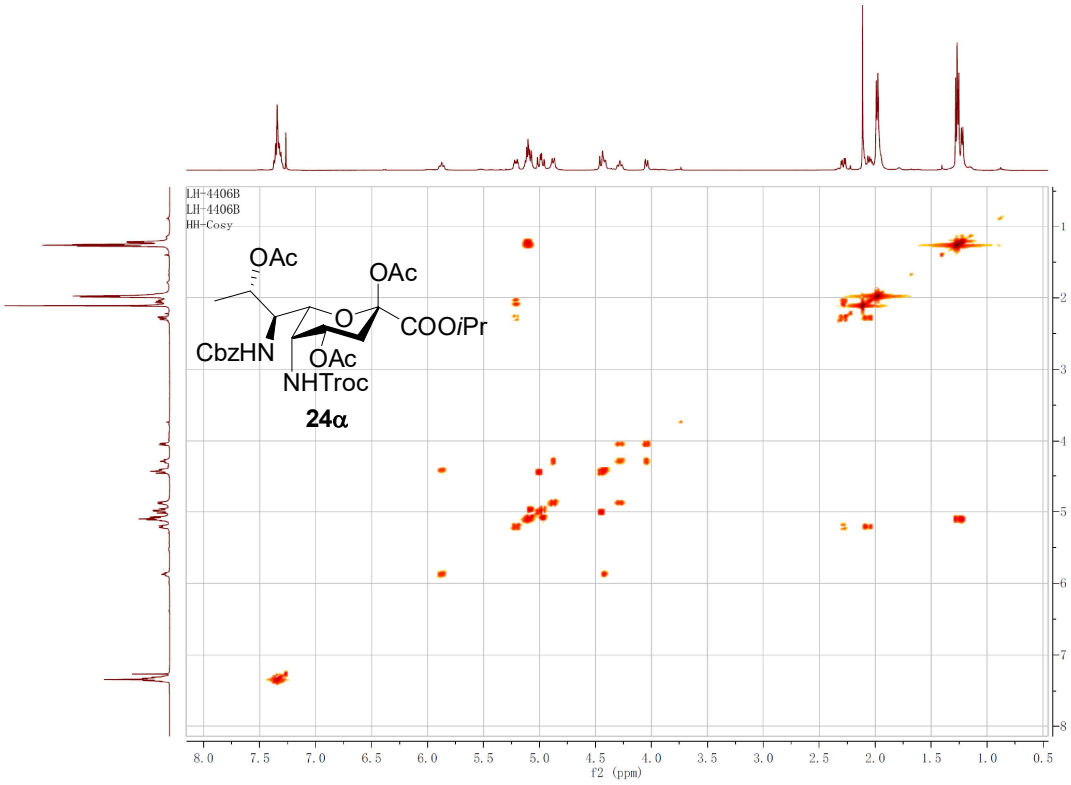
^{1}H NMR of compound 24α



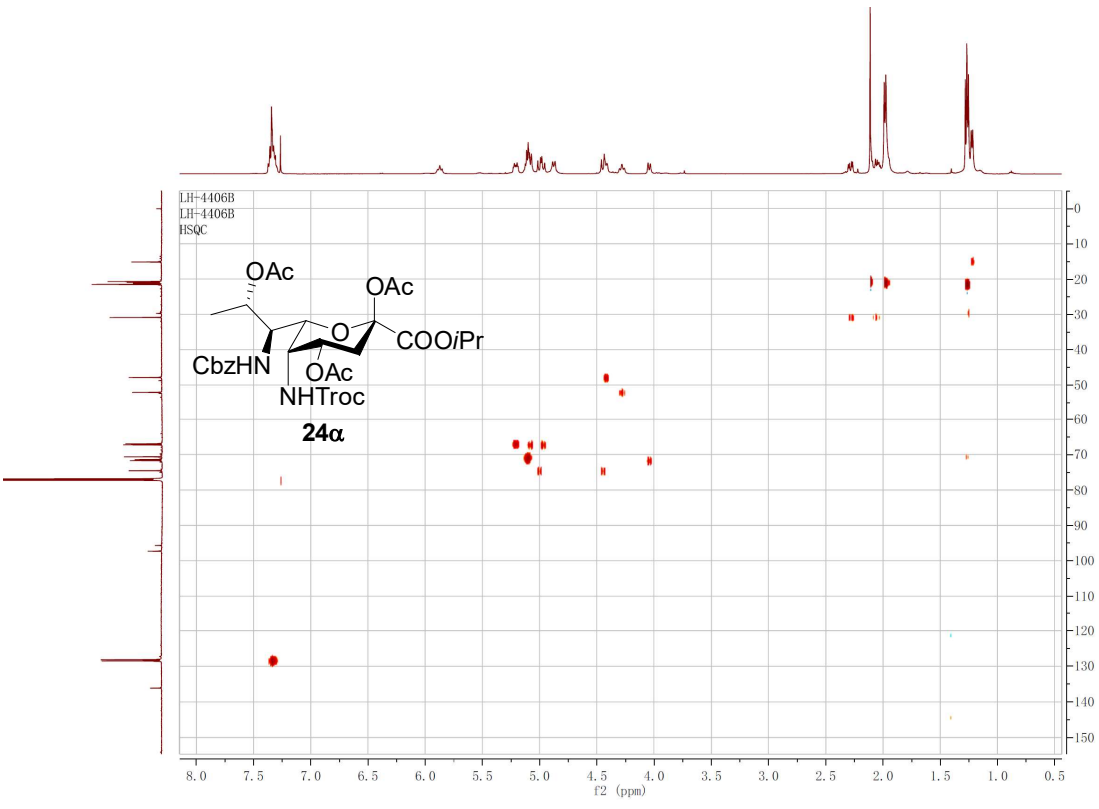
^{13}C NMR of compound 24α



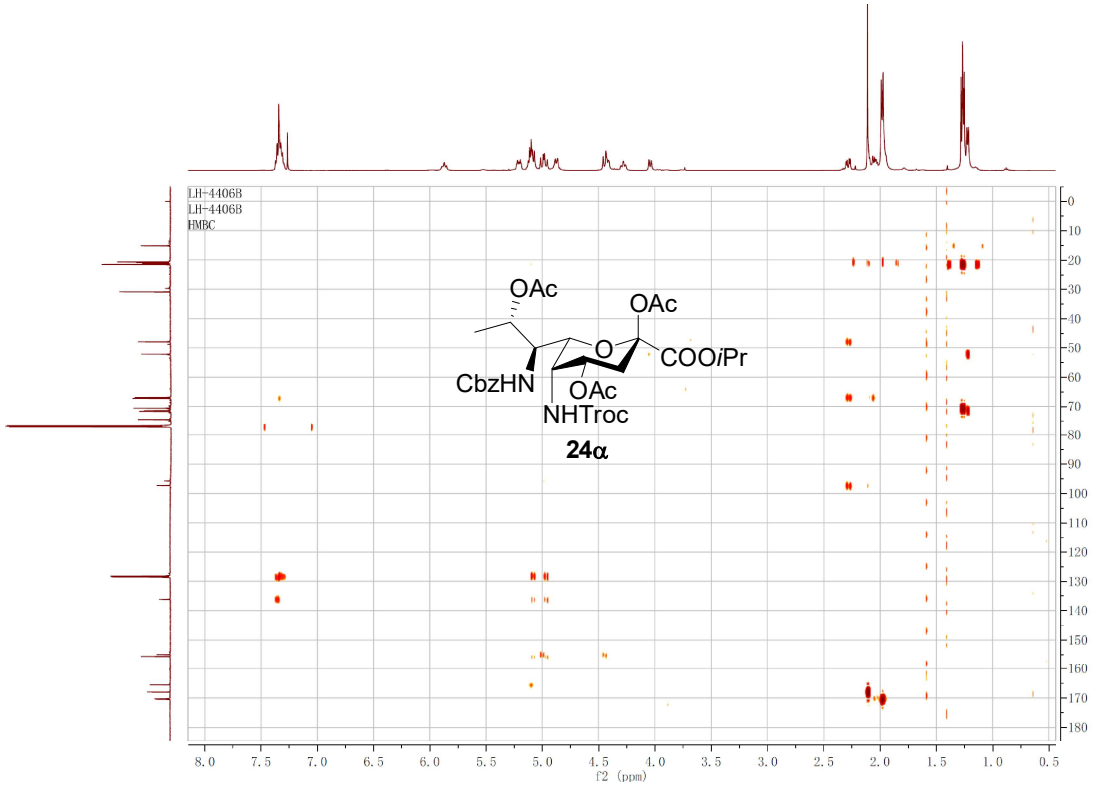
^{1}H-^{1}H COSY of compound 24α



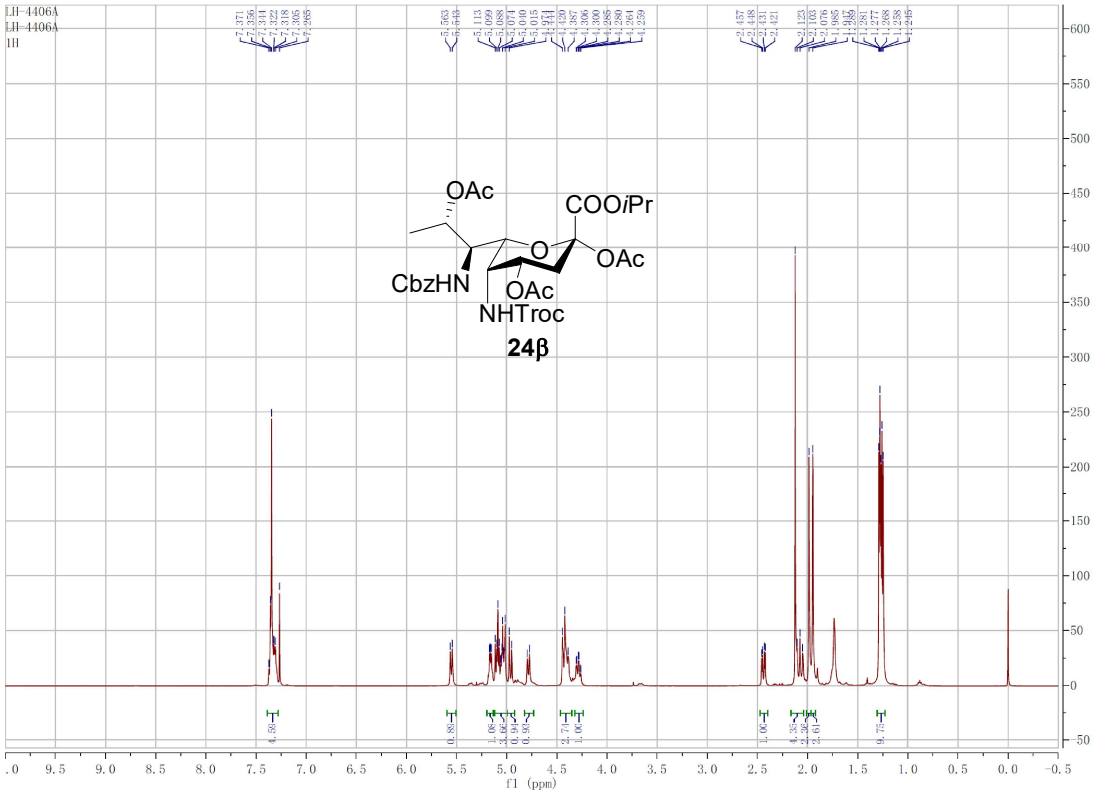
^{1}H-^{13}C HSQC of compound 24α



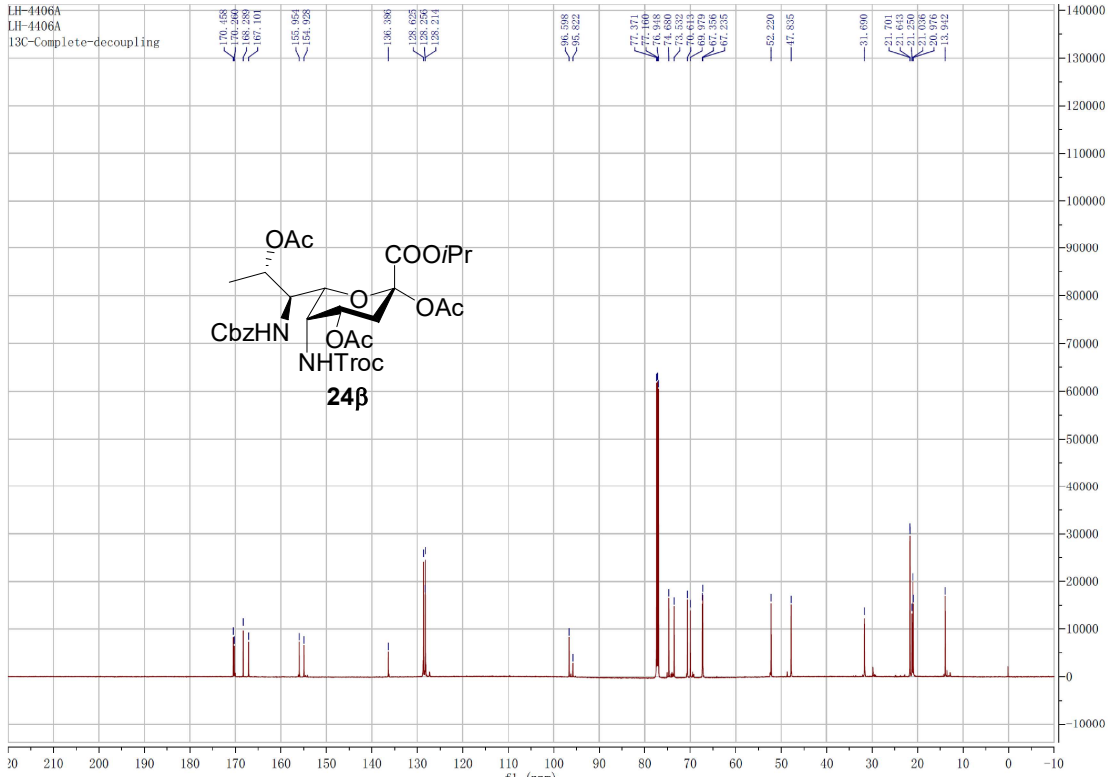
^{1}H-^{13}C HMBC of compound 24α



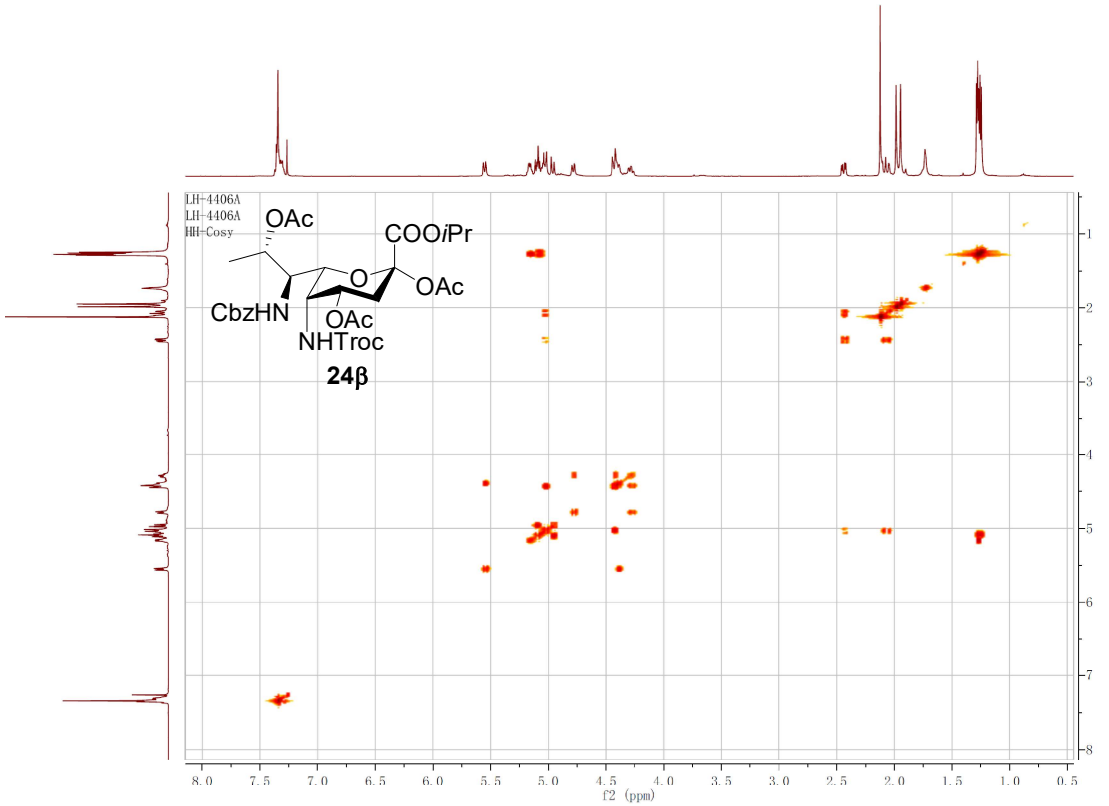
^{1}H NMR of compound 24β



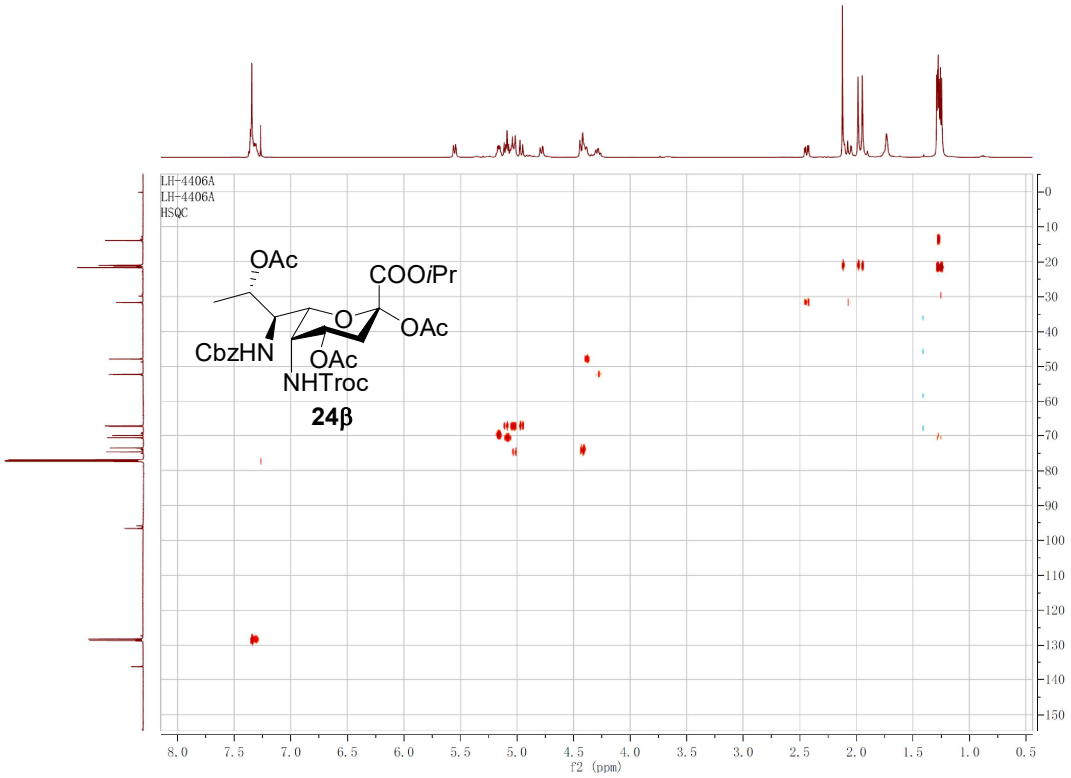
^{13}C NMR of compound 24β



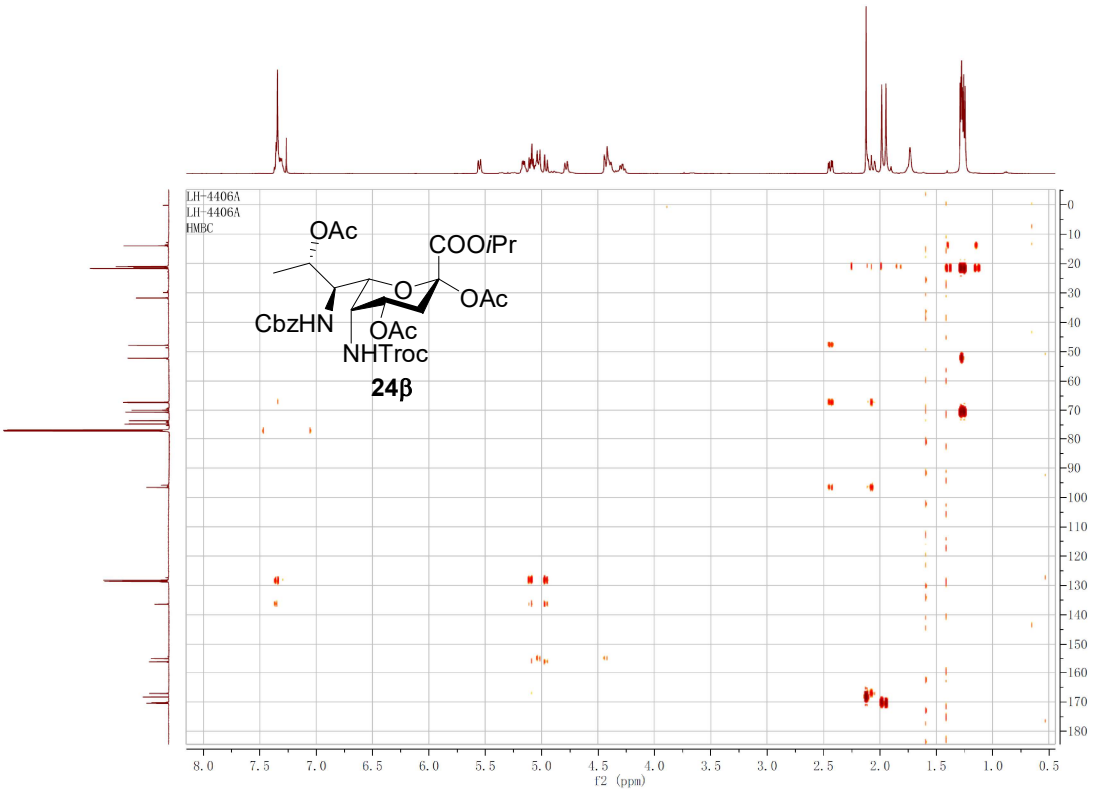
^{1}H-^{1}H COSY of compound 24β



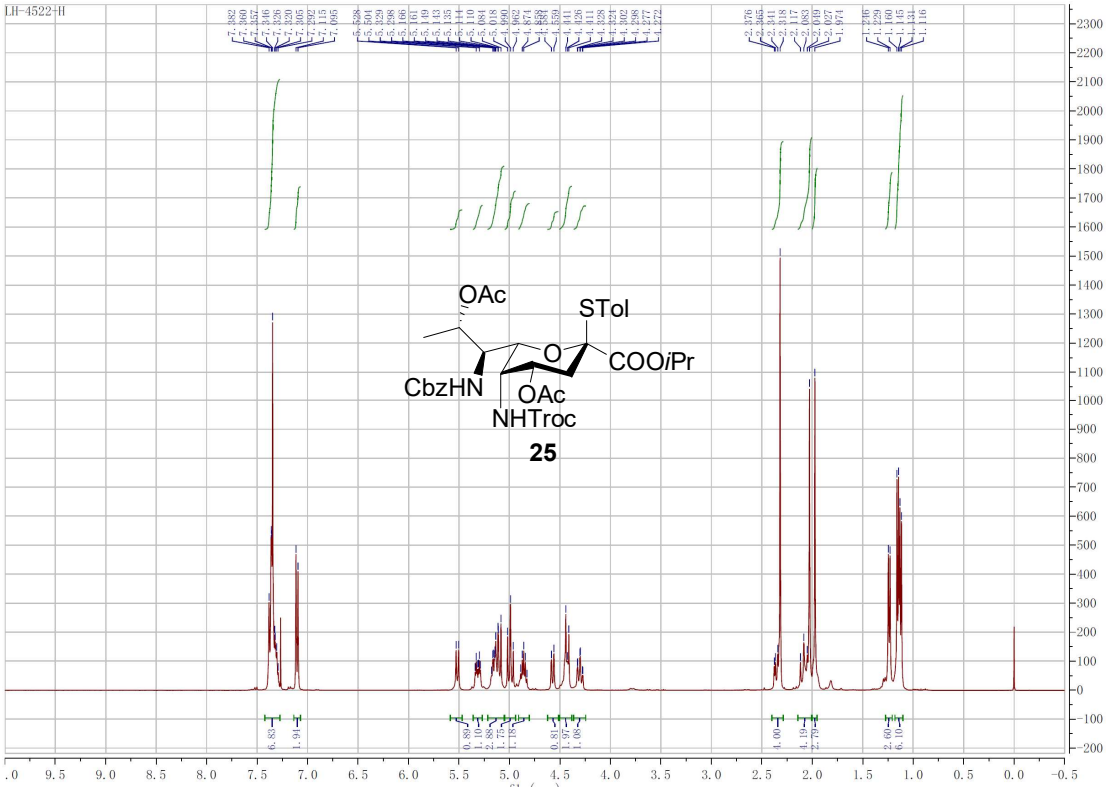
^{1}H-^{13}C HSQC of compound 24β



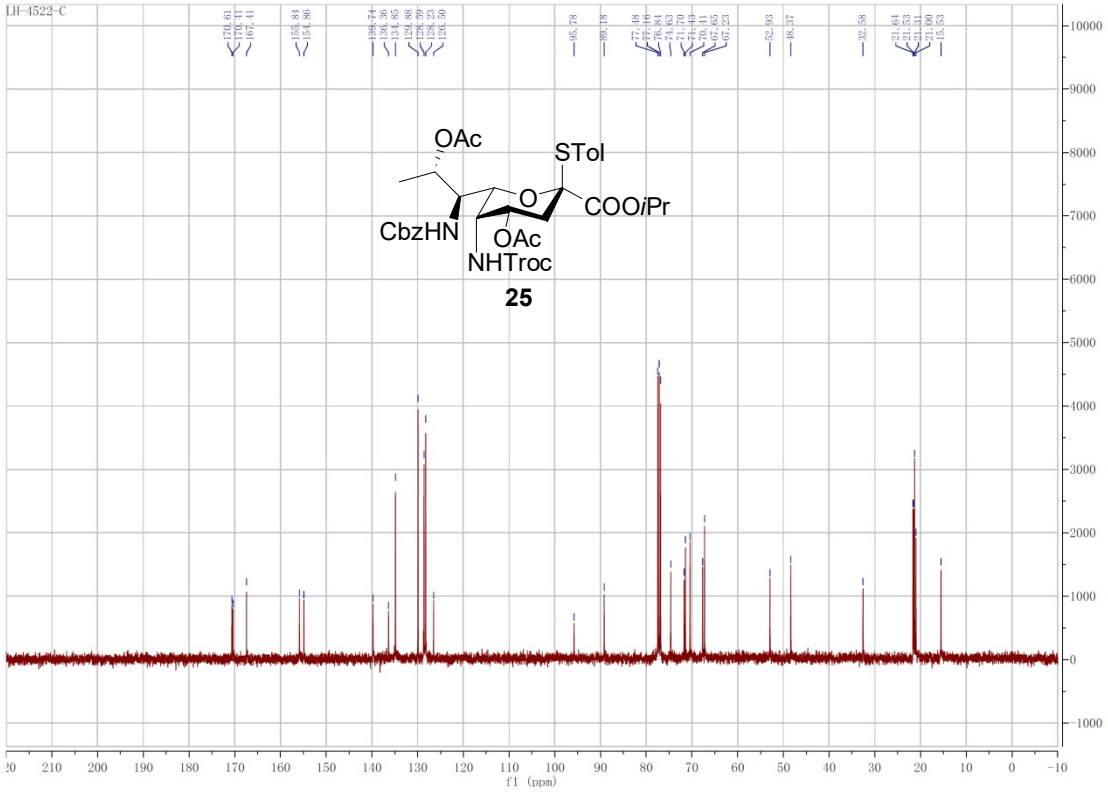
^{1}H-^{13}C HMBC of compound 24β



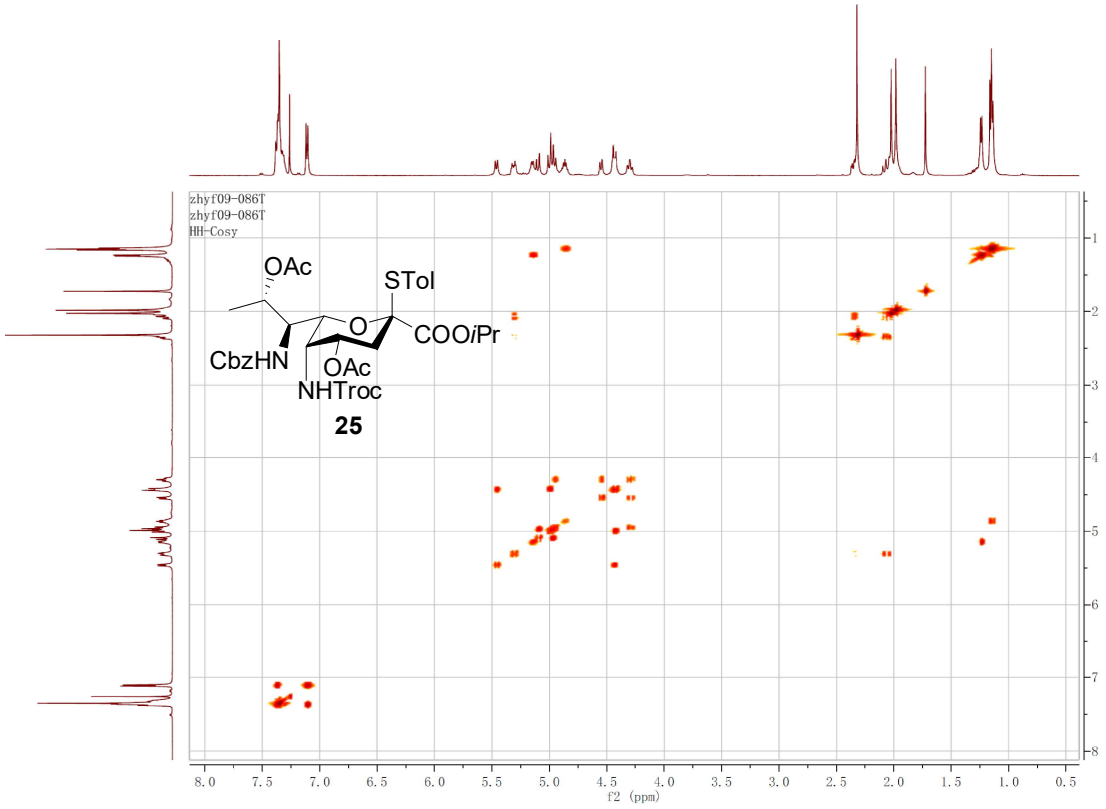
^{1}H NMR of compound 25



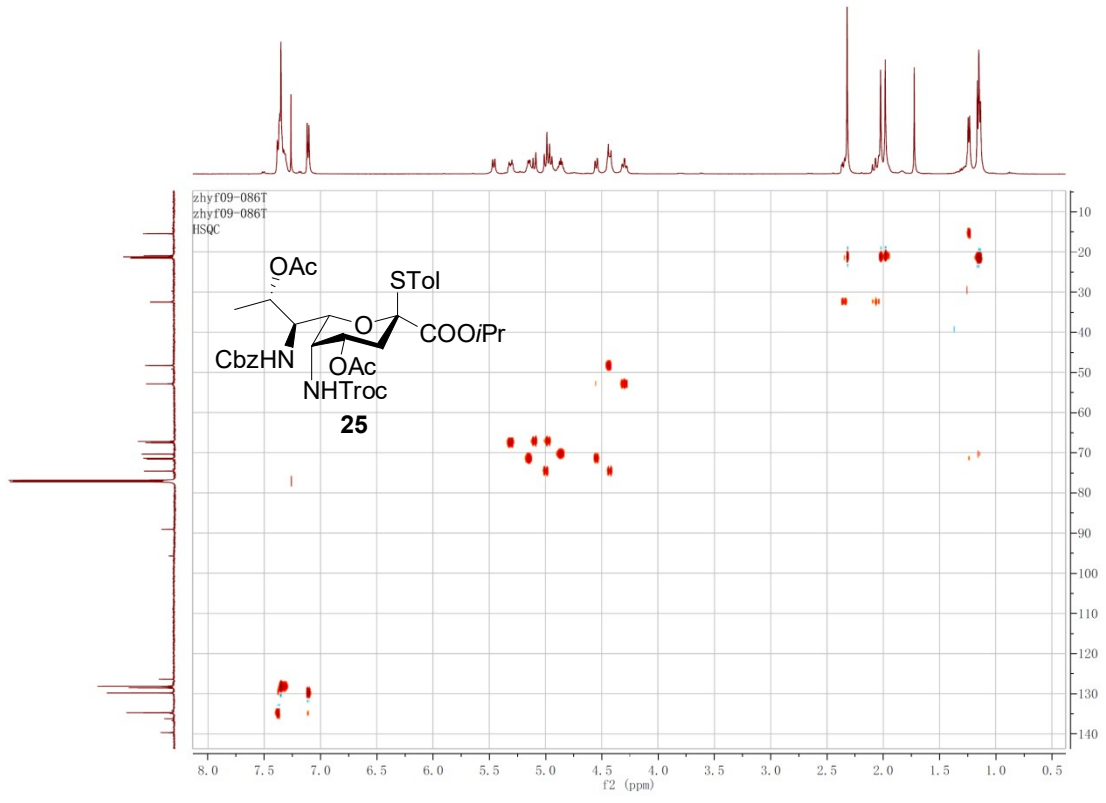
^{13}C NMR of compound 25



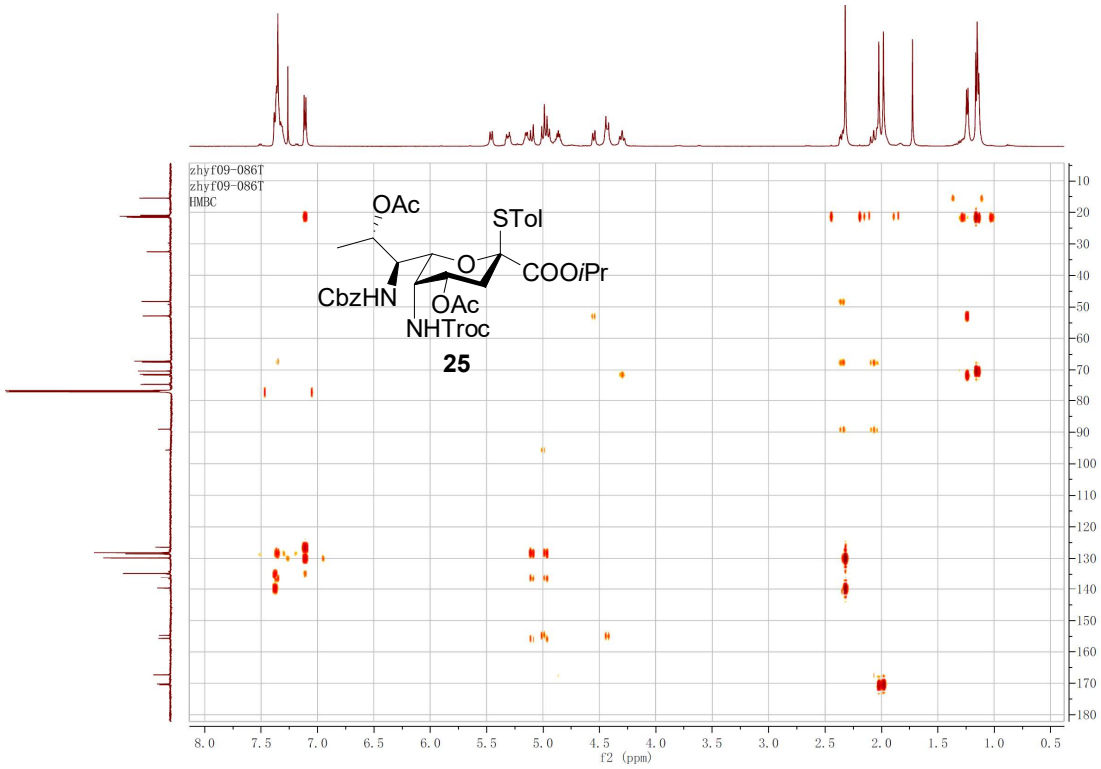
^{1}H-^{1}H COSY of compound 25



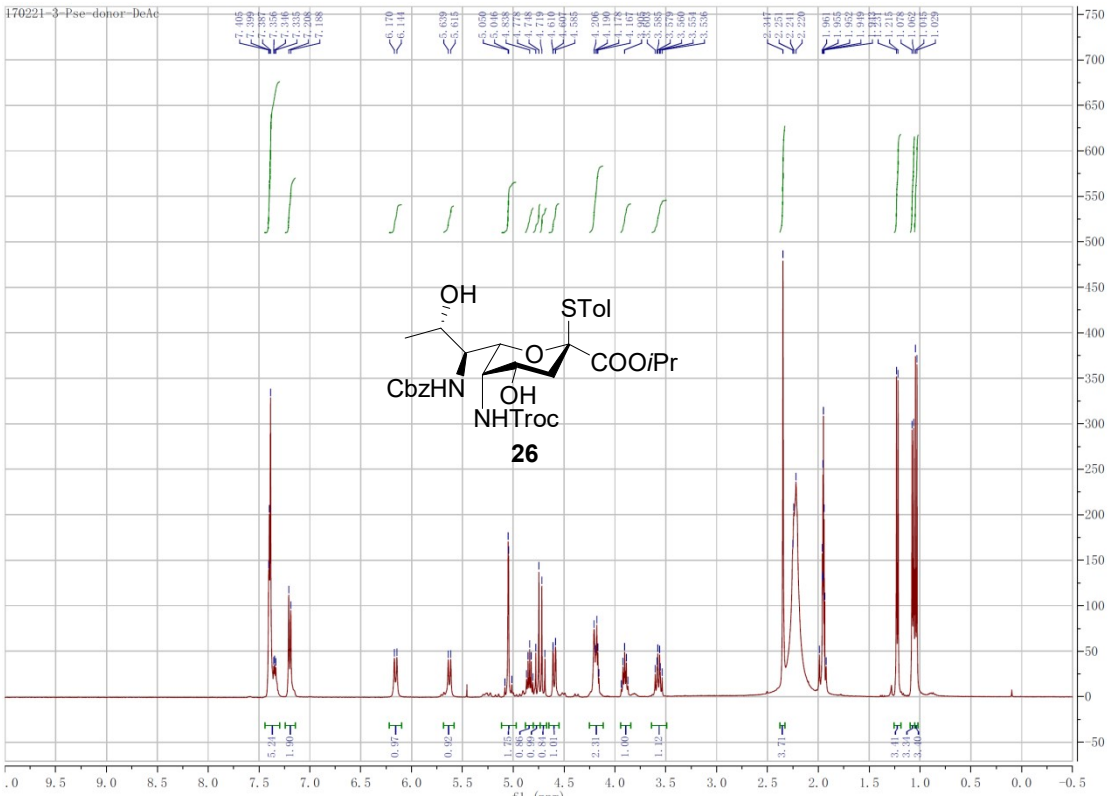
^{1}H-^{13}C HSQC of compound 25



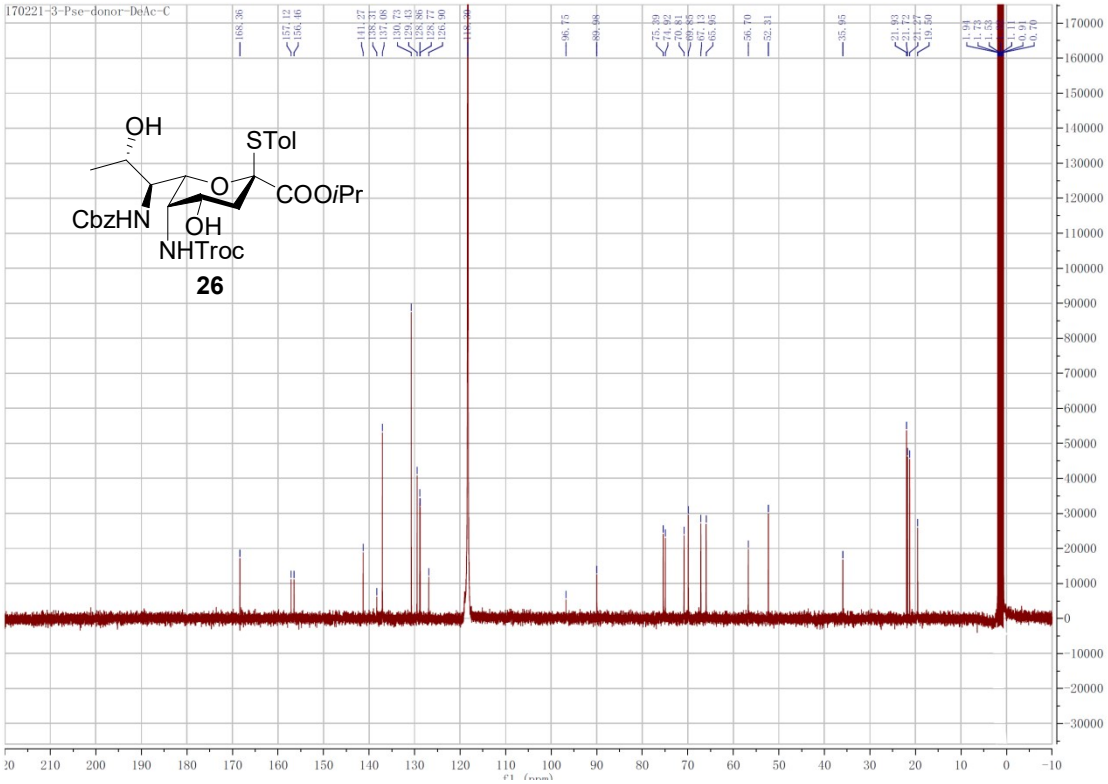
^{1}H-^{13}C HMBC of compound 25



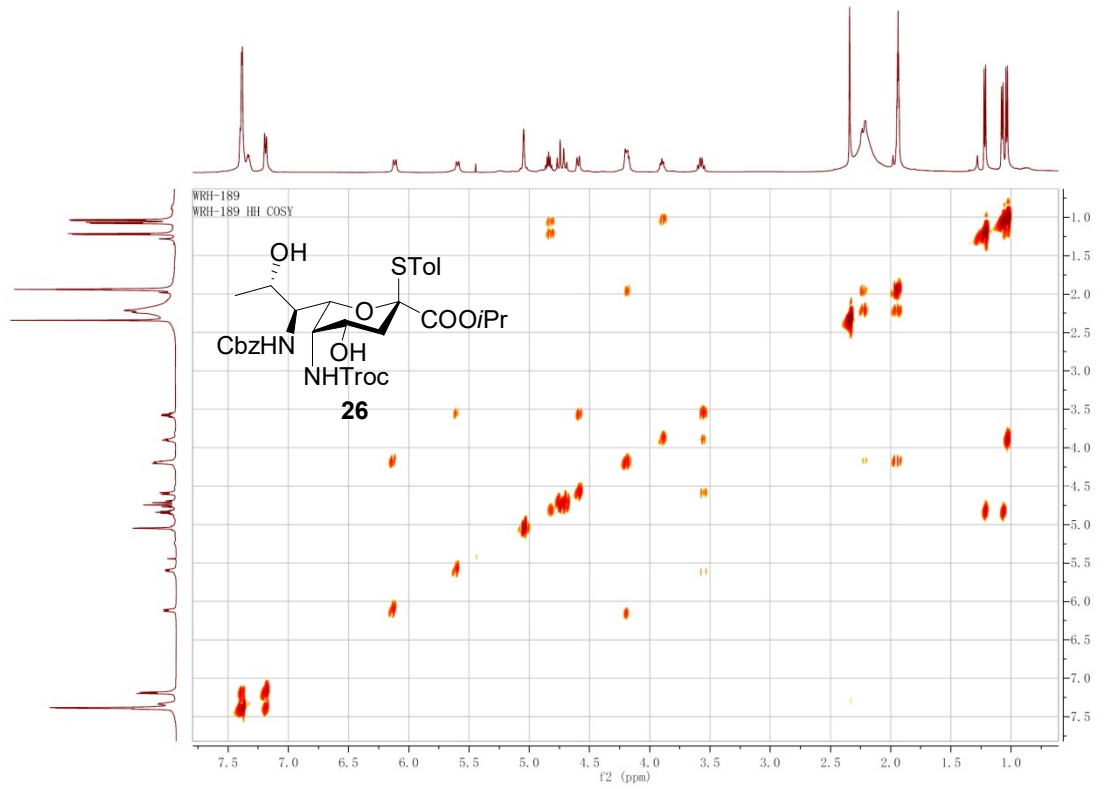
^{1}H NMR of compound 26



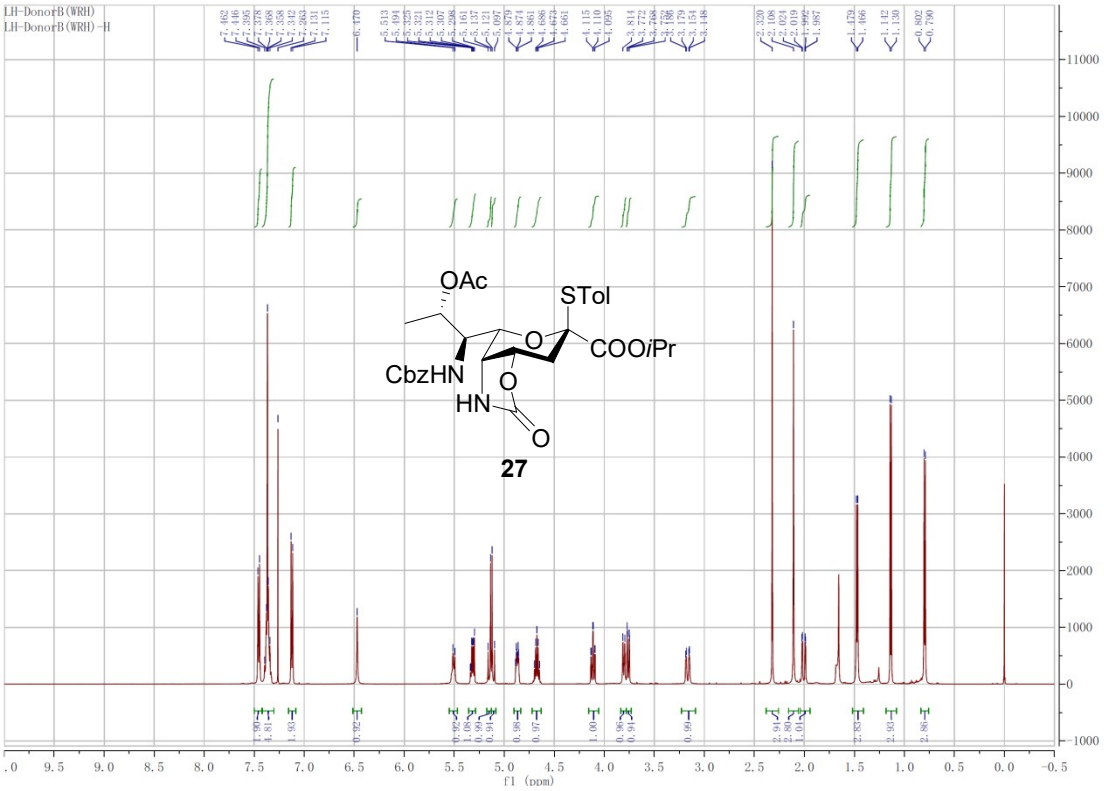
^{13}C NMR of compound 26



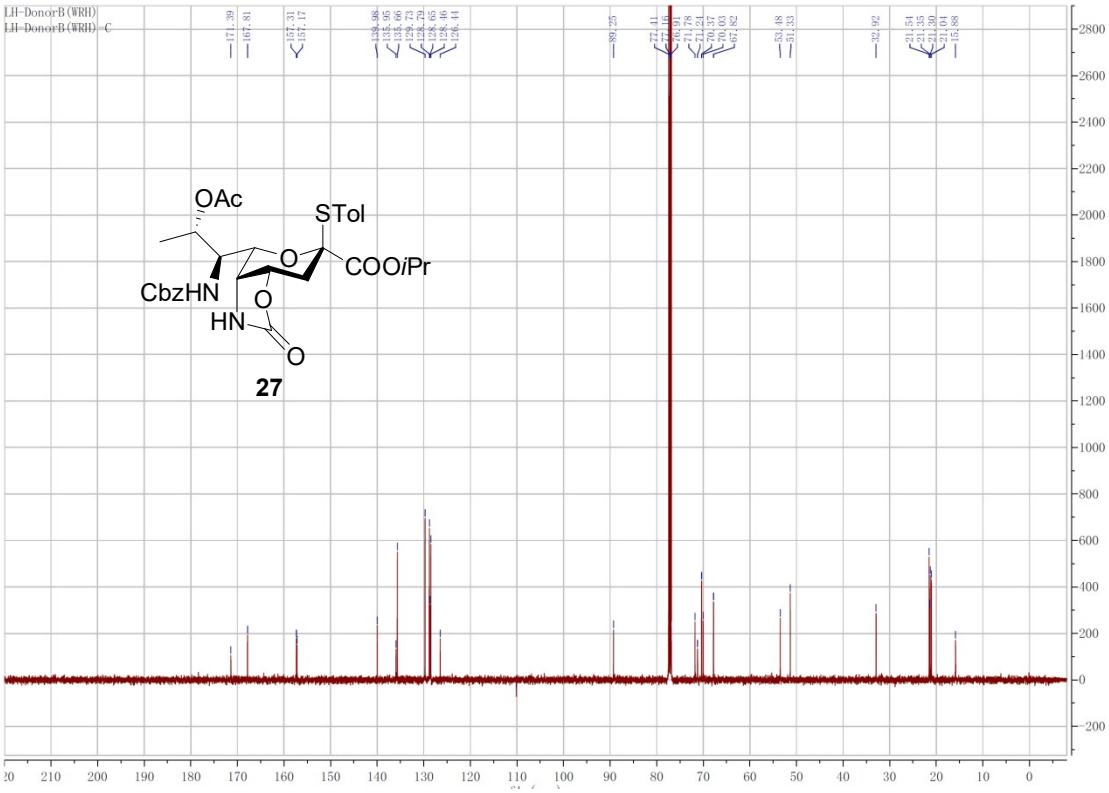
^{1}H-^{1}H COSY of compound 26



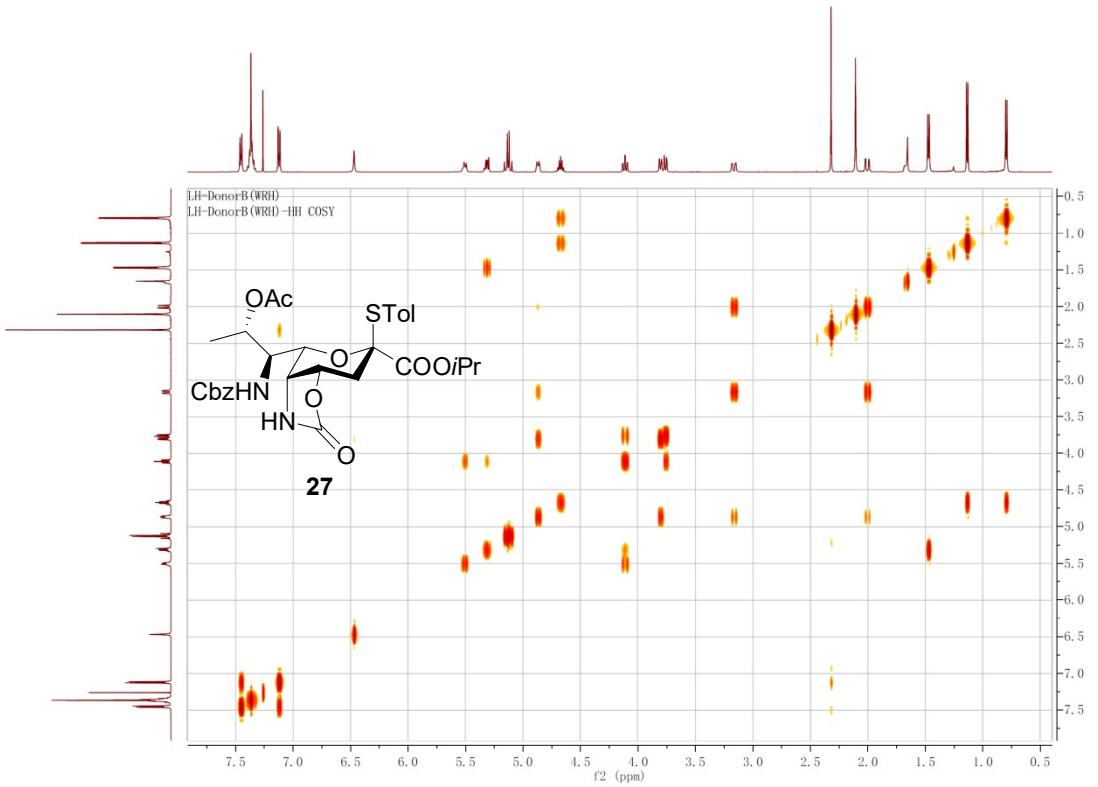
^{1}H NMR of compound 27



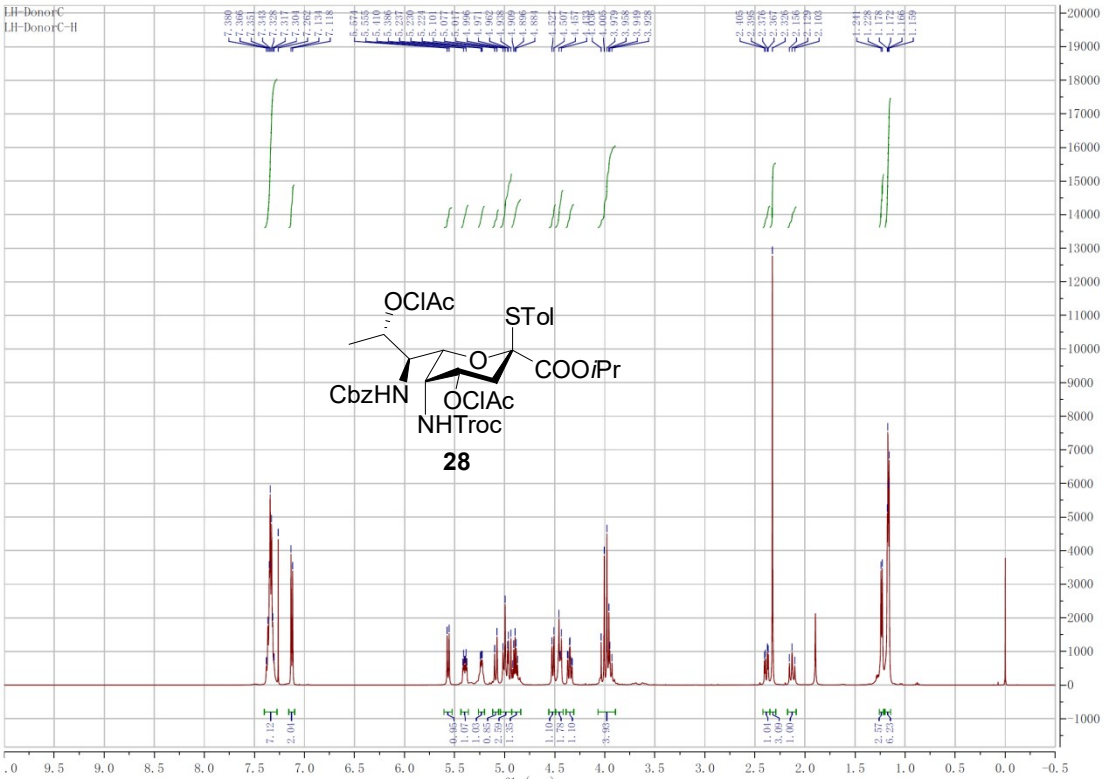
^{13}C NMR of compound 27



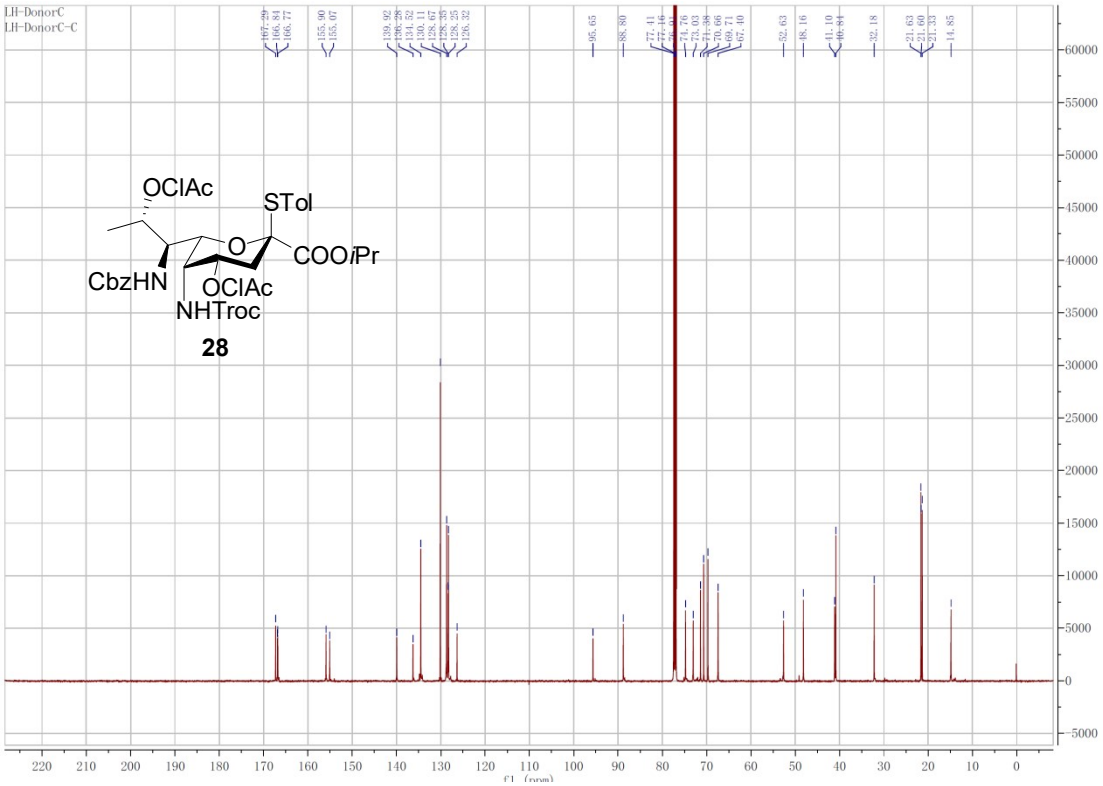
^{1}H-^{1}H COSY of compound 27



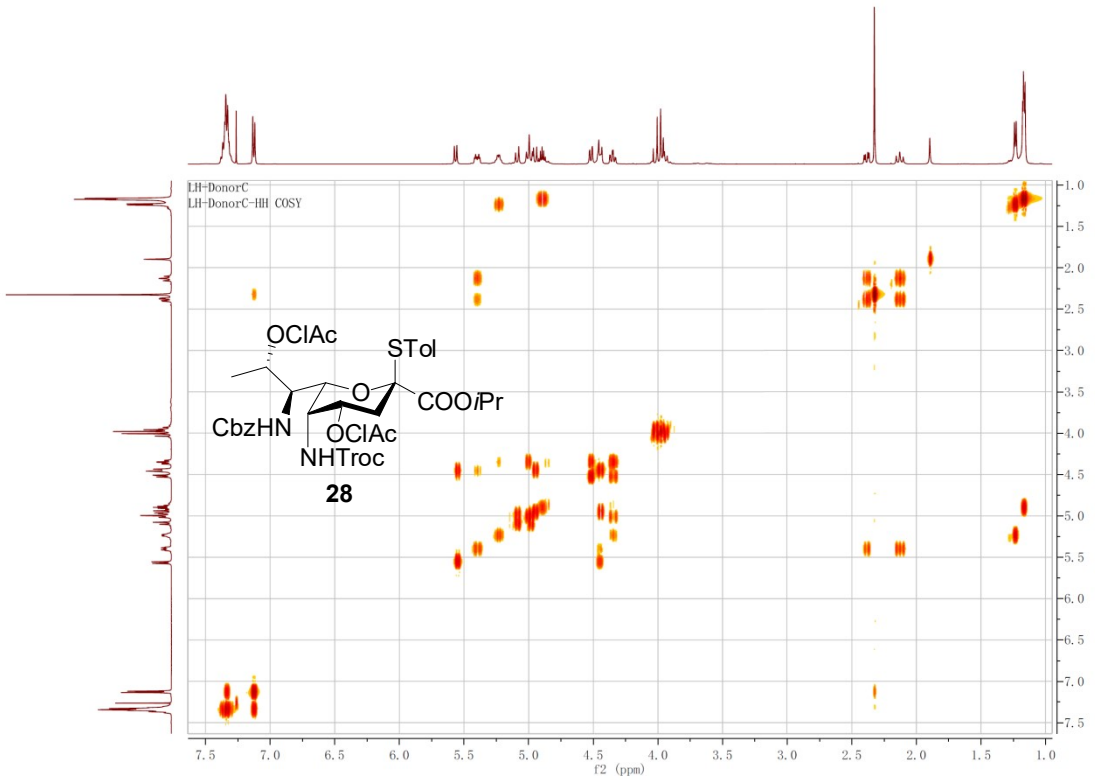
^{1}H NMR of compound 28



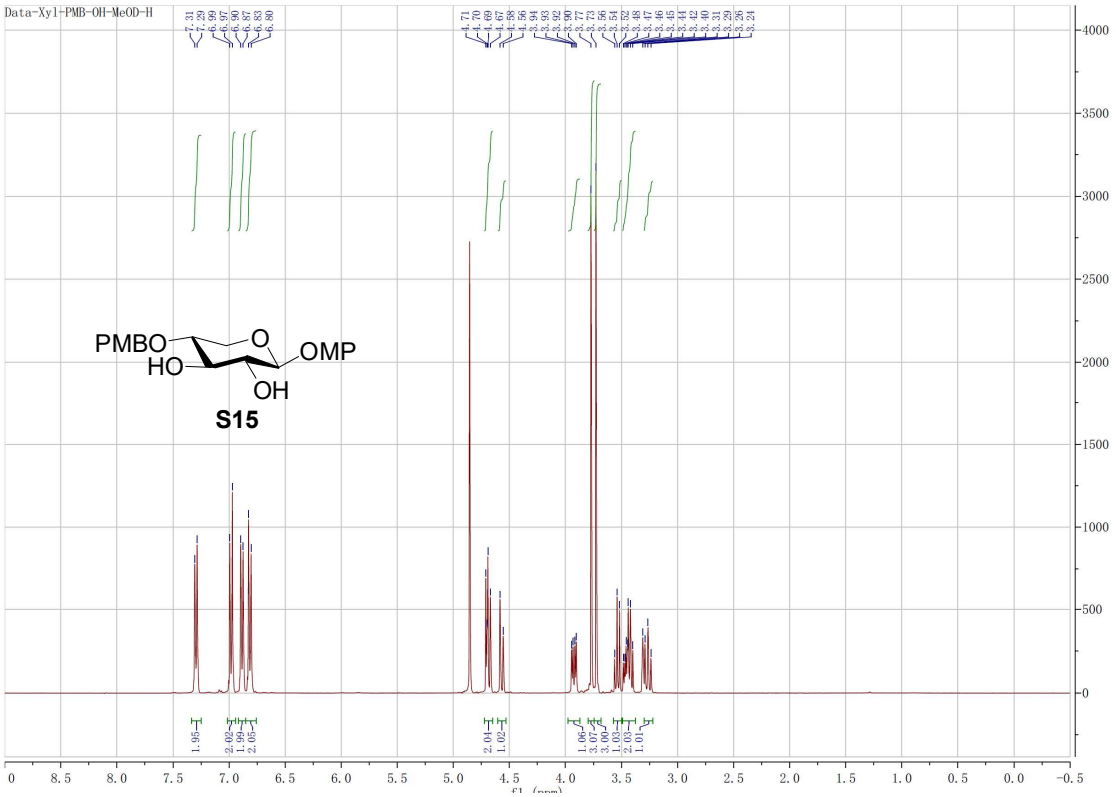
^{13}C NMR of compound 28



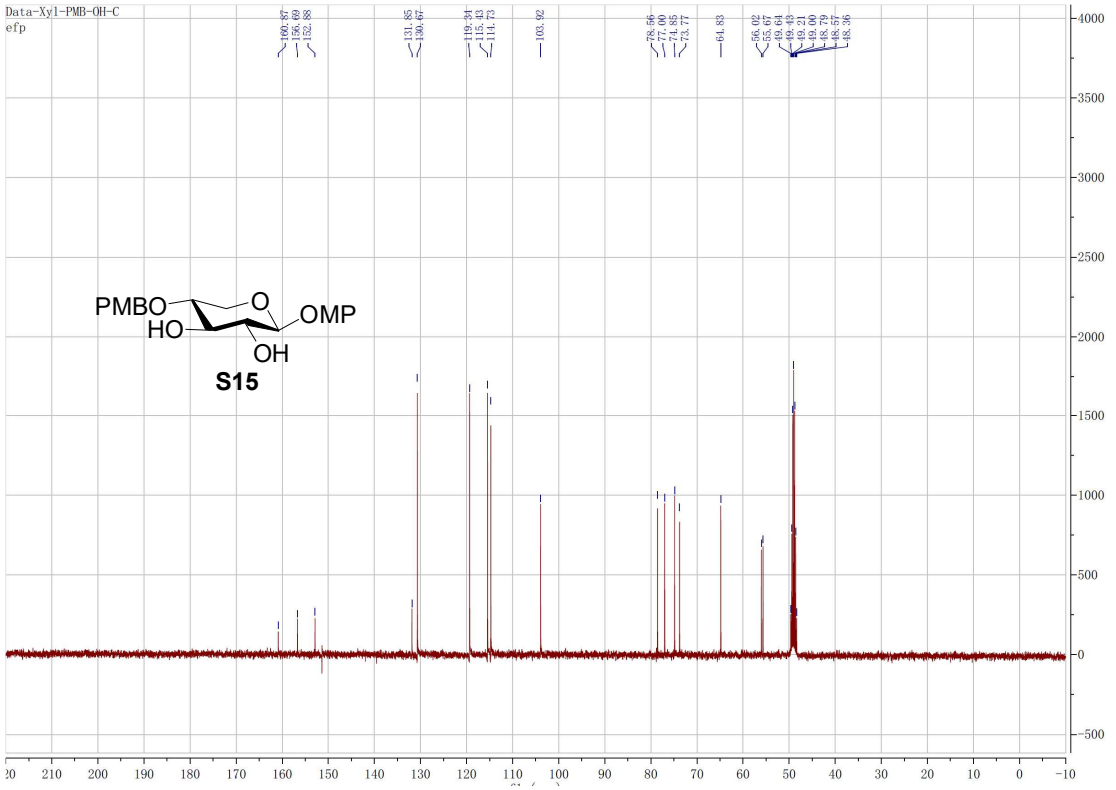
^{1}H-^{1}H COSY of compound 28



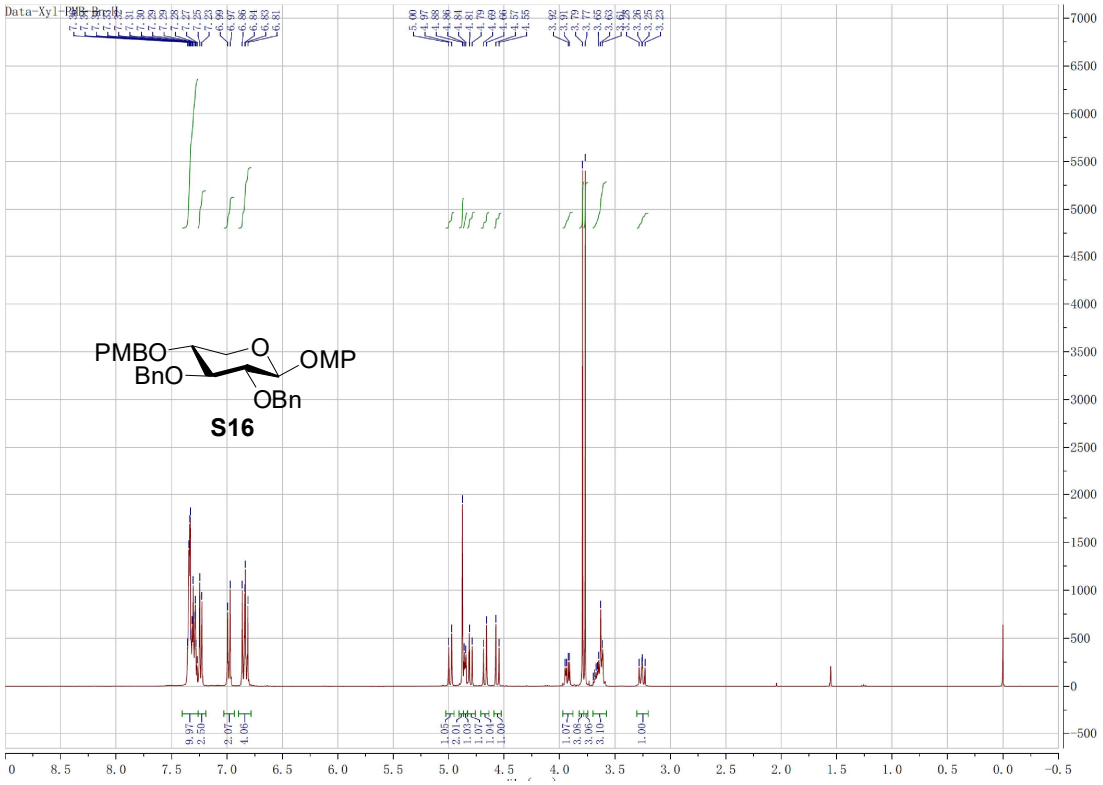
^{1}H NMR of compound S15



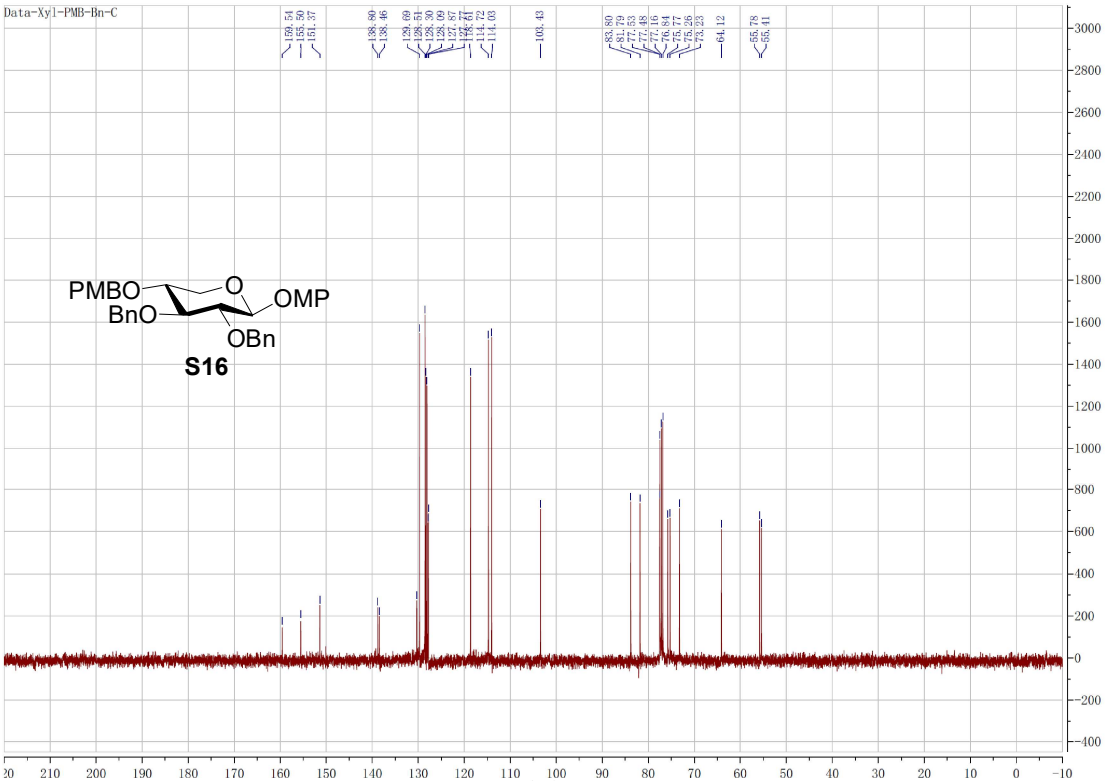
^{13}C NMR of compound S15



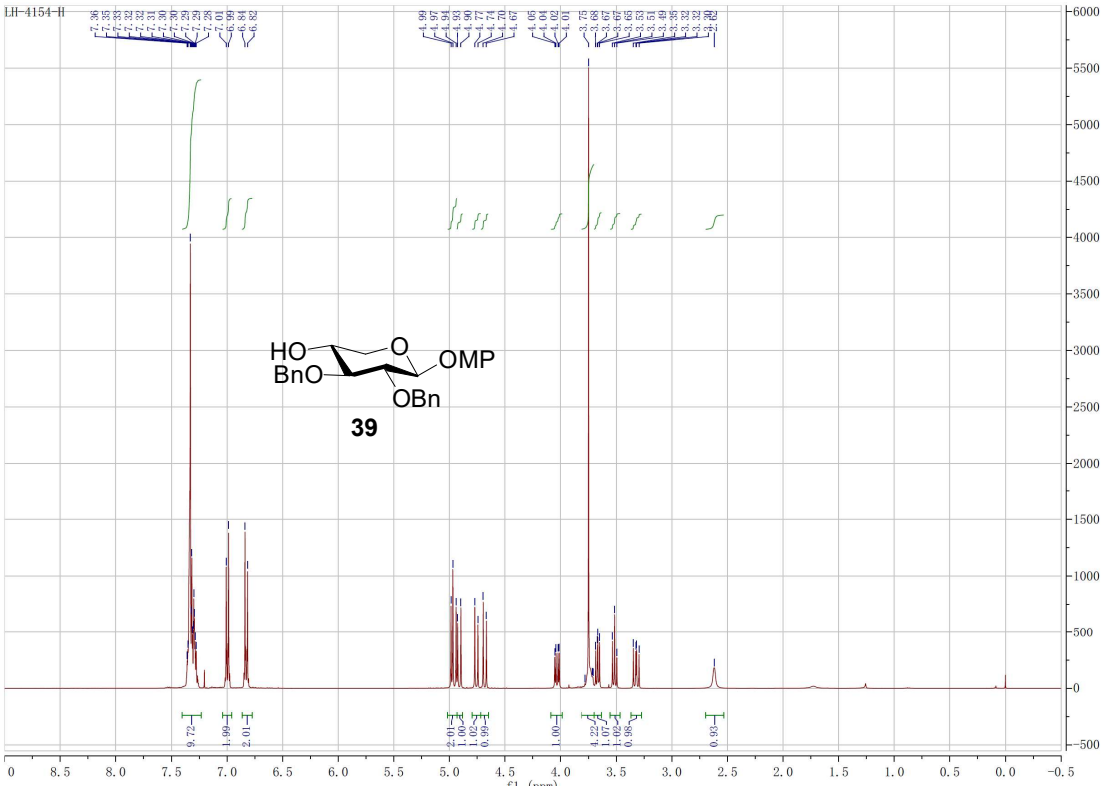
^{1}H NMR of compound S16



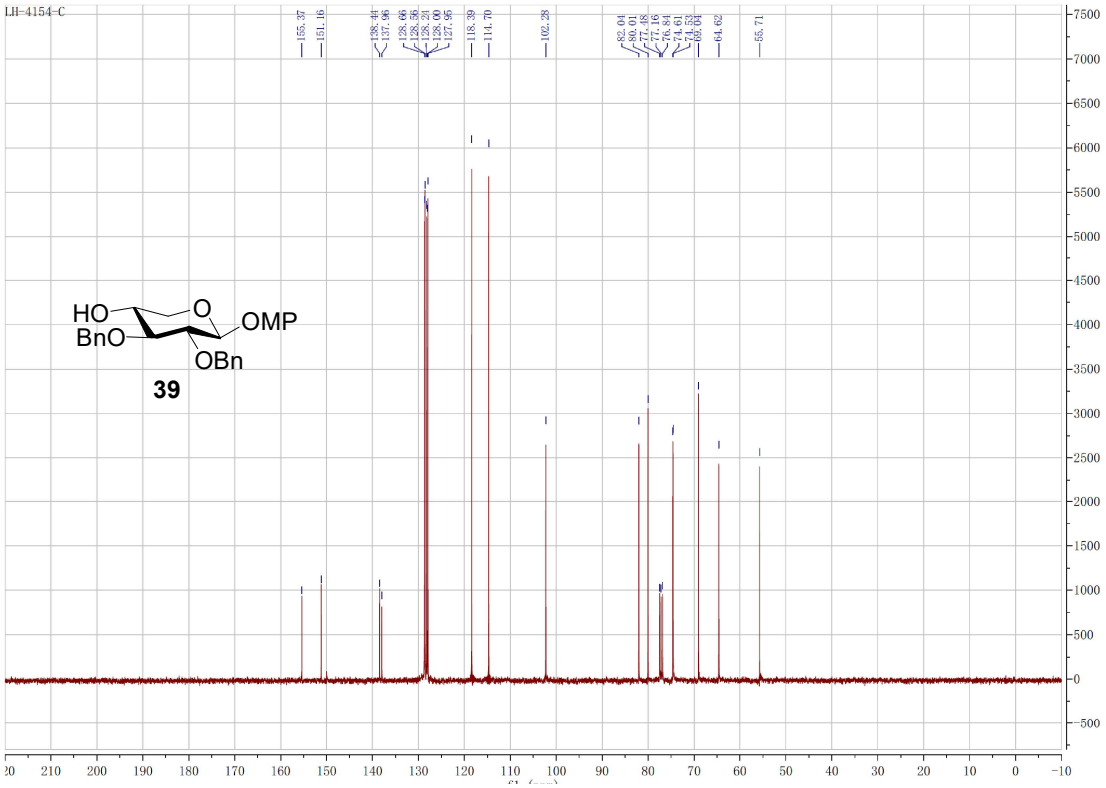
^{13}C NMR of compound S16



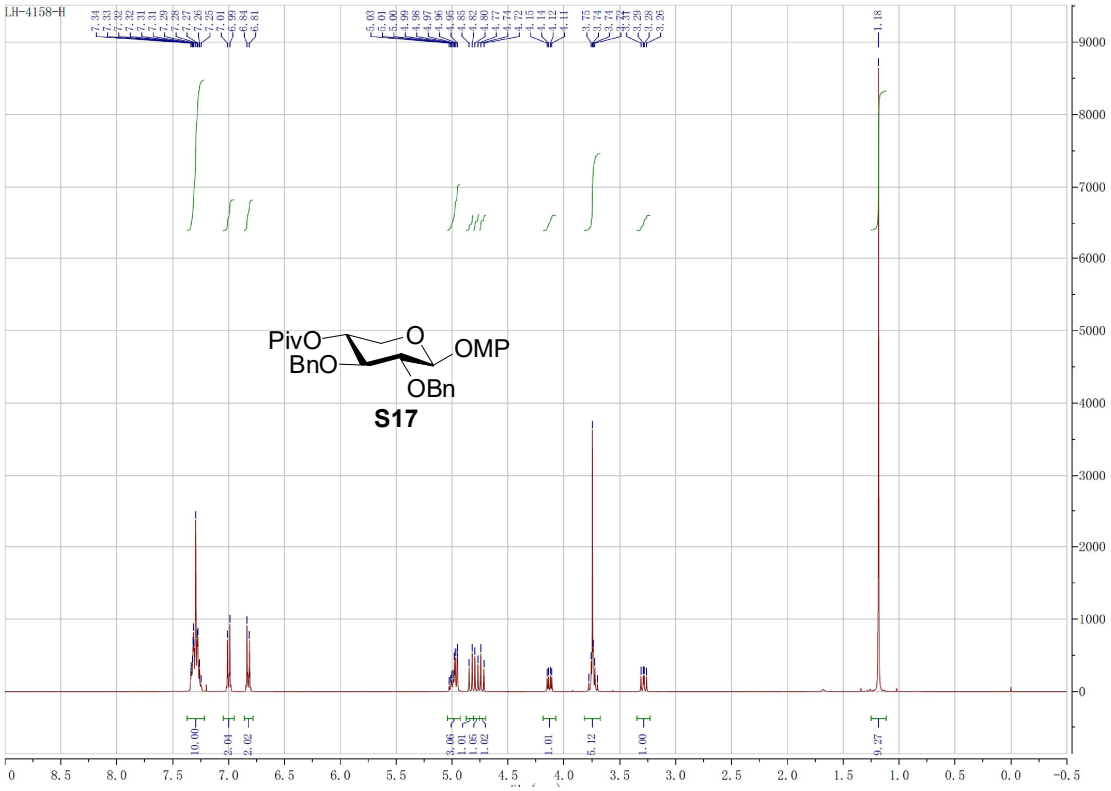
^{1}H NMR of compound 39



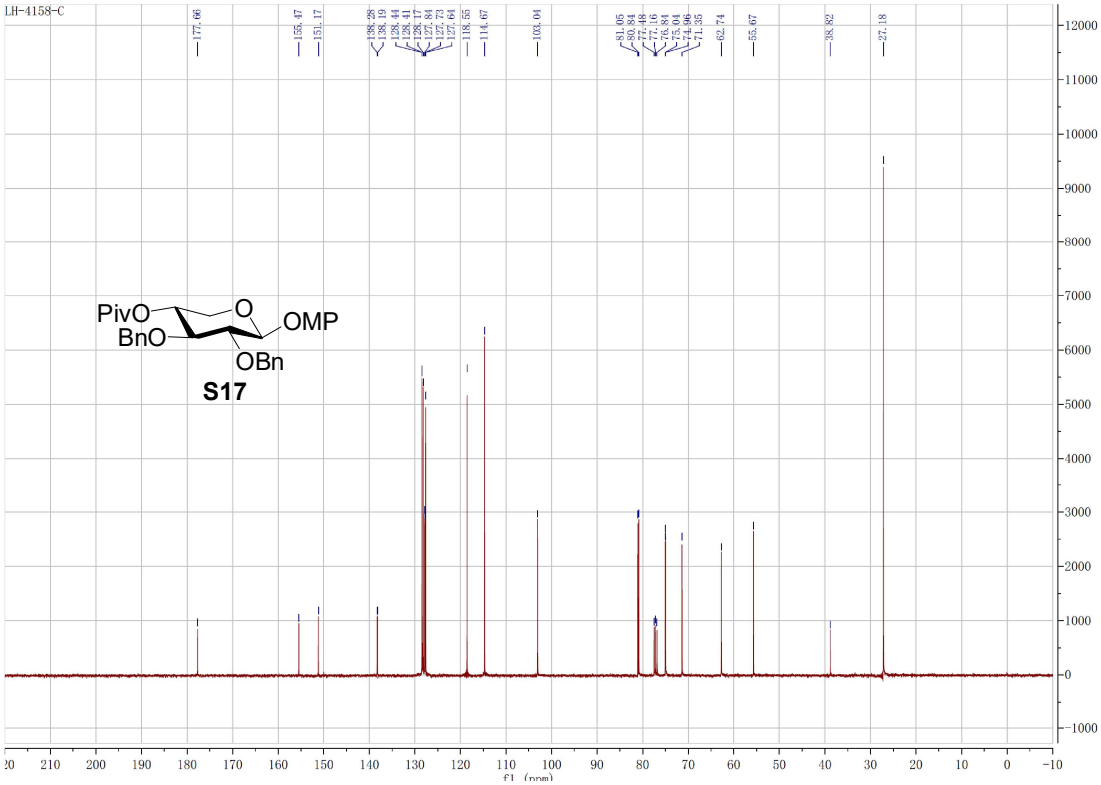
^{13}C NMR of compound 39



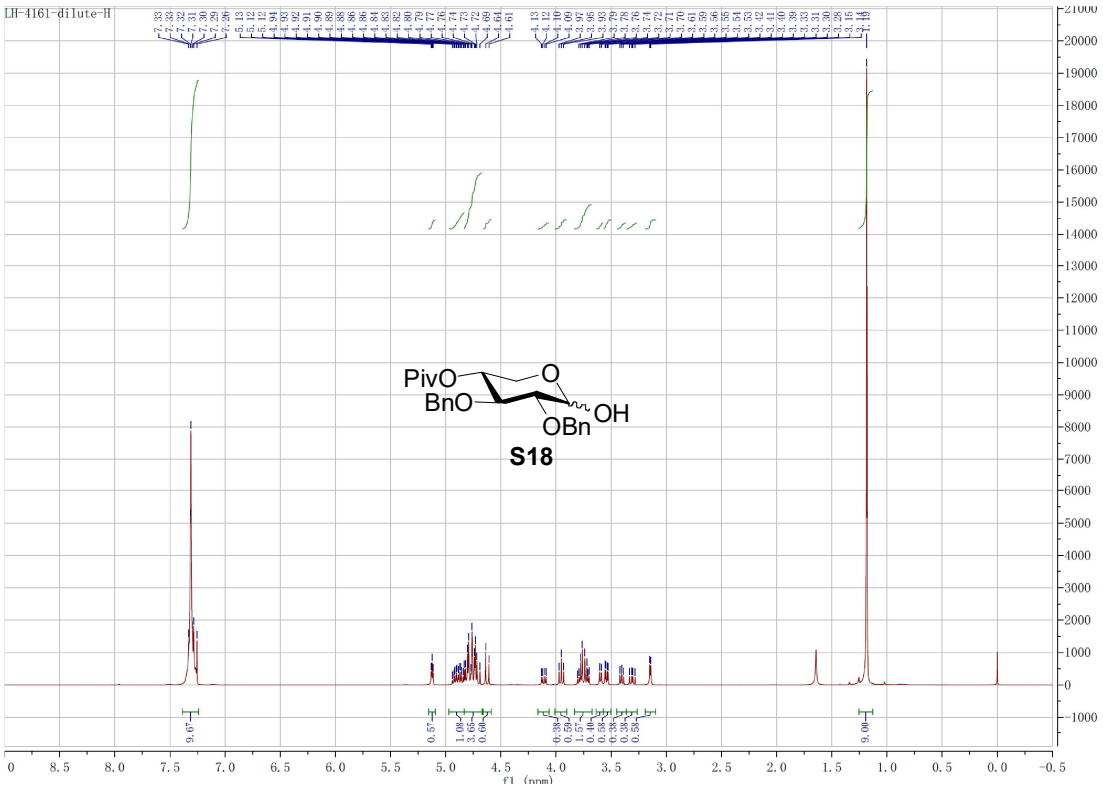
^{1}H NMR of compound S17



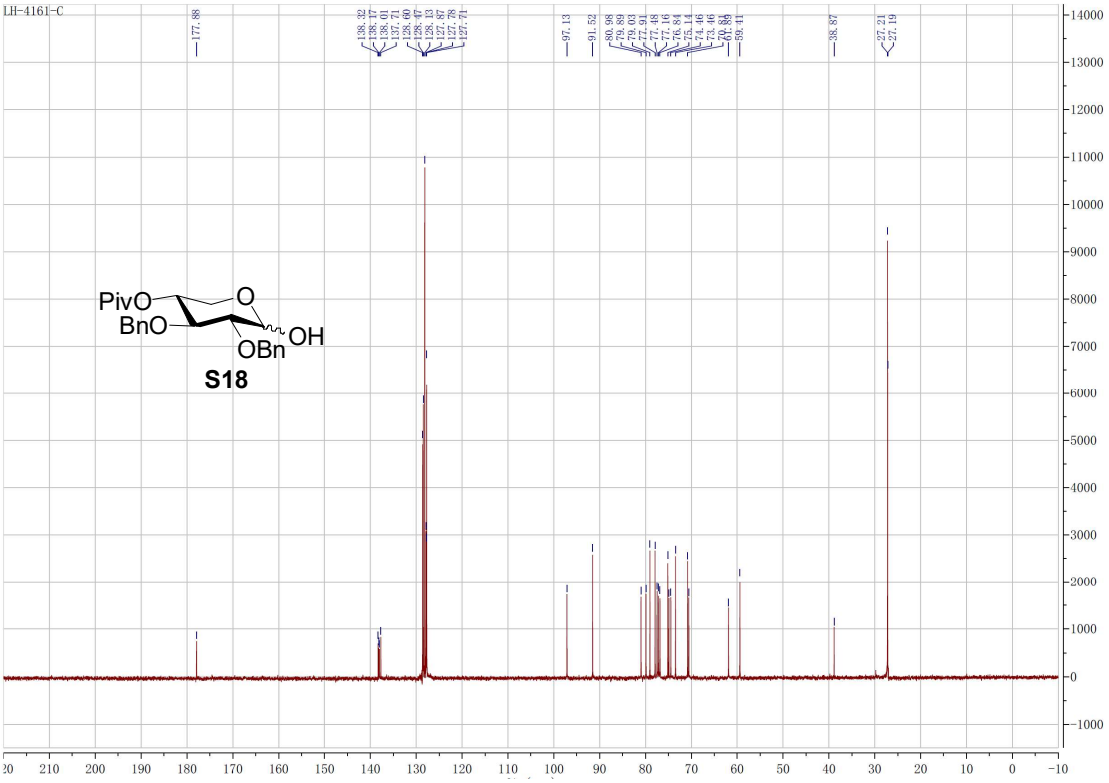
^{13}C NMR of compound S17



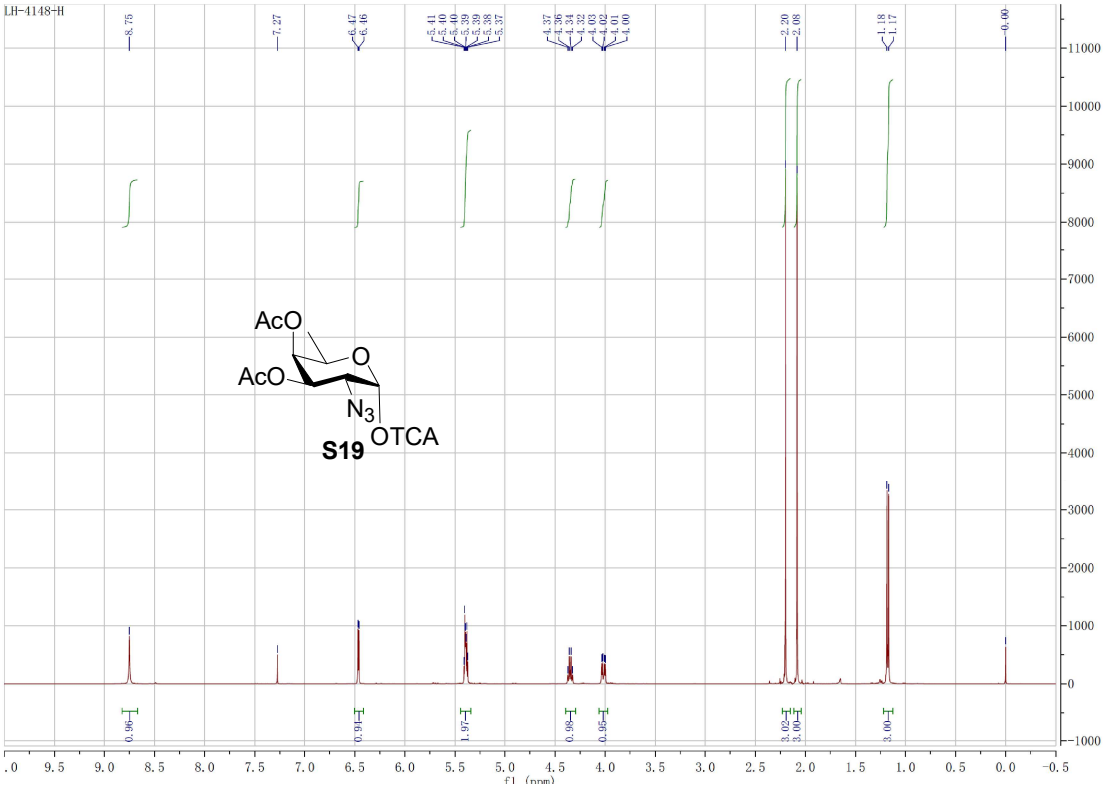
^{1}H NMR of compound S18



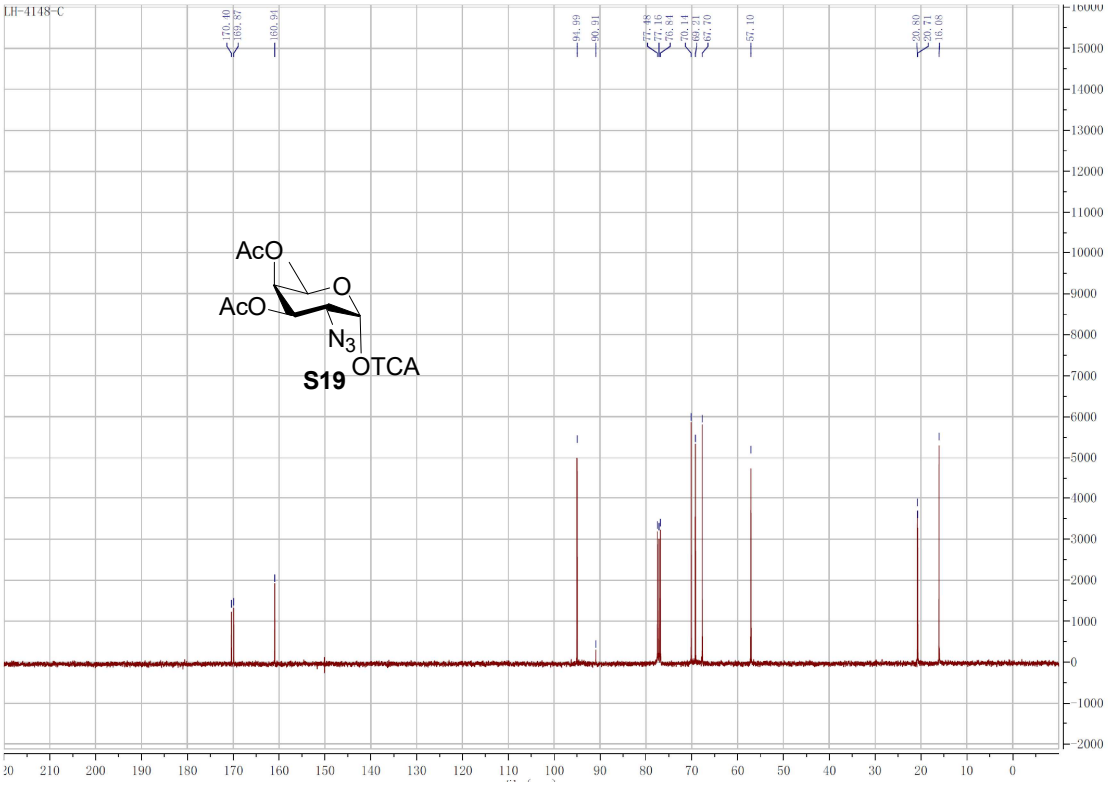
^{13}C NMR of compound S18



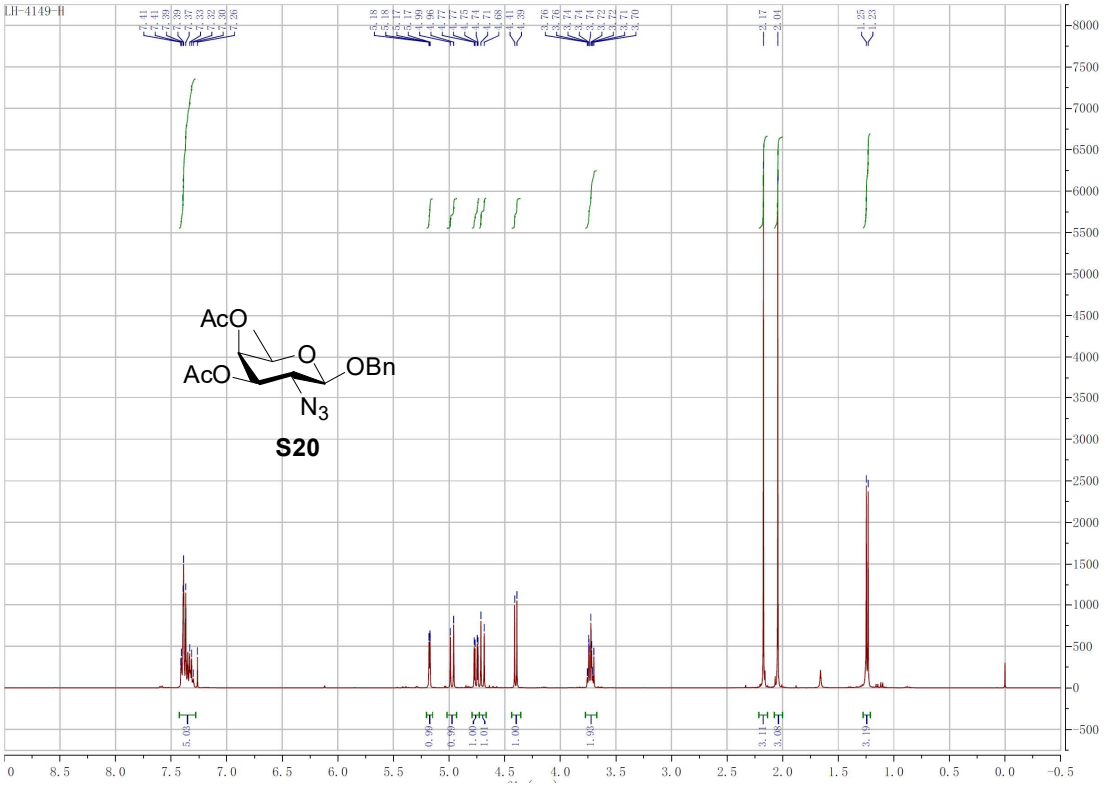
^{1}H NMR of compound S19



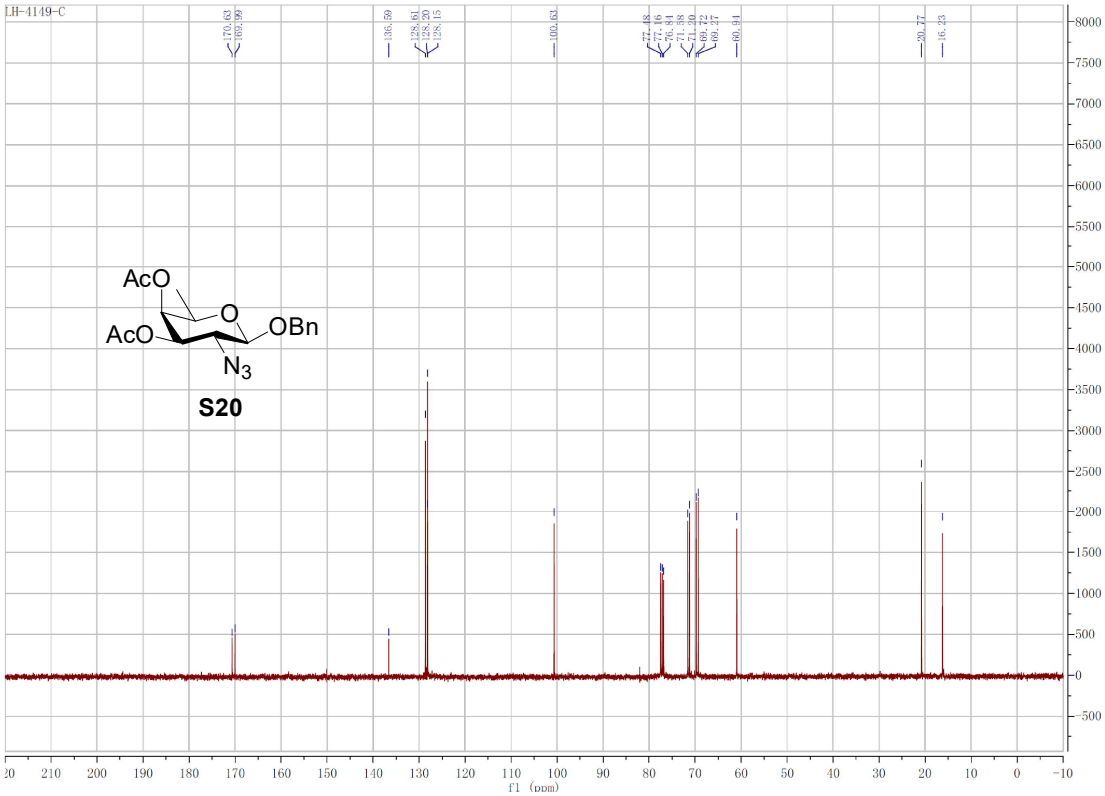
^{13}C NMR of compound S19



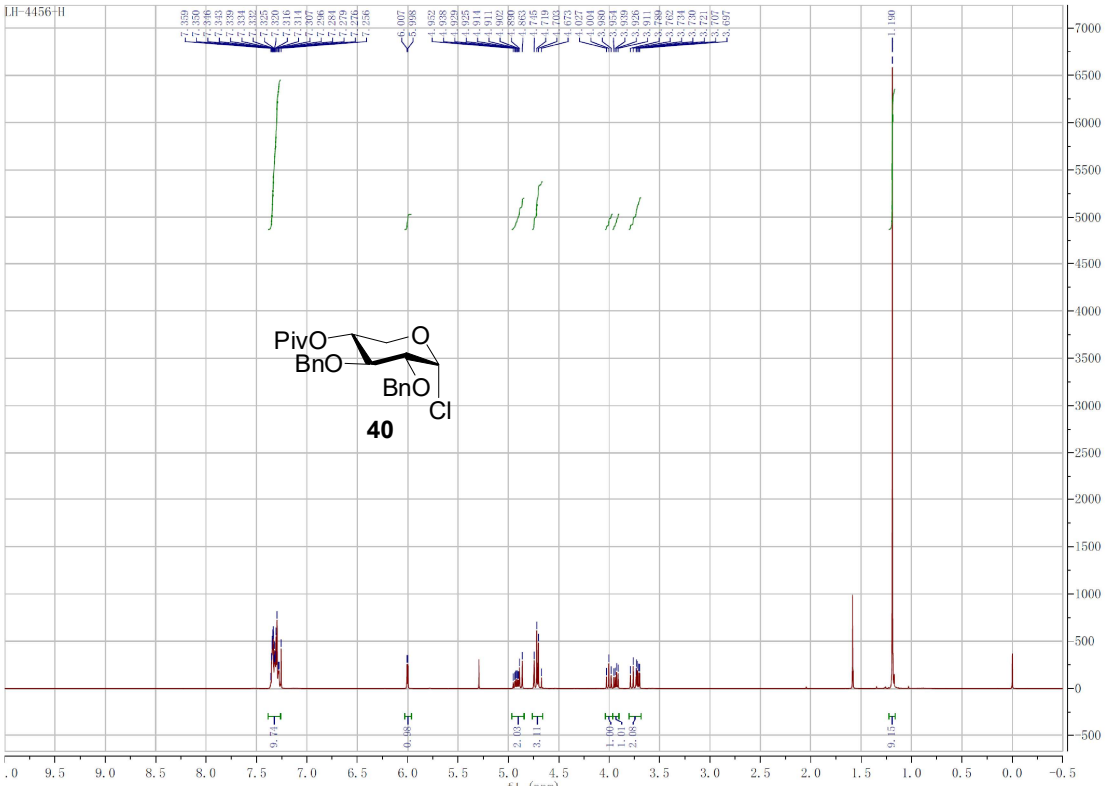
^{1}H NMR of compound S20



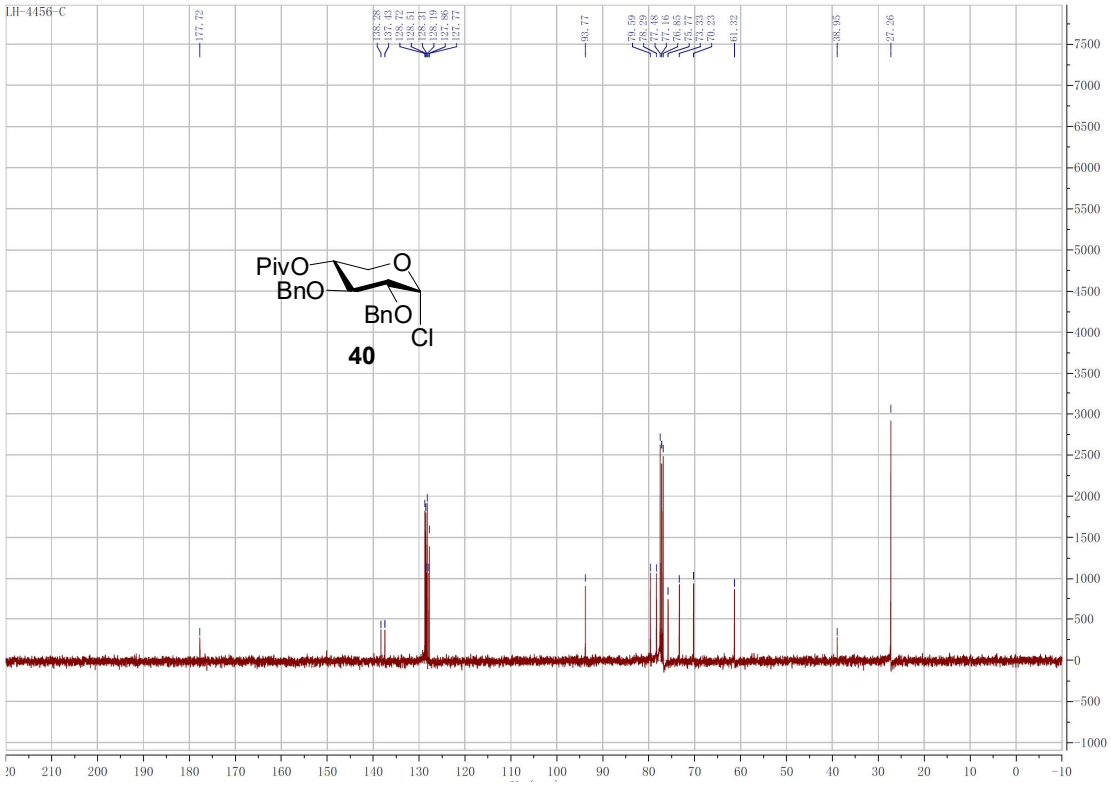
^{13}C NMR of compound S20



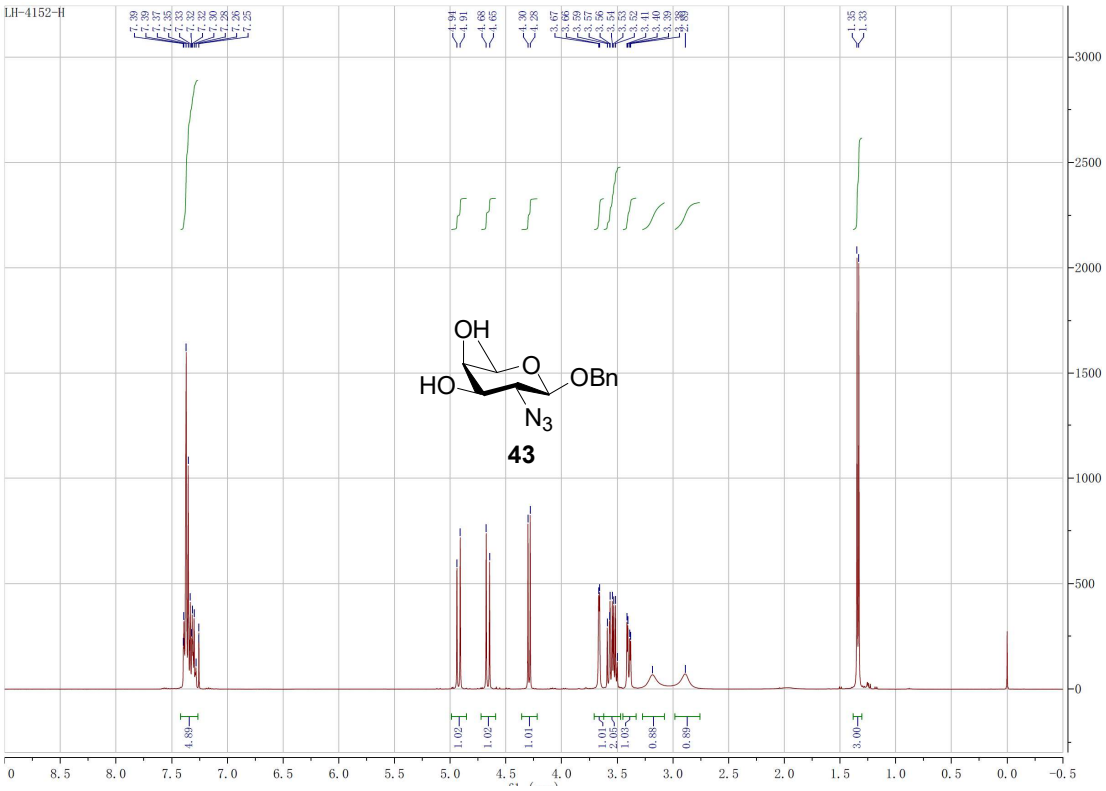
^{1}H NMR of compound 40



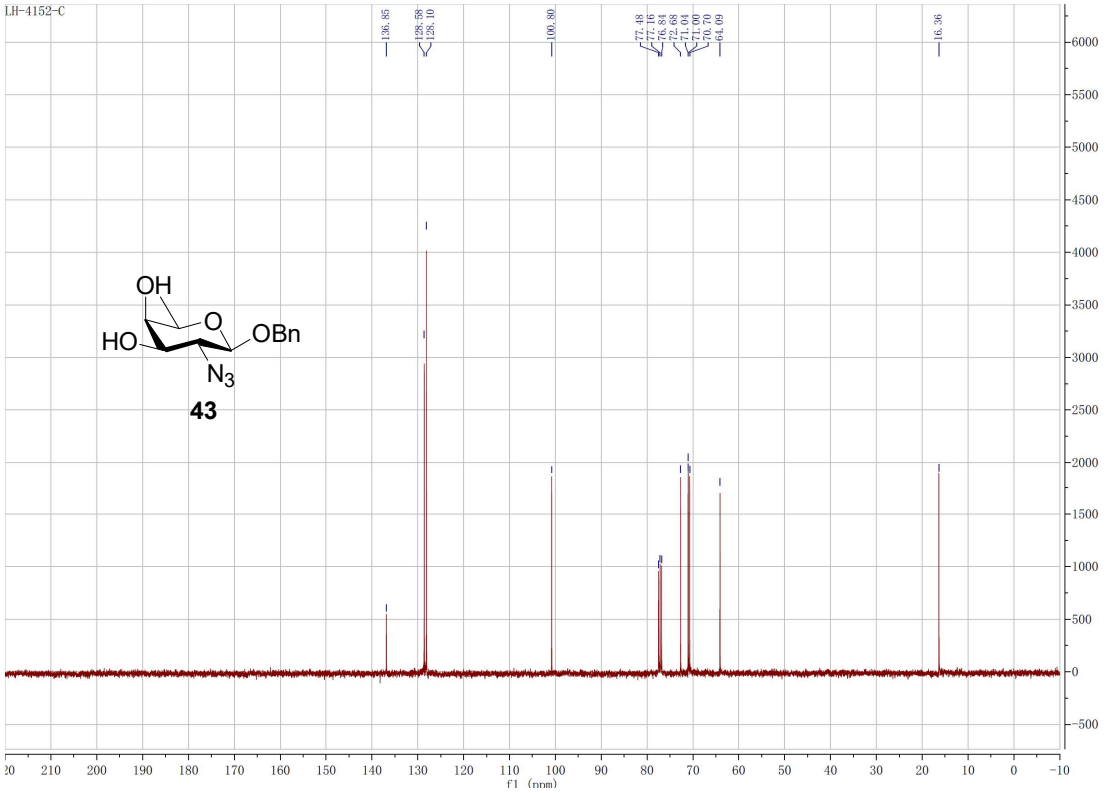
^{13}C NMR of compound 40



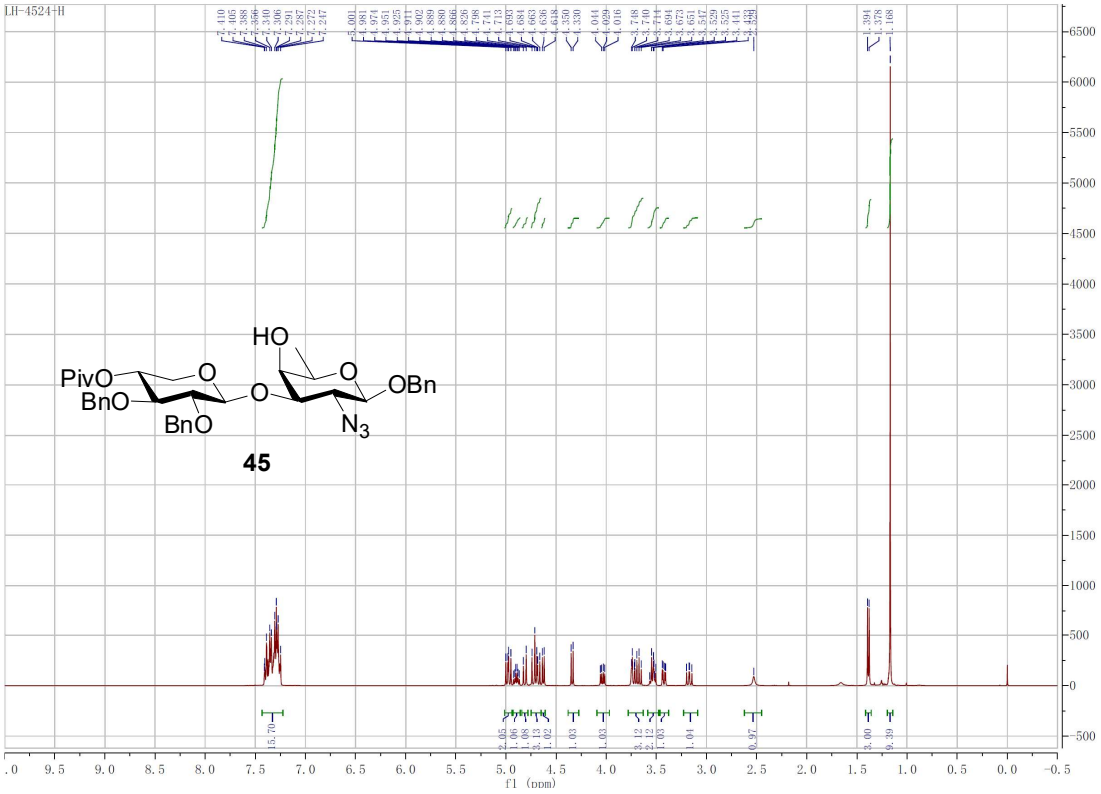
^{1}H NMR of compound 43



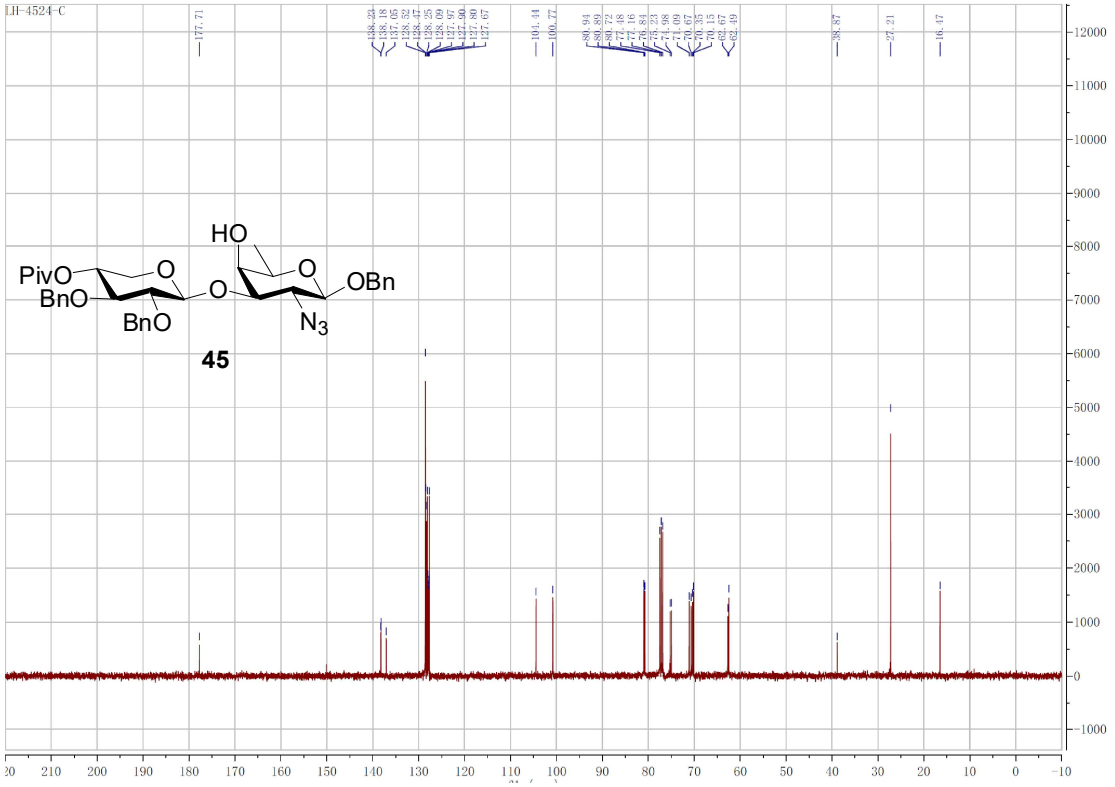
^{13}C NMR of compound 43



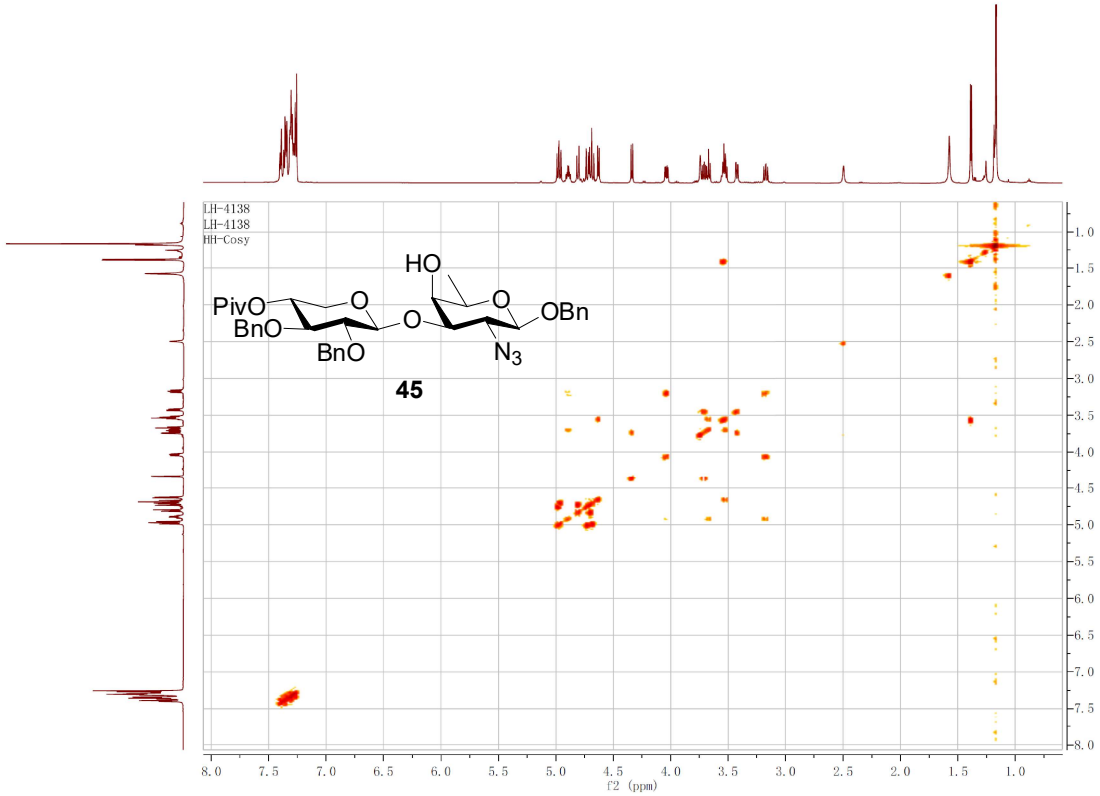
^{1}H NMR of compound 45



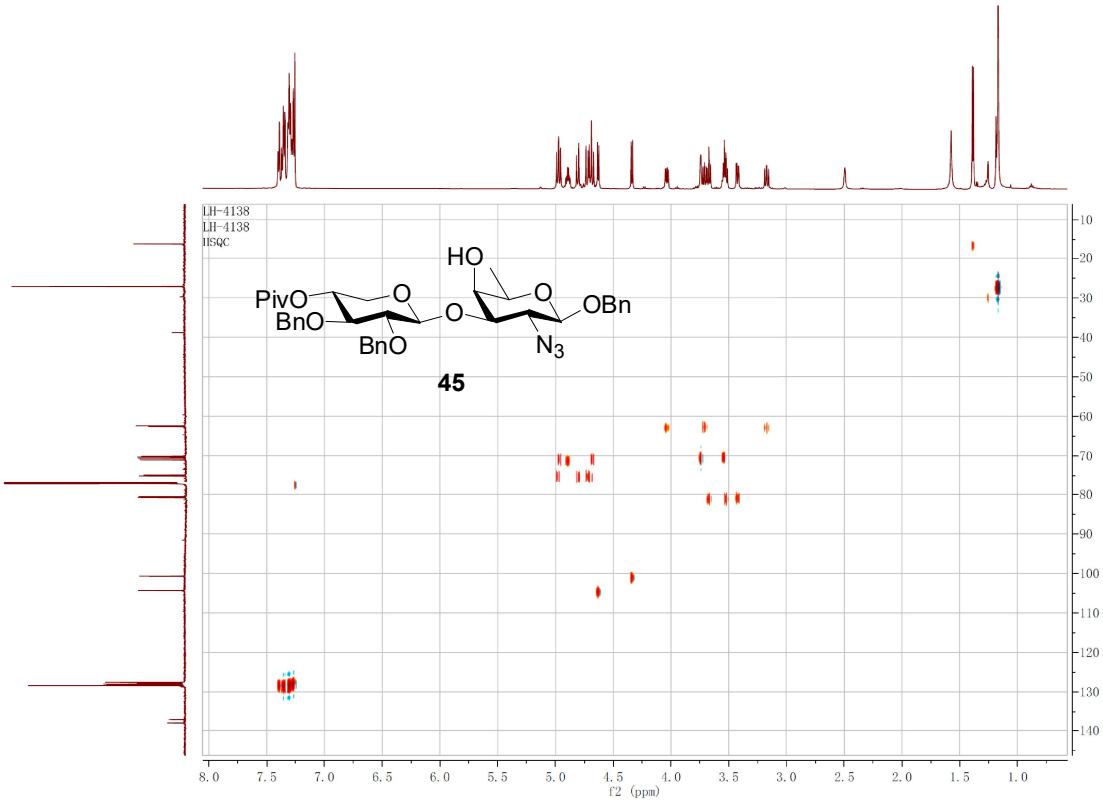
^{13}C NMR of compound 45



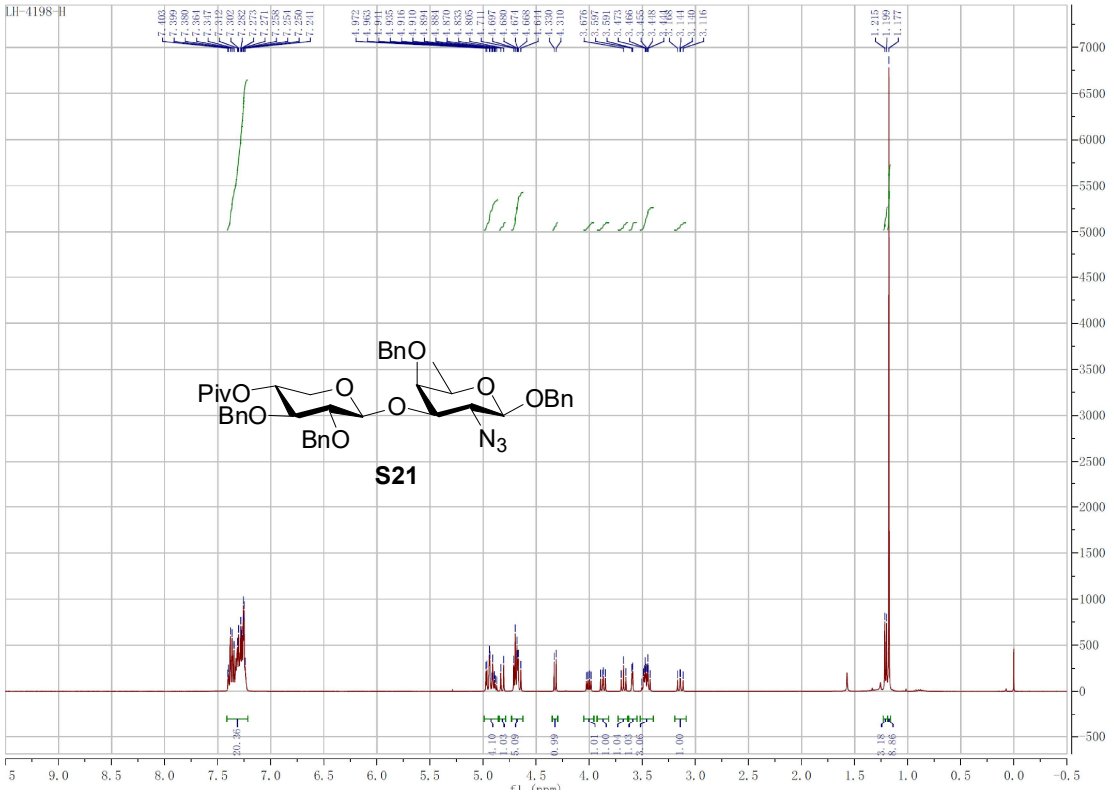
^{1}H-^{1}H COSY of compound 45



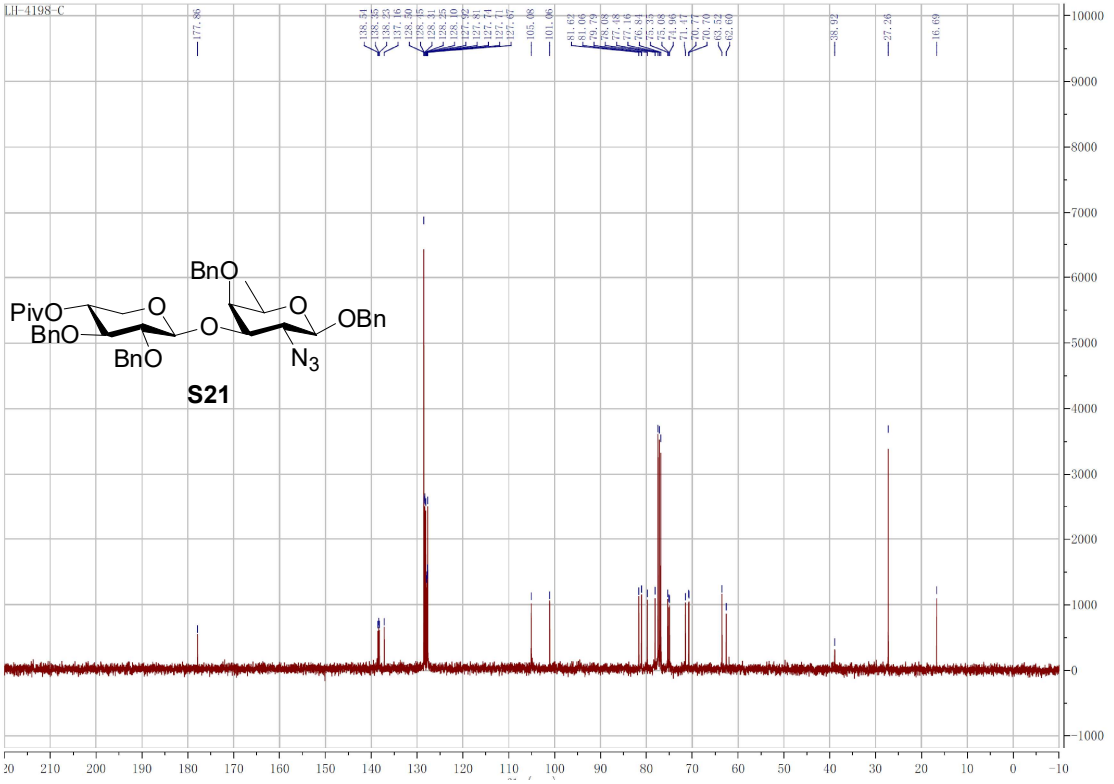
^{1}H-^{13}C HSQC of compound 45



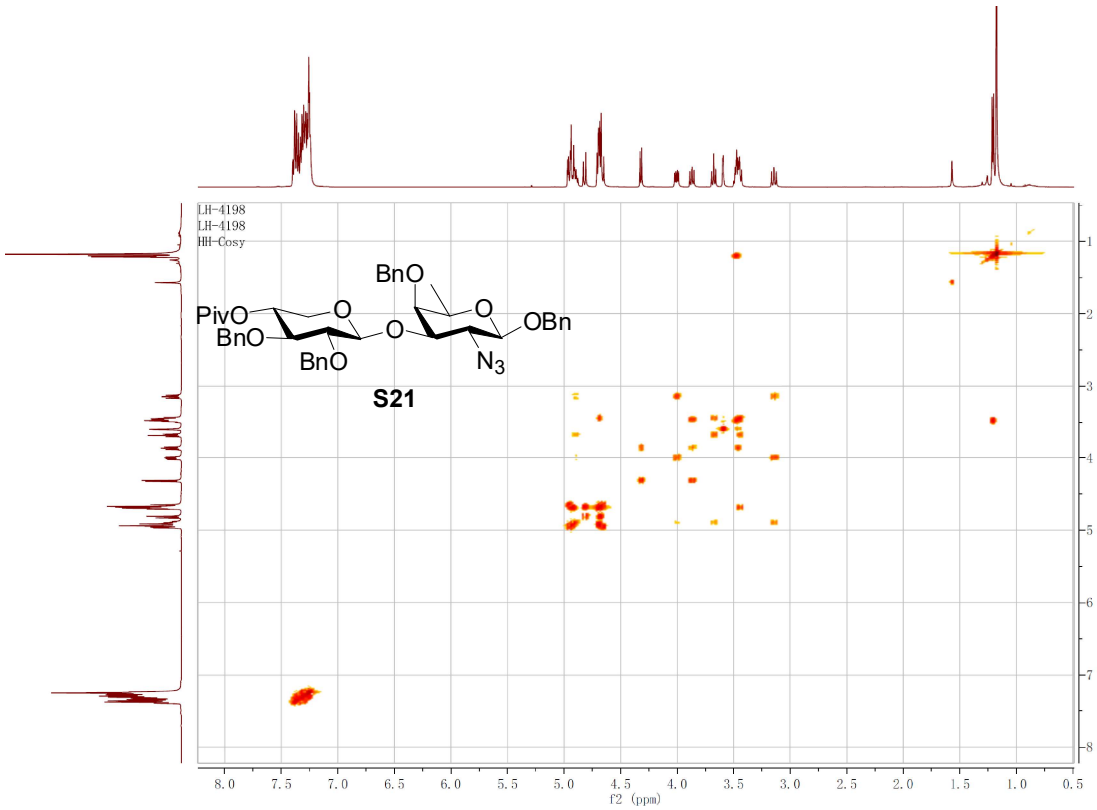
^{1}H NMR of compound S21



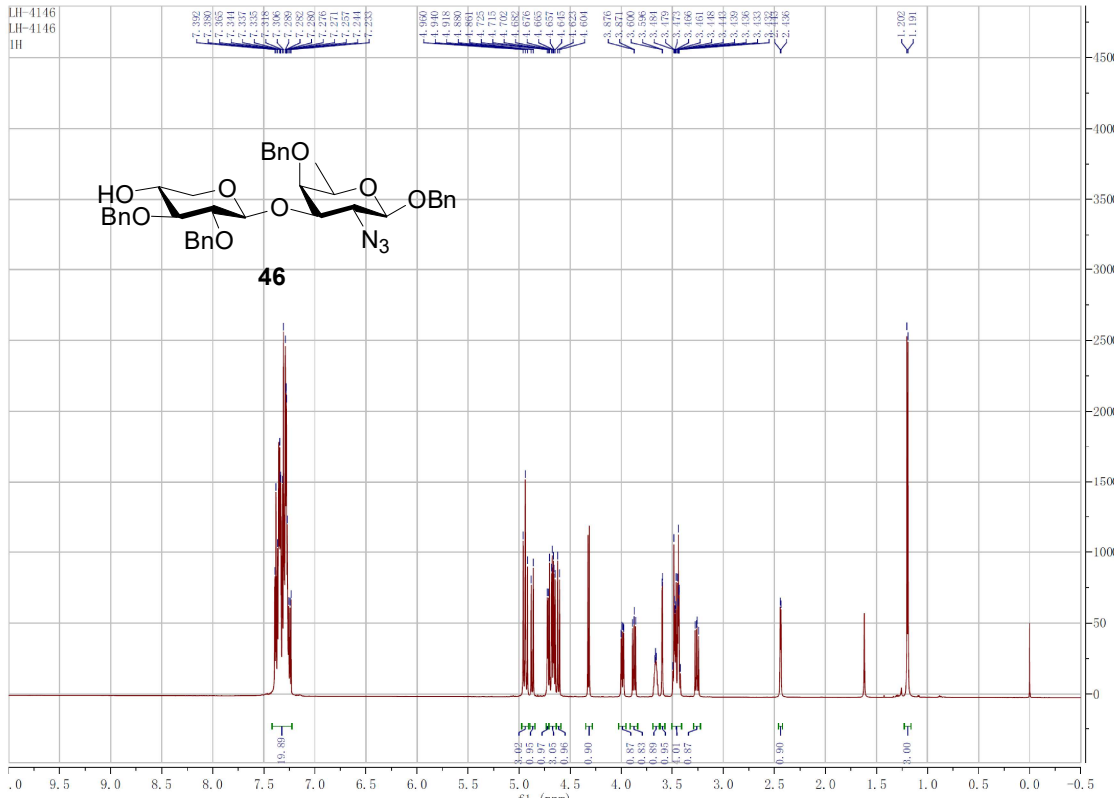
^{13}C NMR of compound S21



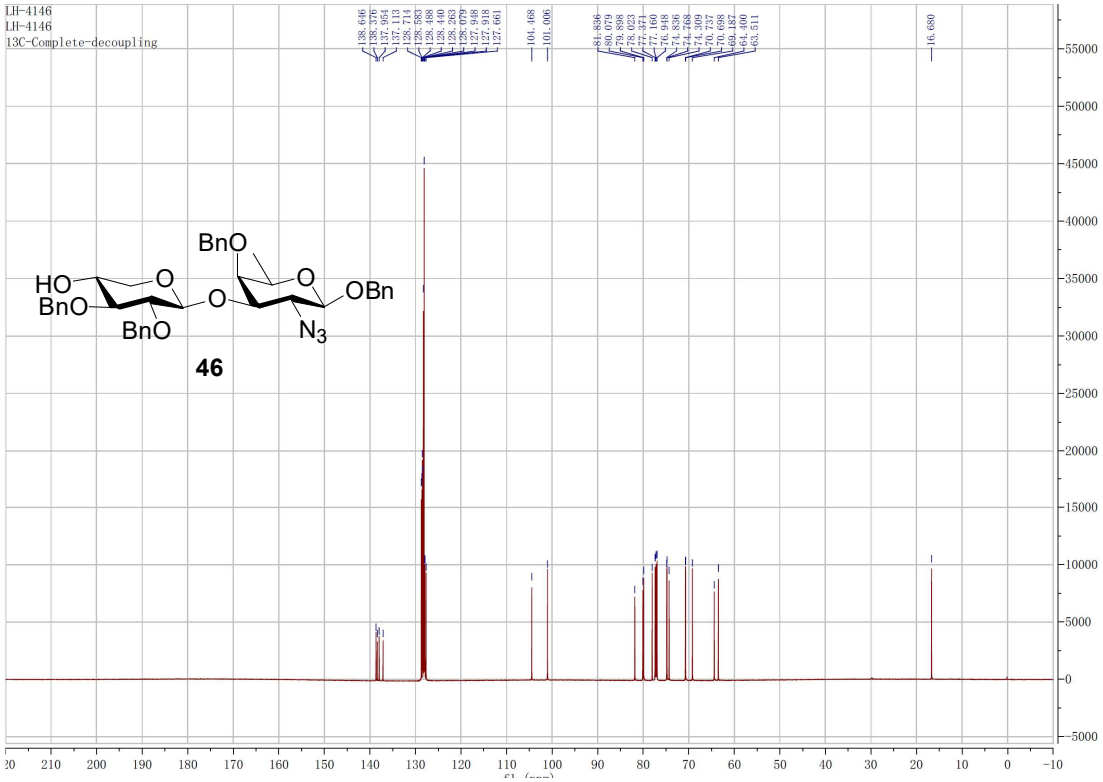
^{1}H-^{1}H COSY of compound S21



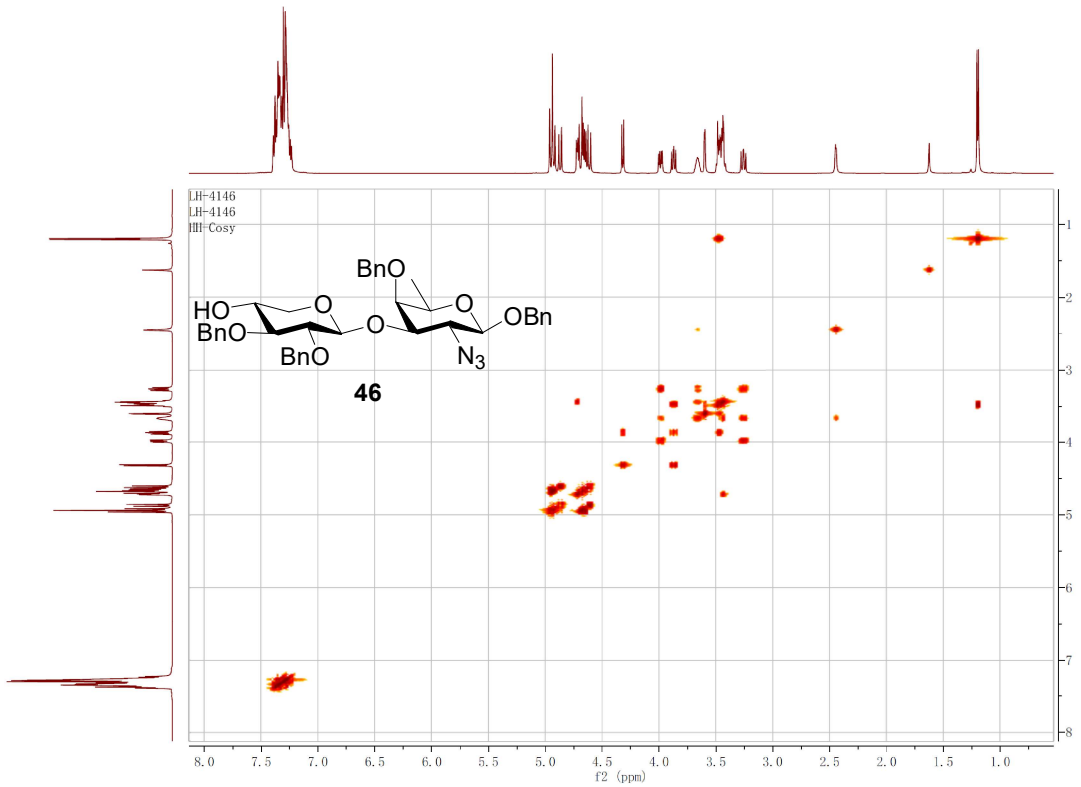
^{1}H NMR of compound 46



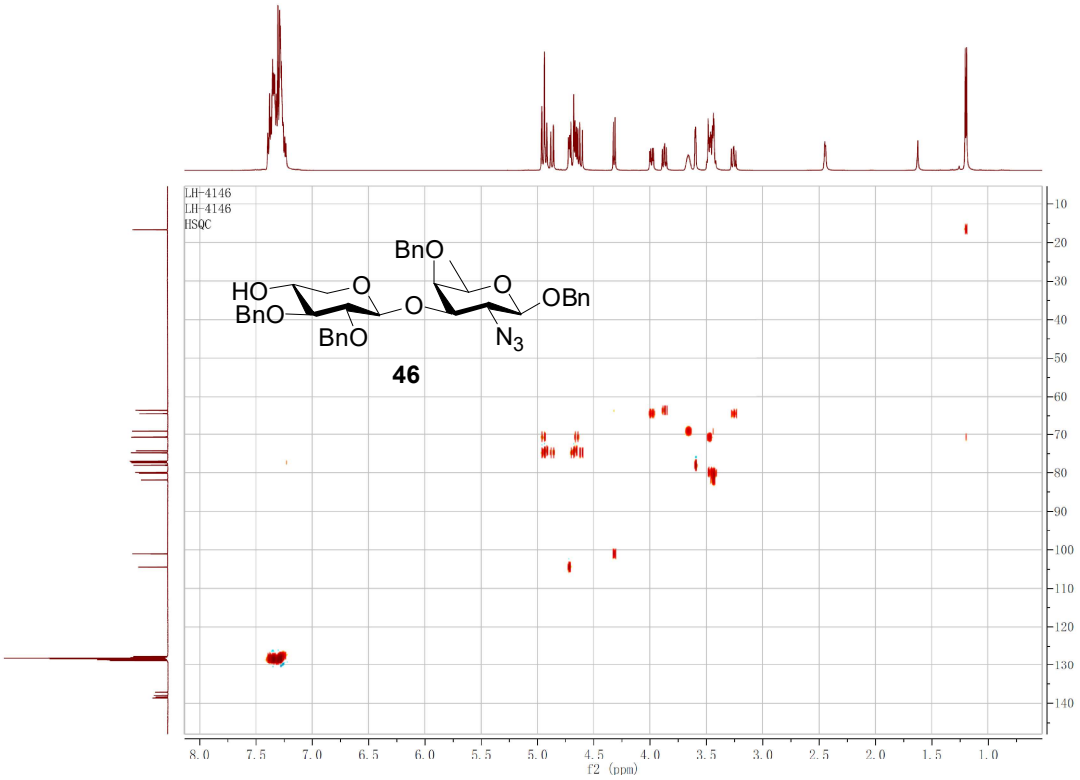
^{13}C NMR of compound 46



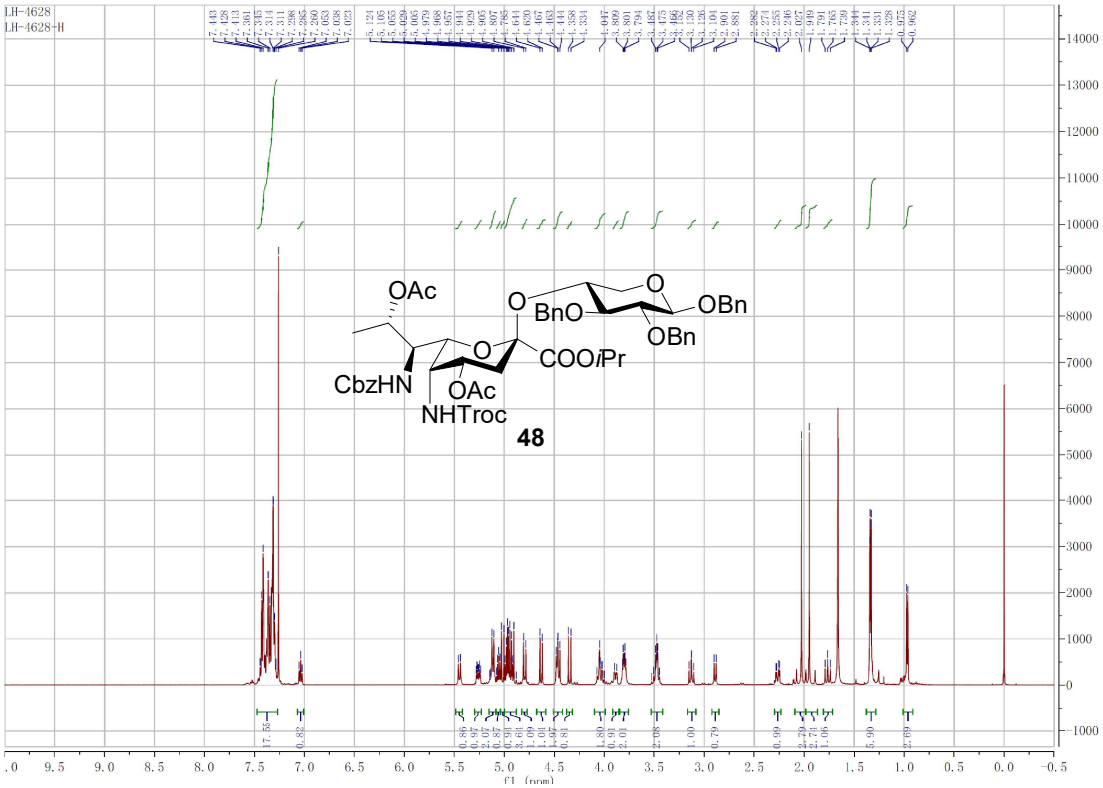
^{1}H-^{1}H COSY of compound 46



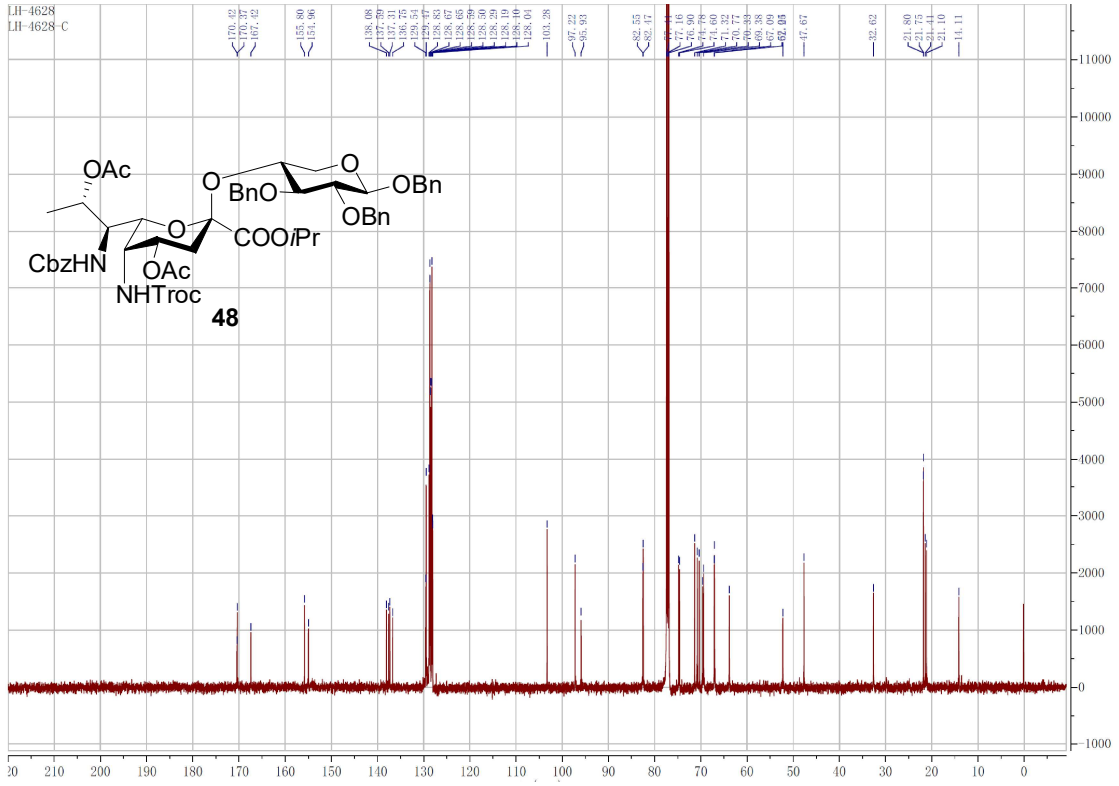
^{1}H-^{13}C HSQC of compound 46



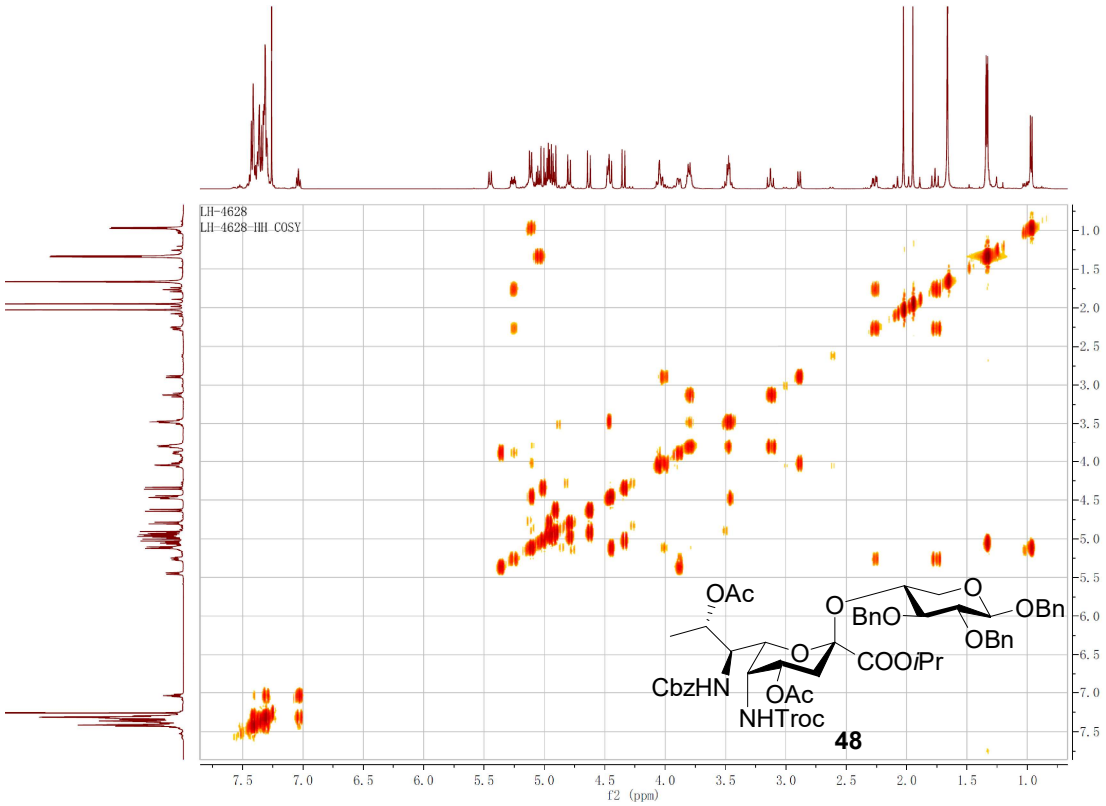
^{1}H NMR of compound 48



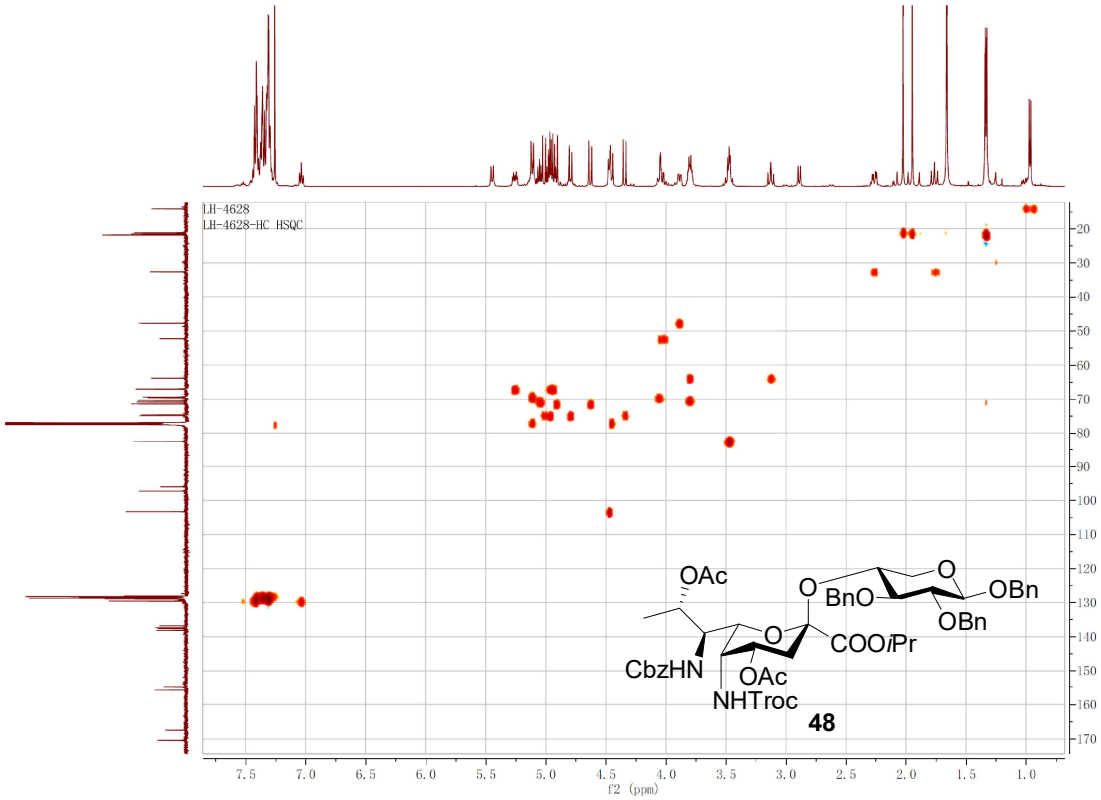
^{13}C NMR of compound 48



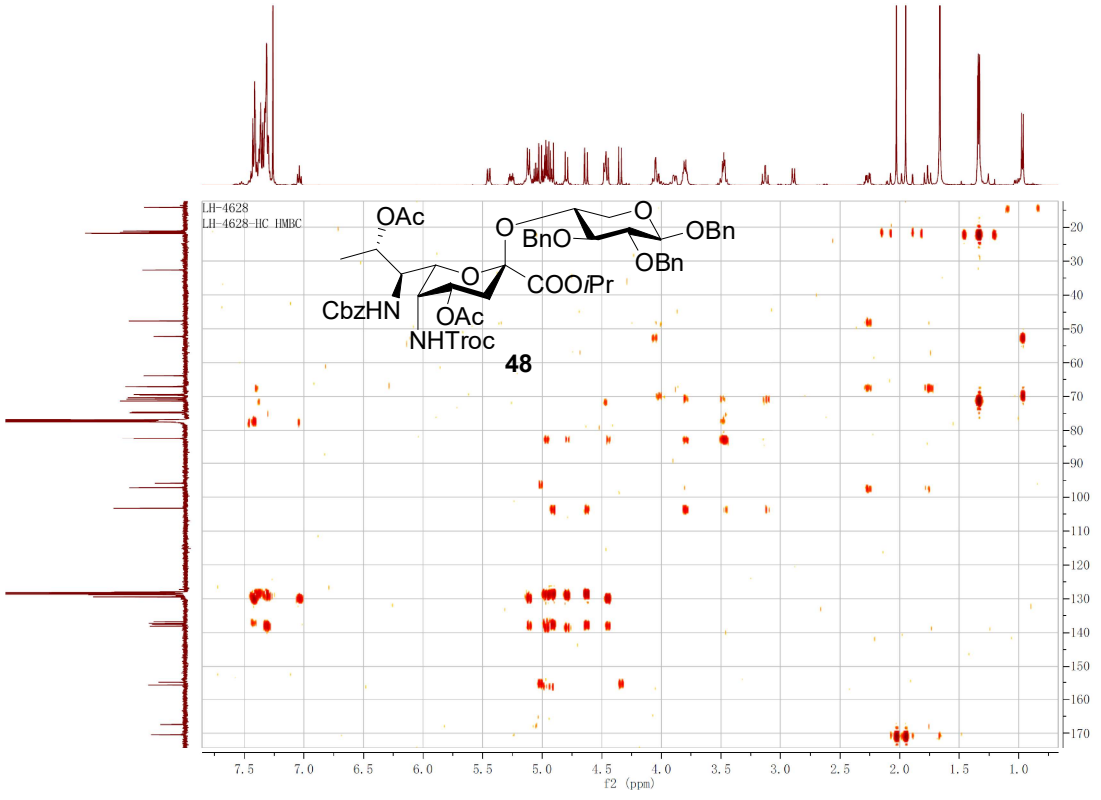
^{1}H -^{1}H COSY of compound 48



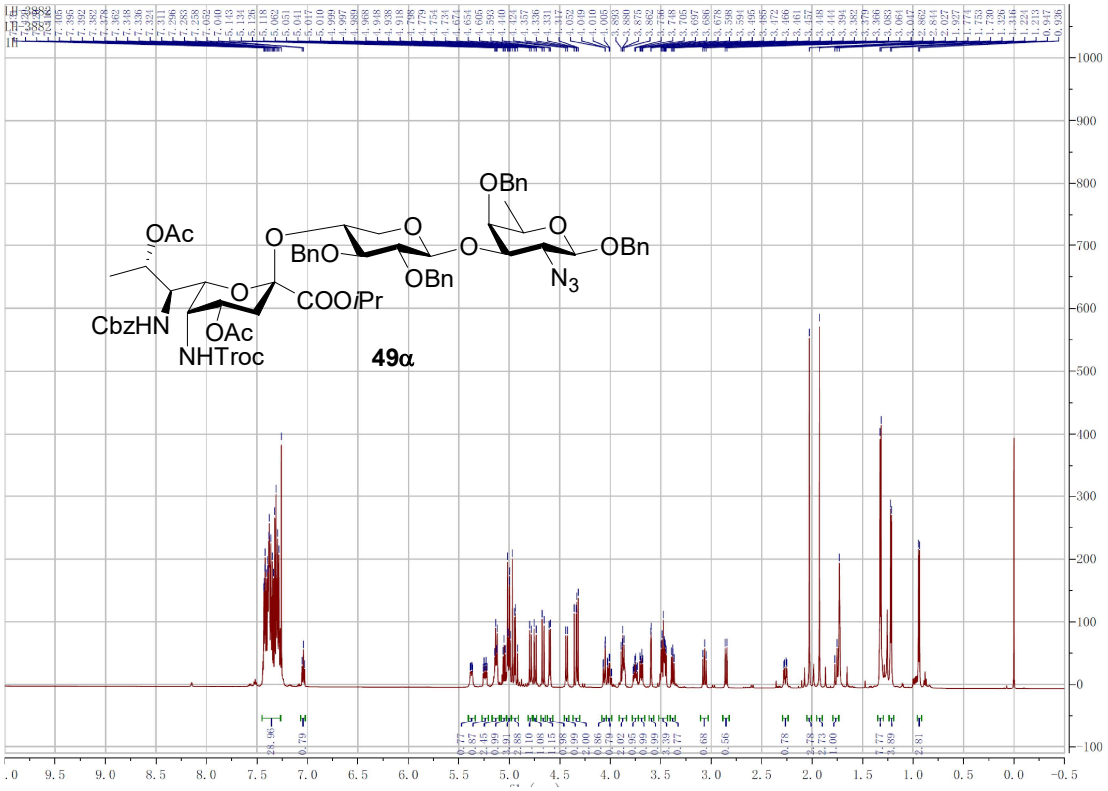
^{1}H-^{13}C HSQC of compound 48



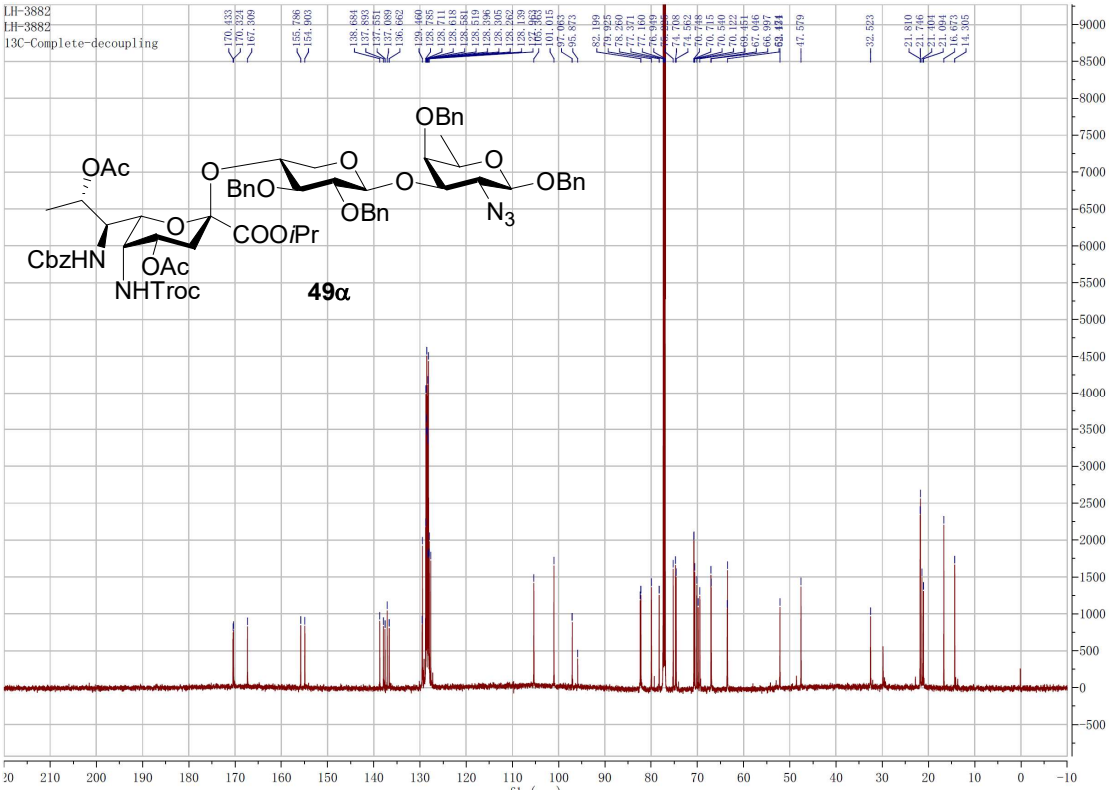
^{1}H-^{13}C HMBC of compound 48



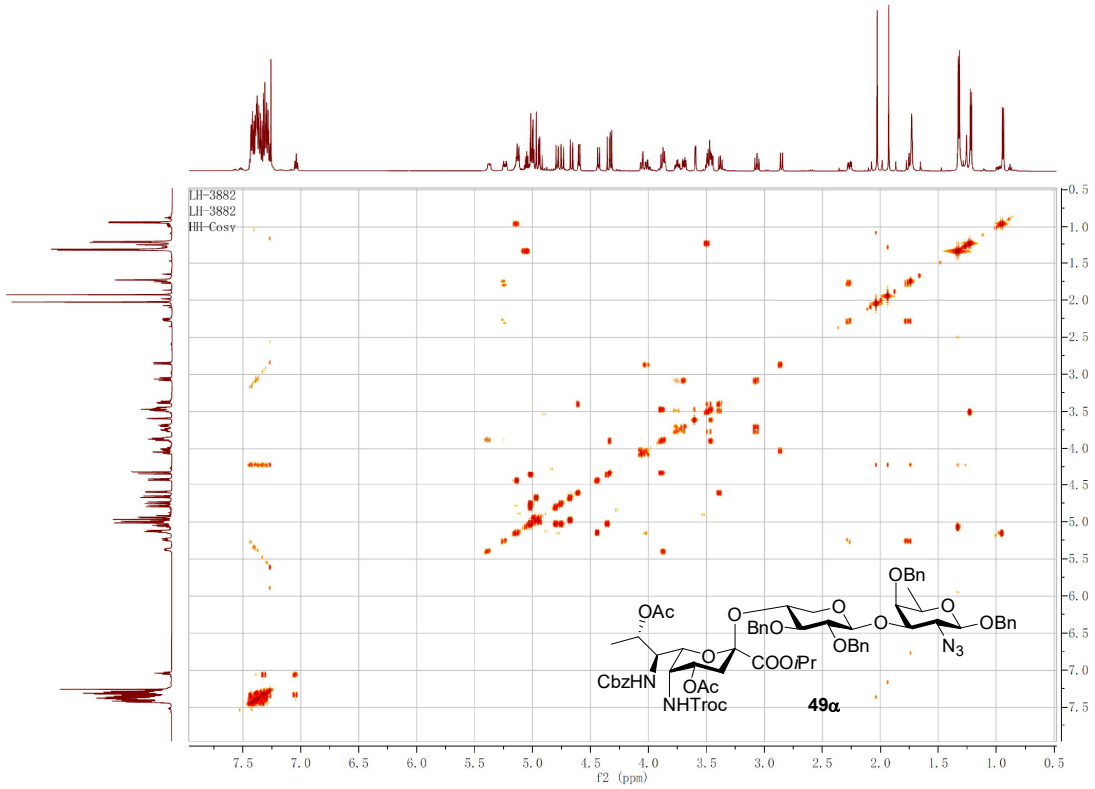
^{1}H NMR of compound 49α



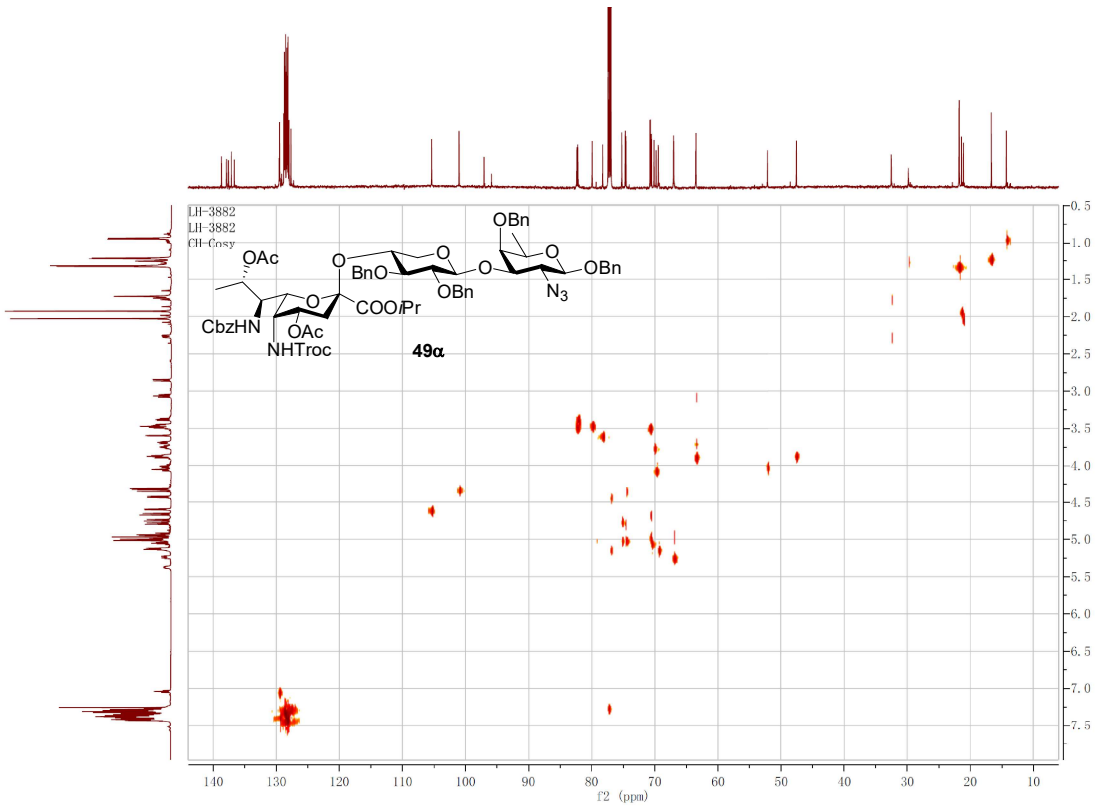
^{13}C NMR of compound 49α



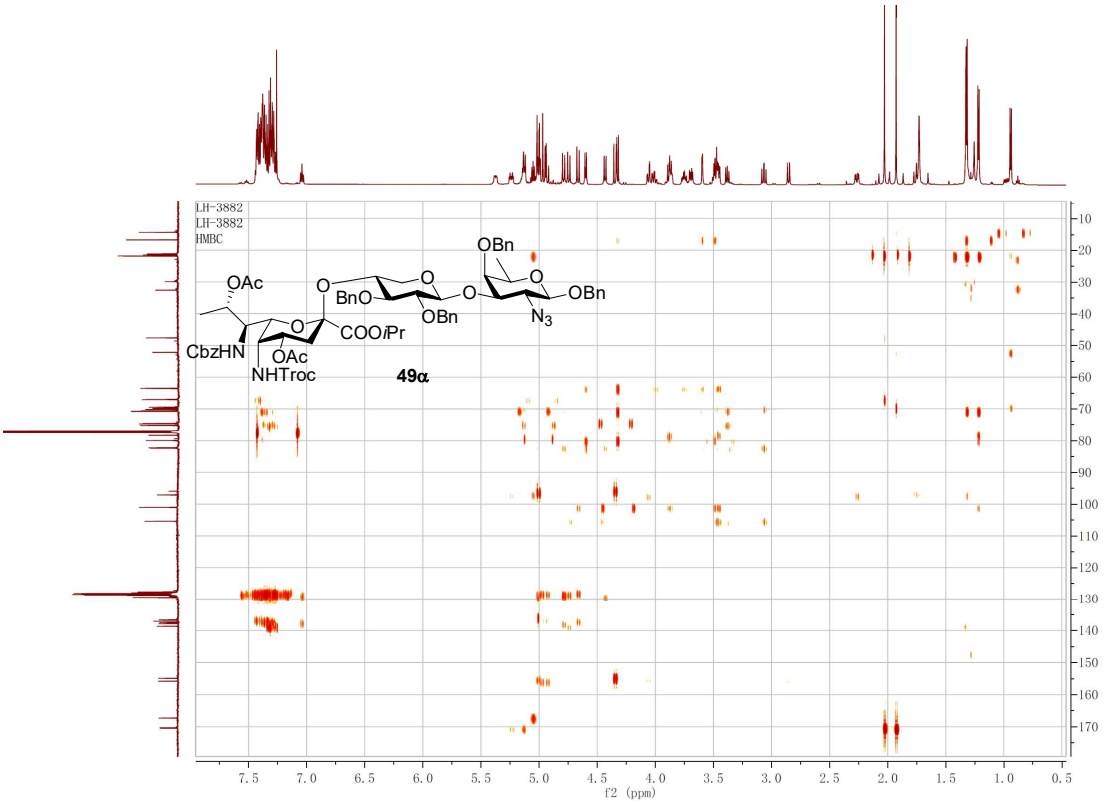
^{1}H-^{1}H COSY of compound 49α



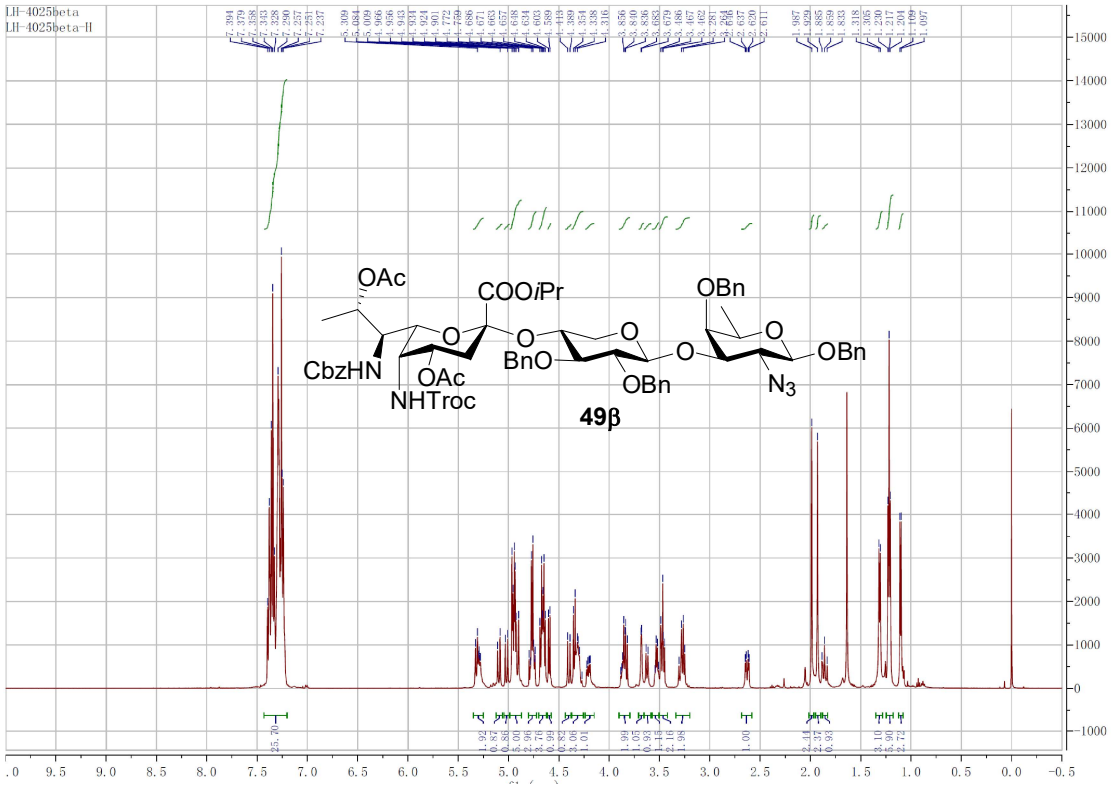
^{1}H-^{13}C COSY of compound 49α



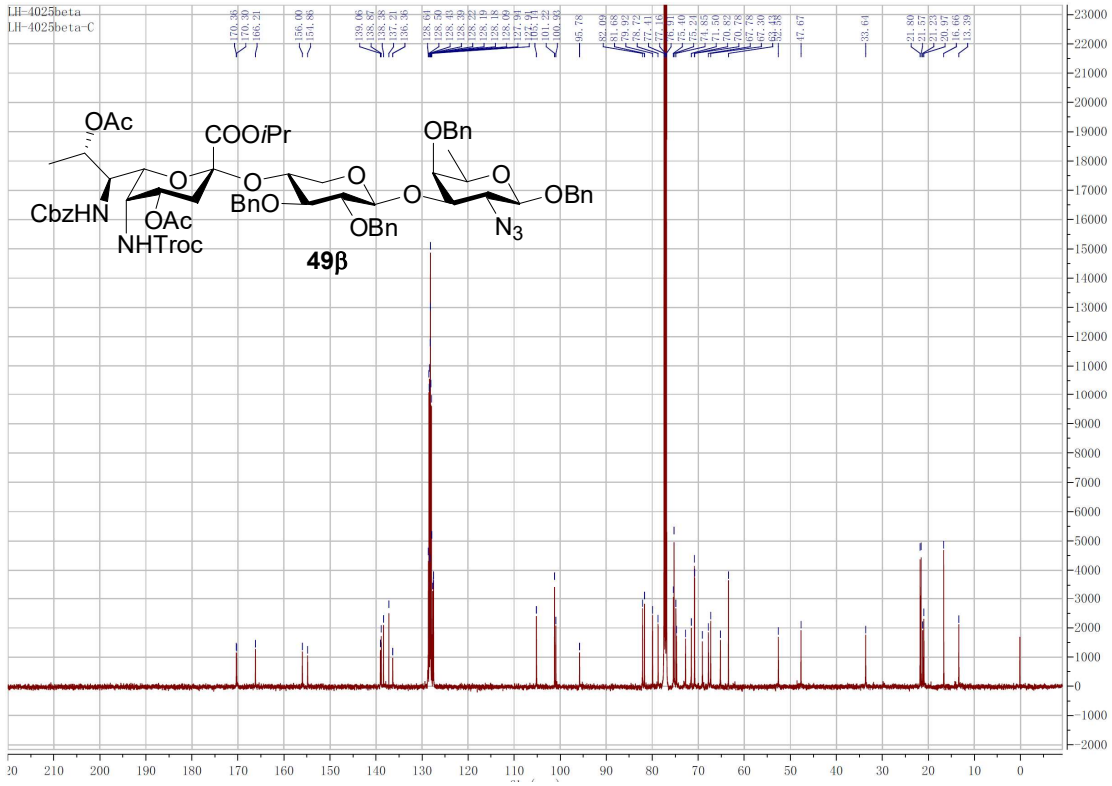
^{1}H-^{13}C HMBC of compound 49α



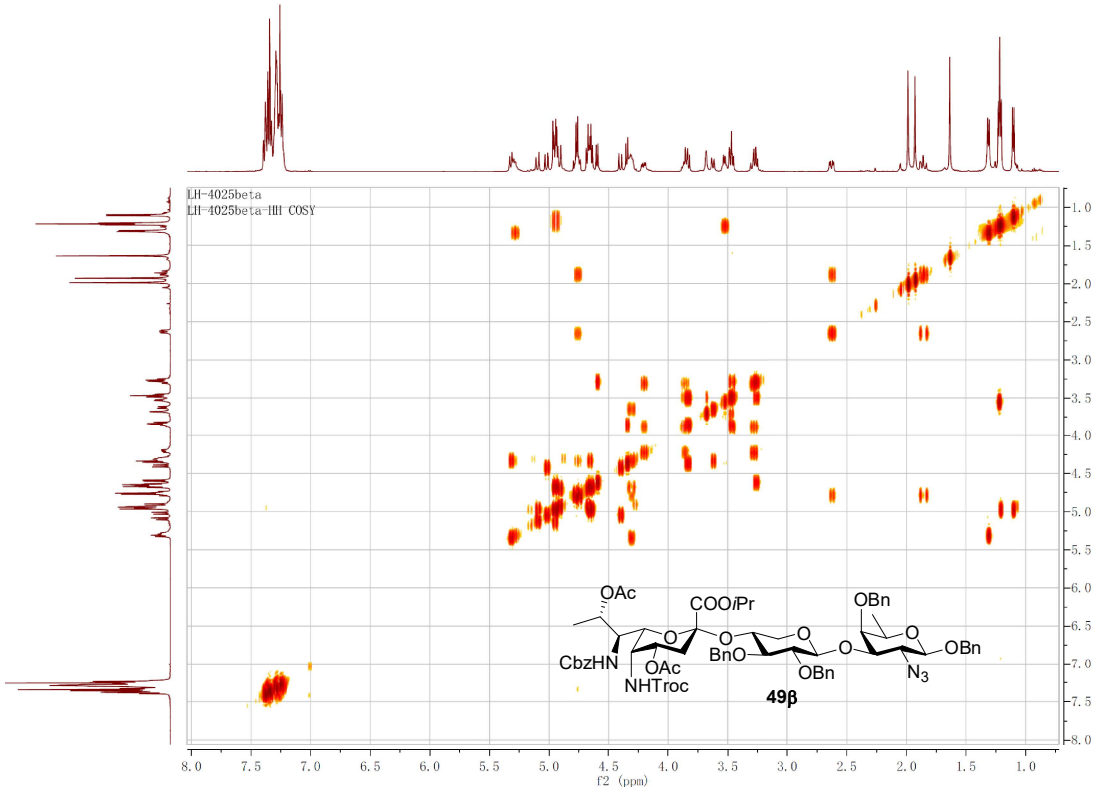
^{1}H NMR of compound 49β



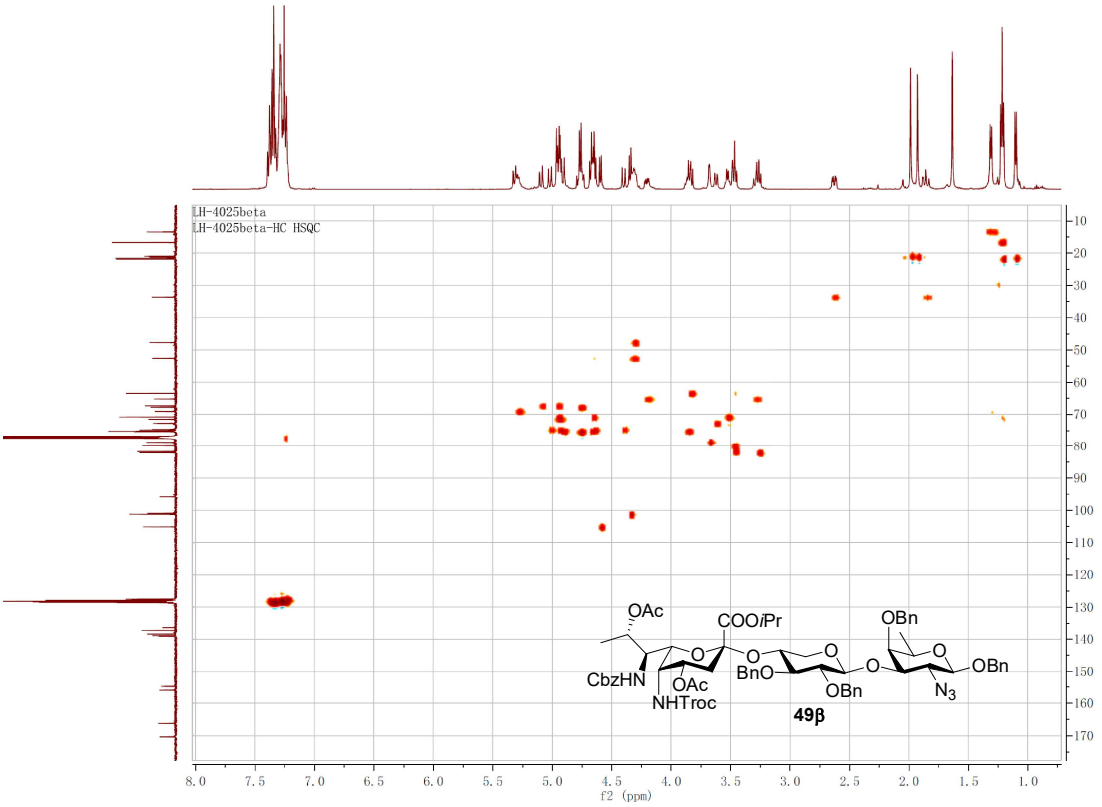
^{13}C NMR of compound 49β



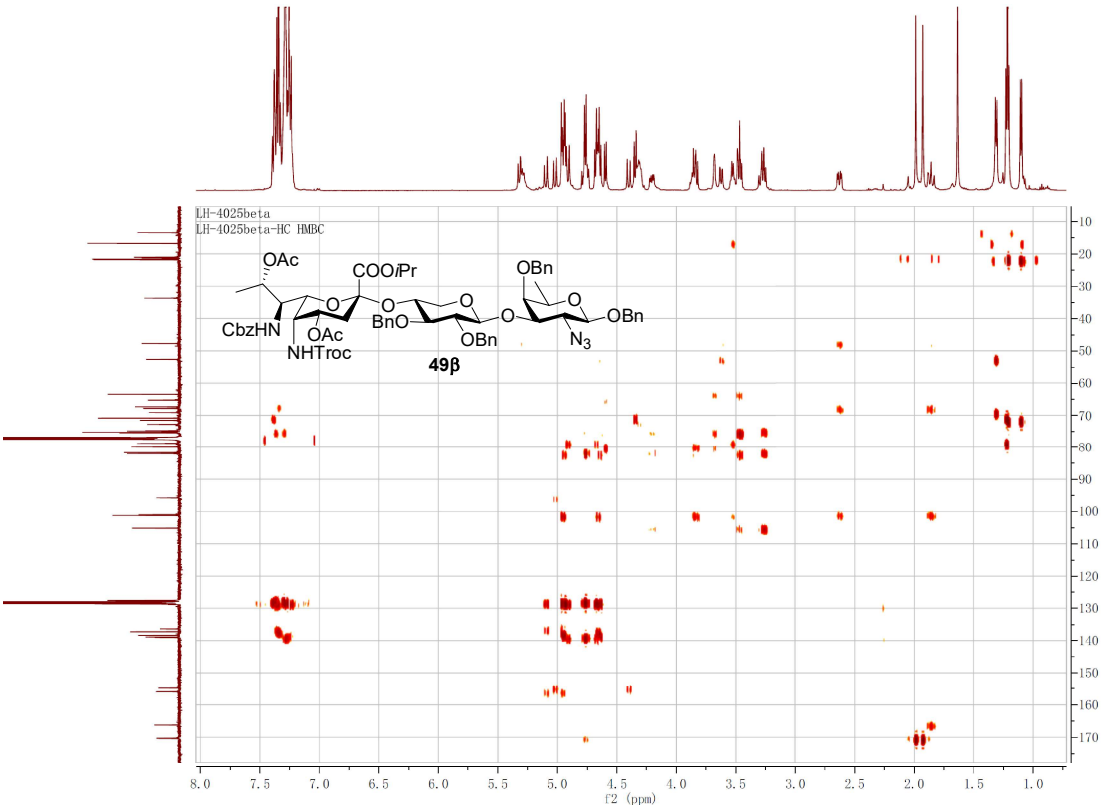
^{1}H-^{1}H COSY of compound 49β



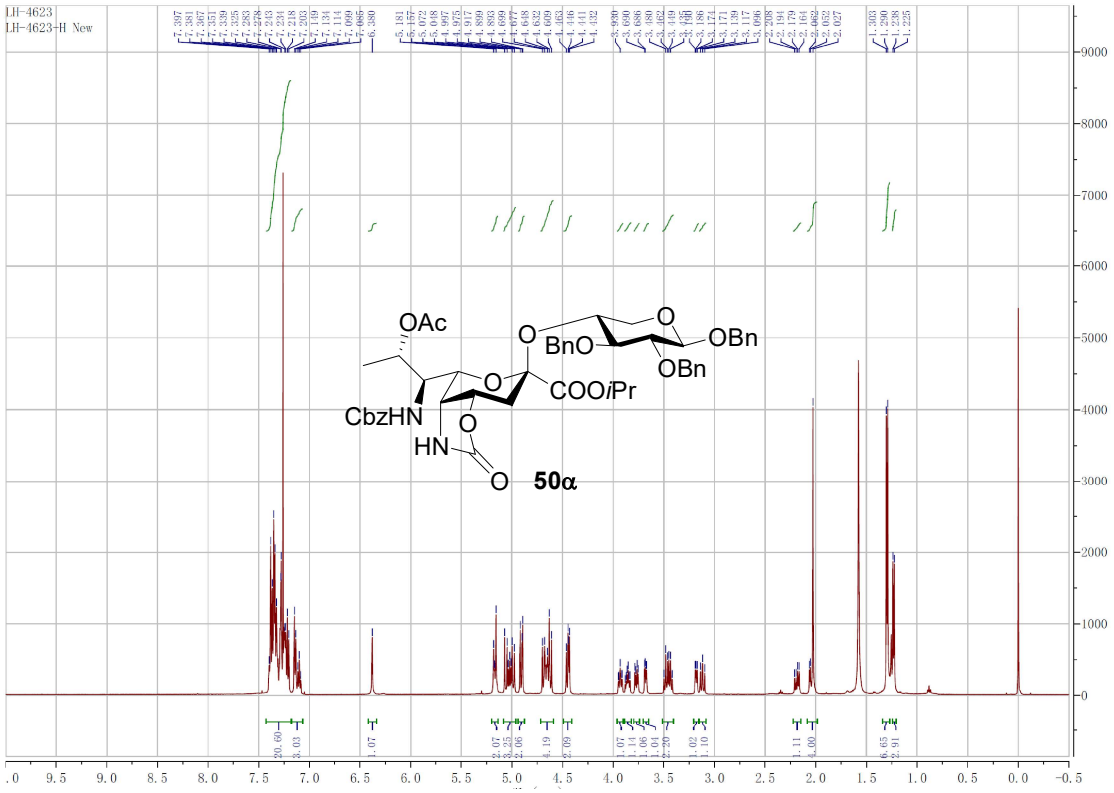
^{1}H-^{13}C HSQC of compound 49β



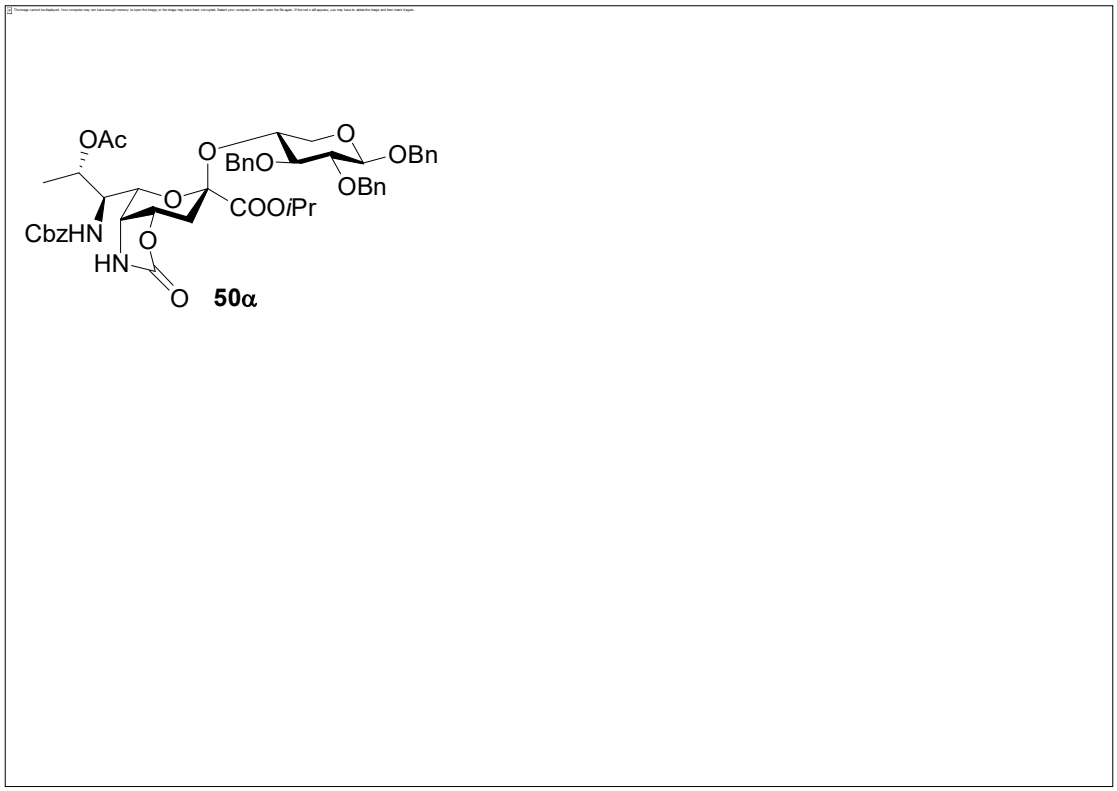
^{1}H-^{13}C HMBC of compound 49β



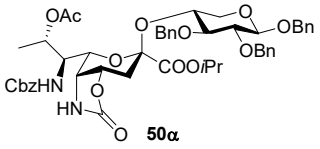
^{1}H NMR of compound 50α



^{13}C NMR of compound 50α

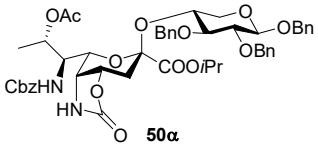


^{1}H-^{1}H COSY of compound 50α



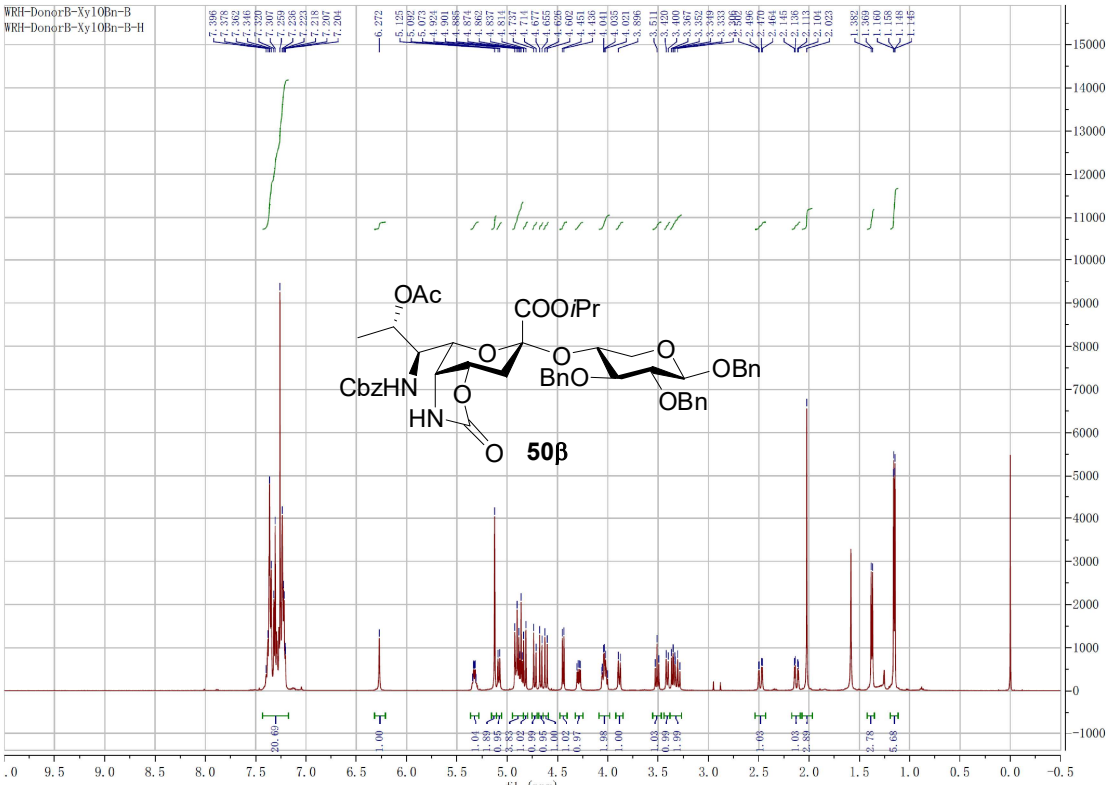
50α

^{1}H-^{13}C HSQC of compound 50α

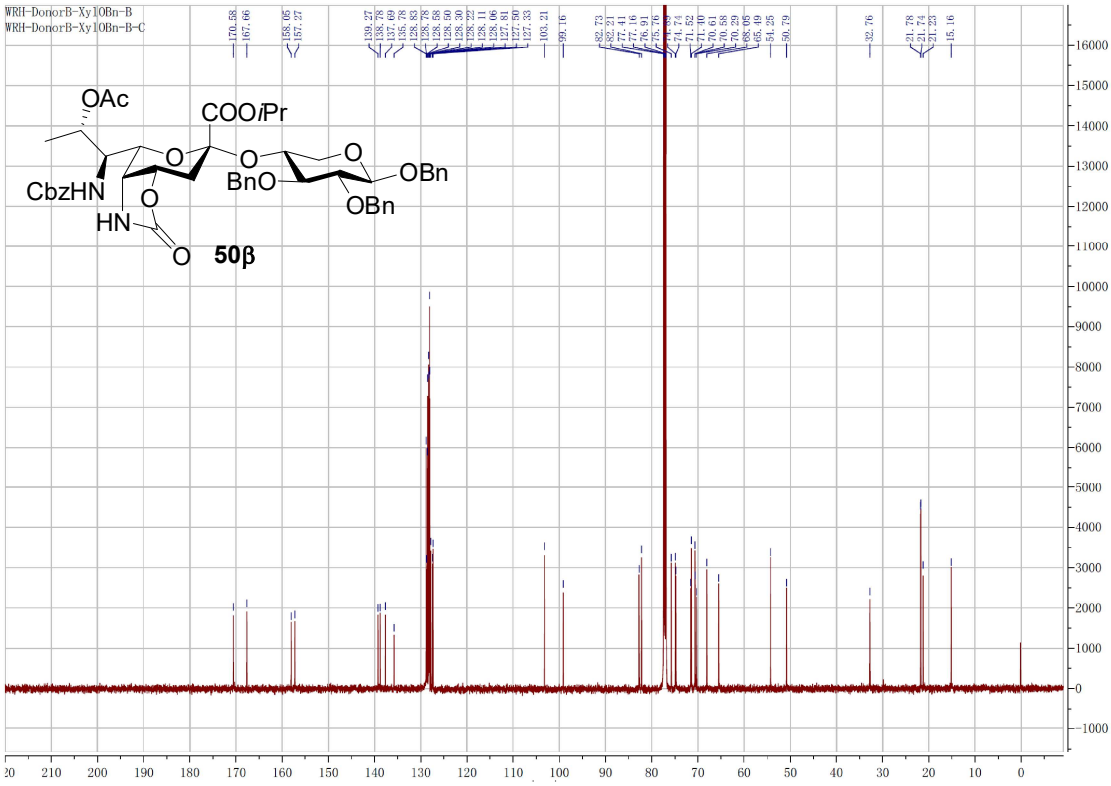


50α

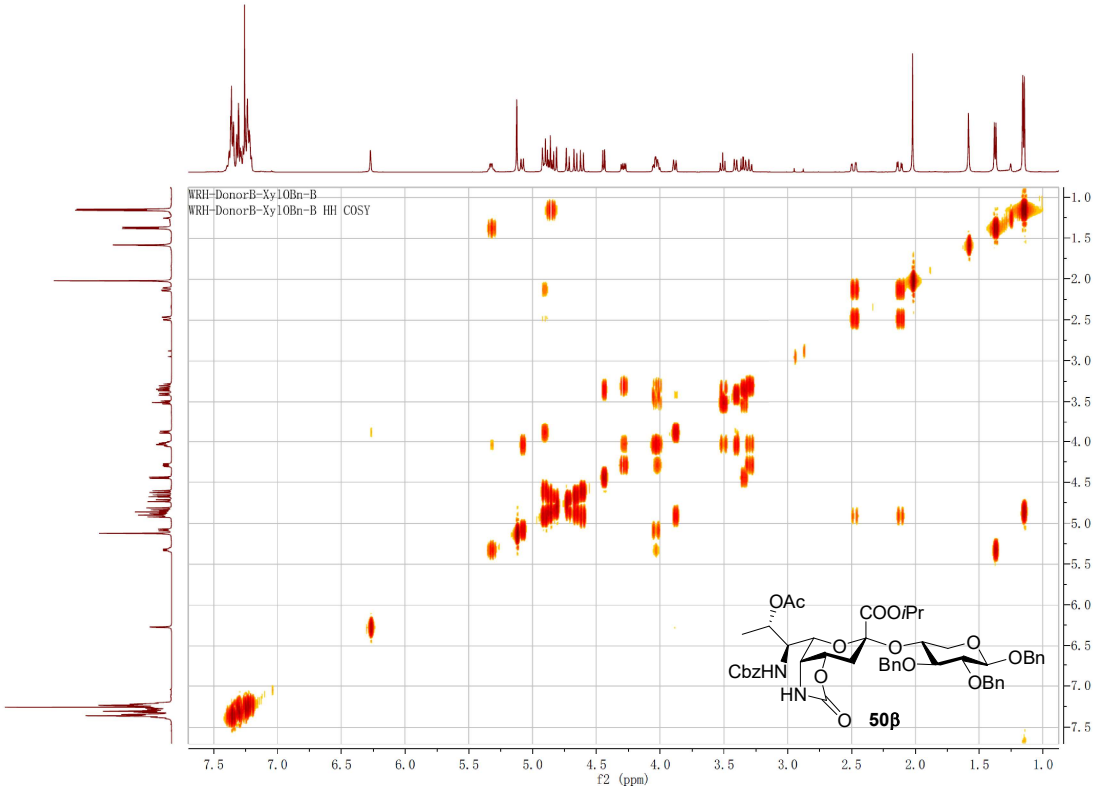
^{1}H NMR of compound 50β



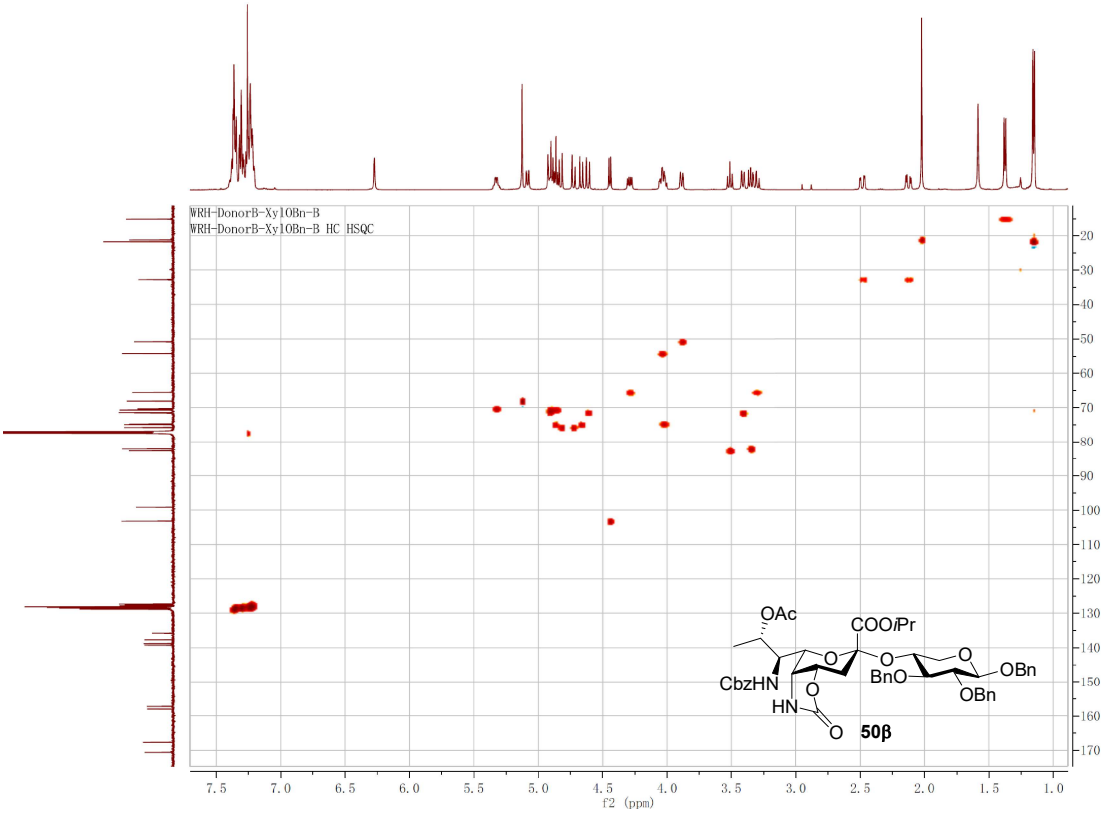
^{13}C NMR of compound 50β



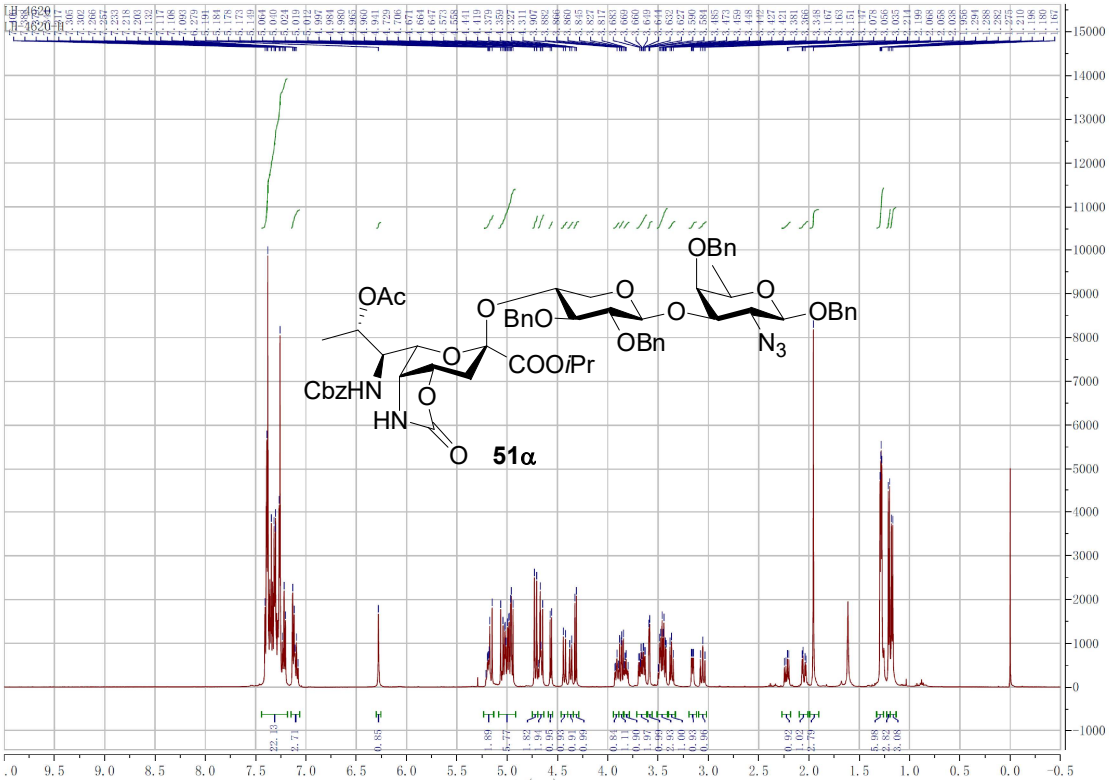
^{1}H-^{1}H COSY of compound 50β



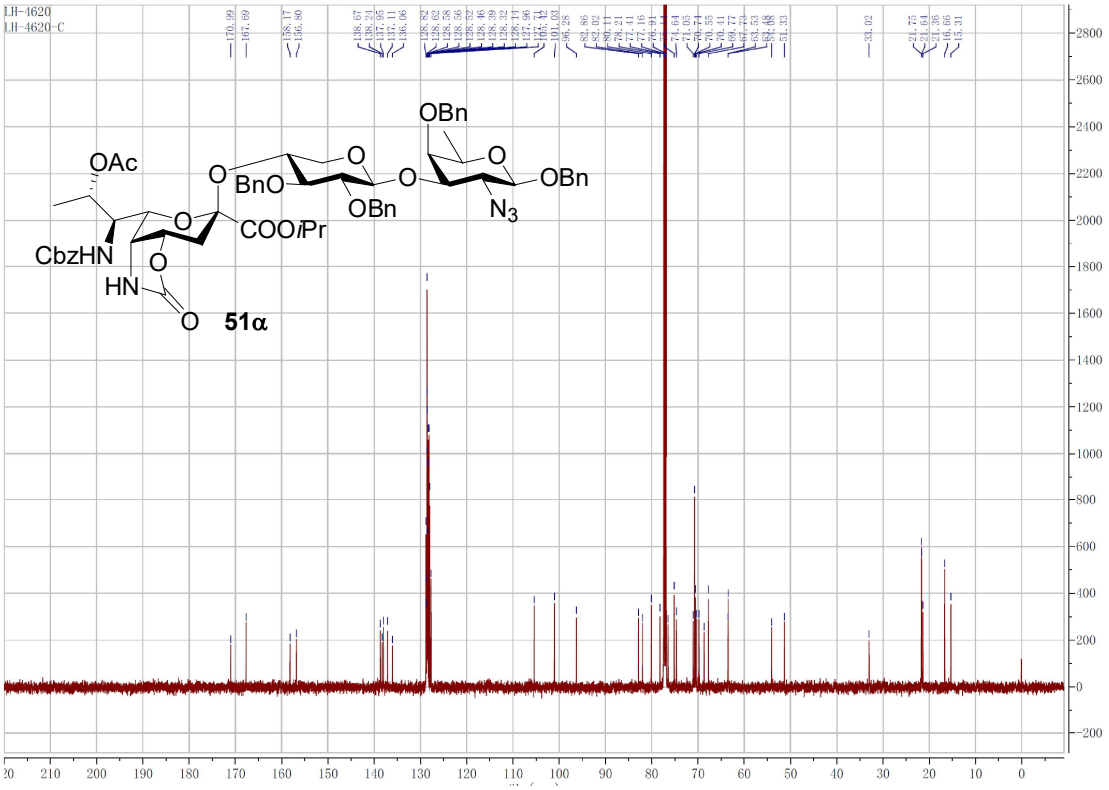
^{1}H-^{13}C HSQC of compound 50β



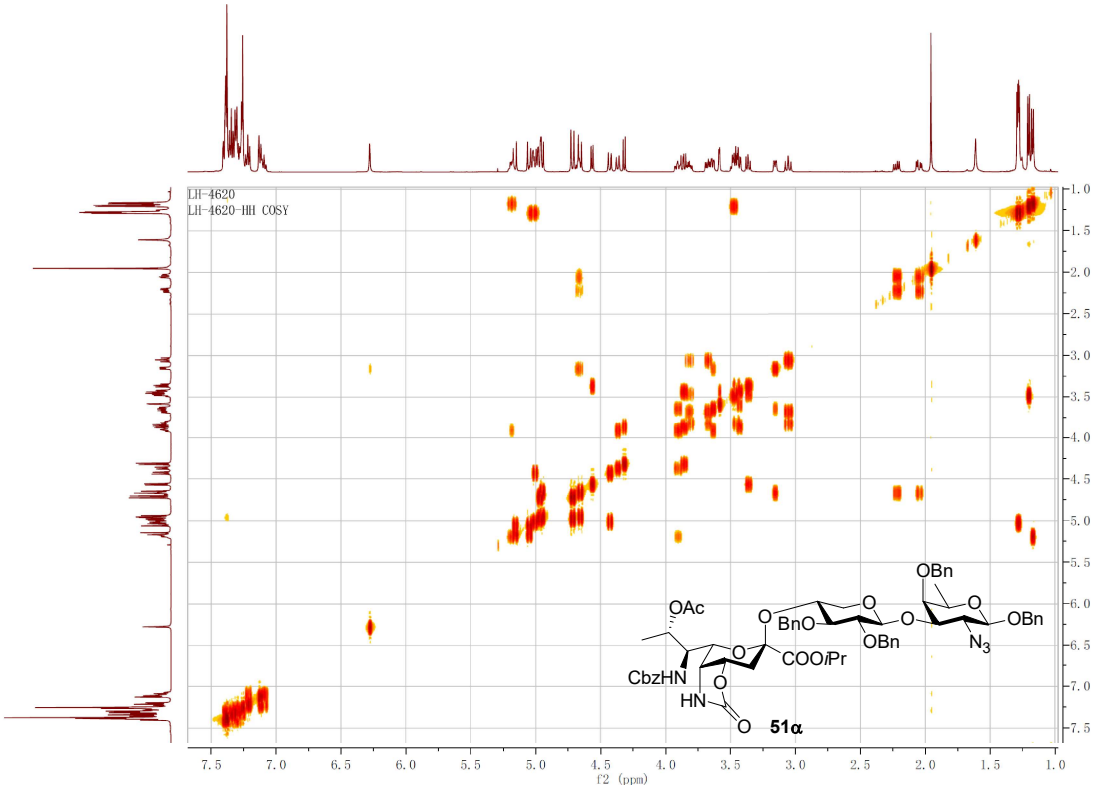
^{1}H NMR of compound 51α



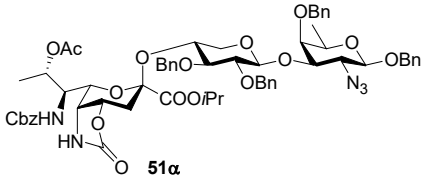
^{13}C NMR of compound 51α



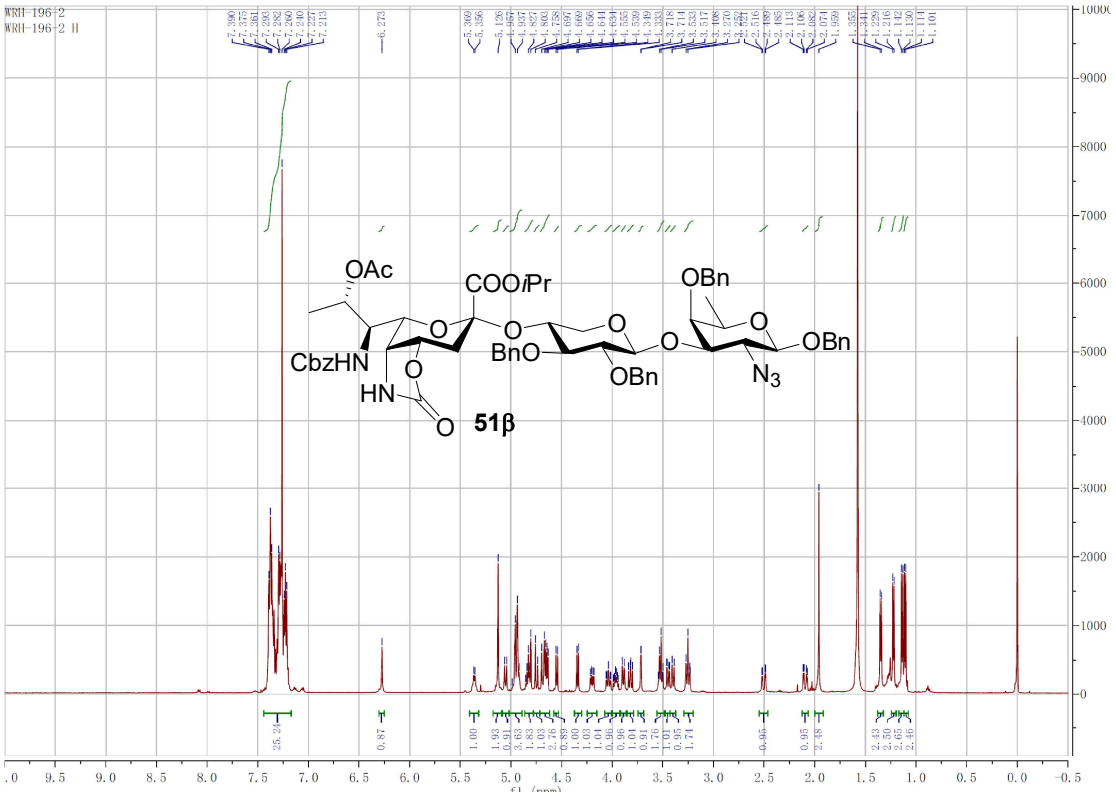
^{1}H-^{1}H COSY of compound 51α



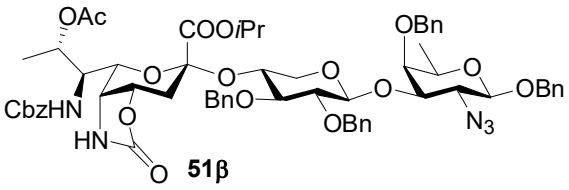
^{1}H-^{13}C HSQC of compound 51α



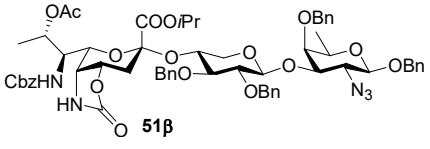
^{1}H NMR of compound 51β



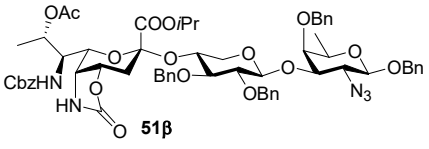
^{13}C NMR of compound 51β



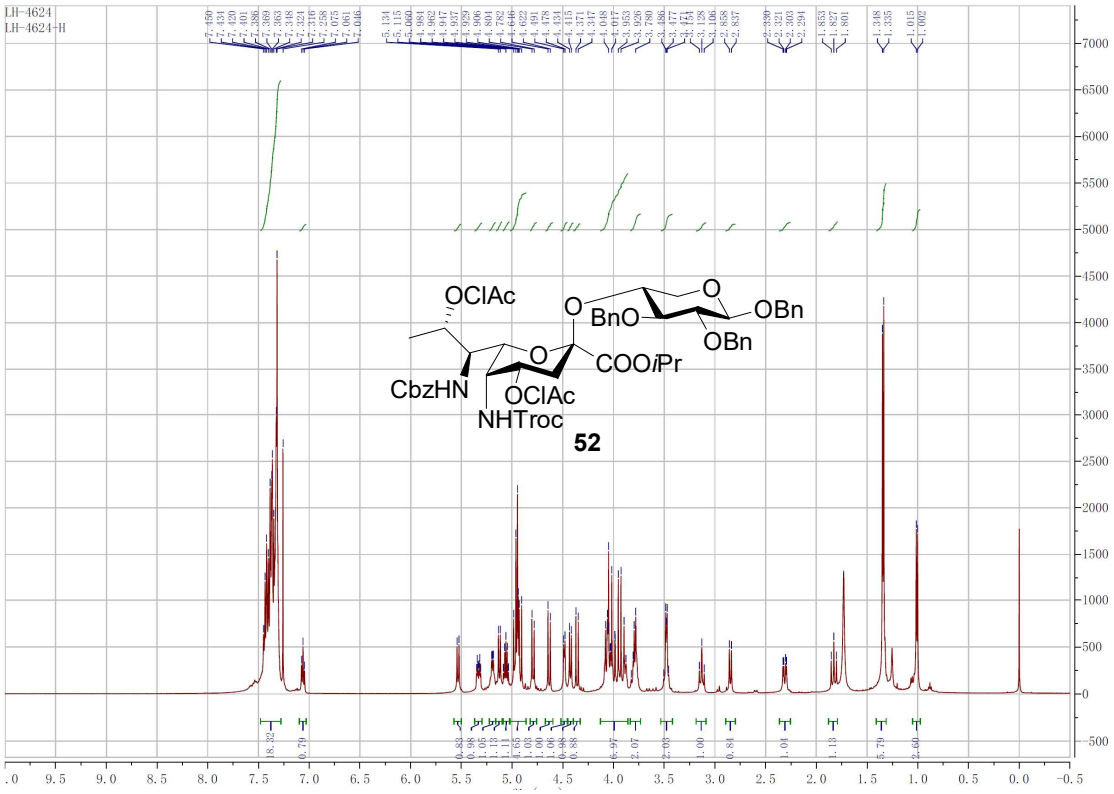
^{1}H-^{1}H COSY of compound 51β



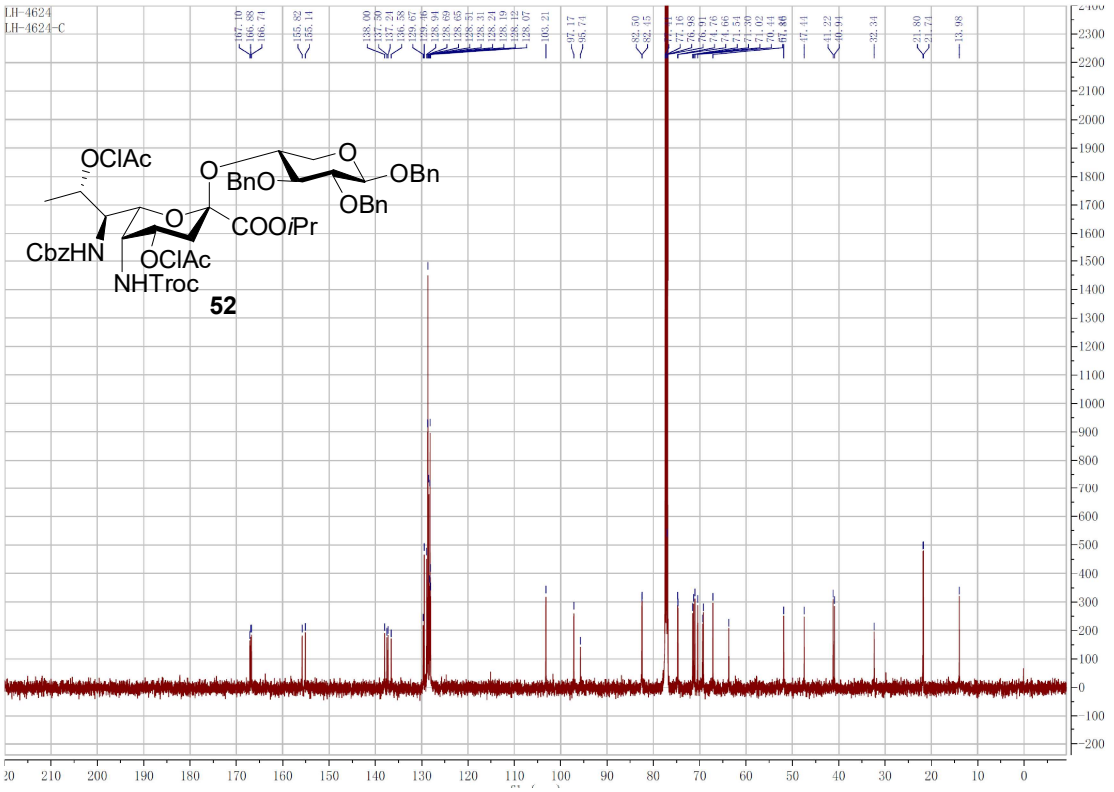
^{1}H-^{13}C HSQC of compound 51β



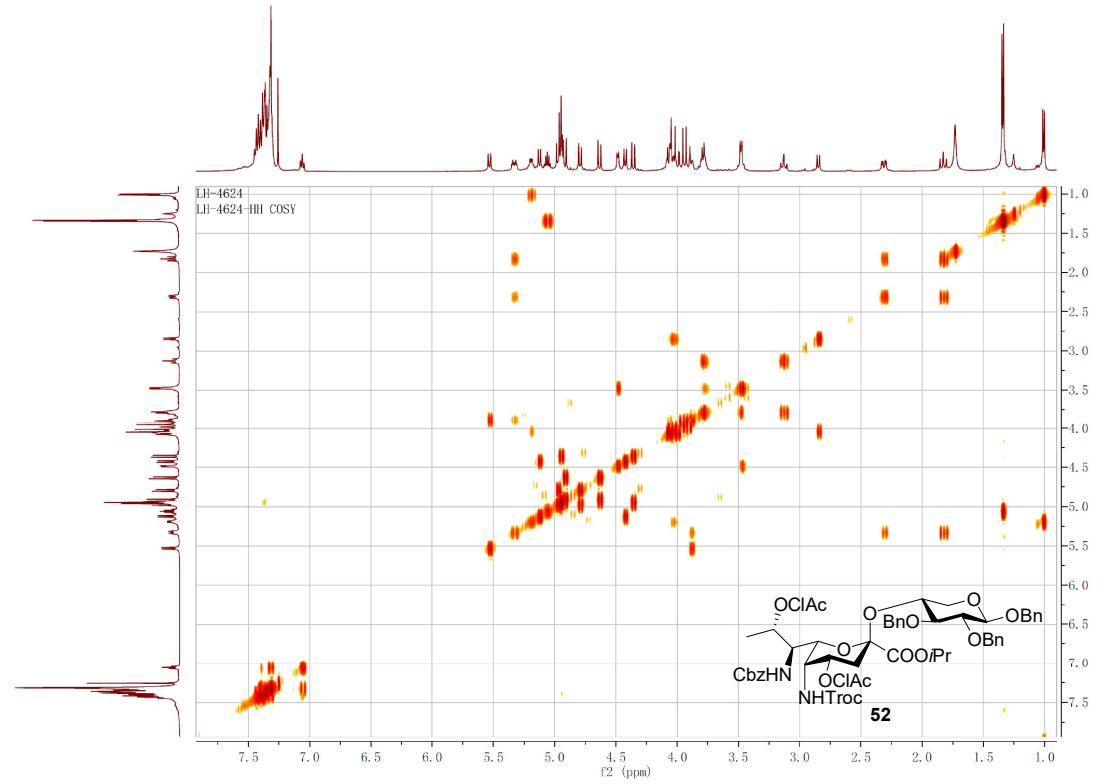
^{1}H NMR of compound 52



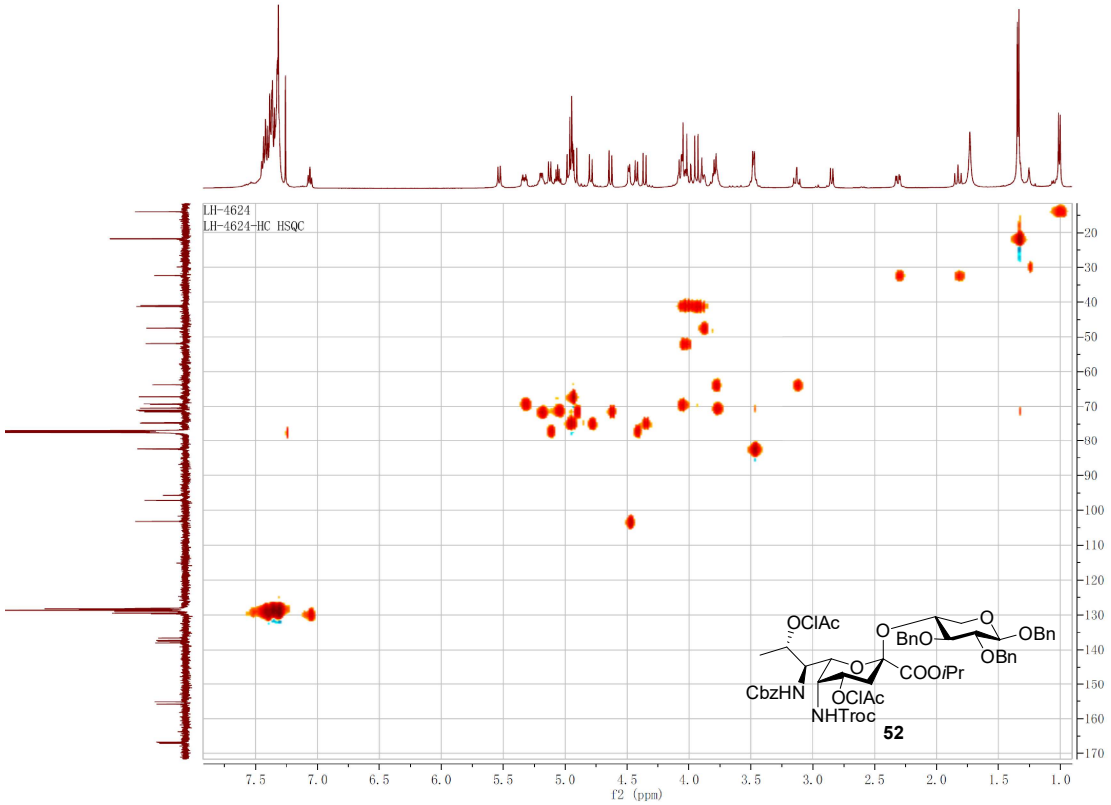
^{13}C NMR of compound 52



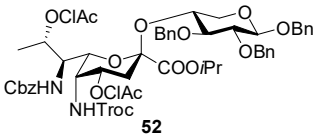
^{1}H-^{1}H COSY of compound 52



^{1}H-^{13}C HSQC of compound 52

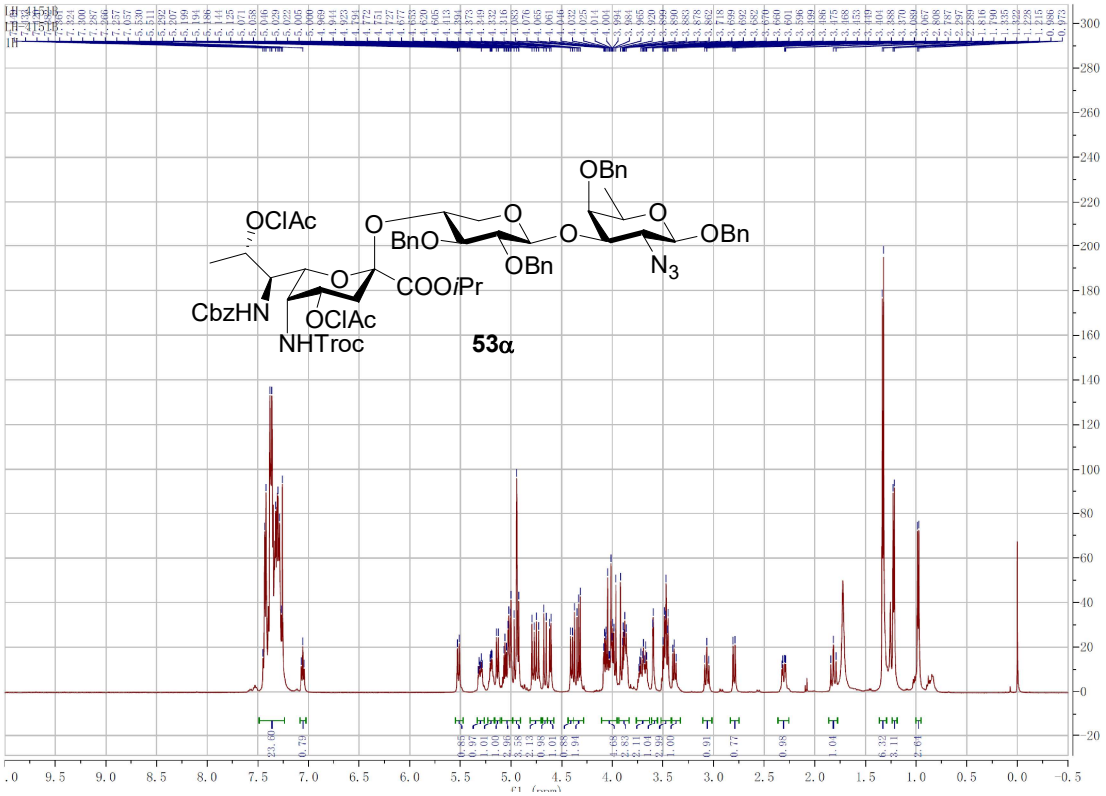


^{1}H-^{13}C HMBC of compound 52



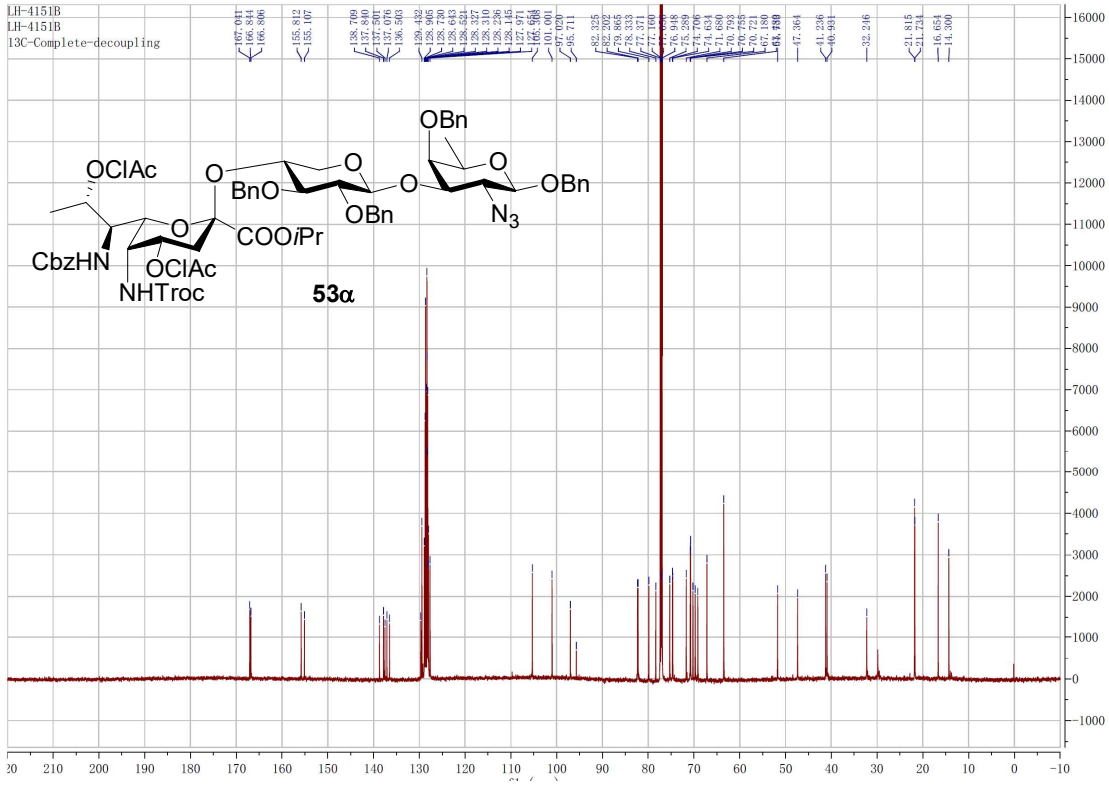
52

^{1}H NMR of compound 53α

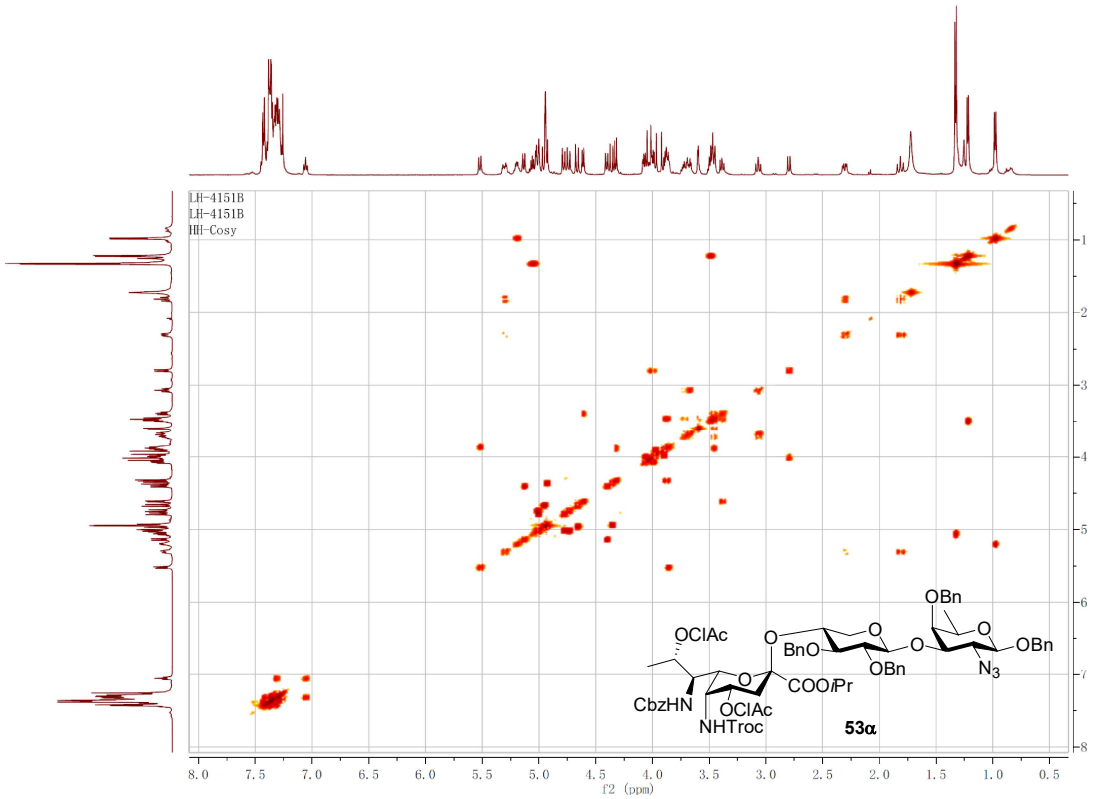


53α

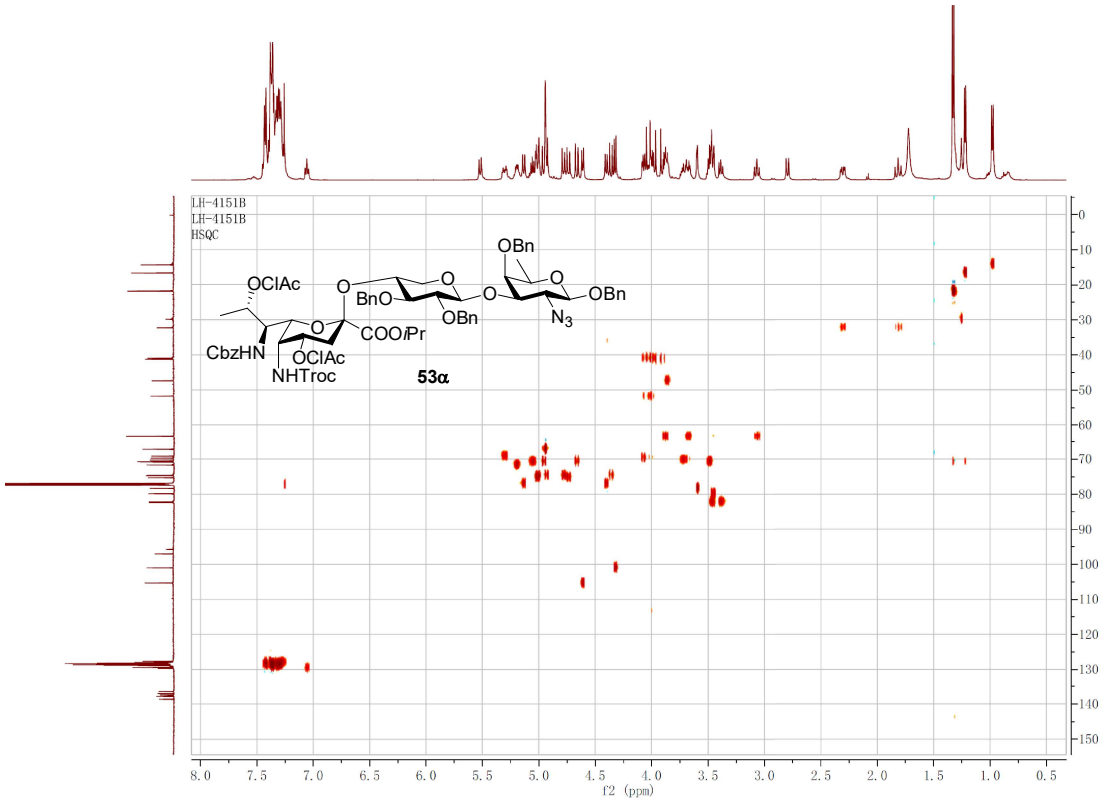
^{13}C NMR of compound 53α



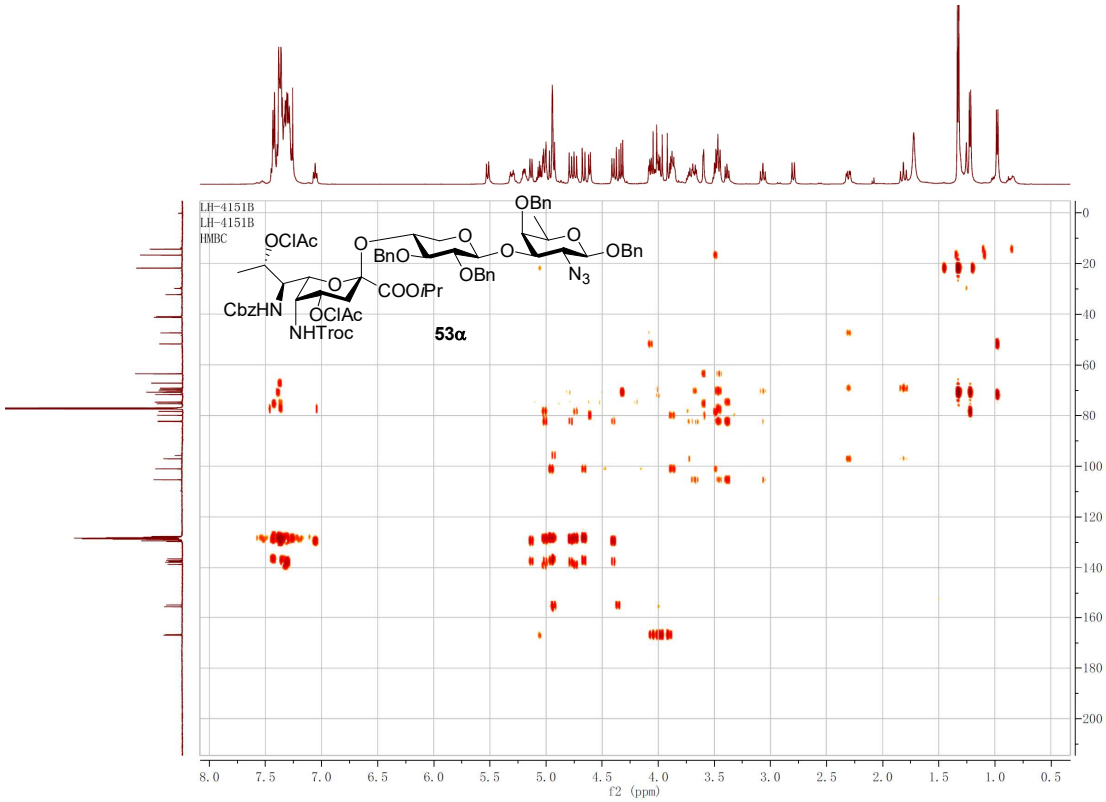
^{1}H-^{1}H COSY of compound 53α



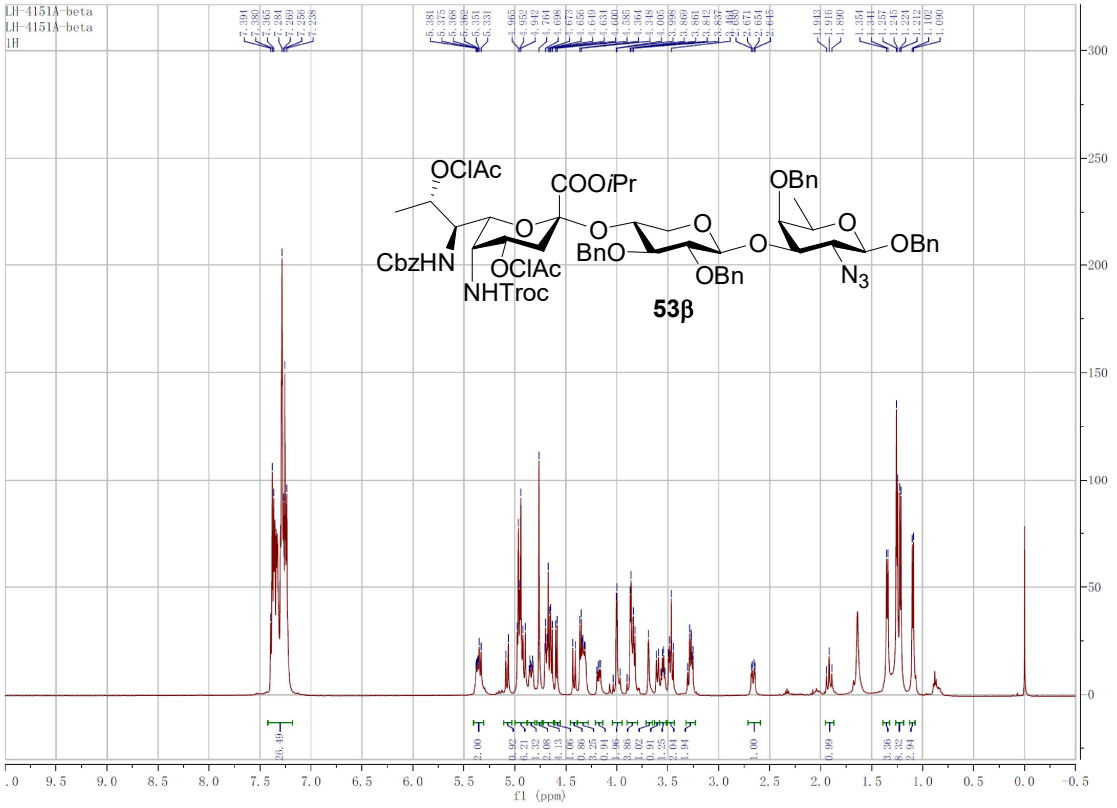
^{1}H-^{13}C HSQC of compound 53α



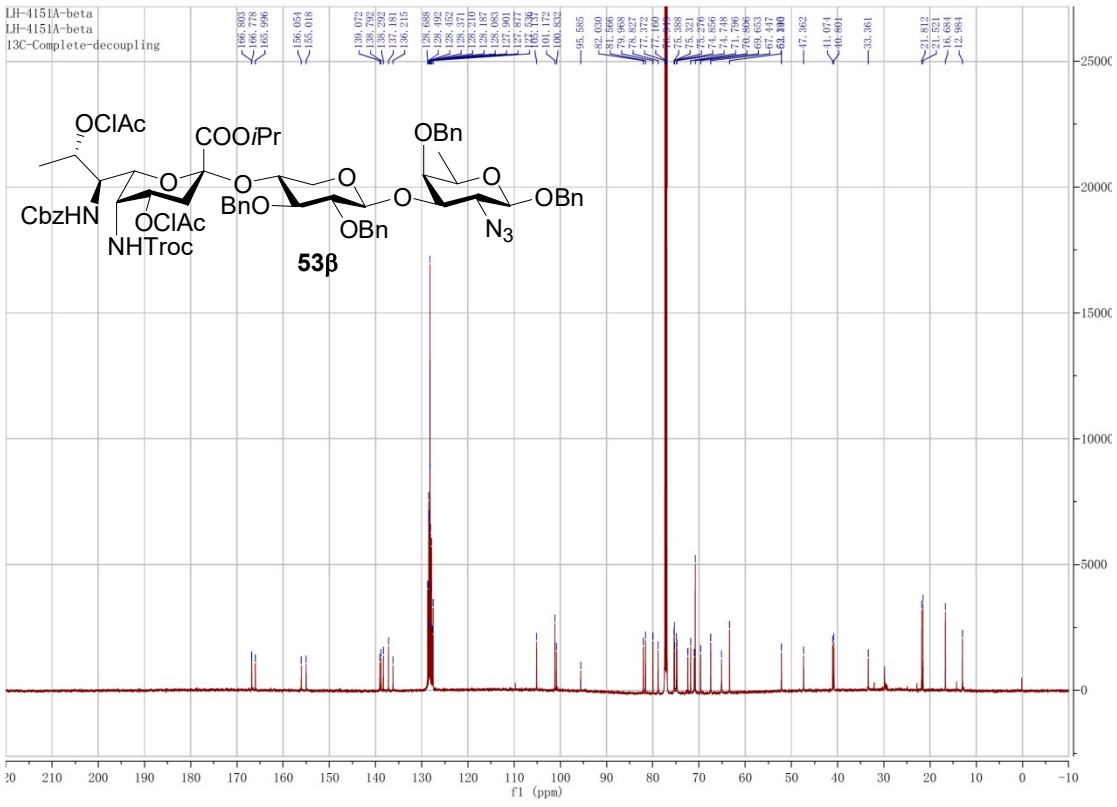
^{1}H-^{13}C HMBC of compound 53α



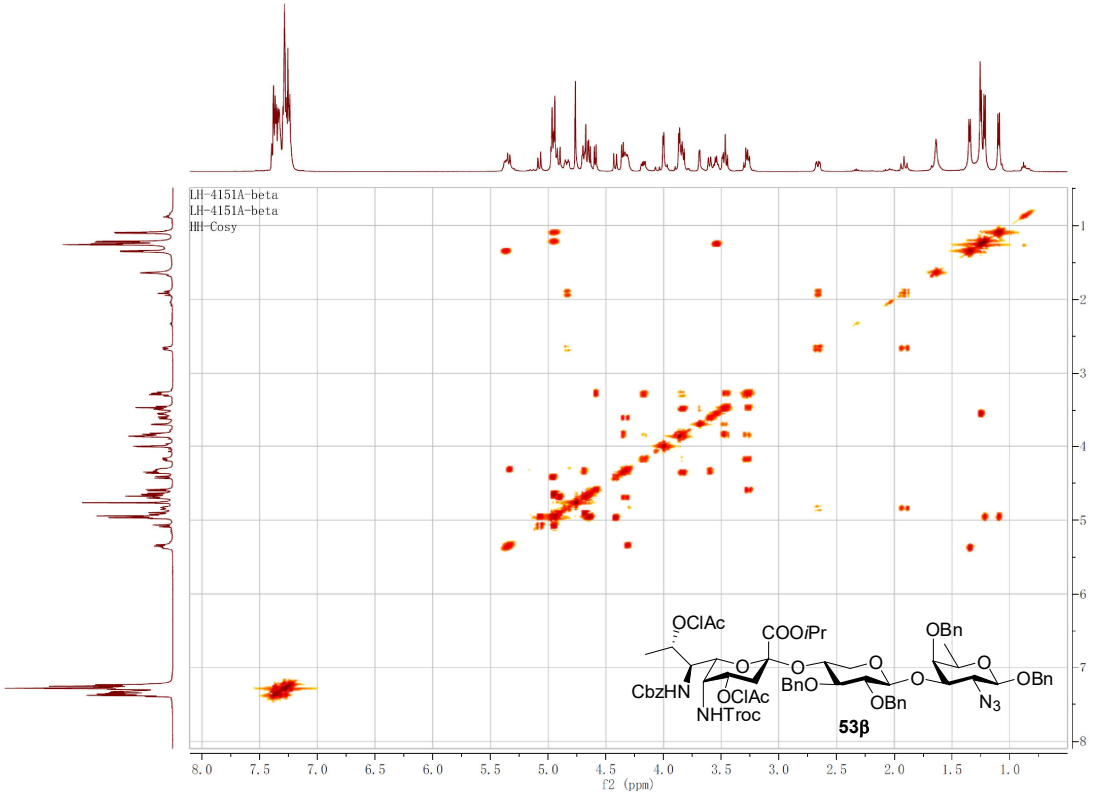
^{1}H NMR of compound 53β



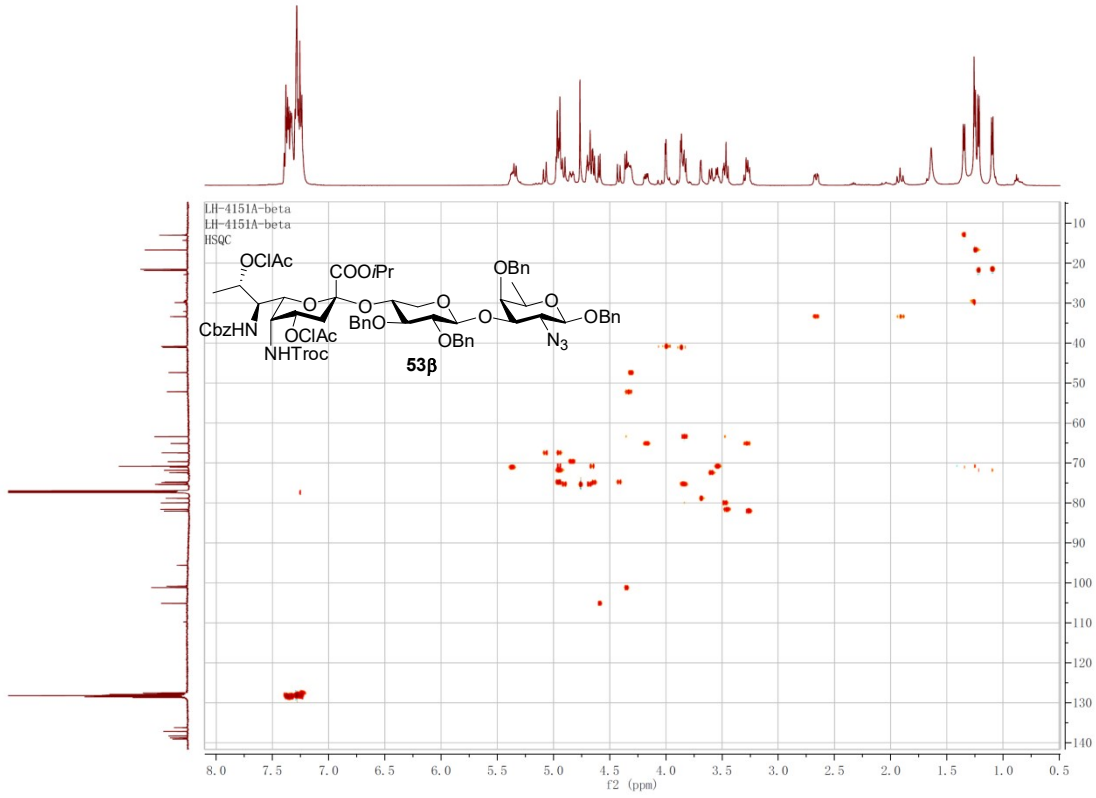
^{13}C NMR of compound 53β



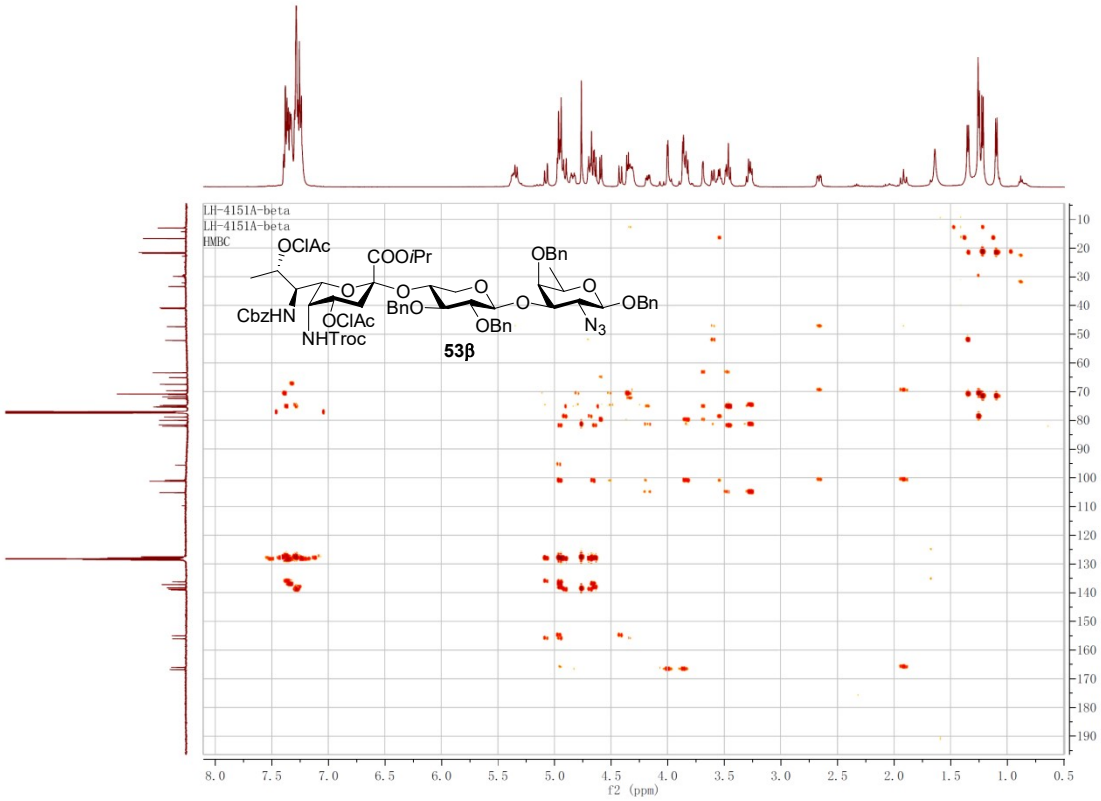
^{1}H-^{1}H COSY of compound 53β



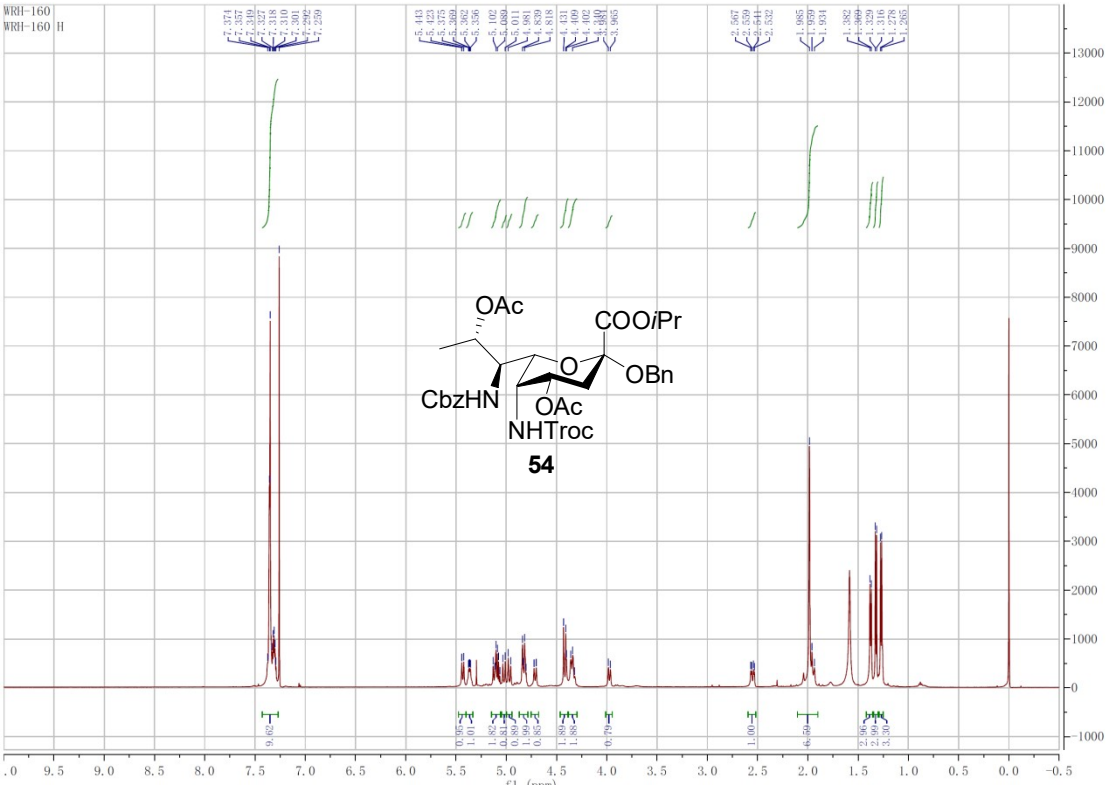
^{1}H-^{13}C HSQC of compound 53β



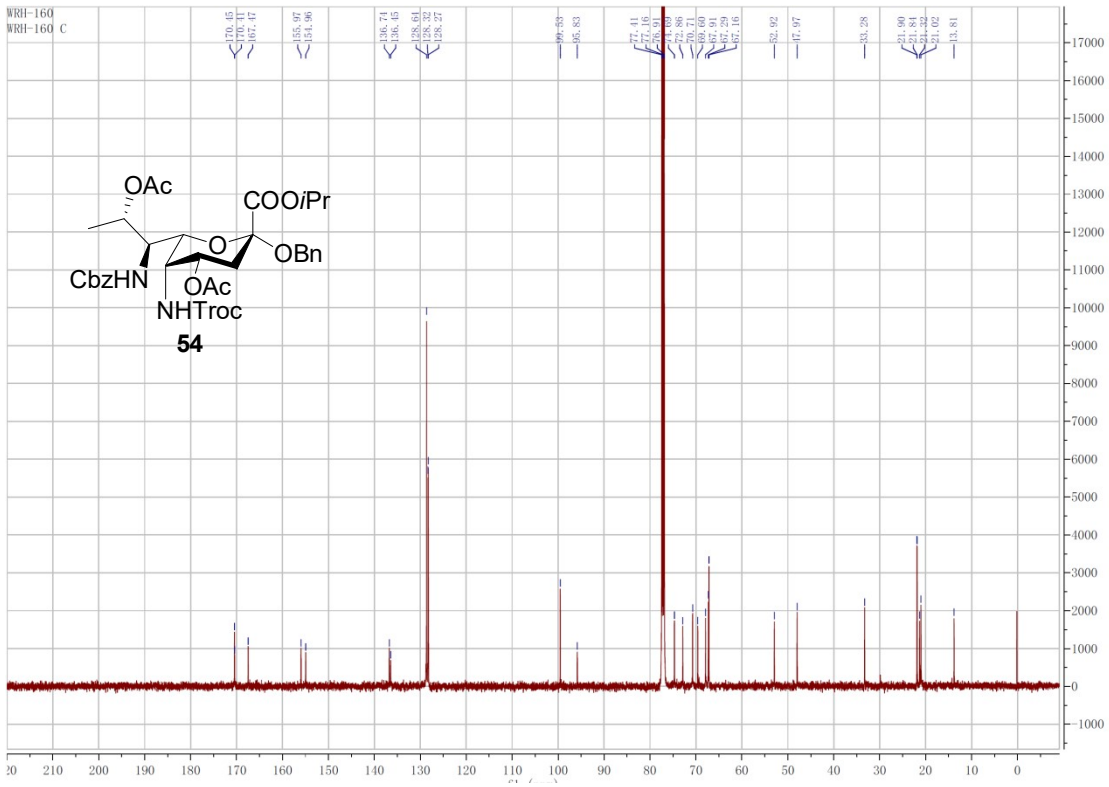
^{1}H-^{13}C HMBC of compound 53β



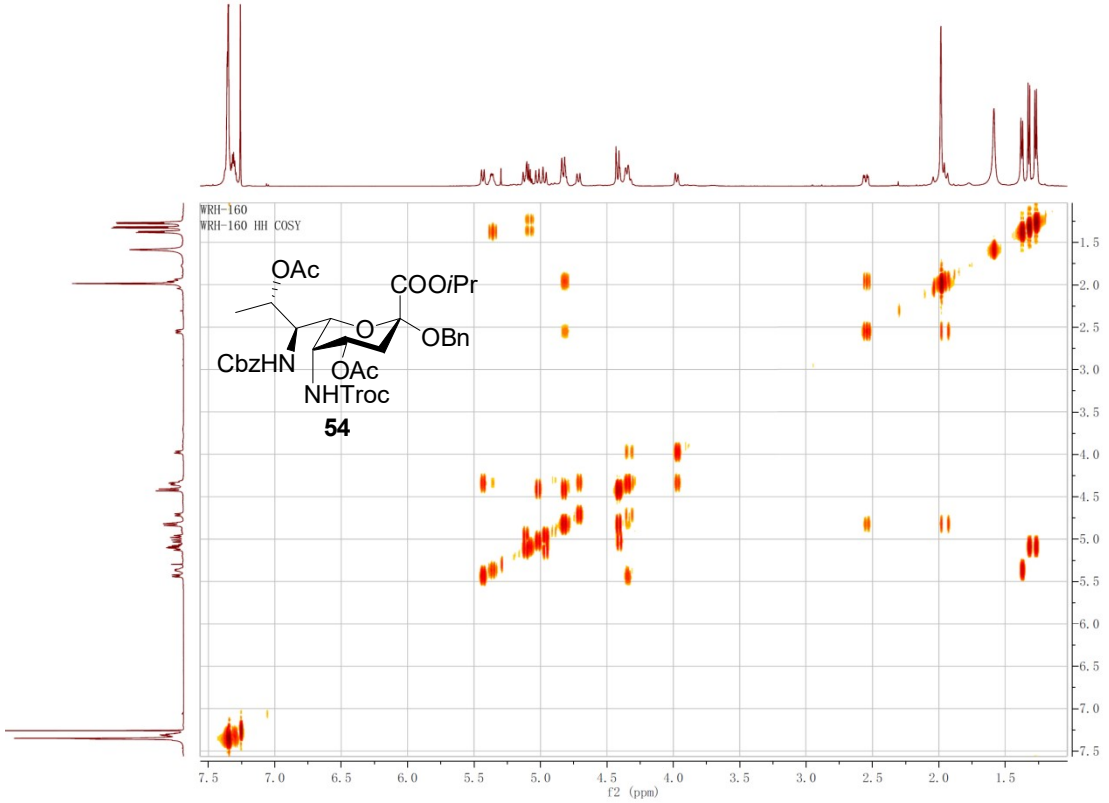
^{1}H NMR of compound 54



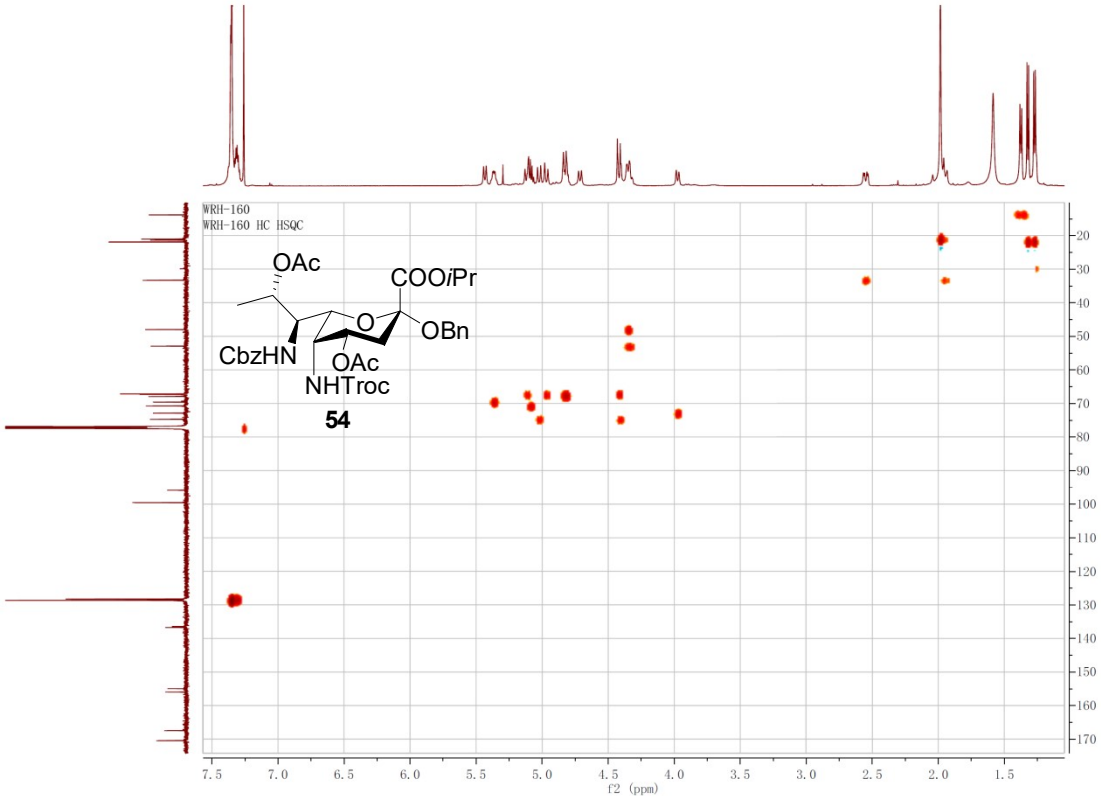
^{13}C NMR of compound 54



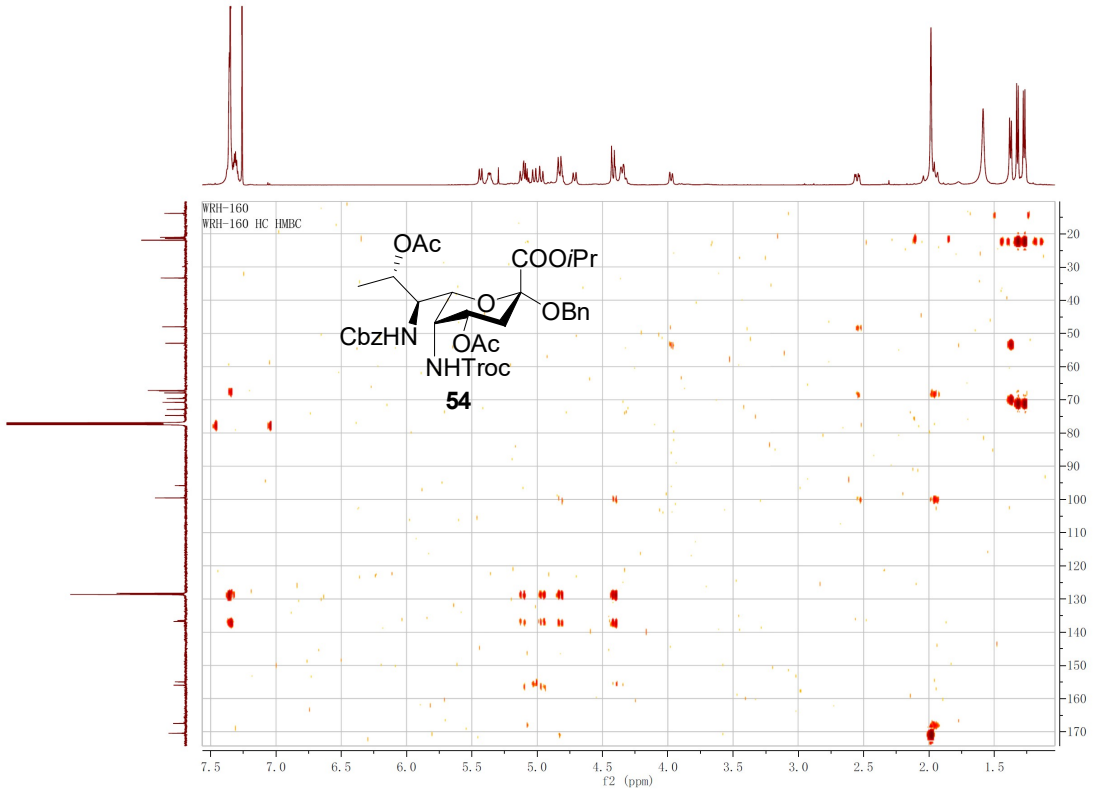
^{1}H-^{1}H COSY of compound 54



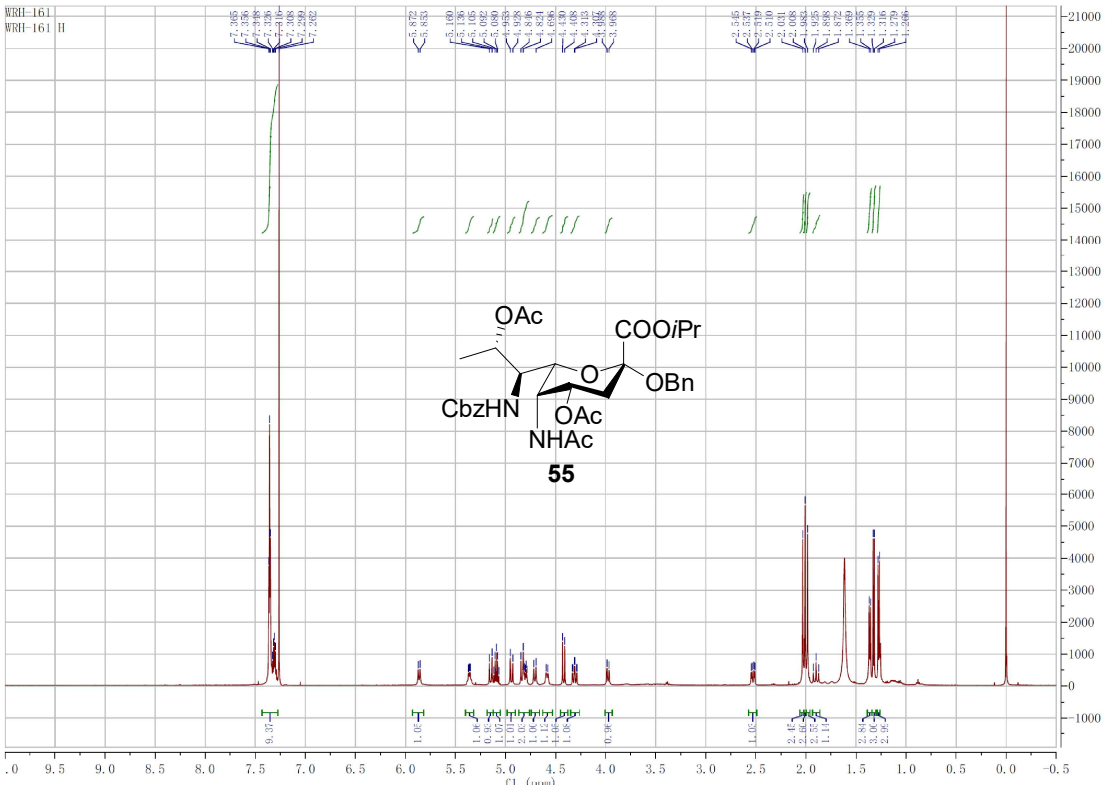
^{1}H-^{13}C HSQC of compound 54



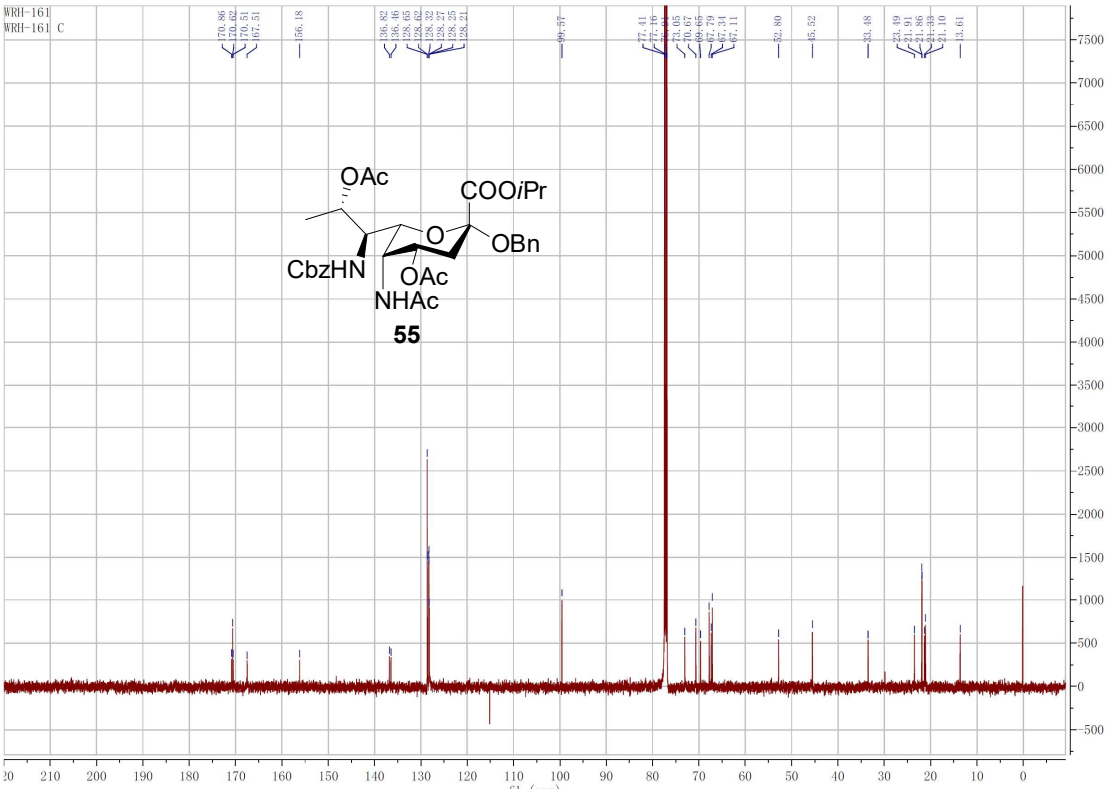
^{1}H-^{13}C HMBC of compound 54



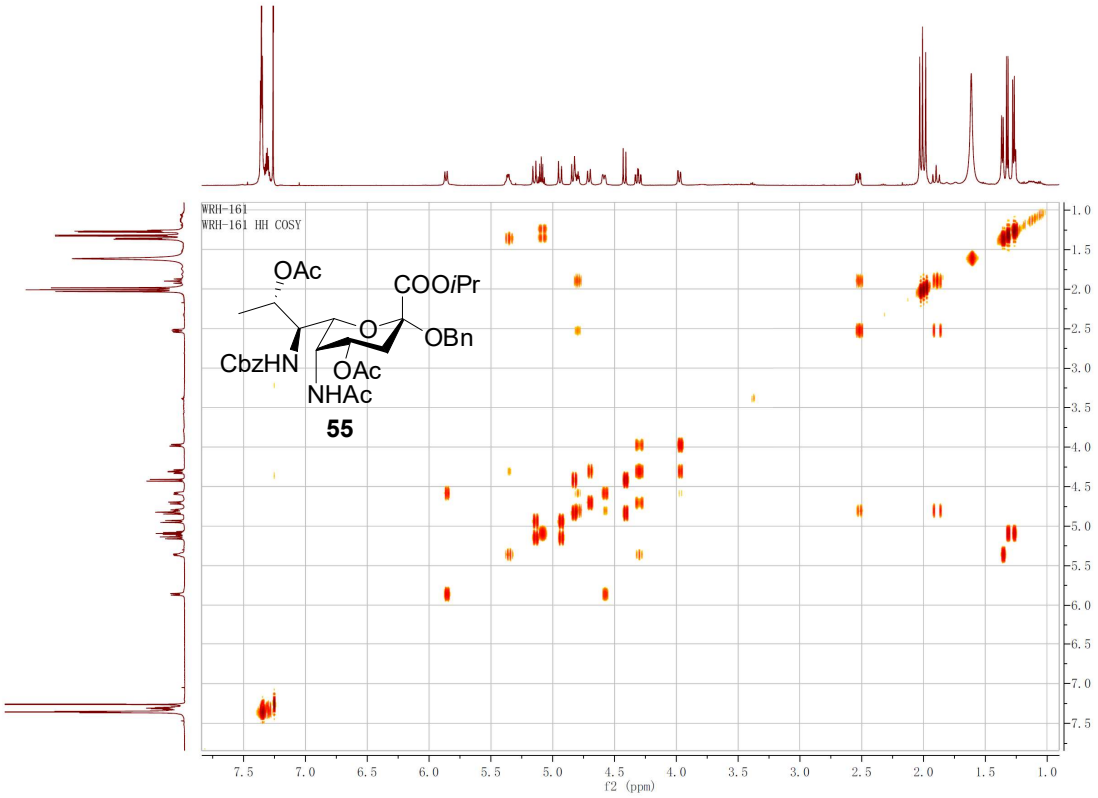
^{1}H NMR of compound 55



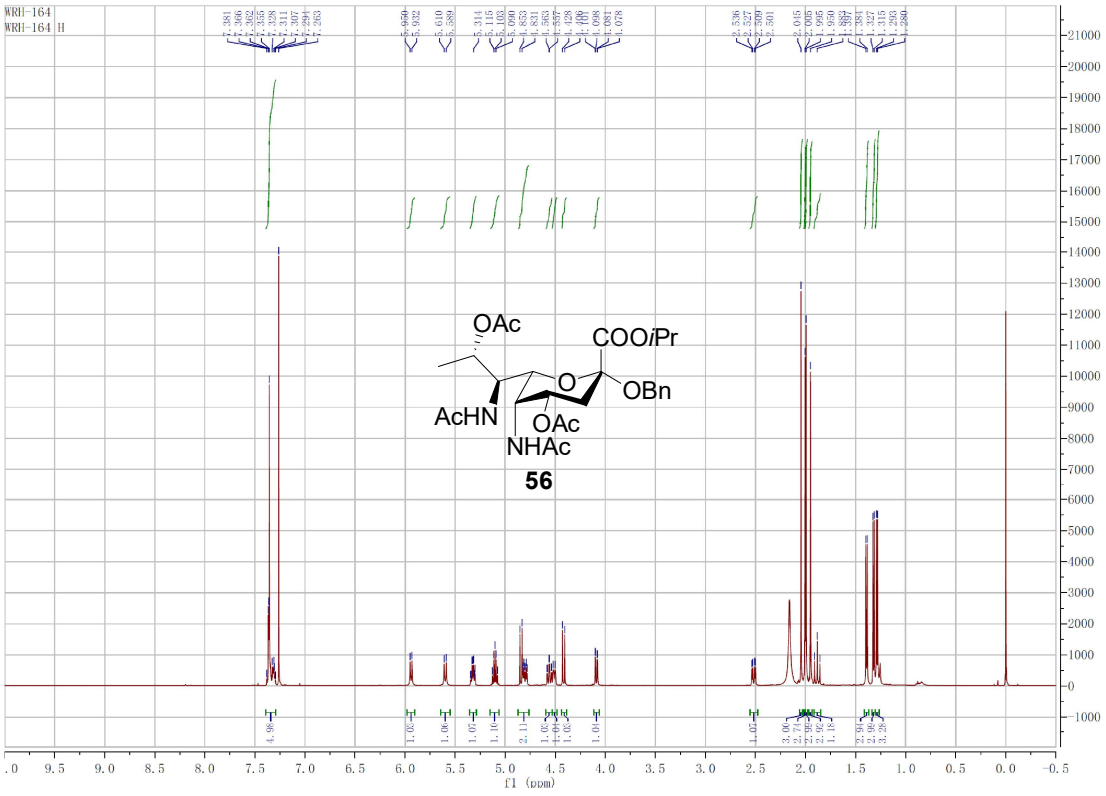
^{13}C NMR of compound 55



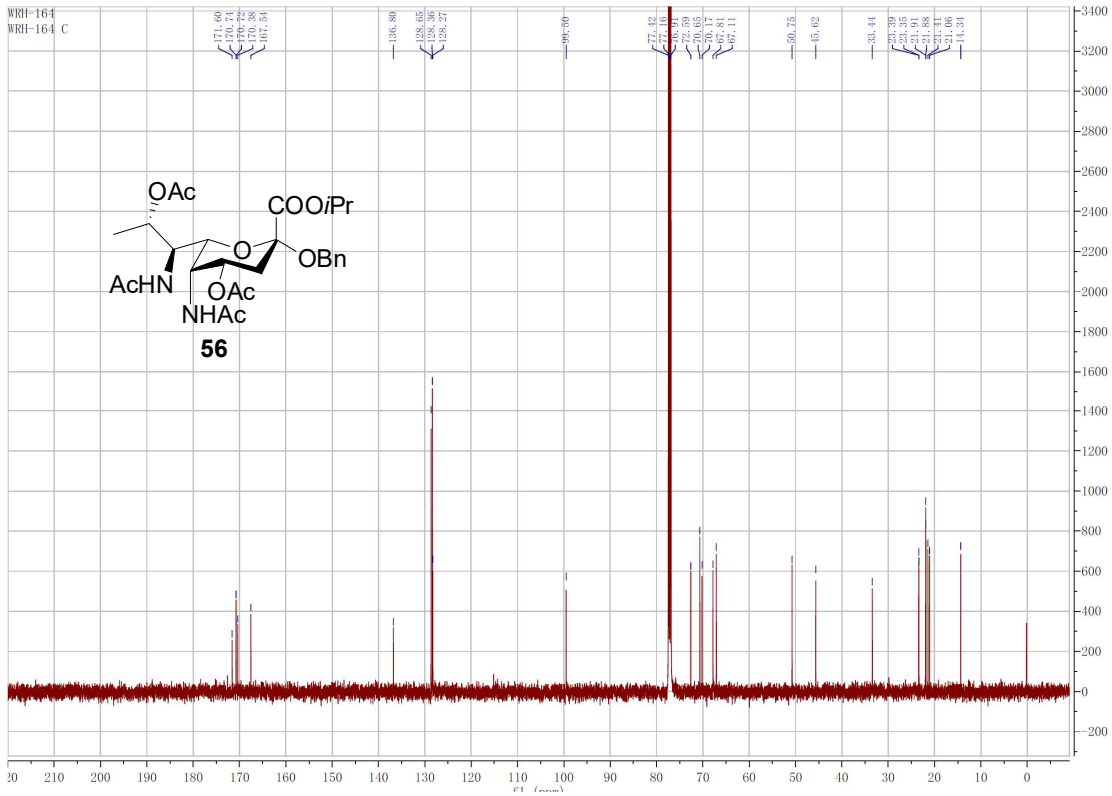
^{1}H-^{1}H COSY of compound 55



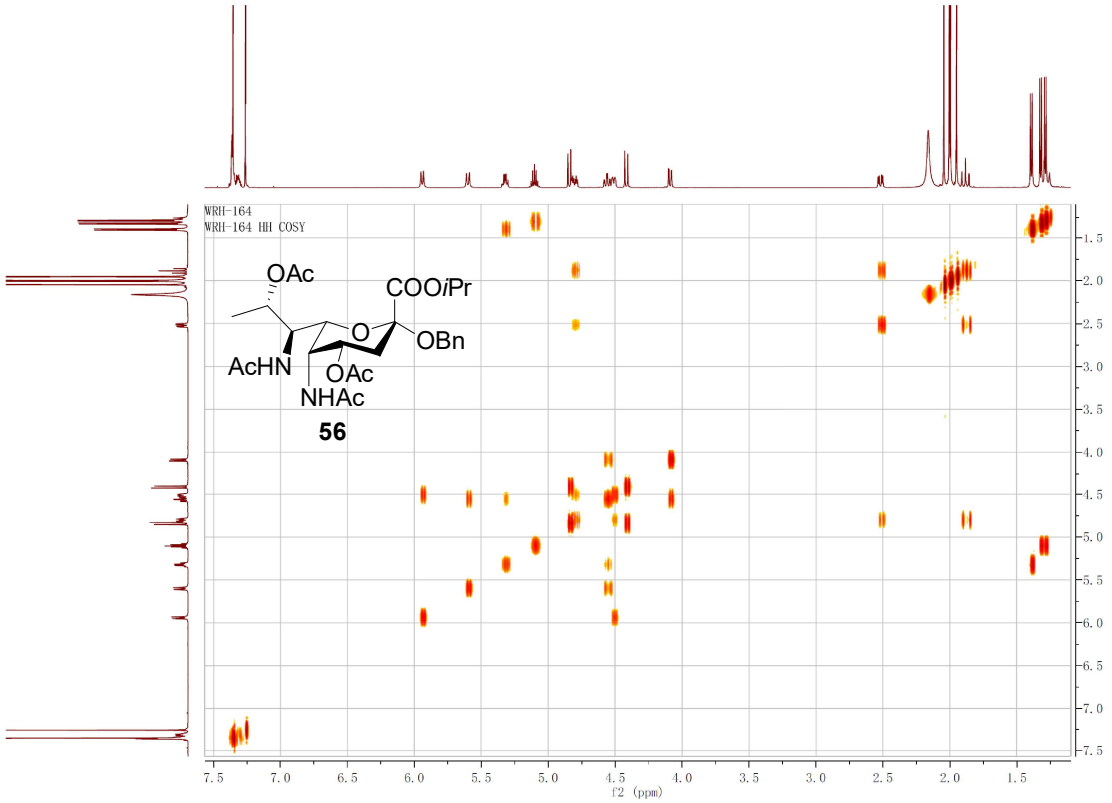
^{1}H NMR of compound 56



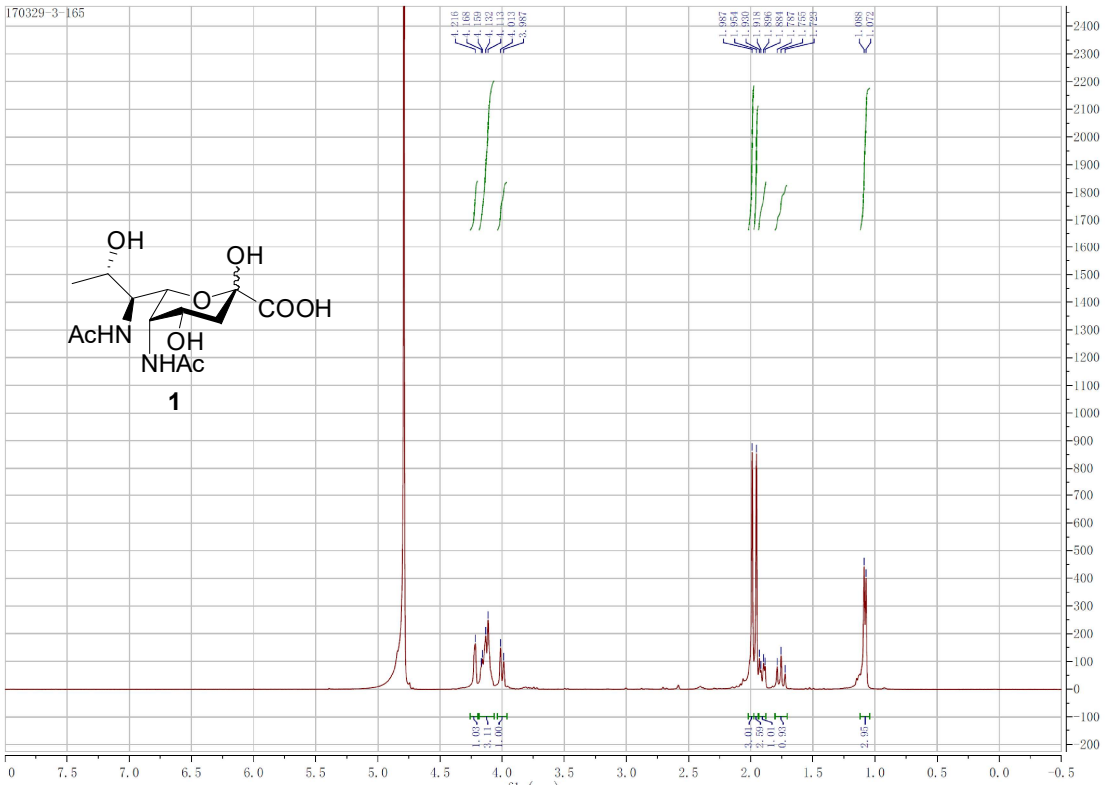
^{13}C NMR of compound 56



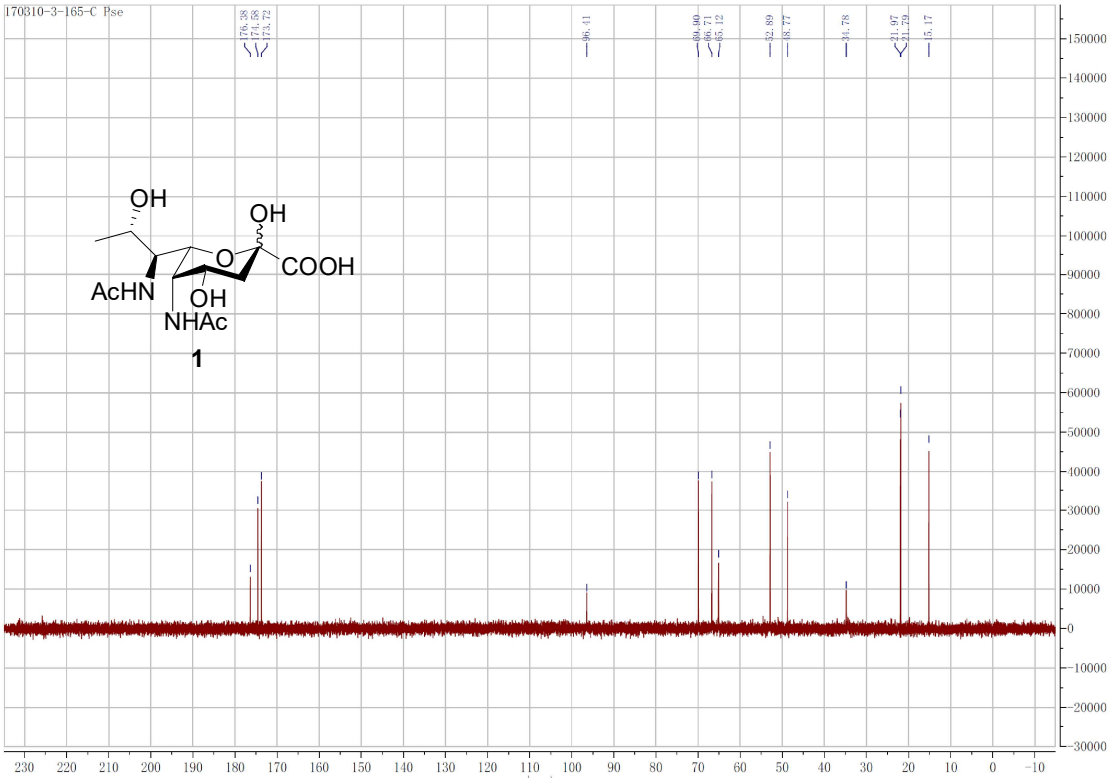
^{1}H-^{1}H COSY of compound 56



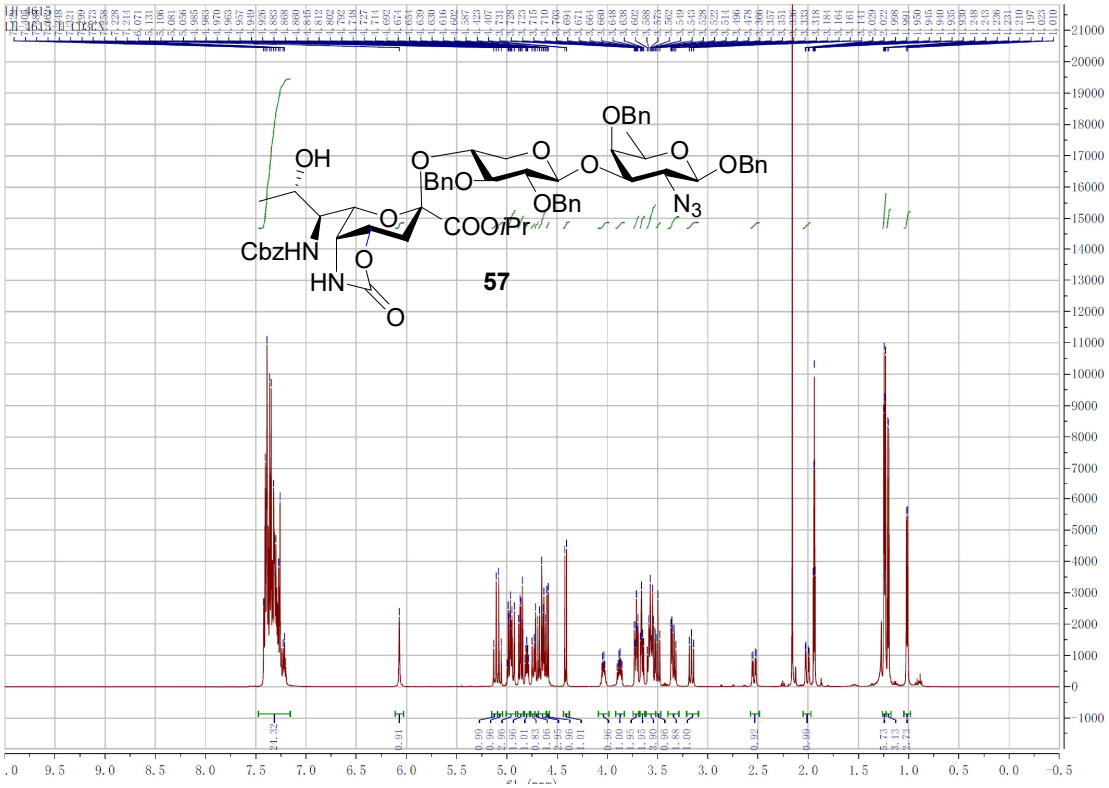
^{1}H NMR of compound 1



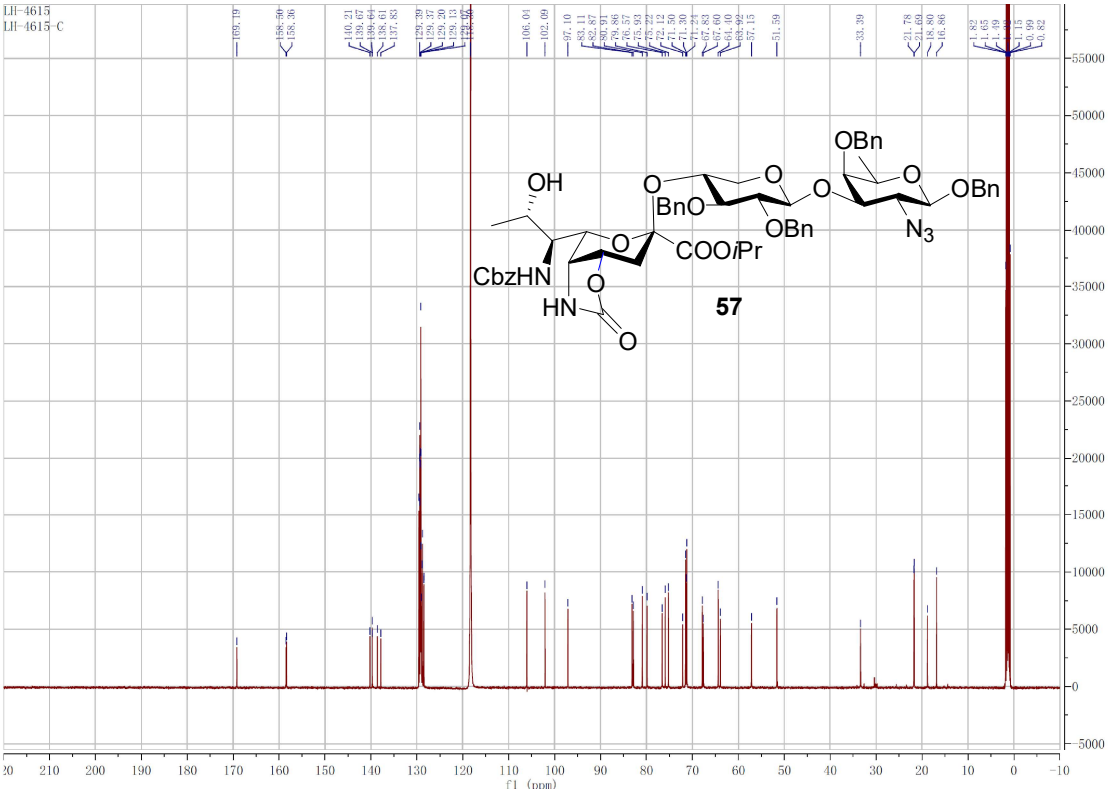
^{13}C NMR of compound 1



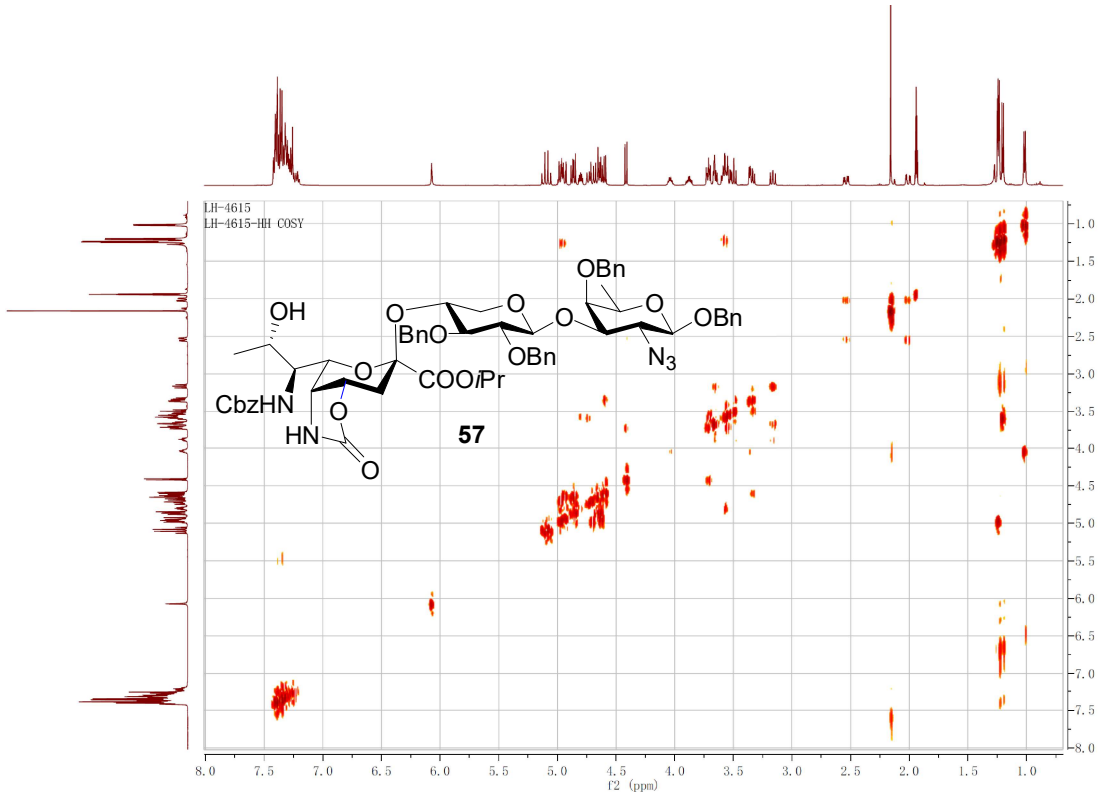
^{1}H NMR of compound 57



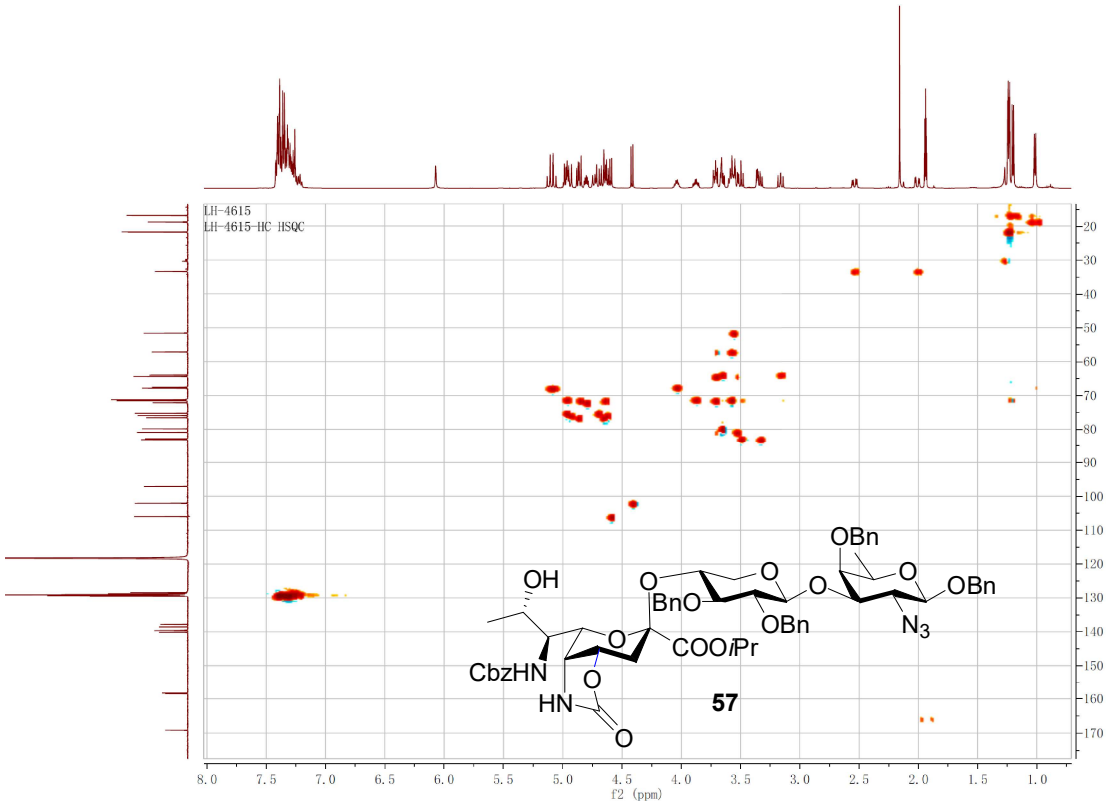
^{13}C NMR of compound 57



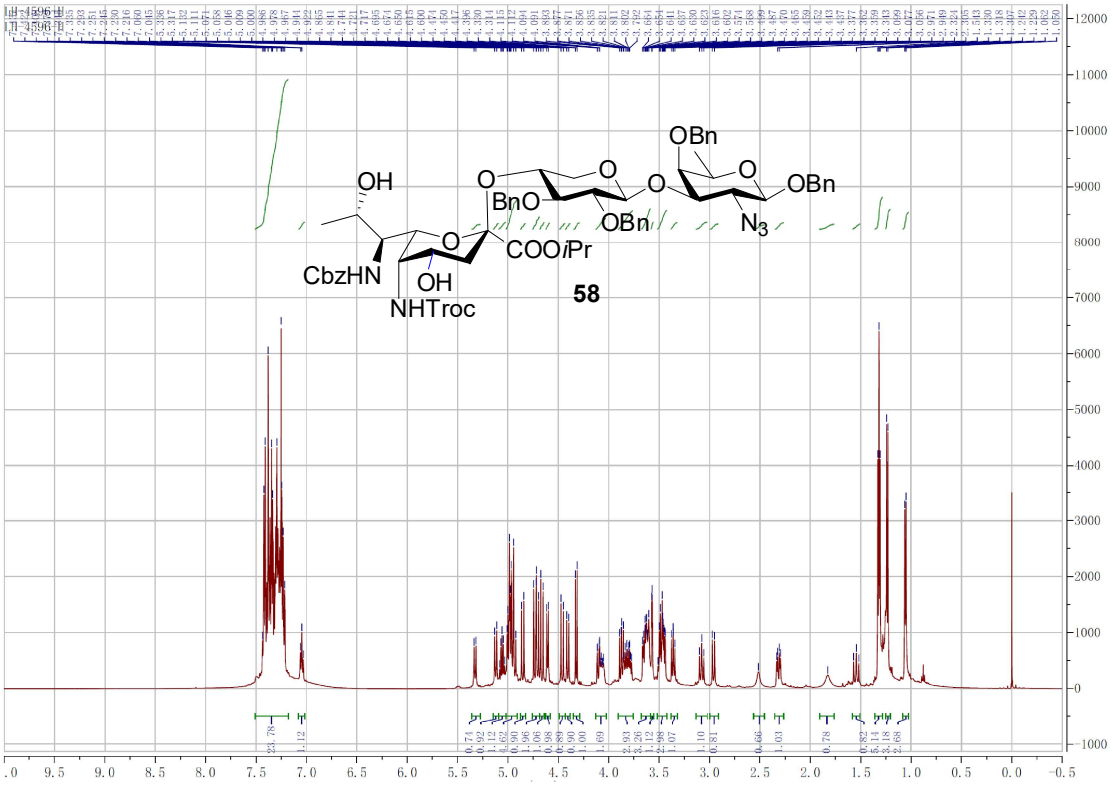
^{1}H-^{1}H COSY of compound 57



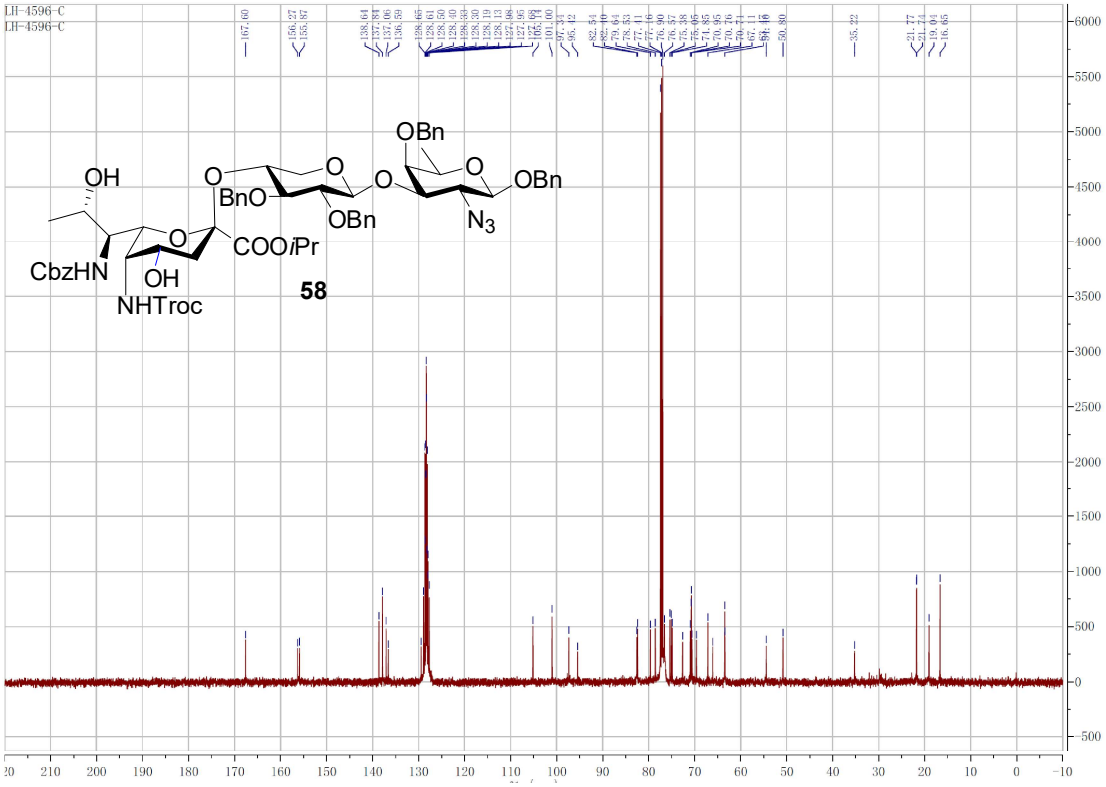
^{1}H-^{13}C HSQC of compound 57



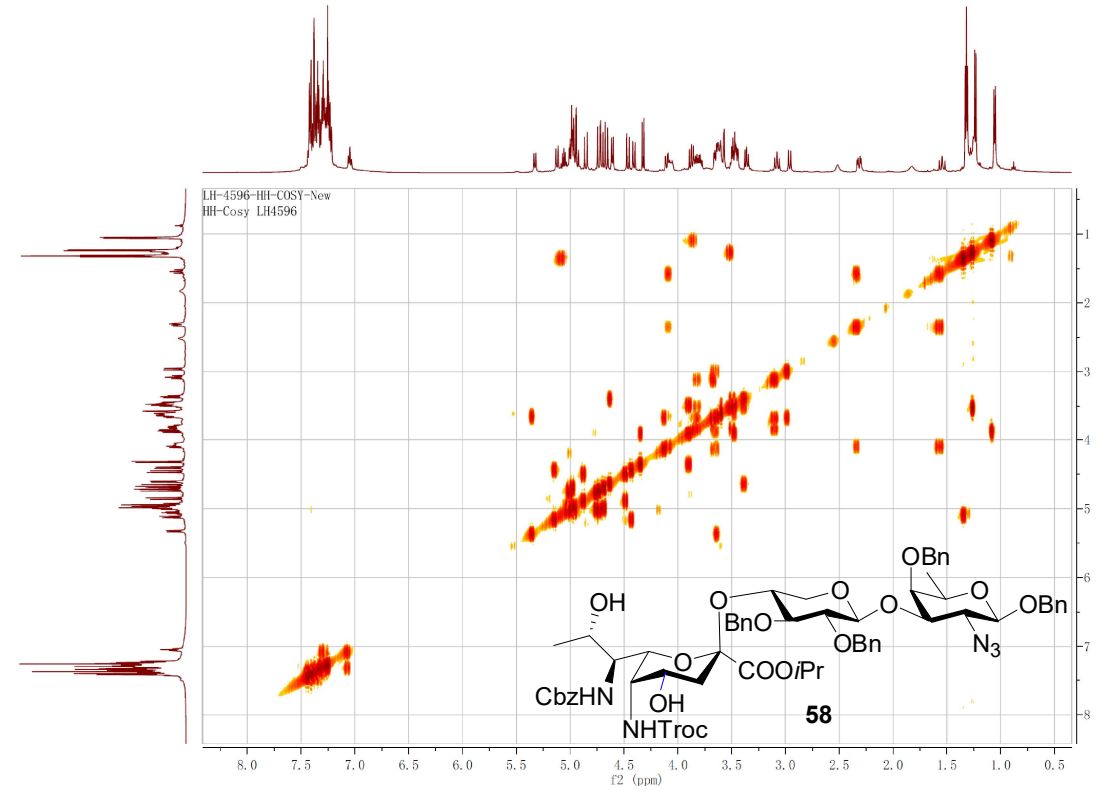
^{1}H NMR of compound 58



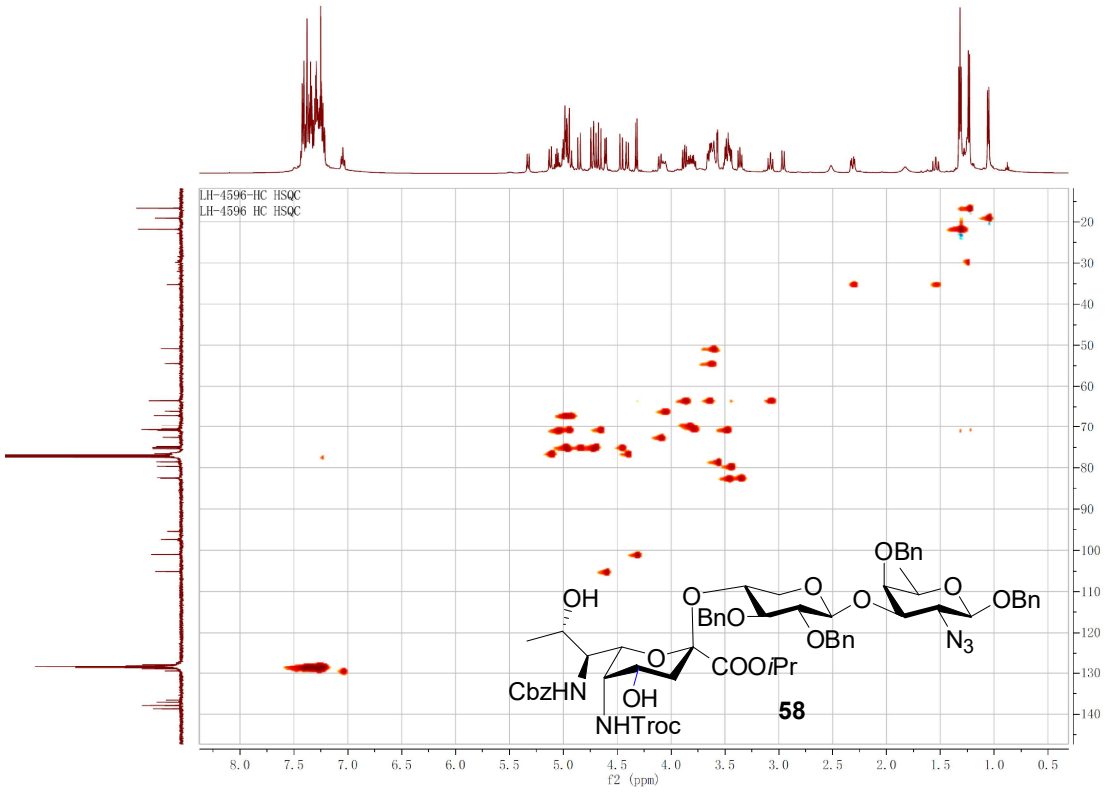
^{13}C NMR of compound 58



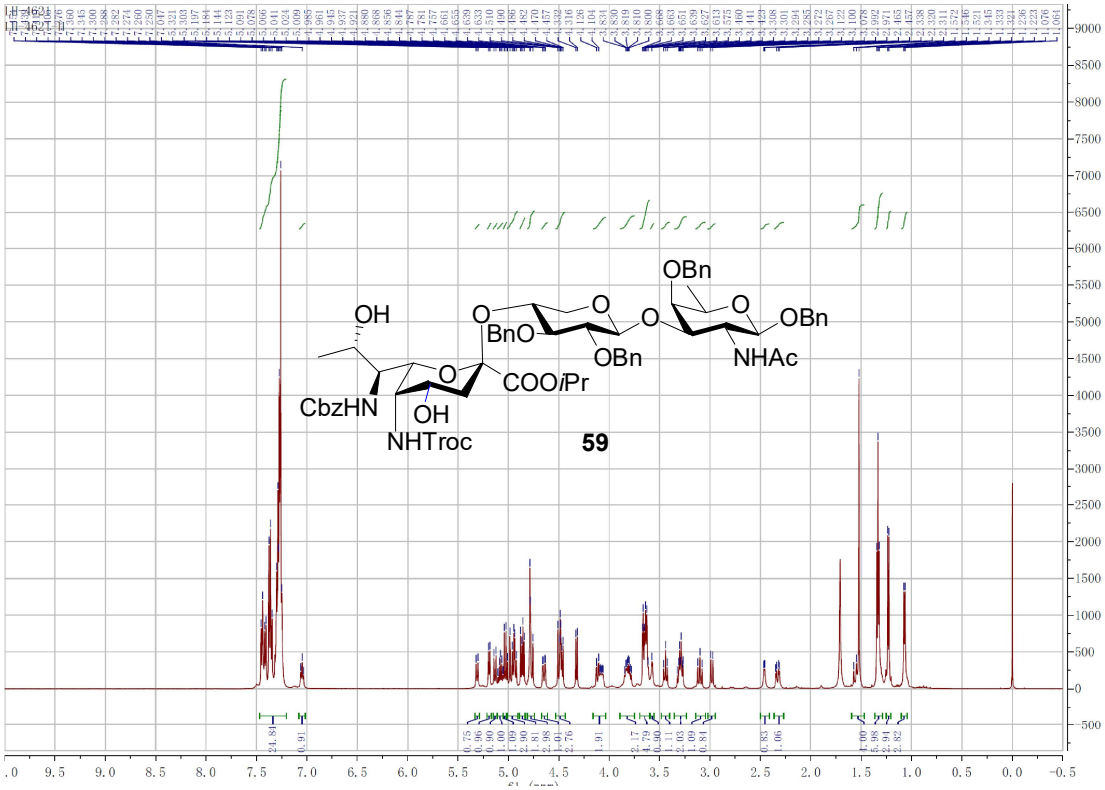
^{1}H-^{1}H COSY of compound 58



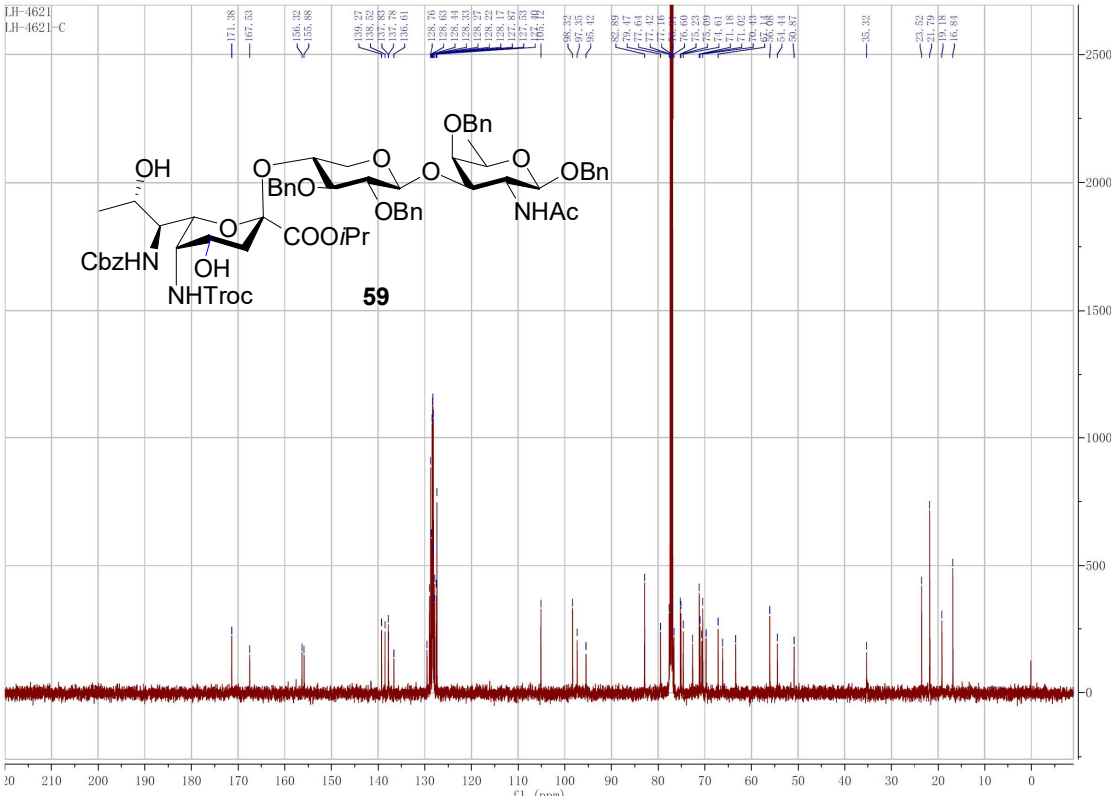
^{1}H-^{13}C HSQC of compound 58



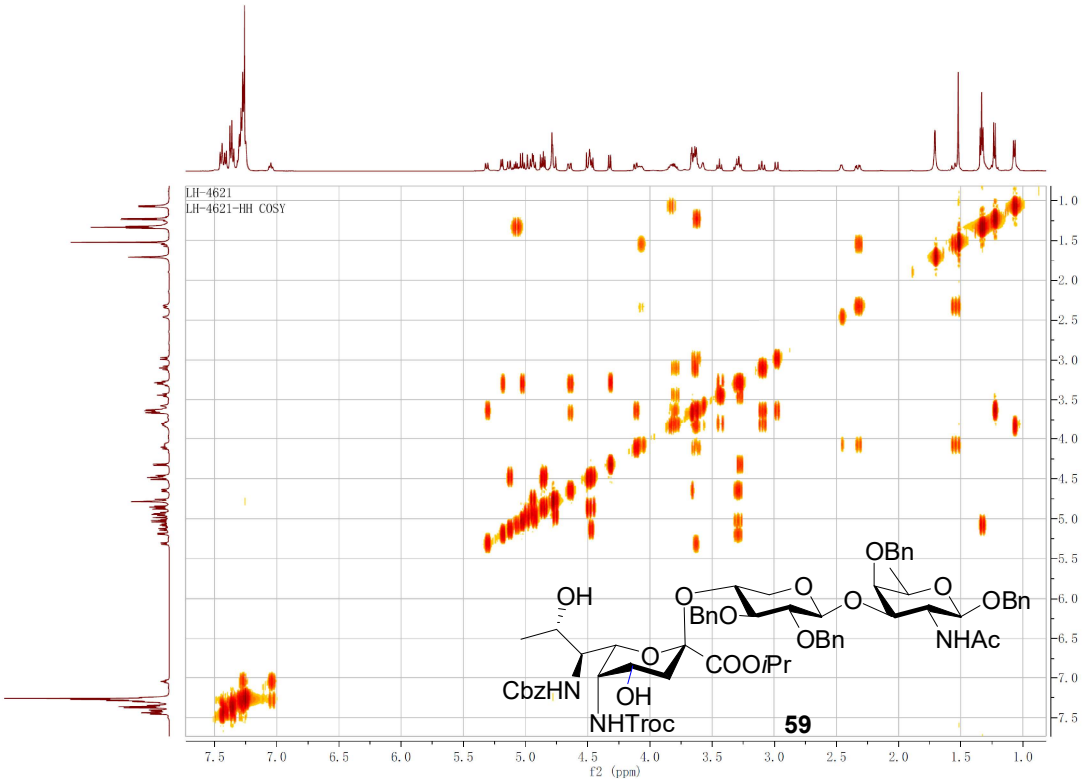
^{1}H NMR of compound 59



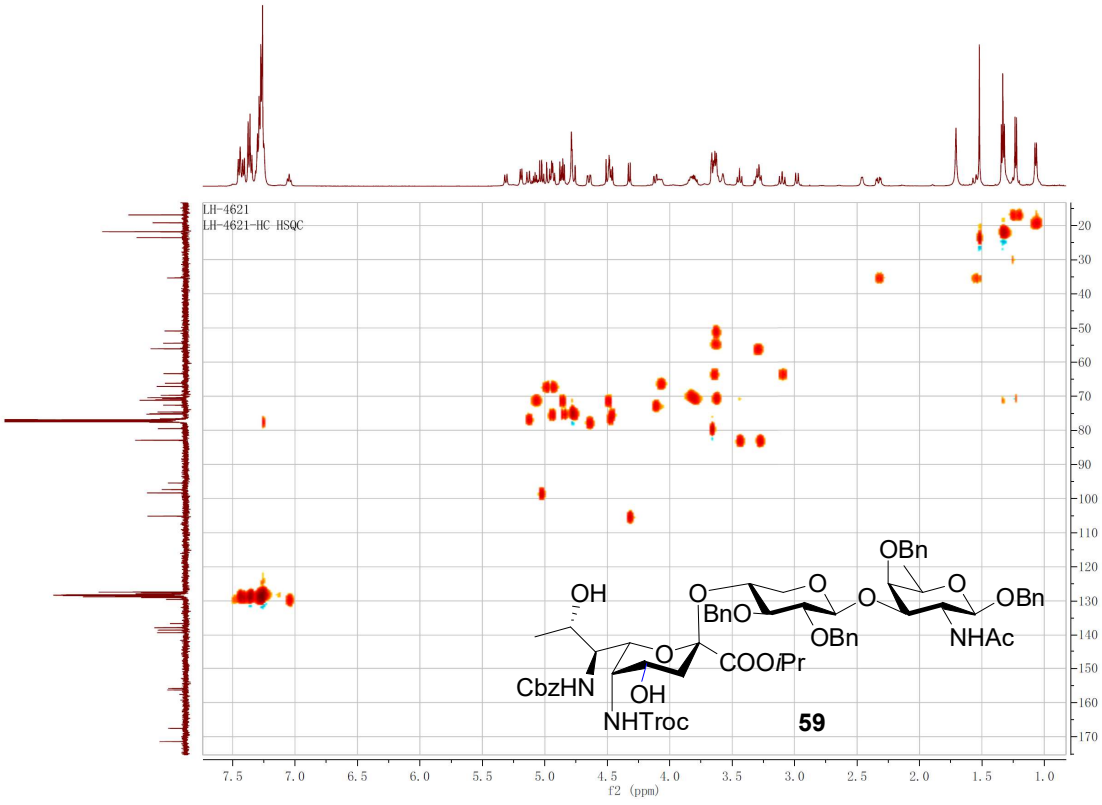
^{13}C NMR of compound 59



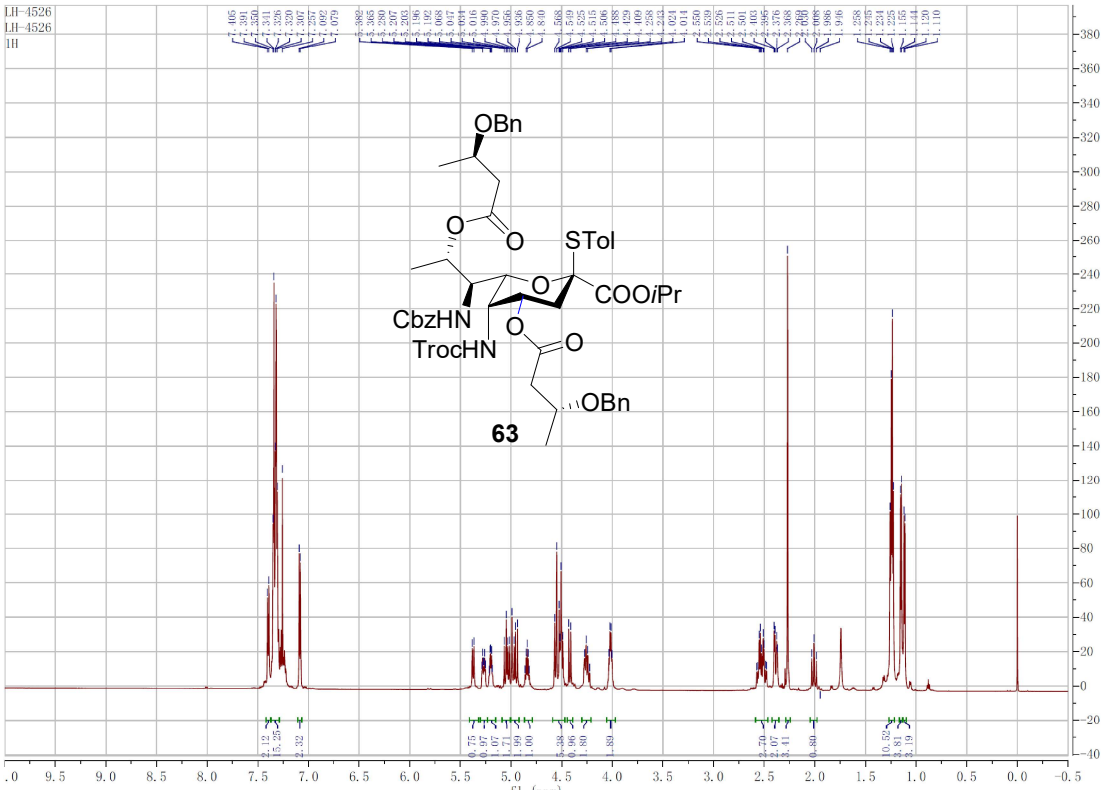
^{1}H-^{1}H COSY of compound 59



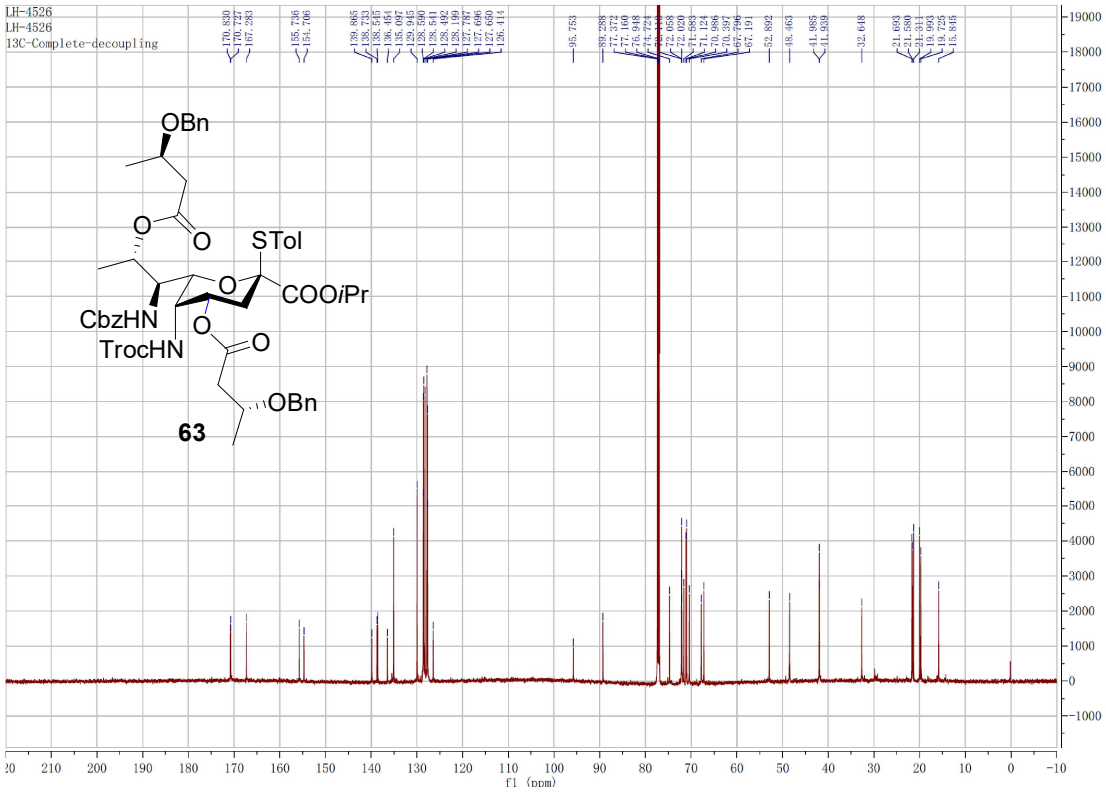
^{1}H-^{13}C HSQC of compound 59



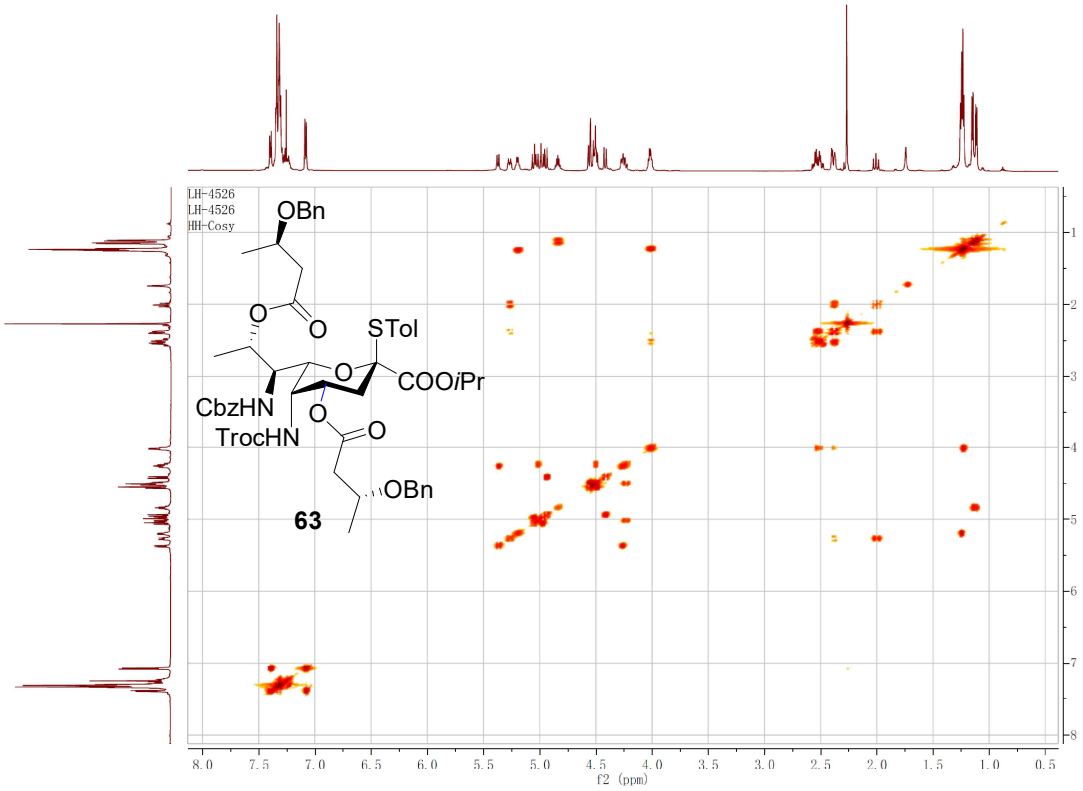
^{1}H NMR of compound 63



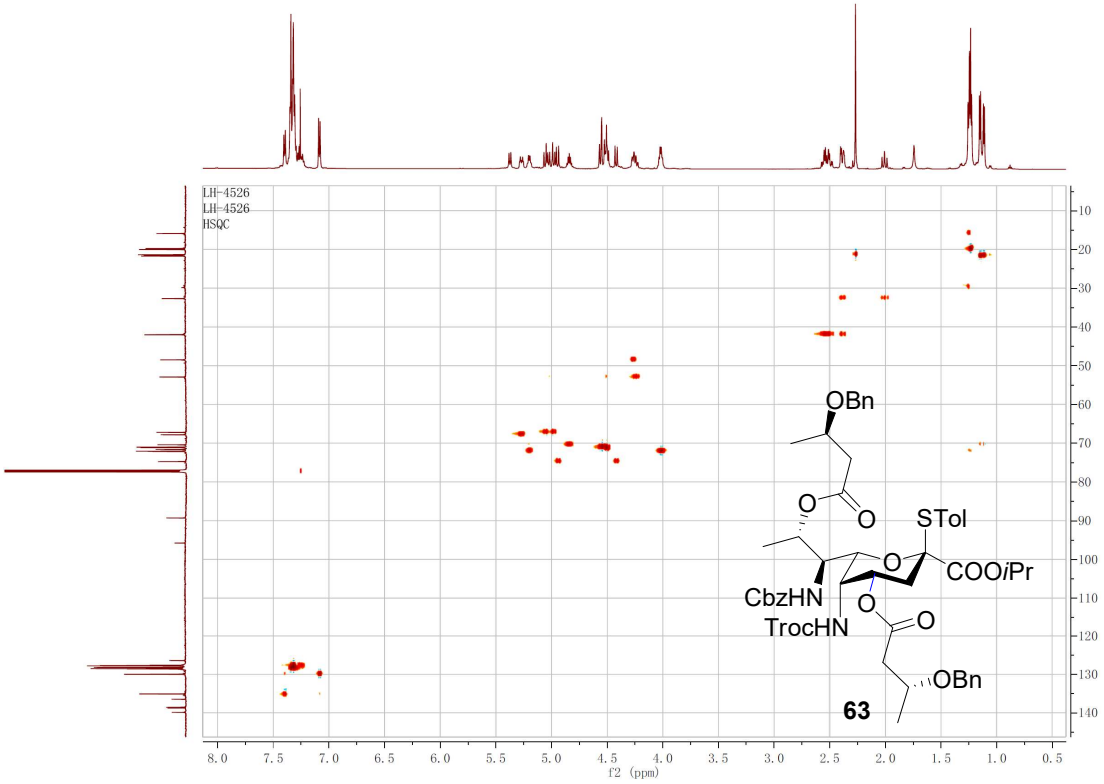
^{13}C NMR of compound 63



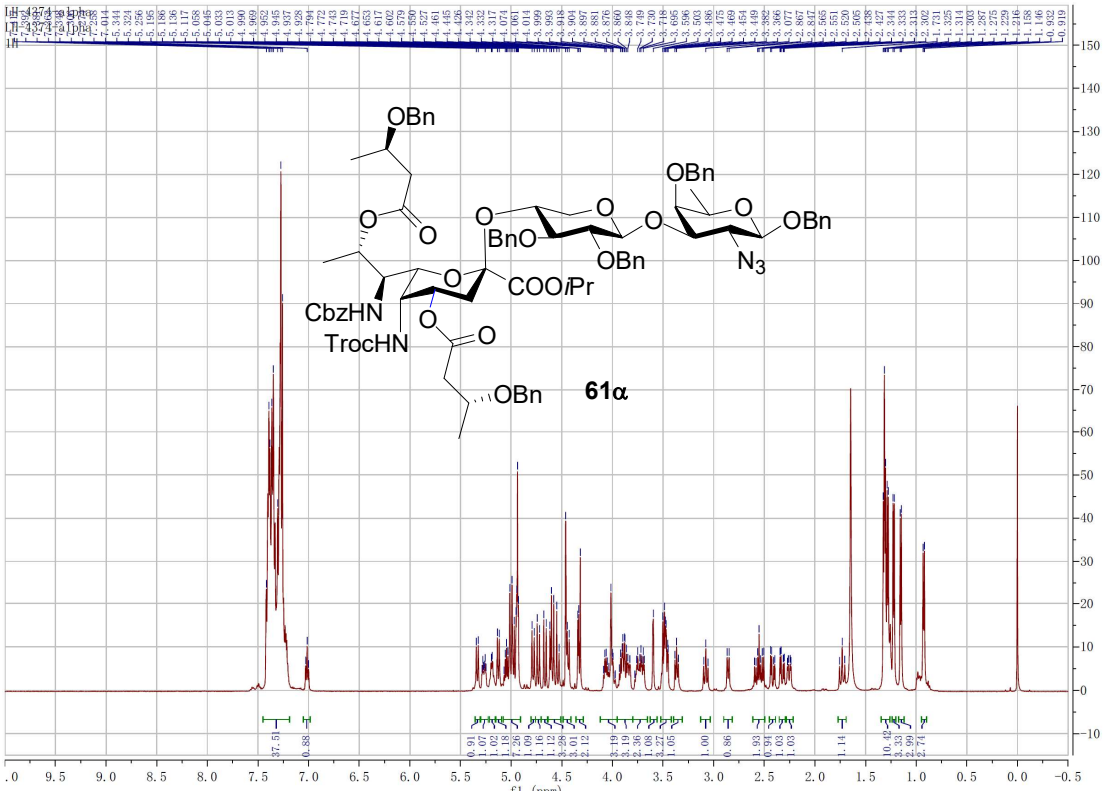
^{1}H-^{1}H COSY of compound 63



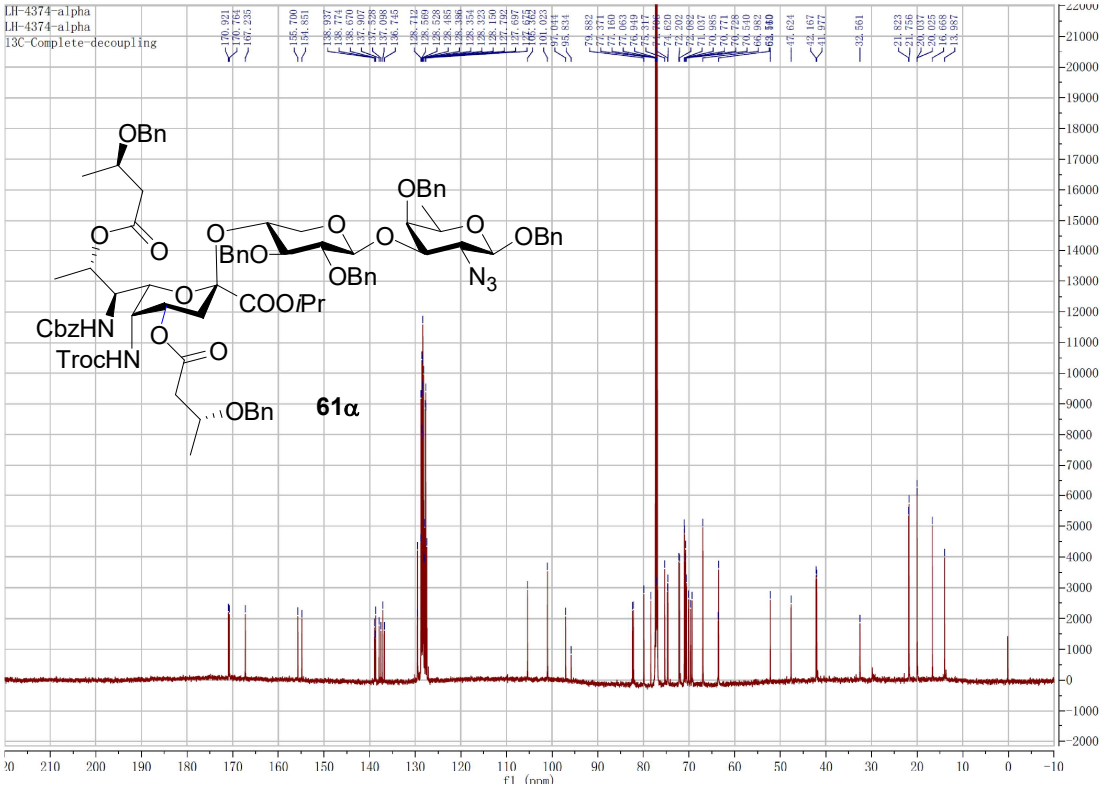
^{1}H-^{13}C HSQC of compound 63



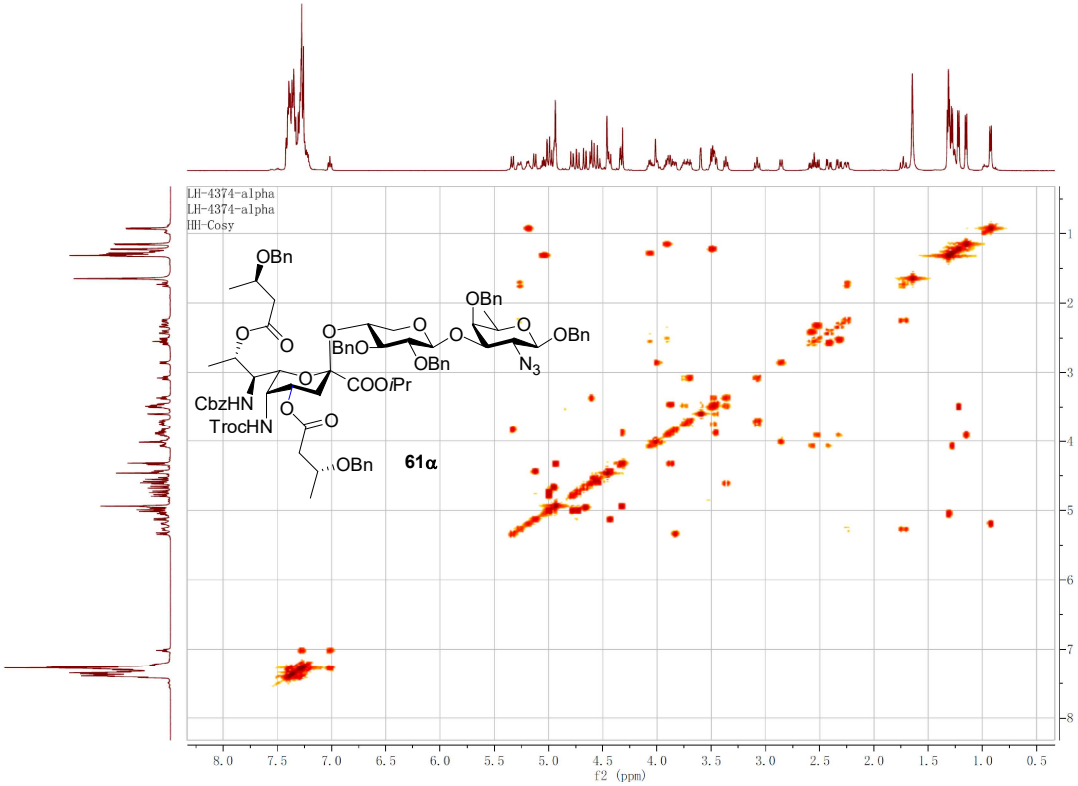
^{1}H NMR of compound 61α



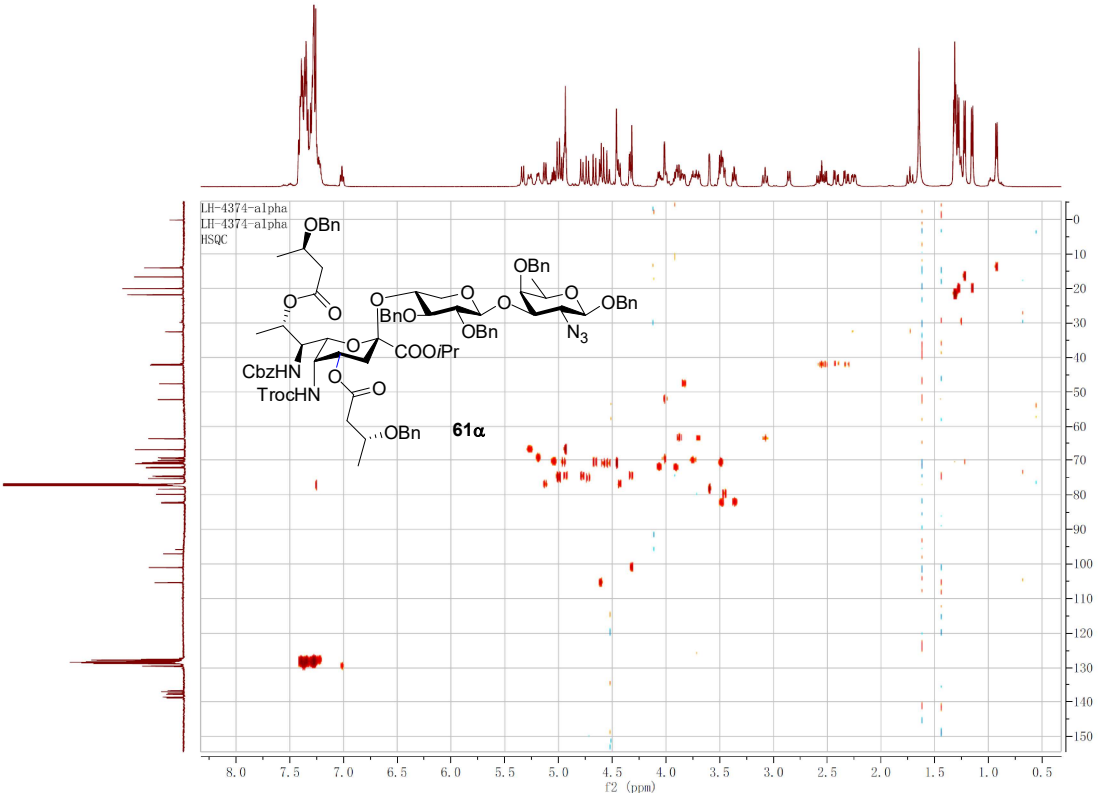
^{13}C NMR of compound 61α



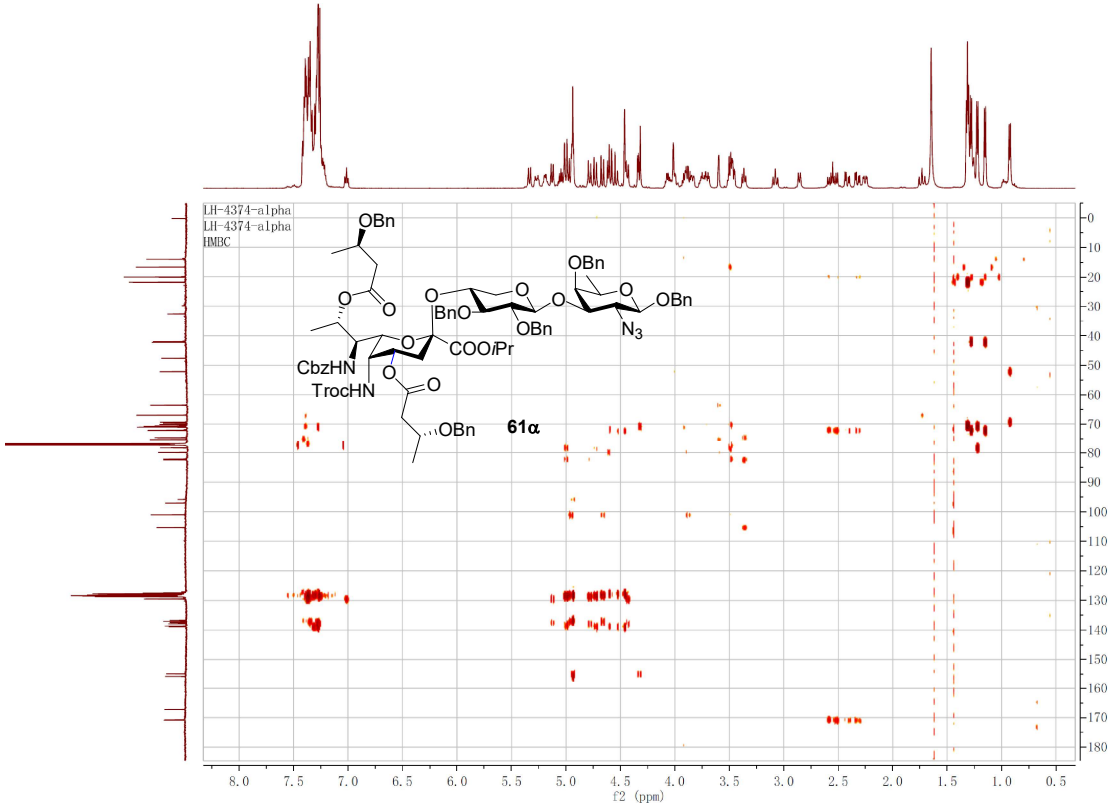
^{1}H-^{1}H COSY of compound 61α



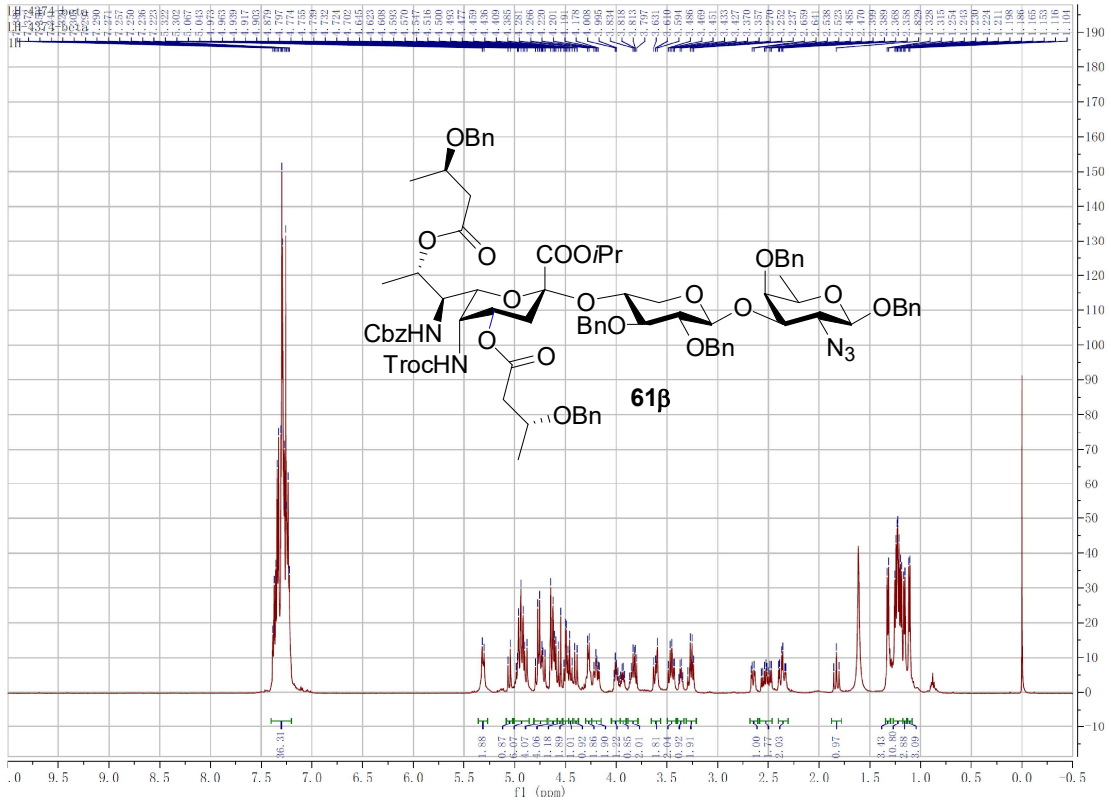
^{1}H-^{13}C HSQC of compound 61α



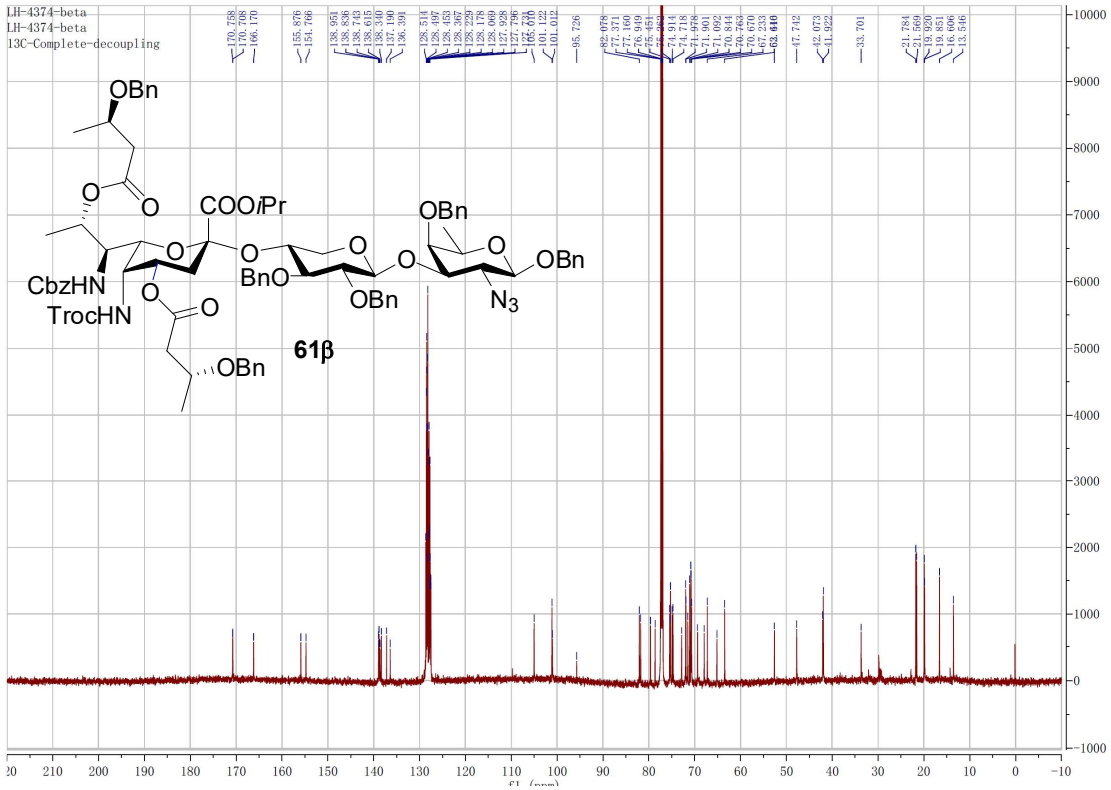
^{1}H-^{13}C HMBC of compound 61α



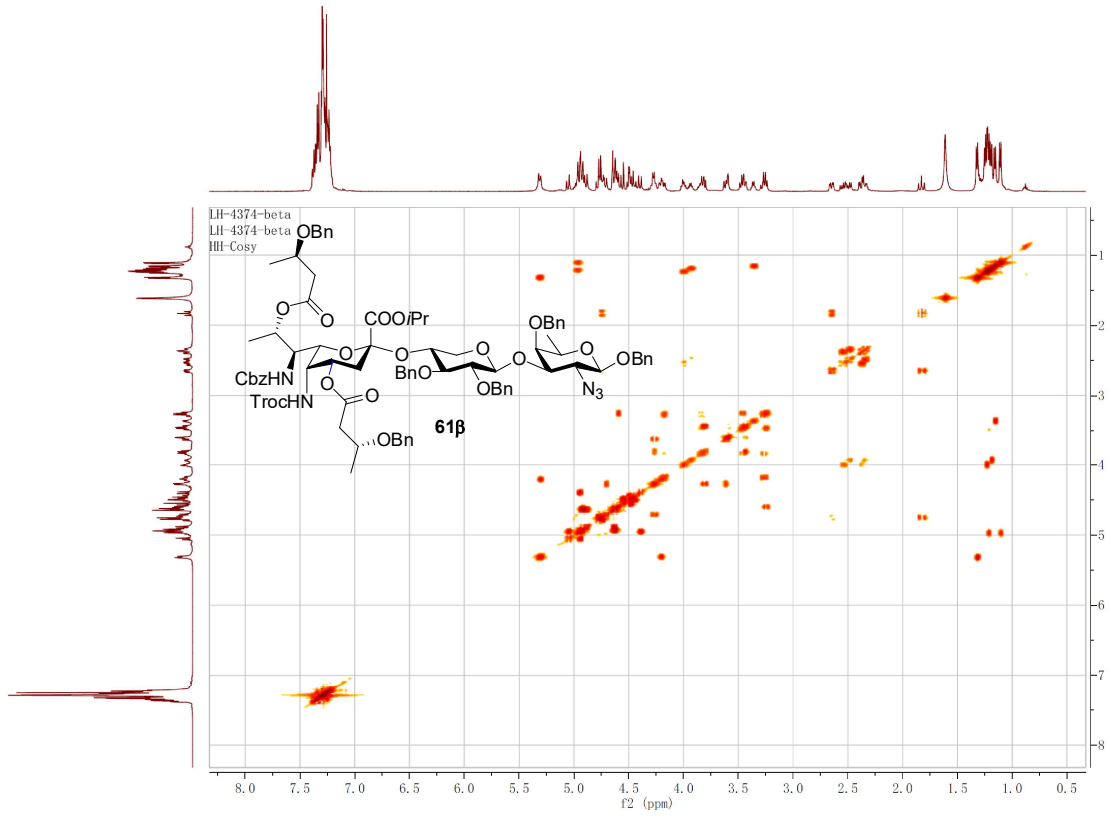
^{1}H NMR of compound 61β



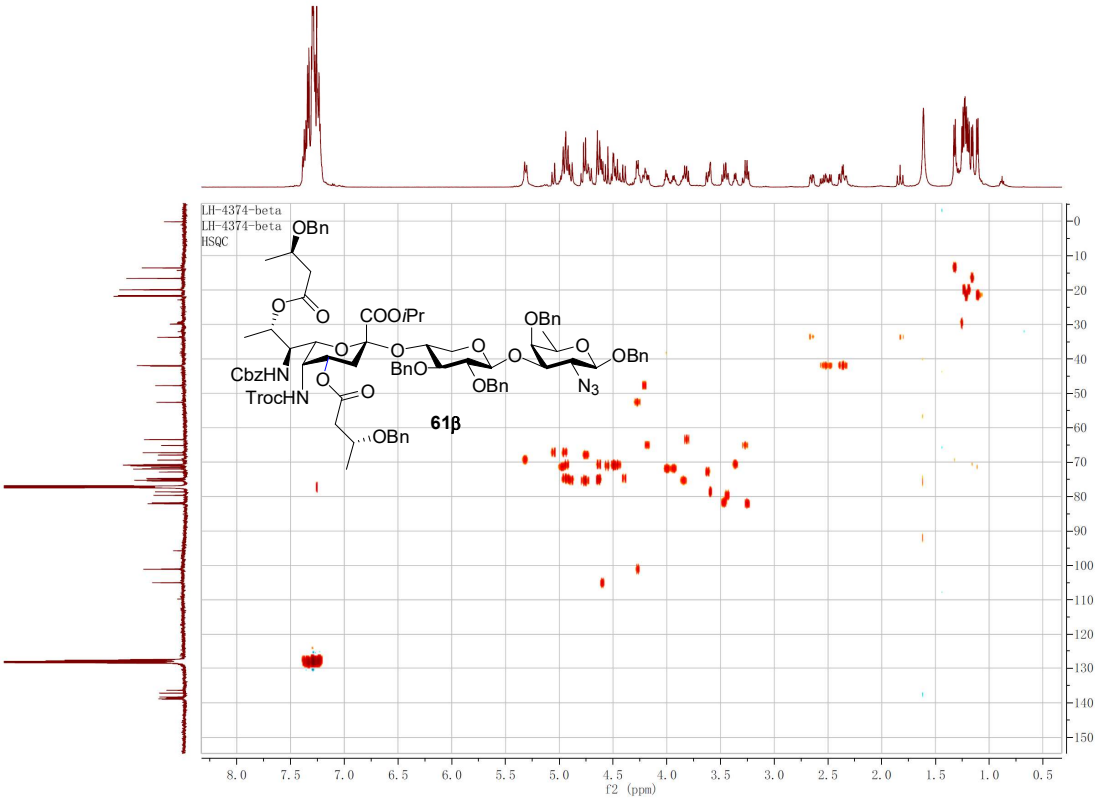
^{13}C NMR of compound 61β



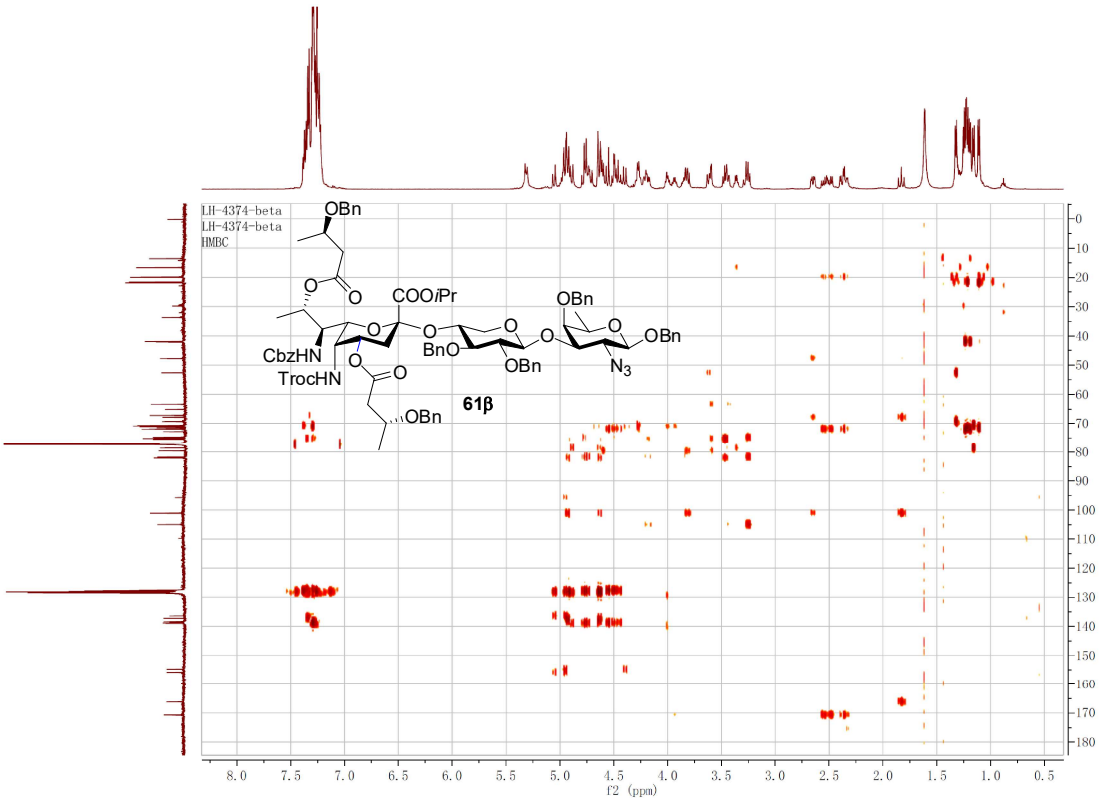
^{1}H-^{1}H COSY of compound 61β



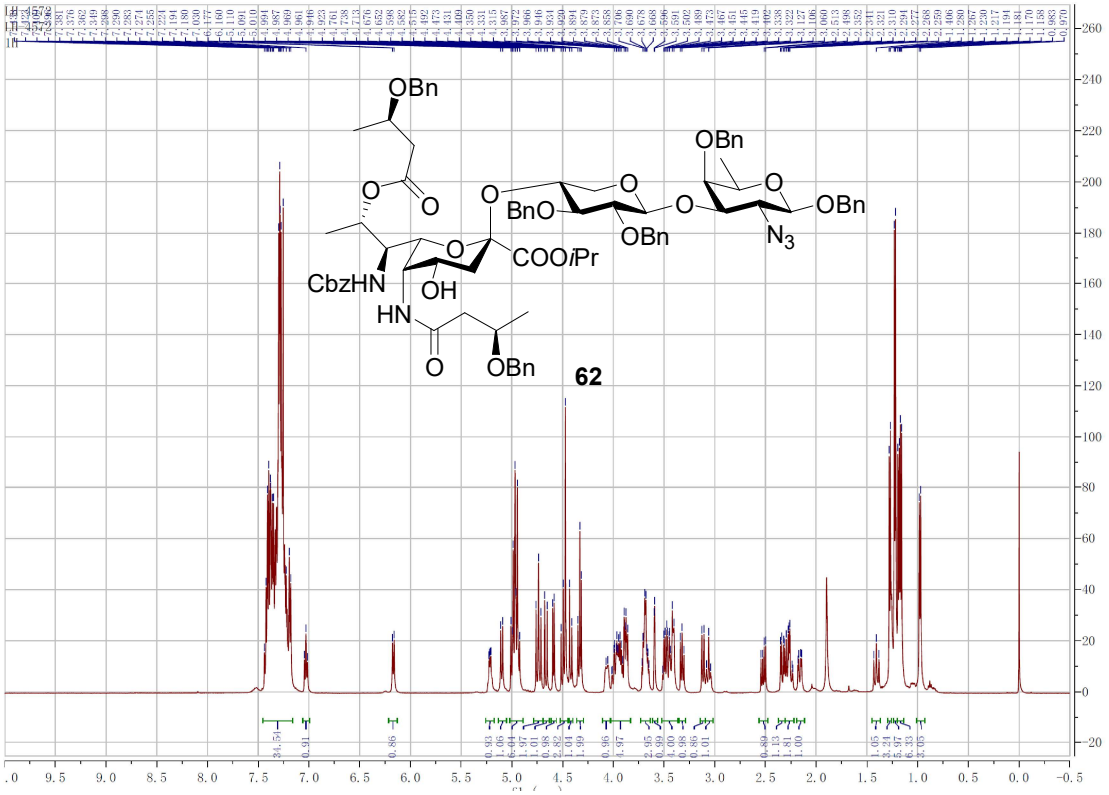
^{1}H-^{13}C HSQC of compound 61β



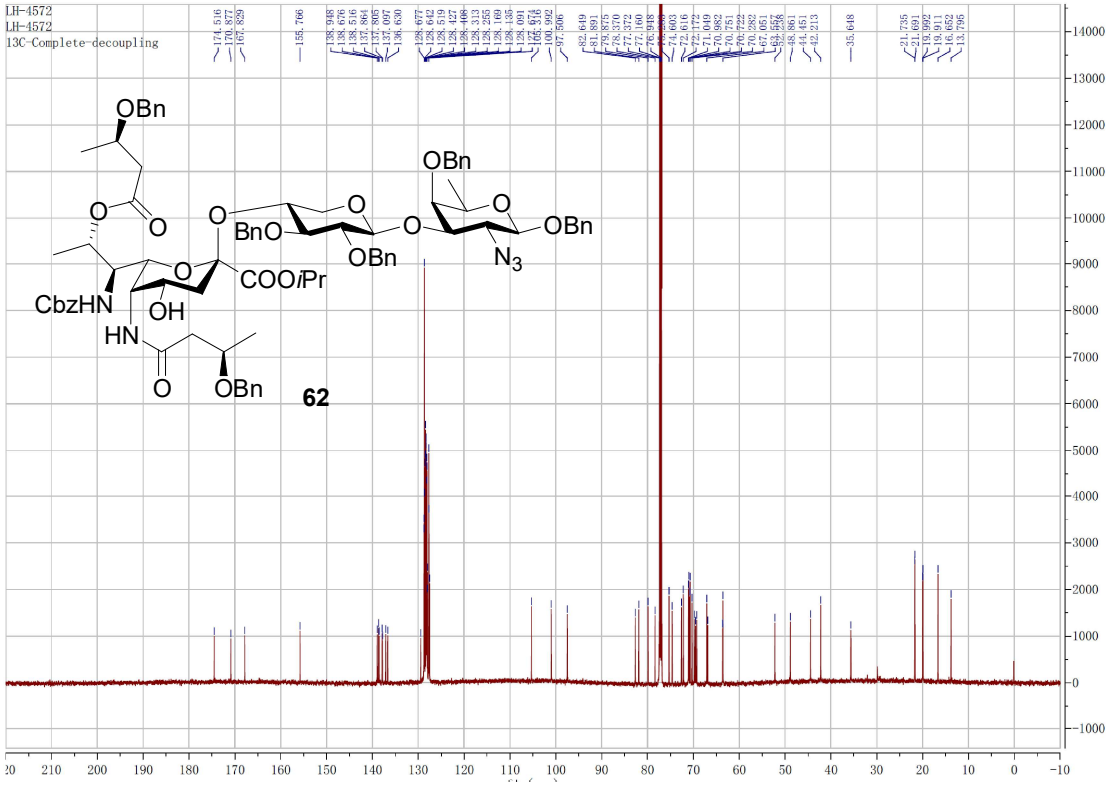
^{1}H-^{13}C HMBC of compound 61β



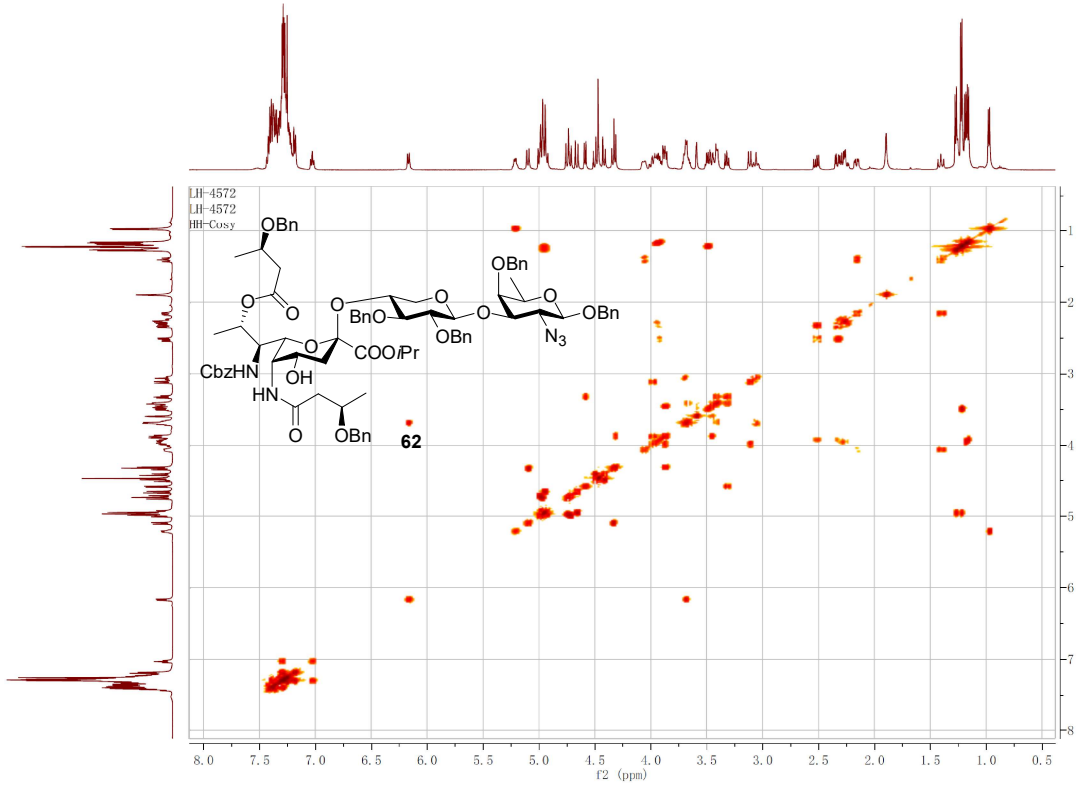
^{1}H NMR of compound 62



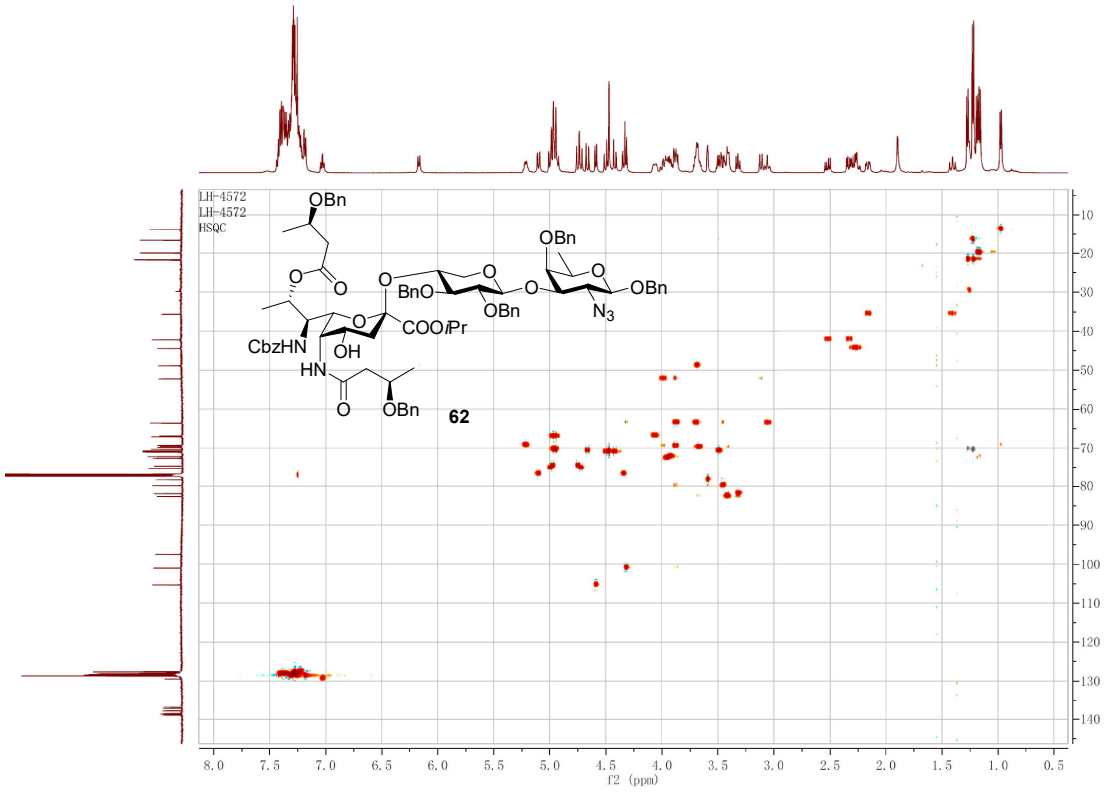
^{13}C NMR of compound 62



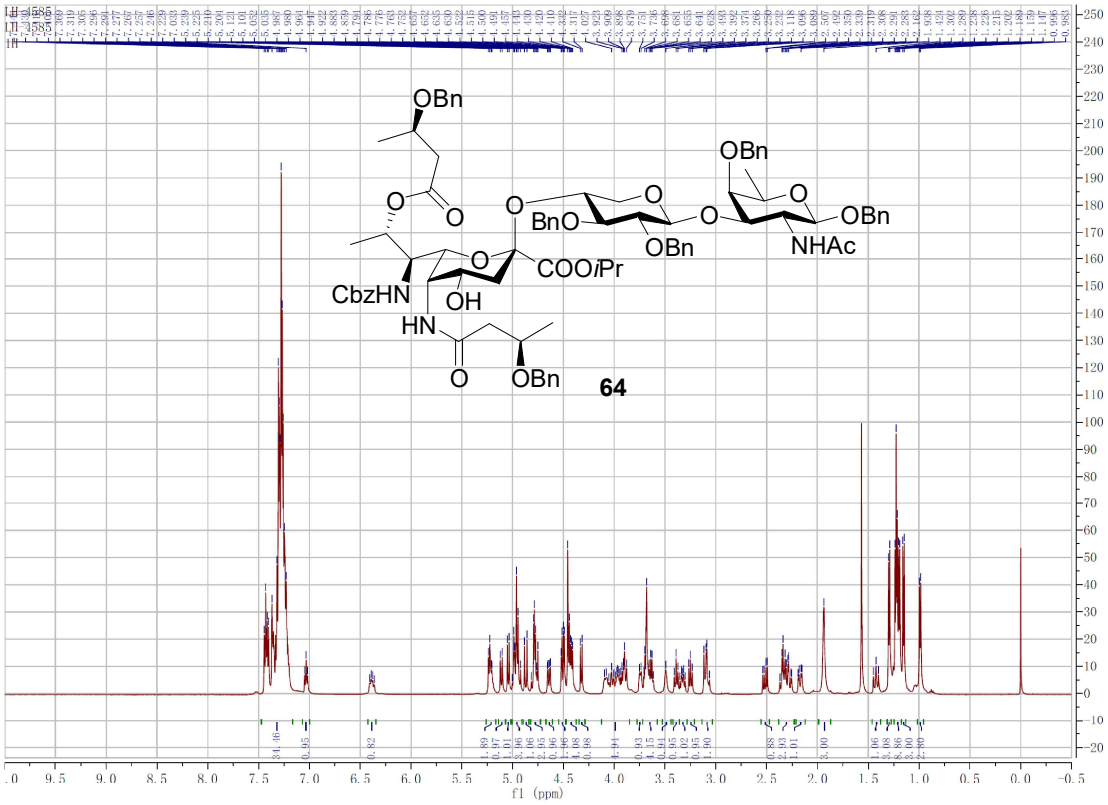
^{1}H-^{1}H COSY of compound 62



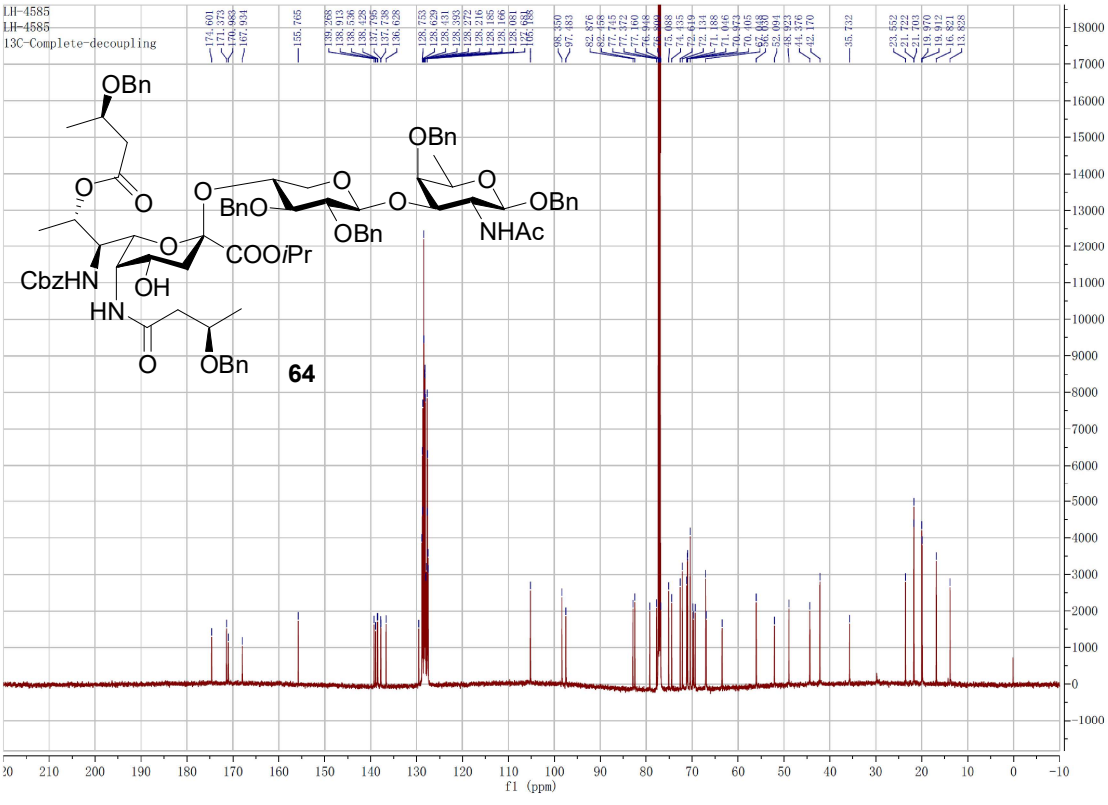
^{1}H-^{13}C HSQC of compound 62



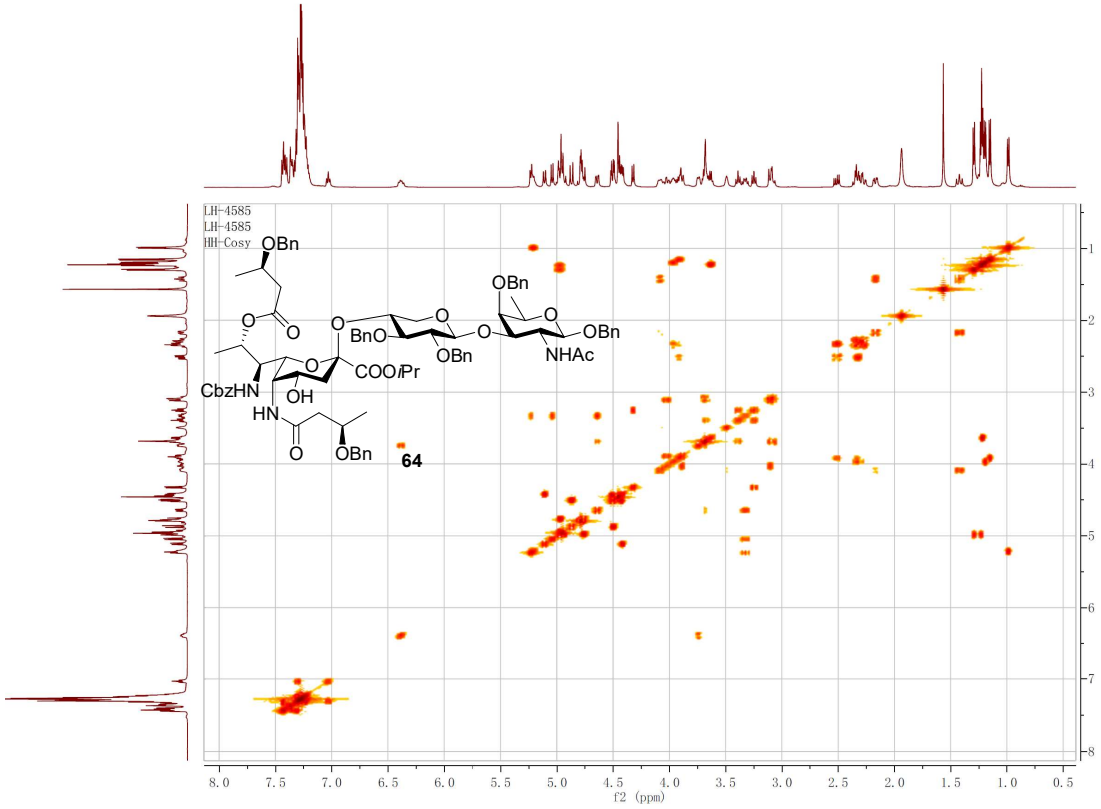
[1]H NMR of compound 64



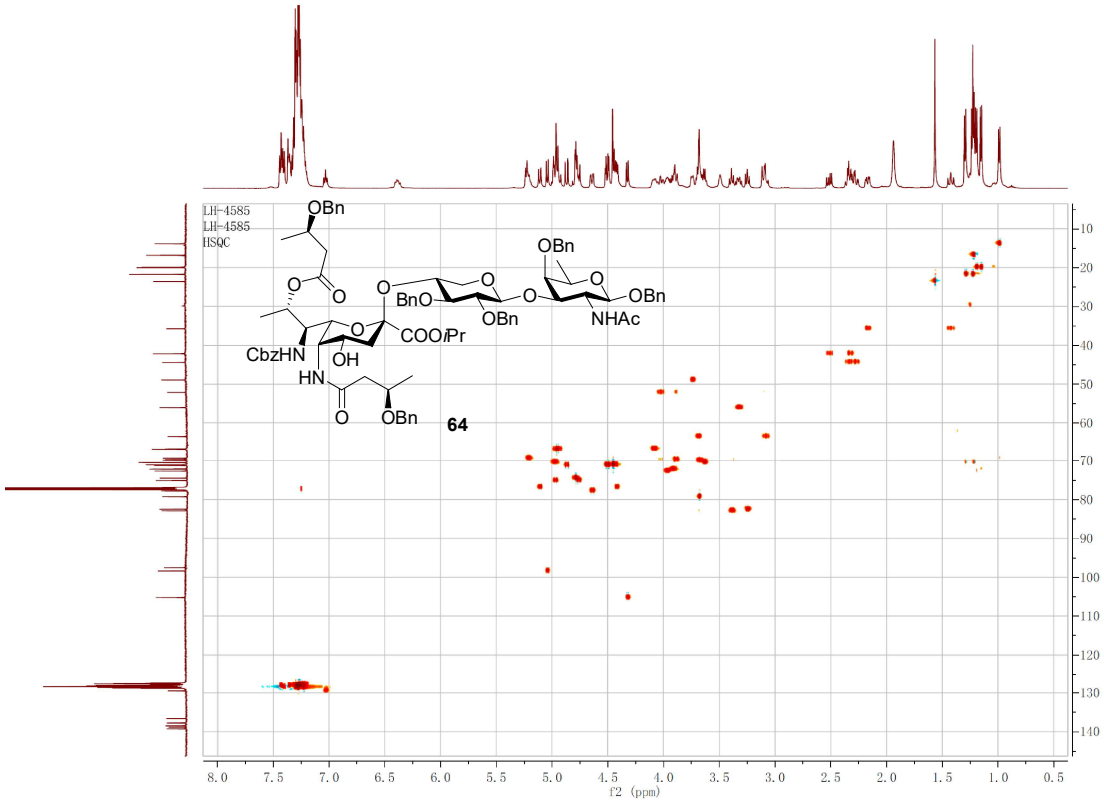
[13]C NMR of compound 64



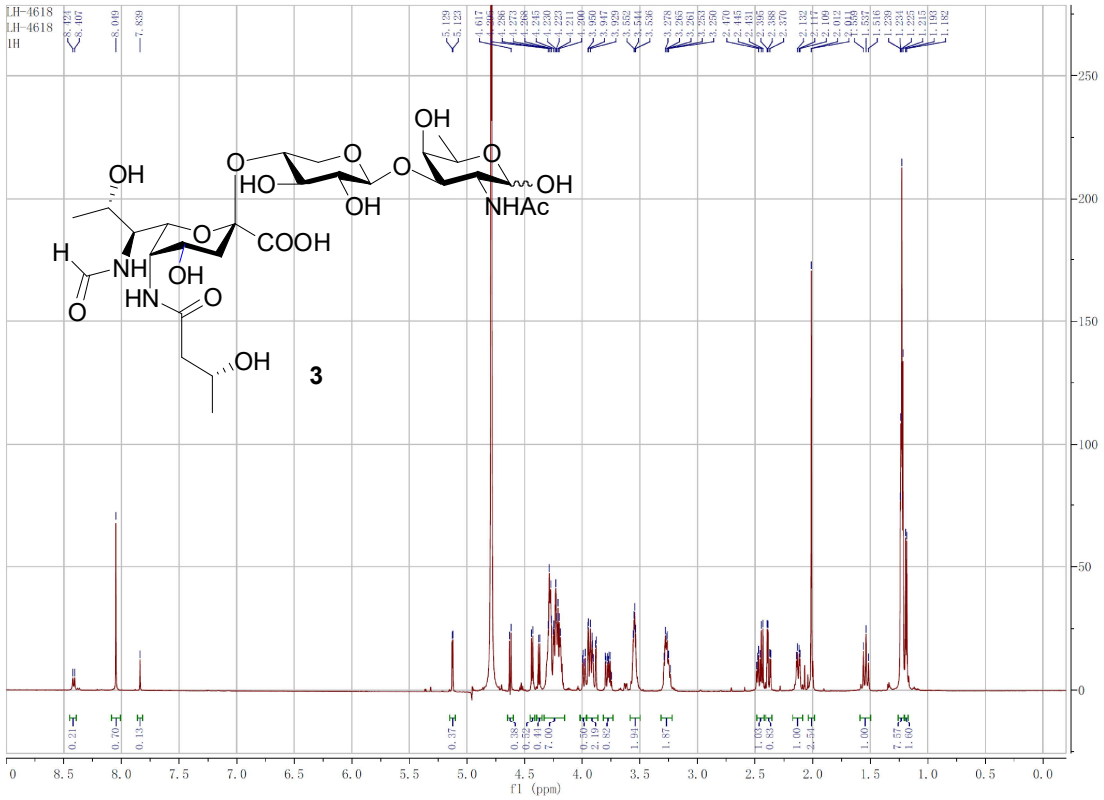
^{1}H-^{1}H COSY of compound 64



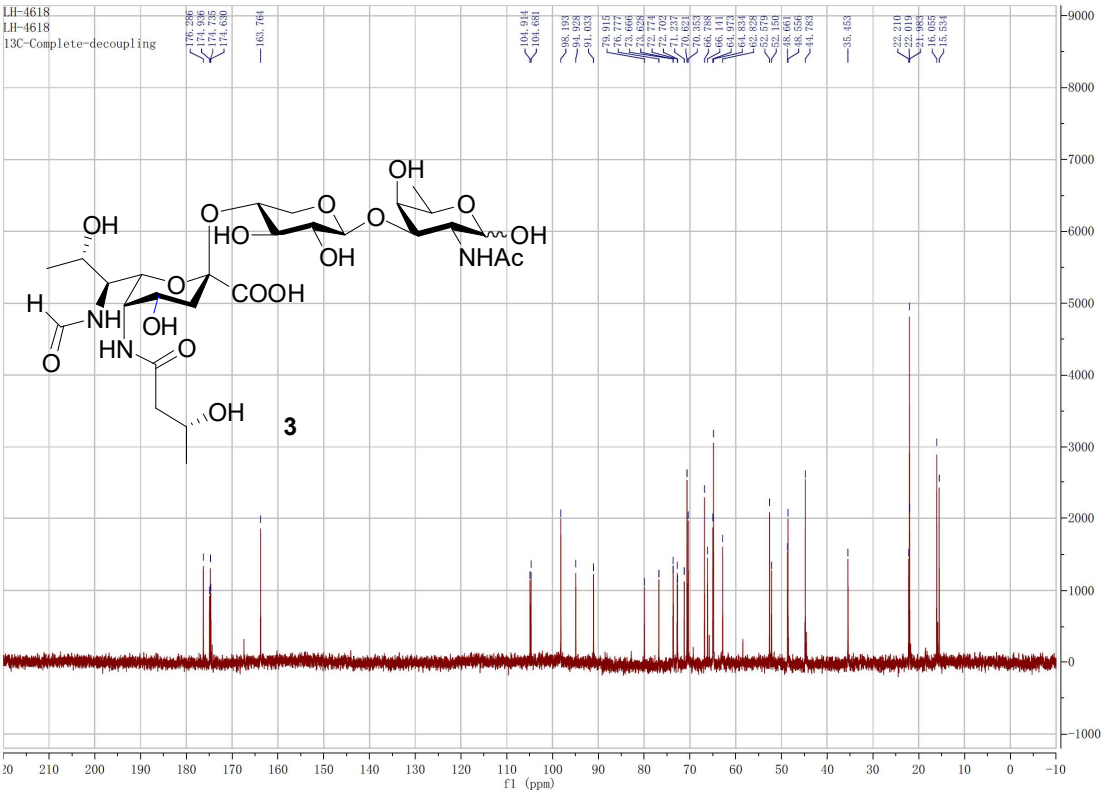
^{1}H-^{13}C HSQC of compound 64



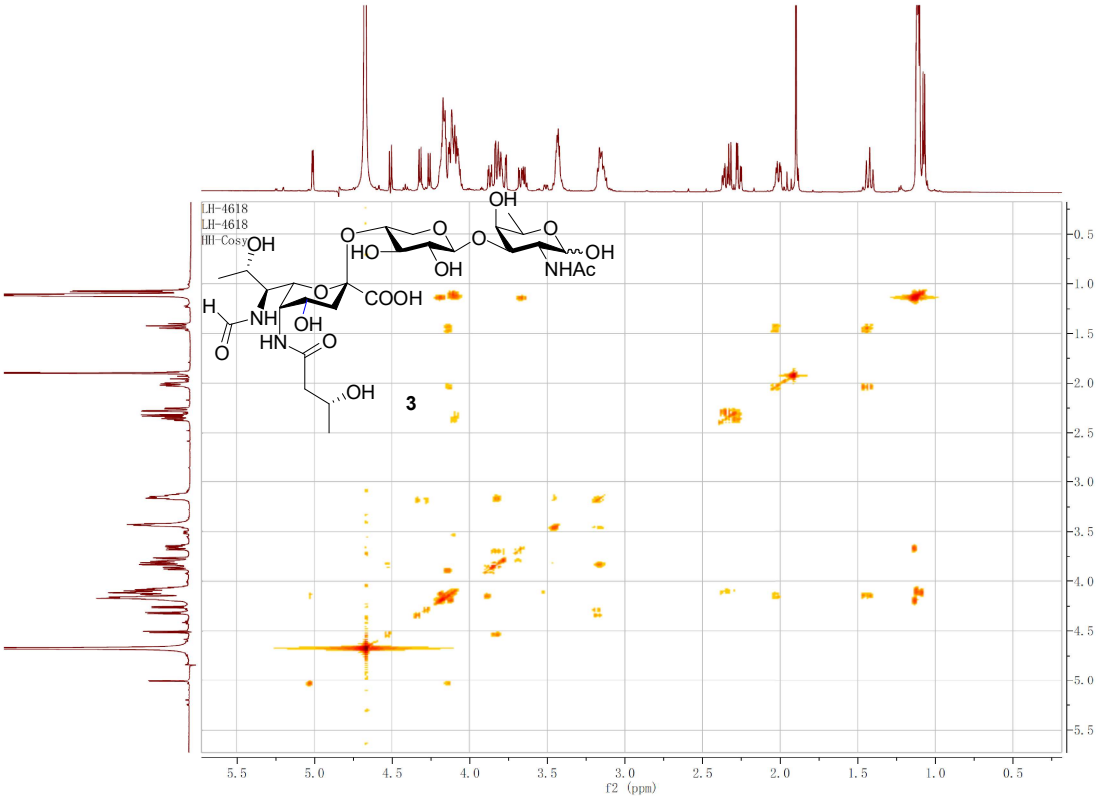
^{1}H NMR of compound 3



^{13}C NMR of compound 3



^{1}H-^{1}H COSY of compound 3



^{1}H-^{13}C HSQC of compound 3