Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information

A light- and heat-driven glycal diazidation approach to nitrogenous carbohydrate derivatives with antiviral activity

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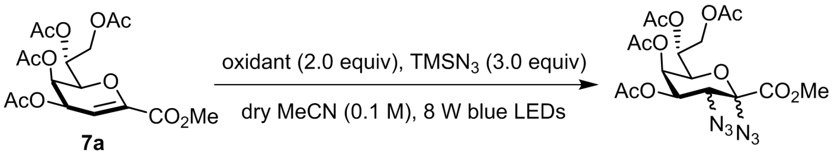
1. General Information

All reactions that require anhydrous conditions were performed in flame-dried glassware under argon atmosphere and all reagents were purchased from commercial suppliers. Solvent purification was conducted according to Purification of Laboratory Chemicals 2nd edn (Perrin, D. D., Armarego, W. L. F. and Perrin, D. R., Pergamon Press: Oxford, 1980). The products were purified by flash column chromatography on silica gel (200 – 300 meshes) from the Anhui Liangchen Silicon Material Company (China). Reactions were monitored by thin layer chromatography (TLC, 0.2 mm, HSGF254) supplied by Yantai Chemicals (China). Visualization was accomplished with UV light, exposure to iodine, stained with ethanolic solution of H_2SO_4/EtOH (1:9, v/v) or basic solution of $KMnO_4$. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian INOVA-400/54 and Agilent DD2-600/54 spectrometer, in the following solvents (reference peaks include ^{1}H and ^{13}C NMR): $CDCl_3$ (^{1}H NMR: 7.26 ppm; ^{13}C NMR: 77.00 ppm), CD_3OD (^{1}H NMR: 3.31 ppm; ^{13}C NMR: 49.00 ppm), D_2O (^{1}H NMR: 4.79 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, td = triple doublet, dt = double triplet, m = multiplet, and coupling constants (*J*) were reported in Hertz (Hz). Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum Two FTIR spectrometer. The specific optical rotation was obtained from Rudolph Research Analytical Autopol VI automatic polarimeter. High-resolution mass spectra (HRMS) were recorded on Bruker Apex IV FTMS or Thermo Scientific LTQ Orbitrap XL ESI mass spectrometers. Melting points were obtained with X-4 precision micro melting point apparatus. Kessil H150BLUE LED and Kessil A160WE TUNA BLUE were purchased from http://www.amazon.com.

2. Optimization Studies

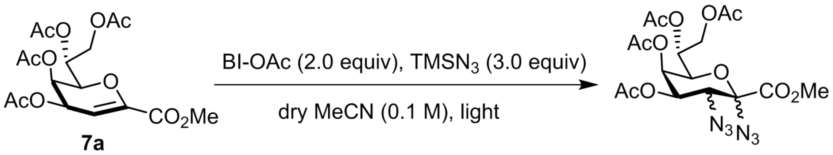
Table S1. Effect of oxidant



Entry[a]	**Oxidant**	**Time**	**Conversion**[b]	**Yield**[c]
1	O_2[d]	15 h	trace	0
2	BQ	15 h	0	0
3	$K_2S_2O_8$	15 h	0	0
4	PhIO	15 h	53%	46%
5	BI-OAc[e]	10 h	100%	69%
6	BI-OH[e]	15 h	87%	60%
7	PIDA	15 h	87%	66%
8	PIFA	15 h	77%	63%
9	$NaIO_4$	12 h	100%	33%
10	IBX	15 h	33%	25%

[a]Reactions were conducted on 0.075 mmol scale unless otherwise stated. [b]Conversions were calculated based on the recovered starting glycal **7a** after column chromatography. [c]Yields were determined according to the isolated material via column chromatography. [d]The reaction was conducted under a balloon of oxygen; [e]BI-OAc and BI-OH were prepared according to the literature method.[1]

Table S2. Effect of light

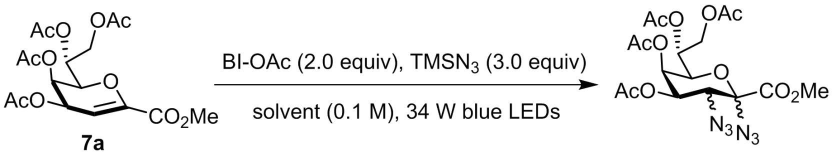


Entry[a]	**Light**	**Time**	**Conversion**[b]	**Yield**[c]
1	26 W CFL	15 h	87%	14%
2	15 W green LEDs	15 h	63%	50%
3	30 W white LEDs	6 h	100%	77%
4	34 W blue LEDs	1.5 h	100%	83%
5	sun light	1.5 h	33%	25%
6	sun light	15 h	67%	41%

[a]Reactions were conducted on 0.075 mmol scale unless otherwise stated. [b]Conversions were calculated

based on the recovered starting glycal **7a** after column chromatography. [c]Yields were determined according to the isolated material via column chromatography.

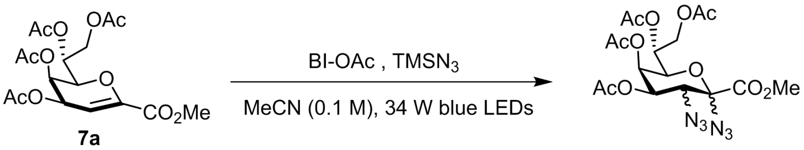
Table S3. Effect of solvent



Entry[a]	**Solvent**	**Time**	**Conversion**[b]	**Yield**[c]
1	MeCN	1.5 h	100%	83%
2	CH_2Cl_2	3 h	100%	36%
3	THF	11 h	<5%	0%
4	DMF	11 h	0%	0%
5	PhMe	11 h	<10%	<5%
6	DMSO	11 h	100%	62%
7	Dioxane	11 h	67%	41%
8	MeOH	11 h	<10%	0%
9	Acetone	3 h	100%	63%

[a]Reactions were conducted on 0.075 mmol scale unless otherwise stated. [b]Conversions were calculated based on the recovered starting glycal **7a** after column chromatography. [c]Yields were determined according to the isolated material via column chromatography.

Table S4. Effect of reagent equivalent

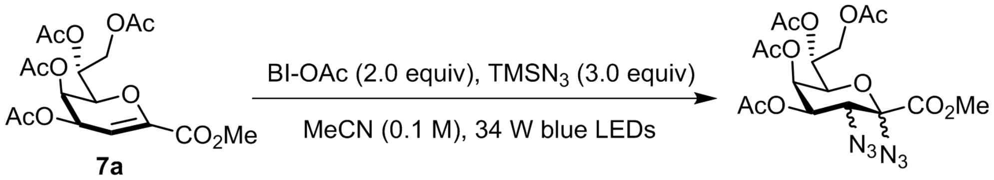


Entry[a]	**Equiv of BI-OAc**	**Equiv of $TMSN_3$**	**Reaction Time**	**Yield**[b]
1	1	3	20 h	55%
2	2	3	1.5 h	83%
3	3	3	2 h	74%
4	4	3	2 h	65%
5	5	3	2 h	58%
6	2	2	3 h	62%
7	2	4	1.5 h	78%
8	2	5	1.5 h	71%

[a]Reactions were conducted on 0.075 mmol scale unless otherwise stated. [b]Yields were determined

according to the isolated material via column chromatography.

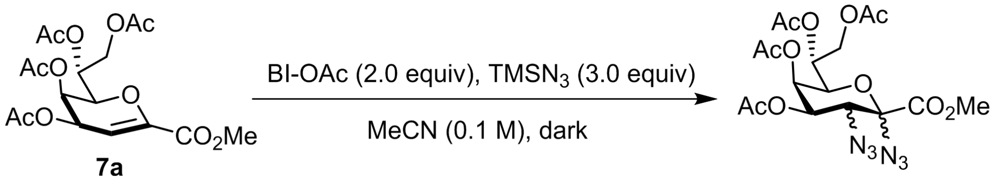
Table S5. Control experiments



Entry[a]	**Variation from standard conditions**	**Time**	**Conversion**[b]	**Yield**[c]
1	none	1.5 h	100%	83%
2	dark	1.5 h	17%	13%
3	dark	15 h	33%	11%
4	no BI-OAc	10 h	0%	0%

[a]Reactions were conducted on 0.075 mmol scale unless otherwise stated. [b]Conversions were calculated based on the recovered starting glycal **7a** after column chromatography. [c]Yields were determined according to the isolated material via column chromatography.

Table S6. Heating experiments

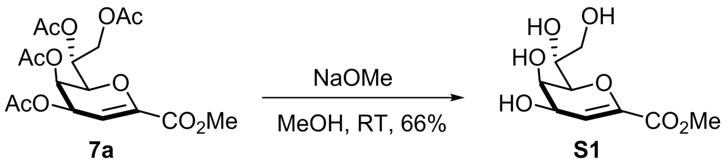


Entry[a]	**Temperature**[b]	**Time**	**Conversion**[c]	**Yield**[d]
1	30 °C	15 h	67%	44%
2	40 °C	15 h	83%	65%
3	50 °C	15 h	83%	55%
4	60 °C	15 h	87%	47%

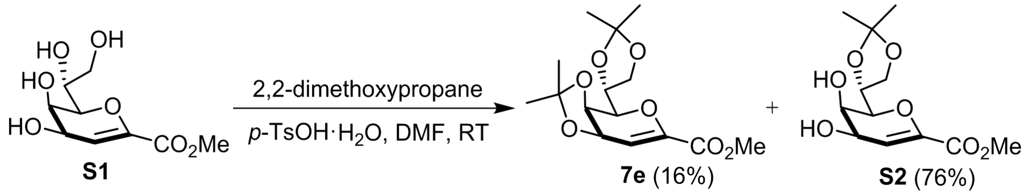
[a]Reactions were conducted on 0.075 mmol scale unless otherwise stated. [b]The ambient temperature of reactor (heating with oil bath). [c]Conversions were calculated based on the recovered starting glycal **7a** after column chromatography. [d]Yields were determined according to the isolated material via column chromatography.

3. Substrate Preparation

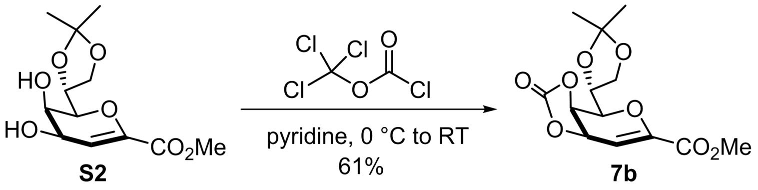
Substrates **7a**[2], **7g**[3], and **7m**[4] were prepared according to the literature methods.



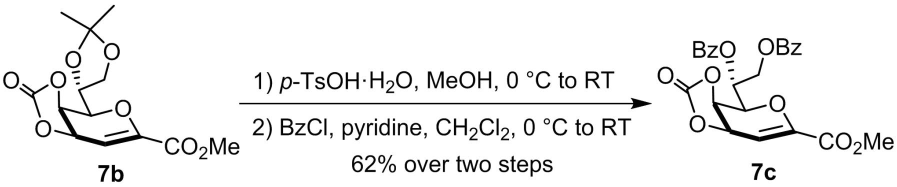
Sodium methoxide (492 mg, 9.10 mmol, 0.3 equiv) was added to a solution of compound **7a** (12.2 g, 30.3 mmol, 1.0 equiv) in MeOH (100 mL) at room temperature. After the reaction was stirred for 30 min, it was carefully neutralized with Amberlite IR 120 (H^+) resin, followed by filtration and concentration. The residue was purified through flash column chromatography (CH_2Cl_2/MeOH = 9:1, v/v) to give **S1** (4.69 g, 66%) as a white amorphous powder. **TLC**: (CH_2Cl_2/MeOH = 9:1, v/v), $R_f = 0.13$; **^{1}H NMR** (400 MHz, CD_3OD) δ 5.84 (t, $J = 2.0$ Hz, 1H), 4.49 – 4.45 (m, 1H), 4.16 – 4.12 (m, 1H), 3.99 – 3.93 (m, 1H), 3.90 – 3.81 (m, 2H), 3.76 (s, 3H), 3.72 (dd, $J = 11.6$, 5.2 Hz, 1H); **^{13}C NMR** (100 MHz, CD_3OD) δ 164.3, 144.6, 113.6, 78.6, 70.5, 66.4, 64.3, 64.1, 52.6. **$[\alpha]_D^{25}$** = −27.5 (*c* 0.38, $CHCl_3$/MeOH = 1:3, v/v); **IR** (neat): ν_{max} = 3348, 2924, 1718, 1648, 1440, 1260, 1154, 1109, 1066, 1021, 863, 844 cm^{-1}; **HRMS (ESI)**: calcd. for $C_9H_{14}NaO_7$ $[M + Na]^+$ *m*/*z* 257.0637; found *m*/*z* 257.0637.



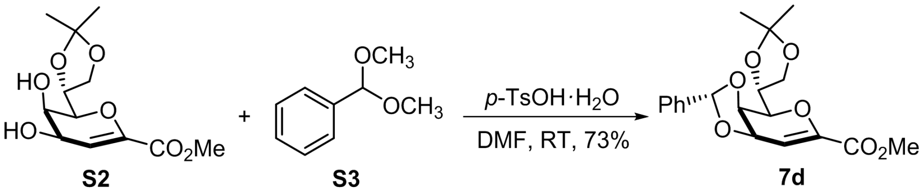
Under argon, to a stirred solution of **S1** (4.69 g, 20.0 mmol, 1.0 equiv) in DMF (80 mL) at room temperature were added 2,2-dimethoxypropane (7.41 mL, 60.1 mmol, 3.0 equiv) and catalytic *p*-toluenesulfonic acid monohydrate (382 mg, 2.00 mmol, 0.1 equiv). After the resulting mixture was stirred for 4 h at the same temperature, Et_3N was added to quench the reaction. Concentration of the mixture and purification of the crude product by column chromatography on silica gel (petroleum ether/EtOAc = 9:1 to 1:1, v/v) afforded **7e** (1.01 g, 16%) and **S2** (4.18 g, 76%), respectively. The spectroscopic data of **7e** were in good agreement with those reported in the literature.[5] Compound **S2**: **TLC**: (petroleum ether/EtOAc = 1:1, v/v), $R_f = 0.20$; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.93 (t, $J = 2.0$ Hz, 1H), 4.55 – 4.43 (m, 2H), 4.23 – 4.14 (m, 2H), 4.06 (dd, $J = 9.0$, 4.8 Hz, 1H), 3.82 – 3.80 (m, 1H), 3.79 (s, 3H), 2.75 – 2.55 (m, 2H), 1.44 (s, 3H), 1.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.2, 143.6, 112.0, 109.9, 77.8, 73.3, 66.8, 64.8, 63.7, 52.4, 26.8, 25.0; **$[\alpha]_D^{25}$** = −14.6 (*c* 0.23, $CHCl_3$); **IR** (neat): ν_{max} = 3451, 2988, 2949, 2934, 1729, 1648, 1372, 1260, 1150, 1077, 1058, 1026, 841, 752 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{12}H_{18}NaO_7$ $[M + Na]^+$ *m*/*z* 297.0950; found *m*/*z* 297.0946.



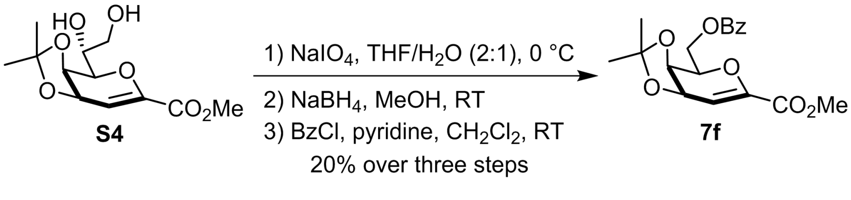
A 100 mL round-bottom flask was charged with compound **S2** (3.68 g, 13.4 mmol, 1.0 equiv) in pyridine (60 mL), diphosgene (3.24 mL, 26.9 mmol, 2.0 equiv) was dropwise added at 0 °C. After being stirred for 30 min at room temperature, the reaction was quenched by water and the mixture was extracted with EtOAc for three times. The combined organic layers were washed with brine and dried over Na_2SO_4, filtered and concentrated. Subjection of the residue to column chromatography on silica gel with petroleum ether/EtOAc (8:1, v/v) yielded **7b** (2.46 g, 61%) as a white amorphous powder. **TLC**: (petroleum ether/EtOAc = 1:1, v/v), R_f = 0.55; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.09 (d, J = 3.2 Hz, 1H), 5.32 (dd, J = 7.6, 3.6 Hz, 1H), 5.07 (d, J = 7.6 Hz, 1H), 4.45 – 4.40 (m, 1H), 4.23 – 4.14 (m, 2H), 3.82 (s, 3H), 3.78 (d, J = 8.8 Hz, 1H), 1.42 (s, 3H), 1.37 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 161.2, 153.2, 147.6, 110.2, 104.8, 75.6, 72.7, 72.2, 68.6, 66.7, 52.8, 26.9, 24.9; **$[\alpha]_D^{25}$** = +1.0 (c 0.40, $CHCl_3$); **IR** (neat): ν_{max} = 2988, 2959, 1800, 1738, 1655, 1373, 1257, 1164, 1013, 841, 769 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{13}H_{16}NaO_8$ $[M + Na]^+$ m/z 323.0743; found m/z 323.0753.



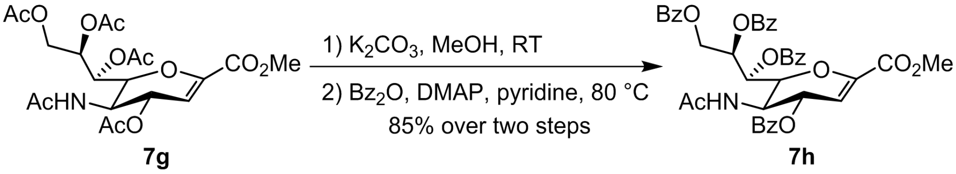
p-Toluenesulfonic acid monohydrate (951 mg, 5.00 mmol, 3.0 equiv) was added to a solution of compound **7b** (500 mg, 1.67 mmol, 1.0 equiv) in MeOH (17 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 6 h. After quench of the reaction with saturated aqueous $NaHCO_3$, the aqueous phase was extracted with EtOAc for three times; the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in *vacuo*. The crude product, dissolved in CH_2Cl_2 (17 mL) and pyridine (1.0 mL), was used directly in the next step. Benzoyl chloride (0.967 mL, 8.33 mmol, 5.0 equiv) was slowly added to the above solution at 0 °C and then the reaction mixture was stirred at room temperature. After disappearance of the crude product as monitored by TLC, the mixture was diluted with CH_2Cl_2, and washed with 0.5% HCl aqueous solution for three times. Next, the organic phase was washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4 and evaporated under reduced pressure to give a residue. Further purification by flash column chromatography (petroleum ether/EtOAc = 3:1, v/v) furnished **7c** (485 mg, 62% over two steps) as white amorphous powder. **TLC**: (petroleum ether/EtOAc = 1:1, v/v), $R_f = 0.38$; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (t, J = 8.4 Hz, 4H), 7.61 – 7.55 (m, 2H), 7.43 (q, J = 7.2 Hz, 4H), 6.17 (d, J = 3.2 Hz, 1H), 5.81 – 5.77 (m, 1H), 5.37 (dd, J = 7.6, 3.6 Hz, 1H), 5.09 (d, J = 8 Hz, 1H), 5.00 (dd, J = 12.8, 2.4 Hz, 1H), 4.78 (dd, J = 12.8, 4.8 Hz, 1H), 4.45 (d, J = 8 Hz, 1H), 3.83 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.9, 164.8, 161.0, 152.8, 147.9, 133.7, 133.3, 129.8, 129.6, 129.6, 128.9, 128.6, 128.5, 104.9, 73.4, 71.7, 69.7, 68.6, 62.0, 52.9; **$[\alpha]_D^{25}$** = −67.1 (c 0.17, $CHCl_3$); **IR** (neat): ν_{max} = 3056, 2958, 2325, 1814, 1728, 1657, 1264, 1095, 1016, 732, 703 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{24}H_{20}NaO_{10}$ $[M + Na]^+$ m/z 491.0954; found m/z 491.0952.



To a stirred solution of **S2** (500 mg, 1.82 mmol, 1.0 equiv) in DMF (10 mL) at room temperature under argon were added benzaldehyde dimethyl acetal (1.31 mL, 8.76 mmol, 4.8 equiv) and catalytic p-toluenesulfonic acid monohydrate (34.7 mg, 0.182 mmol, 0.1 equiv). After the resulting mixture was stirred overnight at the same temperature, Et_3N was added to quench the reaction. Subsequently, the mixture was concentrated in *vacuo* to afford a residue, which was purified by silical gel column chromatography (petroleum ether/EtOAc = 20:1, v/v) to give **7d** (482 mg, 73%) as colorless oil. **TLC**: (petroleum ether/EtOAc = 8:1, v/v), R_f = 0.50; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.46 (m, 2H), 7.37 (t, J = 3.2 Hz, 3H), 6.08 (dd, J = 3.2, 0.8 Hz, 1H), 5.89 (s, 1H), 5.16 (dd, J = 6.4, 3.6 Hz, 1H), 4.62 (d, J = 6.4 Hz, 1H), 4.52 – 4.48 (m, 1H), 4.22 – 4.16 (m, 2 H), 3.86 – 3.85 (m, 1H), 3.84 (s, 3H), 1.45 (s, 3H), 1.37 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 162.1, 147.4, 136.9, 129.5, 128.3, 126.7, 126.6, 109.6, 107.7, 103.0, 77.7, 73.9, 71.9, 69.7, 66.6, 52.5, 29.6, 26.8, 25.2; **$[\alpha]_D^{25}$** = −3.8 (c 0.14, $CHCl_3$); **IR** (neat): ν_{max} = 2955, 1736, 1650, 1438, 1373, 1259, 1220, 1100, 1062, 842, 759 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{19}H_{22}NaO_7$ $[M + Na]^+$ m/z 385.1263; found m/z 385.1262.

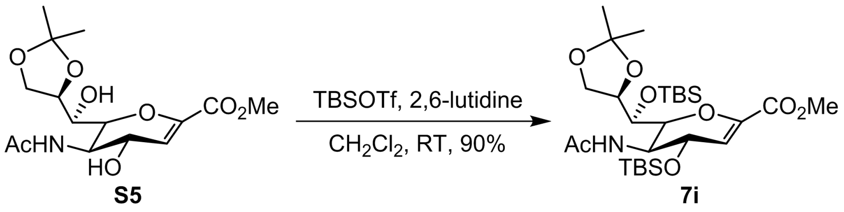


Sodium periodate (817 mg, 3.82 mmol, 1.6 equiv) was added to a solution of compound **S4**[5] (654 mg, 2.39 mmol, 1.0 equiv) in a mixture of THF (16 mL) and water (8 mL) at 0 ºC. After being stirred for 3 h at room temperature, the reaction was extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo*. The residue was dissolved in 10 mL MeOH, to which was added sodium borohydride (110 mg, 2.86 mmol, 1.2 equiv) at 0 ºC. After 30 min, water was added to quench the reaction and MeOH was removed under reduced pressure. The mixture was subsequently extacted with EtOAc for three times, and the combined organic layers were washed with brine, dried, and concentrated to give the crude product. It was directly dissolved in dry CH_2Cl_2 (6 mL), then pyridine (0.5 mL) and benzoyl chloride (0.831 mL, 7.16 mmol, 3.0 equiv) were added slowly at 0 ºC under an argon atmosphere. The reaction mixture was stirred at room temperature until complete consumption of the starting alcohol as monitored by TLC analysis. The mixture was diluted with CH_2Cl_2 and washed with 0.5% aqueous HCl solution for three times. The organic phase was washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4, filtered and concentrated in *vacuo*. Purification of the residue via flash column chromatography (petroleum ether/EtOAc = 9:1, v/v) afforded compound **7f** (166 mg, 20% over three steps). **TLC**: (petroleum ether/EtOAc = 4:1, v/v), $R_f = 0.65$; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.2 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 8.0 Hz, 2H), 6.05 (d, J = 2.0 Hz, 1H), 4.82 (dd, J = 6.0, 3.2 Hz, 1H), 4.76 – 4.67 (m, 2H), 4.41 (d, J = 6.0 Hz, 1H), 4.36 (t, J = 6.8 Hz, 1H), 3.81 (s, 3H), 1.41 (s, 3H), 1.38 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.3, 162.5, 144.0, 133.2, 129.8, 128.4, 111.3, 110.1, 74.1, 71.7, 68.8, 63.8, 52.4, 27.9, 26.5; **$[\alpha]_D^{25}$** = +13.6 (c 0.12, $CHCl_3$); **IR** (neat): ν_{max} = 2919, 1725, 1653, 1451, 1245, 1112, 1028, 712 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{18}H_{20}NaO_7$ $[M + Na]^+$ *m/z* 371.1107; found *m/z* 371.1104.

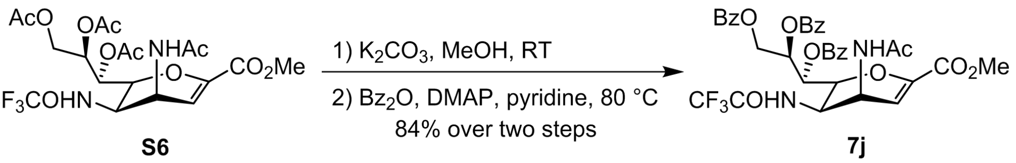


Potassium carbonate (1.46 g, 10.6 mmol, 0.5 equiv) was added to a solution of **7g**[3] (10.0 g, 21.1 mmol, 1.0 equiv) in MeOH (200 mL) at room temperature. After being stirred for 30 min, the mixture was neutralized with Amberlite IR 120 (H^+) resin, followed by filtration and concentration. The residue, benzoic anhydride (47.8 g, 211 mmol, 10.0 equiv) and 4-dimethylaminopyridine (517 mg, 4.23 mmol, 0.2 equiv) were placed in a 200 mL round bottom flask, followed by addition of dry pyridine (100 mL). After being stirred overnight at 80 ºC, the reaction mixture was concentrated in *vacuo*. Flash column chromatography of the residue on silica gel (petroleum ether/EtOAc = 4:1 to 2:1, v/v) gave **7h** (13.1 g, 85%) as a white amorphous powder. **TLC**: (petroleum ether/EtOAc = 1:1, v/v), $R_f = 0.48$; **^{1}H NMR**

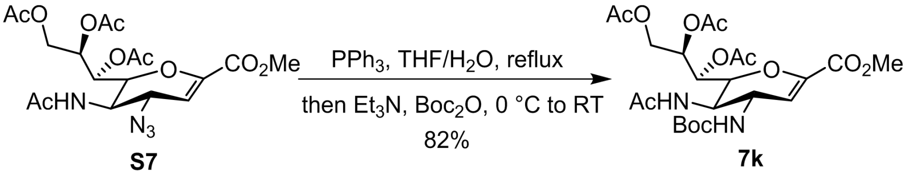
(400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.2 Hz 2H), 8.01 – 7.92 (m, 6H), 7.64 – 7.44 (m, 6H), 7.43 – 7.28 (m, 6H), 6.14 (d, J = 3.2 Hz, 1H), 6.11 – 6.06 (m, 1H), 6.05 – 5.90 (m, 2H), 5.85 – 5.75 (m, 1H), 5.16 (dd, J = 12.4, 3.6 Hz, 1H), 4.96 (dd, J = 9.6, 3.2 Hz, 1H), 4.64 (dd, J = 12.0, 6.4 Hz, 1H), 4.39 (q, J = 8.8 Hz, 1H), 3.76 (s, 3H), 1.89 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.2, 170.2, 166.3, 166.1, 165.6, 165.5, 161.7, 145.4, 133.5, 133.3, 133.3, 133.0, 123.0, 129.8, 129.8, 129.7, 129.4, 129.2, 129.1, 128.5, 128.4, 128.4, 128.3, 108.4, 108.3, 76.5, 71.4, 68.9, 68.8, 62.6, 52.4, 47.9, 23.1; **[α]**$_D^{25}$ = +133.6 (*c* 1.47, $CHCl_3$); **IR** (neat): ν_{max} = 3269, 3065, 2956, 1719, 1248, 1092, 1068, 1025, 708 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{40}H_{35}NNaO_{12}$ $[M + Na]^+$ *m/z* 744.2057; found *m/z* 744.2048.



Under an argon atmosphere, 2,6-lutidine (2.10 mL, 17.4 mmol, 10.0 equiv) and trifluoromethanesulfonic acid *tert*-butyldimethylsilyl ester (2.79 mL, 12.2 mmol, 7.0 equiv) were successively added to a solution of compound **S5**^{6} (600 mg, 1.74 mmol, 1.0 equiv) in dry CH_2Cl_2 (10 mL). The reaction was stirred overnight, before it was quenched by adding water. The resultant mixture was extracted with EtOAc for three times, the combined organic layers were dried over Na_2SO_4, filtered and concentrated. Subjection of the residue to flash column chromatography (petroleum ether/EtOAc = 5:1, v/v) gave **7i** (902 mg, 90%). **TLC**: (petroleum ether/EtOAc = 3:1, v/v), R_f = 0.30; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.97 (d, J = 4.4 Hz, 1H), 5.57 (d, J = 7.6 Hz, 1H), 4.46 (dd, J = 6.8, 2.8 Hz, 1H), 4.37 – 4.27 (m, 2H), 4.22 (t, J = 5.6 Hz, 1H), 4.03 – 3.92 (m, 2H), 3.88 (t, J = 8.0 Hz, 1H), 3.81 (s, 3H), 1.95 (s, 3H), 1.41 (s, 3H), 1.30 (s, 3H), 0.90 (s, 18H), 0.13 (s, 6H), 0.07 (s, 3H), −0.01 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.6, 162.7, 142.8, 110.1, 108.3, 79.4, 75.8, 68.3, 64.0, 63.8, 52.2, 50.3, 26.4, 25.9, 25.7, 25.3, 23.3, 18.2, 17.9, −3.6, −4.6, −4.9, −4.9; **[α]**$_D^{25}$ = +52.1 (*c* 0.73, $CHCl_3$); **IR** (neat): ν_{max} = 3271, 2953, 2930, 2887, 2857, 1738, 1649, 1257, 1063, 834, 777, 756 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{27}H_{51}NNaO_8Si_2$ $[M + Na]^+$ *m/z* 596.3051; found *m/z* 596.3083.

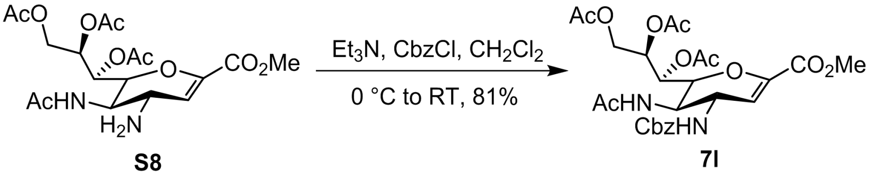


Potassium carbonate (68.3 mg, 0.494 mmol, 0.5 equiv) was added to a solution of **S6**[7] (520 mg, 0.988 mmol, 1.0 equiv) in MeOH (10 mL). After being stirred for 15 min, the mixture was neutralized with Amberlite IR 120 (H^+) resin, then filtered and concentrated to give a white product, which was dissolved in 10 mL anhydrous pyridine. Next, to the solution were added benzoic anhydride (2.24 g, 9.88 mmol, 10.0 equiv) and 4-dimethylaminopyridine (24.2 mg, 0.198 mmol, 0.2 equiv). The reaction mixture was allowed to stir at 80 °C for 5 h, before removal of the solvent in *vacuo*. Flash column chromatography of the residue on silica gel (petroleum ether/EtOAc = 1:1, v/v) yielded **7j** (590 mg, 84%) as a white amorphous powder. **TLC**: (petroleum ether/EtOAc = 1:2, v/v), $R_f = 0.65$; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.2 Hz, 2H), 7.96 – 7.89 (m, 4H), 7.74 (d, J = 8.8 Hz, 1H), 7.60 – 7.29 (m, 9H), 6.35 (d, J = 8.4 Hz, 1H), 6.03 (d, J = 4.8 Hz, 2H), 5.94 – 5.87 (m, 1H), 5.23 (dd, J = 12.4, 3.2 Hz, 1H), 4.97 – 4.88 (m, 1H), 4.71 – 4.60 (m, 2H), 4.45 – 4.35 (m, 1H), 3.72 (s, 3H), 1.91 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 166.2, 166.0, 165.1, 161.7, 157.9 (q, J = 38 Hz), 145.2, 133.7, 133.4, 133.1, 129.9, 129.8, 129.6, 129.5, 129.1, 128.7, 128.6, 128.4, 128.3, 115.5 (q, J = 286 Hz), 108.2, 73.4, 71.7, 69.3, 62.8, 52.5, 48.0, 43.1, 22.8; **$[\alpha]_D^{25}$** = +10.6 (c 0.97, $CHCl_3$); **IR** (neat): ν_{max} = 3260, 3064, 2958, 1721, 1651, 1259, 1163, 1090, 1068, 1025 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{35}H_{31}F_3N_2NaO_{11}$ $[M + Na]^+$ m/z 735.1778; found m/z 735.1768.



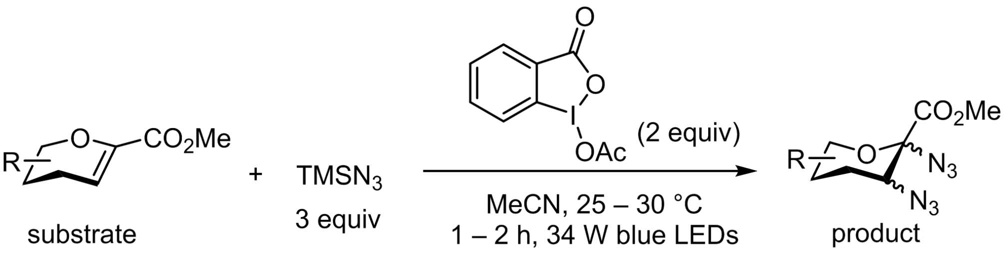
To a solution of compound **S7**[4] (2.40 g, 5.26 mmol, 1.0 equiv) in a mixture of THF (20 mL) and H_2O (4 mL) was added triphenylphosphine (1.66 g, 6.32 mmol, 1.2 equiv) at room temperature. The mixture was refluxed for 4 h at 85 ºC before being cooled to 0 ºC. Triethylamine (1.10 mL, 7.89 mmol, 1.5 equiv) and ditertbutyl dicarbonate (1.81 mL, 7.89 mmol, 1.5 equiv) were added, and the resultant mixture was stirred for 3 h at room temperature. After evaporation of solvent, the residue was purified by silical gel column chromatography (petroleum ether/EtOAc = 1:1, v/v) to give **7k** (2.32 g, 82%) as a white amorphous powder. **TLC**: (petroleum ether/EtOAc = 1:2, v/v), $R_f = 0.25$; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.09 – 5.91 (m, 1H), 5.89 (d, J = 2.4 Hz, 1H), 5.47 (dd, J = 5.2, 2.0 Hz, 1H), 5.32 – 5.25 (m, 1H), 4.89 – 4.78 (m, 1H), 4.68 (dd, J = 12.4, 2.8 Hz, 1H), 4.45 (td, J = 9.6, 2.4 Hz, 1H), 4.27 – 4.10 (m, 3H), 3.77 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.90 (s, 3H), 1.40 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 170.6, 170.2, 170.0, 161.7, 156.2, 144.7, 110.8, 80.2, 77.5, 71.3, 67.8, 62.2, 52.4, 50.0, 47.5, 28.2, 23.1, 20.9, 20.7, 20.7; **$[\alpha]_D^{25}$** = +37.6

(*c* 1.10, $CHCl_3$); **IR** (neat): ν_{max} = 3342, 2978, 1738, 1663, 1527, 1368, 1247, 1215, 1162, 1091, 1043, 1024, 734 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{23}H_{34}N_2NaO_{12}$ [M + Na]$^+$ *m*/*z* 553.2009; found *m*/*z* 553.2005.



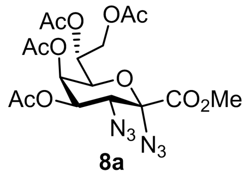
Triethylamine (112 μL, 0.802 mmol, 1.5 equiv) and benzyl chloroformate (150 μL, 1.07 mmol, 2.0 equiv) were added to a solution of **S8**[4] (230 mg, 0.535 mmol, 1.0 equiv) in CH_2Cl_2 (2.5 mL) at 0 °C. After being stirred at room temperature for 2 h, the reaction mixture was directly concentrated in *vacuo*. Purification of the crude product by column chromatography with petroleum ether/acetone (1.5:1, v/v) provided **7l** (244 mg, 81%) as a white amorphous powder. **TLC**: (petroleum ether/EtOAc = 1:3, v/v), R_f = 0.45; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 –7.27 (m, 5H), 6.02 (d, *J* = 9.6 Hz, 1H), 5.88 (d, *J* = 2.4 Hz, 1H), 5.50 – 5.45 (m, 1H), 5.32 – 5.20 (m, 2H), 5.04 (q, *J* = 12.4 Hz, 1H), 4.71 (dd, *J* = 12.4, 2.8 Hz, 1H), 4.52 (td, *J* = 9.6, 2.8 Hz, 1H), 4.31 – 4.11 (m, 3H), 3.74 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.67 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.0, 170.6, 170.4, 170.0, 161.7, 156.8, 144.5, 136.2, 128.5, 128.1, 127.6, 110.6, 77.2, 71.6, 67.8, 67.0, 62.2, 52.4, 50.7, 47.0, 22.9, 20.9, 20.7, 20.6; **$[\alpha]_D^{25}$** = +54.0 (*c* 0.90, $CHCl_3$); **IR** (neat): ν_{max} = 3333, 3060, 2957, 2917, 1739, 1664, 1539, 1371, 1261, 1220, 1094, 1044 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{26}H_{32}N_2NaO_{12}$ [M + Na]$^+$ *m*/*z* 587.1853; found *m*/*z* 587.1848.

4. General Procedure and Product Characterization



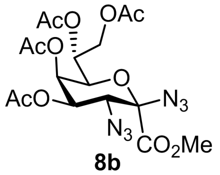
Under an argon atmosphere, to an oven-dried flask were successively added substrate (1.0 equiv), BI-OAc (2.0 equiv), dry MeCN (0.1 M) and azidotrimethylsilane (3.0 equiv). The reaction mixture was stirred with irradiation of two 34 W blue LED lamps (the average distance between the lamp and the flask is about 11 cm). The ambient temperature of reactor was maintained 25 to 30 °C by a fan. After the reaction was completed (identified by TLC analysis), it was quenched with saturated aqueous $KHCO_3$, and the mixture was stirred vigorously at room temperature for 5 min, then extracted with EtOAc for three times. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude residue was purified by silica gel column chromatography using the indicated conditions to afford the corresponding product.

Following the general procedure, the reaction of substrate **7a** (1.01 g, 2.51 mmol, 1.0 equiv), BI-OAc (1.54 g, 5.02 mmol, 2.0 equiv) and azidotrimethylsilane (0.991 mL, 7.53 mmol, 3.0 equiv) proceeded in 1.5 h to afford product **8** as four diastereomers (1.05 g, 86%) after silica gel column chromatography (petroleum ether/acetone = 8:1, v/v). HPLC analysis (Waters e2695 Separations Module; Flow rate: 1.0 mL/min; Column: Agilent ZORBAX 300SB-C8, 5 µm, 4.6 × 150 mm; Detector: Waters 2424 ELSD; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 60:40 → 50:50) indicated the ratio of **8a**–**d** to be 43:30:23:4. Pure products **8a**, **8b**, **8c**, and **8d** were respectively obtained through repeated silica gel column chromatography (petroleum ether/EtOAc = 6:1 or petroleum ether/acetone = 13:1, v/v) combined with reverse-phase C18 HPLC (H_2O/MeOH = 60:40 → 40:60 → 30:70, v/v).



8a

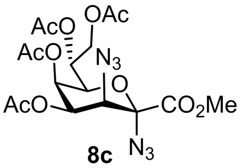
TLC: (petroleum ether/EtOAc = 2:1, v/v), R_f = 0.53; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.48 (d, J = 1.8 Hz, 1H), 5.21 – 5.16 (m, 2H), 4.47 (dd, J = 12.6, 2.4 Hz, 1H), 4.43 (d, J = 9.6 Hz, 1H), 4.23 (d, J = 10.8 Hz, 1H), 4.09 (dd, J = 12.6, 3.2 Hz, 1H), 3.97 (s, 3H), 2.14 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.6, 170.1, 169.6, 169.5, 165.3, 91.6, 69.8, 69.2, 66.8, 65.4, 61.8, 58.0, 56.2, 54.1, 20.7, 20.6, 20.6; **[α]**$_D^{25}$ = +64.5 (*c* 0.11, $CHCl_3$); **IR** (neat): ν_{max} = 2927, 2118, 1752, 1437, 1370, 1226, 1076, 957, 750 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{17}H_{22}N_6NaO_{11}$ $[M + Na]^+$ *m/z* 509.1244; found *m/z* 509.1253; HPLC purity: 93.6% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX 300SB-C8, 5 µm, 4.6 × 150 mm; Detector: Waters 2424 ELSD; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 60:40 → 50:50, v/v; t_R = 21.31).



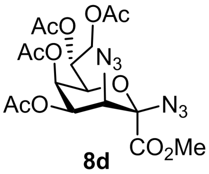
8b

TLC: (petroleum ether/EtOAc = 2:1, v/v), R_f = 0.52; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.48 (d, J = 9.2 Hz, 2H), 5.14 (d, J = 9.2 Hz, 1H), 4.36 (t, J = 8.8 Hz, 2H), 4.22 (dd, J = 12, 2.8 Hz, 1H), 3.92 (s, 3H), 3.76 (d, J = 10 Hz, 1H), 2.14 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.3, 170.1, 169.5, 169.5, 165.7, 91.2, 71.5, 69.4, 67.4, 65.1, 61.8, 61.3, 53.6, 20.7, 20.6, 20.6, 20.6; **[α]**$_D^{25}$ = +32.5 (*c* 0.08, $CHCl_3$); **IR** (neat): ν_{max} = 2926, 2118, 1752, 1437, 1372, 1228, 1080, 804, 735 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{17}H_{22}N_6NaO_{11}$ $[M + Na]^+$ *m/z* 509.1244; found *m/z* 509.1253; HPLC purity: 99.8% (Flow rate: 1.0 mL/min;

Column: Agilent ZORBAX 300SB-C8, 5 µm, 4.6 × 150 mm; Detector: Waters 2424 ELSD; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 60:40 → 50:50, v/v; t_R = 22.76).

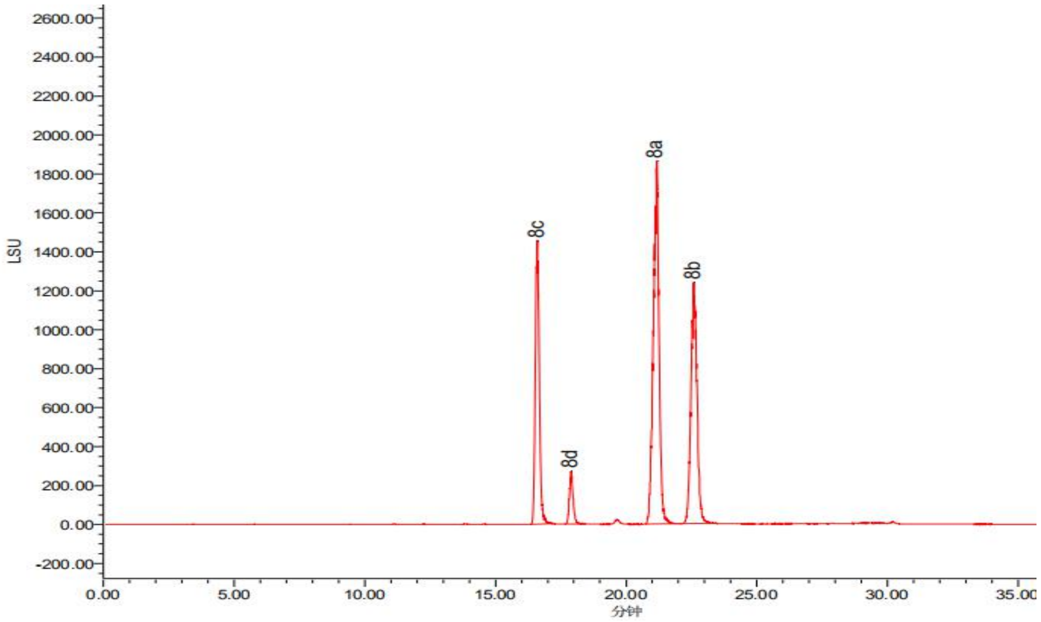

8c

TLC: (petroleum ether/EtOAc = 2:1, v/v), R_f = 0.52; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.42 (d, J = 2.4 Hz, 2H), 5.34 (d, J = 10 Hz, 1H), 4.55 (dd, J = 12.4, 2.0 Hz, 1H), 4.42 (d, J = 9.6 Hz, 1H), 4.24 (dd, J = 12.8, 2.8 Hz, 1H), 4.07 (t, J = 2.0 Hz, 1H), 3.93 (s, 3H), 2.13 (s, 3H), 2.08 (s, 6H), 1.99 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.5, 170.5, 169.4, 169.2, 164.4, 91.5, 69.4, 67.3, 67.1, 63.3, 61.8, 58.5, 53.7, 20.7, 20.6, 20.6, 20.3; **[α]$_D$^{25}** = +116.2 (c 0.32, $CHCl_3$); **IR** (neat): ν_{max} = 2959, 2118, 1748, 1438, 1372, 1223, 1053, 924, 732 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{17}H_{22}N_6NaO_{11}$ $[M + Na]^+$ m/z 509.1244; found m/z 509.1231; HPLC purity: 97.7% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX 300SB-C8, 5 µm, 4.6 × 150 mm; Detector: Waters 2424 ELSD; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 60:40 → 50:50, v/v; t_R = 16.59); The supplementary crystallographic data of **8c** [m.p.: 108 – 110 °C (hexane/$CHCl_3$ = 5:1, v/v)] have been deposited in Cambridge Crystallographic Data Centre (CCDC 1975133). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.


8d

TLC: (petroleum ether/EtOAc = 2:1, v/v), R_f = 0.48; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.34 (s, 1H), 5.30 (d, J = 9.6 Hz, 1H), 5.15 (t, J = 2.8 Hz, 1H), 4.46 (d, J = 12.4 Hz, 1H), 4.29 (dd, J = 12.4, 3.2 Hz, 1H), 4.22 (d, J = 3.2 Hz, 1H), 3.97 (d, J = 9.6 Hz, 1H), 3.92 (s, 3H), 2.16 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H), 1.98 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.5, 170.4, 169.3, 169.3, 165.8, 90.1, 71.9, 67.7, 67.3, 62.9, 61.7, 58.7, 53.9, 20.7, 20.6, 20.5, 20.4; **[α]$_D$^{25}** = +101.8 (c 0.09, $CHCl_3$); **IR** (neat): ν_{max} = 2918, 2115, 1747, 1436, 1372, 1225, 1045, 923, 733 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{17}H_{22}N_6NaO_{11}$ $[M + Na]^+$ m/z 509.1244; found m/z 509.1258; HPLC purity: 99.3% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX 300SB-C8, 5 µm, 4.6 × 150 mm; Detector: Waters 2424 ELSD; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 60:40 → 50:50, v/v; t_R = 17.93); The supplementary crystallographic data of **8d** [m.p.: 126 – 128 °C (hexane/$CHCl_3$ = 5:1, v/v)] have been deposited in Cambridge Crystallographic Data Centre (CCDC 1975134). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

HPLC for measuring d.r. value of 8

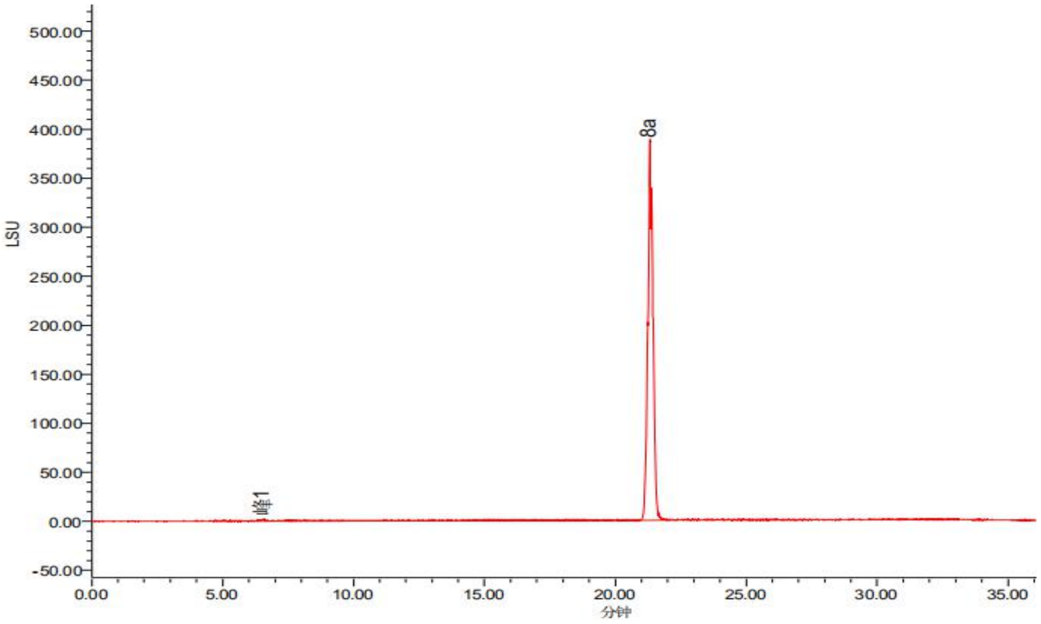


Run information: column: Agilent ZORBAX 300SB-C8, 5 μm, 4.6 × 150 mm; Detector: Waters 2424 ELSD; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 60:40 → 50:50, v/v.

Peak information:

Peak	Isomer	RetTime [min]	Area [mAU*s]	Height [mAU]	Area (%)
1	**8c**	16.588	15071187	1452881	23.11
2	**8d**	17.898	2724899	271171	4.18
3	**8a**	21.174	27853274	1862561	42.72
4	**8b**	22.585	19555577	1234573	29.99

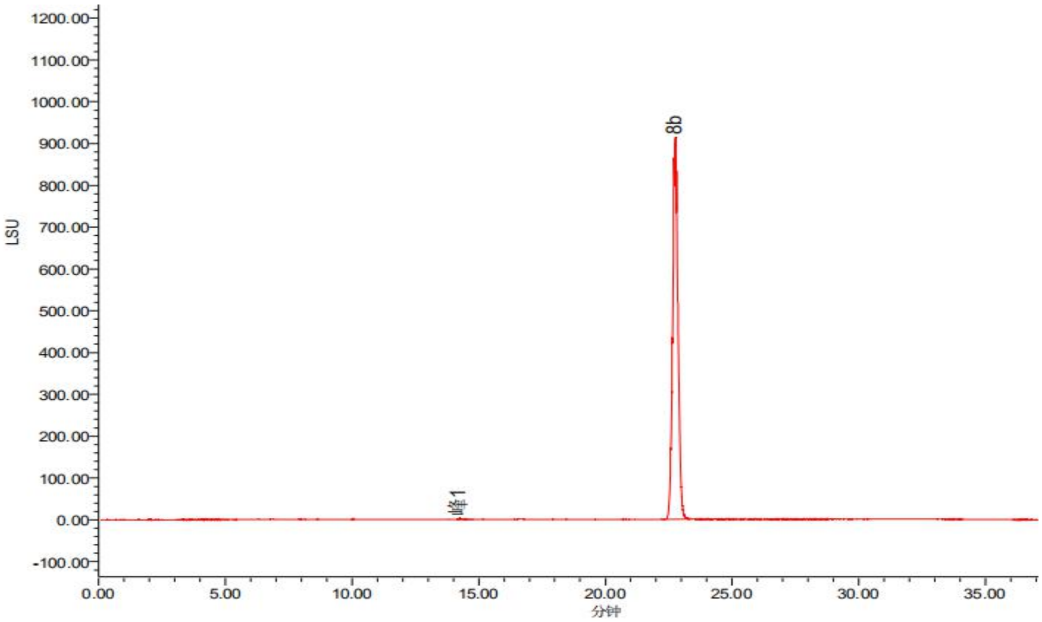
HPLC analysis of 8a under the same condition:



Peak information:

Peak	RetTime [min]	Area [mAU*s]	Height [mAU]	Area (%)
1	6.569	350767	2014	6.40
2	21.315	5132674	388119	93.60

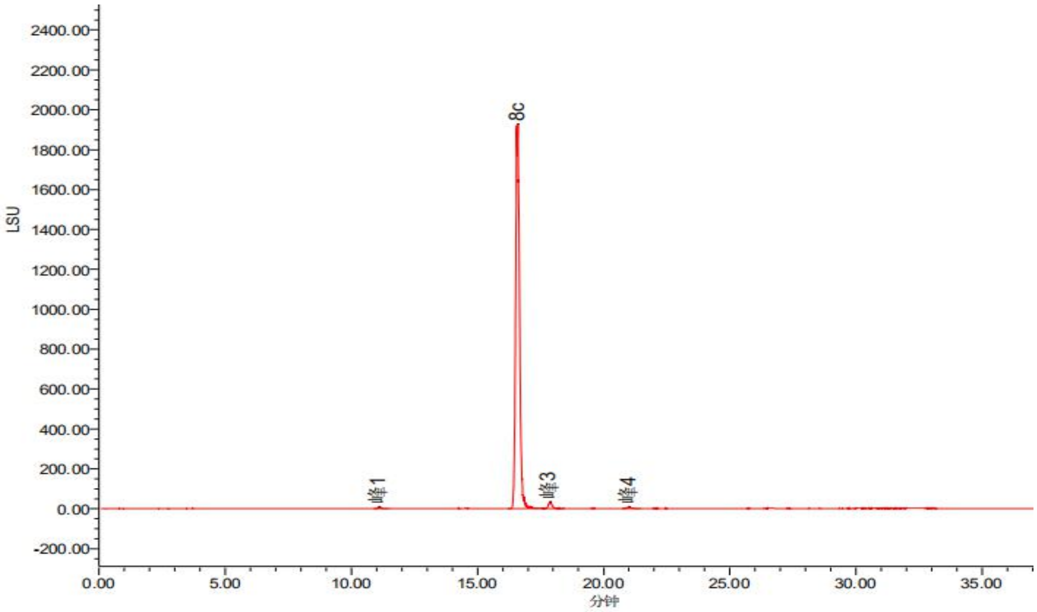
HPLC analysis of 8b under the same condition:



Peak information:

Peak	RetTime [min]	Area [mAU*s]	Height [mAU]	Area (%)
1	14.246	20992	1784	0.15
2	22.766	13601865	914079	99.85

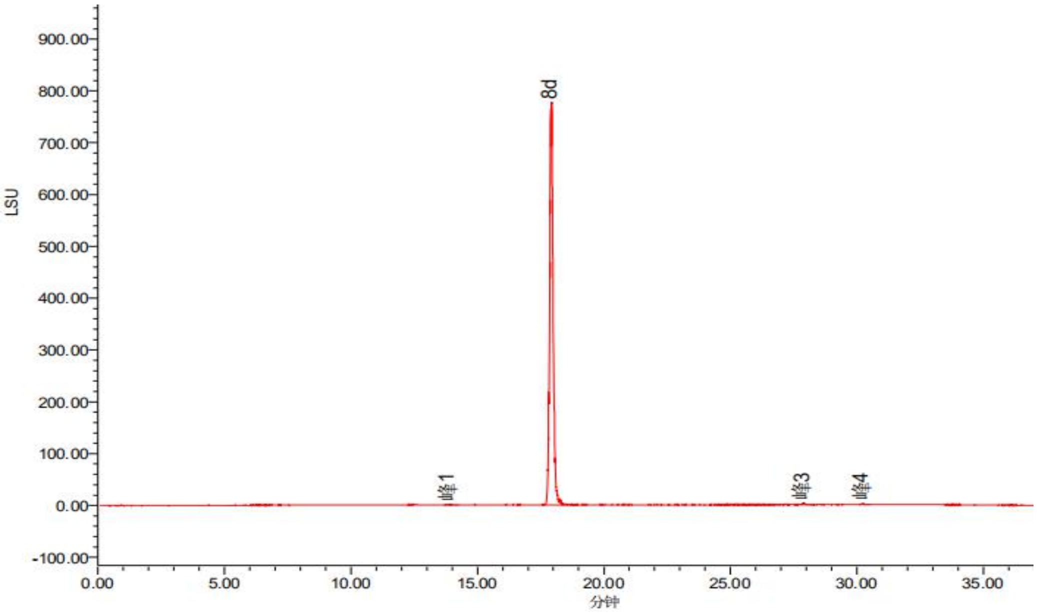
HPLC analysis of 8c under the same condition:



Peak information:

Peak	RetTime [min]	Area [mAU*s]	Height [mAU]	Area (%)
1	11.107	62605	8406	0.30
2	16.590	20660693	1926998	97.68
3	17.880	333054	34312	1.57
4	21.015	95892	7490	0.45

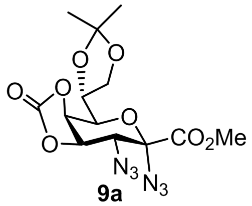
HPLC analysis of 8d under the same condition:



Peak information:

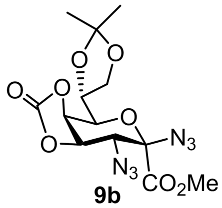
Peak	RetTime [min]	Area [mAU*s]	Height [mAU]	Area (%)
1	13.866	12363	1339	0.16
2	17.927	7617236	775286	99.26
3	27.881	24075	2627	0.31
4	30.233	20293	2382	0.26

Following the general procedure, the mixture of substrate **7b** (1.20 g, 4.00 mmol, 1.0 equiv), BI-OAc (2.45 g, 8.00 mmol, 2.0 equiv) and azidotrimethylsilane (1.58 mL, 12.0 mmol, 3.0 equiv) was subjected to the diazidation reaction in 1 h to afford two isomers **9a** (537 mg, 35%) and **9b** (845 mg, 53%) after purification by silica gel column chromatography (petroleum ether/EtOAc = 8:1 to 5:1, v/v).



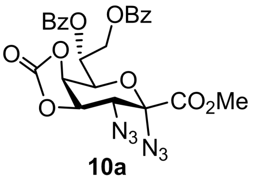
9a

TLC: (petroleum ether/EtOAc = 4:1, v/v), R_f = 0.50; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.91 (dd, J = 6.8, 2.0 Hz, 1H), 4.77 (t, J = 6.8 Hz, 1H), 4.37 – 4.32 (m, 1H), 4.21 (d, J = 6.8 Hz, 1H), 4.18 – 4.12 (m, 1H), 4.01 (d, J = 2.0 Hz, 1H), 3.99 – 3.95 (m, 1H), 3.94 (s, 3H), 1.44 (s, 3H), 1.36 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.1, 152.5, 110.2, 90.0, 74.5, 73.3, 72.7, 71.2, 67.0, 60.1, 54.2, 26.8, 24.8; **[α]**$_D^{25}$ = +76.7 (*c* 0.68, $CHCl_3$); **IR** (neat): ν_{max} = 2988, 2968, 2121, 1820, 1768, 1079, 846, 759 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{13}H_{16}N_6NaO_8$ [M + Na]$^+$ *m*/*z* 407.0927; found *m*/*z* 407.0932; HPLC purity: 99.3% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 μm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 10:90, v/v; t_R = 1.89); The supplementary crystallographic data of **9a** [m.p.: 124 – 126 °C ($CDCl_3$)] have been deposited in Cambridge Crystallographic Data Centre (CCDC 1975130). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

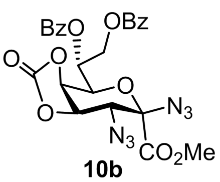

9b

TLC: (petroleum ether/EtOAc = 4:1, v/v), R_f = 0.45; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.02 (dd, *J* = 8.0, 5.2 Hz, 1H), 4.96 (dd, *J* = 8.0, 1.6 Hz, 1H), 4.36 – 4.31 (m, 1H), 4.19 – 4.12 (m, 2H), 3.94 (s, 3H), 3.91 (d, *J* = 4.8 Hz, 1H), 3.79 (dd, *J* = 8.4, 1.6 Hz, 1H), 1.41 (s, 3H), 1.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 152.7, 110.2, 89.3, 73.7, 72.8, 72.5, 72.4, 66.7, 61.2, 53.7, 26.9, 24.8; **[α]**$_D^{25}$ = +40.0 (*c* 0.08, $CHCl_3$); **IR** (neat): ν_{max} = 2988, 2967, 2111, 1820, 1767, 1078, 846, 759 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{13}H_{16}N_6NaO_8$ [M + Na]$^+$ *m*/*z* 407.0927; found *m*/*z* 407.0915; HPLC purity: 99.4% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 μm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 10:90, v/v; t_R = 1.85); The supplementary crystallographic data of **9b** [m.p.: 111 – 113 °C ($CDCl_3$ = 3:1, v/v)] have been deposited in Cambridge Crystallographic Data Centre (CCDC 1975131). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Following the general procedure, the diazidation reaction of **7c** (100 mg, 0.214 mmol, 1.0 equiv) proceeded with BI-OAc (131 mg, 0.427 mmol, 2.0 equiv) and azidotrimethylsilane (84.3 μL, 0.641 mmol, 3.0 equiv) in 1 h to afford two isomers **10a** (32.0 mg, 27%) and **10b** (63.7 mg, 54%) after purification by column chromatography (petroleum ether/EtOAc = 2:1, v/v).


10a

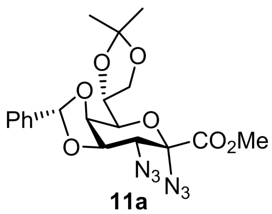
TLC: (petroleum ether/EtOAc = 1:2, v/v), R_f = 0.52; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 – 7.98 (m, 4H), 7.58 (q, *J* = 2.0 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 4H), 5.70 – 5.66 (m, 1H), 5.01 – 4.93 (m, 2H), 4.82 – 4.78 (m, 2H), 4.62 (dd, *J* = 12.4, 3.2 Hz, 1H), 4.28 (d, *J* = 7.2 Hz, 1H), 3.97 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.9, 164.9, 164.6, 152.1, 133.7, 133.3, 129.8, 129.6, 129.5, 128.9, 128.6, 128.5, 90.3, 74.4, 72.7, 69.4, 68.1, 61.7, 59.9, 54.4; **[α]**$_D^{25}$ = +57.4 (c 0.12, $CHCl_3$); **IR** (neat): ν_{max} = 3341, 2960, 2122, 1827, 1729, 1452, 1265, 1094, 736 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{24}H_{20}N_6NaO_{10}$ [M + Na]$^+$ *m*/*z* 575.1139; found *m*/*z* 575.1145.



10b

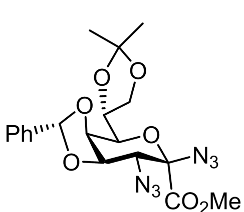
TLC: (petroleum ether/EtOAc = 1:2, v/v), R_f = 0.46; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (t, J = 7.6 Hz, 4H), 7.58 (q, J = 7.6, 2H), 7.48 – 7.43 (m, 4H), 5.68 – 5.65 (m, 1H), 5.05 (t, J = 7.2 Hz, 1H), 4.96 (dd, J = 7.6, 1.6 Hz, 1H), 4.83 – 4.81(m, 2H), 4.50 (dd, J = 9.2, 1.6 Hz, 1H), 3.85 (d, J = 5.6 Hz, 1H), 3.71 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.7, 165.2, 164.5, 152.3, 133.7, 133.4, 129.8, 129.6, 129.5, 128.9, 128.6, 128.5, 89.9, 74.4, 72.1, 69.7, 69.6, 62.1, 61.9, 53.7; **[α]**$_D^{25}$ = +27.6 (c 0.12, $CHCl_3$); **IR** (neat): ν_{max} = 3341, 2961, 2120, 1822, 1730, 1452, 1262, 1094, 736 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{24}H_{20}N_6NaO_{10}$ $[M + Na]^+$ m/z 575.1139; found m/z 575.1135.

Following the general procedure, compound **7d** (320 mg, 0.884 mmol, 1.0 equiv), BI-OAc (541 mg, 1.77 mmol, 2.0 equiv), azidotrimethylsilane (0.349 mL, 2.65 mmol, 3.0 equiv) and dry MeCN (8.8 mL) were used. The reaction was completed in 1 h to provide the isomers **11a** (104 mg, 26%) and **11b** (157 mg, 40%) after purification by column chromatography (petroleum ether/EtOAc = 30:1, v/v).



11a

TLC: (petroleum ether/EtOAc = 7:1, v/v), R_f = 0.45; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 5H), 6.24 (s, 1H), 4.51 (dd, J = 8.0, 5.2 Hz, 1H), 4.43 (dd, J = 12.4, 6.0 Hz, 1H), 4.35 (dd, J = 5.2, 2.4 Hz, 1H), 4.13 (dd, J = 8.8, 6.0 Hz, 1H), 4.07 – 4.00 (m, 3H), 3.95 (s, 3H), 1.41 (s, 3H), 1.36 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.9, 138.2, 129.2, 128.5, 126.0, 109.7, 103.4, 90.9, 75.1, 73.7, 72.6, 72.4, 66.9, 59.5, 53.9, 26.8, 25.3; **[α]**$_D^{25}$ = +53.7 (c 0.20, $CHCl_3$); **IR** (neat): ν_{max} = 2988, 2114, 1756, 1372, 1260, 1225, 1098, 1074, 847, 750 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{19}H_{22}N_6NaO_7$ $[M + Na]^+$ m/z 469.1448; found m/z 469.1469.

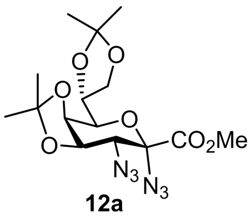


11b

TLC: (petroleum ether/EtOAc = 7:1, v/v), R_f = 0.35; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 5H), 6.25 (s, 1H), 4.77 (t, J = 6.0 Hz, 1H), 4.42 (dd, J = 12.0, 5.2 Hz, 1H), 4.36 (dd, J = 5.6, 1.6 Hz, 1H), 4.14 (d, J = 5.6 Hz, 2H), 3.92 (s, 3H), 3.81 (dd, J = 7.2, 1.6 Hz, 1H), 3.74 (d, J = 6.8 Hz, 1H), 1.40 (s, 3H), 1.36 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 138.1, 129.2, 128.5, 126.1, 109.6, 103.7, 90.1, 75.2, 73.9, 73.8, 72.0, 66.5, 62.6, 53.4, 26.8, 25.2; **[α]**$_D^{25}$ = +24.2 (c 0.16, $CHCl_3$); **IR** (neat): ν_{max} = 2988, 2113, 1745, 1372, 1259, 1221, 1097, 1074, 847, 750 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{19}H_{22}N_6NaO_7$ $[M + Na]^+$ m/z 469.1448; found m/z 469.1463.

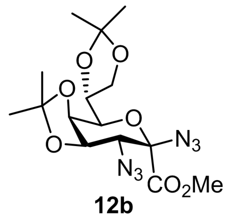
Following the general procedure, the diazidation reaction of **7e** (200 mg, 0.637 mmol, 1.0

equiv) occurred in the presence of BI-OAc (390 mg, 1.27 mmol, 2.0 equiv) and azidotrimethylsilane (0.251 mL, 1.91 mmol, 3.0 equiv) in 30 min to provide **12a** (103 mg, 41%) and **12b** (41.2 mg, 27%) after purification by column chromatography (petroleum ether/EtOAc = 30:1, v/v).



12a

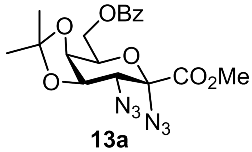
TLC: (petroleum ether/EtOAc = 5:1, v/v), R_f = 0.51; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.40 – 4.28 (m, 3H), 4.11 (dd, J = 9.2, 6.4 Hz, 1H), 4.02 – 3.98 (m, 3H), 3.90 (s, 3H), 1.53 (s, 3H), 1.43 (s, 3H), 1.40 (s, 3H), 1.37 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.0, 110.5, 109.7, 90.7, 74.0, 73.5, 72.6, 72.0, 66.9, 61.3, 53.8, 27.7, 26.9, 26.1, 25.3; **[α]**$_D^{25}$ = +59.7 (*c* 0.31, $CHCl_3$); **IR** (neat): ν_{max} = 2930, 2116, 1757, 1374, 1265, 1074, 810, 733 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{15}H_{22}N_6NaO_7$ [M + Na]$^+$ *m/z* 421.1448; found *m/z* 421.1455; HPLC purity: 91.9% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 μm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 10:90, v/v; t_R = 2.37).



12b

TLC: (petroleum ether/EtOAc = 5:1, v/v), R_f = 0.42; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.57 (t, J = 6.4 Hz, 1H), 4.38 – 4.32 (m, 2H), 4.15 – 4.08 (m, 2H), 3.90 (s, 3H), 3.75 (dd, J = 7.6, 1.2 Hz, 1H), 3.63 (d, J = 6.4 Hz, 1H), 1.56 (s, 3H), 1.42 (s, 3H), 1.40 (s, 3H), 1.37 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.2, 110.4, 109.6, 89.7, 74.3, 73.7, 73.5, 71.5, 66.5, 64.1, 53.4, 27.5, 26.9, 25.7, 25.2; **[α]**$_D^{25}$ = +33.6 (*c* 0.22, $CHCl_3$); **IR** (neat): ν_{max} = 2929, 2117, 1746, 1374, 1264, 1081, 807, 732 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{15}H_{22}N_6NaO_7$ [M + Na]$^+$ *m/z* 421.1448; found *m/z* 421.1443.

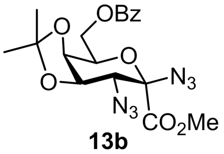
Following the general procedure, the mixture of **7f** (50.2 mg, 0.144 mmol, 1.0 equiv), BI-OAc (88.3 mg, 0.288 mmol, 2.0 equiv), azidotrimethylsilane (56.9 μL, 0.433 mmol, 3.0 equiv) and dry MeCN (1.4 mL) was subjected to the diazidation reaction in 1 h to generate two isomers **13a** (27.5 mg, 45%) and **13b** (13.5 mg, 21%) after purification by silica gel column chromatography (petroleum ether/EtOAc = 25:1, v/v).



13a

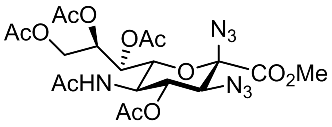
TLC: (petroleum ether/EtOAc = 9:1, v/v), R_f = 0.45; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.2 Hz, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 4.65 (t, J = 8.4 Hz, 1H), 4.59 – 4.53 (m, 2H), 4.33 – 4.32 (m, 2H), 4.00 – 3.97 (m, 1H), 3.93 (s, 3H), 1.56 (s, 3H), 1.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.2, 166.0, 133.3, 129.7, 128.4, 110.8, 90.7, 77.3, 77.0, 76.7, 74.3, 72.4, 70.5, 63.5, 61.4, 53.8, 27.9, 26.1; **[α]**$_D^{25}$ = +59.5 (*c* 0.09, $CHCl_3$); **IR** (neat):

ν_{max} = 2919, 2116, 1723, 1245, 1081, 713 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{18}H_{20}N_6NaO_7$ [M + Na]$^+$ *m*/*z* 455.1291; found *m*/*z* 455.1255.

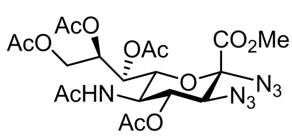

13b

TLC: (petroleum ether/EtOAc = 9:1, v/v), R_f = 0.36; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 4.66 – 4.55 (m, 3H), 4.32 – 4.28 (m, 2H), 3.85 (s, 3H), 3.59 (d, *J* = 7.2, 1H), 1.57 (s, 3H), 1.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.2, 166.1, 133.2, 129.7, 128.5, 110.6, 90.0, 74.8, 71.9, 71.6, 64.7, 63.4, 53.3, 27.8, 25.9; **$[\alpha]_D^{25}$** = +21.7 (c 0.05, $CHCl_3$); **IR** (neat): ν_{max} = 2918, 2115, 1723, 1271, 1081, 712 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{18}H_{20}N_6NaO_7$ [M + Na]$^+$ *m*/*z* 455.1291; found *m*/*z* 455.1282.

Following the general procedure, substrate **7g** (300 mg, 0.634 mmol, 1.0 equiv), BI-OAc (388 mg, 1.27 mmol, 2.0 equiv), azidotrimethylsilane (0.250 mL, 1.90 mmol, 3.0 equiv) and dry MeCN (6 mL) were used. The reaction proceeded in 2 h to provide **14** (307 mg, 87%) after column chromatography (petroleum ether/acetone = 3:1, v/v) on silica gel. HPLC analysis (Waters e2695 Separations Module; Flow rate: 1.0 mL/min; Column: Agilent ZORBAX 300SB-C8, 5 μm, 4.6 × 150 mm; Detector: Waters 2424 ELSD; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 60:40 → 50:50, v/v) indicated that this material was a 5:9:66:20 mixture of four isomers (**14a**, **14b**, **14c**, **14d**). Each pure product was respectively obtained through repeated silica gel column chromatography (petroleum ether/EtOAc = 3.5:1 or petroleum ether/acetone = 5:1, v/v) combined with reverse-phase C18 HPLC (H_2O/MeOH = 50:50 → 40:60 → 30:70, v/v).

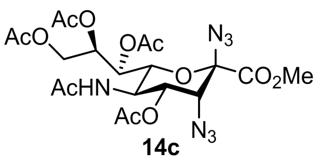

14a

TLC: (petroleum ether/EtOAc = 1:2, v/v), R_f = 0.61; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 10.0 Hz, 1H), 5.45 – 4.28 (m, 2H), 5.17 (td, *J* = 6.0, 2.8 Hz, 1H), 4.46 – 4.32 (m, 2H), 4.24 (q, *J* = 10.0 Hz, 1H), 4.13 – 4.01 (m, 2H), 3.98 (s, 3H), 2.13 (s, 6H), 2.08 (s,3H), 2.03 (s,3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.4, 170.6, 170.2, 169.5, 164.8, 157.8, 157.5, 91.1, 71.7, 70.8, 70.1, 66.7, 62.4, 61.6, 54.2, 49.3, 20.9, 20.6, 20.5, 20.4; **$[\alpha]_D^{25}$** = −25.3 (*c* 0.30, $CHCl_3$); **IR** (neat): ν_{max} = 3254, 2958, 2925, 2114, 1748, 1246, 1210, 1059, 1030 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{20}H_{27}N_7NaO_{12}$ [M + Na]$^+$ *m*/*z* 580.1615; found *m*/*z* 580.1611; HPLC purity: 99.8% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX 300SB-C8, 5 μm, 4.6 × 150 mm; Detector: Waters 2424 ELSD; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 60:40 → 50:50, v/v; t_R = 21.26).



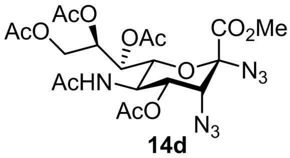
14b

TLC: (petroleum ether/EtOAc = 1:2, v/v), $R_f = 0.59$; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.85 (d, J = 10.0 Hz, 1H), 5.54 (t, J = 10.4 Hz, 1H), 5.35 – 5.28 (m, 1H), 5.25 (dd, J = 8.0, 2.4 Hz, 1H), 4.50 (dd, J = 10.4, 2.0 Hz, 1H), 4.30 – 4.14 (m, 2H), 4.07 (dd, J = 12.4, 5.6 Hz, 1H), 3.93 (s, 3H), 3.62 (d, J = 10.0 Hz, 1H), 2.15 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.8, 170.5, 169.7, 169.6, 166.0, 157.7, 116.3, 90.9, 72.7, 70.6, 68.8, 66.7, 65.0, 62.1, 53.8, 49.3, 20.8, 20.6, 20.6, 20.4; **$[\alpha]_D^{25}$** = −17.0 (c 0.20, $CHCl_3$); **IR** (neat): ν_{max} = 3257, 2959, 2117, 1753, 1289, 1217 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{20}H_{27}N_7NaO_{12}$ [M + Na]$^+$ m/z 580.1615; found m/z 580.1611; HPLC purity: 99.8% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX 300SB-C8, 5 μm, 4.6 × 150 mm; Detector: Waters 2424 ELSD; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 60:40 → 50:50, v/v; t_R = 24.67).



14c

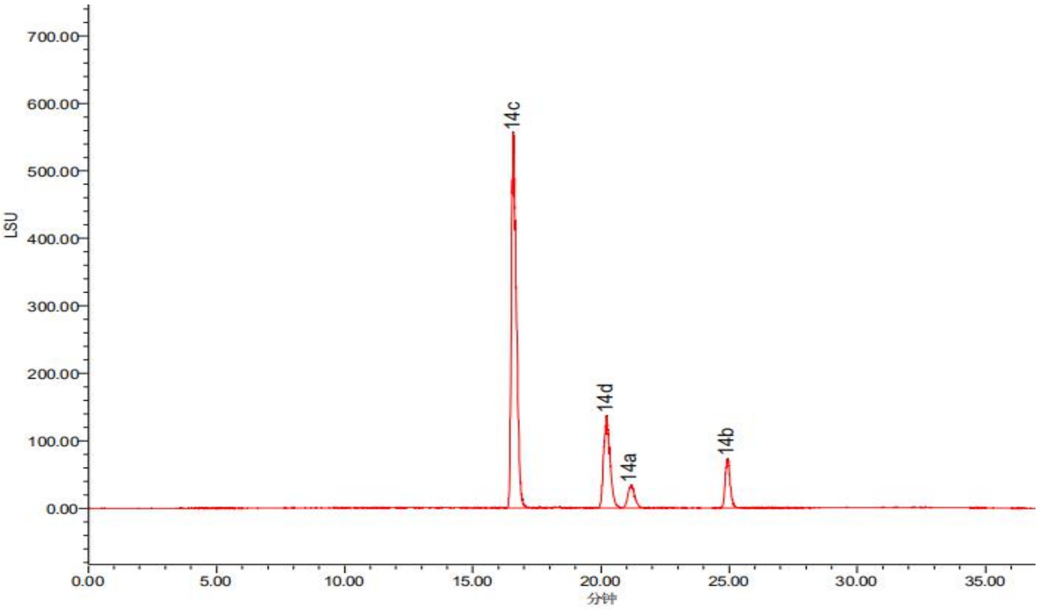
TLC: (petroleum ether/EtOAc = 1:2, v/v), $R_f = 0.59$; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.05 (d, J = 9.2 Hz, 1H), 5.53 (dd, J = 10.0, 3.2 Hz, 1H), 5.37 (dd, J = 5.2, 2.0 Hz, 1H), 5.23 (td, J = 5.2, 2.4 Hz, 1H), 4.65 (dd, J = 12.8, 2.4 Hz, 1H), 4.40 – 4.27 (m, 2H), 4.21 (d, J = 3.2 Hz, 1H), 4.16 (dd, J = 12.8, 6.8 Hz, 1H), 3.94 (s, 3H), 2.17 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.9, 170.6, 170.5, 170.2, 164.2, 157.6, 116.3, 114.4, 90.9, 71.7, 69.1, 67.3, 61.9, 61.9, 53.8, 45.8, 20.9, 20.6, 20.5, 20.3; **$[\alpha]_D^{25}$** = −22.3 (c 0.66, $CHCl_3$); **IR** (neat): ν_{max} = 3275, 2112, 1742, 1370, 1211, 1031 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{20}H_{27}N_7NaO_{12}$ [M + Na]$^+$ m/z 580.1615; found m/z 580.1615; HPLC purity: 98.8% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX 300SB-C8, 5 μm, 4.6 × 150 mm; Detector: Waters 2424 ELSD; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 60:40 → 50:50, v/v; t_R = 16.72); The supplementary crystallographic data of **14c** [m.p.: 203 – 205 °C (petroleum ether/acetone = 5:1, v/v)] have been deposited in Cambridge Crystallographic Data Centre (CCDC 1975132). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.



14d

TLC: (petroleum ether/EtOAc = 1:2, v/v), $R_f = 0.40$; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.72 (d, J = 8.8 Hz, 1H), 5.41 – 5.33 (m, 2H), 5.24 (dd, J = 7.6, 1.6 Hz, 1H), 4.38 – 4.28 (m, 2H), 4.25 – 4.03 (m, 3H), 3.93 (s, 3H), 2.19 (s, 3H), 2.14 (s, 3H), 2.13 (s, 3H), 2.03 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.6, 170.5, 170.3, 170.1, 165.4, 157.5, 116.2, 89.6, 72.3, 68.7, 68.7, 67.2, 62.1, 61.8, 54.0 , 46.1, 20.9, 20.6, 20.6, 20.3; **$[\alpha]_D^{25}$** = +10.4 (c 0.77, $CHCl_3$); **IR** (neat): ν_{max} = 3251, 2923, 2133, 2116, 1368, 1252, 1205, 1036 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{20}H_{27}N_7NaO_{12}$ [M + Na]$^+$ m/z 580.1615; found m/z 580.1612; HPLC purity: 96.8% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX 300SB-C8, 5 μm, 4.6 × 150 mm; Detector: Waters 2424 ELSD; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 60:40 → 50:50, v/v; t_R = 19.79); The supplementary crystallographic data of **14d** [m.p.: 197 – 199 °C (hexane/$CHCl_3$ = 5:1, v/v)] have been deposited in Cambridge Crystallographic Data Centre (CCDC 1975126). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

HPLC for measuring d.r. value of 14

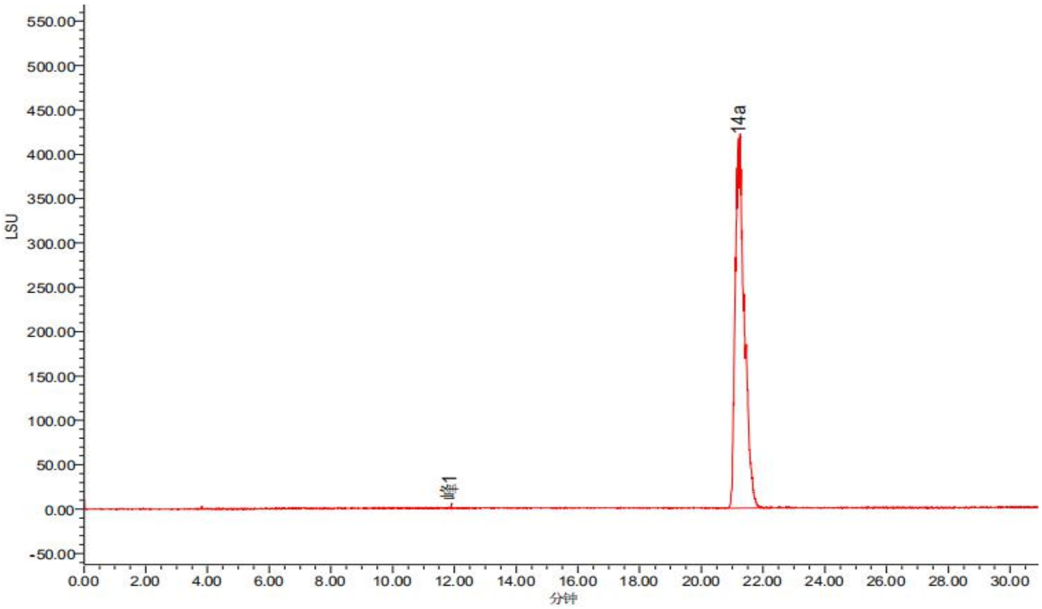


Run information: column: Agilent ZORBAX 300SB-C8, 5 μm, 4.6 × 150 mm; Detector: Waters 2424 ELSD; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 60:40 → 50:50, v/v.

Peak information:

Peak	Isomer	RetTime [min]	Area [mAU*s]	Height [mAU]	Area (%)
1	**14c**	16.579	7581466	557811	66.10
2	**14d**	20.215	2306804	137140	20.11
3	**14a**	21.161	621575	34369	5.42
4	**14b**	24.925	959431	72483	8.37

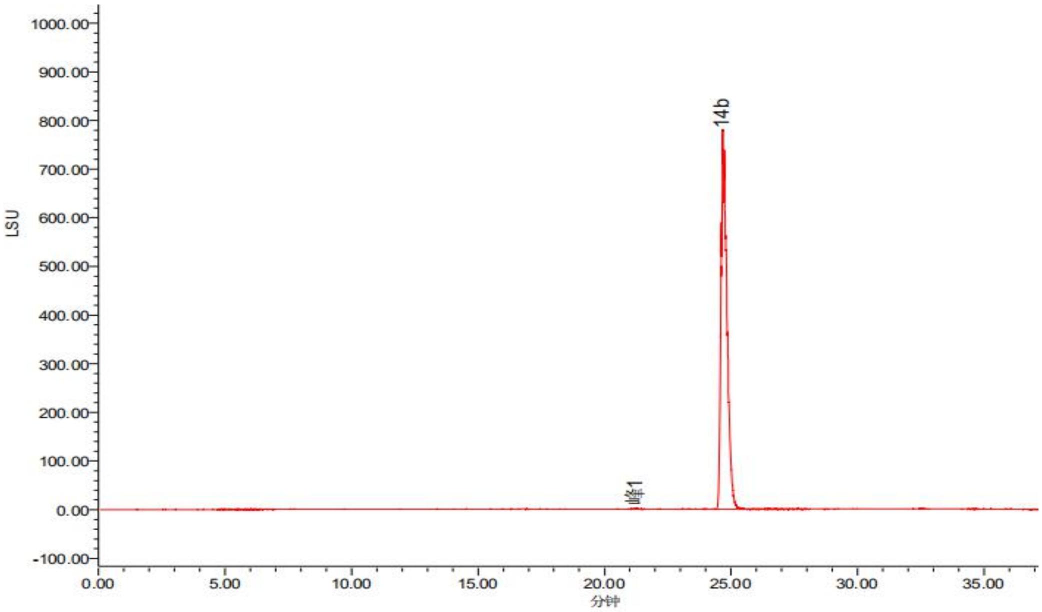
HPLC analysis of 14a under the same condition:



Peak information:

Peak	RetTime [min]	Area [mAU*s]	Height [mAU]	Area (%)
1	11.896	14458	5473	0.17
2	21.256	8552093	422624	99.83

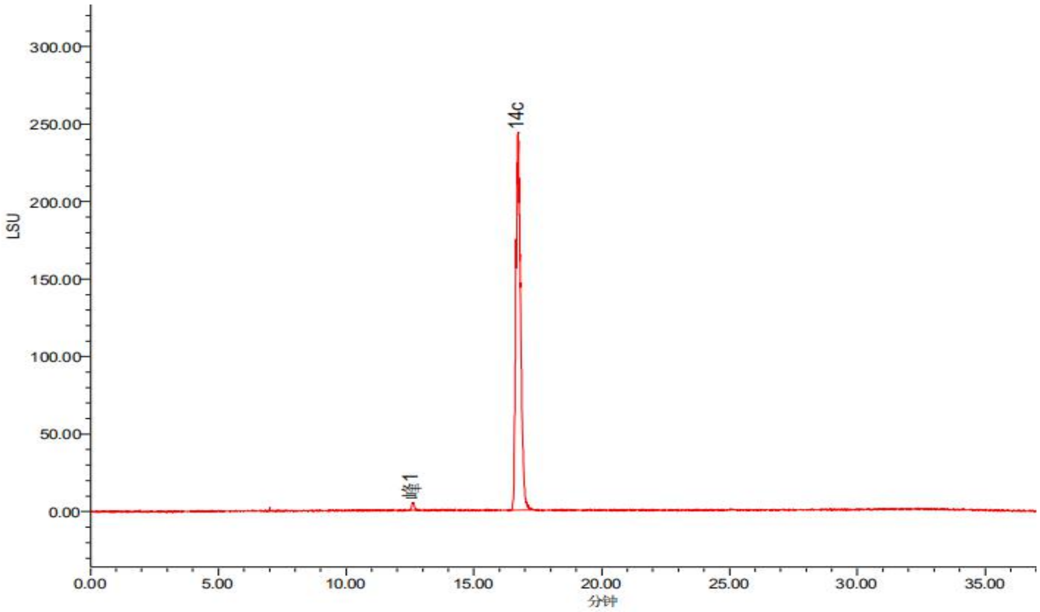
HPLC analysis of 14b under the same condition:



Peak information:

Peak	RetTime [min]	Area [mAU*s]	Height [mAU]	Area (%)
1	21.260	14851	1232	0.12
2	24.669	12730552	781236	99.88

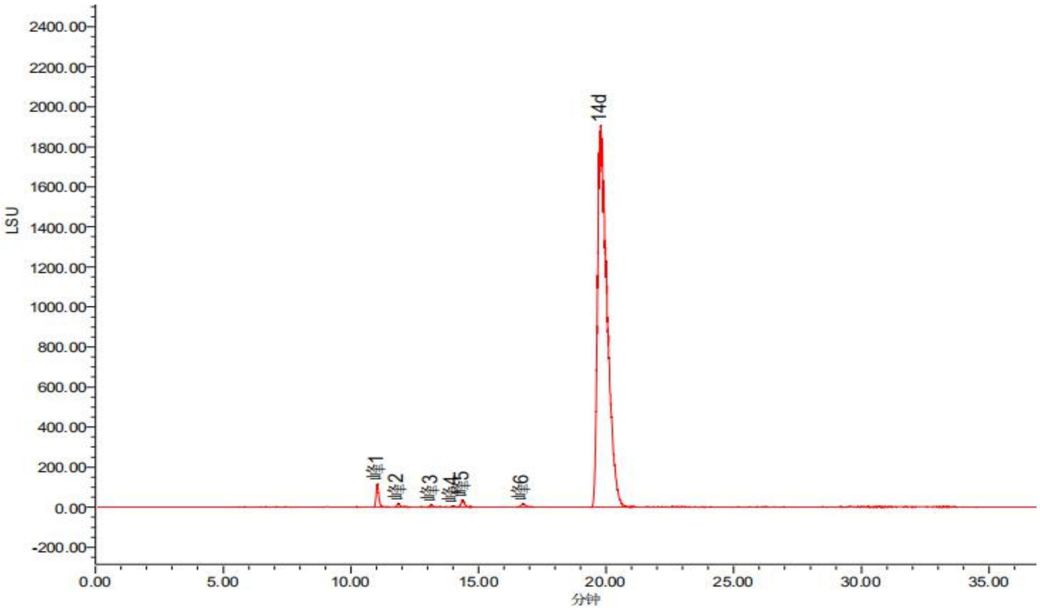
HPLC analysis of 14c under the same condition:



Peak information:

Peak	RetTime [min]	Area [mAU*s]	Height [mAU]	Area (%)
1	12.605	37655	4763	1.17
2	16.721	3173270	243176	98.83

HPLC analysis of 14d under the same condition:

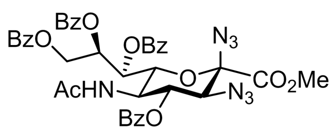


Peak information:

Peak	RetTime [min]	Area [mAU*s]	Height [mAU]	Area (%)
1	11.045	813849	116367	1.59
2	11.854	153570	18705	0.30
3	13.147	85940	11640	0.17
4	13.993	54020	6173	0.11

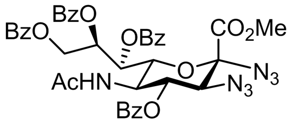
5	14.380	324602	33539	0.63
6	16.734	181810	15181	0.36
7	19.788	49593832	1902242	96.85

Following the general procedure, the diazidation reaction of **7h** (2.03 g, 2.82 mmol, 1.0 equiv) took place with BI-OAc (1.72 g, 5.63 mmol, 2.0 equiv), azidotrimethylsilane (1.11 mL, 8.45 mmol, 3.0 equiv) and dry MeCN (28 mL) in 2 h to give a mixture of three isomers **15a**–**c** (1.50 g, 66.4%) and pure **15d** (420 mg, 18.6%) after column chromatography (petroleum ether/EtOAc = 5:1 to 2:1, v/v). The ratio of **15a**–**c** was indicated to be 14:13:73 by HPLC analysis (Waters e2695 Separations Module; Flow rate: 1.0 mL/min; Column: Agilent ZORBAX 300SB-C8, 5 µm, 4.6 × 150 mm; Detector: Waters 2424 ELSD; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 50:50 → 40:60 → 30:70, v/v). Accordingly, the ratio of four isomers (**15a**–**d**) was 10:10:52:28. Pure **15a**–**c** was respectively obtained through repeated silica gel column chromatography (petroleum ether/EtOAc = 5:1 or petroleum ether/acetone = 8:1, v/v) combined with reverse-phase C18 HPLC (H_2O/MeOH = 40:60 → 30:70, v/v).



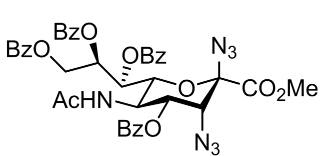
15a

TLC: (petroleum ether/EtOAc = 1.5:1, v/v), $R_f = 0.55$; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 – 7.91 (m, 8H), 7.63 – 7.32 (m, 12H), 5.90 (dd, J = 6.4, 1.6 Hz, 1H), 5.87 – 5.81 (m, 1H), 5.64 (d, J = 9.6 Hz, 1H), 5.55 (t, J =2.0 Hz, 1H), 4.94 (dd, J = 12.4, 3.2 Hz, 1H), 4.64 (dd, J = 10.8, 2.0 Hz, 1H), 4.50 – 4.35 (m, 2H), 4.21 (d, J = 10.0 Hz, 1H), 3.96 (s, 3H), 1.78 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.0, 166.6, 166.0, 165.6, 165.2, 165.2, 133.8, 133.5, 133.4, 133.1, 130.0, 129.9, 129.9, 129.7, 129.5, 129.4, 129.2, 128.6, 128.6, 128.5, 128.3, 91.6, 72.9, 71.5, 70.6, 68.4, 62.9, 62.8, 54.1, 49.8, 23.0; **$[\alpha]_D^{25}$** = +6.1 (c 0.80, $CHCl_3$); **IR** (neat): ν_{max} = 2967, 2132, 2113, 1722, 1451, 1257, 1091, 1067, 1024, 800, 707, 686 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{40}H_{35}N_7NaO_{12}$ $[M + Na]^+$ m/z 828.2241; found m/z 828.2232; HPLC purity: 92.2% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX 300SB-C8, 5 µm, 4.6 × 150 mm; Detector: Waters 2489 UV/Vis; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 40:60 → 30:70, v/v; t_R = 35.69).



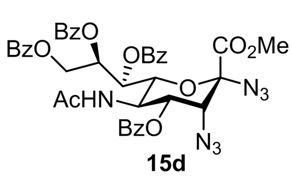
15b

TLC: (petroleum ether/EtOAc = 1.5:1, v/v), $R_f = 0.53$; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 – 7.88 (m, 8H), 7.65 – 7.31 (m, 12H), 5.96 – 5.76 (m, 3H), 5.53 (d, J = 9.6 Hz, 1H), 4.79 (dd, J = 12.4, 2.8 Hz, 1H), 4.67 (dd, J = 10.8, 2.0 Hz, 1H), 4.49 – 4.32 (m, 2H), 3.75 (d, J = 10.0 Hz, 1H), 3.48 (s, 3H), 1.80 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.0, 166.5, 166.0, 165.6, 165.3, 164.8, 133.7, 133.5, 133.0, 130.0, 129.9, 129.9, 129.7, 129.6, 129.2, 129.2, 128.6, 128.6, 128.5, 128.3, 91.2, 73.8, 71.5, 69.3, 67.9, 65.7, 63.0, 53.3, 49.3, 23.0; **$[\alpha]_D^{25}$** = +29.5 (*c* 0.9, $CHCl_3$); **IR** (neat): ν_{max} = 3364, 2963, 2932, 2114, 1726, 1249, 1093, 1068, 1026, 709 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{40}H_{35}N_7NaO_{12}$ $[M + Na]^+$ *m*/*z* 828.2241; found 828.2235; HPLC purity: 96.7% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX 300SB-C8, 5 μm, 4.6 × 150 mm; Detector: Waters 2489 UV/Vis; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 40:60 → 30:70, v/v; t_R = 37.20); The supplementary crystallographic data of **15b** [m.p.: 115 – 117 °C (petroleum ether/acetone = 5:1, v/v)] have been deposited in Cambridge Crystallographic Data Centre (CCDC 1975127). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.



15c

TLC: (petroleum ether/EtOAc = 1.5:1, v/v), R_f = 0.53; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 – 8.13 (m, 2H), 8.05 – 7.98 (m, 4H), 7.98 – 7.92 (m, 2H), 7.64 – 7.45 (m, 6H), 7.45 – 7.31 (m, 6H), 5.94 – 5.86 (m, 2H), 5.84 (dd, *J* = 10.4, 3.2 Hz, 1H), 5.69 – 5.94 (m, 1H), 5.11 (dd, *J* = 12.4, 2.8 Hz, 1H), 4.68 (dd, *J* = 10.8, 2.0 Hz, 1H), 4.59 (dd, *J* = 12.4, 6.4 Hz, 1H), 4.49 (q, *J* = 10.4 Hz, 1H), 4.36 (d, *J* = 3.2 Hz, 1H), 3.96 (s, 3H), 1.81 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.1, 166.1, 166.0, 165.7, 165.6, 164.6, 133.8, 133.5, 133.3, 133.0, 130.1, 130.0, 129.9, 129.7, 129.7, 129.5, 129.2, 128.6, 128.6, 128.4, 128.4, 128.3, 91.2, 72.78, 71.5, 670.0, 69.0, 63.1, 62.5, 53.7, 45.9, 23.2; **$[\alpha]_D^{25}$** = −1.3 (*c* 0.70, $CHCl_3$); **IR** (neat): ν_{max} = 3375, 2970, 2924, 2112, 1723, 1695, 1257, 1092, 1068, 1026, 803, 709 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{40}H_{35}N_7NaO_{12}$ $[M + Na]^+$ *m*/*z* 828.2241; found *m*/*z* 828.2232; HPLC purity: 93.7% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX 300SB-C8, 5 μm, 4.6 × 150 mm; Detector: Waters 2489 UV/Vis; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 40:60 → 30:70, v/v; t_R = 34.73).

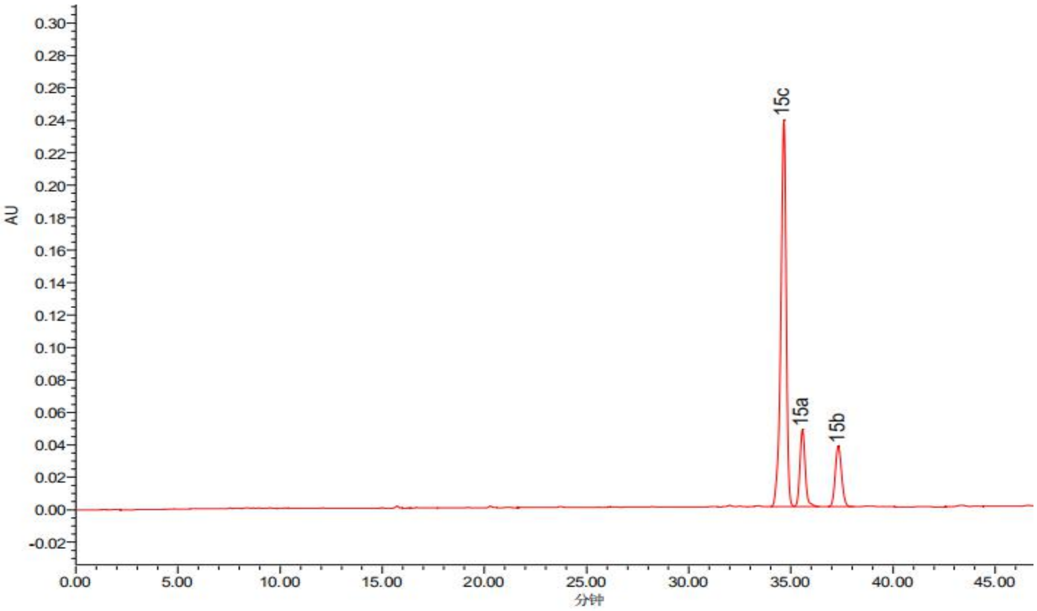


15d

TLC: (petroleum ether/EtOAc = 1.5:1, v/v), R_f = 0.40; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 – 8.13 (m, 2H), 8.07 – 7.98 (m, 4H), 7.97 – 7.92 (m, 2H), 7.67 – 7.32 (m, 12H), 5.97 – 5.90 (m, 1H), 5.86 (dd, *J* = 7.6, 1.6 Hz, 1H), 5.80 (dd, *J* = 10.8, 3.2 Hz, 1H), 5.64 – 5.55 (m, 1H), 4.95 (dd, *J* = 12.4, 3.2 Hz, 1H), 4.64 (dd, *J* = 10.8, 1.6 Hz, 1H), 4.59 – 4.49 (m, 2H), 4.20 – 4.08 (m, 1H), 3.62 (s, 3H), 1.85 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4, 166.0, 165.9, 165.9, 165.7, 165.3, 133.8, 133.7, 133.3, 133.0, 130.2, 123.0, 129.9, 129.7, 129.6, 129.0, 128.7, 128.6, 128.5, 128.3, 89.5, 73.0, 69.9, 69.4, 68.7, 63.1, 62.8, 53.7, 46.6, 23.3; **$[\alpha]_D^{25}$** = +41.2 (*c* 0.70, $CHCl_3$); **IR** (neat): ν_{max} = 3375, 2963, 2111, 1724, 1255, 1106, 1094, 1069, 1026, 709 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{40}H_{35}N_7NaO_{12}$ $[M + Na]^+$ *m*/*z* 828.2241; found *m*/*z* 828.2237; HPLC purity: 96.6% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX 300SB-C8, 5 μm, 4.6 × 150 mm; Detector: Waters 2489 UV/Vis; Temperature:

25 °C; Mobile phase: H_2O/MeOH = 40:60 → 30:70, v/v; $t_R = 36.64$).

HPLC for measuring d.r. value of 15a, 15b and 15c

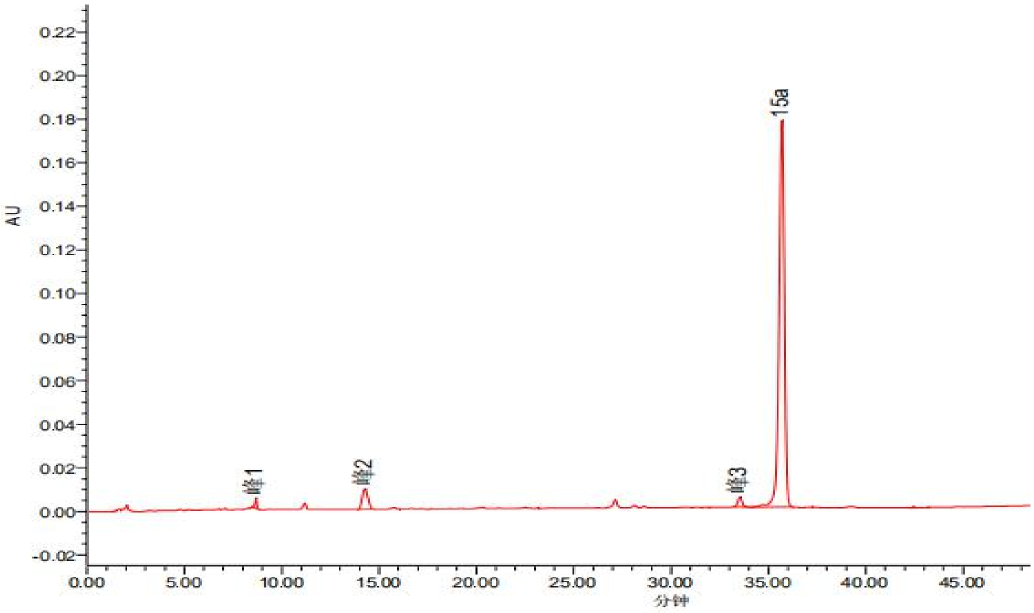


Run information: column: Agilent ZORBAX 300SB-C8, 5 μm, 4.6 × 150 mm; Detector: Waters 2489 UV/Vis; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 40:60 → 30:70, v/v.

Peak information:

Peak	Isomer	RetTime [min]	Area [mAU*s]	Height [mAU]	Area (%)
1	**15c**	34.654	4349581	238456	72.31
2	**15a**	35.563	856881	47596	14.25
3	**15b**	37.313	808326	37360	13.44

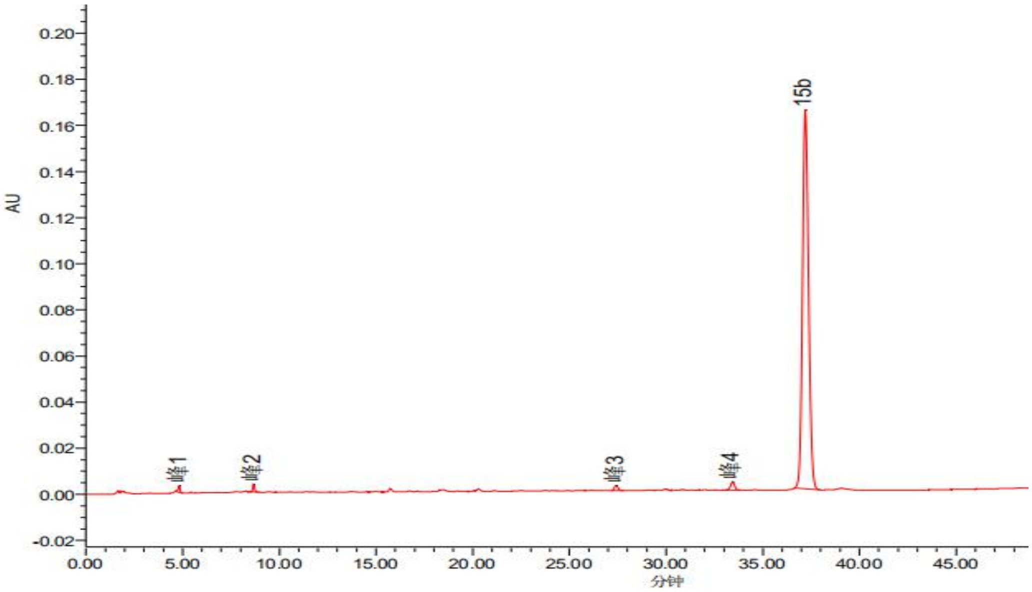
HPLC analysis of 15a under the same condition:



Peak information:

Peak	RetTime [min]	Area [mAU*s]	Height [mAU]	Area (%)
1	8.672	34786	4920	0.95
2	14.265	185201	9208	5.06
3	33.539	65218	4490	1.78
4	35.699	3373911	177500	92.21

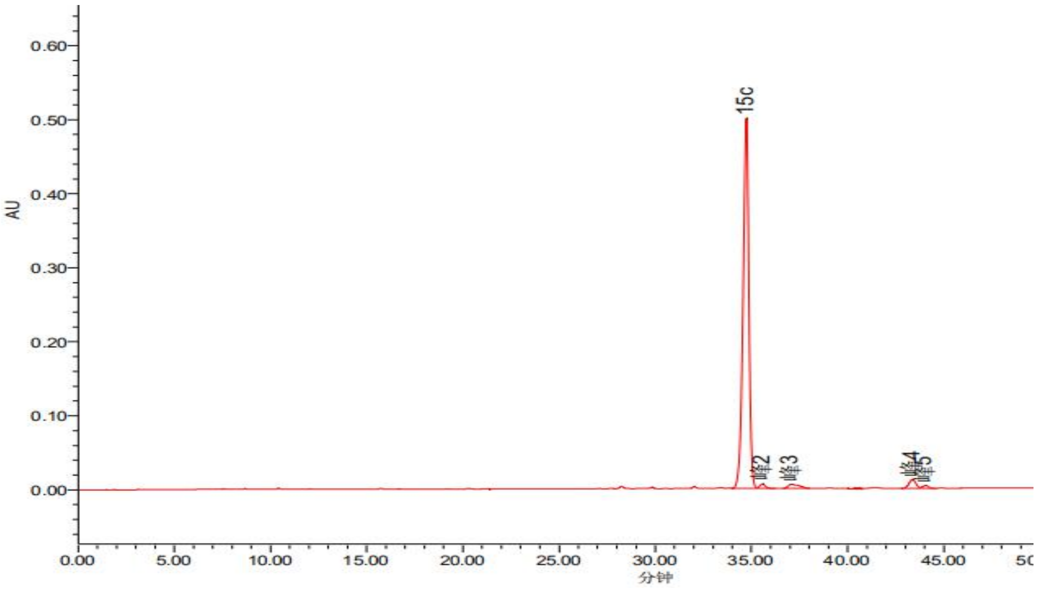
HPLC analysis of 15b under the same condition:



Peak information:

Peak	RetTime [min]	Area [mAU*s]	Height [mAU]	Area (%)
1	4.820	19324	2916	0.53
2	8.673	22458	3402	0.61
3	27.416	27751	2209	0.75
4	33.439	50962	3482	1.38
5	37.200	3559823	164298	96.73

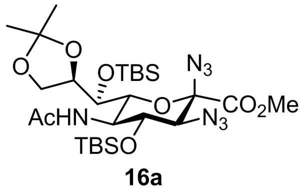
HPLC analysis of 15c under the same condition:



Peak information:

Peak	RetTime [min]	Area [mAU*s]	Height [mAU]	Area (%)
1	34.735	10484801	500193	93.70
2	35.571	114388	6129	1.02
3	37.077	215188	5575	1.92
4	43.361	293747	11800	2.63
5	44.038	81737	4097	0.73

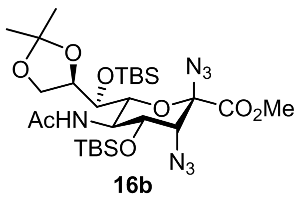
Following the general procedure, substrate **7i** (201 mg, 0.351 mmol, 1.0 equiv), BI-OAc (215 mg, 0.702 mmol, 2.0 equiv) and azidotrimethylsilane (138 µL, 1.05 mmol, 3.0 equiv) were used. The crude product was isolated by silica gel column chromatography (petroleum ether/EtOAc = 12:1 to 8:1, v/v) to afford two isomers **16a** (65.3 mg, 28%) and **16b** (131 mg, 57%).



16a

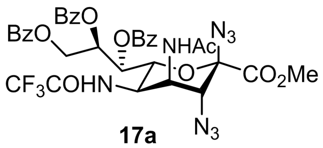
TLC: (petroleum ether/EtOAc = 4:1, v/v), R_f = 0.58; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.26 (d, J = 8.4 Hz, 1H), 4.41 (dd, J = 10.8, 1.2 Hz, 1H), 4.14 (q, J = 6.4 Hz, 1H), 4.07 – 3.86 (m, 3H), 3.92 (s, 3H), 3.85 –3.75 (m, 1H), 3.70 – 3.55 (m, 2H), 1.98 (s, 3H), 1.39 (s, 3H), 1.29 (s, 3H), 0.89 (s, 18H), 0.17 (s, 3H), 0.13 (s, 6H), 0.06 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.6, 166.3, 108.6, 91.4, 76.0, 73.2, 71.5, 70.6, 66.4, 66.3, 53.9, 53.6, 26.6, 25.9, 25.6, 24.8, 23.9, 18.5, 18.0, −3.6, −4.0, −4.6, −4.6; **$[\alpha]_D^{25}$** = −16.0 (c 0.40, $CHCl_3$); **IR** (neat): ν_{max} = 2955, 2930, 2858, 2112, 1757, 1666, 1253, 1120, 1069, 1023, 836, 777, 736 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{27}H_{51}N_7NaO_8Si_2$ $[M + Na]^+$ m/z 680.3235; found m/z 680.3249; HPLC purity: 98.9% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 µm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH

= 10:90, v/v; t_R = 6.46).

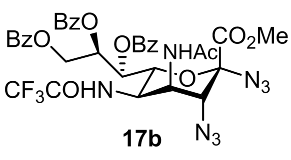

16b

TLC: (petroleum ether/EtOAc = 4:1, v/v), R_f = 0.52; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.29 (d, J = 8.0 Hz, 1H), 4.73 (dd, J = 10.0, 3.6 Hz, 1H), 4.59 (d, J = 10.8 Hz, 1H), 4,24 – 4.16 (m, 1H), 4.07 – 4.01 (m, 2H), 3.97 – 3.83 (m, 2H), 3.85 (s, 3H), 3.67 – 3.55(m, 1H), 1.96 (s, 3H), 1.40 (s, 3H), 1.29 (s, 3H), 0.92 (s, 9H), 0.91 (s, 9H), 0.15 (s, 3H), 0.13 (s, 3H), 0.12 (s, 3H), 0.07 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.2, 165.4, 108.1, 91.0, 72.7, 70.6, 67.8, 65.7, 64.9, 53.2, 50.8, 29.7, 26.4, 25.9, 25.6, 24.7, 23.9, 18.5, 17.9, −3.4, −4.1, −4.4, −5.1; **$[\alpha]_D^{25}$** = −0.9 (c 0.41, $CHCl_3$); **IR** (neat): ν_{max} = 2955, 2930, 2858, 2111, 1758, 1668, 1256, 1068, 1039, 837, 779, 734 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{27}H_{51}N_7NaO_8Si_2$ $[M + Na]^+$ m/z 680.3235; found m/z 680. 3235; HPLC purity: 99.3% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 μm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 10:90, v/v; t_R = 5.10).

Following the general procedure, the diazidation reaction of **7j** (4.21 g, 5.91 mmol, 1.0 equiv) proceeded with BI-OAc (3.62 g, 11.8 mmol, 2.0 equiv) and azidotrimethylsilane (2.33 mL, 17.7 mmol, 3.0 equiv) in 2 h to give two isomers **17a** (2.68 g, 57%) and **17b** (1.50 g, 32%) after purification by silica gel column chromatography (petroleum ether/EtOAc = 2:1, v/v).


17a

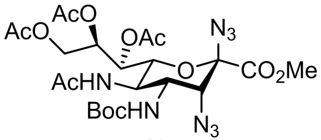
TLC: (petroleum ether/EtOAc = 1:1.5, v/v), R_f = 0.53; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 – 7.98 (m, 4H), 7.97 – 7.90 (m, 2H), 7.65 – 7.31 (m, 9H), 7.16 – 7.07 (m, 1H), 6.72 (d, J = 8.8 Hz, 1H), 5.91 – 5.81 (m, 2H), 5.12 (dd, J = 12.8, 2.4 Hz, 1H), 4.93 (d, J = 10.8 Hz, 1H), 4.70 – 4.61 (m, 1H), 4.53 (dd, J = 12.4, 5.6 Hz, 1H), 4.35 – 4.25 (m, 1H), 4.02 (d, J = 3.6 Hz, 1H), 3.94 (s, 3H), 2.01 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.1, 166.1, 166.0, 165.3, 164.4, 157.9 (q, J = 38 Hz), 133.8, 133.6, 133.1, 130.1, 129.9, 129.6, 129.5, 129.2, 128.8, 128.6, 128.6, 128.5, 128.3, 115.4 (q, J = 286 Hz), 91.2, 71.4, 68.9, 68.5, 62.7, 61.1, 53.7, 49.8, 44.6, 23.2; **$[\alpha]_D^{25}$** = +63.1 (c 1.71, $CHCl_3$); **IR** (Neat): ν_{max} = 2114, 1725, 1259, 1088, 1068, 735, 709 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{35}H_{31}F_3N_8NaO_{11}$ $[M + Na]^+$ m/z 819.1962; found m/z 819.1954; HPLC purity: 98.5% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX 300SB-C8, 5 μm, 4.6 × 150 mm; Detector: Waters 2489 UV/Vis; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 100:0 → 5:95, v/v; t_R = 18.58); The supplementary crystallographic data of **17a** [m.p.: 194 – 196 °C (petroleum ether/acetone = 5:1, v/v)] have been deposited in Cambridge Crystallographic Data Centre (CCDC 1975128). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.



17b

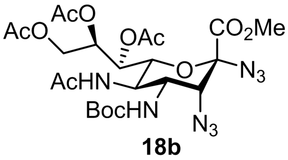
TLC: (petroleum ether/EtOAc = 1:1.5, v/v), R_f = 0.50; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.09 – 7.98 (m, 4H), 7.94 (d, J = 7.6 Hz, 2H), 7.64 – 7.49 (m, 4H), 7.49 – 7.41 (m, 3H), 7.41 – 7.32 (m, 2H), 6.71 – 6.56 (m, 1H), 5.92 – 5.85 (m, 1H), 5.80 (dd, J = 7.6, 1.6 Hz, 1H), 5.22 (d, J = 11.2 Hz, 1H), 4.92 (dd, J = 12.8, 2.8 Hz, 1H), 4.61 (d, J = 7.2 Hz, 1H), 4.46 (dd, J = 12.4, 4.8 Hz, 1H), 4.33 – 4.20 (m, 1H), 4.15 (q, J = 6.8 Hz, 1H), 3.68 (s, 3H), 1.96 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 172.4, 166.4, 166.0, 165.6, 165.5, 158.6 (q, J = 38 Hz), 134.0, 133.6, 133.1, 130.1, 129.8, 129.6, 129.4, 129.2, 128.7, 128.6, 128.3, 128.3, 115.5 (q, J = 287 Hz), 89.6, 70.1, 69.9, 68.5, 62.5, 59.0, 53.6, 50.6, 46.0, 22.9; **[α]$_D^{25}$** = +53.4 (c 1.00, CHCl$_3$); **IR** (neat): ν_{max} = 2116, 1726, 1263, 1247, 1091, 1069, 734, 708 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{35}H_{31}F_3N_8NaO_{11}$ [M + Na]$^+$ m/z 819.1962; found m/z 819.1961; HPLC purity: 97.6% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX 300SB-C8, 5 µm, 4.6 × 150 mm; Detector: Waters 2489 UV/Vis; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 100:0 → 5:95; t_R = 19.90).

Following the general procedure, the diazidation of **7k** (2.20 g, 4.15 mmol, 1.0 equiv) proceeded employing BI-OAc (2.54 g, 8.30 mmol, 2.0 equiv) and azidotrimethylsilane (1.64 mL, 12.4 mmol, 3.0 equiv) in 2 h to afford two isomers **18a** (1.64 g, 64%) and **18b** (650 mg, 26%) after purification by repeated column chromatography (petroleum ether/EtOAc = 1.5:1, v/v).



18a

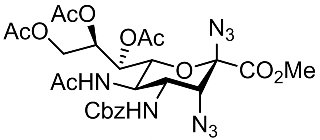
TLC: (petroleum ether/EtOAc = 1:3, v/v), R_f = 0.58; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 5.78 (brs, 1H), 5.41 (dd, J = 5.6, 2.0 Hz, 1H), 5.27 – 5.20 (m, 1H), 5.09 (d, J = 7.6 Hz, 1H), 4.61 (dd, J = 12.8, 2.8 Hz, 1H), 4.18 – 4.04 (m, 5H), 3.94 (s, 3H), 2.12 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.91 (s, 3H), 1.41 (s, 9H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 171.0, 170.6, 170.3, 169.9, 164.8, 155.8, 90.7, 80.5, 73.0, 71.0, 67.5, 63.0, 62.1, 53.6, 50.9, 44.5, 28.2, 28.2, 23.0, 21.0, 20.7, 20.6; **[α]$_D^{25}$** = −9.3 (c 1.07, CHCl$_3$); **IR** (neat): ν_{max} = 3357, 2962, 2113, 1745, 1368, 1248, 1215, 1043, 734 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{23}H_{34}N_8NaO_{12}$ [M + Na]$^+$ m/z 637.2194; found m/z 637.2189; HPLC purity: 99.8% (Flow rate: 1.0 mL/min; Column: HRC-SIL SHIM-PACK, 5 µm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: hexane/2-isopropanol = 80:20, v/v; t_R = 3.22).



18b

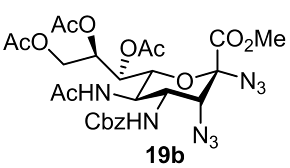
TLC: (petroleum ether/EtOAc = 1:3, v/v), R_f = 0.45; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 5.43 – 5.33 (m, 2H), 5.31 (dd, J = 7.6, 2.0 Hz, 1H), 5.07 (d, J = 9.6 Hz, 1H), 4.32 (dd, J = 12.4, 2.8 Hz, 1H), 4.19 – 4.04 (m, 3H), 3.92 (s, 3H), 3.86 – 3.74 (m, 2H), 2.15 (s, 3H), 2.14 (s, 3H), 2.04 (s, 3H), 1.88 (s, 3H), 1.41 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 170.6, 170.0, 169.9, 165.9, 155.8, 90.5, 80.6, 74.8, 68.9, 67.3, 62.9, 62.1, 53.8, 51.3, 45.1, 28.2, 28.2, 23.1, 21.0, 20.7, 20.7; **[α]**$_D^{25}$ = +20.8 (*c* 0.83, $CHCl_3$); **IR** (neat): ν_{max} = 3357, 2962, 2112, 1747, 1368, 1249, 1214, 1040, 734, 703 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{23}H_{34}N_8NaO_{12}$ $[M + Na]^+$ *m*/*z* 637.2194; found *m*/*z* 637.2186; HPLC purity: 98.3% (Flow rate: 1.0 mL/min; Column: HRC-SIL SHIM-PACK, 5 μm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: hexane/2-isopropanol = 80:20, v/v; t_R = 3.64).

Following the general procedure, the diazidation reaction of **7l** (512 mg, 0.908 mmol, 1.0 equiv) occurred using BI-OAc (556 mg, 1.82 mmol, 2.0 equiv) and azidotrimethylsilane (358 μL, 2.72 mmol, 3.0 equiv) in 2 h to provide two isomers **19a** (387 mg, 66%) and **19b** (52 mg, 9%) after purification by repeated column chromatography (petroleum ether/EtOAc = 3:1, v/v).



19a

TLC: (petroleum ether/EtOAc = 1:2, v/v), R_f = 0.54; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 5H), 5.50 – 5.30 (m, 3H), 5.25 (td, *J* = 6.0, 2.4 Hz, 1H), 5.17 – 5.01 (m, 2H), 4.61 (d, *J* = 12.4 Hz, 1H), 4.22 – 4.05 (m, 5H), 3.95 (s, 3H), 2.12 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 1.75 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 170.6, 170.3, 169.8, 164.7, 156.4, 136.0, 128.6, 128.2, 127.8, 90.7, 72.9, 71.1, 67.4, 67.2, 63.0, 62.1, 53.6, 51.8, 44.4, 22.8, 21.0, 20.7, 20.6; **[α]**$_D^{25}$ = +2.0 (*c* 1.95, $CHCl_3$); **IR** (neat): ν_{max} = 3350, 2959, 2113, 1743, 1672, 1529, 1370, 1246, 1214, 1040, 734 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{26}H_{32}N_8NaO_{12}$ $[M + Na]^+$ *m*/*z* 671.2037; found *m*/*z* 671.2033; HPLC purity: 97.5% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 μm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 10:90; t_R = 1.86).

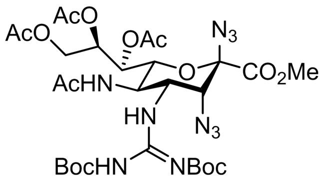


19b

TLC: (petroleum ether/EtOAc = 1:2, v/v), R_f = 0.40; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 5.45 – 5.24 (m, 4H), 5.19 – 4.95 (m, 2H), 4.32 (dd, *J* = 12.4, 2.8 Hz, 1H), 4.18 (d, *J* = 3.2 Hz, 1H), 4.16 – 4.05 (m, 2H), 3.92 (s, 3H), 3.90 – 3.82 (m, 2H), 2.14 (s, 6H), 2.03 (s, 3H), 1.69 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.9, 170.6, 169.9, 169.9, 165.8, 156.4, 135.9, 128.6, 128.3, 127.9, 90.4, 74.6, 68.8, 67.2, 62.7, 62.1, 53.9, 52.1, 44.7, 22.8, 21.0, 20.7, 20.7; **[α]**$_D^{25}$ = +15.5 (*c* 0.37, $CHCl_3$); **IR** (neat): ν_{max} = 3333, 2922, 2115, 1738, 1662, 1537, 1370, 1247, 1216, 1093, 1043 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{26}H_{32}N_8NaO_{12}$ $[M + Na]^+$ *m*/*z* 671.2037; found *m*/*z* 671.2032; HPLC purity: 99.1% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 μm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 10:90, v/v; t_R =

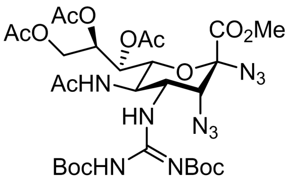
1.91).

Following the general procedure, **7m** (180 mg, 0.268 mmol, 1.0 equiv) was subjected to diazidation in the presence of BI-OAc (164 mg, 0.536 mmol, 2.0 equiv) and azidotrimethylsilane (106 μL, 0.804 mmol, 3.0 equiv) in 2 h to yield two isomers **20a** (142 mg, 70%) and **20b** (48.6 mg, 24%) after purification by silica gel column chromatography (petroleum ether/EtOAc = 2.5:1 to 1.5:1, v/v).



20a

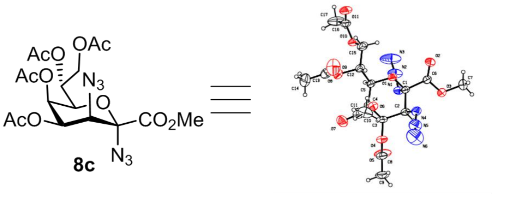
TLC: (petroleum ether/EtOAc = 1:1, v/v), R_f = 0.53; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 11.32 (s, 1H), 8.87 (d, J = 8.4 Hz, 1H), 6.11 (d, J = 9.2 Hz, 1H), 5.34 (dd, J = 5.2, 2.4 Hz, 1H), 5.26 – 5.20 (m, 1H), 4.70 – 4.58 (m, 2H), 4.21 (q, J = 10.0 Hz, 1H), 4.13 – 4,02 (m, 3H), 3.95 (s, 3H), 2.15 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 1.84 (s, 3H), 1.49 (s, 18H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 170.6, 170.5, 170.4, 170.1, 164.9, 162.9, 156.9, 152.6, 90.6, 84.0, 79.8, 73.8, 71.4, 67.9, 62.7, 62.3, 53.6, 49.8, 45.7, 28.2, 28.2, 27.9, 27.9, 22.9, 21.0, 20.8, 20.7; $[\boldsymbol{\alpha}]_D^{25}$ = −62.1 (*c* 0.70, $CHCl_3$); **IR** (neat): ν_{max} = 3270, 2963, 2932, 2114, 1745, 1729, 1643, 1610, 1368, 1255, 1215, 1143, 1113, 1053, 1028, 803 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{29}H_{44}N_{10}NaO_{14}$ $[M + Na]^+$ *m*/*z* 779.2936; found *m*/*z* 779.2934; HPLC purity: 91.3% (Flow rate: 1.0 mL/min; Column: CHIRALCEL OD-H, 5 μm, 4.6 × 250 mm; Detector: Agilent G1314F 1260 VWD; Temperature: 25 °C; Mobile phase: hexane/2-isopropanol = 91:9, v/v; t_R = 6.23).



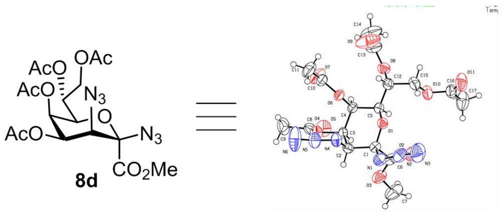
20b

TLC: (petroleum ether/EtOAc = 1:1, v/v), R_f = 0.49; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 11.27 (s, 1H), 8.81 (d, J = 8.0 Hz, 1H), 5.95 (d, J = 9.2 Hz, 1H), 5.40 (td, J = 6.8, 2.8 Hz, 1H), 5.28 (dd, J = 6.8, 2.0 Hz, 1H), 4.40 – 4.30 (m, 2H), 4.28 – 4.16 (m, 2H), 4.12 (dd, J = 12.4, 6.0 Hz, 1H), 3.95 (s, 3H), 3.87 (dd, J = 10.4, 2.0 Hz, 1H), 2.17 (s, 3H), 2.14 (s, 3H), 2.04 (s, 3H), 1.83 (s, 3H), 1.50 (s, 9H), 1.47 (s, 9H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 170.6, 170.5, 170.1, 170.0, 165.8, 162.8, 156.6, 152.4, 90.4, 83.9, 79.6, 75.3, 69.3, 67.6, 62.3, 62.2, 53.7, 50.9, 45.1, 28.2, 28.2, 28.0, 28.0, 23.0, 21.1, 20.8, 20.7; $[\boldsymbol{\alpha}]_D^{25}$ = −5.8 (*c* 1.50, $CHCl_3$); **IR** (neat): ν_{max} = 3312, 2961, 2931, 2111, 1748, 1728, 1643, 1610, 1368, 1300, 1251, 1144, 1074, 1041, 734 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{29}H_{44}N_{10}NaO_{14}$ $[M + Na]^+$ *m*/*z* 779.2936; found *m*/*z* 779.2930; HPLC purity: 93.5% (Flow rate: 1.0 mL/min; Column: CHIRALCEL OD-H, 5 μm, 4.6 × 250 mm; Detector: Agilent G1314F 1260 VWD; Temperature: 25 °C; Mobile phase: hexane/2-isopropanol = 95:5, v/v; t_R = 8.67).

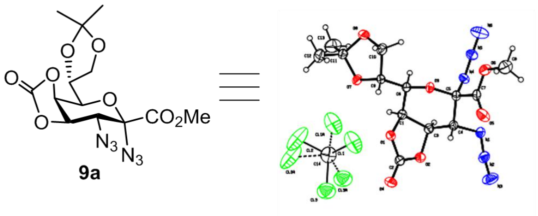
5. Product Interconversion and Stereochemistry Determination



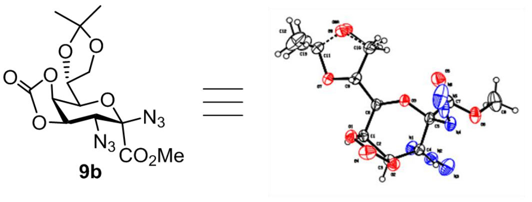
8c



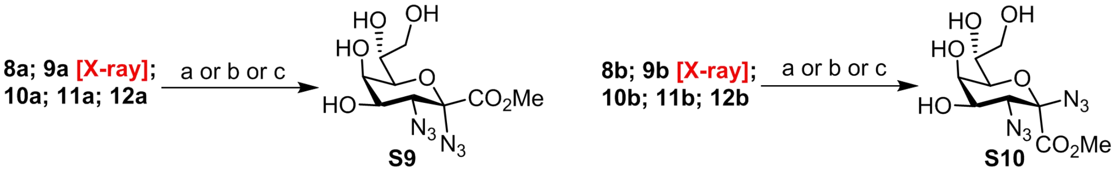
8d



9a

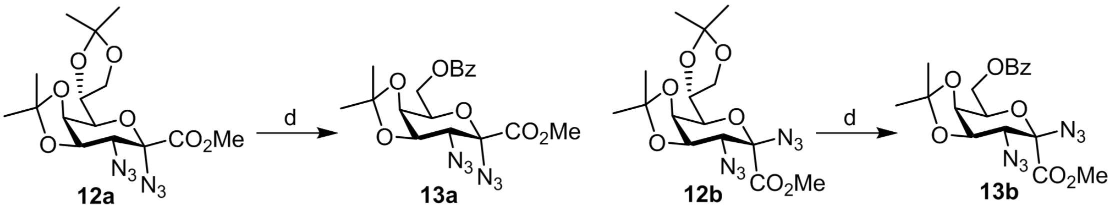


9b



8a, 8b, 10a, 10b: Condition a
9a, 9b: Condition b
11a, 11b, 12a, 12b: Condition c

Condition a: NaOMe, MeOH, RT
Condition b: NaOMe, MeOH, RT; *p*-TsOH·H_2O, MeOH, RT
Condition c: *p*-TsOH·H_2O, MeOH, RT



Condition d: 1) $Zn(NO_3)_2 \cdot 6H_2O$, MeCN, 50 °C
2) $NaIO_4$, THF/H_2O (2:1), 0 °C; $NaBH_4$, MeOH, 0 °C
3) BzCl, pyridine, CH_2Cl_2, 0 °C to RT

Condition a: Sodium methoxide was added to a stirred solution of substrate (1.0 equiv) in MeOH at room temperature. After being stirred overnight, the mixture was neutralized with Amberlite IR 120 (H^+) resin, then filtered and concentrated under *vacuum*. The residue was purified through flash column chromatography.

Condition b: To a stirred solution of substrate (1.0 equiv) in MeOH was added sodium methoxide (5 M in MeOH, 3.0 equiv) at room temperature. When the reaction was completed as indicated by TLC analysis, it was neutralized with Amberlite IR 120 (H+) resin and filtered. The filtrate was evaporated under reduced pressure and dissolved in MeOH, then *p*-toluenesulfonic acid monohydrate (3.0 equiv) was added. After being stirred overnight at room temperature, the reaction was quenched by addition of triethylamine (5.0 equiv). The mixture was concentrated in *vacuo* to afford the crude residue, which was purified through flash column chromatography.

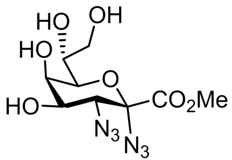
Condition c: *p*-Toluenesulfonic acid monohydrate (3.0 equiv) was added to a stirred solution of substrate (1.0 equiv) in MeOH at room temperature. Triethylamine (5.0 equiv) was added after the reaction was completed (identified by TLC analysis). The mixture was next evaporated under reduced pressure; the resultant crude product was purified by silica gel column chromatography.

Condition d: To a solution of substrate (1.0 equiv) in MeCN at room temperature was added zinc nitrate hexahydrate (3.0 equiv). The resulting mixture was stirred at 50 ºC until the reaction was completed as detected by TLC analysis. Then the mixture was diluted with water and extracted with EtOAc for three times. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated in *vacuo* to afford the crude residue. Sodium periodate (1.6 equiv) was added to the above diol (not shown) in THF/H_2O (2:1, v/v) at 0 ºC. After being stirred for 3 h at the same temperature, the mixture was diluted with water and extracted with EtOAc for three times. The combined organic extracts were dried, filtered and concentrated in *vacuo*. The residue was dissolved in MeOH, to which was slowly added sodium borohydride (1.2 equiv) at 0 ºC. The reaction was completed in 30 min according to TLC. Thus, water was added to quench the reaction and MeOH was removed under reduced pressure. The mixture was extracted with EtOAc for three times, before the combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under *vacuum*. To a solution of the above crude product in dry CH_2Cl_2 were added pyridine and benzoyl chloride (3.0 equiv) at 0 ºC. Then the reaction mixture occurred at room temperature. After removal of solvent in *vacuo*, the residue was purified by silica gel column chromatography.

According to the procedure described for condition a, **8a** or **8b** (20.1 mg, 0.041 mmol, 1.0 equiv), sodium methoxide (1.1 mg, 0.021 mmol, 0.5 equiv) and MeOH (0.5 mL) were used. The mixture was stirred for 20 min at room temperature to give the hydrolyzed products **S9** (9.5 mg, 73%) or **S10** (9.0 mg, 69%), respectively, after purification by silica gel column chromatography (CH_2Cl_2/MeOH = 15:1 to 10:1, v/v). Similarly, **10a** or **10b** (10.0 mg, 0.018 mmol, 1.0 equiv) were converted into the corresponding **S9** (3.7 mg, 64%) or **S10** (3.8 mg, 66%) using sodium methoxide (5 M in MeOH, 10.9 μL, 0.054 mmol, 3.0 equiv) and MeOH (0.5 mL) overnight.

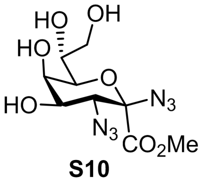
According to the procedure of condition b, compounds **9a** or **9b** (8.2 mg, 0.021 mmol, 1.0 equiv), sodium methoxide (5 M in MeOH, 12.8 μL, 0.064 mmol, 3.0 equiv) and *p*-toluenesulfonic acid monohydrate (12.2 mg, 0.064 mmol, 3.0 equiv) were used. As a result, the corresponding products **S9** (2.9 mg, 43%) or **S10** (2.6 mg, 39%) were prepared.

According to the procedure of condition c, **11a** or **11b** (13.5 mg, 0.030 mmol, 1.0 equiv), *p*-toluenesulfonic acid monohydrate (5.8 mg, 0.091 mmol, 3.0 equiv) and MeOH (0.5 mL) were used. The mixture was stirred overnight at room temperature to respectively give **S9** (6.5 mg, 68%) or **S10** (6.4 mg, 67%). Similarly, both **S9** (5.8 mg, 71%) or **S10** (5.4 mg, 66%) were obtained employing **12a** or **12b** (10.2 mg, 0.026 mmol, 1.0 equiv), *p*-toluenesulfonic acid monohydrate (14.6 mg, 0.077 mmol, 3.0 equiv) and MeOH (0.5 mL).



S9

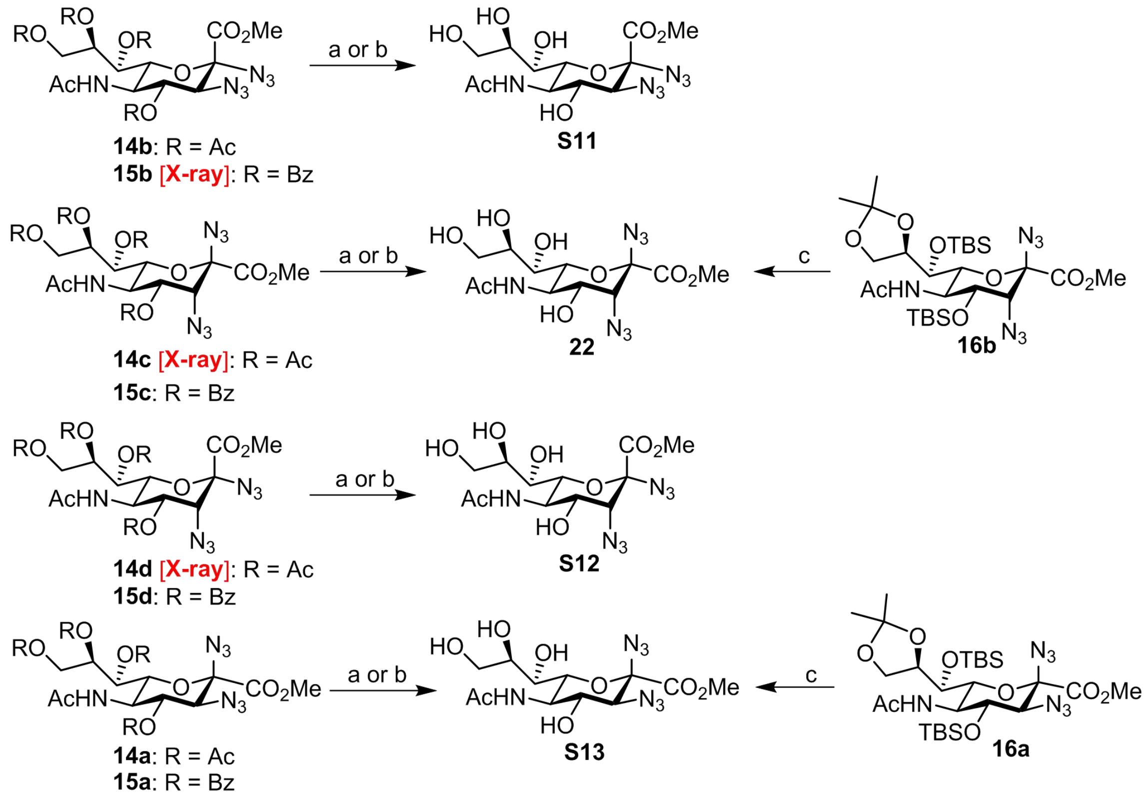
TLC: (CH_2Cl_2/MeOH = 7:1, v/v), R_f = 0.45; **^{1}H NMR** (400 MHz, $CDCl_3/CD_3OD$) δ 4.07 (d, J = 2.8 Hz, 1H), 3.97 (d, J = 10.4 Hz 1H), 3.82 (s, 3H), 3.75 – 3.69 (m, 3H), 3.55 – 3.51 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.4, 91.7, 73.9, 69.3, 69.0, 67.3, 63.0, 60.6, 53.6; **[α]**$_D^{25}$ = +79.0 (*c* 0.07, MeOH); **IR** (neat): ν_{max} = 3374, 2927, 2854, 2117, 1752, 1237, 1079, 925, 798 cm^{-1}; **HRMS (ESI)**: calcd. for $C_9H_{14}N_6NaO_7$ [M + Na]$^+$ *m*/*z* 341.0822; found *m*/*z* 341.0820.



S10

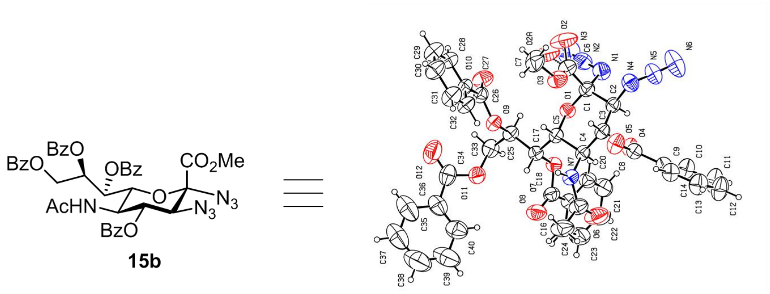
TLC: (CH_2Cl_2/MeOH = 7:1, v/v), R_f = 0.45; **^{1}H NMR** (400 MHz, $CDCl_3/CD_3OD$) δ 4.04 – 4.01 (m, 2H), 3.77 (s, 3H), 3.73 – 3.65 (m, 2H), 3.59 (d, J = 8.0 Hz 1H), 3.54 – 3.46 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 90.7, 75.1, 69.4, 69.2, 66.8, 64.1, 62.9, 52.9; **[α]**$_D^{25}$ = +36.9 (*c* 0.12, MeOH); **IR** (neat): ν_{max} = 3389, 2923, 2852, 2117, 1745, 1245, 1085, 924, 800 cm^{-1}; **HRMS (ESI)**: calcd. for $C_9H_{14}N_6NaO_7$ [M + Na]$^+$ *m*/*z* 341.0822; found *m*/*z* 341.0818.

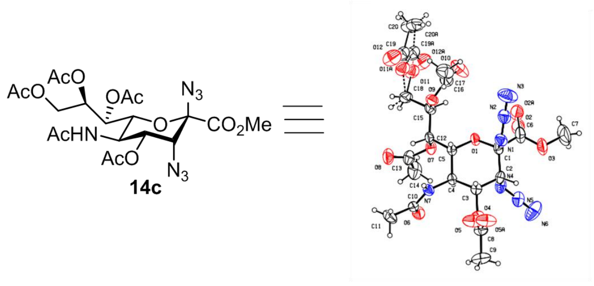
According to the procedure described for condition d, **12a** or **12b** (100 mg, 0.251 mmol, 1.0 equiv) were subjected to a sequence of transformation using zinc nitrate hexahydrate (224 mg, 0.754 mmol, 3.0 equiv), sodium periodate (83.5 mg, 0.402 mmol, 1.6 equiv), sodium borohydride (11.0 mg, 0.302 mmol, 1.2 equiv), and benzoyl chloride (106 μL, 0.754 mmol, 3.0 equiv) in each step. Purification through flash column chromatography (petroleum ether/EtOAc = 25:1, V/V) afforded the corresponding products **13a** (17.4 mg, 16%, 4 steps) or **13b** (21.5 mg, 20%, 4 steps), respectively.

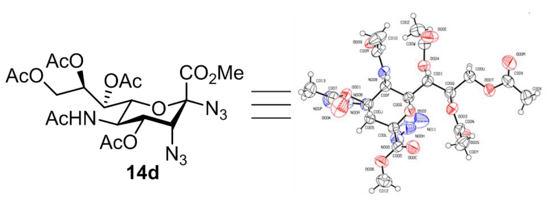


14b, **14c**, **14d**, **14a**: condition a
15b, **15c**, **15d**, **15a**: condition b

condition a: K_2CO_3, MeOH, RT
condition b: NaOMe, MeOH, RT
condition c: 1) TBAF, THF, RT;
2) *p*-TsOH·H_2O, MeOH, RT







Condition a: A mixture of substrate (1.0 equiv) and potassium carbonate (0.5 equiv) in MeOH was stirred for 20 min at room temperature before being neutralized with Amberlite IR 120 (H^+) resin. The mixture was filtered and evaporated to give the crude product, which was purified through column chromatography.

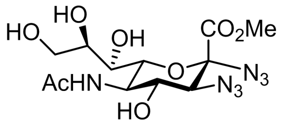
Condition b: Sodium methoxide (3.0 equiv) was added to a stirring solution of substrate (1.0

equiv) in MeOH at room temperature. After being stirred overnight, the mixture was neutralized with Amberlite IR 120 (H^+) resin, then filtered and concentrated under *vacuum*. Purification by silica gel column chromatography with CH_2Cl_2/MeOH afforded the pure product.

Condition c: To a solution of substrate (1.0 equiv) in dry THF was added tetrabutylammonium fluoride (1 M in THF, 3.0 equiv) at room temperature. After being stirred for 3 h, the reaction was quenched by adding saturated NH_4Cl solution. The mixture was extracted with EtOAc for five times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was dissolved in MeOH, to which was added *p*-toluenesulfonic acid monohydrate (1.0 equiv) at room temperature. Triethylamine was used to quench the reaction after overnight. The solvent was removed in *vacuo* and the crude product was purified via column chromatography to yield the corresponding product.

According to the procedure of condition a, compound **14b** (7.5 mg, 0.013 mmol, 1.0 equiv), potassium carbonate (1.0 mg, 0.007 mmol, 0.5 equiv) and MeOH (0.5 mL) were used for the synthesis of **S11** (3.8 mg, 73%) as a white amorphous powder after purification by silica gel column chromatography (CH_2Cl_2/MeOH = 8:1, v/v).

According to the procedure of condition b, compound **15b** (5.0 mg, 0.006 mmol, 1.0 equiv), sodium methoxide (1.0 mg, 0.019 mmol, 3.0 equiv) and MeOH (1 mL) were used for the synthesis of **S11** (1.3 mg, 52%) after purification by silica gel column chromatography (CH_2Cl_2/MeOH = 8:1, v/v).



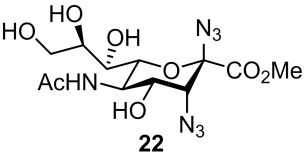
S11

TLC: (CH_2Cl_2/MeOH = 5:1, v/v), R_f = 0.55; **^{1}H NMR** (400 MHz, CD_3OD) δ 4.21 (t, J = 10.0 Hz, 1H), 4.00 (t, J = 10.4 Hz, 1H), 3.91 (dd, J = 10.8, 1.2 Hz, 2H), 3.87 (s, 3H), 3.77 (dd, J = 11.2, 2.8 Hz, 1H), 3.73 3.67 (m, 1H), 3.61 (dd, J = 11.2, 5.2 Hz, 1H), 3.48 (dd, J = 9.6, 1.6 Hz, 1H), 3.35 (d, J = 1.6 Hz, 1H), 2.01 (s, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 175.0, 167.6, 92.0, 75.5, 71.5, 71.1, 69.8, 69.7, 65.0, 53.6, 52.9, 22.6; **$[\alpha]_D^{25}$** = −59.0 (*c* 0.29, $CHCl_3$/MeOH = 5:1, v/v); **IR** (neat): ν_{max} = 3279, 2924, 2113, 1740, 1639, 1555, 1243, 1058, 1022 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{12}H_{19}N_7NaO_8$ $[M + Na]^+$ *m*/*z* 412.1193; found *m*/*z* 412.1192.

According to the procedure described for condition a, compound **14c** (20.0 mg, 0.036 mmol, 1.0 equiv), potassium carbonate (2.5 mg, 0.018 mmol, 0.5 equiv) and MeOH (1 mL) were used for the synthesis of **22** (10.6 mg, 76%) as a white amorphous powder after purification by silica gel column chromatography (CH_2Cl_2/MeOH = 8:1, v/v).

According to the procedure described for condition b, compound **15c** (20.0 mg, 0.025 mmol, 1.0 equiv), sodium methoxide (4.0 mg, 0.075 mmol, 3.0 equiv) and MeOH (1 mL) were used for preparation of **22**. After purification by silica gel column chromatography (CH_2Cl_2/MeOH = 8:1, v/v) to give product **22** (6.1 mg, 63%).

According to the procedure described for condition c, compound **16b** (30.0 mg, 0.046 mmol, 1.0 equiv), tetrabutylammonium fluoride (1 M in THF, 137 μL, 0.137 mmol, 3.0 equiv), 1 mL THF, *p*-toluenesulfonic acid monohydrate (8.7 mg, 0.046 mmol, 1.0 equiv) and MeOH (MeOH) were used for the synthesis of **22** (6.9 mg, 39%) after purification by silica gel column chromatography (CH_2Cl_2/MeOH = 8:1, v/v).

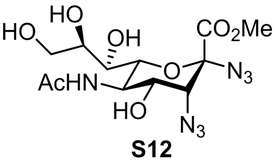


22

TLC: (CH_2Cl_2/MeOH = 5:1, v/v), R_f = 0.54; **^{1}H NMR** (400 MHz, CD_3OD) δ 4.23 – 4.13 (m, 2H), 4.07 – 4.01 (m, 2H), 3.92 (s, 3H), 3.86 – 3.74 (m, 2H), 3.65 (dd, J = 10.8, 4.8 Hz, 1H), 3.53 (dd, J = 9.2, 1.6 Hz, 1H), 2.01 (s, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 175.0, 167.3, 92.6, 74.4, 71.3, 69.7, 69.5, 66.2, 65.1, 53.8, 48.9, 22.7; **$[\alpha]_D^{25}$** = −51.5 (*c* 0.60, $CHCl_3$/MeOH = 5:1, v/v); **IR** (neat): ν_{max} = 3364, 2955, 2923, 2853, 2112, 1018, 800 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{12}H_{19}N_7NaO_8$ $[M + Na]^+$ *m/z* 412.1193; found *m/z* 412.1189; HPLC purity: 99.8% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 μm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 70:30, v/v; t_R = 3.19).

According to the procedure described for condition a, compound **14d** (15.2 mg, 0.027 mmol, 1.0 equiv), potassium carbonate (1.9 mg, 0.014 mmol, 0.5 equiv) and MeOH (1 mL) were used for the synthesis of **S12** (7.5 mg, 71%) as a white amorphous powder after purification by silica gel column chromatography (CH_2Cl_2/MeOH = 8:1, v/v).

According to the procedure of condition b, compound **15d** (20.0 mg, 0.025 mmol, 1.0 equiv), sodium methoxide (4.0 mg, 0.075 mmol, 3.0 equiv) and MeOH (1 mL) were used for the preparation of **S12** (6.5 mg, 67%) after purification by silica gel column chromatography (CH_2Cl_2/MeOH = 8:1, v/v).



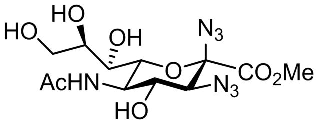
S12

TLC: (CH_2Cl_2/MeOH = 5:1, v/v), R_f = 0.53; **^{1}H NMR** (400 MHz, CD_3OD) δ 4.24 (d, J = 3.2 Hz, 1H), 4.12 (t, J = 10.4 Hz, 1H), 4.01 (dd, J = 10.8, 3.6 Hz, 1H), 3.90 (s, 3H), 3.87 – 3.75 (m, 2H), 3.64 (dd, J = 11.2, 5.2 Hz, 1H), 3.56 (dd, J = 10.4, 1.6 Hz, 1H), 3.48 (dd, J = 9.2, 1.2 Hz, 1H), 1.99 (s, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 175.1, 168.6, 90.9, 76.3, 71.4, 70.3, 70.1, 66.4, 64.9, 54.0, 48.7, 22.7; **[α]**$_D$^{25} = −19.1 (*c* 0.67, $CHCl_3$/MeOH = 5:1, v/v); **IR** (neat): ν_{max} = 3266, 2112, 1744, 1657, 1252, 1034, 589, 568, 552 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{12}H_{19}N_7NaO_8$ [M + Na]$^+$ *m/z* 412.1193; found *m/z* 412.1191; HPLC purity: 99.6% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 μm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 70:30, v/v; t_R = 4.88).

According to the procedure of condition a, compound **14a** (5.1 mg, 0.009 mmol, 1.0 equiv), potassium carbonate (0.6 mg, 0.005 mmol, 0.5 equiv) and MeOH (0.5 mL) were used. Purification by silica gel column chromatography with CH_2Cl_2/MeOH (8:1, v/v) yielded **S13** (2.4 mg, 67%) as a white amorphous powder.

According to the procedure of condition b, compound **15a** (9.3 mg, 0.012 mmol, 1.0 equiv), sodium methoxide (1.9 mg, 0.035 mmol, 3.0 equiv) and MeOH (1 mL) were used for the synthesis of **S13** (2.3 mg, 52%) after purification by silica gel column chromatography (CH_2Cl_2/MeOH = 8:1, v/v).

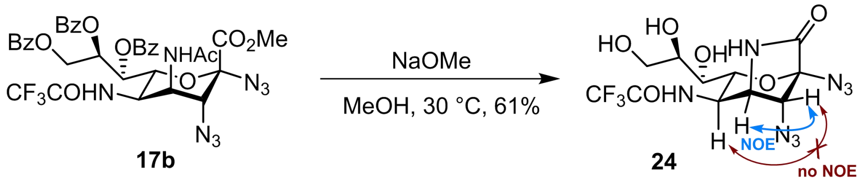
According to the procedure of condition c, compound **16a** (30.1 mg, 0.046 mmol, 1.0 equiv), tetrabutylammonium fluoride (1 M in THF, 137 μL, 0.137 mmol, 3.0 equiv), 1 mL THF, *p*-toluenesulfonic acid monohydrate (8.7 mg, 0.046 mmol, 1.0 equiv) and 1 mL MeOH were used. Purification by silica gel column chromatography with CH_2Cl_2/MeOH (8:1, v/v) provided **S13** (6.2 mg, 35%).



S13

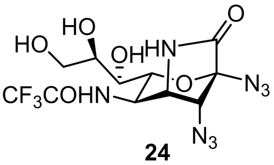
TLC: (CH_2Cl_2/MeOH = 5:1, v/v), R_f = 0.53; **^{1}H NMR** (400 MHz, CD_3OD) δ 4.14 (dd, *J* = 10.8, 1.2 Hz, 1H), 4.04 (t, *J* = 10.0 Hz, 1H), 3.90 (s, 3H), 3.86 (t, *J* = 10.0 Hz, 1H), 3.78 – 3.71 (m, 2H), 3.70 – 3.58 (m, 2H), 3.54 (dd, *J* = 9.2, 1.2 Hz, 1H), 2.02 (s, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 174.8, 167.8, 93.2, 74.7, 71.2, 69.5, 66.2, 65.1, 54.1, 53.1, 29.5, 22.7; **[α]**$_D$^{25} = −88.3 (*c* 0.12, $CHCl_3$/MeOH = 10:1, v/v); **IR** (neat): ν_{max} = 3293, 2954, 2922, 2852, 2114, 1745, 1640, 1557, 1307, 1235, 1115, 1017, 972 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{12}H_{19}N_7NaO_8$ [M + Na]$^+$ *m/z* 412.1193; found *m/z* 412.1190.

17a



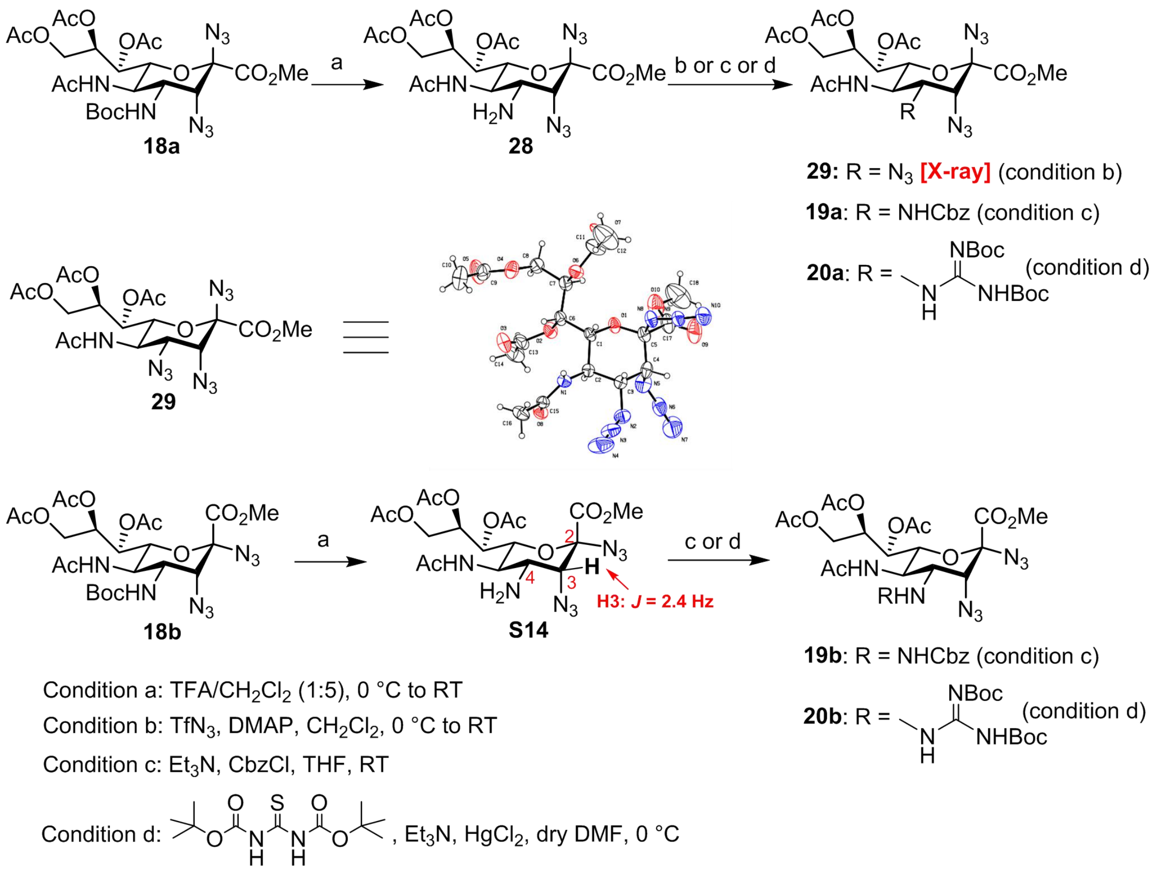
17b **24**

To a stirred solution of compound **17b** (72.0 mg, 0.090 mmol, 1.0 equiv) in MeOH (1 mL) was added sodium methoxide (5 M in MeOH, 54.3 μL, 0.271 mmol, 3.0 equiv) at room temperature. The mixture was stirred at 30 °C overnight, before being neutralized with Amberlite IR 120 (H^+) resin. Then the mixture was filtered, and the filtrate was concentrated under reduced pressure. Purification of the crude residue by column chromatography (CH_2Cl_2/MeOH = 15:1 to 10:1, v/v) afforded **24** (22.6 mg, 61%).



24

TLC: (CH_2Cl_2/MeOH = 7:1, v/v), R_f = 0.50; **^{1}H NMR** (400 MHz, CD_3OD) δ 4.68 (dd, J = 9.6, 1.6 Hz, 1H), 4.23 (dd, J = 9.6, 1.2 Hz, 1H), 4.16 (d, J = 5.6 Hz, 1H), 3.96 (dd, J = 5.6, 1.6 Hz, 1H), 3.87 – 3.78 (m, 2H), 3.66 (dd, J = 11.6, 5.6 Hz, 1H), 3.42 (dd, J = 9.2, 1.2 Hz, 1H); **^{13}C NMR** (100 MHz, CD_3OD) δ 170.1, 159.0 (q, J = 37.5 Hz), 117.2 (q, J = 285.1), 90.1, 74.8, 70.7, 70.2, 64.9, 64.7, 54.9, 46.4; **[α]**$_D^{25}$ = −3.2 (c 0.51, $CHCl_3$/MeOH = 6:1, v/v); **IR** (neat): ν_{max} = 3273, 2926, 2118, 1709, 1213, 1182, 1158, 1072, 1018, 729 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{11}H_{13}F_3N_8NaO_6$ $[M + Na]^+$ m/z 433.0808; found m/z 433.0802; HPLC purity: 99.8% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 μm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 50:50, v/v; t_R = 2.10).



29: R = N_3 **[X-ray]** (condition b)

19a: R = NHCbz (condition c)

20a: R = N(H)C(=NBoc)NHBoc (condition d)

19b: R = NHCbz (condition c)

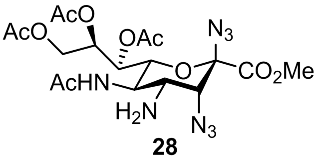
20b: R = N(H)C(=NBoc)NHBoc (condition d)

Condition a: TFA/CH_2Cl_2 (1:5), 0 °C to RT

Condition b: TfN_3, DMAP, CH_2Cl_2, 0 °C to RT

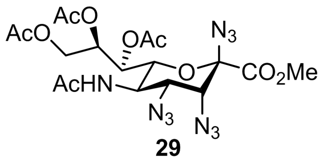
Condition c: Et_3N, CbzCl, THF, RT

Condition d: BocNHC(=S)NHBoc, Et_3N, $HgCl_2$, dry DMF, 0 °C


28

To a stirred solution of compound **18a** (200 mg, 0.326 mmol) in CH_2Cl_2 (4 mL) was added trifluoroacetic acid (0.4 mL) at 0 °C. The mixture was allowed to stir at room temperature for 3 h, before it was concentrated directly in *vacuo*. The crude product was purified by column chromatography (CH_2Cl_2/MeOH = 10:1 to 8:1, +5‰ $NH_3\cdot H_2O$, v/v) to give 140 mg (84%) of product **28** as a white amorphous powder. **TLC**: (CH_2Cl_2/MeOH = 8:1, v/v), R_f = 0.48; ^{1}**H NMR** (400 MHz, $CDCl_3$ + CD_3OD) δ 5.35 (dd, J = 5.4, 2.2 Hz, 1H), 5.22 – 5.14 (m, 1H), 4.61 (dd, J = 12.4, 2.4 Hz, 1H), 4.14 – 4.00 (m, 3H), 3.92 (s, 3H), 3.91 – 3.86 (m, 1H), 3.35 (dd, J = 10.8, 3.6 Hz, 1H), 2.09 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.92 (s, 3H); ^{13}**C NMR** (150 MHz, $CDCl_3$ + MeOD) δ 172.5, 170.8, 170.7, 170.24, 164.9, 90.7, 72.4, 71.2, 67.5, 63.6, 62.0, 53.6, 50.7, 45.84, 22.7, 20.9, 20.6, 20.5; $[\alpha]_D^{25}$ = +15.7 (c 0.70, $CHCl_3$); **IR** (neat): ν_{max} = 3372, 3059, 2119, 1743, 1669, 1373, 1200, 1136, 1047, 722 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{18}H_{26}N_8NaO_{10}$ $[M + Na]^+$ m/z 537.1670; found m/z 537.1668; HPLC purity: 99.9% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 µm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 30:70; t_R = 3.43).

Preparation of TfN_3: Sodium azide (13.0 mg, 0.200 mmol, 10.0 equiv) was dissolved in water (1 mL) and cooled in an ice bath and treated with CH_2Cl_2 (1.5 mL). Trifluoromethanesulfonic anhydride (16.4 μL, 0.100 mmol, 5.0 equiv) was added slowly at 0 °C to the resulting biphasic mixture. The reaction was stirred at 0 °C for 2 h, the organic layer was separated and the aqueous phase was washed with CH_2Cl_2 as less volume as possible. The combined organic layers were washed with saturated $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered and used without further purification.

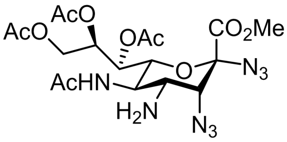


29

To a stirred solution of compound **28** (10.2 mg, 0.019 mmol, 1.0 equiv) in CH_2Cl_2 (1 mL) was added 4-(dimethylamino)pyridine (7.1 mg, 0.058 mmol, 3.0 equiv). The above freshly prepared trifluoromethanesulfonic azide (TfN_3) solution was added dropwise at 0 °C. The ice-bath was removed and the mixture was stirred overnight at room temperature. The reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2, before the combined organic layers were dried and concentrated. Purification of the residue by a flash column chromatography (petroleum ether/EtOAc = 2:1 to 1:1, v/v) furnished **29** (5.0 mg, 47%, 68% brsm) with **28** (3.0 mg) recovered. **TLC**: (petroleum ether/EtOAc = 1:3, v/v), $R_f = 0.54$; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.90 (d, J = 8.0 Hz, 1H), 5.38 – 5.24 (m 2H), 4.81 (d, J = 10.8 Hz, 1H), 4.57 – 4.48 (m, 2H), 4.20 (dd, J = 12.8, 5.2 Hz, 1H), 4.06 (d, J = 3.2 Hz, 1H), 3.93 (s, 3H), 3.45 (s, 1H), 2.17 (s, 3H), 2.07 (3, 3H), 2.04 (s, 3H), 2.03 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 171.1, 170.5, 169.9, 164.6, 90.5, 70.3, 69.9, 67.9, 63.0, 61.8, 57.4, 53.6, 48.2, 23.5, 21.0, 20.8, 20.7; **$[\alpha]_D^{25}$** = −2.0 (c 0.70, $CHCl_3$); **IR** (neat): ν_{max} = 3269, 2960, 2110, 1743, 1370, 1255, 1212, 1048, 1030, 755 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{18}H_{24}N_{10}NaO_{10}$ $[M + Na]^+$ m/z 563.1575; found m/z 563.1573. The supplementary crystallographic data of **29** [m.p.: 186 – 188 °C (hexane/$CHCl_3$ = 5:1, v/v)] have been deposited in Cambridge Crystallographic Data Centre (CCDC 1975129). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Triethylamine (5.41 μL, 0.039 mmol, 2.0 equiv) and benzyl chloroformate (5.48 μL, 0.039 mmol, 2.0 equiv) were successively added to a solution of **28** (10.0 mg, 0.019 mmol, 1.0 equiv) in dry THF (1 mL) under an argon atmosphere. After being stirred for 3 h at room temperature, the reaction mixture was concentrated in *vacuo*. The crude product was purified by column chromatography (petroleum ether/EtOAc = 1.5:1 to 1:2, v/v) to afford **19a** (10.2 mg, 81%).

To a stirred solution of **28** (10.0 mg, 0.019 mmol, 1.0 equiv) in dry DMF (1 mL) were added *N,N'*-bis-tert-butoxycarbonylthiourea (5.9 mg, 0.021 mmol, 1.1 equiv) and triethylamine (54.1 μL, 0.389 mmol, 20.0 equiv). The mixture was cooled to 0 °C, followed by addition of mercurous chloride (9.0 mg, 0.019 mmol, 1.0 equiv). The reaction was concentrated in *vacuo* after being stirred for 5 h at the same temperature. The residue was dissolved in EtOAc, which was further subjected to filtration through Celite®. After the resultant filtrate was washed with water and brine, the organic layer was dried and evaporated under reduced pressure. Purification of the crude product via column chromatography (petroleum ether/EtOAc = 2:1, v/v) yielded **20a** (9.3 mg, 63%).



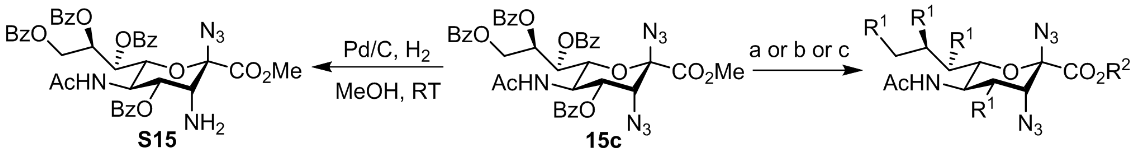
S14

According to the procedure for the synthesis of **28**, the diazidation product **18b** (60.2 mg, 0.098 mmol) and trifluoroacetic acid (0.4 mL) were used for the synthesis of **S14**. The crude product was purified by silica gel column chromatography (petroleum ether/acetone = 3:1 to 1:2 , +5‰ $NH_3{\cdot}H_2O$, v/v) to give **S14** (39.2 mg, 78%). **TLC**: (CH_2Cl_2/MeOH = 8:1, v/v), $R_f = 0.47$; **^{1}H NMR** (600 MHz, CD_3OD) δ 5.38 – 5.30 (m, 2H), 4.33 (dd, J = 12.6, 2.4 Hz, 1H), 4.16 (d, J = 2.4 Hz, 1H), 4.11 (dd, J = 12.0, 4.8 Hz, 1H), 3.95 – 3.84 (m, 5H), 2.79 (dd, J = 10.8, 3.6 Hz, 1H), 2.12 (s, 3H), 2.11 (s, 3H), 2.01 (s, 3H), 1.92 (s, 3H); **^{13}C NMR** (150 MHz, CD_3OD) δ 174.3, 172.4, 171.6, 171.4, 167.5, 91.8, 75.5, 70.0, 68.6, 66.5, 63.2, 54.2, 53.7, 47.6, 22.9, 21.1, 20.8, 20.6; **$[\alpha]_D^{25}$** = +32.8 (c 0.43, $CHCl_3$); **IR** (neat): ν_{max} = 3275, 2959, 2925, 2855, 2109, 1743, 1731, 1368, 1215, 1039, 735 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{18}H_{26}N_8NaO_{10}$ $[M + Na]^+$ m/z 537.1670; found m/z 537.1668; HPLC purity: 99.8% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 μm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 20:80, v/v; t_R = 3.40).

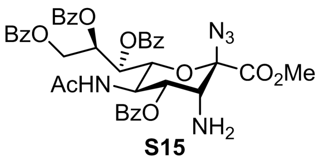
According to the above procedure for synthesis of compound **19a**, triethylamine (4.38 μL, 0.032 mmol, 2.0 equiv), benzyl chloroformate (4.44 μL, 0.032 mmol, 2.0 equiv) and compound **S14** (8.1 mg, 0.016 mmol, 1.0 equiv) were used to access **19b** (7.7 mg, 76%) after the crude product was purified by silica gel column chromatography (petroleum ether/EtOAc = 1.5:1 to 1:2).

According to the above procedure for the synthesis of compound **20a**, compound **S14** (10.2 mg, 0.020 mmol, 1.0 equiv), *N,N'*-bis-tert-butoxycarbonylthiourea (6.0 mg, 0.022 mmol, 1.1 equiv), triethylamine (55.2 μL, 0.397 mmol, 20.0 equiv) and mercurous chloride (7.4 mg, 0.020 mmol, 1.0 equiv) were used. The crude product was purified by silica gel column chromatography (petroleum ether/EtOAc = 2:1 to 1:1, v/v) to afford **20b** (9.2 mg, 61%).

6. Product Diversification

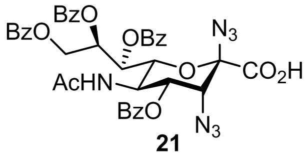


condition a (for **21**): LiI, pyridine, 90 °C **21:** R^1 = OBz, R^2 = H
condition b (for **22**): NaOMe, MeOH, RT **22:** R^1 = OH, R^2 = Me
condition c (for **23**): NaOH, MeOH, RT) **23:** R^1 = OH, R^2 = H



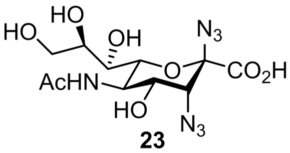
S15

A mixture of compound **15c** (140 mg, 0.174 mmol), 10% Pd/C (14.0 mg), and MeOH (10 mL) was stirred under a balloon of hydrogen at ambient pressure and room temperature for 4 h. The reaction mixture was then filtered through a short plug of Celite® and the filtrate was concentrated in *vacuo*. Purification of the residue by silica gel column chromatography (petroleum ether/EtOAc = 2:1, v/v) afforded **S15** (110 mg, 81%). **TLC**: (petroleum ether/EtOAc = 1:1, v/v), R_f = 0.50; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 – 8.14 (m, 2H), 8.03 – 7.97 (m, 4H), 7.96 – 7.90 (m, 2H), 7.64 – 7.45 (m, 6H), 7.45 – 7.30 (m, 6H), 5.98 (dd, J = 10.8, 3.6 Hz, 1H), 5.95 – 5.80 (m, 1H), 5.84 (dd, J = 5.6, 2.0 Hz, 1H), 5.58 (d, J = 9.6 Hz, 1H), 5.19 (dd, J = 12.4, 2.8 Hz, 1H), 4.81 (dd, J = 10.4, 2.0 Hz, 1H), 4.56 (dd, J = 12.0, 7.6 Hz, 1H), 4.44 (q, J = 10.0 Hz, 1H), 4.32 (d, J = 3.6 Hz, 1H), 3.88 (s, 3H), 2.13 (s, 2H), 1.81 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.3, 170.1, 166.4, 166.2, 165.9, 133.7, 133.4, 132.9, 130.2, 130.0, 129.8, 129.8, 129.6, 129.4, 129.4, 128.6, 128.5, 128.5, 128.5, 128.3, 86.3, 72.0, 71.2, 70.3, 69.5, 63.8, 63.7, 53.0, 46.5, 23.3; **$[\alpha]_D^{25}$** = +4.4 (c 0.50, $CHCl_3$); **IR** (neat): ν_{max} = 3378, 2928, 2855, 2111, 1718, 1261, 1107, 1094, 1069, 1026, 708 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{40}H_{37}N_5NaO_{12}$ $[M + Na]^+$ m/z 802.2336; found m/z 802.2325; HPLC purity: 97.3% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX 300SB-C8, 5 μm, 4.6 × 150 mm; Detector: Waters 2489 UV/Vis; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 100:0 → 5:95, v/v; t_R = 18.64).



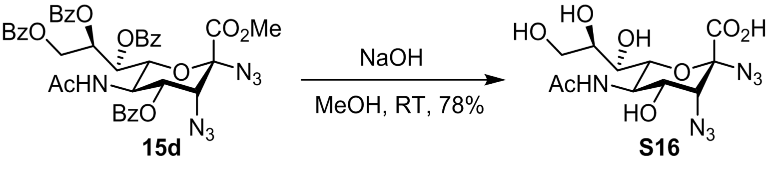
21

A mixture of **15c** (50.3 mg, 0.062 mmol, 1.0 equiv), lithium iodide (83.1 mg, 0.621 mmol, 10.0 equiv), and pyridine (1 mL) was stirred overnight at 90 °C under an argon atmosphere. After being cooled to room temperature, the reaction was concentrated under reduced pressure. Subjection of the crude residue to purification via column chromatography (CH_2Cl_2/MeOH = 20:1, v/v) afforded **21** (42.5 mg, 86%). **TLC**: (CH_2Cl_2/MeOH = 8:1, v/v), R_f = 0.45; **^{1}H NMR** (400 MHz, CD_3OD) δ 8.17 (d, J = 7.2 Hz, 2H), 8.05 (d, J = 7.2 Hz, 2H), 8.00 (d, J = 7.2 Hz, 2H), 7.94 (d, J = 7.2 Hz, 2H), 7.69 – 7.34 (m, 12H), 6.05 – 5.93 (m, 2H), 5.54 (dd, J = 10.4, 3.6 Hz, 1H), 5.08 (dd, J = 12.4, 2.4 Hz, 1H), 4.68 – 4.47 (m, 4H), 4.44 (d, J = 3.6 Hz, 1H), 1.80 (s, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 173.3, 167.6, 167.1, 167.0, 166.8, 150.0, 134.7, 134.6, 134.6, 134.3, 131.3, 131.0, 131.0, 131.0, 130.9, 130.8, 130.7, 130.3, 129.7, 129.6, 129.6, 129.5, 73.3, 73.1, 71.6, 69.6, 64.9, 63.6, 46.0, 30.7, 22.7; **[α]**$_D^{25}$ = +21.4 (c 0.44, $CHCl_3$: MeOH = 4:1, v/v); **IR** (neat): ν_{max} = 3398, 2119, 1725, 1662, 1261, 1090, 1069, 1025, 707, 686 cm^{-1}; **HRMS (ESI)**: calcd.for $C_{39}H_{33}N_7NaO_{12}$ [M + Na]$^+$ m/z 814.2085; found m/z 814.2055; HPLC purity: 99.1% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 μm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 30:70, v/v; t_R = 2.28).



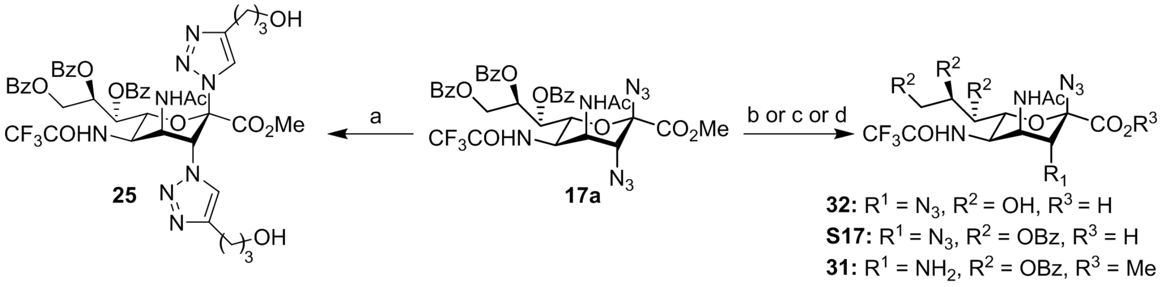
23

To a stirred solution of **15c** (20.0 mg, 0.025 mmol, 1.0 equiv) in MeOH (1 mL) was added NaOH aq. (1 M in H_2O, 50.0 μL, 0.050 mmol, 2.0 equiv) at ambient temperature. The resultant mixture was allowed to stir for 5 h, then neutralized with Amberlite IR 120 (H$^+$) resin and filtered. The filtrate was evaporated under reduced pressure to afford the crude residue, which was purified through reverse phase silica gel column chromatography (MeOH/H_2O = 1:9, v/v) to give acid **23** (8.4 mg, 81%). **^{1}H NMR** (400 MHz, CD_3OD) δ 4.27 – 4.13 (m, 2H), 4.11 – 4.01 (m, 2H), 3.88 – 3.70 (m, 2H), 3.66 (dd, J = 10.8, 4.8 Hz, 1H), 3.57 (d, J = 8.0 Hz, 1H), 2.01 (s, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 174.8, 169.7, 93.7, 74.1, 72.1, 69.9, 66.6, 64.8, 22.8; **[α]**$_D^{25}$ = −82.0 (c 0.60, MeOH); **IR** (neat): ν_{max} = 3277, 2946, 2110, 1631, 1558, 1376, 1070, 1019, 679 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{11}H_{17}N_7NaO_8$ [M + Na]$^+$ m/z 398.1036; found m/z 398.1031; HPLC purity: 97.8% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX 300SB-C8, 5 μm, 4.6 × 150 mm; Detector: Waters 2424 ELSD; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 100:0, v/v; t_R = 1.74).



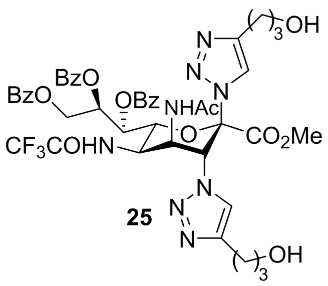
According to the procedure for the preparation of **23**, compound **15d** (20.3 mg, 0.025 mmol, 1.0 equiv), NaOH aq. (1 M in H_2O, 75.6 μL, 0.076 mmol, 3.0 equiv) and MeOH (1 mL) were used for the synthesis of **S16**. The crude product was purified through reverse phase silica gel column chromatography (MeOH/H_2O = 1:9 to 1:4, v/v) to give **S16** (7.4 mg, 78%). **^{1}H NMR** (400 MHz, CD_3OD) δ 4.33 (d, J = 1.6 Hz, 1H), 4.03 (d, J = 6.0 Hz, 2H), 3.95 – 3.82 (m, 2H), 3.67 (dd, J = 11.2, 5.2 Hz, 1H), 3.59 – 3.59 (m, 2H), 2.02 (s, 3H); **^{13}C NMR** (150 MHz, CD_3OD) δ 175.5, 171.6, 92.7, 76.1, 72.6, 71.0, 69.9, 67.6, 64.0, 48.9, 22.7; **[α]**$_D^{25}$ = +2.1 (c

0.57, MeOH); **IR** (neat): ν_{max} = 3273, 2948, 2840, 2109, 1624, 1563, 1375, 1247, 1023 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{11}H_{17}N_7NaO_8$ $[M + Na]^+$ *m/z* 398.1036; found *m/z* 398.1020; HPLC purity: 97.2% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 µm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 90:10, v/v; t_R = 1.68).



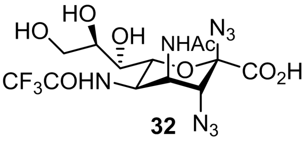
condition a: 4-pentynyl alcohol, $CuSO_4 \cdot 5H_2O$ sodium ascorbate, THF/H_2O, RT

condition b (for **32**): NaOH, MeOH, RT
condition c (for **S17**): LiI, pyridine, 90 °C
condition d (for **31**): Pd/C, H_2, MeOH, RT


25

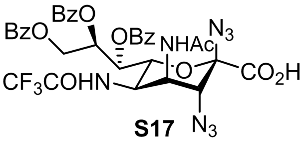
4-Pentynyl alcohol (38.6 µL, 0.414 mmol, 2.2 equiv), $CuSO_4 \cdot 5H_2O$ (18.8 mg, 0.075 mmol, 0.4 equiv) and sodium ascorbate (149 mg, 0.754 mmol, 4.0 equiv) were added sequentially to a stirred solution of **17a** (150 mg, 0.188 mmol, 1.0 equiv) in THF (7.5 mL) and H_2O (7.5 mL) at room temperature. The mixture was allowed to stir at the same temperature for 2 h and diluted with H_2O. Filtration through a pad of Celite® was conducted to remove insoluble salts, and the filtrate was extracted with EtOAc. Next, the combined organic layers were dried over Na_2SO_4, filtered and concentrated. Subjection of the residue to flash column chromatography (CH_2Cl_2/MeOH = 15:1, v/v) on silica gel afforded compound **25** (151 mg, 83%). **TLC**: (CH_2Cl_2/MeOH = 8:1, v/v), R_f = 0.54; **^{1}H NMR** (400 MHz, CD_3OD) δ 8.25 – 8.18 (m, 2H), 8.02 (s, 1H), 7.93 – 7.87 (m, 4H), 7.85 (s, 1H), 7.74 – 7.53 (m, 5H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 1H), 5.95 (dd, *J* = 8.0, 1.6 Hz, 1H), 5.78 – 5.71 (m, 1H), 5.17 – 5.06 (m, 2H), 5.02 (dd, *J* = 10.8, 6.8 Hz, 1H), 4.63 (dd, *J* = 10.8, 1.6 Hz, 1H), 4.60 (s, 1H), 4.39 (dd, *J* = 12.8, 4.8 Hz, 1H), 3.62 (s, 3H), 3.57 – 3.50 (m, 4H), 2.74 (t, *J* = 7.2 Hz, 2H), 2.49 (t, *J* = 7.6 Hz, 2H), 1.88 – 1.70 (m, 4H), 1.82 (s, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 173.7, 167.5, 166.7, 166.6, 165.4, 159.4 (q, *J* = 37 Hz), 150.8, 148.3, 135.1, 134.9, 134.5, 131.3, 130.8, 130.7, 130.7, 130.4, 130.2, 129.9, 129.8, 129.7, 129.6, 129.5, 126.2, 123.0, 117.2 (q, *J* = 285 Hz), 92.6, 71.3, 70.8, 69.8, 63.1, 62.0, 61.8, 58.5, 54.8, 49.9, 47.2, 33.1, 32.5, 22.8, 22.5, 22.4; **$[\alpha]_D^{25}$** = +36.4 (*c* 0.52, $CHCl_3$); **IR** (neat): ν_{max} = 3339, 2936, 1721, 1260, 1106, 1068, 708 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{45}H_{47}F_3N_8NaO_{13}$ [M +

Na]$^+$ *m*/*z* 987.3112; found *m*/*z* 987.3072; HPLC purity: 99.9% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 μm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 10:90, v/v; t_R = 1.90).



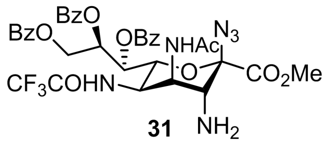
32

According to the procedure for the preparation of **23**, compound **17a** (80.1 mg, 0.101 mmol, 1.0 equiv), NaOH aq. (1 M in H_2O, 0.302 mL, 0.302 mmol, 3.0 equiv) and 2 mL MeOH were employed for synthesis of **32** (32.1 mg, 68%) after the crude product was purified by silica gel column chromatography (CH_2Cl_2/MeOH = 5:1 to 2:1, v/v). **TLC**: (CH_2Cl_2/MeOH = 1:1, v/v), R_f = 0.50; **^{1}H NMR** (400 MHz, CD_3OD) δ 4.68 (t, *J* = 3.6 Hz, 1H), 4.59 (dd, *J* = 11.2, 4.0 Hz, 1H), 4.48 (d, *J* = 11.2 Hz, 1H), 4.02 (d, *J* = 2.8 Hz, 1H), 3.92 – 3.83 (m, 1H), 3.83 – 3.68 (m, 2H), 3.62 (d, *J* = 8.0 Hz, 1H), 2.07 (s, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 173.5, 170.6, 158.9 (q, *J* = 37 Hz), 117.2 (q, *J* = 285 Hz), 93.5, 72.3, 69.4, 69.0, 64.4, 63.1, 49.9, 44.8, 22.9; **$[\alpha]_D^{25}$** = −154.4 (*c* 1.00, MeOH); **IR** (neat): ν_{max} = 3259, 2933, 2113, 1714, 1635, 1380, 1214, 1186, 1153 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{13}H_{17}F_3N_8NaO_8$ [M + Na]$^+$ *m*/*z* 493.1019; found *m*/*z* 493.1018; HPLC purity: 99.8% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 μm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 30:70, v/v; t_R = 1.69).



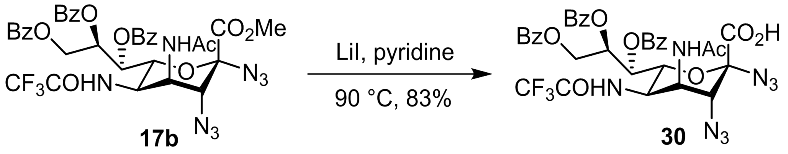
S17

According to the procedure for synthesis of **21**, a mixture of compound **17a** (100 mg, 0.126 mmol, 1.0 equiv), lithium iodide (168 mg, 1.26 mmol, 10.0 equiv) and pyridine (2 mL) was stirred overnight at 90 ºC. Purification of crude product by flash column chromatography (CH_2Cl_2/MeOH = 20:1 to 15:1, v/v) yielded **S17** (74.7 mg, 76%). **TLC**: (CH_2Cl_2/MeOH = 6:1, v/v), R_f = 0.61; **^{1}H NMR** (400 MHz, CD_3OD) δ 8.13 (d, *J* = 7.6 Hz, 2H), 8.02 (d, *J* = 7.2 Hz, 2H), 7.93 (d, *J* = 7.2 Hz, 2H), 7.70 – 7.34 (m, 9H), 6.10 – 6.02 (m, 1H), 5.98 (dd, *J* = 8.0, 2.0 Hz, 1H), 5.16 (dd, *J* = 12.4, 2.0 Hz, 1H), 4.70 (dd, *J* = 11.2, 1.6 Hz, 1H), 4.65 – 4.55 (m, 3H), 4.49 (dd, *J* = 12.4, 4.8 Hz, 1H), 4.39 (dd, *J* = 11.2, 4.4 Hz, 1H), 4.00 (d, *J* = 3.2 Hz, 1H), 2.01 (s, 3H); **^{13}C NMR** (150 MHz, CD_3OD) δ 173.4, 170.3, 167.6, 166.9, 166.7, 158.9 (q, *J* = 37.5 Hz), 134.8, 134.6, 134.4, 131.2, 131.0, 130.9, 130.7, 130.5, 130.5, 129.6, 129.6, 129.5, 129.4, 117.1 (q, *J* = 285 Hz), 93.7, 71.5, 69.9, 68.9, 63.5, 63.3, 50.3, 44.9, 22.9; **$[\alpha]_D^{25}$** = +45.0 (*c* 0.50, $CHCl_3$); **IR** (neat): ν_{max} = 2117, 1718, 1654, 1452, 1259, 1177, 1091, 1068, 709 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{34}H_{29}F_3N_8NaO_{11}$ [M + Na]$^+$ *m*/*z* 805.1806; found *m*/*z* 805.1803; HPLC purity: 99.8% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 μm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 30:70, v/v; t_R = 2.22).

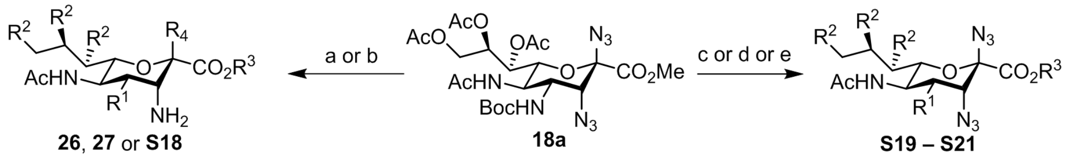


31

According to the procedure for synthesis of **S15**, compound **17a** (100 mg, 0.126 mmol) was subjected to hydrogenation with 10% Pd/C (10.2 mg) in MeOH (5 mL) under a balloon of hydrogen. Amine **31** (58.9 mg, 63%) was obtained after purification by silica gel column chromatography (petroleum ether/EtOAc = 1.5:1, v/v). **TLC**: (petroleum ether/EtOAc = 1:2, v/v), $R_f = 0.56$; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 – 8.07 (m, 2H), 8.06 – 7.99 (m, 2H), 7.98 – 7.89 (m, 2H), 7.72 (d, J = 9.2 Hz, 1H), 7.64 – 7.32 (m, 9H), 6.76 (d, J = 9.2 Hz, 1H), 5.91 – 5.85 (m, 1H), 5.75 (dd, J = 4.8, 1.6 Hz, 1H), 5.31 (dd, J = 12.4, 2.4 Hz, 1H), 4.78 – 4.69 (m, 2H), 4.46 (dd, J = 12.4, 7.2 Hz, 1H), 4.43 – 4.35 (m, 1H), 3.89 (s, 3H), 3.84 (d, J = 3.2 Hz, 1H), 2.02 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 170.0, 166.4, 166.4, 165.3, 157.3 (q, J = 38 Hz), 133.6, 133.5, 133.1, 130.1, 129.9, 129.6, 129.6, 129.2, 129.0, 128.6, 128.6, 128.4, 115.4 (q, J = 286 Hz), 86.0, 72.4, 69.2, 67.6, 63.8, 62.7, 53.2, 49.8, 44.5, 23.5; **$[\alpha]_D^{25}$** = +124.8 (c 0.40, $CHCl_3$); **IR** (neat): ν_{max} = 3377, 3287, 2115, 1718, 1259, 1250, 1089, 1068, 1025, 708 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{35}H_{33}F_3N_6NaO_{11}$ $[M + Na]^+$ m/z 793.2057; found m/z 793.2049; HPLC purity: 92.9% (Flow rate: 1.0 mL/min; Column: CHIRALCEL OD-H, 5 μm, 4.6 × 250 mm; Detector: Agilent G1314F 1260 VWD; Temperature: 25 °C; Mobile phase: hexane/2-isopropanol (0.1% Et_2NH) = 25:75, v/v; t_R = 4.90).



Following the procedure for synthesis of **21**, a mixture of **17b** (52.3 mg, 0.066 mmol, 1.0 equiv), lithium iodide (87.9 mg, 0.657 mmol, 10.0 equiv) and pyridine (1 mL) was stirred overnight at 90 ºC. The residue was purified by column chromatography (CH_2Cl_2/MeOH = 20:1 to 10:1, v/v) to afford acid **30** (42.6 mg, 83%). **TLC**: (CH_2Cl_2/MeOH = 7:1, v/v), R_f = 0.58; **^{1}H NMR** (400 MHz, CD_3OD) δ 8.11 (dd, J = 8.0, 1.2 Hz, 2H), 7.96 (dd, J = 8.0, 1.2 Hz, 2H), 7.90 (dd, J = 8.4, 1.6 Hz, 2H); 7.68 – 7.30 (m, 9H), 5.98 – 5.85 (m, 2H), 5.10 (dd, J = 12.4, 3.2 Hz, 1H), 4.78 (dd, J = 10.4, 2.0 Hz, 1H), 4.70 (dd, J = 12.4, 6.4 Hz, 1H), 4.61 – 4.50 (m, 1H), 4.44 (t, J = 5.2 Hz, 1H), 4.21 (d, J = 4.8 Hz, 1H), 1.95 (s, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 173.8, 172.6, 167.6, 167.0, 166.7, 159.0 (q, J = 38 Hz), 134.7, 134.4, 134.3, 131.1, 131.0, 130.9, 130.8, 130.6, 130.5, 129.7, 129.5, 129.4, 117.1 (q, J = 285 Hz), 93.6, 72.6, 70.9, 63.8, 62.6, 59.5, 50.2, 46.0, 22.9; **$[\alpha]_D^{25}$** = +82.8 (c 0.40, $CHCl_3$); **IR** (neat): ν_{max} = 3276, 3083, 2889, 2114, 1722, 1647, 1262, 1177, 1093, 1069, 707 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{34}H_{29}F_3N_8NaO_{11}$ $[M + Na]^+$ m/z 805.1806; found m/z 805.1811; HPLC purity: 99.8% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 μm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 30:70, v/v; t_R = 1.89).

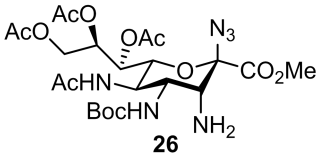


a: Pd/C, H_2, MeOH, RT
26: R^1 = NHBoc, R^2 = OAc, R^3 = Me, R_4 = N_3
27: R^1 = NHBoc, R^2 = OAc, R^3 = Me, R_4 = NH_2

b: 1). TFA/CH_2Cl_2 (1:5); 2). Pd/C, H_2, MeOH, RT
S18: R^1 = NH_2, R^2 = OAc, R^3 = Me, R^4 = N_3

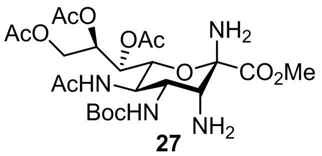
S19: R^1 = NHBoc, R^2 = OH, R^3 = Me (**c**: K_2CO_3, MeOH, RT)
S20: R^1 = NHBoc, R^2 = OH, R^3 = H (**d**: NaOH, MeOH, RT)
S21: R^1 = NH_2, R^2 = OH, R^3 = H (**e**: 1. NaOH, MeOH, RT;
2. TFA/CH_2Cl_2, RT)

Following the procedure for synthesis of **S15**, **18a** (80.1 mg, 0.130 mmol), 10% Pd/C (8.0 mg) and MeOH (2 mL) were used under a balloon of hydrogen to give **26** (47.5 mg, 62%) and **27** (9.0 mg, 12%), which were purified by silica gel column chromatography (petroleum ether/acetone = 3:1 to 1:1, v/v).



26

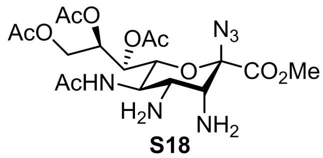
TLC: (petroleum ether/acetone = 2:1, v/v), R_f = 0.35; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.59 (d, J = 10.0 Hz, 1H), 5.39 – 5.24 (m, 2H), 5.12 (d, J = 8.8 Hz, 1H), 4.80 (dd, J = 12.4, 2.4 Hz, 1H), 4.36 (dd, J = 10.4, 2.0 Hz, 1H), 4.30 – 4.20 (m, 1H), 4.15 – 4.02 (m, 3H), 3.84 (s, 3H), 2.13 (s, 3H), 2.07 (s, 3H) , 2.03 (s, 3H), 1.92 (s, 3H), 1.42 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.0, 170.8, 170.6, 170.3, 156.0, 85.8, 80.4, 71.7, 70.5, 68.2, 64.6, 62.9, 53.0, 51.6, 45.4, 28.2, 23.2, 21.0, 20.8, 20.8; **[α]**$_D^{25}$ = +29.8 (c 1.20, $CHCl_3$); **IR** (neat): ν_{max} = 3363, 2979, 2112, 1738, 1368, 1247, 1216, 1161, 1041, 735 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{23}H_{36}N_6NaO_{12}$ $[M + Na]^+$ m/z 611.2289; found m/z 611.2287; HPLC purity: 99.9% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 μm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 30:70, v/v; t_R = 2.70).



27

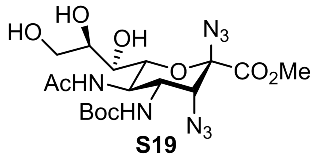
TLC: (petroleum ether/acetone = 1:1, v/v), R_f = 0.32; **^{1}H NMR** (400 MHz, CD_3OD) δ 5.42 – 5.27 (m, 2H), 4.66 (dd, J = 12.4, 2.4 Hz, 1H), 4.59 (s, 1H), 4.47 (dd, J = 10.4, 2.0 Hz, 1H), 4.18 – 4.07 (m, 2H), 3.96 – 3.85 (m, 1H), 3.77 (s, 3H), 3.15 (d, J = 3.6 Hz, 1H), 2.09 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.87 (s, 3H), 1.42 (s, 9H); **^{13}C NMR** (100 MHz, CD_3OD) δ 173.8, 173.2, 172.5, 171.9, 171.8, 157.9, 89.5, 80.5, 72.4, 70.8, 70.1, 63.9, 55.8, 52.9, 52.8, 46.4, 28.6, 22.7, 20.9, 20.8, 20.7; **[α]**$_D^{25}$ = +0.78 (c 0.26, $CHCl_3$); **IR** (neat): ν_{max} =

3332, 2998, 2925, 2854, 1739, 1690, 1368, 1218, 1164, 1040, 734 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{23}H_{39}N_4O_{12}$ [M + H]$^+$ *m*/*z* 563.2564; found *m*/*z* 563.2557; HPLC purity: 98.4% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 µm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 10:90, v/v; t_R = 2.51).



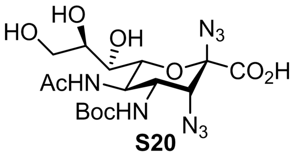
S18

A mixture of **28** (15.0 mg, 0.029 mmol) and 10% Pd/C (1.5 mg) in MeOH (1 mL) was stirred under a balloon of hydrogen at room temperature for 3 h. The reaction mixture was then filtered through a short pad of Celite® and the filtrate was concentrated in *vacuo*. Purification of the residue by column chromatography (CH_2Cl_2/MeOH = 10:1. v/v) afforded **S18** (10.2 mg, 70%). **TLC**: (CH_2Cl_2/MeOH = 6:1, v/v), R_f = 0.50; **^{1}H NMR** (600 MHz, $CDCl_3$ + CD_3OD) δ 5.28 – 5.07 (m, 2H), 4.69 (d, *J* = 8.4 Hz, 1H), 4.13 (d, *J* = 7.2 Hz, 1H), 3.99 – 3.94 (m, 1H), 3.82 (d, *J* = 2.4 Hz, 1H), 3.76 – 3.65 (m, 4H), 3.22 (s, 1H), 3.02 (dd, *J* = 7.2, 2.4 Hz, 1H), 1.99 (s, 3H), 1.94 (s, 3H), 1.91 (s, 3H), 1.80 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$ + CD_3OD) δ 172.3, 171.1, 170.9, 170.7, 170.6, 85.9, 71.8, 69.7, 68.4, 66.2, 62.8, 52.5, 51.2, 47.7, 22.3, 20.5, 20.4, 20.3; **$[\alpha]_D^{25}$** = +30.9 (*c* 0.33, $CHCl_3$); **IR** (neat): ν_{max} = 3360, 2957, 2925, 2856, 2114, 1731, 1372, 1224, 1045 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{18}H_{28}N_6NaO_{10}$ [M + Na]$^+$ *m*/*z* 511.1765; found *m*/*z* 511.1764; HPLC purity: 94.2% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 µm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 10:90, v/v; t_R = 5.73).



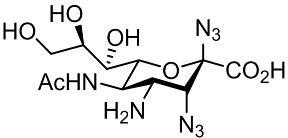
S19

A mixture of compound **18a** (50.0 mg, 0.081 mmol, 1.0 equiv) and potassium carbonate (5.6 mg, 0.041 mmol, 0.5 equiv) in MeOH (1 mL) was stirred for 30 min at room temperature before being neutralized with Amberlite IR 120 (H$^+$) resin. The mixture was filtered and evaporated to give the crude product, which was purified through column chromatography (CH_2Cl_2/MeOH = 10:1, v/v) to deliver **S19** (30.2 mg, 76%). **TLC**: (CH_2Cl_2/MeOH = 6:1, v/v), R_f = 0.62; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.73 (d, *J* = 6.0 Hz, 1H), 5.13 (d, *J* = 10.0 Hz, 1H), 4.69 (d, *J* = 5.2 Hz, 1H), 4.32 – 4.20 (m, 1H), 4.13 – 3.79 (m, 10H), 3.54 (dd, *J* = 9.2, 4.0 Hz, 1H), 2.00 (s, 3H), 1.46 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 173.3, 165.3, 156.8, 90.8, 81.3, 73.9, 69.6, 69.5, 64.8, 63.1, 53.6, 48.9, 48.2, 28.3, 22.9; **$[\alpha]_D^{25}$** = −54.3 (*c* 0.61, $CHCl_3$); **IR** (neat): ν_{max} = 3311, 2959, 2927, 2112, 1691, 1646, 1527, 1250, 1163, 1037, 1020 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{17}H_{28}N_8NaO_9$ [M + Na]$^+$ *m*/*z* 511.1877; found *m*/*z* 511.1874; HPLC purity: 99.8% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 µm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 40:60, v/v; t_R = 5.08).



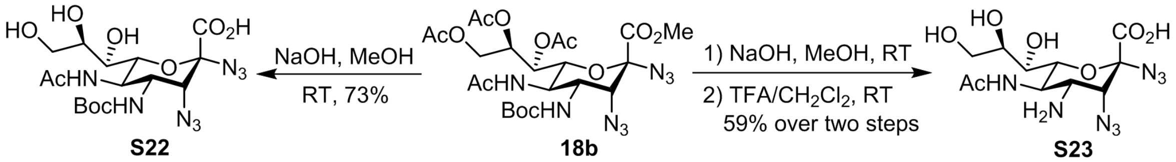
S20

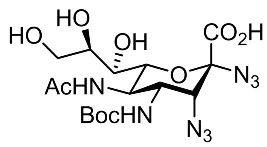
To a stirred solution of **18a** (20.0 mg, 0.032 mmol, 1.0 equiv) in MeOH (1 mL) was added NaOH aq. (1 M in H_2O, 65.1 µL, 0.065 mmol, 2.0 equiv) at ambient temperature. The resultant mixture was allowed to stir for 40 min, then neutralized with Amberlite IR 120 (H^+) resin and filtered. The filtrate was evaporated under reduced pressure to afford the compound **S20** (10.2 mg, 65%), which was pure enough for further characterization. **^{1}H NMR** (400 MHz, CD_3OD) δ 4.25 – 4.07 (m, 4H), 3.83 – 3.76 (m, 2H), 3.67 (dd, J = 12.4, 6.0 Hz, 1H), 3.46 (d, J = 8.8 Hz, 1H), 1.97 (s, 3H), 1.47 (s, 9H); **^{13}C NMR** (150 MHz, CD_3OD) δ 174.2, 170.9, 157.7, 93.9, 80.7, 74.0, 71.7, 70.0, 65.8, 65.0, 52.7, 46.2, 28.7, 22.8; **$[\alpha]_D^{25}$** = −52.1 (c 1.07, $CHCl_3$); **IR** (neat): ν_{max} = 3278, 2956, 2924, 2854, 2113, 1727, 1639, 1534, 1074 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{16}H_{26}N_8NaO_9$ $[M + Na]^+$ m/z 497.1720; found m/z 497.1722; HPLC purity: 98.0% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 µm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 85:15, v/v; t_R = 3.49).



S21

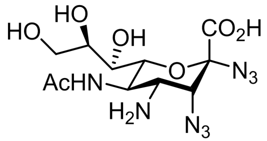
A mixture of **18a** (10.1 mg, 0.016 mmol, 1.0 equiv), NaOH aq. (1 M in H_2O, 49.3 µL, 0.049 mmol, 3.0 equiv) and 1 mL MeOH was stirred for 30 min at room temperature before it was neutralized with Amberlite IR 120 (H^+) resin. After filtration and evaporation, the residue was dissolved in CH_2Cl_2 (1 mL) and trifluoroacetic acid (0.2 mL) was added. The mixture was stirred for 2 h at room temperature and concentrated in *vacuo* to afford a residue. Purification by reverse phase silical gel column chromatography (MeCN/H_2O = 1:9, v/v) yielded product **S21** (3.8 mg, 62%). **^{1}H NMR** (600 MHz, D_2O) δ 4.37 – 4.29 (m, 2H), 4.22 (d, J = 10.2 Hz, 1H), 3.97 (dd, J = 10.8, 3.0 Hz, 1H), 3.93 – 3.88 (m, 1H), 3.86 (dd, J = 12.0, 3.0 Hz, 1H), 3.67 (dd, J = 12.0, 6.0 Hz, 1H), 3.57 (d, J = 9.6 Hz, 1H), 2.06 (s, 3H); **^{13}C NMR** (100 MHz, D_2O) δ 175.0, 169.6, 91.9, 71.6, 69.9, 68.0, 63.3, 61.2, 50.8, 43.8, 22.3; **$[\alpha]_D^{25}$** = −23.6 (c 0.60, MeOH); **IR** (neat): ν_{max} = 3320, 2950, 2839, 2359, 2342, 1685, 1661, 1637, 1013 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{11}H_{18}N_8NaO_7$ $[M + Na]^+$ m/z 397.1196; found m/z 397.1199; HPLC purity: 91.8% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 µm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 90:10, v/v; t_R = 1.49).





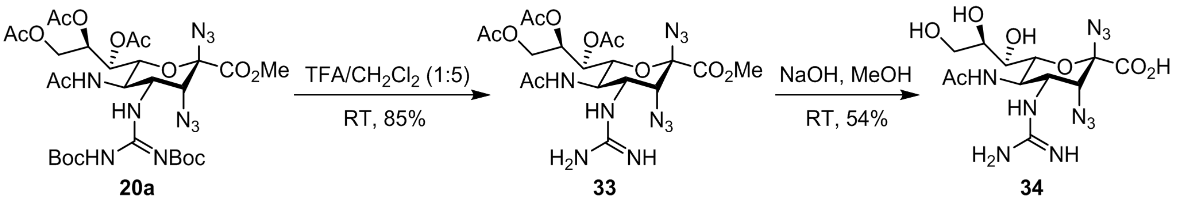
S22

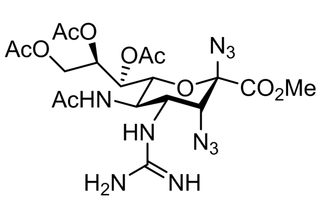
Following the procedure described for synthesis of **S20**, a mixture of **18b** (20.3 mg, 0.033 mmol, 1.0 equiv), NaOH aq. (1 M in H_2O, 99.2 µL, 0.099 mmol, 3.0 equiv) and MeOH (1 mL) was allowed to stir for 40 min at room temperature, neutralized with Amberlite IR 120 (H^+) resin, and filtered. The filtrate was evaporated under reduced pressure to afford product **S22** (11.4 mg, 73%), which was pure enough for further characterization. **^{1}H NMR** (400 MHz, CD_3OD) δ 4.60 (s, 2H), 4.36 (s, 1H), 4.21 – 4.08 (m, 1H), 4.03 (t, J = 10.4 Hz, 1H), 3.93 – 3.76 (m, 2H), 3.69 – 3.54 (m, 2H), 1.96 (s, 3H), 1.46 (s, 8H); **^{13}C NMR** (100 MHz, CD_3OD) δ 175.1, 157.9, 80.9, 76.8, 72.8, 69.9, 65.7, 64.1, 53.5, 46.8, 28.7, 22.7; **$[\alpha]_D^{25}$** = −1.6 (c 0.37, MeOH); **IR** (neat): ν_{max} = 3288, 2927, 2109, 1632, 1534, 1369, 1250, 1161, 1037 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{16}H_{26}N_8NaO_9$ $[M + Na]^+$ m/z 497.1720; found m/z 497.1741; HPLC purity: 97.1% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 µm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 80:20, v/v; t_R = 4.44).



S23

According to the procedure for synthesis of **S21**, compound **18b** (31.2 mg, 0.051 mmol) was used to prepare **S23** (11.2 mg, 59%). **^{1}H NMR** (400 MHz, CD_3OD) δ 4.49 (d, J = 3.2 Hz, 1H), 4.28 (t, J = 10.8 Hz, 1H), 3.91 – 3.72 (m, 4H), 3.71 – 3.57 (m, 2H), 2.03 (s, 3H); **^{13}C NMR** (100 MHz, CD_3OD) δ 175.2, 170.3, 76.1, 72.8, 69.5, 64.3, 62.5, 53.4, 45.3, 23.0; **$[\alpha]_D^{25}$** = +9.5 (c 0.77, MeOH); **IR** (neat): ν_{max} = 3270, 2930, 2121, 1632, 1553, 1375, 1305, 1248, 1037 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{11}H_{18}N_8NaO_7$ $[M + Na]^+$ m/z 397.1196; found m/z 397.1183; HPLC purity: 98.1% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX 300SB-C8, 5 µm, 4.6 × 150 mm; Detector: Waters 2424 ELSD; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 100:0, v/v; t_R = 2.18).

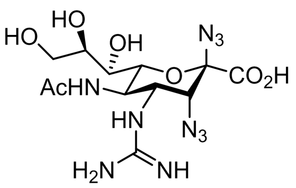




33

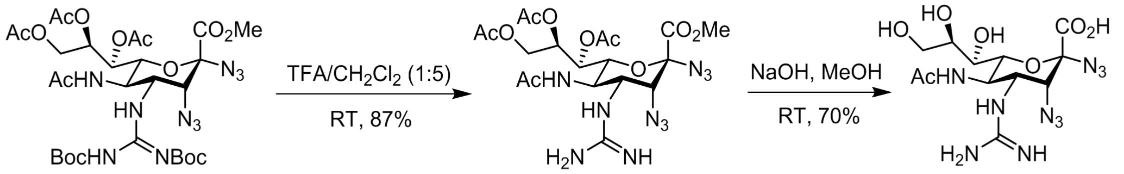
To a solution of **20a** (68.0 mg, 0.090 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) was added trifluoroacetic acid (0.4 mL) at room temperature. The resultant mixture was allowed to stir overnight and then concentrated under *vacuum*. The residue was purified through flash column chromatography (CH_2Cl_2/MeOH = 20:1, v/v) to yield **33** (42.5 mg, 85%). **TLC**: (CH_2Cl_2/MeOH = 8:1, v/v), R_f = 0.55; **^{1}H NMR** (400

MHz, CD_3OD) δ 5.44 (dd, J = 7.2, 2.0 Hz, 1H), 5.31 – 5.25 (m, 1H), 4.52 (dd, J = 12.0, 2.4 Hz, 1H), 4.32 (d, J = 3.2 Hz, 1H), 4.25 (d, J = 10.4 Hz, 1H), 4.21 – 4.14 (m, 1H), 4.11 (dd, J = 12.8, 5.6 Hz, 2H), 3.97 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.91 (s, 3H); **^{13}C NMR** (150 MHz, CD_3OD) δ 173.9, 172.4, 171.5, 171.2, 166.2, 159.1, 92.2, 73.0, 71.0, 68.5, 64.4, 62.9, 54.2, 53.4, 46.3, 22.7, 21.0, 20.6; **$[\alpha]_D^{25}$** = −7.8 (c 1.00, $CHCl_3$); **IR** (neat): ν_{max} = 3338, 2118, 1745,1667, 1372, 1203, 1134, 1046, 734 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{19}H_{29}N_{10}O_{10}$ $[M + H]^+$ m/z 557.2068; found m/z 557.2086; HPLC purity: 99.3% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 μm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 30:70, v/v; t_R = 1.32).

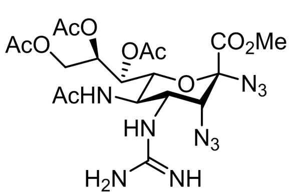


34

A mixture of compound **33** (8.3 mg, 0.015 mmol, 1.0 equiv), NaOH aq. (1 M in H_2O, 44.8 μL, 0.045 mmol, 3.0 equiv) and MeOH (1 mL) was allowed to stir for 1 h at room temperature, then neutralized with Amberlite IR 120 (H^+) resin and filtered. After removal of solvent from the filtrate, the residue was purified by reverse phase silical gel column chromatography (MeOH/H_2O = 1:9, v/v) to give **34** (3.4 mg, 54%). **^{1}H NMR** (600 MHz, CD_3OD/D_2O) δ 4.30 – 4.04 (m, 4H), 3.92 – 3.79 (m, 2H), 3.65 (dd, J = 12.0, 6.0 Hz, 1H), 3.55 (d, J = 9.6 Hz, 1H), 2.00 (s, 3H); **^{13}C NMR** (150 MHz, CD_3OD) δ 173.9, 158.9, 73.3, 71.7, 69.9, 65.5, 64.9, 53.9, 47.3, 45.4, 22.8; **$[\alpha]_D^{25}$** = −63.8 (c 0.13, MeOH); **IR** (neat): ν_{max} = 3195, 2923, 2854, 2113, 1633, 1612, 1374, 1064, 1038, 1019, 610 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{12}H_{21}N_{10}O_7$ $[M + H]^+$ m/z 417.1595; found m/z 417.1581; HPLC purity: 97.4% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 μm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 80:20, v/v; t_R = 1.51).

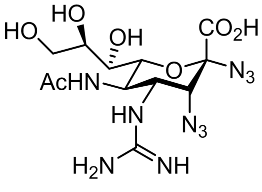


20b **S24** **S25**



S24

According to the procedure described for the synthesis of **33**, a mixture of **20b** (58.2 mg, 0.077 mmol) and trifluoroacetic acid (0.2 mL) in CH_2Cl_2 (1 mL) was stirred for 8 h. The residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH = 20:1, v/v) to afford **S24** (37.2 mg, 87%). **TLC**: (CH_2Cl_2/MeOH = 8:1, v/v), R_f = 0.50; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (brs, 2H), 7.01 (m, 3H), 5.47 – 5.26 (m, 2H), 4.28 (dd, J = 12.8, 2.8 Hz, 1H), 4.23 – 4.05 (m, 4H), 3.91 (s, 3H), 3.90 – 3.85 (m, 1H), 2.12 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.97 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 173.0, 170.8, 167.0, 169.7, 165.8, 157.7, 90.5, 73.6, 68.2, 67.2, 61.7, 53.9, 51.8, 45.4, 29.7, 23.0, 20.8, 20.7, 20.4; **[α]**$_D^{25}$ = +20.7 (*c* 0.58, MeOH); **IR** (neat): ν_{max} = 3339, 2962, 2116, 1746, 1667, 1610, 1372, 1203, 1179, 1135, 1043, 721 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{19}H_{29}N_{10}O_{10}$ $[M + H]^+$ *m/z* 557.2068; found *m/z* 557.2080; HPLC purity: 97.6% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 μm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 30:70, v/v; t_R = 1.35).

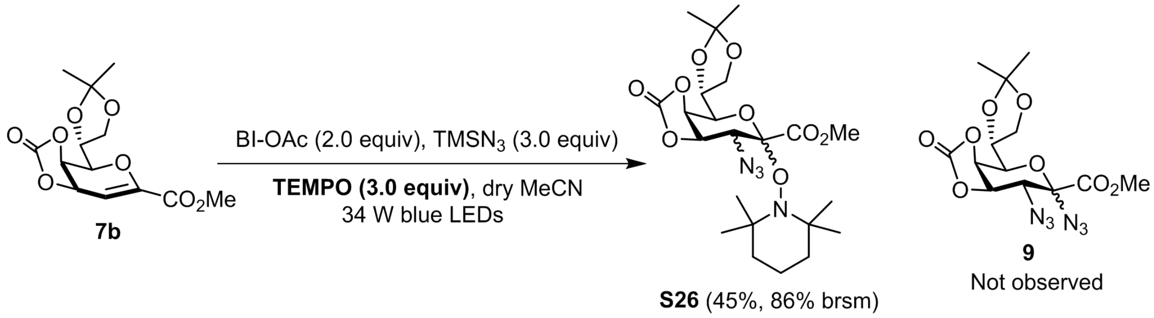


S25

Following the procedure for the preparation of **34**, **S24** (27.3 mg, 0.049 mmol, 1.0 equiv), NaOH aq. (1 M in H_2O, 147 μL, 0.147 mmol, 3.0 equiv) and MeOH (1 mL) were used for the synthesis of **S25** (14.2 mg, 70%) as a white amorphous powder after purification by reverse phase silica gel column chromatography (MeOH/H_2O = 1:9, v/v). **^{1}H NMR** (400 MHz, CD_3OD) *δ* 4.54 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.30 (d, *J* = 3.6 Hz, 1H), 4.21 (t, *J* = 10.4 Hz, 1H), 3.91 – 3.78 (m, 2H), 3.75 – 3.63 (m, 3H), 1.97 (s, 3H); **^{13}C NMR** (100 MHz, CD_3OD) *δ* 174.6, 171.0, 158.7, 93.3, 76.3, 73.5, 69.6, 65.2, 64.5, 54.2, 47.5, 22.7; **[α]**$_D^{25}$ = −9.9 (*c* 0.43, MeOH); **IR** (neat): ν_{max} = 3332, 2944, 2834, 2113, 1634, 1374, 1020 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{12}H_{20}N_{10}NaO_7$ $[M + Na]^+$ *m/z* 439.1414; found *m/z* 439.1487; HPLC purity: 95.3% (Flow rate: 1.0 mL/min; Column: Agilent ZORBAX SB-C18, 5 μm, 4.6 × 150 mm; Detector: Alltech ELSD 2000ES; Temperature: 25 °C; Mobile phase: H_2O/MeOH = 90:10, v/v; t_R = 3.71).

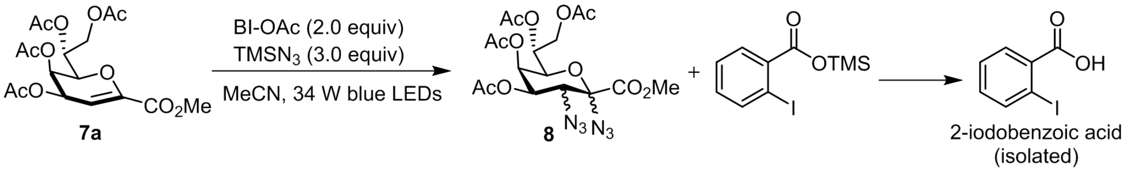
7. Mechanistic Investigations

7.1 Radical Trapping Experiment with TEMPO



To a solution of **7b** (40.0 mg, 0.133 mmol, 1.0 equiv), BI-OAc (81.6 mg, 0.267 mmol, 2.0 equiv) and TEMPO (62.5 mg, 0.400 mmol, 3.0 equiv) in dry MeCN (1 mL) was added TMSN$_3$ (52.6 µL, 0.400 mmol, 3.0 equiv) under an argon atmosphere.The mixture was stirred for 3 h under irradiation of 34 W blue LEDs. Saturated aqueous KHCO$_3$ was added and the mixture was stirred vigorously at room temperature for 5 min. After extraction of the resulting mixture with EtOAc for three times, the organic layers were combined, dried, and concentrated. Purification of the crude residue by silica gel column chromatography (petroleum ether/acetone = 20:1, v/v) afforded **S26** (30.0 mg, 45%, 86% brsm) as a white amorphous powder, along with recovery of **7b** (19.1 mg). Note that **S26** was a mixture of two isomers **S26a** and **S26b**. **S26a**: **TLC**: (petroleum ether/EtOAc = 5:1, v/v), R$_f$ = 0.38; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 4.99 (s, 2 H), 4.51 (t, J = 1.2 Hz, 1H), 4.33 (m, 1H), 4.20 – 4.13 (m, 2H), 3.82 (s, 3H), 3.79 (d, J = 9.2 Hz, 1H), 1.54 – 1.23 (m, 12H), 1.21 (s, 3H), 1.17 (s, 3H), 1.14 (s, 3H), 1.12 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 165.4, 153.0, 110.0, 103.6, 73.1, 72.5, 71.4, 71.0, 67.1, 62.1, 61.5, 59.8, 51.8, 41.2, 40.6, 33.9, 33.4, 26.9, 25.0, 21.7, 21.6, 16.8; **$[\alpha]_D^{25}$** = +52.5 (*c* 0.19, CHCl$_3$); **IR** (neat): $\nu_{\max}$ = 2943, 2936, 2123, 1817, 1258, 1179, 1075 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{22}H_{34}N_4NaO_9$ [M + Na]$^+$ *m*/*z* 521.2223; found *m*/*z* 521.2217. **S26b**: **TLC**: (petroleum ether/EtOAc = 5:1, v/v), R$_f$ = 0.32; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 5.16 (d, J = 4.0 Hz, 1H), 4.95 (dd, J = 8.4, 4.0 Hz, 1H), 4.88 (dd, J = 8.4, 1.6 Hz, 1H), 4.34 – 4.27 (m, 1H), 4.26 – 4.16 (m, 2H), 4.06 (dd, J = 8.8, 4.8 Hz, 1H), 3.76 (s, 3H), 1.62 – 1.34 (m, 12H), 1.26 (s, 3H), 1.24 (s, 3H), 1.20 (s, 3H), 1.18 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 165.9, 152.7, 109.8, 100.8, 72.6, 72.6, 72.3, 71.5, 67.7, 62.1, 61.1, 59.8, 52.4, 41.4, 40.7, 33.7, 33.7, 26.8, 24.9, 21.2, 20.8, 16.6; **$[\alpha]_D^{25}$** = +45.5 (*c* 0.09, CHCl$_3$); **IR** (neat): $\nu_{\max}$ = 2923, 2853, 2119, 1821, 1752, 1370, 1069, 1031 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{22}H_{34}N_4NaO_9$ [M + Na]$^+$ *m*/*z* 521.2223; found *m*/*z* 521.2216.

7.2 Isolation of 2-Iodobenzoic Acid



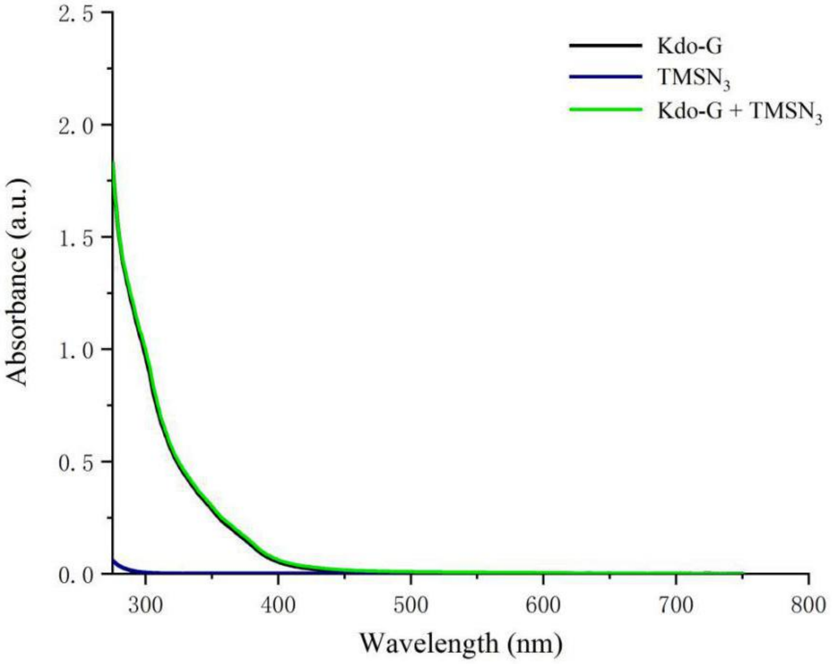
To a solution of **7a** (30.1 mg, 0.075 mmol, 1.0 equiv) and BI-OAc (45.8 mg, 0.15 mmol, 2.0 equiv) in 0.75 mL dry MeCN was added $TMSN_3$ (29.5 µL, 0.22 mmol, 3.0 equiv) under an argon atmosphere. The reaction mixture was stirred under irradiation of 34 W blue LEDs for 2 h. Then saturated $NaHCO_3$ solution was added to quench the reaction. The mixture was stirred for additional 5 min before being acidified with 1M HCl. EtOAc was added to dilute the reaction. After separation of the two layers, the aqueous phase was extracted with EtOAc for three times. The combined organic phase was washed with brine, dried over Na_2SO_4, and evaporated to dryness. 2-Iodobenzoic acid was isolated from the residue through preperative TLC (petroleum ether/EtOAc = 2:1, v/v), which could be confirmed by NMR and MS, as well as by comparison with an authentic sample.

7.3 UV/Vis Absorption

No visible color change was observed when mixing the reaction components between each other (Figure S1).

Figure S1. Appearance of the reaction components and their corresponding mixtures

UV/Vis absorption spectra between substrate **7a** (Kdo-G, 0.04 mmol) and azide donor $TMSN_3$ (0.04 mmol) or oxidant BI-OAc (0.04 mmol) in $CHCl_3$ (2 mL) were recorded in 1 cm path quartz cuvettes using a Quawell scientific Q6000+ micro volume spectrophotometer. As shown in Figure S2, no bathochromic shift was observed.



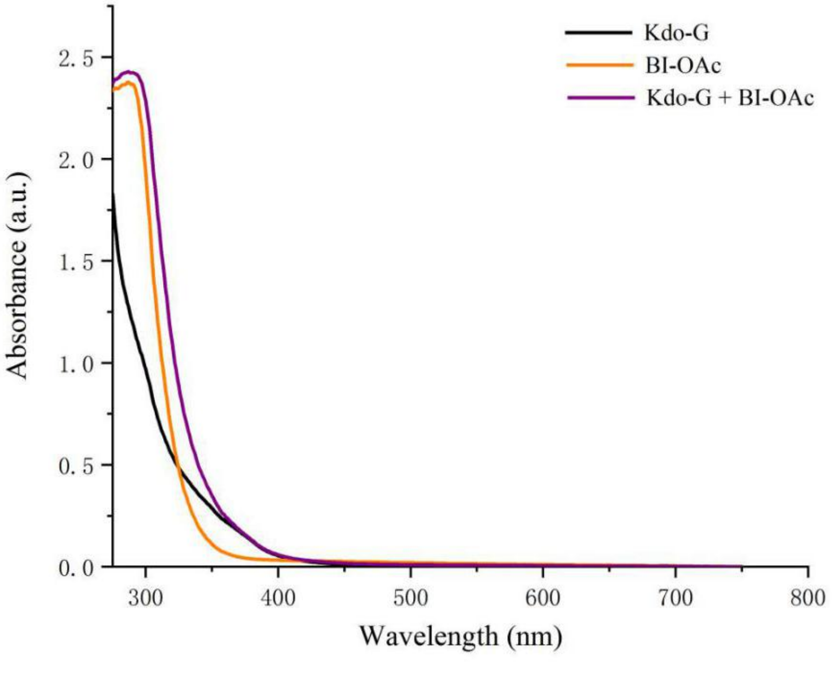


Figure S2. UV/Vis absorption spectra between Kdo-G (**7a**) and $TMSN_3$ or BI-OAc

UV/Vis absorption spectra between oxidant BI-OAc (0.04 mmol) and azide donor $TMSN_3$ (0.04 mmol) in $CHCl_3$ (2 mL) were recorded in 1 cm path quartz cuvettes using a Quawell scientific Q6000+ micro volume spectrophotometer. As shown in Figure S3, no bathochromic shift was observed.

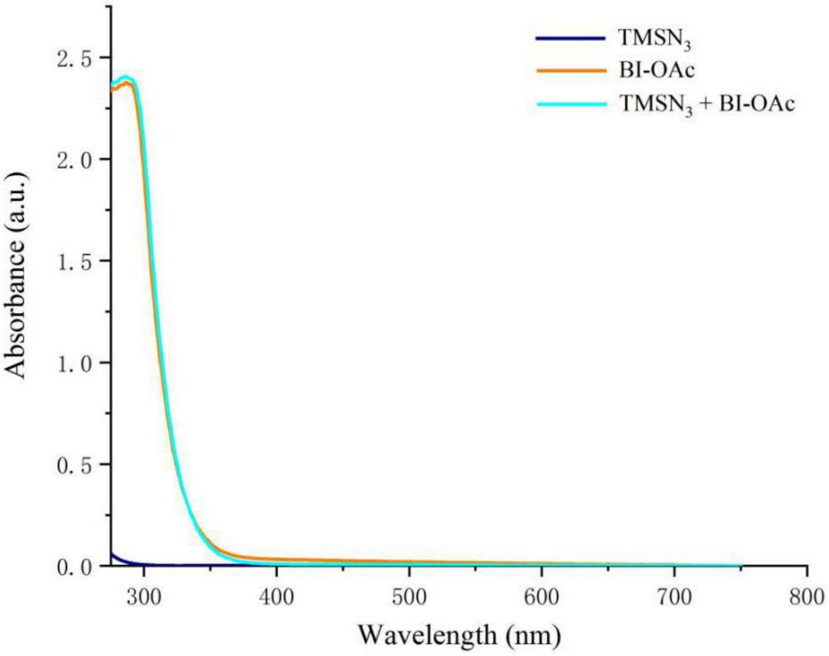


Figure S3. UV/Vis absorption spectra between TMSN$_3$ and BI-OAc

UV/Vis absorption spectra between substrate **7a** (Kdo-G, 0.04 mmol) and oxidant BI-N$_3$ (0.04 mmol) in 2 mL CHCl$_3$ were recorded in 1 cm path quartz cuvettes using a Quawell scientific Q6000+ micro volume spectrophotometer. As shown in Figure S4, no bathochromic shift was observed.

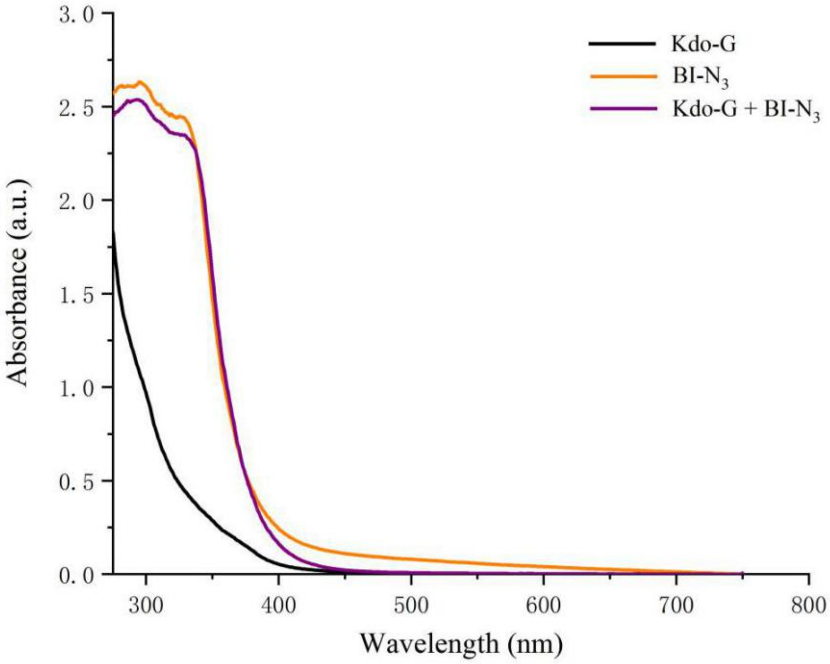


Figure S4. UV/Vis absorption spectra between Kdo-G (**7a**) and BI-N$_3$

UV/Vis absorption spectra between BI-N_3 (0.04 mmol) and azide donor $TMSN_3$ (0.04 mmol) in 2 mL $CHCl_3$ were recorded in 1 cm path quartz cuvettes using a Quawell scientific Q6000+ micro volume spectrophotometer. As shown in Figure S5, no bathochromic shift was observed.

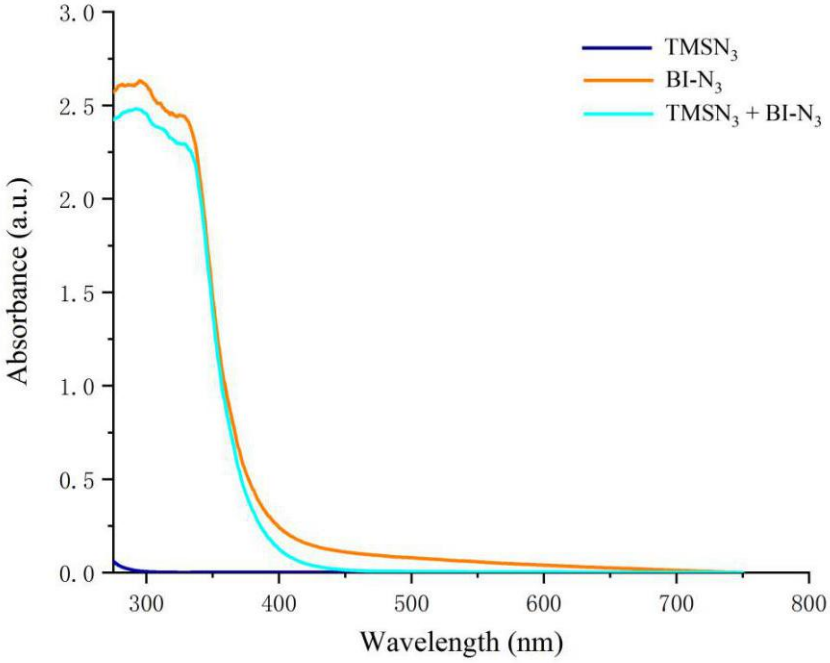
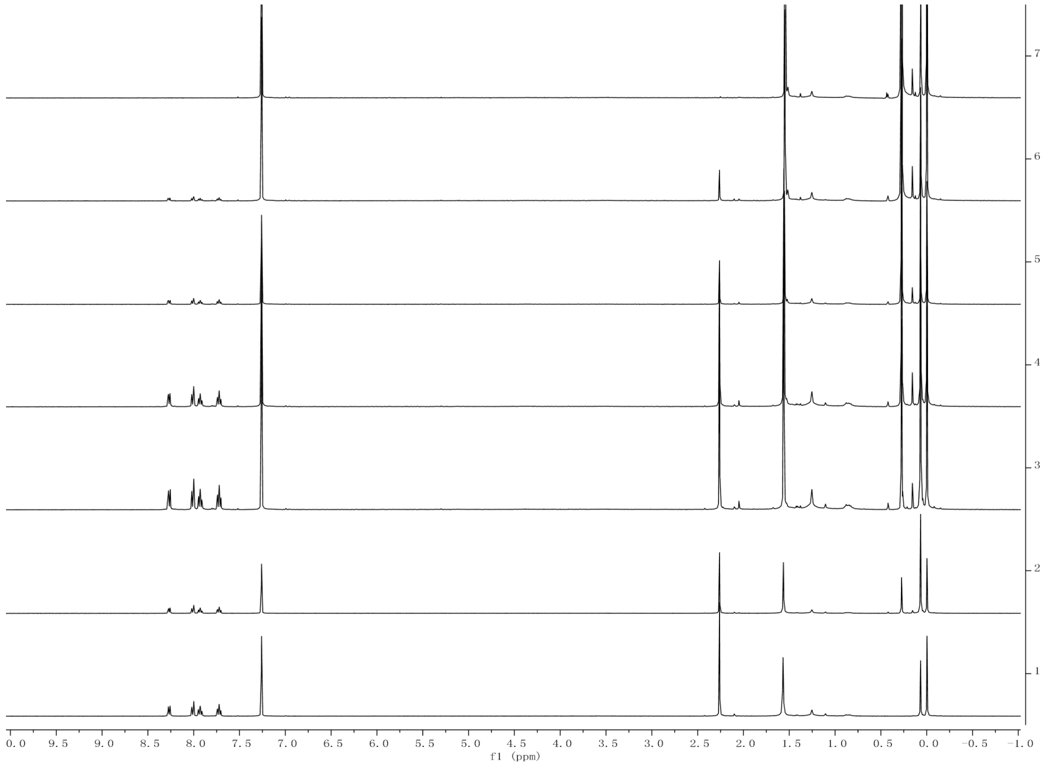
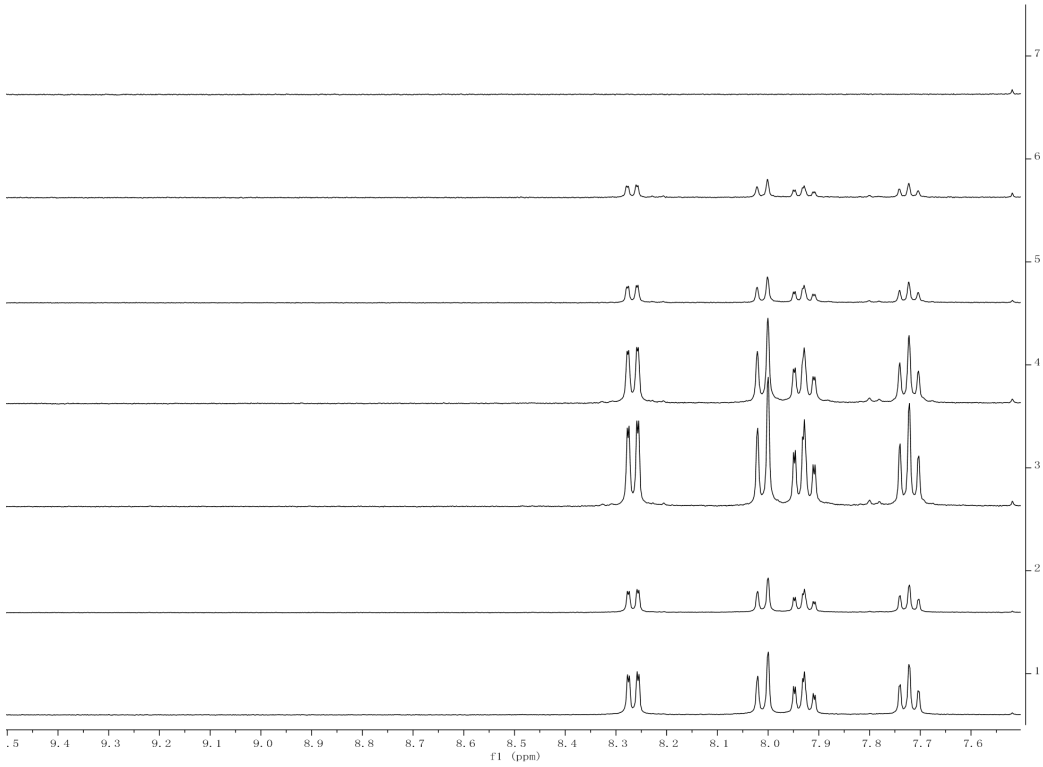


Figure S5. UV/Vis absorption spectra between $TMSN_3$ and BI-N_3

7.4 NMR Titration Experiments

^{1}H NMR experiments of solutions containing different ratios of oxidant (BI-OAc) and azide donor ($TMSN_3$) (covering the ratio 0%, 10%, 20%, 40%, 60%, 80% and 100% $TMSN_3$, from 1 to 7 in Figure S6) were performed, with constant concentration of the two components (0.01 M in $CDCl_3$). No resonance signal shift was observed in BI-OAc upon addition of $TMSN_3$.





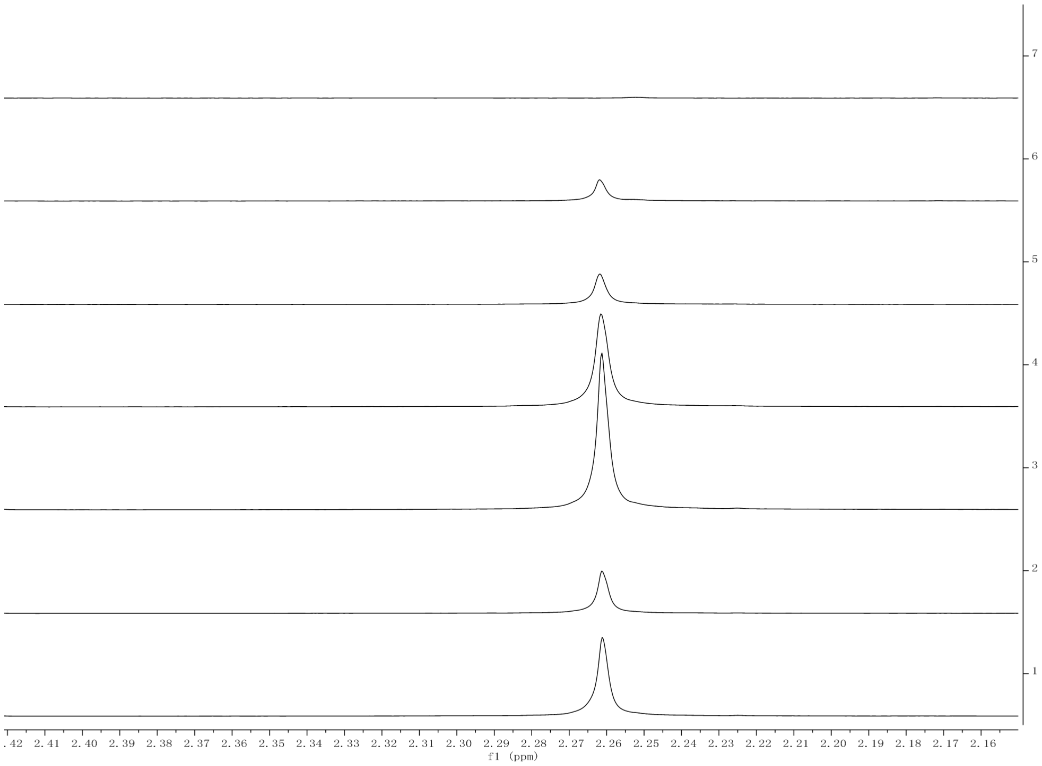
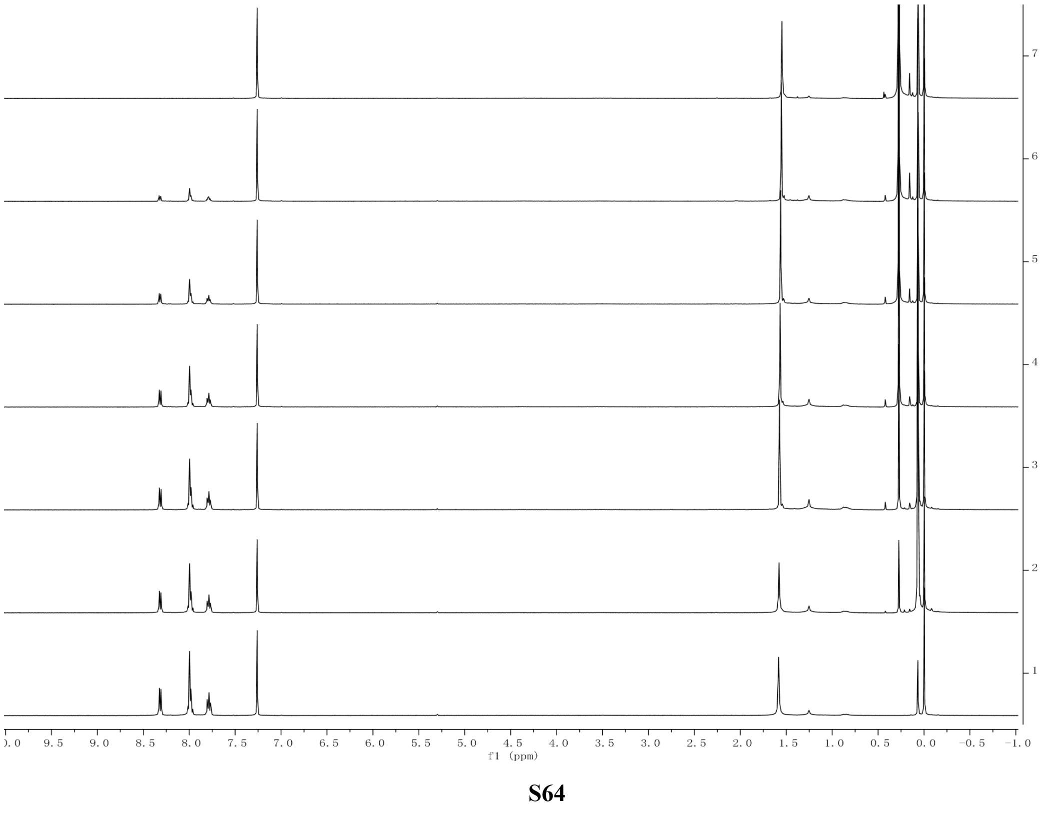


Figure S6. ^{1}H NMR titration between oxidant (BI-OAc) and $TMSN_3$

^{1}H NMR experiments of solutions containing different ratios of BI-N_3 and azide donor $TMSN_3$ (covering the ratio 0%, 10%, 20%, 40%, 60%, 80% and 100% $TMSN_3$, from 1 to 7 in Figure S7) were performed, with constant concentration of the two components (0.02 M in $CDCl_3$). No resonance signal shift was observed in BI-N_3 upon addition of $TMSN_3$.



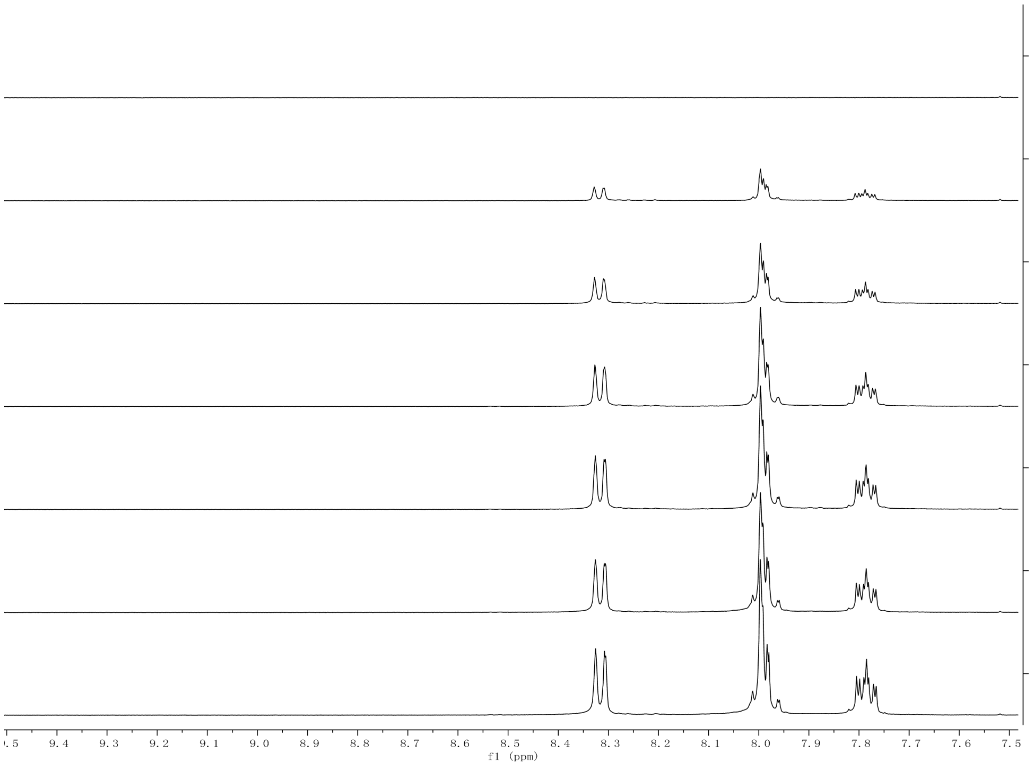


Figure S7. ^{1}H NMR titration between BI-N_3 and $TMSN_3$

8. Antiviral Activities

Materials and Methods

Cells and Viruses. BHK and H1 Hela cells were obtained from National Infrastructure of Cell Line Resource, China. Cells were cultured in Dulbecco's modified Eagle's medium (DMEM, Gibco) supplemented with 10% fetal bovine serum (FBS, Gibco) and 100 U/ml penicillin/streptomycin at 37 °C in 5% CO_2. ZIKV (SMGC-1 strain) was produced by infecting Vero cells one day post-seeding at a multiplicity of infection (MOI) of 0.001. The virus titers were determined by 50% tissue culture infectious dose ($TCID_{50}$) assay. Human rhinovirus 1059 strain belongs to Enterovirus Rhinovirus B and genotype 14 (ATCC, VR-284), and the virus stocks were propagated in H1 Hela cells according standard protocol.

***In Vitro* Cytopathic Effect (CPE) Assay.** BHK or H1 Hela cells were used for antiviral assays of ZIKV or HRV, respectively. Briefly, 5×10^3 cells were seeded in 96-well plates. At 24 hours post infection (hpi), cells were infected with 100 $TCID_{50}$ of virus in the presence of gradient dilutions of indicated drugs and cultured for 8 days for ZIKV, and 3 days for HRV. Then, the protection of CPE was measured with CellTiter-Glo® Luminescent Cell Viability Assay (Promega, USA) kit according to the manufacturer's instructions. Values for the vitro efficacy were calculated using OriginPro 8.0 Software.

Cytotoxicity Assay. The cytotoxicity was evaluated using a CellTiter-Glo® Luminescent Cell

Viability Assay (Promega, USA) kit following the manufacturer's instructions. Briefly, 5×10^3 cells were seeded in 96-well plates and incubated with gradient dilutions of drugs for the 8 days or 3 days for BHK and H1 Hela cells, respectively. Values for the cytotoxicity were calculated using the OriginPro 8.0 Software.

Table S7. Antiviral Activity

compd.	anti-ZIKV (BHK)			anti-HRV (H1 Hela)		
	IC$_{50}$ (μM)[a]	CC$_{50}$ (μM)[b]	SI[c]	IC$_{50}$ (μM)[a]	CC$_{50}$ (μM)[b]	SI[c]
NITD008[d]	0.87	>20	>22.99			
Rupintrivir[d]				0.08	>10	>125
8a	>200	--	--	95.24	>200	>2.10
8b	166.11	--	--	59.81	--	--
8c	>200	--	--	178.09	>200	>1.12
8d	>200	--	--	171.99	>200	>1.16
9a	>200	--	--	178.95	>200	>1.12
9b	>200	--	--	>200	--	--
12a	>200	--	--	71.1	199.79	2.81
14a	>200	--	--	81.04	>200	>2.47
14b	>200	--	--	68.77	--	--
14c	>200	--	--	>200	--	--
14d	>200	--	--	>200	--	--
15a	31.05	>200	>6.44	>200	--	--
15b	8.67	>200	>23.07	>200	--	--
15c	9.24	>200	>21.65	>200	--	--
15d	9.20	>200	>21.74	>200	--	--
16a	1.41	7.68	5.45	4.58	9.25	2.02
16b	1.90	>200	>105.26	18.89	49.11	2.60
17a	5.50	21.89	3.98	0.93	6.68	7.18
17b	7.30	20.29	2.78	2.05	5.74	2.80
18a	>200	--	--	>200	--	--
18b	>200	--	--	193.78	>200	>1.03
19a	>200	--	--	>200	--	--
19b	>200	--	--	59.38	>200	>3.37
20a	69.63	128.12	1.84	74.56	>200	>2.68
20b	165.03	>200	>1.21	104.97	>200	>1.91
21	44.95	>200	>4.45	19.16	200.03	10.44
22	177.50	>200	>1.13	>200	--	--
23	140.65	>200	>1.42	67.39	>200	>2.97
24	108.41	>200	>1.84	>200	--	--

25	15.02	193.31	12.87	>200	--	--
26	>200	--	--	83.06	>200	>2.41
27	69.32	--	--	>200	--	--
28	>200	--	--	>200	--	--
30	22.73	29.32	1.29	1.87	64.70	34.60
31	25.05	67.89	2.71	5.39	41.02	7.61
32	>200	--	--	113.99	>200	>1.75
33	105.56	>200	>1.89	>200	--	--
34	>200	--	--	70.49	>200	>2.84
S12	192.98	>200	>1.04	>200	--	--
S14	>200	--	--	>200	--	--
S15	9.64	>200	>20.75	>200	--	--
S16	>200	--	--	>200	--	--
S17	74.64	>200	>2.68	12.53	>200	>15.96
S18	>200	--	--	181.77	>200	>1.10
S19	>200	--	--	>200	--	--
S20	199.68	>200	>1.00	98.73	>200	>2.03
S21	185.68	>200	>1.08	82.09	>200	>2.44
S22	156.62	>200	>1.28	185.29	>200	>1.08
S23	154.46	>200	>1.29	18.89	200.05	10.59
S24	>200	--	--	176.55	>200	>1.13
S25	>200	--	--	>200	--	--

[a]IC_{50}: the concentration of test compounds that reduced the activity by 50% of the untreated (control) cell cultures. Each value was calculated from duplicate assays. [b]CC_{50}: the concentration of test compounds that reduced cell viability to 50% of the untreated (control) cell cultures. Each value was calculated from duplicate assays. [c]SI: selectivity index, the ratio of CC_{50} to IC_{50} (CC_{50}/IC_{50}). [d]NITD008[8] and rupintrivir[9] were used as positive controls, respectively.

9. References

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10.X-Ray Crystallographic Data

X-ray Crystallographic Data for Compound 8c: CCDC 1975133 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

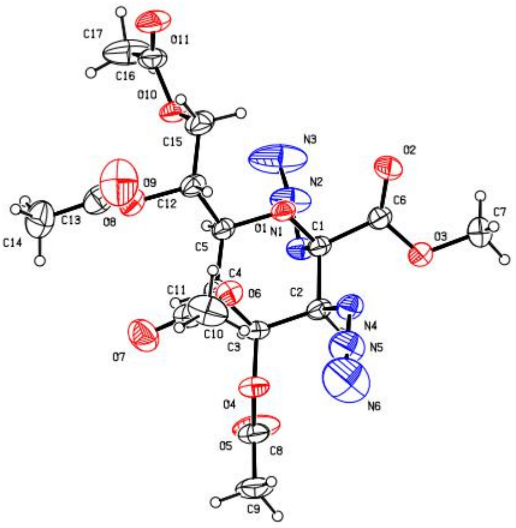


Table S8. Crystal data and structure refinement for 190419_s1_hh_yd0417a.

Identification code	190419_s1_hh_yd0417a
Empirical formula	$C_{17}H_{22}N_6O_{11}$
Formula weight	486.40
Temperature/K	293.15
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.2129(4)
b/Å	40.7685(17)
c/Å	12.8563(5)
α/°	90
β/°	90.320(3)

γ/°	90
Volume/Å^3	4828.7(3)
Z	8
ρ_{calc}g/cm^3	1.338
μ/mm^{-1}	0.113
F(000)	2032.0
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.81 to 52.744
Index ranges	$-11 \leq h \leq 11, -50 \leq k \leq 49, -15 \leq l \leq 16$
Reflections collected	35580
Independent reflections	16488 [R_{int} = 0.0264, R_{sigma} = 0.0466]
Data/restraints/parameters	16488/1/1253
Goodness-of-fit on F^2	1.015
Final R indexes [I>=2σ (I)]	R_1 = 0.0499, wR_2 = 0.1143
Final R indexes [all data]	R_1 = 0.0741, wR_2 = 0.1318
Largest diff. peak/hole / e Å^{-3}	0.28/-0.24
Flack parameter	0.1(4)

X-ray Crystallographic Data for Compound 8d: CCDC 1975134 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

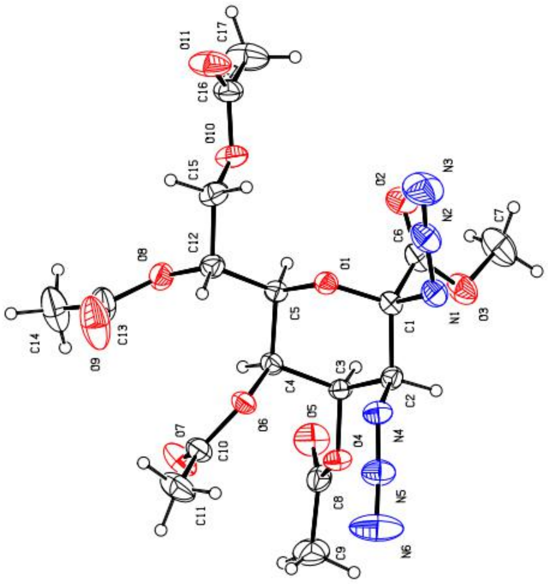


Table S9. Crystal data and structure refinement for 190419_s1_hh_yd0417b.

Identification code	190419_s2_hh_yd0417b
Empirical formula	$C_{17}H_{22}N_6O_{11}$

Formula weight	486.40
Temperature/K	293.15
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.7778(5)
b/Å	13.2995(10)
c/Å	11.4128(6)
α/°	90
β/°	91.458(5)
γ/°	90
Volume/Å^3	1180.18(13)
Z	2
ρ_{calc}g/cm^3	1.369
μ/mm^{-1}	0.116
F(000)	508.0
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.07 to 52.738
Index ranges	$-9 \leq h \leq 9$, $-16 \leq k \leq 9$, $-14 \leq l \leq 12$
Reflections collected	5262
Independent reflections	3233 [R_{int} = 0.0190, R_{sigma} = 0.0362]
Data/restraints/parameters	3233/1/312
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0410, wR_2 = 0.0881
Final R indexes [all data]	R_1 = 0.0617, wR_2 = 0.0994
Largest diff. peak/hole / e Å^{-3}	0.19/-0.18
Flack parameter	0.3(7)

X-ray Crystallographic Data for Compound 9a: CCDC 1975130 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

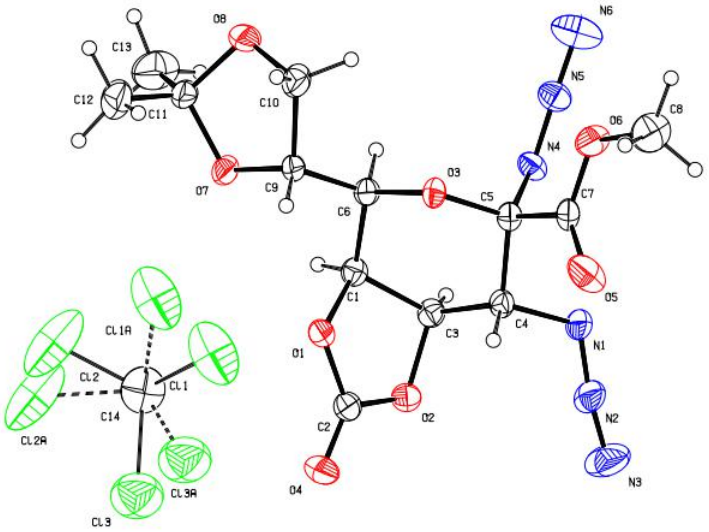


Table S10. Crystal data and structure refinement for 190226_s3_yd_1.

Identification code	190226_s3_yd_1
Empirical formula	$C_{14}H_{16}Cl_3N_6O_8$
Formula weight	502.68
Temperature/K	293.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.6304(6)
b/Å	10.8741(9)
c/Å	22.9325(14)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2152.2(3)
Z	4
ρ_{calc}g/cm^3	1.551
μ/mm^{-1}	0.480
F(000)	1028.0
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.026 to 52.728
Index ranges	$-10 \leq h \leq 10$, $-8 \leq k \leq 13$, $-28 \leq l \leq 28$
Reflections collected	9826
Independent reflections	4407 [R_{int} = 0.0216, R_{sigma} = 0.0399]
Data/restraints/parameters	4407/0/293
Goodness-of-fit on F^2	1.030

Final R indexes [I>=2σ (I)]	$R_1 = 0.0594$, $wR_2 = 0.1420$
Final R indexes [all data]	$R_1 = 0.0806$, $wR_2 = 0.1562$
Largest diff. peak/hole / e Å^{-3}	0.31/-0.43
Flack parameter	0.04(3)

X-ray Crystallographic Data for Compound 9b: CCDC 1975131 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

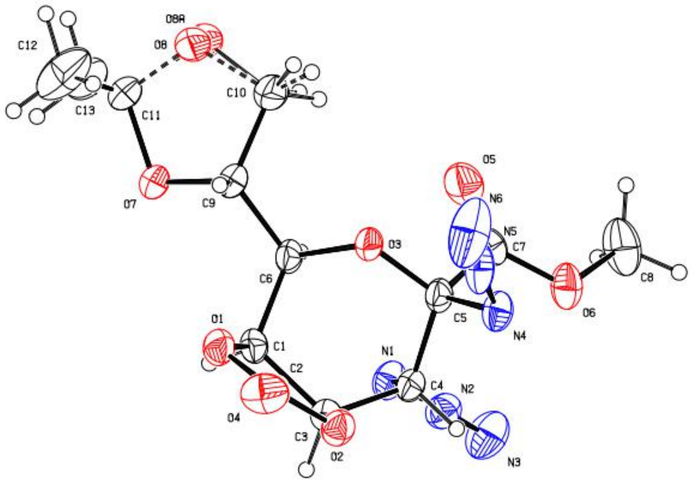


Table S11. Crystal data and structure refinement for 190226_s4_yd_2.

Identification code	190226_s4_yd_2
Empirical formula	$C_{13}H_{16}N_6O_8$
Formula weight	384.32
Temperature/K	293.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.2784(7)
b/Å	9.2019(10)
c/Å	26.166(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1752.4(3)
Z	4
ρ_{calc}g/cm^3	1.457
μ/mm^{-1}	0.123

F(000)	800.0
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.228 to 52.732
Index ranges	$-9 \leq h \leq 8$, $-11 \leq k \leq 10$, $-23 \leq l \leq 32$
Reflections collected	6084
Independent reflections	3278 [R_{int} = 0.0229, R_{sigma} = 0.0467]
Data/restraints/parameters	3278/0/251
Goodness-of-fit on F^2	1.018
Final R indexes [I>=2σ (I)]	R_1 = 0.0461, wR_2 = 0.0845
Final R indexes [all data]	R_1 = 0.0687, wR_2 = 0.0950
Largest diff. peak/hole / e Å^{-3}	0.14/-0.14
Flack parameter	0.2(10)

X-ray Crystallographic Data for Compound 14c: CCDC 1975132 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

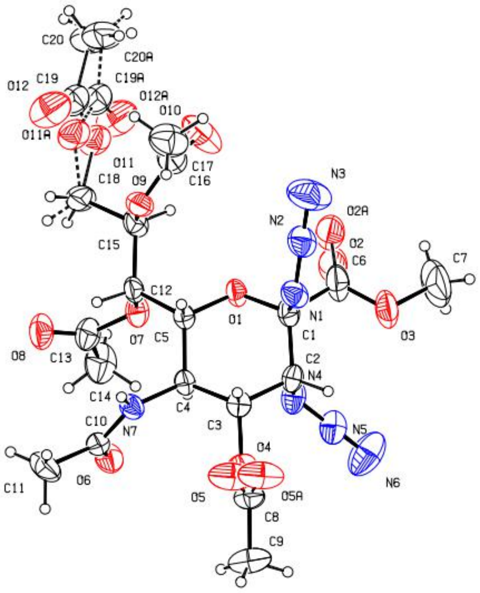


Table S12. Crystal data and structure refinement for 190321_s2_hh.

Identification code	190321_s2_hh
Empirical formula	$C_{20}H_{27}N_7O_{12}$
Formula weight	557.48
Temperature/K	293.15
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.6273(12)
b/Å	8.8714(10)
c/Å	16.549(2)
α/°	90
β/°	101.469(11)
γ/°	90
Volume/Å^3	1385.2(3)
Z	2
ρ_{calc}g/cm^3	1.337
μ/mm^{-1}	0.112
F(000)	584.0
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.938 to 52.74
Index ranges	$-11 \leq h \leq 12, -11 \leq k \leq 7, -20 \leq l \leq 13$
Reflections collected	5951
Independent reflections	4170 [R_{int} = 0.0233, R_{sigma} = 0.0662]
Data/restraints/parameters	4170/5/381
Goodness-of-fit on F^2	0.965
Final R indexes [I>=2σ (I)]	R_1 = 0.0484, wR_2 = 0.0959
Final R indexes [all data]	R_1 = 0.1013, wR_2 = 0.1171
Largest diff. peak/hole / e Å^{-3}	0.23/-0.16
Flack parameter	0.8(10)

X-ray Crystallographic Data for Compound 14d: CCDC 1975126 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

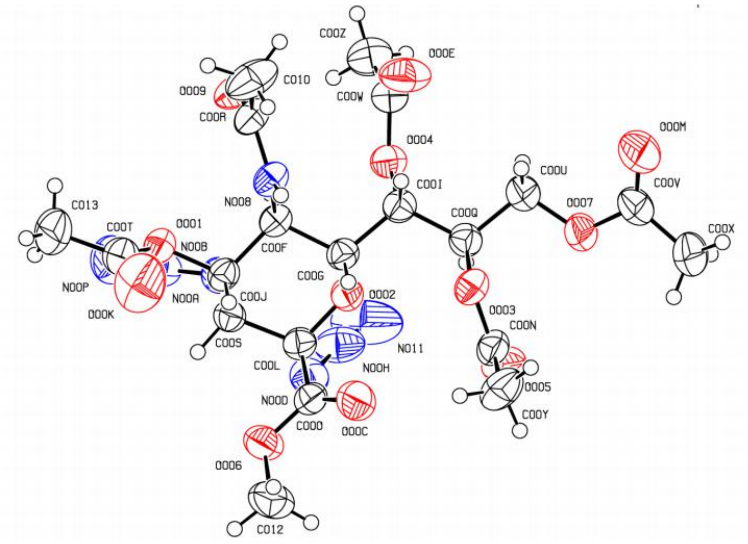


Table S13. Crystal data and structure refinement for qy-hh181126e.

Identification code	qy-hh181126e
Empirical formula	$C_{20}H_{27}N_7O_{12}$
Formula weight	557.48
Temperature/K	291.6(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.29096(14)
b/Å	14.5006(2)
c/Å	20.3184(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2737.38(7)
Z	4
ρ_{calc}g/cm^3	1.353
μ/mm^{-1}	0.975
F(000)	1168.0
Crystal size/mm^3	0.7 × 0.4 × 0.3
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.49 to 145.916
Index ranges	$-11 \leq h \leq 7, -17 \leq k \leq 16, -23 \leq l \leq 24$
Reflections collected	15433
Independent reflections	5368 [R_{int} = 0.0320, R_{sigma} = 0.0264]
Data/restraints/parameters	5368/0/358
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0540, wR_2 = 0.1430

Final R indexes [all data]	$R_1 = 0.0574$, $wR_2 = 0.1492$
Largest diff. peak/hole / e Å^{-3}	0.24/-0.32
Flack parameter	-0.10(10)

X-ray Crystallographic Data for Compound 15b: CCDC 1975127 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

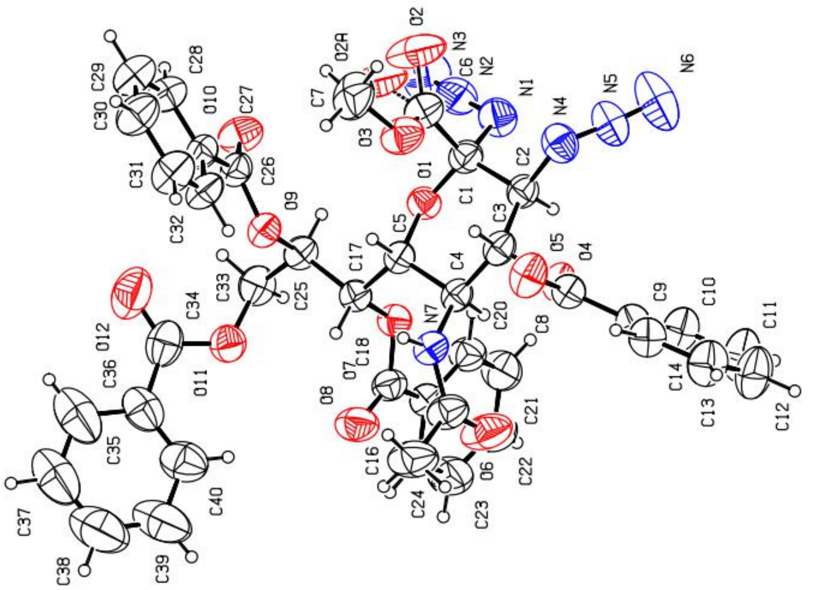


Table S14. Crystal data and structure refinement for 190510_s5_hh_0405b.

Identification code	190510_s5_hh_0405b
Empirical formula	$C_{40}H_{35}N_7O_{12}$
Formula weight	805.75
Temperature/K	293.15
Crystal system	trigonal
Space group	$P3_121$
a/Å	19.7672(8)
b/Å	19.7672(8)
c/Å	23.6968(12)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	8018.8(8)
Z	6
ρ_{calc}g/cm^3	1.001

μ/mm^{-1}	0.076
F(000)	2520.0
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.872 to 52.74
Index ranges	$-24 \leq h \leq 20$, $-24 \leq k \leq 23$, $-29 \leq l \leq 29$
Reflections collected	34678
Independent reflections	10925 [R_{int} = 0.0321, R_{sigma} = 0.0489]
Data/restraints/parameters	10925/0/536
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0819, wR_2 = 0.2096
Final R indexes [all data]	R_1 = 0.1515, wR_2 = 0.2662
Largest diff. peak/hole / e Å^{-3}	0.47/-0.30
Flack parameter	0.8(4)

X-ray Crystallographic Data for Compound 17a: CCDC 1975128 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

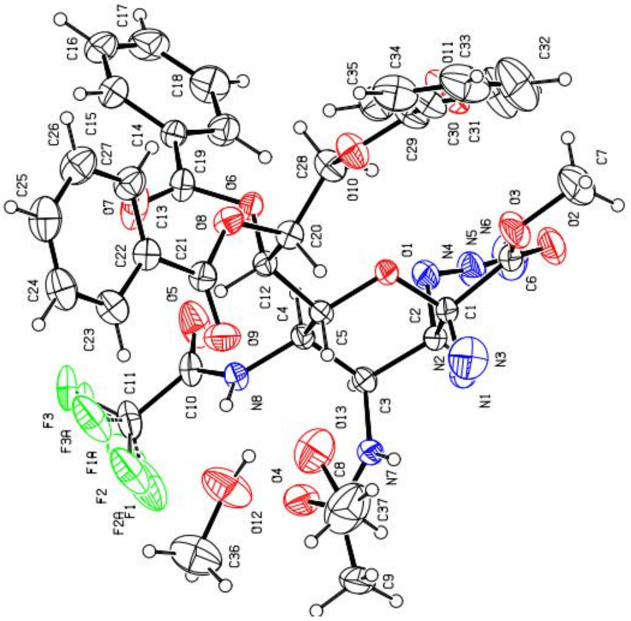


Table S15. Crystal data and structure refinement for 190419_s2_hh_hh190410a.

Identification code	190419_s2_hh_hh190410a
Empirical formula	$C_{37}H_{39}F_3N_8O_{13}$
Formula weight	860.76
Temperature/K	293.15
Crystal system	monoclinic

Space group	$P2_1$
a/Å	12.9906(4)
b/Å	11.1438(4)
c/Å	14.8377(7)
α/°	90
β/°	103.257(4)
γ/°	90
Volume/Å^3	2090.74(15)
Z	2
ρ_{calc}g/cm^3	1.367
μ/mm^{-1}	0.113
F(000)	896.0
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.99 to 52.738
Index ranges	$-15 \leq h \leq 16$, $-13 \leq k \leq 13$, $-18 \leq l \leq 12$
Reflections collected	9421
Independent reflections	7012 [R_{int} = 0.0172, R_{sigma} = 0.0448]
Data/restraints/parameters	7012/1/569
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0533, wR_2 = 0.1204
Final R indexes [all data]	R_1 = 0.0802, wR_2 = 0.1378
Largest diff. peak/hole / e Å^{-3}	0.26/-0.24
Flack parameter	-0.5(5)

X-ray Crystallographic Data for Compound 29: CCDC 1975129 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

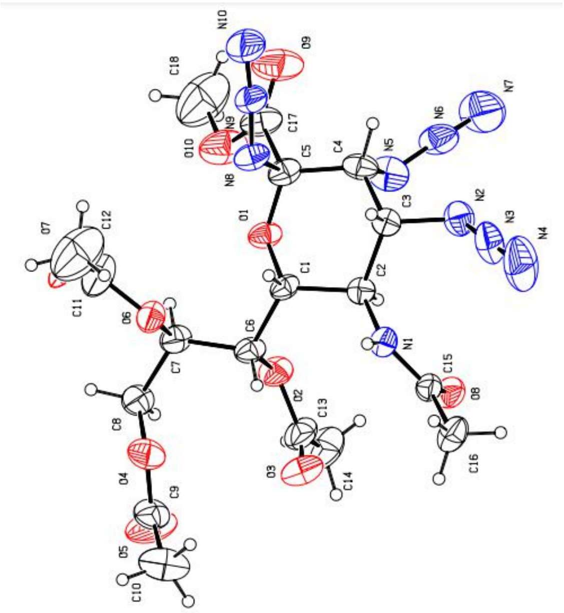
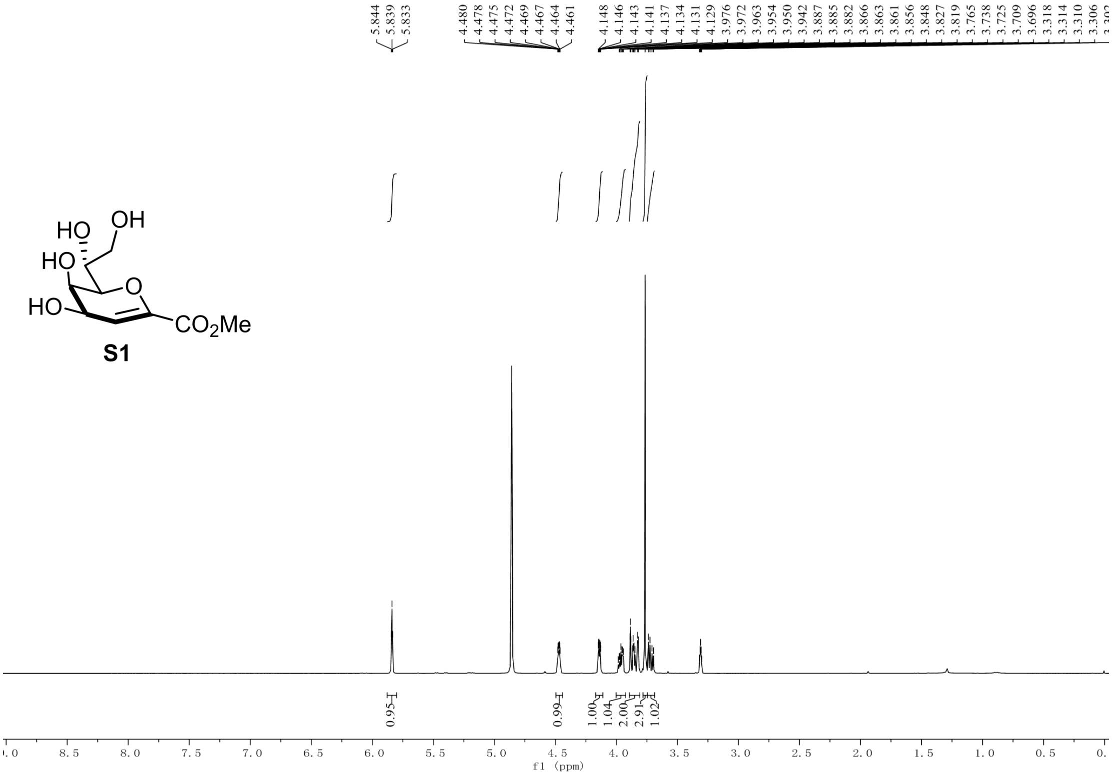


Table S16. Crystal data and structure refinement for 190226_s5_yd_hh181130b.

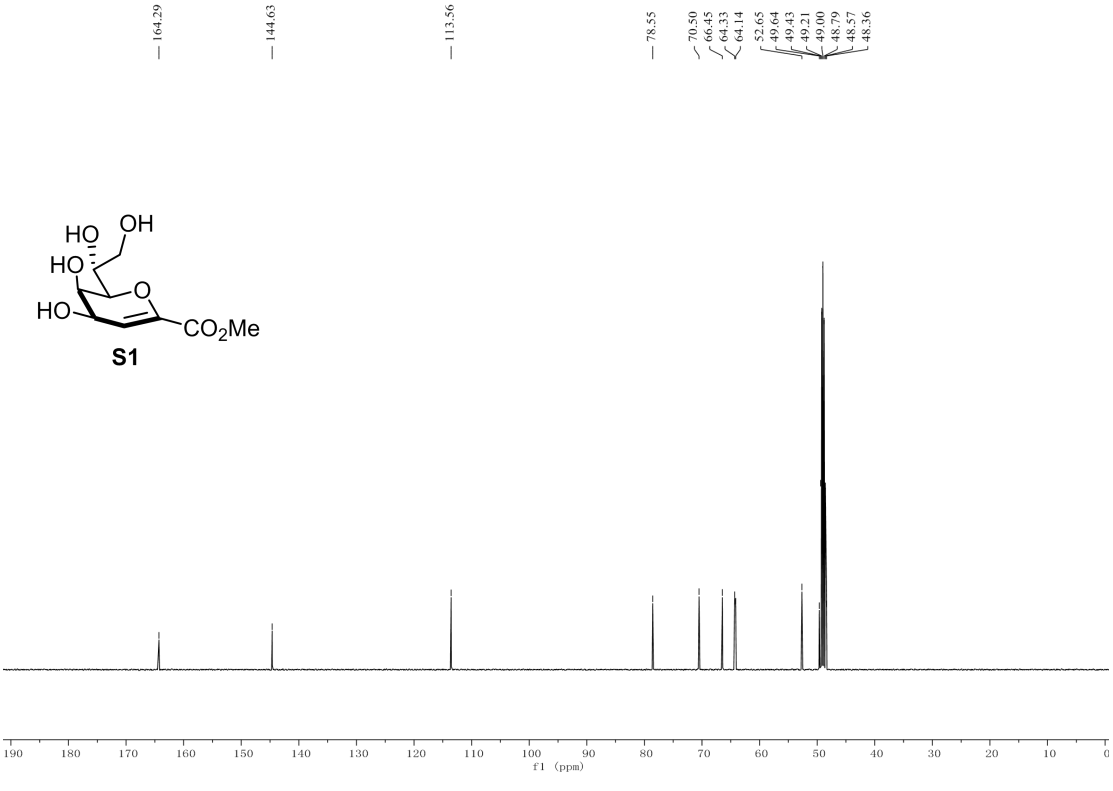
Identification code	190226_s5_yd_hh181130b
Empirical formula	$C_{18}H_{24}N_{10}O_{10}$
Formula weight	540.47
Temperature/K	293.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.6075(7)
b/Å	10.7485(9)
c/Å	33.736(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3121.1(5)
Z	4
ρ_{calc}g/cm^3	1.150
μ/mm^{-1}	0.095
F(000)	1128.0
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.96 to 52.74
Index ranges	$-10 \le h \le 10$, $-9 \le k \le 13$, $-24 \le l \le 42$
Reflections collected	9470
Independent reflections	5968 [R_{int} = 0.0270, R_{sigma} = 0.0541]
Data/restraints/parameters	5968/0/342
Goodness-of-fit on F^2	0.966

Final R indexes [I>=2σ (I)]	$R_1 = 0.0717$, $wR_2 = 0.1976$
Final R indexes [all data]	$R_1 = 0.0974$, $wR_2 = 0.2188$
Largest diff. peak/hole / e Å^{-3}	0.29/-0.28
Flack parameter	0.7(10)

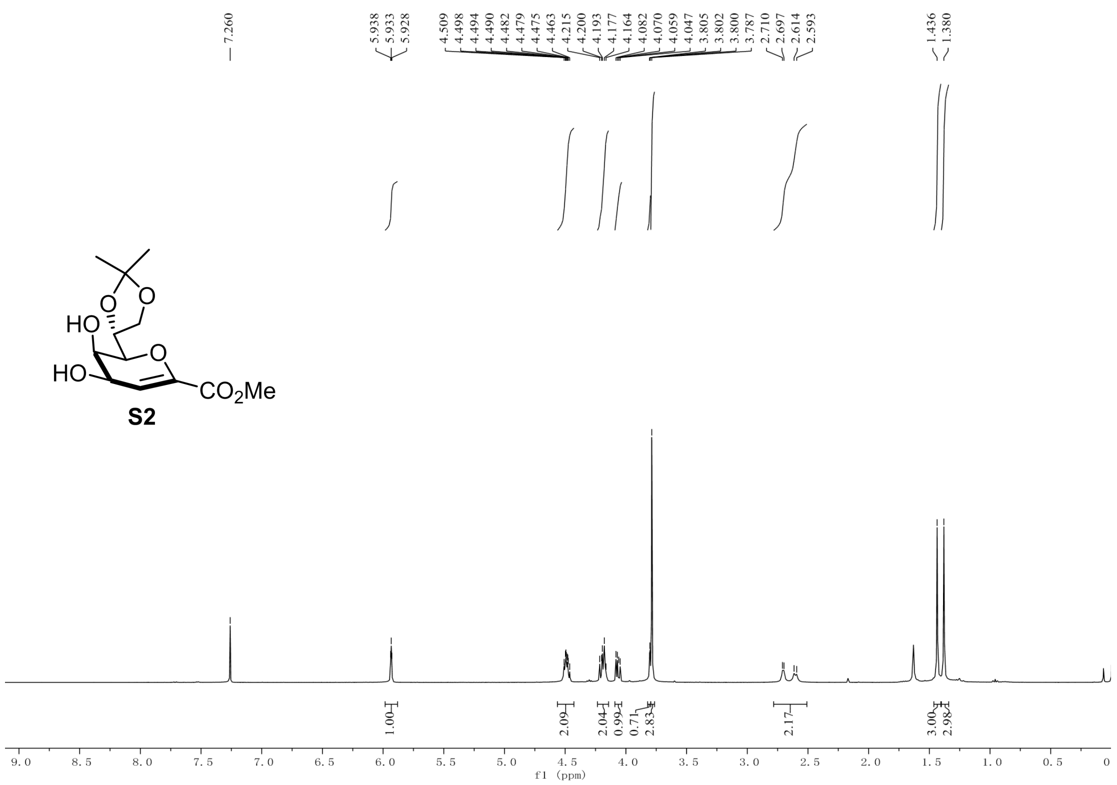
11. NMR Spectra



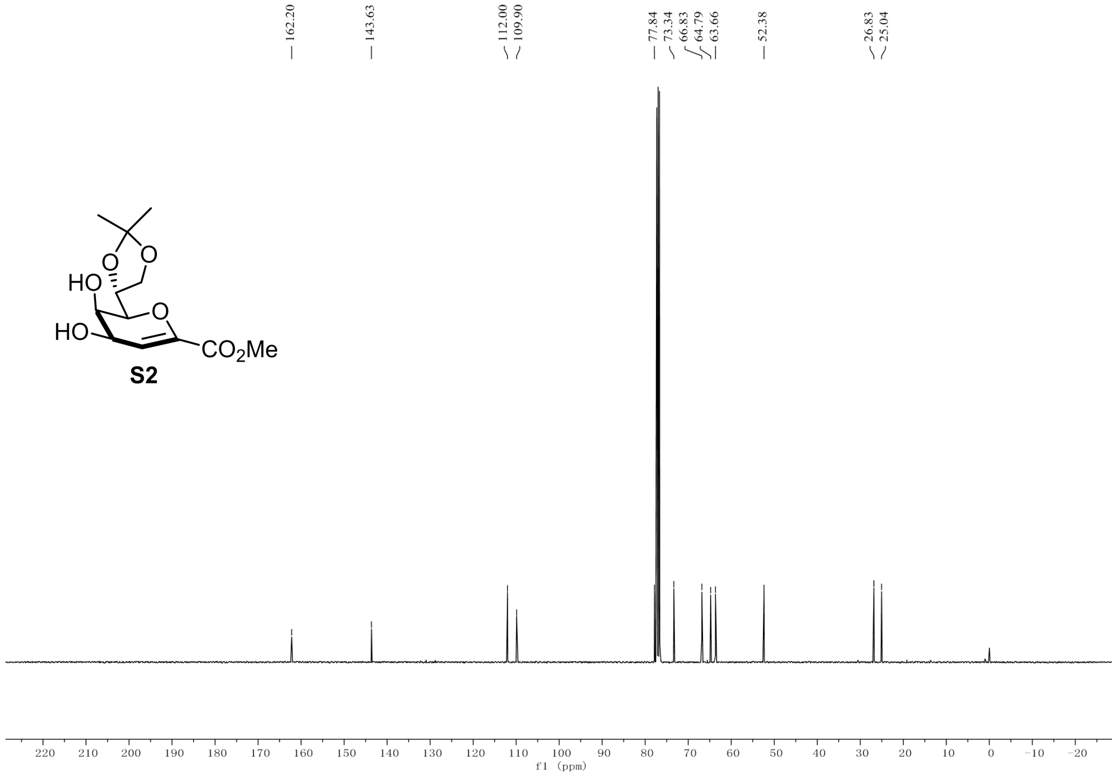
^{1}H NMR spectrum of compound **S1**



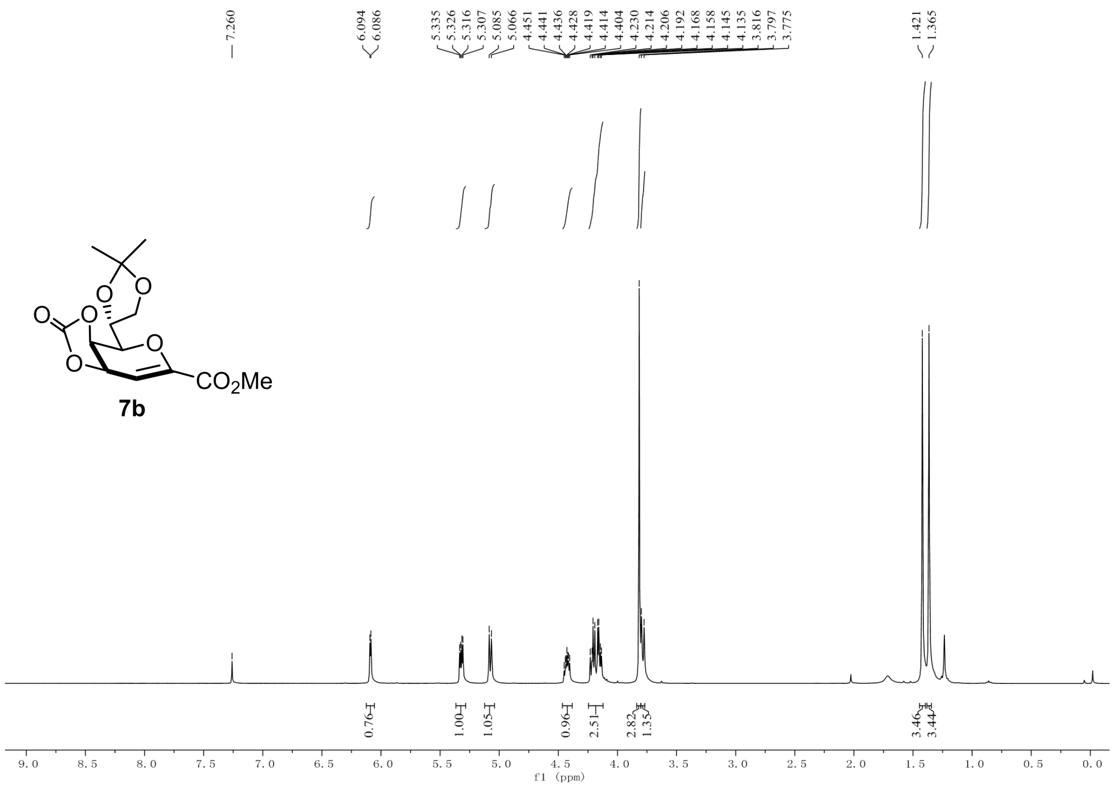
^{13}C NMR spectrum of compound **S1**



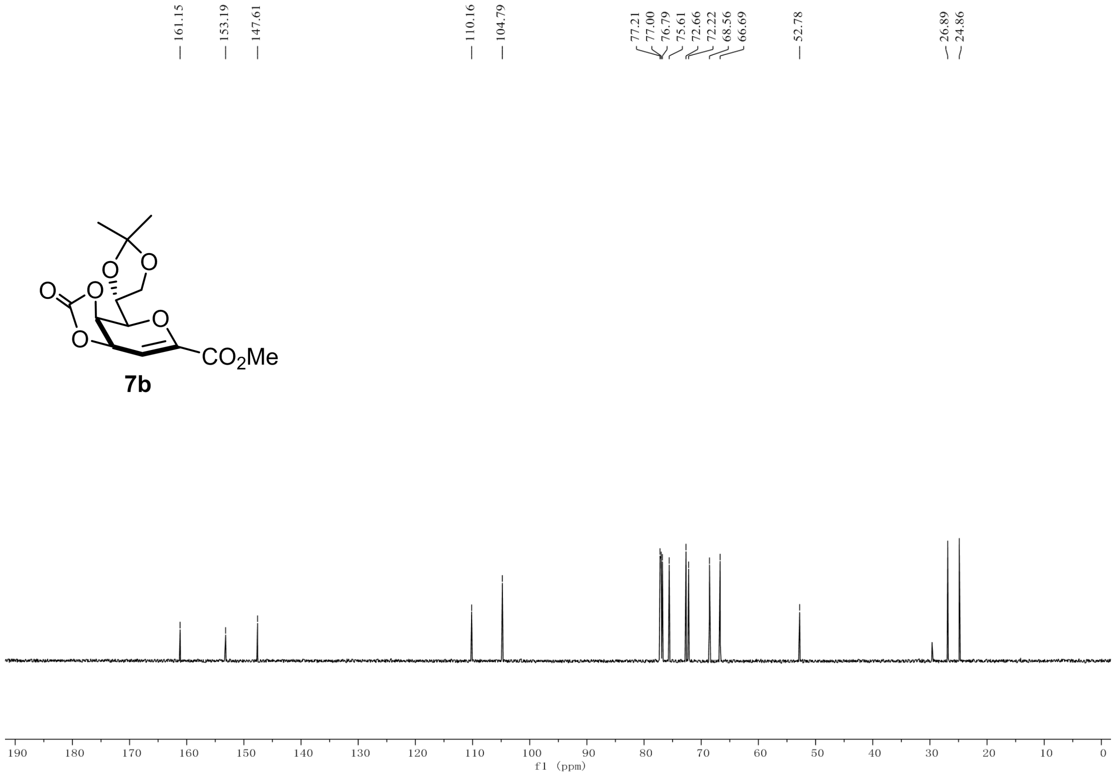
^{1}H NMR spectrum of compound **S2**



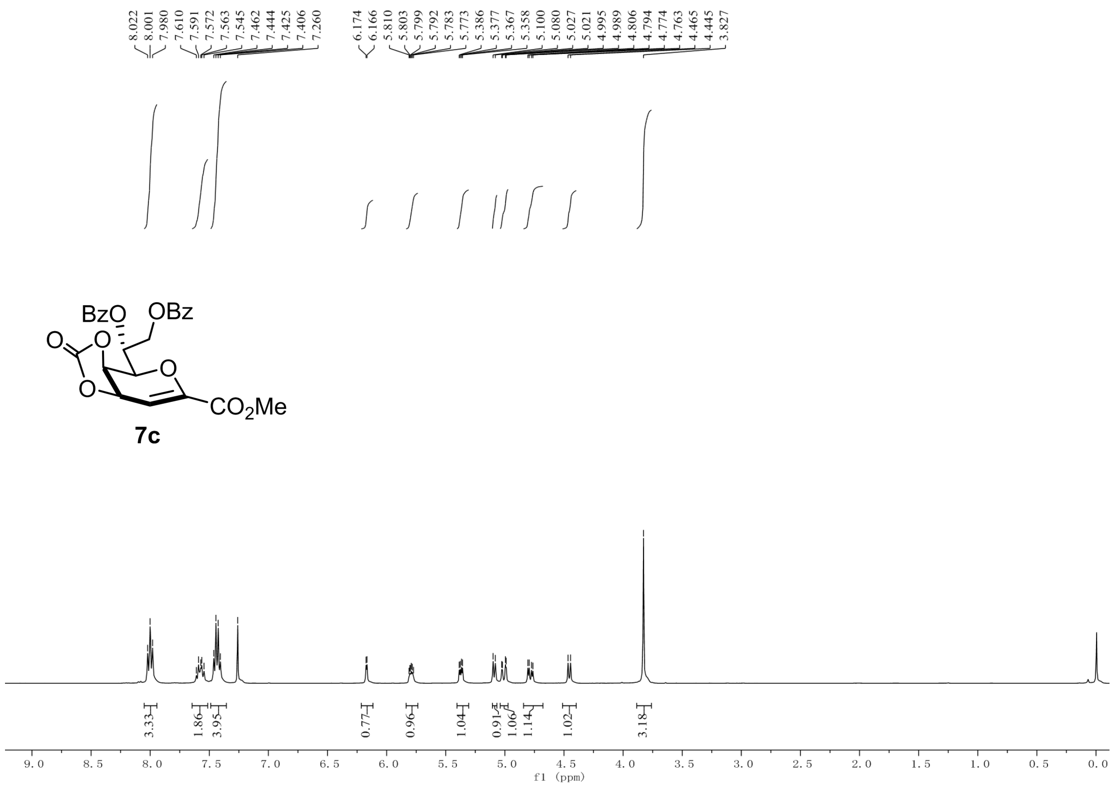
^{13}C NMR spectrum of compound **S2**



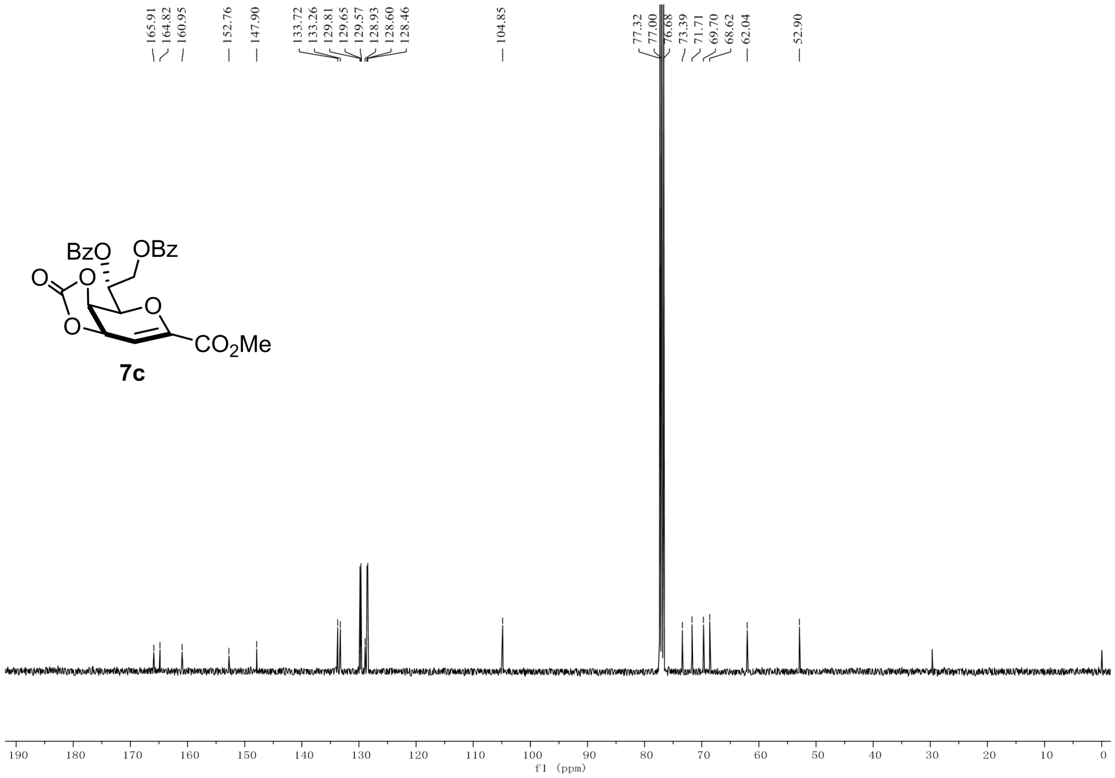
^{1}H NMR spectrum of compound **7b**



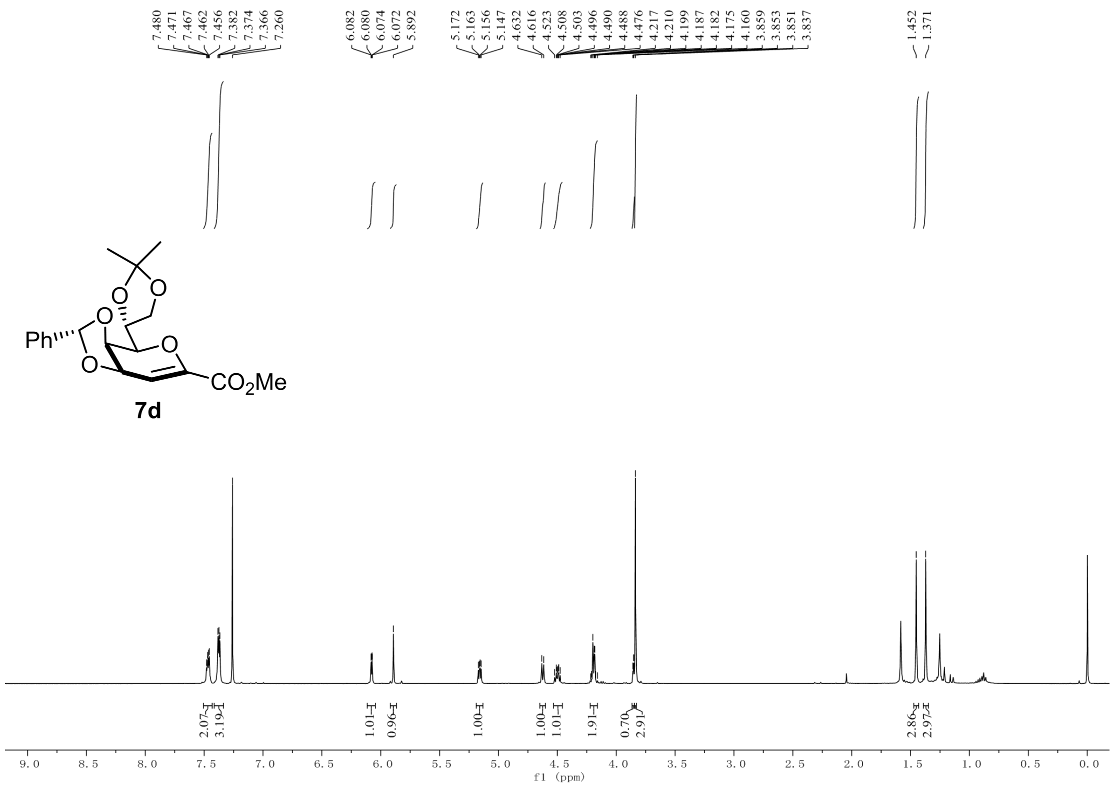
^{13}C NMR spectrum of compound **7b**



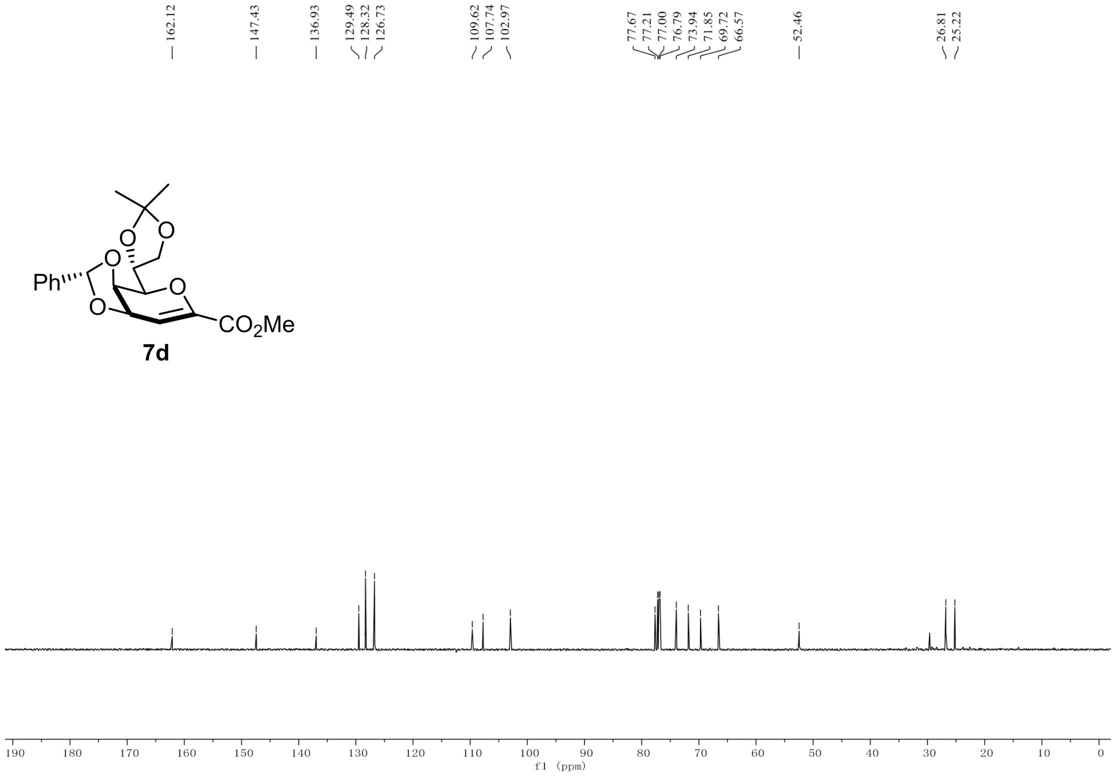
^{1}H NMR spectrum of compound **7c**



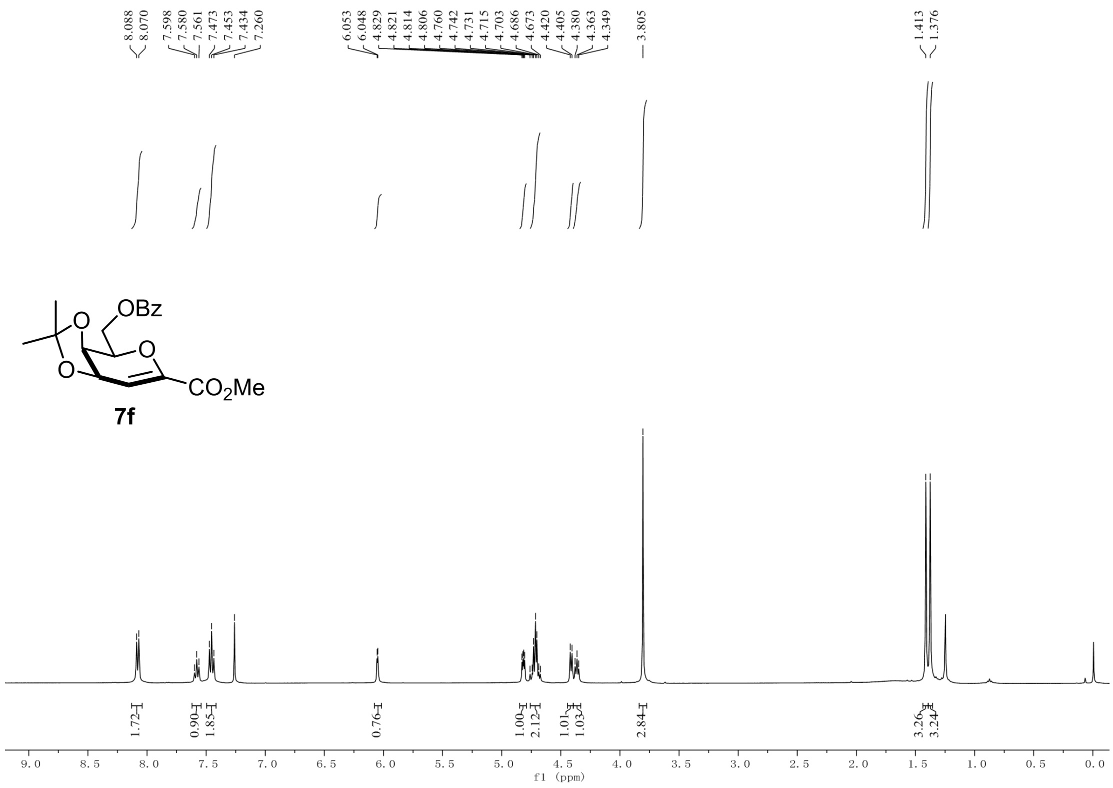
^{13}C NMR spectrum of compound **7c**



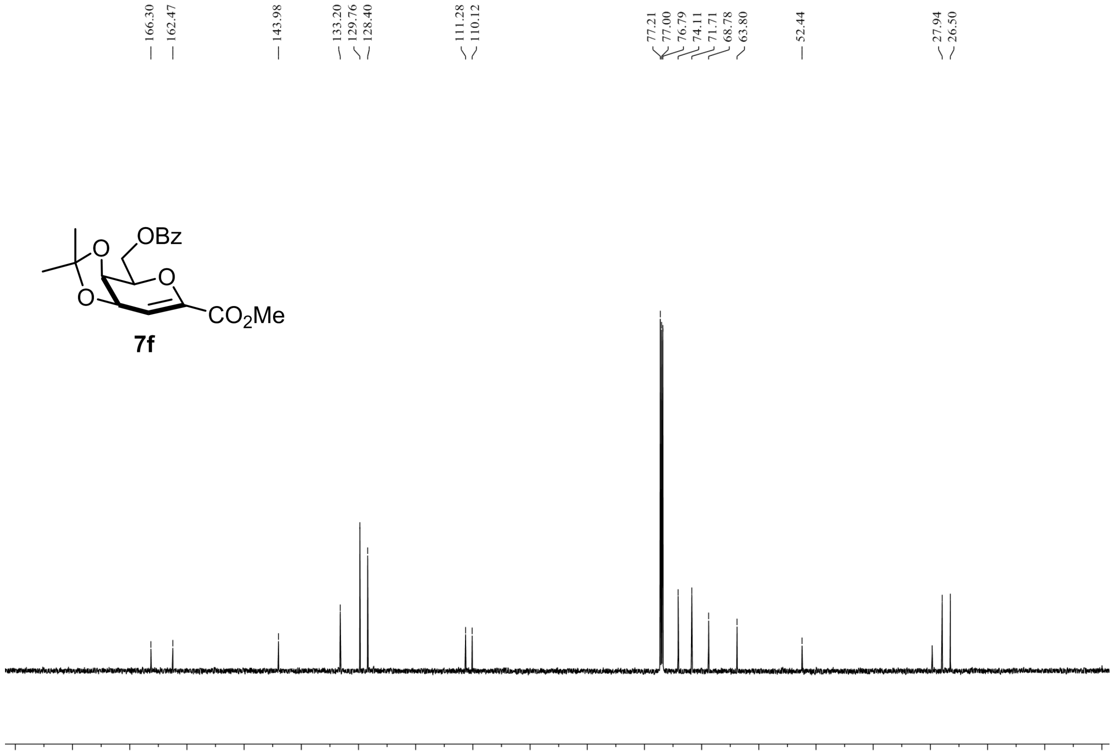
^{1}H NMR spectrum of compound **7d**



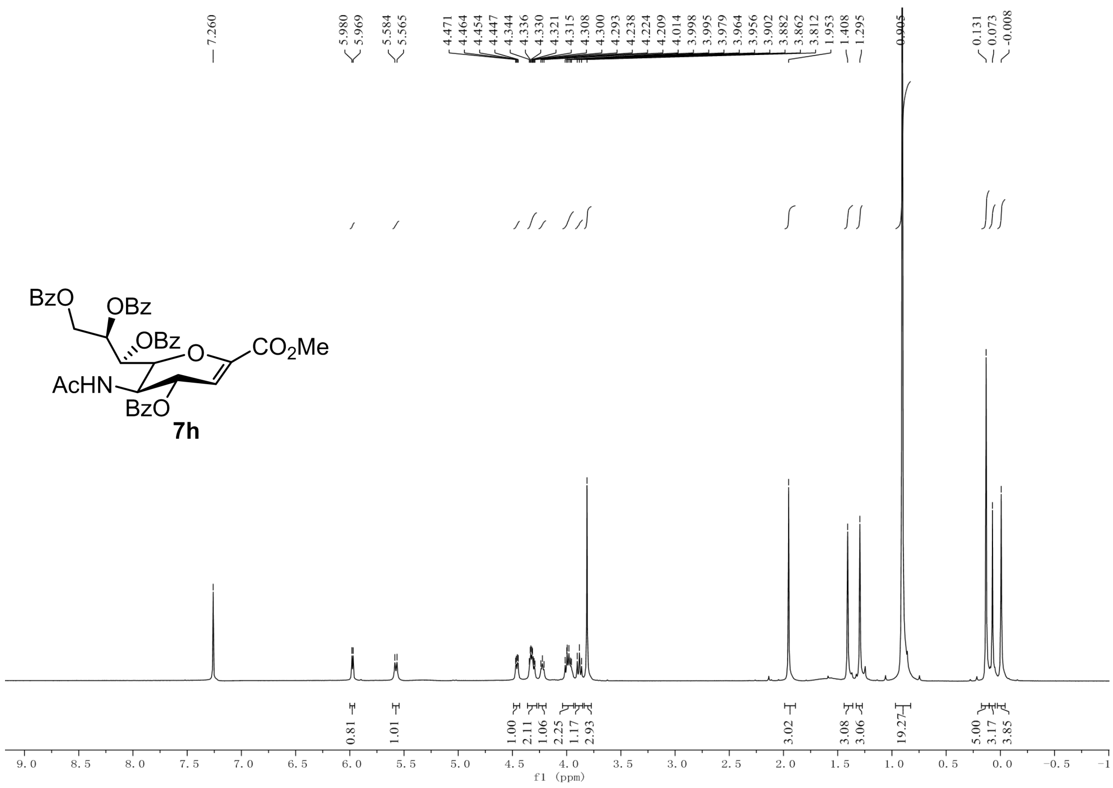
^{13}C NMR spectrum of compound **7d**



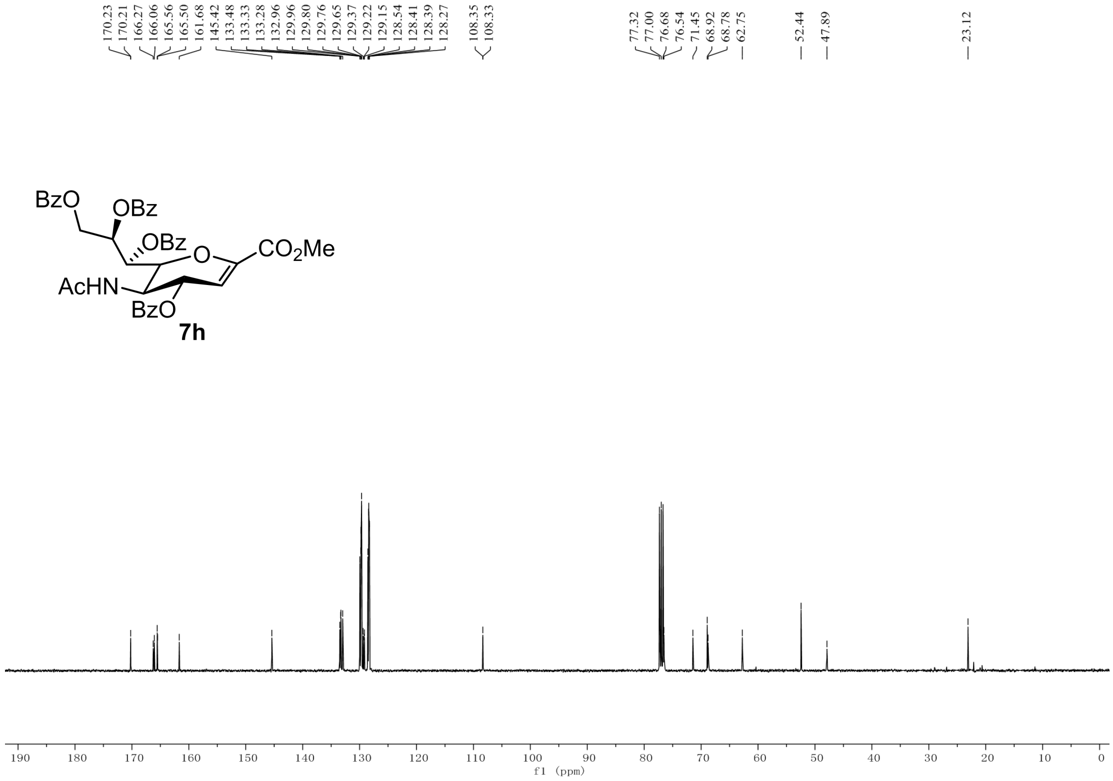
^{1}H NMR spectrum of compound **7f**



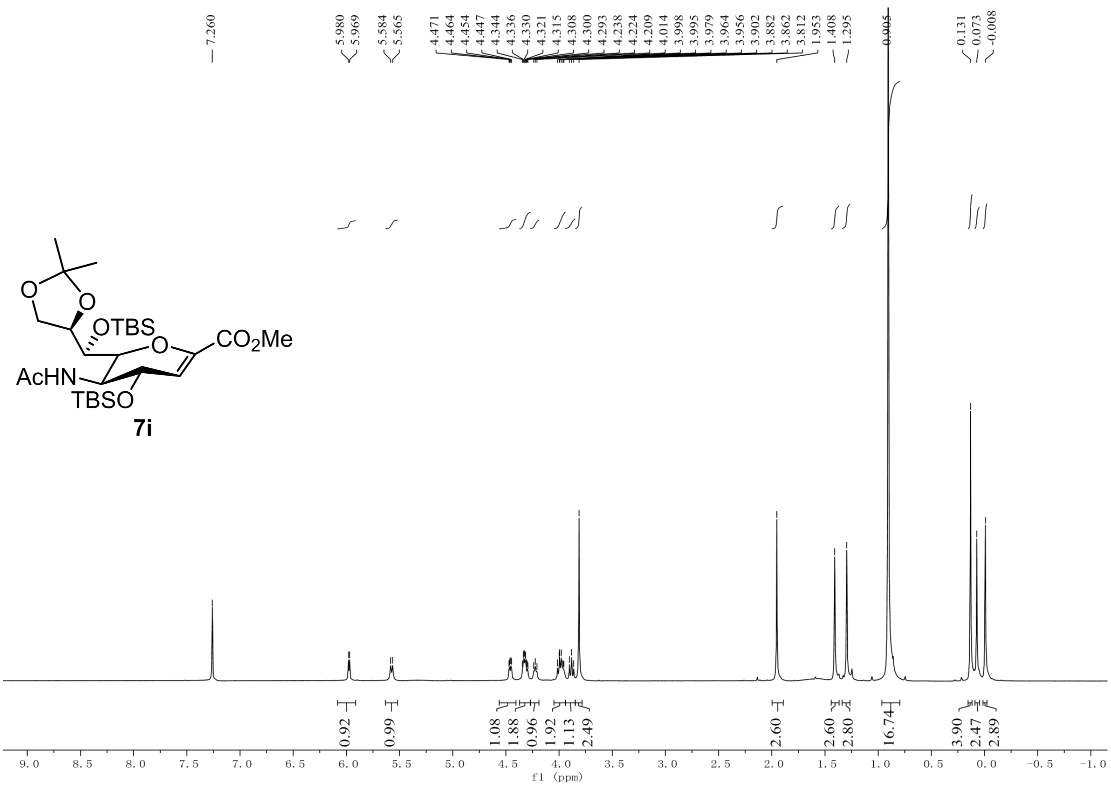
^{13}C NMR spectrum of compound **7f**



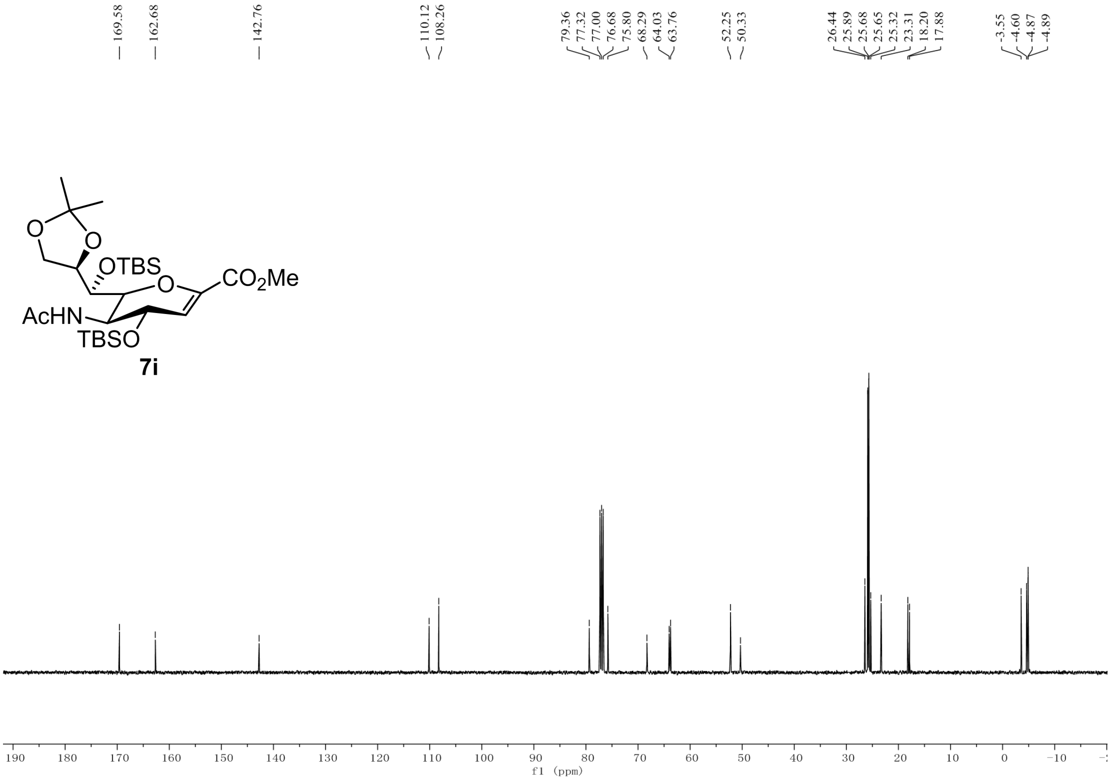
^{1}H NMR spectrum of compound **7h**



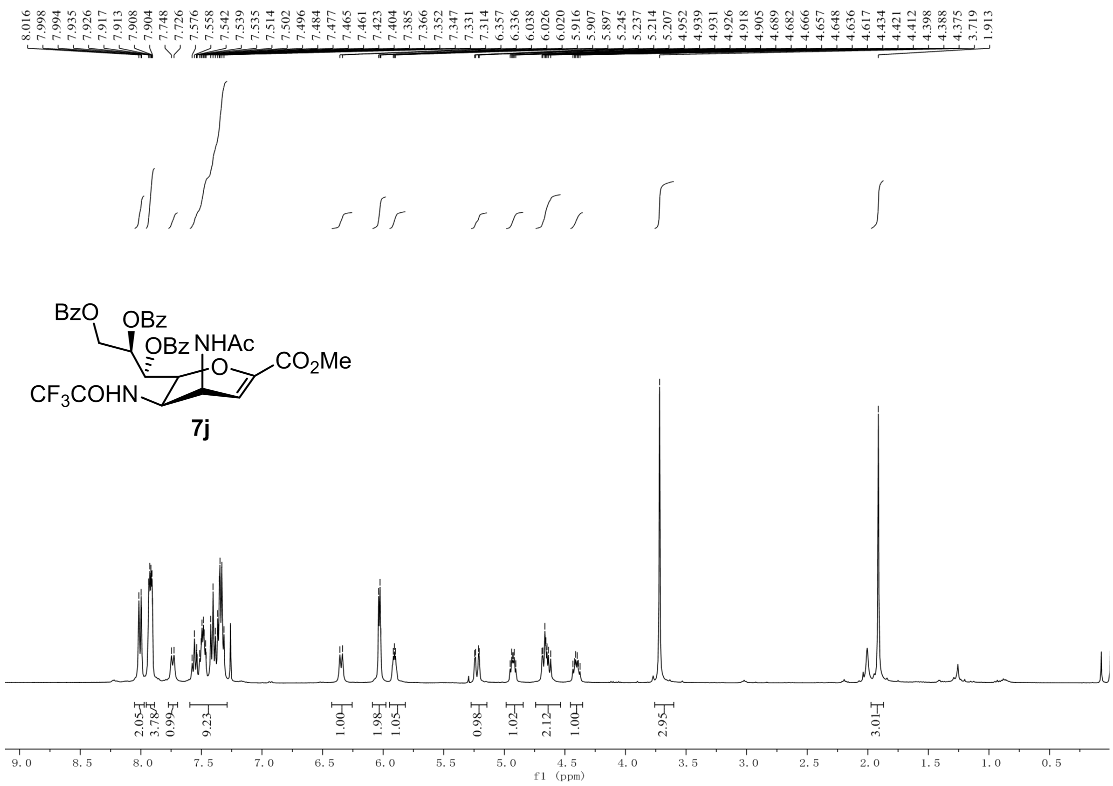
^{13}C NMR spectrum of compound **7h**



^{1}H NMR spectrum of compound **7i**



^{13}C NMR spectrum of compound **7i**



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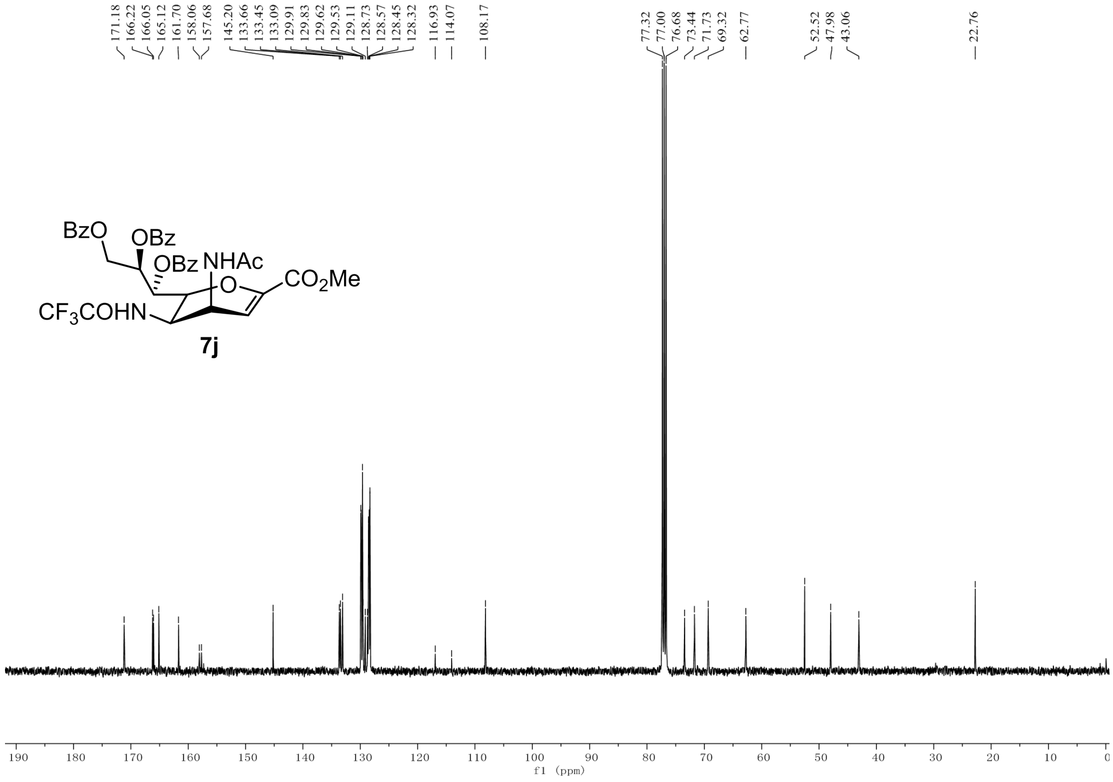
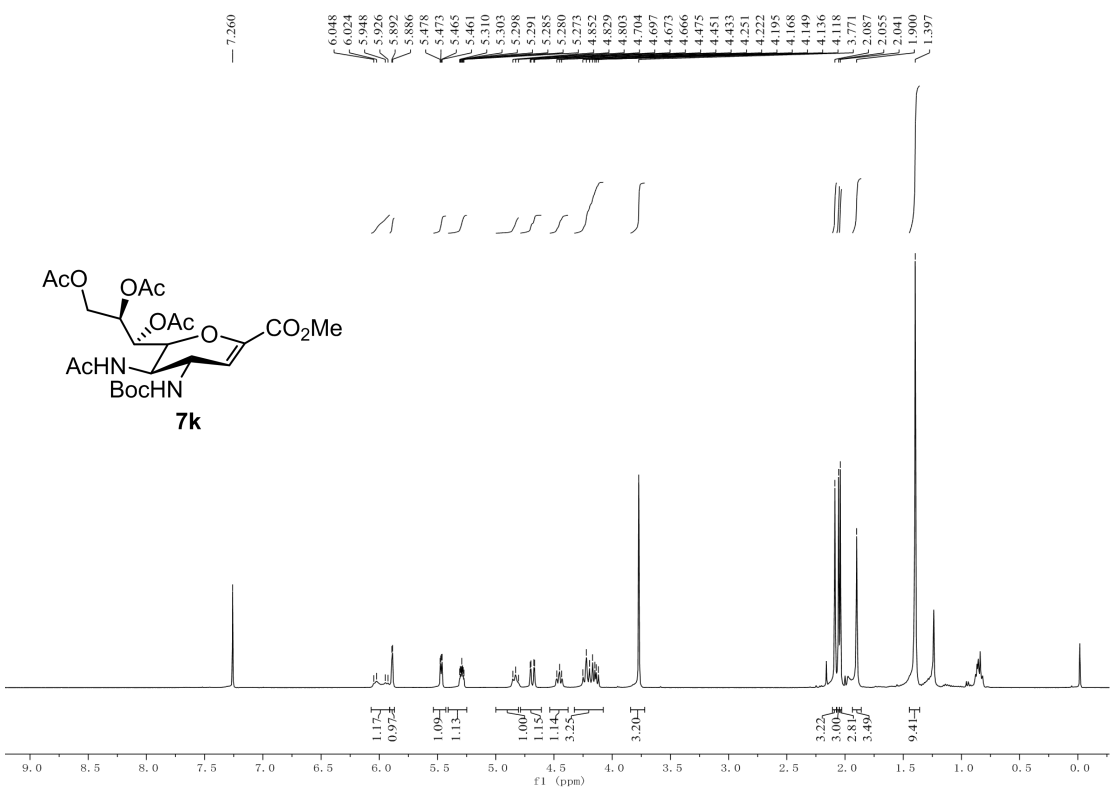
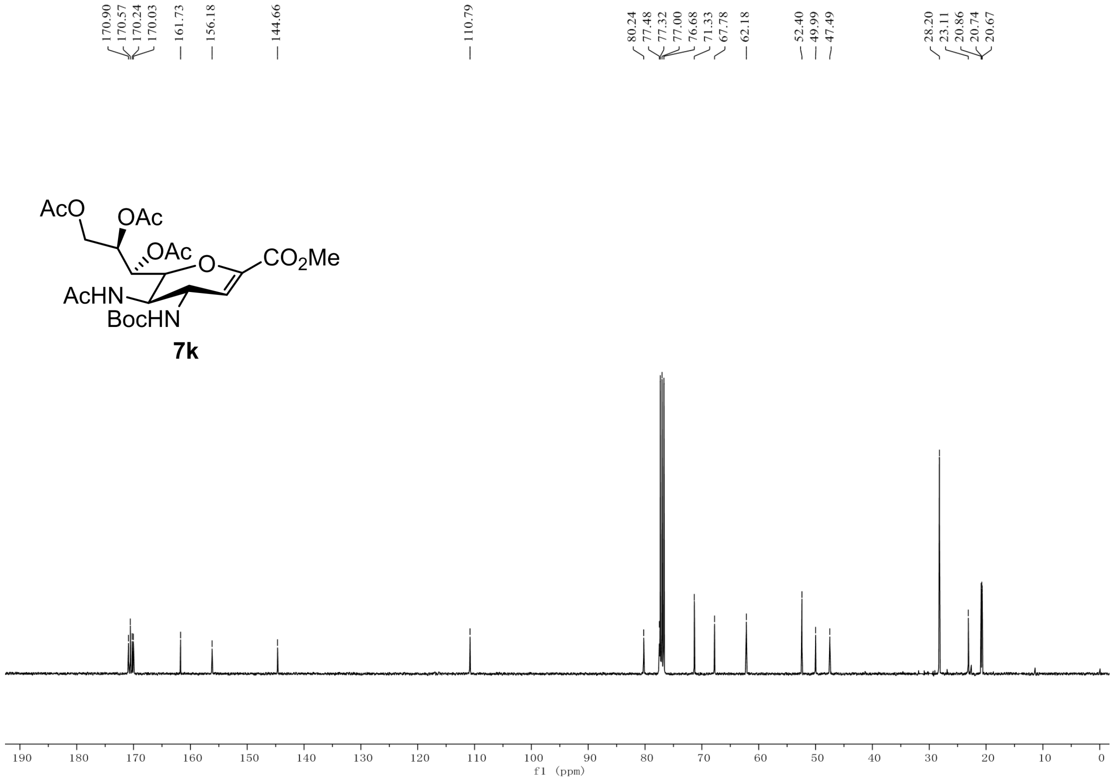


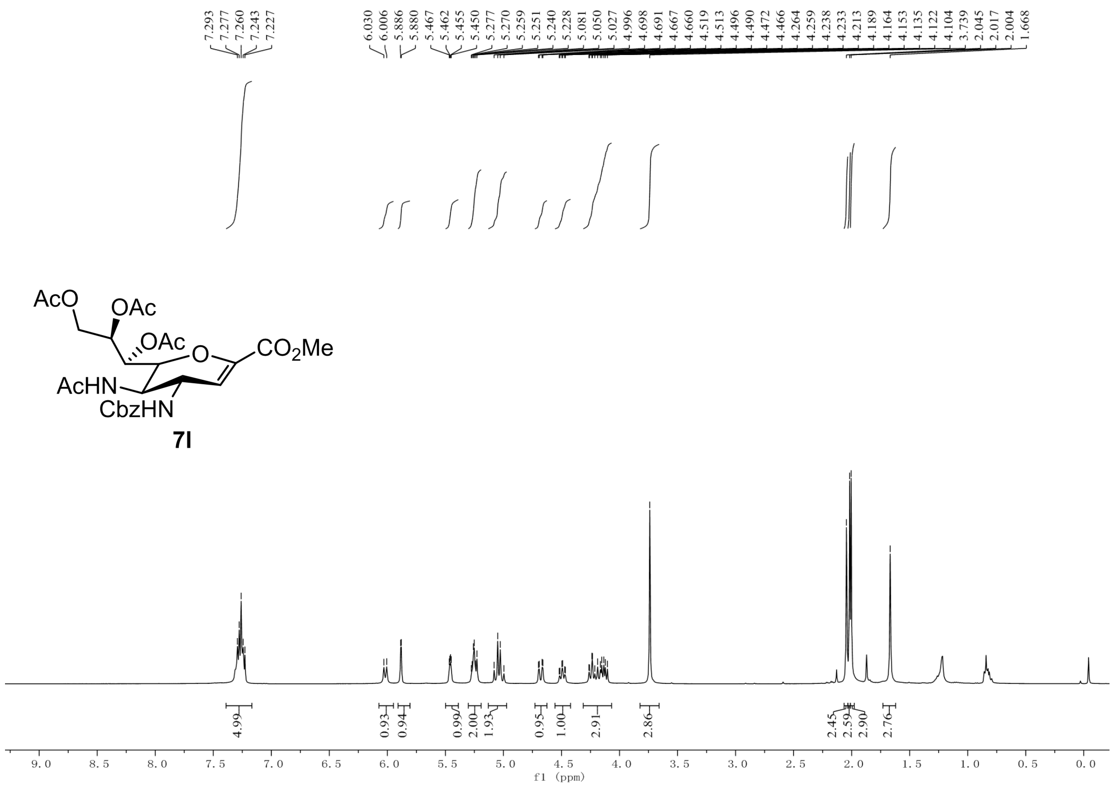
^{13}C NMR spectrum of compound **7j**



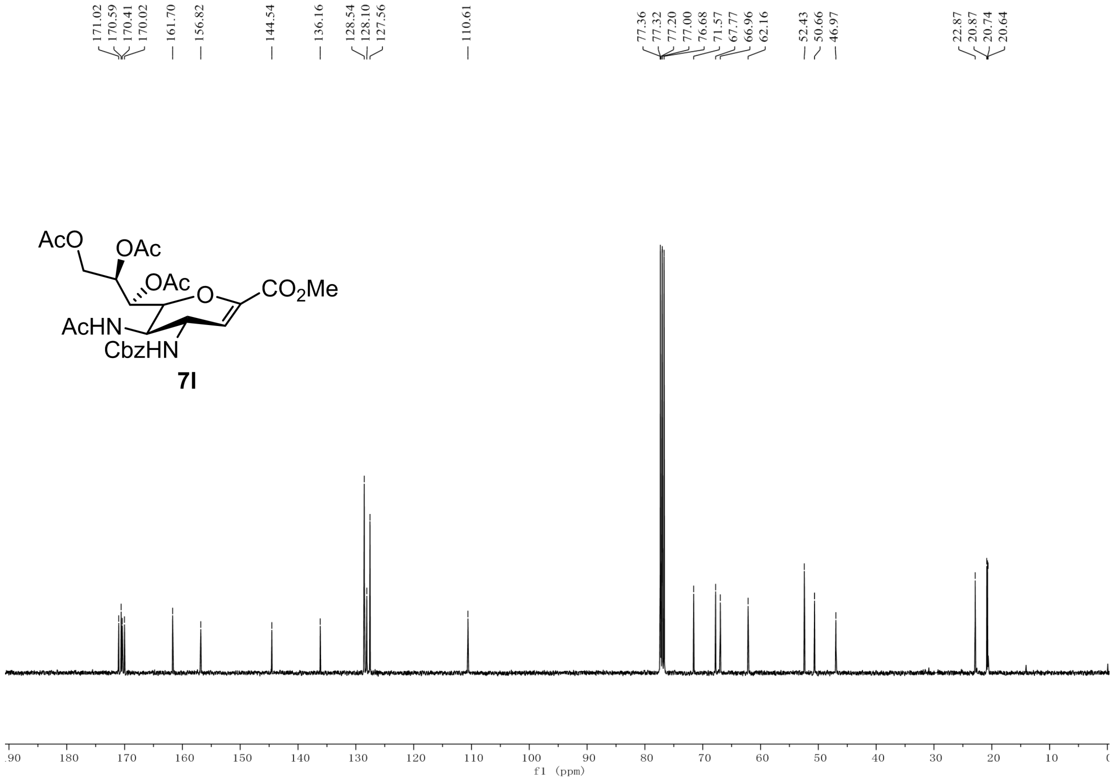
^{1}H NMR spectrum of compound **7k**



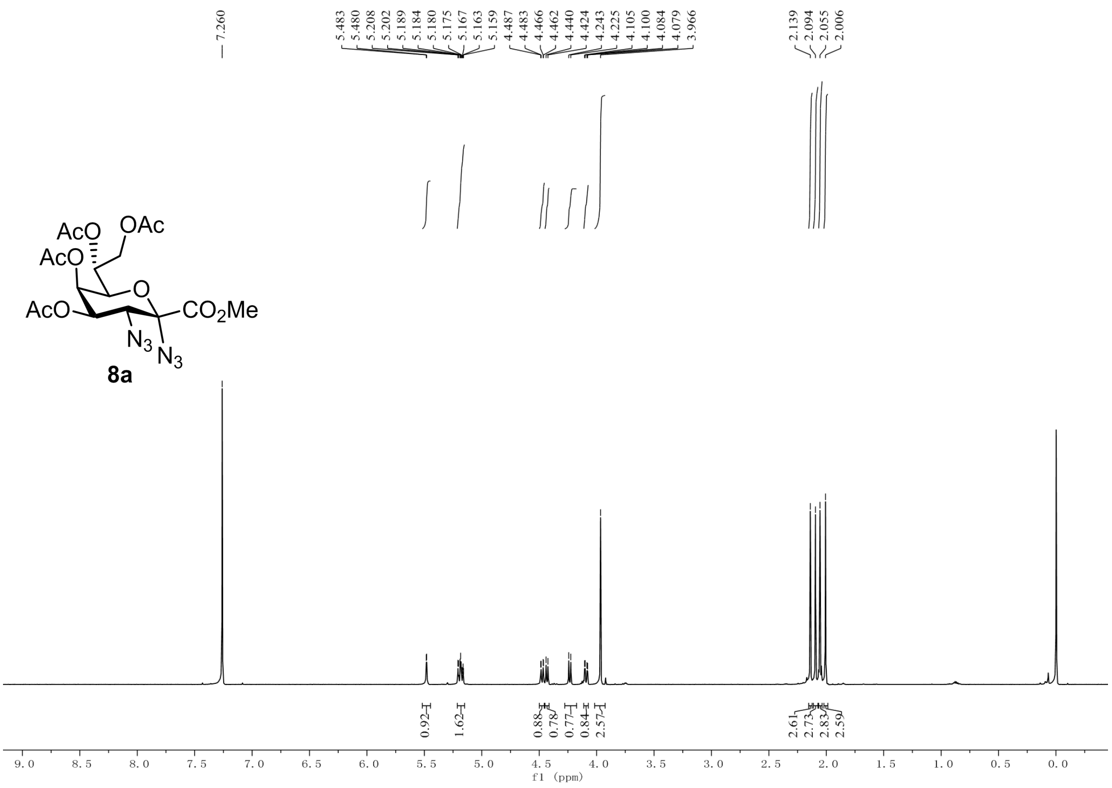
^{13}C NMR spectrum of compound **7k**



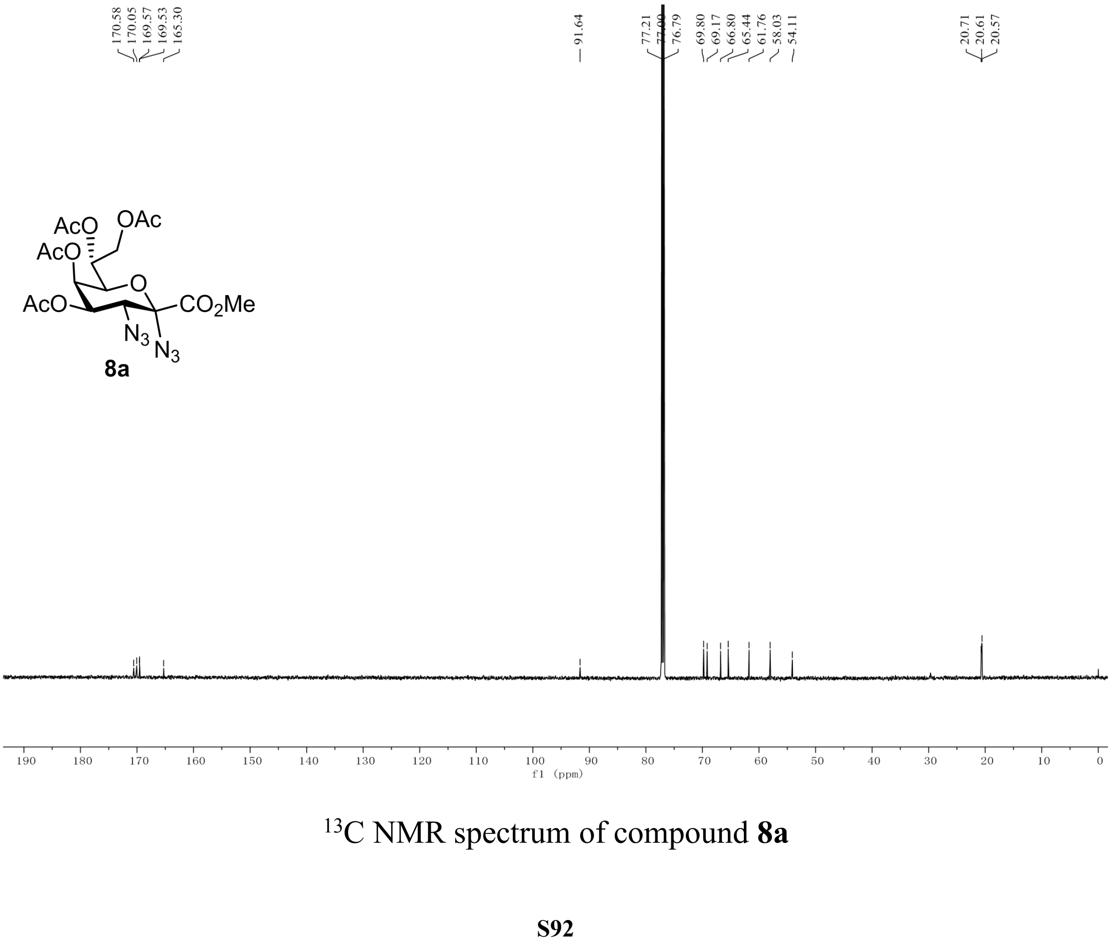
^{1}H NMR spectrum of compound **7l**



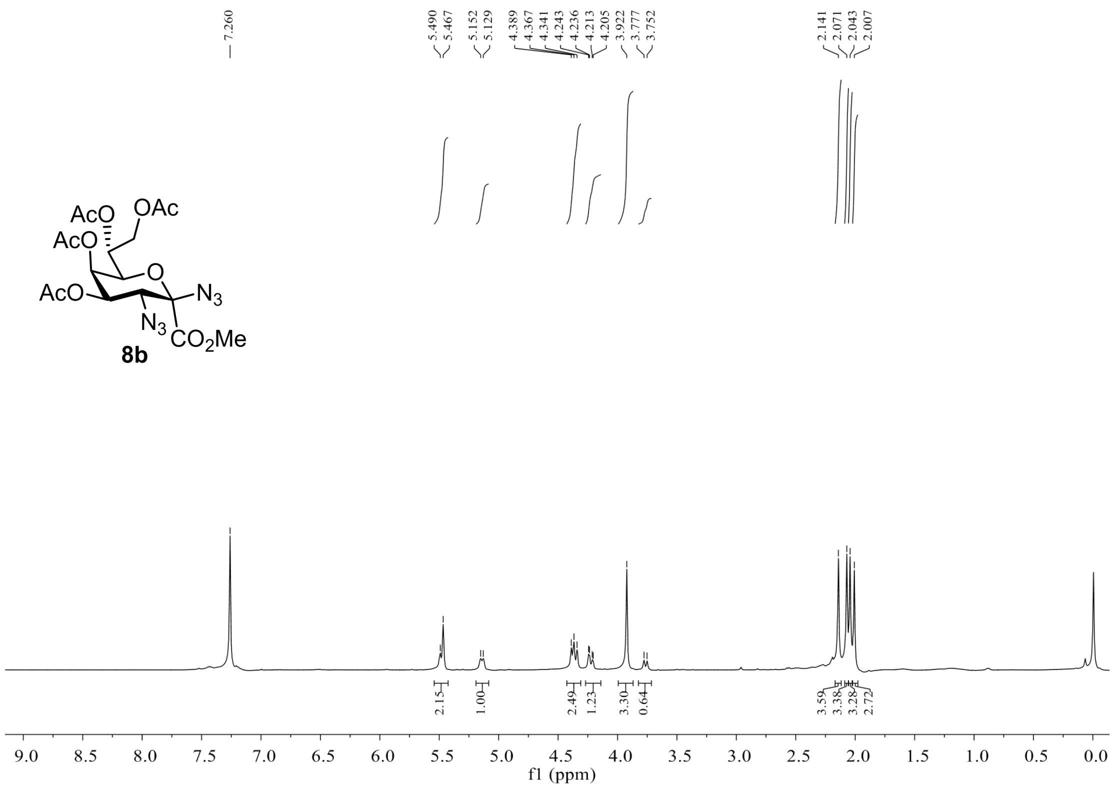
^{13}C NMR spectrum of compound **7l**



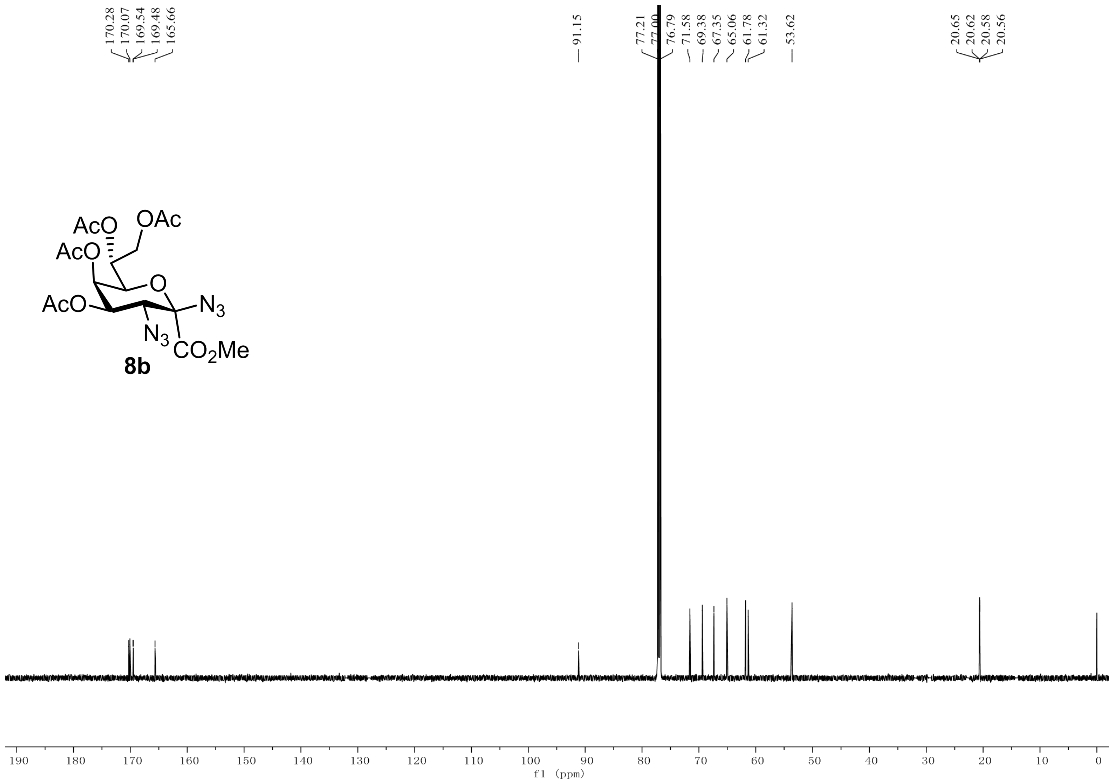
^{1}H NMR spectrum of compound **8a**



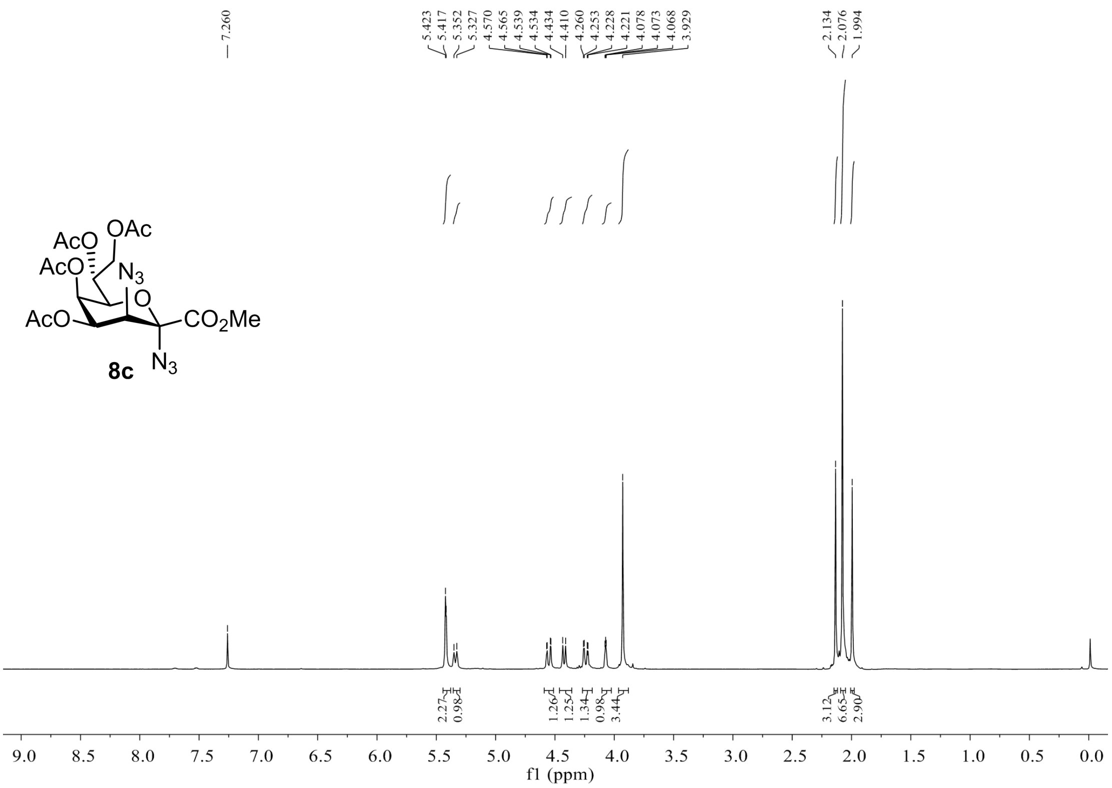
^{13}C NMR spectrum of compound **8a**



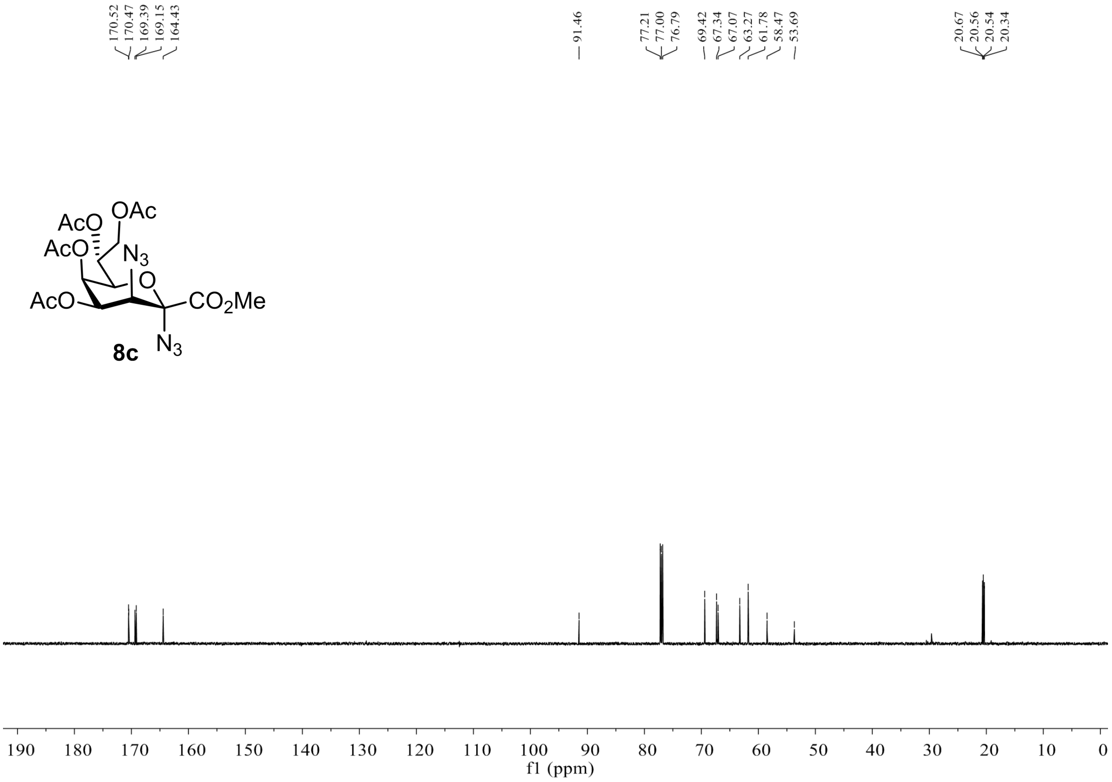
^{1}H NMR spectrum of compound **8b**



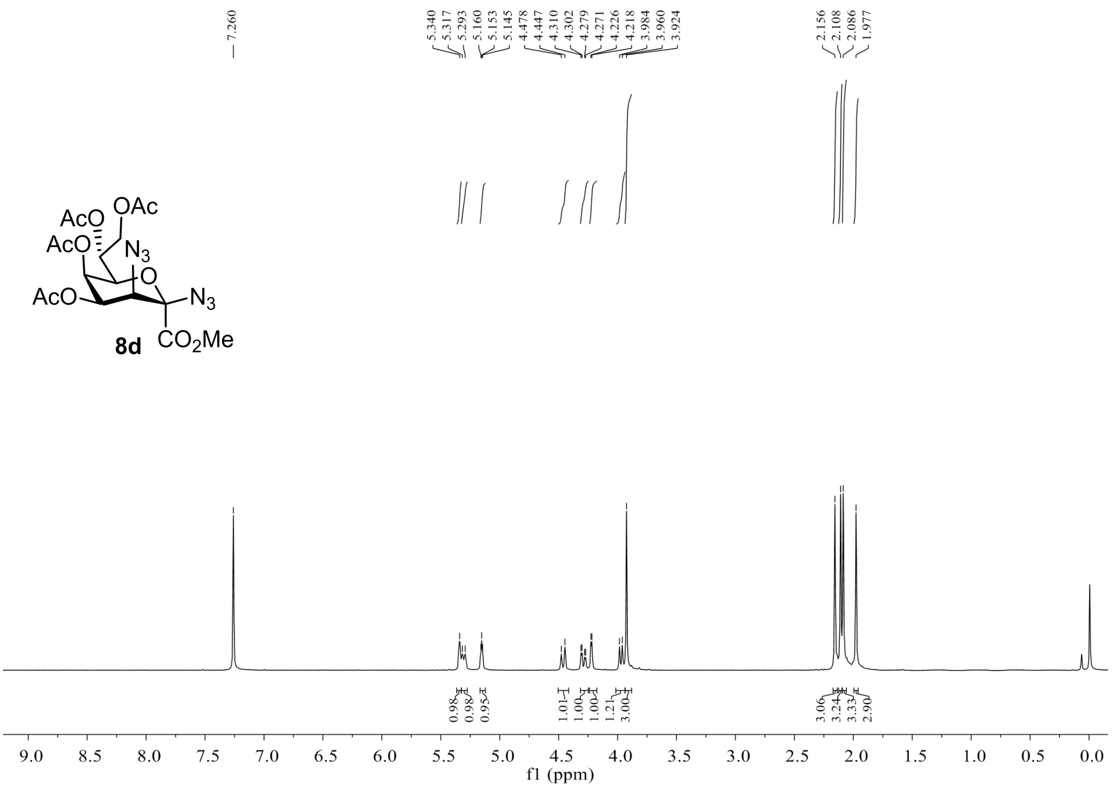
^{13}C NMR spectrum of compound **8b**



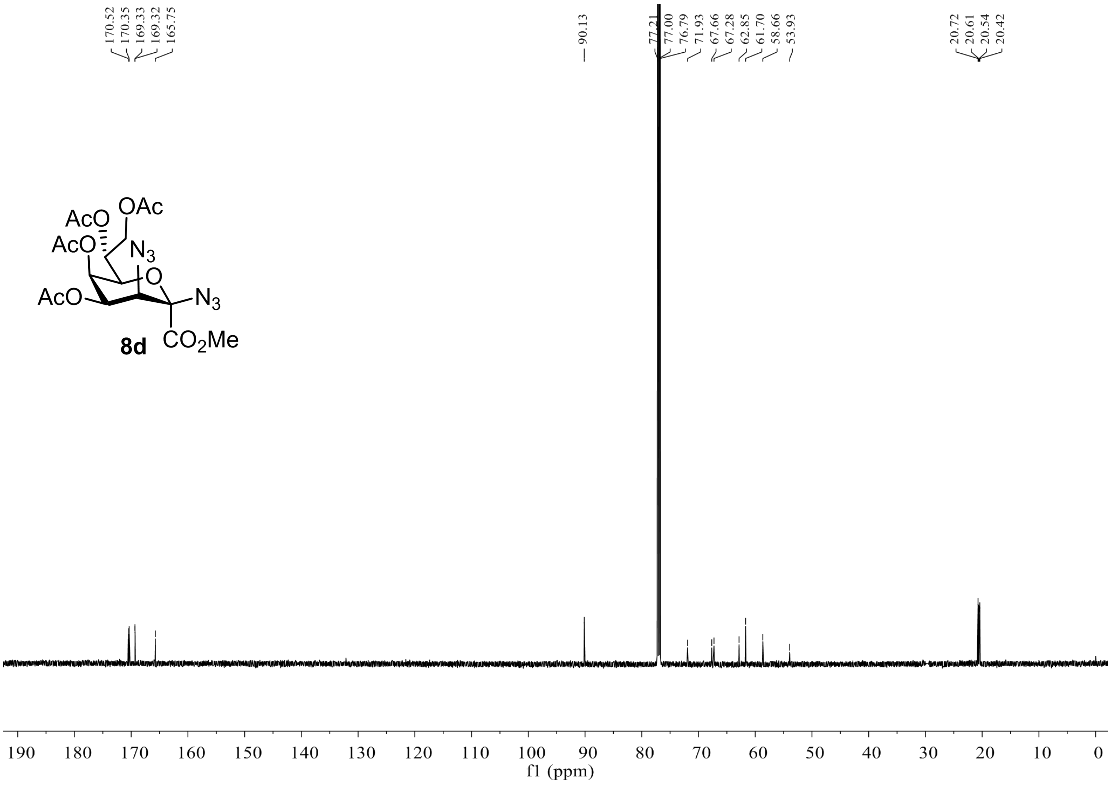
^{1}H NMR spectrum of compound **8c**



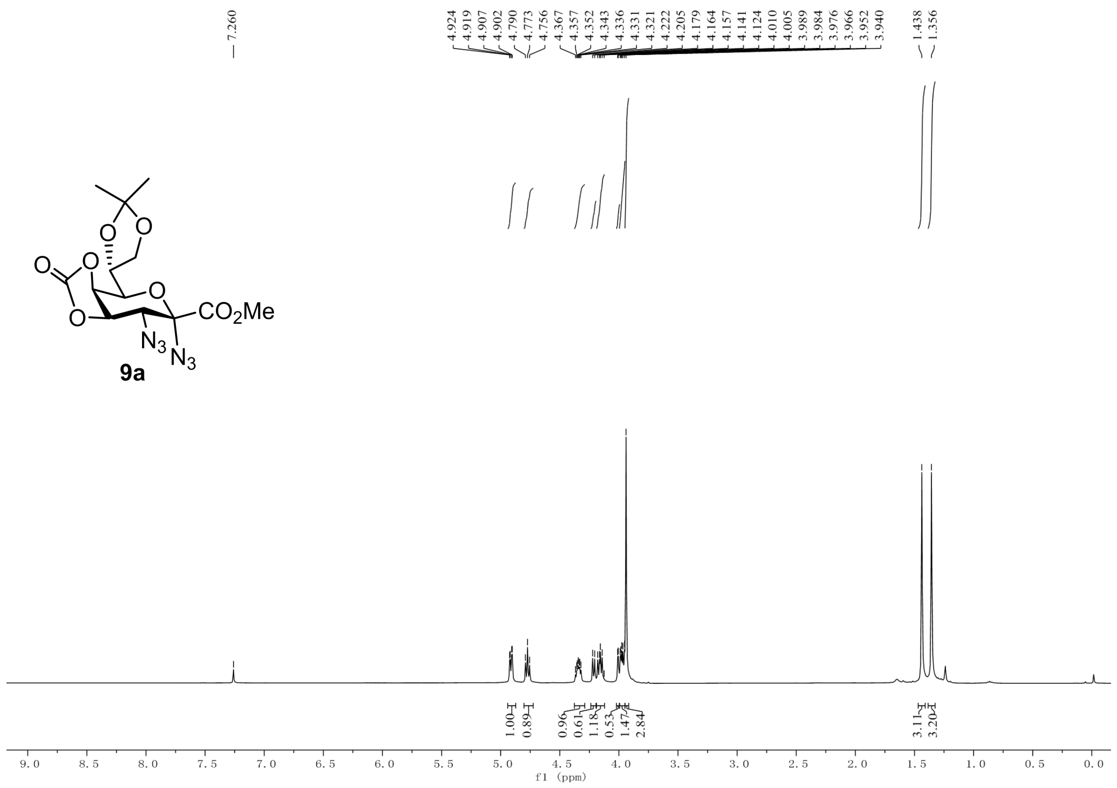
^{13}C NMR spectrum of compound **8c**



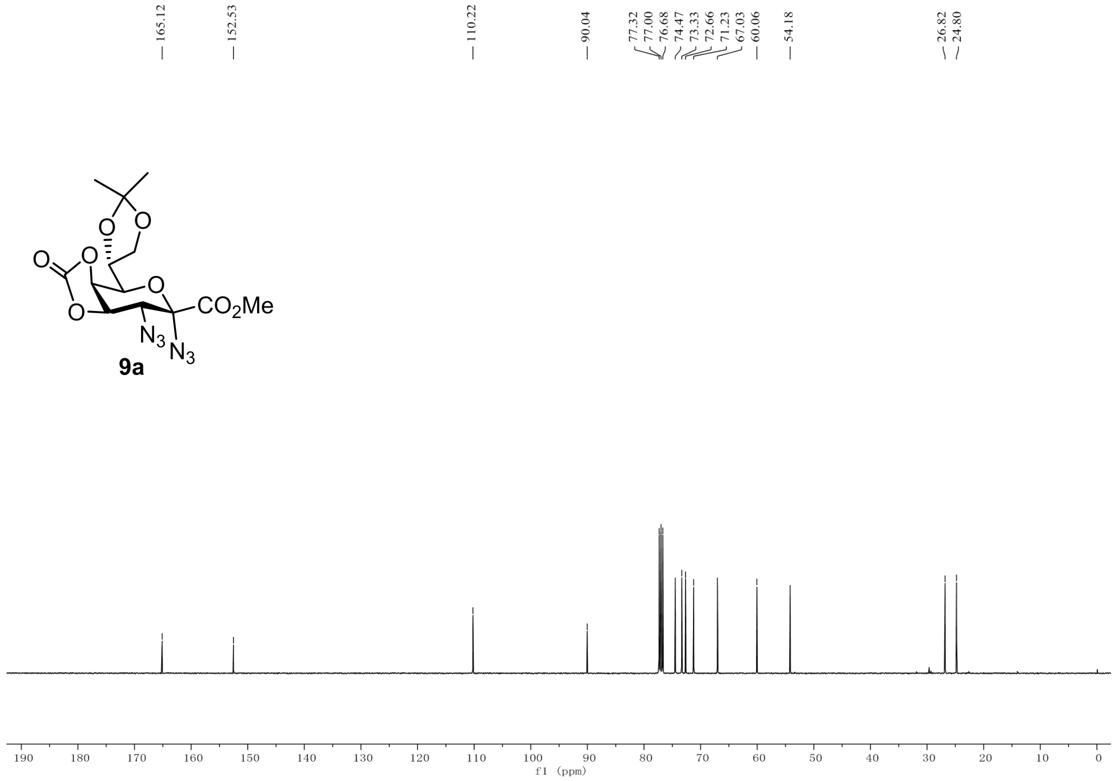
^{1}H NMR spectrum of compound **8d**



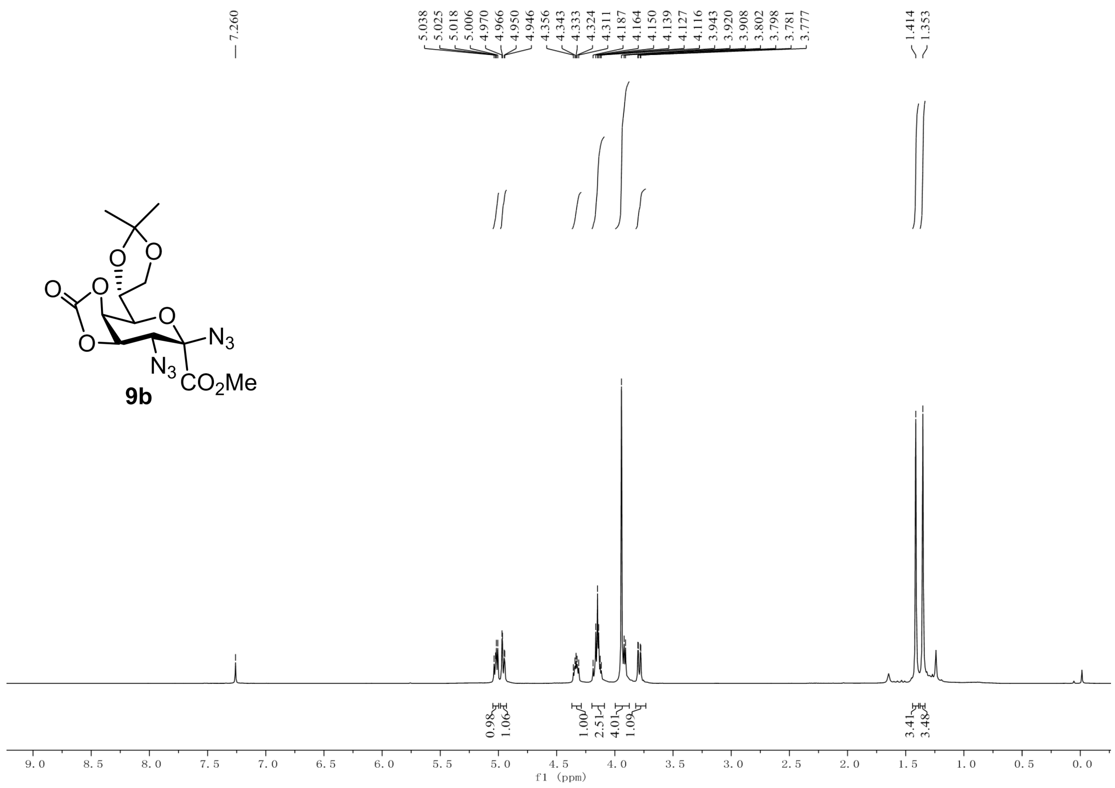
^{13}C NMR spectrum of compound **8d**



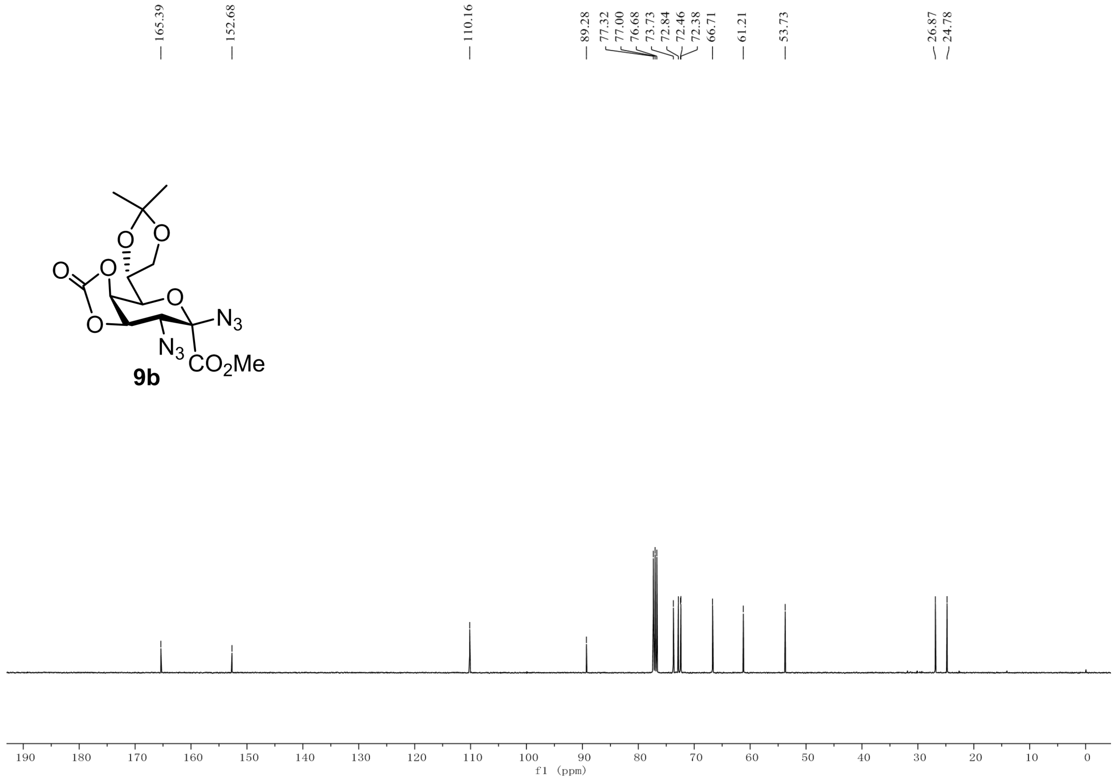
^{1}H NMR spectrum of compound **9a**



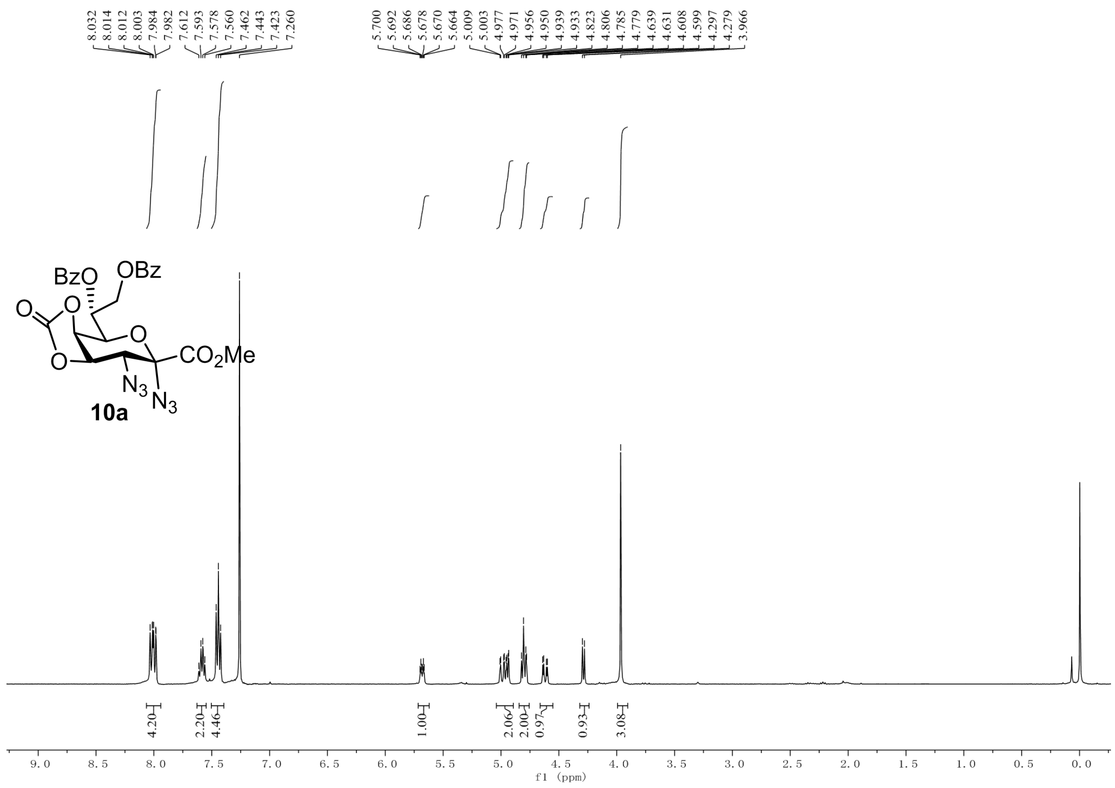
^{13}C NMR spectrum of compound **9a**



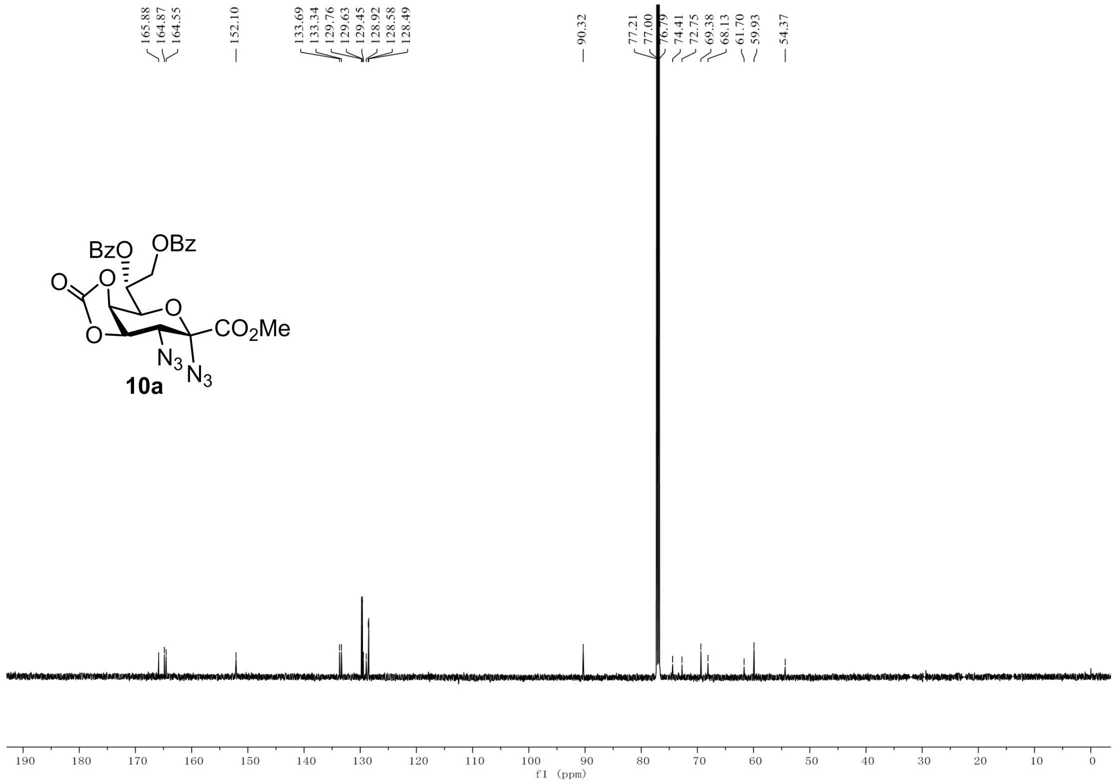
^{1}H NMR spectrum of compound **9b**



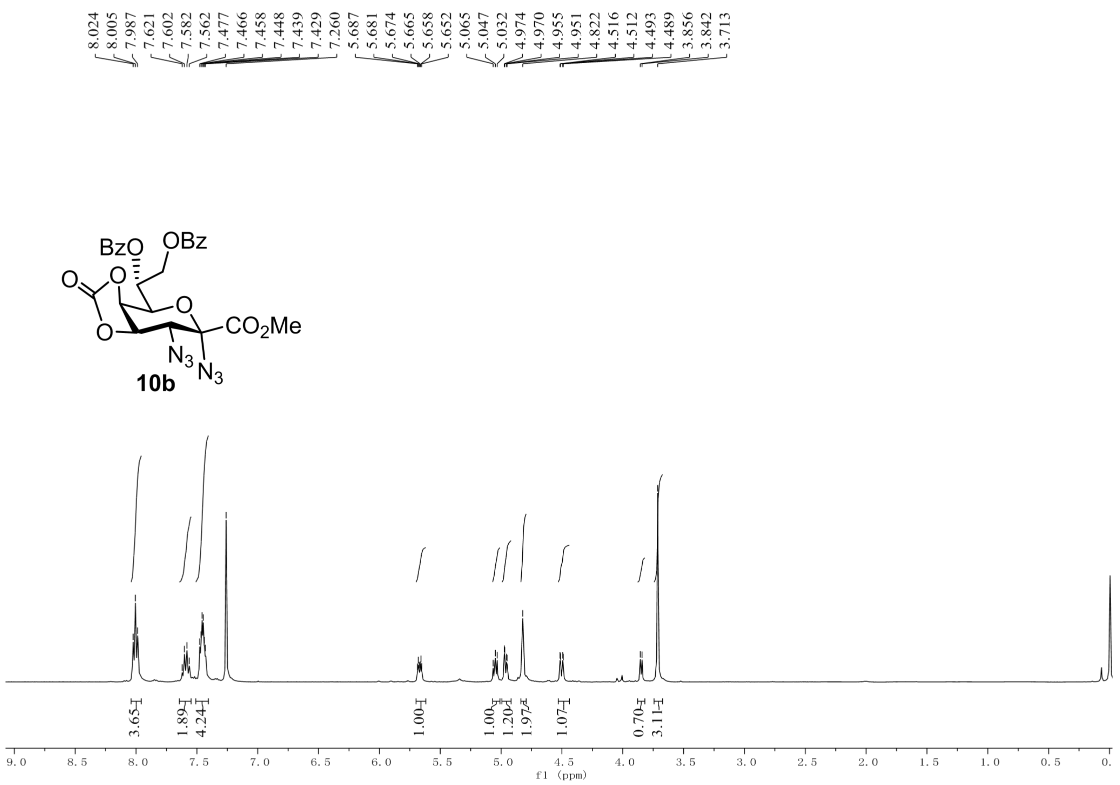
^{13}C NMR spectrum of compound **9b**



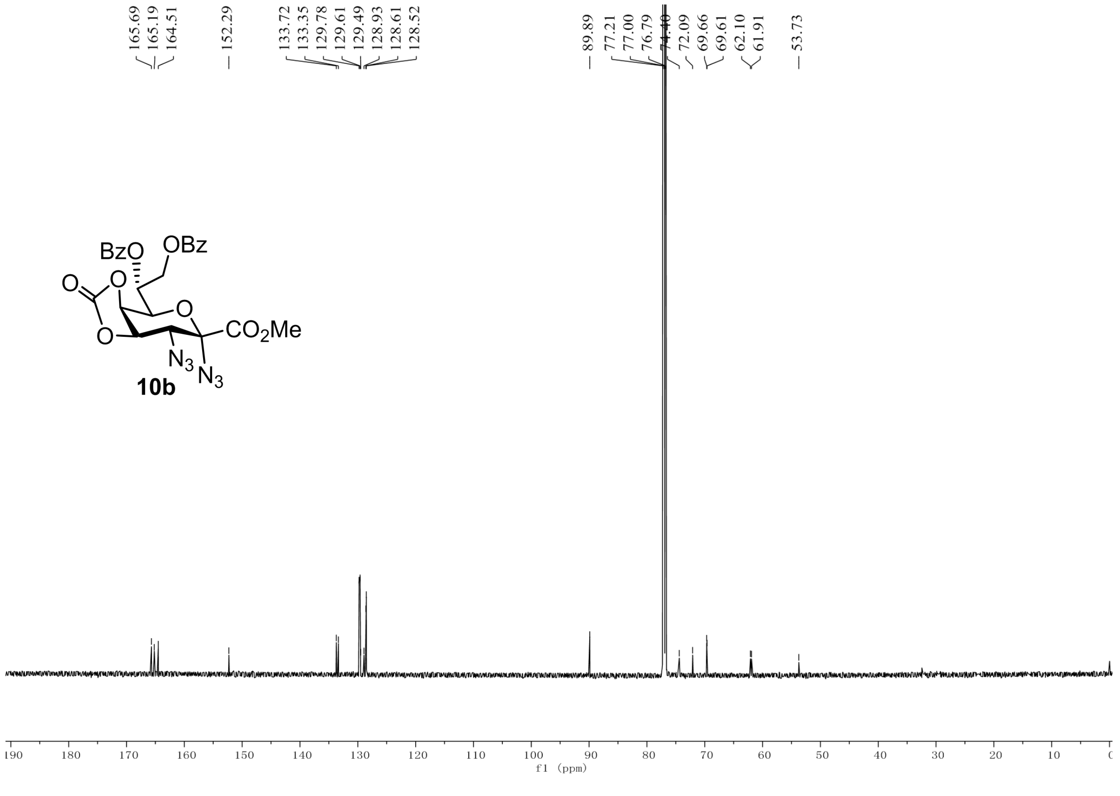
^{1}H NMR spectrum of compound **10a**



^{13}C NMR spectrum of compound **10a**



^{1}H NMR spectrum of compound **10b**



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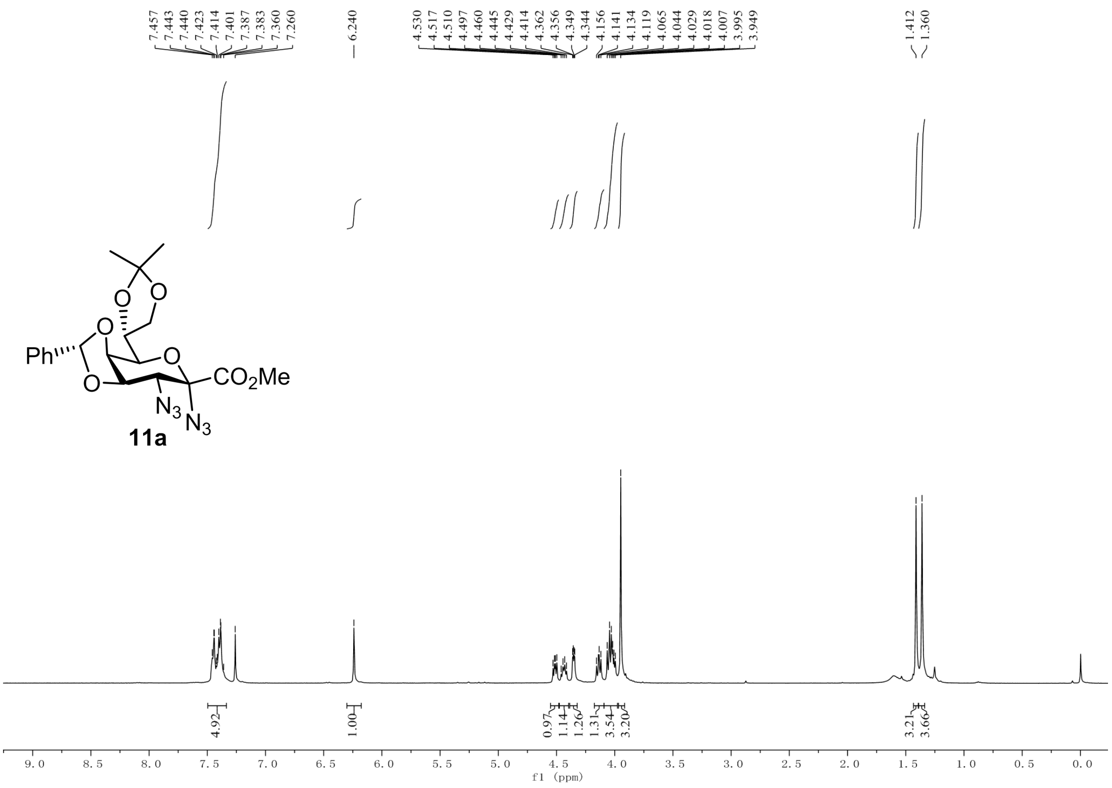
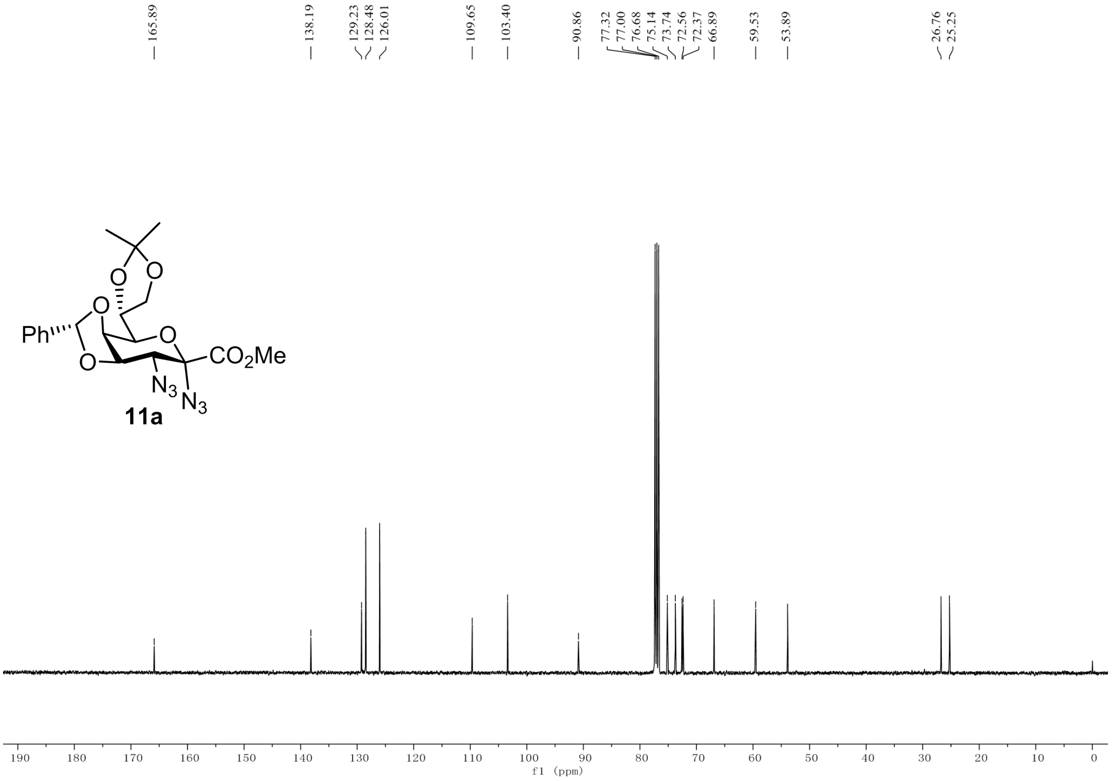
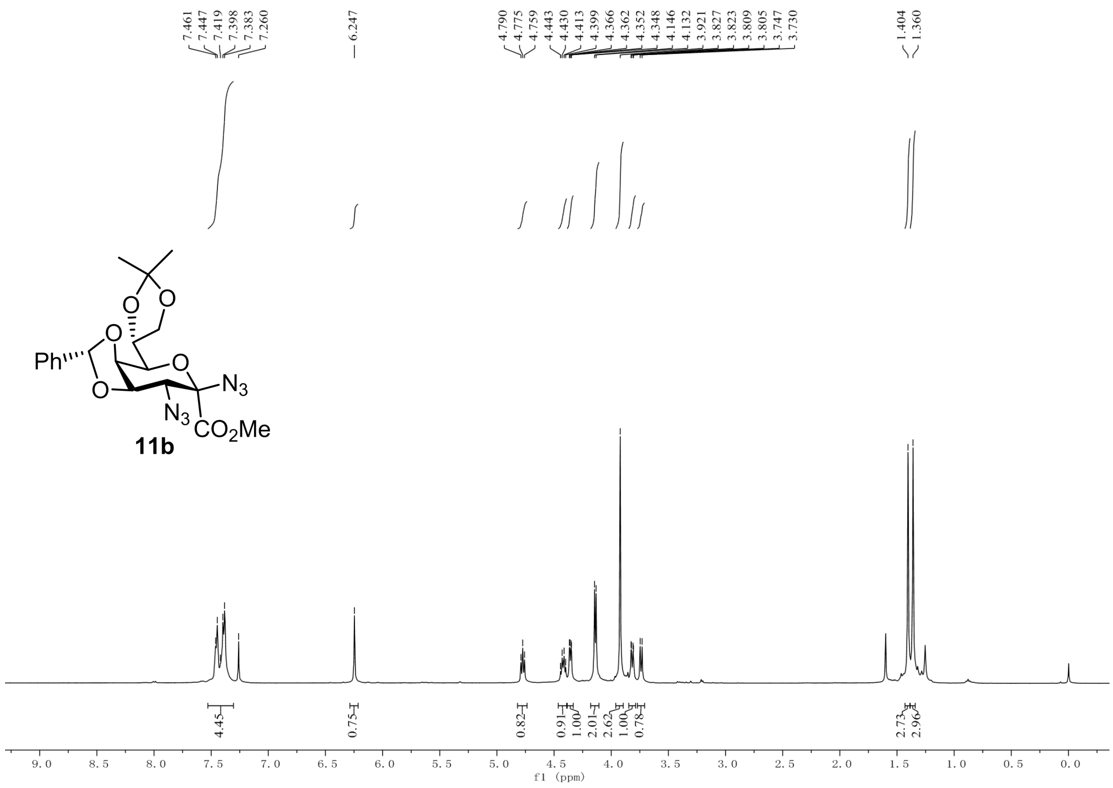


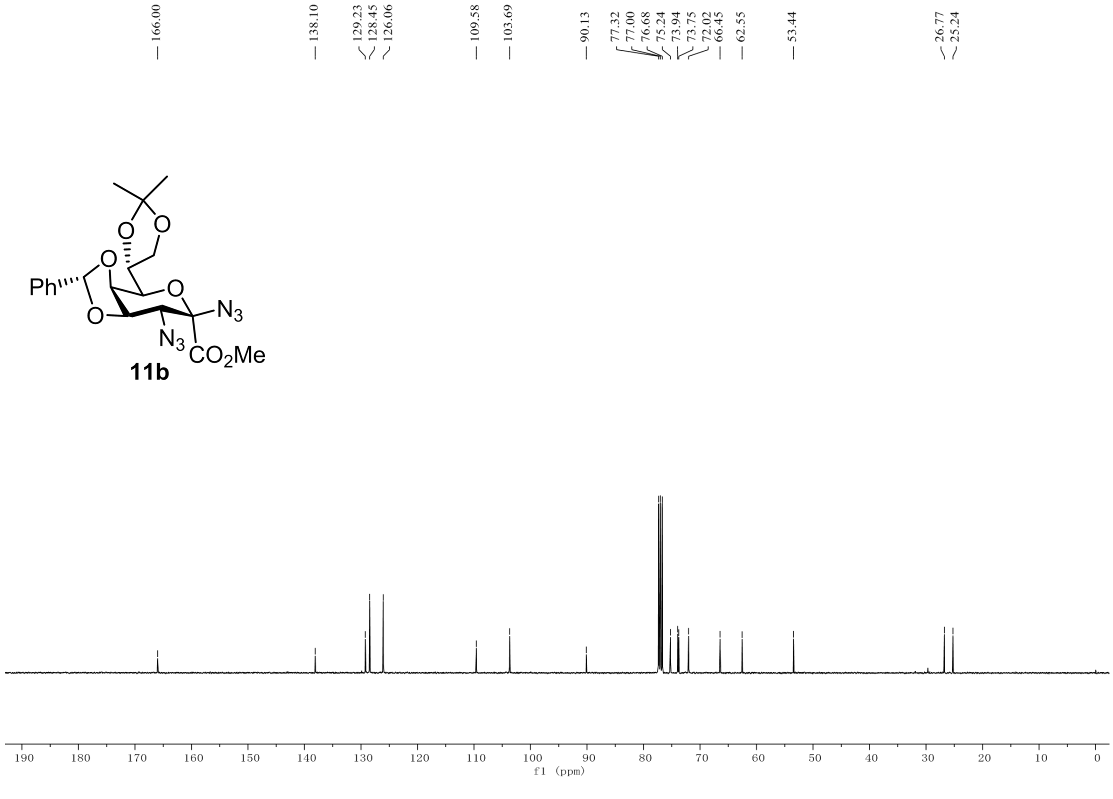
^{1}H NMR spectrum of compound **11a**



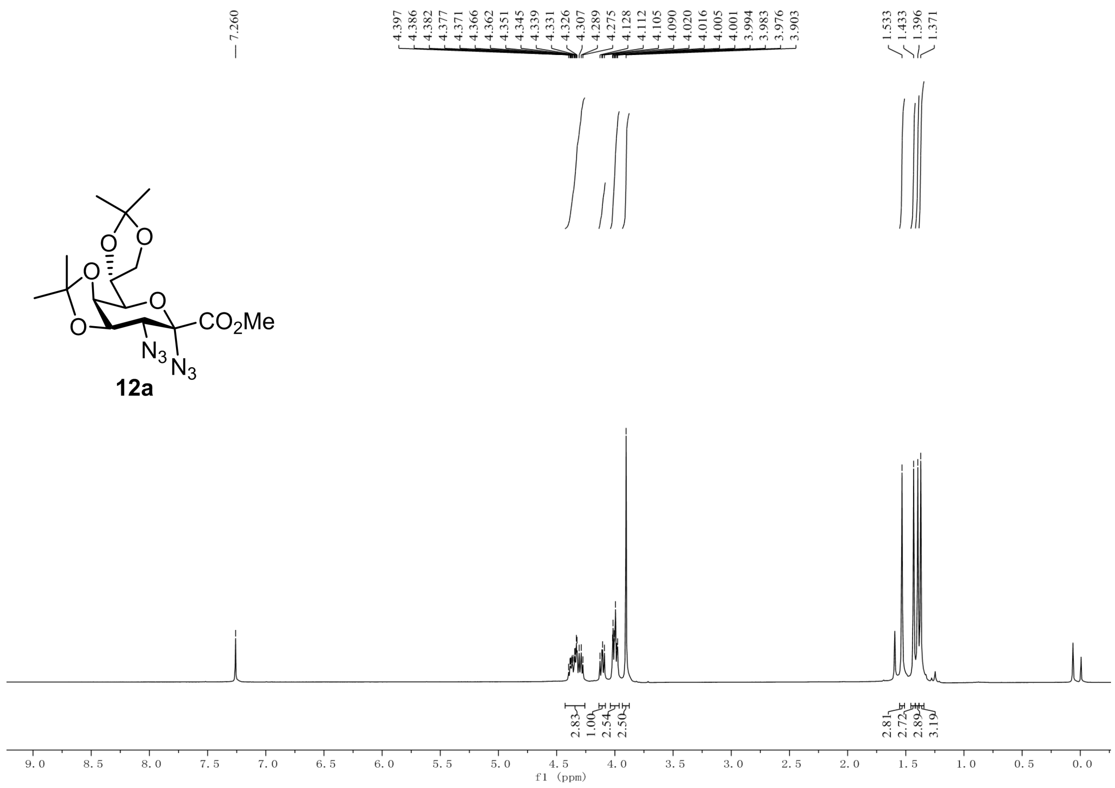
^{13}C NMR spectrum of compound **11a**



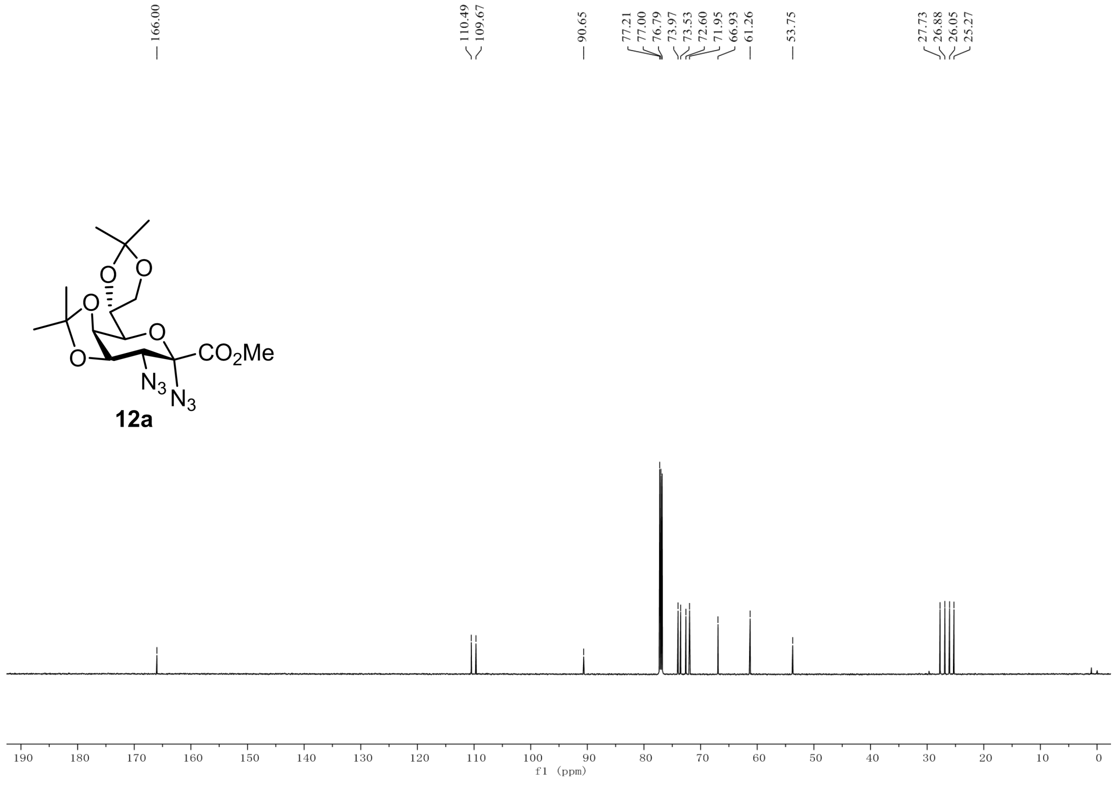
^{1}H NMR spectrum of compound **11b**



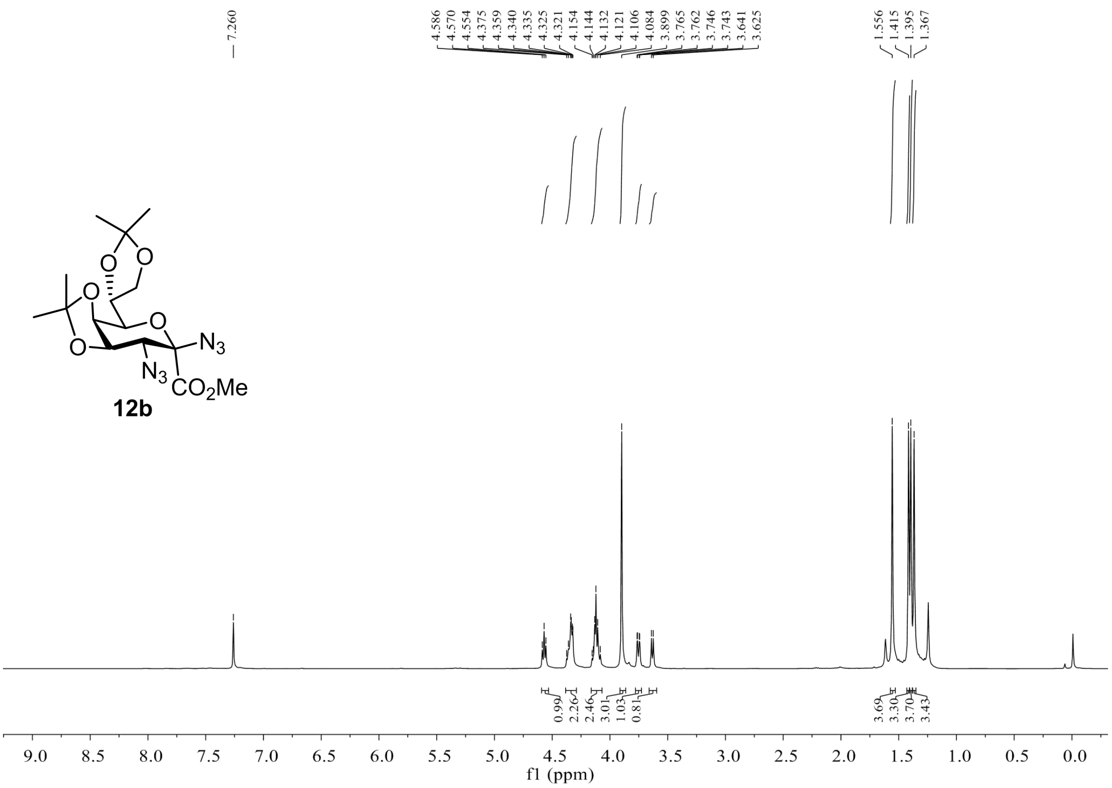
^{13}C NMR spectrum of compound **11b**



^{1}H NMR spectrum of compound **12a**



^{13}C NMR spectrum of compound **12a**



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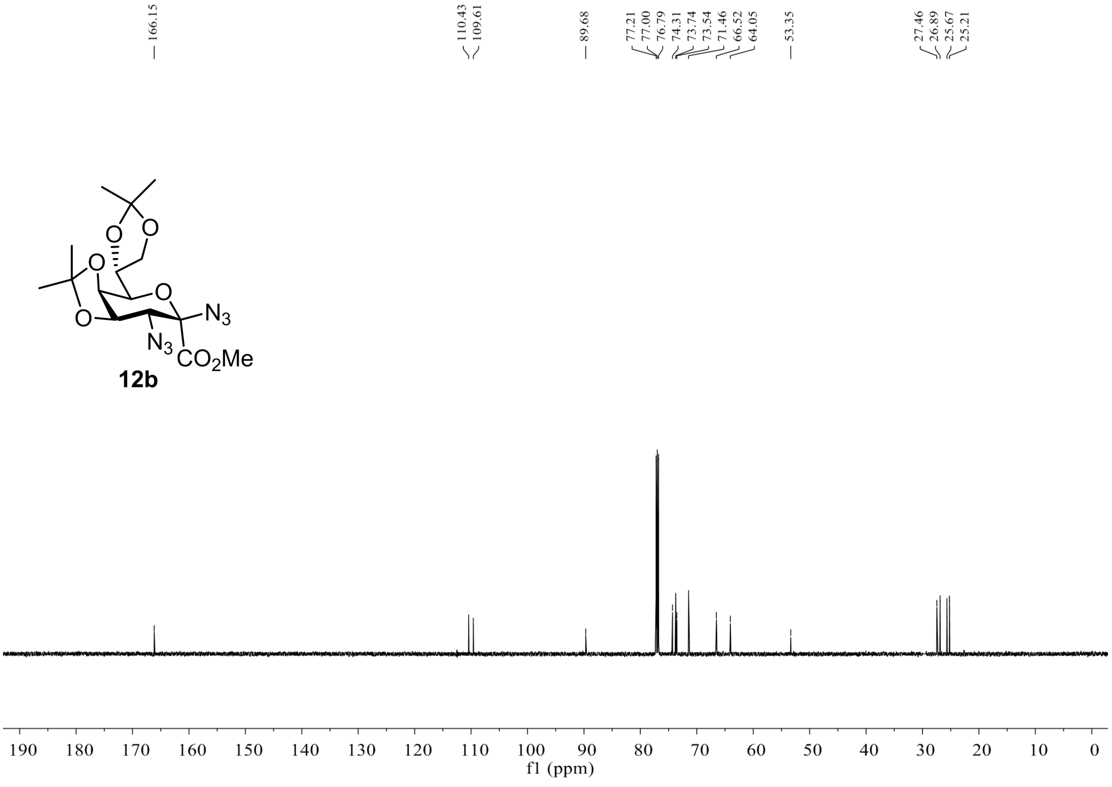

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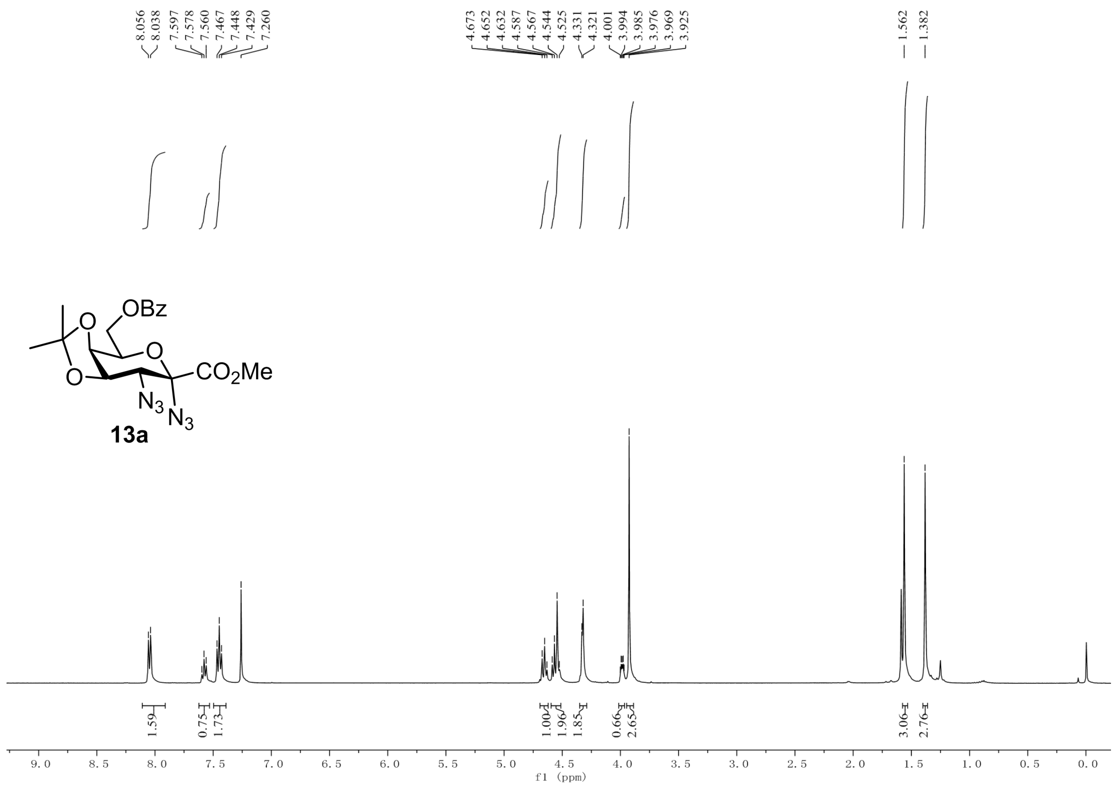
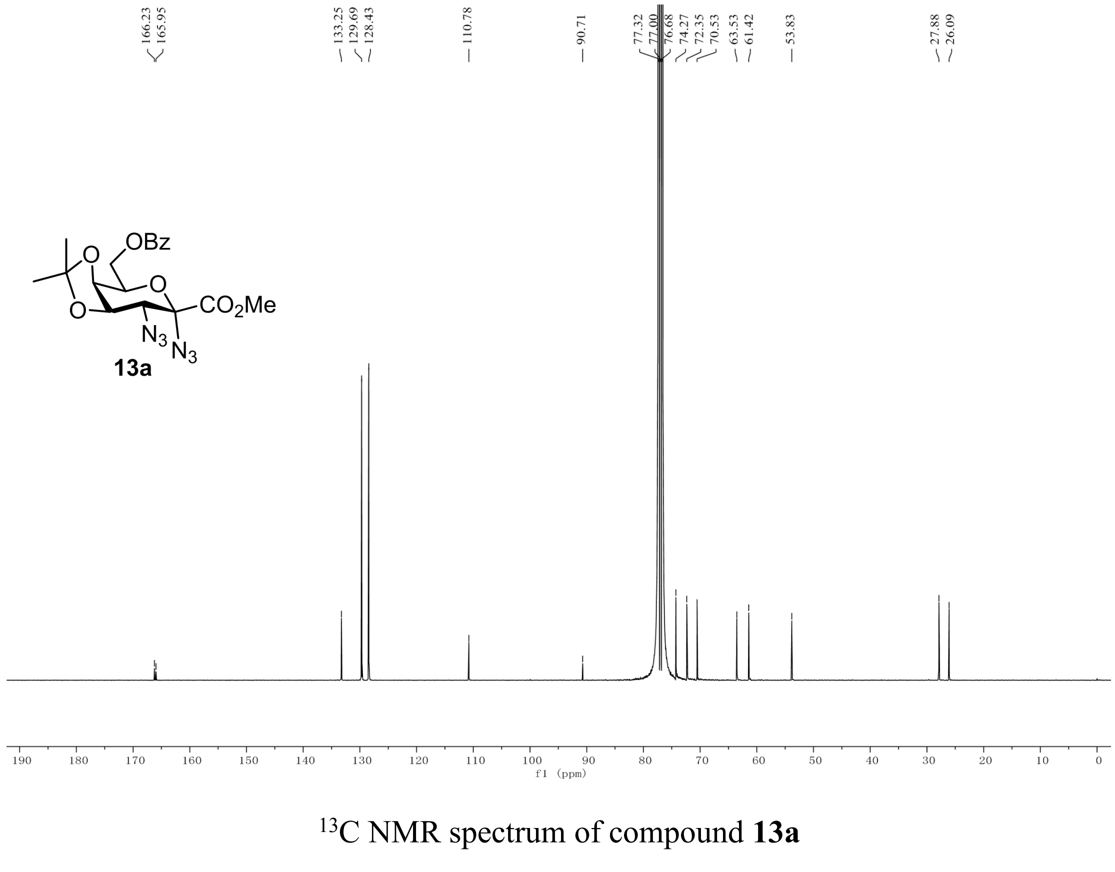
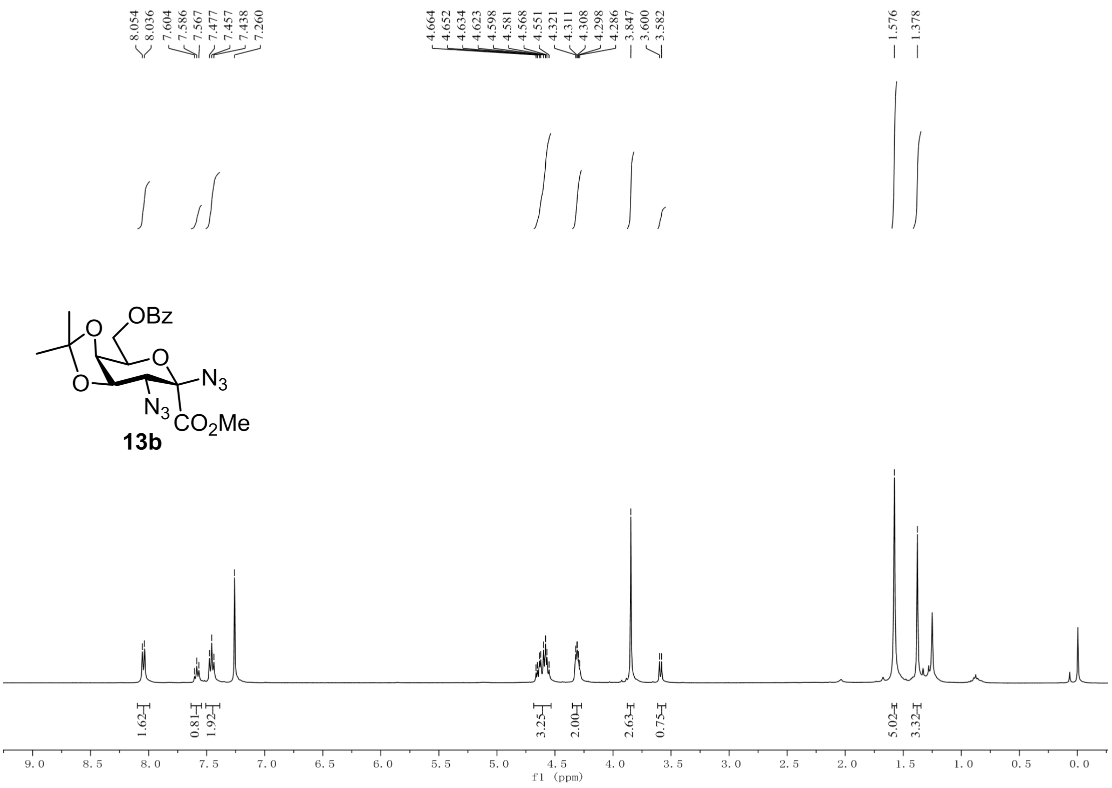


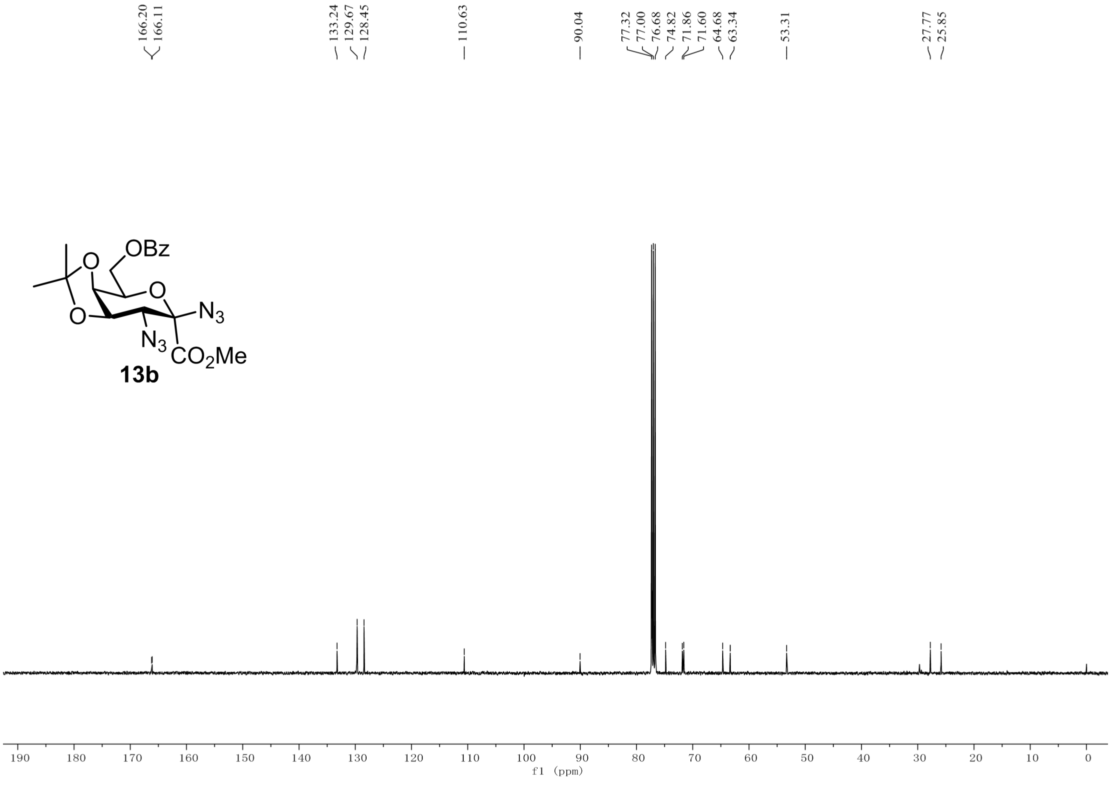
^{1}H NMR spectrum of compound **13a**



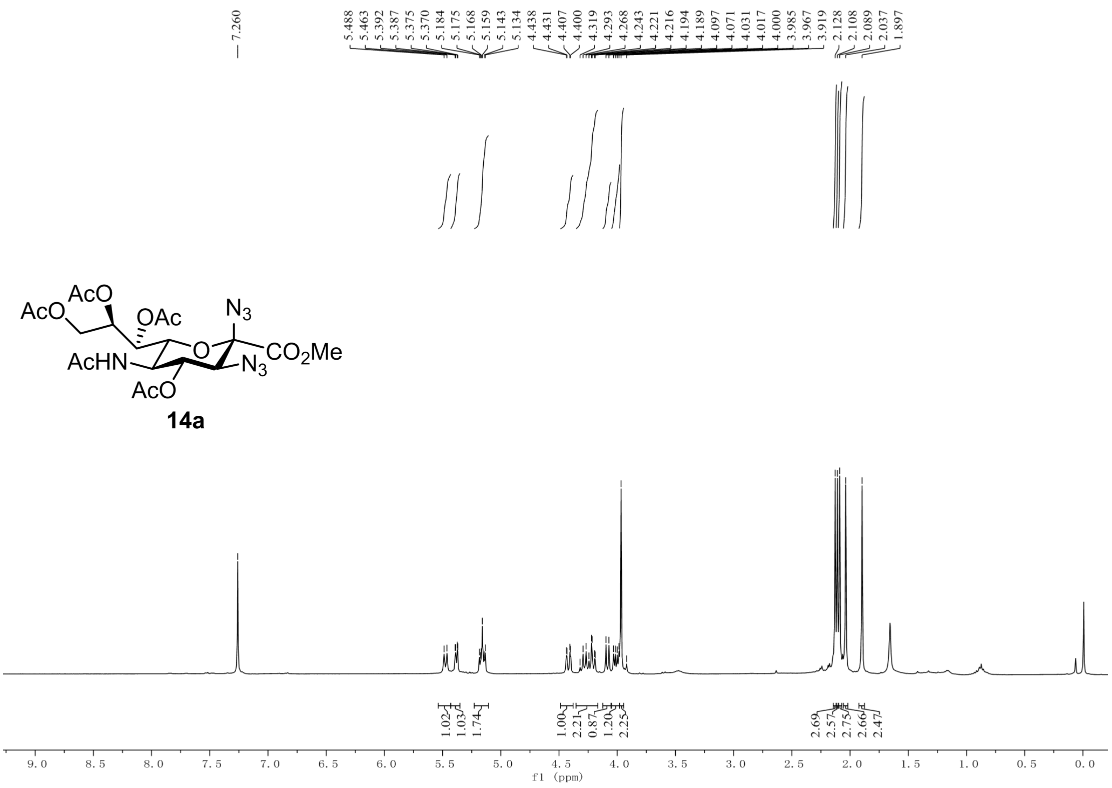
^{13}C NMR spectrum of compound **13a**



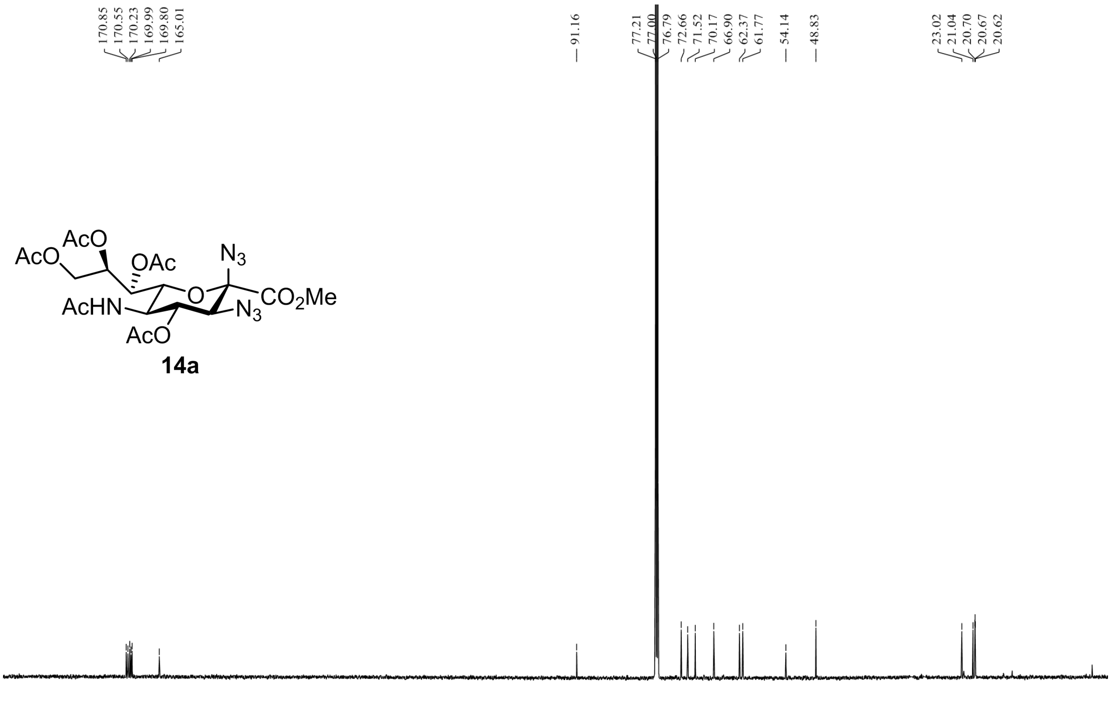
^{1}H NMR spectrum of compound **13b**



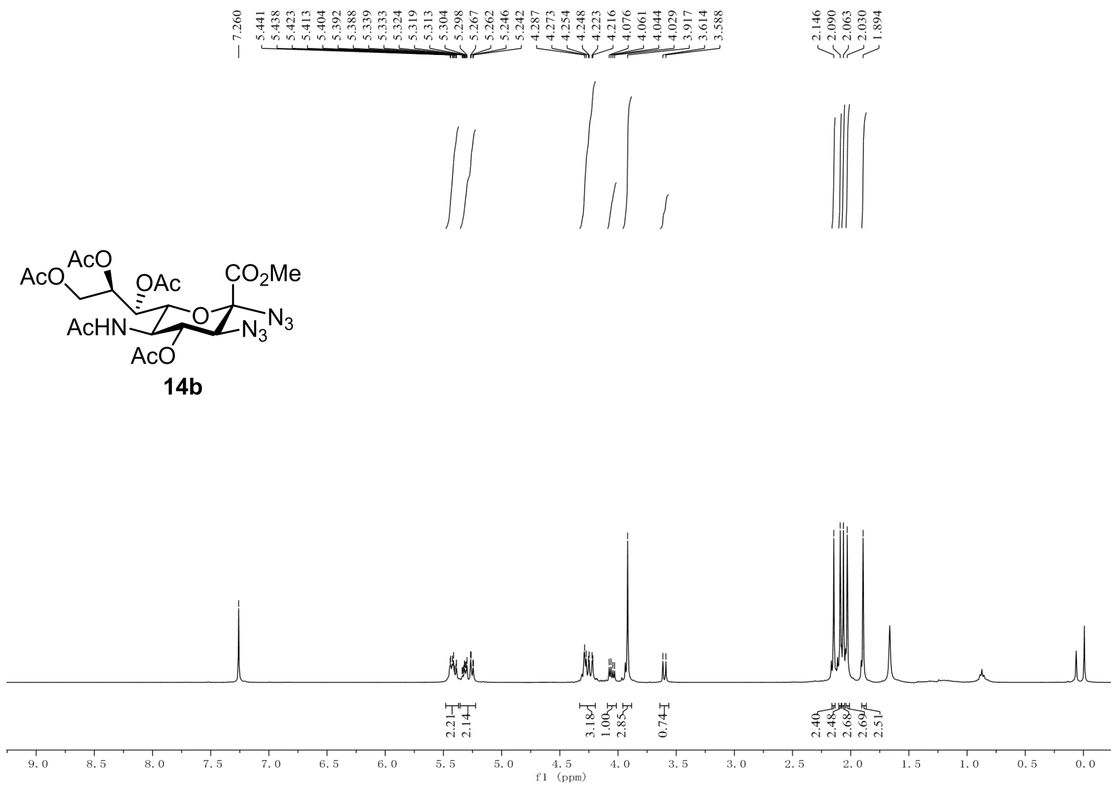
^{13}C NMR spectrum of compound **13b**



^{1}H NMR spectrum of compound **14a**



^{13}C NMR spectrum of compound **14a**



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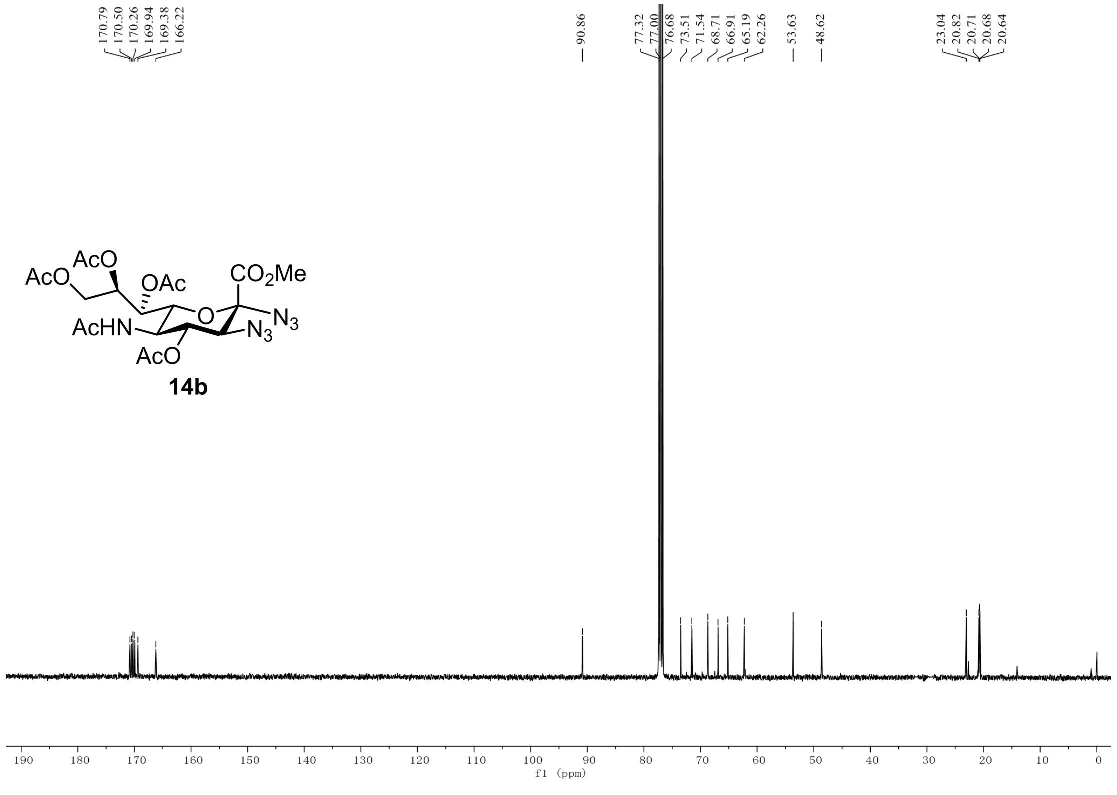

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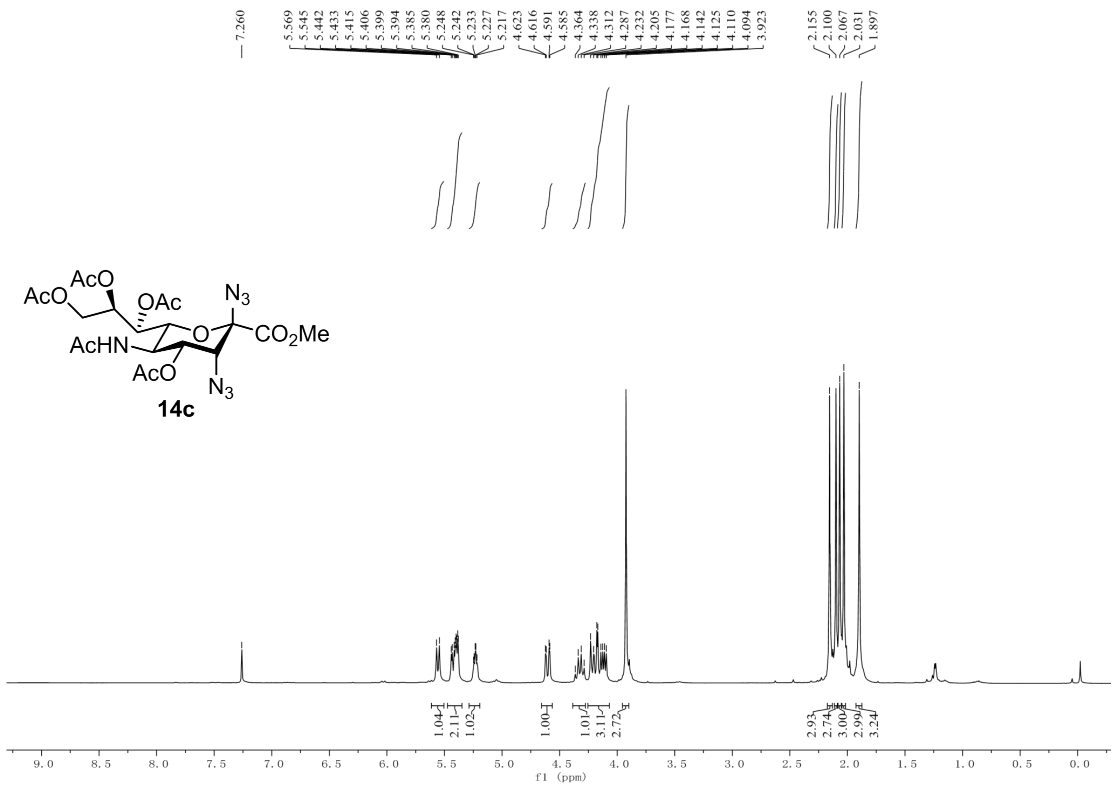
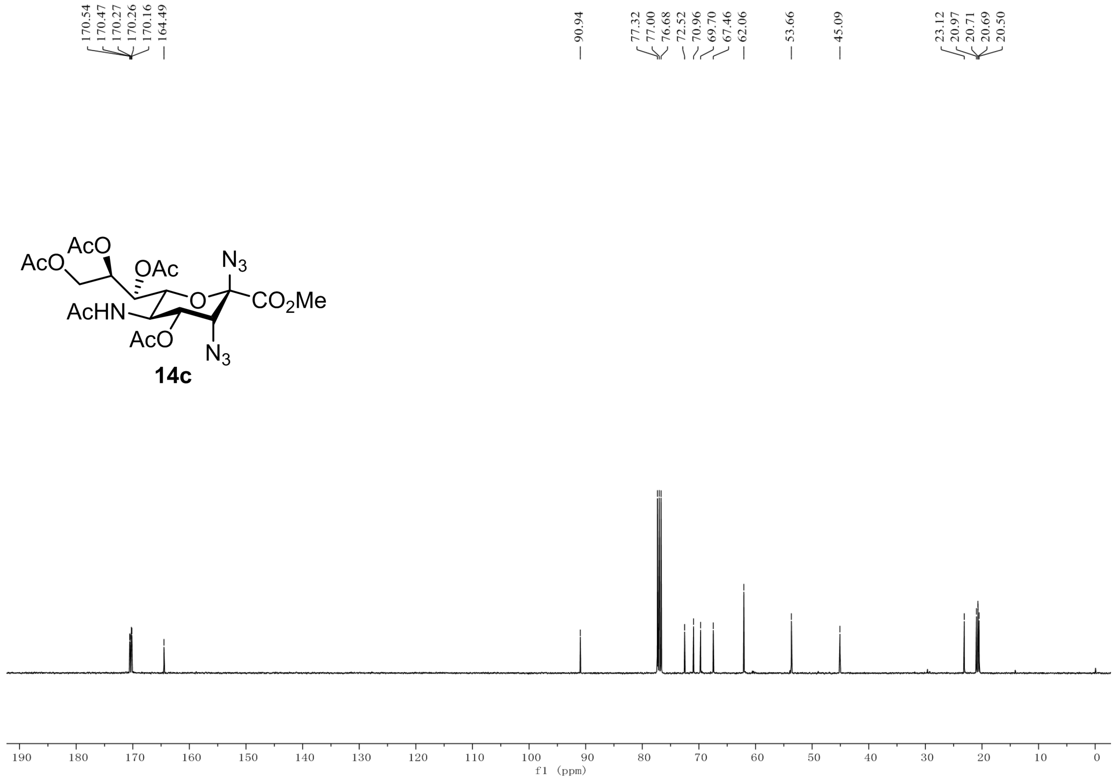
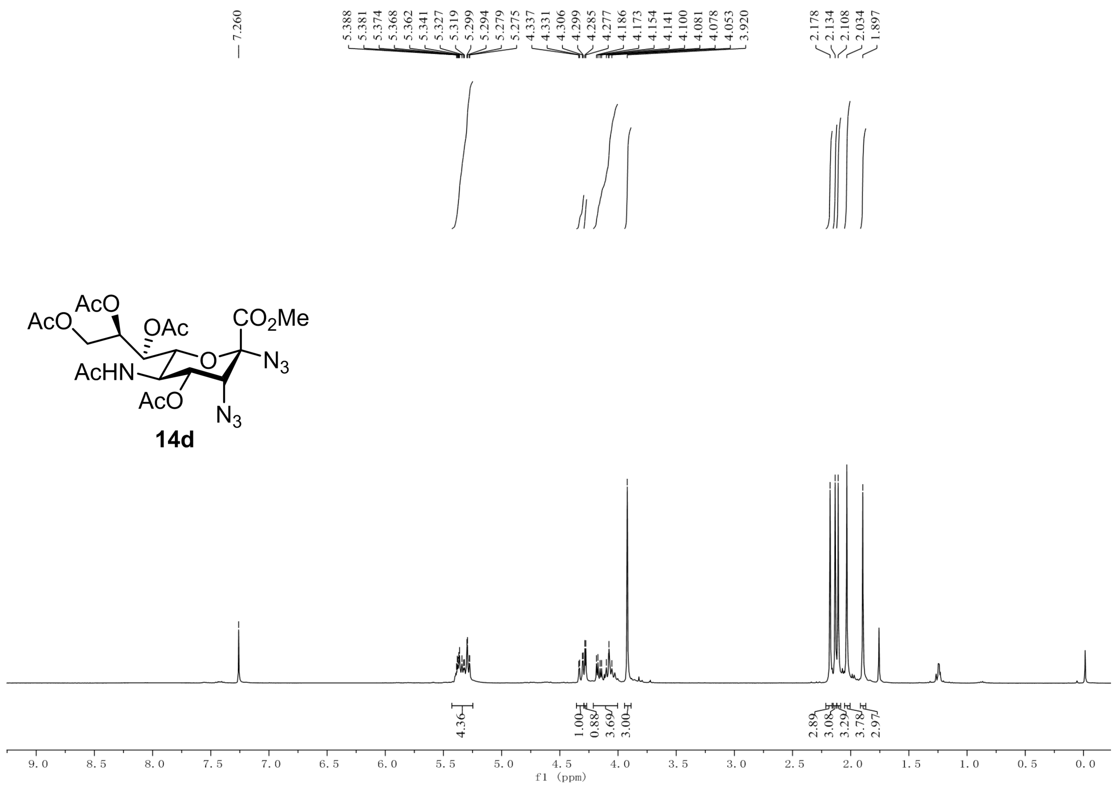


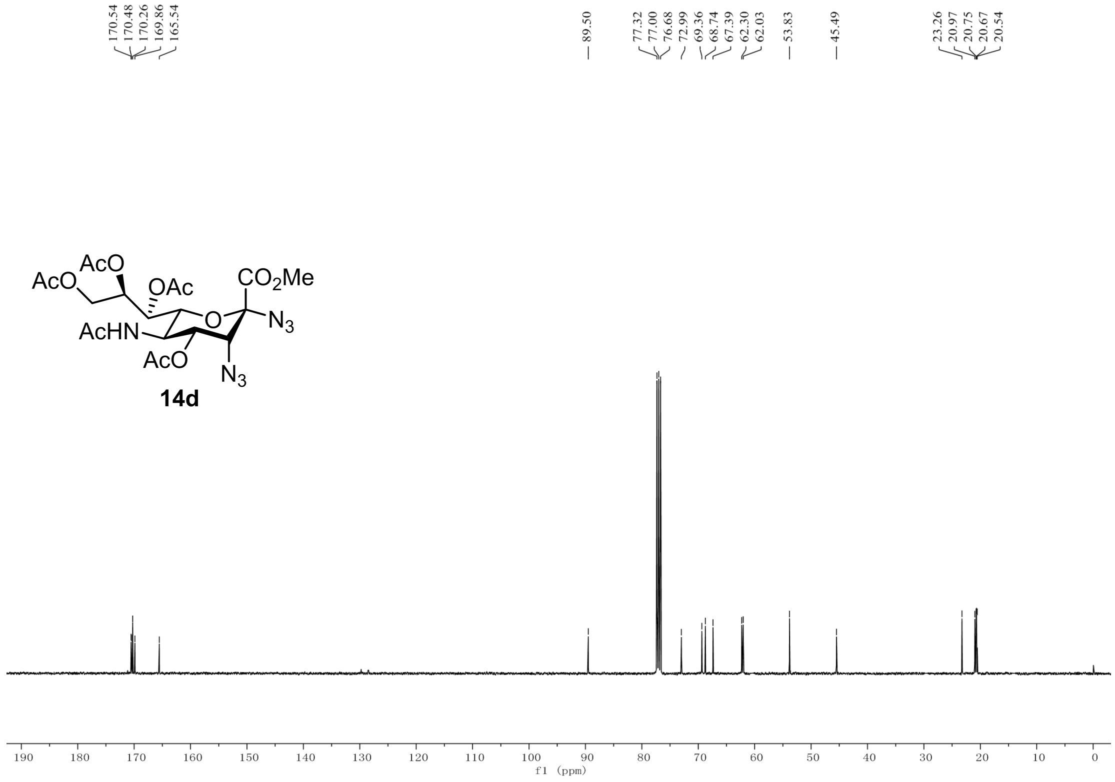
^{1}H NMR spectrum of compound **14c**



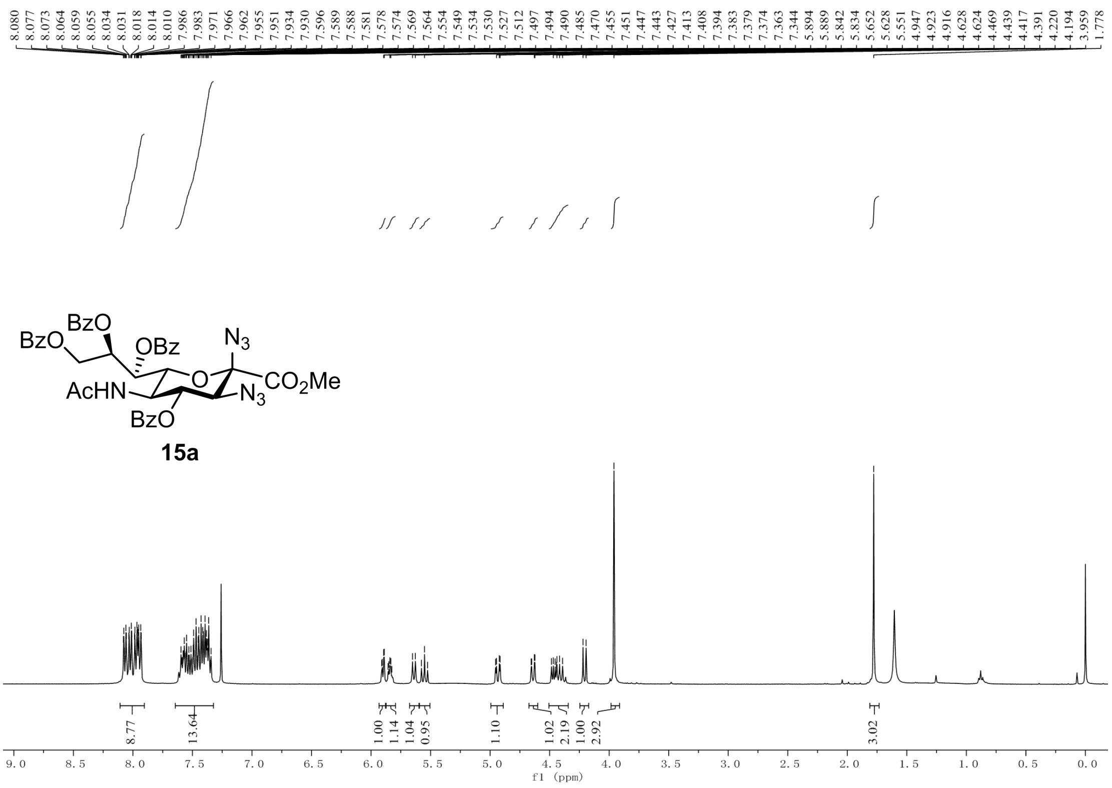
^{13}C NMR spectrum of compound **14c**



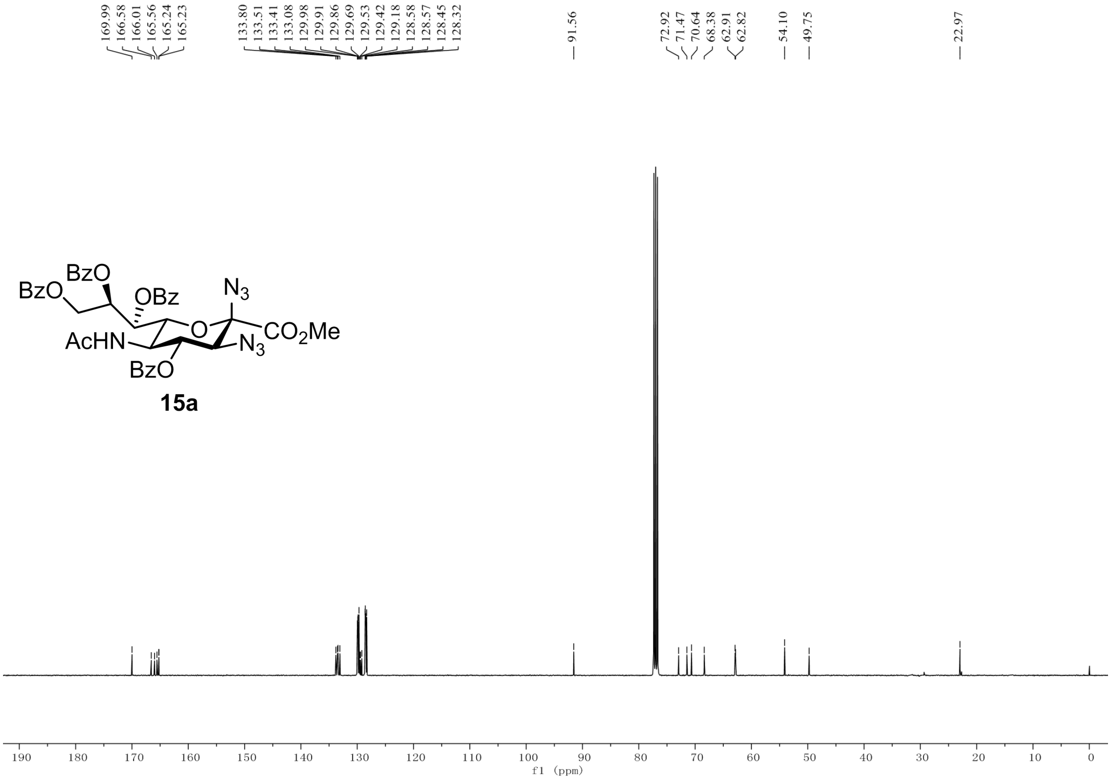
^{1}H NMR spectrum of compound **14d**



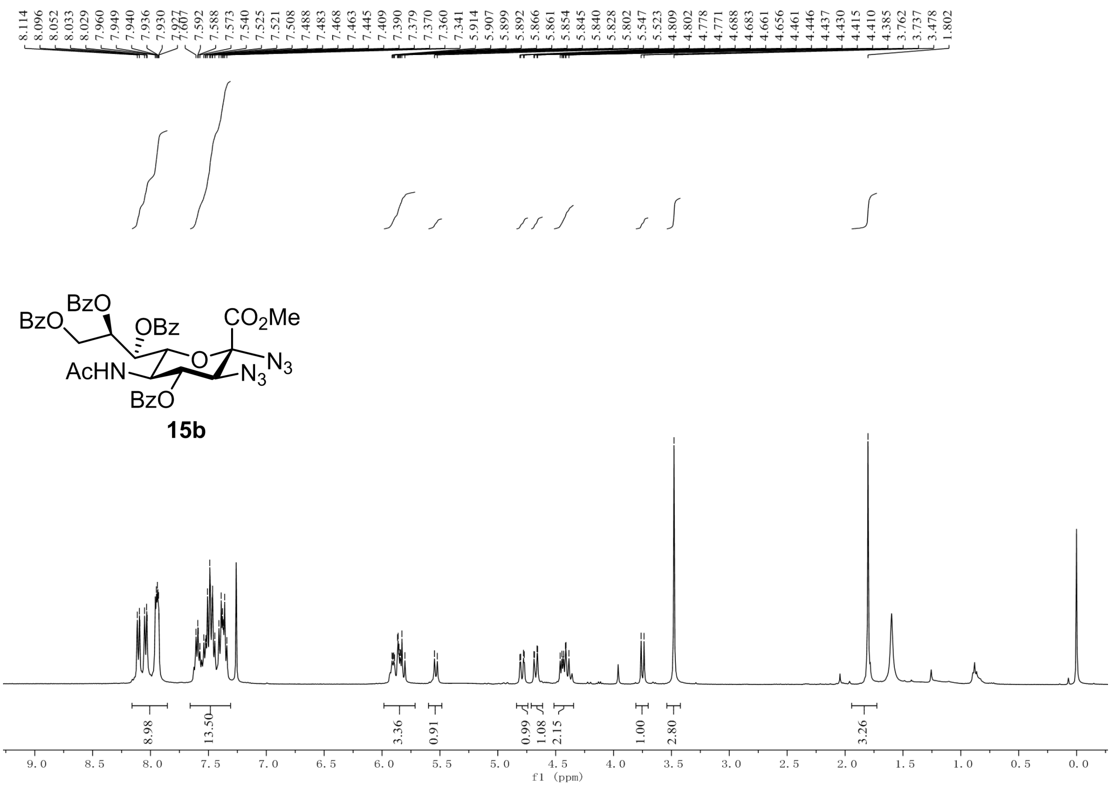
^{13}C NMR spectrum of compound **14d**



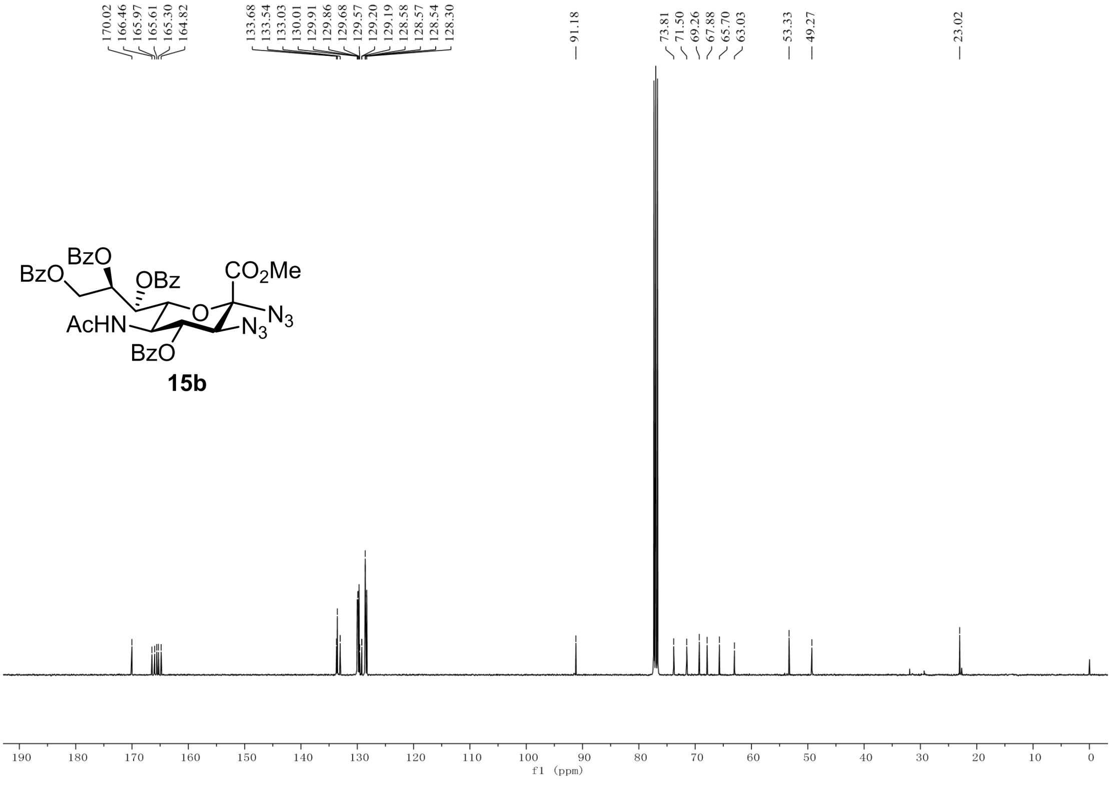
^{1}H NMR spectrum of compound **15a**



^{13}C NMR spectrum of compound **15a**



^{1}H NMR spectrum of compound **15b**



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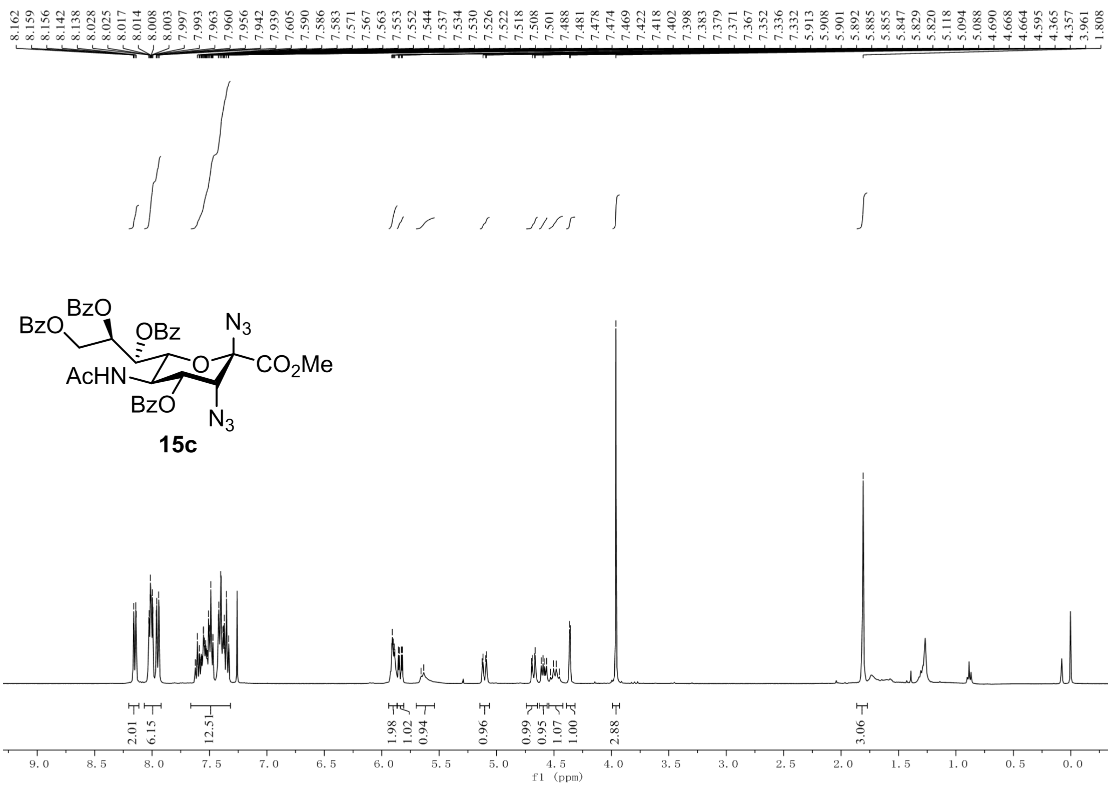
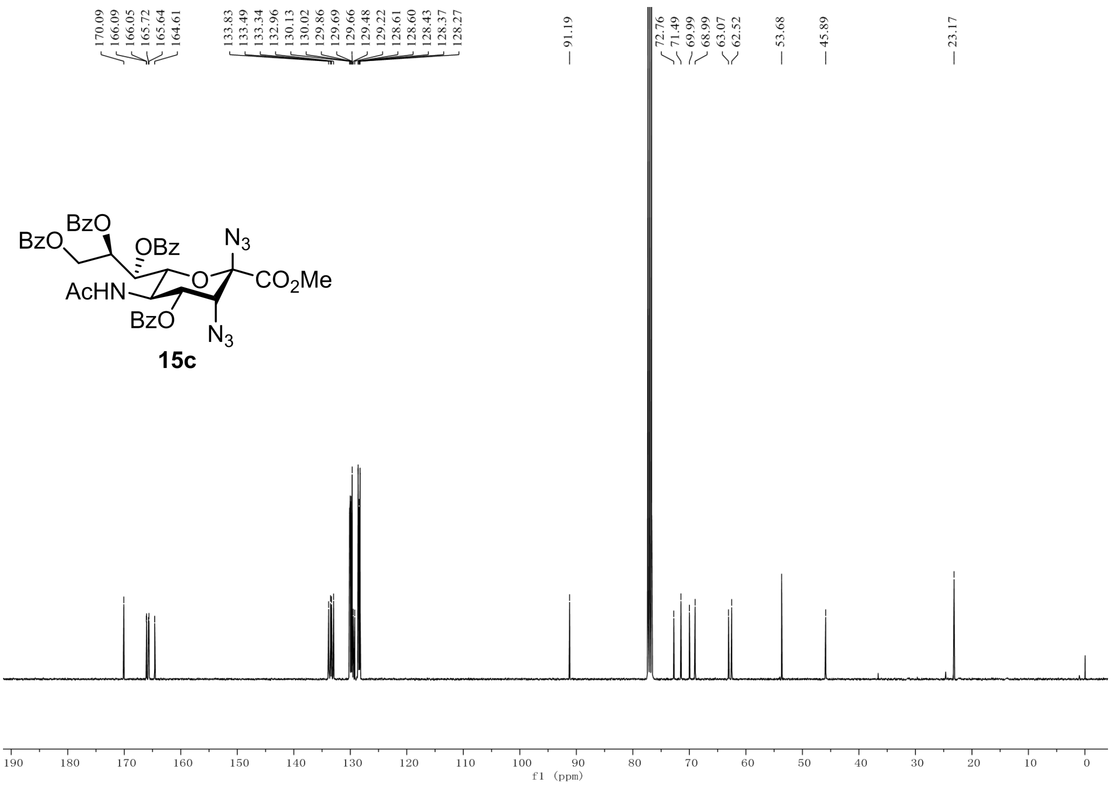


^{1}H NMR spectrum of compound **15c**



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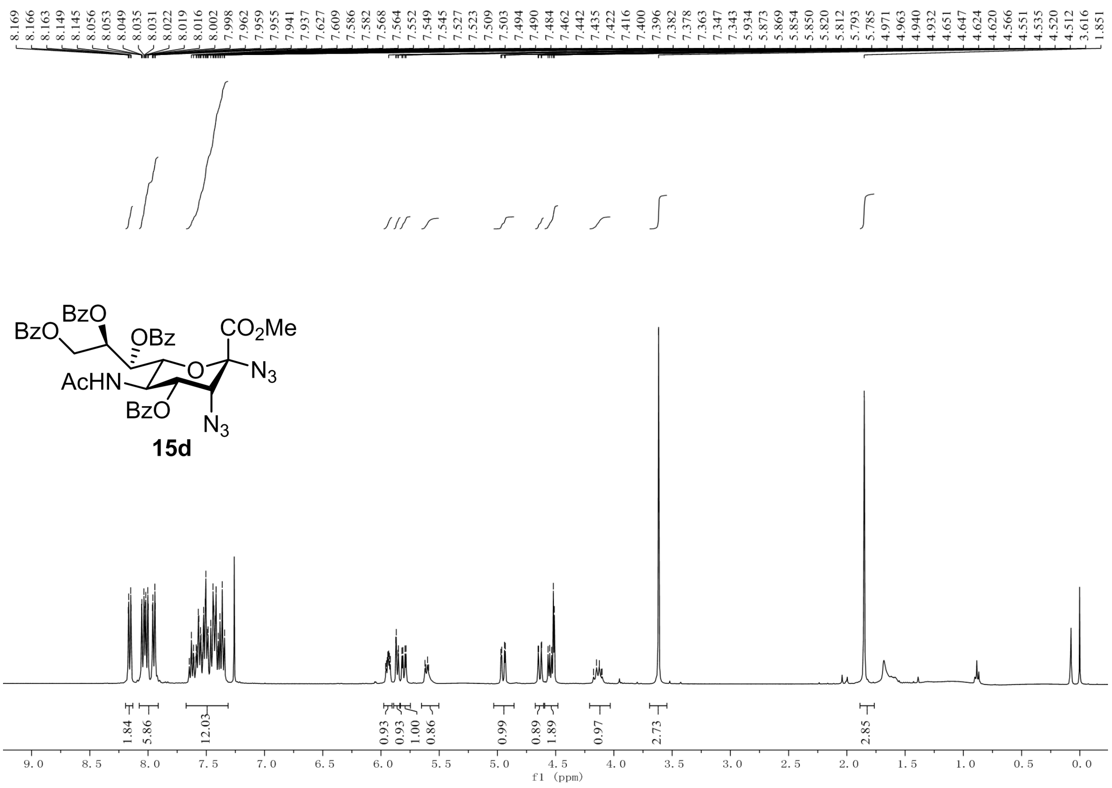

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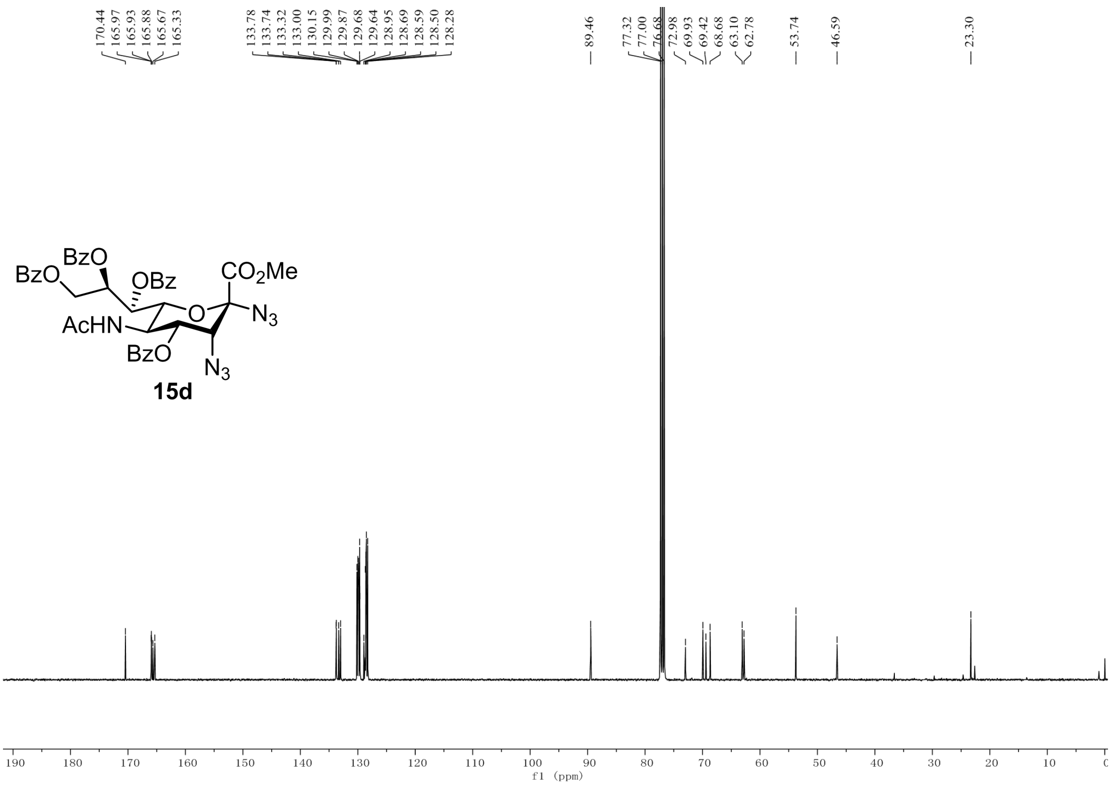
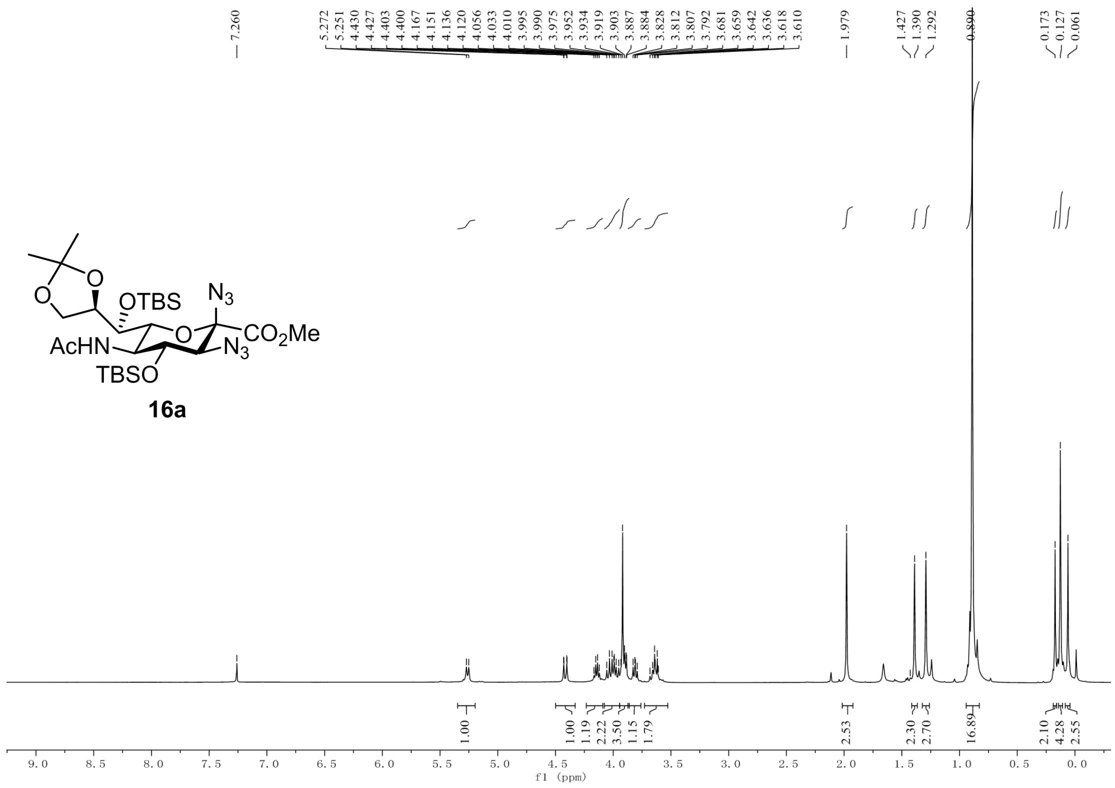
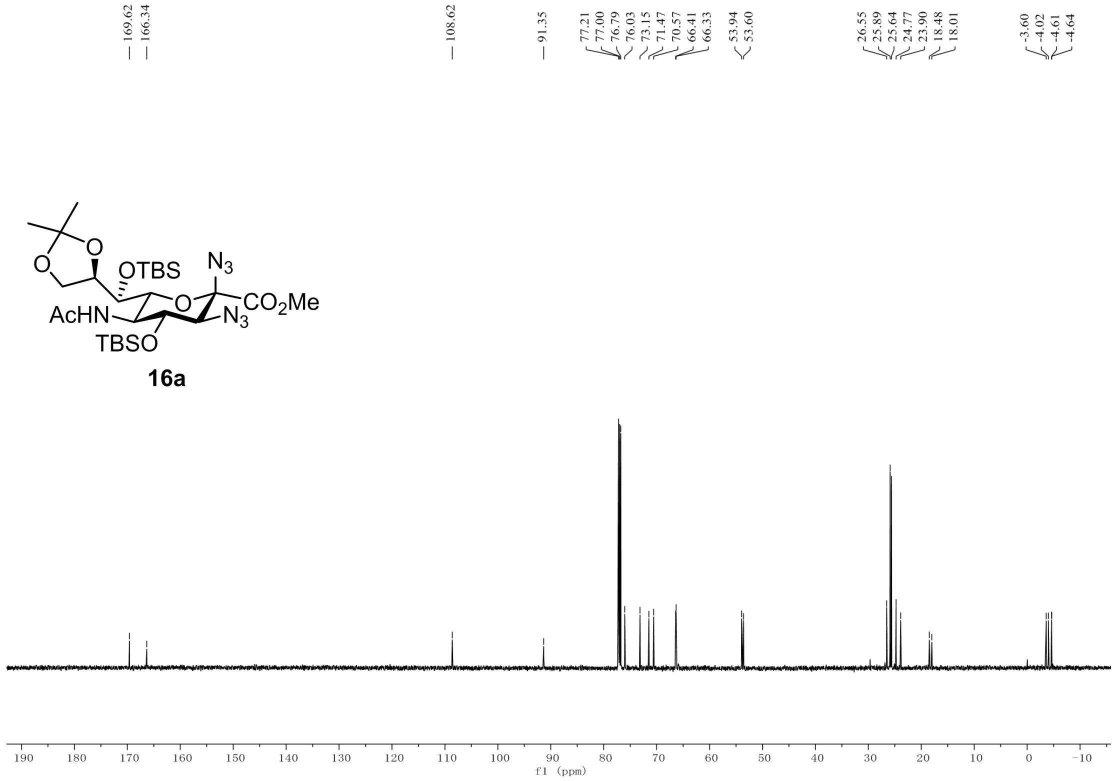


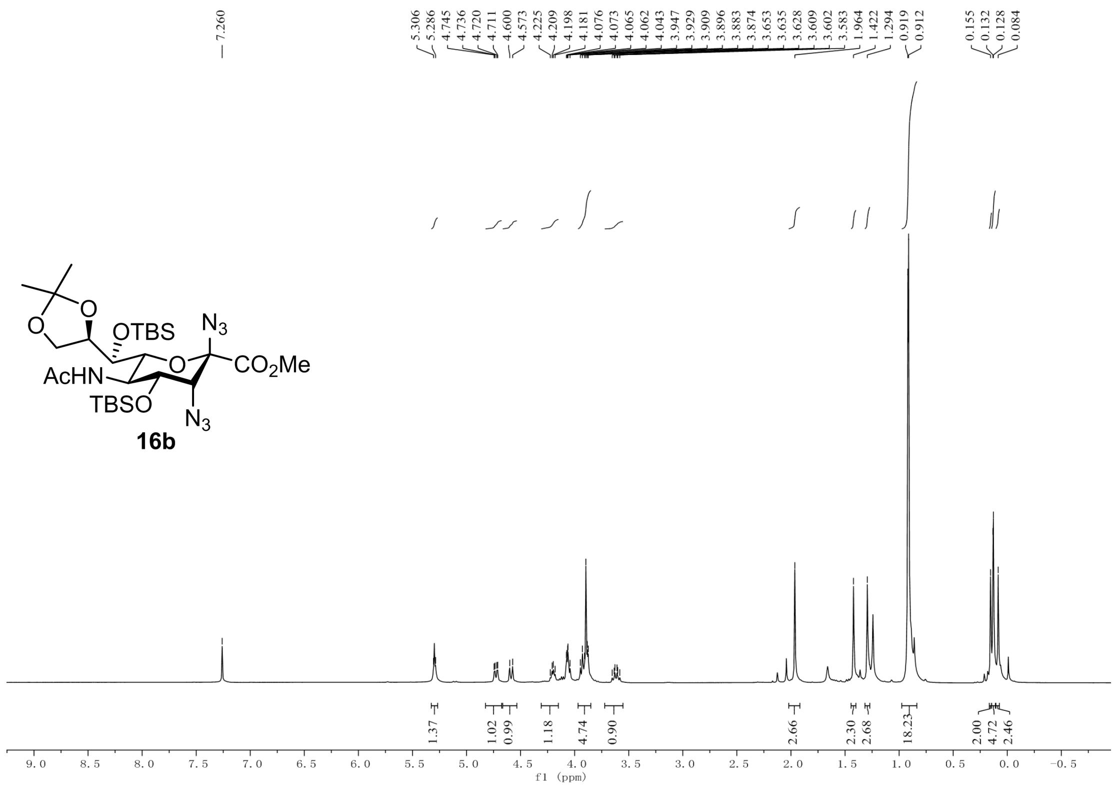
^{13}C NMR spectrum of compound **15d**



^{1}H NMR spectrum of compound **16a**



^{13}C NMR spectrum of compound **16a**



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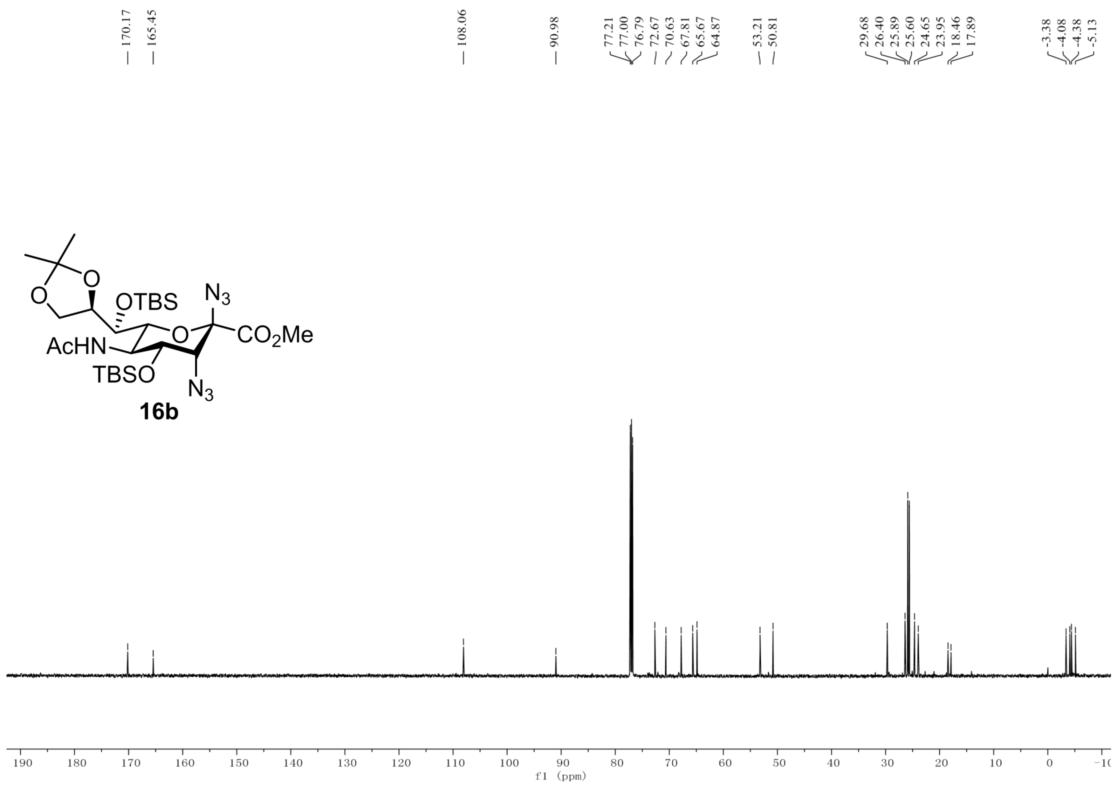
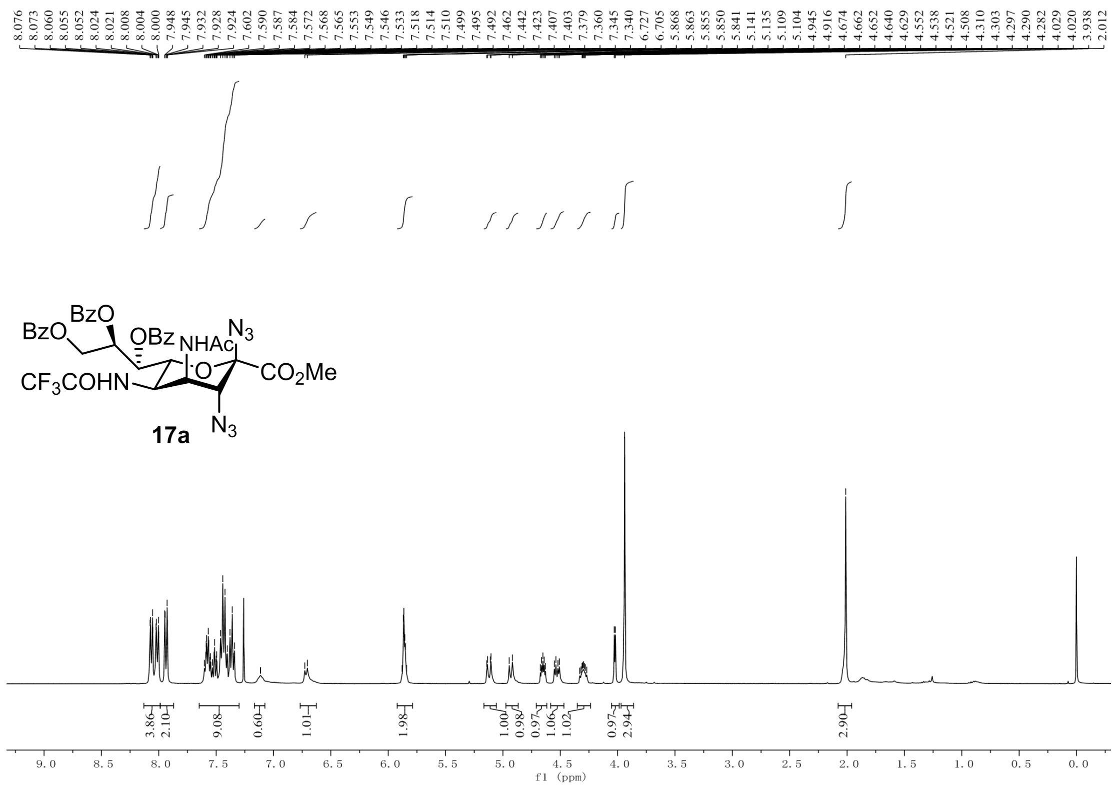
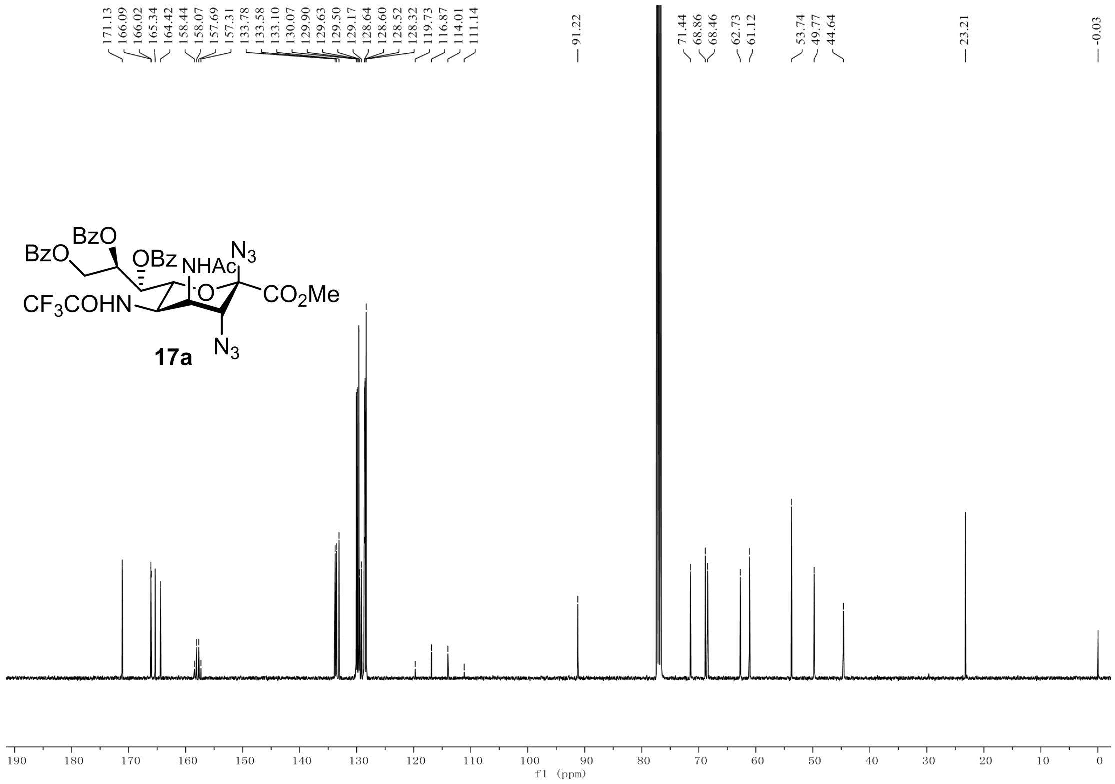


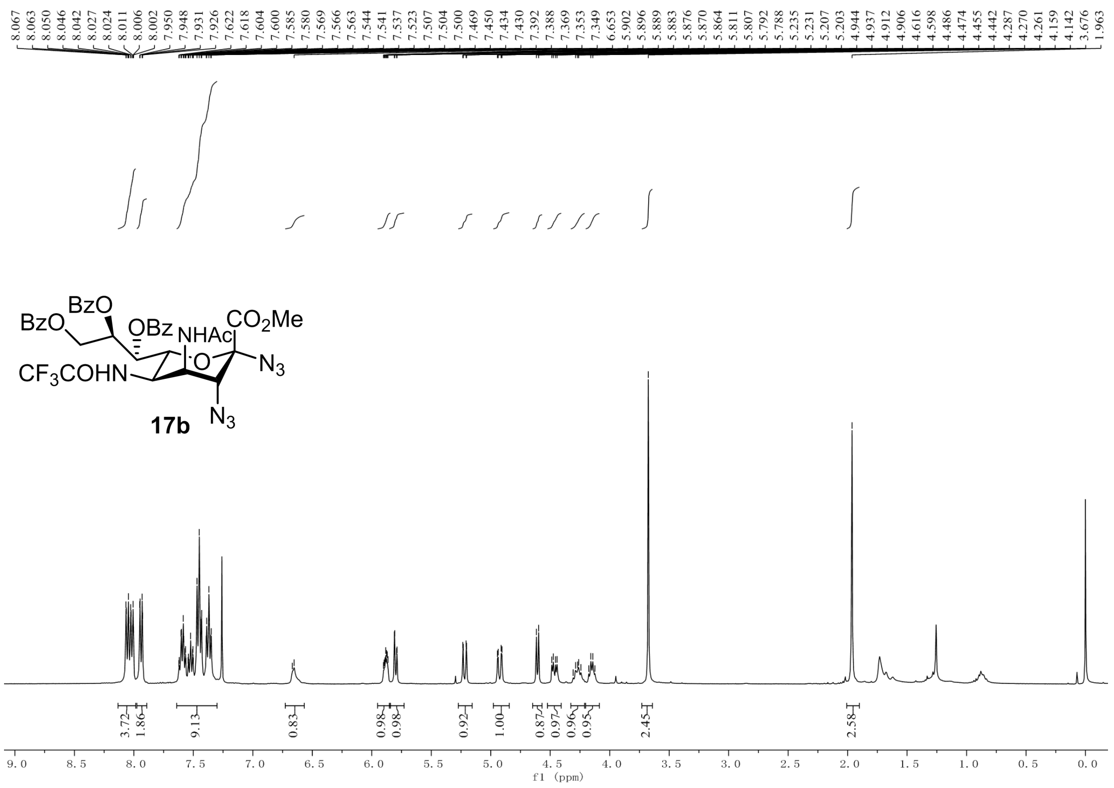
^{13}C NMR spectrum of compound **16b**



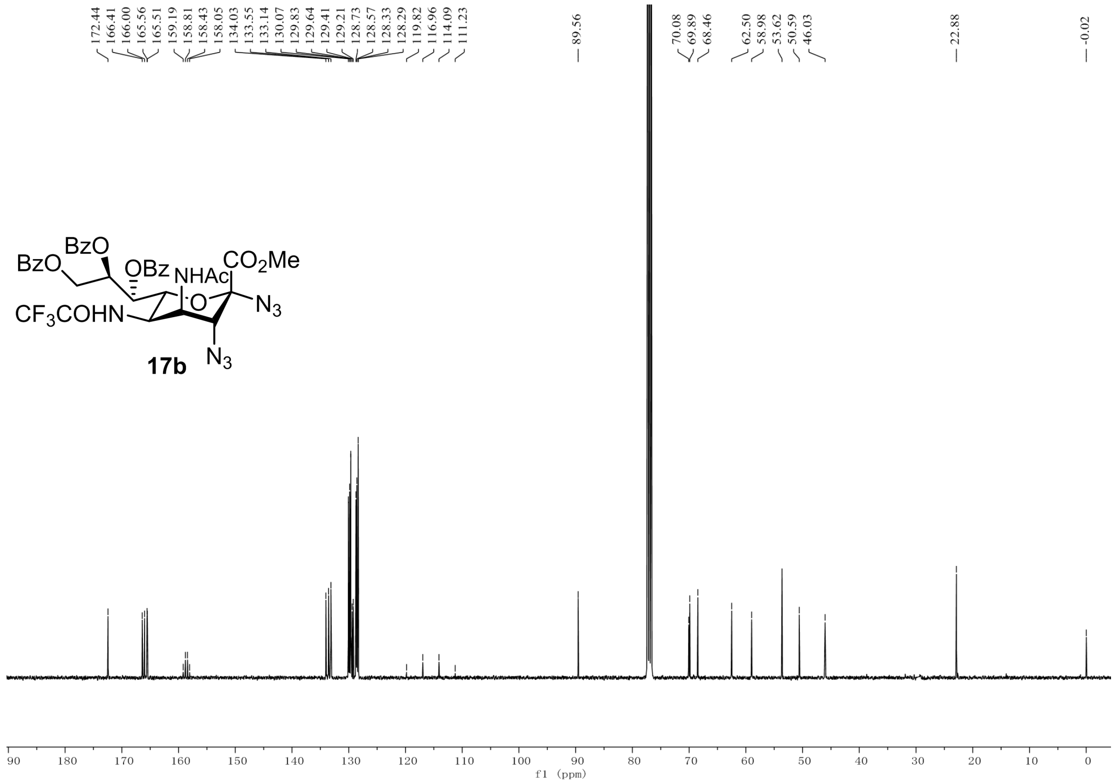
^{1}H NMR spectrum of compound **17a**



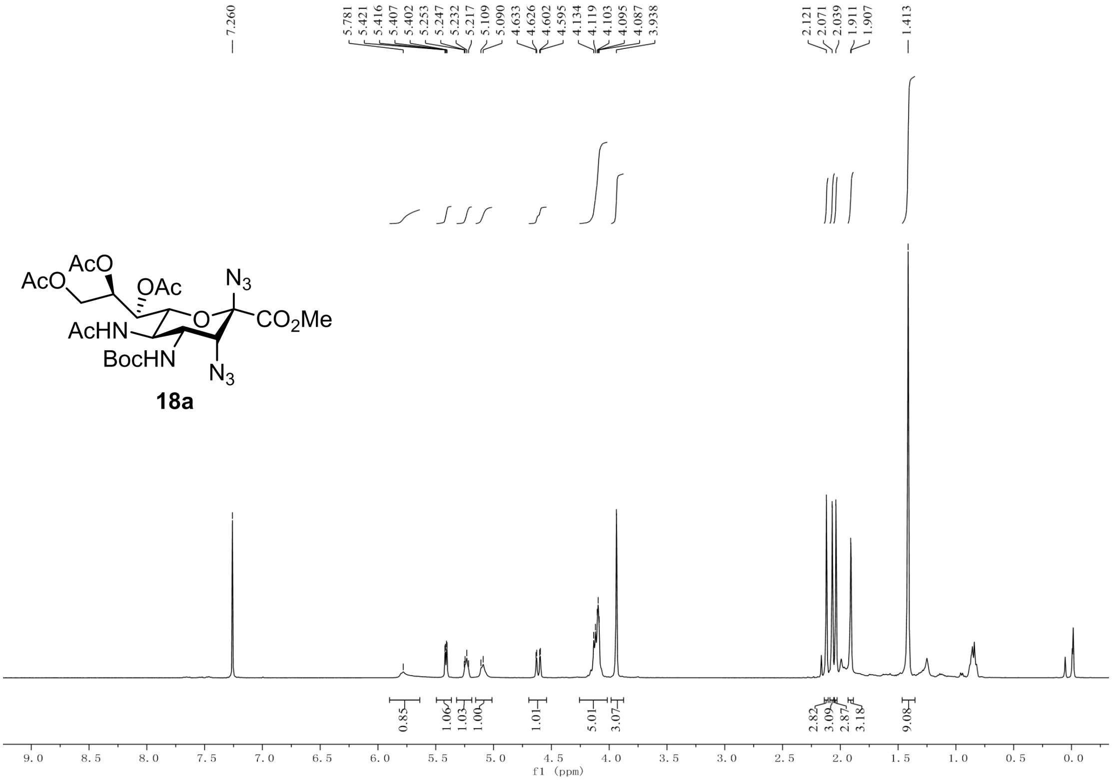
^{13}C NMR spectrum of compound **17a**



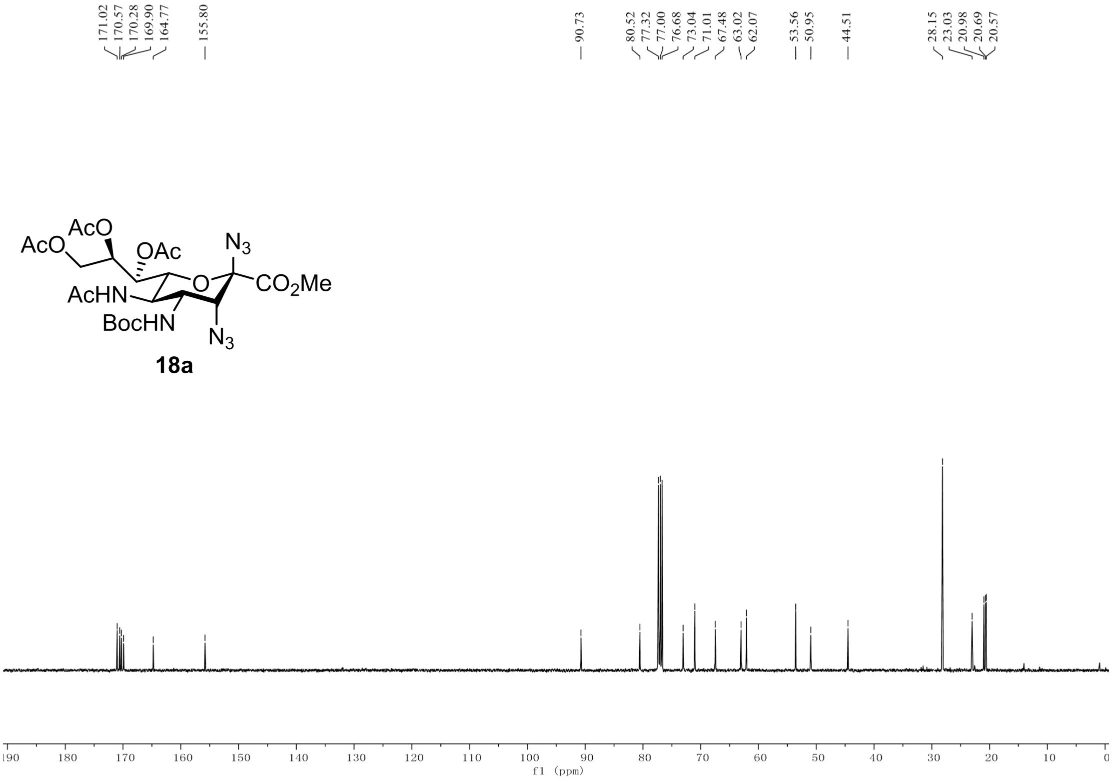
^{1}H NMR spectrum of compound **17b**



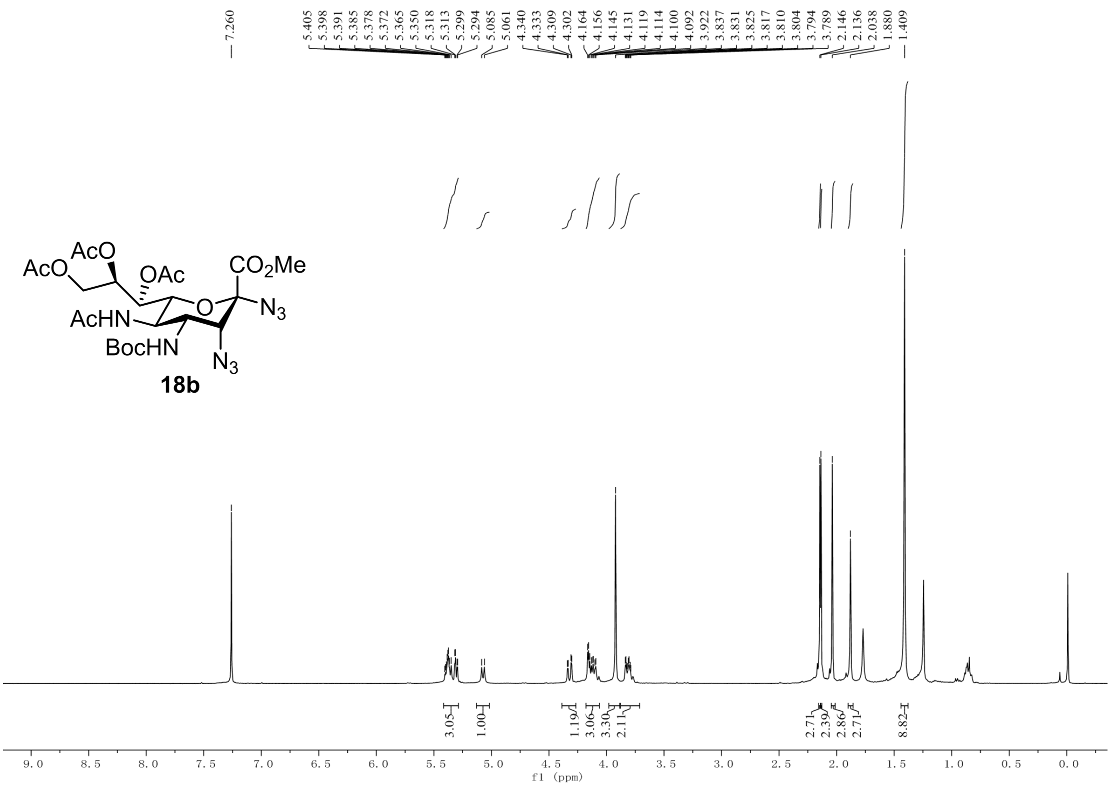
^{13}C NMR spectrum of compound **17b**



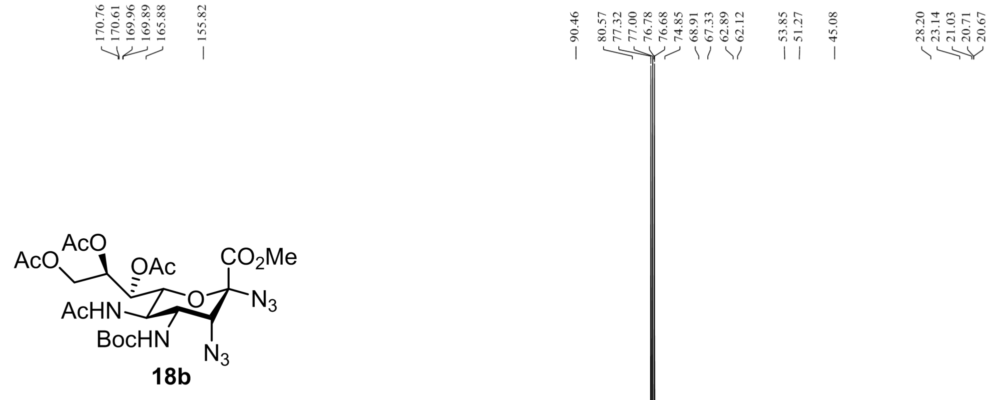
^{1}H NMR spectrum of compound **18a**



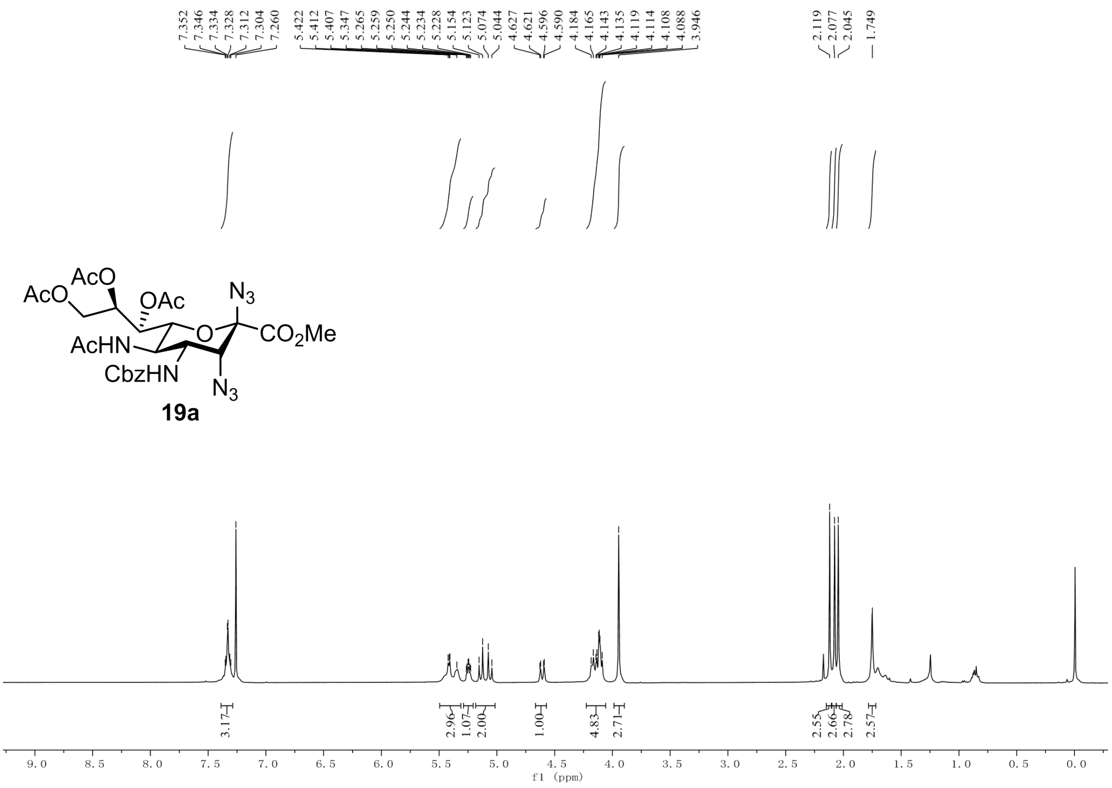
^{13}C NMR spectrum of compound **18a**



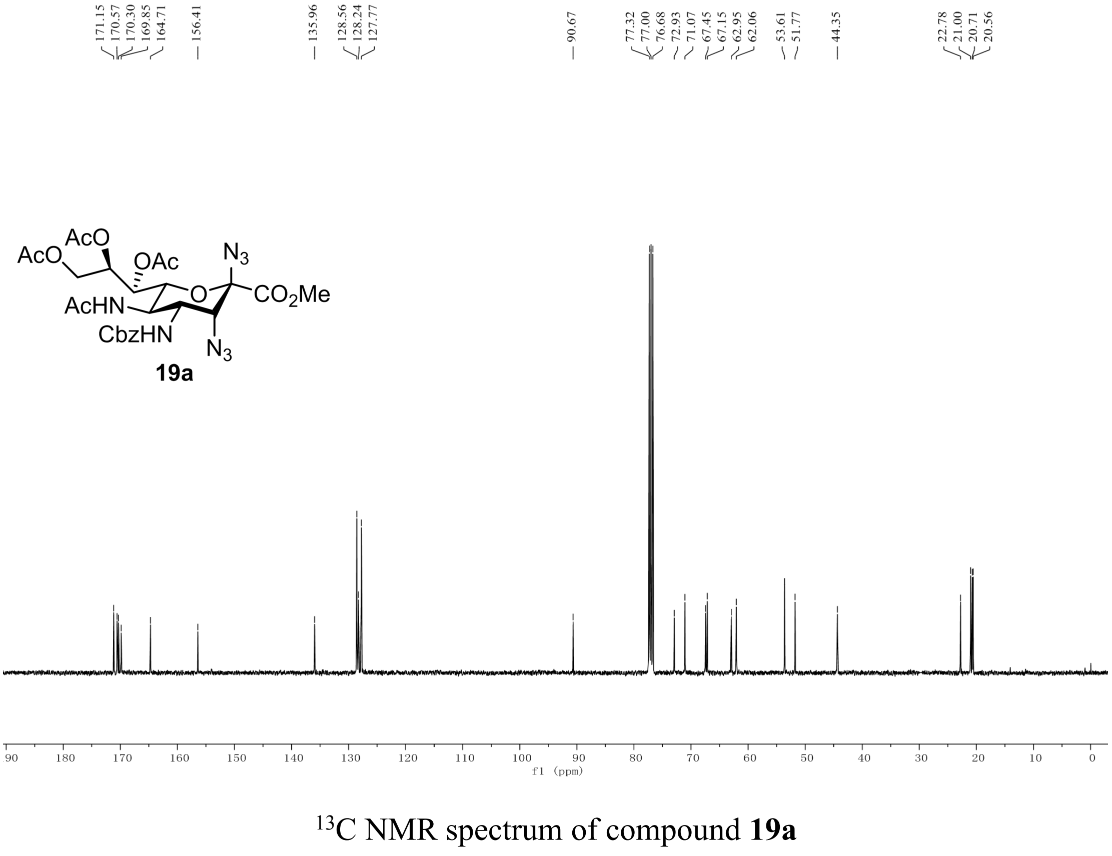
^{1}H NMR spectrum of compound **18b**



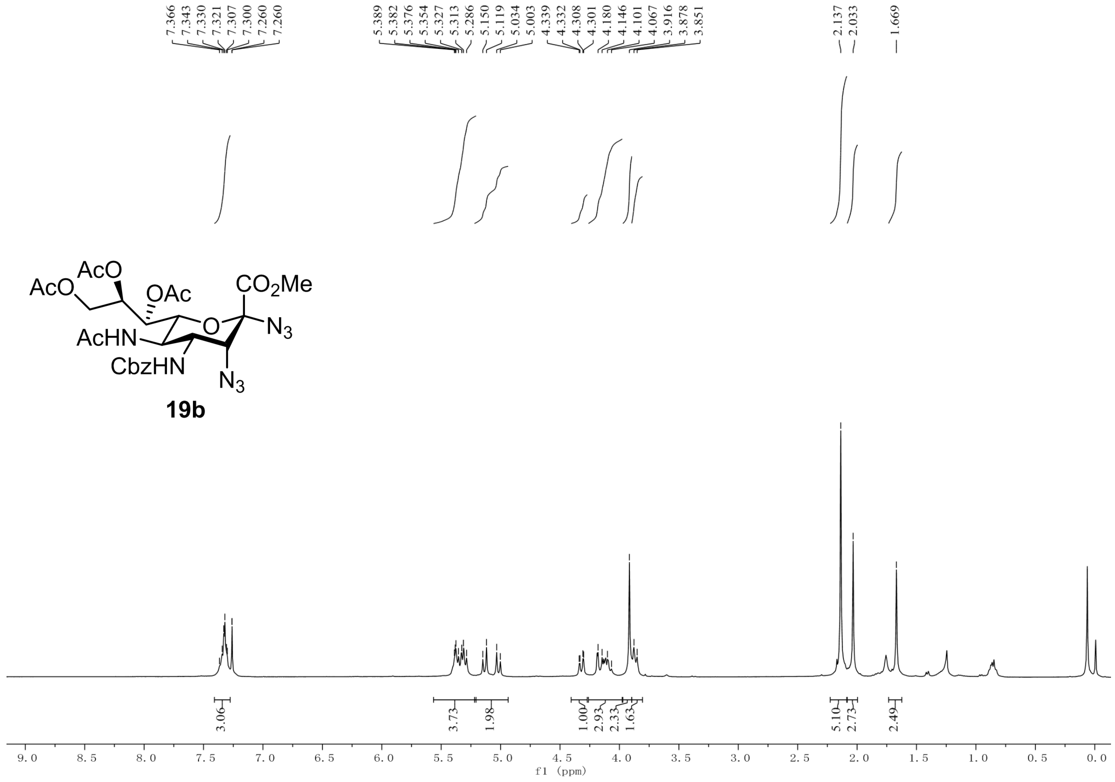
^{13}C NMR spectrum of compound **18b**



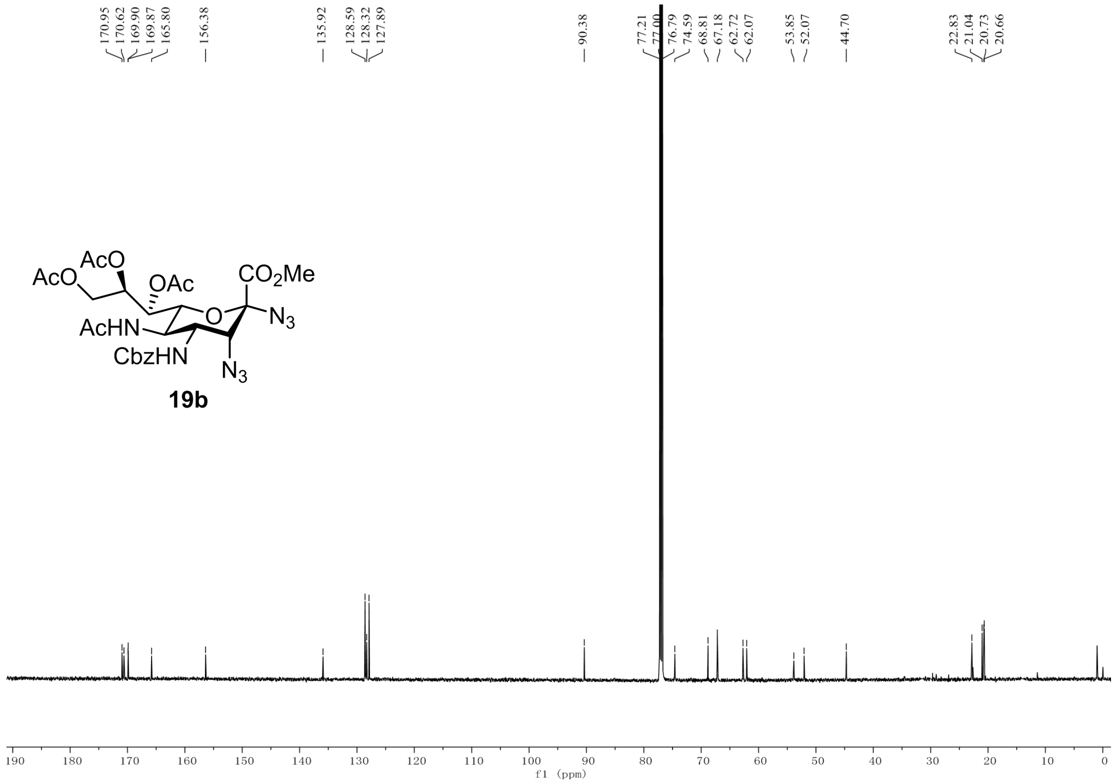
^{1}H NMR spectrum of compound **19a**



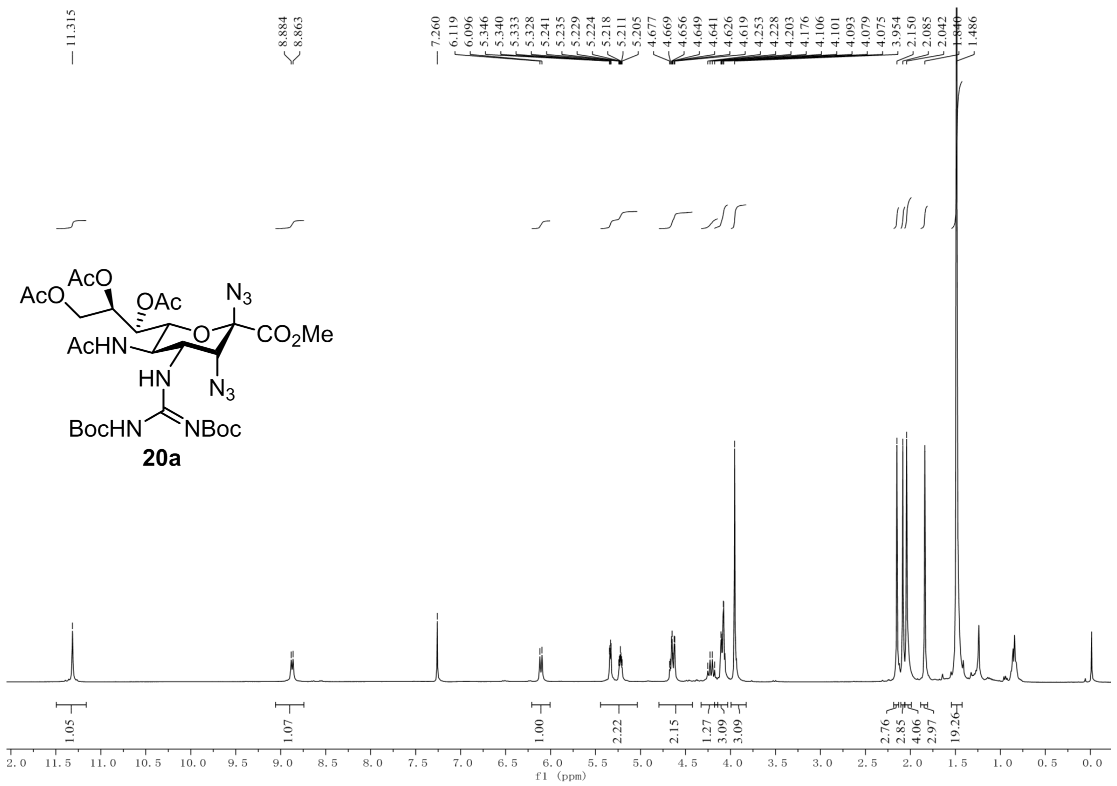
^{13}C NMR spectrum of compound **19a**



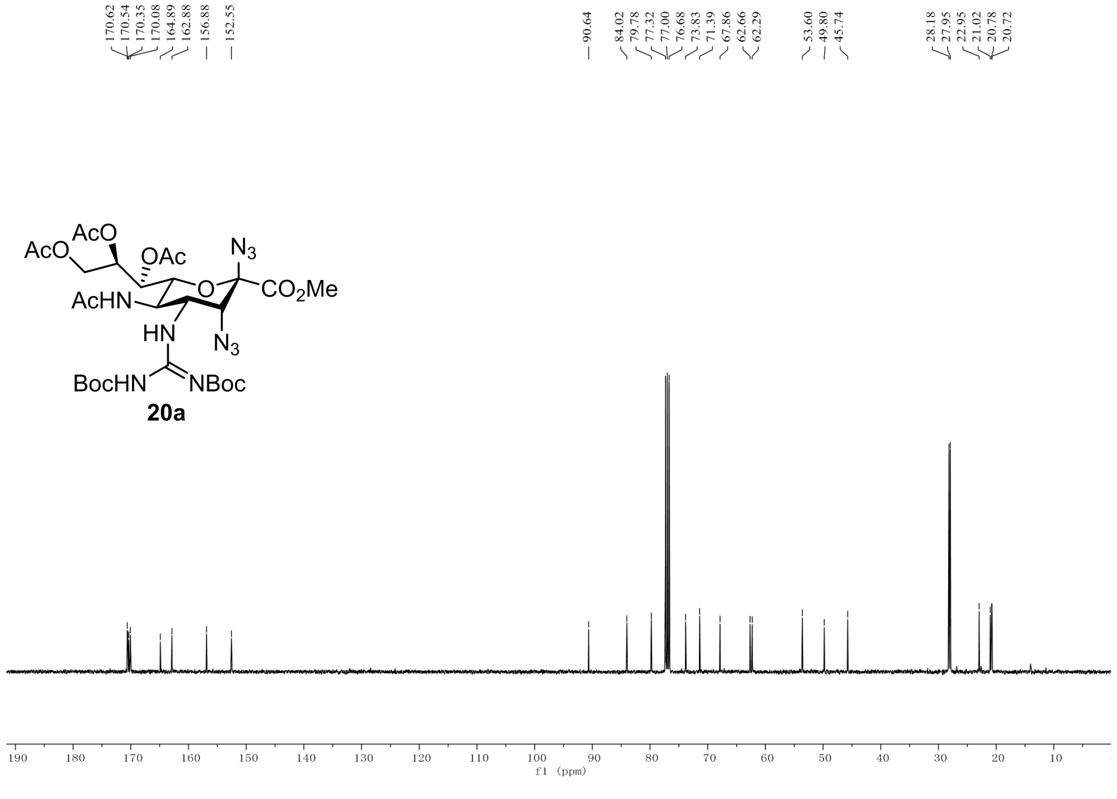
^{1}H NMR spectrum of compound **19b**



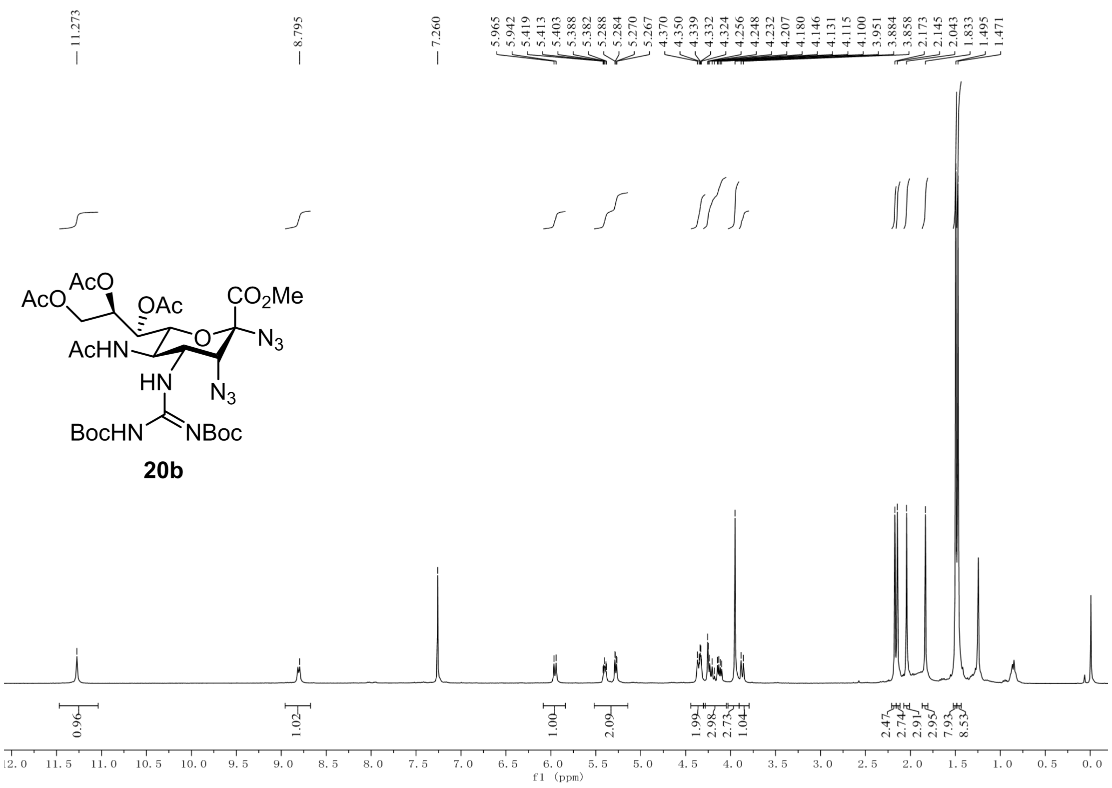
^{13}C NMR spectrum of compound **19b**



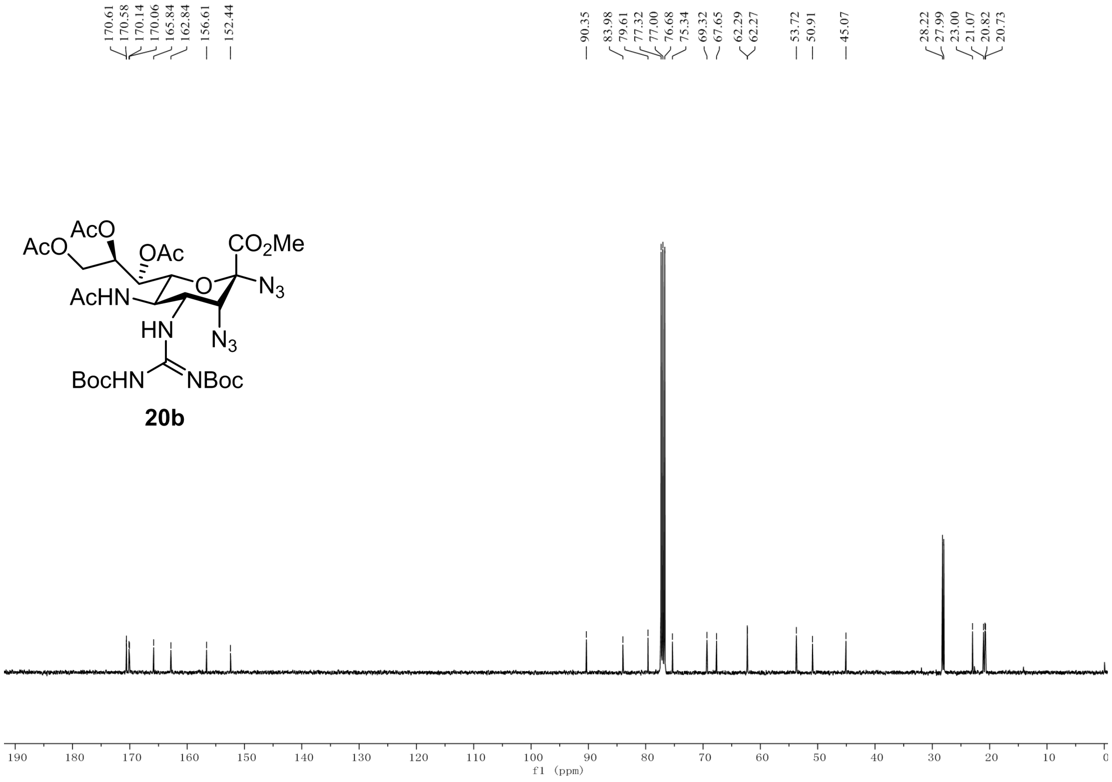
^{1}H NMR spectrum of compound **20a**



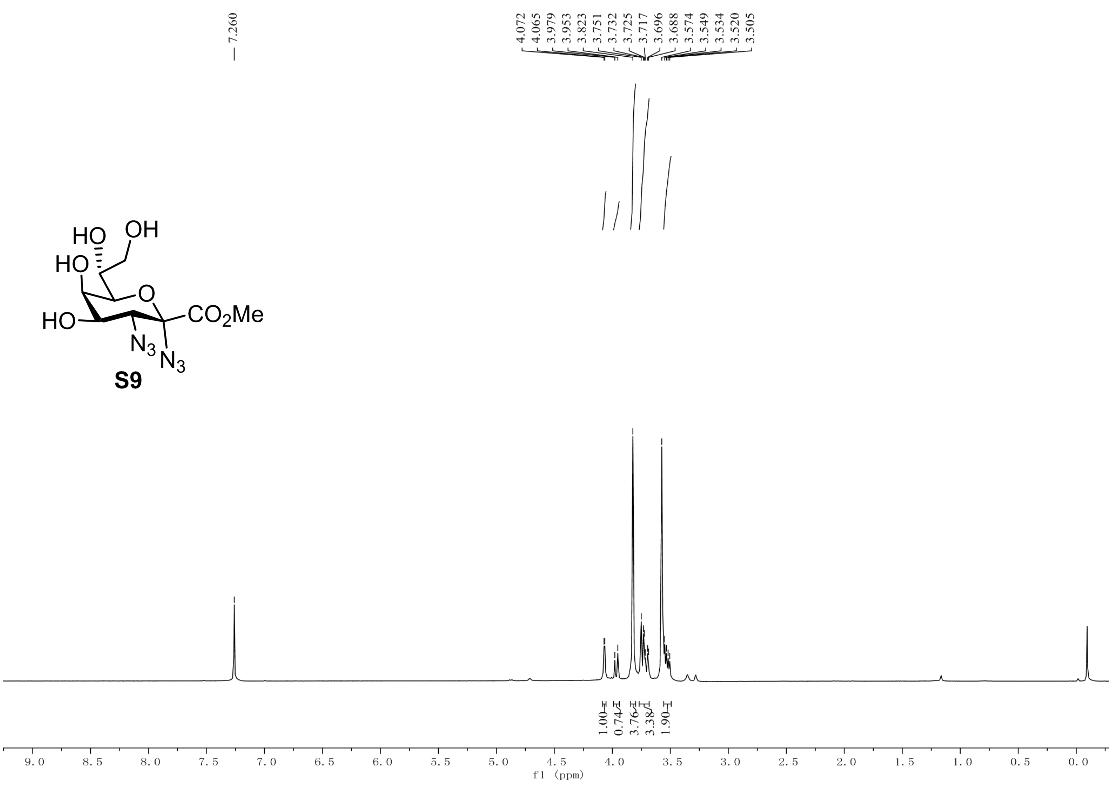
^{13}C NMR spectrum of compound **20a**



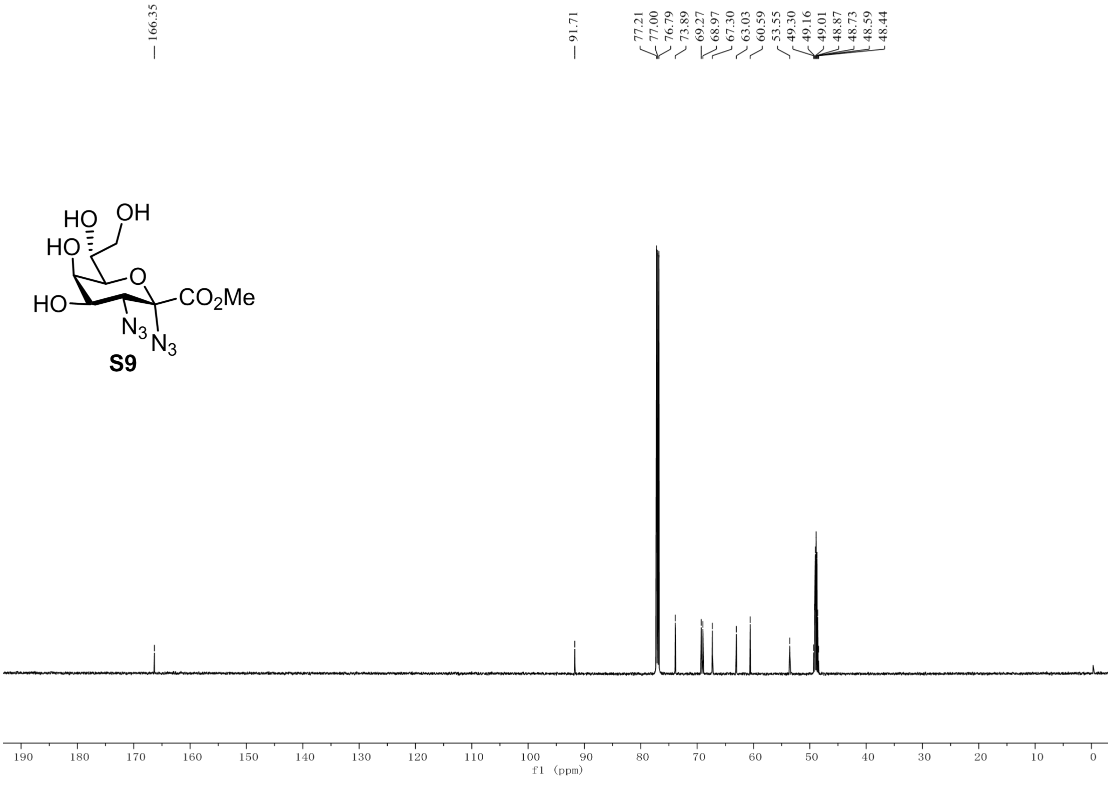
^{1}H NMR spectrum of compound **20b**



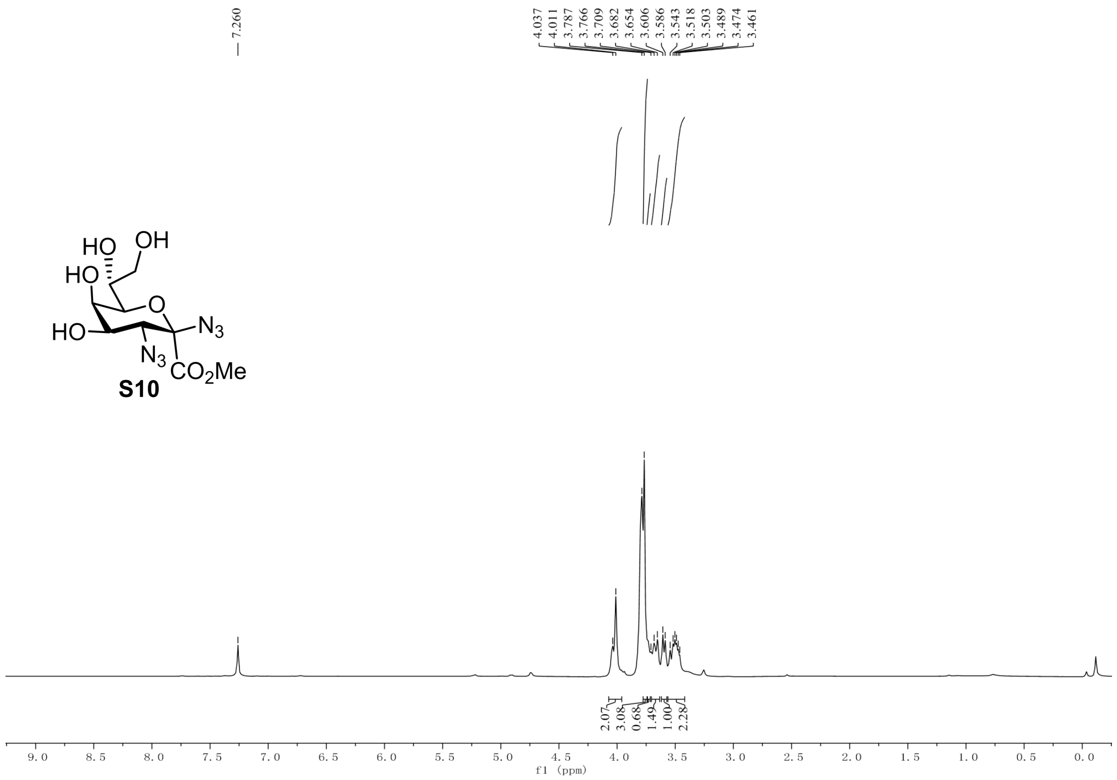
^{13}C NMR spectrum of compound **20b**



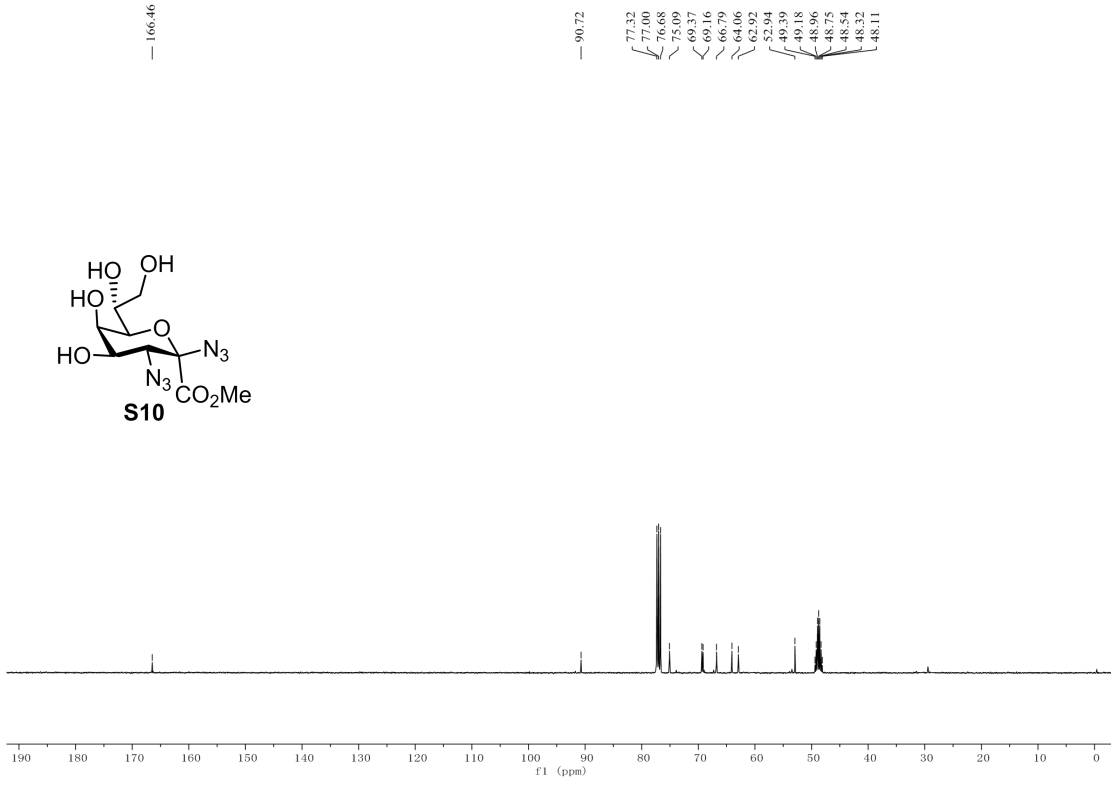
^{1}H NMR spectrum of compound **S9**



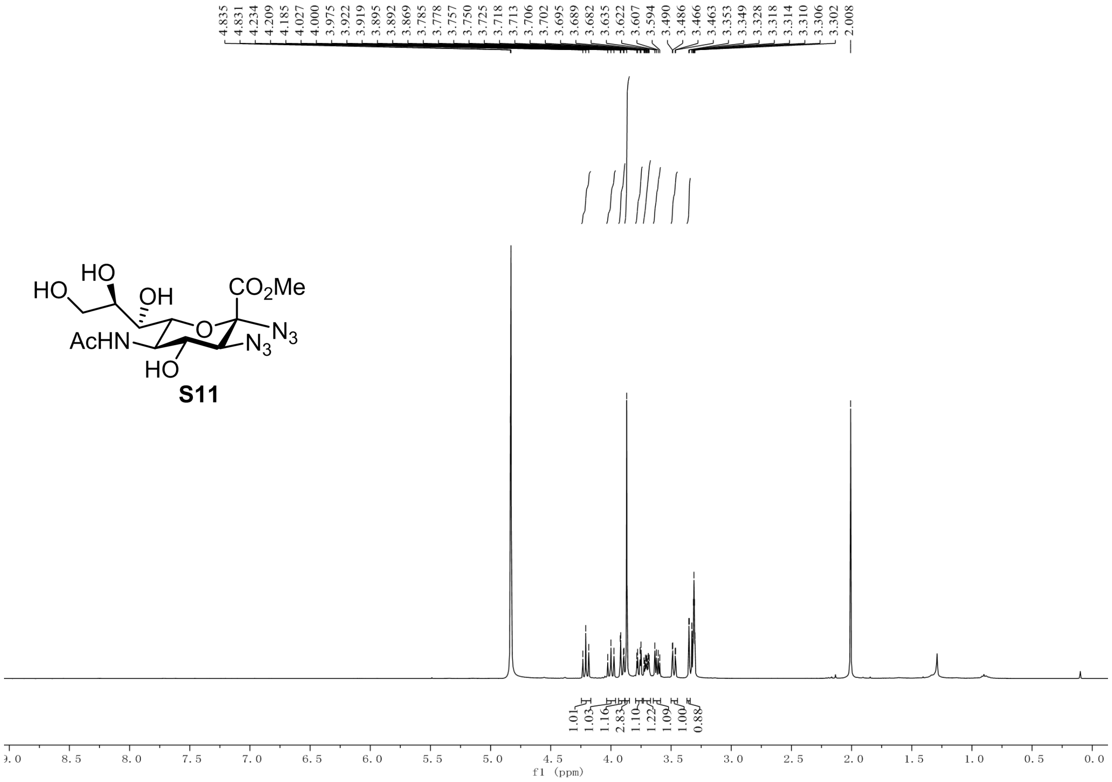
^{13}C NMR spectrum of compound **S9**



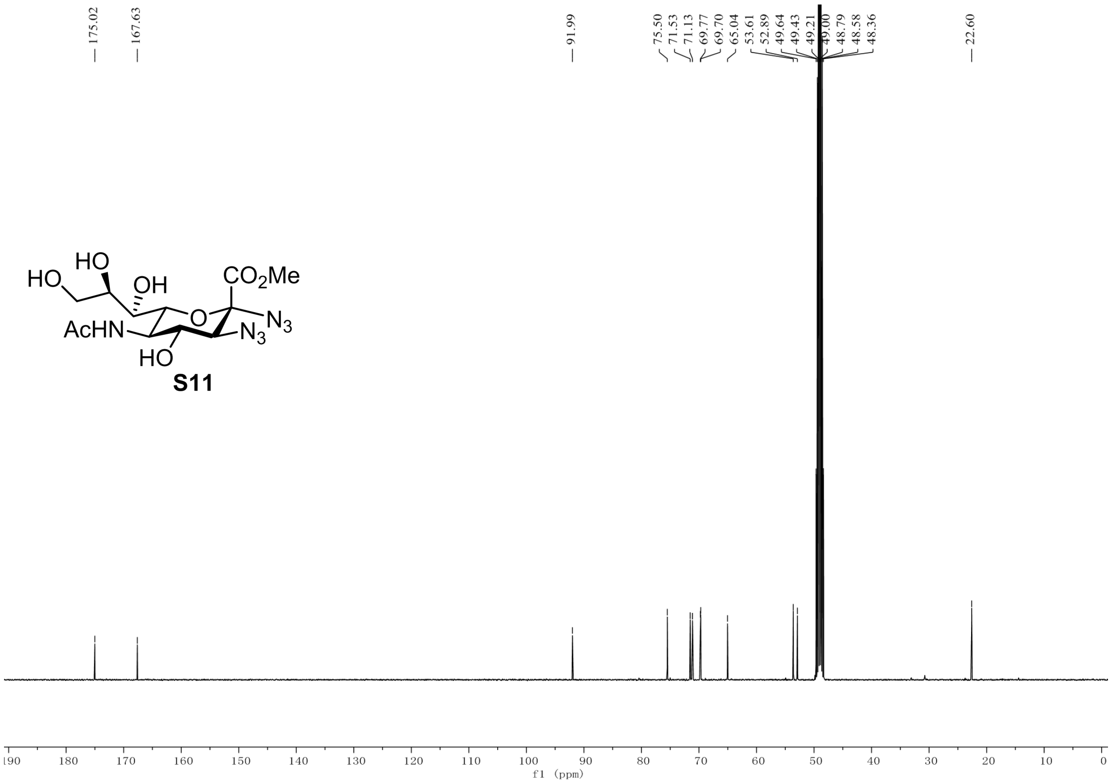
^{1}H NMR spectrum of compound **S10**



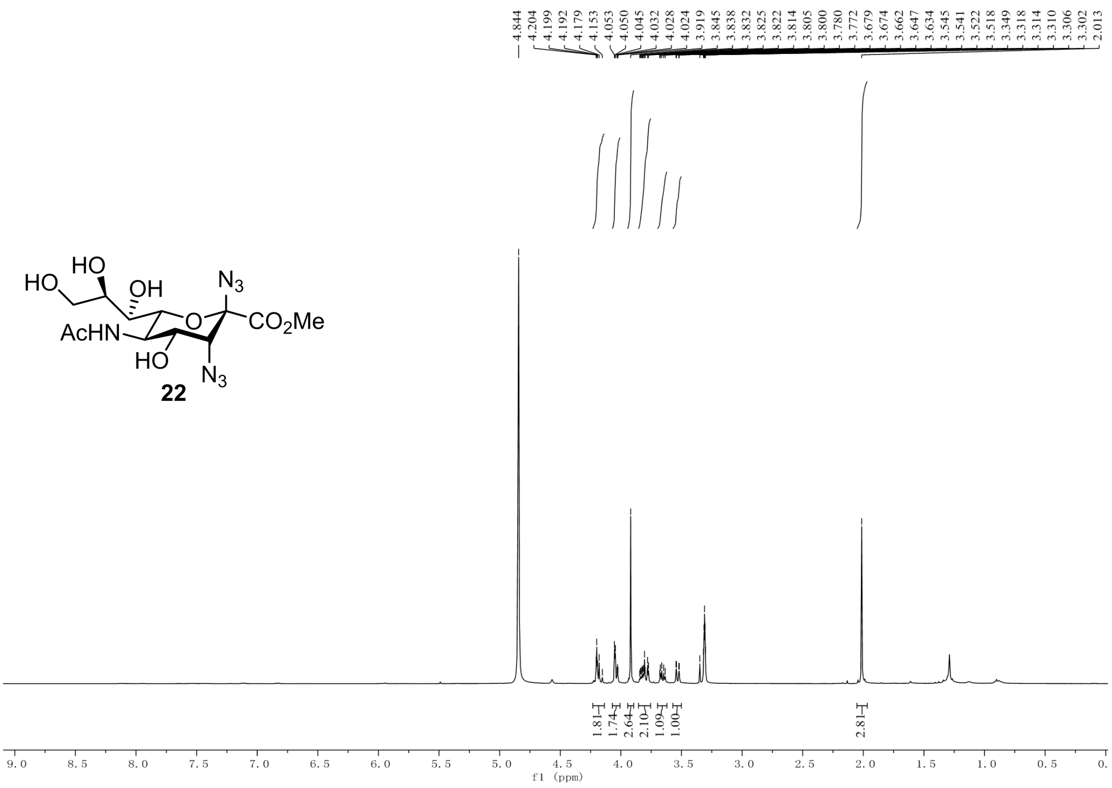
^{13}C NMR spectrum of compound **S10**



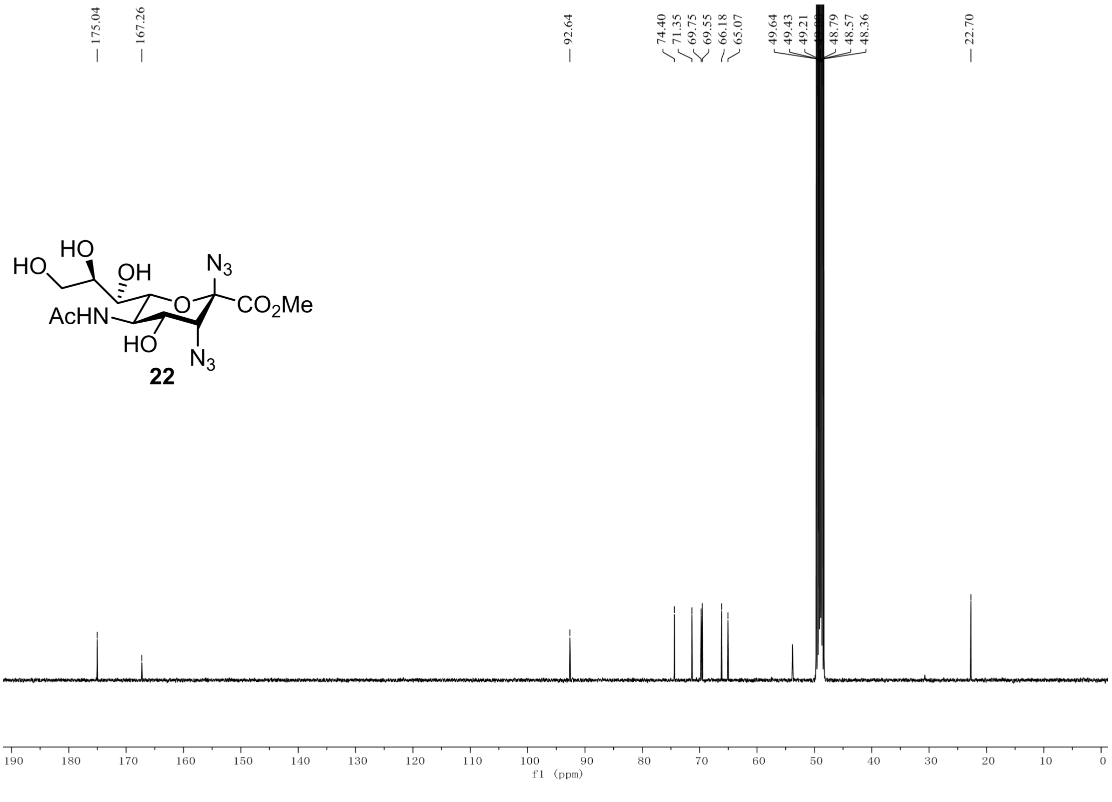
^{1}H NMR spectrum of compound **S11**



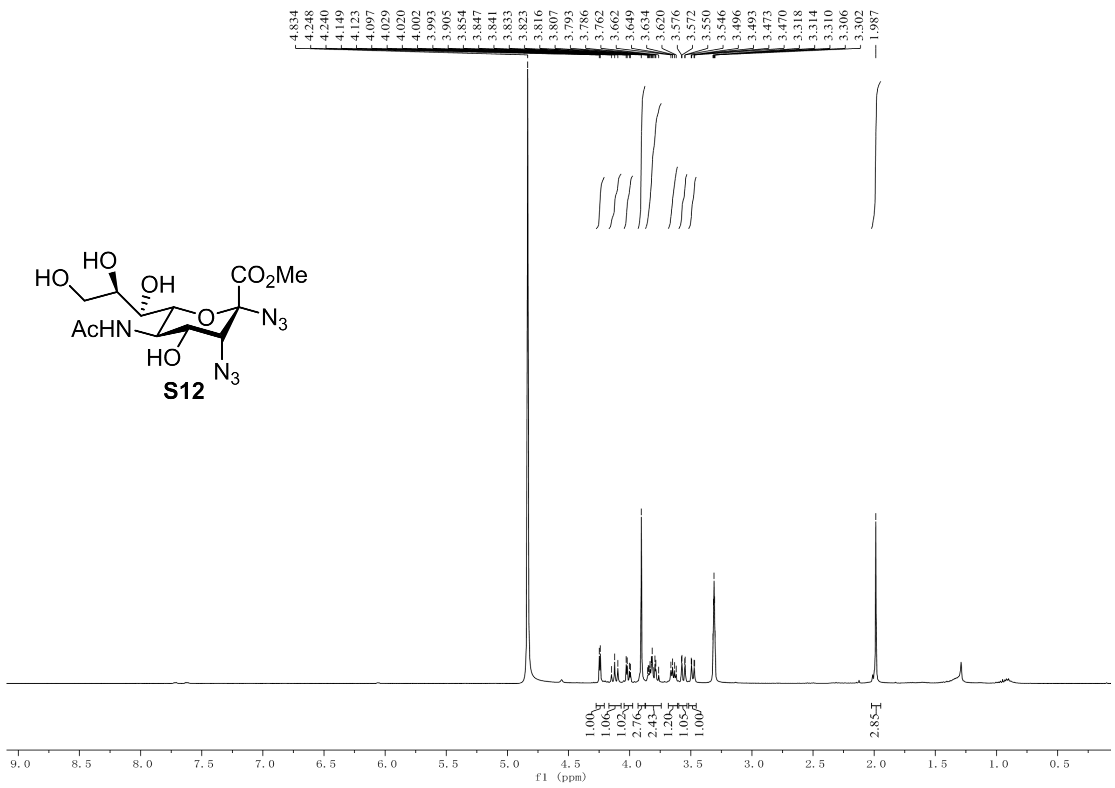
^{13}C NMR spectrum of compound **S11**



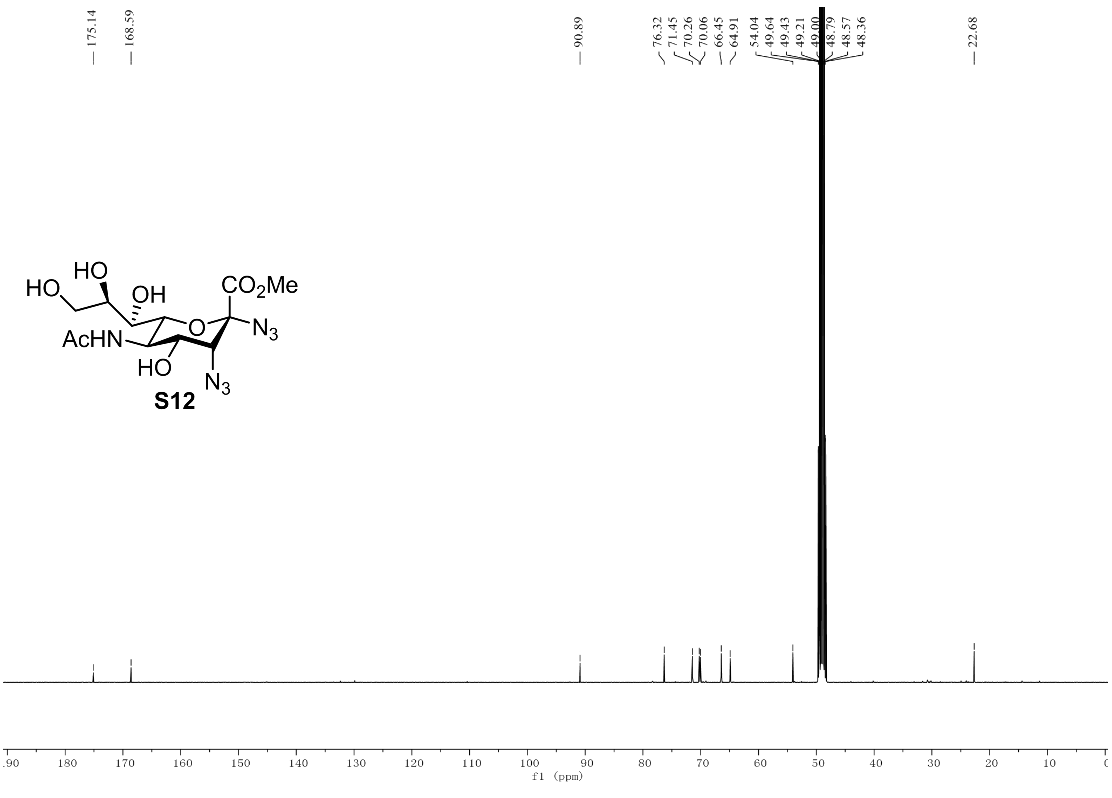
^{1}H NMR spectrum of compound **22**



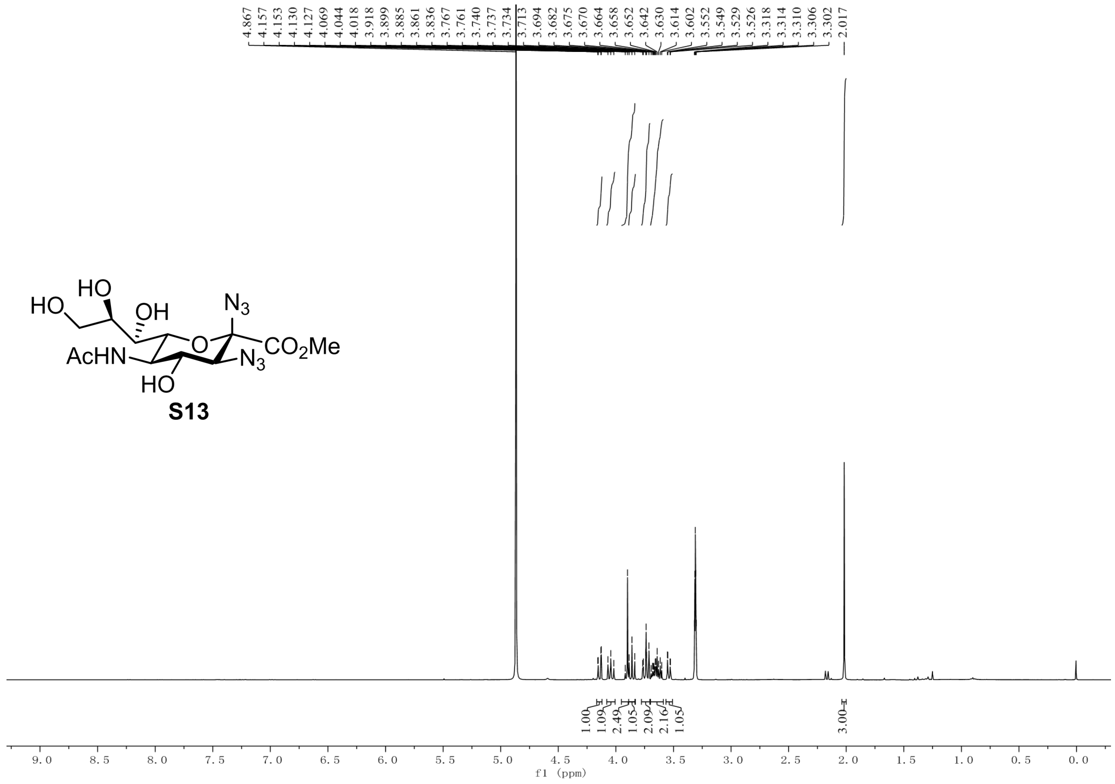
^{13}C NMR spectrum of compound **22**



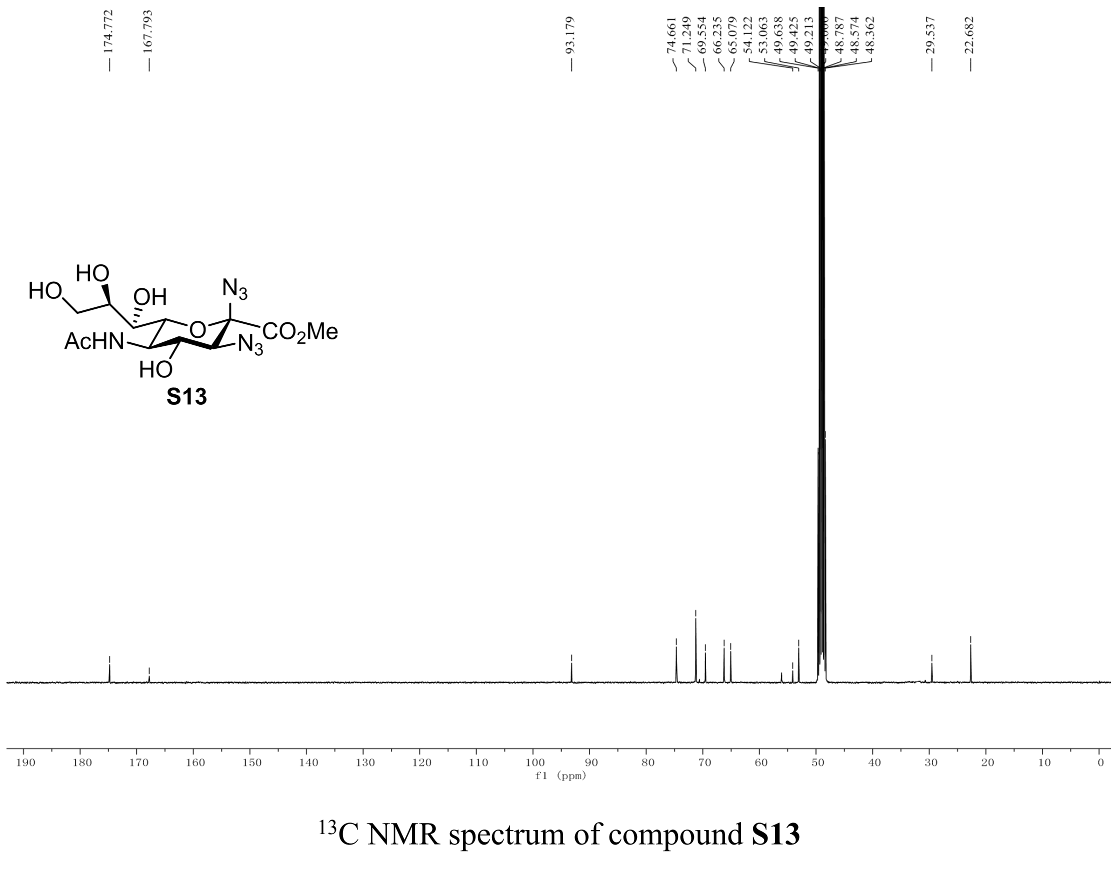
^{1}H NMR spectrum of compound **S12**



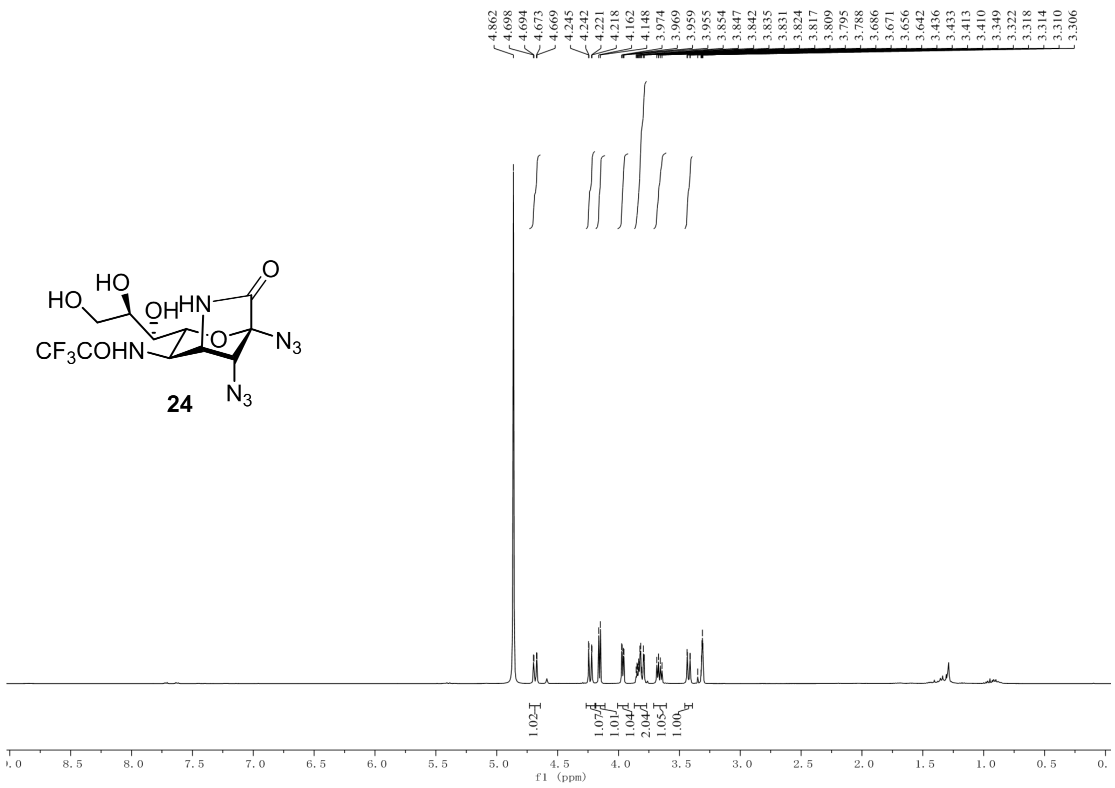
^{13}C NMR spectrum of compound **S12**



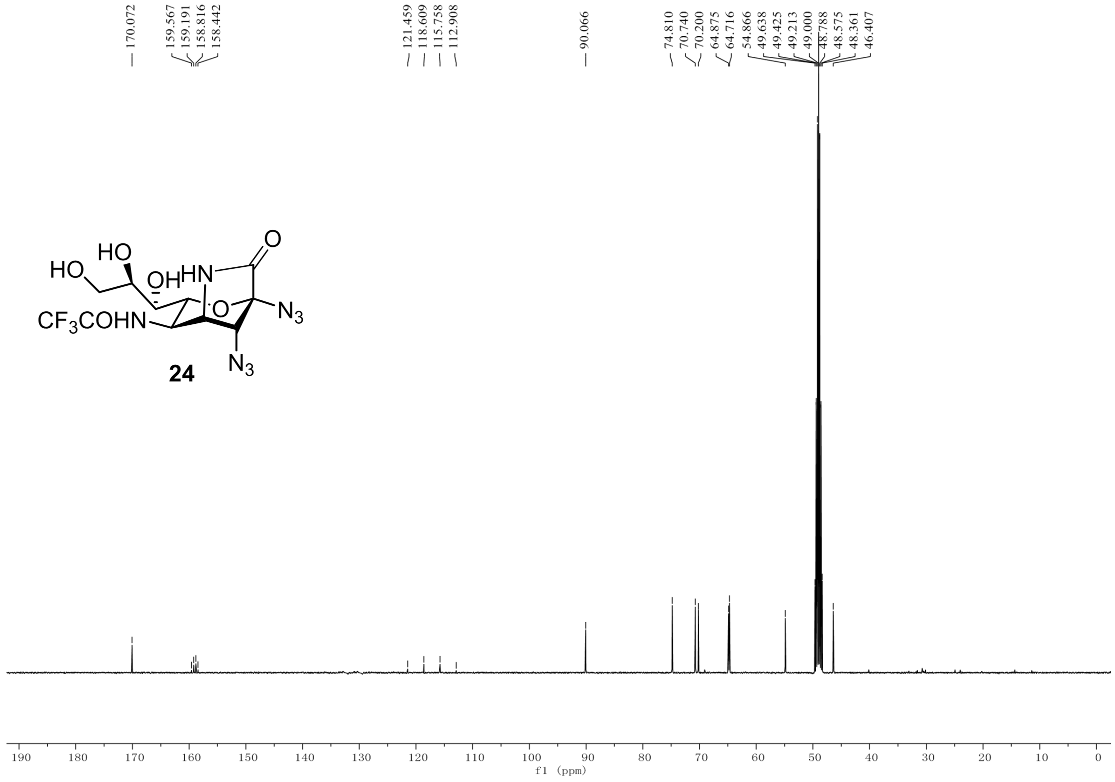
^{1}H NMR spectrum of compound **S13**



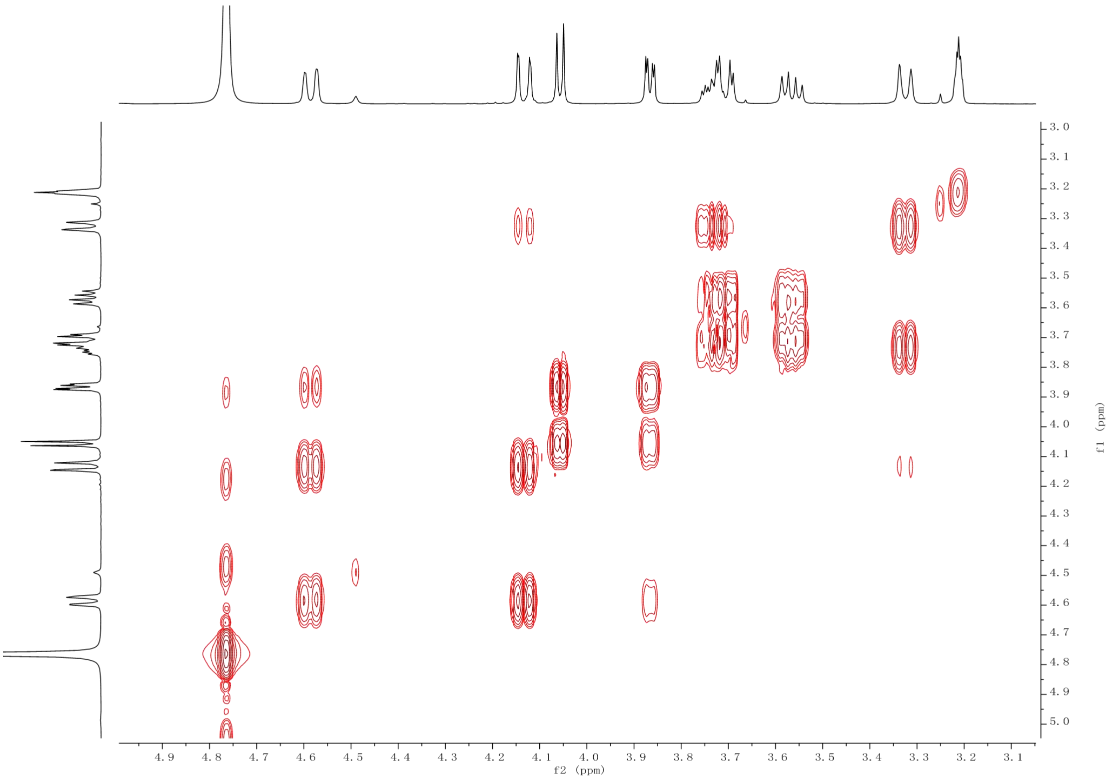
^{13}C NMR spectrum of compound **S13**



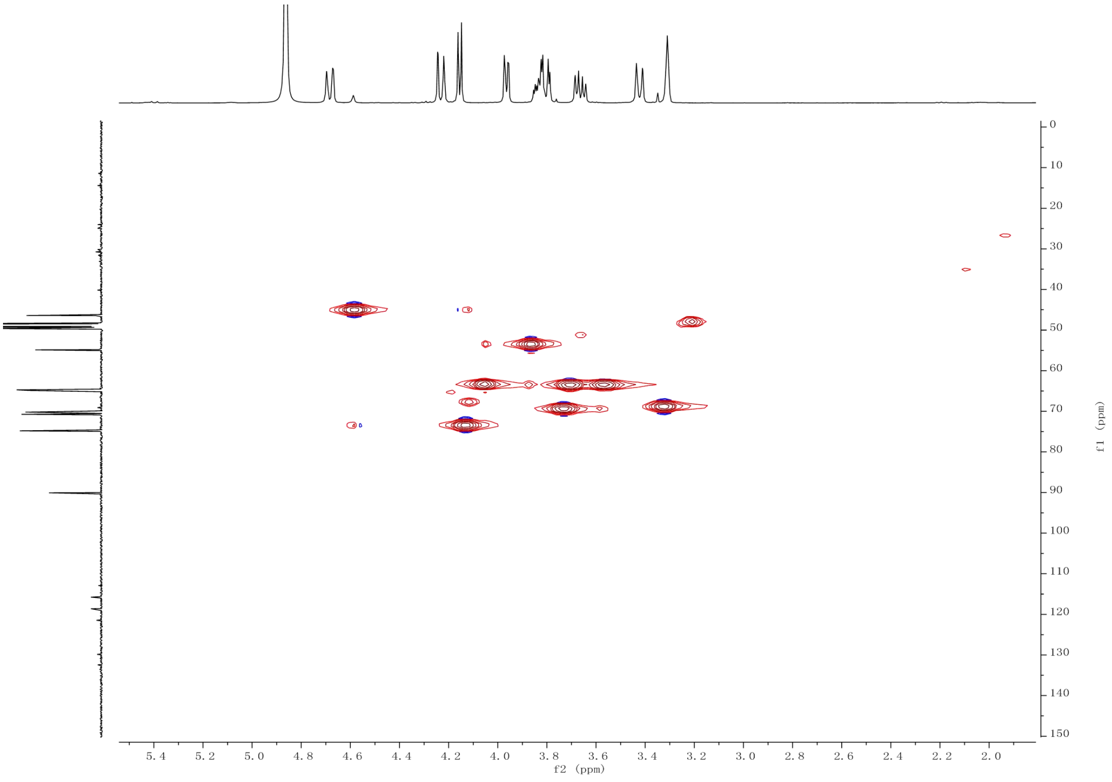
^{1}H NMR spectrum of compound **24**



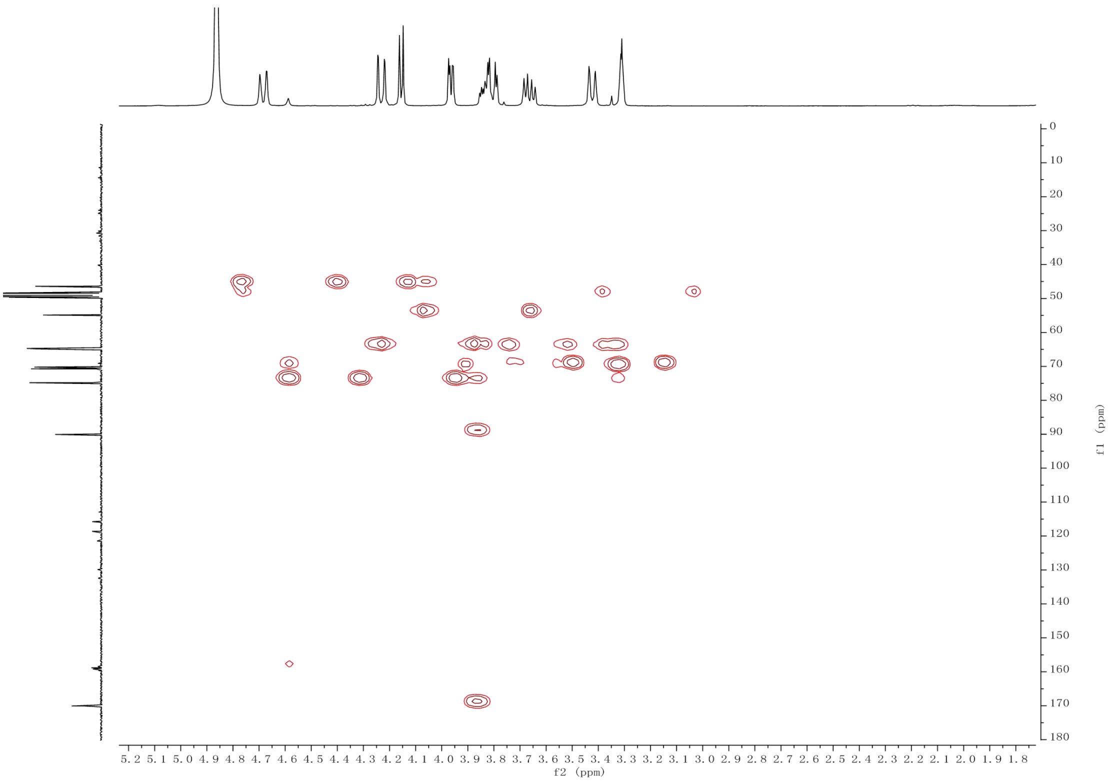
^{13}C NMR spectrum of compound **24**



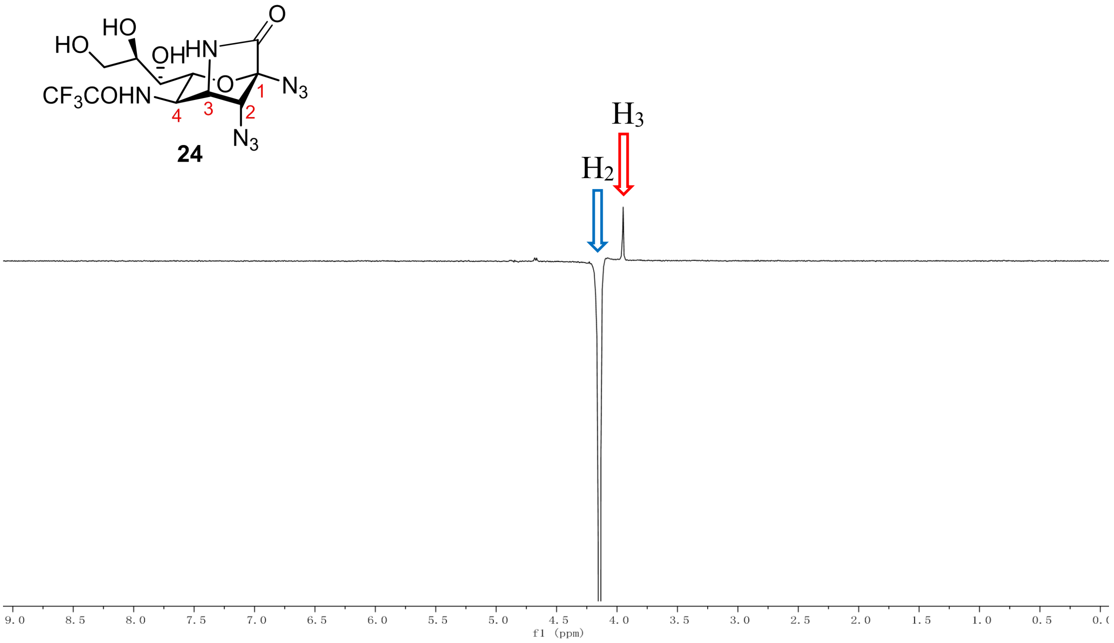
H-H COSY spectrum of compound **24**



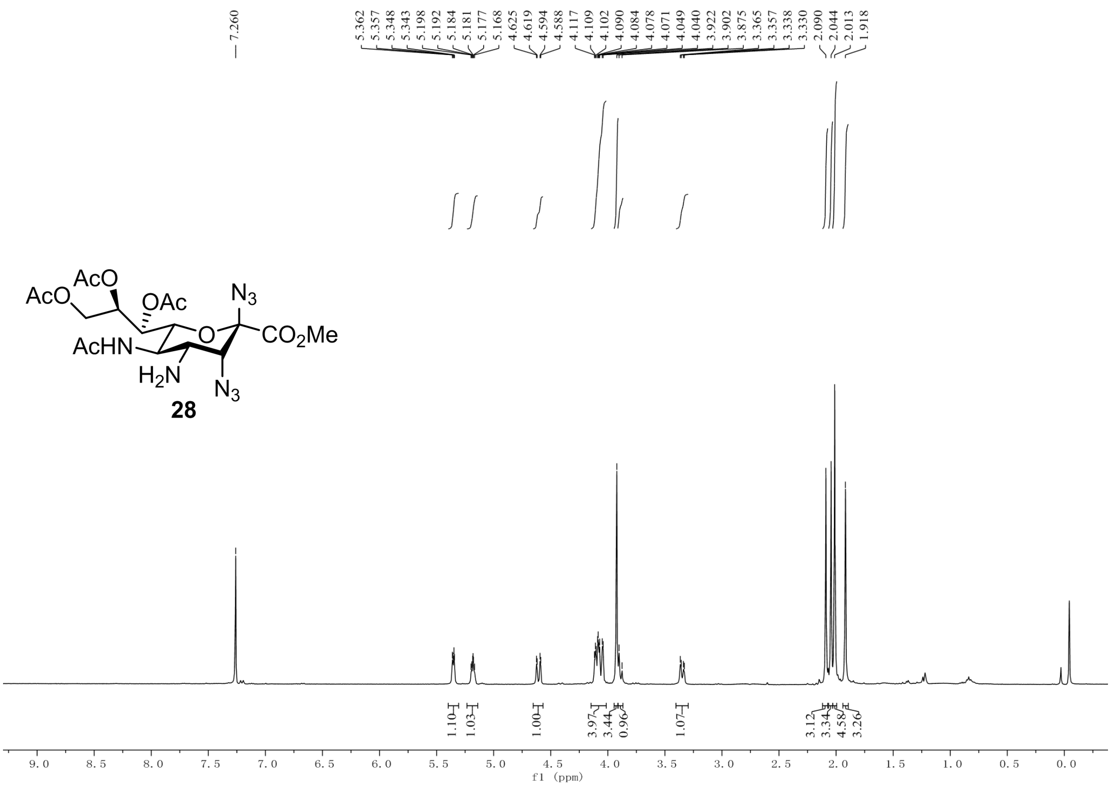
HSQC spectrum of compound **24**



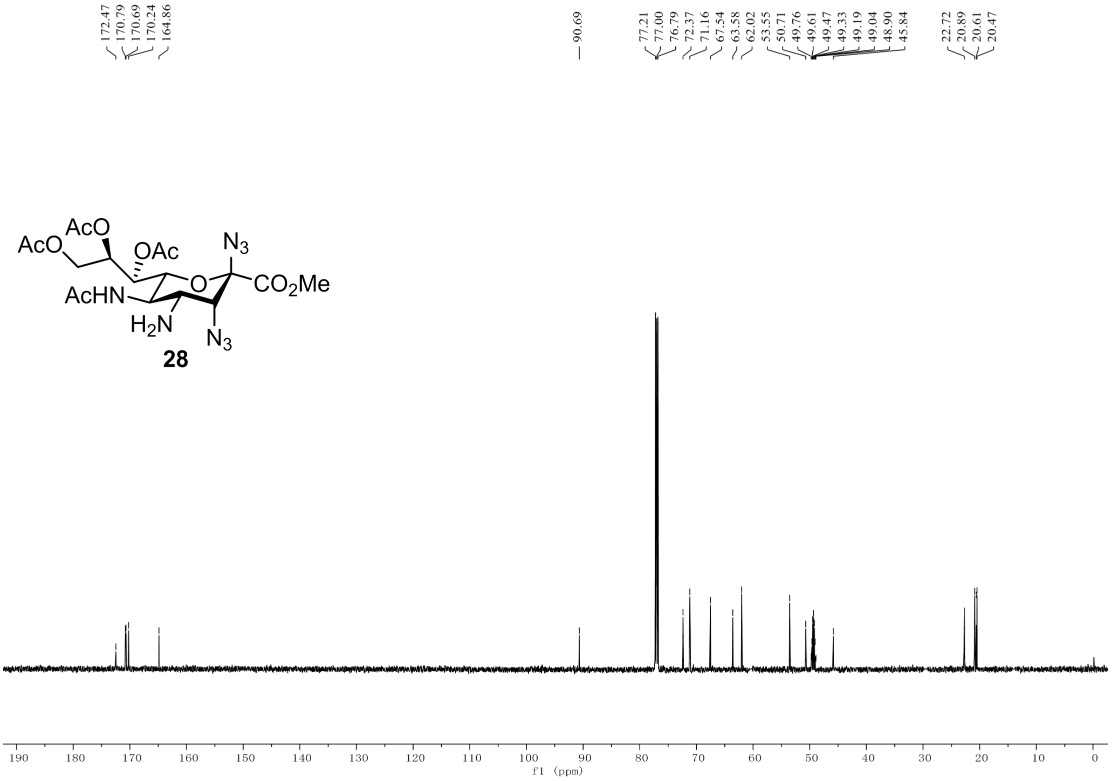
HMBC spectrum of compound **24**



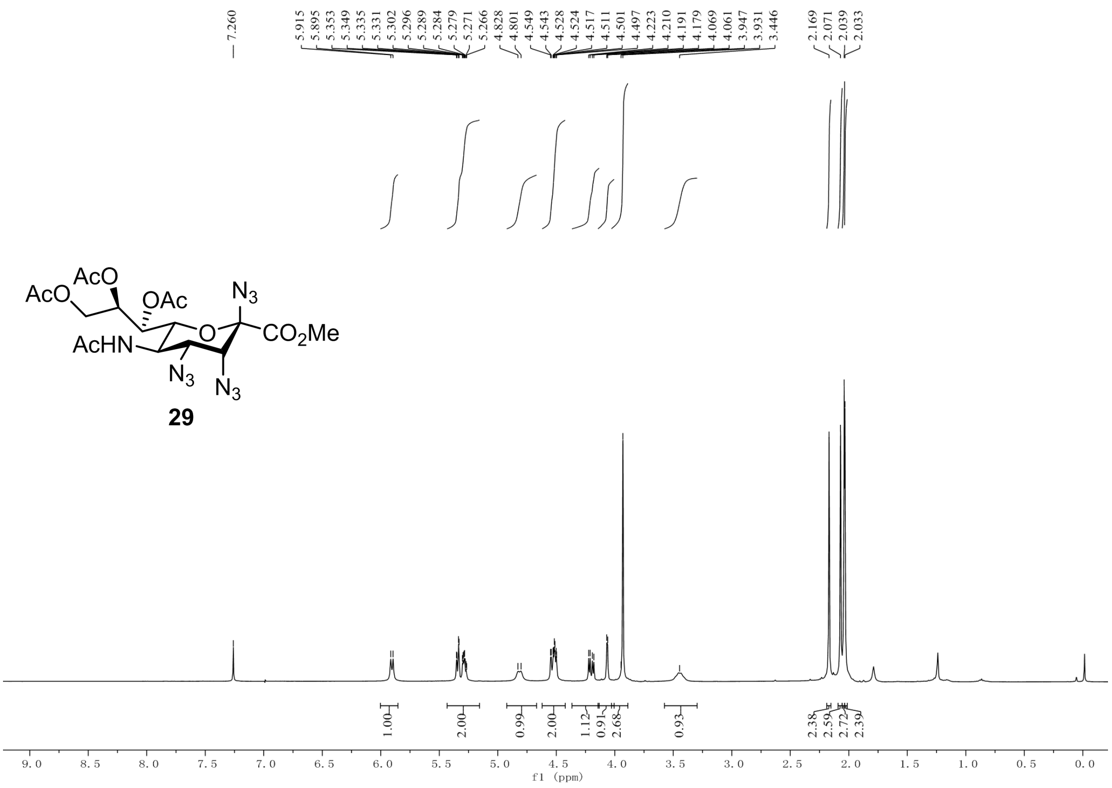
NOE spectrum of compound **24**



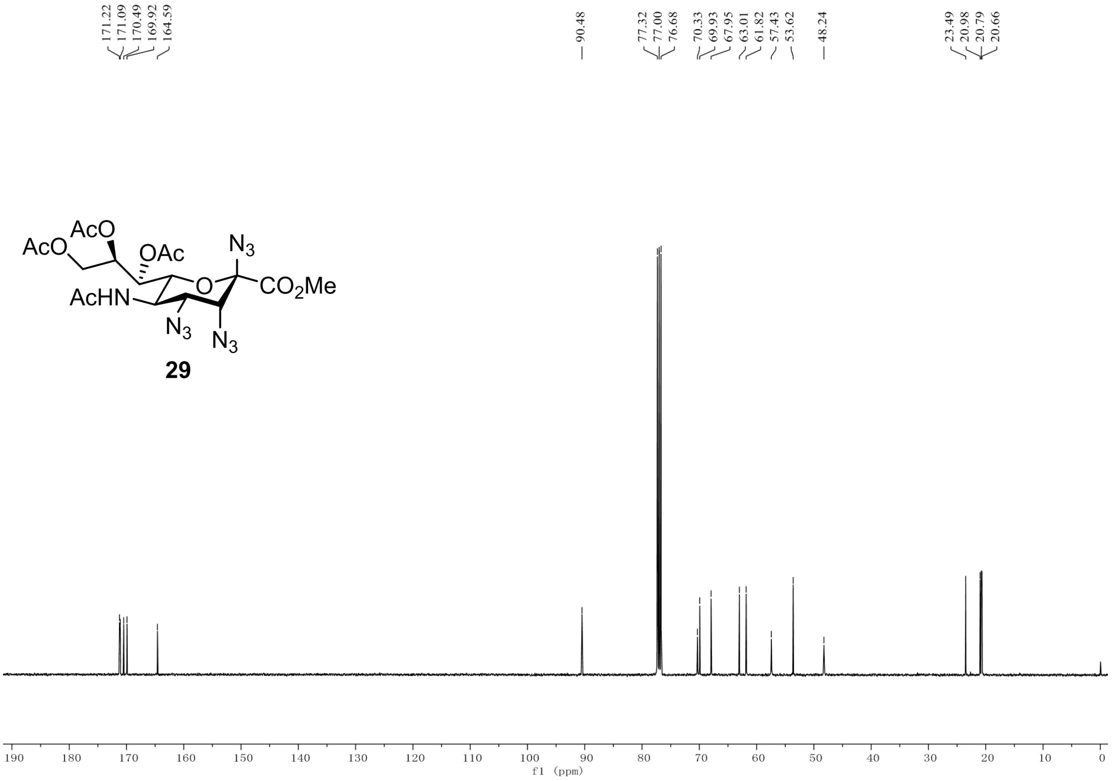
^{1}H NMR spectrum of compound **28**



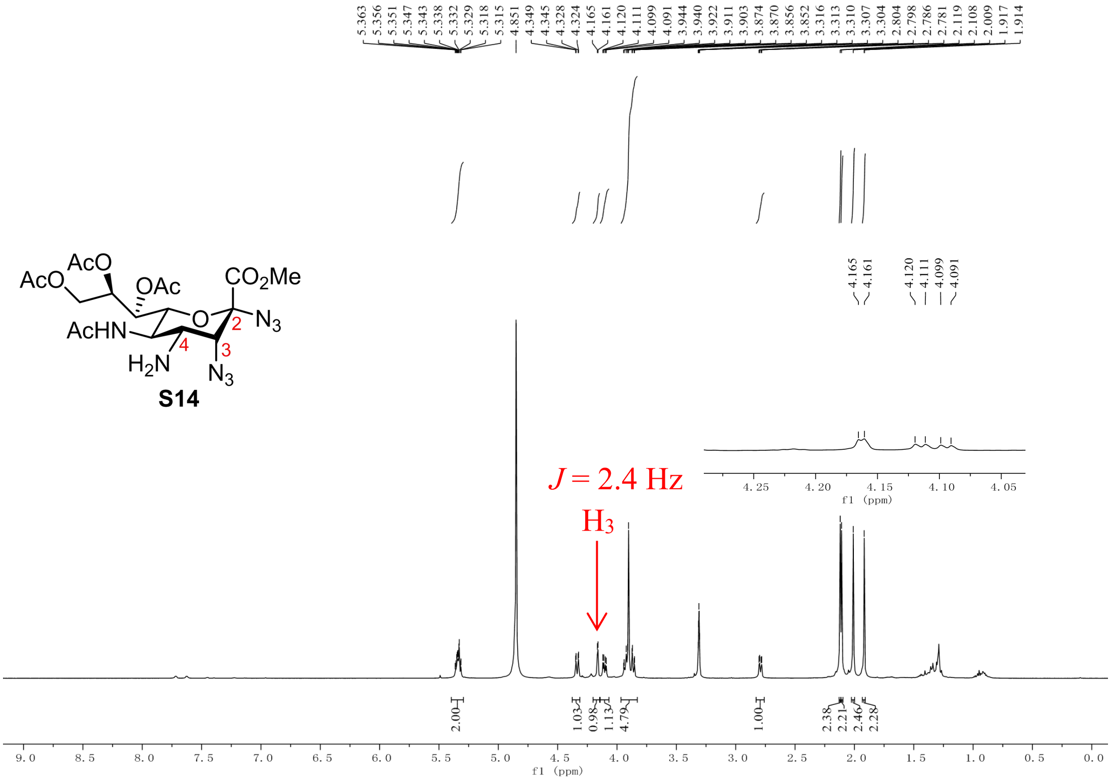
^{13}C NMR spectrum of compound **28**



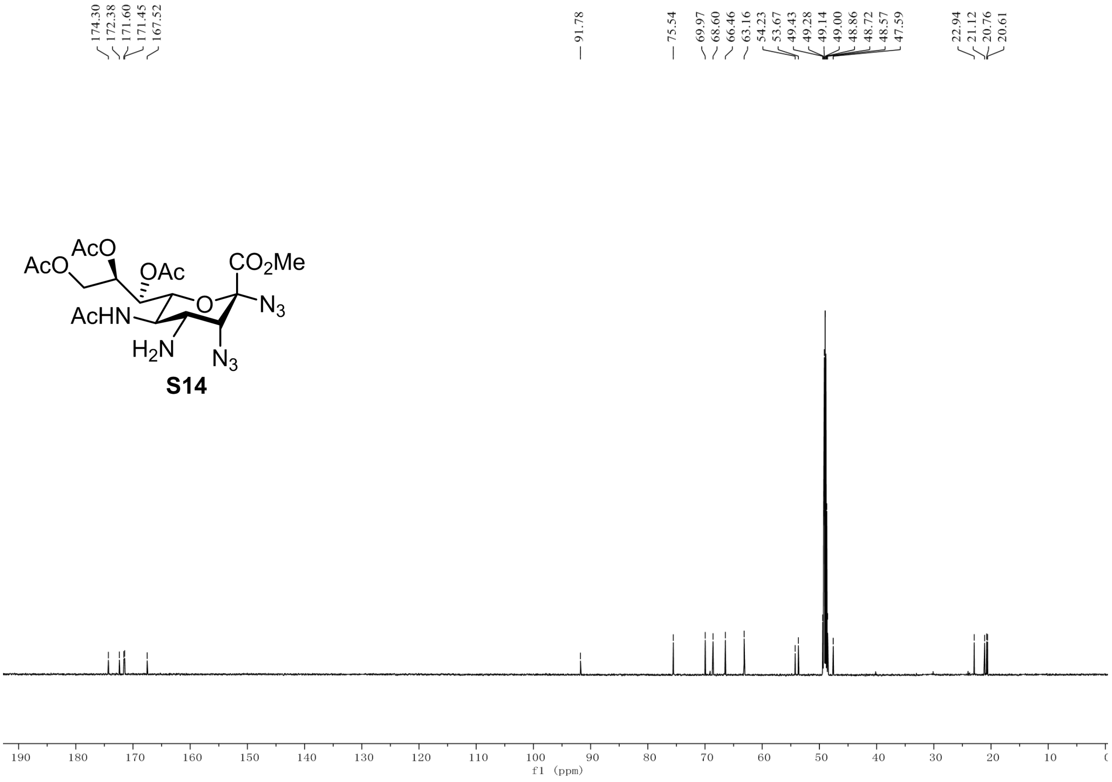
^{1}H NMR spectrum of compound **29**



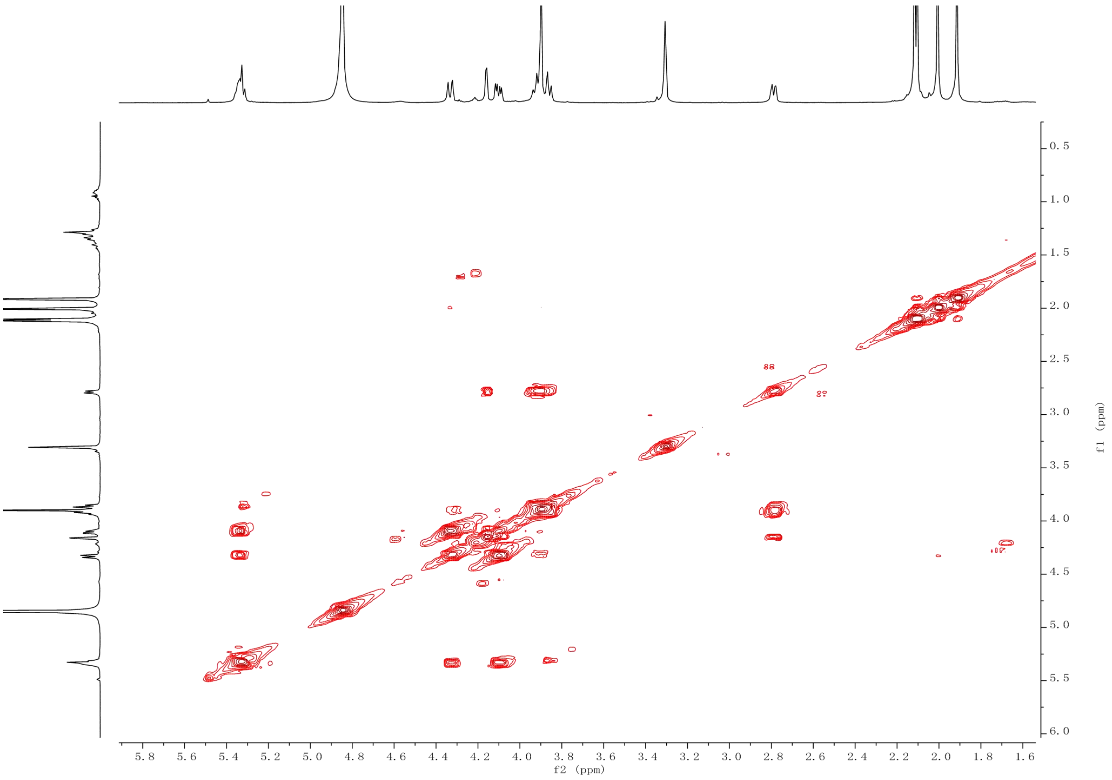
^{13}C NMR spectrum of compound **29**



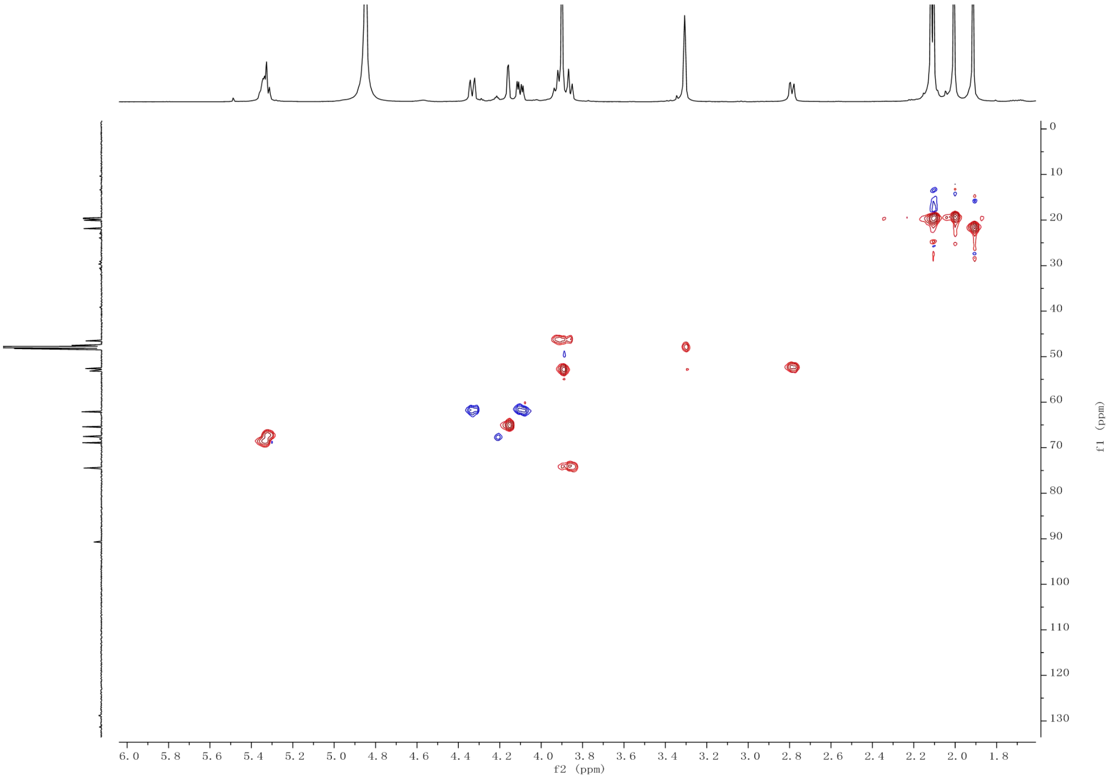
^{1}H NMR spectrum of compound **S14**



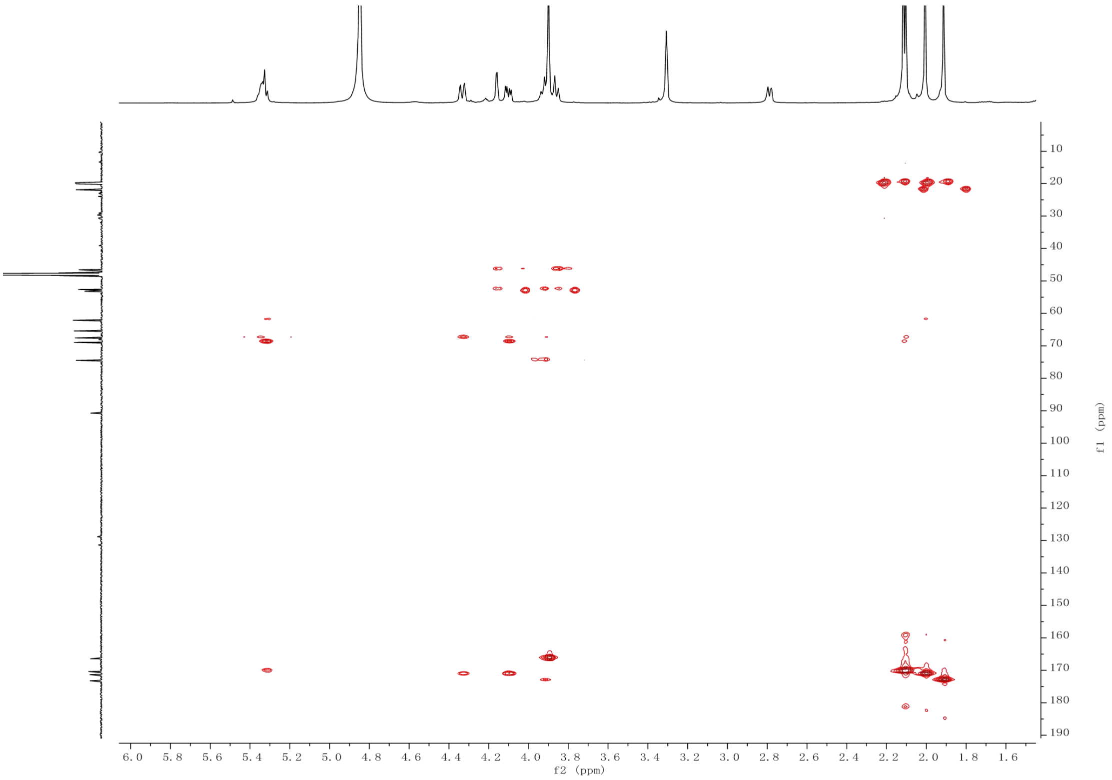
^{13}C NMR spectrum of compound **S14**



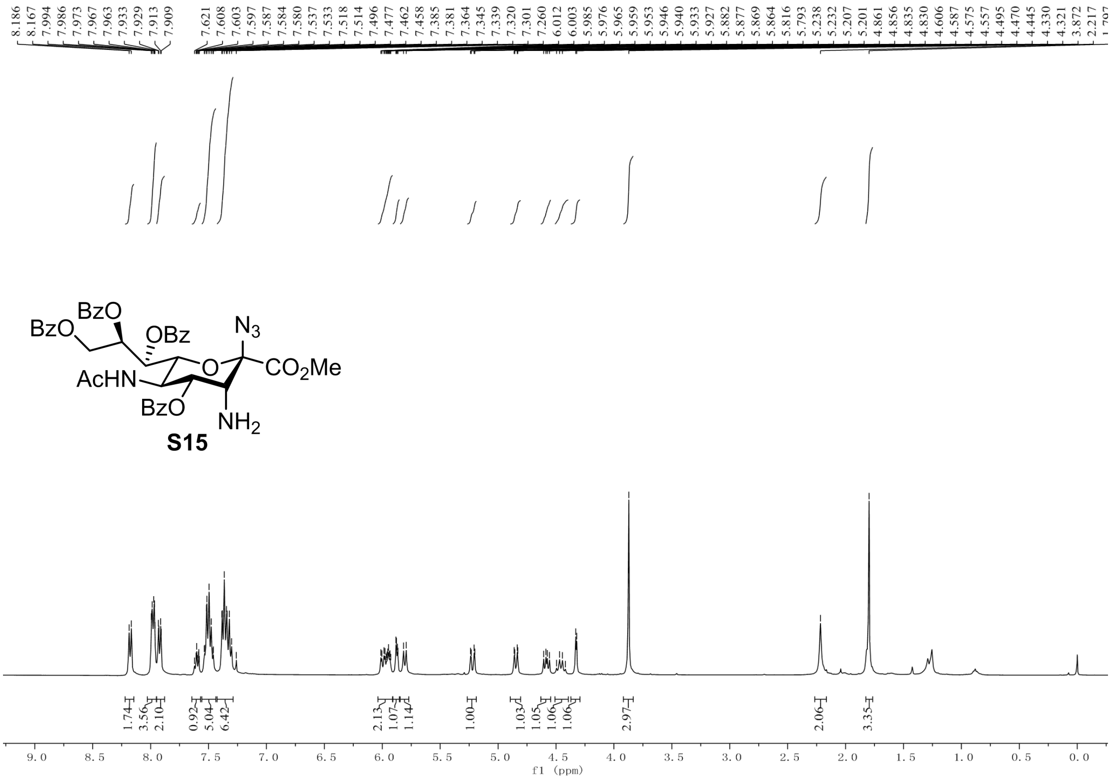
H-H COSY spectrum of compound **S14**



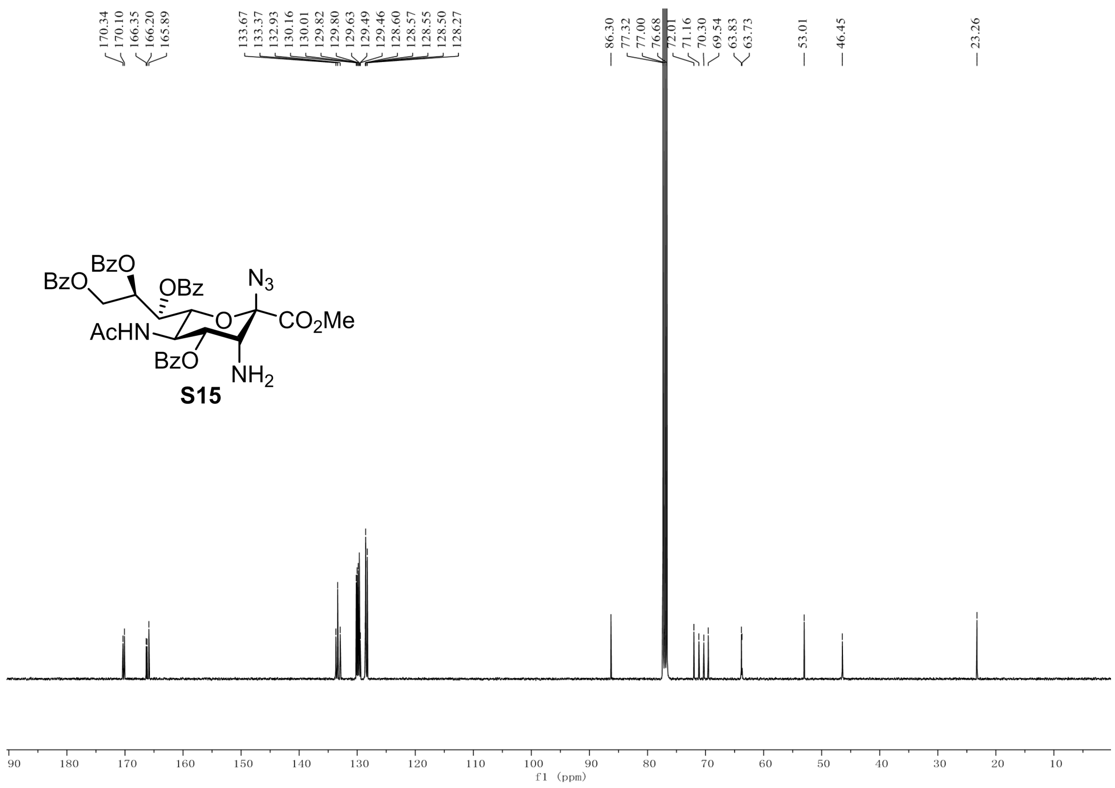
HSQC spectrum of compound **S14**



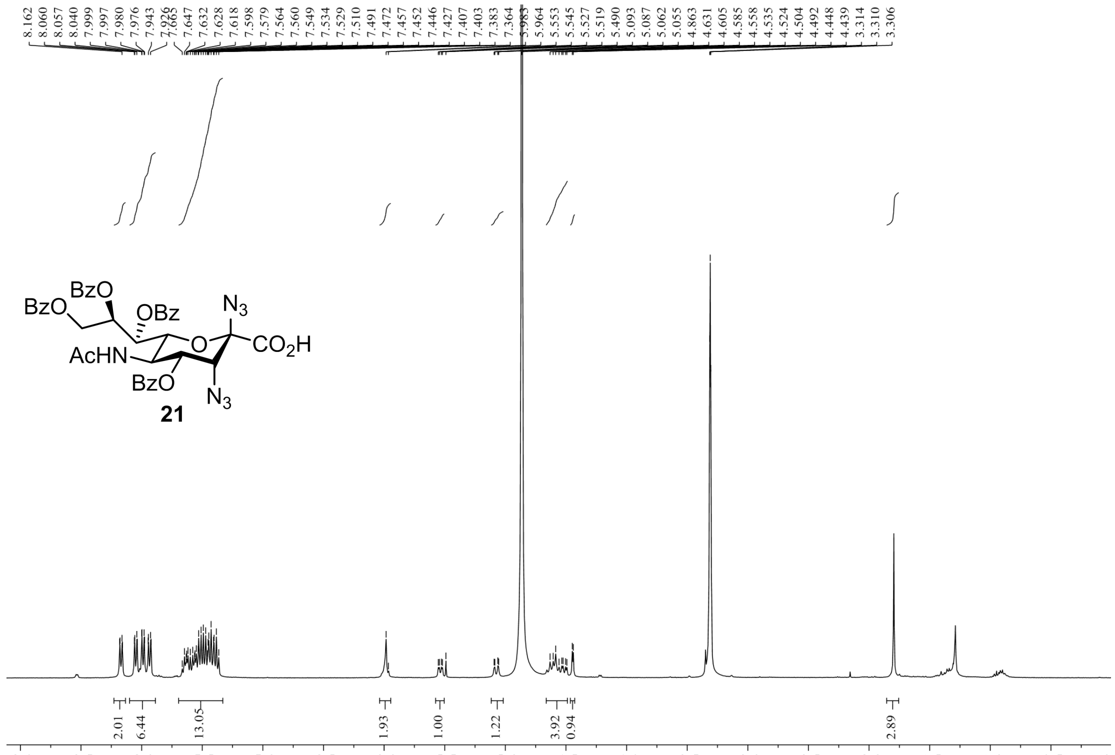
HMBC spectrum of compound **S14**



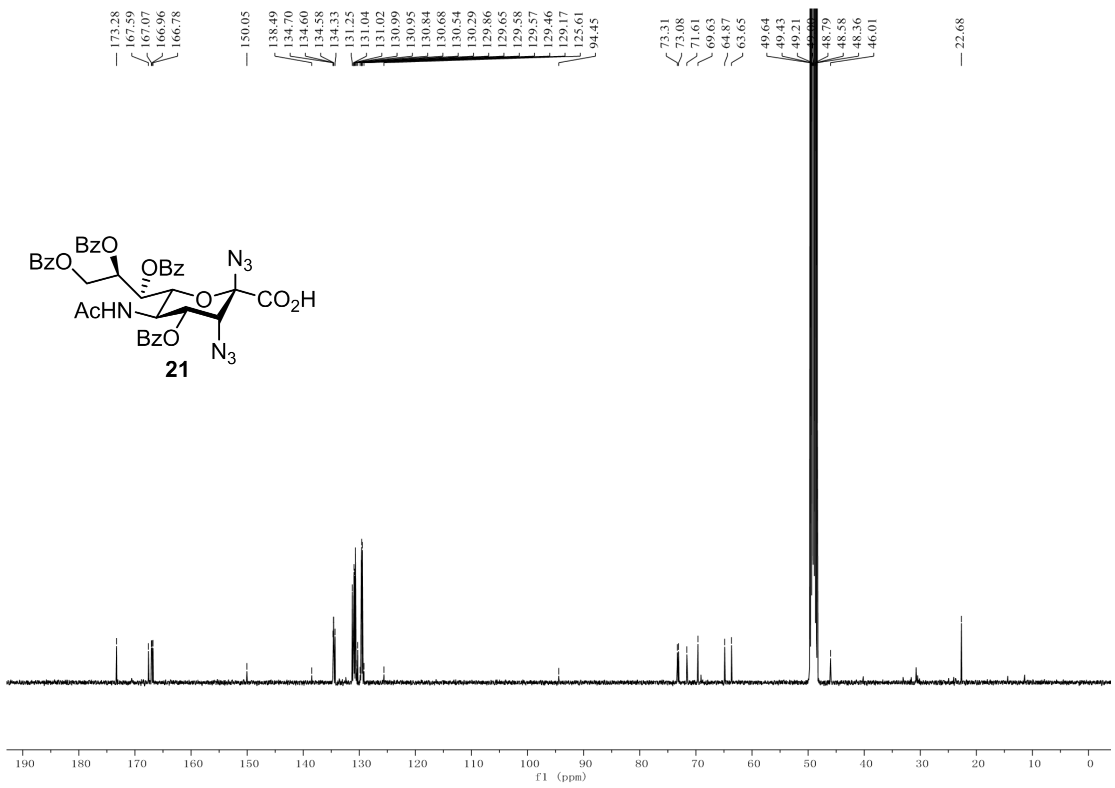
^{1}H NMR spectrum of compound **S15**



^{13}C NMR spectrum of compound **S15**

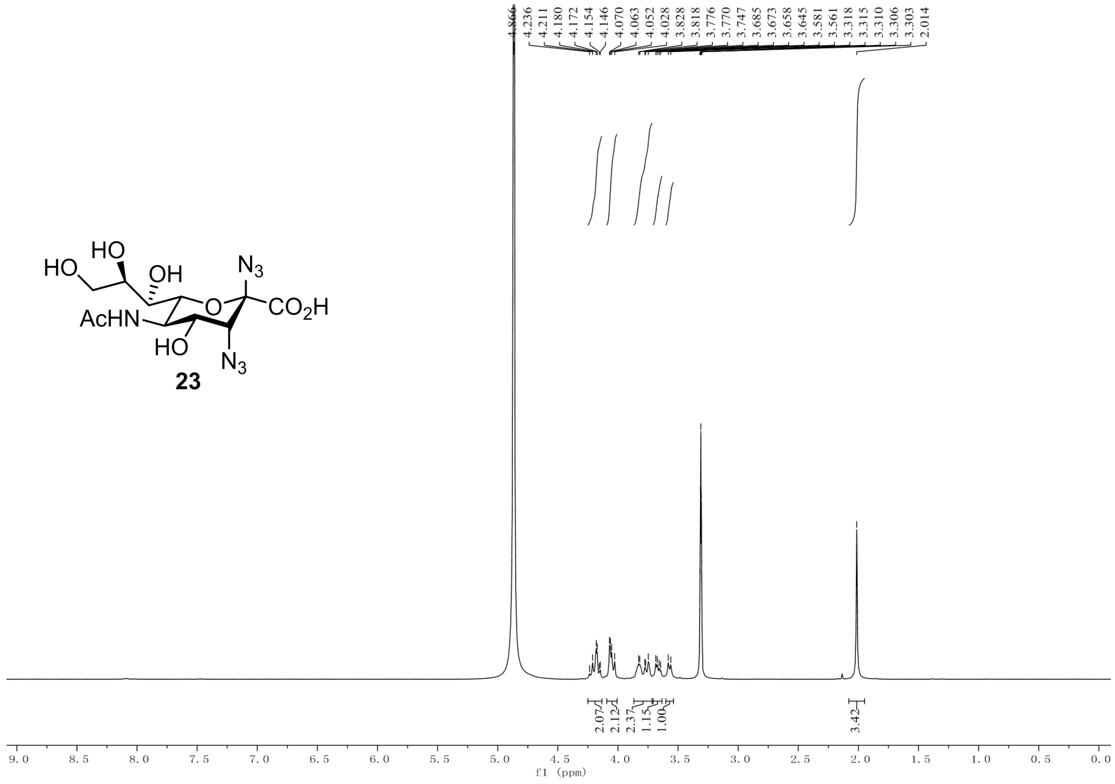


^{1}H NMR spectrum of compound **21**



21

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



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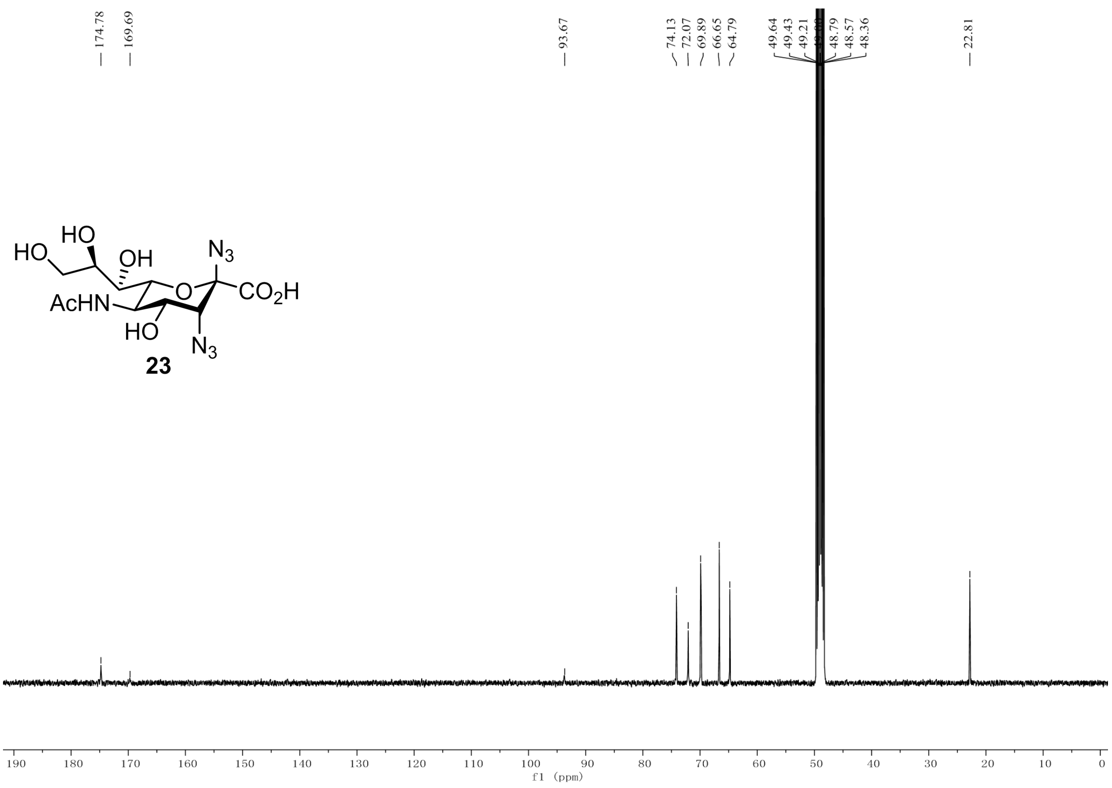
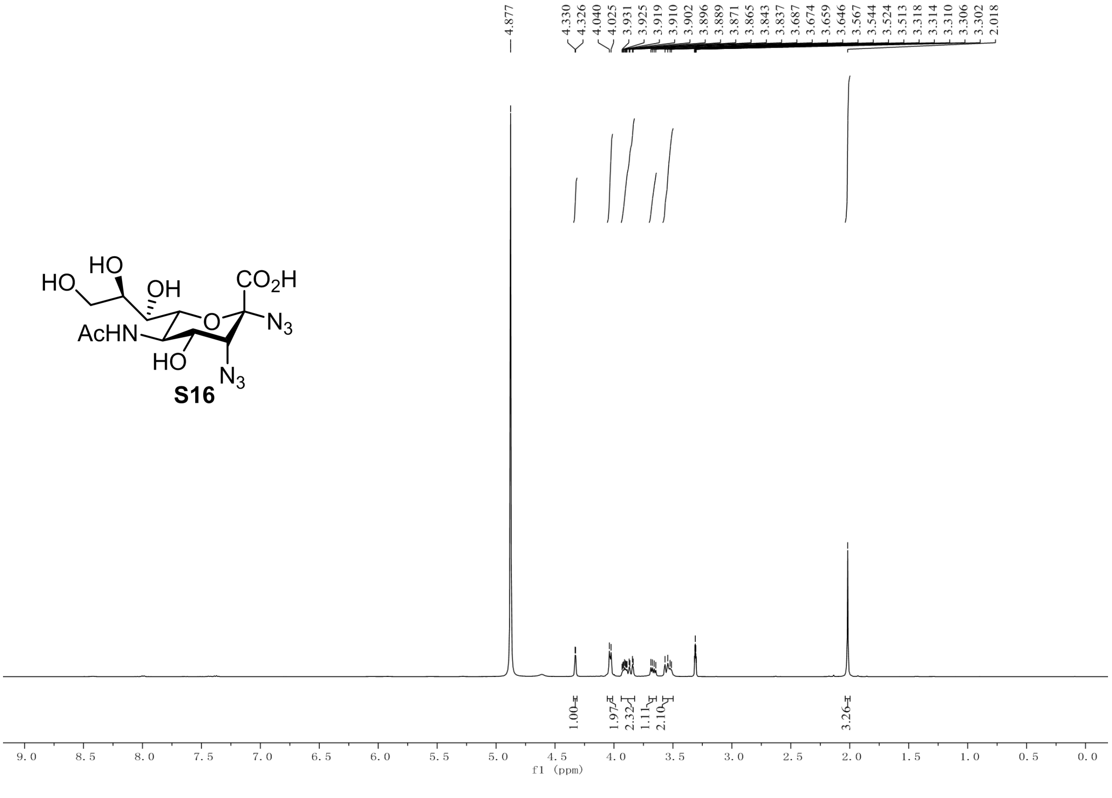
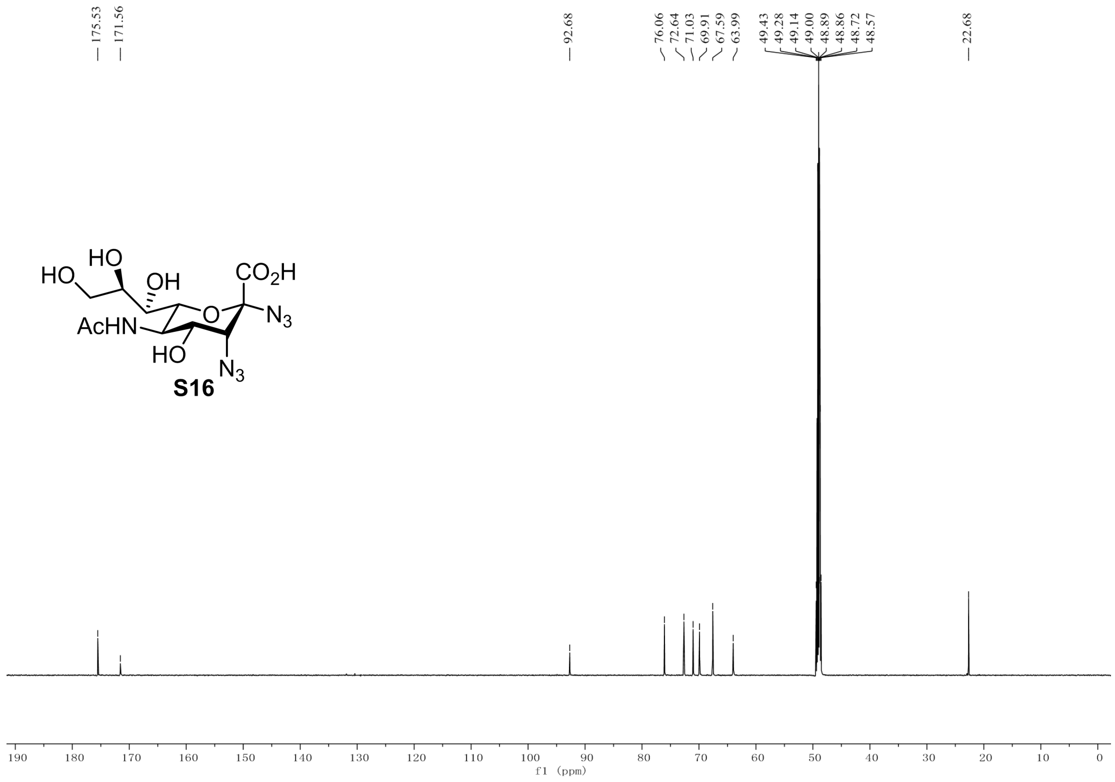
^{1}H NMR spectrum of compound **23**



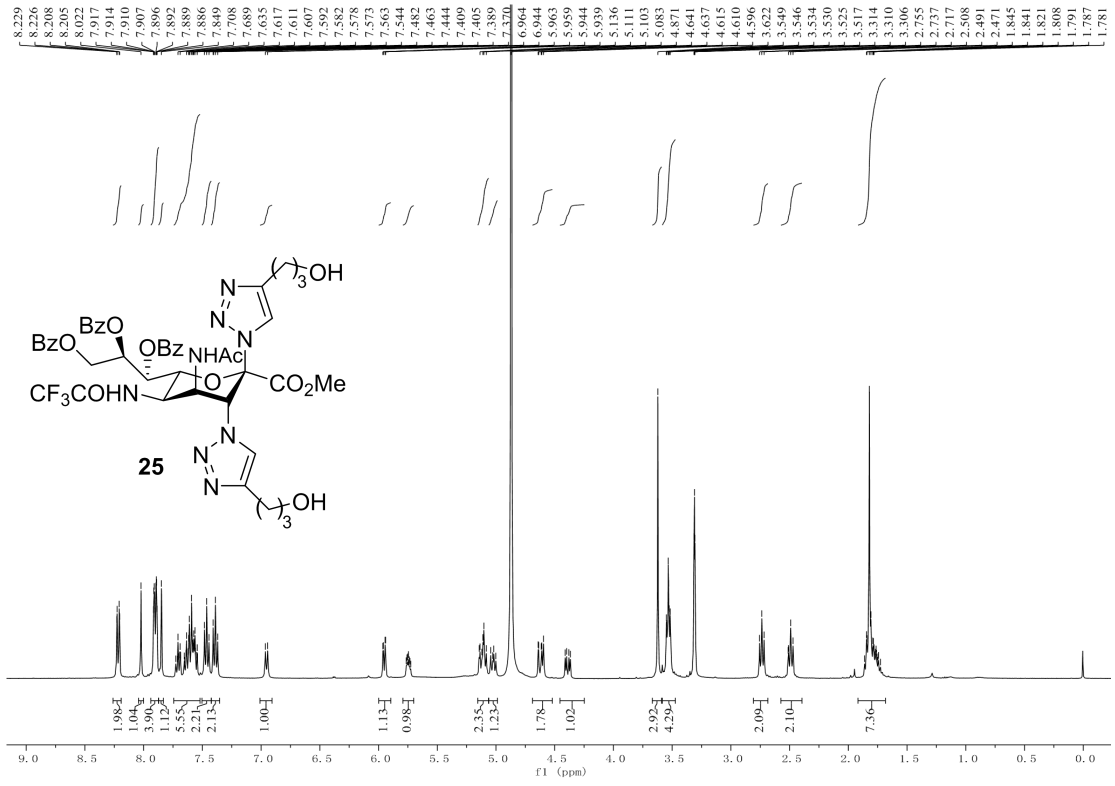
^{13}C NMR spectrum of compound **23**



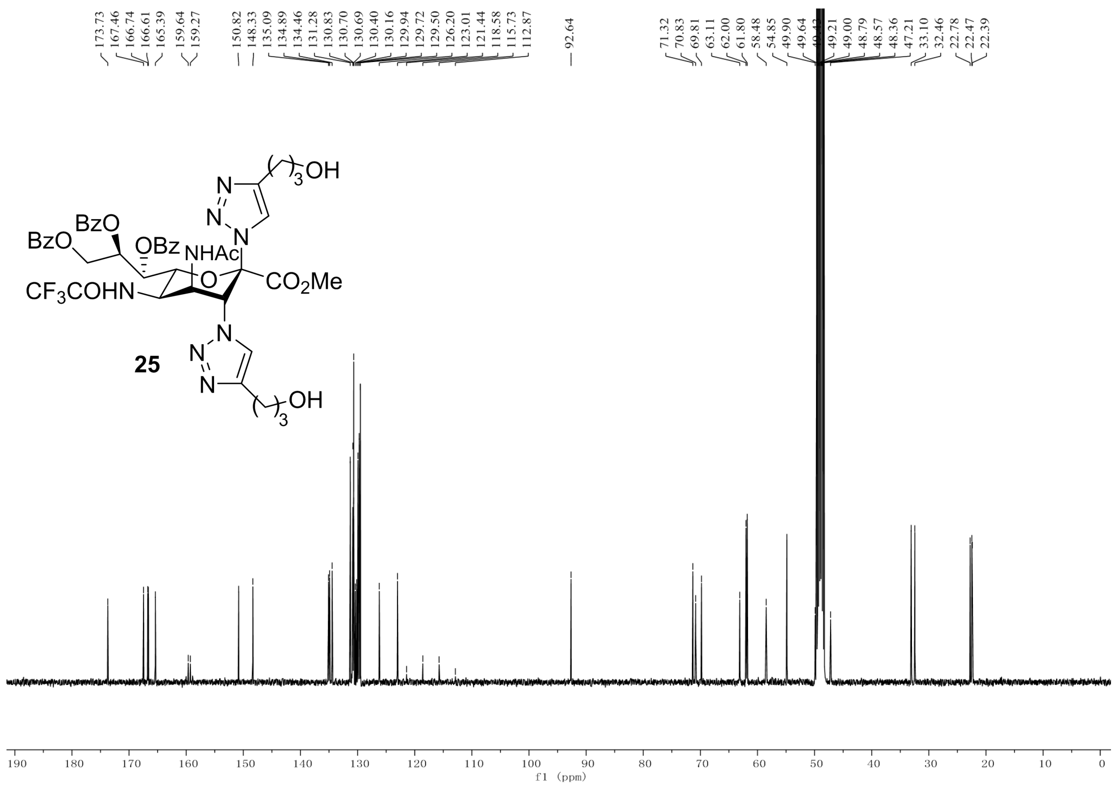
^{1}H NMR spectrum of compound **S16**



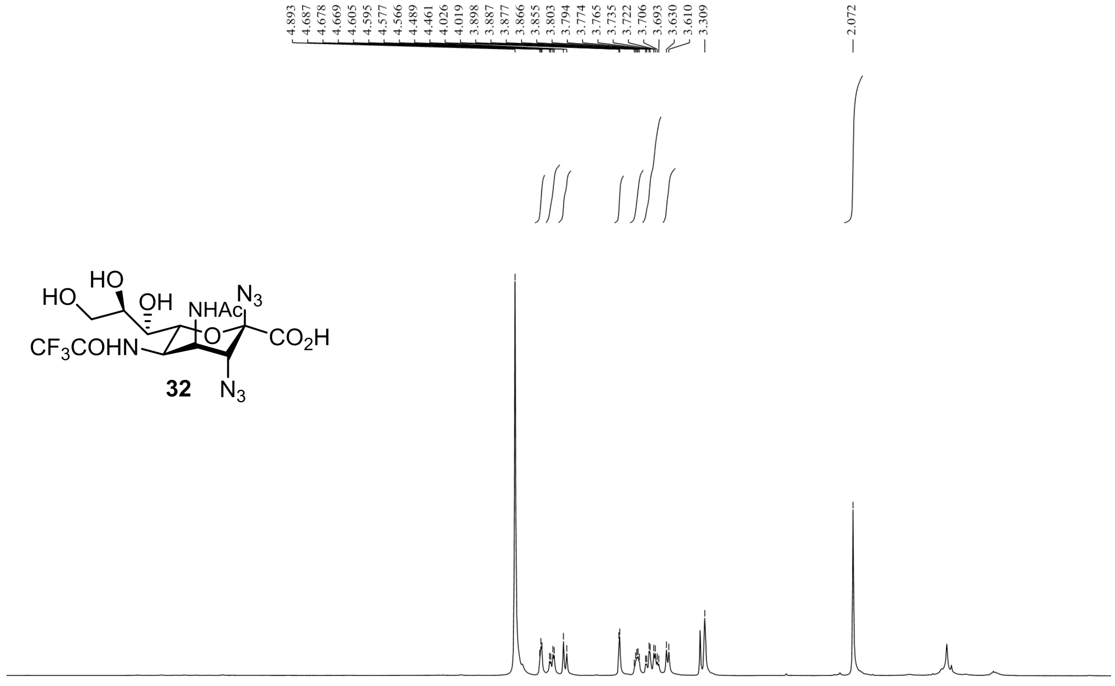
^{13}C NMR spectrum of compound **S16**



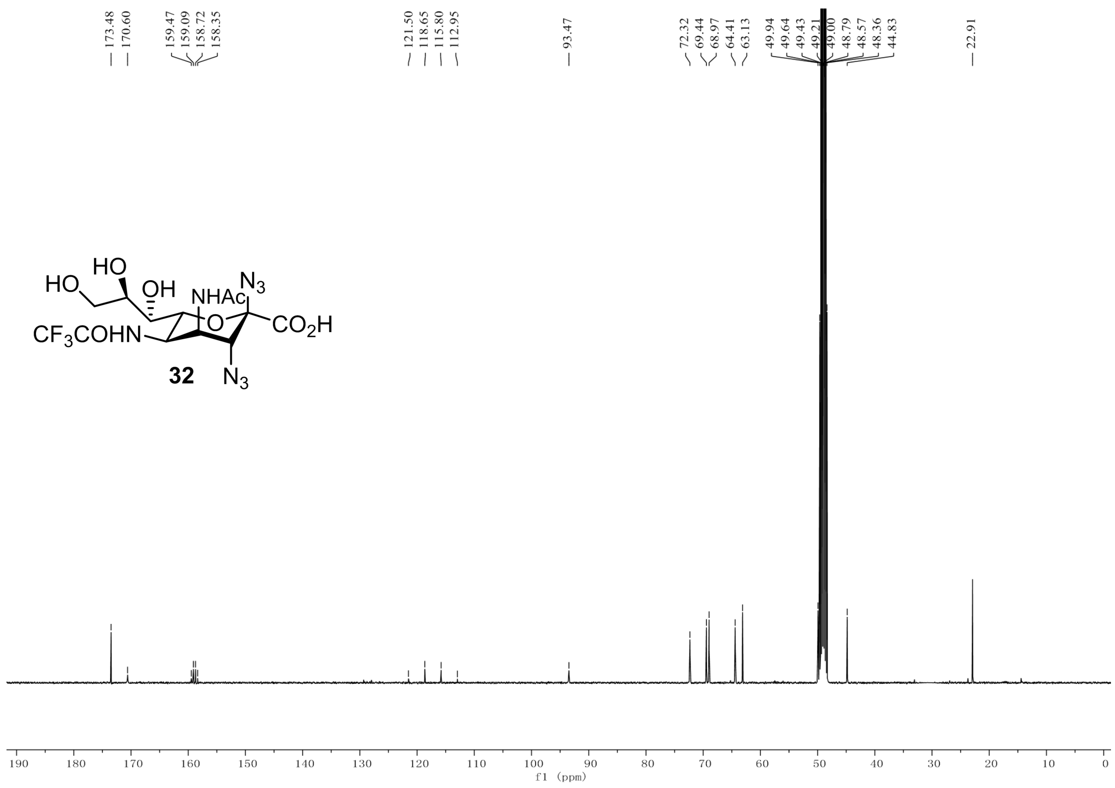
^{1}H NMR spectrum of compound **25**



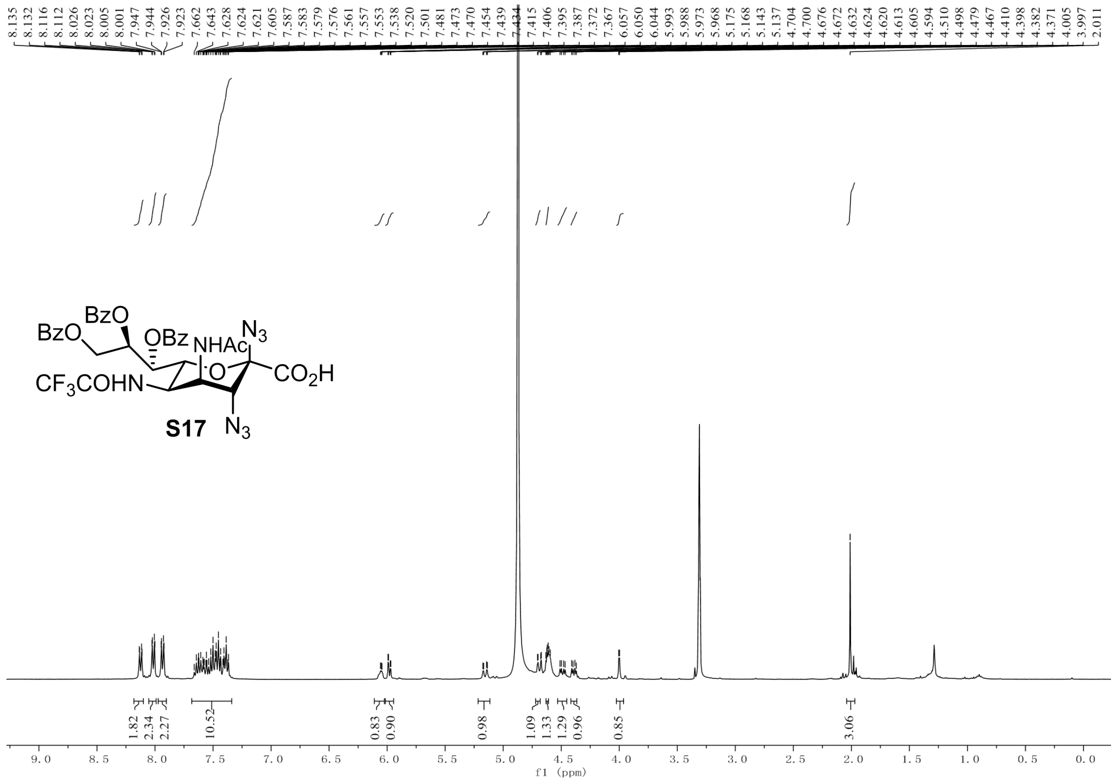
^{13}C NMR spectrum of compound **25**



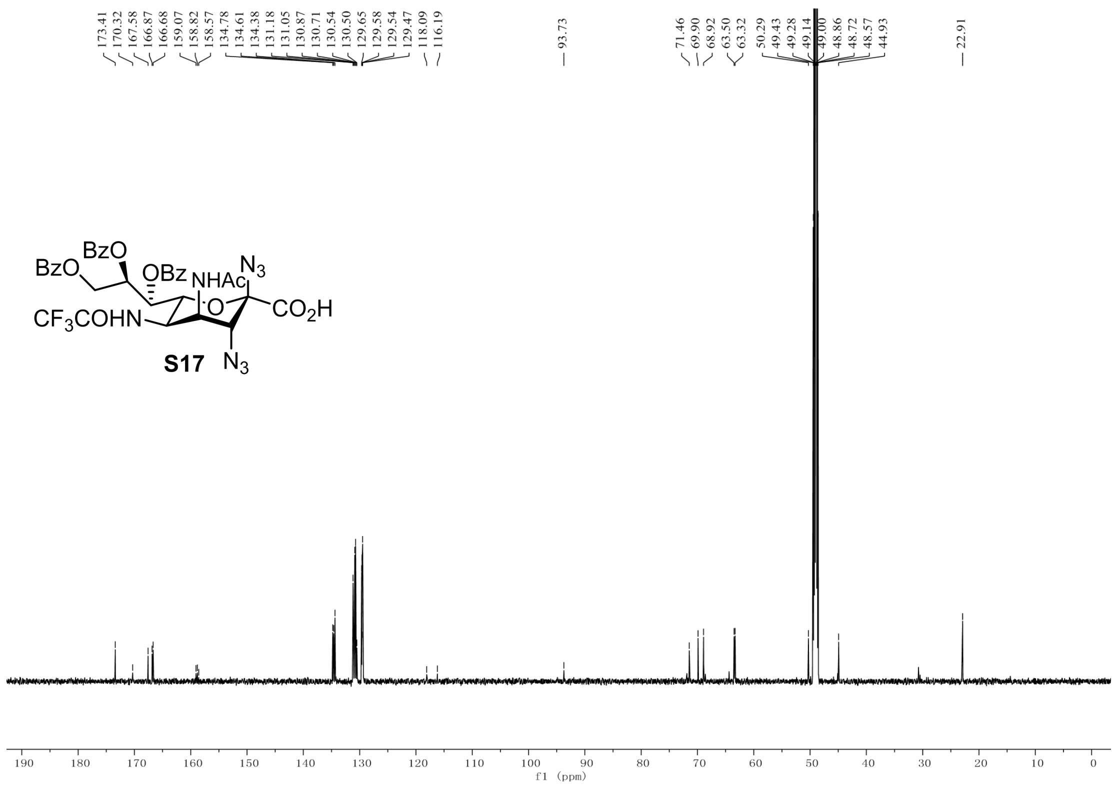
^{1}H NMR spectrum of compound **32**



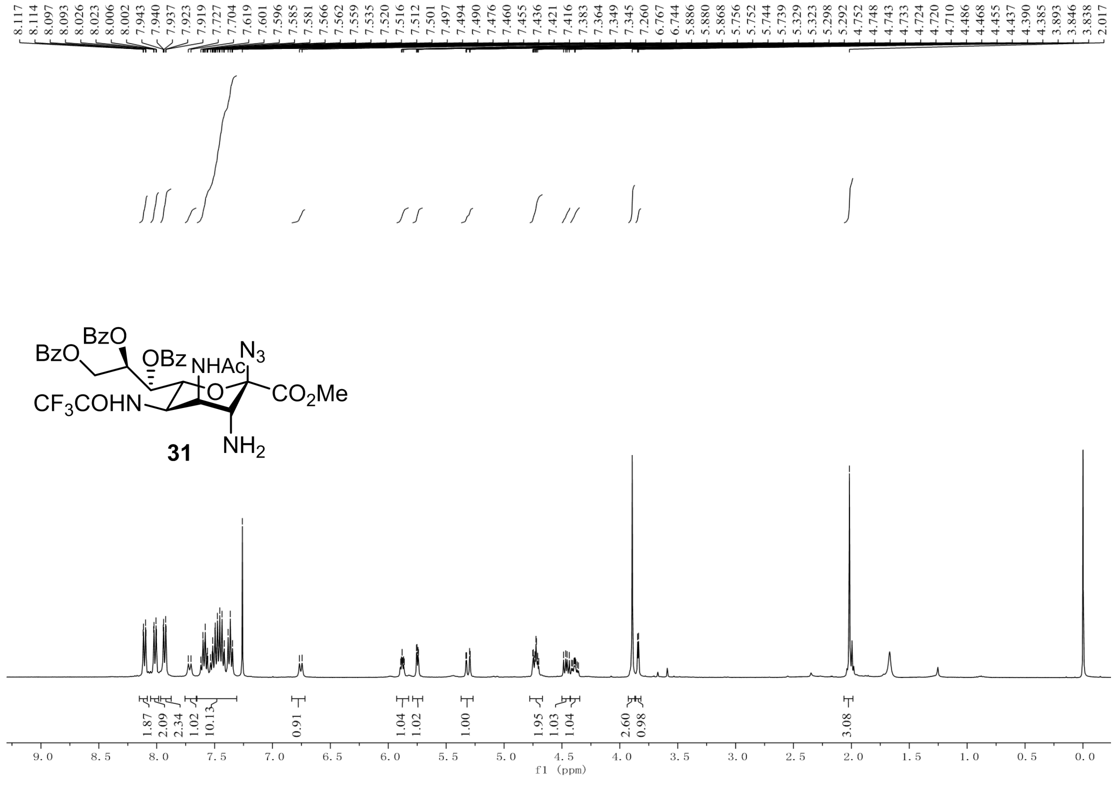
^{13}C NMR spectrum of compound **32**



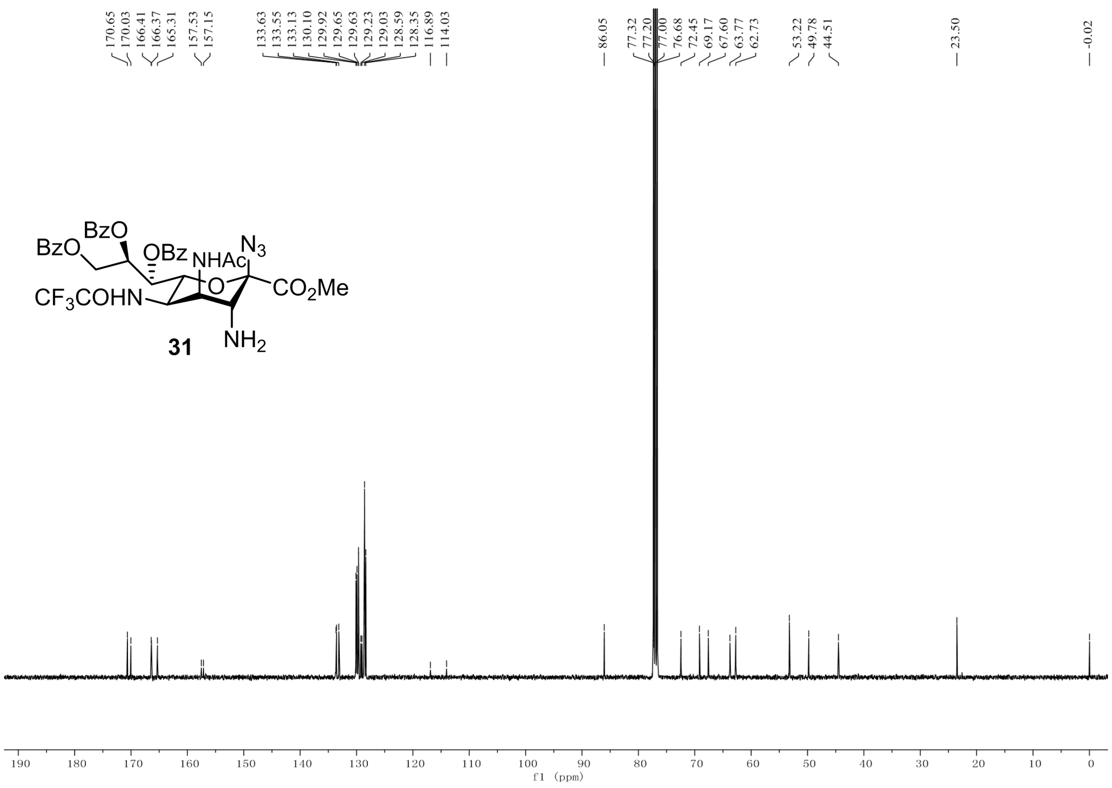
^{1}H NMR spectrum of compound **S17**



^{13}C NMR spectrum of compound **S17**



^{1}H NMR spectrum of compound **31**



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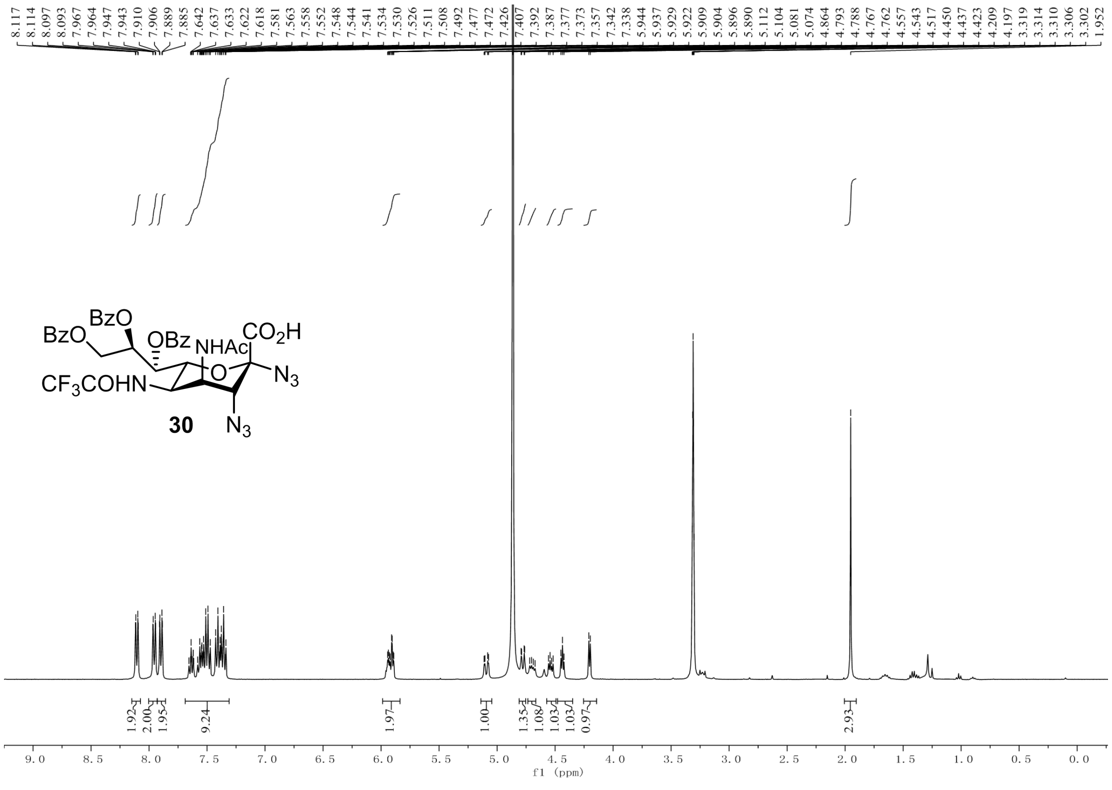
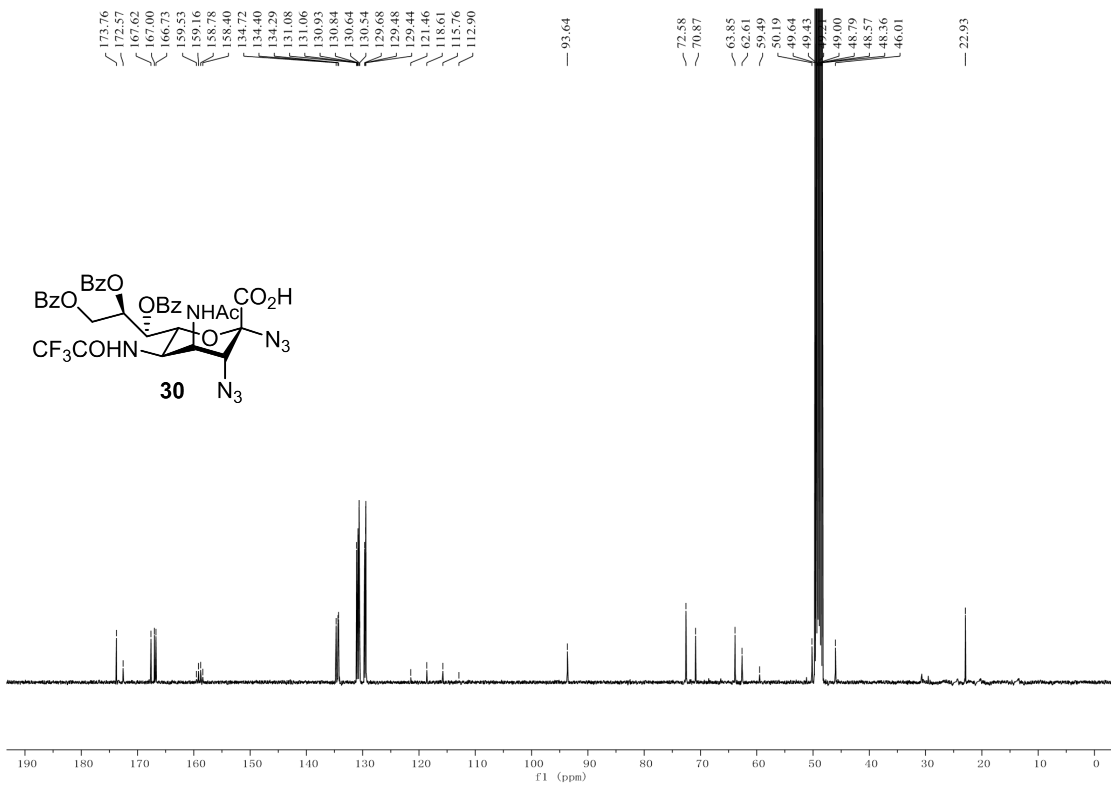
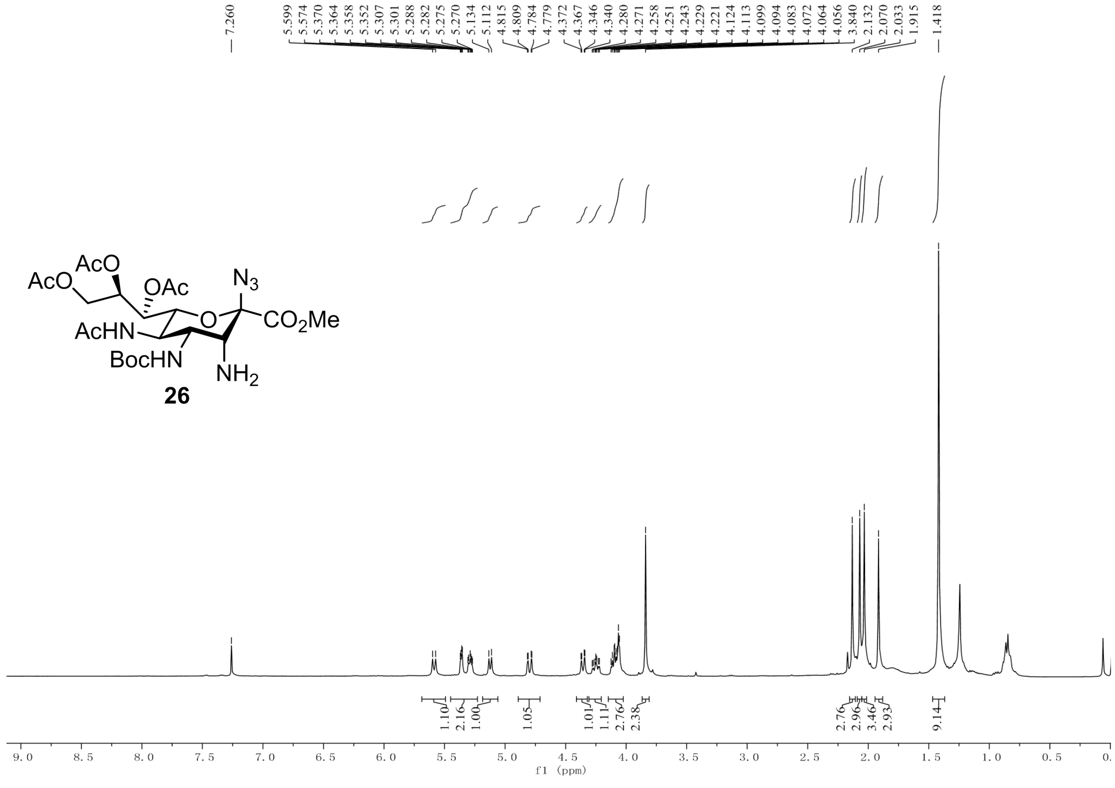


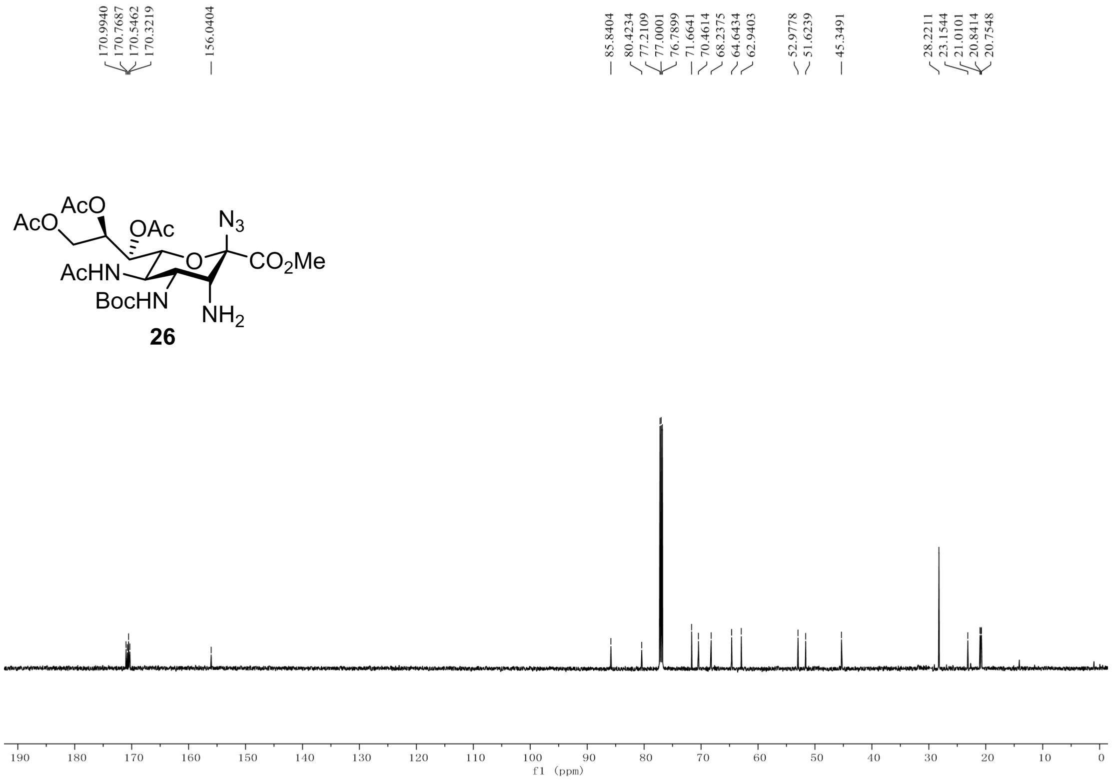
^{1}H NMR spectrum of compound **30**



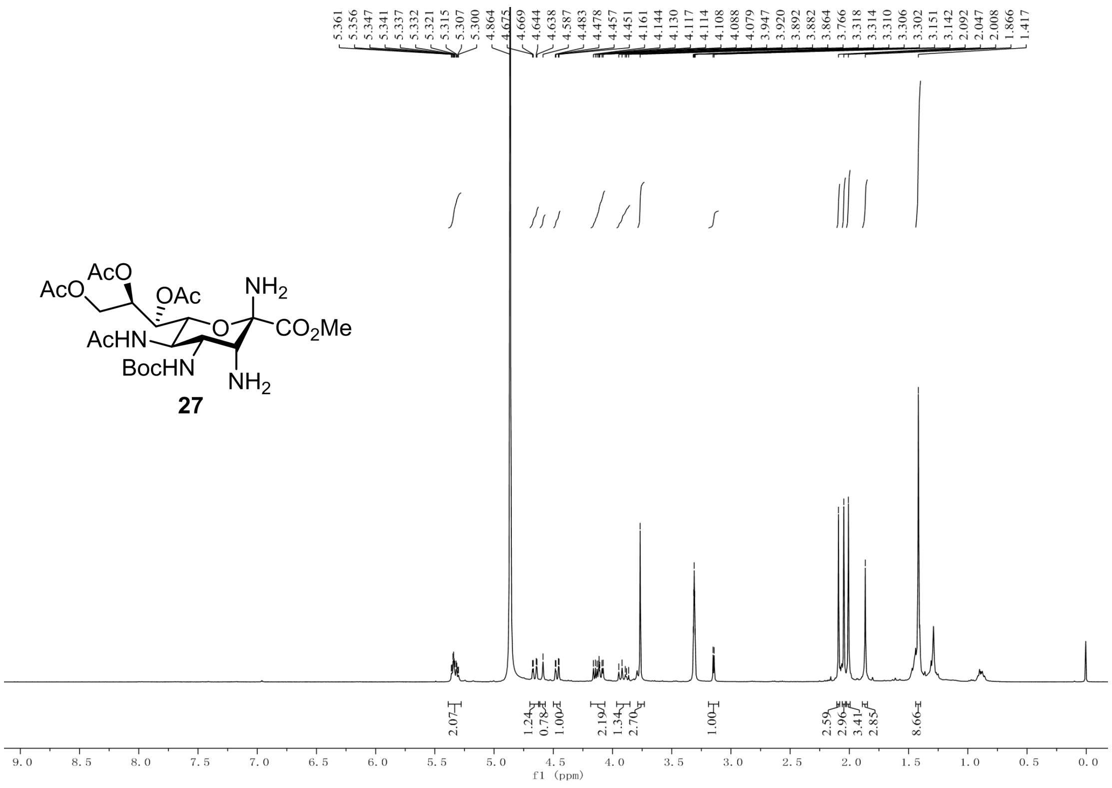
^{13}C NMR spectrum of compound **30**



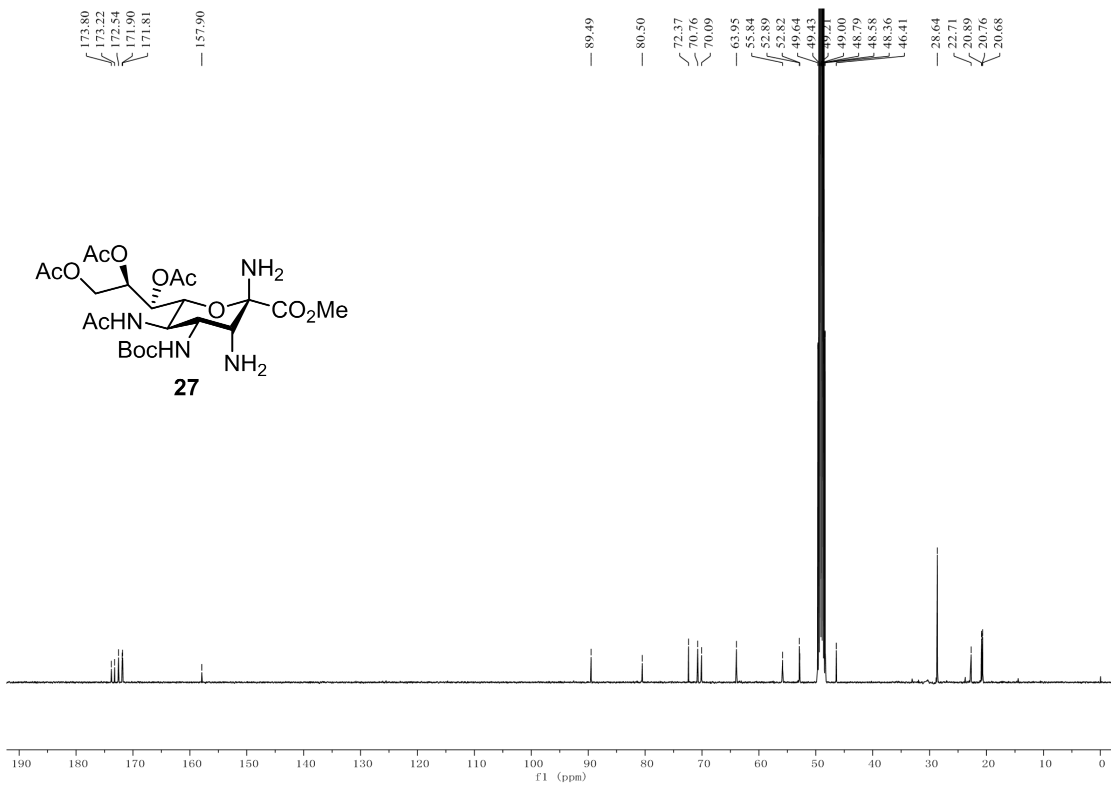
^{1}H NMR spectrum of compound **26**



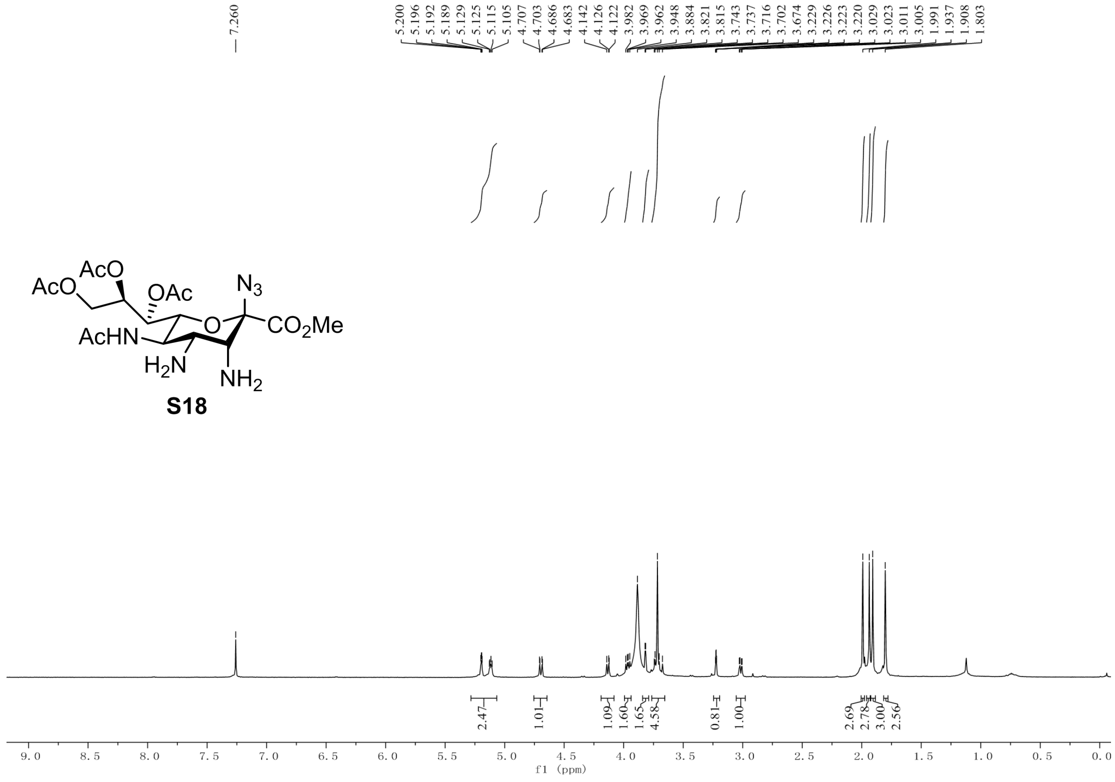
^{13}C NMR spectrum of compound **26**



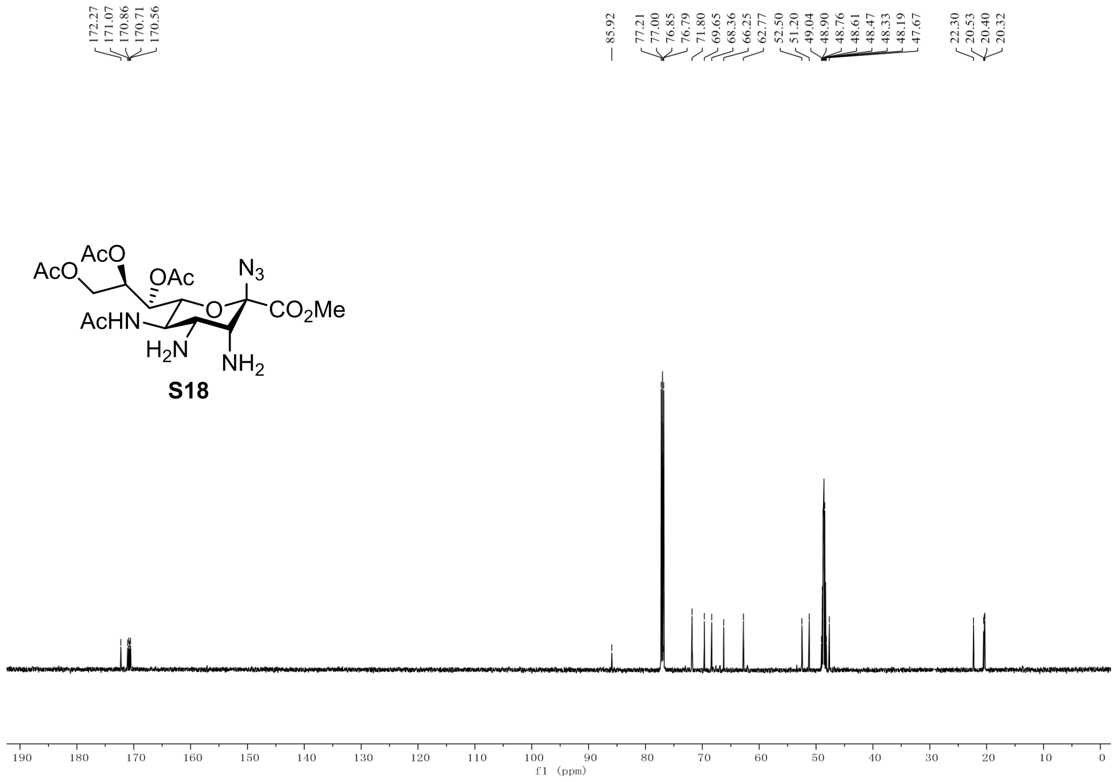
^{1}H NMR spectrum of compound **27**



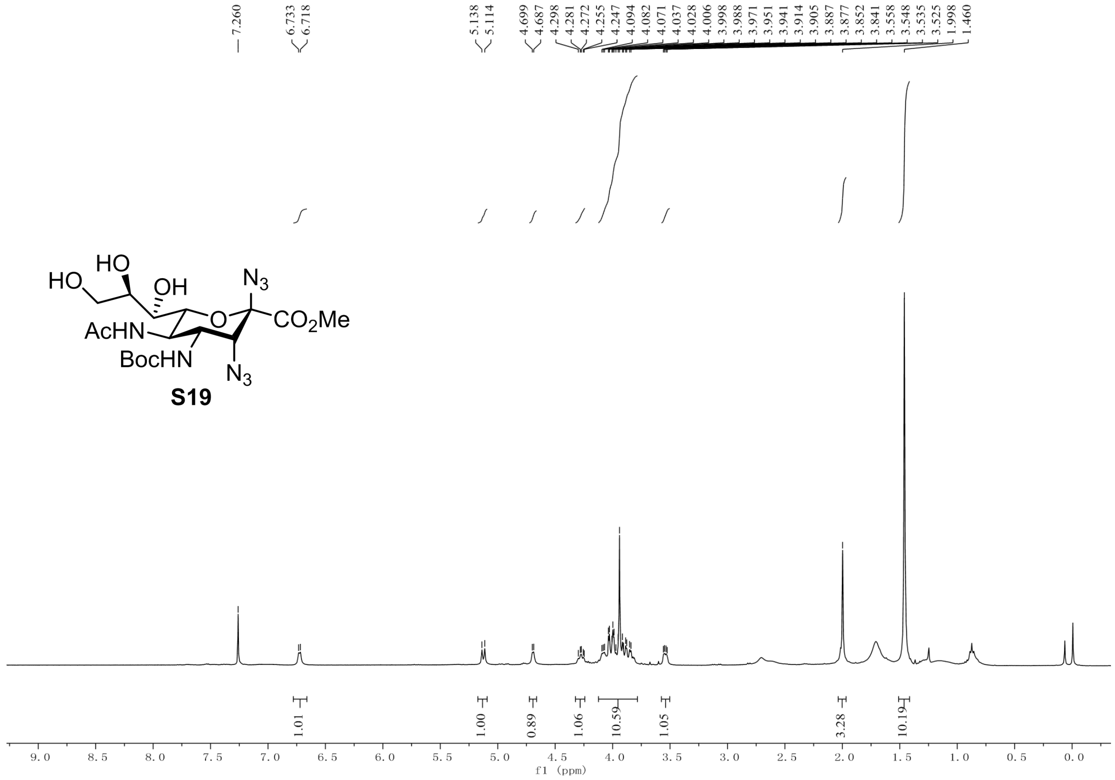
^{13}C NMR spectrum of compound **27**



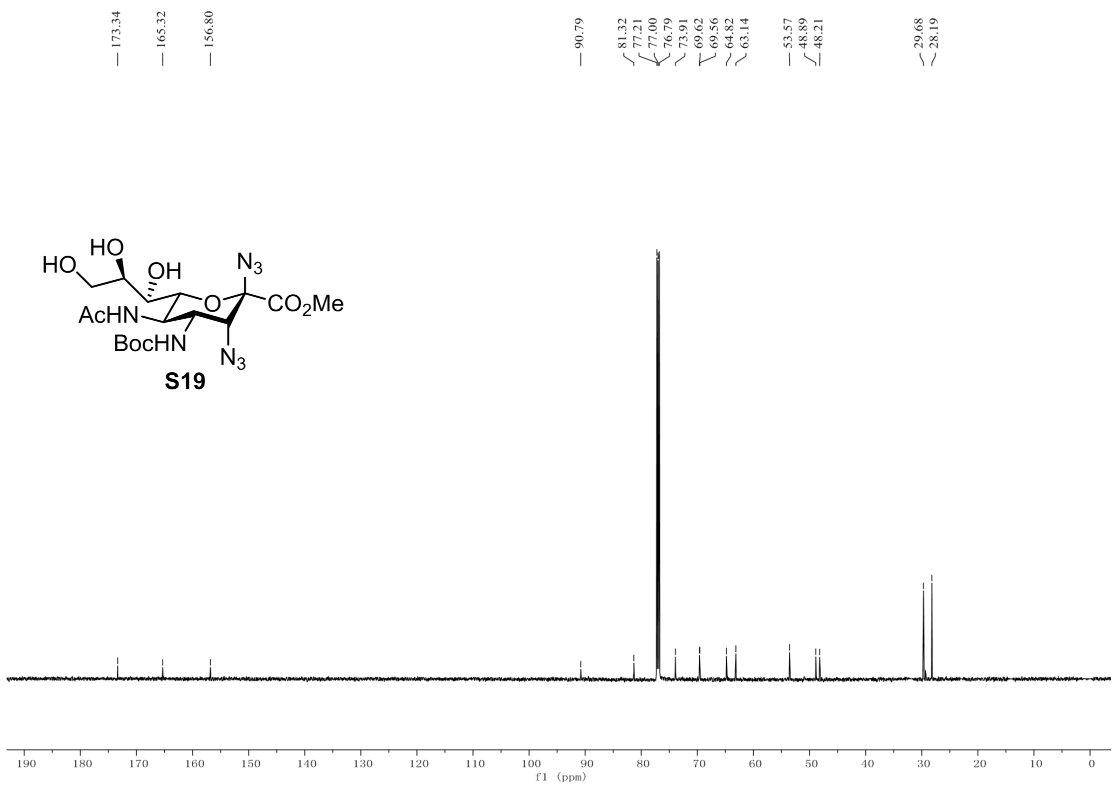
^{1}H NMR spectrum of compound **S18**



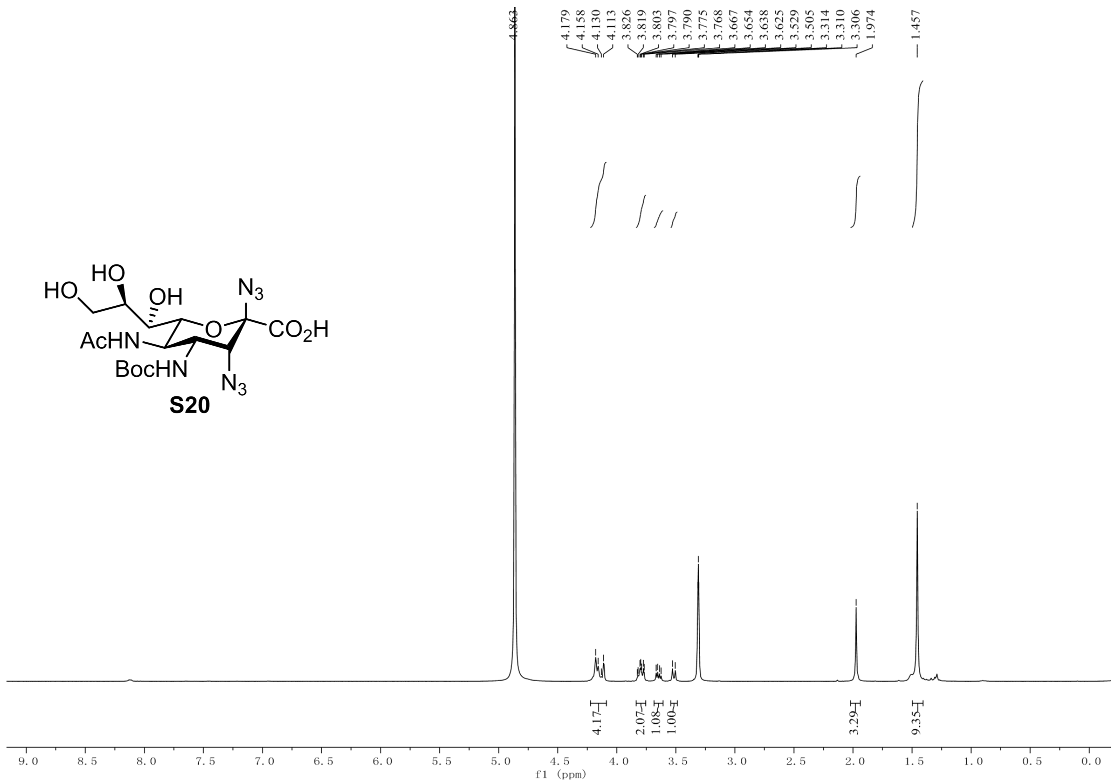
^{13}C NMR spectrum of compound **S18**



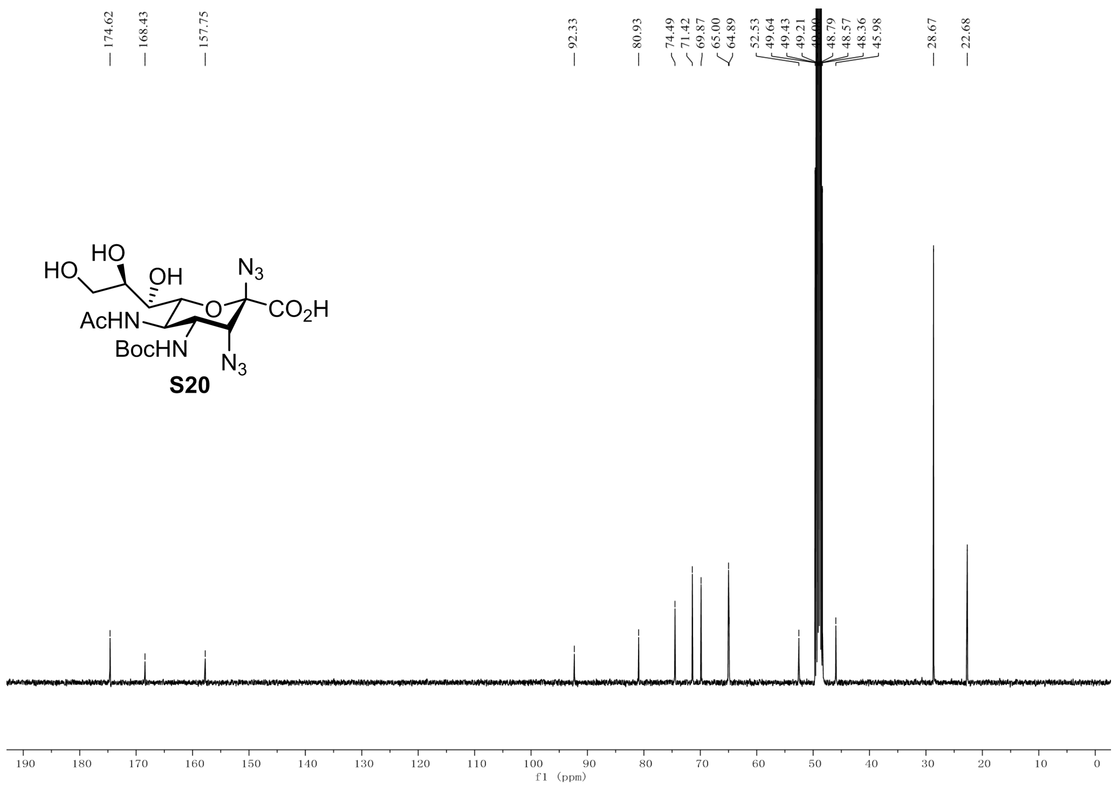
^{1}H NMR spectrum of compound **S19**



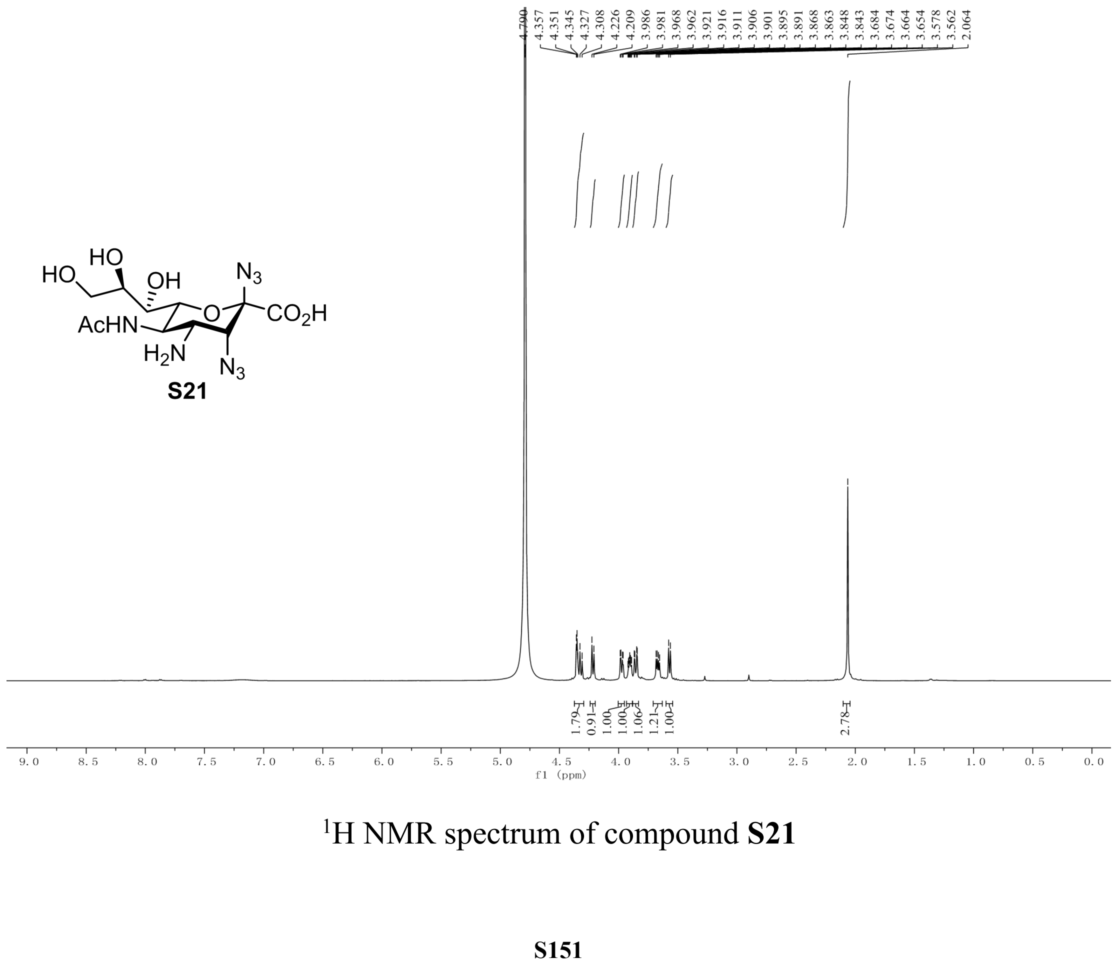
^{13}C NMR spectrum of compound **S19**



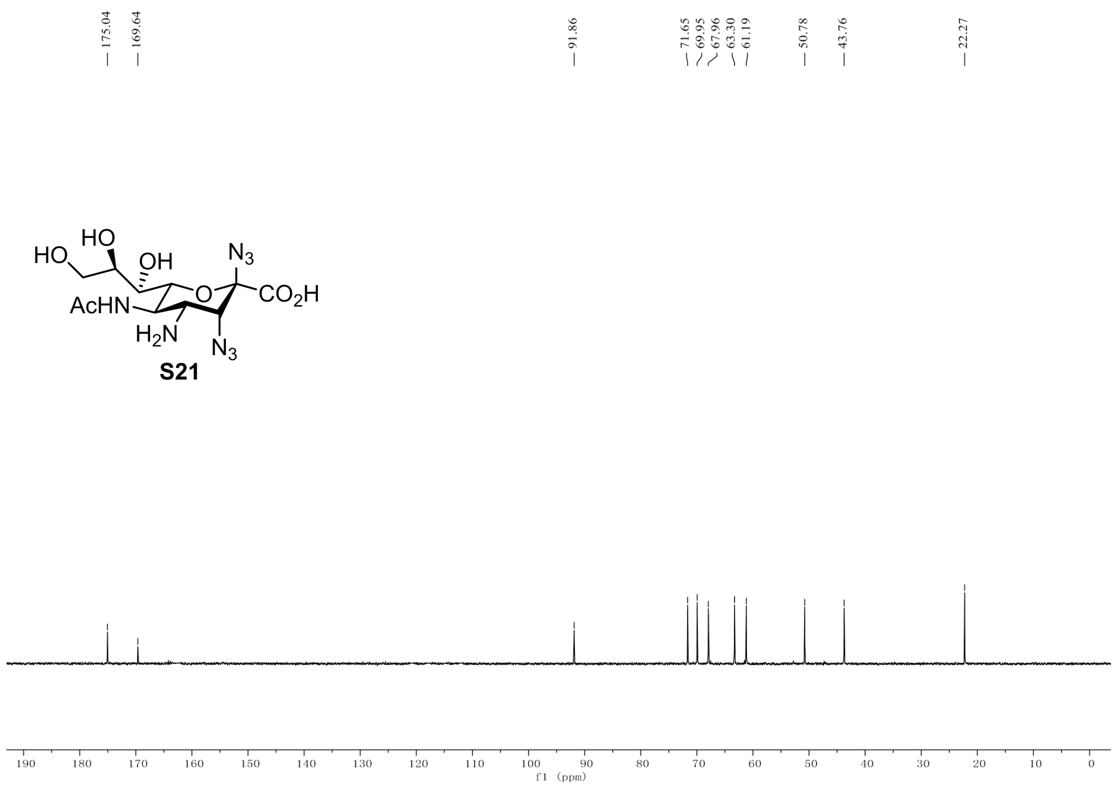
^{1}H NMR spectrum of compound **S20**



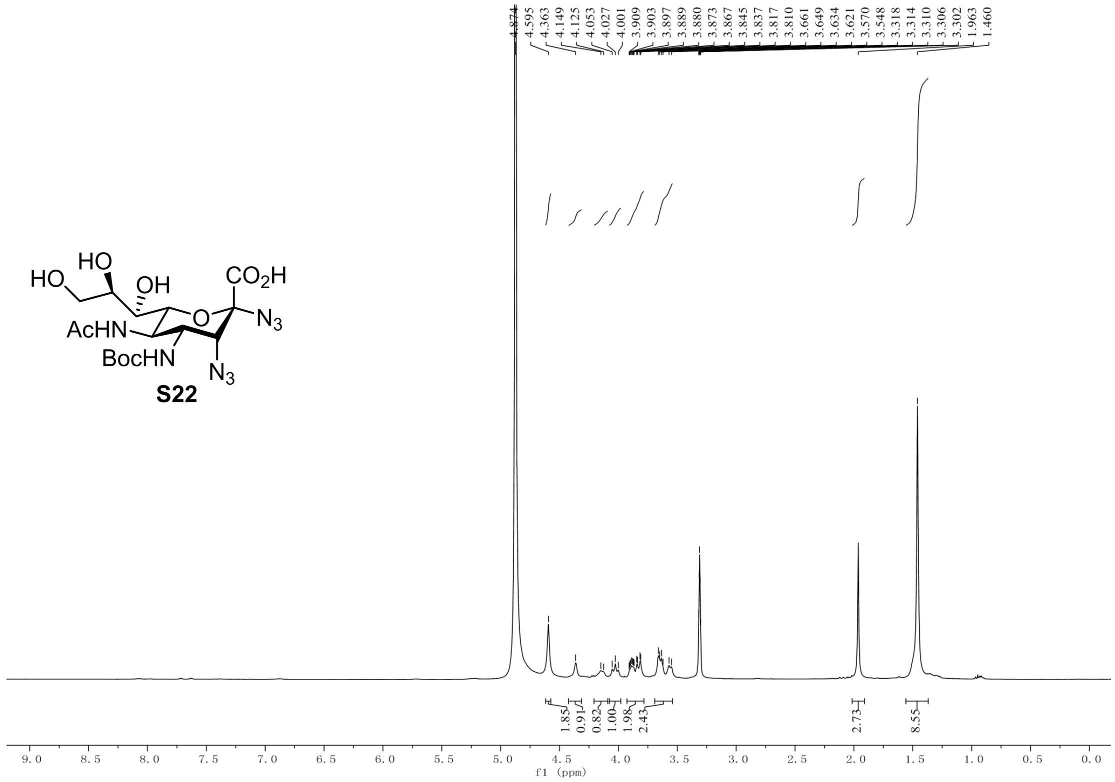
^{13}C NMR spectrum of compound **S20**



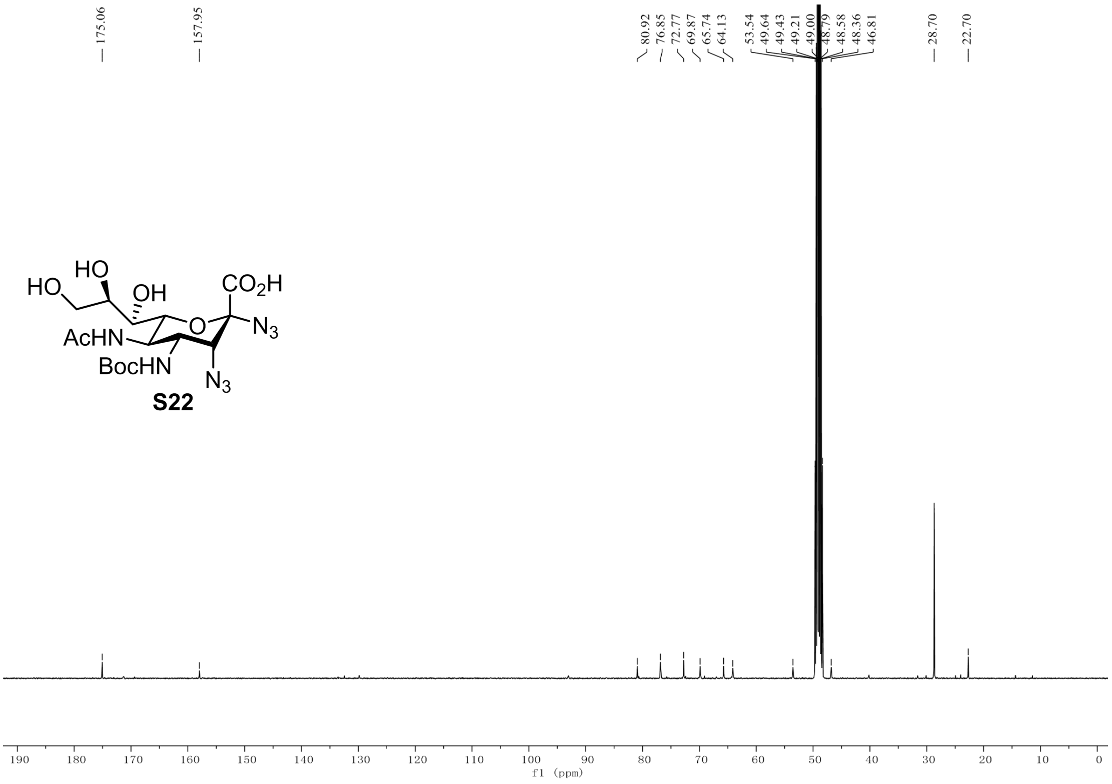
^{1}H NMR spectrum of compound **S21**



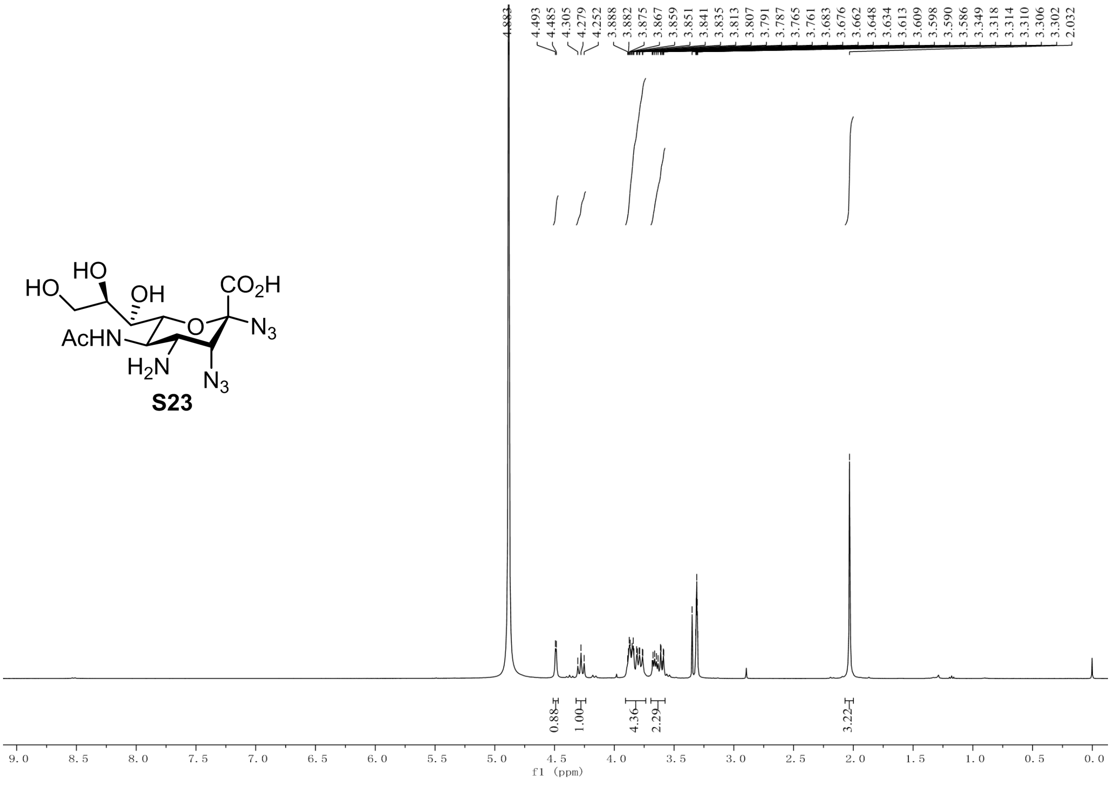
^{13}C NMR spectrum of compound **S21**



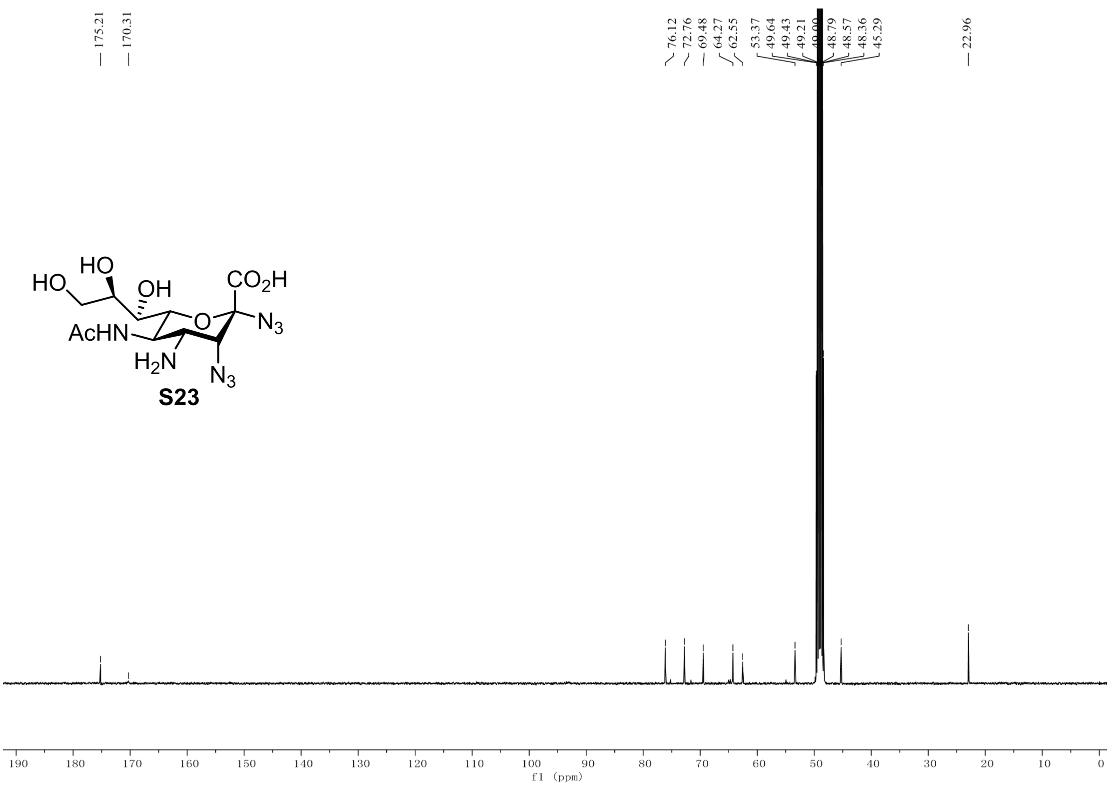
^{1}H NMR spectrum of compound **S22**



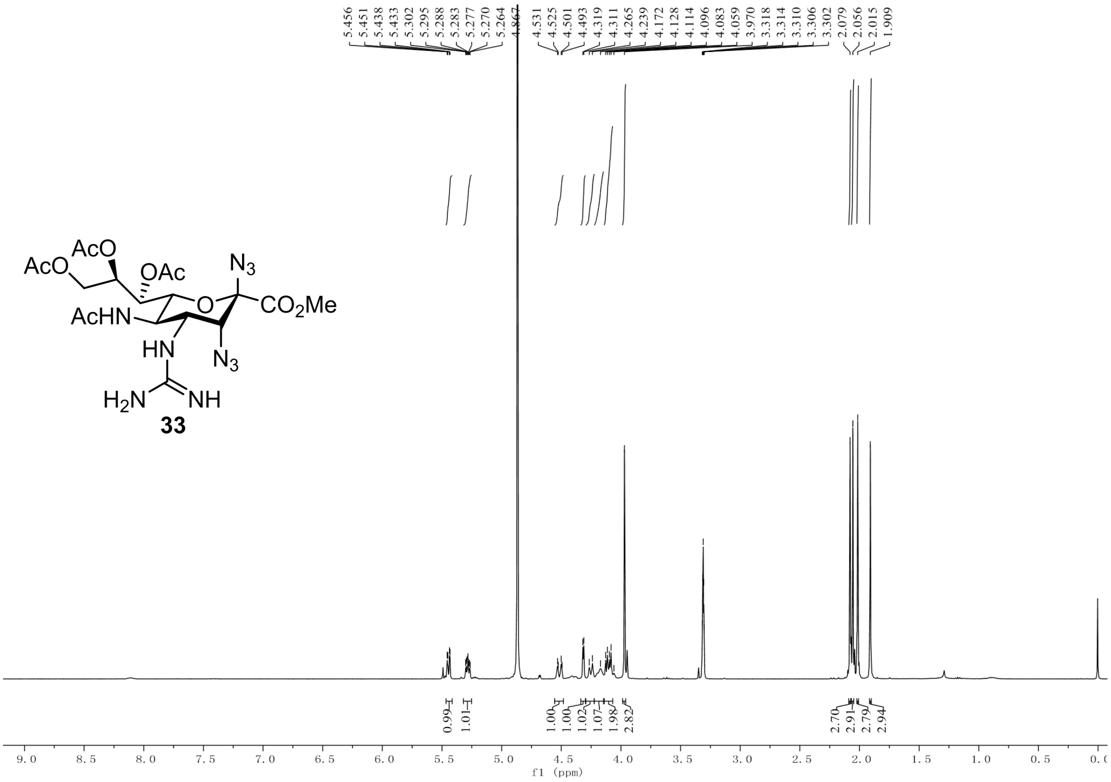
^{13}C NMR spectrum of compound **S22**



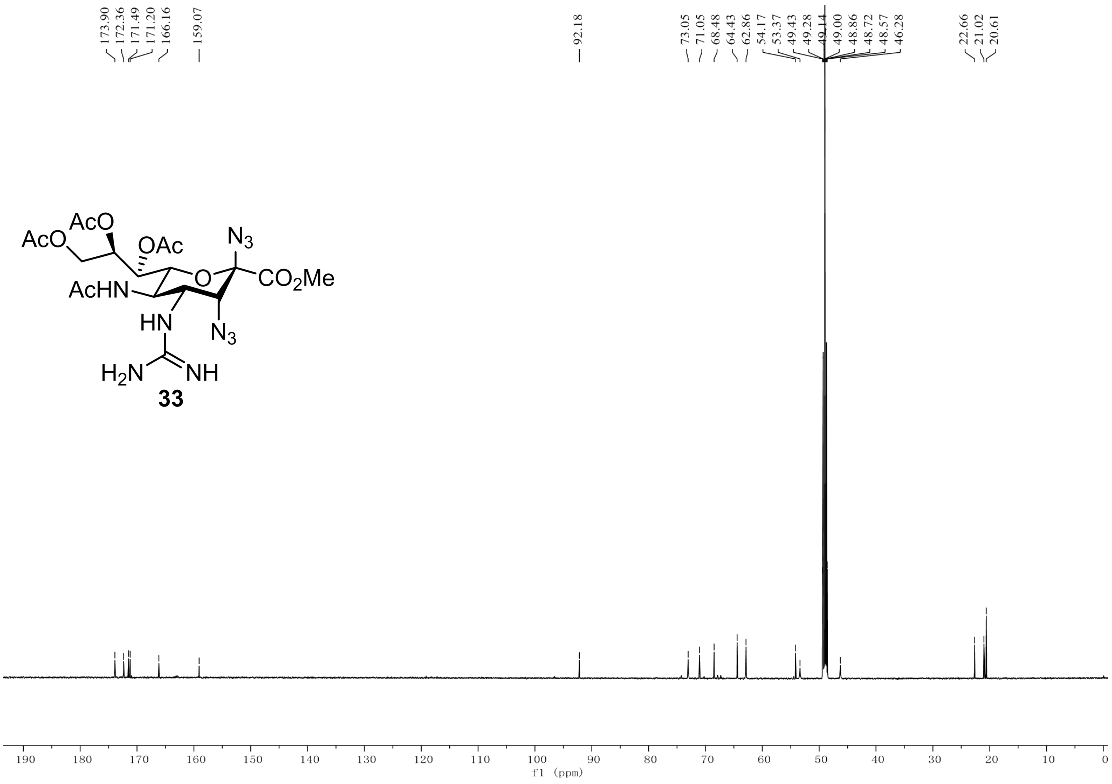
^{1}H NMR spectrum of compound **S23**



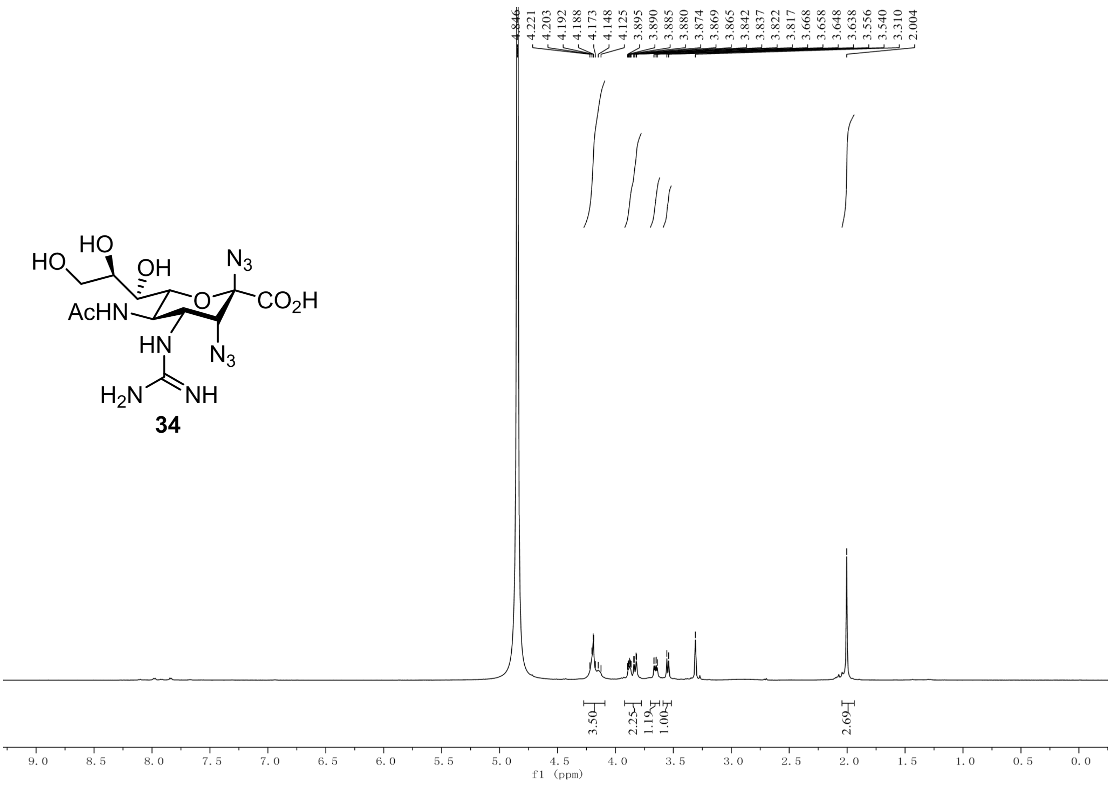
^{13}C NMR spectrum of compound **S23**



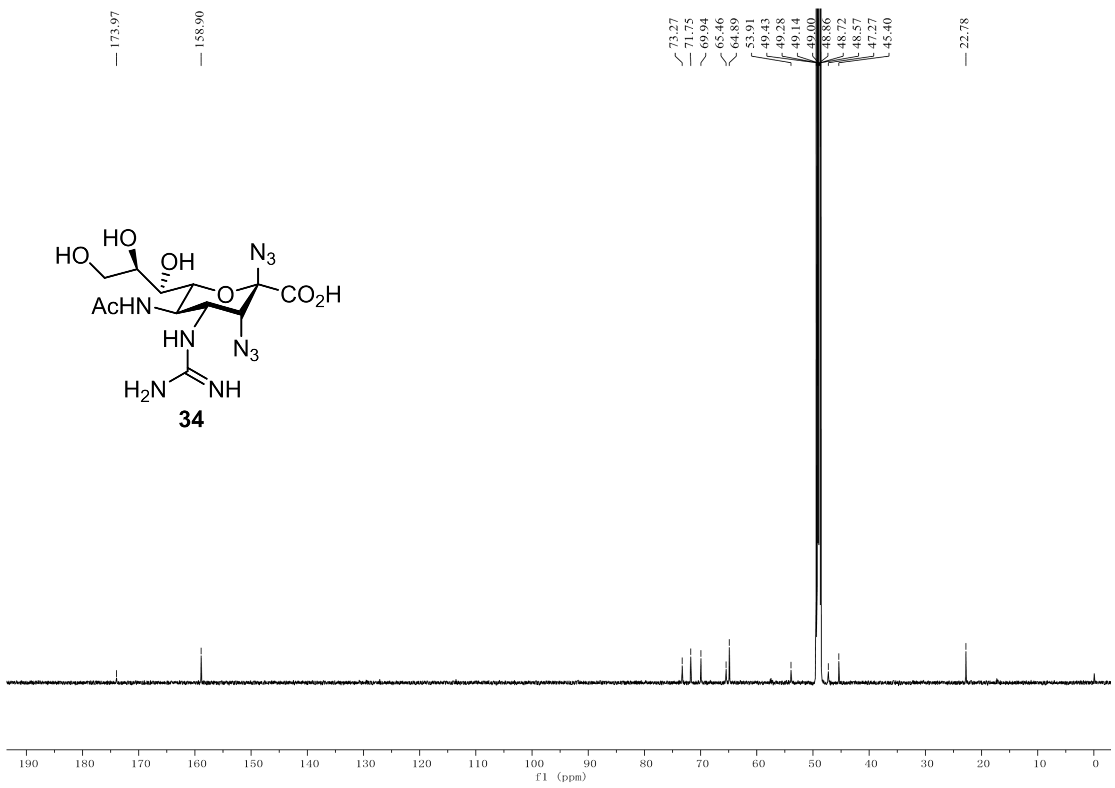
^{1}H NMR spectrum of compound **33**



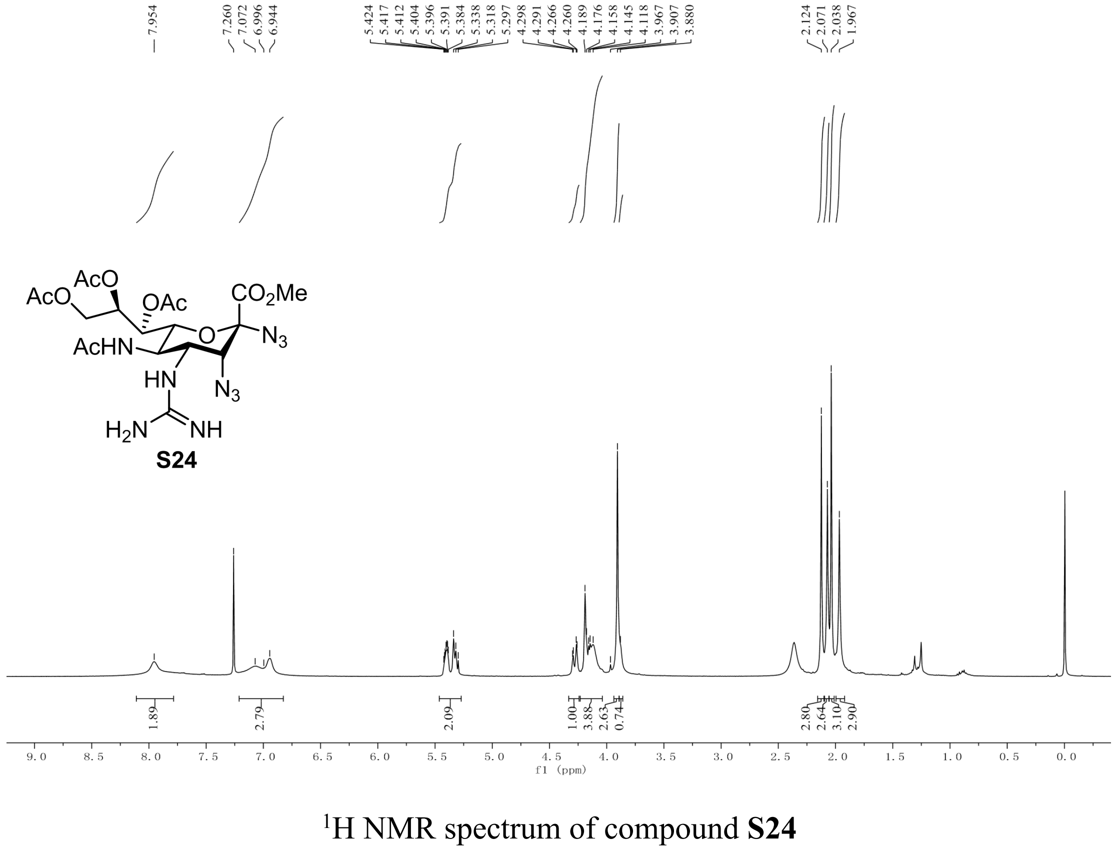
^{13}C NMR spectrum of compound **33**



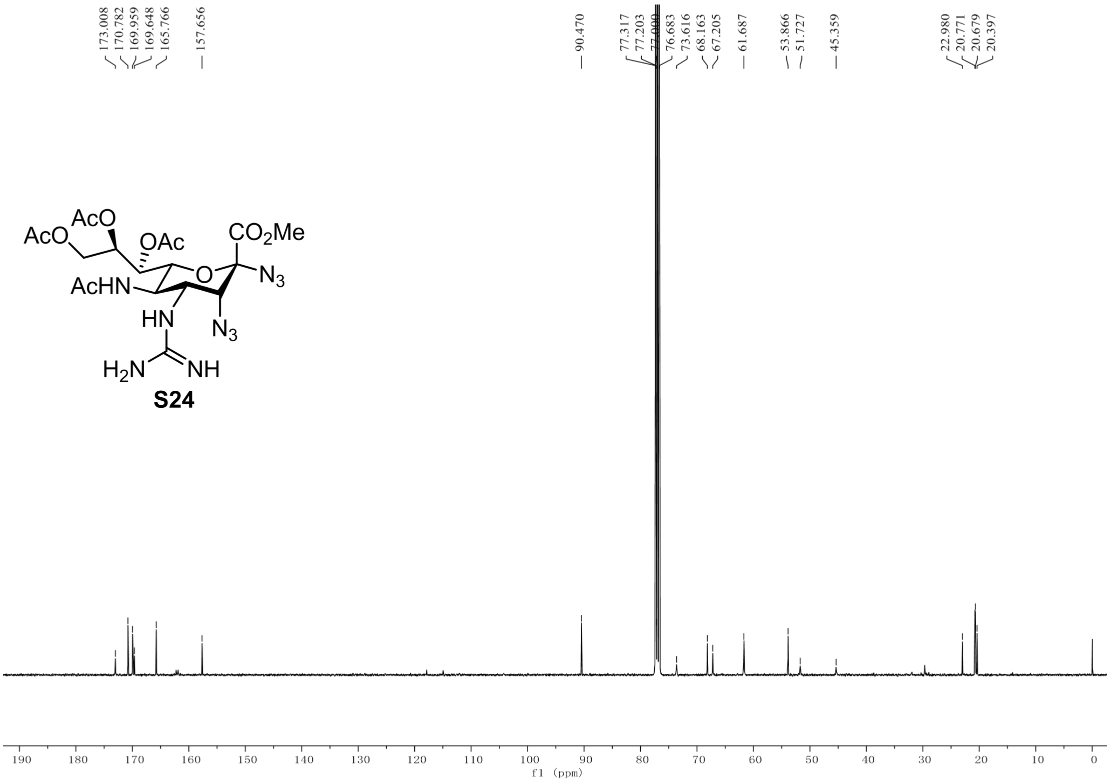
^{1}H NMR spectrum of compound **34**



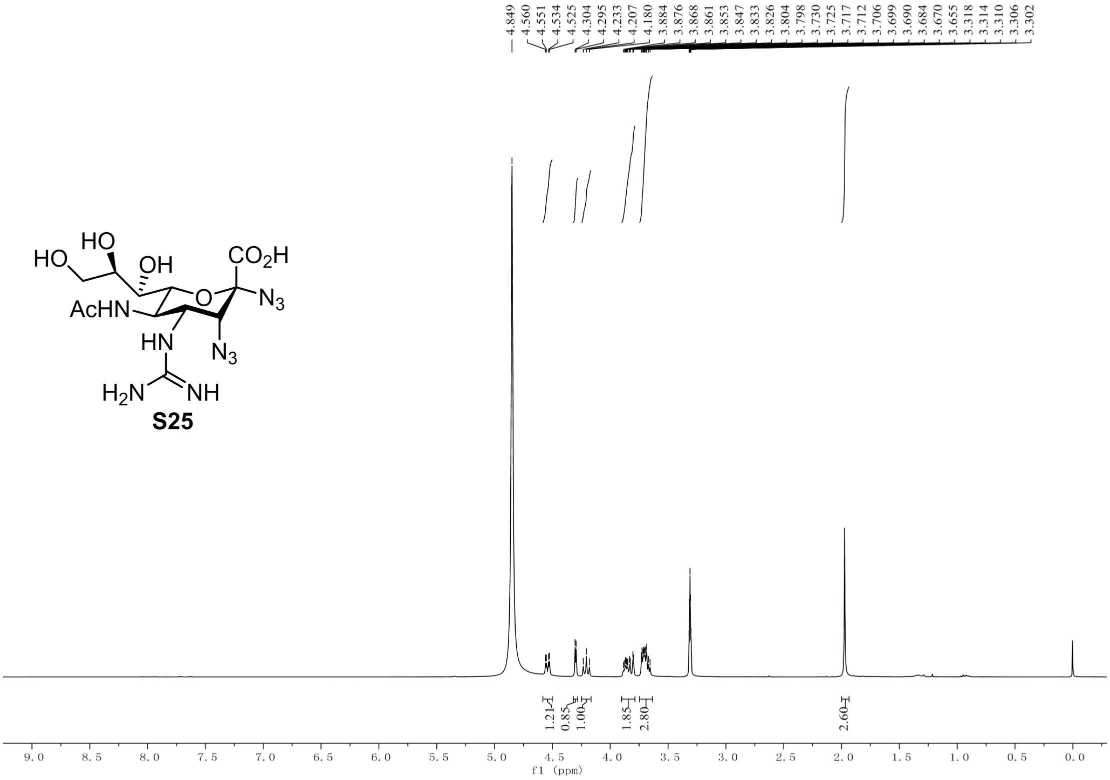
^{13}C NMR spectrum of compound **34**



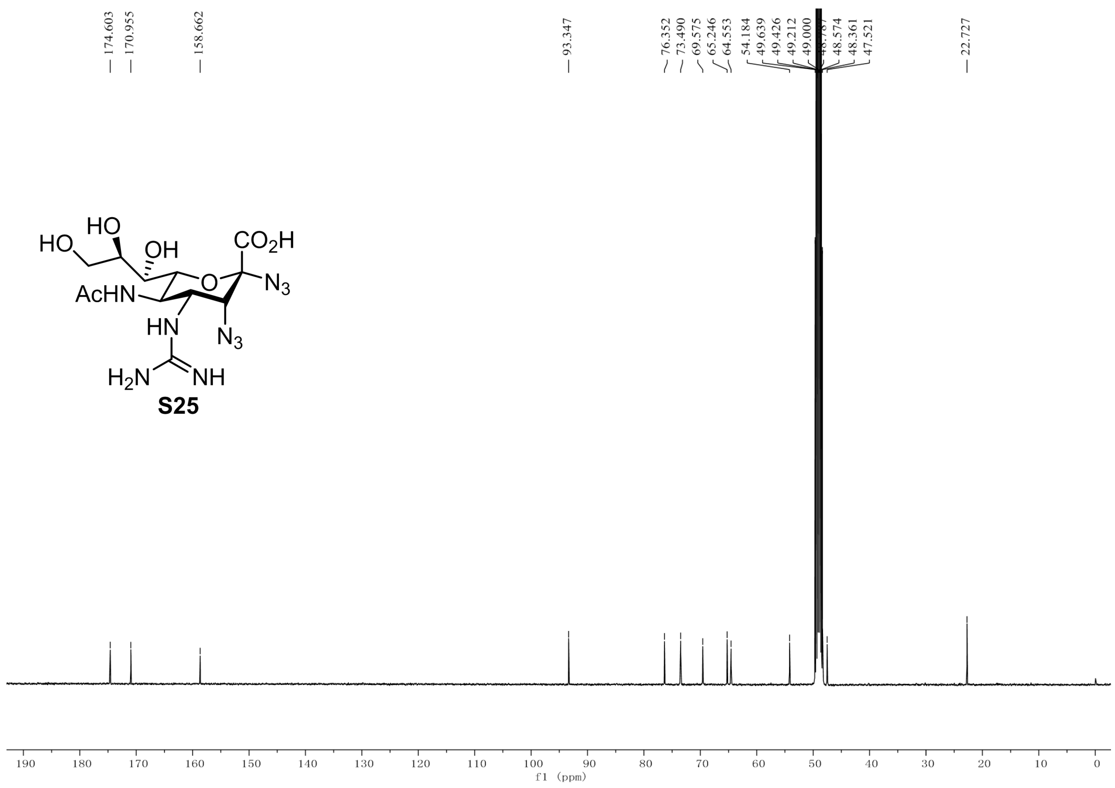
^{1}H NMR spectrum of compound **S24**



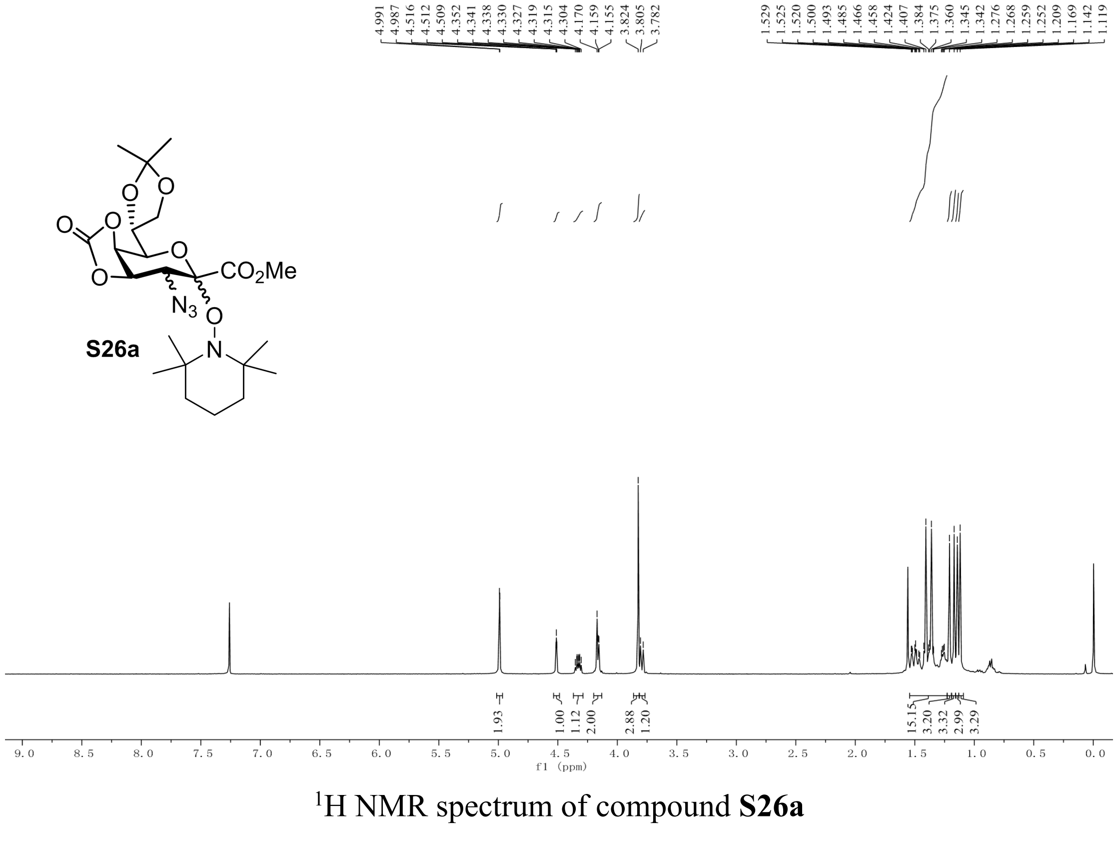
^{13}C NMR spectrum of compound **S24**



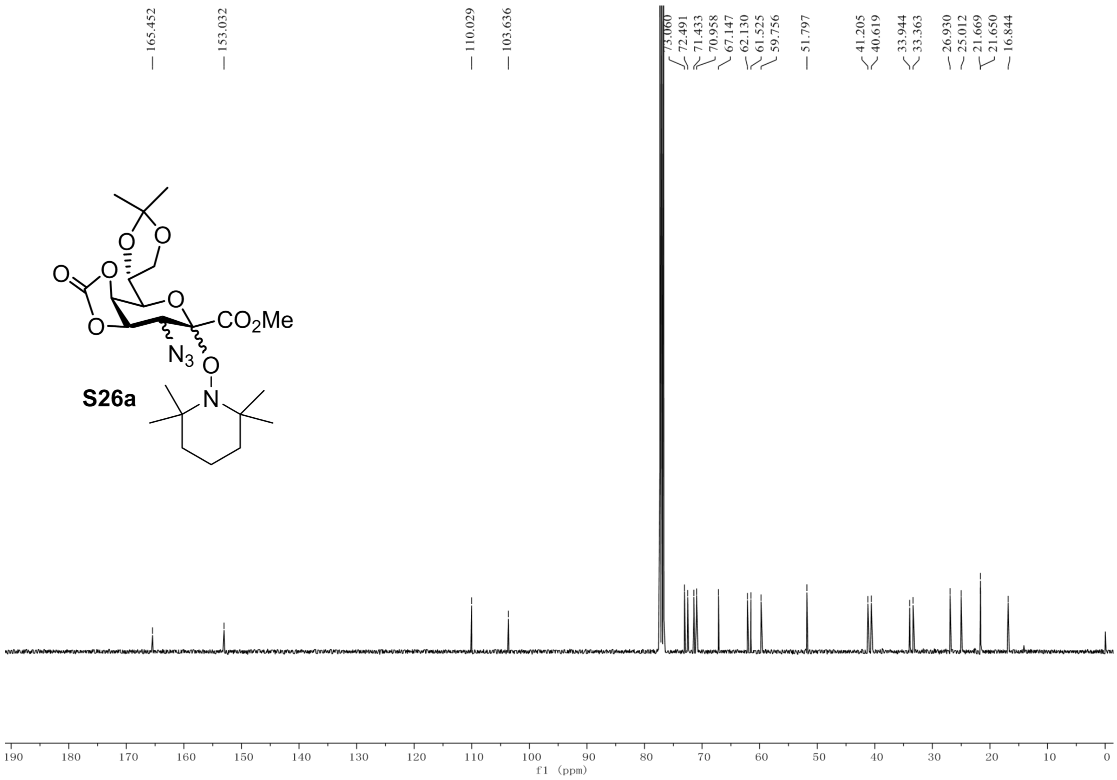
^{1}H NMR spectrum of compound **S25**



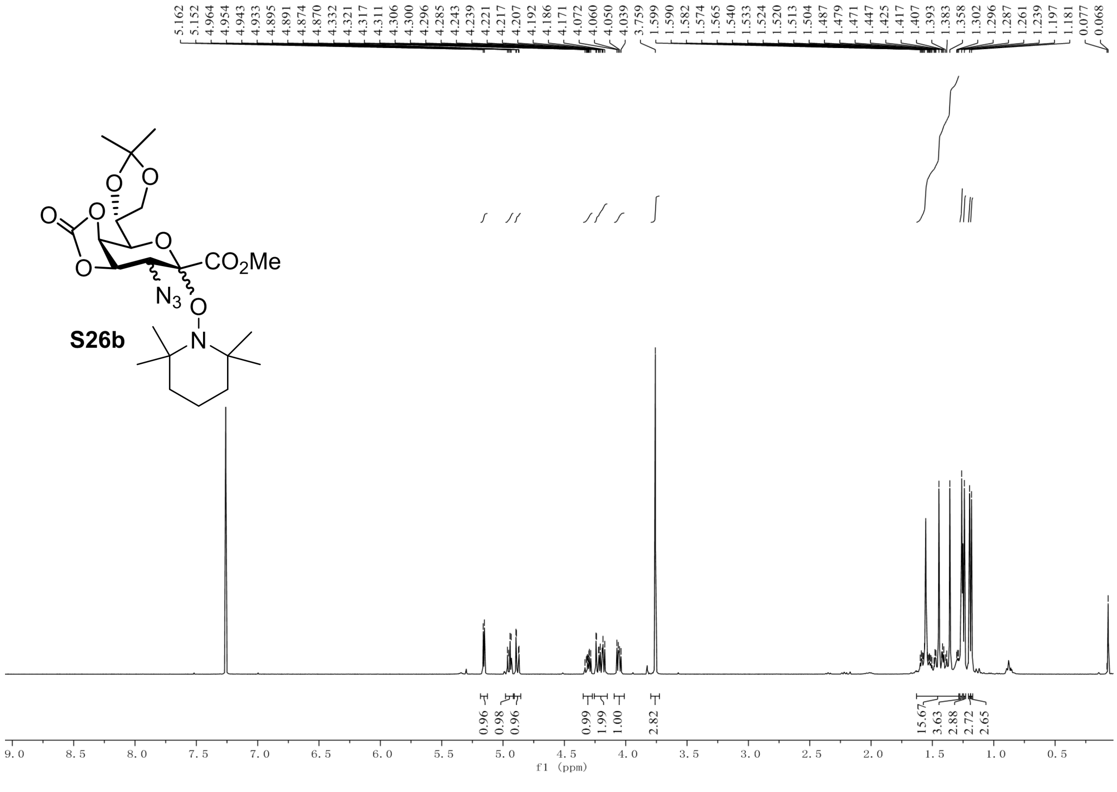
^{13}C NMR spectrum of compound **S25**



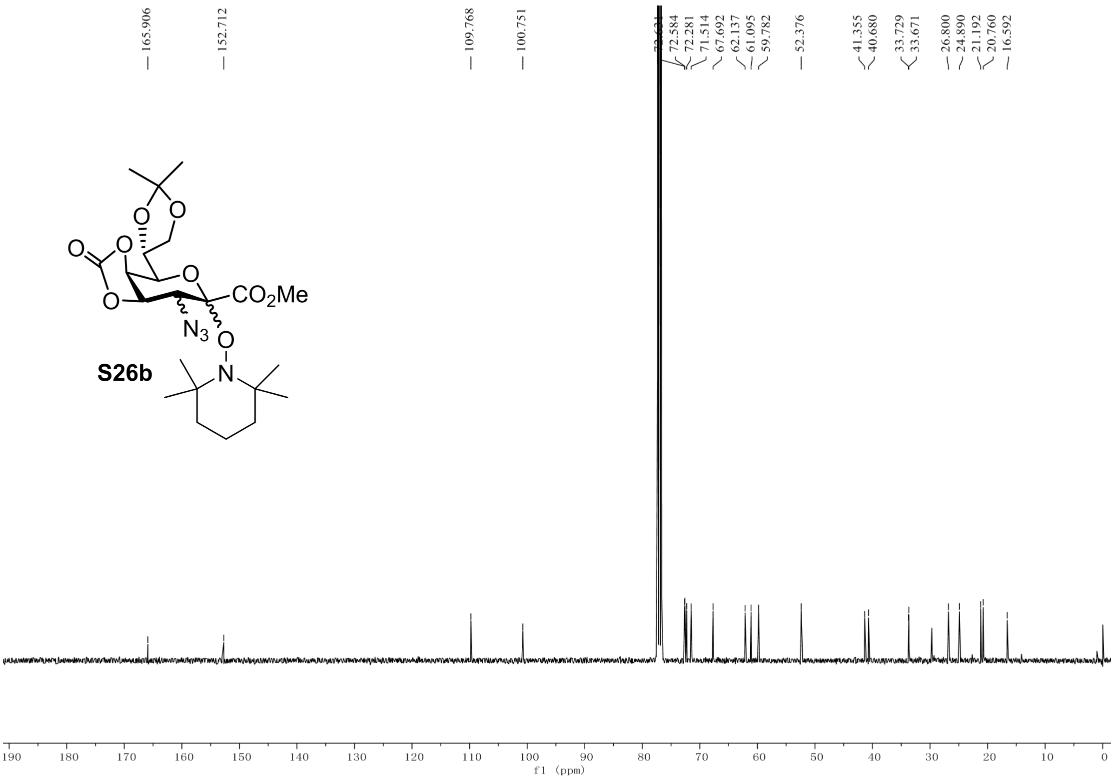
^{1}H NMR spectrum of compound **S26a**



^{13}C NMR spectrum of compound **S26a**



^{1}H NMR spectrum of compound **S26b**



^{13}C NMR spectrum of compound **S26b**