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

Supporting Information

One Step Stereoselective Synthesis of Oxazoline-fused Saccharides and Their Conversion into the Corresponding 1, 2-cis Glycosylamines Bearing Various Protected Groups

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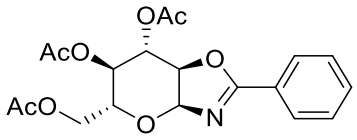
Contents

1. General Information

All starting materials were obtained from commercial suppliers and used without further purification. The ^{1}H NMR and ^{13}C NMR spectra were taken on Bruker Avance-600, 500 or 400, Varian- MERCURY Plus-600 or 400 NMR spectrometer operating at 600 MHz or 400 MHz for ^{1}H NMR, 125 MHz or 100 MHz for ^{13}C NMR, using TMS as internal standard and $CDCl_3$ or DMSO-d_6 as solvent. ^{13}C NMR spectra were recorded with complete proton decoupling. The ESI-MS or EI-MS was recorded on Finnigan LCQ/DECA or Thermo-DFS, respectively. The HRMS were obtained from Micromass Ultra Q-TOF (ESI) or Thermo-DFS (EI) spectrometer. Flash column chromatography was carried out using silica gel (200~400 mesh). Thin layer chromatography (TLC) was used silica gel F254 fluorescent treated silica which were visualised under UV light (254 nm).

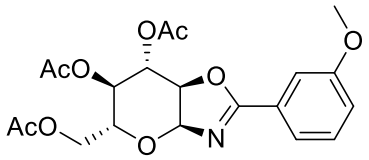
2. Synthetic Procedures and Characterization for Oxazolinoses

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-phenyl-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3A)



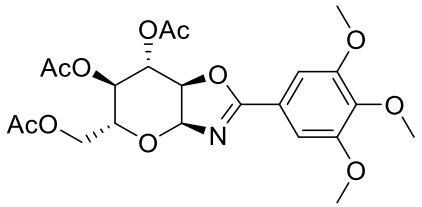
To a solution of β-D-glucose pentaacetate (195 mg, 0.5 mmol), benzonitrile (50 μL, 0.5 mmol) in dry DCM (dichloromethane), water (10 μL) was added. After the reaction mixture was stirred well, TfOH (90 μL, 1 mmol) was added and stirred for 2 hours at room temperature. Then the mixture was poured into water (20 mL) and extracted with ethyl acetate (20 mL) for three times. The organic layer was combined and washed with water and brine, dried over anhydrous sodium sulfate, and concentrated in vacuo to give the crude product which was purified by a silica gel column (petroleum ether/ ethyl acetate 2:1) to give product **3A** (144.3 mg, yield 74%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.07 – 7.99 (m, 2H), 7.59 – 7.53 (m, 1H), 7.46 (dd, *J* = 8.4, 7.1 Hz, 2H), 6.09 (d, *J* = 7.7 Hz, 1H, H-1), 5.33 – 5.29 (m, 1H, H-3), 4.98 (ddd, *J* = 8.4, 4.5, 0.9 Hz, 1H, H-4), 4.63 (ddd, *J* = 7.7, 3.6, 0.9 Hz, 1H, H-2), 4.31 (dd, *J* = 12.1, 5.2 Hz, 1H, H-6), 4.19 (dd, *J* = 12.1, 2.9 Hz, 1H, H-6), 3.75 (ddd, *J* = 8.2, 5.1, 2.9 Hz, 1H, H-5), 2.16 (s, 3H), 2.09 (s, 3H), 1.94 (s, 3H).^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.68, 169.54, 169.47, 166.59, 132.68, 128.90, 128.59, 126.21, 93.22, 75.82, 70.55, 68.07, 67.30, 63.28, 20.87, 20.78, 20.61. HRMS (ESI): $C_{19}H_{22}NO_8$ $[M+H]^+$, calculated for: 392.134, found: 392.1351. $[\alpha]_D^{20}$=33.5 (c=0.064, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(3-methoxyphenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3B)



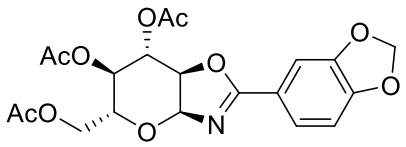
3-Methoxybenzonitrile (66.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3B** (123.1 mg, yield 57%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.60 (m, 1H), 7.55 (m, 1H), 7.36 (m, 1H), 7.10 (m, 1H), 6.08 (d, *J* = 7.7 Hz, 1H, H-1), 5.30 (d, *J* = 4.1 Hz, 1H, H-3), 4.98 (m, 1H, H-4), 4.63 (m, 1H, H-2), 4.31 (m, 1H, H-6), 4.19 (dd, *J* = 12.1, 2.9 Hz, 1H, H-6), 3.85 (s, 3H), 3.75 (m, 1H, H-5), 2.15 (s, 3H), 2.09 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.57, 169.44, 169.35, 166.46, 159.51, 129.56, 127.29,121.20, 119.35, 113.05, 93.07, 75.70, 70.33, 67.93, 67.16, 63.16, 55.40, 20.78, 20.69, 20.54. HRMS (ESI): $C_{20}H_{24}NO_9$ $[M+H]^+$, calculated for: 422.1446, found: 422.1449. $[\alpha]^{20}_{D}$ =40.5 (c=0.074, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(3,4,5-trimethoxyphenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3C)



3,4,5-Methoxybenzonitrile (96.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3C** (161.9 mg, yield 67%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.27 (s, 2H), 6.07 (d, *J* = 7.6 Hz, 1H, H-1), 5.34 – 5.29 (m, 1H, H-3), 4.99 (m, 1H, H-4), 4.62 (m, 1H, H-2), 4.32 (dd, *J* = 12.1, 4.9 Hz, 1H, H-6), 4.19 (dd, *J* = 12.1, 2.9 Hz, 1H, H-6), 3.91 (d, *J* = 2.0 Hz, 9H), 3.79 – 3.71 (m, 1H, H-5), 2.16 (s, 3H), 2.09 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.23, 169.06, 165.99, 152.72, 141.51, 120.69, 105.64, 92.71, 75.60, 70.05, 67.43, 66.89, 62.75, 60.54, 55.90, 29.25, 20.45, 20.36, 20.23. HRMS (ESI): $C_{22}H_{28}NO_{11}$ $[M+H]^+$, calculated for: 482.1657, found: 482.1662. $[\alpha]^{20}_{D}$=35.5 (c=0.093, MeOH).

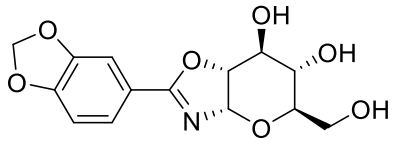
(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(benzo[d][1,3]dioxol-5-yl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3D)



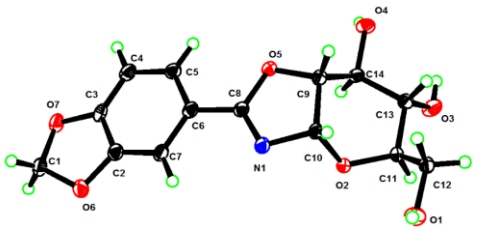
Piperonylonitrile (73.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3D** (135.5 mg, yield 62%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.59 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.47 (d, *J* = 1.6 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.05 (m, 3H, H-1 and CH_2), 5.28 (m, 1H, H-3), 4.97 (ddd, *J* = 8.6, 4.6, 0.9 Hz, 1H, H-4), 4.60 (ddd, *J* = 7.7, 3.8, 0.9 Hz, 1H, H-2), 4.30 (dd, *J* = 12.1, 5.1 Hz, 1H, H-6), 4.22 – 4.16

(m, 1H, H-6), 3.74 (ddd, *J* = 8.2, 5.0, 2.8 Hz, 1H, H-5), 2.16 (s, 3H), 2.09 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.68, 169.54, 169.46, 166.14, 151.43, 147.88, 124.35, 119.98, 108.80, 108.29, 101.82, 93.16, 75.91, 70.62, 67.98, 67.31, 63.26, 20.85, 20.77, 20.64. HRMS (ESI): $C_{20}H_{22}NO_{10}$ $[M+H]^+$, calculated for: 436.1238, found: 436.1248. $[\alpha]_D^{20}$=97.5 (c=0.002, MeOH).

Compound **3D** was deprotected with triethylamine in MeOH to give compound **3S**, the structure of compound **3S** was identified via X-ray crystallography.

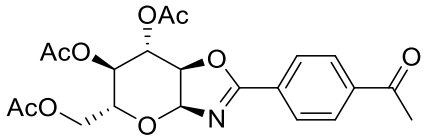


3S



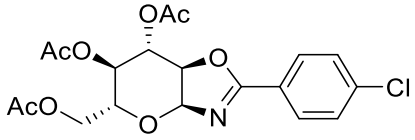
X-ray crastallography of **3S**

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(4-acetylphenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3E)



4-Acetybenzonitrile (72.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3E** (79.6 mg, yield 35%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.14 – 8.08 (m, 2H), 8.02 (d, *J* = 8.7 Hz, 2H), 6.11 (d, *J* = 7.8 Hz, 1H, H-1), 5.32 – 5.26 (m, 1H, H-3), 4.98 (m, 1H, H-4), 4.66 (m, 1H, H-2), 4.31 (dd, *J* = 12.2, 5.1 Hz, 1H, H-6), 4.19 (dd, *J* = 12.1, 2.9 Hz, 1H, H-6), 3.74 (m, 1H, H-5), 2.64 (s, 3H), 2.16 (s, 3H), 2.08 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.20, 170.54, 169.36, 165.48, 139.90, 130.03, 129.03, 128.30, 128.27, 93.18, 76.03, 70.40, 68.27, 67.00, 63.06, 26.73, 20.76, 20.68, 20.52. HRMS (ESI): $C_{21}H_{24}NO_9$ $[M+H]^+$, calculated for: 434.1446, found: 434.1453. $[\alpha]_D^{20}$=60.3 (c=0.105, MeOH).

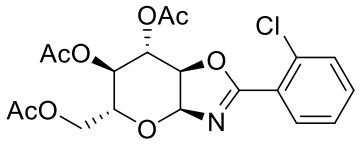
(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(4-chlorophenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3F)



4-Chlorobenzonitrile (68.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3F** (57.5 mg, yield 27%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.6 Hz, 2H), 7.46 – 7.39 (m, 2H), 6.07 (d, *J* = 7.7 Hz, 1H, H-1), 5.30 – 5.24 (m, 1H, H-3), 4.97 (m, 1H, H-4), 4.63 (m, 1H, H-2), 4.30 (dd, *J* = 12.1, 5.1 Hz, 1H, H-6), 4.18 (dd, *J* = 12.1, 2.9 Hz, 1H, H-6), 3.76 – 3.67 (m, 1H, H-5), 2.15 (s, 3H), 2.08 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.54, 169.36, 165.53, 138.98, 130.09, 128.86,

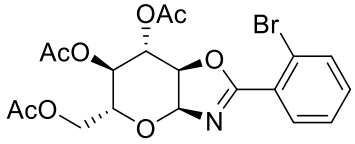
124.56, 93.15, 75.97, 70.44, 68.11, 67.05, 63.08, 20.76, 20.68, 20.52. HRMS (ESI): $C_{19}H_{21}ClNO_8$ $[M+H]^+$, Calculated for: 426.0950, found: 426.0955. $[\alpha]_D^{20}$=39.2 (c=0.1, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(2-chlorophenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3G)



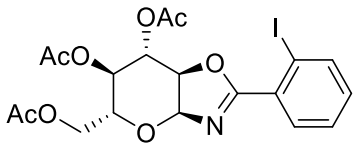
2- Chlorobenzonitrile (72.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3G** (74.4 mg, yield 35%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.8 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.5 – 7.4 (m, 2H), 7.4 (td, *J* = 7.5, 1.4 Hz, 1H), 6.1 (d, *J* = 7.8 Hz, 1H, H-1), 5.3 (t, *J* = 4.1 Hz, 1H, H-3), 5.0 (ddd, *J* = 8.7, 4.5, 0.9 Hz, 1H, H-4), 4.6 (ddd, *J* = 7.8, 3.7, 0.9 Hz, 1H, H-2), 4.3 (dd, *J* = 12.1, 5.2 Hz, 1H, H-6), 4.2 (dd, *J* = 12.1, 2.8 Hz, 1H, H-6), 3.8 (ddd, *J* = 8.4, 5.2, 2.8 Hz, 1H, H-5), 2.2 (s, 3H), 2.1 (s, 3H), 2.0 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 170.2, 169.1, 168.9, 164.7, 133.5, 132.2, 131.2, 130.6, 126.2, 125.4, 93.0, 70.1, 67.6, 66.8, 62.7, 59.9, 20.4, 20.3, 20.2. HRMS (ESI): $C_{19}H_{21}ClNO_8$ $[M+H]^+$, calculated for: 426.095,found: 426.0958. $[\alpha]_D^{20}$=59.1 (c=0.095, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(2-bromophenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3H)



2-Bromobenzonitrile (91.0 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3H** (84.5 mg, yield 38%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.8 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.7 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.4 (dtd, *J* = 22.4, 7.5, 1.6 Hz, 2H), 6.1 (d, *J* = 7.8 Hz, 1H, H-1), 5.3 (t, *J* = 4.2 Hz, 1H, H-3), 5.0 (ddd, *J* = 8.8, 4.6, 0.8 Hz, 1H, H-4), 4.7 (ddd, *J* = 7.9, 3.8, 0.8 Hz, 1H, H-2), 4.3 (dd, *J* = 12.2, 5.2 Hz, 1H, H-6), 4.2 (dd, *J* = 12.1, 2.8 Hz, 1H, H-6), 3.9 (ddd, *J* = 8.3, 5.2, 2.7 Hz, 1H, H-5), 2.2 (s, 3H), 2.1 (s, 3H), 2.0 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 170.7, 169.6, 169.4, 165.8, 134.3, 132.7, 131.7, 128.0, 127.3, 122.2, 93.4, 75.9, 70.7, 68.1, 67.4, 63.2, 20.9, 20.8, 20.7. HRMS (ESI): $C_{19}H_{21}BrNO_8$ $[M+H]^+$, calculated for: 470.0455, found: 470.0457. $[\alpha]_D^{20}$=19.1 (c=0.115, MeOH).

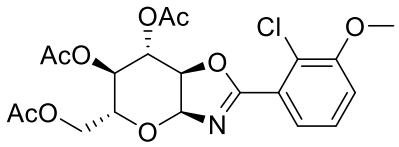
(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(2-iodophenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3I)



2-Iodobenzonitrile (114.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3I** (142.9 mg, yield 56%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.0 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.8 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.5 (td, *J* =

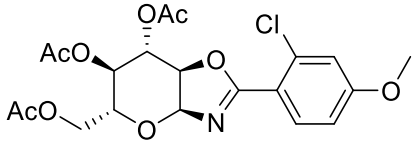
7.6, 1.2 Hz, 1H), 7.2 (td, *J* = 7.7, 1.7 Hz, 1H), 6.2 (d, *J* = 7.8 Hz, 1H, H-1), 5.4 (t, *J* = 4.1 Hz, 1H, H-3), 5.0 (ddd, *J* = 8.8, 4.7, 0.9 Hz, 1H, H-4), 4.7 (ddd, *J* = 7.8, 3.7, 0.9 Hz, 1H, H-2), 4.4 (dd, *J* = 12.1, 5.2 Hz, 1H, H-6), 4.3 (dd, *J* = 12.2, 2.8 Hz, 1H, H-6), 3.9 (ddd, *J* = 8.4, 5.2, 2.8 Hz, 1H, H-5), 2.2 (s, 3H), 2.1 (s, 3H), 2.0 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.7, 169.6, 169.4, 166.5, 141.2, 132.6, 131.6, 131.2, 128.0, 94.7, 93.4, 76.1, 70.7, 68.2, 67.4, 63.1, 20.8, 20.8, 20.7. HRMS (ESI): $C_{19}H_{21}INO_8$ $[M+H]^+$, calculated ford: 518.0306, found: 518.0317. $[\alpha]_D^{20}$=24.7 (c=0.502, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(2-chloro-3-methoxyphenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3J)



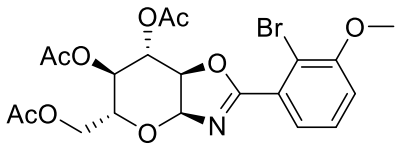
2-Chloro-3methoxybenzonitrile (110.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3J** (54.0 mg, yield 24%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.09 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.12 (d, *J* = 7.8 Hz, 1H, H-1), 5.33 (t, *J* = 4.0 Hz, 1H, H-3), 4.98 (dd, *J* = 8.8, 4.3 Hz, 1H, H-4), 4.63 (dd, *J* = 7.9, 3.7 Hz, 1H, H-2), 4.31 (dd, *J* = 12.2, 5.3 Hz, 1H, H-6), 4.21 (dd, *J* = 12.2, 2.7 Hz, 1H, H-6), 3.94 (s, 3H), 3.84 (s, 1H, H-5), 2.15 (s, 3H), 2.09 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 170.69, 169.58, 169.36, 165.45, 127.52, 127.28, 122.99, 122.62, 114.84, 93.29, 75.59, 70.45, 67.95, 67.35, 63.23, 56.53, 20.83, 20.78, 20.68. HRMS (ESI): $C_{20}H_{23}ClNO_9$ $[M+H]^+$, calculated for: 456.1056, found: 456.1060. $[\alpha]_D^{20}$=34.4 (c=0.125, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(2-chloro-4-methoxyphenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3K)



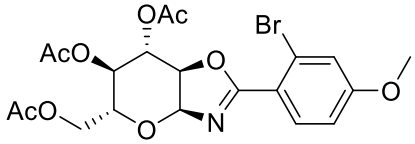
2-Chloro-4methoxybenzonitrile (110.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3K** (151.2 mg, yield 67%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.8 Hz, 1H), 7.04 (d, *J* = 2.5 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.13 (d, *J* = 7.7 Hz, 1H, H-1), 5.37 – 5.31 (m, 1H, H-3), 5.00 (m, 1H, H-4), 4.61 (m, 1H, H-2), 4.33 (dd, *J* = 12.1, 5.2 Hz, 1H, H-6), 4.23 (dd, *J* = 12.1, 2.9 Hz, 1H, H-6), 3.88 (s, 3H), 3.83 (m, 1H, H-5), 2.17 (s, 3H), 2.11 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.67, 169.55, 169.41, 164.86, 162.48, 135.50, 133.03, 117.76, 116.40, 112.81, 93.44, 75.29, 70.60, 68.05, 67.33, 63.25, 55.72, 20.84, 20.77, 20.65. HRMS (ESI): $C_{20}H_{23}ClNO_9$ $[M+H]^+$, calculated for: 456.1056, found: 456.1049. $[\alpha]_D^{20}$=62.0 (c=0.079, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(2-bromo-3-methoxyphenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3L)



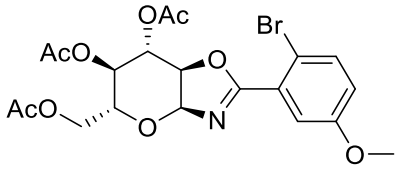
2-Bromo-3methoxybenzonitrile (105.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3L** (116.8 mg, yield 47%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 (t, *J* = 8.0 Hz, 1H), 7.32 – 7.29 (m, 1H), 7.05 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.12 (d, *J* = 7.8 Hz, 1H, H-1), 5.36 (t, *J* = 4.0 Hz, 1H, H-3), 4.99 (m, 1H, H-4), 4.65 (m, 1H, H-2), 4.32 (dd, *J* = 12.1, 5.3 Hz, 1H, H-6), 4.22 (dd, *J* = 12.1, 2.7 Hz, 1H, H-6), 3.93 (d, *J* = 7.9 Hz, 4H, H-5 and MeO), 2.15 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.66, 169.56, 169.33, 166.22, 156.62, 130.03, 128.17, 123.22, 114.52, 112.07, 93.28, 75.96, 70.70, 68.00, 67.42, 63.15, 56.61, 20.78, 20.73, 20.66. HRMS (ESI): $C_{20}H_{23}BrNO_9$ $[M+H]^+$, calculated for: 500.0551, found: 500.0556. $[\alpha]^{20}_{D}$=33.5 (c=0.181, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(2-bromo-4-methoxyphenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3M)



2-Bromo-4methoxybenzonitrile (105.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3M** (151.2mg, yield 67%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.8 Hz, 1H), 7.23 (d, *J* = 2.5 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.11 (d, *J* = 7.8 Hz, 1H, H-1), 5.33 (t, *J* = 4.2 Hz, 1H, H-3), 4.98 (m, 1H, H-4), 4.63 – 4.58 (m, 1H, H-2), 4.32 (dd, *J* = 12.1, 5.2 Hz, 1H, H-6), 4.21 (dd, *J* = 12.1, 2.7 Hz, 1H, H-6), 3.87 – 3.83 (m, 4H, H-5 and MeO), 2.16 (s, 3H), 2.10 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 170.70, 169.58, 169.43, 162.24, 133.05, 123.34, 121.47, 119.78, 119.76, 113.26, 93.42, 75.52, 70.65, 68.04, 67.37, 63.22, 55.73, 20.86, 20.80, 20.69. HRMS (ESI): $C_{20}H_{23}BrNO_9$ $[M+H]^+$, calculated for: 500.0551, found: 500.0558. $[\alpha]^{20}_{D}$=32.0 (c=0.125, MeOH).

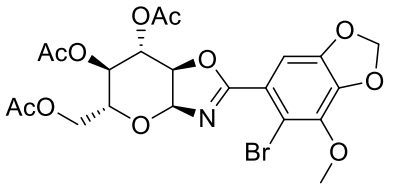
(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(2-bromo-5-methoxyphenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3N)



2-Bromo-5methoxybenzonitrile (105.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3N** (123.0mg, yield 50%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.9 Hz, 1H), 7.33 (d, *J* = 3.1 Hz, 1H), 6.93 (dd, *J* = 8.9, 3.1 Hz, 1H), 6.14 (d, *J* = 7.8 Hz, 1H, H-1), 5.36 (t, *J* = 4.2 Hz, 1H, H-3), 5.00 (m, 1H, H-4), 4.66 (m, 1H, H-2), 4.34 (dd, *J* = 12.2, 5.2 Hz, 1H, H-6), 4.23 (dd, *J* = 12.2, 2.8 Hz, 1H, H-6), 3.88 (m, 1H, H-5), 3.84 (s, 3H), 2.16 (s, 3H), 2.10 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.66, 169.55, 169.37, 158.57, 135.05, 119.21, 116.64, 112.37, 93.40, 77.24,

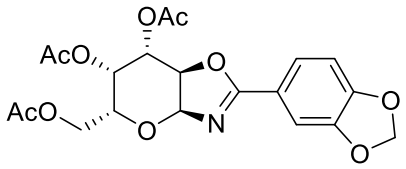
76.02, 70.72, 68.15, 67.31, 63.13, 60.36, 55.68, 20.82, 20.76, 20.67. HRMS (ESI): $C_{20}H_{23}BrNO_9$ $[M+H]^+$, calculated for: 500.0551, found: 500.0556. $[\alpha]_D^{20}$=32.4 (c=0.074, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(6-bromo-7-methoxybenzo[d][1,3]dioxol-5-yl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (**3O**)



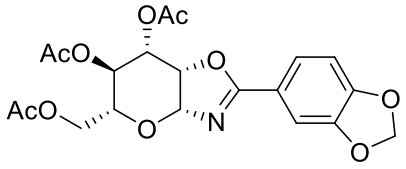
6-Bromo-7-methoxybenzo[d][1,3]dioxole-5-carbonitrile(128 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3O** (147 mg, yield 54%) as a yellow oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.00 (s, 1H), 6.09 (d, J = 7.8 Hz, 1H, H-1), 6.06 (s, 2H), 5.32 (t, J = 4.1 Hz, 1H, H-3), 5.01 – 4.95 (m, 1H, H-4), 4.63 – 4.58 (m, 1H, H-2), 4.31 (dd, J = 12.2, 5.2 Hz, 1H, H-6), 4.20 (dd, J = 12.2, 2.7 Hz, 1H, H-6), 4.04 (s, 3H), 3.84 (ddd, J = 8.2, 5.1, 2.5 Hz, 1H, H-5), 2.15 (s, 3H), 2.09 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 170.86, 169.73, 169.54, 165.95, 148.70, 141.36, 140.71, 122.17, 109.61, 105.99, 102.64, 93.50, 75.99, 70.87, 68.19, 67.57, 63.35, 60.51, 21.00, 20.96, 20.88. HRMS (ESI): $C_{21}H_{23}BrNO_{11}$ $[M+H]^+$, calculated for: 544.0449, found: 544.0463. $[\alpha]_D^{20}$= 51.061 (c=0.110, MeOH).

(3aS,5R,6S,7S,7aR)-5-(acetoxymethyl)-2-(benzo[d][1,3]dioxol-5-yl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3Da)



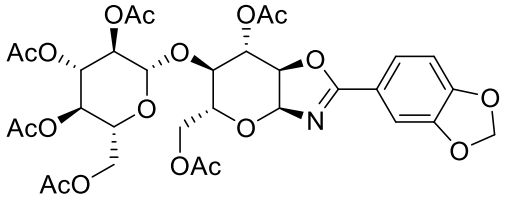
Piperonylonitrile (73.5 mg, 0.5 mmol) and β-D-Galactose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3Da** (98.3 mg, yield 62%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.37 (d, *J* = 1.7 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 6.03 – 5.93 (m, 3H, H-1 and OCH_2O), 5.41 (s, 1H, H-3), 4.98 (dd, *J* = 7.2, 3.1 Hz, 1H, H-4), 4.61 (t, *J* = 7.1 Hz, 1H, H-2), 4.22 (m, 1H, H-6), 4.13 (m, 2H, H-6 and H-5), 2.10 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.98, 169.53, 169.51, 165.17, 150.85, 147.32, 123.75, 119.90, 108.19, 107.72, 101.32, 93.63, 76.17, 71.33, 68.80, 65.72, 60.88, 20.29, 20.22, 20.15. HRMS (ESI): $C_{20}H_{22}NO_{10}$ $[M+H]^+$, calculated for: 436.1238, found: 436.1247. $[\alpha]_D^{20}$=85.3 (c=0.068, MeOH).

(3aR,5R,6R,7S,7aS)-5-(acetoxymethyl)-2-(benzo[d][1,3]dioxol-5-yl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3Db)



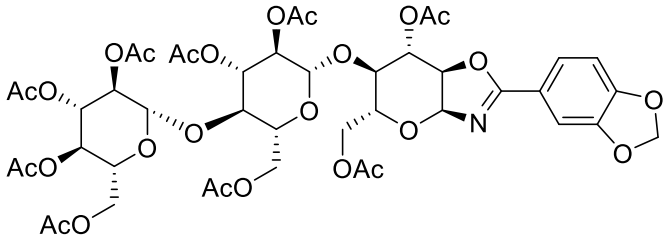
Piperonylonitrile (73.5 mg, 0.5 mmol) and α-D-Mannose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3Db** (96.7 mg, yield 62%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.62 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.49 (d, *J* = 1.6 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.05 (s, 2H), 5.74 (d, *J* = 5.5 Hz, 1H, H-1), 5.40 (dd, *J* = 8.4, 4.9 Hz, 1H, H-3), 5.14 (t, *J* = 8.2 Hz, 1H, H-4), 4.81 (t, *J* = 5.2 Hz, 1H, H-2), 4.24 (dd, *J* = 12.0, 6.4 Hz, 1H, H-6), 4.16 (dd, *J* = 12.0, 3.4 Hz, 1H, H-6), 3.83 (m, 1H, H-5), 2.12 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.30, 169.76, 168.95, 167.85, 151.03, 147.36, 124.17, 119.55, 108.52, 107.79, 101.35, 93.19, 76.32, 72.86, 68.52, 66.09, 63.27, 20.33, 20.29, 20.27. HRMS (ESI): $C_{20}H_{22}NO_{10}$ $[M+H]^+$, calculated for: 436.1238, found: 436.1238. $[\alpha]_D^{20}$=-76.2 (c=0.042, MeOH).

(2S,3R,4S,5R,6R)-2-(((3aS,5R,6R,7S,7aR)-7-acetoxy-5-(acetoxymethyl)-2-(benzo[d][1,3]dioxol-5-yl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazol-6-yl)oxy)-6-(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3Dc)



Piperonylonitrile (73.5 mg, 0.5 mmol) and α-D-Cellobiose octaacetate (339 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3Dc** (94.5 mg, yield 42%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.61 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.48 (d, *J* = 1.7 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.05 (s, 2H), 5.97 (d, *J* = 7.4 Hz, 1H), 5.63 (s, 1H), 5.19 – 5.08 (m, 2H), 4.89 (dd, *J* = 9.3, 8.0 Hz, 1H), 4.66 (d, *J* = 8.1 Hz, 1H), 4.54 (ddd, *J* = 7.4, 3.3, 1.1 Hz, 1H), 4.26 (dd, *J* = 12.3, 4.4 Hz, 1H), 4.22 (dd, *J* = 12.0, 2.5 Hz, 1H), 4.17 (dd, *J* = 12.3, 2.6 Hz, 1H), 4.15 – 4.11 (m, 1H), 3.76 – 3.66 (m, 2H), 3.46 (ddd, *J* = 9.0, 5.1, 2.5 Hz, 1H), 2.15 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H), 2.02 (s, 3H), 1.97 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.54, 170.10, 169.28, 169.26, 169.11, 166.80, 151.33, 147.73, 124.45, 119.66, 108.86, 108.22, 101.67, 101.54, 92.45, 76.56, 75.35, 72.84, 71.84, 71.21, 69.76, 67.99, 67.21, 63.48, 61.64, 20.82, 20.77, 20.62, 20.48, 20.45, 20.34. HRMS (ESI): $C_{32}H_{38}NO_{18}$ $[M+H]^+$, calculated for: 724.2083, found: 724.2100. $[\alpha]_D^{20}$ =17.0 (c=0.053, MeOH).

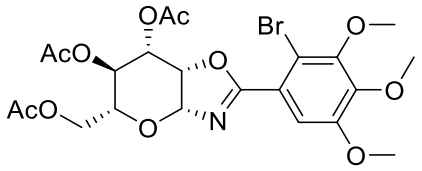
(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(((2R,3R,4S,5R,6S)-4,5-diacetoxy-6-(((3aS,5R,6R,7S,7aR)-7-acetoxy-5-(acetoxymethyl)-2-(benzo[d][1,3]dioxol-5-yl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazol-6-yl)oxy)-2-(acetoxymethyl)tetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3Dd)



Piperonylonitrile (73.5 mg, 0.5 mmol) and D-Maltotriose pearcetate (483 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3Dd** (94.5 mg, yield 18%) as a white powder. ^{1}H

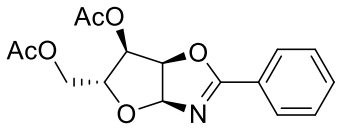
NMR (500 MHz, Chloroform-*d*) δ 7.68 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.55 (d, *J* = 1.7 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.05 (d, *J* = 1.5 Hz, 2H), 5.39 (d, *J* = 4.0 Hz, 1H), 5.36 – 5.29 (m, 3H), 5.24 (dd, *J* = 3.4, 1.6 Hz, 1H), 5.07 (d, *J* = 9.9 Hz, 1H), 4.85 (ddd, *J* = 15.8, 10.3, 4.0 Hz, 2H), 4.59 – 4.54 (m, 1H), 4.43 (dd, *J* = 12.4, 1.8 Hz, 1H), 4.31 – 4.21 (m, 4H), 4.18 – 4.13 (m, 1H), 4.07 – 4.03 (m, 1H), 3.93 (dd, *J* = 7.1, 2.5 Hz, 3H), 3.72 (dt, *J* = 8.6, 1.7 Hz, 1H), 3.61 (td, *J* = 5.3, 2.6 Hz, 1H), 2.16 (s, 6H), 2.14 (s, 6H), 2.11 (s, 3H), 2.04 (s, 6H), 2.01 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.67, 170.50, 170.48, 170.40, 170.21, 169.83, 169.63, 169.51, 169.42, 167.23, 151.37, 147.88, 124.62, 119.85, 108.99, 108.63, 101.66, 95.77, 95.55, 92.32, 74.82, 73.86, 72.85, 72.05, 70.68, 70.04, 69.42, 68.88, 68.58, 68.52, 67.88, 67.39, 64.02, 62.55, 61.41, 20.96, 20.90, 20.89, 20.73, 20.69, 20.66, 20.57, 20.51.HRMS (ESI): $C_{44}H_{53}NNaO_{26}$ $[M+Na]^+$, calculated for: 1034.2748, found: 1034.2722. $[\alpha]_D^{20}$=104.5 (c=0.089, MeOH).

(3aR,5R,6R,7S,7aS)-5-(acetoxymethyl)-2-(2-bromo-3,4,5-trimethoxyphenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3Ra)



2-Bromo-3,4,5-trimethoxybenzonitrile (135.5 mg, 0.5 mmol) and α-D-Mannose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3Ra** (63.9 mg, yield 23%) as a colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.27 (s, 1H), 6.40 (d, *J* = 6.2 Hz, 1H, H-1), 5.01 (d, *J* = 6.2 Hz, 1H, H-3), 4.95 (ddd, *J* = 10.4, 4.7, 2.6 Hz, 1H, H-4), 4.46 (dd, *J* = 12.3, 2.6 Hz, 1H, H-2), 4.31 (t, *J* = 6.7 Hz, 1H, H-6), 4.27 – 4.21 (m, 2H, H-6 and H-5), 4.01 – 3.79 (m, 9H), 2.15 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.87, 171.56, 170.92, 167.13, 154.11, 153.03, 147.40, 132.31, 124.44, 111.73, 104.31, 87.02, 83.62, 79.64, 70.71, 64.19, 62.59, 62.47, 57.81, 22.26, 22.16, 20.61. HRMS (ESI): $C_{22}H_{27}BrNO_{11}$ $[M+H]^+$ calculated for: 560.0762, found: 560.0764. $[\alpha]_D^{20}$= -9.5 (c=0.084, MeOH).

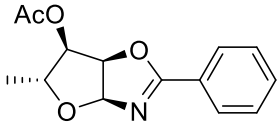
((3aS,5R,6R,6aR)-6-acetoxy-2-phenyl-3a,5,6,6a-tetrahydrofuro[2,3-d]oxazol-5-yl)methyl acetate (3a)



Benzonitrile (51.5 mg, 0.5 mmol) and beta-D-Ribofuranose tetraacetate (159 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3a** (94.5 mg, yield 81%) as a yellow oil.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.07 – 7.99 (m, 2H), 7.60 – 7.52 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 6.32 (d, *J* = 6.2 Hz, 0.2H, minor, H-1), 6.28 (d, *J* = 5.6 Hz, 0.8H, major H-1), 5.34 (s, 0.2H, minor, H-3), 5.23 (t, *J* = 5.8 Hz, 0.8H, major, H-3), 5.06 (d, *J* = 6.1 Hz, 0.2H, minor, H-2), 4.87 (dd, *J* = 9.2, 5.9 Hz, 0.8H, major, H-2), 4.42 (dd, *J* = 12.3, 2.7 Hz, 0.8H, major, H-5), 4.33 (td, *J* = 5.9, 2.4 Hz, 0.2H, minor, H-5), 4.23 (dd, *J* = 12.3, 5.0 Hz, 0.8H, major, H-5), 4.07 (qd, *J* = 11.8, 6.0 Hz, 0.5H, minor, H-5 and H-4), 3.92 (ddd, *J* = 9.3, 5.0, 2.7 Hz, 0.8H, major, H-4), 2.17 (d, *J* = 4.5 Hz, 3H major+minor), 2.10 (s, 2.5H, major), 1.90 (s, 0.6H, minor). ^{13}C NMR (125 MHz,

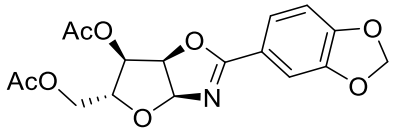
Chloroform-*d*) δ 170.66(major), 170.52(minor), 170.07 (major), 169.87(minor), 167.49 (major), 166.47 (minor), 132.62(minor), 132.54(major), 129.03(minor), 128.94(major), 128.57(minor), 128.52(major), 126.34(minor), 126.08(major), 102.19(minor), 100.68(major), 86.15(minor), 81.65(minor),78.78(minor), 78.08 (major), 74.03(major), 73.04(major), 63.42(minor), 62.02(major), 20.80(minor), 20.75(major), 20.53(minor), 20.49(major).

(3aS,5R,6R,6aR)-5-methyl-2-phenyl-3a,5,6,6a-tetrahydrofuro[2,3-d]oxazol-6-yl acetate (3b)



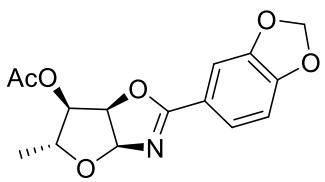
Benzonitrile (51.5 mg, 0.5 mmol) and 1,2,3-Triacetyl-5-deoxy-D-ribose (130 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3b** (94.5 mg, yield 81%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.07 – 7.95 (m, 2H), 7.52 (m, 1H), 7.49 – 7.39 (m, 2H), 6.18 (d, *J* = 5.6 Hz, 1H, H-1), 5.17 (t, *J* = 5.6 Hz, 1H, H-3), 4.49 (dd, *J* = 9.3, 5.6 Hz, 1H, H-2), 3.80 – 3.69 (m, 1H, H-4), 2.15 (s, 3H), 1.32 (d, *J* = 6.1 Hz, 3H, H-5). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.34, 167.25, 132.35, 128.85, 128.44, 126.21, 100.00, 78.46, 78.23, 71.61, 20.54, 16.60. HRMS (ESI): $C_{14}H_{16}NO_4$ $[M+H]^+$, calculated for: 262.1074, found: 262.1075. $[\alpha]^{20}_{D}$=95.0 (c=0.040, MeOH).

((3aS,5R,6R,6aR)-6-acetoxy-2-(benzo[d][1,3]dioxol-5-yl)-3a,5,6,6a-tetrahydrofuro[2,3-d]oxazol-5-yl)methyl acetate (3c)



Piperonylonitrile (73.5 mg, 0.5 mmol) and beta-D-Ribofuranose tetraacetate (159 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3c** (130.6 mg, yield 72%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.47 (d, *J* = 1.7 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.24 (d, *J* = 5.6 Hz, 1H, H-1), 6.06 (q, *J* = 1.4 Hz, 2H), 5.20 (t, *J* = 5.7 Hz, 1H, H-3), 4.85 (dd, *J* = 9.3, 5.8 Hz, 1H, H-2), 4.42 (dd, *J* = 12.3, 2.7 Hz, 1H, H-5), 4.22 (dd, *J* = 12.3, 5.0 Hz, 1H, H-5), 3.91 (ddd, *J* = 9.3, 5.0, 2.7 Hz, 1H, H-4), 2.18 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.25, 169.63, 166.65, 150.85, 147.37, 123.92, 119.40, 108.45, 107.80, 101.34, 100.19, 77.67, 73.49, 72.56, 61.57, 20.33, 20.07. HRMS (ESI): $C_{17}H_{18}NO_8$ $[M+H]^+$, calculated for: 364.1027, found: 364.1026. $[\alpha]^{20}_{D}$=940.5 (c=0.007, MeOH)

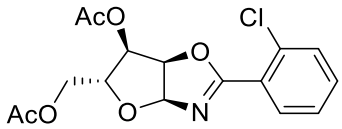
(3aS,5R,6R,6aR)-2-(benzo[d][1,3]dioxol-5-yl)-5-methyl-3a,5,6,6a-tetrahydrofuro[2,3-d]oxazol-6-yl acetate (3d)



Piperonylonitrile (73.5 mg, 0.5 mmol) and 1,2,3-Triacetyl-5-deoxy-D-ribose (130 mg, 0.5 mmol)

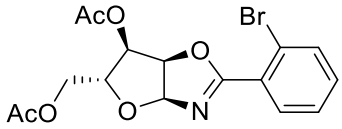
were used as described in (**3A**) and give compound **3d** (77.5 mg, yield 51%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.7 (ddd, *J* = 8.2, 3.1, 1.7 Hz, 1H), 7.5 (dd, *J* = 4.1, 1.7 Hz, 1H), 6.9 (d, *J* = 8.2 Hz, 1H), 6.1 (s, 2H), 5.6 – 5.4 (m, 1H, H-1), 5.4 – 5.3 (m, 1H, H-3), 5.3 – 5.1 (m, 1H, H-2), 4.5 – 4.3 (m, 1H, H-4), 2.1 (d, *J* = 46.9 Hz, 3H), 1.4 (dd, *J* = 35.9, 6.4 Hz, 3H, H-5). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.0, 164.8, 152.1, 147.8, 125.7, 123.2, 109.5, 108.1, 101.9, 100.1, 95.4, 76.4, 75.0, 20.6, 20.3. HRMS (ESI): $C_{15}H_{16}NO_6$ $[M+H]^+$, calculated for: 306.0972, found: 306.0978. $[\alpha]^{20}_{D}$=465.3 (c=0.120, MeOH).

((3aS,5R,6R,6aR)-6-acetoxy-2-(2-chlorophenyl)-3a,5,6,6a-tetrahydrofuro[2,3-d]oxazol-5-yl) methyl acetate (3e)



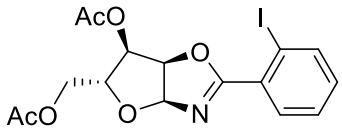
2-Chlorobenzonitrile (72.5 mg, 0.5 mmol) and beta-D-Ribofuranose tetraacetate (159 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3e** (126.0 mg, yield 71%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.50 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.45 (td, *J* = 8.1, 7.7, 1.7 Hz, 1H), 7.35 (td, *J* = 7.5, 1.4 Hz, 1H), 6.32 (d, *J* = 5.7 Hz, 1H, H-1), 5.26 (t, *J* = 5.8 Hz, 1H, H-3), 4.86 (dd, *J* = 9.4, 5.8 Hz, 1H, H-2), 4.46 (dd, *J* = 12.3, 2.7 Hz, 1H, H-5), 4.26 (dd, *J* = 12.3, 5.1 Hz, 1H, H-5), 4.02 (m, 1H, H-4), 2.16 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.67, 170.09, 166.60, 133.71, 132.50, 131.73, 130.91, 126.66, 126.15, 100.61, 78.20, 74.00, 73.01, 61.93, 20.76, 20.52. HRMS (ESI): $C_{16}H_{17}ClNO_6$ $[M+H]^+$, calculated for: 354.0739, found: 354.0742. $[\alpha]^{20}_{D}$=162.3 (c=0.268, MeOH).

((3aS,5R,6R,6aR)-6-acetoxy-2-(2-bromophenyl)-3a,5,6,6a-tetrahydrofuro[2,3-d]oxazol-5-yl) methyl acetate (3f)



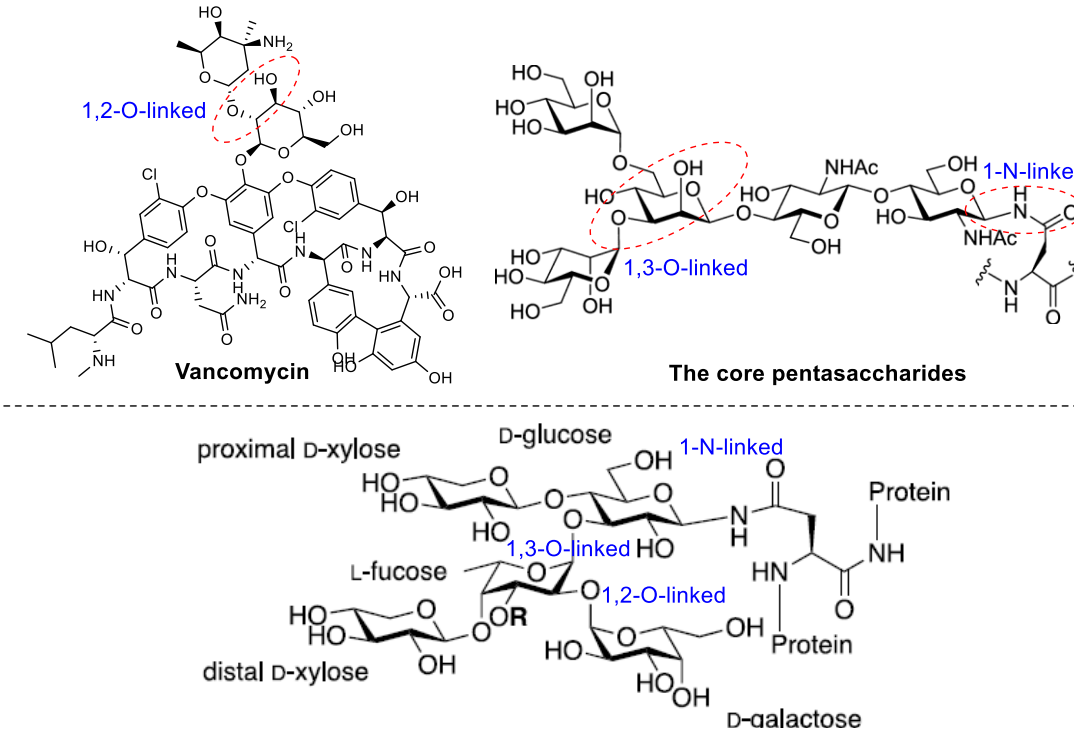
2-Bromobenzonitrile (91.0 mg, 0.5 mmol) and beta-D-Ribofuranose tetraacetate (159 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3f** (159.0 mg, yield 79%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79 – 7.73 (m, 1H), 7.68 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.37 (m, 2H), 6.30 (d, *J* = 5.7 Hz, 1H, H-1), 5.25 (t, *J* = 5.8 Hz, 1H, H-3), 4.86 (dd, *J* = 9.5, 5.8 Hz, 1H, H-2), 4.45 (dd, *J* = 12.4, 2.7 Hz, 1H, H-5), 4.25 (dd, *J* = 12.4, 5.0 Hz, 1H, H-5), 4.06 (m, 1H, H-4), 2.15 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.65, 170.07, 167.24, 134.10, 132.49, 131.78, 128.44, 127.20, 121.78, 100.57, 78.37, 74.00, 73.03, 61.93, 20.76, 20.57. HRMS (ESI): $C_{16}H_{17}BrNO_6$ $[M+H]^+$, calculated for: 398.0234, found: 398.0229. $[\alpha]^{20}_{D}$=129.3 (c=0.163, MeOH).

((3aS,5R,6R,6aR)-6-acetoxy-2-(2-iodophenyl)-3a,5,6,6a-tetrahydrofuro[2,3-d]oxazol-5-yl)methyl acetate (3g)



2-Iodobenzonitrile (114.5 mg, 0.5 mmol) and beta-D-Ribofuranose tetraacetate (159 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3g** (142.0 mg, yield 64%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.71 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H), 7.17 (td, *J* = 7.7, 1.7 Hz, 1H), 6.30 (d, *J* = 5.7 Hz, 1H, H-1), 5.25 (t, *J* = 5.7 Hz, 1H, H-3), 4.88 (dd, *J* = 9.5, 5.7 Hz, 1H, H-2), 4.45 (dd, *J* = 12.3, 2.7 Hz, 1H, H-5), 4.25 (dd, *J* = 12.4, 5.0 Hz, 1H, H-5), 4.17 – 4.08 (m, 1H, H-4), 2.15 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.64, 170.05, 167.93, 140.95, 132.43, 132.17, 131.32, 127.88, 100.57, 94.27, 78.44, 74.06, 73.07, 61.96, 20.77, 20.68. HRMS (ESI): $C_{16}H_{17}INO_6$ $[M+H]^+$, calculated for: 446.0095, found: 446.0094. $[\alpha]_D^{20}$=24.7 (c=0.502, MeOH).

3. Supplementary Data



Scheme S1. glycopeptides and glycoproteins

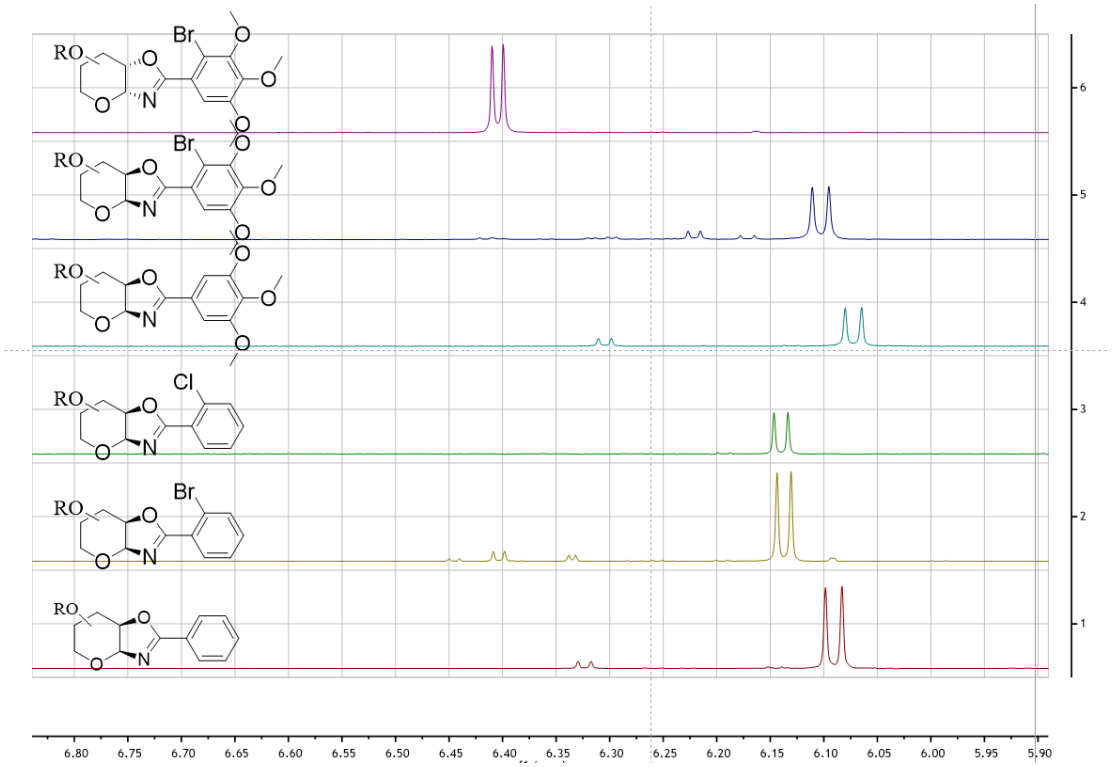
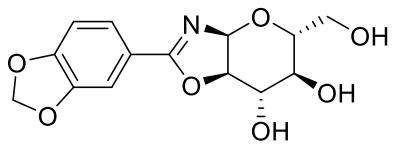


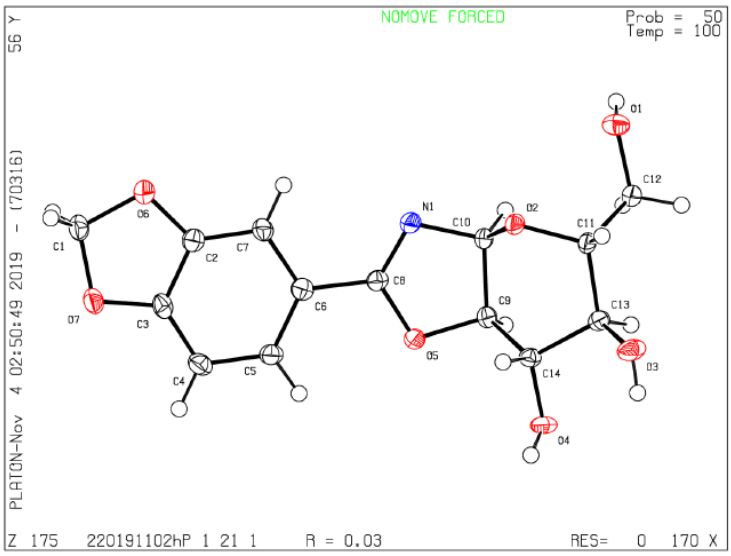
Fig S1. the ^{1}H-NMR spectra of several oxazolinoses

We have compared the ^{1}H-NMR spectra of several oxazolinoses and found visible differences of the hydrogen chemical shift at 1 position between 1-*α* and 1-*β* C-N configurations. The chemical shifts of hydrogen atom on C-1 for 1-*α* oxazolionses are around at 6.10 ppm. Electron-donating or withdrawing substitutes can make the chemical shifts fluctuate slightly. Meanwhile, the chemical shifts of hydrogen atom on C-1 for 1-*β* oxazolinoses are around at 6.40 ppm. Therefore, the difference of two isomers can be recognized *via* ^{1}H-NMR spectra.

4. Crystal Data and Structure Refinement (3S)



3S



Bond precision: C-C = 0.0030 A Wavelength=1.54184

Cell: a=4.7659(3) b=12.6787(7) c=11.0168(6)
alpha=90 beta=95.803(2) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	662.28(7)	662.28(7)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C14 H15 N O7	C14 H15 N O7
Sum formula	C14 H15 N O7	C14 H15 N O7
Mr	309.27	309.27
Dx,g cm-3	1.551	1.551
Z	2	2
Mu (mm-1)	1.078	1.078
F000	324.0	324.0
F000'	325.22	
h,k,lmax	5,15,13	5,15,13
Nref	2344[1230]	2250
Tmin,Tmax	0.937,0.979	0.624,0.754
Tmin'	0.908	

Correction method= # Reported T Limits: Tmin=0.624 Tmax=0.754
AbsCorr = MULTI-SCAN

Data completeness= 1.83/0.96 Theta(max)= 66.583

R(reflections)= 0.0279(2196) wR2(reflections)= 0.0663(2250)

S = 1.042 Npar= 202

The CheckCIF report for the crystal data is provided in another single file.

5. DFT Studies

5.1 Computational Methods

All of the DFT calculations were performed with the Gaussian 16 B.01.[1] The geometry optimizations and frequency analysis of the two intramolecular cyclization mechanisms were carried out with the M06-2*X*/6-311G(d) basic set.[2] The frequency analysis was used to confirm the optimized structures as local energy minima or saddle point and acquire Gibbs free energy corrections. The solvent effects of dichloromethane (DCM) were taken into consideration by using solvation model based on density (SMD).[3] The calculated energies are summarized in Table S2. And the computed structures are presented in Figure S2 using CYLview.[4]

Table S2. Summary of the optimized geometries calculated at M06-2*X*/6-311G(d) level.

Geometry	Single-point Energy(a.u.)	Thermal correction of Gibbs Free Energy(a.u.)	Gibbs Free Energy(a.u.)	IF*
A1	-1546.102291	0.374225	-1545.728066	-
TS1	-1546.075232	0.377057	-1545.698175	-268.05
B1	-1546.095596	0.375021	-1545.720575	-
C1	-1393.087355	0.331425	-1392.755930	-
A2	-1546.098542	0.378431	-1545.720111	-
TS2	-1546.060748	0.377981	-1545.682767	-311.18
B2	-1546.078531	0.375146	-1545.703385	-
C2	-1393.067373	0.333863	-1392.733510	-
S1	-1037.981062	0.015921	-1037.965141	-
S2	-1191.054380	0.061245	-1190.993135	-

* The calculated imaginary frequencies for transition states.

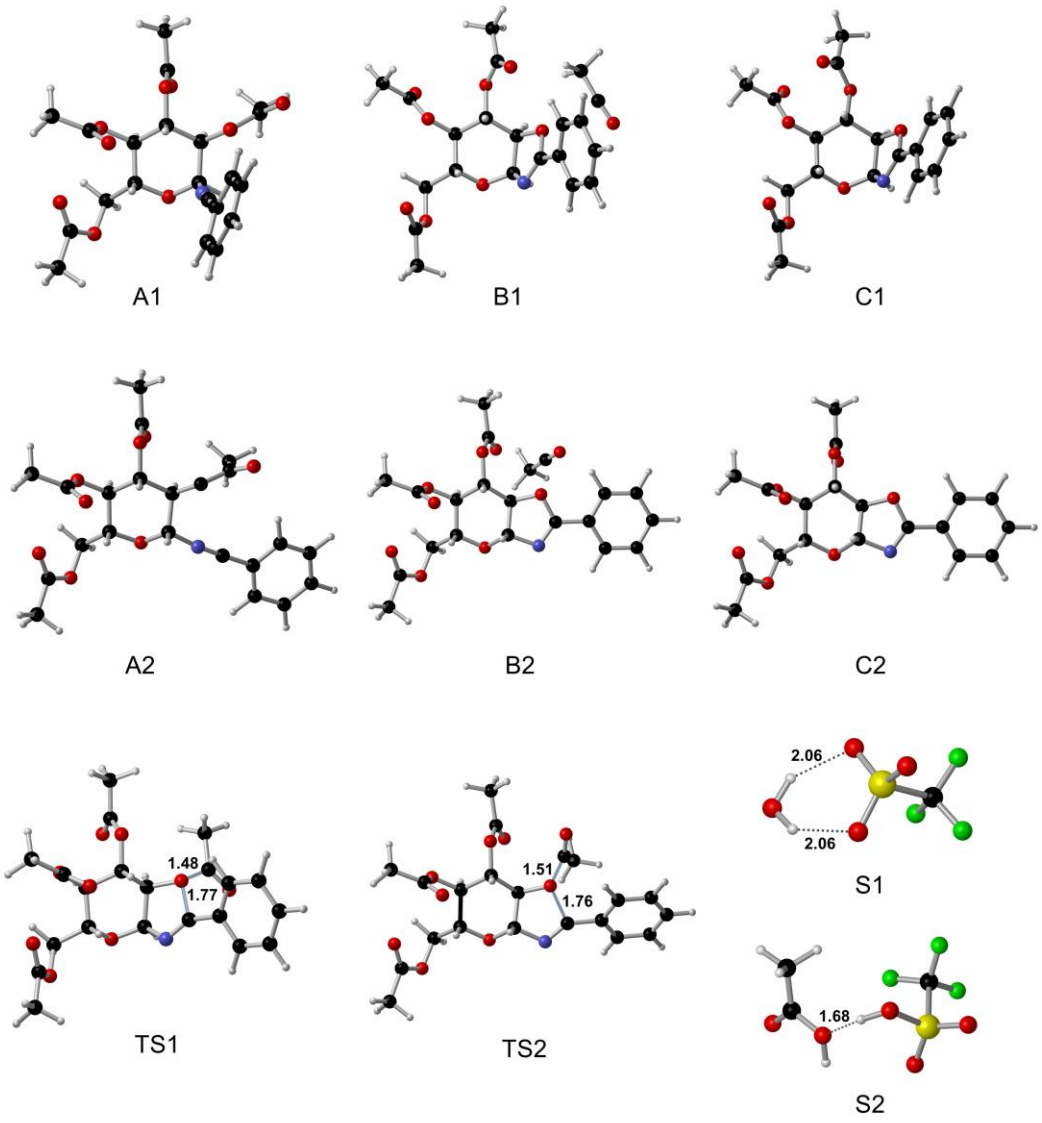


Figure S2. All of the optimized geometries calculated at M06-2*X*/6-311G(d) level. The essential distances are shown in Å.

5.2 M06-2*X* geometries for all the optimized compounds and transition states.

A1				O	-0.43306100	2.62237700	-0.51673100
C	-1.78622700	-0.81825000	-0.10210700	N	1.25941300	0.67548500	-1.17096200
C	-0.72283900	-1.47590100	-0.98869700	C	2.27239200	0.81049500	-0.65521900
O	-0.44523500	-0.62596500	-2.11837300	C	3.50383100	1.00118900	0.01037100
C	-0.05663800	0.65696900	-1.83585400	C	3.58124500	2.02191200	0.96990700
C	-1.04024600	1.41553900	-0.92739700	C	4.78550100	2.21490900	1.62486400
C	-1.33047000	0.58114800	0.31640100	C	5.87970500	1.40437600	1.32590500
C	-1.22294100	-2.79500200	-1.55480000	C	5.78818500	0.39398400	0.36913300
O	-0.15080000	-3.70766100	-1.79074300	C	4.59646300	0.18098700	-0.30218800
C	0.30114800	-4.35591000	-0.69883800	C	-0.89240200	3.86312500	-0.87565400
C	1.39681800	-5.31487500	-1.04539800	O	-0.29619200	4.80065200	-0.43843200
O	-0.14796300	-4.16056700	0.40136900	C	-2.08546500	3.94824900	-1.78200200

O	-2.12407900	-1.64828500	1.00605700	O	-4.20525700	-1.62939900	0.76366600
C	-1.18844600	-1.94836600	1.94291400	O	1.94816500	0.66136400	-0.54286100
O	-0.08450800	-1.47543900	1.94804300	N	0.91144300	-1.38366000	-1.20027800
C	-1.73838800	-2.91976100	2.93695900	C	1.88230400	-1.10904800	-0.53786200
O	-2.22820700	1.21719600	1.22261100	C	2.97113400	-1.62759400	0.24317500
C	-3.49289900	1.50030100	0.84140400	C	3.47174100	-0.92610900	1.34533400
O	-3.90567900	1.29213100	-0.26987700	C	4.49470000	-1.49226000	2.08920800
C	-4.26642300	2.10314100	1.97025900	C	5.01125400	-2.73685100	1.73289000
H	-2.71377400	-0.74542900	-0.67204700	C	4.50770300	-3.42807000	0.63344800
H	0.19982400	-1.62808000	-0.42222400	C	3.48273300	-2.87887000	-0.12147700
H	0.08970200	1.18628600	-2.77765400	C	3.15288700	1.28734200	-1.13259500
H	-1.93993600	1.56964400	-1.51933900	O	3.83131300	0.59557200	-1.79489900
H	-0.41103100	0.50485200	0.89375900	C	3.29823000	2.69183600	-0.68126700
H	-1.94609900	-3.24852300	-0.87830600	O	-2.65053400	1.23077500	0.74792100
H	-1.68746700	-2.62020100	-2.52400600	C	-2.59379600	0.45271500	1.85957800
H	1.75723000	-5.80260400	-0.14328300	O	-1.74360100	-0.37504000	2.04198900
H	1.01951800	-6.06019800	-1.74791800	C	-3.70786000	0.79745600	2.79457900
H	2.21259000	-4.78099900	-1.53577800	O	-0.02854700	2.40663000	0.79053600
H	2.71657600	2.63999200	1.17957800	C	-0.25727000	3.59016100	0.17091500
H	4.87163900	2.99695500	2.36890800	O	-0.59754100	3.66817700	-0.97943800
H	6.81779700	1.56285900	1.84515300	C	-0.02061500	4.73353200	1.10481200
H	6.64756100	-0.22616100	0.14695700	H	-2.02013500	1.76581800	-1.06621100
H	4.50038500	-0.59653700	-1.05001300	H	-1.63439000	-1.16135900	-0.27474700
H	-2.96641100	3.49544600	-1.32168400	H	0.74226900	-0.23008300	-2.91133100
H	-2.28292000	4.99914000	-1.97579100	H	0.72902000	1.85859900	-1.74103500
H	-1.89728300	3.43555300	-2.72833300	H	-0.05087800	0.42414500	0.83188300
H	-1.00387300	-3.09525600	3.71897400	H	-4.03821700	0.04706100	-0.90116000
H	-2.66416700	-2.53318800	3.36577000	H	-3.39134300	-0.28969600	-2.52388600
H	-1.96554700	-3.85563500	2.42385000	H	-5.36271100	-3.93232700	-0.97881900
H	-5.27975300	2.32178300	1.64342200	H	-3.72554800	-4.40610800	-0.52891200
H	-4.28372900	1.40910500	2.81228400	H	-4.93429700	-4.09699800	0.74702500
H	-3.77236200	3.01772500	2.30329900	H	3.05614100	0.03587000	1.62195300
				H	4.88935300	-0.96456400	2.94871400
TS1				H	5.81445500	-3.17093100	2.31695200
C	-1.74422700	1.01202100	-0.32894900	H	4.91657900	-4.39335000	0.36109200
C	-1.91691300	-0.36769700	-0.97340800	H	3.07953000	-3.39788200	-0.98283700
O	-1.07183900	-0.42470900	-2.13265300	H	3.28604600	2.71356000	0.41048300
C	0.27153800	-0.26381700	-1.92828900	H	4.23551300	3.08814400	-1.06429900
C	0.64812000	0.98896100	-1.09260400	H	2.46653700	3.29995600	-1.04540400
C	-0.28422200	1.19006200	0.09305100	H	-3.64045300	0.17678000	3.68448000
C	-3.34154800	-0.56513700	-1.47172300	H	-3.65006300	1.85321800	3.06559700
O	-3.74057600	-1.93374600	-1.40542600	H	-4.66082900	0.62656800	2.29242300
C	-4.16922800	-2.35251400	-0.19845400	H	-0.71637400	4.66408500	1.94322900
C	-4.57810000	-3.79183300	-0.23358800	H	0.99195500	4.67985800	1.50827700

H	-0.16630900	5.67255400	0.57714300	H	2.98565200	0.39483400	1.25025200
				H	4.86558300	-0.34809900	2.69698300
B1				H	5.61590600	-2.70749000	2.62913300
C	-1.93903000	0.87179700	-0.42543600	H	4.49375700	-4.32717700	1.13000200
C	-2.14879600	-0.63473800	-0.55956000	H	2.62497500	-3.57885800	-0.32701900
O	-1.51377500	-1.06207700	-1.75726000	H	3.37921800	2.35312900	-0.00749300
C	-0.13476200	-0.89119700	-1.80242300	H	4.44283300	3.10491700	-1.26542200
C	0.36194700	0.51530500	-1.40089500	H	2.72174100	2.71656500	-1.64841900
C	-0.45370900	1.14218900	-0.27202700	H	-4.46437000	3.71763300	1.97488800
C	-3.61781400	-0.97661000	-0.69263900	H	-4.47648000	1.98685400	2.41497200
O	-3.80908500	-2.38960800	-0.77715400	H	-3.04458200	2.95824500	2.74656600
C	-3.79126800	-3.06951200	0.38461300	H	1.39975900	4.96535700	1.20991200
C	-3.99462600	-4.53597000	0.15225800	H	0.70045600	4.94904200	-0.43630700
O	-3.63137300	-2.53936700	1.45252400	H	-0.36585800	4.88883600	0.96237800
O	1.68022400	0.21794000	-0.89791500				
N	0.62339800	-1.77588800	-0.90472100	C1			
C	1.61429000	-1.10120900	-0.49957200	C	1.77956700	-0.16675200	-0.54040500
C	2.71951200	-1.54566000	0.35852700	C	1.22782400	1.25785900	-0.56840200
C	3.34652100	-0.62819800	1.20628500	O	0.56115100	1.45567300	-1.80355800
C	4.38611300	-1.05140000	2.02603200	C	-0.57864700	0.67481900	-1.98537900
C	4.80151000	-2.38028400	1.99269900	C	-0.38358200	-0.82858400	-1.70775600
C	4.16981000	-3.29326900	1.15075900	C	0.60941300	-1.14346500	-0.58700500
C	3.12468300	-2.88052800	0.33451100	C	2.33759900	2.28636000	-0.49551500
C	4.01685900	1.13702300	-1.52616000	O	1.80258300	3.61216700	-0.48755900
O	4.40698500	0.16531800	-1.89816300	C	1.33655900	4.06533100	0.69000000
C	3.60747000	2.42266200	-1.07658600	C	0.77375900	5.44758500	0.55040800
O	-2.58353600	1.32652100	0.76047400	O	1.37483400	3.42021500	1.70480100
C	-3.31753600	2.46664300	0.69400900	O	-1.69585200	-1.22060700	-1.26704600
O	-3.48810500	3.08288100	-0.31983200	N	-1.70910200	1.02903100	-1.12121700
C	-3.86660200	2.81225600	2.04347300	C	-2.28195500	-0.06812800	-0.83247900
O	-0.27963500	2.56157300	-0.24162500	C	-3.52954700	-0.22873100	-0.07054300
C	0.66297100	3.07274600	0.57409200	C	-3.99307900	-1.50021000	0.27067800
O	1.43553400	2.39099700	1.19807800	C	-5.16972800	-1.63237900	0.99984400
C	0.60616700	4.56809700	0.58210300	C	-5.88123900	-0.50094400	1.38720500
H	-2.34690500	1.38982200	-1.29573200	C	-5.41759000	0.76871200	1.04543300
H	-1.71699000	-1.15177100	0.30560400	C	-4.24509400	0.90729400	0.31667300
H	0.14944100	-1.12280800	-2.83154800	O	2.47770400	-0.30779300	0.69941800
H	0.45144700	1.19186400	-2.24892600	C	3.50266100	-1.18349700	0.76630800
H	-0.12449800	0.72153900	0.68204100	O	3.88155500	-1.82599500	-0.17638100
H	-4.17748300	-0.57367500	0.15095700	C	4.05715900	-1.24387700	2.15482200
H	-4.00739600	-0.57294800	-1.62723400	O	1.05136200	-2.48486000	-0.81751500
H	-3.98744300	-5.06385600	1.10261100	C	1.33348000	-3.26451300	0.24655200
H	-4.94374700	-4.70009400	-0.36086900	O	1.19730300	-2.90411200	1.38536400
H	-3.19893200	-4.91494400	-0.49167600	C	1.85247800	-4.59669700	-0.19667400

H	2.46300700	-0.33123600	-1.37695000
H	0.53169000	1.39905800	0.26745500
H	-0.87223500	0.84109500	-3.02448000
H	-0.13594400	-1.39427900	-2.60328200
H	0.09564400	-1.09326200	0.37661300
H	2.94904500	2.12550600	0.39102000
H	2.95419400	2.22863500	-1.39253300
H	0.47643900	5.82371400	1.52623400
H	1.51435300	6.10964000	0.09960100
H	-0.09246100	5.41607400	-0.11364700
H	-3.43435900	-2.37766600	-0.03153100
H	-5.52966100	-2.61945700	1.26630500
H	-6.79851900	-0.60670300	1.95564600
H	-5.97257200	1.64975800	1.34655400
H	-3.87409700	1.88783200	0.04188500
H	4.96442800	-1.84307900	2.16341500
H	4.25831800	-0.23953700	2.52916100
H	3.30618300	-1.70007100	2.80368200
H	1.91020800	-5.27102700	0.65435300
H	1.21501600	-5.01609200	-0.97526200
H	2.84968100	-4.45074000	-0.61852100

A2

C	1.99379500	-0.45303300	-0.54456600
C	1.70953300	1.03646000	-0.29950700
O	0.29935200	1.26948100	-0.45305700
C	-0.44024900	0.54567500	0.47079300
C	-0.34469400	-0.96258100	0.18793800
C	1.12819100	-1.33110500	0.36794700
C	2.41545900	1.89836700	-1.33252000
O	2.73488800	3.18901700	-0.81364000
C	3.82730200	3.23650200	-0.02518600
C	4.10274200	4.63090400	0.44368000
O	4.47674100	2.25774200	0.24006800
O	-1.11237100	-1.64896100	1.15305800
N	-1.81618400	0.93695500	0.30940900
C	-2.93685100	1.13764400	0.19605200
C	-4.32596800	1.34502400	0.05024100
C	-4.80403700	2.61157000	-0.31449100
C	-6.17080300	2.77735300	-0.45719700
C	-7.03177800	1.70250000	-0.23771000
C	-6.54242300	0.44848900	0.12577800
C	-5.17994200	0.25348400	0.27285700
C	-2.25458600	-2.34040100	0.84859300
O	-2.88483200	-2.77183500	1.76780900
C	-2.62583700	-2.52291100	-0.59635200
O	3.38476500	-0.74394100	-0.43676200
C	4.02905100	-0.56767800	0.74542500
O	3.46854800	-0.26722200	1.76355900
C	5.49495400	-0.81030700	0.58168300
O	1.38558400	-2.72276100	0.20354200
C	1.13092200	-3.32876900	-0.97602200
O	0.64162100	-2.75826100	-1.91649700
C	1.52647000	-4.77028200	-0.92942100
H	1.75750900	-0.67583900	-1.58608800
H	2.00740300	1.31779700	0.71393700
H	-0.16498500	0.77147200	1.50821000
H	-0.68196800	-1.14259400	-0.83092200
H	1.38852700	-1.14691400	1.40922800
H	3.32404700	1.40759300	-1.67982200
H	1.74822600	2.07069000	-2.17585000
H	4.93944600	4.62720600	1.13766600
H	4.33753000	5.26137400	-0.41623100
H	3.21418800	5.04241800	0.92466500
H	-4.11417200	3.43016600	-0.47767500
H	-6.56736500	3.74488800	-0.73817700
H	-8.10026200	1.84497000	-0.35046200
H	-7.22372800	-0.37567400	0.29568400
H	-4.77371900	-0.70894600	0.56173000
H	-1.82260200	-3.01311800	-1.15076300
H	-3.51873800	-3.14143800	-0.63253800
H	-2.83356100	-1.56728600	-1.08458300
H	5.98527800	-0.74191500	1.54954200
H	5.66503700	-1.79247600	0.13823800
H	5.90151900	-0.05610400	-0.09410700
H	1.29925000	-5.24285800	-1.88150200
H	2.59423200	-4.84795900	-0.71699200
H	0.99031900	-5.27162900	-0.12177500

TS2

C	-1.82590200	0.65701600	-0.45611600
C	-2.08248500	-0.87226800	-0.43768900
O	-0.89322200	-1.61080300	-0.76720400
C	0.11281700	-1.23565800	0.10234100
C	0.52657400	0.20033500	-0.21594500
C	-0.57256200	1.08354500	0.34266200
C	-3.14104800	-1.23090100	-1.46560700
O	-3.86028500	-2.40483400	-1.08844400

C	-4.79013800	-2.22604100	-0.13027200	H	-0.97607200	4.93166000	-0.41597800
C	-5.50804000	-3.50185900	0.18052400	H	0.65090100	4.87299500	0.26154500
O	-4.98809200	-1.15650200	0.38816600	H	0.43731700	5.09077900	-1.49925500
O	1.82909100	0.30030900	0.38666300				
N	1.34297800	-2.00024400	-0.02387800	B2			
C	2.35396600	-1.36724600	0.18609100	C	-1.73202600	0.67755700	-0.18951100
C	3.78365800	-1.43847600	0.34042000	C	-2.00684800	-0.83031200	-0.45505700
C	4.42741500	-0.67479600	1.31988900	O	-0.82631700	-1.53141900	-0.85634000
C	5.80627100	-0.76425300	1.43521700	C	0.15496600	-1.32709300	0.11992200
C	6.52537400	-1.59845300	0.58126600	C	0.57247500	0.13220500	0.10351800
C	5.87304200	-2.35846300	-0.38705800	C	-0.53027100	0.92738900	0.74872400
C	4.49385200	-2.28695900	-0.51549800	C	-3.02961900	-0.97660800	-1.56966700
C	2.67597300	1.44277000	-0.13513700	O	-3.79449100	-2.17496900	-1.42336500
O	2.76533600	2.35060100	0.59557300	C	-4.77654000	-2.12380500	-0.50469300
C	3.26034500	1.18627200	-1.47395700	C	-5.52855200	-3.41654300	-0.43525500
O	-2.99856700	1.35311200	-0.05172800	O	-4.99585200	-1.14215700	0.15906500
C	-3.46930700	1.20968800	1.21494100	O	1.86240900	0.07585300	0.71275300
O	-2.88469000	0.59892200	2.06752300	N	1.42469400	-2.00496000	-0.07579800
C	-4.77455600	1.92009400	1.37114200	C	2.29731000	-1.18366000	0.35909100
O	-0.39561300	2.49609900	0.30951400	C	3.73487700	-1.43483200	0.51897600
C	0.07278600	3.12309900	-0.78990700	C	4.57660800	-0.44142100	1.02364100
O	0.47700700	2.53079800	-1.75806100	C	5.93632100	-0.69621000	1.16356700
C	0.04750500	4.60555400	-0.60829800	C	6.45453700	-1.93532100	0.79967700
H	-1.67986800	0.96925800	-1.49434700	C	5.61260500	-2.92742100	0.29853200
H	-2.40378800	-1.16508300	0.56486700	C	4.25420900	-2.68220900	0.16091900
H	-0.20780000	-1.34413500	1.14689900	C	2.80179200	2.08456000	-1.89649200
H	0.63877900	0.28828000	-1.29530600	O	3.33603000	2.12025200	-0.92281400
H	-0.69804300	0.86579600	1.40141400	C	2.21518000	2.01488900	-3.19140500
H	-3.83742400	-0.40350200	-1.59895000	O	-2.92485800	1.32883700	0.23897900
H	-2.66228800	-1.46537400	-2.41507500	C	-3.48972400	1.00083200	1.42808700
H	-6.00767700	-3.86827200	-0.71804200	O	-2.98044200	0.25244600	2.21654600
H	-4.78839400	-4.26058200	0.49293100	C	-4.79213700	1.71517800	1.60107500
H	-6.23682600	-3.33106300	0.96874500	O	-0.33365600	2.32941700	0.98260400
H	3.85730600	-0.03935000	1.98884200	C	0.18025600	3.13933400	0.05747400
H	6.31924900	-0.18494600	2.19297000	O	0.55558300	2.75900600	-1.03137400
H	7.60355200	-1.65826500	0.67321200	C	0.23349500	4.55326100	0.53949300
H	6.43928100	-3.00529600	-1.04600500	H	-1.50914800	1.15706500	-1.14662900
H	3.96885000	-2.86549900	-1.26656600	H	-2.38731500	-1.27835100	0.46739000
H	2.71921800	0.42597300	-2.03401900	H	-0.24191600	-1.62695300	1.10228800
H	3.27260400	2.12746400	-2.02134500	H	0.70602400	0.41249300	-0.94437200
H	4.29255500	0.85488000	-1.32469000	H	-0.72861800	0.53729500	1.74406100
H	-5.10044000	1.85728200	2.40637800	H	-3.70155200	-0.11932300	-1.59415500
H	-4.67188300	2.96317500	1.06830600	H	-2.51508100	-1.06943100	-2.52500800
H	-5.51090000	1.44591000	0.72054100	H	-5.97296700	-3.63353500	-1.40830000

H	-4.84032300	-4.22909000	-0.19625500
H	-6.30507600	-3.34957400	0.32255900
H	4.16825800	0.51908500	1.31395900
H	6.59006800	0.07215000	1.55978800
H	7.51510600	-2.13172600	0.91004600
H	6.01685900	-3.89365300	0.01997400
H	3.58762400	-3.44684500	-0.22075000
H	2.98393500	1.63469200	-3.87127800
H	1.35505700	1.34260800	-3.13490100
H	1.90074800	3.02651600	-3.46347500
H	-5.21986300	1.46209600	2.56800900
H	-4.63639200	2.79296400	1.52885900
H	-5.47045200	1.41298300	0.80229100
H	-0.78076100	4.89936300	0.74774200
H	0.79788600	4.60210700	1.47195800
H	0.69429700	5.18504800	-0.21534800

C2

C	-1.51782400	0.72803900	-0.43932100
C	-1.66400300	-0.81846000	-0.47933800
O	-0.45262600	-1.45925700	-0.88728900
C	0.56631500	-1.02943600	-0.03127300
C	0.85621700	0.43976500	-0.27780900
C	-0.27220100	1.22736500	0.33072700
C	-2.74545200	-1.19913800	-1.47650200
O	-3.37960200	-2.43028100	-1.11735100
C	-4.29249000	-2.34446600	-0.13434200
C	-4.89391700	-3.68173500	0.17130500
O	-4.56600700	-1.30673700	0.41446500
O	2.17159700	0.55892800	0.27660700
N	1.87488000	-1.63595400	-0.20104400
C	2.69174800	-0.69498900	0.07267300
C	4.15050000	-0.81775700	0.19636100
C	4.94290900	0.31424400	0.39377400
C	6.32265100	0.17943400	0.50148100
C	6.90992000	-1.07885200	0.41061500
C	6.11748500	-2.20888000	0.21309600
C	4.73991900	-2.08177500	0.10861200
O	-2.72952800	1.32831800	0.02089200
C	-3.15611800	1.11231300	1.28714700
O	-2.52026600	0.50984400	2.10929600
C	-4.49832800	1.73898900	1.50057900
O	-0.16340000	2.65393500	0.32471800
C	0.03074000	3.33092300	-0.82412800
O	0.12602500	2.80596700	-1.90188400
C	0.11240500	4.80365700	-0.55926400
H	-1.43284600	1.08036300	-1.46810200
H	-1.93166100	-1.17174000	0.52059600
H	0.25178300	-1.19942400	1.01193100
H	0.93016800	0.60817900	-1.35479600
H	-0.35562200	0.98667400	1.38826100
H	-3.49729900	-0.41417900	-1.55137300
H	-2.29423000	-1.37217900	-2.45226900
H	-5.31942600	-4.11309200	-0.73597300
H	-4.11245500	-4.35724300	0.52484300
H	-5.66235100	-3.57418600	0.93278500
H	4.48063000	1.29156200	0.46034000
H	6.93866400	1.05793100	0.65517900
H	7.98610800	-1.18134300	0.49453700
H	6.57538600	-3.18883200	0.14356300
H	4.11123200	-2.95185800	-0.04059700
H	-4.79960900	1.61080400	2.53741900
H	-4.46029600	2.79950300	1.24686500
H	-5.22063100	1.25563300	0.84128900
H	-0.80138700	5.13906900	-0.06600300
H	0.94739100	5.00796600	0.11340800
H	0.24988800	5.33689400	-1.49657700

S1

S	0.26480300	0.68415300	0.00000000
O	0.97317600	0.32002100	-1.23161900
O	-0.35622700	2.00266500	-0.00000400
O	0.97317100	0.32002700	1.23162300
C	-1.17025000	-0.47094500	0.00000000
F	-1.93028800	-0.28372300	-1.07869400
F	-1.93029200	-0.28371900	1.07869100
F	-0.75688000	-1.73763600	0.00000300
H	2.73660600	-0.62136000	0.75169300
O	3.26845200	-0.90925800	0.00000000
H	2.73661300	-0.62135800	-0.75169600

S2

O	-3.71520000	0.12093100	-1.02831000
C	-3.00487200	0.62224800	1.22829500
H	-3.86108400	1.28908300	1.28266600
H	-3.06376600	-0.12840500	2.01863000
H	-2.08446500	1.19218700	1.37371800
C	-2.97630800	-0.04893200	-0.10627800

S	1.34512600	-0.82853200	0.03580500	F	1.66131200	1.59161400	0.95796300
O	0.84450600	-1.38534300	-1.19299000	F	0.00947900	1.35698500	-0.41350600
O	2.64243200	-1.14197800	0.55508800	H	-0.62651000	-1.08660100	0.83372100
O	0.29867800	-1.02441700	1.19161400	O	-1.94742700	-0.94781200	-0.18897900
C	1.26110800	1.00840900	-0.15449600	H	-1.93018700	-1.35944300	-1.0700230
F	2.03815500	1.37232200	-1.15646900				

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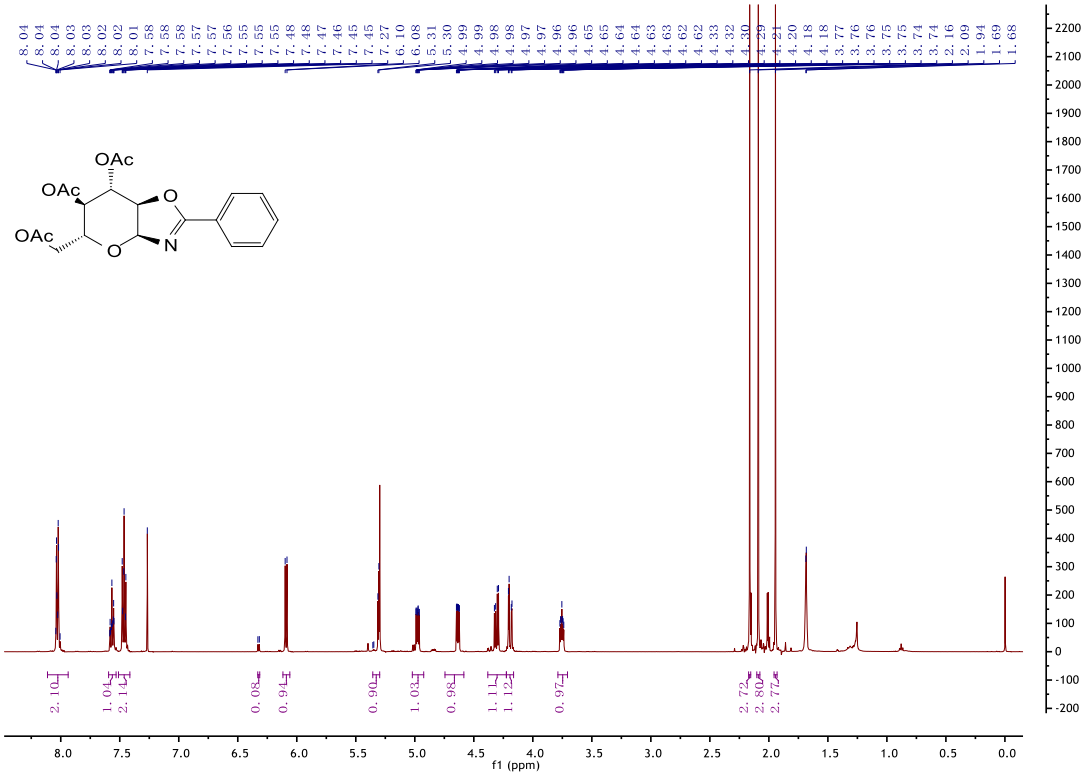
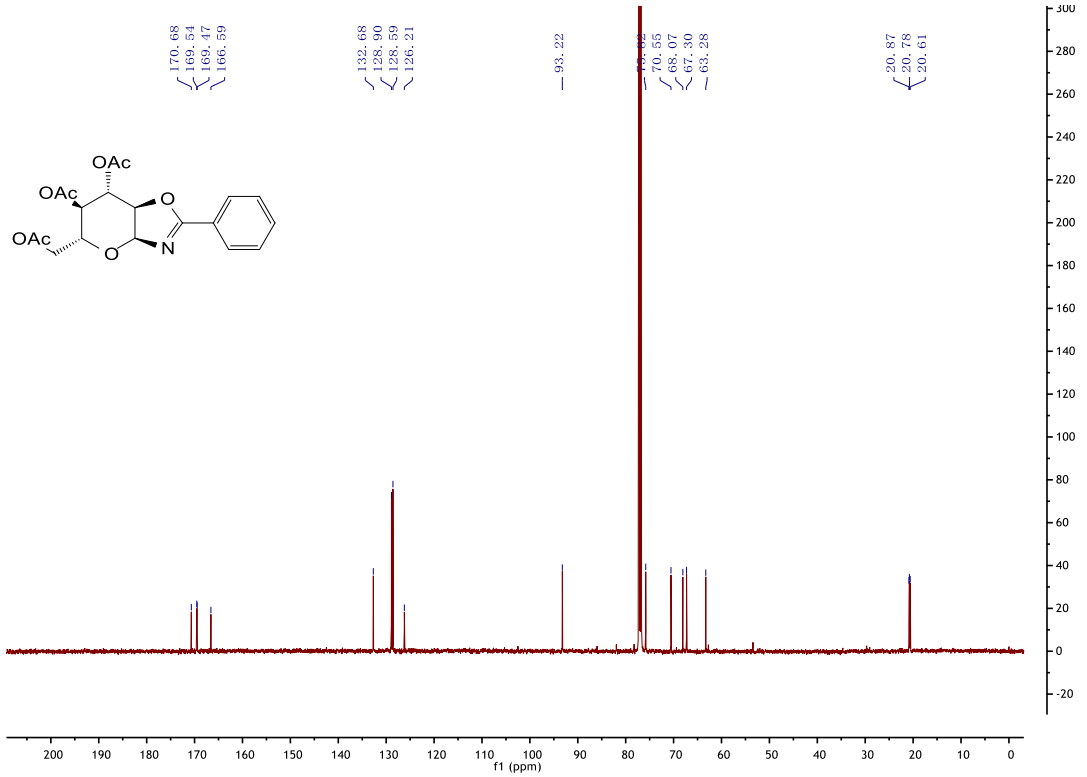
6. NMR spectra

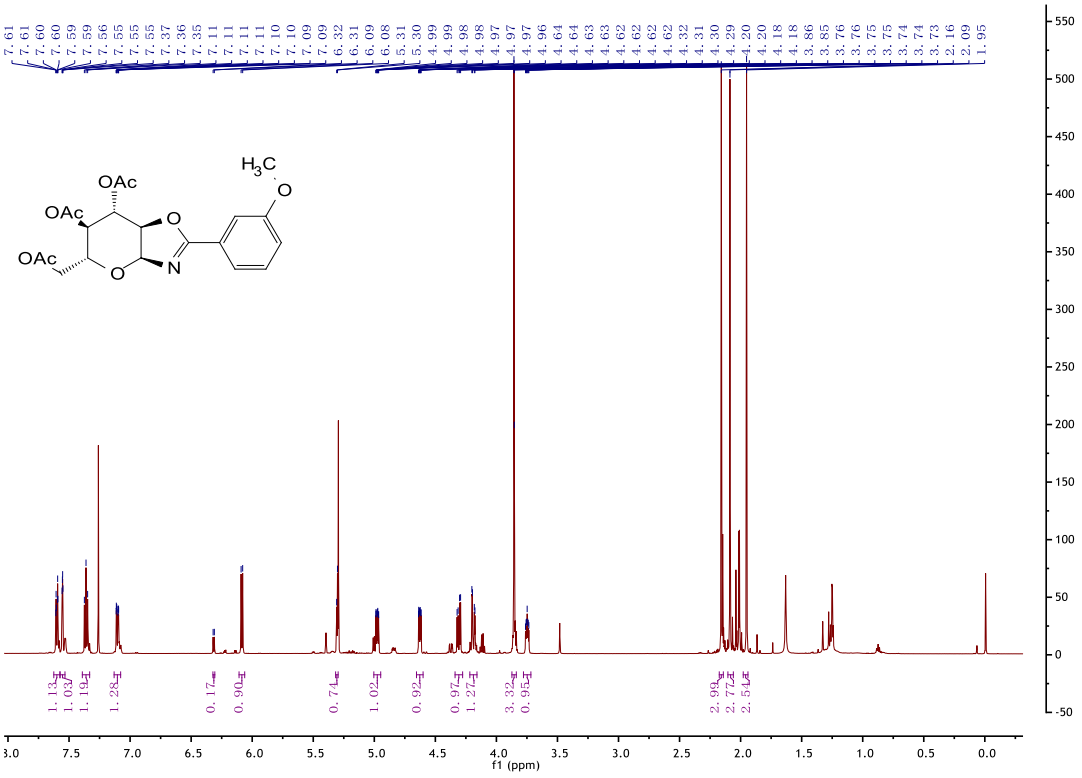
^{1}H NMR spectrum of 3A



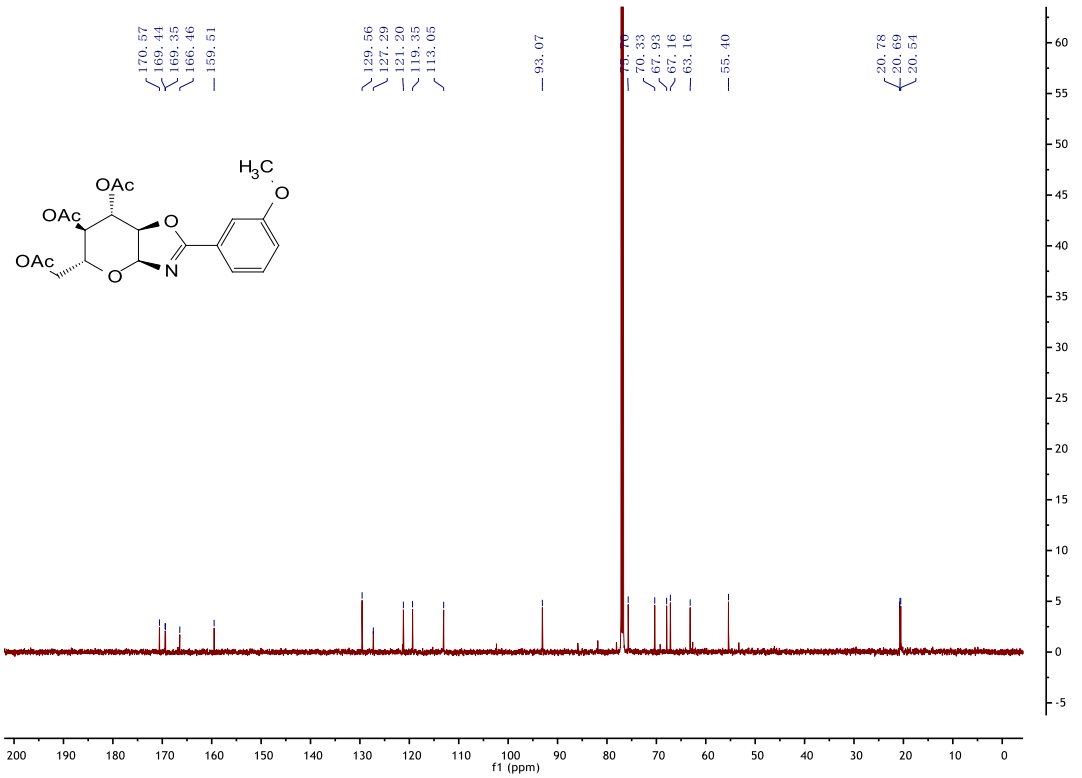
^{13}C NMR spectrum of 3A



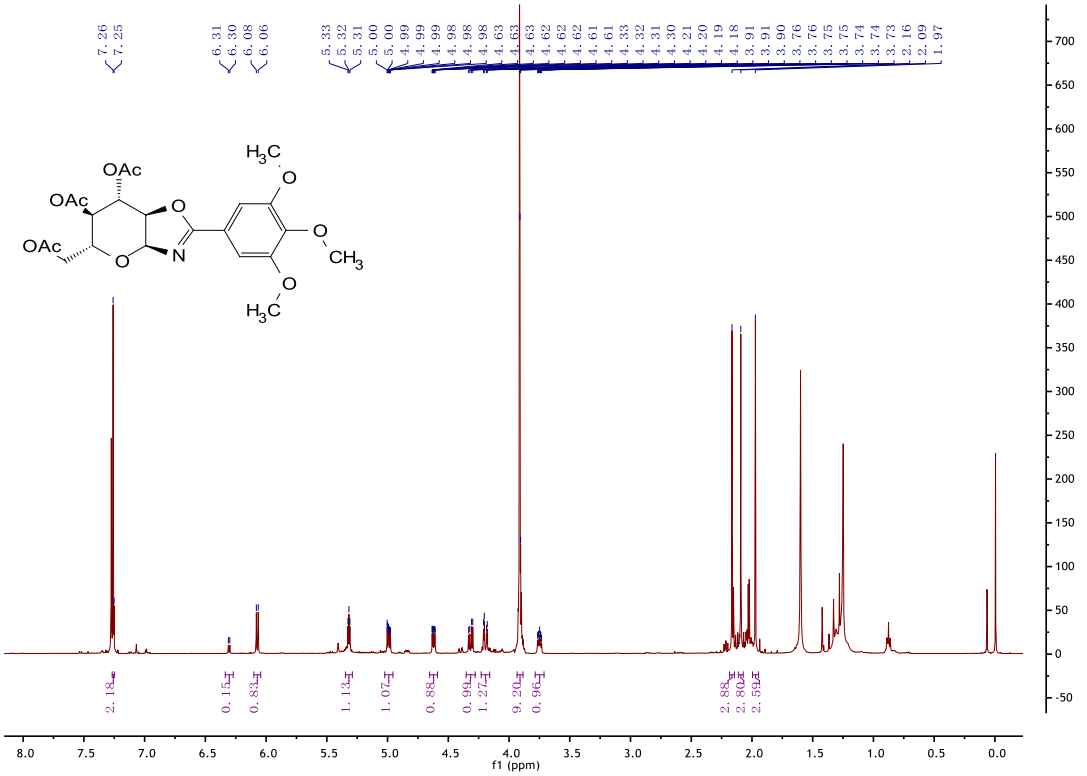
^{1}H NMR spectrum of 3B



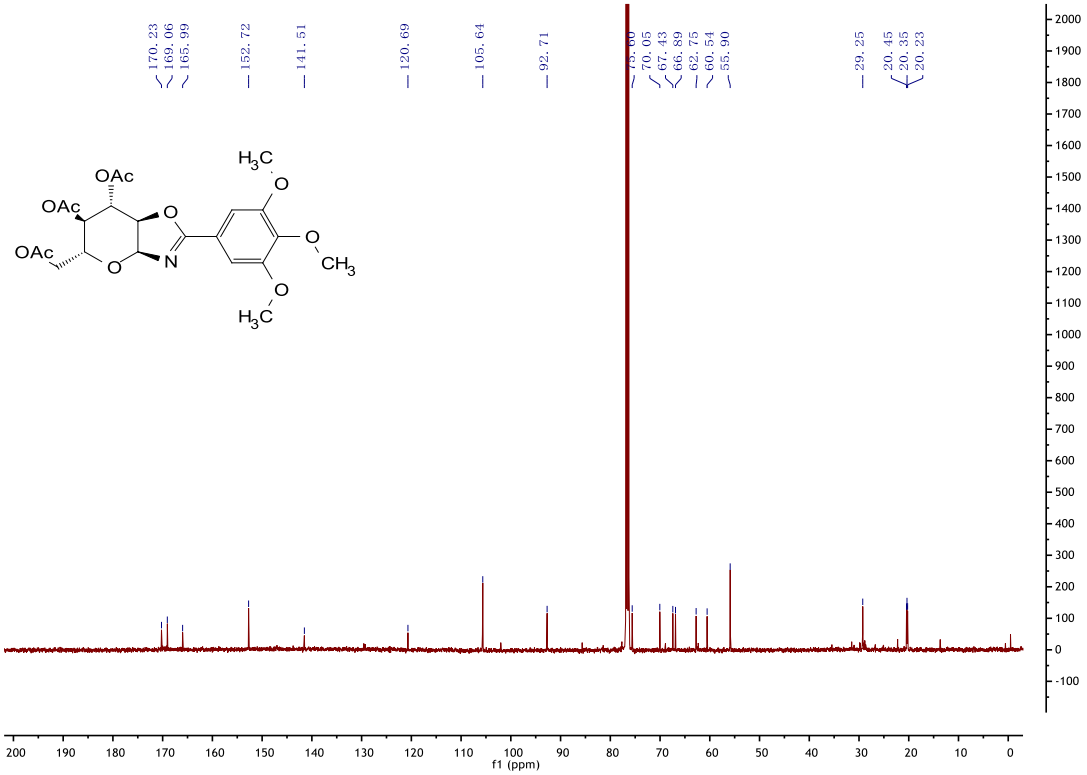
^{13}C NMR spectrum of 3B



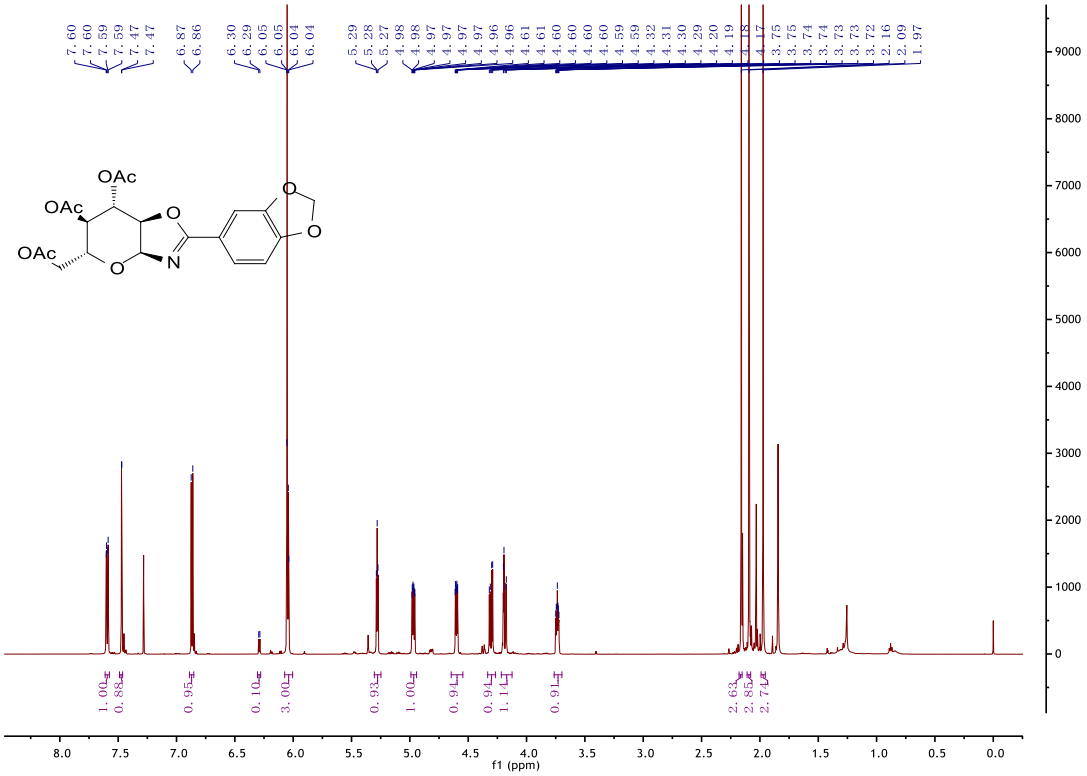
^{1}H NMR spectrum of 3C



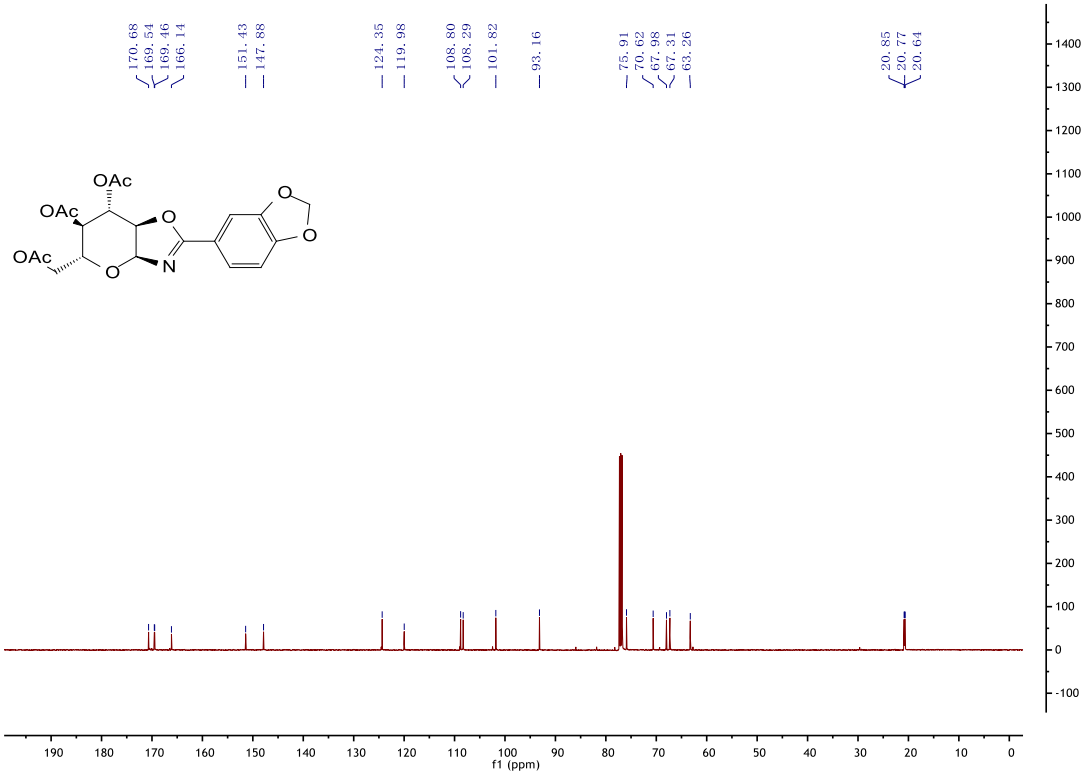
^{13}C NMR spectrum of 3C



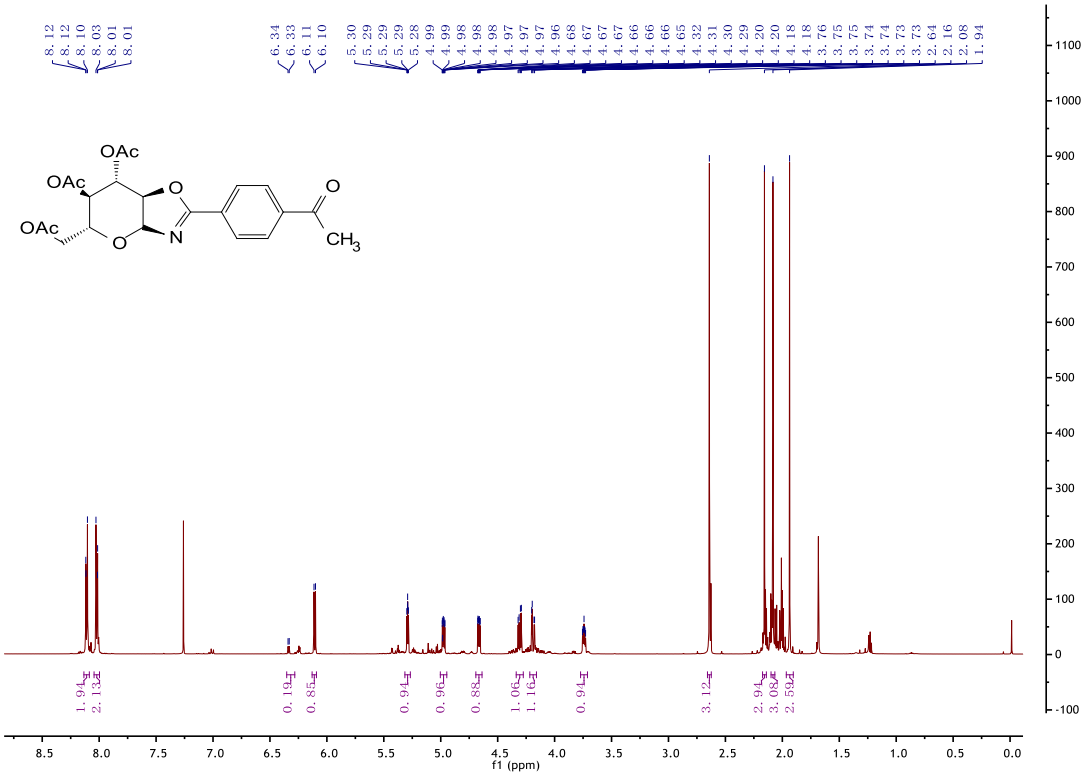
^{1}H NMR spectrum of 3D



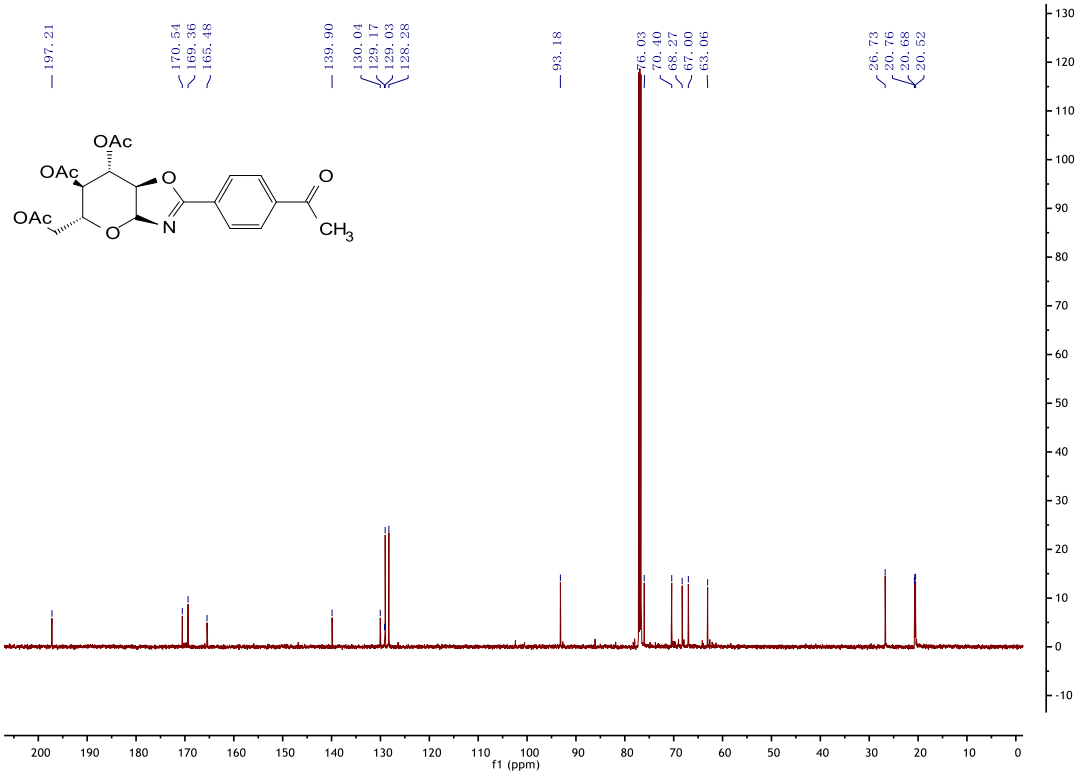
^{13}C NMR spectrum of 3D



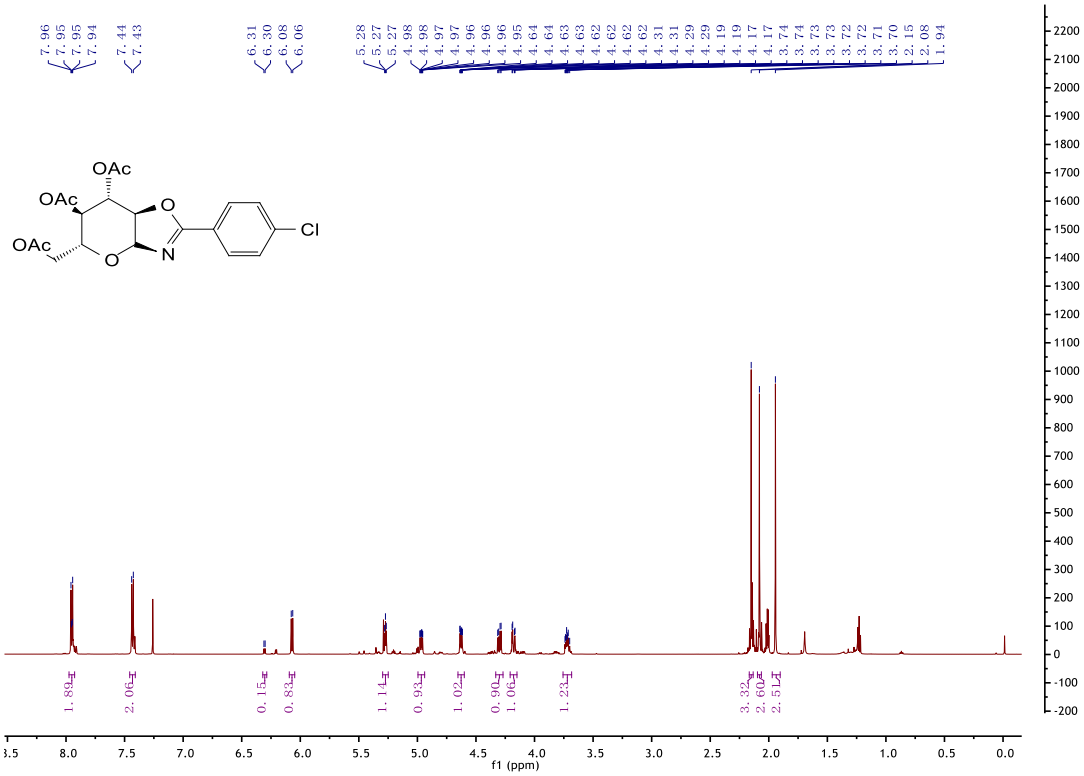
^{1}H NMR spectrum of 3E



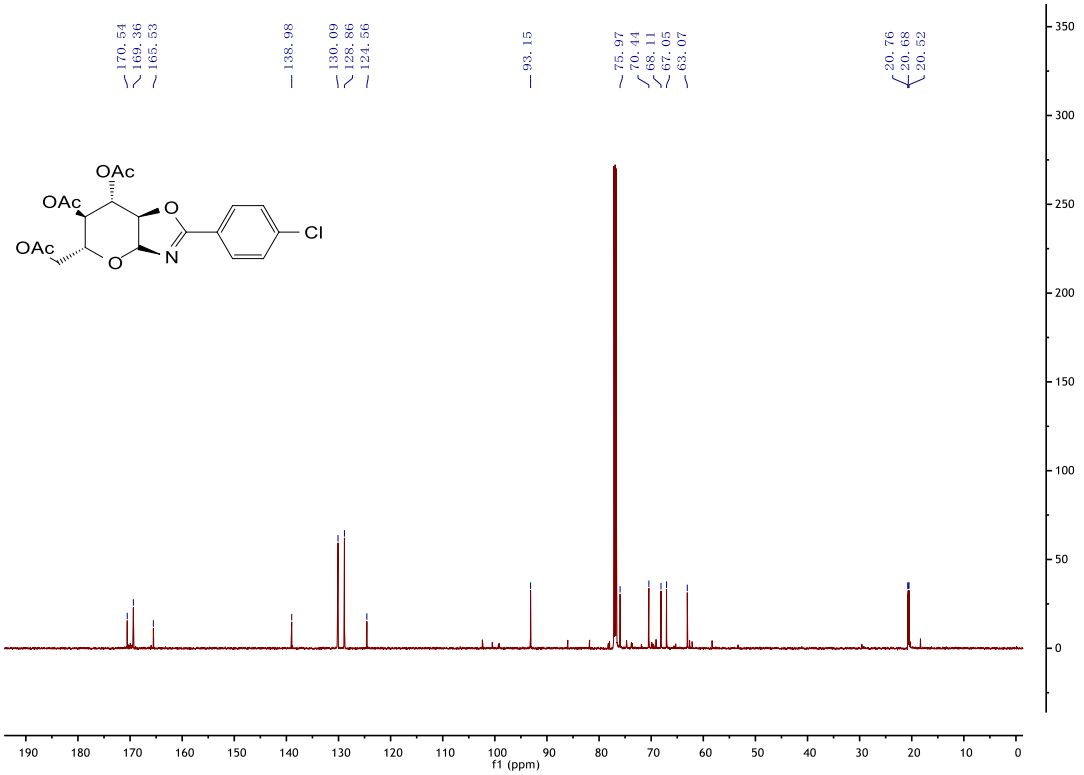
^{13}C NMR spectrum of 3E



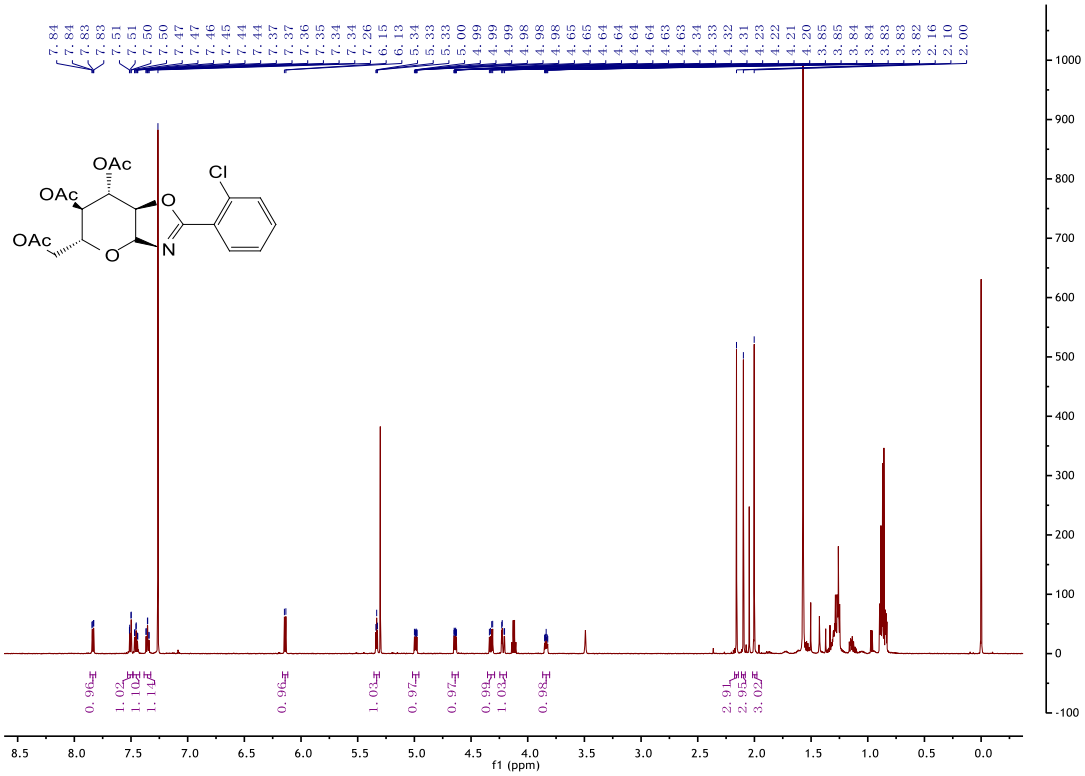
^{1}H NMR spectrum of 3F



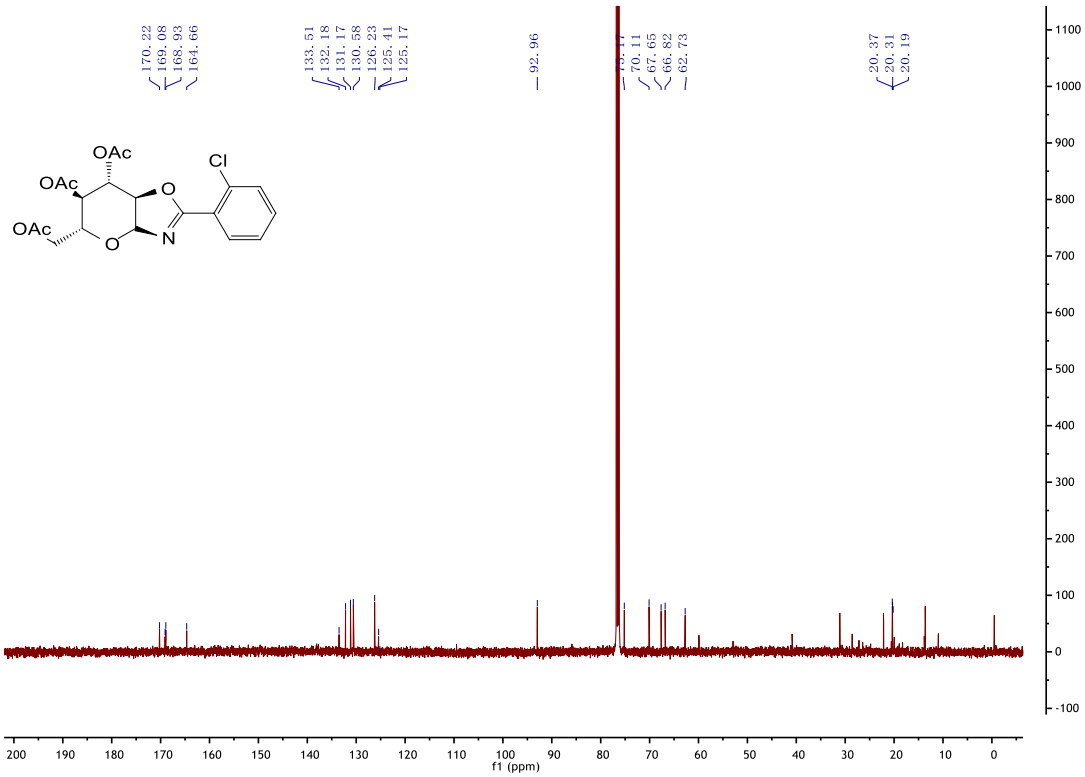
^{13}C NMR spectrum of 3F



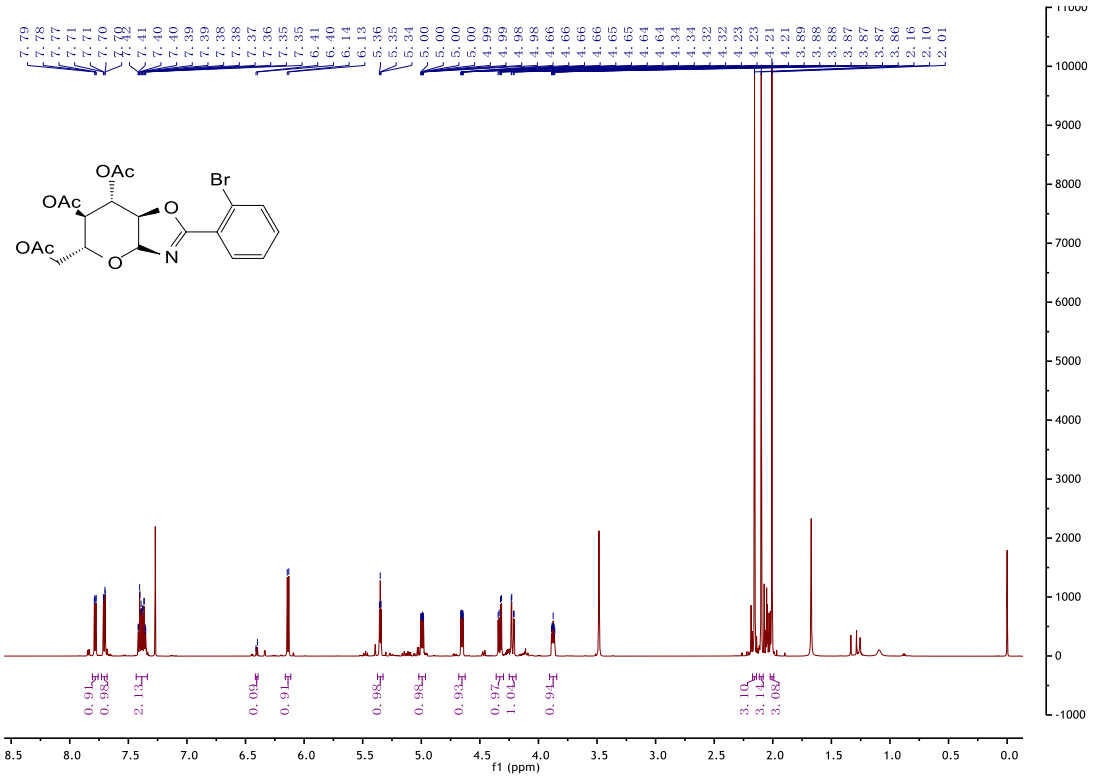
^{1}H NMR spectrum of 3G



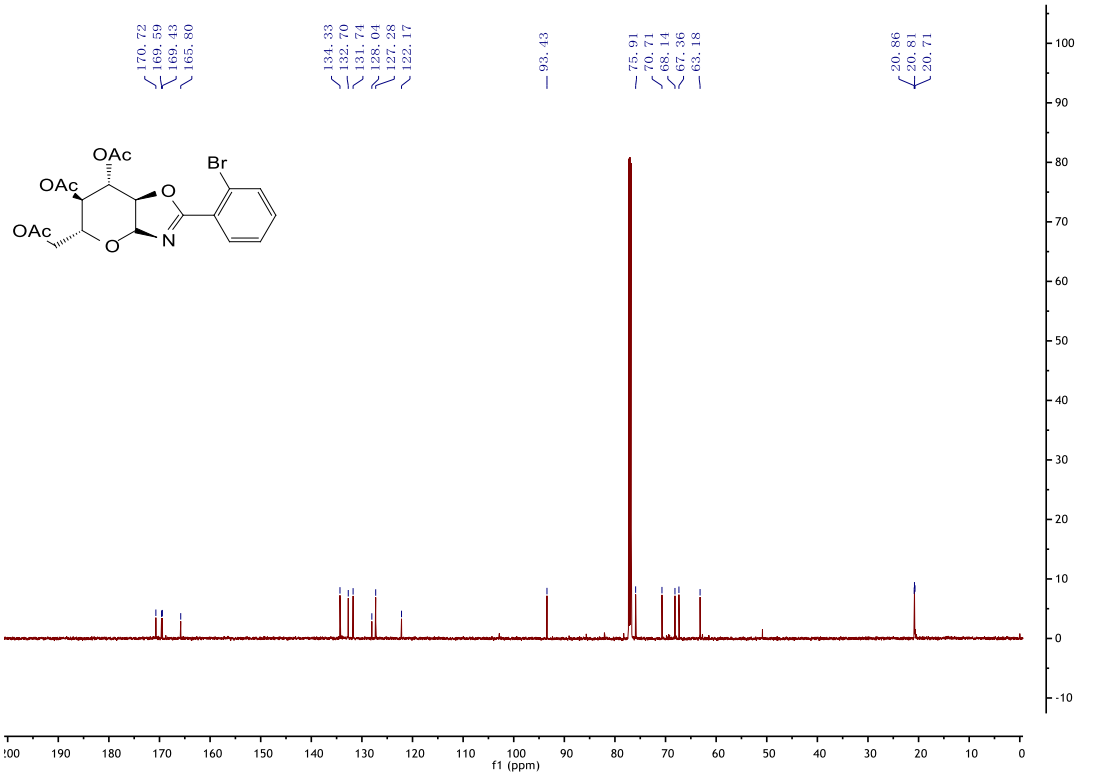
^{13}C NMR spectrum of 3G



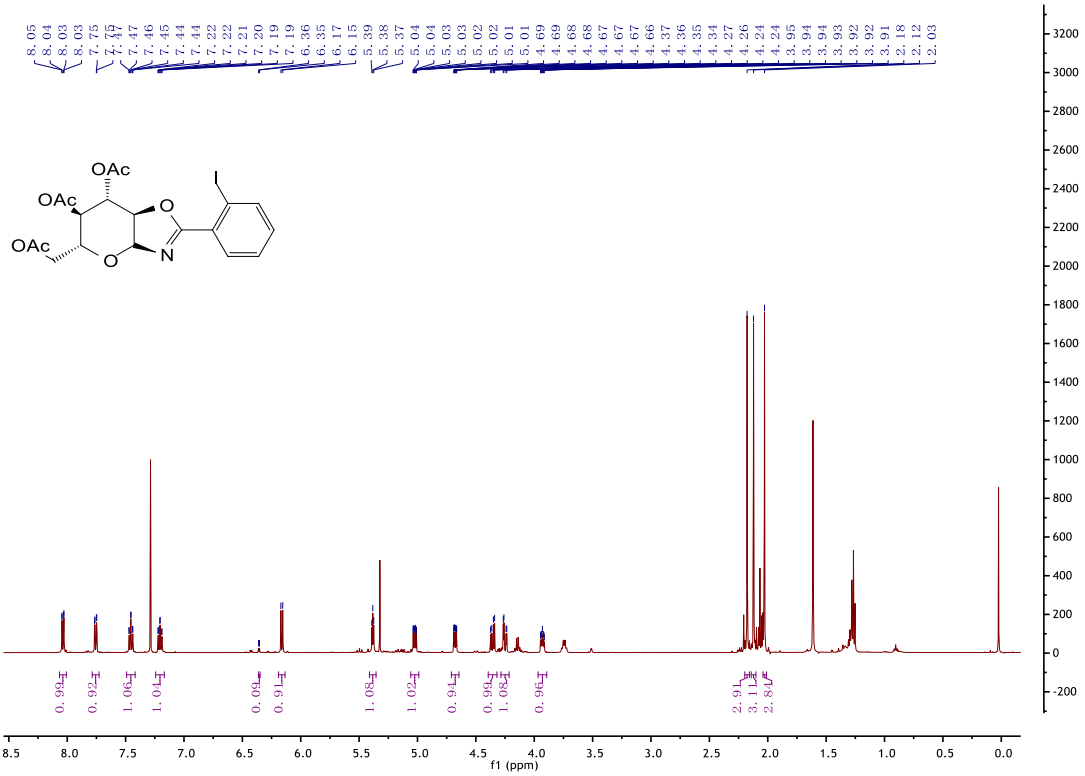
^{1}H NMR spectrum of 3H



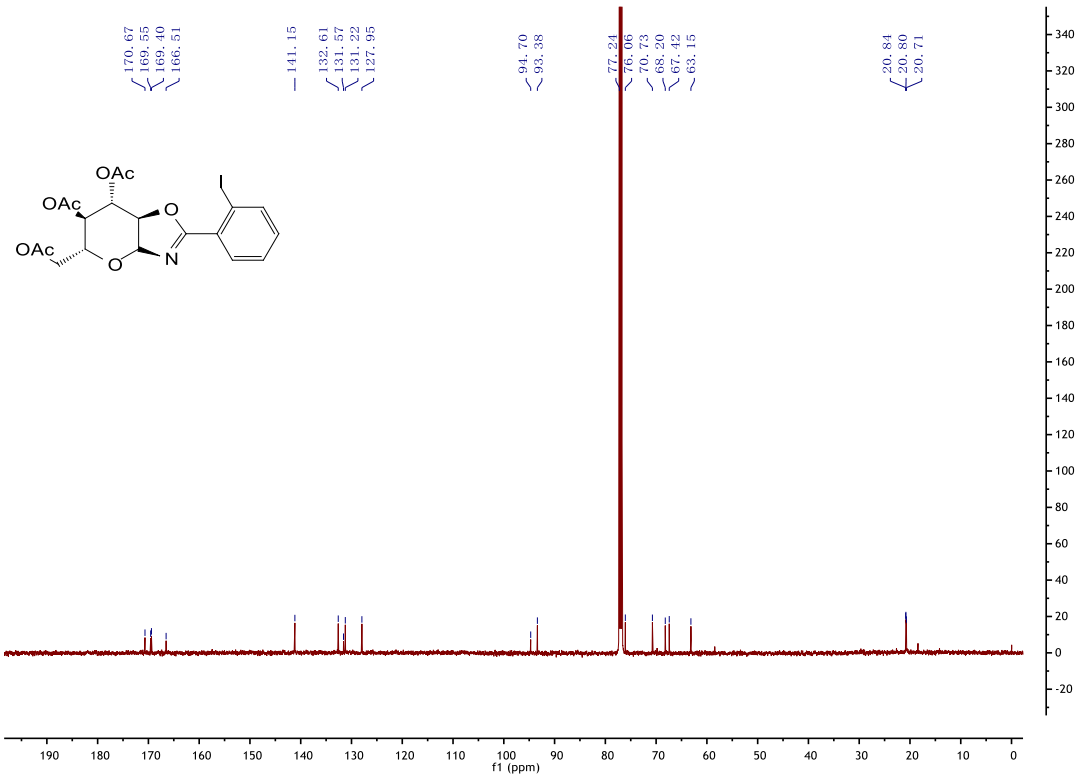
^{13}C NMR spectrum of 3H



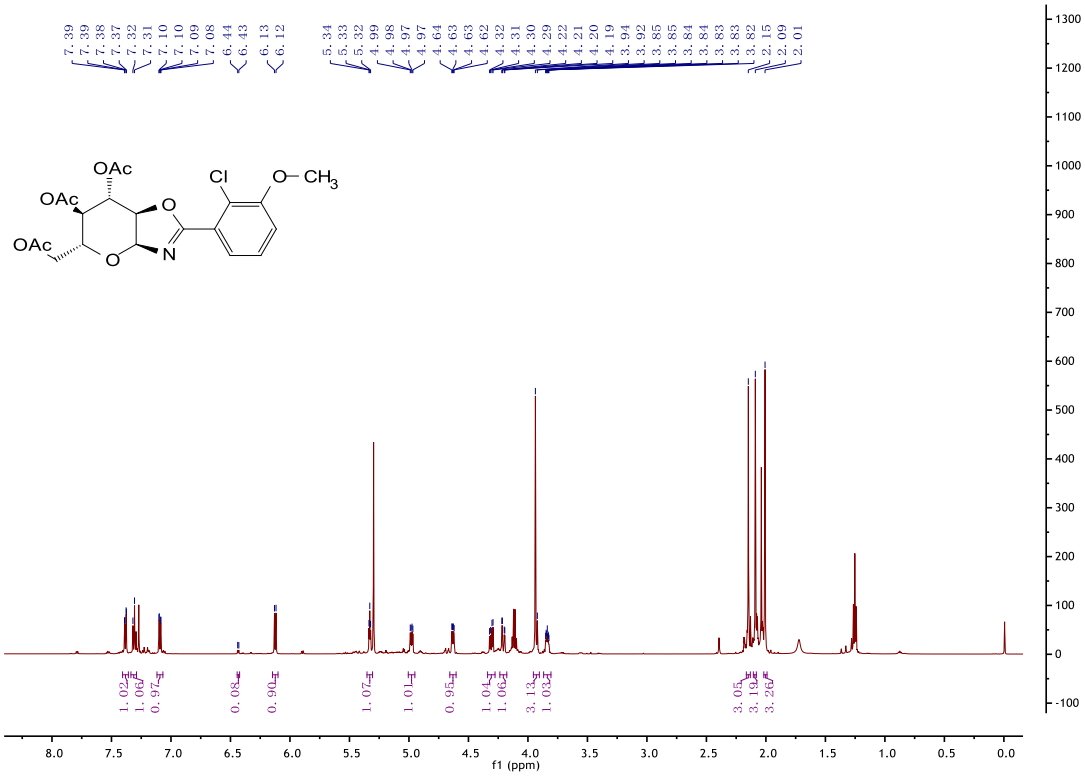
^{1}H NMR spectrum of 3I



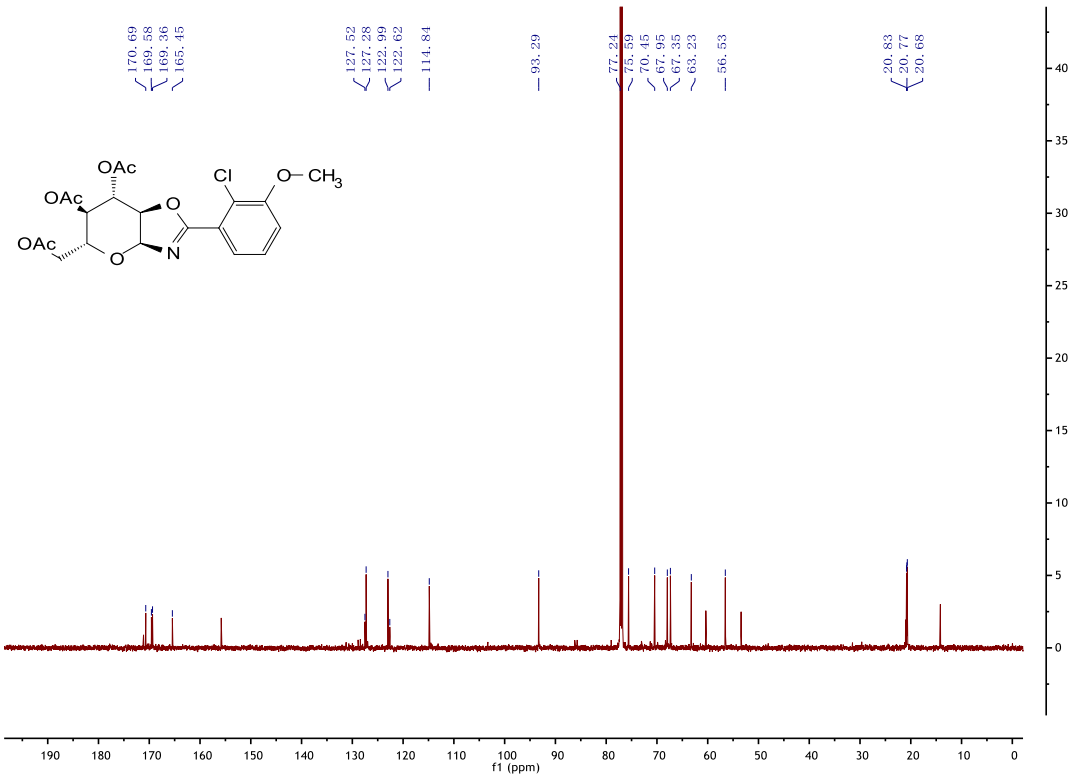
^{13}C NMR spectrum of 3I



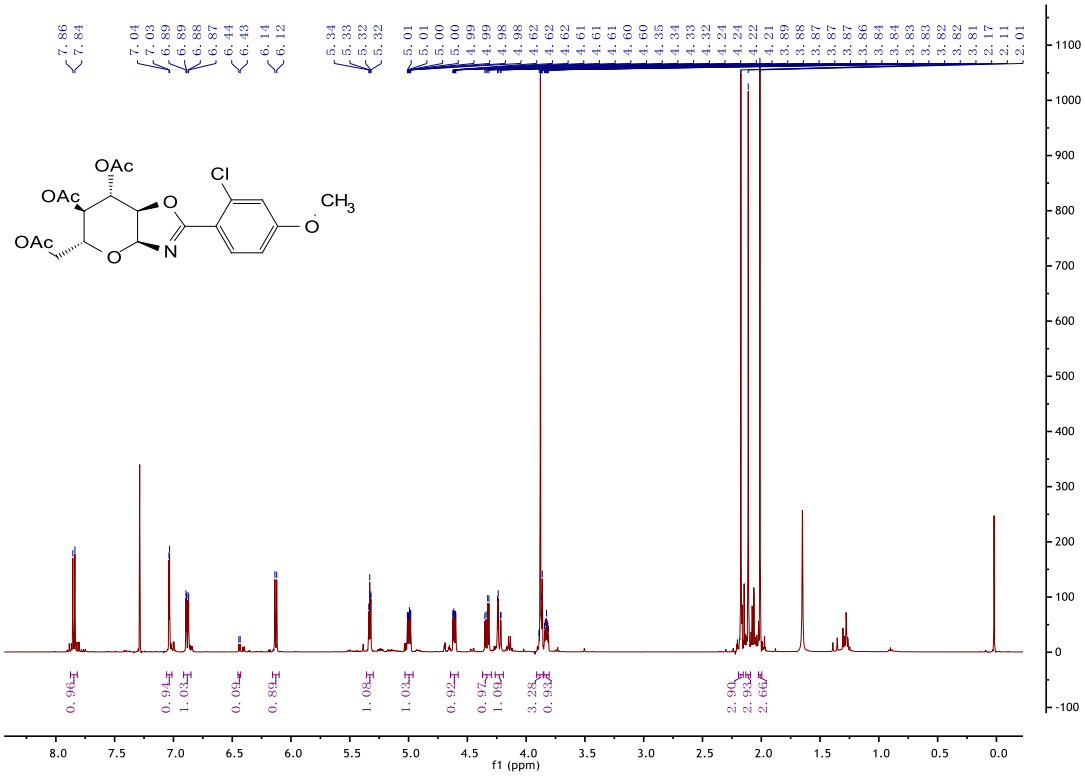
^{1}H NMR spectrum of 3J



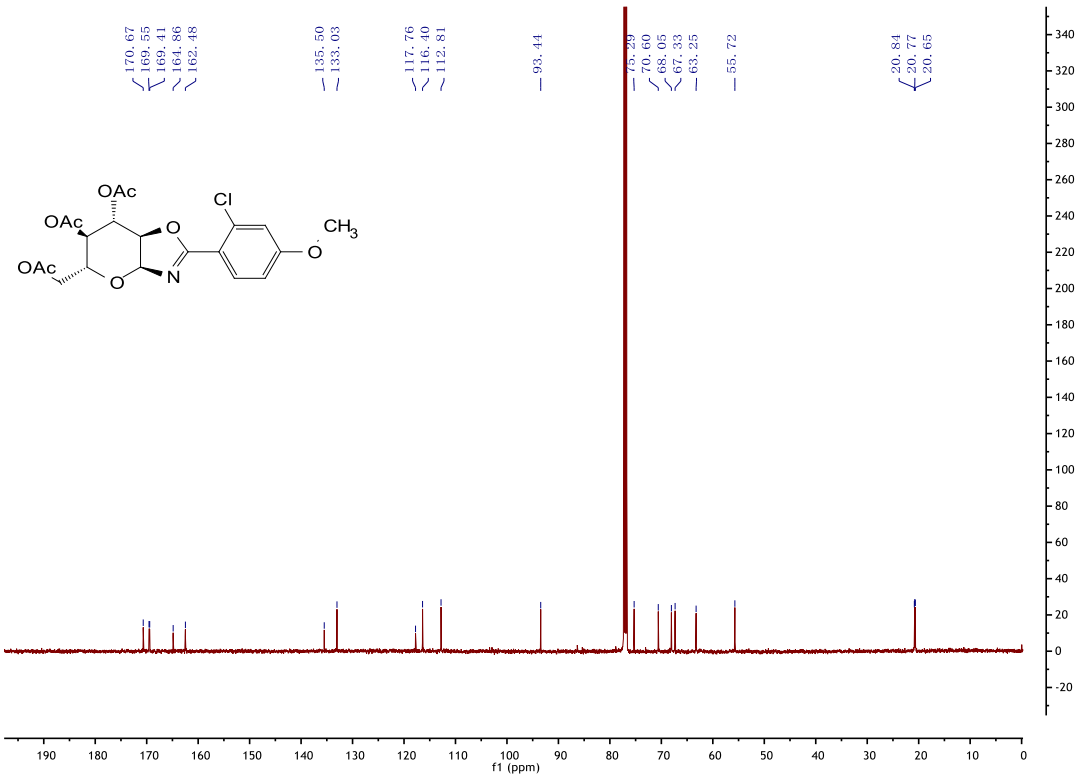
^{13}C NMR spectrum of 3J



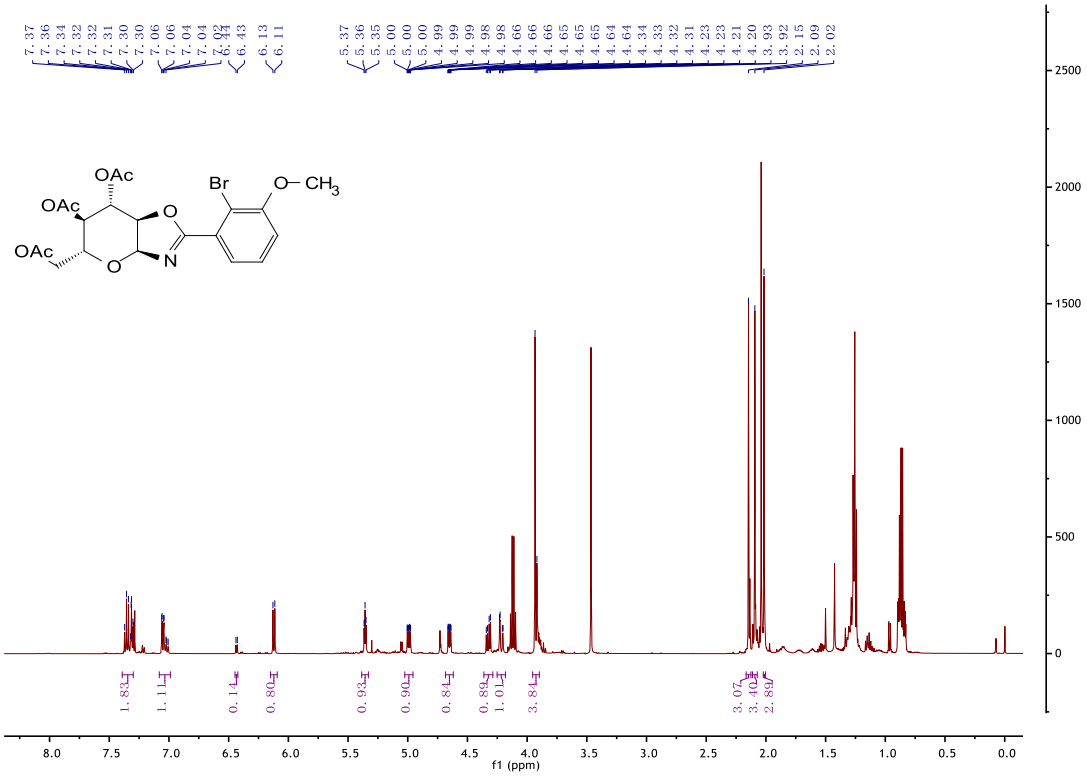
^{1}H NMR spectrum of 3K



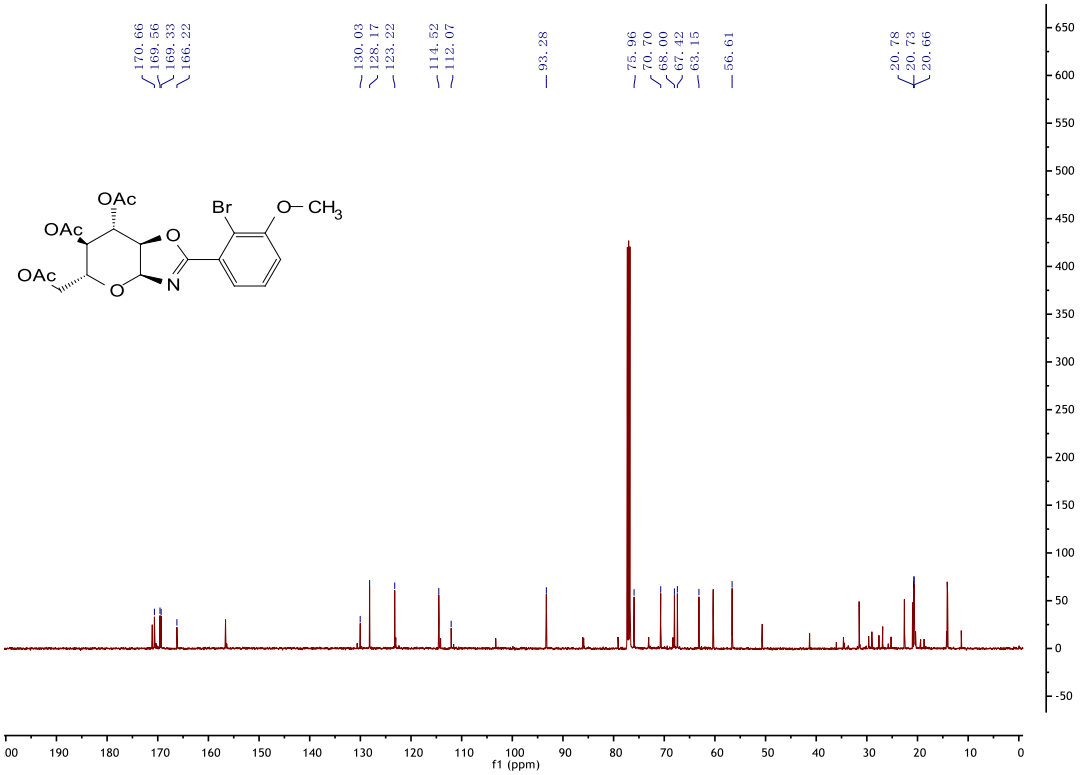
^{13}C NMR spectrum of 3K



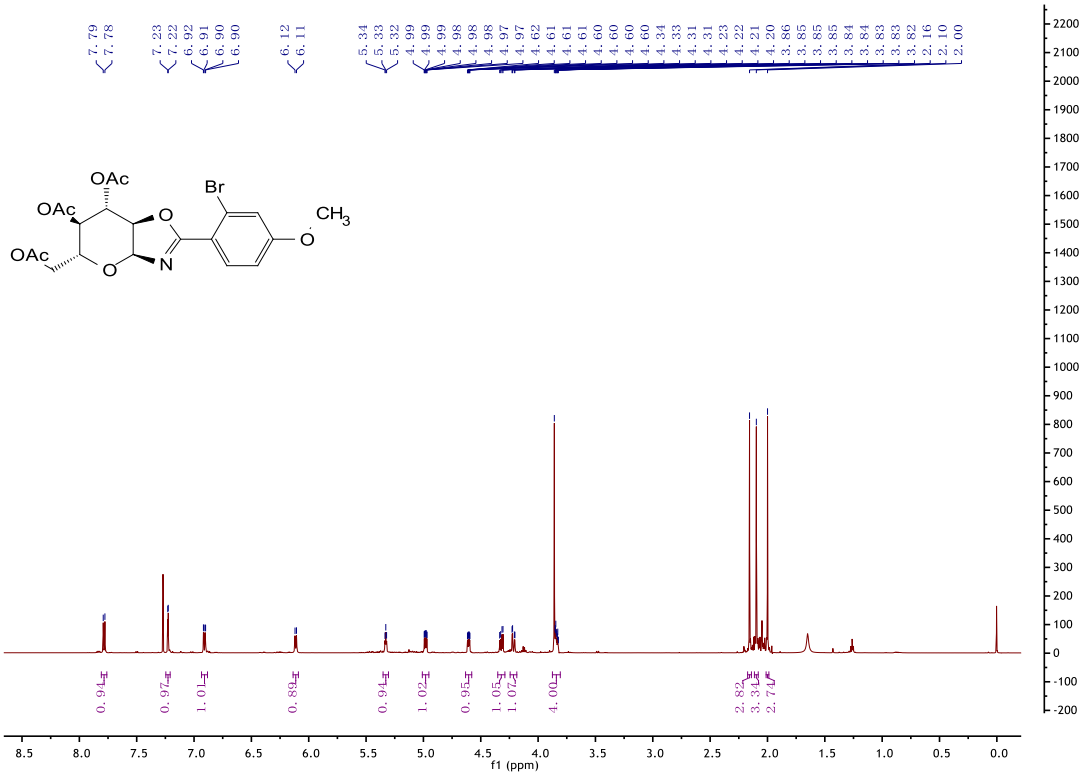
^{1}H NMR spectrum of 3L



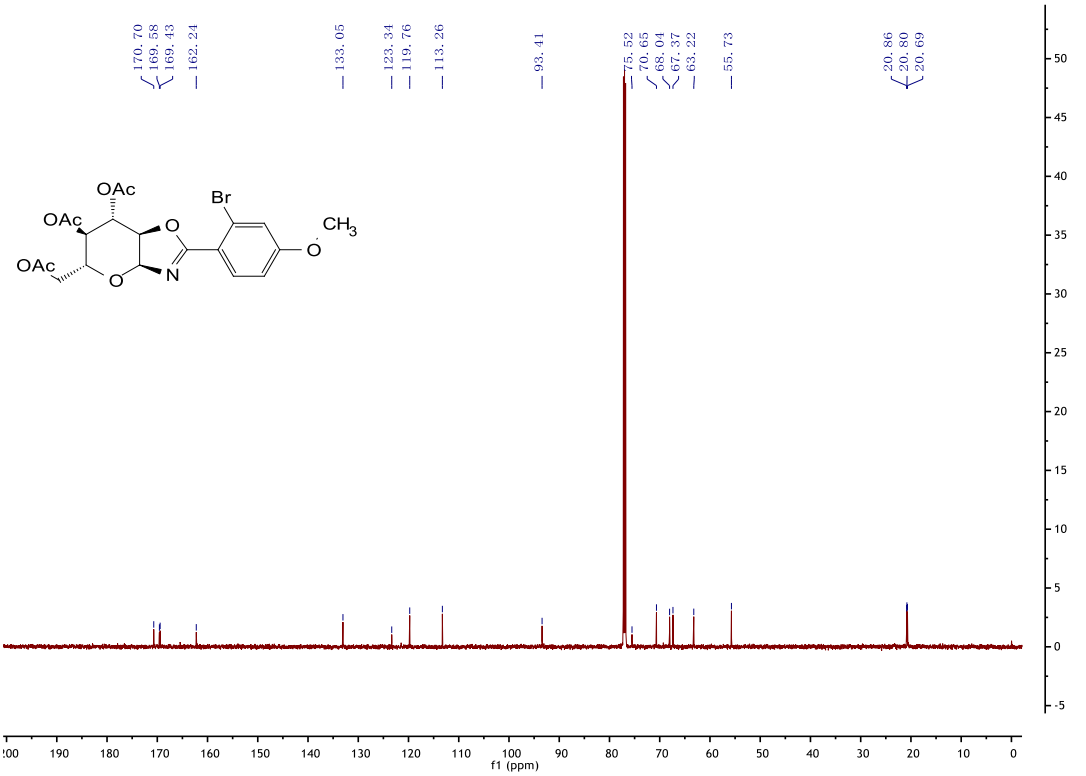
^{13}C NMR spectrum of 3L



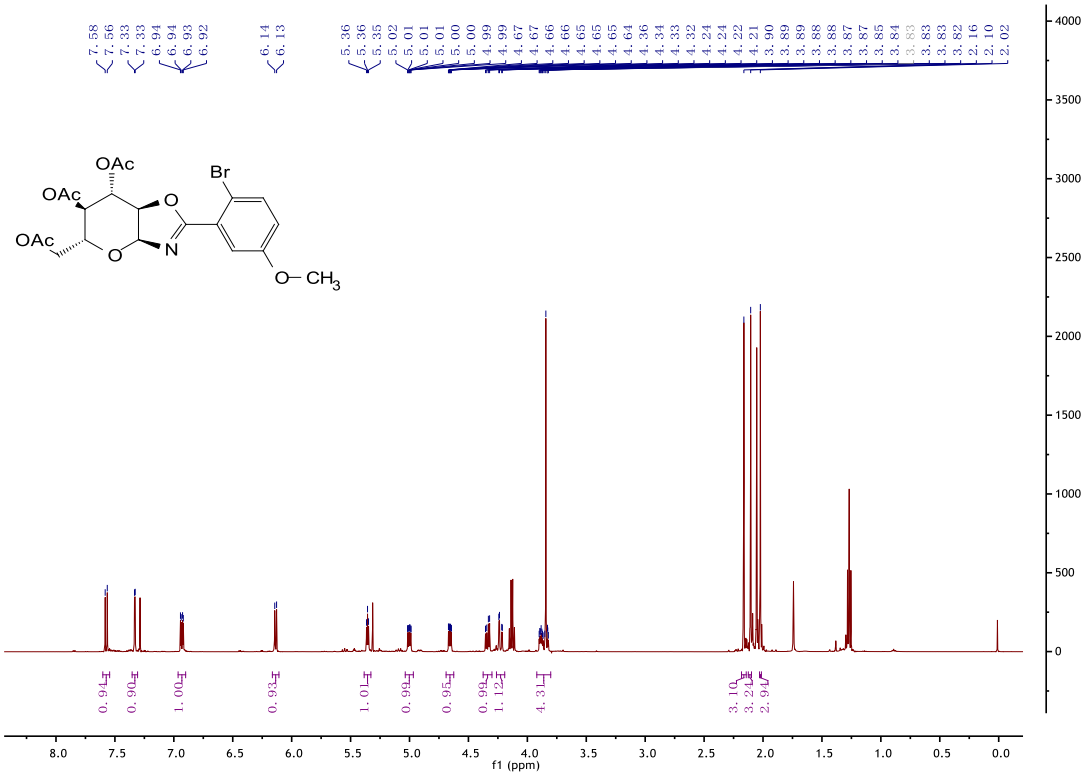
^{1}H NMR spectrum of 3M



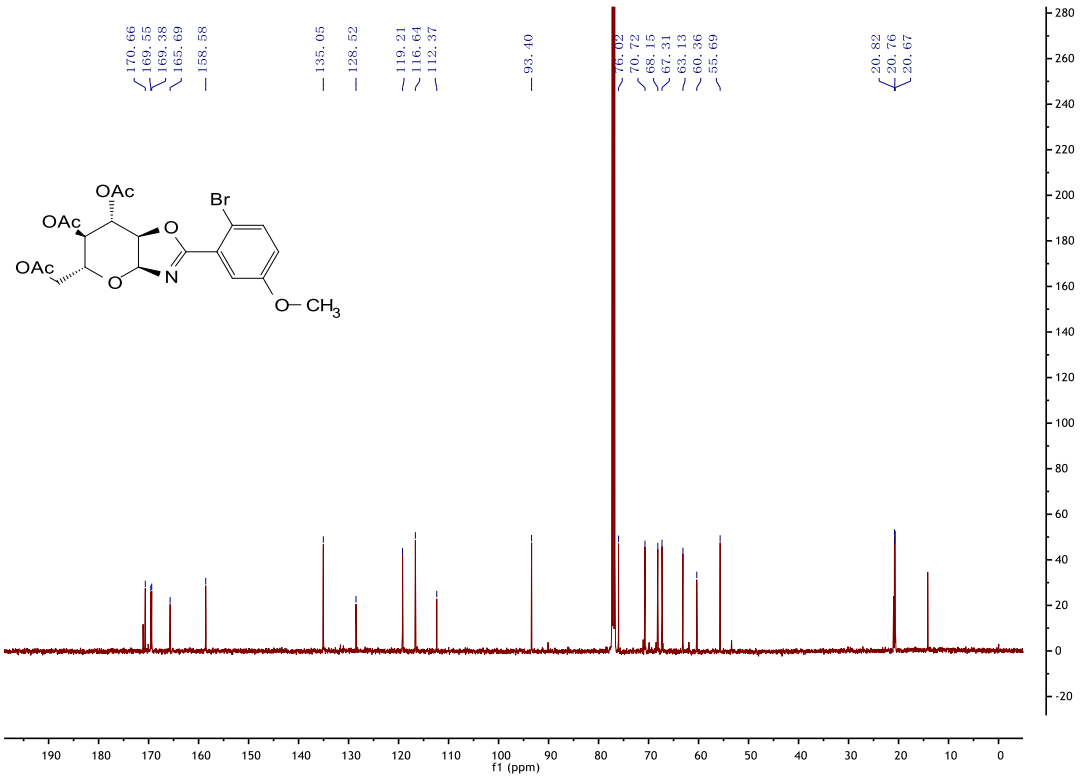
^{13}C NMR spectrum of 3M



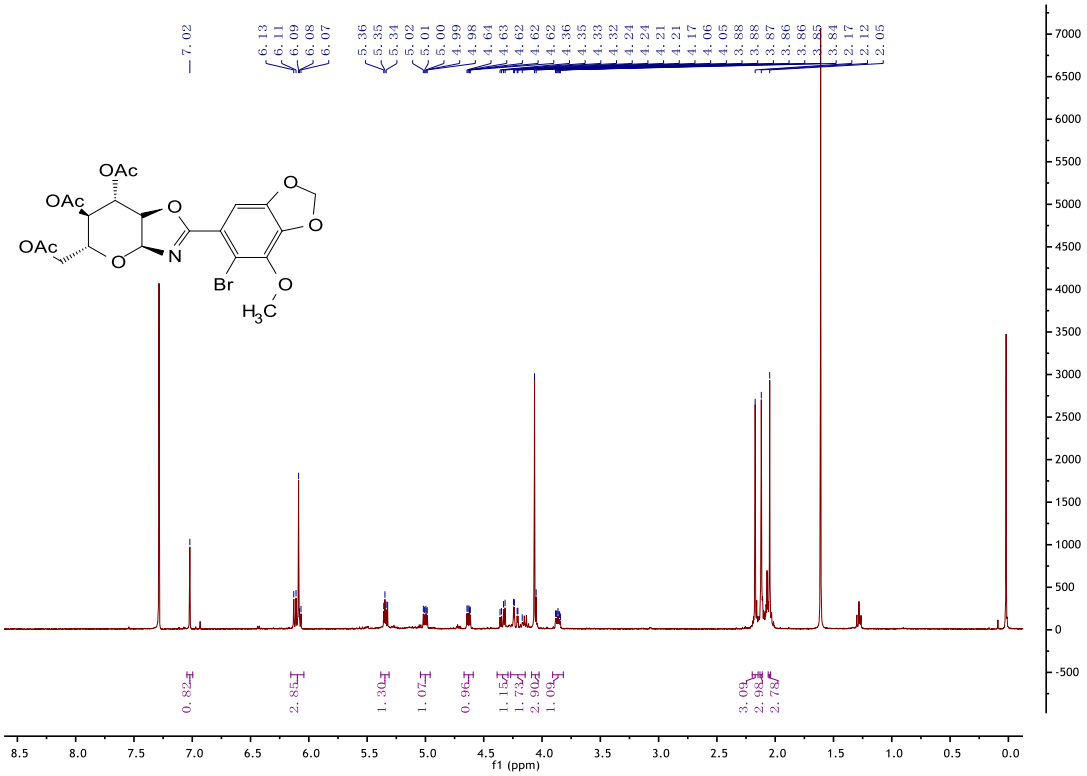
^{1}H NMR spectrum of 3N



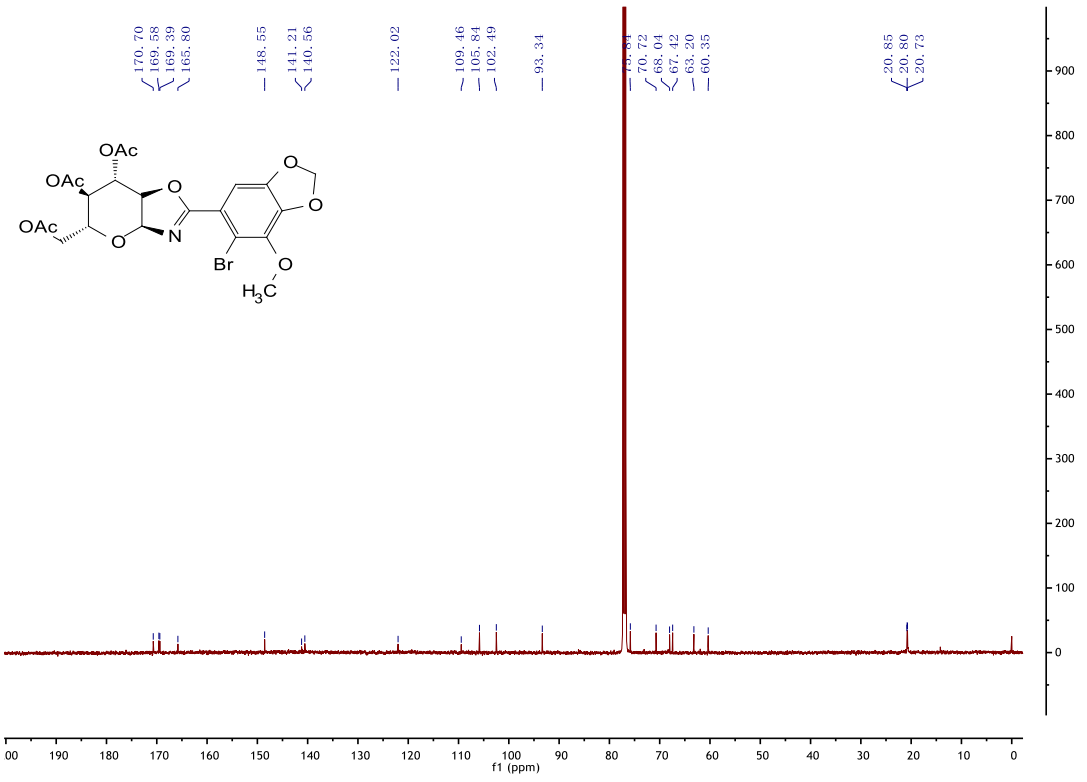
^{13}C NMR spectrum of 3N



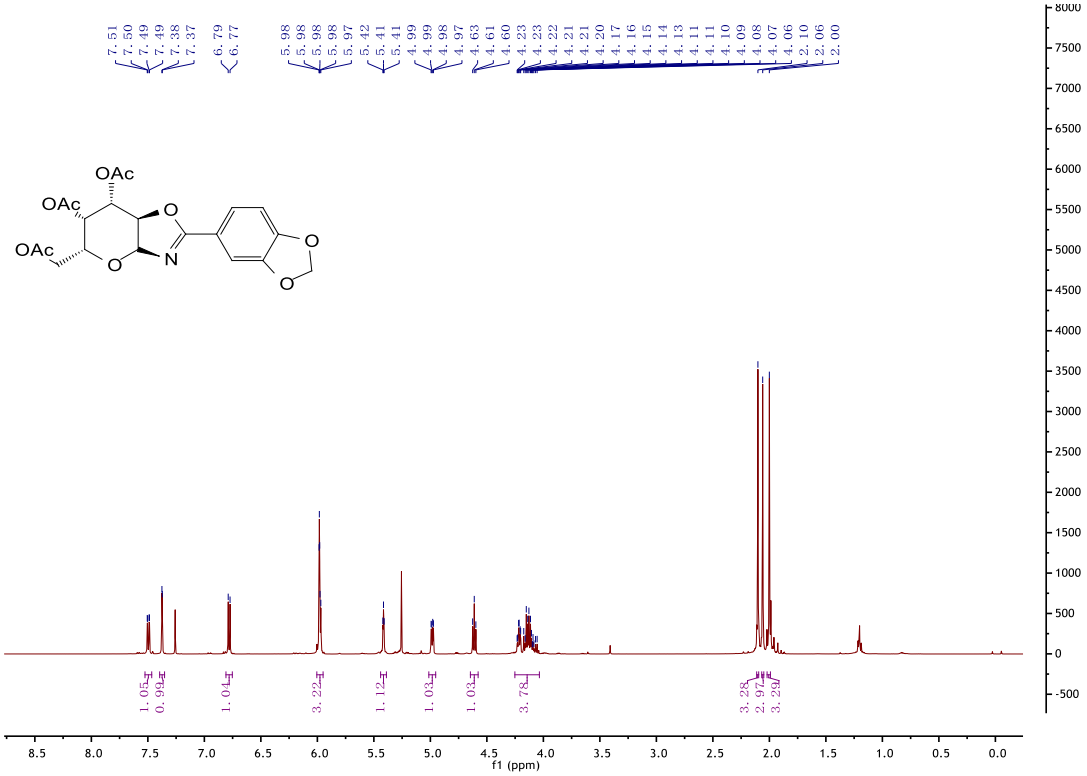
^{1}H NMR spectrum of 3O



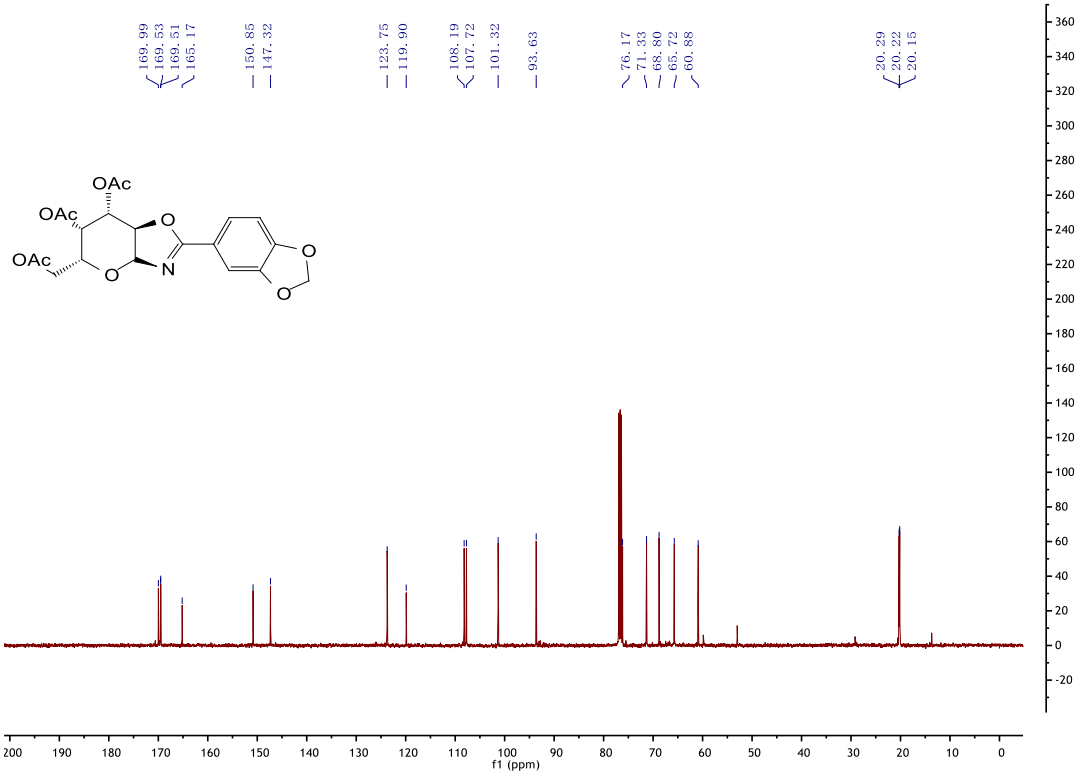
^{13}C NMR spectrum of 3O



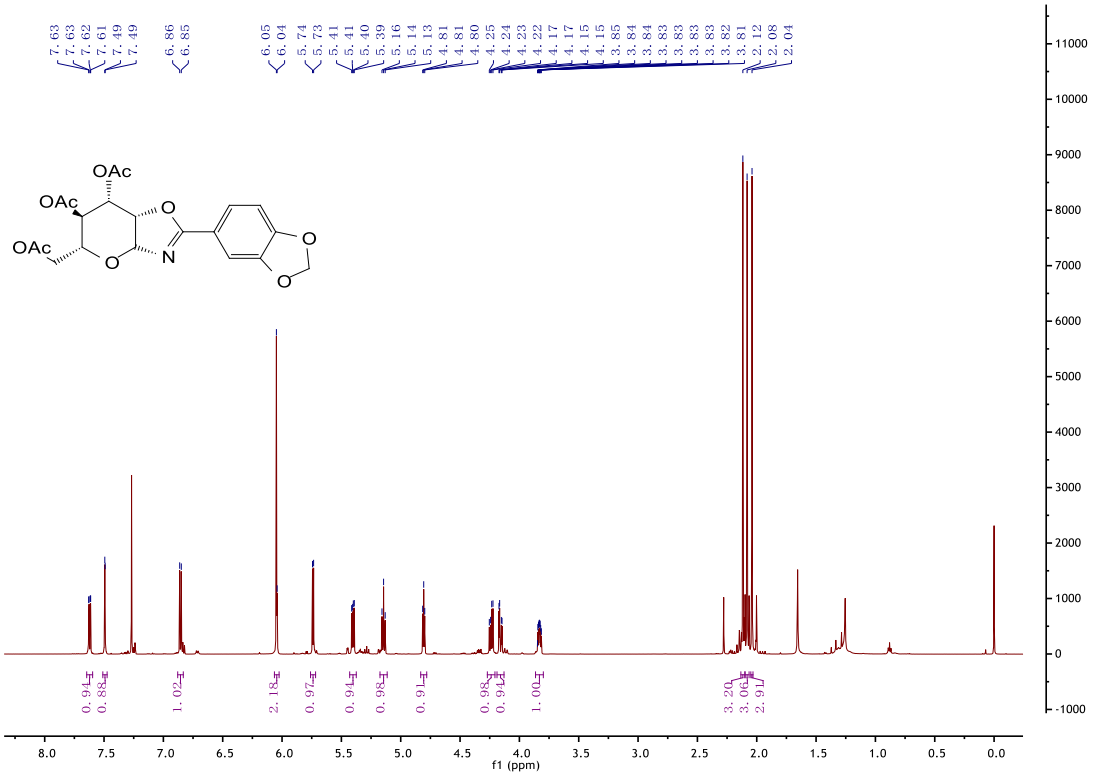
^{1}H NMR spectrum of 3Da



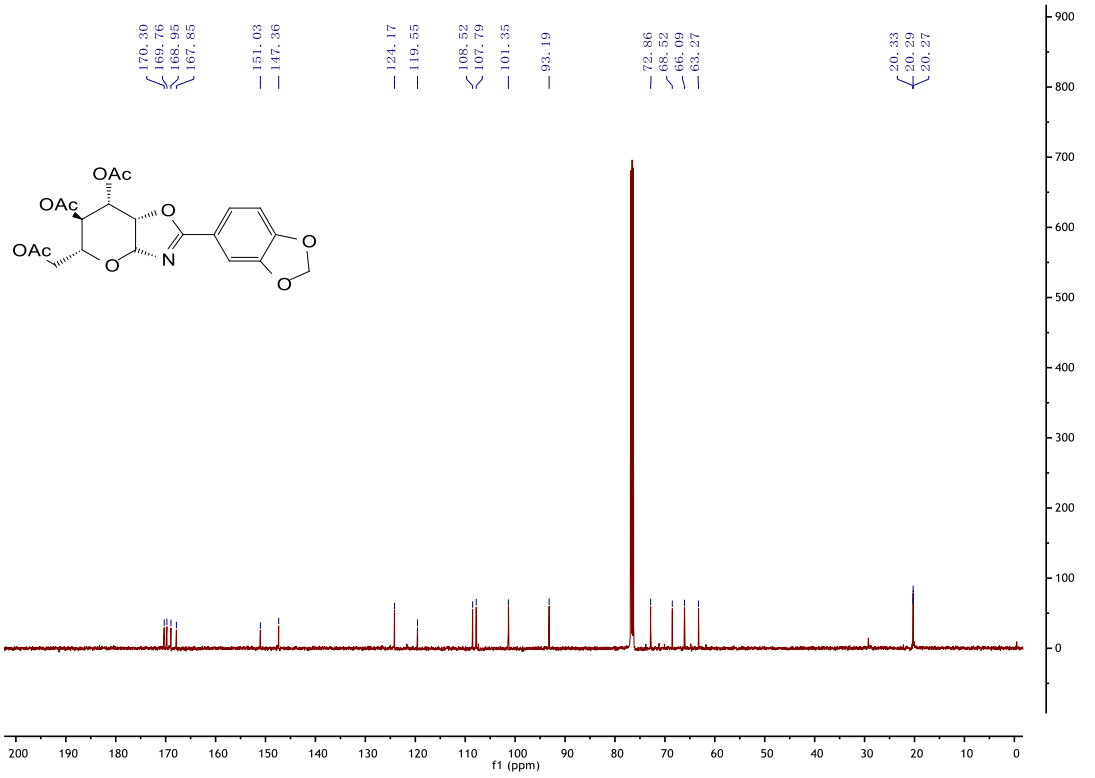
^{13}C NMR spectrum of 3Da



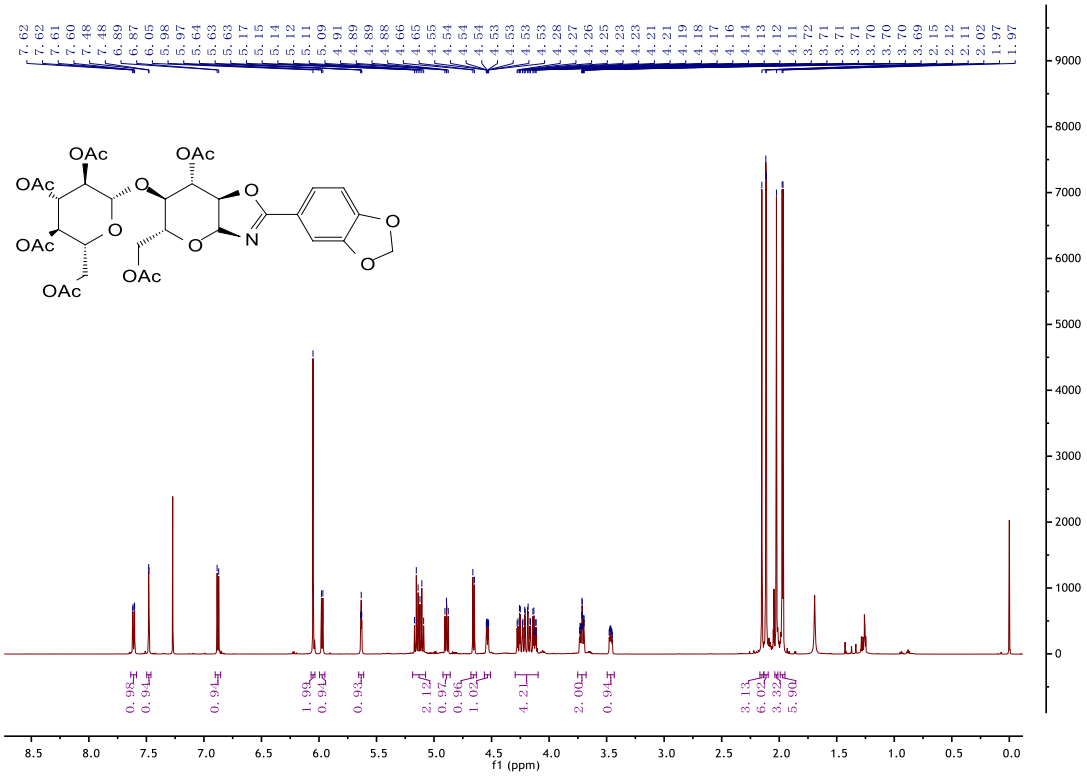
^{1}H NMR spectrum of 3Db



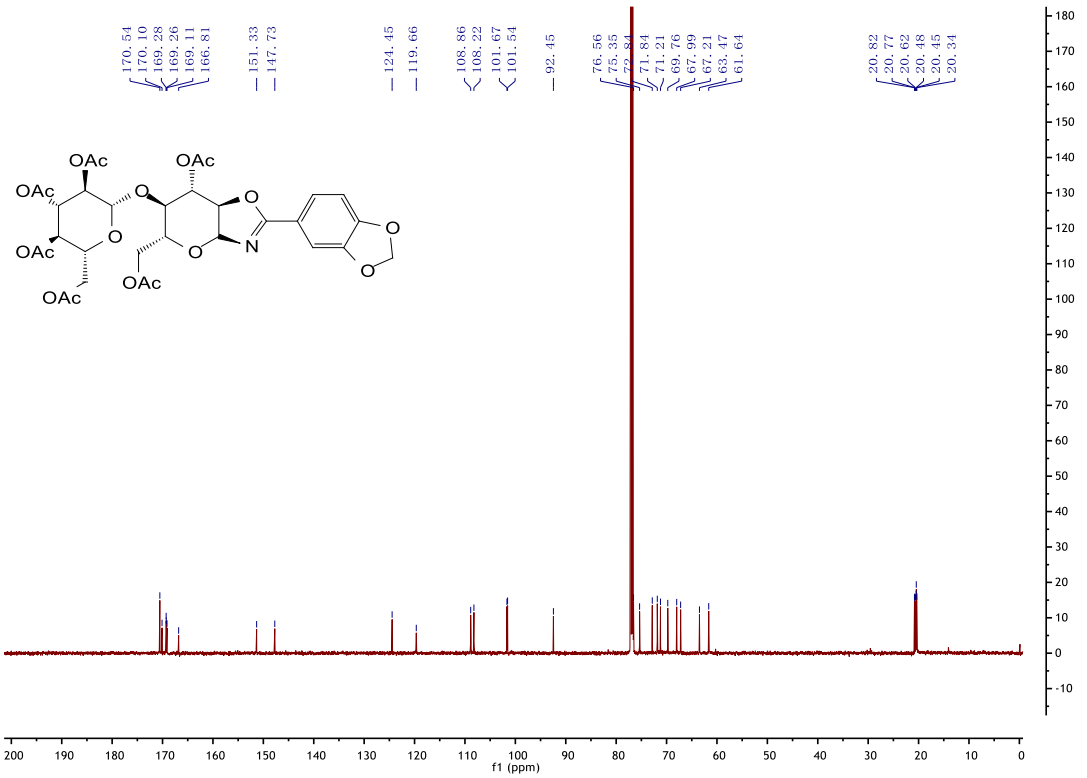
^{13}C NMR spectrum of 3Db



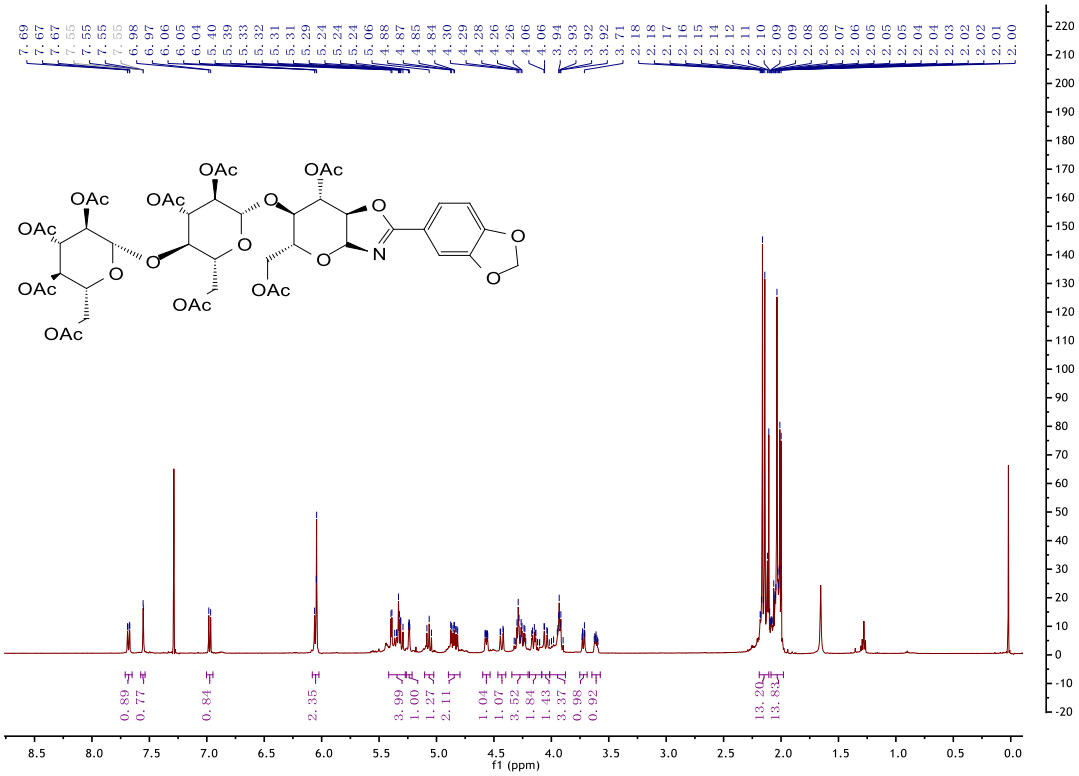
^{1}H NMR spectrum of 3Dc



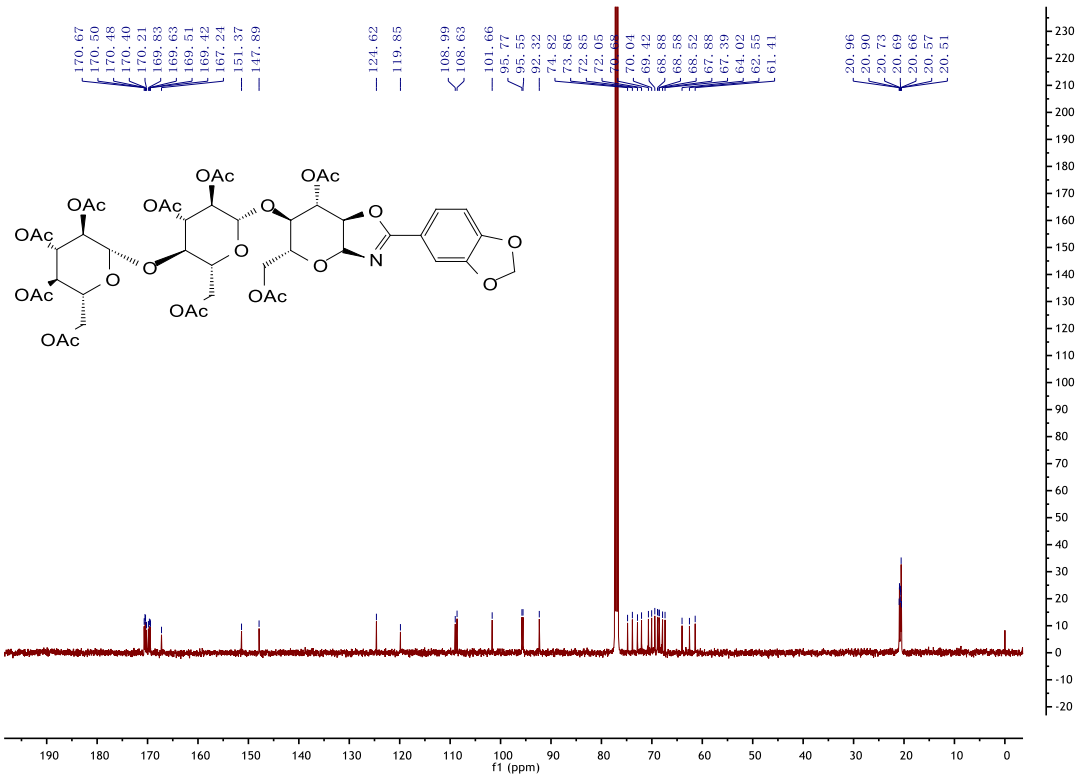
^{13}C NMR spectrum of 3Dc



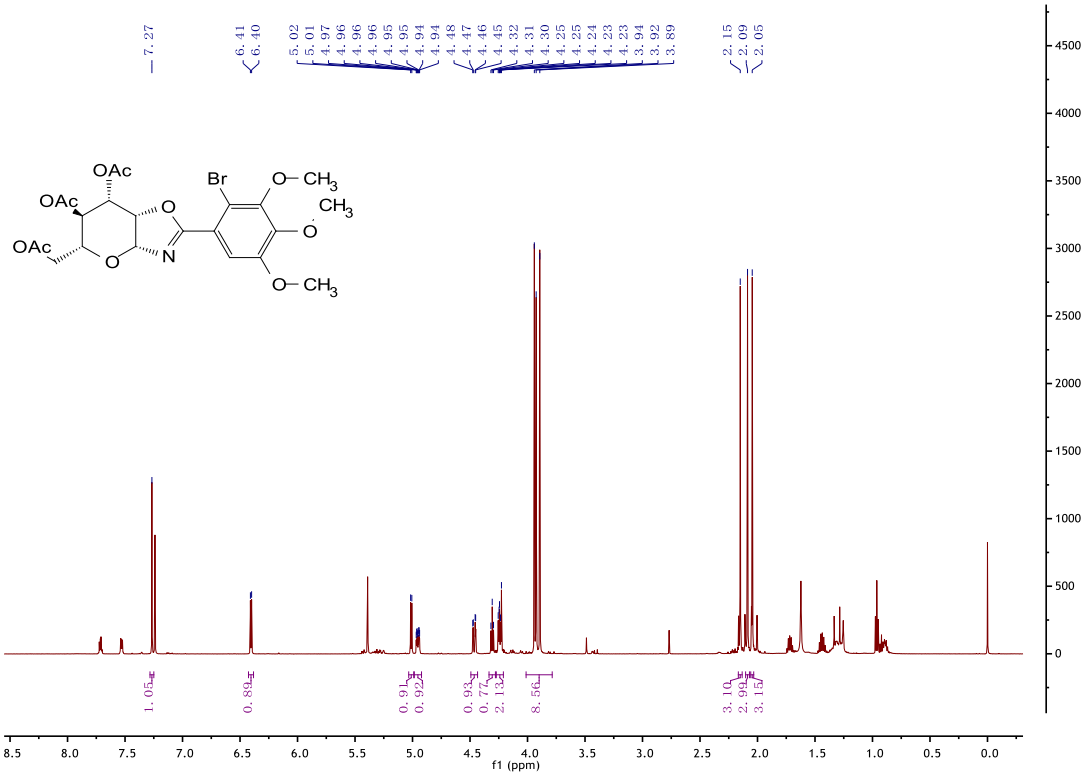
^{1}H NMR spectrum of 3Dd



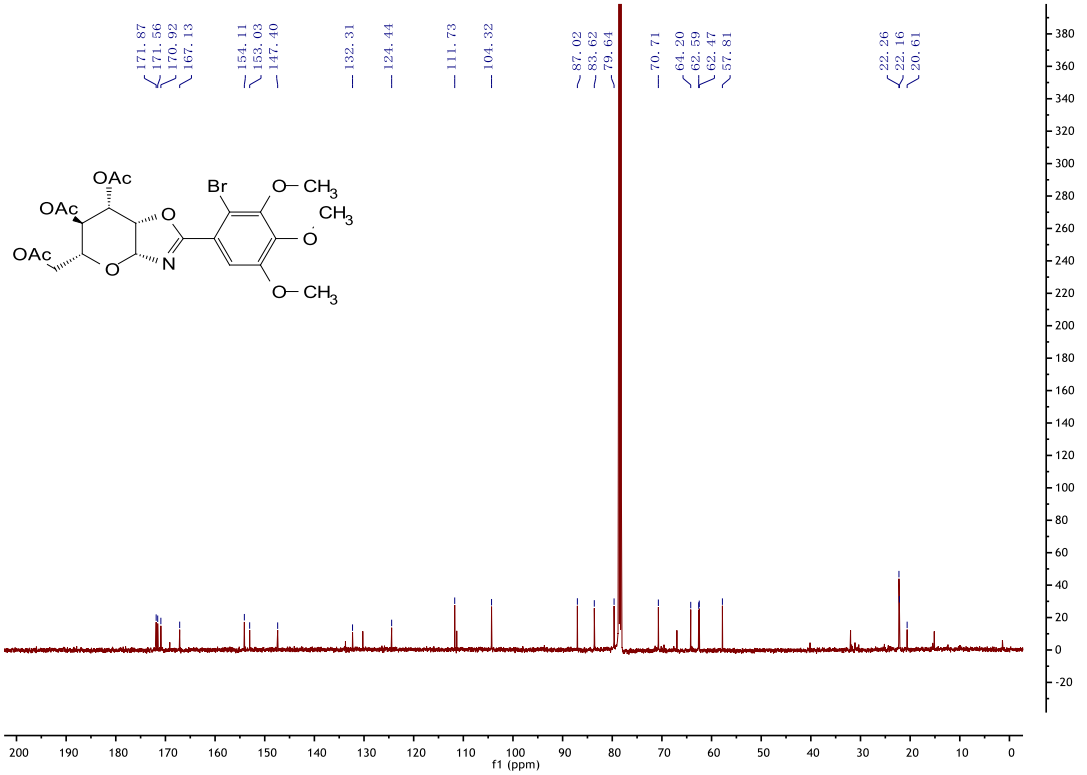
^{13}C NMR spectrum of 3Dd



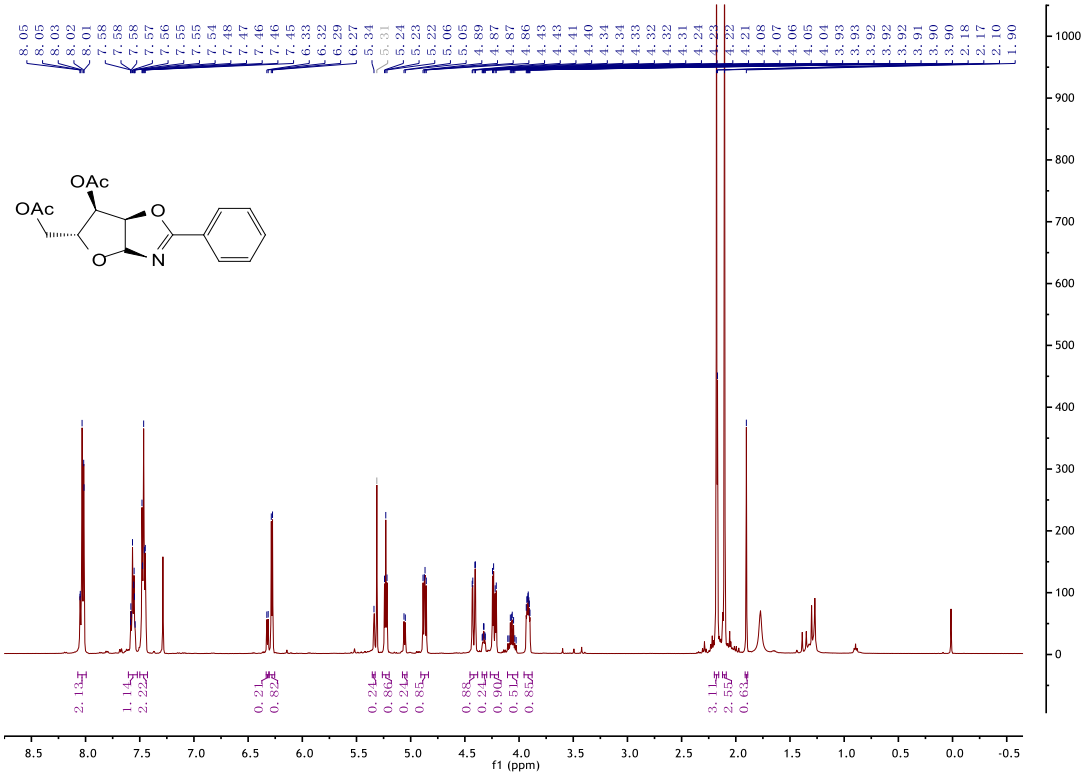
^{1}H NMR spectrum of 3Ra



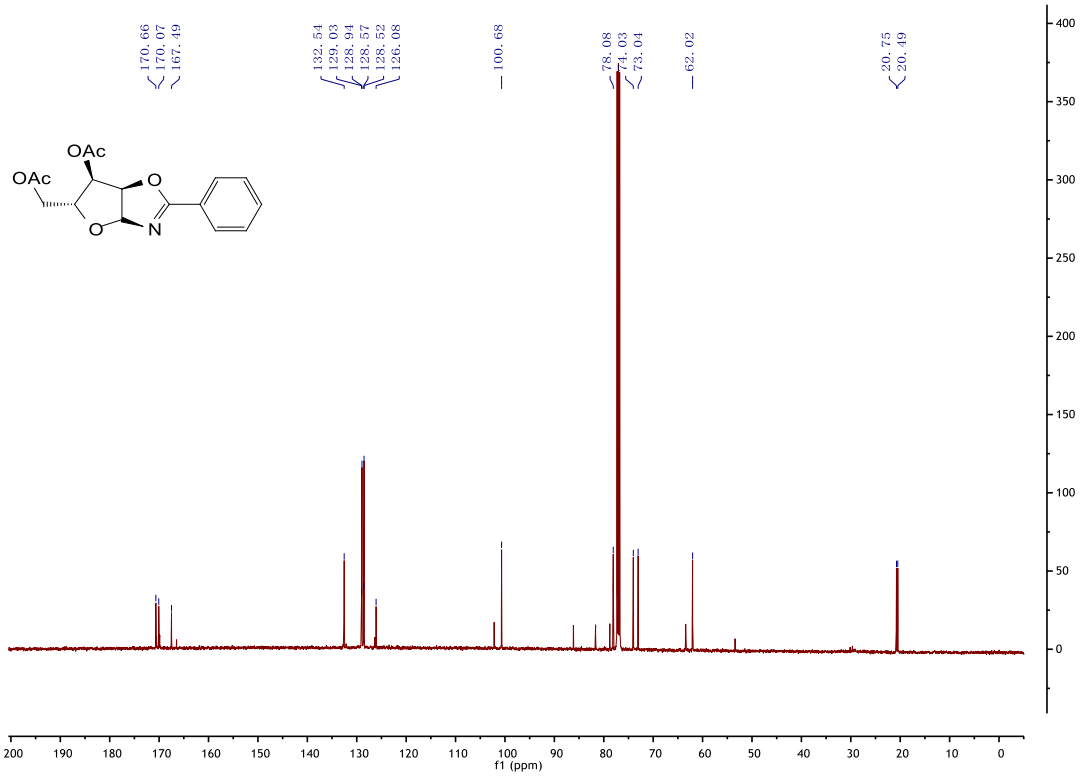
^{13}C NMR spectrum of 3Ra



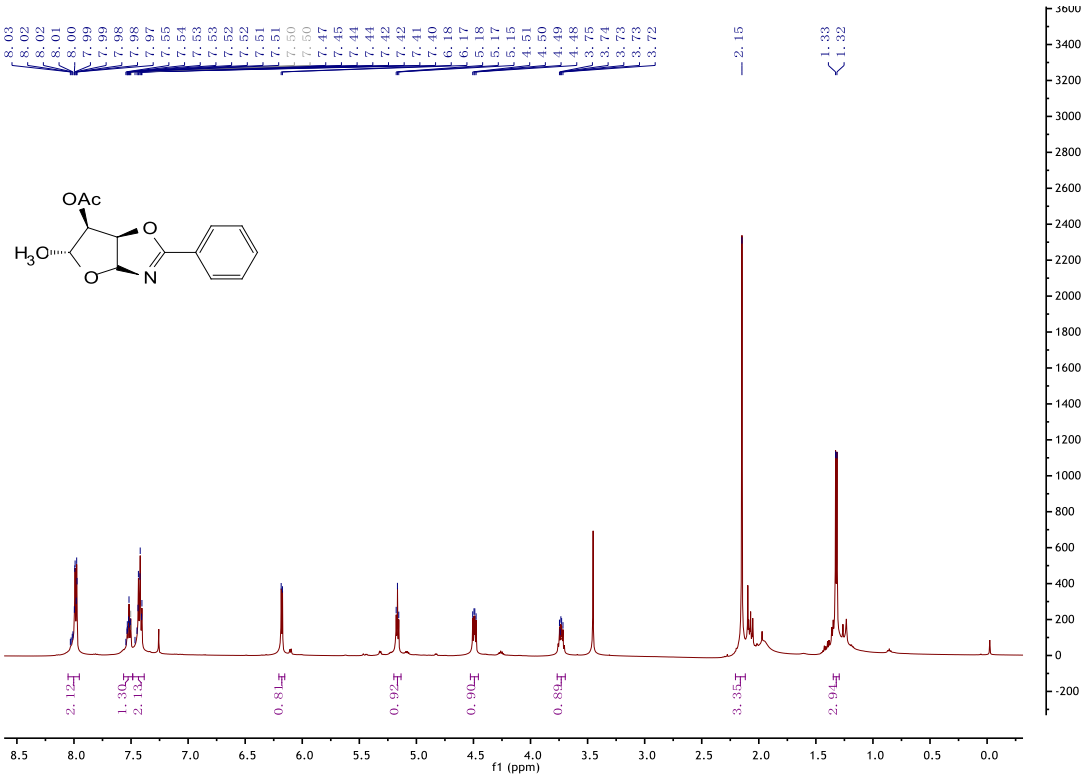
^{1}H NMR spectrum of 3a



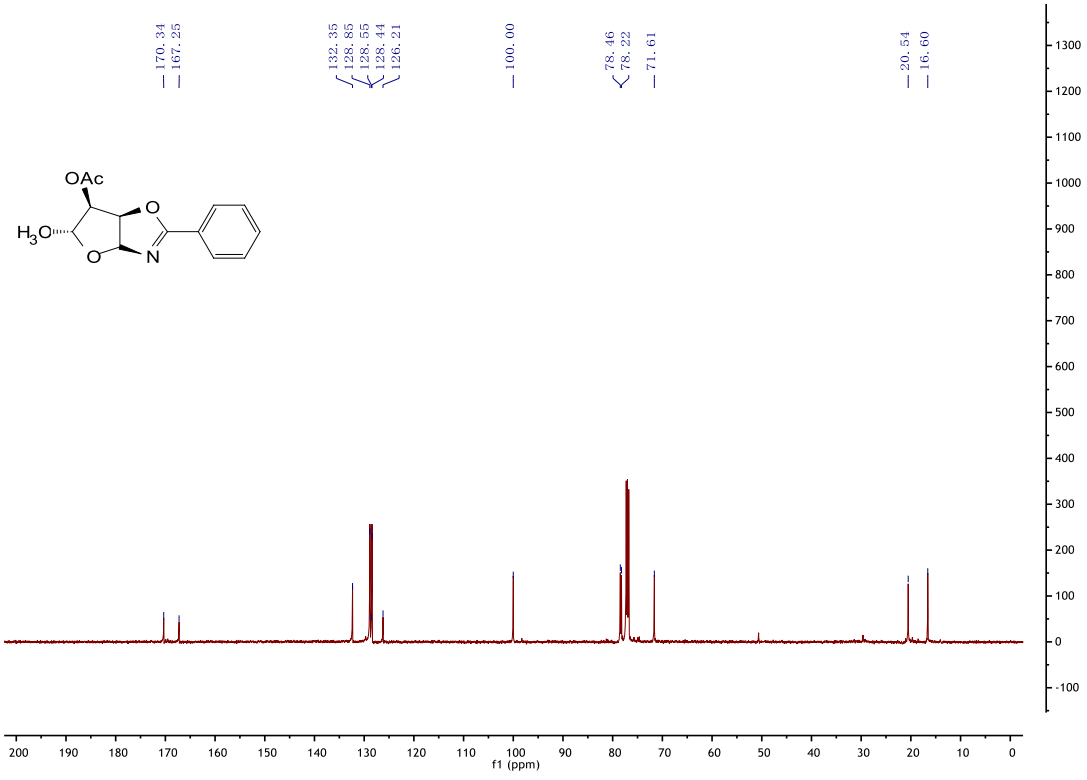
^{13}C NMR spectrum of 3a



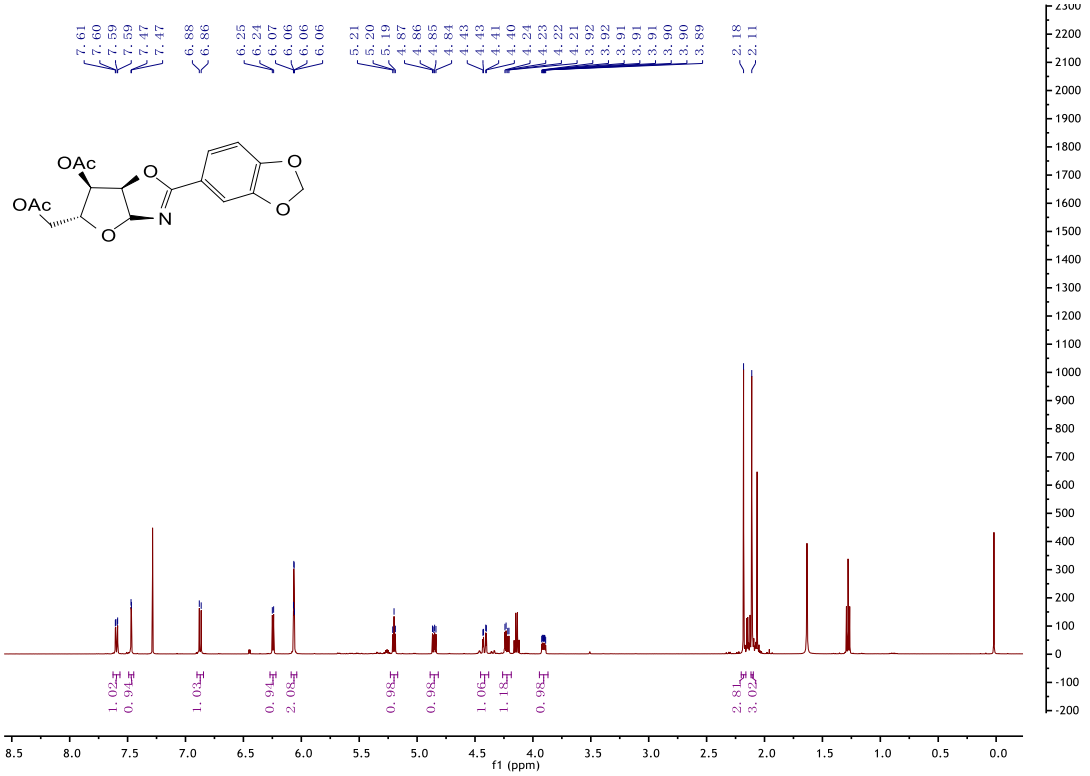
^{1}H NMR spectrum of 3b



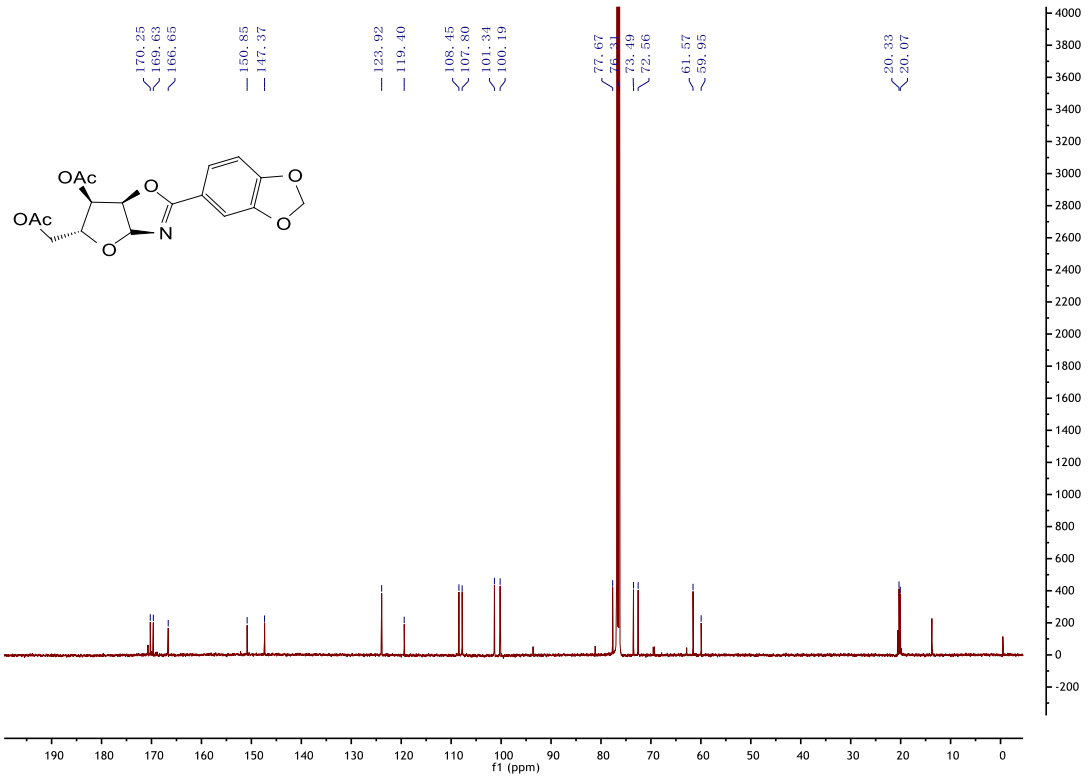
^{13}C NMR spectrum of 3b



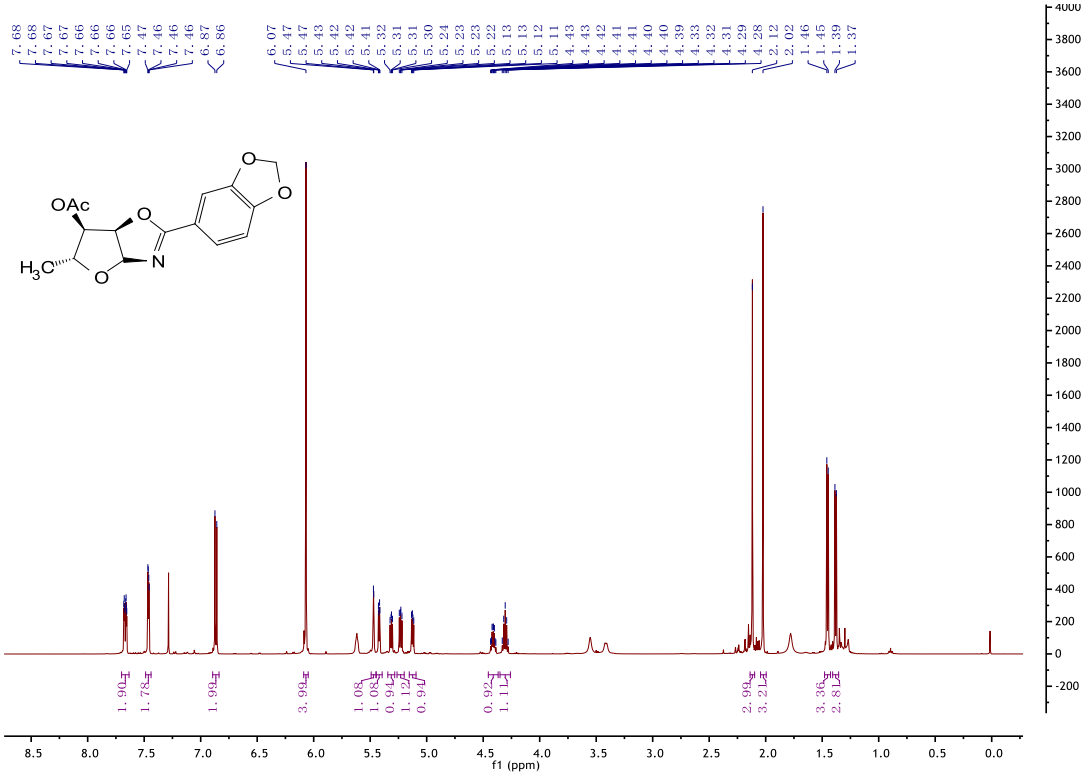
^{1}H NMR spectrum of 3c



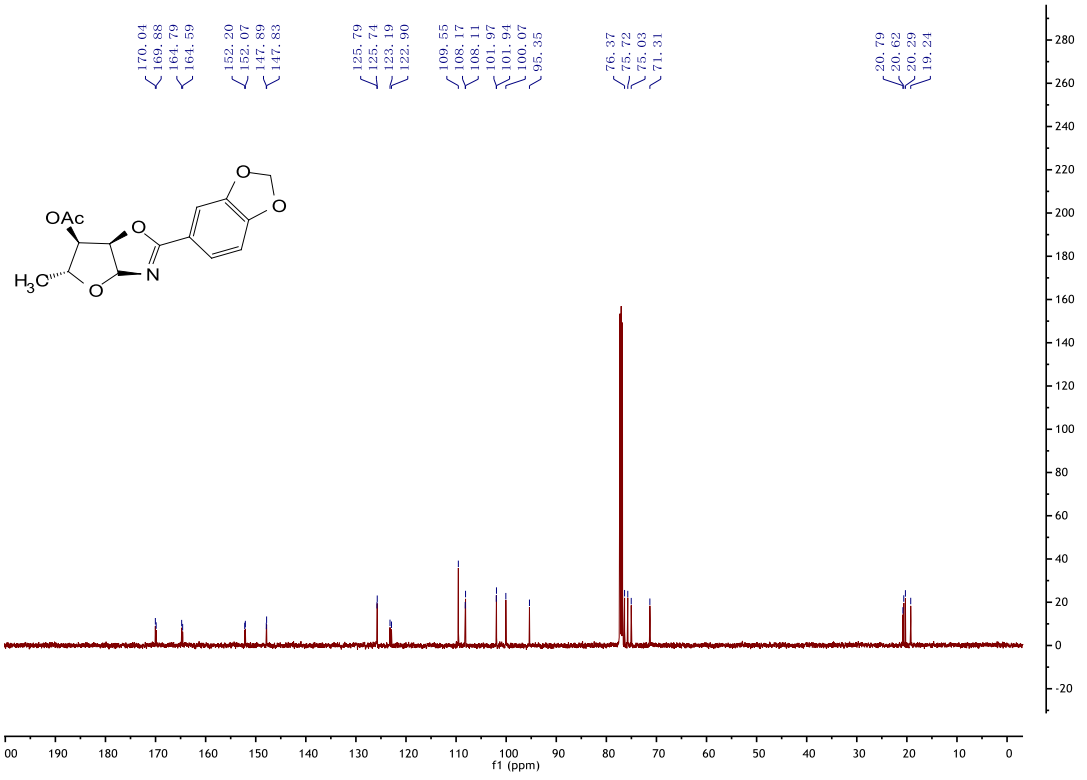
^{13}C NMR spectrum of 3c



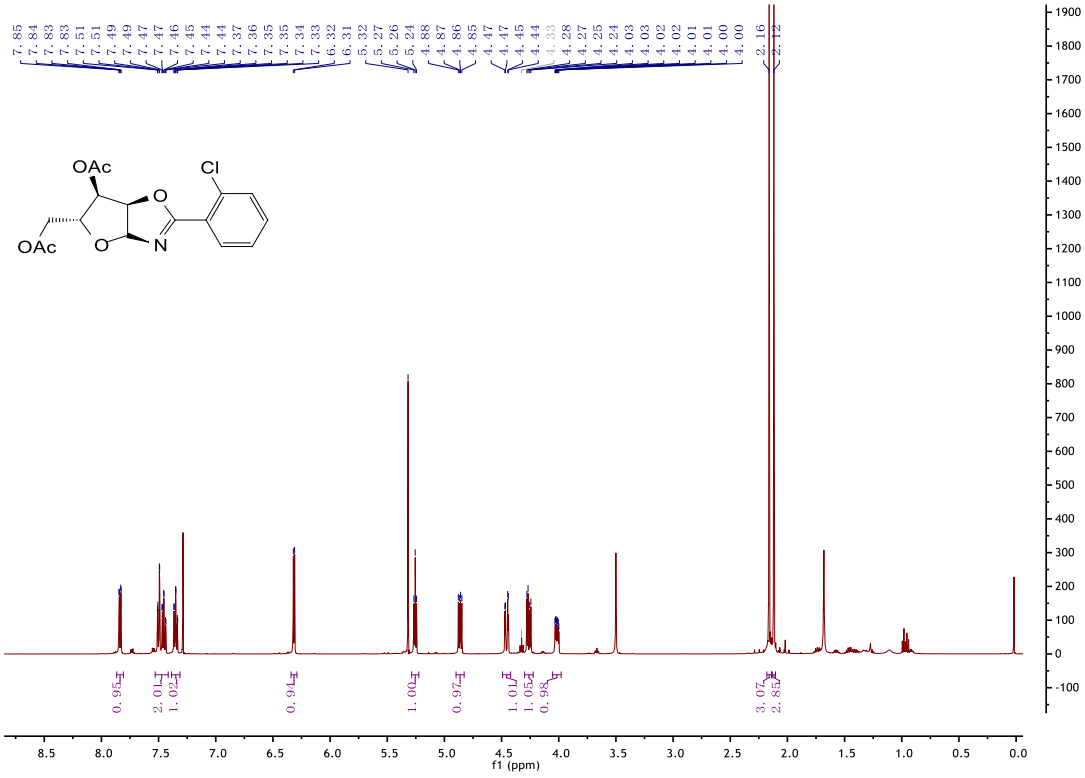
^{1}H NMR spectrum of 3d



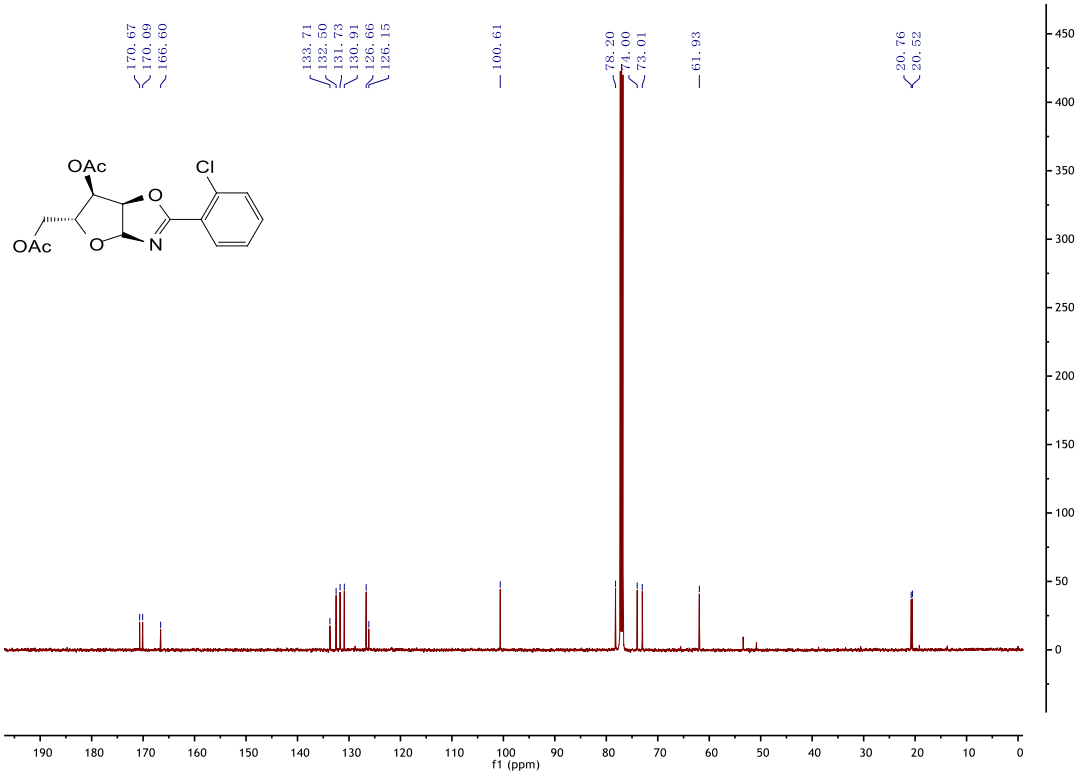
^{13}C NMR spectrum of 3d



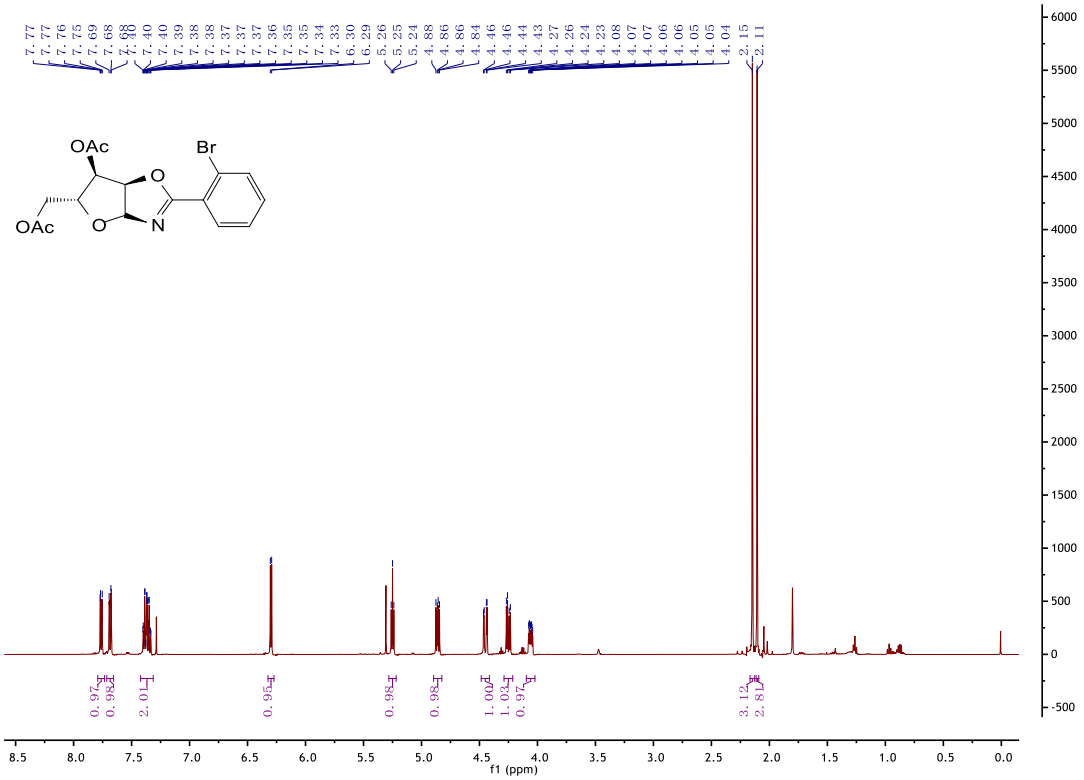
^{1}H NMR spectrum of 3e



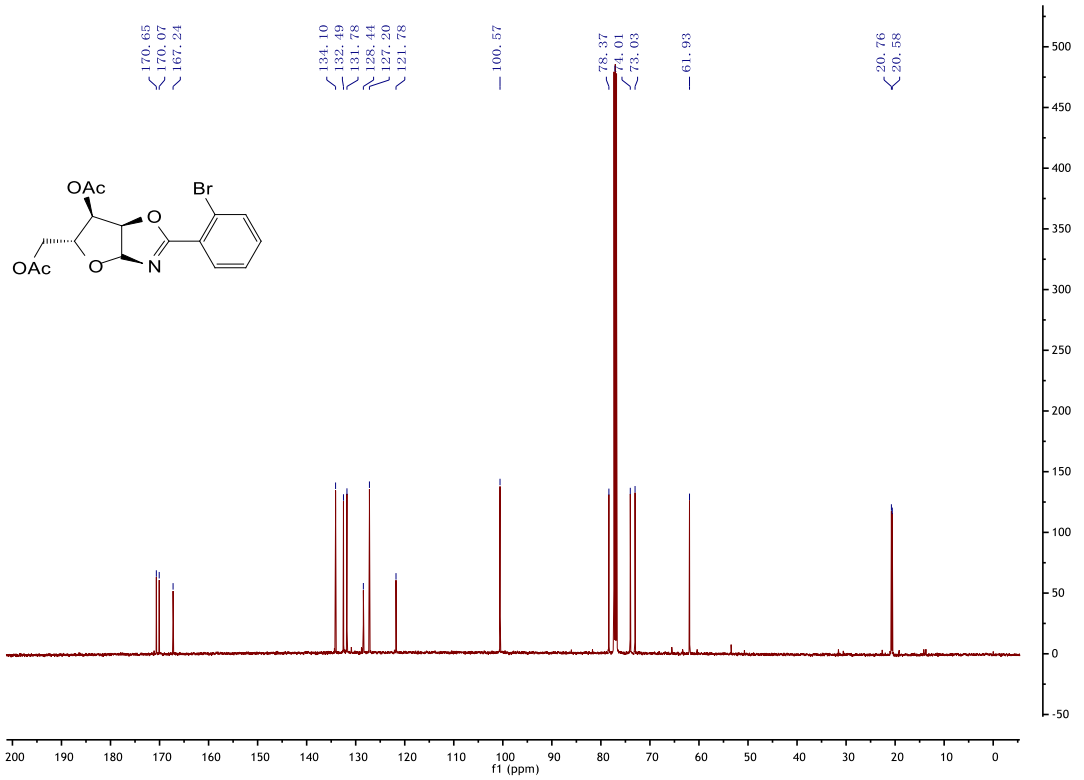
^{13}C NMR spectrum of 3e



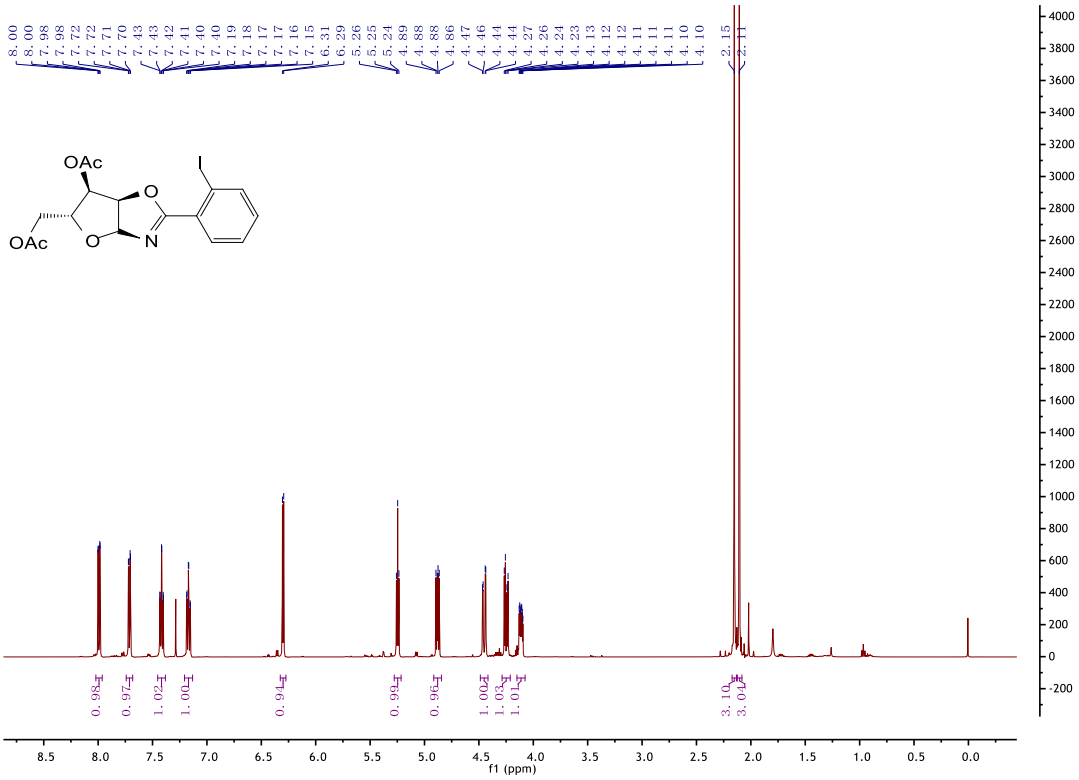
^{1}H NMR spectrum of 3f



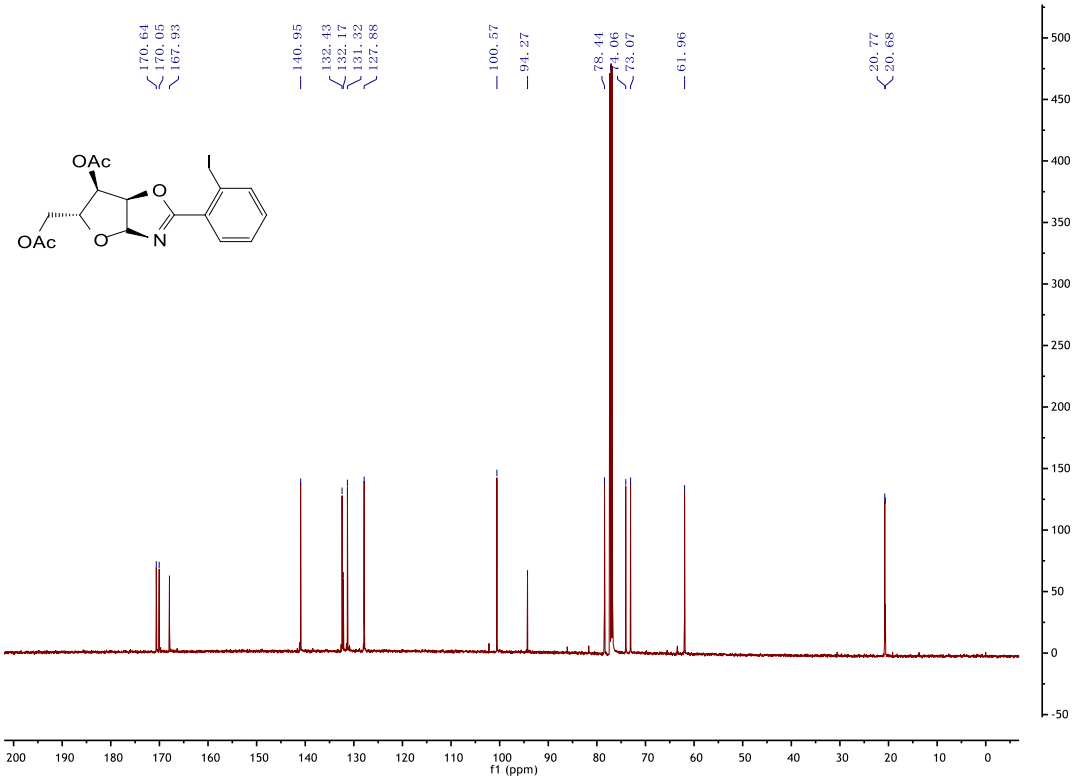
^{13}C NMR spectrum of 3f



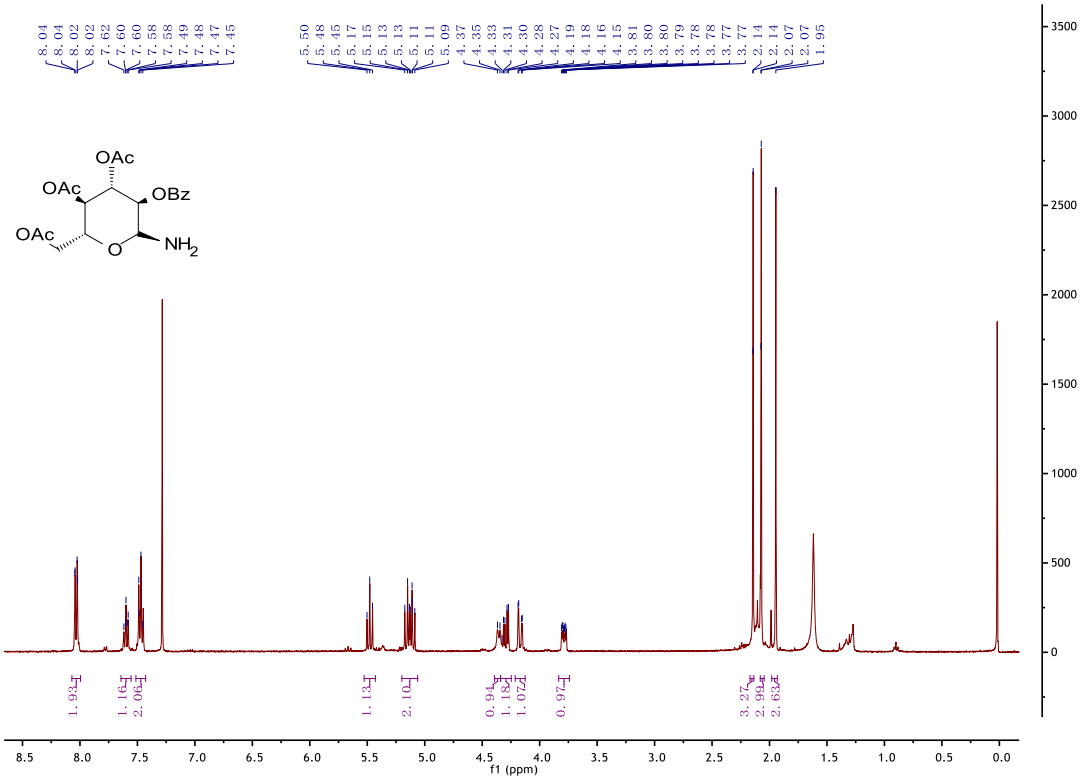
^{1}H NMR spectrum of 3g



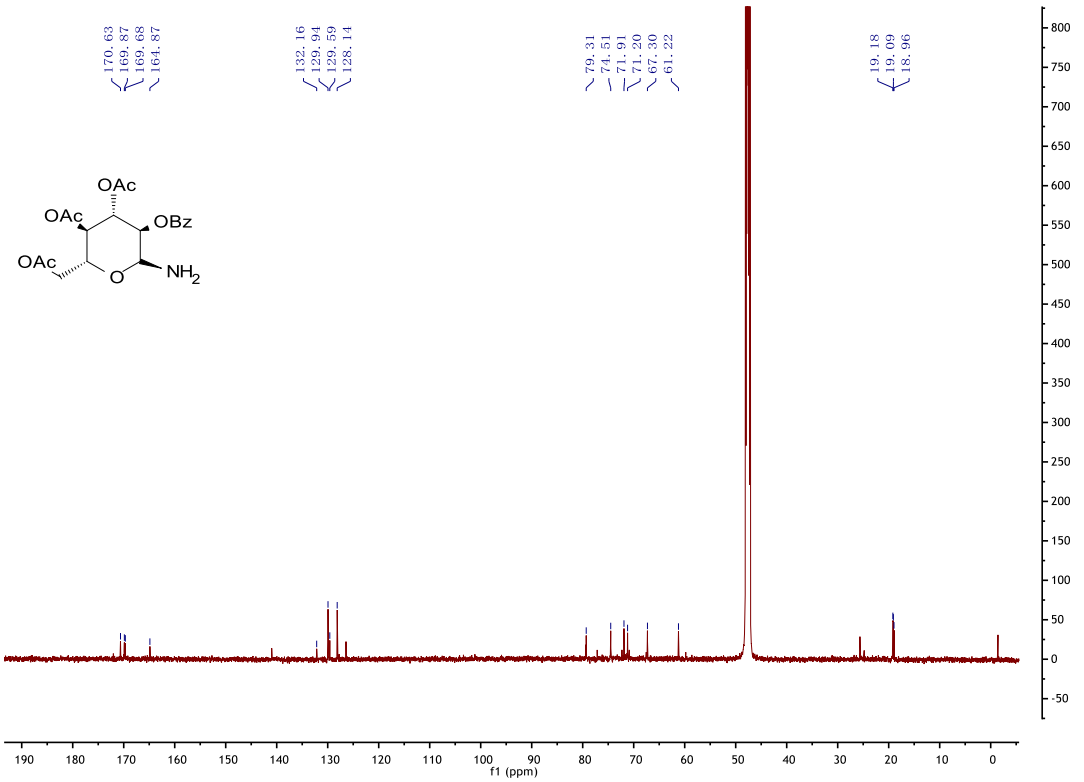
^{13}C NMR spectrum of 3g



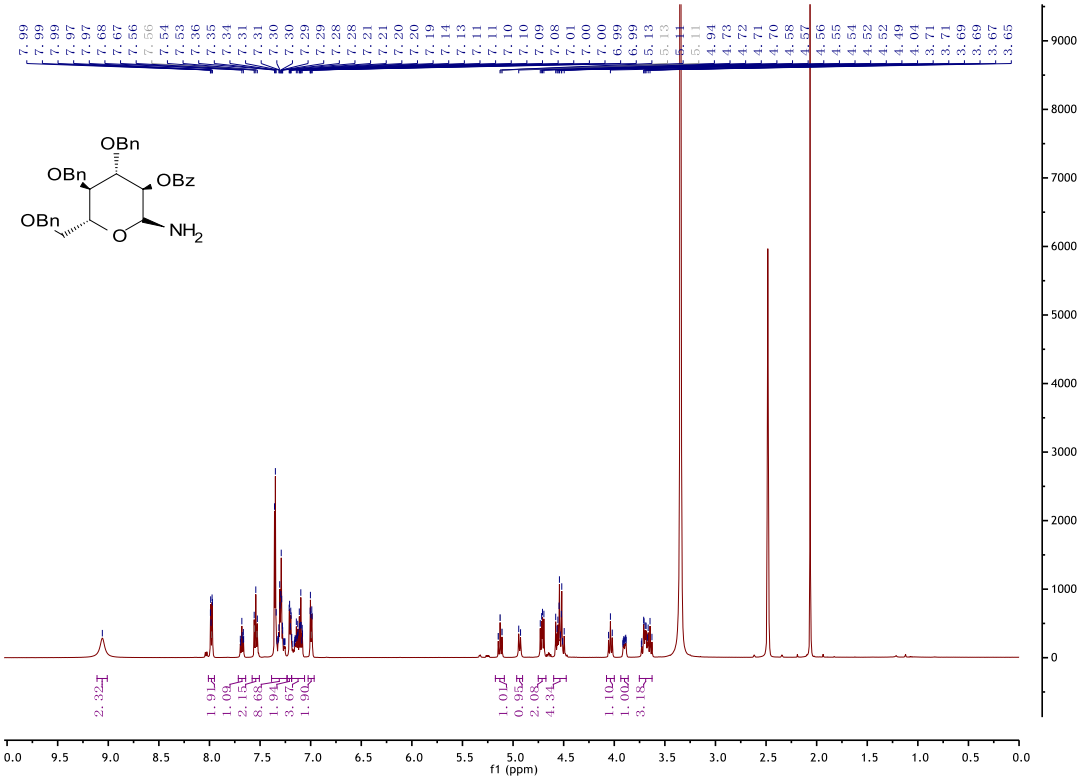
^{1}H NMR spectrum of 4A



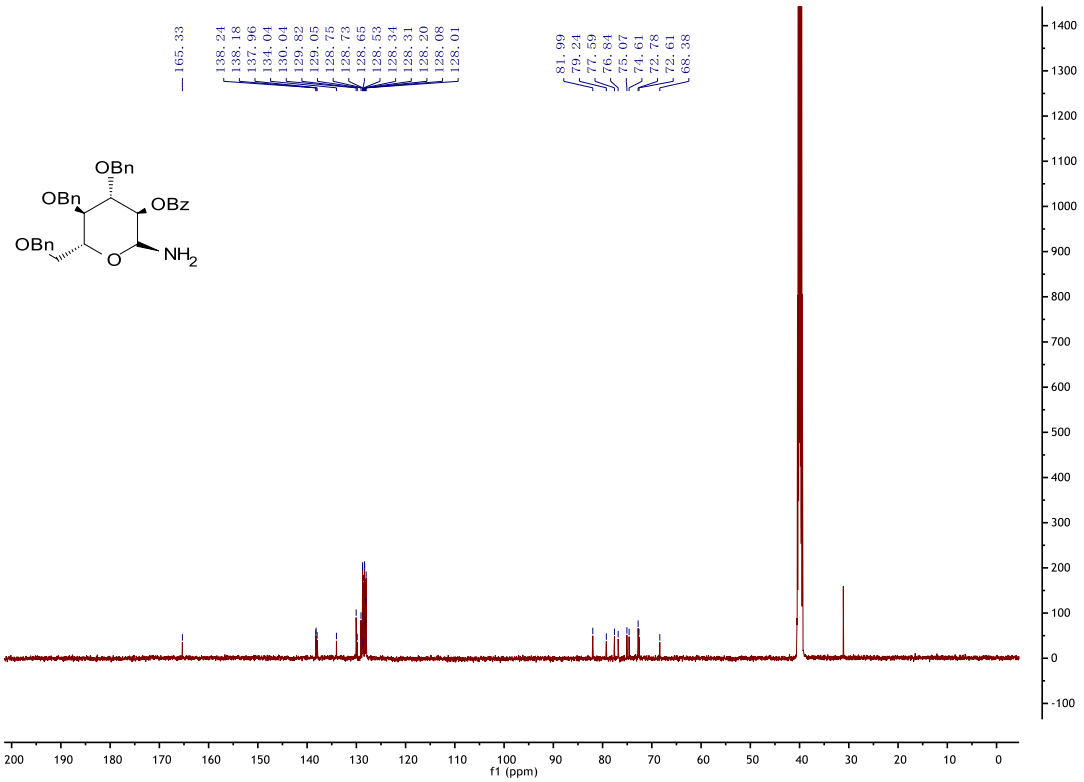
^{13}C NMR spectrum of 4A



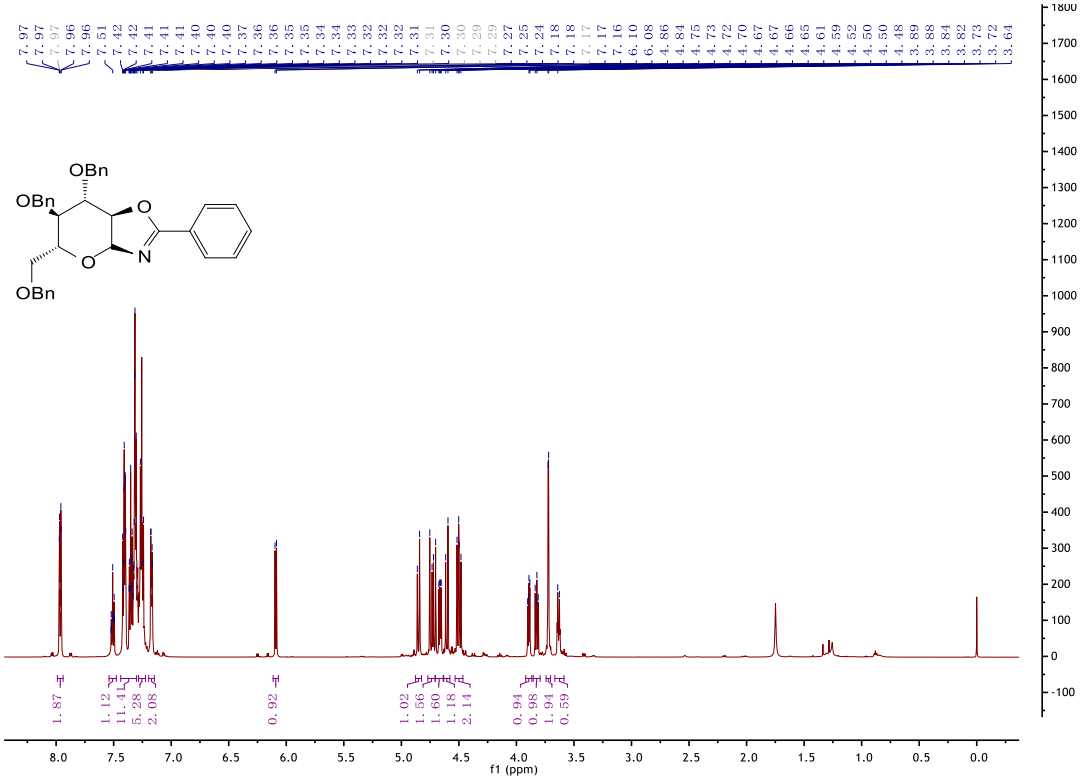
^{1}H NMR spectrum of 4B



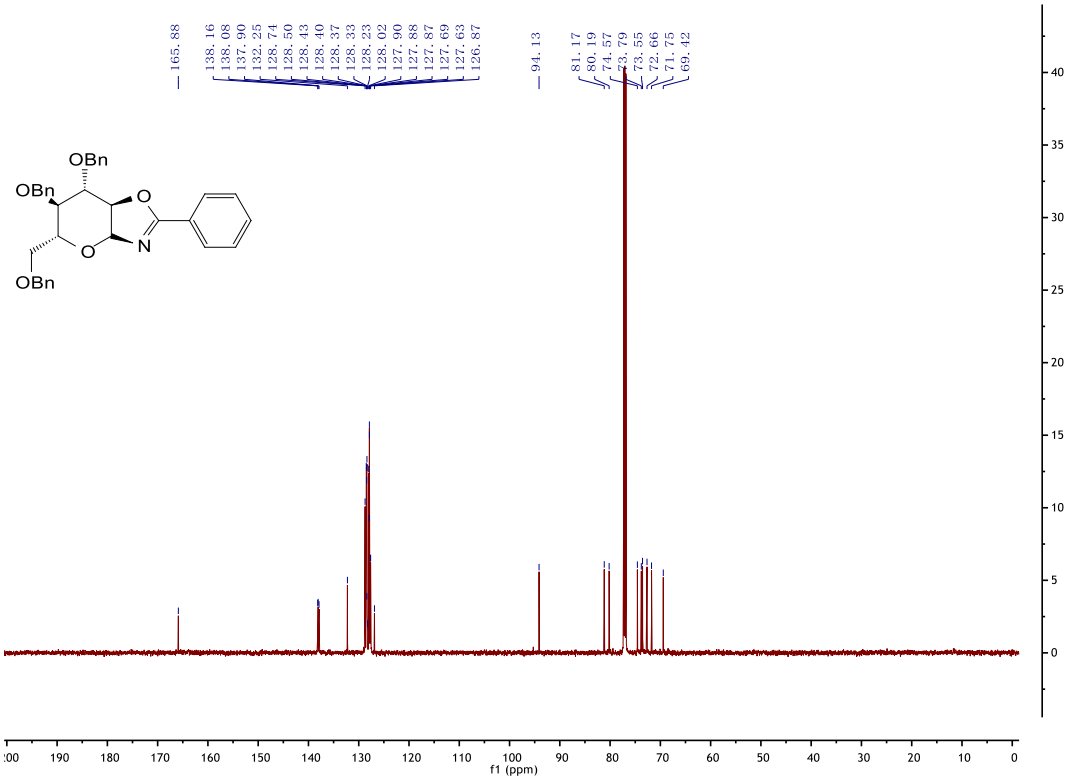
^{13}C NMR spectrum of 4B



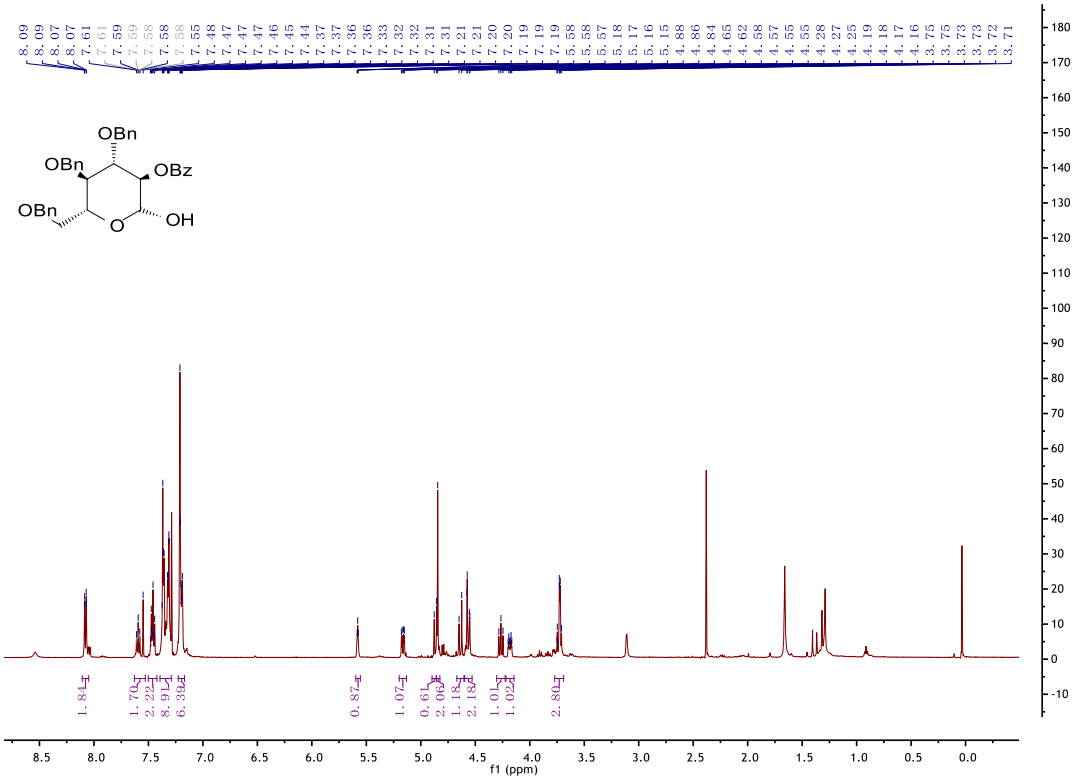
^{1}H NMR spectrum of 6



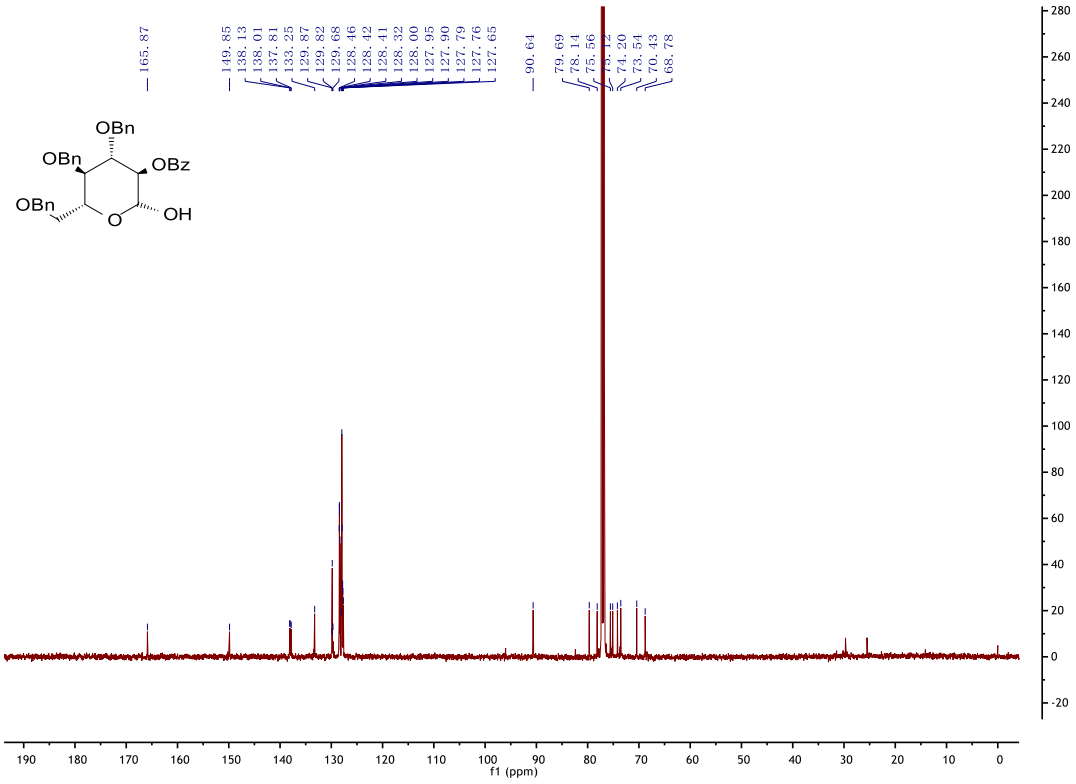
^{13}C NMR spectrum of 6



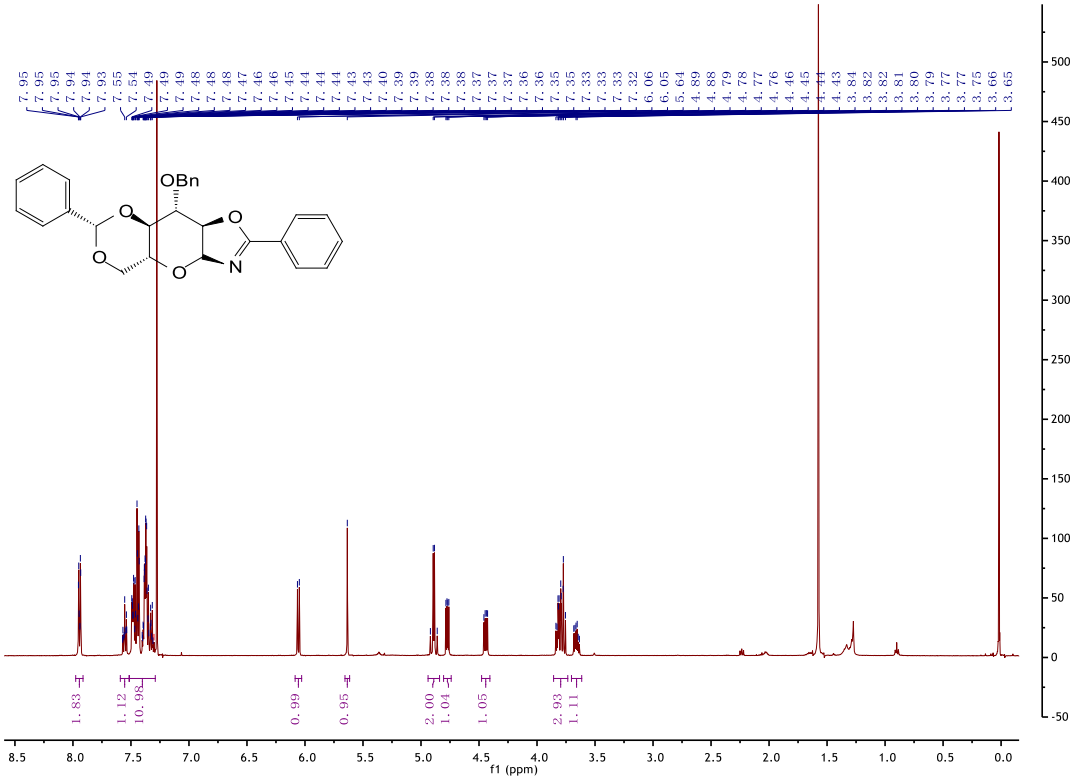
^{1}H NMR spectrum of 7



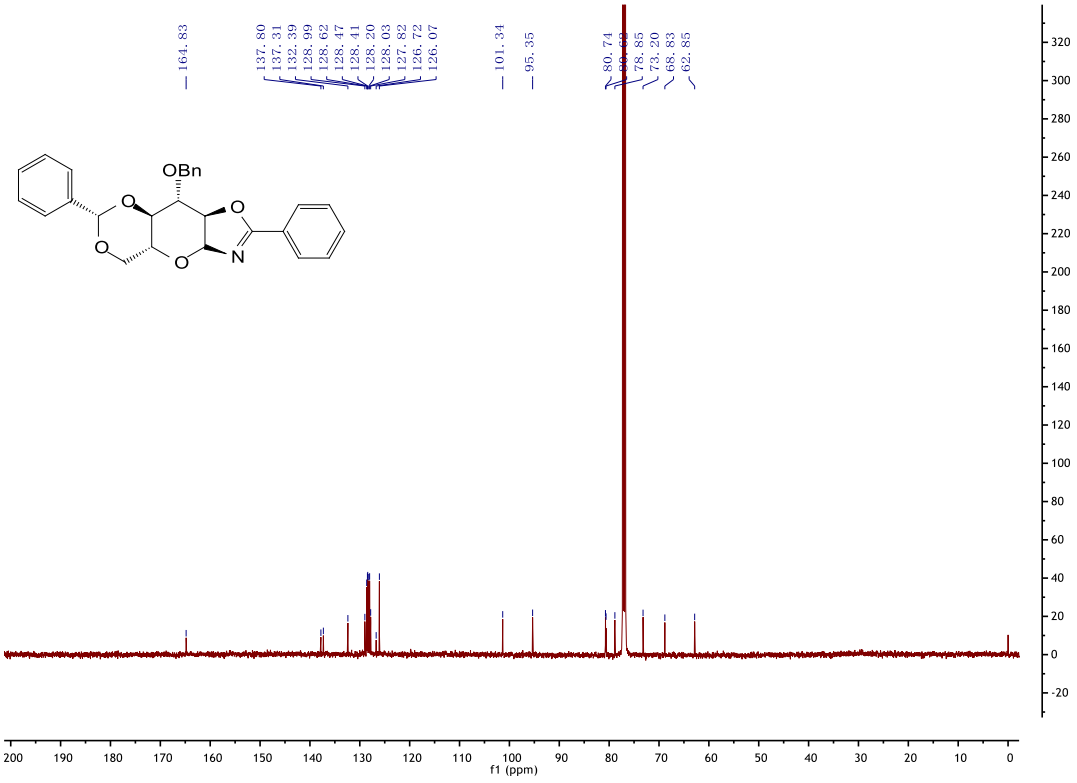
^{13}C NMR spectrum of 7



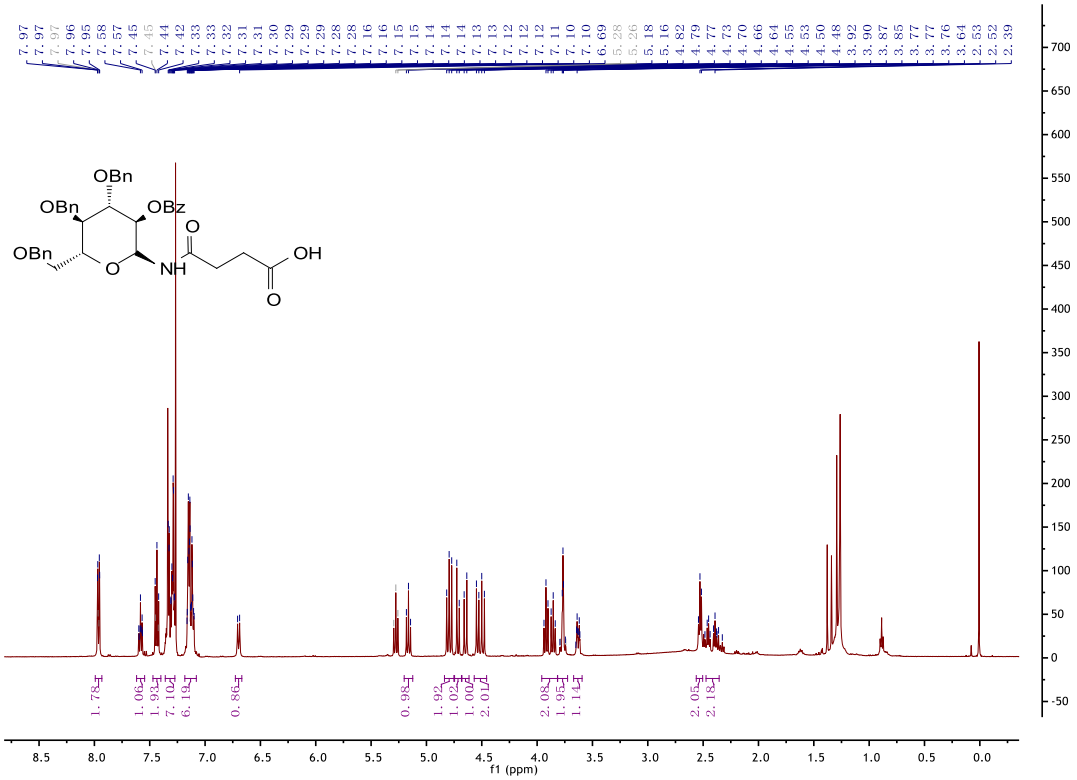
^{1}H NMR spectrum of 9



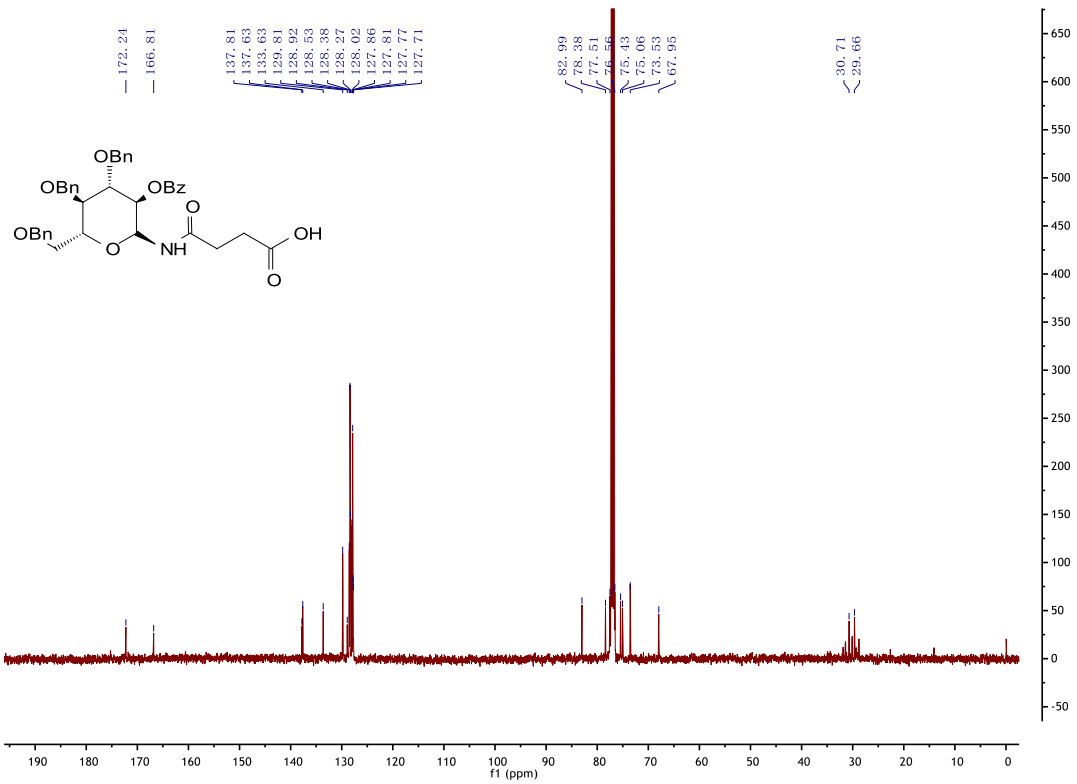
^{13}C NMR spectrum of 9



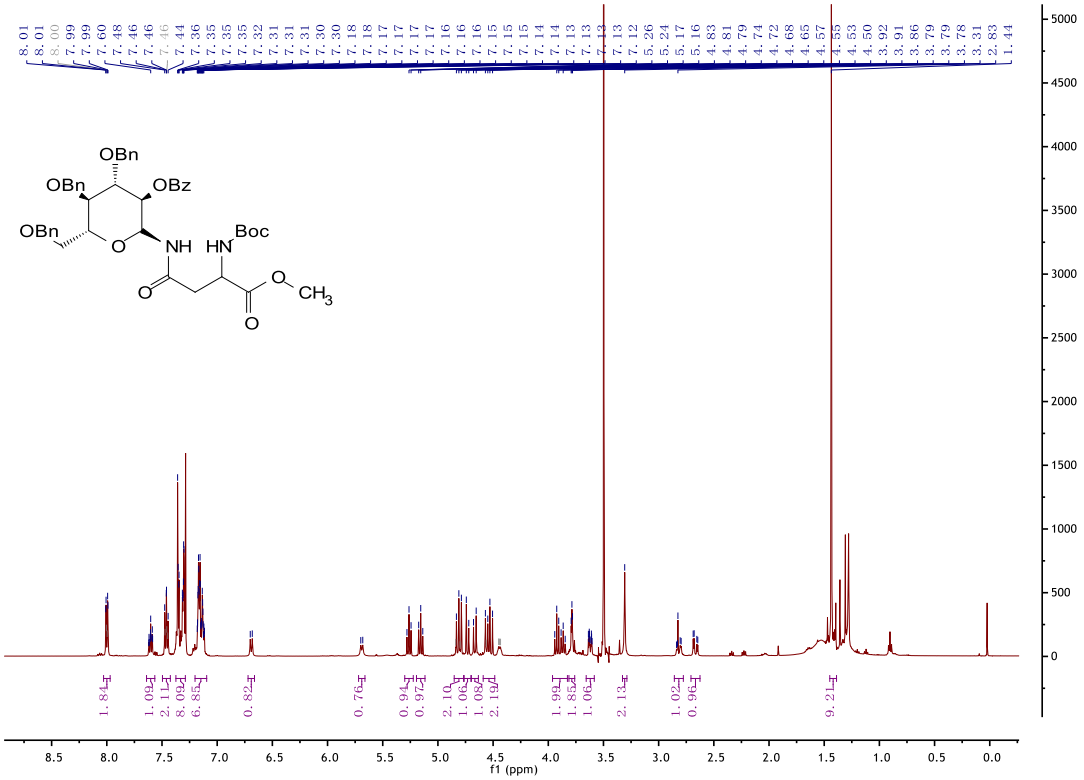
^{1}H NMR spectrum of 10a



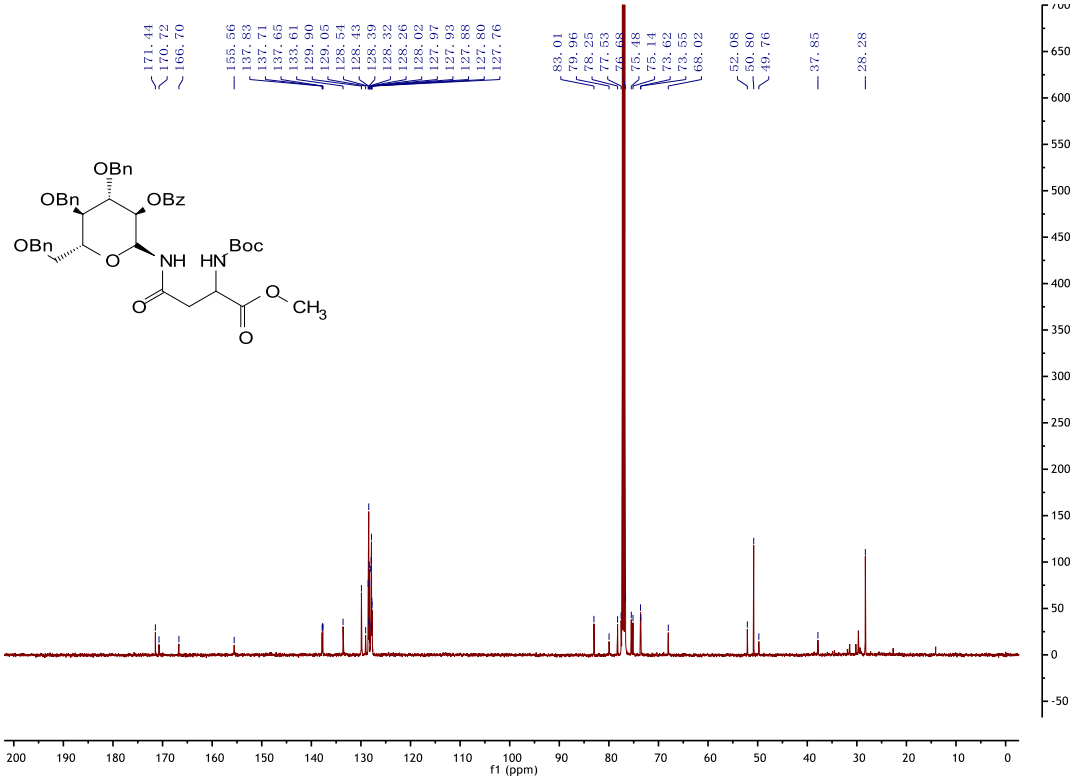
^{13}C NMR spectrum of 10a



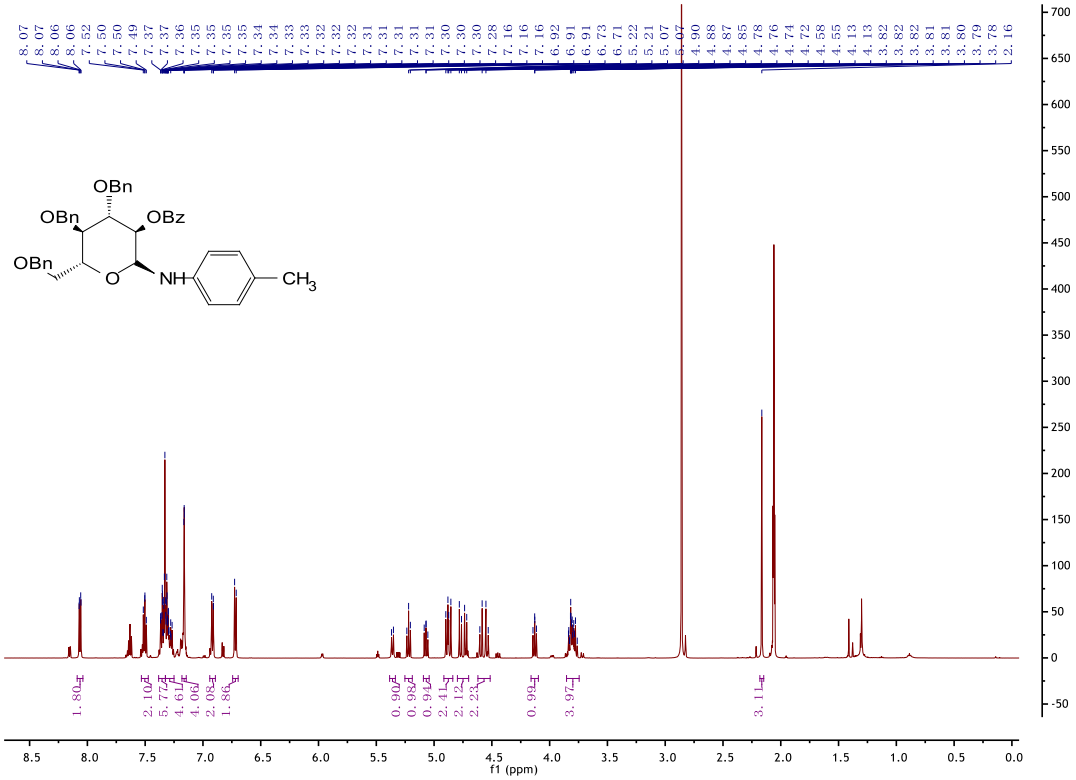
^{1}H NMR spectrum of 10b



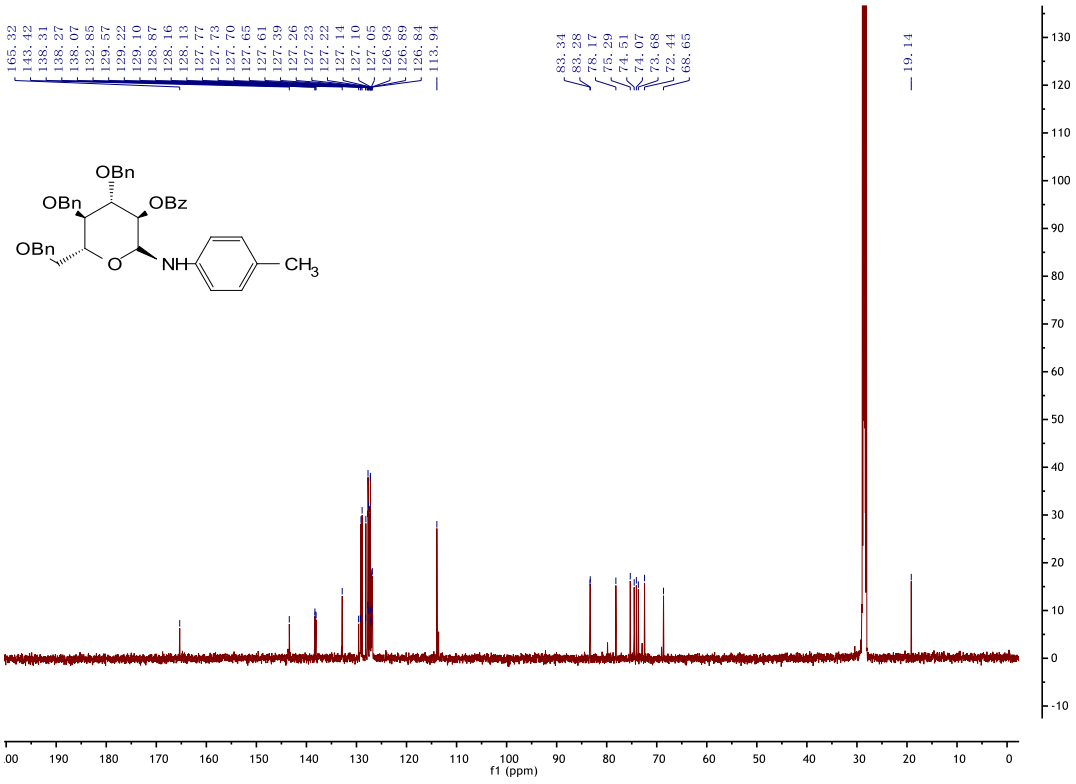
^{13}C NMR spectrum of 10b



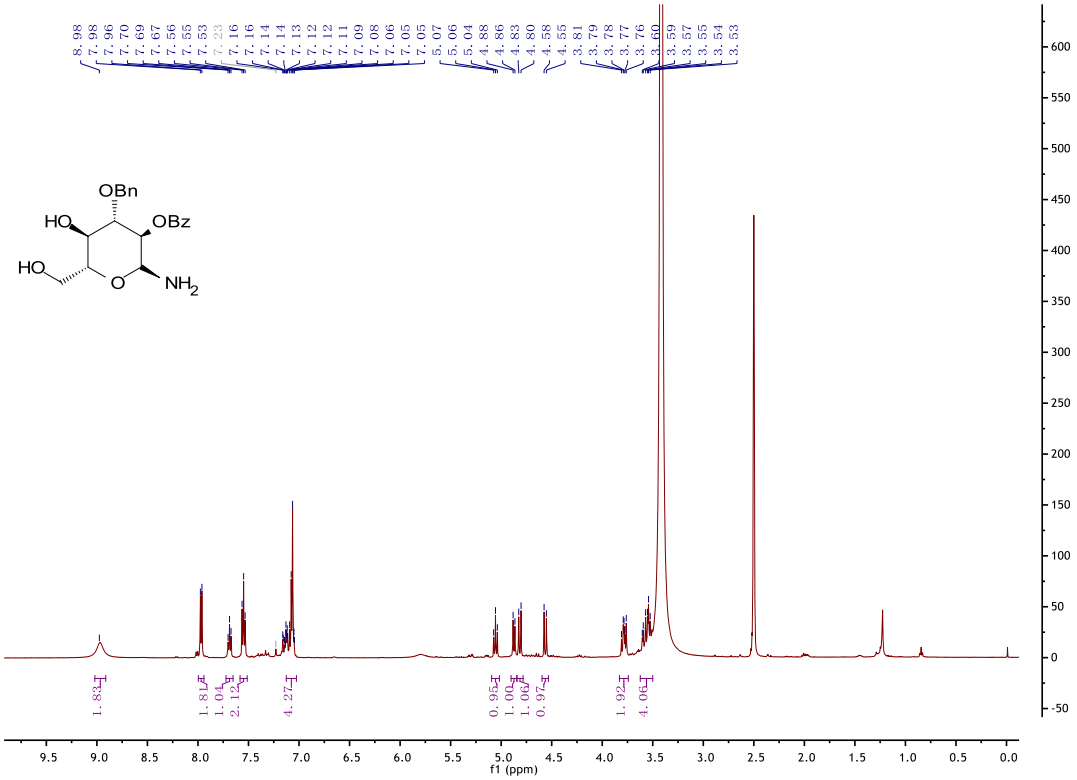
^{1}H NMR spectrum of 10c



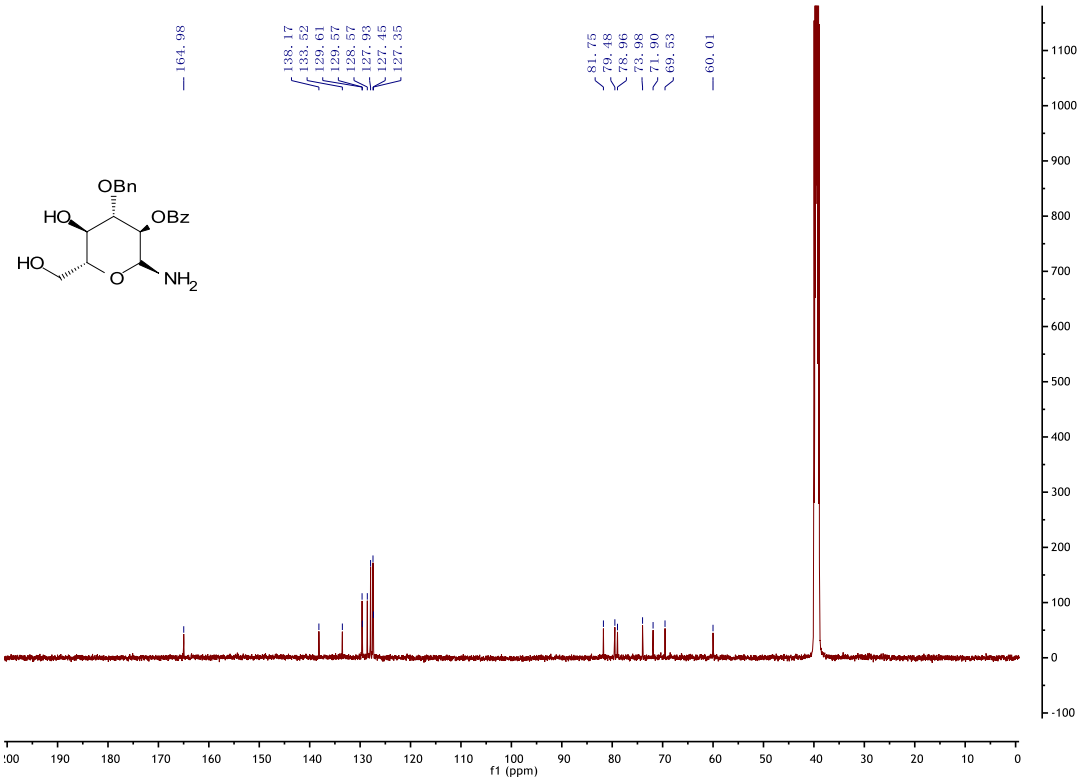
^{13}C NMR spectrum of 10c



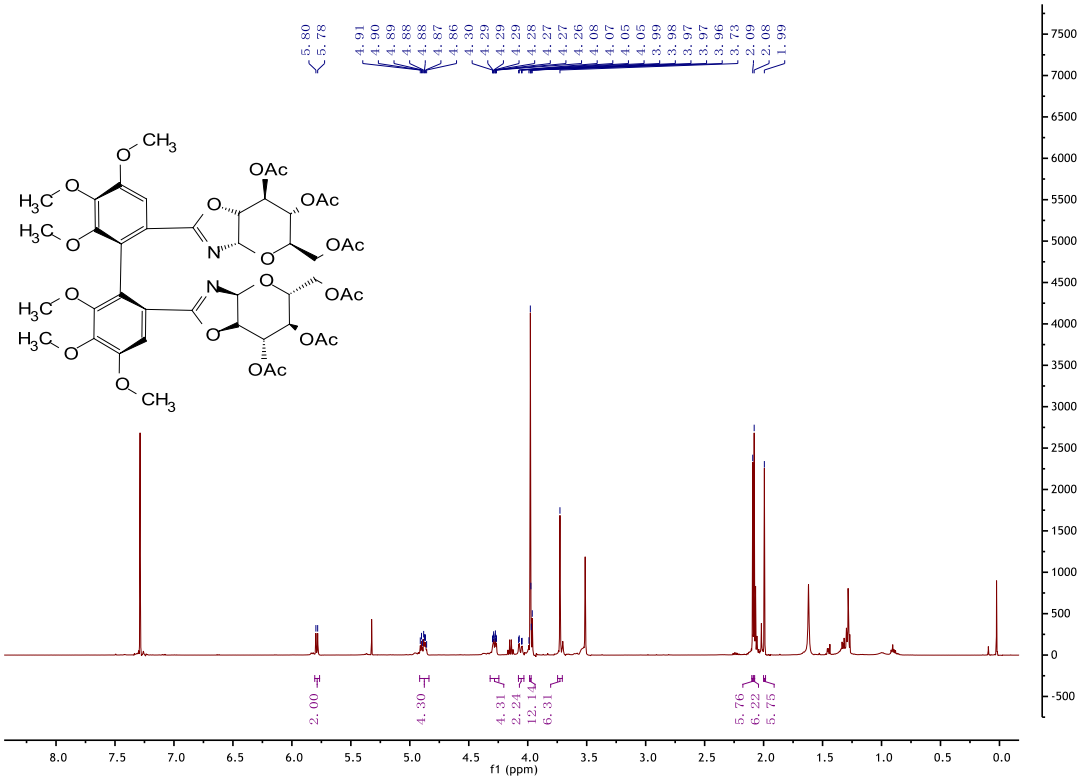
^{1}H NMR spectrum of 10d



^{13}C NMR spectrum of 10d



^{1}H NMR spectrum of 11



^{13}C NMR spectrum of 11