Supporting Information

Fragmentation of Glucosylphosphonium-ylides for Synthesis of Glycals

Chao Chen, Zhichao Mei, Mengyao You, Ziwei Zhang, Haiyang Huang,* Qiang Xiao*

Jiangxi Provincial Key Laboratory of Organic Functional Molecules; Institute of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang 330013, China

huanghaiyang1209@163.com ; xiaoqiang@tsinghua.org.cn

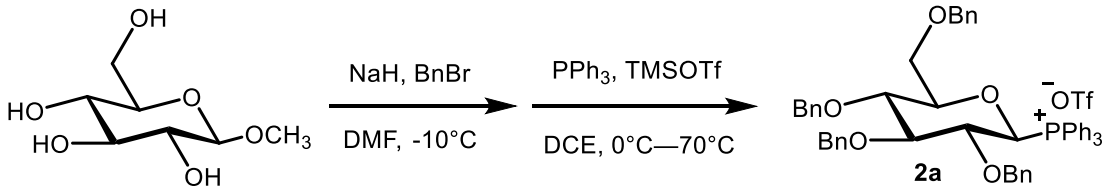
Fragmentation of Glucosylphosphonium-ylides for Synthesis of Glycals 1

1. **Materials and Instruments** 2
2. **General procedure for the synthesis of compounds 2a** 2
3. **General procedure for the synthesis of compounds 3a.** 4
4. **Computation of reaction mechanism** 4
5. **The Analytical and Spectral Characterization Data of Compounds 3** 7
6. **Copies of ^{1}H NMR, ^{13}C NMR Spectra of Compounds 3.** 14
7. **Cartesian coordinates of calculated structures** 34

1. Materials and Instruments

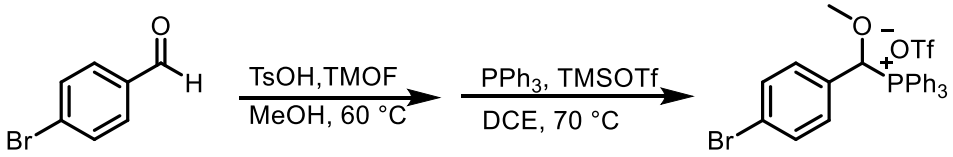
All reactions were routinely performed under an inert atmosphere of nitrogen by using standard Schlenk techniques and dry deoxygenated solvents. Dry DCM were purchased from J&K Scientific Ltd.Dry DCE were purchased from J&K Scientific Ltd. Dry MeOH were purchased from J&K Scientific Ltd.Dry DMF were purchased from J&K Scientific Ltd. Dry CH_3CN were purchased from J&K Scientific Ltd. Dry THF was distillation from CaH_2. Dry toluene was obtained by distillation from P_4O_{10}. Silica gel (200 - 300 mesh) purchased from Qingdao Hai Yang Chemical Industry Co. Ltd. was used for chromatographic separations. NMR spectra (400 MHz/100 MHz) were recorded on an Advance DPX spectrometer (Bruker, Billerica, MA, USA) at room temperature with Chloroform-d as solvent. Tetramethylsilane (TMS) was used as an internal reference. High resolution mass spectrometry (HRMS) data were measured with an AB Sciex TOF 4600 instrument (Billerica, MA, USA).

2. General procedure for the synthesis of compounds 2a

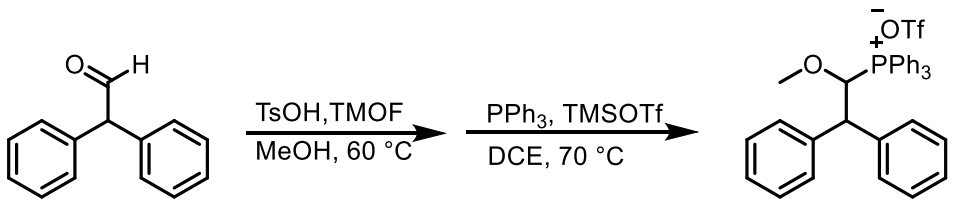


2.0 g (50.0 mmol) of NaH were added to a suspension of (10.0 mmol) of 1-Methylglucoside in DMF of 30 mL at -10 ℃, add BnBr after 50 minutes of reaction. The mixture was then stirred for 2 h at the same temperature, then mixture was stirred at room temperature for 12 h. The aqueous layer was extracted with ethyl acetate (3 × 30 mL). The extract was washed with brine and dried over with Na_2SO_4, then concentrated under reduced pressure and purified by silica gel flash chromatography to afford the product as yellow liquid. The yellow liquid 4.4g (8.0 mmol) and triphenylphosphine (8.8 mmol) were dissolved in DCE (25mL) in a Schlenk bottle under argon gas atmosphere, TMSOTf (9.6 mmol) was amed under 0 ℃. The mixture was stirred at 70 ℃ for 12-72h. The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The extract was washed with brine and dried over with Na_2SO_4, then

concentrated under reduced pressure and purified by silica gel flash chromatography to afford the product as white powder.



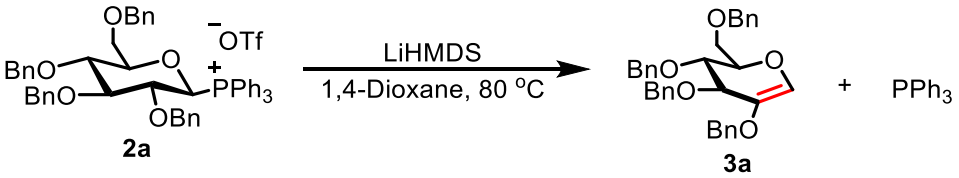
To 4-Bromobenzaldehyde 0.5 ml (5.0 mmol) and TsOH 380 mg (2 mmol) into the Schlenk bottle, evacuate and replace with argon gas for 3 times. Then add MeOH 15 mL and Trimethoxymethane 1.72 mL (20 mmol), the mixture was then stirred for 12 h at 60 ℃. After the reaction is complete, add sodium carbonate and evaporate the excess solvent. Filter and evaporate the filtrate to obtain the product as yellow liquid. The yellow liquid 1.15 g (5.0 mmol) and triphenylphosphine (5.5 mmol) were dissolved in DCE (15mL) in a Schlenk bottle under argon gas atmosphere, TMSOTf (6 mmol) was added under 0 ℃. The mixture was stirred at 70 ℃ for 12h. The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The extract was washed with brine and dried over with Na_2SO_4, then concentrated under reduced pressure and purified by silica gel flash chromatography to afford the product as white powder.



To Diphenylacetaldehyde 0.9 ml (5.0 mmol) and TsOH 380 mg (2 mmol) into the Schlenk bottle, evacuate and replace with argon gas for 3 times. Then add MeOH 15 mL and Trimethoxymethane 1.72 mL (20 mmol), the mixture was then stirred for 12 h at 60 ℃. After the reaction is complete, add sodium carbonate and evaporate the excess solvent. Filter and evaporate the filtrate to obtain the product as yellow liquid. The yellow liquid 1.21 g (5.0 mmol) and triphenylphosphine (5.5 mmol) were dissolved in DCE (15mL) in a Schlenk bottle under argon gas atmosphere, TMSOTf (6 mmol) was added under 0 ℃. The mixture was stirred at 70 ℃ for 12h. The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The extract was washed with

brine and dried over with Na_2SO_4, then concentrated under reduced pressure and purified by silica gel flash chromatography to afford the product as white powder.

3. General procedure for the synthesis of compounds 3a.



To 2a (0.5 mmol) into the Schlenk bottle, evacuate and replace with argon gas for 3 times ,then add to 1,4-Dioxane (1.5 mL) and LiHMDS 92 mg (1.1 mmol) in the Schlenk bottle under argon gas atmosphere. After stirred at 100 ^{o}C for 2 h, the reaction mixture was cooled to room temperature. The aqueous layer was extracted with Dichloromethane (3 × 10 mL). The extract was washed with brine and dried over with Na_2SO_4, then concentrated under reduced pressure. The crude material was purified by silica gel flash column chromatography (EA/ PE= 10/1) to obtain the product **3a**. All Olefin sugar 3**a**–3**l** were synthesized according to this method.

4. Computation of reaction mechanism

Computational Methods :

All density functional theory calculations were carried out with the Gaussian 16 programs. The geometry optimizations, Intrinsic reaction coordinate (IRC), and frequency analyses of the reactants, transition states, and products were performed using the B3LYP-D3 method at the 6-31G(d,p)/SMD(1,4-dioxane level. Frequency calculations at the same level of theory were performed to identify the number of imaginary frequencies (zero for local minimum and one for transition states) and provide the thermal corrections of Gibbs free energy. Transition states were submitted to intrinsic reaction coordinate (IRC) calculations to determine two corresponding minima. The single-point energy calculations were performed at the M06-2X-D3/def2-TZVP/SMD(1,4-dioxane) level of theory for solution-phase. The corrections of Gibbs free energy calculations (at the 6-31G(d,p)/SMD(1,4-dioxane)

level) were added to the single-point energies (at the M06-2X-D3/def2-TZVP/SMD(1,4-dioxane)) to obtain the Gibbs free energy in solution.

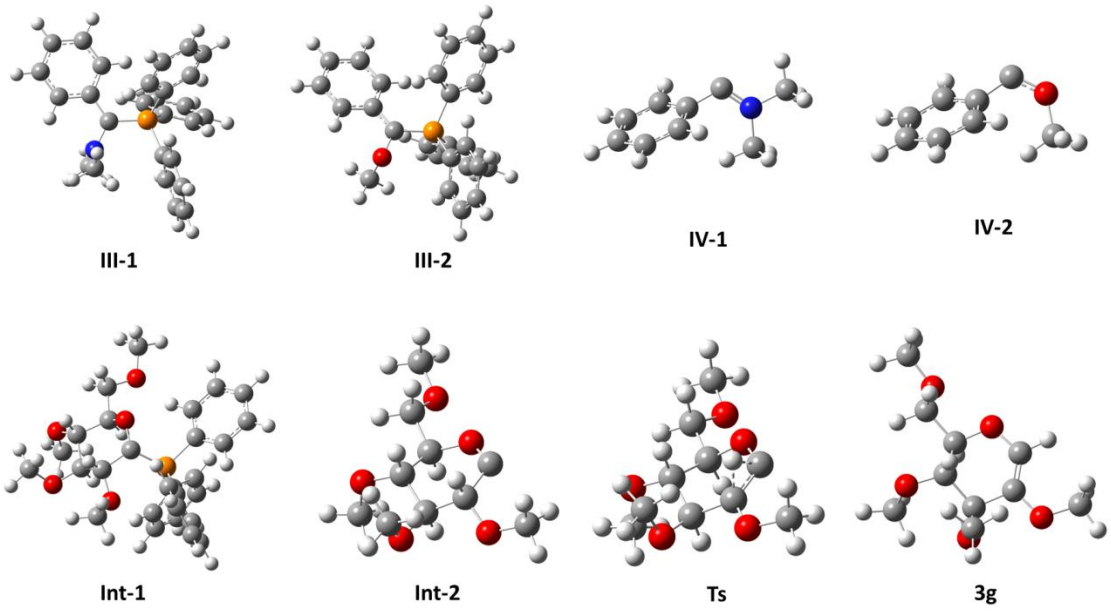


Figure S3. The main geometries calculated at the B3LYP-D3/6-31G(d,p)/SMD(1,4-dioxane) level.

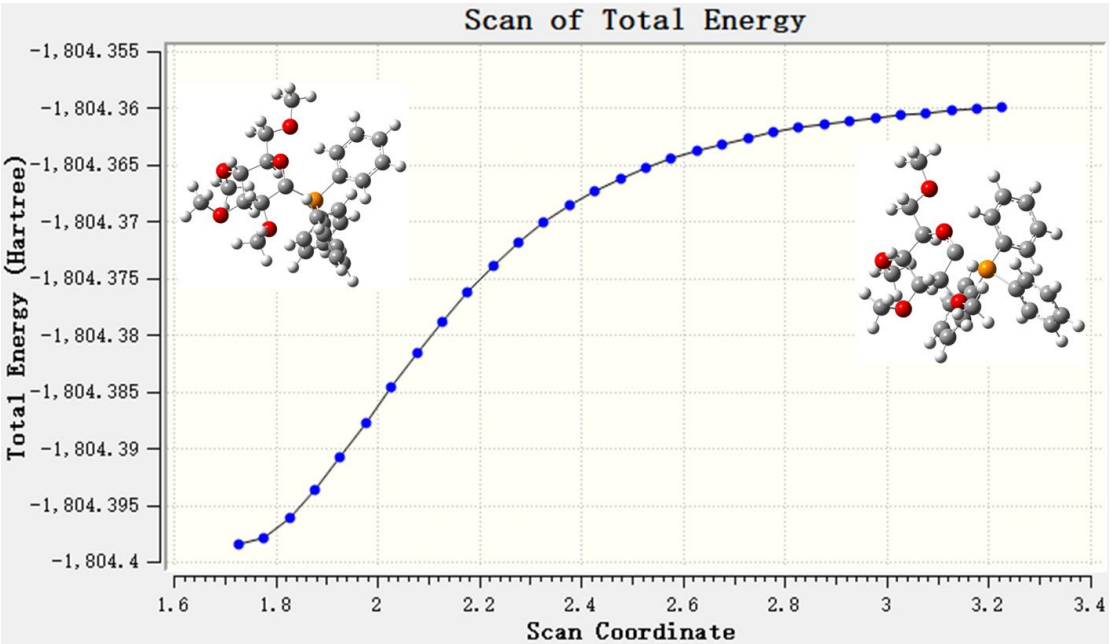


Figure S4. The scan plot along prolonged P-C bond-length from **int-1** calculated at the B3LYP-D3/6-31G(d,p)/SMD(1,4-dioxane) level.

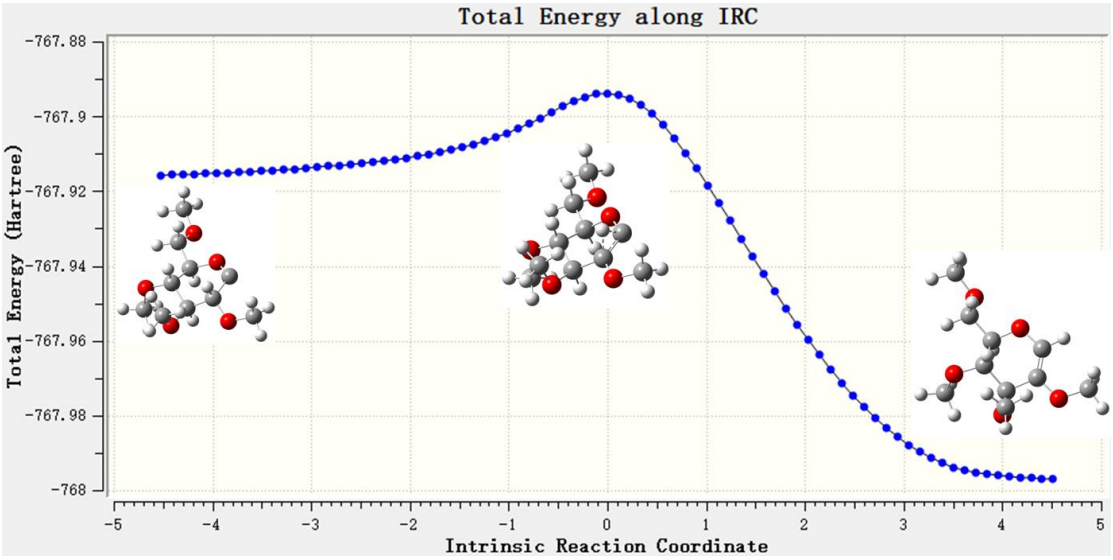


Figure S5. The IRC plots of **TS** calculated at the B3LYP-D3/6-31G(d,p)/SMD(1,4-dioxane) level.

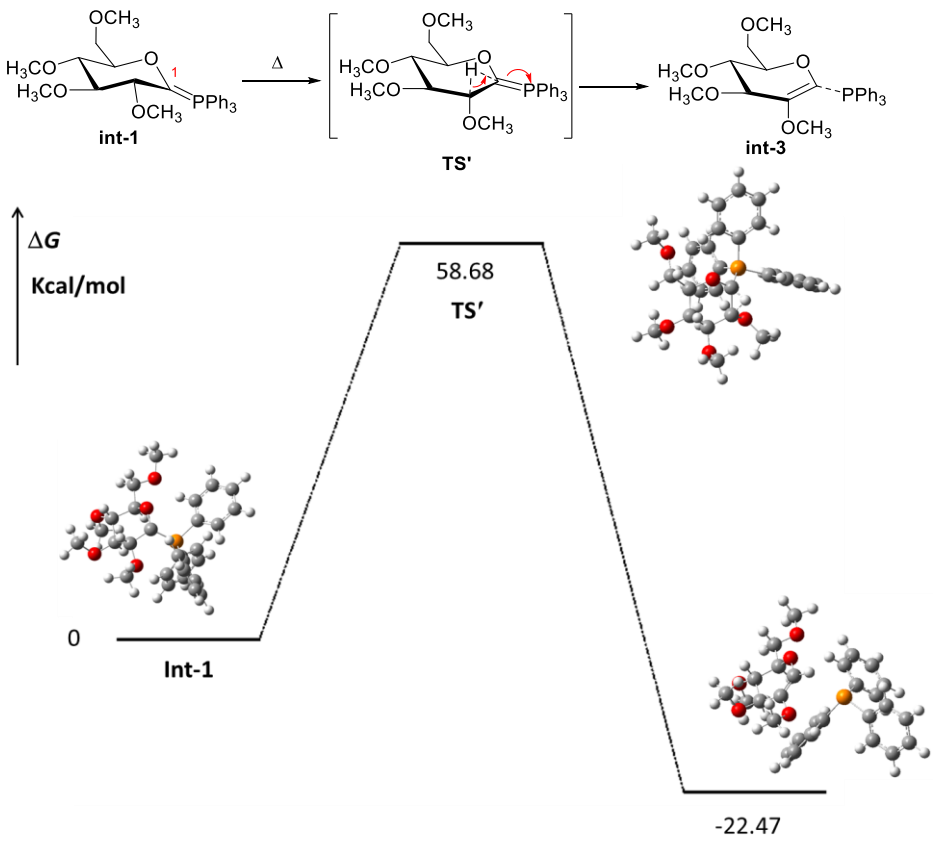
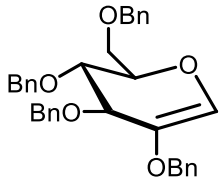


Figure S6. Computed energy profile (kcal/mol) for the reaction of H-abstraction mechanism at the m06-2x-D3/def2-TZVP/SMD(1,4-dioxane)// b3lyp-D3/6-311G(d,p)/SMD(1,4-dioxane) level.

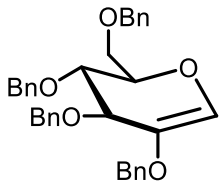
Table S2. Thermal Free Energies with thermal correction (Hartree/Particle).

Intermediates or transition states	Thermal correction to Gibbs Free Energy (B3LYP-D3/6-31G(d,p)/SMD(1,4-dioxane)	Single-point energies (M06-2X-D3/def2-TZVP/ SMD(1,4-dioxane))	Thermal Free Energies with thermal correction
III-1	0.397135	-1440.5138483	-1440.116713
III-TS	0.395495	-1440.4822301	-1440.086735
III-2	0.358068	-1421.0791401	-1420.721072
IV-1	0.142825	-404.2272796	-404.0844546
IV-2	0.103767	-384.7593187	-384.6555517
PPh_3	0.227674	-1036.2573595	-1036.029686
int-1	0.490484	-1804.1485526	-1803.658069
int-2	0.234985	-767.8359259	-767.6009409
int-3	0.488089	-1804.1819608	-1803.693872
TS	0.231215	-767.8139120	-767.582697
TS′	0.485191	-1804.0497544	-1803.564563
3g	0.236648	-767.9160740	-767.679426

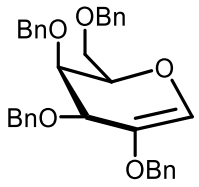
5. The Analytical and Spectral Characterization Data of Compounds 3



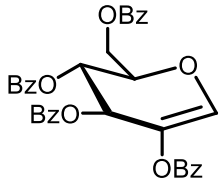
3a: Colorless oil; yield (72%). R_f 0.4 (Petroluem Ether/ Ethyl Acetate = 7 : 1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (t, *J* = 5.0 Hz, 5H), 7.32 – 7.27 (m, 12H), 7.26 – 7.22 (m, 3H), 6.31 (s, 1H), 4.77 – 4.67 (m, 4H), 4.63 – 4.53 (m, 4H), 4.26 (d, *J* = 4.6 Hz, 1H), 4.09 (d, *J* = 3.4 Hz, 1H), 3.90 (m, *J* = 6.6, 4.8 Hz, 1H), 3.76 (d, *J* = 6.0 Hz, 1H), 3.68 (m, *J* = 10.6, 3.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.9 (s, C), 138.4 (s, C), 138.1 (s, C), 138.0 (s, C), 137.2(s, C), 128.5 (d, *J* = 2.2 Hz, 4CH), 128.4 (d, *J* = 3.7 Hz, 4CH), 128.0 (d, *J* = 2.8 Hz, 4CH), 127.9 (d, *J* = 1.8 Hz, 2CH), 127.8 (s, 2CH), 127.7 (d, *J* = 2.7 Hz, 2CH), 127.6 (s, 2CH), 76.3 (s, CH), 75.6 (s, CH), 74.3 (s, CH), 73.5 (s, CH_2), 72.9 (s, CH_2), 72.3 (s, CH_2), 71.1 (s, CH_2), 68.3 (s, CH_2). HRMS Calcd. For $C_{34}H_{34}O_5[M+H]^+$, m/z 523.2406. Found: 523.2409.



3a': Colorless oil; yield (61%). R_f 0.4 (Petroluem Ether/ Ethyl Acetate = 7 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 6.5 Hz, 4H), 7.25 (d, *J* = 4.4 Hz, 4H), 7.22 (d, *J* = 3.5 Hz, 4H), 7.19 (d, *J* = 2.6 Hz, 3H), 7.18 (d, *J* = 3.6 Hz, 3H), 7.11 – 7.07 (m, 2H), 4.90 (s, 1H), 4.80 (d, *J* = 10.7 Hz, 1H), 4.66 – 4.57 (m, 4H), 4.46 (d, *J* = 6.1 Hz, 1H), 4.37 (d, *J* = 11.9 Hz, 1H), 3.93 (d, *J* = 9.2 Hz, 1H), 3.89 (d, *J* = 2.9 Hz, 1H), 3.78 – 3.62 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.52 (s, C), 137.46 (s, C), 137.41 (s, C), 137.27 (s, C), 136.34 (s, C), 127.37 (s, 2CH), 127.29 (d, *J* = 2.5 Hz, 6CH), 126.99 (s, 2CH), 126.81 (s, 2CH), 126.74 (s, 2CH), 126.63 (s, 2CH), 126.55 (s, 2CH), 126.50 (s, CH), 126.44 (s, CH), 79.23 (s, CH), 74.13 (s, CH), 73.74 (s, CH), 72.36 (s, CH_2), 71.58 (s, CH_2), 71.19 (s, CH_2), 68.27 (s, CH_2), 67.93 (s, CH_2). HRMS Calcd. For $C_{34}H_{34}O_5[M+H]^+$, m/z 523.2406. Found: 523.2408.

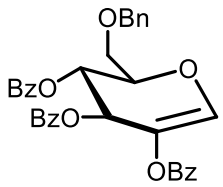


3b: Colorless oil; yield (58%). R_f 0.4 (Petroluem Ether/ Ethyl Acetate = 7 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 4H), 7.26 (s, 3H), 7.24 (d, *J* = 3.8 Hz, 6H), 7.22 (s, 3H), 7.21 (d, *J* = 1.7 Hz, 3H), 7.18 (d, *J* = 2.9 Hz, 1H), 6.34 – 6.26 (m, 1H), 4.80 (d, *J* = 12.0 Hz, 2H), 4.64 – 4.52 (m, 4H), 4.41 (s, 1H), 4.35 (d, *J* = 11.9 Hz, 1H), 4.11 (s, 2H), 3.87 (d, *J* = 2.4 Hz, 1H), 3.72 – 3.68 (m, 1H), 3.57 (m, *J* = 10.1, 5.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.17 (s, C), 137.48 (s, C), 137.35 (s, C), 137.17 (s, C), 136.98 (s, C), 127.36 (s, 7CH), 127.30 (s, 3CH), 127.12 (s, 2CH), 126.87 (s, 2CH), 126.67 (s, 3CH), 126.53 (s, 2CH), 126.42 (s, 2CH), 74.68 (s, CH), 72.40 (s, CH_2), 72.30 (s, CH_2), 70.29 (s, CH), 69.87 (s, CH_2), 69.74 (s, CH), 68.30 (s, CH_2), 67.42 (s, CH_2). HRMS Calcd. For $C_{34}H_{34}O_5[M+H]^+$, m/z 523.2406. Found: 523.2408.

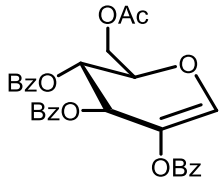


3c: Colorless oil; yield (64%). R_f 0.4 (Petroluem Ether/ Ethyl Acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.2 Hz, 2H), 7.94 (d, *J* = 7.1 Hz, 2H), 7.86 (d, *J* = 7.2 Hz, 2H), 7.82 – 7.76 (m, 4H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 3H), 7.31 (d, *J* = 7.6 Hz, 3H), 7.20 (d, *J* = 7.0 Hz, 3H), 6.79 (d, *J* = 3.7 Hz, 1H), 6.25 (t, *J* = 10.0 Hz, 1H), 5.80 (t, *J* = 9.8 Hz, 1H), 5.62 (m, *J* = 10.3, 3.7 Hz, 1H), 4.60 – 4.51 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.02 (s, C), 164.86 (s, C), 164.31 (s, C), 164.09 (s, C), 163.35 (s, C), 132.89 (s, CH), 132.48 (s, CH),132.46 (s, CH),132.33 (s,

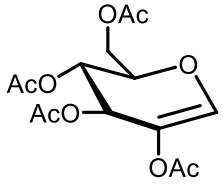
CH), 132.10 (s, CH), 128.97 (s, 2CH), 128.76 (m, 8CH, *J* = 9.8, 4.8 Hz), 128.48 (s, C), 127.91 (s, C), 127.76 (s, 2CH), 127.63 (s, C), 127.49 (s, C), 127.47 – 127.28 (m, 8CH), 89.00 (s, CH), 69.44 (s, CH), 67.79 (s, CH), 61.42 (s, CH_2). HRMS Calcd. For $C_{34}H_{26}O_9[M+H]^+$, m/z 579.1577. Found: 579.1575.



3d: Colorless oil; yield (44%). R_f 0.5 (Petroluem Ether/ Ethyl Acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.94 (m, 4H), 7.51 (d, *J* = 4.0 Hz, 2H), 7.39 (s, 2H), 7.29 (d, *J* = 4.6 Hz, 2H), 7.12 (s, 5H), 7.06 (s, 5H), 5.81 (t, *J* = 9.5 Hz, 1H), 4.68 (d, *J* = 3.4 Hz, 1H), 4.62 (s, 1H), 4.51 (d, *J* = 1.3 Hz, 1H), 4.44 (s, 1H), 4.02 (md, *J* = 9.9, 4.7, 2.2 Hz, 1H), 3.65 (t, *J* = 9.6 Hz, 1H), 3.56 (m, *J* = 10.0, 3.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.21 (s, C), 164.41 (s, C), 163.82 (s, C), 139.90 (s, C), 138.83 (s, C), 136.67 (s, C), 136.04 (s, C), 132.07 (d, *J* = 30.5 Hz, 2CH), 129.90 (s, C), 128.72 (d, *J* = 47.2 Hz, 4CH), 127.55 (s, CH), 127.37 (d, *J* = 25.0 Hz, 7CH), 127.20 (s, 2CH), 126.86 (t, *J* = 20.3 Hz, 4CH), 125.96 (s, CH), 75.33 (s, CH), 73.23 (s, CH_2), 67.54 (s, CH), 64.37 (s, CH_2), 54.30 (s, CH). HRMS Calcd. For $C_{34}H_{28}O_8[M+H]^+$, m/z 565.1784. Found: 565.1788.

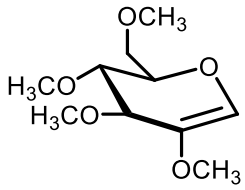


3e: Colorless oil; yield (62%). R_f 0.3 (Petroluem Ether/ Ethyl Acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.70 (m, 5H), 7.44 (t, *J* = 21.6, 14.2 Hz, 2H), 7.43 – 7.2 (m, 6H), 7.21 (m, *J* = 13.2, 5.4 Hz, 2H), 6.08 (t, *J* = 9.8 Hz, 1H), 5.53 (t, *J* = 9.7 Hz, 1H), 5.35 – 4.93 (m, 2H), 4.28 – 4.15 (m, 2H), 2.09 – 1.90 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.64 (s, C), 164.82 (s, C), 164.76 (s, C), 163.60 (s, C), 132.42 (s, CH), 132.37 (s, CH), 132.09 (s, 2CH), 128.93 (s, 2CH), 128.82 (s, 2CH), 128.66 (s, 2CH), 128.20 (s, C), 128.11 (s, C), 128.03 (s, C), 127.90 (s, C), 127.42 (s, 4CH), 127.27 (s, 2CH), 71.00 (s, CH), 66.52 (s, CH_2), 61.45 (s, CH), 54.66 (s, CH), 19.70 (s, CH_3). HRMS Calcd. For $C_{29}H_{24}O_9[M+H]^+$, m/z 517.1420. Found: 517.1423.

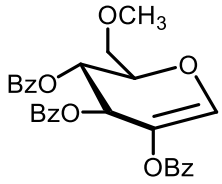


3f: Colorless oil; yield (46%). R_f 0.4 (Petroluem Ether/ Ethyl Acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 – 5.32 (m, 1H), 5.22 (m, *J* = 7.5, 5.8 Hz, 1H), 4.85 (m, *J* = 6.1, 3.2 Hz, 1H), 4.40 (m, *J* = 12.0, 5.7 Hz, 1H), 4.25 (m, *J* = 7.7, 5.5 Hz, 1H), 4.20 (m, *J* = 12.0, 3.0 Hz, 1H), 2.29 – 2.27 (m, 3H), 2.10 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.60 (s, C), 170.42 (s, C), 169.59 (s, C),

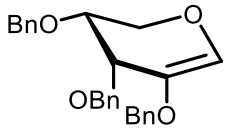
168.80 (s, C), 145.65 (s, C), 99.02 (s, CH), 73.98 (s, CH), 67.45 (s, CH), 67.24 (s, CH), 61.41 (s, CH_2), 21.05 (s, CH_3), 20.99 (s, CH_3), 20.80 (s, CH_3), 20.72 (s, CH_3). HRMS Calcd. For $C_{14}H_{18}O_9[M+H]^+$, m/z 331.0951. Found: 331.0954.



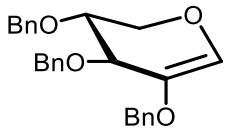
3g: Colorless oil; yield (47%). R_f 0.4 (Petroluem Ether/ Ethyl Acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 (d, *J* = 7.8 Hz, 1H), 3.88 (m, *J* = 9.4, 7.1 Hz, 1H), 3.55 (s, 3H), 3.51 (s, 3H), 3.46 (s, 3H), 3.33 (s, 3H), 3.23 – 3.17 (m, 1H), 3.07 (t, *J* = 7.0 Hz, 2H), 2.92 (t, *J* = 8.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 102.17 (s, C), 85.43 (s, CH), 82.72 (s, CH), 78.46 (s, CH), 73.55 (s, CH), 70.46 (s, CH_2), 64.36 (s, CH_3), 59.74 (s, CH_3), 59.40 (s, CH_3), 58.33 (s, CH_3). HRMS Calcd. For $C_{10}H_{18}O_5[M+H]^+$, m/z 219.1154. Found: 219.1156.



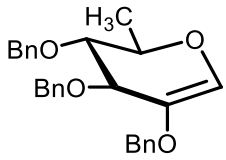
3h: Colorless oil; yield (46%). R_f 0.4 (Petroluem Ether/ Ethyl Acetate = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.94 (m, 4H), 7.51 (m, *J* = 4.7, 2.7 Hz, 2H), 7.39 (d, *J* = 3.9 Hz, 2H), 7.26 (m, *J* = 8.1, 4.0 Hz, 2H), 7.12 (s, 5H), 5.81 (t, *J* = 9.5 Hz, 1H), 4.68 (d, *J* = 3.4 Hz, 1H), 4.53 – 4.50 (m, 3H), 4.06 – 3.99 (m, 1H), 3.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.25 (s, C), 165.45 (s, C), 164.68 (s, C), 137.72 (s, C), 137.09 (s, C), 136.50 (s, C), 133.10 (d, *J* = 31.0 Hz, 2CH), 130.23 (s, C), 129.75 (d, *J* = 47.0 Hz, 4CH), 128.41 (d, *J* = 25.2 Hz, 4CH), 128.23 (s, 2CH), 127.88 (s, 4CH), 76.38 (s, CH), 74.27 (s, CH_2), 72.71 (s, CH), 68.59 (s, CH_3), 55.34 (s, CH). HRMS Calcd. For $C_{28}H_{24}O_8[M+H]^+$, m/z 489.1471. Found: 489.1475.



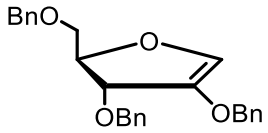
3i: Colorless oil; yield (41%). R_f 0.4 (Petroluem Ether/ Ethyl Acetate = 7 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 3H), 7.25 (s, 4H), 7.23 (s, 4H), 7.21 (d, *J* = 2.2 Hz, 4H), 4.88 (d, *J* = 4.2 Hz, 1H), 4.62 (m, *J* = 12.0, 8.4 Hz, 2H), 4.55 (s, 1H), 4.48 (d, *J* = 3.7 Hz, 2H), 4.42 (m, *J* = 12.0, 7.3 Hz, 2H), 4.11 – 4.05 (m, 2H), 4.02 – 3.97 (m, 1H), 3.55 – 3.45 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.18 (s, C), 137.06 (s, C), 136.65 (s, C), 136.41 (s, C), 127.34 (d, *J* = 4.2 Hz, 5CH), 127.24 (s, 2CH), 126.96 (s, 2CH), 126.80 (d, *J* = 2.8 Hz, 2CH), 126.73 (d, *J* = 2.7 Hz, 2CH), 126.61 (d, *J* = 3.3 Hz, 2CH), 83.21 (s, CH), 82.32 (s, CH),79.43 (s, CH), 72.31 (s, CH_2), 71.58 (s, CH_2), 71.33 (s, CH_2), 67.72 (s, CH_2). HRMS Calcd. For $C_{26}H_{26}O_4[M+H]^+$, m/z 403.1831. Found: 403.1838.



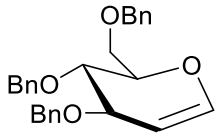
3j: Colorless oil; yield (69%). R_f 0.4 (Petroluem Ether/ Ethyl Acetate = 7 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 3.9 Hz, 5H), 7.24 (d, *J* = 5.1 Hz, 5H), 7.22 (d, *J* = 5.0 Hz, 5H), 6.33 (s, 1H), 4.64 – 4.55 (m, 4H), 4.50 (s, 2H), 4.00 (m, *J* = 11.8, 2.5, 1.6 Hz, 1H), 3.90 – 3.88 (m, 1H), 3.71 (m, *J* = 11.7, 0.9 Hz, 1H), 3.58 – 3.54 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.45 (s, C), 137.30 (s, C), 136.77 (s, C), 136.30 (s, C), 128.24 (s, CH), 127.47 (s, 2CH), 127.35 (d, *J* = 1.8 Hz, 4CH), 126.85 (d, *J* = 3.1 Hz, 3CH), 126.76 (s, 3CH), 126.64 (s, CH), 126.54 (s, 2CH), 71.46 (s, CH), 70.74 (s, CH_2), 70.04 (s, CH_2), 69.99 (s, CH), 69.85 (s, CH_2), 62.37 (s, CH_2). HRMS Calcd. For $C_{26}H_{26}O_4[M+H]^+$, m/z 403.1831. Found: 403.1833.



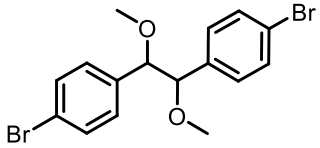
3k: Colorless oil; yield (65%). R_f 0.4 (Petroluem Ether/ Ethyl Acetate = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (s, 3H), 7.22 (d, *J* = 4.2 Hz, 7H), 7.19 (d, *J* = 6.7 Hz, 5H), 4.86 (d, *J* = 10.8 Hz, 1H), 4.77 (s, 1H), 4.63 (d, *J* = 5.8 Hz, 1H), 4.55 (m, *J* = 12.9, 4.7 Hz, 3H), 4.33 (d, *J* = 11.9 Hz, 1H), 3.83 (m, *J* = 9.2, 3.1 Hz, 1H), 3.73 (d, *J* = 1.9 Hz, 1H), 3.56 (t, *J* = 9.4 Hz, 1H), 1.29 (m, *J* = 29.8, 6.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.59 (s, C), 137.57 (s, C), 137.27 (s, C), 136.41 (s, C), 127.36 (s, 2CH), 127.30 (d, *J* = 2.2 Hz, 4CH), 127.01 (s, 2CH), 126.88 (s, 2CH), 126.71 (s, 2CH), 126.60 (s, 2CH), 126.47 (s, CH),79.53 (s, CH), 79.16 (s, CH), 74.39 (s, CH), 71.75 (s, CH), 71.17 (s, CH_2), 67.86 (s, CH_2), 67.27 (s, CH_2), 17.00 (s, CH_3). HRMS Calcd. For $C_{27}H_{28}O_4[M+H]^+$, m/z 417.1988. Found: 417.1990.



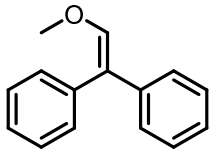
3l: Colorless oil; yield (48%). R_f 0.4 (Petroluem Ether/ Ethyl Acetate = 5 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 3.3 Hz, 5H), 7.26 – 7.23 (m, 7H), 7.22 (s, 3H), 6.10 (s, 1H), 4.70 (d, *J* = 11.4 Hz, 1H), 4.60 (md, *J* = 19.7, 13.9, 10.6 Hz, 4H), 4.48 (t, *J* = 5.5 Hz, 2H), 4.44 (dt, *J* = 6.1, 3.2 Hz, 1H), 3.47 (m, *J* = 10.1, 6.3 Hz, 1H), 3.33 (m, *J* = 10.2, 5.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.44 (s, C), 137.32 (s, C), 136.89 (s, C), 135.70 (s, C), 127.47 (s, 2CH), 127.40 (s, 2CH), 127.31 (s, 2CH), 127.01 (s, CH), 126.84 (s, 2CH), 126.70 (d, *J* = 2.8 Hz, 2CH), 126.55 (s, CH), 126.46 (s, 2CH), 126.07 (s, CH), 82.36 (s, CH), 80.16 (s, CH), 72.42 (s, CH_2), 71.53 (s, CH_2), 69.51 (s, CH_2), 68.81 (s, CH_2). HRMS Calcd. For $C_{26}H_{26}O_4[M+H]^+$, m/z 403.1831. Found: 403.1835.



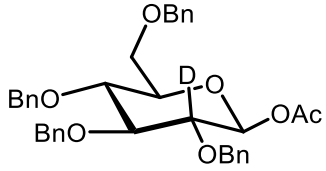
3m: Colorless oil; yield (69%). R_f 0.4 (Petroluem Ether/ Ethyl Acetate = 7 : 1);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.21 (m, 15H), 6.47 (dd, *J* = 6.1, 1.0 Hz, 1H), 4.97 – 4.81 (m, 2H), 4.65 (ddd, *J* = 29.4, 14.3, 7.3 Hz, 5H), 4.26 (ddd, *J* = 6.1, 2.2, 1.4 Hz, 1H), 4.16 – 4.06 (m, 1H), 3.95 – 3.77 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.75 (s, CH), 138.38 (s, C), 138.22 (s, C), 138.03 (s, C), 128.53 – 128.26 (m, 6CH), 127.93 (s, 2CH), 127.78 (d, *J* = 5.5 Hz, 5CH), 127.67 (s, 2CH), 99.98 (s, CH), 76.79 (s, CH), 75.77 (s, CH), 74.44 (s, CH), 73.77 (s, CH_2), 73.54 (s, CH_2), 70.49 (s, CH_2), 68.57 (s, CH_2). HRMS Calcd. For $C_{27}H_{28}O_4[M+H]^+$, m/z 417.1988. Found: 417.1991.



IV-3: white solid; yield (19%). R_f 0.4 (Petroluem Ether/ Dichloromethane = 2 : 1);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.3 Hz, 4H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 6.7 Hz, 1H), 5.37 (s, 1H), 3.29 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.36 (s, C), 140.83 (s, C), 137.11 (s, 2C), 128.78 (s, 2CH), 127.38 (s, 2CH), 127.16 (d, *J* = 0.9 Hz, 2CH), 126.99 (s, 2CH), 103.08 (s, 2CH), 52.78 (s, $2CH_3$). HRMS Calcd. For $C_{16}H_{16}Br_2O_2[M+H]^+$, m/z 399.9497. Found: 399.9495.

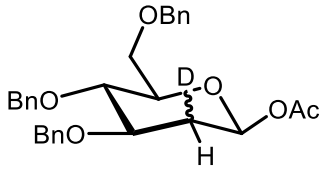


IV-4: Colorless liquid; yield (33%). R_f 0.4 (Petroluem Ether/ Dichloromethane = 2 : 1); 1H NMR (400 MHz, CDCl3) δ 7.31 (d, J = 7.4 Hz, 2H), 7.22 (dd, J = 14.7, 7.4 Hz, 4H), 7.15 (t, J = 7.3 Hz, 4H), 6.38 (s, 1H), 3.69 (s, 3H).13C NMR (101 MHz, CDCl3) δ 146.37 (s, CH), 140.46 (s, C), 137.66 (s, C), 129.87 (s, 2CH), 128.26 (d, J = 3.0 Hz, 4CH), 127.98 (s, 2CH), 126.60 (s, C), 126.44 (s, C), 120.59 (s, C), 60.59 (s, CH_3). HRMS Calcd. For $C_{15}H_{14}O[M+H]^+$, m/z 211.1045. Found: 211.1042.

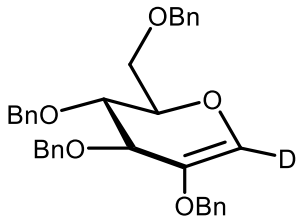


2*D*-2a: Colorless oil; yield (89%). R_f 0.4 (Petroluem Ether/ Ethyl Acetate = 5 : 1);^{1}H NMR (400 MHz,) δ 7.29 (ddd, *J* = 49.5, 29.6, 18.6 Hz), 5.64 (d, *J* = 8.1 Hz), 4.92 (t, *J* = 8.2 Hz), 4.90 – 4.77 (m), 4.67 (d, *J* = 12.1 Hz), 4.54 (dd, *J* = 19.3, 11.4 Hz), 3.82 – 3.72 (m), 3.63 (dd, *J* = 15.4, 7.6 Hz), 2.09 (s). ^{13}C NMR (400 MHz,) δ 169.27 (s, C), 138.46 (s, C), 138.20 (s, C), 138.13 (s, C), 138.00 (s, C), 128.44 (s, 8CH), 127.92 (d, *J* = 30.9 Hz, 12CH), 94.11 (s, CH), 84.87 (s, CH), 81.15 (s, CH), 78.82 (s, CH), 77.34 (s, CH), 75.72 (s, CH_2), 75.60 (s, CH_2), 75.04 (s, CH_2), 73.57 (s, CH_2), 68.24 (s, CH_2),

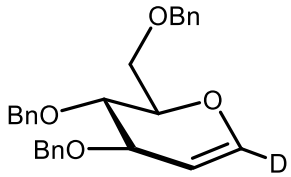
21.08 (s, CH_3). HRMS Calcd. For $C_{36}H_{37}DO_7$ $[M+H]^+$, m/z 584.2680. Found: 584.2683.



2*D*-2m: Colorless oil; yield (85%). R_f 0.4 (Petroluem Ether/ Ethyl Acetate = 7 : 1); ^{1}H NMR (400 MHz,) δ 7.25 (dt, *J* = 18.4, 6.0 Hz), 6.57 (s), 4.60 (d, *J* = 3.5 Hz), 4.55 – 4.40 (m), 4.33 (t, *J* = 7.3 Hz), 4.15 (d, *J* = 11.6 Hz), 3.99 (d, *J* = 5.9 Hz), 3.71 (d, *J* = 3.1 Hz), 2.13 (s), 1.76 (s), 1.66 (s). ^{13}C NMR (400 MHz,) δ 169.24 (s, C), 140.95 (s, C), 137.54 (s, C), 137.43 (s, C), 128.58 (s, 2CH), 128.51 (s, 2CH), 128.40 (d, *J* = 15.6 Hz, 5CH), 128.02 (s, CH), 127.93 (s, CH), 127.82 (s, 2CH), 127.65 (s, CH), 127.00 (s, CH), 105.20 (s, CH), 81.05 (s, CH), 78.35 (s, CH), 74.61 (s, CH), 74.14 (s, CH_2), 73.64 (s, CH_2), 67.90 (s, CH_2), 65.37 (s, CH_2), 27.21 (s, CH_2), 19.89 (s, CH_3). HRMS Calcd. For $C_{29}H_{31}DO_6[M+H]^+$, m/z 478.2262. Found: 478.2261.



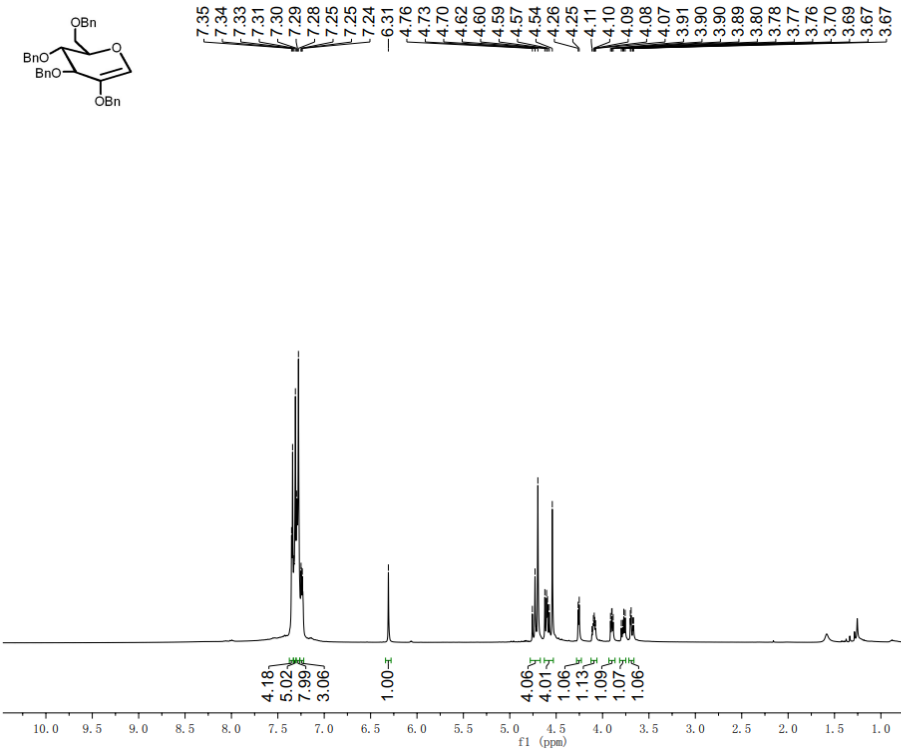
1*D*-3a: Colorless oil; yield (71%). R_f 0.4 (Petroluem Ether/ Ethyl Acetate = 7 : 1); ^{1}H NMR (400 MHz,) δ 7.44 – 7.26 (m, 20H), 6.31 (s, 1D), 4.77 – 4.68 (m, 4H), 4.64 – 4.53 (m, 4H), 4.26 (d, *J* = 4.5 Hz, 1H), 4.13 – 4.05 (m, 1H), 3.90 (dd, *J* = 6.5, 4.8 Hz, 1H), 3.80 – 3.74 (m, 1H), 3.69 (dd, *J* = 10.6, 3.4 Hz, 1H). ^{13}C NMR (400 MHz,) δ 138.94 (s, C), 138.43 (s, C), 138.09 (s, C), 137.97 (s, C), 137.22 (s, C), 128.91 (s, 2CH), 128.44 (s, 3CH), 128.37 (d, *J* = 14.8 Hz, 3CH), 127.94 (d, *J* = 12.0 Hz, 5CH), 127.81 (d, *J* = 18.2 Hz, 5CH), 127.61 (d, *J* = 12.8 Hz, 2CH), 76.26 (s, CH), 75.60 (s, CH), 74.31 (s, CH), 73.46 (s, CH_2), 72.88 (s, CH_2), 72.30 (s, CH_2), 71.09 (s, CH_2), 68.31 (s, CH_2). HRMS Calcd. For $C_{34}H_{33}DO_5[M+H]^+$, m/z 524.2469. Found: 524.2466.



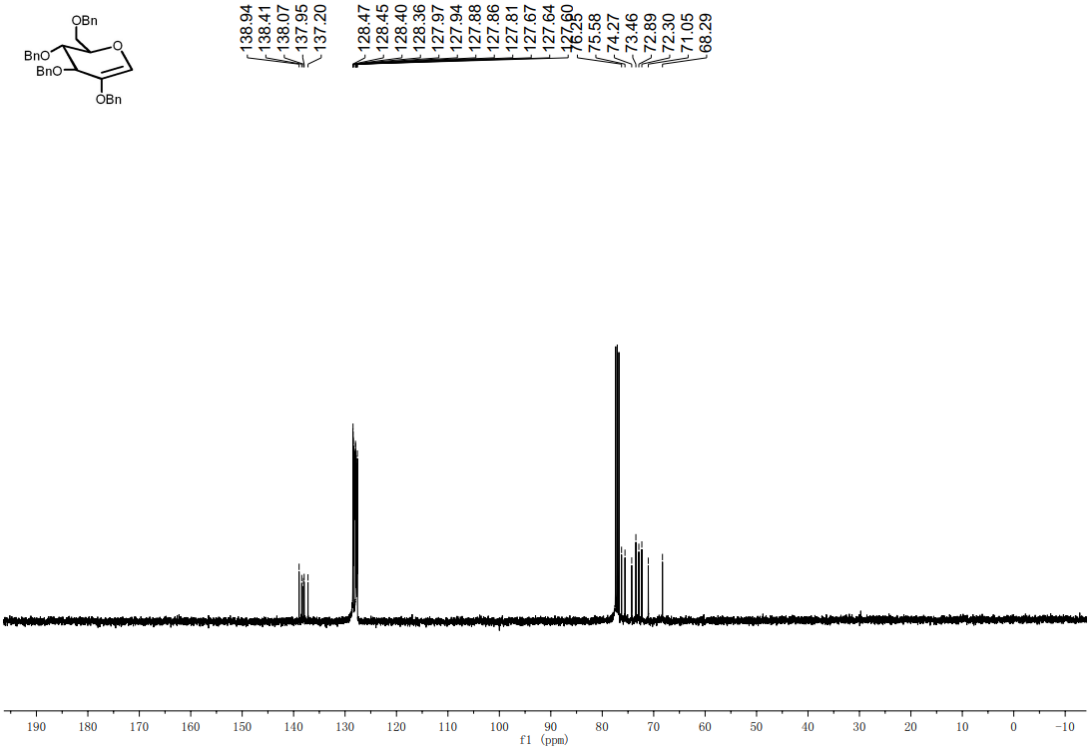
1*D*-3m: Colorless oil; yield (67%). R_f 0.4 (Petroluem Ether/ Ethyl Acetate = 10 : 1); ^{1}H NMR (400 MHz,) δ 7.31 – 7.13 (m, 15H), 6.33 (d, *J* = 5.8 Hz, 1D), 4.82 – 4.70 (m, 2H), 4.59 – 4.43 (m, 5H), 4.13 (d, *J* = 4.9 Hz, 1H), 4.02 – 3.94 (m, 1H), 3.82 – 3.62 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.02 (s, CH), 138.65 (s, C), 138.50 (s, C), 138.30 (s, C), 128.70 (d, *J* = 1.7 Hz, 6CH), 128.21 (s, 2CH), 128.06 (d, *J* = 5.5 Hz, 5CH), 127.95 (s, 2CH), 100.25 (s, CH), 77.04 (s, CH), 76.04 (s, CH), 74.71 (s, CH), 74.04 (s, CH_2), 73.80 (s, CH_2), 70.76 (s, CH_2), 68.83 (s, CH_2). HRMS Calcd. For

$C_{27}H_{27}DO_4[M+H]^+$, m/z 418.2050. Found: 418.2053.

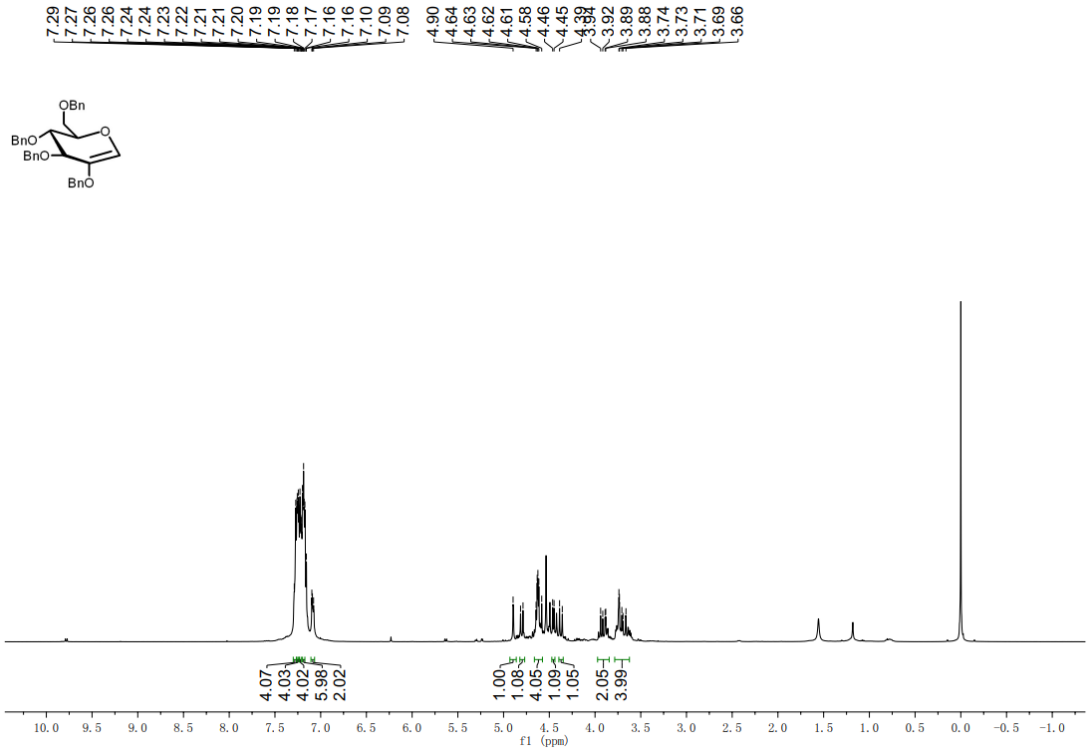
6. Copies of ^{1}H NMR, ^{13}C NMR Spectra of Compounds 3.



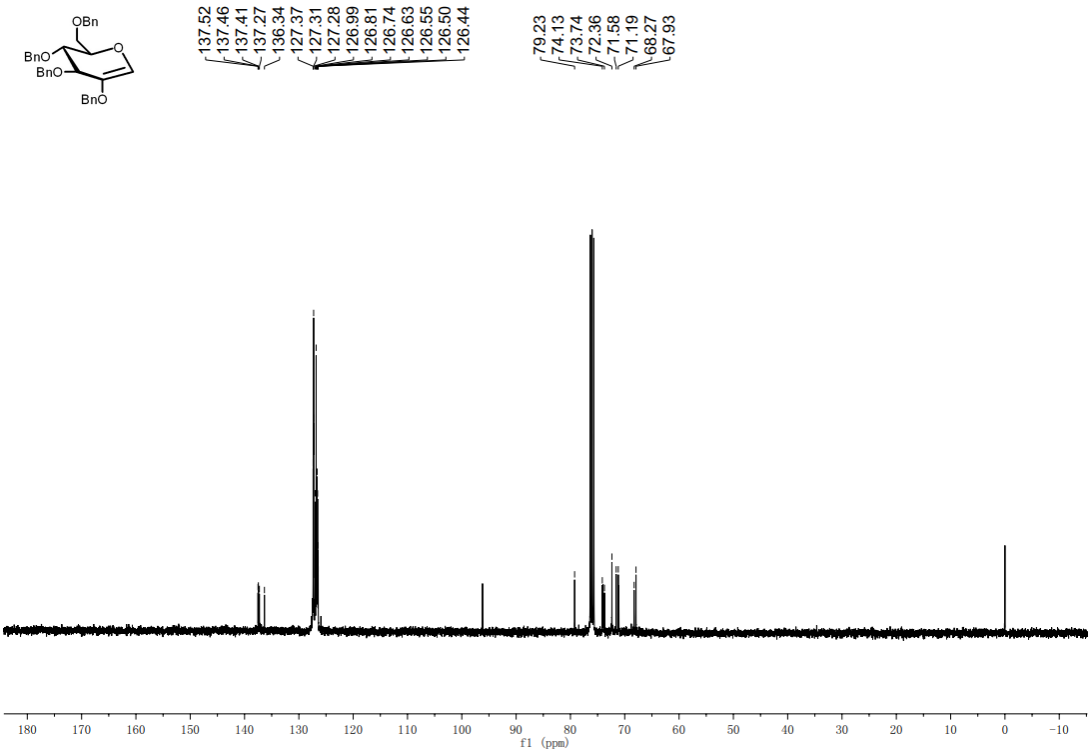
^{1}H NMR ($CDCl_3$-*d*) of **3a**



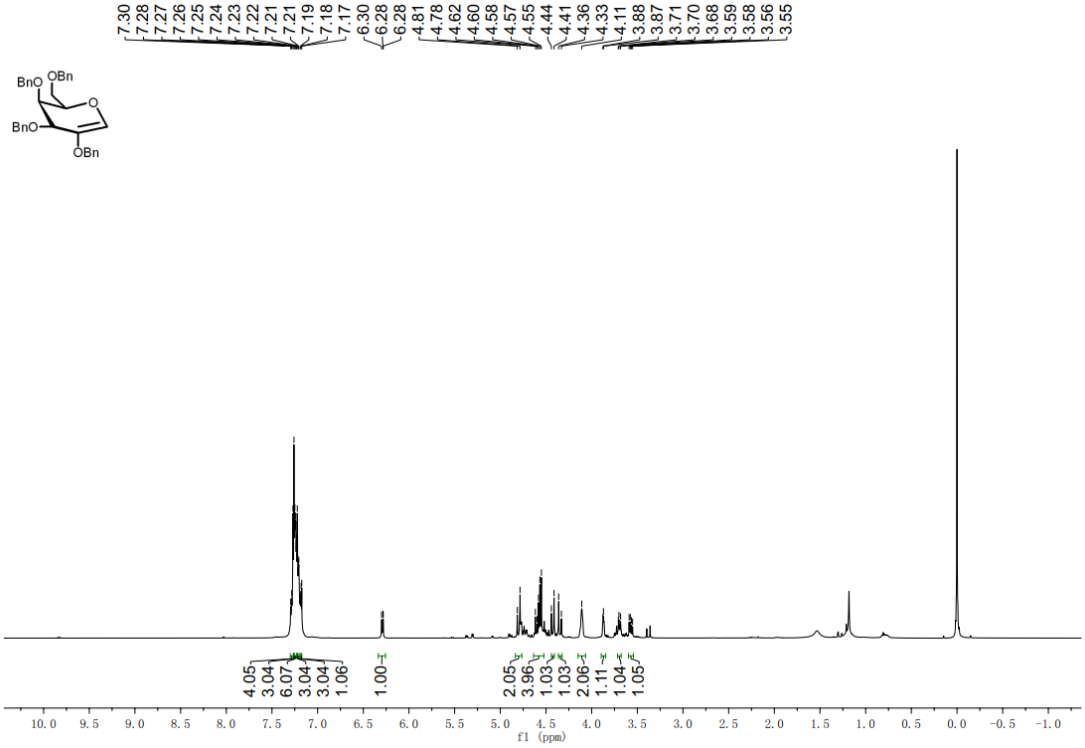
^{13}C NMR ($CDCl_3$-*d*) of **3a**



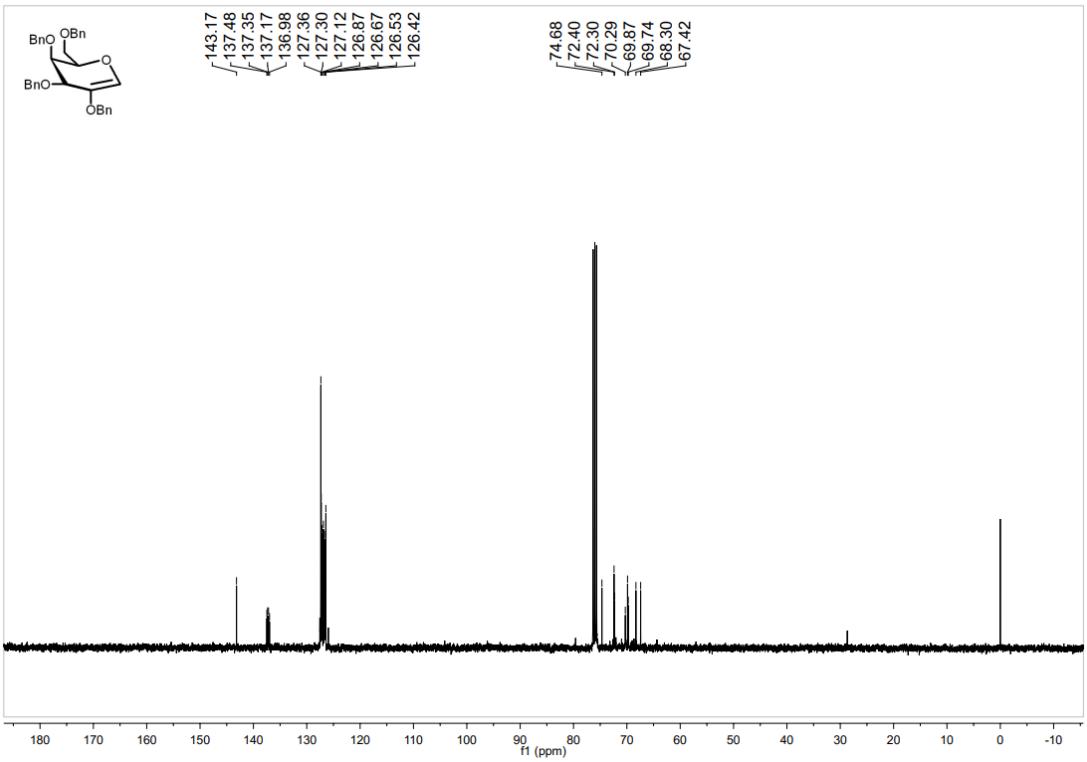
^{1}H NMR ($CDCl_3$-*d*) of **3a'**



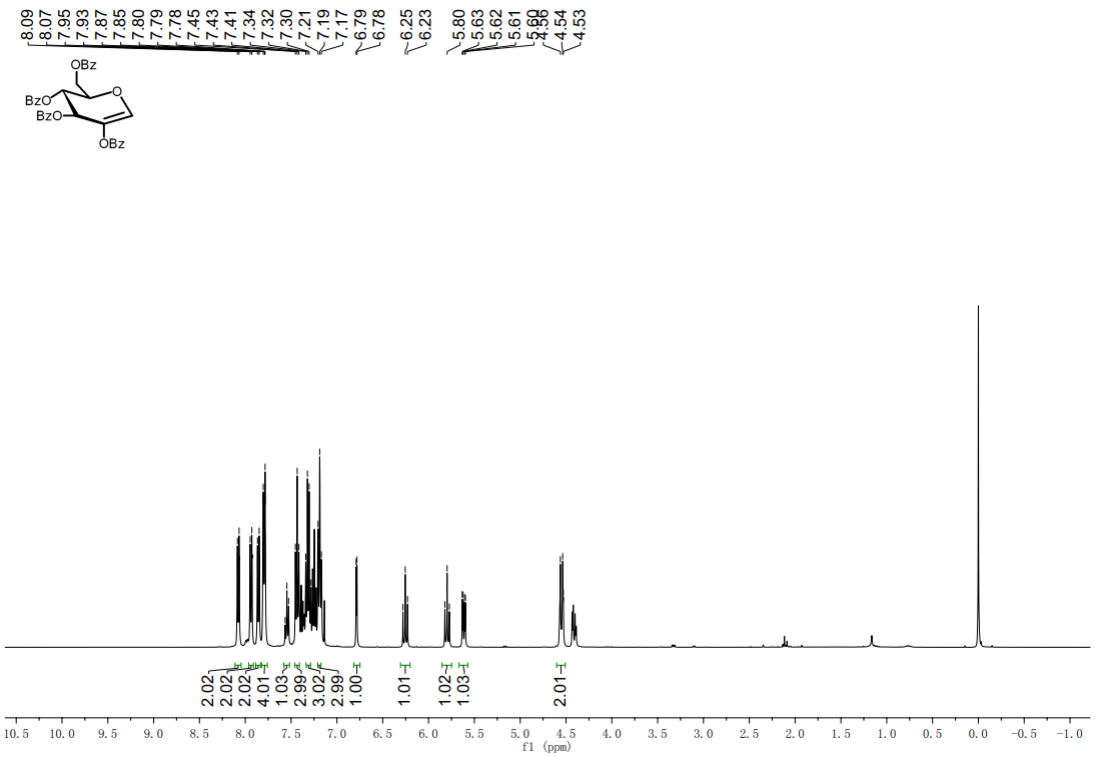
^{13}C NMR ($CDCl_3$-*d*) of **3a'**



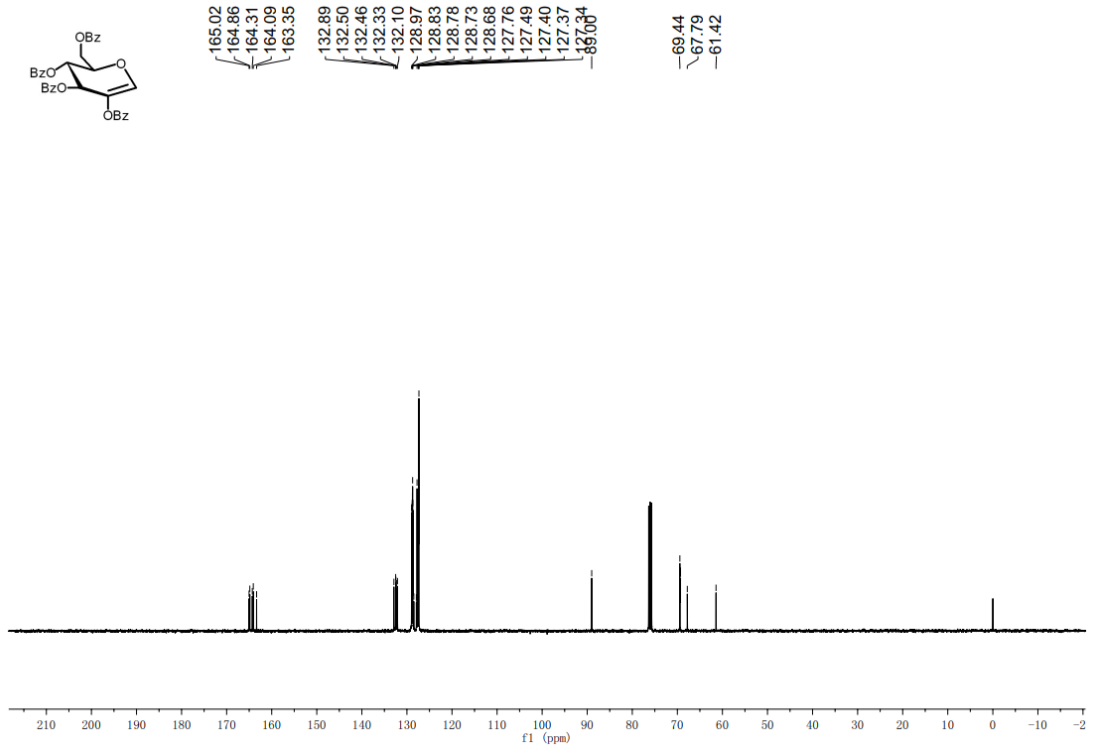
^{1}H NMR ($CDCl_3$-*d*) of **3b**



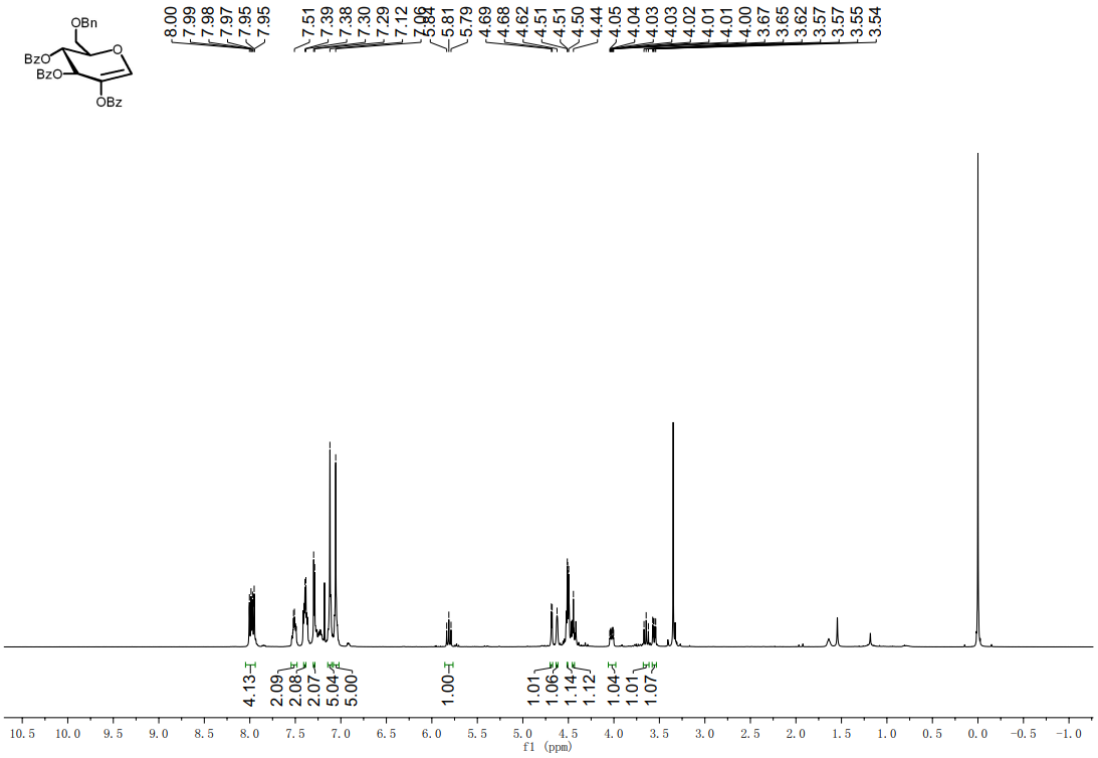
^{13}C NMR ($CDCl_3$-*d*) of **3b**



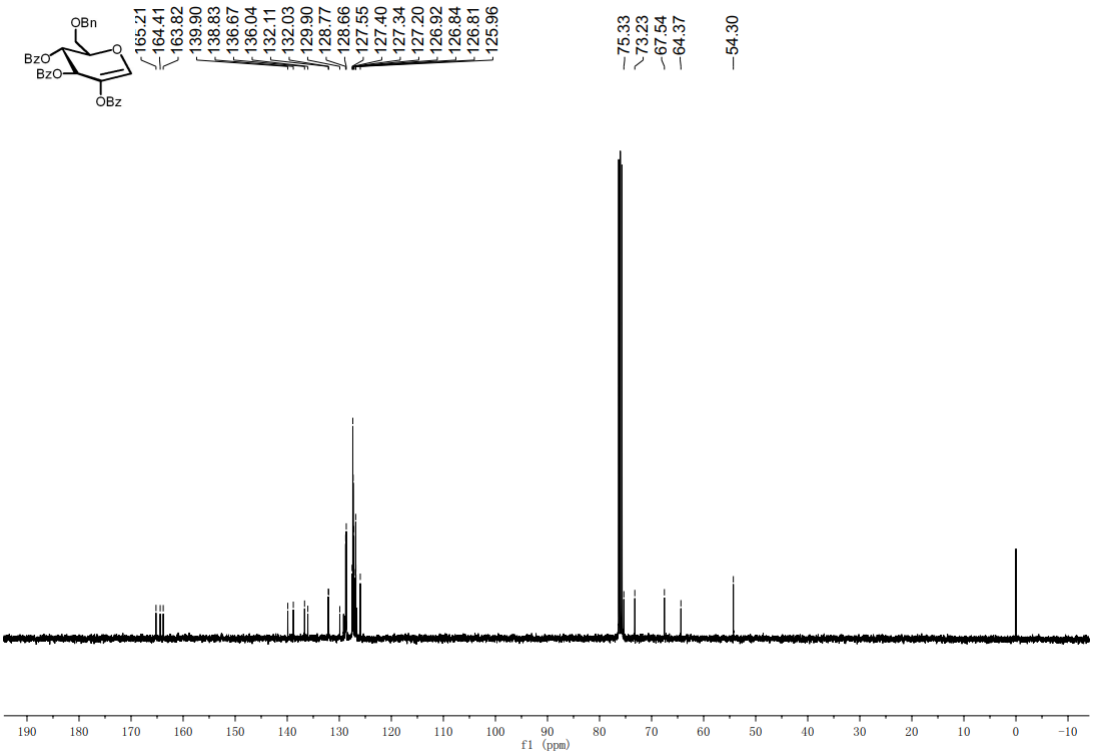
^{1}H NMR ($CDCl_3$-*d*) of **3c**



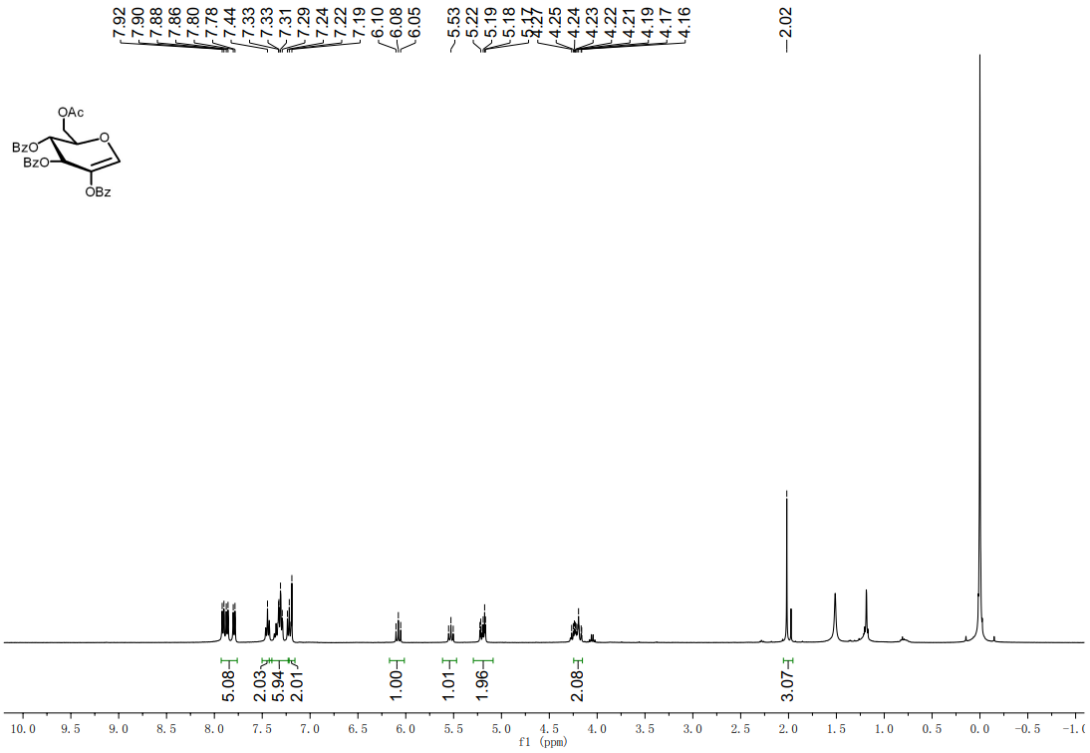
^{13}C NMR ($CDCl_3$-*d*) of **3c**



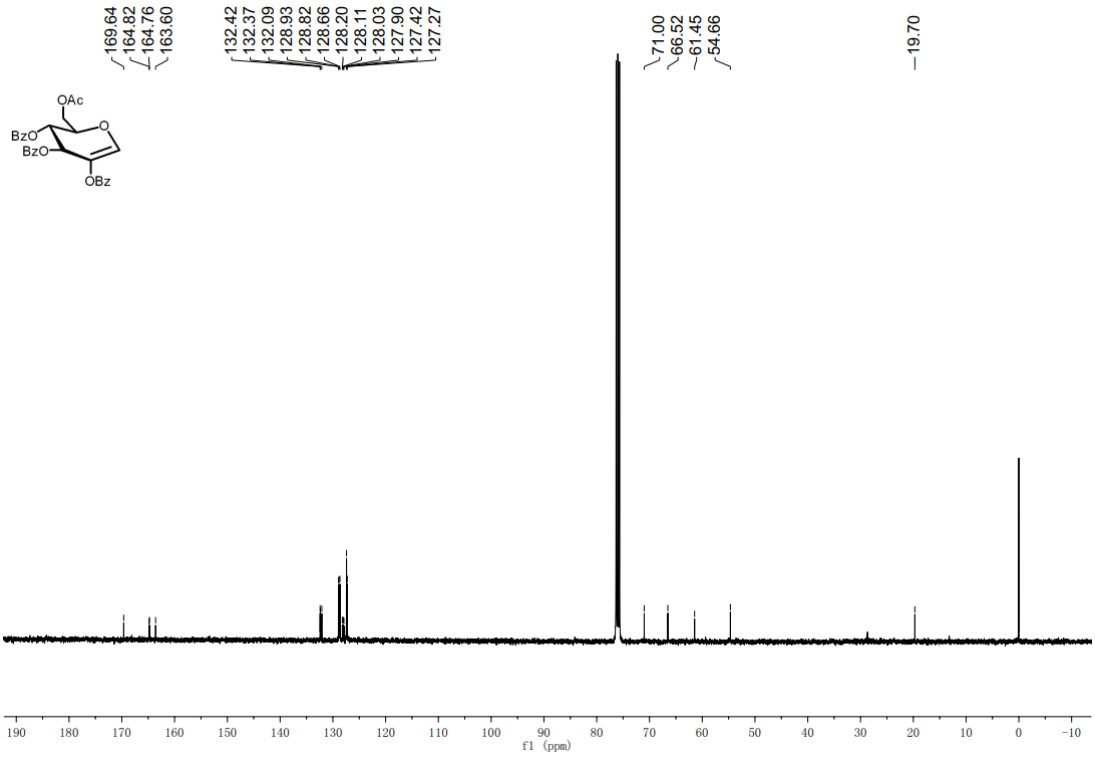
^{1}H NMR ($CDCl_3$-*d*) of **3d**



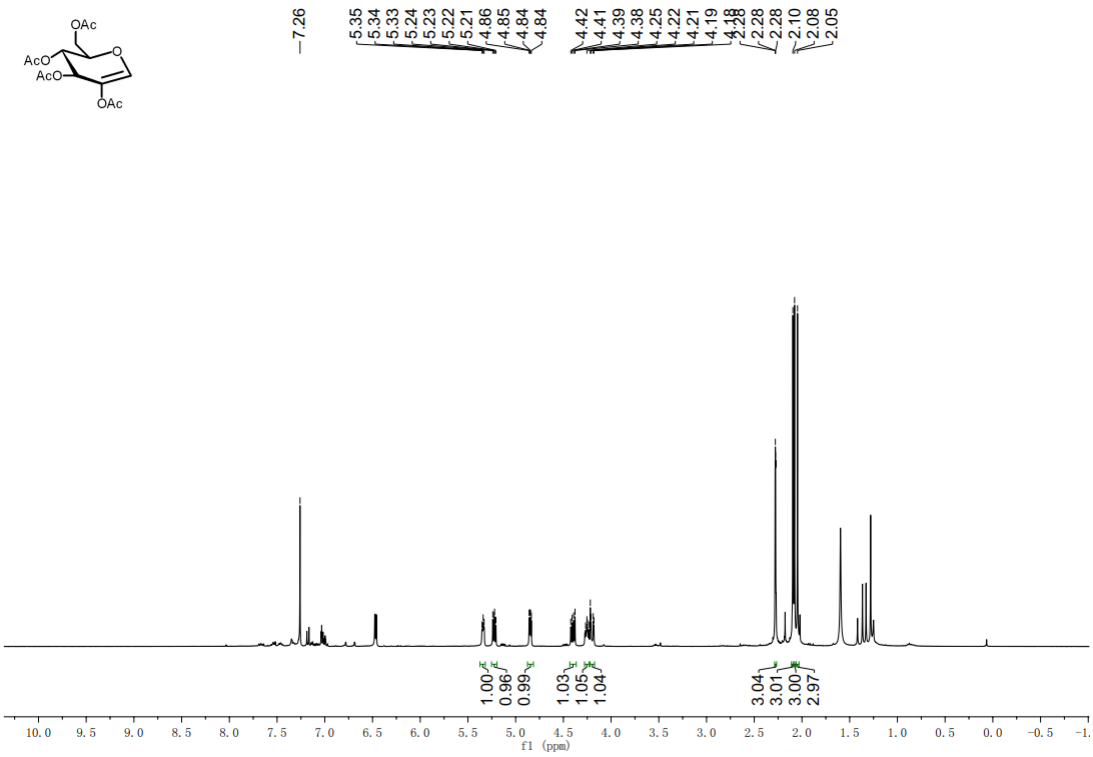
^{13}C NMR ($CDCl_3$-*d*) of **3d**



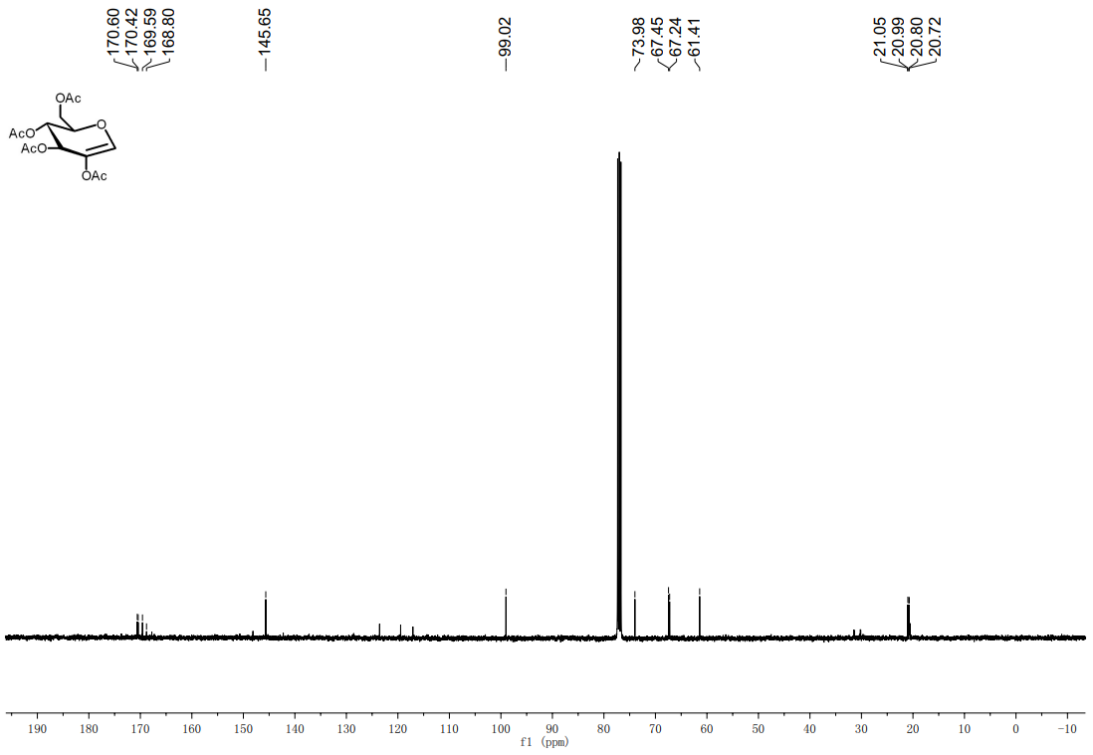
^{1}H NMR ($CDCl_3$-*d*) of **3e**



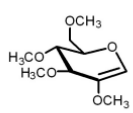
^{13}C NMR ($CDCl_3$-*d*) of **3e**

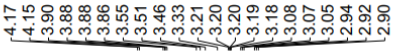


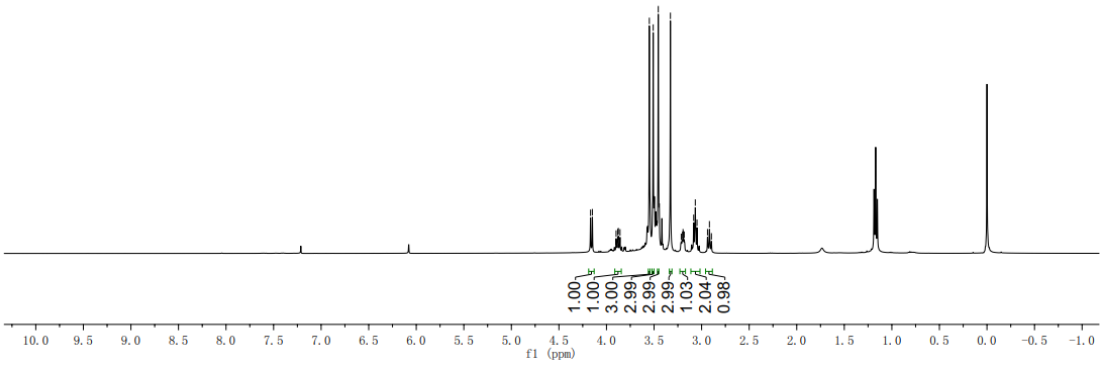
^{1}H NMR ($CDCl_3$-*d*) of **3f**



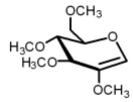
^{13}C NMR ($CDCl_3$-*d*) of **3f**

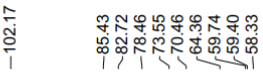


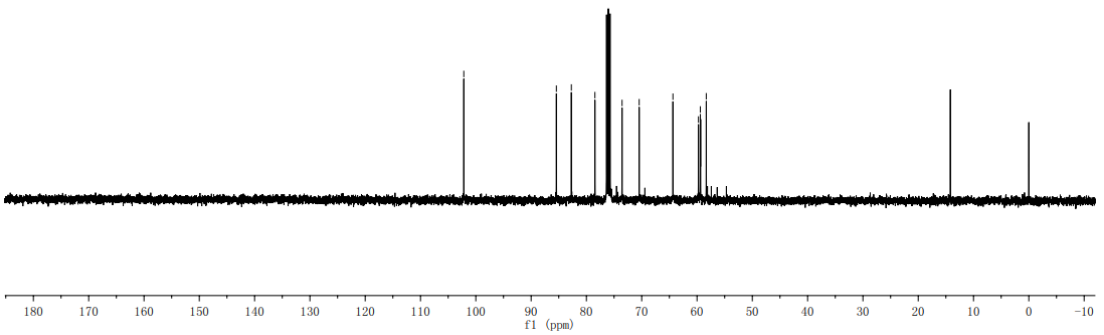




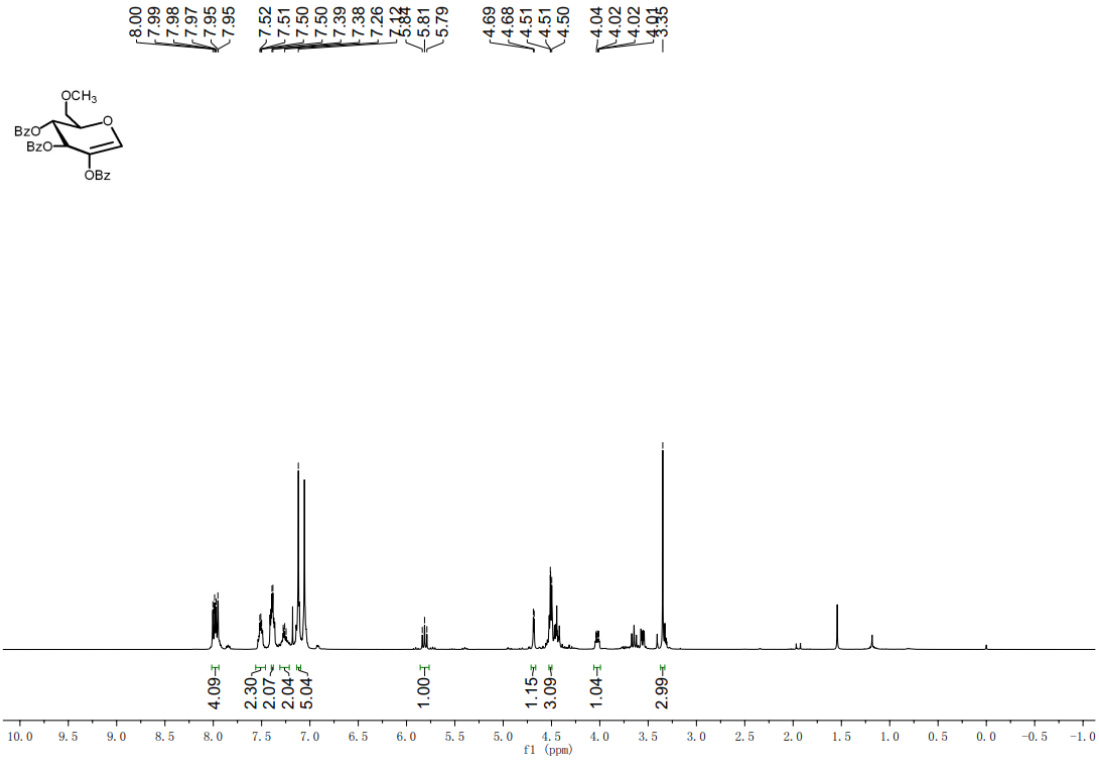
^{1}H NMR ($CDCl_3$-*d*) of **3g**



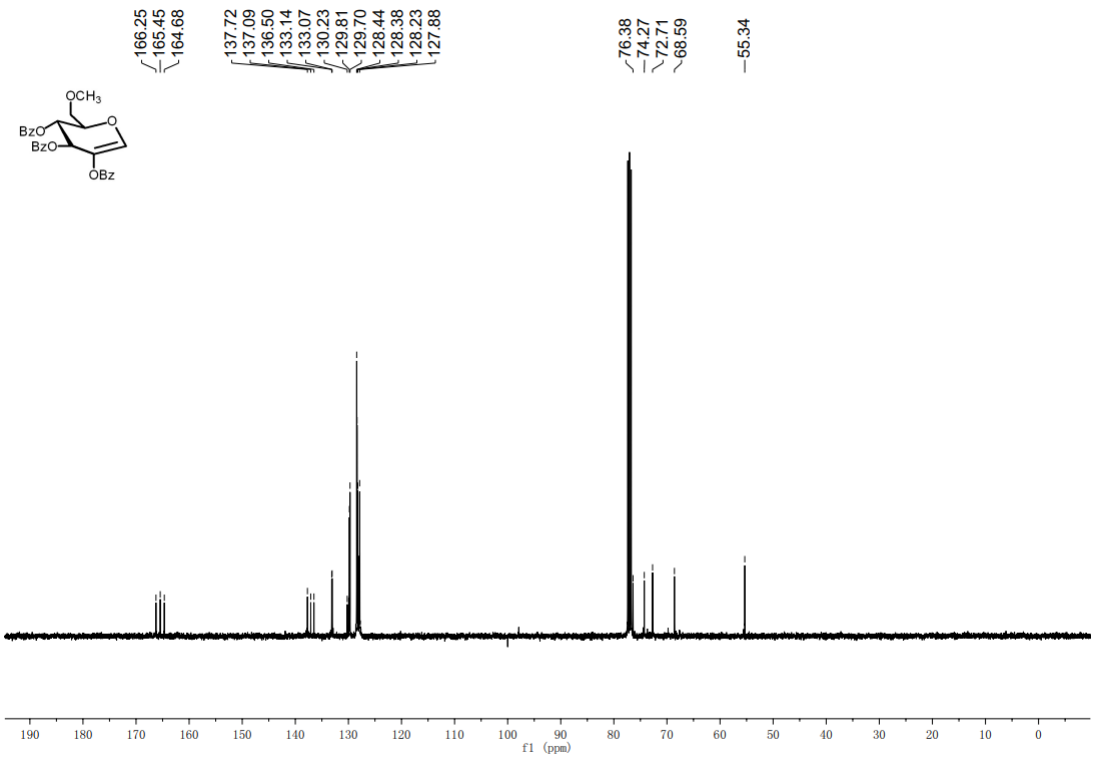




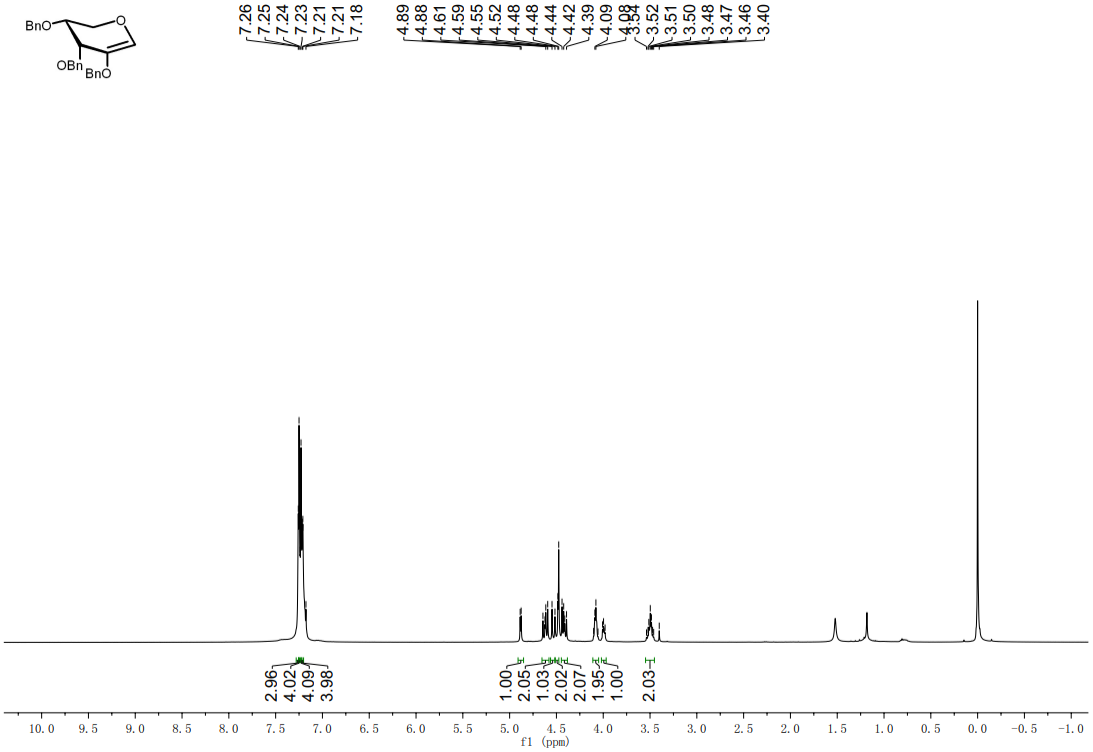
^{13}C NMR ($CDCl_3$-*d*) of **3g**



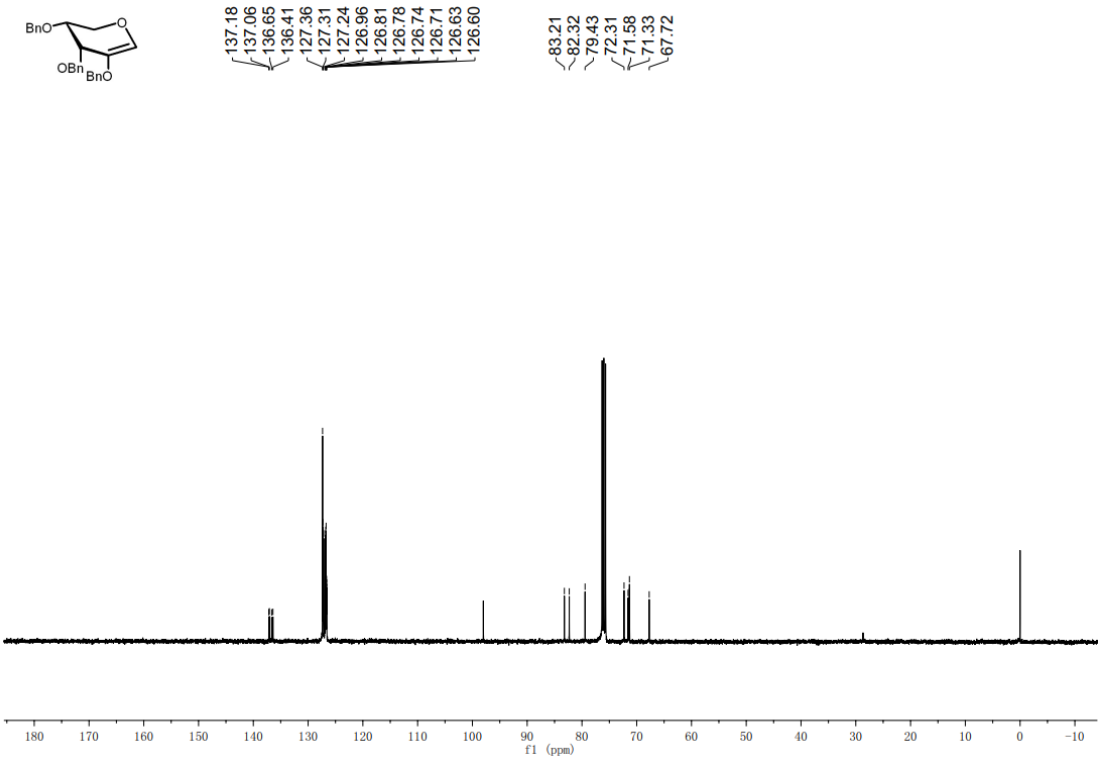
^{1}H NMR ($CDCl_3$-*d*) of **3h**



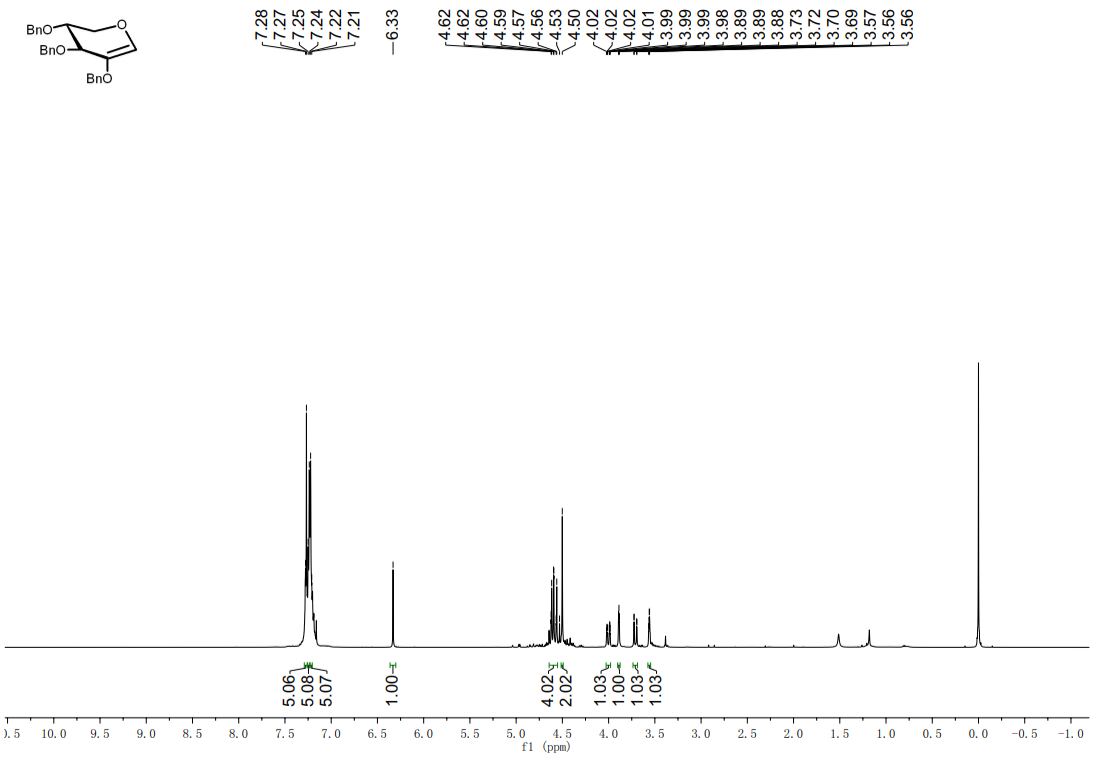
^{13}C NMR ($CDCl_3$-*d*) of **3h**



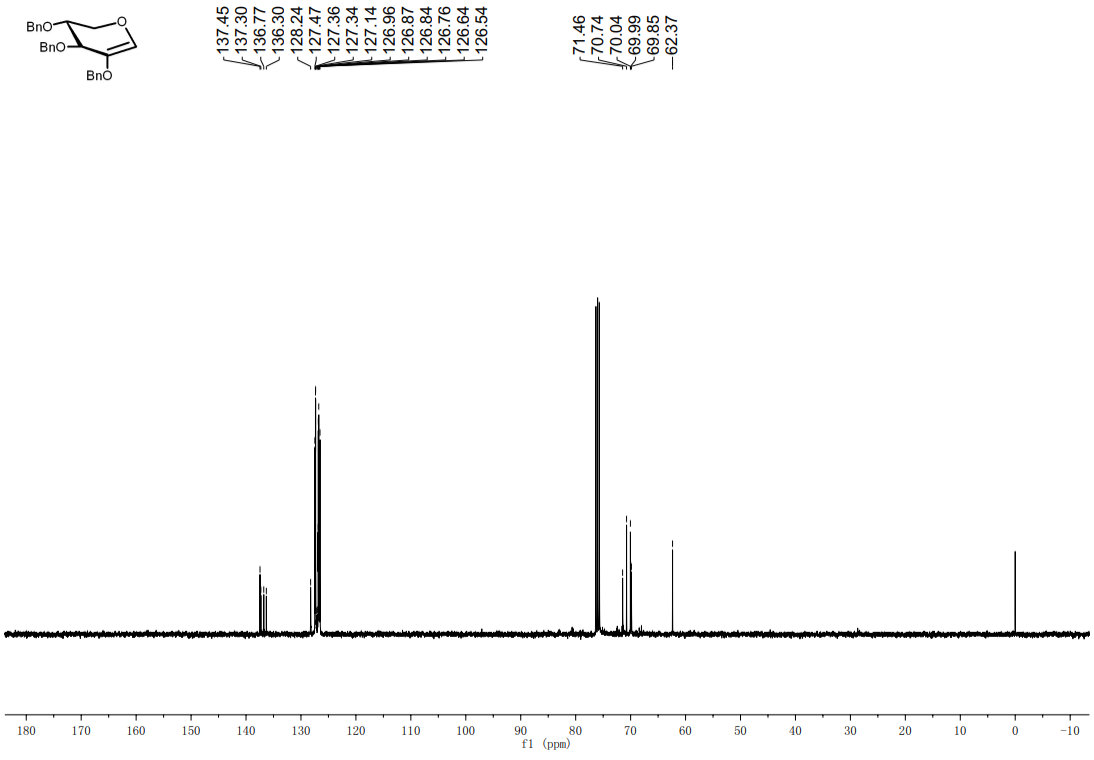
^{1}H NMR ($CDCl_3$-*d*) of **3i**



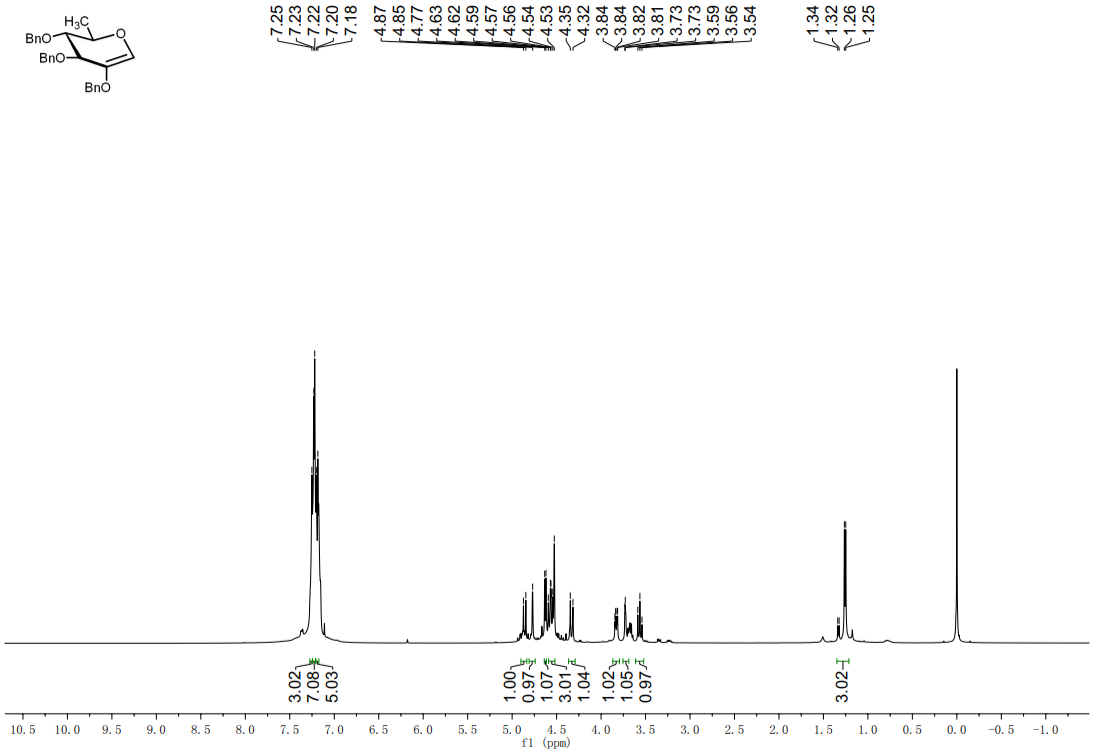
^{13}C NMR ($CDCl_3$-*d*) of **3i**



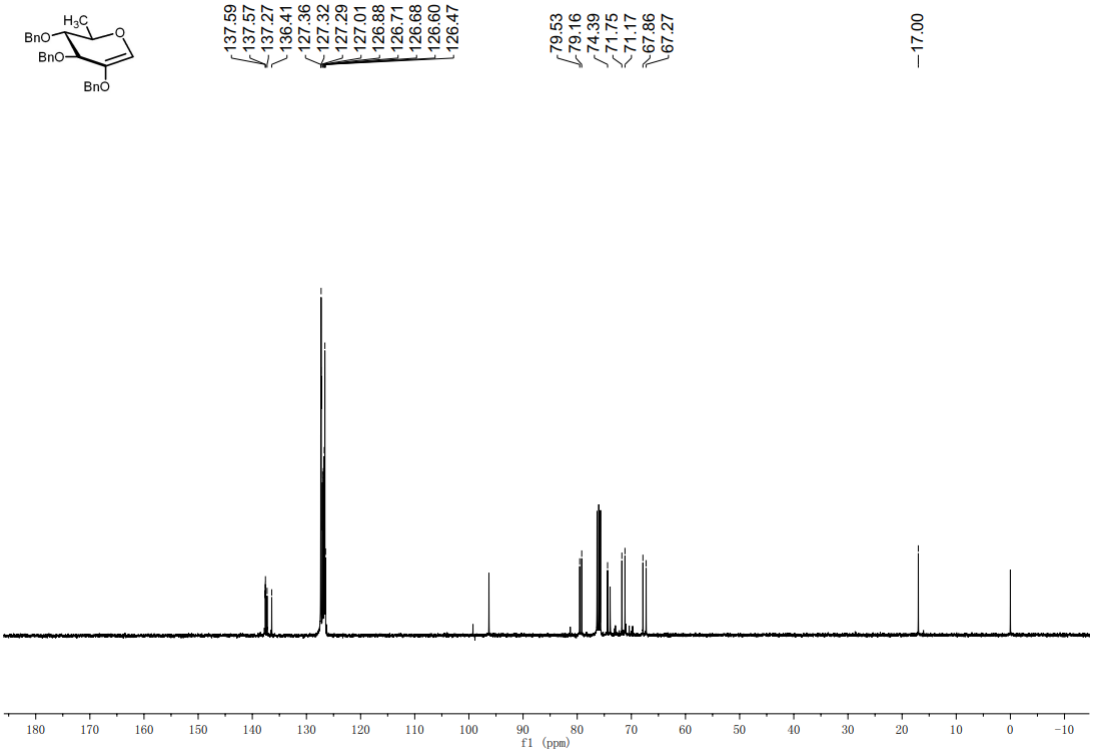
^{1}H NMR ($CDCl_3$-*d*) of **3j**



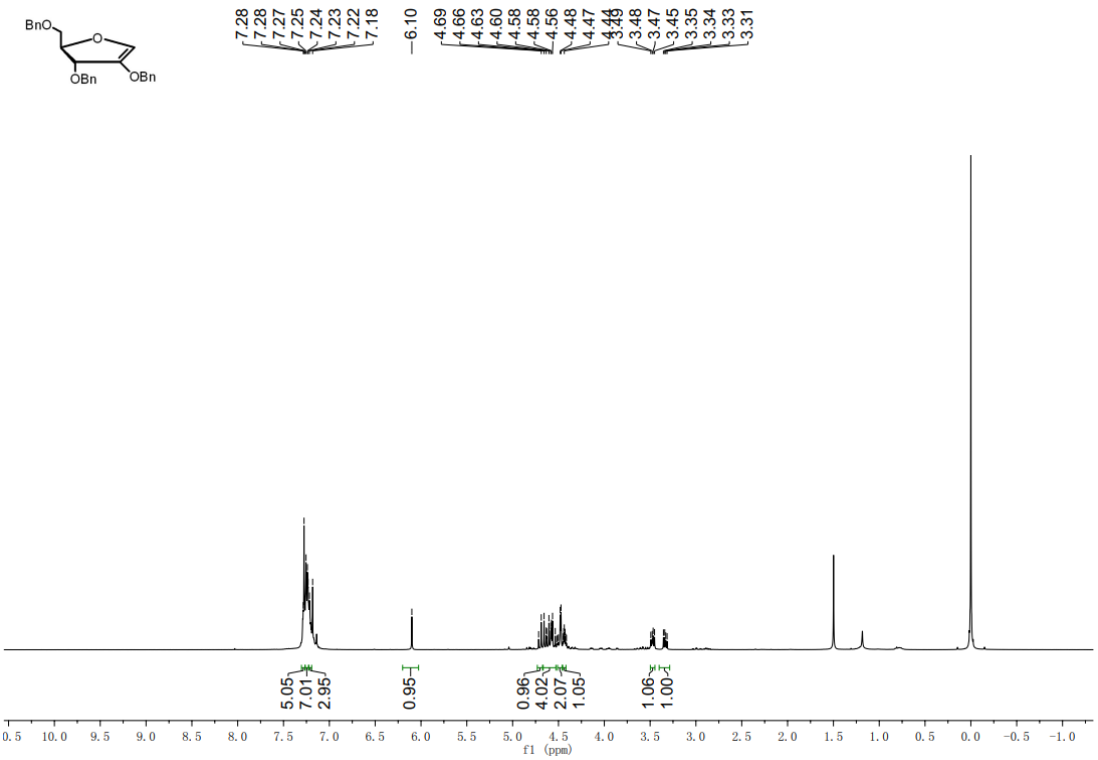
^{13}C NMR ($CDCl_3$-*d*) of **3j**



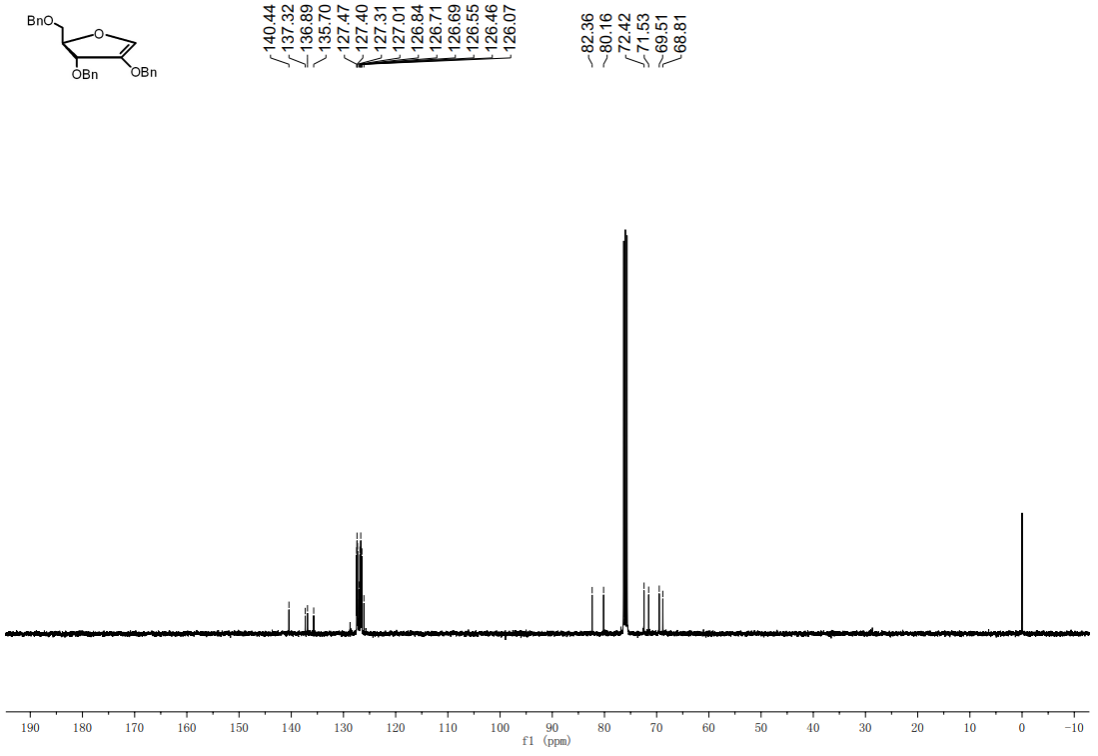
^{1}H NMR ($CDCl_3$-*d*) of **3k**



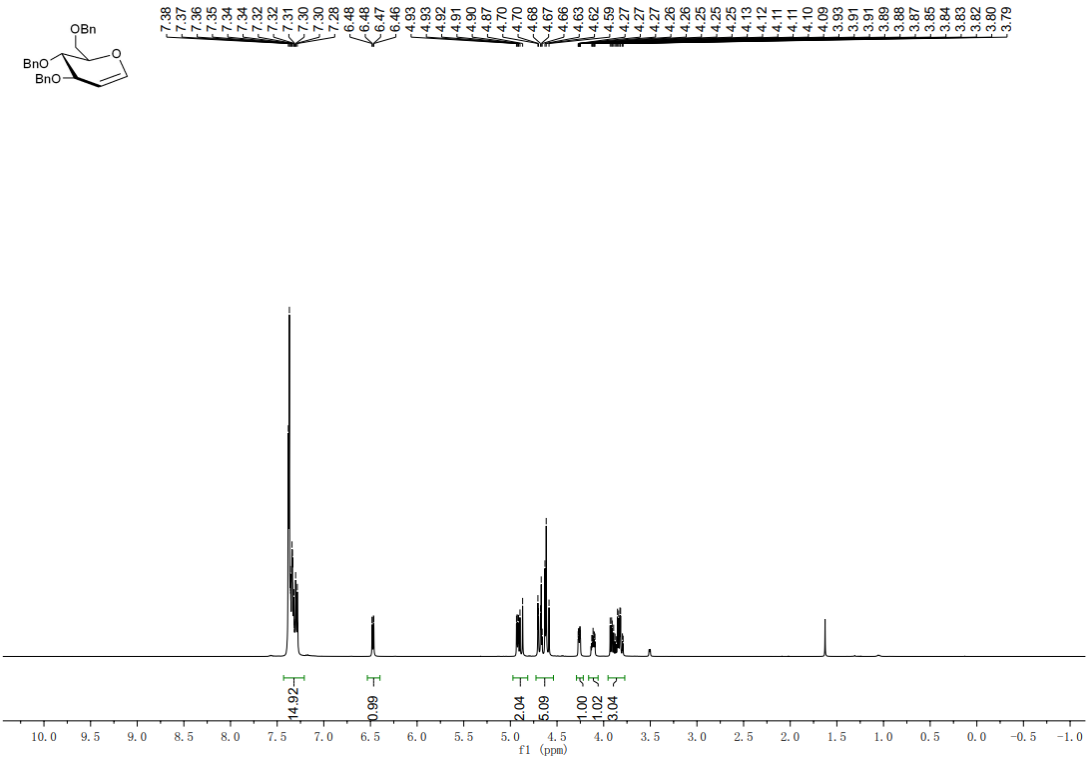
^{13}C NMR ($CDCl_3$-*d*) of **3k**



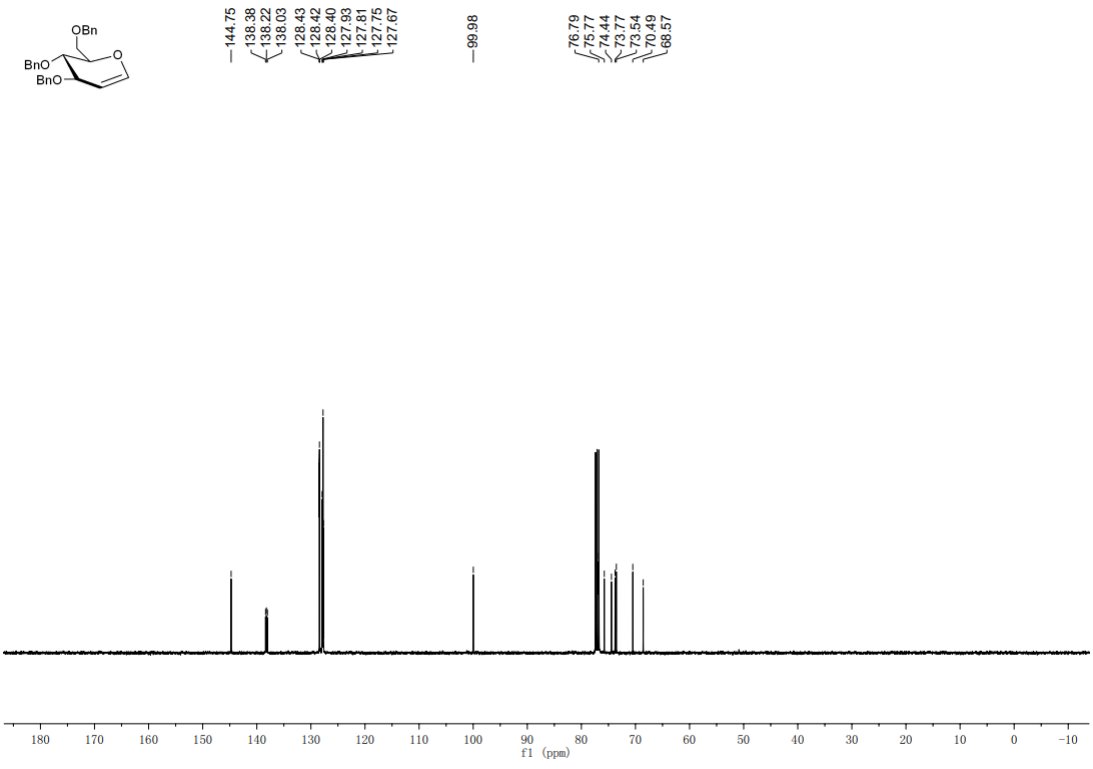
^{1}H NMR ($CDCl_3$-*d*) of **3l**



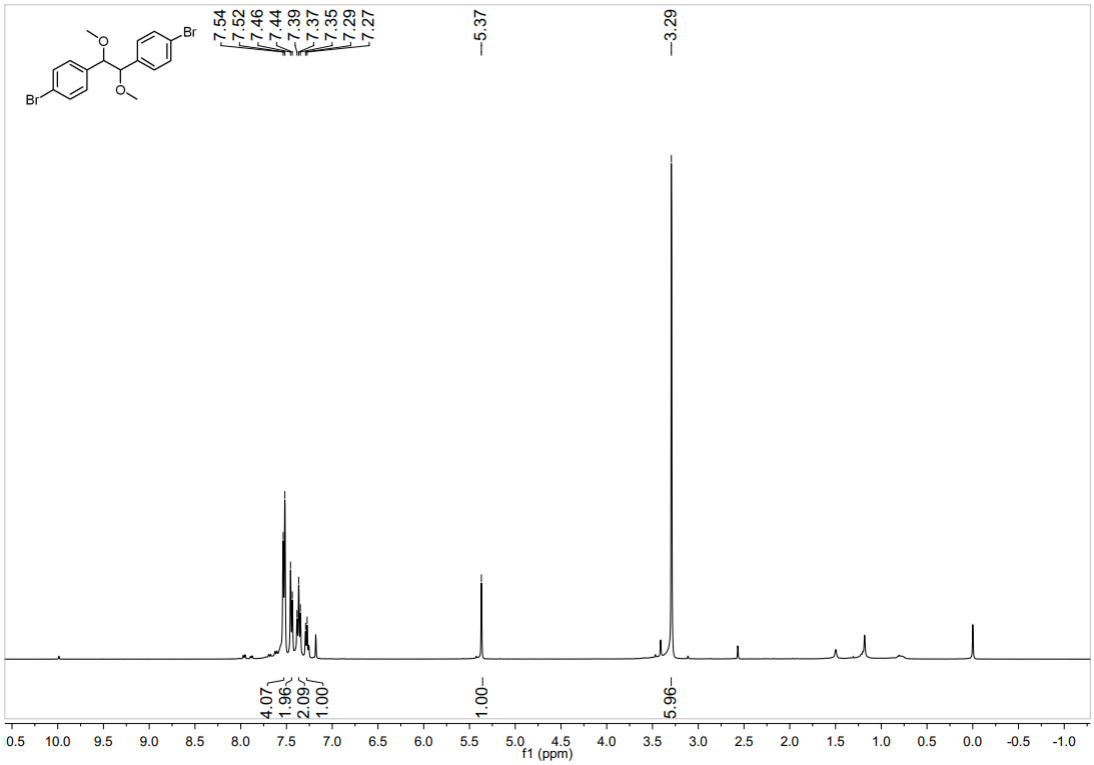
^{13}C NMR ($CDCl_3$-*d*) of **3l**



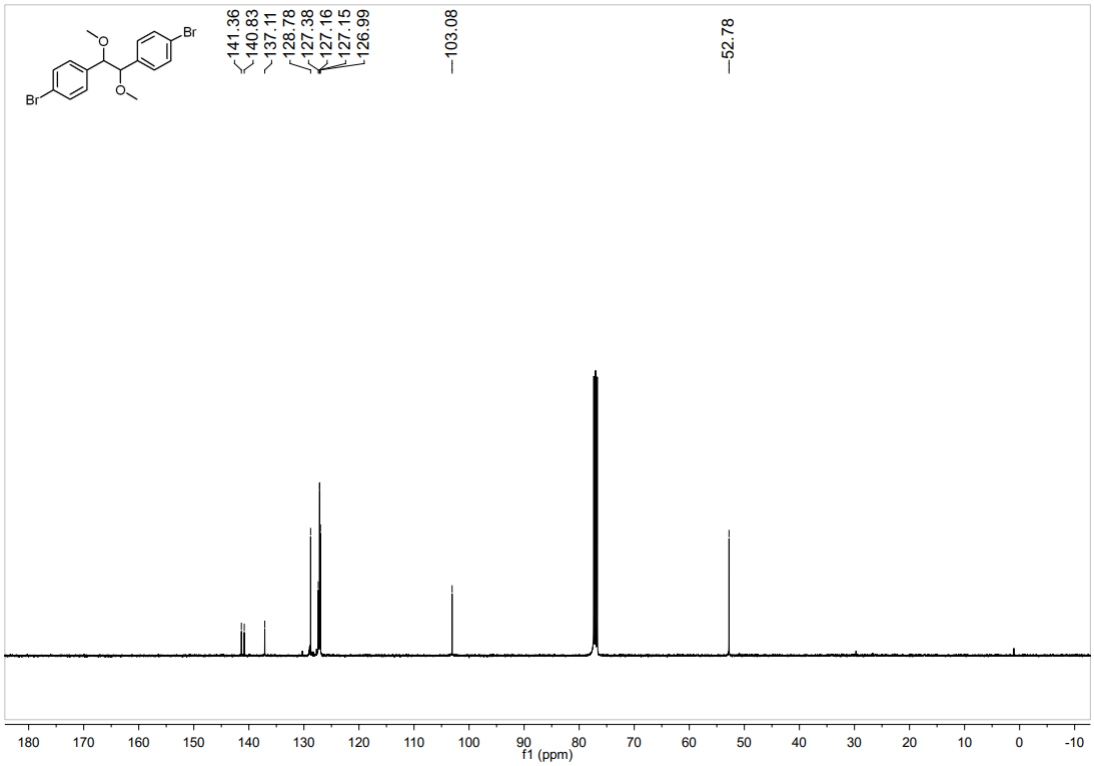
^{1}H NMR ($CDCl_3$-*d*) of **3m**



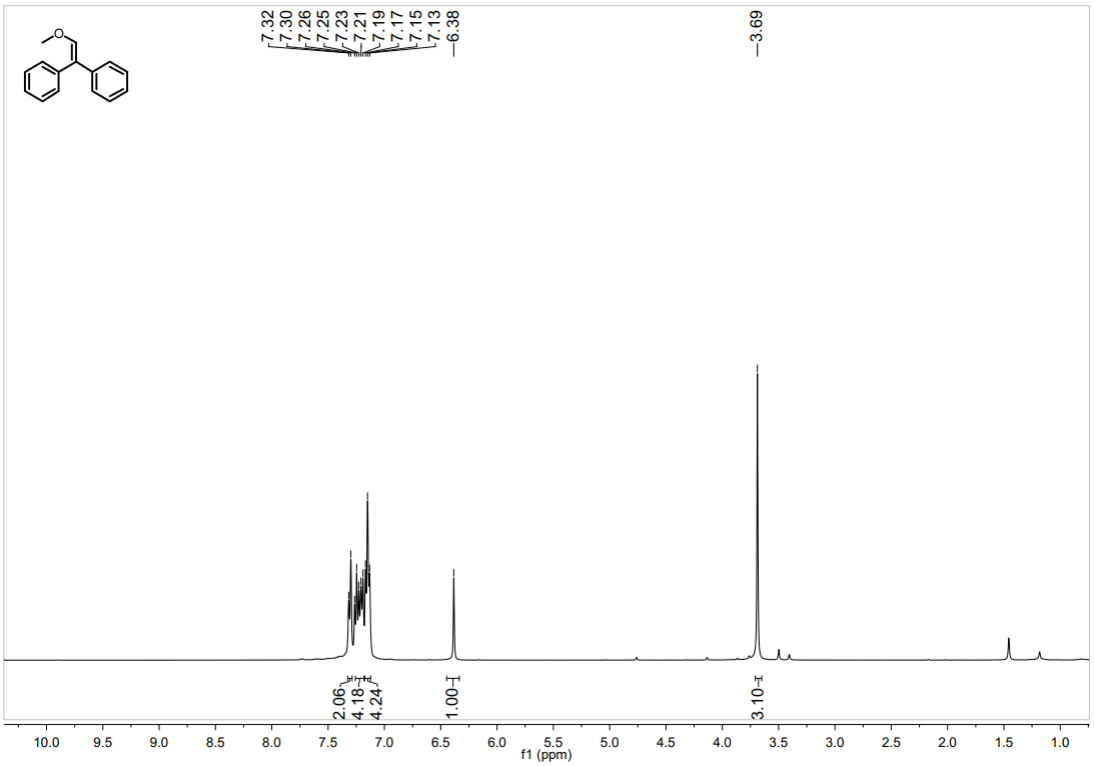
^{13}C NMR ($CDCl_3$-*d*) of **3m**



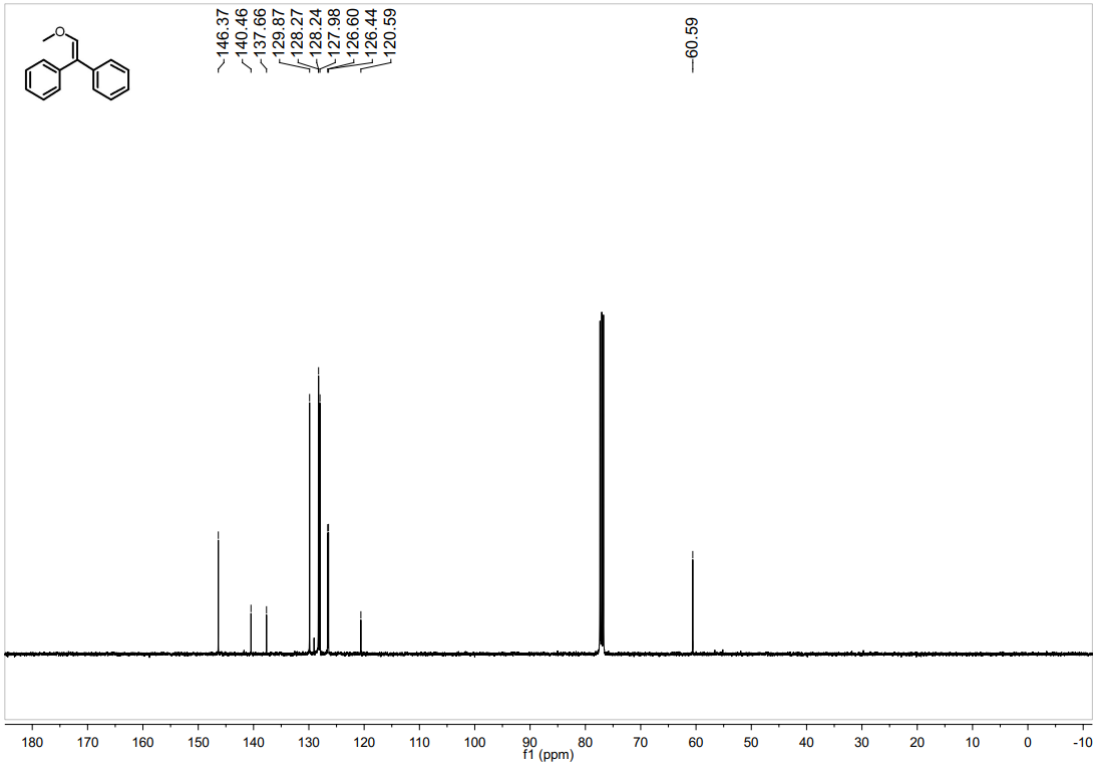
^{1}H NMR ($CDCl_3$-*d*) of **IV-3**



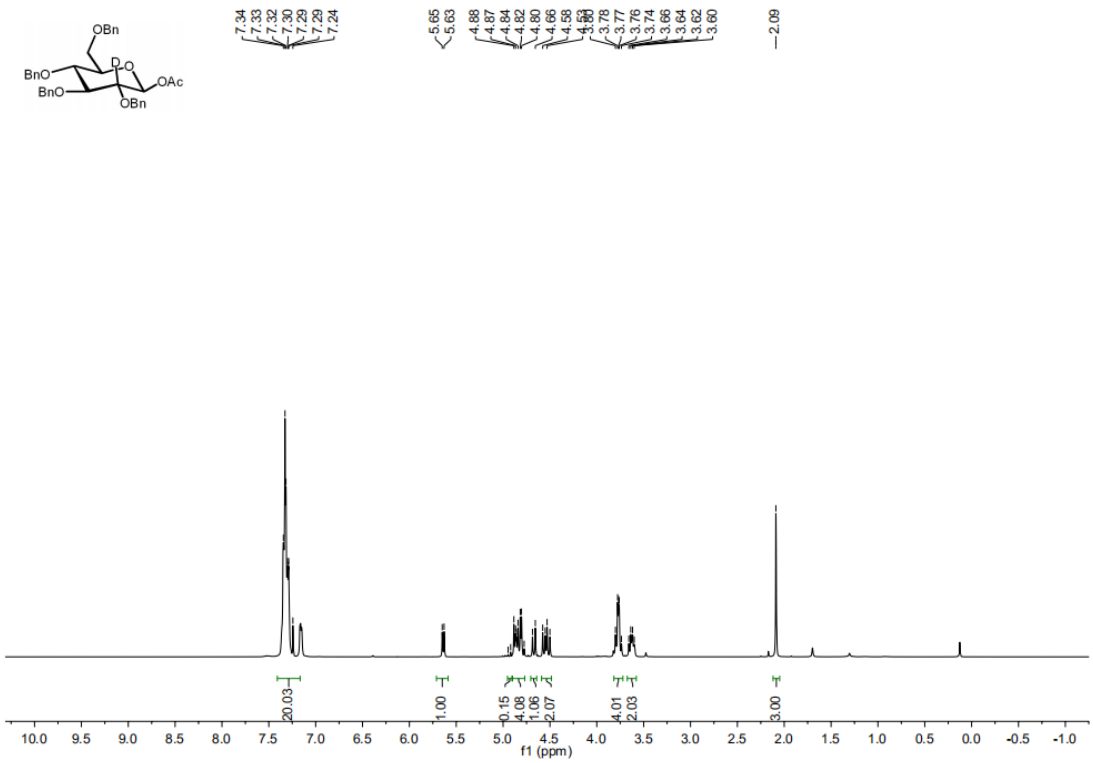
^{13}C NMR ($CDCl_3$-*d*) of **IV-3**



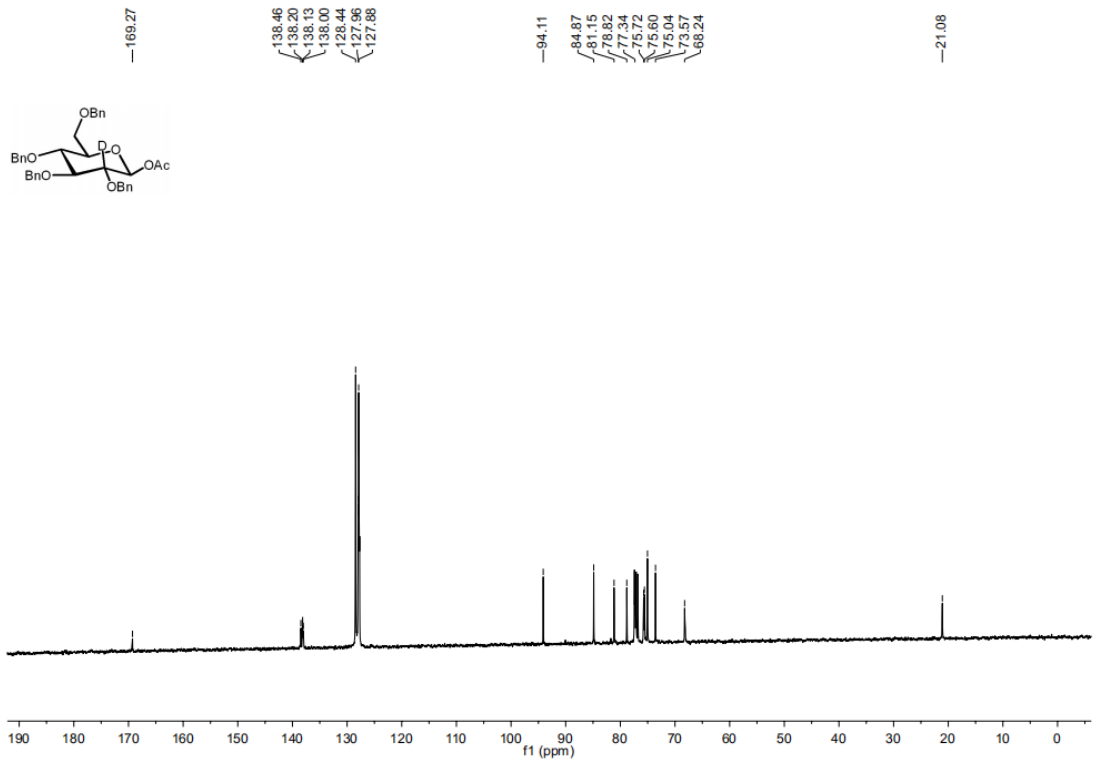
^{1}H NMR ($CDCl_3$-*d*) of **IV-4**



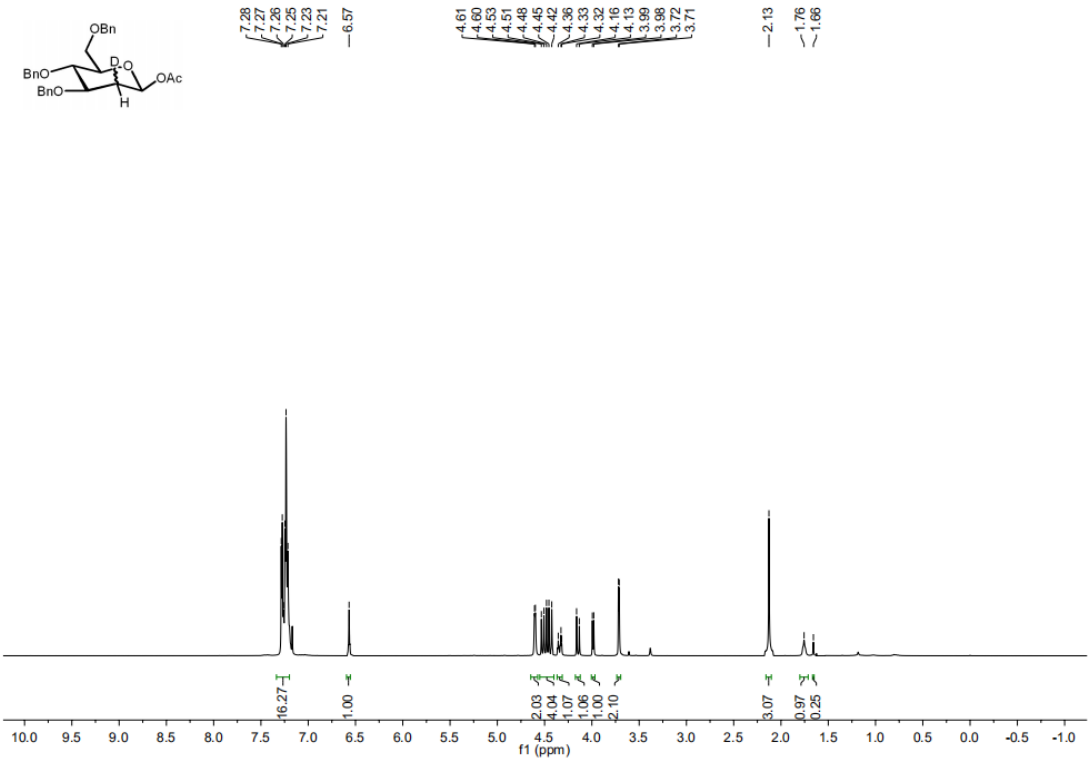
^{13}C NMR ($CDCl_3$-*d*) of **IV-4**



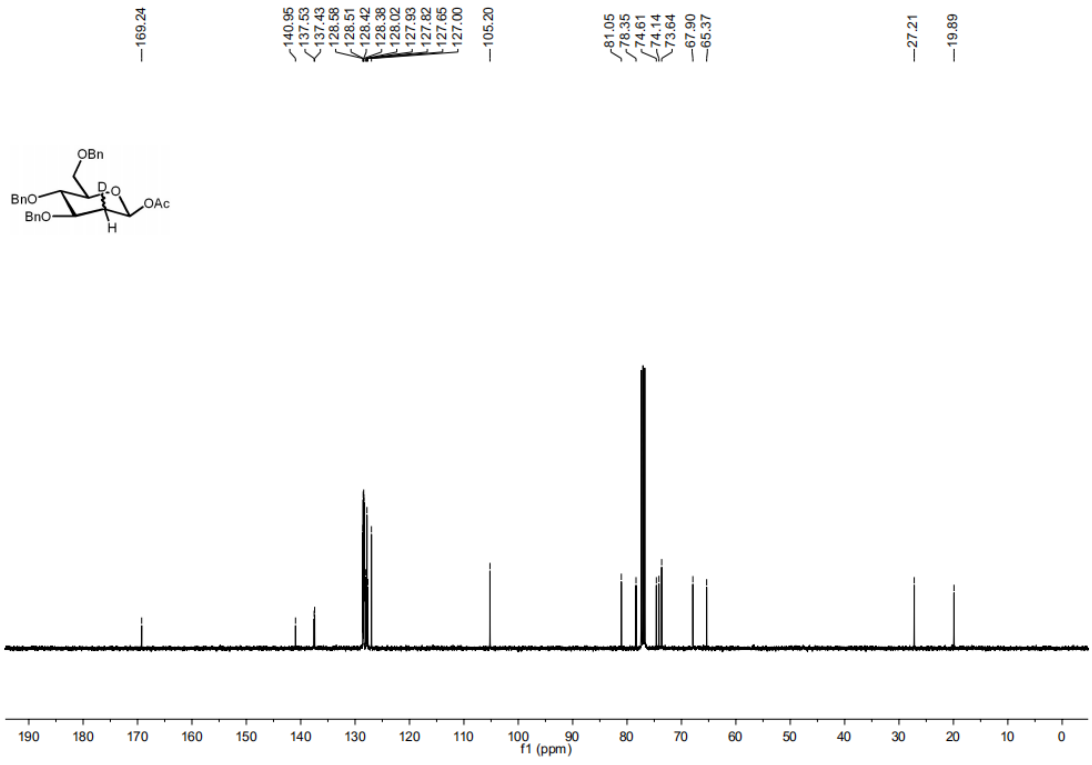
^{1}H NMR ($CDCl_3$-*d*) of **2*D*-2a**



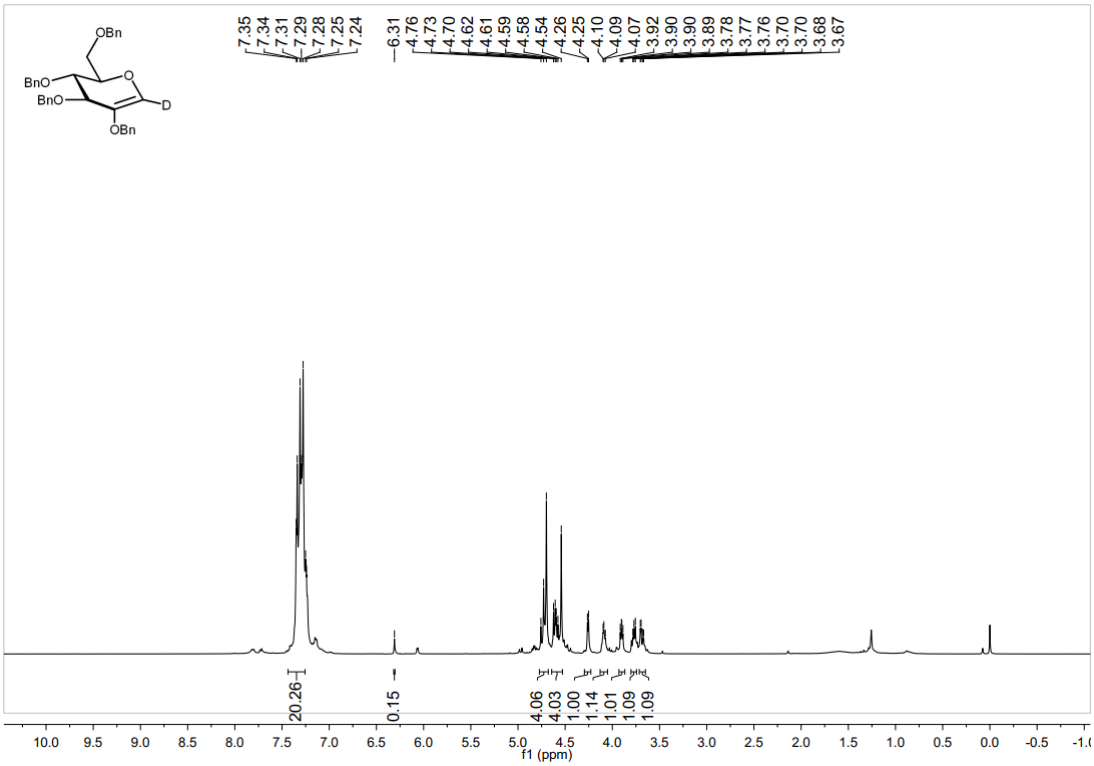
^{13}C NMR ($CDCl_3$-*d*) of **2*D*-2a**



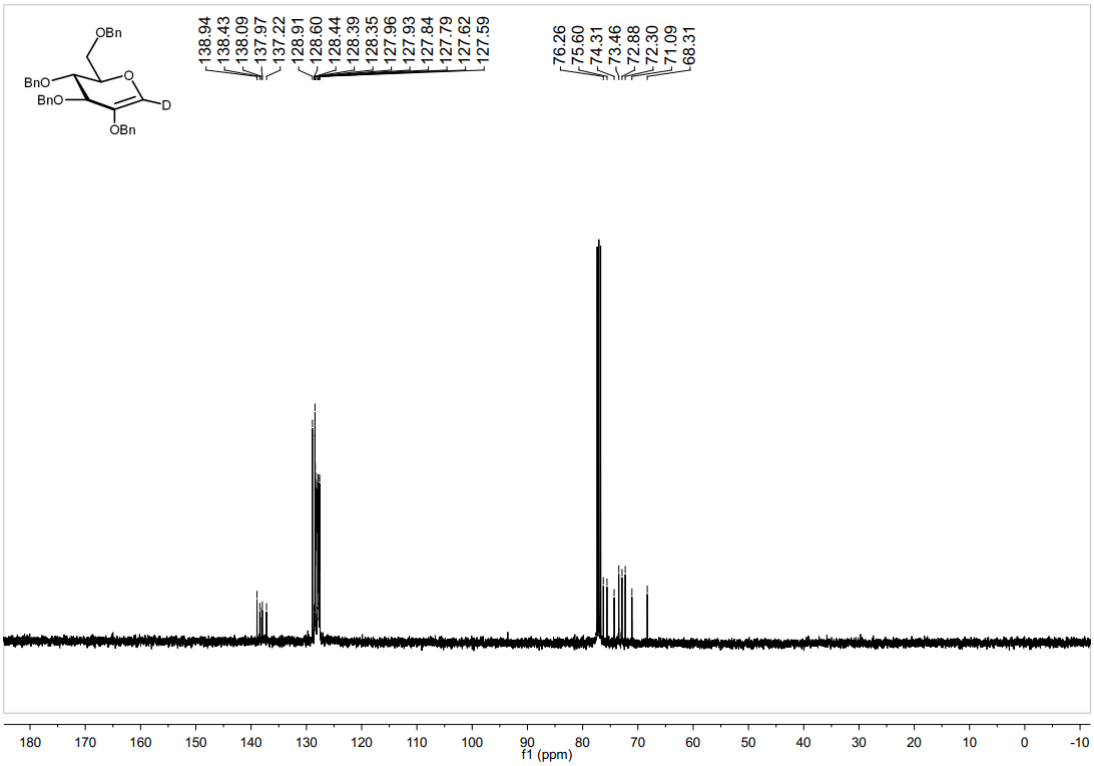
^{1}H NMR ($CDCl_3$-*d*) of **2*D*-2m**



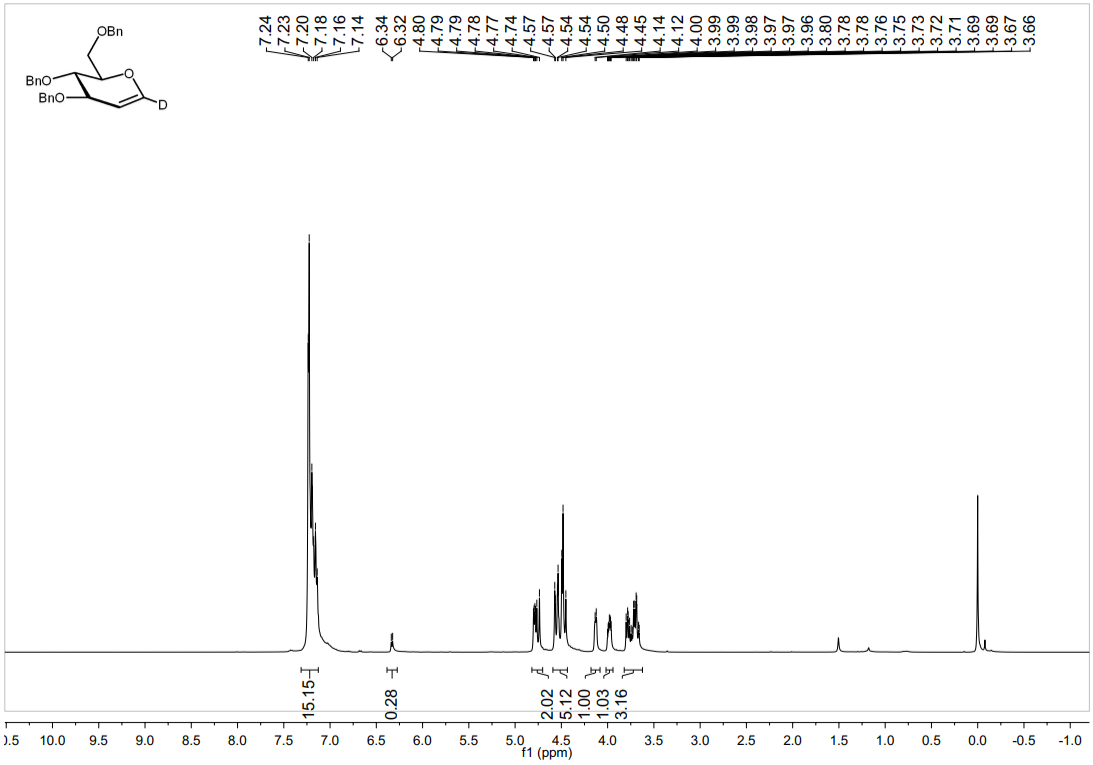
^{13}C NMR ($CDCl_3$-*d*) of **2*D*-2m**



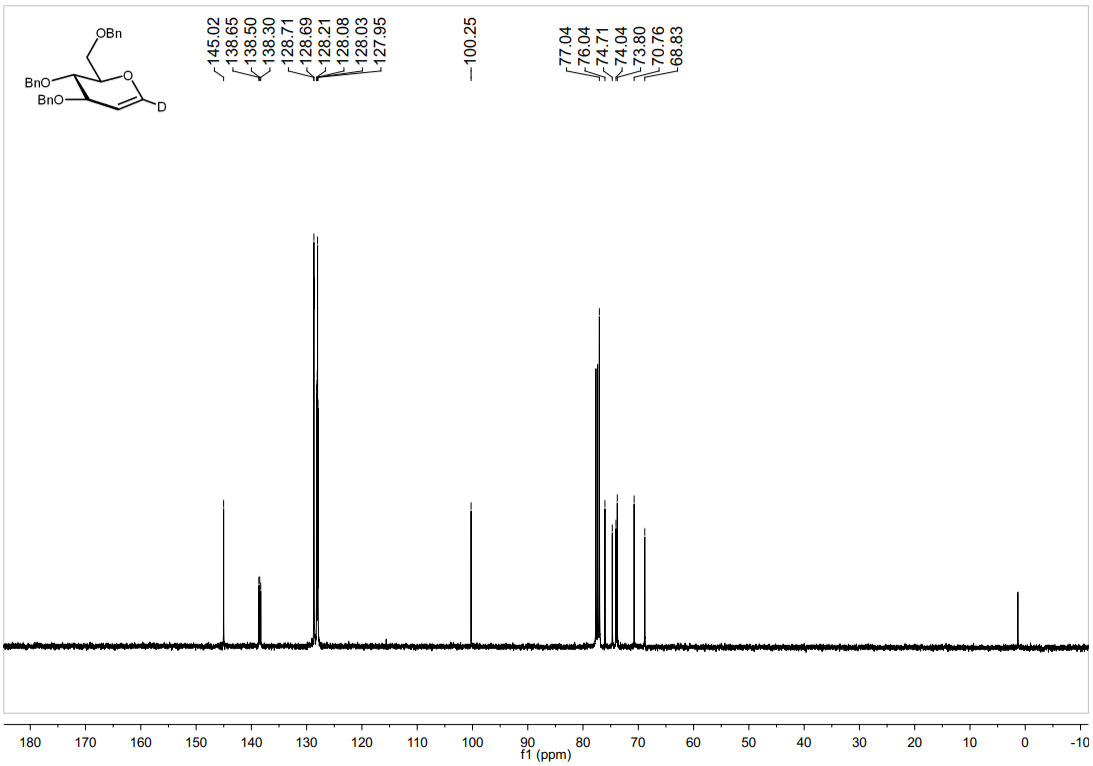
^{1}H NMR ($CDCl_3$-*d*) of **1*D*-3a**



^{13}C NMR ($CDCl_3$-*d*) of **1*D*-3a**



^{1}H NMR ($CDCl_3$-*d*) of **1*D*-3m**



^{13}C NMR ($CDCl_3$-*d*) of **1*D*-3m**

7. Cartesian coordinates of calculated structures

III-1

0 1

C	-0.78947300	-1.21740200	-0.23697600
P	0.33866800	0.06559300	0.02288600
C	0.70092500	1.22318000	-1.36463900
C	1.85058000	2.02724800	-1.40069700
C	-0.19940300	1.25916400	-2.43660200
C	2.08451200	2.86659700	-2.48872500
H	2.56922300	1.98605600	-0.58803900
C	0.03396900	2.10586700	-3.52014700
H	-1.07735200	0.62194100	-2.41832000
C	1.17400000	2.90972500	-3.54681300
H	2.97881800	3.48206900	-2.51356600
H	-0.67112900	2.13206700	-4.34526100
H	1.35842300	3.56358200	-4.39384300
C	1.96561900	-0.63937800	0.43375100
C	2.30238900	-0.89428900	1.76857000
C	2.85717500	-0.99637700	-0.58623500
C	3.51150800	-1.51410700	2.07786600
H	1.61971000	-0.61309600	2.56285400
C	4.06178500	-1.62418300	-0.27313900
H	2.61191300	-0.78371300	-1.62044600
C	4.38926100	-1.88503600	1.05800200
H	3.76698000	-1.70829800	3.11489900
H	4.74427700	-1.90632500	-1.06875900
H	5.32893300	-2.37190700	1.30053300
C	-0.14465200	1.13956600	1.42768500
C	-0.84512500	0.54349500	2.48657900
C	0.17772800	2.50062600	1.49300500
C	-1.20086000	1.29657700	3.60298600
H	-1.12163400	-0.50282600	2.41307900
C	-0.18037100	3.25034600	2.61316700
H	0.69414300	2.98084300	0.67030300
C	-0.86604300	2.65014700	3.66940800
H	-1.74889400	0.82908000	4.41513700
H	0.07209300	4.30543700	2.65673700
H	-1.14678600	3.23751800	4.53843000
C	-2.22398400	-0.97194000	-0.31720100
C	-3.11334500	-2.06583600	-0.46511400
C	-2.82078700	0.31398700	-0.25359700
C	-4.49097700	-1.88749300	-0.51468400
H	-2.68673400	-3.06041300	-0.53528700
C	-4.20129500	0.48251000	-0.29548300

H	-2.20088900	1.20117800	-0.17907600
C	-5.05788000	-0.61285300	-0.42438200
H	-5.13283000	-2.75861300	-0.62561800
H	-4.61031000	1.48847800	-0.23926500
H	-6.13416300	-0.47635600	-0.46436400
C	0.10166500	-2.78743700	-1.94103200
H	-0.50451100	-2.19436100	-2.63027300
H	1.16586900	-2.56724700	-2.14414000
H	-0.05550600	-3.84947800	-2.17871900
N	-0.30308200	-2.50918100	-0.57976200
C	0.26009000	-3.39369700	0.41870700
H	1.35932800	-3.34394300	0.49639500
H	-0.15987200	-3.14667200	1.39601900
H	0.00040700	-4.43868400	0.19006600

III-2

0 1

C	0.84539200	-0.77915400	-1.00953200
P	-0.36901100	0.00994900	-0.09037700
C	-0.94752300	-0.76065600	1.48338300
C	-2.20094600	-0.48197900	2.04772900
C	-0.09504100	-1.67878200	2.10879800
C	-2.58864500	-1.10864700	3.23124900
H	-2.87474400	0.21415800	1.55787100
C	-0.48295700	-2.29798100	3.29667500
H	0.86409200	-1.91049800	1.65568300
C	-1.72891300	-2.01384900	3.85746000
H	-3.56238200	-0.89548300	3.66206200
H	0.18319400	-3.00683100	3.77883200
H	-2.03413300	-2.50271600	4.77771100
C	-1.88587100	0.12783800	-1.08805200
C	-2.21977000	1.32082500	-1.73841300
C	-2.70373200	-1.00011700	-1.24096200
C	-3.36166500	1.38371100	-2.53634300
H	-1.59186200	2.19729900	-1.62236200
C	-3.83848400	-0.93447400	-2.04564500
H	-2.45858900	-1.92288900	-0.72657500
C	-4.16958600	0.25748100	-2.69278800
H	-3.61854600	2.31312700	-3.03505600
H	-4.46539700	-1.81263400	-2.16559100
H	-5.05728700	0.30787900	-3.31594900
C	0.15571600	1.69562200	0.36714600
C	0.92955200	2.41603400	-0.55509300

C	-0.21797800	2.29255000	1.57720100
C	1.31679700	3.72250600	-0.26865000
H	1.23234600	1.93700500	-1.47986100
C	0.17162800	3.60203300	1.85715800
H	-0.80076100	1.73730300	2.30295500
C	0.93690800	4.31745700	0.93619000
H	1.92192900	4.27281300	-0.98224500
H	-0.11902300	4.06014400	2.79752400
H	1.24189400	5.33550900	1.15876500
C	2.26512500	-0.75199900	-0.74653600
C	3.16012500	-1.30799900	-1.69661200
C	2.84724700	-0.18585400	0.41717400
C	4.53615500	-1.27632600	-1.50209300
H	2.74789900	-1.74604100	-2.59894500
C	4.22614800	-0.14377200	0.59100800
H	2.21289500	0.21578400	1.20049300
C	5.09111500	-0.68857300	-0.36179000
H	5.18613000	-1.71195200	-2.25738100
H	4.62890400	0.30522900	1.49568000
H	6.16627900	-0.66531800	-0.21422600
O	0.36137700	-1.63804100	-2.01673800
C	0.29610600	-3.00290400	-1.61231500
H	1.27644200	-3.37696000	-1.29107600
H	-0.41559900	-3.14760800	-0.78763500
H	-0.04096200	-3.58017500	-2.47919100

IV-1:

0 1

C	1.09929400	-0.63461500	-0.70406900
C	-0.28312900	-0.30457400	-0.34796400
C	-0.82619100	0.97521800	-0.58161700
C	-1.14099100	-1.31400200	0.13022200
C	-2.17431100	1.23196300	-0.34010400
H	-0.18479500	1.76214100	-0.96878400
C	-2.47771100	-1.04070500	0.40408600
H	-0.74315100	-2.31271100	0.28454100
C	-3.00562800	0.23090100	0.16452400
H	-2.57436000	2.22294700	-0.53656700
H	-3.11689000	-1.82908100	0.79181800
H	-4.05395000	0.43489500	0.35942900
C	1.90957300	0.83254600	1.16302500
H	0.86728000	0.89213500	1.46706800
H	2.51119200	0.43574900	1.98655600
H	2.27684800	1.83471100	0.91983600

N	2.04729700	-0.05771200	-0.00968000
C	3.44855400	-0.30205200	-0.36674900
H	3.97487300	-0.77431800	0.47023700
H	3.46693600	-0.95595100	-1.23652100
H	3.94817500	0.64538800	-0.59797900

IV-2:

0 1

C	1.43874700	-0.95361100	-0.69014400
C	0.12342200	-0.40374400	-0.30507000
C	-0.24671700	0.94354100	-0.48561300
C	-0.85927500	-1.32560700	0.10117400
C	-1.55674700	1.35247800	-0.24809500
H	0.48337000	1.66200300	-0.84481400
C	-2.15053800	-0.90090200	0.39557000
H	-0.58608000	-2.37316700	0.18575600
C	-2.50599000	0.43833600	0.21279600
H	-1.83534400	2.38940500	-0.41160400
H	-2.89020700	-1.61737500	0.73997400
H	-3.52259700	0.76363200	0.41139000
O	2.50287500	-0.36216000	-0.21932000
C	2.53027100	0.71337100	0.78660200
H	2.65427800	1.67158200	0.27967700
H	1.62512100	0.71133200	1.39306800
H	3.40942000	0.50670000	1.39779300

PPh_3:

0 1

P	0.00069400	-0.00126300	-1.26719600
C	-0.33241700	1.61701200	-0.44363100
C	0.25734900	2.75798500	-1.00951100
C	0.06988000	4.01437900	-0.43651200
C	-0.72582900	4.15092500	0.70236400
C	-1.32682400	3.02494200	1.26552700
C	-1.12993600	1.76485100	0.69929300
C	1.56824900	-0.52163600	-0.44319200
C	2.09434200	0.09572200	0.69968000
C	3.28428200	-0.36301700	1.26598600
C	3.95951000	-1.44634300	0.70310000
C	3.44375400	-2.06804200	-0.43548400
C	2.26182400	-1.60283200	-1.00878000
C	-1.23493000	-1.09729300	-0.44315000

C	-2.51737900	-1.15656700	-1.01026500
C	-3.51292500	-1.94563200	-0.43734000
C	-3.23496400	-2.70184300	0.70274700
C	-1.95968700	-2.65988100	1.26690800
C	-0.96559900	-1.86086300	0.70064200
H	0.86763800	2.65875900	-1.90336700
H	0.53701100	4.88706500	-0.88337200
H	-0.87975000	5.13043200	1.14514600
H	-1.94862300	3.12550700	2.15044100
H	-1.59588800	0.89475900	1.14888400
H	1.57330100	0.93465700	1.14795000
H	3.68199600	0.12592000	2.15063300
H	4.88485400	-1.80203500	1.14623000
H	3.96635400	-2.90893100	-0.88181000
H	1.87090800	-2.08191000	-1.90273600
H	-2.73506000	-0.57907200	-1.90500900
H	-4.50201000	-1.97682400	-0.88472400
H	-4.00704500	-3.32361100	1.14598900
H	-1.73696800	-3.24767400	2.15273800
H	0.02069000	-1.82929800	1.15065000

INT-1

0 1

C	0.85388400	-1.73538200	-0.99767300
C	2.17248200	-1.77349800	-0.20027400
C	3.11501700	-0.65123800	-0.64289800
C	2.36835600	0.68893100	-0.52848200
P	-1.03047300	0.12990900	-0.06919400
C	-2.45791900	-0.95712300	-0.39709300
C	-2.69219300	-1.35716100	-1.71986500
C	-3.78986600	-2.15817600	-2.02401700
C	-4.66729500	-2.55863000	-1.01346400
C	-4.44548800	-2.14917200	0.30114000
C	-3.34628100	-1.34665000	0.61064300
C	-1.55595900	1.81938900	-0.51707100
C	-2.91945200	2.08574200	-0.70991500
C	-3.34914500	3.37633200	-1.01688600
C	-2.42423500	4.41356900	-1.13133400
C	-1.06734200	4.15376200	-0.93434100
C	-0.62841800	2.86741800	-0.62543900
C	-0.90698300	0.18151400	1.78408800
C	-0.51461200	-0.99267800	2.45249100
C	-0.27709900	-0.97608800	3.82402300
C	-0.41255700	0.21293900	4.54680500

C	-0.79339000	1.38227200	3.89025300
C	-1.04278500	1.36854700	2.51638600
H	-1.99431000	-1.04485200	-2.48944700
H	-3.96225300	-2.46958500	-3.05000200
H	-5.52265100	-3.18397100	-1.25152200
H	-5.12622400	-2.45512700	1.08984300
H	-3.17805500	-1.03338400	1.63457500
H	-3.64781200	1.28759300	-0.62314100
H	-4.40739200	3.56800800	-1.16694100
H	-2.75908400	5.41842500	-1.37153700
H	-0.33919500	4.95503600	-1.02114900
H	0.42974600	2.69396800	-0.48604700
H	-0.39229400	-1.91030500	1.88527100
H	0.01849000	-1.89031200	4.33071600
H	-0.21914800	0.22589000	5.61531600
H	-0.90090500	2.30903000	4.44648700
H	-1.34169100	2.28336600	2.01694300
C	3.22914600	1.86608200	-0.93241500
H	4.24173100	1.74696500	-0.52283300
H	3.30270600	1.89146500	-2.03088100
C	0.27339500	-0.34001300	-1.10052800
O	1.23700400	0.64380200	-1.41643400
H	1.04915100	-2.13316400	-2.00688700
H	1.89279700	-1.60499100	0.84437400
H	3.36864300	-0.77667800	-1.70198500
O	-0.08086900	-2.58443700	-0.33077500
O	2.76774300	-3.07095200	-0.19956700
O	4.37458900	-0.66044100	0.02455600
O	2.63014600	3.05544100	-0.43876800
C	3.24995000	4.22201100	-0.93685900
H	2.74513800	5.07939200	-0.48387500
H	4.31824900	4.26238700	-0.67250800
H	3.16307300	4.29569800	-2.03181200
C	4.33072900	-0.77466800	1.44138200
H	3.99603900	-1.76917300	1.75807700
H	5.35553600	-0.62267600	1.79001800
H	3.69183400	-0.01440500	1.90980100
C	3.51625500	-3.41883700	-1.35318700
H	3.76238500	-4.47943400	-1.25160300
H	2.95020100	-3.28903600	-2.28600800
H	4.45030300	-2.84775500	-1.42175300
C	-0.39373800	-3.78651800	-1.00518900
H	-1.17831200	-4.27964400	-0.42489700
H	-0.77894300	-3.59798200	-2.01653600

H	0.47775800	-4.45084900	-1.06754100
H	2.01597100	0.84411400	0.50160400

INT-2

0 1

C	-1.49656200	-0.90246500	0.00277000
C	-1.18976600	0.55442500	-0.35379000
C	0.18145100	0.85738100	0.26068600
C	1.23919500	-0.07564800	-0.34107000
C	2.45912500	-0.20414100	0.54280200
H	2.72873100	0.80502000	0.89362600
H	2.20830300	-0.81075400	1.42962200
C	-0.47783300	-1.90051500	-0.52001400
O	0.74036700	-1.46169000	-0.61638800
H	-1.45225100	-1.02388800	1.10597100
H	-1.13538700	0.63054600	-1.44522400
H	0.12812600	0.67352000	1.34046600
O	-2.79193000	-1.22155600	-0.46833700
O	-2.17972700	1.49608500	0.01283400
O	0.61162100	2.20542600	0.15951200
O	3.50995600	-0.78504800	-0.19451000
C	4.67774200	-0.95536300	0.58444000
H	5.43932900	-1.39457000	-0.06413800
H	5.05293900	0.00371600	0.97449300
H	4.50555700	-1.63107200	1.43634300
C	0.41622500	2.83924000	-1.10124000
H	-0.64673600	3.00011500	-1.30808000
H	0.91619700	3.80787800	-1.03017700
H	0.86813200	2.28229600	-1.93303200
C	-2.62185400	1.44938700	1.35871500
H	-3.33030100	2.27302600	1.47380500
H	-3.14274500	0.51019000	1.58444200
H	-1.80724400	1.59639400	2.08037800
C	-3.29794200	-2.43394100	0.07014200
H	-4.28201900	-2.59205500	-0.37750000
H	-2.64646900	-3.28276400	-0.16478500
H	-3.41110400	-2.36782200	1.16433100
H	1.54596000	0.28433100	-1.32607000

INT-3:

0 1

C	2.37471400	-1.41271400	-1.04927900
C	3.15470200	-0.85072100	0.11678800

C	3.37651000	0.65962600	-0.08051700
C	2.12435200	1.30353100	-0.69755300
P	-1.59159500	-0.17444400	-0.53453400
C	-2.90553400	-1.46894900	-0.60829300
C	-3.45165300	-1.75339500	-1.86866700
C	-4.46668400	-2.69891100	-2.00834500
C	-4.94047400	-3.38477200	-0.88922300
C	-4.39767200	-3.11709600	0.36843500
C	-3.38896600	-2.16417800	0.50968500
C	-2.56989500	1.34200800	-0.14341900
C	-3.87825000	1.32419100	0.35894000
C	-4.53762600	2.51772200	0.65276700
C	-3.89570900	3.74190600	0.45830600
C	-2.59320400	3.76786600	-0.04193200
C	-1.93641600	2.57699800	-0.35281200
C	-0.82311600	-0.54309400	1.10555400
C	-0.07693600	-1.72830100	1.21935000
C	0.55623200	-2.05634200	2.41638600
C	0.47086200	-1.19841000	3.51617800
C	-0.25619200	-0.01322900	3.40856100
C	-0.90257600	0.31196700	2.21340100
H	-3.07536600	-1.23123200	-2.74438800
H	-4.88066400	-2.90641800	-2.99070500
H	-5.72533400	-4.12754700	-0.99705100
H	-4.76188800	-3.64906400	1.24266500
H	-2.97449500	-1.96026000	1.49115600
H	-4.38292300	0.37776500	0.52093400
H	-5.55298700	2.49099700	1.03795200
H	-4.41041300	4.66959000	0.69109100
H	-2.08800600	4.71686500	-0.19888500
H	-0.92811900	2.61125600	-0.75573100
H	0.02593000	-2.39080200	0.36608800
H	1.12858100	-2.97677000	2.48380100
H	0.97027800	-1.45148300	4.44658200
H	-0.32876000	0.66036700	4.25770000
H	-1.47362300	1.23134300	2.14676500
C	2.28502700	2.79787000	-0.86975300
H	2.53003400	3.23937900	0.10646700
H	3.12620500	3.00503200	-1.55086300
C	1.82991100	-0.63177300	-1.99181000
O	1.90447100	0.72990800	-1.99974600
H	2.56208000	-1.02031200	1.01934200
H	4.17856400	0.80434500	-0.81122500
O	2.02778800	-2.75130500	-1.03691100

O	4.37270400	-1.55325400	0.38877500
O	3.83842900	1.32914300	1.08436700
O	1.08306800	3.33619800	-1.38544400
C	1.11028500	4.74626800	-1.46495700
H	0.15854200	5.06608500	-1.89618500
H	1.22948900	5.21042600	-0.47335600
H	1.92627900	5.10217700	-2.11228600
C	3.04763200	1.16292300	2.25667000
H	3.18164200	0.17284300	2.70741200
H	3.39667300	1.91572300	2.96825700
H	1.97845300	1.32294400	2.07663300
C	5.40501900	-1.38853200	-0.57208200
H	6.09526600	-2.22658300	-0.44207300
H	5.02442800	-1.40604600	-1.60177800
H	5.96341900	-0.45620700	-0.41676400
C	3.07222000	-3.69364200	-1.29073100
H	2.58366100	-4.66441700	-1.40795200
H	3.60415400	-3.45112200	-2.21938100
H	3.78432300	-3.74051000	-0.46290900
H	1.23415700	1.09486400	-0.09142600
H	1.24328700	-1.03499000	-2.81008300

Ts:

0 1

C	-1.58243400	-0.82652900	-0.14416400
C	-1.17026900	0.62556800	-0.37952400
C	0.17855100	0.84168900	0.32095400
C	1.12673000	-0.26732200	-0.15325400
C	2.52439100	-0.12041200	0.40619000
H	2.85022600	0.92400800	0.28881200
H	2.50688600	-0.34546700	1.48527900
C	-0.69084800	-1.90365200	0.12173100
O	0.61833700	-1.56501100	0.28284600
H	-1.42545800	-1.31568800	1.08273100
H	-1.02880700	0.73019200	-1.46102000
H	0.05302200	0.72250400	1.40340800
O	-2.88554600	-1.02709700	-0.46484200
O	-2.16208800	1.57308300	-0.05802400
O	0.69861100	2.15178600	0.17244800
O	3.38674600	-1.00097200	-0.28458300
C	4.70693100	-0.94786500	0.21333500
H	5.30782300	-1.64160900	-0.38010600
H	5.13970100	0.06160100	0.12403000
H	4.75906700	-1.25074800	1.27077900

C	0.74286500	2.66978300	-1.15238300
H	-0.26000300	2.88502700	-1.53921800
H	1.29925400	3.60786800	-1.09070600
H	1.26641300	2.00503200	-1.85199800
C	-2.53429500	1.63083400	1.31076100
H	-3.38874800	2.30880600	1.36639900
H	-2.84636100	0.65067400	1.69606000
H	-1.73138500	2.03024800	1.94267600
C	-3.37126800	-2.37278000	-0.39822600
H	-4.39288700	-2.33120100	-0.77922000
H	-2.75176500	-3.04438900	-0.99850800
H	-3.37491200	-2.73987600	0.63430600
H	1.18732800	-0.28718800	-1.24898200

Ts’

0 1

C	1.02538200	-1.74445500	-0.83586000
C	2.38812200	-1.69990000	-0.19095400
C	3.19698800	-0.50015200	-0.69698200
C	2.34814100	0.76240300	-0.48243400
P	-1.08319200	0.10131700	-0.01899500
C	-2.38373400	-1.13442500	-0.31002300
C	-2.60927000	-1.57893400	-1.62119400
C	-3.60160200	-2.52119900	-1.87828400
C	-4.38388300	-3.01928500	-0.83427500
C	-4.17552500	-2.56299900	0.46735500
C	-3.18261200	-1.61955300	0.73115900
C	-1.72864100	1.68406300	-0.64426400
C	-3.09064100	1.81806700	-0.94990600
C	-3.59340300	3.04186300	-1.38971500
C	-2.74297000	4.13888800	-1.52668500
C	-1.38790900	4.00974200	-1.21890200
C	-0.87537800	2.79138500	-0.77658500
C	-0.94414400	0.28711700	1.79887000
C	-0.40720300	-0.78537500	2.53503400
C	-0.17629000	-0.64677600	3.89999200
C	-0.45292900	0.56347900	4.54315100
C	-0.97340800	1.63304700	3.81414200
C	-1.22260300	1.49957800	2.44848100
H	-1.99967500	-1.19069000	-2.42960500
H	-3.76475100	-2.86621100	-2.89472500
H	-5.15613500	-3.75534400	-1.03601000
H	-4.78456500	-2.94219200	1.28224400
H	-3.02248700	-1.27356700	1.74569800

H	-3.75749400	0.96959800	-0.84742300
H	-4.64913800	3.13563900	-1.62512200
H	-3.13544700	5.09107100	-1.87117000
H	-0.72004800	4.85969100	-1.32390200
H	0.17994900	2.71165800	-0.54794700
H	-0.17064200	-1.71418400	2.02232300
H	0.23032600	-1.48190100	4.46288200
H	-0.25776400	0.67259100	5.60565900
H	-1.19225000	2.57447300	4.30946600
H	-1.63380600	2.33412900	1.89179000
C	3.07655900	2.04162800	-0.82280500
H	4.08736500	2.02059700	-0.39380500
H	3.17203200	2.11983700	-1.91689200
C	0.33082500	-0.37256300	-1.07156200
O	1.21019000	0.67104700	-1.36875100
H	0.34970800	-1.23992100	-1.94767000
H	2.25409400	-1.58685400	0.89665000
H	3.34766700	-0.58955700	-1.77773900
O	0.10729600	-2.52997100	-0.09791200
O	3.09598800	-2.94393500	-0.29704200
O	4.51396900	-0.40766100	-0.16347700
O	2.33442300	3.13501200	-0.30047900
C	2.81471800	4.38368600	-0.75289900
H	2.20703400	5.15872700	-0.27840600
H	3.86782900	4.54220800	-0.47344200
H	2.72965000	4.48266500	-1.84594200
C	4.63354300	-0.54666700	1.24513800
H	4.43107800	-1.57305400	1.57109300
H	5.67087700	-0.29975400	1.48780600
H	3.97868900	0.14042600	1.79885700
C	3.48965000	-3.29056900	-1.61394800
H	3.76492400	-4.34928500	-1.59495000
H	2.66868000	-3.14554700	-2.32766700
H	4.36351300	-2.71245800	-1.94650200
C	-0.10282400	-3.84297300	-0.58738200
H	-0.92320700	-4.27419400	-0.00429700
H	-0.38246200	-3.83195500	-1.64847000
H	0.79442400	-4.46133600	-0.46418700
H	1.99122500	0.82427900	0.55562700

3g:

0 1

C	-1.59482600	-0.77208000	-0.23285600
C	-1.18635000	0.68077800	-0.36773800
C	0.18753800	0.87561600	0.29358500

C	1.11663600	-0.27220800	-0.13938500
C	2.52975200	-0.10169200	0.37303400
H	2.87578500	0.91408600	0.13330700
H	2.53247000	-0.20413000	1.47058600
C	-0.72667800	-1.73121500	0.12621300
O	0.60131000	-1.50167500	0.39508100
H	-0.97978800	-2.77824400	0.23148100
H	-1.11295100	0.91672100	-1.43552300
H	0.07216700	0.78549500	1.37880100
O	-2.90887500	-0.96873900	-0.55558800
O	-2.16983200	1.58828000	0.10338800
O	0.74497700	2.16682300	0.10325500
O	3.35708100	-1.07646500	-0.23081600
C	4.69125200	-0.98991900	0.22213800
H	5.26402000	-1.76242200	-0.29751200
H	5.13865300	-0.00775700	-0.00039000
H	4.76877600	-1.16270500	1.30713900
C	0.77707700	2.65635300	-1.23068700
H	-0.21758600	2.95784800	-1.58069000
H	1.41940100	3.54042200	-1.21482900
H	1.20328800	1.93516100	-1.94086400
C	-2.50496800	1.46971400	1.47698000
H	-3.41169200	2.06164800	1.62480600
H	-2.71415200	0.43156000	1.76441800
H	-1.72132000	1.86990600	2.13413700
C	-3.39584100	-2.29666600	-0.45076800
H	-4.45017100	-2.26239400	-0.73003200
H	-2.86167000	-2.97469100	-1.13044000
H	-3.30491400	-2.67738200	0.57541300
H	1.14084600	-0.36099100	-1.23546100