Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Site-Selective C−H Alkylation of *Myo*-Inositol via Organic Photoredox Catalysis

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Content

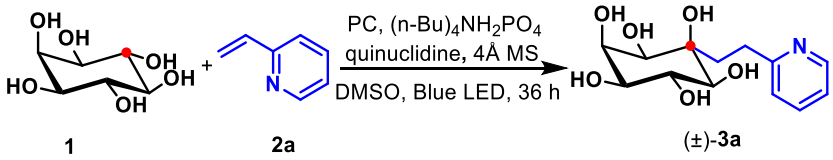
1. General Information

Unless otherwise noted, all reactions sensitive to water and oxygen were operated under argon atmosphere in a dry reaction vessel. Air and/or moisture-sensitive liquids were transferred with microliter syringes. Thin-layer chromatography (TLC) was performed on silica gel plates (GF254). Visualization of the developed chromatogram was achieved by Phosphomolybdic acid （10% mass fraction in EtOH）stain which developed upon heating. Column chromatography was performed with silica gel (200-300 mesh). ^{1}H and ^{13}C NMR data were acquired at Bruker AVANCE III HD 400 MHz and Bruker AVANCE NEO 600 MHz. Chemical shifts (δ) are reported in ppm relative to residual DMSO (2.50 ppm) or tetramethylsilane (0.00 ppm) in the ^{1}H NMR and residual DMSO (39.52 ppm) in the ^{13}C NMR. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet; br, broad. HRMS were performed on Thermo Scientific LTQ-Obitrap-ETD HRMS-TOF with electron spray ionization (ESI). LC-MS data were performed on Agilent 1260-6125b which employed a NanoChrom Unisil 5-120 C18 Ultra column(5 μm, 4.6x150mm). All commercially available reagents and dry DMSO were purchased from Energy Chemcial used without purification, unless otherwise indicated. Extraction and chromatography solvents were reagent grade and used without purification. All preparative reverse phase chromatography employed a Elitehplc SinoChrom ODS-BP column (10 μm, 10.0 mmX250 mm) and NanoMicro UniSil® 5-120 C18 Aq (5 μm, 10 mmX250 mm). Purification instruments (monitoring at 210 nm and 254 nm). Solvent A, H_2O; Solvent B, methanol. All samples were loaded onto the column at 2% B and the column was allowed to equilibrate at 2% B for 5 Column volume (CV) before a linear gradient was started. Cyclic voltammetry was performed on a CH Instruments Electrochemical Analyzer (CHI600D). A 0.005 M CH3CN solution of HAT reagent 13 was prepared with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte and the solution was sparged with Ar for 15 minutes. The cyclic voltammogram was obtained using a glassy carbon working electrode, a Pt counter electrode, and a saturated calomel reference electrode. Scan rate = 0.05 V/s. Melting points were determined in Tech X-4 melting point detector and apparatu was uncorrected.

2. Experimental Section

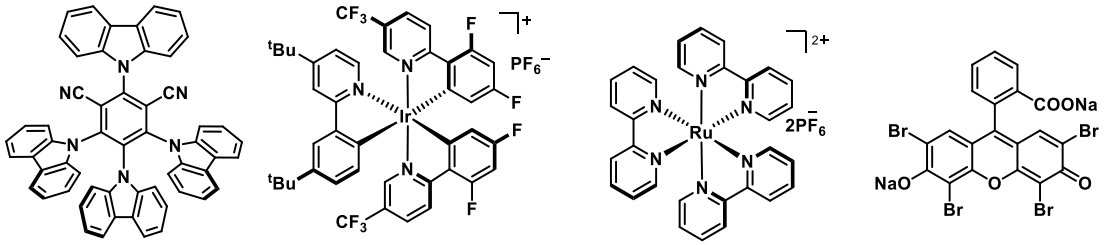
2.1 Condition Screening

Table S1 Screening of photocatalysts [a].

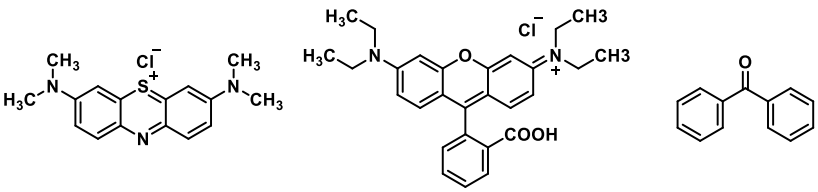


1 2a (±)-3a

Entry	**PC**（x mol %）	Yield [b] (%)
1	4-CzIPN (5 mol %)	39
2	$Ir[dF(CF_3)ppy]_2(dtbbty)PF_6$ (3 mol %)	<5
3	$[Ru(bpy)_3](PF_6)_2$ (3 mol %)	n.d.[c]
4	Eosin Y (5 mol %)	n.d.
5	Methylene Blue (5 mol %)	n.d.
6	Phodamine B (5 mol %)	n.d.
7	Benzophenone (5 mol %)	n.d.



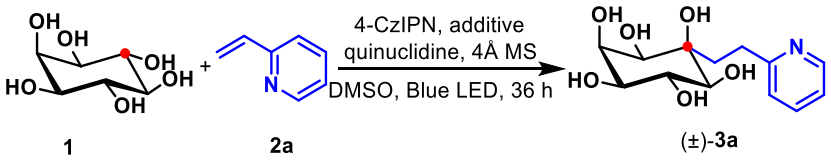
4-CzIPN $Ir[(dF(CF_3)ppy)_2(dtbpy)]PF_6$ $Ru(bpy)_3(PF_6)_2$ Eosin Y



Methylene Blue Phodamine B Benzophenone

[a] Reaction condition: 40 W blue LEDs, **1** (0.2 mmol, 1.0 equiv.), **2a** (0.2 mmol, 1 equiv.), PC (3 - 5 mol %), quinuclidine (0.02 mmol, 10 mol %), $(n\text{-}Bu)_4NH_2PO_4$ (0.1 mmol, 50 mol%), DMSO (1 mL), Ar, room temperature, 36 h, unless otherwise noted. [b] Isolated yield determined by silica gel column chromatography. [c] Not detected.

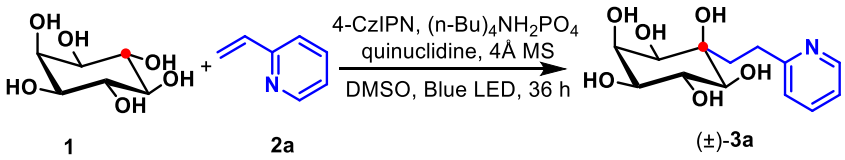
Table S2 Screening of additives. [a]



Entry	Additive	Yield [b] (%)
1	$(n\text{-}Bu)_4NH_2PO_4$	39
2	$(n\text{-}Bu)_4NN_3$	n.d.[c]
3	BPh_2OH	n.d.
4	$4\text{-}ClOBz(n\text{-}Bu)_4N$	n.d.

[a] Reaction condition: 40 W blue LEDs, **1** (0.2 mmol, 1.0 equiv.), **2a** (0.2 mmol, 1 equiv.), 4-CzIPN (5 mol %), quinuclidine (0.02 mmol, 10 mol %), additive (0.1 mmol, 50 mol%),DMSO (1 mL), Ar, room temperature, 36 h. [b] Isolated yield determined by silica gel column chromatography. [c] Not detected.

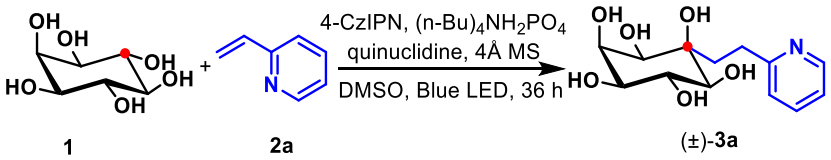
Table S3 Screening of solvents and concentration. [a]



Entry	Solvent and concentration	Yield [b] (%)
1	DMSO (1 mL)	39
2	ACN (1 mL)	n.d.[c]
3	DMSO (2 mL)	34
4	DMSO (10 mL)	32

[a] Reaction condition: 40 W blue LEDs, **1** (0.2 mmol, 1.0 equiv.), **2a** (0.2 mmol, 1 equiv.), 4-CzIPN (5 mol %), quinuclidine (0.02 mmol, 10 mol %), $(n\text{-}Bu)_4NH_2PO_4$ (0.1 mmol, 50 mol%), Ar, room temperature, 36 h. [b] Isolated yield determined by silica gel column chromatography. [c] Not detected.

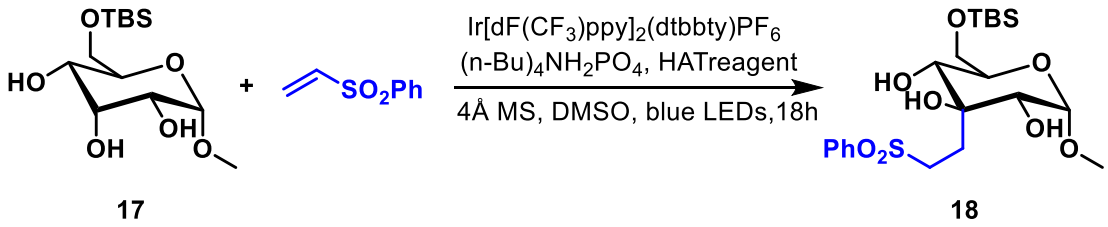
Table S4 Screening of substrates ratio. [a]



Entry	**2a**(mmol)	Yield [b] (%)
1	0.2	39
2	0.6	24
3	1.2	33
4	0.18	38
5	0.1	65
6	0.05	56
7	0.15	56

[a] Reaction condition: 40 W blue LEDs, **1** (0.2 mmol, 1.0 equiv.), 4-CzIPN (5 mol %), quinuclidine (0.02 mmol, 10 mol %), $(n\text{-}Bu)_4NH_2PO_4$ (0.1 mmol, 50 mol%), DMSO (1 mL), Ar, room temperature, 36 h. [b] Isolated yield determined by silica gel column chromatography.

Table S5 Application of **13** on α-*D*-Mehylglucoside [a]

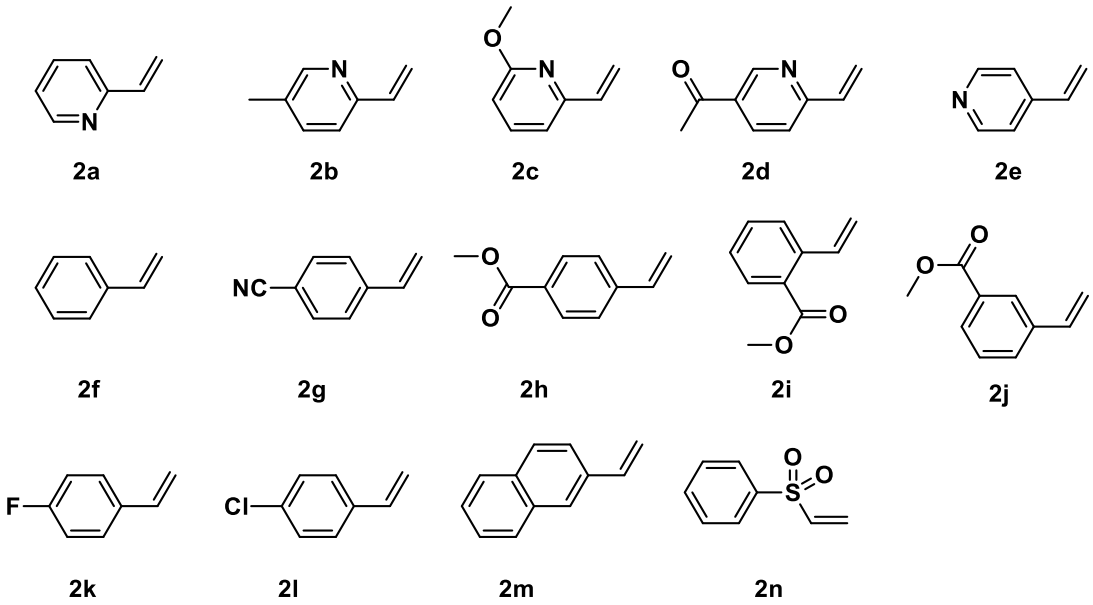


Entry	HAT reagent	Yield [b] (%)
1	Quinuclidine	58
2	13	59

[a] Reaction condition: 40 W blue LEDs, **17** (0.2 mmol, 1.0 equiv.), Phenyl vinyl sulfone (0.3 mmol, 1.5 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbty)PF_6$ (1 mol %), HAT reagent (0.02 mmol, 10 mol %), $(n\text{-}Bu)_4NH_2PO_4$ (0.5 mmol, 25 mol%), DMSO (1 mL), Ar, room temperature, 18 h. [b] Isolated yield determined by silica gel column chromatography.

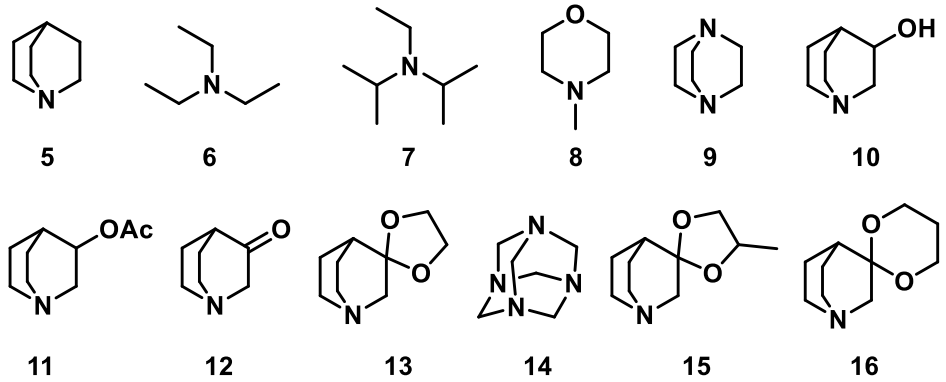
2.2 Preparation of Substrates

Preparation of alkenes



Note: Substrate **2b**, **2c**, **2d**, **2e**, **2g**, **2h**,**2i**, **2j** were prepared using established method.[1] Others were brought from Energy Chemcial.

Preparation of HAT reagents



Note: The cstalyst **10, 11, 13 ,15,** and **16** were prepared using established method[2-4]. Others were brought from Energy Chemcial.

2.3 General procedure

General procedure A (for solid **2**)

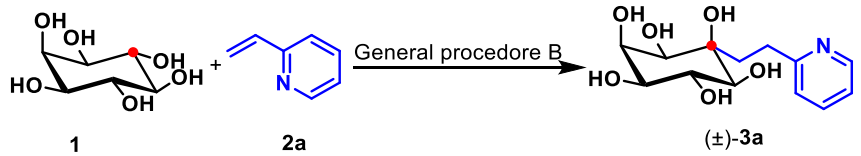
Into a 10 mL reaction tube, **1** (0.4 mmol, 2.0 equiv.), 4-CzIPN (5 mol %), **13** (10 mol %), $Bu_4NH_2PO_4$ (50 mol %) and 4Å MS (granular form, 100mg), olefin (0.2 mmol, 1.0 equiv.) were subsequently added. A PTFE magnetic stir bar and degassed DMSO (1 mL)

were added. The reaction mixture was subjected to a three-times freeze-pump-thaw procedure under Ar-atmosphere. The reaction tube was then irradiated by blue LEDs lamp and stirred at 300 rpm, which was cooled with fans. After 36 hours, the crude reaction mixture was lyophilized, and the remaining solid was dissolved in MeOH. To remove $Bu_4NH_2PO_4$, KPF_6 (1.1 equiv. based on equivalent of $Bu_4NH_2PO_4$) was added to form $TBAPF_6$. Then the solution underwent a quick purification with flash column chromatography to get product. Preparative reverse phase chromatography was employed to obtain further purity.

General procedure B (for liquid **2**)

Into a 10 mL reaction tube, **1** (0.4 mmol, 1.0 equiv.), 4-CzIPN (5 mol %), **13** (10 mol %), $Bu_4NH_2PO_4$ (50 mol %) and 4Å MS (granular form, 100mg) were subsequently added. A PTFE magnetic stir bar and degassed DMSO (1 mL) were added. The reaction mixture was subjected to a three-times freeze-pump-thaw procedure under Ar-atmosphere and then olefin (0.2 mmol, 2.0 equiv.) was added via syringe. The reaction tube was then irradiated by blue LEDs lamp and stirred at 300 rpm, which was cooled with fans. After 36 hours, the crude reaction mixture was lyophilized, and the remaining solid was dissolved in MeOH. To remove $Bu_4NH_2PO_4$, KPF_6 (1.1 equiv. based on equivalent of $Bu_4NH_2PO_4$) was added to form $TBAPF_6$. Then the solution underwent a quick purification with flash column chromatography to get product. Preparative reverse phase chromatography was employed to obtain further purity.

2.4 Product Characterization.



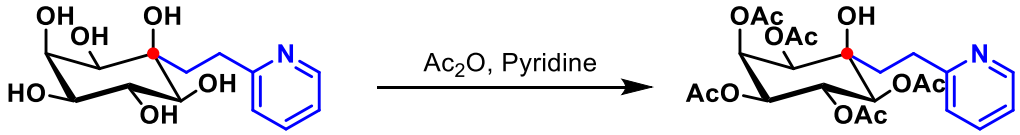
Prepared following general procedure B using *Myo*-Inositol 1 (72 mg, 0.4 mmol, 2.0 equiv.), 4-CzIPN (7.9 mg, 5 mol %, 0.05 equiv.), **13** (3.2 mg, 10 mol %, 0.1 equiv.), $Bu_4NH_2PO_4$ (34.0 mg, 50 mol %, 0.5 equiv.), 4Å MS (granular form, 100 mg), olefin **2a** (21 mg, 0.2 mmol, 1.0 equiv.) and DMSO (1 mL, 0.2 M). Purification by chromatography to give the **3a** (65% yield) as a yellow waxy solid.

Gram scale prepared following general procedure B using *Myo*-Inositol **1** (1440 mg, 8 mmol, 2.0 equiv.), 4-CzIPN (160 mg, 5 mol %, 0.05 equiv.), **13** (120 mg, 10 mol %, 0.1 equiv.), $Bu_4NH_2PO_4$ (780 mg, 50 mol %, 0.5 equiv.), 4Å MS (granular form, 2000 mg), olefin **2a** (420 mg, 0.2 mmol, 1.0 equiv.) and DMSO (20 mL, 0.2 M). Purification by chromatography to give the **3a** (44% yield).

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.44 (d, *J* = 4.0 Hz, 1H), 7.68 (td, *J* = 7.7, 1.8 Hz, 1H), 7.25 – 7.13 (m, 2H), 5.08 (d, *J* = 5.9 Hz, 1H), 4.76 (s, 1H), 4.66 (d, *J* = 7.2 Hz, 1H), 4.52 (s, 1H), 4.44 (s, 1H), 4.35 (d, *J* = 6.1 Hz, 1H), 3.84-3.78 (m, 1H), 3.56 (t, *J* = 9.3 Hz, 1H), 3.37 – 3.35 (m, 1H), 3.17 (d, *J* = 9.3 Hz, 1H), 3.10 – 3.04 (m, 1H), 2.68 (t, J = 8.6 Hz, 2H), 2.01 – 1.81 (m, 2H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 162.7, 149.2, 136.9, 122.9, 121.4, 79.3, 76.1, 73.2, 72.3 72.0, 67.5, 34.2, 32.7.

HRMS: m/z (ESI) calcd. for $C_{13}H_{19}NO_6$ $[M+H]^+$ 286.1285, found 286.1292.



(±)-**3a** (±)-**4a**

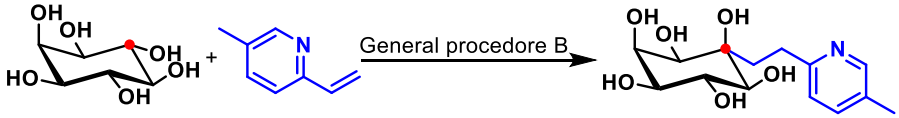
Into a 25 mL reaction flask, **3a** (0.2 mmol, 1.0 equiv.), Ac_2O (2 mmol), Pyridine (1 mmol), The reaction flask stirred at 300 rpm. After 5 hours, the crude reaction mixture was concentrated under vacuum and purified by flash column chromatography on silica gel (DCM: MeOH, 80:1) to give compound **4a** as a yellow solid(50% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 – 8.48 (m, 1H), 7.60 (td, J = 7.7, 1.9 Hz, 1H), 7.16 – 7.13 (m, 1H), 7.12 – 7.09 (m, 1H), 5.85 – 5.73 (m, 2H), 5.62 (t, J = 3.4 Hz, 1H), 5.14 (dd, J = 10.7, 3.5 Hz, 1H), 5.09 (d, J = 9.9 Hz, 1H), 5.02 (d, J = 3.4 Hz, 1H), 3.00 – 2.83 (m, 2H), 2.20 (s, 3H), 2.06 (s, 3H), 2.01 (d, J = 1.5 Hz, 6H), 2.00 (s, 3H), 1.95 – 2.00 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.5, 170.1, 169.8, 169.7, 169.5, 160.8, 148.5, 137.0, 123.2, 121.4, 75.0, 73.5, 70.4, 69.1, 69.0, 68.5, 34.8, 31.5, 21.0, 20.7, 20.9, 20.6, 20.5.

MS: m/z (ESI) calcd. for $C_{23}H_{29}NO_{11}$ $[M+H]^+$ 496.2, found 496.2.

Melting point: 160-161℃



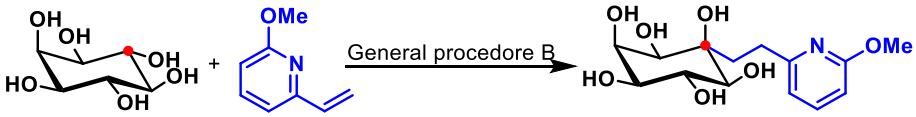
1 **2b** (±)-**3b**

Prepared following general procedure B using *Myo*-Inositol **1** (72 mg, 0.4 mmol, 2.0 equiv.), 4-CzIPN (7.9 mg, 5 mol %, 0.05 equiv.), **13** (3.2 mg, 10 mol %, 0.1 equiv.), $Bu_4NH_2PO_4$ (34.0 mg, 50 mol %, 0.5 equiv.), 4Å MS (granular form, 100 mg), olefin **2b** (23.8 mg, 0.2 mmol, 1.0 equiv.) and DMSO (1 mL, 0.2 M). Purification by chromatography to give the **3b** (44% yield) as a yellow waxy solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.28 – 8.26 (m, 1H), 7.50 (dd, *J* = 8.1, 2.3 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 1H), 5.09 (d, *J* = 6.2 Hz, 1H), 4.77 (s, 1H), 4.72 – 4.67 (m, 1H), 4.57 – 4.53 (m, 1H), 4.48 – 4.44 (m, 1H), 4.38 (d, *J* = 6.4 Hz, 1H), 3.84 – 3.80 (m, 1H), 3.60 – 3.53 (m, 1H), 3.38 – 3.33 (m, 1H), 3.20 – 3.14 (m, 1H), 3.05 (m, 1H), 2.63 (t, *J* = 8.6 Hz, 2H), 2.24 (s, 3H), 1.99 – 1.78 (m, 2H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 159.7, 149.3, 137.3, 130.2, 122.4, 79.3, 76.1, 73.2, 72.3, 72.0, 67.5, 34.2, 32.1, 18.0.

HRMS: m/z (ESI) calcd. for $C_{14}H_{21}NO_6$ $[M+H]^+$ 300.1442, found 300.1449.



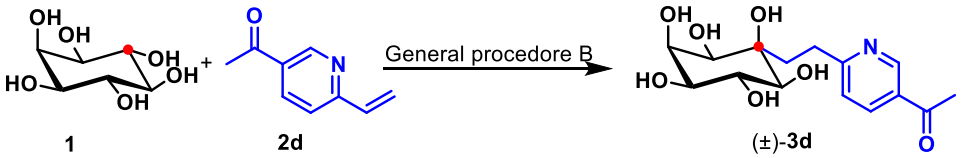
1 2c (±)-3c

Prepared following general procedure B using *Myo*-Inositol **1** (72 mg, 0.4 mmol, 2.0 equiv.), 4-CzIPN (7.9 mg, 5 mol %, 0.05 equiv.), **13** (3.2 mg, 10 mol %, 0.1 equiv.), $Bu_4NH_2PO_4$ (34.0 mg, 50 mol %, 0.5 equiv.), 4Å MS (granular form, 100mg), olefin **2c** (27 mg, 0.2 mmol, 1.0 equiv.) and DMSO (1 mL, 0.2 M). Purification by chromatography to give the desired product (40% yield) as a a yellow waxy solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.57 – 7.61 (m, 1H), 6.80 (d, *J* = 7.3, 1H), 6.59 (d, *J* = 8.2, 1H), 5.10 (d, *J* = 6.1 Hz, 1H), 4.74 (s, 1H), 4.61 (d, *J* = 7.8 Hz, 1H), 4.53 (d, *J* = 4.4 Hz, 1H), 4.45 (d, *J* = 5.9 Hz, 1H), 4.31 (d, *J* = 6.7 Hz, 1H), 3.83 (s, 3H), 3.82 – 3.79 (m, 1H), 3.56 (td, *J* = 9.5, 4.2 Hz, 1H), 3.35 – 3.33 (m, 1H), 3.20 – 3.14 (m, 1H), 3.07 (dd, *J* = 9.3, 6.6 Hz, 1H), 2.66 – 2.52 (m, 2H), 2.05 – 1.83 (m, 2H).

^{13}C NMR (101 MHz, DMSjO-*d*$_6$) δ 163.2, 160.7, 139.7, 115.4, 107.6, 79.2, 76.1, 73.3, 72.2, 72.0, 67.6, 53.2, 33.7, 32.4.

HRMS: m/z (ESI) calcd. for $C_{14}H_{21}NO_7$ $[M+H]^+$ 316.1391, found 316.1398.



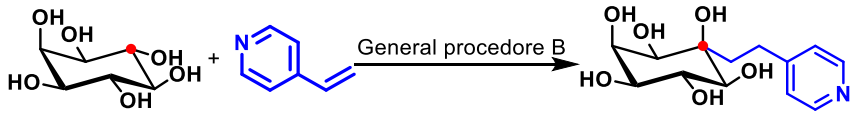
1 2d (±)-3d

Prepared following general procedure B using *Myo*-Inositol **1** (72 mg, 0.4 mmol, 2.0 equiv.), 4-CzIPN (7.9 mg, 5 mol %, 0.05 equiv.), **13** (3.2 mg, 10 mol %, 0.1 equiv.), $Bu_4NH_2PO_4$ (34.0 mg, 50 mol %, 0.5 equiv.), 4Å MS (granular form, 100mg), olefin **2d** (29.4 mg, 0.2 mmol, 1.0 equiv.) and DMSO (1 mL, 0.2 M). Purification by chromatography to give the **3d** (46 % yield) as a yellow waxy solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.01 (d, *J* = 1.7 Hz, 1H), 8.19 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 5.23 – 4.18 (m, 6H), 3.83 (t, *J* = 2.8 Hz, 1H), 3.57 (t, *J* = 9.5 Hz, 2H), 3.45 – 3.40 (m, 1H), 3.17 (dt, *J* = 10.6, 5.3 Hz, 1H), 3.12 – 3.07 (m, 1H), 2.78 (t, *J* = 9.7 Hz, 2H), 2.60 (s, 3H), 2.03 – 1.80 (m, 2H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 197.6, 167.6, 149.5, 136.4, 130.2, 123.0, 79.2, 76.1, 73.2, 72.2, 72.0, 67.6, 34.0, 32.9, 27.3.

HRMS: m/z (ESI) calcd. for $C_{15}H_{21}NO_7$ $[M+H]^+$ 328.1391, found 328.1398.



1 2e (±)-3e

Prepared following general procedure B using *Myo*-Inositol **1** (72 mg, 0.4 mmol, 2.0 equiv.), 4-CzIPN (7.9 mg, 5 mol %, 0.05 equiv.), **13** (3.2 mg, 10 mol %, 0.1 equiv.), $Bu_4NH_2PO_4$ (34.0 mg, 50 mol %, 0.5 equiv.), 4Å MS (granular form, 100mg), olefin **2e** (21 mg, 0.2 mmol, 1.0 equiv.) and DMSO (1 mL, 0.2 M). Purification by chromatography to give the **3e** (47% yield) as a yellow solid.

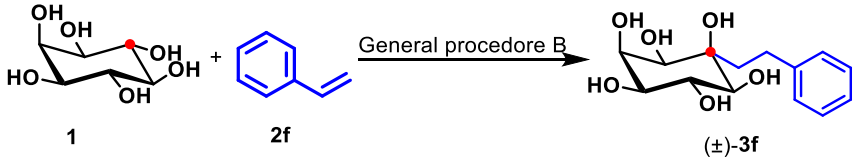
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.42 (m, 2H), 7.20 (d, *J* = 5.`9 Hz, 2H), 5.14 – 5.07 (m, 1H), 4.75 – 4.64 (m, 2H), 4.55 (s, 1H), 4.45 – 4.40 (m, 1H), 3.83 – 3.78 (m, 1H), 3.55

(t, J = 9.4 Hz, 1H), 3.43 - 3.38 (m, 1H), 3.19 – 3.13 (m, 1H), 3.07 (d, J = 9.2 Hz, 1H), 2.58 – 2.51 (m, 2H), 1.91 – 1.71 (m, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 152.3, 149.9, 124.2, 79.2, 76.1, 73.1, 72.2, 71.9, 67.4, 35.1, 29.5.

HRMS: m/z (ESI) calcd. for $C_{13}H_{19}NO_6$ $[M+H]^+$ 286.1285, found 286.1291.

Melting point: 223-225℃



1 2f (±)-3f

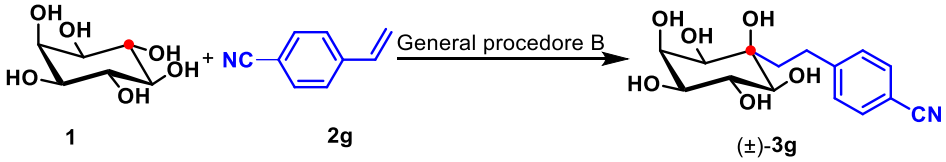
Prepared following general procedure B using *Myo*-Inositol **1** (72 mg, 0.4 mmol, 2.0 equiv.), 4-CzIPN (7.9 mg, 5 mol %, 0.05 equiv.), **13** (3.2 mg, 10 mol %, 0.1 equiv.), $Bu_4NH_2PO_4$ (34.0 mg, 50 mol %, 0.5 equiv.), 4Å MS (granular form, 100mg), olefin **2f** (20.8 mg, 0.2 mmol, 1.0 equiv.) and DMSO (1 mL, 0.2 M). Purification by chromatography to give the **3f** (38% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.29 – 7.24 (m, 2H), 7.21 – 7.12 (m, 3H), 5.20 – 4.02 (m, 6H), 3.83 (t, J = 2.7 Hz, 1H), 3.57 (t, J = 9.4 Hz, 1H), 3.38 (d, J = 2.7 Hz, 1H), 3.18 (dd, J = 9.6, 2.9 Hz, 1H), 3.10 (d, J = 9.3 Hz, 1H), 2.48 (d, J = 9.1 Hz, 2H), 1.91 – 1.71 (m, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 143.4, 128.7, 128.6, 125.9, 79.3, 76.1, 73.0, 72.3, 72.0, 67.3, 36.2, 30.2.

HRMS: m/z (ESI) calcd. for $C_{14}H_{20}O_6$ $[M+Na]^+$ 307.1152, found 307.1153.

Melting point: 204-206℃



1 2g (±)-3g

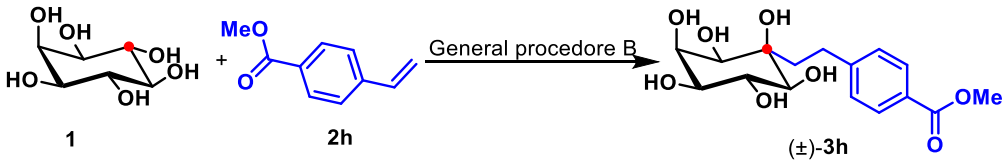
Prepared following general procedure B using *Myo*-Inositol **1** (72 mg, 0.4 mmol, 2.0 equiv.), 4-CzIPN (7.9 mg, 5 mol %, 0.05 equiv.), **13** (3.2 mg, 10 mol %, 0.1 equiv.), $Bu_4NH_2PO_4$ (34.0 mg, 50 mol %, 0.5 equiv.), 4Å MS (granular form, 100mg), olefin **2g** (25.8 mg, 0.2 mmol, 1.0 equiv.) and DMSO (1 mL, 0.2 M). Purification by chromatography to give the **3g** (56% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.74 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.3 Hz, 2H), 4.62 - 3.49 (m, 6H), 3.83 (t, J = 2.8 Hz, 1H), 3.57 (t, J = 9.4 Hz, 1H), 3.37 (d, J = 2.8 Hz, 1H), 3.18 (dd, J = 9.6, 3.0 Hz, 1H), 3.08 (d, J = 9.3 Hz, 1H), 2.64 – 2.55 (m, 2H), 1.80 (m, J = 18.0, 12.9, 7.3 Hz, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 149.6, 132.7, 129.7, 119.6, 108.8, 79.2, 76.1, 73.0, 72.3, 71.9, 67.4, 35.8, 30.4.

HRMS: m/z (ESI) calcd. for $C_{15}H_{19}NO_6$ $[M+Na]^+$ 332.1105, found 332.1105.

Melting point: 200-203℃



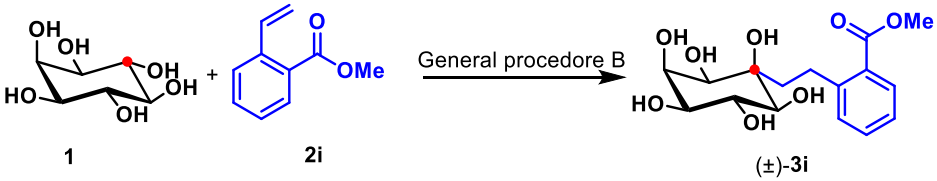
Prepared following general procedure B using *Myo*-Inositol **1** (72 mg, 0.4 mmol, 2.0 equiv.), 4-CzIPN (7.9 mg, 5 mol %, 0.05 equiv.), **13** (3.2 mg, 10 mol %, 0.1 equiv.), $Bu_4NH_2PO_4$ (34.0 mg, 50 mol %, 0.5 equiv.), 4Å MS (granular form, 100mg), olefin **2h** (32.4 mg, 0.2 mmol, 1.0 equiv.) and DMSO (1 mL, 0.2 M). Purification by chromatography to give the **3h** (52% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 4.34 – 3.87 (m, 6H), 3.83 (s, 2H), 3.57 (t, *J* = 9.5 Hz, 1H), 3.38 (d, *J* = 2.7 Hz, 1H), 3.18 (dd, *J* = 9.7, 2.9 Hz, 1H), 3.09 (d, *J* = 9.3 Hz, 1H), 2.61 – 2.55 (m, 1H), 1.92 – 1.73 (m, 1H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 166.7, 149.4, 129.7, 129.0, 127.5, 79.3, 76.1, 73.0, 72.3, 71.9, 67.3, 52.4, 35.9, 30.3.

HRMS: m/z (ESI) calcd. for $C_{16}H_{22}O_8$ $[M+Na]^+$ 365.1207, found 365.1210.

Melting point: 210-211℃



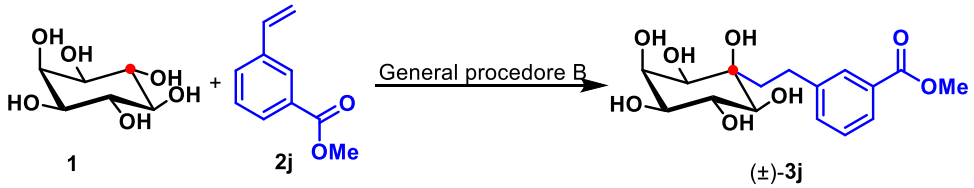
Prepared following general procedure B using *Myo*-Inositol **1** (72 mg, 0.4 mmol, 2.0 equiv.), 4-CzIPN (7.9 mg, 5 mol %, 0.05 equiv.), **13** (3.2 mg, 10 mol %, 0.1 equiv.), $Bu_4NH_2PO_4$ (34.0 mg, 50 mol %, 0.5 equiv.), 4Å MS (granular form, 100mg), olefin **2i** (32.4 mg, 0.2 mmol, 1.0 equiv.) and DMSO (1 mL, 0.2 M). Purification by chromatography to give the **3i** (37% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.72-7.65 (m, 1H), 7.53 - 7.45 (m, 1H), 7.36 – 7.251 (m, 2H), 4.43 - 3.90 (m, 6H), 4.02 (s, 1H), 3.84 (s, 3H), 3.56 (t, *J* = 9.4 Hz, 1H), 3.37 (d, *J* = 2.7 Hz, 1H), 3.18 (dd, *J* = 9.6, 2.9 Hz, 1H), 3.10 (d, *J* = 9.3 Hz, 1H), 2.83 – 2.74 (m, 2H), 1.86 – 1.68 (m, 2H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 168.6, 143.8, 132.3, 130.9, 130.5, 130.1, 126.3, 79.3, 76.0, 73.1, 72.3, 72.0, 67.4, 52.6, 36.3, 28.5.

HRMS: m/z (ESI) calcd. for $C_{16}H_{22}O_8$ $[M+Na]^+$ 365.1207, found 365.1206.

Melting point: 189-191℃



Prepared following general procedure B using *Myo*-Inositol **1** (72 mg, 0.4 mmol, 2.0 equiv.), 4-CzIPN (7.9 mg, 5 mol %, 0.05 equiv.), **13** (3.2 mg, 10 mol %, 0.1 equiv.), $Bu_4NH_2PO_4$ (34.0 mg, 50 mol %, 0.5 equiv.), 4Å MS (granular form, 100mg), olefin **2j** (32.4 mg, 0.2 mmol, 1.0 equiv.) and DMSO (1 mL, 0.2 M). Purification by

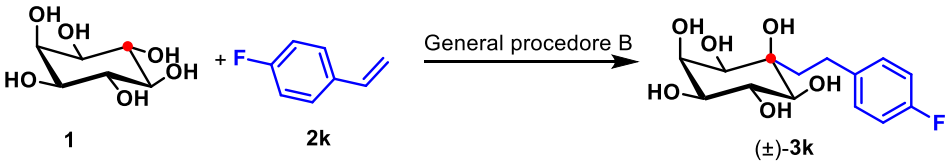
chromatography to give the **3j** (37% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.82 (s, 1H), 7.77 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.55 – 7.37 (m, 2H), 4.34 - 4.04 (m, 6H), 3.85 (s, 2H), 3.83 (t, *J* = 2.8 Hz, 1H), 3.57 (t, *J* = 9.5 Hz, 1H), 3.39 (d, *J* = 2.8 Hz, 1H), 3.18 (dd, *J* = 9.6, 3.0 Hz, 1H), 3.10 (d, *J* = 9.3 Hz, 1H), 2.56 (q, *J* = 8.7 Hz, 2H), 1.91 – 1.71 (m, 2H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 166.8, 144.1, 133.7, 130.1, 129.2, 129.2, 126.9, 79.3, 76.1, 73.0, 72.3, 71.9, 67.3, 52.5, 36.3, 30.0.

HRMS: m/z (ESI) calcd. for $C_{16}H_{22}O_8$ $[M+Na]^+$ 365.1207, found 365.1215.

Melting point: 179-181℃



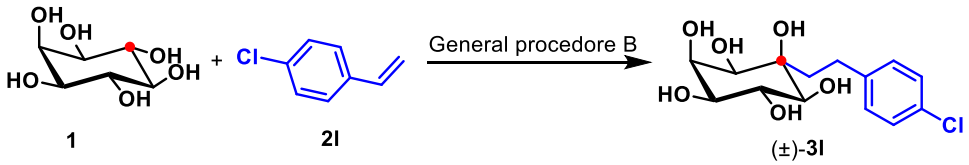
Prepared following general procedure B using *Myo*-Inositol **1** (72 mg, 0.4 mmol, 2.0 equiv.), 4-CzIPN (7.9 mg, 5 mol %, 0.05 equiv.), **13** (3.2 mg, 10 mol %, 0.1 equiv.), $Bu_4NH_2PO_4$ (34.0 mg, 50 mol %, 0.5 equiv.), 4Å MS (granular form, 100mg), olefin **2k** (24.4 mg, 0.2 mmol, 1.0 equiv.) and DMSO (1 mL, 0.2 M). Purification by chromatography to give the **3k** (21% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.20 (dd, *J* = 8.5, 5.7 Hz, 1H), 7.09 (t, *J* = 8.9 Hz, 1H), 3.84 – 3.81 (m, 1H), 3.56 (t, *J* = 9.5 Hz, 1H), 3.36 (d, *J* = 2.8 Hz, 1H), 3.17 (dd, *J* = 9.6, 2.9 Hz, 1H), 3.08 (d, *J* = 9.3 Hz, 0H), 2.46 (d, *J* = 8.9 Hz, 2H), 1.88 – 1.69 (m, 2H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 139.4, 130.3, 130.2, 115.4, 115.2, 79.3, 76.1, 73.0, 72.3, 71.9, 67.3, 36.4, 29.3.

HRMS: m/z (ESI) calcd. for $C_{14}H_{19}FO_6$ $[M+K]^+$ 341.0797, found 341.0770.

Melting point: 184-186℃



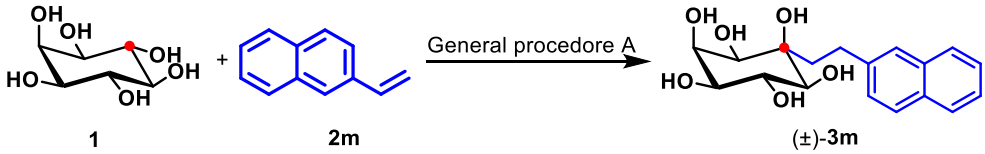
Prepared following general procedure B using *Myo*-Inositol **1** (72 mg, 0.4 mmol, 2.0 equiv.), 4-CzIPN (7.9 mg, 5 mol %, 0.05 equiv.), **13** (3.2 mg, 10 mol %, 0.1 equiv.), $Bu_4NH_2PO_4$ (34.0 mg, 50 mol %, 0.5 equiv.), 4Å MS (granular form, 100mg), olefin **2l** (27.6 mg, 0.2 mmol, 1.0 equiv.) and DMSO (1 mL, 0.2 M). Purification by chromatography to give the **3l** (37% yield) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.32 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 5.13 – 5.07 (m, 1H), 4.76 – 4.63 (m, 1H), 4.55 (s, 1H), 4.43 (d, *J* = 11.4 Hz, 1H), 3.82 (s, 1H), 3.56 (t, *J* = 9.4 Hz, 1H), 3.37 (s, 1H), 3.17(d, *J* = 9.2 Hz, 1H), 3.08 (d, *J* = 6.5 Hz, 1H), 2.53 – 2.44 (m, 2H), 1.88 – 1.69 (m, 2H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 142.4, 130.5, 128.6, 79.3, 76.1, 73.0, 72.3, 71.9, 67.3, 36.1, 29.5.

HRMS: m/z (ESI) calcd. for $C_{14}H_{19}ClO_6$ $[M+Na]^+$ 341.0762, found 341.0761.

Melting point: 222-225℃



1 2m (±)-3m

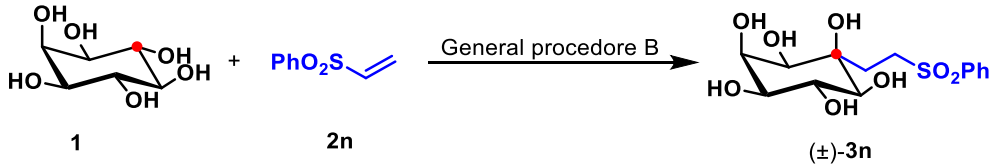
Prepared following general procedure A using *Myo*-Inositol **1** (72 mg, 0.4 mmol, 2.0 equiv.), 4-CzIPN (7.9 mg, 5 mol %, 0.05 equiv.), **13** (3.2 mg, 10 mol %, 0.1 equiv.), $Bu_4NH_2PO_4$ (34.0 mg, 50 mol %, 0.5 equiv.), 4Å MS (granular form, 100mg), olefin **2m** (30.8 mg, 0.2 mmol, 1.0 equiv.) and DMSO (1 mL, 0.2 M). Purification by chromatography to give the **3m** (47% yield) as a gray solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.89 – 7.80 (m, 3H), 7.66 (s, 1H), 7.51 – 7.35 (m, 4H), 7.40 – 7.35 (m, 1H), 5.11 (d, *J* = 6.1 Hz, 1H), 4.75 (s, 1H), 4.69 (d, *J* = 7.7 Hz,1H), 4.56 (d, *J* = 4.1 Hz, 1H), 4.44 (dd, *J* = 14.9, 6.2 Hz, 1H), 3.88 – 3.82 (m, 1H), 3.59 (td, *J* = 9.4, 3.8 Hz, 1H), 3.43 (dd, *J* = 7.5, 2.4 Hz, 1H), 3.23 – 3.12 (m, 2H), 2.67 (t, *J* = 8.7 Hz, 2H), 2.00 – 1.87 (m, 2H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 141.0, 133.7, 131.9, 128.1, 128.0, 127.9, 127.7, 126.4, 126.1, 125.5, 79.4, 76.1, 73.1, 72.3, 72.0, 67.4, 36.1, 30.4.

HRMS: m/z (ESI) calcd. for $C_{18}H_{22}O_6$ $[M+Na]^+$ 357.1309, found 357.1310.

Melting point: 242-243℃



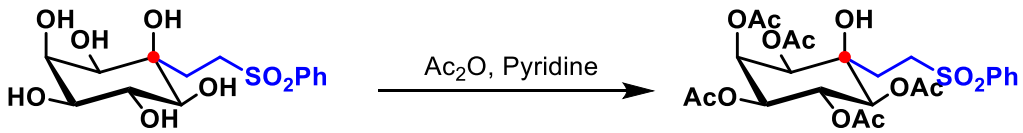
1 2n (±)-3n

Prepared following general procedure B using *Myo*-Inositol **1** (72 mg, 0.4 mmol, 2.0 equiv.), 4-CzIPN (7.9 mg, 5 mol %, 0.05 equiv.), **13** (3.2 mg, 10 mol %, 0.1 equiv.), $Bu_4NH_2PO_4$ (34.0 mg, 50 mol %, 0.5 equiv.), 4Å MS (granular form, 100mg), olefin **2n** (33.6 mg, 0.2 mmol, 1.0 equiv.) and DMSO (1 mL, 0.2 M). Purification by chromatography to give the **3n** (61% yield) as a collorless waxy solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.87 – 7.81 (m, 2H), 7.77 – 7.71 (m, 1H), 7.68 – 7.63 (m, 2H), 5.16 (d, J = 5.5 Hz, 1H), 4.67 (t, *J* = 4.0 Hz, 2H), 4.50 (d, *J* = 4.4 Hz, 2H), 4.46 (d, *J* = 5.7 Hz, 1H), 4.37 (d, *J* = 6.8 Hz, 1H), 3.73 – 3.70 (m, 1H), 3.45 (td, *J* = 9.4, 4.3 Hz, 1H), 3.36 – 3.34 (m, 1H), 3.20 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.16 (d, *J* = 5.3 Hz, 1H), 3.12 – 3.04 (m, 1H), 2.86 (dd, *J* = 9.3, 6.7 Hz, 1H), 1.94 – 1.74 (m, 2H).

^{13}C NMR (101 MHz, DMSO)-*d*$_6$) δ 139.7, 134.1, 129.9, 128.0, 78.0, 75.9, 74.5, 71.9, 71.6, 68.7, 52.0, 28.1.

HRMS: m/z (ESI) calcd. for $C_{14}H_{20}O_8S$ $[M+Na]^+$ 371.0771, found 371.0778.



3n (±)-4n

Into a 25 mL reaction flask, **3n** (0.2 mmol, 1.0 equiv.), Ac_2O (2 mmol), Pyridine (1 mmol), The reaction flask stirred at 300 rpm. After 5 hours, the crude reaction mixture

was concentrated under vacuum and purified by flash column chromatography on silica gel (PE: EA,2:1) to give compound **4n** as a yellow waxy solid (85% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.82 (m, 2H), 7.70 – 7.62 (m, 1H), 7.53 – 7.62 (m, 2H), 5.65 (t, *J* = 10.3 Hz, 1H), 5.59 (t, *J* = 3.4 Hz, 1H), 3.23 - 3.13 (m, 1H), 3.08 - 2.98 (m, 1H), 2.16 (s, 3H), 2.04 – 2.04 (m, 6H), 1.99 (s, 3H), 1.96 (s, 3H), 1.91 - 1.83 (m, 2H)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.9, 169.7, 169.5, 169.5, 169.3, 138.5, 133.9, 129.4, 128.2, 75.9, 71.5, 69.4, 68.2, 68.2, 67.3, 50.5, 27.3, 20.8, 20.5, 20.4, 20.4, 20.4.

MS: m/z (ESI) calcd. for $C_{24}H_{30}O_{13}S$ $[M+H]^+$ 559.1, found 559.1.

3. Mechanistic Studies

3.1 Stern-Volmer Experiment

Stern-Volmer Plot of 4-CzIPN with varying concentration of quenchers: 2.0 mL sample solution (in DMSO) containing 10^{-5}M of 4-CzIPN together with 10^{-4}M-10^{-2}M of **13**.and 10^{-4}M-10^{-2}M of **1**. All of solutions were excited at 360 nm and the emission intensity at 530 nm was observed.

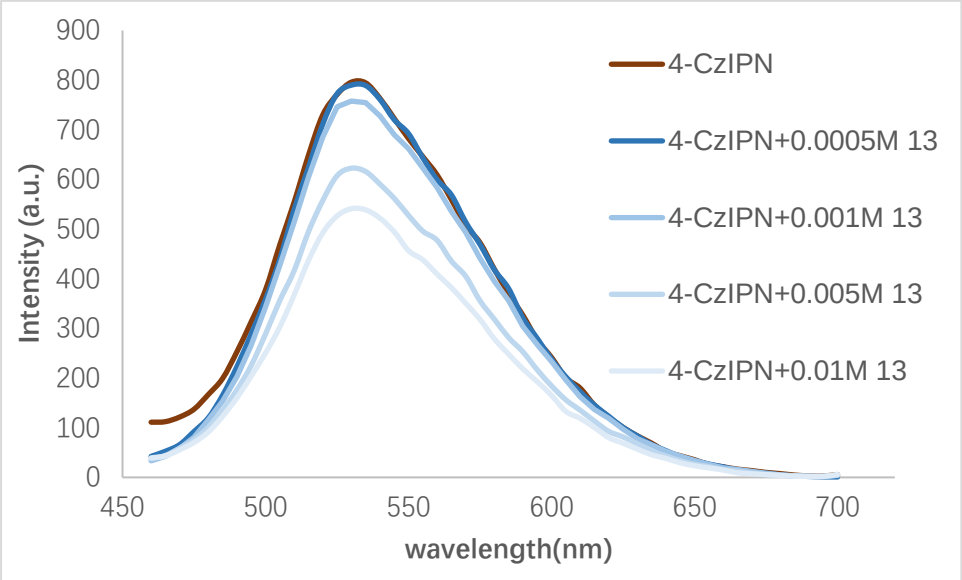


Figure S1 The fluorescence emission spectra of 4-CzIPN with different concentration of **13** excited at 360 nm

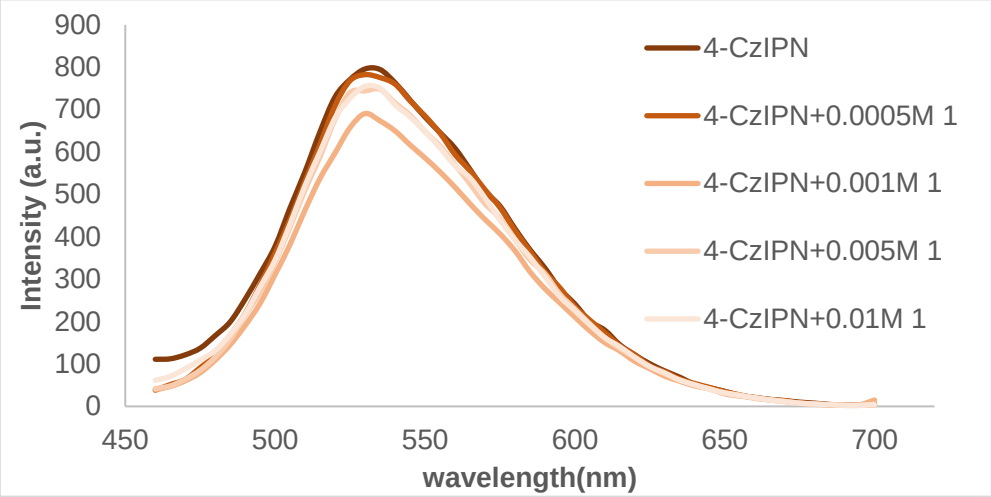


Figure S2 The fluorescence emission spectra of 4-CzIPN with different concentration of **1** excited at 360 nm

3.2 UV-Vis spectroscopy, fluorescence emission and lifetime

UV-Vis absorbance was performed on a BioTek Epoch2 Fluorescence emission was performed on Perkin Elmer LS55 and fluorescence lifetime was performed on Edinburgh Instruments F900.

UV-Vis absorbance and fluorescence emission between different solution from the same 4-CzIPN concentration show nearly no differences. A superposition of some examples is depicted in the following figures, followed by more detailed depiction of the individual spectra. All spectra were recorded at a concentration of $1x10^{-5}$mol/L for 4-CzIPN. The excitation wavelength for recording of fluorescence emission spectra was 360 nm.

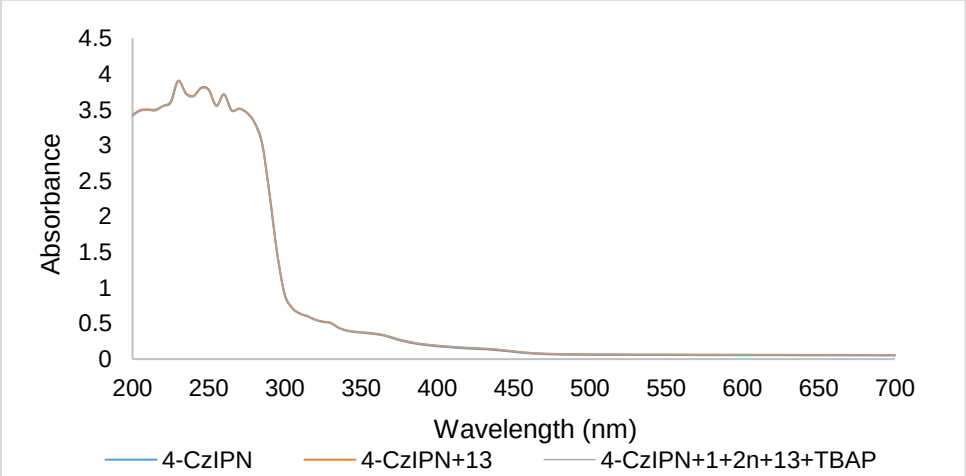


Figure S3 Superposition of the absorption spectra of 4-CzIPN and reaction component

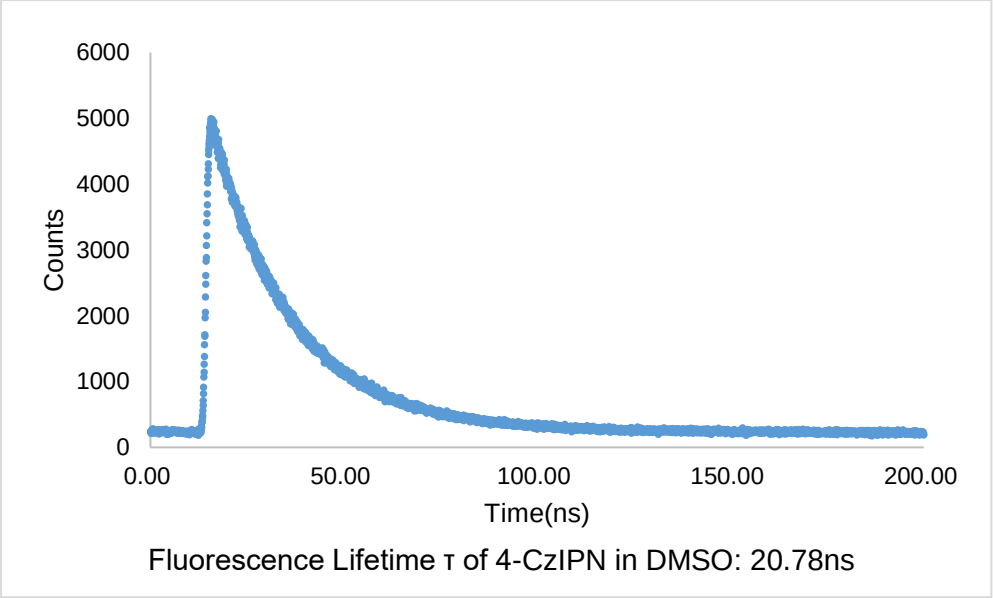


Figure S4 Fluorescence Lifetime of 4-CzIPN in DMSO

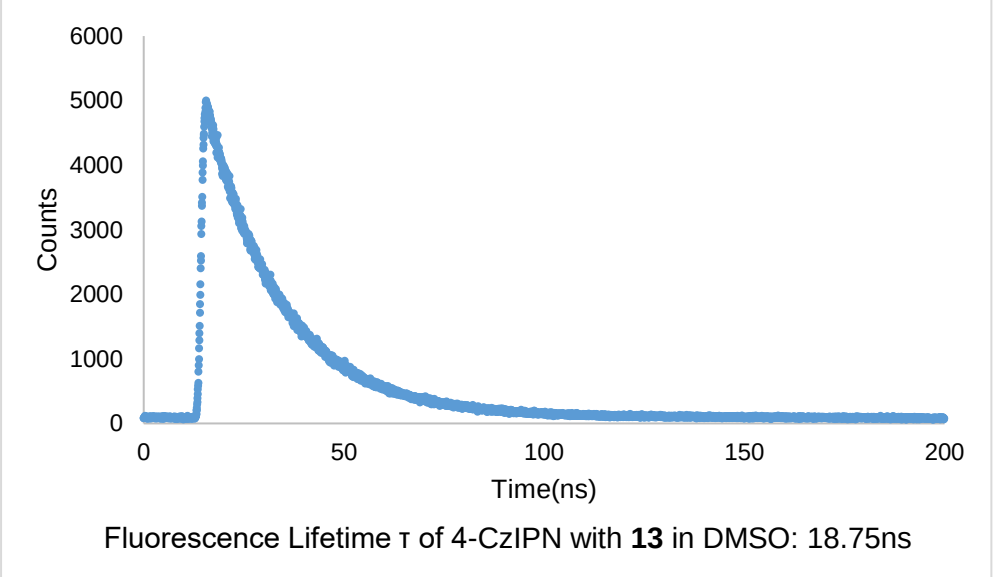


Figure S5 Fluorescence Lifetime of 4-CzIPN with **13** in DMSO

3.3 Regioselectivity Study

Solutions of **1** (9.0 mg, 0.05 mmol, 1.0 equiv.)in DMSO-*d*6 (0.5 mL, 0.1 M) were prepared and both tetra-n-butylammonium phosphate (8.5 mg, 0.025 mmol, 0.5 equiv.) were added, Proton-decoupled ^{13}C NMR spectra were acquired at 101 MHz.

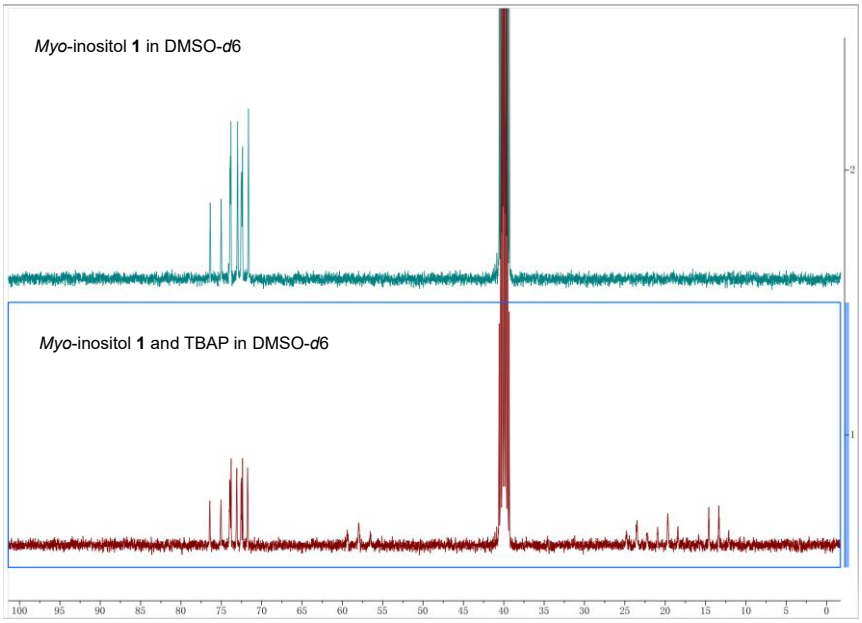


Figure S6 Proton-decoupled ^{13}C NMR spectra

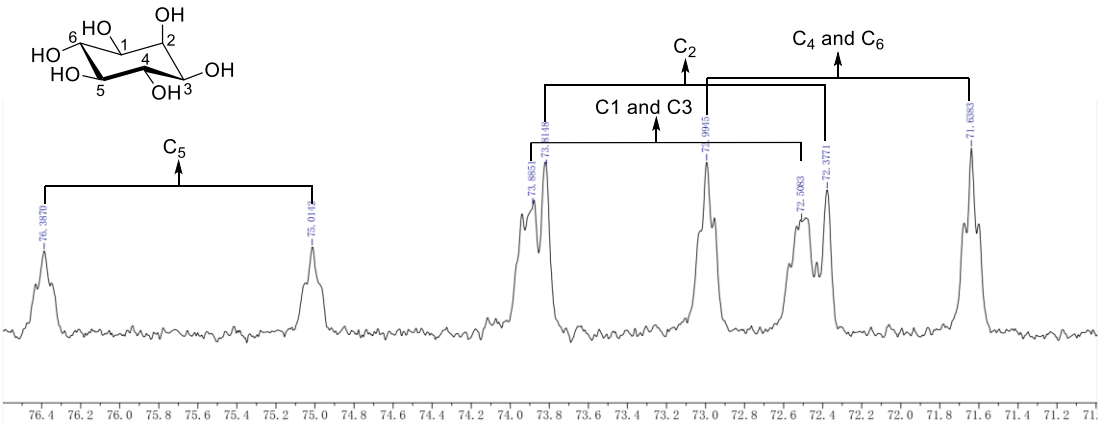


Figure S7 Proton-decoupled ^{13}C NMR spectra of *myo*-inositol **1**

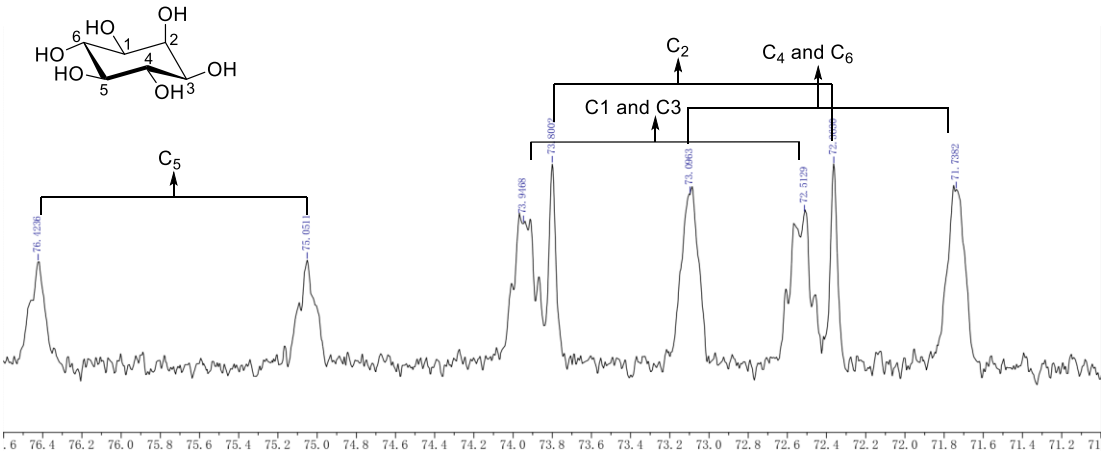


Figure S8 Proton-decoupled ^{13}C NMR spectra of the mixture of *myo*-inositol **1** and TBAP

Table S6 Data of $^{1}J_{CH}$ and δ

1 in d_6-DMSO	**C1 / C3**	**C2**	**C4 / C6**	**C5**
δ (ppm)	72.72	72.68	71.91	75.28
$^{1}J_{CH}$ (Hz)	152.51	145.44	136.35	138.37
1+ TBAP in d_6-DMSO				
δ (ppm)	72.78	72.65	71.98	75.05
Δδ(ppm)	0.06	-0.03	0.07	-0.23
$^{1}J_{CH}$ (Hz)	141.40	145.44	136.35	138.37
Δ$^{1}J_{CH}$ (Hz)	-11.11	0	0	0

In summary, according to the literature[5-9], both chemical shift of NMR and the $^{1}J_{CH}$ coupling constant are decrease after the hydrogen bond is formed between the alcohol and TBAP. However, The result is inconsistent with the experimental result. In addition, we cannot obtain a definite value of the change in the $^{1}J_{CH}$ coupling constant caused by hydrogen bonding due to the hydrogen bonds complexity and the mechanical error of the NMR instrument.

3.4 HPLC Analysis of Reaction Mixture

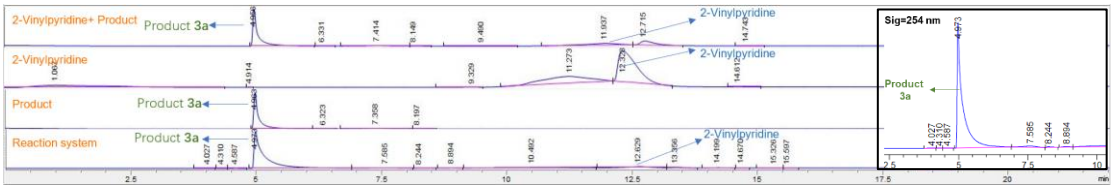


Figure S9 HPLC data of **3a** reaction mixture

4. X-Ray Crystallographic Data.

The crystals were obtained from a solution of hexane and dichloromethane upon slow volatilization. The X-ray intensity data were measured at 293K.

Table S7 Crystal data and structure refinement for **4a**

Item	Value
Identification code	4a
Empirical formula	$C_{23}H_{29}NO_{11}$
Formula weight	495.47
Temperature/K	294.4(6)
Crystal system	triclinic
Space group	P-1
a/Å	9.59580(9)

b/Å	11.62912(10)
c/Å	11.80883(10)
α/°	96.0575(7)
β/°	90.7961(7)
γ/°	107.8097(8)
Volume/Å^3	1246.12(2)
Z	2
ρ_{calc}g/cm^3	1.320
μ /mm^{-1}	0.899
F(000)	524.0
Crystal size/mm^3	0.12 × 0.08 × 0.07
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.538 to 152.47
Index ranges	-11 ≤ h ≤ 12, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14
Reflections collected	35365
Independent reflections	4922 [R_{int} = 0.0257, R_{sigma} = 0.0111]
Data/restraints/parameters	4922/0/323
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1= 0.0458, wR_2= 0.1179
Final R indexes [all data]	R_1= 0.0475, wR_2= 0.1191
Largest diff. peak/hole / e Å^{-3}	0.46/-0.29

5.References

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2. *CN Pat.,* CN107721999 (A) 2018.
3. S. Takemura, Y. Miki, M. Hoshida, M. Shibano and A. Suzuki, *CHEMICAL & PHARMACEUTICAL BULLETIN*, 1981, **213**, 3019-3025.
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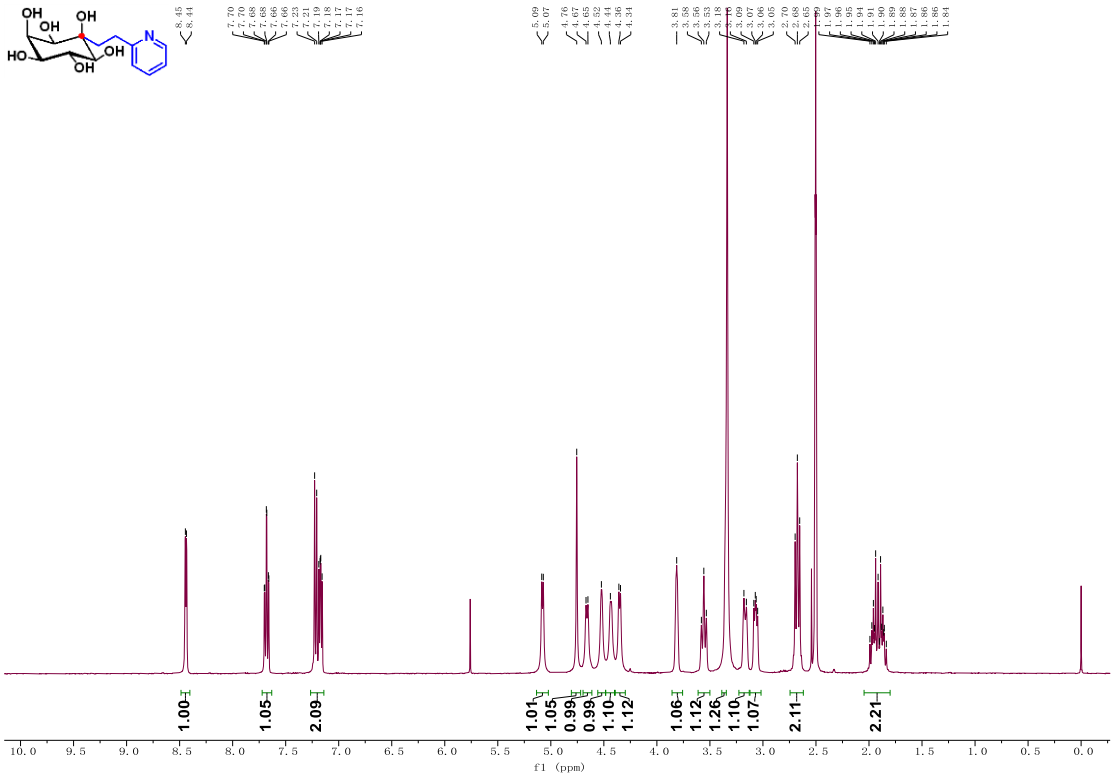
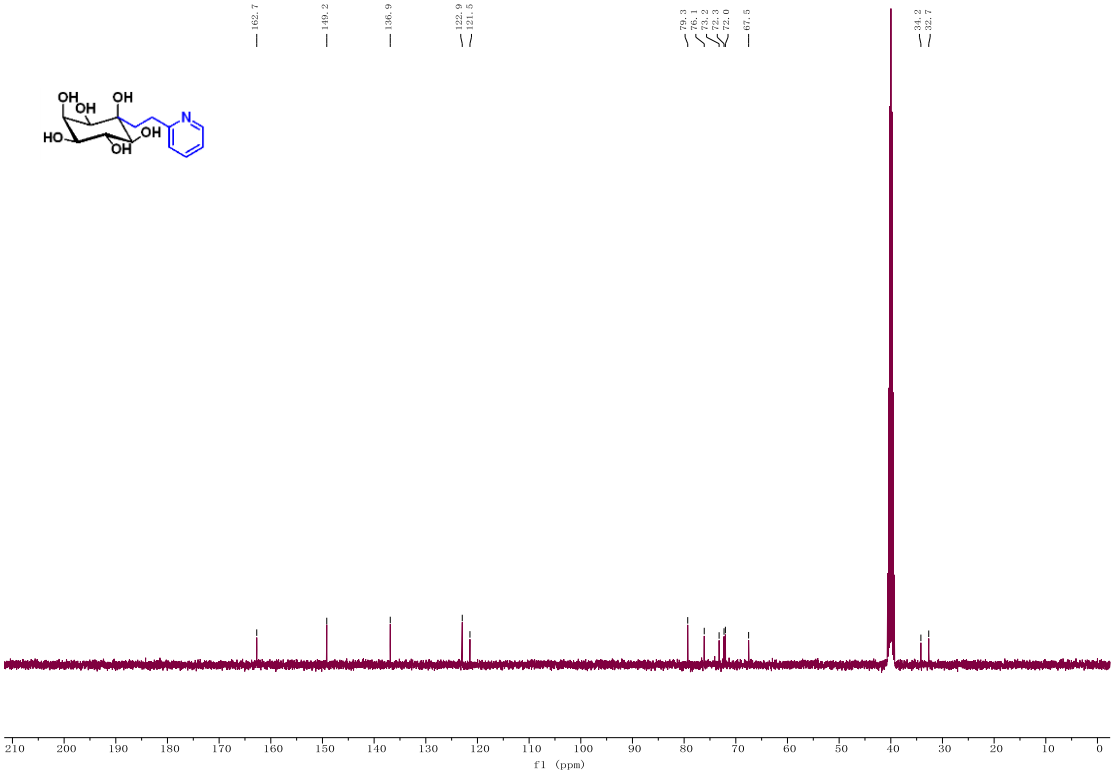
6. NMR Spectra of the Products

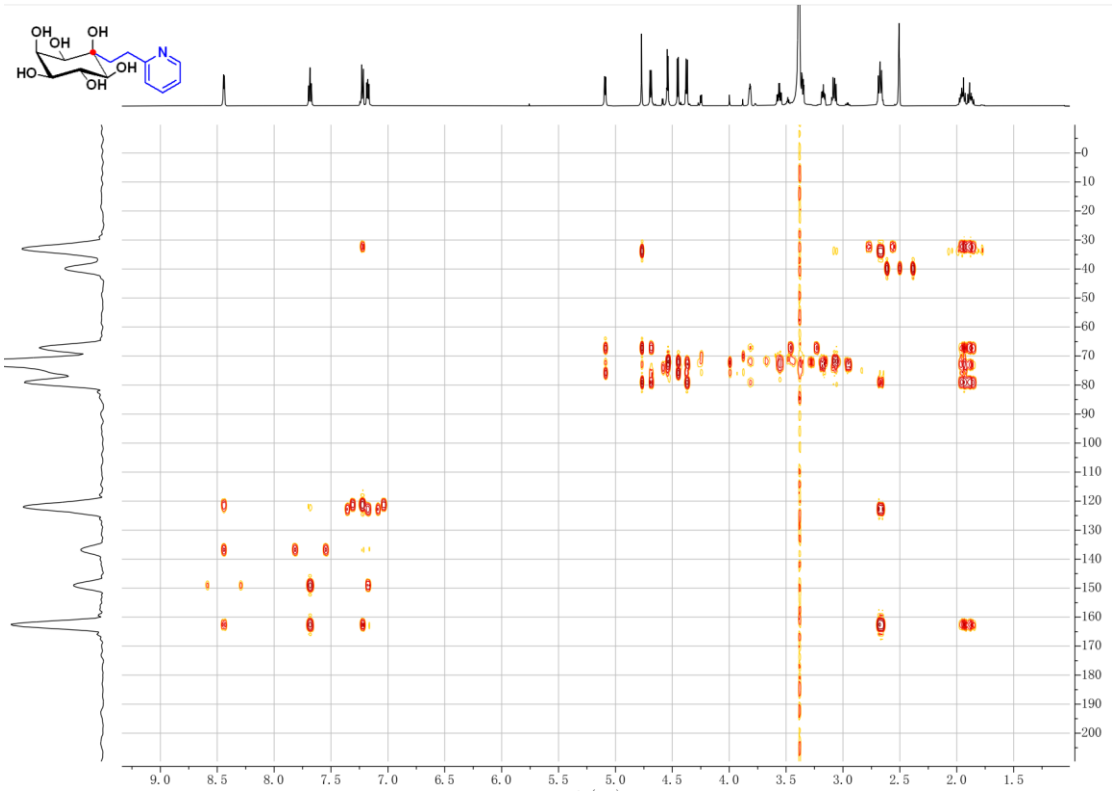
3a (^{1}H NMR, 400 MHz, DMSO-d_6)



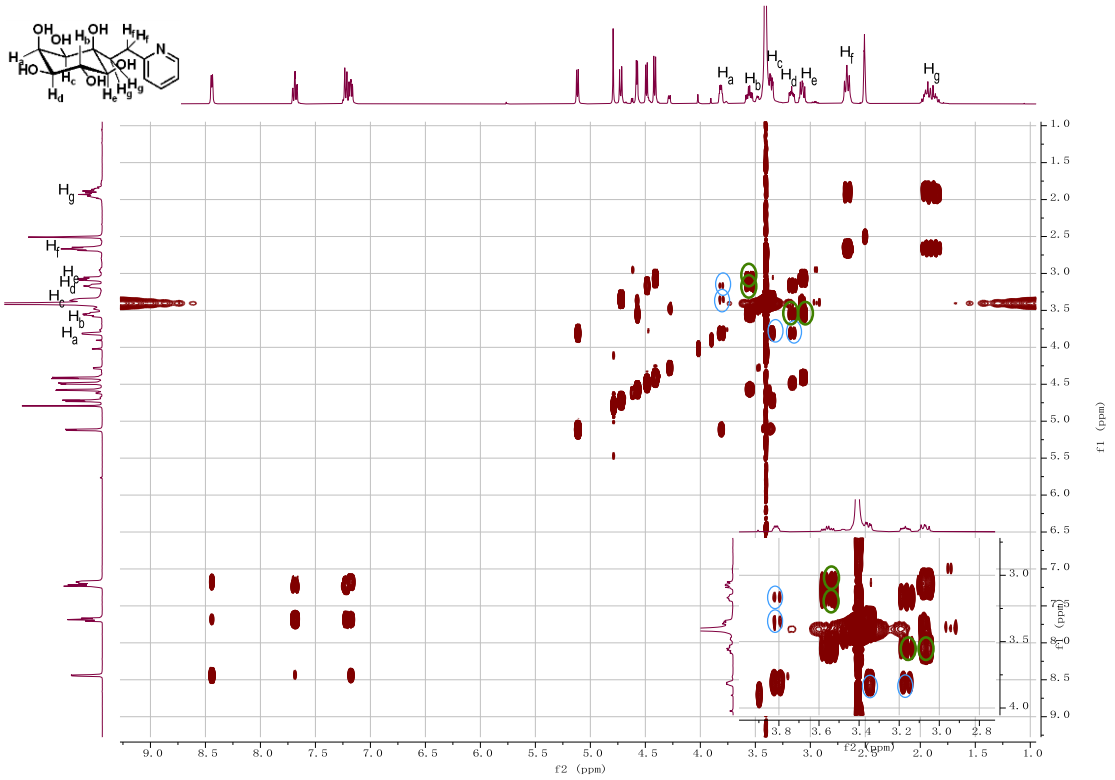
3a (^{13}C NMR, 101 MHz, DMSO-d_6)

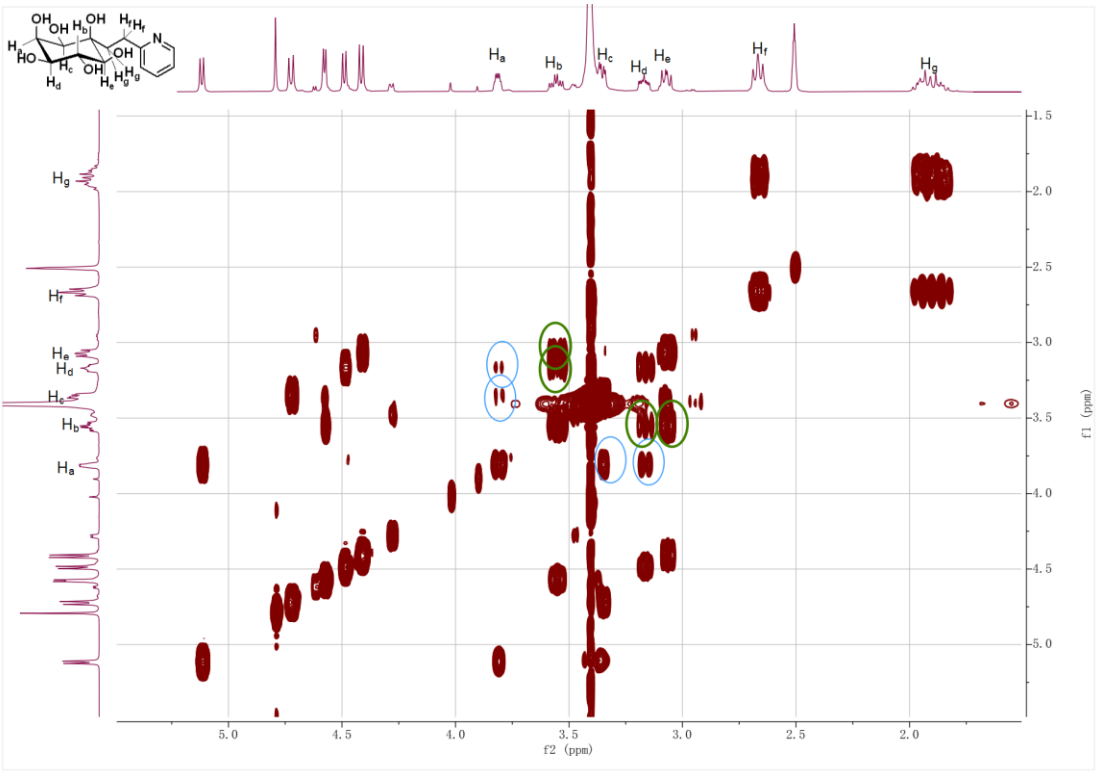


3a (HMBC, 600 MHz, DMSO-d_6)

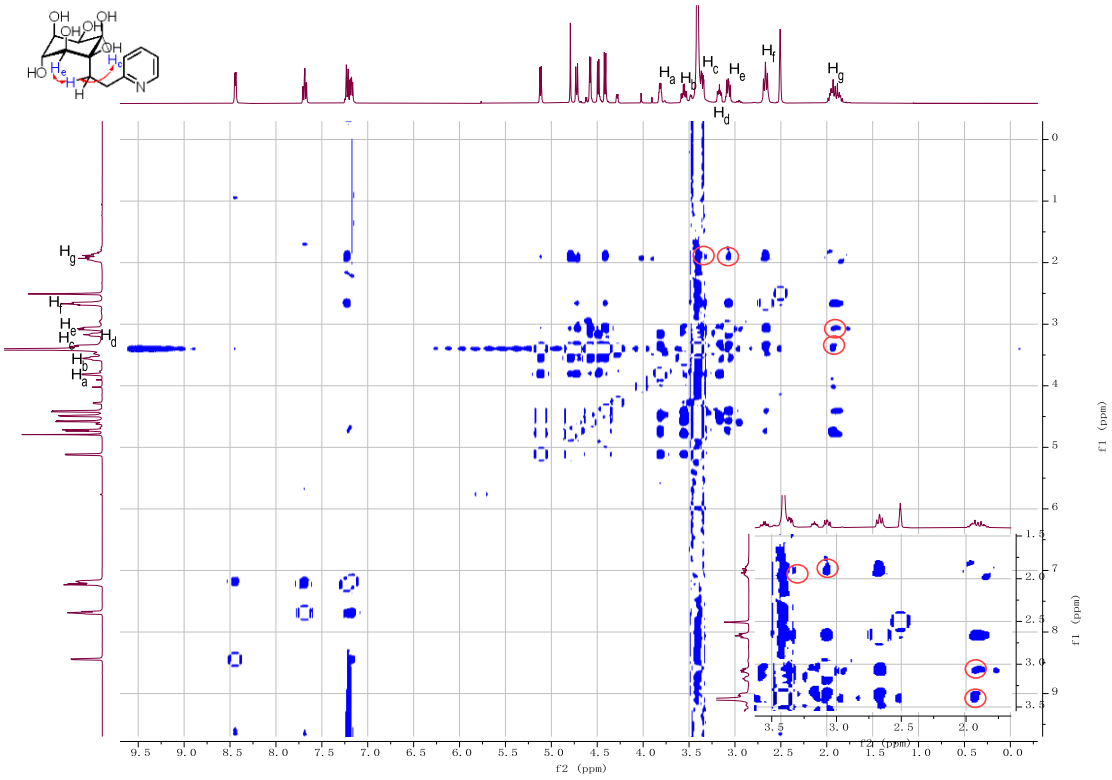


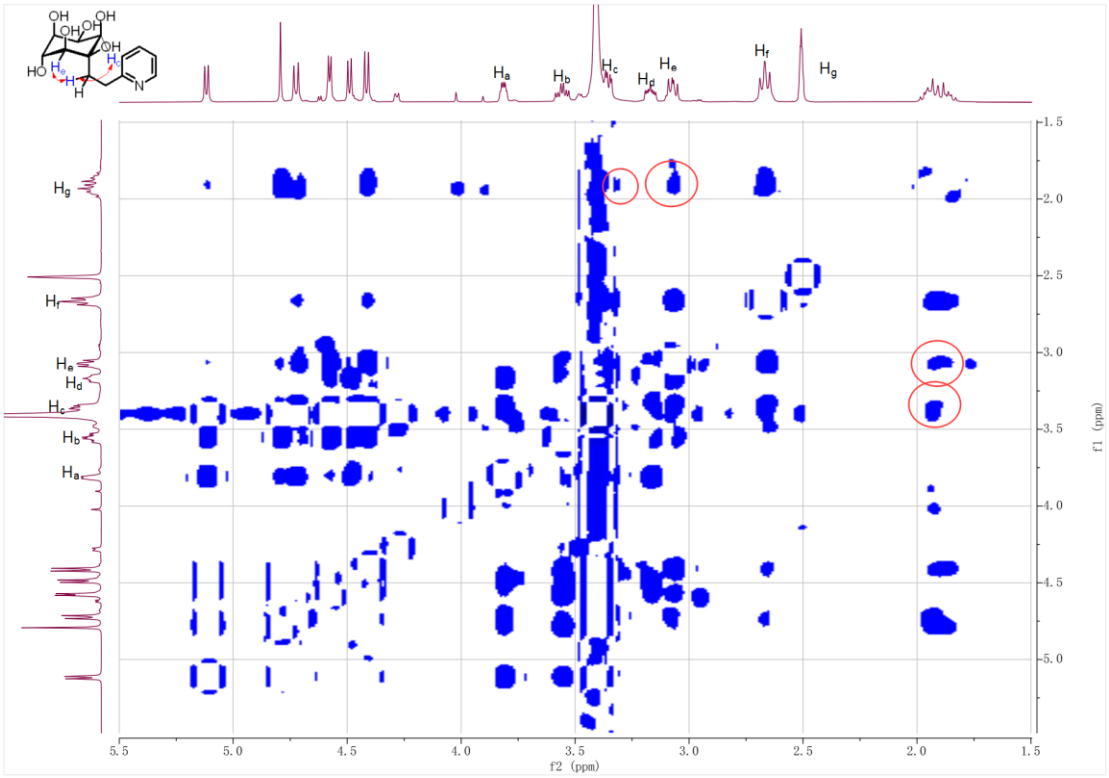
3a (COSY, 400 MHz, DMSO-d_6)



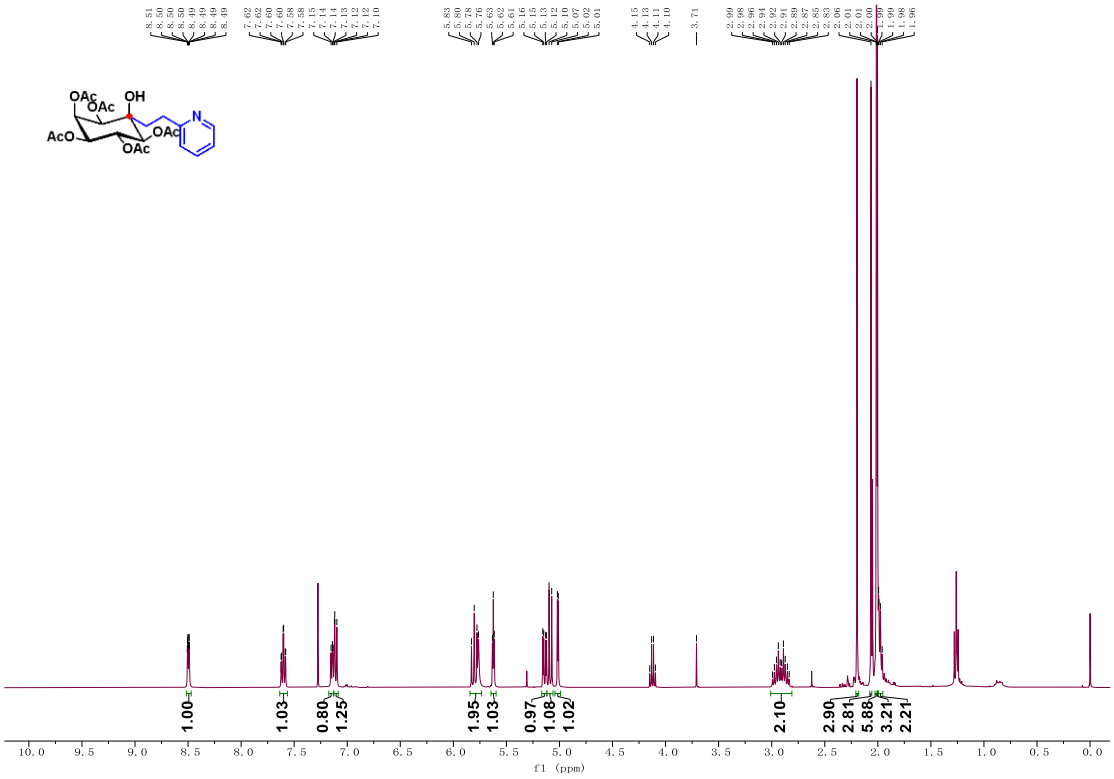


3a (NOESY, 400 MHz, DMSO-d_6)

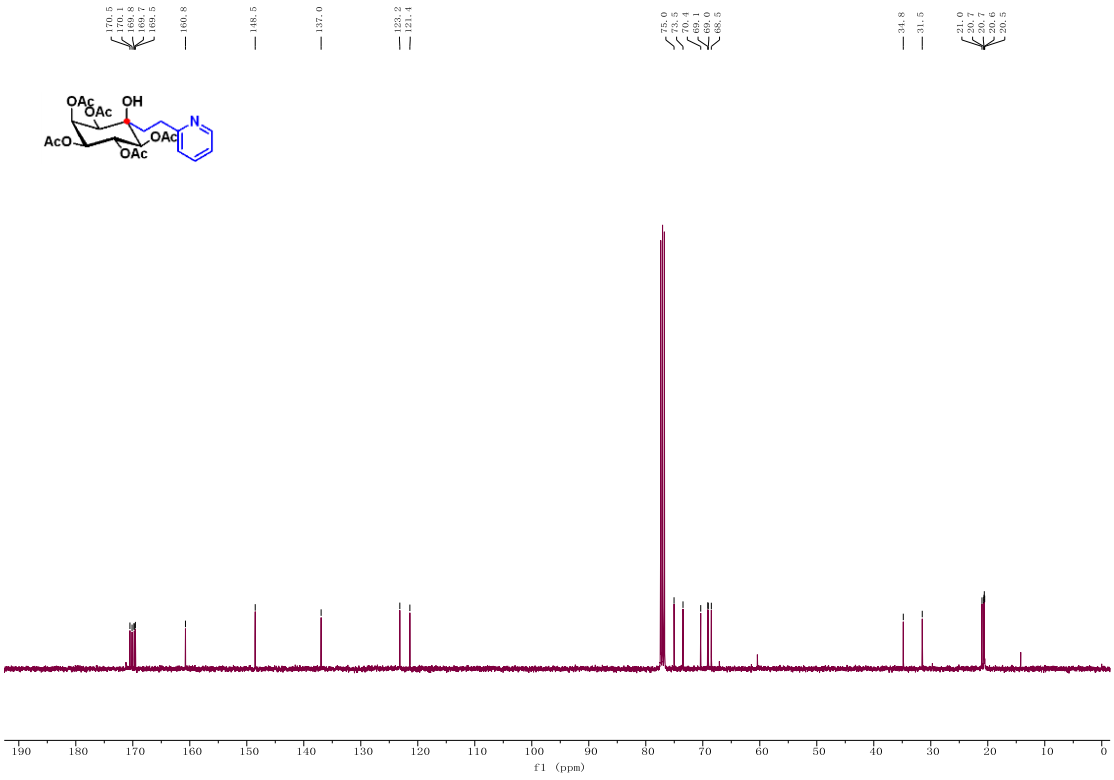



OH
OH
OH
OH
OH
HO
H
H
H
N
Ha
Hb
Hc
Hd
He
Hf
Hg
f2 (ppm)
f1 (ppm)

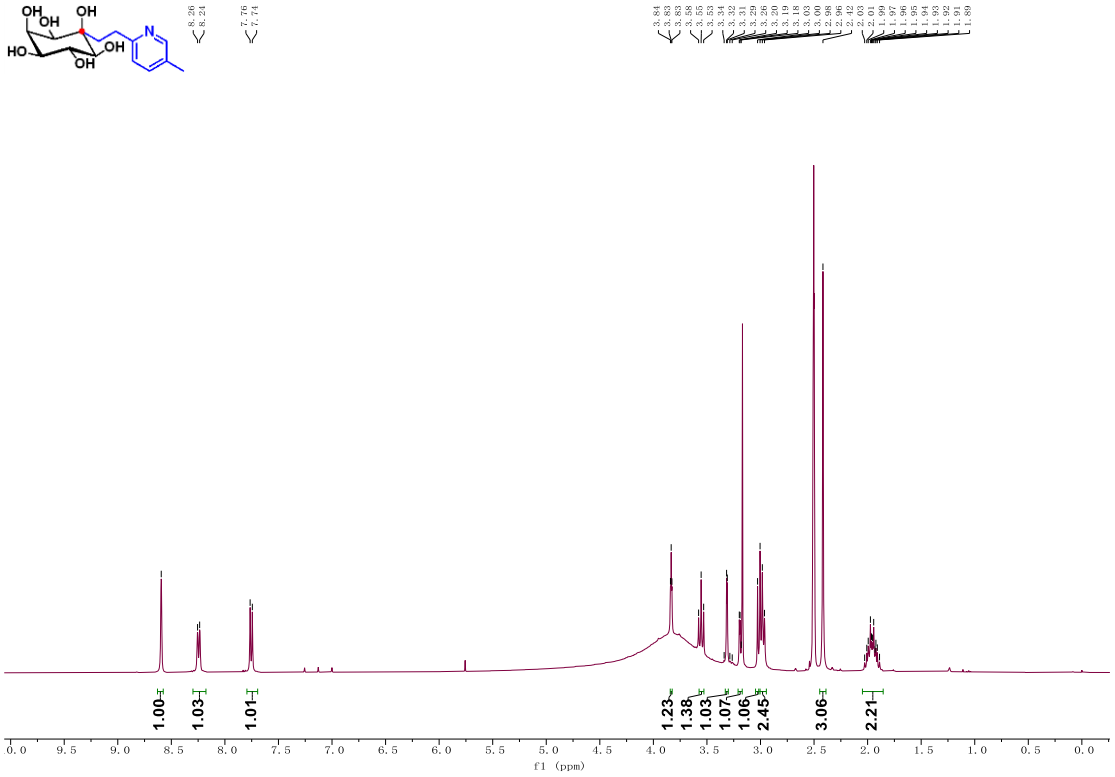
4a (^{1}H NMR, 400 MHz, $CDCl_3$)



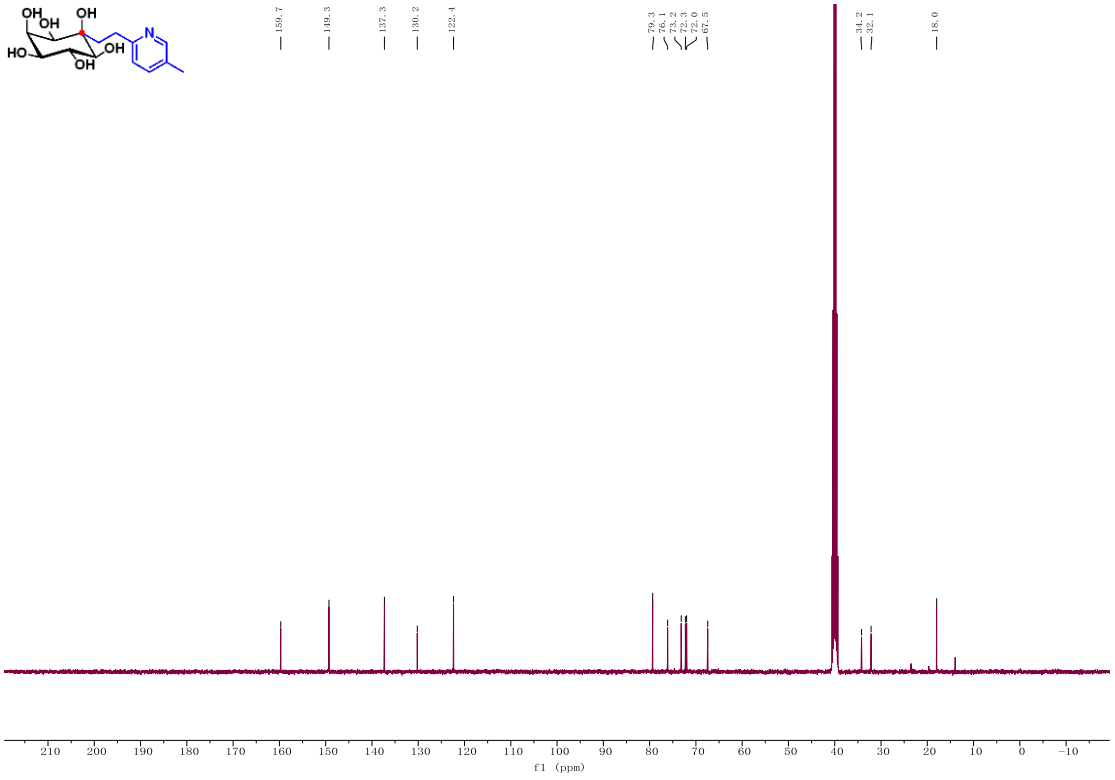
4a (^{13}C NMR, 101 MHz, $CDCl_3$)



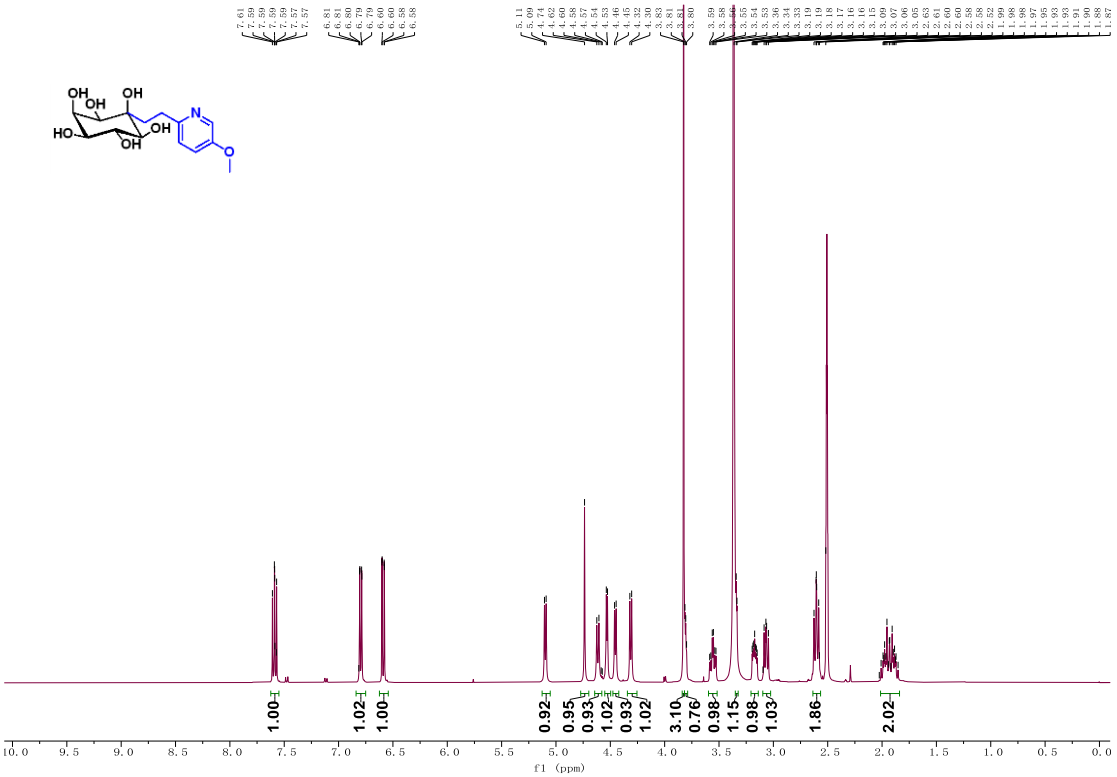
3b (^{1}H NMR, 400 MHz, DMSO-d_6)



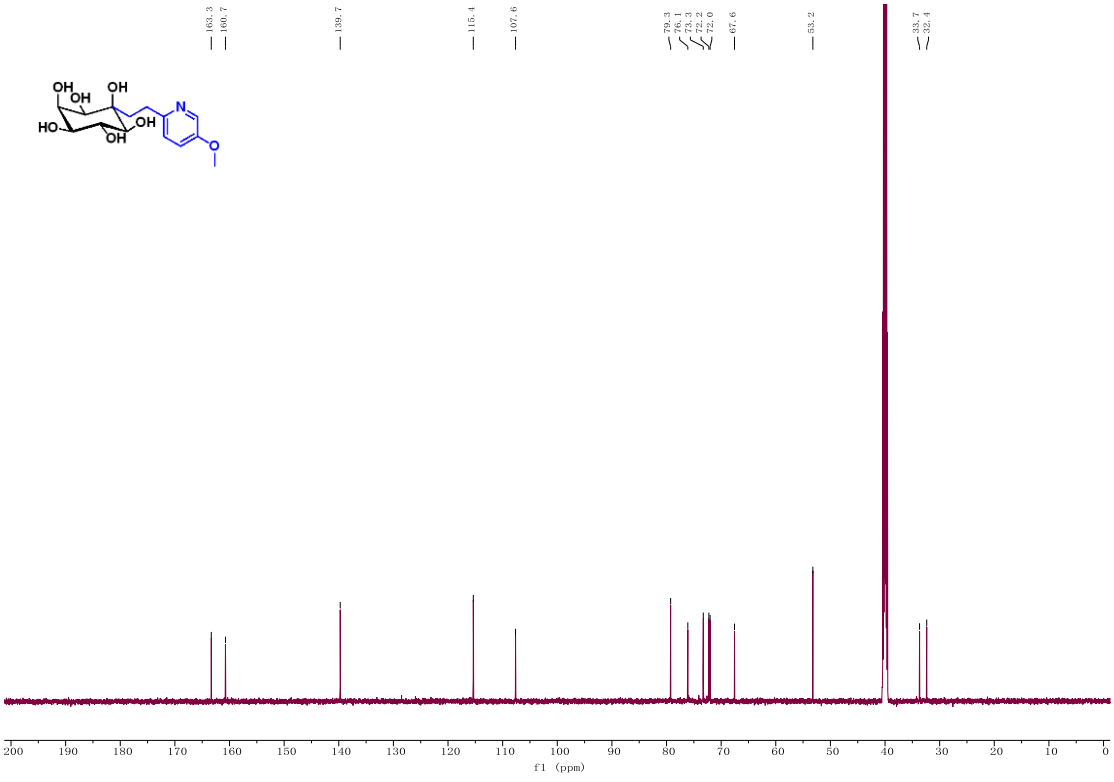
3b (^{13}C NMR, 101 MHz, DMSO-d_6)



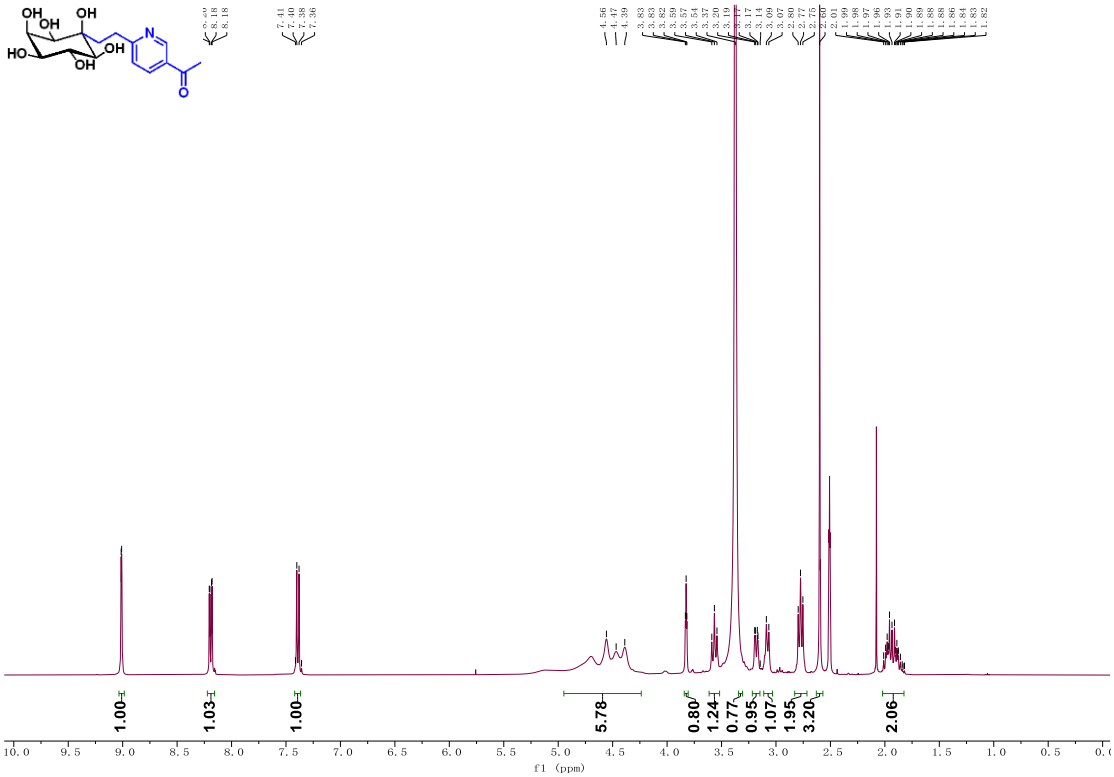
3c (^{1}H NMR, 400 MHz, DMSO-d_6)



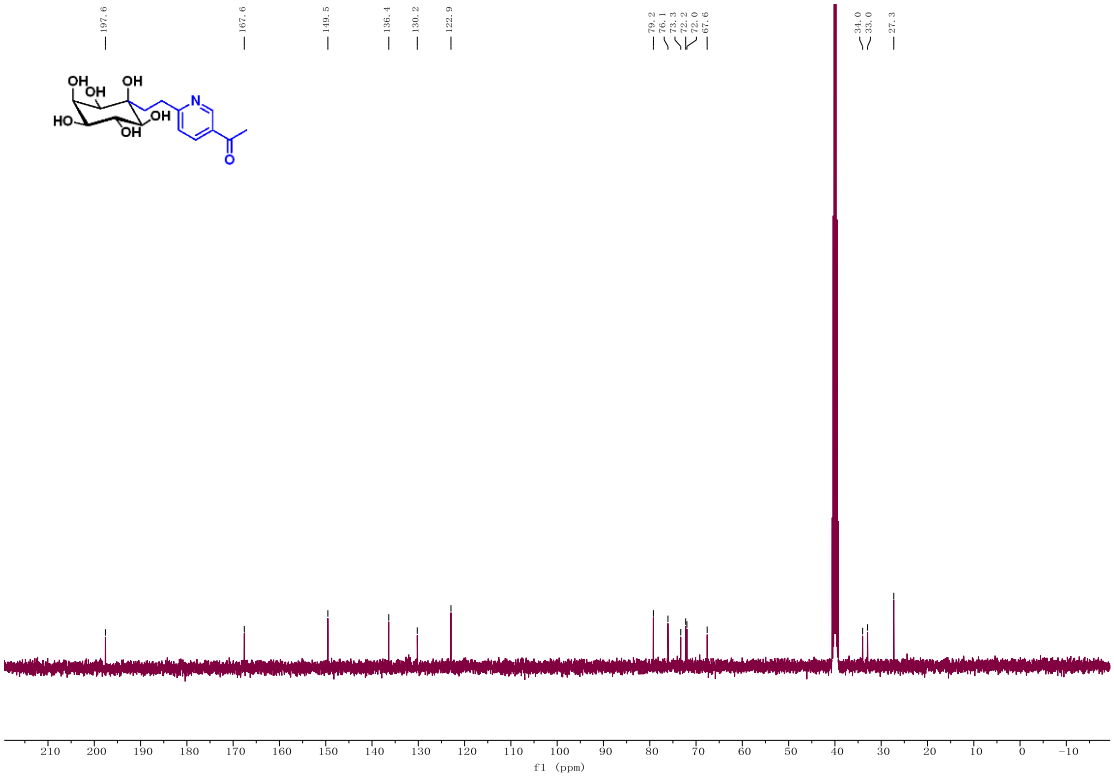
3c (^{13}C NMR, 101 MHz, DMSO-d_6)



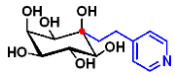
3d (^{1}H NMR, 400 MHz, DMSO-d_6)



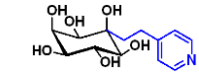
3d (^{13}C NMR, 101 MHz, DMSO-d_6)



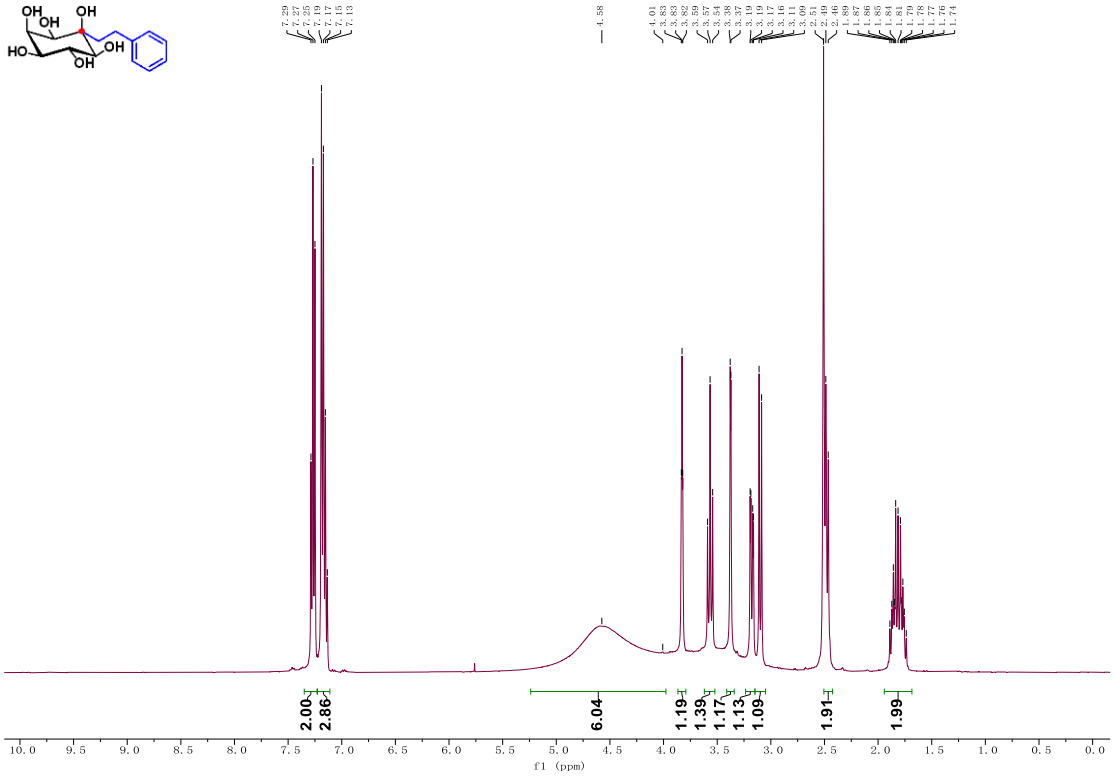
3e (^{1}H NMR, 400 MHz, DMSO-d_6)



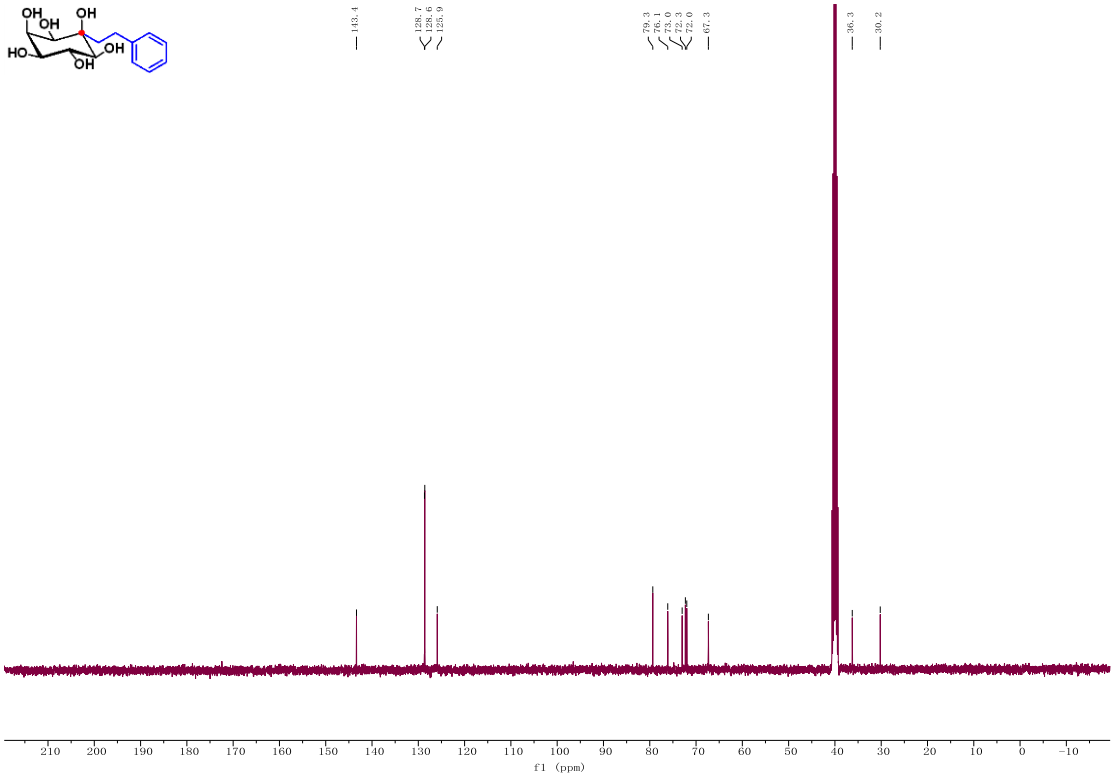
3e (^{13}C NMR, 101 MHz, DMSO-d_6)



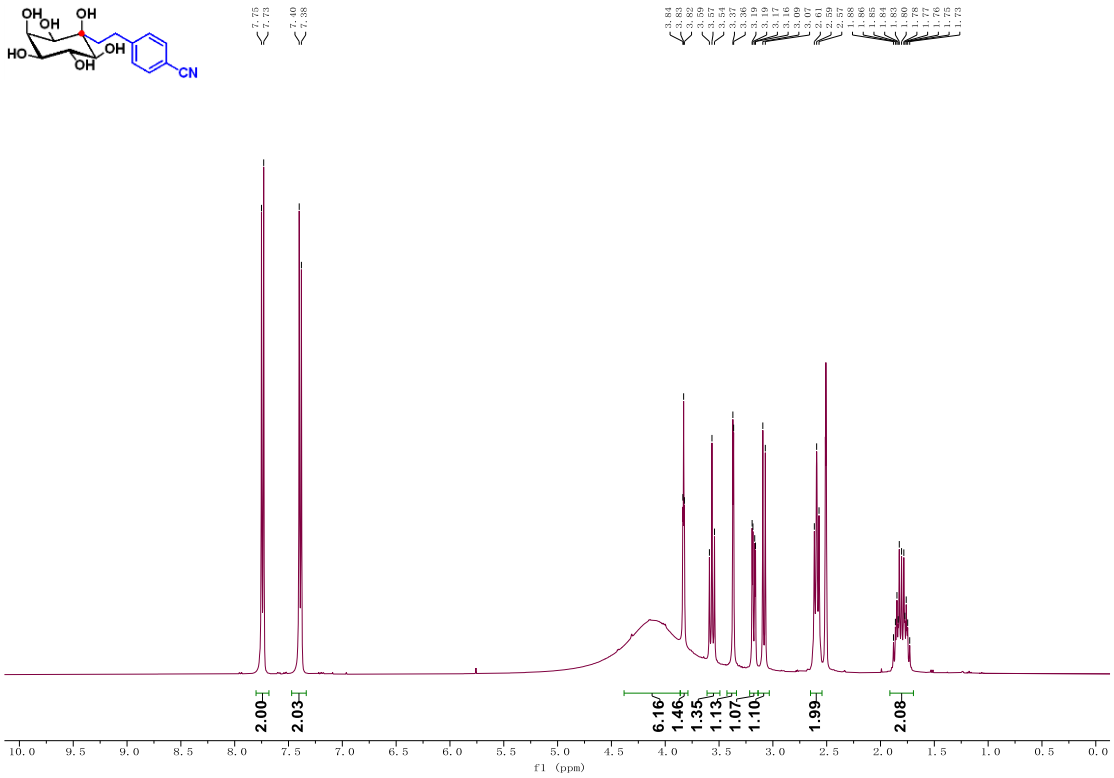
3f (^{1}H NMR, 400 MHz, DMSO-d_6)



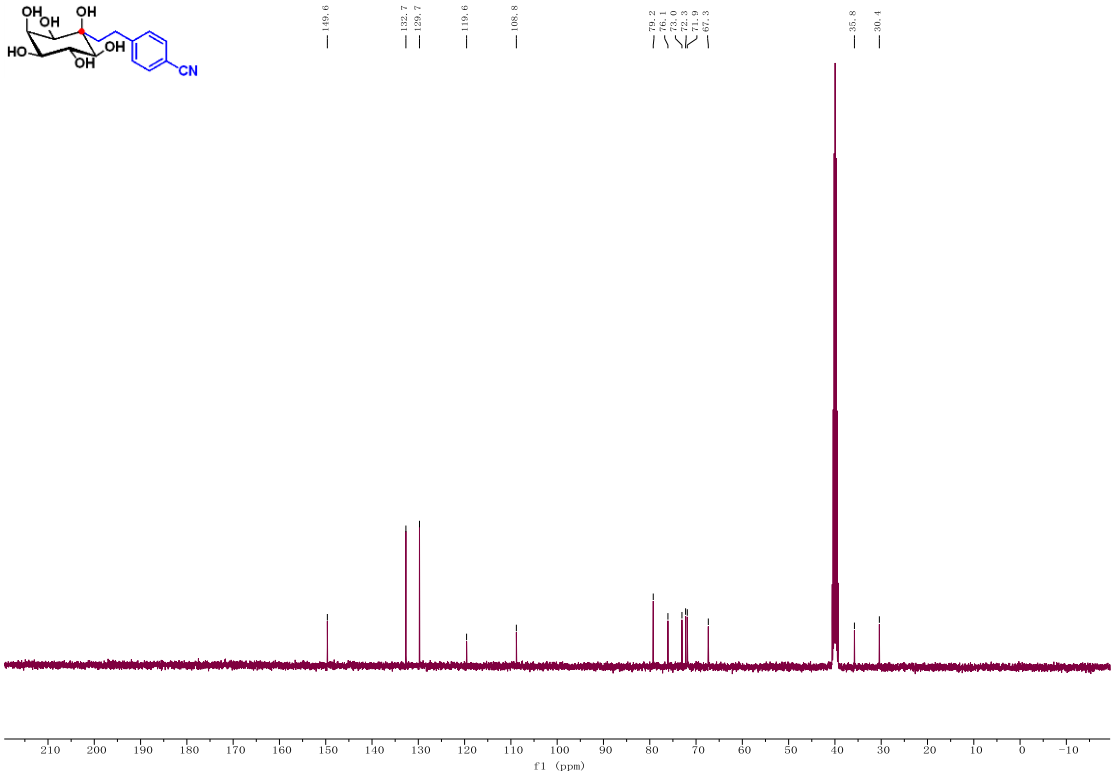
3f (^{13}C NMR, 101 MHz, DMSO-d_6)



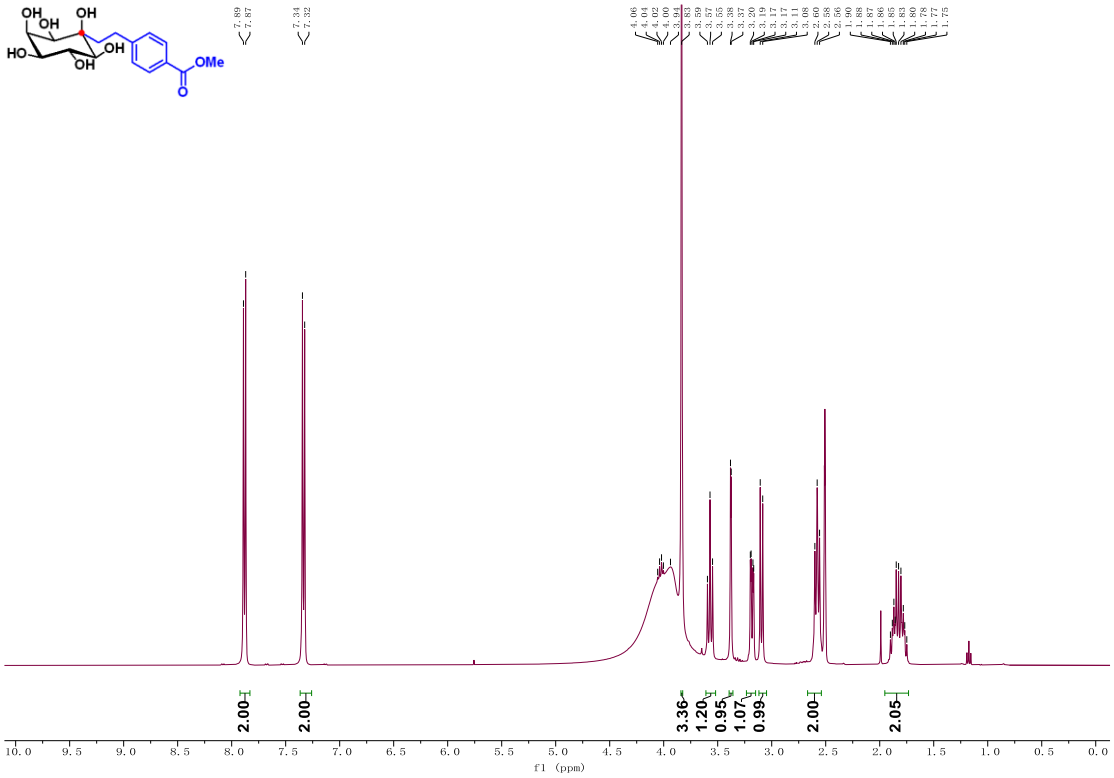
3g (^{1}H NMR, 400 MHz, DMSO-d_6)



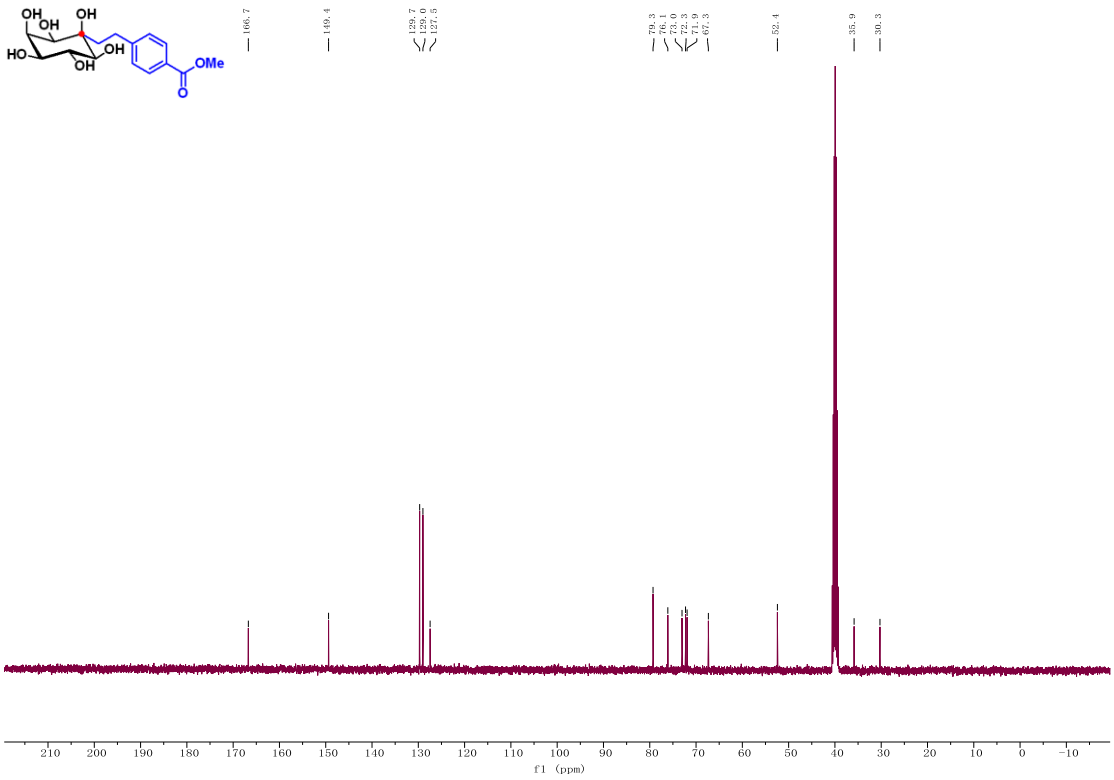
3g (^{13}C NMR, 101 MHz, DMSO-d_6)



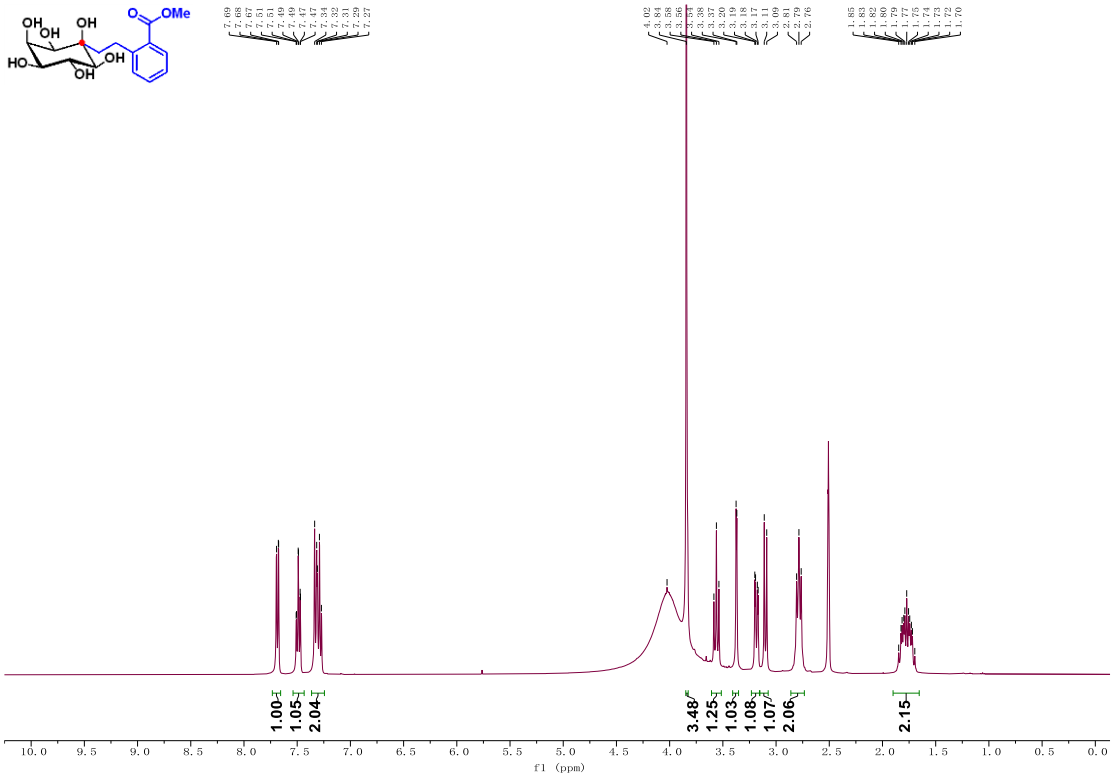
3h (^{1}H NMR, 400 MHz, DMSO-d_6)



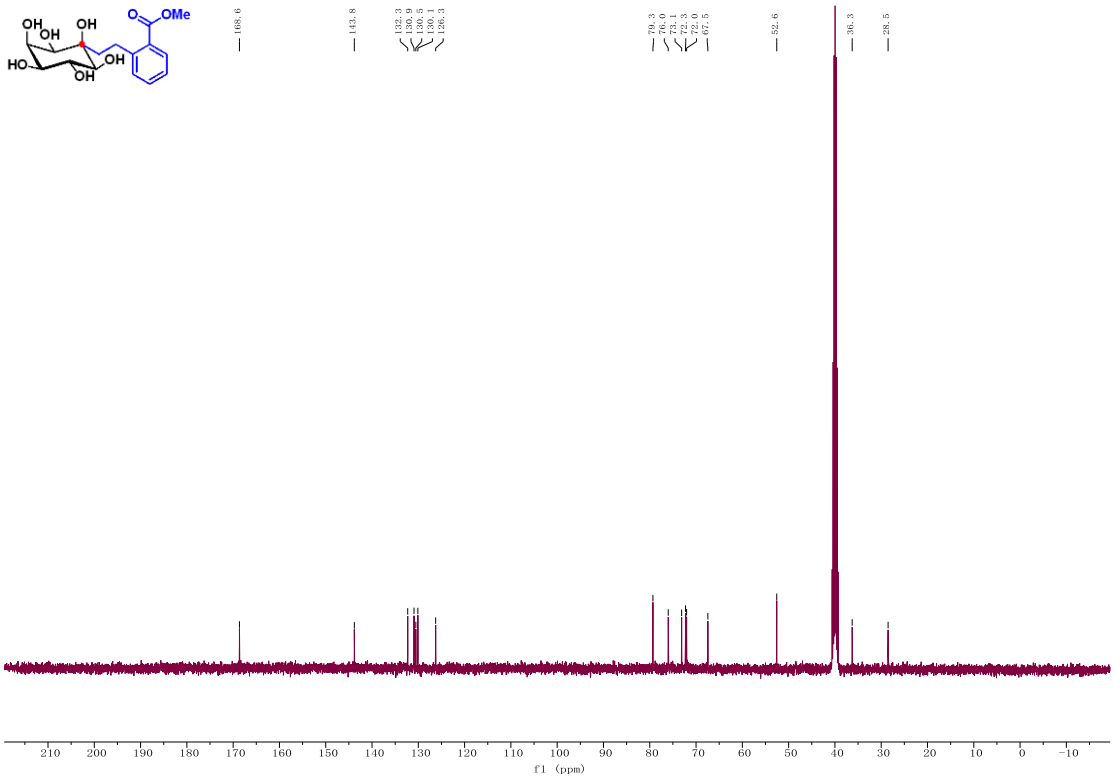
3h (^{13}C NMR, 101 MHz, DMSO-d_6)



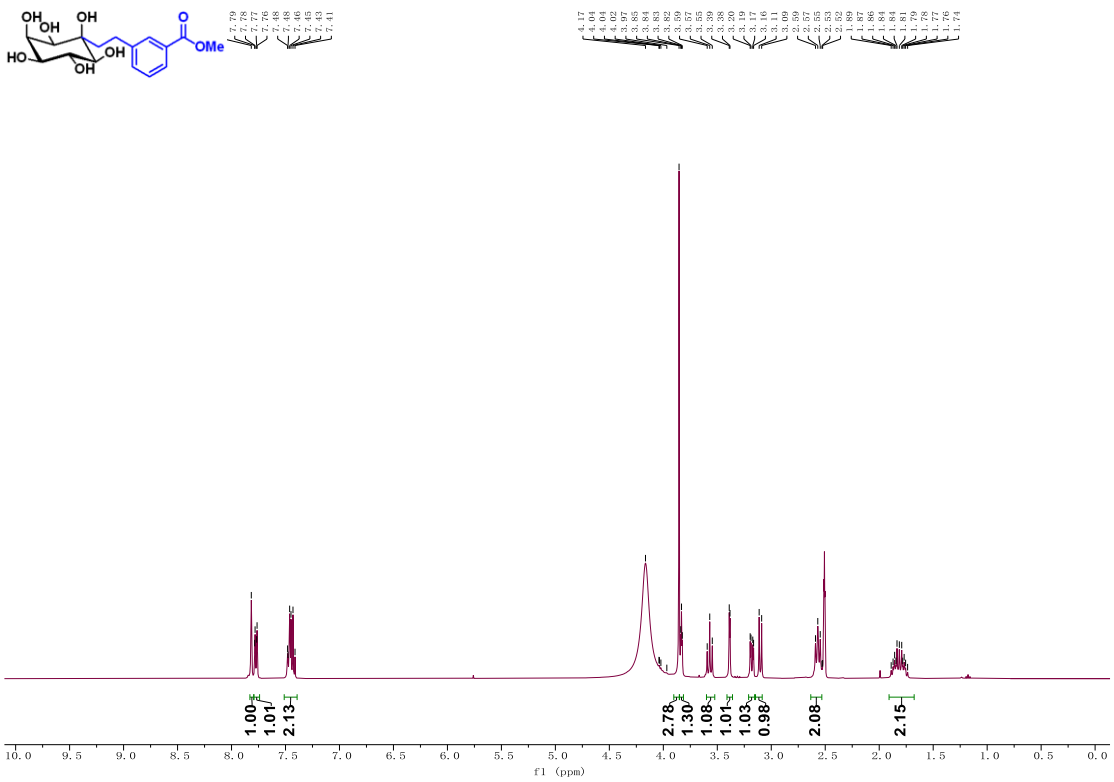
3i (^{1}H NMR, 400 MHz, DMSO-d_6)



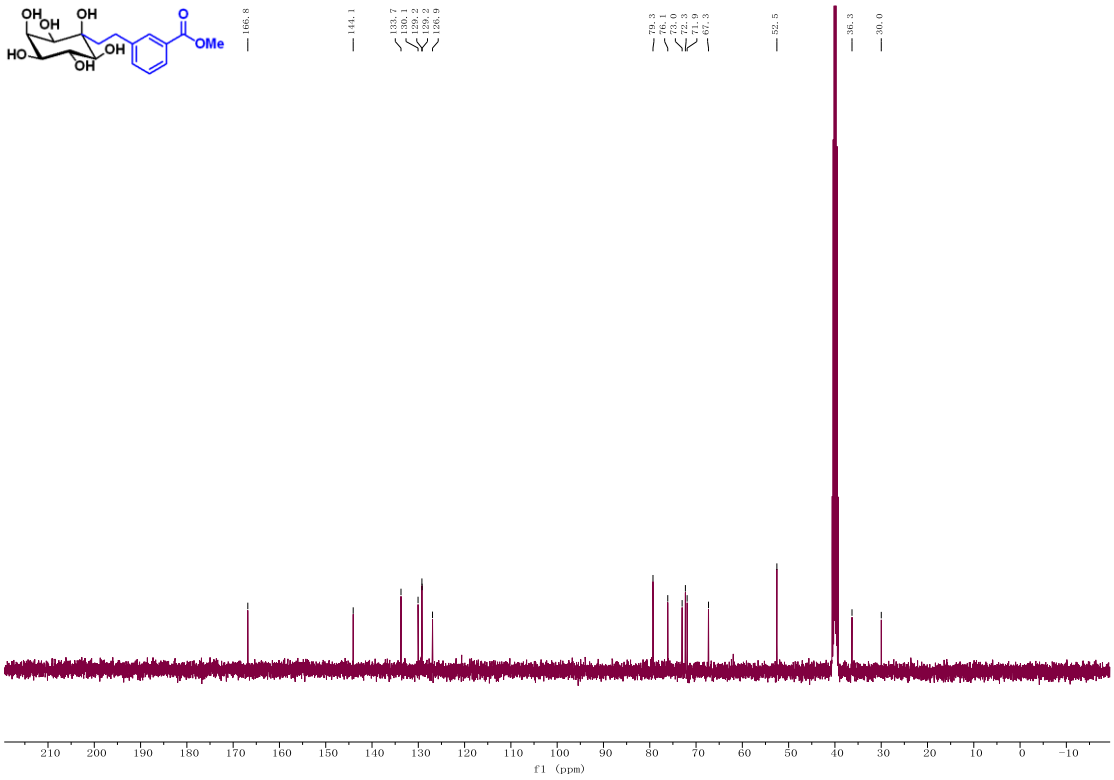
3i (^{13}C NMR, 101 MHz, DMSO-d_6)



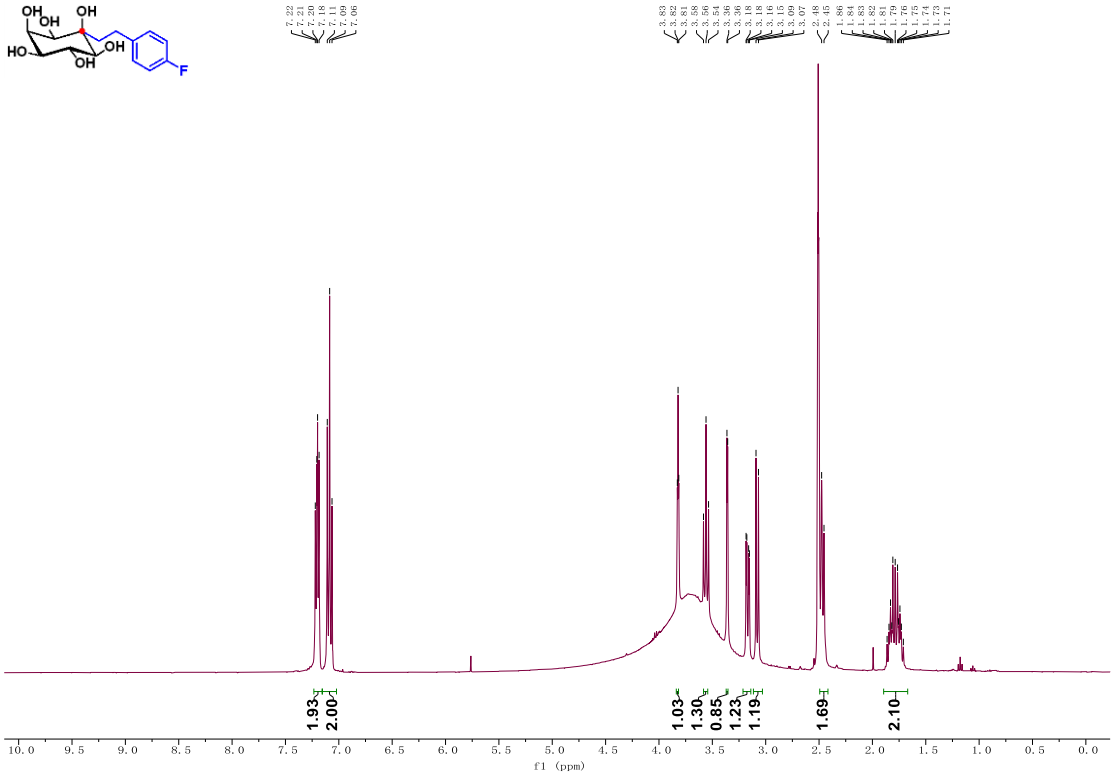
3j (^{1}H NMR, 400 MHz, DMSO-d_6)



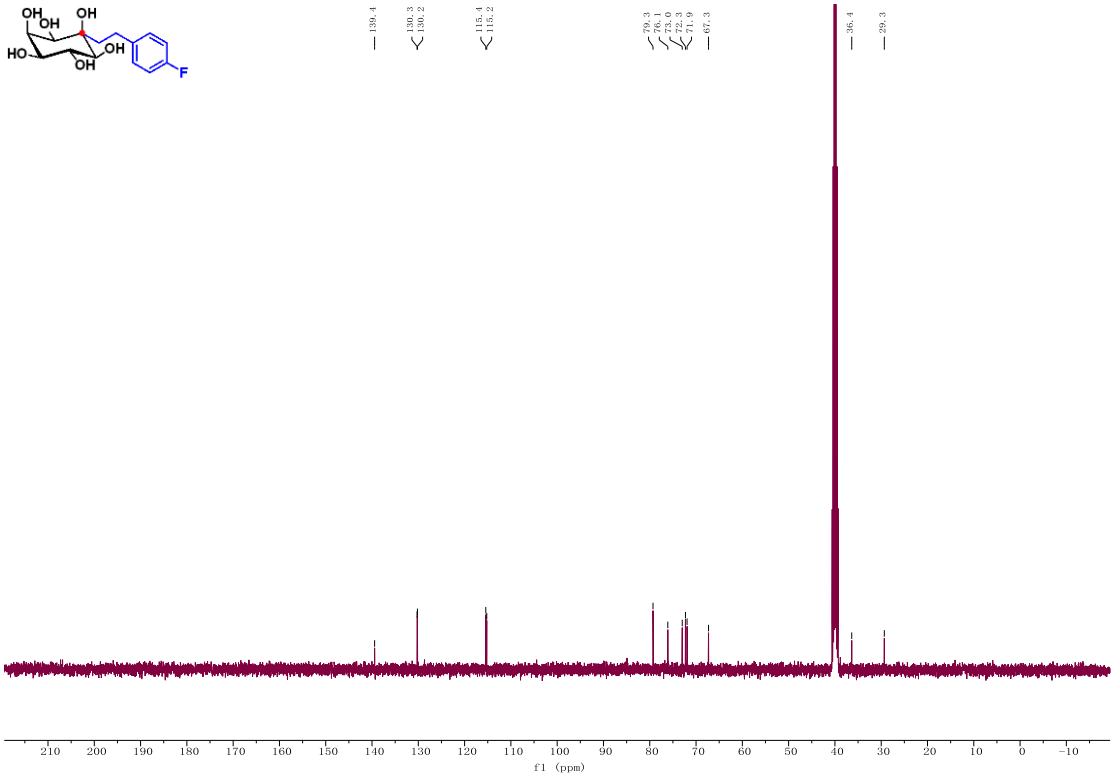
3j (^{13}C NMR, 101 MHz, DMSO-d_6)



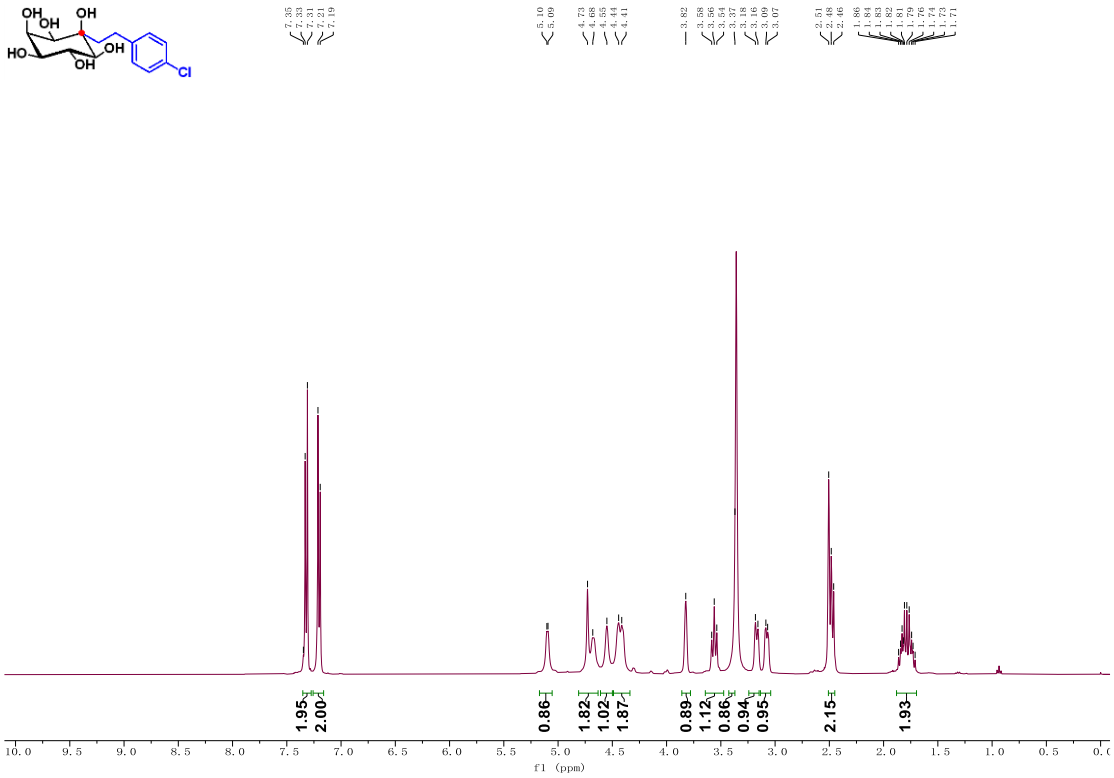
3k (^{1}H NMR, 400 MHz, DMSO-d_6)



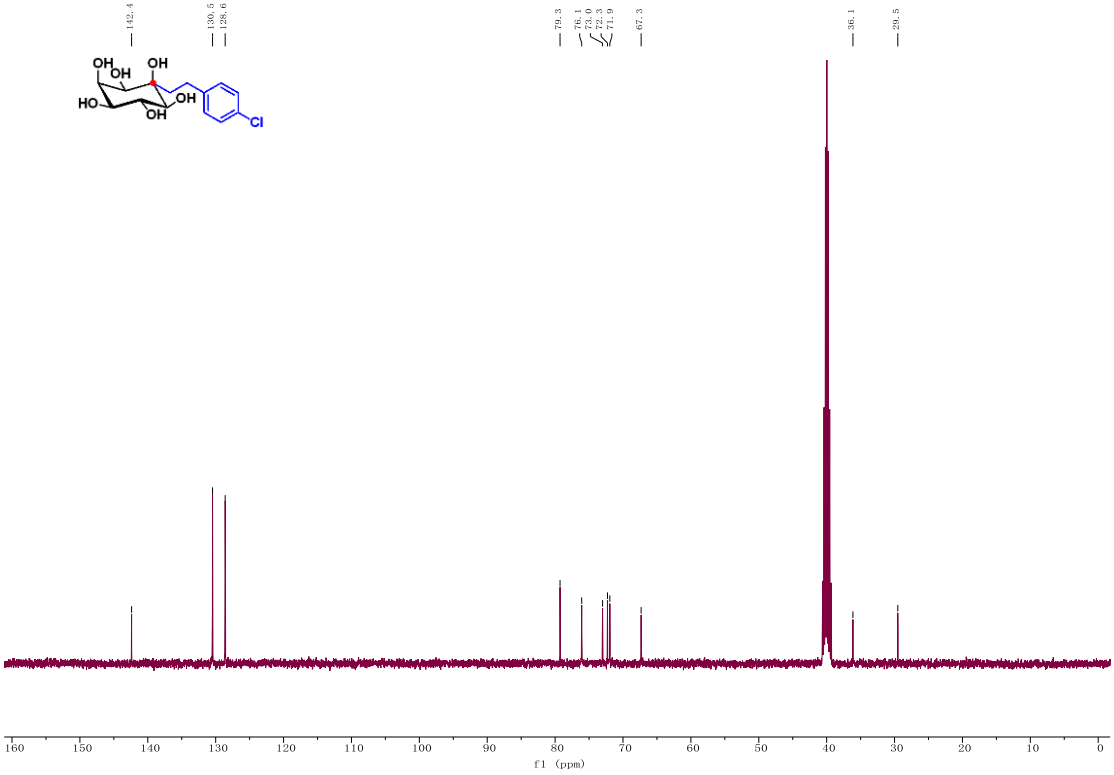
3k (^{13}C NMR, 101 MHz, DMSO-d_6)



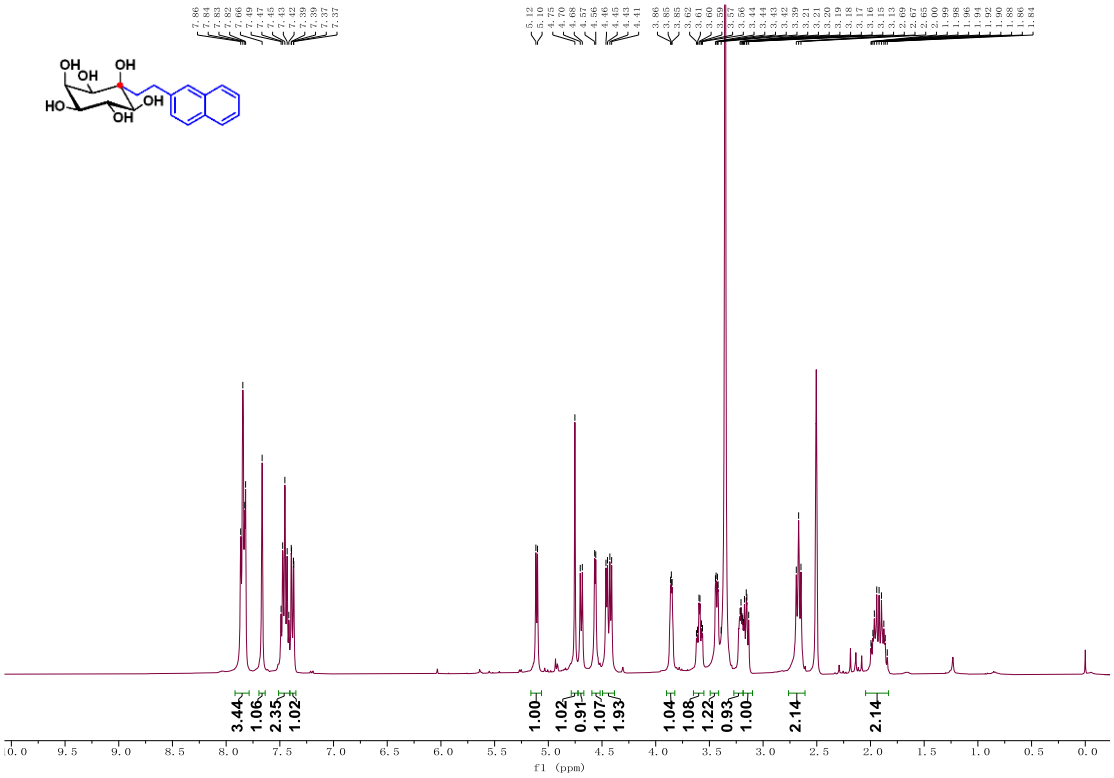
3l (^{1}H NMR, 400 MHz, DMSO-d_6)



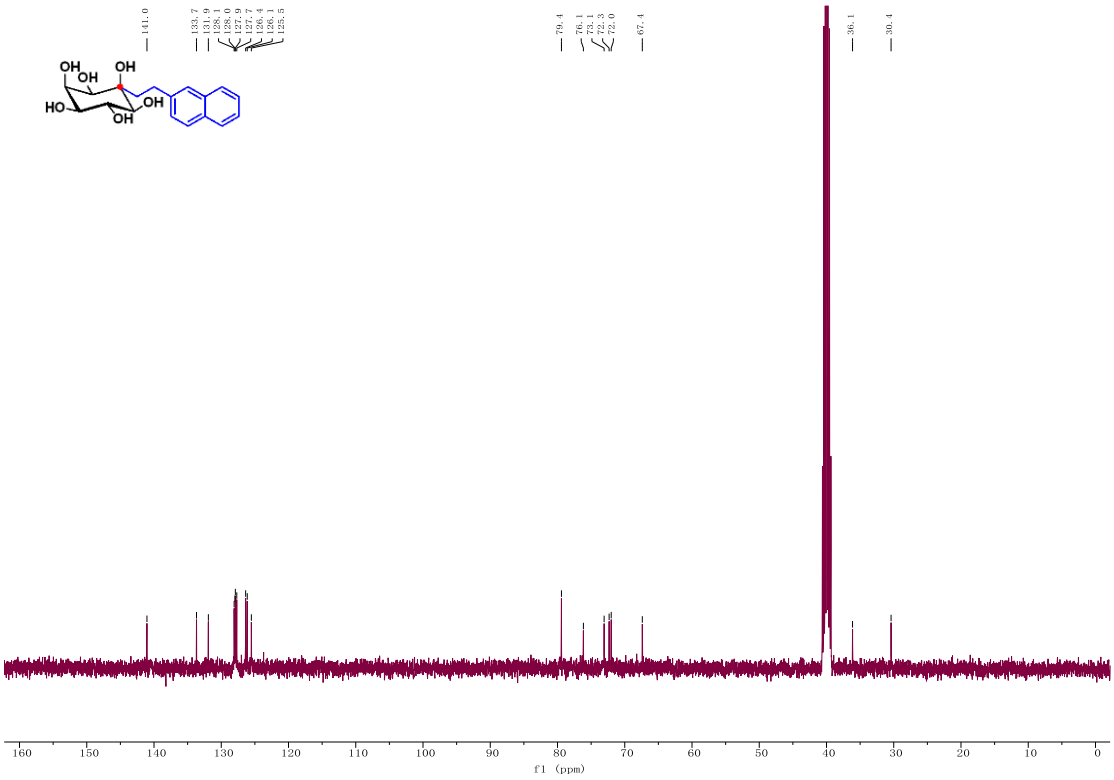
3l (^{13}C NMR, 101 MHz, DMSO-d_6)



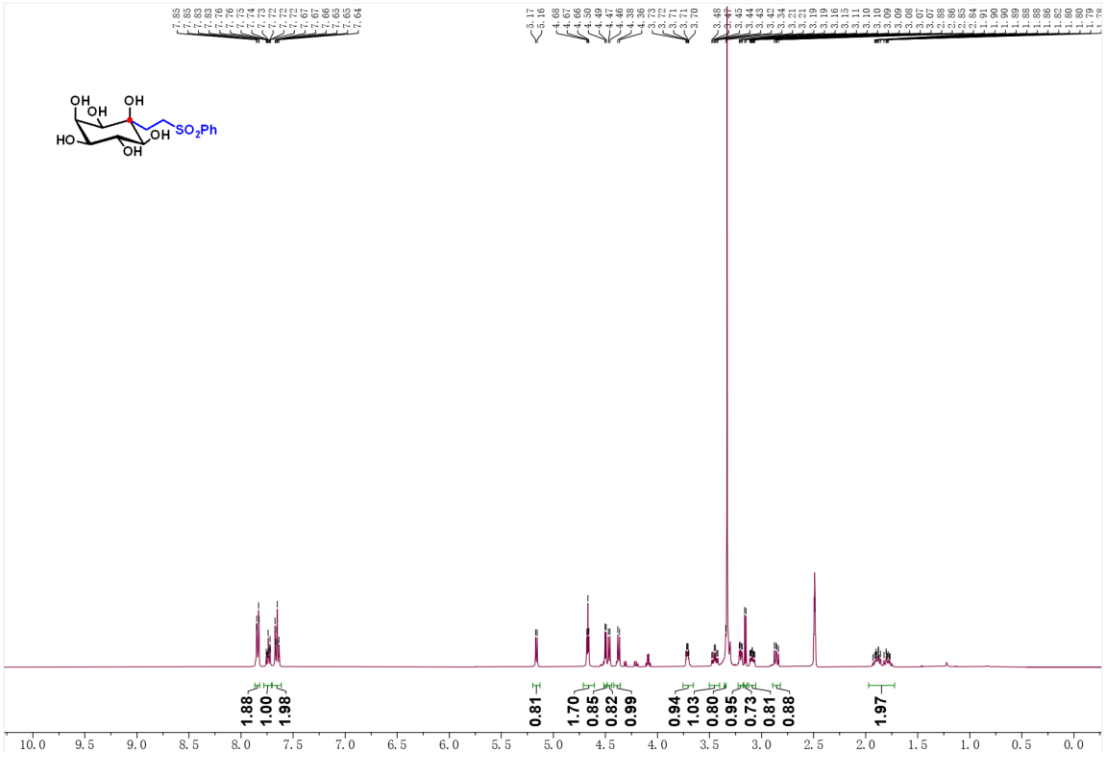
3m (^{1}H NMR, 400 MHz, DMSO-d_6)



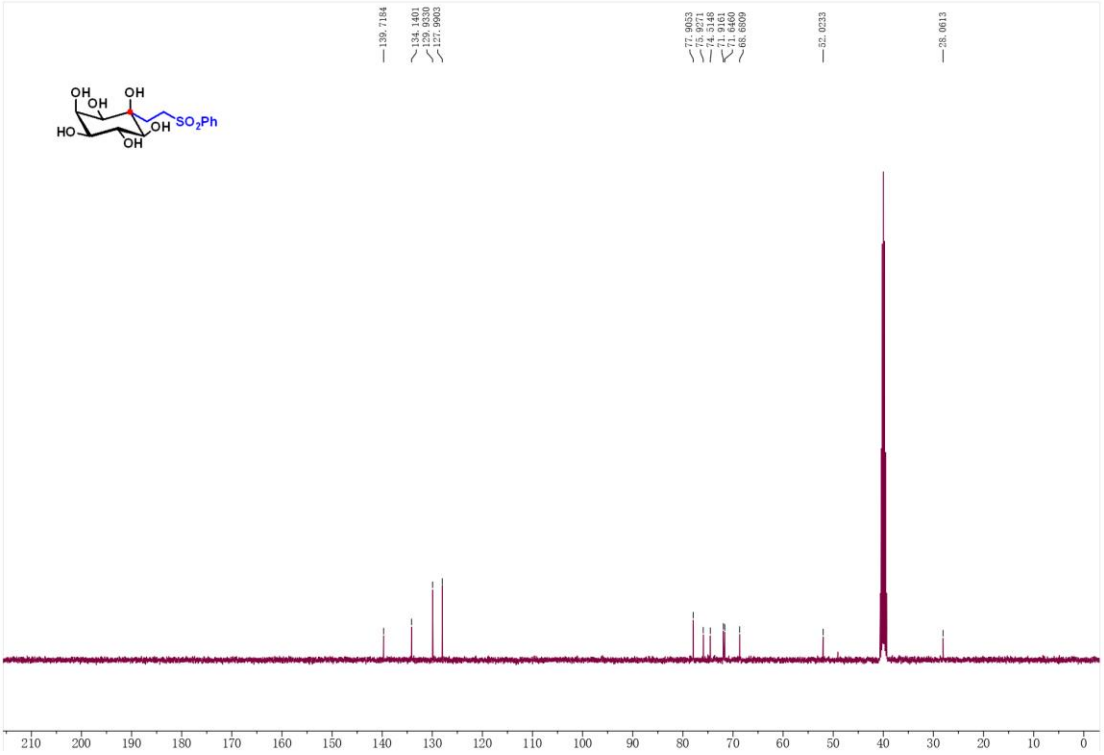
3m (^{13}C NMR, 101 MHz, DMSO-d_6)



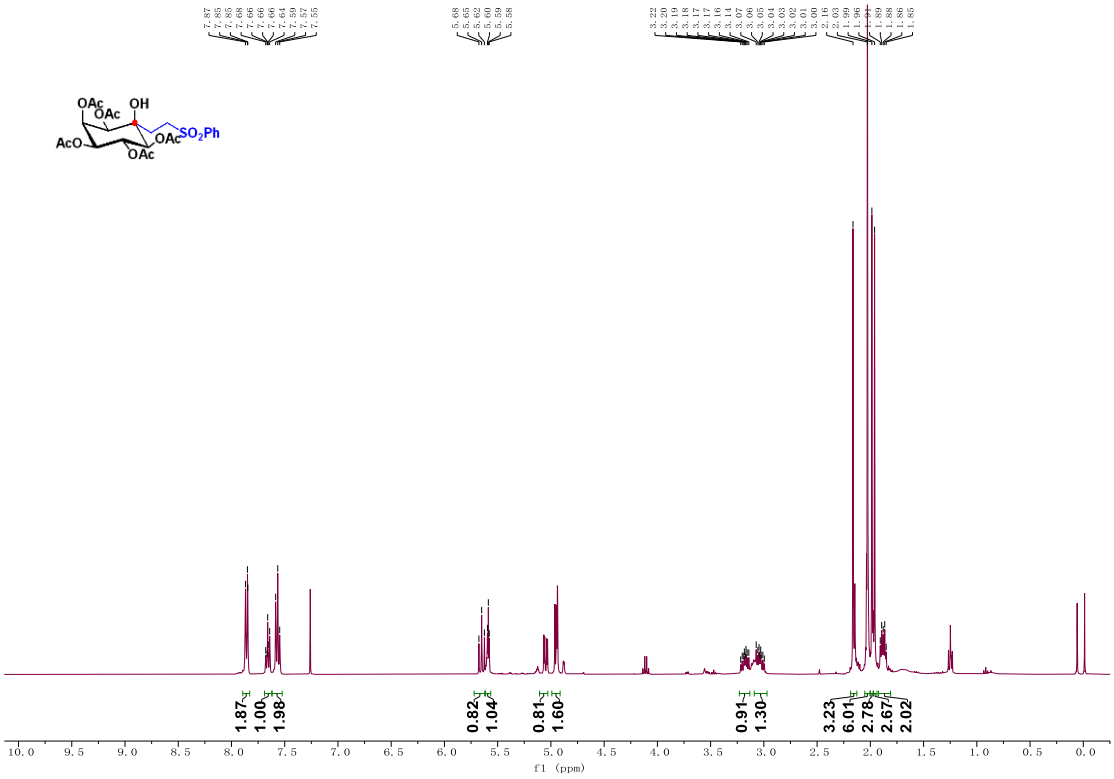
3n (^{1}H NMR, 400 MHz, DMSO-d_6)



3n (^{13}C NMR, 101 MHz, DMSO-d_6)



4n (^{1}H NMR, 600 MHz, DMSO-d_6)



4n (^{13}C NMR, 151 MHz, DMSO-d_6)