Supporting Information for

A Stereoselective Organocatalyzed C-Glycosylation of Indole Involving Acceptor-Catalyst-Donor Interaction

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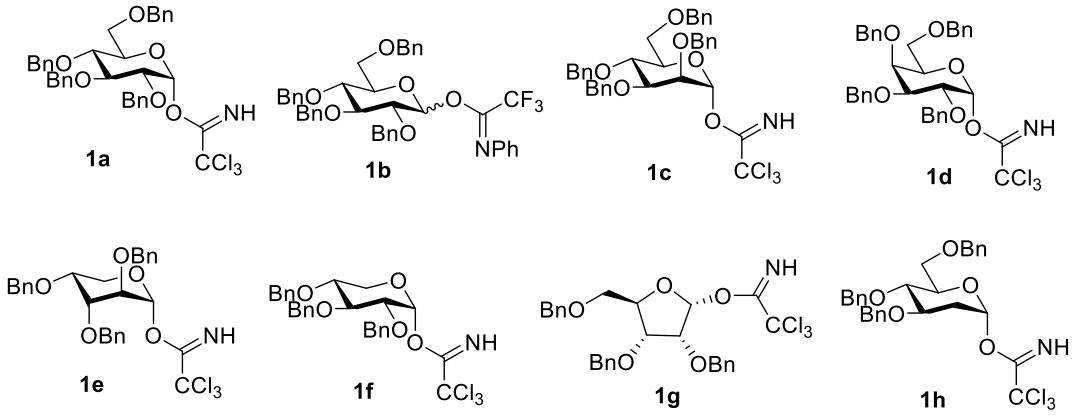
1. General information

Unless otherwise stated, all reactions were set up under inert atmosphere (N_2) utilizing glassware that were oven dried and cooled under nitrogen purging. Silica Gel Flash Column Chromatography was performed on deactivated silica gel or basified silica gel. Basified silica gel was obtained by immersing silica in the 5% NEt_3/pentane overnight, and then the solvent was removed in vacuo. Starting materials were purchased directly from commercial suppliers (Energy Chemical, Bidepharm) and used without further purifications unless otherwise stated. All solvents were dried according to standard procedures or brought from commercial suppliers. Reactions were monitored using thin-layer chromatography (TLC) with F254 indicator. Visualization of the developed plates was performed under UV light (254 nm) or H_2SO_4-EtOH (10% H_2SO_4 v/v). ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded using Bruker AVIII 400 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as the external standard and low field is positive. Coupling constants (J) are reported in Hertz (Hz). The residual solvent peak was used as an internal reference: ^{1}H NMR ($CDCl_3$ δ 7.26), ^{13}C NMR ($CDCl_3$ δ 77.16), ^{1}H NMR (DMSO-*d*$_6$ δ 2.50) and ^{13}C NMR (DMSO-*d*$_6$ δ 39.50). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiple, br = broad.

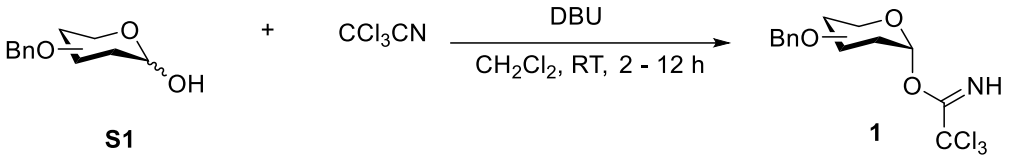
2. Experimental Section

2.1 Synthesis of glycosyl trichloroacetimidates



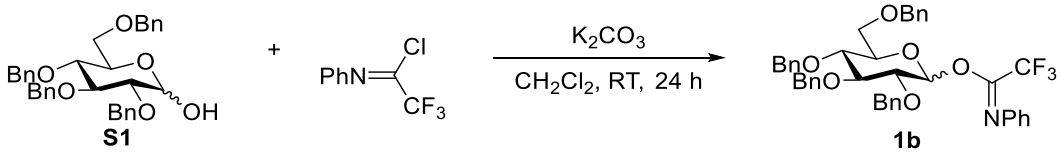
Scheme 1. Library of glycosyl donor

2.1.1 Synthesis of *α*-glycosyl trichloroacetimidate (General procedure A)



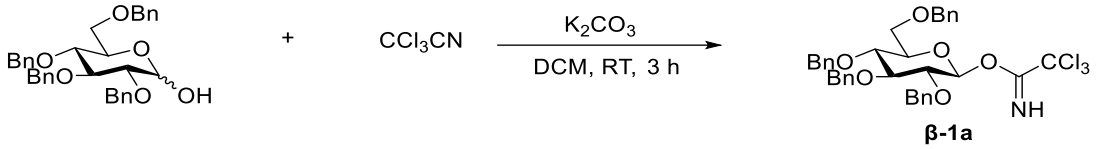
Trichloroacetonitrile (10.0 equiv.) and DBU (0.2 equiv.) were added to a stirring solution of hemiacetal sugar **S1** (1.0 equiv.) in anhydrous CH_2Cl_2 (0.25 M) at RT. The reaction was stirred for 2 - 12 h and evaporated onto celite under reduced pressure. The residue was purified by flash column chromatography (Basified silica gel, 1:10 ethyl acetate/petroleum) to afford glycosyl trichloroacetimidates (**1a**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**).[1]

2.1.2 Synthesis of glycosyl *N*-Ph-trifluoroacetimidate (General procedure B)



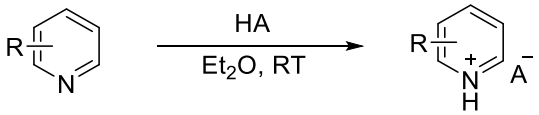
K_2CO_3 (6.0 equiv.) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (2.0 equiv.) was added to a stirred solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (1.0 equiv.) in anhydrous CH_2Cl_2 (0.25 M). The solution was stirred at RT for 24 h and evaporated in vacuo onto celite. The residue was purified by flash column chromatography (Basified silica gel, 10:1 petroleum ether/ethyl acetate) to afford the desired product **1b**.[2]

2.1.3 Synthesis of glycosyl β-glycosyl trichloroacetimidate (General procedure C)



K_2CO_3 (9.7 equiv.) and trichloroacetonitrile (10. 0 equiv.) was added to a stirred solution of 2,3,4,6-tetra-O-benzyl-D-glucopyranose (1.0 equiv.) in dry DCM (0.25 M). The solution was stirred at RT for 3 h and evaporated in vacuo onto celite. The crude product was purified by flash column chromatography (Basified silica gel, 10:1 petroleum ether/ethyl acetate) to afford the desired product **β-1a**.[3]

2.2 Synthesis of pyridinium catalyst (General procedure D)

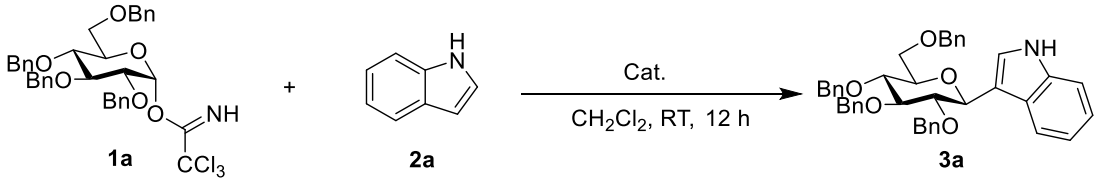


To a sample bottle equipped with a stirring bar was added an ethyl ether solution of pyridine, then the corresponding acid was added. A precipitation was observed. After the reaction is completed, the precipitation was washed with ethyl ether three times. Afterwards, the solid was dried under vacuum to afford the targeted product.

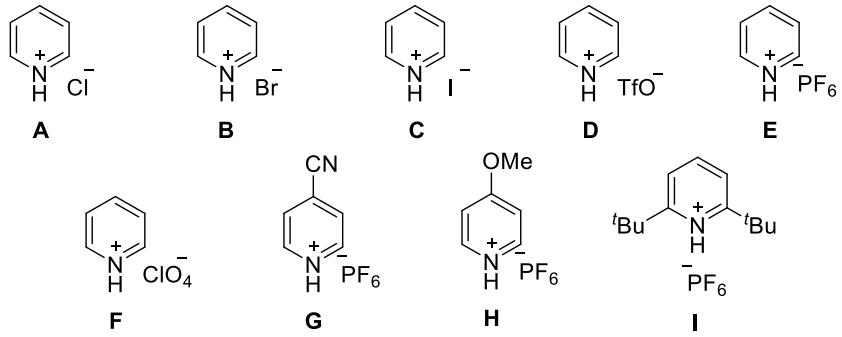
2.3 Reaction optimization (General procedure E)

In a glove box filled with nitrogen, to an oven-dried 5 mL tube equipped with a stir bar was added glycosyl trichloroacetimidates, indole, pyridinium catalyst and anhydrous CH_2Cl_2. The reaction mixture was stirred at dedicated temperature. The mixture was analyzed by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

Table S1. Screening of catalyst[a]

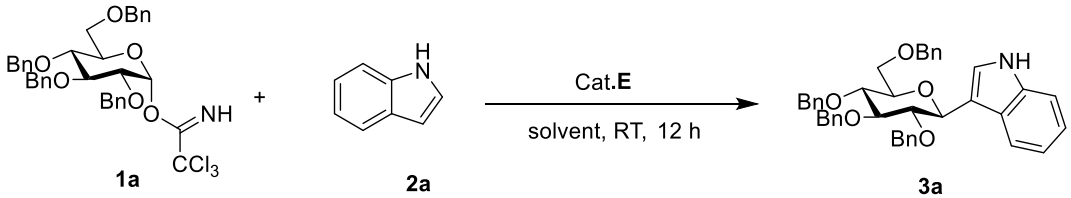


Entries	Cat.	Yield (%)
1	**A**	<5
2	**B**	<5
3	**C**	<5
4	**D**	52
5	**E**	65
6	**F**	44
7	**G**	36
8	**H**	59
9	**I**	53



[a]Reaction conditions: **1a** (0.075 mmol, 1.5 equiv.), **2a** (0.05 mmol, 1.0 equiv.), anhydrous CH_2Cl_2 (1 mL), 20 mol% cat., under N_2 atmosphere; 12 h, RT; the yield was determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

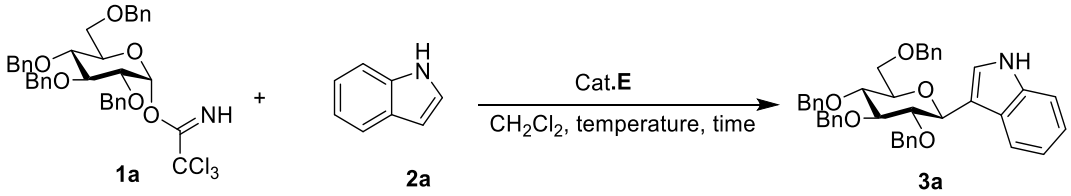
Table S2. Screening of solvent[a]



Entries	Solvent	Yield (%)
1	DMF	9
2	DMSO	trace
3	CH_3CN	23
4	ethyl acetate	36
5	CH_2Cl_2	65
6	$ClCH_2CH_2Cl$	40
7	Et_2O	25
8	^{t}Butyl methyl ether	21
9	THF	8
10	toluene	36

[a]Reaction conditions: **1a** (0.075 mmol, 1.5 equiv.), **2a** (0.05 mmol, 1.0 equiv.), solvent (1 mL), 20 mol% cat., under N_2 atmosphere; 12 h, RT; the yield was determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

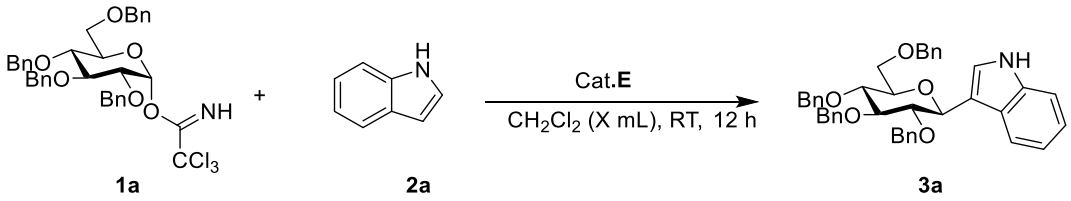
Table S3. Screening of temperature and time[a]



Entries	temperature/°C	time	Yield (%)
1	0	12	49
2	RT	12	65
3	45	12	51
4	RT	10	58
5	RT	14	57

[a]Reaction conditions: **1a** (0.075 mmol, 1.5 equiv.), **2a** (0.05 mmol, 1.0 equiv.), anhydrous CH_2Cl_2 (1 mL), 20 mol% cat., under N_2 atmosphere; time, temperature; the yield was determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

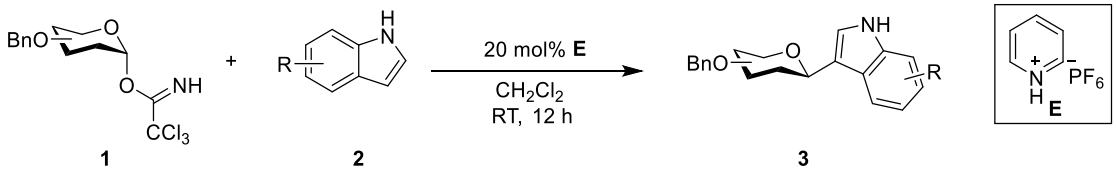
Table S4. Screening of substrate ratio and concentration[a]



Entries	1a:2a	X	Yield (%)
1	1:1.5	1	45
2	1:1	1	50
3	1.5:1	1	65(77)[b]
4	2:1	1	75(89)[b]
5	1.5:1	0.5	50
6	1.5:1	2	61

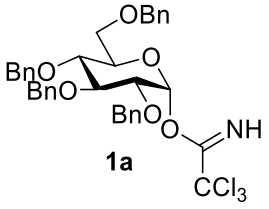
[a]Reaction conditions: **1a** :**2a** = 1:1.5 to 2:1, anhydrous CH_2Cl_2 (X mL), 20 mol% cat., under N_2 atmosphere; 12 h, RT; the yield was determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yield.

2.4 Synthesis of 3-indolyl-C-glycosides (General procedure F)



In a glove box filled with nitrogen, to an oven-dried 5 mL tube equipped with a stir bar was added glycosyl trichloroacetimidates **1** (0.1 mmol, 2.0 equiv.), indole **2** (0.05 mmol, 1.0 equiv.), cat.**E** (20 mol%) and anhydrous CH_2Cl_2 (1mL). The reaction mixture was stirred at room temperature for 12 h. After the reaction is completed, the solvent was removed under reduced pressure with a rotary evaporator. The crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate as an eluent.

3. NMR data

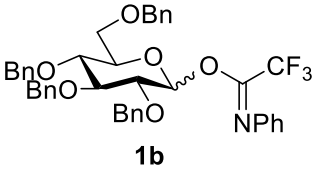


1a

(2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 2,2,2-trichloroacetimidate

1a was synthesized according to the general procedure A. Trichloroacetonitrile (5.4 mL, 56.0 mmol) and DBU (165.0 μL, 1.1 mmol) were added to a stirring solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (3.0 g, 5.6 mmol) in anhydrous CH_2Cl_2 (0.25 M) at RT. The reaction was stirred for 2 h and evaporated onto celite under reduced pressure. The crude product was purified by flash-column chromatography (Basified silica gel, 1:10 ethyl acetate/petroleum) to afford the product as a white solid (3.5 g, 86%).[4]

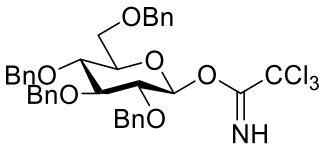
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.37 - 7.32 (m, 18H), 7.22 - 7.20 (m, 2H), 6.59 (d, *J* = 3.4 Hz, 1H), 5.02 (d, *J* = 10.9 Hz, 1H), 4.92 - 4.87 (m, 2H), 4.80 (d, *J* = 11.7 Hz, 1H), 4.73 (d, *J* = 11.7 Hz, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 10.7 Hz, 1H), 4.52 (d, *J* = 12.1 Hz, 1H), 4.11 (t, *J* = 9.3 Hz, 1H), 4.07 - 4.03 (m, 1H), 3.87 - 3.81 (m, 3H), 3.74 - 3.70 (m, 1H).



1b

1b was synthesized according to the general procedure B. K_2CO_3 (153.4 mg, 1.11 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (58 μL, 0.37 mmol) was added to a stirred solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (0.10 g, 0.185 mmol) in anhydrous CH_2Cl_2 (0.25 M). The solution was stirred at RT for 24 h and evaporated in vacuo onto celite. The crude product was purified by flash column chromatography (Basified silica gel, 10:1 petroleum ether/ethyl acetate) to afford the product as a colorless sugar (127.0 mg, 96%).[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 - 7.25 (m, 20H), 7.19 - 7.15 (m, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.83 - 6.81 (m, 2H), 4.94 (d, *J* = 11.0 Hz, 1H), 4.88 - 4.78 (m, 4H), 4.65 (d, *J* = 12.1 Hz, 1H), 4.57 - 4.54 (m, 2H), 3.78 - 3.72 (m, 5H).

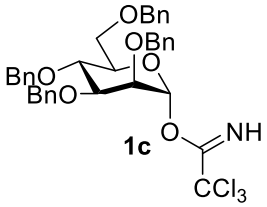


β-1a

(2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 2,2,2-trichloroacetimidate

β-1a was synthesized according to the general procedure A. K_2CO_3 (0.51 g, 3.6 mmol) and trichloroacetonitrile (0.37ml, 3.7 mmol) was added to a stirred solution of 2,3,4,6-tetra-O-benzyl-D-glucopyranose (0.20 g, 0.37 mmol) in dry DCM (0.25 M). The solution was stirred at RT for 3 h and evaporated in vacuo onto celite. The crude product was purified by flash column chromatography (Basified silica gel, 10:1 petroleum ether/ethyl acetate) to afford the product as a colorless sugar (89.0 mg, 35%).[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.34 - 7.27 (m, 18H), 7.19 - 7.17 (m, 2H), 5.84 - 5.78 (m, 1H), 4.95 (d, *J* = 10.9 Hz, 1H), 4.92 (d, *J* = 11.0 Hz, 1H), 4.83 (d, *J* = 10.1 Hz, 2H), 4.77 (d, *J* = 10.8 Hz, 1H), 4.64 - 4.54 (m, 3H), 3.78 - 3.76 (m, 5H), 3.67 - 3.64 (m, 1H).



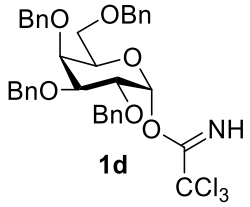
1c

((2*R*,3*R*,4*S*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 2,2,2-trichloroacetimidate

1c was synthesized according to the general procedure A. Trichloroacetonitrile (2.0 mL, 24.0 mmol) and DBU (61.0 μL, 0.48 mmol) were added to a stirring solution of 2,3,4,6-

tetra-*O*-benzyl-D-mannopyranse (1.1 g, 2.4 mmol) in anhydrous CH_2Cl_2 (0.25 M) at RT. The reaction was stirred for 4 h and evaporated onto celite under reduced pressure. The crude product was purified by flash-column chromatography (Basified silica gel, 1:10 ethyl acetate/petroleum) to afford the product as a colorless sugar (1.1 g, 68%).[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.44 - 7.41 (m, 2H), 7.36 - 7.28 (m, 16H), 7.20 (m, 2H), 6.38 (d, *J* = 2.0 Hz, 1H), 4.91 (d, *J* = 10.6 Hz, 1H), 4.79 - 4.75 (m, 2H), 4.69 (d, *J* = 11.9 Hz, 1H), 4.62 (d, *J* = 8.1 Hz, 1H), 4.59 - 4.51 (m, 3H), 4.15 (d, *J* = 9.7 Hz, 1H), 4.00 - 3.92 (m, 2H), 3.88 (t, *J* = 2.7 Hz, 1H), 3.86 - 3.82 (m, 1H), 3.75 - 3.72 (m, 1H).

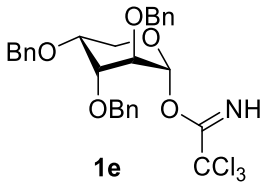


1d

(2*R*,3*R*,4*S*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl 2,2,2-trichloroacetimidate

1d was synthesized according to the general procedure A. Trichloroacetonitrile (3.7 mL, 37.0 mmol) and DBU (110.0 μL, 0.74 mmol) were added to a stirring solution of 2,3,4,6-tetra-*O*-benzyl-D-galactopyranose (2.0 g, 3.7 mmol) in anhydrous CH_2Cl_2 (0.25 M) at RT. The reaction was stirred for 3 h and evaporated onto celite under reduced pressure. The crude product was purified by flash-column chromatography (Basified silica gel, 1:10 ethyl acetate/petroleum) to afford the product as a colorless sugar (1.9 g, 76%).[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.39 - 7.23 (m, 20H), 6.53 (d, *J* = 3.4 Hz, 1H), 4.99 (d, *J* = 11.3 Hz, 1H), 4.84 (d, *J* = 11.9 Hz, 1H), 4.78 - 4.76 (m, 3H), 4.61 (d, *J* = 11.5 Hz, 1H), 4.49 - 4.40 (m, 2H), 4.27 - 4.24 (m, 1H), 4.17 (t, *J* = 6.7 Hz, 1H), 4.08 - 4.02 (m, 2H), 3.65 - 3.55 (m, 2H).



1e

(2*R*,3*S*,4*R*,5*R*)-3,4,5-tris(benzyloxy)tetrahydro-2*H*-pyran-2-yl 2,2,2-trichloroacetimidate

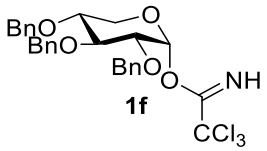
1e was synthesized according to the general procedure A. Trichloroacetonitrile (4.0 mL, 40.0 mmol) and DBU (120.0 μL, 0.80 mmol) were added to a stirring solution of 2,3,4-tri-*O*-benzyl-D-arabinopyranose (1.7 g, 4.0 mmol) in anhydrous CH_2Cl_2 (0.25 M) at RT.

The reaction was stirred for 3 h and evaporated onto celite under reduced pressure. The crude product was purified by flash-column chromatography (Basified silica gel, 1:10 ethyl acetate/petroleum) to afford the product as a yellow sugar (0.87 g, 38%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.42 - 7.29 (m, 15H), 6.51 (d, *J* = 3.4 Hz, 1H), 4.84 - 4.69 (m, 6H), 4.28 - 4.25 (m, 1H), 4.03 - 4.00 (m, 1H), 3.93 - 3.84 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.27, 138.49, 138.43, 138.12, 128.49, 128.43, 128.32, 128.28, 127.94, 127.87, 127.80, 127.76, 127.59, 127.50, 127.43, 95.67, 91.44, 76.35, 75.69, 73.56, 73.11, 72.66, 71.86, 62.89.

Note: Due to its instability in acidic condition (HCOOH, MeOH), the HRMS signal observed is the methyl glycoside.

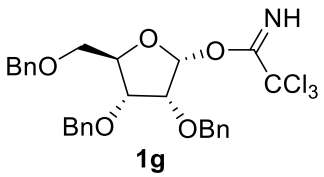


1f

(2*R*,3*R*,4*S*,5*R*)-3,4,5-tris(benzyloxy)tetrahydro-2*H*-pyran-2-yl 2,2,2-trichloroacetimidate

1f was synthesized according to the general procedure A. Trichloroacetonitrile (2.5 mL, 25.0 mmol) and DBU (80.0 μL, 0.50 mmol) were added to a stirring solution of 2,3,4-tri-*O*-benzyl-D-xylopyranose (1.0 g, 2.5 mmol) in anhydrous CH_2Cl_2 (0.25 M) at RT. The reaction was stirred for 12 h and evaporated onto celite under reduced pressure. The crude product was purified by flash-column chromatography (Basified silica gel, 1:10 ethyl acetate/petroleum) to afford the product as a yellow sugar (α:β = 2.9:1, 1.3 g, 92%).[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.34 - 7.27 (m, 15H), 6.35 (d, *J* = 3.5 Hz, 1H), 4.94 - 4.85 (m, 2H), 4.80 - 4.58 (m, 4H), 3.98 (t, *J* = 9.0 Hz, 1H), 3.82 - 3.62 (m, 4H).



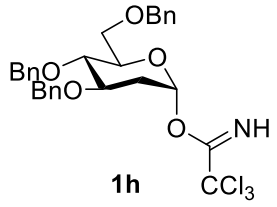
1g

(2*R*,3*R*,4*R*,5*R*)-3,4-bis(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-2-yl 2,2,2-trichloroacetimidate

1g was synthesized according to the general procedure A. Trichloroacetonitrile (2.8 mL, 28.0 mmol) and DBU (84.5 μL, 0.56 mmol) were added to a stirring solution of 2,3,5-tri-*O*-benzyl-D-ribofuranose (1.18 g, 2.8 mmol) in anhydrous CH_2Cl_2 (0.25 M) at RT. The reaction was stirred for 3 h and evaporated onto celite under reduced pressure. The

crude product was purified by flash-column chromatography (Basified silica gel, 1:10 ethyl acetate/petroleum) to afford the product as a yellow sugar (1.1 g, 70%).[7]

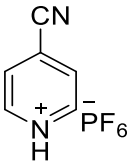
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.46 - 7.32 (m, 15H), 6.27 (d, *J* = 6.7 Hz, 1H), 4.89 - 4.82 (m, 3H), 4.74 (d, *J* = 12.1 Hz, 1H), 4.67 - 4.59 (m, 2H), 4.14 - 4.08 (m, 2H), 3.97 - 3.93 (m, 1H), 3.70 - 3.66 (m, 1H), 3.65 - 3.62 (m, 1H).



1h

1h was synthesized according to the general procedure A. Trichloroacetonitrile (1.65 mL, 16.5 mmol) and DBU (49.0 μL, 0.33 mmol) were added to a stirring solution of 3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranose (0.717 g, 1.65 mmol) in anhydrous CH_2Cl_2 (0.25 M) at RT. The reaction was stirred for 4 h and evaporated onto celite under reduced pressure. The crude product was purified by flash-column chromatography (Basified silica gel, 1:10 ethyl acetate/petroleum) to afford the product as a yellow sugar (0.65 g, 68%).[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.36 - 7.18 (m, 15H), 6.39 (d, *J* = 3.1 Hz, 1H), 4.91 (d, *J* = 10.7 Hz, 1H), 4.68 (s, 2H), 4.63 (d, *J* = 12.1 Hz, 1H), 4.56 (d, *J* = 10.8 Hz, 1H), 4.50 (d, *J* = 12.1 Hz, 1H), 4.06 - 3.96 (m, 2H), 3.84 - 3.74 (m, 2H), 3.70 - 3.67 (m, 1H), 2.45 - 2.40 (m, 1H), 1.91 - 1.84 (m, 1H).



Cat.**G**

4-cyanopyridin-1-ium hexafluorophosphate

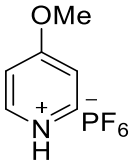
Cat. **G** was synthesized according to the general procedure C, to a sample bottle equipped with a stirring bar was added an ethyl ether (1 mL) solution of 4-cyanopyridin (52.1 mg 0.5 mmol), then the hexafluorophosphoric acid (60% w/w in H_2O, 73.7 μL) was added. A precipitation was observed. After the reaction is completed, the precipitation was washed with ethyl ether three times. Afterwards, the solid was dried under vacuum to afford the product as an orange solid (97.7 mg, 78%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.85 (d, *J* = 5.1 Hz, 2H), 7.88 (d, *J* = 5.0 Hz, 2H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -70.15 (d, *J* = 711.3 Hz).

^{13}C NMR (126 MHz, DMSO-d_6) δ 149.62, 126.68, 121.21, 116.68.

ESI-HRMS: Calculated for $C_6H_5N_2$ (M-PF_6^-): 105.0447, Found: 105.0449.



Cat.**H**

4-methoxypyridin-1-ium hexafluorophosphate

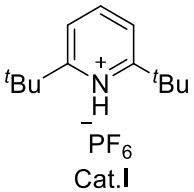
Cat. **H** was synthesized according to the general procedure C, to a sample bottle equipped with a stirring bar was added an ethyl ether (1 mL) solution of 4-methoxypyridin (50.8 μL, 0.5 mmol), then the hexafluorophosphoric acid (60% w/w in H_2O, 73.7 μL) was added. A precipitation was observed. After the reaction is completed, the precipitation was washed with ethyl ether three times. Afterwards, the solid was dried under vacuum to afford the product as a white solid (119.6 mg, 93%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.72 (d, *J* = 6.6 Hz, 2H), 7.52 (d, *J* = 6.6 Hz, 2H), 4.07 (s, 3H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -70.14 (d, *J* = 711.2 Hz).

^{13}C NMR (101 MHz, DMSO-d_6) δ 171.35, 143.66, 112.68, 57.67.

ESI-HRMS: Calculated for C_6H_8NO (M-PF_6^-): 110.0600, Found: 110.0600.



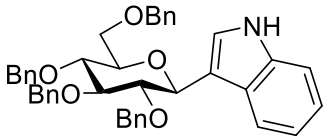
Cat.**I**

2,6-di-tert-butylpyridin-1-ium hexafluorophosphate

Cat. **I** was synthesized according to the general procedure C, to a sample bottle equipped with a stirring bar was added an ethyl ether (2 mL) solution of 2-methylpyridin (224.5 μL, 1.0 mmol), then the hexafluorophosphoric acid (60% w/w in H_2O, 147.4 μL) was added. A precipitation was observed. After the reaction is completed, the precipitation was washed with ethyl ether three times. Afterwards, the solid was dried under vacuum to afford the product as a white solid (325.1 mg, 96%).[9]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.76 (br, 1H), 7.31 (br, 2H), 1.33 (s, 18H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -70.12 (d, *J* = 711.2 Hz).



3a

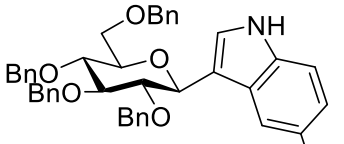
3-((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-1*H*-indole

3a was synthesized according to the General procedure E and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, giving the target product as a white syrup (28.5 mg, 89%).[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.65 (s, 1H), 7.39 - 7.27 (m, 16H), 7.22 - 7.20 (m, 4H), 7.12 -7.05 (m, 3H), 5.73 (d, *J* = 5.8 Hz, 1H), 5.07 (d, *J* = 10.8 Hz, 1H), 4.86 (d, *J* = 10.8 Hz, 1H), 4.81 (d, *J* = 10.7 Hz, 1H), 4.71 - 4.65 (m, 3H), 4.47 - 4.41 (m, 2H), 4.22 (t, *J* = 9.1 Hz, 1H), 4.14 - 4.10 (m, 1H), 3.81 (t, *J* = 9.3 Hz, 1H), 3.67 - 3.64 (m, 1H), 3.59 - 3.56 (m, 1H), 3.39 - 3.36 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.00, 138.47, 138.42, 138.15, 135.99, 128.52, 128.49, 128.42, 128.27, 128.20, 128.11, 127.95, 127.81, 127.74, 127.71, 127.34, 124.76, 122.45, 120.72, 119.95, 111.00, 110.86, 82.87, 81.19, 78.42, 75.71, 75.10, 73.59, 72.48, 71.61, 70.85, 68.98.

R_f (5:1 petroleum ether/ethyl acetate) = 0.50.



3b

5-methyl-3-((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-1*H*-indole

3b was synthesized according to the General procedure E and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, giving the target product as a white syrup (23.1 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.70 (s, 1H), 7.59 (s, 1H), 7.39 - 7.20 (m, 19H), 7.08 - 7.06 (m, 2H), 7.01 (dd, *J* = 8.3, 1.6 Hz, 1H), 5.70 (d, *J* = 5.7 Hz, 1H), 5.07 (d, *J* = 10.9 Hz, 1H), 4.86 (d, *J* = 10.9 Hz, 1H), 4.81 (d, *J* = 10.9 Hz, 1H), 4.69 - 4.63 (m, 3H), 4.48 - 4.42 (m, 2H), 4.22 (t, *J* = 9.2 Hz, 1H), 4.13 - 4.09 (m, 1H), 3.80 (t, *J* = 9.2 Hz, 1H), 3.66 - 3.63 (m, 1H), 3.59 - 3.56 (m, 1H), 3.40 - 3.36 (m, 1H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.09, 138.57, 138.48, 138.23, 134.36, 129.18, 128.59, 128.53, 128.50, 128.47, 128.42, 128.17, 128.15, 128.09, 127.94, 127.78, 127.69,

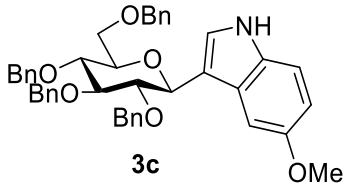
124.95, 124.05, 120.35, 110.63, 110.33, 82.97, 81.23, 78.58, 75.67, 75.07, 73.53, 72.45, 71.54, 70.87, 69.05, 21.64.

IR (thin film, cm^{-1}): 3370, 2922. 2852, 1496, 1453, 1259, 1084, 800, 695.

ESI-HRMS: Calculated for $C_{43}H_{44}NO_5$ ($M+H^+$): 654.3214, Found: 654.3209.

$[\alpha]_D^{25}$ = +111.3 (*c* = 0.20, $CHCl_3$)

R$_f$ (5:1 petroleum ether/ethyl acetate) = 0.50.



3c

5-methoxy-3-((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-1*H*-indole

3c was synthesized according to the General procedure E and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, giving the target product as a white solid (32.7 mg, 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.63 (s, 1H), 7.39 - 7.21 (m, 20H), 7.09 - 7.07 (m, 2H), 6.85 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.71 (d, *J* = 5.7 Hz, 1H), 5.07 (d, *J* = 10.8 Hz, 1H), 4.86 (d, *J* = 10.8 Hz, 1H), 4.82 (d, *J* = 10.8 Hz, 1H), 4.75 - 4.68 (m, 2H), 4.61 (d, *J* = 11.8 Hz, 1H), 4.49 - 4.44 (m, 2H), 4.22 (t, *J* = 9.2 Hz, 1H), 4.13 - 4.09 (m, 1H), 3.81 (t, *J* = 9.3 Hz, 1H), 3.75 (s, 3H), 3.67 - 3.63 (m, 1H), 3.59 - 3.56 (m, 1H), 3.39 - 3.35 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.26, 139.01, 138.49, 138.43, 138.04, 131.07, 128.62, 128.52, 128.50, 128.45, 128.20, 128.13, 128.03, 127.96, 127.81, 127.78, 127.74, 125.46, 112.95, 111.76, 110.55, 102.02, 91.97, 82.85, 81.24, 78.50, 75.70, 75.11, 73.59, 72.53, 71.53, 70.93, 69.06, 55.88.

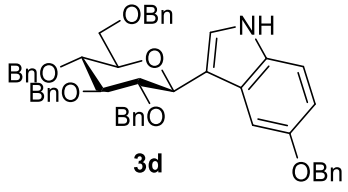
IR (thin film, cm^{-1}): 3377, 2922, 2852, 1507, 1454, 1259, 1087, 801, 692.

ESI-HRMS: Calculated for $C_{43}H_{44}NO_6$ ($M+H^+$): 670.3163, Found: 670.3160.

$[\alpha]_D^{25}$ = +36.1 (*c* = 0.23, $CHCl_3$)

M.p.:154.0 - 154.7 ℃.

R$_f$ (5:1 petroleum ether/ethyl acetate) = 0.40.



3d

5-(benzyloxy)-3-((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-1*H*-indole

3d was synthesized according to the General procedure E and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, giving the target product as a white syrup (33.2 mg, 89%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.63 (s, 1H), 7.44 - 7.17 (m, 25H), 7.10 - 7.05 (m, 2H), 6.94 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.70 (d, *J* = 5.7 Hz, 1H), 5.08 - 5.00 (m, 3H), 4.86 (d, *J* = 10.8 Hz, 1H), 4.81 (d, *J* = 10.8 Hz, 1H), 4.74 - 4.66 (m, 2H), 4.60 (d, *J* = 12.1 Hz, 1H), 4.47 - 4.40 (m, 2H), 4.22 (t, *J* = 9.2 Hz, 1H), 4.12 - 4.08 (m, 1H), 3.81 (t, *J* = 9.2 Hz, 1H), 3.63 - 3.60 (m, 1H), 3.49 (d, *J* = 10.5 Hz, 1H), 3.36 (d, *J* = 9.3 Hz, 1H).

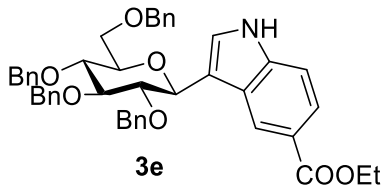
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.47, 138.98, 138.48, 138.41, 138.04, 137.81, 131.27, 128.61, 128.51, 128.48, 128.46, 128.43, 128.19, 128.06, 127.95, 127.85, 127.81, 127.78, 127.73, 127.69, 125.55, 113.65, 111.81, 110.52, 82.81, 81.19, 78.43, 75.67, 75.09, 73.54, 72.50, 71.56, 70.87, 70.77, 69.01.

IR (thin film, cm^{-1}): 3374, 2923, 2854, 1618, 1454, 1260, 1070, 835, 681.

ESI-HRMS: Calculated for $C_{49}H_{48}NO_6$ ($M+H^+$): 746.3476, Found: 746.3470.

$[\alpha]_D^{25}$ = +65.2 (*c* = 0.16, $CHCl_3$)

R_f (5:1 petroleum ether/ethyl acetate) = 0.40.



3e

Ethyl-3-((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-1*H*-indole-5-carboxylate

3e was synthesized according to the General procedure E (0.1 mmol scale) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, giving the target product as a white syrup (43.4 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.34 (s, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.70 (s, 1H), 7.34 (m, 19H), 7.07 - 7.05 (m, 2H), 5.74 (d, *J* = 5.4 Hz, 1H), 5.07 (d, *J* = 10.8 Hz, 1H), 4.87 (d, *J* = 11.2 Hz, 1H), 4.81 (d, *J* = 10.4 Hz, 1H), 4.72 - 4.70 (m, 3H), 4.48 - 4.42 (m, 2H), 4.40 - 4.35 (m, 2H), 4.20 - 4.11 (m, 2H), 3.86 (t, *J* = 9.1 Hz, 1H), 3.70 - 3.67 (m, 1H), 3.61 (d, *J* = 10.6 Hz, 1H), 3.34 (d, *J* = 10.0 Hz, 1H), 1.40 (t, *J* = 7.2 Hz, 3H).

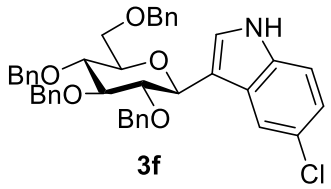
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.85, 138.93, 138.59, 138.39, 138.29, 138.12, 128.52, 128.44, 128.14, 128.07, 128.00, 127.95, 127.88, 127.76, 127.72, 126.92, 125.92, 123.99, 123.55, 122.46, 112.39, 110.76, 82.81, 81.03, 78.32, 75.66, 75.16, 73.71, 72.71, 72.00, 70.66, 68.93, 60.65, 14.63.

IR (thin film, cm^{-1}): 3328, 2924, 2854, 1709, 1496, 1241, 1092, 819, 700.

ESI-HRMS: Calculated for $C_{45}H_{46}NO_7$ ($M+H^+$): 712.3269, Found: 712.3266.

$[\alpha]_D^{25}$ = +123.7 (*c* = 0.20, $CHCl_3$)

R$_f$ (4:1 petroleum ether/ethyl acetate) = 0.20.



3f

5-chloro-3-((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-1*H*-indole

3f was synthesized according to the General procedure E (0.1 mmol scale) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, giving the target product as a white syrup (49.2 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.90 (d, *J* = 2.0 Hz, 1H), 7.65 - 7.20 (m, 20H), 7.14 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.08 - 7.02 (m, 2H), 5.64 (d, *J* = 5.6 Hz, 1H), 5.05 (d, *J* = 10.8 Hz, 1H), 4.86 (t, *J* = 9.6 Hz, 1H), 4.79 (d, *J* = 10.7 Hz, 1H), 4.70 - 4.67 (m, 3H), 4.46 - 4.43 (m, 2H), 4.19 - 4.12 (m, 1H), 4.11 - 4.07 (m, 1H), 3.81 - 3.77 (m, 1H), 3.67 - 3.64 (m,1H), 3.61 - 3.56 (m, 1H), 3.34 - 3.30 (m, 1H).

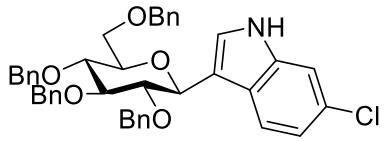
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.96, 138.40, 138.33, 138.11, 134.37, 128.52, 128.51, 128.48, 128.45, 128.16, 128.14, 128.03, 128.00, 127.97, 127.94, 127.88, 127.76, 126.02, 125.73, 122.83, 120.23, 112.00, 110.89, 82.78, 81.08, 78.46, 75.65, 75.15, 73.59, 72.72, 71.87, 70.69, 68.90.

IR (thin film, cm^{-1}): 3324, 2923. 2853, 1497, 1453, 1259, 1073, 801, 695.

ESI-HRMS: Calculated for $C_{42}H_{40}ClNO_5Na$ ($M+Na^+$): 696.2487, Found: 696.2484.

$[\alpha]_D^{25}$ = +95.7 (*c* = 0.23, $CHCl_3$)

R$_f$ (4:1 petroleum ether/ethyl acetate) = 0.40.



3g

6-chloro-3-((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-1*H*-indole

3g was synthesized according to the General procedure E (0.1 mmol scale) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, giving the target product as a white syrup (44.3 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.63 (s, 1H), 7.40 - 7.23 (m, 19H), 7.10 - 7.04 (m, 3H), 5.68 (d, *J* = 5.7 Hz, 1H), 5.08 (d, *J* = 10.8 Hz, 1H), 4.88 - 4.81 (m, 2H), 4.68 (m, 3H), 4.49 - 4.43 (m, 2H), 4.20 (t, *J* = 9.1 Hz, 1H), 4.14 - 4.10 (m, 1H), 3.80 (t, *J* = 9.2 Hz, 1H), 3.69 - 3.66 (m, 1H), 3.60 - 3.57 (m, 1H), 3.37 - 3.33 (m, 1H).

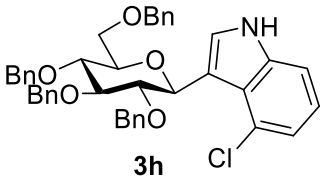
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.92, 138.36, 138.31, 138.05, 136.38, 128.79, 128.59, 128.52, 128.45, 128.39, 128.26, 128.20, 128.15, 128.10, 127.98, 127.93, 127.87, 127.78, 127.76, 125.89, 125.28, 121.64, 120.69, 111.20, 110.94, 82.74, 81.07, 78. 45, 75.62, 75.15, 73.61, 72.67, 71.78, 70.72, 69.07.

IR (thin film, cm^{-1}): 3302, 2924. 2855, 1496, 1454, 12606, 1071, 800, 697.

ESI-HRMS: Calculated for $C_{42}H_{40}ClNO_5Na$ ($M+Na^+$): 696.2487, Found: 696.2484.

$[\alpha]_D^{25}$ = +93.7 (*c* = 0.25, $CHCl_3$)

R_f (4:1 petroleum ether/ethyl acetate) = 0.50.



3h

4-chloro-3-((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-1*H*-indole

3h was synthesized according to the General procedure E (0.1 mmol scale) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, giving the target product as a white syrup (46.7 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.50 (s, 1H), 7.33 - 7.00 (m, 23H), 6.10 (s, 1H), 4.96 - 4.92 (m, 1H), 4.84 - 4.80 (m, 1H), 4.76 - 4.72 (m, 1H), 4.61 - 4.55 (m, 2H), 4.52 - 4.43 (m, 3H), 4.17 - 4.15 (m, 2H), 3.82 - 3.78 (m, 1H), 3.71 - 3.67 (m, 1H), 3.61 - 3.55 (m, 2H).

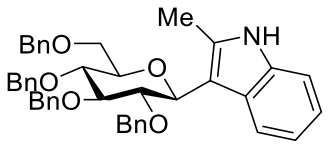
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.80, 138.35, 138.19, 137.67, 128.52, 128.37, 128.34, 128.18, 128.07, 127.99, 127.91, 127.87, 127.77, 127.71, 127.58, 126.98, 126.48, 124.37, 122.66, 121.23, 110.50, 110.07, 82.27, 79.69, 78.08, 74.93, 74.76, 73.53, 72.27, 71.73, 69.09, 68.71.

IR (thin film, cm^{-1}): 3248, 2924. 2853, 1561, 1503, 1260, 1090, 801, 695.

ESI-HRMS: Calculated for $C_{42}H_{41}ClNO_5$ ($M+H^+$): 674.2668, Found: 674.2666.

$[\alpha]_D^{25}$ = +63.5 (*c* = 0.23, $CHCl_3$)

R_f (4:1 petroleum ether/ethyl acetate) = 0.40.



3i

2-methyl-3-((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-1*H*-indole

3i was synthesized according to the General procedure E (0.1 mmol scale) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, giving the target product as a white syrup (45.7 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 - 7.79 (m, 2H), 7.20 - 7.09 (m, 18H), 7.02 - 6.94 (m, 5H), 5.47 (d, *J* = 4.5 Hz, 1H), 4.81 (d, *J* = 11.1 Hz, 1H), 4.74 - 4.67 (m, 2H), 4.52 - 4.46 (m, 2H), 4.43 - 4.34 (m, 3H), 4.09 (t, *J* = 7.1 Hz, 1H), 3.89 - 3.86 (m, 1H), 3.81 (t, *J* = 8.4 Hz, 1H), 3.68 - 3.65 (m, 1H), 3.63 - 3.60 (m, 1H), 3.57 - 3.53 (m, 1H), 2.38 (s, 3H).

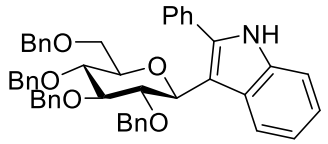
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.67, 138.58, 138.36, 138.32, 135.23, 134.18, 121.04, 120.76, 119.56, 110.04, 108.54, 82.81, 81.10, 77.93, 74.29, 73.99, 73.50, 73.11, 72.65, 70.76, 69.69, 13.99.

IR (thin film, cm^{-1}): 3351, 2921. 2853, 1496, 1456, 1259, 1085, 798, 698.

ESI-HRMS: Calculated for $C_{43}H_{44}NO_5$ ($M+H^+$): 654.3214, Found: 654.3213.

$[\alpha]_D^{25}$ = +24.2 (*c* = 0.19, $CHCl_3$)

R_f (4:1 petroleum ether/ethyl acetate) = 0.50.



3j

2-phenyl-3-((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-1*H*-indole

3j was synthesized according to the General procedure E (0.1 mmol scale) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, giving the target product as a yellow syrup (61.6 mg, α:β = 1:5.6, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 - 8.09 (m, 2H), 7.43 - 7.41 (m, 2H), 7.34 - 7.06 (m, 24H), 6.88 - 6.86 (m, 2H), 5.55 (d, *J* = 3.5 Hz, 1H), 4.76 (d, *J* = 11.3 Hz, 1H), 4.57 - 4.53 (m, 3H), 4.47 (d, *J* = 12.1 Hz, 1H), 4.34 (d, *J* = 12.2 Hz, 1H), 4.27 (d, *J* = 11.8 Hz, 1H), 4.20 (d, *J* = 11.6 Hz, 1H), 4.15 - 4.09 (m, 1H), 4.05 - 4.02 (m, 1H), 3.99 - 3.94 (m, 1H), 3.85 (t, *J* = 4.0 Hz, 1H), 3.69 - 3.66 (m, 1H), 3.61 - 3.58 (m, 1H).

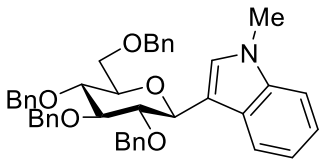
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.75, 138.53, 138.10, 136.15, 135.88, 133.22, 128.97, 128.71, 128.60, 128.52, 128.42, 128.39, 128.34, 128.15, 128.09, 127.93, 127.87, 127.77, 127.66, 127.55, 127.47, 123.49, 122.37, 120.10, 111.26, 110.46, 83.12, 81.91, 77.23, 73.93, 73.80, 73.49, 73.09, 73.01, 70.31, 70.01.

IR (thin film, cm^{-1}): 3382, 2924. 2854, 1496, 1454, 1260, 1086, 799, 698.

ESI-HRMS: Calculated for $C_{48}H_{46}NO_5$ ($M+H^+$): 716.3371, Found: 716.3365.

$[\alpha]_D^{25}$ = +9.2 (*c* = 0.16, $CHCl_3$)

R_f (4:1 petroleum ether/ethyl acetate) = 0.40.



3k-β

1-methyl-3-((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-1*H*-indole

3k-β was synthesized according to the General procedure E (0.1 mmol scale) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, giving the target product as a light yellow solid (41.2 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.9 Hz, 1H), 7.45 (s, 1H), 7.42 - 7.40 (m, 2H), 7.37 - 7.21 (m, 18H), 7.12 - 7.05 (m, 3H), 5.72 (d, *J* = 5.7 Hz, 1H), 5.10 (d, *J* = 10.9 Hz, 1H), 4.89 (d, *J* = 11.0 Hz, 1H), 4.81 (d, *J* = 10.6 Hz, 1H), 4.74 - 4.65 (m, 3H), 4.46 - 4.40 (m, 2H), 4.23 (t, *J* = 9.2 Hz, 1H), 4.12 - 4.08 (m, 1H), 3.82 (t, *J* = 9.4 Hz, 1H), 3.74 (s, 3H), 3.67 - 3.63 (m, 1H), 3.56 (d, *J* = 10.6 Hz, 1H), 3.37 (d, *J* = 10.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.03, 138.45, 138.15, 136.84, 129.34, 128.50, 128.44, 128.40, 128.22, 128.11, 127.99, 127.91, 127.81, 127.72, 127.70, 121.98, 120.75, 119.45, 109.12, 109.09, 82.76, 81.10, 78.47, 75.64, 75.11, 73.57, 72.44, 71.41, 70.83, 68.98, 32.95.

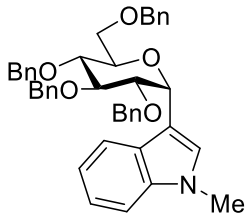
IR (thin film, cm^{-1}): 2921. 2854, 1497, 1453, 1260, 1084, 800, 696.

ESI-HRMS: Calculated for $C_{43}H_{44}NO_5$ ($M+H^+$): 654.3214, Found: 654.3214.

$[\alpha]_D^{25}$ = +87.5 (*c* = 0.20, $CHCl_3$)

M.p.:91.0 - 91.9 ℃

R_f (4:1 petroleum ether/ethyl acetate) = 0.50.



3k-α

1-methyl-3-((2*R*,3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-1*H*-indole

3k-α was synthesized according to the General procedure E (0.1 mmol scale) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, giving the target product as a pale yellow syrup (18.7 mg, 29%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.9 Hz, 1H), 7.29 - 7.15 (m, 17H), 7.04 (m, 5H), 6.72 - 6.71 (m, 2H), 4.91 - 4.82 (m, 3H), 4.63 - 4.58 (m, 2H), 4.48 - 4.45 (m, 2H), 4.27 (d, *J* = 10.4 Hz, 1H), 3.89 - 3.70 (m, 6H), 3.69 (s, 3H), 3.56 (d, *J* = 9.4 Hz, 1H).

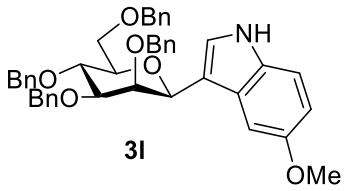
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.97, 138.72, 138.53, 138.14, 137.53, 128.55, 128.53, 128.43, 128.28, 128.17, 128.01, 127.94, 127.85, 127.69, 127.58, 127.53, 126.84, 122.04, 120.87, 119.53, 112.82, 109.47, 86.98, 83.21, 79.50, 78.63, 76.53, 75.80, 75.29, 74.84, 73.56, 69.42, 32.86.

IR (thin film, cm^{-1}): 2922, 2851, 1497, 1454, 1260, 1062, 801, 698.

ESI-HRMS: Calculated for $C_{43}H_{44}NO_5$ ($M+H^+$): 654.3214, Found: 654.3214.

$[\alpha]_D^{25}$ = +12.0 (*c* = 0.22, $CHCl_3$)

R_f (4:1 petroleum ether/ethyl acetate) = 0.25.



3l

5-methoxy-3-((2*S*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-1*H*-indole

3l was synthesized according to the General procedure E (0.1 mmol scale, reaction time 18 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, giving the target product as a white solid (28.5 mg, 43%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.42 - 7.40 (m, 2H), 7.34 - 7.20 (m, 17H), 7.18 - 7.13 (m, 3H), 6.82 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.36 (d, *J* = 2.5 Hz, 1H), 5.50 (d, *J* = 2.7 Hz, 1H), 4.85 - 4.80 (m, 2H), 4.71 - 4.64 (m, 4H), 4.54 - 4.48 (m, 2H), 4.19 (t, *J* = 3.0 Hz, 1H), 4.12 (t, *J* = 8.7 Hz, 1H), 3.97 - 3.94 (m, 1H), 3.81 - 3.78 (m, 1H), 3.73 (d, *J* = 2.5 Hz, 1H), 3.70 (s, 3H), 3.58 - 3.56 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.38, 138.78, 138.71, 138.52, 138.50, 131.31, 128.56, 128.46, 128.43, 128.41, 128.31, 128.28, 128.02, 127.98, 127.85, 127.73, 127.65, 127.59, 127.19, 122.43, 113.47, 112.58, 111.76, 102.08, 79.18, 77.37, 75.87, 75.12, 74.72, 73.46, 72.47, 71.73, 71.21, 69.61, 55.78.

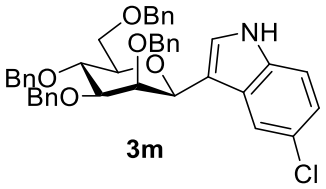
IR (thin film, cm^{-1}): 3266, 2923. 2853, 1496, 1453, 1259, 1086, 800, 698.

ESI-HRMS: Calculated for $C_{43}H_{44}NO_6$ ($M+H^+$): 670.3163, Found: 670.3163.

$[\alpha]_D^{25}$ = +47.1 (*c* = 0.14, $CHCl_3$)

M.p.:208.4 - 209.0 ℃

R_f (2:1 petroleum ether/ethyl acetate) = 0.33.



3m

5-chloro-3-((2*S*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-1*H*-indole

3m was synthesized according to the General procedure E (0.1 mmol scale, reaction time 18 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, giving the target product as a white solid (33.9 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.82 (s, 1H), 7.29 (m, 18H), 7.16 - 7.12 (m, 3H), 7.07 (d, *J* = 8.8 Hz, 1H), 6.40 (s, 1H), 5.39 (d, *J* = 3.2 Hz, 1H), 4.79 (d, *J* = 10.9 Hz, 1H), 4.72 - 4.59 (m, 5H), 4.53 - 4.49 (m, 2H), 4.14 (d, *J* = 4.0 Hz, 1H), 4.07 (t, *J* = 8.2 Hz, 1H), 3.89 - 3.87 (m, 1H), 3.83 - 3.80 (m, 1H), 3.75 - 3.71 (m, 1H), 3.64 (t, *J* = 6.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.58, 138.51, 138.43, 138.28, 134.69, 128.55, 128.48, 128.44, 128.40, 128.23, 128.19, 128.04, 128.00, 127.88, 127.81, 127.73, 127.62, 125.73, 123.37, 122.92, 120.34, 112.76, 112.13, 78.61, 75.72, 75.21, 74.47, 73.83, 73.46, 72.54, 71.86, 70.63, 69.32.

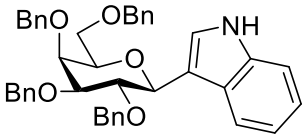
IR (thin film, cm^{-1}): 3292, 2923. 2854, 1496, 1453, 1258, 1090, 799, 696.

ESI-HRMS: Calculated for $C_{42}H_{41}ClNO_5$ ($M+H^+$): 674.2668, Found: 674.2668.

$[\alpha]_D^{25}$ = +74.3 (*c* = 0.14, $CHCl_3$)

M.p.:193.7 - 194.4 ℃

R_f (2:1 petroleum ether/ethyl acetate) = 0.40.



3n

3-((2*S*,3*S*,4*R*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-1*H*-indole

3n was synthesized according to the General procedure E (0.1 mmol scale) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, giving the target product as a white syrup (49.1 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.48 (s, 1H), 7.39 - 7.16 (m, 22H), 7.06 (t, *J* = 7.5 Hz, 1H), 5.69 (d, *J* = 5.1 Hz, 1H), 4.92 (d, *J* = 11.5 Hz, 1H), 4.78 (m, 2H), 4.63 - 4.60 (m, 3H), 4.39 - 4.32 (m, 3H), 4.07 - 4.05 (m, 1H), 4.00 (s, 1H), 3.68 (s, 3H).

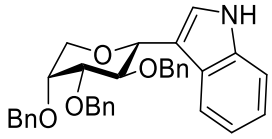
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.03, 138.78, 138.33, 136.04, 128.48, 128.40, 128.36, 128.24, 127.87, 127.82, 127.73, 127.61, 124.19, 122.33, 120.69, 119.85, 111.56, 110.93, 78.48, 77.68, 74.97, 74.47, 73.38, 72.95, 72.88, 71.48, 68.48.

IR (thin film, cm^{-1}): 3320, 2923, 2853, 1498, 1455, 1260, 1101, 800, 699.

ESI-HRMS: Calculated for $C_{42}H_{42}NO_5$ ($M+H^+$): 640.3057, Found: 640.3055.

$[\alpha]_D^{25}$ = +24.7 (*c* = 0.22, $CHCl_3$)

R_f (4:1 petroleum ether/ethyl acetate) = 0.33.



3o

3-((2*R*,3*R*,4*R*,5*R*)-3,4,5-tris(benzyloxy)tetrahydro-2*H*-pyran-2-yl)-1*H*-indole

3o was synthesized according to the General procedure E (0.1 mmol scale, reaction time 36 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, giving the target product as a white solid (21.3 mg, 41%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.34 - 7.04 (m, 17H), 6.92 - 6.90 (m, 2H), 5.21 (s, 1H), 4.78 (d, *J* = 12.3 Hz, 1H), 4.59 - 4.52 (m, 3H), 4.17 (d, *J* = 12.0 Hz, 1H), 4.01 - 3.98 (m, 2H), 3.95 - 3.92 (m, 2H), 3.87 (t, *J* = 3.5 Hz, 1H), 3.73 (d, *J* = 4.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.91, 138.65, 138.11, 136.02, 128.58, 128.56, 128.30, 128.05, 127.97, 127.83, 127.75, 126.13, 122.92, 122.10, 119.66, 119.21, 113.73, 111.18, 77.37, 74.22, 73.39, 73.26, 72.98, 71.54, 71.26, 65.09.

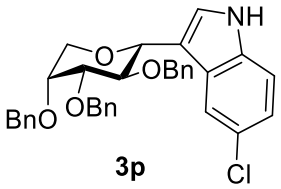
IR (thin film, cm^{-1}): 3342, 2924, 2854, 1496, 1455, 1260, 1085, 799, 697.

ESI-HRMS: Calculated for $C_{34}H_{34}NO_4$ ($M+H^+$): 520.2482, Found: 520.2483.

$[\alpha]_D^{25}$ = +11.2 (*c* = 0.14, $CHCl_3$).

M.p.:139.3 - 140.0 ℃

R_f (4:1 petroleum ether/ethyl acetate) = 0.33.



3p

5-chloro-3-((2*R*,3*R*,4*R*,5*R*)-3,4,5-tris(benzyloxy)tetrahydro-2*H*-pyran-2-yl)-1*H*-indole

3p was synthesized according to the General procedure E (0.1 mmol scale, reaction time 36 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, giving the target product as a light yellow solid (16.9 mg, 31%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.39 - 7.10 (m, 16H), 6.90 - 6.88 (m, 2H), 5.12 (s, 1H), 4.85 (d, *J* = 12.3 Hz, 1H), 4.63 - 4.54 (m, 3H), 4.16 - 4.01 (m, 3H), 3.96 - 3.91 (m, 3H), 3.63 (d, *J* = 4.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.79, 138.57, 137.76, 134.37, 128.68, 128.58, 128.28, 128.07, 128.04, 128.02, 127.88, 127.85, 127.82, 127.20, 125.37, 124.26, 122.41, 119.06, 113.66, 112.13, 77.56, 73.85, 73.47, 73.21, 72.93, 71.63, 71.16, 65.03.

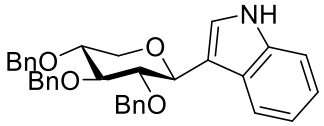
IR (thin film, cm^{-1}): 3333, 2923. 2853, 1495, 1454, 1260, 1076, 798, 697.

ESI-HRMS: Calculated for $C_{34}H_{33}ClNO_4$ ($M+H^+$): 554.2093, Found: 554.2094.

$[\alpha]_D^{25}$ = +27.6 (*c* = 0.18, $CHCl_3$)

M.p.:187.3 - 188.0 ℃

R_f (3:1 petroleum ether/ethyl acetate) = 0.33.



3q

3-((2*S*,3*S*,4*S*,5*R*)-3,4,5-tris(benzyloxy)tetrahydro-2*H*-pyran-2-yl)-1*H*-indole

3q was synthesized according to the General procedure E (0.1 mmol scale, reaction time 36 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, giving the target product as a white solid (29.1 mg, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.40 - 7.13 (m, 17H), 6.85 - 6.83 (m, 2H), 5.01 - 4.91 (m, 2H), 4.83 (d, *J* = 11.6 Hz, 1H), 4.75 (d, *J* =

11.6 Hz, 1H), 4.51 (d, *J* = 9.5 Hz, 1H), 4.38 (d, *J* = 10.4 Hz, 1H), 4.22 - 4.18 (m, 1H), 3.91 - 3.75 (m, 4H), 3.43 (t, *J* = 10.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.99, 138.48, 138.12, 136.65, 128.65, 128.62, 128.54, 128.51, 128.25, 128.22, 128.20, 128.12, 128.09, 127.98, 127.96, 127.72, 127.61, 126.16, 123.40, 123.38, 122.59, 122.56, 120.41, 120.39, 120.15, 120.12, 114.36, 111.46, 111.43, 86.28, 82.54, 78.94, 77.33, 75.88, 74.95, 73.51, 68.63.

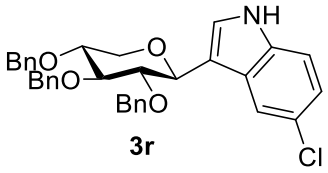
IR (thin film, cm^{-1}): 3317, 2923. 2854, 1497, 1455, 1261, 1078, 805, 694.

ESI-HRMS: Calculated for $C_{34}H_{34}NO_4$ ($M+H^+$): 520.2482, Found: 520.2484.

$[\alpha]_D^{25}$ = +0.6 (*c* = 0.23, $CHCl_3$)

M.p.:132.2 - 132.7 ℃

R_f (4:1 petroleum ether/ethyl acetate) = 0.20.



3r

5-chloro-3-((2*S*,3*S*,4*S*,5*R*)-3,4,5-tris(benzyloxy)tetrahydro-2*H*-pyran-2-yl)-1*H*-indole

3r was synthesized according to the General procedure E (0.1 mmol scale, reaction time 36 h) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, giving the target product as a white solid (24.5 mg, 44%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.72 (s, 1H), 7.37 - 7.13 (m, 16H), 6.84 - 6.82 (m, 2H), 4.98 (d, *J* = 10.9 Hz, 1H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.81 (d, *J* = 11.5 Hz, 1H), 4.73 (d, *J* = 11.6 Hz, 1H), 4.44 - 4.40 (m, 2H), 4.20 - 4.16 (m, 1H), 3.88 - 3.81 (m, 2H), 3.79 - 3.73 (m, 2H), 3.39 (t, *J* = 10.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.85, 138.38, 137.88, 134.91, 128.66, 128.55, 128.24, 128.17, 128.10, 128.02, 127.97, 127.78, 127.70, 127.05, 125.85, 124.68, 122.94, 119.88, 114.19, 112.46, 86.21, 82.20, 78.90, 77.04, 75.92, 75.02, 73.57, 68.60.

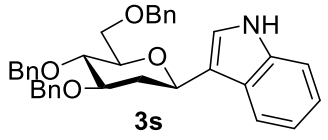
IR (thin film, cm^{-1}): 3296, 2923. 2855, 1497, 1462, 1261, 1086, 804, 698.

ESI-HRMS: Calculated for $C_{34}H_{34}NO_4$ ($M+H^+$): 554.2093, Found: 554.2096.

$[\alpha]_D^{25}$ = -19.8 (*c* = 0.15, $CHCl_3$)

M.p.:226.1 - 227.2 ℃

R_f (4:1 petroleum ether/ethyl acetate) = 0.20.



3s

3-((2*R*,4*R*,5*S*,6*R*)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-1*H*-indole

3s was synthesized according to the General procedure E (0.1 mmol scale) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, giving the target product as a white syrup (31.3 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.40 - 7.14 (m, 17H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.73 (s, 1H), 5.48 (d, *J* = 5.5 Hz, 1H), 4.84 (d, *J* = 11.0 Hz, 1H), 4.72 (s, 2H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.53 (d, *J* = 10.9 Hz, 1H), 4.47 (d, *J* = 12.1 Hz, 1H), 4.01 - 3.98 (m, 1H), 3.79 - 3.69 (m, 2H), 3.64 (d, *J* = 10.4 Hz, 1H), 3.47 (d, *J* = 8.6 Hz, 1H), 2.60 - 2.55 (m, 1H), 2.18 - 2.10 (m, 1H).

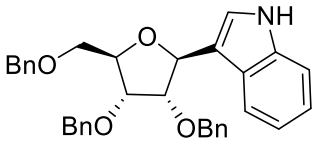
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.95, 138.82, 138.48, 136.69, 128.60, 128.42, 128.13, 128.03, 127.95, 127.85, 127.65, 126.71, 122.56, 122.36, 120.89, 119.98, 115.29, 111.02, 78.74, 77.79, 74.68, 73.60, 72.62, 71.96, 69.52, 69.06, 33.45.

IR (thin film, cm^{-1}): 3020, 2962, 2921, 1264, 1214, 1016, 747, 672.

ESI-HRMS: Calculated for $C_{35}H_{36}NO_4$ ($M+H^+$): 534.2639, Found: 534.2629.

$[\alpha]_D^{25}$ = +12.8 (*c* = 0.12, $CHCl_3$)

R_f (4:1 petroleum ether/ethyl acetate) = 0.25.



3t

3-((2*S*,3*S*,4*R*,5*R*)-3,4-bis(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-2-yl)-1*H*-indole

3t was synthesized according to the General procedure E (0.1 mmol scale) and isolated by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, giving the target product as a white syrup (26.1 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.48 - 7.46 (m, 2H), 7.38 - 7.06 (m, 15H), 6.88 - 6.86 (m, 2H), 5.03 (d, *J* = 9.7 Hz, 1H), 4.99 - 4.92 (m, 2H), 4.63 - 4.56 (m, 2H), 4.28 (s, 1H), 4.12 (d, *J* = 11.9 Hz, 1H), 4.06 - 3.94 (m, 3H), 3.70 - 3.67 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.55, 138.51, 138.28, 136.70, 128.61, 128.56, 128.51, 128.35, 128.30, 128.23, 128.18, 128.09, 128.04, 127.99, 127.84, 127.80, 127.74, 127.67, 127.56, 127.49, 127.42, 126.57, 123.37, 122.29, 120.56, 119.83, 114.78, 111.28, 79.33, 76.53, 74.69, 74.22, 71.98, 71.80, 71.33, 64.67.

IR (thin film, cm^{-1}): 3018, 2923, 1457, 1214, 751, 668.

ESI-HRMS: Calculated for $C_{34}H_{34}NO_4$ ($M+H^+$): 520.2482, Found: 520.2473.

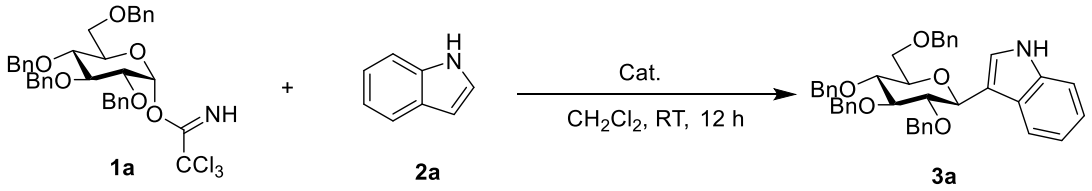
$[\alpha]_D^{25}$ = -1.1 (*c* = 0.18, $CHCl_3$)

R_f (4:1 petroleum ether/ethyl acetate) = 0.25.

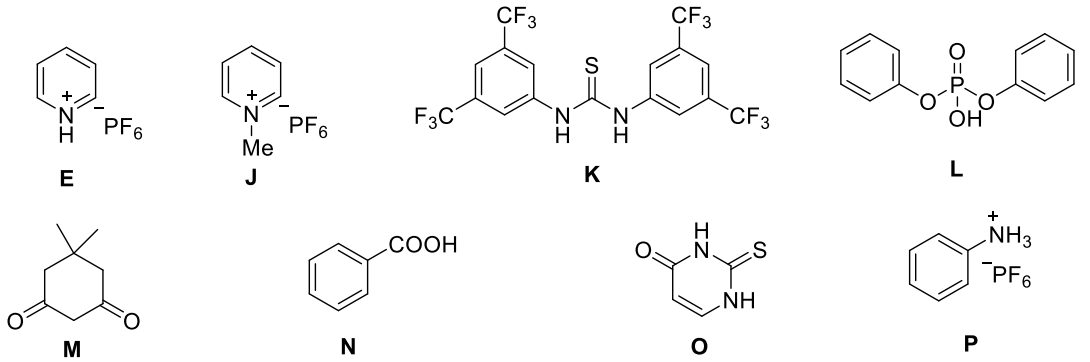
4. Mechanistic studies

4.1 NMR study for catalysts comparison

Table S5. Comparison with other types of catalysts[a]



Entries	Catalyst	Yield (%)
1	**E**	77[b]
2	**J**	no reaction
3	**K**	no reaction
4	**L**	no reaction
5	**M**	no reaction
6	**N**	no reaction
7	**O**	no reaction
8	**P**	no product



[a]Procedure: **1a** (0.075 mmol, 1.5 equiv.), **2a** (0.05 mmol, 1.0 equiv.), anhydrous CH_2Cl_2 (1 mL), 20 mol% cat., under N_2 atmosphere; 12 h, RT; the yield was determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yield.

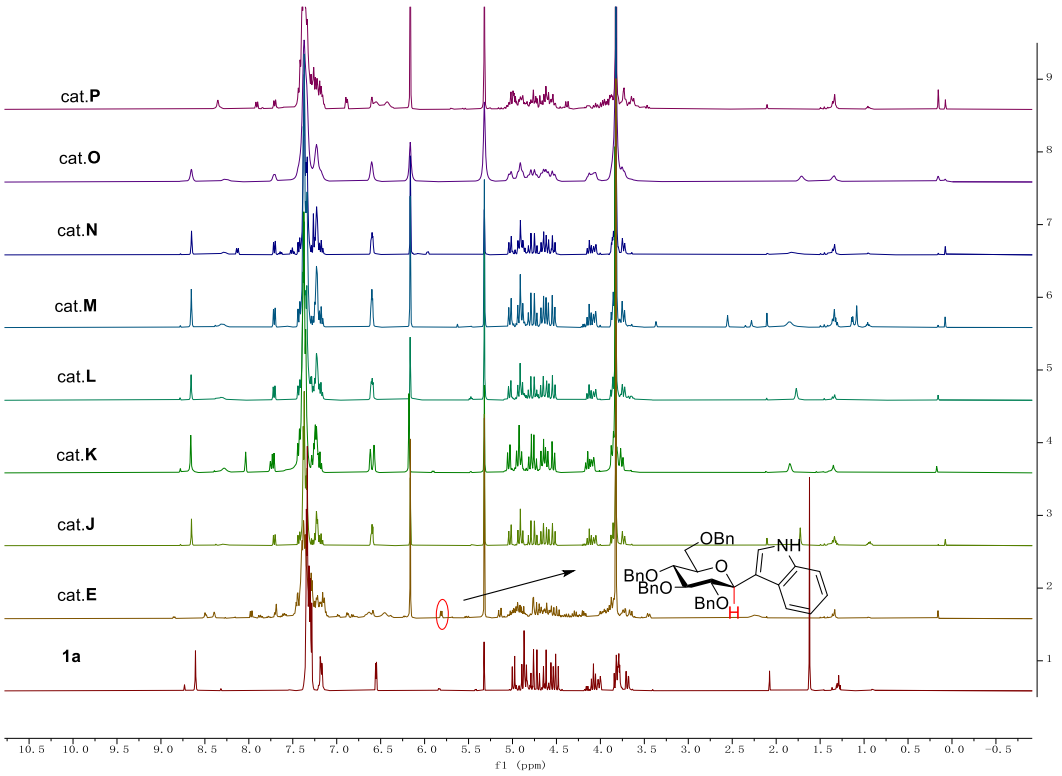


Figure S1. Crude ^{1}H NMR spectra for catalysts comparison

4.2 NMR study for E and 1a

Procedure: A mixture of glycosyl donor **1a** (0.0375 mmol, 7.5 equiv.) and cat. **E** (0.005 mmol, 1.0 equiv.) were dissolved in 0.5 mL CD_2Cl_2 in an anhydrous NMR tube, then test ^{1}H NMR, we found that yielding the rearrangement product, trichloroacetamide-based *N*-glycoside.[11] Glycosyl donor **1a** (0.075 mmol, 1.0 equiv.) were dissolved in 0.5 mL CD_2Cl_2 in an anhydrous NMR tube, then test ^{1}H NMR.

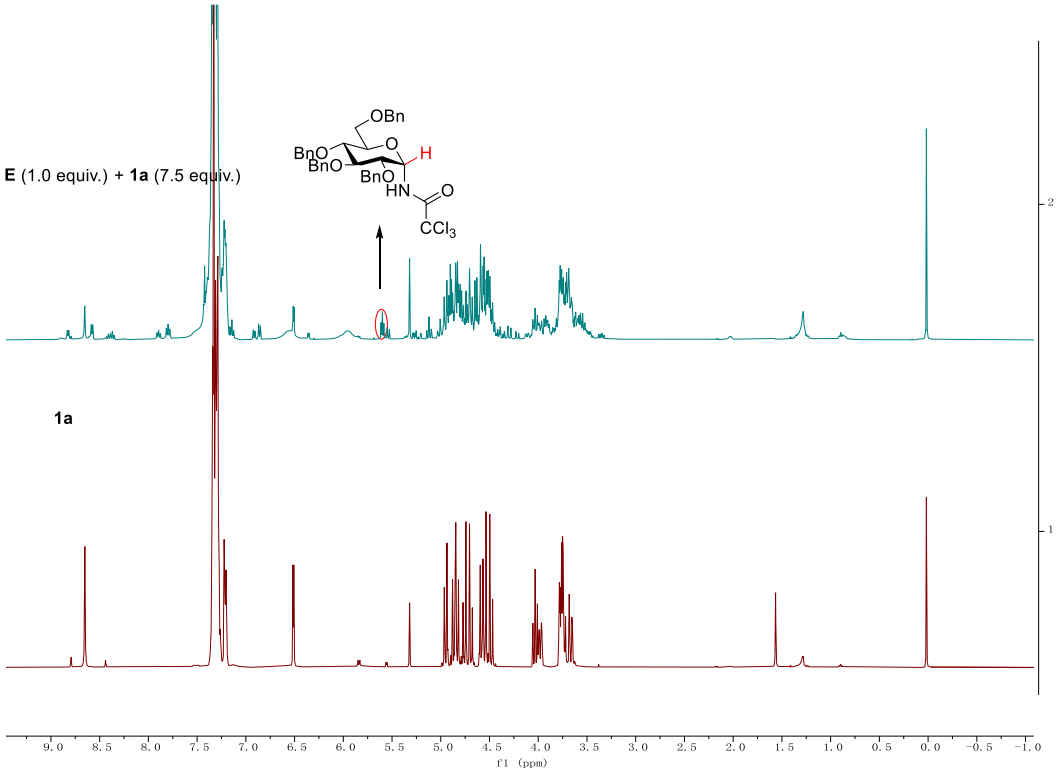


Figure S2. Crude ^{1}H NMR spectra for E and 1a

4.3 Study for E and 2a

4.3.1 NMR study for E and 2a

Procedure: A mixture of indole **2a** (0.025 mmol, 5.0 equiv.) and cat. **E** (0.005 mmol, 1.0 equiv.) were dissolved in 0.5 mL CD_2Cl_2 in an anhydrous NMR tube, then test ^{1}H NMR. Cat. **E** (20 mol%) were dissolved in 0.5 mL CD_2Cl_2 in an anhydrous NMR tube, then test ^{1}H NMR.

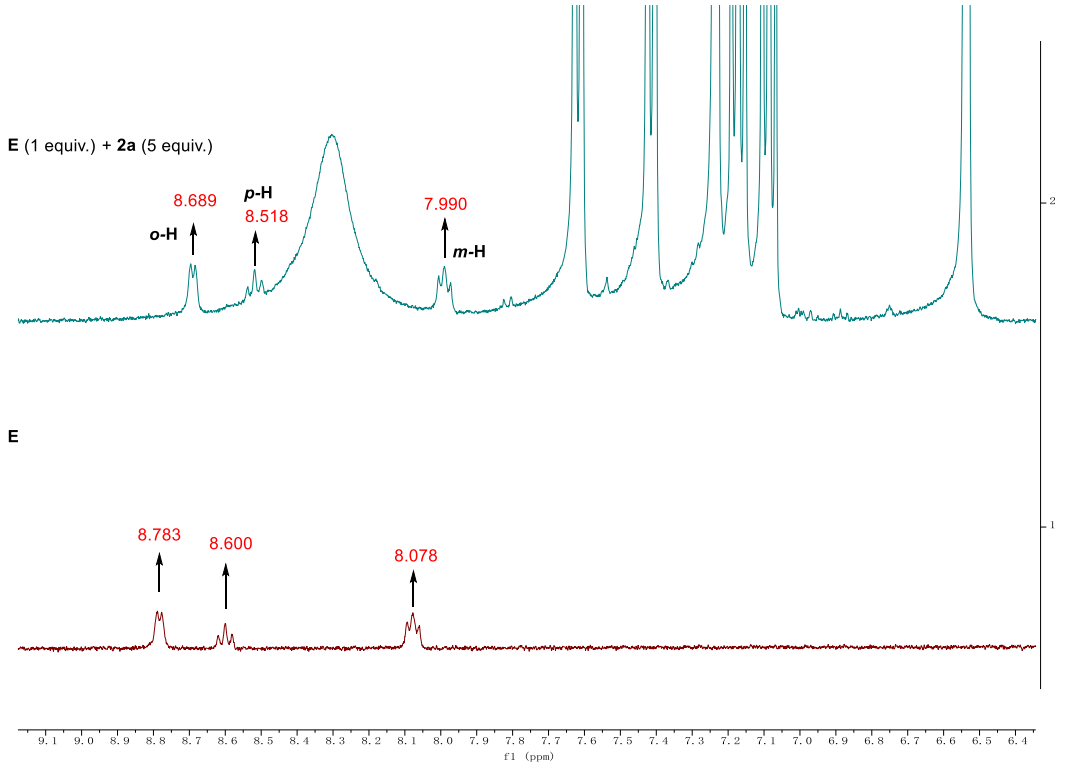


Figure S3. Crude ^{1}H NMR spectra for E and 2a

4.3.2 UV spectra for E, 2a and complex

Procedure: Prepare a CH_2Cl_2 solution with a concentration of 4×10^{-5} mol/L for cat.**E**, **2a**, and their complex separately, and then measure the UV absorption wavelength using a UH5300 spectrophotometer.

The ultraviolet absorption spectrum of indole exhibits two absorption bands, E bands and B bands, in the regions of 220-240 nm and 260-280 nm, respectively. Both bands are attributed to π→π* electron transition. When indole coordinates with a pyridinium salt catalyst (**E**), a notable blue shift occurs in the B bands, while the change in absorption intensity is minimal. In contrast, the E bands shows no significant shift in peak position, but there is a pronounced decrease in absorption intensity. This description has been included in SI.

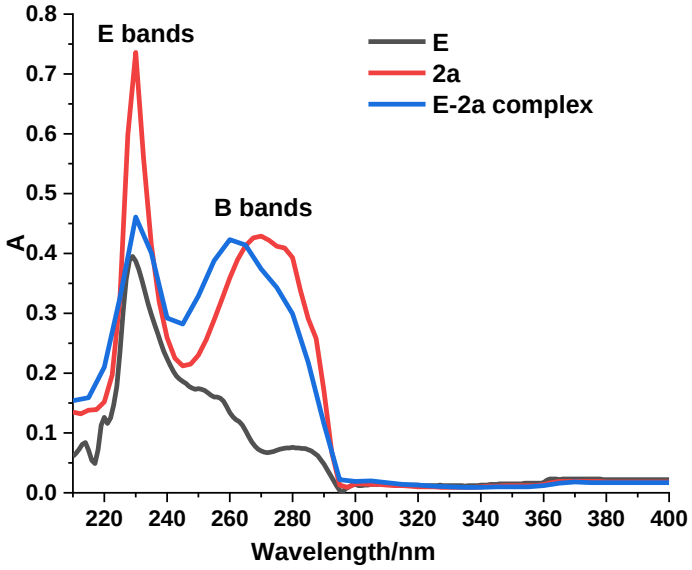
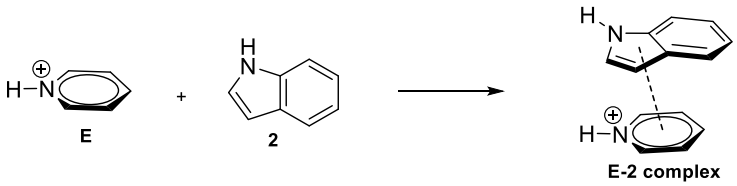
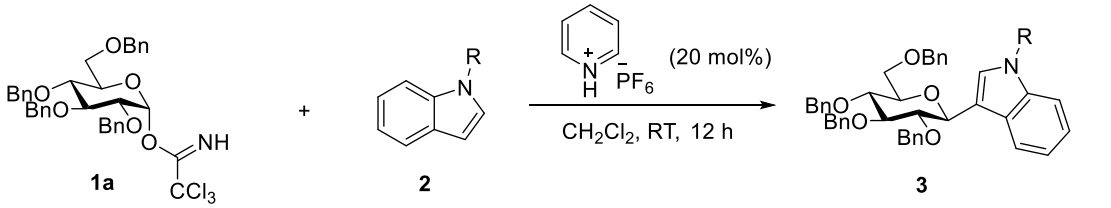


Figure S4. UV absorption spectra

The ^{1}H NMR analysis revealed an upfield shift of the hydrogen on the pyridine scaffold upon mixing with five equivalents of indole, while UV spectroscopy indicated a significant red shift in the absorption band and alterations in absorption intensity. Based on the above experimental phenomena, we believe that indole **2** will generate a force with cat. **E** to form a complex (**E-2 complex**).



4.4 Reaction for Boc-, Ts- and Me-protected indole



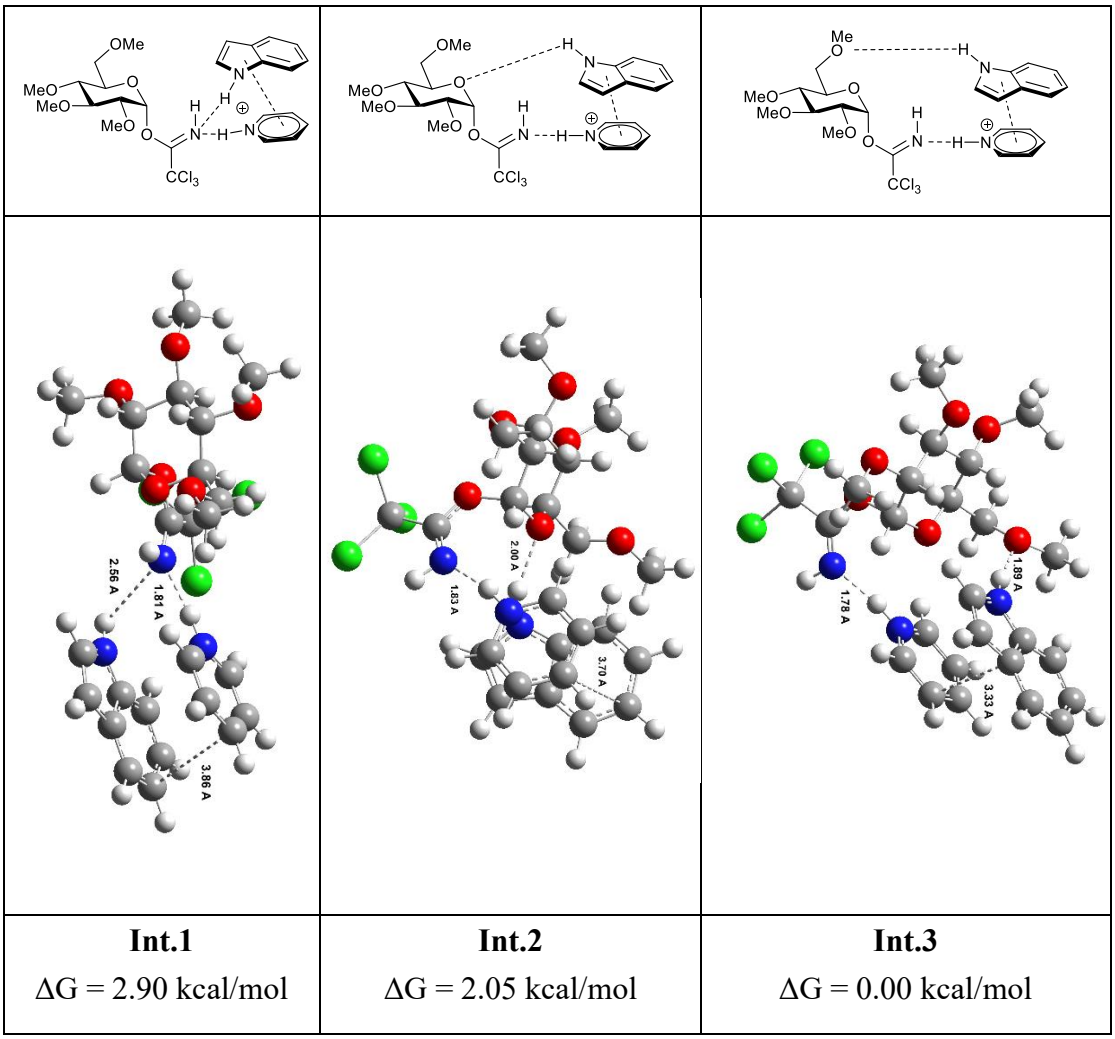
Procedure for Boc- or Ts-protected indole: In a glove box filled with nitrogen, to an oven-dried 5 mL tube equipped with a stir bar was added glycosyl trichloroacetimidate **1a** (0.075 mmol, 1.5 equiv.), **2** (0.05 mmol, 1.0 equiv.), cat.**E** (20 mol%) and anhydrous CH_2Cl_2 (1mL). The reaction mixture was stirred at room temperature for 12 h. Then we find that the reaction did not proceed.

Procedure for Me-protected indole: In a glove box filled with nitrogen, to an oven-dried 5 mL tube equipped with a stir bar was added glycosyl trichloroacetimidate **1a** (0.2 mmol, 2.0 equiv.), **2** (0.1 mmol, 1.0 equiv.), cat.**E** (20 mol%) and anhydrous CH_2Cl_2 (1mL). The reaction mixture was stirred at room temperature for 12 h. The crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate as an eluent. Then we found that the substrate had poor stereoselectivity.

Based on the above experiments, we believe that the importance of the indole N-H and its nucleophilicity in the glycosylation process.

4.5 DFT calculations

All density functional theory (DFT) calculations were performed using Gaussian 16 package.[12] The geometries and frequency calculations were performed by the B3LYP[13] density functional with Grimme's dispersion correction (D3BJ) in conjunction with the 6-31+G(d,p) basis set in dichloromethane solution with the SMD continuum solvation models.[14] To obtain more accurate electronic energies, the single-point energy calculations were performed at the M062X/6-311+G(d,p) level with the optimized structures. Structures are generated using Gaussian View.



Int.1	**Int.2**	**Int.3**
ΔG = 2.90 kcal/mol	ΔG = 2.05 kcal/mol	ΔG = 0.00 kcal/mol

Scheme S2. Calculated structures of **Int.1**, **Int.2** and **Int.3**

Table S6. Summary of single point energy (E) and G for compounds

Entry	E (Hartree)	G (Hartree)
Int.1	-2968.2934405	-2967.8040185
Int.2	-2968.3016161	-2967.8053771
Int.3	-2968.3034922	-2967.8086402

Coordinates and total energies

Int.1

Thermal correction to Gibbs Free Energy = 0.489422

E (SP) = -2968.2934405 hartree

C	-4.51161100	-0.06266800	0.15542900
C	-3.75184200	-0.58069400	1.38106800
C	-2.24757800	-0.29245000	1.26407200
C	-2.59359600	1.51504200	-0.26744000
C	-4.11395100	1.37918400	-0.15897300
H	-1.70864100	-0.50828300	2.19019300
H	-4.09928600	-0.02250200	2.26391900
H	-4.26102400	-0.68898600	-0.71112400
H	-2.23841300	0.91872300	-1.11732000
H	-4.46420400	2.03185700	0.64818800
O	-1.97166500	1.03149000	0.94879200
C	-2.12947200	2.94009100	-0.47643900
H	-1.02747000	2.96357800	-0.47832800
H	-2.47423700	3.26748000	-1.46752600
O	-2.65276100	3.76578300	0.54374400
C	-2.31155500	5.12787200	0.35515800
H	-2.69630200	5.51351800	-0.60055100
H	-2.76333000	5.69277200	1.17402600
H	-1.22162100	5.28008300	0.37590200
O	-4.66180900	1.77666900	-1.40637500
O	-5.90961100	-0.08192000	0.39608300
O	-4.02430400	-1.95691900	1.51810900
C	-3.66031000	-2.51000400	2.77702600
H	-4.06694500	-3.52322800	2.80402700
H	-2.57126500	-2.56885800	2.90414300
H	-4.08505200	-1.92997500	3.60763600
C	-6.58373200	-1.21990800	-0.12921800
H	-6.23043600	-2.14869400	0.33075600
H	-7.64528300	-1.08626300	0.09490700
H	-6.45838500	-1.28849000	-1.21891700
C	-5.77597500	2.65534600	-1.29395800
H	-6.60455100	2.18304400	-0.75496800
H	-5.49806500	3.58746800	-0.78304200
H	-6.09545400	2.89116600	-2.31246700
O	-1.74265900	-1.21324200	0.24783100
C	-0.44471900	-1.18210200	-0.05442300
N	0.44708300	-0.34462300	0.28202500
C	-0.11524700	-2.37273500	-0.97622500

Cl	-0.99096800	-2.12943400	-2.53119800
Cl	-0.66520100	-3.89481900	-0.19739000
Cl	1.64128900	-2.49599400	-1.29926400
C	5.15633600	0.50248600	1.58685200
C	4.58821800	-0.71045000	1.09395600
C	5.24303600	-1.51626200	0.15640000
C	6.49055700	-1.09358800	-0.29200800
C	7.07156000	0.10171100	0.18027900
C	6.41811200	0.90063400	1.11154700
C	4.20038000	1.06675200	2.50025500
C	3.12187400	0.21534500	2.53115700
H	4.79498700	-2.43765400	-0.20301500
H	7.02690900	-1.69652000	-1.01837000
H	8.04656800	0.40024300	-0.19287500
H	6.87298300	1.82050800	1.46739500
H	2.70009000	-1.60186900	1.51547600
N	3.35152500	-0.85023000	1.68570500
H	2.19870600	0.27675200	3.08905800
H	4.30334200	1.98434500	3.06184500
C	2.73676600	2.17889500	-0.18080700
C	3.74958200	3.06931500	-0.49261900
C	4.70890900	2.69767300	-1.43488900
C	4.62475000	1.45138200	-2.05967600
C	3.59200100	0.59926600	-1.71681300
N	2.68623400	0.98259100	-0.79564100
H	5.51691300	3.37631700	-1.68463000
H	1.96065600	2.38013400	0.54448600
H	3.78833100	4.02942300	0.00619100
H	5.35501200	1.13542000	-2.79309000
H	3.45748900	-0.37989600	-2.15291400
H	1.92555900	0.33005800	-0.50530400
H	0.04901400	0.41265900	0.84140400

Int.2

Thermal correction to Gibbs Free Energy = 0.496239

E (SP) = -2968. 3016161 hartree

C	-3.11421	1.59046	0.75705
C	-2.15248	0.85251	1.68782
C	-1.06008	0.12809	0.8914
C	-1.24597	1.66579	-0.94932
C	-2.32329	2.46877	-0.21172
H	-0.30662	-0.29801	1.54771

H	-1.63843	1.59865	2.3121
H	-3.69336	0.8596	0.17803
H	-1.73381	0.93596	-1.60527
H	-1.83657	3.27219	0.35287
O	-0.39423	0.95423	-0.00905
C	-0.3482	2.54039	-1.79925
H	0.42516	1.92525	-2.28141
H	-0.96662	2.98658	-2.59004
O	0.23786	3.5434	-0.98913
C	1.04505	4.4331	-1.74509
H	0.45535	4.95046	-2.51552
H	1.45076	5.1717	-1.04986
H	1.87752	3.90758	-2.23319
O	-3.1811	2.99956	-1.20988
O	-3.97906	2.43339	1.50143
O	-2.88556	-0.04897	2.48792
C	-2.19561	-0.49494	3.64982
H	-2.9051	-1.09163	4.22681
H	-1.32998	-1.12465	3.40336
H	-1.85527	0.35091	4.26272
C	-5.26064	1.87306	1.76594
H	-5.18836	0.96557	2.37456
H	-5.82721	2.63119	2.31288
H	-5.79243	1.63847	0.83322
C	-3.53747	4.36275	-1.00618
H	-4.07998	4.49758	-0.0644
H	-2.65046	5.01121	-1.00778
H	-4.18437	4.64615	-1.84048
O	-1.72233	-0.95121	0.18049
C	-1.06356	-2.07957	-0.06588
N	0.11189	-2.34631	0.32504
C	-1.97958	-3.00032	-0.9107
Cl	-2.35409	-2.15678	-2.45536
Cl	-3.49246	-3.31283	0.00177
Cl	-1.17983	-4.56208	-1.28002
C	4.29034	0.00882	-1.21478
C	3.07461	0.66566	-0.86032
C	3.04594	1.91829	-0.23704
C	4.27069	2.51813	0.03859
C	5.48775	1.88485	-0.29044
C	5.50937	0.64187	-0.91462
C	3.92073	-1.24638	-1.8122
C	2.54667	-1.31131	-1.79581
H	2.10313	2.40029	-0.00028

H	4.29011	3.49276	0.51707
H	6.42406	2.38303	-0.05694
H	6.45305	0.16639	-1.16632
H	1.06561	0.0207	-1.00437
N	2.03742	-0.16474	-1.22492
H	1.88	-2.08601	-2.14642
H	4.58903	-1.99786	-2.20846
C	2.65312	-0.19402	2.21554
C	3.9135	0.18428	2.64011
C	4.998	-0.65079	2.36297
C	4.79414	-1.85293	1.68415
C	3.51378	-2.18871	1.28155
N	2.49008	-1.3581	1.55893
H	5.99646	-0.36584	2.67523
H	1.76336	0.40132	2.37132
H	4.04208	1.12474	3.15975
H	5.6169	-2.51788	1.4539
H	3.26799	-3.09301	0.74239
H	1.5469	-1.61487	1.20233
H	0.41371	-3.27606	0.03868

Int.3

Thermal correction to Gibbs Free Energy = 0.494852

E (SP) = -2968.3034922 hartree

C	-1.82698	2.54878	0.46079
C	-1.39423	1.47035	1.45619
C	-1.08809	0.14559	0.73966
C	-0.61427	1.24381	-1.32839
C	-0.83497	2.62377	-0.69875
H	-0.65386	-0.5976	1.40945
H	-0.45499	1.79897	1.92567
H	-2.81726	2.29488	0.06017
H	-1.55076	0.90549	-1.78799
H	0.12556	2.99249	-0.3204
O	-0.20496	0.28705	-0.32351
C	0.44934	1.25939	-2.40363
H	0.58776	0.25016	-2.81402
H	0.1034	1.91579	-3.21111
O	1.66676	1.75081	-1.85861
C	2.64913	2.00663	-2.85574
H	2.27928	2.73582	-3.58808
H	3.52302	2.41963	-2.34926

H	2.93273	1.08701	-3.38612
O	-1.33293	3.4708	-1.72262
O	-1.85517	3.82081	1.08889
O	-2.40714	1.32291	2.42626
C	-1.99931	0.63871	3.60458
H	-2.81843	0.73039	4.32102
H	-1.81424	-0.42843	3.42285
H	-1.09381	1.08782	4.03531
C	-3.14554	4.23587	1.52304
H	-3.55358	3.56187	2.28349
H	-3.02568	5.23439	1.95133
H	-3.8487	4.29434	0.68048
C	-0.73343	4.76209	-1.7501
H	-0.90408	5.30157	-0.81255
H	0.34766	4.69612	-1.93641
H	-1.20159	5.30856	-2.57286
O	-2.37579	-0.35586	0.28681
C	-2.48845	-1.6453	-0.00967
N	-1.5276	-2.47144	-0.02607
C	-3.97842	-1.95455	-0.29742
Cl	-4.54753	-0.88299	-1.62416
Cl	-4.922	-1.63156	1.1973
Cl	-4.21139	-3.66299	-0.78608
C	4.69626	-0.08959	1.72805
C	4.28944	0.28926	0.41242
C	5.17902	0.28697	-0.66931
C	6.49012	-0.10691	-0.42571
C	6.91049	-0.49677	0.86476
C	6.02909	-0.49015	1.93879
C	3.53434	0.01778	2.56462
C	2.50011	0.43106	1.75809
H	4.85429	0.57026	-1.6644
H	7.20368	-0.11839	-1.24426
H	7.94149	-0.80198	1.01699
H	6.3621	-0.78951	2.92877
H	2.38198	0.91782	-0.32074
N	2.94603	0.58795	0.46324
H	1.47273	0.6428	2.00957
H	3.47528	-0.18645	3.62457
C	2.10815	-2.72027	0.70218
C	3.45471	-2.89141	0.43062
C	3.90691	-2.717	-0.8776
C	3.0044	-2.37453	-1.88736
C	1.66888	-2.21918	-1.56458

N	1.26431	-2.3977	-0.29418
H	4.95928	-2.83689	-1.10604
H	1.67365	-2.83445	1.68637
H	4.13572	-3.14298	1.23228
H	3.32978	-2.22848	-2.90981
H	0.89828	-1.9628	-2.27919
H	0.24069	-2.30775	-0.09392
H	-1.82144	-3.42235	-0.24326

5. Proposed mechanism

Based on the above mechanistic studies, we propose the following possible mechanisms. The process begins with the catalyst **E** forming a complex (**E-2 complex**) with indole **2**. This complex subsequently interacts with the glycosyl donor **1** to generate an intermediate **1-E-2**. In this intermediate, the proton of N-H of pyridinium engages in a hydrogen bond with the lone pair electrons on the nitrogen of trichloroacetimidate, while the proton of N-H of indole potentially forms a hydrogen bond with the oxygen atom at the C6 position of the glycosyl donor. This arrangement facilitates an intramolecular-like S_N2 reaction, leading to the departure of trichloroacetamide and the deprotonation of the catalyst. As a result, intermediate **4** and pyridine are formed. Subsequently, the newly generated pyridine abstracts the proton from the C3 position of intermediate **4**, yielding the final product C-indolyl glycoside and regenerating the catalyst, thereby completing the catalytic cycle.

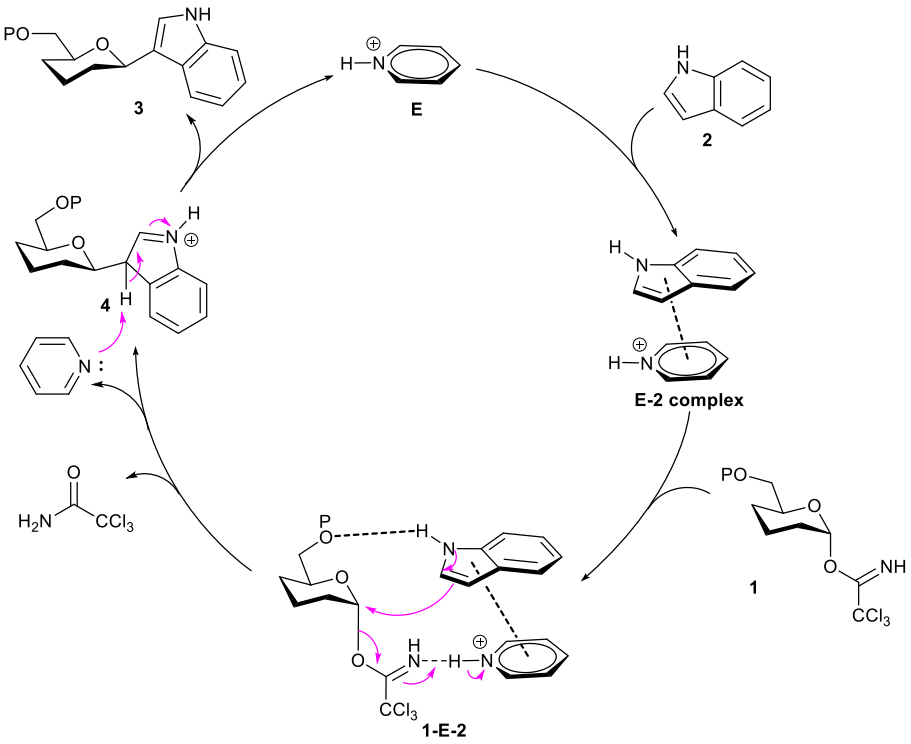


Figure S5. Proposed mechanism

6. Reference

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7. NMR spectra

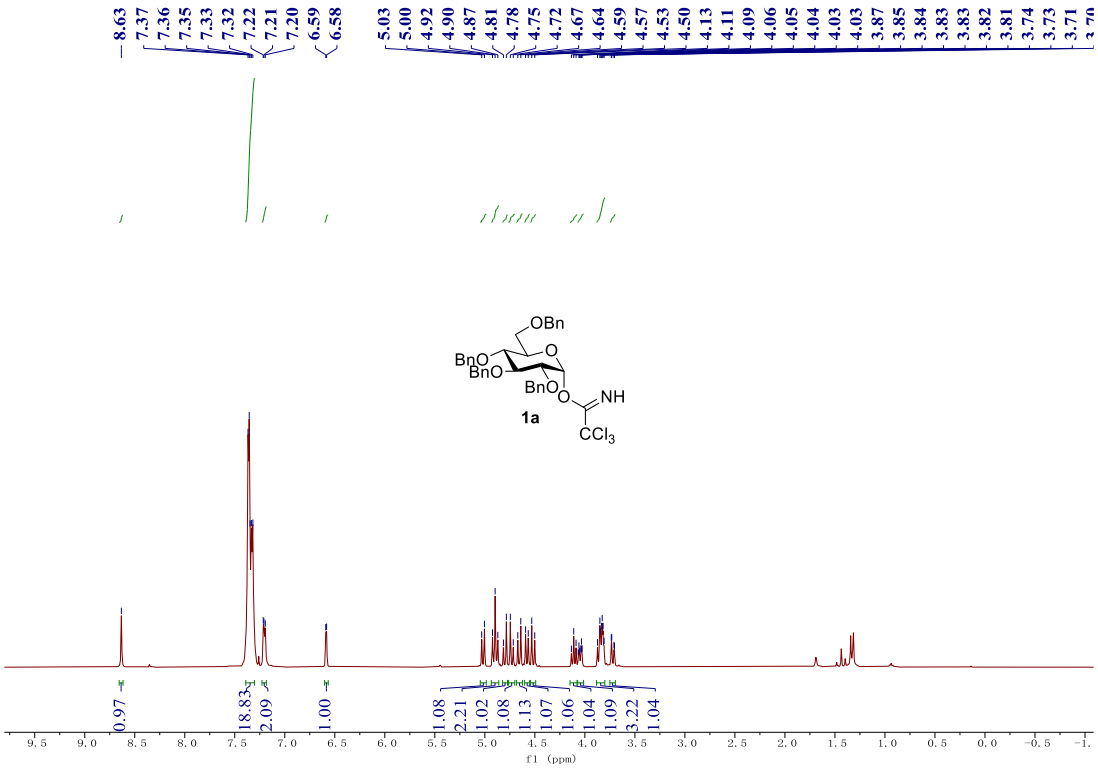

Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 1a

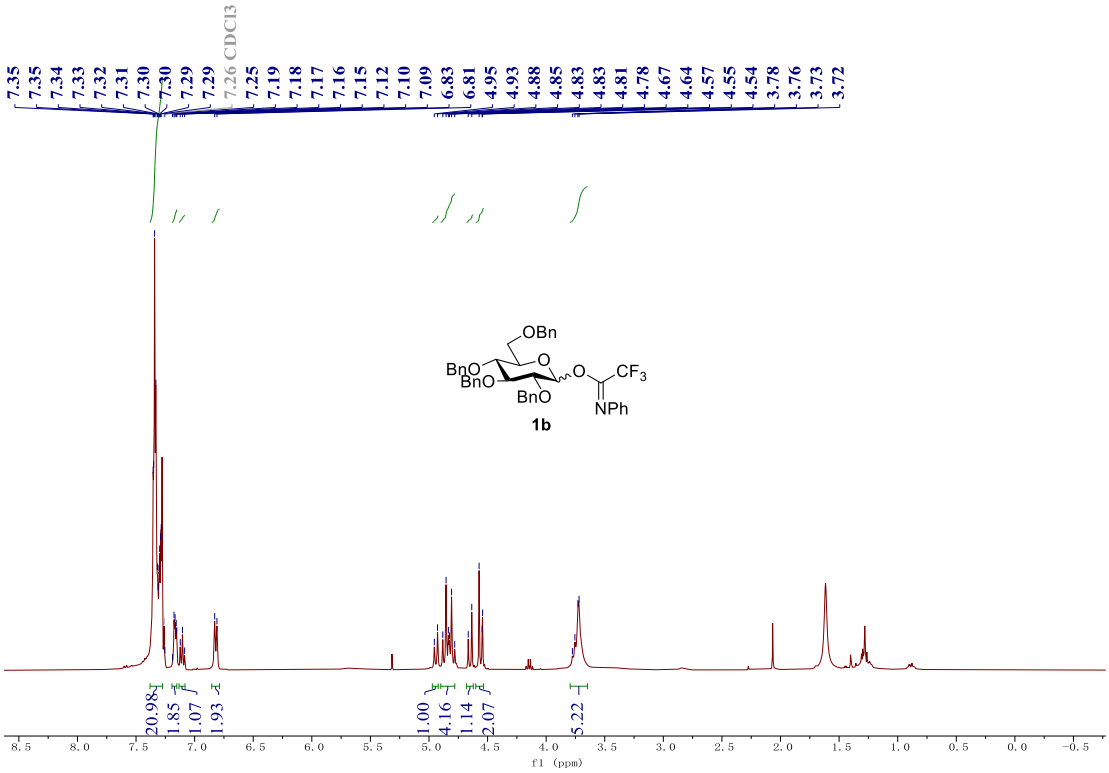

Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 1b

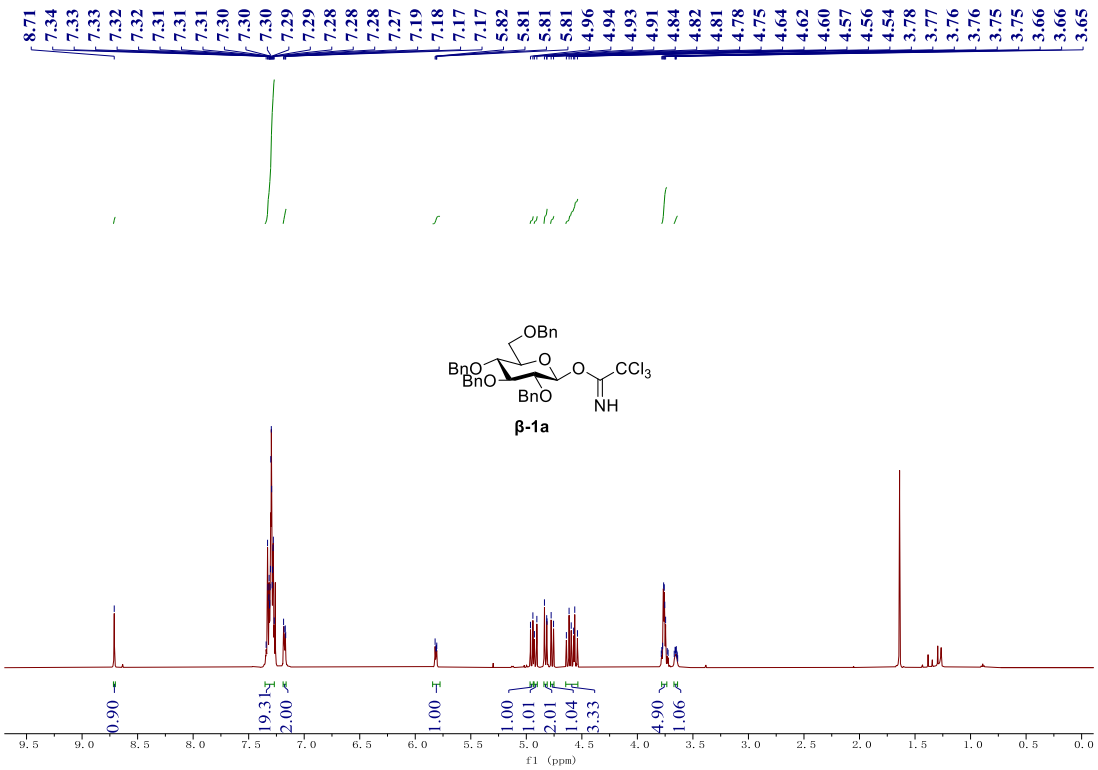

Figure S8. ^{1}H NMR (500 MHz, $CDCl_3$) Spectra for compound β-1a

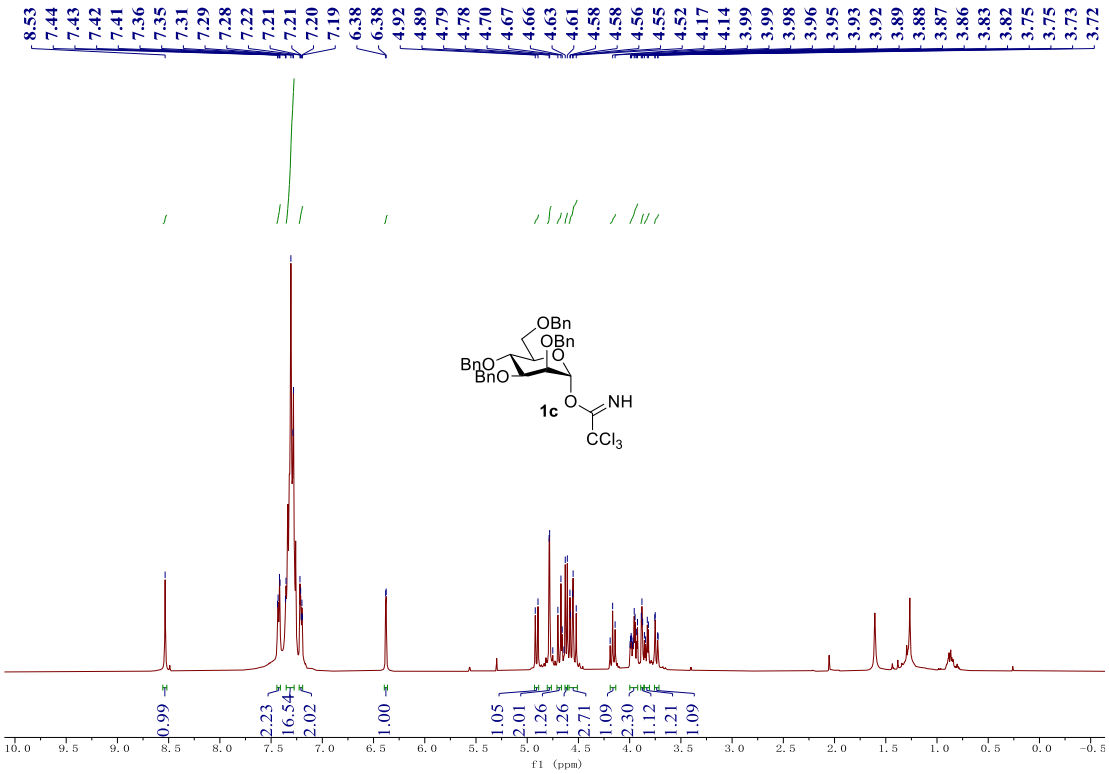

Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 1c

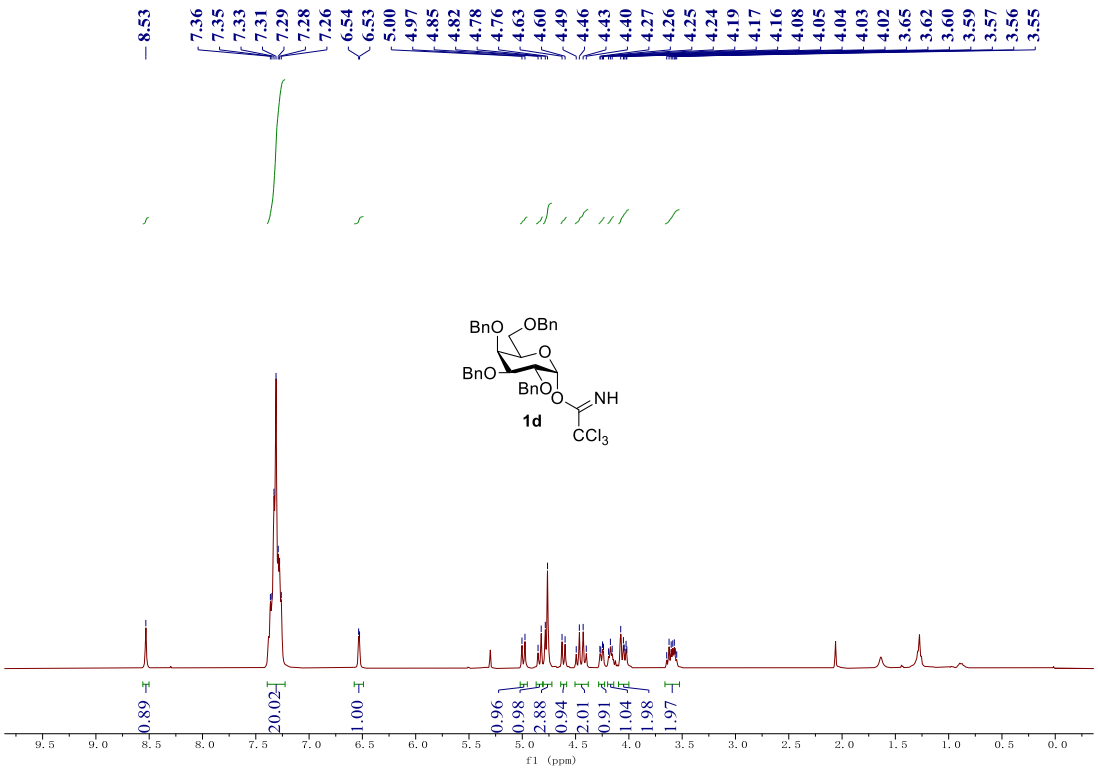

Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 1d

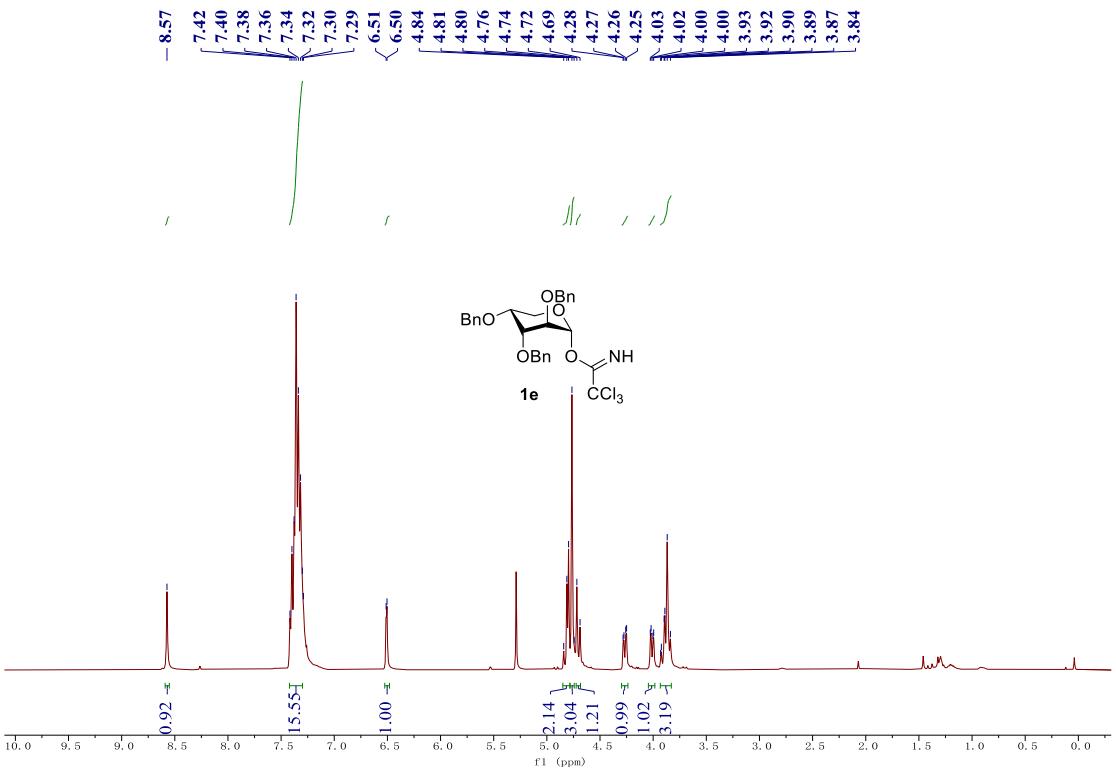

Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 1e

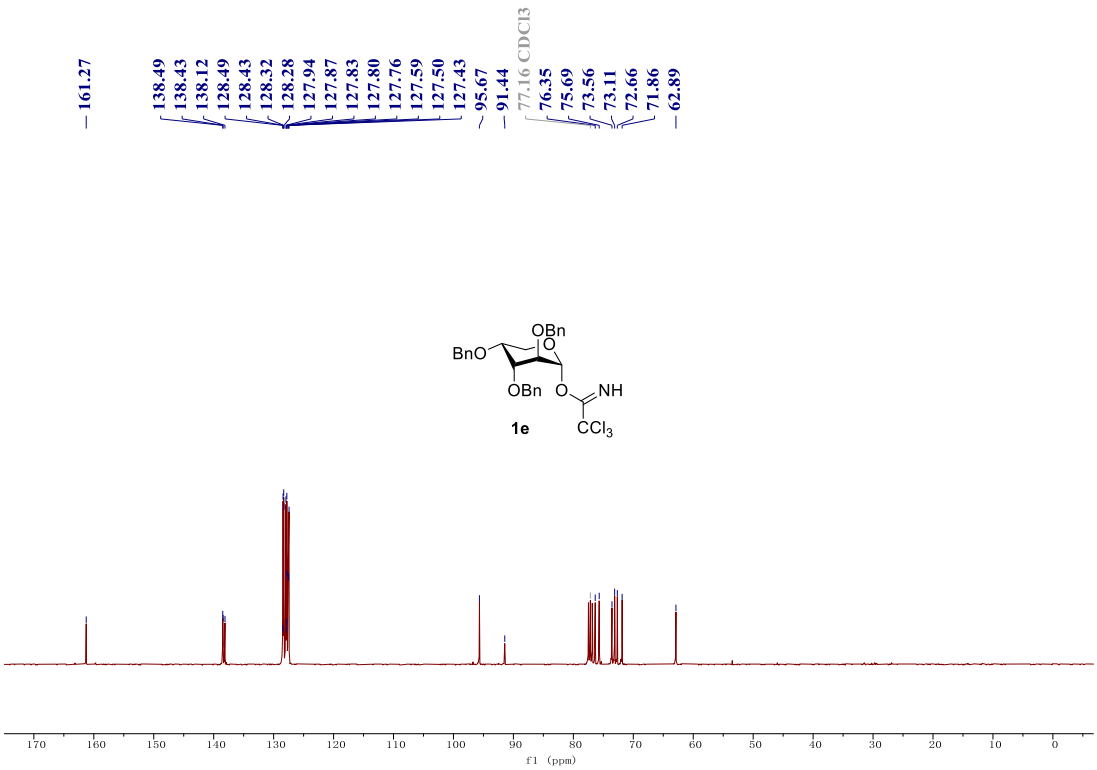

Figure S12. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound 1e

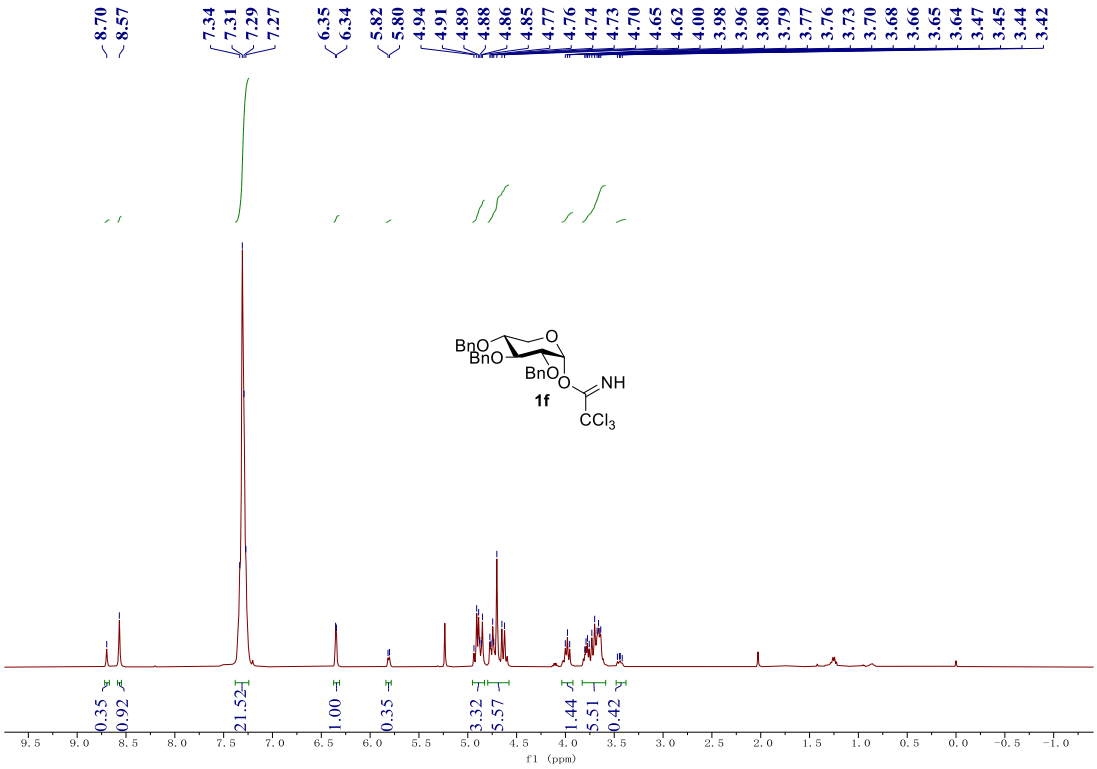

Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 1f

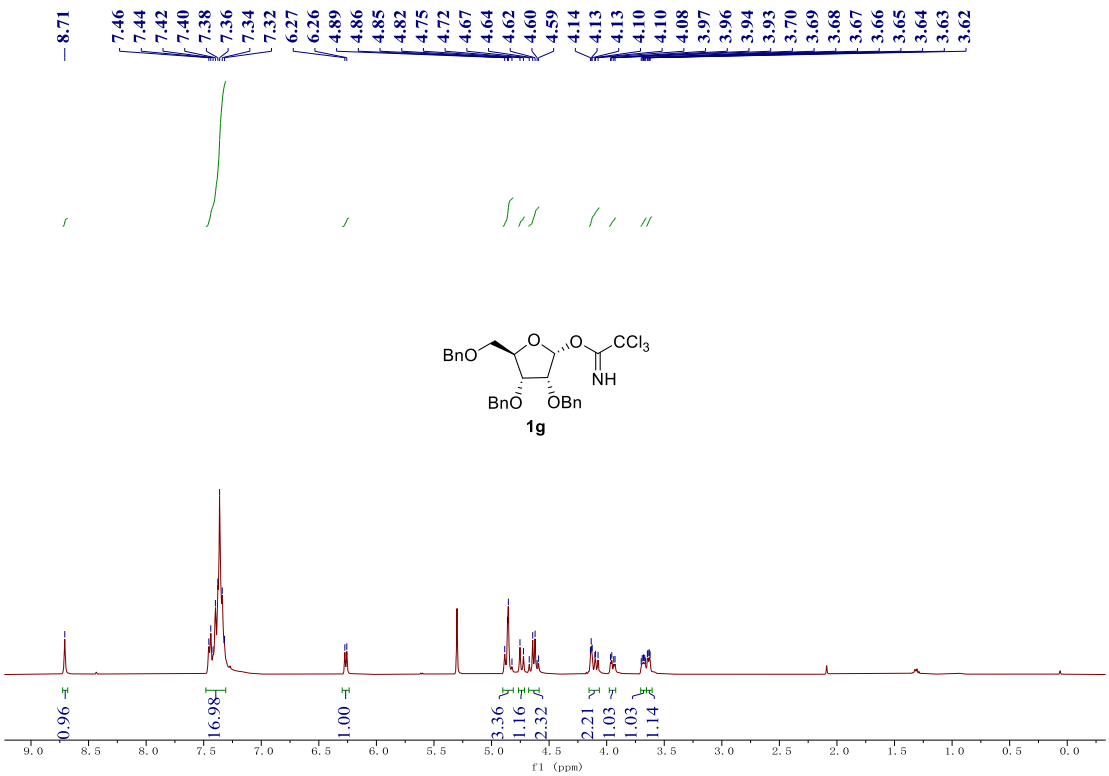

Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 1g

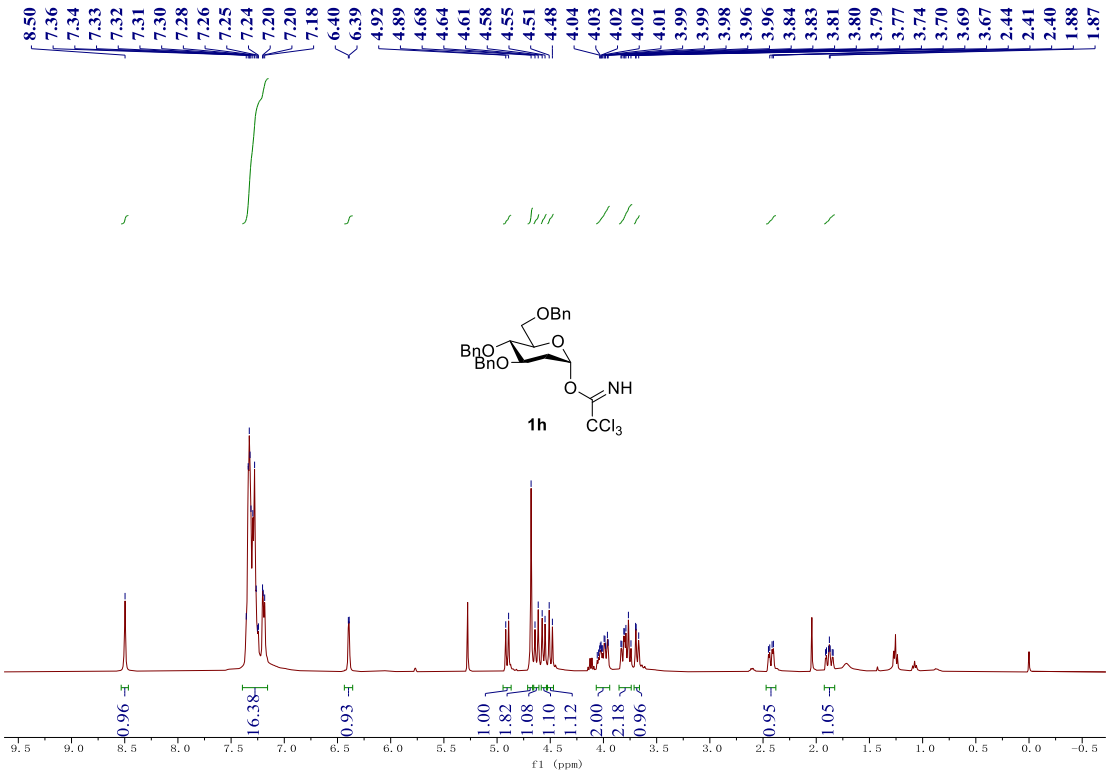

Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 1h

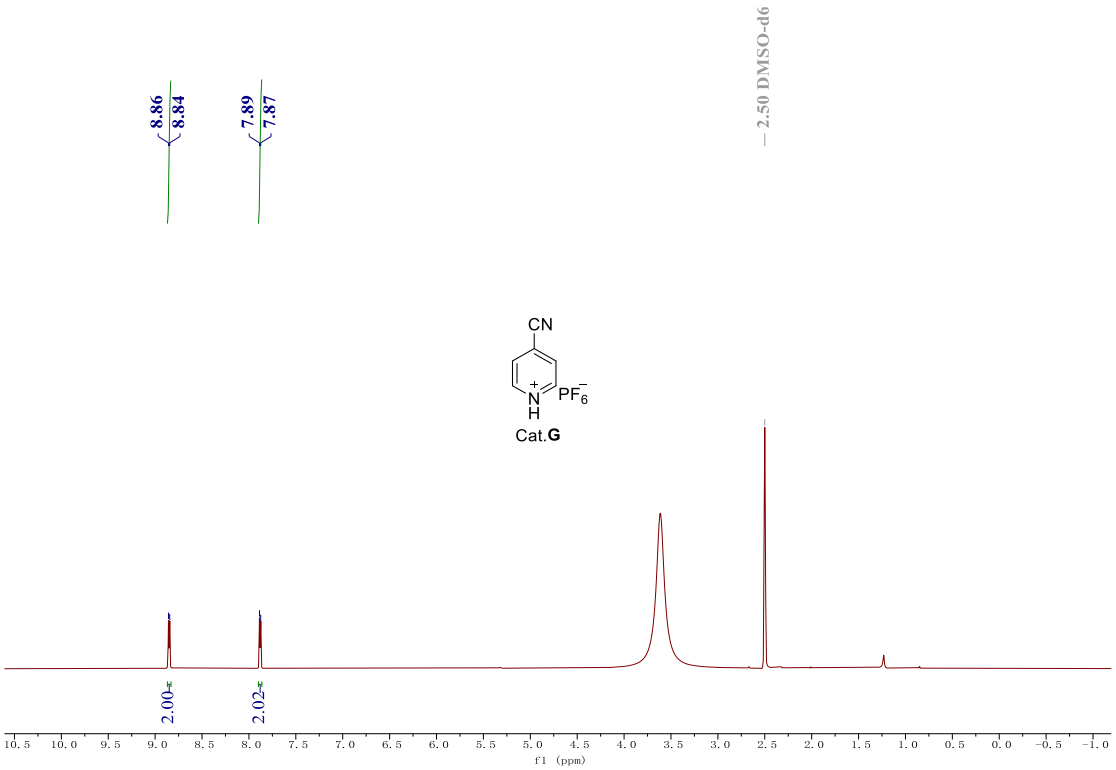

Figure S16. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) Spectra for compound Cat.G

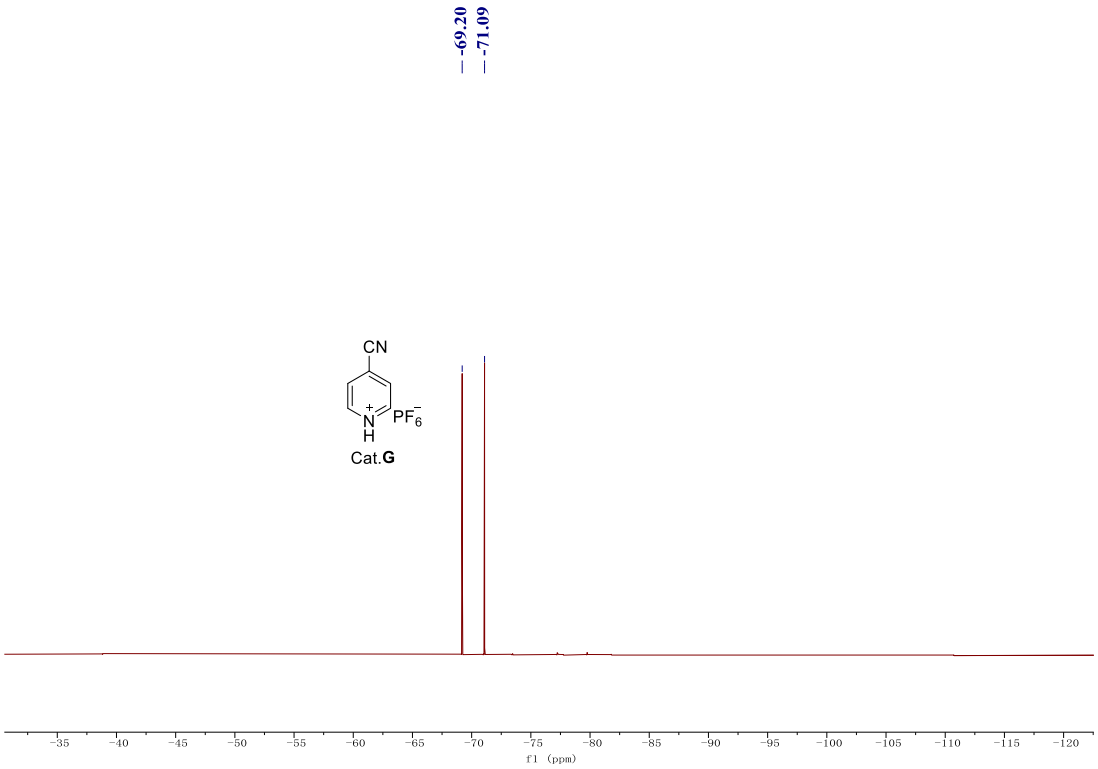

Figure S17. ^{19}F NMR (376 MHz, DMSO-*d*$_6$) Spectra for compound Cat.G

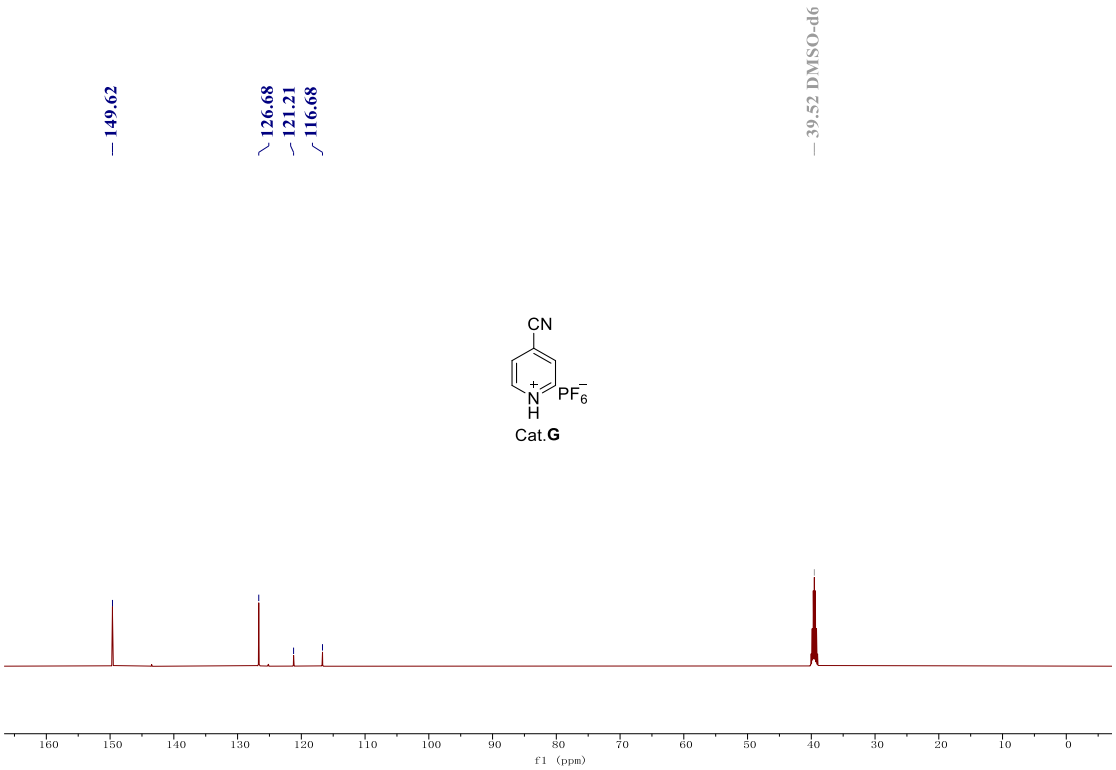

Figure S18. ^{13}C NMR (126 MHz, DMSO-*d*$_6$) Spectra for compound Cat.G

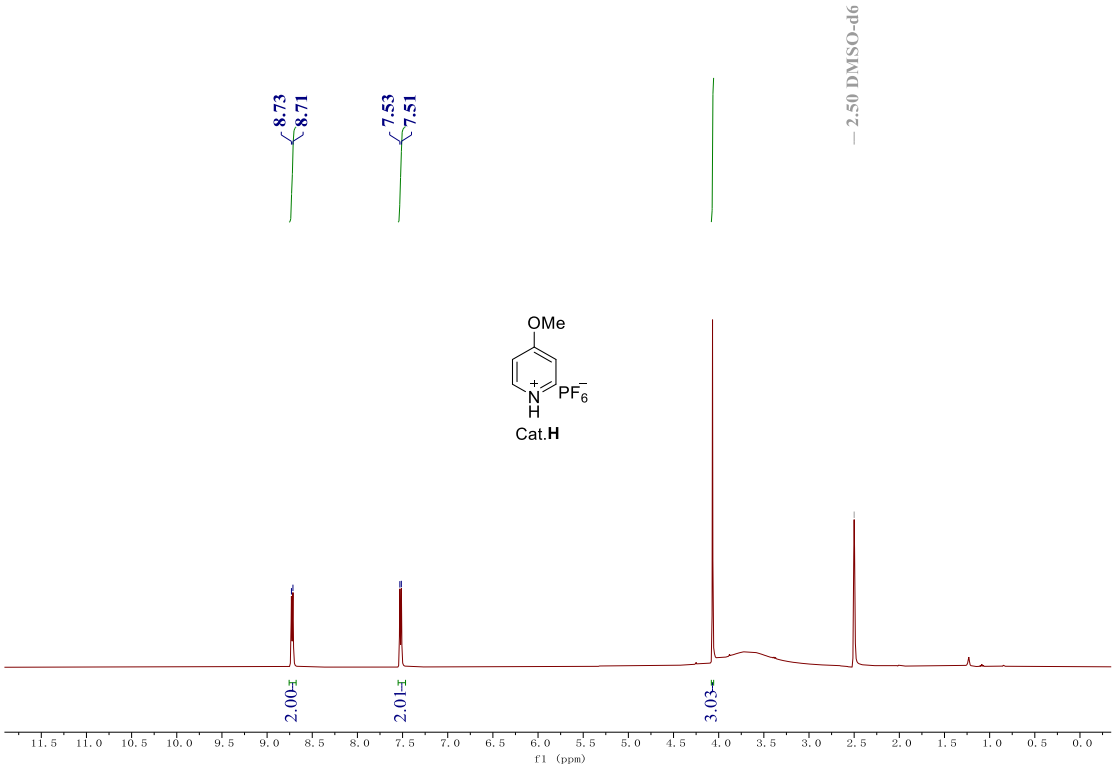

Figure S19. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) Spectra for compound Cat.H

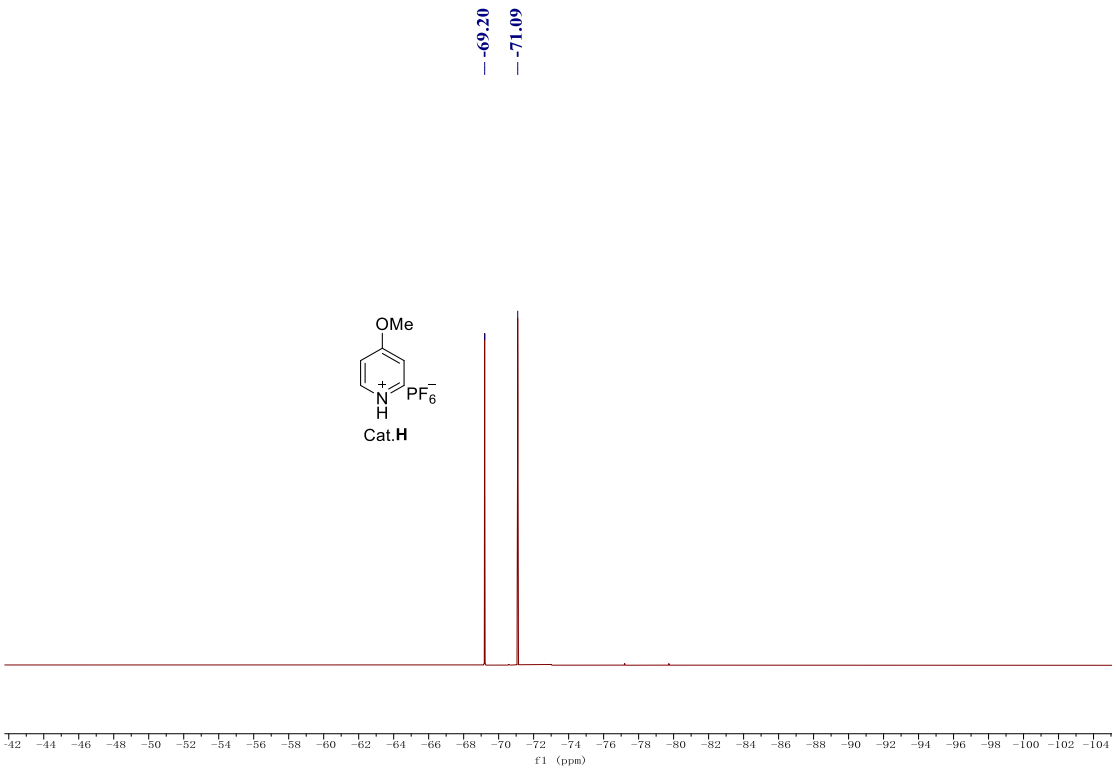

Figure S20. ^{19}F NMR (376 MHz, DMSO-*d*$_6$) Spectra for compound Cat.H

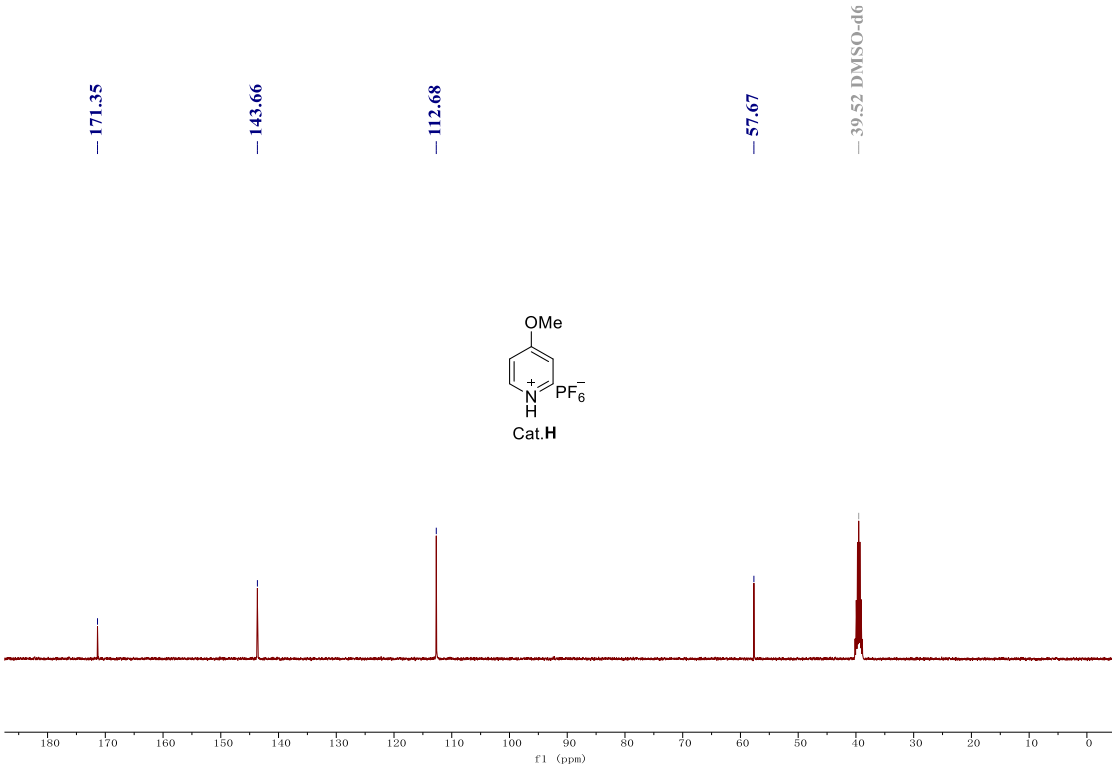

Figure S21. ^{13}C NMR (101 MHz, DMSO-*d*$_6$) Spectra for compound Cat.G

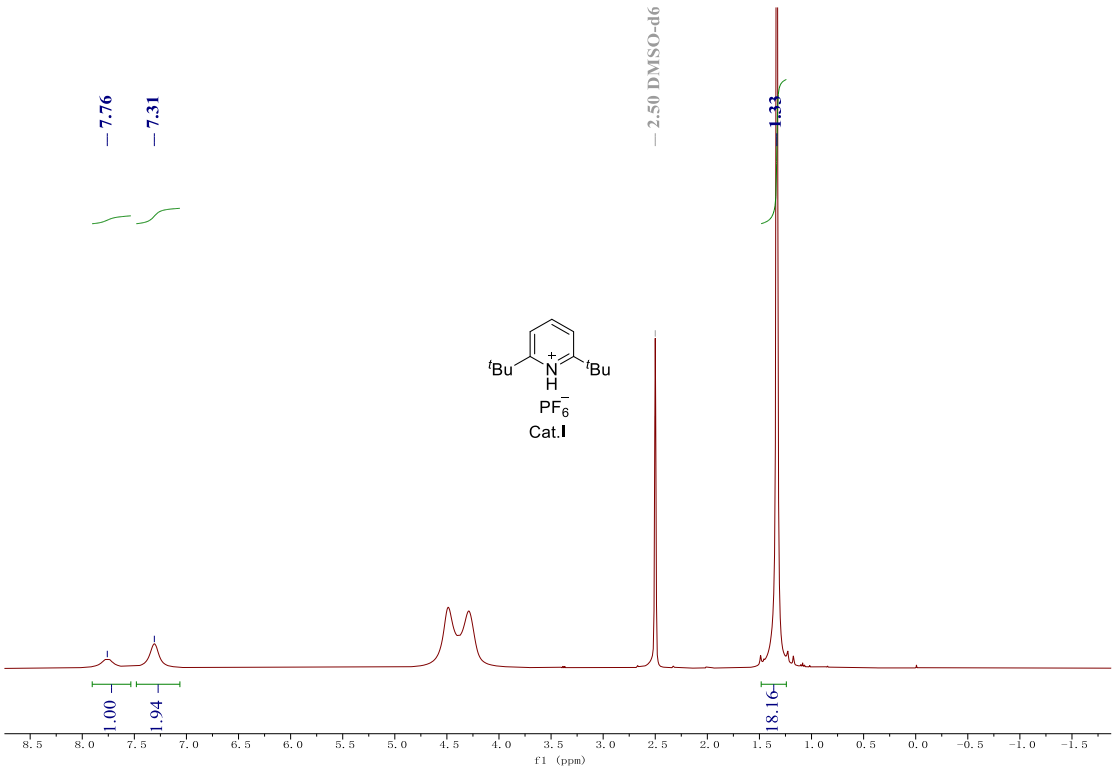

Figure S22. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) Spectra for compound Cat.I

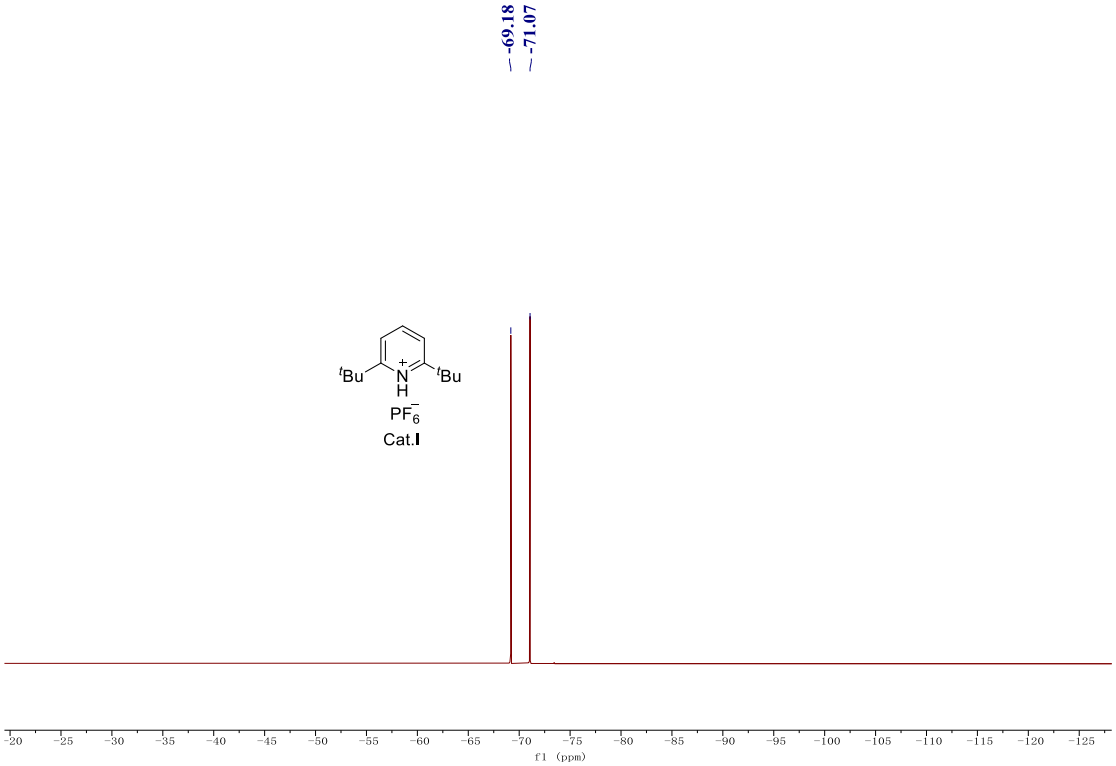

Figure S23. ^{19}F NMR (376 MHz, DMSO-*d*$_6$) Spectra for compound Cat.I

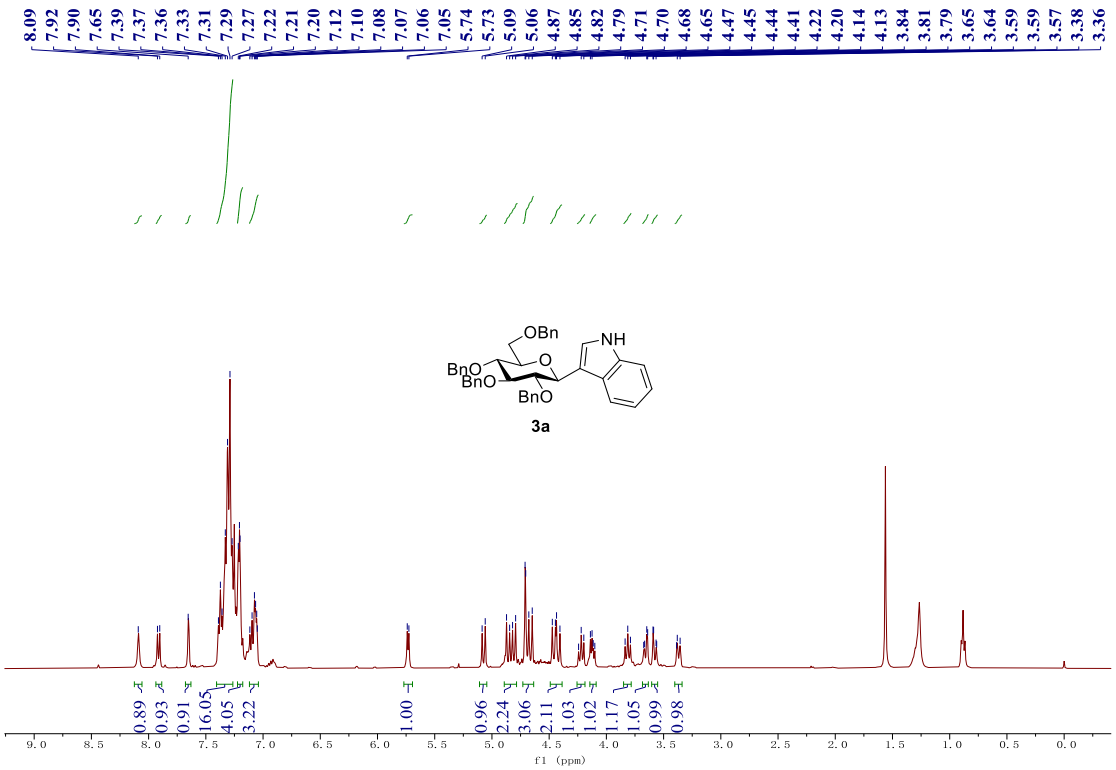

Figure S24. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 3a

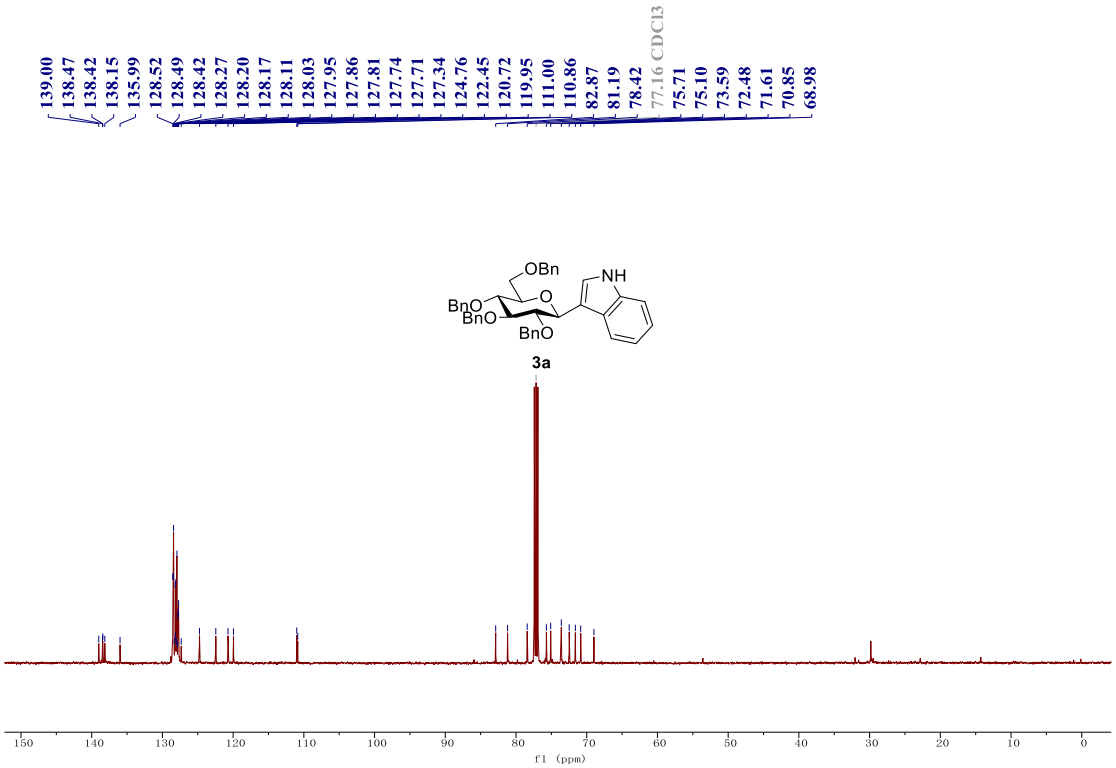

Figure S25. ^{13}C NMR (126 MHz, $CDCl_3$) Spectra for compound 3a

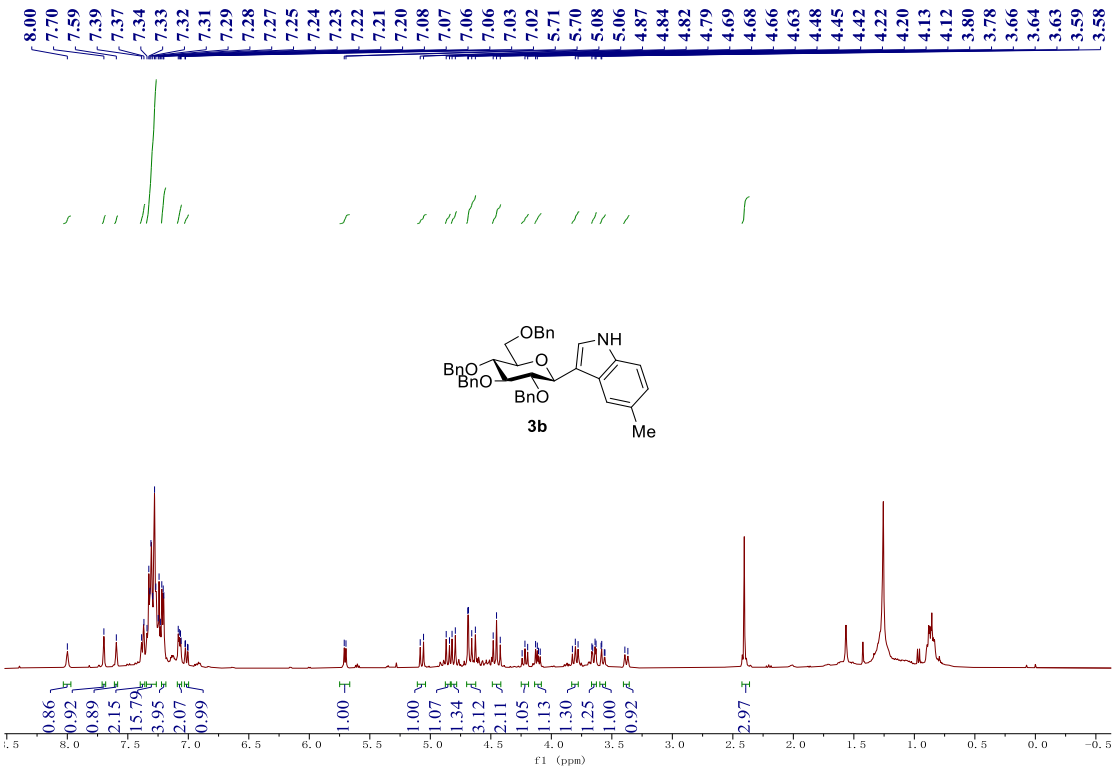

Figure S26. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 3b

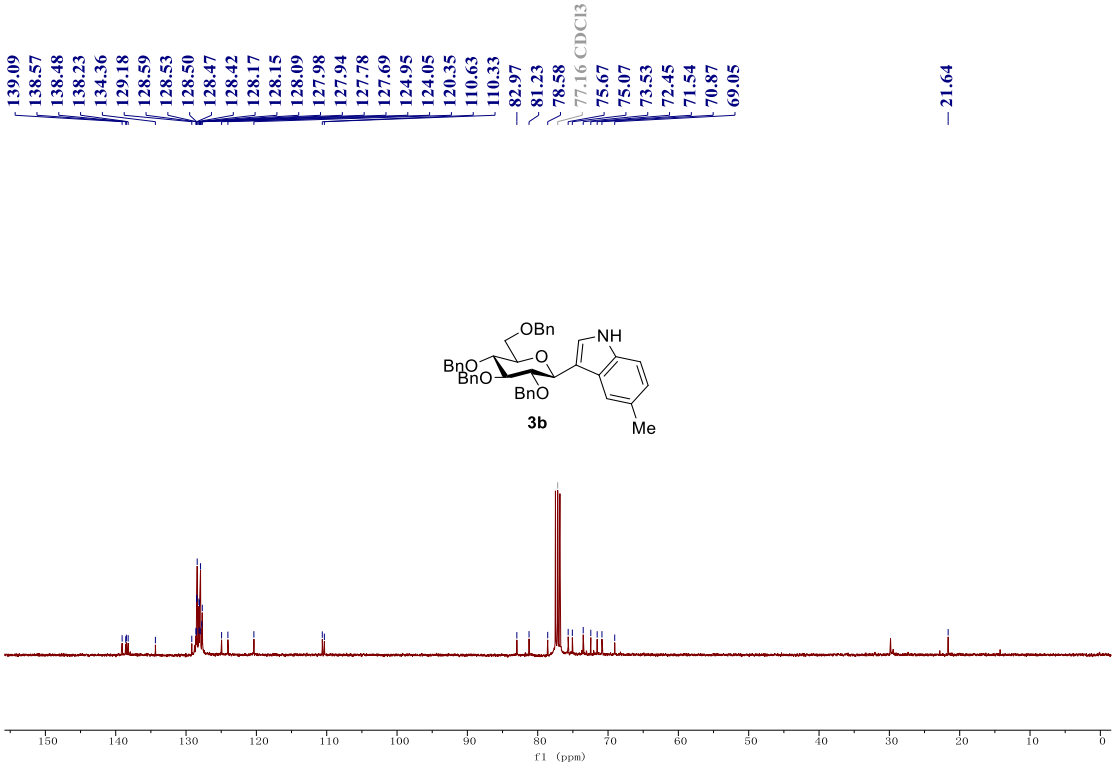

Figure S27. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound 3b

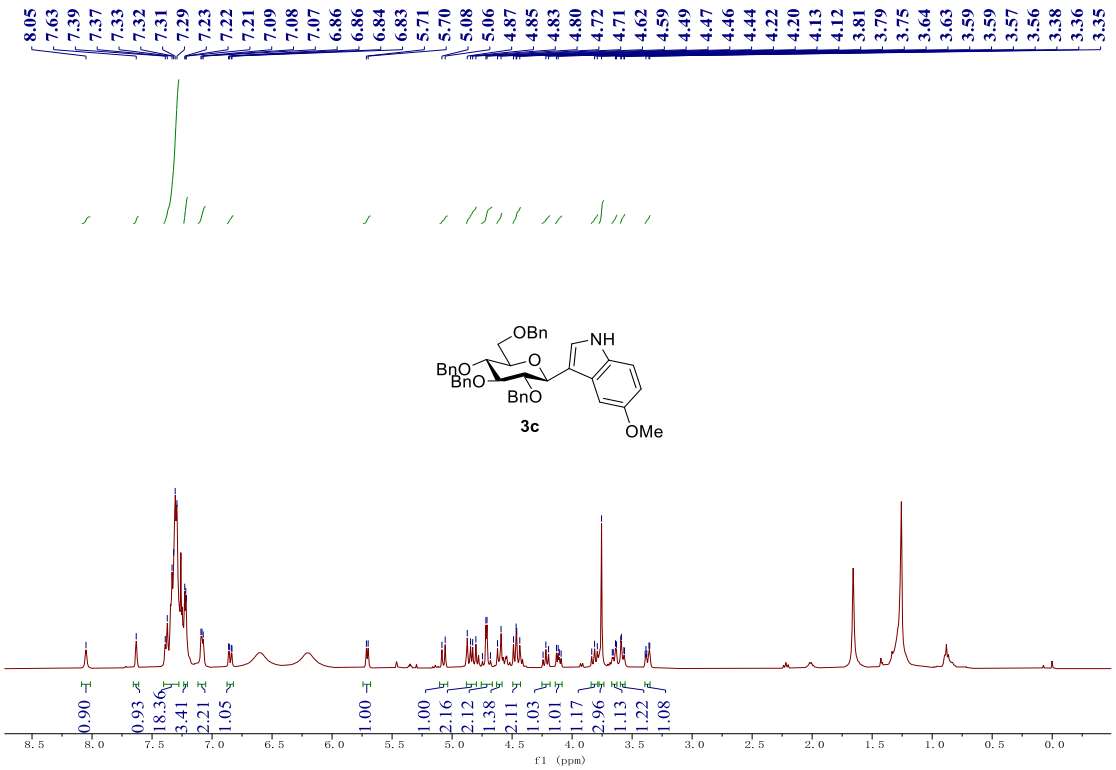

Figure S28. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 3c

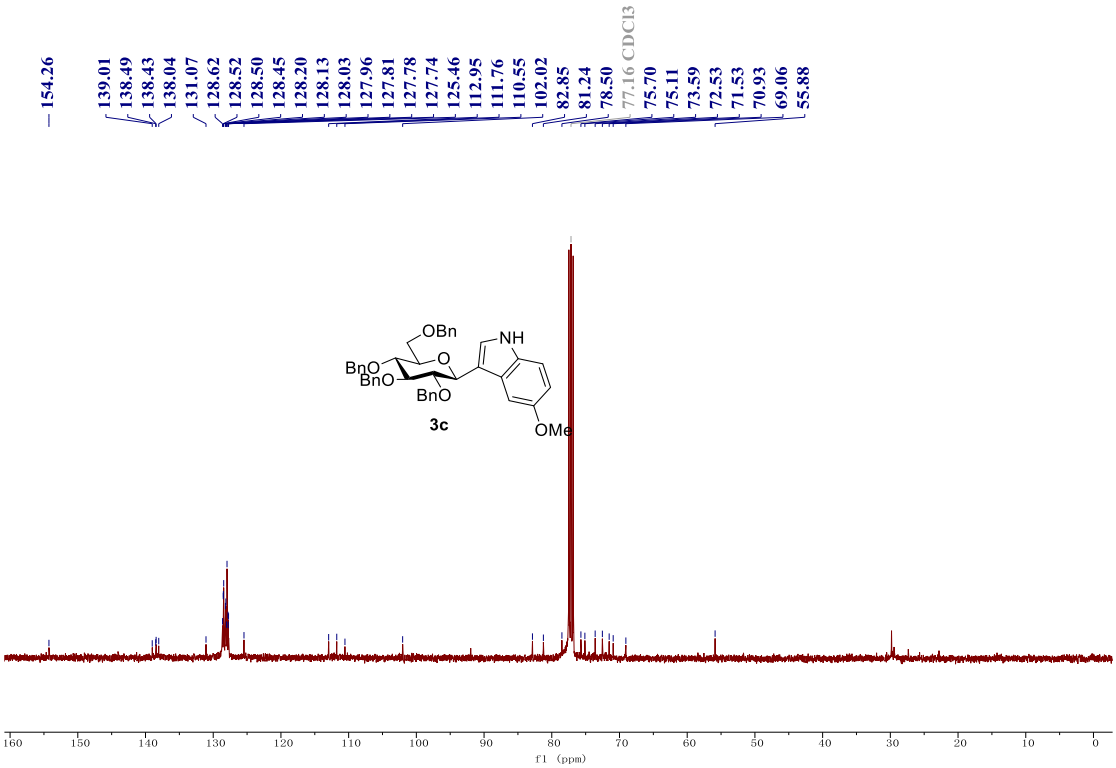

Figure S29. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound 3c

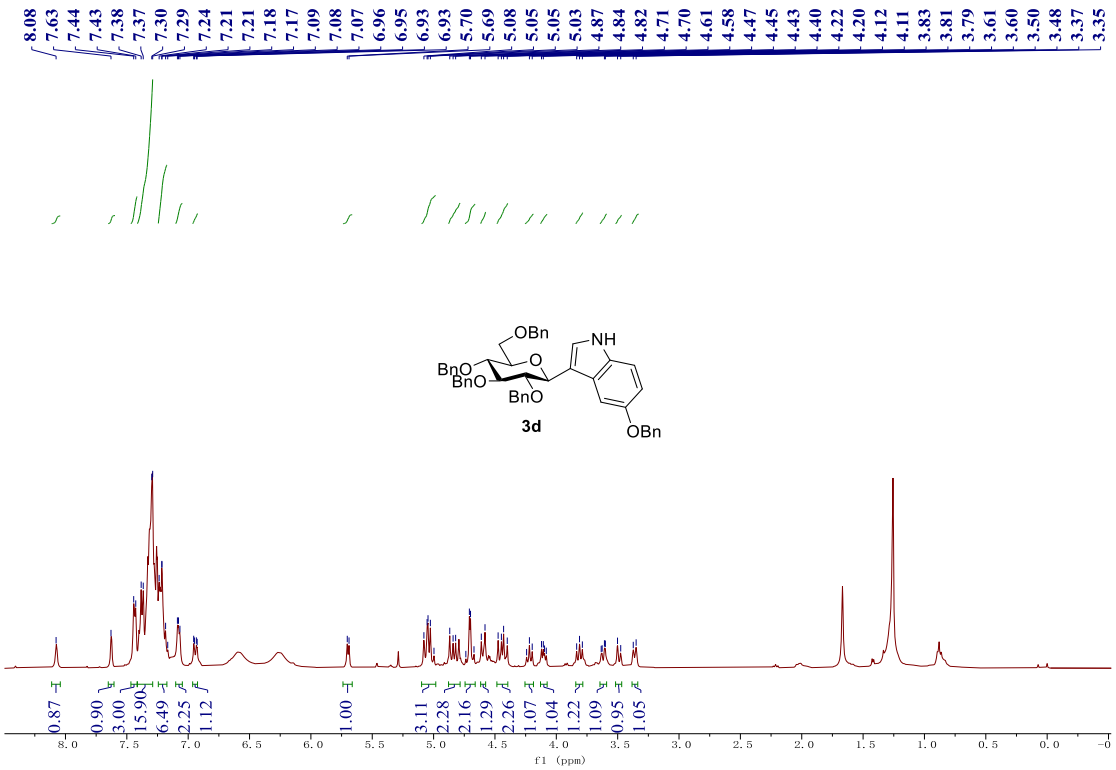

Figure S30. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 3d

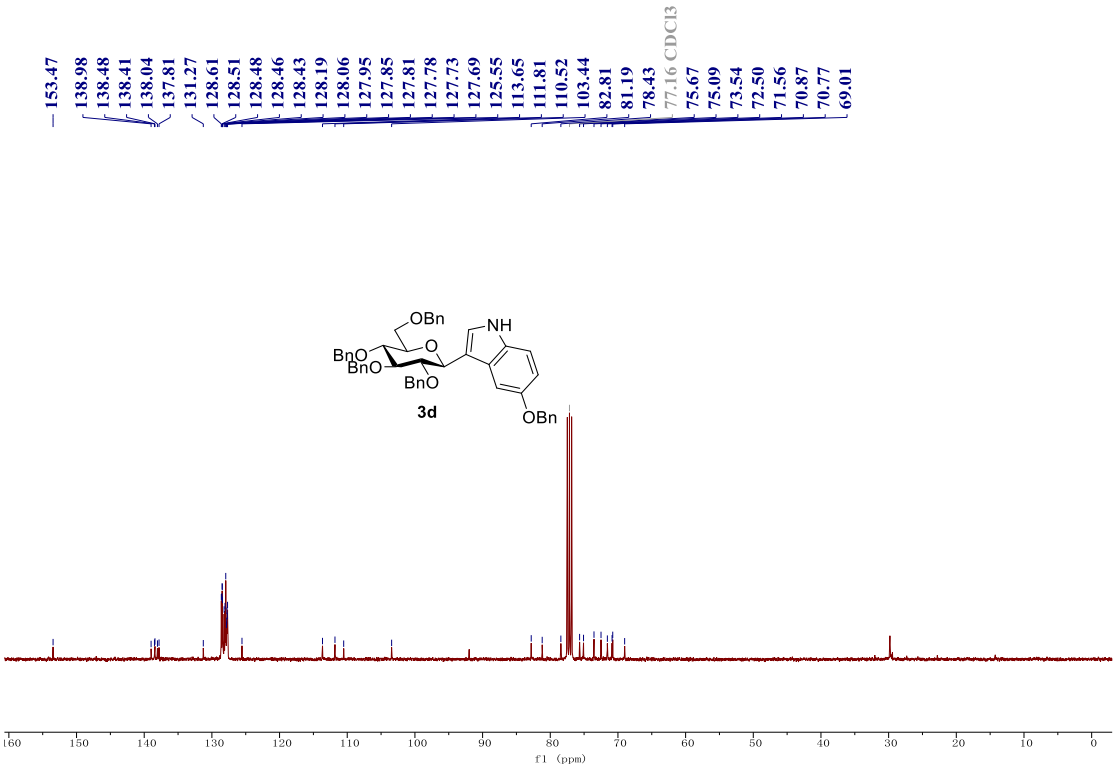

Figure S31. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound 3d

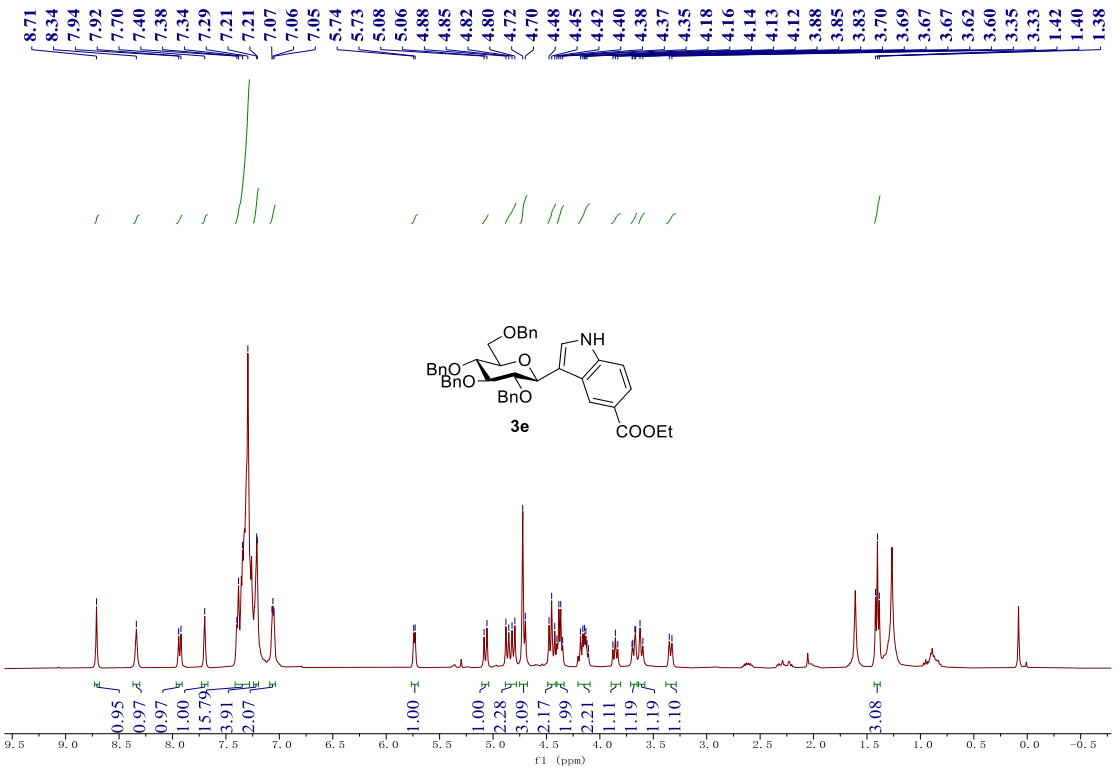

Figure S32. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 3e

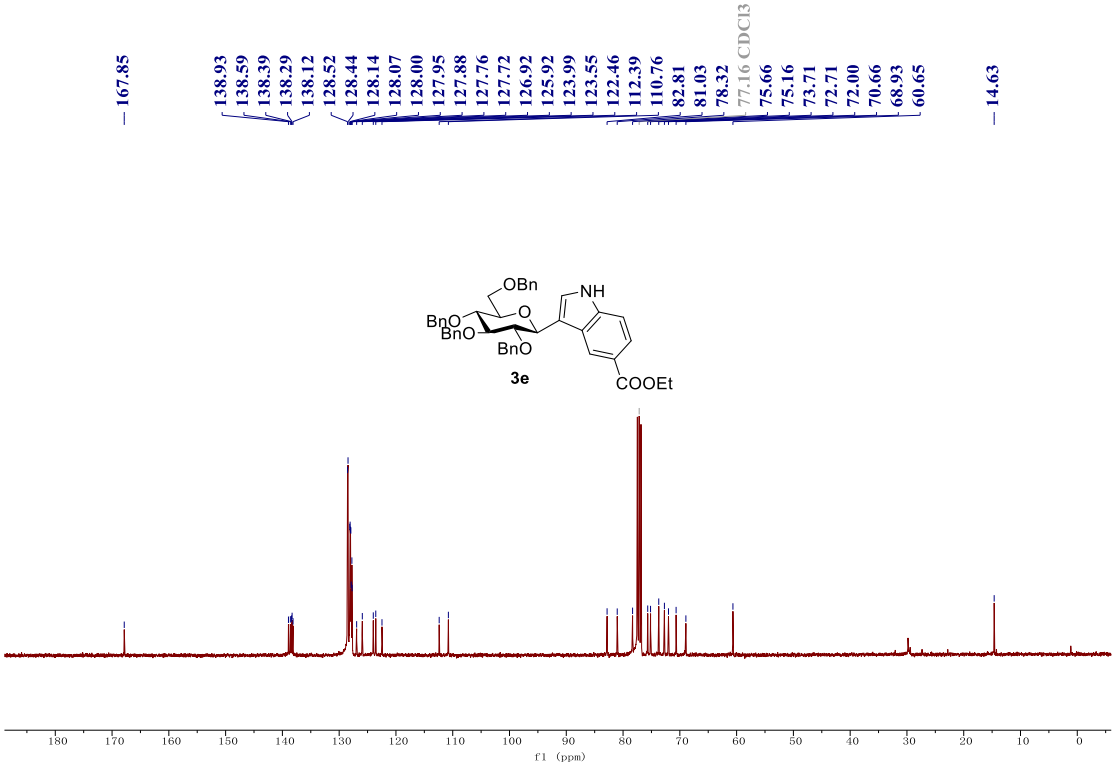

Figure S33. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound 3e

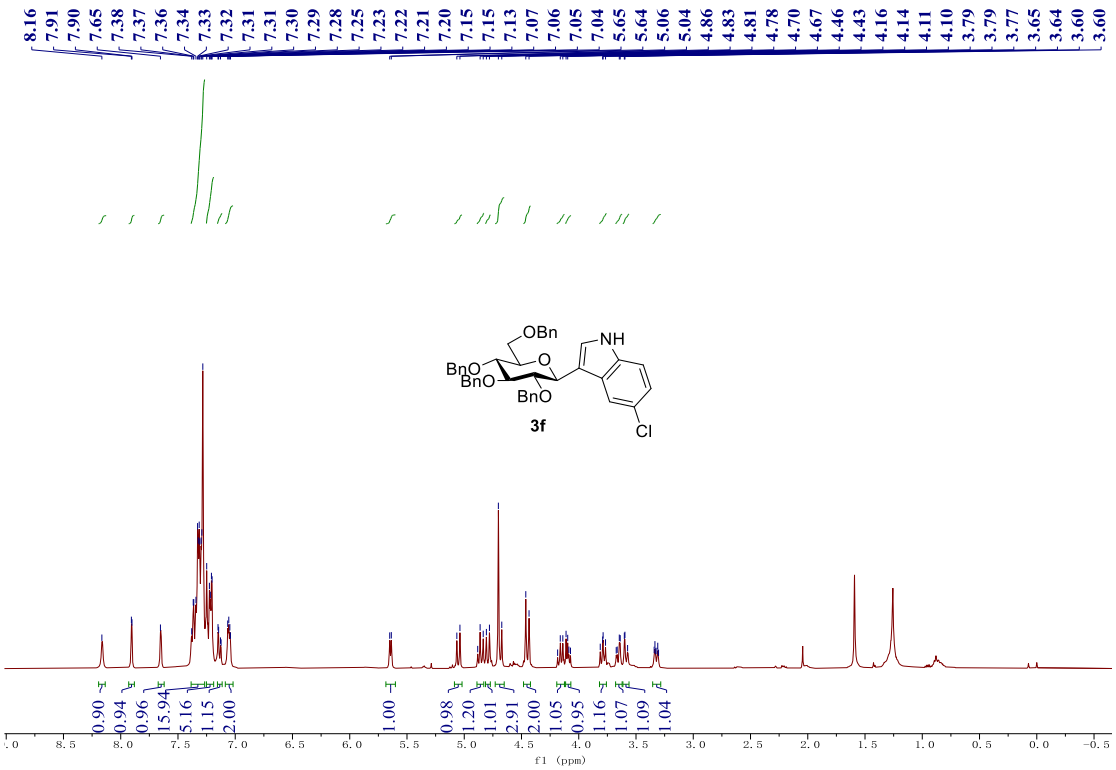

Figure S34. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 3f

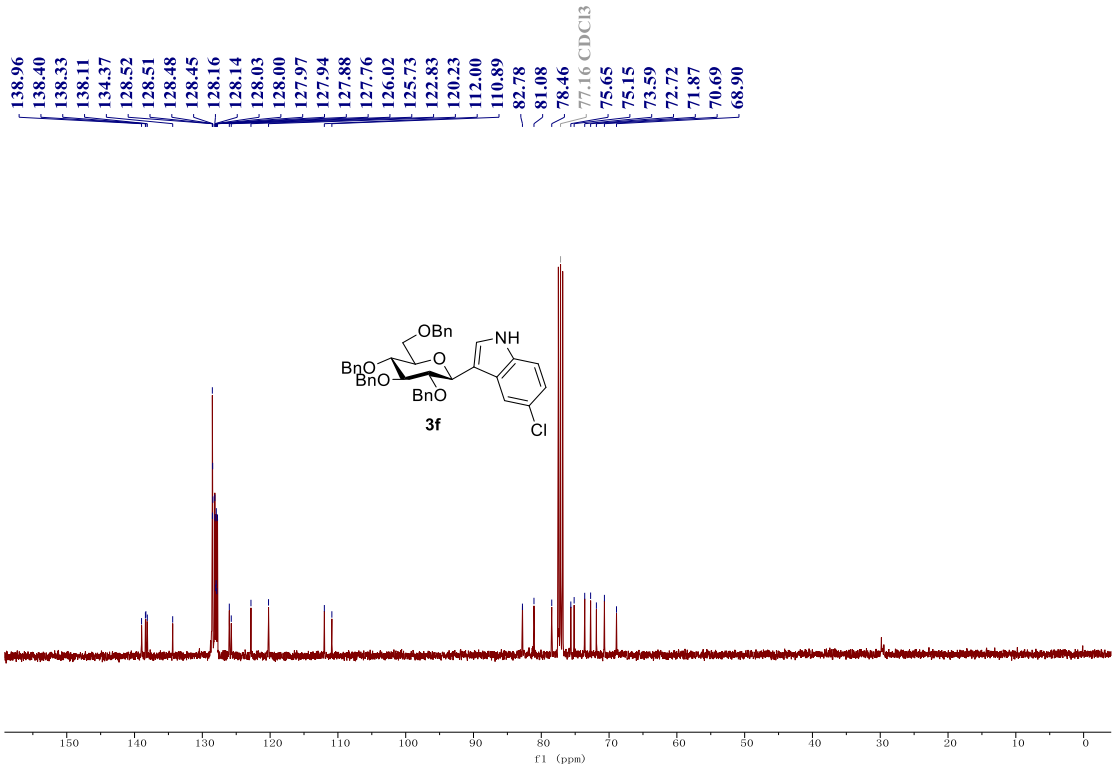

Figure S35. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound 3f

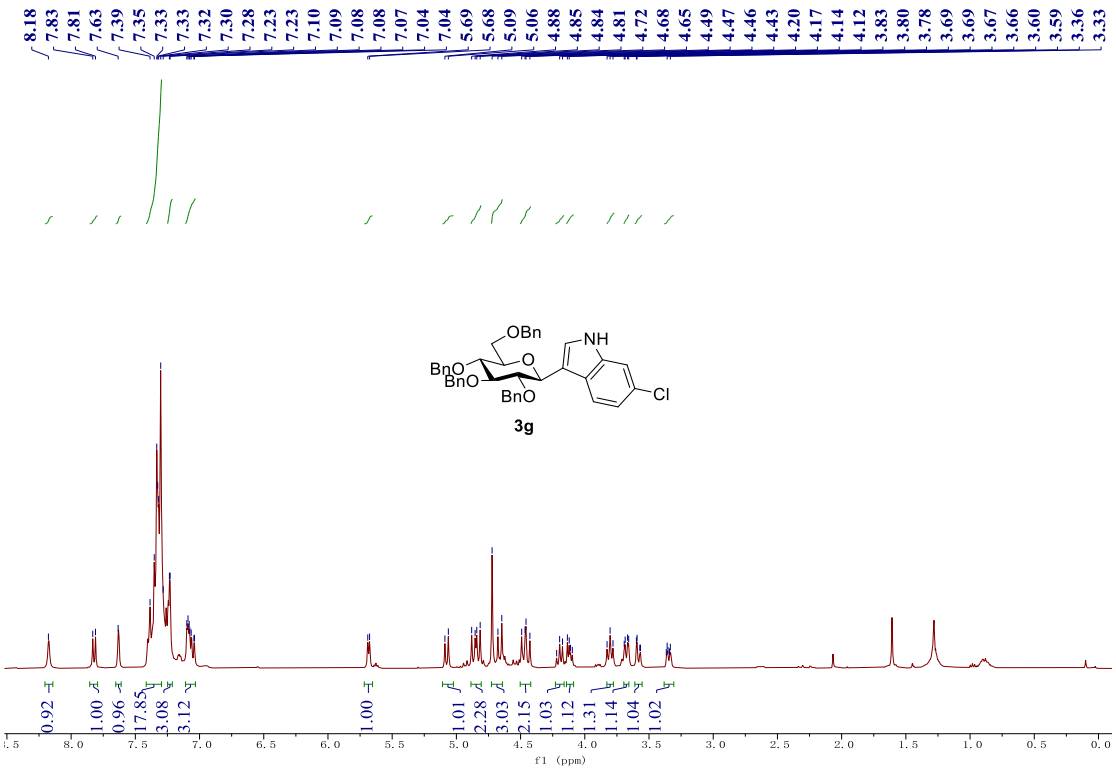

Figure S36. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 3g

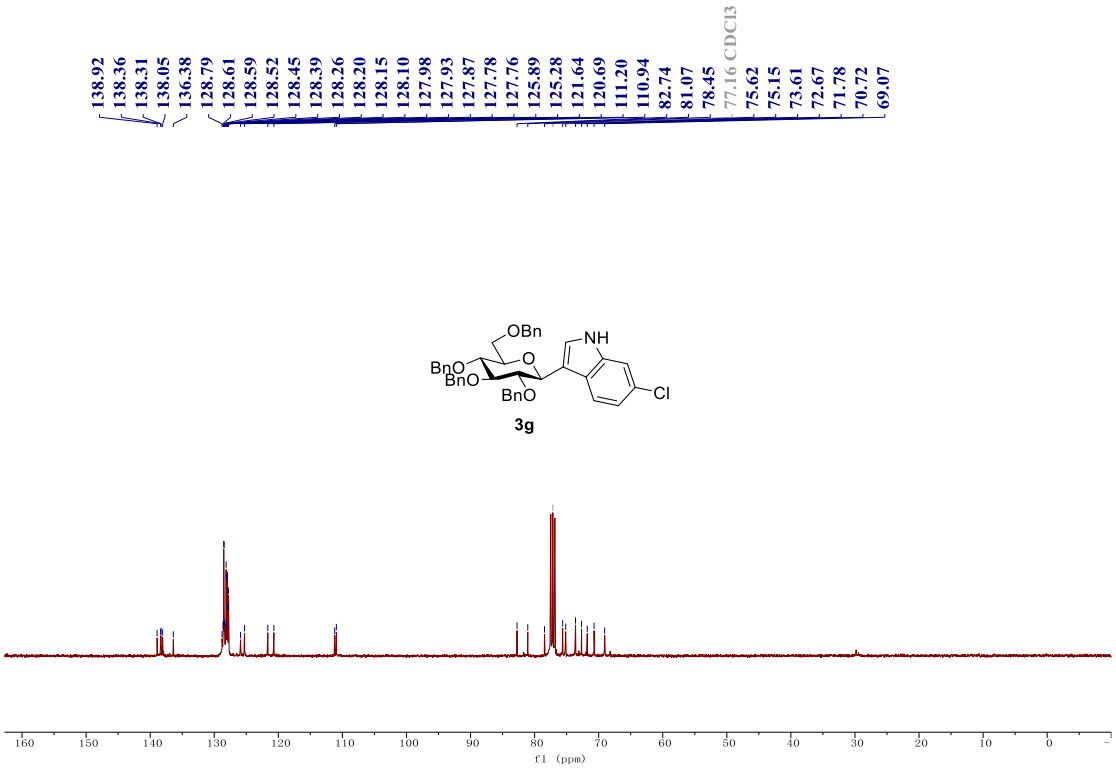

Figure S37. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound 3g

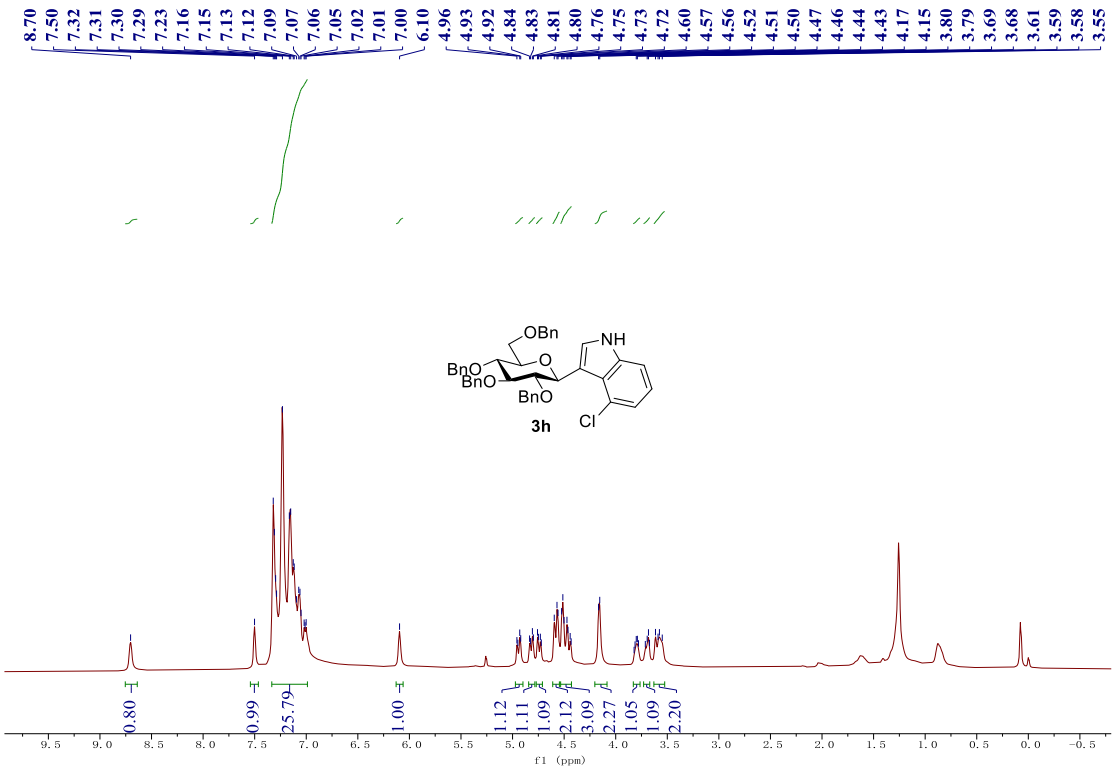

Figure S38. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 3h

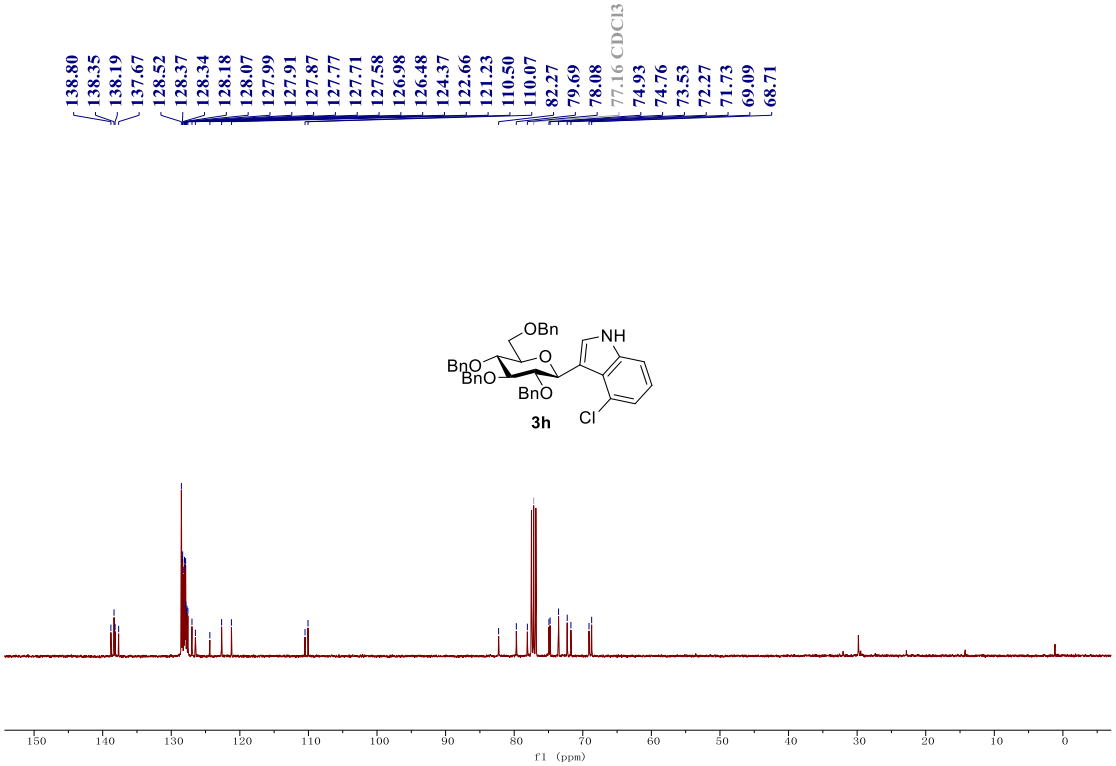

Figure S39. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound 3h

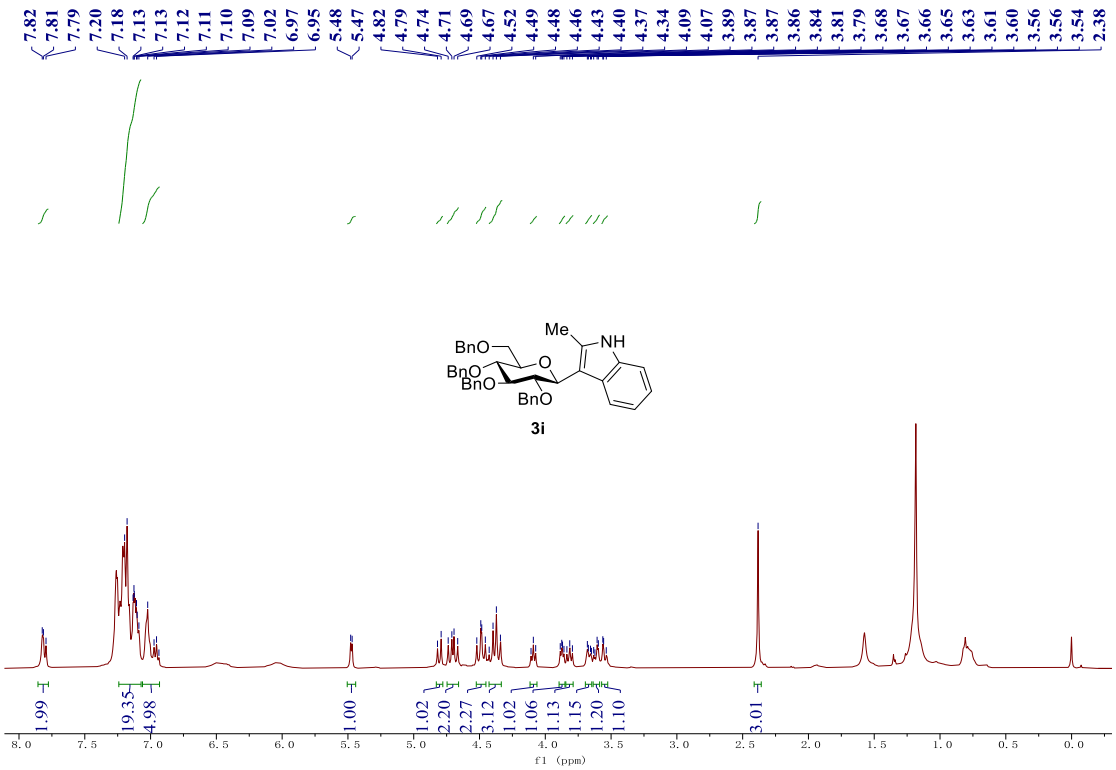

Figure S40. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 3i

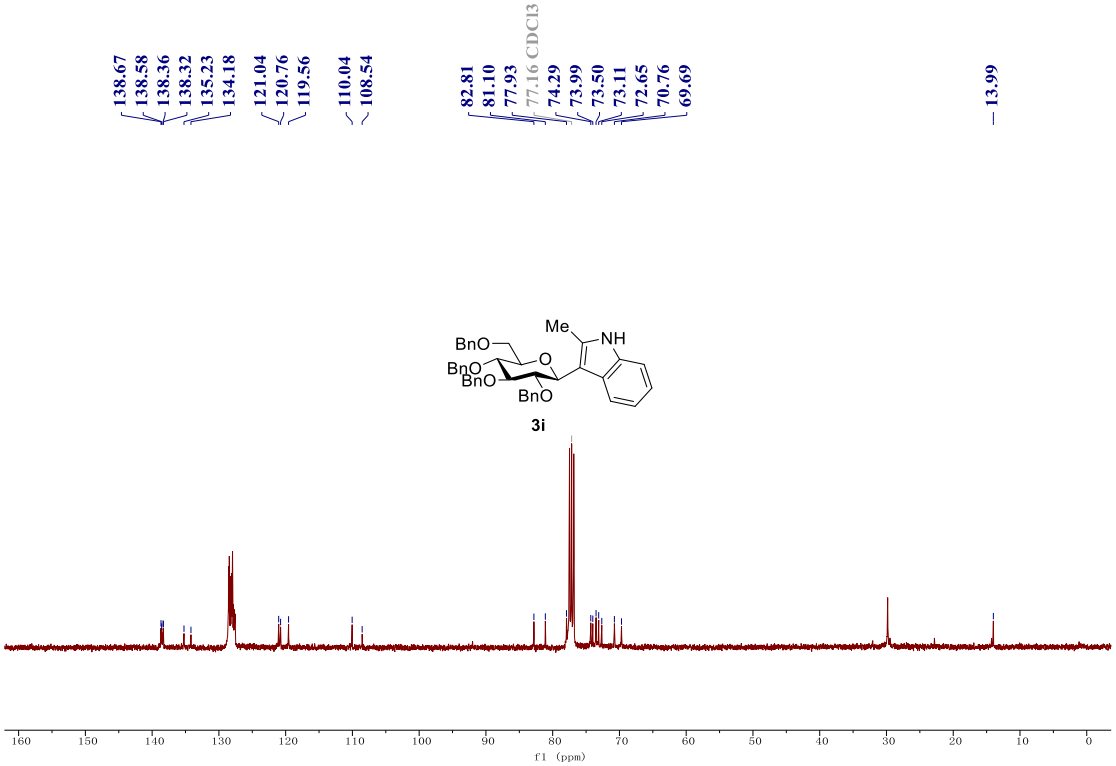

Figure S41. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound 3i

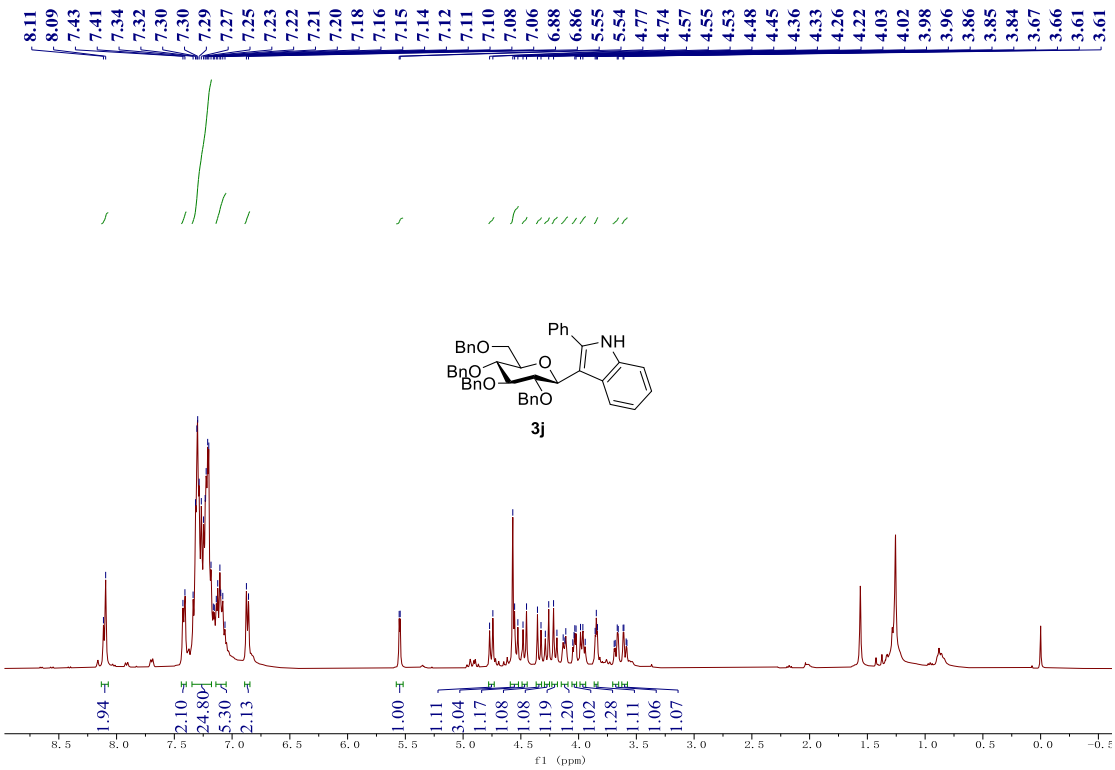

Figure S42. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 3j

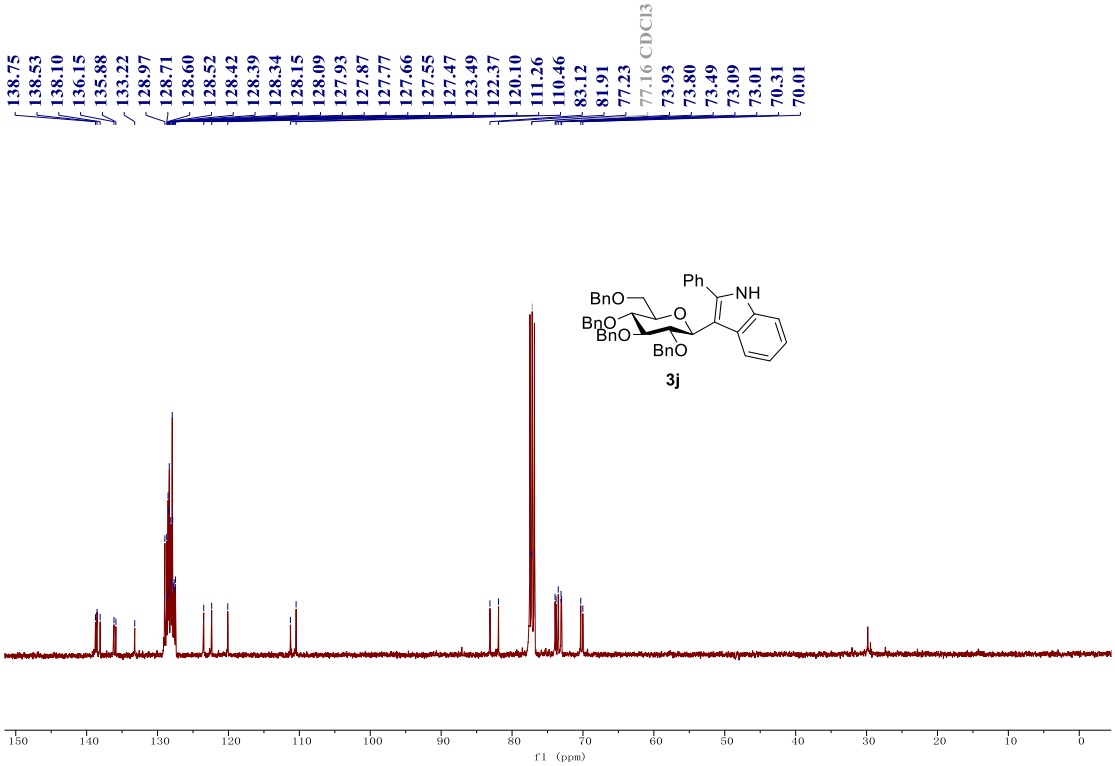

Figure S43. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound 3j

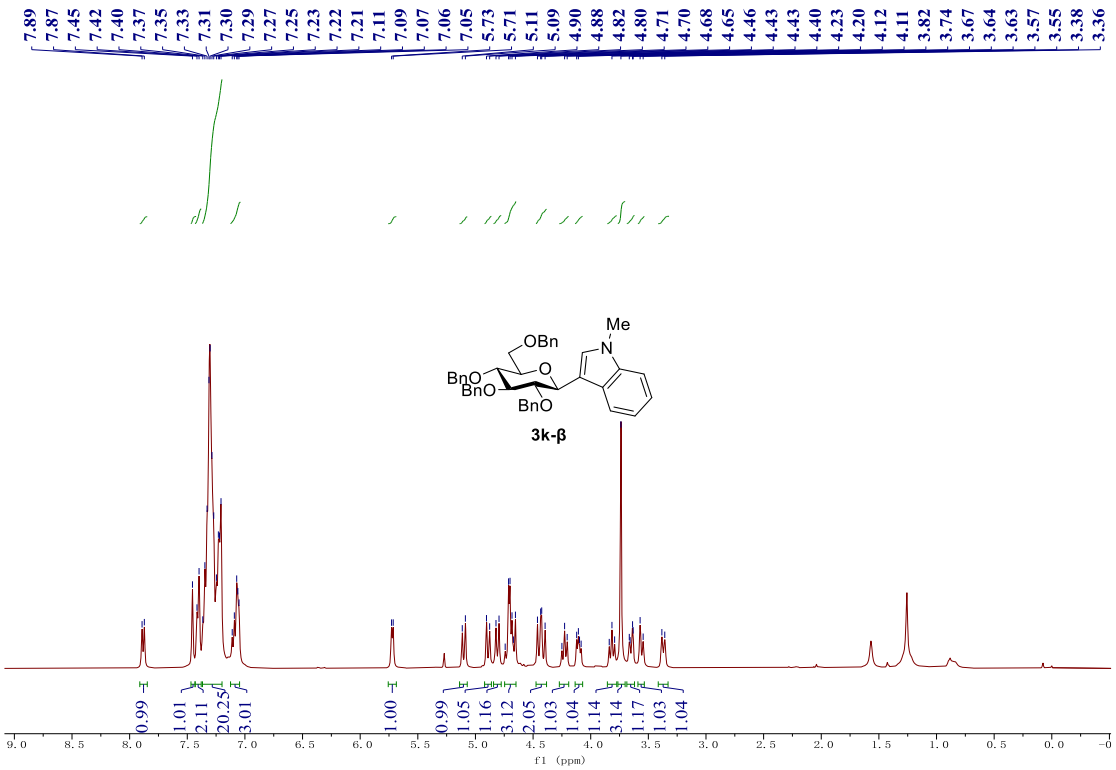

Figure S44. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 3k-β

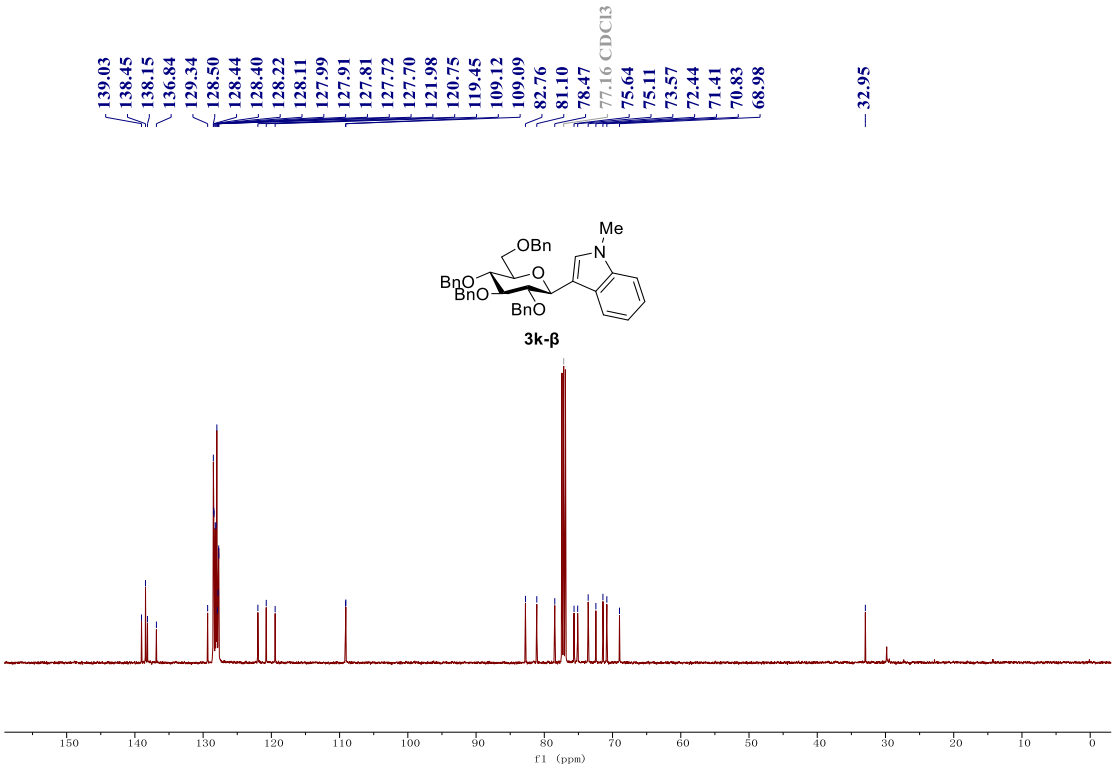

Figure S45. ^{13}C NMR (126 MHz, $CDCl_3$) Spectra for compound 3k-β

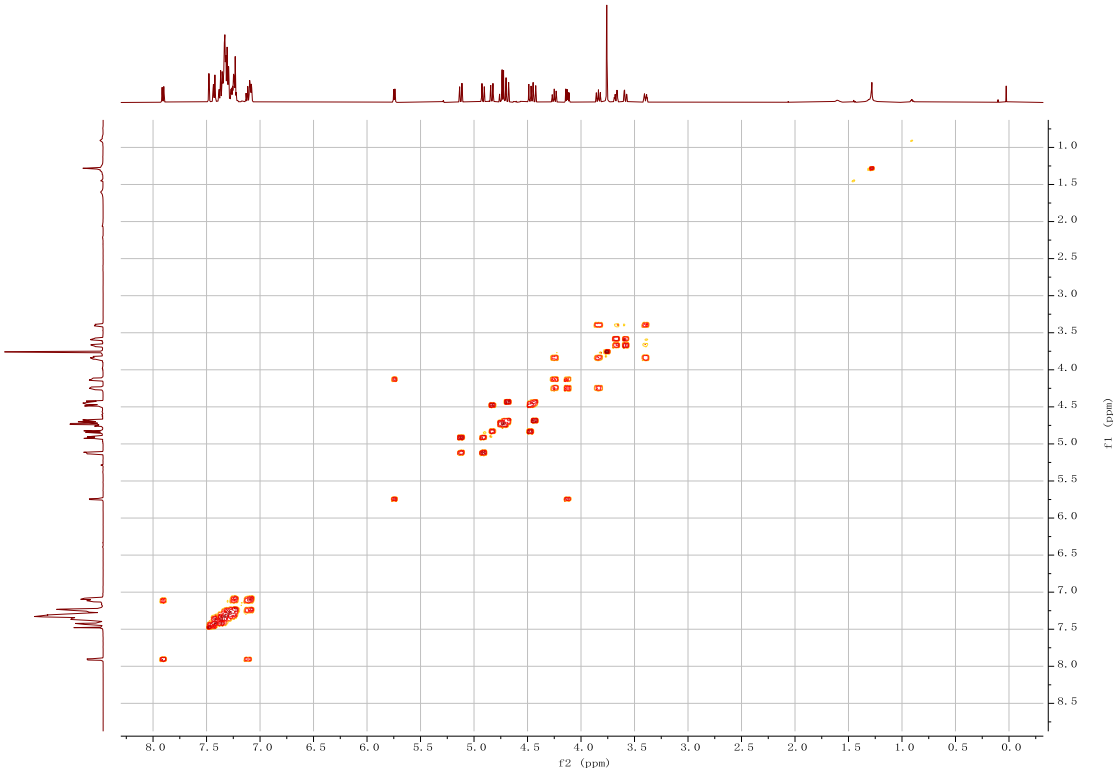

Figure S46. COSY Spectra for compound 3k-β

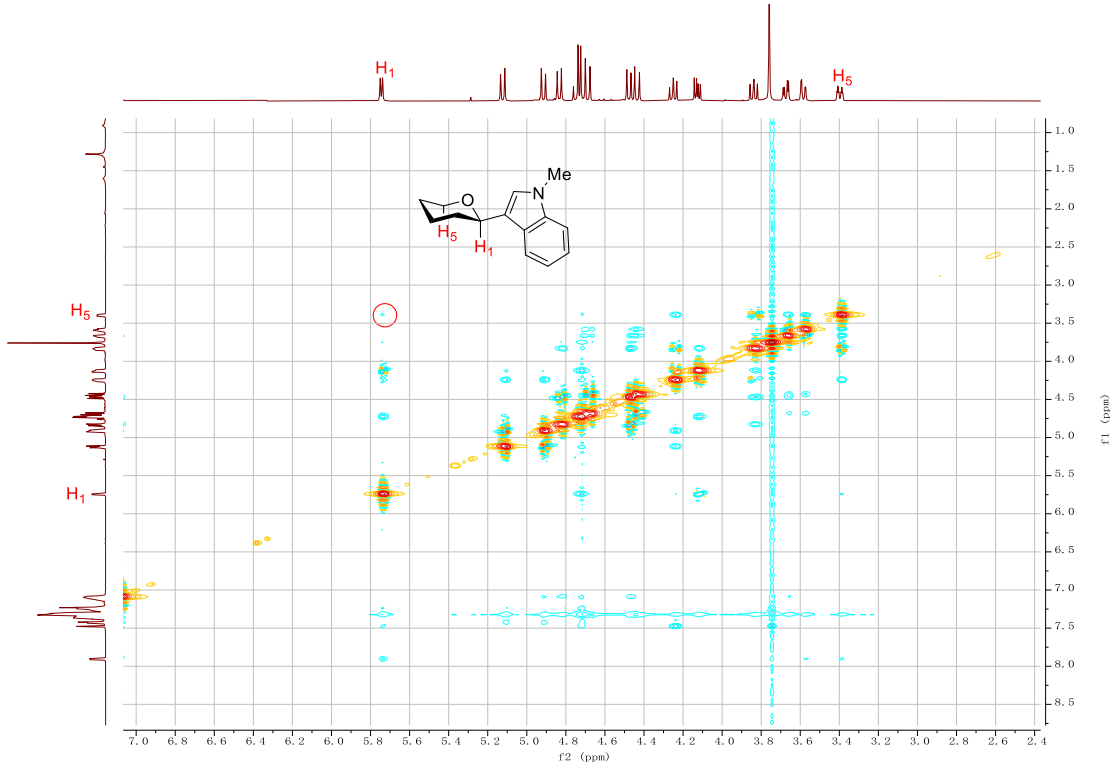

Figure S47. NOESY Spectra for compound 3k-β

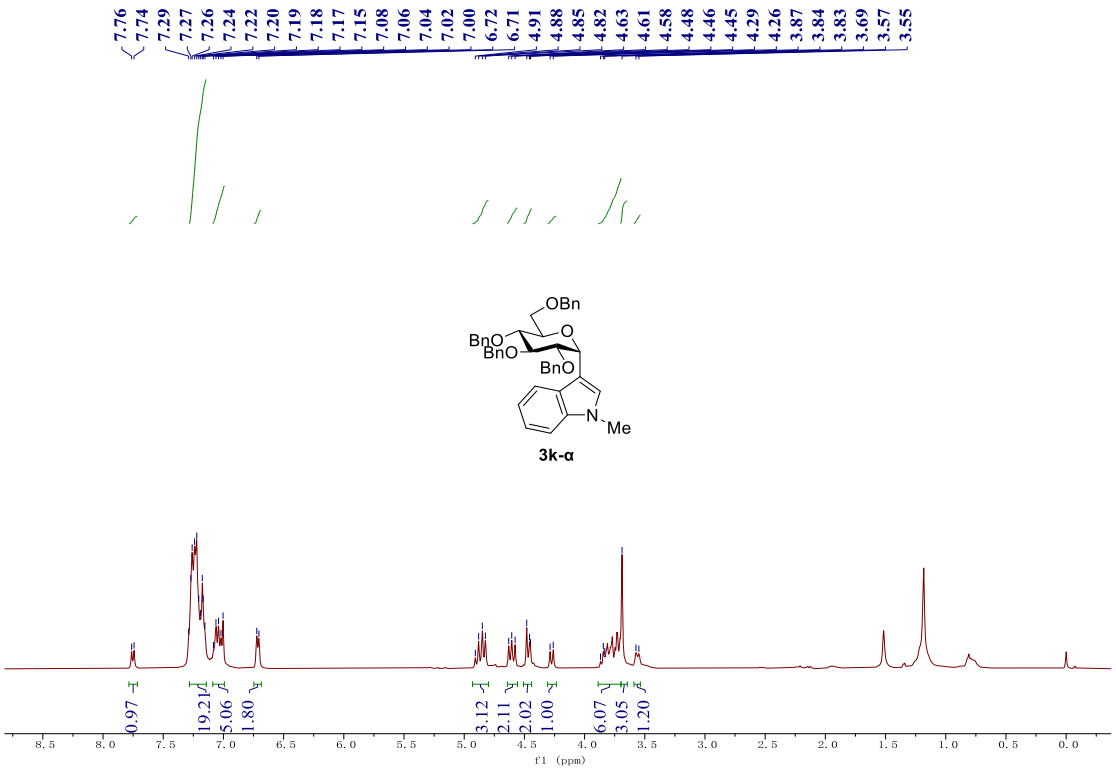

Figure S48. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 3k-α

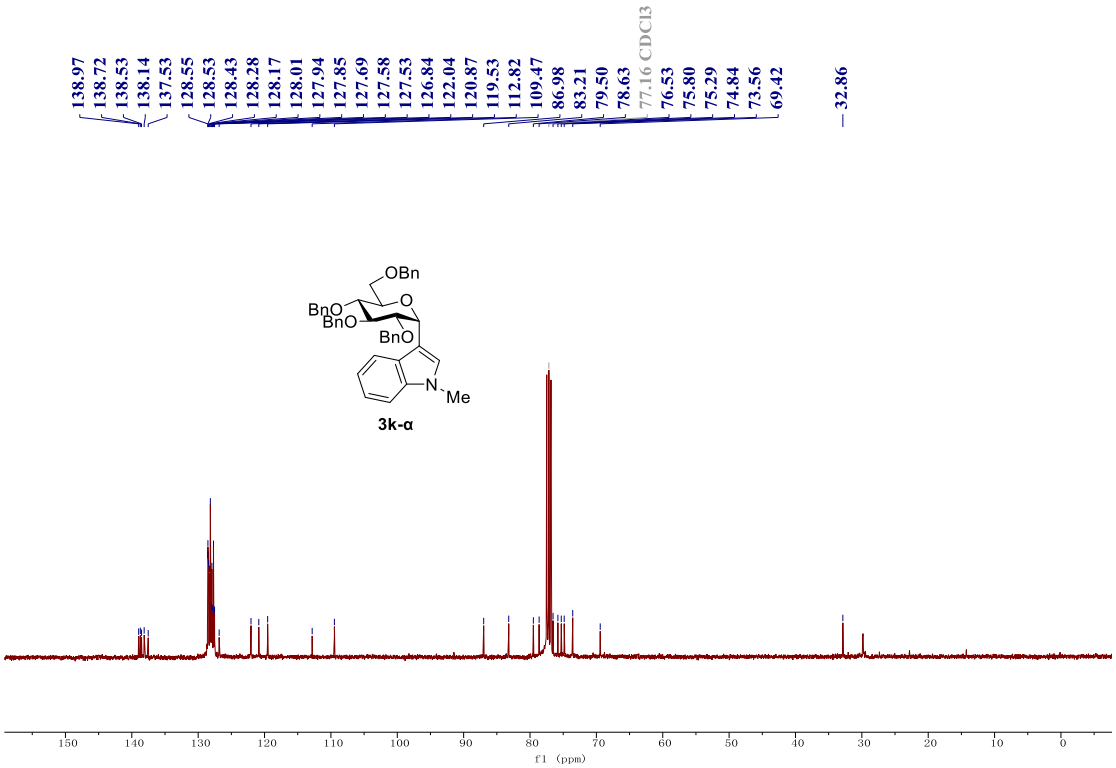

Figure S49. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound 3k-α

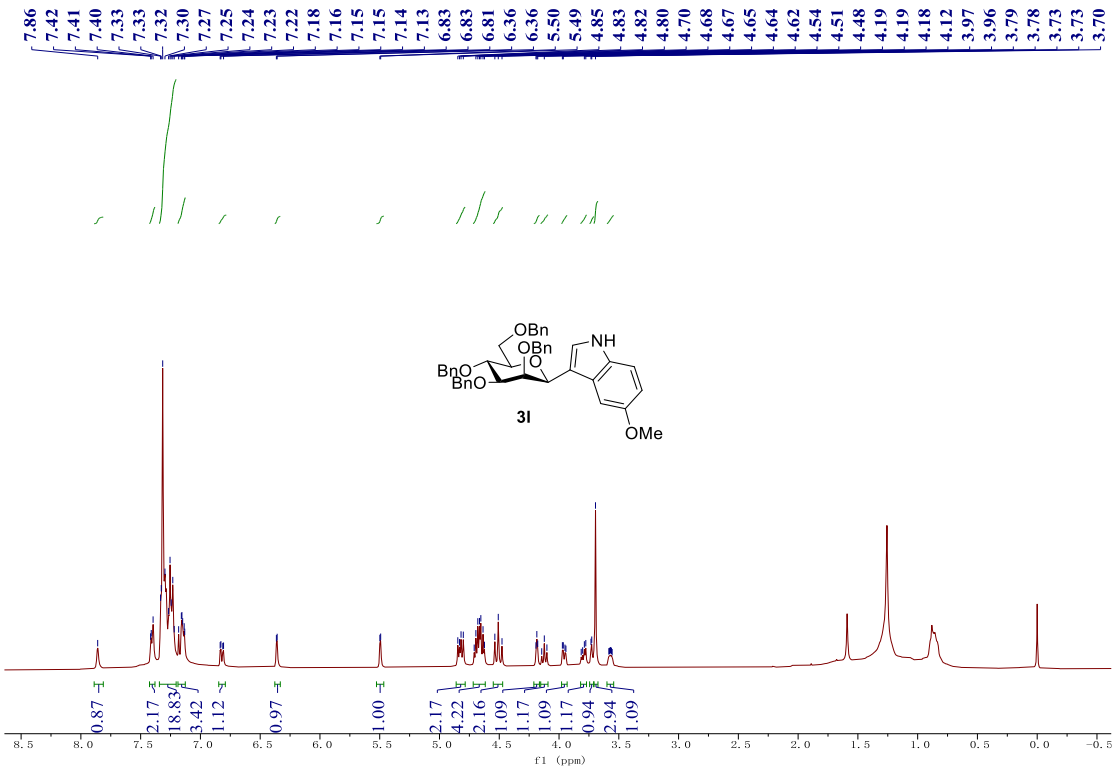

Figure S50. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 3l

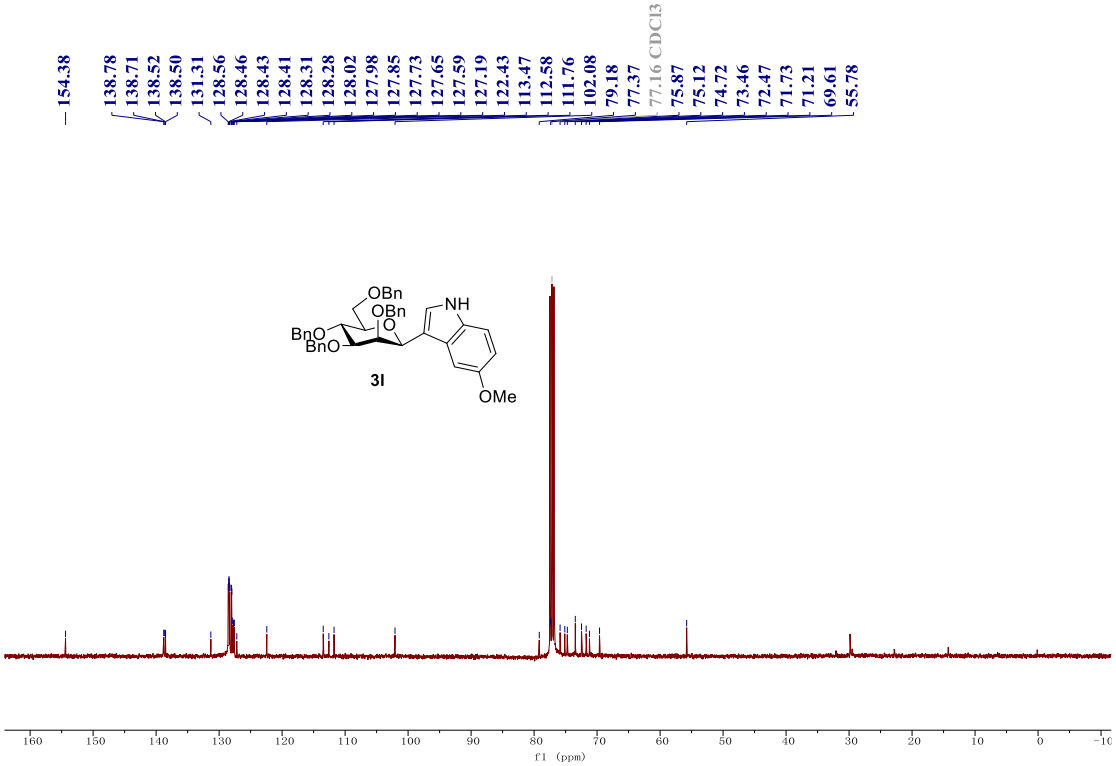

Figure S51. ^{13}C NMR (101MHz, $CDCl_3$) Spectra for compound 3l

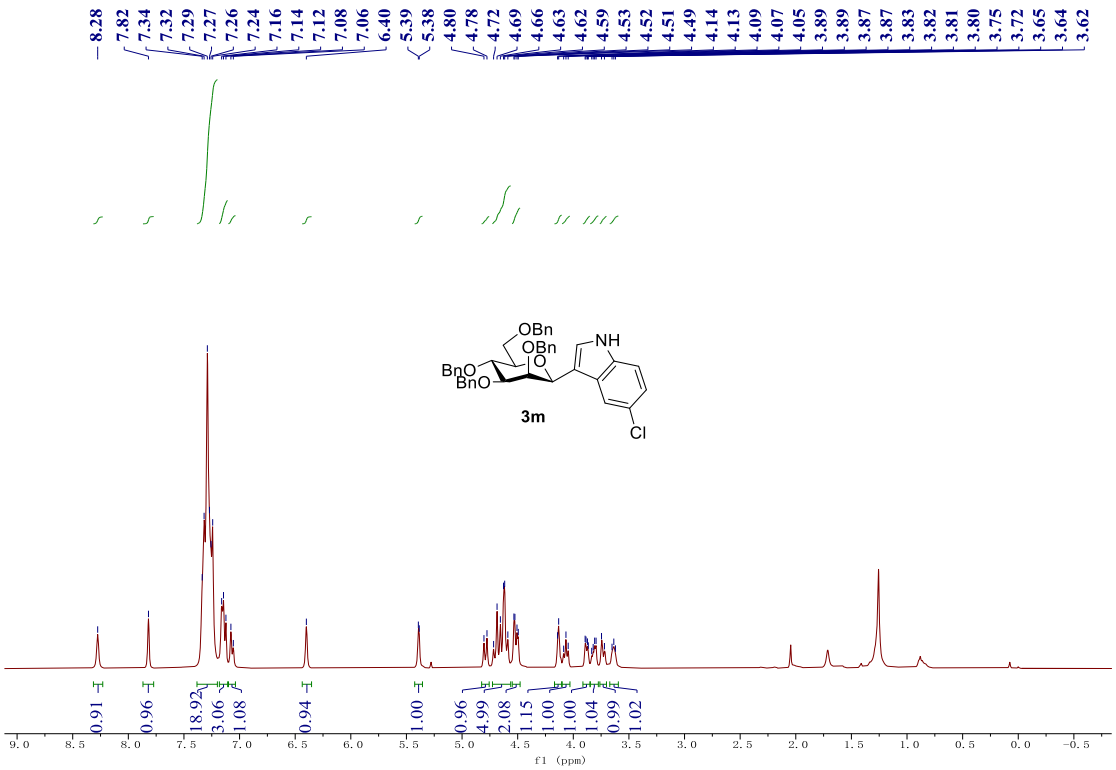

Figure S52. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 3m

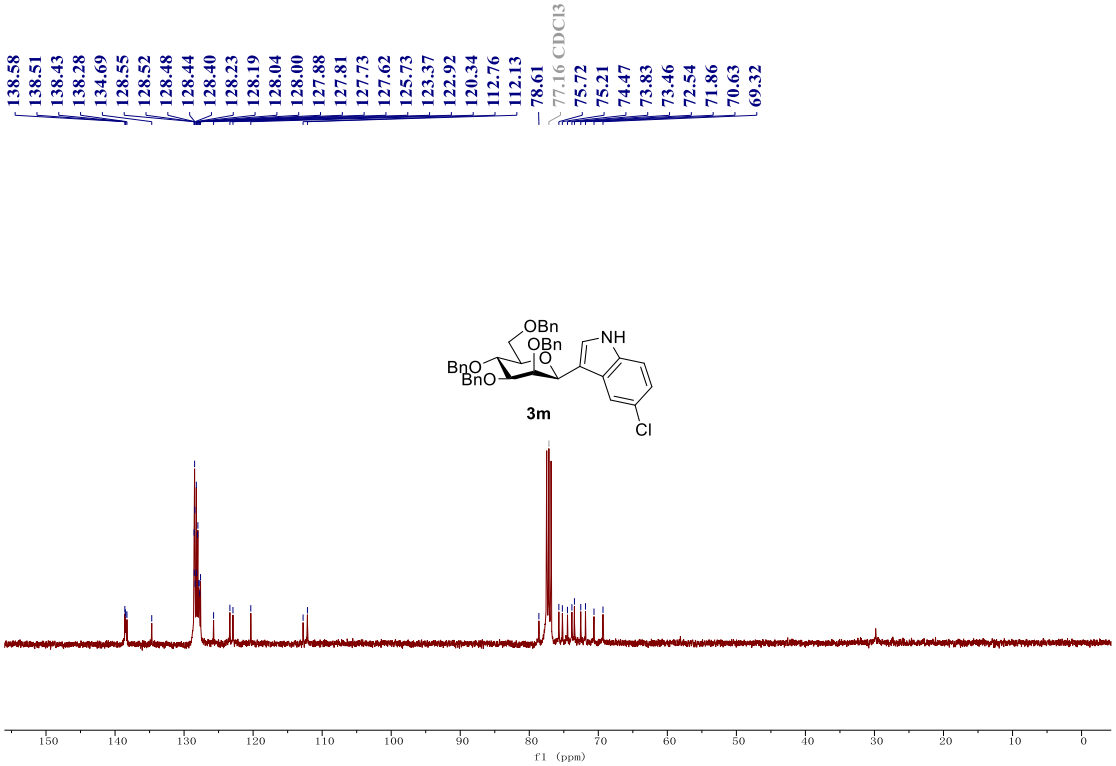

Figure S53. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound 3m

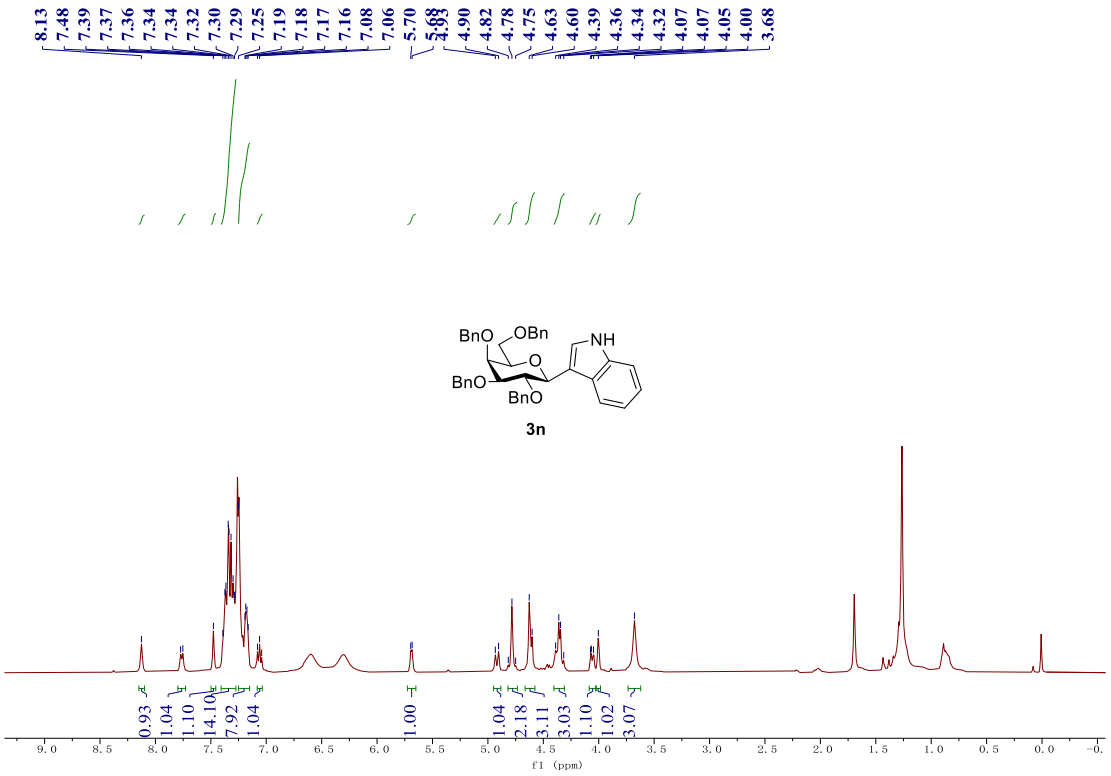

Figure S54. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 3n

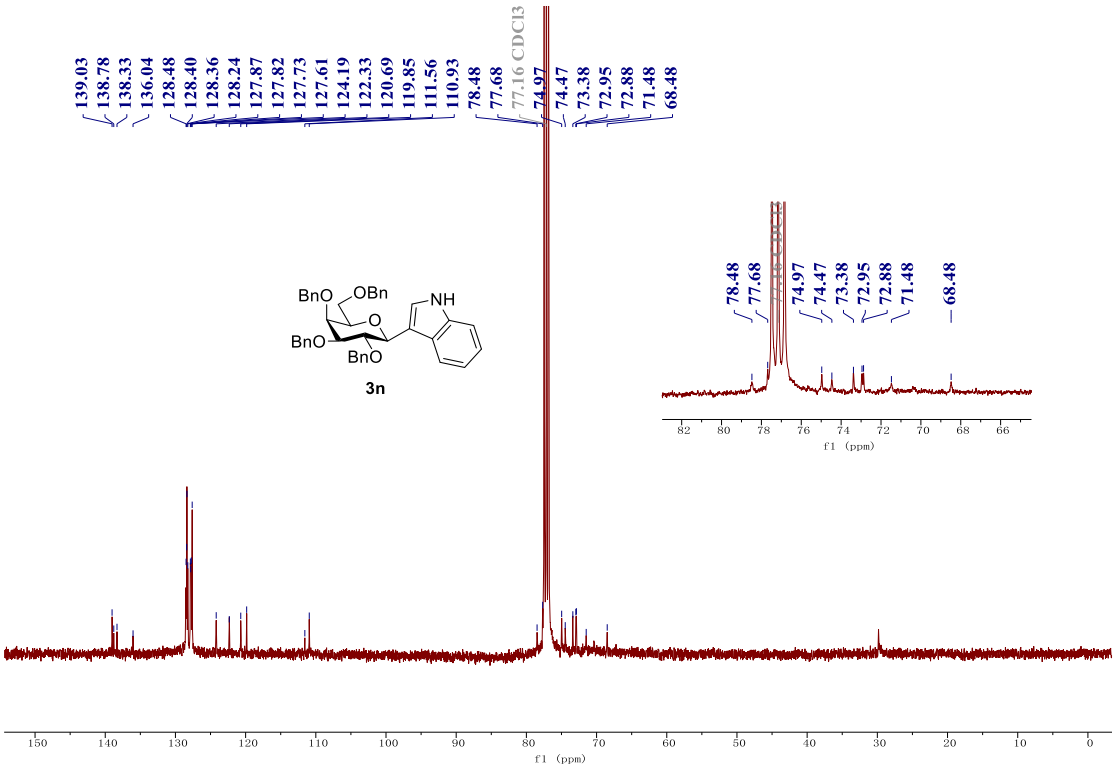

Figure S55. ^{13}C NMR (101MHz, $CDCl_3$) Spectra for compound 3n

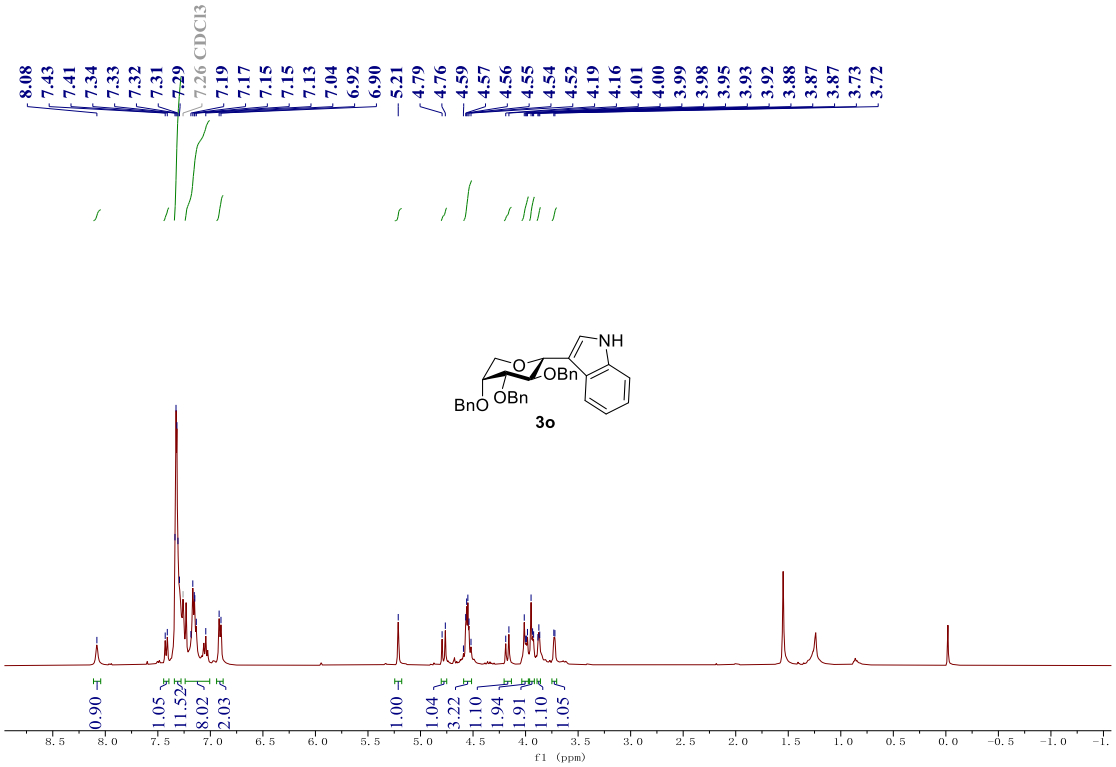

Figure S56. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 3o

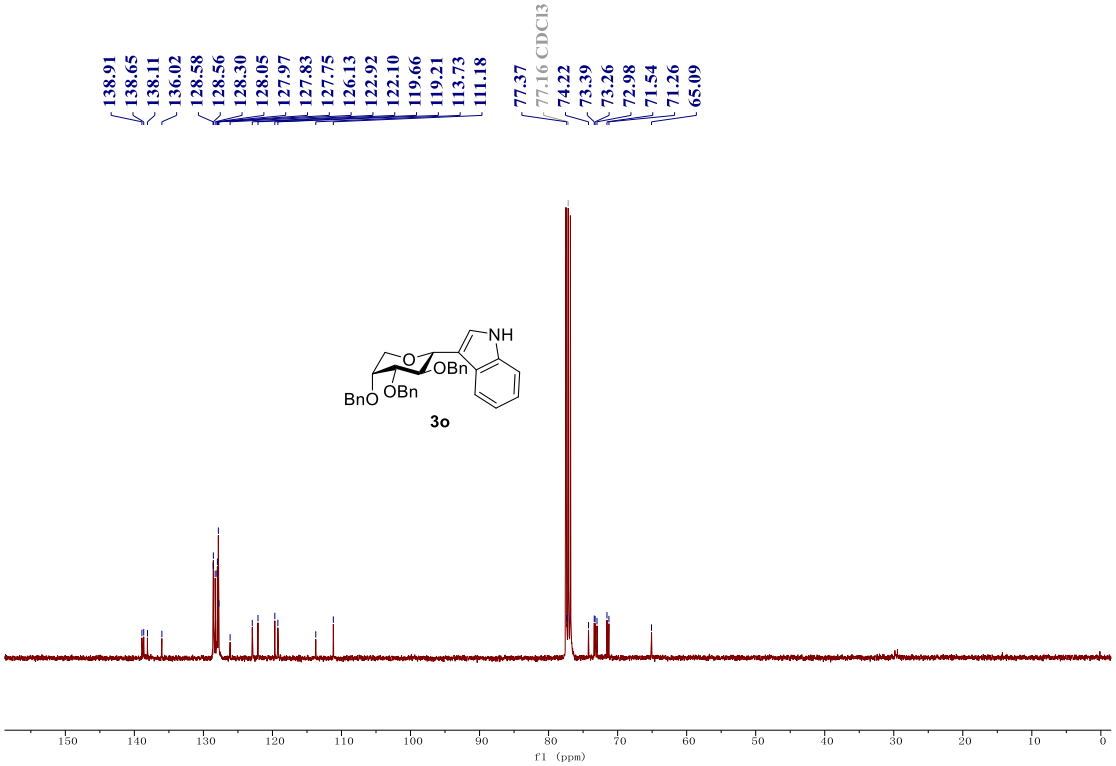

Figure S57. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound 3o

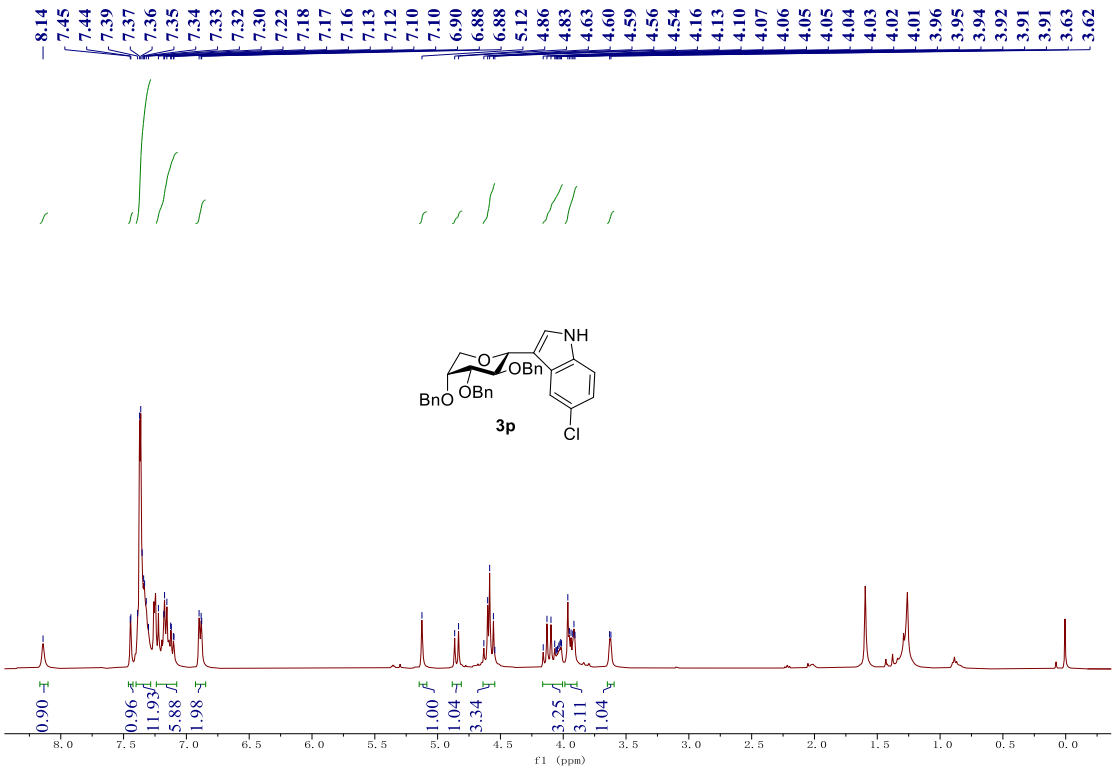

Figure S58. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 3p

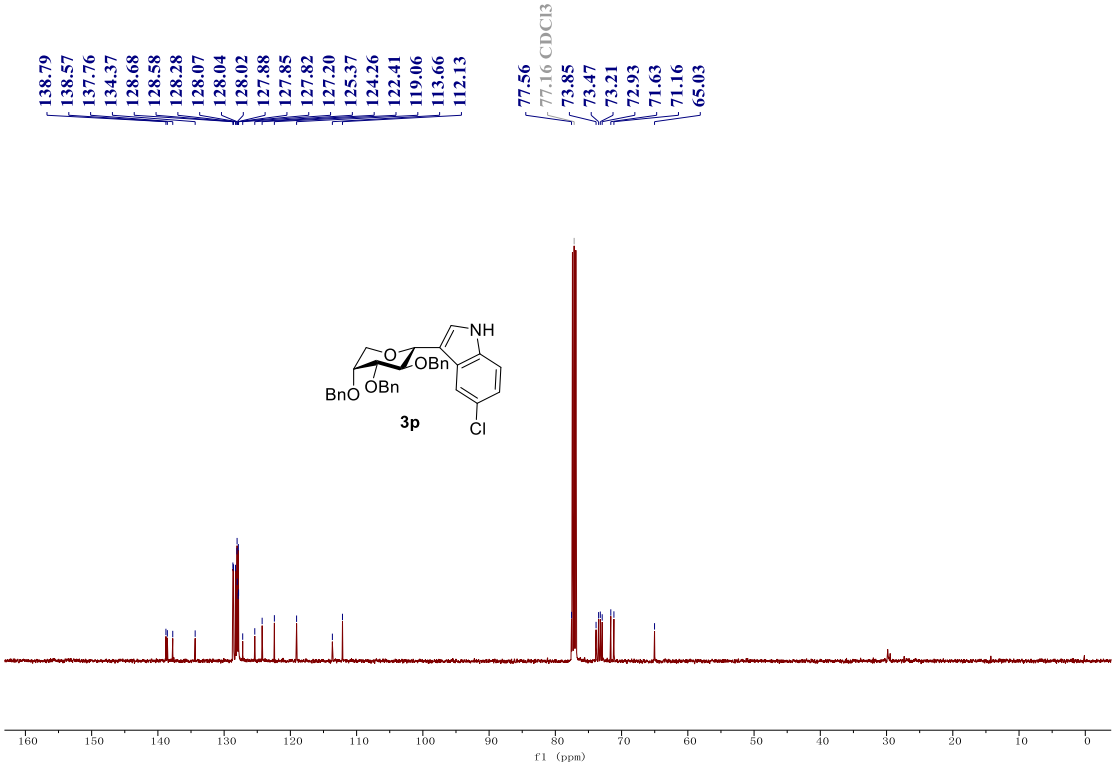

Figure S59. ^{13}C NMR (126 MHz, $CDCl_3$) Spectra for compound 3p

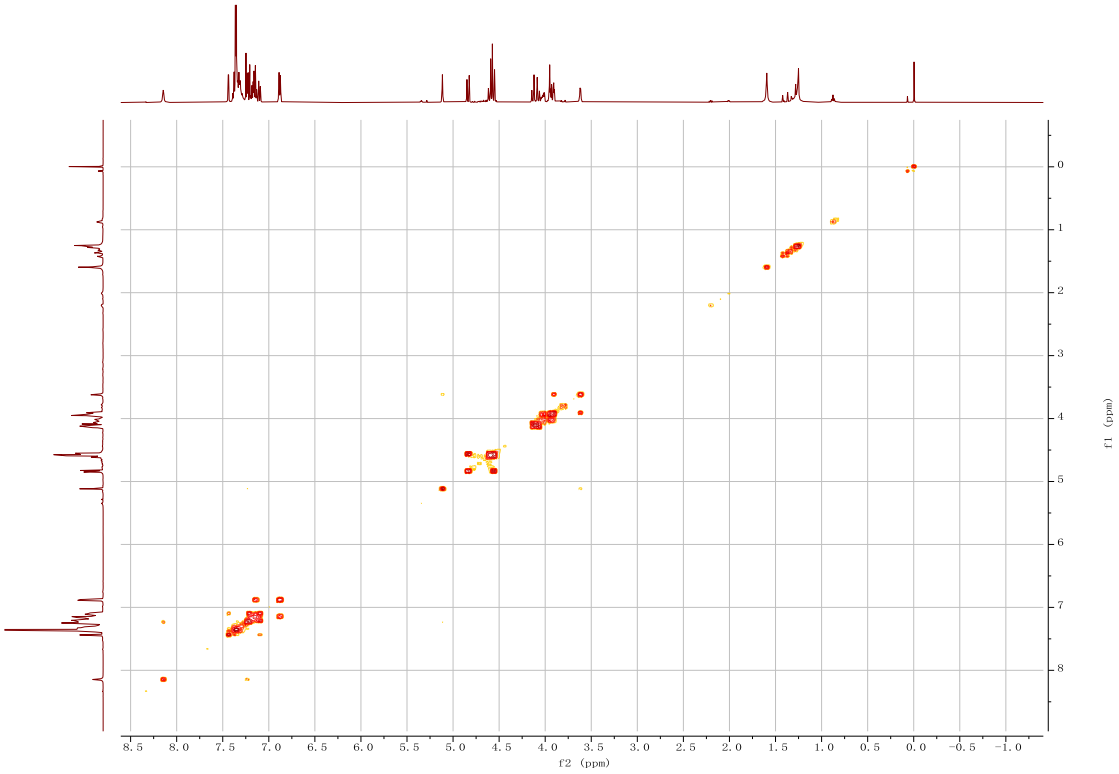

Figure S60. COSY Spectra for compound 3p

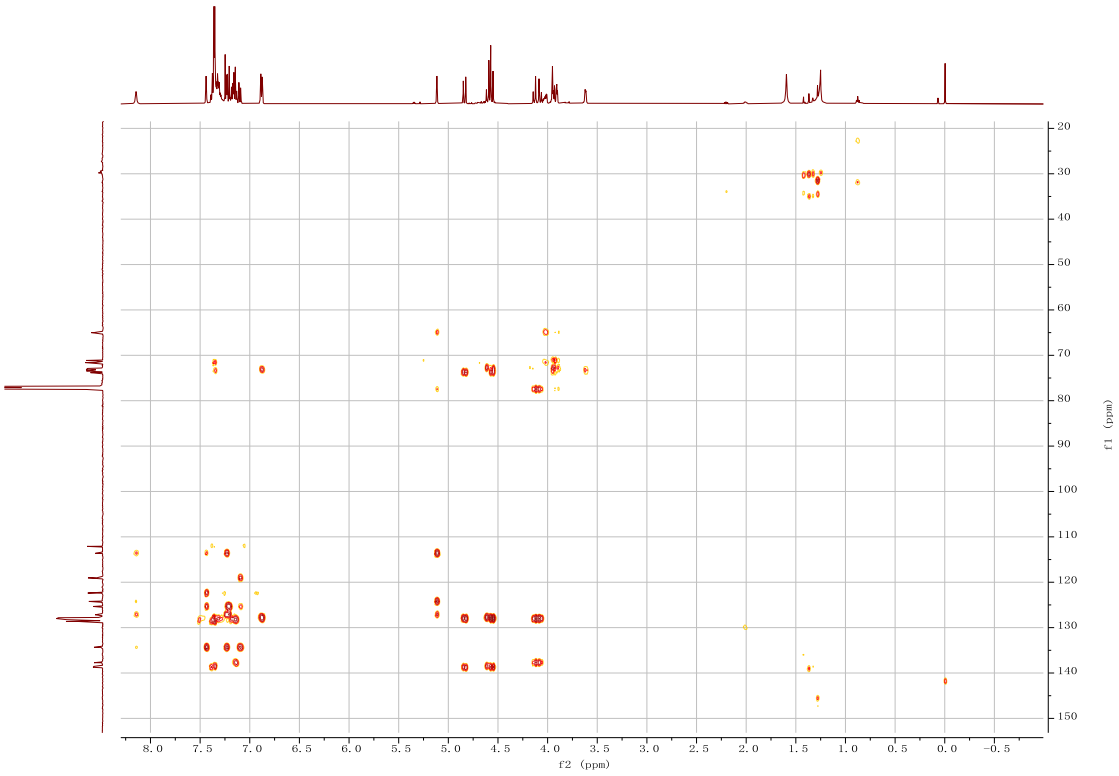

Figure S61. HMBC Spectra for compound 3p

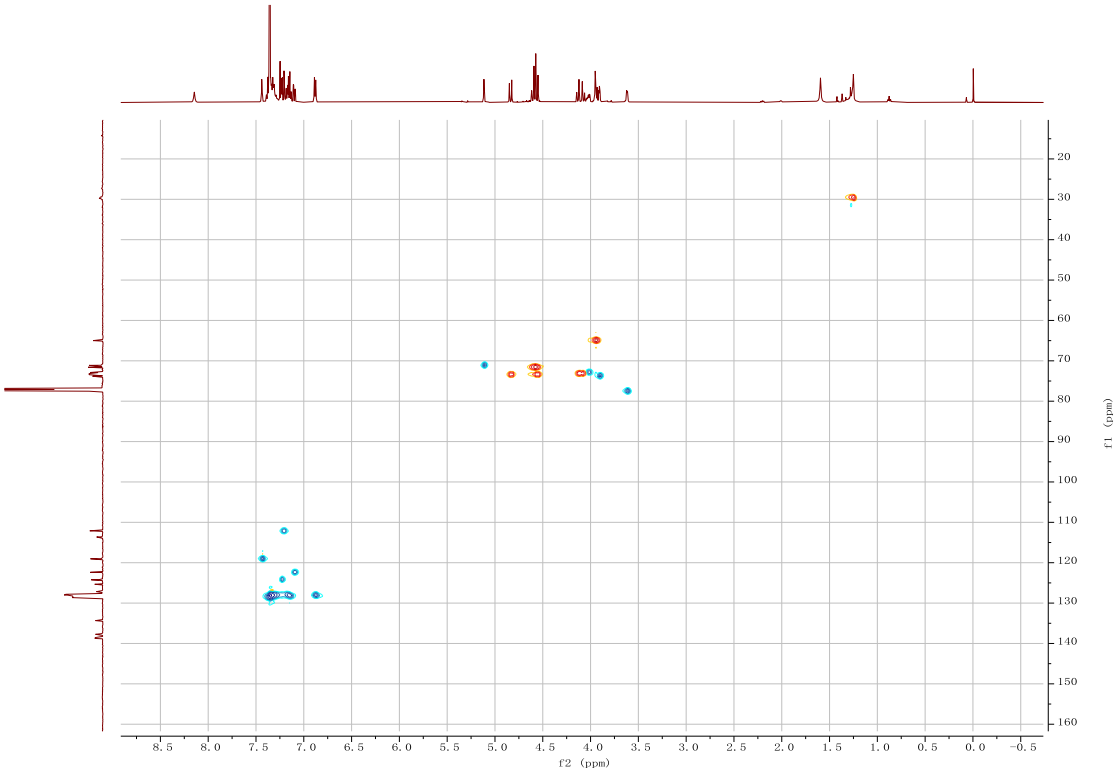

Figure S62. HSQC Spectra for compound 3p

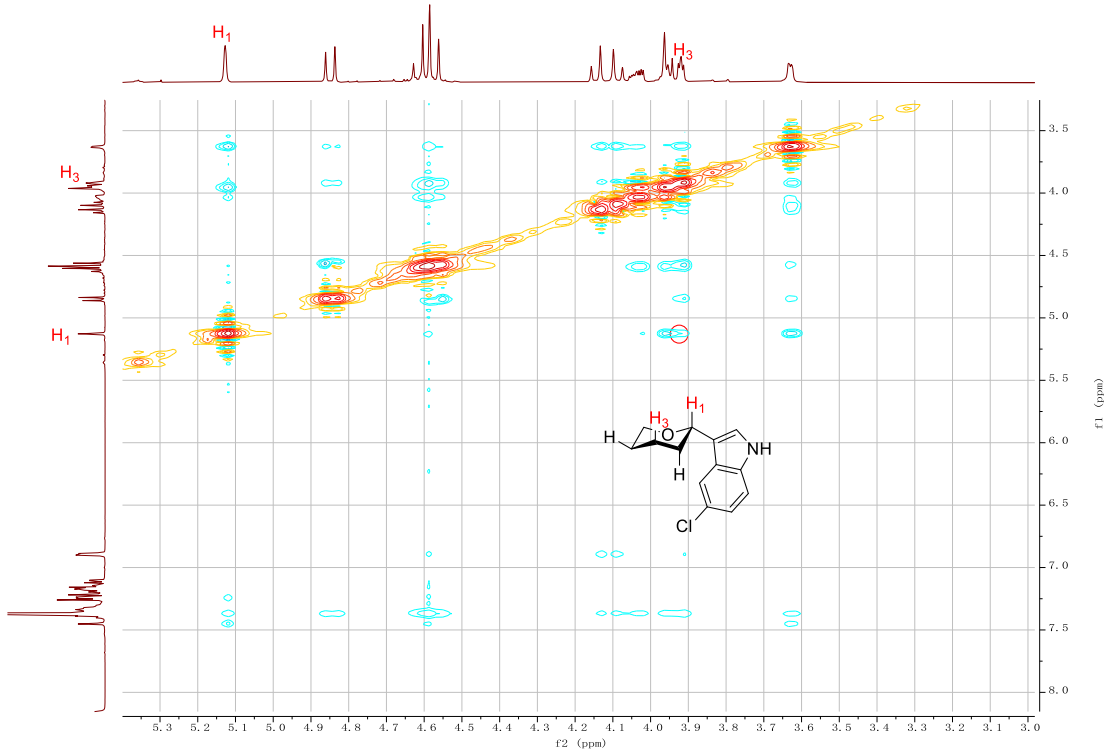

Figure S63. NOESY Spectra for compound 3p

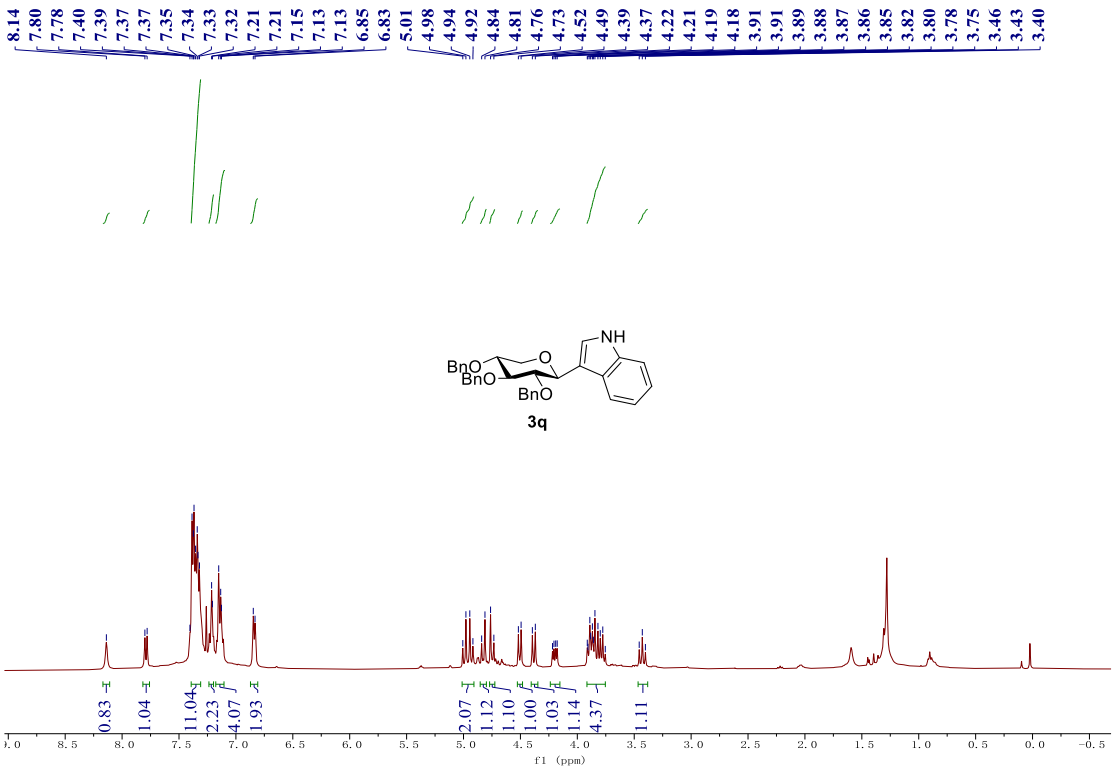

Figure S64. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 3q

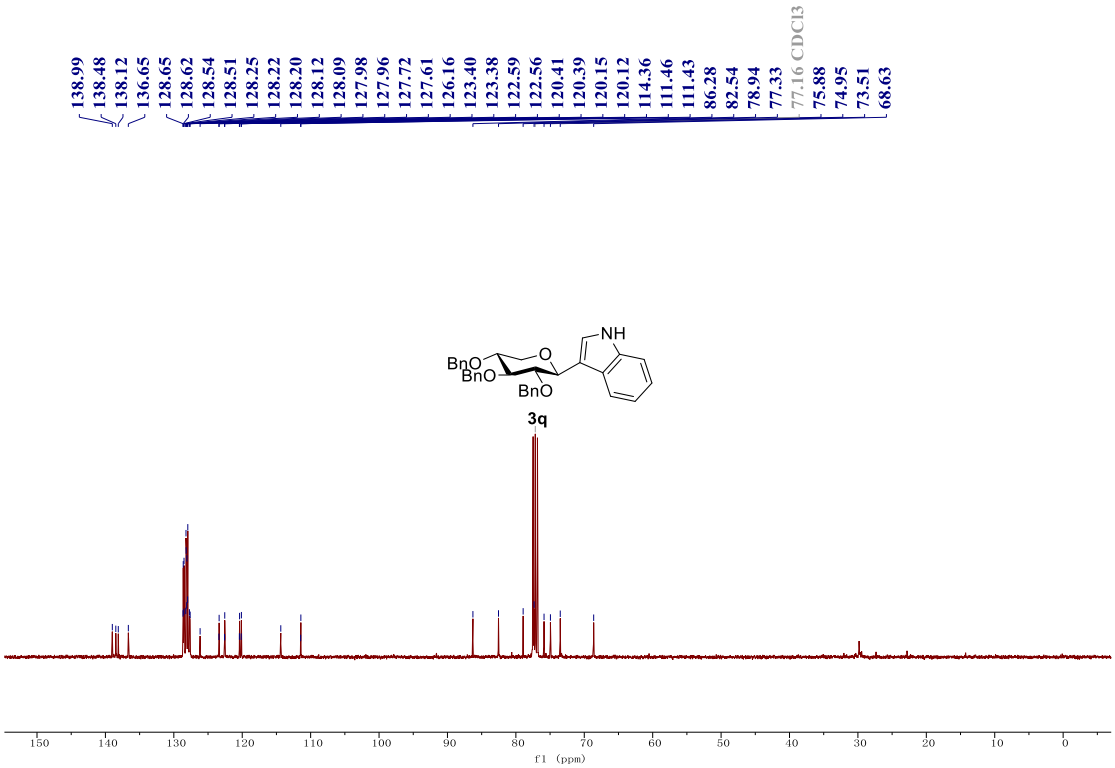

Figure S65. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound 3q

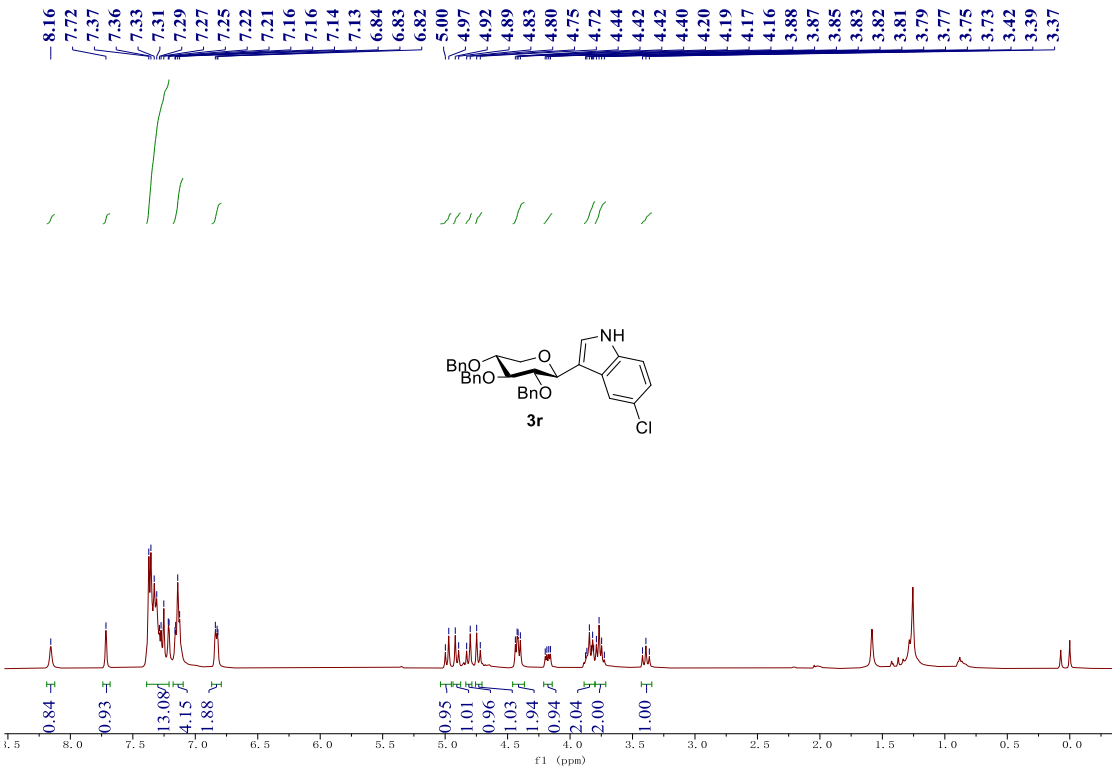

Figure S66. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 3r

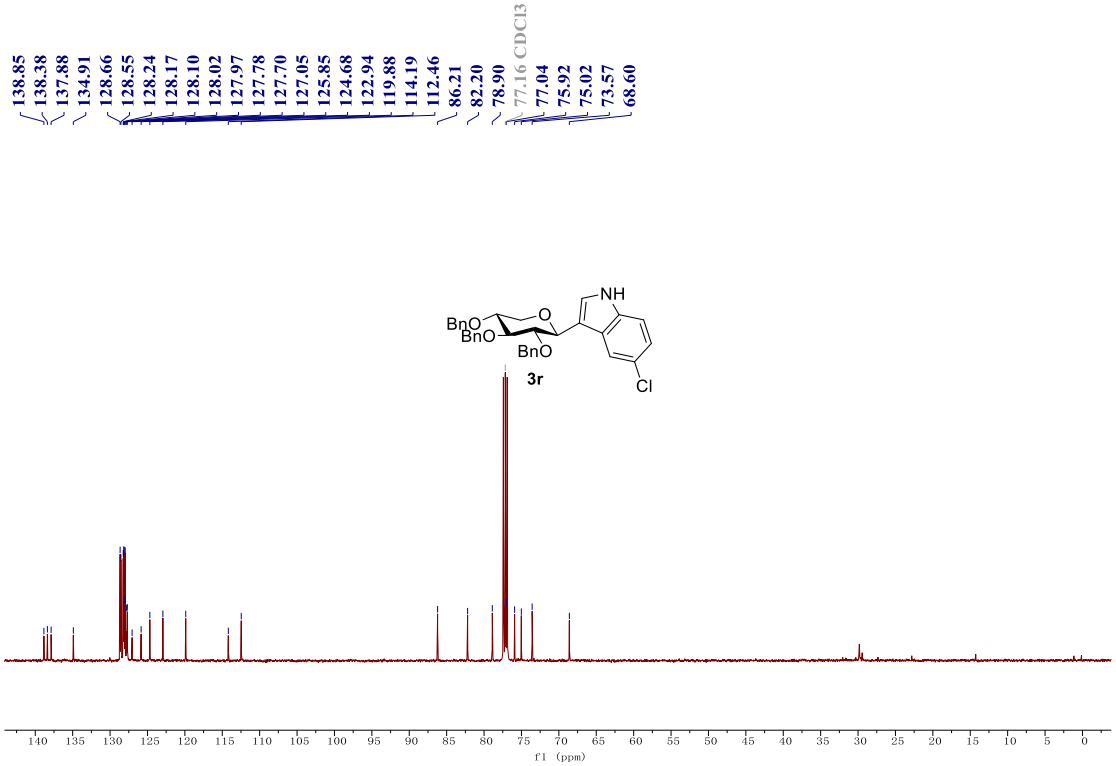

Figure S67. ^{13}C NMR (126 MHz, $CDCl_3$) Spectra for compound 3r

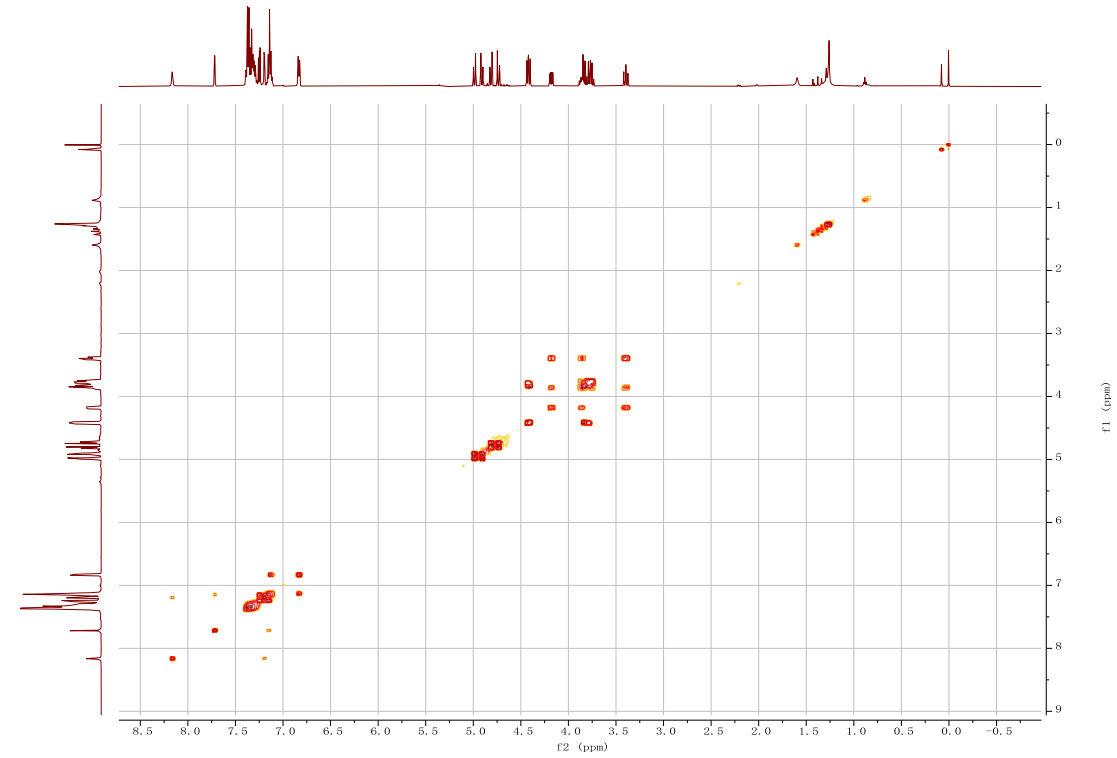

Figure S68. COSY Spectra for compound 3r

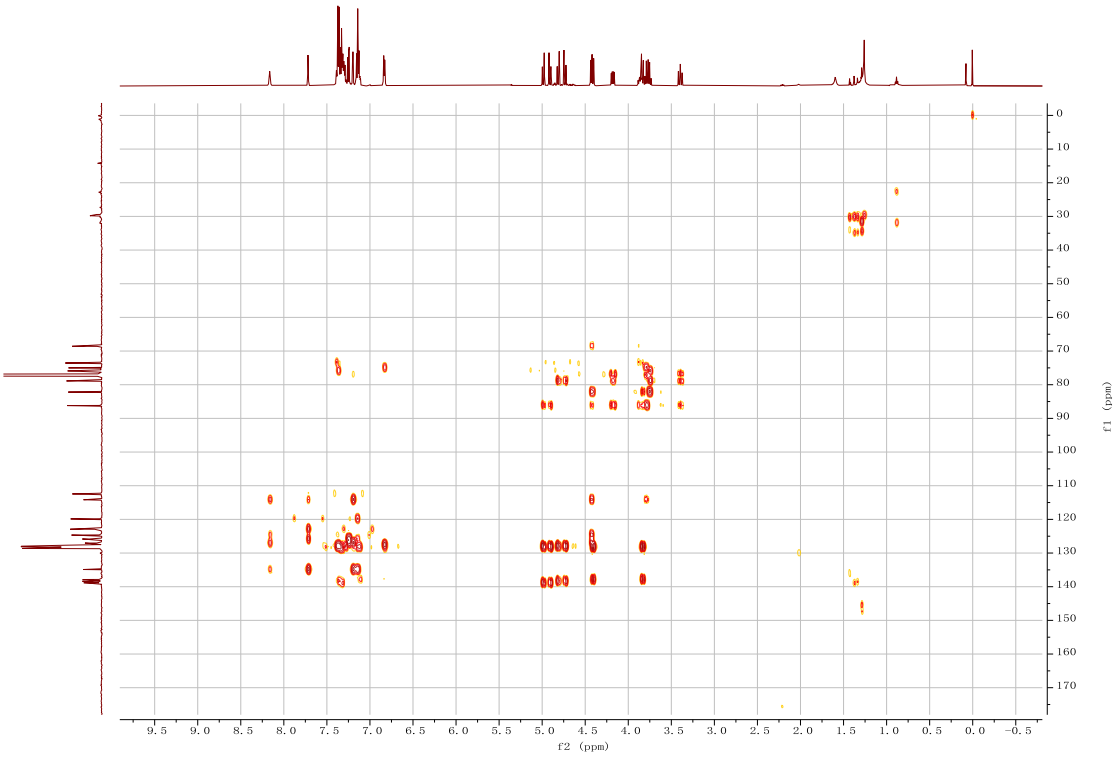

Figure S69. HMBC Spectra for compound 3r

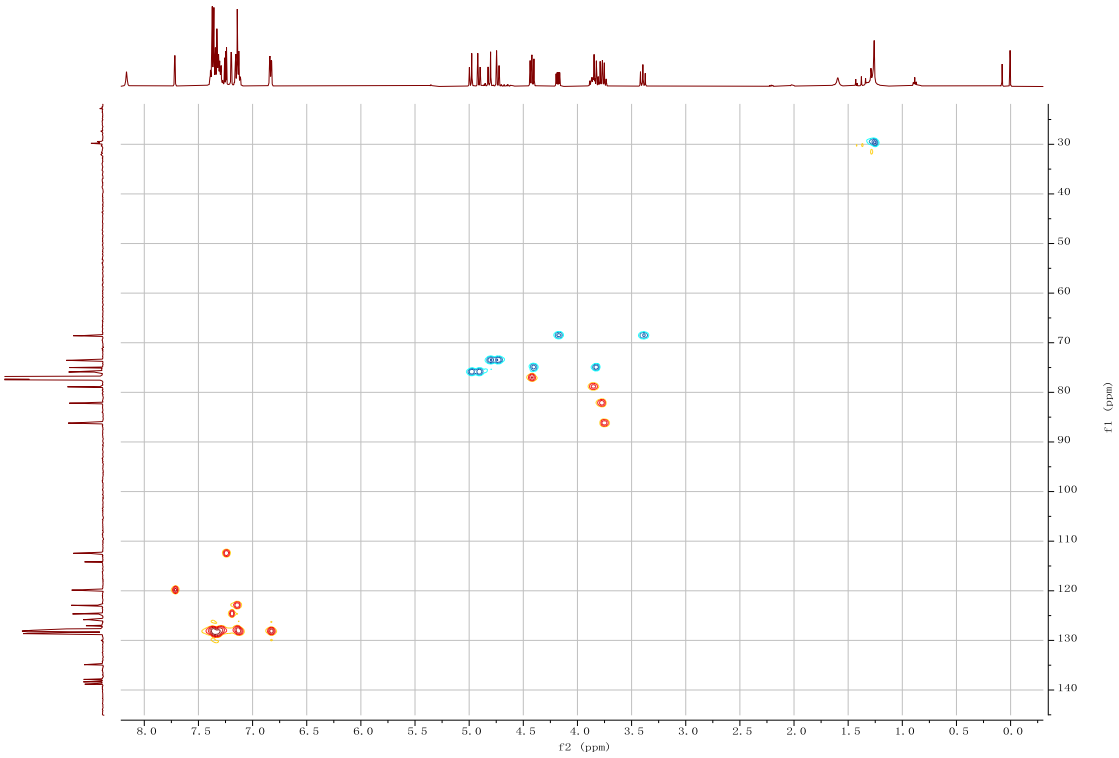

Figure S70. HSQC Spectra for compound 3r

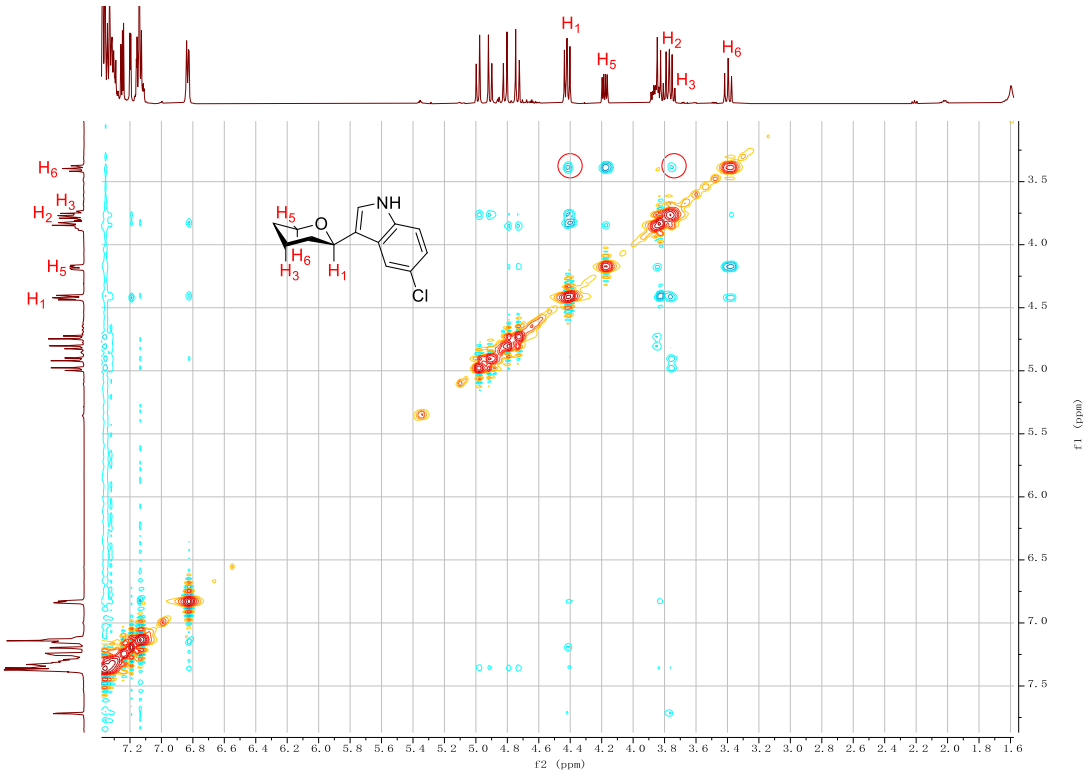

Figure S71. NOESY Spectra for compound 3r

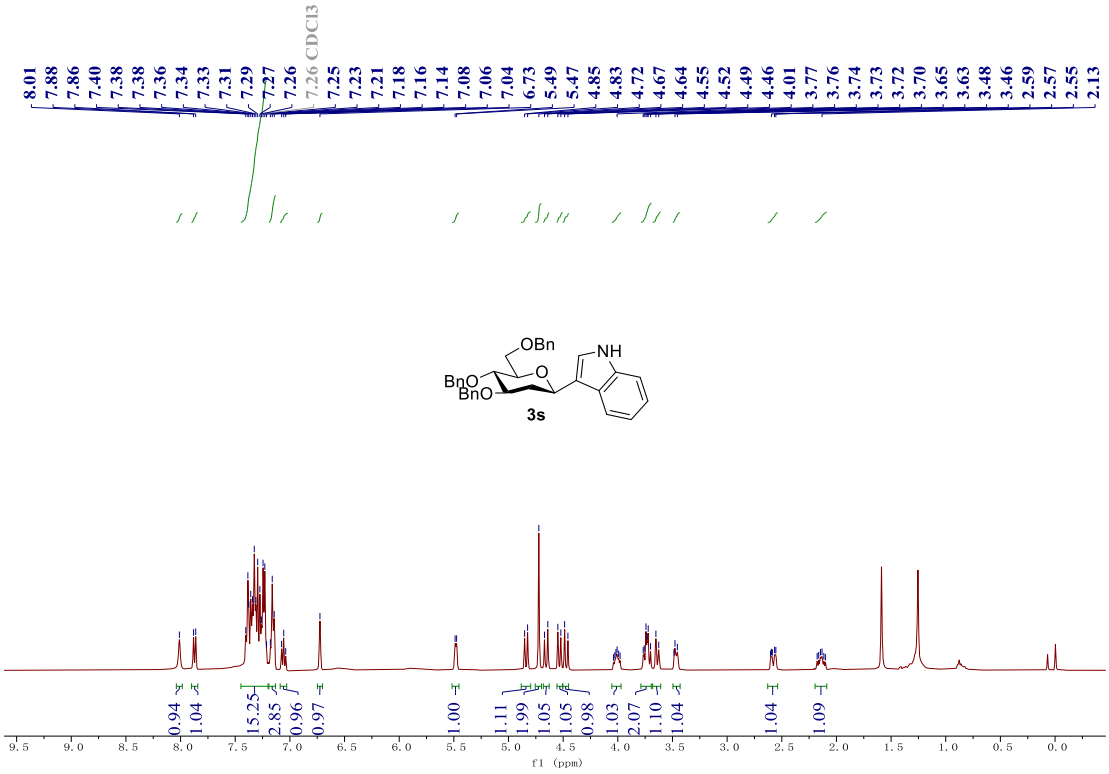

Figure S72. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 3s

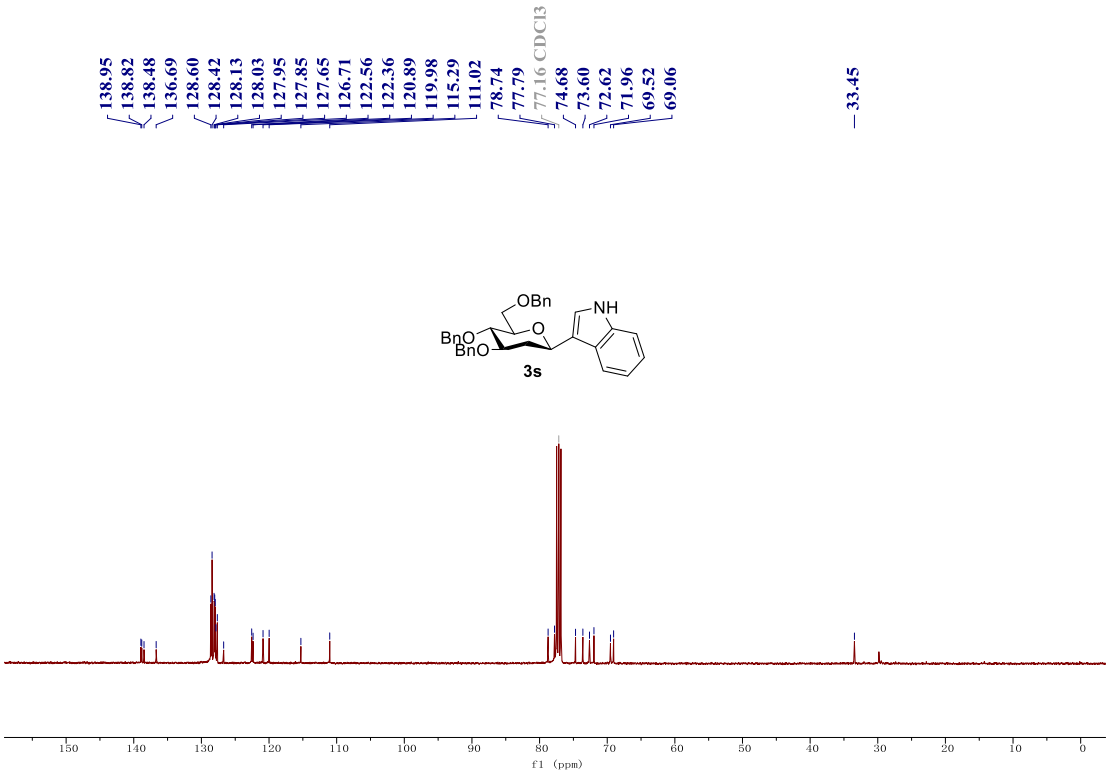

Figure S73. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound 3s

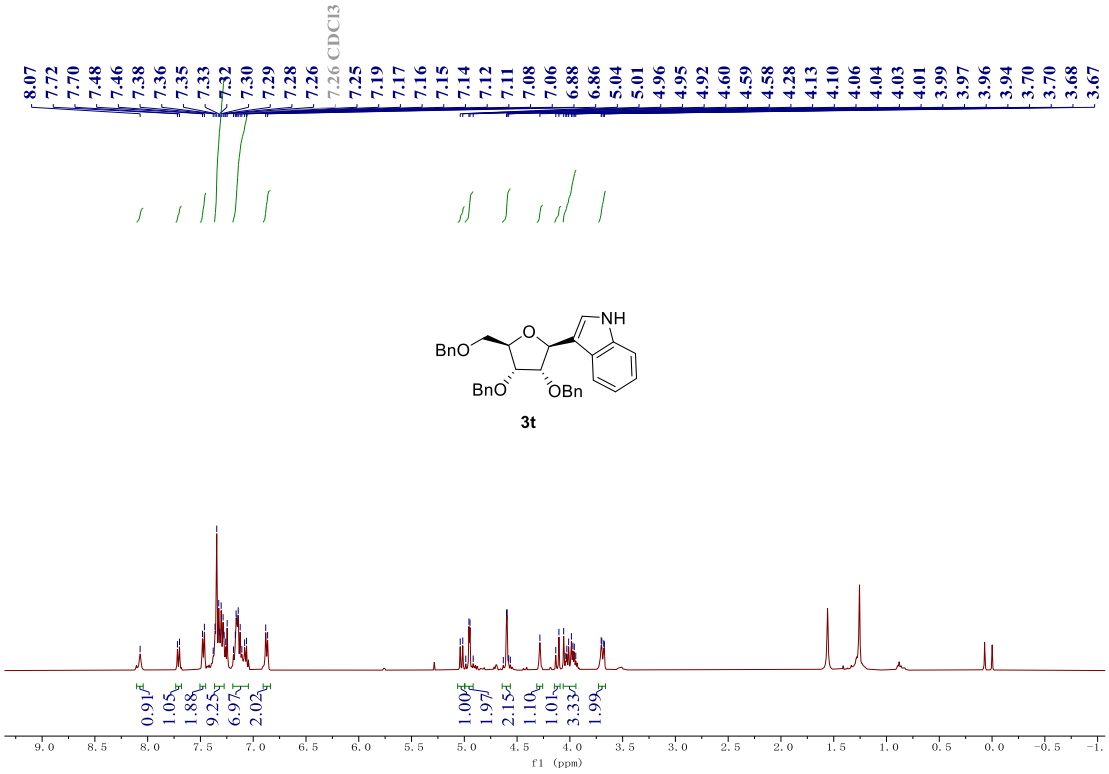

Figure S74. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra for compound 3t

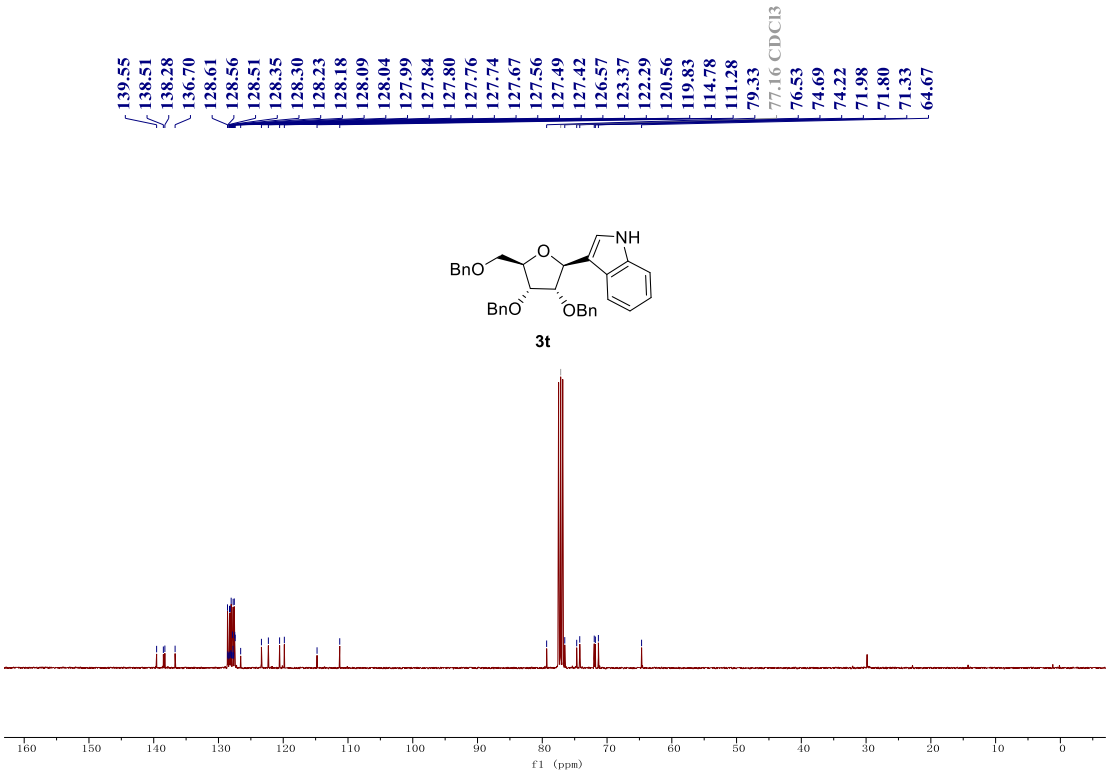

Figure S75. ^{13}C NMR (101 MHz, $CDCl_3$) Spectra for compound 3t