Supporting Information

Radical N-Glycosylation of Heterocycles with 1-Hydroxycarbohydrates Enabled by Metallaphotoredox Catalysis

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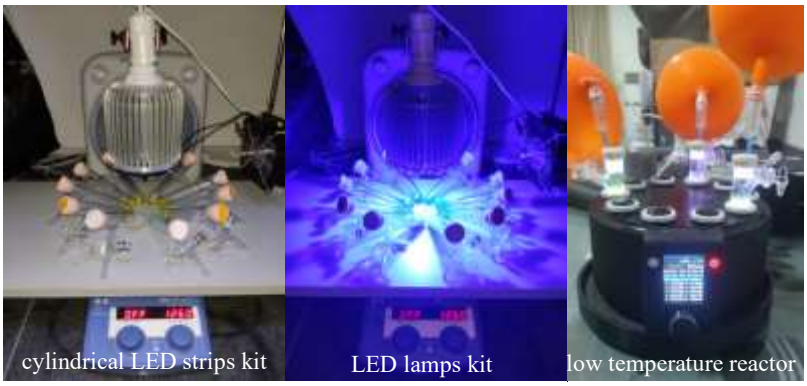
1. General information

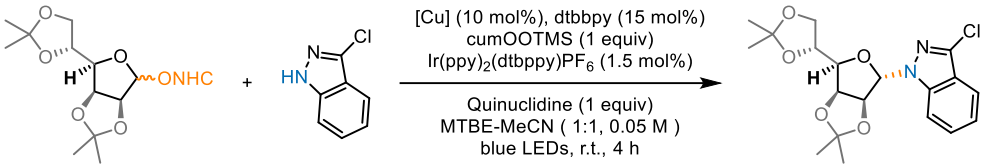
All purchased reagents were used without further purification unless otherwise specified. Solvents were dried over 4Å molecular sieves before use, unless stated otherwise. Reactions were stirred using Teflon-coated magnetic stirrers. Analytical thin-layer chromatography (TLC) was performed using 0.20 mm silica gel 60F plates with a 254 nm fluorescent indicator. TLC plates were visualized by ultraviolet light or by treatment with a spray of Pancaldi reagent {$(NH_4)_6MoO_4$, $Ce(SO_4)_2$, H_2SO_4, H_2O}, or a 10% H_2SO_4 in ethanol solution. Products were purified through flash column chromatography on silica gel (200-300 mesh). Melting points were determined using a WRX-4 visual melting point apparatus. Both melting points and boiling points are uncorrected. Infrared spectra were recorded using an IR Affinity-1 spectrometer. Nuclear magnetic resonance spectra (^{1}H NMR, ^{13}C NMR, and ^{19}F NMR) were acquired using a Bruker AV 400 spectrometer operating at the following frequencies: 400 MHz for ^{1}H, 100 MHz for ^{13}C, and 376 MHz for ^{19}F. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hz. The following abbreviations were used for multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. ESI mass spectra were recorded on an AB sciex Triple-TOF 5600+ mass instrument. The samples for the irradiation reaction were positioned at a distance of 5 cm from a 40 W blue LED lamp (λmax = 420 nm, purchased from Shenzhen Hongye Optoelectronics Technology Corporation). Alternatively, a parallel light low-temperature reactor (purchased from Shanghai Shanshi Technology Corporation) was also utilized. The reaction temperature was maintained at approximately 25ºC by fans or 0ºC by a low-temperature reactor.



2. Experimental section

2.1 Optimization of the reaction conditions

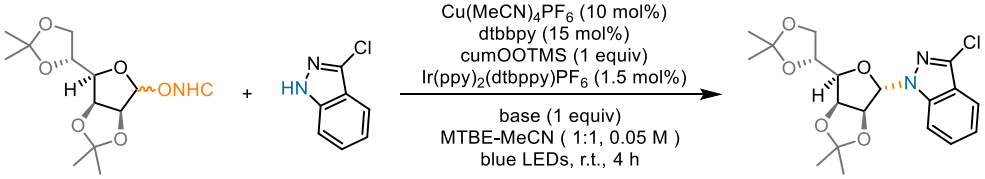
Table S1 | Evaluation of copper catalyst



1a' **1b** **2a**

Entry	Copper source	Yield (%)
1	$CuBr_2$	31
2	CuBr	35
3	CuTc	32
4	$Cu(hfac)_2$	38
5	$Cu(MeCN)_4PF_6$	42
6	$Cu(OAc)_2$	39
7	$Cu(acac)_2$	9
8	$Cu(OTf)_2$	30
9	$Cu(TMHD)_2$	42

Table S2 | Evaluation of base

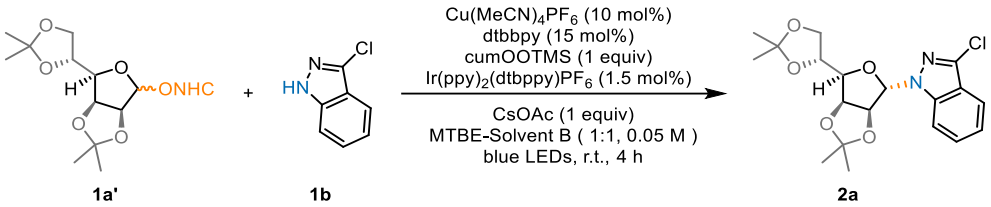


1a' **1b** **2a**

Entry	Base	Yield (%)
1	Quinuclidne	42
2	NaOAc	27
3	CsOAc	43
4	Cs_2CO_3	12
5	K_3PO_4	12
6	*t*-BuOLi	12

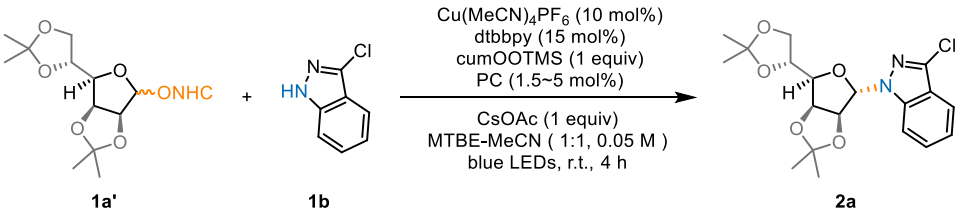
7	DABCO	11
8	CsF	13
9	Et_3N	—
10	DBU	9
11	TMG	41
12	BTMG	10

Table S3 | Evaluation of solvent B



Entry	Solvent B	Yield (%)
1	MeCN	43
2	MTBE	23
3	DCM	<10
4	1,4-Dioxane	20
5	Acetone	<10
6	THF	trace
7	DMF	7
8	DMSO	22
9	EtOAc	40
10	$PhCF_3$	26

Table S4 | Evaluation of PC source



Entry	PC source	Yield (%)
1	4CzIPN (5 mol%)	43
2	PTH1 (5 mol%)	trace

3	PTH2 (5 mol%)	trace
4	PTH4 (5 mol%)	13
5	PTH6 (5 mol%)	13
6	----	16
7	EoSinY (5 mol%)	15
8	Acridine (5 mol%)	14
9	$Ru(bpy)_3(PF_6)_2$ (1.5 mol%)	28
10	*fac*-$Ir(ppy)_3$ (1.5 mol%)	29
11	$Ir[(ppy)_2dtbppy]PF_6$ (1.5 mol%)	42
12	$Ir[dF(CF_3)ppy]_2(dtbppy)PF_6$ (1.5 mol%)	42

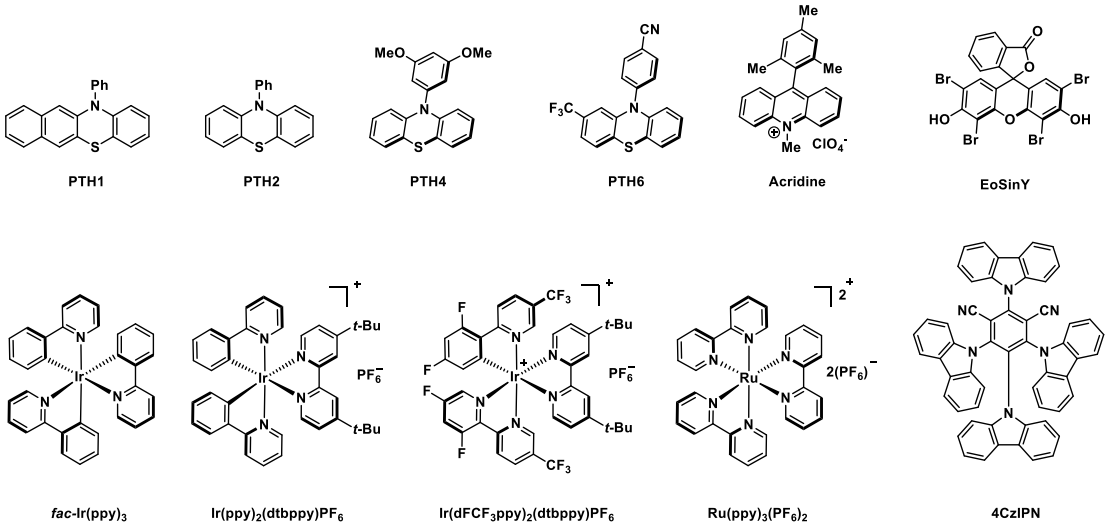
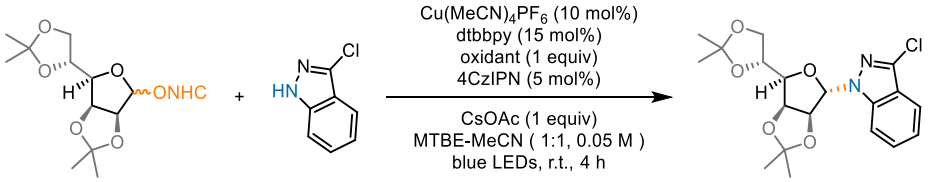


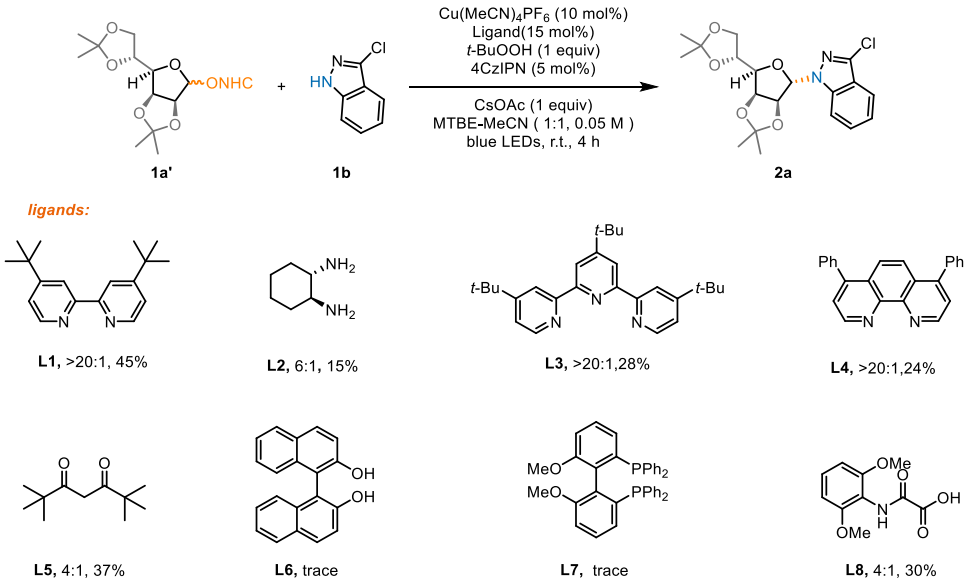
Table S5 | Evaluation of oxidants



Entry	Oxidant	Yield (%)
1	*t*-BuOOH (70% wt in H_2O)	45
2	cumOOH	41
3	（*t*-BuO)$_2$	-
4	BzOO*t*Bu	31
5	BPO	-
6	LPO	12

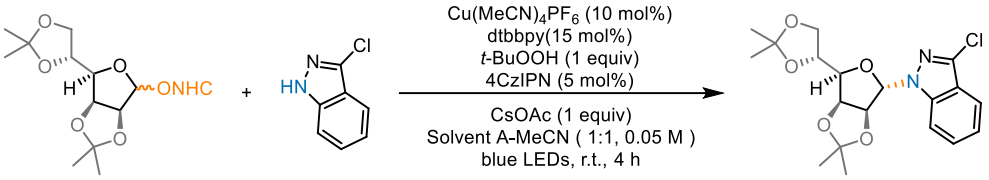
7	$Na_2S_2O_8$	-
8	DDQ	-
9	cumOOTMS	43
10	O_2	-
11	$PhI(OAc)_2$	5
12	$NaNO_2$	-

Table **S6** | Evaluation of ligands



Entry	Ligand source	Yield (%)	Ratio
1	-----	24	14:1
2	L1	45	>20:1
3	L2	15	6:1
4	L3	28	>20:1
5	L4	24	>20:1
6	L5	37	4:1
7	L6	trace	---
8	L7	trace	---
9	L8	30	4:1

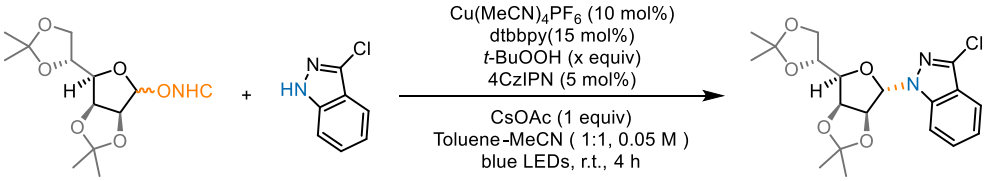
Table S7 | Evaluation of solvent A



1a' 1b 2a

Entry	Solvent A	Yield (%)
1	*t*-BuOMe	45
2	PhCl	54
3	$PhCF_3$	43
4	ethyl acetate	42
5	PhF	42
6	$(i\text{-Pr})_2O$	43
7	toluene	55
8	MeCN	n.r.

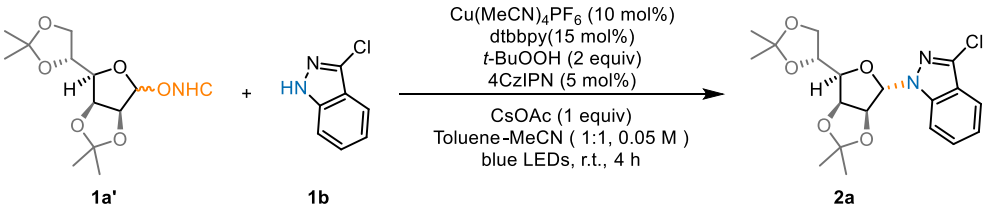
Table S8 | Evaluation of the oxidant loading



1a' 1b 2a

Entry	Oxidant loading (*t*-BuOOH)	Yield (%)
1	------	trace
2	1 equiv (70% wt in H_2O)	55
3	1.5 equiv (70% wt in H_2O)	62
4	2 equiv (70% wt in H_2O)	76
5	2.5 equiv (70% wt in H_2O)	75
6	2 equiv (5 M in decane)	87

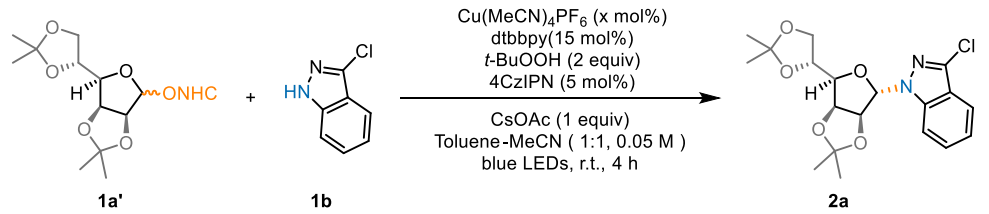
Table S9 | Evaluation of the loading of NHC-adduct (**1a'**)



1a' **1b** **2a**

Entry	**1a'**	Yield (%)
1	1.2 equiv	65
2	1.8 equiv	87
3	2.4 equiv	83
4	3.0 equiv	70

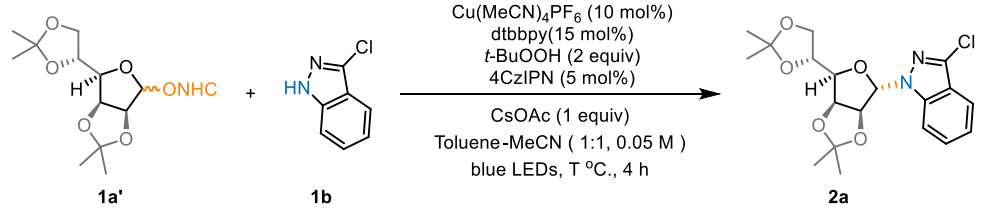
Table S10 | Evaluation of the loading of copper catalyst



1a' **1b** **2a**

Entry	Copper loading	Yield (%)*
1	20 mol%	85
2	15 mol%	86
3	10 mol%	87
4	5 mol%	70
5	1 mol%	12

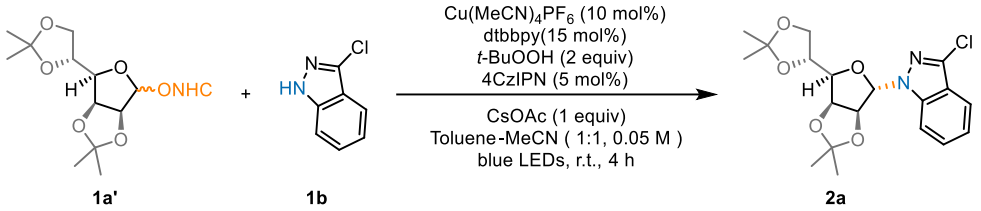
Table S11 | Evaluation of the temperature



1a' **1b** **2a**

Entry	T °C	Yield (%)*
1	0 °C	89
2	rt	87
3	50 °C	76

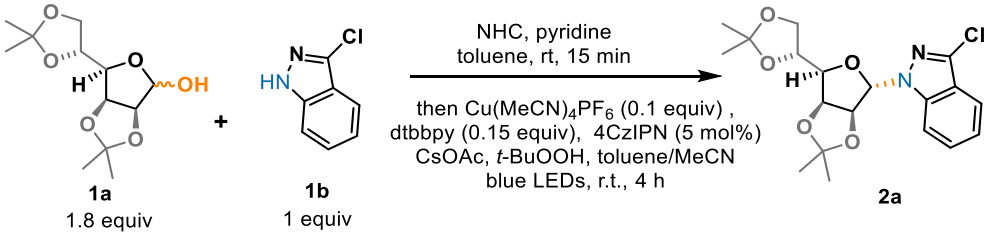
Table S12 | Evaluation of the light source

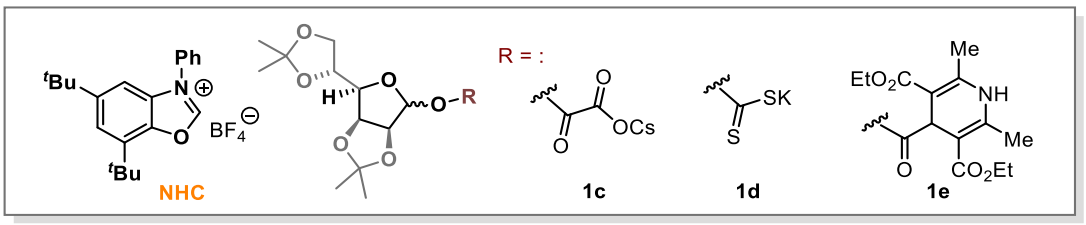


Entry	Deviations from standard	Yield (%)	N1:N2
1	12 W blue light	87	>20:1
2	12 W white light	85	9:1
3	Sun light	77	9:1

The reaction proceeded smoothly under both white light and sunlight, which can be attributed to the wide absorption range of the photocatalyst (250-470 nm). However, blue light showed better results.

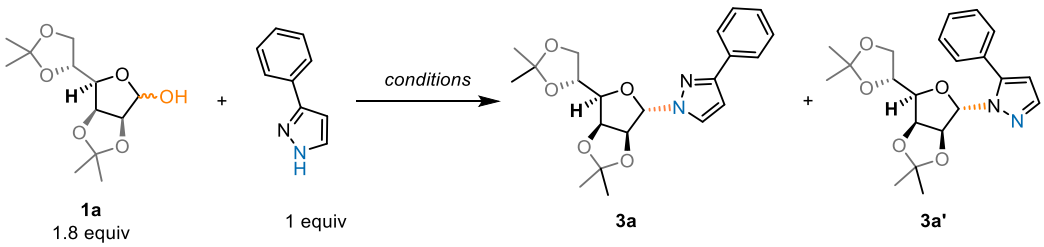
Table S13 | Varation from optimal conditions





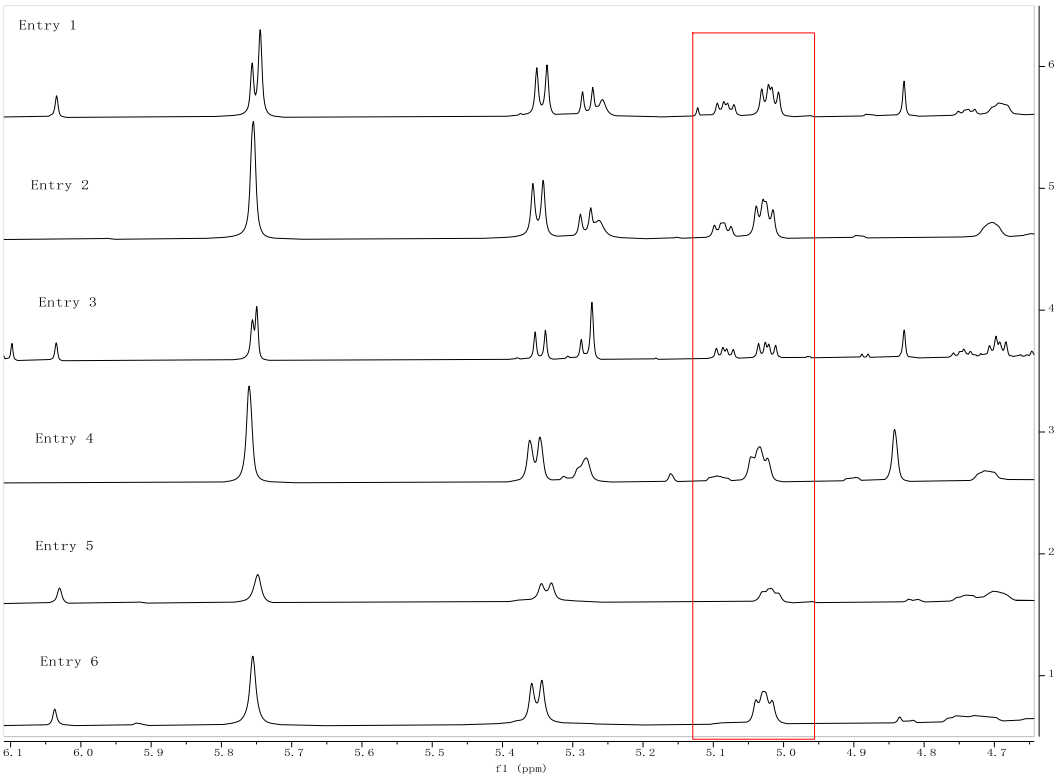
entry	Varation from optimal conditions	Yield(%)[c]
1	------	87%
	No [Cu]	N.D.
2	No base	N.D.
3	No PC	trace
4	No [O]	N.D.
5	No light	trace
6	No ligand	71 (N1:N2=9:1)
7	$Cu(TMHD)_2$ as catalyst	66 (N1:N2 = 3:2)
8	Bphen as ligand	75
9	BTMG as base	57
10	$Ir[dF(CF_3)ppy]_2(dtbppy)PF_6$ (1.5 mol%)	84
11	cumOOTMS as oxidant	81
12	DMSO as solvent	55
13	under air	86
14	10 equiv H_2O	78
15	**1c** instead of **1a**+NHC	N.D.
16	**1d** instead of **1a**+NHC	N.D.
17	**1e** instead of **1a**+NHC	trace

Table S14 | The regioselectivity of 3-phenyl pyrozole



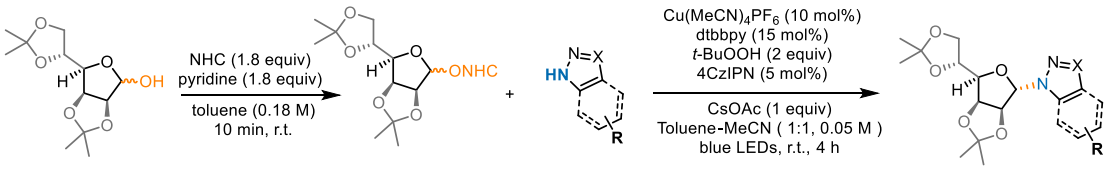
Entry	Conditions	Yield (%)	N1 : N2 (**3a**:**3a'**)
1	standard conditions	74	2.1:1
2	TMG as base	78	2.4:1
3	$Cu(TMHD)_2$ as cat.	54	1.3:1
4	$CH_3COOCH(CH_3)_2$ as solvent	74	5.1:1
5	Bphen as Ligand	55	>20:1
6	10 mol% CuTc + 10 mol% Bphen as cat.	71	>20:1

The regioselectivity of the regioisomers was determined from the C_3-H signals observed in the spectra shown below.



2.2 General procedures for N-glycosylation of heterocycles

Procedure A:



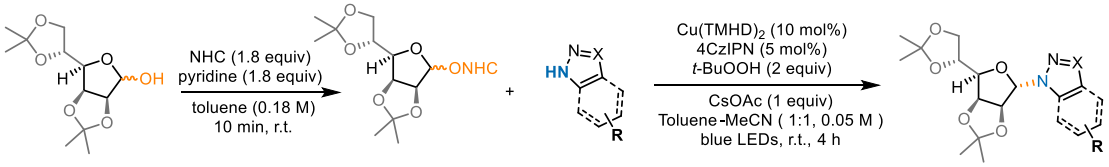
An oven-dried 10 mL Schlenk tube was charged with 1-hydroxylmannose **1a** (93.6 mg, 0.36 mmol, 1.8 equiv), NHC (142.4 mg, 0.36 mmol, 1.8 equiv) and a magnetic stir bar. After the Schlenk tube was vacuumed and refilled with nitrogen gas three times, dry toluene (2.0 mL) was added and the reaction was stirred at r.t. for 5 min. Then, pyridine (29.1 μL, 0.36 mmol, 1.8 equiv) was added dropwise at room temperature. The resulting solution was stirred at r.t. for 10 min. A white solid precipitated out during this time.

Another 10 mL Schlenk tube was charged with 1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN, 5 mg, 0.01 mmol, 0.05 equiv), $Cu(MeCN)_4PF_6$ (7.4 mg, 0.02 mmol, 0.1 equiv), dtbbpy (4,4-di-*tert*-butyl bipyridine, 8.0 mg, 0.03 mmol, 0.15 equiv), CsOAc (38.2 mg, 0.2 mmol, 1.0 equiv), *N*-heterocycle (0.2 mmol, 1.0 equiv) and a magnetic stir bar. This Schlenk tube was vacuumed and refilled with nitrogen gas three times. Dry acetonitrile (2.0

mL) was added to this Schlenk tube under an atmosphere of nitrogen and stirred at room temperature.

The toluene suspension was transferred to a 5 mL syringe under an atmosphere of nitrogen. Then a syringe filter and new needle were installed on the syringe, and the toluene solution was injected through the syringe filter into the MeCN solution. *t*-BuOOH (80 μL, 5-6 M in decane, 2.0 equiv) was added, before subjecting the reaction mixture to irradiation by 420 nm blue LEDs at room temperature for a duration of 4 hours. The organic layers were evaporated and then purified by flash column chromatography on silica gel.

Procedure B:

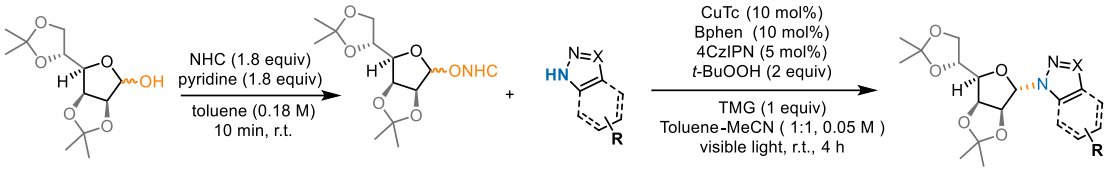


An oven-dried 10 mL Schlenk tube was charged with 1-hydroxylmannose **1a** (93.6 mg, 0.36 mmol, 1.8 equiv), NHC (142.4 mg, 0.36 mmol, 1.8 equiv) and a magnetic stir bar. After the Schlenk tube was vacuumed and refilled with nitrogen gas three times, dry toluene (2.0 mL) was added and the reaction was stirred at r.t. for 5 min. Then, pyridine (29.1 μL, 0.36 mmol, 1.8 equiv) was added dropwise at room temperature. The resulting solution was stirred at r.t. for 10 min. A white solid precipitated out during this time.

Another 10 mL Schlenk tube was charged with 4CzIPN (7.5 mg, 0.01 mmol, 0.05 equiv), 2,2,6,6-Tetramethyl-3,5-heptanedione copper (II) ($Cu(TMHD)_2$, 8.6 mg, 0.02 mmol, 0.1 equiv), CsOAc (38.2 mg, 0.2 mmol, 1.0 equiv), *N*-heterocycle (0.2 mmol, 1.0 equiv) and a magnetic stir bar. And this Schlenk tube was vacuumed and refilled with nitrogen gas three times. Dry MeCN (2.0 mL) was added to this Schlenk tube under an atmosphere of nitrogen and stirred at r.t.

The toluene suspension was transferred to a 5 mL syringe under an atmosphere of nitrogen. Then a syringe filter and new needle were installed on the syringe, and the toluene solution was injected through the syringe filter into the MeCN solution. *t*-BuOOH (80 μL, 5-6 M in decane, 2.0 equiv) was added, before subjecting the reaction mixture to irradiation by 420 nm blue LEDs at room temperature for a duration of 4 hours. The organic layers were evaporated and then purified by flash column chromatography on silica gel.

Procedure C:



An oven-dried 10 mL Schlenk tube was charged with 1-hydroxylmannose 1a (93.6 mg, 0.36 mmol, 1.8 equiv), NHC (142.4 mg, 0.36 mmol, 1.8 equiv) and a magnetic stir bar. After the Schlenk tube was vacuumed and refilled with nitrogen gas three times, dry toluene (2.0 mL) was added and the reaction was stirred at r.t. for 5 min. Then, pyridine (29.1 μL, 0.36 mmol, 1.8 equiv) was added dropwise at room temperature. The resulting solution was stirred at r.t. for 10 min. A white solid precipitated out during this time.

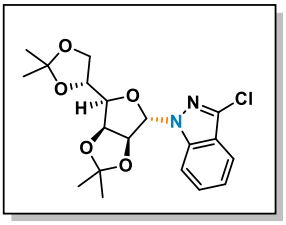
Another 10 mL Schlenk tube was charged with 4CzIPN (7.5 mg, 0.01 mmol, 0.05 equiv), copper(I) thiophene-2-carboxylate (CuTc, 3.8 mg, 0.02 mmol, 0.1 equiv), 4,7-diphenyl-1,10-phenanthroline (Bphen, 10.0 mg, 0.03 mmol, 0.15 equiv), 1,1,3,3-Tetramethylguanidine (TMG, 25.1 μL, 0.2 mmol, 1.0 equiv), *N*-heterocycle (0.2 mmol, 1.0 equiv) and a magnetic stir bar. This Schlenk tube was vacuumed and refilled with nitrogen gas three times. Dry acetonitrile (2.0 mL) was added to this Schlenk tube under an atmosphere of nitrogen and stirred at r.t..

The toluene suspension was transferred to a 5 mL syringe under an atmosphere of nitrogen. Then a syringe filter and new needle were installed on the syringe, and the toluene solution was injected through the syringe filter into the MeCN solution. *t*-BuOOH (80 μL, 5-6 M in decane, 2.0 equiv) was added, before subjecting the reaction mixture to irradiation by 420 nm blue LEDs at room temperature for a duration of 4 hours. The organic layers were evaporated and then purified by flash column chromatography on silica gel.

Table S15 | Synthesis method for substrate

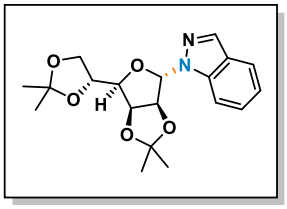
Substrate	Synthesis method
2a-2k, 3d, 3f, 3g, 8l	according to procedure A
3e, 4f, 4g, 5a-5n, 9f	according to procedure B
3h, 3i, 4i, 6b-6g, 7b-7d, 9b, 9c, 9e	according to procedure C
4a-4e, 4h, 9a	according to procedure B, but base CsOAc replaced with TMG
3a, 3b, 3c	according to procedure C, but base replaced TMG with CsOAc
6a	according to procedure C, but solvent MeCN replaced with DMSO
7a	according to procedure A, but base CsOAc replaced with TMG
8a-8k, 8m-8p	according to procedure A, but reaction irradiated at 0 °C, base CsOAc replaced with TMG
9d	according to procedure A, but solvent MeCN replaced with DMSO

3-Chloro-1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-indazole (2a)



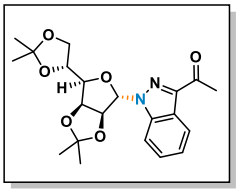
Purified by flash column chromatography (ethyl acetate/ petroleum ether = 1:33, v:v); white solid (67 mg, 85%), mp: 90-95 °C; $[\alpha]_D^{25}$ = +90.6 (*c* = 0.4, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 1H), 7.54–7.44 (m, 2H), 7.30–7.22 (m, 1H), 6.20 (s, 1H), 5.55 (d, *J* = 5.9 Hz, 1H), 5.16 (dd, *J* = 5.9, 3.8 Hz, 1H), 4.45–4.38 (m, 1H), 4.10 (dd, *J* = 7.3, 3.8 Hz, 1H), 4.04 (dd, *J* = 8.7, 6.3 Hz, 1H), 3.89 (dd, *J* = 8.7, 4.7 Hz, 1H), 1.59 (s, 3H), 1.42 (s, 3H), 1.40 (s, 3H), 1.35 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.3, 135.4, 128.5, 122.4, 121.86, 120.0, 113.0, 109.9, 109.3, 90.0, 84.6, 82.7, 80.6, 73.4, 66.7, 26.9, 26.1, 25.2, 24.5; **HRMS (ESI)** m/z cald for $C_{19}H_{24}ClN_2O_5^+$ $[M+H]^+$ 395.1368, found 395.1346.

1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-indazole (2b)



Purified by flash column chromatography (ethyl acetate/petroleum ether = 1:28, v:v); white solid (60 mg, 83%), mp: 96-98 °C; $[\alpha]_D^{25}$ = +78.3 (*c* = 0.8, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.46–7.37 (m, 1H), 7.24–7.16 (m, 1H), 6.27 (s, 1H), 5.59 (d, *J* = 5.9 Hz, 1H), 5.17 (dd, *J* = 5.9, 3.9 Hz, 1H), 4.46–4.37 (m, 1H), 4.10–3.99 (m, 2H), 3.87 (dd, *J* = 8.7, 4.4 Hz, 1H), 1.60 (s, 3H), 1.43 (s, 3H), 1.39 (s, 3H), 1.35 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.1, 134.9, 127.2, 124.5, 121.7, 121.2, 112.9, 109.4, 109.3, 89.7, 84.7, 82.6, 80.7, 73.4, 66.8, 27.0, 26.1, 25.3, 24.5; **HRMS (ESI)** m/z cald for $C_{19}H_{25}N_2O_5^+$ $[M+H]^+$ 361.1758, found 361.1747.

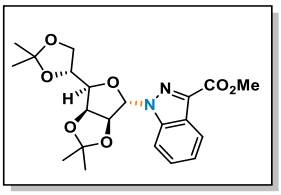
1-(1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-indazol-3-yl)ethan-1-one (2c)



Purified by flash column chromatography (acetone / petroleum ether = 1:24, v:v); Colorless oil (67 mg, 83%); $[\alpha]_D^{25}$ = -76.2 (*c* = 3.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37-8.33 (m, 1H), 7.60–7.52 (m, 1H), 7.50–7.42 (m, 1H), 7.37–7.31 (m, 1H), 6.31 (s, 1H), 5.60 (d, *J* = 5.8 Hz, 1H), 5.17 (dd, *J* = 5.9, 3.8 Hz, 1H), 4.45 (ddd, *J* = 7.4, 6.3, 4.5 Hz, 1H), 4.12 (dd, *J* = 7.3, 3.8 Hz, 1H), 4.04 (dd, *J* = 8.7, 6.3 Hz, 1H), 3.90 (dd, *J* = 8.7, 4.5 Hz, 1H), 2.67 (s, 3H), 1.60 (s, 3H), 1.44 (s, 3H), 1.38 (s, 3H), 1.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.7, 143.6, 141.2,

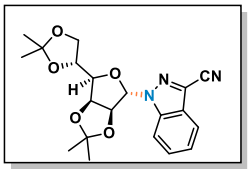
127.8, 124.3, 123.1, 122.7, 113.3, 109.6, 109.3, 90.3, 84.6, 83.0, 80.6, 73.2, 66.6, 26.9, 26.8, 26.1, 25.2, 24.6; **HRMS (ESI)** m/z cald for $NaC_{21}H_{26}N_2O_6^+$ $[M+Na]^+$ 425.1683, found 425.1676.

Methyl1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-indazole-3-carboxylate (2d)



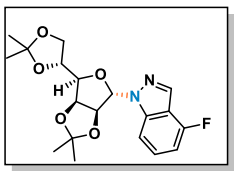
Purified by flash column chromatography (acetone/petroleum ether = 1:20, v:v); Colorless oil (54 mg, 64%); $[\alpha]_D^{25}$ = +59.2 (*c* = 1.2, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23-8.17 (m, 1H), 7.63-7.58 (m, 1H), 7.49-7.45 (m, 1H), 7.38-7.32 (m, 1H), 6.31 (s, 1H), 5.72 (d, *J* = 5.8 Hz, 1H), 5.20 (dd, *J* = 5.9, 3.7 Hz, 1H), 4.43 (ddd, *J* = 7.2, 6.4, 4.7 Hz, 1H), 4.07–4.02 (m, 5H), 3.87 (dd, *J* = 8.7, 4.7 Hz, 1H), 1.59 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H), 1.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.0, 141.1, 136.6, 127.7, 123.9, 123.9, 122.5, 113.1, 110.1, 109.3, 90.6, 84.3, 82.8, 80.5, 73.2, 66.7, 52.2, 26.9, 26.1, 25.2, 24.6; **HRMS (ESI)** m/z cald for $C_{21}H_{27}N_2O_7^+$ $[M+H]^+$ 419.1813, found 419.1805.

1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-indazole-3-carbonitrile (2e)



Purified by flash column chromatography (acetone/petroleum ether = 1:17, v:v); white solid (49 mg, 64%), mp: 132-134°C; $[\alpha]_D^{25}$ = +62.1 (*c* = 0.4, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88-7.85 (m, 1H), 7.70–7.62 (m, 1H), 7.60–7.50 (m, 1H), 7.44–7.38 (m, 1H), 6.30 (s, 1H), 5.58 (d, *J* = 5.9 Hz, 1H), 5.16 (dd, *J* = 5.9, 3.8 Hz, 1H), 4.46–4.38 (m, 1H), 4.07–4.02 (m, 2H), 3.89 (dd, *J* = 8.8, 4.5 Hz, 1H), 1.60 (s, 3H), 1.43 (s, 3H), 1.40 (s, 3H), 1.35 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.1, 128.8, 125.5, 124.5, 119.9, 119.8, 113.4, 113.3, 110.6, 109.5, 90.6, 84.5, 83.1, 80.4, 73.2, 66.6, 27.0, 26.1, 25.2, 24.5; **HRMS (ESI)** m/z cald for $C_{20}H_{24}N_3O_5^+$ $[M+H]^+$ 386.1710, found 386.1710.

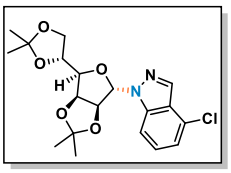
1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-4-fluoro-1*H*-indazole (2f)



Purified by flash column chromatography (acetone / petroleum ether = 1:27, v:v); Colorless oil (70 mg, 92%); $[\alpha]_D^{25}$ = +103.2 (*c* = 1.4, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.38–7.28 (m, 2H), 6.83 (dd,

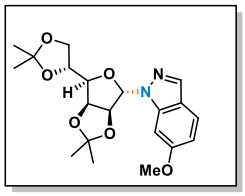
J = 9.8, 7.2 Hz, 1H), 6.23 (s, 1H), 5.57 (d, *J* = 5.8 Hz, 1H), 5.16 (dd, *J* = 5.9, 3.8 Hz, 1H), 4.42 (td, *J* = 6.9, 4.5 Hz, 1H), 4.13–3.98 (m, 2H), 3.83-3.91 (m, 1H), 1.59 (s, 3H), 1.42 (s, 3H), 1.39 (s, 3H), 1.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.8 (d, *J* = 253.0 Hz), 141.5 (d, *J* = 8.8 Hz), 130.2, 127.1 (d, *J* = 7.6 Hz), 113.7 (d, *J* = 23.2 Hz), 111.9, 108.2, 104.9 (d, *J* = 18.4 Hz), 104.4 (d, *J* = 4.2 Hz), 88.9, 83.5, 81.6 , 79.5, 72.2, 65.6, 25.8, 24.9, 24.1, 23.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.73 (dd, *J* = 9.8, 4.6 Hz, 1F); **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$) δ -117.73 (s, 1F); **HRMS (ESI)** m/z cald for $C_{19}H_{24}FN_2O_5^+$ $[M+H]^+$ 379.1664, found 379.1674.

4-Chloro-1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-indazole (2g)



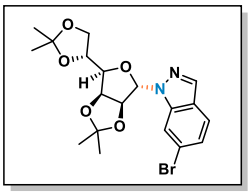
Purified by flash column chromatography (acetone/petroleum ether = 1:35, v:v); Colorless oil (59 mg, 76%); $[\alpha]_D^{25}$ = +84.3 (*c* = 2.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.32 (dd, *J* = 8.4, 7.4 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 6.22 (s, 1H), 5.58 (d, *J* = 5.9 Hz, 1H), 5.16 (dd, *J* = 5.9, 3.8 Hz, 1H), 4.41 (ddd, *J* = 7.5, 6.3, 4.5 Hz, 1H), 4.11–3.97 (m, 2H), 3.86 (dd, *J* = 8.7, 4.5 Hz, 1H), 1.59 (s, 3H), 1.42 (s, 3H), 1.39 (s, 3H), 1.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.0, 133.5, 127.8, 126.9, 123.8, 121.3, 113.0, 109.3, 108.1, 90.0, 84.6, 82.8, 80.7, 73.3, 66.8, 26.9, 26.1, 25.3, 24.5; **HRMS (ESI)** m/z cald for $C_{19}H_{24}ClN_2O_5^+$ $[M+H]^+$ 395.1368, found 395.1362.

1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-6-methoxy-1H-indazole (2h)



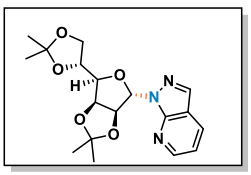
Purified by flash column chromatography (ethyl acetate/petroleum ether = 1:25, v:v); white solid (54 mg, 67%), mp: 140-141 °C; $[\alpha]_D^{25}$ = +101.4 (*c* = 2.7, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 6.87 (d, *J* = 2.0 Hz, 1H), 6.84 (dd, *J* = 8.8, 2.1 Hz, 1H), 6.19 (s, 1H), 5.58 (d, *J* = 5.9 Hz, 1H), 5.16 (dd, *J* = 5.9, 3.8 Hz, 1H), 4.42 (ddd, *J* = 7.6, 6.3, 4.4 Hz, 1H), 4.08 (dd, *J* = 7.6, 3.9 Hz, 1H), 4.04 (dd, *J* = 8.7, 6.3 Hz, 1H), 3.89 (dd, *J* = 8.7, 4.4 Hz, 1H), 3.86 (s, 3H), 1.59 (s, 3H), 1.42 (s, 3H), 1.39 (s, 3H), 1.34 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.9, 141.3, 134.7, 121.8, 118.9, 113.8, 112.7, 109.2, 90.5, 89.5, 84.5, 82.4, 80.6, 73.3, 66.7, 55.5, 26.9, 26.0, 25.1, 24.4; **HRMS (ESI)** m/z cald for $C_{20}H_{27}N_2O_6^+$ $[M+H]^+$ 391.1864, found 391.1854

6-Bromo-1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-indazole (2i)



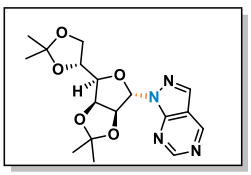
Purified by flash column chromatography (ethyl acetate/petroleum ether = 1:25, v:v); white solid (57 mg, 65%), mp: 140-143 °C; $[\alpha]_D^{25}$ = +139.0 (*c* = 2.5, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.73 (s, 1H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.29 (dd, *J* = 8.5, 1.6 Hz, 1H), 6.17 (s, 1H), 5.57 (d, *J* = 5.9 Hz, 1H), 5.13 (dd, *J* = 5.9, 3.8 Hz, 1H), 4.41 (ddd, *J* = 7.6, 6.3, 4.5 Hz, 1H), 4.08–4.01 (m, 2H), 3.88 (dd, *J* = 8.8, 4.5 Hz, 1H), 1.58 (s, 3H), 1.41 (s, 3H), 1.39 (s, 3H), 1.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.8, 135.0, 125.3, 123.3, 122.3, 121.7, 113.0, 112.6, 109.3, 89.9, 84.5, 82.7, 80.6, 73.3, 66.7, 26.9, 26.1, 25.2, 24.5; **HRMS (ESI)** m/z cald for $C_{19}H_{24}BrN_2O_5$ $[M+H]^+$ 439.0863, found 439.0872.

1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-pyrazolo[3,4-*b*]pyridine (2j)



Purified by flash column chromatography (ethyl acetate/petroleum ether = 1:12, v:v); white solid (44 mg, 61%), mp: 107-109 °C; $[\alpha]_D^{25}$ = +77.8 (*c* = 2.1, $CHCl_3$); **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 8.60 (dd, *J* = 4.5, 1.5 Hz, 1H), 8.30 (d, *J* = 8.0 Hz, 2H), 7.30 (dd, *J* = 8.0, 4.5 Hz, 1H), 6.50 (s, 1H), 5.35 (d, *J* = 5.8 Hz, 1H), 5.14 (dd, *J* = 5.9, 3.3 Hz, 1H), 4.36–4.26 (m, 2H), 3.95 (dd, *J* = 8.4, 5.8 Hz, 1H), 3.73 (dd, *J* = 8.5, 5.0 Hz, 1H), 1.49 (s, 3H), 1.33 (s, 3H), 1.26 (s, 4H), 1.23 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 150.9, 150.4, 135.4, 132.1, 119.0, 116.4, 113.2, 108.9, 89.1, 85.4, 83.6, 81.3, 73.7, 66.6, 27.5, 26.9, 26.0, 25.3; **HRMS (ESI)** m/z cald for $C_{18}H_{24}N_3O_5^+$ $[M+H]^+$ 362.1710, found 362.1699.

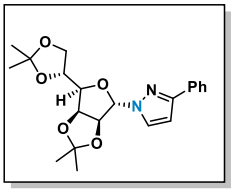
1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-pyrazolo[3,4-*d*]pyrimidine (2k)



Purified by flash column chromatography (ethyl acetate/ petroleum ether = 2:1, v:v); Colorless oil (38 mg, 52%); $[\alpha]_D^{25}$ = +71.8 (*c* = 1.9, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 9.21 (s, 1H), 9.04 (s, 1H), 8.15 (s, 1H), 6.61 (s, 1H), 5.40 (d, *J* = 5.9 Hz, 1H), 5.20 (dd, *J* = 5.9, 3.8 Hz, 1H), 4.42 (ddd, *J* = 7.7, 6.2, 4.3 Hz, 1H), 4.26 (dd, *J* = 7.7, 3.8 Hz, 1H), 4.03 (dd, *J* = 8.8, 6.2 Hz, 1H), 3.90 (dd, *J* = 8.8, 4.3 Hz, 1H), 1.57 (s, 3H), 1.40 (s, 6H), 1.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 155.7, 152.9, 152.6, 133.9, 114.7, 113.4, 109.3, 89.0, 84.9, 83.4, 80.9, 73.4, 66.8, 27.0, 26.2, 25.3, 24.71; **HRMS (ESI)** m/z cald for $C_{17}H_{23}N_4O_5^+$ $[M+H]^+$ 363.1663, found

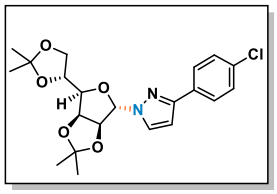
363.1655.

1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-3-phenyl-1*H*-pyrazole (3a)



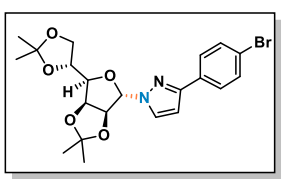
Purified by flash column chromatography (ethyl acetate/petroleum ether = 1:30, v:v); white solid (57 mg, 74%), mp: 77-78 °C; $[\alpha]_D^{25}$ = -50.1 (*c* = 1.4, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82–7.75 (m, 2H), 7.54 (d, *J* = 2.4 Hz, 1H), 7.44–7.37 (m, 2H), 7.36–7.28 (m, 1H), 6.59 (d, *J* = 2.4 Hz, 1H), 5.85 (s, 1H), 5.46 (d, *J* = 5.9 Hz, 1H), 5.13 (dd, *J* = 5.9, 3.8 Hz, 1H), 4.47–4.40 (m, 1H), 4.35 (dd, *J* = 7.2, 3.9 Hz, 1H), 4.09 (dd, *J* = 8.6, 6.3 Hz, 1H), 4.00 (dd, *J* = 8.6, 4.8 Hz, 1H), 1.56 (s, 3H), 1.43 (s, 3H), 1.40 (s, 3H), 1.37 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.8, 133.2, 131.1, 128.7, 128.1, 125.9, 113.0, 109.2, 103.7, 92.9, 84.9, 83.1, 80.7, 73.4, 66.7, 26.9, 26.1, 25.3, 24.6; **HRMS (ESI)** m/z cald for $C_{21}H_{27}N_2O_5^+$ $[M+H]^+$ 387.1914, found 387.1907.

3-(4-Chlorophenyl)-1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-pyrazole (3b)



Purified by flash column chromatography (acetone / petroleum ether = 1:40, v:v); white solid (64 mg, 77%), mp: 127-133 °C; $[\alpha]_D^{25}$ = -62.2 (*c* = 0.8, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74–7.67 (m, 2H), 7.54 (d, *J* = 2.4 Hz, 1H), 7.39–7.33 (m, 2H), 6.56 (d, *J* = 2.4 Hz, 1H), 5.84 (s, 1H), 5.43 (d, *J* = 5.9 Hz, 1H), 5.10 (dd, *J* = 5.9, 3.8 Hz, 1H), 4.47–4.40 (m, 1H), 4.32 (dd, *J* = 7.0, 3.8 Hz, 1H), 4.08 (dd, *J* = 8.6, 6.3 Hz, 1H), 3.99 (dd, *J* = 8.7, 4.8 Hz, 1H), 1.56 (s, 3H), 1.43 (s, 3H), 1.40 (s, 3H), 1.37 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.7, 133.8, 131.7, 131.3, 128.9, 127.1, 113.1, 109.3, 103.7 (d, *J* = 3.4 Hz), 93.0 (d, *J* = 3.8 Hz), 84.9 (d, *J* = 5.5 Hz), 83.1, 80.7 (d, *J* = 2.1 Hz), 73.4, 66.7, 27.0, 26.1, 25.3, 24.6; **HRMS (ESI)** m/z cald for $C_{21}H_{26}ClN_2O_5^+$ $[M+H]^+$ 421.1525, found 421.1518.

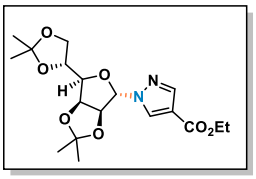
3-(4-bromophenyl)-1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-pyrazole (3c)



Purified by flash column chromatography (acetone/petroleum ether = 1:40, v:v); colorless oil (79 mg, 85%); $[\alpha]_D^{25}$ = -56.2 (*c* = 1.5, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.6 Hz, 2H), 7.48–7.41 (m, 3H), 6.48 (d, *J* = 2.4 Hz, 1H), 5.77 (s, 1H), 5.35 (d, *J* = 5.9 Hz, 1H), 5.03 (dd, *J* = 5.9, 3.8 Hz, 1H), 4.40–4.31 (m, 1H), 4.24 (dd, *J* = 7.1, 3.8 Hz, 1H), 4.01 (dd,

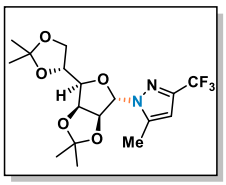
J = 8.6, 6.3 Hz, 1H), 3.92 (dd, *J* = 8.7, 4.8 Hz, 1H), 1.48 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H), 1.29 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.7, 132.2, 131.8, 131.3, 127.4, 122.0, 113.1, 109.2, 103.7 (d, *J* = 2.6 Hz), 93.0 (d, *J* = 3.5 Hz), 84.8 (d, *J* = 3.7 Hz), 83.1, 80.7, 73.4, 66.6, 26.9, 26.1, 25.2, 24.6; **HRMS (ESI)** m/z cald for $C_{21}H_{25}BrN_2O_5Na^+$ $[M+Na]^+$ 487.0839, found 487.0840.

Ethyl 1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-pyrazole-3-carboxylate (3d)



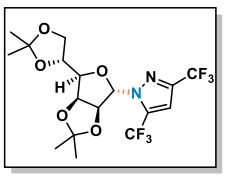
Purified by flash column chromatography (ethyl acetate/ petroleum ether = 1:12, v:v); colorless oil (47 mg, 62%); $[\alpha]_D^{25}$ = -56.2 (*c* = 1.7, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.90 (s, 1H), 5.81 (s, 1H), 5.35 (d, *J* = 5.9 Hz, 1H), 5.05 (dd, *J* = 5.9, 3.8 Hz, 1H), 4.43–4.36 (m, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.21 (dd, *J* = 7.3, 3.8 Hz, 1H), 4.06 (dd, *J* = 8.7, 6.3 Hz, 1H), 3.95 (dd, *J* = 8.7, 4.5 Hz, 1H), 1.53 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H), 1.36–1.31 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.7, 141.9, 133.0, 116.0, 113.2, 109.3, 93.1, 84.6, 83.2, 80.4, 73.1, 66.6, 60.4, 26.8, 25.9, 25.1, 24.4, 14.4; **HRMS (ESI)** m/z cald for $C_{18}H_{27}N_2O_7^+$ $[M+H]^+$ 383.1813, found 383.1820.

1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-5-methyl-3-(trifluoromethyl)-1*H*-pyrazole (3e)



Purified by flash column chromatography (ethyl acetate/ petroleum ether = 1:28, v:v); Colorless oil (61 mg, 77%); $[\alpha]_D^{25}$ = +20.9 (*c* = 0.8, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.30 (s, 1H), 5.86 (s, 1H), 5.46 (d, *J* = 5.8 Hz, 1H), 5.08 (dd, *J* = 5.9, 4.0 Hz, 1H), 4.44–4.32 (m, 1H), 4.10–4.02 (m, 2H), 3.94 (dd, *J* = 8.7, 4.7 Hz, 1H), 2.36 (s, 3H), 1.41 (s, 3H), 1.39 (s, 3H), 1.35 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.4 (q, *J* = 38.1 Hz), 141.4, 121.3 (q, *J* = 268.6 Hz), 113.0, 109.3, 104.8, 89.9, 84.3, 82.4, 80.6, 73.3, 66.5, 26.9, 26.0, 25.3, 24.5, 11.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.46 (s, 3F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -62.46 (s, 3F); **HRMS (ESI)** m/z cald for $C_{17}H_{24}F_3N_2O_5^+$ $[M+H]^+$ 393.1632, found 393.1630.

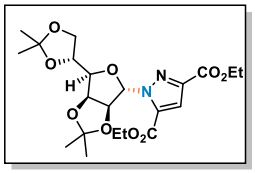
1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-3,5-bis(trifluoromethyl)-1*H*-pyrazole (3f)



Purified by flash column chromatography (ethyl acetate/ petroleum ether = 1:40, v:v); Colorless oil (52 mg, 58%); $[\alpha]_D^{25}$ = +30.2 (*c* = 0.7, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.94 (s, 1H), 6.06 (s, 1H), 5.42 (d, *J* = 5.8

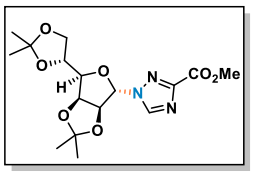
Hz, 1H), 5.09 (dd, *J* = 5.9, 3.9 Hz, 1H), 4.45-4.37 (m, 1H), 4.12 (dd, *J* = 7.3, 3.9 Hz, 1H), 4.06 (dd, *J* = 8.9, 6.2 Hz, 1H), 3.95 (dd, *J* = 8.8, 4.5 Hz, 1H), 1.55 (s, 3H), 1.41 (s, 3H), 1.40 (s, 3H), 1.36 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.8 (q, *J* = 39.6 Hz), 134.5 (q, *J* = 41.0 Hz), 120.2 (q, *J* = 269.1 Hz), 119.0 (q, *J* = 269.0 Hz), 113.5, 109.5, 107.1, 92.2, 84.7, 83.5, 80.3, 73.2, 66.5, 26.9, 26.0, 25.4, 24.5; **^{19}F NMR** (376 MHz, $CHCl_3$) δ -59.04 (s, 3F), -62.56 (s, 3F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -59.04 (s, 3F), -62.56 (s, 3F); **HRMS (ESI)** m/z cald for $C_{17}H_{21}F_6N_2O_5^+$ $[M+H]^+$ 447.1349, found 447.1332.

Diethyl 1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-pyrazole-3,5-dicarboxylate (3g)



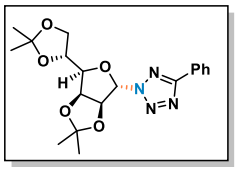
Purified by flash column chromatography (ethyl acetate/ petroleum ether = 1:25, v:v); Colorless oil (62 mg, 69%), $[\alpha]_D^{25}$ = +26.1 (*c* = 1.2, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 6.96 (s, 1H), 5.42 (d, *J* = 5.9 Hz, 1H), 5.14 (dd, *J* = 5.9, 3.8 Hz, 1H), 4.47–4.33 (m, 5H), 4.18 (dd, *J* = 7.6, 3.8 Hz, 1H), 4.04 (dd, *J* = 8.8, 6.2 Hz, 1H), 3.91 (dd, *J* = 8.7, 4.6 Hz, 1H), 1.55 (s, 3H), 1.42–1.34 (m, 15H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.4, 158.8, 143.5, 134.6, 114.5, 113.1, 109.3, 91.9, 84.8, 83.1, 80.8, 73.3, 66.8, 61.9, 61.4, 27.0, 26.1, 25.3, 24.7, 14.4, 14.3; **HRMS (ESI)** m/z cald for $NaC_{21}H_{30}N_2O_9^+$ $[M+Na]^+$ 477.1844, found 477.1835.

Methyl 1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-1,2,4-triazole-3-carboxylate (3h)



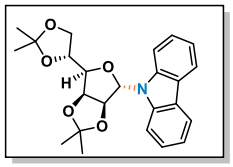
Purified by flash column chromatography (ethyl acetate/petroleum ether = 1:4, v:v); white solid (44 mg, 72%), mp: 124-125 °C; $[\alpha]_D^{25}$ = +66.2 (*c* = 1.2, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 6.92 (s, 1H), 5.22 (d, *J* = 5.9 Hz, 1H), 5.08 (dd, *J* = 5.9, 3.8 Hz, 1H), 4.39 (ddd, *J* = 7.8, 6.2, 4.3 Hz, 1H), 4.24 (dd, *J* = 7.7, 3.8 Hz, 1H), 4.04 (dd, *J* = 8.8, 6.2 Hz, 1H), 4.01 (s, 3H), 3.90 (dd, *J* = 8.8, 4.4 Hz, 1H), 1.54 (s, 3H), 1.41 (s, 3H), 1.37 (s, 3H), 1.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 151.2, 144.8, 113.4, 109.4, 91.3, 85.2, 83.6, 80.6, 73.2, 66.8, 53.5, 27.0, 26.1, 25.3, 24.6; **HRMS (ESI)** m/z cald for $C_{16}H_{24}N_3O_7^+$ $[M+H]^+$ 370.1609, found 370.1622.

2-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-5-phenyl-2*H*-tetrazole (3i)



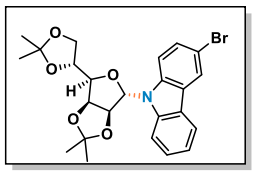
Purified by flash column chromatography (ethyl acetate/petroleum ether = 1:4.5, v:v); Colorless oil (49 mg, 65%); $[\alpha]_D^{25}$ = +16.6 (*c* = 0.9, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17-8.12 (m, 2H), 7.53-7.47 (m, 3H), 6.49 (s, 1H), 5.35 (d, *J* = 5.8 Hz, 1H), 5.18 (dd, *J* = 5.9, 3.7 Hz, 1H), 4.47 (ddd, *J* = 7.5, 6.2, 4.5 Hz, 1H), 4.35 (dd, *J* = 7.5, 3.7 Hz, 1H), 4.09 (dd, *J* = 8.9, 6.2 Hz, 1H), 3.98 (dd, *J* = 8.9, 4.5 Hz, 1H), 1.59 (s, 3H), 1.44 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.5, 129.7, 127.9, 126.0, 125.8, 112.8, 108.4, 93.2, 83.8, 82.8, 79.1, 71.9, 65.5, 25.8, 25.0, 24.1, 23.5; **HRMS (ESI)** m/z cald for $C_{19}H_{25}N_4O_5^+$ $[M+H]^+$ 389.1819, found 389.1816.

9-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-9*H*-carbazole (4a)



Purified by flash column chromatography (ethyl acetate/petroleum ether = 1:28, v:v); white solid (50 mg, 61%), mp: 84-85 °C; $[\alpha]_D^{25}$ = +15.2 (*c* = 1.9, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.09-8.06 (m, 2H), 7.48–7.39 (m, 4H), 7.29–7.24 (m, 2H), 6.39 (d, *J* = 1.5 Hz, 1H), 5.52 (dd, *J* = 5.9, 1.6 Hz, 1H), 5.21 (dd, *J* = 5.9, 3.7 Hz, 1H), 4.55–4.49 (m, 1H), 4.42 (dd, *J* = 7.2, 3.7 Hz, 1H), 4.11 (dd, *J* = 8.8, 6.2 Hz, 1H), 4.04 (dd, *J* = 8.9, 4.7 Hz, 1H), 1.66 (s, 3H), 1.44 (s, 6H), 1.39 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 139.6, 126.3, 124.2, 120.5, 120.2, 113.9, 110.1, 109.4, 92.2, 84.5, 83.6, 81.2, 73.7, 66.7, 27.0, 26.6, 25.4, 24.9. **HRMS (ESI)** m/z cald for $C_{24}H_{28}NO_5^+$ $[M+H]^+$ 410.1962, found 410.1953.

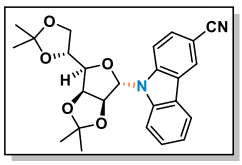
3-Bromo-9-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-9*H*-carbazole (4b)



Purified by flash column chromatography (ethyl acetate/petroleum ether = 1:30, v:v); Colorless oil (64 mg, 66%); $[\alpha]_D^{25}$ = +33.3 (*c* = 2.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 1.9 Hz, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.53 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.48 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.33 (d, *J* = 8.8 Hz, 1H), 7.31-7.26 (m, 1H), 6.33 (d, *J* = 1.6 Hz, 1H), 5.45 (dd, *J* = 5.9, 1.6 Hz, 1H), 5.17 (dd, *J* = 5.8, 3.6 Hz, 1H), 4.56–4.49 (m, 1H), 4.41 (dd, *J* = 6.9, 3.7 Hz, 1H), 4.12 (dd, *J* = 8.8, 6.3 Hz, 1H), 4.06 (dd, *J* = 8.9, 4.8 Hz, 1H), 1.66 (s, 3H), 1.45 (s, 3H), 1.44 (s, 3H), 1.40 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.8, 138.3, 128.9, 127.0, 125.9, 123.2, 123.2, 120.7, 120.6, 114.1, 113.1, 111.7, 110.4, 109.4, 92.5,

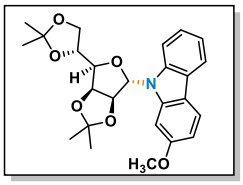
84.6, 83.6, 81.0, 73.7, 66.6, 27.0, 26.6, 25.3, 25.0; **HRMS (ESI)** m/z cald for $C_{24}H_{27}BrNO_5^+$ $[M+H]^+$ 488.1067, found 488.1070.

9-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-9*H*-carbazole-3-carbonitrile (4c)



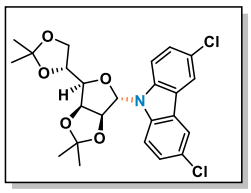
Purified by flash column chromatography (ethyl acetate/ petroleum ether = 1:25, v:v); white solid (55 mg, 63%), mp: 79-80 °C; $[\alpha]_D^{25}$ = +33.4 (*c* = 1.3, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 1.6 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.61 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.51–7.42 (m, 2H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 6.28 (d, *J* = 1.7 Hz, 1H), 5.32 (dd, *J* = 5.8, 1.7 Hz, 1H), 5.06 (dd, *J* = 5.8, 3.6 Hz, 1H), 4.52–4.37 (m, 2H), 4.04 (qd, *J* = 8.9, 5.5 Hz, 2H), 1.59 (s, 3H), 1.39 (s, 3H), 1.36 (s, 3H), 1.33 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.4, 139.8, 129.5, 127.7, 125.1, 124.3, 123.1, 121.5, 120.9, 120.2, 114.3, 111.2, 110.8, 109.4, 103.1, 93.0, 84.9, 83.7, 80.8, 73.7, 66.4, 26.9, 26.7 , 25.3, 25.0; **HRMS (ESI)** m/z cald for $C_{25}H_{27}N_2O_5^+$ $[M+H]^+$ 435.1914., found 435.1919.

9-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-3-methoxy-9*H*-carbazole (4d)



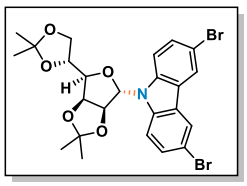
Purified by flash column chromatography (ethyl acetate/petroleum ether = 1:30, v:v); white solid (52 mg, 59%), mp: 124-125 °C; $[\alpha]_D^{25}$ = +21.1 (*c* = 1.6, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 16.8, 8.1 Hz, 2H), 7.32–7.24 (m, 2H), 7.18-7.13 (m, 1H), 6.87 (d, *J* = 2.1 Hz, 1H), 6.80 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.24 (d, *J* = 1.4 Hz, 1H), 5.39 (dd, *J* = 5.8, 1.4 Hz, 1H), 5.09 (dd, *J* = 5.9, 3.6 Hz, 1H), 4.48-4.42 (m, 1H), 4.37 (dd, *J* = 7.0, 3.7 Hz, 1H), 4.06–3.97 (m, 2H), 3.84 (s, 3H), 1.58 (s, 3H), 1.36 (d, *J* = 5.7 Hz, 6H), 1.31 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.3, 141.0, 139.4, 124.9, 124.4, 121.0, 120.3, 119.6, 117.9, 113.9, 109.9, 109.3, 108.4, 95.2, 92.4, 84.6, 83.5, 81.1, 73.7, 66.6, 55.9, 27.0, 26.6, 25.3, 24.9; **HRMS (ESI)** m/z cald for $C_{25}H_{30}NO_6^+$ $[M+H]^+$ 440.2068., found 440.2072.

3,6-dichloro-9-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-9*H*-carbazole (4e)



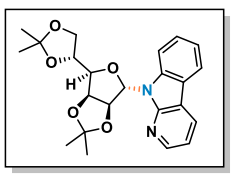
Purified by flash column chromatography (ethyl acetate/ petroleum ether = 1:25, v:v); white solid (56 mg, 59%), mp: 180-181 °C; $[\alpha]_D^{25}$ = +35.4 (*c* = 1.2, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 2.0 Hz, 2H), 7.42 (dd, *J* = 8.8, 2.1 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 6.28 (d, *J* = 1.6 Hz, 1H), 5.36 (dd, *J* = 5.9, 1.6 Hz, 1H), 5.12 (dd, *J* = 5.8, 3.6 Hz, 1H), 4.56–4.48 (m, 1H), 4.41 (dd, *J* = 6.6, 3.7 Hz, 1H), 4.15–4.04 (m, 2H), 1.66 (s, 3H), 1.46 (s, 3H), 1.43 (s, 3H), 1.40 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.3, 127.0, 126.1, 124.4, 120.4, 114.3, 111.6, 109.4, 92.9, 84.8, 83.6, 80.8, 73.7, 66.4, 27.0, 26.7, 25.3, 25.0; **HRMS (ESI)** m/z cald for $NaC_{24}H_{25}Cl_2NO_5^+$ $[M+Na]^+$ 500.1002, found 500.1009.

3,6-dibromo-9-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-9*H*-carbazole (4f)



Purified by flash column chromatography (ethyl acetate/petroleum ether = 1:20, v:v); Colorless oil (70 mg, 62%) $[\alpha]_D^{25}$ = +25.0 (*c* = 2.1, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 2.0 Hz, 2H), 7.54 (d, *J* = 2.0 Hz, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.31 (s, 1H), 7.29 (s, 1H), 6.25 (d, *J* = 1.5 Hz, 1H), 5.34 (dd, *J* = 5.8, 1.6 Hz, 1H), 5.11 (dd, *J* = 5.8, 3.6 Hz, 1H), 4.52 (td, *J* = 6.4, 4.9 Hz, 1H), 4.39 (dd, *J* = 6.5, 3.6 Hz, 1H), 4.19 – 4.02 (m, *J* = 5.5 Hz, 2H), 1.66 (s, 3H), 1.46 (s, 3H), 1.43 (s, 3H), 1.40 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.4, 129.7, 124.8, 123.4, 114.2, 113.4, 112.0, 109.4, 92.9, 84.8, 83.6, 80.8, 73.7, 66.4, 26.9, 26.6, 25.3, 25.0; **HRMS (ESI)** m/z cald for $C_{24}H_{26}Br_2NO_5^+$ $[M+H]^+$ 566.0172, found 566.0186.

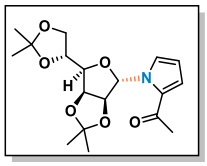
9-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-9*H*-pyrido[2,3-*b*]indole (4g)



Purified by flash column chromatography (ethyl acetate/petroleum ether = 1:25, v:v); colorless oil (49 mg, 60%); $[\alpha]_D^{25}$ = +15.0 (*c* = 0.5, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.38 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.29 (dd, *J* = 7.7, 1.6 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.52 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.33–7.29 (m, 1H), 7.18 (dd, *J* = 7.7, 4.9 Hz, 1H), 6.33 (s, 1H), 5.92 (d, *J* = 5.9 Hz, 1H), 5.48 (dd, *J* = 5.9, 2.8 Hz, 1H), 4.53–4.42 (m, 2H), 4.07–4.01 (m, 1H), 3.97–3.91 (m, 1H), 1.63 (s, 3H), 1.46 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.4, 145.7, 139.8, 128.2, 127.2, 121.1, 121.0, 120.9, 116.8, 116.2, 112.8, 109.9, 109.1, 89.0, 85.0, 84.3, 82.3, 73.9, 66.7, 27.0, 26.4, 25.4, 24.7; **HRMS (ESI)** m/z cald

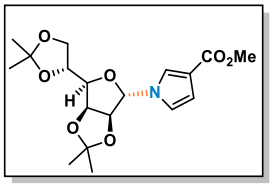
for $C_{23}H_{27}N_2O_5^+$ $[M+H]^+$ 411.1914., found 411.1921.

1-(1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-pyrrol-2-yl)ethan-1-one (4h)



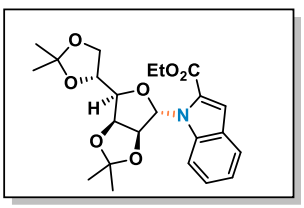
Purified by flash column chromatography (acetone / petroleum ether = 1:25, v:v); White solid; (29 mg, 42%), mp: 102-103 °C; $[\alpha]_D^{25}$ = -16.0 (c =0.6, $CHCl_3$);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.05–7.02 (m, 2H), 6.44 (s, 1H), 6.20 (dd, *J* = 3.9, 2.8 Hz, 1H), 4.80 (d, *J* = 2.4 Hz, 2H), 4.53–4.47 (m, 1H), 4.24 (dd, *J* = 7.0, 2.6 Hz, 1H), 4.16–4.13 (m, 2H), 2.44 (s, 3H), 1.58 (s, 3H), 1.46 (s, 3H), 1.39 (s, 3H), 1.36 (s, 3H),**^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.9, 129.4, 124.6, 120.2, 112.1, 108.2, 107.7, 93.3, 87.2, 82.3, 78.8, 72.4, 65.6, 25.9, 25.8, 25.2, 24.1, 23.8; **HRMS (ESI)** m/z cald for $C_{18}H_{26}NO_6^+$ $[M+H]^+$ 352.1755, found 352.1748.

Methyl1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)- 1*H*-pyrrole-3-carboxylate (4i)



Purified by flash column chromatography (ethyl acetate/petroleum ether = 1:25, v:v); colorless oil (40 mg, 55%), $[\alpha]_D^{25}$ = +96.3 (*c* =0.5, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 1H), 6.67–6.63 (m, 1H), 6.64–6.59 (m, 1H), 5.71 (s, 1H), 5.06 (d, *J* = 5.8 Hz, 1H), 4.93 (dd, *J* = 5.9, 3.7 Hz, 1H), 4.41 (ddd, *J* = 7.4, 6.3, 4.5 Hz, 1H), 4.09 (dd, *J* = 8.8, 6.3 Hz, 1H), 4.03–3.95 (m, 2H), 3.78 (s, 3H), 1.53 (s, 3H), 1.41 (s, 3H), 1.36 (s, 3H), 1.35 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.0, 123.6 (d, *J* = 1.9 Hz), 119.9, 117.4, 113.7, 111.2, 109.5, 92.7 (d, *J* = 4.2 Hz), 85.5, 82.8, 80.3, 73.0, 66.8, 51.2 (d, *J* = 4.1 Hz), 26.9, 26.0, 25.2, 24.6; **HRMS (ESI)** m/z cald for $C_{18}H_{26}NO_7^+$ $[M+H]^+$ 368.1704, found 368.1701.

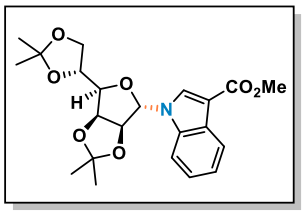
Ethyl1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-indole-2-carboxylate (5a)



Purified by flash column chromatography (acetone/petroleum ether = 1:30, v:v); colorless oil (49 mg, 57%), $[\alpha]_D^{25}$ = +29.9 (*c* =1.5, $CHCl_3$); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.74 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.43 (s, 1H), 7.42-7.36 (m, 1H), 7.23-7.17 (m, 1H), 6.93 (d, *J* = 3.1 Hz, 1H), 5.38 (dd, *J* = 5.8, 3.2 Hz, 1H), 5.22 (dd, *J* = 5.8, 4.0 Hz, 1H), 4.55 (dd, *J* = 6.0, 4.0 Hz, 1H), 4.38–4.27 (m, 3H), 4.00 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.81 (dd, *J* = 8.6, 5.6 Hz, 1H), 1.56 (s, 3H), 1.35–1.25 (m, 12H); **^{13}C**

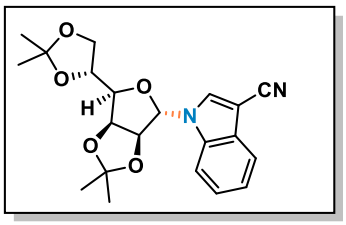
NMR (101 MHz, DMSO-d_6) δ 162.2, 138.7, 128.5, 127.3, 126.9, 123.9, 122.4, 114.4, 113.9, 113.2, 109.0, 92.5, 85.1, 83.6, 81.7, 74.5, 66.5, 61.9, 27.7, 27.5, 26.0, 25.9, 15.1; **HRMS (ESI)** m/z cald for $NaC_{23}H_{29}NO_7^+$ $[M+Na]^+$ 454.1836, found 454.1827.

Methyl1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-indole-3-carboxylate (5b)



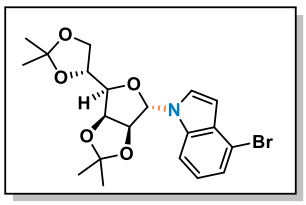
Purified by flash column chromatography (ethyl acetate/petroleum ether = 1:15, v:v); colorless oil (42 mg, 51%), $[\alpha]_D^{25}$ = +55.3 (*c* =0.7, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21-8.16 (m, 1H), 7.77 (s, 1H), 7.53–7.44 (m, 1H), 7.38–7.28 (m, 2H), 6.13 (s, 1H), 5.20 (d, *J* = 5.8 Hz, 1H), 5.01 (dd, *J* = 5.9, 3.6 Hz, 1H), 4.49 (ddd, *J* = 7.3, 6.3, 4.5 Hz, 1H), 4.17–4.06 (m, 2H), 4.03 (dd, *J* = 8.9, 4.5 Hz, 1H), 3.93 (s, 3H), 1.62 (s, 3H), 1.44 (s, 3H), 1.42 (s, 3H), 1.38 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.4, 136.0, 130.1, 127.0, 123.7, 122.8, 122.1, 114.0, 110.8, 109.6, 109.0, 91.2, 85.3, 83.1, 80.4, 73.2, 66.8, 51.3, 27.0, 26.3, 25.2, 24.8. **HRMS (ESI)** m/z cald for $C_{22}H_{28}NO_7^+$ $[M+H]^+$ 418.1860, found 418.1862.

1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-indole-3-carbonitrile (5c)



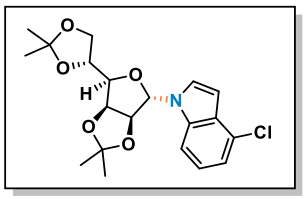
Purified by flash column chromatography (ethyl acetate/ petroleum ether = 1:25, v:v); Colorless oil (39 mg, 51%), $[\alpha]_D^{25}$ = +50.1 (*c* =1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80–7.75 (m, 1H), 7.63 (s, 1H), 7.53–7.48 (m, 1H), 7.31–7.41 (m, 2H), 6.08 (s, 1H), 5.14 (d, *J* = 5.9 Hz, 1H), 4.96 (dd, *J* = 5.8, 3.5 Hz, 1H), 4.51 (td, *J* = 6.6, 4.5 Hz, 1H), 4.18–4.13 (m, 2H), 4.08 (dd, *J* = 9.0, 4.5 Hz, 1H), 1.62 (s, 3H), 1.46 (s, 3H), 1.42 (s, 3H), 1.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 134.3, 130.8, 128.4, 124.6, 123.0, 120.3, 115.5, 114.3, 111.4, 109.7, 92.1, 87.6, 85.4, 83.5, 80.3, 73.1, 66.6, 27.0, 26.3, 25.2, 24.9; **HRMS (ESI)** m/z cald for $C_{21}H_{25}N_2O_5^+$ $[M+H]^+$ 385.1758, found 385.1760.

4-bromo-1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-indole (5d)



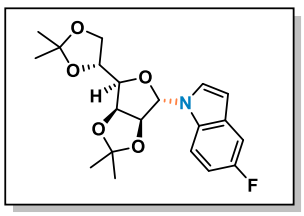
Purified by flash column chromatography (acetone/petroleum ether = 1:35, v:v); colorless oil; (55 mg, 62%), $[\alpha]_D^{25}$ = +57.3 (*c* =1, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.3 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.14–7.08 (m, 2H), 6.61 (d, *J* = 3.4 Hz, 1H), 6.10 (s, 1H), 5.20 (d, *J* = 5.8 Hz, 1H), 5.00 (dd, *J* = 5.8, 3.7 Hz, 1H), 4.48 (td, *J* = 6.8, 4.4 Hz, 1H), 4.11 (dd, *J* = 8.9, 6.3 Hz, 1H), 4.06–3.97 (m, 2H), 1.61 (s, 3H), 1.42 (s, 6H), 1.38 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.9 , 129.7 , 124.4 (d, *J* = 2.4 Hz), 123.5 , 123.3 , 115.0 , 113.7 , 109.4 , 109.4 , 103.5 (d, *J* = 2.2 Hz), 90.7 , 85.0 , 82.6 , 80.3 , 73.1 , 66.7 , 26.9 , 26.1 , 25.1 , 24.7; **HRMS (ESI)** m/z cald for $C_{20}H_{25}BrNO_5^+$ $[M+H]^+$ 438.0911, found 438.0925.

4-chloro-1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-indole (5e)



Purified by flash column chromatography (ethyl acetate/petroleum ether = 1:40, v:v); white solid; (42 mg, 54%), mp: 125 °C; $[\alpha]_D^{25}$ = +49.0 (*c* =0.5, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39–7.33 (m, 1H), 7.18–7.15 (m, 2H), 7.08 (d, *J* = 3.4 Hz, 1H), 6.67 (dd, *J* = 3.4, 0.8 Hz, 1H), 6.11 (s, 1H), 5.21 (d, *J* = 5.8 Hz, 1H), 5.01 (dd, *J* = 5.8, 3.6 Hz, 1H), 4.47 (ddd, *J* = 7.6, 6.3, 4.4 Hz, 1H), 4.11 (dd, *J* = 8.9, 6.3 Hz, 1H), 4.06–3.97 (m, 2H), 1.61 (s, 3H), 1.42 (s, 6H), 1.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.5, 128.0, 126.5, 124.6, 123.2, 120.4, 113.8, 109.6, 109.0, 101.9, 90.9, 85.2, 82.8, 80.5, 73.2, 66.9, 27.0, 26.3, 25.3, 24.8; **HRMS (ESI)** m/z cald for $C_{20}H_{25}ClNO_5^+$ $[M+H]^+$ 394.1416, found 394.1409.

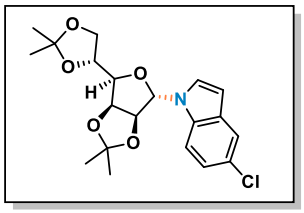
1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-5-fluoro-1*H*-indole (5f)



Purified by flash column chromatography (ethyl acetate/ petroleum ether = 1:35, v:v); Colorless oil; (43 mg, 58%), $[\alpha]_D^{25}$ = + 68.5 (*c* =0.8, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 8.9, 4.3 Hz, 1H), 7.31–7.22 (m, 1H), 7.07 (d, *J* = 3.3 Hz, 1H), 7.00 (td, *J* = 9.1, 2.6 Hz, 1H), 6.51 (d, *J* = 3.3 Hz, 1H), 6.09 (s, 1H), 5.20 (d, *J* = 5.8 Hz, 1H), 5.00 (dd, *J* = 5.9, 3.6 Hz, 1H), 4.47 (ddd, *J* = 7.6, 6.3, 4.3 Hz, 1H), 4.11 (dd, *J* = 8.9, 6.3 Hz, 1H), 4.03–3.97 (m, 2H), 1.61 (s, 3H), 1.42 (s, 6H), 1.38 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.43 (d, *J* = 235.6 Hz), 132.4 , 129.5 (d, *J* = 10.1 Hz), 125.6, 113.7, 111.0 (d, *J* = 2.7 Hz), 110.9 (d, *J* = 13.8 Hz), 109.6, 106.0 (d, *J* = 23.5 Hz), 103.3 (d, *J* = 4.6 Hz), 90.7, 85.1, 82.6, 80.5, 73.2, 66.9, 27.0, 26.2, 25.2, 24.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -123.97 (td,

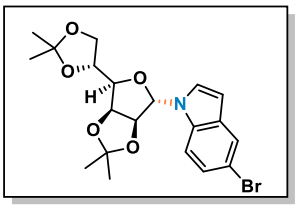
J = 9.4, 2.9 Hz, 1F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -123.97 (s, 1F); **HRMS (ESI)** m/z cald for $C_{20}H_{25}FNO_5^+$ $[M+H]^+$ 378.1711, found 378.1703.

5-chloro-1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-indole (5g)



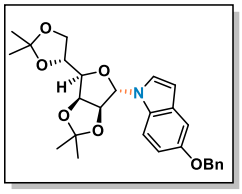
Purified by flash column chromatography (ethyl acetate/ petroleum ether = 1:35, v:v); colorless oil; (41 mg, 53%), $[\alpha]_D^{25}$ = +47.5 (c = 0.7, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, J = 1.9 Hz, 1H), 7.37 (d, J = 8.8 Hz, 1H), 7.20 (dd, J = 8.7, 1.9 Hz, 1H), 7.06 (d, J = 3.4 Hz, 1H), 6.49 (d, J = 3.3 Hz, 1H), 6.09 (s, 1H), 5.20 (d, J = 5.8 Hz, 1H), 5.00 (dd, J = 5.9, 3.7 Hz, 1H), 4.47 (td, J = 6.8, 4.4 Hz, 1H), 4.11 (dd, J = 9.0, 6.3 Hz, 1H), 4.03-3.98 (m, 2H), 1.57 (s, 3H), 1.42 (s, 6H), 1.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.2, 130.2, 126.4, 125.3, 122.9, 120.6, 113.8, 111.3, 109.6, 103.0, 90.6, 85.1, 82.7, 80.4, 73.2, 66.9, 27.0, 26.2, 25.2, 24.8; **HRMS (ESI)** m/z cald for $NaC_{20}H_{24}ClNO_5^+$ $[M+Na]^+$ 416.1241, found 416.1236.

5-Bromo-1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-indole (5h)



Purified by flash column chromatography (ethyl acetate/ petroleum ether = 1:35, v:v); colorless oil; (49 mg, 56%), $[\alpha]_D^{25}$ = +63.3 (c =0.9, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.30 (s, 2H) 7.04 (d, J = 3.3 Hz, 1H), 6.49 (d, J = 3.3 Hz, 1H), 6.08 (s, 1H), 5.19 (d, J = 5.8 Hz, 1H), 5.00 (dd, J = 5.9, 3.6 Hz, 1H), 4.50–4.44 (m, 1H), 4.11 (dd, J = 8.8, 6.3 Hz, 1H), 4.05 – 3.96 (m, 2H), 1.61 (s, 3H), 1.42 (s, 6H), 1.37 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.3, 129.7, 124.2, 124.0, 122.6, 112.8, 112.6, 110.6, 108.4, 101.7, 89.5, 84.0, 81.6, 79.3, 72.0, 65.7, 25.9, 25.1, 24.1, 23.6. **HRMS (ESI)** m/z cald for $C_{20}H_{25}BrNO_5^+$ $[M+H]^+$ 438.0911, found 438.0914.

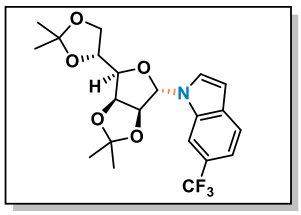
5-(benzyloxy)-1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-indole (5i)



Purified by flash column chromatography (acetone/ petroleum ether = 1:40, v:v); colorless oil; (34 mg, 24%), $[\alpha]_D^{25}$ = +62.1 (c =0.8, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.0 Hz, 2H), 7.42–7.29 (m, 4H), 7.17 (d, J = 2.4 Hz, 1H), 7.00 (dd, J = 8.5, 2.7 Hz, 2H), 6.47 (d, J = 3.2

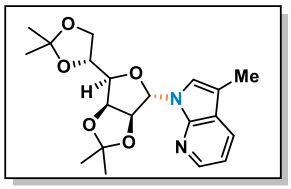
Hz, 1H), 6.08 (s, 1H), 5.22 (d, J = 5.8 Hz, 1H), 5.12 (s, 2H), 5.00 (dd, J = 5.9, 3.7 Hz, 1H), 4.47 (ddd, J = 7.6, 6.2, 4.4 Hz, 1H), 4.11 (dd, J = 8.8, 6.3 Hz, 1H), 4.00 (ddd, J = 10.9, 8.2, 4.0 Hz, 2H), 1.61 (s, 3H), 1.42 (s, 6H), 1.38 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.0, 137.7, 131.3, 129.6, 128.7, 127.9, 127.6, 124.7, 113.6, 113.5, 111.0, 109.5, 104.6, 103.1, 90.6, 85.1, 82.5, 80.5, 73.3, 71.0, 66.9, 27.0, 26.2, 25.3, 24.8; **HRMS (ESI)** m/z cald for $C_{27}H_{31}NO_6Na^+$ $[M+Na]^+$ 488.2044, found 488.2047.

1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-6-(trifluoromethyl)-1*H*-indole (5j)



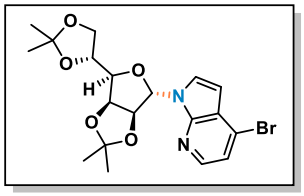
Purified by flash column chromatography (ethyl acetate/ petroleum ether = 1:35, v:v); Colorless oil; (51 mg, 60%), $[\alpha]_D^{25}$ = +44.9 (c =2.2, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.71 (d, J = 8.3 Hz, 1H), 7.40 (dd, J = 8.4, 1.5 Hz, 1H), 7.18 (d, J = 3.3 Hz, 1H), 6.62 (dd, J = 3.3, 0.8 Hz, 1H), 6.17 (s, 1H), 5.24 (d, J = 5.9 Hz, 1H), 5.03 (dd, J = 5.8, 3.6 Hz, 1H), 4.48 (ddd, J = 7.4, 6.3, 4.3 Hz, 1H), 4.11 (dd, J = 8.9, 6.3 Hz, 1H), 4.04–3.96 (m, 2H), 1.62 (s, 3H), 1.43 (s, 3H), 1.42 (s, 3H), 1.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 133.8, 130.3, 124.0 (q, J = 272 Hz), 125.5, 123.6 (q, J = 32 Hz), 120.4, 116.2 (q, J = 3.4 Hz), 112.7, 108.4, 106.8, 102.5, 89.4, 83.9, 81.5, 79.3, 72.0, 65.6, 25.8, 25.0, 24.1, 23.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -60.6 (s, 3F); **^{19}F {H}NMR** (376 MHz, $CDCl_3$) δ -60.6 (s, 3F); **HRMS (ESI)** m/z cald for $C_{21}H_{25}F_3NO_5^+$ $[M+H]^+$ 428.1679, found 428.1674.

1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-3-methyl-1*H*-pyrrolo[2,3-b]pyridine (5k)



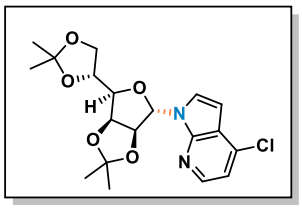
Purified by flash column chromatography (acetone/petroleum ether = 1:50, v:v); Colorless oil; (34 mg, 45%), $[\alpha]_D^{25}$ = -25.4 (c =2.4, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (dd, J = 4.7, 1.6 Hz, 1H), 7.81 (dd, J = 7.8, 1.6 Hz, 1H), 7.05 (dd, J = 7.8, 4.7 Hz, 1H), 6.94 (d, J = 1.3 Hz, 1H), 6.01 (s, 1H), 5.62 (d, J = 5.9 Hz, 1H), 5.31 (dd, J = 5.9, 3.7 Hz, 1H), 4.44 (ddd, J = 7.4, 6.1, 4.4 Hz, 1H), 4.38 (dd, J = 7.3, 3.7 Hz, 1H), 4.05 (dd, J = 8.7, 6.1 Hz, 1H), 3.97 (dd, J = 8.7, 4.4 Hz, 1H), 2.27 (d, J = 1.2 Hz, 3H), 1.58 (s, 3H), 1.41 (s, 3H), 1.40 (s, 3H), 1.35 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.5, 142.9, 127.2, 125.4, 122.1, 115.9, 112.9, 110.4, 109.1, 91.5, 85.2, 83.7, 81.7, 73.7, 66.7, 27.0, 26.3, 25.2, 24.7, 9.7; **HRMS (ESI)** m/z cald for $C_{20}H_{27}N_2O_5^+$ $[M+H]^+$ 375.1914, found 375.1910.

4-Bromo-1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-pyrrolo[2,3-b]pyridine (5l)



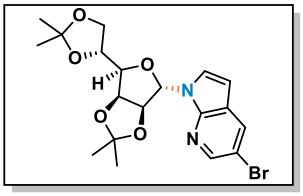
Purified by flash column chromatography (acetone/ petroleum ether = 1:50, v:v); Colorless oil; (45 mg, 51%), $[\alpha]_D^{25}$ = -9.0 (*c* =2.1, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 5.1 Hz, 1H), 7.29–7.24 (m, 2H), 6.51 (d, *J* = 3.6 Hz, 1H), 6.02 (s, 1H), 5.59 (d, *J* = 5.9 Hz, 1H), 5.28 (dd, *J* = 5.9, 3.3 Hz, 1H), 4.49–4.37 (m, 2H), 4.06 (dd, *J* = 8.8, 5.8 Hz, 1H), 3.98 (dd, *J* = 8.7, 4.0 Hz, 1H), 1.57 (s, 3H), 1.41 (s, 3H), 1.40 (s, 3H), 1.35 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.9, 143.2, 128.8, 125.4, 123.1, 119.9, 113.1, 109.1, 101.2, 92.3, 85.2, 84.2, 81.6, 73.6, 66.5, 27.0, 26.2, 25.2, 24.7; **HRMS (ESI)** m/z cald for $C_{19}H_{24}BrN_2O_5^+$ $[M+H]^+$ 439.0863., found 439.0869.

4-chloro-1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-pyrrolo[2,3-b]pyridine (5m)



Purified by flash column chromatography (acetone/ petroleum ether = 1:50, v:v); Colorless oil; (37 mg, 47%), $[\alpha]_D^{25}$ = -16.7 (*c* =3.2, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 5.2 Hz, 1H), 7.23 (d, *J* = 3.6 Hz, 1H), 7.10 (d, *J* = 5.2 Hz, 1H), 6.56 (d, *J* = 3.6 Hz, 1H), 6.02 (s, 1H), 5.59 (d, *J* = 5.9 Hz, 1H), 5.28 (dd, *J* = 5.9, 3.2 Hz, 1H), 4.48–4.40 (m, 2H), 4.06 (dd, *J* = 8.7, 5.7 Hz, 1H), 3.98 (dd, *J* = 8.7, 3.9 Hz, 1H), 1.56 (s, 3H), 1.41 (s, 3H), 1.40 (s, 3H), 1.35 (s, 3H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.7, 143.4, 136.2, 128.7, 120.9, 116.8, 113.1, 109.1, 99.6, 92.3, 85.2, 84.1, 81.6, 73.6, 66.5, 26.9, 26.2, 25.2, 24.7; **HRMS (ESI)** m/z cald for $C_{19}H_{24}ClN_2O_5^+$ $[M+H]^+$ 395.1368, found 395.1378.

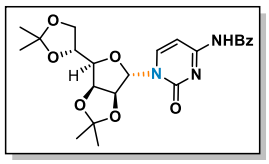
5-bromo-1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-pyrrolo[2,3-*b*]pyridine (5n)



Purified by flash column chromatography (ethyl acetate/ petroleum ether = 1:40, v:v); White solid; (39 mg, 45%), mp: 136 °C; $[\alpha]_D^{25}$ = +15.7(*c* =0.45, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 2.2 Hz, 1H), 8.01 (d, *J* = 2.2 Hz, 1H), 7.22 (d, *J* = 3.6 Hz, 1H), 6.42 (d, *J* = 3.6 Hz, 1H), 6.00 (s, 1H), 5.58 (d, *J* = 5.9 Hz, 1H), 5.27 (dd, *J* = 5.9, 3.4 Hz, 1H), 4.48–4.39 (m, 2H), 4.06 (dd, *J* = 8.8, 5.7 Hz, 1H), 3.98 (dd, *J* = 8.7, 4.1 Hz, 1H), 1.58 (s, 3H), 1.41 (s, 6H), 1.36 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.6,

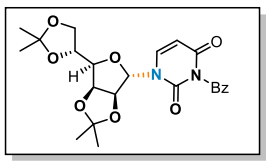
143.7, 131.1, 129.9, 123.3, 113.2, 112.7, 109.2, 100.7, 92.2, 85.3, 84.2 , 81.7, 73.7, 66.6, 27.0, 26.3, 25.3, 24.7; **HRMS (ESI)** m/z cald for $C_{19}H_{24}BrN_2O_5^+$ $[M+H]^+$ 439.0863, found 439.0854.

_N_-(1-((3a_S_,4_S_,6_R_,6a_S_)-6-((_R_)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-_d_][1,3]dioxol-4-yl)-2-oxo-1,2-dihydropyrimidin-4-yl)benzamide (6a)



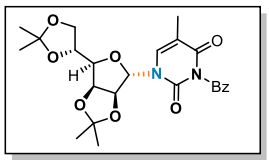
Purified by flash column chromatography (ethyl acetate / petroleum ether = 1:6, v:v); White solid; (50 mg, 55%), m.p.: 190 °C; $[\alpha]_D^{25}$ = +57.3 (_c_ = 1.0, $CHCl_3$); **^{1}H NMR** [1] (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.50 (d, _J_ = 5.7 Hz, 1H), 8.03 (d, _J_ = 5.6 Hz, 1H), 7.93–7.86 (m, 2H), 7.65–7.56 (m, 1H), 7.51 (dd, _J_ = 8.3, 6.8 Hz, 2H), 6.46 (s, 1H), 4.95–4.87 (m, 2H), 4.43 (ddd, _J_ = 8.2, 6.1, 3.9 Hz, 1H), 4.19 (dd, _J_ = 8.3, 3.1 Hz, 1H), 4.08 (dd, _J_ = 8.9, 6.1 Hz, 1H), 4.00 (dd, _J_ = 8.9, 3.9 Hz, 1H), 1.52 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H), 1.35 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 163.0, 161.0, 159.4, 133.2, 133.1, 129.2, 127.5, 113.4, 109.6, 105.2, 103.2, 85.2, 82.3, 79.6, 73.0, 67.1, 27.1, 26.2, 25.3, 24.8; **HRMS (ESI)** m/z cald for $C_{23}H_{27}N_3O_7Na^+$ $[M+Na]^+$ 480.1741, found 480.1735.

3-Benzoyl-1-((3a_S_,4_S_,6_R_,6a_S_)-6-((_R_)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-_d_][1,3]dioxol-4-yl)pyrimidine-2,4(1_H_,3_H_)-dione (6b)



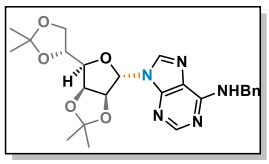
Purified by flash column chromatography (MeOH/toluene = 1:5, v:v); White solid (43 mg, 47%), m.p.: 156-157 °C; $[\alpha]_D^{25}$ = +22.2 (_c_ = 0.6, $CHCl_3$); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.79 (d, _J_ = 5.4 Hz, 1H), 8.18–8.09 (m, 2H), 7.84–7.77 (m, 1H), 7.68–7.60 (m, 2H), 7.30 (d, _J_ = 5.4 Hz, 1H), 6.32 (s, 1H), 4.92 (dd, _J_ = 5.9, 3.4 Hz, 1H), 4.88 (d, _J_ = 5.9 Hz, 1H), 4.35–4.26 (m, 1H), 4.15 (dd, _J_ = 6.4, 3.4 Hz, 1H), 4.00 (dd, _J_ = 8.5, 6.5 Hz, 1H), 3.82 (dd, _J_ = 8.5, 5.3 Hz, 1H), 1.41 (s, 3H), 1.32 (s, 3H), 1.29 (s, 3H), 1.26 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 166.5, 163.2, 163.1, 162.5, 135.0, 130.2, 129.3, 127.8, 112.2, 108.6, 108.2, 103.3, 84.5, 82.0, 78.9, 72.5, 65.7, 26.6, 25.8, 25.2, 24.4; **HRMS (ESI)** m/z cald for $C_{23}H_{26}N_2O_8Na^+$ $[M+Na]^+$ 481.1581, found 481.1584.

3-benzoyl-1-((3a_S_,4_S_,6_R_,6a_S_)-6-((_R_)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-_d_][1,3]dioxol-4-yl)-5-methylpyrimidine-2,4(1_H_,3_H_)-dione (6c)



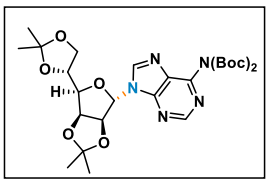
Purified by flash column chromatography (MeOH/toluene = 1:5, v:v); White solid (44 mg, 46%), m.p.: 88-89 ºC; $[\alpha]_D^{25}$ = +49.8 (*c* = 0.3, $CHCl_3$); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.67 (d, *J* = 1.0 Hz, 1H), 8.22–8.12 (m, 2H), 7.86–7.78 (m, 1H), 7.72–7.61 (m, 2H), 6.28 (s, 1H), 4.91 (dd, *J* = 5.9, 3.4 Hz, 1H), 4.86 (d, *J* = 5.9 Hz, 1H), 4.30 (td, *J* = 6.4, 5.3 Hz, 1H), 4.13 (dd, *J* = 6.4, 3.4 Hz, 1H), 3.99 (dd, *J* = 8.5, 6.4 Hz, 1H), 3.81 (dd, *J* = 8.5, 5.3 Hz, 1H), 2.12 (s, 2H), 1.40 (s, 3H), 1.31 (s, 3H), 1.28 (s, 3H), 1.26 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 164.9, 162.9, 162.5, 161.7, 135.0, 130.2, 129.4, 127.5, 117.1, 112.1, 108.2, 103.2, 84.4, 81.9, 78.9, 72.5, 65.7, 26.6, 25.8, 25.2, 24.4, 11.6; **HRMS (ESI)** m/z cald for $C_{24}H_{28}N_2O_8Na^+$ $[M+Na]^+$ 495.1738, found 495.1730.

_N_-benzyl-9-((3a_S_,4_S_,6_R_,6a_S_)-6-((_R_)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-_d_][1,3]dioxol-4-yl)-9_H_-purin-6-amine (6d)



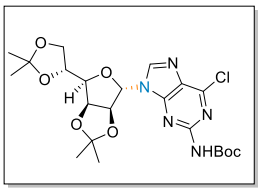
Purified by flash column chromatography (ethyl acetate / petroleum ether = 1:8, v:v); colorless oil; (45 mg, 49%), $[\alpha]_D^{25}$ = -1.1 (*c* = 0.7, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.61 (s, 1H), 7.35–7.19 (m, 5H), 6.33 (s, 1H), 5.88 (s, 1H), 5.47 (d, *J* = 5.7 Hz, 1H), 5.21 (dd, *J* = 6.0, 2.9 Hz, 1H), 4.80 (s, 2H), 4.48–4.33 (m, 2H), 3.96-4.00 (m, 1H), 3.88-3.95 (m, 1H), 1.50 (s, 3H), 1.35 (s, 6H), 1.29 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.8, 153.4, 147.6, 140.0, 138.4, 128.8, 127.8, 127.7, 119.2, 113.5, 109.2, 90.6, 84.8, 84.1, 81.4, 73.5, 66.4, 43.6, 26.9, 26.2, 25.2, 24.7; **HRMS (ESI)** m/z cald for $C_{24}H_{30}N_5O_5^+$ $[M+H]^+$ 468.2241, found 468.2239.

***Tert*-butyl (*tert*-butoxycarbonyl)(9-((3a_S_,4_S_,6_R_,6a_S_)-6-((_R_)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-_d_][1,3]dioxol-4-yl)-9_H_-purin-6-yl)carbamate (6e)**



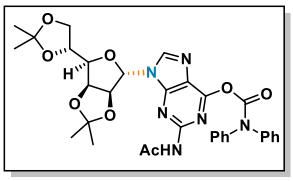
Purified by flash column chromatography (acetatone / petroleum ether = 1:20, v:v); colorless oil; (54 mg, 48%), $[\alpha]_D^{25}$ = -7.0 (*c* = 0.4, $CHCl_3$); **^{1}H NMR** (400 MHz, Acetone-d_6) δ 8.82 (s, 1H), 8.59 (s, 1H), 6.32 (s, 1H), 5.64 (d, *J* = 5.8 Hz, 1H), 5.32 (dd, *J* = 5.9, 3.5 Hz, 1H), 4.52 (dd, *J* = 6.3, 3.6 Hz, 1H), 4.46–4.40 (m, 1H), 4.03 (dd, *J* = 8.5, 6.4 Hz, 1H), 3.90 (dd, *J* = 8.5, 5.5 Hz, 1H), 1.53 (s, 3H), 1.45 (s, 18H), 1.39 (s, 3H), 1.29 (s, 3H), 1.27 (s, 3H); **^{13}C NMR** (101 MHz, Acetone-d_6) δ 153.8, 152.6, 151.3, 151.3, 146.4 129.7, 113.7, 109.3, 91.3, 85.6, 85.1, 84.0, 82.0, 74.1, 66.8, 27.9, 26.9, 26.4, 25.5, 24.7; **HRMS (ESI)** m/z cald for $C_{27}H_{40}N_5O_9^+$ $[M+H]^+$ 578.2821, found 578.2829.

***Tert*-butyl (6-chloro-9-((3a*S*,4*S*,6*R*,6a*S*)-6-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-9*H*-purin-2-yl)carbamate (6f)**



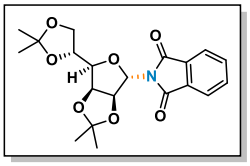
Purified by flash column chromatography (acetatone / DCM = 1:30, v:v); colorless oil; (44 mg, 43%), $[\alpha]_D^{25}$ = -92.8 (*c* =1.2, $CHCl_3$); **^{1}H NMR** (400 MHz, Acetone-d_6) δ 9.23 (s, 1H), 8.39 (s, 1H), 6.15 (s, 1H), 5.66–5.56 (m, 2H), 4.57 (dd, *J* = 6.2, 3.5 Hz, 1H), 4.39–4.30 (m, 1H), 3.96 (dd, *J* = 8.4, 6.4 Hz, 1H), 3.85 (dd, *J* = 8.4, 5.4 Hz, 1H), 1.49 (s, 9H), 1.46 (s, 3H), 1.34 (s, 3H), 1.26 (s, 3H), 1.22 (s, 3H); **^{13}C NMR** (101 MHz, Acetone-d_6) 153.6, 153.4, 151.3, 151.2, 146.3, 128.7, 113.1, 109.1, 91.1, 85.4, 85.2, 82.1, 81.0, 74.4, 66.7, 28.4, 27.0, 26.3, 25.5, 24.5; **HRMS (ESI)** m/z cald for $C_{22}H_{31}ClN_5O_7^+$ $[M+H]^+$ 512.1907, found 512.1894.

2-acetamido-9-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-9*H*-purin-6-yl diphenylcarbamate (6g)



Purified by flash column chromatography (acetatone / DCM = 1:10, v:v); white solid (52 mg, 41%), m.p.: 88-89 °C;, $[\alpha]_D^{25}$ = -92.8 (*c* =1.2, $CHCl_3$); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.84 (s, 1H), 8.55 (s, 1H), 7.53–7.41 (m, 8H), 7.36–7.29 (m, 2H), 6.27 (s, 1H), 5.53 (dd, *J* = 5.9, 3.8 Hz, 1H), 5.43 (d, *J* = 5.9 Hz, 1H), 4.56 (dd, *J* = 5.5, 3.8 Hz, 1H), 4.31 (q, *J* = 5.9 Hz, 1H), 3.95 (dd, *J* = 8.4, 6.5 Hz, 1H), 3.83 (dd, *J* = 8.4, 5.7 Hz, 1H), 2.16 (s, 3H), 1.48 (s, 3H), 1.32 (s, 3H), 1.26 (s, 3H), 1.24 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 168.2, 155.2, 154.1, 151.9, 150.0, 145.4, 141.5, 129.4, 127.3, 126.9, 120.3, 111.9, 107.8, 88.9, 84.1, 83.6, 80.6, 73.1, 65.1, 26.3, 25.7, 25.0, 24.5, 24.2; **HRMS (ESI)** m/z cald for $C_{32}H_{34}N_6O_8Na^+$ $[M+Na]^+$ 653.2330, found 653.2341.

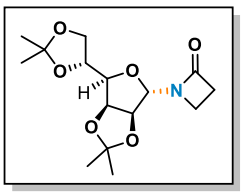
2-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)isoindoline-1,3-dione (7a)



Purified by flash column chromatography (ether / DCM = 1:10, v:v); White solid; (45 mg, 58%), $[\alpha]_D^{25}$ = +23.8 (*c* = 1.1, $CHCl_3$); mp: 114 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90–7.84 (m, 2H), 7.80–7.73 (m, 2H), 5.91 (s, 1H), 5.26 (d, *J* = 5.9 Hz, 1H), 5.17 (dd, *J* = 6.0, 3.8 Hz, 1H), 4.39 (ddd, *J* = 7.3, 6.1, 4.7 Hz, 1H), 4.29 (dd, *J* = 7.3, 3.8 Hz, 1H), 4.05 (dd, *J* = 8.8, 6.1 Hz, 1H), 3.99 (dd, *J* = 8.8, 4.7 Hz, 1H), 1.54 (s, 3H), 1.44 (s, 3H), 1.38 (s, 3H), 1.36 (s, 3H); **^{13}C**

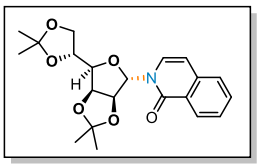
NMR (101 MHz, $CDCl_3$) δ 168.1, 134.8, 131.9, 124.0, 113.3, 109.3, 84.9, 84.7, 84.2, 81.7, 73.8, 66.8, 27.2, 26.3, 25.5, 24.7; **HRMS (ESI)** m/z cald for $C_{20}H_{24}NO_7^+$ $[M+H]^+$ 390.1547, found 390.1543.

1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)azetidin-2-one (7b)



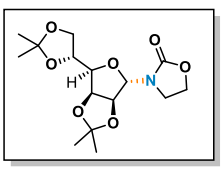
Purified by flash column chromatography (ether / DCM = 1:10, v:v); Colorless oil; (38 mg, 62%), $[\alpha]_D^{25}$ = +4.3 (*c* = 1, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.32 (d, *J* = 5.9 Hz, 1H), 4.86 (dd, *J* = 5.9, 3.7 Hz, 1H), 4.70 (s, 1H), 4.33 (td, *J* = 6.5, 4.7 Hz, 1H), 4.04–3.94 (m, 2H), 3.88 (dd, *J* = 6.9, 3.6 Hz, 1H), 3.32 (td, *J* = 5.6, 3.1 Hz, 1H), 3.17 (td, *J* = 5.5, 3.0 Hz, 1H), 2.95-2.80 (m, 2H), 1.40 (s, 3H), 1.39 (s, 3H), 1.30 (s, 3H), 1.27 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 111.9, 108.2, 88.2, 81.9, 80.9, 79.3, 72.4, 65.7, 37.2, 35.6, 26.0, 25.0, 24.2, 23.6; **HRMS (ESI)** m/z cald for $C_{15}H_{23}NO_6Na^+$ $[M+Na]^+$ 336.1418, found 336.1423.

2-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)isoquinolin-1(2*H*)-one (7c)



Purified by flash column chromatography (ethyl acetate/ petroleum ether = 1:12, v:v); Colorless oil; (36 mg, 47%), $[\alpha]_D^{25}$ = +28.2 (*c* = 0.5, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 5.8 Hz, 1H), 7.80 – 7.73 (m, 1H), 7.72–7.63 (m, 1H), 7.60–7.51 (m, 1H), 7.24-7.31 (m, 1H), 6.70 (s, 1H), 5.06–4.97 (m, 2H), 4.43-4.55 (m, 1H), 4.22 (dd, *J* = 8.2, 3.3 Hz, 1H), 4.12 (dd, *J* = 8.9, 6.0 Hz, 1H), 4.04 (dd, *J* = 8.8, 4.1 Hz, 1H), 1.56 (s, 3H), 1.46 (s, 3H), 1.40 (s, 3H), 1.38 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.4, 138.7, 137.1, 129.6, 125.7, 125.3, 122.8, 118.4, 114.8, 112.2, 108.3, 101.6, 84.5, 81.3, 78.6, 72.0, 66.1, 26.0, 25.1, 24.1, 23.7; **HRMS (ESI)** m/z cald for $C_{21}H_{26}NO_6^+$ $[M+H]^+$ 388.1755, found 388.1765.

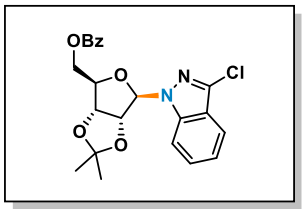
3-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)oxazolidin-2-one (7d)



Purified by flash column chromatography (ethyl acetate/petroleum ether = 1:8, v:v); colorless oil; (54 mg, 41%), $[\alpha]_D^{25}$ = +23.9 (*c* = 0.7, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.38 (d, *J* = 5.9 Hz, 1H), 5.00 (d, *J* = 5.8 Hz, 2H), 4.43–4.29 (m, 3H), 4.21 (dd, *J* = 6.7, 3.7 Hz, 1H), 4.10–3.98 (m, 2H), 3.82 (q, *J* = 8.7 Hz, 1H), 3.63–3.52 (m, 1H), 1.48 (s, 3H), 1.44 (s, 3H), 1.36 (s, 3H),

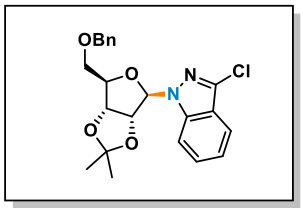
1.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.9, 112.8, 109.2, 91.0, 83.7, 83.5, 80.9, 73.7, 66.5, 62.5, 45.3, 26.9, 26.1, 25.2, 24.5; **HRMS (ESI)** m/z cald for $C_{15}H_{23}NO_7Na^+$ $[M+Na]^+$ 352.1367, found 352.1364.

((3a*R*,4*R*,6*R*,6a*R*)-6-(3-chloro-1*H*-indazol-1-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methyl benzoate (8a)



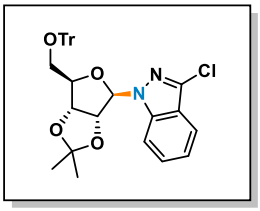
Purified by flash column chromatography (acetone / petroleum ether = 1:25, v:v); colorless oil; (61 mg, 70%), $[\alpha]_D^{25}$ = +68.4 (*c* = 0.9, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01–7.94 (m, 2H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.58–7.50 (m, 2H), 7.49–7.37 (m, 3H), 7.27–7.22 (m, 1H), 6.34 (d, *J* = 1.2 Hz, 1H), 5.62 (dd, *J* = 6.1, 1.2 Hz, 1H), 5.12 (dd, *J* = 6.0, 2.5 Hz, 1H), 4.58 (td, *J* = 6.3, 2.5 Hz, 1H), 4.35 (dd, *J* = 11.6, 6.4 Hz, 1H), 4.23 (dd, *J* = 11.6, 6.2 Hz, 1H), 1.63 (s, 3H), 1.43 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 166.2, 141.6, 135.9, 133.2, 129.9, 129.7, 128.6, 128.5, 122.5, 122.0, 120.1, 113.8, 110.0, 91.5, 85.3, 84.4, 82.4, 64.4, 27.1, 25.4; **HRMS (ESI)** m/z cald for $C_{22}H_{22}ClN_2O_5^+$ $[M+H]^+$ 429.1212, found 429.1210.

1-((3a*R*,4*R*,6*R*,6a*R*)-6-((benzyloxy)methyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-3-chloro-1*H*-indazole (8b)



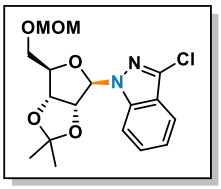
Purified by flash column chromatography (ethyl acetate/ petroleum ether = 1:30, v:v); colorless oil; (83 mg, 67%), $[\alpha]_D^{25}$ = -78.4 (*c* =2.6, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.39-7.47 (m, 1H), 7.13–7.28 (m, 6H), 6.28 (d, *J* = 1.3 Hz, 1H), 5.53 (dd, *J* = 6.1, 1.3 Hz, 1H), 4.98 (dd, *J* = 6.1, 2.5 Hz, 1H), 4.44 (td, *J* = 6.5, 2.4 Hz, 1H), 4.37 (d, *J* = 1.7 Hz, 2H), 3.47 (dd, *J* = 10.1, 6.3 Hz, 1H), 3.34 (dd, *J* = 10.1, 6.8 Hz, 1H), 1.61 (s, 3H), 1.40 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.5, 137.8, 135.2, 128.4, 128.4, 127.7, 127.7, 122.3, 121.9, 119.9, 113.5, 110.2, 91.6, 86.5, 84.1, 82.5, 73.4, 70.3, 27.1, 25.4; **HRMS (ESI)** m/z cald for $C_{22}H_{24}ClN_2O_4^+$ $[M+H]^+$ 415.1419, found 415.1425.

3-Chloro-1-((3a*R*,4*R*,6*R*,6a*R*)-2,2-dimethyl-6-((trityloxy)methyl)tetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-indazole (8c)



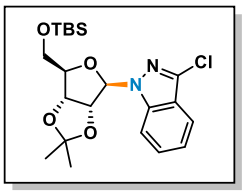
Purified by flash column chromatography (diethyl ether/petroleum ether = 1:30, v:v); colorless oil; (84 mg, 74%), $[\alpha]_D^{25}$ = -24.9 (*c* = 0.8, $CHCl_3$); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.98 (d, *J* = 8.6 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.58–7.52 (m, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.24–7.13 (m, 15H), 6.59 (d, *J* = 1.2 Hz, 1H), 5.38 (dd, *J* = 6.0, 1.2 Hz, 1H), 4.83 (dd, *J* = 6.0, 2.5 Hz, 1H), 4.31 (td, *J* = 6.0, 2.4 Hz, 1H), 3.00–2.89 (m, 2H), 1.53 (s, 3H), 1.32 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 144.4, 142.1, 134.8, 129.5, 129.0, 128.7, 127.9, 123.6, 121.9, 120.2, 113.6, 112.0, 91.4, 87.2, 86.9, 84.4, 82.7, 65.3, 27.8, 26.0; **HRMS (ESI)** m/z cald for $C_{34}H_{31}ClN_2O_4Na^+$ $[M+Na]^+$ 589.1865, found 589.1877.

3-chloro-1-((3a*R*,4*R*,6*R*,6a*R*)-6-((methoxymethoxy)methyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-indazole (8d)



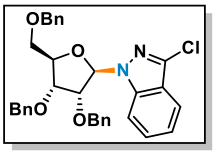
Purified by flash column chromatography (acetone/petroleum ether = 1:35, v:v); colorless oil; (55 mg, 71%), $[\alpha]_D^{25}$ = +68.1(*c* =3.8, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67–7.62 (m, 1H), 7.55–7.51 (m, 1H), 7.48–7.41 (m, 1H), 7.27–7.19 (m, 1H), 6.30 (d, *J* = 1.2 Hz, 1H), 5.55 (d, *J* = 1.2 Hz, 1H), 4.99 (dd, *J* = 6.1, 2.4 Hz, 1H), 4.49 (d, *J* = 6.6 Hz, 1H), 4.45–4.38 (m, 2H), 3.51-3.39 (m, 2H), 3.16 (s, 3H), 1.61 (s, 3H), 1.41 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.5, 135.3, 128.3, 122.3, 121.9, 119.9, 113.5, 110.1, 96.6, 91.5, 86.5, 84.2, 82.5, 67.9, 55.1, 27.0, 25.3. **HRMS (ESI)** m/z cald for $C_{17}H_{21}ClN_2NaO_5^+$ $[M+Na]^+$ 391.1031, found 391.1041.

1-((3a*R*,4*R*,6*R*,6a*R*)-6-(((*tert*-butyldimethylsilyl)oxy)methyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-3-chloro-1*H*-indazole (8e)



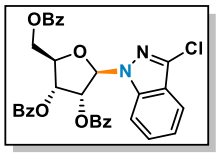
Purified by flash column chromatography (diethyl ether/ petroleum ether = 1:50, v:v); Colorless oil; (57 mg, 65%), $[\alpha]_D^{25}$ = +42.9 (*c* =0.5, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70–7.64 (m, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.50–7.44 (m, 1H), 7.28–7.23 (m, 1H), 6.28 (d, *J* = 1.3 Hz, 1H), 5.56 (dd, *J* = 6.1, 1.3 Hz, 1H), 4.99 (dd, *J* = 6.1, 2.1 Hz, 1H), 4.30 (ddd, *J* = 7.8, 6.2, 2.1 Hz, 1H), 3.55 (dd, *J* = 10.5, 7.4 Hz, 1H), 3.43 (dd, *J* = 10.5, 6.2 Hz, 1H), 1.61 (s, 3H), 1.42 (s, 3H), 0.81 (s, 9H), -0.07 (s, 3H), -0.09 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.6, 135.2, 128.4, 122.4, 122.0, 119.9, 113.3, 110.2, 91.8, 88.3, 84.1, 82.4, 63.4, 27.1, 26.0, 25.4, 18.5, -5.4, -5.4; **HRMS (ESI)** m/z cald for $C_{22}H_{32}ClN_2O_4Si^+$ $[M+H]^+$ 439.1814, found 439.1828.

1-((2*R*,3*R*,4*R*,5*R*)-3,4-bis(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-2-yl)-3-chloro-1*H*-indazole (8f)



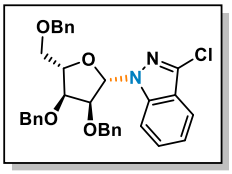
Purified by flash column chromatography (ethyl acetate/ petroleum ether = 1:32, v:v); colorless oil; (70 mg, 63%), $[\alpha]_D^{25}$ = -40.3 (*c* = 1.9, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.1 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 1H), 7.32–7.17 (m, 11H), 7.13 (td, *J* = 6.3, 2.4 Hz, 6H), 6.12 (d, *J* = 4.7 Hz, 1H), 4.73 (t, *J* = 5.0 Hz, 1H), 4.64–4.54 (m, 2H), 4.54–4.34 (m, 4H), 4.32 (q, *J* = 4.7 Hz, 1H), 4.24 (t, *J* = 4.9 Hz, 1H), 3.55 (dd, *J* = 10.6, 4.4 Hz, 1H), 3.48 (dd, *J* = 10.6, 5.0 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.8, 138.1, 137.8, 137.6, 135.4, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 128.0, 128.0, 127.8, 127.7, 127.7, 122.2, 122.0, 119.8, 110.1, 89.1, 81.9, 79.6, 77.4, 73.5, 73.0, 72.6, 70.4; **HRMS (ESI)** m/z cald for $C_{33}H_{32}ClN_2O_4^+$ $[M+H]^+$ 555.2045, found 555.2048.

(2*R*,3*R*,4*R*,5*R*)-2-((benzoyloxy)methyl)-5-(3-chloro-1*H*-indazol-1-yl) tetrahydrofuran-3,4-diyl dibenzoate (8g)



Purified by flash column chromatography (DCM / petroleum ether = 1:1.5, v:v); colorless oil; (41 mg, 35%), $[\alpha]_D^{25}$ = -55.7 (*c* = 0.9, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.1 Hz, 2H), 7.93 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.80–7.75 (m, 2H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.62–7.53 (m, 2H), 7.53–7.39 (m, 5H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.26–7.18 (m, 3H), 6.48 (t, *J* = 3.3 Hz, 1H), 6.32 (d, *J* = 6.6 Hz, 1H), 6.17 (dd, *J* = 6.6, 3.4 Hz, 1H), 5.70 (ddd, *J* = 7.1, 5.1, 3.2 Hz, 1H), 4.25–4.18 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6, 165.3, 165.1, 141.2, 136.0, 133.6, 133.5, 133.4, 130.0, 130.0, 129.9, 129.6, 129.4, 129.1, 128.8, 128.6, 128.6, 128.4, 122.7, 122.5, 120.3, 110.3, 83.9, 68.5, 68.4, 67.2, 63.9; **HRMS (ESI)** m/z cald for $C_{33}H_{25}ClN_2O_7Na^+$ $[M+Na]^+$ 619.1242, found 619.1248.

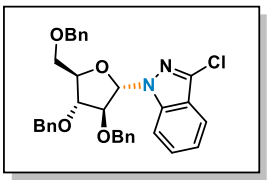
1-((2*S*,3*S*,4*S*,5*S*)-3,4-bis(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-2-yl)-3-chloro-1*H*-indazole (8h)



Purified by flash column chromatography (ethyl acetate/ petroleum ether = 1:30, v:v); Colorless oil; (69 mg, 61%), $[\alpha]_D^{25}$ = +38.9 (*c* =2.9, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.1 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 1H), 7.31–7.17 (m, 11H), 7.15–7.10 (m, 6H), 6.13 (d, *J* = 4.7 Hz, 1H), 4.74 (t, *J* = 4.9 Hz, 1H), 4.64–4.54 (m, 2H), 4.54–4.35 (m, 4H), 4.32 (q, *J* = 4.7 Hz, 1H), 4.25 (t, *J* = 4.9 Hz, 1H), 3.55 (dd, *J* = 10.7, 4.4 Hz, 1H), 3.48 (dd, *J* = 10.6, 5.1 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.8, 138.1, 137.8, 137.6, 135.4, 128.5,

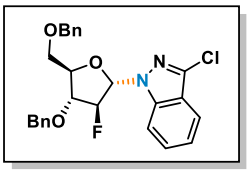
128.4, 128.4, 128.3, 128.1, 128.0, 128.0, 128.0, 127.7, 127.6, 122.2, 122.0, 119.8, 110.1, 89.1, 81.9, 79.6, 77.4, 73.5, 73.0, 72.6, 70.4; **HRMS (ESI)** m/z cald for $NaC_{33}H_{31}ClN_2O_4^+$ $[M+Na]^+$ 577.1865, found 577.1863.

1-((2*S*,3*S*,4*R*,5*R*)-3,4-bis(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-2-yl)-3-chloro-1*H*-indazole (8i)



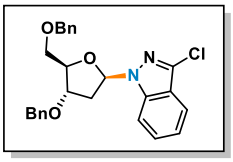
Purified by flash column chromatography (ethyl acetate/ petroleum ether = 1:30, v:v); White solid; (66 mg, 60%), mp: 58 °C; $[\alpha]_D^{25}$ = +44.2(*c* =0.7, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.1 Hz, 1H), 7.39–7.30 (m, 3H), 7.28–7.19 (m, 10H), 7.16–7.04 (m, 5H), 6.06 (d, *J* = 4.6 Hz, 1H), 5.14 (t, *J* = 5.0 Hz, 1H), 4.63 (d, *J* = 11.7 Hz, 1H), 4.55–4.49 (m, 2H), 4.47–4.34 (m, 3H), 4.34–4.31 (m, 1H), 4.27 (dd, *J* = 7.6, 5.5 Hz, 1H), 3.61 (dd, *J* = 11.0, 3.0 Hz, 1H), 3.53 (dd, *J* = 11.0, 4.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.4, 138.1, 138.0, 137.4, 135.5, 128.5, 128.4, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 122.2, 122.2, 119.9, 110.2, 90.3, 86.5, 82.7, 81.0, 73.6, 73.0, 72.6, 69.3; **HRMS (ESI)** m/z cald for $NaC_{33}H_{31}ClN_2O_4^+$ $[M+Na]^+$ 577.1865, found 577.1879.

1-((2*S*,3*S*,4*R*,5*R*)-4-(benzyloxy)-5-((benzyloxy)methyl)-3-fluorotetrahydrofuran-2-yl)-3-chloro-1*H*-indazole (8j)



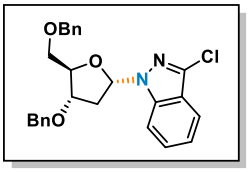
Purified by flash column chromatography (ethyl acetate/ petroleum ether = 1:35, v:v); Colorless oil; (56 mg, 60%), $[\alpha]_D^{25}$ = +103.1(*c* =1.6, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.41–7.33 (m, 1H), 7.14-7.30 (m, 11H), 6.23 (dd, *J* = 16.3, 3.3 Hz, 1H), 6.08 (dt, *J* = 53.2, 3.6 Hz, 1H), 4.73 (d, *J* = 11.8 Hz, 1H), 4.57–4.46 (m, 2H), 4.46–4.29 (m, 3H), 3.65–3.57 (m, 1H), 3.53 (dd, *J* = 11.1, 3.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 137.9, 137.3, 136.0, 128.6, 128.6, 128.4, 128.1, 128.1, 127.9, 127.8, 122.4, 122.3, 120.1, 110.1, 99.5 (d, *J* = 187.0 Hz), 89.3 (d, *J* = 36.0 Hz), 81.9 (d, *J* = 23.2 Hz), 81.6 (d, *J* = 7.1 Hz), 73.7, 72.7, 68.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -187.44 – -190.67 (m, 1F); **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -189.51 (s, 1F); **HRMS (ESI)** m/z cald for $C_{26}H_{24}ClFN_2O_3Na^+$ $[M+Na]^+$ 489.1352, found 489.1356.

1-((2*R*,4*S*,5*R*)-4-(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-2-yl)-3-chloro-1*H*-indazole (8ka)



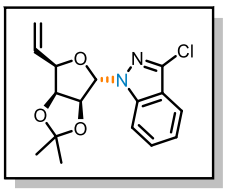
Purified by flash column chromatography (ethyl acetate/ petroleum ether = 1:30, v:v); colorless oil; (30.7 mg, 34%), $[\alpha]_D^{25}$ = -32.2 (*c* =0.4, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60–7.53 (m, 1H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.37–7.28 (m, 1H), 7.30–7.25 (m, 3H), 7.27–7.10 (m, 8H), 6.38 (t, *J* = 6.3 Hz, 1H), 4.58–4.46 (m, 2H), 4.39 (s, 2H), 4.38–4.34 (m, 1H), 4.27 (td, *J* = 5.7, 3.0 Hz, 1H), 3.48 (dd, *J* = 10.2, 5.8 Hz, 1H), 3.42 (dd, *J* = 10.3, 5.7 Hz, 1H), 3.15–3.04 (m, 1H), 2.41 (ddd, *J* = 13.7, 6.5, 3.5 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.5, 138.2, 138.0, 134.8, 128.6, 128.5, 128.1, 128.0, 128.0, 127.8, 127.7, 122.2, 122.1, 119.9, 110.2, 87.0, 83.8, 80.1, 73.53, 71.8, 70.9, 36.2; **HRMS (ESI)** m/z cald for $C_{26}H_{26}ClN_2O_3^+$ $[M+H]^+$ 449.1626, found 449.1610.

1-((2*S*,4*S*,5*R*)-4-(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-2-yl)-3-chloro-1*H*-indazole (8kb)



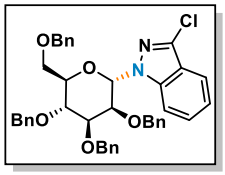
Purified by flash column chromatography (ethyl acetate/ petroleum ether = 1:30, v:v); colorless oil; (26.0 mg, 29%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66–7.55 (m, 2H), 7.35–7.30 (m, 1H), 7.30–7.20 (m, 10H), 7.16–7.12 (m, 1H), 6.32 (dd, *J* = 7.2, 5.2 Hz, 1H), 4.60–4.50 (m, 2H), 4.49–4.39 (m, 2H), 4.34–4.29 (m, 1H), 4.28–4.20 (m, 1H), 3.62 (dd, *J* = 10.7, 3.0 Hz, 1H), 3.53 (dd, *J* = 10.7, 3.8 Hz, 1H), 3.09–3.00 (m, 1H), 2.72–2.60 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.8, 137.0, 136.8, 133.2, 127.4, 127.4, 126.8, 126.7, 126.7, 126.7, 126.6, 121.2, 120.8, 118.7, 109.7, 86.8, 81.8, 77.5, 72.5, 70.9, 68.9, 35.0.

3-chloro-1-((3a*S*,4*S*,6*R*,6a*S*)-2,2-dimethyl-6-vinyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1*H*-indazole (8l)



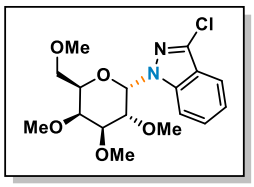
Purified by flash column chromatography (MeOH/toluene/ petroleum ether = 1:20:50, v:v:v); white solid; (52 mg, 81%), mp: 86 °C; $[\alpha]_D^{25}$ = +34.6 (c = 2.5, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.47 (ddd, *J* = 8.4, 6.8, 1.1 Hz, 1H), 7.30–7.21 (m, 1H), 6.24 (s, 1H), 6.03-5.93 (m, 1H), 5.57 (d, *J* = 5.8 Hz, 1H), 5.38–5.28 (m, 2H), 5.09 (dd, *J* = 5.8, 3.9 Hz, 1H), 4.57 (dd, *J* = 7.5, 3.9 Hz, 1H), 1.60 (s, 3H), 1.41 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.5, 135.3, 132.0, 128.5, 122.4, 121.8, 119.9, 119.8, 113.0, 110.0, 89.8, 84.8, 83.9, 82.4, 26.3, 24.9; **HRMS (ESI)** m/z cald for $C_{16}H_{17}ClN_2O_3Na^+$ $[M+Na]^+$ 343.0820, found 343.0820.

3-chloro-1-((2*S*,3*S*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-1*H*-indazole (8m)



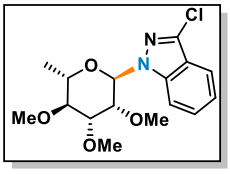
Purified by flash column chromatography (acetone/petroleum ether = 1:50, v:v); colorless oil; (92 mg, 68%), $[\alpha]_D^{25}$ = +53.9 (*c* = 2.9, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.6 Hz, 2H), 7.43–7.36 (m, 2H), 7.34–7.23 (m, 6H), 7.25–7.11 (m, 12H), 7.13–7.04 (m, 2H), 6.02 (d, *J* = 3.1 Hz, 1H), 4.78–4.65 (m, 5H), 4.64–4.46 (m, 2H), 4.45–4.33 (m, 3H), 4.01 (dd, *J* = 9.1, 7.9 Hz, 1H), 3.68 (dd, *J* = 11.0, 5.1 Hz, 1H), 3.60–3.50 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.5, 138.4, 138.3, 138.2, 138.1, 134.3, 128.5, 128.5, 128.4, 128.3, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 122.3, 121.9, 119.7, 111.3, 84.2, 78.8, 74.9, 74.5, 74.5, 73.9, 73.4, 73.3, 72.6, 69.1; **HRMS (ESI)** m/z cald for $C_{41}H_{39}ClN_2O_5Na^+$ $[M+Na]^+$ 697.2440, found 697.2432.

3-chloro-1-((2*R*,3*R*,4*S*,5*S*,6*R*)-3,4,5-trimethoxy-6-(methoxymethyl)tetrahydro-2*H*-pyran-2-yl)-1*H*-indazole (8n)



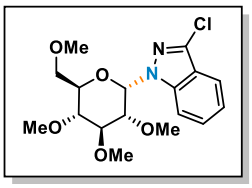
Purified by flash column chromatography (acetone / petroleum ether = 1:50, v:v); colorless oil; (49 mg, 66%), $[\alpha]_D^{25}$ = +57.2 (*c* =2.7, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70–7.62 (m, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.49–7.39 (m, 1H), 7.27–7.19 (m, 1H), 6.11 (d, *J* = 4.6 Hz, 1H), 4.88 (t, *J* = 4.9 Hz, 1H), 4.23 (dd, *J* = 7.3, 2.8 Hz, 1H), 4.07 (dd, *J* = 7.2, 5.2 Hz, 1H), 3.59–3.44 (m, 9H), 3.32 (s, 3H), 3.31 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.3, 135.4, 128.1, 122.2, 122.2, 119.9, 110.2, 90.3, 87.9, 84.8, 81.7, 79.6, 72.5, 59.7, 59.6, 59.2, 58.3; **HRMS (ESI)** m/z cald for $C_{17}H_{24}ClN_2O_5^+$ $[M+H]^+$ 371.1368, found 371.1364.

3-Chloro-1-((2*R*,3*R*,4*R*,5*S*,6*S*)-3,4,5-trimethoxy-6-methyltetrahydro-2*H*-pyran-2-yl)-1*H*-indazole (8o)



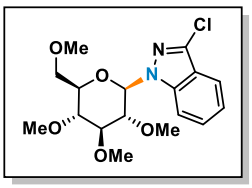
Purified by flash column chromatography (acetone / petroleum ether = 1:50, v:v); White solid; (47 mg, 70%), mp: 69 °C; $[\alpha]_D^{25}$ = -66.5 (c =2.8, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70–7.59 (m, 2H), 7.49–7.40 (m, 1H), 7.28–7.20 (m, 1H), 6.01 (d, *J* = 2.7 Hz, 1H), 4.53 (t, *J* = 3.1 Hz, 1H), 4.12 (dd, *J* = 8.0, 3.4 Hz, 1H), 3.63 (s, 3H), 3.55 (s, 3H), 3.54 (s, 3H), 3.35–3.26 (m, 1H), 3.24 (dd, *J* = 9.0, 8.0 Hz, 1H), 1.23 (d, *J* = 6.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.5, 134.3, 128.2, 122.3, 121.9, 119.8, 111.0, 83.1, 82.1, 80.7, 76.6, 70.1, 60.5, 59.5, 58.1, 18.0; **HRMS (ESI)** m/z cald for $C_{16}H_{22}ClN_2O_4^+$ $[M+H]^+$ 341.1263, found 341.1263.

3-chloro-1-((2*S*,3*R*,4*S*,5*R*,6*R*)-3,4,5-trimethoxy-6-(methoxymethyl)tetrahydro-2*H*-pyran-2-yl)-1*H*-indazole (8pa)



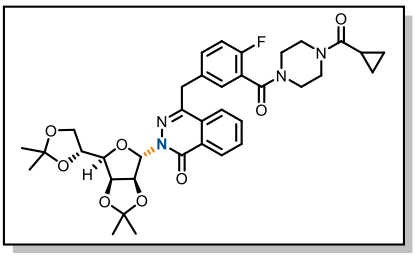
Purified by flash column chromatography (acetone/petroleum ether = 1:25, v:v); white solid; (19 mg, 26%), mp: 159 °C; $[\alpha]_D^{25}$ = +98.5 (c = 1.2, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 3.8 Hz, 2H), 7.27–7.21 (m, 1H), 6.30 (d, *J* = 6.0 Hz, 1H), 4.60 (t, *J* = 9.2 Hz, 1H), 3.82–3.75 (m, 2H), 3.73 (s, 3H), 3.60 (s, 3H), 3.51 (dd, *J* = 10.6, 3.1 Hz, 1H), 3.44 (dd, *J* = 10.2, 8.9 Hz, 1H), 3.40–3.35 (m, 4H), 3.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.3, 135.1, 128.1, 122.1, 121.6, 120.0, 109.5, 83.6, 81.4, 80.1, 79.5, 72.8, 70.7, 61.0, 60.5, 59.7, 59.2.

3-chloro-1-((2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-trimethoxy-6-(methoxymethyl)tetrahydro-2*H*-pyran-2-yl)-1*H*-indazole (8pb)



Purified by flash column chromatography (acetone/petroleum ether = 1:40, v:v); white solid; (31 mg, 42%), mp: 137 °C; $[\alpha]_D^{25}$ = -5.8 (c = 1.3, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70–7.62 (m, 1H), 7.50–7.41 (m, 2H), 7.29–7.20 (m, 1H), 5.38 (d, *J* = 8.9 Hz, 1H), 4.02 (t, *J* = 9.0 Hz, 1H), 3.68 (s, 3H), 3.63–3.53 (m, 6H), 3.39 (t, *J* = 9.1 Hz, 1H), 3.35 – 3.27 (m, 4H), 3.14 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.58, 134.26, 127.07, 121.10, 120.92, 118.82, 108.76, 86.76, 84.94, 80.04, 78.22, 76.50, 70.23, 59.94, 59.62, 59.24, 58.30; **HRMS (ESI)** m/z cald for $C_{17}H_{24}ClN_2O_5^+$ $[M+H]^+$ 371.1368, found 371.1368.

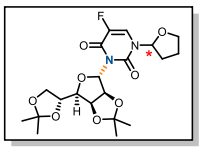
4-(3-(4-(cyclopropanecarbonyl)piperazine-1-carbonyl)-4-fluorobenzyl)-2-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)phthalazin-1(2*H*)-one (9a)



Purified by flash column chromatography (acetone/ petroleum ether = 1 : 4, v:v); colorless oil (61 mg, 45%); $[\alpha]_D^{25}$ = +39.8 (*c* = 0.9, $CHCl_3$); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.27–8.19 (m, 2H), 8.04–7.94 (m, 2H), 7.49-7.45 (m, 1H), 7.39 (s, 1H), 7.26-7.20 (m, 1H), 6.64 (s, 1H), 5.00 (d, *J* = 5.9 Hz, 1H), 4.94 (dd, *J* = 6.0, 2.6 Hz, 1H), 4.63 (s, 2H), 4.40–4.31 (m, 2H), 4.08–4.00 (m, 1H), 3.91–3.83 (m, 1H), 3.78–3.47 (m, 5H), 3.40–3.34 (m, 1H), 3.12-3.12 (m, 2H), 2.34-1.85 (m, 1H), 1.46 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H), 1.28 (s, 3H), 0.77–0.69 (m,

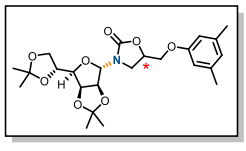
4H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 172.3, 165.0, 159.0, 158.5, 156.5, 156.1, 136.3 (d, J = 3.2 Hz), 134.1, 133.5, 132.7 (d, J = 8.2 Hz), 129.8, 128.3, 125.8, 124.6, 124.5, 124.1, 120.1, 116.9 (d, J = 21.8 Hz), 113.0, 109.1, 104.0, 85.6, 83.1, 79.8, 73.5, 66.7, 38.1, 27.5, 26.7, 26.1, 25.3, 11.3, 8.1; **^{19}F NMR** (376 MHz, DMSO-d_6) δ -119.67 (s, 1F); **^{19}F {^{1}H} NMR** (376 MHz, DMSO-d_6) δ -119.65 (s, 1F)； **HRMS (ESI)** m/z cald for $C_{36}H_{41}FN_4O_8Na^+$ $[M+Na]^+$ 699.2801, found 699.2791.

3-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-5-fluoro-1-(tetrahydrofuran-2-yl)pyrimidine-2,4(1*H*,3*H*)-dione (9b)



Purified by flash column chromatography (ethyl acetate / petroleum ether = 1:6, v:v); colorless oil (76 mg, 58%); $[\alpha]_D^{25}$ = +17.4 (c =1.3, $CHCl_3$); **^{1}H NMR** (600 MHz, Acetone-d_6) δ 7.77 (dd, J = 6.4, 1.7 Hz, 1H), 6.39 (d, J = 3.0 Hz, 1H), 6.02–5.93 (m, 1H), 5.23 (dd, J = 11.4, 6.1 Hz, 1H), 5.03 (dd, J = 6.1, 4.1 Hz, 1H), 4.61–4.56 (m, 1H), 4.38–4.33 (m, 1H), 4.31 (q, J = 6.2 Hz, 1H), 4.00 (dd, J = 8.3, 6.5 Hz, 1H), 3.97–3.91 (m, 1H), 3.87 (dd, J = 8.4, 5.9 Hz, 1H), 2.40–2.31 (m, 1H), 2.23–2.15 (m, 1H), 2.07-2.04 (m, 1H), 2.04–2.01 (m, 1H), 1.47 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H), 1.28 (s, 3H); **^{13}C NMR** (151 MHz, Acetone-d_6) δ 158.14 (d, J = 4.0 Hz), 157.97 (d, J = 4.2 Hz), 150.2, 150.1, 141.5, 140.0, 124.56 (d, J = 4.6 Hz), 124.34 (d, J = 4.4 Hz), 113.0, 112.9, 108.9, 108.9, 89. 7, 89.0, 89.0, 87.3, 85.8, 85.8, 83.0, 83.0, 74.7, 74.7, 70.9, 70.9, 66.8, 66.8, 33.2, 33.1, 30.6, 27.0, 27.0, 26.5, 26.5, 25.5, 24.5, 24.4, 24.3, 24.3 (two groups of ^{13}C-NMR peaks exist due to isomers as indicated by the red star); **^{19}F NMR** (565 MHz, Acetone-d_6) δ-167.61 (s, 1F); **^{19}F {^{1}H} NMR** (565 MHz, Acetone-d_6) δ -167.61(s, 1F); **HRMS (ESI)** m/z cald for $C_{20}H_{27}FN_2O_8Na^+$ $[M+Na]^+$ 465.1644, found 465.1650.

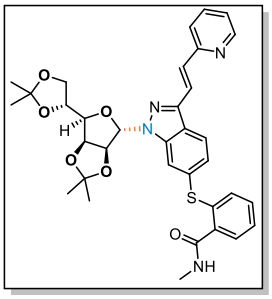
3-((3a*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-5-((3,5-dimethylphenoxy)methyl)oxazolidin-2-one (9c)



Purified by flash column chromatography (ethyl acetate/ petroleum ether = 1 : 2.7, v:v); colorless oil (34 mg, 37%); $[\alpha]_D^{25}$ = +44.5 (c =0.5, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.64 (s, 1H), 6.54 (s, 1H), 6.53 (s, 1H), 5.40 (dd, J = 9.7, 5.8 Hz, 1H), 5.05–4.97 (m, 2H), 4.90–4.80 (m, 1H), 4.42–4.33 (m, 1H), 4.27–4.18 (m, 1H), 4.18–4.00 (m, 4H), 3.98–3.55 (m, 2H), 2.29 (s, 6H), 1.49 (d, J = 1.6 Hz, 3H), 1.45 (d, J = 4.6 Hz, 3H), 1.37 (s, 3H), 1.36 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.2, 157.1, 157.0, 139.6, 123.6, 123.6, 112.8, 112.8, 112.5, 112.5, 109.3, 109.3, 90.9, 90.8,

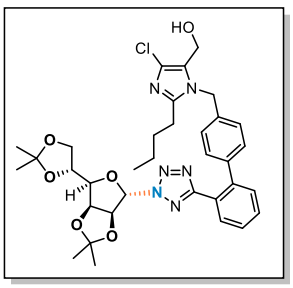
83.6, 83.6, 83.6, 83.4, 80.9, 73.7, 73.6, 71.9, 71.6, 67.9, 67.8, 66.7, 66.5, 47.3, 47.3, 27.0, 26.9, 26.1, 26.1, 25.3, 25.2, 24.5, 24.5, 21.5, 21.5 (two groups of ^{13}C-NMR peaks exist due to isomers as indicated by the red star); **HRMS (ESI)** m/z cald for $C_{24}H_{33}NO_8Na^+$ $[M+Na]^+$ 486.2098, found 486.2097.

2-((1-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-3-((*E*)-2-(pyridin-2-yl)vinyl)-1*H*-indazol-6-yl)thio)-*N*-methylbenzamide (9d)



Purified by flash column chromatography (MeOH/DCM = 1:20, v:v); colorless oil; (59 mg, 47%), $[\alpha]_D^{25}$ = +50.3 (*c* =0.6, $CHCl_3$); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.65–8.59 (m, 1H), 8.40 (q, *J* = 4.5 Hz, 1H), 8.28–8.22 (m, 1H), 8.14 (s, 1H), 7.93 (d, *J* = 16.4 Hz, 1H), 7.83 (td, *J* = 7.7, 1.8 Hz, 1H), 7.72–7.61 (m, 2H), 7.54–7.48 (m, 1H), 7.35–7.27 (m, 4H), 7.24 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.06–7.01 (m, 1H), 6.63 (s, 1H), 5.49 (d, *J* = 5.9 Hz, 1H), 5.15 (dd, *J* = 5.9, 3.8 Hz, 1H), 4.39–4.29 (m, 1H), 4.18 (dd, *J* = 5.7, 3.8 Hz, 1H), 3.96 (dd, *J* = 8.5, 6.6 Hz, 1H), 3.77 (dd, *J* = 8.4, 5.9 Hz, 1H), 2.78 (d, *J* = 4.6 Hz, 3H), 1.50 (s, 3H), 1.37 (s, 3H), 1.26 (s, 3H), 1.24 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 168.3, 154.9, 150.1, 143.3, 142.0, 137.4, 137.4, 136.1, 134.5, 131.5, 130.8, 130.5, 128.2, 127.2, 126.6, 123.4, 123.3, 123.0, 122.5, 121.7, 115.4, 112.5, 108.3, 89.5, 84.6, 82.7, 80.5, 73.3, 65.8, 26.9, 26.6, 26.2, 25.5, 24.7; **HRMS (ESI)** m/z cald for $C_{34}H_{36}N_4O_6SNa^+$ $[M+Na]^+$ 651.2248, found 651.2235.

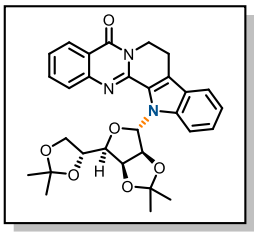
(2-butyl-4-chloro-1-((2'-(2-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-2*H*-tetrazol-5-yl)-[1,1'-biphenyl]-4-yl)methyl)-1*H*-imidazol-5-yl)methanol (9e)



Purified by flash column chromatography (ethyl acetate / petroleum ether = 1:3.5, v:v); colorless oil; (81 mg, 61%), $[\alpha]_D^{25}$ = +19.2 (*c* =1.3, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.58–7.46 (m, 2H), 7.39 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.33 (s, 1H), 5.24 (s, 2H), 5.05 (d, *J* = 5.8 Hz, 1H), 4.87 (dd, *J* = 5.9, 3.8 Hz, 1H), 4.50 (s, 2H), 4.39 (td, *J* = 6.8, 4.4 Hz, 1H), 4.04 (dt, *J* = 7.3, 5.2 Hz, 2H), 3.85 (dd, *J* = 8.8, 4.4 Hz, 1H), 2.58 (t, *J* = 7.8 Hz, 2H), 1.63 (ddd, *J* = 15.4, 8.8, 6.6 Hz, 2H), 1.54 (s, 3H), 1.41 (s, 3H), 1.33 (d, *J* = 7.5 Hz, 9H), 0.86 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.4, 147.5, 140.2,

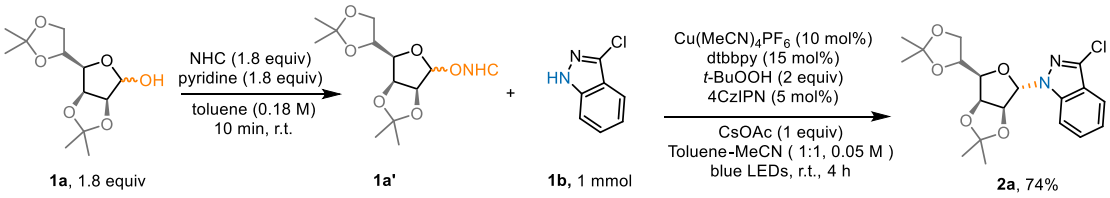
139.7, 133.9, 129.9, 129.4, 129.3, 128.8, 126.8, 125.8, 124.8, 124.4, 124.1, 112.8, 108.4, 92.7, 83.7, 82.6, 78.9, 71.8, 65.4, 52.0, 46.6, 28.7, 25.8, 25.7, 24.9, 24.1, 23.5, 21.4, 12.7; **HRMS (ESI)** m/z cald for $C_{34}H_{41}ClN_6O_6Na^+$ $[M+Na]^+$ 687.2668, found 687.2675.

13-((3a*S*,4*S*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-8,13-dihydroindolo[2',3':3,4]pyrido[2,1-*b*]quinazolin-5(7*H*)-one (9f)



Purified by flash column chromatography (acetone/DCM = 1:20, v:v); white solid (112 mg, 53%), m.p.: 218-220 °C; $[\alpha]_D^{25}$ = -15.2 (*c* =0.6, $CHCl_3$); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.75–7.69 (m, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 3.0 Hz, 1H), 7.50–7.35 (m, 3H), 7.22 (t, *J* = 7.3 Hz, 1H), 5.61 (dd, *J* = 5.9, 3.0 Hz, 1H), 5.23 (dd, *J* = 5.9, 4.0 Hz, 1H), 4.69 (dd, *J* = 7.3, 4.1 Hz, 1H), 4.66–4.58 (m, 1H), 4.56–4.51 (m, 1H), 4.51–4.44 (m, 1H), 4.14 (dd, *J* = 8.8, 6.3 Hz, 1H), 4.06 (dd, *J* = 8.8, 4.9 Hz, 1H), 3.13 (t, *J* = 6.7 Hz, 2H), 1.69 (s, 3H), 1.43 (s, 3H), 1.42 (s, 3H), 1.40 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.6, 147.1, 145.2, 139.6, 134.4, 127.3, 127.3, 126.9, 126.6, 126.2, 125.5, 123.1, 121.4, 121.0, 120.5, 113.9, 112.1, 109.3, 93.2, 85.5, 83.3, 81.6, 74.1, 66.8, 40.4, 27.2, 27.0, 25.5, 25.4, 20.0; **HRMS (ESI)** m/z cald for $C_{30}H_{31}N_3O_6Na^+$ $[M+Na]^+$ 552.2105, found 552.2111.

2.3 N-glycosylation procedure on 1 mmol scale



An oven-dried 50 mL Schlenk tube was charged with 1-hydroxylmannose **1a** (470.3 mg, 1.8 mmol, 1.8 equiv), NHC (395.3 mg, 1.8 mmol, 1.8 equiv) and a magnetic stir bar. After the Schlenk tube was vacuumed and refilled with nitrogen gas three times, dry toluene (10 mL) was added and the reaction stirred at r.t. for 5 min. Then, pyridine (145.5 μL, 1.8 mmol, 1.8 equiv) was added dropwise at room temperature. The resulting solution stirred at r.t. for 10 min. A white solid precipitated out during this time.

Another 10 mL Schlenk tube was charged with 4CzIPN (38 mg, 0.1 mmol, 0.05 equiv),

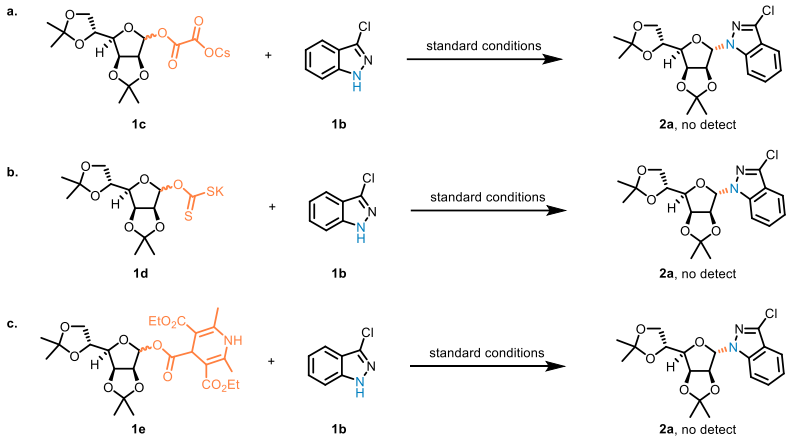
$Cu(MeCN)_4PF_6$ (37.4 mg, 0.1 mmol, 0.1 equiv), dtbbpy (40.0 mg, 0.15 mmol, 0.15 equiv) CsOAc (192 mg, 1 mmol, 1.0 equiv), 3-chlorideindazole (156 mg, 1 mmol, 1.0 equiv) and a magnetic stir bar. And this Schlenk tube was vacuumed and refilled with nitrogen gas three times. Dry MeCN (10 mL) was added to this Schlenk tube under an atmosphere of nitrogen and stirred at r.t.

The toluene suspension was transferred to a 10 mL syringe under an atmosphere of nitrogen (twice). Then a syringe filter and new needle were installed on the syringe, before the toluene solution was injected through the syringe filter into the MeCN solution. *t*-BuOOH (400 μL, 5-6 M in decane, 2.0 equiv) was added before placing under 420 nm blue LEDs. The mixture then irradiates at r.t. for 4 h. The organic layers were evaporated and then purified by flash column chromatography (petroleum ether/acetone = 150:1 ~ 80:1) on silica gel to give the desired product **2a** (288 mg, 74%) as a white solid.

2.4 Oxalate, DHP ester, xanthate salt as glycosyl donors

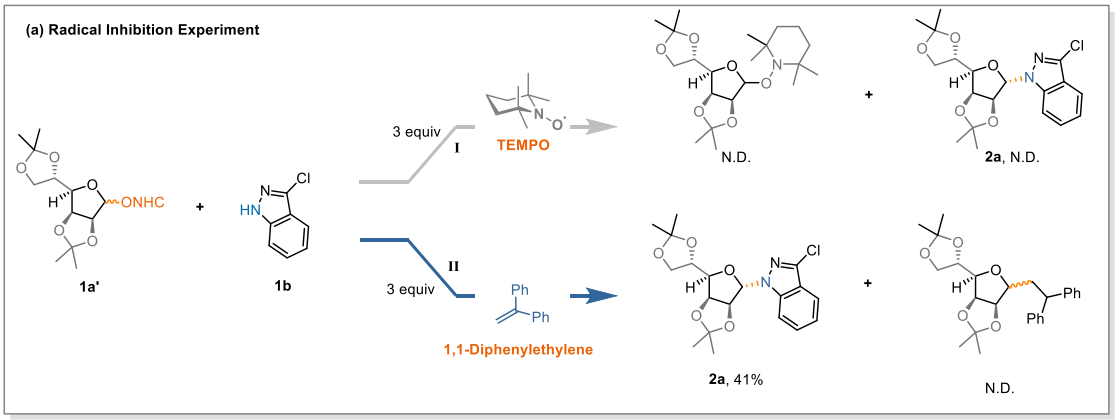
Glycosyl oxalate (**1c**) [3], glycosyl xanthate salt (**1d**) [4], glycosyl DHP ester [2] (**1e**) were synthesized according to the reported procedures. Due to the instability of **1c** and **1d**, they were used directly without purification. **1e** was purified by column chromatography on silica gel.

An oven-dried 10 mL Schlenk tube was charged with glycosyl donor (**1c**, **1d,** or **1e,** 0.36 mmol, 1.8 equiv), 4CzIPN (7.5 mg, 0.01 mmol, 0.05 equiv), $Cu(MeCN)_4PF_6$ (7.4 mg, 0.02 mmol, 0.1 equiv), dtbbpy (8.0 mg, 0.03 mmol, 0.15 equiv), CsOAc (38.4 mg, 0.2 mmol, 1.0 equiv), 3-chlorideindazole (31.2 mg, 0.2 mmol, 1.0 equiv) and a magnetic stir bar. And this Schlenk tube was vacuumed and refilled with nitrogen gas three times. Dry MeCN (2.0 mL) was added to this Schlenk tube under an atmosphere of nitrogen and stirred for 5 min. *t*-BuOOH (80 μL, 5-6 M in decane, 2 equiv) was added before placing under 420 nm blue LEDs. The mixture then irradiates at r.t. for 4 h. Virtually no products were observed in each reaction.



2.5 Mechanistic studies

2.5.1 Radical trapping experiments



(I) *With TEMPO:* An oven-dried 10 mL Schlenk tube was charged with 1-hydroxylmannose **1a** (94 mg, 0.36 mmol, 1.8 equiv), NHC (142.4 mg, 0.36 mmol, 1.8 equiv) and a magnetic stir bar. After the Schlenk tube was vacuumed and refilled with nitrogen gas three times, dry toluene (2.0 mL) was added and the reaction stirred at r.t. for 5 min. Then, pyridine (29.1 μL, 0.36 mmol, 1.8 equiv) was added dropwise at room temperature. The resulting solution stirred at r.t. for 10 min. A white solid precipitated out during this time.

Another 10 mL Schlenk tube was charged with TEMPO (93.5 mg, 0.6 mmol, 3.0 equiv), 4CzIPN (7.5 mg, 0.01 mmol, 0.05 equiv), $Cu(MeCN)_4PF_6$ (7.4 mg, 0.02 mmol, 0.1 equiv), dtbbpy (8.0 mg, 0.03 mmol, 0.15 equiv), CsOAc (38.4 mg, 0.2 mmol, 1.0 equiv), 3-chlorideindazole (31.2 mg, 0.2 mmol, 1.0 equiv) and a magnetic stir bar. And this Schlenk tube was vacuumed and refilled with nitrogen gas three times. Dry MeCN (2.0 mL) was added to this Schlenk tube under an atmosphere of nitrogen and stirred at r.t.

The toluene suspension was transferred to a 5 mL syringe under an atmosphere of nitrogen.

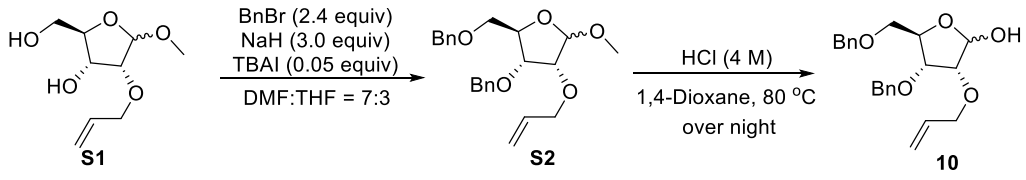
Then a syringe filter and new needle were installed on the syringe, before the toluene solution was injected through the syringe filter into the MeCN solution. *t*-BuOOH (80 μL 5-6 M in decane, 2.0 equiv) was added before placing under 420 nm blue LEDs. The mixture then irradiates at r.t. for 4 h.

(II): *With 1,1-Diphenylethylene:* An oven-dried 10 mL Schlenk tube was charged with 1-hydroxylmannose **1a** (94 mg, 0.36 mmol, 1.8 equiv), NHC (142.4 mg, 0.36 mmol, 1.8 equiv) and a magnetic stir bar. After the Schlenk tube was vacuumed and refilled with nitrogen gas three times, dry toluene (2.0 mL) was added and the reaction stirred at r.t. for 5 min. Then, pyridine (29.1 μL, 0.36 mmol, 1.8 equiv) was added dropwise at room temperature. The resulting solution stirred at r.t. for 10 min. A white solid precipitated out during this time.

Another 10 mL Schlenk tube was charged with 1,1-Diphenylethylene (108 mg, 0.6 mmol, 3.0 equiv), 4CzIPN (7.5 mg, 0.01 mmol, 0.05 equiv), $Cu(MeCN)_4PF_6$ (7.4 mg, 0.02 mmol, 0.1 equiv), dtbbpy (8.0 mg, 0.03 mmol, 0.15 equiv), CsOAc (38.4 mg, 0.2 mmol, 1.0 equiv), 3-chlorideindazole (31.2 mg, 0.2 mmol, 1.0 equiv) and a magnetic stir bar. And this Schlenk tube was vacuumed and refilled with nitrogen gas three times. Dry MeCN (2.0 mL) was added to this Schlenk tube under an atmosphere of nitrogen and stirred at r.t.

The toluene suspension was transferred to a 5 mL syringe under an atmosphere of nitrogen. Then a syringe filter and new needle were installed on the syringe, before the toluene solution was injected through the syringe filter into the MeCN solution. *t*-BuOOH (80 μL, 5-6 M in decane, 2.0 equiv) was added before placing under 420 nm blue LEDs. The mixture then irradiates at r.t. for 4 h.

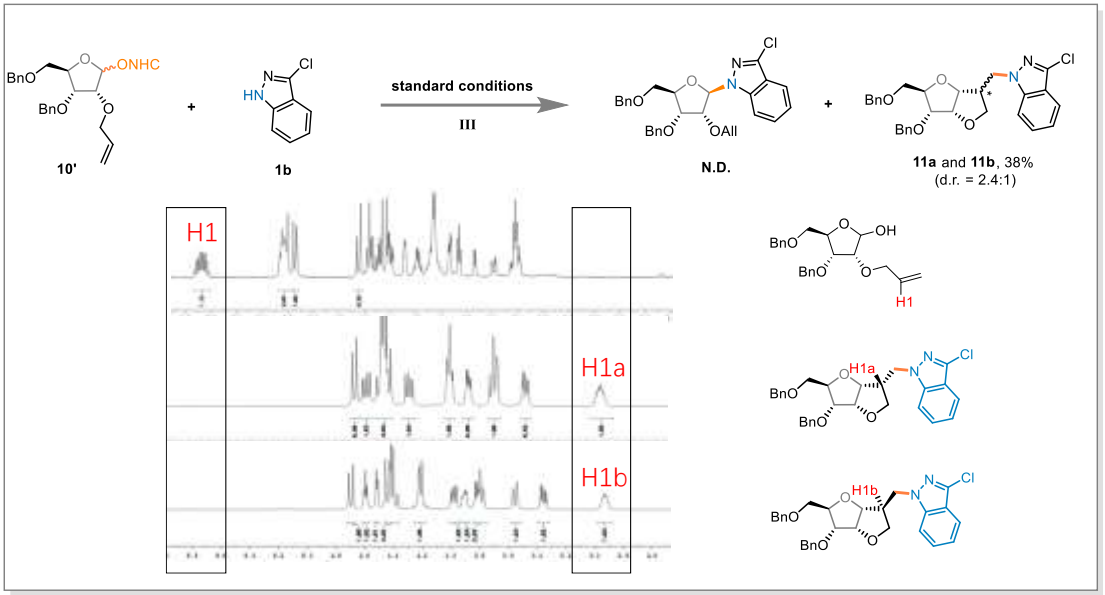
2.5.2 Radical clock experiments



Compound **S1** [1] (1.02 g, 5 mmol, 1.0 equiv) and TBAI (92 mg) were placed in a 100 mL round-bottom flask, along with a magnetic stirring bar. The flask was evacuated and backfilled with N_2 three times, and a N_2 balloon was attached before adding DMF (35 mL) and THF (15 mL, 0.1 M). The mixture was cooled to 0 °C. Subsequently, NaH was added in batches (600 mg, 15 mmol, 3.0 equiv) and stirred at the same temperature for 1 hour. The reaction mixture was then allowed to warm up to room temperature. BnBr (1.43 mL, 12 mmol, 2.4 equiv) was

added dropwise to the reaction mixture. After vigorous stirring for 8 hours, the reaction mixture was quenched with water (2 mL), and then concentrated under reduced pressure. Compound **S2** (1.42 g, 74%) was obtained as a mixture of diastereomers by column chromatography (silica gel, EtOAc / petroleum ether, 0:100 to 1:20) and used directly for the next step.

Compound **S2** (1.42 g, 3.7 mmol) was dissolved in 10 mL of 1,4-dioxane and added to a 50 mL round-bottom flask equipped with a magnetic stirring bar. Subsequently, 10 mL of 4 M HCl was introduced. The resulting mixture was heated to 80 °C and stirred for 18 hours. Following this, the mixture was concentrated under reduced pressure. Purification of the mixture was performed through column chromatography on silica gel using an eluent mixture of ethyl acetate and petroleum ether in increasing proportions ranging from 0:100 to 1:5. This technique afforded compound **10** (790 mg, 58%) [1]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.16 (m, 10H), 5.87 (m, 1H), 5.26–5.18 (m, 2H), 5.13 (d, J = 10.4 Hz, 1H), 4.67–4.35 (m, 4H), 4.31–3.99 (m, 4H), 3.95–3.35 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.0, 137.8, 137.6, 137.5, 134.5, 134.2, 128.6, 128.6, 128.5, 128.5, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 117.9, 117.8, 100.5, 96.3, 81.0, 81.0, 80.9, 77.8, 77.7, 77.3, 73.6, 73.6, 72.9, 72.6, 71.7, 71.6, 70.1, 69.6.



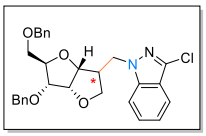
(III): 1d *as radical donor:* An oven-dried 10 mL Schlenk tube was charged with 1-hydroxylmannose **10** (133 mg, 0.36 mmol, 1.8 equiv), NHC (142.4 mg, 0.36 mmol, 1.8 equiv.) and a magnetic stir bar. After the Schlenk tube was vacuumed and refilled with nitrogen gas three times, dry toluene (2.0 mL) was added and the reaction stirred at r.t. for 5 min. Then, pyridine (29.1 μL, 0.36 mmol, 1.8 equiv) was added dropwise at room temperature. The resulting solution stirred at r.t. for 10 min. A white solid precipitated out during this time.

Another 10 mL Schlenk tube was charged with 4CzIPN (7.5 mg, 0.01 mmol, 0.05 equiv),

$Cu(MeCN)_4PF_6$ (7.4 mg, 0.02 mmol, 0.1 equiv), dtbbpy (8 mg, 0.03 mmol, 0.15 equiv) CsOAc (38.4 mg, 0.2 mmol, 1.0 equiv), 3-chlorideindazole (31.2 mg, 0.2 mmol, 1.0 equiv) and a magnetic stir bar. And this Schlenk tube was vacuumed and refilled with nitrogen gas three times. Dry MeCN (2.0 mL) was added to this Schlenk tube under an atmosphere of nitrogen and stirred in a parallel light low-temperature reactor (0 ºC, 420 nm blue LEDs).

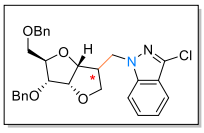
The toluene suspension was transferred to a 5 mL syringe under an atmosphere of nitrogen. Then a syringe filter and new needle were installed on the syringe, before the toluene solution was injected through the syringe filter into the MeCN solution. *t*-BuOOH (80 μL, 5-6 M in decane, 2 equiv) was added and irradiated at 0 ºC for 4 h. The organic layers were evaporated and then purified by flash column chromatography (petroleum ether/ ethyl acetate = 100:1~20:1) on silica gel.

1-(((3aR,5R,6R,6aS)-6-(benzyloxy)-5-((benzyloxy)methyl)hexahydrofuro[3,2-b]furan-3-yl)methyl)-3-chloro-1*H*-indazole (11a)



Purified by flash column chromatography (petroleum ether/ ethyl acetate = 100:1~20:1, v:v); (26.7 mg, 27%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.31–7.15 (m, 11H), 7.09 (t, *J* = 7.5 Hz, 1H), 4.66 (d, *J* = 11.8 Hz, 1H), 4.58 (dd, *J* = 14.1, 7.4 Hz, 1H), 4.51–4.38 (m, 4H), 4.27 (dd, *J* = 14.1, 7.0 Hz, 1H), 3.98 (td, *J* = 8.1, 7.7, 3.2 Hz, 2H), 3.84 (dd, *J* = 8.4, 4.1 Hz, 1H), 3.71 – 3.62 (m, 2H), 3.44 (dd, *J* = 10.9, 4.6 Hz, 1H), 2.97–2.83 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.2, 138.2, 137.8, 133.3, 128.5, 128.5, 128.1, 128.0, 127.7, 127.7, 127.6, 121.4, 121.0, 119.7, 109.9, 82.5, 81.8, 81.7, 80.2, 73.6, 72.3, 72.3, 70.2, 46.7, 45.5; **HRMS (ESI)** m/z cald for $C_{29}H_{29}ClN_2O_4Na^+$ $[M+Na]^+$ 527.1708, found 527.1697.

1-(((3aR,5R,6R,6aS)-6-(benzyloxy)-5-((benzyloxy)methyl)hexahydrofuro[3,2-b]furan-3-yl)methyl)-3-chloro-1*H*-indazole (11b)



Purified by flash column chromatography (petroleum ether/ ethyl acetate = 100:1~20:1, v:v); (11.1 mg, 11%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 1H), 7.36 (dd, *J* = 8.3, 7.0 Hz, 1H), 7.30–7.17 (m, 11H), 7.13 (t, *J* = 7.5 Hz, 1H), 4.70 (d, *J* = 11.8 Hz, 1H), 4.60 (t, *J* = 4.5 Hz, 1H), 4.52 (d, *J* = 4.4 Hz, 1H), 4.48–4.35 (m, 3H), 4.28–4.14 (m, 2H), 3.98 (dd, *J* = 9.4, 5.6 Hz, 1H), 3.91 (ddd, *J* = 7.4, 4.8, 2.3 Hz, 1H), 3.80 (ddd, *J* = 11.4, 8.9, 3.6 Hz, 2H), 3.56 (dd, *J* = 10.7, 2.3 Hz, 1H), 3.36 (dd, *J* = 10.8, 4.8 Hz, 1H), 2.94 (dd, *J* = 10.5, 4.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.1, 138.1, 137.8, 133.4, 128.6, 128.5, 128.1, 128.1, 128.0, 127.9, 127.8, 121.6, 121.4, 120.1, 109.1,

85.1, 80.7, 80.1, 79.7, 73.6, 72.4, 72.0, 69.9, 49.3, 48.6; **HRMS (ESI)** m/z cald for $C_{29}H_{29}ClN_2O_4Na^+$ $[M+Na]^+$ 527.1708, found 527.1703.

2.5.2 Cyclic voltammetry data

Cyclic voltammetry experiment was performed in a three-electrode cell connected to an undivided three-necked bottle with stir bar under nitrogen at room temperature. The working electrode was a glass carbon electrode, while the counter electrode was a platinum wire. The reference electrode was an Ag/AgCl electrode submerged in a saturated aqueous KCl solution. After adding 0.01 mmol substrates (if solid), the mixture then purged with nitrogen. Under the protection of N_2, anhydrous and degassed 10 mL 0.01M $^n Bu_4N^+BF_4^-$ solution (in CH_3CN) were injected into the electrochemical cell. The scan rate was set at 0.1 V/s, covering a voltage range from 0 V to 3 V.

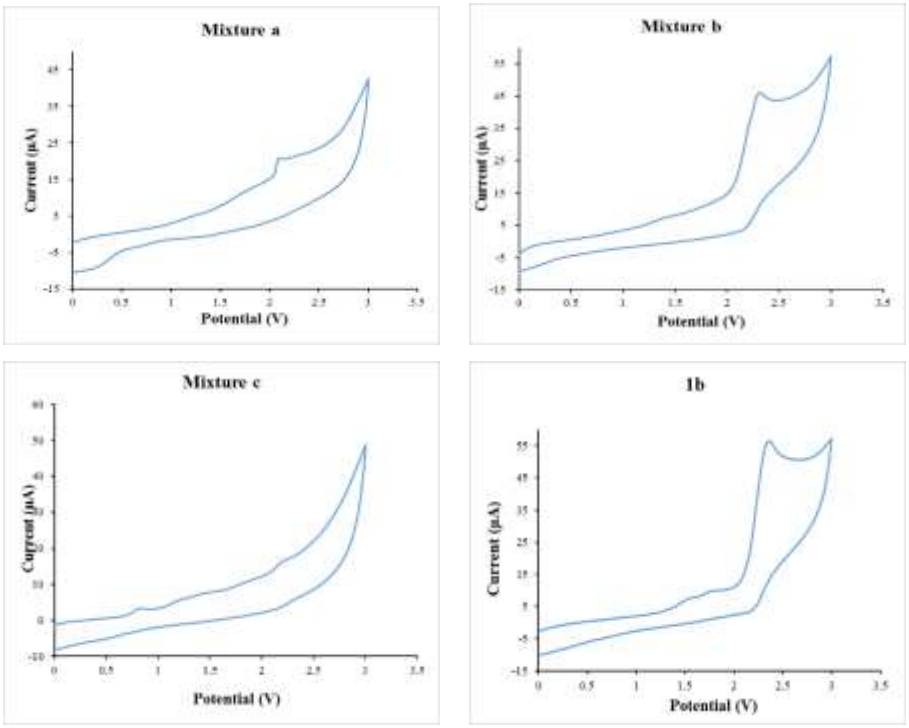
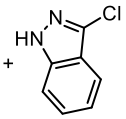
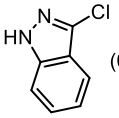


Figure S1 | Cyclic voltammetry data of catalyst system.

Mixture a: 0.01 mmol $Cu(MeCN)_4PF_6$ + 0.01 mmol dtbbpy

Mixture b: 0.01 mmol $Cu(MeCN)_4PF_6$ + 0.01 mmol dtbbpy +  (0.01 mmol)

Mixture c: 0.01 mmol $Cu(MeCN)_4PF_6$ + 0.01 mmol dtbbpy + CsOAc +  (0.01 mmol)

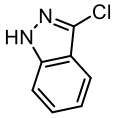
1b:  (0.01 mmol)

Table S16 | Cyclic voltammetry data of catalyst system

Mixture	*E* (V)
Mixture a	E_{ox} = 2.10 V
Mixture b	E_{ox} = 2.32 V
Mixture c	E_{ox} = 0.83 V
1b	E_{ox} = 2.36 V

2.5.3 Stern-Volmer experiment

The fluorescence quenching studies were performed using an Agilent Cary Eclipse Fluorescence Spectrophotometer. In each experiment, the photocatalyst and different concentrations of quencher were mixed in a 1:1 MeCN/toluene mixture in screw top 1.0 cm quartz cuvettes. Both MeCN and toluene were degassed by sparging with argon for 30 minutes. The emission quenching of 4CzIPN involved a photocatalyst concentration of 5.0 x 10^{-4} M. The solution was then irradiated at 420 nm, and the resulting emission intensity was observed at 550 nm. Plots were constructed according to the Stern–Volmer equation $I_0/I = 1 + k_q\tau_0[Q]$.

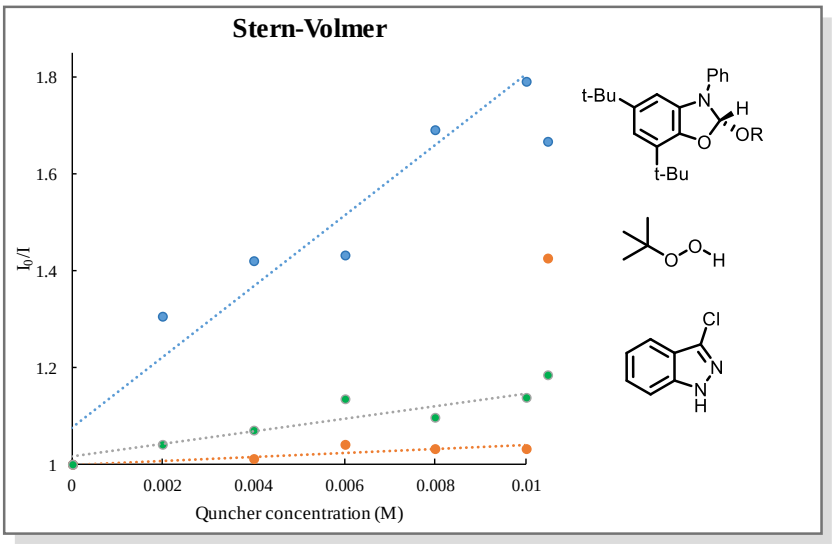


Figure S2 | Emission quenching study of three different substrates with 4CzIPN in MeCN/toluene = 1 : 1 mixture.

2.5.4 UV-Vis spectra

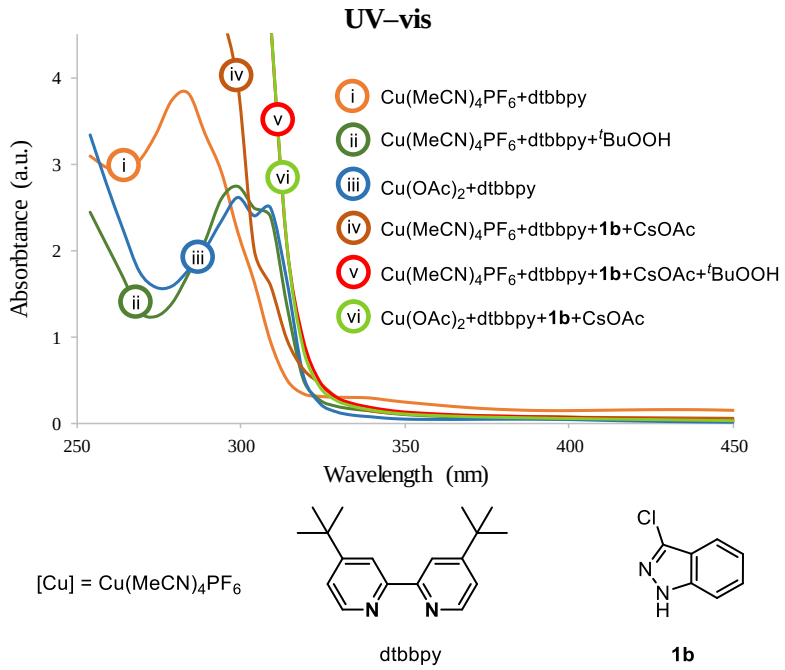


Figure S3 | UV-Vis spectra of 0.1 mM solutions of copper salt mixture in MeCN.

2.5.5 Oxidation of copper salts

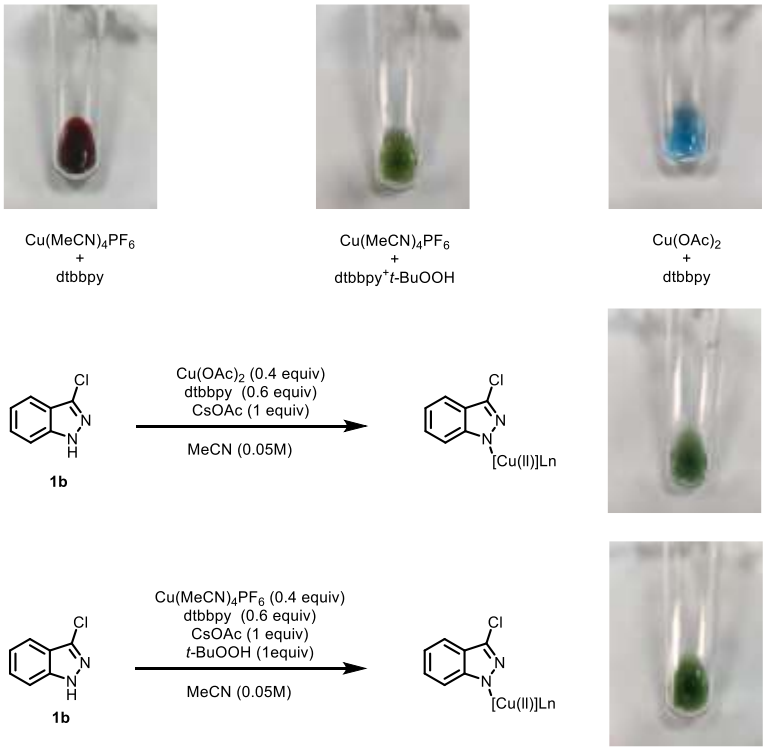


Figure S4 | Oxidation of copper salt mixture in MeCN.

3. References

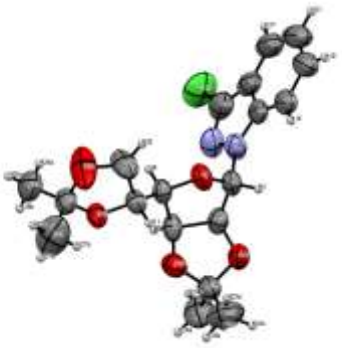
[1] Li, Y.; Wang, Z.; Li, L.; Tian, X.; Shao, F.; Li, C., Chemoselective and Diastereoselective Synthesis of C-Aryl Nucleoside Analogues by Nickel-Catalyzed Cross-Coupling of Furanosyl Acetates with Aryl Iodides. *Angew. Chem. Int. Ed.* **2022**, *61*, e202110391.

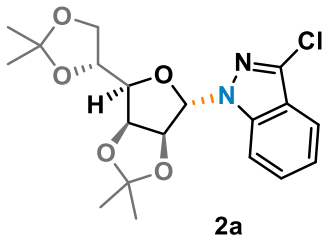
[2] Wei, Y.; Ben-Zvi, B.; Diao, T., Diastereoselective Synthesis of Aryl C-Glycosides from Glycosyl Esters via C-O Bond Homolysis. *Angew. Chem. Int. Ed. Engl.* **2021**, *60*, 9433-9438.

[3] Nawrat, C. C.; Jamison, C. R.; Slutskyy, Y.; MacMillan, D. W. C.; Overman, L. E., Oxalates as Activating Groups for Alcohols in Visible Light Photoredox Catalysis: Formation of Quaternary Centers by Redox-Neutral Fragment Coupling. *J Am Chem Soc.* **2015**, *137*, 11270-11273.

[4] Guo, H. M.; Wu, X., Selective deoxygenative alkylation of alcohols via photocatalytic domino radical fragmentations. *Nat Commun.* **2021**, *12*, 5365.

4. X-ray crystal structure data





2a

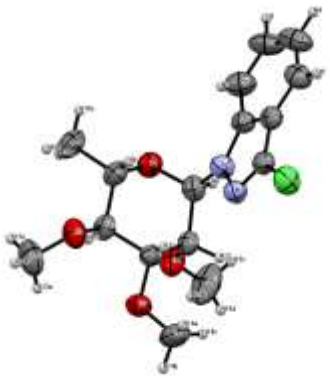
The crystal structure has been deposited at the Cambridge Crystallographic Date Center and allocated the deposition number CCDC 2305000

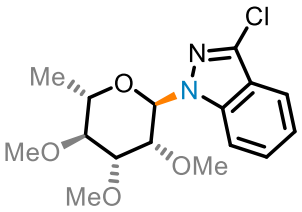
This data can be obtained free of charge from the Cambridge Crystallographic Date Center via www.ccdc.cam.ac.uk/data_request/cif

Table 1. Crystal data and structure refinement for **2a**.

Identification code	**2a**	
Empirical formula	C19 H23 Cl N2 O5	
Formula weight	394.84	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.946(3) Å	α= 90°.
	b = 13.868(4) Å	β= 90°.
	c = 14.628(4) Å	γ = 90°.
Volume	2017.7(9) $Å^3$	
Z	4	
Density (calculated)	1.300 Mg/m^3	
Absorption coefficient	0.221 mm^{-1}	
F(000)	832	
Crystal size	0.240 x 0.220 x 0.210 mm^3	
Theta range for data collection	2.024 to 25.498°.	
Index ranges	-12<=h<=11, -16<=k<=16, -17<=l<=17	
Reflections collected	15818	
Independent reflections	3752 [R(int) = 0.0243]	
Completeness to theta = 25.242°	100.0 %	

Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3752 / 0 / 249
Goodness-of-fit on F^2	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0447, wR2 = 0.1115
R indices (all data)	R1 = 0.0579, wR2 = 0.1252
Absolute structure parameter	0.019(19)
Extinction coefficient	0.0113(16)
Largest diff. peak and hole	0.408 and -0.310 e.Å^{-3}





8o

The crystal structure has been deposited at the Cambridge Crystallographic Date Center and allocated the deposition number CCDC 2305001
This data can be obtained free of charge from the Cambridge Crystallographic Date Center via www.ccdc.cam.ac.uk/data_request/cif

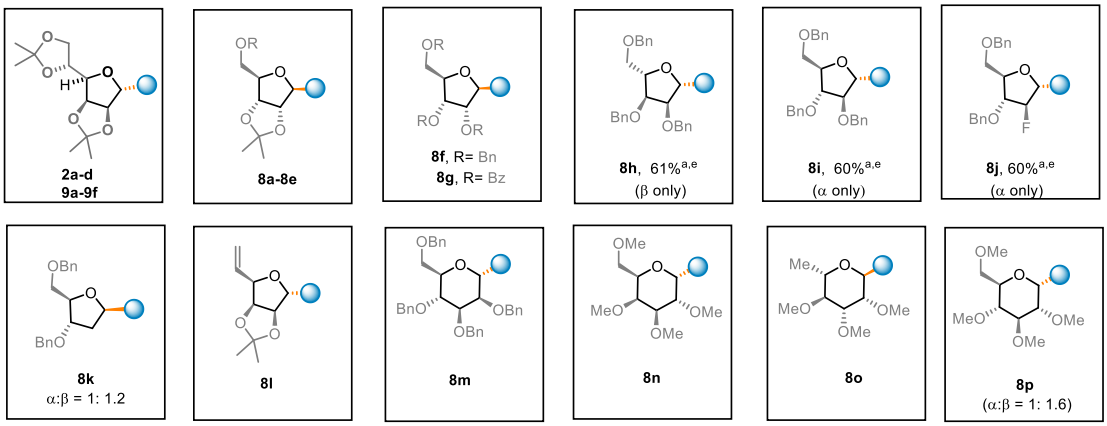
Table 2. Crystal data and structure refinement for **8o**

Identification code	**8o**	
Empirical formula	C16 H21 Cl N2 O4	
Formula weight	340.80	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 8.025(2) Å	= 90°.
	b = 8.715(2) Å	= 95.615(3)°.
	c = 12.609(3) Å	= 90°.
Volume	877.6(4) Å^3	

Z	2
Density (calculated)	1.290 Mg/m^3
Absorption coefficient	0.238 mm^{-1}
F(000)	360
Crystal size	0.220 x 0.180 x 0.170 mm^3
Theta range for data collection	2.550 to 25.498°.
Index ranges	-9<=h<=9, -9<=k<=10, -15<=l<=15
Reflections collected	6825
Independent reflections	2978 [R(int) = 0.0138]
Completeness to theta = 25.242°	99.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2978 / 1 / 212
Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0282, wR2 = 0.0776
R indices (all data)	R1 = 0.0300, wR2 = 0.0792
Absolute structure parameter	0.960(18)
Extinction coefficient	n/a
Largest diff. peak and hole	0.123 and -0.130 $e.Å^{-3}$

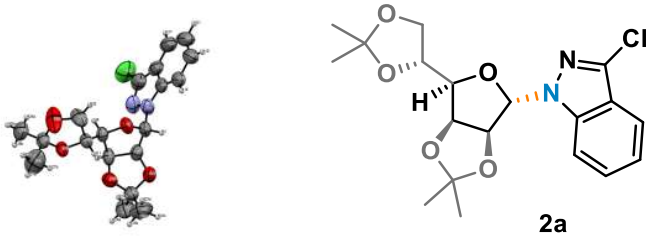
5. Structure Determination

5.1 Determination of the anomeric stereochemistry

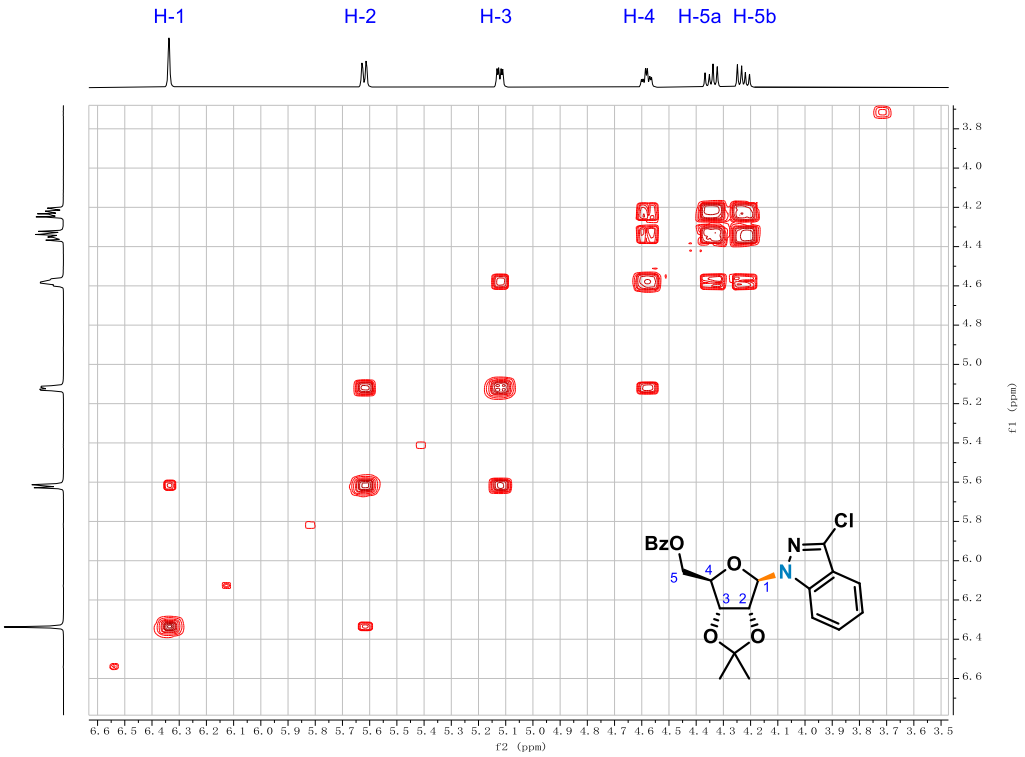


As shown in the figure above, there are 12 types of sugars used in this work. To determine the stereochemistry of the anomeric carbon, compound **2a**, **8a**, **8f**, **8h**, **8i**, **8j**, **8ka**, **8l**, **8m**, **8n**, **8o**, **8pb** were selected for detailed NMR analyses. Firstly, most meaningful protons were assigned with the aid of COSY. Then, characteristic NOE signals between H1 and H4 on the sugar ring were identified as shown in the following spectra (**8a**, **8f**, **8h**, **8i**, **8j**, **8ka**). For **8m**, **8n**, **8o** and **8pb**, the coupling constant *J* of anomeric hydrogen can judge their spatial configuration. Under such circumstances, the stereochemistry is determined as *α* when *J* < 6Hz. This conclusion is consistent with the X-Ray of **8o**. For **2a** and **8l**, there is no characteristic NOE signals between H1 and H4, indicating 1,4-trans relationship, which is consistent with X-ray crystal structure of **2a**. Therefore, the stereochemistry of **8l** was assigned in analogy to **2a**.

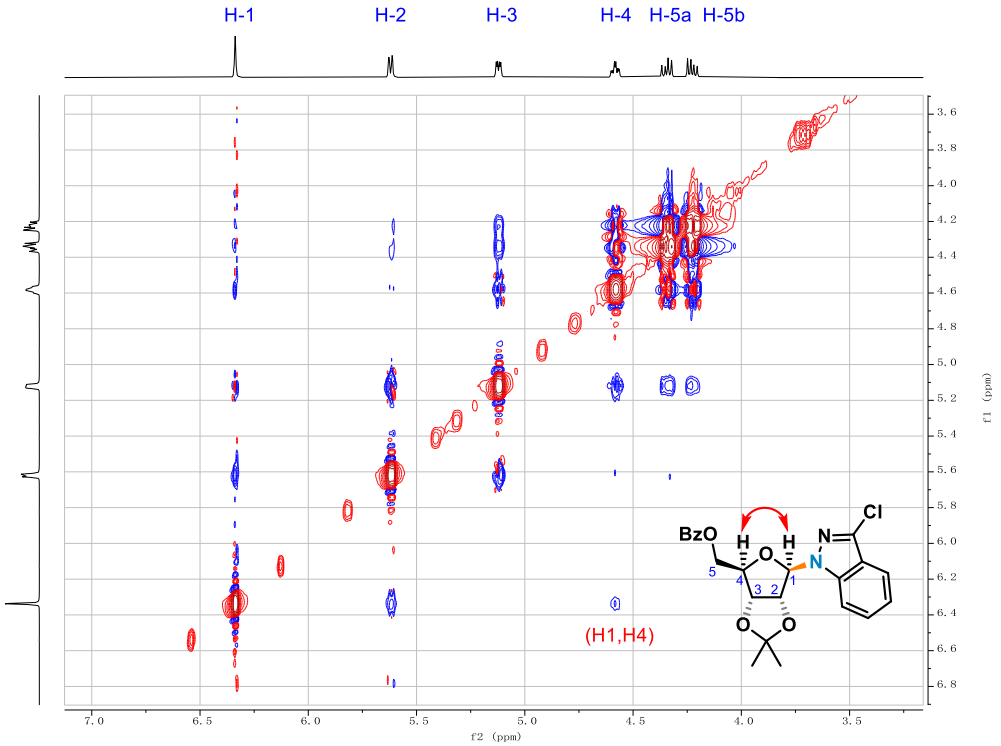
Anomeric stereochemistry of **2a** determined by X-Ray



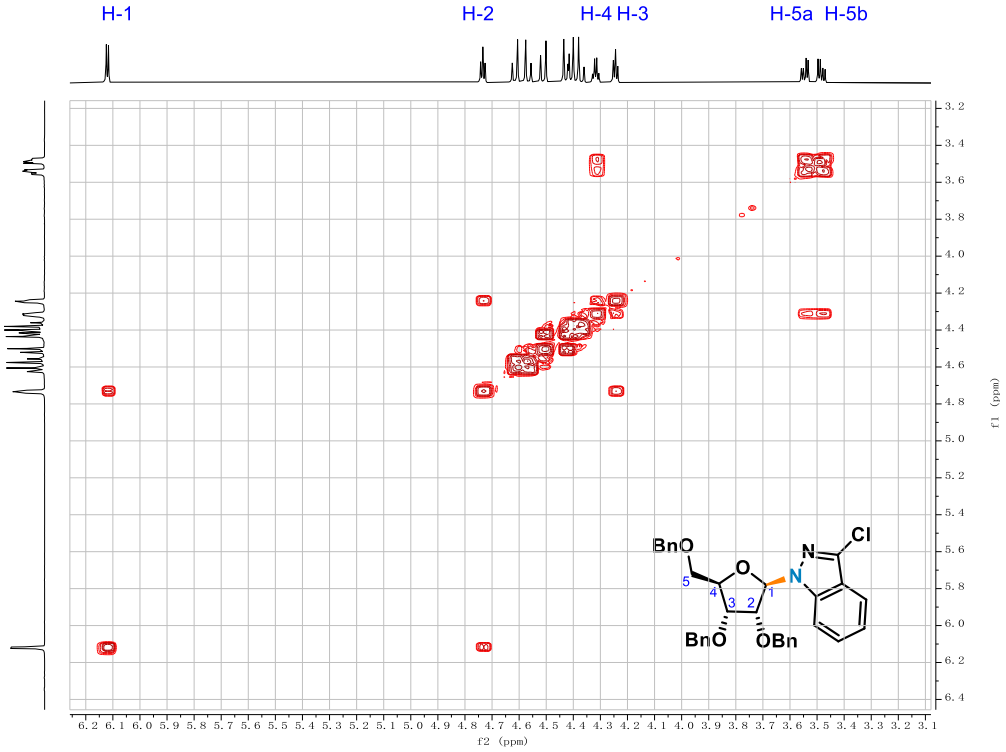
^{1}H-^{1}H-COSY of **8a**



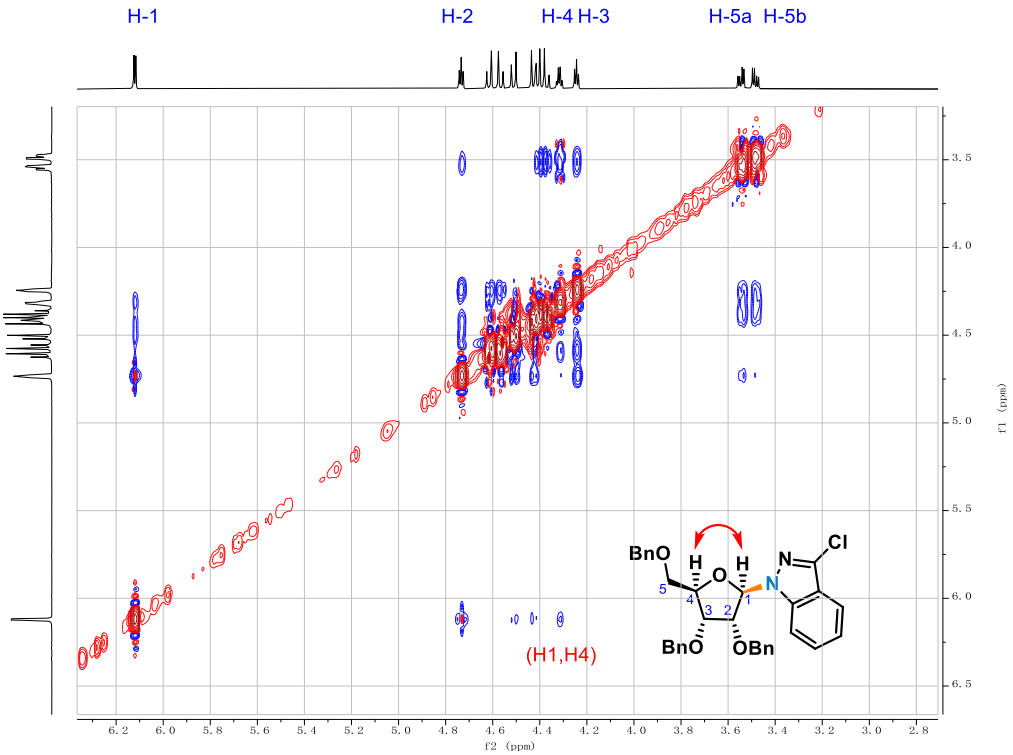
NOESY of **8a**



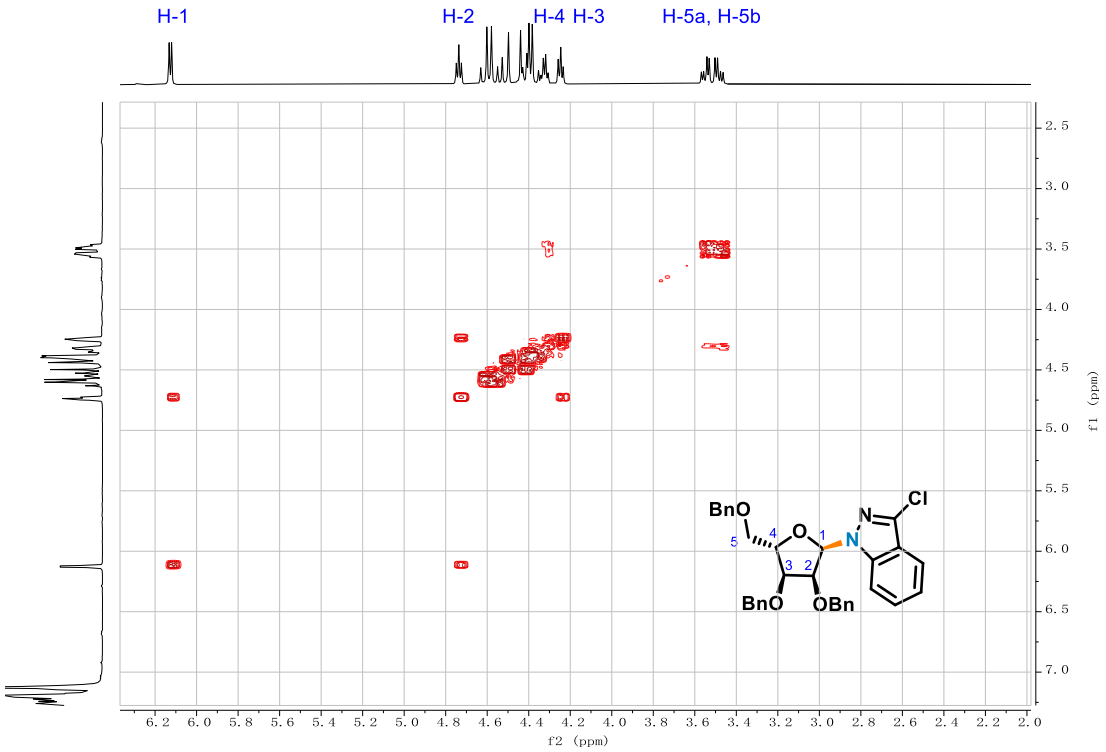
^{1}H-^{1}H-COSY of **8f**



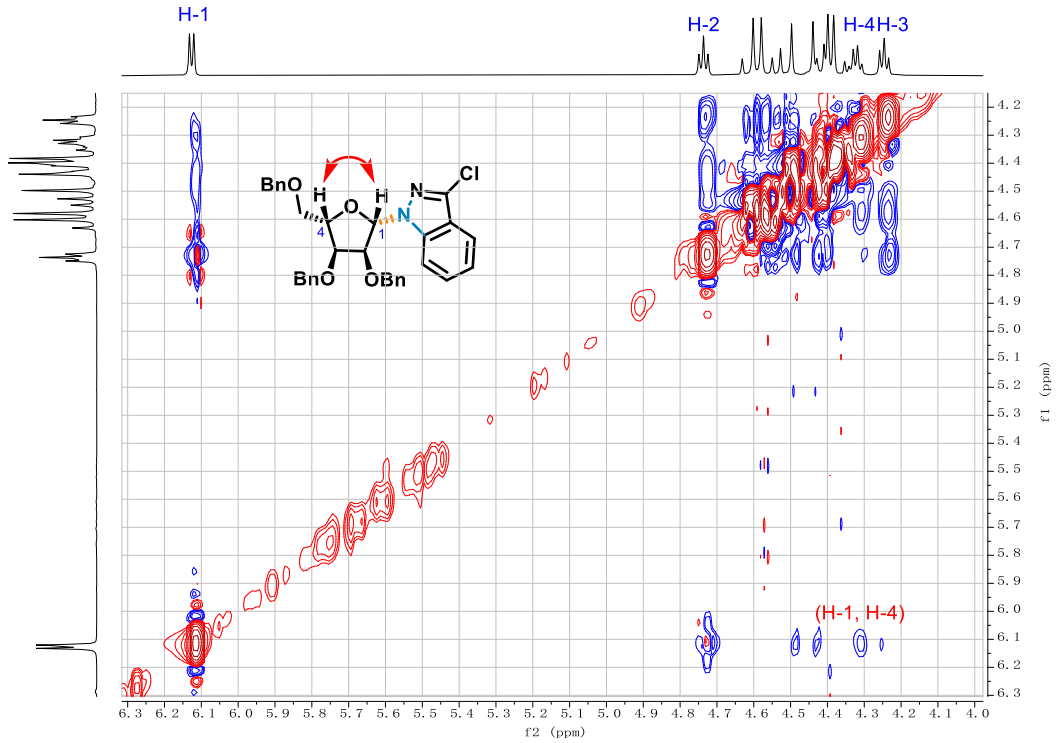
NOESY of **8f**



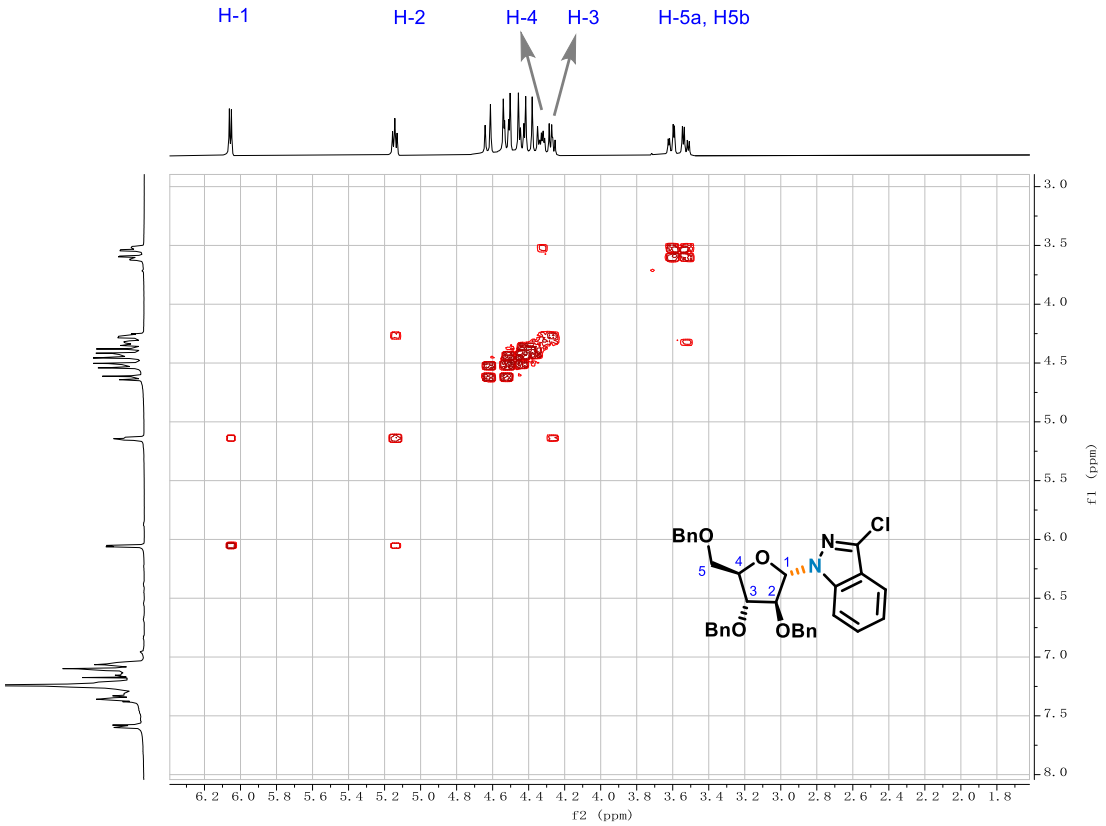
^{1}H-^{1}H-COSY of **8h**



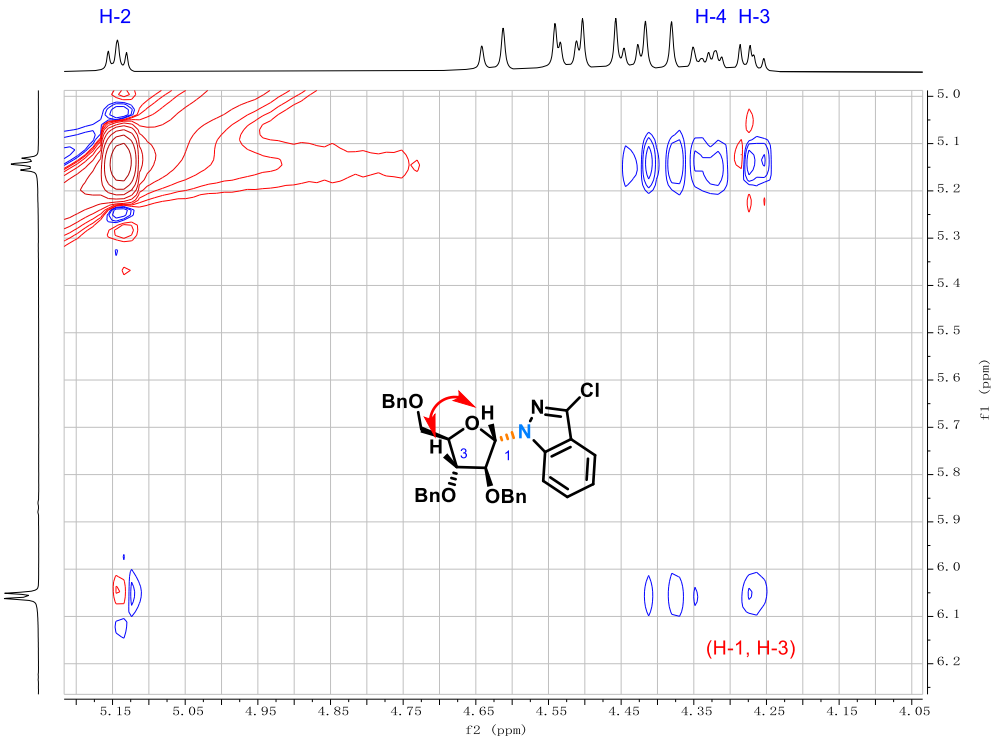
NOESY of **8h**



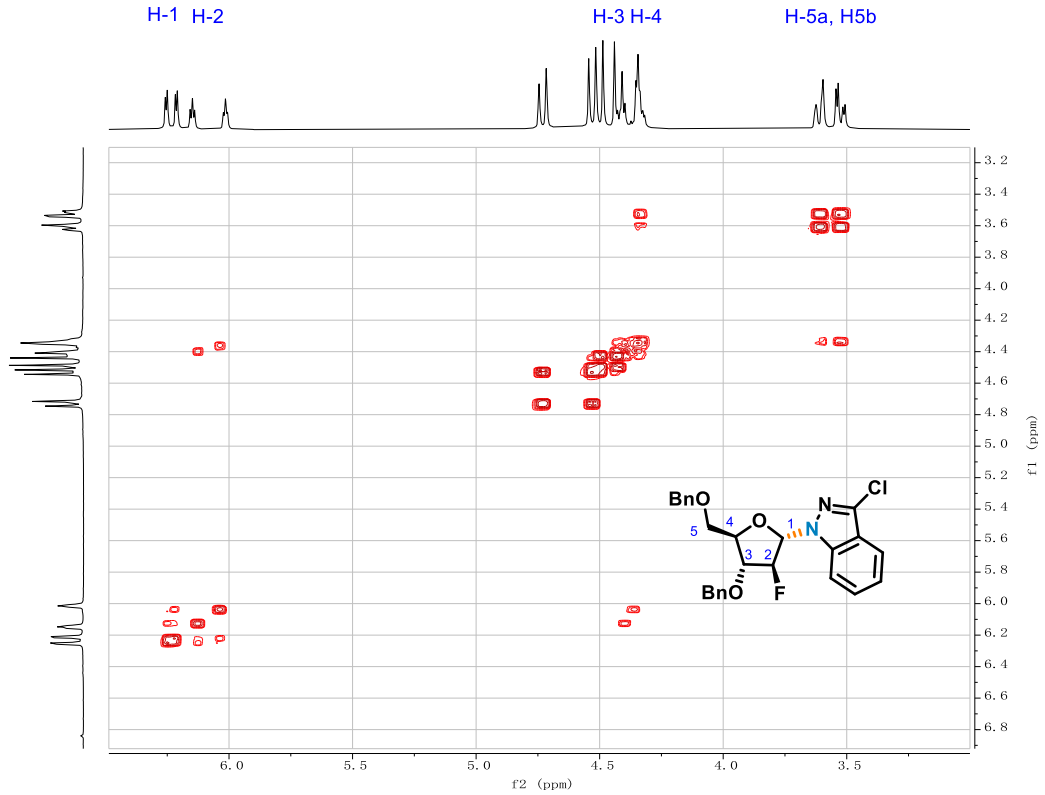
^{1}H-^{1}H-COSY of **8i**



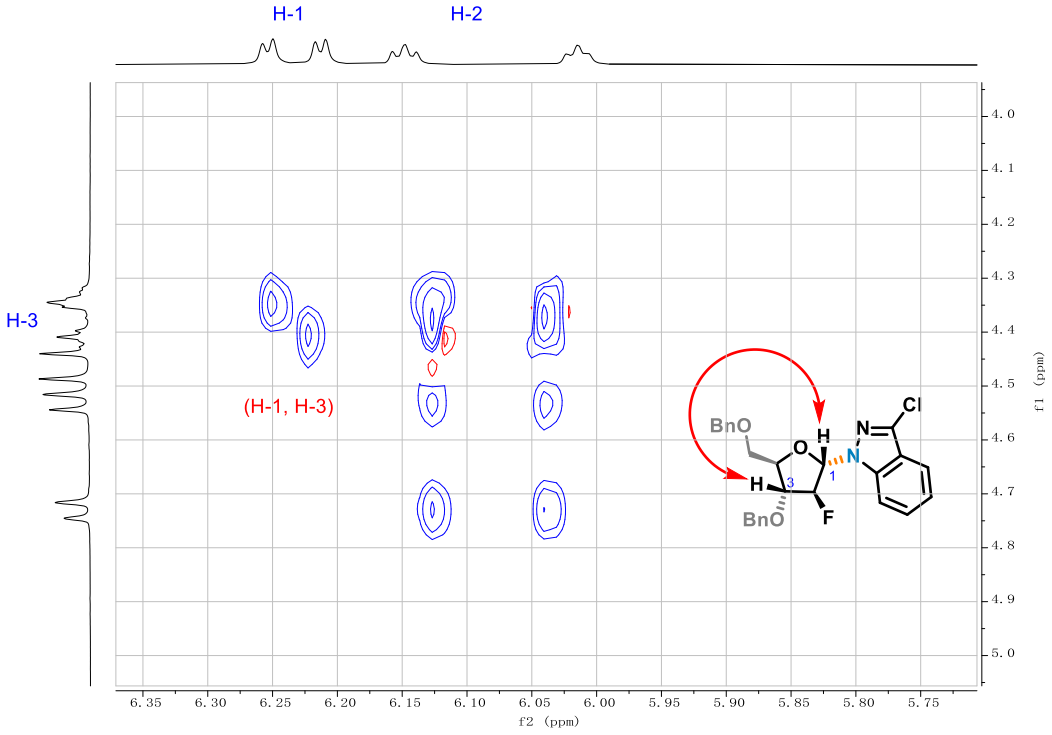
NOESY of **8i**



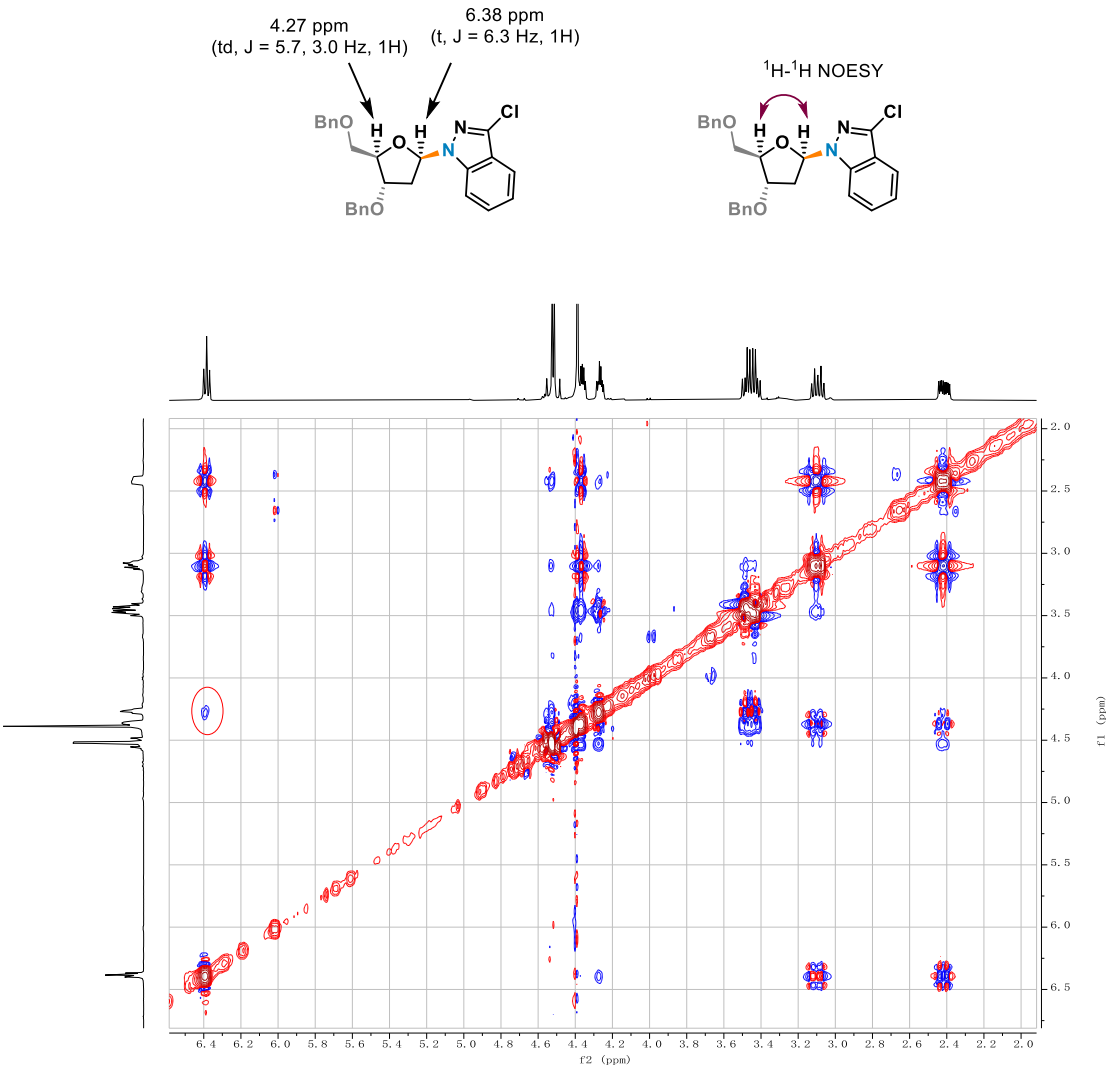
^{1}H-^{1}H-COSY of **8j**



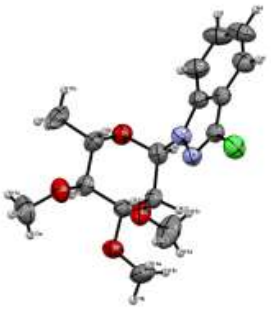
NOESY of **8j**

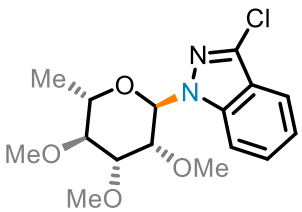


NOESY of **8ka**



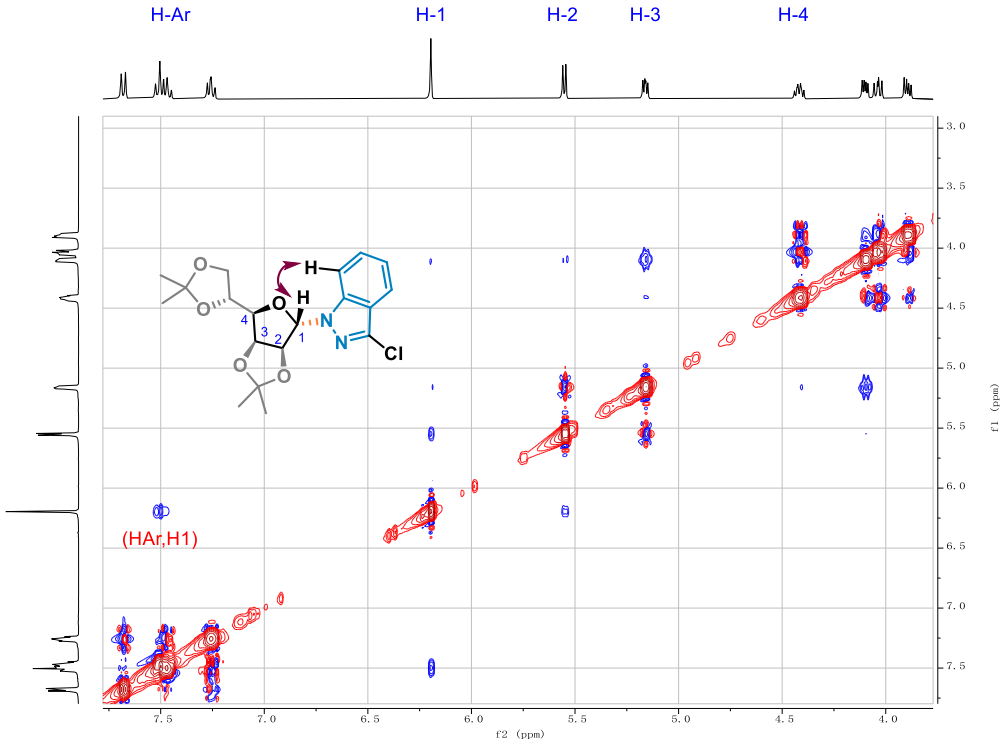
Anomeric stereochemistry of **8o** determined by X-Ray



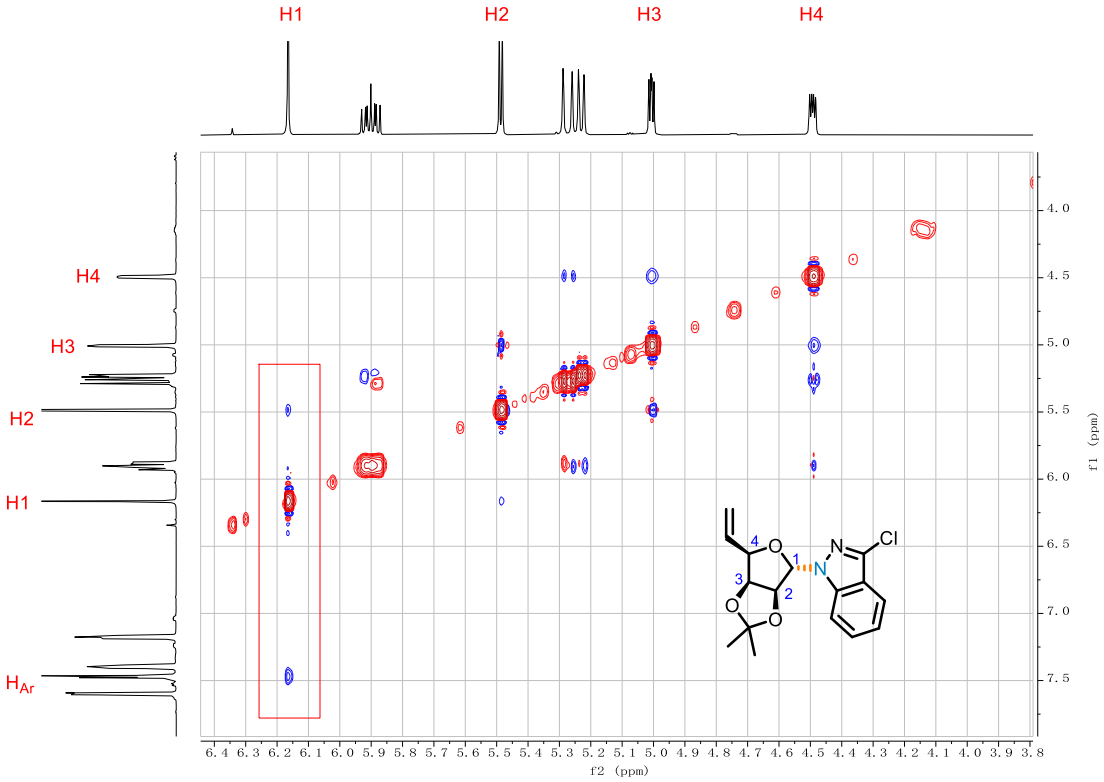


8o

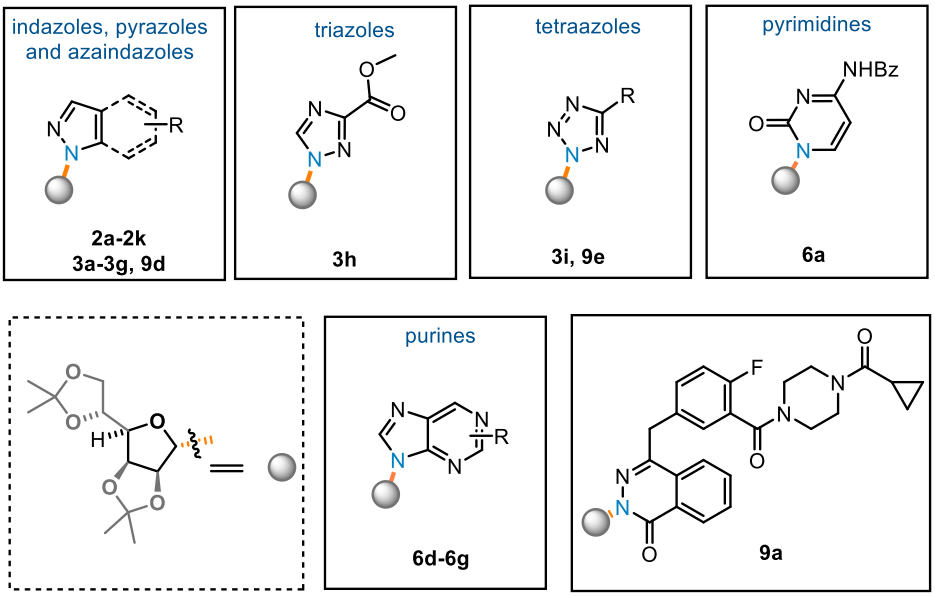
NOESY of **2a**



NOESY of **8l**

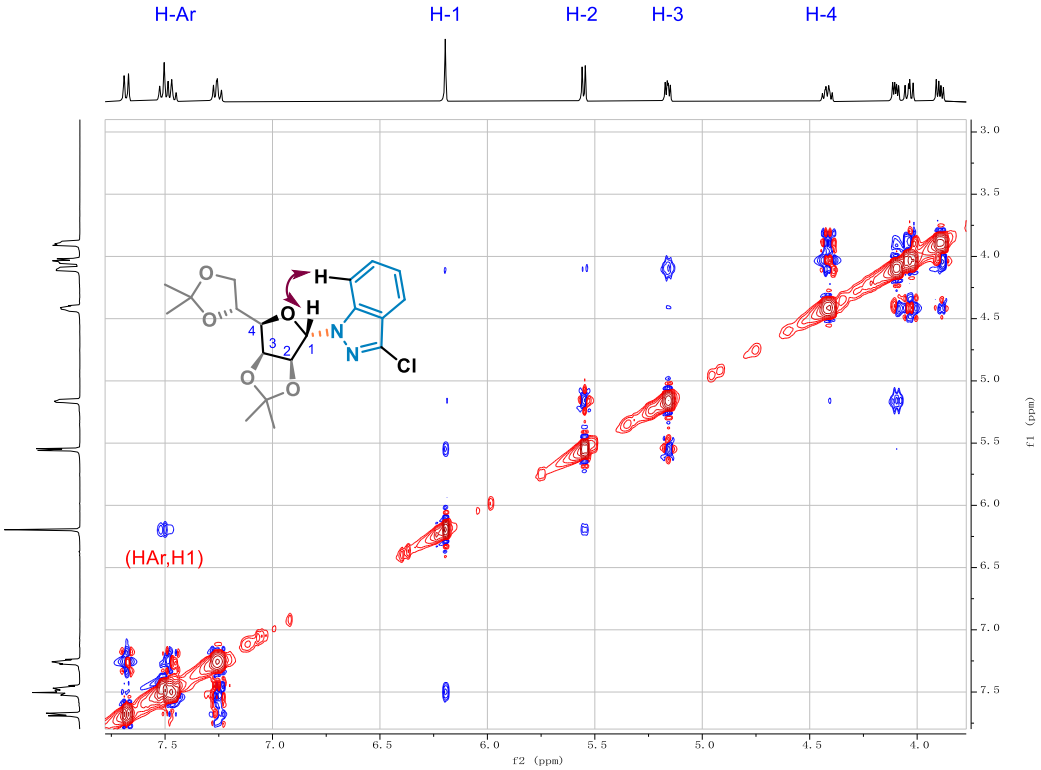


5.2 Determination of the regioisomer

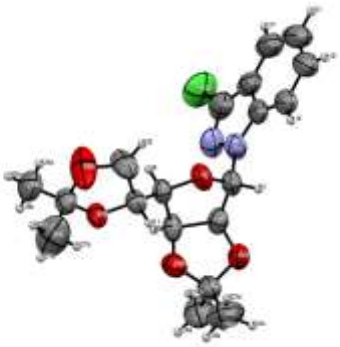


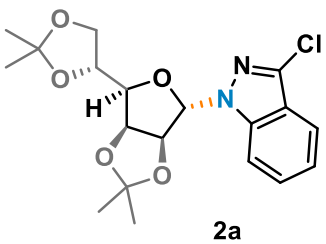
As shown above, there are 6 types of N-htereocycles in this paper that may yield regioisomers. To determine the regiochemistry, compound **2a**, **3h**, **3i, 6a**, **6e** and **9a** were selected for detailed NMR analyses. For **2a**, characteristic NOE signals between H1 and H_{Ar} were identified as shown in the following spectra. In addition, X-ray crystal structure data of **2a** was also obtained. For **3h**, C_{Ar1} have characteristic correlation with H_1 in HMBC. For **3i**, H1 have no correlation with H_{Ar} and C_{Ar} in both NOE and HMBC . For **6a**, we identified meaningful carbons and protons through 2D NMR, then we find C_{Ar5} have characteristic HMBC reference with H1. For **6e**, C_{ar8} was identified by its HMBC correlation with H1. Then, H_{ar8} and H_{ar2} could be assigned from C_{ar8}. From H_{ar8} and H_{ar2}, we then identified C_{ar4} and C_{ar5}. Because H1 has strong correlation with C_{ar4} rather than C_{ar5}, **6e** was assigned as N9 isomer. For **9a**, C_{Ar1} has characteristic HMBC correlation with H1.

NOESY of **2a**



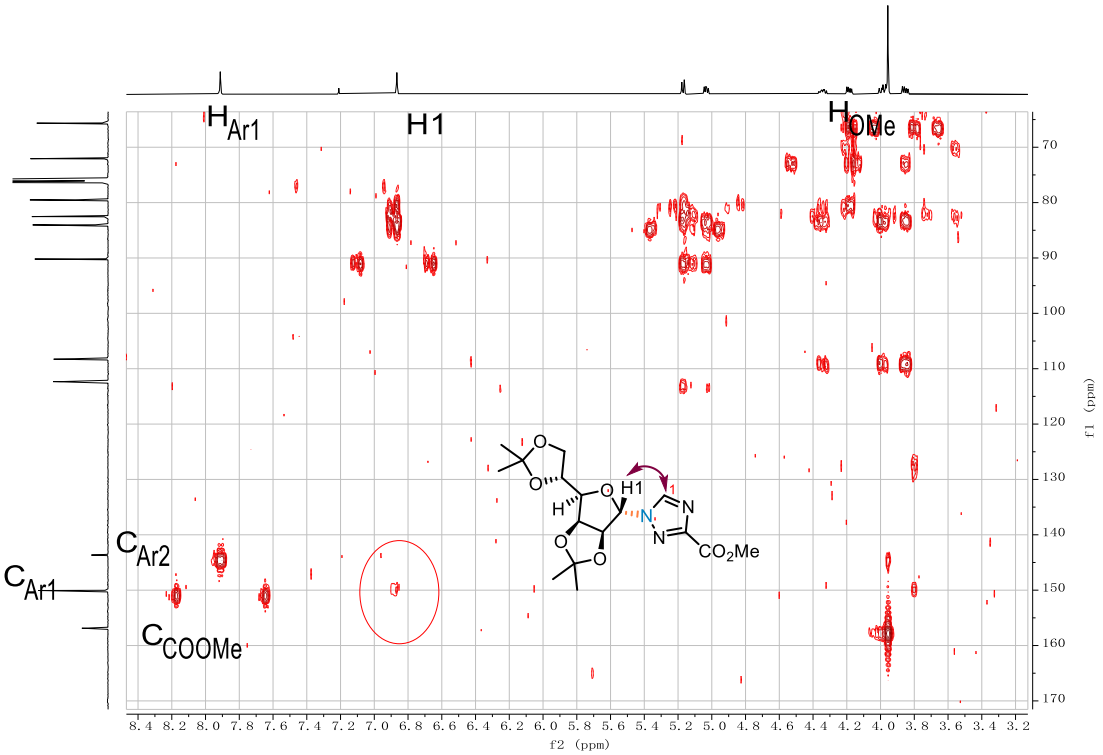
Regiochemistry of **2a** determined by X-ray



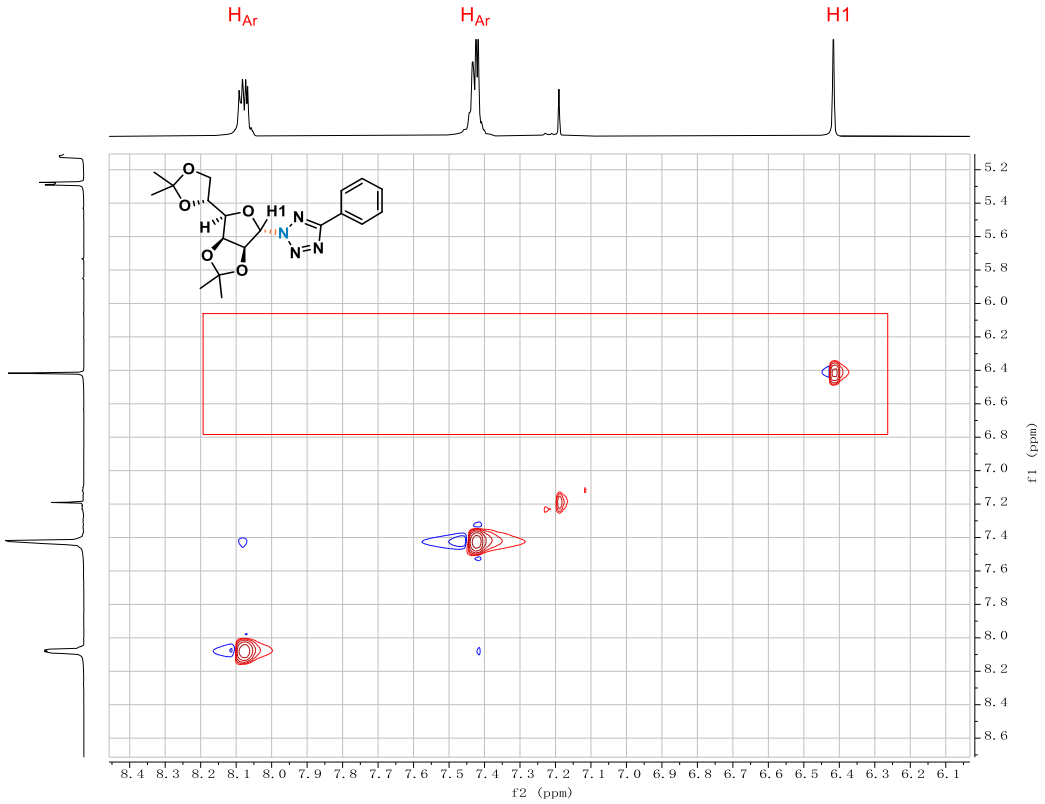


2a

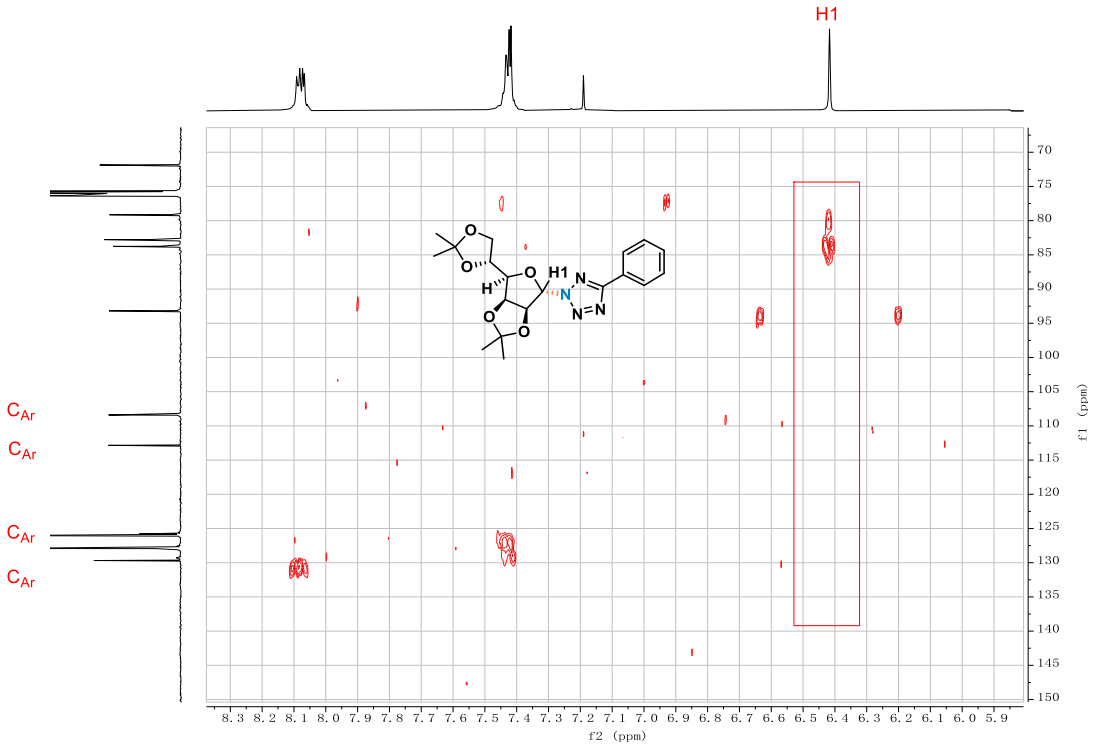
HMBC of **3h**



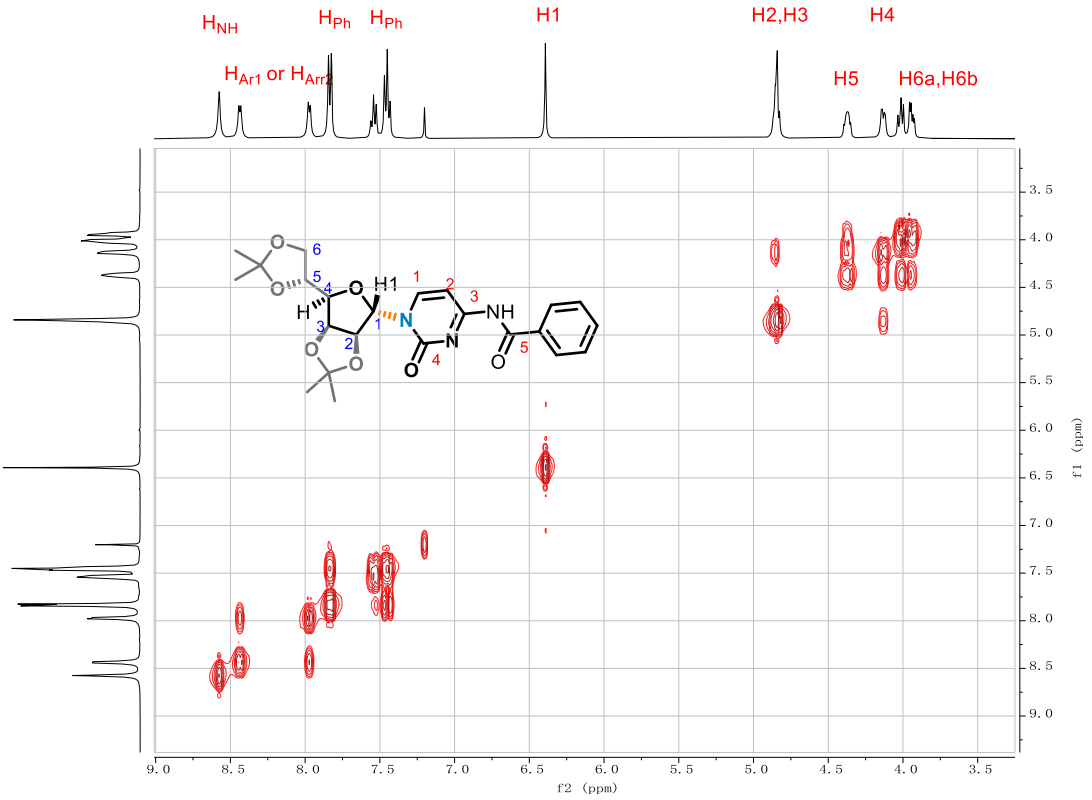
NOESY of **3i**



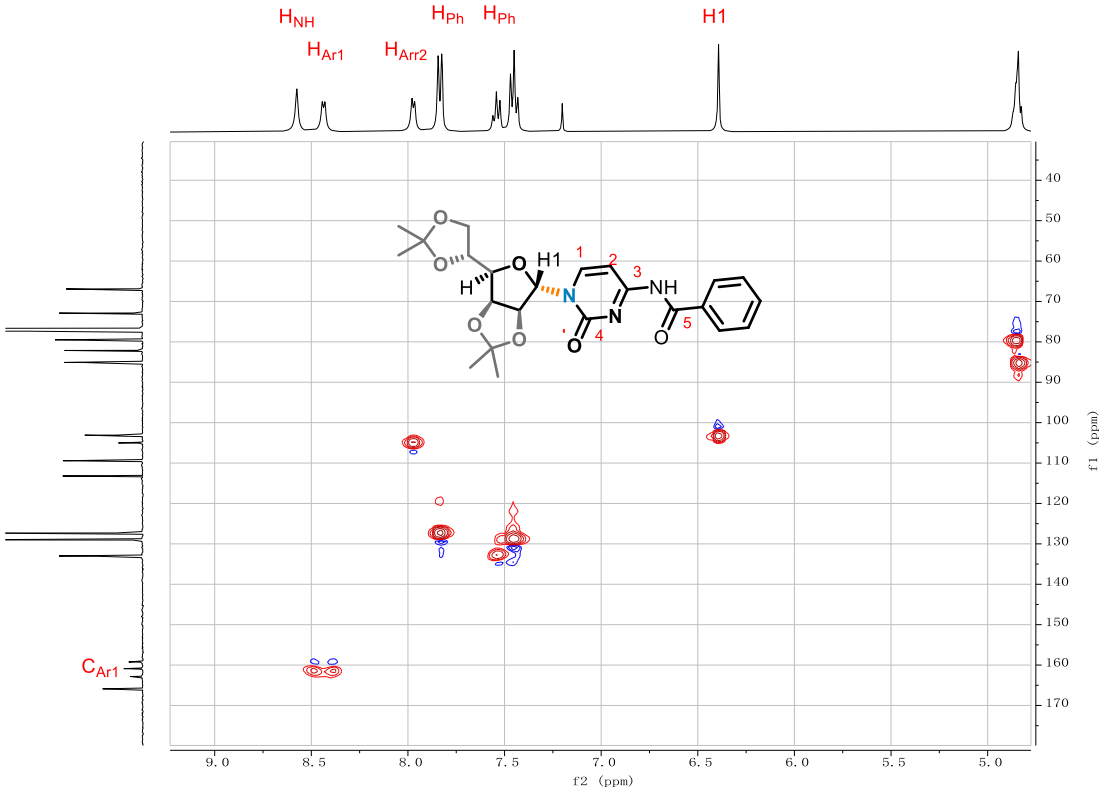
HMBC of **3i**



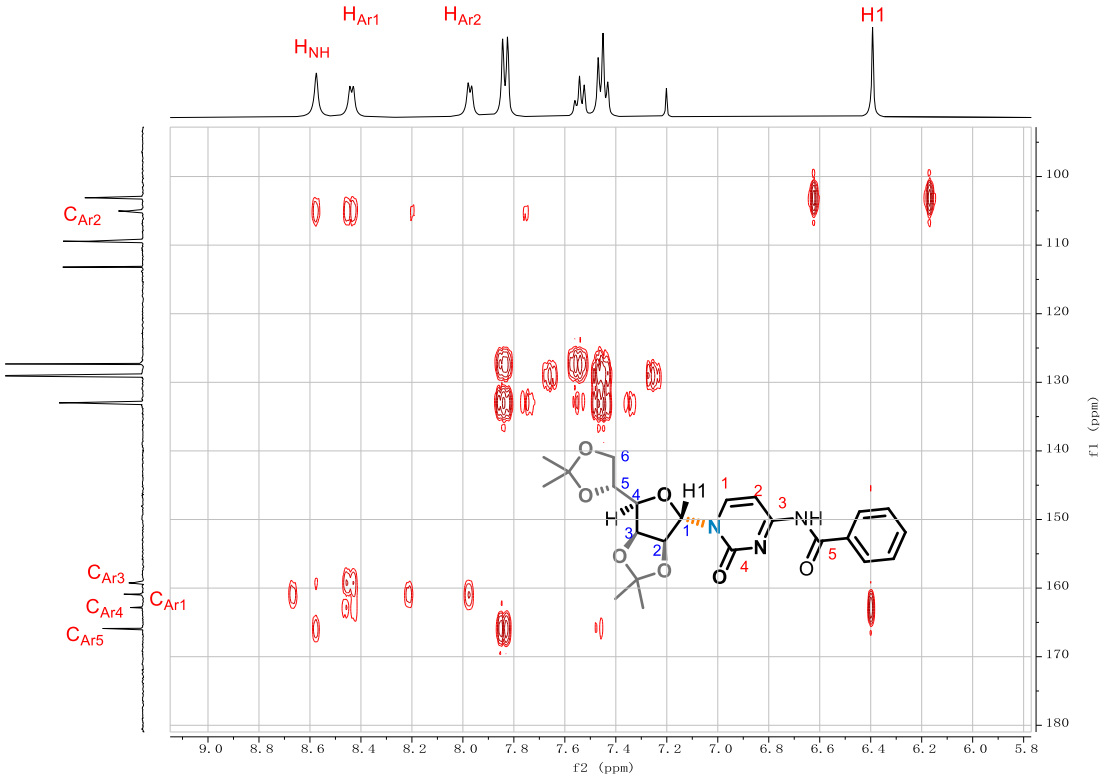
H-HCOY of **6a**



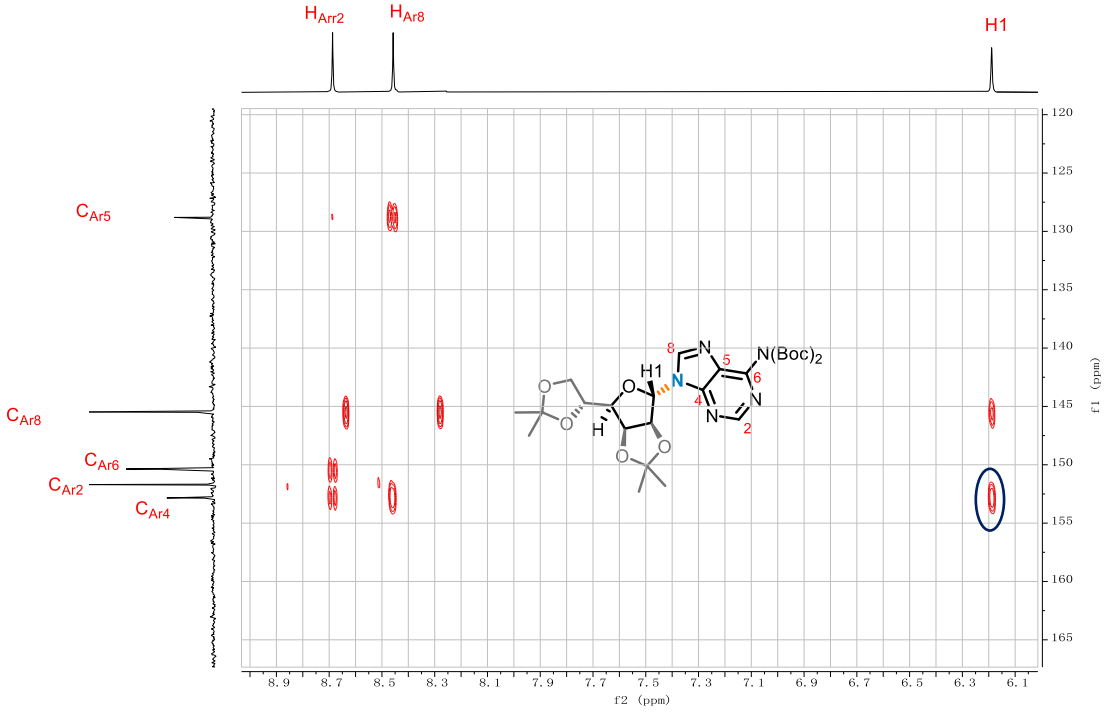
HSQC of **6a**



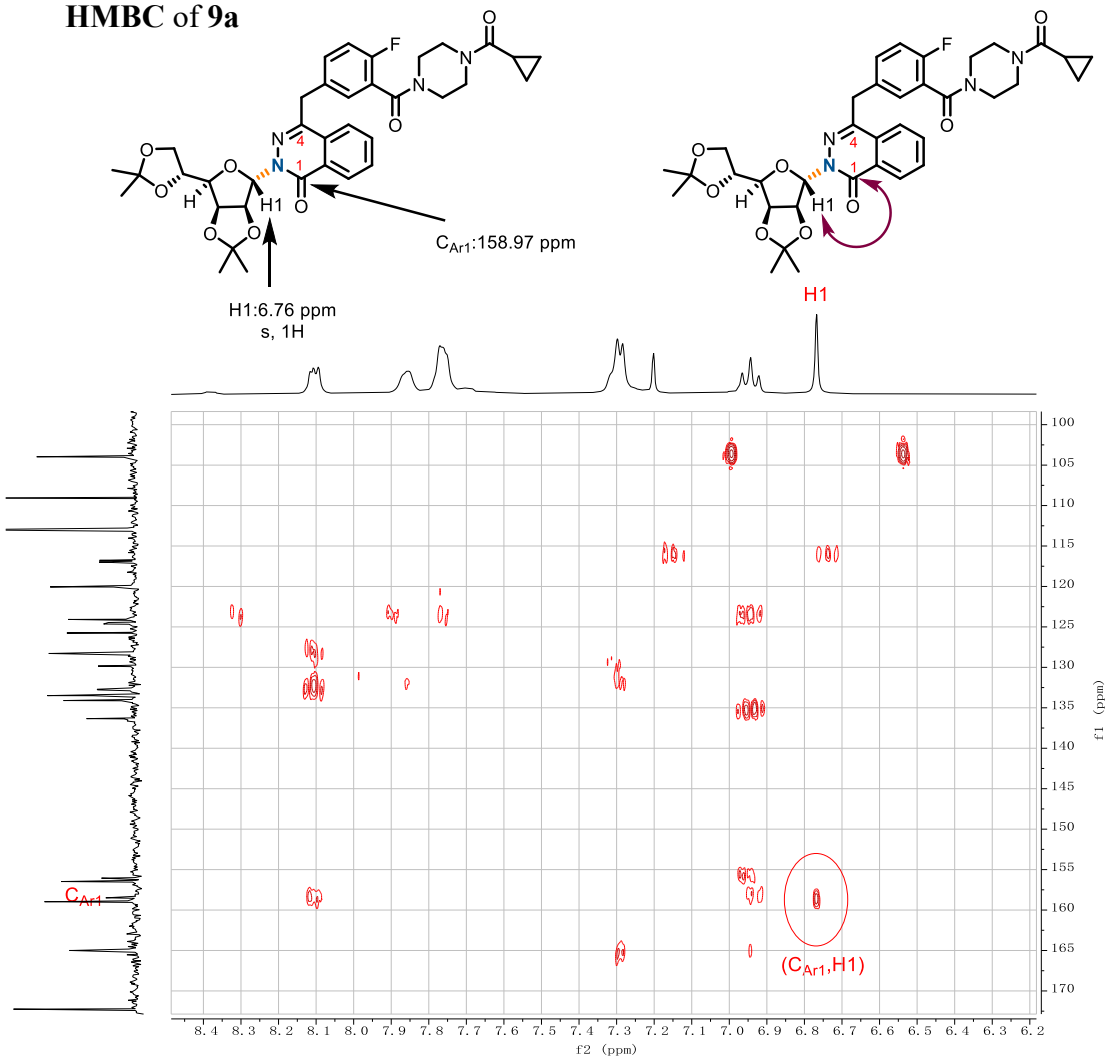
HMBC of **6a**



HMBC of **6e**

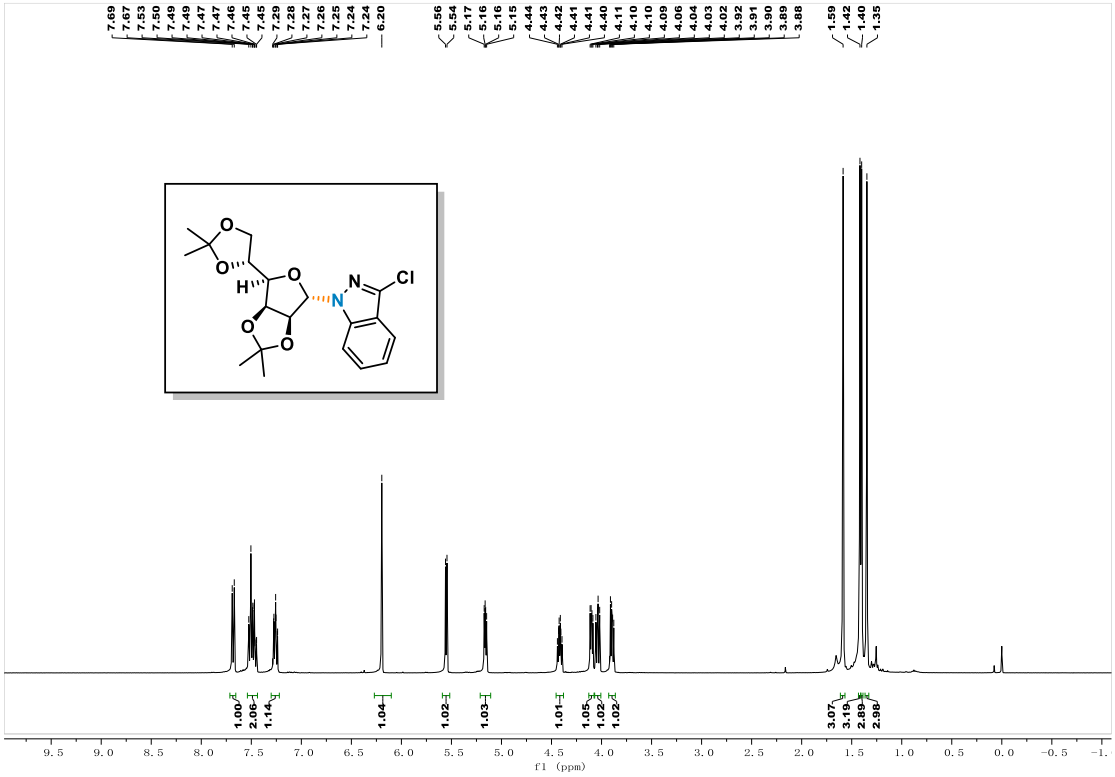


HMBC of **9a**

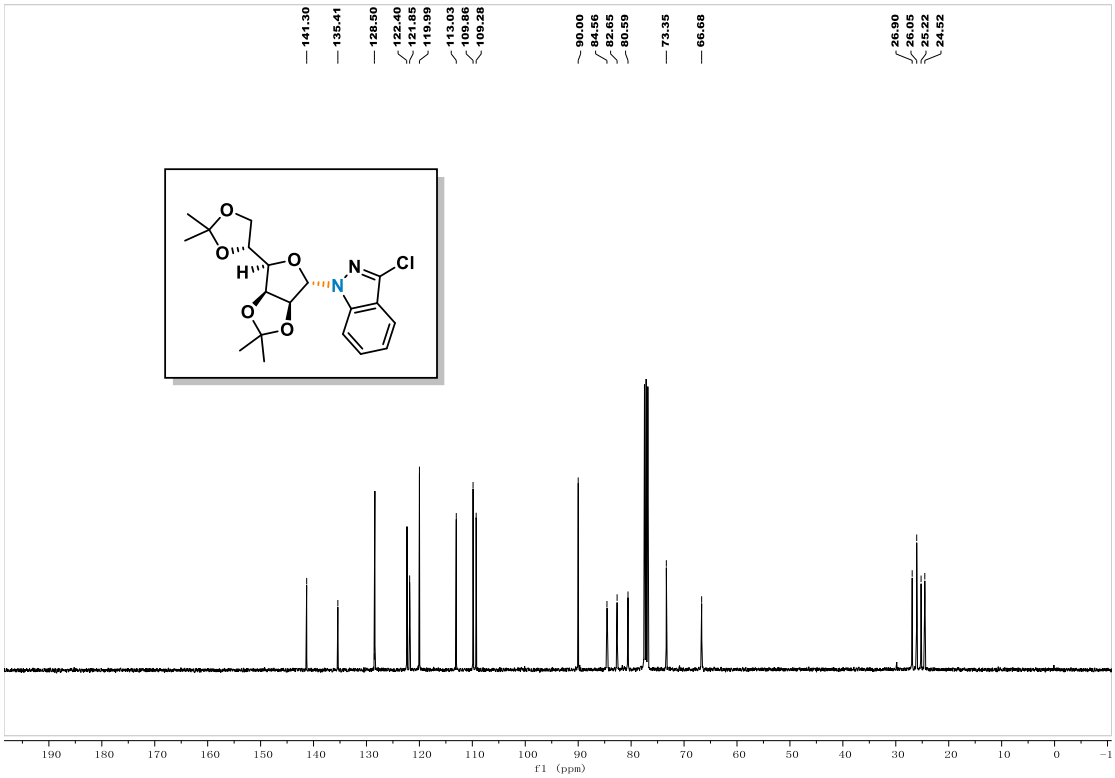


6. Copies of NMR spectra

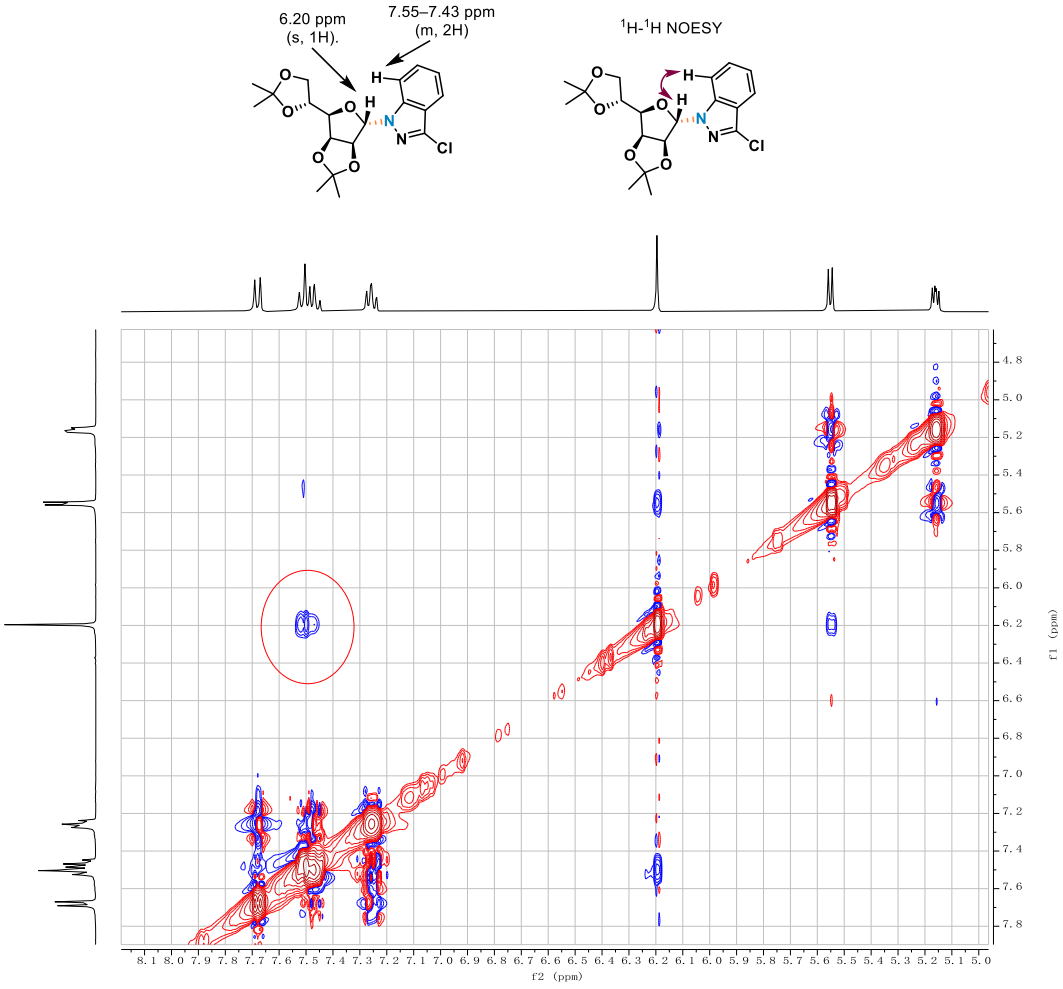
^{1}H NMR (400 MHz, $CDCl_3$) **(2a)**



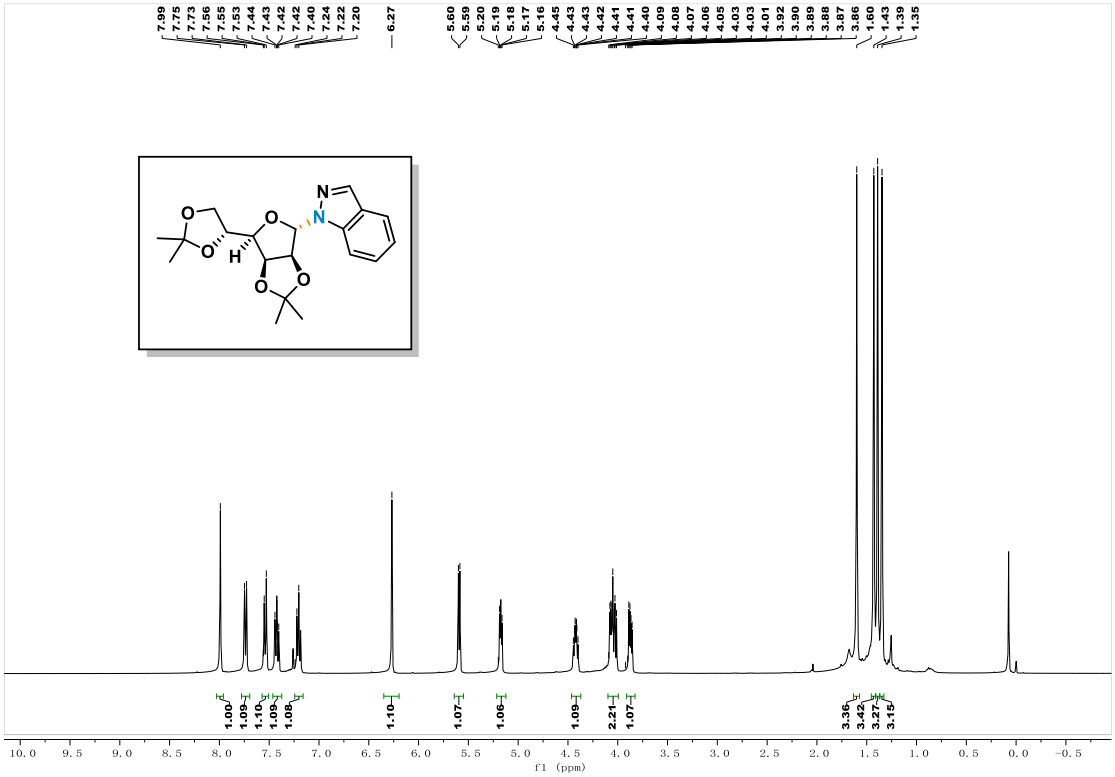
^{13}C NMR (101 MHz, $CDCl_3$) **(2a)**



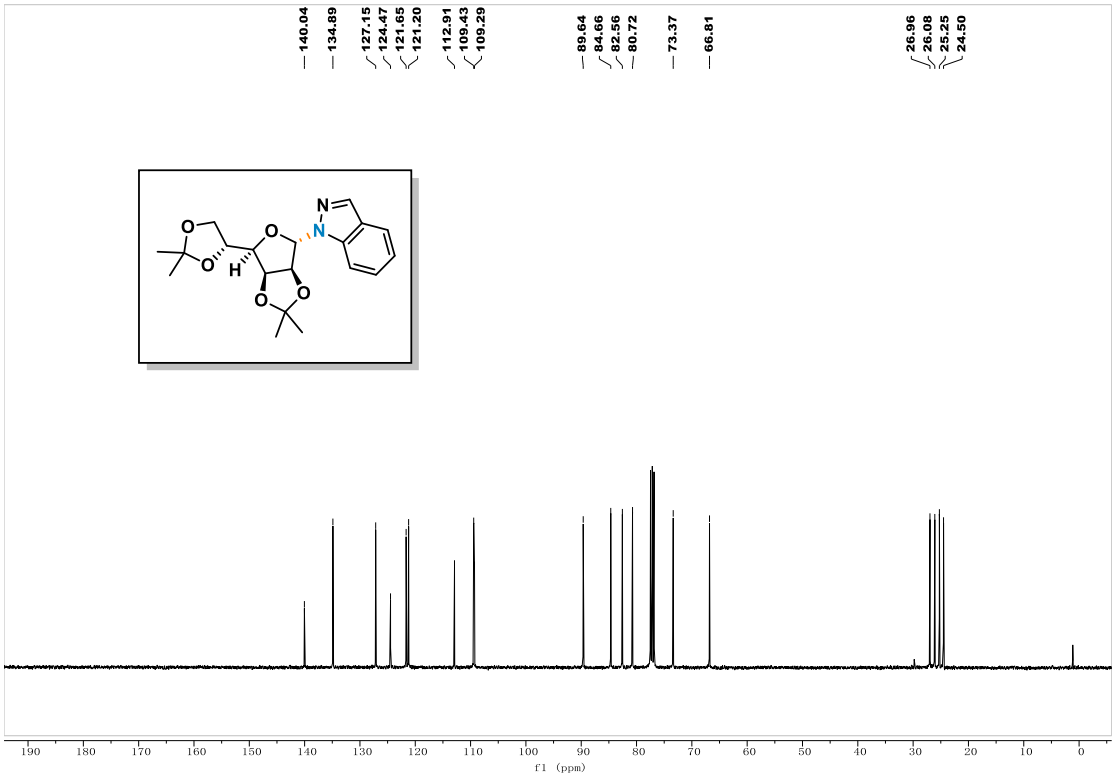
NOESY of **2a**



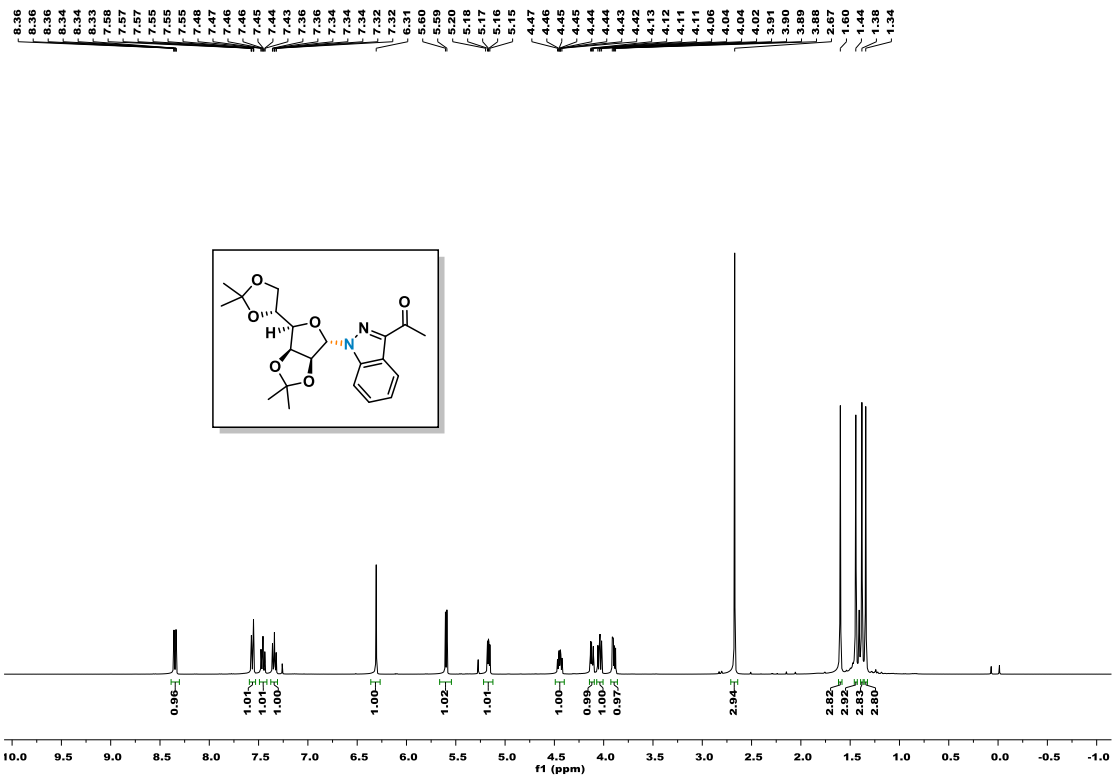
^{1}H NMR (400 MHz, $CDCl_3$) **(2b)**



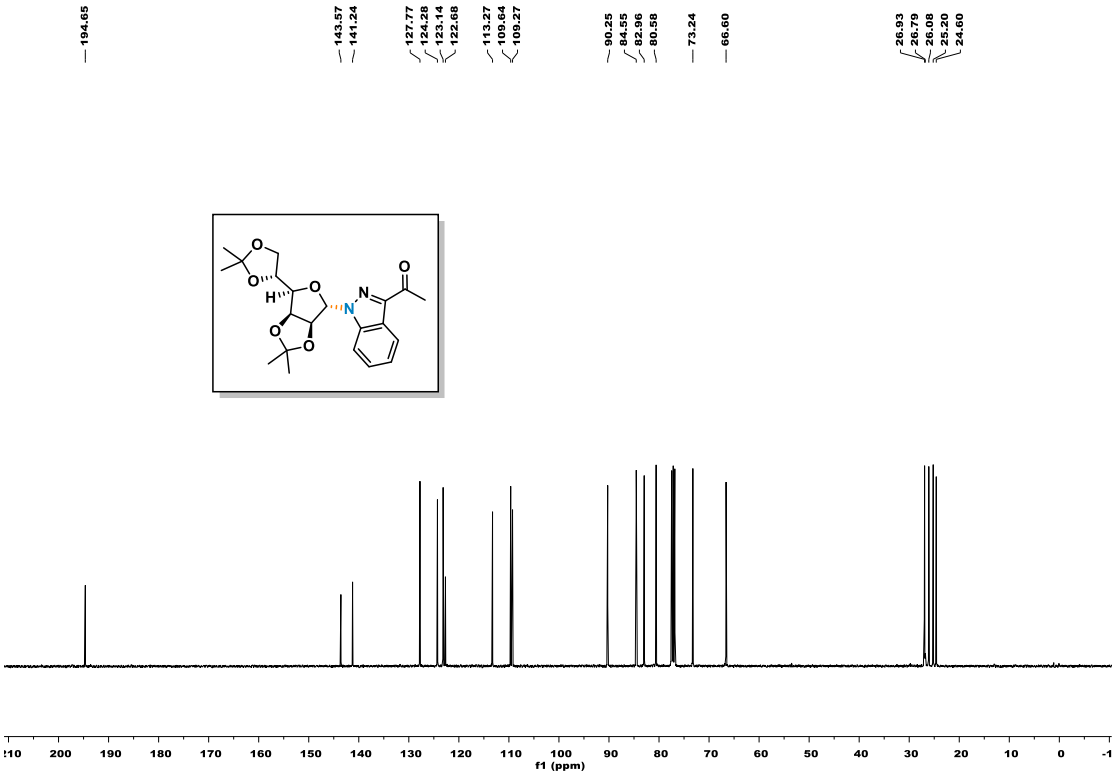
^{13}C NMR (101 MHz, $CDCl_3$) **(2b)**



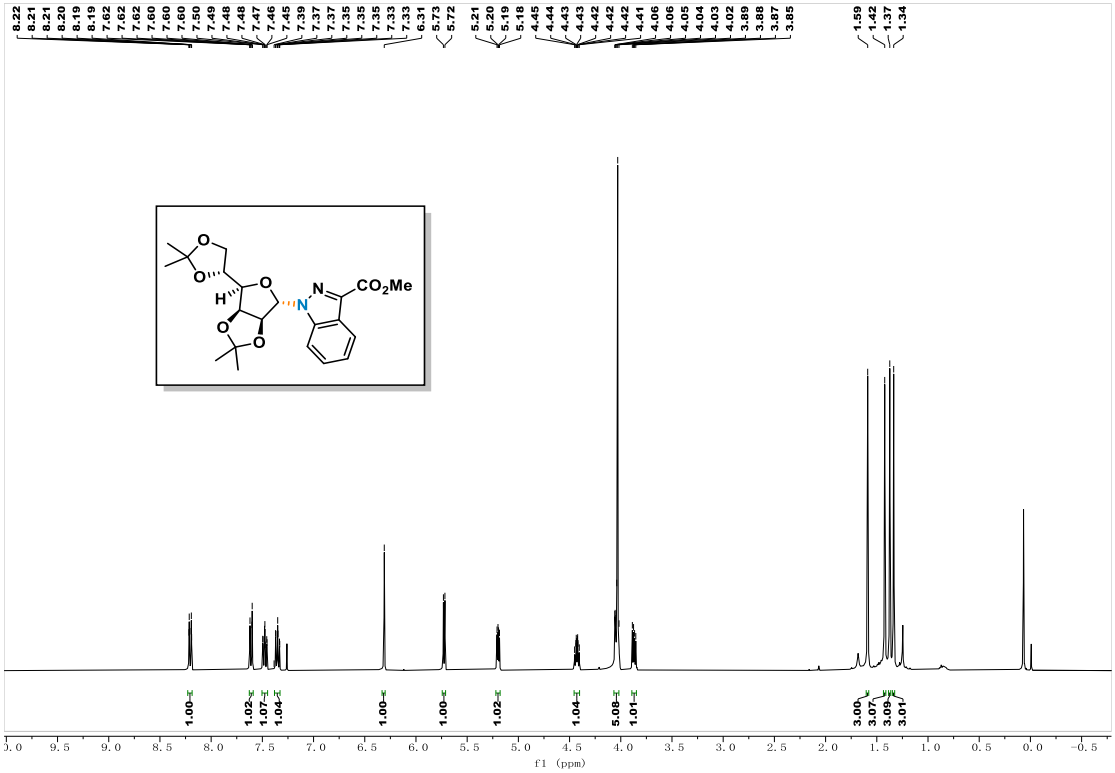
^{1}H NMR (400 MHz, $CDCl_3$) **(2c)**



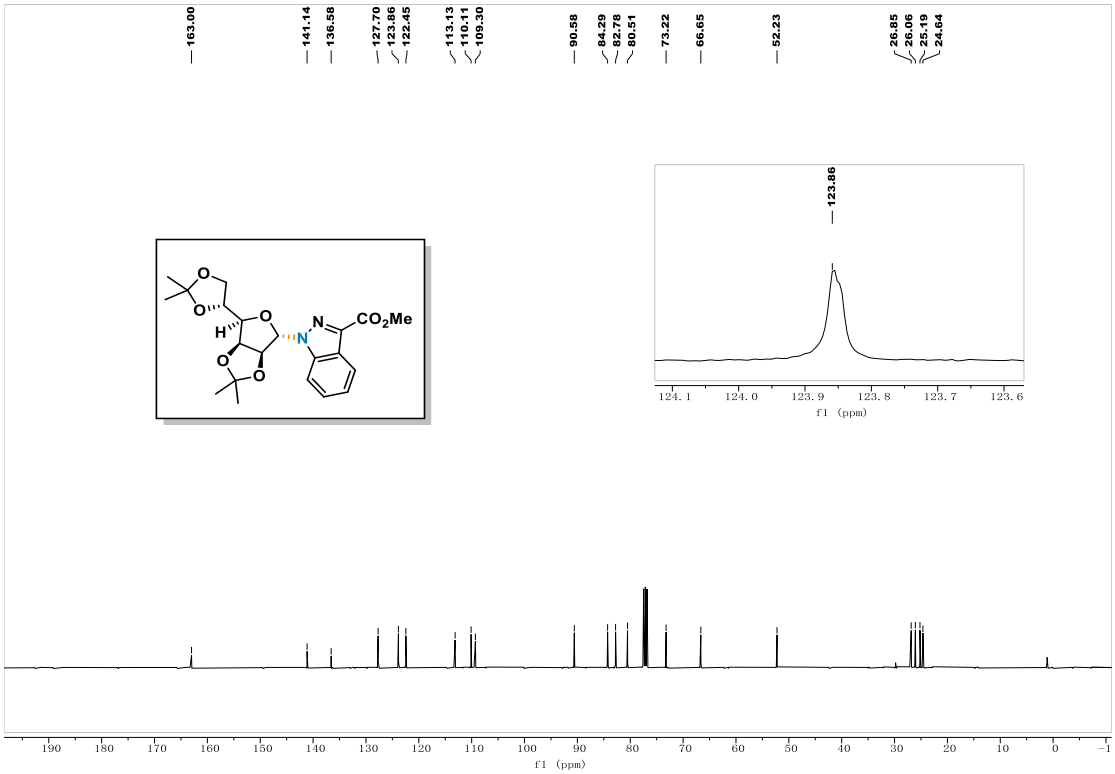
^{13}C NMR (101 MHz, $CDCl_3$) **(2c)**



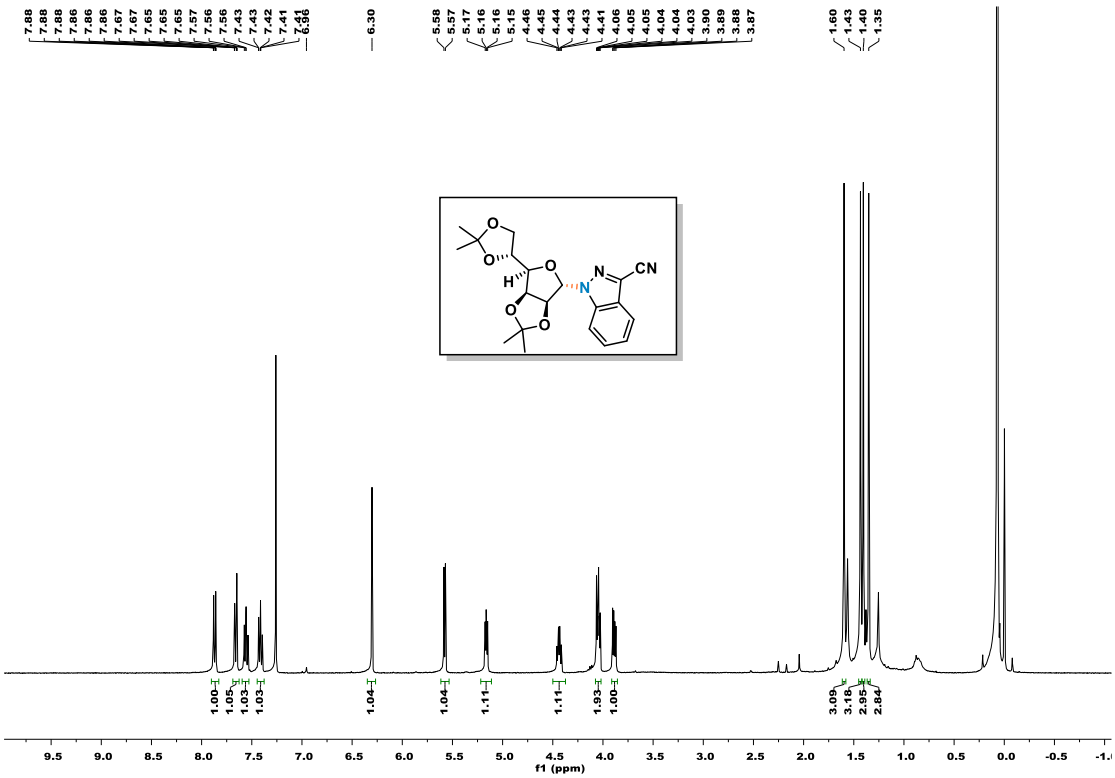
^{1}H NMR (400 MHz, $CDCl_3$) **(2d)**



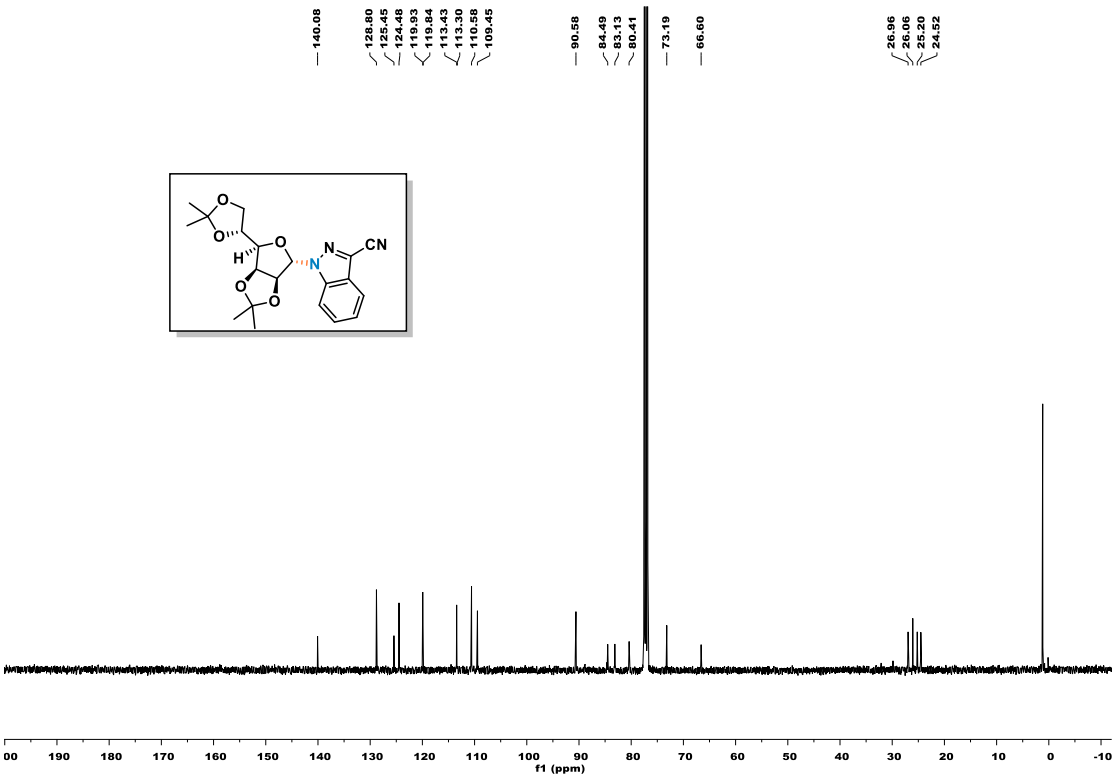
^{13}C NMR (101 MHz, $CDCl_3$) **(2d)**



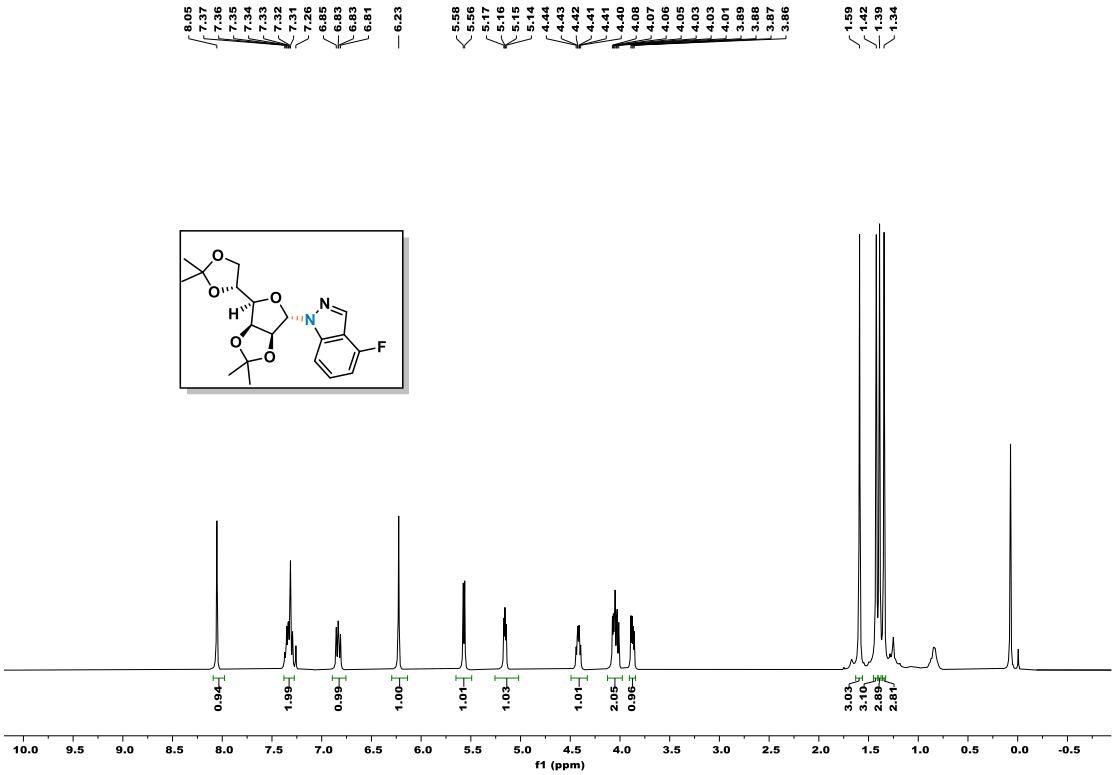
^{1}H NMR (400 MHz, $CDCl_3$) **(2e)**



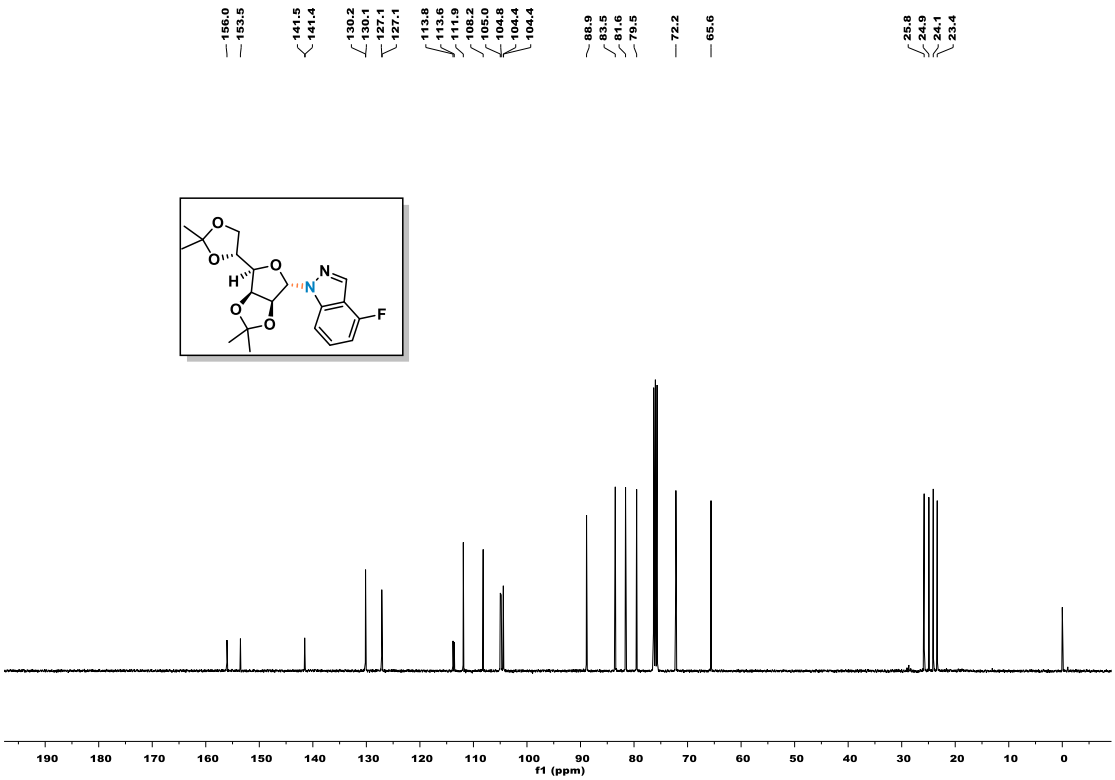
^{13}C NMR (101 MHz, $CDCl_3$) **(2e)**



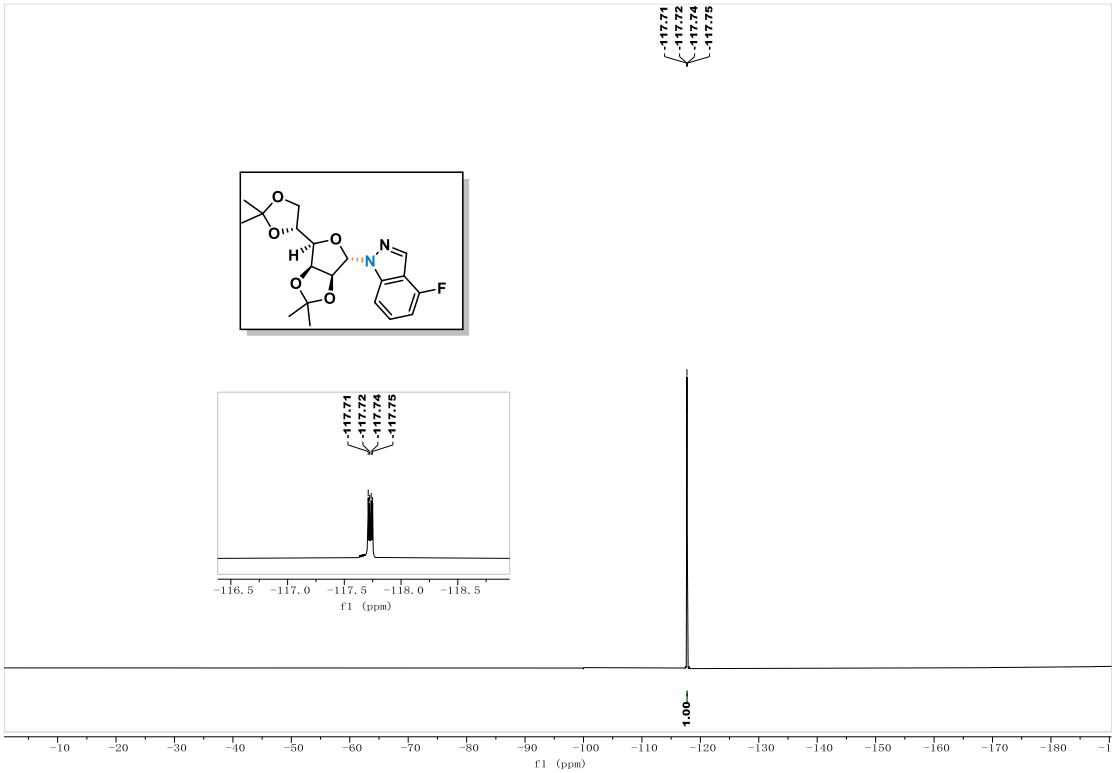
^{1}H NMR (400 MHz, $CDCl_3$) **(2f)**



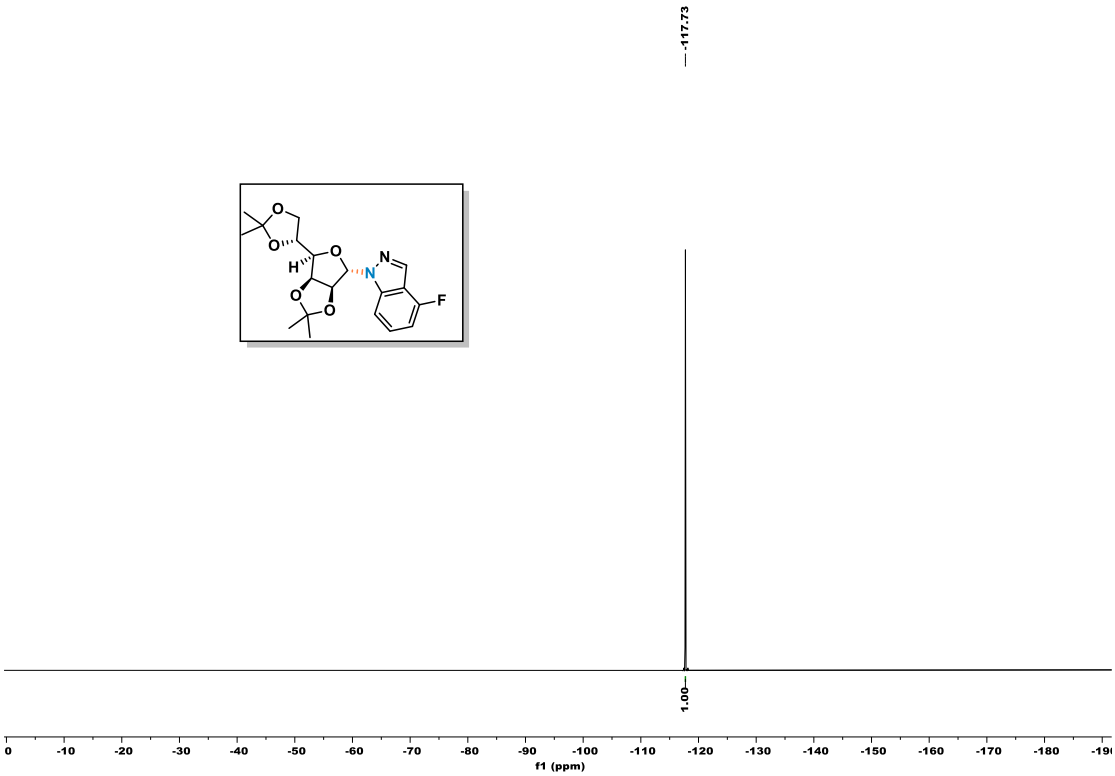
^{13}C NMR (101 MHz, $CDCl_3$) **(2f)**



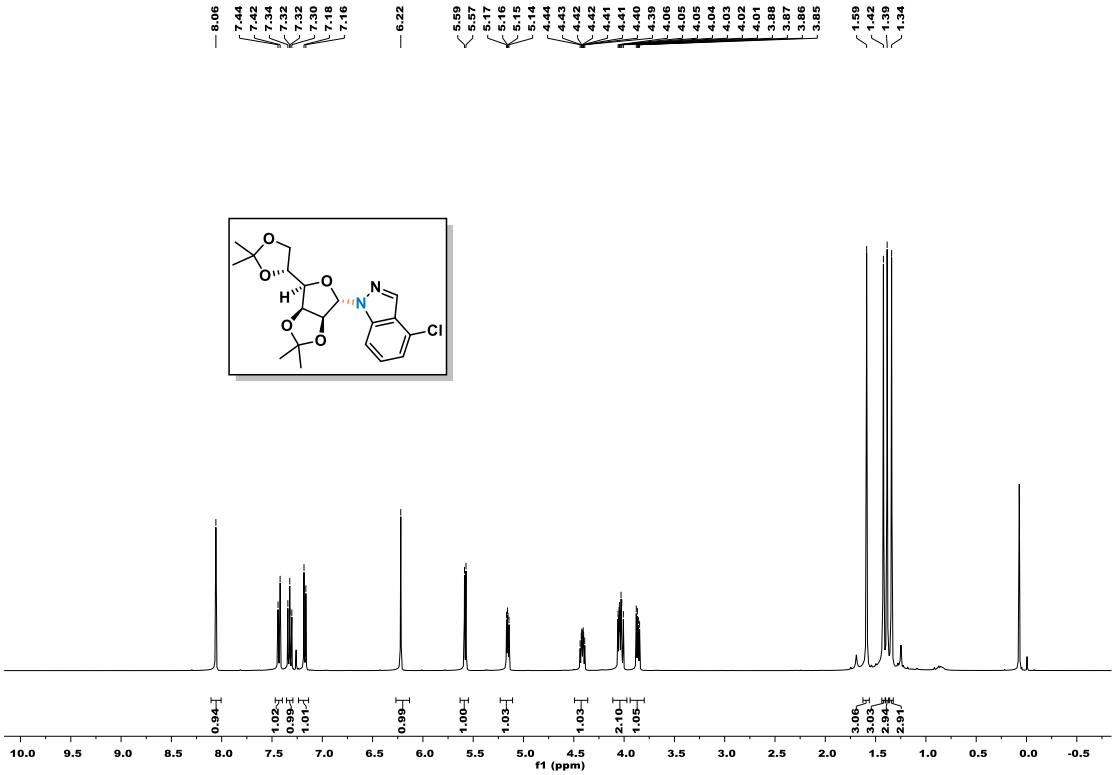
^{19}F NMR (376 MHz, $CDCl_3$) (**2f**)



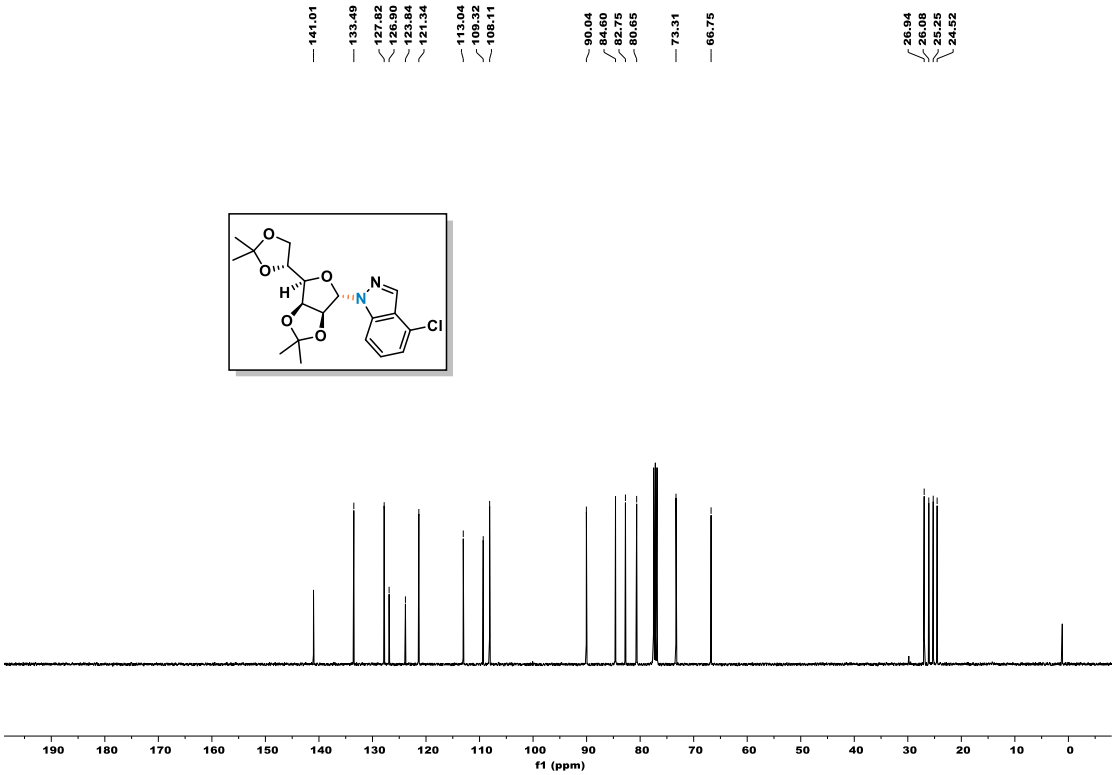
^{19}F{H} NMR (376 MHz, $CDCl_3$) (**2f**)



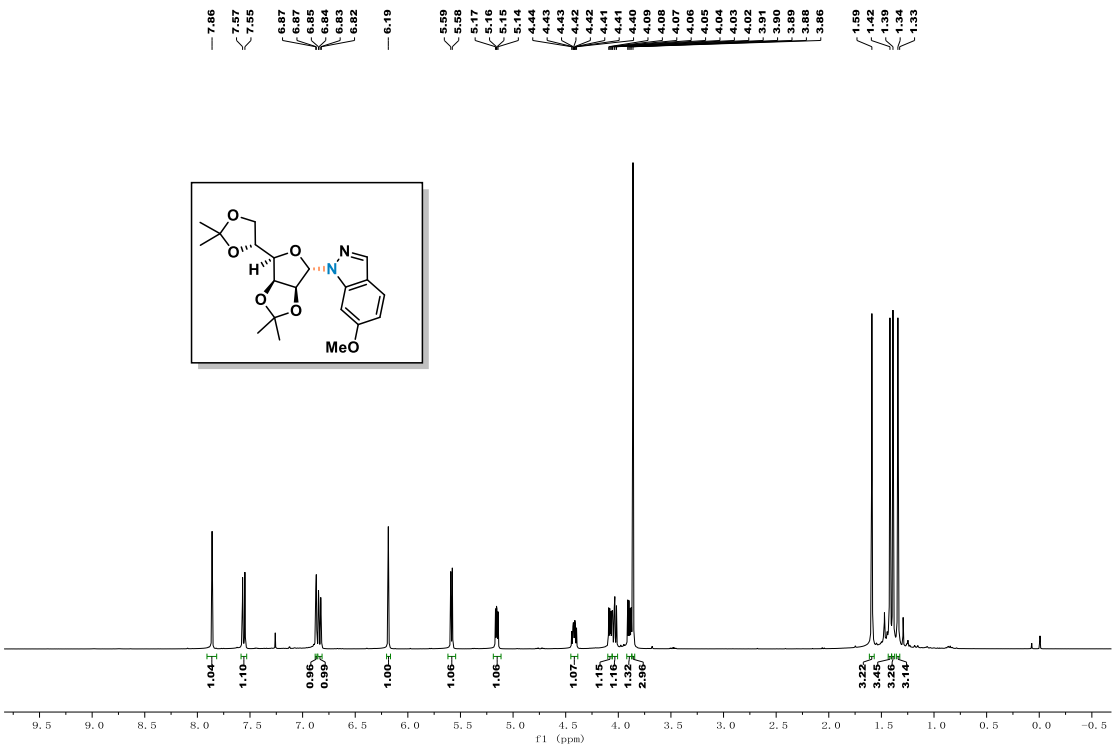
^{1}H NMR (400 MHz, $CDCl_3$) **(2g)**



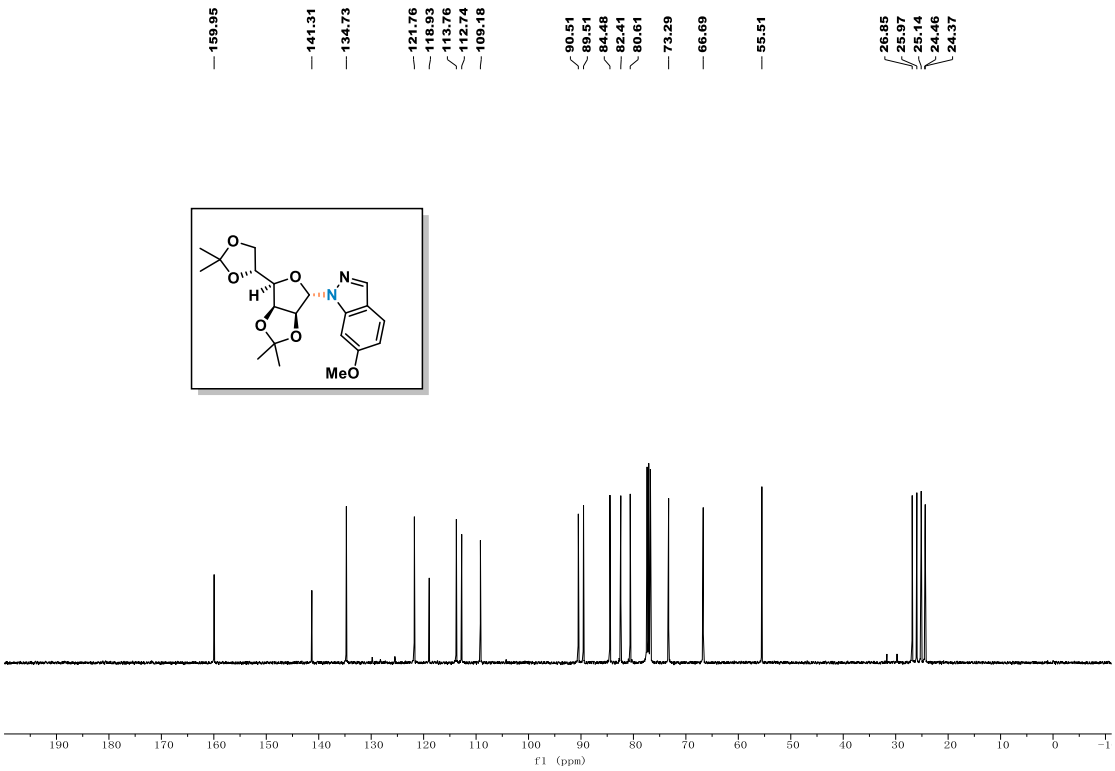
^{13}C NMR (101 MHz, $CDCl_3$) **(2g)**



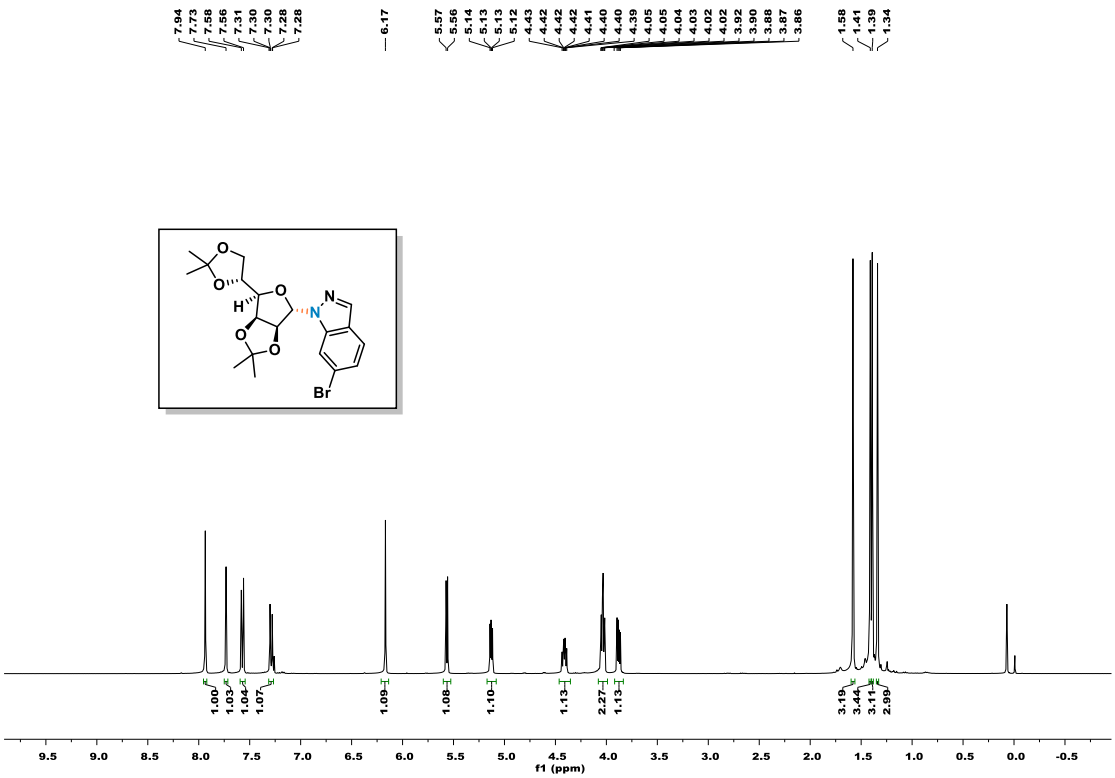
^{1}H NMR (400 MHz, $CDCl_3$) **(2h)**



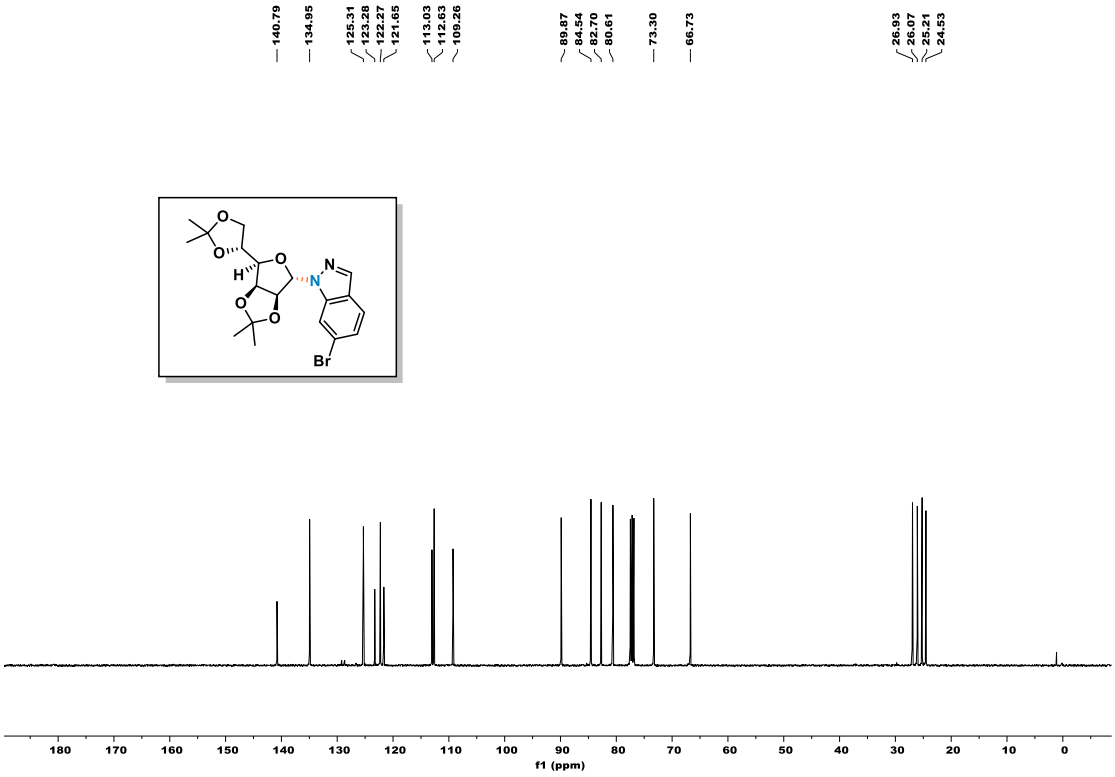
^{13}C NMR (101 MHz, $CDCl_3$) **(2h)**



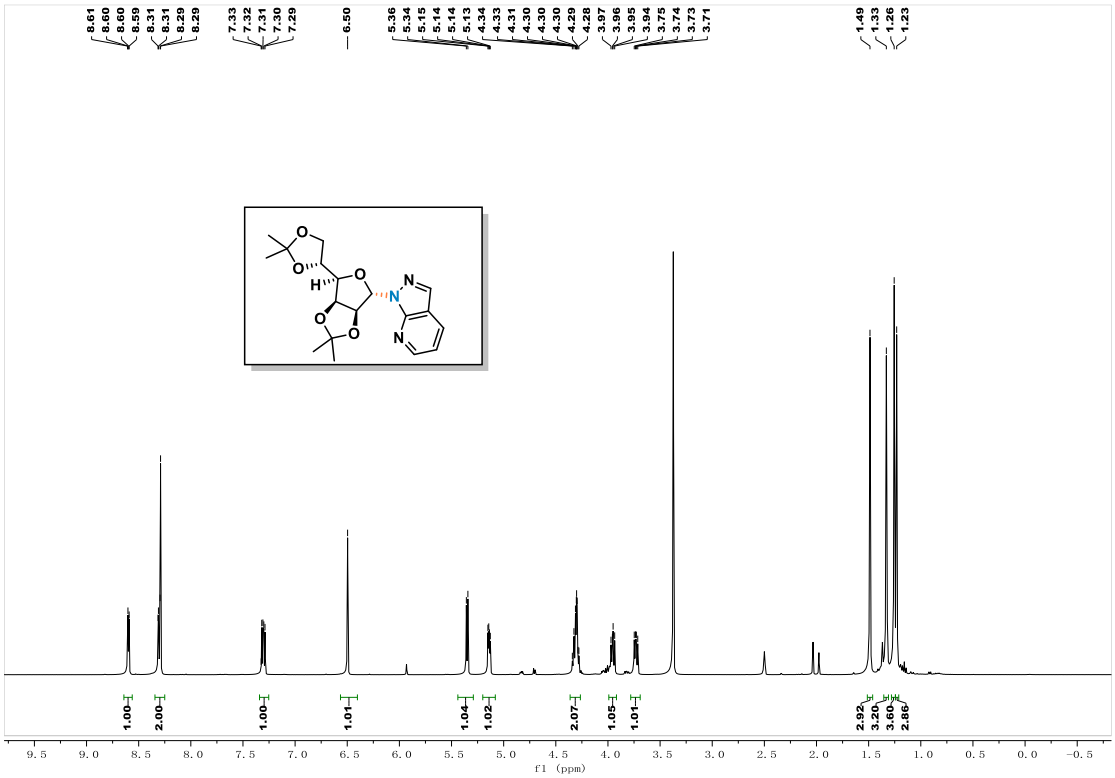
^{1}H NMR (400 MHz, $CDCl_3$) **(2i)**



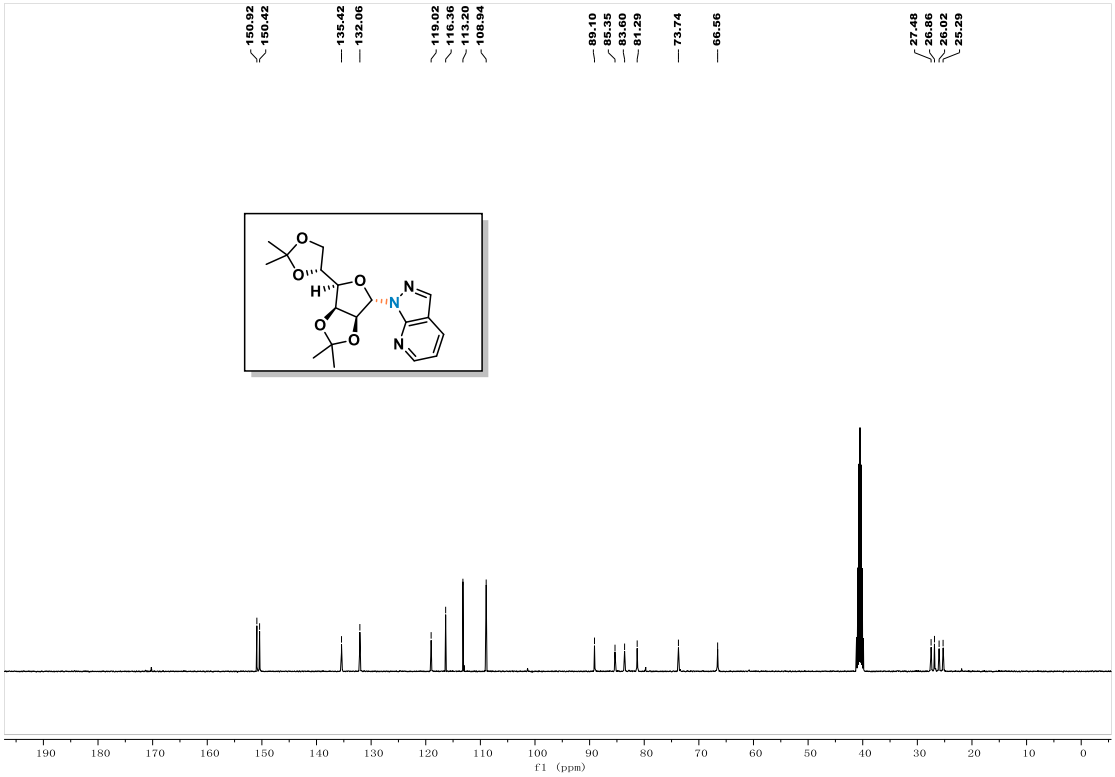
^{13}C NMR (101 MHz, $CDCl_3$) **(2i)**



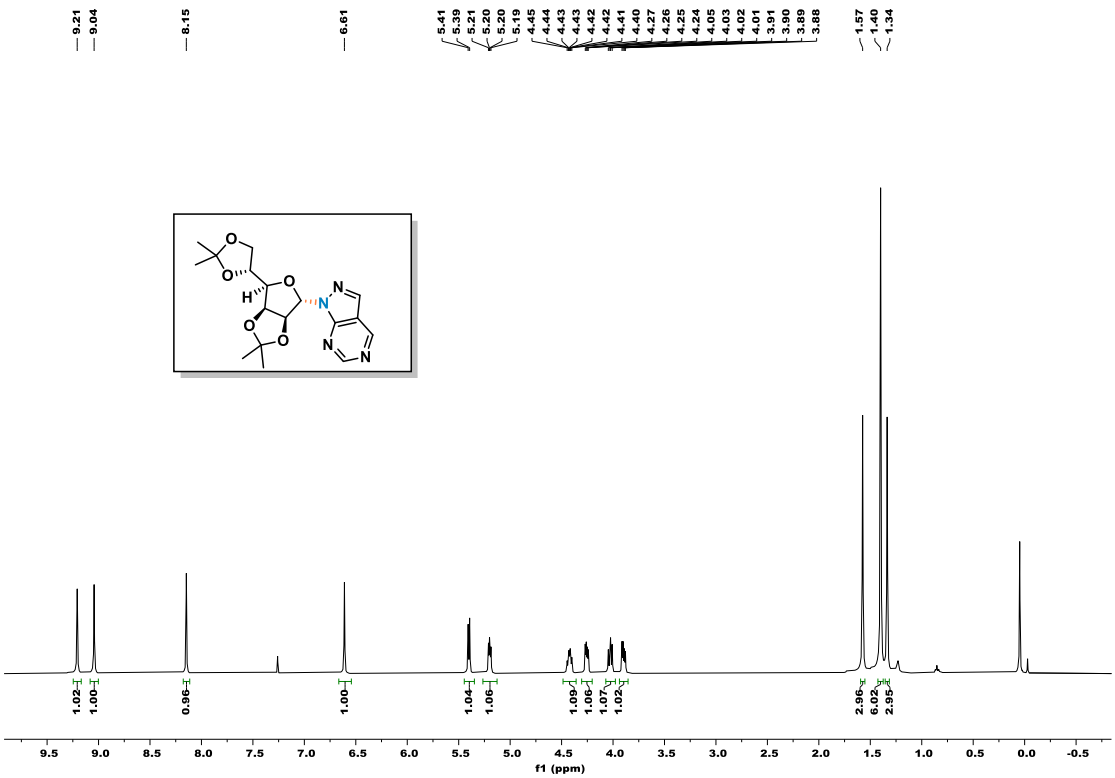
^{1}H NMR (400 MHz, DMSO-d_6) **(2j)**



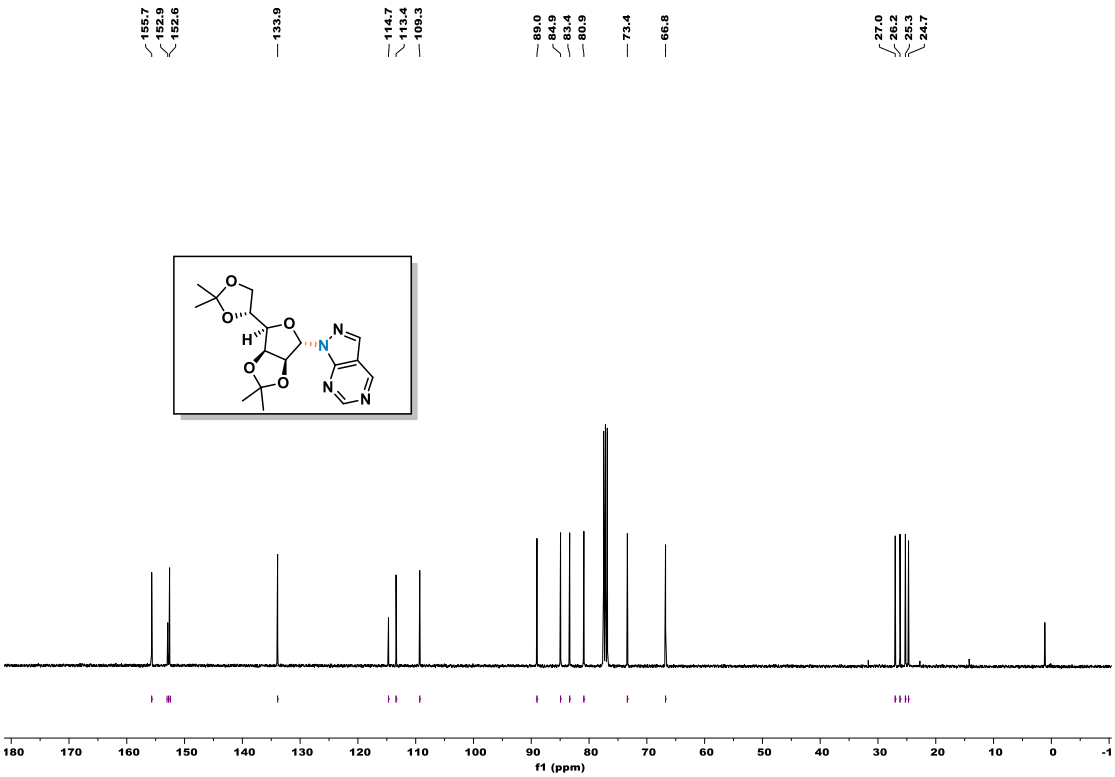
^{13}C NMR (101 MHz, DMSO-d_6) **(2j)**



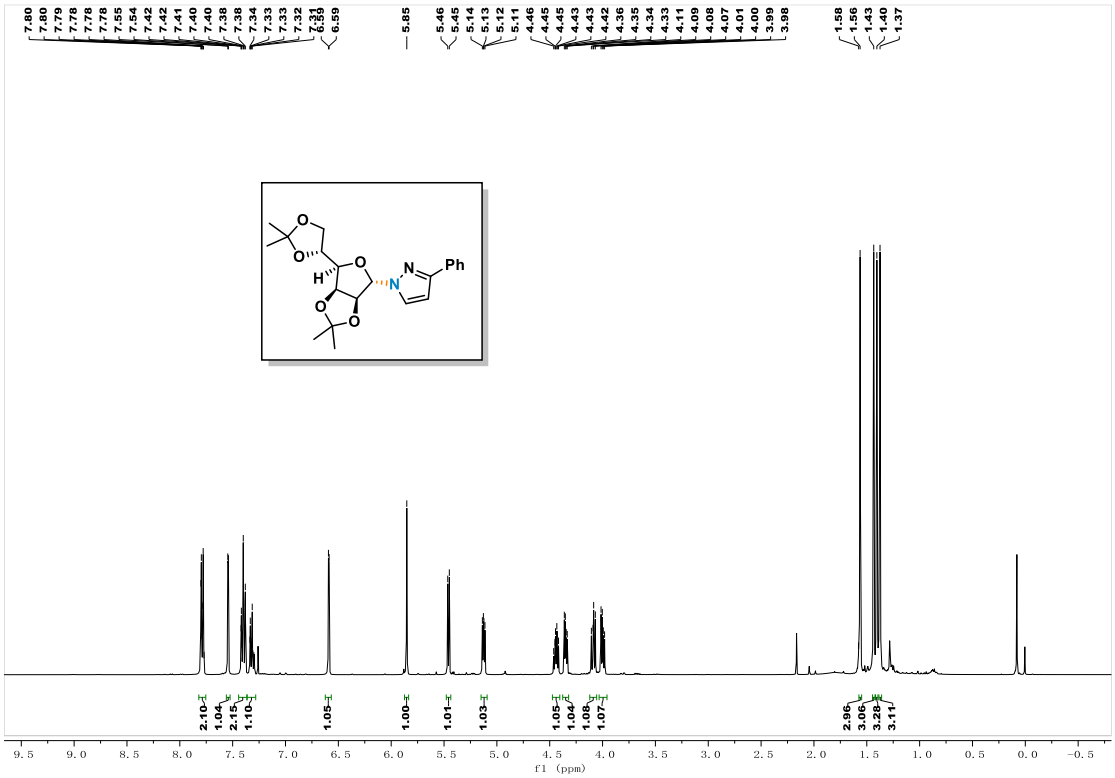
^{1}H NMR (400 MHz, $CDCl_3$) **(2k)**



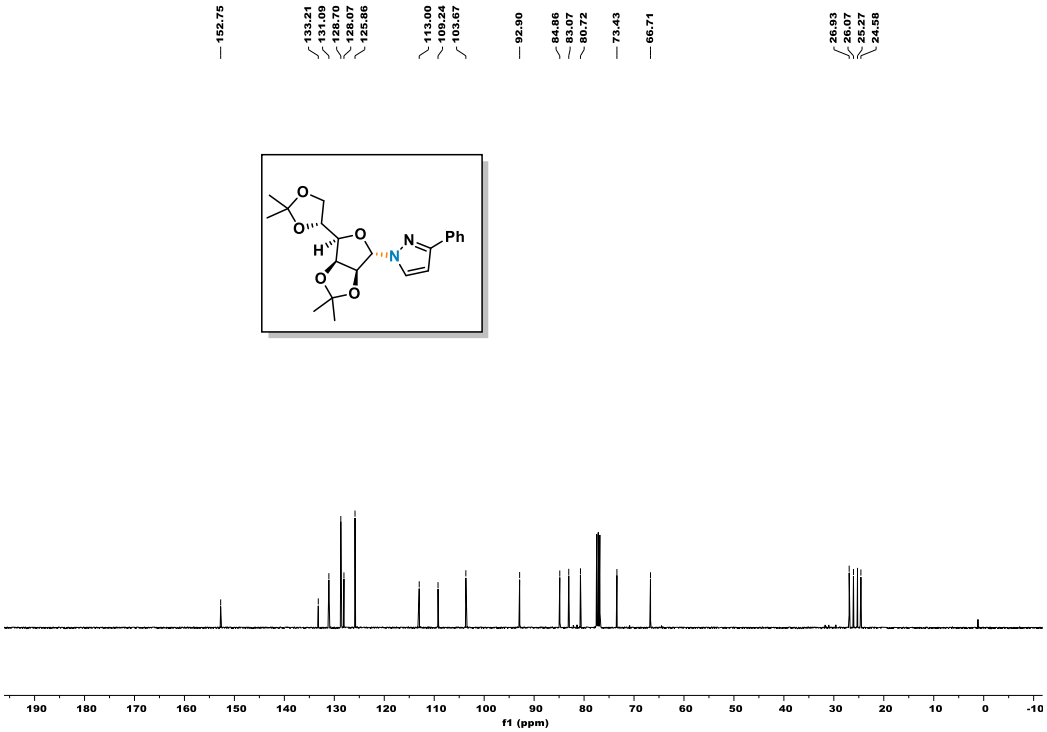
^{13}C NMR (101 MHz, $CDCl_3$) **(2k)**



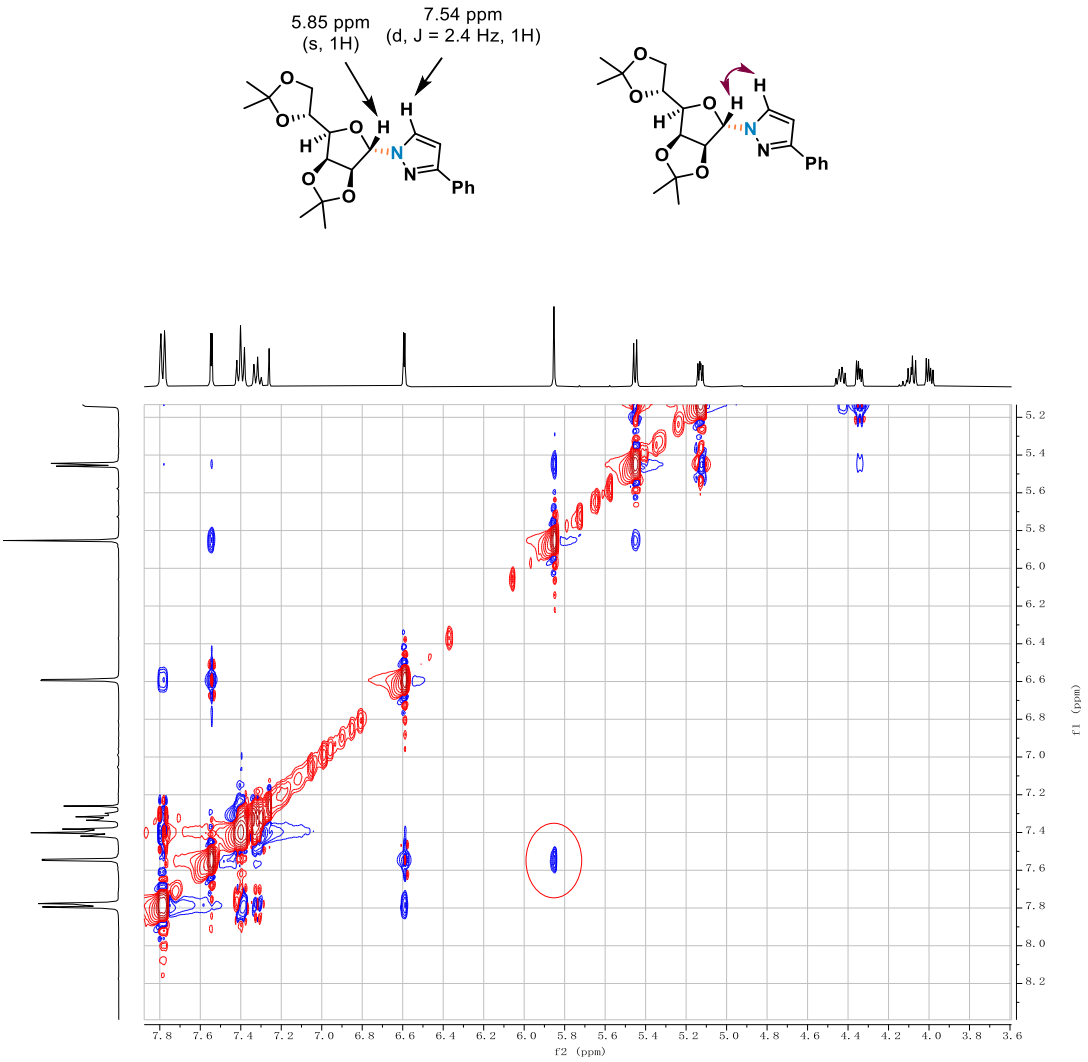
^{1}H NMR (400 MHz, $CDCl_3$) **(3a)**



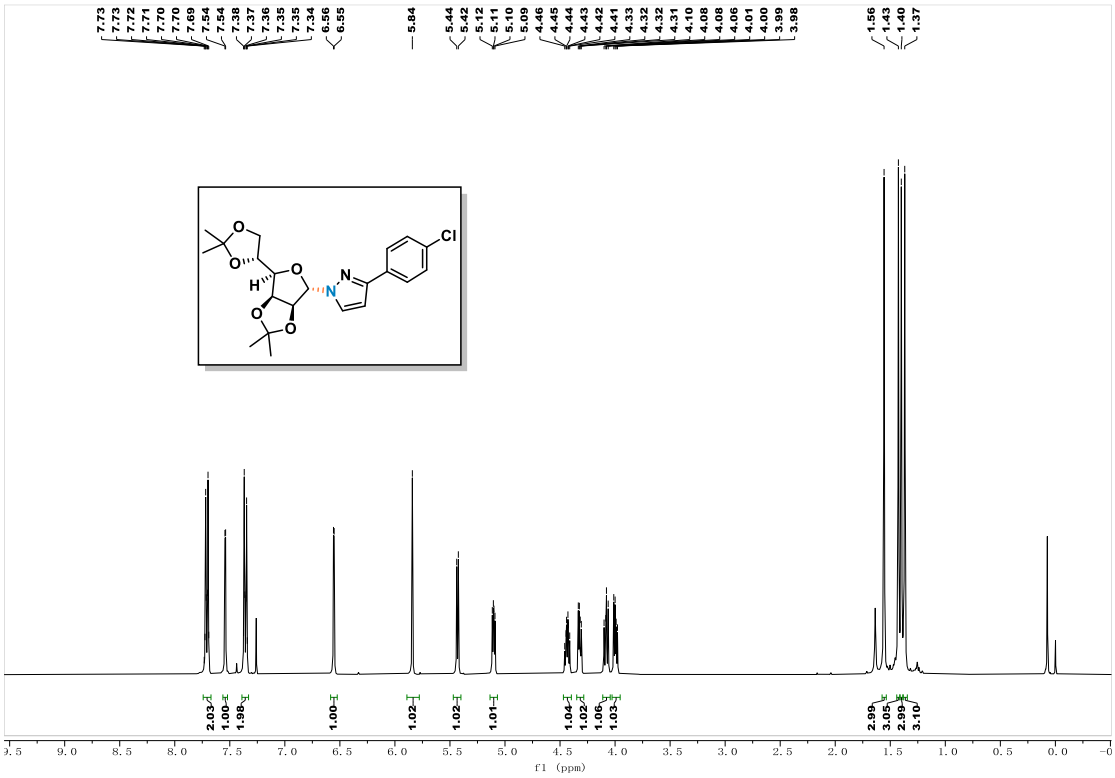
^{13}C NMR (101 MHz, $CDCl_3$) **(3a)**



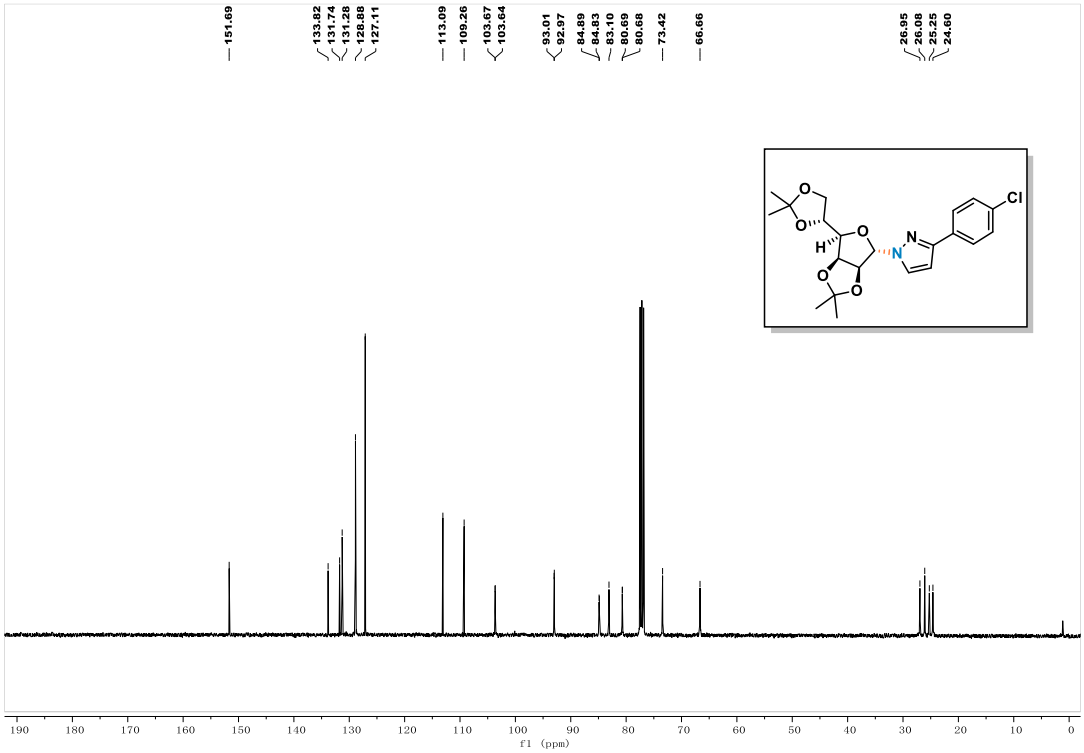
NOESY of **3a**



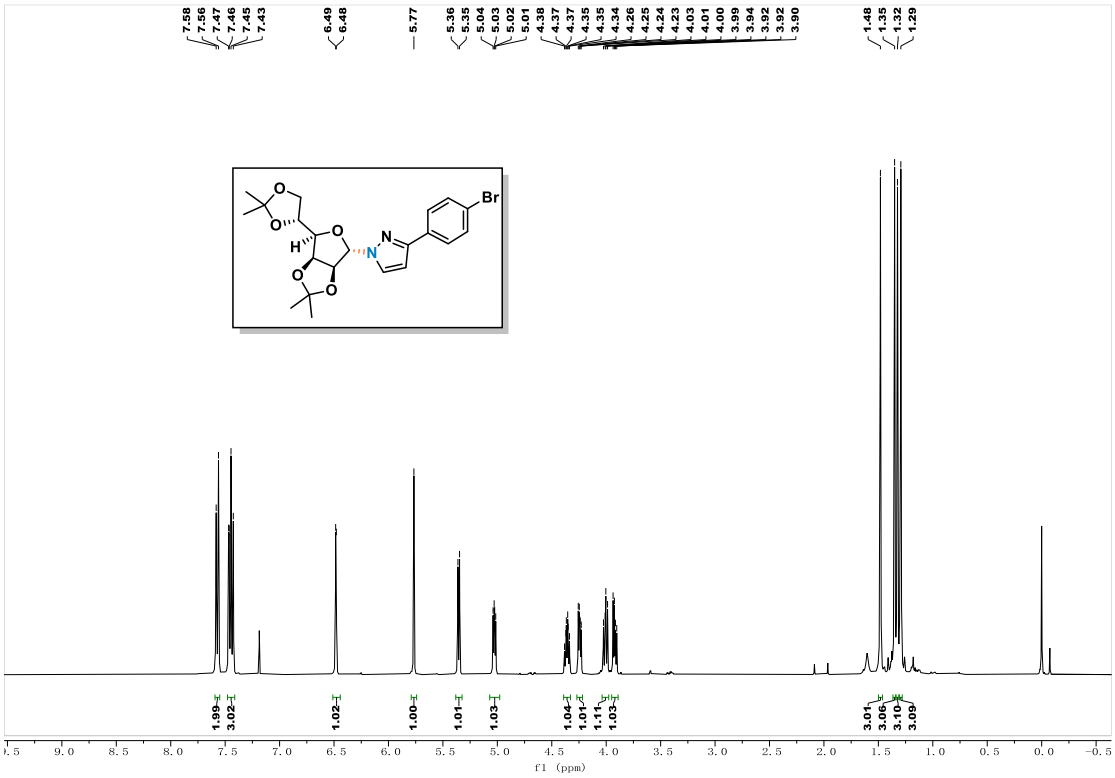
^{1}H NMR (400 MHz, $CDCl_3$) **(3b)**



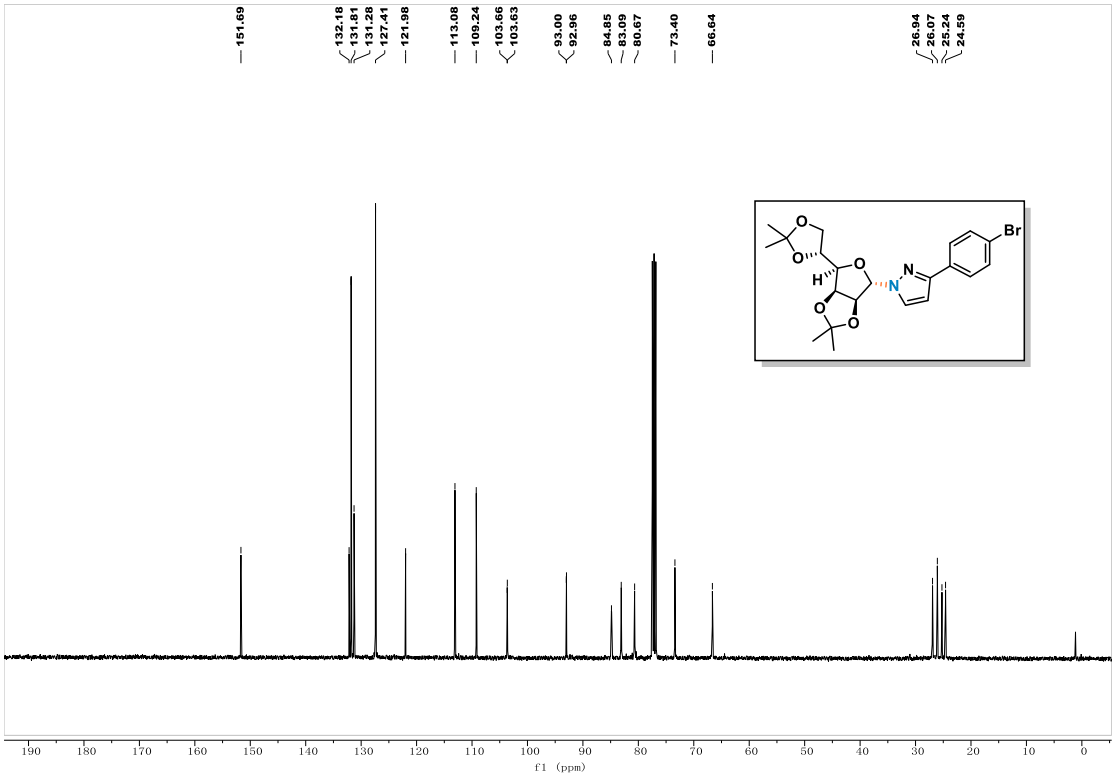
^{13}C NMR (101 MHz, $CDCl_3$) **(3b)**



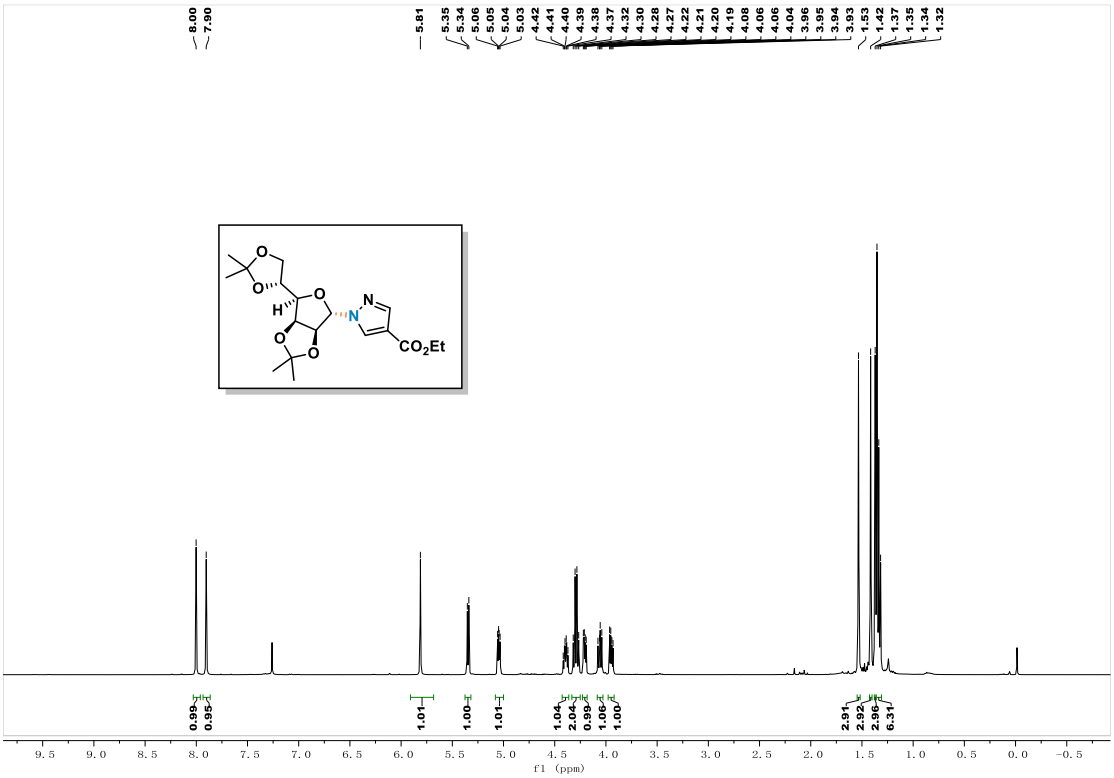
^{1}H NMR (400 MHz, $CDCl_3$) **(3c)**



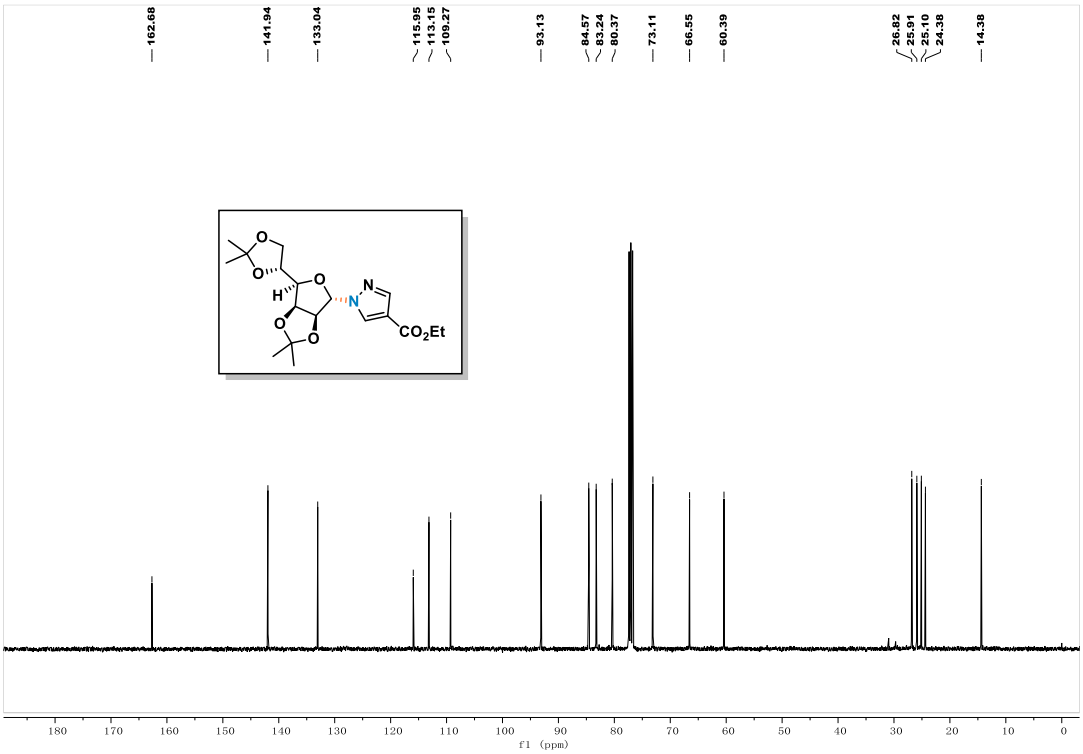
^{13}C NMR (101 MHz, $CDCl_3$) **(3c)**



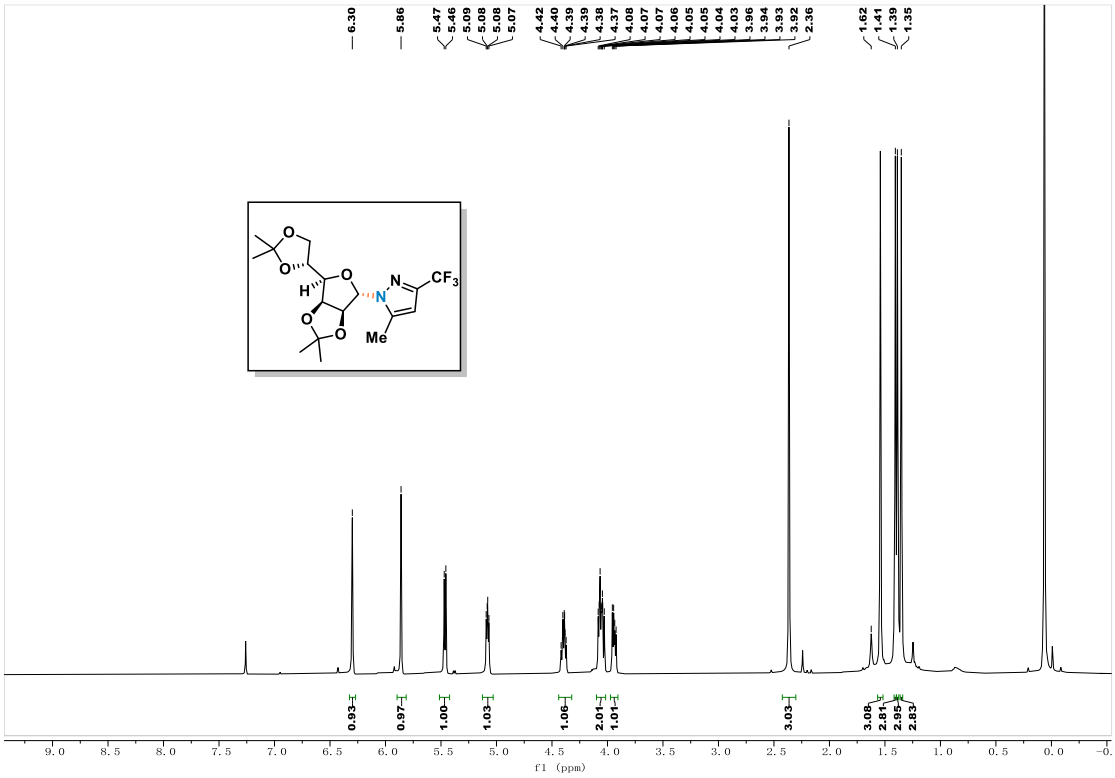
^{1}H NMR (400 MHz, $CDCl_3$) **(3d)**



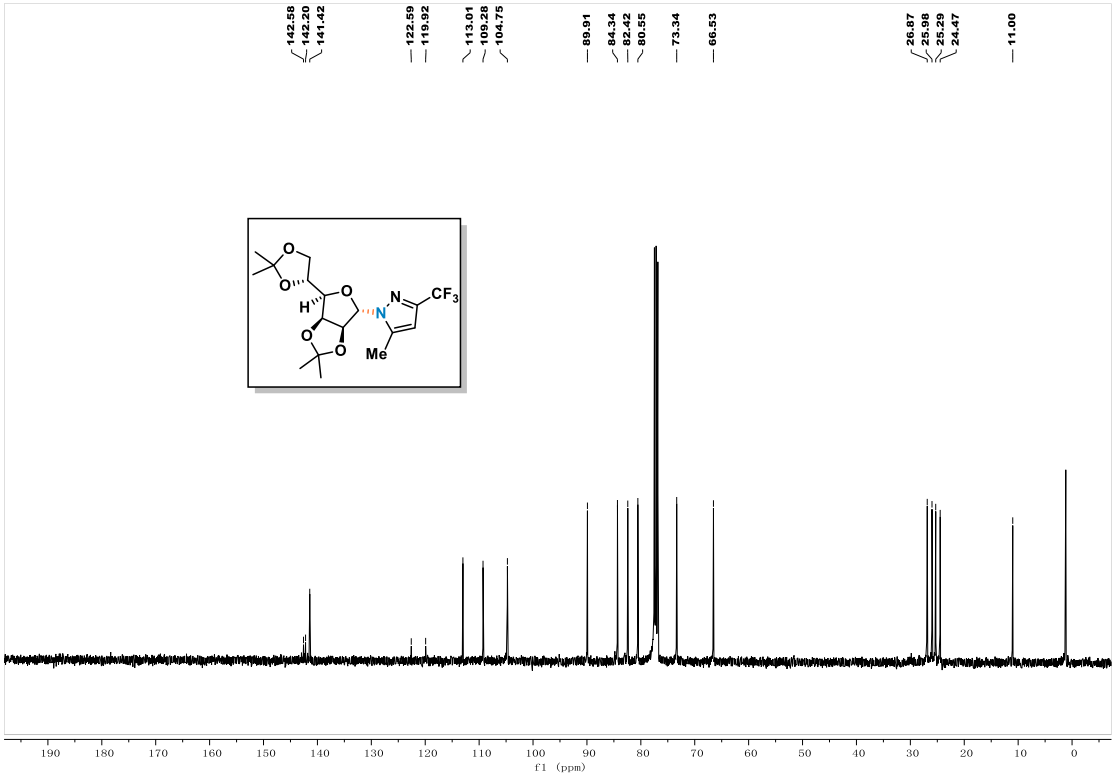
^{13}C NMR (101 MHz, $CDCl_3$) **(3d)**



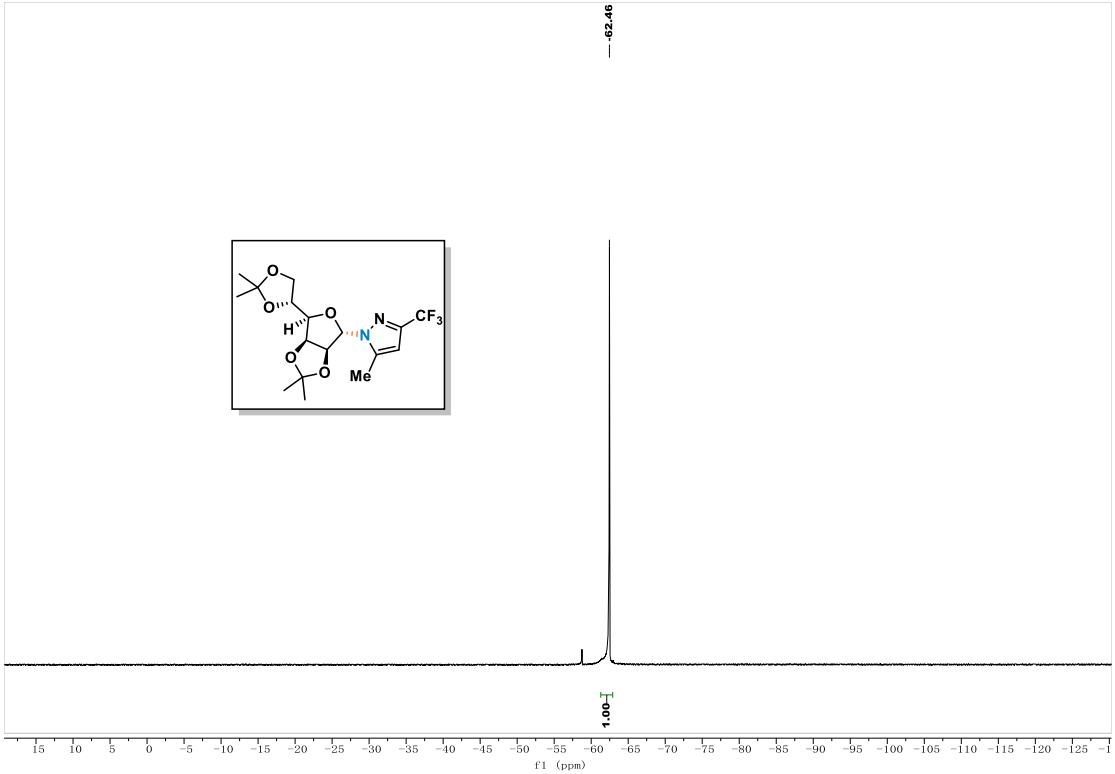
^{1}H NMR (400 MHz, $CDCl_3$) **(3e)**



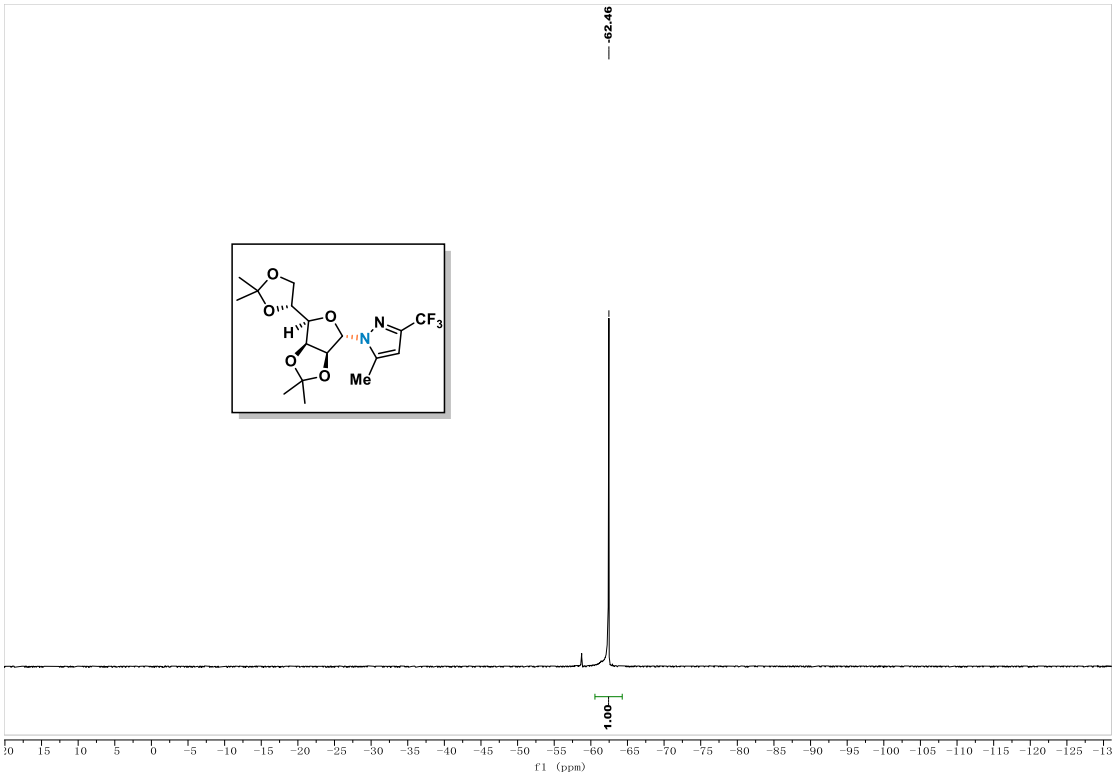
^{13}C NMR (101 MHz, $CDCl_3$) **(3e)**



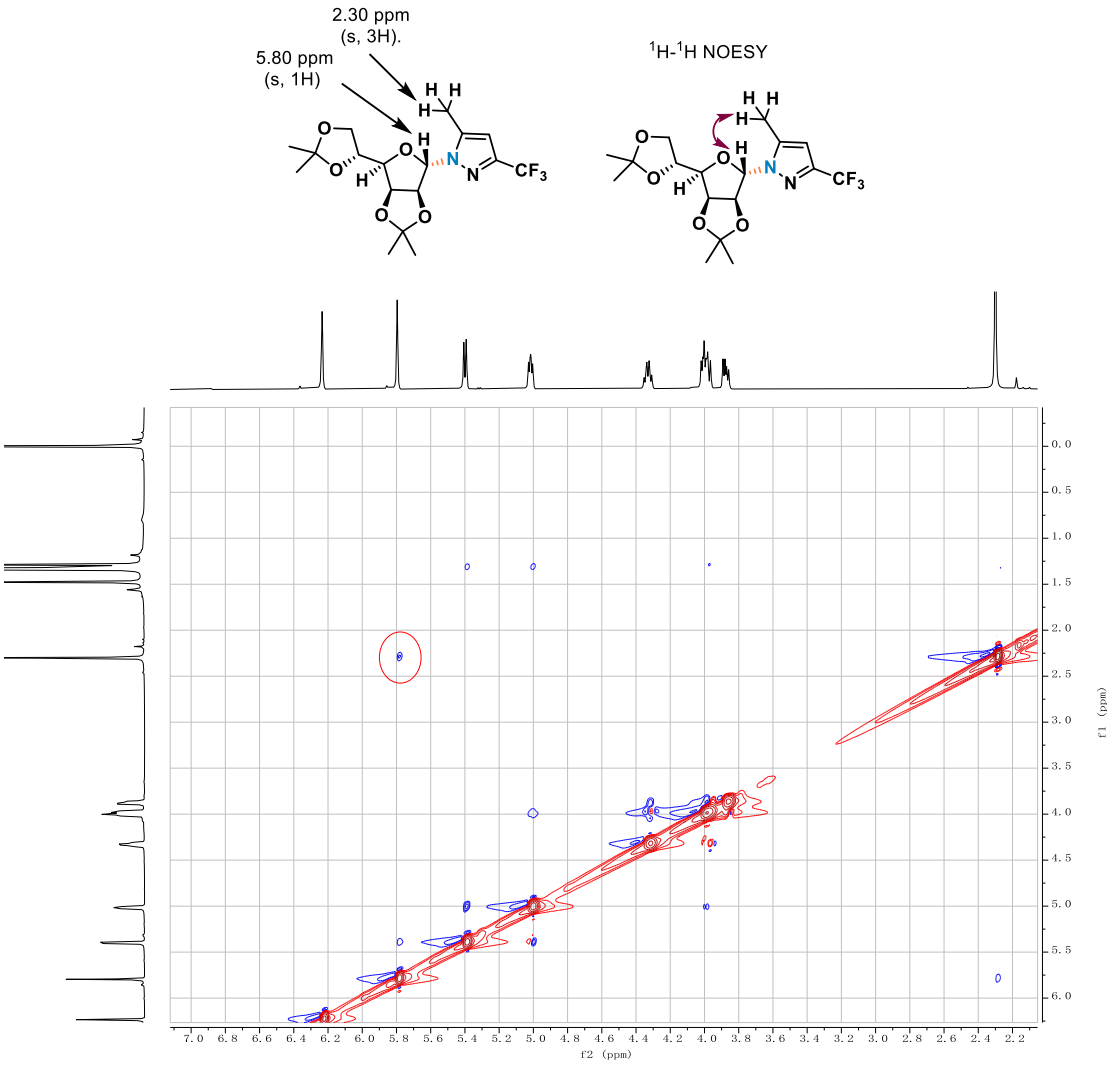
^{19}F NMR (376 MHz, $CDCl_3$) **(3e)**



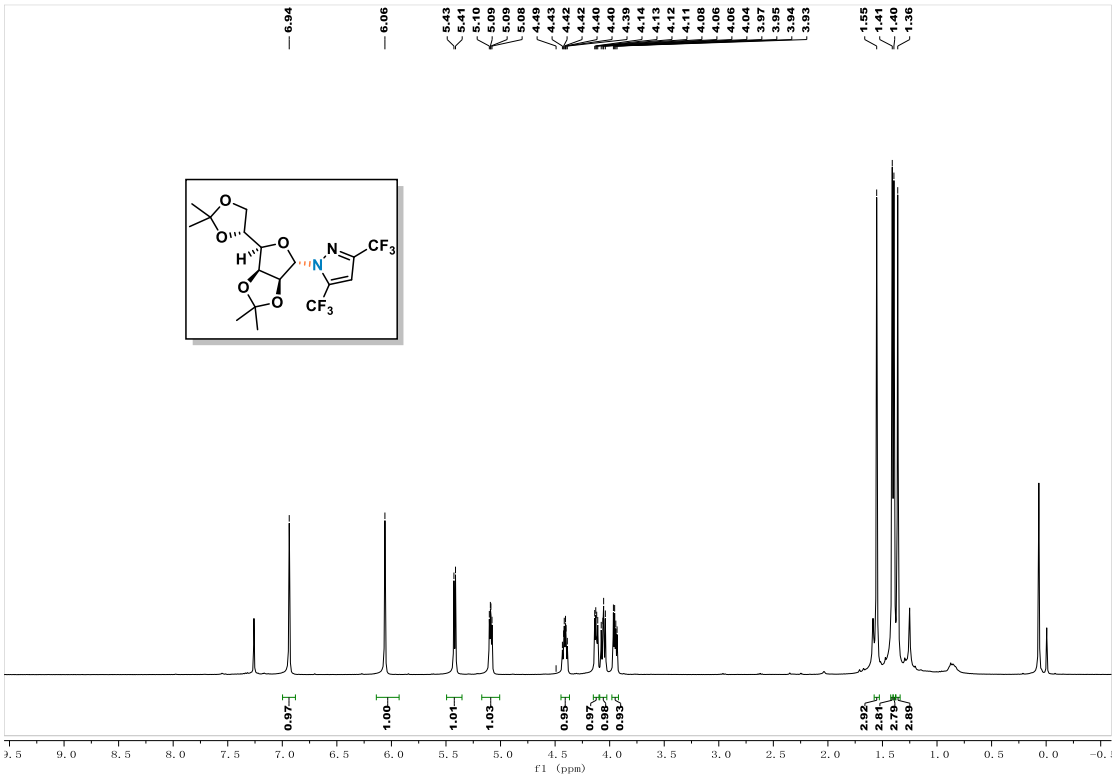
^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) **(3e)**



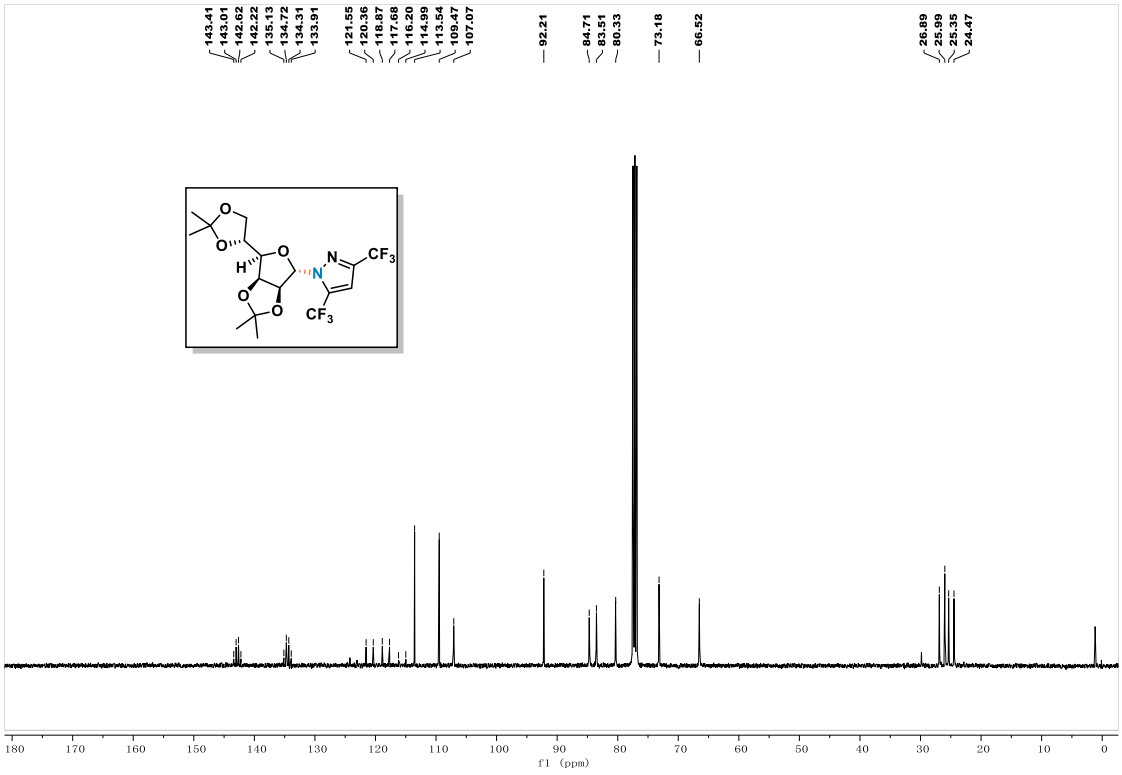
NOESY of **3e**



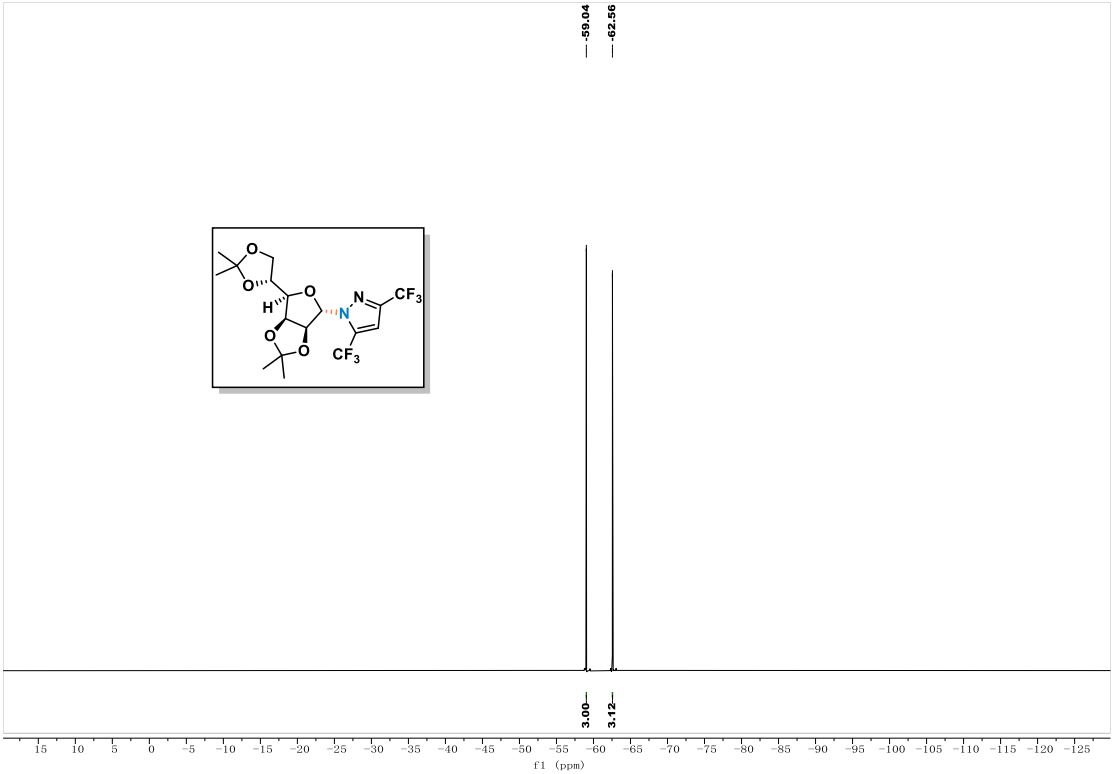
^{1}H NMR (400 MHz, $CDCl_3$) **(3f)**



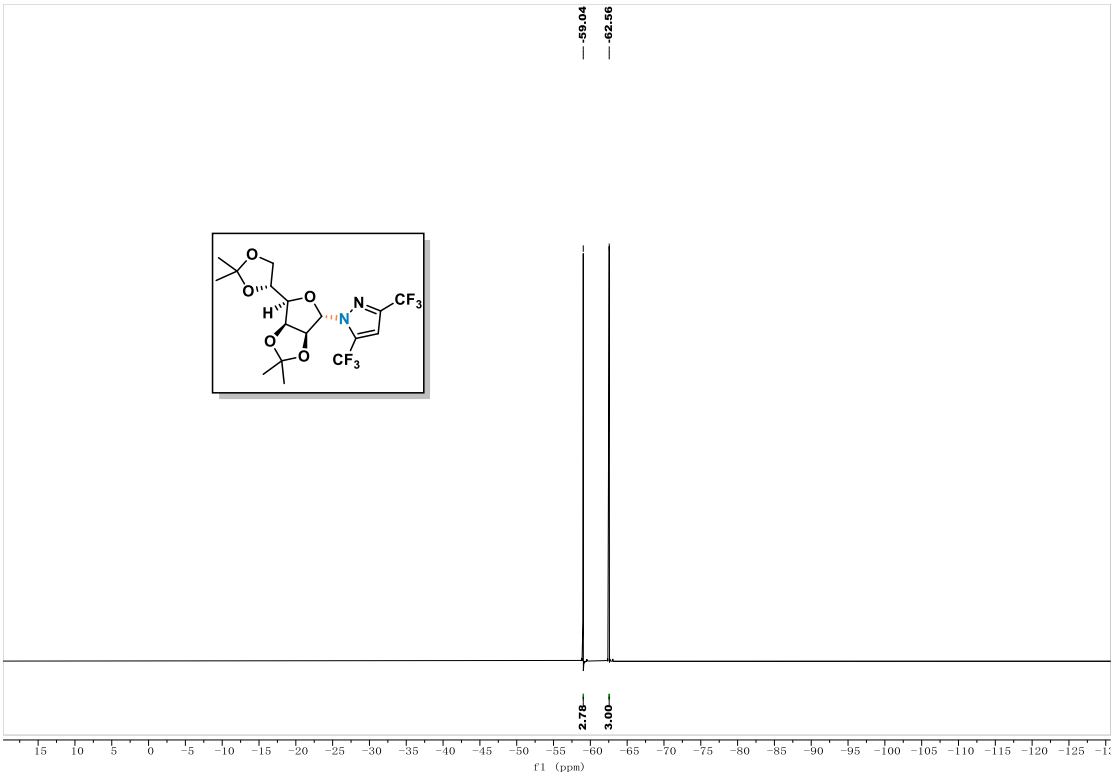
^{13}C NMR (101 MHz, $CDCl_3$) **(3f)**



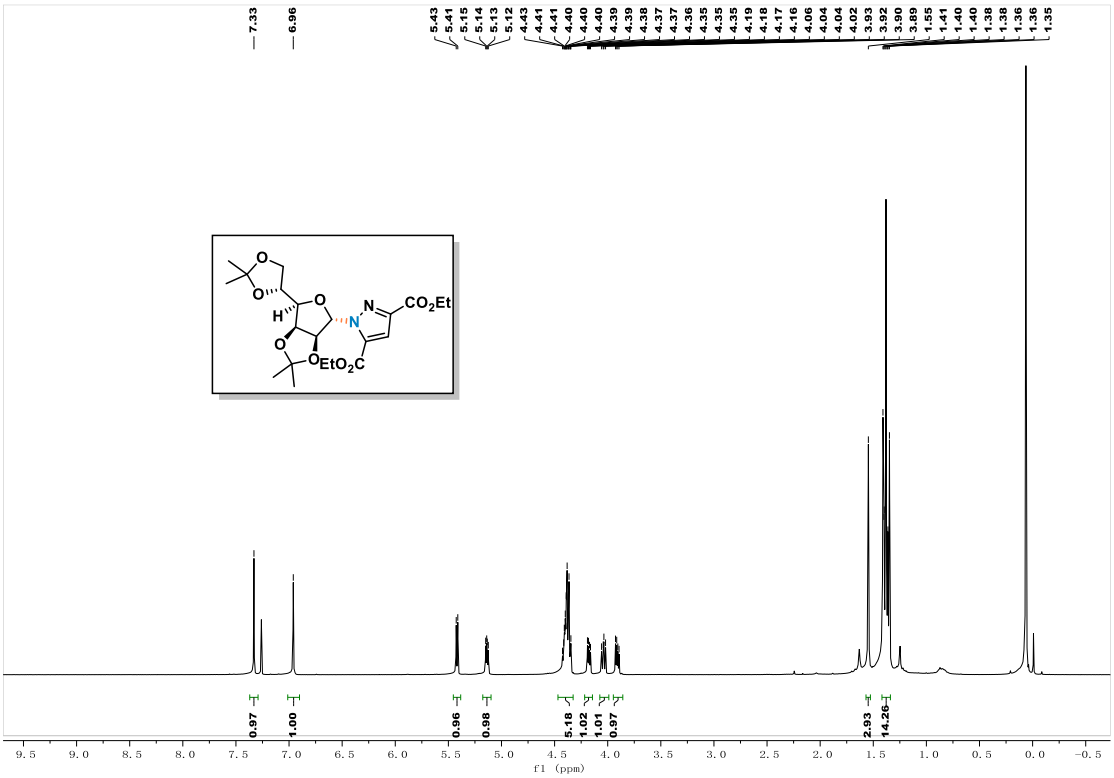
^{19}F NMR (376 MHz, $CDCl_3$) **(3f)**



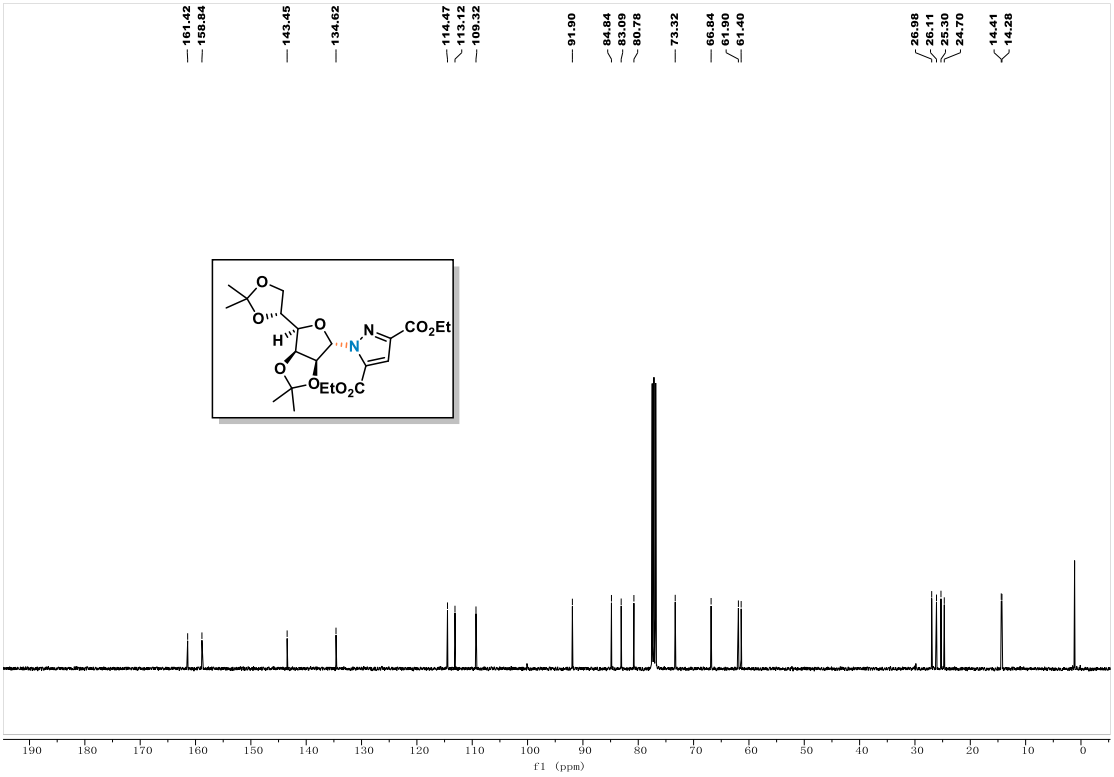
^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) **(3f)**



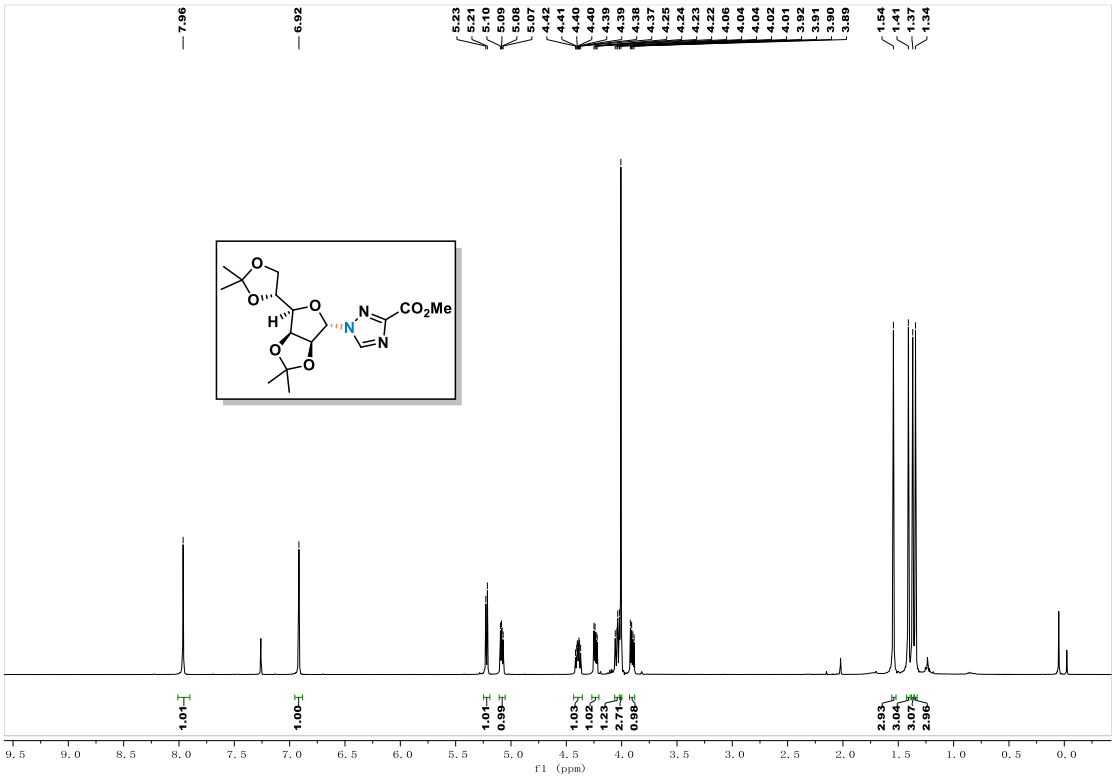
^{1}H NMR (400 MHz, $CDCl_3$) **(3g)**



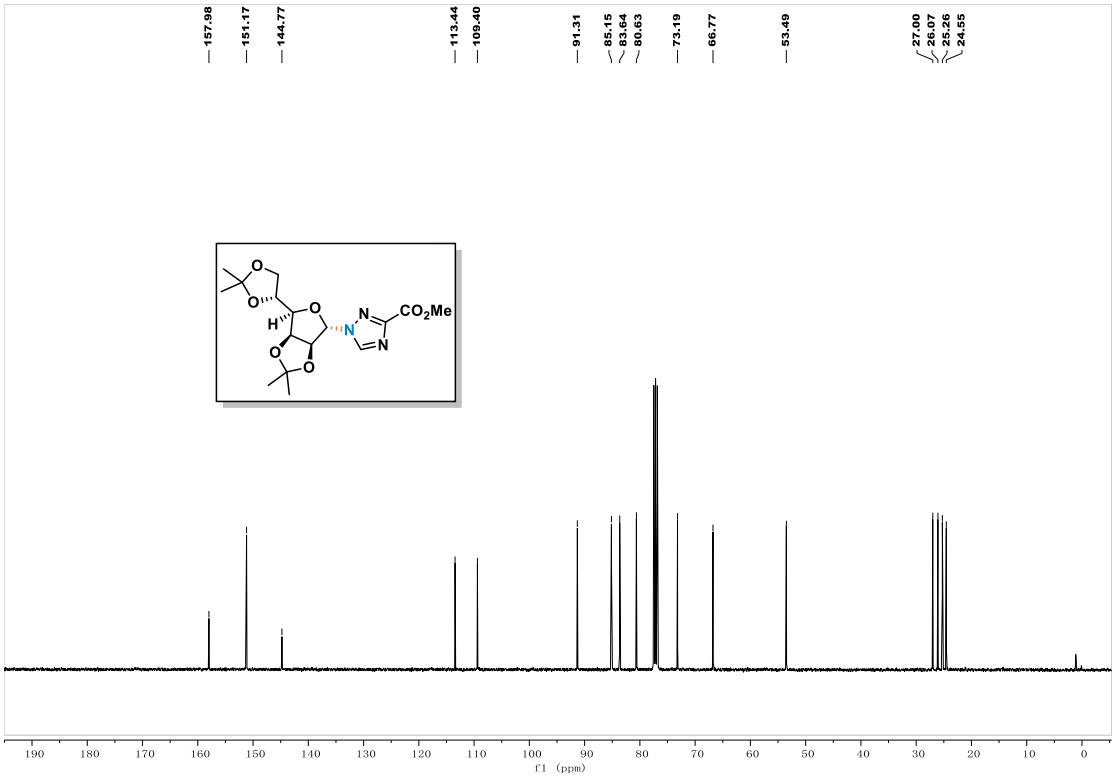
^{13}C NMR (101 MHz, $CDCl_3$) **(3g)**



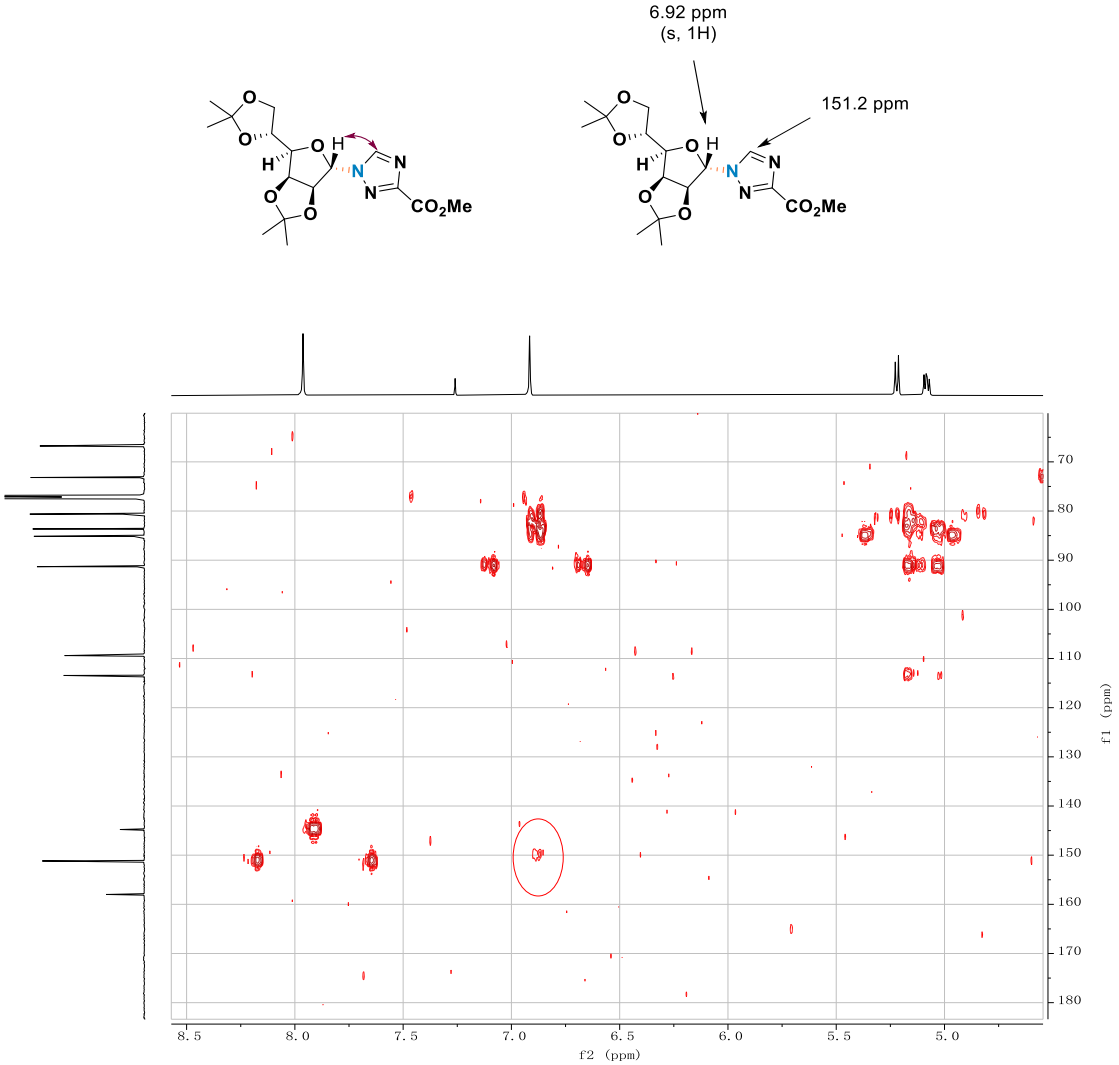
^{1}H NMR (400 MHz, $CDCl_3$) **(3h)**



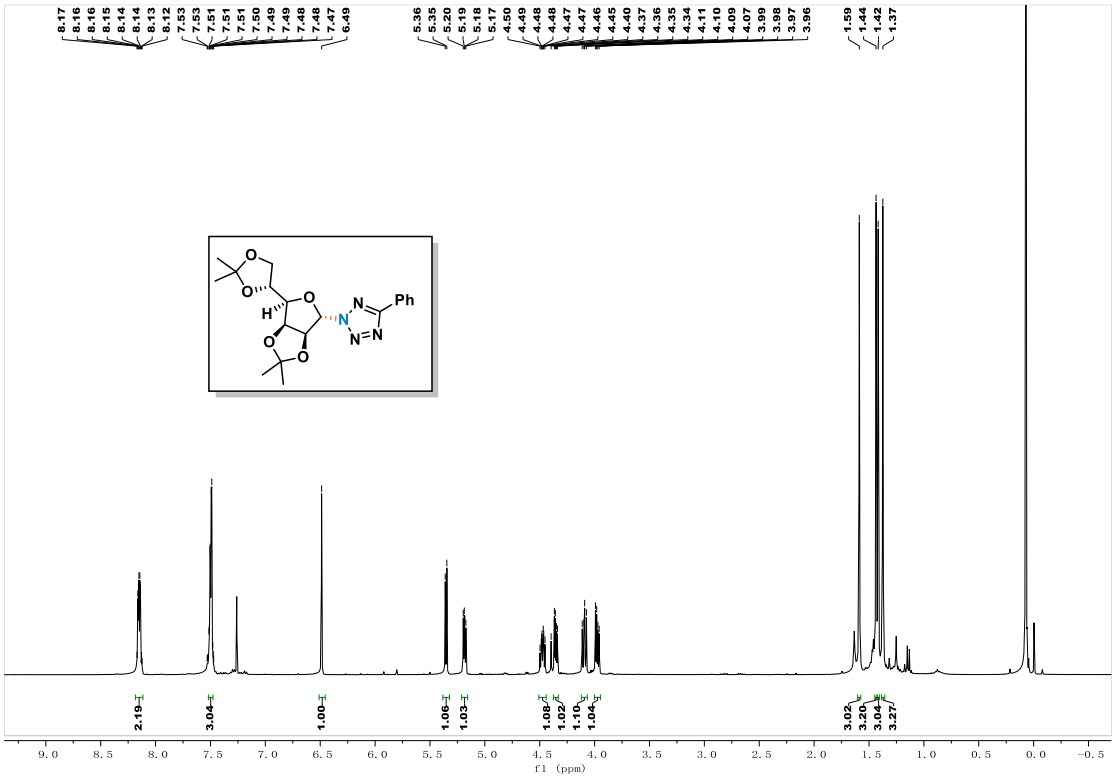
^{13}C NMR (101 MHz, $CDCl_3$) **(3h)**



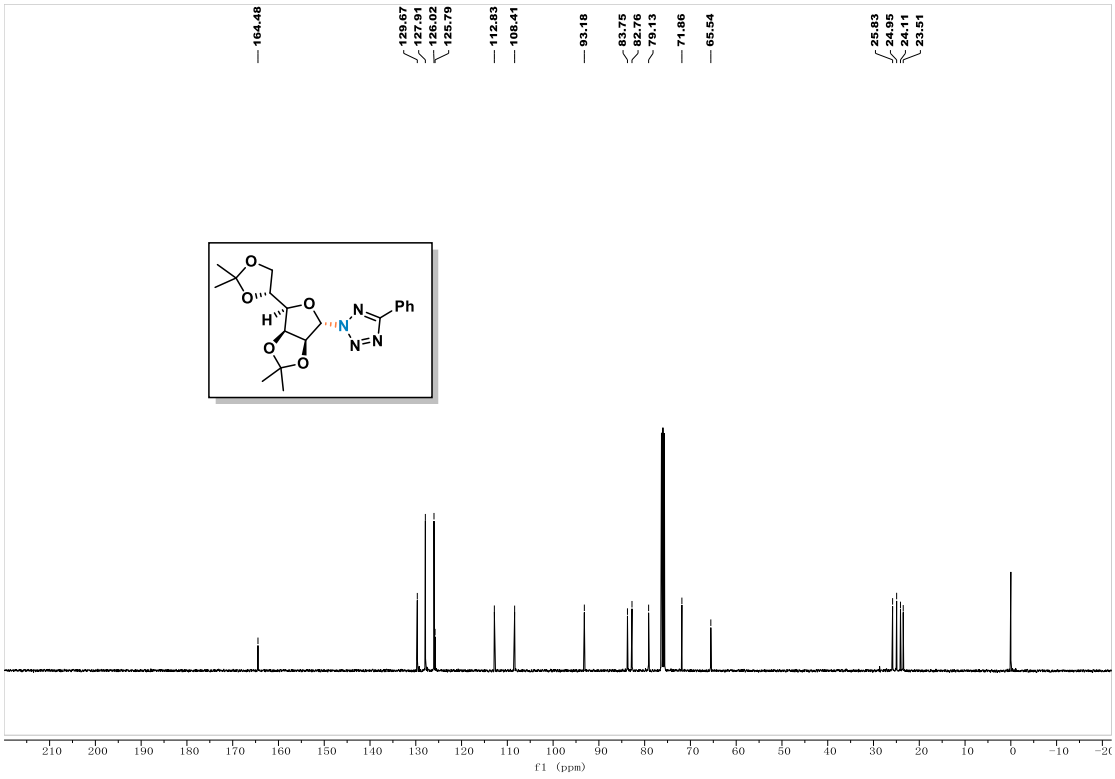
HMBC of **3h**



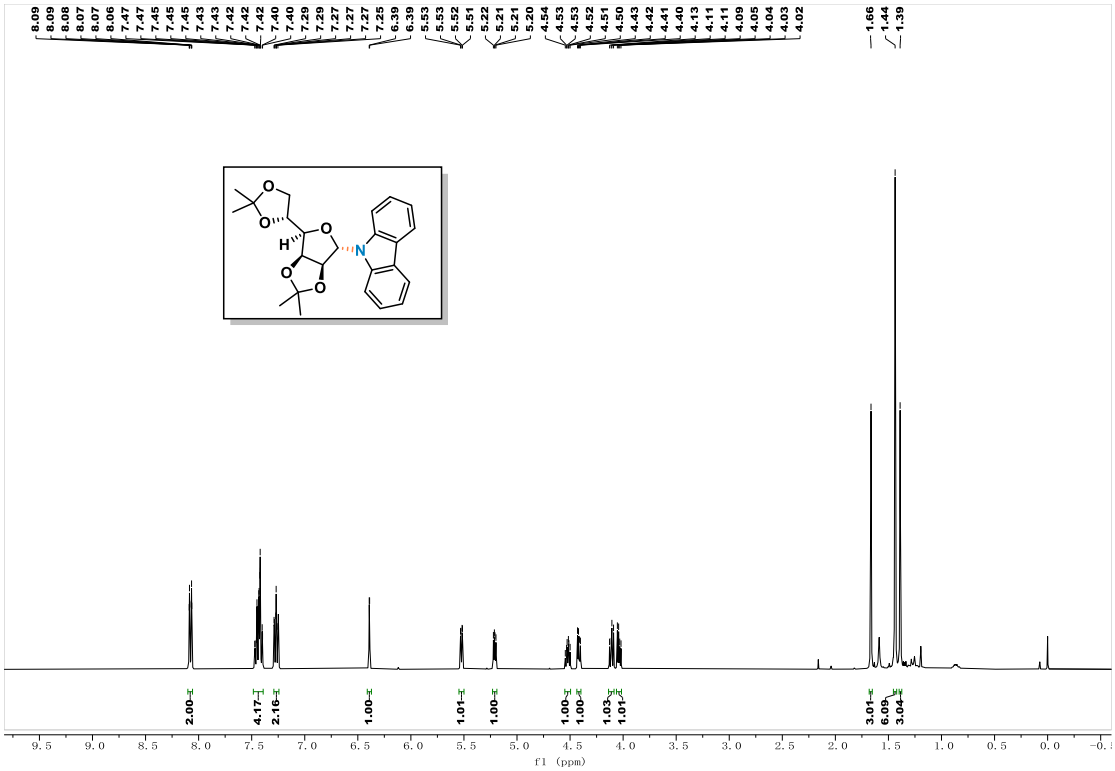
^{1}H NMR (400 MHz, $CDCl_3$) **(3i)**



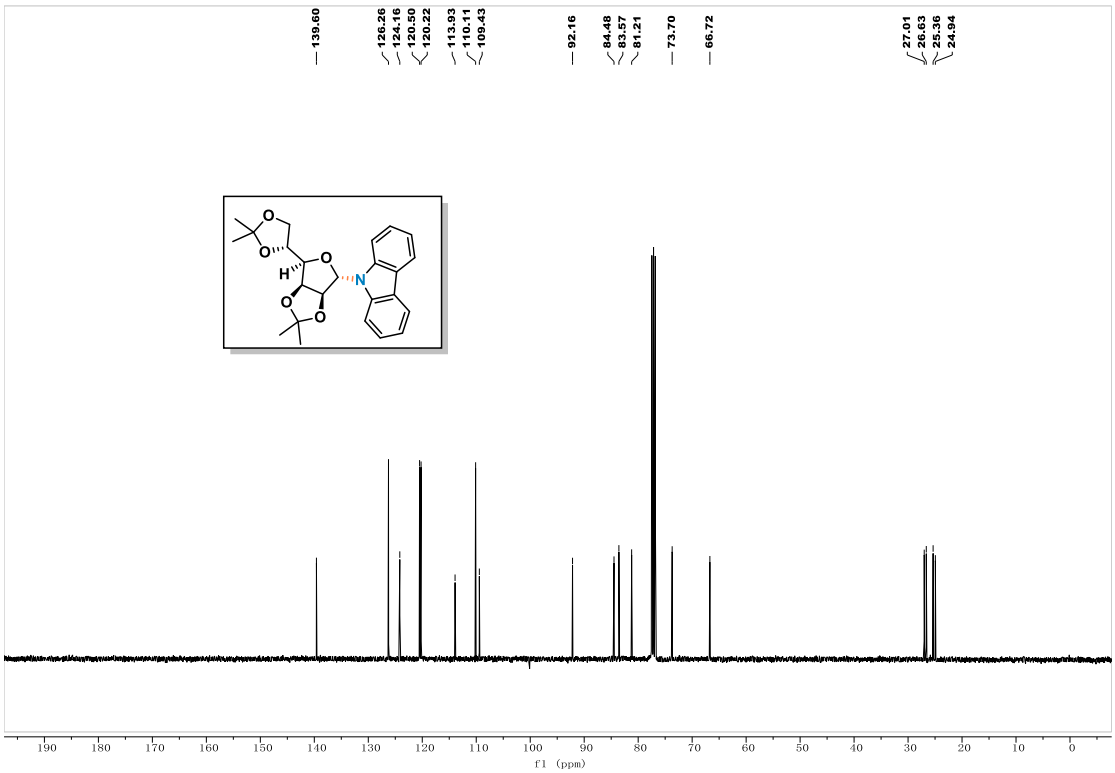
^{13}C NMR (101 MHz, $CDCl_3$) **(3i)**



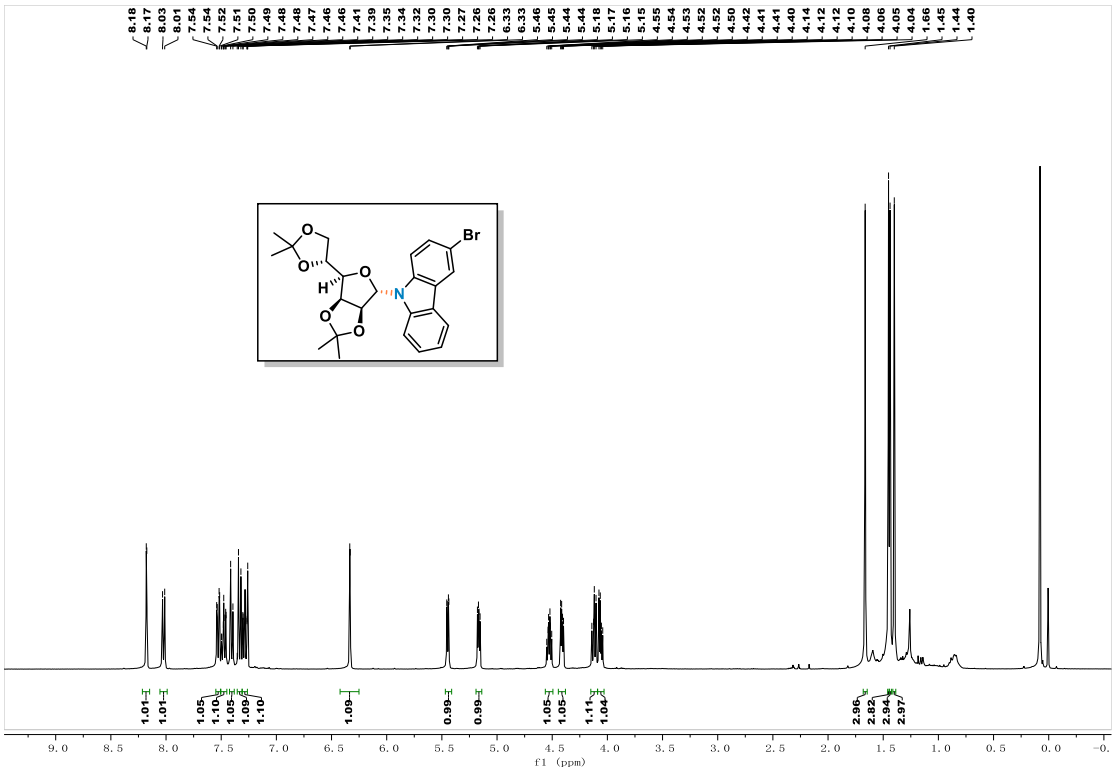
^{1}H NMR (400 MHz, $CDCl_3$) **(4a)**



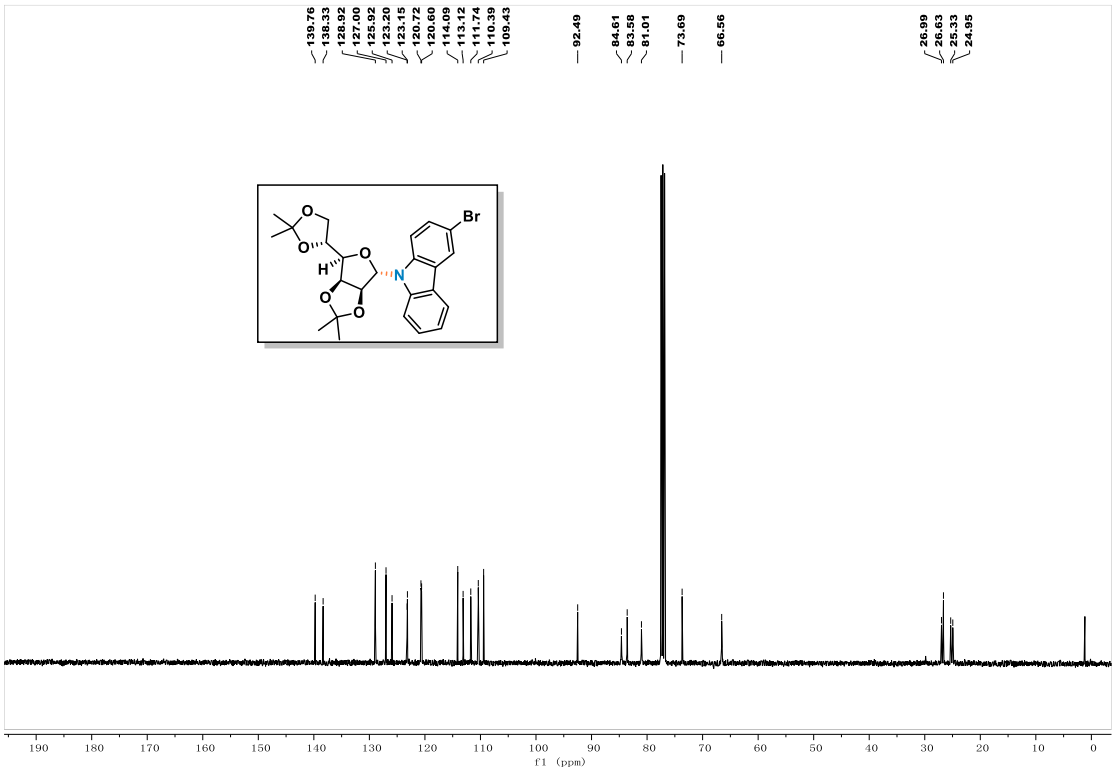
^{13}C NMR (101 MHz, $CDCl_3$) **(4a)**



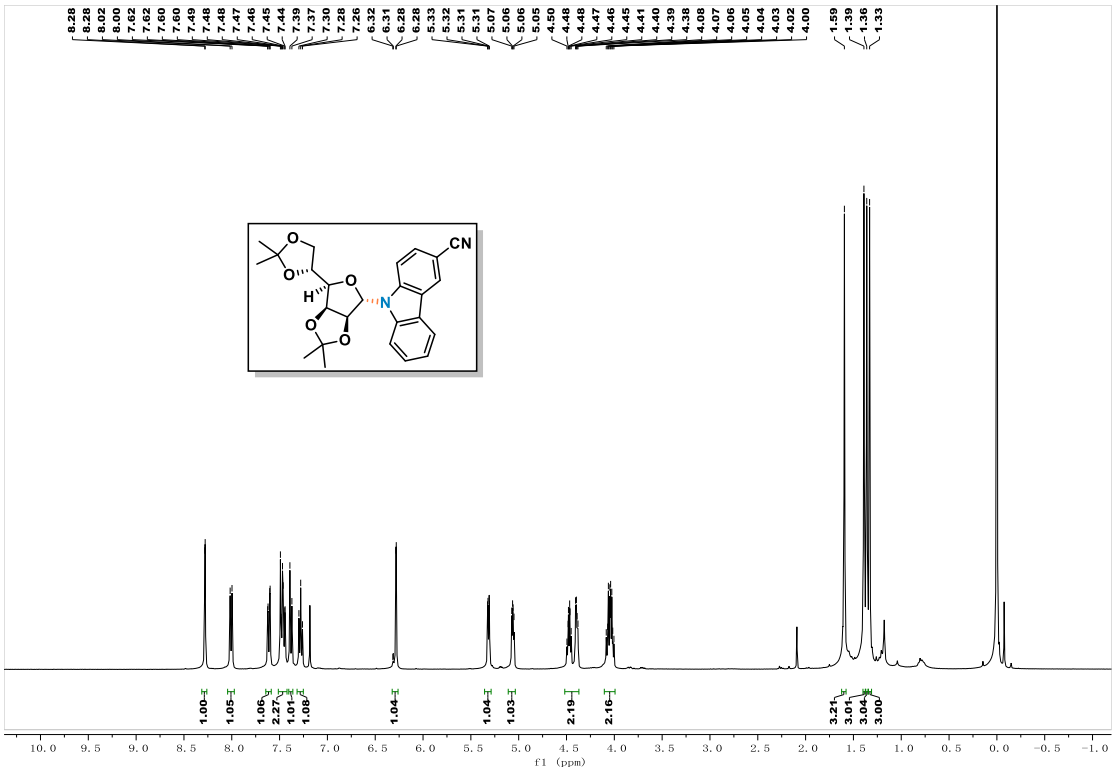
^{1}H NMR (400 MHz, $CDCl_3$) **(4b)**



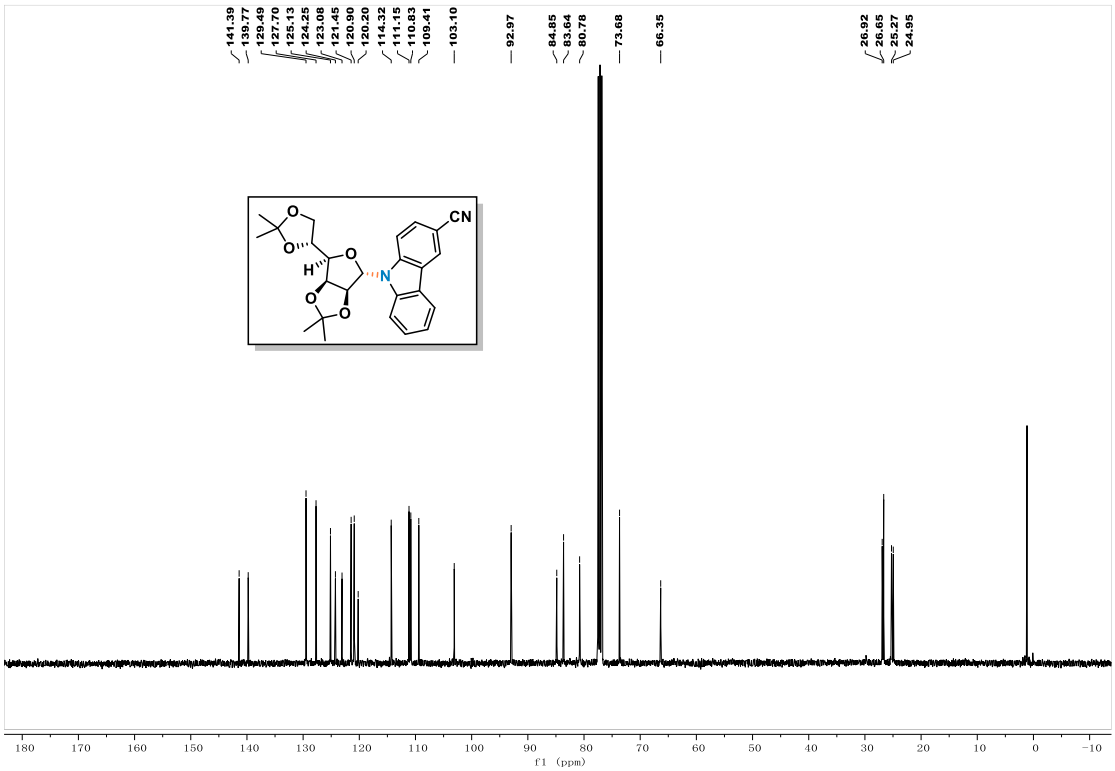
^{13}C NMR (101 MHz, $CDCl_3$) **(4b)**



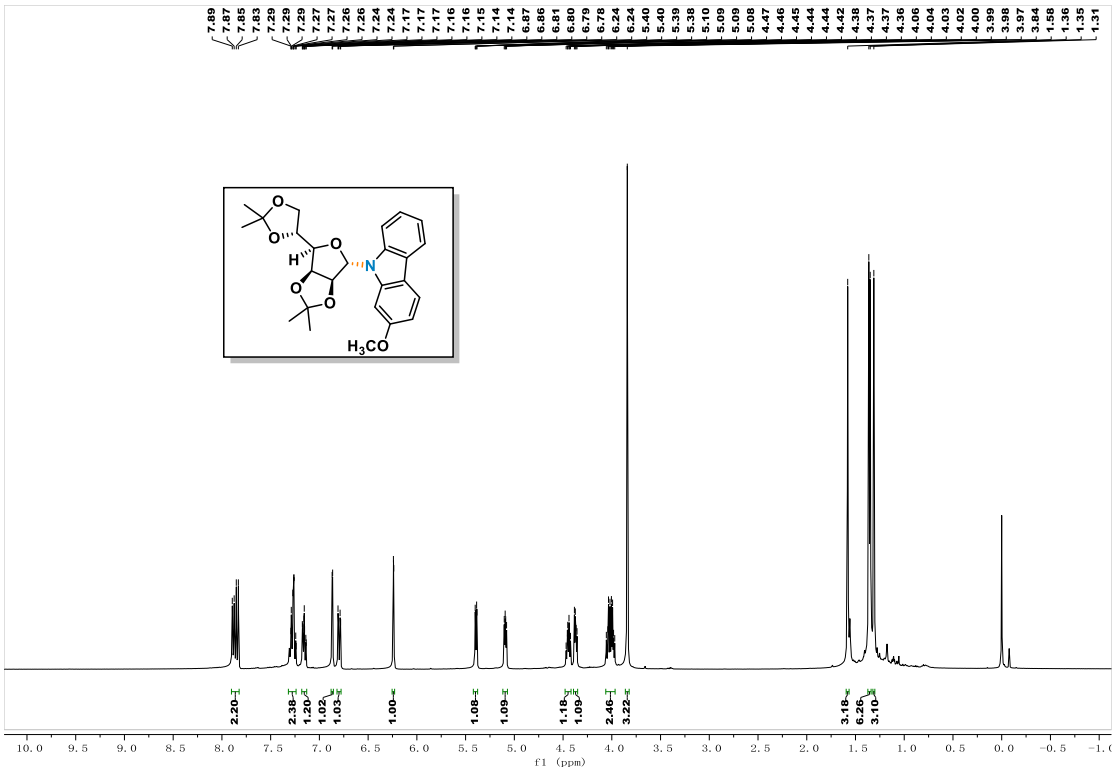
^{1}H NMR (400 MHz, $CDCl_3$) **(4c)**



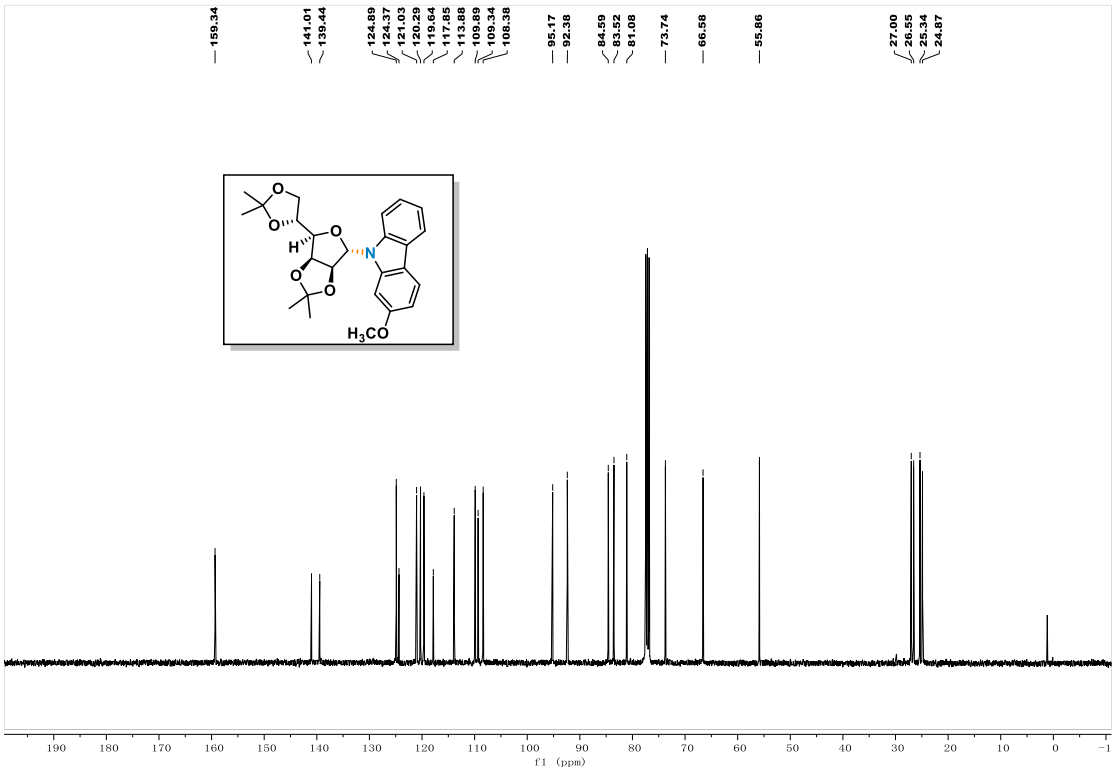
^{13}C NMR (101 MHz, $CDCl_3$) **(4c)**



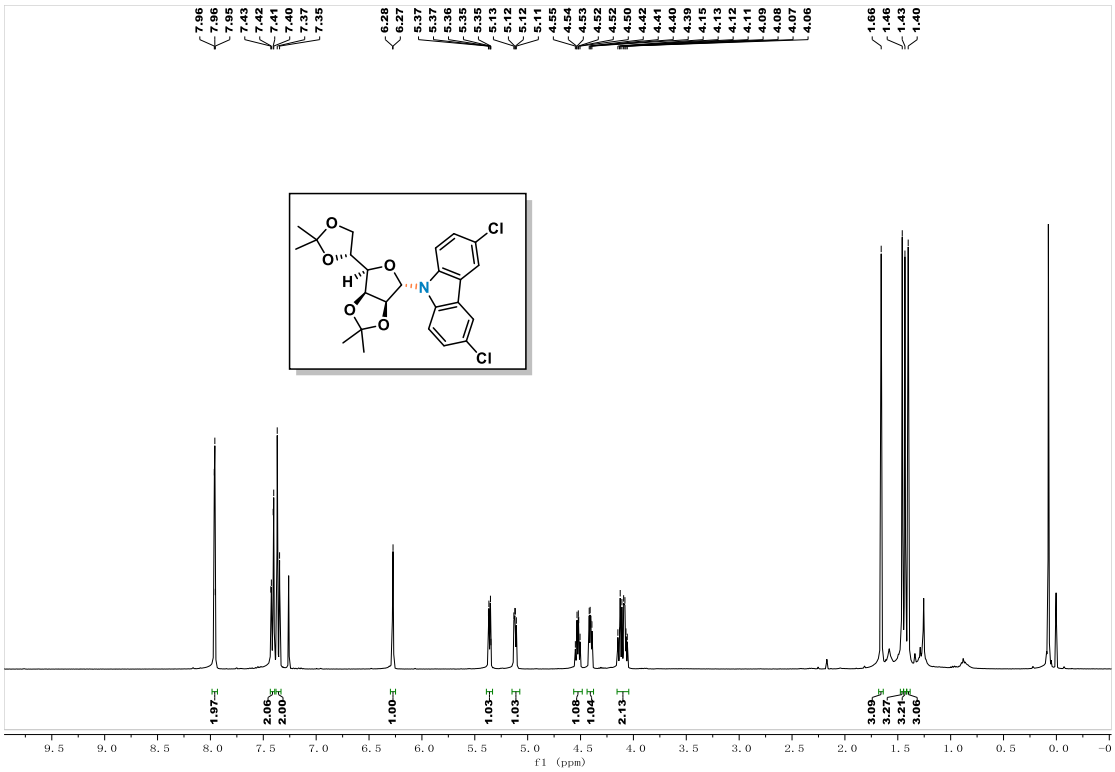
^{1}H NMR (400 MHz, $CDCl_3$) **(4d)**



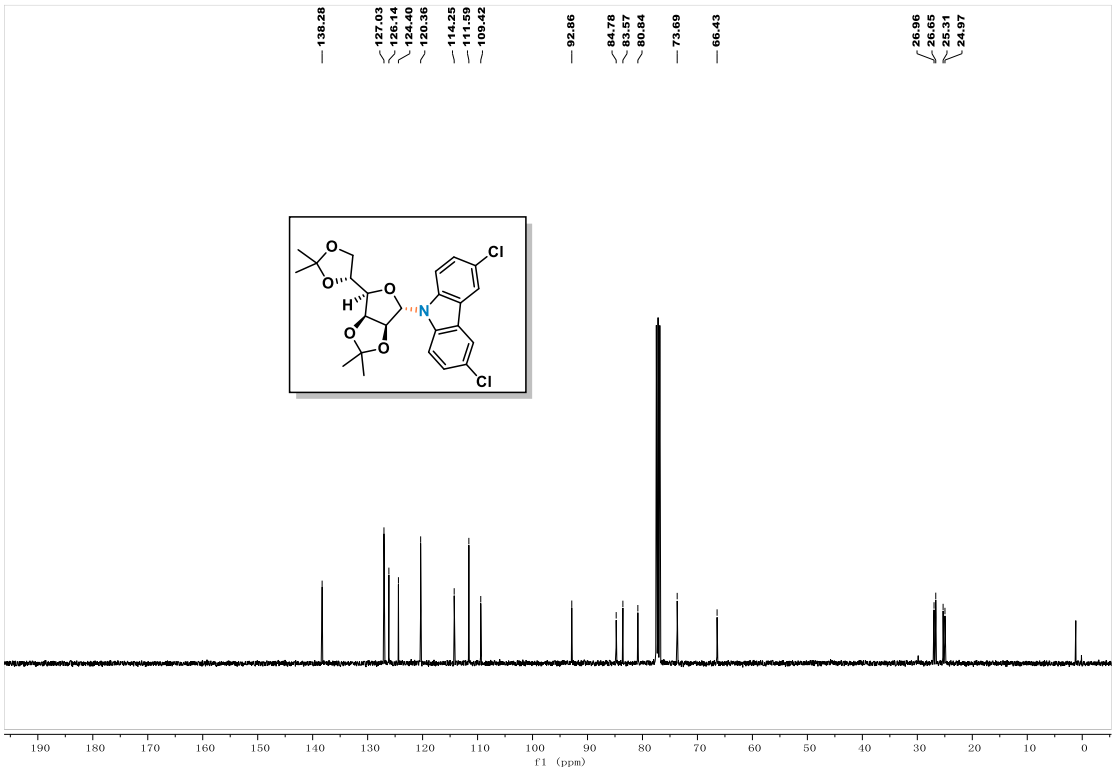
^{13}C NMR (101 MHz, $CDCl_3$) **(4d)**



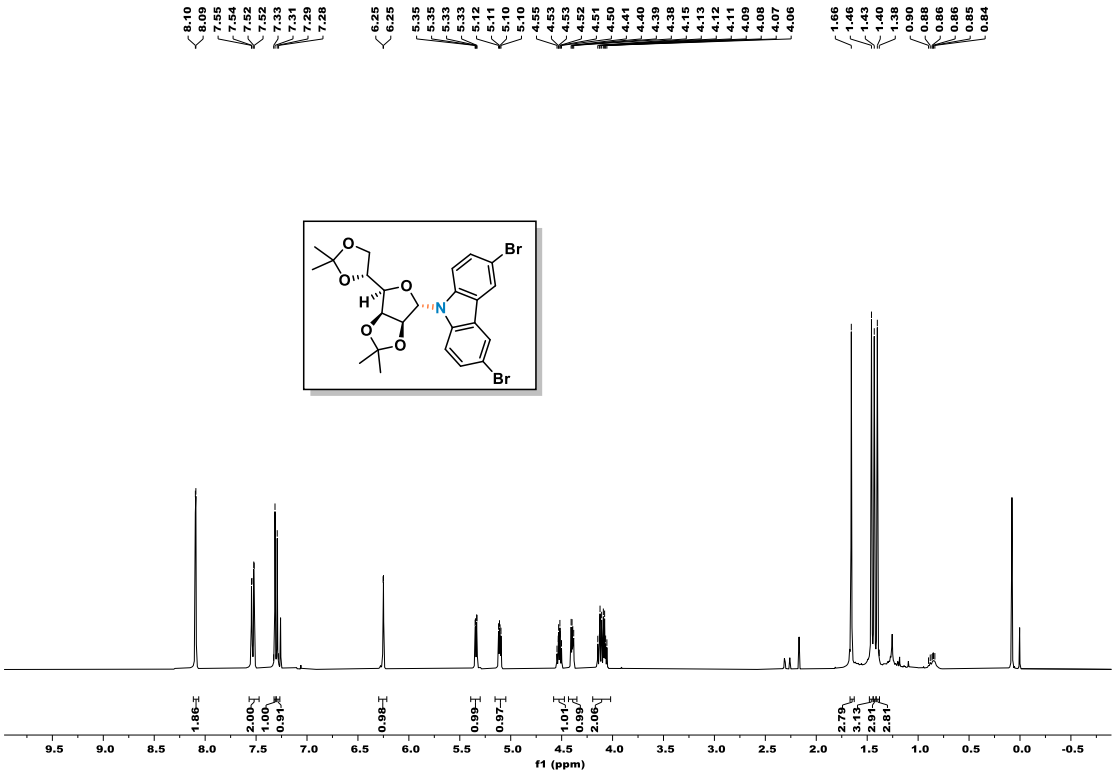
^{1}H NMR (400 MHz, $CDCl_3$) **(4e)**



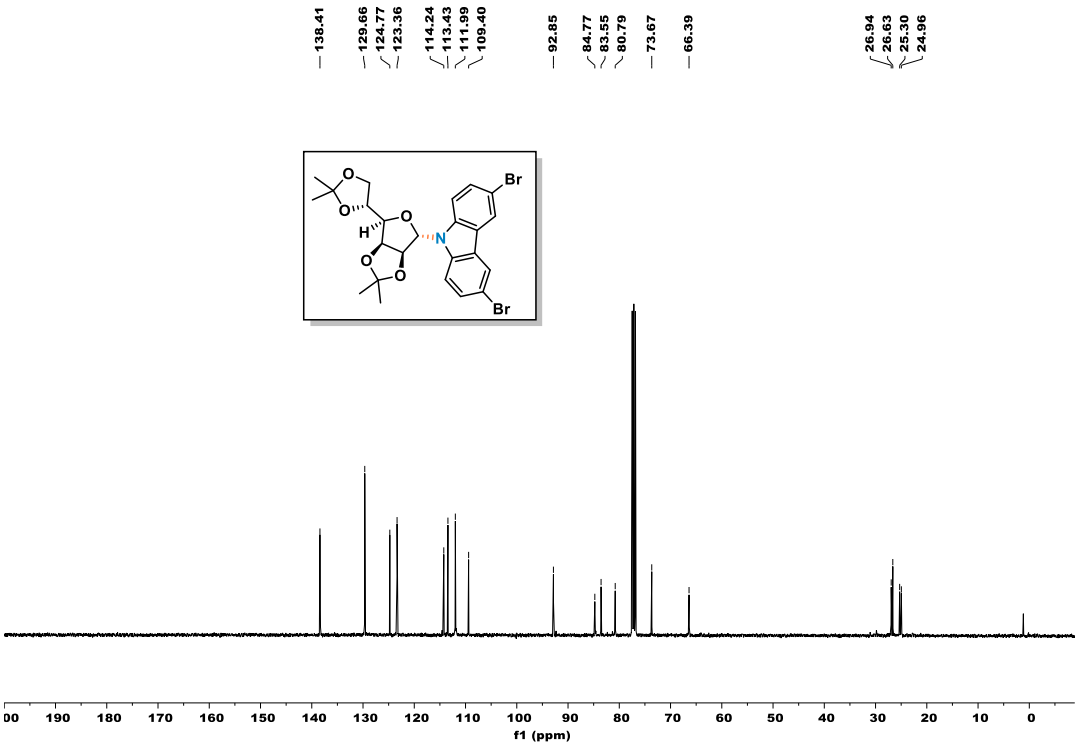
^{13}C NMR (101 MHz, $CDCl_3$) **(4e)**



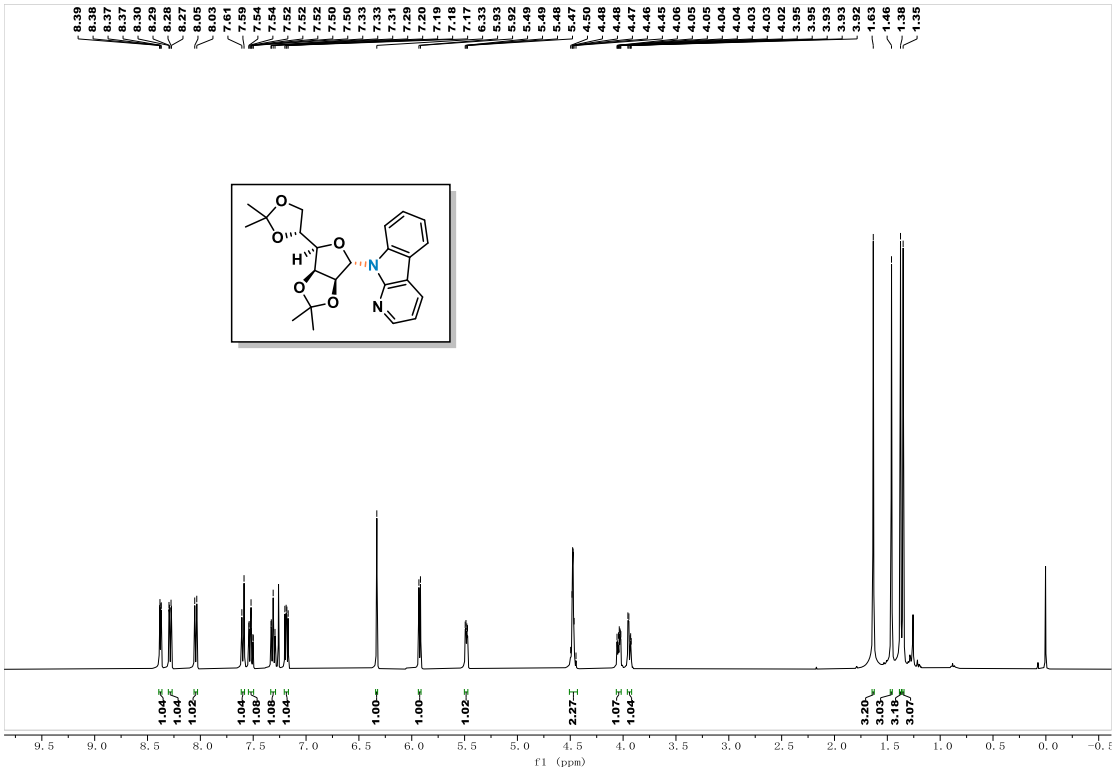
^{1}H NMR (400 MHz, $CDCl_3$) **(4f)**



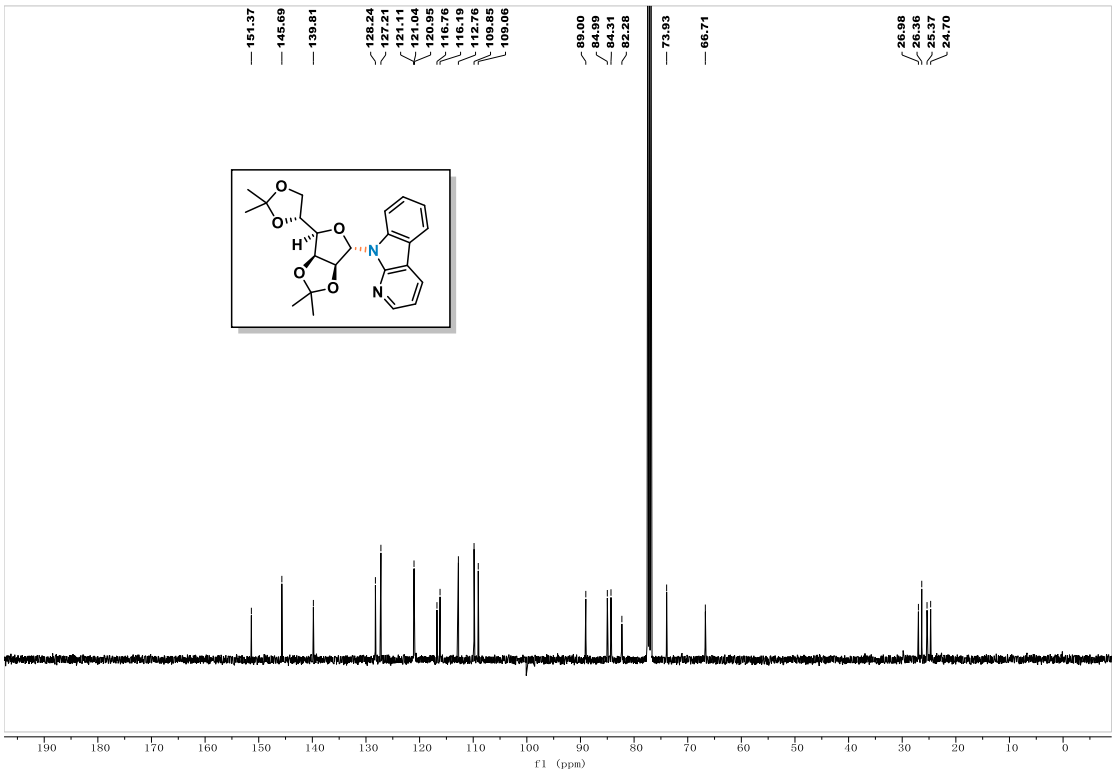
^{13}C NMR (101 MHz, $CDCl_3$) **(4f)**



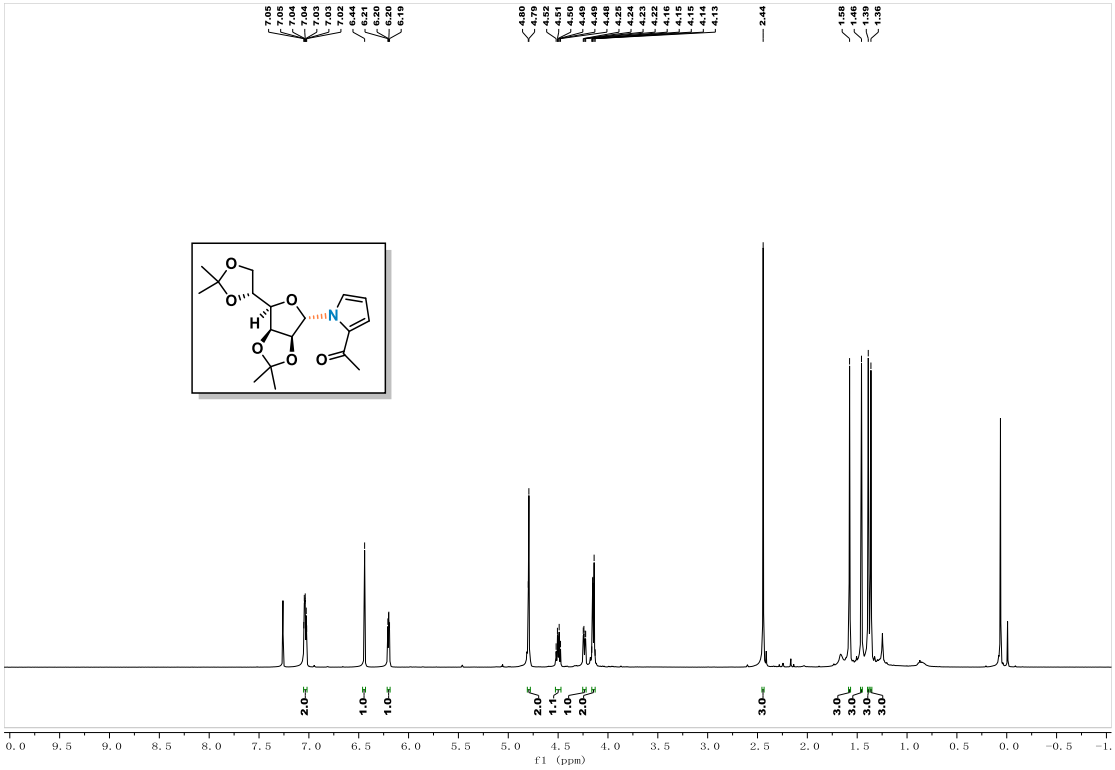
^{1}H NMR (400 MHz, $CDCl_3$) **(4g)**



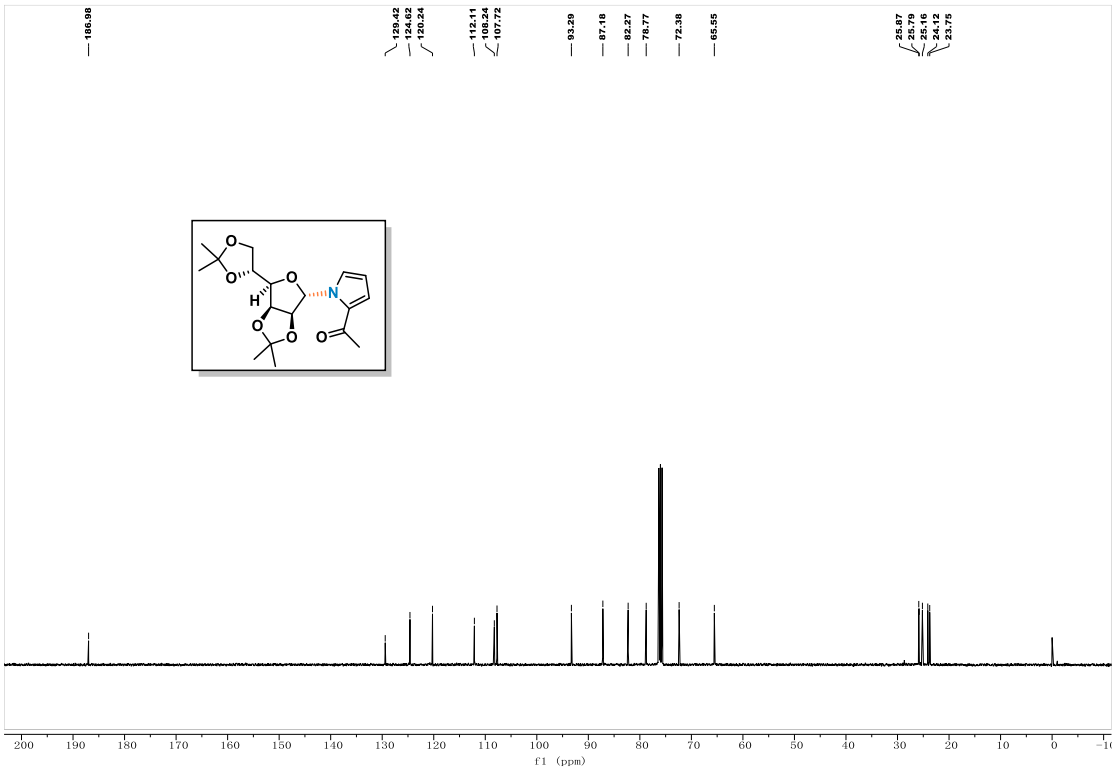
^{13}C NMR (101 MHz, $CDCl_3$) **(4g)**



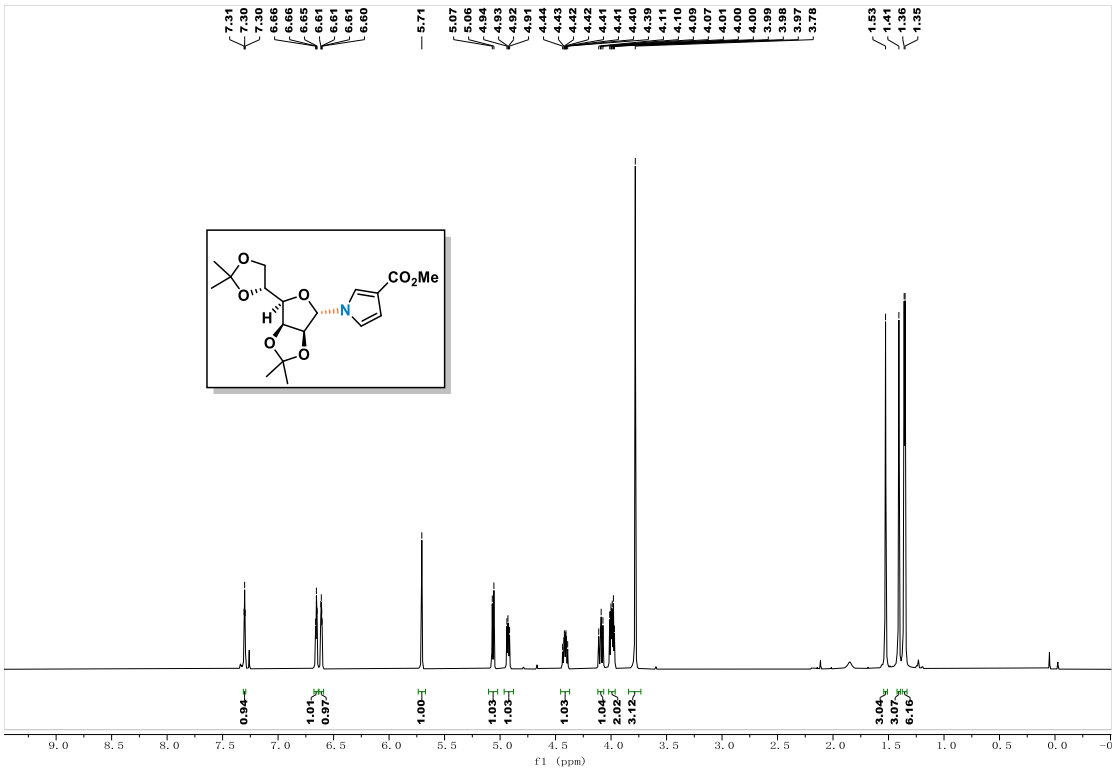
^{1}H NMR (400 MHz, $CDCl_3$) **(4h)**



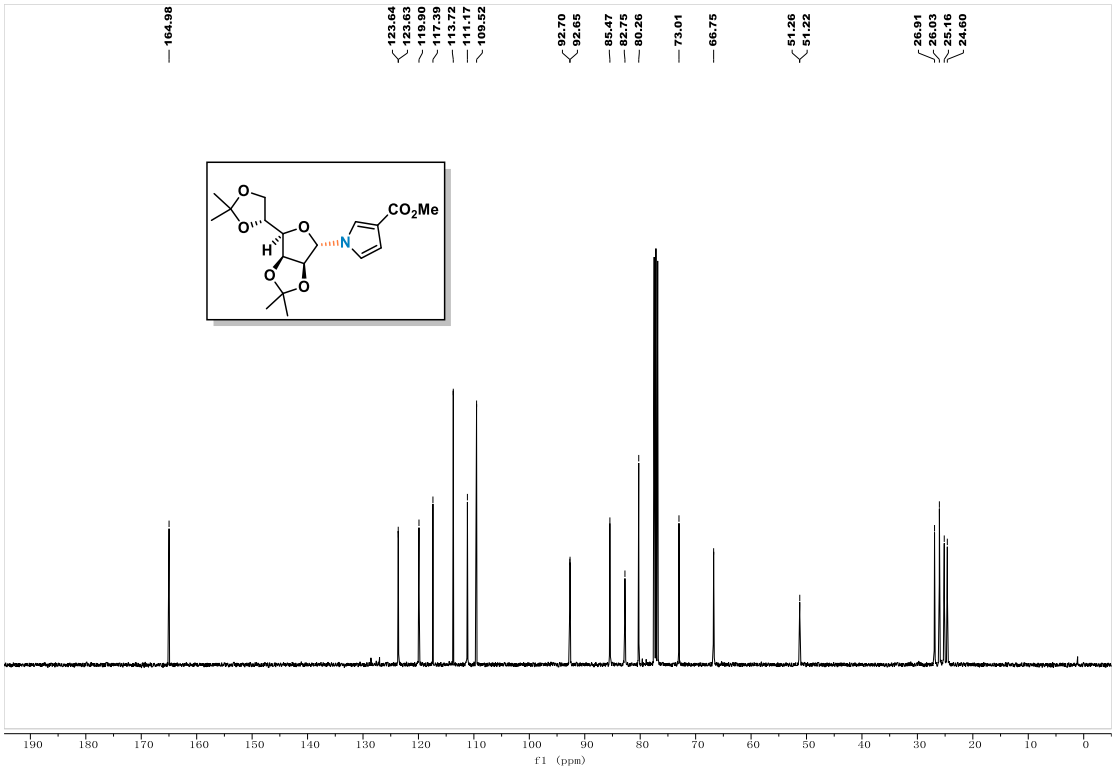
^{13}C NMR (101 MHz, $CDCl_3$) **(4h)**



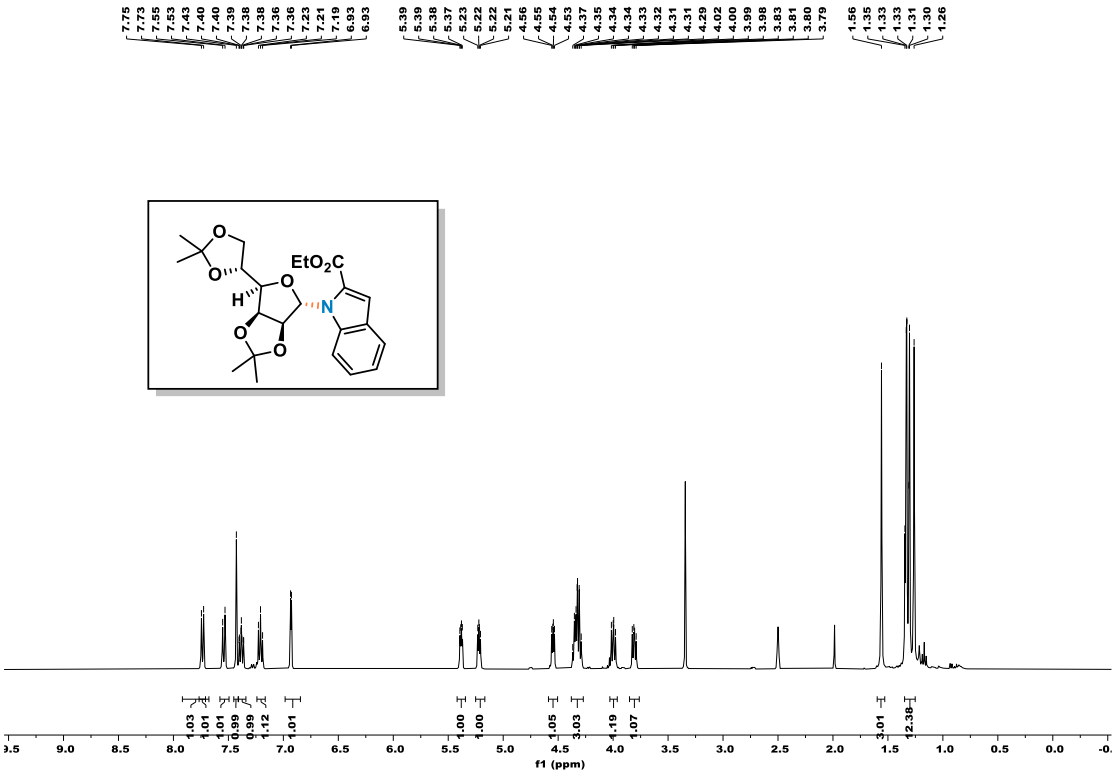
^{1}H NMR (400 MHz, $CDCl_3$) **(4i)**



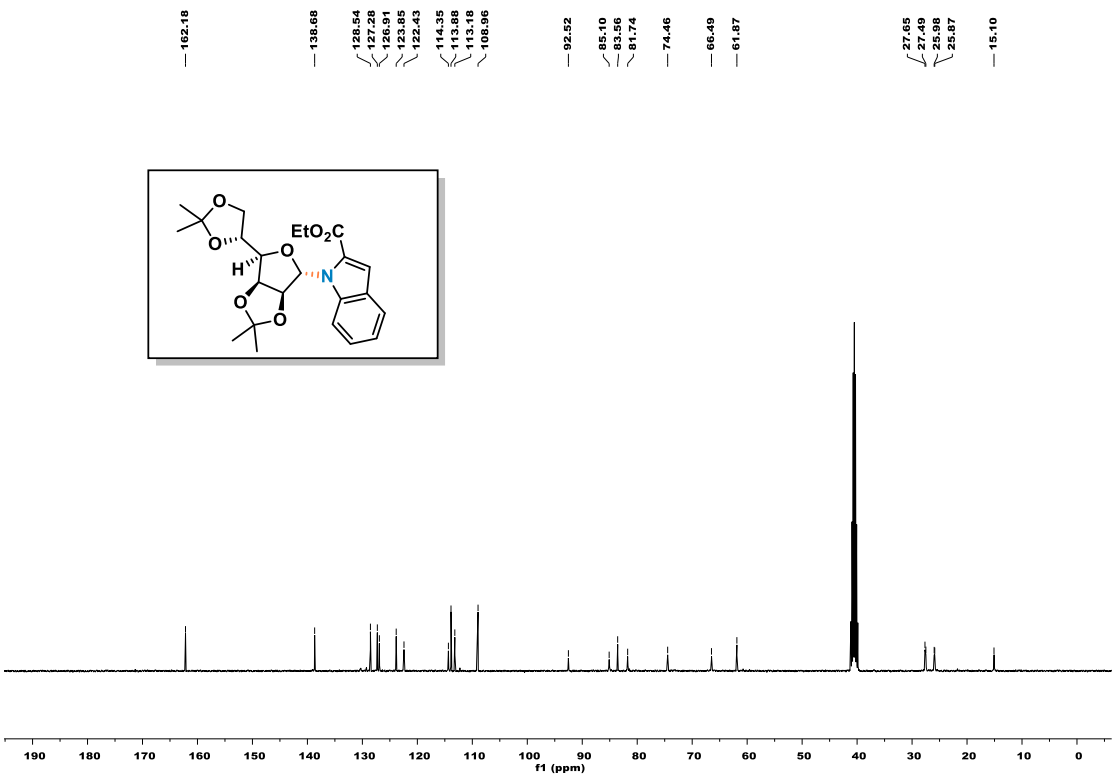
^{13}C NMR (101 MHz, $CDCl_3$) **(4i)**



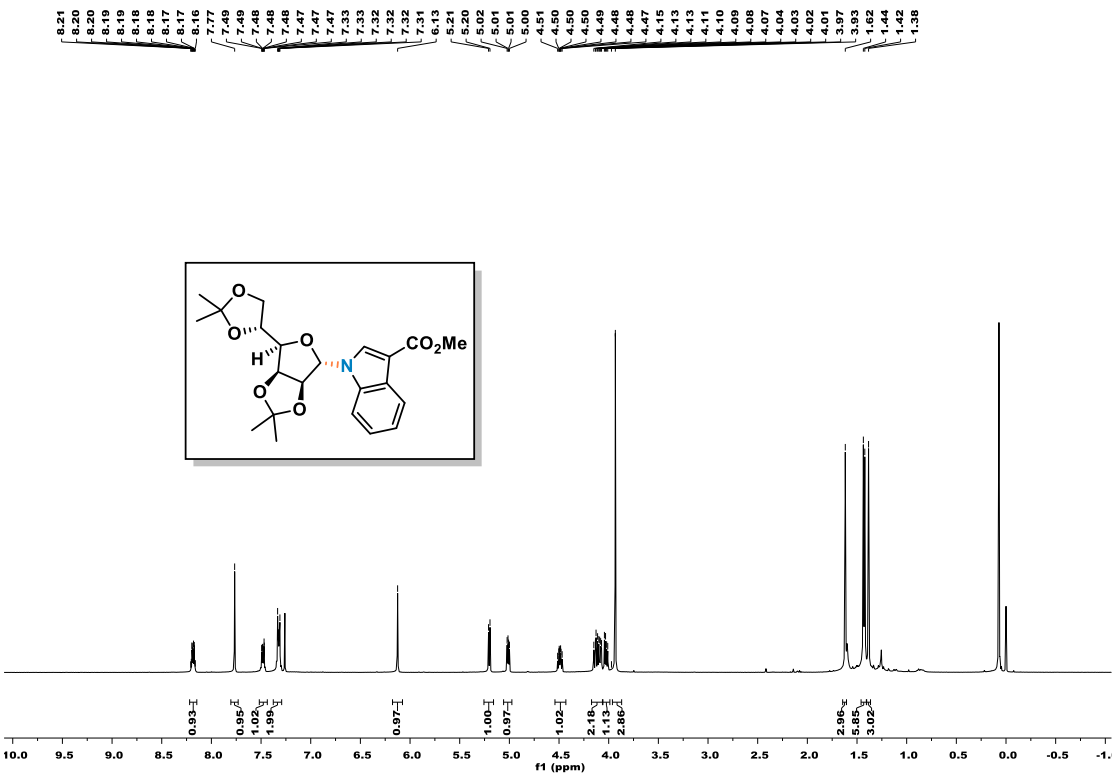
^{1}H NMR (400 MHz, DMSO-*d6*) **(5a)**



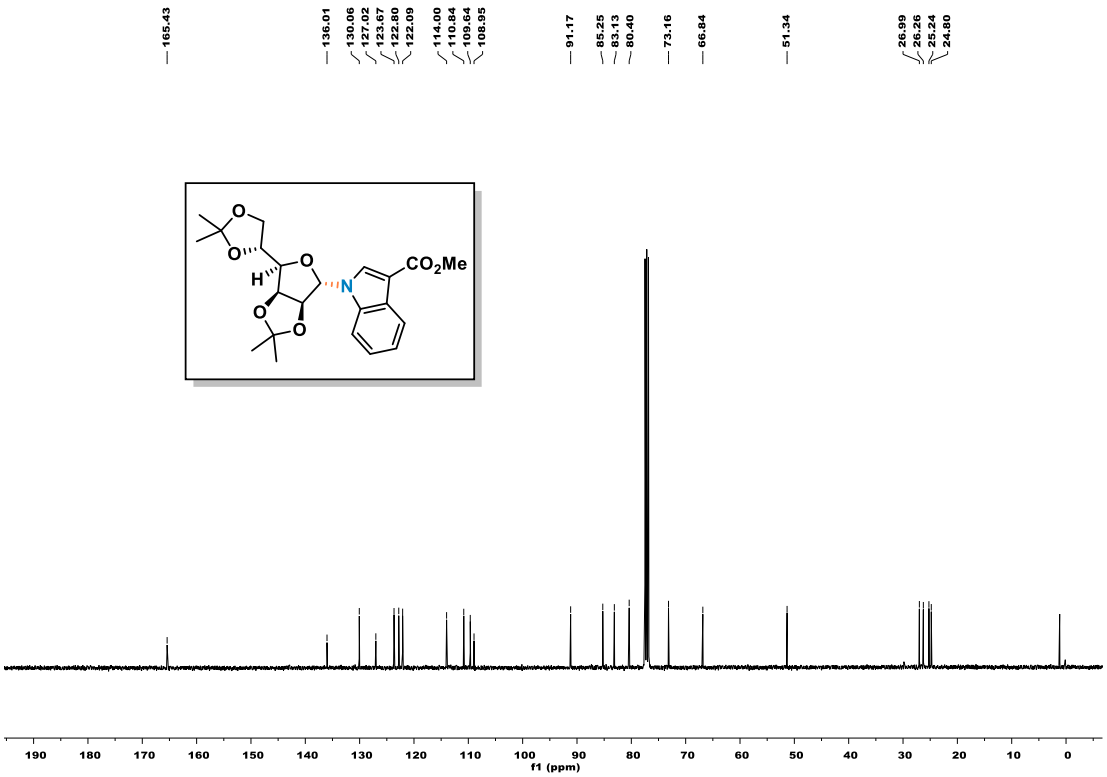
^{13}C NMR (101 MHz, DMSO-*d6*) **(5a)**



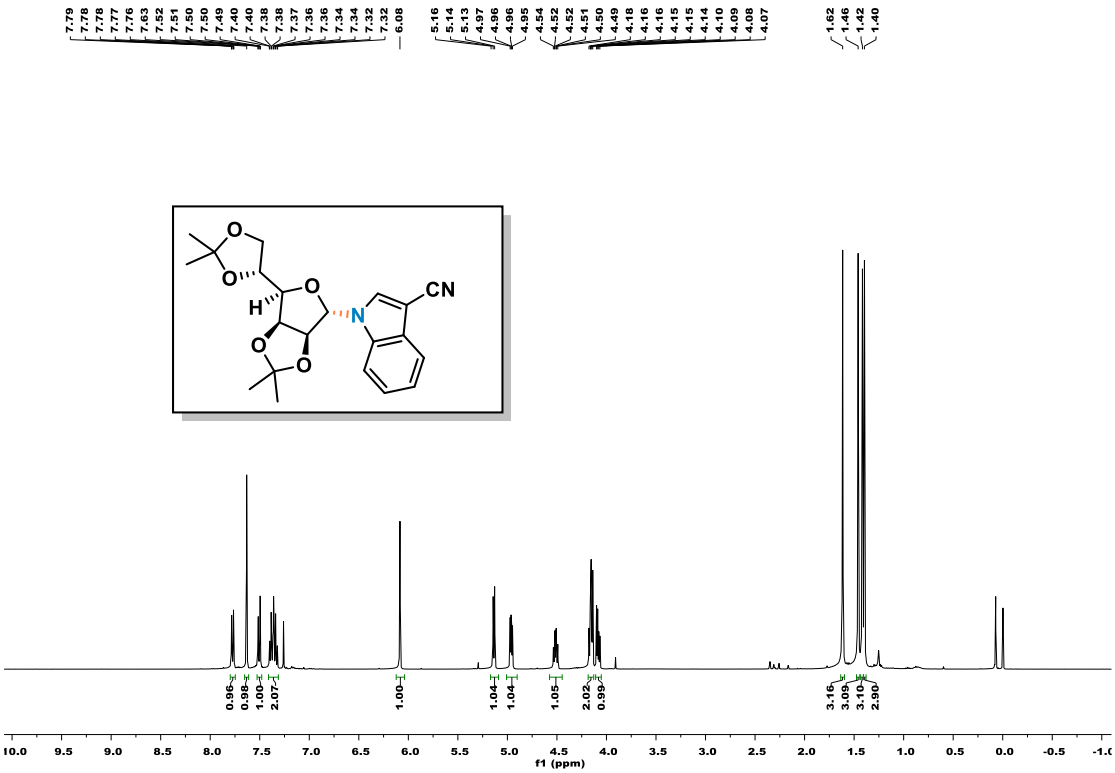
^{1}H NMR (400 MHz, $CDCl_3$) **(5b)**



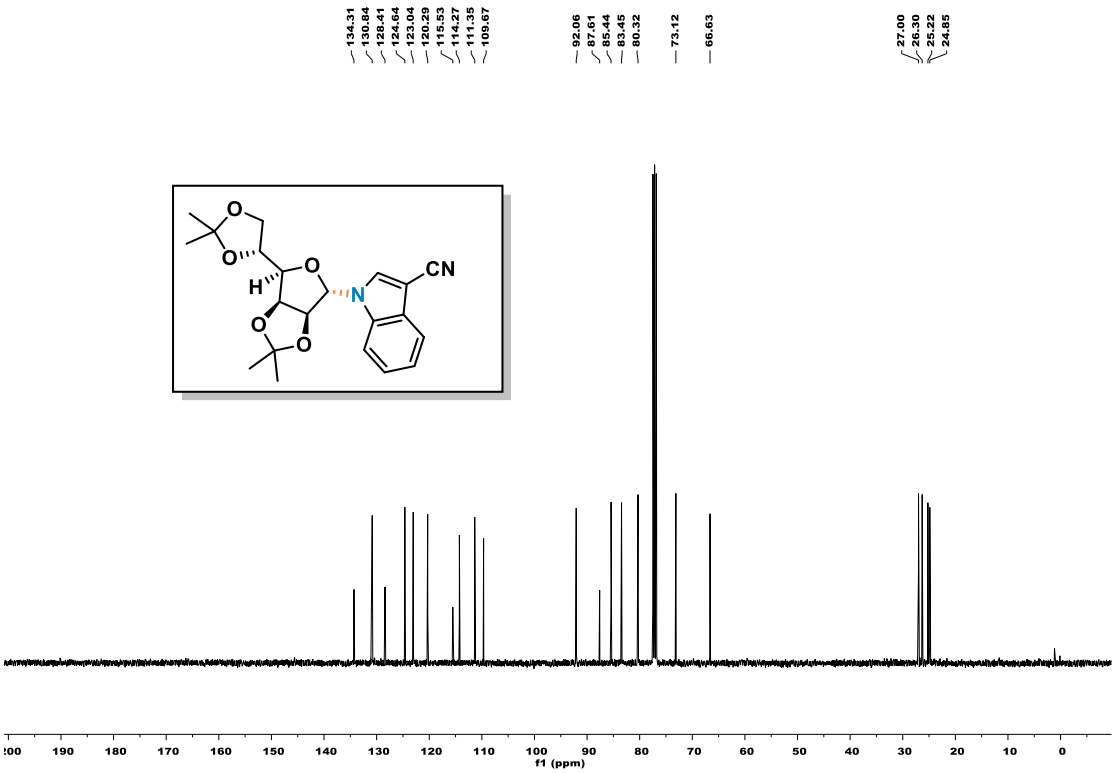
^{13}C NMR (101 MHz, $CDCl_3$) **(5b)**



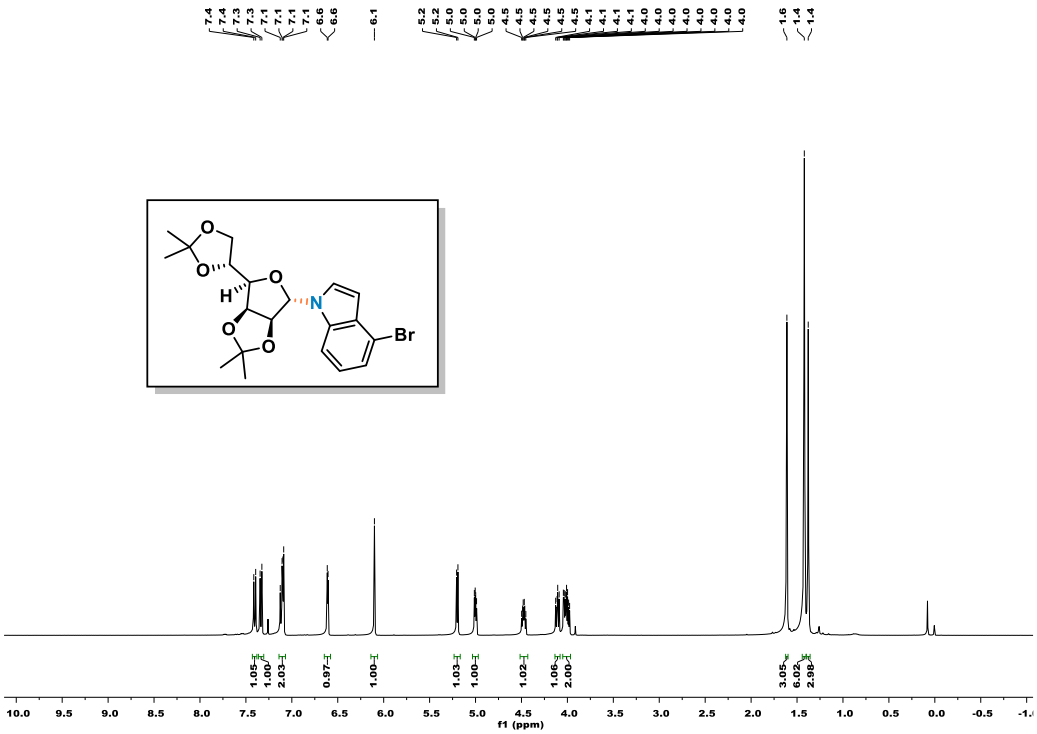
^{1}H NMR (400 MHz, $CDCl_3$) **(5c)**



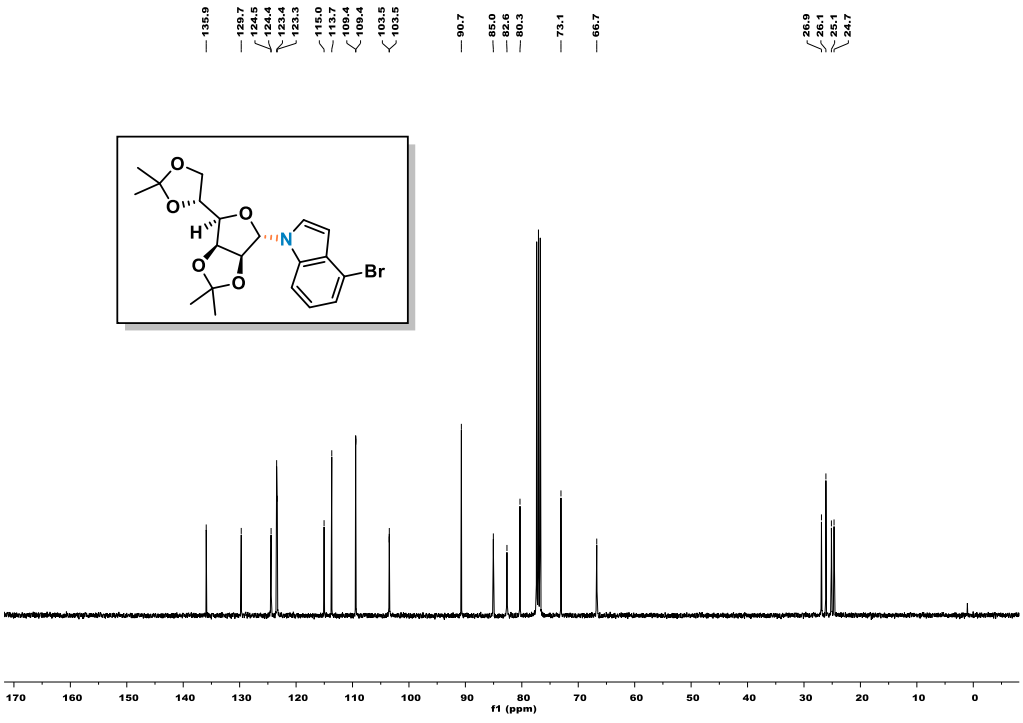
^{13}C NMR (101 MHz, $CDCl_3$) **(5c)**



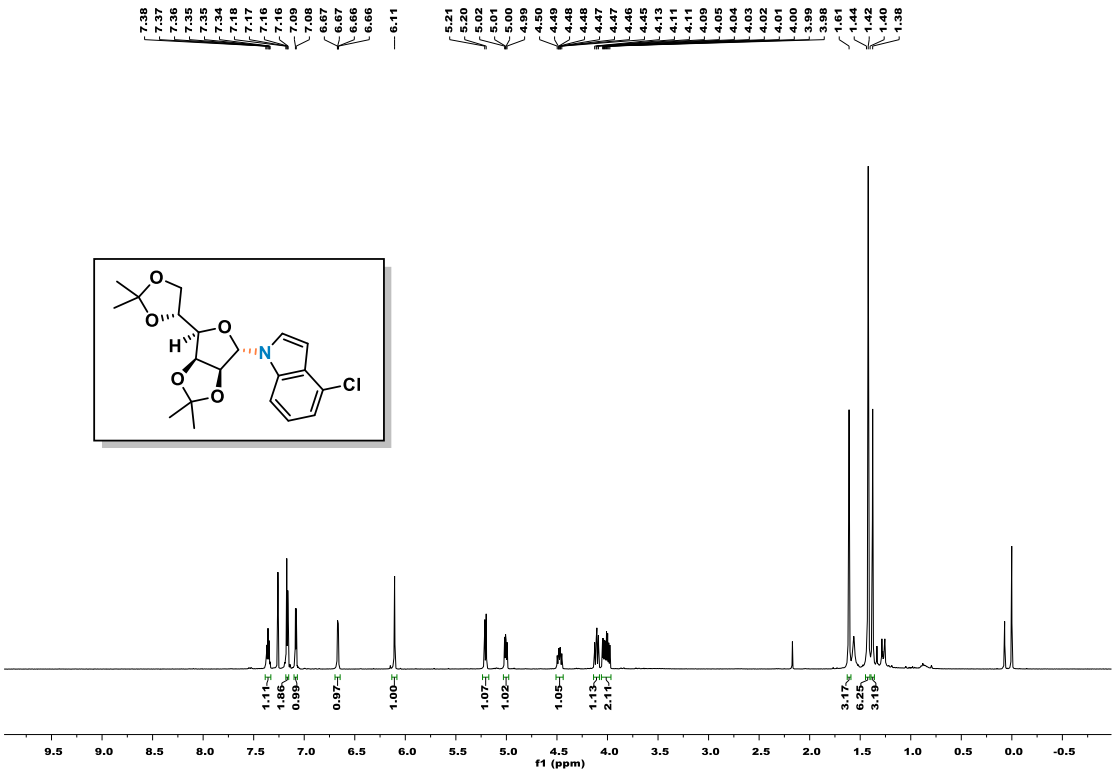
^{1}H NMR (400 MHz, $CDCl_3$) **(5d)**



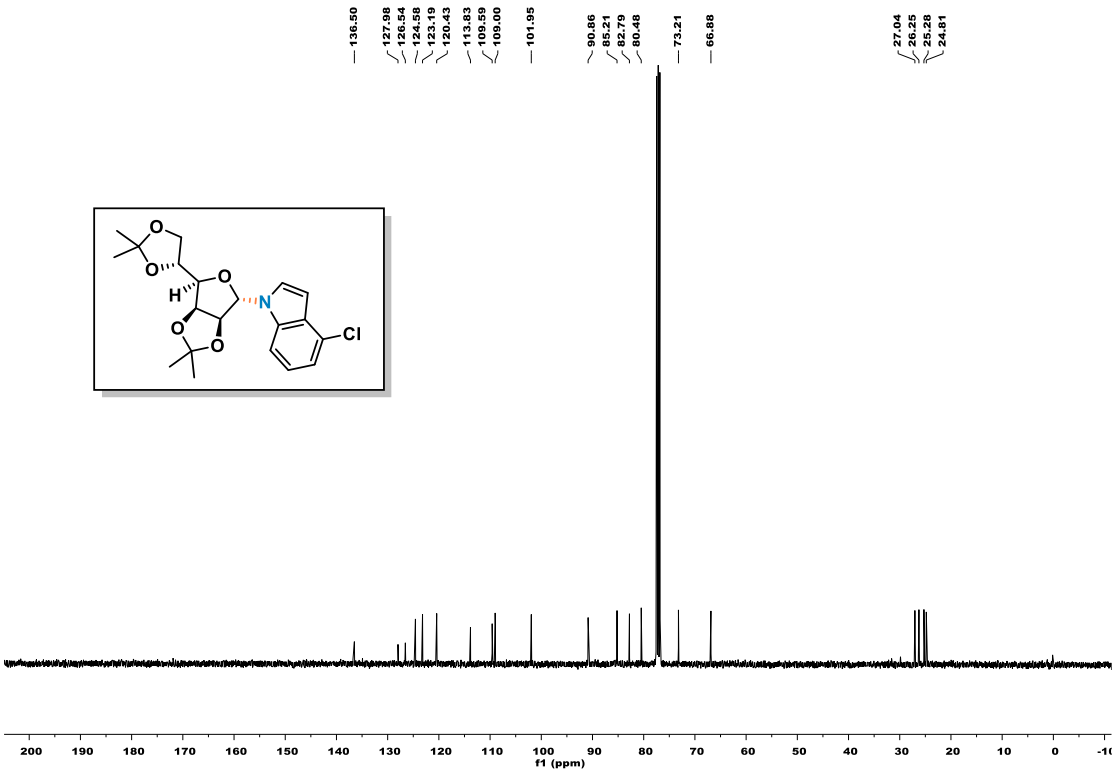
^{13}C NMR (101 MHz, $CDCl_3$) **(5d)**



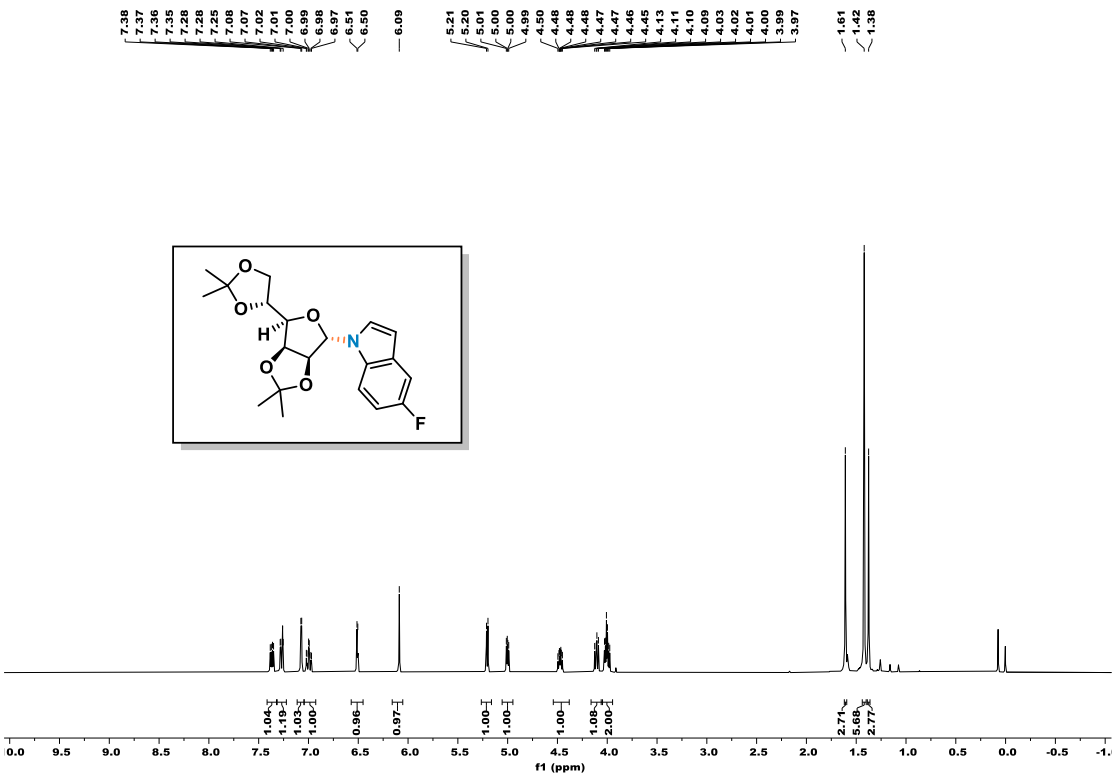
^{1}H NMR (400 MHz, $CDCl_3$) **(5e)**



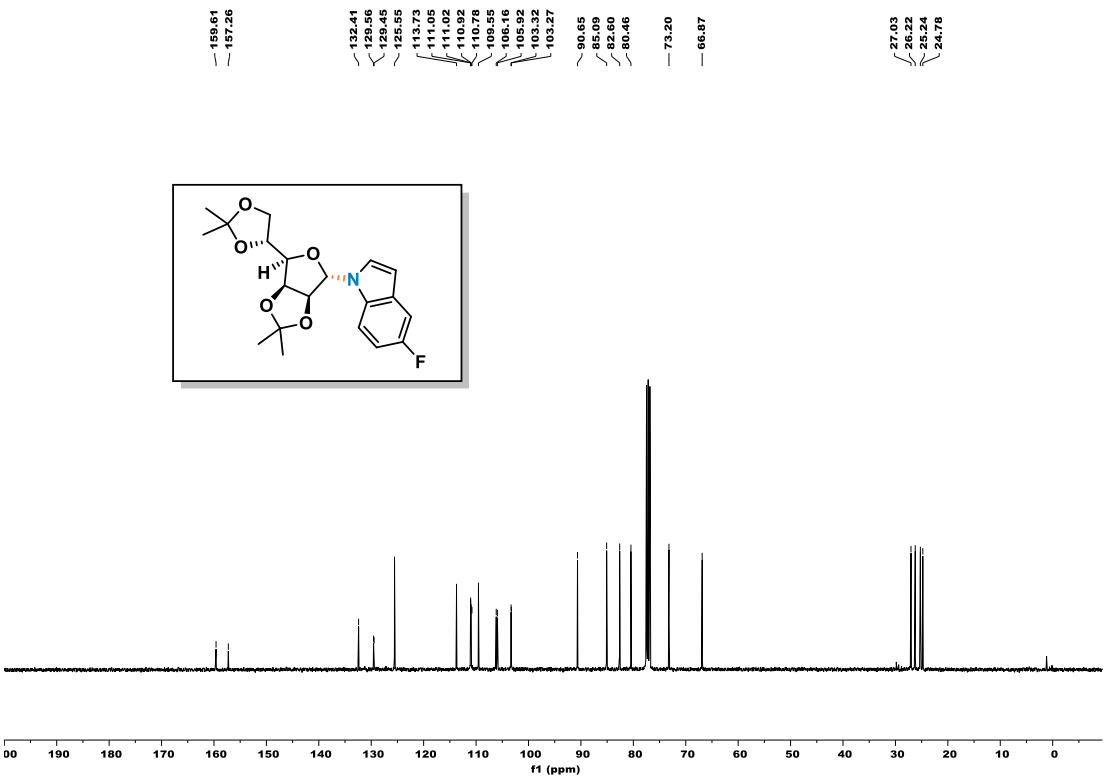
^{13}C NMR (101 MHz, $CDCl_3$) **(5e)**



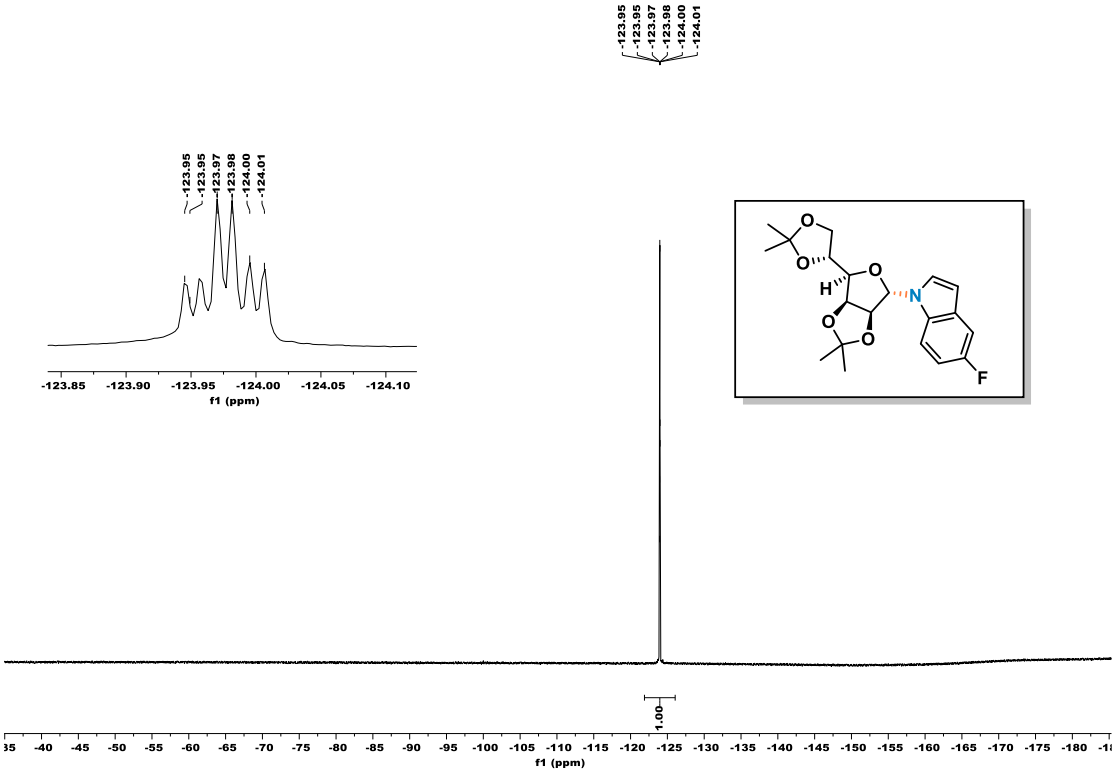
^{1}H NMR (400 MHz, $CDCl_3$) **(5f)**



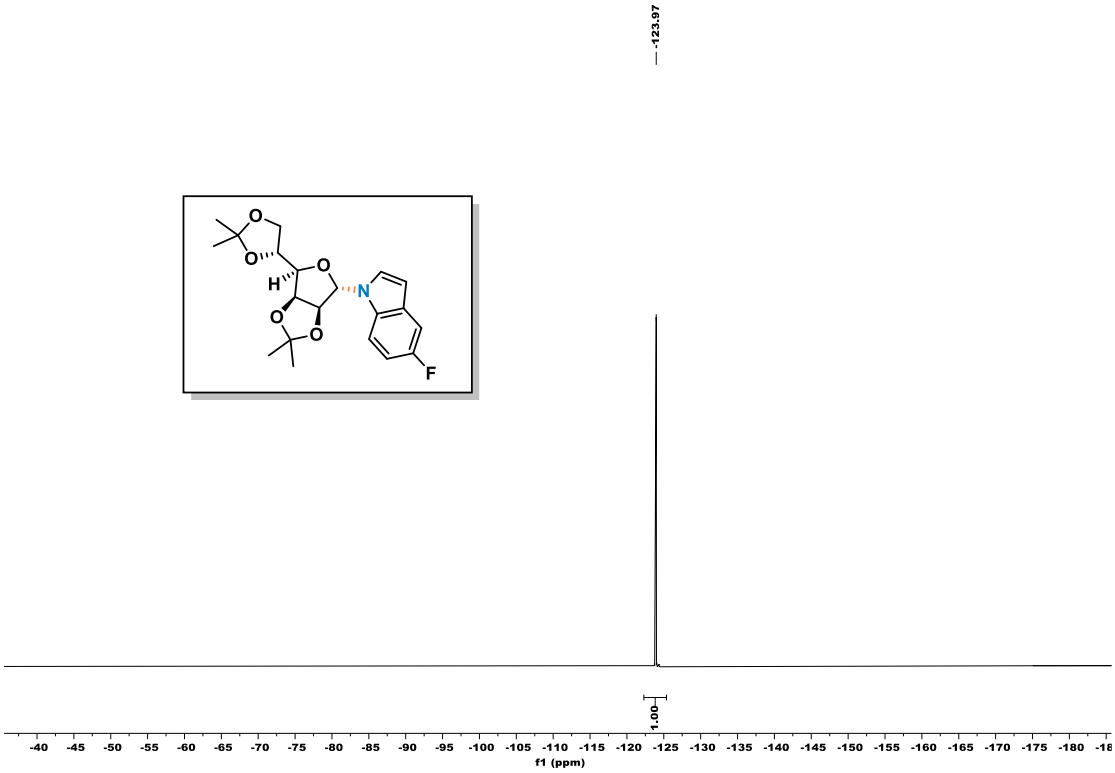
^{13}C NMR (101 MHz, $CDCl_3$) **(5f)**



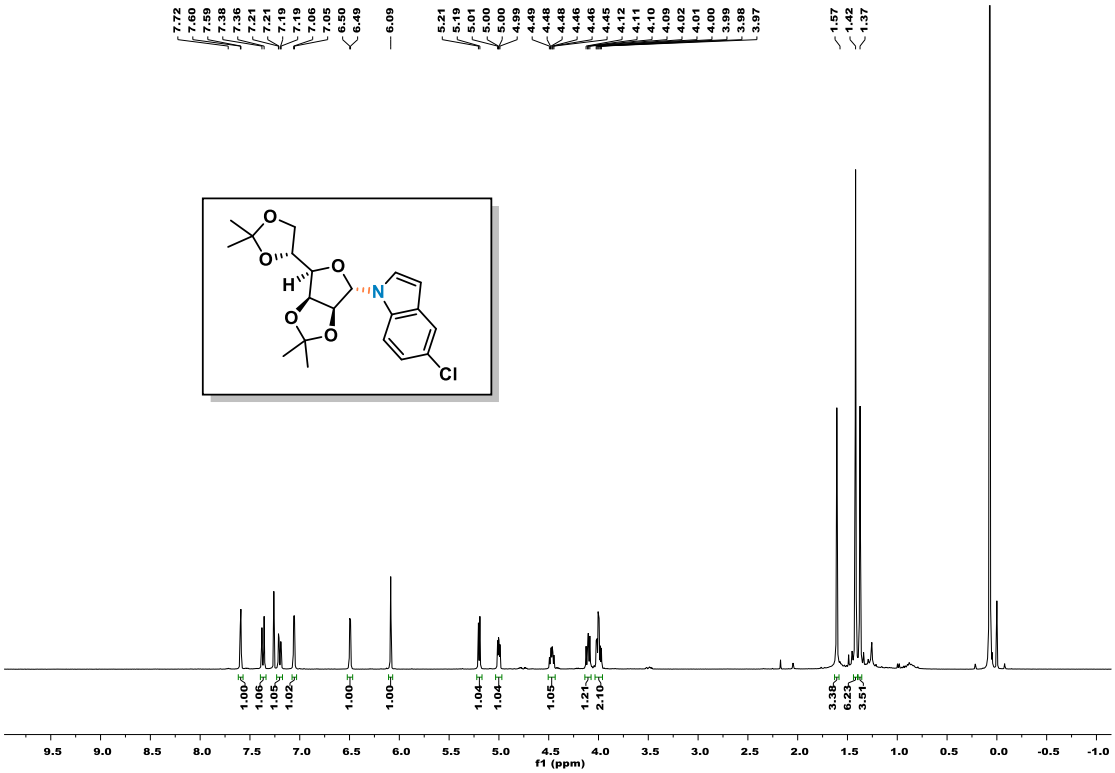
^{19}F NMR (376 MHz, $CDCl_3$) **(5f)**



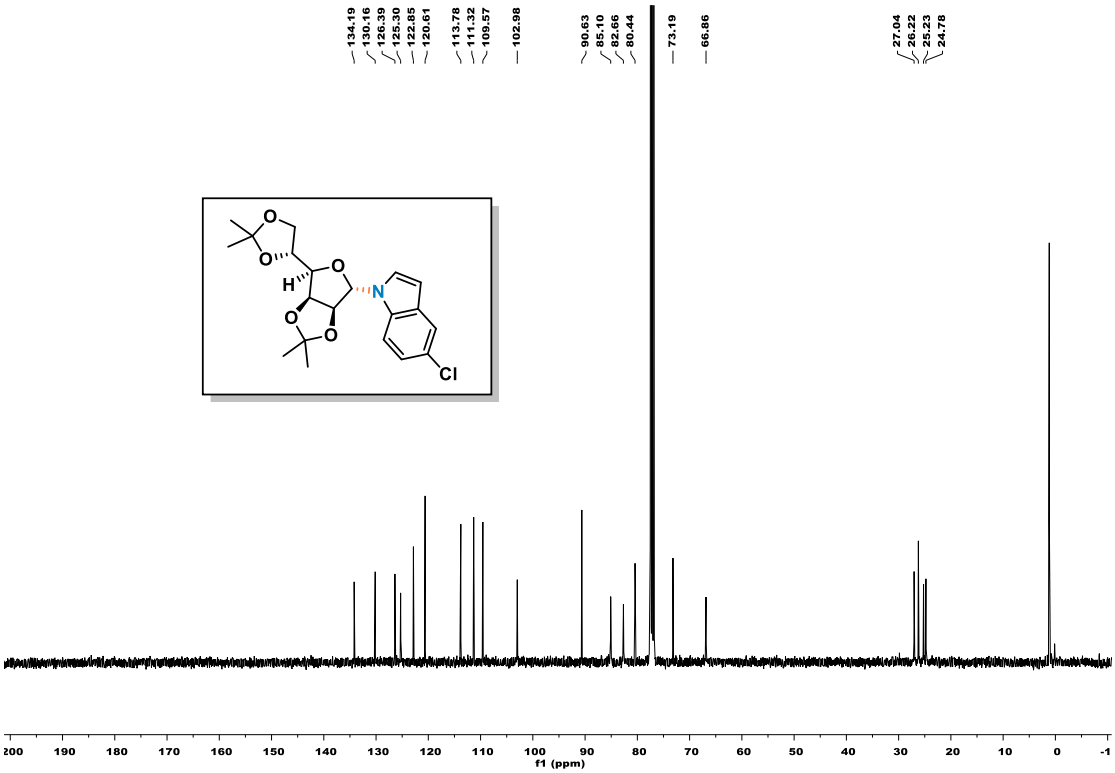
^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) **(5f)**



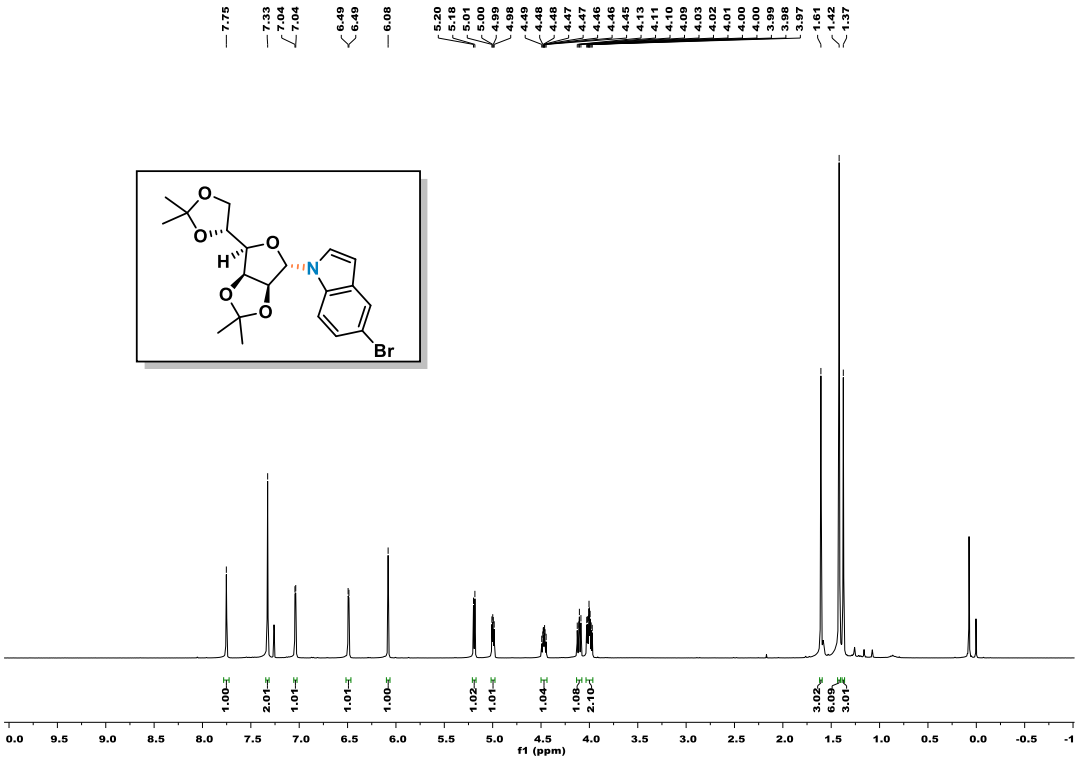
^{1}H NMR (400 MHz, $CDCl_3$) **(5g)**



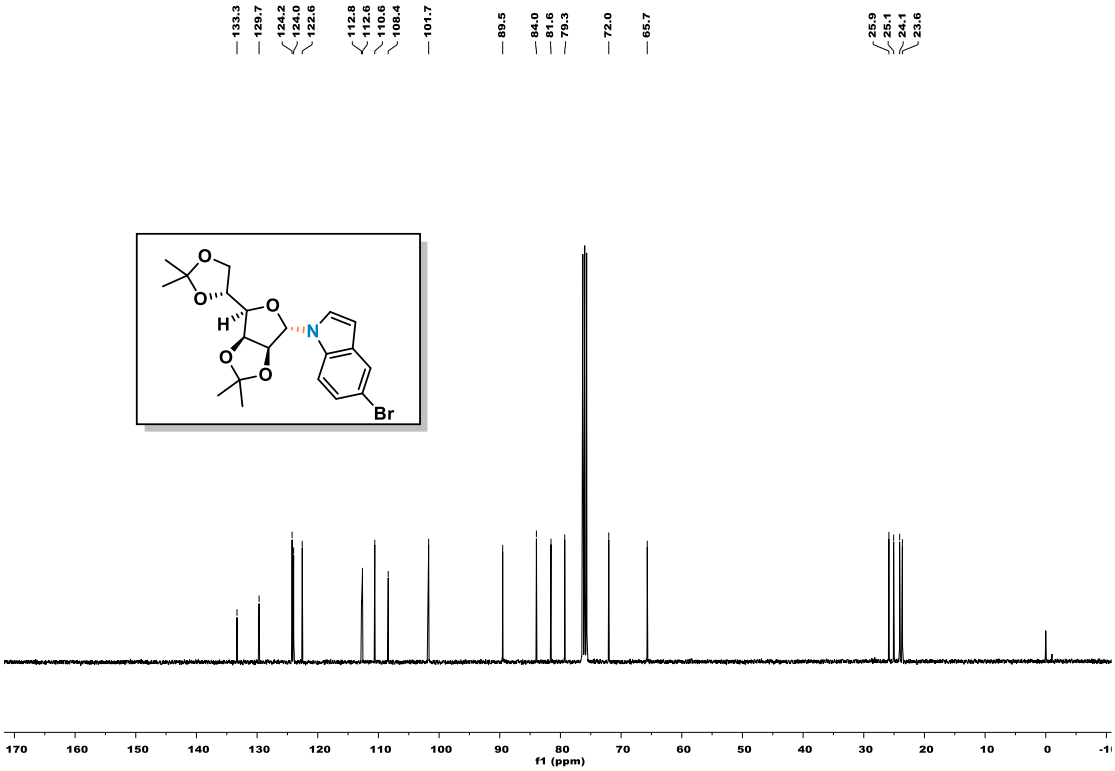
^{13}C NMR (101 MHz, $CDCl_3$) **(5g)**



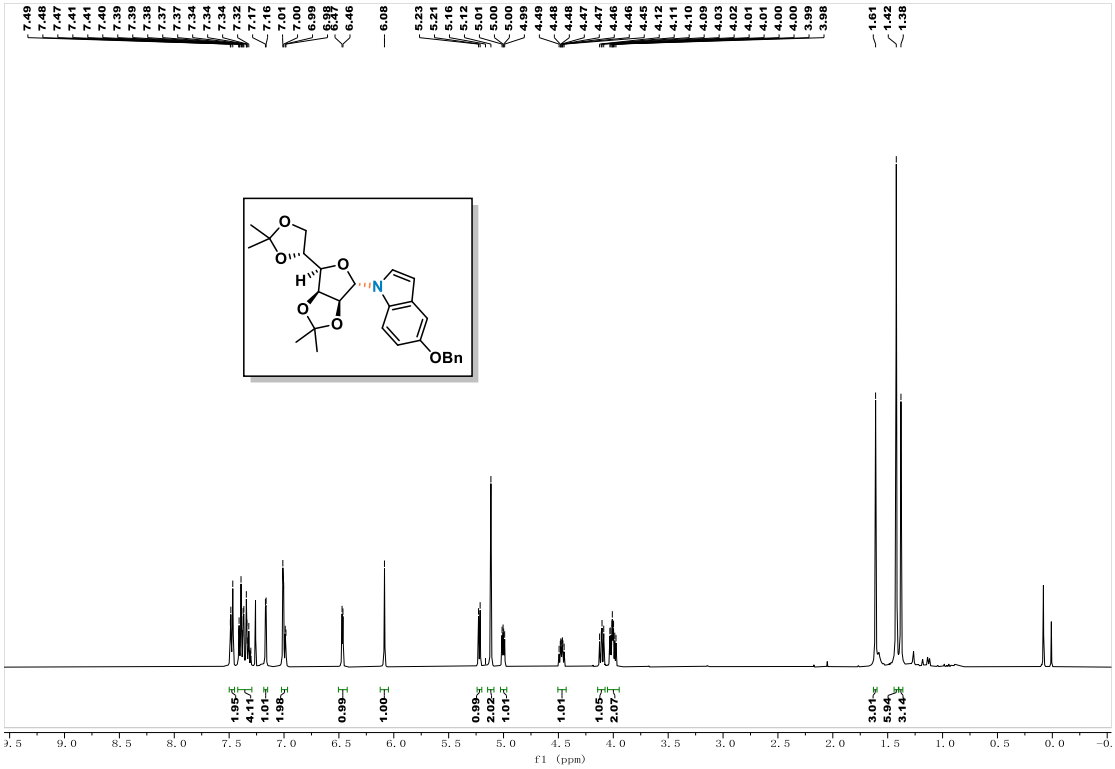
^{1}H NMR (400 MHz, $CDCl_3$) **(5h)**



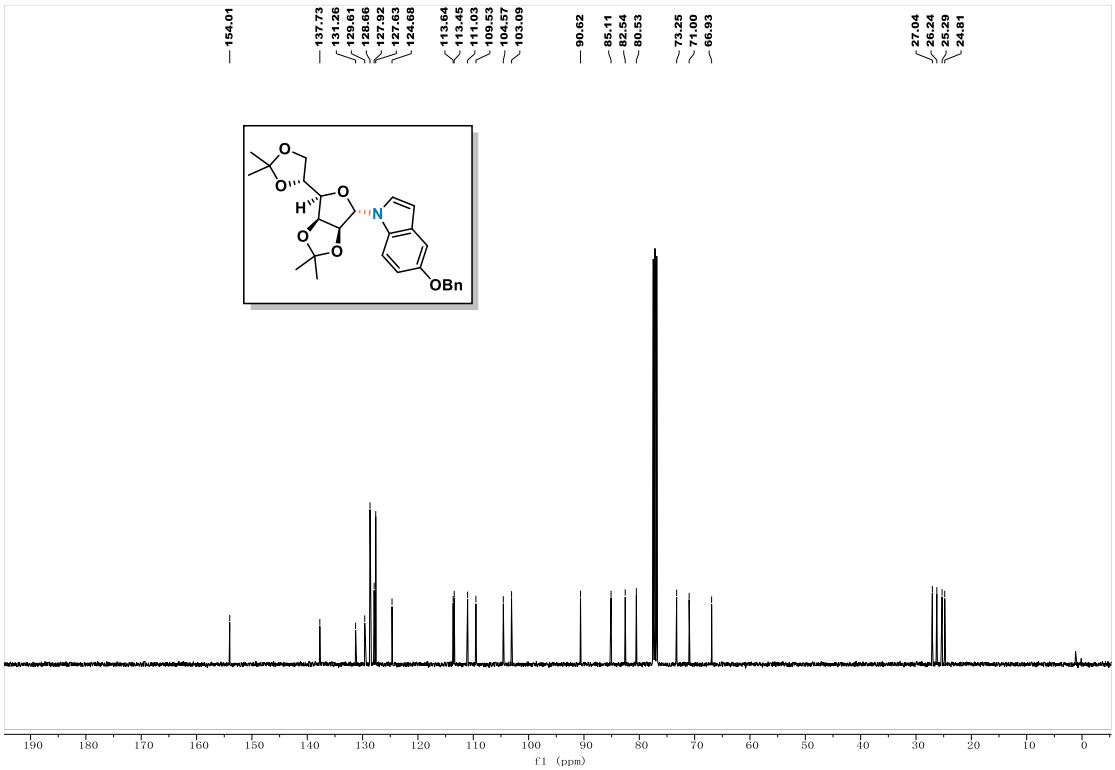
^{13}C NMR (101 MHz, $CDCl_3$) **(5h)**



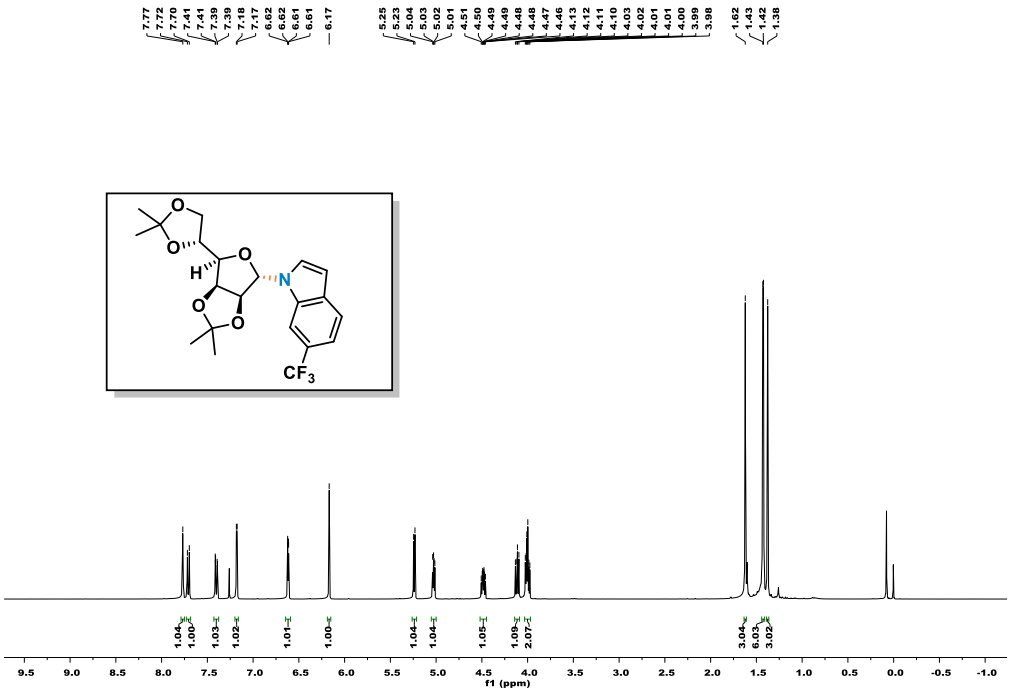
^{1}H NMR (400 MHz, $CDCl_3$) **(5i)**



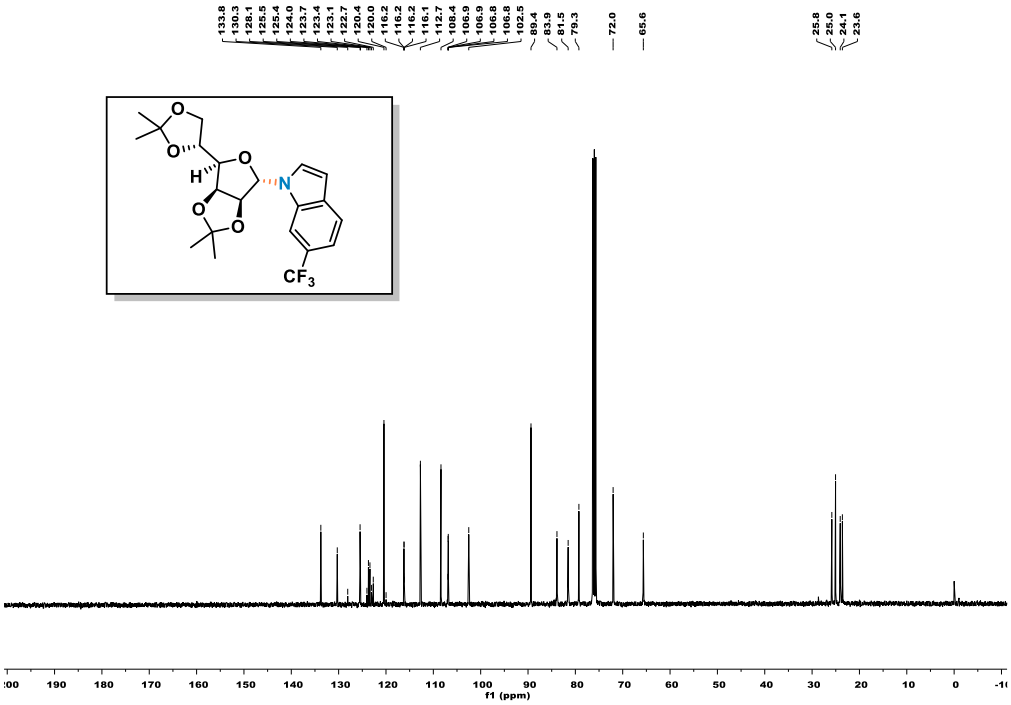
^{13}C NMR (101 MHz, $CDCl_3$) **(5i)**



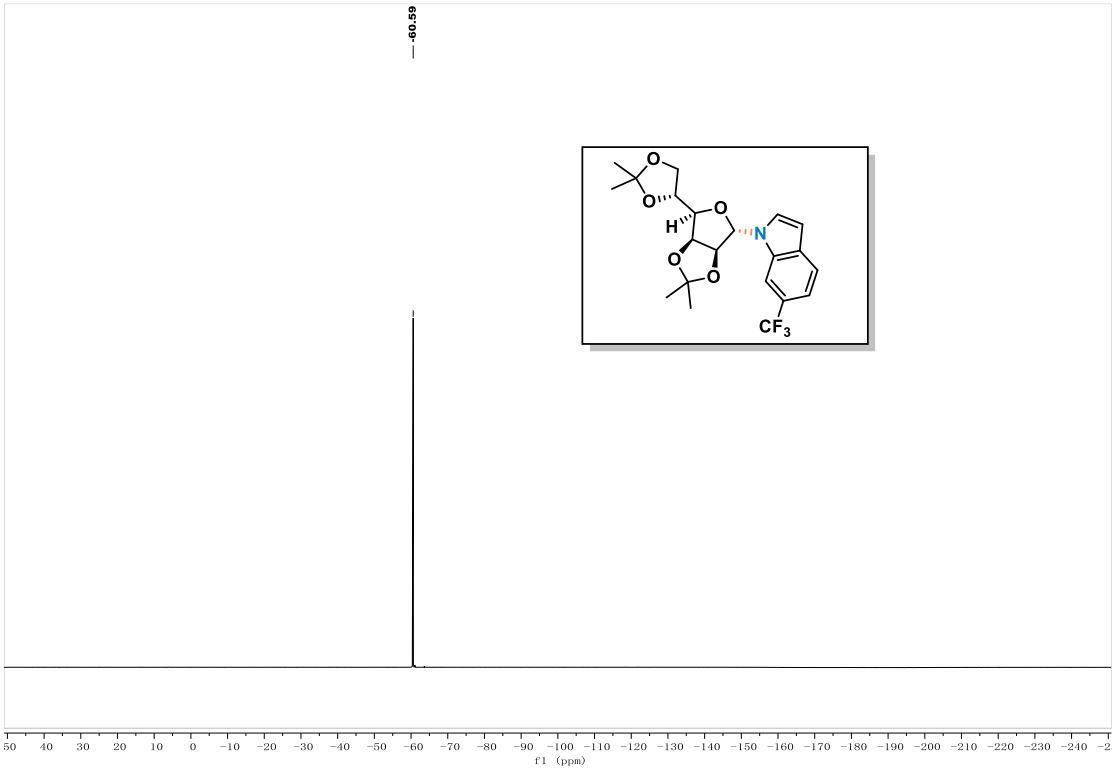
^{1}H NMR (400 MHz, $CDCl_3$) **(5j)**



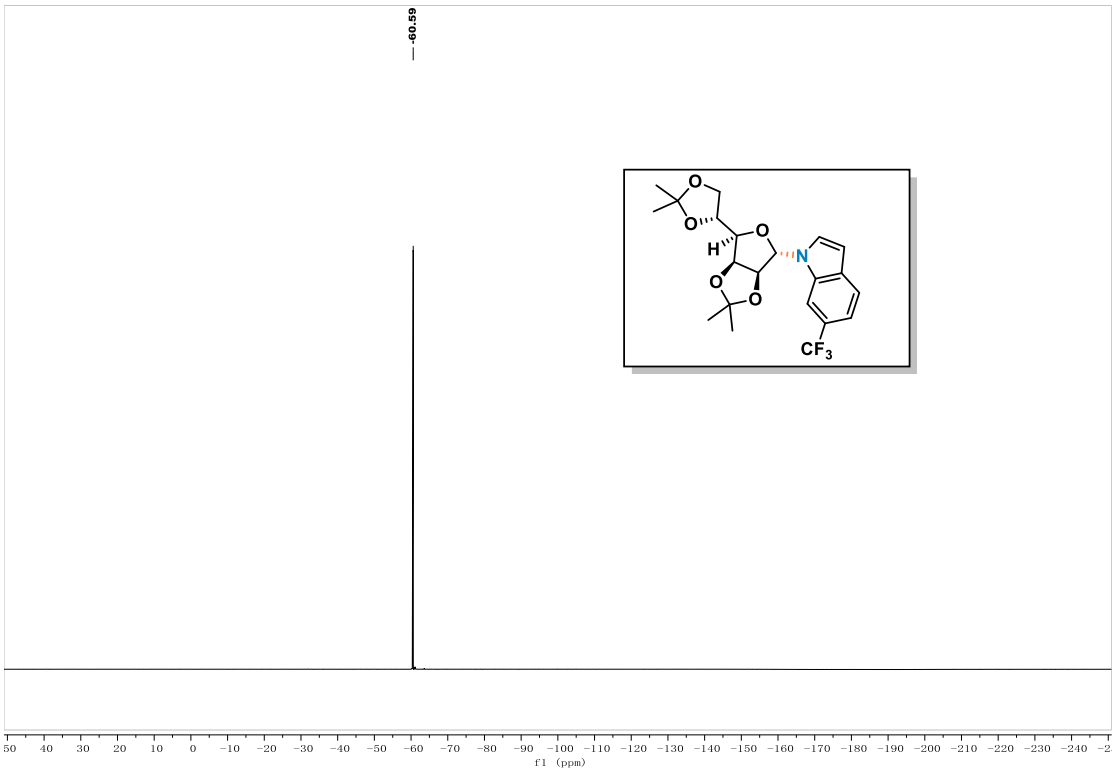
^{13}C NMR (101 MHz, $CDCl_3$) **(5j)**



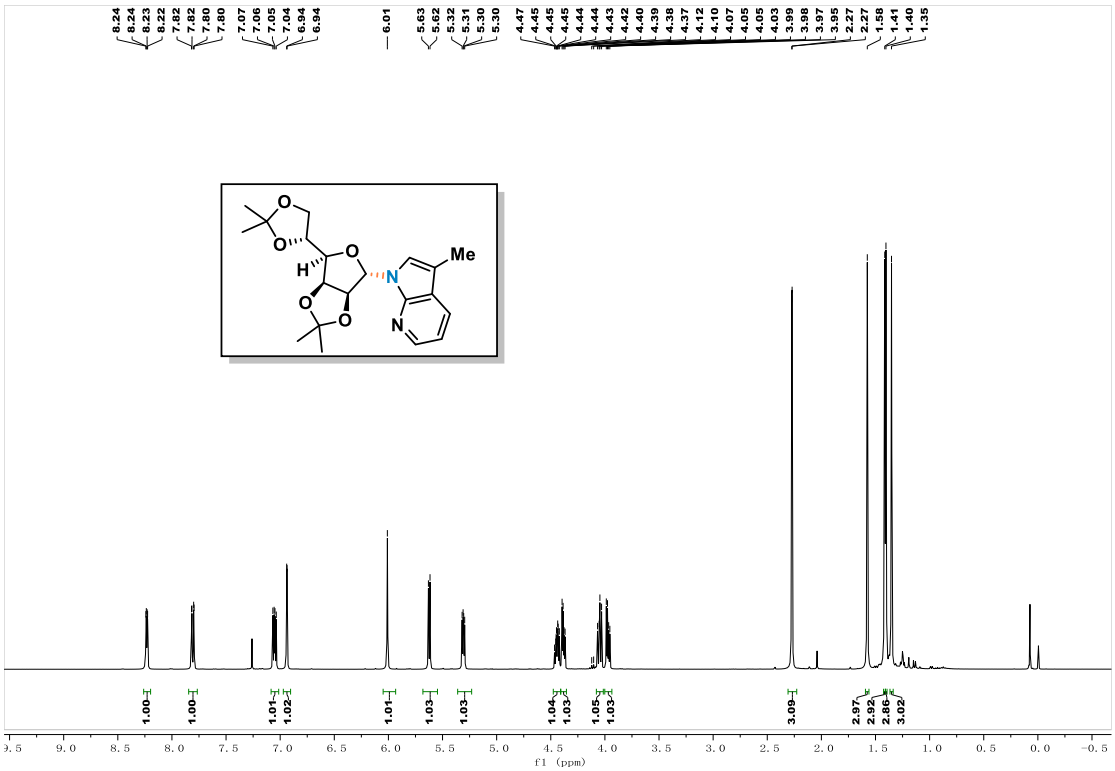
^{19}F NMR (376 MHz , $CDCl_3$) **(5j)**



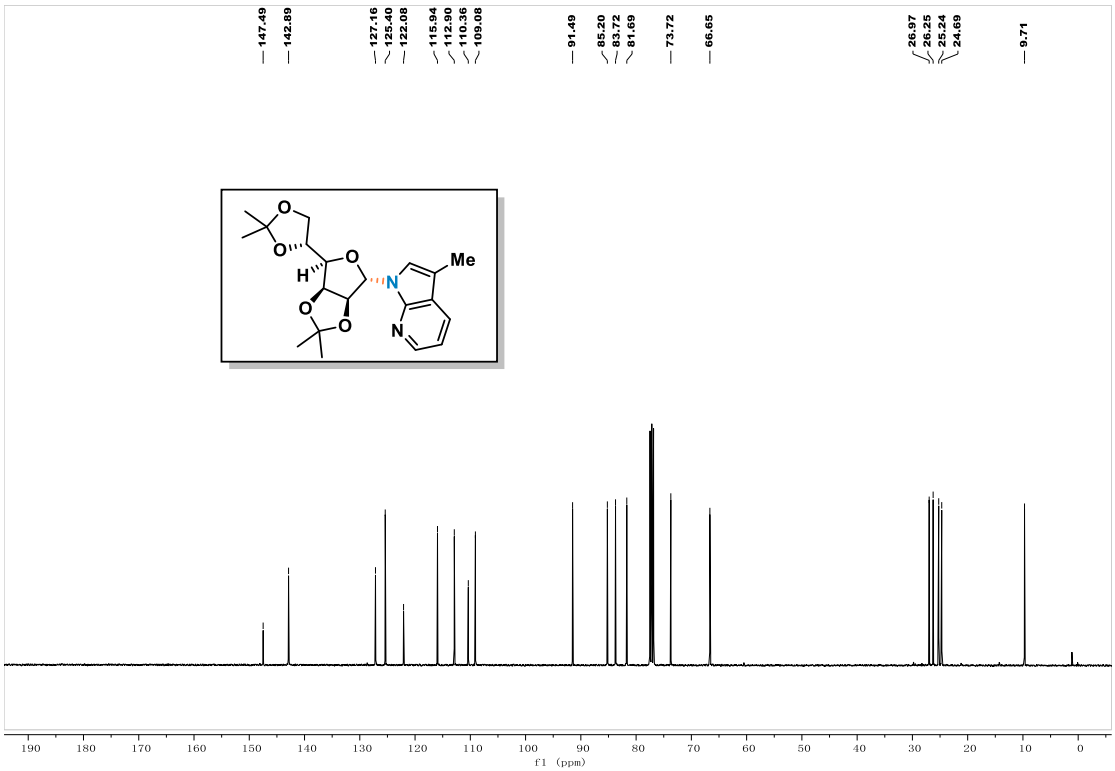
^{19}F {^{1}H} NMR (376 MHz , $CDCl_3$) **(5j)**



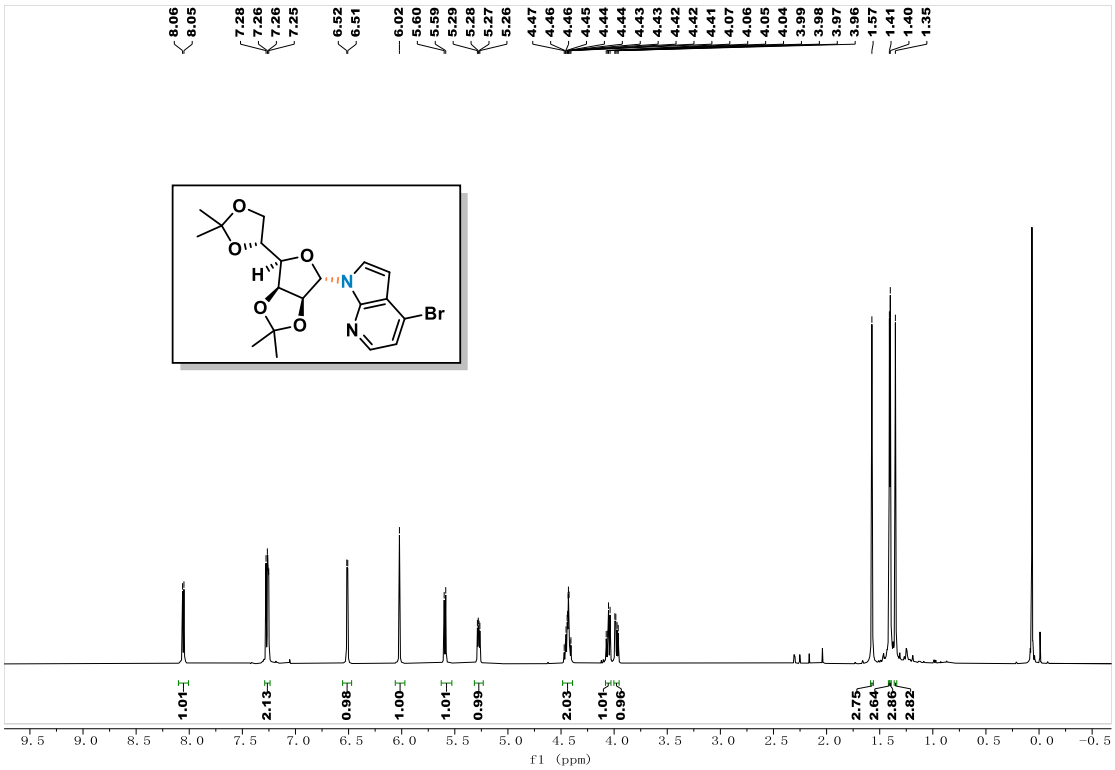
^{1}H NMR (400 MHz, $CDCl_3$) **(5k)**



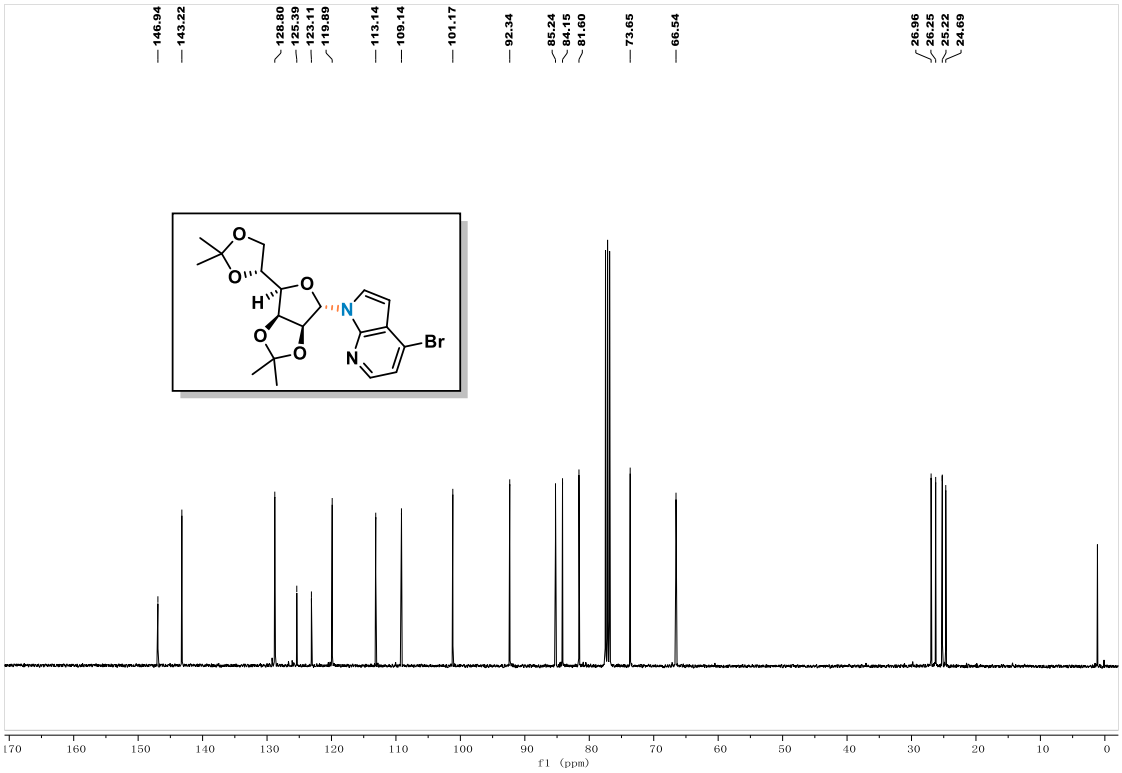
^{13}C NMR (101 MHz, $CDCl_3$) **(5k)**



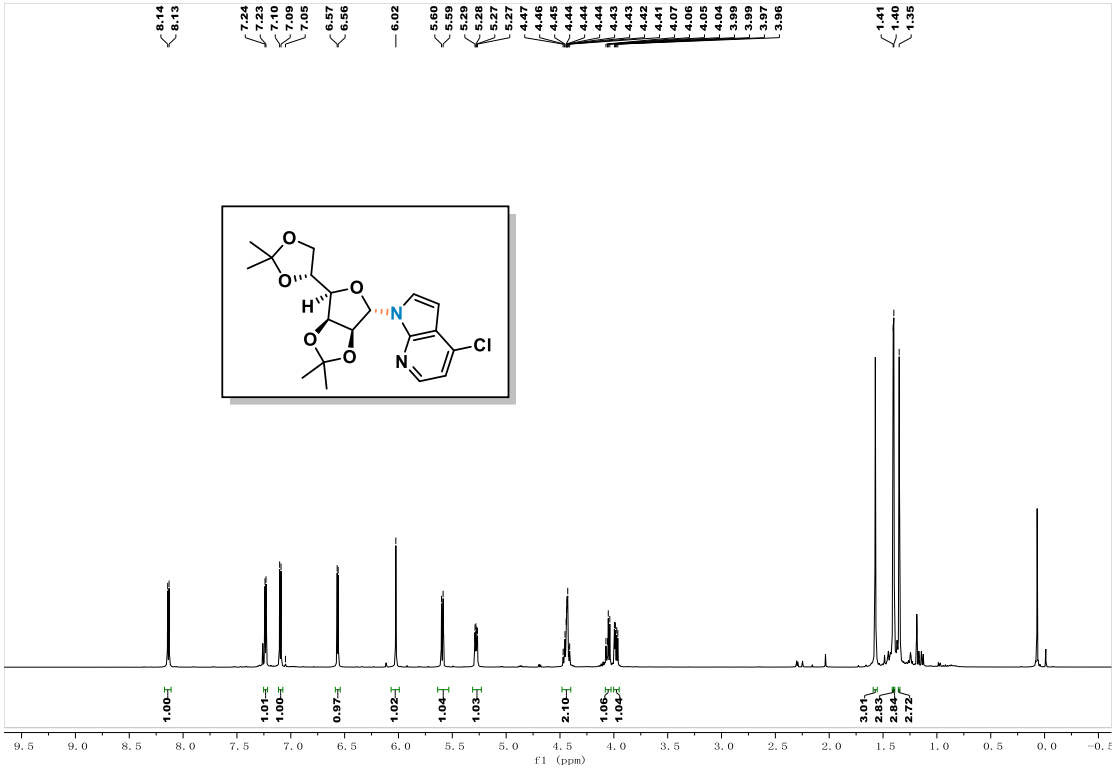
^{1}H NMR (400 MHz, $CDCl_3$) **(5l)**



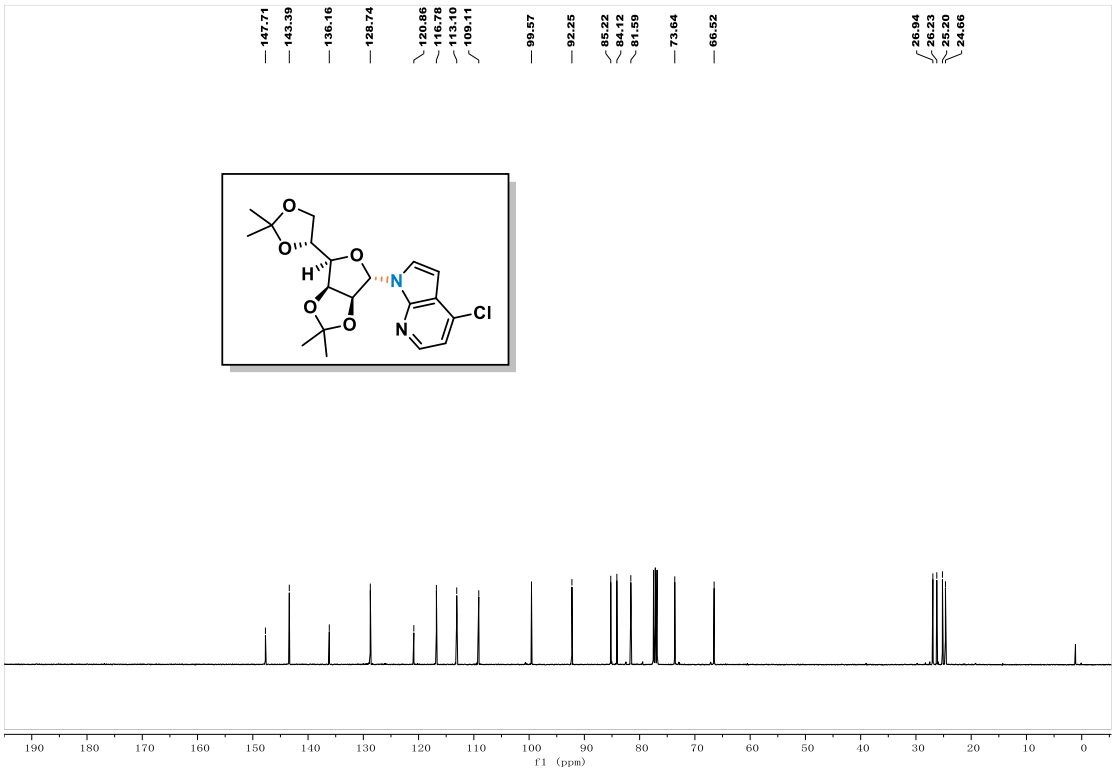
^{13}C NMR (101 MHz, $CDCl_3$) **(5l)**



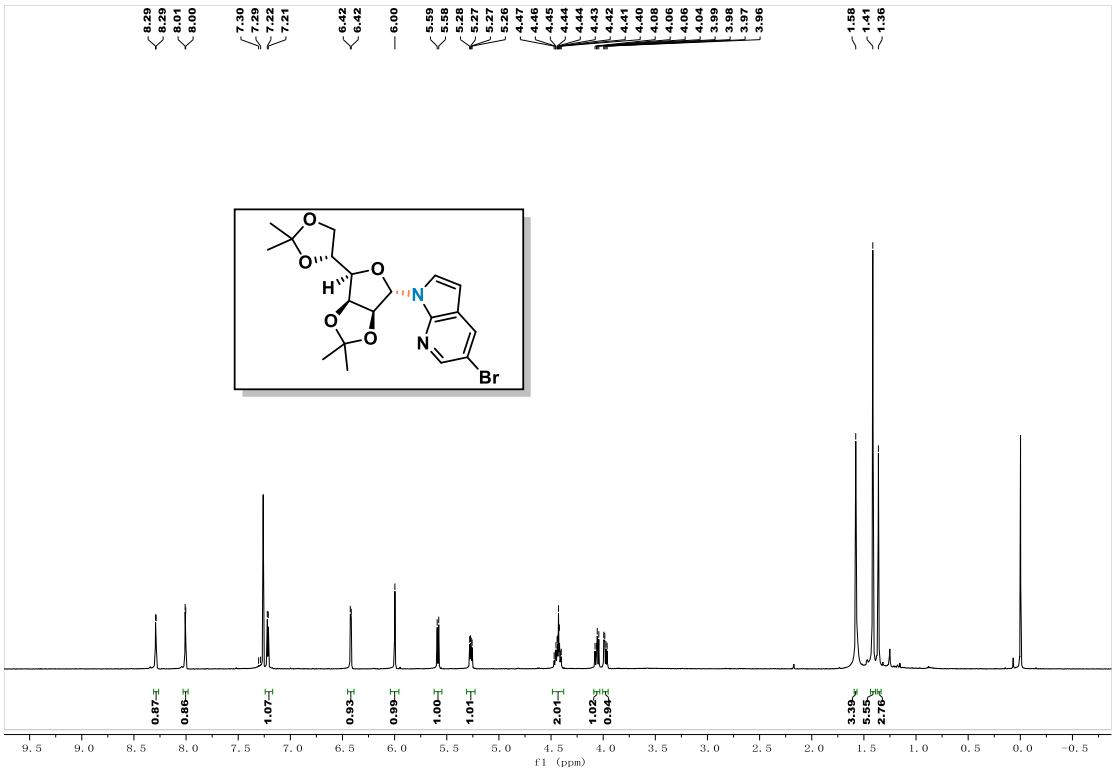
^{1}H NMR (400 MHz, $CDCl_3$) **(5m)**



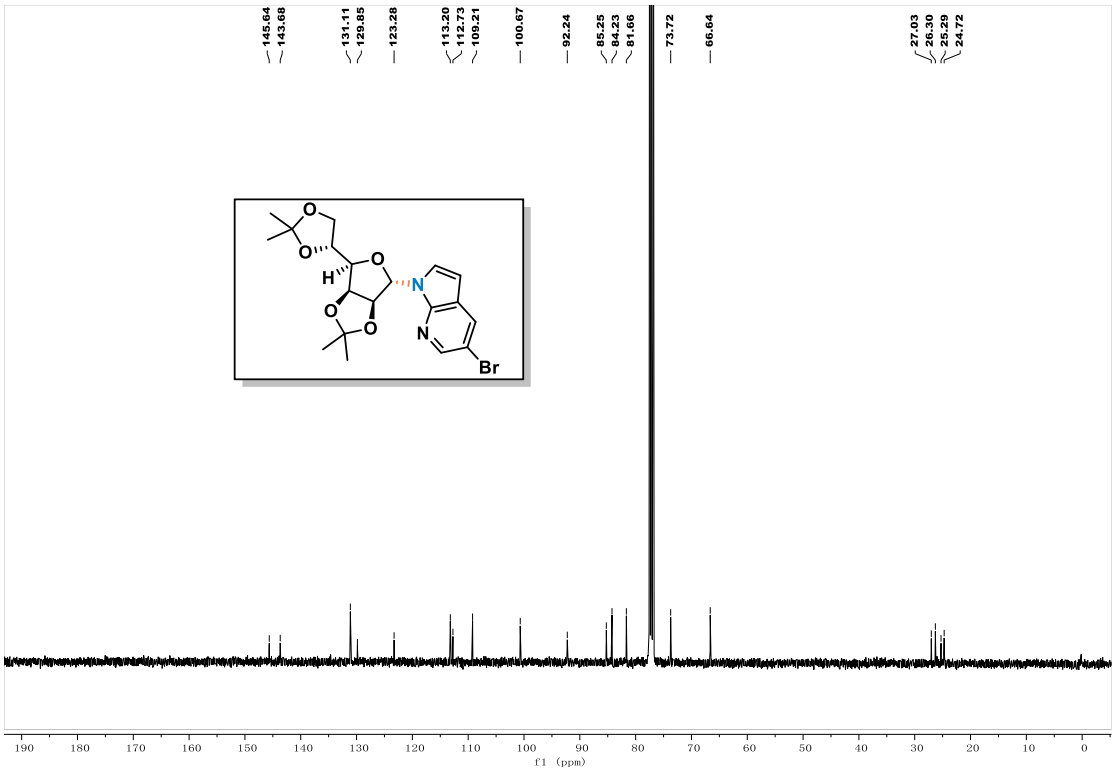
^{13}C NMR (101 MHz, $CDCl_3$) **(5m)**



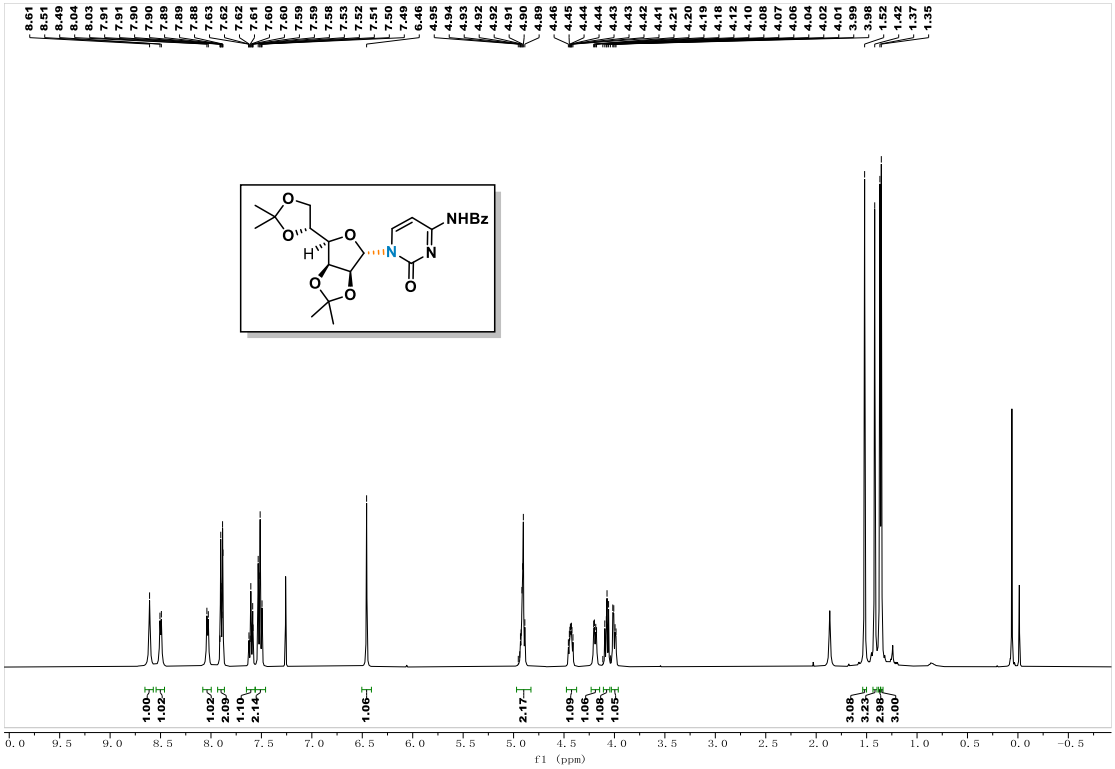
^{1}H NMR (400 MHz, $CDCl_3$) **(5n)**



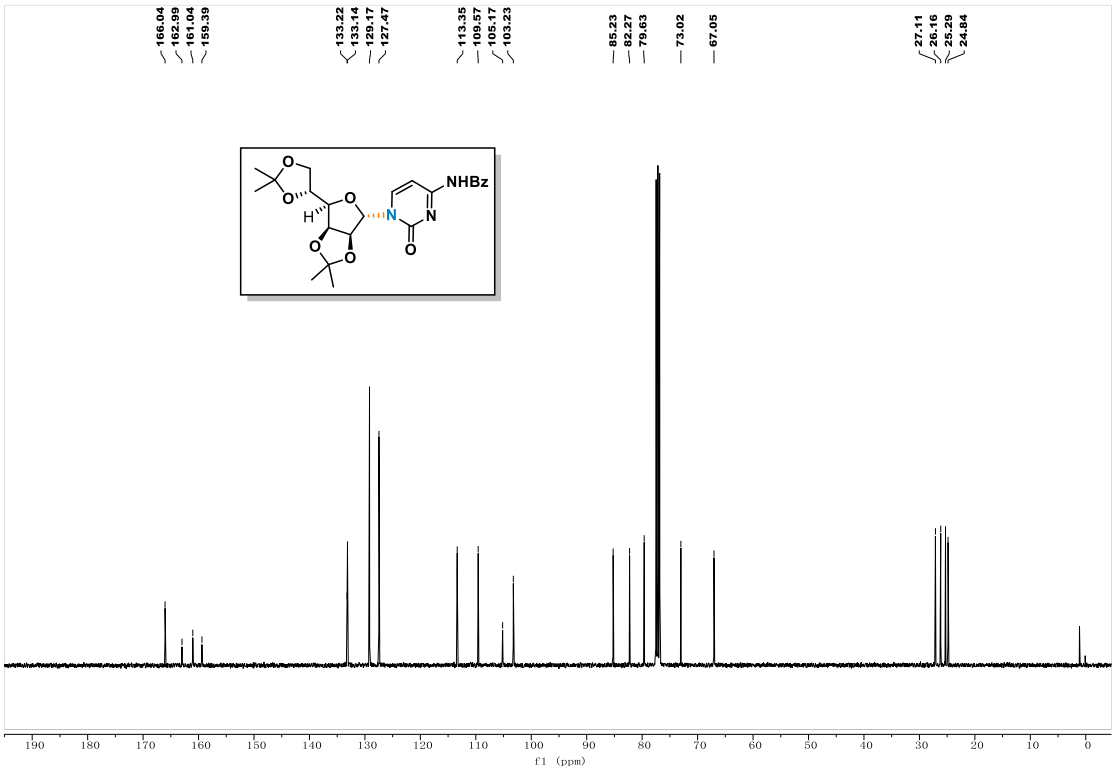
^{13}C NMR (101 MHz, $CDCl_3$) **(5n)**



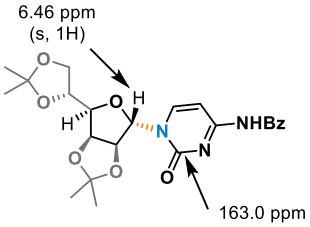
^{1}H NMR (400 MHz, $CDCl_3$) **(6a)**

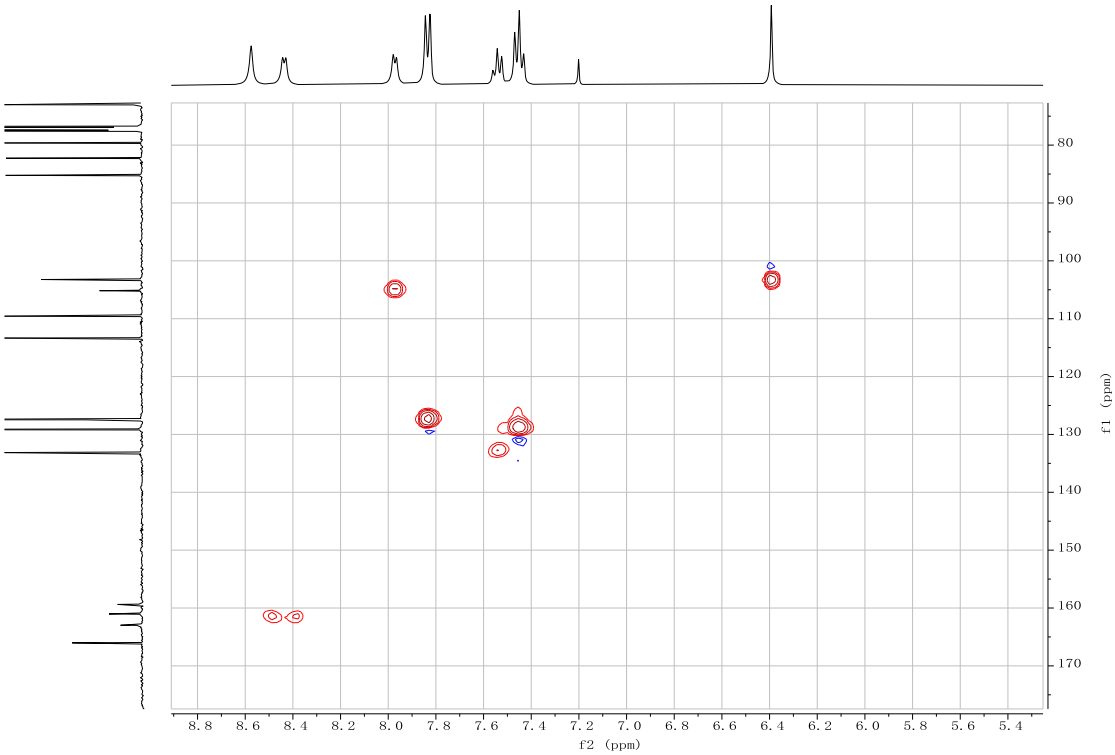


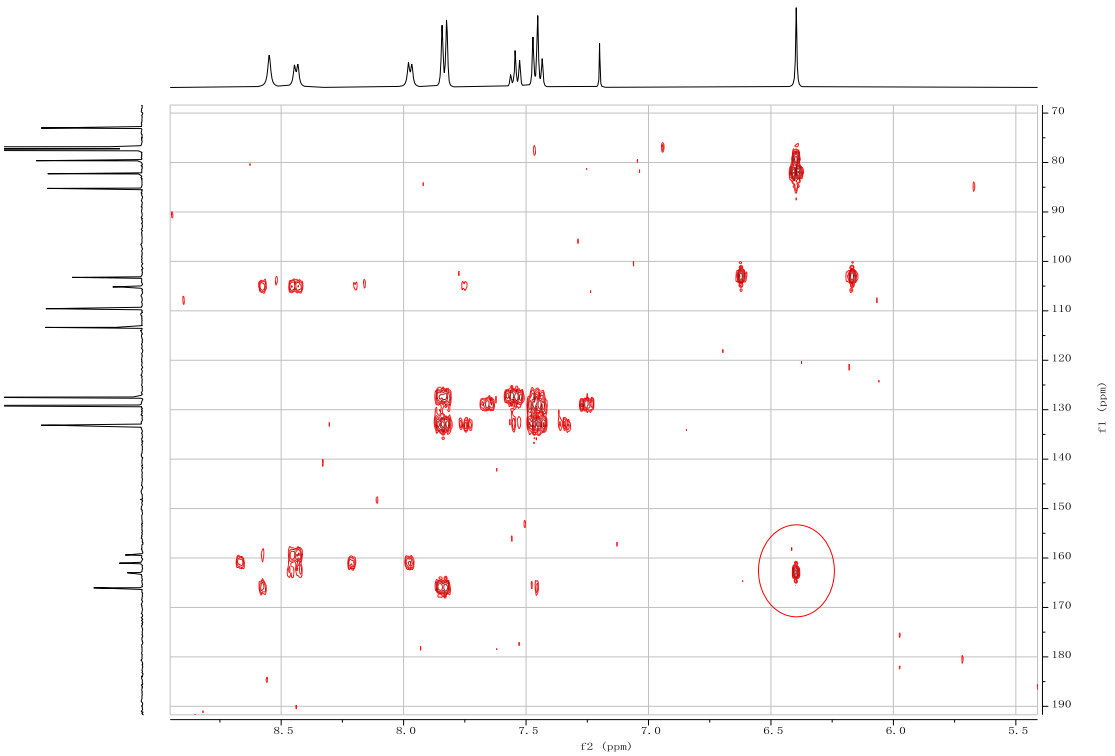
^{13}C NMR (101 MHz, $CDCl_3$) **(6a)**



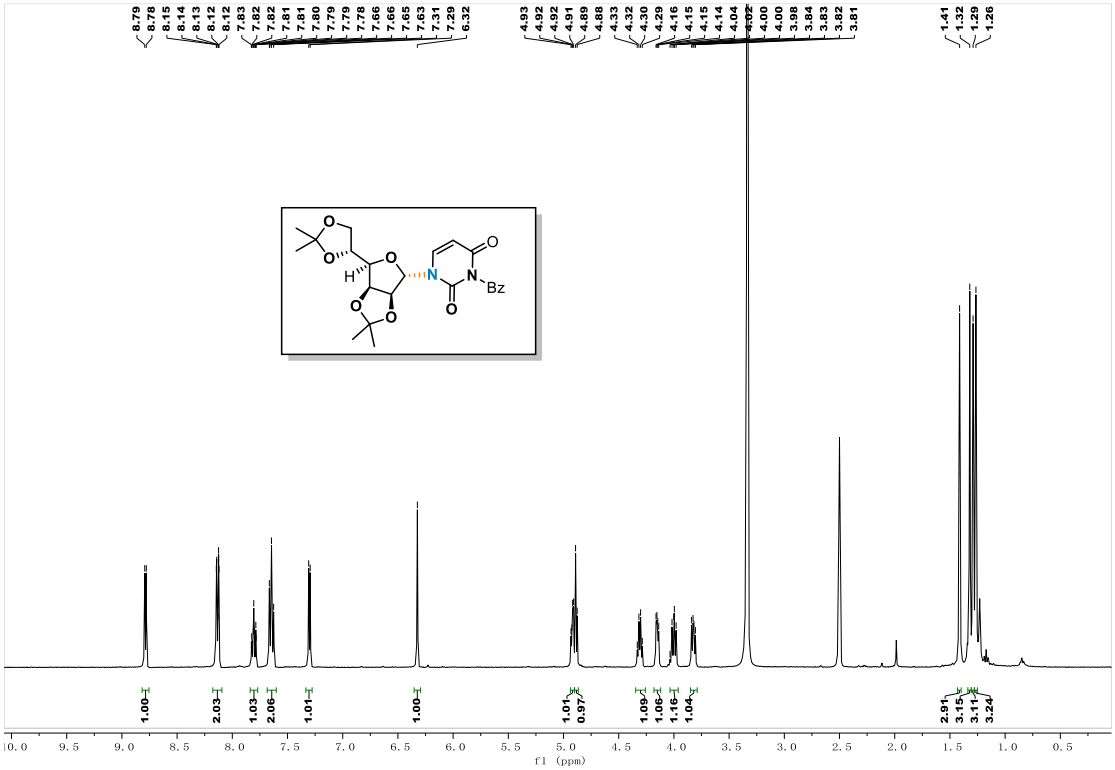
HMBC of **6a**



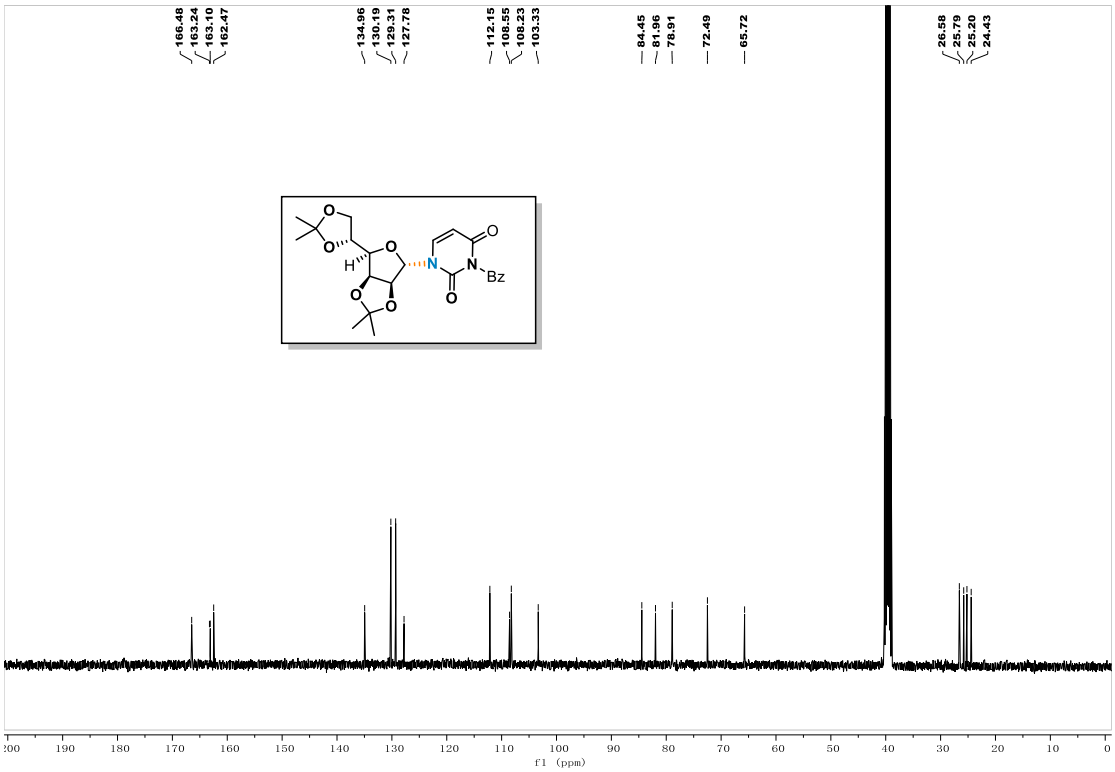




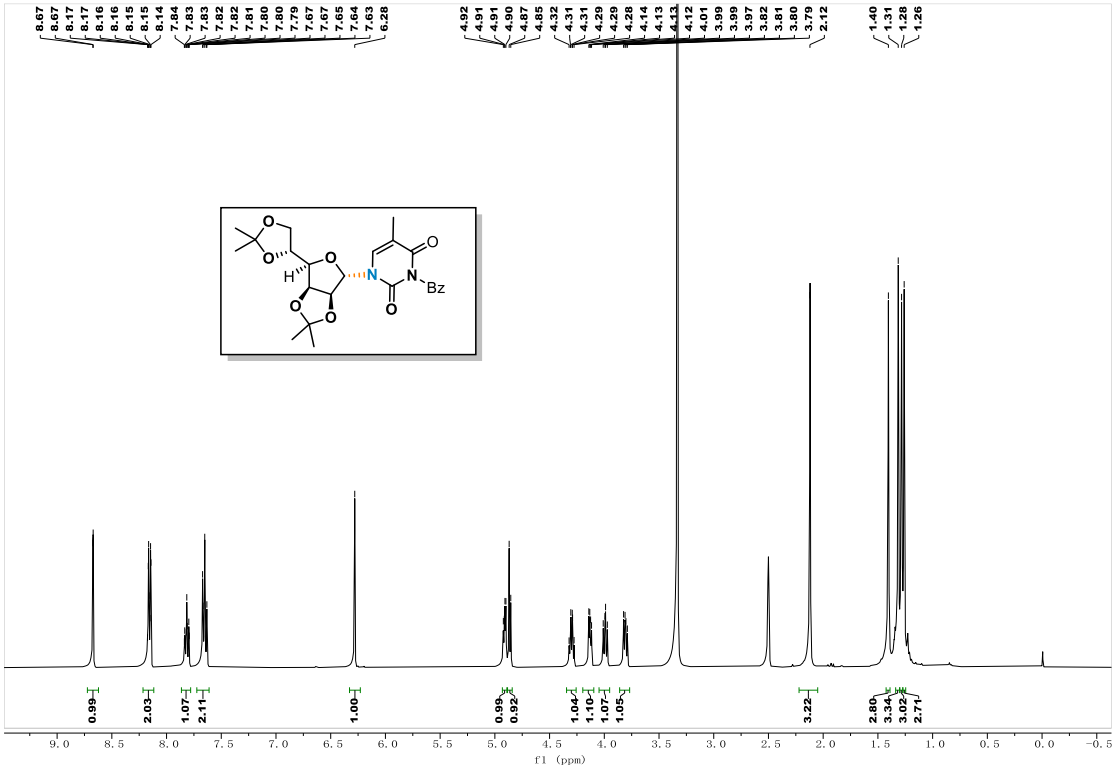
^{1}H NMR (400 MHz, DMSO-d_6) **(6b)**



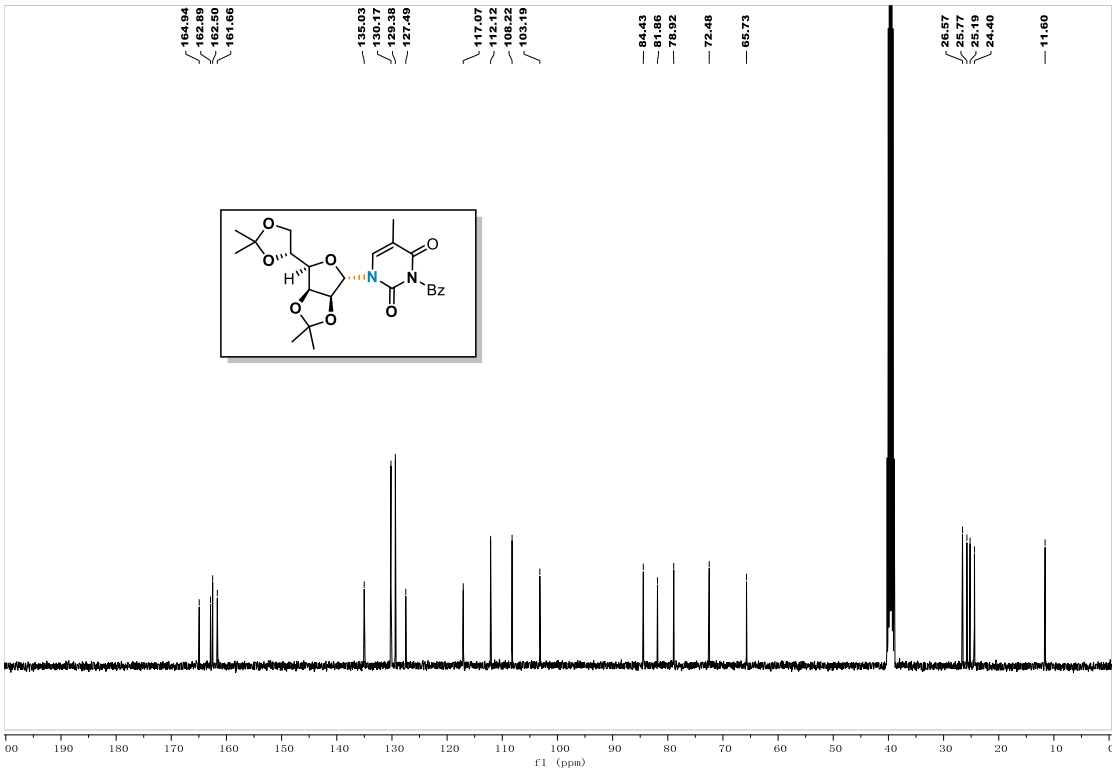
^{13}C NMR (101 MHz, DMSO-d_6) **(6b)**



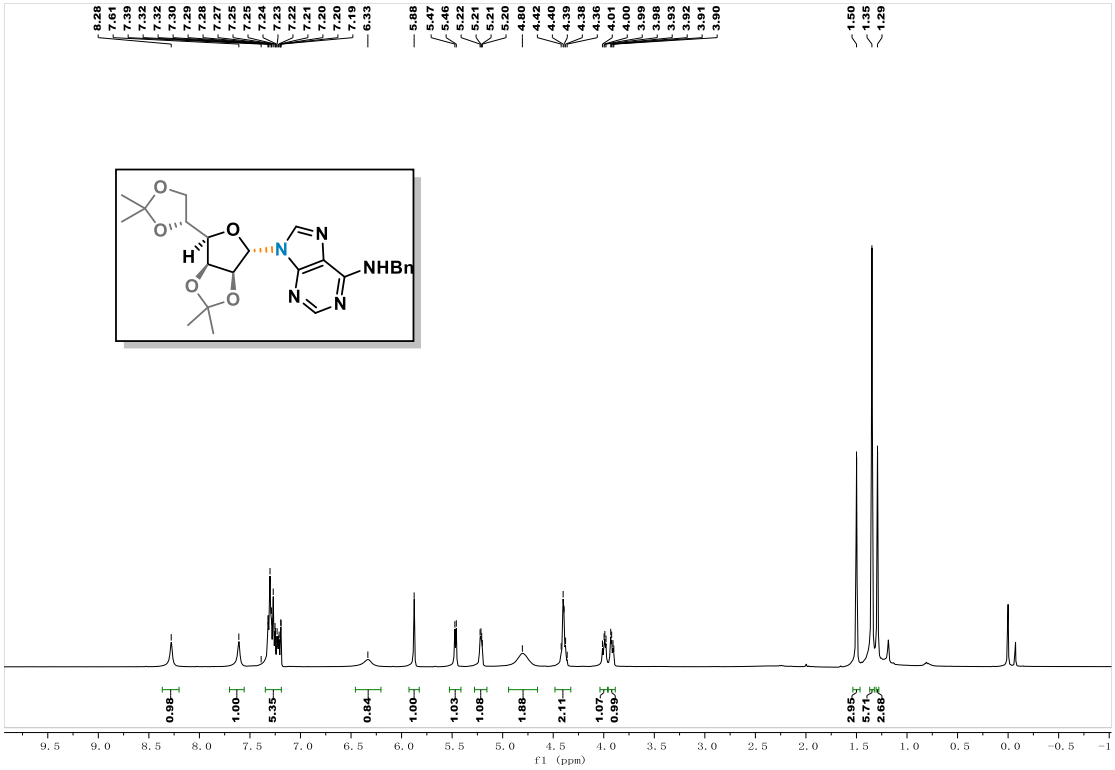
^{1}H NMR (400 MHz, DMSO-d_6) **(6c)**



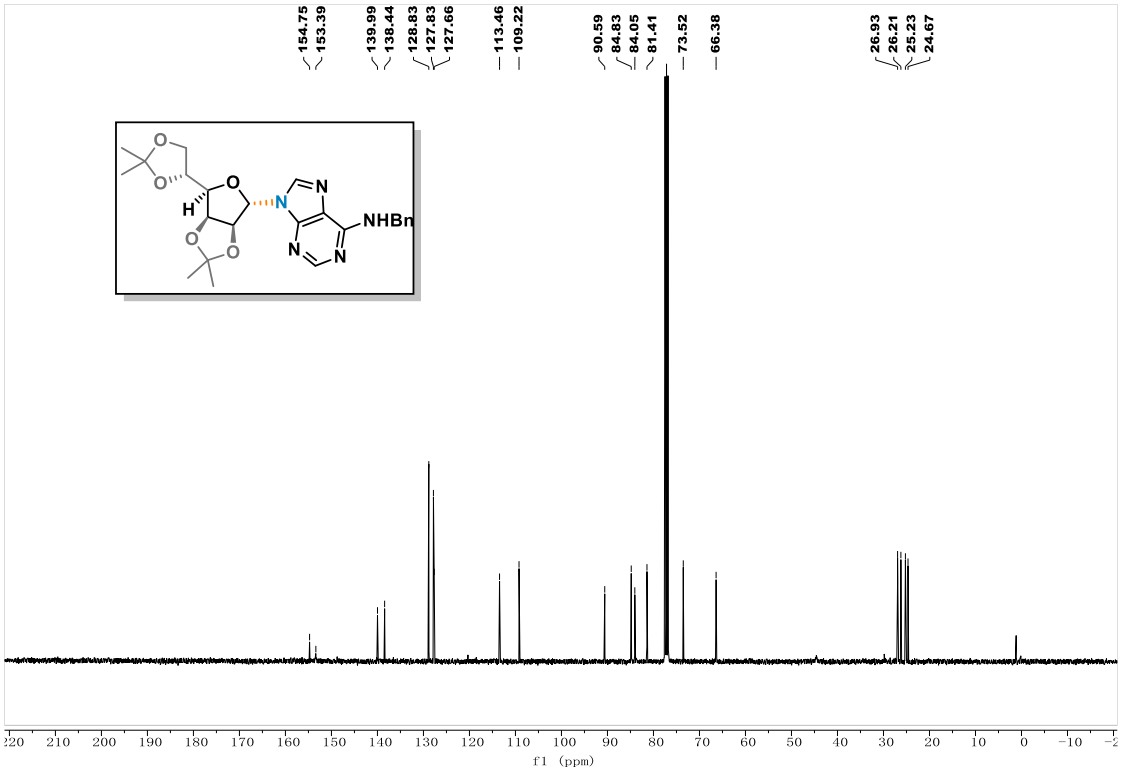
^{13}C NMR (101 MHz, DMSO-d_6) **(6c)**



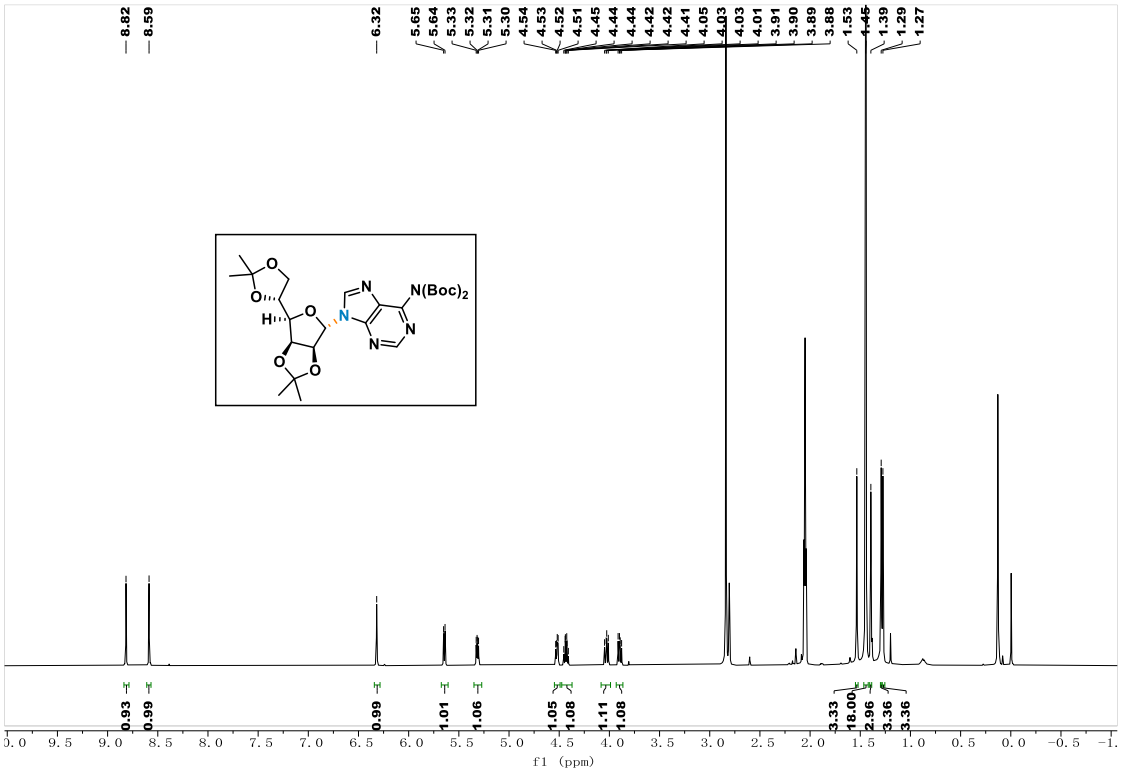
^{1}H NMR (400 MHz, $CDCl_3$) **(6d)**



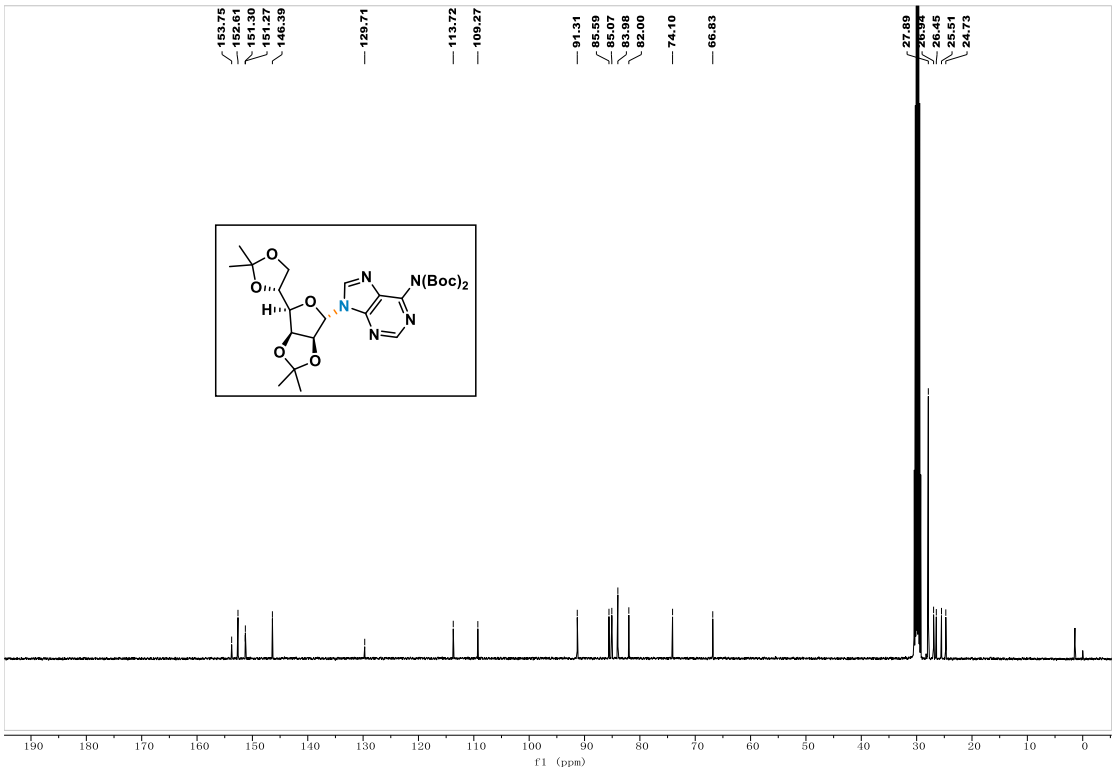
^{13}C NMR (101 MHz, $CDCl_3$) **(6d)**



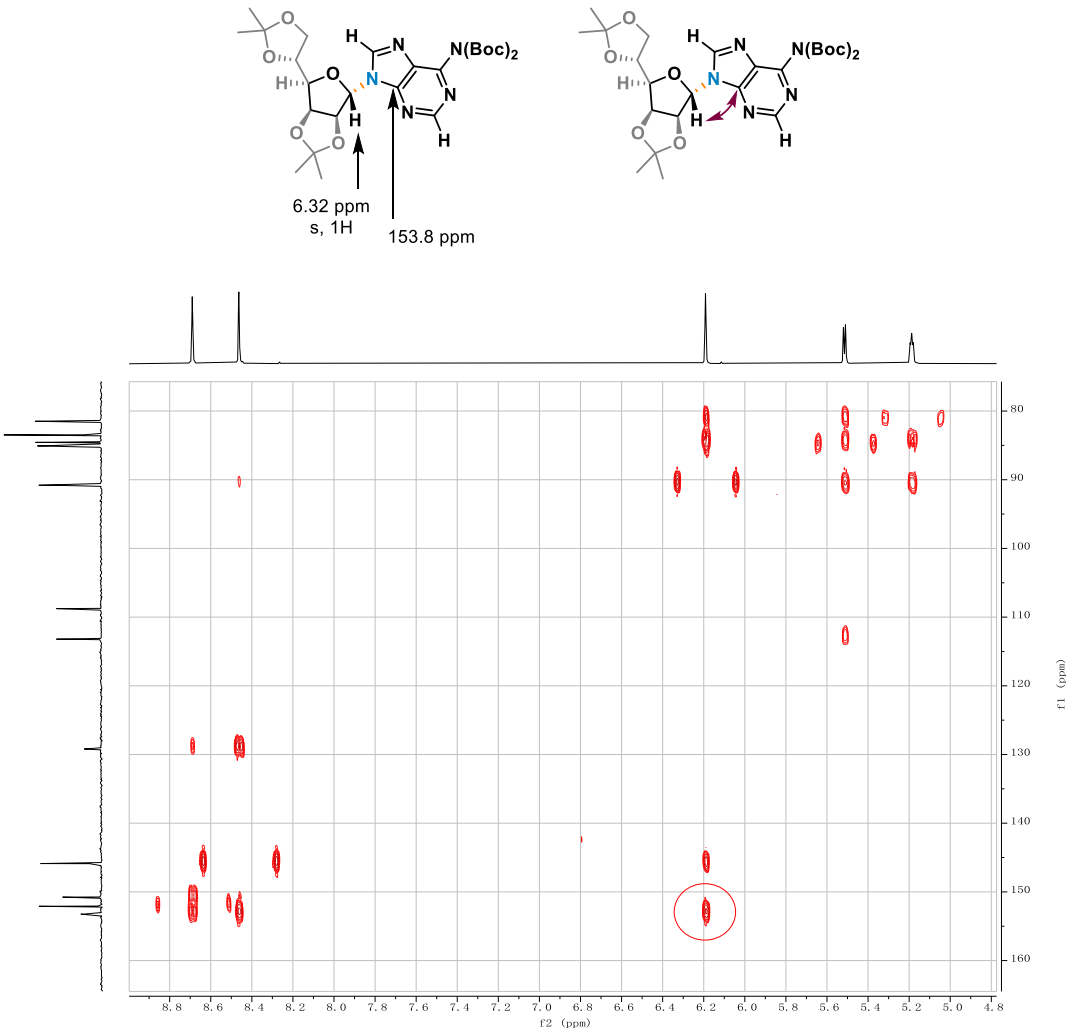
^{1}H NMR (400 MHz, Acetone-d_6) **(6e)**



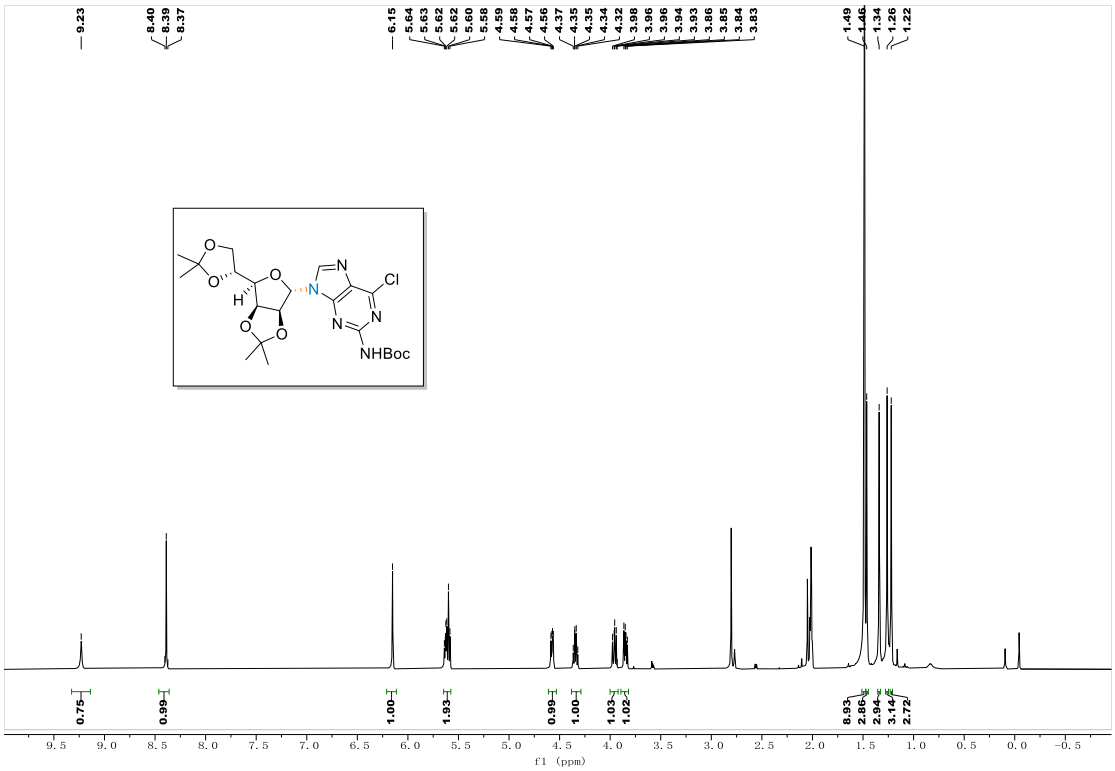
^{13}C NMR (101 MHz, Acetone-d_6) **(6e)**



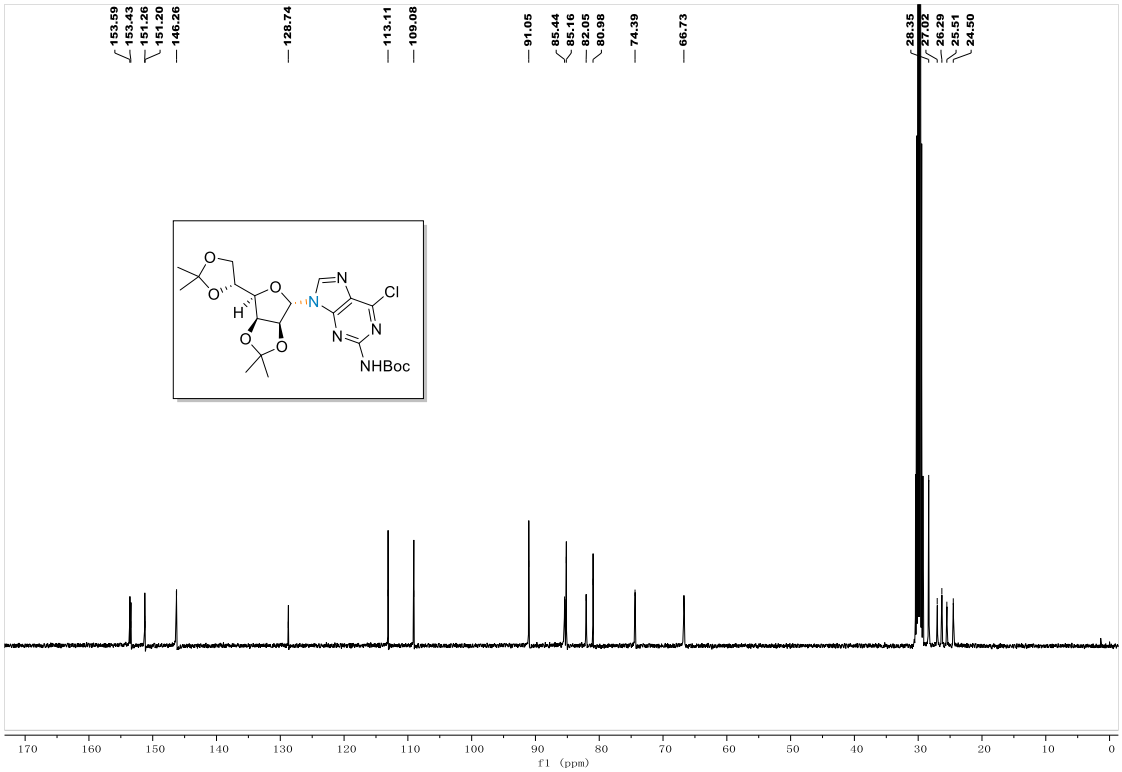
HMBC of **6e**



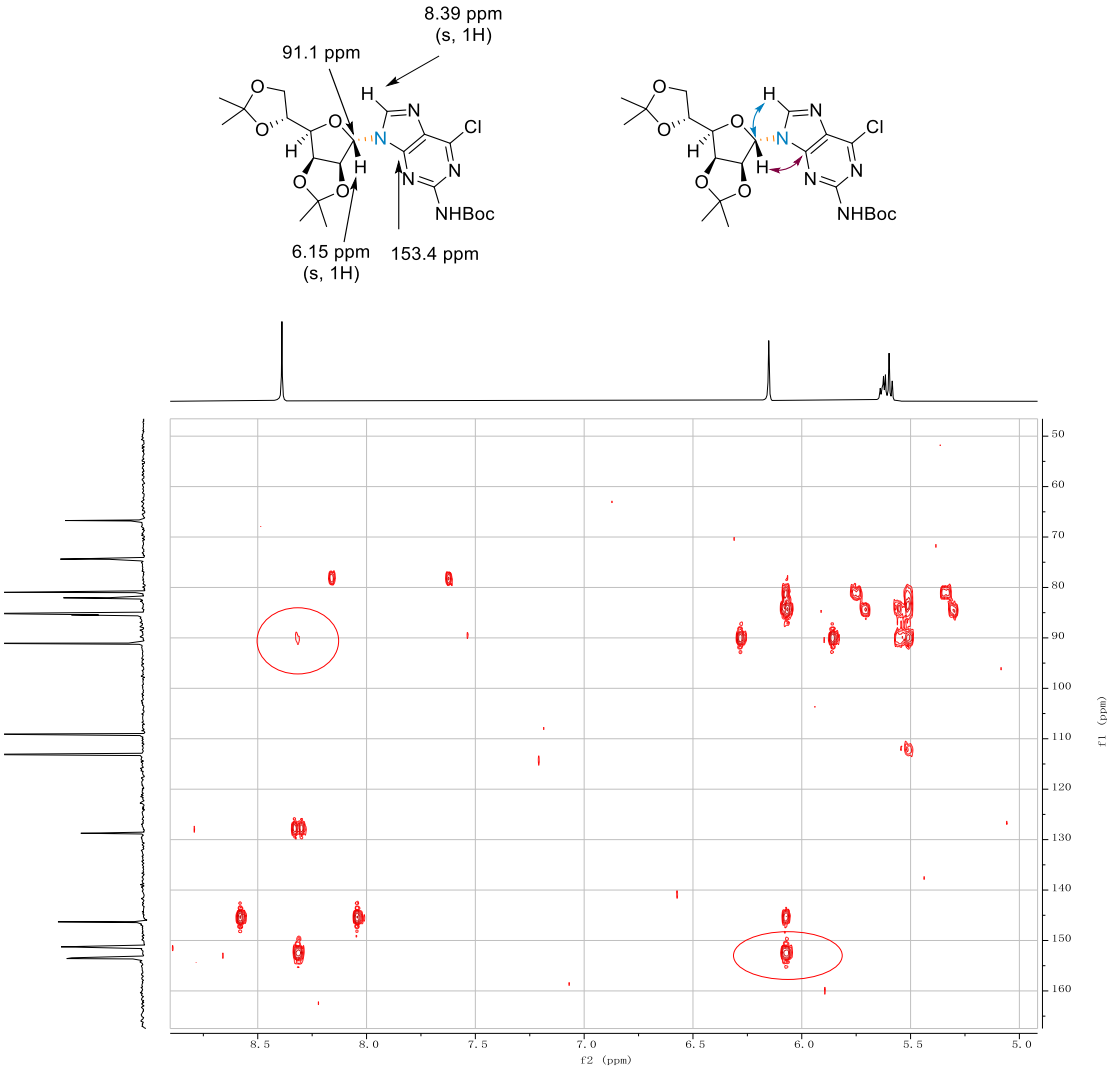
^{1}H NMR (400 MHz, Acetone-d_6) **(6f)**



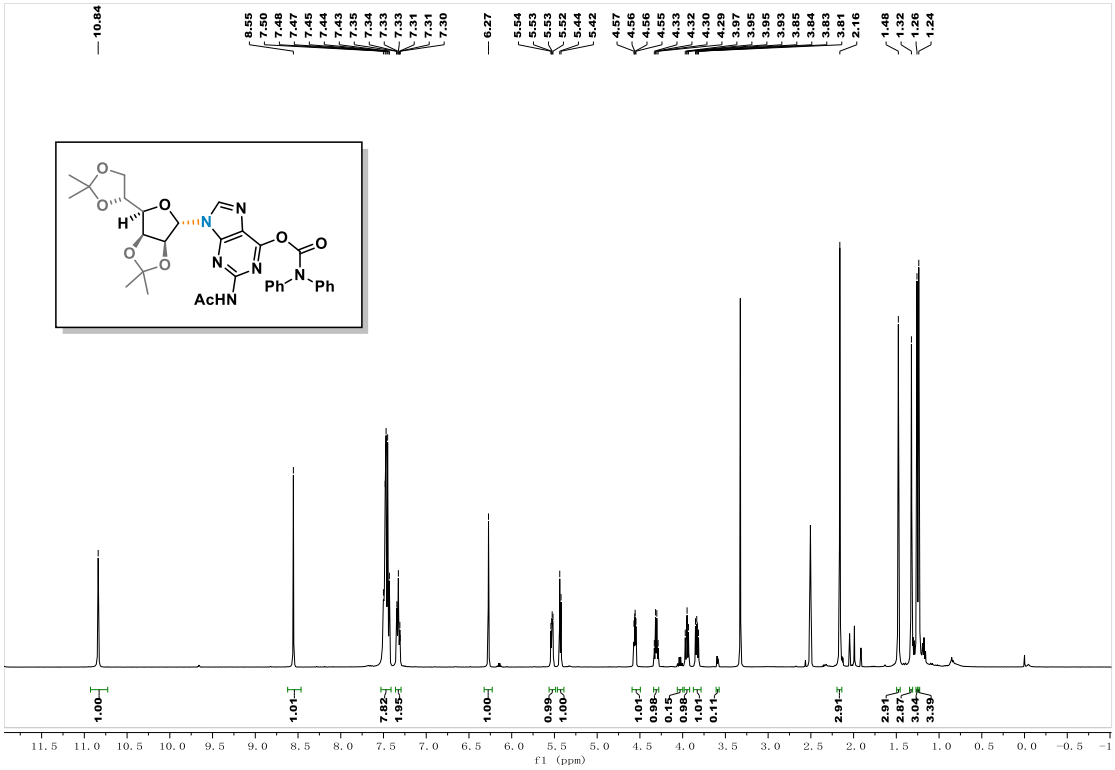
^{13}C NMR (101 MHz, Acetone-d_6) **(6f)**



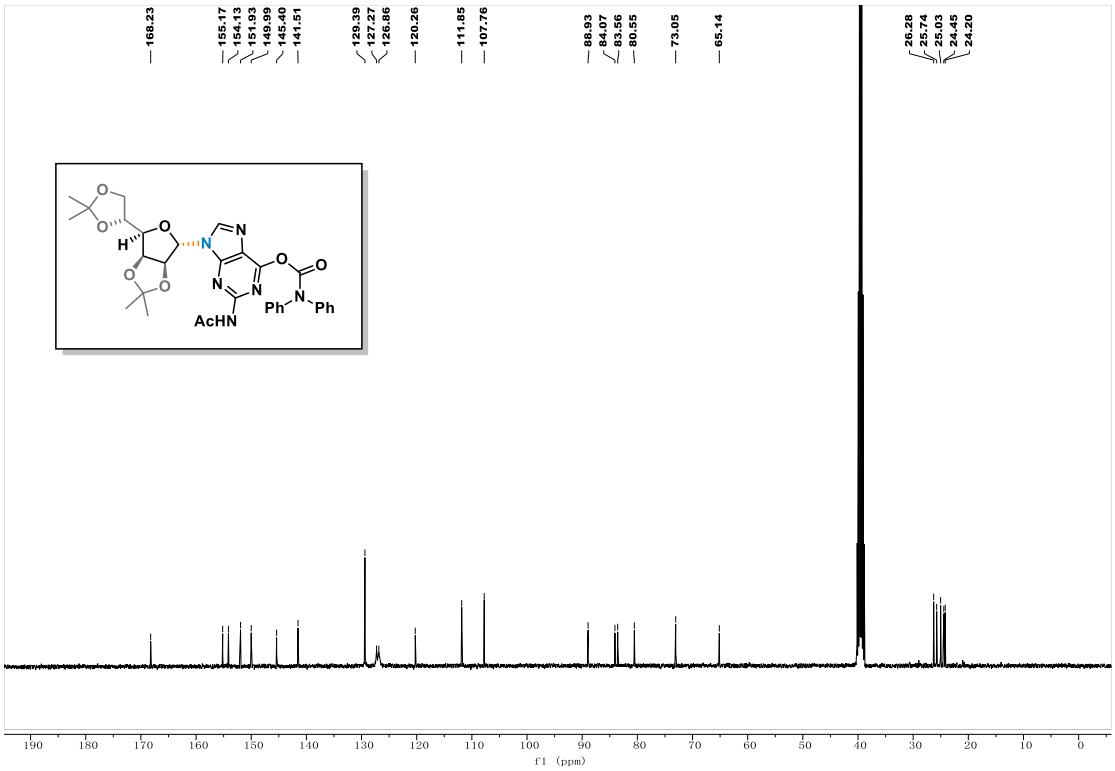
HMBC of **6f**



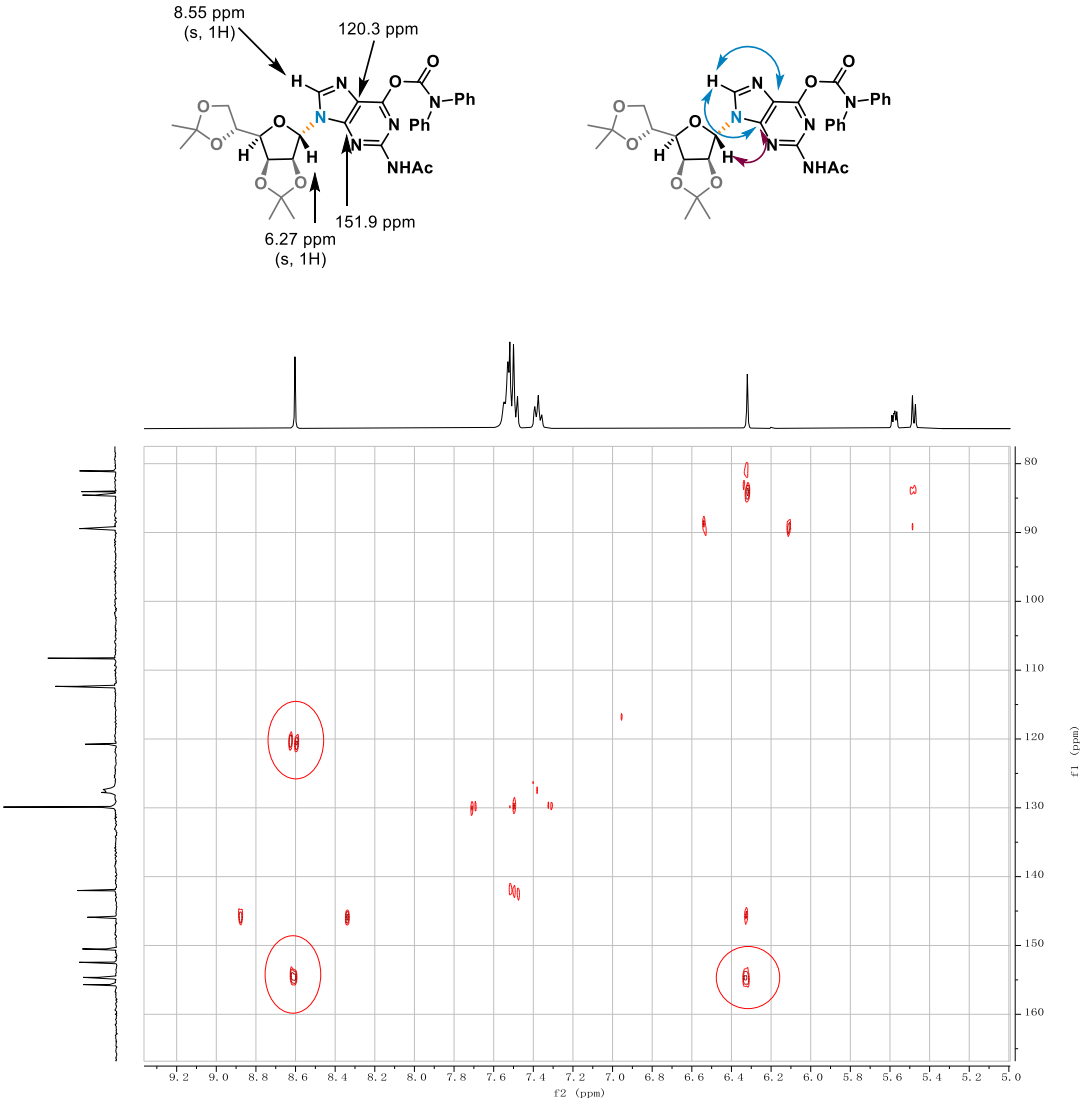
^{1}H NMR (400 MHz, DMSO-d_6) **(6g)**



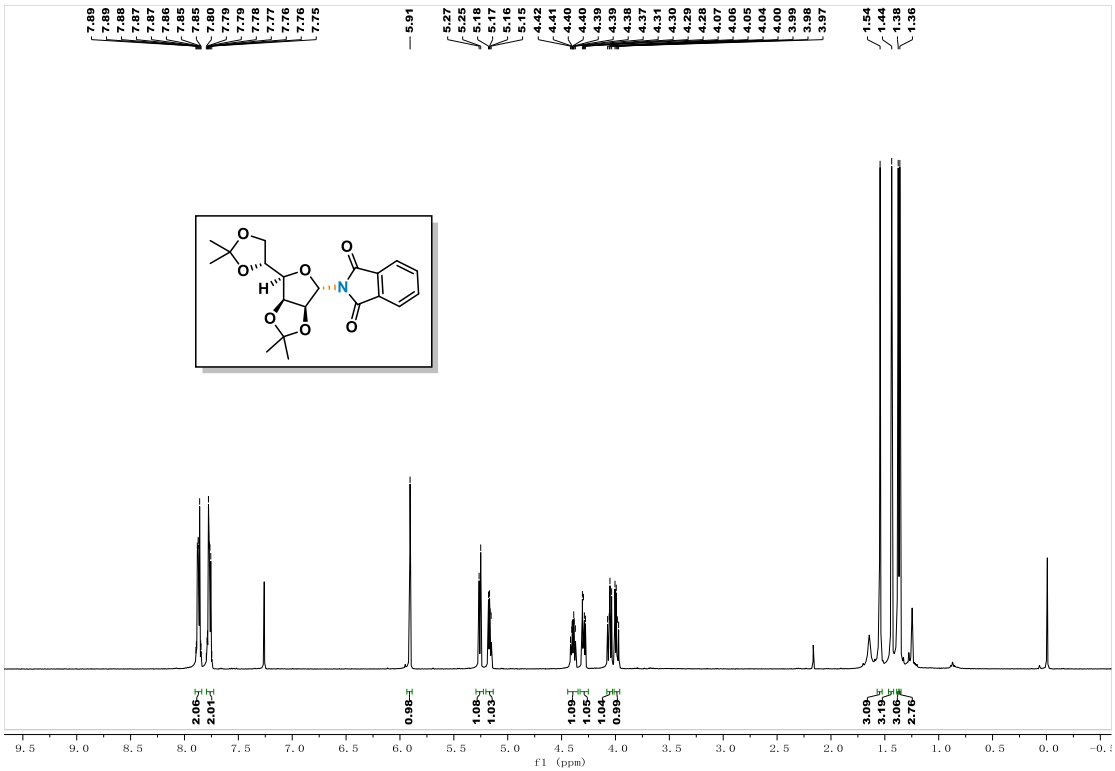
^{13}C NMR (101 MHz, DMSO-d_6) **(6g)**



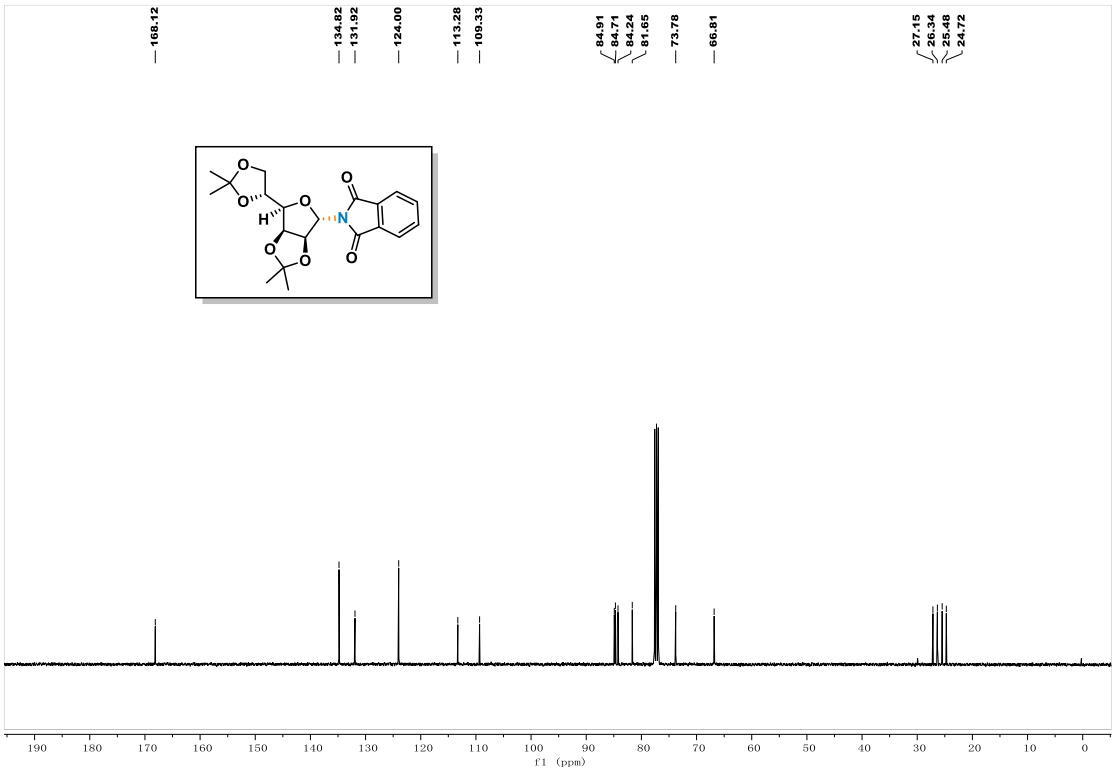
HMBC of **6g**


8.55 ppm
(s, 1H)
120.3 ppm
6.27 ppm
(s, 1H)
151.9 ppm
NHAc
N–Ph
Ph
f2 (ppm)
f1 (ppm)

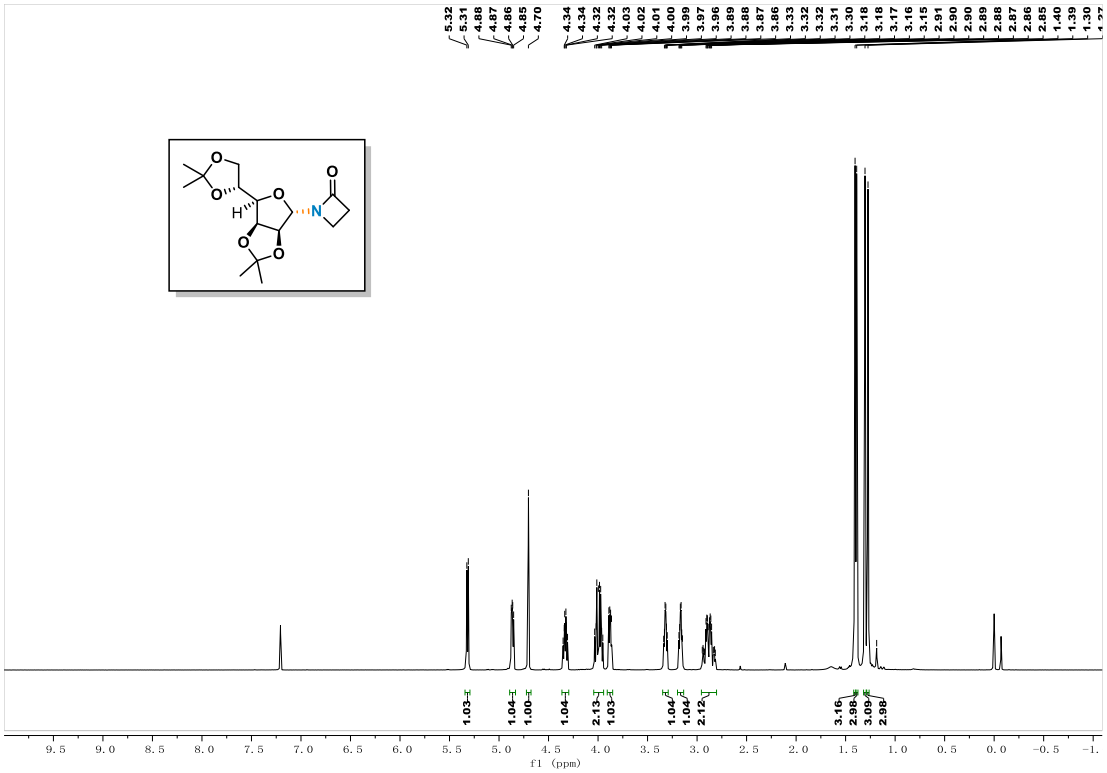
^{1}H NMR (400 MHz, $CDCl_3$) **(7a)**



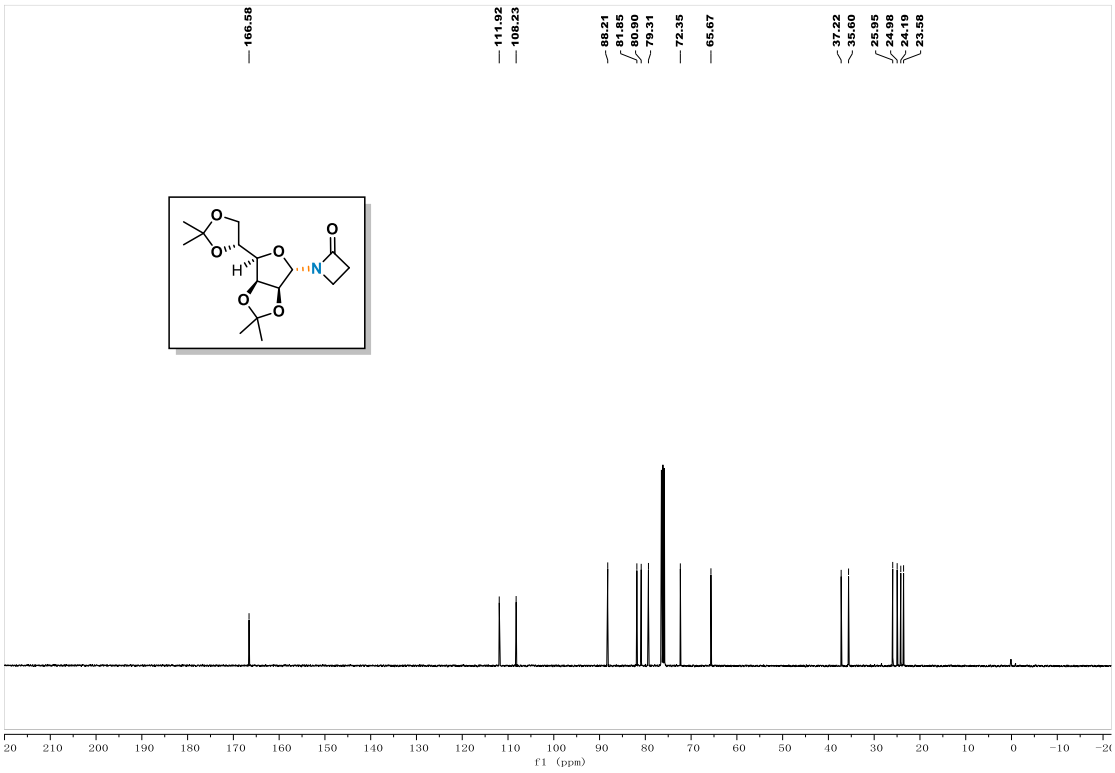
^{13}C NMR (101 MHz, $CDCl_3$) **(7a)**



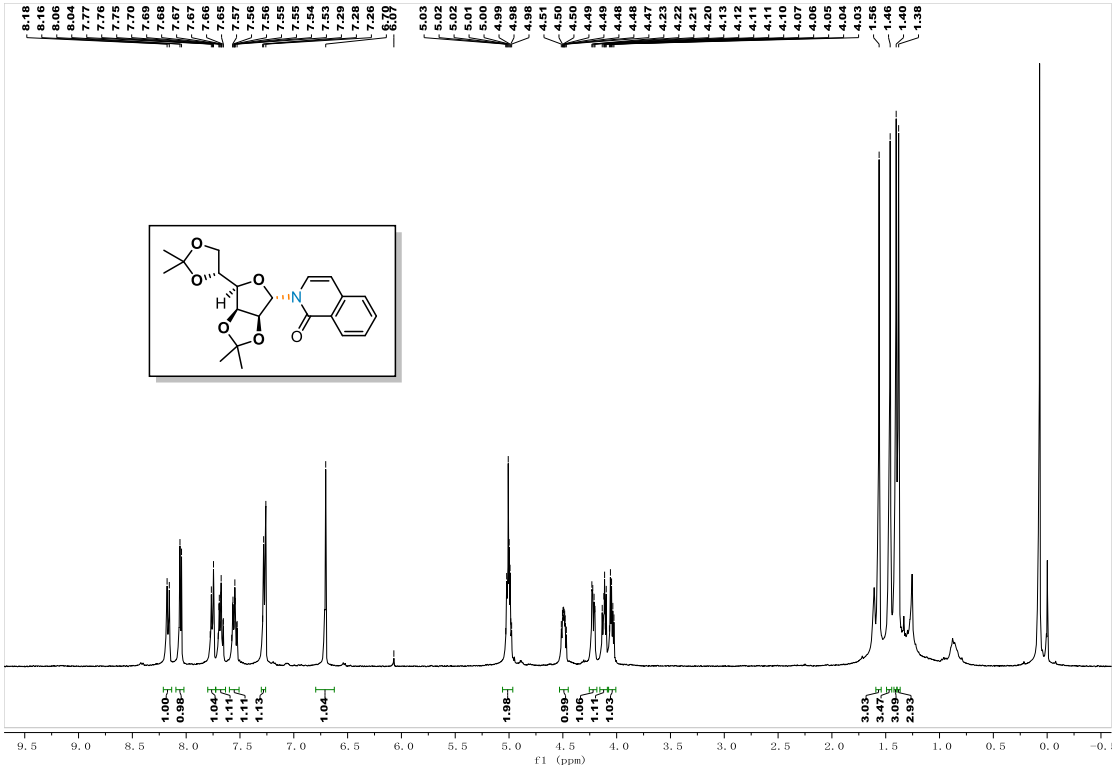
^{1}H NMR (400 MHz, $CDCl_3$) **(7b)**



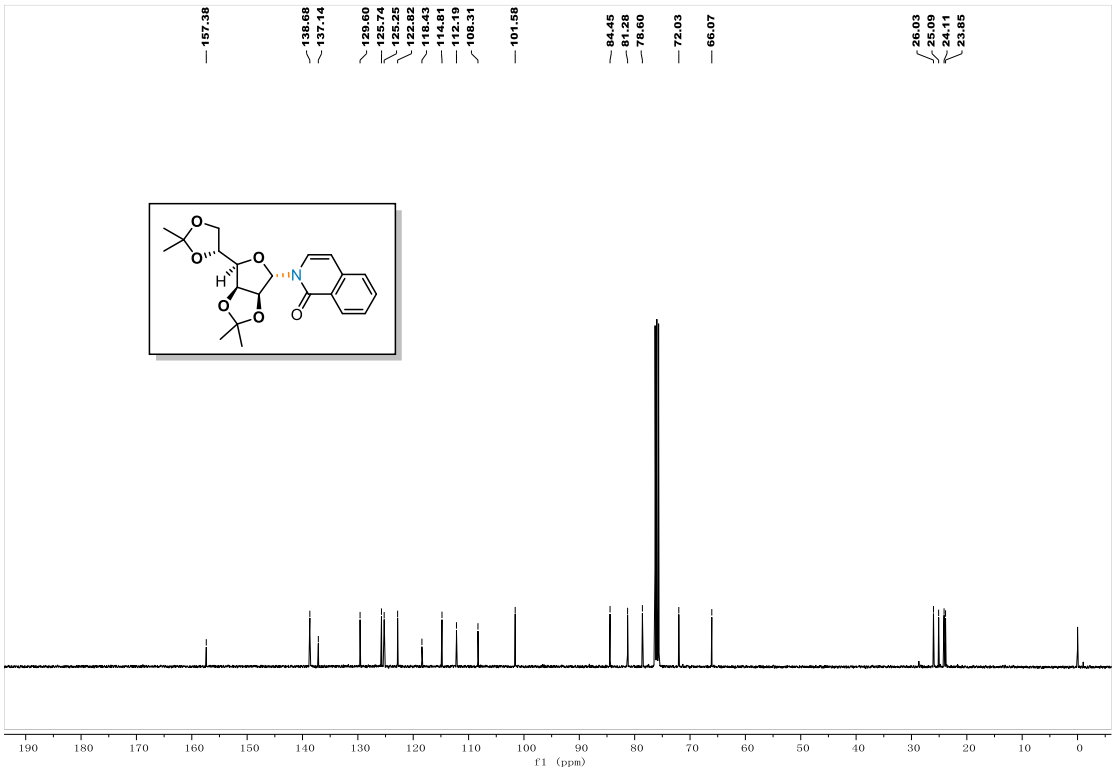
^{13}C NMR (101 MHz, $CDCl_3$) **(7b)**



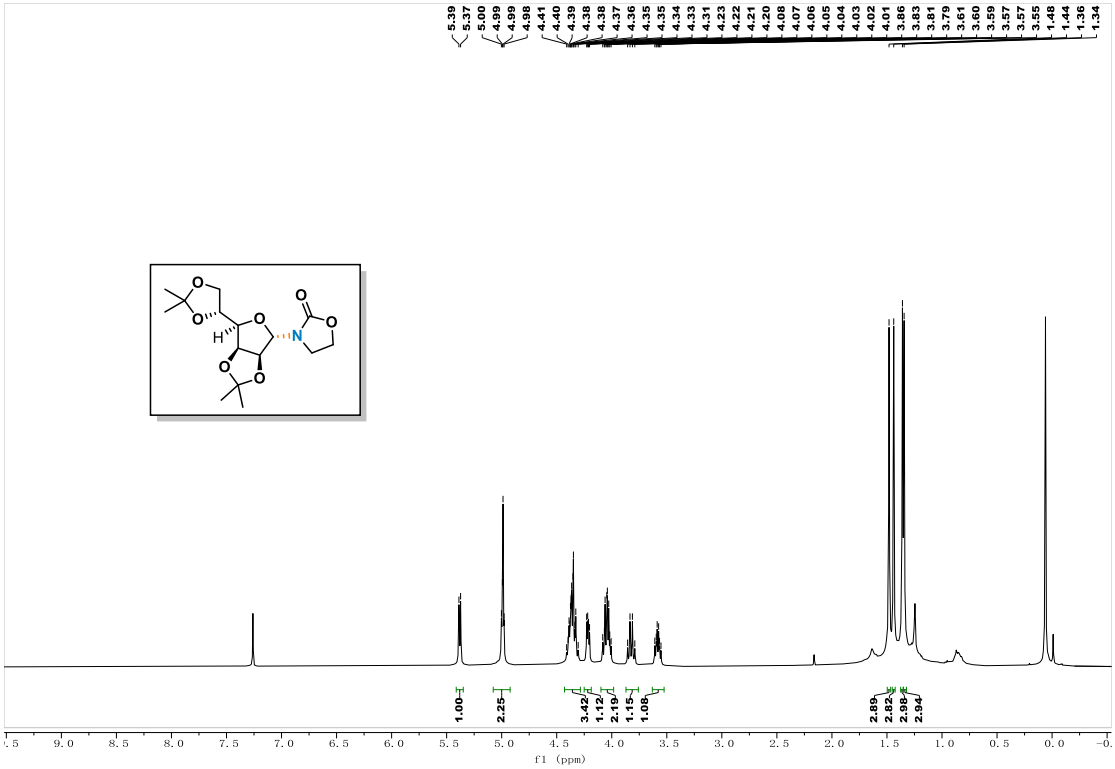
^{1}H NMR (400 MHz, $CDCl_3$) **(7c)**



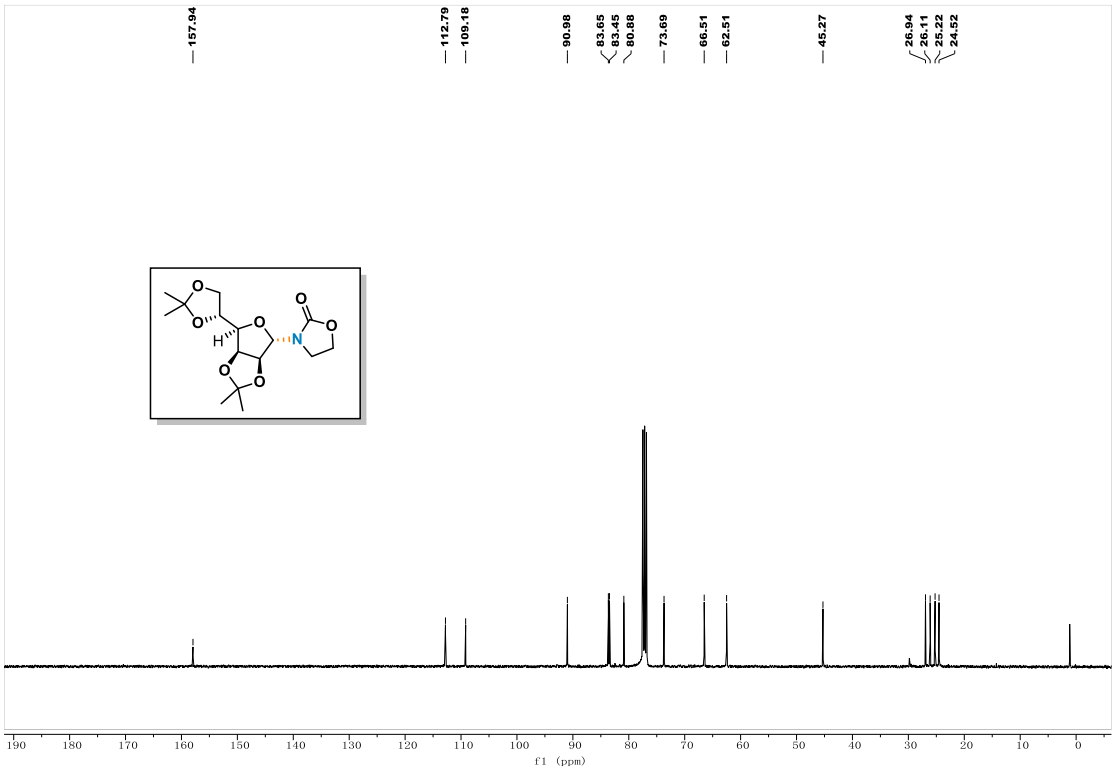
^{13}C NMR (101 MHz, $CDCl_3$) **(7c)**



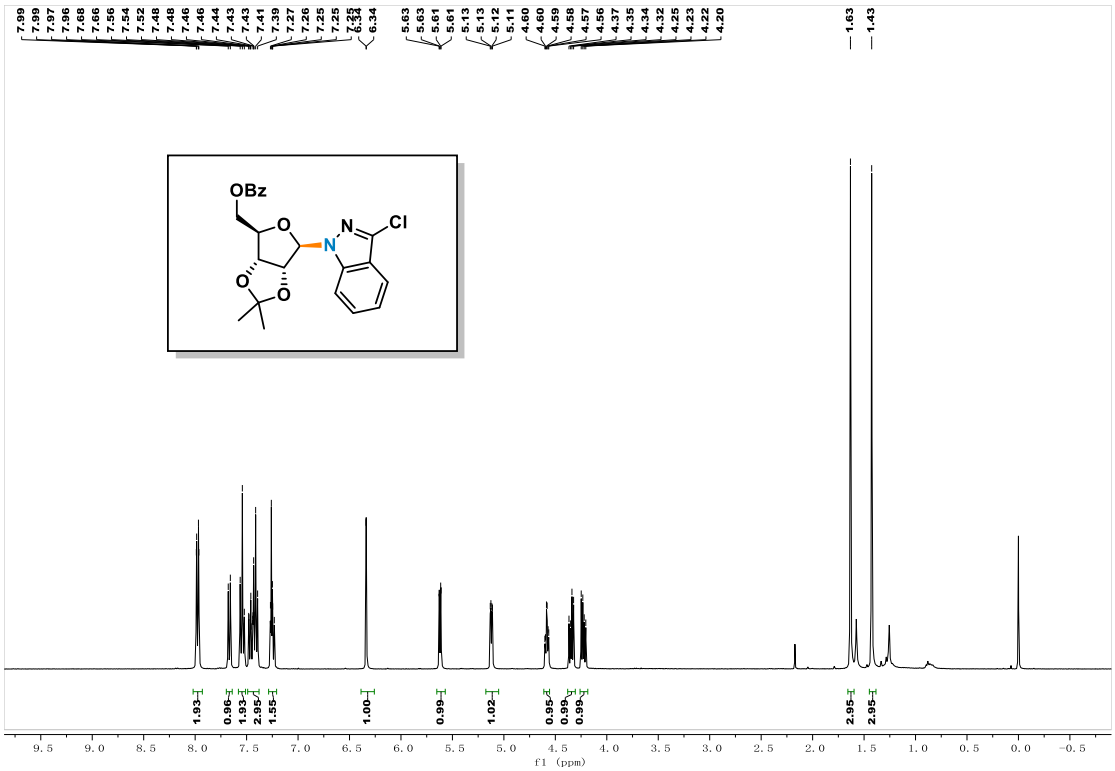
^{1}H NMR (400 MHz, $CDCl_3$) **(7d)**



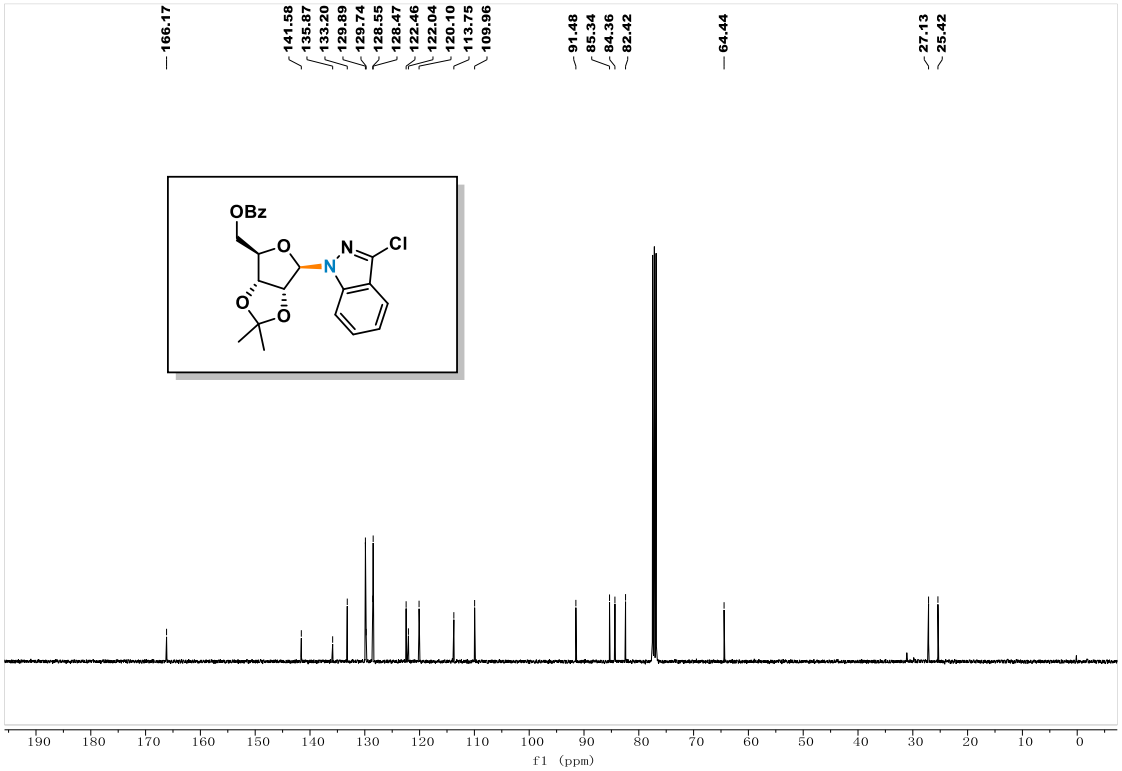
^{13}C NMR (101 MHz, $CDCl_3$) **(7d)**



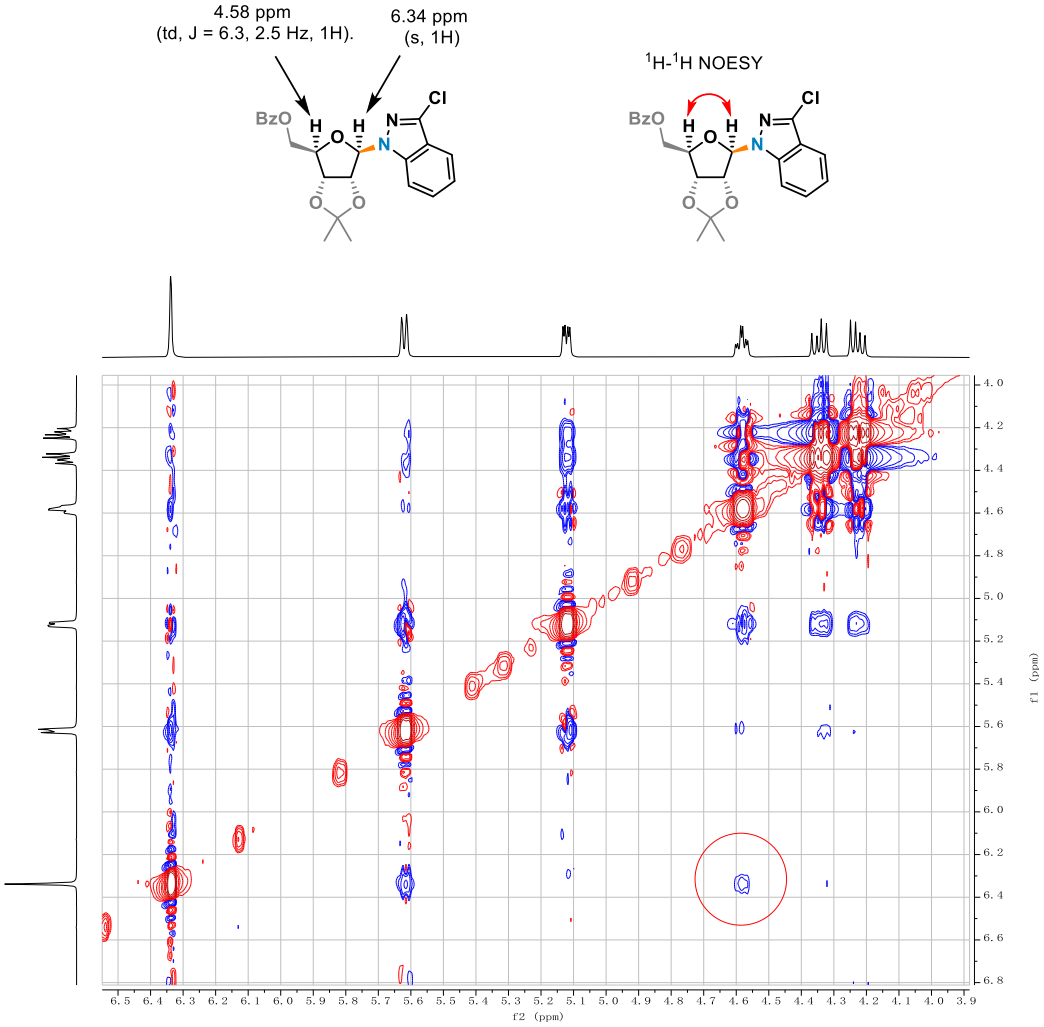
^{1}H NMR (400 MHz, $CDCl_3$) **(8a)**



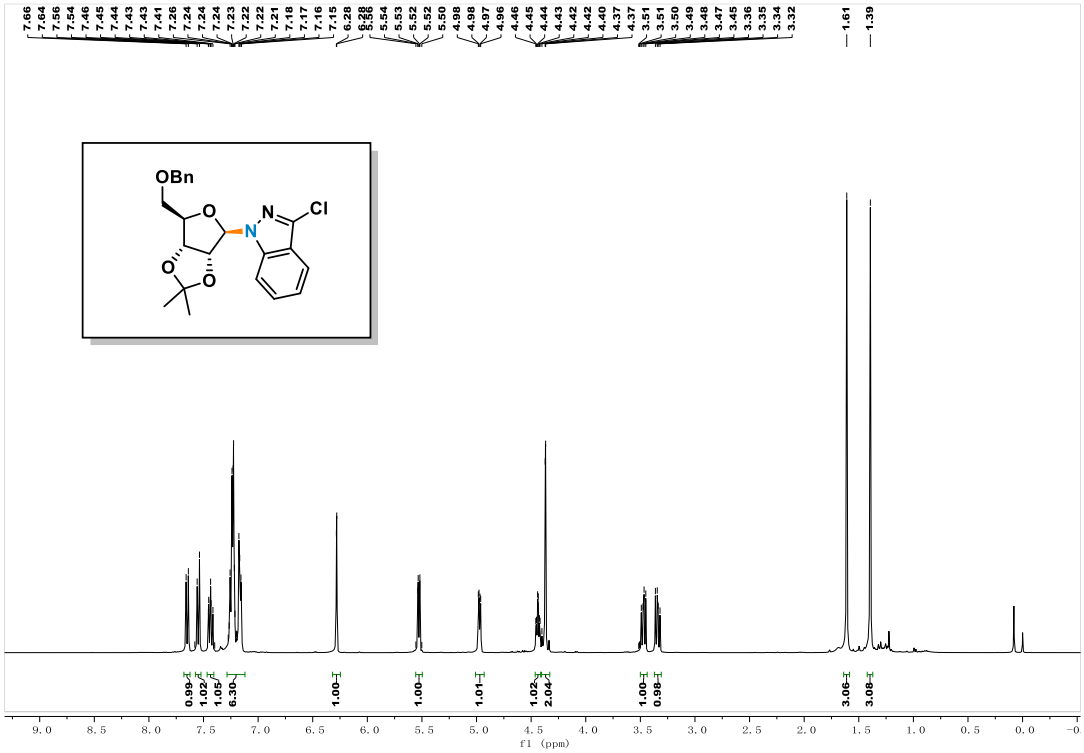
^{13}C NMR (101 MHz, $CDCl_3$) **(8a)**



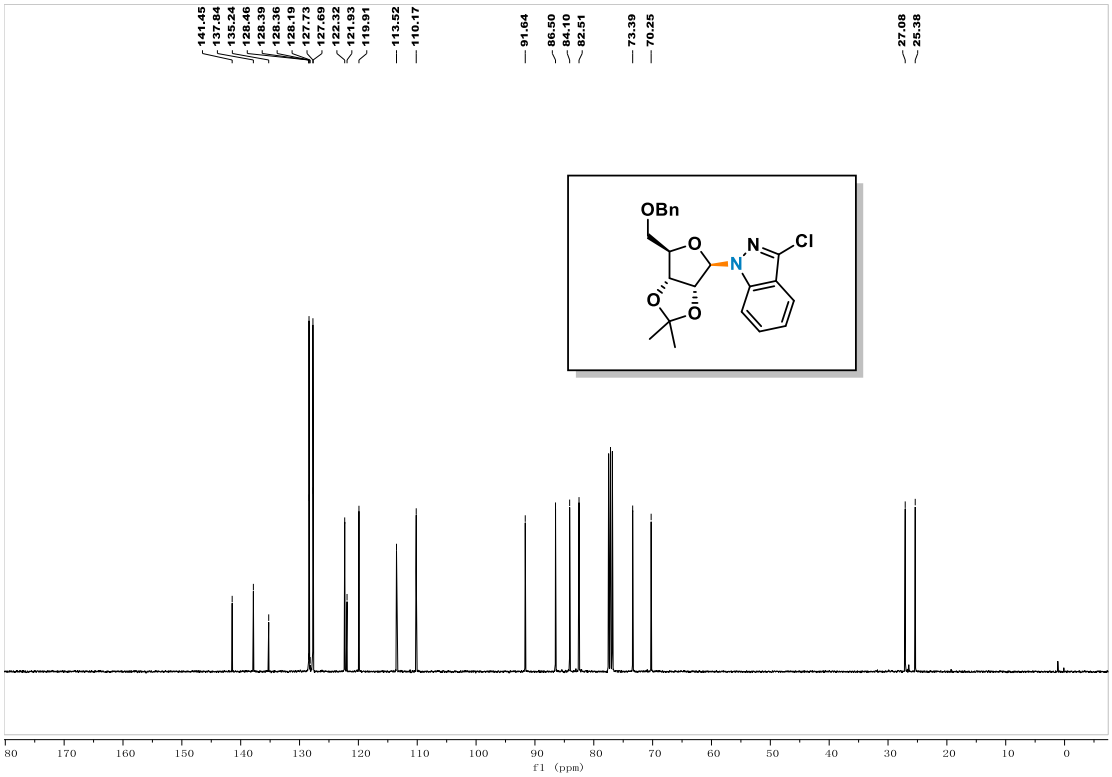
NOESY of **8a**


4.58 ppm
(td, J = 6.3, 2.5 Hz, 1H).
6.34 ppm
(s, 1H)
^{1}H-^{1}H NOESY
BzO
H
O
H
N
N
Cl
O
O
f2 (ppm)
f1 (ppm)

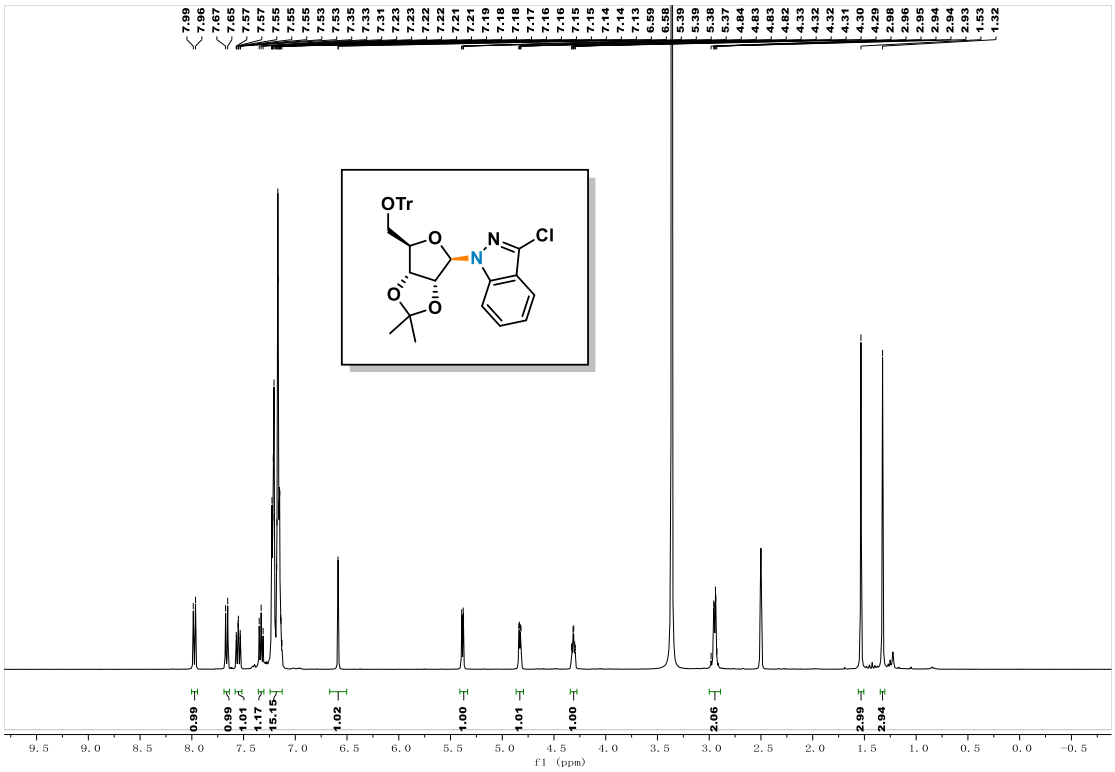
^{1}H NMR (400 MHz, $CDCl_3$) **(8b)**



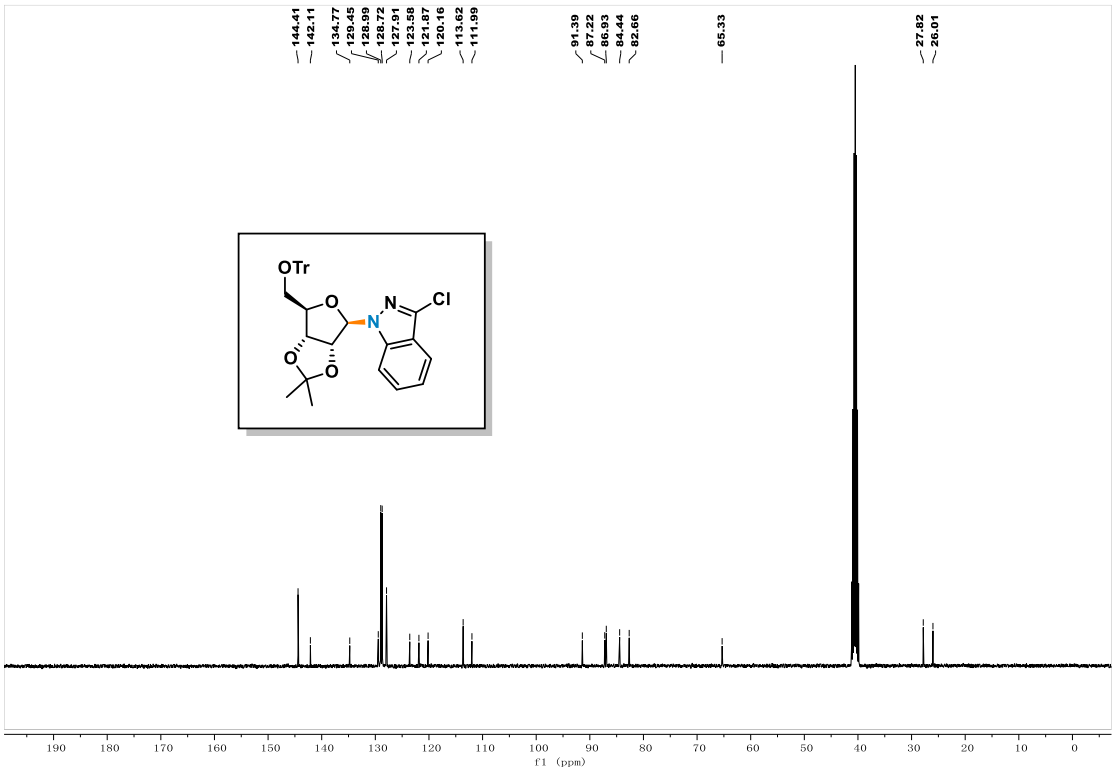
^{13}C NMR (101 MHz, $CDCl_3$) **(8b)**



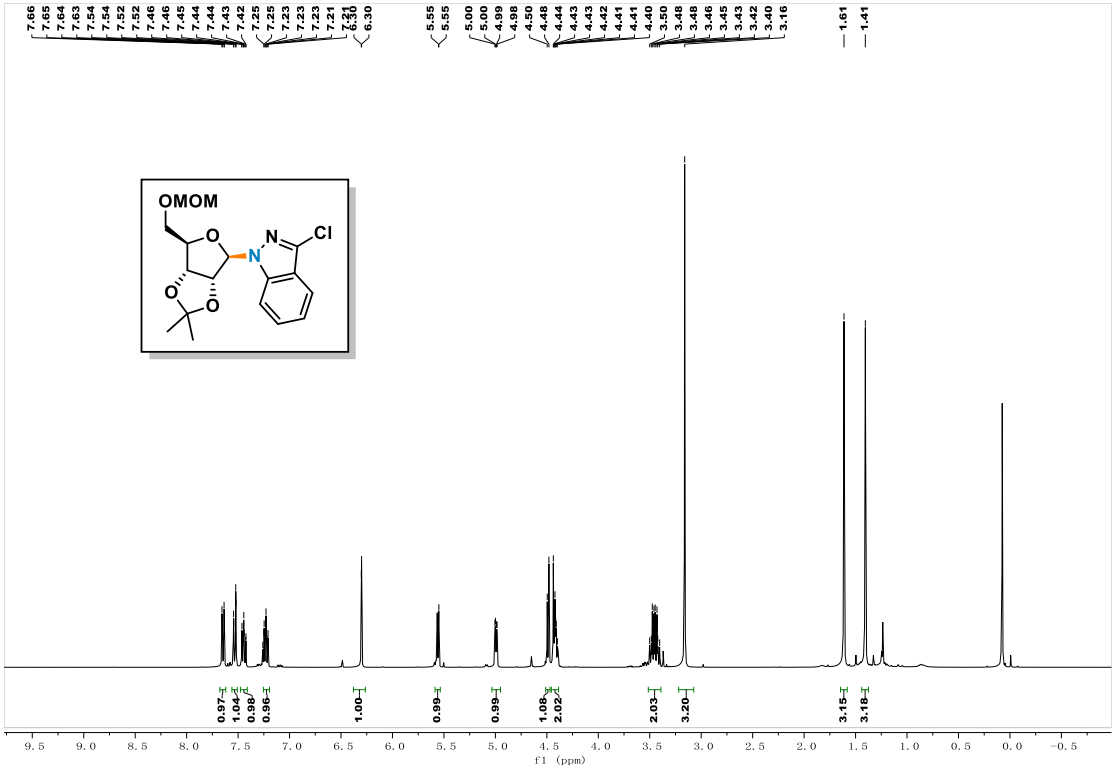
^{1}H NMR (400 MHz, $CDCl_3$) **(8c)**



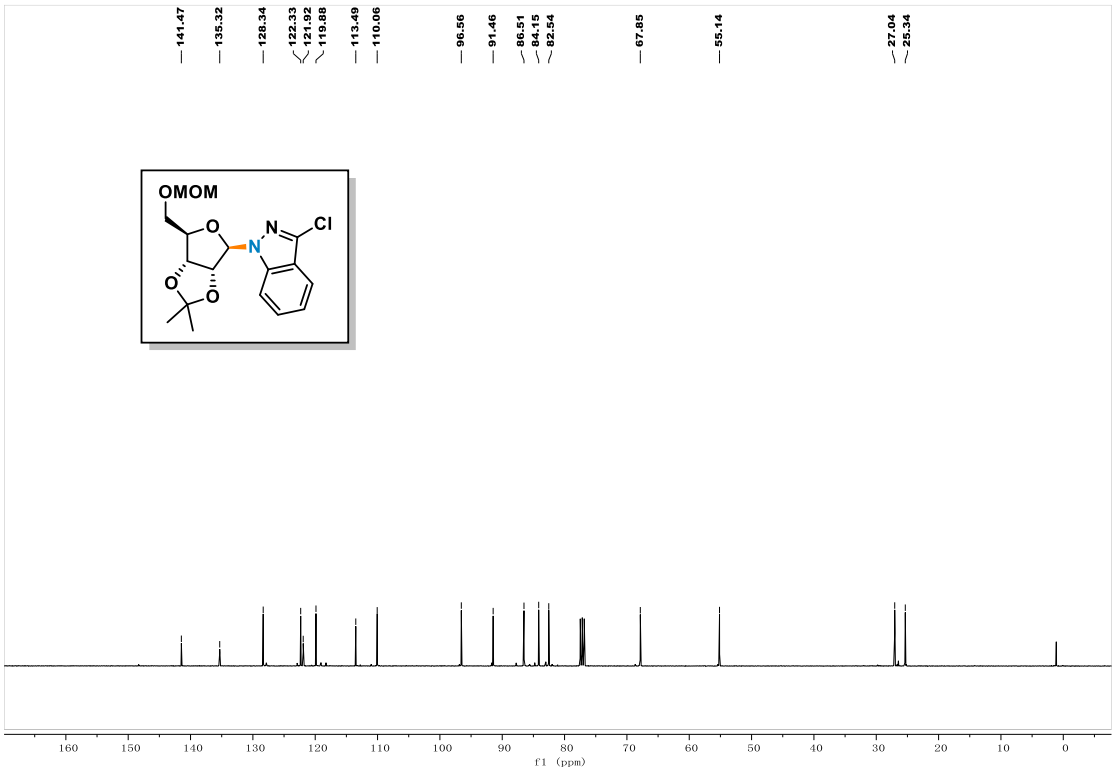
^{13}C NMR (101 MHz, $CDCl_3$) **(8c)**



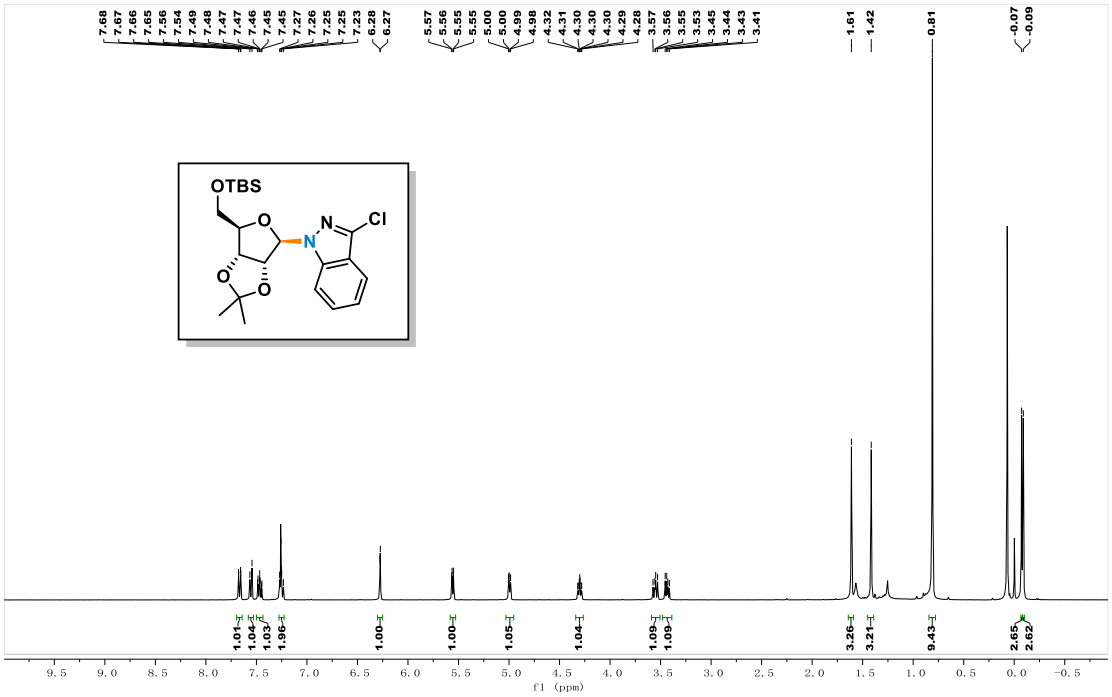
^{1}H NMR (400 MHz, $CDCl_3$) **(8d)**



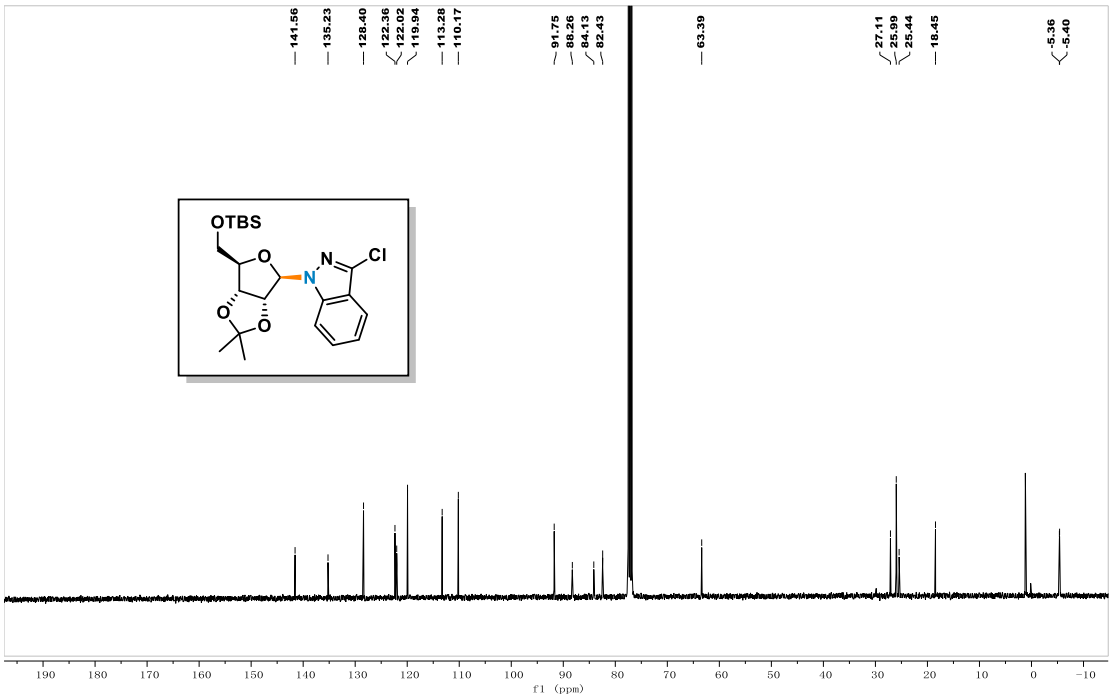
^{13}C NMR (101 MHz, $CDCl_3$) **(8d)**



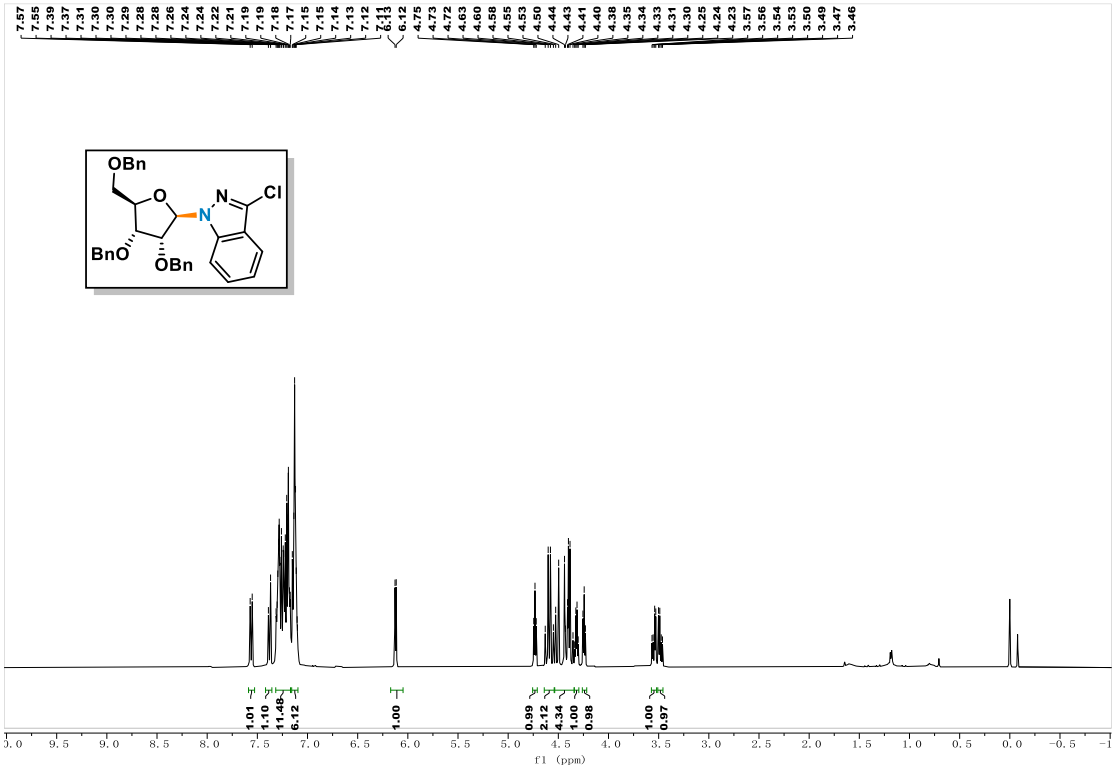
^{1}H NMR (400 MHz, $CDCl_3$) **(8e)**



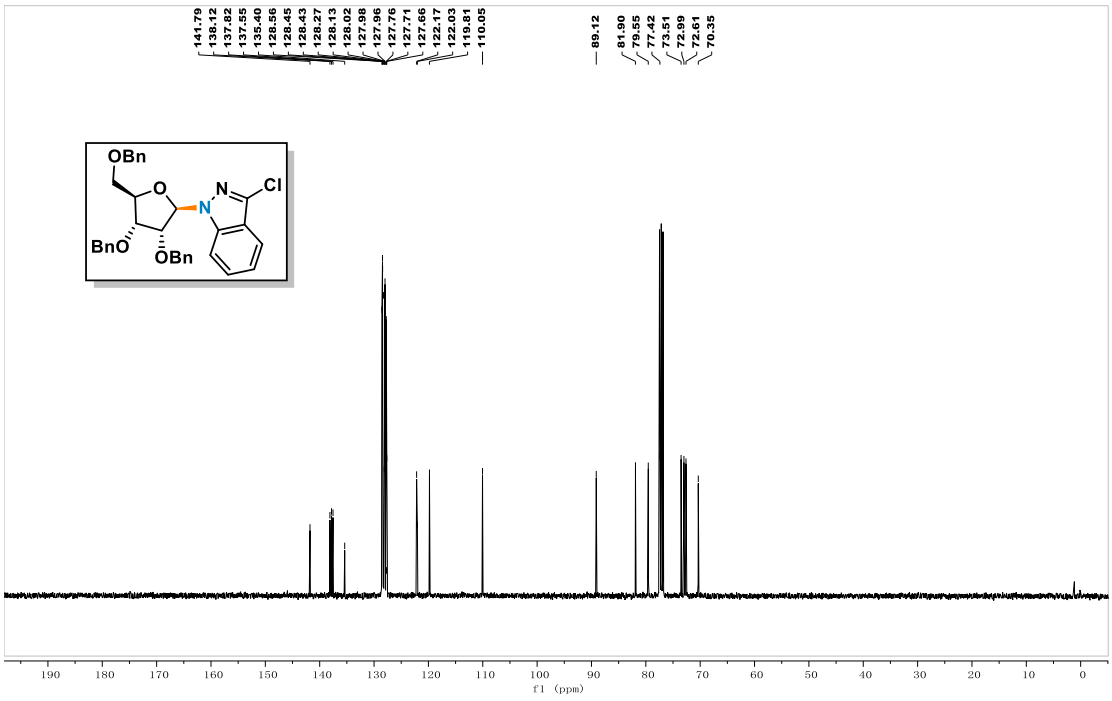
^{13}C NMR (101 MHz, $CDCl_3$) **(8e)**



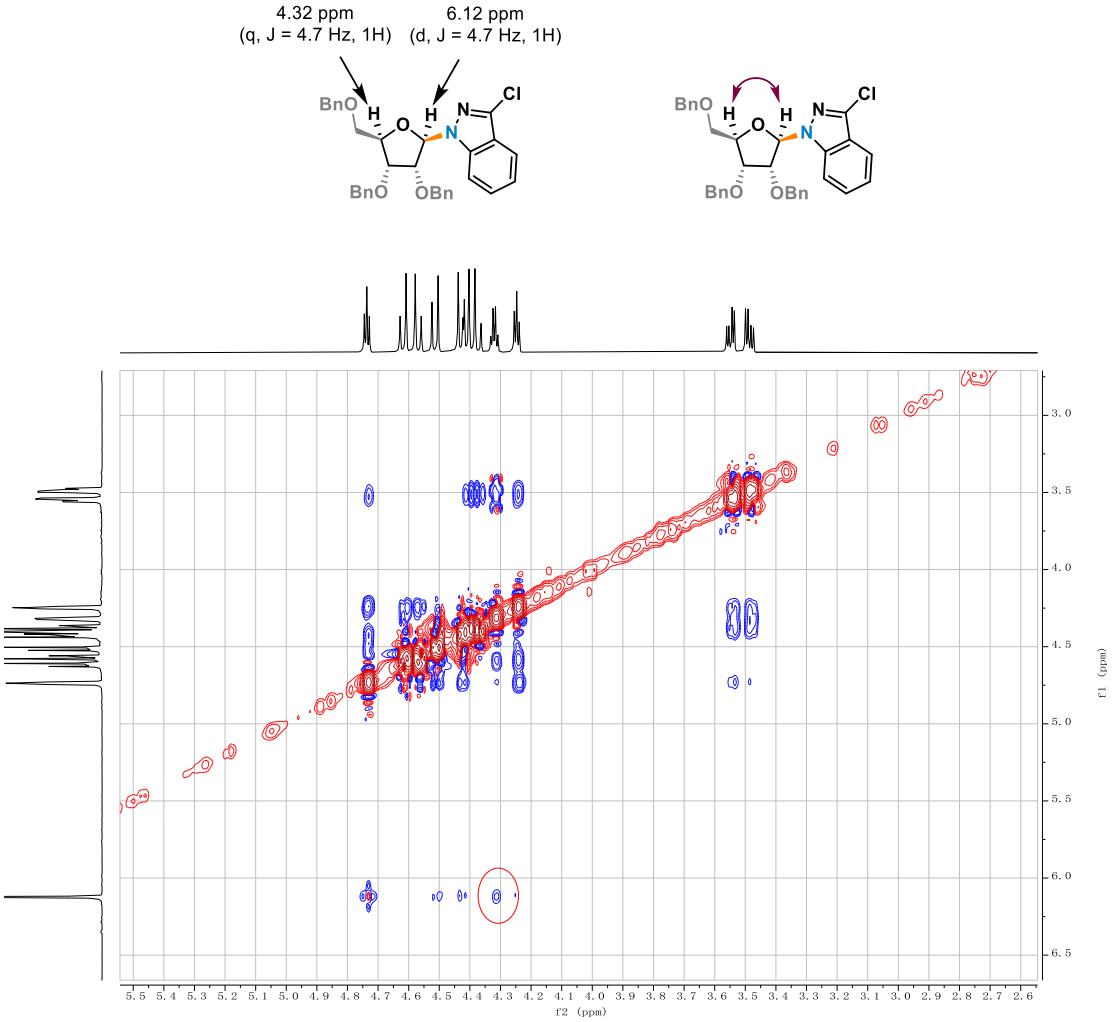
^{1}H NMR (400 MHz, $CDCl_3$) **(8f)**



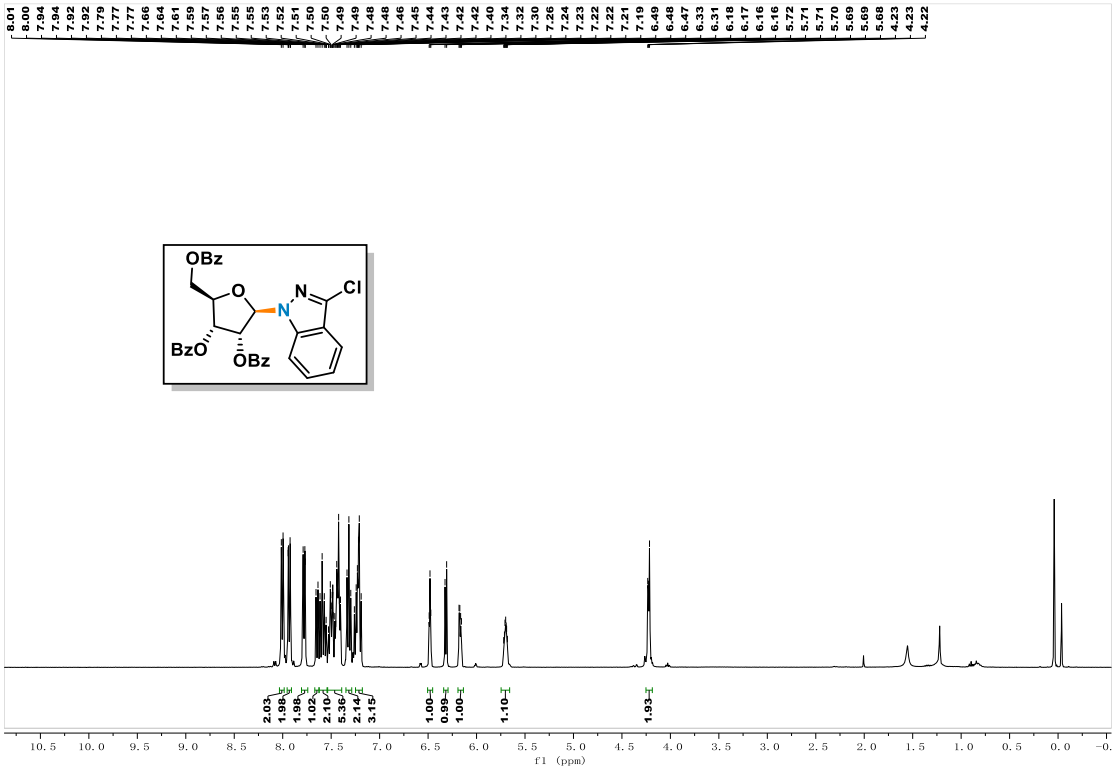
^{13}C NMR (101 MHz, $CDCl_3$) **(8f)**



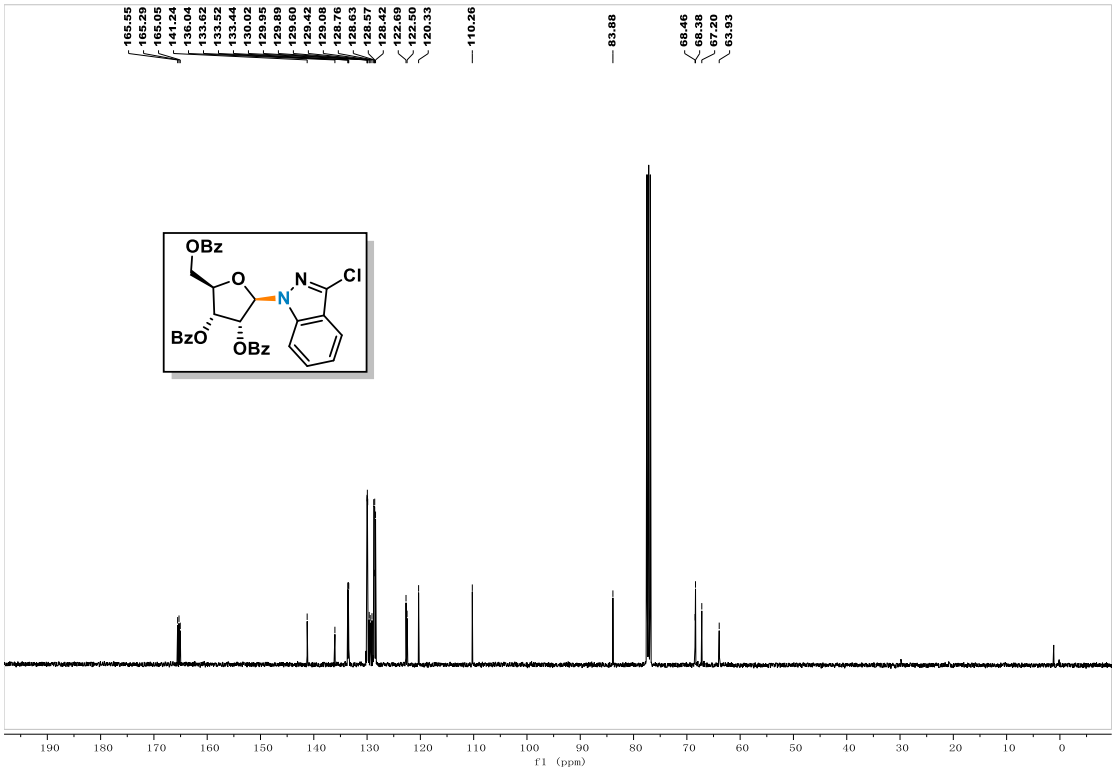
NOESY of **8f**


4.32 ppm
(q, J = 4.7 Hz, 1H)
6.12 ppm
(d, J = 4.7 Hz, 1H)
BnO
H
O
H
N
N
Cl
BnO
OBn
f2 (ppm)
f1 (ppm)

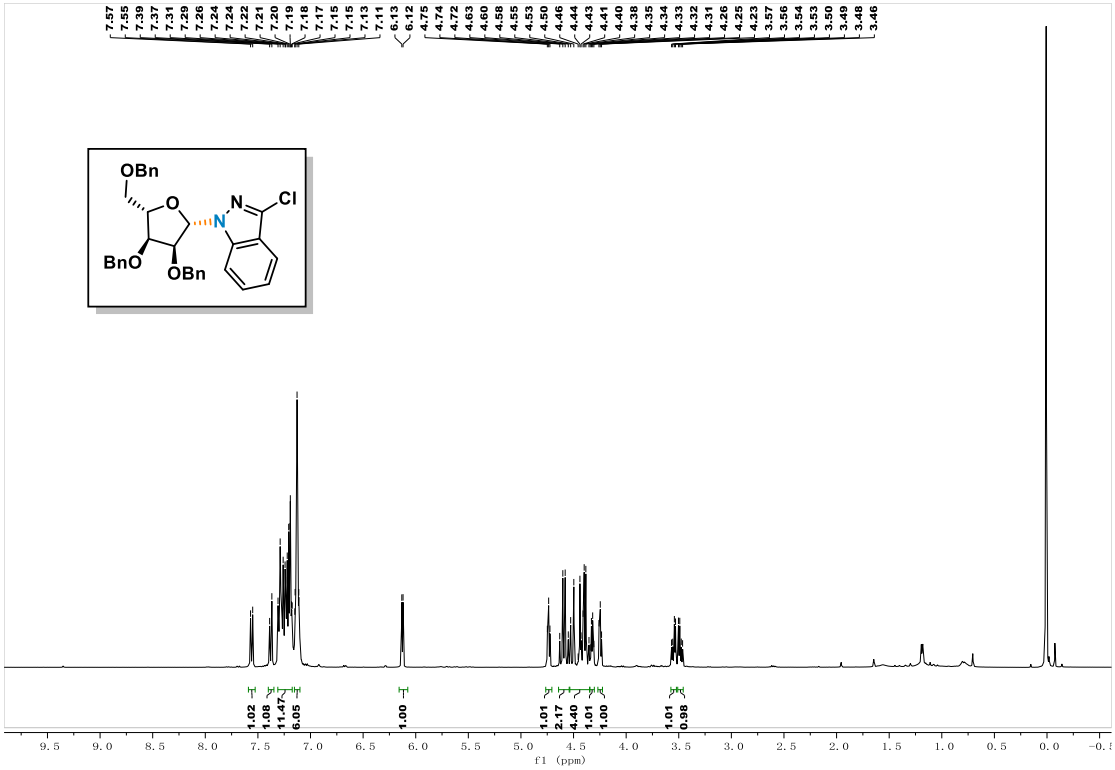
^{1}H NMR (400 MHz, $CDCl_3$) **(8g)**



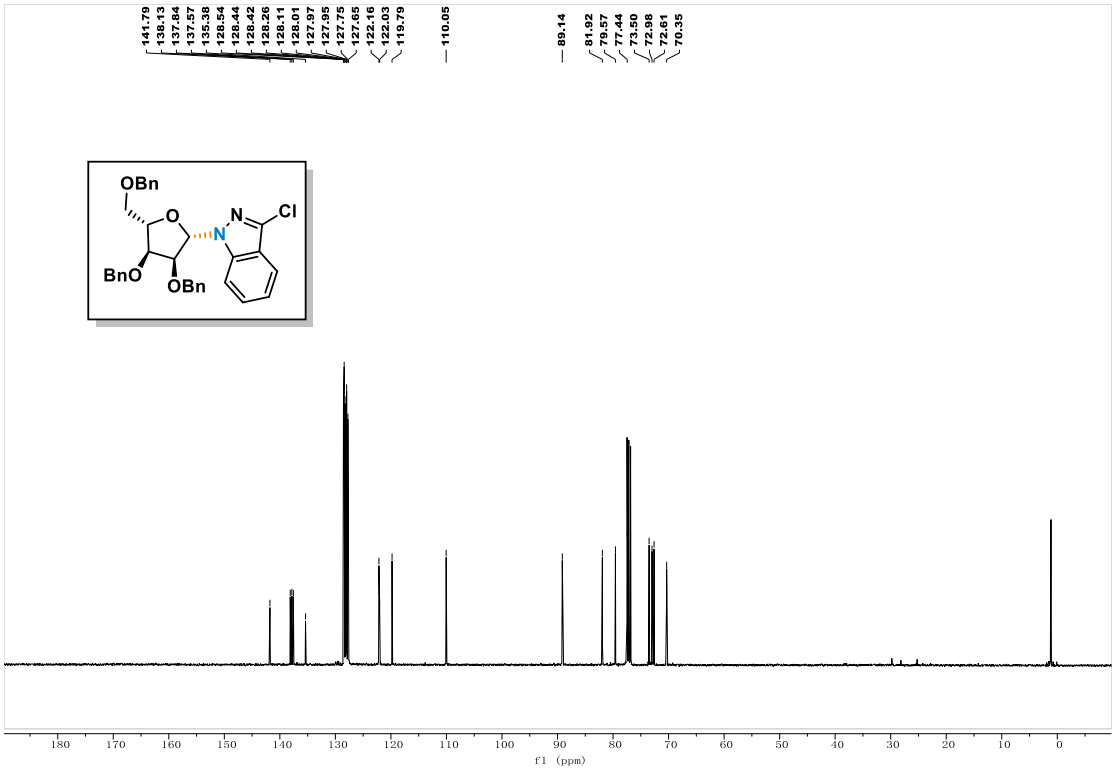
^{13}C NMR (101 MHz, $CDCl_3$) **(8g)**



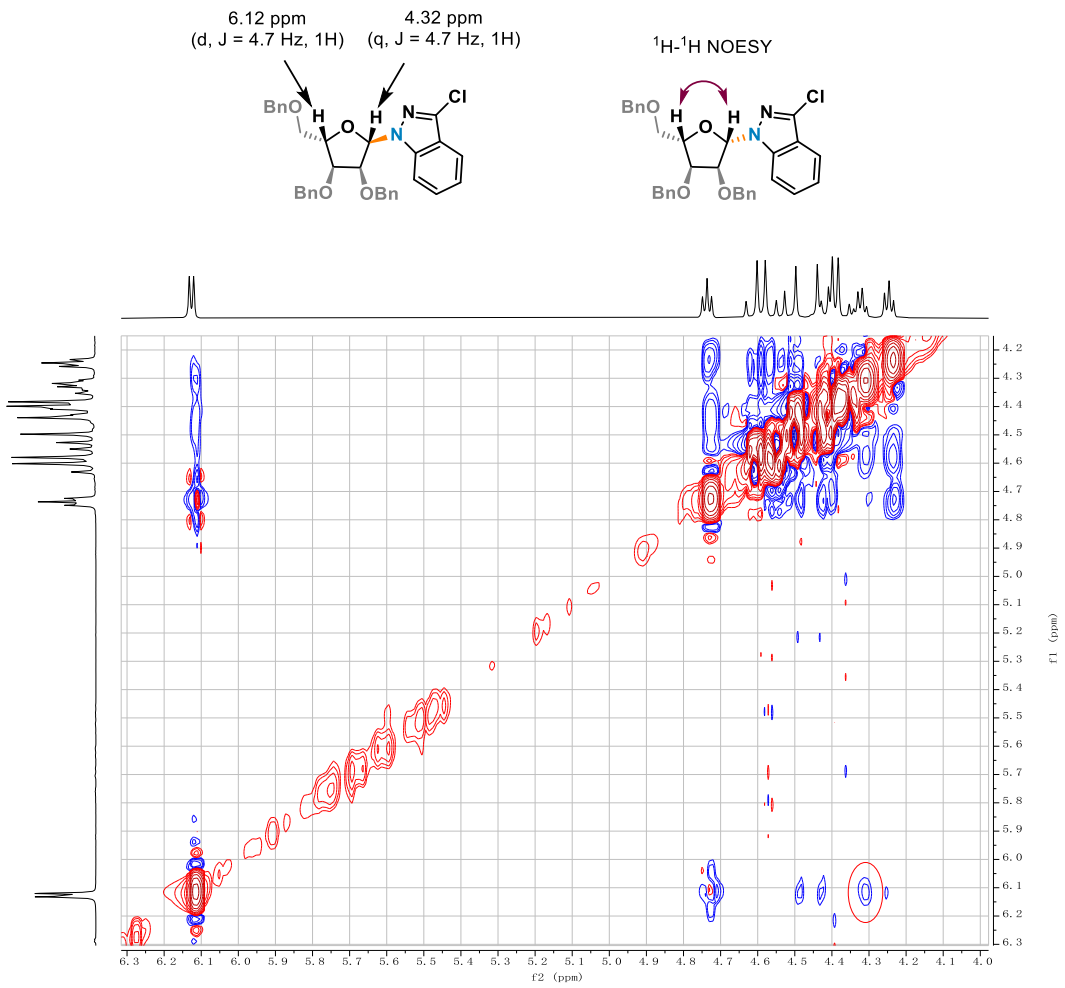
^{1}H NMR (400 MHz, $CDCl_3$) **(8h)**



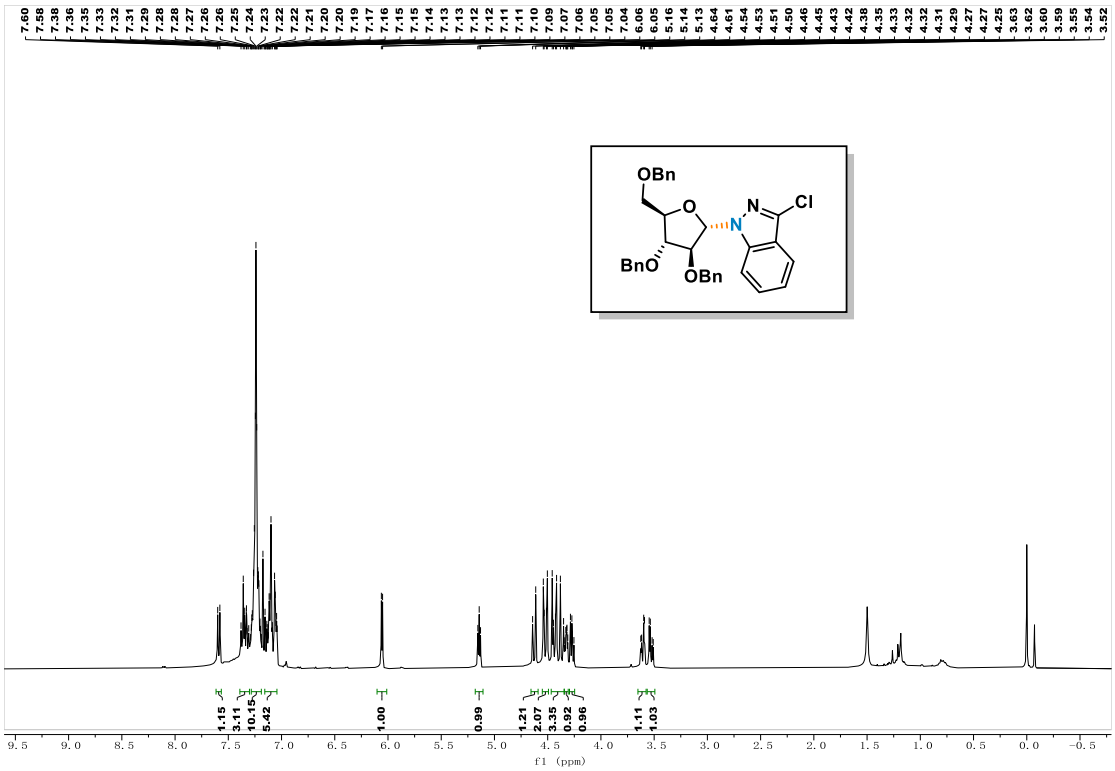
^{13}C NMR (101 MHz, $CDCl_3$) **(8h)**



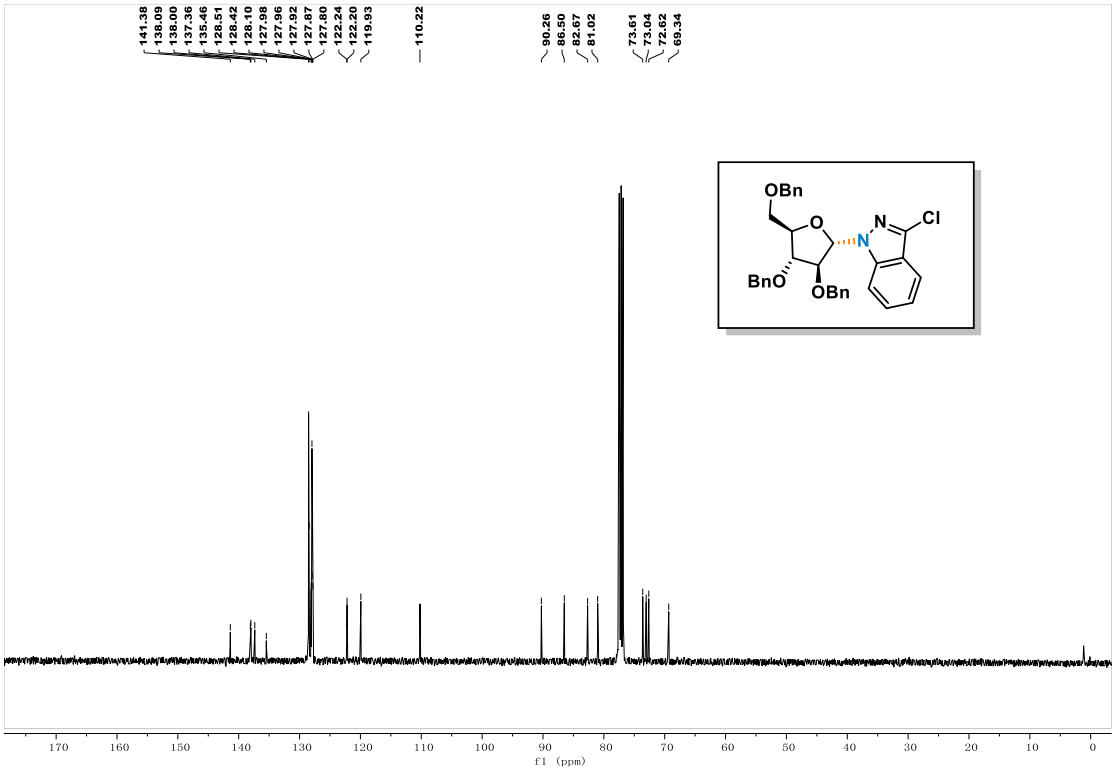
NOESY of **8h**


6.12 ppm
(d, J = 4.7 Hz, 1H)
4.32 ppm
(q, J = 4.7 Hz, 1H)
^{1}H-^{1}H NOESY
BnO
OBn
Cl
N
O
H
f2 (ppm)
f1 (ppm)

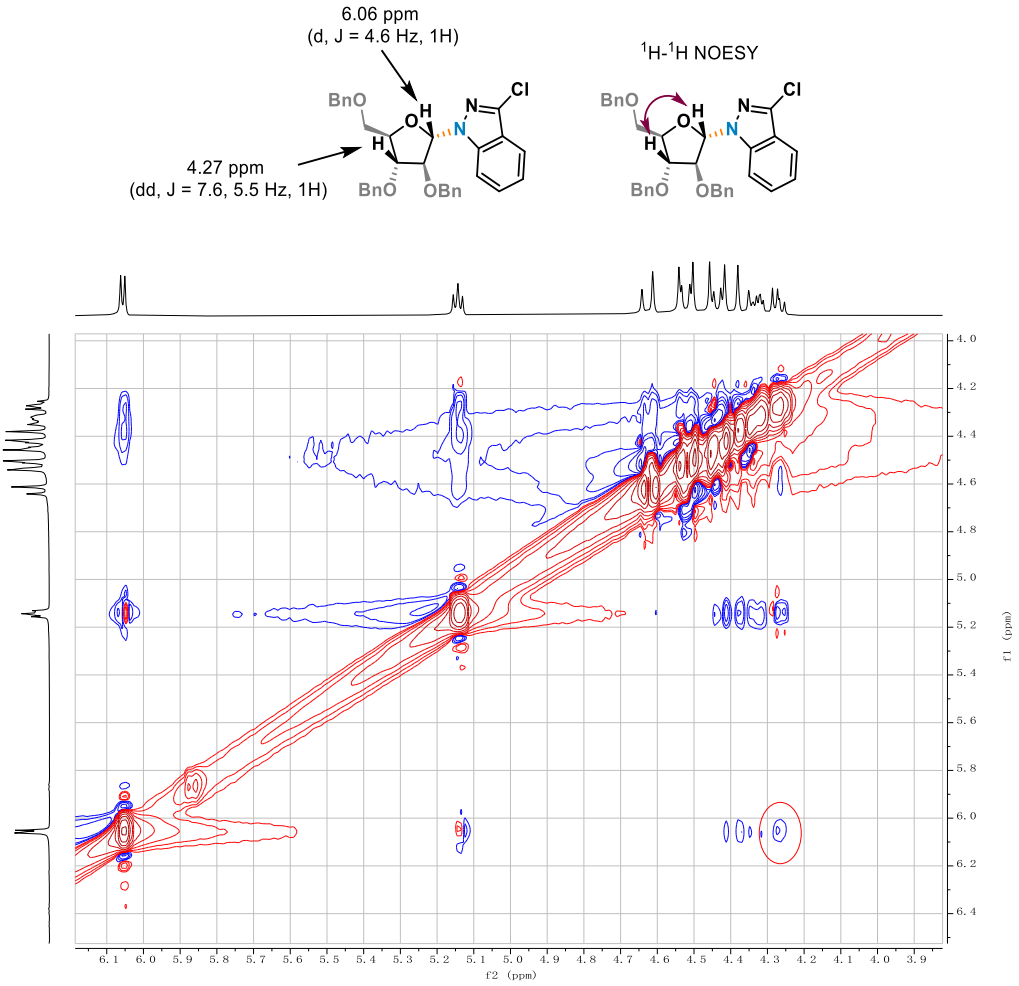
^{1}H NMR (400 MHz, $CDCl_3$) **(8i)**



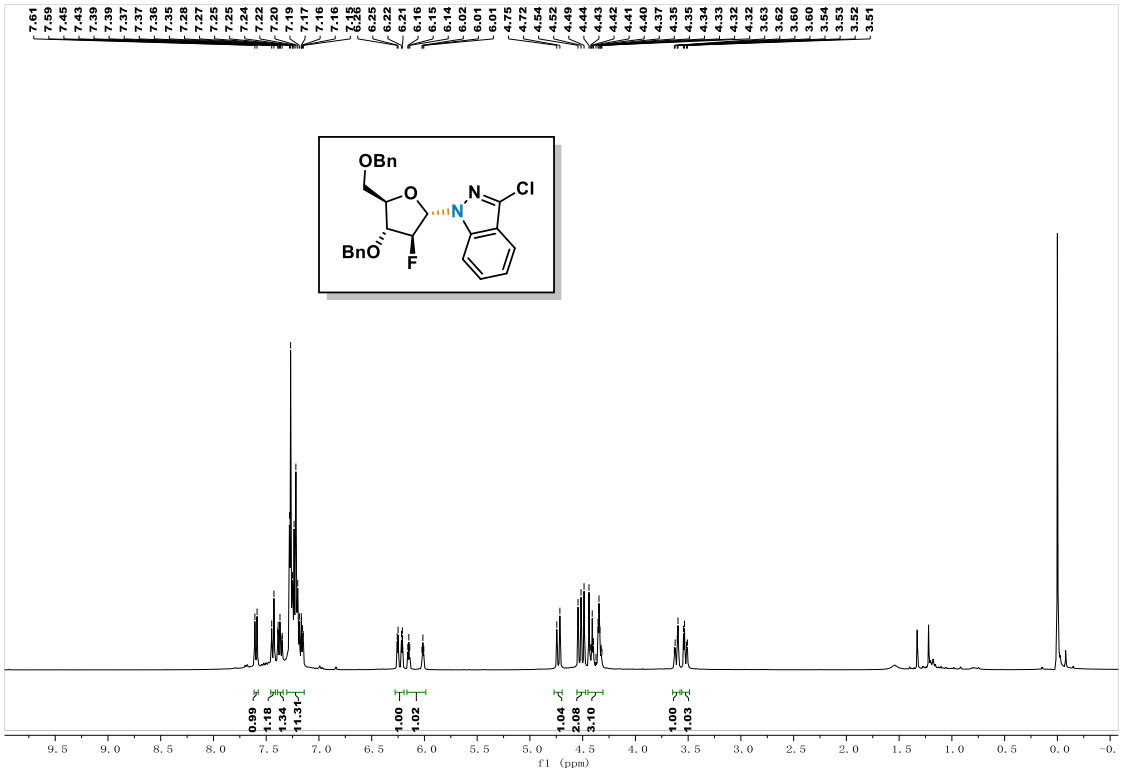
^{13}C NMR (101 MHz, $CDCl_3$) **(8i)**



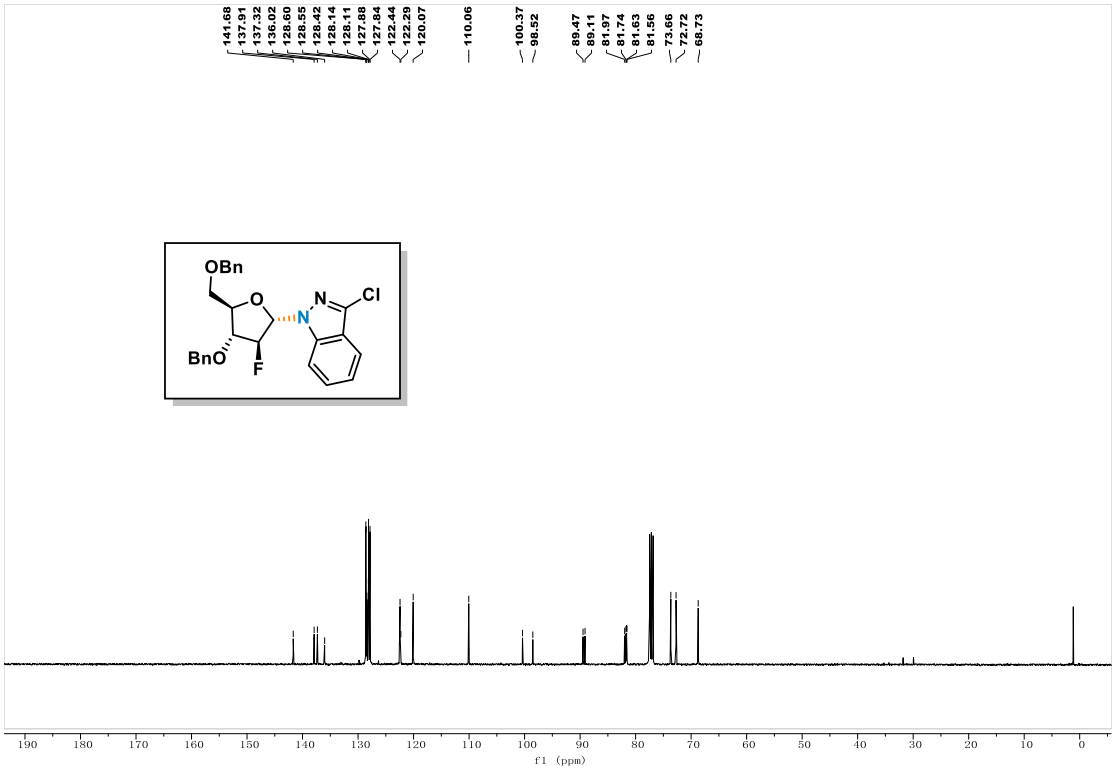
NOESY of **8i**


6.06 ppm
(d, J = 4.6 Hz, 1H)
4.27 ppm
(dd, J = 7.6, 5.5 Hz, 1H)
BnO
OBn
Cl
N
O
H
^{1}H-^{1}H NOESY
f2 (ppm)
f1 (ppm)

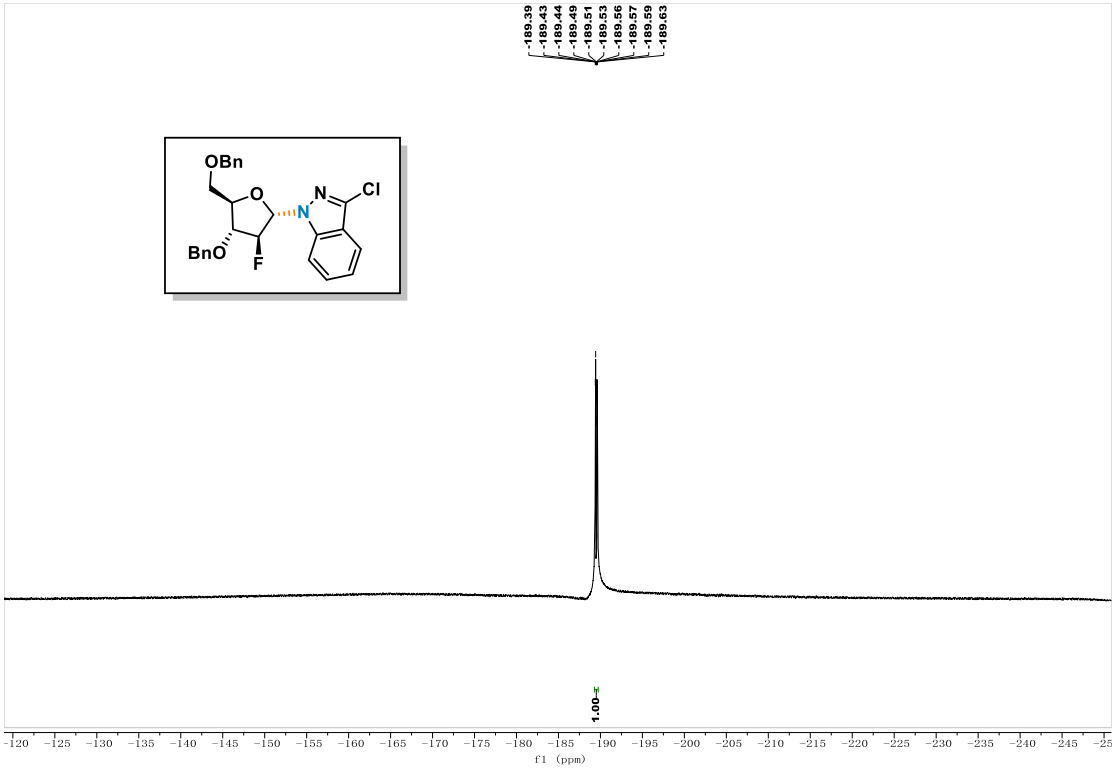
^{1}H NMR (400 MHz, $CDCl_3$) **(8j)**



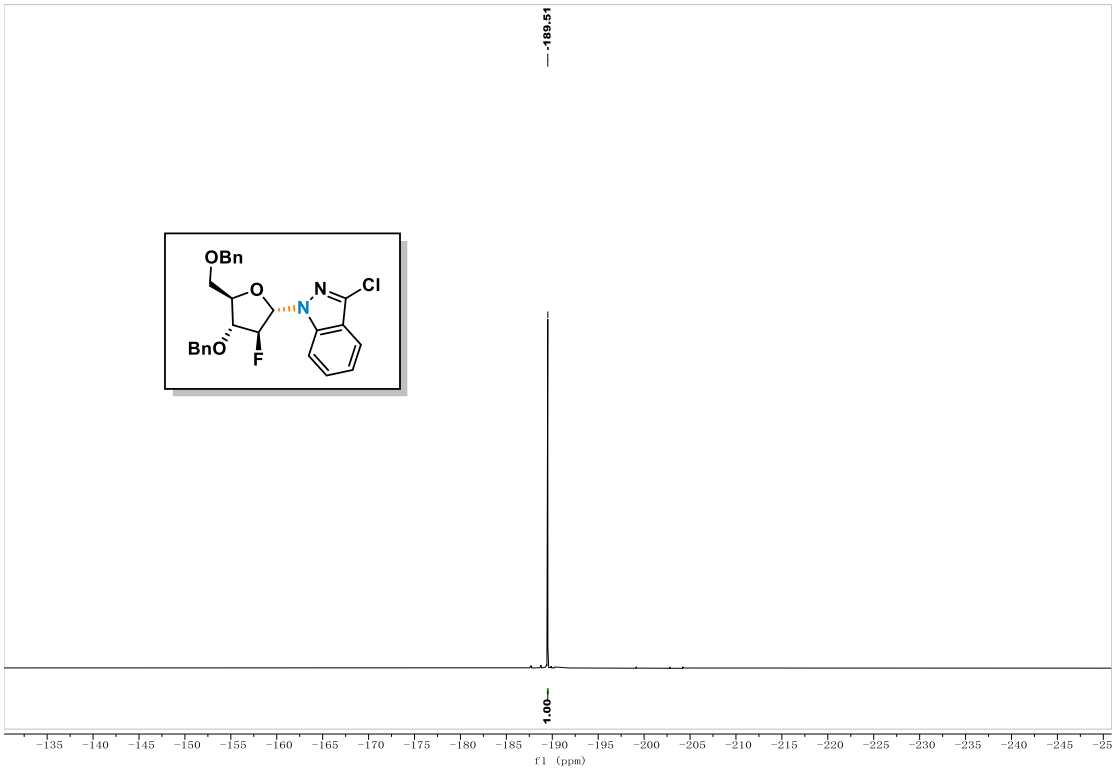
^{13}C NMR (101 MHz, $CDCl_3$) **(8j)**



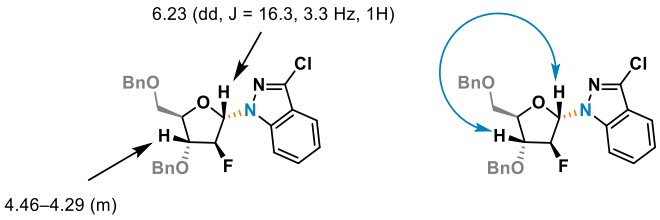
^{19}F NMR (376 MHz, $CDCl_3$) **(8j)**

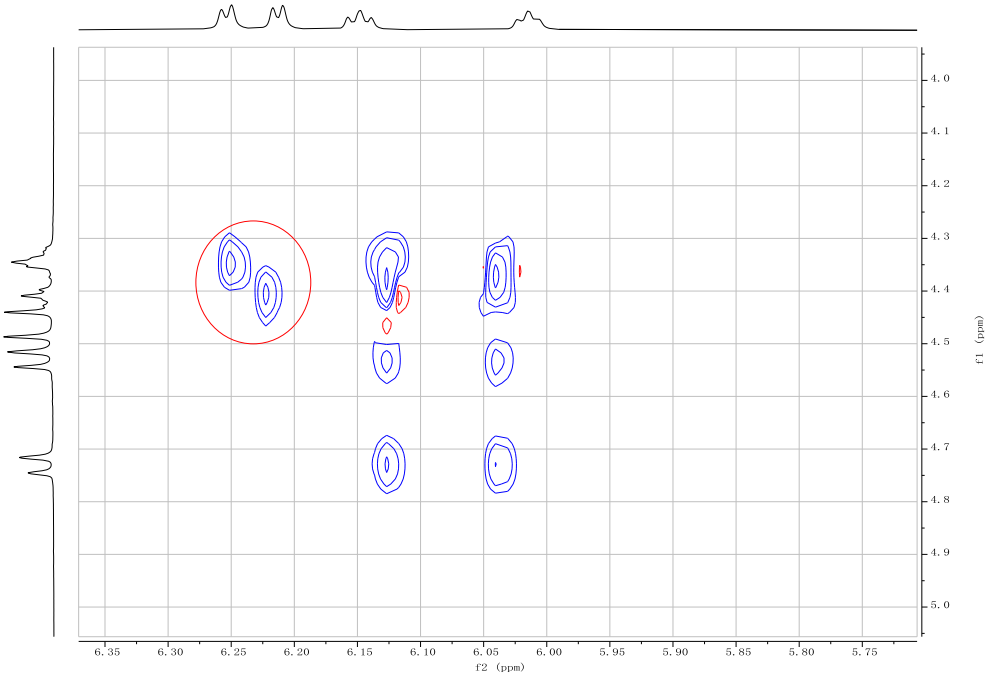


^{19}F{H} NMR (376 MHz, $CDCl_3$) **(8j)**

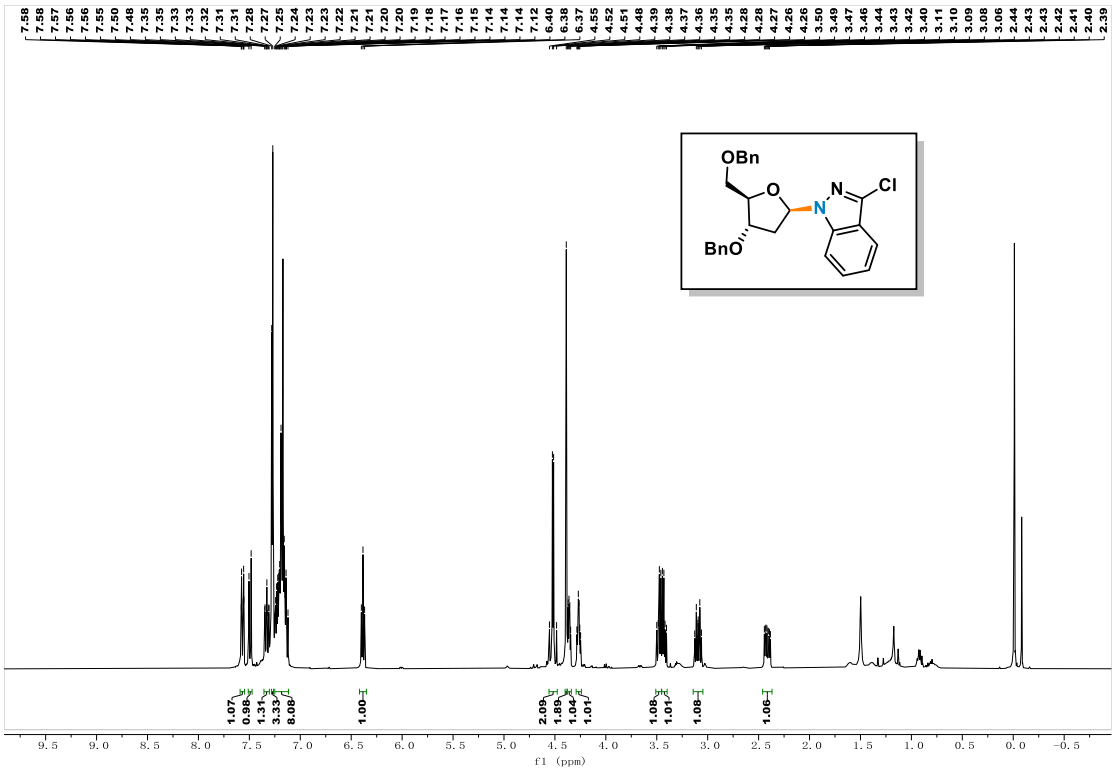


NOESY of **8j**

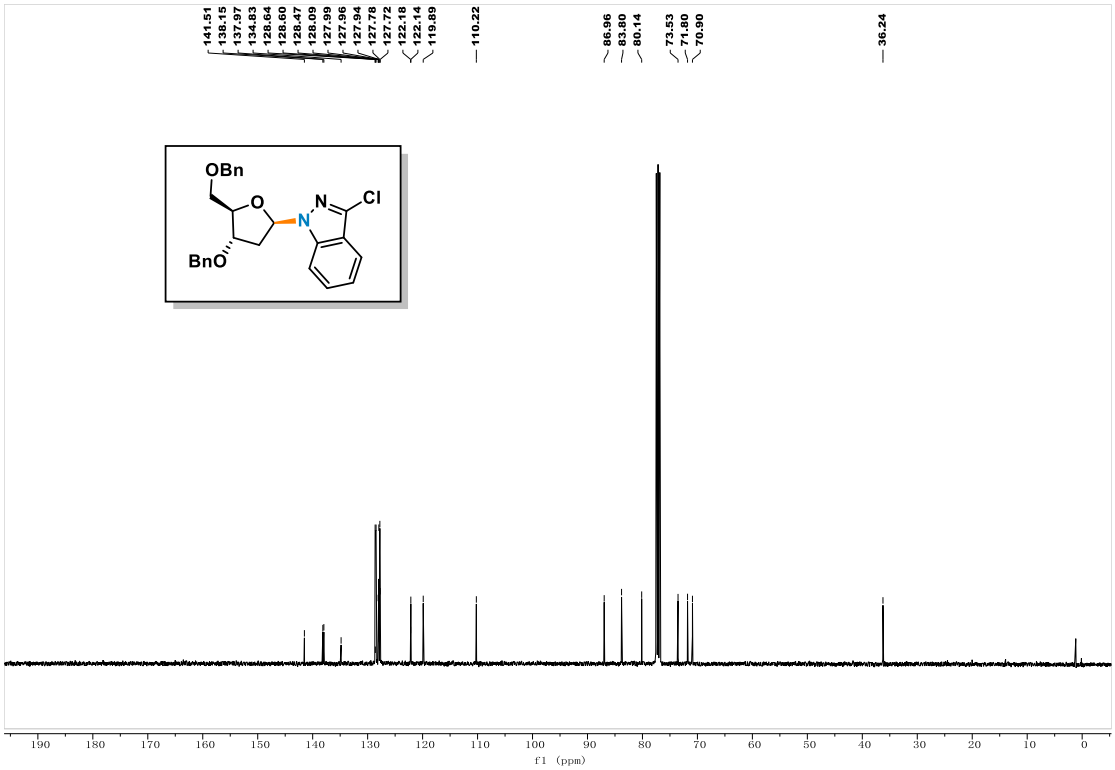

6.23 (dd, J = 16.3, 3.3 Hz, 1H)
4.46–4.29 (m)
BnO
Cl
N
O
H
F


4.0
4.1
4.2
4.3
4.4
4.5
4.6
4.7
4.8
4.9
5.0
f1 (ppm)
6.35
6.30
6.25
6.20
6.15
6.10
6.05
6.00
5.95
5.90
5.85
5.80
5.75
f2 (ppm)

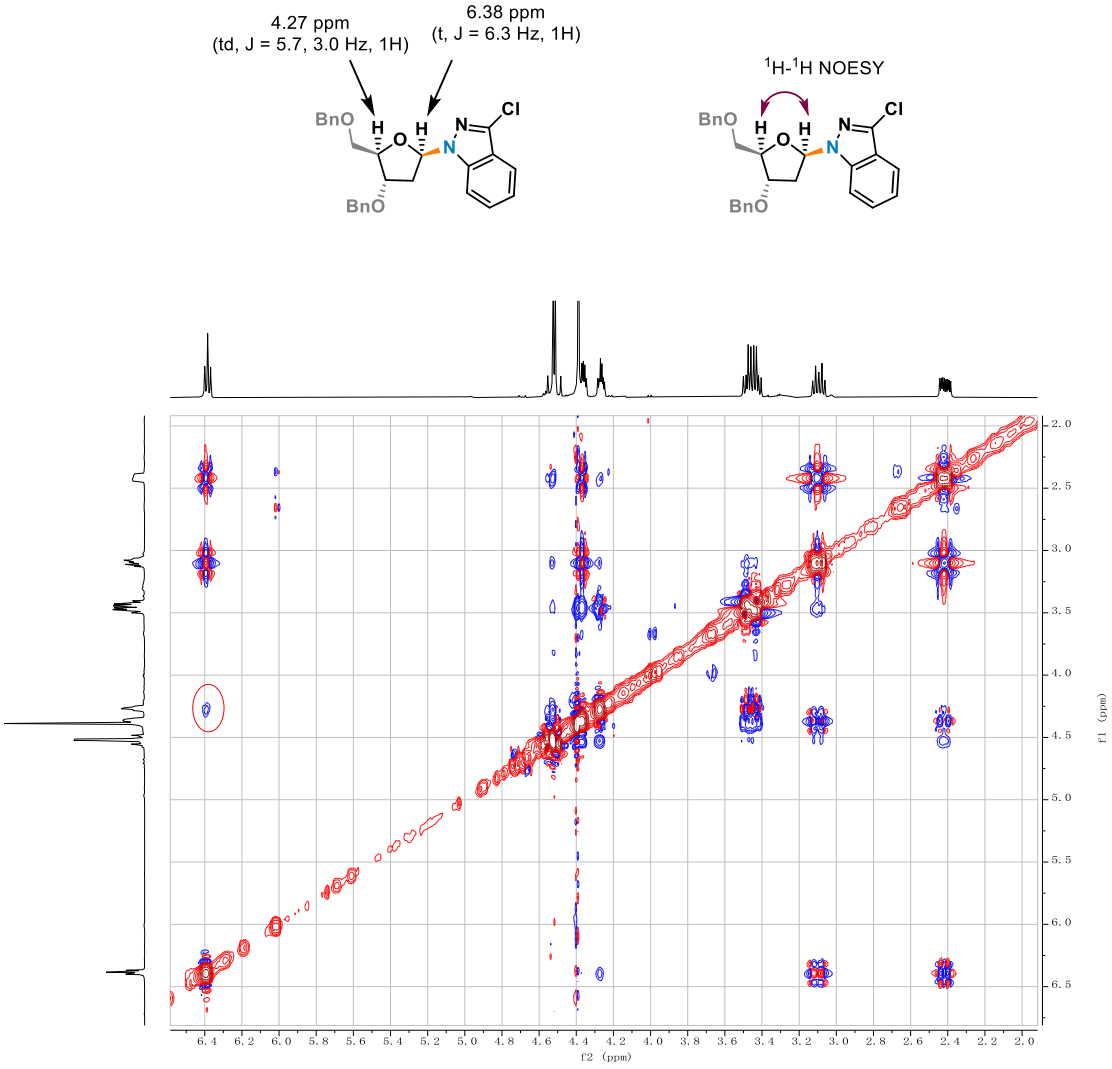
^{1}H NMR (400 MHz, $CDCl_3$) **(8ka)**



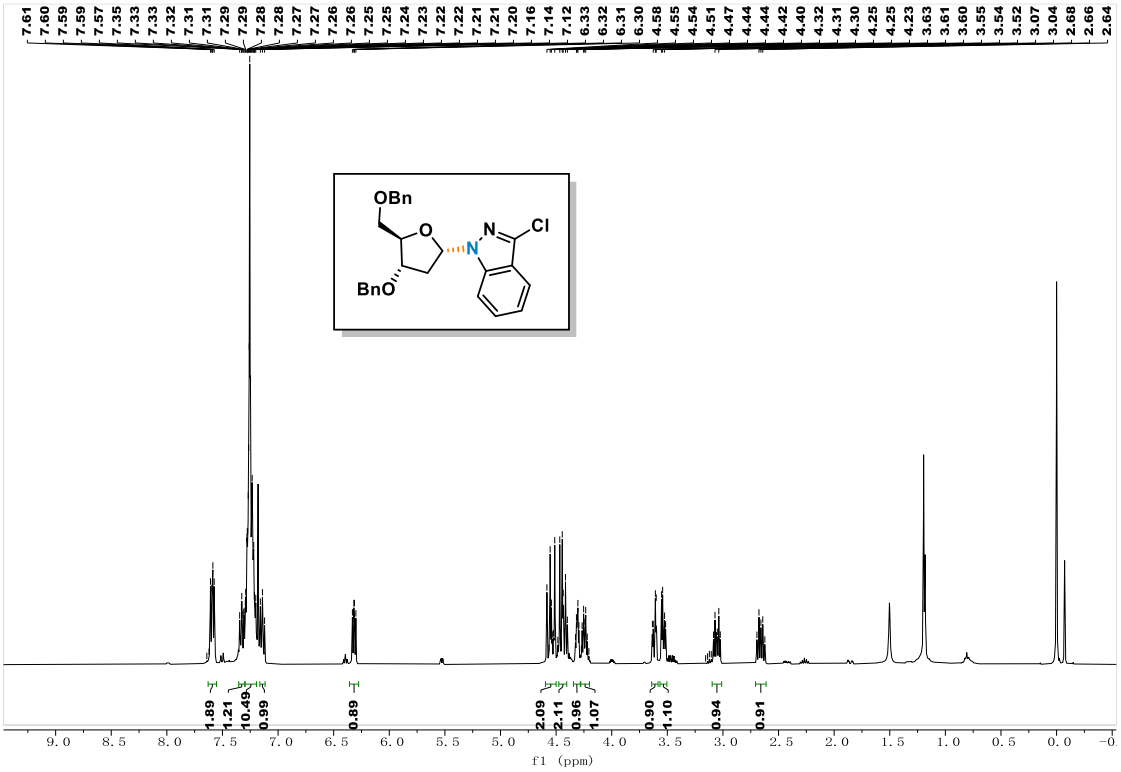
^{13}C NMR (101 MHz, $CDCl_3$) **(8ka)**



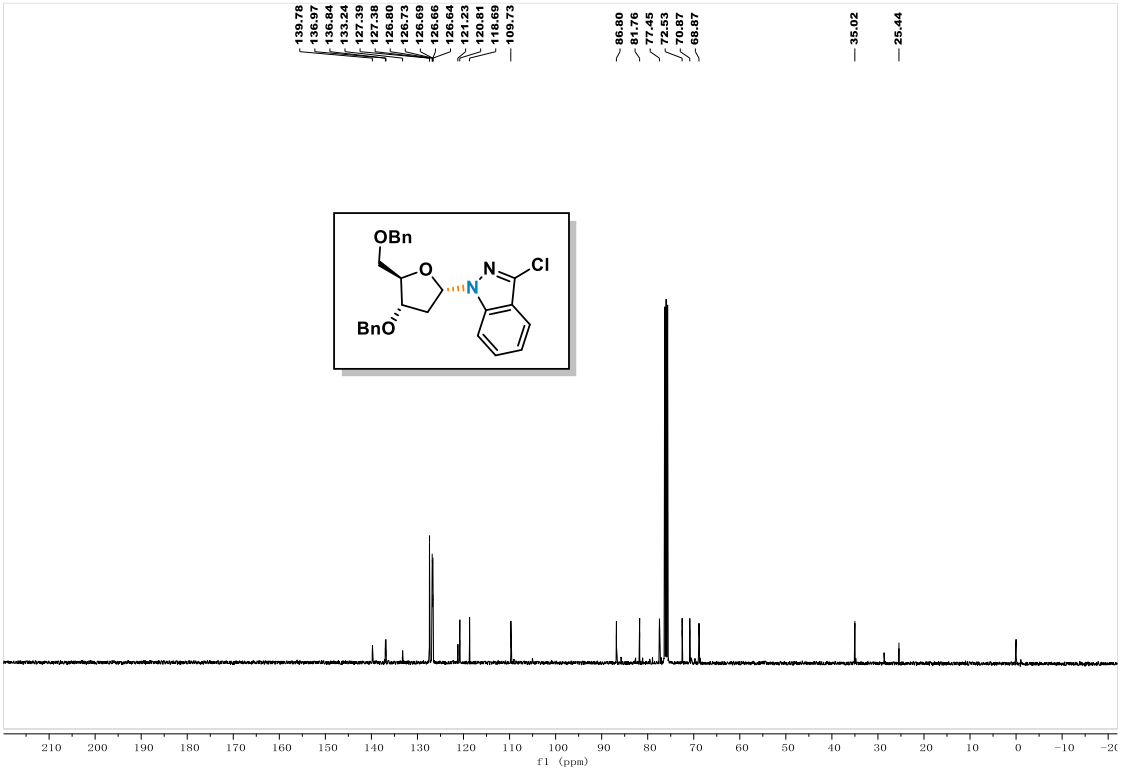
NOESY of **8ka**


4.27 ppm
(td, J = 5.7, 3.0 Hz, 1H)
6.38 ppm
(t, J = 6.3 Hz, 1H)
BnO
H
O
H
N
N
Cl
BnO
^{1}H-^{1}H NOESY
f2 (ppm)
f1 (ppm)

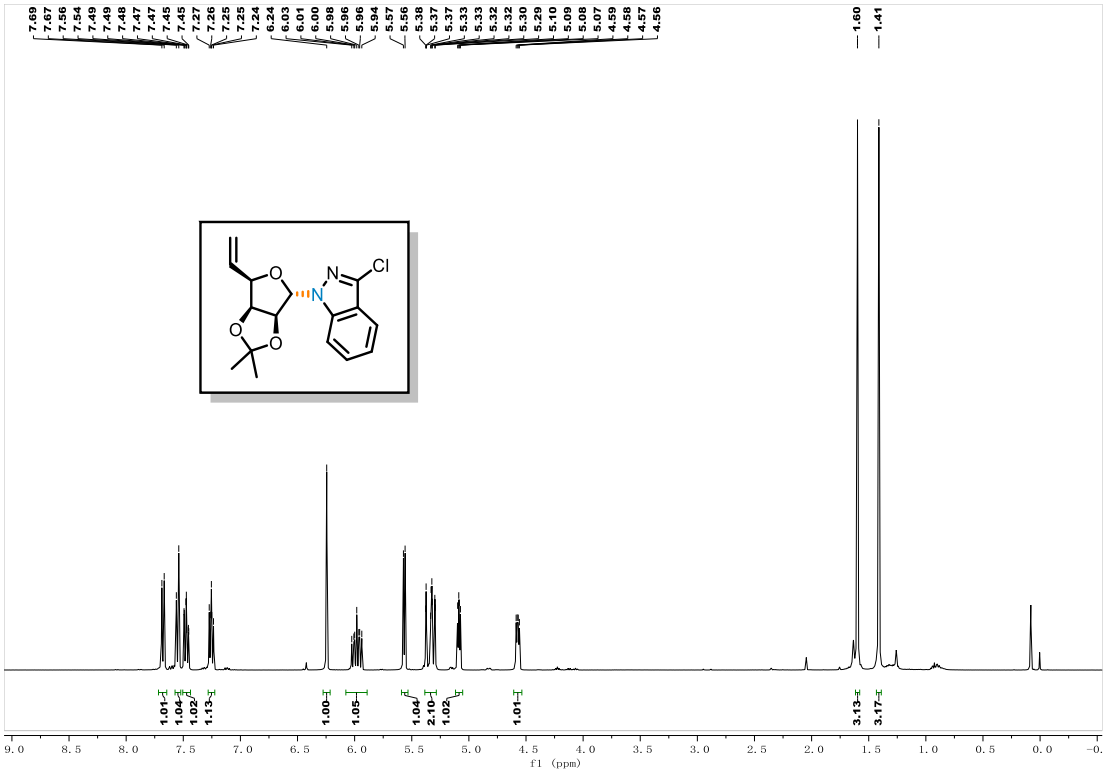
^{1}H NMR (400 MHz, $CDCl_3$) **(8kb)**



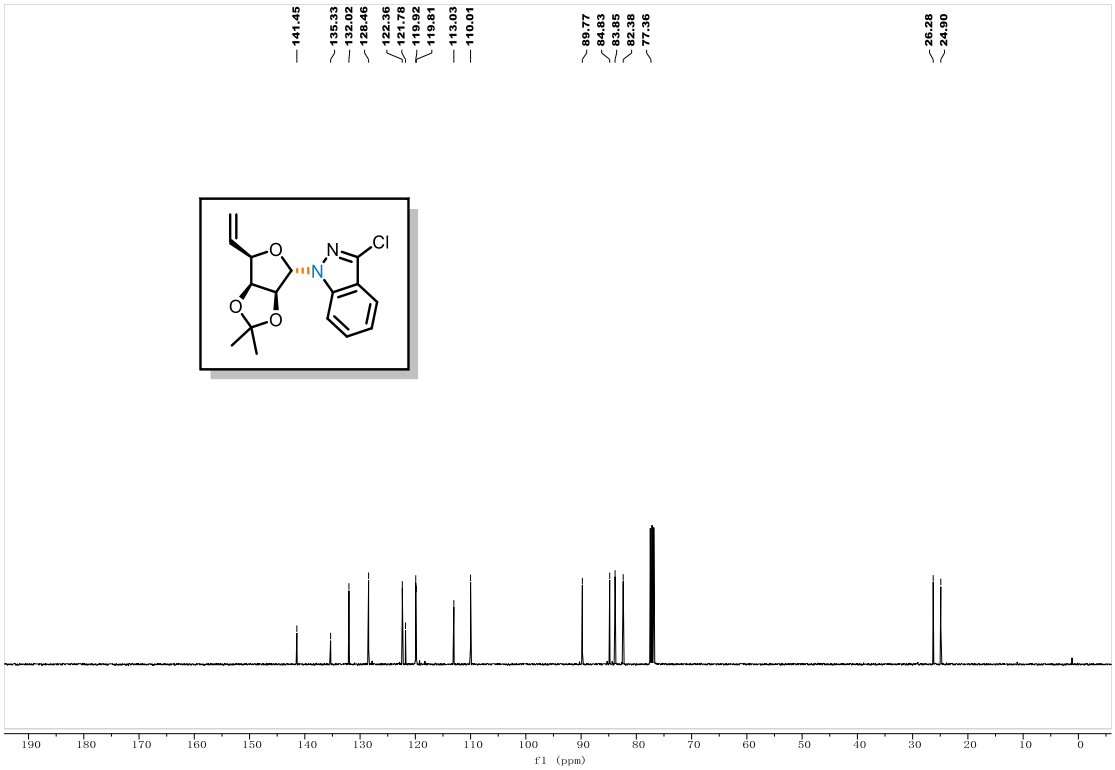
^{13}C NMR (101 MHz, $CDCl_3$) **(8kb)**



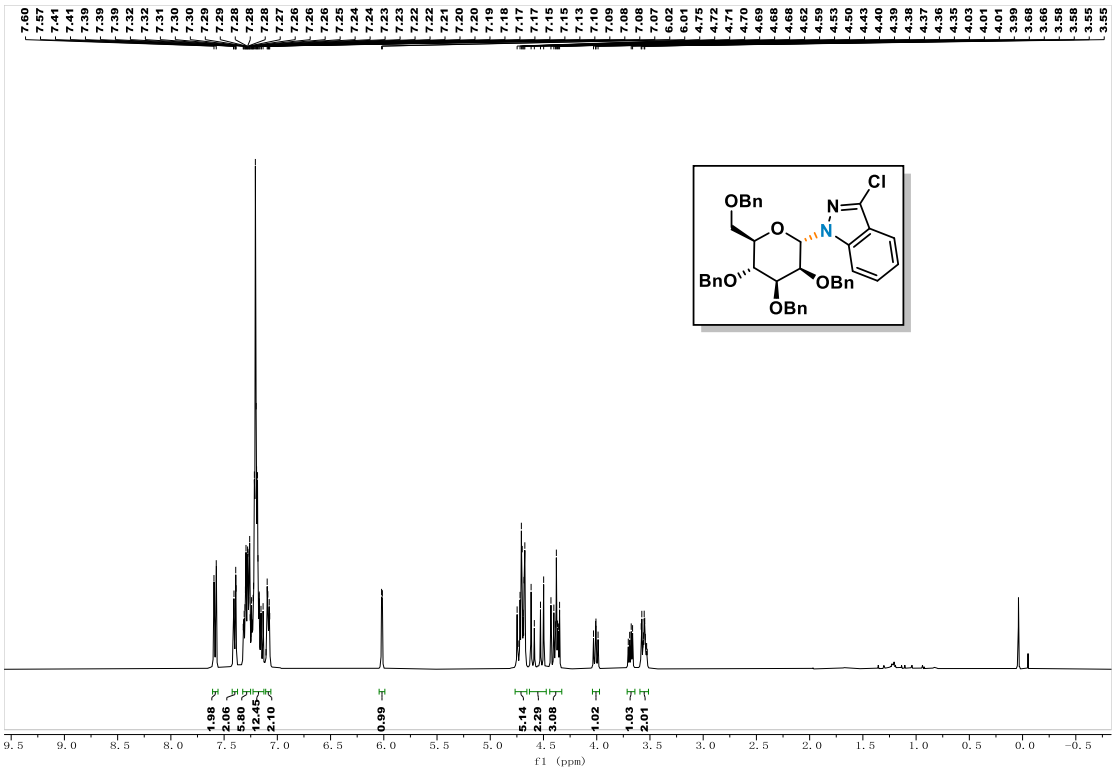
^{1}H NMR (400 MHz, $CDCl_3$) **(8l)**



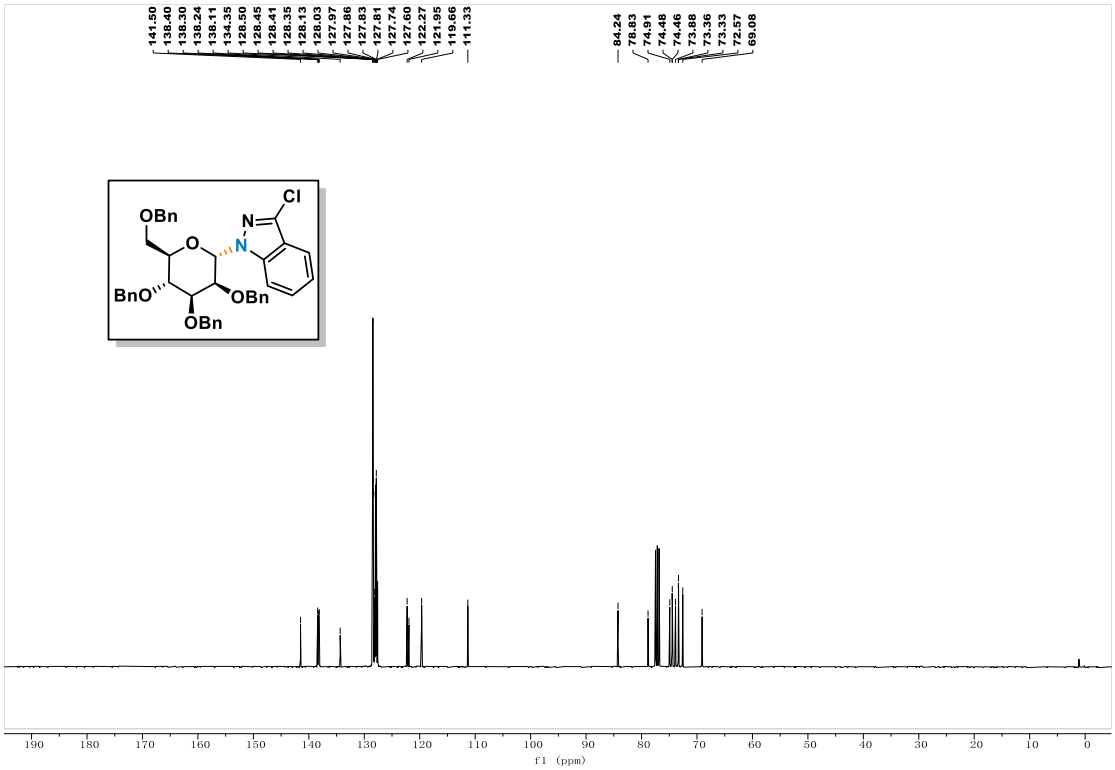
^{13}C NMR (101 MHz, $CDCl_3$) **(8l)**



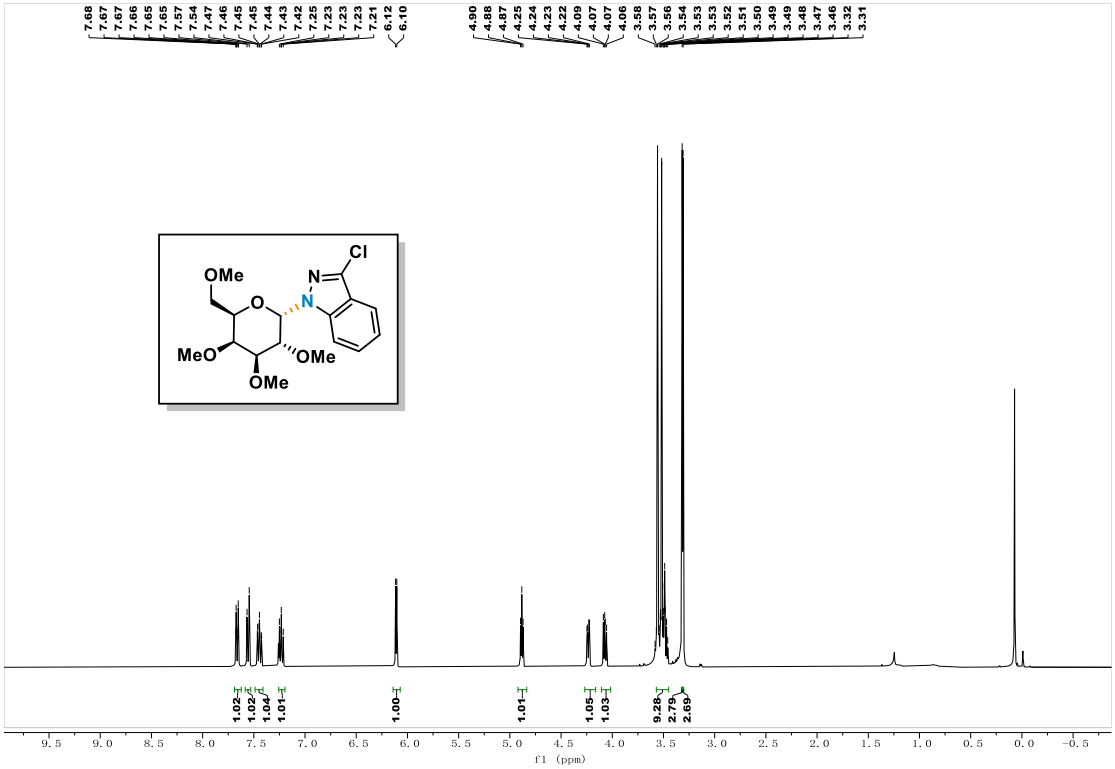
^{1}H NMR (400 MHz, $CDCl_3$) **(8m)**



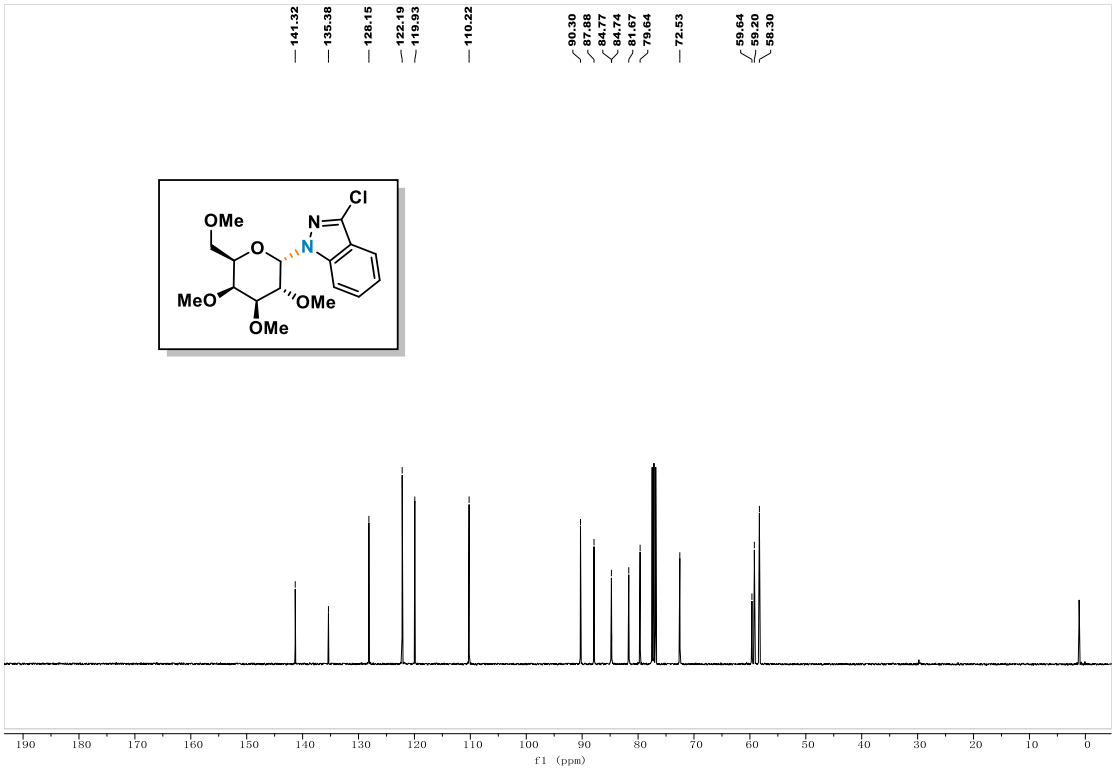
^{13}C NMR (101 MHz, $CDCl_3$) **(8m)**



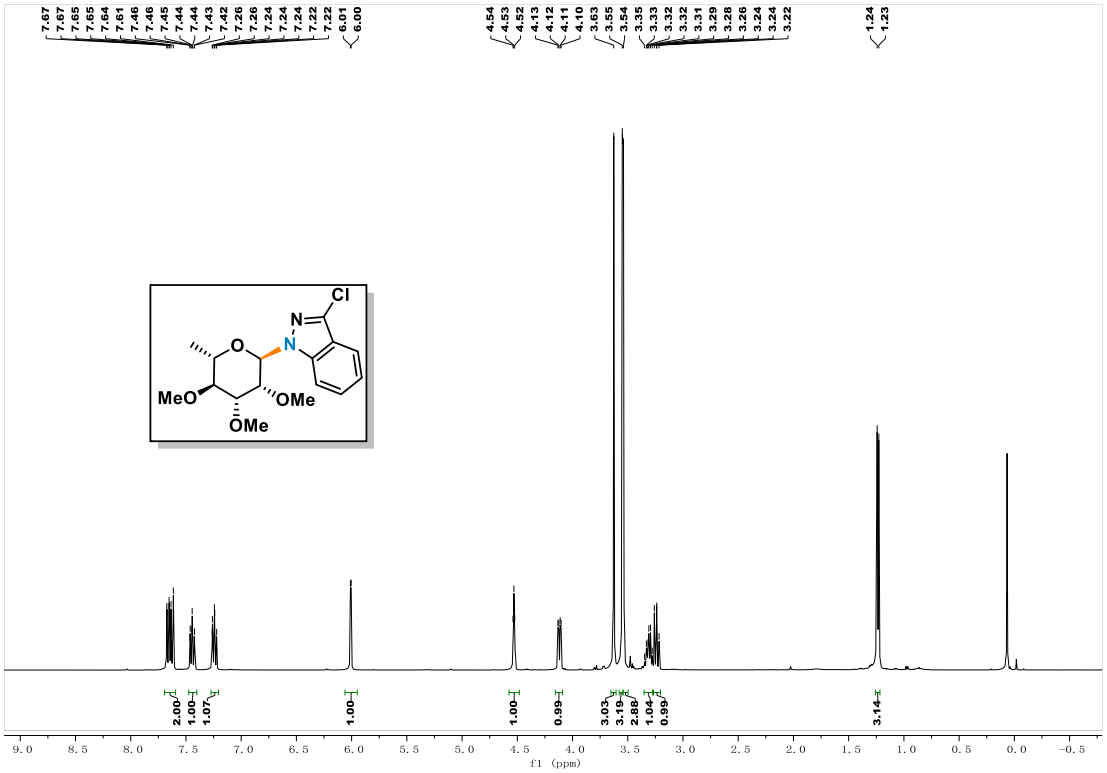
^{1}H NMR (400 MHz, $CDCl_3$) **(8n)**



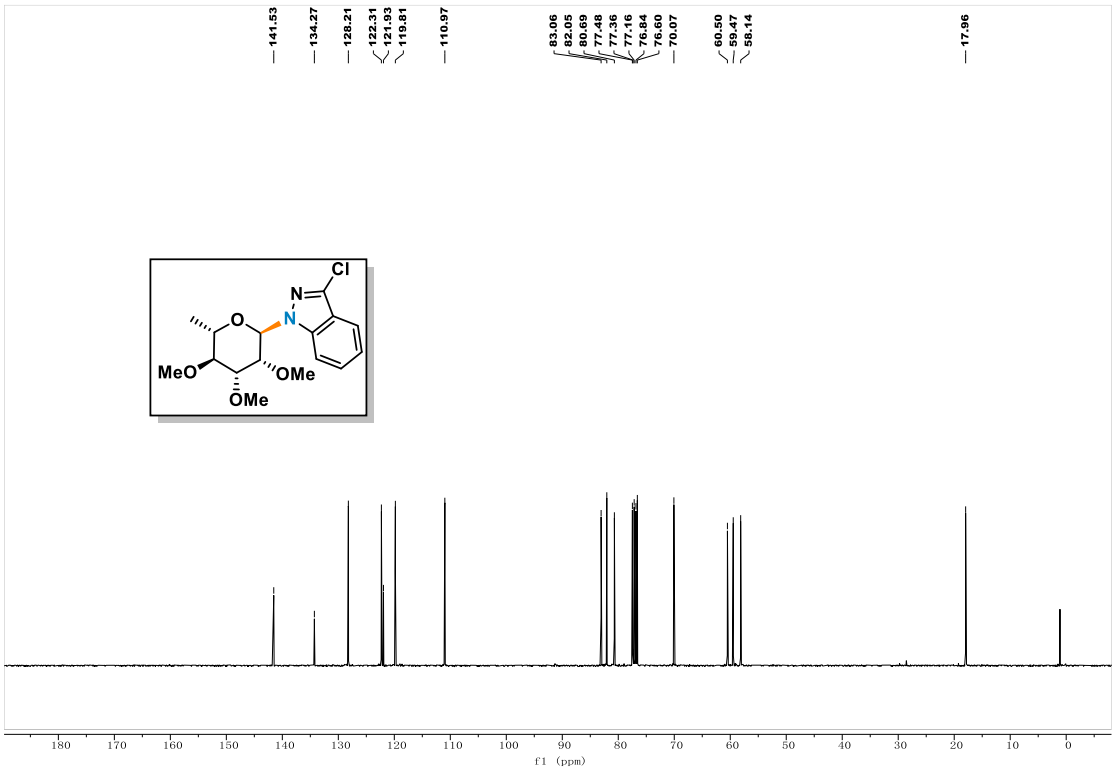
^{13}C NMR (101 MHz, $CDCl_3$) **(8n)**



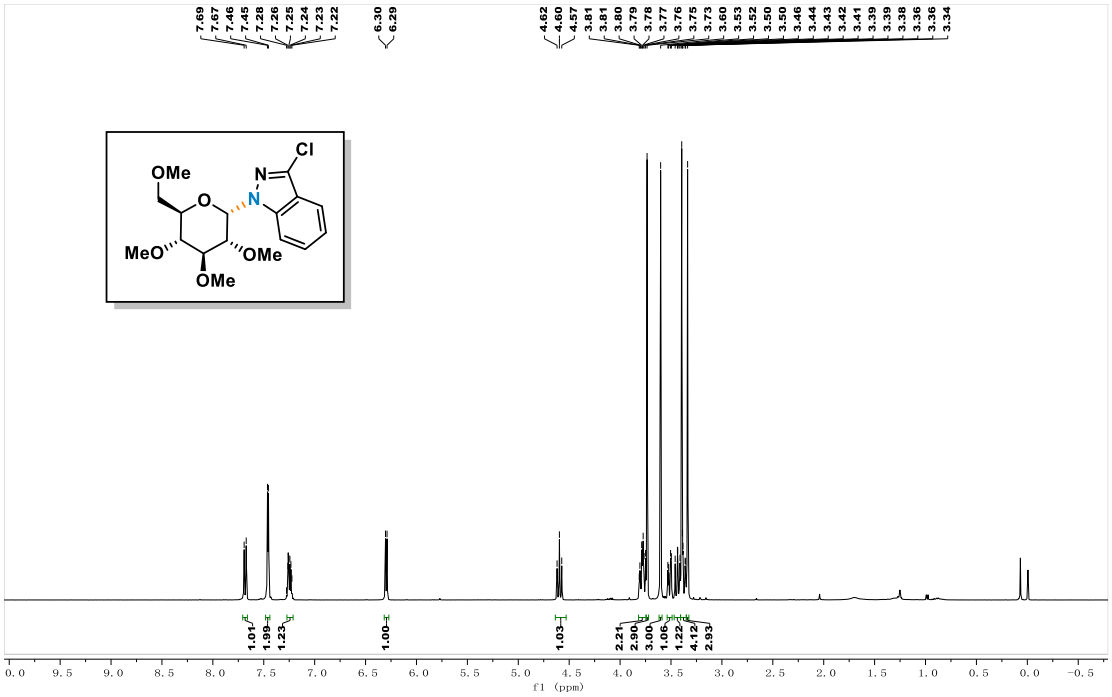
^{1}H NMR (400 MHz, $CDCl_3$) **(8o)**



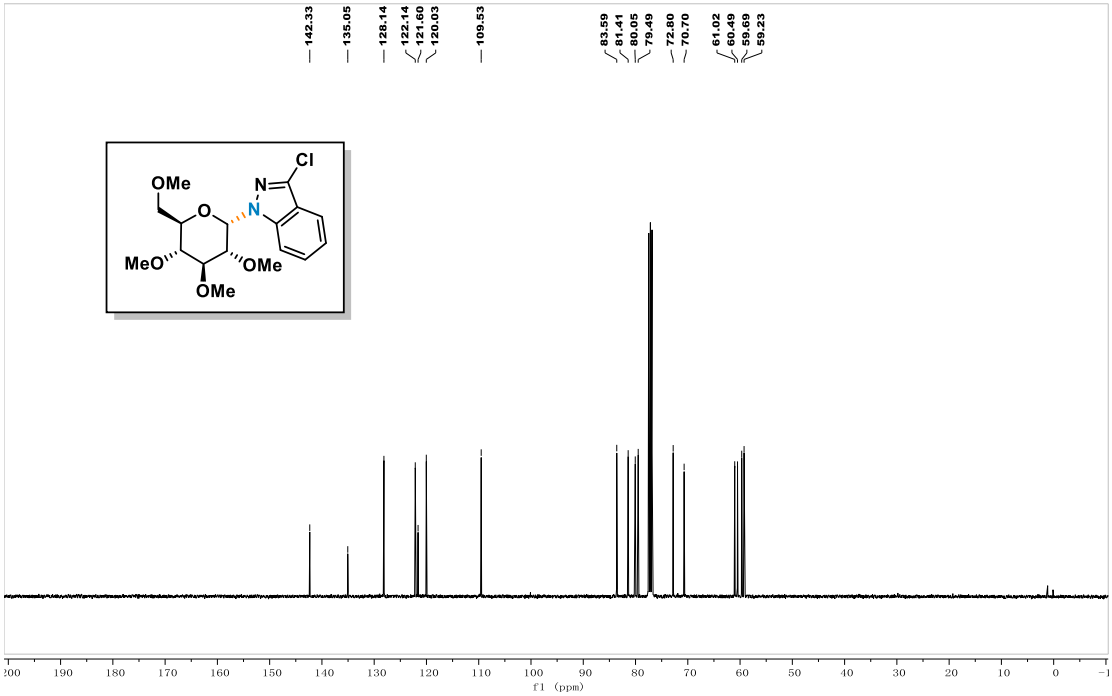
^{13}C NMR (101 MHz, $CDCl_3$) **(8o)**



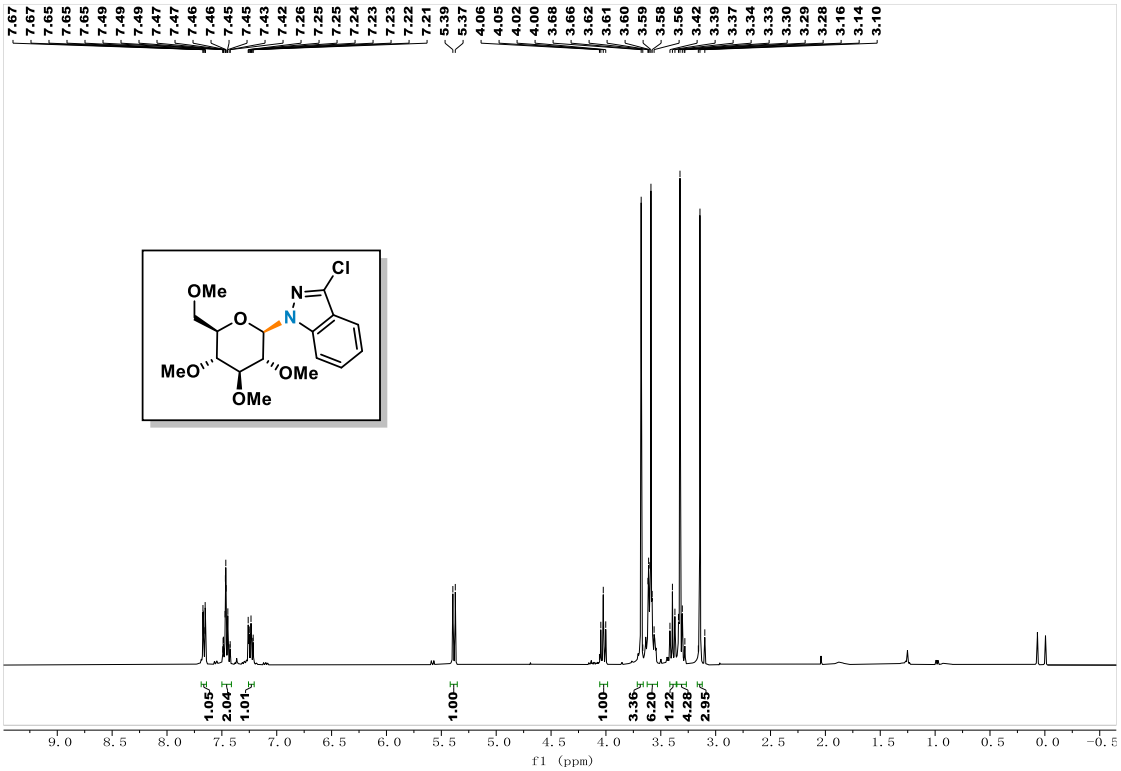
^{1}H NMR (400 MHz, $CDCl_3$) **(8pa)**



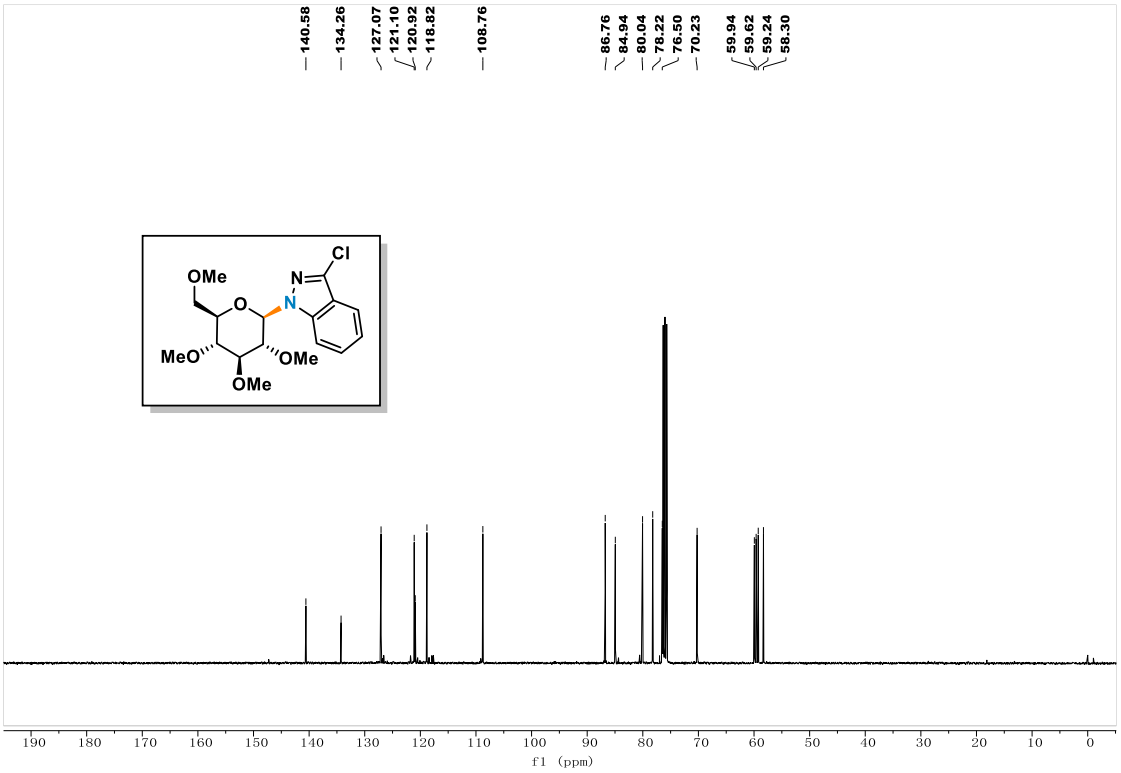
^{13}C NMR (101 MHz, $CDCl_3$) **(8pa)**



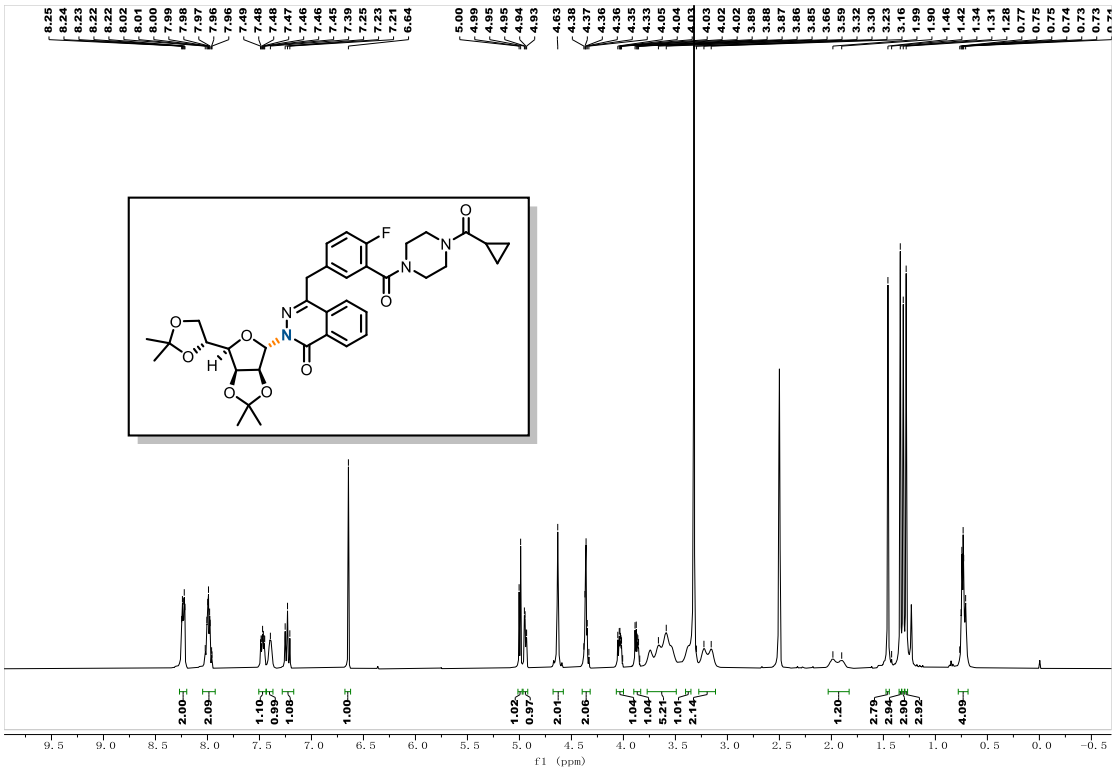
^{1}H NMR (400 MHz, $CDCl_3$) **(8pb)**



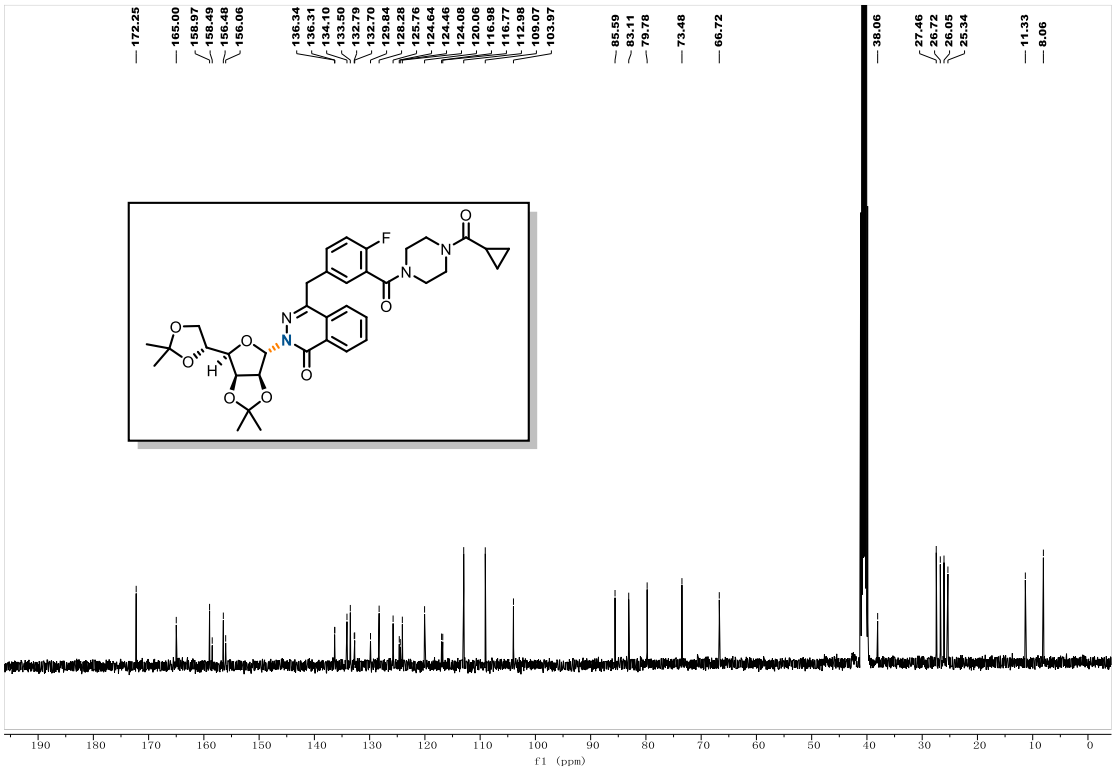
^{13}C NMR (101 MHz, $CDCl_3$) **(8pb)**



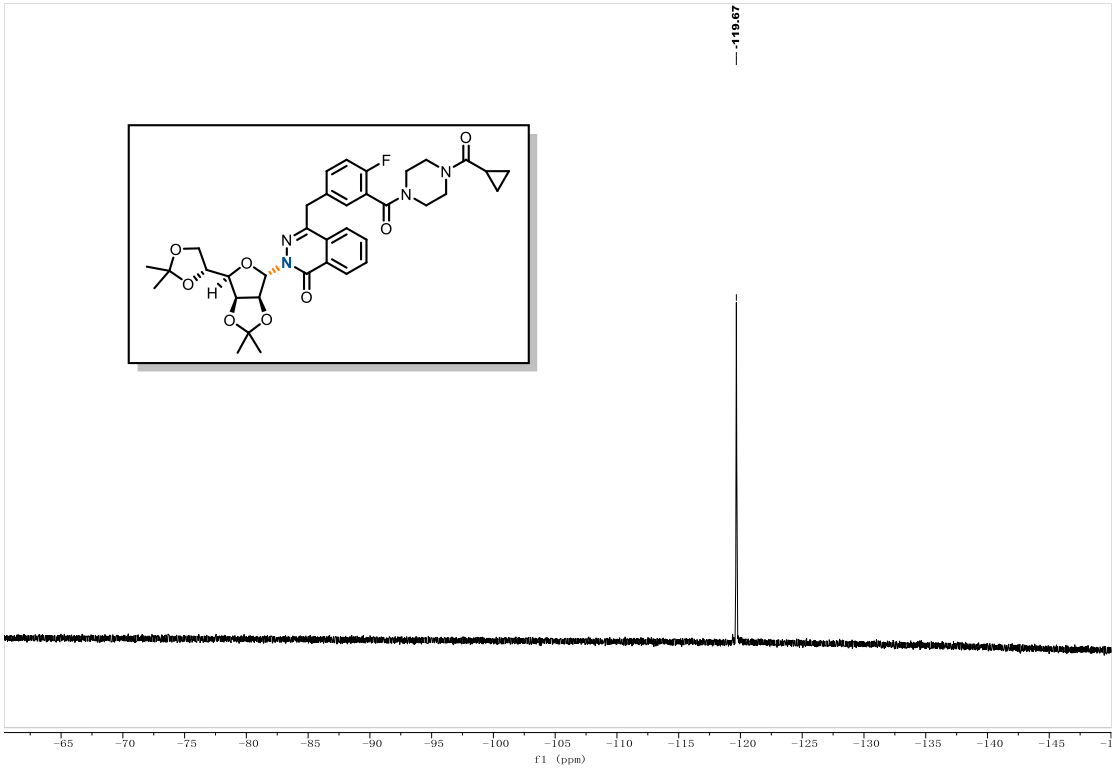
^{1}H NMR (400 MHz, DMSO-d_6) **(9a)**



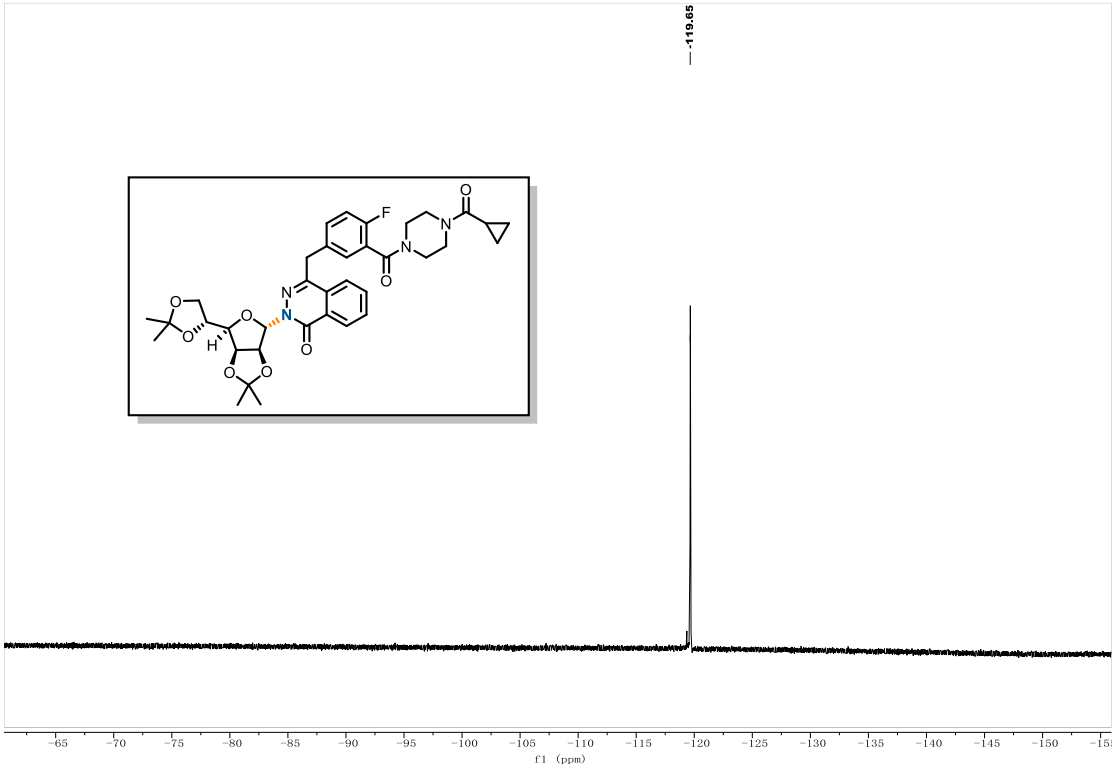
^{13}C NMR (101 MHz, DMSO-d_6) **(9a)**



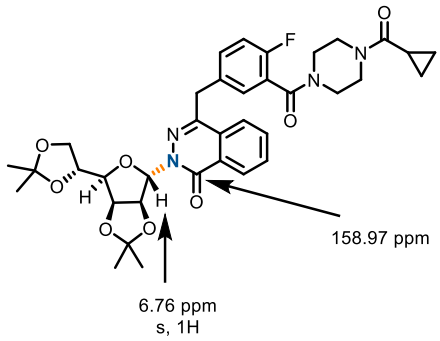
^{19}F NMR (376 MHz, DMSO-d_6) **(9a)**

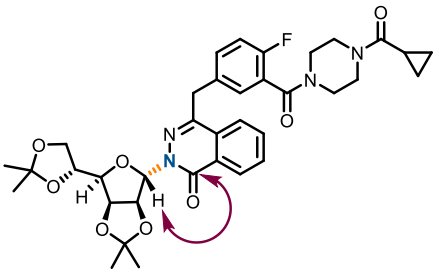


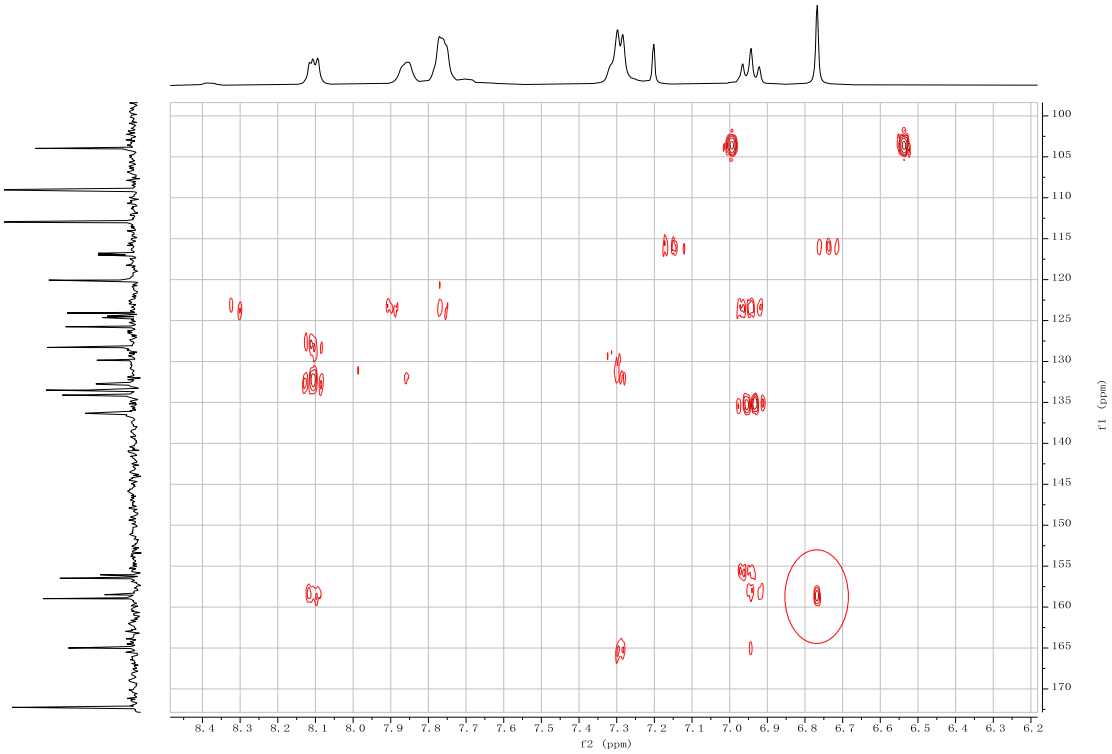
^{19}F {^{1}H} NMR (376 MHz, DMSO-d_6) **(9a)**



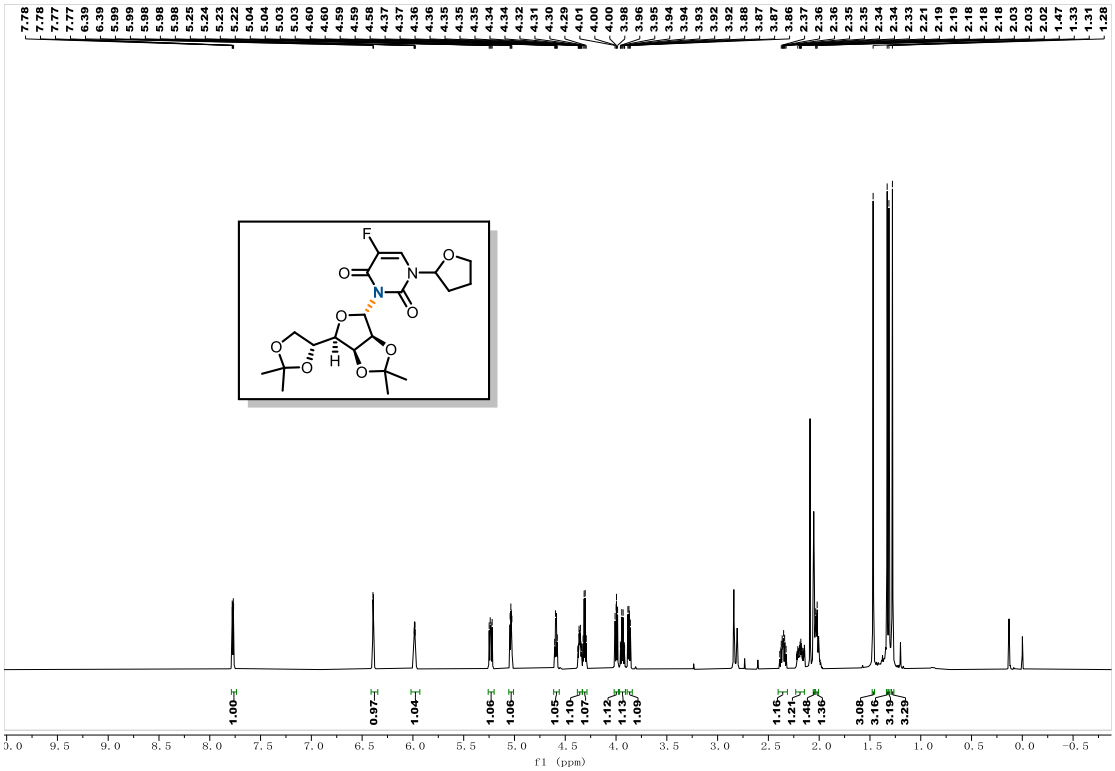
HMBC of **9a**



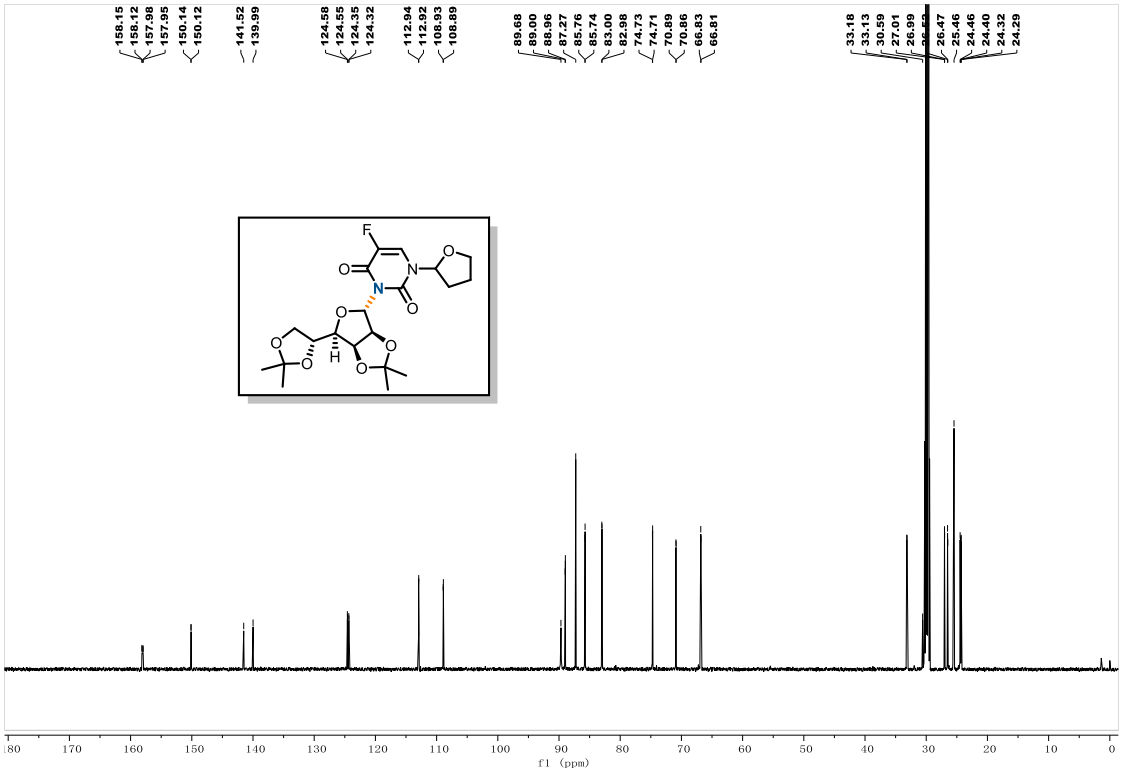




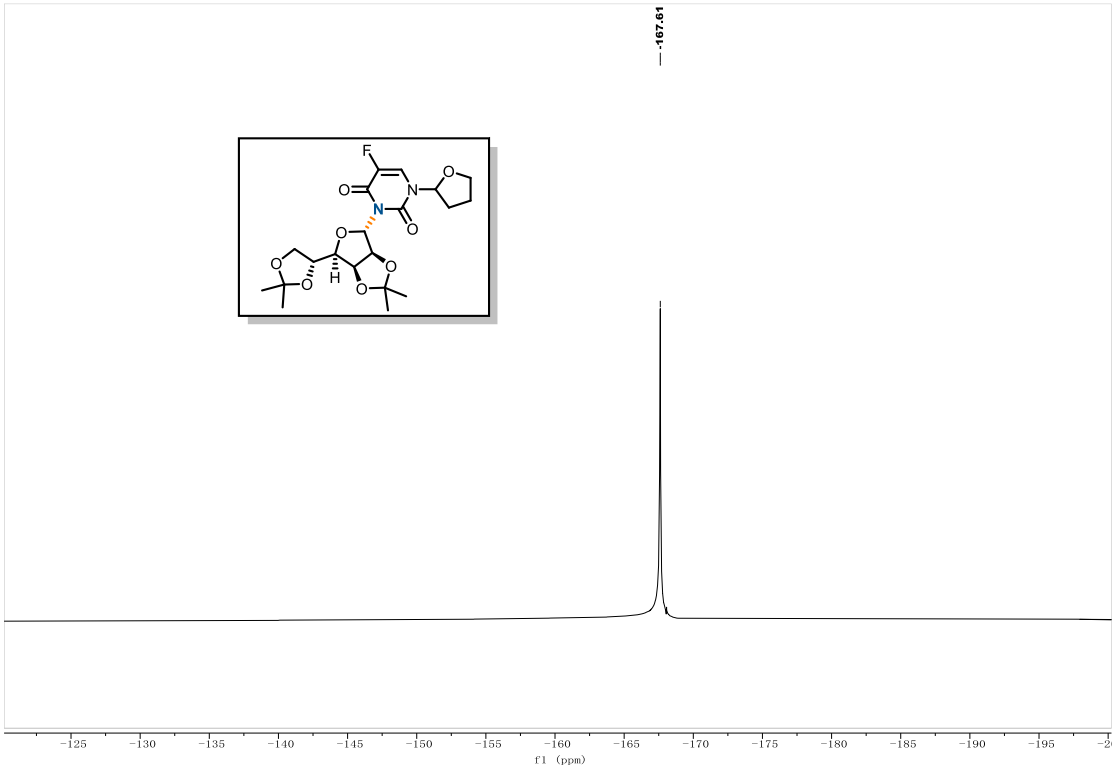
^{1}H NMR (600 MHz, Acetone-d_6) **(9b)**



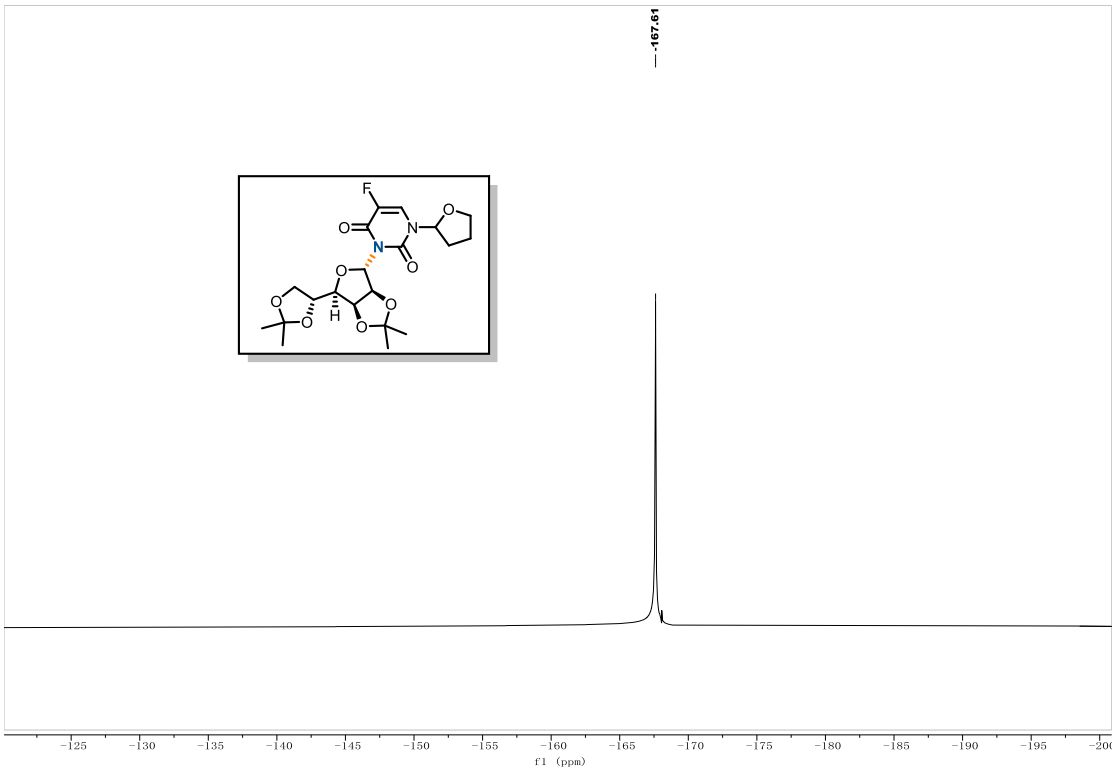
^{13}C NMR (151 MHz, Acetone-d_6) **(9b)**



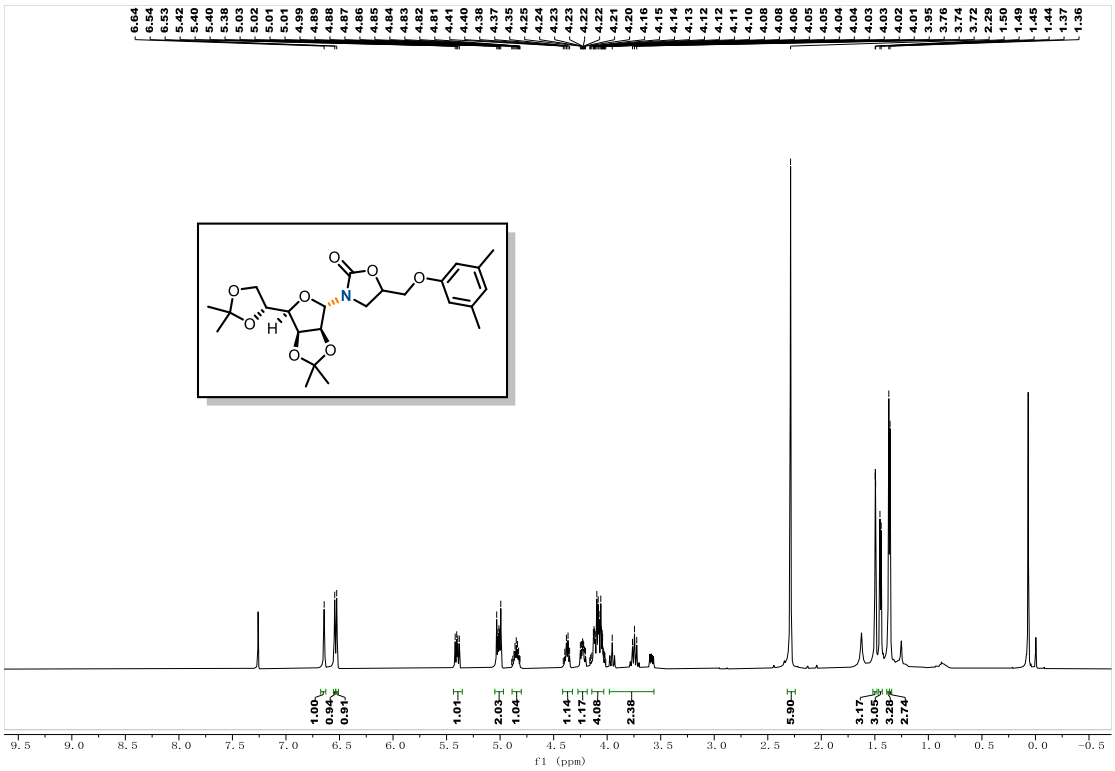
^{19}F NMR (565 MHz, Acetone-d_6) (**9b**)



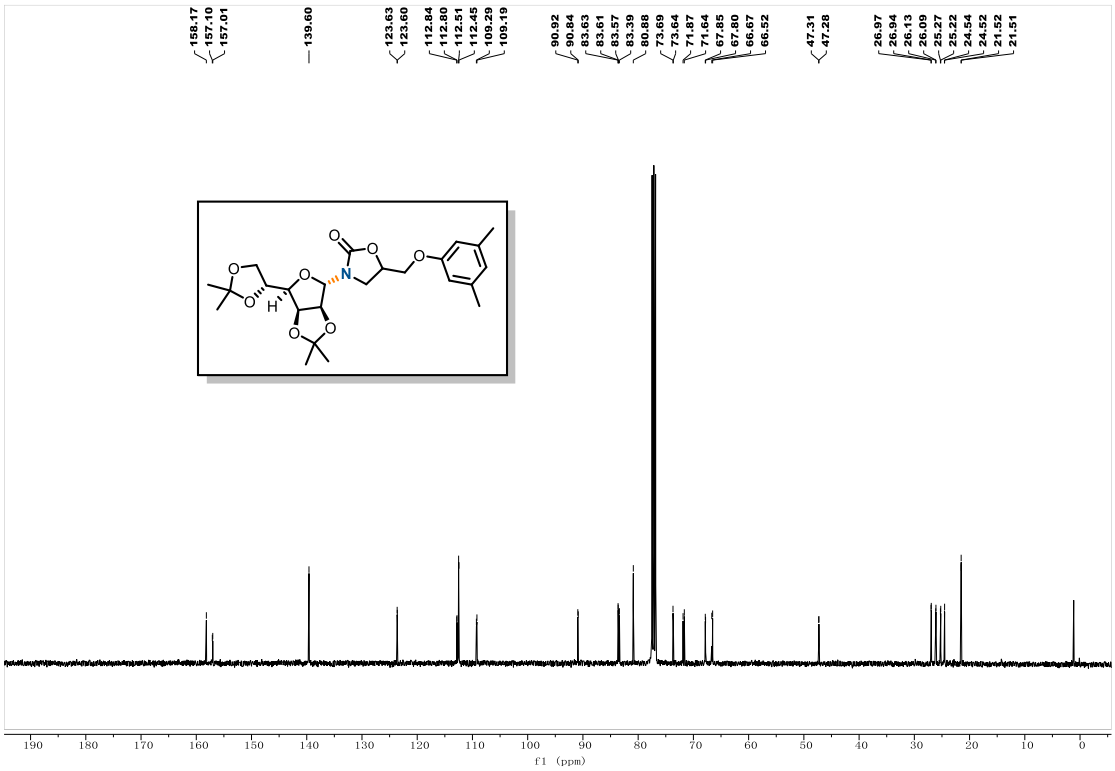
^{19}F {^{1}H} NMR (565 MHz, Acetone-d_6)



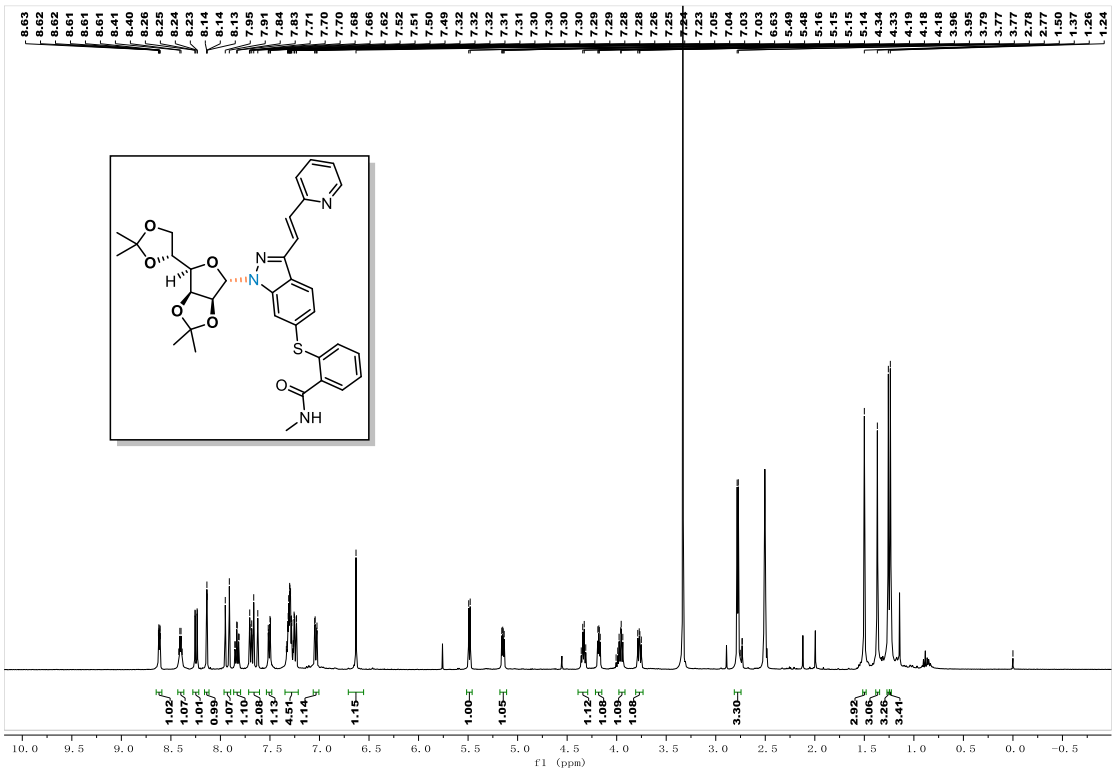
^{1}H NMR (400 MHz, $CDCl_3$) **(9c)**



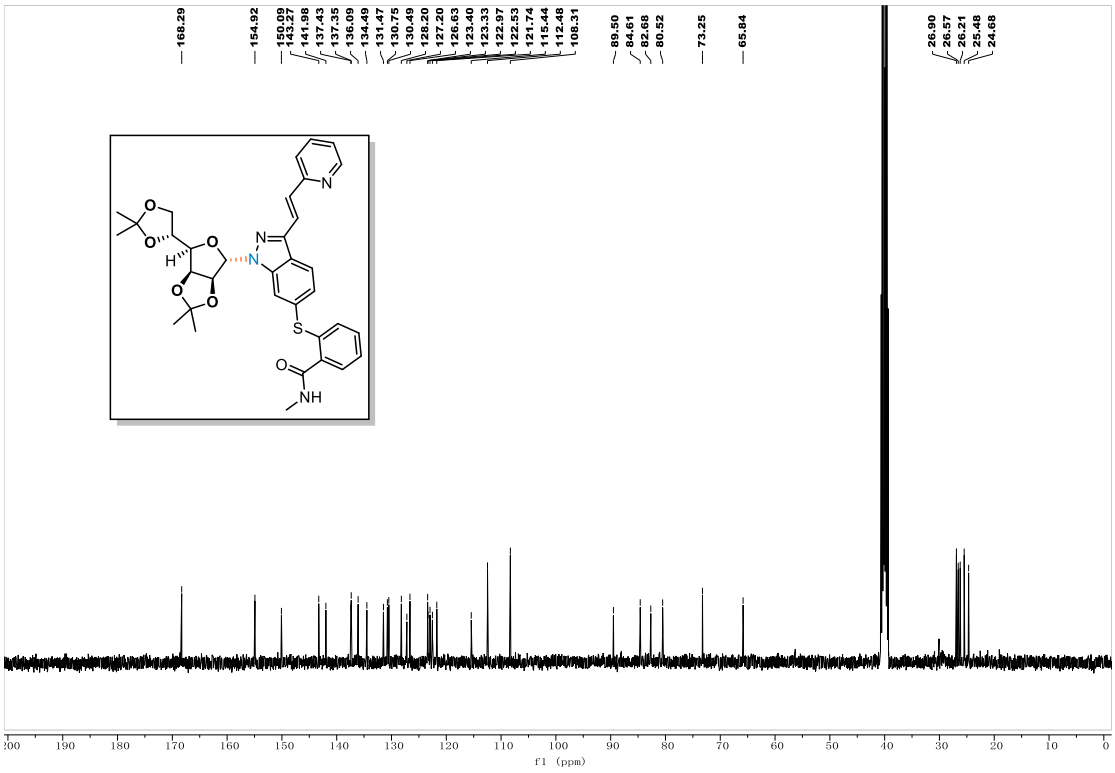
^{13}C NMR (101 MHz, $CDCl_3$) **(9c)**



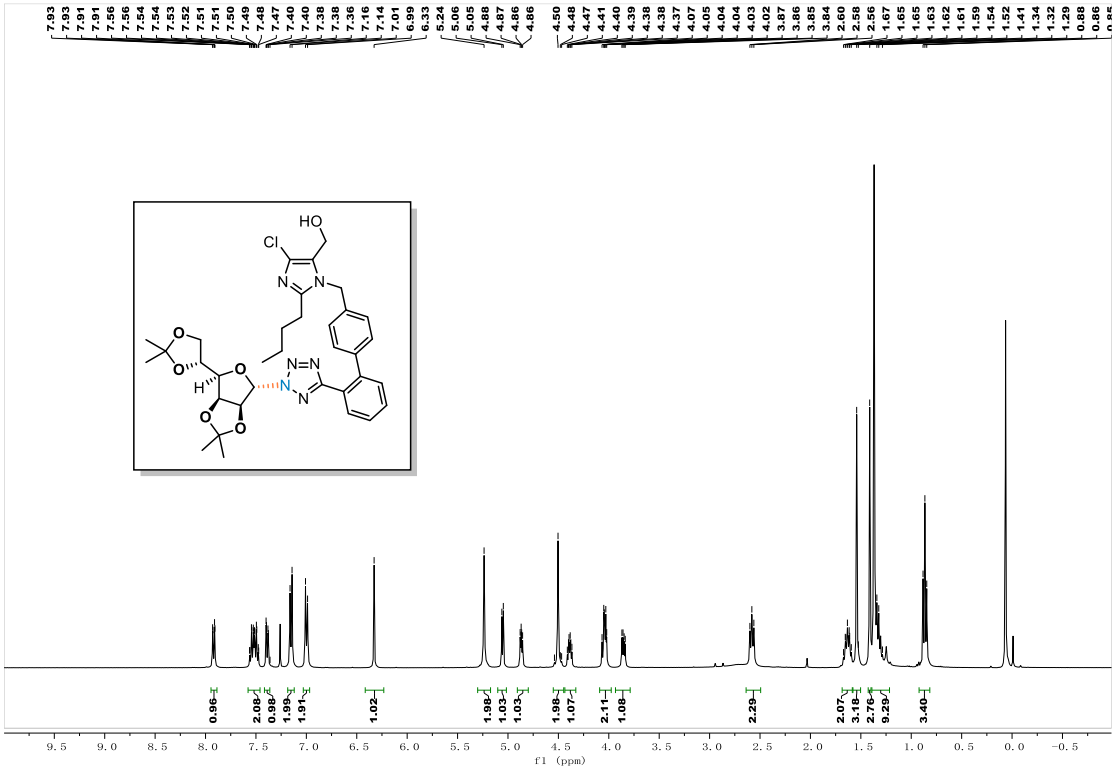
^{1}H NMR (400 MHz, DMSO-d_6) **(9d)**



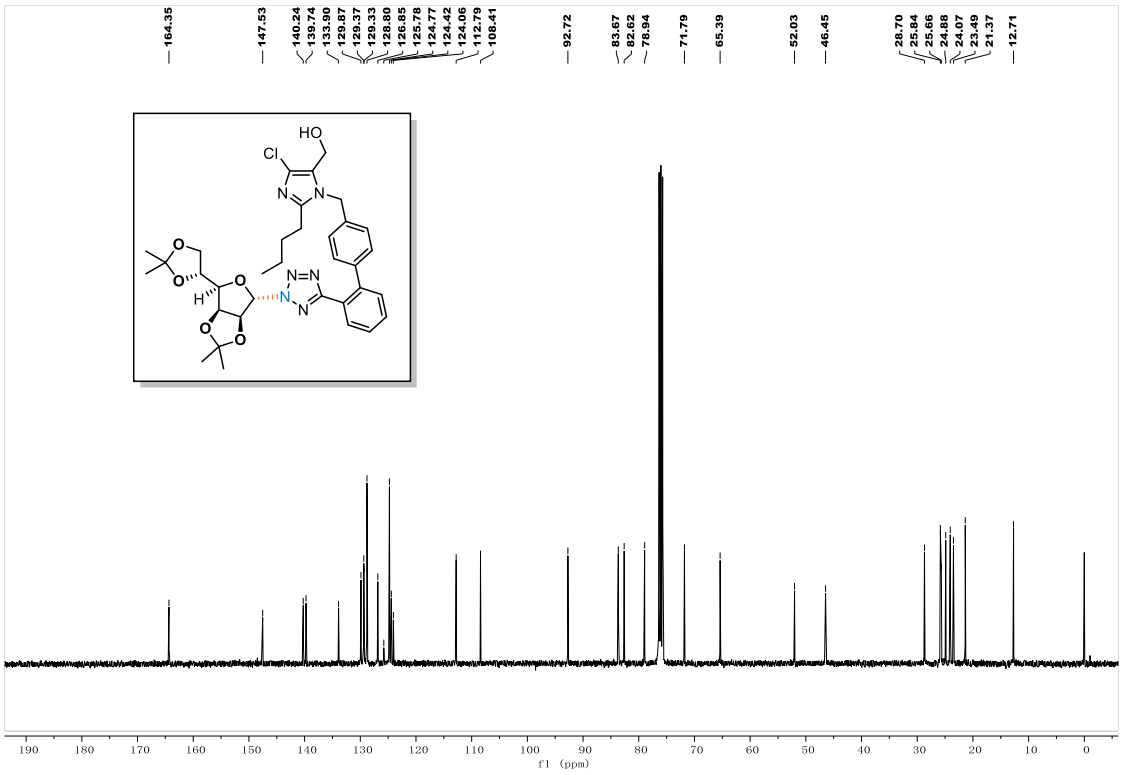
^{13}C NMR (101 MHz, DMSO-d_6) **(9d)**



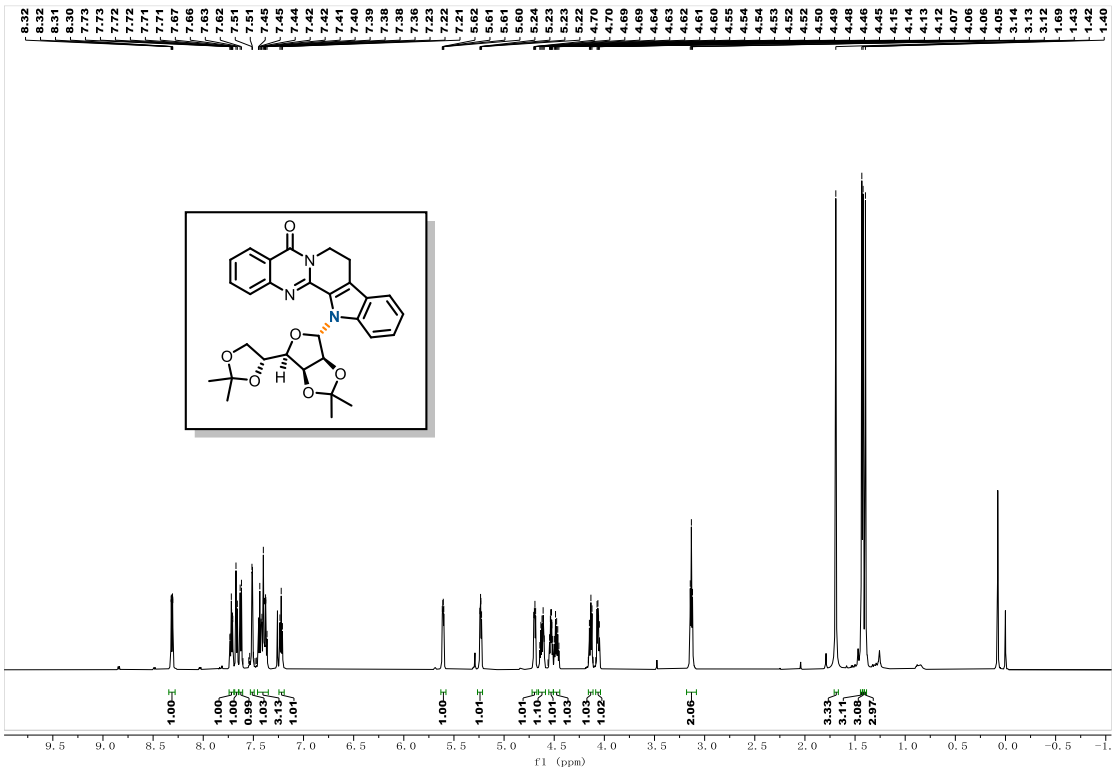
^{1}H NMR (400 MHz, $CDCl_3$) **(9e)**



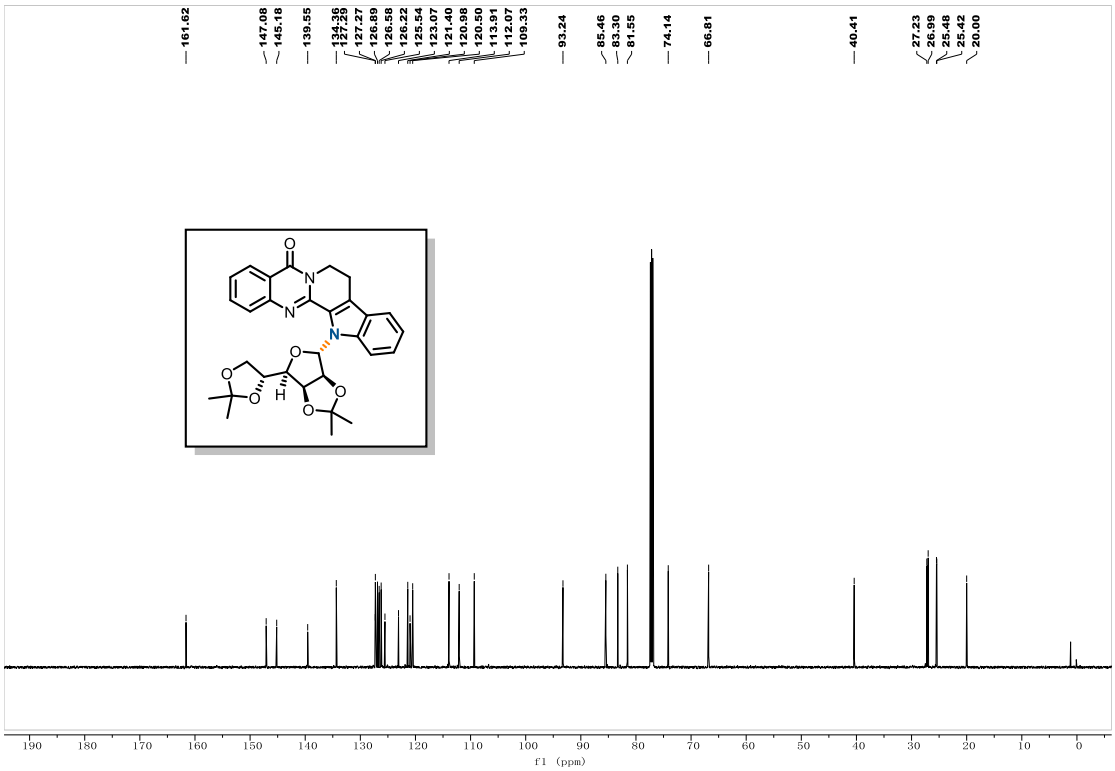
^{13}C NMR (101 MHz, $CDCl_3$) **(9e)**



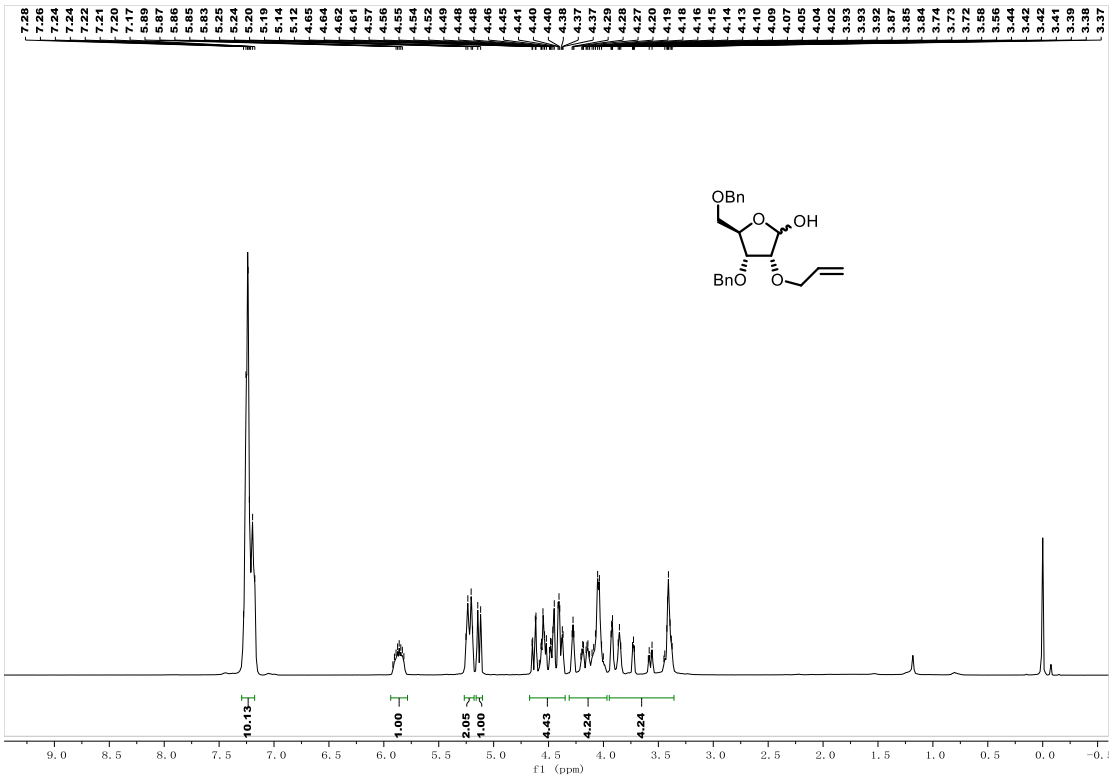
^{1}H NMR (600 MHz, $CDCl_3$) (**9f**)



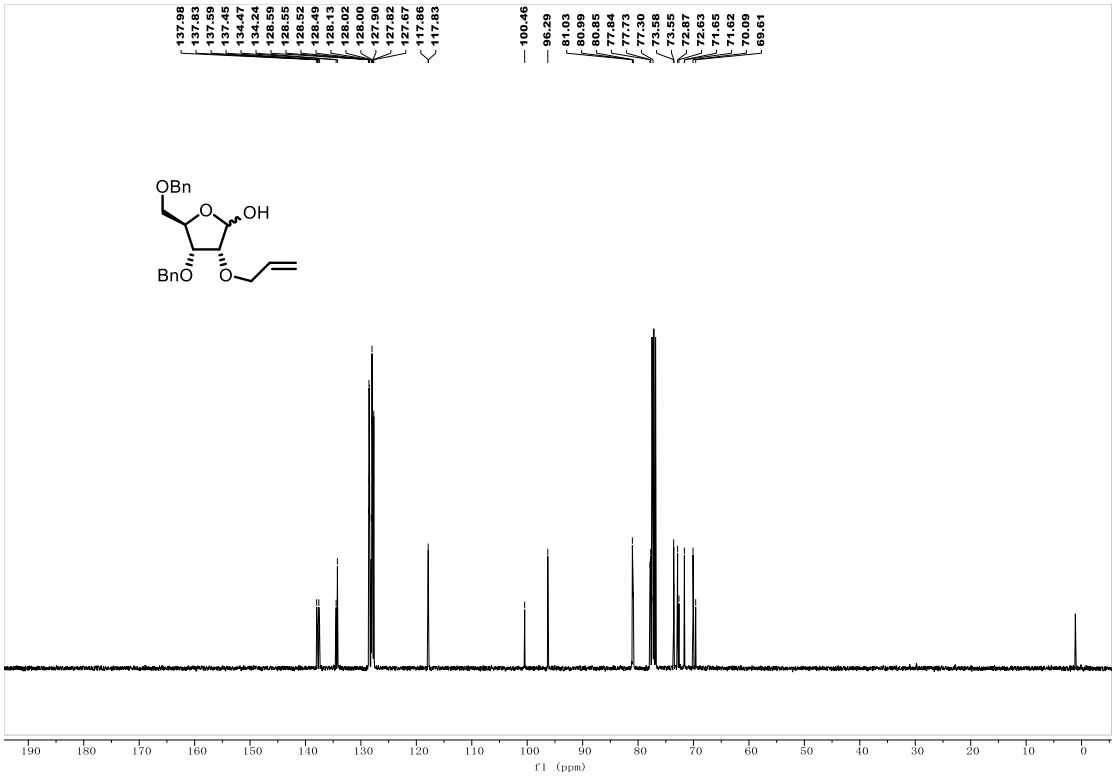
^{13}C NMR (151 MHz, $CDCl_3$) (**9f**)



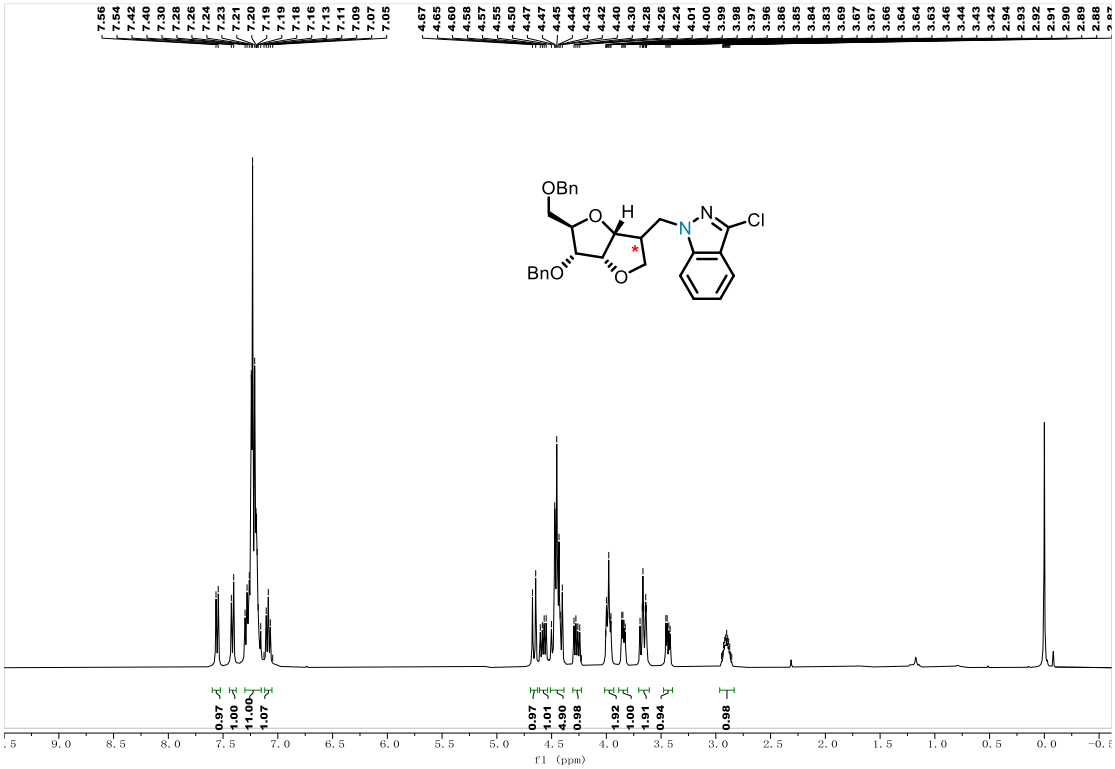
^{1}H NMR (400 MHz, $CDCl_3$) **(10)**



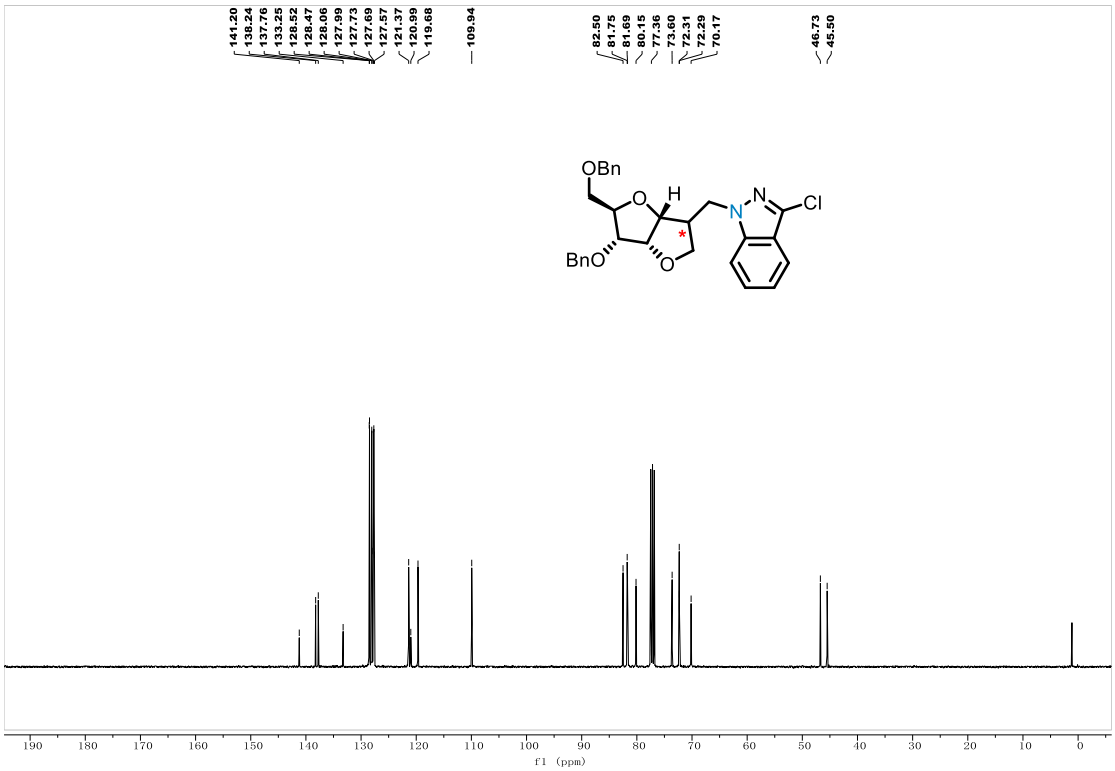
^{13}C NMR (101 MHz, $CDCl_3$) **(10)**



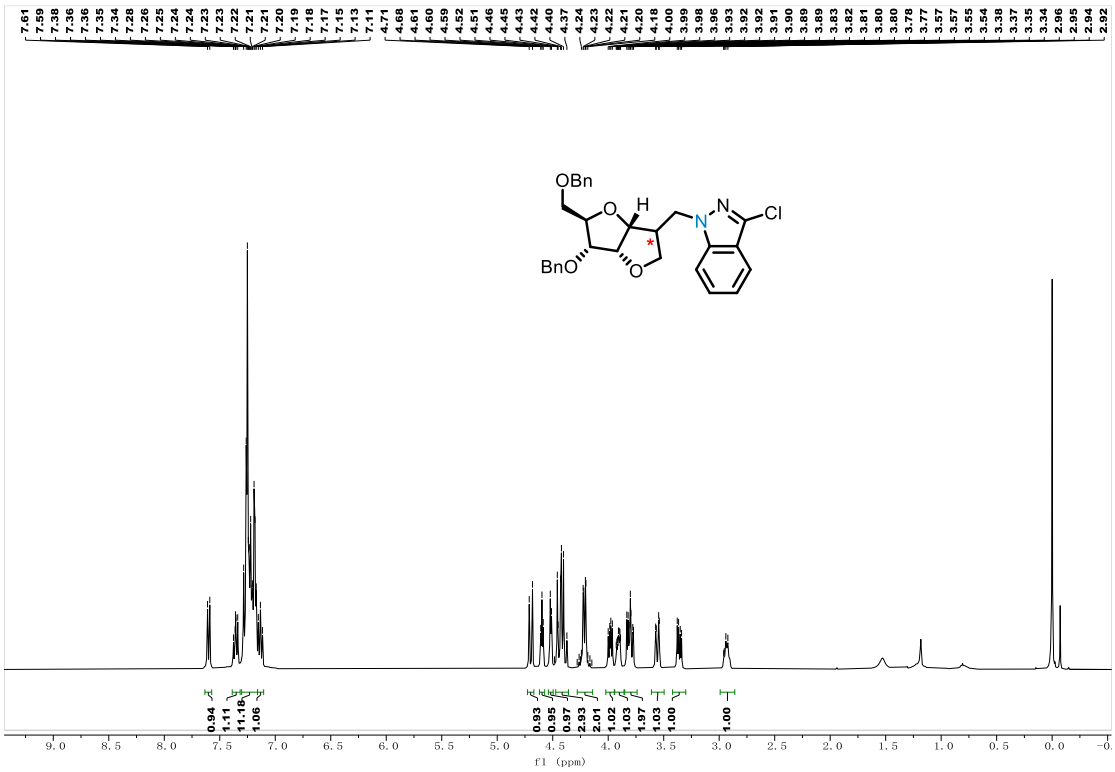
^{1}H NMR (400 MHz, $CDCl_3$) **(11a)**



^{13}C NMR (101 MHz, $CDCl_3$) **(11a)**



^{1}H NMR (400 MHz, $CDCl_3$) **(11b)**



^{13}C NMR (101 MHz, $CDCl_3$) **(11b)**