Synthesis of 2-glycosyl-quinazolines and 5-glycosyl-pyrazolo[1,2-a]cinnolines by Cp*Ir(III)-catalyzed C-H activation/cyclization

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1. General Information

Unless otherwise noted, all reactions were carried out under an atmosphere of nitrogen in flame-dried glassware. If reaction was not carried out at room temperature, reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The dry solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under nitrogen. Commercially available chemicals were obtained from commercial suppliers and used without further purification unless otherwise stated.

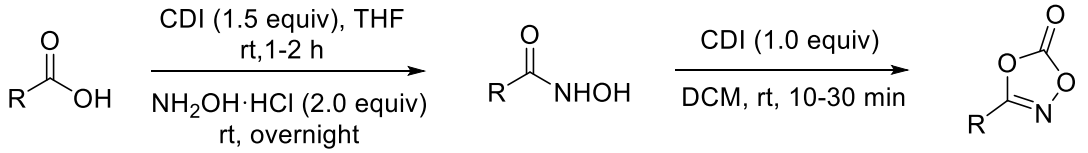
Proton NMR (^{1}H) were recorded at 300/400/500/600 MHz, and Carbon NMR (^{13}C) at 75/101/126/151 MHz NMR spectrometer unless otherwise stated. The following abbreviations are used for the multiplicities: s: singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s: broad singlet for proton spectra. Coupling constants (*J*) are reported in Hertz (Hz).

High–resolution mass spectra (HRMS, LCMS-IT-TOF) were recorded on a Bruker VPEXII spectrometer with EI and ESI mode unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. Visualization was accomplished with short wave UV light, or PhosPhomolybdic Acid staining solutions followed by heating. Flash column chromatography was performed using silica gel (300-400 mesh) or PrepTLC with solvents distilled prior to use.

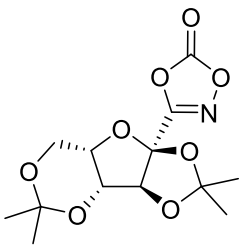
2. Synthesis of Starting Materials

2.1 The preparation of dioxazolones glycogen anomeric substrates [1]: (General procedure 1)

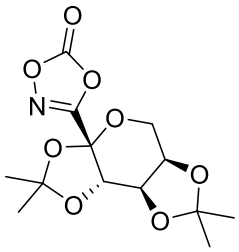


Step 1. Synthesis of hydroxamic acids: 1,1'-Carbonyldiimidazole (CDI, 1.5 equiv) was added to a mixture of carboxylic acid (1.0 equiv) in dry tetrahydrofuran (THF, 1.0 M) at room temperature. The reaction mixture was stirred for 1-2 hours. Afterward, powdered hydroxylamine hydrochloride (2.0 equiv) was added. The resulting mixture was stirred overnight. The reaction direct vacuum concentration. The resulting residue was purified by silica gel flash chromatography (DCM/methanol = 50:1 ~ 20:1) to give the hydroxamic acid.

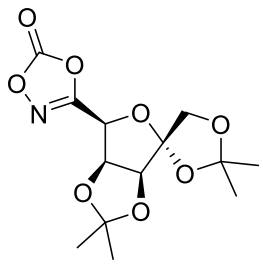
Step 2. Synthesis of dioxazolone substrates: To a stirred solution of hydoxamic acid (1.0 equiv) in freshly distilled dichloromethane, 1,1′-carbonyldiimidazole (1.0 equiv) was added in one portion at room temperature. After being stirred for 10-30 minutes, the reaction mixture was quenched with 1 N HCl, and extracted with EtOAc. The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified quickly by short silica pad (PE/EA = 10:1 ~ 5:1) to give the desired dioxazolones glycogen anomeric.



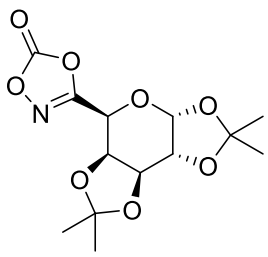
SI-1-1 64%
[gram scale]



SI-1-2 58%
[gram scale]

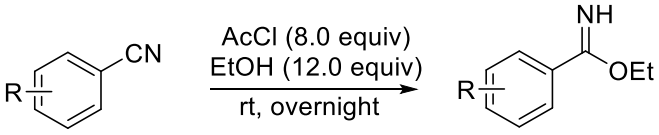


SI-1-3 45%
[gram scale]

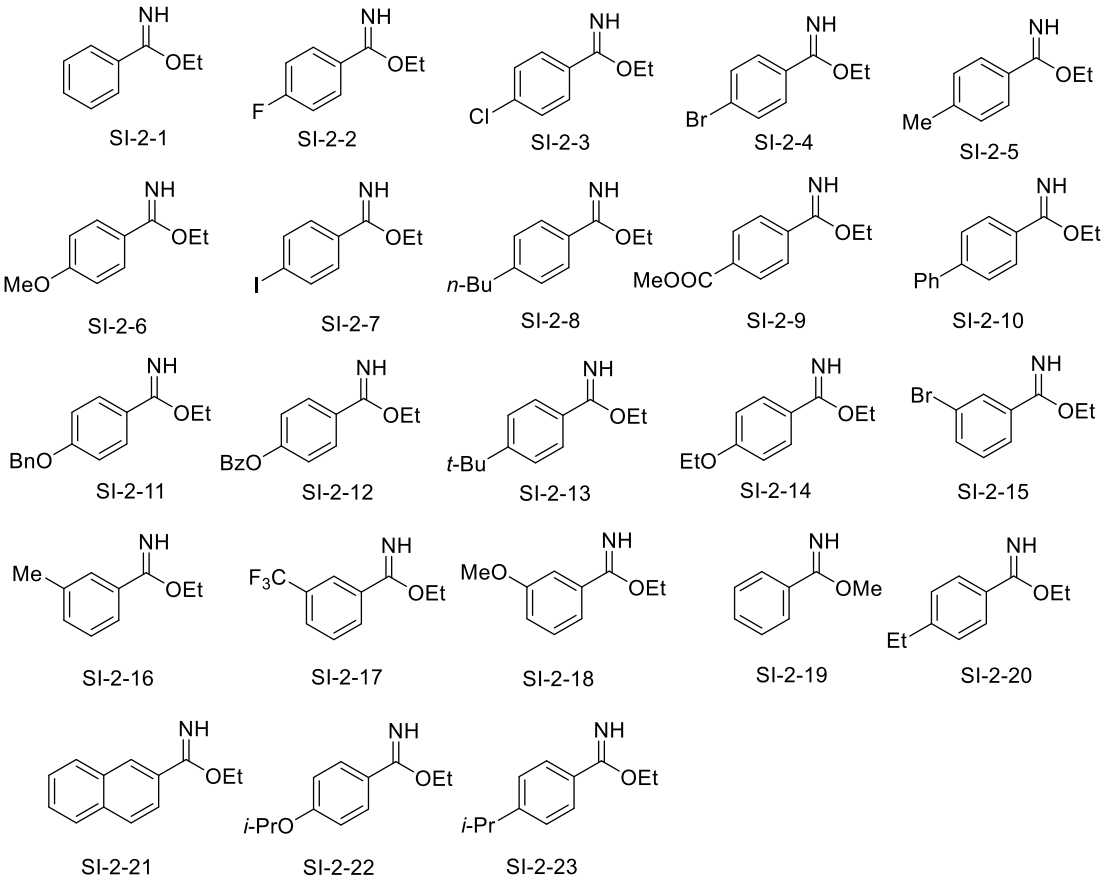


SI-1-4 46%
[gram scale]

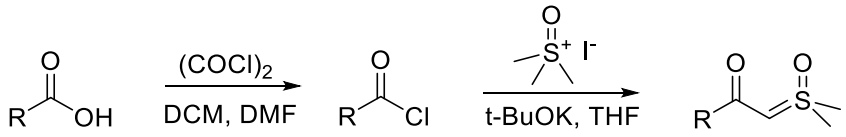
2.2 General Procedure for the Preparation of Imidates [2]:



Acetyl chloride (8.0 equiv) was added dropwise over 15 minutes to a stirred solution of the required nitrile in ethanol (12.0 equiv). The mixture was stirred at room temperature overnight. The solution was cooled to 0 °C before the addition of saturated aqueous sodium hydrogen carbonate until the evolution of gas ceased. The solution was then warmed to room temperature and extracted with diethyl ether (3 x 150 mL). The combined organic fractions were washed with brine (50 mL) and dried ($MgSO_4$) before the solvent was removed under reduced pressure to yield the crude compound. The title compound was reacted on without further purification.

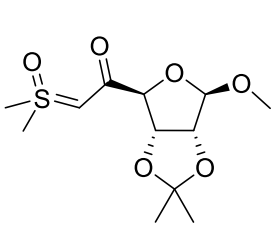


2.3 Synthesis of Carbonyl sulfoxonium ylides glycogen anomeric [3]:

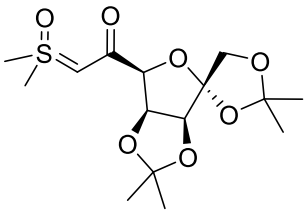


Step-I: To a stirred solution of a carboxylic acid (5 mmol) and DMF (2 drops) in CH_2Cl_2 (25 mL), $(COCl)_2$ (10 mmol, 0.9 mL) was added dropwise. The reaction was allowed to stir at room temperature 2 h. Evaporation of the reaction mixture gave a residue which was dissolved in THF (20 mL). The resulting solution was used as acid chloride solution in subsequent reactions.

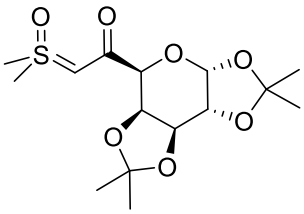
Step-II: To a stirred solution of potassium tert-butoxide (16.75 mmol, 2.1 g) in dry THF (20 mL), trimethylsulfoxonium iodide (10.25 mmol, 5.5 g) was added and the reaction was allowed to reflux (oil bath) for 2 h under N_2. The reaction mixture was cooled to 0 ℃ and the solution of the acid chloride (obtained by step-I) was added dropwise to it. Then, the reaction was allowed to stir at room temperature for additional 1-2 h. Next, the solvent was evaporated, water and ethyl acetate were then added to the resulting slurry. The layers were separated and the aqueous layer was extracted with ethyl acetate and the organic layers were combined. The organic solution was dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The crude product was purified by flash chromatography over silica gel using CH_2Cl_2 and MeOH to afford the corresponding carbonyl sulfoxonium ylides glycogen anomeric.



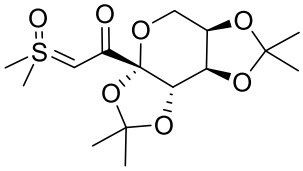
SI-3-1 54%
[gram scale]



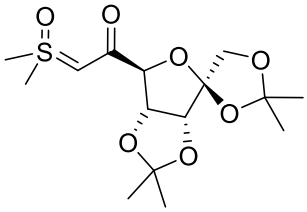
SI-3-2 50%
[gram scale]



SI-3-3 42%
[gram scale]

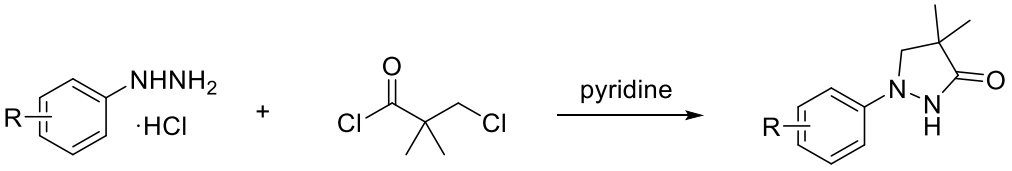


SI-3-4 57%
[gram scale]

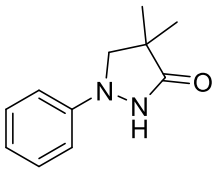


SI-3-5 55%
[gram scale]

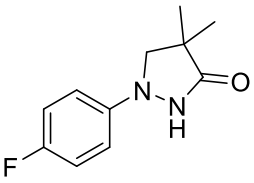
2.4 General synthetic procedure for the preparation of 1-arylpyrazolidinones [4]:



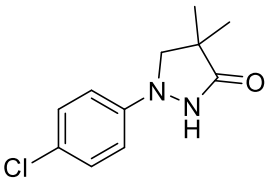
To a flask containing anhydrous pyridine (5 mL) and arylhydrazine hydrocholoride (1 mmol) was slowly added 3-chloro-2,2-dimethylpropionyl chloride (1 mmol) at 0 °C. The resulting mixture was stirred and allowed to warm to room temperature in 4 h. It was then stirred at 100 °C (oil bath) for 8 h. Upon completion, it was cooled to room temperature, diluted with DCM, and neutralized to pH = 2 using aqueous HCl (1 M). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified through silica gel column chromatography by using petroleum ether/ethyl acetate (3:1) as the eluent to afford 1-arylpyrazolidinone.



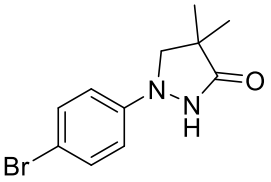
SI-4-1



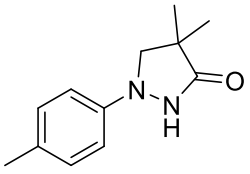
SI-4-2



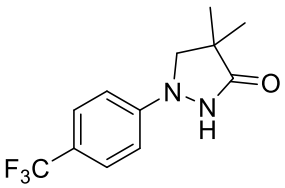
SI-4-3



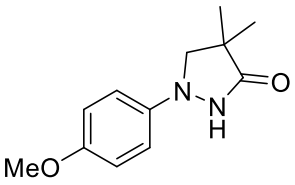
SI-4-4



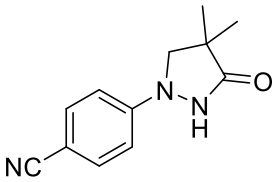
SI-4-5



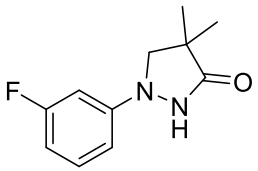
SI-4-6



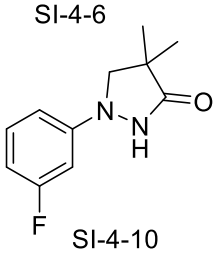
SI-4-7



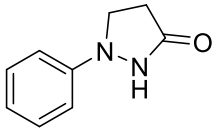
SI-4-8



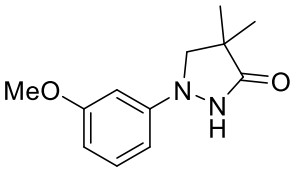
SI-4-9



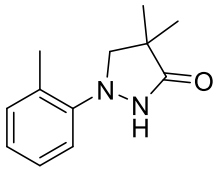
SI-4-10



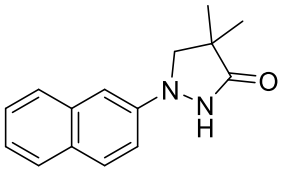
SI-4-11



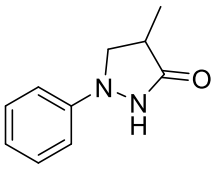
SI-4-12



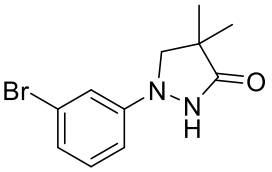
SI-4-13



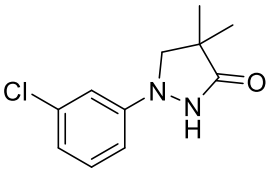
SI-4-14



SI-4-15



SI-4-16

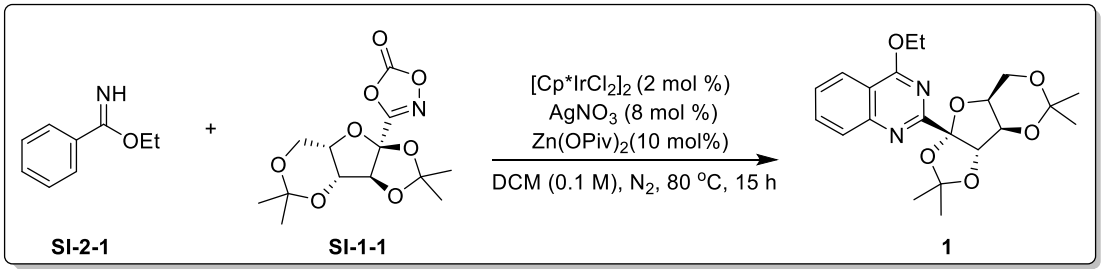


SI-4-17

3. General procedure for the Ir-catalyzed C–H functionalization

3.1 Optimization reactions

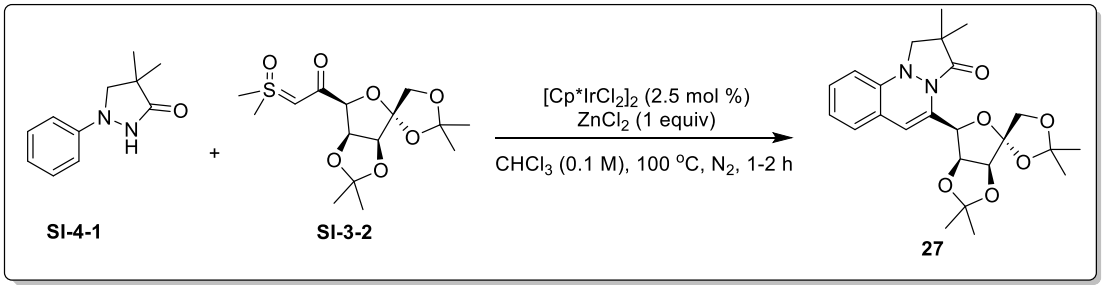
Table S1. Reaction of benzimidates **SI-2-1** with dioxazolones glycogen anomeric **SI-1-1**.



entry	A gsalts	Solvent	Additive	Yield of **1**(%)
1[a]	$AgNO_3$	DCE	-	37
2[a]	Ag_2CO_3	DCM	-	30
3[a]	$AgNTf_2$	DCM	-	15
4[a]	AgO	DCM	-	28
5[a]	$AgBF_4$	DCM	-	16
6[a]	$AgNO_3$	DMSO	-	/
7[a]	$AgNO_3$	DMF	-	/
8[a]	$AgNO_3$	THF	-	40
9[a]	$AgNO_3$	MeCN	-	65
10[a]	$AgNO_3$	DCM	-	81
11[a]	$AgNO_3$	DCM	$Zn(OPiv)_2$	74
12[a]	$AgNO_3$	DCM	$Zn(OAc)_2$	64
13[a]	$AgNO_3$	DCM	$ZnCl_2$	27
14[a,b]	$AgNO_3$	DCM	$Zn(OPiv)_2$	46
15[a,c]	$AgNO_3$	DCM	$Zn(OPiv)_2$	95
16[a,d]	$AgNO_3$	DCM	$Zn(OPiv)_2$	90

Reaction conditions: [a] **SI-2-1** (0.1 mmol, 1.0 equiv), **SI-1-1** (0.15 mmol, 1.5 equiv), $[Cp^*IrCl_2]_2$ (2 mol %), $AgNO_3$ (8 mol %), Additive (1.0 equiv), Solvent (0.1 M), 80 °C, N_2, 15 h, Isolated yields. [b] Additive (2.0 equiv). [c] Additive (10 mol %). [d] Additive (20 mol %).

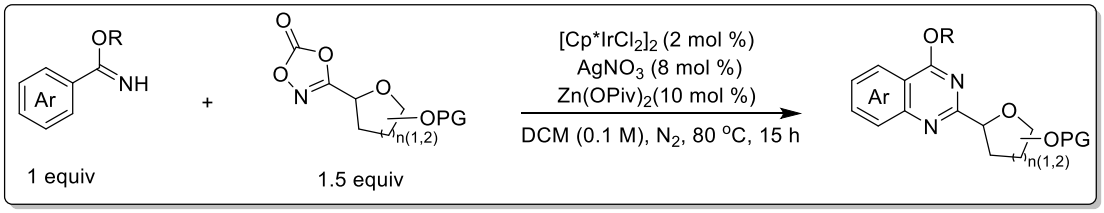
Table S2. Reaction of Narylpyrazolidin-3-ones **SI-4-1** with Carbonyl sulfoxonium ylides glycogen anomeric **SI-3-2**.



entry	Additive	Solvent	Catalysis	Yield of **27** [b]
1[a]	$Zn(OPiv)_2$	$CHCl_3$	$[Cp^*IrCl_2]_2$	<5%
2[a]	$Zn(OAc)_2$	$CHCl_3$	$[Cp^*IrCl_2]_2$	10%
3[a]	$MgCl_2$	$CHCl_3$	$[Cp^*IrCl_2]_2$	38%
4[a]	$Zn(CN)_2$	$CHCl_3$	$[Cp^*IrCl_2]_2$	ND
5[a]	ZnI_2	$CHCl_3$	$[Cp^*IrCl_2]_2$	<5%
6[a]	$ZnCl_2$	$CHCl_3$	$[Cp^*IrCl_2]_2$	81%
7[a]	$ZnBr_2$	$CHCl_3$	$[Cp^*IrCl_2]_2$	36%
8[a]	$ZnCl_2$	DCM	$[Cp^*IrCl_2]_2$	56%
9[a]	$ZnCl_2$	DCE	$[Cp^*IrCl_2]_2$	66%
10[a]	$ZnCl_2$	MeCN	$[Cp^*IrCl_2]_2$	20%
11[a]	$ZnCl_2$	CCl_4	$[Cp^*IrCl_2]_2$	12%
12[a,c]	$ZnCl_2$	$CHCl_3$	$[Cp^*IrCl_2]_2$	60%
13[a,d]	$ZnCl_2$	$CHCl_3$	$[Cp^*IrCl_2]_2$	28%
14[a,e]	$ZnCl_2$	$CHCl_3$	$[Cp^*IrCl_2]_2$	45%
15[a]	$ZnCl_2$	$CHCl_3$	/	ND

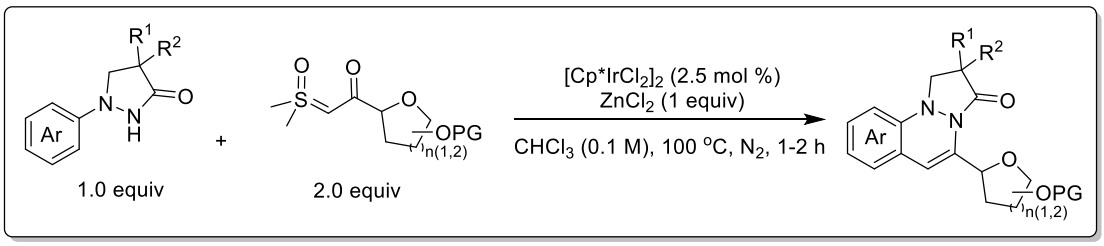
Reaction conditions: [a] **SI-4-1** (0.1 mmol, 1.0 equiv), **SI-3-2** (0.2 mmol, 2.0 equiv), $[Cp^*IrCl_2]_2$ (2.5 mol %), Additive (1.0 equiv), Solvent (0.1 M), 100 °C, N_2, 1-2 h. [b] Isolated yields. [c] **SI-3-2** (0.15 mmol, 1.5 equiv). [d] Additive (2.0 equiv). [e] Additive (0.5 equiv).

3.2 Procedure for the annulation of benzimidates with dioxazolones glycogen anomeric (General procedure 2)



A Schlenk tube (15 mL) equipped with a magnetic stir bar and a Teflon-lined screwed cap was charged with benzimidates SI-2 (0.1 mmol), dioxazolones glycogen anomeric SI-1 (0.15 mmol), $[Cp^*IrCl_2]_2$ (2 mol %, 1.6 mg), $AgNO_3$ (8 mol %, 1.4 mg), $Zn(OPiv)_2$ (10 mol %, 2.6 mg) and DCM (0.1 M, 1 mL). The vial was then sealed and heated at 80 ℃ for 15 h under N_2. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography or PrepTLC using PE/EA to afford the product.

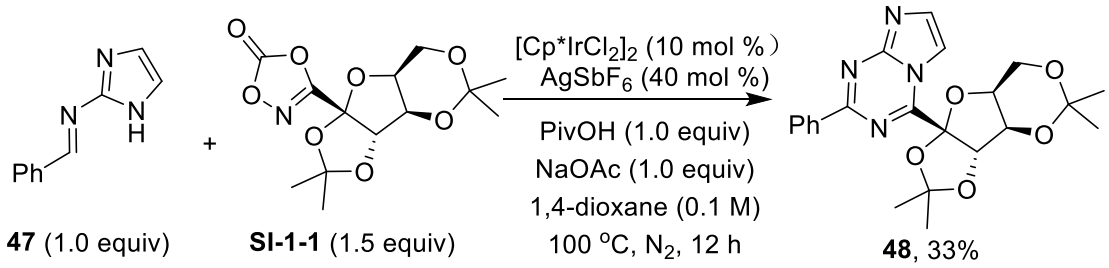
3.3 Procedure for the annulation of Narylpyrazolidin-3-ones with carbonyl sulfoxonium ylides glycogen anomeric (General procedure 3)



A Schlenk tube (15 mL) equipped with a magnetic stir bar and a Teflon-lined screwed cap was charged with substituted Narylpyrazolidin-3-ones SI-4 (0.1 mmol), carbonyl sulfoxonium ylides glycogen anomeric SI-3 (0.15 mmol or 0.2 mmol), $[Cp^*IrCl_2]_2$ (2.5 mol %, 2 mg), $ZnCl_2$ (13.6 mg, 0.1 mmol, 1.0 equiv) and $CHCl_3$ (1 mL, 0.1 M). The vial was then sealed and heated at 100 ℃ for 1-2 hour under N_2. After cooling to room temperature, the solvent was removed in vacuo and the residue was purified using column chromatography or PrepTLC to afford product.

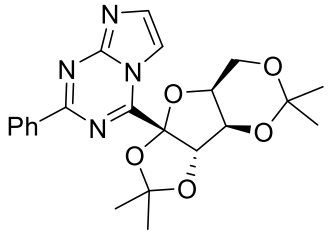
4 Miscellaneous Reactions

4.1



A Schlenk tube (15 mL) equipped with a magnetic stir bar and a Teflon-lined screwed cap was charged with substituted benzimidates **47**[5] (0.1 mmol, 1.0 equiv), dioxazolones glycogen anomeric **SI-1-1** (0.15 mmol, 1.5 equiv), $[Cp^*IrCl_2]_2$ (10 mol %), $AgSbF_6$ (40 mol %), NaOAc (1.0 equiv), PivOH(1.0 equiv) and 1,4-dioxane (0.1 M). The vial was then sealed and heated at 100 ℃ for 12 h under N_2. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography or PrepTLC using PE/EA to afford the product **48** (33% yield) as white solid.

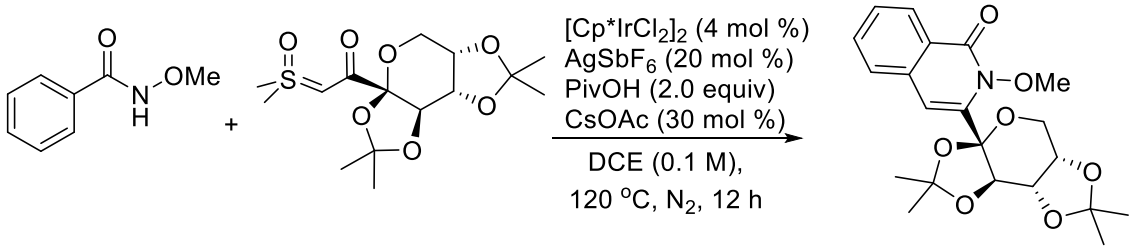
2-phenyl-4-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)-6,7-dihydroimidazo[1,2-*a*][1,3,5]triazine(48)[1]



TLC: R*f* = 0.35 (acetone/hexanes = 2/5)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 – 8.55 (m, 2H), 8.09 (d, *J* = 1.7 Hz, 1H), 7.78 (d, *J* = 1.7 Hz, 1H), 7.54 – 7.47 (m, 3H), 5.73 (s, 1H), 4.50 (d, *J* = 2.4 Hz, 1H), 4.41 (q, *J* = 2.1 Hz, 1H), 4.16 (dd, *J* = 13.8, 2.4 Hz, 1H), 4.08 (d, *J* = 13.9 Hz, 1H), 1.62 (s, 3H), 1.45 (s, 3H), 1.37 (s, 3H), 1.15 (s, 3H).

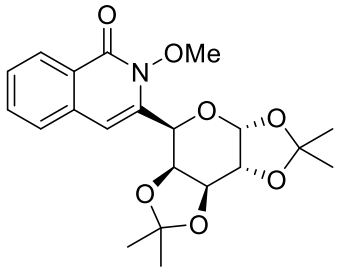
4.2



49 (1.0 equiv) **SI-3-3** (1.5 equiv) **50**, 52%

A Schlenk tube (15 mL) equipped with a magnetic stir bar and a Teflon-lined screwed cap was charged with substituted benzimidates **49**[6] (0.1 mmol, 1.0 equiv), dioxazolones glycogen anomeric **SI-3-3** (0.15 mmol, 1.5 equiv), $[Cp^*IrCl_2]_2$ (4 mol %), $AgSbF_6$ (20 mol %), PivOH (2.0 equiv.), CsOAc (30 mol %) and DCE (0.1 M). The vial was then sealed and heated at 120 ℃ for 12 h under N_2. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the product **50** (52% yield) as yellow solid.

2-methoxy-3-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)isoquinolin-1(2*H*)-one(50)[3]

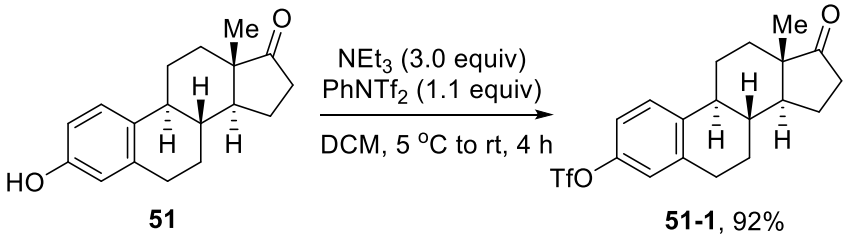


TLC: R*f* = 0.50 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.62 (ddd, *J* = 8.2, 7.0, 1.4 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.49 – 7.42 (m, 1H), 6.75 (s, 1H), 5.73 (d, *J* = 5.0 Hz, 1H), 5.13 – 5.09 (m, 1H), 4.74 (dd, *J* = 7.8, 2.4 Hz, 1H), 4.66 (dd, *J* = 7.8, 1.8 Hz, 1H), 4.44 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.15 (s, 3H), 1.61 (s, 3H), 1.44 (s, 3H), 1.39 (s, 3H), 1.30 (s, 3H).

5 Synthetic application

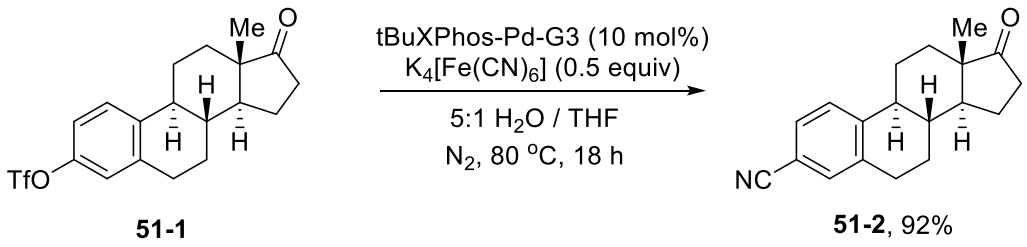
5.1 Transformations of 51 to 51-1 [7]



51 **51-1**, 92%

To a solution of estrone (2.7 g, 10.0 mmol, 1.0 equiv) and triethylamine (4.2 mL, 30.0 mmol, 3.0 equiv) in dichloromethane at 5 °C was charged dropwise a solution of 1,1,1-trifluoro-*N*-phenyl-*N*-((trifluoromethyl)sulfonyl)methanesulfonamide (3.9 g, 11.0 mmol, 1.1 equiv) in dichloromethane and the resulting mixture was stirred at rt for 4 h and then concentrated. The residue was purified by silica gel column chromatography to give pure product **51-1** (3.7 g, 92%) as white solid.

5.2 Transformations of 51-1 to 51-2 [8]

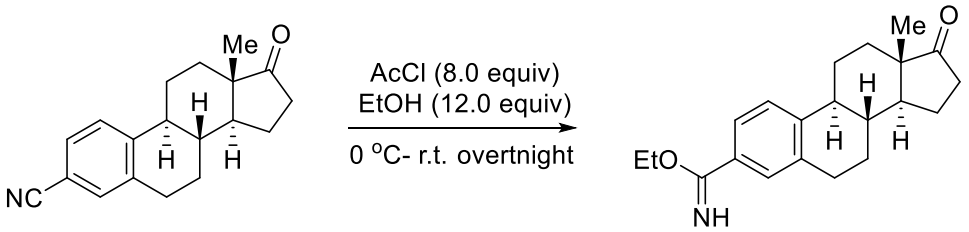


51-1 **51-2**, 92%

51-1 (402 mg, 1.0 mmol, 1.0 equiv), $K_4[Fe(CN)_6]$ (0.53 g, 0.5 mmol, 0.5 equiv) and *t*BuXPhos-Pd-G3 (79 mg, 0.1 mmol, 0.1 equiv) were added to a 4 mL screwcap vial fitted with a septum cap prior to evacuation and backfill with N_2. Degassed water (5.0 mL) and degassed THF (1.0 mL) were added prior to heating at 80 ℃ with vigorous stirring for 18 h. After cooling to room temperature, the reaction mixture was diluted with water (10 mL) and extracted with 1:1 ethyl acetate / dichloromethane (3x10 mL), the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Silica gel column chromatography (elute: *n*-hexane / ethyl acetate) afforded the desired product **51-2** as a white solid (1.28 mg,

92%).

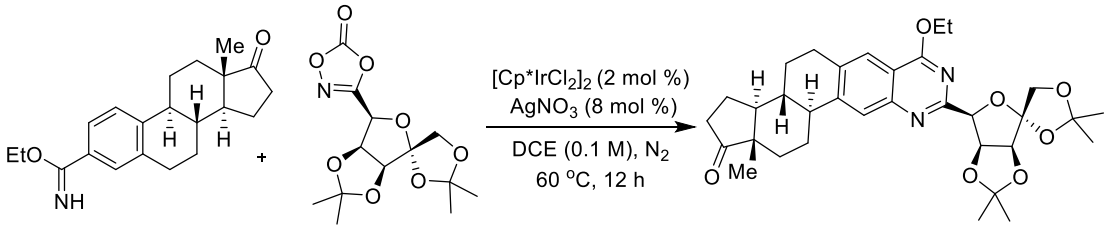
5.3 Transformations of 51-2 to 52 [9]



51-2 **52**, 72%

AcCl (1.14 mL, 16 mmol, 8.0 equiv) was added to a stirred solution of a **51-2** (559 mg, 2 mmol, 1.0 equiv) and an alcohol (1.4 mL, 24 mmol, 12.0 equiv). The reaction flask was stoppered tightly and the stirring was continued at 25 ℃. After the reaction was complete by TLC, the volatiles were removed under reduced pressure to isolate the imidate hydrochloride. Alternatively, the reaction mixture was cooled to 0 ℃ and mixed slowly with saturated aqueous $NaHCO_3$ solution, until gas evolution had ceased. The product was extracted into Et_2O (3×5 mL) and the organic solution was washed with H_2O (1×5 mL) and brine (1×5 mL) and Silica gel column chromatography (elute: *n*-hexane / ethyl acetate) afforded the desired product **52** as a yellow oil (0.47 g, 72%).

5.4 Transformations of 52 to 53

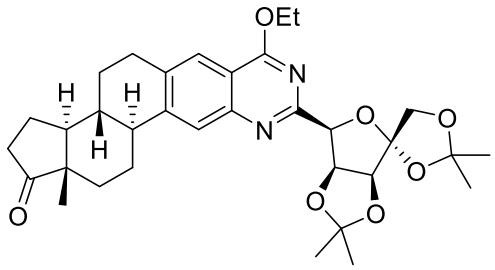


52 (1.0 equiv) SI-1-3(1.5 equiv) **53**, 46%

A Schlenk tube (15 mL) equipped with a magnetic stir bar and a Teflon-lined screwed cap was charged with substituted **52** (32.5 mg, 0.1 mmol, 1.0 equiv), dioxazolones glycogen anomeric **SI-1-3** (47.3 mg, 0.15 mmol, 1.5 equiv), $[Cp^*IrCl_2]_2$ (1.5 mg, 2 mol %), $AgNO_3$ (1.5 mg, 8 mol %) and DCE (1.0 mL, 0.1 M). The vial was then sealed and heated at 60 ℃ for 12 h under N_2. After that, the solvent was removed

under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the product **53** (26.9 mg, 46% yield) as white solid.

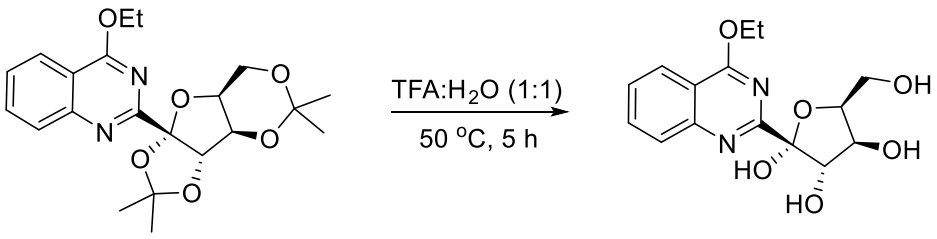
(3a*S*,3b*R*,11b*S*,13a*S*)-7-ethoxy-13a-methyl-9-((3a*S*,4*R*,6*R*,6a*S*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)-2,3,3a,3b,4,5,11b,12,13,13a-decahydro-1*H*-cyclopenta[5,6]naphtho[2,1-*g*]quinazolin-1-one(53)[1]



TLC: R*f* = 0.45 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.82 (s, 1H), 5.25 (d, *J* = 6.0 Hz, 2H), 4.70 (dd, *J* = 5.3, 1.3 Hz, 1H), 4.65 – 4.56 (m, 2H), 4.44 – 4.38 (m, 2H), 3.15 – 3.00 (m, 2H), 2.60 – 2.48 (m, 2H), 2.44 (td, *J* = 11.3, 4.2 Hz, 1H), 2.16 (dt, *J* = 18.5, 8.8 Hz, 1H), 2.08 (td, *J* = 10.2, 8.3, 5.5 Hz, 2H), 2.01 (dt, *J* = 13.1, 3.2 Hz, 1H), 1.83 (s, 2H), 1.71 – 1.60 (m, 3H), 1.58 – 1.53 (m, 2H), 1.52 (s, 3H), 1.50 – 1.47 (m, 3H), 1.44 (s, 3H), 1.31 (s, 3H), 1.23 (s, 3H), 0.91 (s, 3H).

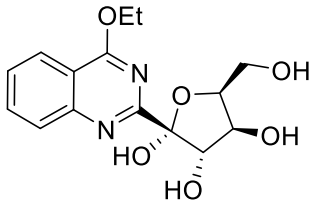
5.5 Deprotection reaction of 1



1 (0.1 mmol) **D1**, 49%

Dissolve the reactant **1** (0.1 mmol, 1.0 equiv) in 1 mL of a solution of 50% TFA (aq.) and stir at 50 ℃ for 5 h. Remove the solvent under reduced pressure. Purify the residue by column chromatography (silica, CH_2Cl_2/MeOH) to give the corresponding product **D1** (15.7 mg, 49%) as color oil.

(2*R*,3*S*,4*S*,5*S*)-2-(4-ethoxyquinazolin-2-yl)-5-(hydroxymethyl)tetrahydrofuran-2,3,4-triol(D1)[1]

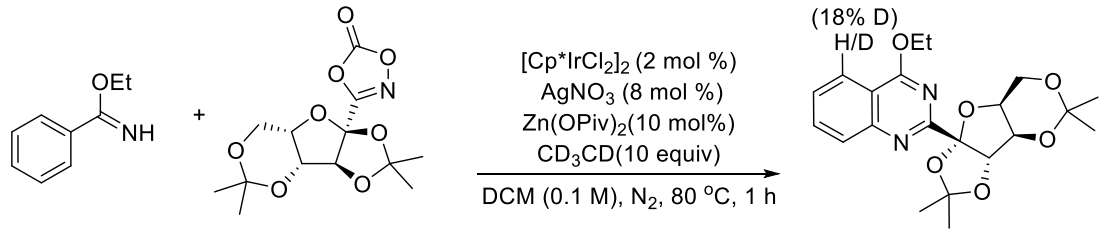


TLC: R*f* = 0.3 (DCM/MeOH = 10/1)

^{1}H NMR (400 MHz, CD_3OD): δ 8.20 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.99 – 7.88 (m, 2H), 7.64 (ddd, *J* = 8.1, 6.8, 1.4 Hz, 1H), 4.77 – 4.70 (m, 2H), 4.28 (d, *J* = 9.4 Hz, 1H), 3.94 – 3.86 (m, 1H), 3.80 (t, *J* = 8.9 Hz, 1H), 3.76 – 3.70 (m, 2H), 1.54 (t, *J* = 7.1 Hz, 3H).

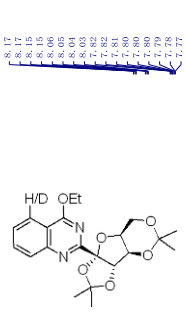
6 H/D Exchange Experiment

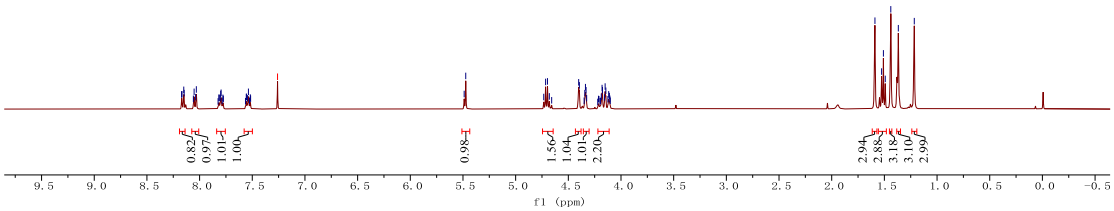
6.1 H/D Exchange for 1



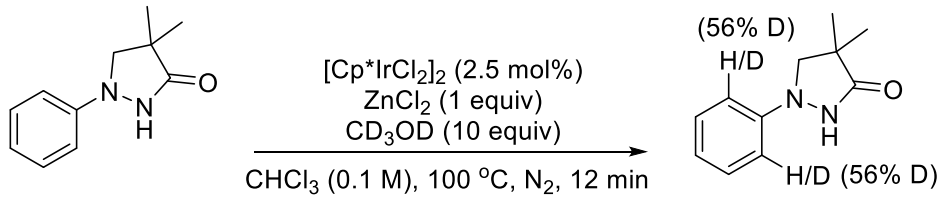
SI-2-1 (0.1 mmol) **SI-1-1** (0.15 mmol) **1-d_n**, 57%

A Schlenk tube (15 mL) equipped with a magnetic stir bar and a Teflon-lined screwed cap was charged with substituted benzimidates **SI-2-1** (14.9 mg, 0.1 mmol, 1.0 equiv), dioxazolones glycogen anomeric **SI-1-1** (47 mg, 0.15 mmol, 1.5 equiv), $[Cp^*IrCl_2]_2$ (2 mol %), $AgNO_3$ (8 mol %), $Zn(OPiv)_2$ (10 mol%), CD_3OD (41 μL, 1.0 mmol, 10.0 equiv) and DCM (1.0 mL, 0.1 M). The vial was then sealed and heated at 80 ℃ for 1 h under N_2. After that, the solvent was removed under reduced pressure and the residue was purified by PrepTLC using PE/EA to afford **1-d_n** in 57% yield. Upon analyzing the ^1H NMR spectrum of the product, the deuteration percentage was determined as 18%.





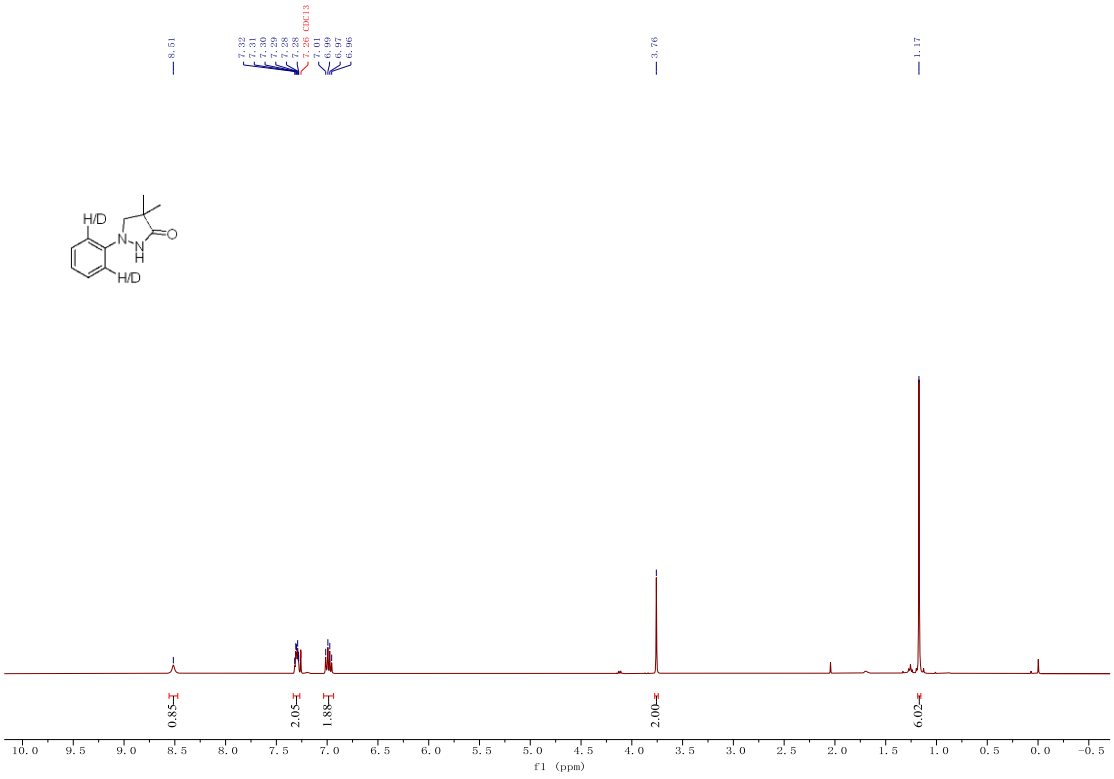
6.2 H/D Exchange for SI-4-1



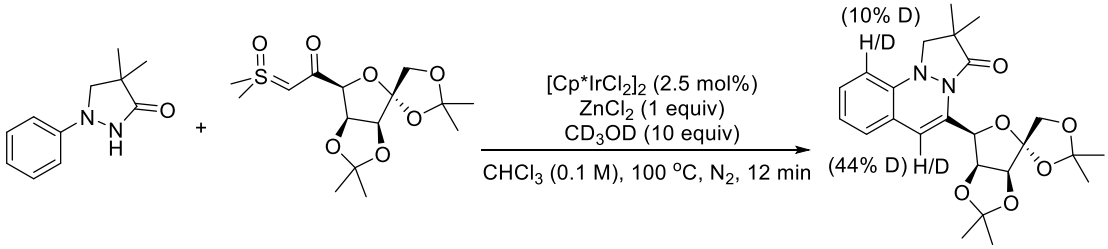
SI-4-1 (0.1 mmol)

SI-4-1-*d*$_n$, 63%

A Schlenk tube (15 mL) equipped with a magnetic stir bar and a Teflon-lined screwed cap was charged with substituted 4,4-dimethyl-1-phenylpyrazolidin-3-one **SI-4-1** (19 mg, 0.1 mmol, 1.0 equiv), $[Cp^*IrCl_2]_2$ (2 mg, 2.5 mol %), $ZnCl_2$ (13.6 mg, 0.1 mmol, 1.0 equiv), CD_3OD (41 μL, 1.0 mmol, 10.0 equiv) and $CHCl_3$ (1 mL, 0.1 M). The vial was then sealed and heated at 100 ℃ (oil bath) for 12 min under N_2. After cooling to room temperature, the solvent was removed in vacuo and the residue was purified using PrepTLC (ethyl acetate/petroleum ether = 1:1) to afford **SI-4-1-*d*$_n$** in 63% yield. Upon analyzing the ^{1}H NMR spectrum of the product, the deuteration percentage was determined as 56%.

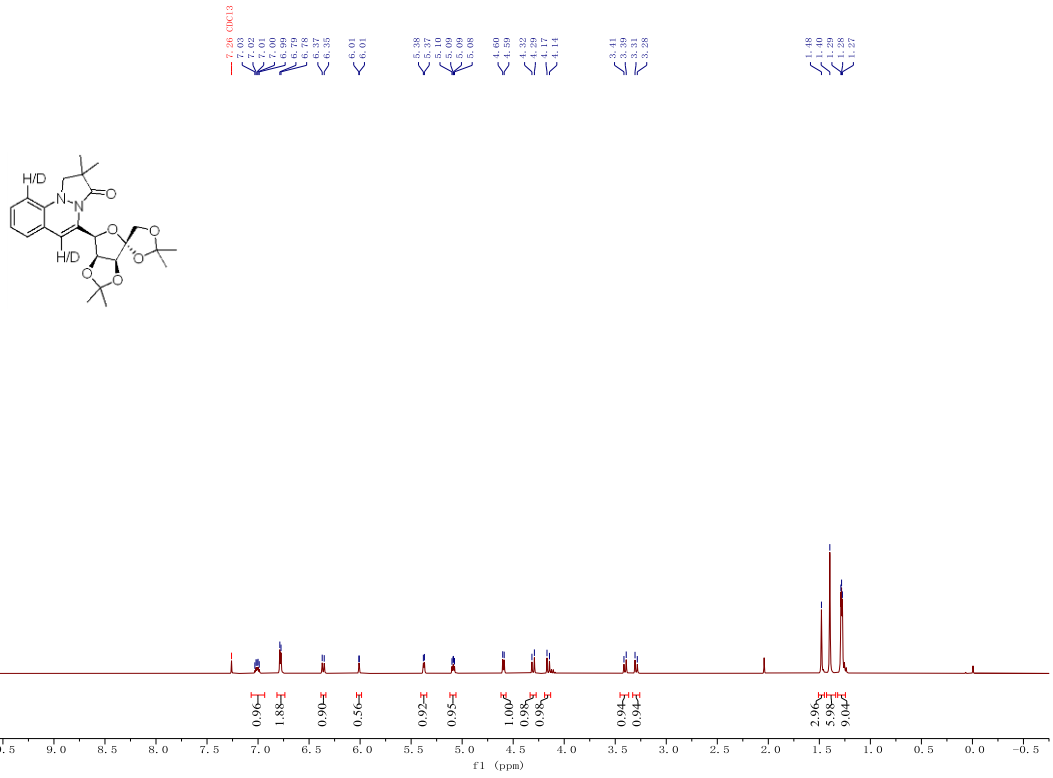


6.3 H/D Exchange for 27



SI-4-1 (0.1 mmol) **SI-3-2** (0.2 mmol) **27-d_n**, 59%

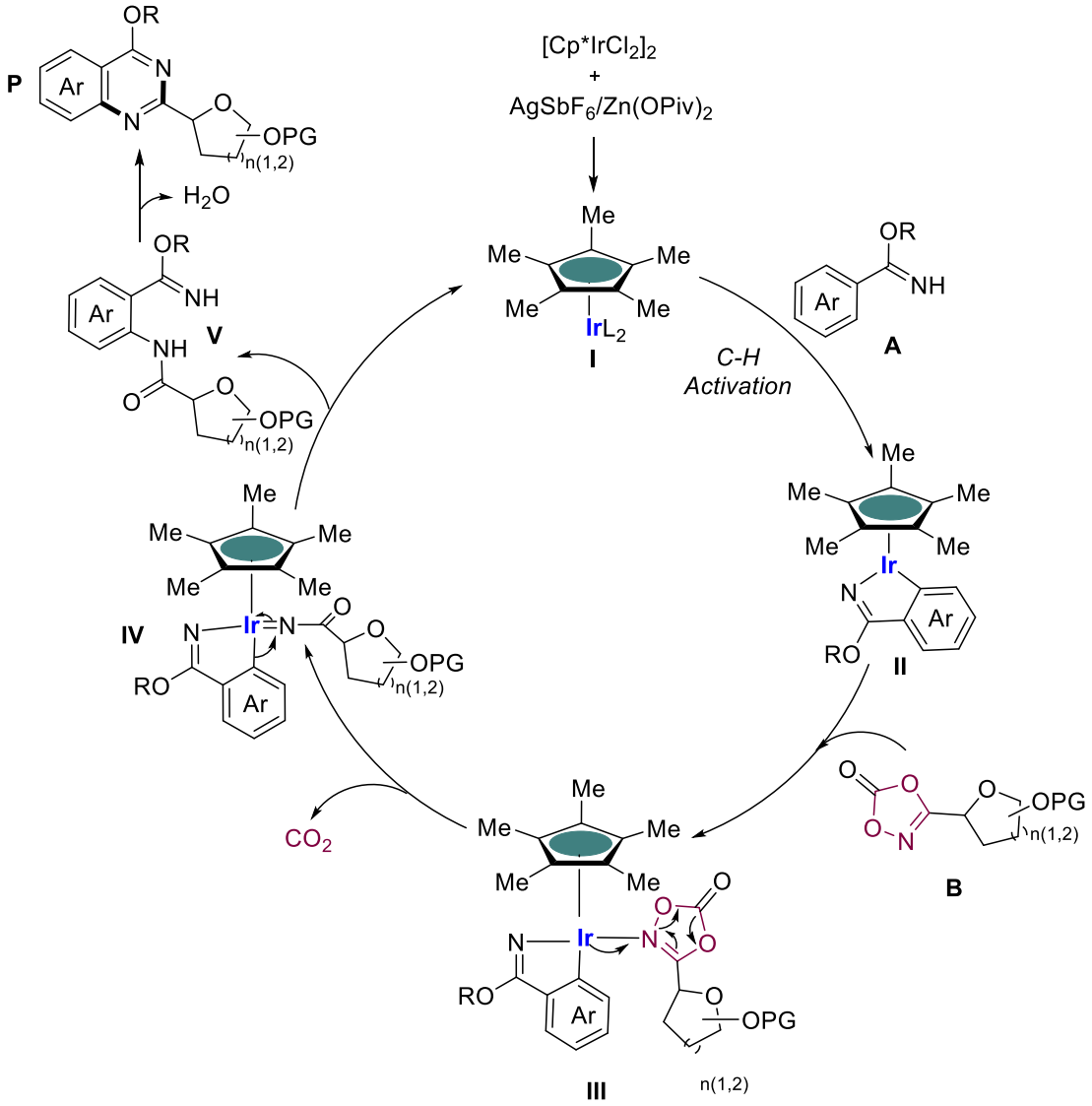
A Schlenk tube (15 mL) equipped with a magnetic stir bar and a Teflon-lined screwed cap was charged with substituted 4,4-dimethyl-1-phenylpyrazolidin-3-one **SI-4-1** (19 mg, 0.1 mmol, 1.0 equiv), carbonyl sulfoxonium ylides glycogen anomeric **SI-3-2** (69.6 mg, 0.2 mmol, 2.0 equiv), $[Cp^*IrCl_2]_2$ (2 mg, 2.5 mol %), $ZnCl_2$ (13.6 mg, 0.1 mmol, 1.0 equiv), CD_3OD (41 μL, 1.0 mmol, 10.0 equiv) and $CHCl_3$ (1 mL, 0.1 M). The vial was then sealed and heated at 100 ℃ (oil bath) for 12 min under N_2. After cooling to room temperature, the solvent was removed in vacuo and the residue was purified using PrepTLC (ethyl acetate/petroleum ether = 1:3) to afford **27-d_n** in 59% yield. Upon analyzing the ^1H NMR spectrum of the product, the deuteration percentage was determined as 44%.



6.4 Proposed reaction mechanism

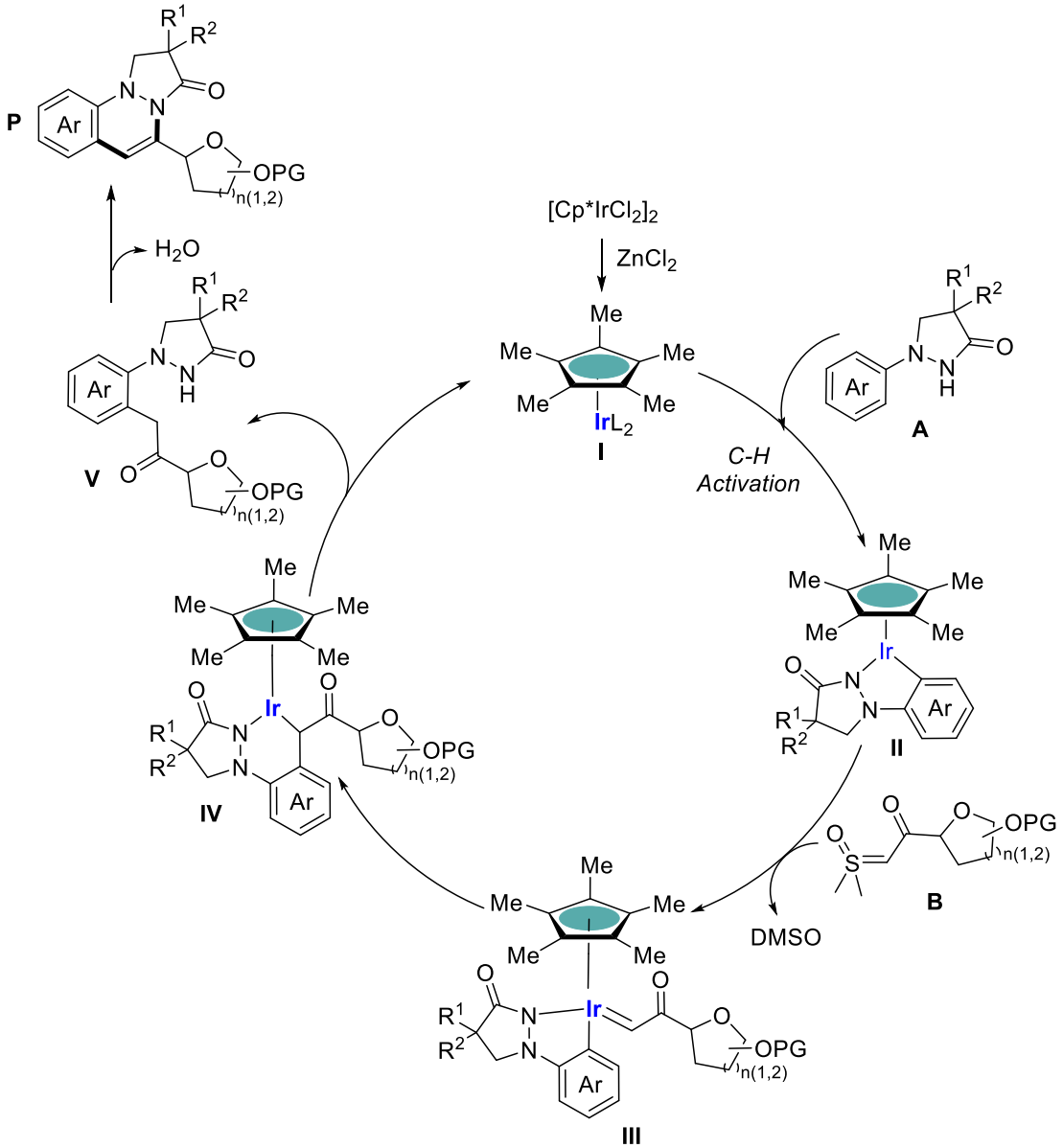
6.4.1 General catalytic pathway for Cp*Ir(III) to the annulation of benzimidates with dioxazolones glycogen anomeric

Based on literature report, we propose a plausible mechanism for these reactions. Cyclometalation of A forms a Ir-cyclic intermediate II. Coordination of dioxazolones glycogen anomeric B to afford the formation of Ir-carbene species III. This species is then proposed to undergo migratory insertion of the Ir-C bond, leading to the formation of a six-membered Ir-cyclic intermediate IV. Protonolysis releases the acylmethylated intermediate V while regenerating the active catalyst. The intermediate V undergoes cyclization and dehydration to generate product P.



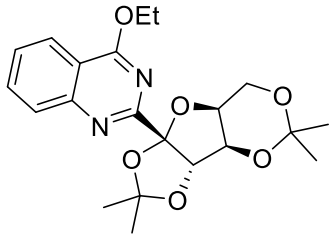
6.4.2 General catalytic pathway for Cp*Ir(III) to the annulation of Narylpyrazolidin-3-ones with carbonyl sulfoxonium ylides glycogen anomeric

Based on literature report, we propose a plausible mechanism for these reactions. C–H activation under the assistance of directing group delivers a cyclometallated intermediate **II**. Coordination of sulfoxonium ylide glycol-reagents B occurs after subsequent α elimination of DMSO, resulting in the formation of Ir-carbene species **III**. This species is then proposed to undergo migratory insertion of the Ir-C bond, leading to the formation of a six-membered Ir-cyclic intermediate **IV**. Protonolysis releases the acylmethylated intermediate **V** while regenerating the active catalyst. The intermediate **V** undergoes cyclization and dehydration to generate product P.



7 Spectra Data of substrates and products

4-ethoxy-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)quinazoline(1)



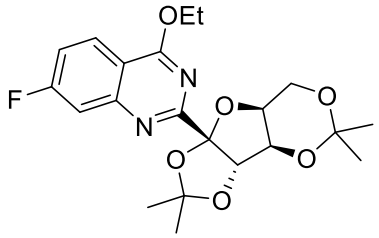
Prepared from **SI-2-1** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **1** (38.2 mg, 95% yield) as yellow oil.

TLC: R*f* = 0.40 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.06 – 8.01 (m, 1H), 7.79 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.53 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 5.46 (s, 1H), 4.70 (qd, *J* = 7.2, 0.8 Hz, 2H), 4.39 (d, *J* = 2.5 Hz, 1H), 4.33 (q, *J* = 2.3 Hz, 1H), 4.23 – 4.11 (m, 2H), 1.58 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H), 1.43 (s, 3H), 1.37 (s, 3H), 1.21 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.17, 160.37, 151.16, 133.37, 128.51, 127.03, 123.32, 115.80, 114.40, 112.34, 97.43, 87.21, 28.63, 27.10, 26.54, 18.93, 14.36.

4-ethoxy-7-fluoro-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)quinazoline(2)



Prepared from **SI-2-2** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl

acetate/Petroleum Ether = 1/5) afforded **2** (17.6 mg, 42% yield) as yellow oil.

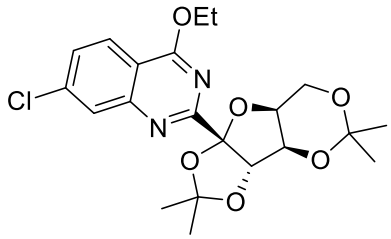
TLC: R*f* = 0.40 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (dd, *J* = 9.0, 6.1 Hz, 1H), 7.67 (dd, *J* = 10.0, 2.5 Hz, 1H), 7.32 – 7.26 (m, 1H), 5.43 (s, 1H), 4.70 (q, *J* = 7.1 Hz, 2H), 4.39 (d, *J* = 2.4 Hz, 1H), 4.33 (t, *J* = 2.2 Hz, 1H), 4.16 (dd, *J* = 11.9, 2.1 Hz, 2H), 1.59 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H), 1.44 (s, 3H), 1.38 (s, 3H), 1.21 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.37, 165.51 (d, *J* = 225.5 Hz), 161.70, 153.07 (d, *J* = 13.8 Hz), 126.04 (d, *J* = 10.5 Hz), 116.97 (d, *J* = 24.8 Hz), 114.24, 112.90, 112.67 (d, *J* = 8.2 Hz), 112.46, 97.42, 87.21, 74.01, 73.49, 63.49, 60.10, 28.65, 27.07, 26.51, 18.89, 14.33.

^{19}F NMR (376 MHz, $CDCl_3$): δ -103.82.

7-chloro-4-ethoxy-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)quinazoline(3)[1]



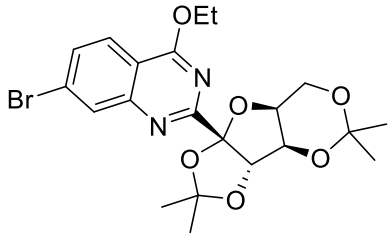
Prepared from **SI-2-3** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **3** (21.4 mg, 49% yield) as yellow oil.

TLC: R*f* = 0.60 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.7 Hz, 1H), 8.04 (d, *J* = 2.0 Hz, 1H), 7.48 (dd, *J* = 8.7, 2.0 Hz, 1H), 5.44 (s, 1H), 4.70 (q, *J* = 7.1 Hz, 2H), 4.39 (d, *J* = 2.5 Hz, 1H), 4.33 (q, *J* = 2.2 Hz, 1H), 4.15 (dd, *J* = 9.1, 2.1 Hz, 2H), 1.58 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H), 1.43 (s, 3H), 1.36 (s, 3H), 1.21 (s, 3H).

7-bromo-4-ethoxy-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-

[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)quinazoline(4)



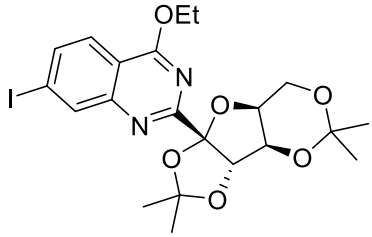
Prepared from **SI-2-4** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **4** (21.6 mg, 45% yield) as yellow oil.

TLC: R*f* = 0.50 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 1.9 Hz, 1H), 8.01 (d, *J* = 8.7 Hz, 1H), 7.62 (dd, *J* = 8.7, 1.9 Hz, 1H), 5.43 (s, 1H), 4.69 (q, *J* = 7.1 Hz, 2H), 4.39 (d, *J* = 2.5 Hz, 1H), 4.32 (d, *J* = 2.1 Hz, 1H), 4.21 – 4.09 (m, 2H), 1.58 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H), 1.43 (s, 3H), 1.36 (s, 3H), 1.20 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.27, 161.55, 151.96, 130.96, 130.60, 128.07, 124.83, 114.50, 114.21, 112.45, 97.41, 87.16, 73.98, 73.51, 63.62, 60.11, 28.67, 27.06, 26.48, 18.88, 14.30.

4-ethoxy-7-iodo-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)quinazoline(5)



Prepared from **SI-2-7** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **5** (25.3mg, 48% yield) as yellow oil.

TLC: R*f* = 0.50 (Ethyl acetate/Petroleum Ether = 1/2)

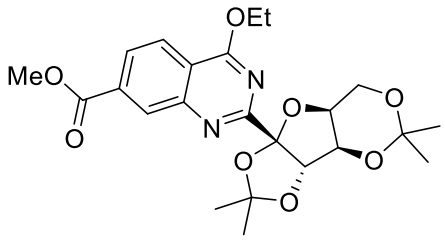
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 1.7 Hz, 1H), 7.88 – 7.79 (m, 2H), 5.45 (s,

1H), 4.70 (qd, *J* = 7.2, 1.6 Hz, 2H), 4.39 (d, *J* = 2.4 Hz, 1H), 4.32 (q, *J* = 2.2 Hz, 1H), 4.21 – 4.09 (m, 2H), 1.58 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H), 1.43 (s, 3H), 1.35 (s, 3H), 1.21 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.39, 161.32, 151.84, 137.54, 135.93, 124.51, 114.94, 114.26, 112.42, 100.58, 97.41, 87.17, 74.02, 73.58, 63.59, 60.14, 28.63, 27.07, 26.49, 18.93, 14.28.

HRMS (ESI): m/z calculated for $C_{21}H_{26}IN_2O_6^+$ $[M+H]^+$, 529.0830; found, 529.0835.

methyl 4-ethoxy-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)quinazoline-7-carboxylate(6)[1]

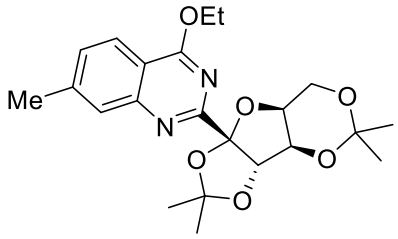


Prepared from **SI-2-9** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **6** (27.6 mg, 60% yield) as yellow oil.

TLC: R*f* = 0.40 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 1.6 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 8.13 (dd, *J* = 8.5, 1.6 Hz, 1H), 5.46 (s, 1H), 4.72 (q, *J* = 7.1 Hz, 2H), 4.40 (d, *J* = 2.5 Hz, 1H), 4.33 (q, *J* = 2.2 Hz, 1H), 4.21 – 4.11 (m, 2H), 3.97 (s, 3H), 1.58 (s, 3H), 1.51 (t, *J* = 7.1 Hz, 3H), 1.43 (s, 3H), 1.37 (s, 3H), 1.19 (s, 3H).

4-ethoxy-7-methyl-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)quinazoline(7)[1]

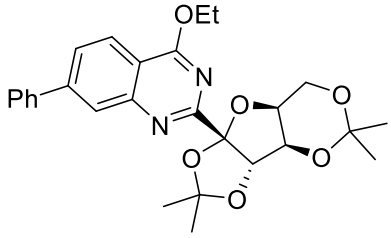


Prepared from **SI-2-5** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **7** (38.3 mg, 92% yield) as yellow oil.

TLC: R*f* = 0.30 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.3 Hz, 1H), 7.82 (s, 1H), 7.35 (dd, *J* = 8.4, 1.7 Hz, 1H), 5.46 (s, 1H), 4.68 (q, *J* = 7.1 Hz, 2H), 4.39 (d, *J* = 2.5 Hz, 1H), 4.32 (q, *J* = 2.3 Hz, 1H), 4.16 (qd, *J* = 13.5, 2.2 Hz, 2H), 2.52 (s, 3H), 1.58 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H), 1.43 (s, 3H), 1.36 (s, 3H), 1.21 (s, 3H).

4-ethoxy-7-phenyl-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)quinazoline(8)[1]



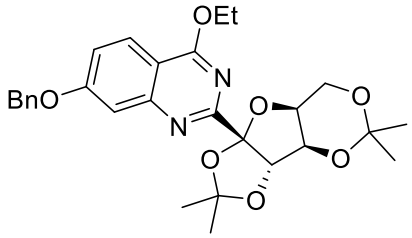
Prepared from **SI-2-10** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **8** (37.8 mg, 79% yield) as yellow oil.

TLC: R*f* = 0.40 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 1.7 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 7.81 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.76 – 7.72 (m, 2H), 7.49 (dd, *J* = 8.3, 6.7 Hz, 2H), 7.44 – 7.39 (m, 1H), 5.48 (s, 1H), 4.76 – 4.69 (m, 2H), 4.41 (d, *J* = 2.5 Hz, 1H), 4.35 (d, *J* = 2.1 Hz, 1H), 4.24 – 4.12 (m, 2H), 1.60 (s, 3H), 1.53 (t, *J* = 7.1 Hz, 3H), 1.44 (s,

3H), 1.40 (s, 3H), 1.23 (s, 3H).

7-(benzyloxy)-4-ethoxy-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)quinazoline(9)[1]

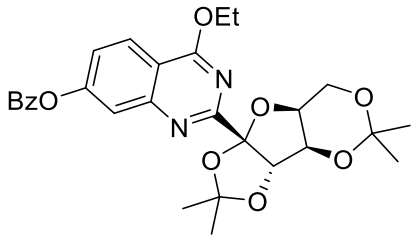


Prepared from **SI-2-11** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **9** (25.4 mg, 50% yield) as yellow oil.

TLC: R*f* = 0.30 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 9.0 Hz, 1H), 7.49 – 7.43 (m, 3H), 7.42 – 7.36 (m, 2H), 7.36 – 7.32 (m, 1H), 7.21 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.44 (s, 1H), 5.17 (s, 2H), 4.66 (qd, *J* = 7.1, 2.5 Hz, 2H), 4.39 (d, *J* = 2.5 Hz, 1H), 4.32 (d, *J* = 2.1 Hz, 1H), 4.23 – 4.10 (m, 2H), 1.58 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 3H), 1.43 (s, 3H), 1.38 (s, 3H), 1.22 (s, 3H).

4-ethoxy-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)quinazolin-7-yl benzoate(10)



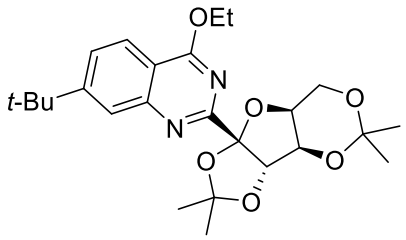
Prepared from **SI-2-12** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **10** (18.8 mg, 36% yield) as yellow oil.

TLC: R*f* = 0.50 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 – 8.21 (m, 3H), 7.89 (d, *J* = 2.2 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.54 (dd, *J* = 8.4, 7.1 Hz, 2H), 7.44 (dd, *J* = 8.9, 2.3 Hz, 1H), 5.48 (s, 1H), 4.73 (q, *J* = 7.1 Hz, 2H), 4.40 (d, *J* = 2.5 Hz, 1H), 4.34 (d, *J* = 2.1 Hz, 1H), 4.16 (qd, *J* = 13.5, 2.2 Hz, 2H), 1.59 (s, 3H), 1.52 (t, *J* = 7.1 Hz, 3H), 1.44 (s, 3H), 1.38 (s, 3H), 1.23 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.12, 164.72, 161.37, 154.82, 152.39, 133.99, 130.37, 129.07, 128.74, 124.99, 122.38, 119.92, 114.29, 113.80, 112.46, 97.47, 87.25, 74.03, 73.52, 63.51, 60.12, 28.69, 27.09, 26.53, 18.92, 14.36.

7-(tert-butyl)-4-ethoxy-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)quinazoline(11)



Prepared from **SI-2-13** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **11** (18.3 mg, 40% yield) as colorless oil.

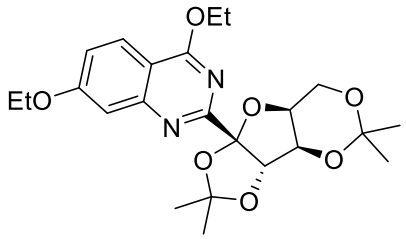
TLC: R*f* = 0.50 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.7 Hz, 1H), 8.02 (d, *J* = 1.8 Hz, 1H), 7.61 (dd, *J* = 8.6, 1.8 Hz, 1H), 5.49 (s, 1H), 4.73 – 4.65 (m, 2H), 4.39 (d, *J* = 2.5 Hz, 1H), 4.33 (q, *J* = 2.3 Hz, 1H), 4.22 – 4.10 (m, 2H), 1.59 (s, 3H), 1.49 (t, *J* = 7.0 Hz, 3H), 1.44 (s, 3H), 1.40 (d, *J* = 1.5 Hz, 9H), 1.36 (s, 3H), 1.23 (s, 3H).

^{13}C NMR (75 MHz,$CDCl_3$): δ 166.85, 160.48, 157.01, 151.62, 125.58, 124.31, 122.75, 114.54, 113.56, 112.15, 97.42, 87.08, 74.26, 73.46, 63.05, 60.16, 35.48, 31.09, 28.57, 27.08, 26.60, 19.02, 14.38.

HRMS (ESI): m/z calculated for $C_{25}H_{35}N_2O_6^+$ $[M+H]^+$, 459.2490; found, 459.2498.

4,7-diethoxy-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)quinazoline(12)



Prepared from **SI-2-14** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **12** (26.7 mg, 60% yield) as colorless oil.

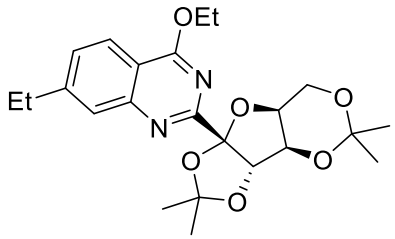
TLC: R*f* = 0.30 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 9.0 Hz, 1H), 7.36 (d, *J* = 2.5 Hz, 1H), 7.12 (dd, *J* = 9.0, 2.4 Hz, 1H), 5.44 (s, 1H), 4.66 (qd, *J* = 7.1, 2.2 Hz, 2H), 4.38 (d, *J* = 2.5 Hz, 1H), 4.32 (t, *J* = 2.3 Hz, 1H), 4.22 – 4.12 (m, 4H), 1.58 (s, 3H), 1.47 (td, *J* = 7.0, 4.9 Hz, 6H), 1.44 (s, 3H), 1.37 (s, 3H), 1.23 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 166.67, 163.03, 161.07, 153.77, 124.52, 119.57, 114.49, 112.21, 109.97, 107.74, 97.41, 87.21, 74.19, 73.50, 63.92, 62.95, 60.15, 28.56, 27.09, 26.57, 19.02, 14.62, 14.40.

HRMS (ESI): m/z calculated for $C_{23}H_{31}N_2O_7^+$ $[M+H]^+$, 447.2126, found, 447.2135.

4-ethoxy-7-ethyl-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)quinazoline(13)



Prepared from **SI-2-20** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **13** (22.8 mg, 53% yield) as colorless oil.

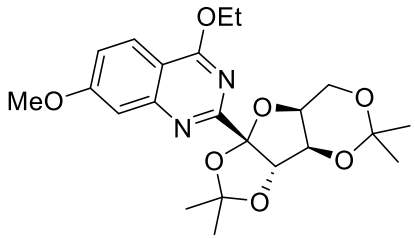
TLC: R*f* = 0.30 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.85 (s, 1H), 7.38 (dd, *J* = 8.4, 1.6 Hz, 1H), 5.48 (s, 1H), 4.69 (q, *J* = 7.1 Hz, 2H), 4.39 (d, *J* = 2.5 Hz, 1H), 4.33 (q, *J* = 2.4 Hz, 1H), 4.21 – 4.11 (m, 2H), 2.83 (q, *J* = 7.6 Hz, 2H), 1.58 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H), 1.44 (s, 3H), 1.36 (s, 3H), 1.32 (t, *J* = 7.6 Hz, 3H), 1.22 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.00, 160.46, 151.65, 150.17, 128.01, 126.45, 123.05, 114.50, 113.83, 112.18, 97.41, 87.15, 74.19, 73.48, 63.07, 60.16, 29.25, 28.58, 27.08, 26.55, 19.00, 14.97, 14.37.

HRMS (ESI): m/z calculated for $C_{23}H_{31}N_2O_6^+$ $[M+H]^+$, 431.2177, found, 431.2186.

4-ethoxy-7-methoxy-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)quinazoline(14)[1]

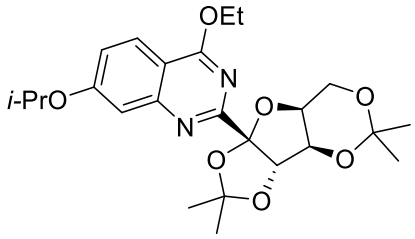


Prepared from **SI-2-6** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **14** (32.0 mg, 74% yield) as yellow oil.

TLC: R*f* = 0.30 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 9.0 Hz, 1H), 7.39 (d, *J* = 2.5 Hz, 1H), 7.12 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.44 (s, 1H), 4.66 (qd, *J* = 7.1, 2.3 Hz, 2H), 4.38 (d, *J* = 2.5 Hz, 1H), 4.32 (dq, *J* = 4.0, 2.2 Hz, 1H), 4.20 – 4.11 (m, 2H), 3.92 (s, 3H), 1.58 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 3H), 1.43 (s, 3H), 1.37 (s, 3H), 1.22 (s, 3H).

4-ethoxy-7-isopropoxy-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)quinazoline(15)



Prepared from **SI-2-22** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **15** (23.4 mg, 51% yield) as colorless oil.

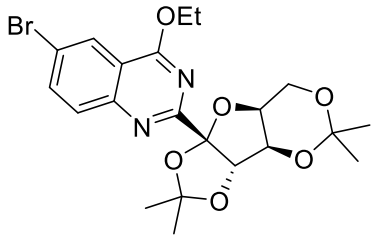
TLC: R*f* = 0.20 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 9.0 Hz, 1H), 7.37 (d, *J* = 2.5 Hz, 1H), 7.08 (dd, *J* = 9.0, 2.4 Hz, 1H), 5.43 (s, 1H), 4.76 – 4.68 (m, 1H), 4.64 (ddt, *J* = 10.7, 6.6, 3.9 Hz, 2H), 4.38 (d, *J* = 2.4 Hz, 1H), 4.32 (q, *J* = 2.2 Hz, 1H), 4.23 – 4.12 (m, 2H), 1.58 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 3H), 1.44 (s, 3H), 1.40 (s, 3H), 1.39 (s, 3H), 1.37 (s, 3H), 1.23 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 166.64, 162.09, 161.01, 153.73, 124.63, 120.36, 114.47, 112.25, 109.74, 108.44, 97.43, 87.24, 74.17, 73.49, 70.29, 62.94, 60.13, 28.58, 27.10, 26.58, 21.82, 19.01, 14.41.

HRMS (ESI): m/z calculated for $C_{24}H_{33}N_2O_7^+$ $[M+H]^+$, 461.2282, found, 461.2292.

6-bromo-4-ethoxy-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)quinazoline(16)[1]

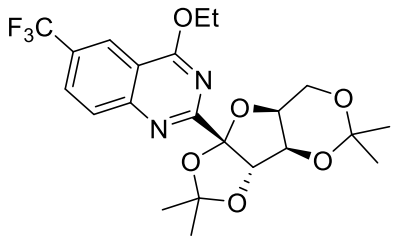


Prepared from **SI-2-15** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **16** (16.8 mg, 35% yield) as yellow oil.

TLC: R*f* = 0.40 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 2.2 Hz, 1H), 7.95 – 7.84 (m, 2H), 5.41 (s, 1H), 4.70 (q, *J* = 7.1 Hz, 2H), 4.39 (d, *J* = 2.5 Hz, 1H), 4.33 (d, *J* = 2.3 Hz, 1H), 4.16 (qd, *J* = 13.6, 2.2 Hz, 2H), 1.58 (s, 3H), 1.51 (t, *J* = 7.1 Hz, 3H), 1.43 (s, 3H), 1.38 (s, 3H), 1.20 (s, 3H).

4-ethoxy-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)-6-(trifluoromethyl)quinazoline(17)[1]

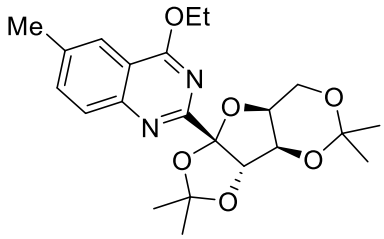


Prepared from **SI-2-17** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **17** (22.1 mg, 47% yield) as yellow oil.

TLC: R*f* = 0.40 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 – 8.43 (m, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 7.98 (dd, *J* = 8.8, 2.1 Hz, 1H), 5.44 (s, 1H), 4.74 (q, *J* = 7.1 Hz, 2H), 4.41 (d, *J* = 2.4 Hz, 1H), 4.34 (d, *J* = 2.1 Hz, 1H), 4.23 – 4.11 (m, 2H), 1.59 (s, 3H), 1.54 (t, *J* = 7.1 Hz, 3H), 1.43 (s, 3H), 1.38 (s, 3H), 1.19 (s, 3H).

4-ethoxy-6-methyl-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)quinazoline(18)



Prepared from **SI-2-16** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl

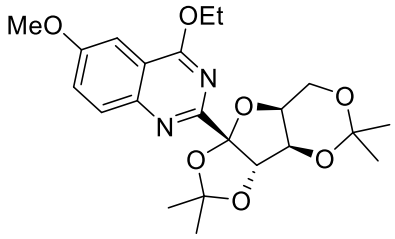
acetate/Petroleum Ether = 1/5) afforded **18** (27.0 mg, 65% yield) as yellow oil.

TLC: R*f* = 0.50 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 – 7.89 (m, 2H), 7.62 (dd, *J* = 8.6, 2.1 Hz, 1H), 5.43 (s, 1H), 4.68 (qd, *J* = 7.1, 1.2 Hz, 2H), 4.38 (d, *J* = 2.5 Hz, 1H), 4.32 (q, *J* = 2.3 Hz, 1H), 4.23 – 4.10 (m, 2H), 2.52 (s, 3H), 1.58 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H), 1.43 (s, 3H), 1.38 (s, 3H), 1.21 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 166.70, 159.55, 149.52, 137.18, 135.39, 128.16, 122.19, 115.61, 114.40, 112.32, 97.42, 87.27, 74.08, 73.46, 63.15, 60.11, 28.60, 27.10, 26.52, 21.69, 18.94, 14.38.

4-ethoxy-6-methoxy-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)quinazoline(19)



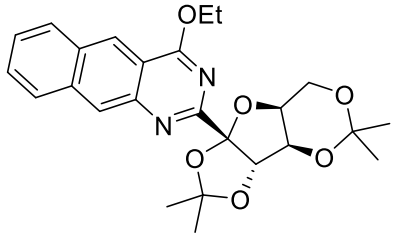
Prepared from **SI-2-18** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **19** (16.8 mg, 39% yield) as yellow oil.

TLC: R*f* = 0.30 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 9.1 Hz, 1H), 7.43 (dd, *J* = 9.1, 2.9 Hz, 1H), 7.39 (d, *J* = 2.8 Hz, 1H), 5.44 (s, 1H), 4.71 (q, *J* = 7.1 Hz, 2H), 4.39 (d, *J* = 2.5 Hz, 1H), 4.33 (q, *J* = 2.2 Hz, 1H), 4.22 – 4.12 (m, 2H), 3.94 (s, 3H), 1.59 (s, 3H), 1.52 (t, *J* = 7.2 Hz, 3H), 1.44 (s, 3H), 1.36 (s, 3H), 1.22 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 175.82, 165.32, 158.26, 147.23, 130.09, 125.37, 116.26, 114.29, 112.19, 101.19, 97.42, 87.21, 74.18, 73.42, 63.17, 60.15, 55.75, 28.61, 27.08, 26.54, 18.96, 14.44.

4-ethoxy-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)benzo[g]quinazoline(20)[1]

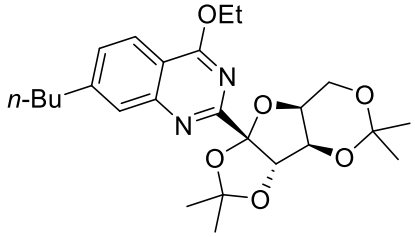


Prepared from **SI-2-21** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **20** (14.9 mg, 33% yield) as white solid.

TLC: R*f* = 0.30 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 8.59 (s, 1H), 8.02 (t, *J* = 8.5 Hz, 2H), 7.56 (ddd, *J* = 8.2, 6.5, 1.4 Hz, 1H), 7.50 (ddd, *J* = 8.0, 6.5, 1.3 Hz, 1H), 5.51 (s, 1H), 4.78 (q, *J* = 7.1 Hz, 2H), 4.42 (d, *J* = 2.5 Hz, 1H), 4.37 (q, *J* = 2.3 Hz, 1H), 4.23 (dd, *J* = 13.5, 1.6 Hz, 1H), 4.15 (dd, *J* = 13.6, 2.8 Hz, 1H), 1.61 (s, 3H), 1.57 (t, *J* = 7.1 Hz, 3H), 1.44 (s, 3H), 1.42 (s, 3H), 1.22 (s, 3H).

7-butyl-4-ethoxy-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)quinazoline(21)



Prepared from **SI-2-8** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **21** (23.3 mg, 51% yield) as colorless oil.

TLC: R*f* = 0.40 (Ethyl acetate/Petroleum Ether = 1/2)

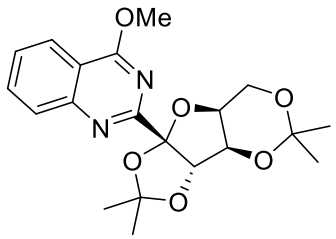
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 1.6 Hz, 1H), 7.37 (dd, *J* = 8.3, 1.7 Hz, 1H), 5.47 (s, 1H), 4.69 (q, *J* = 7.1 Hz, 2H), 4.39 (d, *J* = 2.5

Hz, 1H), 4.33 (q, *J* = 2.3 Hz, 1H), 4.16 (qd, *J* = 13.4, 2.2 Hz, 2H), 2.79 (t, *J* = 7.7 Hz, 2H), 1.73 – 1.64 (m, 2H), 1.59 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H), 1.44 (s, 3H), 1.37 (d, *J* = 6.5 Hz, 5H), 1.22 (s, 3H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 166.99, 160.45, 151.57, 148.91, 128.37, 127.18, 122.99, 114.51, 113.83, 112.19, 97.42, 87.19, 74.20, 73.51, 63.05, 60.17, 35.95, 32.99, 28.56, 27.09, 26.56, 22.28, 19.02, 14.37, 13.92.

HRMS (ESI): m/z calculated for $C_{25}H_{35}N_2O_6^+$ $[M+H]^+$, 459.2490, found, 459.2496

4-methoxy-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)quinazoline(22)[1]

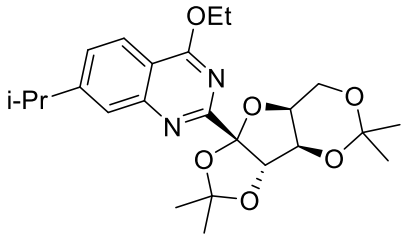


Prepared from **SI-2-19** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **22** (23.3 mg, 66% yield) as yellow oil.

TLC: R*f* = 0.30 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (dd, *J* = 8.3, 1.5 Hz, 1H), 8.06 (dd, *J* = 8.6, 1.1 Hz, 1H), 7.80 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.54 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 5.49 (s, 1H), 4.42 (d, *J* = 2.5 Hz, 1H), 4.35 (q, *J* = 2.3 Hz, 1H), 4.23 (s, 3H), 4.20 (d, *J* = 1.6 Hz, 1H), 4.15 (dd, *J* = 13.6, 2.8 Hz, 1H), 1.60 (s, 3H), 1.44 (s, 3H), 1.41 (s, 3H), 1.23 (s, 3H).

4-ethoxy-7-isopropyl-2-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)quinazoline(23)



Prepared from **SI-2-23** (0.1 mmol, 1.0 equiv) and **SI-1-1** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **23** (20.0mg, 45% yield) as colorless oil.

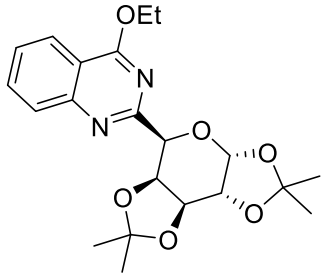
TLC: R*f* = 0.30 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 1.7 Hz, 1H), 7.42 (dd, *J* = 8.4, 1.7 Hz, 1H), 5.48 (s, 1H), 4.69 (q, *J* = 7.1 Hz, 2H), 4.39 (d, *J* = 2.5 Hz, 1H), 4.33 (q, *J* = 2.3 Hz, 1H), 4.21 – 4.10 (m, 2H), 3.08 (p, *J* = 6.9 Hz, 1H), 1.58 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H), 1.44 (s, 3H), 1.36 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H), 1.23 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 166.95, 160.46, 154.76, 151.72, 126.86, 125.09, 123.08, 114.52, 113.95, 112.17, 97.42, 87.12, 74.22, 73.47, 63.06, 60.16, 34.53, 28.57, 27.08, 26.58, 23.65, 19.01, 14.38.

HRMS (ESI): m/z calculated for $C_{24}H_{33}N_2O_6^+$ $[M+H]^+$, 445.2333, found, 445.2339.

4-ethoxy-2-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-*d*]pyran-5-yl)quinazoline(24)



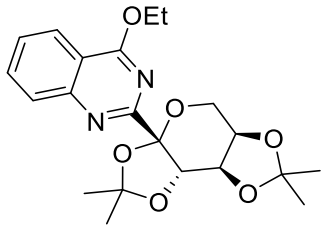
Prepared from **SI-2-1** (0.1 mmol, 1.0 equiv) and **SI-1-4** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **24** (29.7 mg, 74% yield) as yellow oil.

TLC: R*f* = 0.40 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (dd, *J* = 8.2, 1.5 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.76 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.49 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 5.92 (d, *J* = 5.1 Hz, 1H), 5.08 (d, *J* = 2.1 Hz, 1H), 4.97 (dd, *J* = 7.8, 2.2 Hz, 1H), 4.77 (dd, *J* = 7.8, 2.4 Hz, 1H), 4.62 (qq, *J* = 7.4, 3.6 Hz, 2H), 4.46 (dd, *J* = 5.1, 2.4 Hz, 1H), 1.58 (s, 3H), 1.49 (t, *J* = 7.0 Hz, 3H), 1.43 (s, 3H), 1.39 (s, 3H), 1.29 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 166.42, 161.27, 151.23, 133.20, 128.15, 126.41, 123.37, 115.70, 109.49, 108.69, 97.13, 73.59, 71.10, 70.78, 62.94, 26.19, 25.84, 24.97, 24.44, 14.33.

4-ethoxy-2-((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-b:4',5'-*d*]pyran-3a-yl)quinazoline(25)[1]

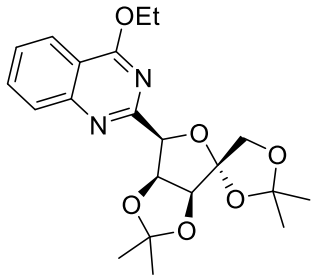


Prepared from **SI-2-1** (0.1 mmol, 1.0 equiv) and **SI-1-2** (0.3 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **25** (15.2 mg, 38% yield) as yellow oil.

TLC: R*f* = 0.30 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (dd, *J* = 8.2, 1.5 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.79 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.53 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H), 5.35 (d, *J* = 2.6 Hz, 1H), 4.67 (dddd, *J* = 20.4, 10.6, 7.2, 3.1 Hz, 3H), 4.34 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 4.18 – 4.06 (m, 2H), 1.62 (s, 3H), 1.57 (s, 3H), 1.51 (t, *J* = 7.1 Hz, 3H), 1.29 (s, 3H), 1.27 (s, 3H).

4-ethoxy-2-((3a*S*,4*R*,6*R*,6a*S*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)quinazoline(26)



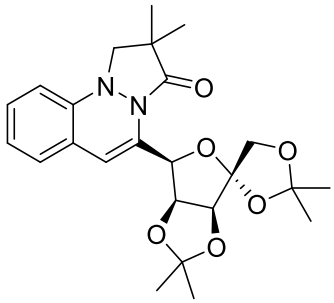
Prepared from **SI-2-1** (0.1 mmol, 1.0 equiv) and **SI-1-3** (0.3 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **26** (18.1 mg, 45% yield) as white solid.

TLC: R*f* = 0.60 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.76 (ddd, *J* = 8.5, 6.7, 1.5 Hz, 1H), 7.49 (dd, *J* = 8.2, 6.9 Hz, 1H), 5.27 (d, *J* = 2.7 Hz, 2H), 4.71 (p, *J* = 2.5 Hz, 1H), 4.63 (p, *J* = 7.0 Hz, 2H), 4.42 (d, *J* = 2.1 Hz, 2H), 1.52 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H), 1.44 (s, 3H), 1.32 (s, 3H), 1.23 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 166.44, 160.29, 151.11, 133.15, 127.96, 126.46, 123.45, 115.74, 113.27, 112.27, 111.84, 84.98, 82.51, 82.29, 69.18, 62.92, 26.61, 26.07, 25.72, 14.38.

2,2-dimethyl-5-((3a*S*,4*R*,6*R*,6a*S*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)-1,2-dihydro-3*H*-pyrazolo[1,2-*a*]cinnolin-3-one(27)



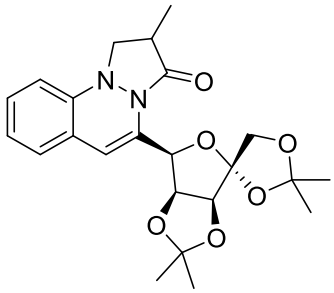
Prepared from **SI-4-1** (0.1 mmol, 1.0 equiv) and **SI-3-2** (0.2 mmol, 2.0 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/6) afforded **27** (35.9 mg, 81% yield) as yellow solid.

TLC: R*f* = 0.80 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.01 (dt, *J* = 7.8, 4.5 Hz, 1H), 6.78 (d, *J* = 4.5 Hz, 2H), 6.36 (d, *J* = 7.9 Hz, 1H), 6.01 (d, *J* = 1.6 Hz, 1H), 5.37 (dd, *J* = 4.2, 1.6 Hz, 1H), 5.08 (dd, *J* = 5.8, 4.1 Hz, 1H), 4.59 (d, *J* = 5.8 Hz, 1H), 4.30 (d, *J* = 9.7 Hz, 1H), 4.16 (d, *J* = 9.7 Hz, 1H), 3.40 (d, *J* = 8.9 Hz, 1H), 3.29 (d, *J* = 8.9 Hz, 1H), 1.48 (s, 3H), 1.40 (s, 6H), 1.28 (d, *J* = 2.5 Hz, 6H), 1.27 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 169.96, 146.54, 133.67, 128.66, 124.88, 123.75, 122.74, 84.97, 81.24, 76.43, 69.43, 60.88, 41.25, 26.54, 26.46, 26.12, 25.18, 22.96, 22.84.

2-methyl-5-((3a*S*,4*R*,6*R*,6a*S*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)-1,2-dihydro-3*H*-pyrazolo[1,2-*a*]cinnolin-3-one(28)[3]

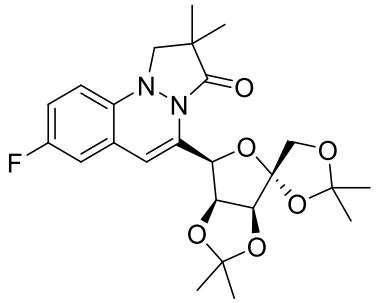


Prepared from **SI-4-15** (0.1 mmol, 1.0 equiv) and **SI-3-2** (0.2 mmol, 2.0 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **28** (36.6 mg, 85% yield) as yellow solid.

TLC: R*f* = 0.60 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 – 6.97 (m, 1H), 6.82 – 6.75 (m, 2H), 6.38 (d, *J* = 7.9 Hz, 1H), 6.00 (d, *J* = 1.8 Hz, 1H), 5.39 (ddd, *J* = 97.6, 4.1, 1.5 Hz, 1H), 5.12 (ddd, *J* = 77.2, 5.7, 4.1 Hz, 1H), 4.61 (dd, *J* = 5.7, 1.6 Hz, 1H), 4.30 (dd, *J* = 9.6, 1.6 Hz, 1H), 4.16 (dd, *J* = 9.8, 1.1 Hz, 1H), 3.89 (dt, *J* = 28.3, 8.9 Hz, 1H), 3.09 (ddd, *J* = 24.6, 10.6, 9.0 Hz, 1H), 2.85 (dddd, *J* = 10.4, 8.7, 7.1, 3.7 Hz, 1H), 1.47 (s, 3H), 1.40 (t, *J* = 3.5 Hz, 6H), 1.31 (dd, *J* = 7.0, 2.0 Hz, 3H), 1.29 (s, 3H).

8-fluoro-2,2-dimethyl-5-((3a*S*,4*R*,6*R*,6a*S*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)-1,2-dihydro-3*H*-pyrazolo[1,2-*a*]cinnolin-3-one(29)



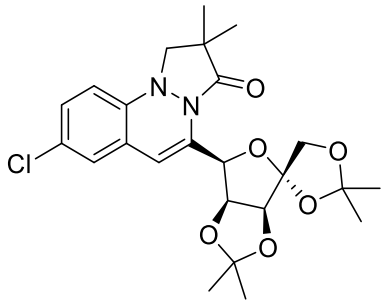
Prepared from **SI-4-2** (0.1 mmol, 1.0 equiv) and **SI-3-2** (0.2 mmol, 2.0 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/6) afforded **29** (35.8 mg, 78% yield) as yellow oil.

TLC: R*f* = 0.80 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.69 (td, *J* = 8.5, 2.8 Hz, 1H), 6.53 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.29 (dd, *J* = 8.7, 4.4 Hz, 1H), 5.96 (d, *J* = 1.6 Hz, 1H), 5.38 (dd, *J* = 4.2, 1.6 Hz, 1H), 5.08 (dd, *J* = 5.8, 4.2 Hz, 1H), 4.59 (d, *J* = 5.8 Hz, 1H), 4.30 (d, *J* = 9.7 Hz, 1H), 4.15 (d, *J* = 9.7 Hz, 1H), 3.37 (d, *J* = 8.8 Hz, 1H), 3.26 (d, *J* = 8.8 Hz, 1H), 1.48 (s, 3H), 1.40 (s, 6H), 1.29 – 1.27 (m, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 170.20, 159.01 (d, *J* = 240.6 Hz), 142.52, 135.30, 125.79 (d, *J* = 8.5 Hz), 113.88 (d, *J* = 22.8 Hz), 112.89, 112.00 (d, *J* = 16.1 Hz), 111.78, 111.59 (d, *J* = 8.2 Hz), 111.06, 109.87, 84.93, 81.20, 76.38, 69.41, 61.15, 41.36, 26.51, 26.43, 26.08, 25.13, 22.89, 22.76.

8-chloro-2,2-dimethyl-5-((3a*S*,4*R*,6*R*,6a*S*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)-1,2-dihydro-3*H*-pyrazolo[1,2-*a*]cinnolin-3-one(30)



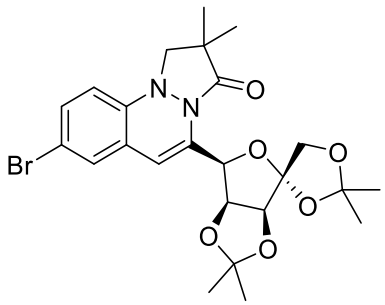
Prepared from **SI-4-3** (0.1 mmol, 1.0 equiv) and **SI-3-2** (0.2 mmol, 2.0 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/6) afforded **30** (27.5 mg, 58% yield) as yellow solid.

TLC: R*f* = 0.80 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.75 (d, *J* = 2.3 Hz, 1H), 6.26 (d, *J* = 8.4 Hz, 1H), 5.93 (d, *J* = 1.6 Hz, 1H), 5.36 (dd, *J* = 4.3, 1.6 Hz, 1H), 5.08 (dd, *J* = 5.7, 4.2 Hz, 1H), 4.59 (d, *J* = 5.8 Hz, 1H), 4.30 (d, *J* = 9.7 Hz, 1H), 4.14 (d, *J* = 9.6 Hz, 1H), 3.36 (d, *J* = 8.9 Hz, 1H), 3.25 (d, *J* = 8.9 Hz, 1H), 1.47 (s, 3H), 1.40 (s, 6H), 1.29 (s, 3H), 1.28 (d, *J* = 1.6 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 170.02, 144.99, 135.20, 127.88, 125.58, 124.51, 112.90, 111.90, 111.71, 111.06, 109.67, 84.92, 81.20, 76.38, 69.41, 60.81, 41.30, 26.50, 26.43, 26.10, 25.14, 22.92, 22.80.

8-bromo-2,2-dimethyl-5-((3a*S*,4*R*,6*R*,6a*S*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)-1,2-dihydro-3*H*-pyrazolo[1,2-*a*]cinnolin-3-one(31)



Prepared from **SI-4-4** (0.1 mmol, 1.0 equiv) and **SI-3-2** (0.2 mmol, 2.0 equiv) according to the general procedure **3**. Purification by flash column (Ethyl

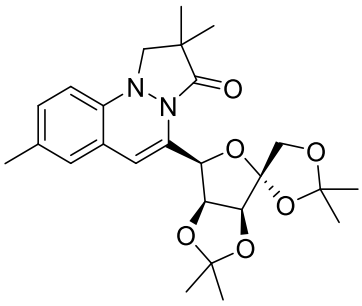
acetate/Petroleum Ether = 1/6) afforded **31** (25.5 mg, 49% yield) as yellow oil.

TLC: R*f* = 0.80 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.88 (d, *J* = 2.2 Hz, 1H), 6.20 (d, *J* = 8.4 Hz, 1H), 5.93 (d, *J* = 1.6 Hz, 1H), 5.36 (dd, *J* = 4.2, 1.6 Hz, 1H), 5.07 (dd, *J* = 5.8, 4.2 Hz, 1H), 4.59 (d, *J* = 5.7 Hz, 1H), 4.30 (d, *J* = 9.7 Hz, 1H), 4.14 (d, *J* = 9.7 Hz, 1H), 3.36 (d, *J* = 8.9 Hz, 1H), 3.25 (d, *J* = 8.9 Hz, 1H), 1.47 (s, 3H), 1.40 (s, 6H), 1.29 (s, 3H), 1.28 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 169.98, 145.49, 135.19, 130.89, 127.27, 125.92, 115.26, 112.91, 112.13, 111.91, 111.06, 109.55, 84.92, 81.20, 76.38, 69.41, 60.72, 41.29, 26.50, 26.45, 26.11, 25.15, 22.93, 22.81.

2,2,8-trimethyl-5-((3a*S*,4*R*,6*R*,6a*S*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)-1,2-dihydro-3*H*-pyrazolo[1,2-*a*]cinnolin-3-one(32)



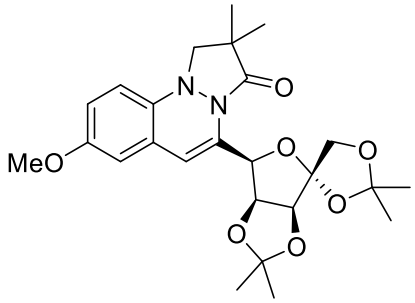
Prepared from **SI-4-5** (0.1 mmol, 1.0 equiv) and **SI-3-2** (0.2 mmol, 2.0 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/6) afforded **32** (37.1 mg, 81% yield) as yellow solid.

TLC: R*f* = 0.80 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.63 (d, *J* = 1.9 Hz, 1H), 6.28 (d, *J* = 8.0 Hz, 1H), 6.00 (d, *J* = 1.6 Hz, 1H), 5.38 (dd, *J* = 4.1, 1.5 Hz, 1H), 5.08 (dd, *J* = 5.8, 4.2 Hz, 1H), 4.59 (d, *J* = 5.7 Hz, 1H), 4.30 (d, *J* = 9.7 Hz, 1H), 4.15 (d, *J* = 9.6 Hz, 1H), 3.39 (d, *J* = 8.9 Hz, 1H), 3.27 (d, *J* = 8.9 Hz, 1H), 2.18 (s, 3H), 1.48 (s, 3H), 1.40 (s, 6H), 1.28 (s, 3H), 1.28 (d, *J* = 1.8 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 170.17, 144.37, 133.73, 132.21, 128.86, 125.90, 123.78, 112.95, 111.93, 111.29, 111.17, 110.82, 85.15, 81.38, 76.58, 69.56, 61.26, 41.40, 26.64, 26.59, 26.26, 25.33, 23.08, 22.95, 20.62.

8-methoxy-2,2-dimethyl-5-((3a*S*,4*R*,6*R*,6a*S*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)-1,2-dihydro-3*H*-pyrazolo[1,2-*a*]cinnolin-3-one(33)[3]

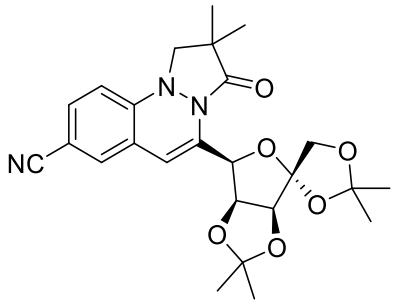


Prepared from **SI-4-7** (0.1 mmol, 1.0 equiv) and **SI-3-2** (0.2 mmol, 2.0 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/6) afforded **33** (43.7 mg, 92% yield) as yellow oil.

TLC: R*f* = 0.80 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.54 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.43 (d, *J* = 2.8 Hz, 1H), 6.32 (d, *J* = 8.6 Hz, 1H), 6.00 (d, *J* = 1.5 Hz, 1H), 5.40 (dd, *J* = 4.2, 1.6 Hz, 1H), 5.09 (dd, *J* = 5.8, 4.2 Hz, 1H), 4.60 (d, *J* = 5.9 Hz, 1H), 4.30 (d, *J* = 9.6 Hz, 1H), 4.16 (d, *J* = 9.7 Hz, 1H), 3.72 (s, 3H), 3.38 (d, *J* = 8.9 Hz, 1H), 3.26 (d, *J* = 8.9 Hz, 1H), 1.48 (s, 3H), 1.40 (s, 6H), 1.28 (d, *J* = 1.9 Hz, 6H), 1.27 (s, 3H).

2,2-dimethyl-3-oxo-5-((3a*S*,4*R*,6*R*,6a*S*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)-2,3-dihydro-1*H*-pyrazolo[1,2-*a*]cinnoline-8-carbonitrile(34)[3]

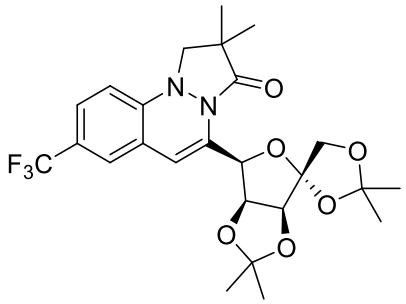


Prepared from **SI-4-8** (0.1 mmol, 1.0 equiv) and **SI-3-2** (0.2 mmol, 2.0 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/6) afforded **34** (17.0 mg, 36% yield) as yellow oil.

TLC: R*f* = 0.60 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.90 (d, *J* = 1.8 Hz, 1H), 6.26 (d, *J* = 8.3 Hz, 1H), 5.88 (d, *J* = 1.6 Hz, 1H), 5.32 (dd, *J* = 4.3, 1.6 Hz, 1H), 5.06 (dd, *J* = 5.7, 4.2 Hz, 1H), 4.59 (d, *J* = 5.7 Hz, 1H), 4.30 (d, *J* = 9.8 Hz, 1H), 4.14 (d, *J* = 9.8 Hz, 1H), 3.39 (d, *J* = 9.1 Hz, 1H), 3.28 (d, *J* = 9.1 Hz, 1H), 1.47 (s, 3H), 1.40 (d, *J* = 1.7 Hz, 6H), 1.30 (s, 3H), 1.28 (s, 3H), 1.28 (s, 3H).

2,2-dimethyl-5-((3a*S*,4*R*,6*R*,6a*S*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)-8-(trifluoromethyl)-1,2-dihydro-3*H*-pyrazolo[1,2-*a*]cinnolin-3-one(35)[3]

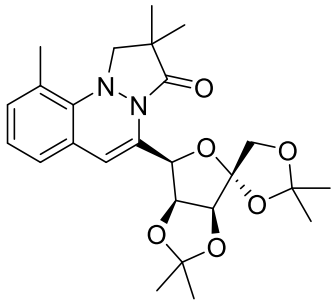


Prepared from **SI-4-6** (0.1 mmol, 1.0 equiv) and **SI-3-2** (0.2 mmol, 2.0 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/6) afforded **35** (21.9 mg, 43% yield) as yellow oil.

TLC: R*f* = 0.80 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 – 7.20 (m, 1H), 6.96 (d, *J* = 2.0 Hz, 1H), 6.34 (d, *J* = 8.3 Hz, 1H), 5.98 (d, *J* = 1.6 Hz, 1H), 5.35 (dd, *J* = 4.2, 1.6 Hz, 1H), 5.07 (dd, *J* = 5.7, 4.2 Hz, 1H), 4.59 (d, *J* = 5.7 Hz, 1H), 4.31 (d, *J* = 9.7 Hz, 1H), 4.14 (d, *J* = 9.7 Hz, 1H), 3.41 (d, *J* = 9.0 Hz, 1H), 3.29 (d, *J* = 9.0 Hz, 1H), 1.47 (s, 3H), 1.41 (s, 3H), 1.40 (s, 3H), 1.30 (s, 3H), 1.29 (s, 3H), 1.28 (s, 3H).

2,2,10-trimethyl-5-((3a*S*,4*R*,6*R*,6a*S*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)-1,2-dihydro-3*H*-pyrazolo[1,2-*a*]cinnolin-3-one(36)



Prepared from **SI-4-13** (0.1 mmol, 1.0 equiv) and **SI-3-2** (0.2 mmol, 2.0 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/6) afforded **36** (30.7 mg, 67% yield) as yellow oil.

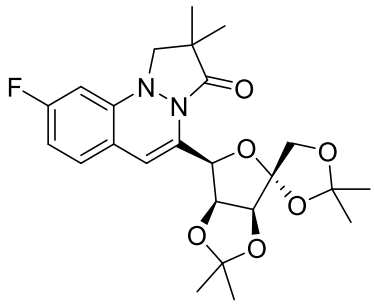
TLC: R*f* = 0.80 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 (dd, *J* = 7.4, 1.8 Hz, 1H), 6.73 – 6.64 (m, 2H), 5.96 (d, *J* = 1.5 Hz, 1H), 5.33 (dd, *J* = 4.0, 1.5 Hz, 1H), 5.09 (dd, *J* = 5.8, 4.0 Hz, 1H), 4.59 (d, *J* = 5.7 Hz, 1H), 4.29 (d, *J* = 9.6 Hz, 1H), 4.13 (d, *J* = 9.7 Hz, 1H), 3.69 (d, *J* = 8.8 Hz, 1H), 3.61 (d, *J* = 8.8 Hz, 1H), 2.27 (s, 3H), 1.48 (s, 3H), 1.41 (s, 3H), 1.39 (s, 3H), 1.29 (s, 3H), 1.27 (s, 3H), 1.26 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 170.02, 147.26, 133.37, 132.25, 124.32, 123.69, 122.88, 121.60, 113.94, 112.89, 111.91, 111.14, 85.19, 81.38, 69.57, 65.12, 40.34, 26.67, 26.61, 26.29, 25.32, 22.58.

9-fluoro-2,2-dimethyl-5-((3a*S*,4*R*,6*R*,6a*S*)-2,2,2',2'-tetramethyldihydro-6*H*-

spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)-1,2-dihydro-3*H*-pyrazolo[1,2-*a*]cinnolin-3-one(37)



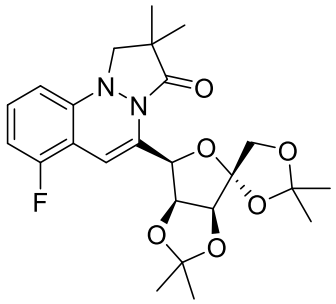
Prepared from **SI-4-9** (0.1 mmol, 1.0 equiv) and **SI-3-2** (0.2 mmol, 2.0 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/6) afforded **37** (18.0 mg, 39% yield) as yellow oil.

TLC: R*f* = 0.70 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (td, *J* = 8.3, 6.0 Hz, 1H), 6.53 (t, *J* = 8.7 Hz, 1H), 6.21 (d, *J* = 1.6 Hz, 1H), 6.15 (d, *J* = 8.0 Hz, 1H), 5.35 (dd, *J* = 4.2, 1.5 Hz, 1H), 5.10 (dd, *J* = 5.7, 4.2 Hz, 1H), 4.60 (d, *J* = 5.7 Hz, 1H), 4.32 (d, *J* = 9.7 Hz, 1H), 4.17 (d, *J* = 9.7 Hz, 1H), 3.38 (d, *J* = 9.0 Hz, 1H), 3.31 (d, *J* = 9.0 Hz, 1H), 1.48 (s, 3H), 1.41 (s, 3H), 1.40 (s, 3H), 1.29 (s, 3H), 1.28 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 170.29, 157.42 (d, *J* = 249.2 Hz), 148.17 (d, *J* = 14.3 Hz), 134.35 (d, *J* = 2.2 Hz), 129.44 (d, *J* = 9.4 Hz), 113.08, 111.98, 111.25, 110.25, 109.96, 106.61 (d, *J* = 2.7 Hz), 104.16 (d, *J* = 5.4 Hz), 85.15, 81.34, 69.52, 61.11, 41.39, 26.60, 26.16, 25.33, 23.03.

7-fluoro-2,2-dimethyl-5-((3a*S*,4*R*,6*R*,6a*S*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)-1,2-dihydro-3*H*-pyrazolo[1,2-*a*]cinnolin-3-one(37')



Prepared from **SI-4-10** (0.1 mmol, 1.0 equiv) and **SI-3-2** (0.2 mmol, 2.0 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/6) afforded**37'** (5.5 mg, 12% yield) as yellow oil.

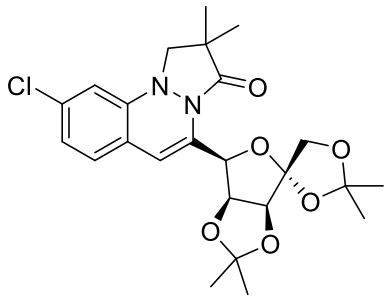
TLC: R*f* = 0.60 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.72 (dd, *J* = 8.2, 6.0 Hz, 1H), 6.45 (td, *J* = 8.5, 2.4 Hz, 1H), 6.10 (dd, *J* = 10.0, 2.4 Hz, 1H), 5.98 (d, *J* = 1.6 Hz, 1H), 5.35 (dd, *J* = 4.2, 1.6 Hz, 1H), 5.07 (dd, *J* = 5.7, 4.2 Hz, 1H), 4.59 (d, *J* = 5.7 Hz, 1H), 4.30 (d, *J* = 9.7 Hz, 1H), 4.15 (d, *J* = 9.8 Hz, 1H), 3.37 (d, *J* = 8.9 Hz, 1H), 3.26 (d, *J* = 8.9 Hz, 1H), 1.48 (s, 3H), 1.40 (s, 6H), 1.29 (s, 3H), 1.28 (d, *J* = 2.0 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 169.79, 163.10 (d, *J* = 246.5 Hz), 148.19 (d, *J* = 9.6 Hz), 132.75 (d, *J* = 2.7 Hz), 125.91 (d, *J* = 9.3 Hz), 119.76 (d, *J* = 3.4 Hz), 112.84, 111.86, 111.02, 110.30, 108.30 (d, *J* = 21.6 Hz), 99.33 (d, *J* = 27.7 Hz), 84.95, 81.18, 77.48, 77.05, 76.63, 76.34, 69.41, 60.62, 41.19, 26.53, 26.43, 26.10, 25.15, 22.96, 22.84.

HRMS (ESI): m/z calculated for $C_{24}H_{29}FN_2NaO_6^+$ [M+Na], 483.1902, found, 483.1911.

9-chloro-2,2-dimethyl-5-((3a*S*,4*R*,6*R*,6a*S*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)-1,2-dihydro-3*H*-pyrazolo[1,2-*a*]cinnolin-3-one(38)



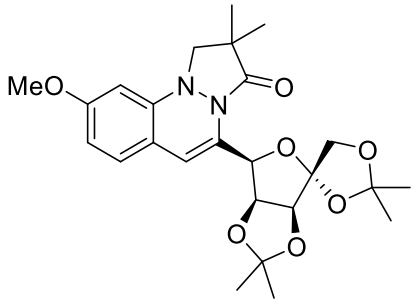
Prepared from **SI-4-17** (0.1 mmol, 1.0 equiv) and **SI-3-2** (0.2 mmol, 2.0 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/6) afforded **38** (14.3 mg, 30% yield) as yellow oil.

TLC: R*f* = 0.80 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$):δ 6.74 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.67 (d, *J* = 7.9 Hz, 1H), 6.32 (d, *J* = 1.9 Hz, 1H), 5.96 (s, 1H), 5.35 (dd, J = 4.2, 1.5 Hz, 1H), 5.07 (dd, *J* = 5.8, 4.3 Hz, 1H), 4.59 (d, *J* = 5.8 Hz, 1H), 4.30 (d, *J* = 9.7 Hz, 1H), 4.15 (d, *J* = 9.6 Hz, 1H), 3.37 (d, *J* = 8.9 Hz, 1H), 3.26 (d, *J* = 8.9 Hz, 1H), 1.47 (s, 3H), 1.39 (s, 6H), 1.29 (s, 3H), 1.28 (d, J = 2.3 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 169.86, 147.53, 134.08, 133.90, 125.52, 122.37(2), 112.88, 111.89, 111.17, 111.04, 109.96, 84.92, 81.19, 76.41, 69.41, 60.62, 41.24, 26.53, 26.43, 26.08, 25.15, 22.96, 22.81.

9-methoxy-2,2-dimethyl-5-((3a*S*,4*R*,6*R*,6a*S*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)-1,2-dihydro-3*H*-pyrazolo[1,2-*a*]cinnolin-3-one(39)



Prepared from **SI-4-12** (0.1 mmol, 1.0 equiv) and **SI-3-2** (0.2 mmol, 2.0 equiv)

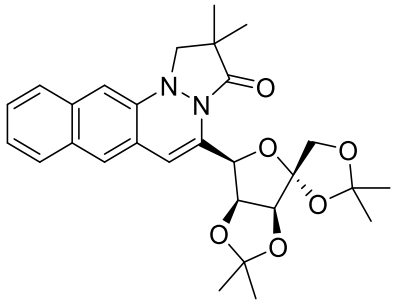
according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **39** (24 mg, 51% yield) as yellow oil.

TLC: R*f* = 0.80 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.73 (d, *J* = 8.2 Hz, 1H), 6.29 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.04 – 5.95 (m, 2H), 5.36 (dd, *J* = 4.0, 1.9 Hz, 1H), 5.08 (dd, *J* = 5.7, 4.1 Hz, 1H), 4.60 (d, *J* = 5.8 Hz, 1H), 4.30 (d, *J* = 9.7 Hz, 1H), 4.15 (d, *J* = 9.7 Hz, 1H), 3.76 (s, 3H), 3.40 (d, *J* = 9.0 Hz, 1H), 3.29 (d, *J* = 9.0 Hz, 1H), 1.48 (s, 3H), 1.40 (s, 6H), 1.29 (s, 3H), 1.28 (d, *J* = 1.4 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 169.79, 160.39, 147.97, 131.01, 125.89, 112.79, 111.80, 111.17, 110.99, 105.36, 99.18, 85.01, 81.24, 76.43, 69.43, 60.82, 55.36, 41.18, 26.55, 26.46, 26.13, 25.19, 22.99, 22.92.

2,2-dimethyl-5-((3a*S*,4*R*,6*R*,6a*S*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)-1,2-dihydro-3*H*-benzo[g]pyrazolo[1,2-*a*]cinnolin-3-one(40)[3]



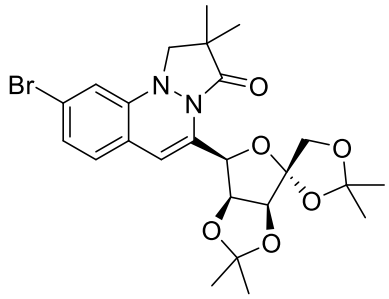
Prepared from **SI-4-14** (0.1 mmol, 1.0 equiv) and **SI-3-2** (0.2 mmol, 2.0 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/6) afforded **40** (27.2 mg, 55% yield) as yellow oil.

TLC: R*f* = 0.80 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.5 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 8.7 Hz, 1H), 7.44 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 1H), 7.33 – 7.28 (m, 1H), 6.77 (d, *J* = 8.7 Hz, 1H), 6.69 (d, *J* = 1.6 Hz, 1H), 5.42 (dd, *J* = 4.1, 1.5 Hz, 1H), 5.14 (dd, *J* = 5.7, 4.2 Hz, 1H), 4.64 (d, *J* = 5.8 Hz, 1H), 4.36 (d, *J* = 9.7 Hz, 1H), 4.25 (d, *J* = 9.7 Hz, 1H), 3.54 (d, *J* = 8.9 Hz, 1H), 3.46 (d, *J* = 8.8 Hz, 1H), 1.52 (s, 3H), 1.42 (d,

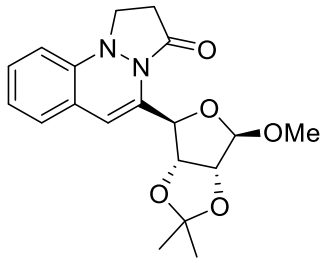
J = 1.3 Hz, 6H), 1.32 (s, 3H), 1.31 (s, 3H), 1.29 (s, 3H).

9-bromo-2,2-dimethyl-5-((3a*S*,4*R*,6*R*,6a*S*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)-1,2-dihydro-3*H*-pyrazolo[1,2-*a*]cinnolin-3-one(41)



Prepared from **SI-4-16** (0.1 mmol, 1.0 equiv) and **SI-3-2** (0.2 mmol, 2.0 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/6) afforded **41** (28.3 mg, 54% yield) as yellow oil.
TLC: R*f* = 0.80 (Ethyl acetate/Petroleum Ether = 1/2)
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.89 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.61 (d, *J* = 7.9 Hz, 1H), 6.47 (d, *J* = 1.8 Hz, 1H), 5.94 (s, 1H), 5.34 (dd, *J* = 4.3, 1.6 Hz, 1H), 5.07 (dd, *J* = 5.7, 4.2 Hz, 1H), 4.59 (d, *J* = 5.7 Hz, 1H), 4.30 (d, *J* = 9.7 Hz, 1H), 4.14 (d, *J* = 9.7 Hz, 1H), 3.37 (d, *J* = 8.9 Hz, 1H), 3.26 (d, *J* = 8.9 Hz, 1H), 1.47 (s, 3H), 1.39 (d, *J* = 1.8 Hz, 6H), 1.29 (s, 3H), 1.27 (d, *J* = 1.9 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 169.86, 147.53, 134.08, 133.90, 125.52, 122.37(2), 112.88, 111.89, 111.17, 111.04, 109.96, 84.92, 81.19, 76.41, 69.41, 60.62, 41.24, 26.53, 26.43, 26.08, 25.15, 22.96, 22.81.

5-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1,2-dihydro-3*H*-4l4,11l4-pyrazolo[1,2-*a*]cinnolin-3-one(42)[3]

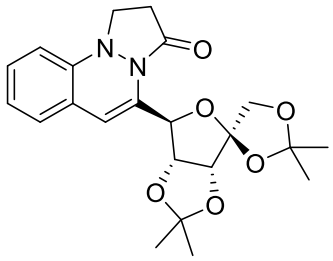


Prepared from **SI-4-11** (0.1 mmol, 1.0 equiv) and **SI-3-1** (0.15 mmol, 1.5 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/4) afforded **40** (33.7 mg, 94% yield) as yellow oil.

TLC: R*f* = 0.50 (Ethyl acetate/Petroleum Ether = 1/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (ddd, *J* = 8.4, 6.4, 2.7 Hz, 1H), 6.86 – 6.82 (m, 2H), 6.49 (d, *J* = 8.0 Hz, 1H), 6.13 – 6.07 (m, 1H), 5.80 (s, 1H), 5.11 (s, 1H), 4.94 (d, *J* = 5.9 Hz, 1H), 4.65 (d, *J* = 6.0 Hz, 1H), 3.73 (t, *J* = 8.3 Hz, 2H), 3.49 (s, 3H), 2.73 (t, *J* = 8.3 Hz, 2H), 1.53 (s, 3H), 1.35 (s, 3H).

5-((3a*R*,4*S*,6*R*,6a*R*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)-1,2-dihydro-3*H*-pyrazolo[1,2-*a*]cinnolin-3-one (43)[3]

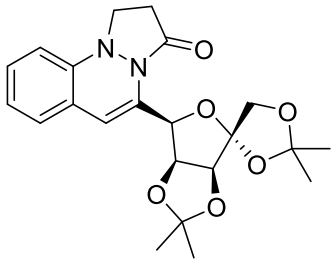


Prepared from **SI-4-11** (0.1 mmol, 1.0 equiv) and **SI-3-5** (0.15 mmol, 1.5 equiv) according to the general procedure **4**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/4) afforded **43** (24.8 mg, 60% yield) as yellow oil.

TLC: R*f* = 0.55 (Ethyl acetate/Petroleum Ether = 1/1)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.08 (d, *J* = 6.8 Hz, 1H), 6.82 (d, *J* = 3.6 Hz, 2H), 6.48 (d, *J* = 8.0 Hz, 1H), 6.37 (s, 1H), 5.73 (s, 1H), 4.95 (d, *J* = 5.9 Hz, 1H), 4.68 (d, *J* = 5.9 Hz, 1H), 4.41 (d, *J* = 9.8 Hz, 1H), 4.13 (d, *J* = 9.9 Hz, 1H), 3.73 (q, *J* = 8.4 Hz, 2H), 2.72 (t, *J* = 8.3 Hz, 2H), 1.61 (s, 3H), 1.49 (s, 3H), 1.40 (s, 3H), 1.35 (s, 3H).

5-((3a*S*,4*R*,6*R*,6a*S*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)-1,2-dihydro-3*H*-4l4,11l4-pyrazolo[1,2-*a*]cinnolin-3-one(44)[3]

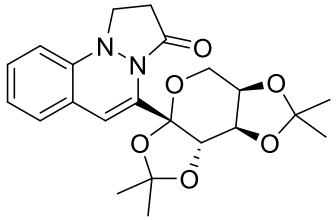


Prepared from **SI-4-11** (0.1 mmol, 1.0 equiv) and **SI-3-2** (0.15 mmol, 1.5 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **44** (29.4 mg, 71% yield) as yellow solid.

TLC: R*f* = 0.60 (Ethyl acetate/Petroleum Ether = 1/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (ddd, *J* = 8.4, 5.9, 3.2 Hz, 1H), 6.78 (q, *J* = 4.2, 3.5 Hz, 2H), 6.37 (d, *J* = 7.9 Hz, 1H), 5.99 (d, *J* = 1.5 Hz, 1H), 5.40 (dd, *J* = 4.3, 1.5 Hz, 1H), 5.12 (dd, *J* = 5.7, 4.2 Hz, 1H), 4.61 (d, *J* = 5.7 Hz, 1H), 4.30 (d, *J* = 9.7 Hz, 1H), 4.16 (d, *J* = 9.7 Hz, 1H), 3.61 (dq, *J* = 25.0, 8.8 Hz, 2H), 2.74 (t, *J* = 8.5 Hz, 2H), 1.48 (s, 3H), 1.40 (d, *J* = 2.1 Hz, 6H), 1.30 (s, 3H).

5-((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-b:4',5'-*d*]pyran-3a-yl)-1,2-dihydro-3*H*-pyrazolo[1,2-*a*]cinnolin-3-one(45)[3]



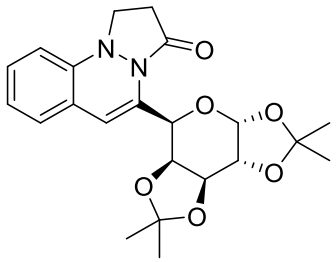
Prepared from **SI-4-11** (0.1 mmol, 1.0 equiv) and **SI-3-4** (0.15 mmol, 1.5 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **45** (34.7 mg, 84% yield) as white solid.

TLC: R*f* = 0.60 (Ethyl acetate/Petroleum Ether = 1/1)

^{1}H NMR (300 MHz, $CDCl_3$):δ 7.21 (t, *J* = 6.7 Hz, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.24 (s, 1H), 4.91 (d, *J* = 2.6 Hz, 1H), 4.62 (dd, *J* = 8.0, 2.6 Hz, 1H), 4.23 (d, *J* = 8.1 Hz, 1H), 3.97 (dt, *J* = 8.7, 2.3 Hz, 1H), 3.70 (td, *J* = 12.0, 7.6 Hz,

1H), 3.47 (d, *J* = 14.7 Hz, 1H), 2.98 (d, *J* = 14.7 Hz, 1H), 2.86 (ddd, *J* = 16.5, 8.3, 3.9 Hz, 1H), 2.58 – 2.46 (m, 1H), 1.52 (s, 3H), 1.46 (s, 3H), 1.37 (s, 3H), 1.32 (s, 3H).

5-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)-1,2-dihydro-3*H*-4l4,11l4-pyrazolo[1,2-*a*]cinnolin-3-one(46)[3]



Prepared from **SI-4-11** (0.1 mmol, 1.0 equiv) and **SI-3-3** (0.15 mmol, 1.5 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/4) afforded **46** (31.1 mg, 75% yield) as yellow solid.

TLC: R*f* = 0.50 (Ethyl acetate/Petroleum Ether = 1/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (ddd, *J* = 8.2, 7.1, 2.0 Hz, 1H), 6.87 – 6.76 (m, 2H), 6.43 (d, *J* = 8.0 Hz, 1H), 6.09 (d, *J* = 1.6 Hz, 1H), 5.68 (t, *J* = 1.8 Hz, 1H), 5.64 (d, *J* = 5.1 Hz, 1H), 4.69 (dd, *J* = 7.7, 2.5 Hz, 1H), 4.45 (dd, *J* = 7.7, 2.0 Hz, 1H), 4.39 (dd, *J* = 5.1, 2.6 Hz, 1H), 3.80 (dt, *J* = 9.6, 7.6 Hz, 1H), 3.59 (q, *J* = 9.5 Hz, 1H), 2.72 (dd, *J* = 9.3, 7.7 Hz, 2H), 1.62 (s, 3H), 1.46 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H).

8 References

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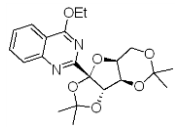
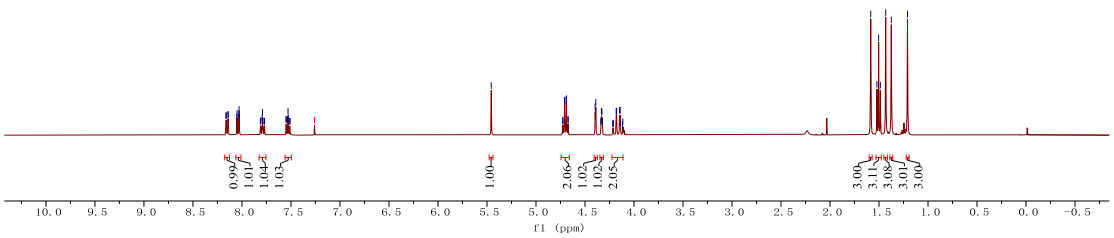
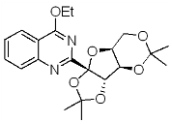
9 NMR Spectra of Substrates and Products

^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 1

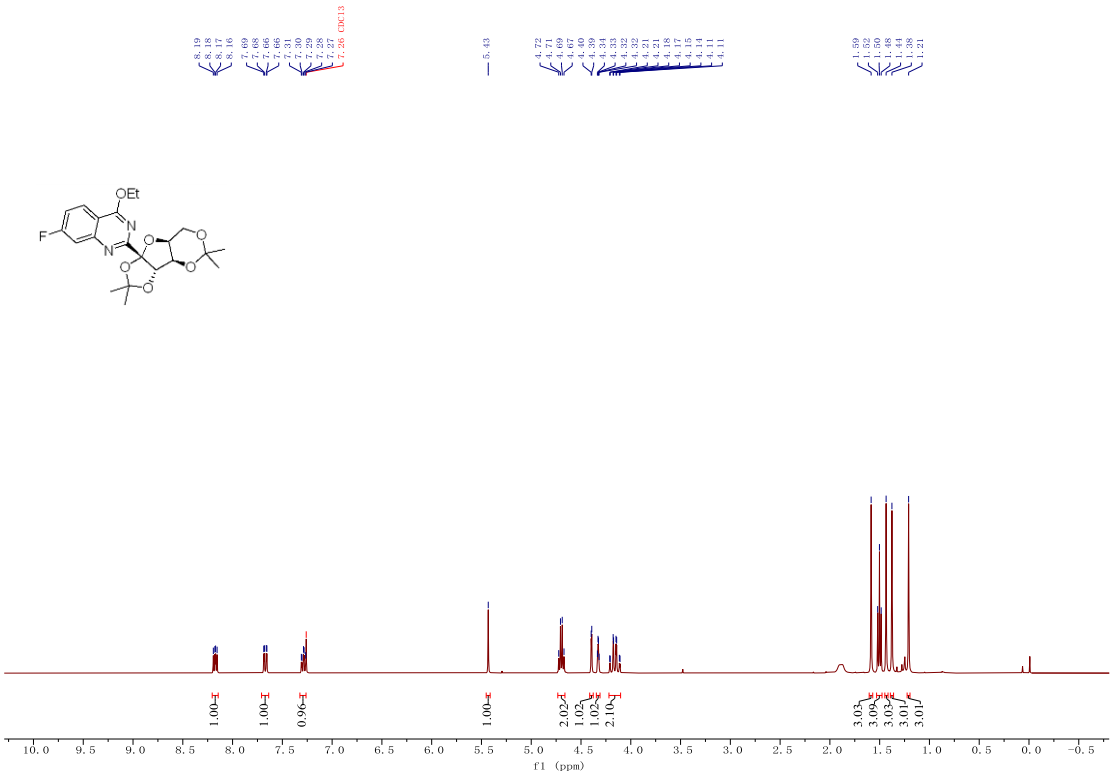




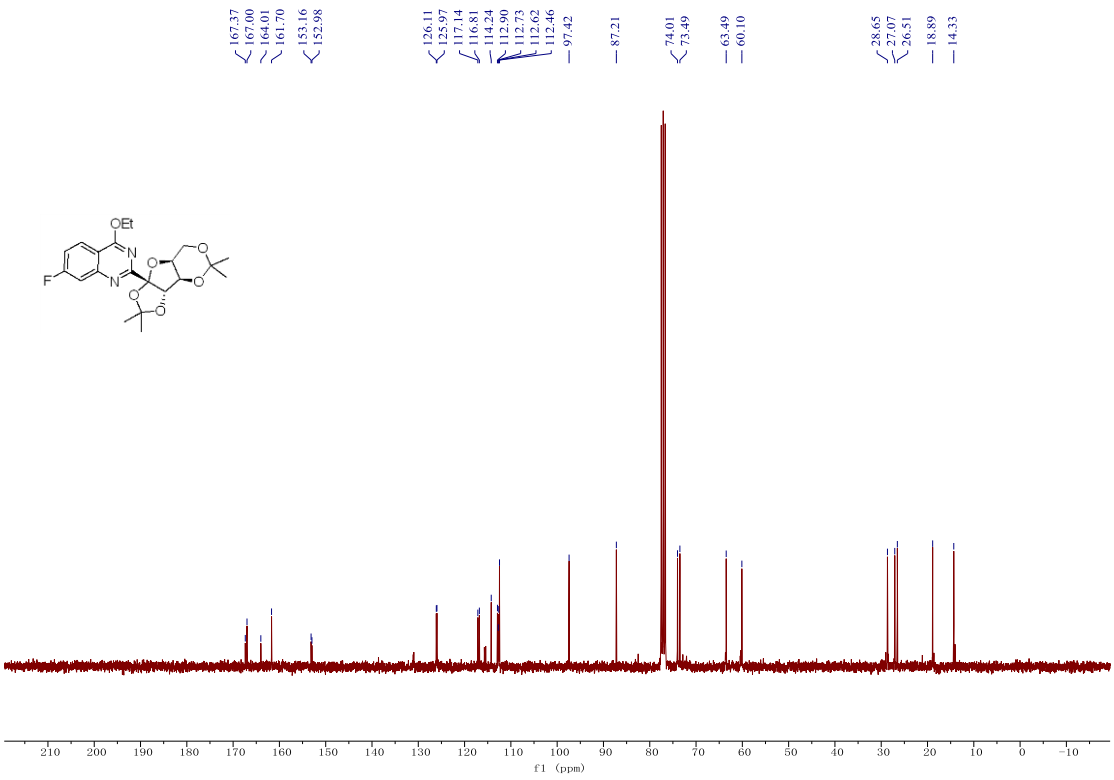
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 1



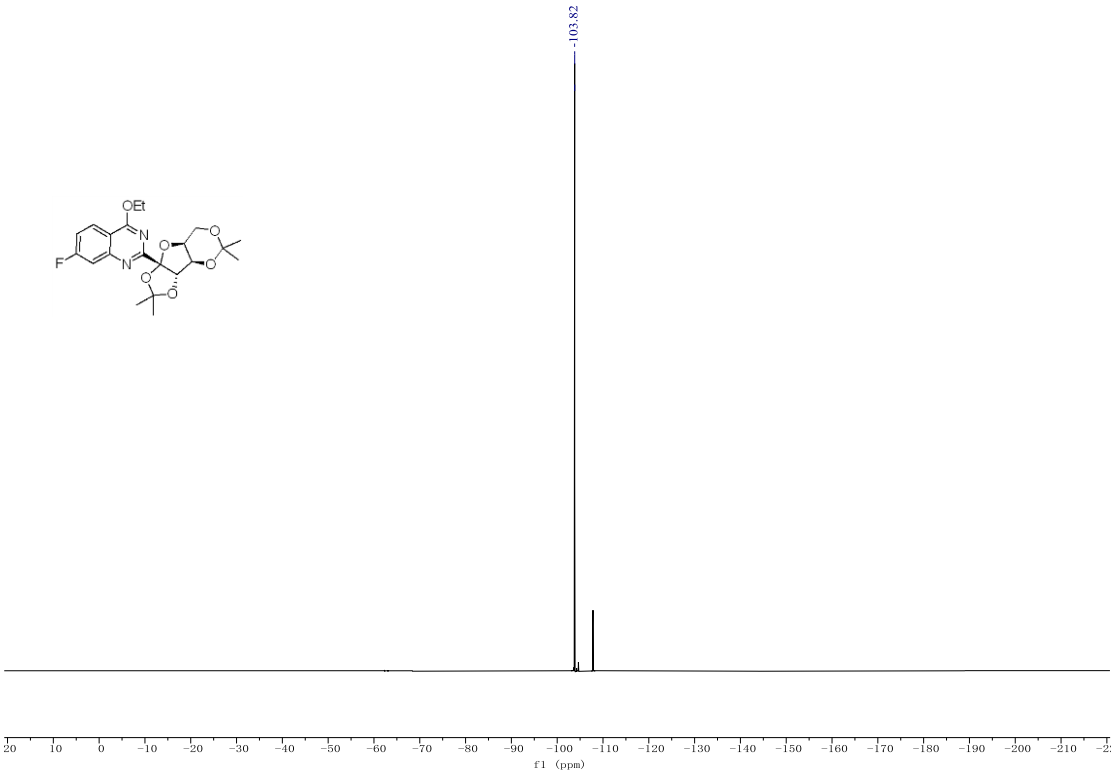
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 2



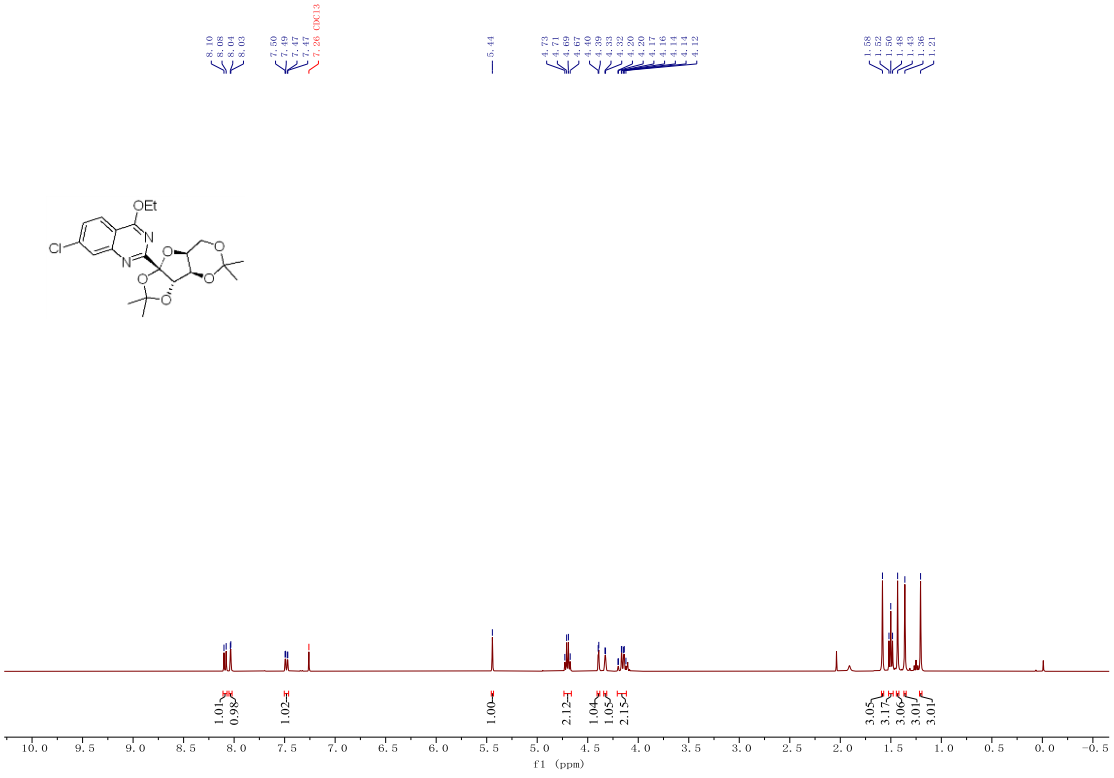
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 2



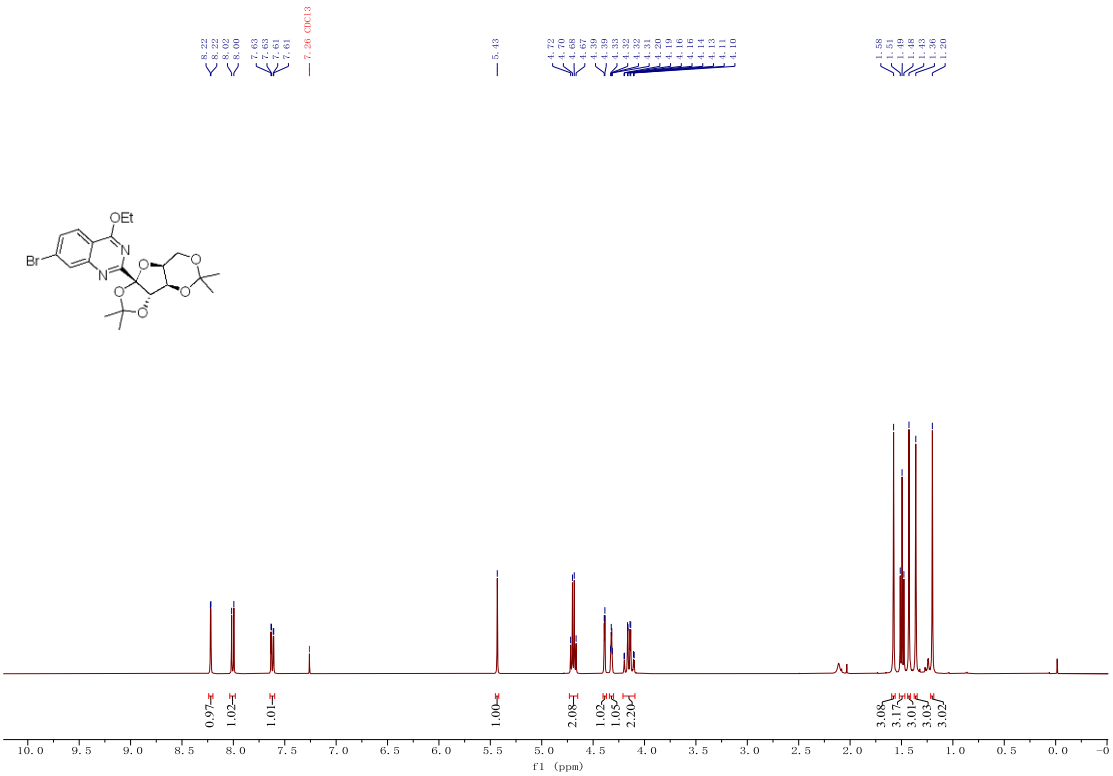
^{19}F NMR (376 MHz, $CDCl_3$) Spectra of compound 2



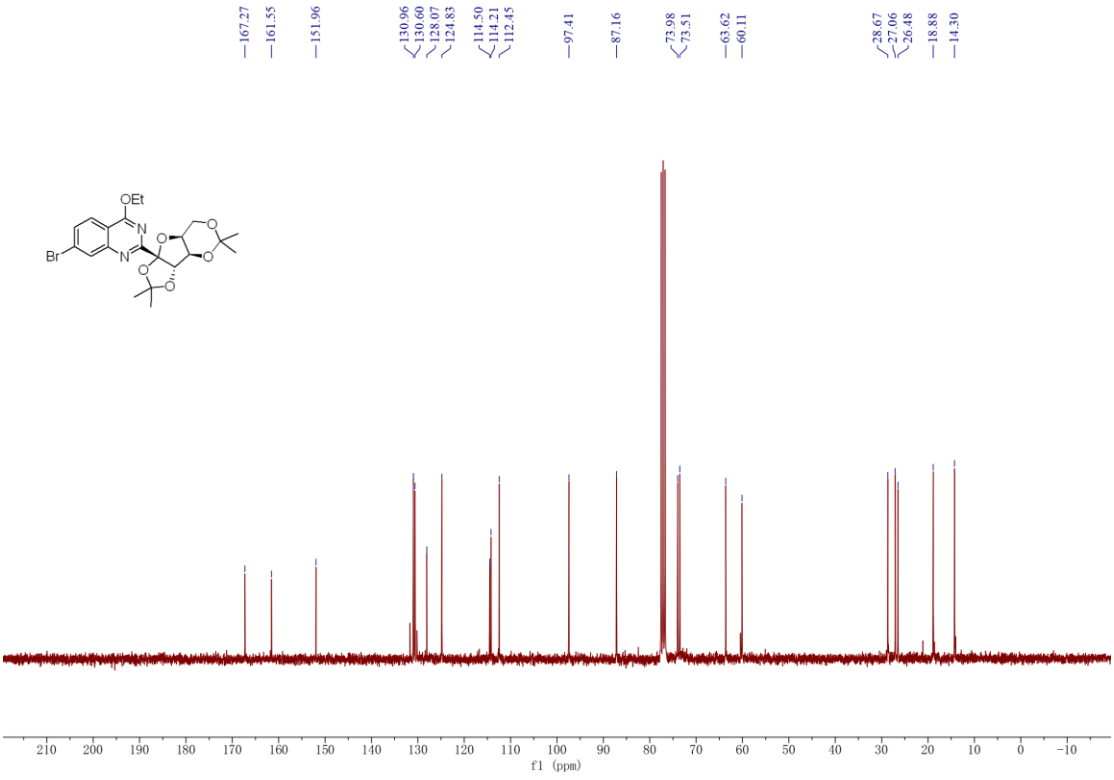
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 3[1]



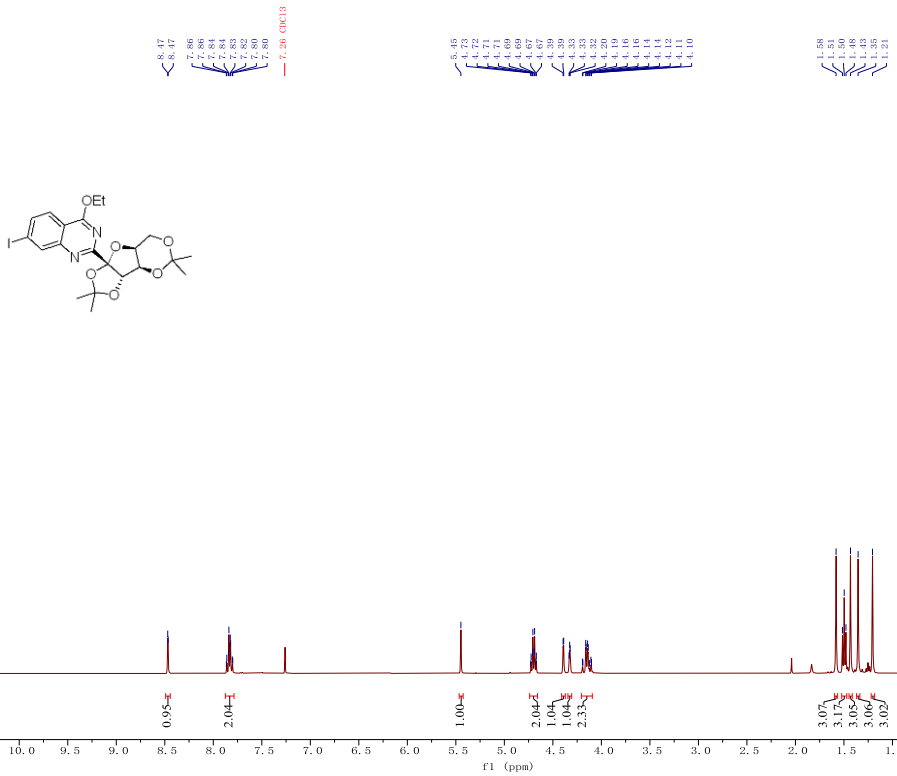
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 4



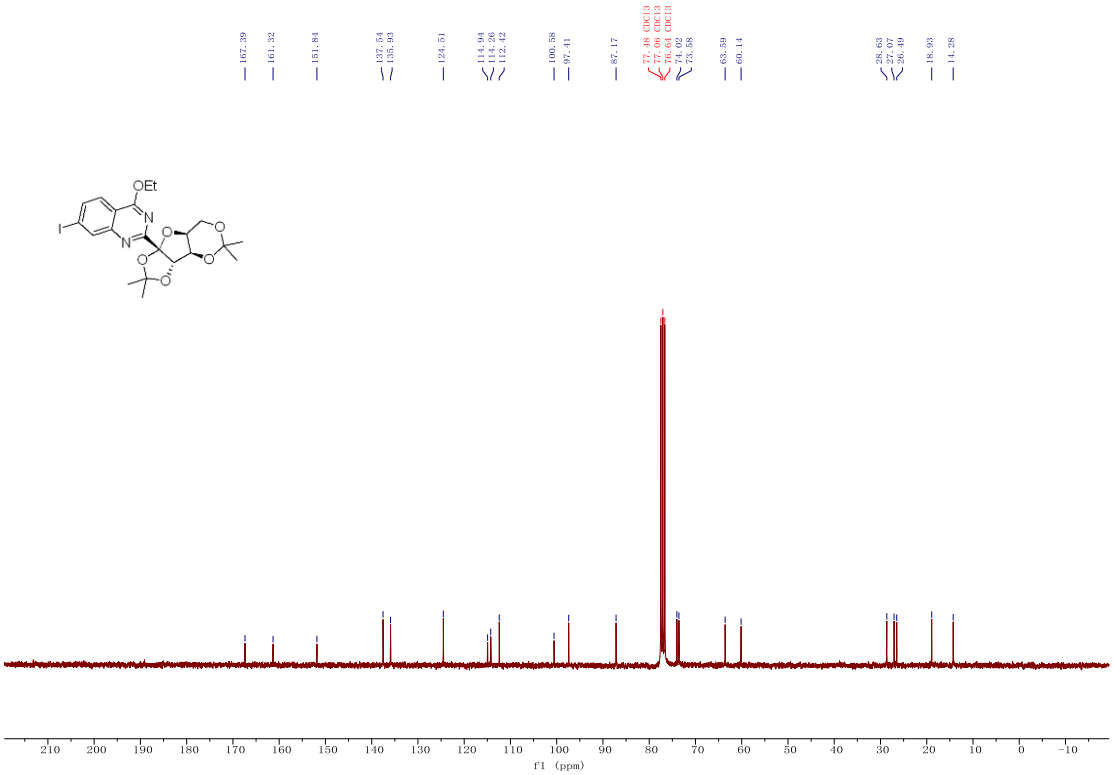
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 4



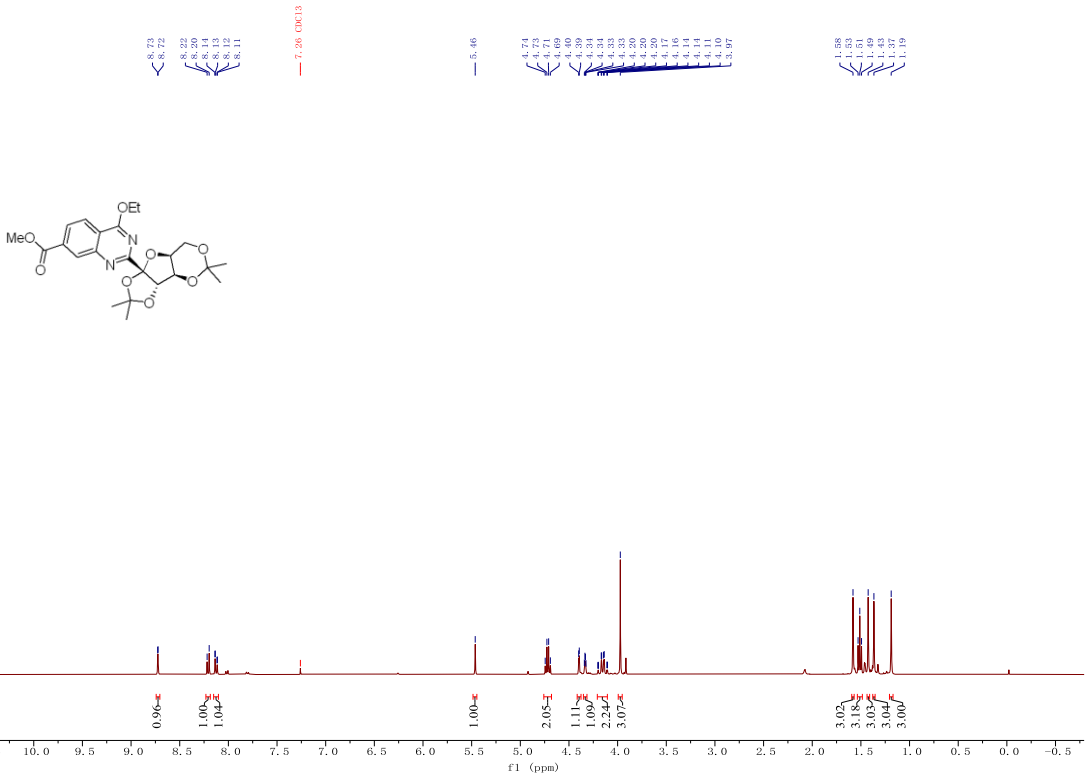
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 5



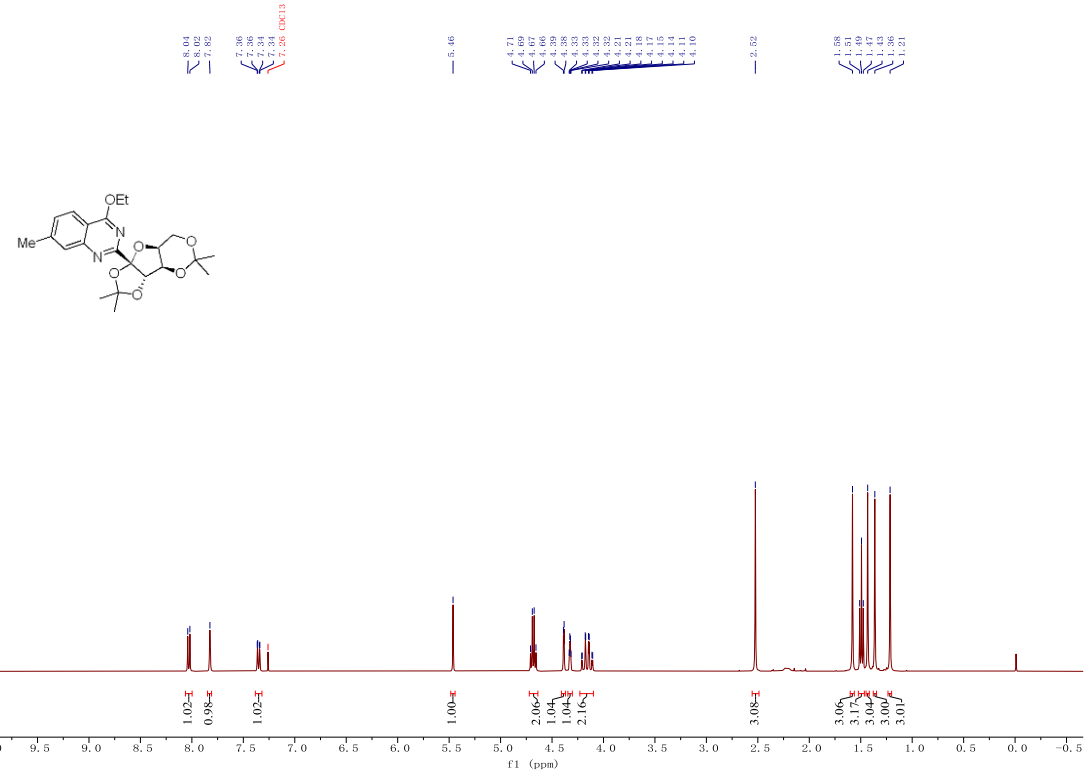
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 5



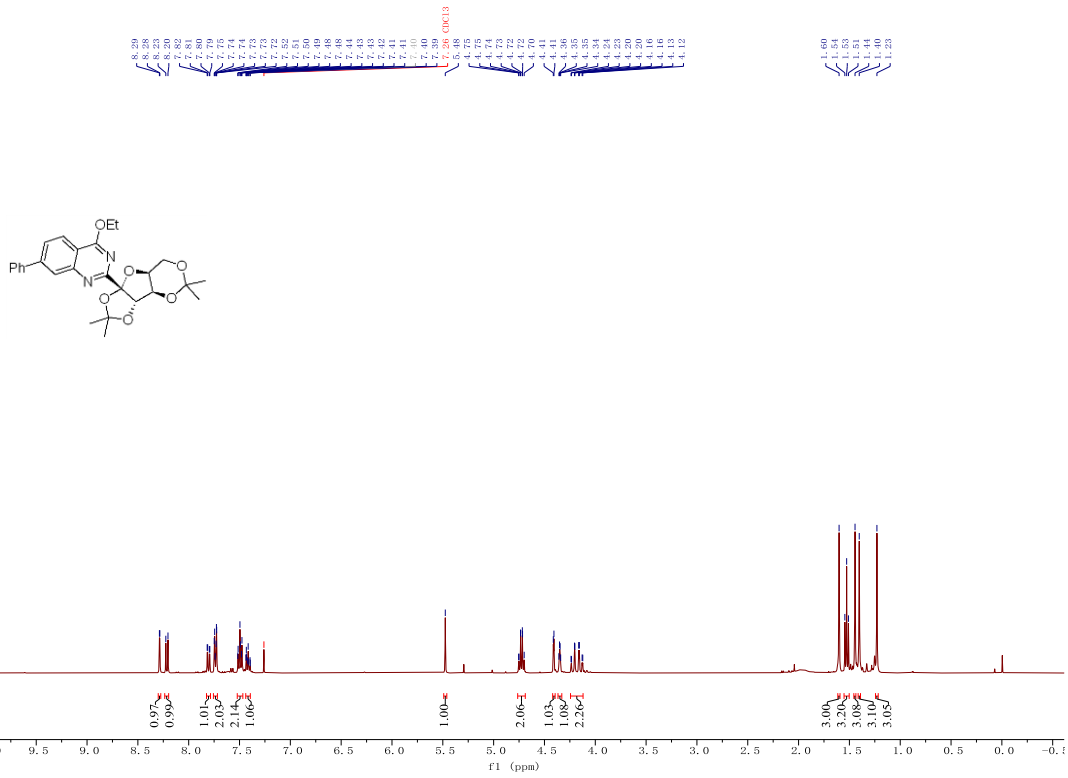
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 6[1]



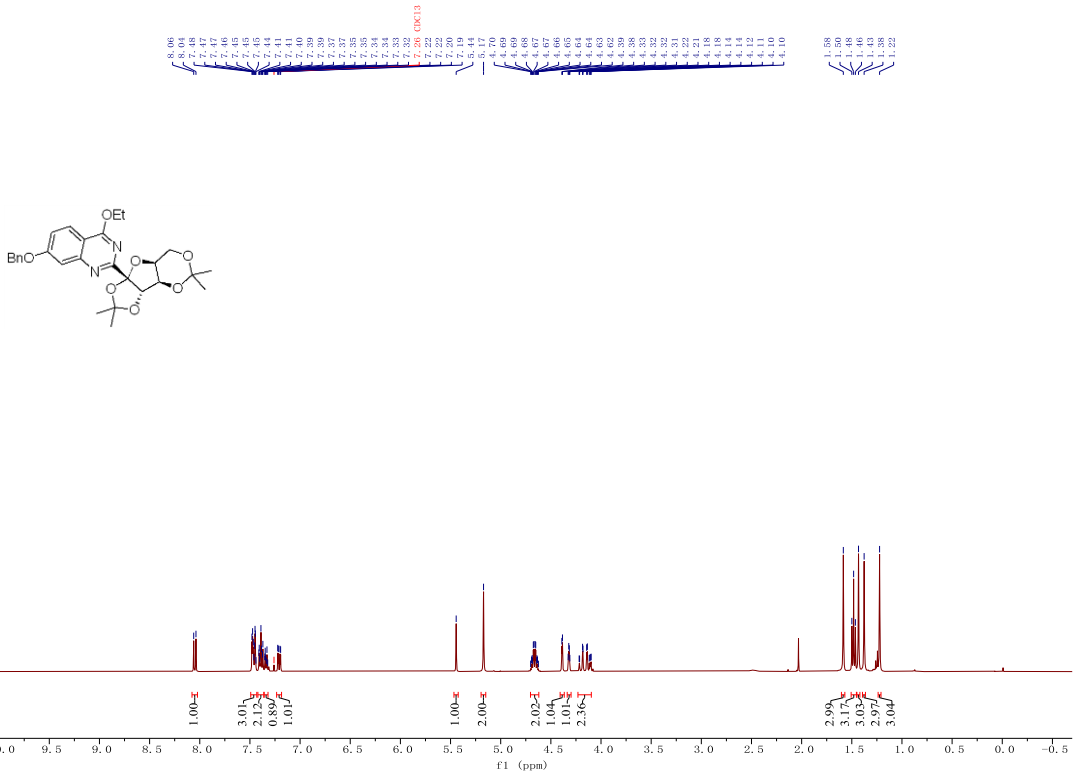
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 7[1]



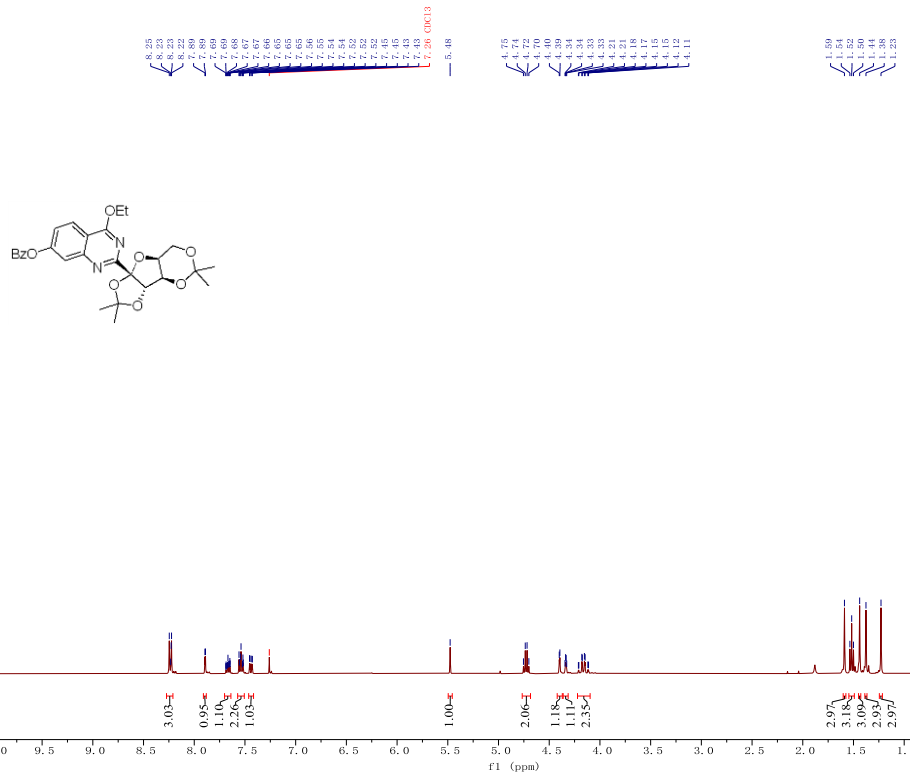
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 8[1]



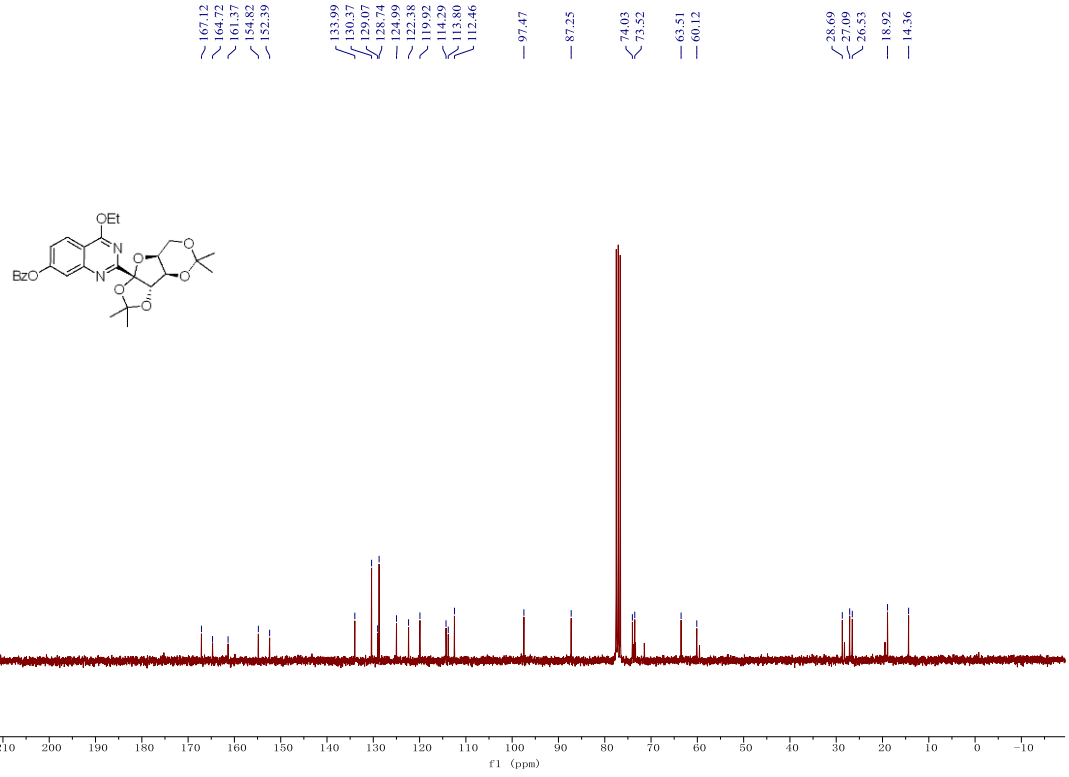
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 9[1]



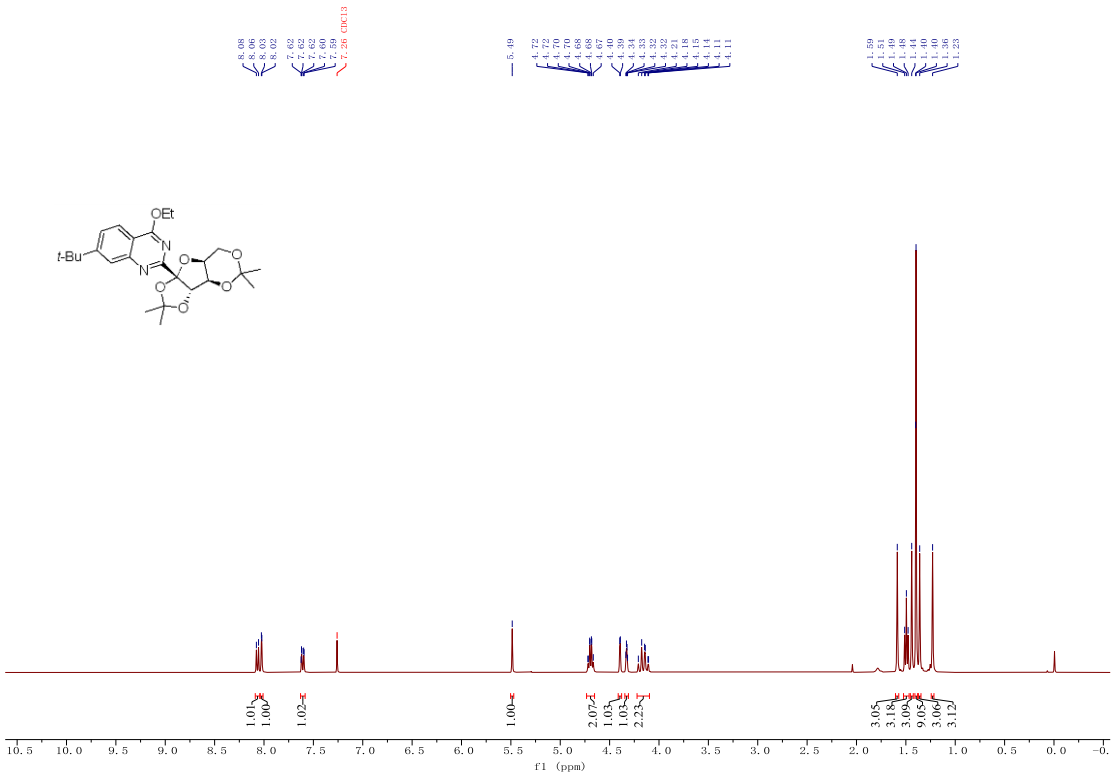
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 10



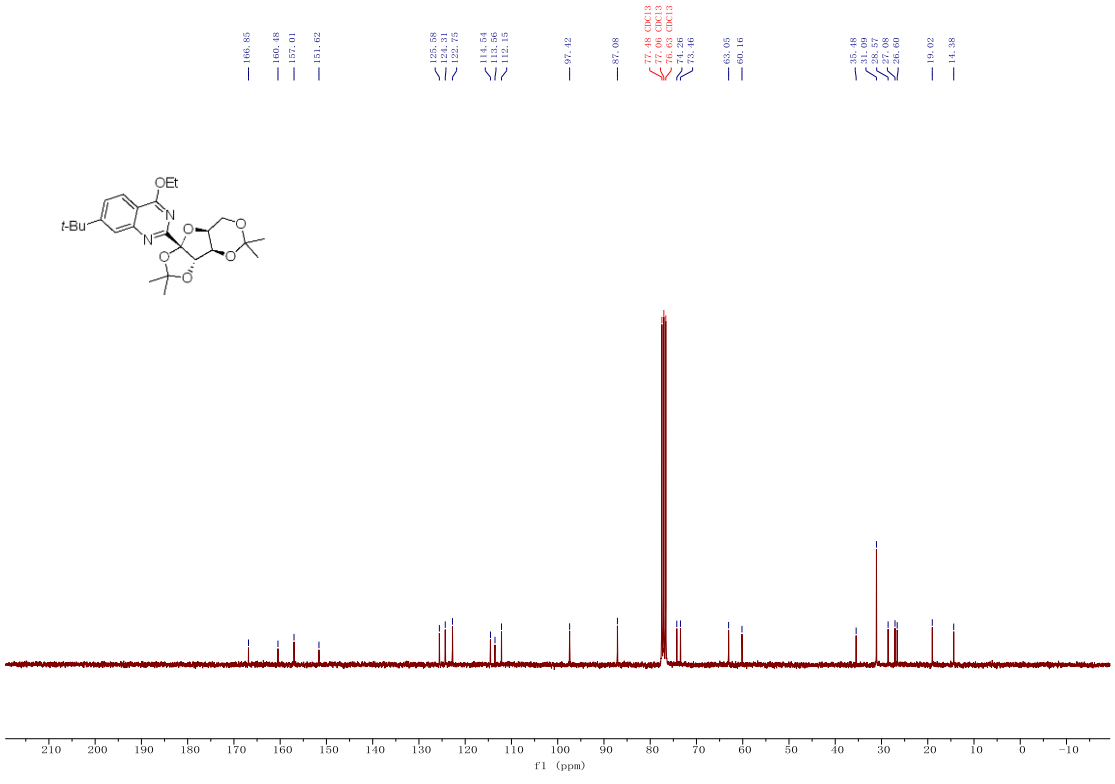
^{13}C NMR (400 MHz, $CDCl_3$) Spectra of compound 10



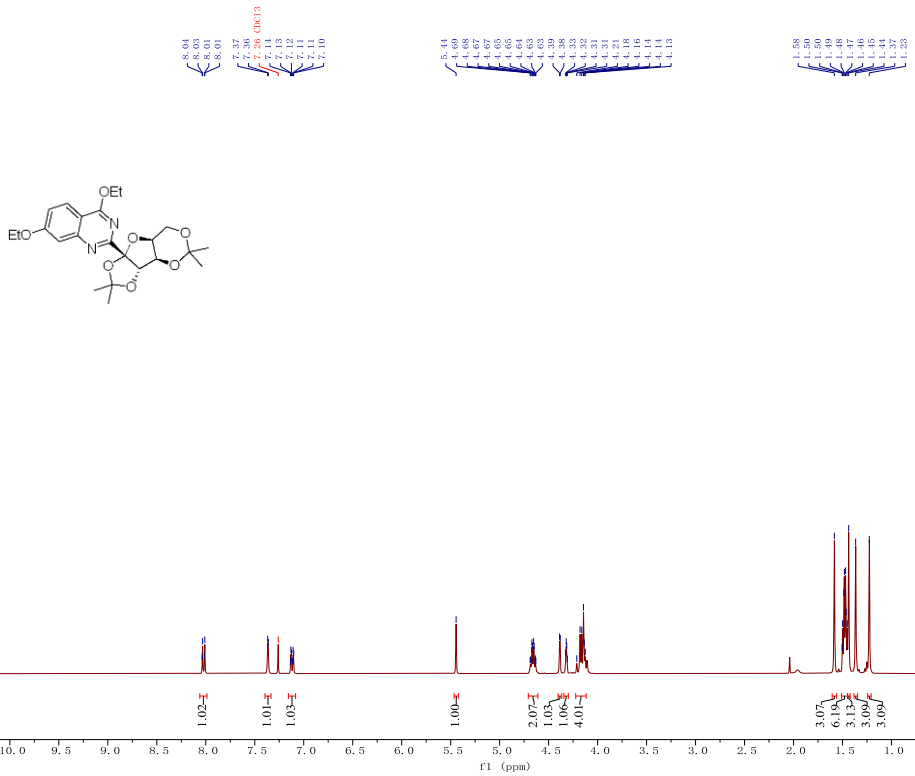
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 11



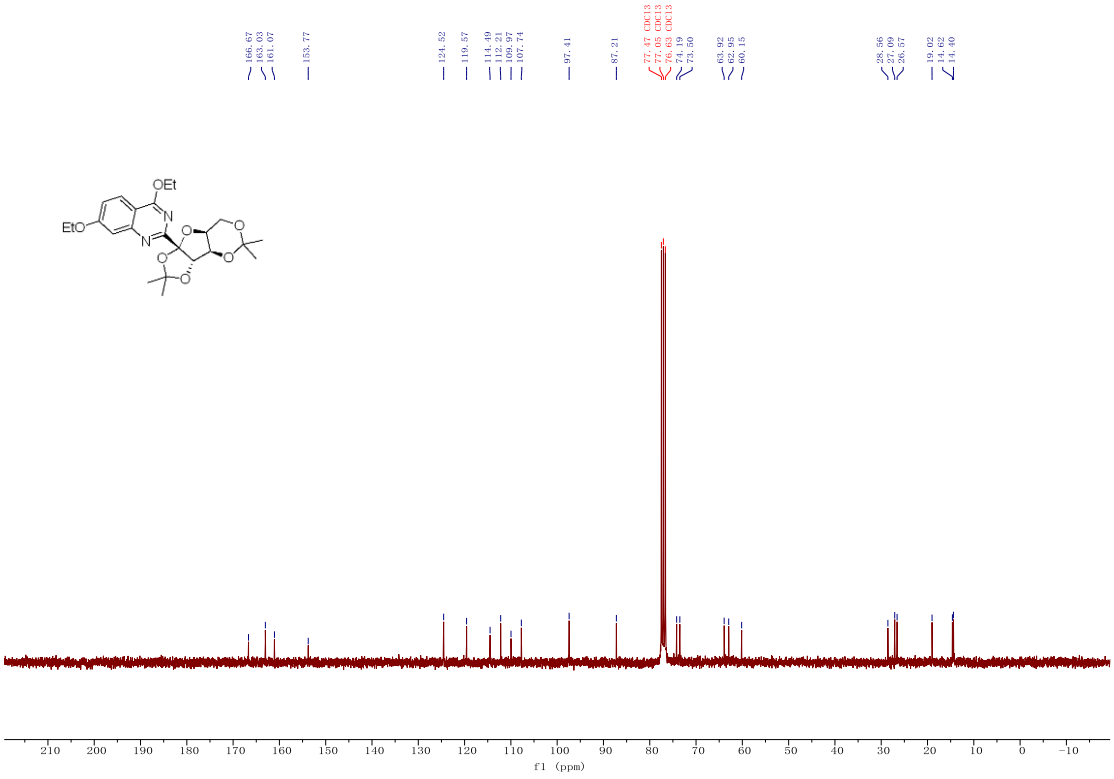
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 11



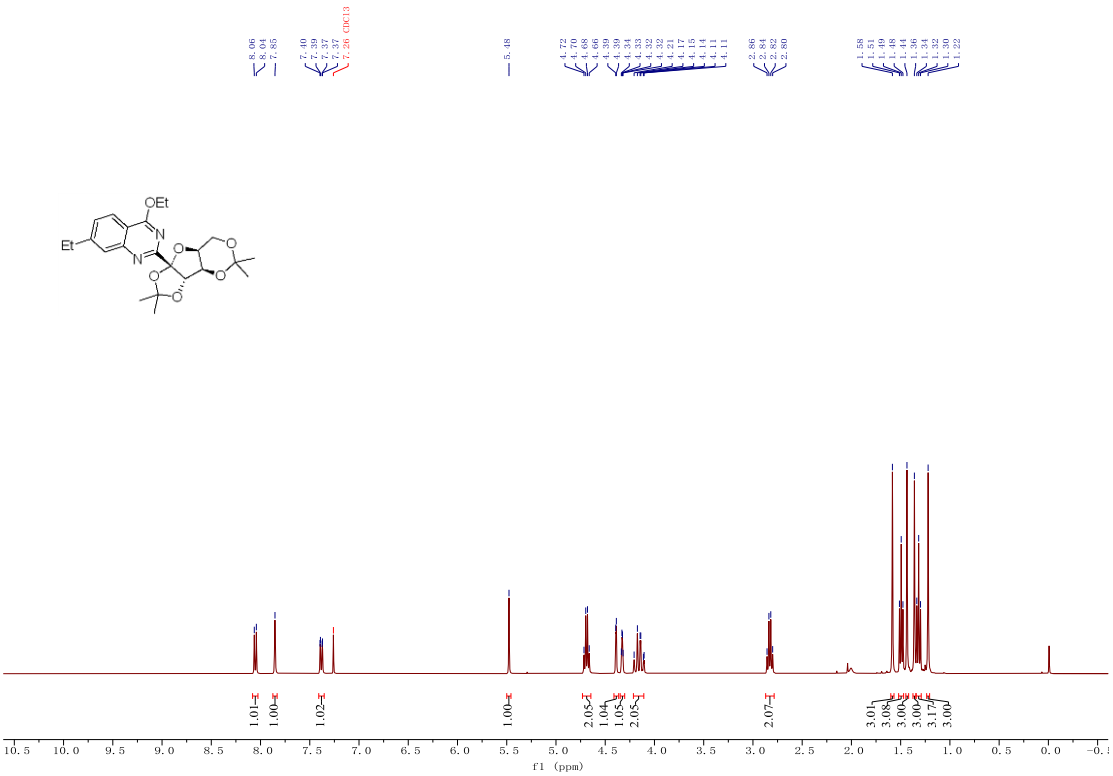
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 12



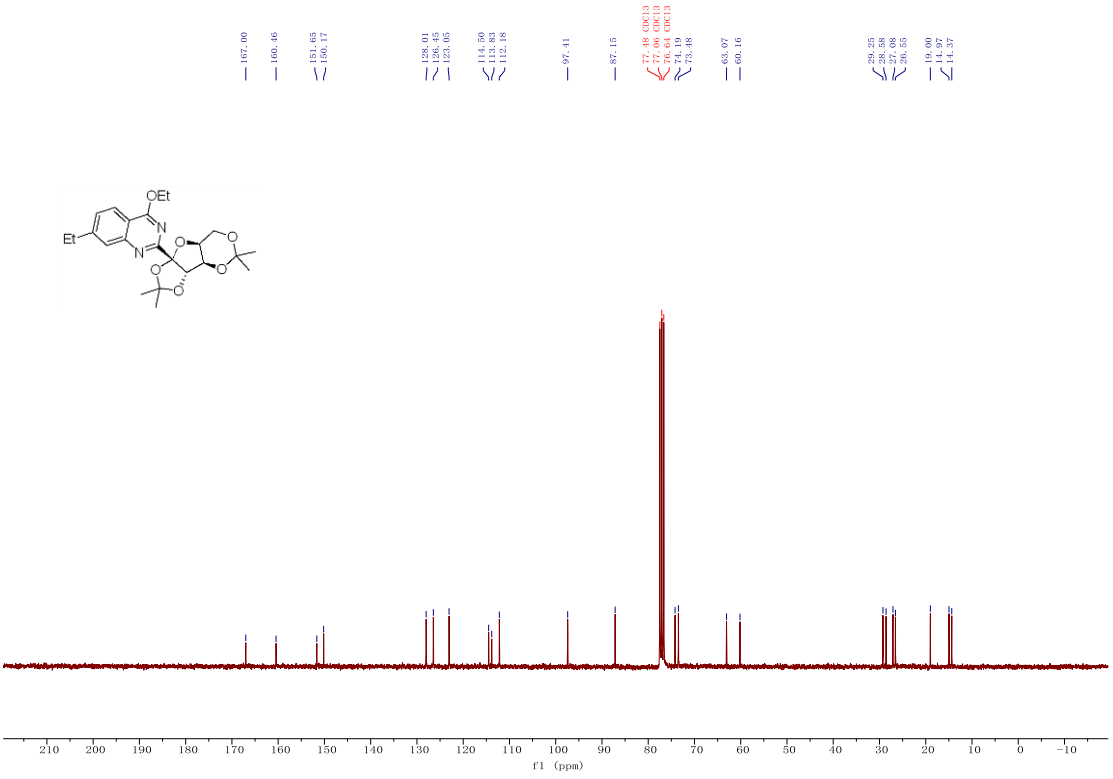
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 12



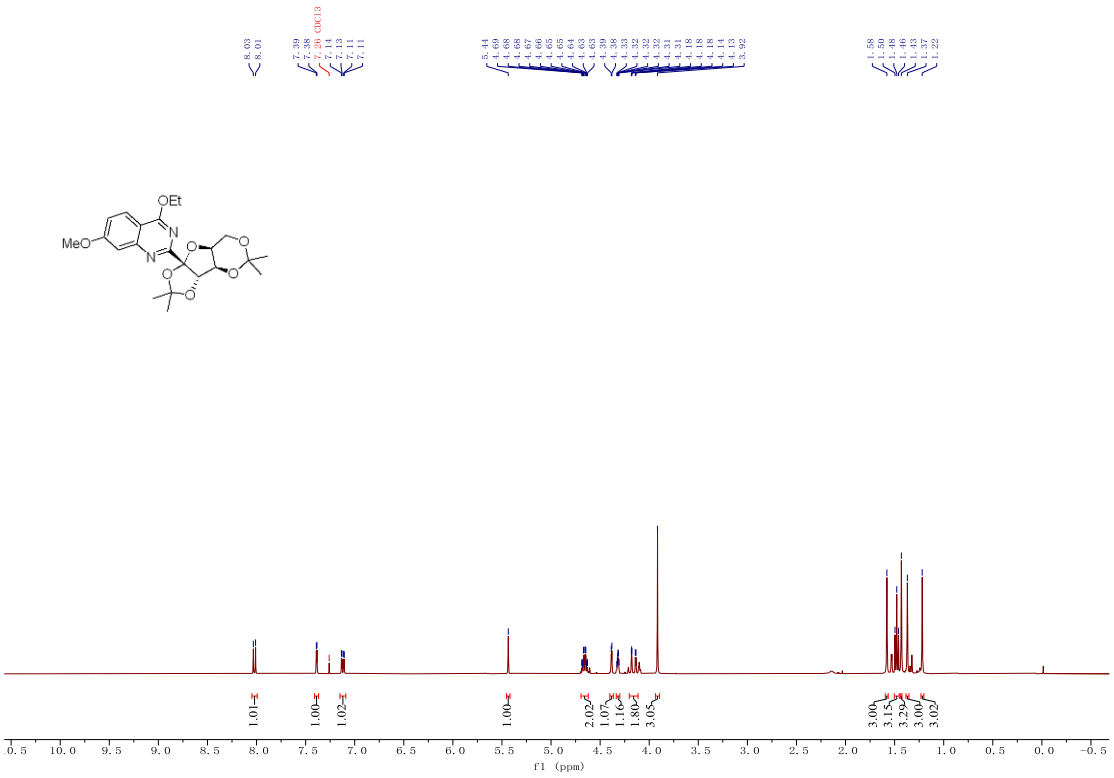
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 13



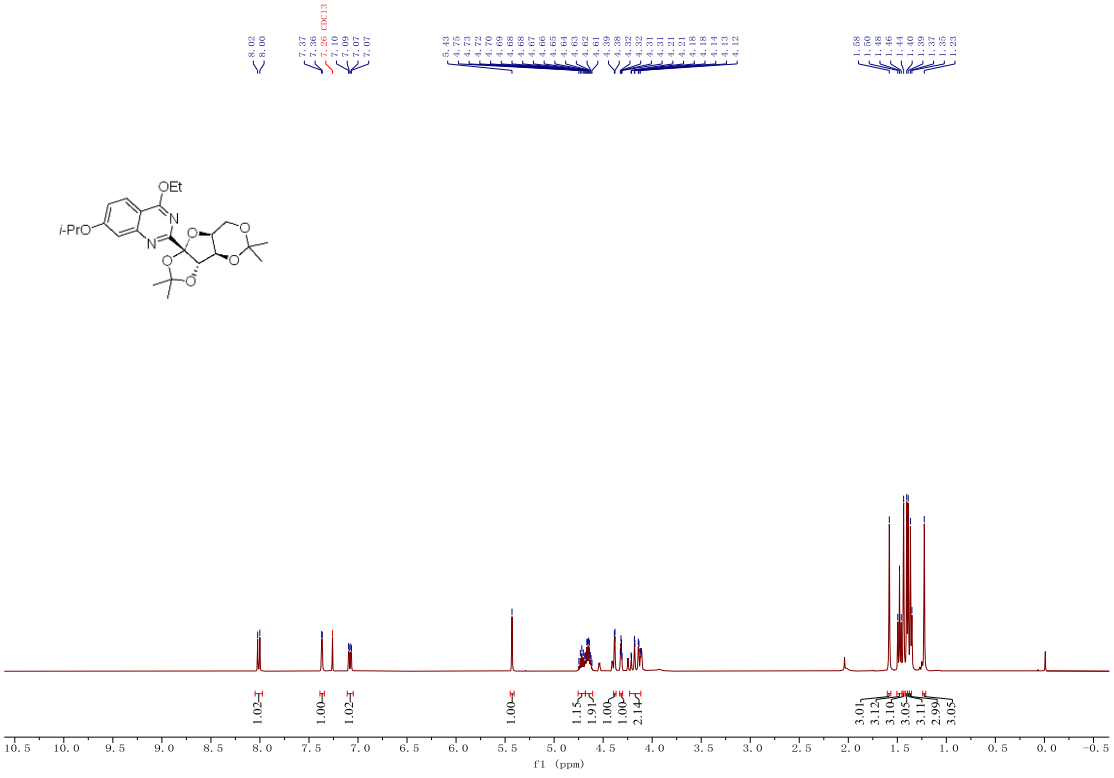
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 13



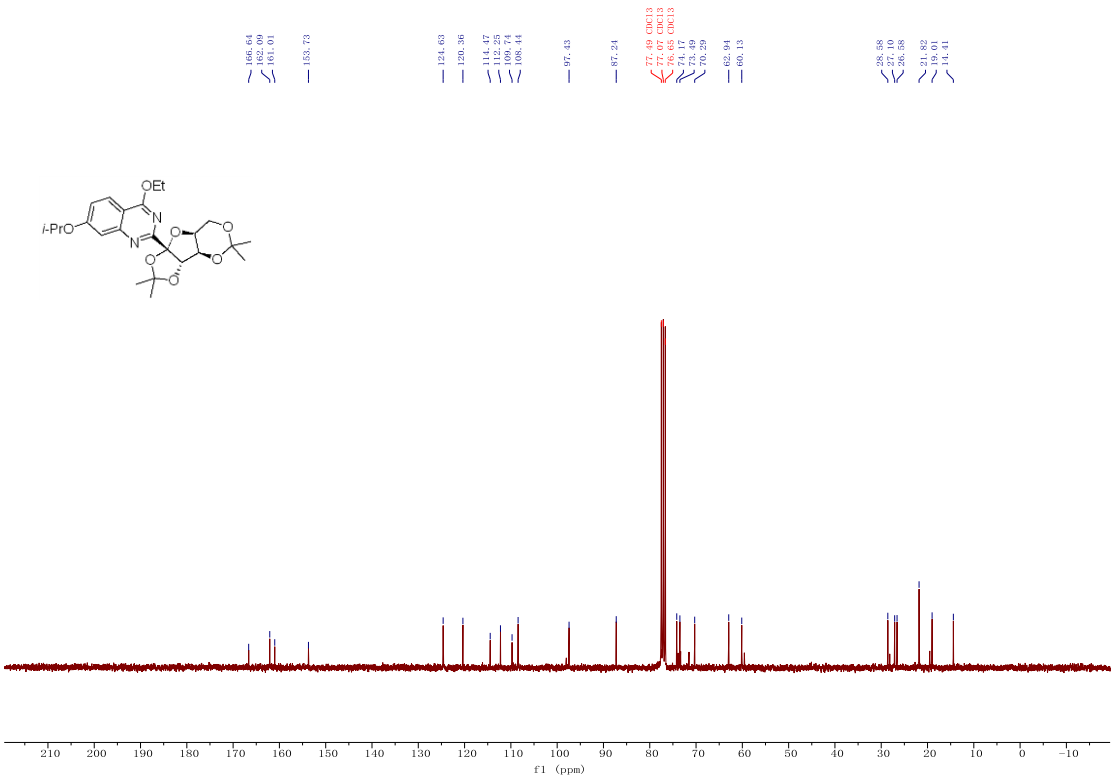
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 14[1]



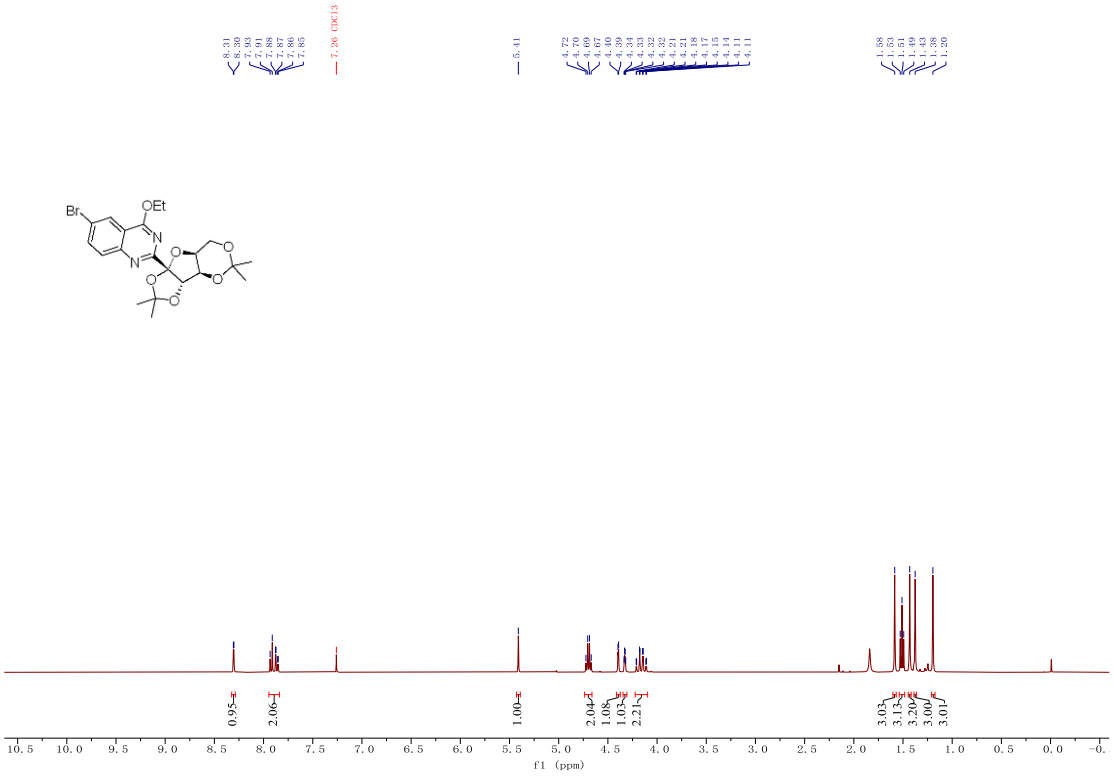
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 15



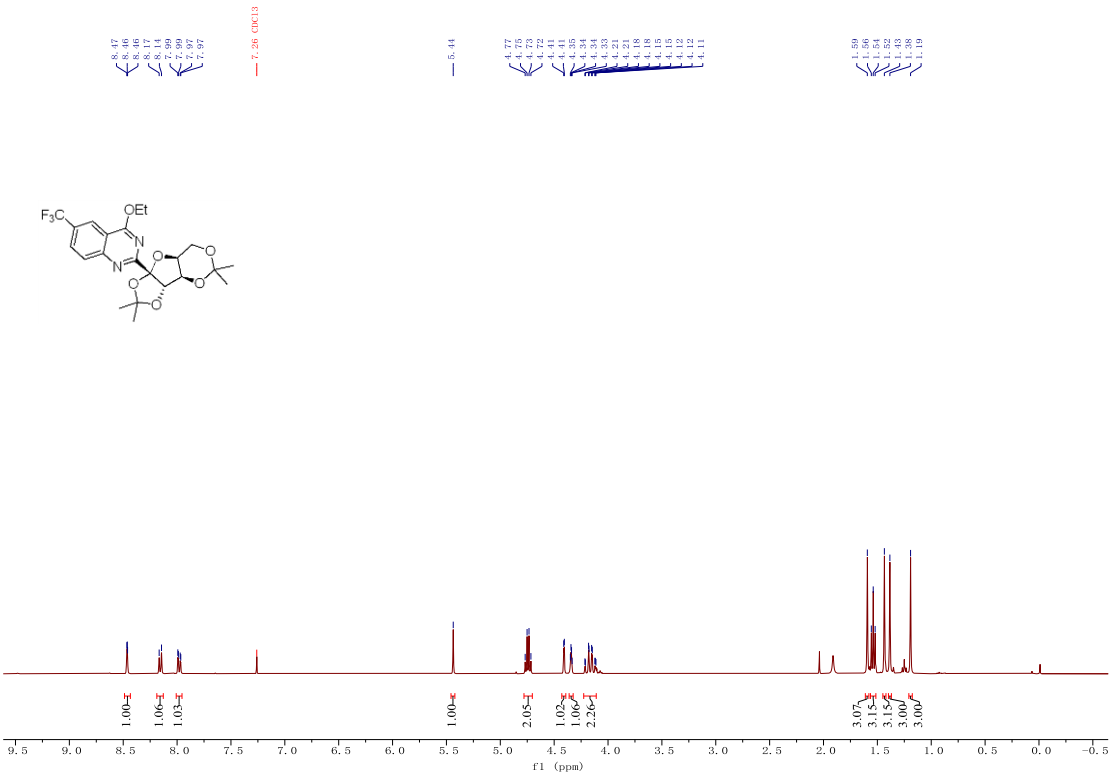
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 15



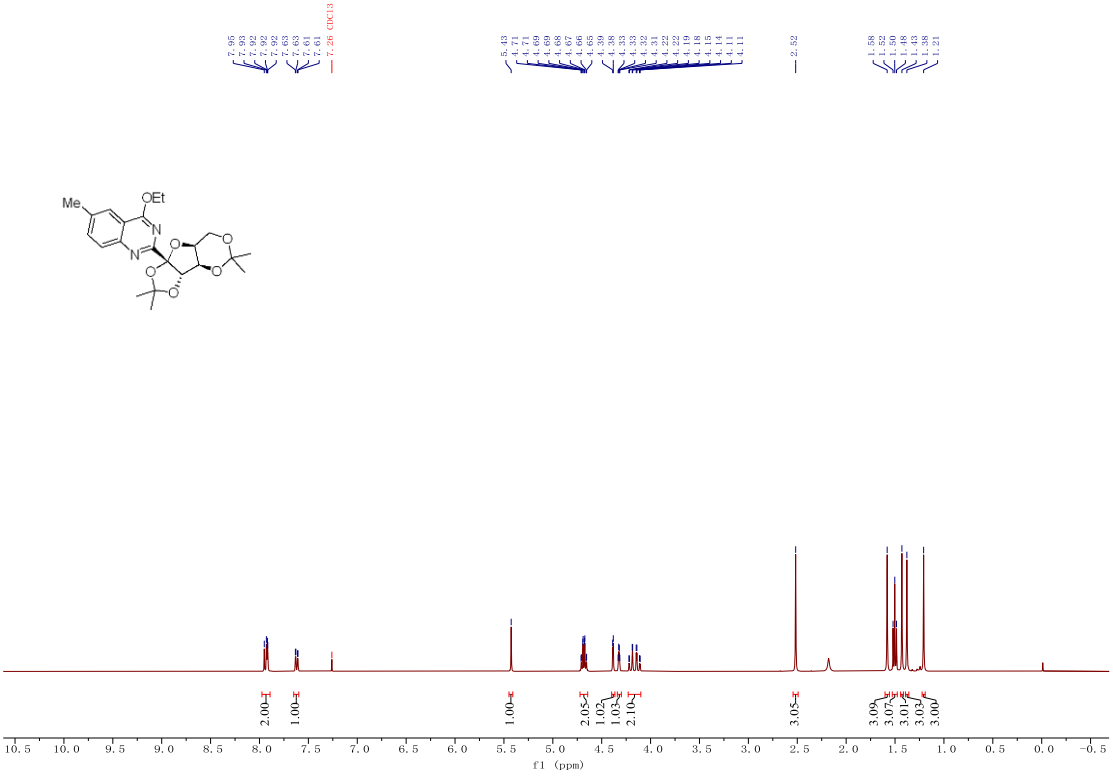
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 16[1]



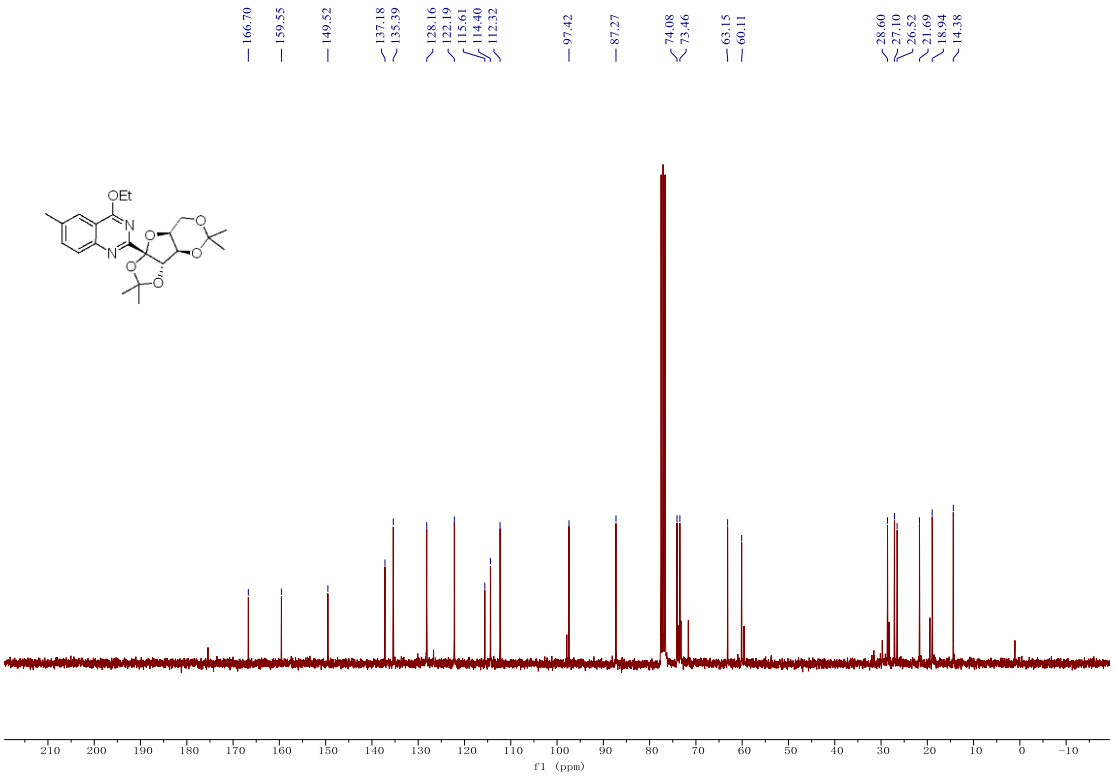
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 17[1]



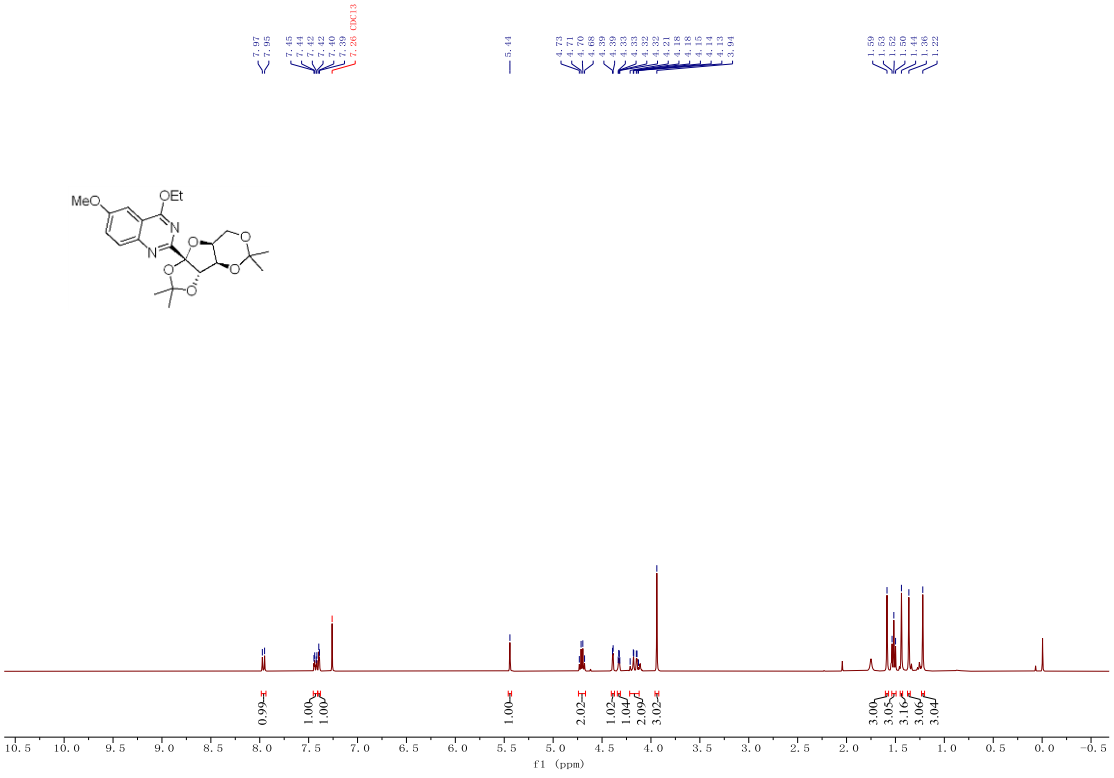
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 18



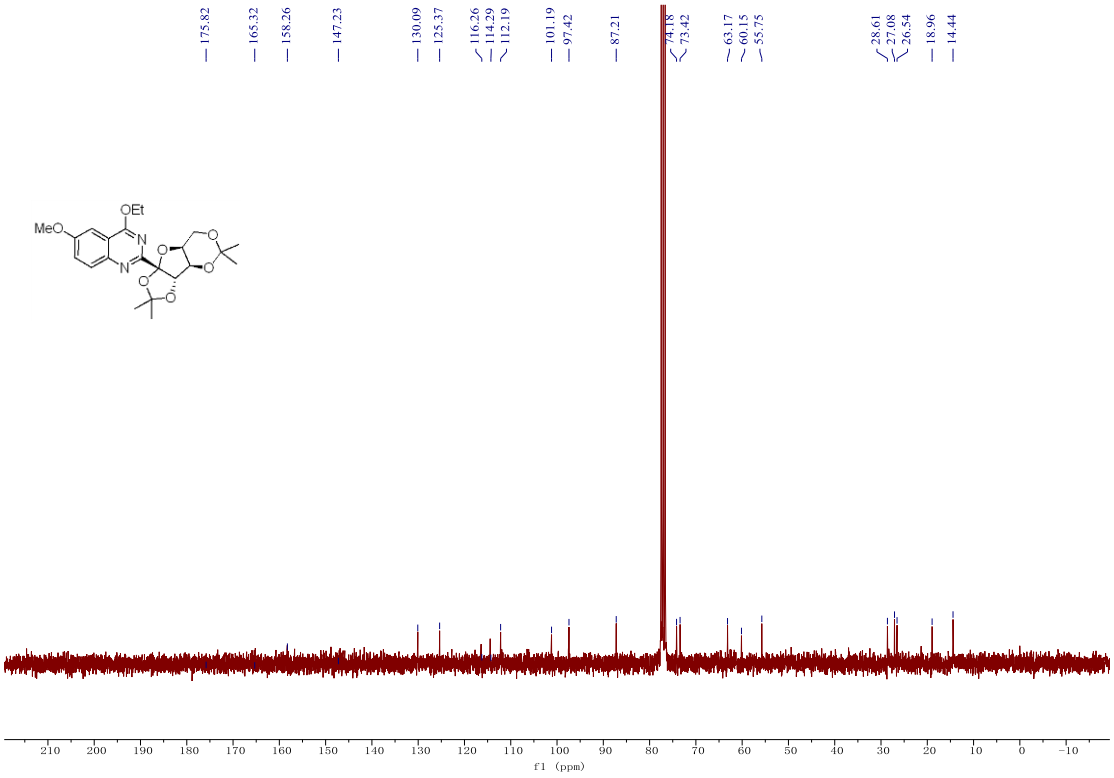
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 18



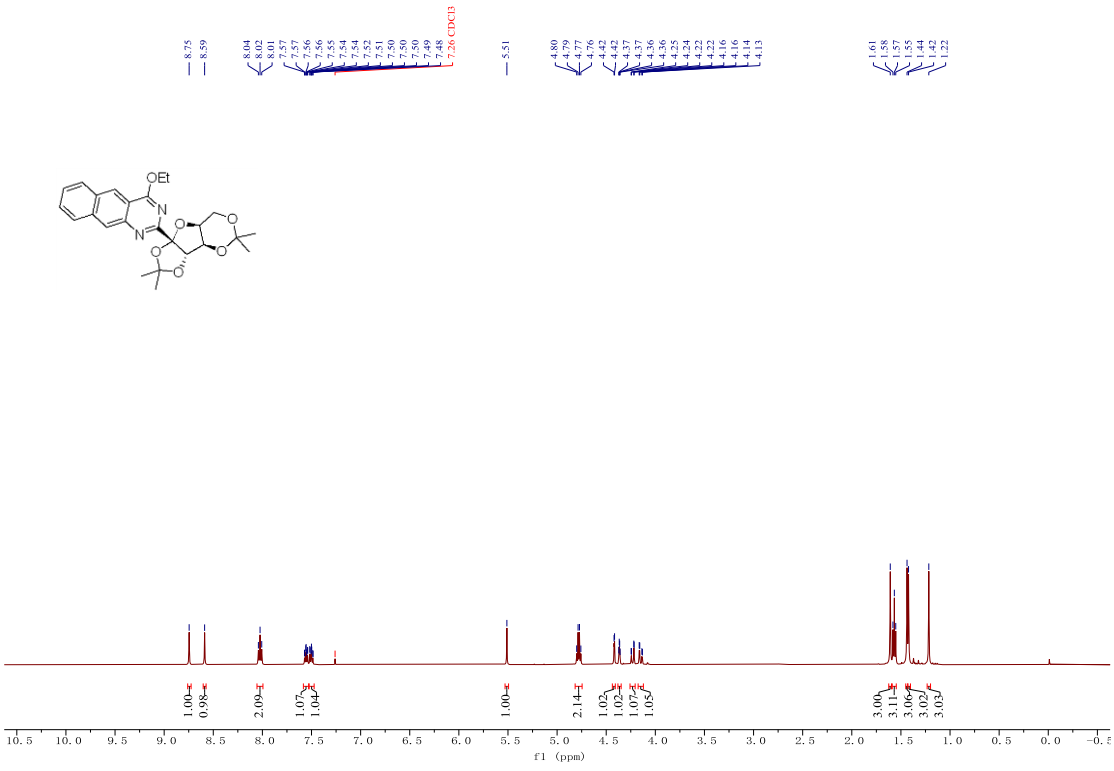
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 19



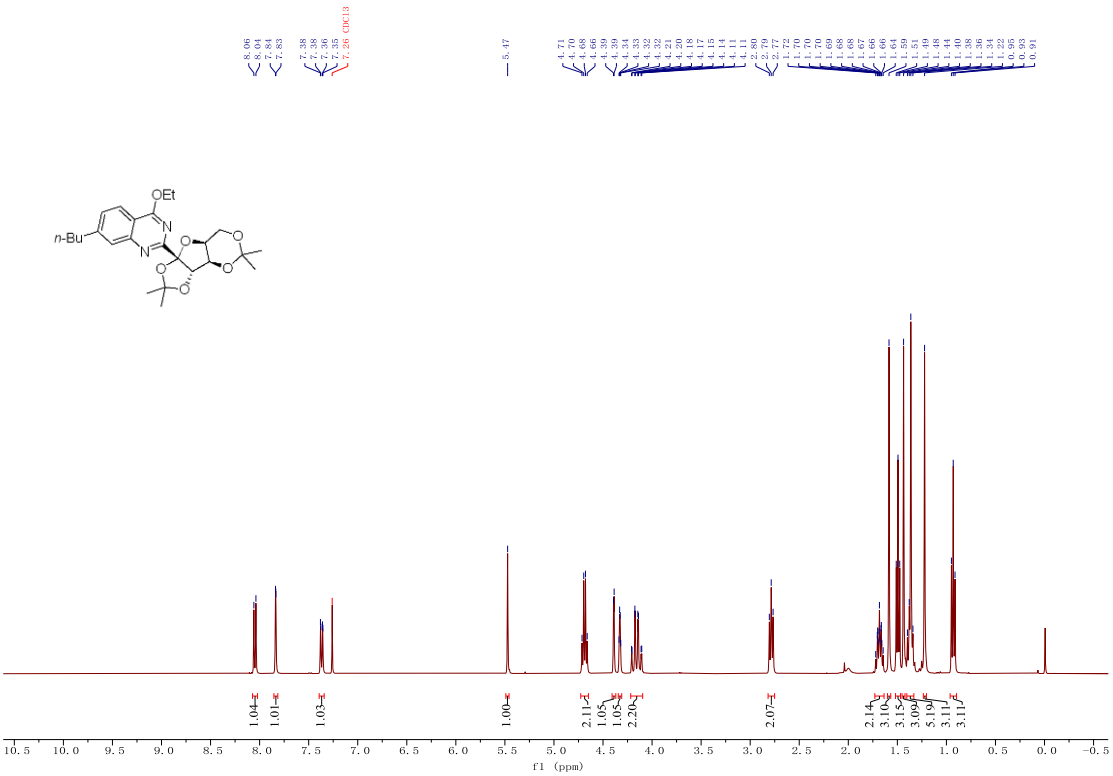
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 19



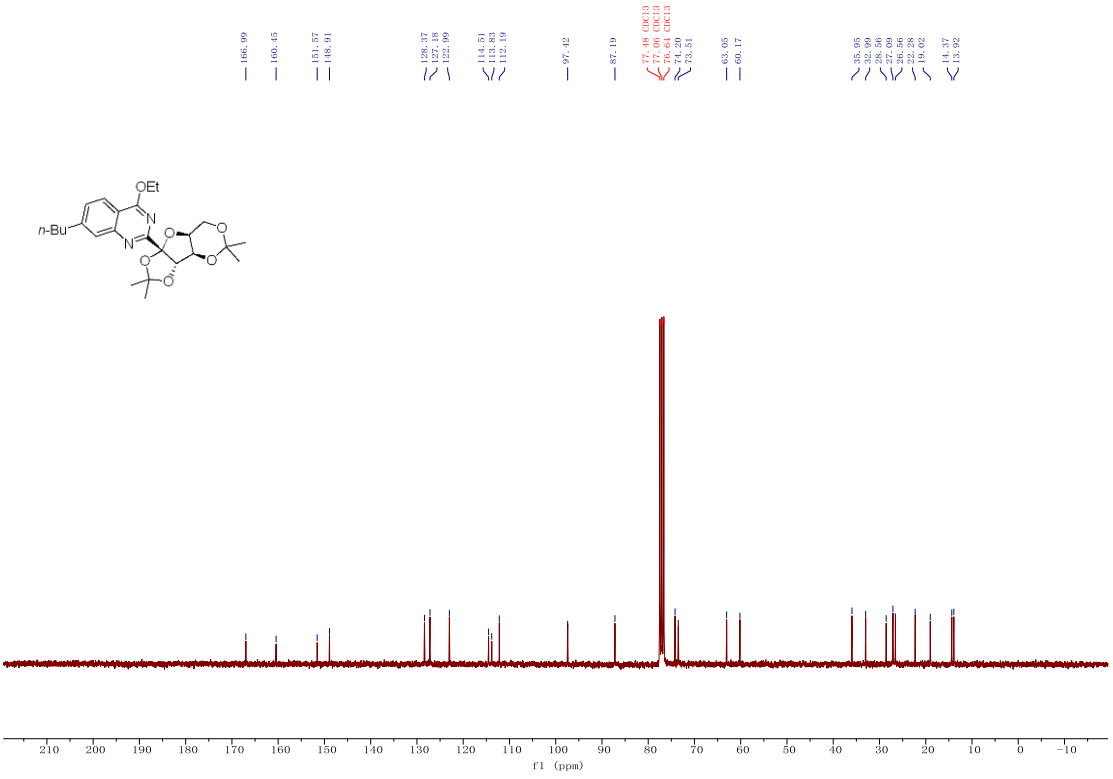
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 20[1]



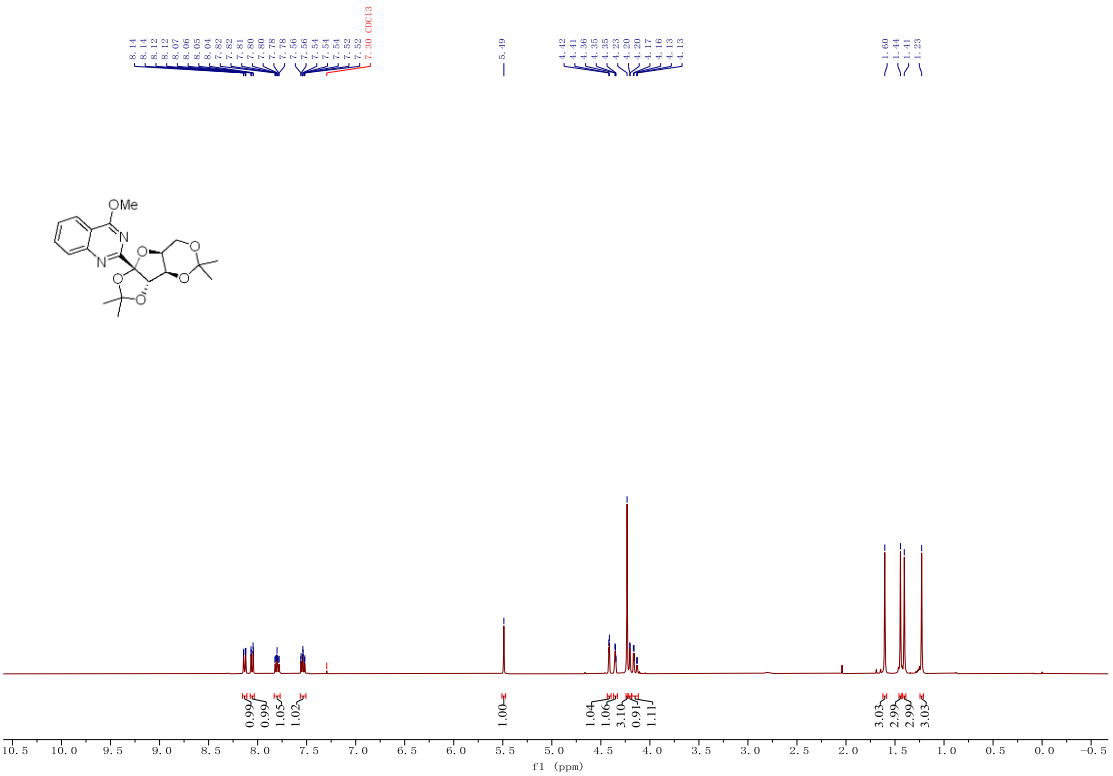
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 21



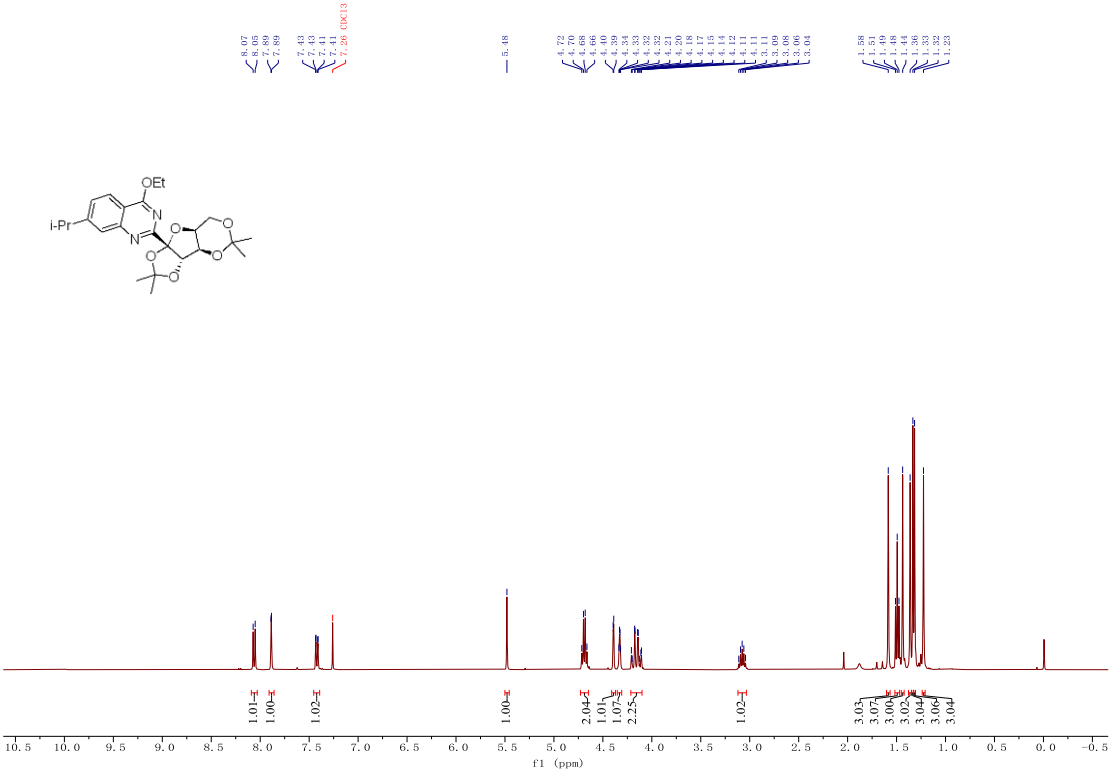
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 21



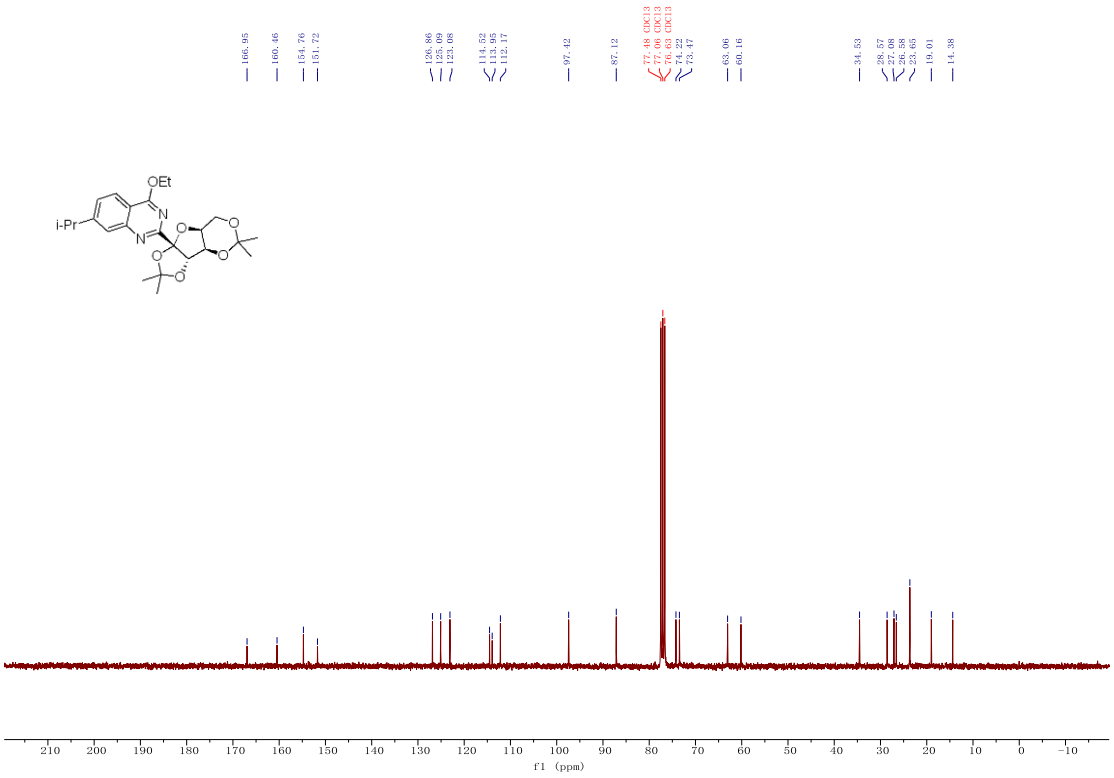
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 22[1]



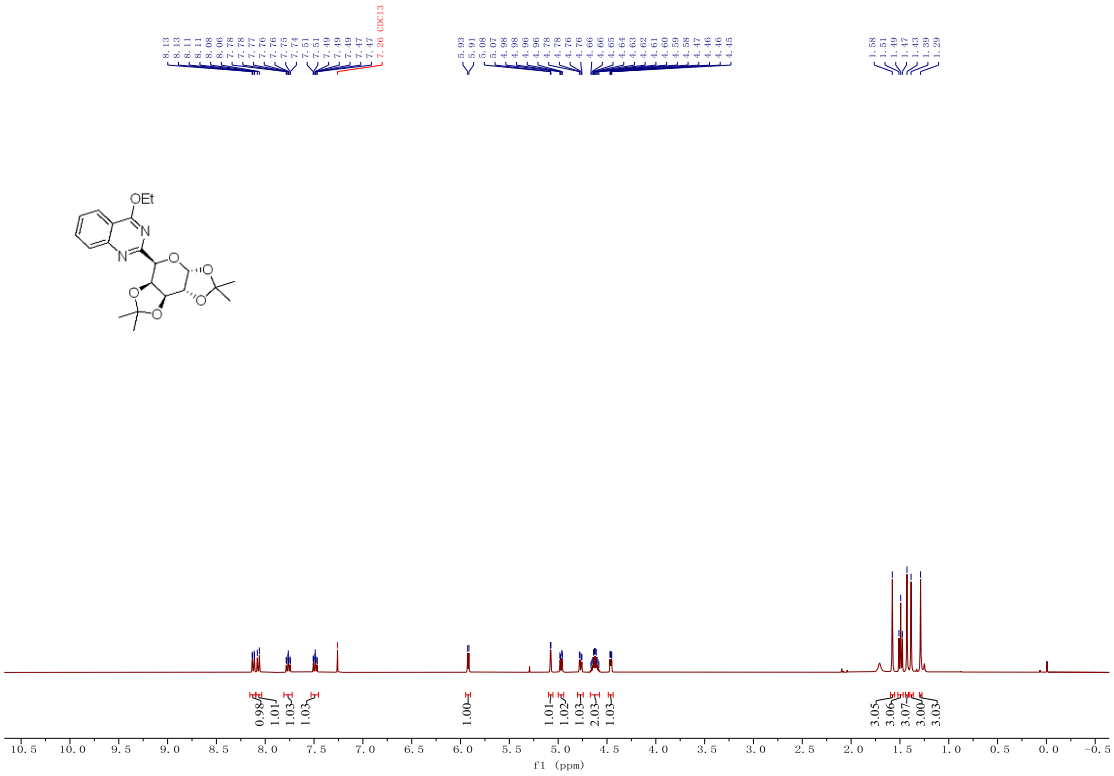
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 23



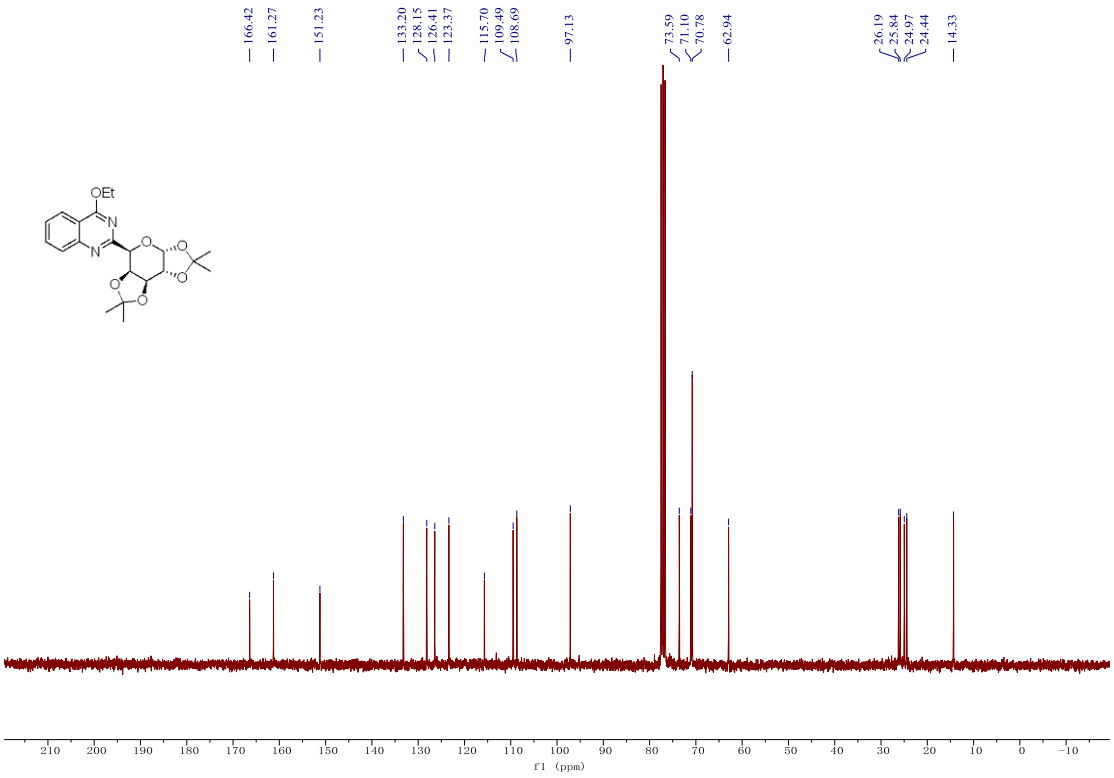
^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound 23



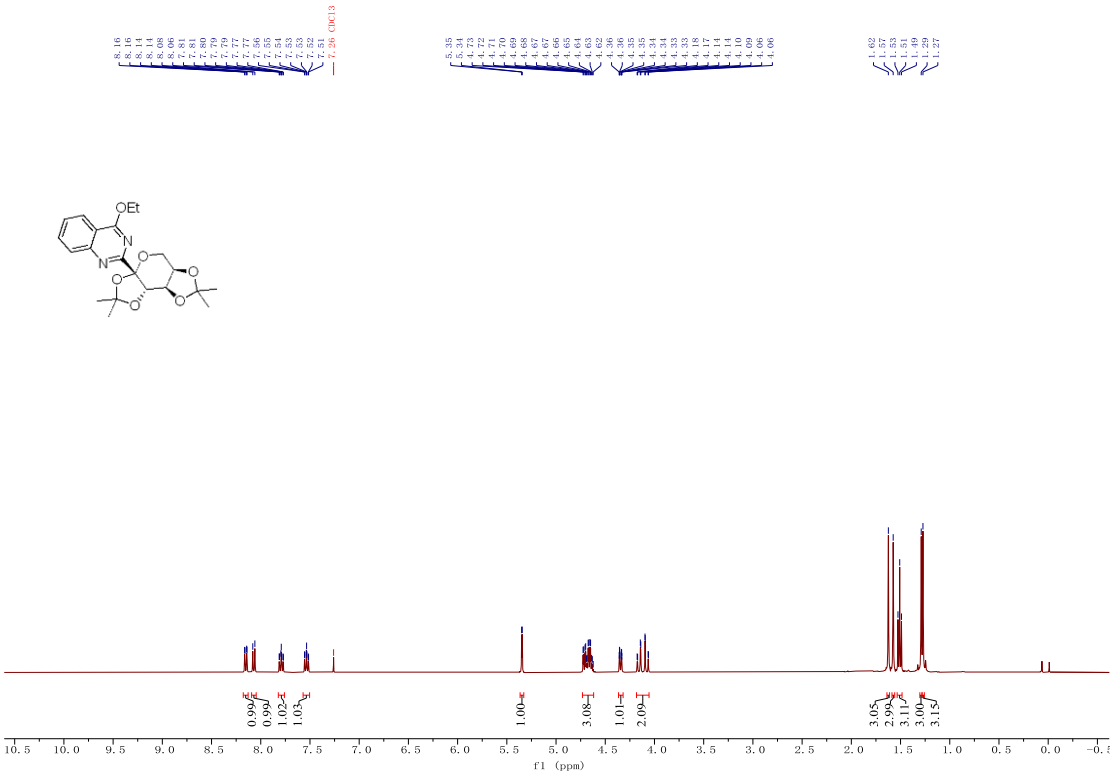
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 24



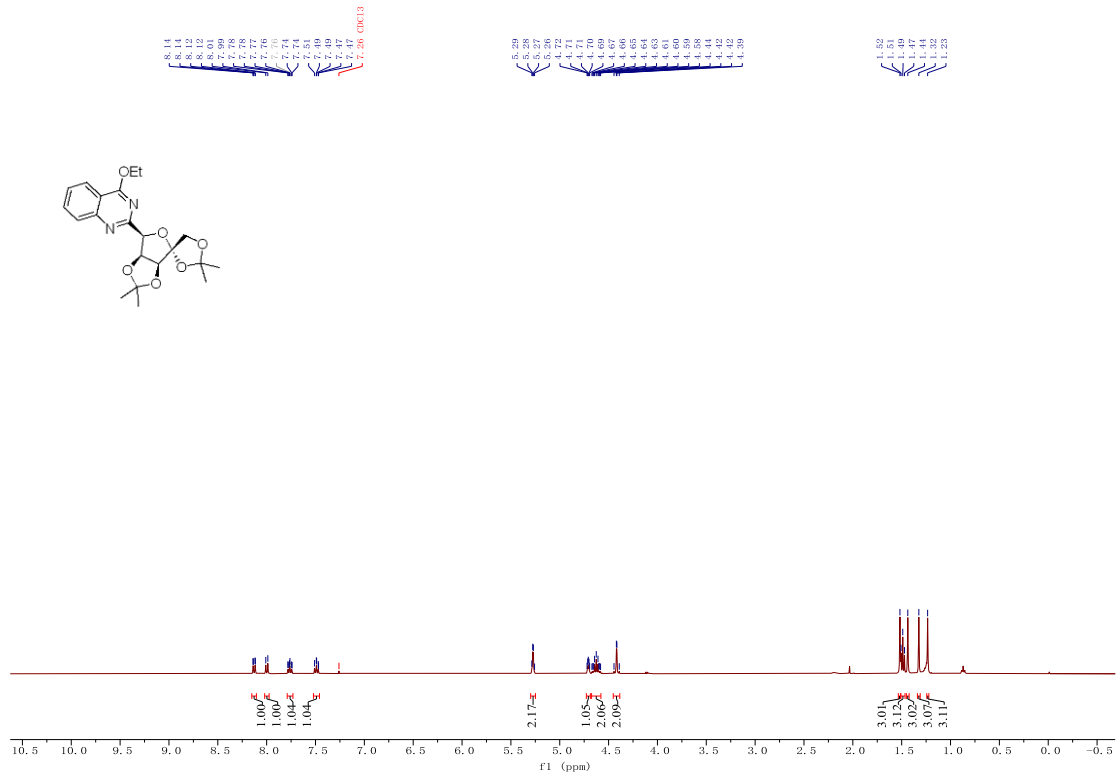
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 24



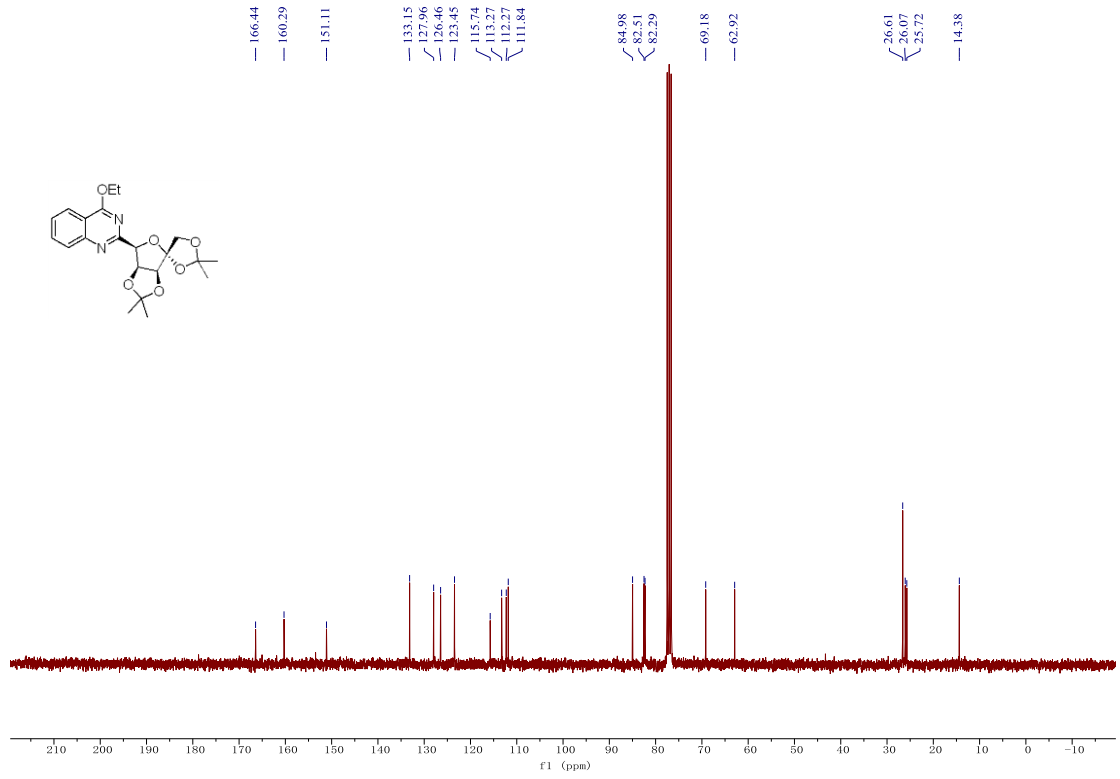
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 25[1]



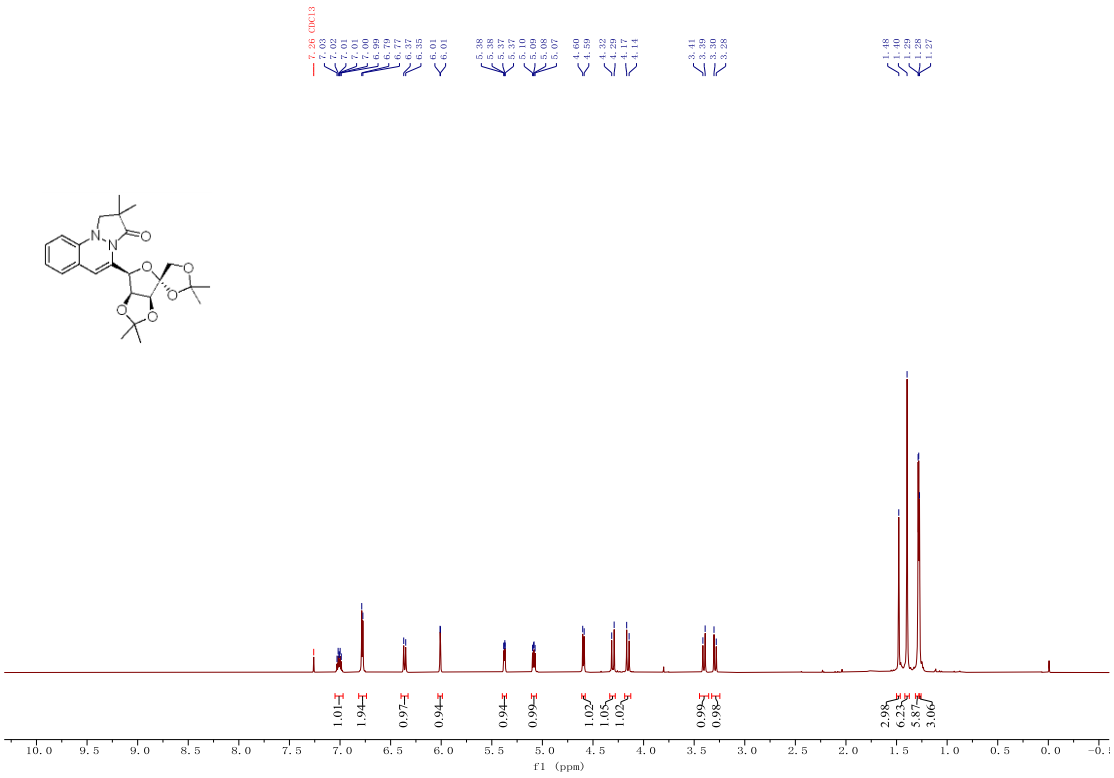
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 26



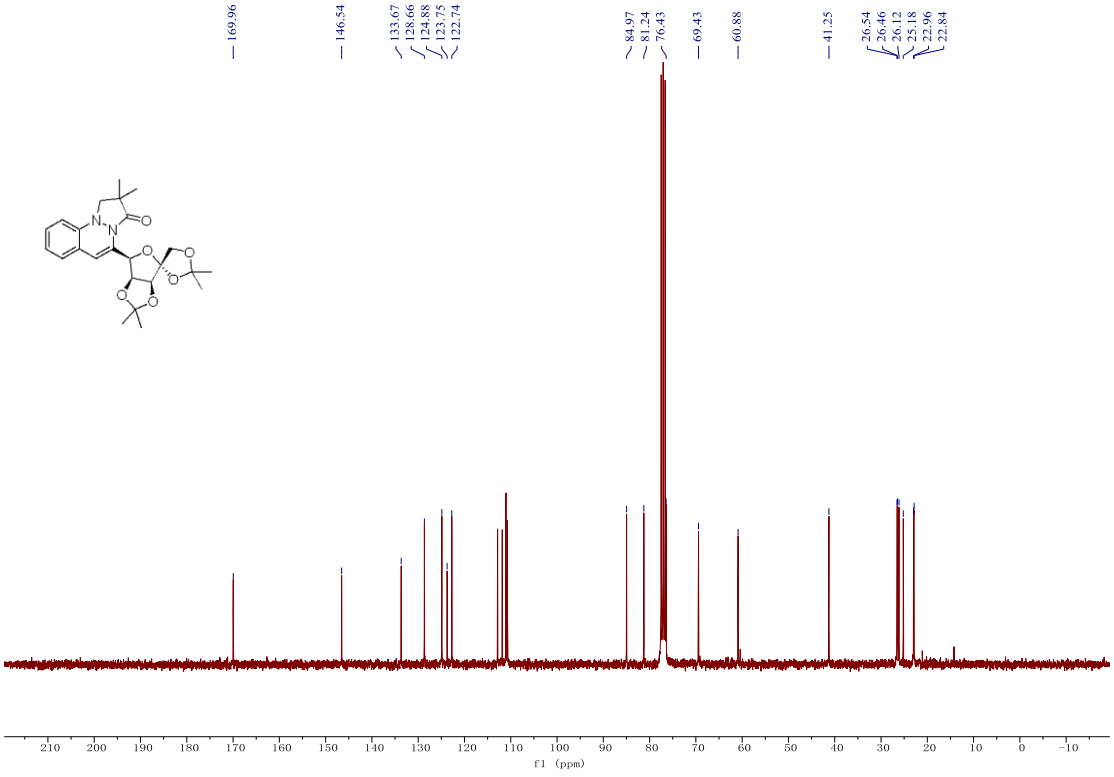
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 26



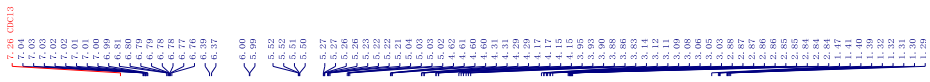
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 27

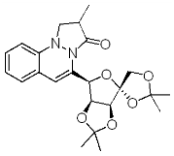


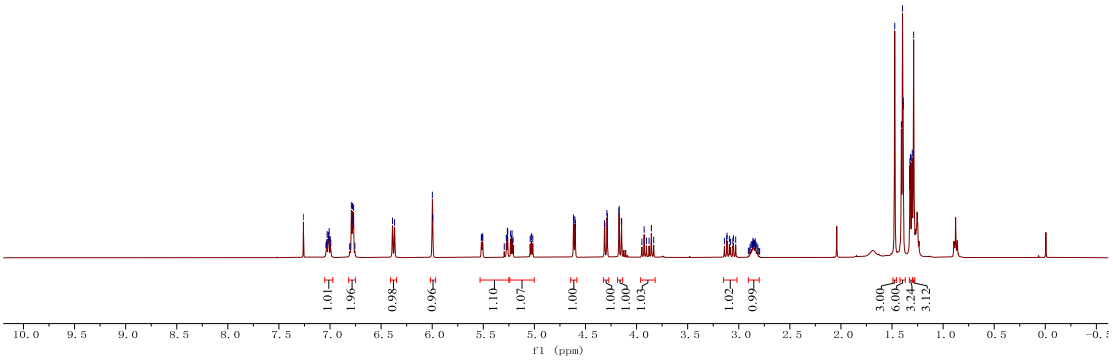
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 27



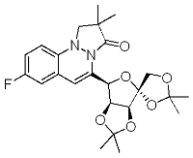
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 28[3]

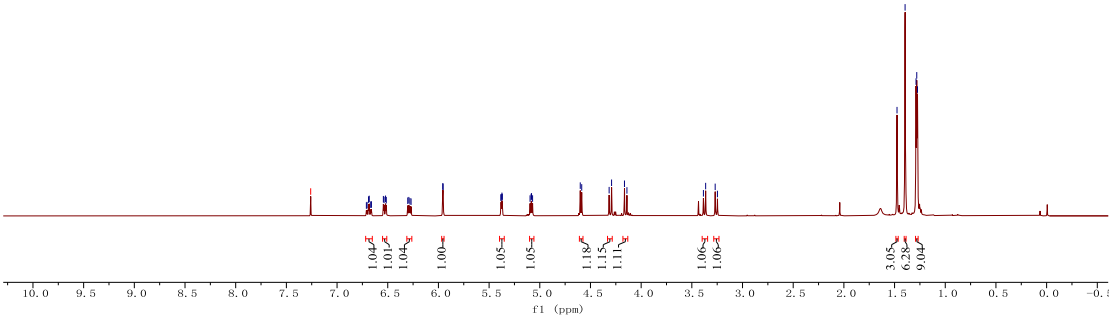




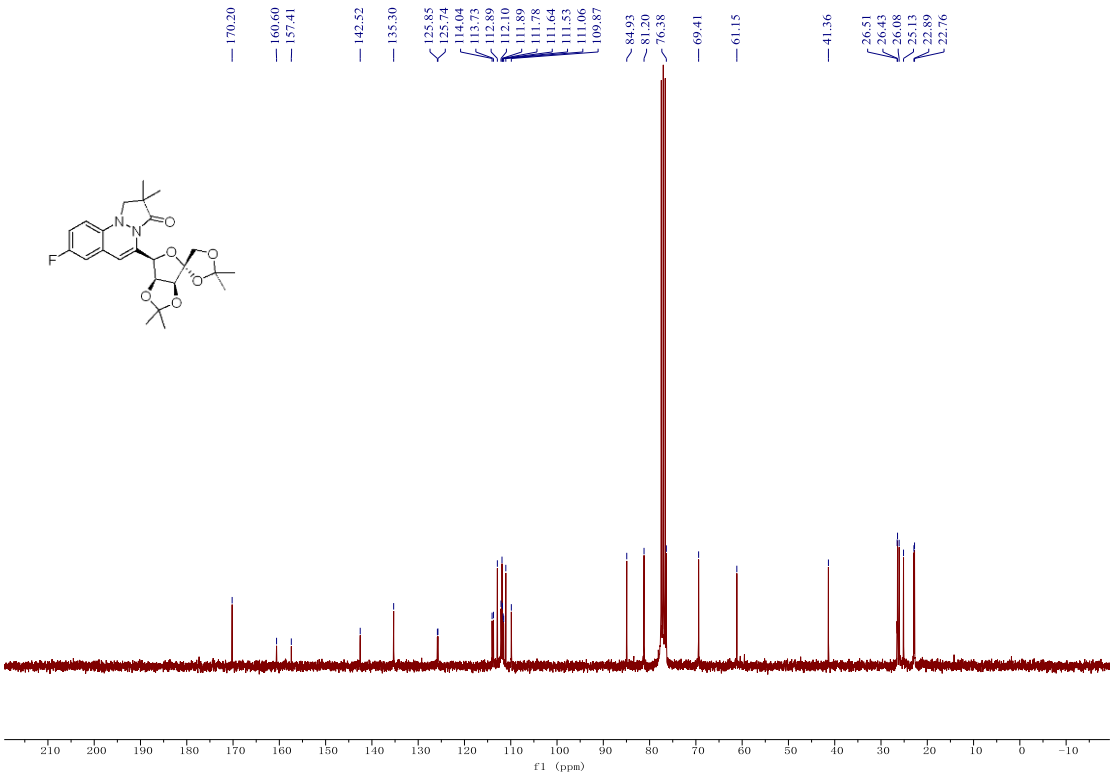


^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 29

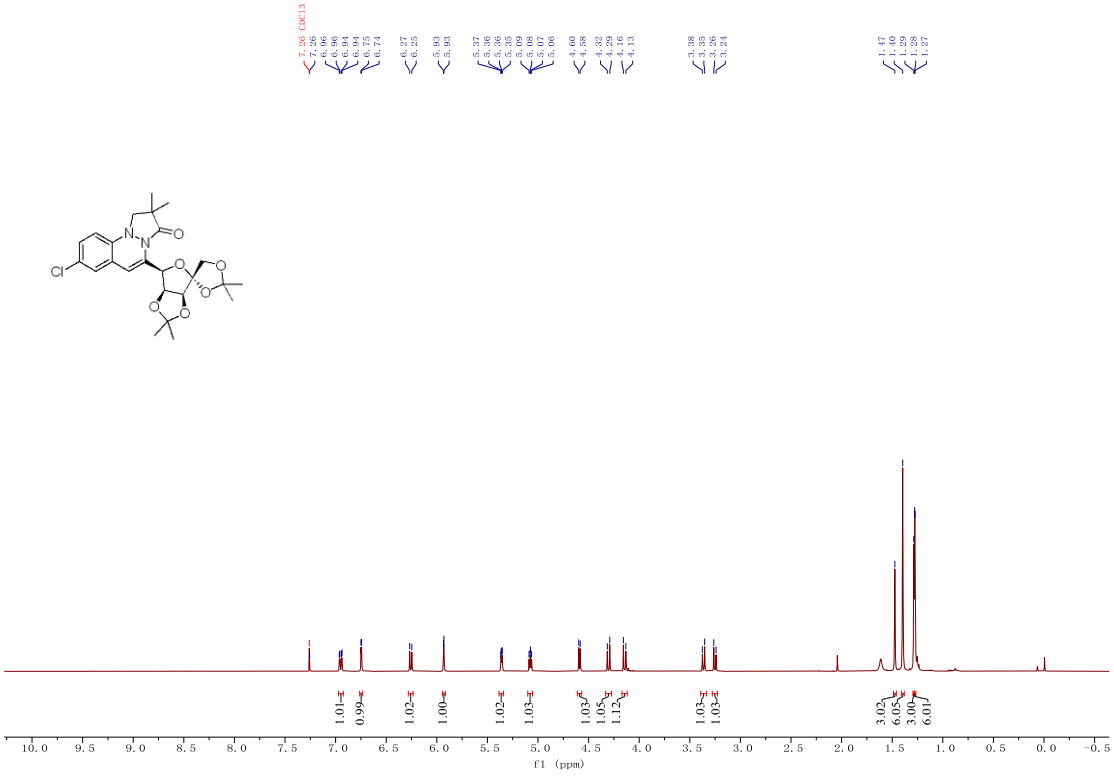




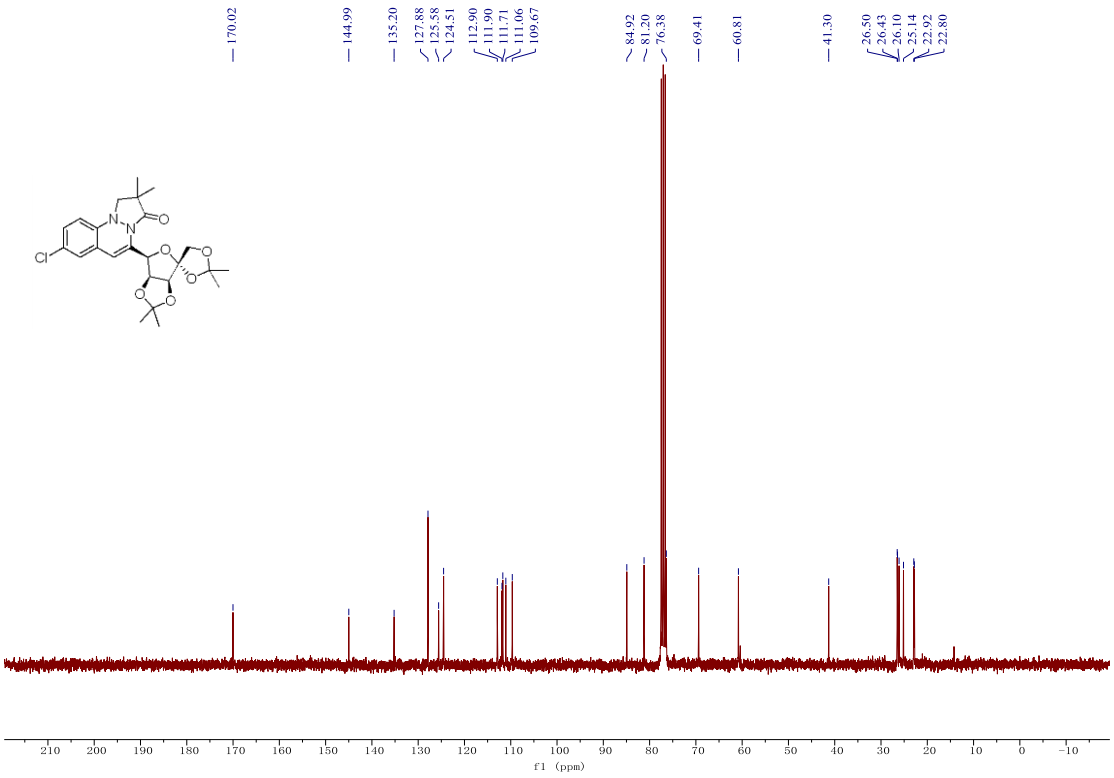
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 29



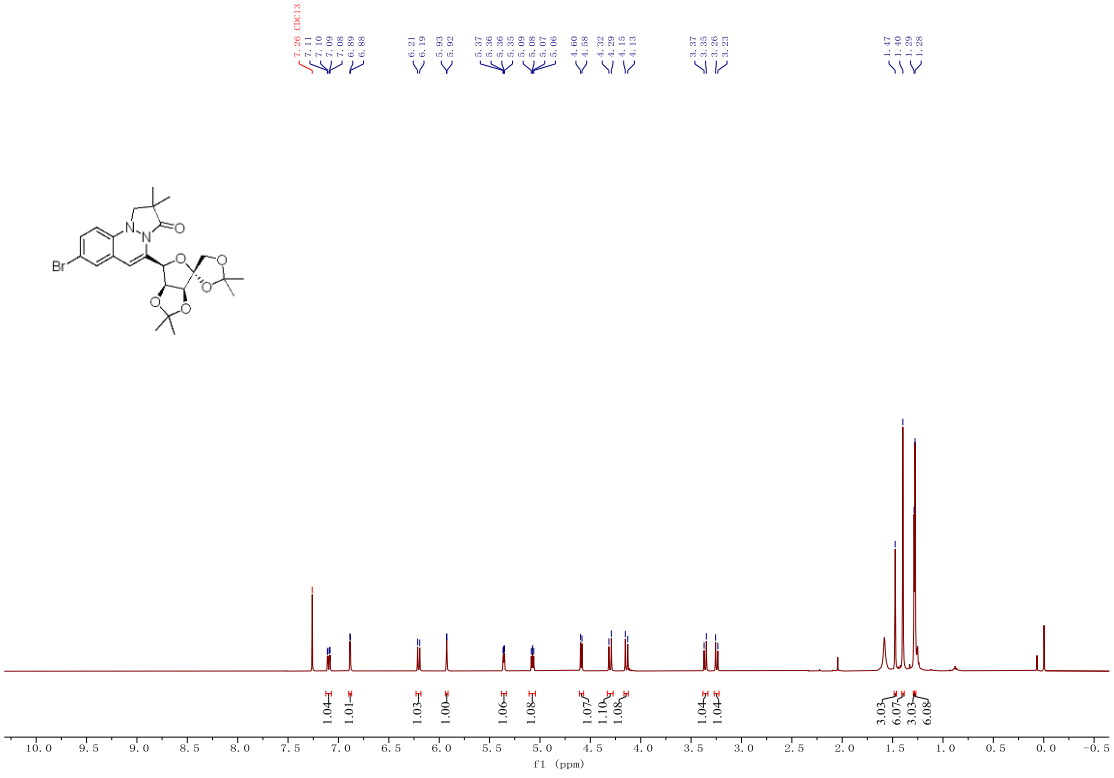
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 30



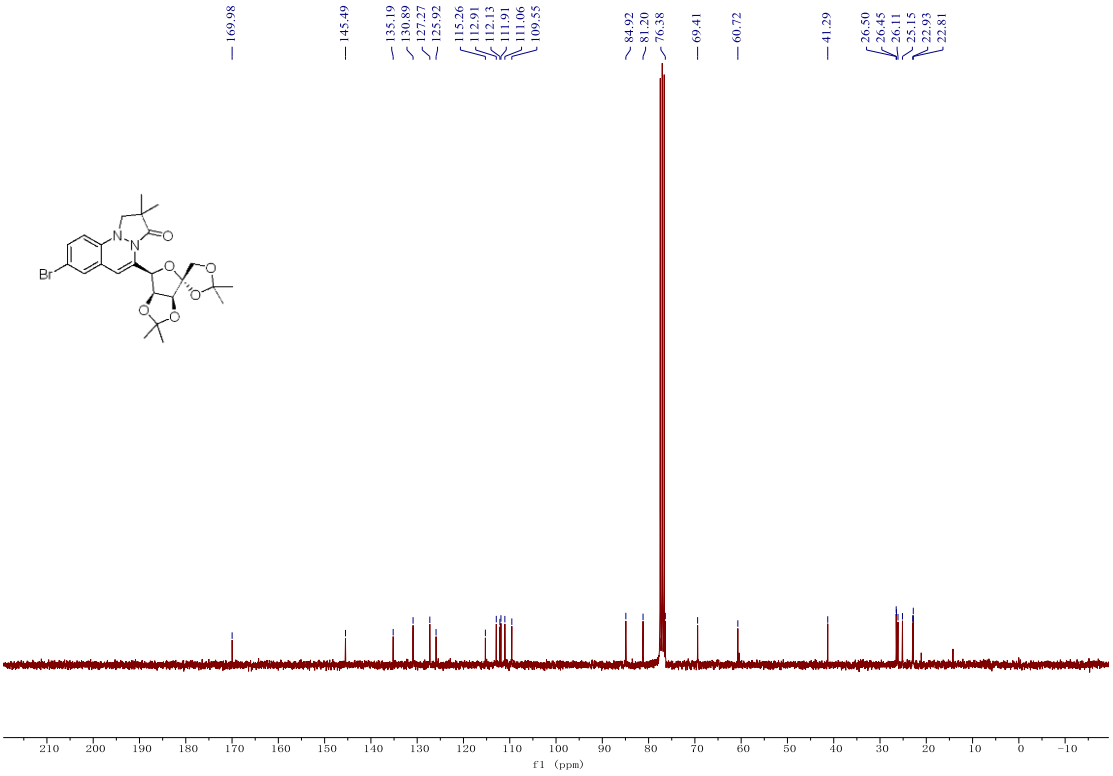
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 30



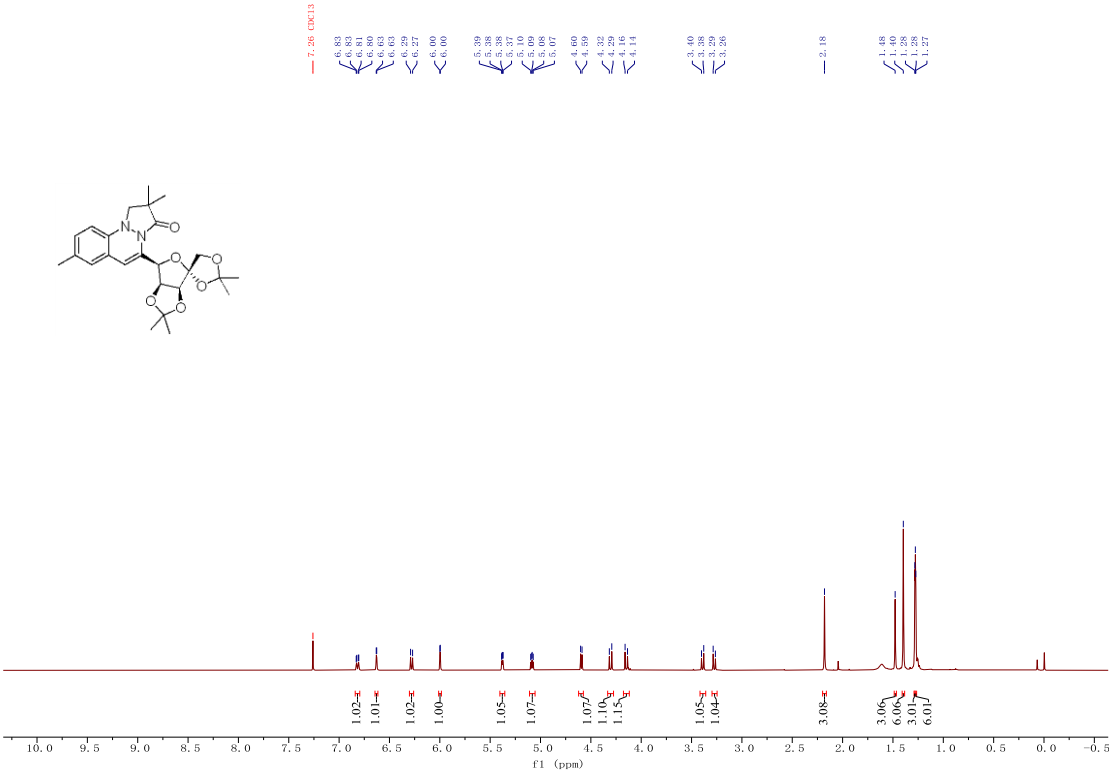
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 31



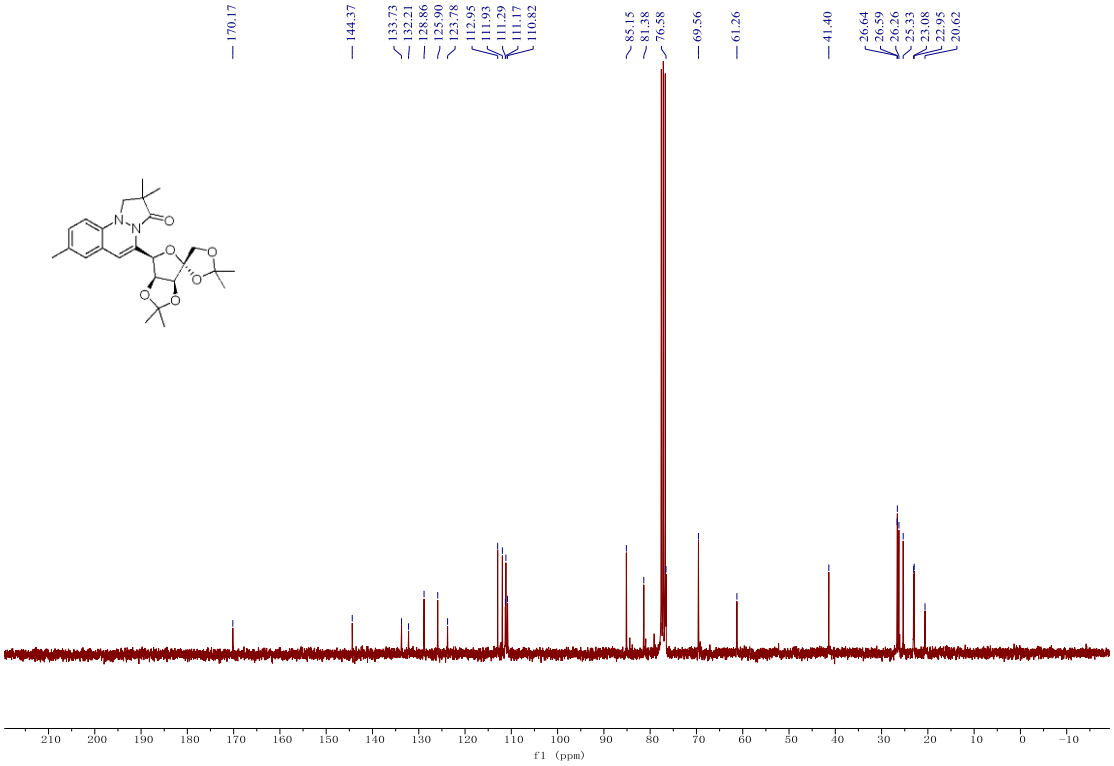
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 31



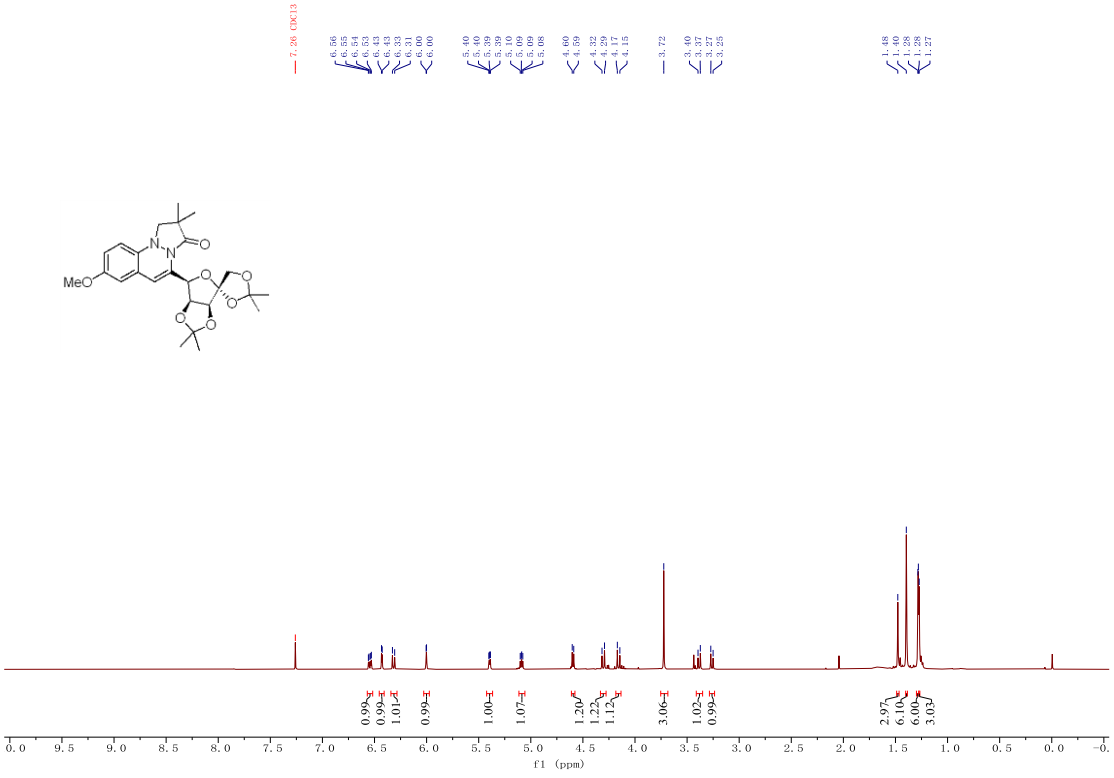
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 32



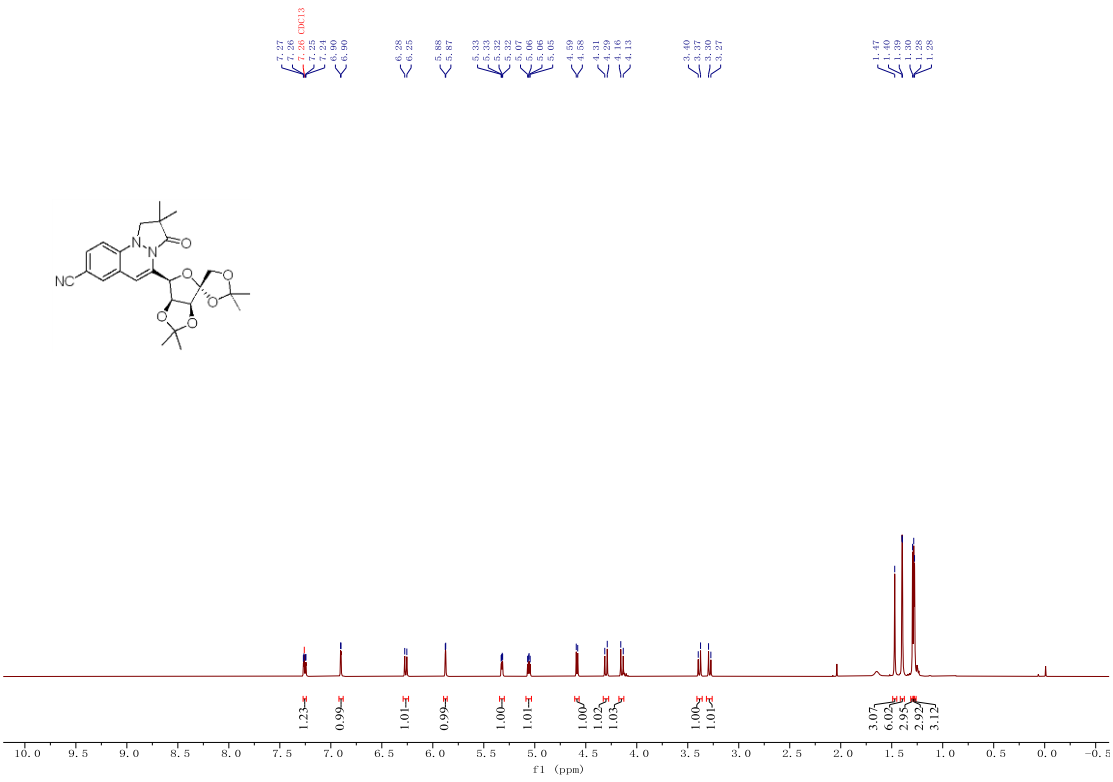
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 32



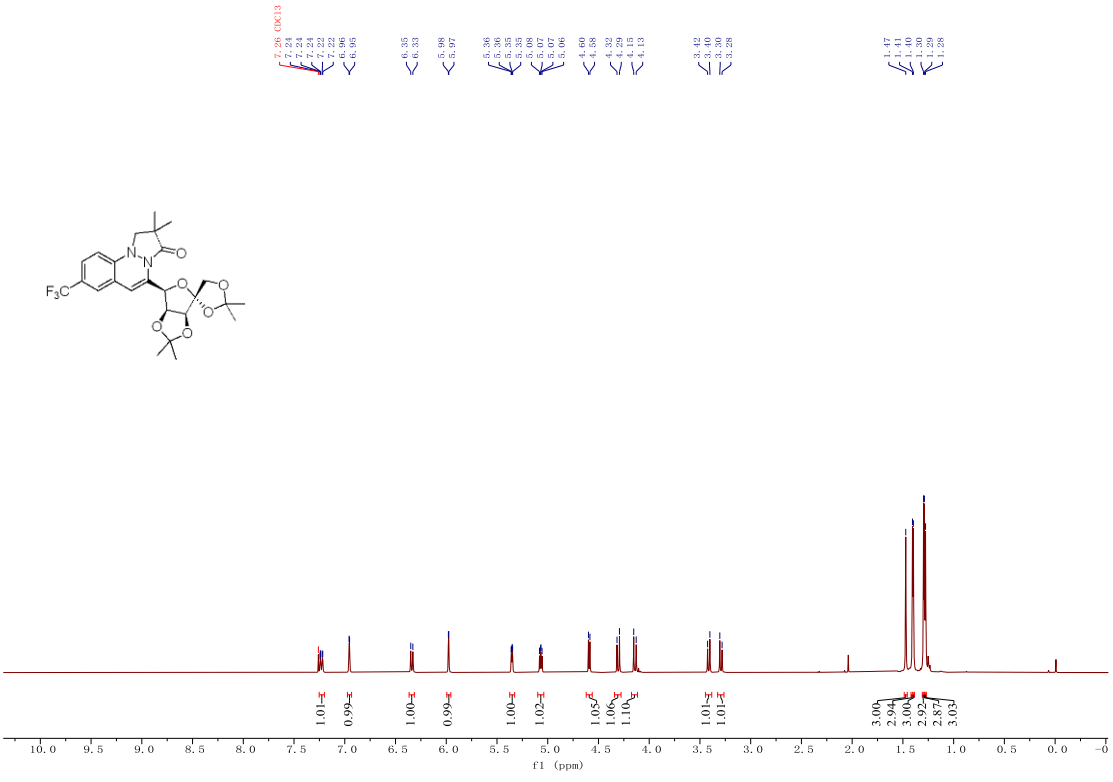
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 33[3]



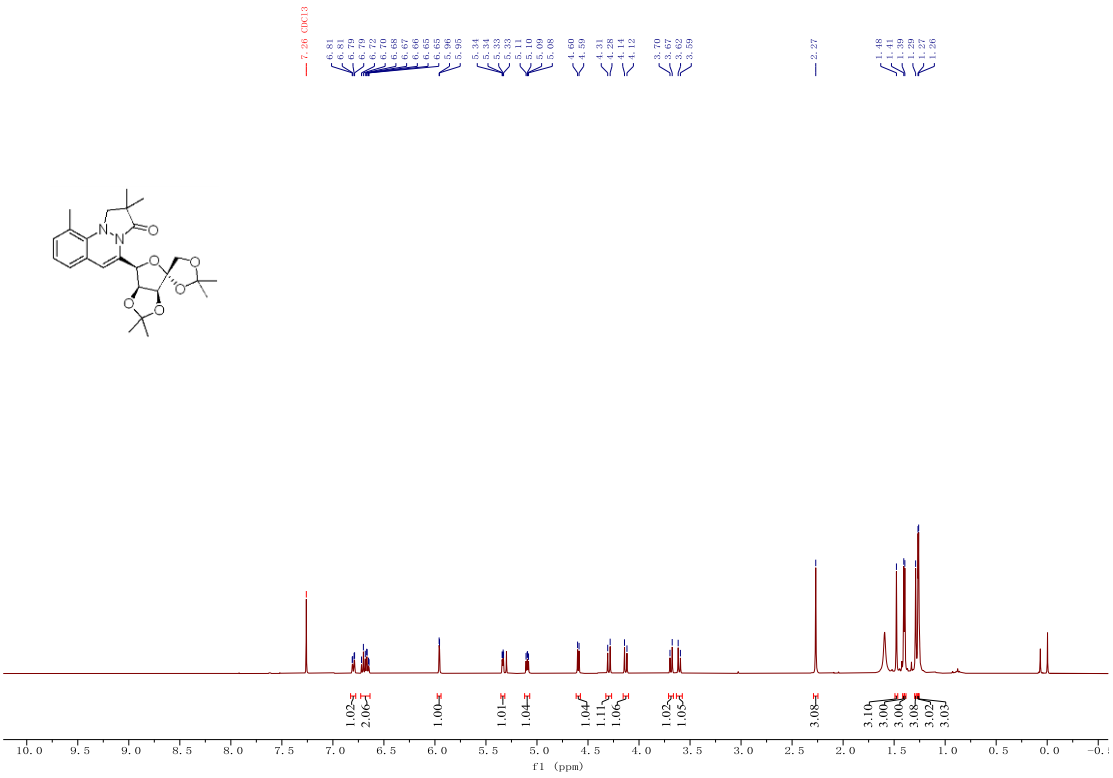
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 34[3]



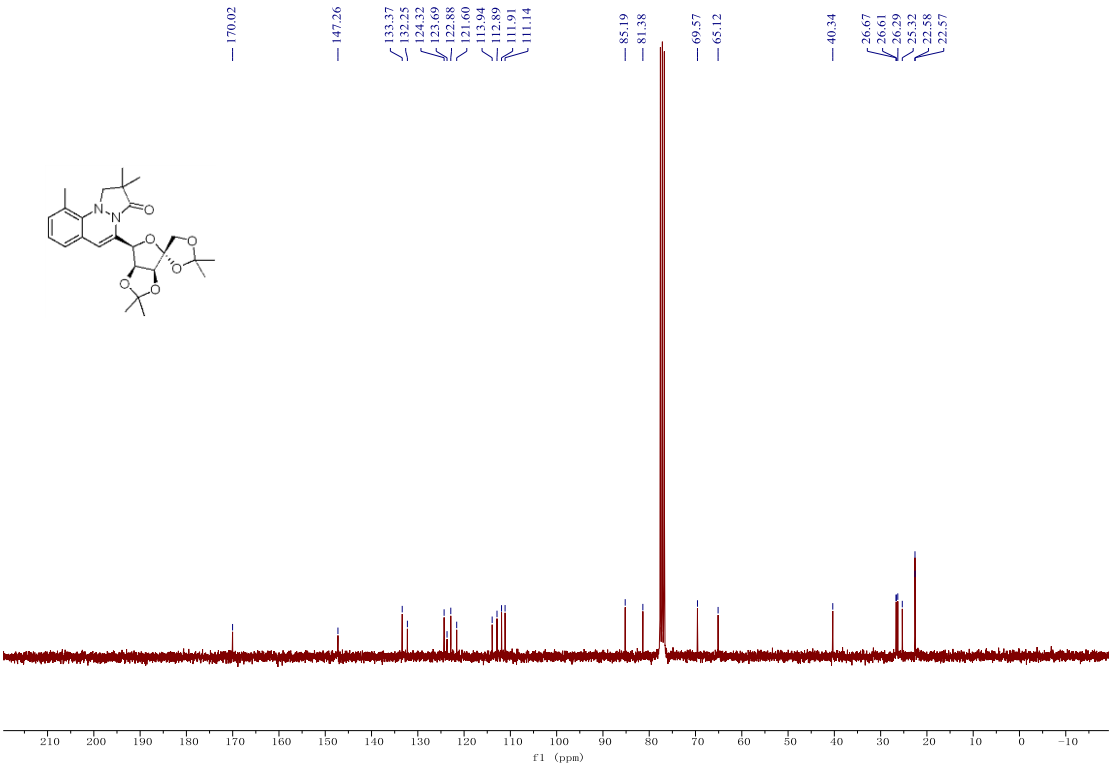
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 35[3]



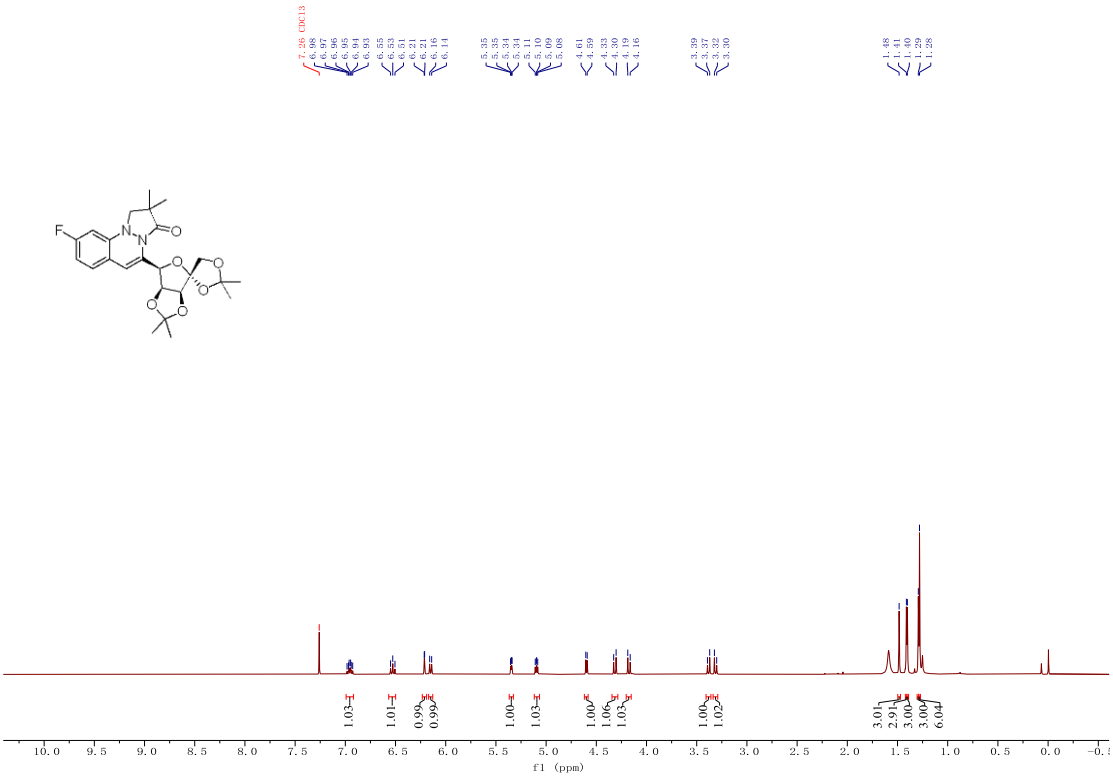
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 36



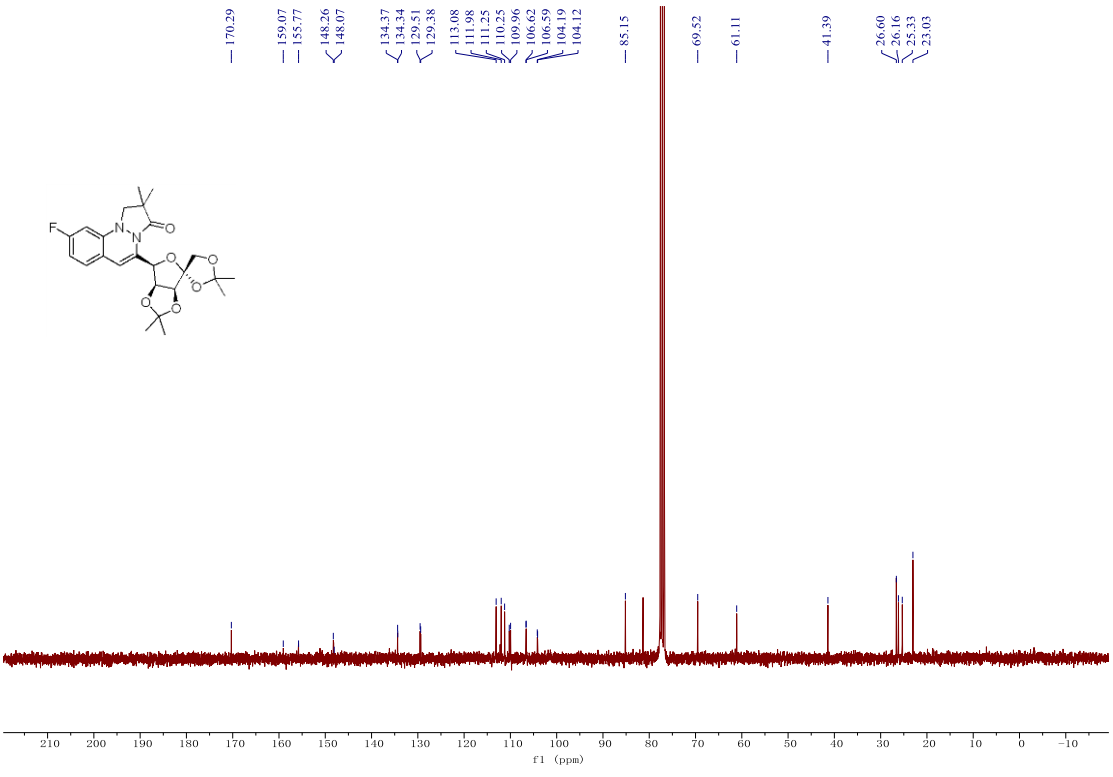
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 36



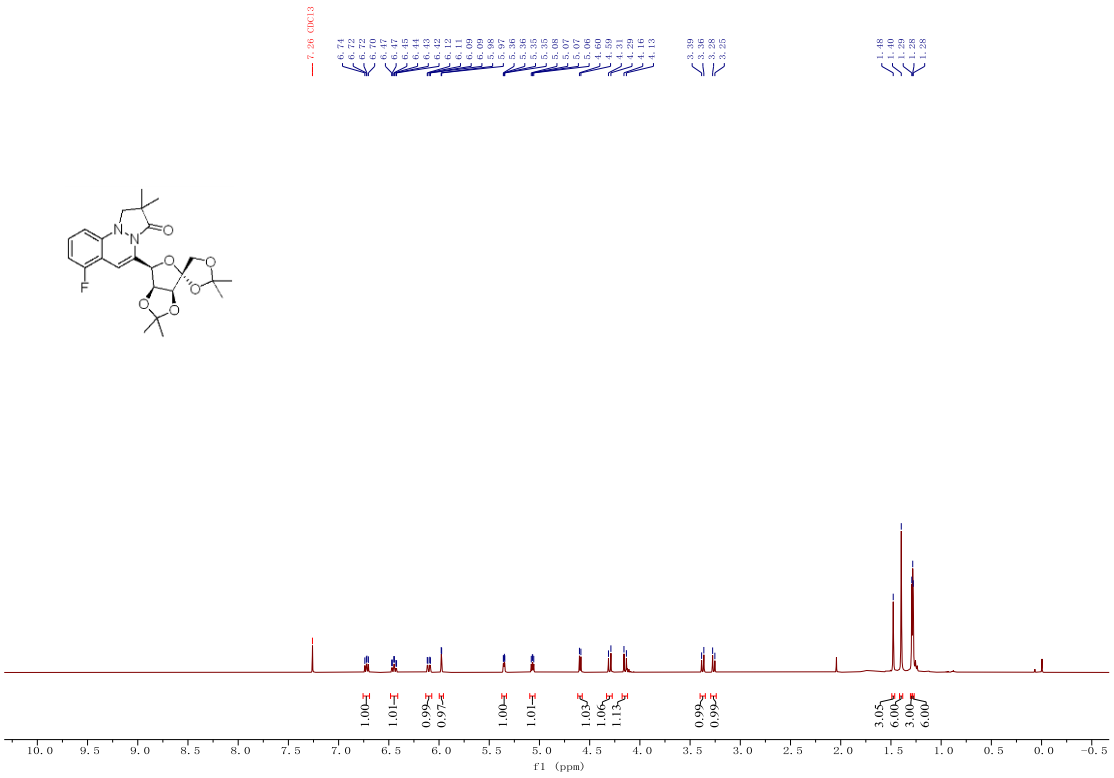
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 37



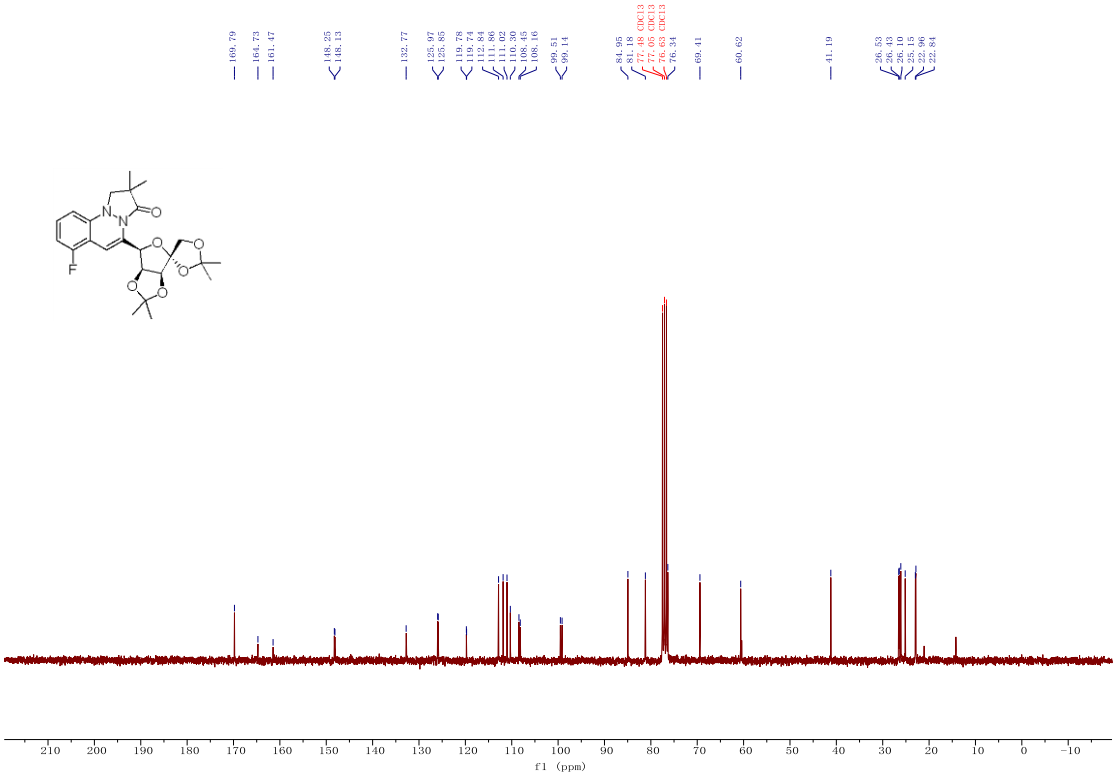
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 37



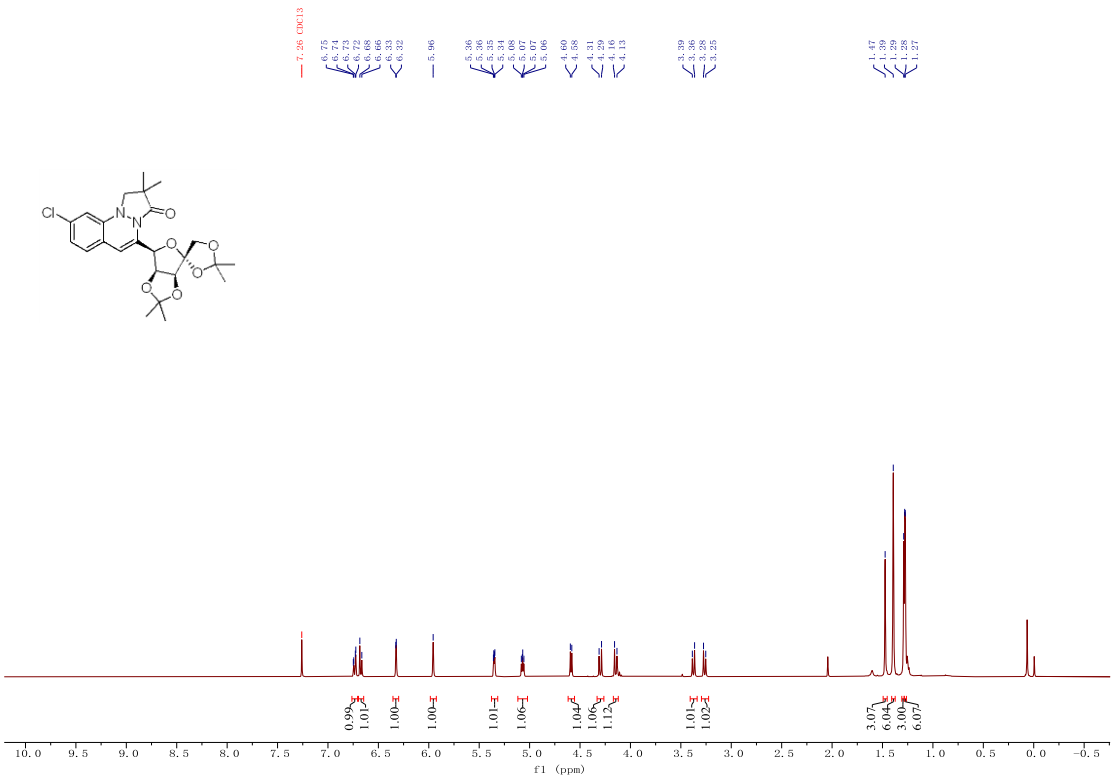
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 37’



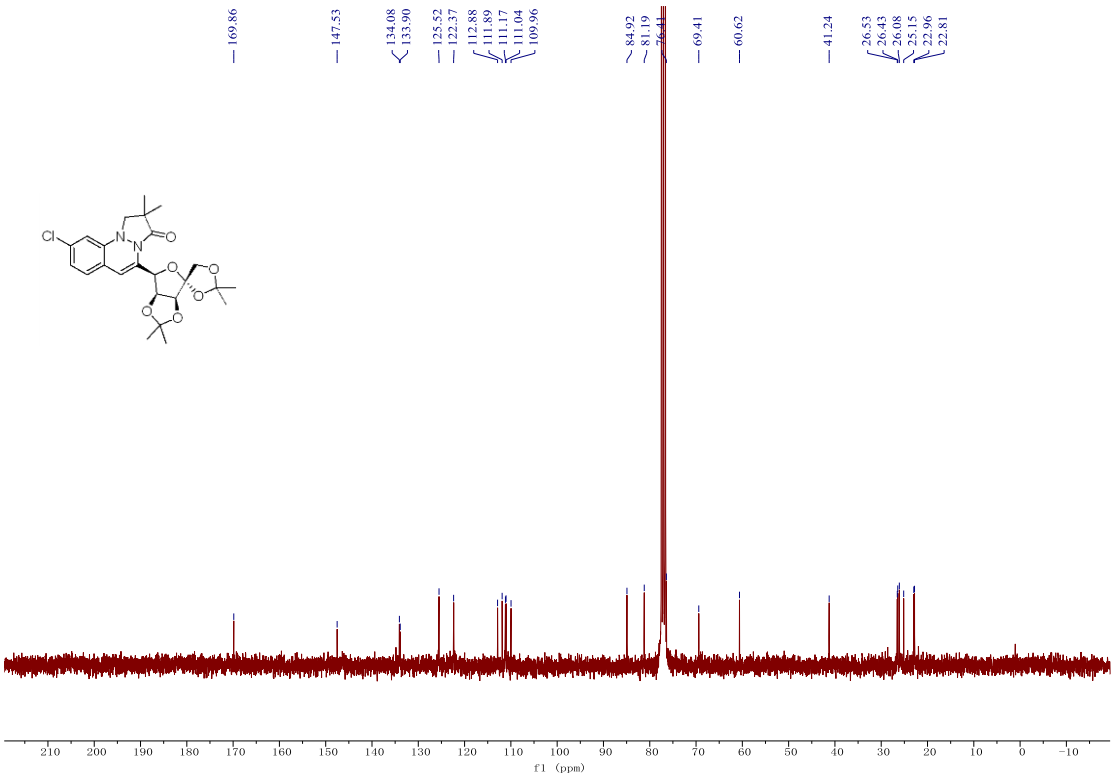
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 37'



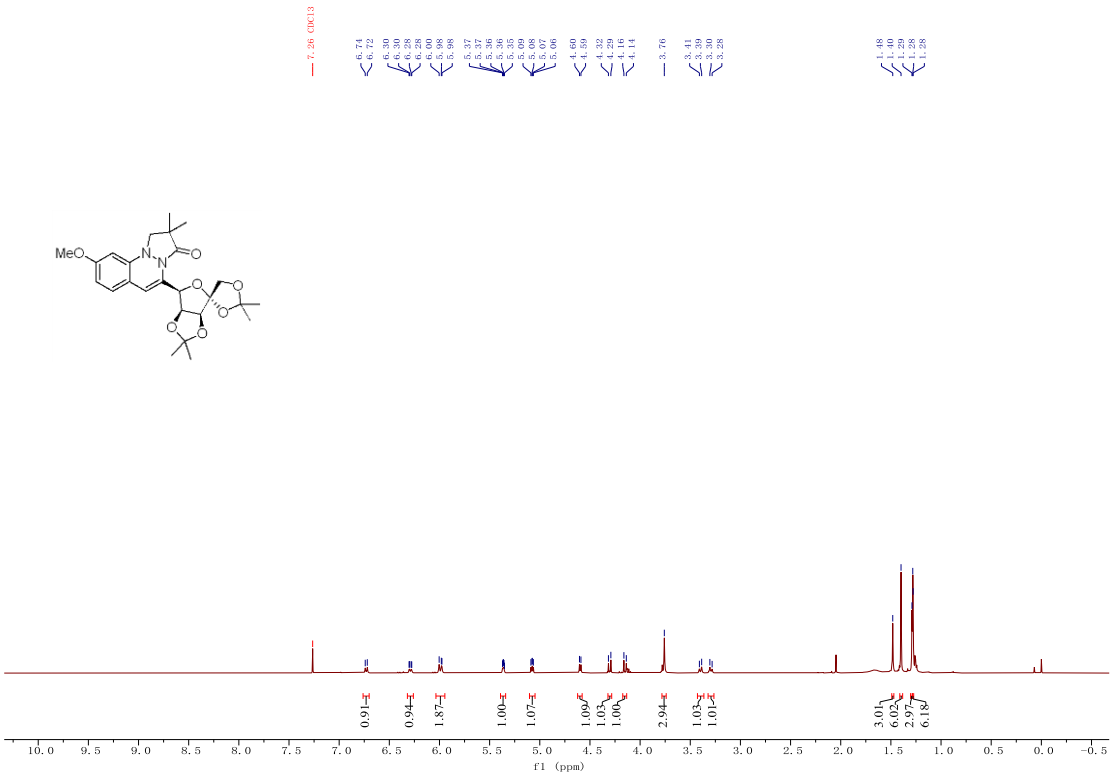
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 38



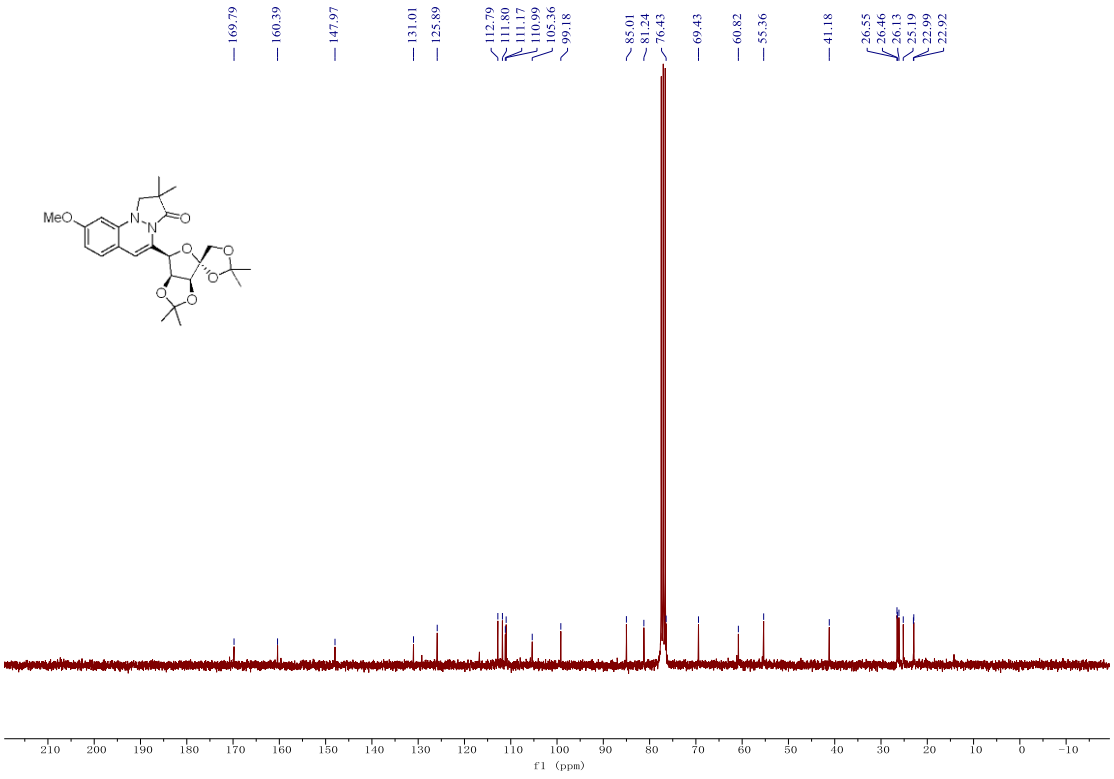
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 38



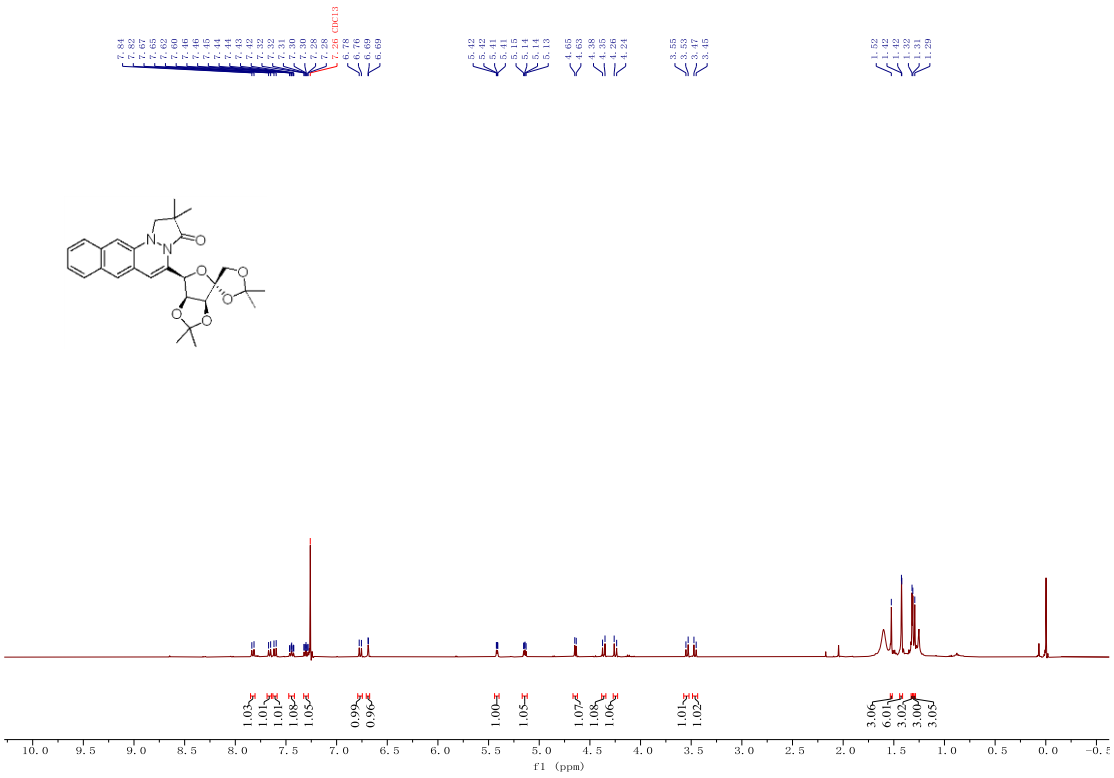
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 39



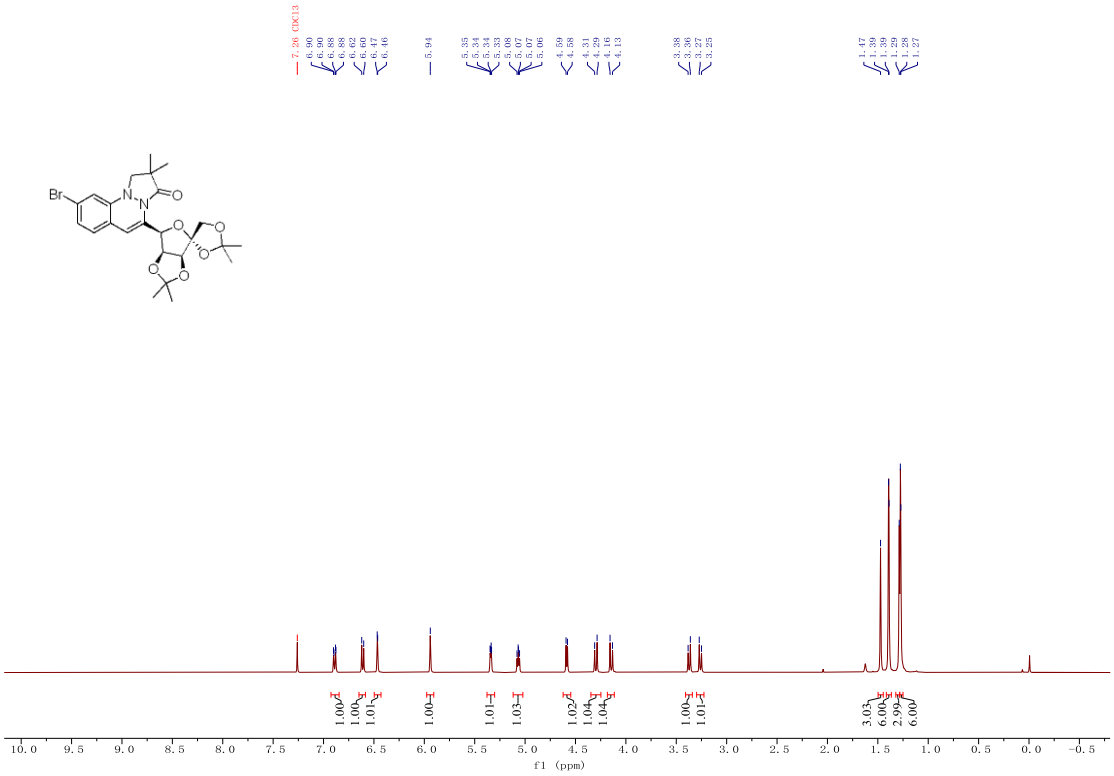
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 39



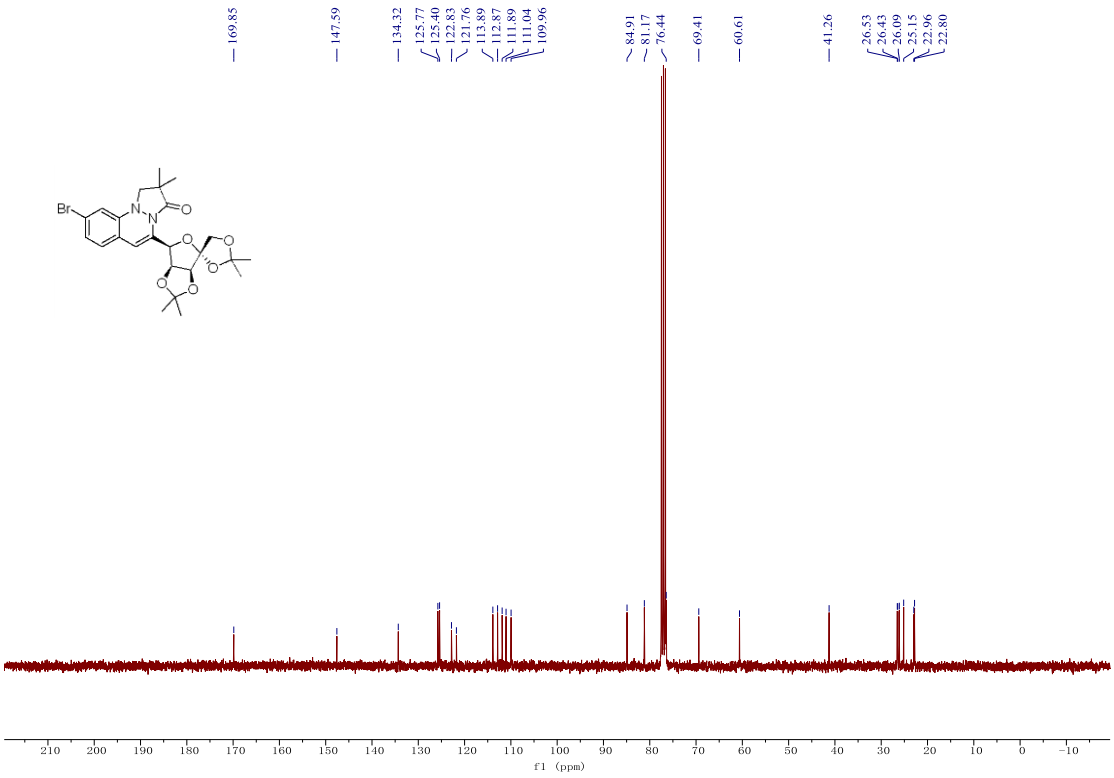
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 40[3]



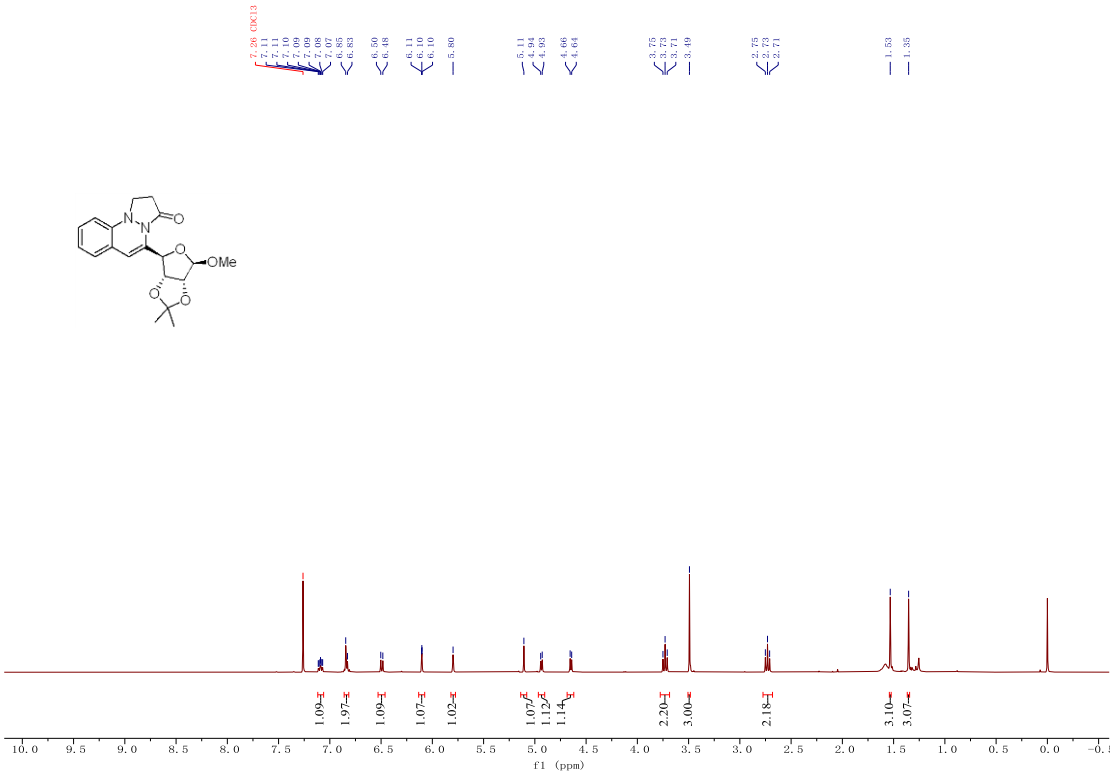
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 41



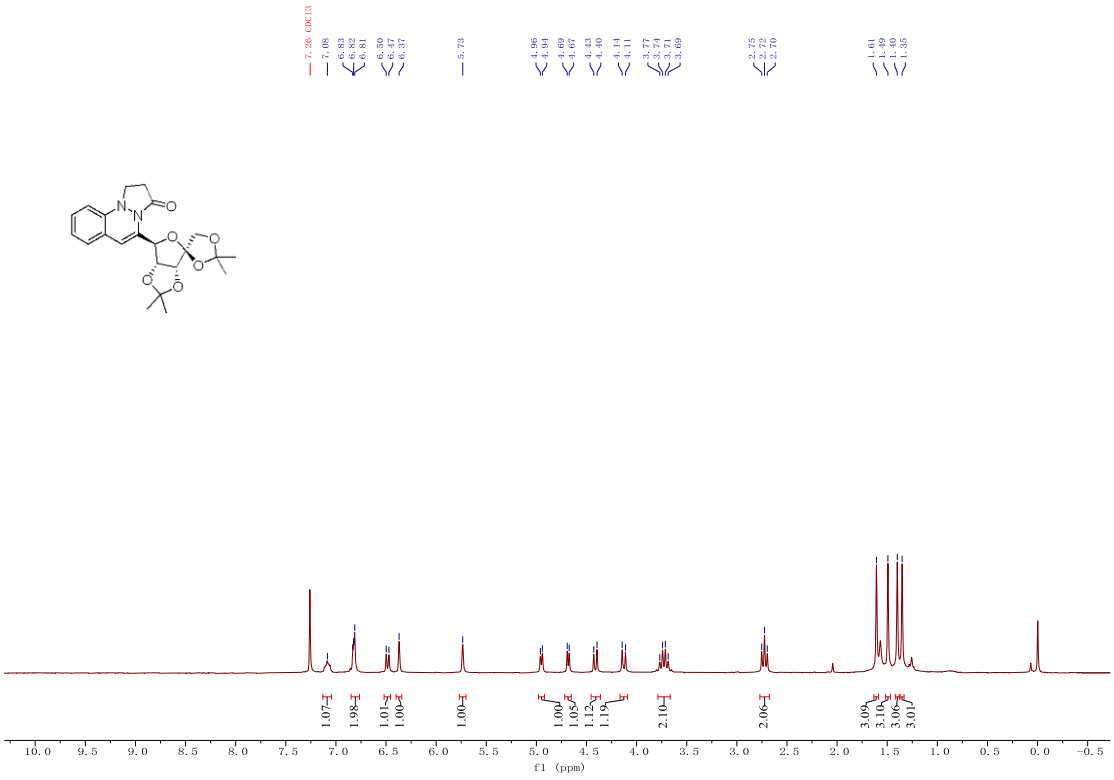
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 41



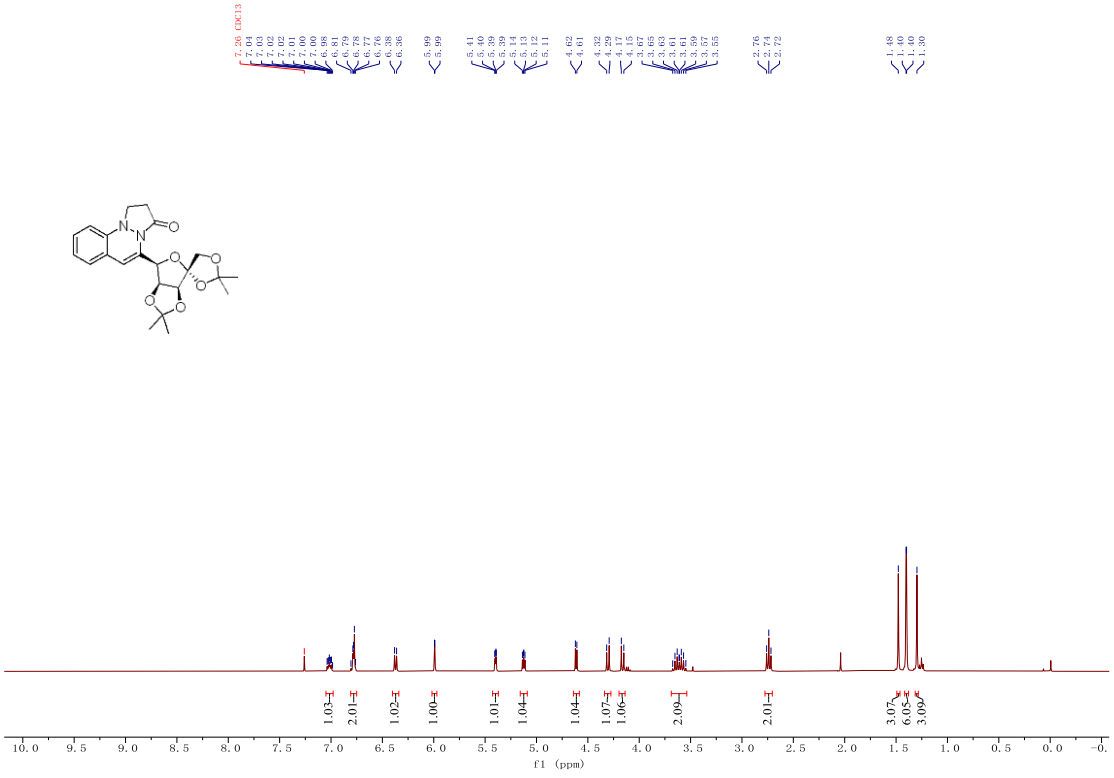
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 42[3]



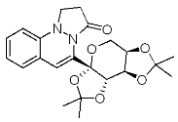
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 43[3]

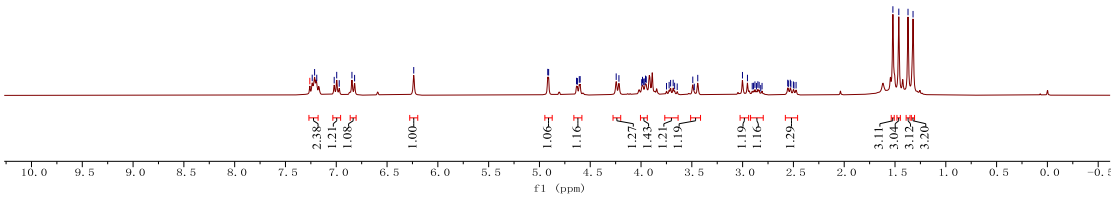


^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 44[3]

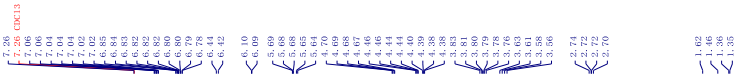


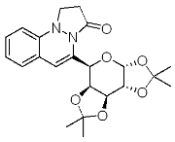
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 45[3]

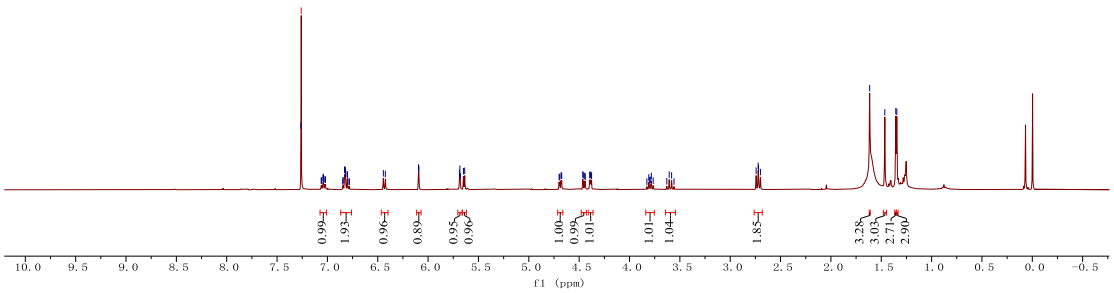




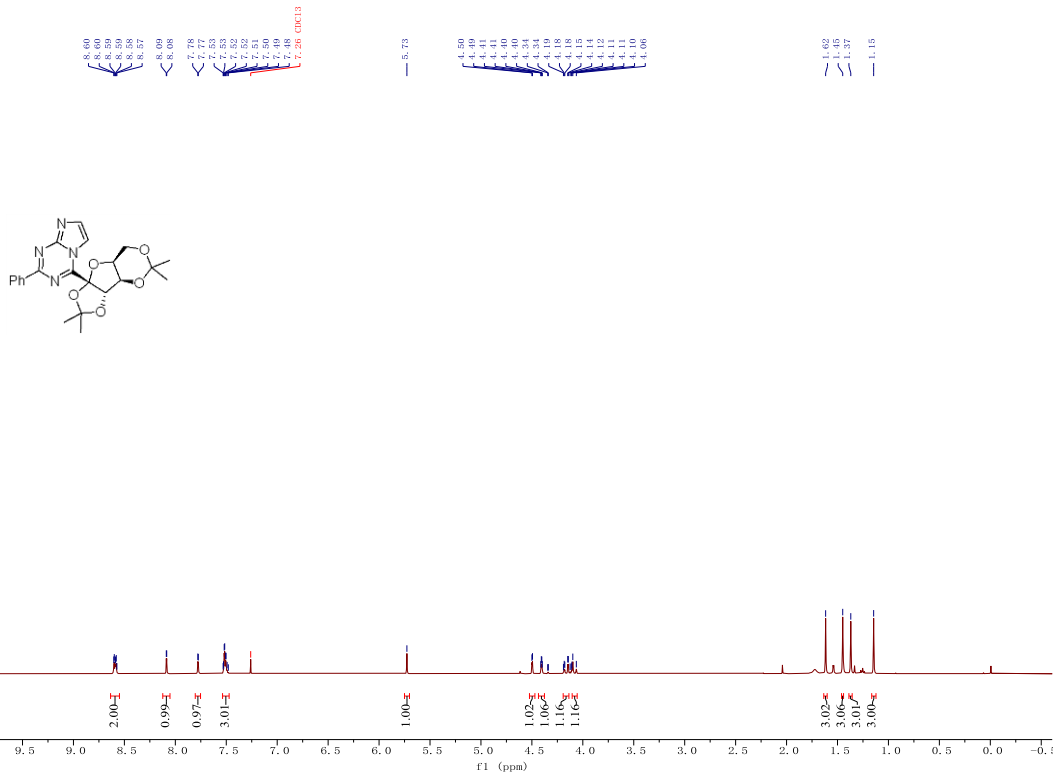
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 46[3]



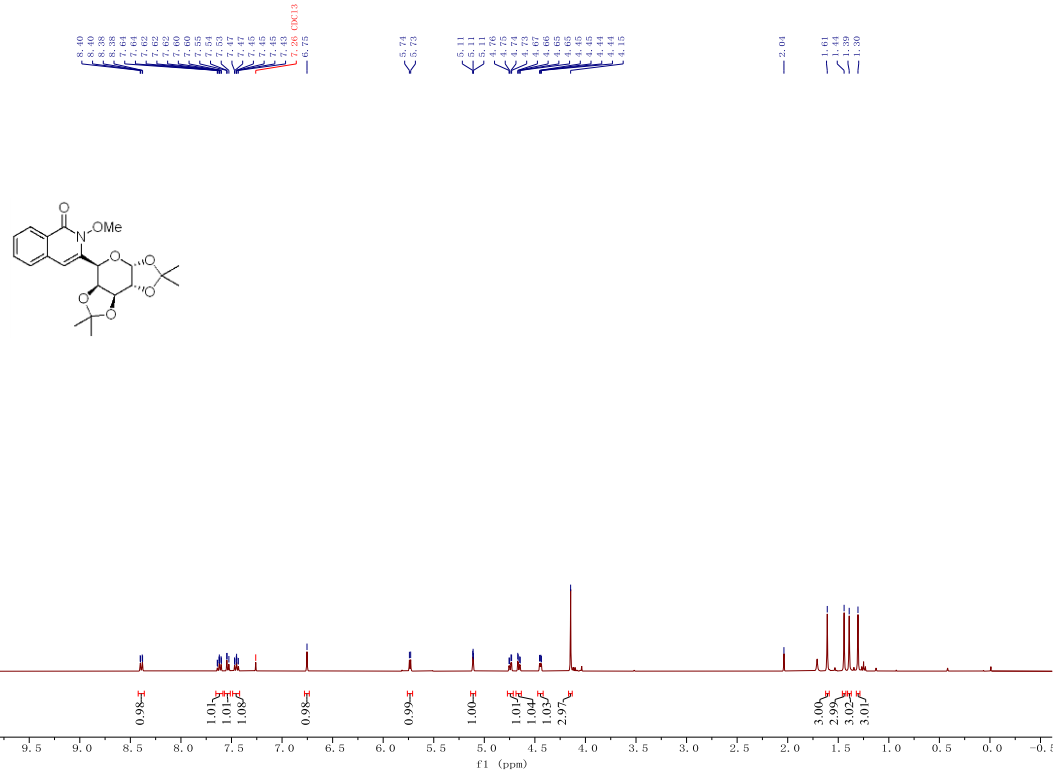




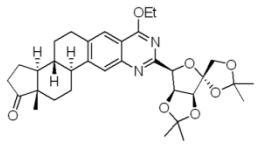
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 48[1]

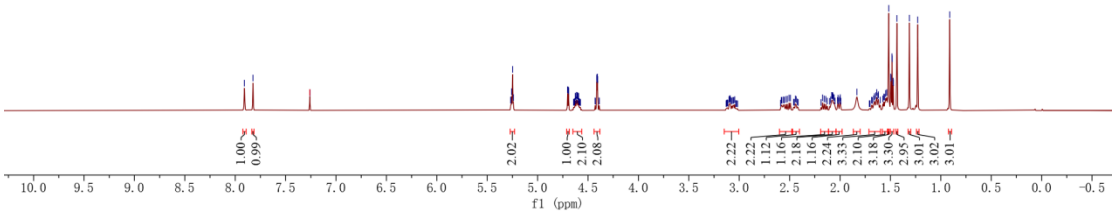


^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 50[3]



^{1}H NMR (600 MHz, $CDCl_3$) Spectra of compound 53[1]


OEt
N
N
H
H
H
O
O
O
O
O
O


1.00
0.99
2.02
1.00
2.10
2.08
2.22
2.22
1.12
1.16
2.18
1.16
2.24
3.33
2.10
3.18
3.30
2.95
3.01
3.02
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)