Supporting Information

Visible-light-induced synthesis of heteroaryl C-glycosides via decarboxylative C-H glycosylation

CuiMei Zhang,[a] Dongqin He,[c] Zhaohui Ma,[b] Mi Wang,[a] Yafei Zhu,[a] Yan Liu,[c] Jian Chen,[a] Guanghui Lv*[a,b] and Yong Wu*[a]

[a] Key Laboratory of Drug-Targeting and Drug Delivery System of Education Ministry, Department of Medicinal Chemistry, West China School of Pharmacy, Sichuan University, No. 17, 3rd Section, South Renmin Road, Chengdu 610041, P. R. China.

[b] Department of Pharmacy, Hubei Provincial Clinical Research Center for Umbilical Cord Blood Hematopoietic Stem Cells, Taihe Hospital, Hubei University of Medicine, Shiyan 442000 Hubei, China.

[c] Department of Pediatrics, Hubei Provincial Clinical Research Center for Umbilical Cord Blood Hematopoietic Stem Cells, Taihe Hospital, Hubei University of Medicine, Shiyan 442000 Hubei, China.

*E-mails: wyong@scu.edu.cn；lvguanghui0725@163.com.

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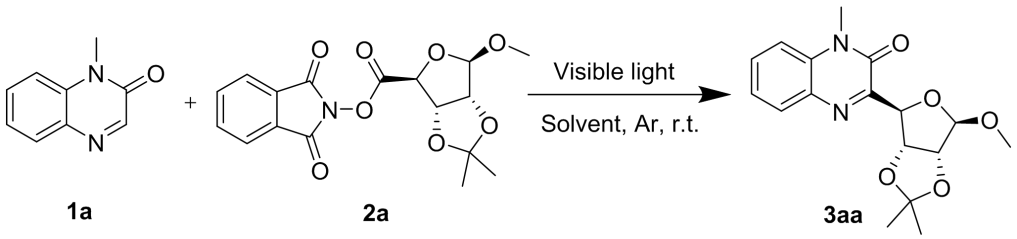
1. General information

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. All of the reactions were carried out in pressure tubes. Except for the specially mentioned dry solvent, all the solvents were treated according to general methods. All the reactions were monitored by thin-layer chromatography (TLC) and were visualized using UV light. Product purification was done using silica gel column chromatography. Thin-layer chromatography (TLC) characterization was performed with precoated silica gel GF254 (0.2 mm), while column chromatography characterization was performed with silica gel (100-200 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded with tetramethylsilane (TMS, δ = 0.00 ppm) as the internal standard. ^{1}H NMR spectra were recorded at 400 or 600 MHz (Varian) and ^{13}C NMR spectra were recorded at 100 or 150 MHz (Varian). Shifts are reported in ppm downfield from $CDCl_3$ (δ =7.26 ppm) or DMSO-d_6 (δ = 2.50 ppm; H_2O signal was found at δ = 3.34 ppm) for ^{1}H NMR and chemical shifts for ^{13}C NMR spectra are reported in ppm relative to the central $CDCl_3$ (δ = 77.0ppm) or DMSO-d_6 (δ = 39.6 ppm). Coupling constants were given in Hz. The following notations were used: br-broad, s-singlet, d-doublet, t-triplet, q-quartet, m-multiplet, dd-doublet of doublet, dt-doublet of triplet, td-triplet of doublet. HRMS spectra were recorded a MicrOTOF-QIII(Bruker.Daltonics). Melting points were measured with YRT-3 melting point apparatus (Shantou Keyi Instrument &Equipment Co., Ltd., Shantou, China). Quinoxalin-2(1*H*)-ones and glycosyl NHP esters were synthesized according to the literature.

2. Condition Optimization

Table 1. Optimization of reaction conditions for **3aa**.[a]



1a **2a** **3aa**

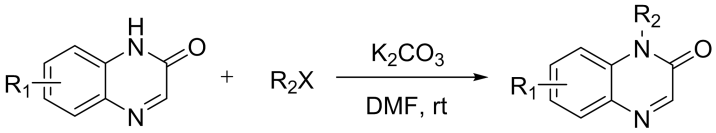
Entry	Light source	Solvent	Time(h)	Yield(%)[b]
1	390-395nm	DMSO	24	65
2	420-425nm	DMSO	24	77
3	425-430nm	DMSO	24	79
4	450-455nm	DMSO	24	91
5	520-525nm	DMSO	24	82
6	427nm Kessil lamps	DMSO	24	75
7	456nm Kessil lamps	DMSO	24	84

8	Dark conditions	DMSO	24	N.R.
9	450-455nm	DCE	24	47
10	450-455nm	DMA	24	64
11	450-455nm	DMF	24	71
12	450-455nm	MeCN	24	41
13	450-455nm	Dioxane	24	75
14	450-455nm	THF	24	25
15	450-455nm	Tol	24	36
16[c]	450-455nm	DMSO	24	77
17	450-455nm	DMSO	36	91
18	450-455nm	DMSO	12	71
19[d]	450-455nm	DMSO	24	91

[a] Reaction condition: **1a** (0.1 mmol), **2a** (0.12 mmol), solvent (1.0ml), at rt for 24 h under Ar. [b] Isolated yield. [c] Open to air. [d] **2a** (0.15 mmol). N.R.= No Reaction

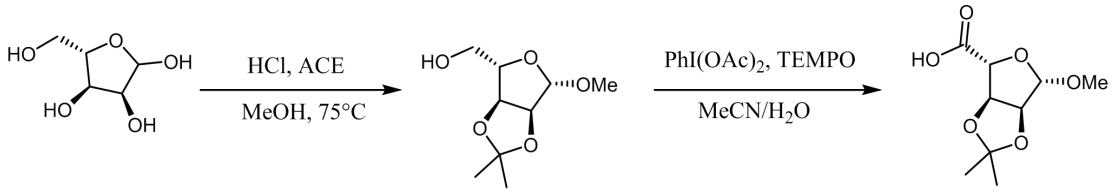
3. Experimental Information

3.1 Synthesis of Quinoxalin-2(1*H*)-ones (1a as an example)



Following a literature procedures [1], to a 100 mL round bottom flask with a stir bar was added *N*-free quinoxalin-2(1*H*)-one derivatives (6.8 mmol), DMF (15 mL) and K_2CO_3 (8.2 mmol), followed by dropwise addition of alkyl halide (10.9 mmol). The reaction mixture was stirred for 1-12 h at room temperature. Then reaction mixture was partitioned in water and EtOAc, and extracted with EtOAc thrice. The combined EtOAc extracts were dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography (PET ether/ EtOAc) to afford the desired *N*-alkylated quinoxalin-2(1*H*)-ones.

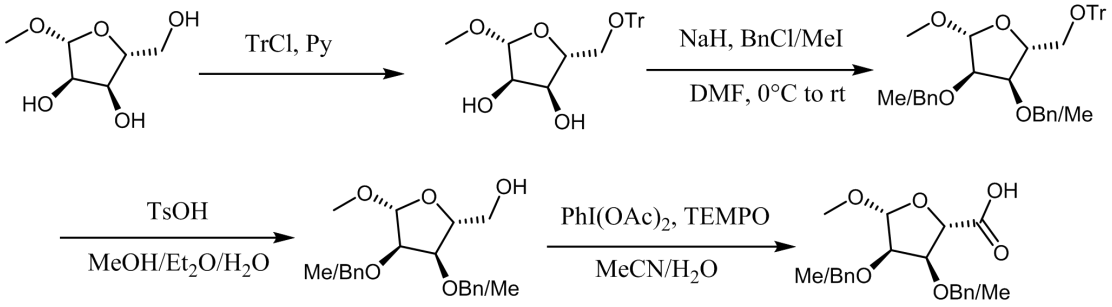
3.2 Examples of general procedures for the synthesis of carboxylic acid



Scheme S1. Procedure for the synthesis of ribose-derived carboxylic acid.

Step 1[2]**:** To a 250 mL round bottom flask was added D-ribose (10 g, 66 mmol, 1.0 equiv.), methanol (40 mL), and acetone (40 mL). Next, concentrated HCl (1.0 mL) was added at room temperature, the flask was heated to 75 °C for 4 h. The solution was cooled to room temperature and filtered to remove the solid then sat. Na_2CO_3 was added to adjust pH above 7. The solution was extracted by ethyl acetate (50 mL × 2), washed by brine (50 mL × 2) , dried by Na_2SO_4, combined the organic phase and concentrated with reduced pressure. The desired crude product was obtained as a faint yellow oil (10 g, 80% yield).

Step 2[3]**:** The acid was prepared according to the reported paper. TEMPO (0.63 g, 4.0 mmol, 0.20 equiv.) and $PhI(OAc)_2$ (19 g, 60 mmol, 3.0 equiv.) were added to a solution of alcohol obtained from above step (4.1 g, 20 mmol, 1.0 equiv.) in $MeCN/H_2O$ (50 mL/50 mL, 0.20 M) at room temperature. The reaction mixture was stirred for 9 h at room temperature, and then saturated aqueous $Na_2S_2O_3$ (5.0 mL) was added. After being stirred for 20 min at room temperature, the resultant mixture was extracted with CH_2Cl_2 (30 mL × 2). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluant to afford carboxylic acid (3.8 g, 89% yield).



Scheme S2. Procedure for the synthesis of Bn/Me-protected ribose-derived carboxylic acid.

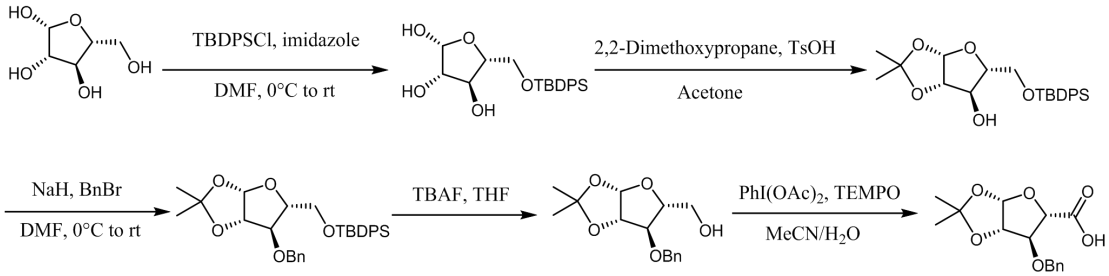
Step 1[4]**:** To a solution of methyl beta D-ribofuranoside (5.0 g, 30 mmol, 1.0 equiv) in pyridine (60 mL, 0.50 M) was added trityl chloride (9.2 g, 33 mmol, 1.1 equiv) and the reaction mixture was stirred at room temperature overnight. The solvent was removed in vacuo and the residue was coevaporated with toluene, dissolve in EtOAc (90 mL) and washed with 1.0 M aqueous $CuSO_4$ solution (50 mL × 3), brine (50 mL × 2), dried over Na_2SO_4, filtered, and concentrated to afford desired product. Purification by flash column chromatography (cyclohexane/EtOAc) yielded product as a white foam (12g, 86% yield).

Step 2[5]**:** The obtained compound (5.0 g, 12 mmol, 1.0 equiv) from above step was dissolved in DMF (60 mL, 0.20 M) and cooled to 0 °C. Sodium hydride (60% in mineral oil, 1.9 g, 48 mmol, 4.0 equiv) was added portion-wise. Then, BnCl/MeI (4.3 mL/2.3 mL, 36mmol, 3.0 equiv) was added dropwise. The mixture was stirred overnight and allowed to warm to room temperature. The reaction was quenched with MeOH and thiourea, and stirred for another 2 h at room temperature. The solvents were evaporated in vacuo and the residue was dissolved in EtOAc (50 mL) and then washed with water (50 mL × 2). The aqueous phase was extracted with EtOAc (30 mL), the combined organic phases were washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to obtain crude product Purification by flash column chromatography (cyclohexane/CH_2Cl_2/EtOAc) yielded product as a white foam (5.6 g, 80% yield).

Step 3[3]**:** The obtained compound (take the Bn-protected as an example, 5.0 g, 8.5 mmol, 1.0 equiv) from above step was dissolved in $MeOH/Et_2O/H_2O$ (42 mL/4.2 mL/0.42 mL, 0.20 M) followed by addition of TsOH (0.73 g, 4.3 mmol, 0.50 equiv). After being stirred for 20 min at

room temperature, the resultant mixture was extracted with EtOAc (30 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluent to get the alcohol (2.3 g, 80% yield).

Step 4[3]**:** The acid was prepared according to the reported paper. TEMPO (0.18 g， 1.2 mmol, 0.20 equiv.) and $PhI(OAc)_2$ (5.6 g, 17 mmol, 3.0 equiv.) were added to a solution of alcohol obtained from above step (take the Bn-protected as an example, 2.0 g， 5.8 mmol， 1.0 equiv.) in $MeCN/H_2O$ (15 mL/15 mL, 0.20 M) at room temperature. The reaction mixture was stirred for 9 h at room temperature, and then saturated aqueous $Na_2S_2O_3$ (5.0 mL) was added. After being stirred for 20 min at room temperature, the resultant mixture was extracted with CH_2Cl_2 (30 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluant to afford carboxylic acid (1.6 g, 78% yield).



Scheme S3. Procedure for the synthesis of arabinose-derived carboxylic acid.

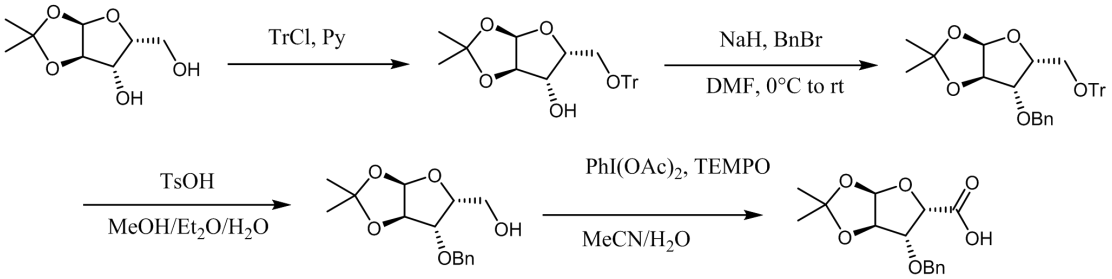
Step 1[6]**:** To a solution of beta D-arabinose (8.0 g, 53 mmol, 1.0 equiv) in DMF(0.27 L, 0.20 M) was added imidazole (5.4 g, 80 mmol, 1.5 equiv) at 50 °C. Then TBDPSCl (21 mL,80 mmol, 1.5 equiv) was added dropwise. The mixture was stirred at 50 °C overnight . The solvents were evaporated in vacuo and the residue was dissolved in EtOAc (90 mL), and then washed with water (50 mL × 2). The aqueous phase was extracted with EtOAc (30 mL), the combined organic phases were washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to obtain crude product Purification by flash column chromatography (cyclohexane/ EtOAc) yielded product as a colorless oil (17 g, 83% yield).

Step 2[7]**:** The obtained compound (11 g, 28 mmol, 1.0 equiv) from above step was dissolved in acetone (30 mL) and 2, 2-dimethoxypropane (10 mL) and *p*-toluenesulfonic acid (0.20 g) was added. The reaction was neutralized by triethylamine and concentrated after stired 30 min at room temperature. The solvents were evaporated in vacuo, purification by flash column chromatography (cyclohexane / EtOAc). yielded product as a colorless oil (10 g, 84% yield).

Step 3[5]**:** The obtained compound (10 g, 23 mmol, 1.0 equiv) from above step was dissolved in DMF (0.12 L, 0.20 M) and cooled to 0 °C. Sodium hydride (60% in mineral oil, 1.8 g, 46 mmol, 2.0 equiv) was added portion wise. Then, BnCl (4.1 mL, 35 mmol, 1.5 equiv) was added dropwise. The mixture was stirred overnight and allowed to warm to room temperature. The reaction was quenched with MeOH and thiourea, and stirred for another 2 h at room temperature. The solvents were evaporated in vacuo and the residue was dissolved in EtOAc (90 mL), and then washed with water (50 mL × 2). The aqueous phase was extracted with EtOAc (30 mL), the combined organic phases were washed with water, dried over Na_2SO_4, filtered, and concentrated in vacuo to obtain crude product as an oil. Purification by flash column chromatography (cyclohexane / EtOAc). yielded product as a white solid (10 g, 87% yield).

Step 4[6]**:** The obtained compound (10 g, 19 mmol, 1.0 equiv) from above step was dissolved in anhydrous THF (40 mL, 0.50 M), was reacted with TBAF (1.0 M in THF, 23 mL,1.2 equiv). The solution was stirred at room temperature for 2 h. The solvents were evaporated in vacuo, purification by flash column chromatography (cyclohexane / EtOAc). yielded product as a white solid (4.2 g, 79% yield).

Step 5[3]**:** The acid was prepared according to the reported paper. TEMPO (0.17 g, 0.20 equiv.) and $PhI(OAc)_2$ (5.2 g, 3.0 equiv.) were added to a solution of alcohol (1.5 g, 5.4 mmol, 1.0 equiv.) obtained from above step (1.0 equiv.) in $MeCN/H_2O$ (15 mL/15 mL, 0.20 M) at room temperature. The reaction mixture was stirred for 9 h at room temperature, and then saturated aqueous $Na_2S_2O_3$ (5.0 mL) was added. After being stirred for 20 min at room temperature, the resultant mixture was extracted with CH_2Cl_2 (30 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluant to afford carboxylic acid 78% yield (white solid, 1.2 g).



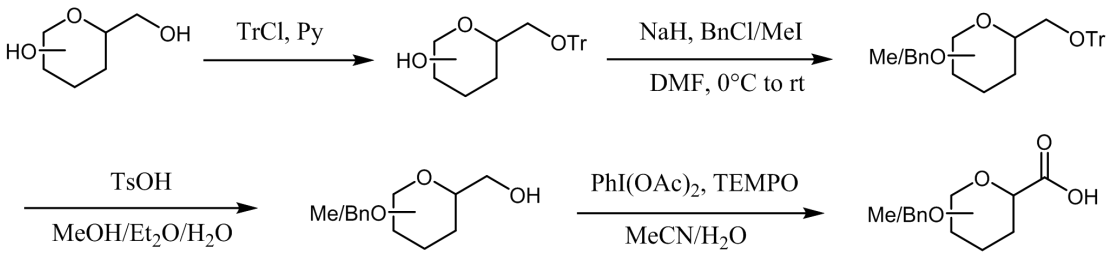
Scheme S4. Procedure for the synthesis of xylose-derived carboxylic acid.

Step 1[4]**:** To a solution of 1,2-O-Isopropylidene-alpha-D-xylofuranose (5.0 g, 26 mmol, 1.0 equiv) in pyridine (52 mL,0.50 M) was added trityl chloride (8.0 g, 29 mmol, 1.1 equiv) and the reaction mixture was stirred at room temperature overnight. The solvent was removed in vacuo and the residue was coevaporated with toluene, dissolve in EtOAc (90 mL) and washed with 1 M aqueous $CuSO_4$ solution (50 mL × 3), brine (50 mL × 2), dried over Na_2SO_4, filtered, and concentrated to afford desired product. Purification by flash column chromatography (cyclohexane/EtOAc) yielded product as a white foam (8.7 g, 83% yield).

Step 2[5]**:** The obtained compound (6.0 g, 14 mmol, 1.0 equiv) from above step was dissolved in DMF (70 mL, 0.2 M) and cooled to 0 °C. Sodium hydride (60% in mineral oil, 1.1 g, 28 mmol, 2.0 equiv) was added portion-wise. Then, BnCl (2.5 mL, 21 mmol, 1.5 equiv) was added dropwise. The mixture was stirred overnight and allowed to warm to room temperature. The reaction was quenched with MeOH and thiourea, and stirred for another 2 h at room temperature. The solvents were evaporated in vacuo and the residue was dissolved in EtOAc (90 mL), and then washed with water (50 mL × 2). The aqueous phase was extracted with EtOAc (30 mL), the combined organic phases were washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to obtain crude product Purification by flash column chromatography (cyclohexane/CH_2Cl_2/EtOAc) yielded product as a white foam (5.9 g, 81% yield).

Step 3[3]**:** The obtained compound (5.4 g, 10 mmol, 1.0 equiv) from above step was dissolved in $MeOH/Et_2O/H_2O$ (50 mL/5.0 mL/0.50 mL, 0.20 M) followed by addition of TsOH (0.86 g, 5.0 mmol, 0.50 equiv). After being stirred for 20 min at room temperature, the resultant mixture was extracted with EtOAc (30 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluent to get the alcohol (2.3g. 85%).

Step 4[3]**:** The acid was prepared according to the reported paper. TEMPO (0.17 g, 1.1 mmol, 0.20 equiv.) and $PhI(OAc)_2$ (5.2 g, 16 mmol, 3.0 equiv.) were added to a solution of alcohol (1.5 g, 5.4 mmol, 1.0 equiv.)obtained from above step in $MeCN/H_2O$ (15 mL/15 mL, 0.20 M) at room temperature. The reaction mixture was stirred for 9 h at room temperature, and then saturated aqueous $Na_2S_2O_3$ (5.0 mL) was added. After being stirred for 20 min at room temperature, the resultant mixture was extracted with CH_2Cl_2 (30 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluant to afford carboxylic acid 78% yield (1.2 g).



Scheme S5. Procedure for the synthesis of Bn/Me-protected hexose-derived carboxylic acid.

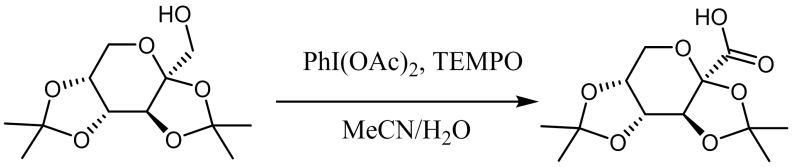
Step 1[4]**:**To a solution of methyl-α-D-glucopyranoside (10 g, 51 mmol, 1.0 equiv) in pyridine (0.10 L, 0.50 M) was added trityl chloride (16 g, 56 mmol, 1.1 equiv) and the reaction mixture was stirred at room temperature overnight. The solvent was removed in vacuo and the residue was coevaporated with toluene, dissolve in EtOAc (90 mL) and washed with 1 M aqueous $CuSO_4$ solution (50 mL × 3), brine (50 mL × 2), dried over Na_2SO_4, filtered, and concentrated to afford desired product. Purification by flash column chromatography (cyclohexane/EtOAc) yielded product as a white foam (17 g, 80% yield).

Step.2[2,5]**:** The obtained compound (8.0 g, 18 mmol, 1.0 equiv.) from above step was dissolved in DMF (90 mL, 0.20 M) and cooled to 0 °C. Sodium hydride (60% in mineral oil, 4.3 g, 0.11 mol 6.0 equiv) was added portion-wise. Then, BnCl (9.6 mL, 81 mmol, 4.5 equiv) /MeI was added dropwise. The mixture was stirred overnight and allowed to warm to room temperature. The reaction was quenched with MeOH and thiourea, and stirred for another 2 h at room temperature. The solvents were evaporated in vacuo and the residue was dissolved in EtOAc (90 mL), and then washed with water (50 mL × 2). The aqueous phase was extracted with EtOAc (30mL), the combined organic phases were washed with brine (50mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to obtain crude product Purification by flash column chromatography (cyclohexane/CH_2Cl_2/EtOAc) yielded product as a white foam (9.9 g, 78% yield).

Step.3[3]**:** The obtained compound (8.0 g, 11 mmol, 1.0 equiv.) from above step was dissolved in $MeOH/Et_2O/H_2O$ (50 mL/5.0 mL/0.50 mL, 0.20 M) followed by addition of TsOH (0.95 g, 5.5 mmol, 0.50 equiv). After being stirred for 20 min at room temperature, the resultant mixture was extracted with EtOAc (30 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluent to get the alcohol (4.2 g, 82% yield).

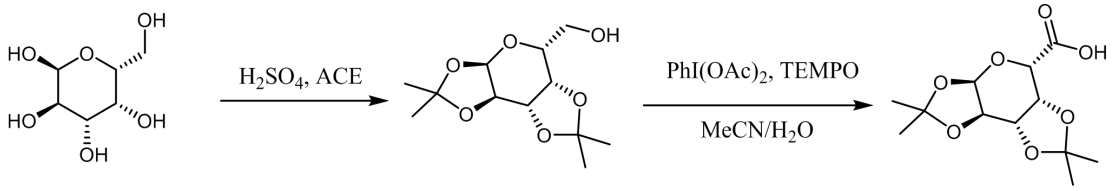
Step.4[3]**:** The acid was prepared according to the reported paper. TEMPO (0.20 g, 1.3 mmol, 0.20 equiv.) and $PhI(OAc)_2$ (6.3 g, 20 mmol, 3.0 equiv.) were added to a solution of alcohol (3.0g 6.5 mmol, 1.0 equiv.) obtained from above step in $MeCN/H_2O$ (16 mL/16 mL, 0.20 M) at room temperature. The reaction mixture was stirred for 9 h at room temperature, and then saturated aqueous $Na_2S_2O_3$ (5.0 mL) was added. After being stirred for 20 min at room temperature, the

resultant mixture was extracted with CH_2Cl_2 (30 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluant to afford carboxylic acid (2.4 g, 80% yield).



Scheme S6. Procedure for the synthesis of fructose-derived carboxylic acid.

(3aR,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-carboxylic acid[3]**:** To a 50 mL flask, the diacetonefructose (3.0 g, 12 mmol, 1.0 equiv) was treated with TEMPO (0.36 g, 2.3 mmol, 0.20 equiv.) and $PhI(OAc)_2$ (11 g, 35 mmol, 3.0 equiv.) in $MeCN/H_2O$ (30 mL/30 mL, 0.20 M) at room temperature for 9 h, and then saturated aqueous $Na_2S_2O_3$ (5.0 mL) was added. After being stirred for 20 min at room temperature, the resultant mixture was extracted with CH_2Cl_2 (30 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluant to afford carboxylic acid(2.6 g, 83%).

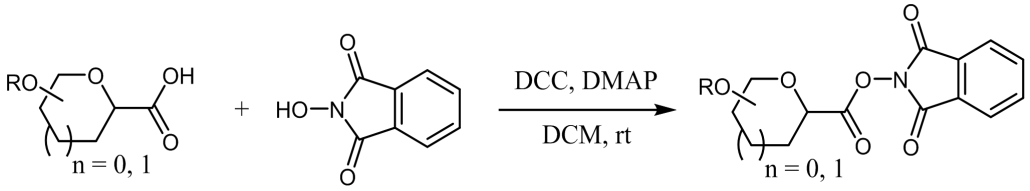


Scheme S7. Procedure for the synthesis of galactose-derived carboxylic acid.

((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methanol[8]**:**To a round bottom flask was added D-galactose (7.0 g, 39 mmol, 1.0 equiv.), acetone (0.25 L). Next, concentrated H_2SO_4 (7.7 mL) was added at 0 °C. The reaction mixtures were stirred at room temperature for 5 h and then neutralized by the addition of sat. Na_2CO_3 until pH = 7. The precipitate was removed by filtration and the filtrates were combined and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluent to get the product as a colorless oil.(8.5 g, 84%).

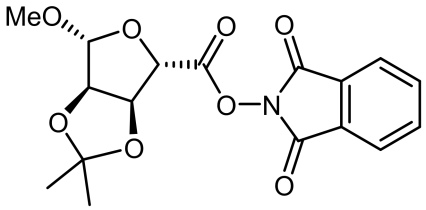
(3aR,5S,5aR,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-carboxylic acid[3]**:** The acid was prepared according to the reported paper. TEMPO (0.84 g, 5.4 mmol, 0.20 equiv.) and $PhI(OAc)_2$ (26 g, 81 mmol, 3.0 equiv.) were added to a solution of alcohol (7.0 g, 27 mmol, 1.0 equiv.) obtained from above step in $MeCN/H_2O$ (67 mL/67 mL, 0.20 M) at room temperature. The reaction mixture was stirred for 9 h at room temperature, and then saturated aqueous $Na_2S_2O_3$ (5.0 mL) was added. After being stirred for 20 min at room temperature, the resultant mixture was extracted with CH_2Cl_2 (30 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel using hexane/EtOAc as eluant to afford carboxylic acid (5.1 g, 87% yield).

3.3 Synthetic procedure of N-hydroxyphthalimide esters

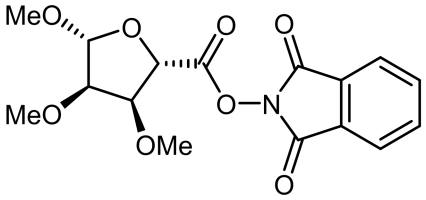


Scheme S8. Procedure for the synthesis of N-hydroxyphthalimide esters.

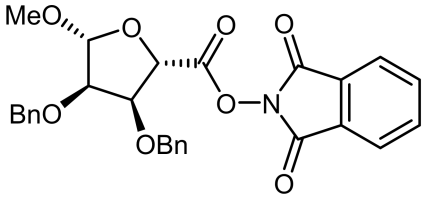
A round-bottom flask or culture tube was charged with carboxylic acid derived from sugar (1.0 equiv), N-hydroxyphthalimide (1.1 equiv) and 4-dimethylaminopyridine (0.050 equiv). Dichloromethane was added (0.10 – 0.20 M), and the mixture was stirred vigorously. Dicyclohexylcarbodiimide (DCC, 1.1 equiv) was added, and then the mixture was allowed to stir until the acid was consumed (determined by TLC). Typical reaction times were between 0.5 h to 12 h. The mixture was filtered through a thin pad of Celite and rinsed with additional CH_2Cl_2. The solvent was removed under reduced pressure, and purification of the crude mixture by column chromatography (DCM/hexane/ethyl acetate as eluent) afforded the desired N-hydroxyphthalimide esters.



1,3-dioxoisoindolin-2-yl(3aS,4S,6R,6aR)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole-4-carboxylate (2a): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 5.36 (d, *J* = 5.8 Hz, 1H), 5.14 (s, 1H), 5.00 (s, 1H), 4.66 (d, *J* = 5.8 Hz, 1H), 3.50 (s, 3H), 1.52 (s, 3H), 1.35 (s, 3H). The compound was identified by spectral comparison with literature data.[5]

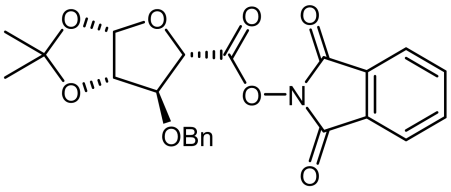


1,3-dioxoisoindolin-2-yl(2S,3S,4R,5R)-3,4,5-trimethoxytetrahydrofuran-2-carboxylate (2b): ^{1}H-NMR (600 MHz, Chloroform-*d*) δ 7.93 – 7.85 (m, 2H), 7.85 – 7.76 (m, 2H), 5.05 (s, 1H), 4.85 (d, *J* = 4.5 Hz, 1H), 4.47 (s, 1H), 3.83 (s, 1H), 3.57 (s, 3H), 3.53 (s, 3H), 3.46 (s, 3H). The compound was identified by spectral comparison with literature data. [5]

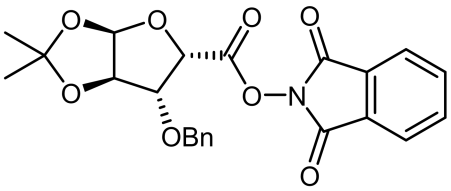


1,3-dioxoisoindolin-2-yl(2S,3S,4R,5R)-3,4-bis(benzyloxy)-5-methoxytetrahydrofuran-2-carboxylate (2c): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.42 – 7.28 (m, 10H), 5.00 (d, *J* = 6.6 Hz, 2H), 4.79 (d, *J* = 11.7 Hz, 1H), 4.71 –

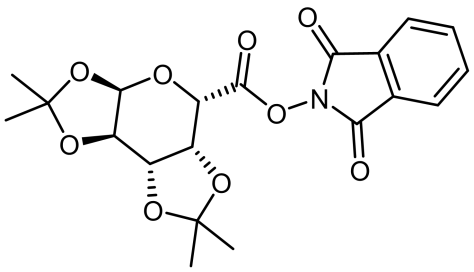
4.60 (m, 4H), 3.87 (d, *J* = 4.5 Hz, 1H), 3.42 (s, 3H). The compound was identified by spectral comparison with literature data. [5]



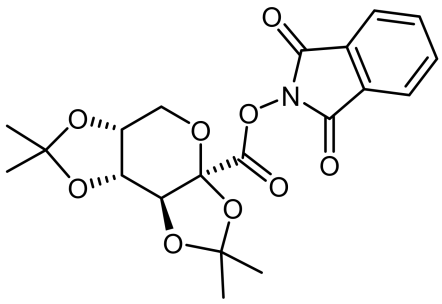
1,3-dioxoisoindolin-2-yl(3aS,5S,6S,6aS)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole-5-carboxylate (2d): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.39 – 7.28 (m, 5H), 6.07 (d, *J* = 3.4 Hz, 1H), 5.07 (d, *J* = 0.8 Hz, 1H), 4.78 – 4.72 (m, 2H), 4.71 – 4.65 (m, 2H), 1.50 (s, 3H), 1.33 (s, 3H). **^{13}C-NMR (100 MHz, Chloroform-*d*)** δ 166.3, 161.4, 136.5, 134.9, 128.8, 128.7, 128.3, 128.0, 124.1, 113.8, 107.0, 84.4, 82.9, 80.7, 72.5, 25.9, 25.7. HRMS (ESI) m/z $[M + Na]^+$ calculated for 462.1159, found 462.1161.



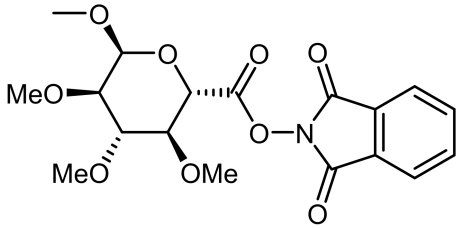
1,3-dioxoisoindolin-2-yl(3aR,5S,6R,6aR)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole-5-carboxylate (2e): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.46 – 7.27 (m, 5H), 6.11 (d, *J* = 3.4 Hz, 1H), 5.20 (d, *J* = 3.5 Hz, 1H), 4.92 (d, *J* = 11.9 Hz, 1H), 4.69 (d, *J* = 11.9 Hz, 1H), 4.56 (d, *J* = 3.4 Hz, 1H), 4.46 (d, *J* = 3.5 Hz, 1H), 1.51 (s, 3H), 1.32 (s, 3H). The compound was identified by spectral comparison with literature data. [5]



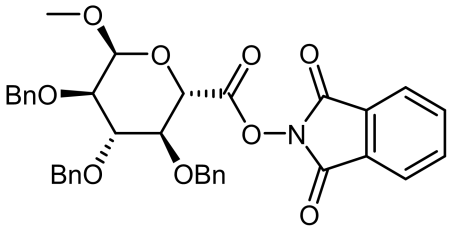
1,3-dioxoisoindolin-2-yl(3aR,5S,5aR,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-carboxylate (2f): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H), 5.70 (d, *J* = 5.0 Hz, 1H), 4.84 (d, *J* = 2.2 Hz, 1H), 4.74 (qd, *J* = 7.5, 2.4 Hz, 2H), 4.46 (dd, *J* = 5.0, 2.6 Hz, 1H), 1.61 (s, 3H), 1.54 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H). The compound was identified by spectral comparison with literature data. [5]



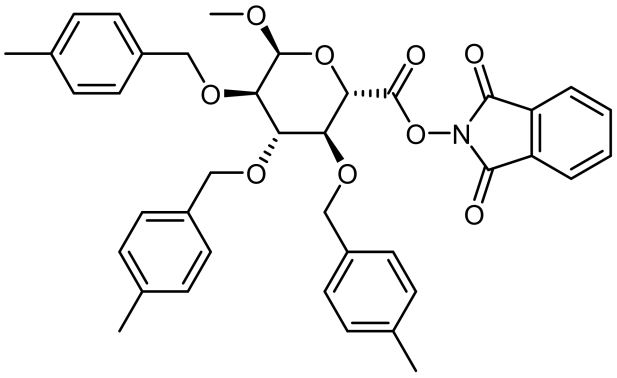
1,3-dioxoisoindolin-2-yl(3aR,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-carboxylate (2g): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.88 (d, *J* = 2.5 Hz, 1H), 4.69 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.31 (d, *J* = 7.9 Hz, 1H), 3.96 (s, 2H), 1.62 (s, 3H), 1.57 (s, 3H), 1.51 (s, 3H), 1.37 (s, 3H). The compound was identified by spectral comparison with literature data. [5]



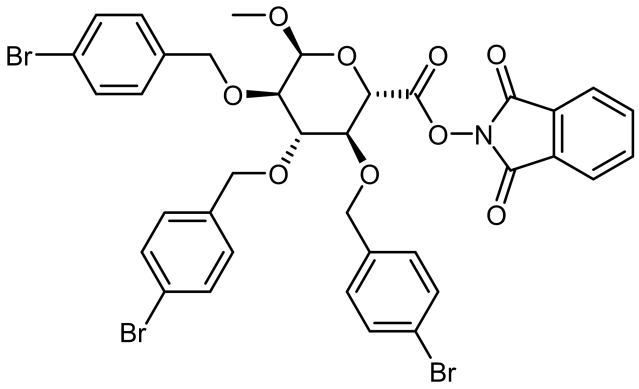
1,3-dioxoisoindolin-2-yl(2S,3S,4S,5R,6S)-3,4,5,6-tetramethoxytetrahydro-2H-pyran-2-carboxylate (2h): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.81 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.95 (d, *J* = 3.5 Hz, 1H), 4.42 (d, *J* = 9.9 Hz, 1H), 3.65 (d, *J* = 1.7 Hz, 6H), 3.57 (d, *J* = 9.6 Hz, 1H), 3.54 (s, 3H), 3.52 (s, 3H), 3.50 (d, *J* = 2.9 Hz, 1H), 3.30 (dd, *J* = 9.5, 3.5 Hz, 1H). The compound was identified by spectral comparison with literature data. [5]



1,3-dioxoisoindolin-2-yl(2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-carboxylate (2i): ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.43 – 7.26 (m, 15H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.93 (d, *J* = 10.1 Hz, 1H), 4.86 (d, *J* = 11.0 Hz, 2H), 4.82 (d, *J* = 2.4 Hz, 1H), 4.71 (d, *J* = 3.4 Hz, 1H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.58 (d, *J* = 10.0 Hz, 1H), 4.07 (t, *J* = 9.2 Hz, 1H), 3.96 – 3.90 (m, 1H), 3.63 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.49 (s, 3H). The compound was identified by spectral comparison with literature data. [5]

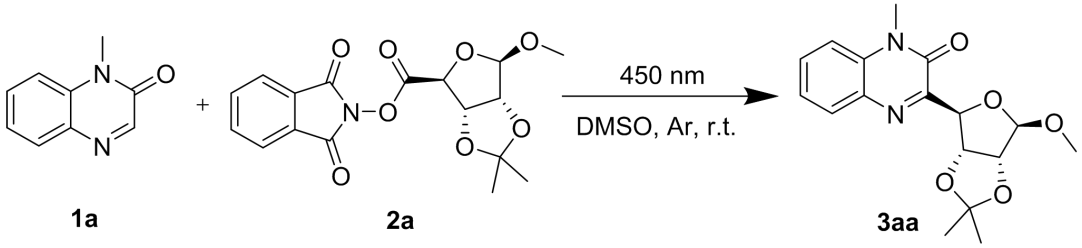


1,3-dioxoisoindolin-2-yl(2S,3S,4S,5R,6S)-6-methoxy-3,4,5-tris((4-methylbenzyl)oxy)tetrahydro-2H-pyran-2-carboxylate(2j): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.26 – 7.07 (m, 12H), 4.91 (d, *J* = 10.6 Hz, 1H), 4.85 – 4.76 (m, 4H), 4.62 – 4.58 (m, 2H), 4.52 (d, *J* = 10.0 Hz, 1H), 4.01 (t, *J* = 9.2 Hz, 1H), 3.86 (t, *J* = 9.4 Hz, 1H), 3.56 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.45 (s, 3H), 2.35 (s, 3H), 2.34 (s, 3H), 2.30 (s, 3H).



1,3-dioxoisoindolin-2-yl(2S,3S,4S,5R,6S)-3,4,5-tris((4-bromobenzyl)oxy)-6-methoxytetrahydro-2*H*-pyran-2-carboxylate(2k):^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.81 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.47 – 7.40 (m, 6H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.14 – 7.12 (m, 4H), 4.85 (d, *J* = 11.1 Hz, 2H), 4.78 (d, *J* = 3.4 Hz, 1H), 4.72 (d, *J* = 11.5 Hz, 1H), 4.69 – 4.65 (m, 2H), 4.60 (d, *J* = 12.2 Hz, 1H), 4.54 (d, *J* = 9.9 Hz, 1H), 3.98 (t, *J* = 9.2 Hz, 1H), 3.86 (dd, *J* = 10.0, 8.8 Hz, 1H), 3.57 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.50 (s, 3H).

3.4 General procedure for the synthesis of desired products 3 and 4 (3aa as an example)

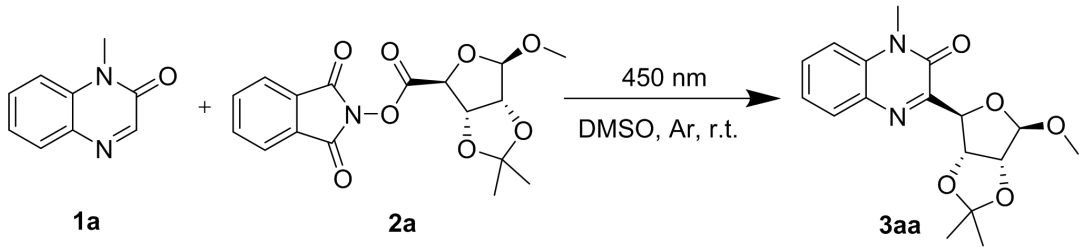


1a **2a** **3aa**

To an oven-dried 10 mL glass tube equipped with a stir bar, was added glycosyl NHP ester (0.12 mmol), *N*-methylquinoxalin-2(1*H*)-one (0.1 mmol). The tube was evacuated and back-filled with Ar (three times), then sealed with rubber stopper and parafilm. Then, anhydrous DMSO (1.0 mL) was added using a syringe. The solution was then stirred at room temperature under the

irradiation of 12 W Blue LEDs for 24 h . After completion of the reaction, 5.0 mL water was added and extracted by ethyl acetate (3 × 5.0 mL). The combined organic layer was washed with brine (5.0 mL) and then dried over anhydrous Na_2SO_4 and evaporated in vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on silica gel eluting with hexane/ethyl acetate or hexane/dichloromethane.

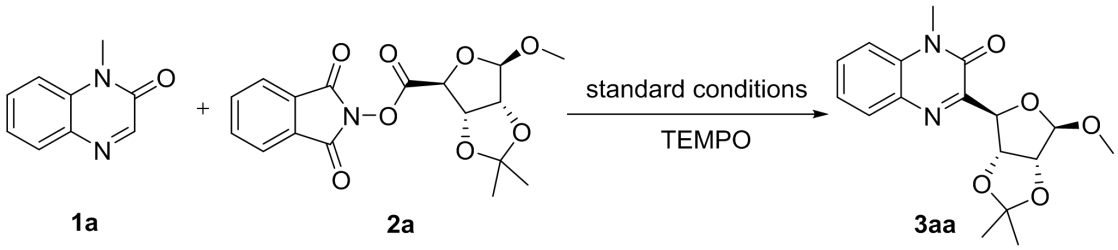
4. Scale-Up Synthesis of 3aa



1a **2a** **3aa**

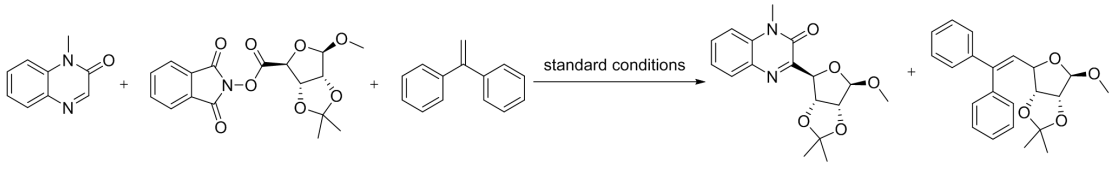
To an oven-dried 50ml schlenk tube equipped with a stir bar, was added glycosyl NHP ester (1.36 g, 3.75 mmol), *N*-methylquinoxalin-2(1*H*)-one (500 mg, 3.12 mmol). The tube was evacuated and back-filled with Ar (three times), then sealed with rubber stopper and parafilm. Then, anhydrous DMSO (20 mL) was added using a syringe. The solution was then stirred at room temperature under the irradiation of 12 W Blue LEDs for 24 h. After completion of the reaction, 50 mL water was added and extracted by ethyl acetate (3 × 10 mL). The combined organic layer was washed with brine (20 mL) and then dried over anhydrous Na_2SO_4 and evaporated in vacuum. The residue was directly purified by a silica gel column chromatography using ethyl acetate/petroleum as the eluent to afford product **3aa** (0.83 g, 86%).

5. Control experiments



1a **2a** **3aa**

To an oven-dried 10 mL glass tube equipped with a stir bar, was added glycosyl NHP ester (0.12 mmol), *N*-methylquinoxalin-2(1*H*)-one (0.10 mmol),TEMPO (0.45 mmol). The tube was evacuated and back-filled with Ar (three times), then sealed with rubber stopper and parafilm. Then, anhydrous DMSO (1.0 mL) was added using a syringe. The solution was then stirred at room temperature under the irradiation of 12 W 450nm Blue LEDs for 24 h using electronic fan to cool the tube. After 24 h, no corresponding product **3aa** was formed by TLC analysis, suggesting that the in-situ formed glycosyl radical might act as a key intermediate during this transformation.



1a **2a** **3aa**, 51% **5**, 26%

To an oven-dried 10 mL glass tube equipped with a stir bar, was added glycosyl NHP ester (0.15 mmol), *N*-methylquinoxalin-2(1*H*)-one (0.10 mmol), 1,1-diphenylethylene (0.30 mmol).

The tube was evacuated and back-filled with Ar (three times), then sealed with rubber stopper and parafilm. Then, anhydrous DMSO (1.0 mL) was added using a syringe. The solution was then stirred at room temperature under the irradiation of 12 W Blue LEDs for 24 h using electronic fan to cool the tube. After completion of the reaction, corresponding product **3aa** was isolated in 51% yield and the heck-type product **5** was isolated in 26% yield, indicating that this photo-induced thioglycosidation protocol may proceed through a radical-based mechanism. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.21 (m, 10H), 6.08 (d, *J* = 10.5 Hz, 1H), 5.00 (s, 1H), 4.75 – 4.70 (m, 3H), 3.38 (s, 3H), 1.41 (s, 3H), 1.30 (s, 3H).

6. Stern-Volmer fluorescence quenching experiments

DMSO was degassed with a stream of argon for 30 min. Substrate **1a** or product **3aa** (5.0 μmol) was dissolved in 1.0 mL DMSO to prepare a 5×10^{-3} M solution. 100 μL of this solution was added to each of a set of 6 volumetric flasks (10 mL). Subsequently, the solution of quencher **2a** in DMSO (1.5 mL, 0.125 M) was added in increasing amounts (0, 100 μL, 200 μL, 300 μL, 400 μL, 500 μL) to the volumetric flasks and the volume of volumetric flasks were adjusted to 10 mL by adding DMSO. All solutions were excited at 350 nm and the emission intensity at 418 nm was observed. All fluorescence measurements were recorded by a F-98 FL Spectrophotometer. Control experiments showed that the excited state substrate **1a** and product **3aa** were both mainly quenched by **2a**.

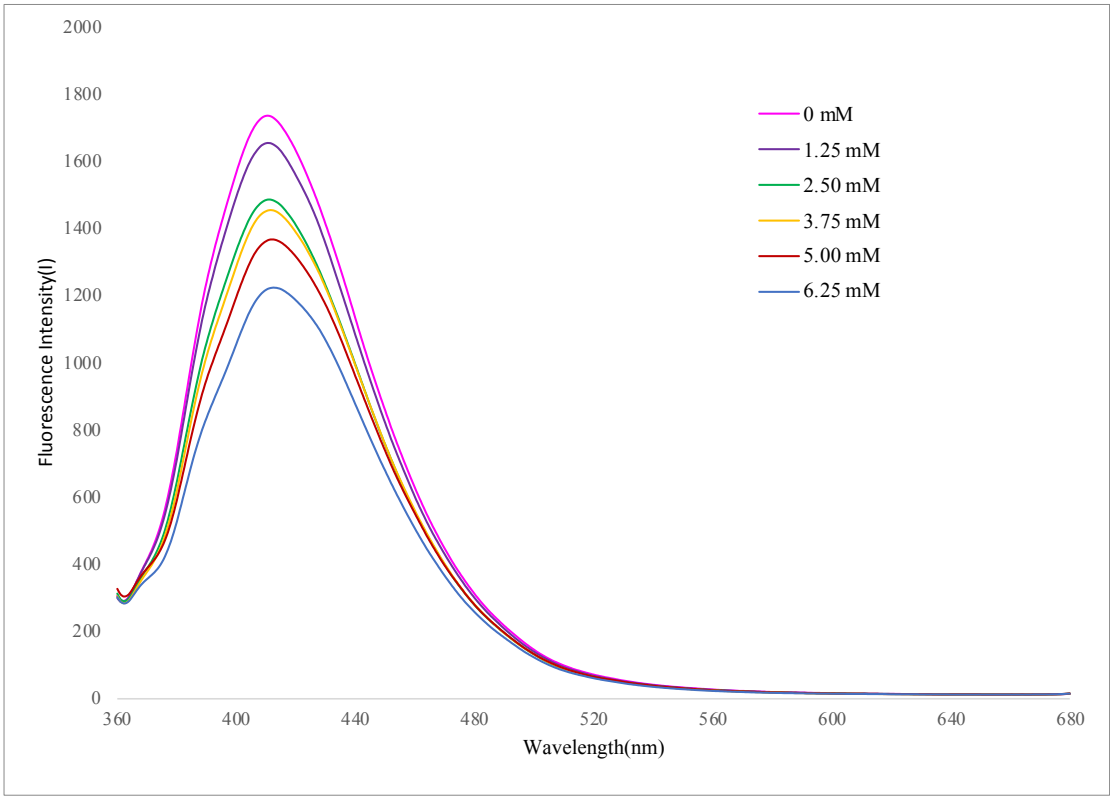


Figure S1 Emission spectra of **1a** with varying concentrations **2a**

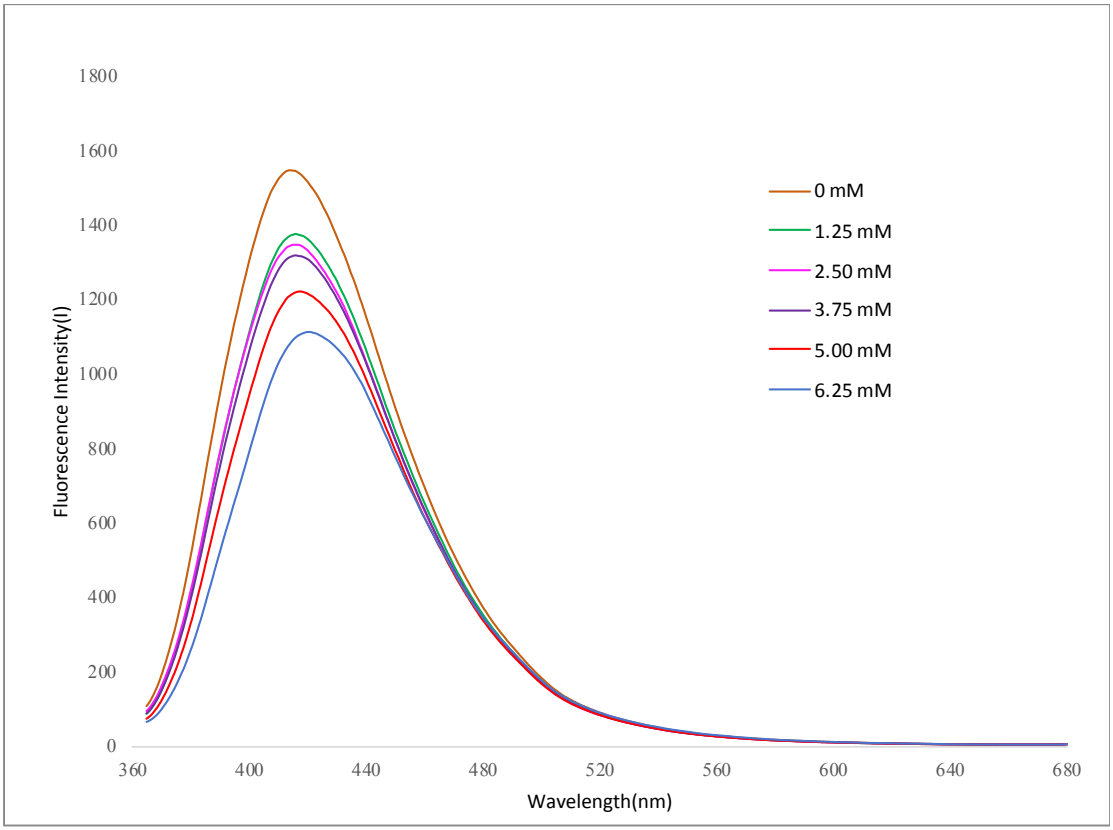


Figure S2 Emission spectra of **3aa** with varying concentrations **2a**

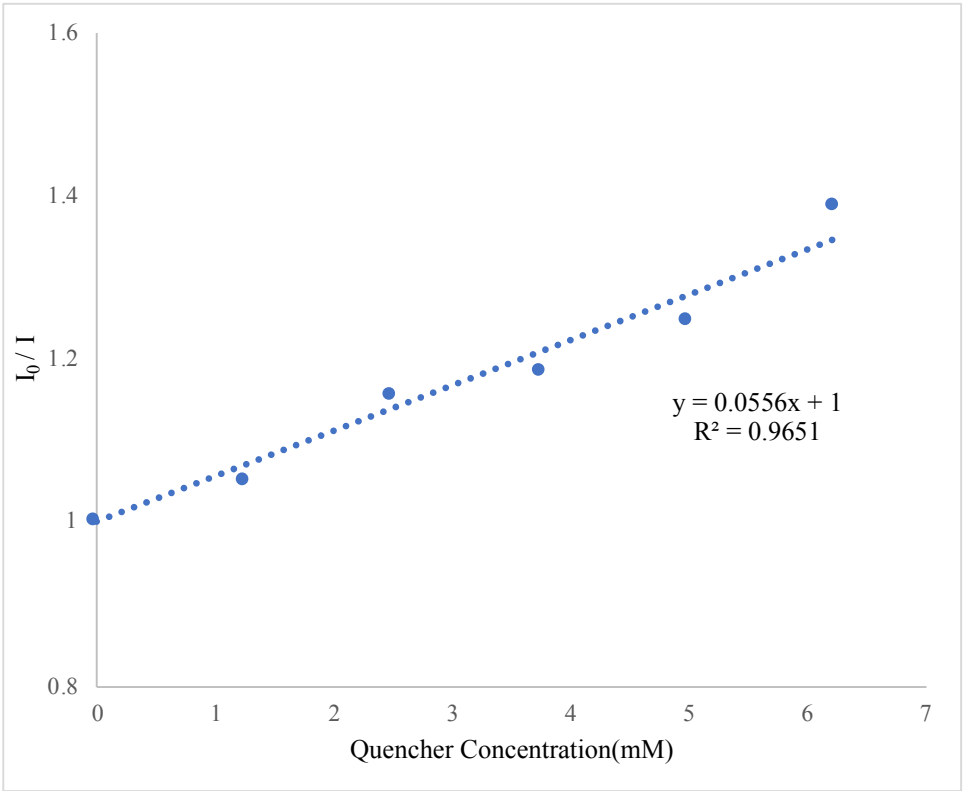


Figure S3 Stern-Volmer plot of fluorescence quenching of **1a** by **2a**

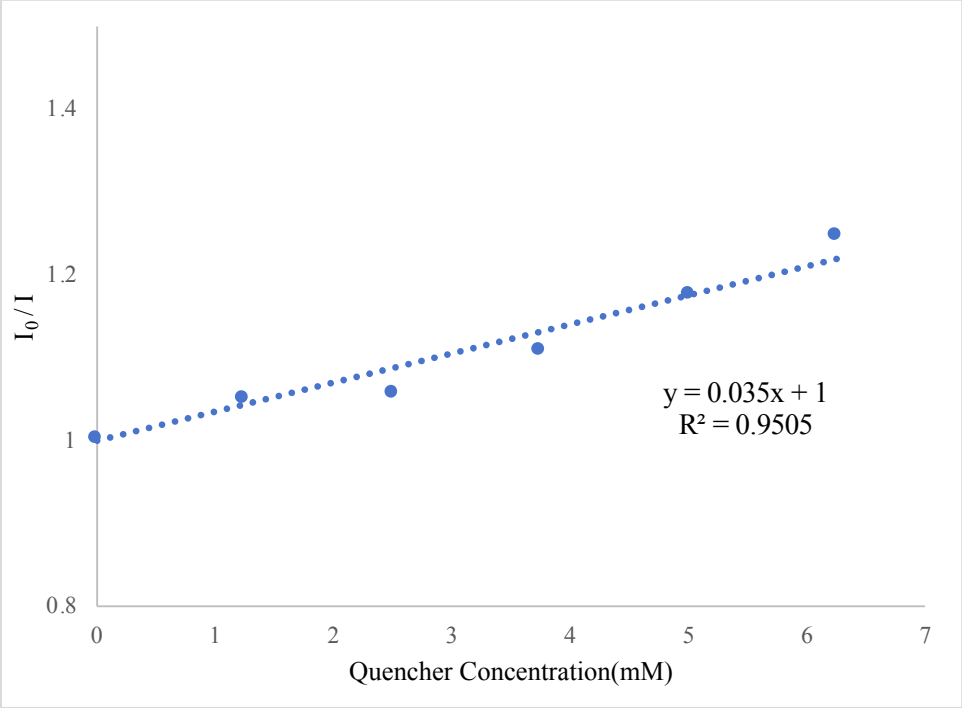


Figure S4 Stern-Volmer plot of fluorescence quenching of **3aa** Y by **2a**

7. Investigation of potential EDA complex formation

The UV/VIS spectra of all the reaction components were measured in DMSO in a quartz cuvette using a GENESYS 180 UV-visible spectrophotometer in a 10.0 mm quartz cuvette with the aim of investigating the possible formation of an excited donor-acceptor (EDA) complex (exciplex). Spectra were measured for **1a**, **2a**, **1a**+**2a** in different combinations at various concentrations mimicking the reaction concentration in DMSO. The following measurements were conducted: **1a** (0.1 M); **2a** (0.12 M); **1a**(0.1 M) + **2a** (0.12 M). In each case, no EDA complex (Electron-Donor Acceptor) was detected. These spectra are shown in (Figure S5) below along with the spectra for each component in isolation at these concentrations for comparison.

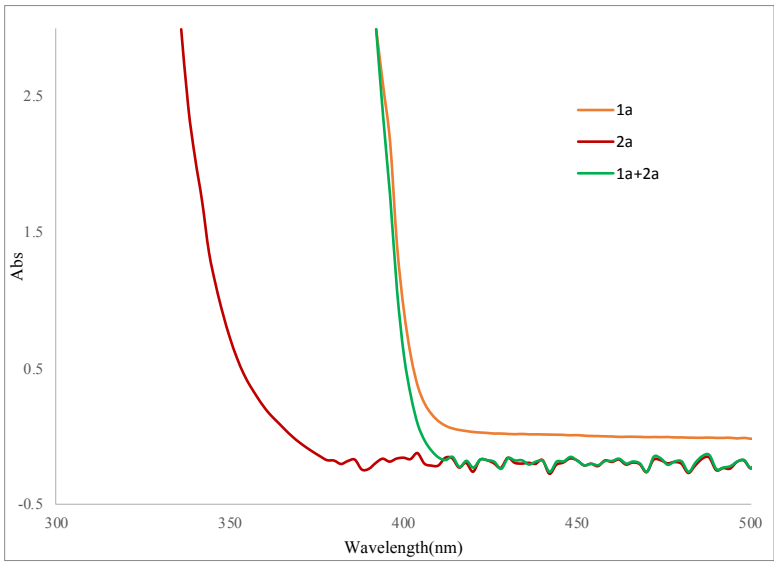


Figure S5 Absorption spectra of **1a**, **2a**, **1a+2a**

8. EDA complex exclusion

The NMR signal of the mixture of **1a** and **2a** shows no shifting change. Combining with the results of investigation of potential EDA complex formation, we conclude that the pathway to generate C-centered radicals through formation of EDA complex is unlikely in this reaction.

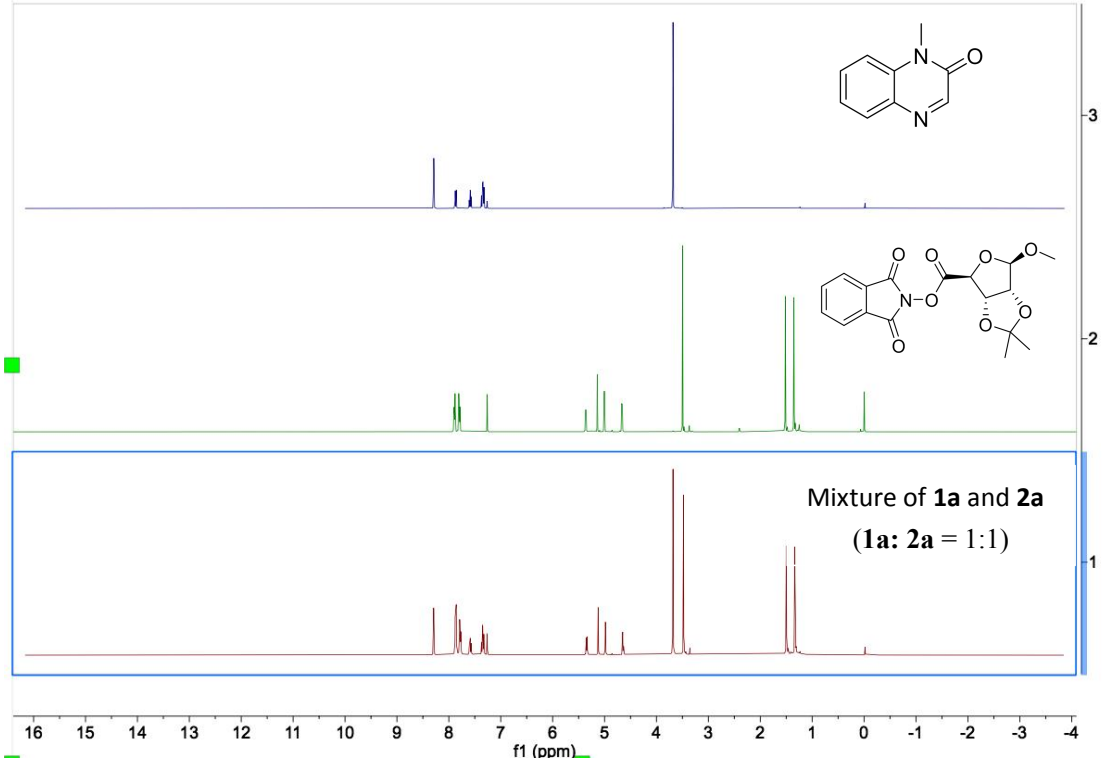
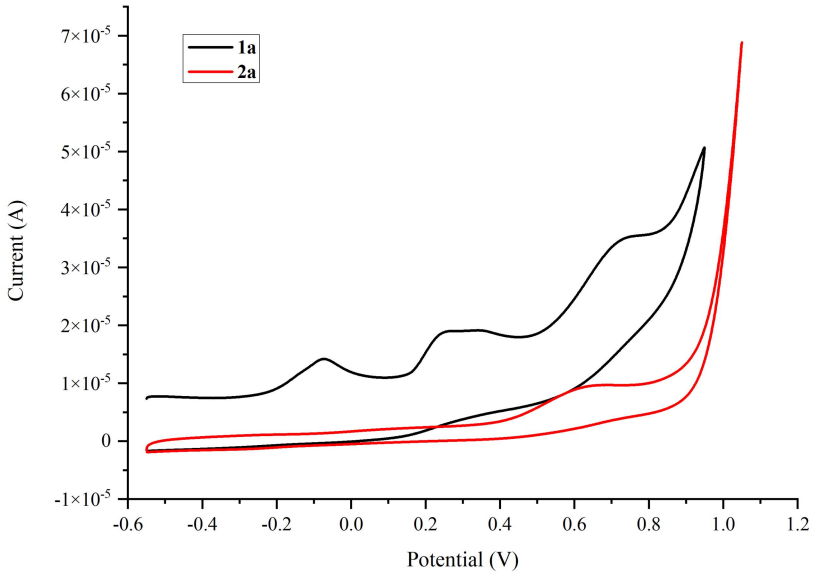


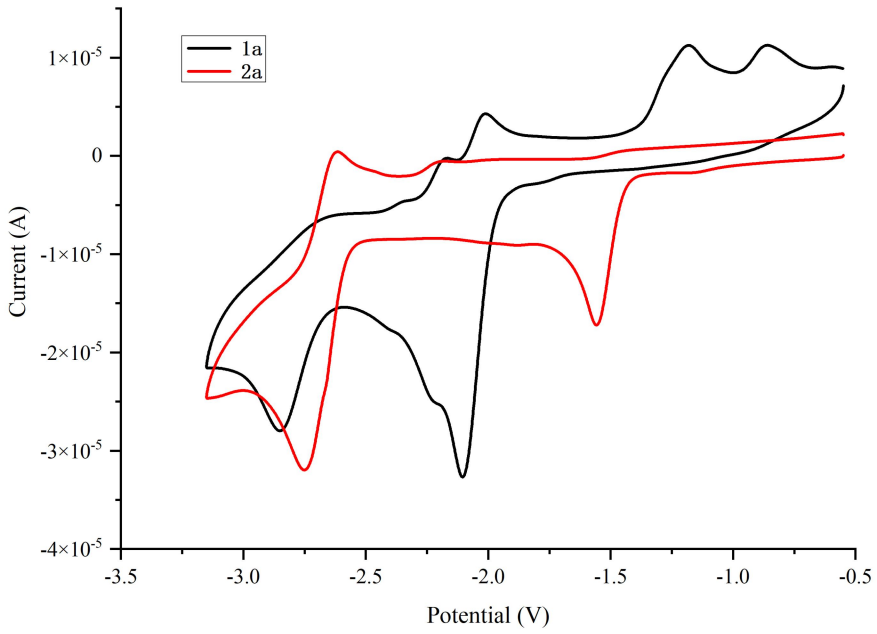
Figure S6 ^{1}H NMR spectra of **1a**, **2a** and **1a**+**2a**

9. Cyclic voltammetry measurements

Cyclic Voltammetry was performed using a CHI760E Electrochemical workstation with a glassycarbon as the working electrode, the Ag/AgCl electrode (3 M KCl) as the reference electrode, and a platinum electrode as the counter electrode. The testing solution of **1a**, **2a** were prepared by dissolving the sample (0.05 mmol) into DMSO (5 mL) with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$).



(a)



(b)

Figure S7 Cyclic voltammograms for **1a** and **2a** (a)oxidation (b)reduction

10. Quantum yield measurement

Determination of the light intensity at 450 nm:

According to the literature, [9,10] the photon flux of the blue LED (λmax = 450 nm) was determined by standard ferrioxalate actinometry. Potassium ferrioxalate hydrate (2.21 g) was dissolved in H_2SO_4 (0.05 M, 30 mL) to prepare a solution of ferrioxalate (0.15 M). Phenanthroline (50 mg) and sodium acetate (11.25 g) were dissolved in 0.5 M H_2SO_4 (50 mL) to give a buffered solution of phenanthroline. The freshly prepared solutions were stored in dark. Then, the ferrioxalate solution (2.0 mL) was placed in a 3 mL cuvette and irradiated for 90.0 seconds at λmax = 450 nm to determine the photon flux of the blue LED. After irradiation, the phenanthroline solution (0.35 mL) was added to the cuvette, and the resulting solution was then allowed to stand for 1 h to ensure the complete coordination of the ferrous ions to the phenanthroline. The absorbance of the solution was measured at 510 nm. Similarly, a non-irradiated sample was prepared, whose absorbance at 510 nm was also measured. The results were shown as below:

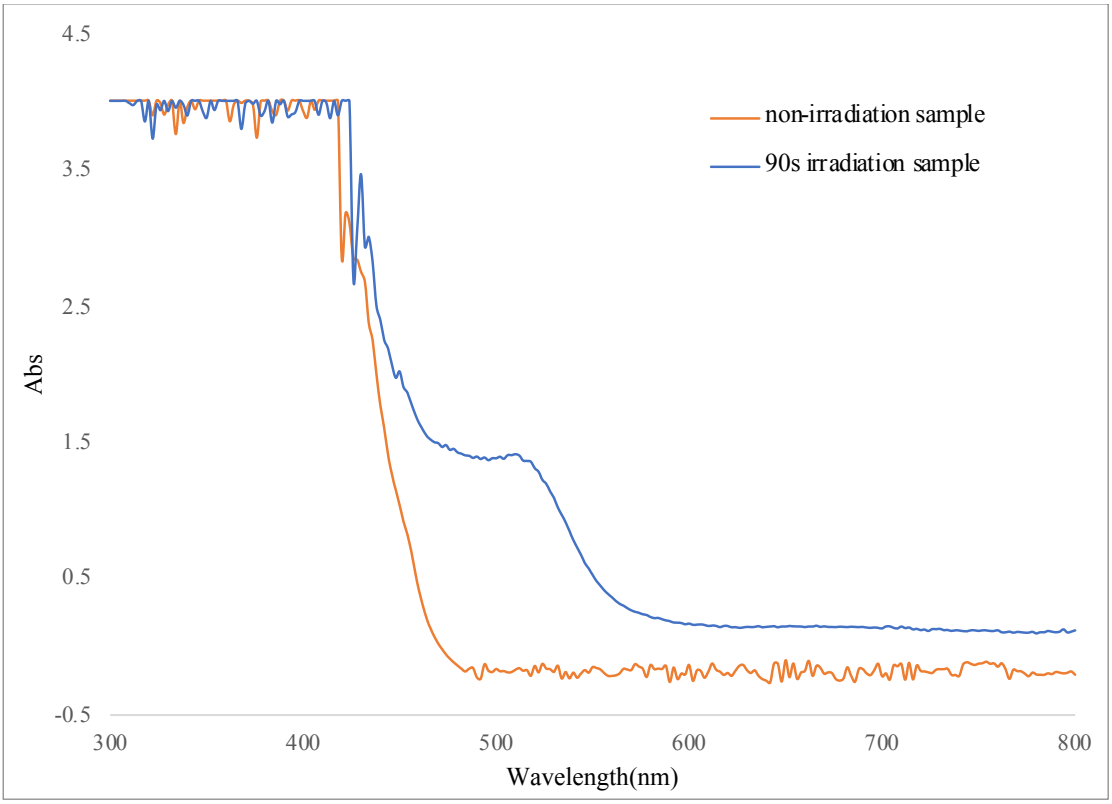


Figure S8 UV-vis spectrum of irradiation and non-irradiation sample

Conversion was calculated using equation 1.

$$mol\ Fe^{2+} = \frac{v \cdot \Delta A(510nm)}{l \cdot \varepsilon} = \frac{0.00235 \times 1.58}{1 \times 11100} = 3.3 \times 10^{-7} \qquad (1)$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.0 cm), and ε is the molar absorptivity at 510 nm (1.11×10^4 L mol^{-1} cm^{-1}).

The photon flux can be calculated using equation 2.

$$\text{photon flux} = \frac{mol\ Fe^{2+}}{\Phi \cdot t \cdot f} = \frac{3.3 \times 10^{-7}}{0.845 \times 90 \times 0.988} = 4.39 \times 10^{-9} \qquad (2)$$

Where Φ is the quantum yield for the ferrioxalate actinometer (0.845 for a 0.15 M solution at λ =

450 nm), [11] t is the time (90 s), and f is the fraction of light absorbed at λ = 450 nm. This value is calculated using equation 3 where A is the absorbance of the ferrioxalte solution at 450 nm.

$$f = 1 - 10^{-A} = 1 - 10^{-1.915} = 0.988 \qquad (3)$$

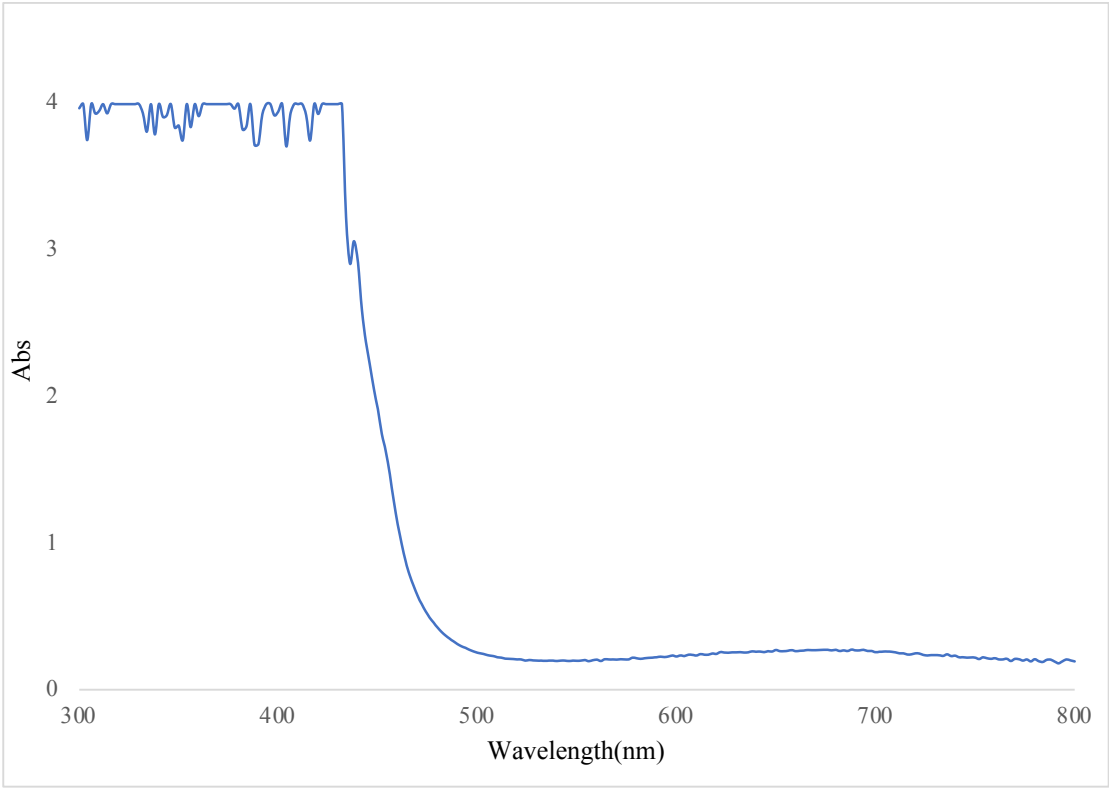


Figure S9 UV-vis spectrum of ferrioxalate actinometer solution

Determination of the reaction quantum yield (Φ):

Three parallel standard reactions were proceeded on a 0.10 mmol scale according to the general procedure. The standard reaction was stirred and irradiated (24 W blue LEDs, λ = 450 nm) at room temperature for 10 h. The yield of three parallel standard reactions was determined by ^{1}H NMR. All of the following NMR yields were afford 64%, 65%, and 66% respectively, therefore, the average yield was obtained 65%. The quantum yield for the reaction was calculated using equation 4. The reaction quantum yield (Φ) was thus determined to be 0.41.

$$\Phi = \frac{mol\ of\ product\ formed}{photon\ flux \cdot t \cdot f} = \frac{6.5\times10^{-5}}{4.39\times10^{-9}\times10\times60\times60\times0.999} = 0.41 \qquad (4)$$

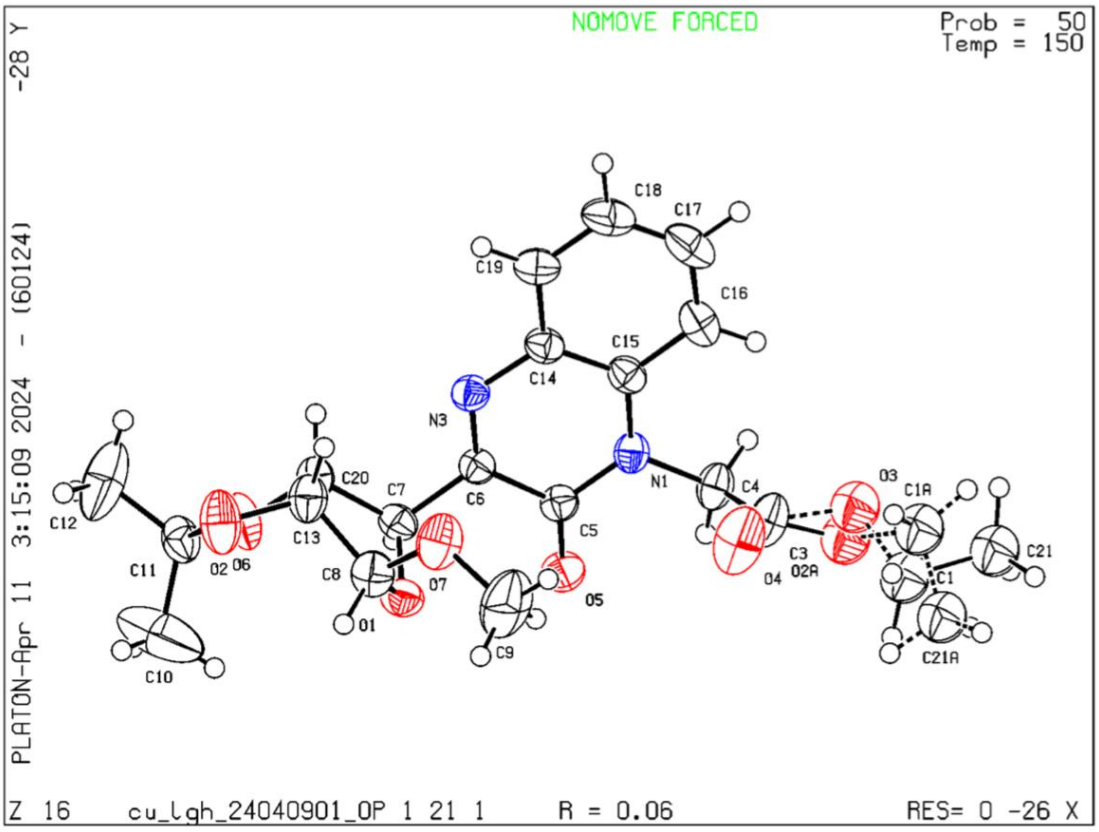
where photon flux was determined as above described, t is the reaction time, f is the fraction of incident light absorbed by the reaction mixture. This value is calculated using equation 3 where A is the absorbance of the reaction mixture at 450 nm. The absorbance of the reaction mixture at 450 nm was measured to be 2.893, so the value of f is 0.999.

11. Configuration determination

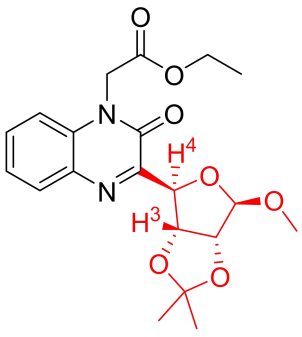
11.1 X-ray diffraction parameters and data of 3aj

Method for crystallization:

The purified compound **3aj** was dissolved in a mixed solvent of petroleum ether/n-Hexane (1:3), and placed in a dark cabinet for slowly evaporation. Colorless crystals were collected after few days for X-ray analysis.



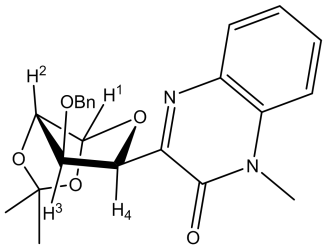
```
Bond precision:   C-C = 0.0051 A          Wavelength=1.54178

Cell:             a=9.9830(8)     b=9.6498(8)         c=10.6876(9)
                  alpha=90        beta=98.928(4)      gamma=90
Temperature:      150 K

                  Calculated                  Reported
Volume            1017.11(15)                 1017.10(15)
Space group       P 21                        P 1 21 1
Hall group        P 2yb                       P 2yb
Moiety formula    C20 H24 N2 O7               C20 H24 N2 O7
Sum formula       C20 H24 N2 O7               C20 H24 N2 O7
Mr                404.41                      404.41
Dx,g cm-3         1.321                       1.320
Z                 2                           2
Mu (mm-1)         0.843                       0.843
F000              428.0                       428.0
F000'             429.47
h,k,lmax          12,11,13                    12,11,13
Nref              4015[ 2135]                 3936
Tmin,Tmax         0.737,0.817                 0.616,0.754
Tmin'             0.668

Correction method= # Reported T Limits: Tmin=0.616 Tmax=0.754
AbsCorr = MULTI-SCAN

Data completeness= 1.84/0.98        Theta(max)= 72.204

R(reflections)= 0.0578( 3785)                wR2(reflections)=
                                             0.1510( 3936)
S = 1.054                   Npar= 267
```



3aj

We can conclude that H^3 and H^4 are on the different side of the sugar ring based on the X-ray crystallographic analysis of the molecular structure of product **3aj**. So it is easy to conclude that **3aj** was β isomer. The stereochemical outcome of other furanoses(**3ab-3pa**, **4aa-4ab**) was same to the compound **3aj**.

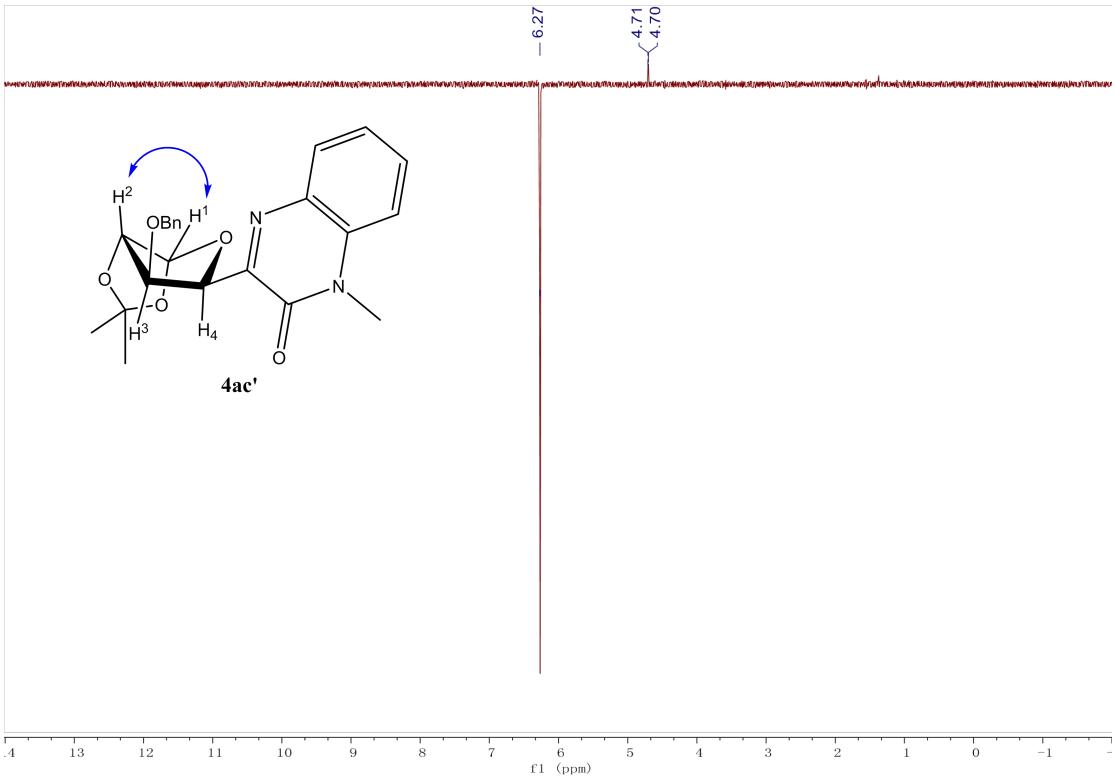
11.2 NOE experiments



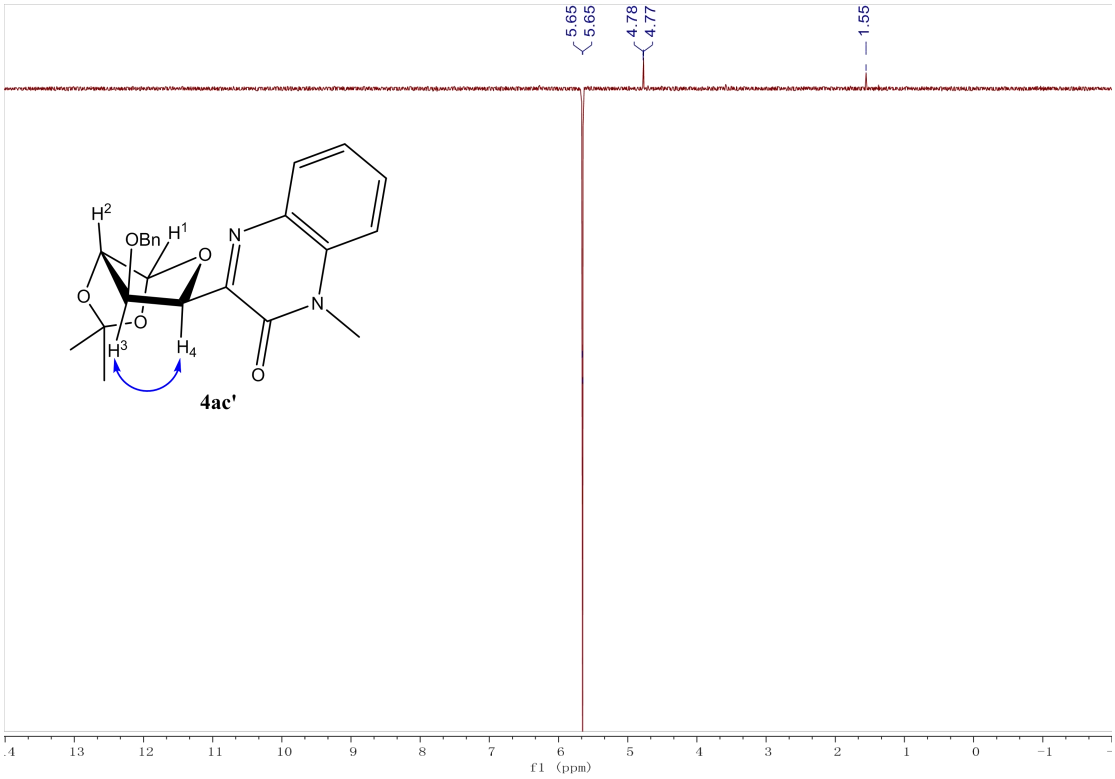
4ac'

3-((3a*S*,5*S*,6*R*,6a*S*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)-1-methylquinoxalin-2(1*H*)-one(4ac'): ^{1}H NMR (400 MHz, Chloroform-*d*, minor diastereomer) δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.14 – 7.11 (m, 1H), 7.07 (t, *J* = 7.3 Hz, 2H), 6.95 (d, *J* = 7.3 Hz, 2H), **6.27 (d, *J* = 3.8 Hz, H^1)**, **5.65 (d, *J* = 3.5 Hz, H^4), 4.77 (d, *J* = 3.5 Hz, H^3), 4.70 (d, *J* = 3.8 Hz, H^2)**, 4.56 (d, *J* = 12.2 Hz, 1H), 4.32 (d, *J* = 12.2 Hz, 1H), 3.58 (s, 3H), 1.55 (s, 3H), 1.37 (s, 3H).

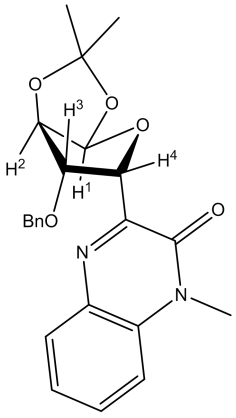
We identified H^1 and H^2 through NOE experiment because they are on the same side. By comparing the data of another NOE experiment, it is clearly found H^3 and H^4 of the isomer **4ac'** are coupled to each other that they are on the same side. So we concluded that **4ac'** was α isomer and **4ac** was β isomer .



1D-NOE spectrum of compound **4ac'**



1D-NOE spectrum of compound **4ac'**

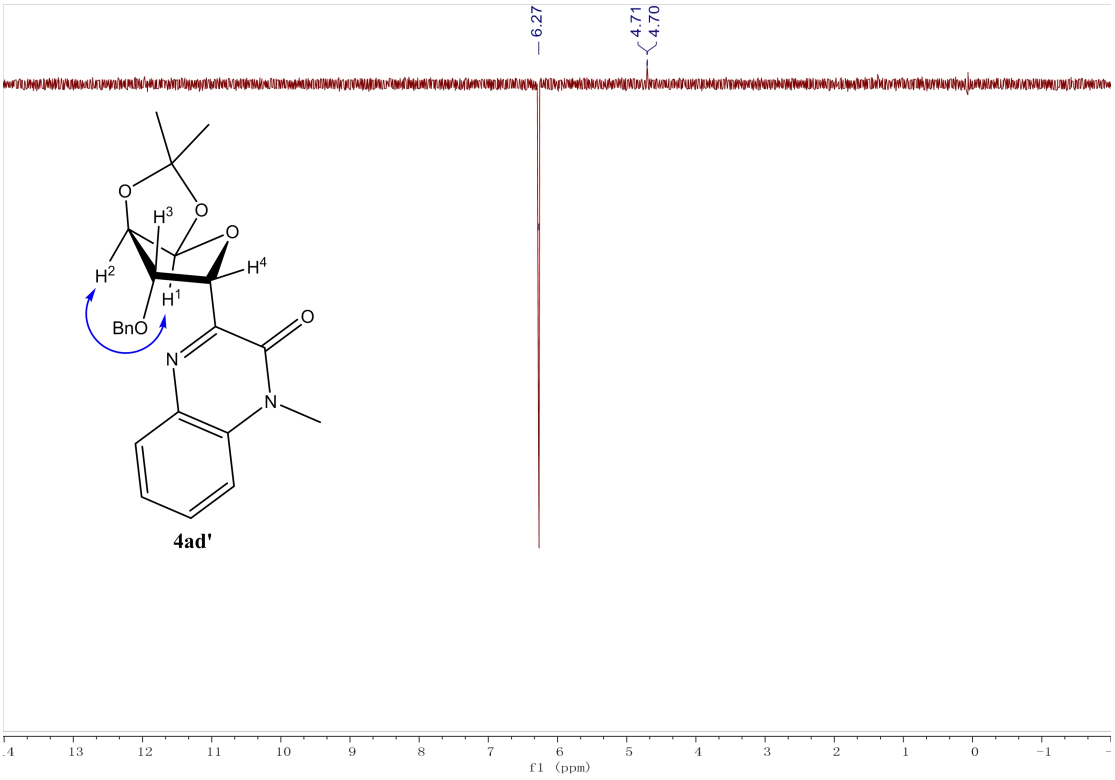


4ad'

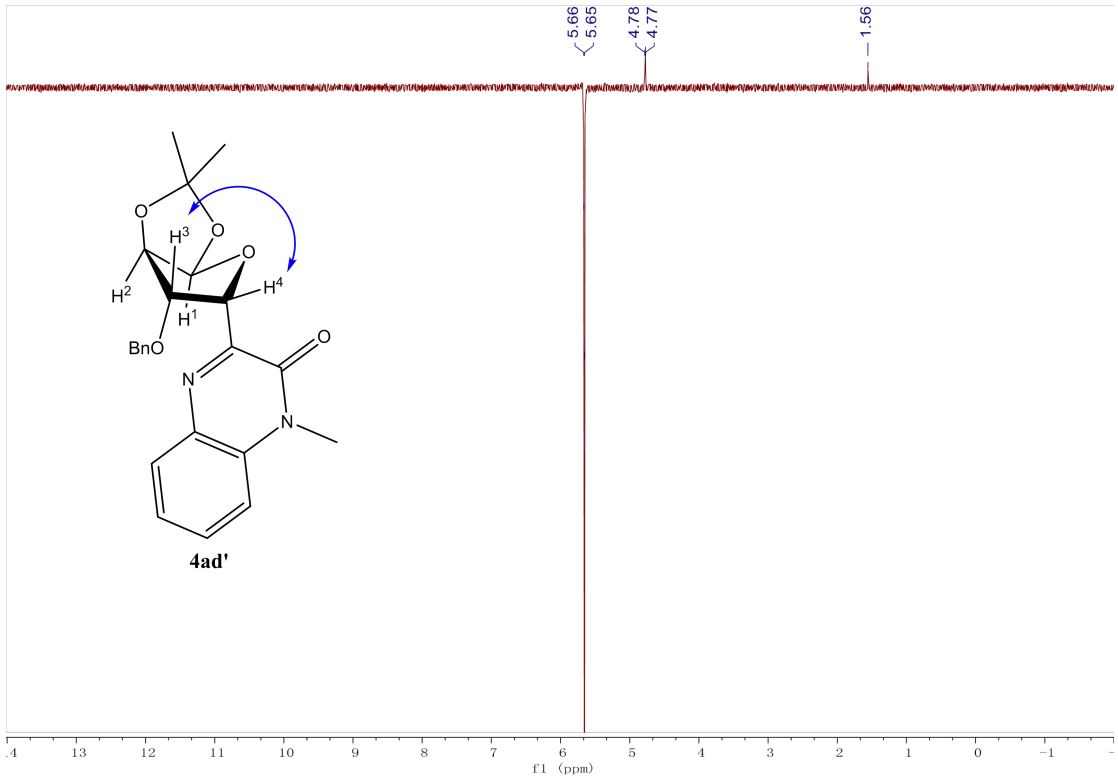
3-((3a*R*,5*R*,6*S*,6a*R*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)-1-methylquinoxalin-2(1*H*)-one(4ad'): ^{1}H NMR (600 MHz, Chloroform-*d*, minor diastereomer) δ 8.08 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.57 (td, *J* = 7.9, 1.5 Hz, 1H), 7.37 (td, *J* = 7.7, 1.2 Hz, 1H), 7.30 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.15 – 7.12 (m, 1H), 7.08 – 7.06 (m, 2H), 6.96 – 6.94 (m, 2H), **6.27 (d, *J* = 3.8 Hz, H^1), 5.66 (d, *J* = 3.5 Hz, H^4), 4.77 (d, *J* = 3.6 Hz, H^3), 4.70 (d, *J* = 3.8 Hz, H^2)**, 4.56 (d, *J* = 12.3 Hz, 1H), 4.33 (d, *J* = 12.3 Hz, 1H), 3.58 (s, 3H), 1.55 (s, 3H), 1.37 (s, 3H).

We identified H^1 and H^2 through NOE experiment because they are on the same side. Then it was clearly found H^3 and H^4 are coupled to each

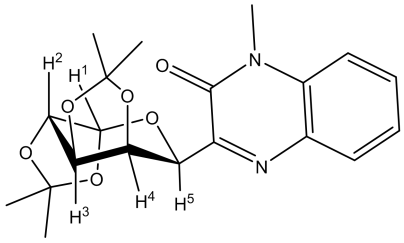
other that they are on the same side through another NOE experiment. So we concluded that **4ad'** was α isomer and **4ad** was β isomer .



1D-NOE spectrum of compound **4ad'**



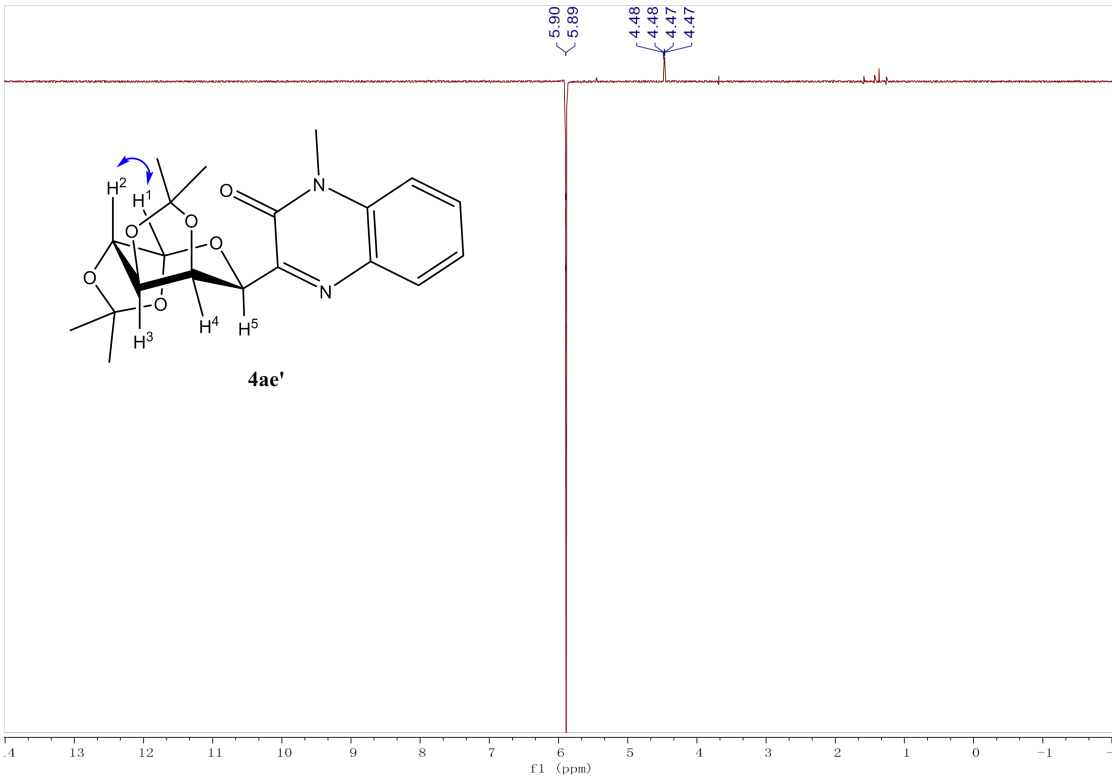
1D-NOE spectrum of compound **4ad'**



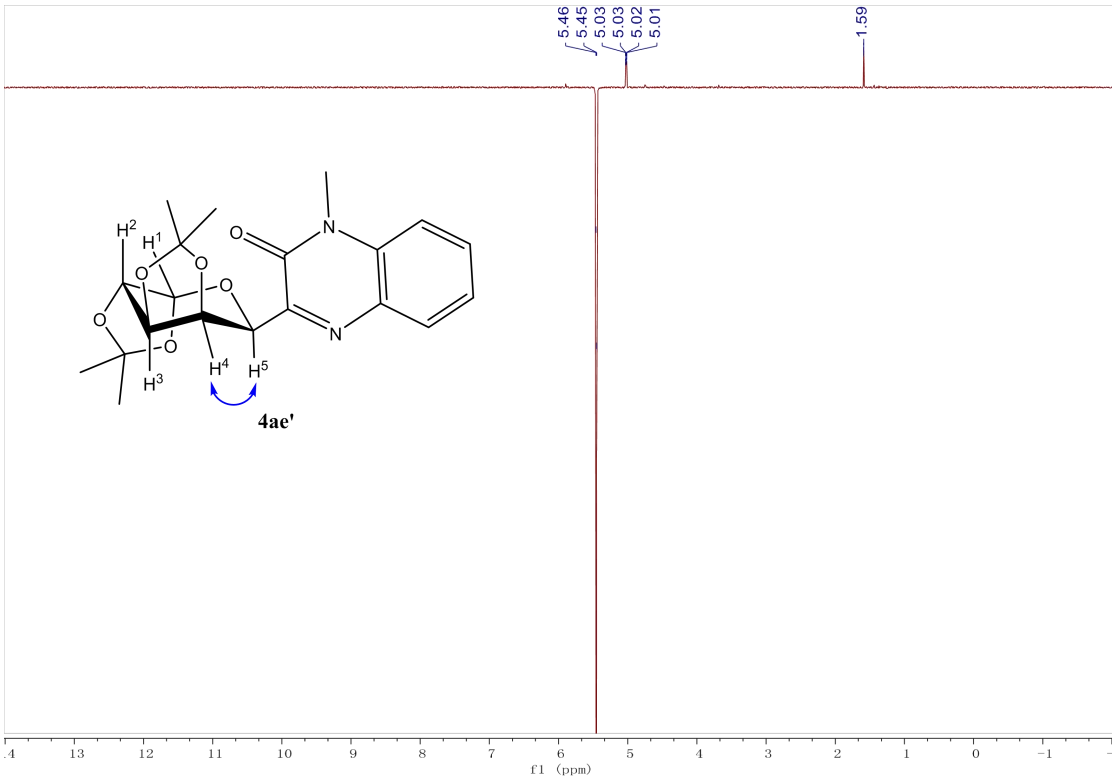
4ae'

1-methyl-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)quinoxalin-2(1*H*)-one(4ae'): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.34 (td, *J* = 7.7, 1.2 Hz, 1H), 7.30 (dd, *J* = 8.4, 1.2 Hz, 1H), **5.90 (d, *J* = 5.1 Hz, H^1), 5.46 (d, *J* = 2.3 Hz, H^5), 5.02 (dd, *J* = 7.7, 2.3 Hz, H^4), 4.75 (dd, *J* = 7.7, 2.5 Hz, H^3), 4.47 (dd, *J* = 5.2, 2.6 Hz, H^2)**, 3.68 (s, 3H), 1.59 (s, 3H), 1.44 (s, 3H), 1.37 (s, 3H), 1.26 (s, 3H).

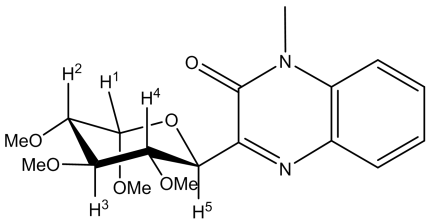
We identified H^1 and H^2 through NOE experiment because they are on the same side. Then it was clearly found H^4 and H^5 are coupled to each other that they are on the same side through another NOE experiment. So we concluded that **4ae'** was α isomer and **4ae** was β isomer .



1D-NOE spectrum of compound **4ae'**



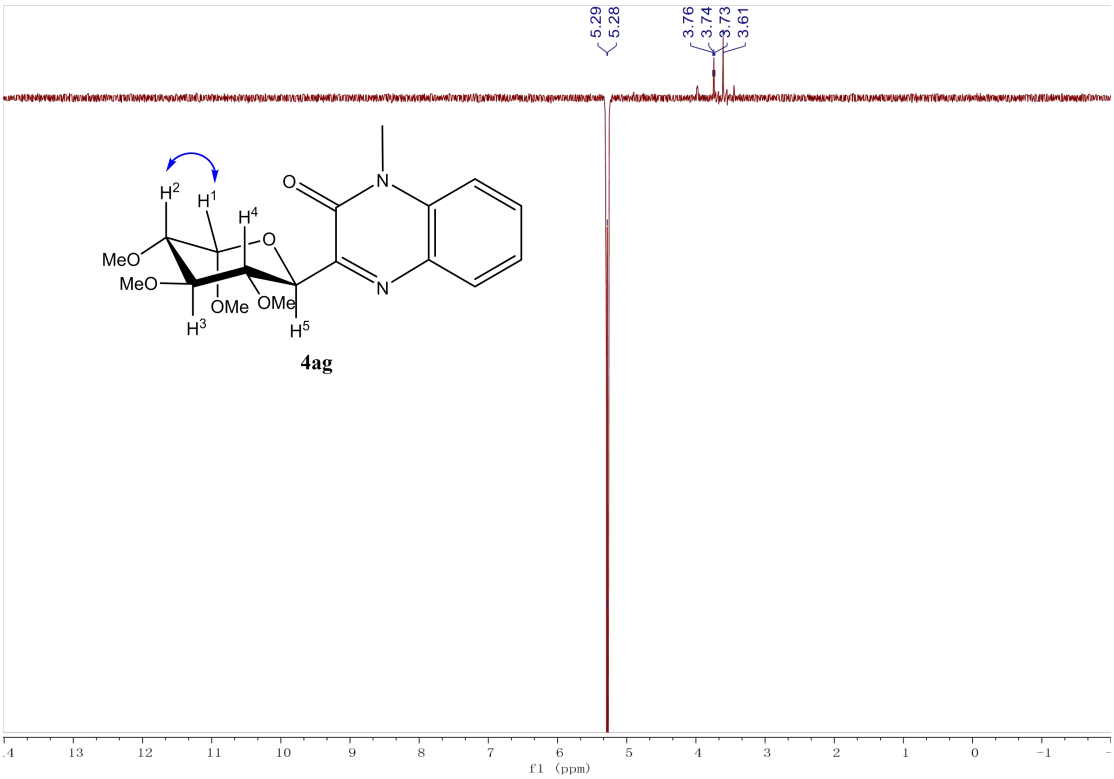
1D-NOE spectrum of compound **4ae'**



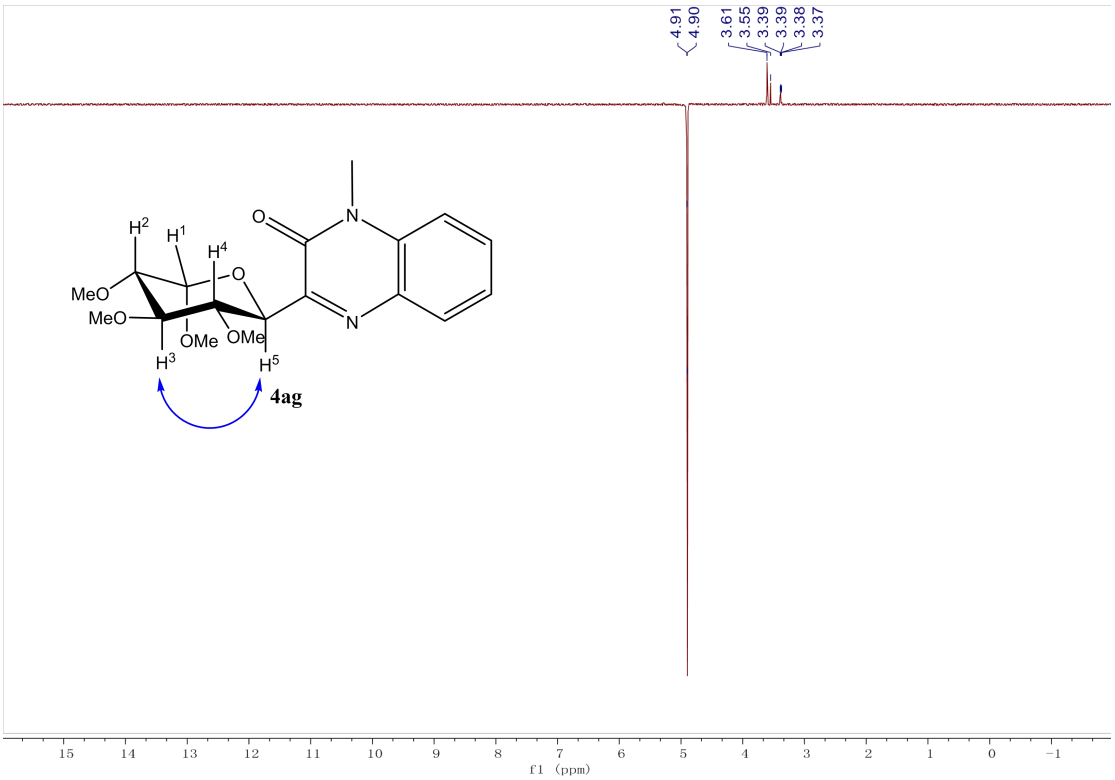
4ag

1-**methyl-3-((2*R*,3*R*,4*S*,5*R*,6S)-3,4,5,6-tetramethoxytetrahydro-2*H*-pyran-2-yl)quinoxalin-2(1*H*)-one(4ag):** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.60 (td, *J* = 7.9, 1.5 Hz, 1H), 7.37 (td, *J* = 8.3, 1.2 Hz, 1H), 7.33 (dd, *J* = 8.5, 1.2 Hz, 1H), **5.29 (d, *J* = 10.1 Hz, H^1), 4.91 (d, *J* = 3.5 Hz, H^5)**, 4.01 (dd, *J* = 10.1, 9.0 Hz, 1H), **3.76 (t, *J* = 9.3 Hz, H^2)**, 3.72 (s, 3H), 3.68 (s, 3H), 3.62 (s, 3H), 3.56 (s, 3H), 3.46 (s, 3H), **3.39 (dd, *J* = 9.7, 3.6 Hz, H^3)**.

We identified H^1 and H^2 through NOE experiment because they are on the same side. Then it was clearly found H^3 and H^5 are coupled to each other that they are on the same side through another NOE experiment. So we concluded that **4ag** was β isomer. The stereochemical outcome of benzyl-protected glucose products (**4ah-4aj**) was same to the compound **4ag**.



1D-NOE spectrum of compound **4ag**



1D-NOE spectrum of compound **4ag**

12. References

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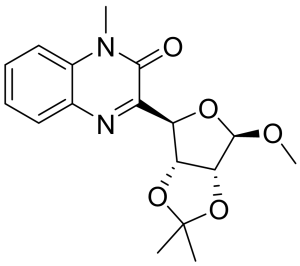
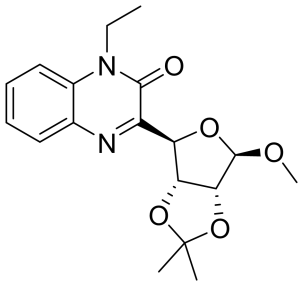
13. Characterization of the Products

3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1-methylquinoxalin-2(1*H*)-one(3aa)



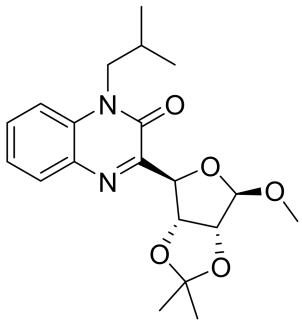
Colorless wax; 30.2 mg, 91% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.87 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.56 (td, *J* = 8.6, 1.5 Hz, 1H), 7.37 – 7.31 (m, 2H), 5.58 (d, *J* = 1.7 Hz, 1H), 5.41 (dd, *J* = 6.0, 1.7 Hz, 1H), 5.14 (s, 1H), 4.66 (d, *J* = 5.9 Hz, 1H), 3.72 (s, 3H), 3.37 (s, 3H), 1.59 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 156.3, 153.9, 133.4, 132.3, 130.64, 130.59, 123.7, 113.6, 112.7, 109.9, 86.0, 85.2, 82.2, 55.3, 28.8, 26.8, 25.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{21}N_2O_5$ 333.1450; Found 333.1453.

1-ethyl-3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)quinoxalin-2(1*H*)-one(3ab)



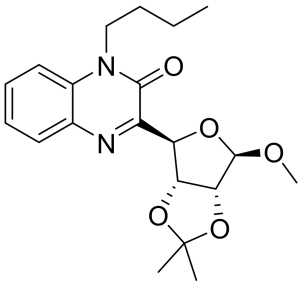
White solid, mp: 100-102 °C; 31.2 mg, 90% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.55 (td, *J* = 8.6, 1.6 Hz, 1H), 7.34 – 7.30 (m, 2H), 5.58 (d, *J* = 1.6 Hz, 1H), 5.41 (dd, *J* = 6.0, 1.7 Hz, 1H), 5.14 (s, 1H), 4.65 (d, *J* = 5.9 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 3.38 (s, 3H), 1.58 (s, 3H), 1.39 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.3, 152.3, 131.6, 131.3, 129.9, 129.5, 122.5, 112.4, 111.7, 108.7, 85.0, 84.1, 81.3, 54.2, 36.0, 25.8, 24.4, 11.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{23}N_2O_5$ 347.1607; Found 347.1605.

1-isobutyl-3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)quinoxalin-2(1*H*)-one(3ac)



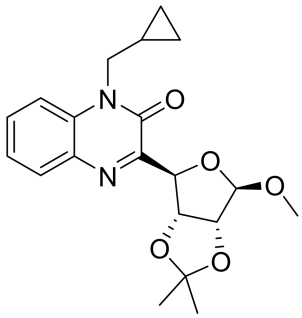
White solid, mp: 128-130 °C; 31.1 mg, 83% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.34 – 7.30 (m, 2H), 5.58 (d, *J* = 1.6 Hz, 1H), 5.39 (dd, *J* = 5.9, 1.7 Hz, 1H), 5.15 (s, 1H), 4.66 (d, *J* = 5.9 Hz, 1H), 4.24 (dd, *J* = 13.7, 7.9 Hz, 1H), 4.05 (dd, *J* = 13.7, 7.1 Hz, 1H), 3.40 (s, 3H), 2.26 (dq, *J* = 13.8, 6.9 Hz, 1H), 1.59 (s, 3H), 1.40 (s, 3H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.4, 154.1, 133.0, 132.5, 130.9, 130.3, 123.4, 114.1, 112.7, 109.9, 86.2, 85.2, 82.3, 55.3, 48.8, 27.2, 26.8, 25.4, 20.3, 20.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{27}N_2O_5$ 375.1920; Found 375.1916.

1-butyl-3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)quinoxalin-2(1*H*)-one(3ad)



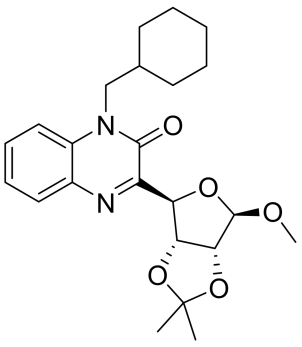
White solid, mp: 107-109 °C; 34.4 mg, 92% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.54 (td, *J* = 7.7, 1.6 Hz, 1H), 7.33 – 7.29 (m, 2H), 5.57 (d, *J* = 1.7 Hz, 1H), 5.39 (dd, *J* = 5.9, 1.7 Hz, 1H), 5.14 (s, 1H), 4.64 (d, *J* = 5.9 Hz, 1H), 4.33 – 4.18 (m, 2H), 3.39 (s, 3H), 1.76 – 1.69 (m, 2H), 1.58 (s, 3H), 1.51 – 1.42 (m, 2H), 1.39 (s, 3H), 0.98 (t, *J* = 7.4 Hz,3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.4, 153.6, 132.61, 132.58, 130.8, 130.4, 123.5, 113.6, 112.7, 109.8, 86.2, 85.2, 82.3, 55.2, 41.9, 29.3, 26.8, 25.4, 20.3, 13.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{27}N_2O_5$ 375.1920; Found 375.1925.

1-(cyclopropylmethyl)-3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)quinoxalin-2(1*H*)-one(3ae)



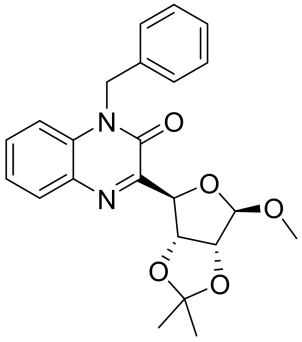
White solid, mp: 108-110 °C; 31.3 mg, 84% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.56 (td, *J* = 7.8, 1.6 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.35 – 7.31 (m, 1H), 5.57 (d, *J* = 1.7 Hz, 1H), 5.41 (dd, *J* = 5.9, 1.7 Hz, 1H), 5.15 (s, 1H), 4.65 (d, *J* = 5.9 Hz, 1H), 4.27 – 4.16 (m, 2H), 3.40 (s, 3H), 1.59 (s, 3H), 1.40 (s, 3H), 1.33 – 1.26 (m, 1H), 0.61 – 0.47 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.5, 152.9, 131.8, 131.5, 129.8, 129.4, 122.4, 112.9, 111.7, 108.8, 85.2, 84.1, 81.3, 54.2, 44.9, 25.8, 24.4, 8.6, 3.1, 3.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{25}N_2O_5$ 373.1763; Found 373.1758.

1-(cyclohexylmethyl)-3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)quinoxalin-2(1*H*)-one(3af)



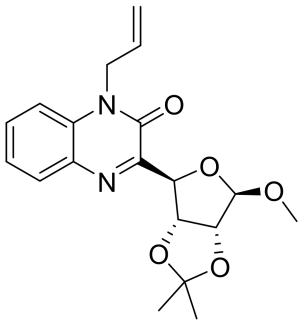
White solid, mp: 83-85 °C; 35.6 mg, 86% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.53 (td, *J* = 8.6, 1.6 Hz, 1H), 7.34 – 7.29 (m, 2H), 5.57 (d, *J* = 1.7 Hz, 1H), 5.38 (dd, *J* = 6.0, 1.7 Hz, 1H), 5.15 (s, 1H), 4.65 (d, *J* = 5.9 Hz, 1H), 4.23 (dd, *J* = 13.7, 7.6 Hz, 1H), 4.06 (dd, *J* = 13.8, 7.1 Hz, 1H), 3.40 (s, 3H), 1.96 – 1.86 (m, 1H), 1.73 – 1.63 (m, 5H), 1.59 (s, 3H), 1.40 (s, 3H), 1.21 – 1.11 (m, 5H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.4, 154.1, 133.1, 132.5, 130.8, 130.3, 123.4, 114.1, 112.7, 109.9, 86.3, 85.2, 82.4, 55.3, 47.8, 36.5, 30.9, 30.8, 26.8, 26.2, 25.79, 25.75, 25.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{31}N_2O_5$ 415.2233; Found 415.2239.

1-benzyl-3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)quinoxalin-2(1*H*)-one(3ag)



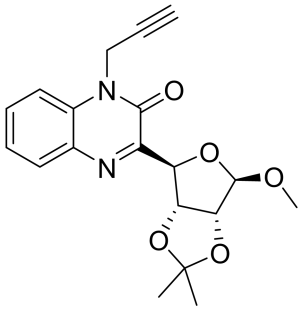
Colorless oil; 38.4 mg, 94% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.31 – 7.22 (m, 7H), 5.65 (d, *J* = 1.7 Hz, 1H), 5.58 (d, *J* = 15.6 Hz, 1H), 5.49 (dd, *J* = 5.9, 1.6 Hz, 1H), 5.44 (d, *J* = 15.6 Hz, 1H), 5.16 (s, 1H), 4.70 (d, *J* = 5.9 Hz, 1H), 3.38 (s, 3H), 1.60 (s, 3H), 1.41 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.5, 154.0, 135.2, 132.8, 132.5, 130.7, 130.6, 128.9, 127.8, 127.0, 123.8, 114.4, 112.7, 109.9, 86.0, 85.3, 82.2, 55.3, 45.6, 26.8, 25.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{25}N_2O_5$ 409.1763; Found 409.1766.

1-allyl-3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)quinoxalin-2(1*H*)-one(3ah)



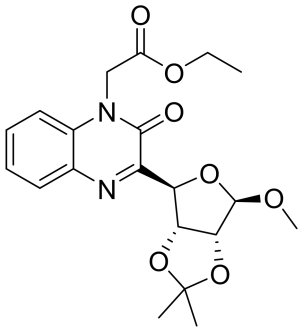
White solid, mp: 139-141 °C; 33.3 mg, 93% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.35 – 7.28 (m, 2H), 5.97 – 5.87 (m, 1H), 5.59 (d, *J* = 1.6 Hz, 1H), 5.44 (dd, *J* = 5.9, 1.7 Hz, 1H), 5.27 – 5.24 (m, 1H), 5.18 – 5.13 (m, 2H), 5.00 – 4.84 (m, 2H), 4.67 (d, *J* = 5.9 Hz, 1H), 3.37 (s, 3H), 1.58 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.4, 153.4, 132.6, 132.4,130.7, 130.6, 130.5, 123.7, 118.3, 114.2, 112.7, 109.8, 85.9, 85.2, 82.2, 55.2, 44.2, 26.8, 25.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{23}N_2O_5$ 359.1607; Found 359.1601.

3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1-(prop-2-yn-1-yl)quinoxalin-2(1*H*)-one(3ai)



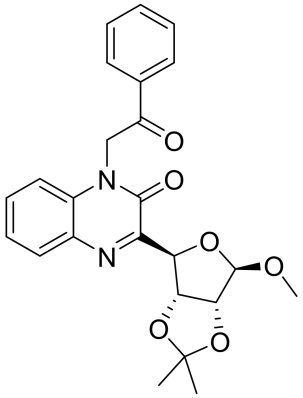
White solid, mp: 161-163 °C; 31 mg, 87% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.59 (td, *J* = 7.8, 1.5 Hz, 1H), 7.47 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.37 (td, *J* = 7.6, 1.2 Hz, 1H), 5.57 (d, *J* = 1.7 Hz, 1H), 5.44 (dd, *J* = 5.9, 1.7 Hz, 1H), 5.13 (s, 1H), 5.12 – 5.01 (m, 2H), 4.66 (d, *J* = 5.9 Hz, 1H), 3.36 (s, 3H), 2.27 (t, *J* = 2.5 Hz, 1H), 1.58 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.3, 151.8, 131.4, 130.8, 129.71, 129.66, 123.1, 113.2, 111.7, 108.8, 84.8, 84.1, 81.1, 75.7, 72.3, 54.2, 30.1, 25.8, 24.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}N_2O_5$ 357.1450; Found 357.1458.

Ethyl2-(3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-2-oxoquinoxalin-1(2*H*)-yl)acetate(3aj)



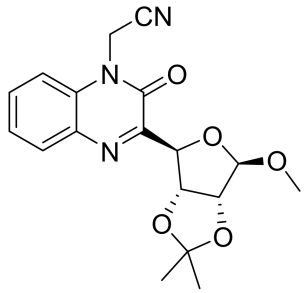
White solid, mp: 159-161 °C; 32.4 mg, 80% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.52 (td, *J* = 7.9, 1.5 Hz, 1H), 7.36 – 7.32 (m, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 5.57 (d, *J* = 1.6 Hz, 1H), 5.47 (dd, *J* = 5.9, 1.6 Hz, 1H), 5.13 (s, 1H), 5.08 – 4.99 (m, 2H), 4.67 (d, *J* = 5.9 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.34 (s, 3H), 1.58 (s, 3H), 1.39 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.9, 155.2, 152.4, 131.5, 131.3, 129.9, 129.7, 123.0, 112.1, 111.6, 108.8, 84.7, 84.2, 81.0, 61.1, 54.1, 42.2, 25.7, 24.3, 13.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{25}N_2O_7$ 405.1662; Found 405.1657.

3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1-(2-oxo-2-phenylethyl)quinoxalin-2(1*H*)-one(3ak)



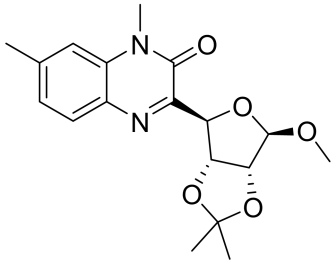
White solid, mp: 191-193 °C; 35.4 mg, 87% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 8.04 (m, 2H), 7.90 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.55 – 7.51 (m, 2H), 7.45 (td, *J* = 7.9, 1.6 Hz, 1H), 7.32 (td, *J* = 7.7, 1.2 Hz, 1H), 6.96 (dd, *J* = 8.5, 1.2 Hz, 1H), 5.80 – 5.70 (m, 2H), 5.58 (d, *J* = 1.5 Hz, 1H), 5.49 (dd, *J* = 5.9, 1.6 Hz, 1H), 5.14 (s, 1H), 4.69 (d, *J* = 5.9 Hz, 1H), 3.37 (s, 3H), 1.57 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.9, 156.1, 153.7, 134.5, 134.4, 132.9, 132.4, 130.9, 130.7, 129.1, 128.1, 123.9, 113.5, 112.6, 109.8, 85.7, 85.3, 82.1, 55.2, 48.2, 26.8, 25.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{25}N_2O_6$ 437.1713; Found 437.1721.

2-(3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-2-oxoquinoxalin-1(2*H*)-yl)acetonitrile(3al)



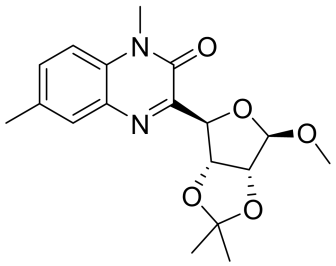
White solid, mp: 81-83 °C; 24 mg, 67% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.65 (td, *J* = 8.3, 1.5 Hz, 1H), 7.44 (td, *J* = 7.7, 1.2 Hz, 1H), 7.34 (dd, *J* = 8.4, 1.2 Hz, 1H), 5.54 (d, *J* = 1.5 Hz, 1H), 5.45 (dd, *J* = 5.9, 1.6 Hz, 1H), 5.27 – 5.18 (m, 2H), 5.12 (s, 1H), 4.66 (d, *J* = 5.9 Hz, 1H), 3.33 (s, 3H), 1.58 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.0, 152.5, 132.3, 131.4, 131.3, 131.1, 125.0, 113.6, 113.1, 112.8, 110.0, 85.5, 85.2, 81.9, 55.3, 29.1, 26.8, 25.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}N_3O_5$ 358.1403; Found 358.1399.

3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1,7-dimethylquinoxalin-2(1*H*)-one(3ba)



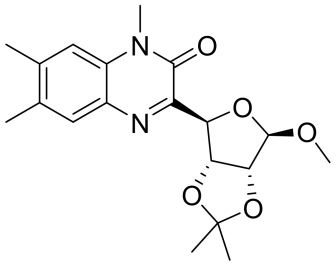
Colorless oil; 27 mg, 78% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.1 Hz, 1H), 7.15 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.10 (s, 1H), 5.56 (d, *J* = 1.6 Hz, 1H), 5.41 (dd, *J* = 6.0, 1.6 Hz, 1H), 5.13 (s, 1H), 4.66 (d, *J* = 5.9 Hz, 1H), 3.69 (s, 3H), 3.36 (s, 3H), 2.51 (s, 3H), 1.58 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.0, 154.1, 141.5, 133.3, 130.5, 130.3, 125.1, 113.8, 112.6, 109.8, 85.9, 85.2, 82.2, 55.2, 28.8, 26.8, 25.3, 22.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{23}N_2O_5$ 347.1607; Found 347.1613.

3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1,6-dimethylquinoxalin-2(1*H*)-one(3ca)



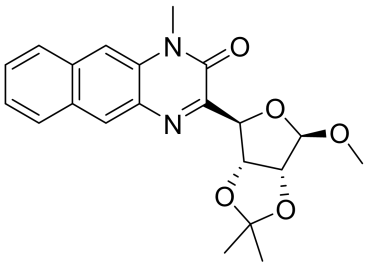
Colorless oil; 27.7 mg, 80% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 1.9 Hz, 1H), 7.38 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.21 (d, *J* = 8.5 Hz, 1H), 5.58 (d, *J* = 1.6 Hz, 1H), 5.41 (dd, *J* = 5.9, 1.6 Hz, 1H), 5.13 (s, 1H), 4.66 (d, *J* = 5.9 Hz, 1H), 3.69 (s, 3H), 3.36 (s, 3H), 2.44 (s, 3H), 1.59 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.2, 153.9, 133.6, 132.2, 131.8, 131.2, 130.4, 113.4, 112.6, 109.9, 85.9, 85.2, 82.2, 55.3, 28.9, 26.8, 25.3, 20.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{23}N_2O_5$ 347.1607; Found 347.1603.

3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1,6,7-trimethylquinoxalin-2(1*H*)-one(3da)



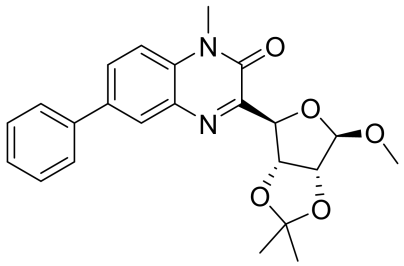
Colorless oil; 32.1 mg, 89% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (s, 1H), 7.07 (s, 1H), 5.56 (d, *J* = 1.9 Hz, 1H), 5.43 (dd, *J* = 5.9, 2.1 Hz, 1H), 5.11 (s, 1H), 4.66 (dd, *J* = 6.1, 1.9 Hz, 1H), 3.67 (s, 3H), 3.32 (s, 3H), 2.40 (s, 3H), 2.33 (s, 3H), 1.57 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 154.9, 154.0, 140.5, 132.6, 131.5, 130.7, 130.6, 114.2, 112.6, 109.9, 85.7, 85.3, 82.1, 55.1, 28.7, 26.8, 25.4, 20.6, 19.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{25}N_2O_5$ 361.1763; Found 361.1771.

3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1-methylbenzo[*g*]quinoxalin-2(1*H*)-one(3ea)



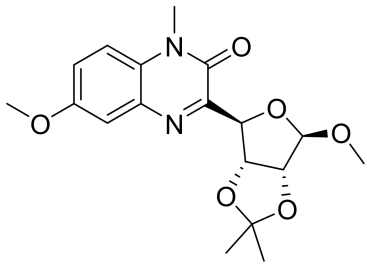
Yellow solid, mp: 79-81 °C; 36 mg, 94% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.36 (s, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.59 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 5.63 (d, *J* = 1.7 Hz, 1H), 5.49 (dd, *J* = 5.9, 1.6 Hz, 1H), 5.16 (s, 1H), 4.71 (d, *J* = 5.9 Hz, 1H), 3.76 (s, 3H), 3.38 (s, 3H), 1.61 (s, 3H), 1.42 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.9, 153.8, 133.8, 131.8, 131.6, 130.0, 129.7, 128.5, 128.1, 127.2, 125.4, 112.7, 110.0, 109.9, 85.8, 85.3, 82.2, 55.3, 28.8, 26.8, 25.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}N_2O_5$ 383.1607; Found 383.1601.

3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1-methyl-6-phenylquinoxalin-2(1*H*)-one(3fa)



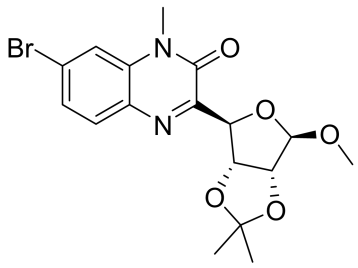
Yellow solid, mp: 99-101 °C; 38.1 mg, 93% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 2.2 Hz, 1H), 7.81 (dd, *J* = 2.2, 8.7 Hz, 1H), 7.65 – 7.62 (m, 2H), 7.49 – 7.45 (m, 2H), 7.40 – 7.36 (m, 2H), 5.61 (d, *J* = 1.6 Hz, 1H), 5.44 (dd, *J* = 5.9, 1.6 Hz, 1H), 5.16 (s, 1H), 4.68 (d, *J* = 5.9 Hz, 1H), 3.74 (s, 3H), 3.39 (s, 3H), 1.60 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.8, 153.8, 139.3, 136.9, 132.6, 132.5, 129.5, 129.1, 128.6, 127.7, 127.0, 114.1, 112.7, 109.9, 86.0, 85.2, 82.2, 55.3, 29.0, 26.8, 25.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{25}N_2O_5$ 409.1763; Found 409.1767.

6-methoxy-3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1-methylquinoxalin-2(1*H*)-one(3ga)



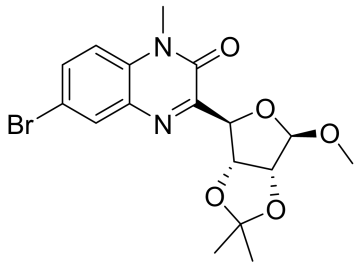
White solid, mp: 153-155 °C; 31.9 mg, 88% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 2.8 Hz, 1H), 7.23 (d, *J* = 9.1 Hz, 1H), 7.18 (dd, *J* = 9.1, 2.8 Hz, 1H), 5.58 (d, *J* = 1.6 Hz, 1H), 5.43 (dd, *J* = 5.9, 1.7 Hz, 1H), 5.13 (s, 1H), 4.67 (d, *J* = 5.9 Hz, 1H), 3.87 (s, 3H), 3.70 (s, 3H), 3.34 (s, 3H), 1.58 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.8, 156.0, 153.6, 133.0, 127.7, 119.7, 114.5, 112.7, 112.1, 109.9, 85.9, 85.2, 82.1, 55.8, 55.2, 29.0, 26.79, 25.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{23}N_2O_6$ 363.1556; Found 363.1553.

7-bromo-3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1-methylquinoxalin-2(1*H*)-one(3ha)



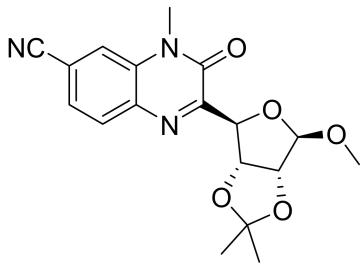
White solid, mp: 109-111 °C; 33.7 mg, 82% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.4 Hz, 1H), 7.47 – 7.43 (m, 2H), 5.54 (d, *J* = 1.6 Hz, 1H), 5.39 (dd, *J* = 6.0, 1.7 Hz, 1H), 5.13 (s, 1H), 4.65 (d, *J* = 5.9 Hz, 1H), 3.68 (s, 3H), 3.35 (s, 3H), 1.58 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.8, 153.6, 134.4, 131.8, 131.1, 127.0, 124.8, 116.8, 112.8, 109.9, 85.9, 85.2, 82.1, 55.3, 29.0, 26.8, 25.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}BrN_2O_5$ 411.0556; Found 411.0562.

6-bromo-3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1-methylquinoxalin-2(1*H*)-one(3ia)



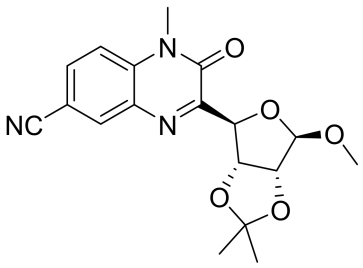
White solid, mp: 79-81 °C; 32.5 mg, 79% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 2.3 Hz, 1H), 7.64 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.19 (d, *J* = 8.9 Hz, 1H), 5.56 (d, *J* = 1.6 Hz, 1H), 5.37 (dd, *J* = 6.0, 1.6 Hz, 1H), 5.12 (s, 1H), 4.64 (d, *J* = 5.9 Hz, 1H), 3.69 (s, 3H), 3.35 (s, 3H), 1.58 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.8, 152.5, 132.3, 132.0, 131.9, 131.5, 115.3, 114.1, 111.7, 108.9, 84.8, 84.1, 81.1, 54.3, 28.0, 25.7, 24.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}BrN_2O_5$ 411.0556; Found 411.0551.

2-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-][1,3]dioxol-4-yl)-4-methyl-3-oxo-3,4-dihydroquinoxaline-6-carbonitrile(3ja)



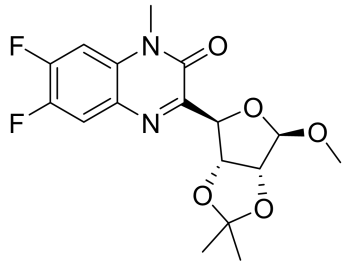
White solid, mp: 152-154 °C; 23.2 mg, 65% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.1 Hz, 1H), 7.62 – 7.58 (m, 2H), 5.57 (d, *J* = 1.6 Hz, 1H), 5.36 (dd, *J* = 5.9, 1.7 Hz, 1H), 5.14 (s, 1H), 4.63 (d, *J* = 5.9 Hz, 1H), 3.72 (s, 3H), 3.37 (s, 3H), 1.58 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.0, 152.3, 133.3, 132.8, 130.4, 125.6, 117.0, 116.9, 112.7, 111.9, 108.9, 85.0, 84.0, 81.0, 54.4, 28.1, 25.7, 24.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}N_3O_5$ 358.1403; Found 358.1407.

3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1-methyl-2-oxo-1,2-dihydroquinoxaline-6-carbonitrile(3ka)



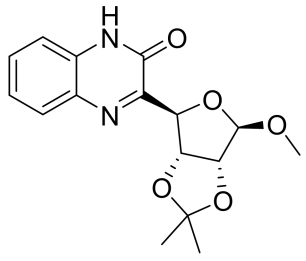
White solid, mp: 179-181 °C; 24.3 mg, 68% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 1.9 Hz, 1H), 7.78 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.41 (d, *J* = 8.7 Hz, 1H), 5.54 (d, *J* = 1.6 Hz, 1H), 5.34 (dd, *J* = 5.9, 1.6Hz, 1H), 5.12 (s, 1H), 4.62 (d, *J* = 5.9 Hz, 1H), 3.72 (s, 3H), 3.35 (s, 3H), 1.57 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.9, 153.5, 136.7, 134.8, 133.1, 131.8, 117.8, 114.9, 112.9, 110.0, 107.3, 85.8, 85.0, 82.0, 55.4, 29.2, 26.7, 25.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}N_3O_5$ 358.1403; Found 358.1396.

6,7-difluoro-3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-1-methylquinoxalin-2(1*H*)-one(3la)



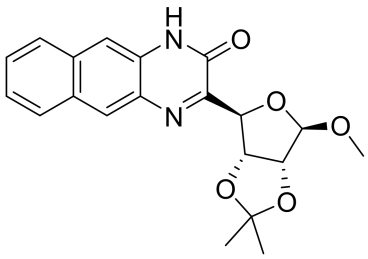
White solid, mp: 77-79 °C; 31.3 mg, 85% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (q, *J* = 10.1, 8.1 Hz, 1H), 7.12 (q, *J* = 11.2, 7.0 Hz, 1H), 5.53 (d, *J* = 1.6 Hz, 1H), 5.35 (dd, *J* = 5.9, 1.7 Hz, 1H), 5.12 (s, 1H), 4.63 (d, *J* = 5.9 Hz, 1H), 3.66 (s, 3H), 3.34 (s, 3H), 1.57 (s, 3H), 1.38 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -129.92 – 129.81(m), -141.82 – 141.71(m). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.0 (d, *J* = 3.5 Hz), 153.4, 151.7(dd, *J* = 254.3 Hz, 14.4 Hz), 146.7 (dd, *J* = 247.5, 14.0 Hz), 130.7 (dd, *J* = 9.1, 1.9 Hz), 128.5 (dd, *J* = 9.2, 2.9 Hz), 118.1 (dd, *J* = 17.9, 2.3 Hz), 112.8, 109.9, 102.4 (d, *J* = 23.3 Hz), 85.8, 85.1, 82.1, 55.3, 29.4, 26.7, 25.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{19}F_2N_2O_5$ 369.1262; Found 369.1269.

3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)quinoxalin-2(1*H*)-one(3ma)



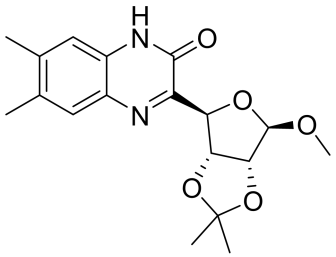
White solid, mp: 230-232 °C; 27.4 mg, 86% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.49 (s, 1H), 7.85 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.52 (td, *J* = 8.3, 1.4 Hz, 1H), 7.43 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.35 (td, *J* = 7.6, 1.4 Hz, 1H), 5.68 (d, *J* = 6.2 Hz, 1H), 5.66 (d, *J* = 1.2 Hz, 1H), 5.12 (s, 1H), 4.76 (d, *J* = 5.8 Hz, 1H), 3.22 (s, 3H), 1.61 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.5, 155.9, 132.2, 131.3, 130.8, 129.7, 124.4, 116.0, 112.5, 110.1, 85.6, 84.5, 81.6, 55.0, 26.7, 25.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{19}N_2O_5$ 319.1294; Found 319.1286.

3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)benzo[g]quinoxalin-2(1*H*)-one(3na)



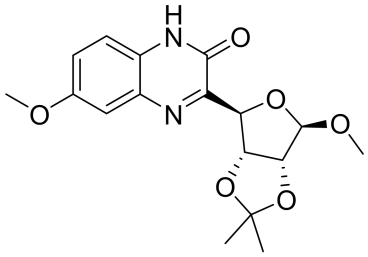
Yellow solid, mp: 219-221 °C; 33.9 mg, 92% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.04 (s, 1H), 8.36 (s, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.81 (s, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 5.75 (d, *J* = 5.7 Hz, 2H), 5.14 (s, 1H), 4.81 (d, *J* = 5.7 Hz, 1H), 3.22 (s, 3H), 1.65 (s, 3H), 1.46 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.1, 155.6, 134.1, 131.4, 130.3, 129.3, 129.1, 128.8, 128.1, 127.0, 125.3, 112.5, 111.9, 110.2, 85.7, 84.3, 81.5, 55.0, 26.8, 25.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}N_2O_5$ 369.1450; Found 369.1457.

3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-6,7-dimethylquinoxalin-2(1*H*)-one(3oa)



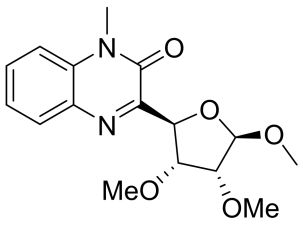
White solid, mp: 200-202 °C; 30.8 mg, 89% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.72 (s, 1H), 7.60 (s, 1H), 7.22 (s, 1H), 5.70 (d, *J* = 6.0 Hz, 1H), 5.68 (s, 1H), 5.10 (s, 1H), 4.77 (d, *J* = 5.8 Hz, 1H), 3.17 (s, 3H), 2.38 (s, 3H), 2.34 (s, 3H), 1.61 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.2, 155.0, 141.1, 133.5, 130.8, 129.5, 129.4, 116.3, 112.4, 110.1, 85.8, 84.2, 81.6, 54.8, 26.8, 25.3, 20.1, 19.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{23}N_2O_5$ 347.1607; Found 347.1604.

6-methoxy-3-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)quinoxalin-2(1*H*)-one(3pa)



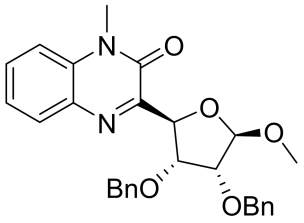
Yellow solid, mp: 194-196 °C; 28.9 mg, 83% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.76 (s, 1H), 7.37 (d, *J* = 8.9 Hz, 1H), 7.29 (d, *J* = 2.8 Hz, 1H), 7.17 (dd, *J* = 8.9, 2.8 Hz, 1H), 5.70 (dd, *J* = 6.0, 1.2 Hz, 1H), 5.66 (d, *J* = 1.2 Hz, 1H), 5.11 (s, 1H), 4.77 (d, *J* = 5.9 Hz, 1H), 3.88 (s, 3H), 3.20 (s, 3H), 1.61 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.7, 156.6, 155.7, 133.0, 125.6, 120.8, 117.0, 112.5, 110.5, 110.1, 85.7, 84.3, 81.5, 55.8, 54.9, 26.7, 25.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{21}N_2O_6$ 349.1400; Found 349.1405.

1-methyl-3-((2*R*,3*R*,4*R*,5*R*)-3,4,5-trimethoxytetrahydrofuran-2-yl)quinoxalin-2(1H)-one(4aa)



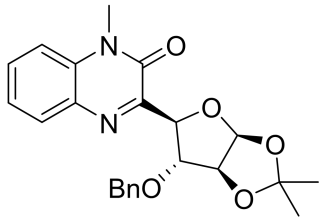
Colorless oil; 29.5 mg, 92% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.56 (td, *J* = 7.9, 1.6 Hz, 1H), 7.36 – 7.29 (m, 2H), 5.57 (d, *J* = 5.1 Hz, 1H), 5.10 (d, *J* = 2.8 Hz, 1H), 4.61 (t, *J* = 4.9 Hz, 1H), 3.92 (dd, *J* = 4.8, 2.8 Hz, 1H), 3.70 (s, 3H), 3.52 (s, 3H), 3.51 (s, 3H), 3.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 154.9, 153.5, 132.5, 131.4, 129.84, 129.81, 122.6, 112.6, 105.5, 81.6, 79.6, 77.9, 57.33, 57.28, 54.9, 28.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{21}N_2O_5$ 321.1450; Found 321.1445.

3-((2*R*,3*R*,4*R*,5*R*)-3,4-bis(benzyloxy)-5-methoxytetrahydrofuran-2-yl)-1-methylquinoxalin-2(1*H*)-one(4ab)



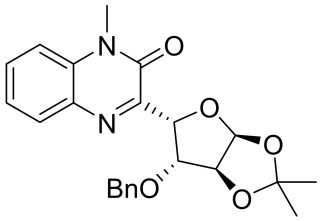
Colorless oil; 36.4 mg, 77% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.42– 7.39 (m, 2H), 7.37 – 7.19 (m, 10H), 5.69 (d, *J* = 5.5 Hz, 1H), 5.15 (d, *J* = 2.5 Hz, 1H), 4.85 (t, *J* = 5.1 Hz, 1H), 4.73 – 4.66(m, 4H), 4.08 (dd, *J* = 4.7, 2.4 Hz, 1H), 3.69 (s, 3H), 3.36 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.8, 154.5, 138.2, 138.0, 133.6, 132.4, 130.81, 130.78, 128.4, 128.2, 128.0, 127.9, 127.7, 127.6, 123.6, 113.6, 107.2, 80.7, 79.4, 78.6, 72.42, 72.39, 55.8, 29.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{29}N_2O_5$ 473.2076; Found 473.2071.

3-((3a*S*,5*R*,6*R*,6a*S*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)-1-methylquinoxalin-2(1*H*)-one(4ac)



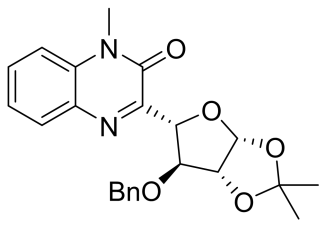
Colorless oil; 19.9 mg, 49% yield. ^{1}H NMR (400 MHz, Chloroform-*d*, major diastereomer) δ 7.97 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.57 (td, *J* = 8.6, 1.5 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.39 – 7.28 (m, 5H), 6.17 (d, *J* = 3.6 Hz, 1H), 5.65 (d, *J* = 1.9 Hz, 1H), 4.98 (d, *J* = 11.7 Hz, 1H), 4.85 (d, *J* = 11.7 Hz, 1H), 4.70 – 4.68 (m, 2H), 3.72 (s, 3H), 1.46 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*, major diastereomer) δ 154.4, 153.0, 136.9, 132.4, 131.3, 129.5, 129.4, 127.3, 126.9, 126.7, 122.9, 112.6, 112.1, 105.9, 83.9, 83.4, 82.6, 71.1, 27.8, 25.2, 25.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{25}N_2O_5$ 409.1763; Found 409.1771.

3-((3a*S*,5*S*,6*R*,6a*S*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)-1-methylquinoxalin-2(1*H*)-one(4ac')



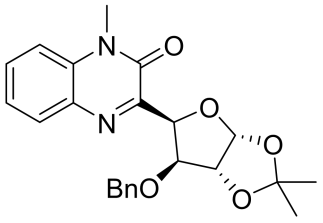
Colorless oil; 13.2 mg, 32% yield. ^{1}H NMR (400 MHz, Chloroform-*d*, minor diastereomer) δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.14 – 7.11 (m, 1H), 7.07 (t, *J* = 7.3 Hz, 2H), 6.95 (d, *J* = 7.3 Hz, 2H), 6.27 (d, *J* = 3.8 Hz, 1H), 5.65 (d, *J* = 3.5 Hz, 1H), 4.77 (d, *J* = 3.5 Hz, 1H), 4.70 (d, *J* = 3.8 Hz, 1H), 4.56 (d, *J* = 12.2 Hz, 1H), 4.32 (d, *J* = 12.2 Hz, 1H), 3.58 (s, 3H), 1.55 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*, minor diastereomer) δ 153.4, 152.4, 136.5, 131.8, 131.7, 129.8, 129.2, 127.0, 126.5, 126.4, 122.7, 112.4, 111.1, 104.1, 82.7, 82.0, 79.1, 71.3, 27.7, 26.0, 25.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{25}N_2O_5$ 409.1763; Found 409.1760.

3-((3a*R*,5*S*,6*S*,6a*R*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)-1-methylquinoxalin-2(1*H*)-one(4ad)



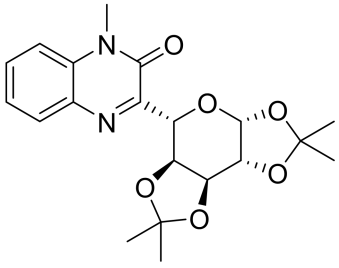
Colorless oil; 20.3 mg, 50% yield. ^{1}H NMR (600 MHz, Chloroform-*d*, major diastereomer) δ 7.97 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.57 (td, *J* = 7.8, 1.5 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.38 – 7.33 (m, 4H), 7.28 (d, *J* = 7.5 Hz, 1H), 6.17 (d, *J* = 3.6 Hz, 1H), 5.65 (d, *J* = 1.9 Hz, 1H), 4.97 (d, *J* = 11.7 Hz, 1H), 4.85 (d, *J* = 11.7 Hz, 1H), 4.70 – 4.68 (m, 2H), 3.72 (s, 3H), 1.46 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*, major diastereomer) δ 155.4, 154.0, 137.9, 133.4, 132.3, 130.51, 130.46, 128.4, 127.9, 127.7, 123.9, 113.7, 113.1, 106.9, 84.9, 84.4, 83.6, 72.2, 28.9, 26.2, 26.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{25}N_2O_5$ 409.1763; Found 409.1756.

3-((3a*R*,5*R*,6*S*,6a*R*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)-1-methylquinoxalin-2(1*H*)-one(4ad')



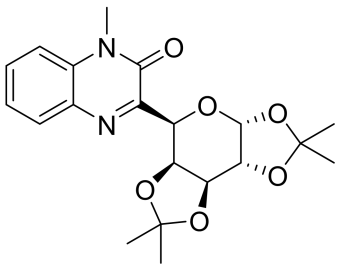
Colorless oil; 13.6 mg, 33% yield. ^{1}H NMR (600 MHz, Chloroform-*d*, minor diastereomer) δ 8.08 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.57 (td, *J* = 7.9, 1.5 Hz, 1H), 7.37 (td, *J* = 7.7, 1.2 Hz, 1H), 7.30 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.15 – 7.12 (m, 1H), 7.08 – 7.06 (m, 2H), 6.96 – 6.94 (m, 2H), 6.27 (d, *J* = 3.8 Hz, 1H), 5.66 (d, *J* = 3.5 Hz, 1H), 4.77 (d, *J* = 3.6 Hz, 1H), 4.70 (d, *J* = 3.8 Hz, 1H), 4.56 (d, *J* = 12.3 Hz, 1H), 4.33 (d, *J* = 12.3 Hz, 1H), 3.58 (s, 3H), 1.55 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*, minor diastereomer) δ 154.3, 153.4, 137.5, 132.8, 132.7, 130.8, 130.3, 128.0, 127.5, 127.4, 123.8, 113.4, 112.1, 105.1, 83.7, 83.0, 80.1, 72.3, 28.7, 27.0, 26.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{25}N_2O_5$ 409.1763; Found 409.1761.

1-methyl-3-((3a*R*,5*S*,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)quinoxalin-2(1*H*)-one(4ae)



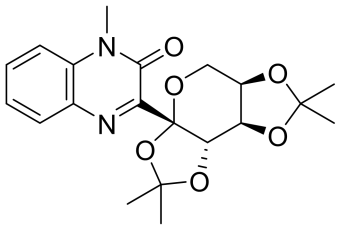
Colorless oil; 17.5 mg, 45% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.35 – 7.30 (m, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 5.55 (d, *J* = 2.5 Hz, 1H), 5.09 (dd, *J* = 9.9, 5.1 Hz, 1H), 5.01 (d, *J* = 10.0 Hz, 1H), 4.72 (d, *J* = 5.1 Hz, 1H), 4.37 (d, *J* = 2.2 Hz, 1H), 3.68 (s, 3H), 1.53 (s, 3H), 1.50 (s, 3H), 1.40 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 154.7, 154.0, 133.6, 132.5, 131.13, 131.08, 123.6, 113.5, 111.1, 109.1, 97.8, 77.3, 76.2, 74.7, 70.4, 69.2, 29.2, 28.0, 26.0, 25.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{25}N_2O_6$ 389.1713; Found 389.1719.

1-methyl-3-((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)quinoxalin-2(1H)-one(4ae')



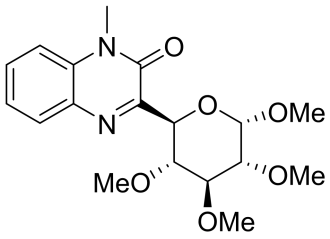
Colorless oil; 17.4 mg, 45% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.34 (td, *J* = 7.7, 1.2 Hz, 1H), 7.30 (dd, *J* = 8.4, 1.2 Hz, 1H), 5.90 (d, *J* = 5.1 Hz, 1H), 5.46 (d, *J* = 2.3 Hz, 1H), 5.02 (dd, *J* = 7.7, 2.3 Hz, 1H), 4.75 (dd, *J* = 7.7, 2.5 Hz, 1H), 4.47 (dd, *J* = 5.2, 2.6 Hz, 1H), 3.68 (s, 3H), 1.59 (s, 3H), 1.44 (s, 3H), 1.37 (s, 3H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 154.5, 153.6, 133.0, 132.9, 130.8, 130.2, 123.7, 113.5, 109.8, 109.0, 97.1, 71.9, 71.2, 70.7, 68.2, 28.9, 26.1, 25.9, 25.0, 24.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{25}N_2O_6$ 389.1713; Found 389.1712.

1-methyl-3-((3aS,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)quinoxalin-2(1*H*)-one(4af)



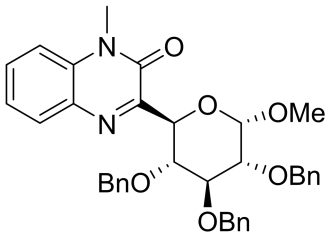
Colorless oil; 33.8 mg, 87% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.35 – 7.30 (m, 2H), 5.73 (d, *J* = 2.4 Hz, 1H), 4.75 (dd, *J* = 8.0, 2.3 Hz, 1H), 4.32 (d, *J* = 8.0 Hz, 1H), 4.14 (dd, *J* = 12.9, 2.1 Hz, 1H), 3.96 (d, *J* = 13.0 Hz, 1H), 3.71 (s, 3H), 1.62 (s, 3H), 1.33 (s, 3H), 1.27 (s, 3H), 1.20 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.2, 152.8, 134.0, 131.1, 130.9, 123.4, 113.5, 109.0, 108.7, 103.1, 70.9, 70.5, 70.2, 61.4, 29.0, 26.3, 25.9, 25.1, 24.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{25}N_2O_6$ 389.1713; Found 389.1721.

1-methyl-3-((2*R*,3*R*,4*S*,5*R*,6S)-3,4,5,6-tetramethoxytetrahydro-2*H*-pyran-2-yl)quinoxalin-2(1*H*)-one(4ag)



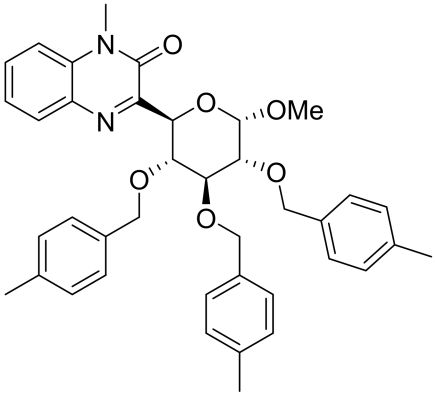
White solid, mp: 113-115 °C; 32.4 mg, 89% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.60 (td, *J* = 7.9, 1.5 Hz, 1H), 7.37 (td, *J* = 8.3, 1.2 Hz, 1H), 7.33 (dd, *J* = 8.5, 1.2 Hz, 1H), 5.29 (d, *J* = 10.1 Hz, 1H), 4.91 (d, *J* = 3.5 Hz, 1H), 4.01 (dd, *J* = 10.1, 9.0 Hz, 1H), 3.76 (t, *J* = 9.3 Hz, 1H), 3.72 (s, 3H), 3.68 (s, 3H), 3.62 (s, 3H), 3.56 (s, 3H), 3.46 (s, 3H), 3.39 (dd, *J* = 9.7, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.1, 154.9, 133.7, 132.4, 131.1, 130.7, 123.7, 113.7, 98.2, 83.9, 81.9, 80.5, 67.1, 61.0, 60.3, 59.1, 55.7, 29.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{25}N_2O_6$ 365.1713; Found 365.1718.

1-methyl-3-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)quinoxalin-2(1*H*)-one(4ah)



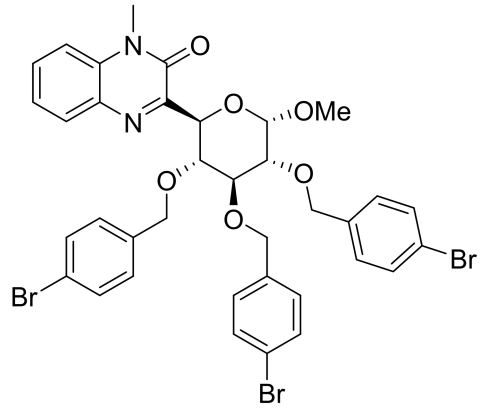
White solid, mp: 85-87 °C; 50.4 mg, 85% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.33 – 7.29 (m, 4H), 7.27 – 7.13 (m, 8H), 6.86 (s, 5H), 5.31 (d, *J* = 8.9 Hz, 1H), 4.96 (d, *J* = 10.9 Hz, 1H), 4.82 (d, *J* = 10.9 Hz, 1H), 4.76 (dd, *J* = 11.9, 2.6 Hz, 2H),4.63 (d, *J* = 10.2 Hz, 1H), 4.61 (s, 1H), 4.50 (d, *J* = 11.6 Hz, 1H), 4.20 – 4.12 (m, 2H), 3.64 (dd, *J* = 9.3, 3.5 Hz, 1H), 3.52 (s, 3H), 3.47 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 155.2, 154.6, 138.9, 138.4, 138.2, 133.6, 132.3, 131.0, 130.6, 128.5, 128.4, 128.2, 128.0, 127.9, 127.8, 127.59, 127.57, 127.0, 123.6, 113.6, 98.8, 82.5, 79.8, 79.6, 75.9, 74.7, 73.5, 55.6, 29.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{36}H_{37}N_2O_6$ 593.2652; Found 593.2645.

3-((2*R*,3*R*,4*S*,5*R*,6*S*)-6-methoxy-3,4,5-tris((4-methylbenzyl)oxy)tetrahydro-2*H*-pyran-2-yl)-1-methylquinoxalin-2(1*H*)-one(4ai)



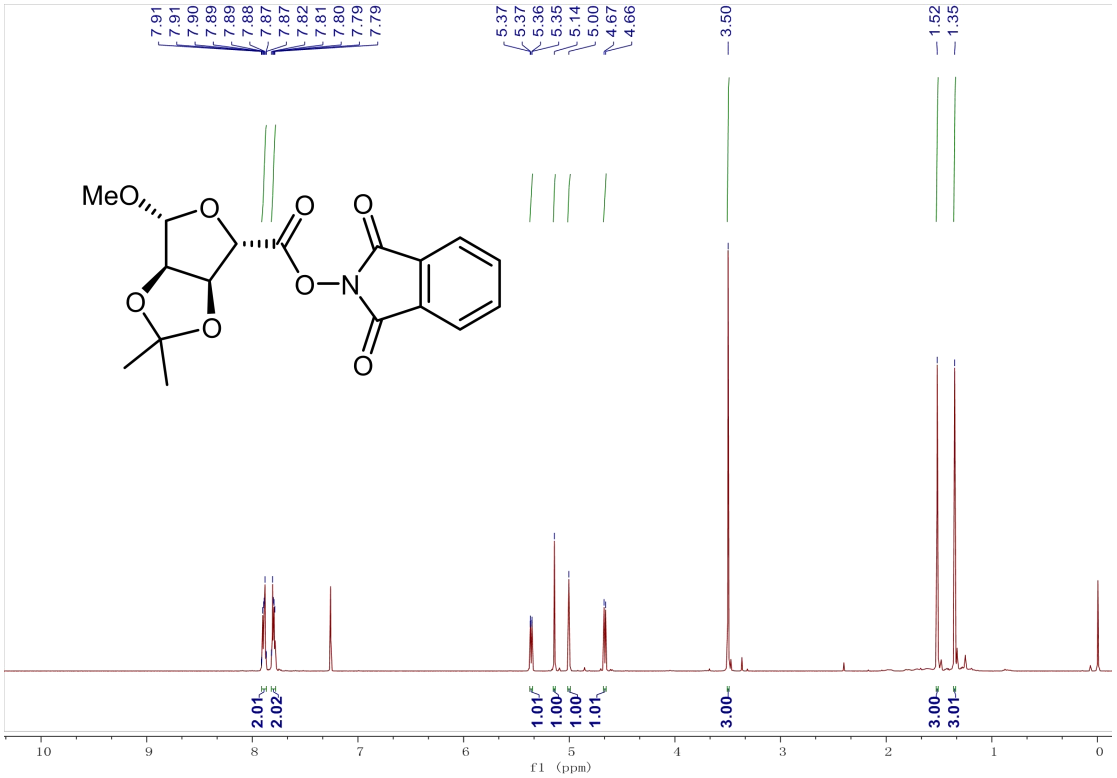
White solid, mp: 93-95 °C; 55.8 mg, 88% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.35 – 7.30 (m, 5H), 7.24 (d, *J* = 8.3 Hz, 1H), 7.16 (t, *J* = 7.3 Hz, 4H), 6.85 (d, *J* = 7.7 Hz, 2H), 6.75 (d, *J* = 7.7 Hz, 2H), 5.40 – 5.38 (m, 1H), 5.02 (d, *J* = 10.6 Hz, 1H), 4.90 – 4.81 (m, 3H), 4.71 – 4.67 (m, 2H), 4.56 (d, *J* = 11.5 Hz, 1H), 4.26 – 4.20 (m, 2H), 3.73 – 3.70 (m, 1H), 3.61 (s, 3H), 3.55 (s, 3H), 2.37 (s, 3H), 2.36 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.4, 154.6, 137.6, 137.2, 136.7, 136.0, 135.5, 135.3, 133.6, 132.4, 130.9, 130.6, 129.2, 129.1, 128.5, 128.4, 128.3, 127.8, 123.5, 113.5, 99.0, 82.5, 79.58, 79.55, 77.4, 75.8, 74.5, 73.4, 55.6, 29.0, 21.3, 21.2, 21.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{39}H_{43}N_2O_6$ 635.3121; Found 635.3114.

1-methyl-3-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris((4-bromobenzyl)oxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)quinoxalin-2(1*H*)-one(4aj)

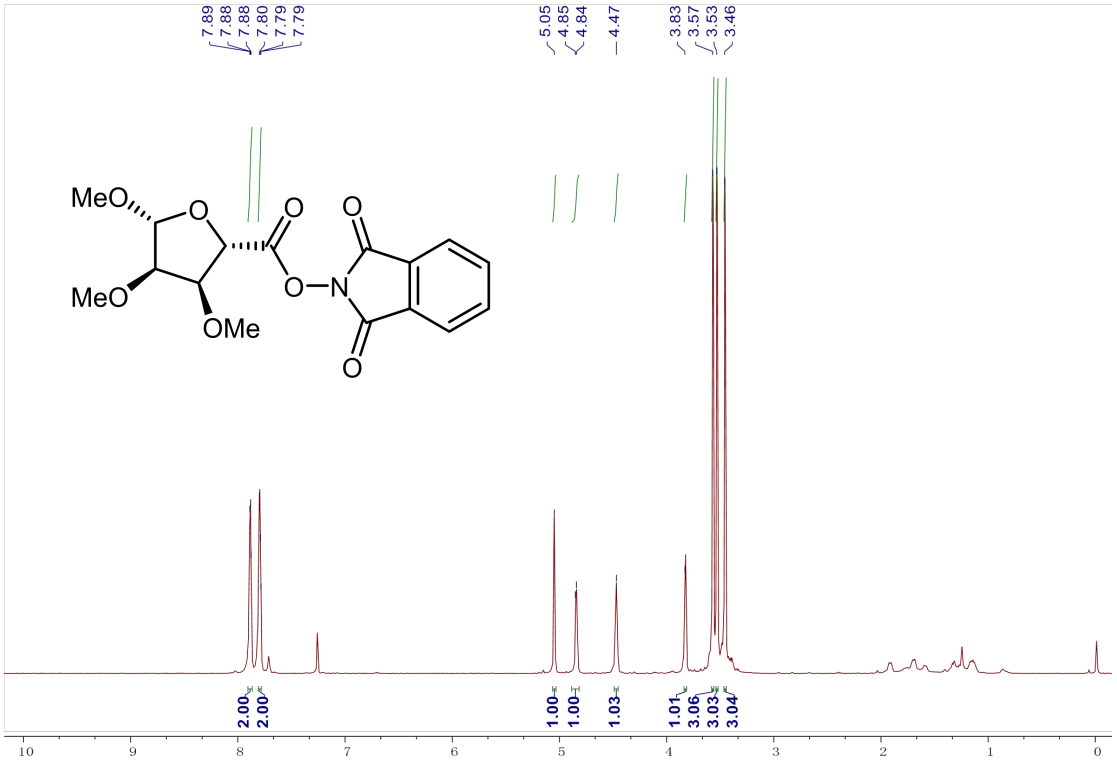


White solid, mp: 101-103 °C; 68.8 mg, 83% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.43 (dd, *J* = 8.2, 1.5 Hz, 4H), 7.37 – 7.33 (m, 1H), 7.28 – 7.26 (m, 1H), 7.23 – 7.18 (m, 4H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 2H), 5.30 (d, *J* = 9.0 Hz, 1H), 4.91 (d, *J* = 11.5 Hz, 1H), 4.79 (d, *J* = 11.5 Hz, 1H), 4.74 (d, *J* = 3.4 Hz, 1H), 4.71 – 4.63 (m, 3H), 4.47 (d, *J* = 12.3 Hz, 1H), 4.23 (t, *J* = 9.4 Hz, 1H), 4.14 (t, *J* = 9.2 Hz, 1H), 3.68 (dd, *J* = 9.5, 3.4 Hz, 1H), 3.60 (s, 3H), 3.54 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 154.8, 154.4, 137.8, 137.4, 137.1, 133.5, 132.2, 131.6, 131.5, 131.3, 130.9, 130.4, 129.7, 129.4, 129.2, 123.8, 121.9, 121.5, 121.1, 113.7, 98.5, 82.3, 79.8, 77.3, 74.9, 73.9, 72.5, 55.7, 29.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{36}H_{34}Br_3N_2O_6$ 826.9967; Found 826.9976.

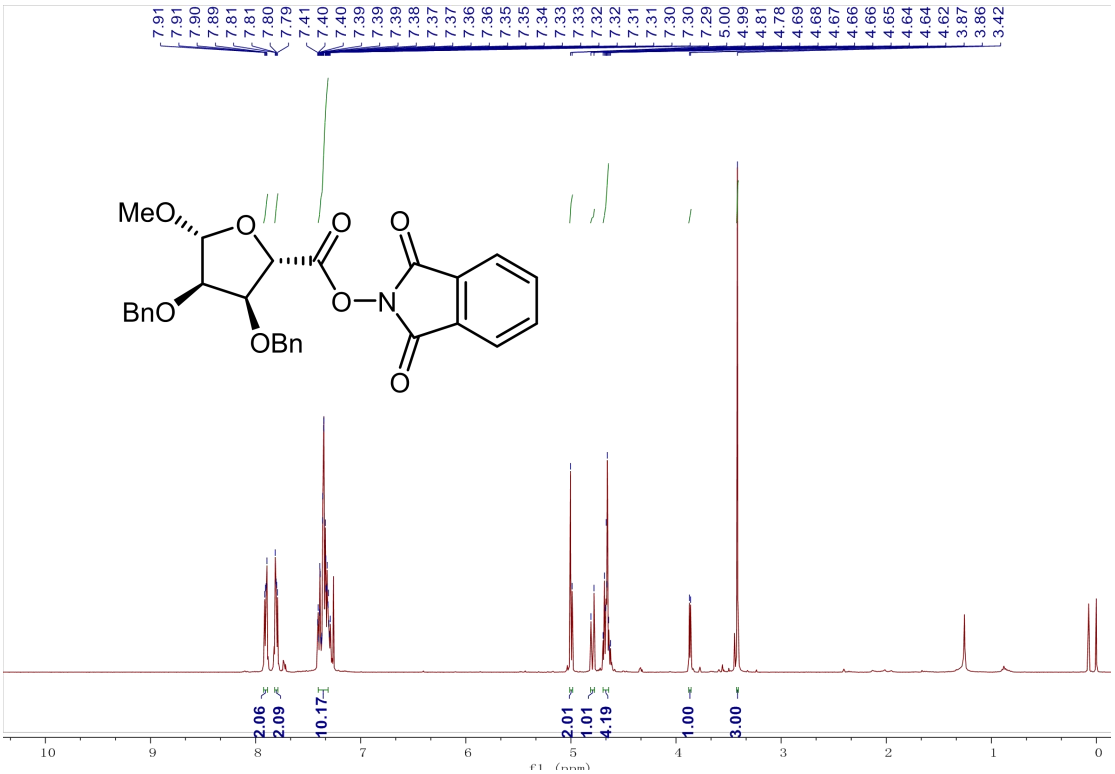
14. NMR spectra of compounds



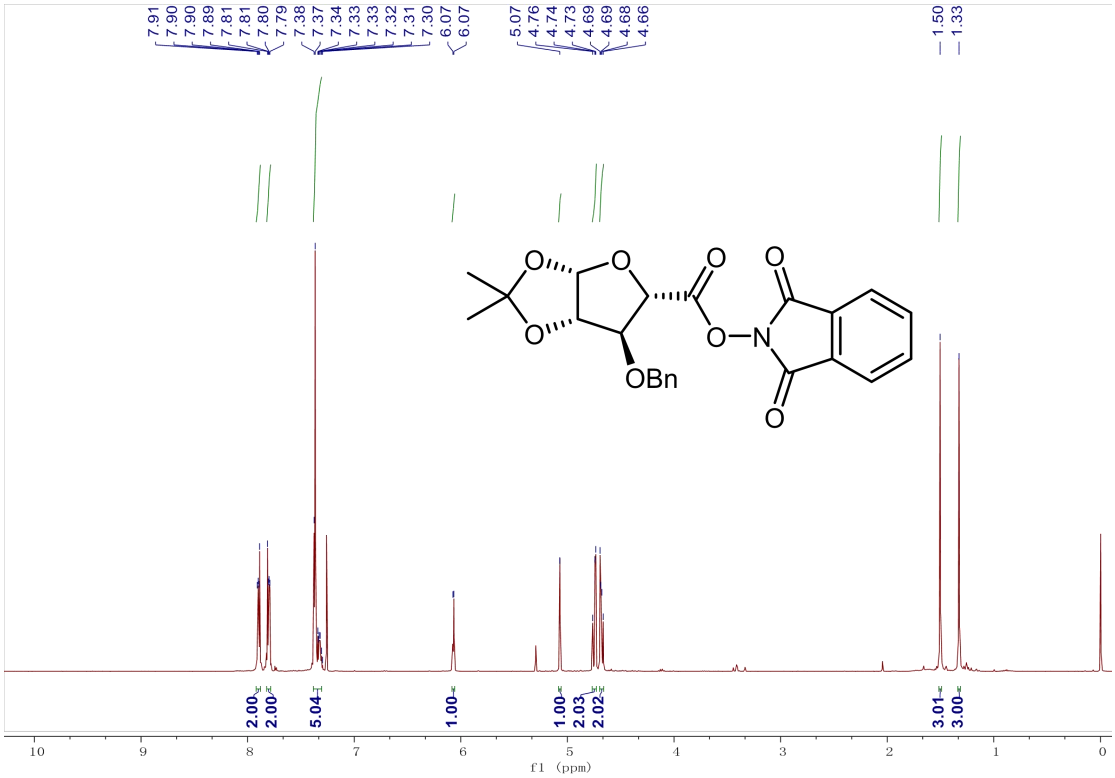
S1. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2a**



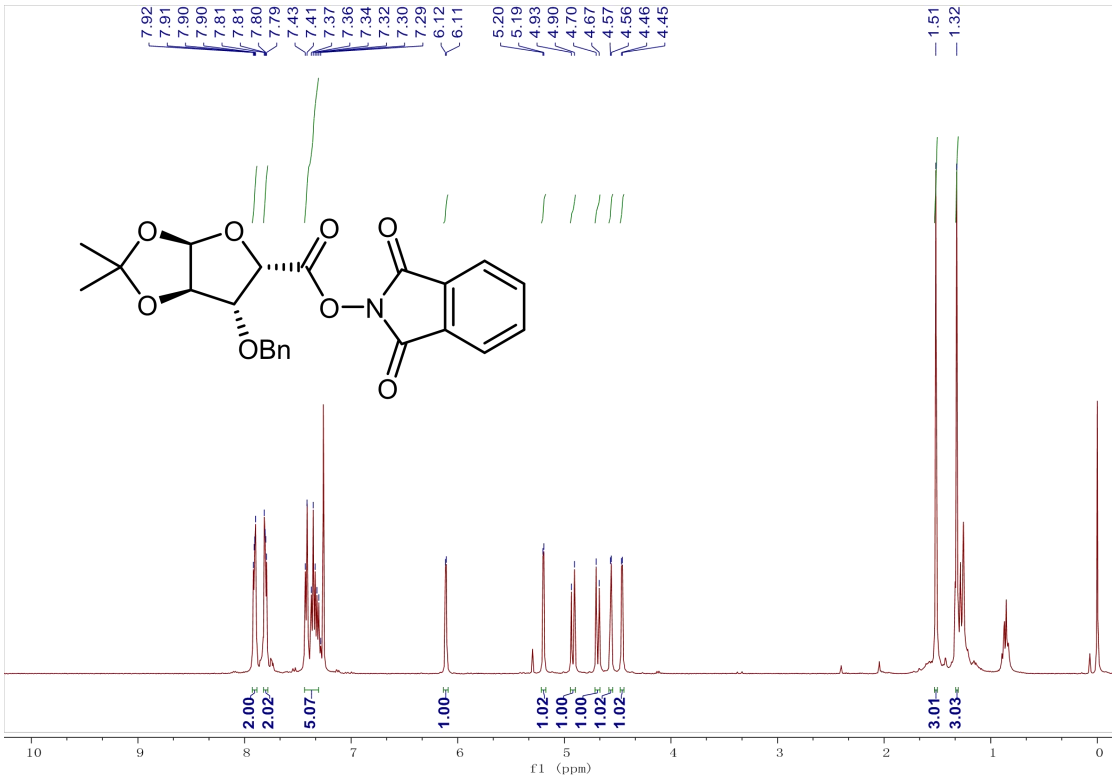
S2. ^{1}H NMR spectra (600 MHz, $CDCl_3$) of compound **2b**



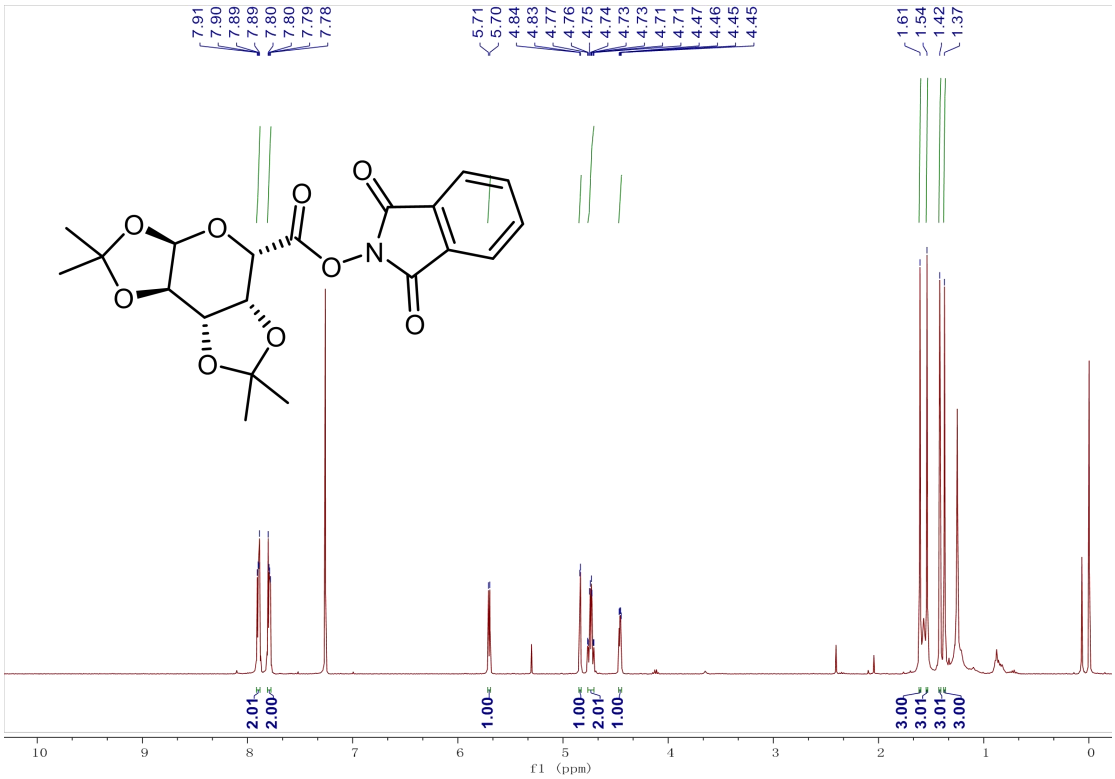
S3. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2c**



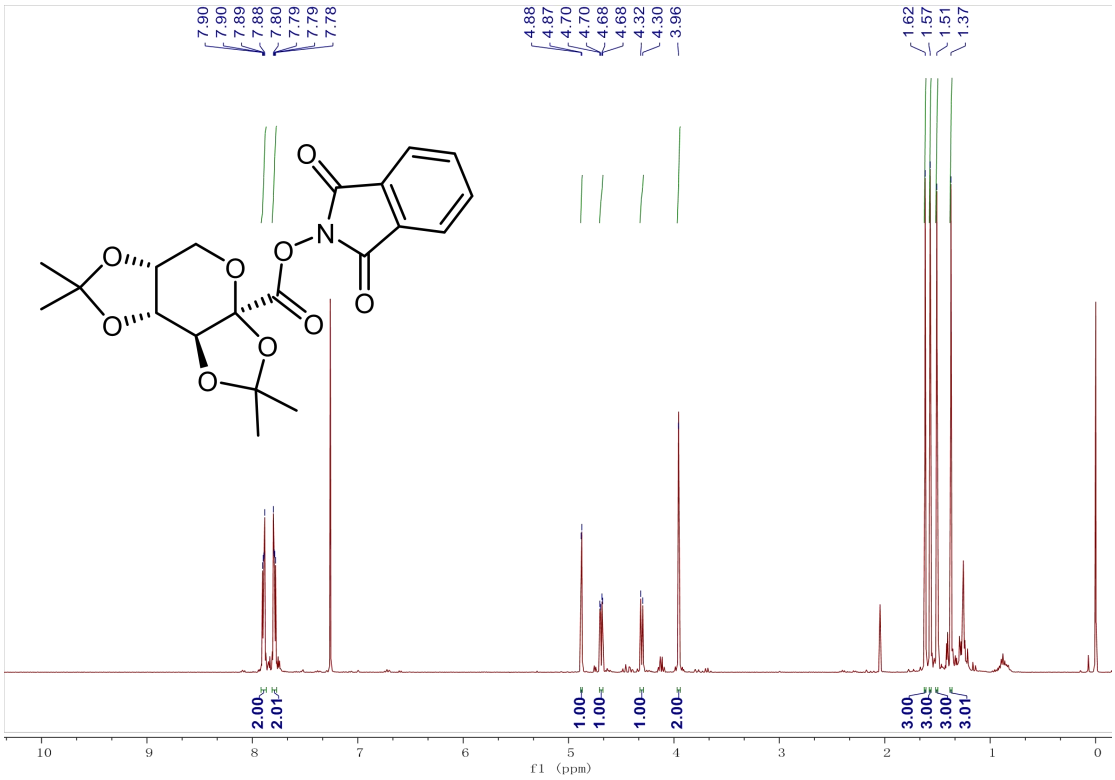
S4. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2d**



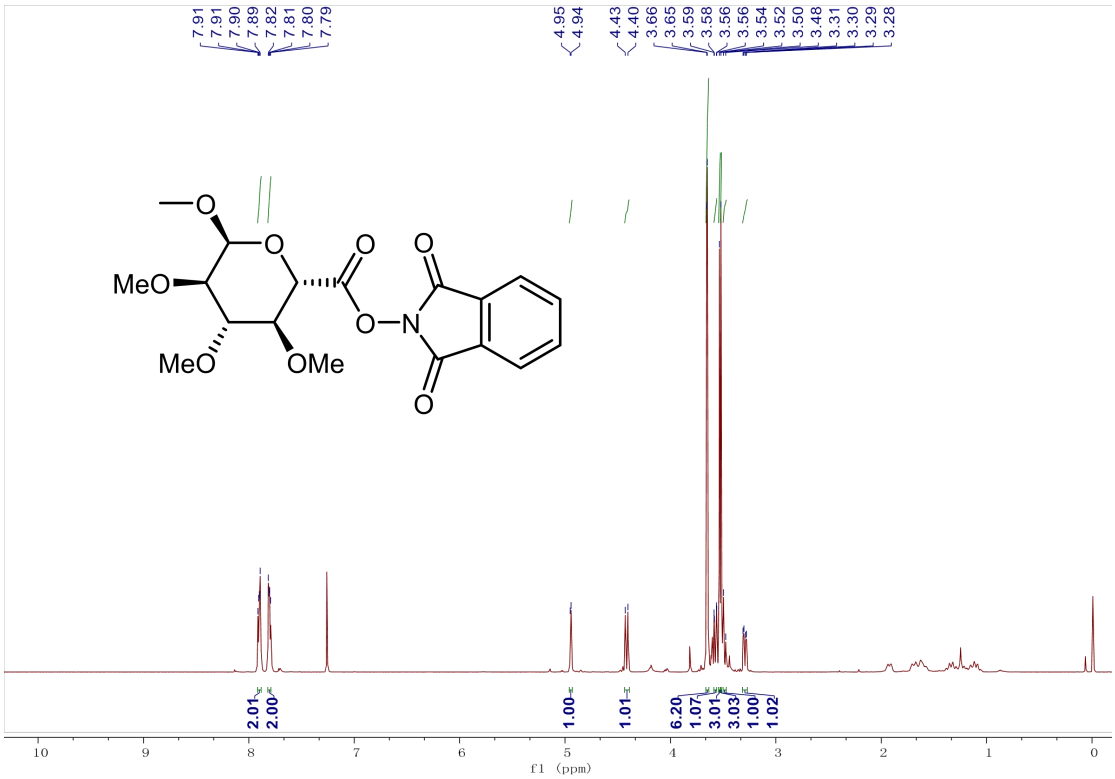
S5. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2e**



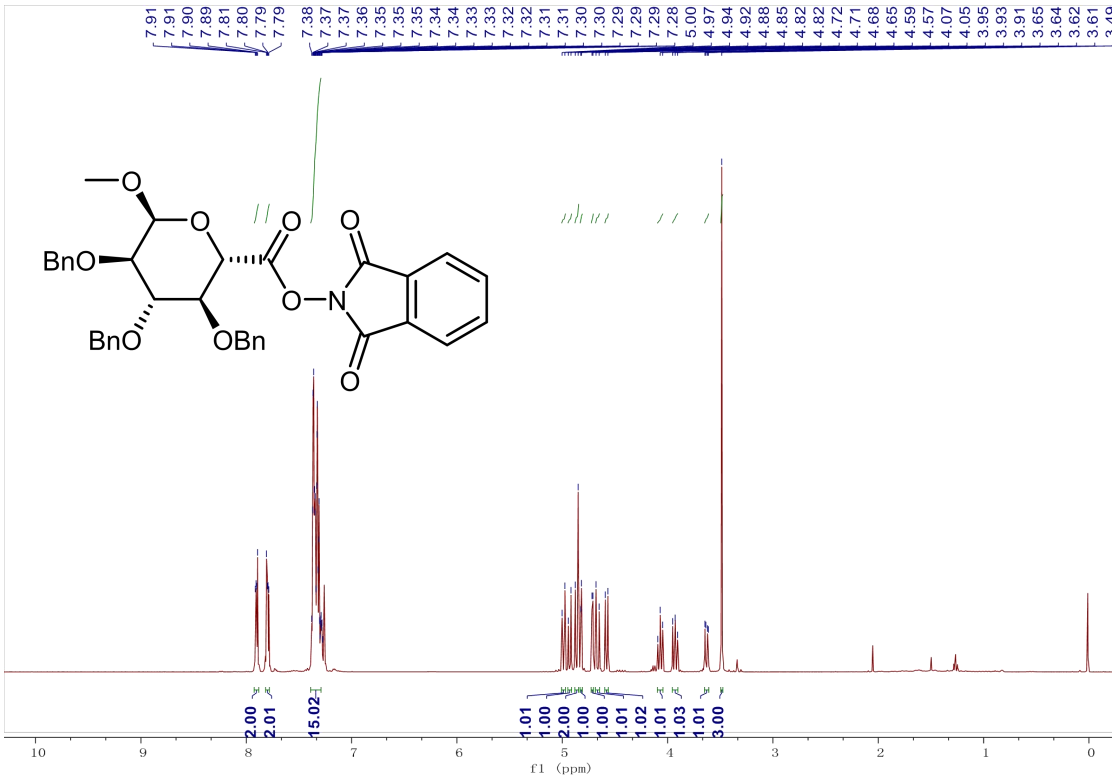
S6. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2f**



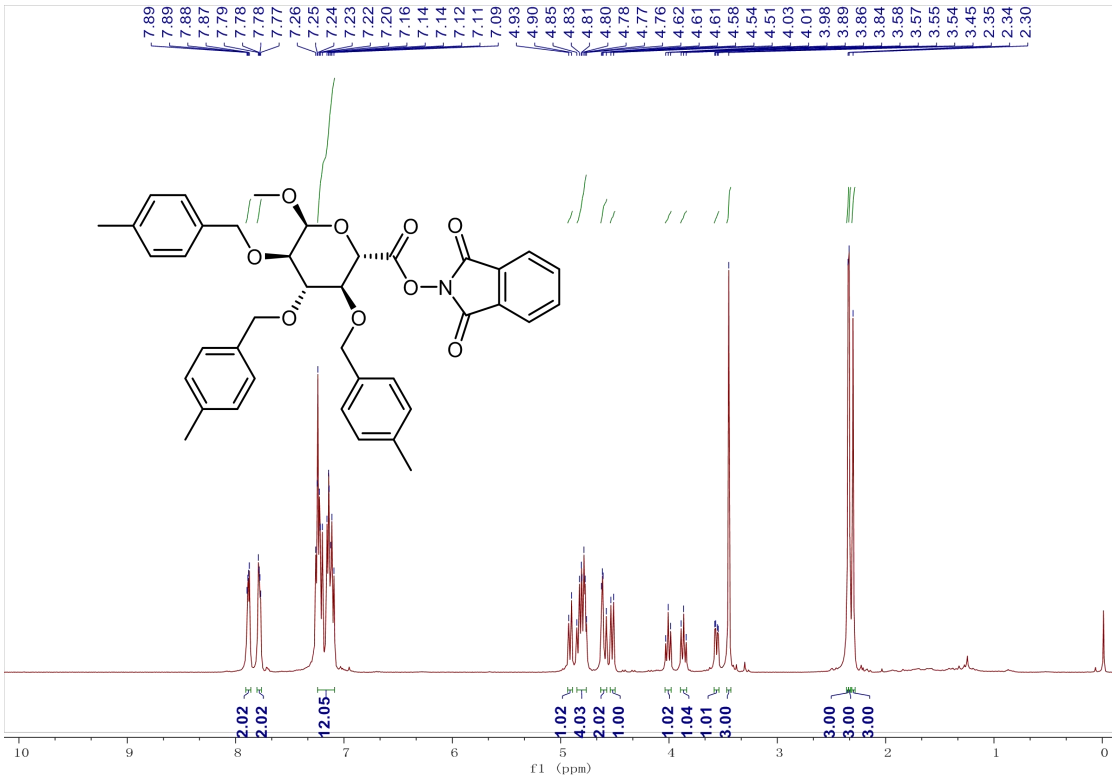
S7. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2g**



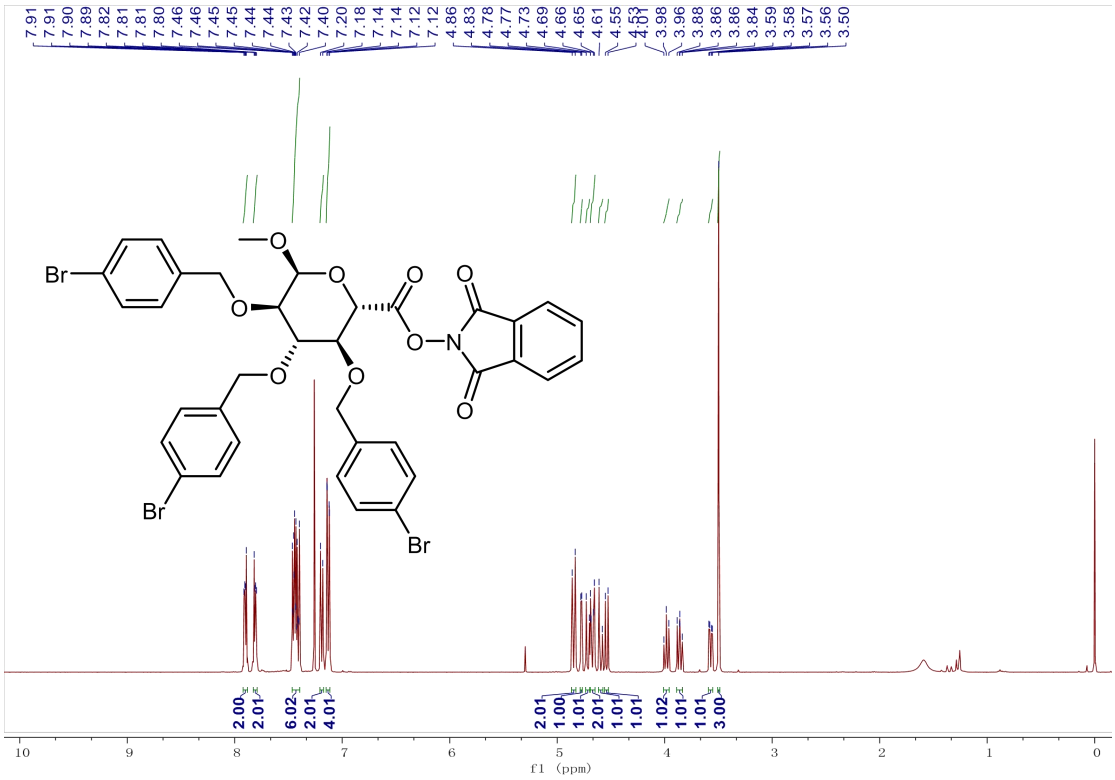
S8. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2h**



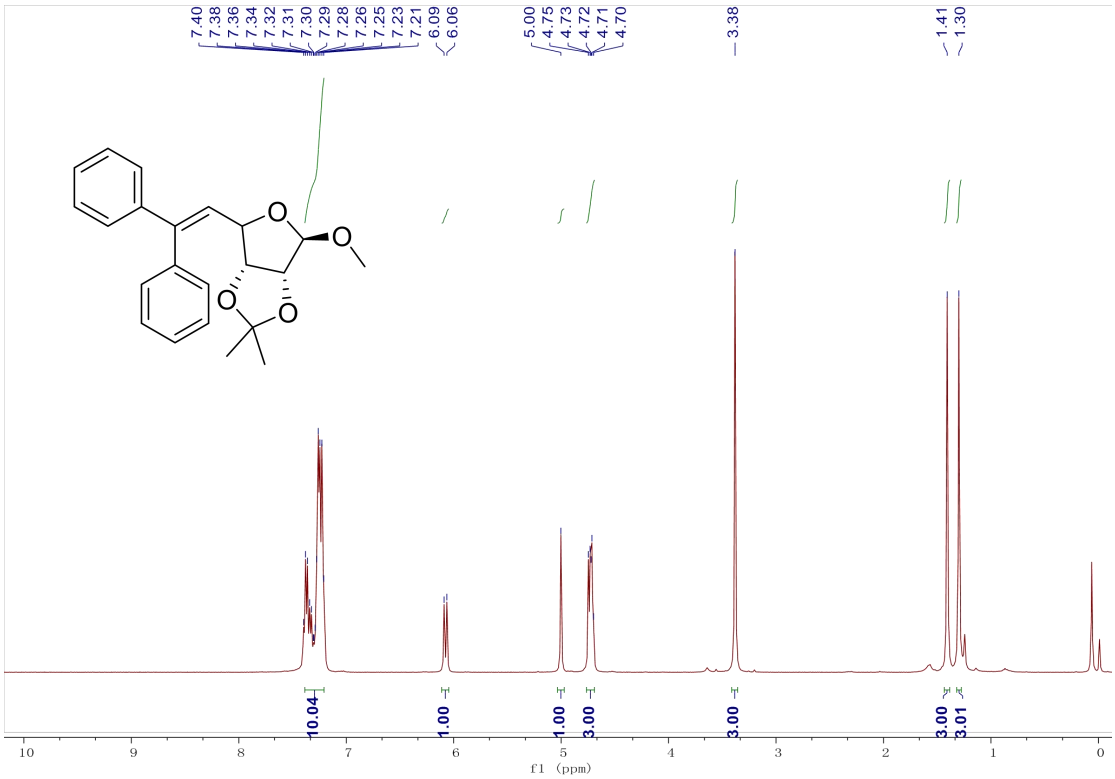
S9. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2i**



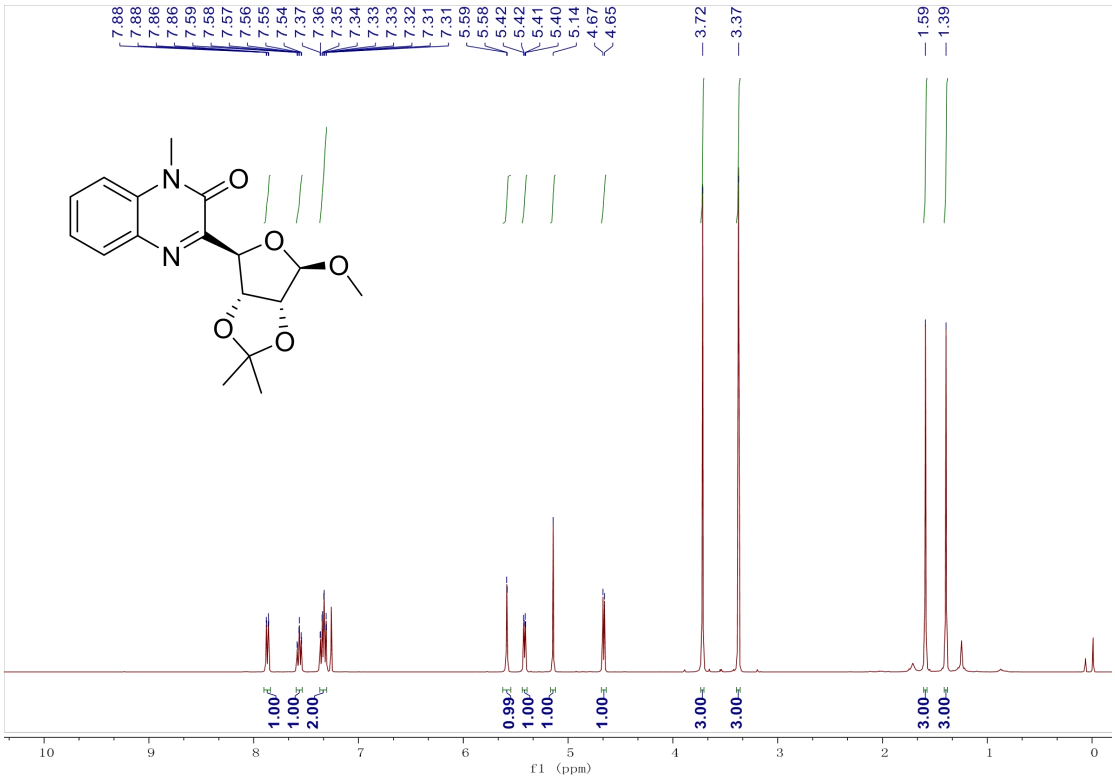
S10. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2j**



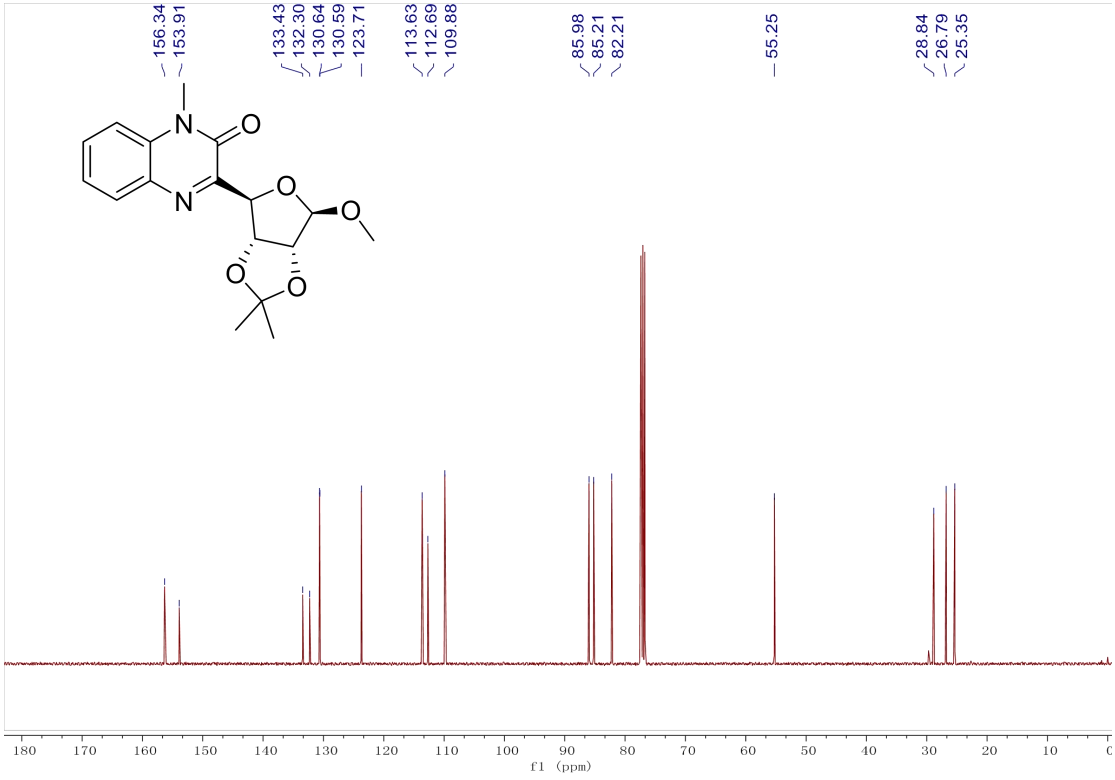
S11. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2k**



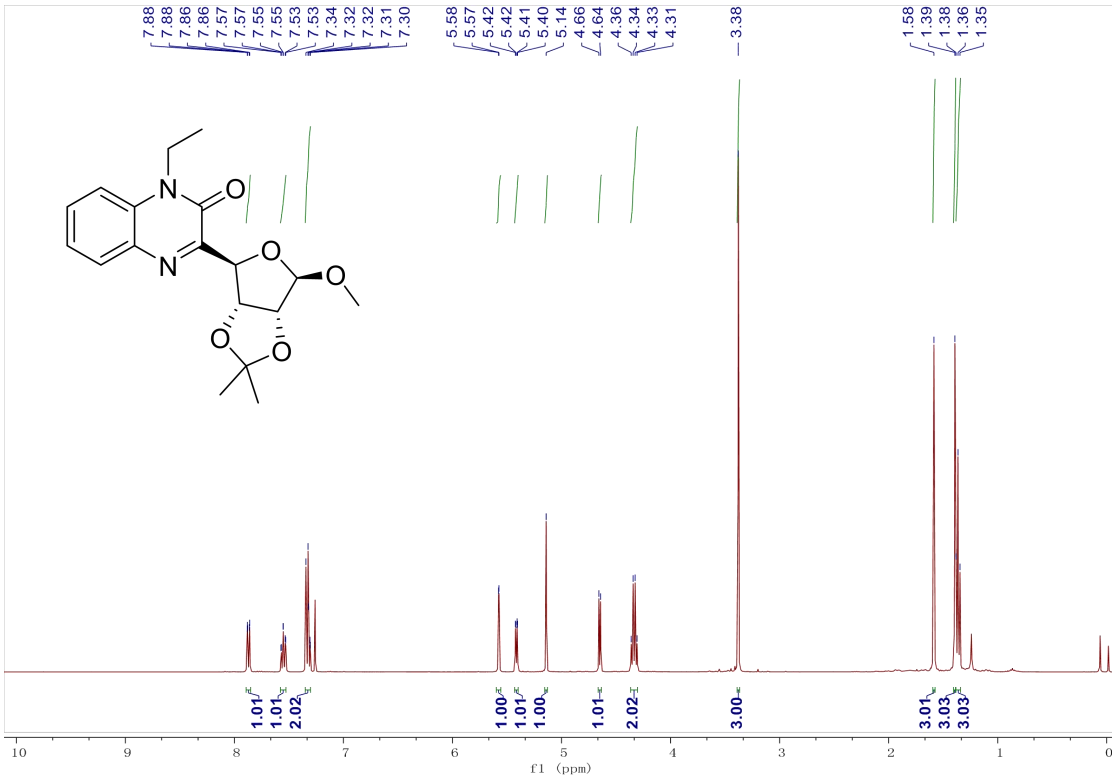
S12. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5**



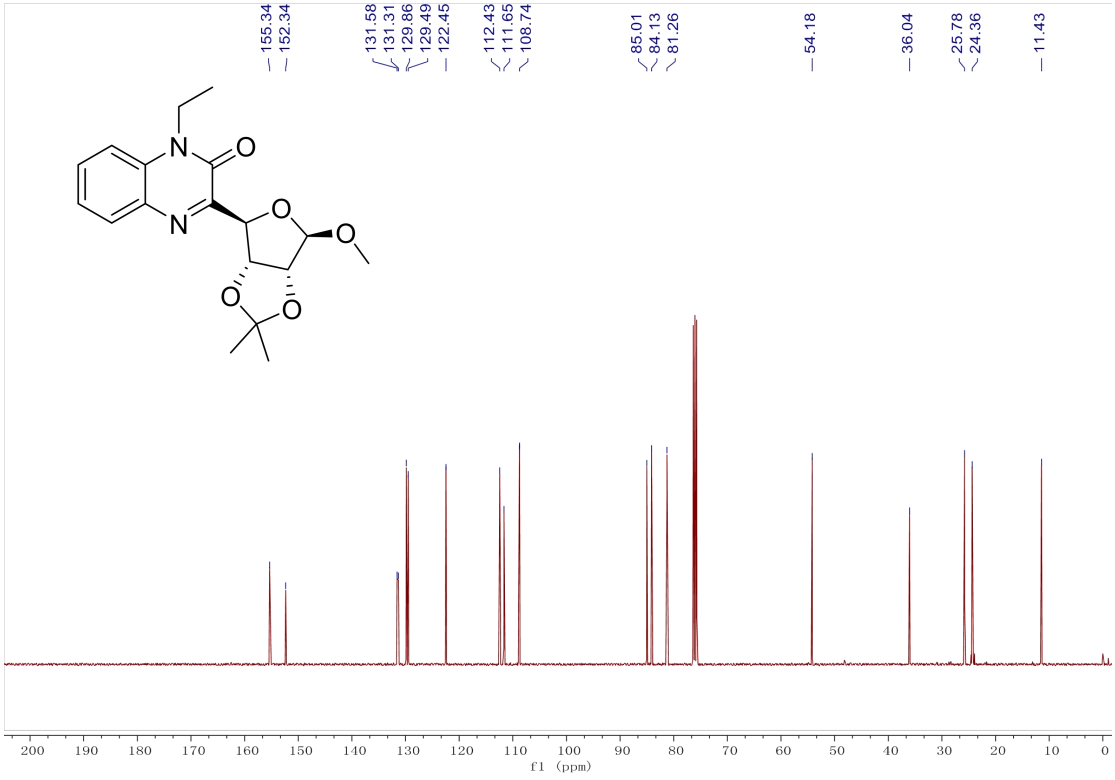
S13. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3aa**



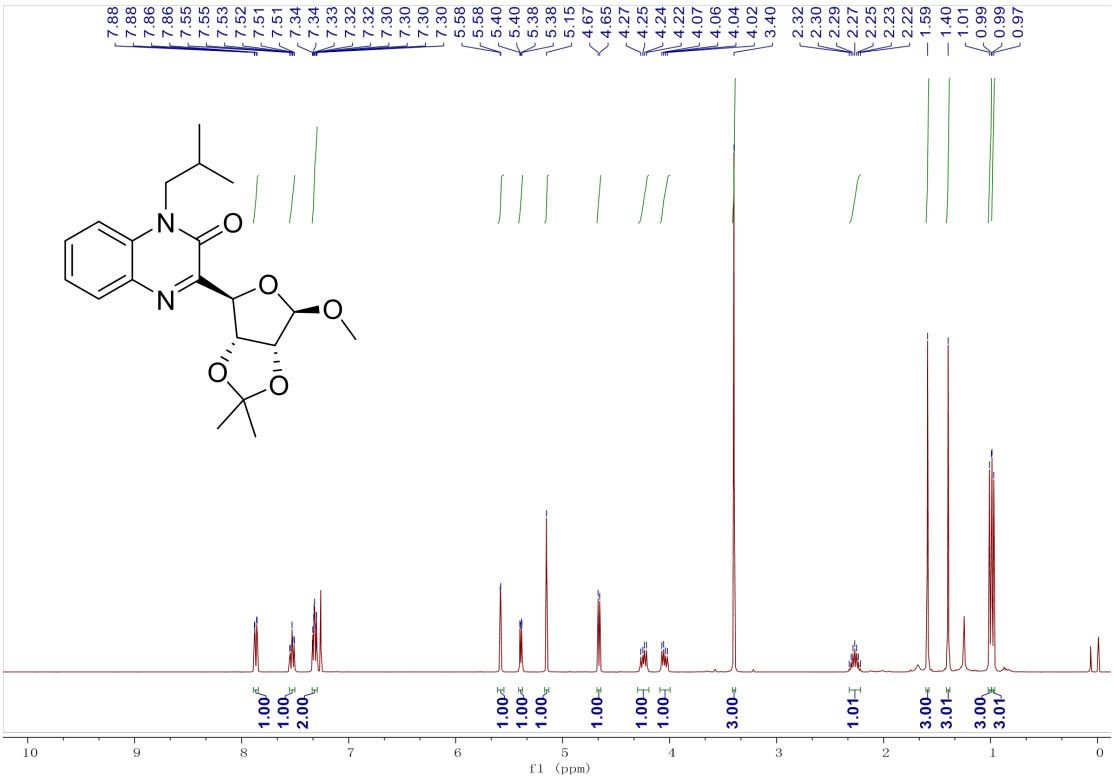
S14. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3aa**



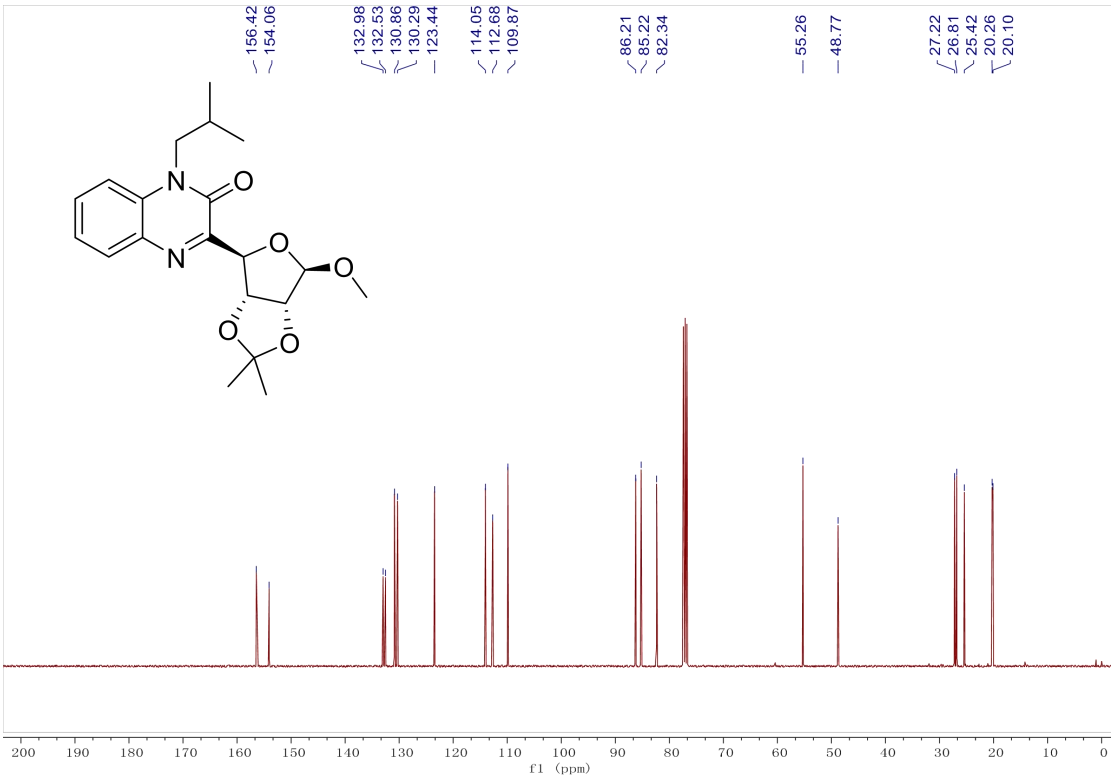
S15. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3ab**



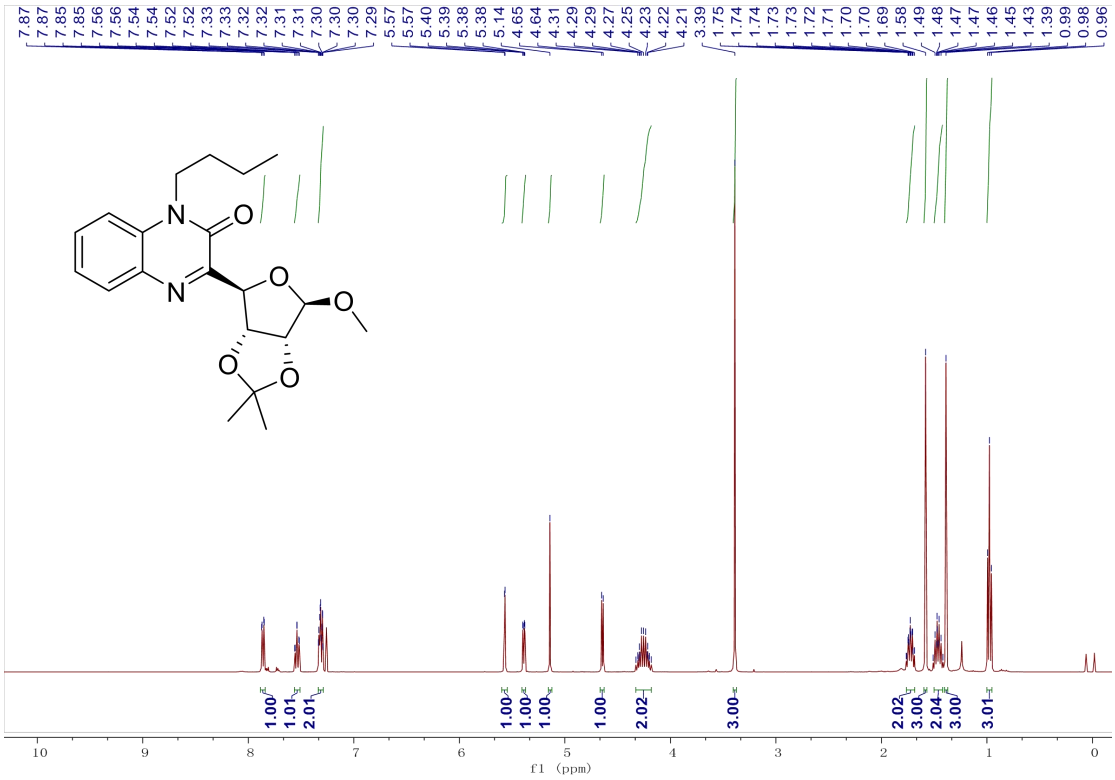
S16. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3ab**



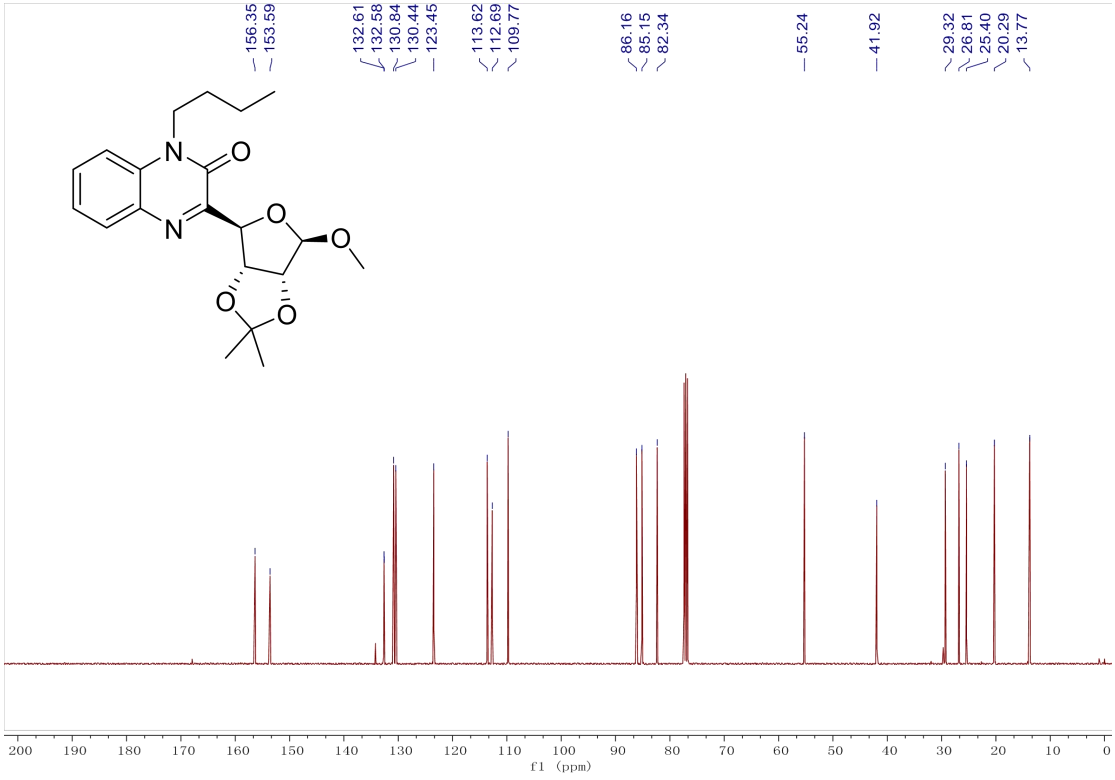
S17. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3ac**



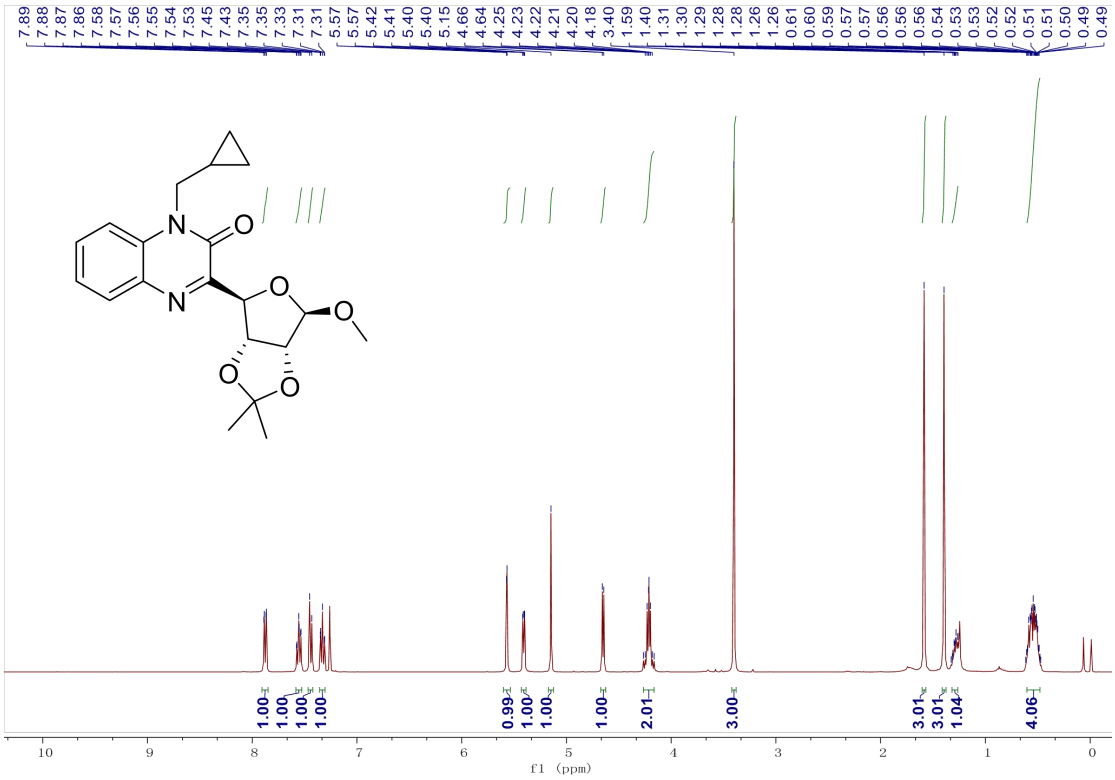
S18. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3ac**



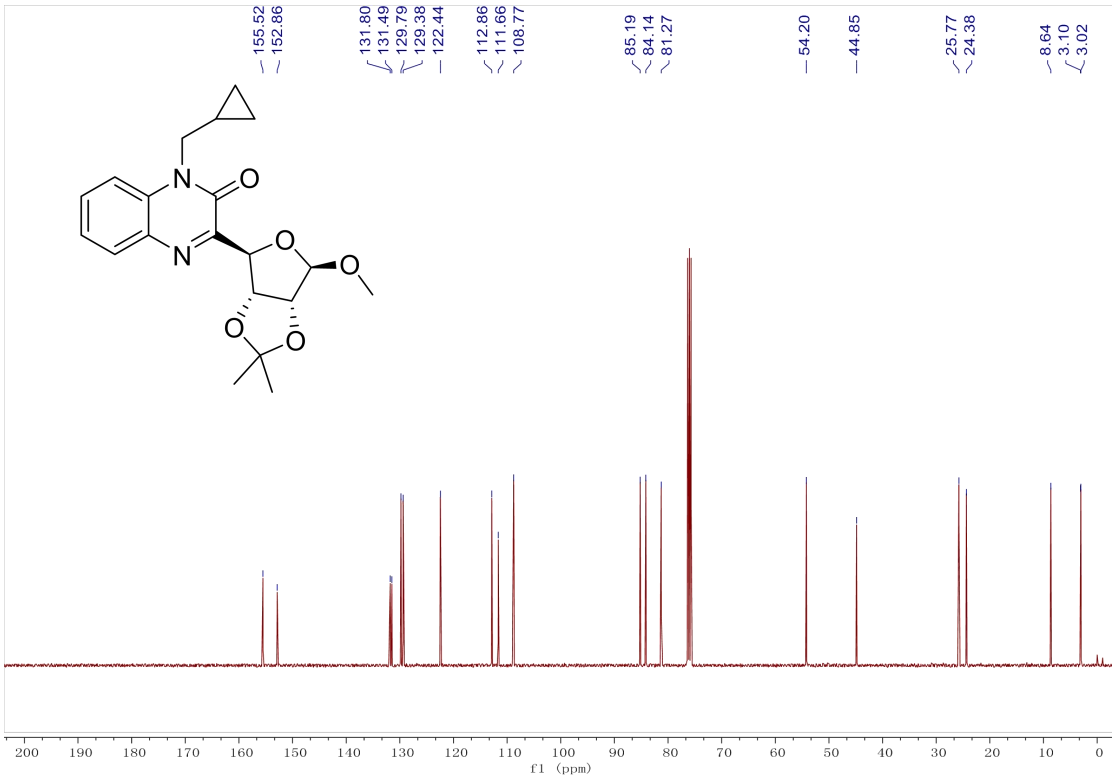
S19. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3ad**



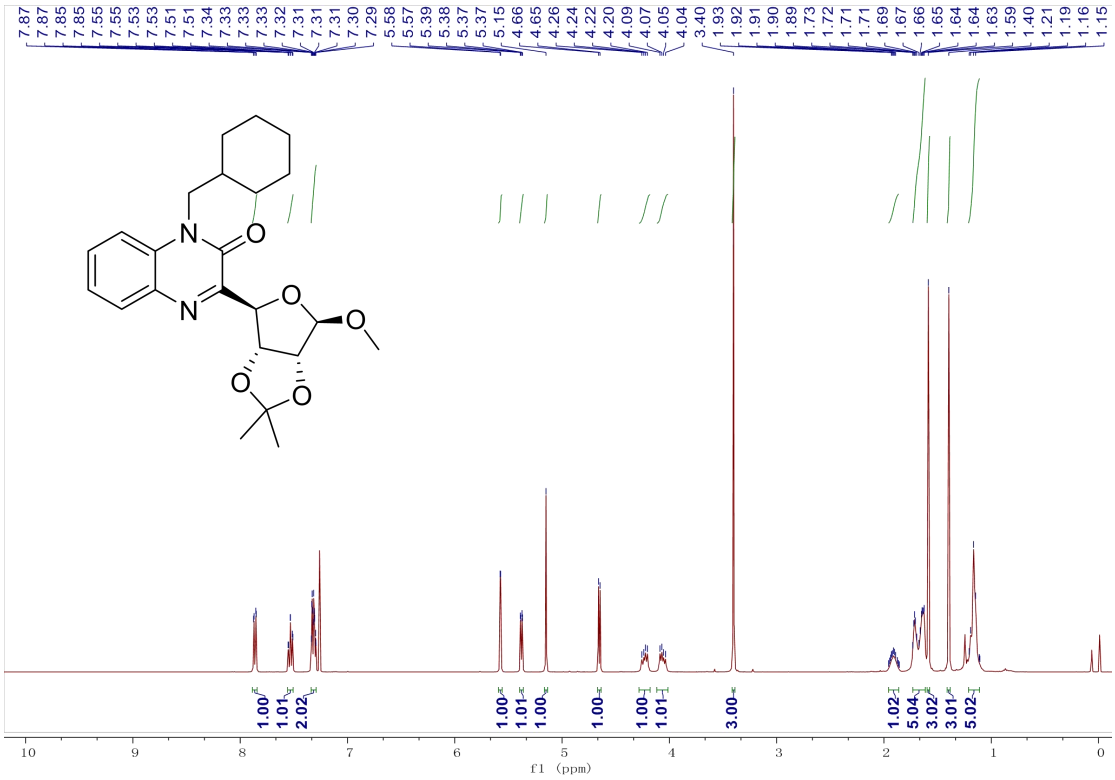
S20. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3ad**



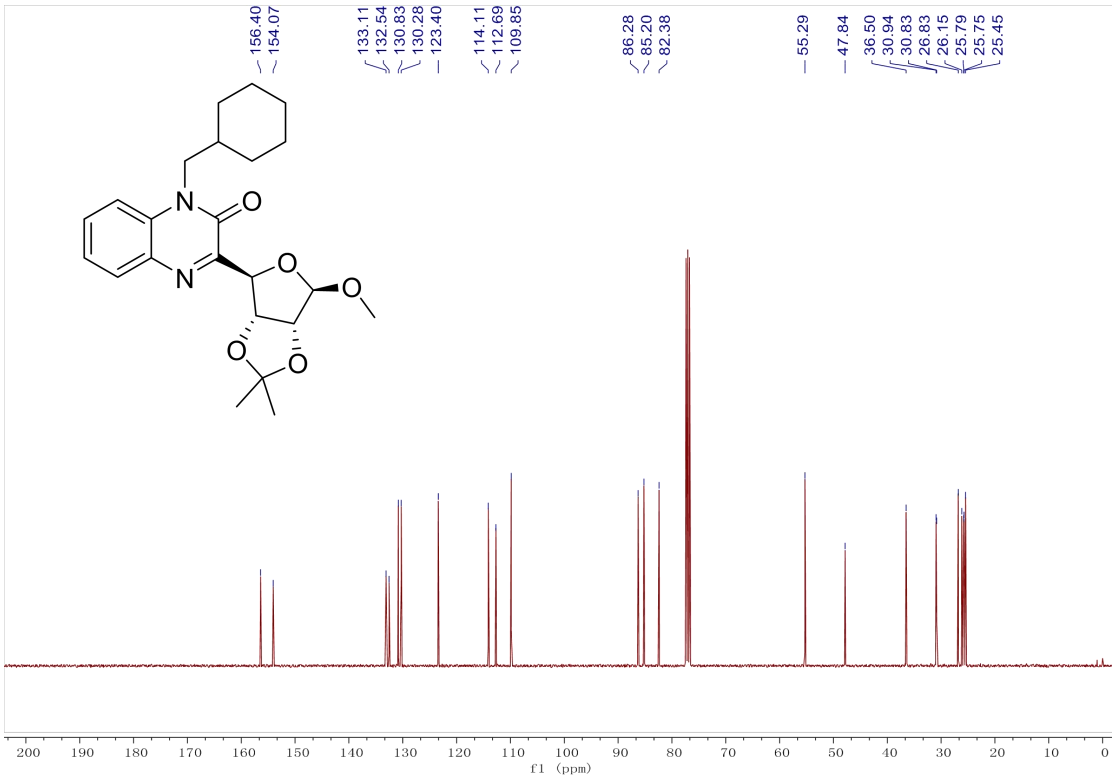
S21. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3ae**



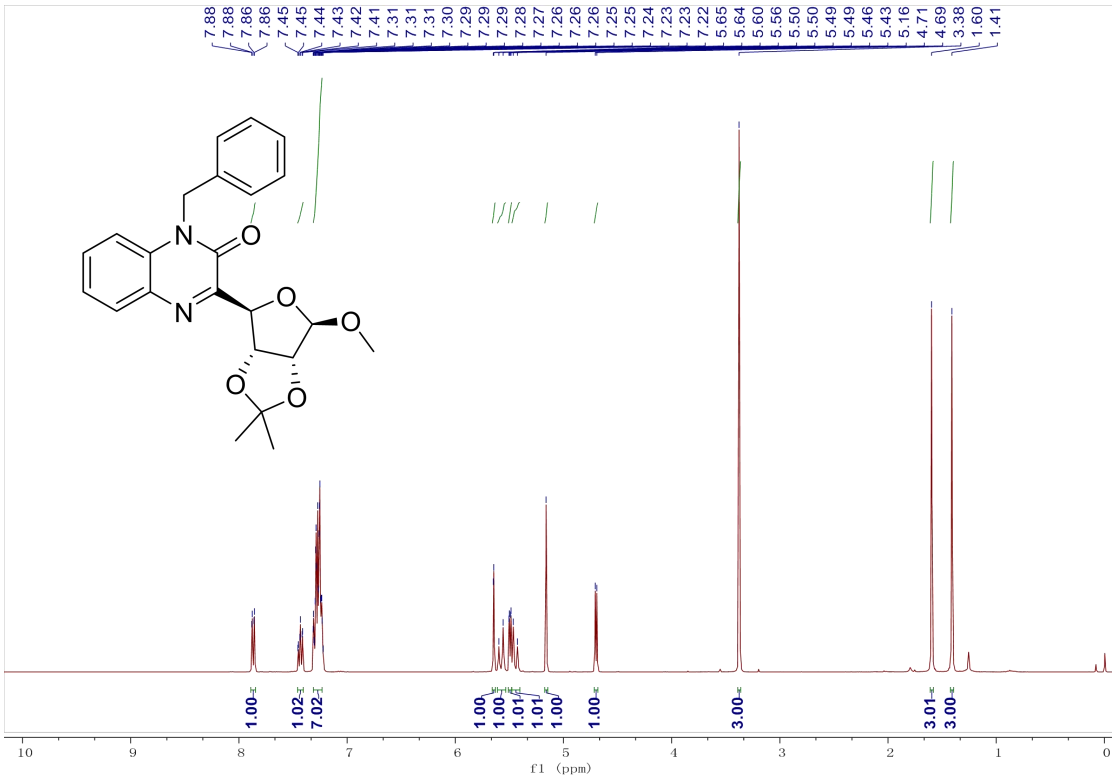
S22. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3ae**



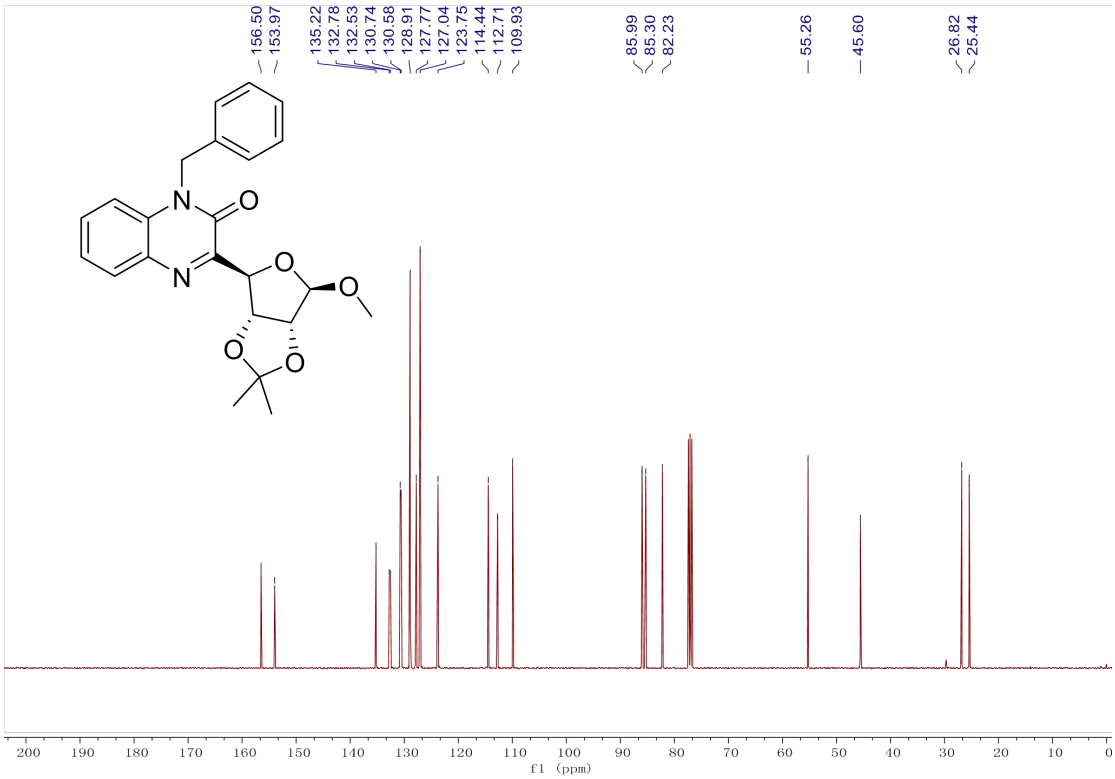
S23. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3af**



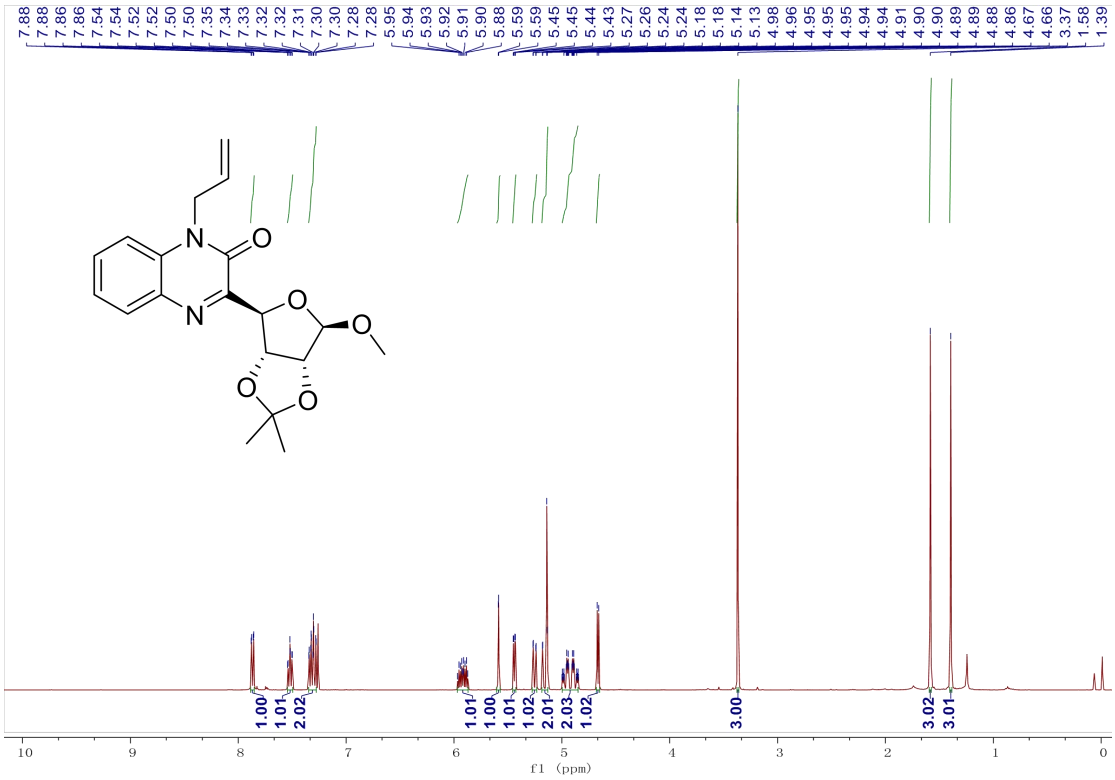
S24. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3af**



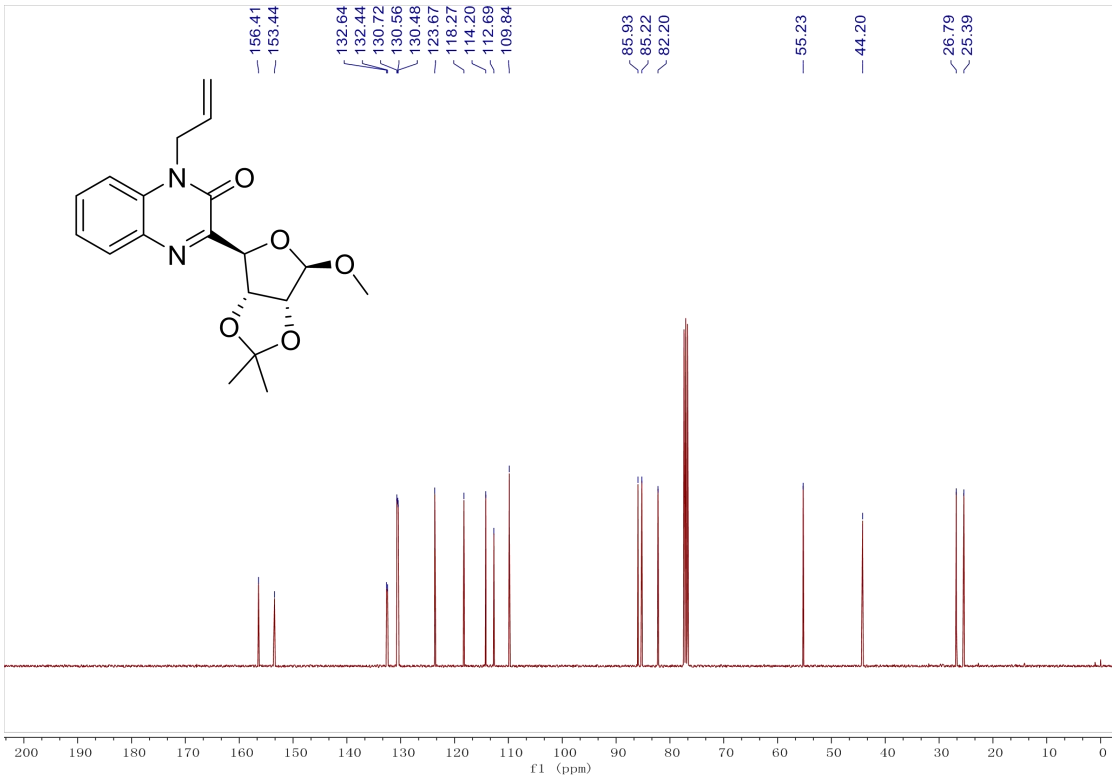
S25. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3ag**



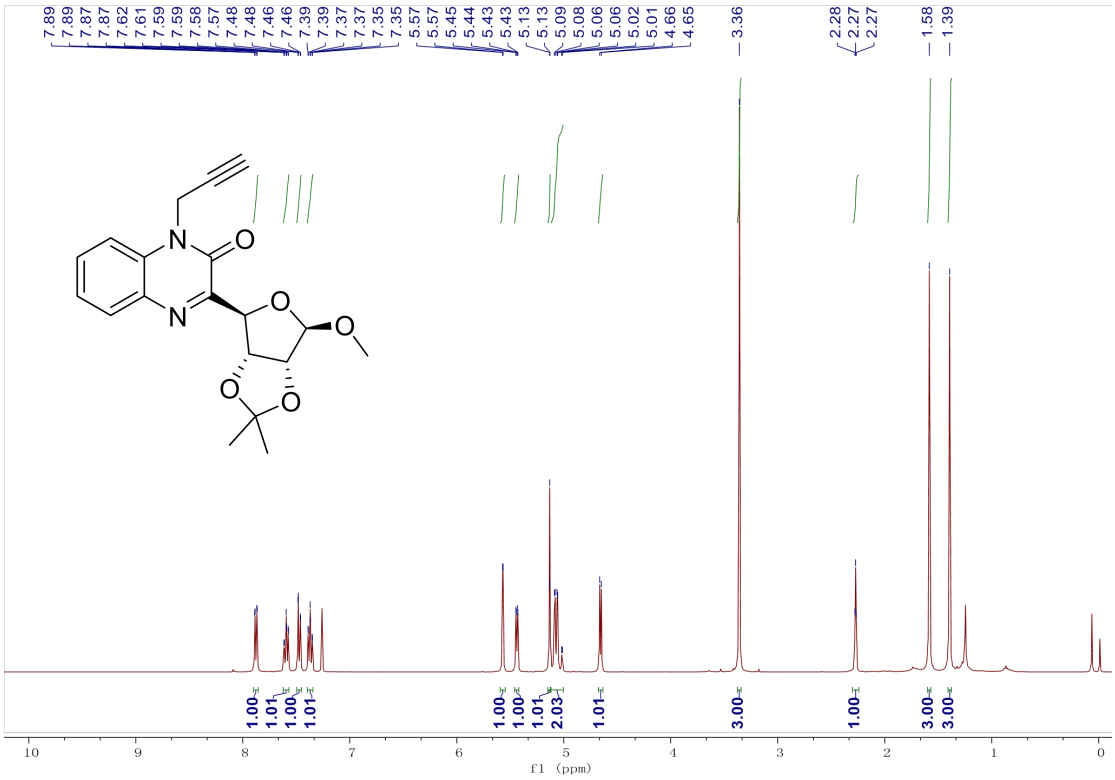
S26. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3ag**



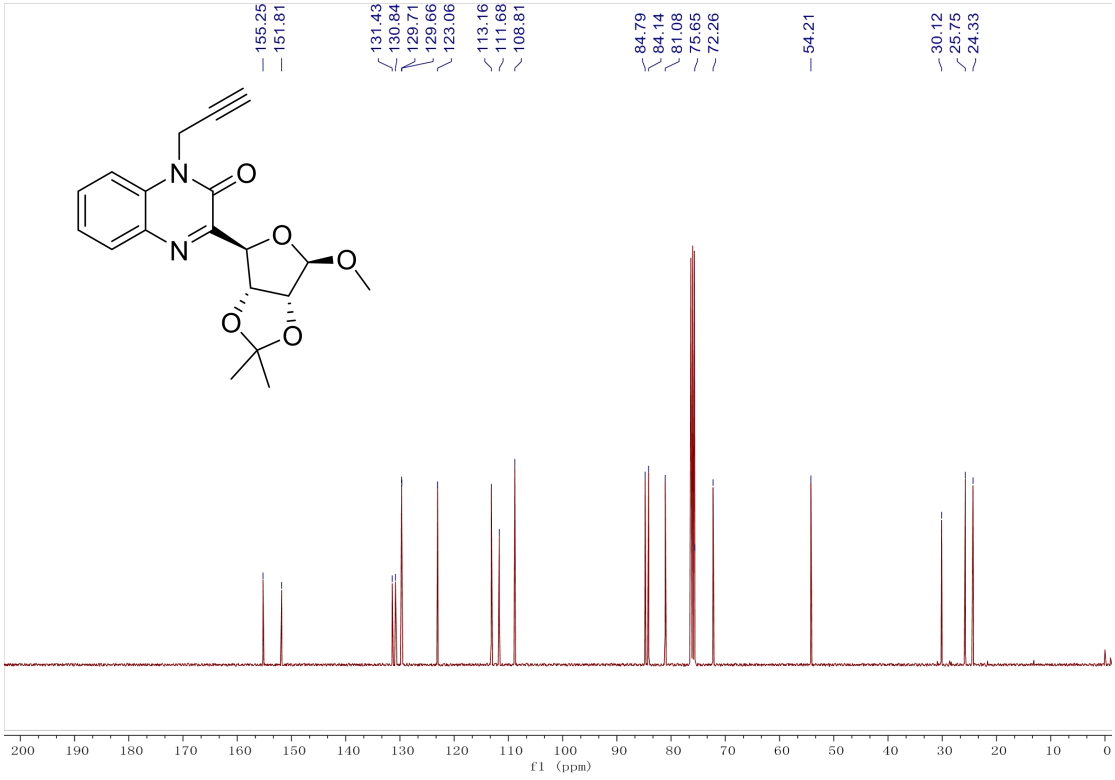
S27. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3ah**



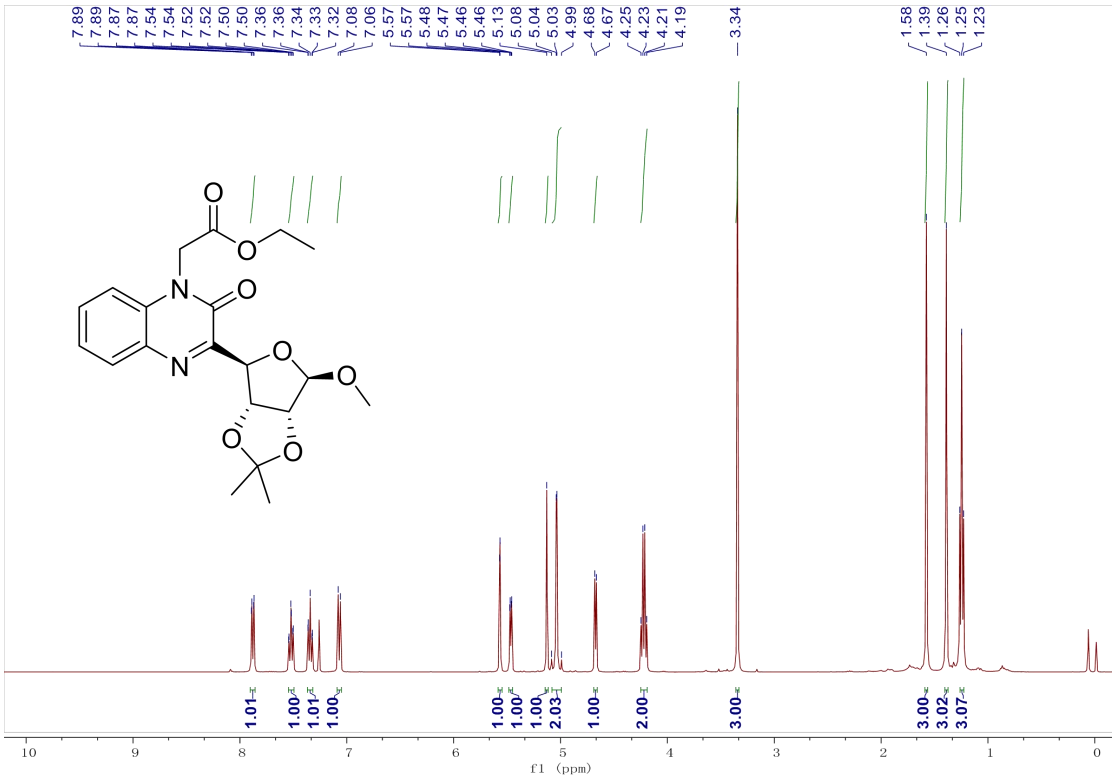
S28. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3ah**



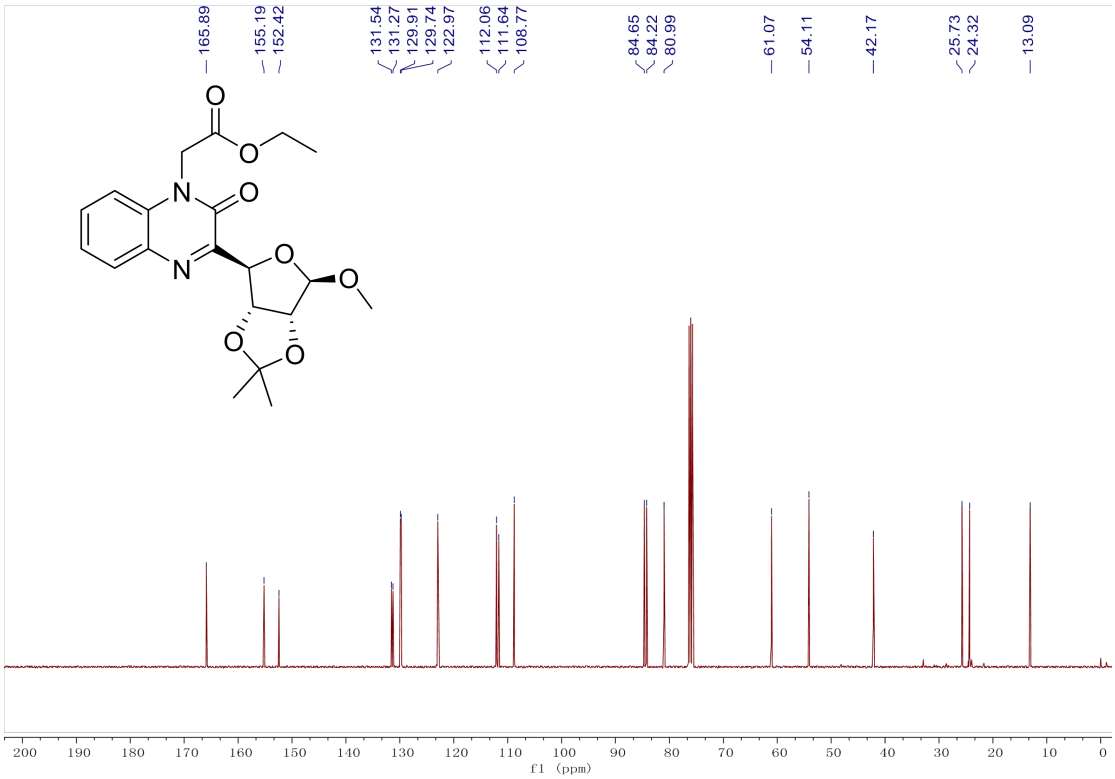
S29. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3ai**



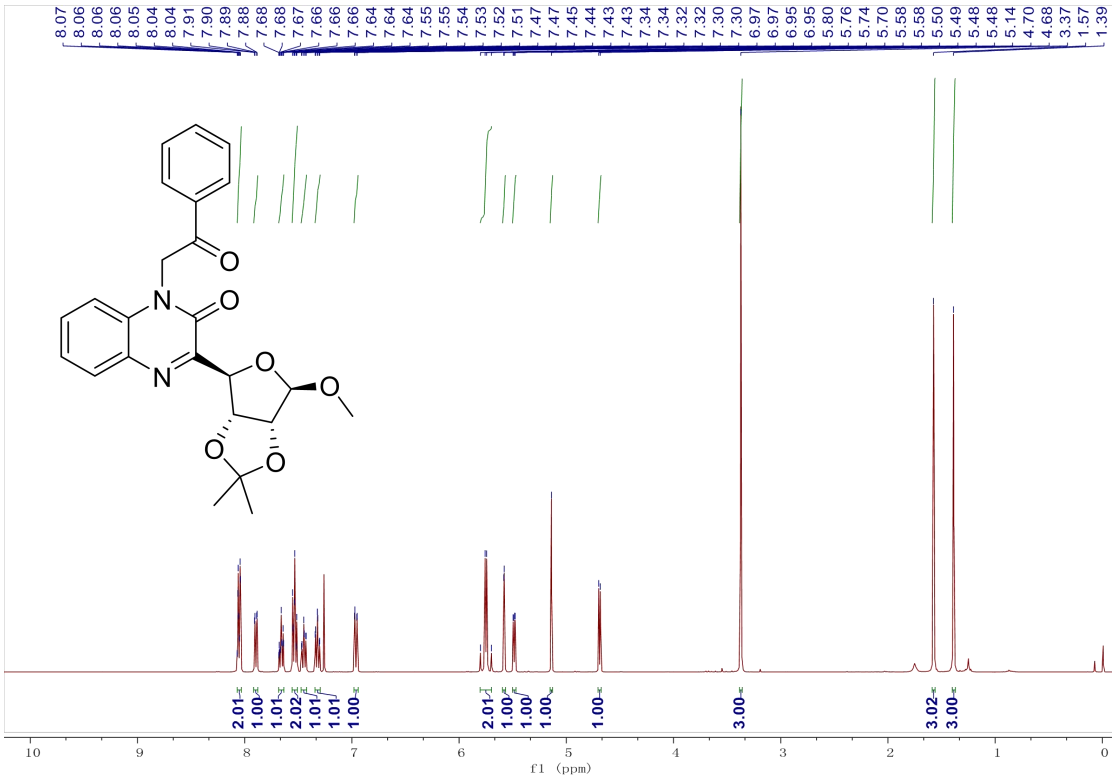
S30. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3ai**



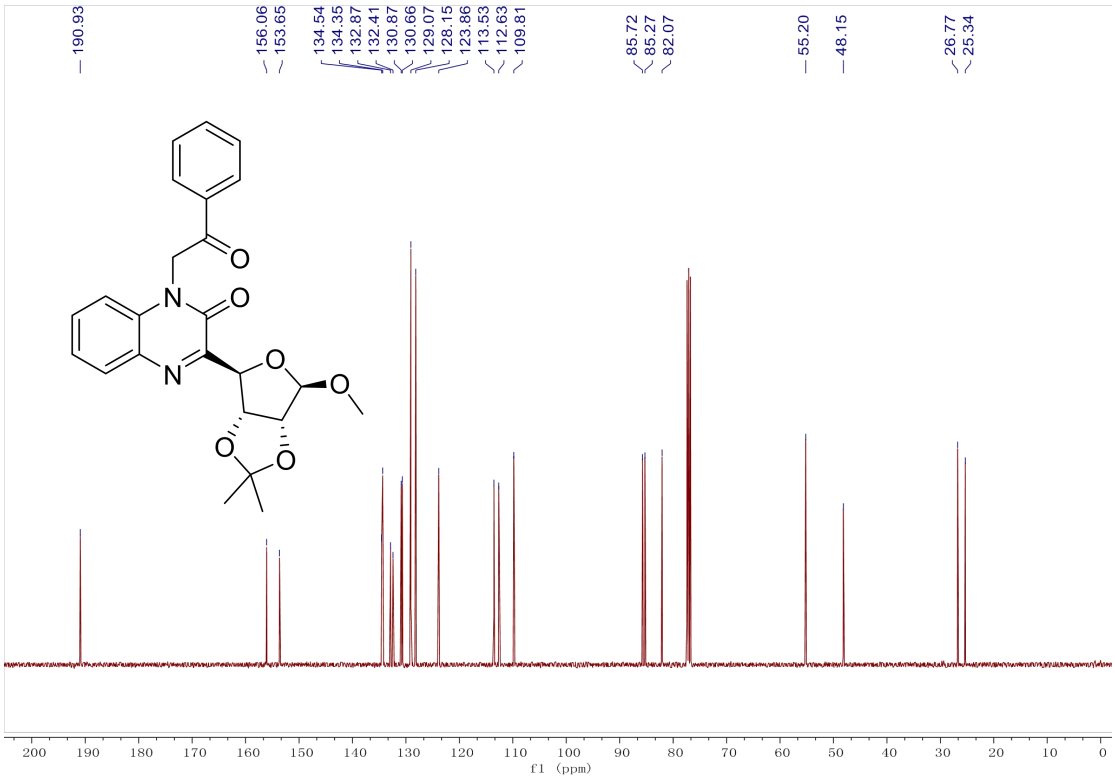
S31. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3aj**



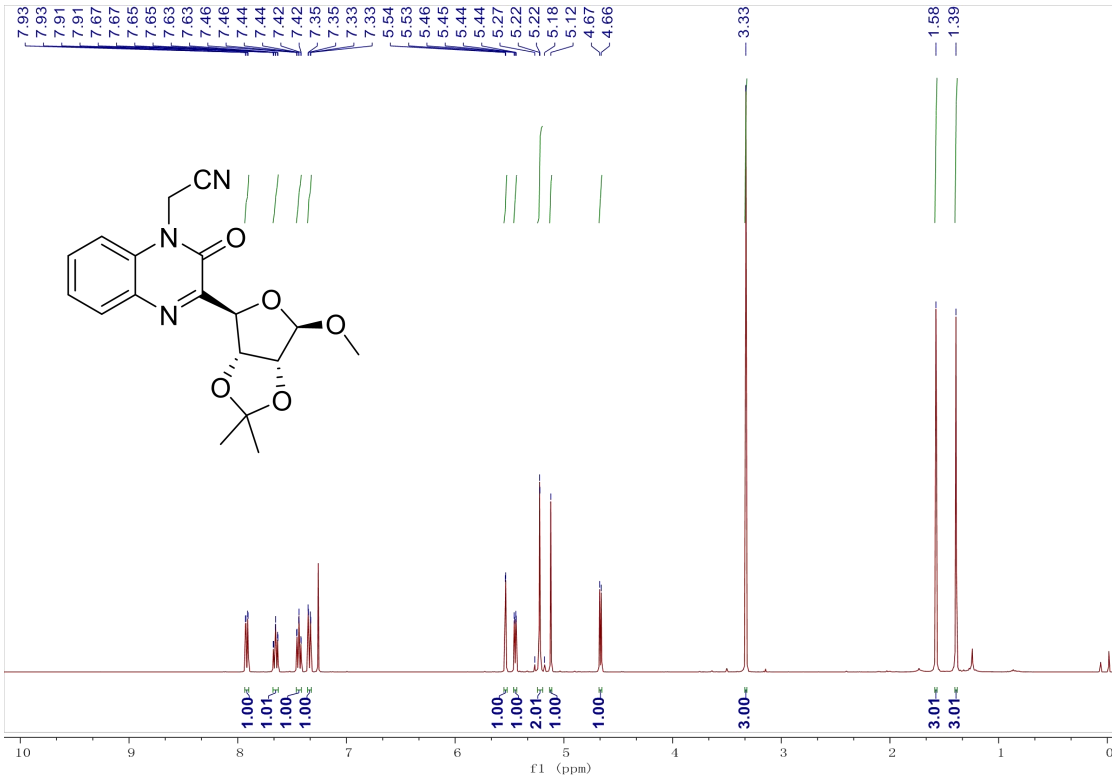
S32. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3aj**



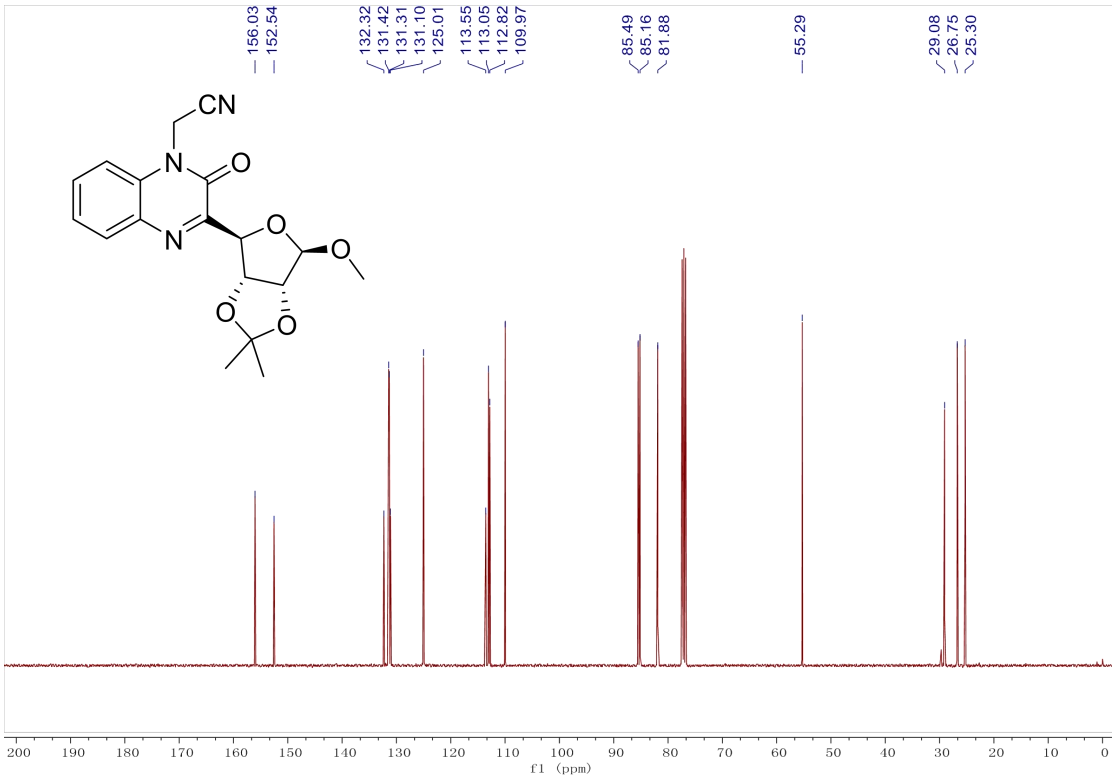
S33. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3ak**



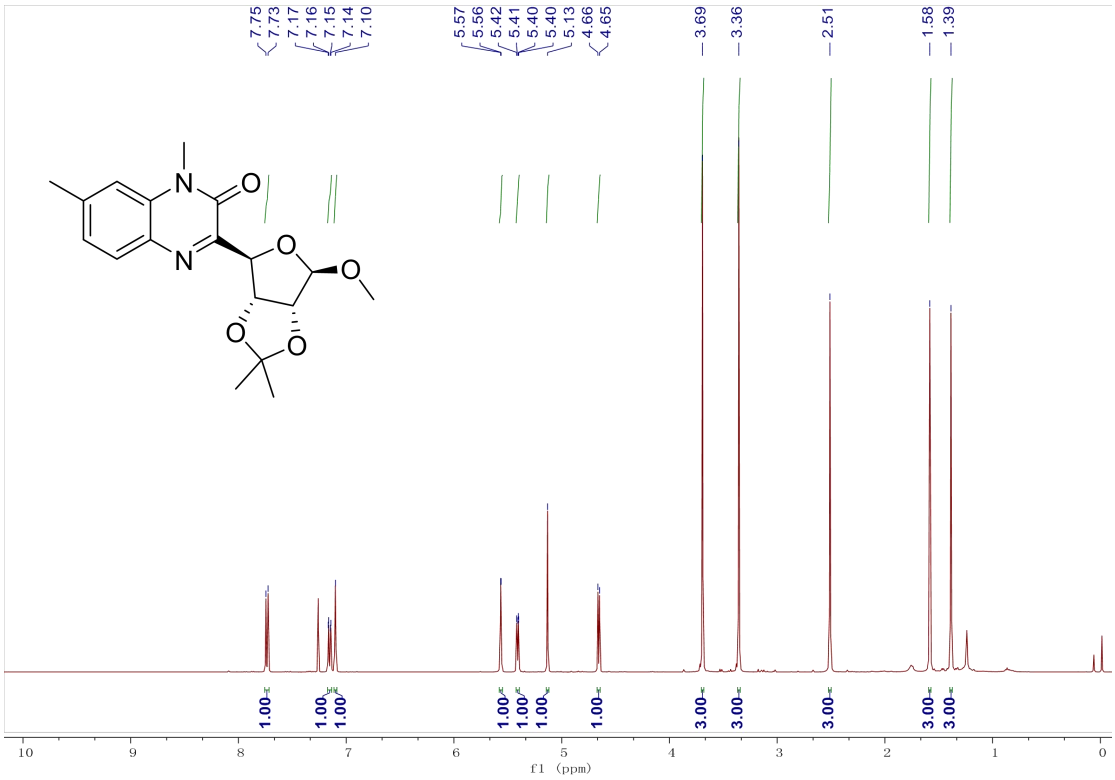
S34. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3ak**



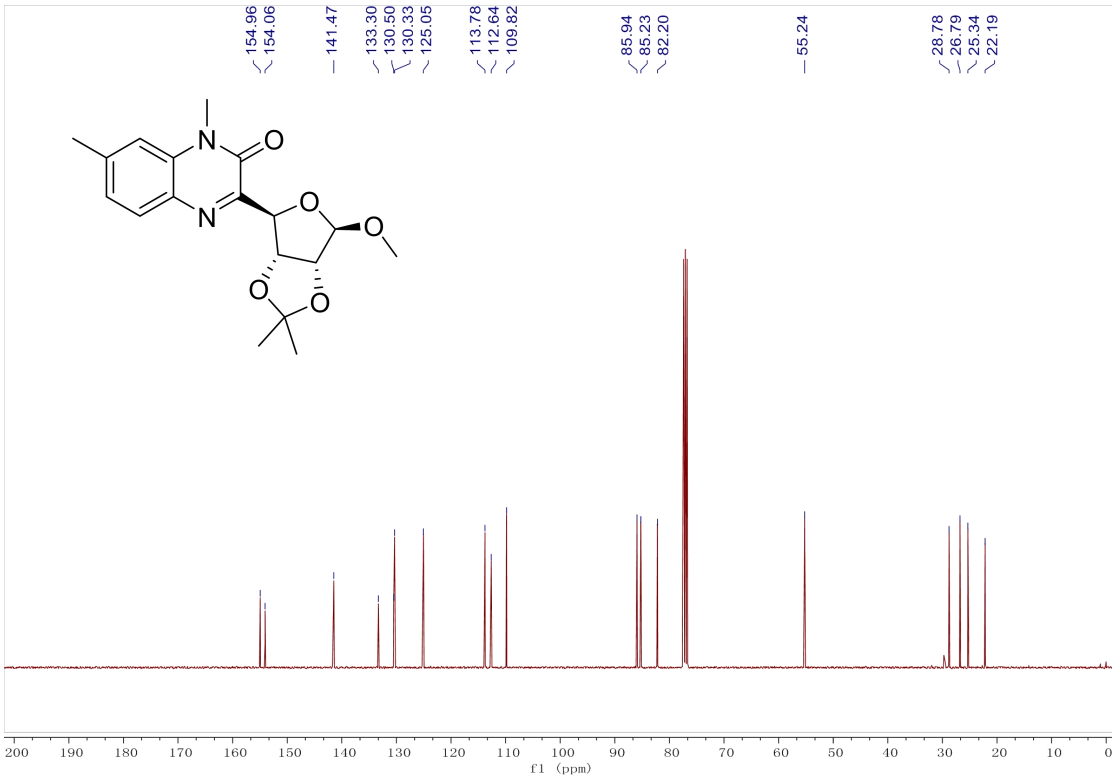
S35. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3al**



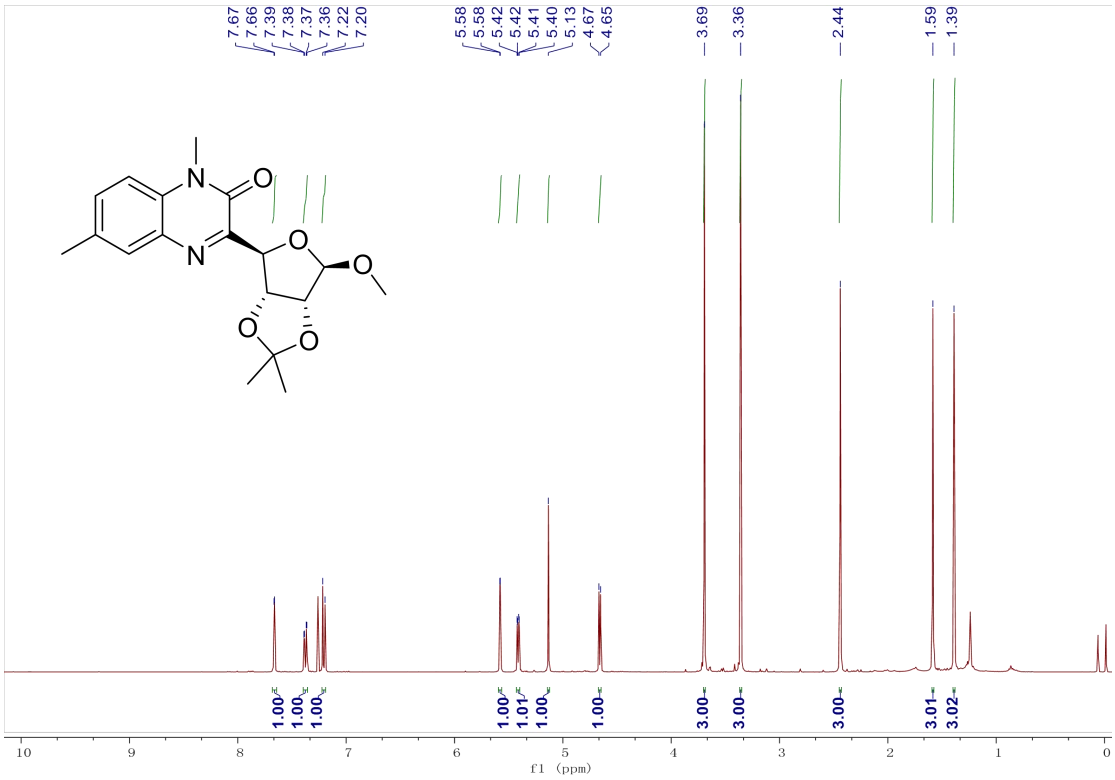
S36. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3al**



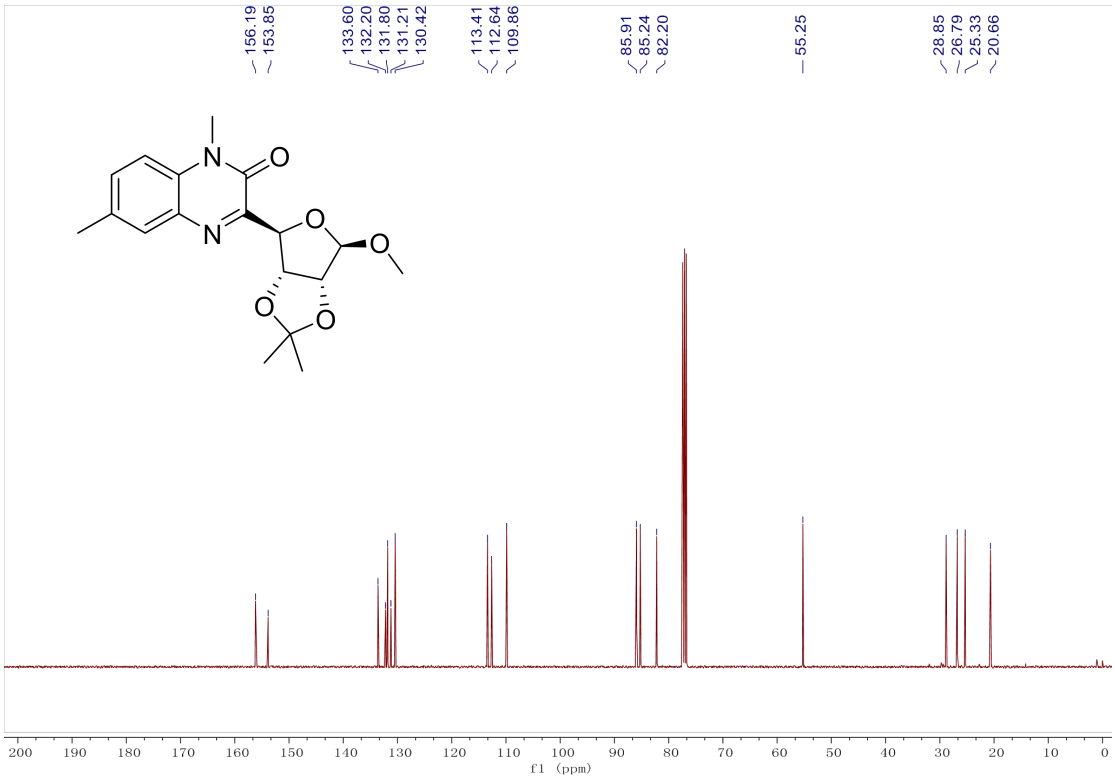
S37. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3ba**



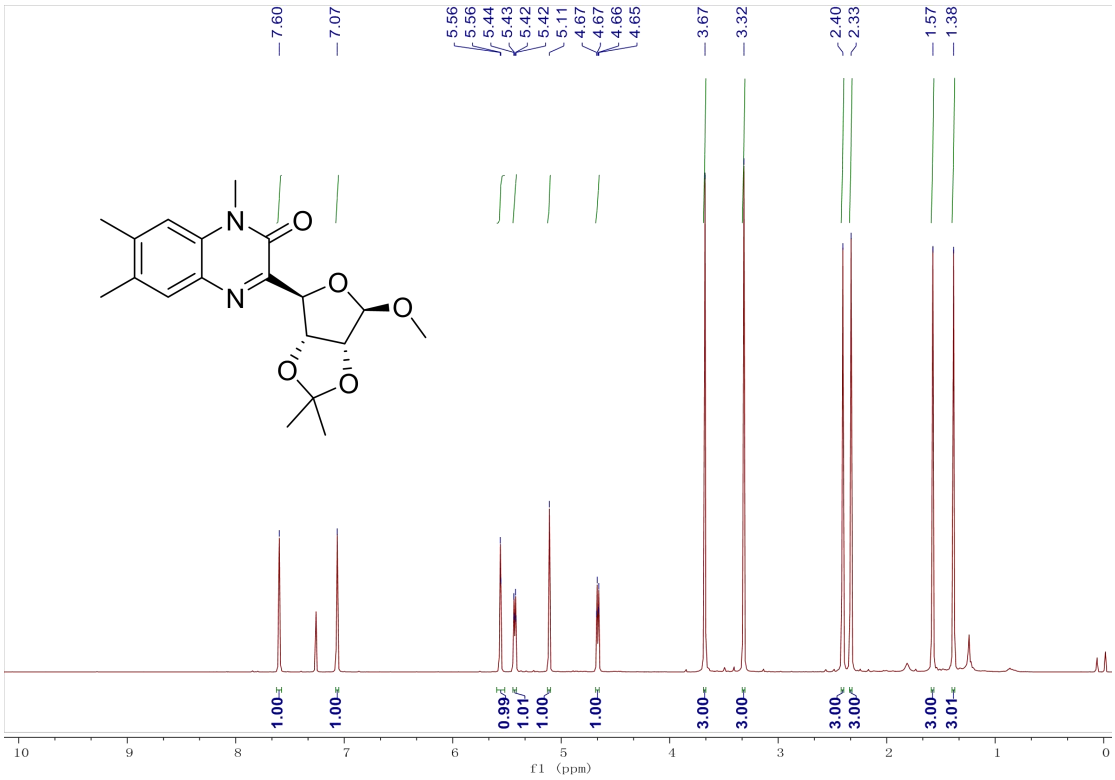
S38. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3ba**



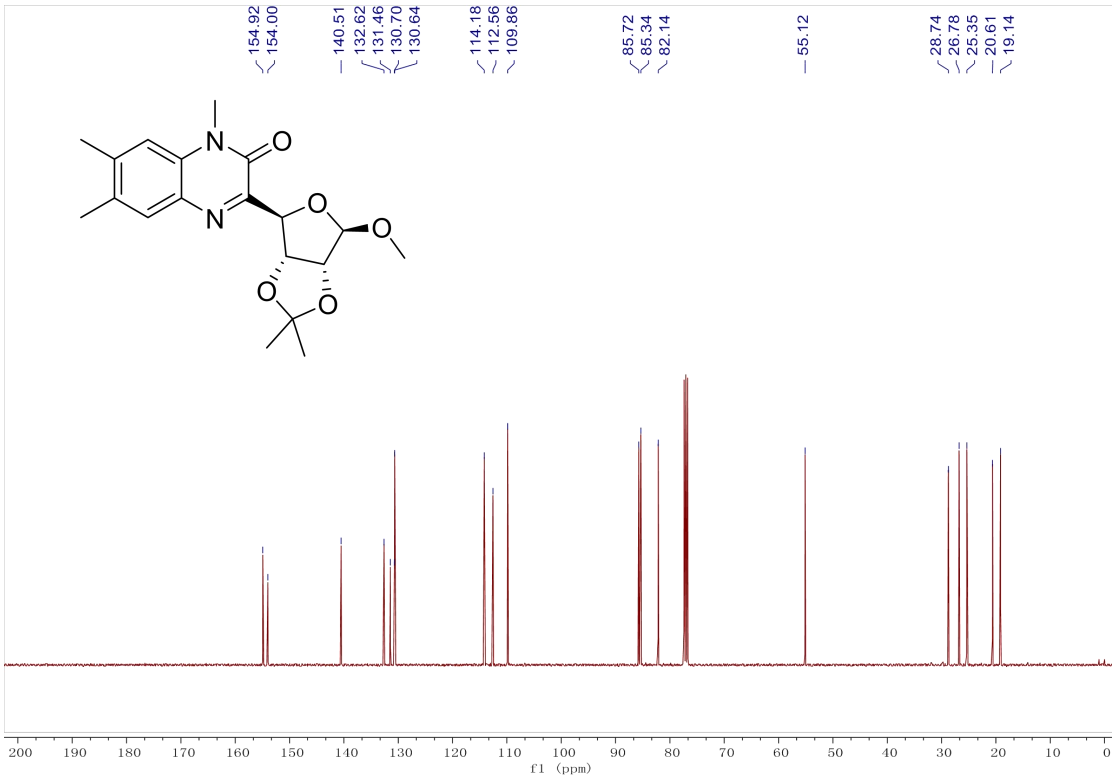
S39. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3ca**



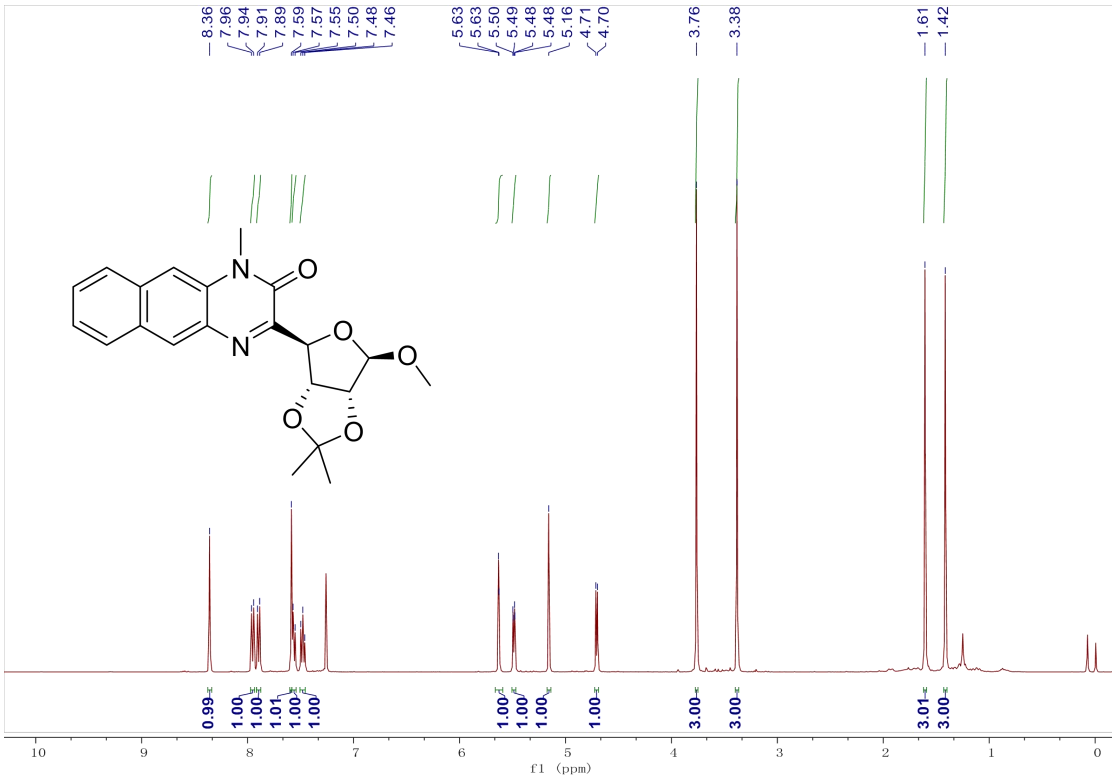
S40. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3ca**



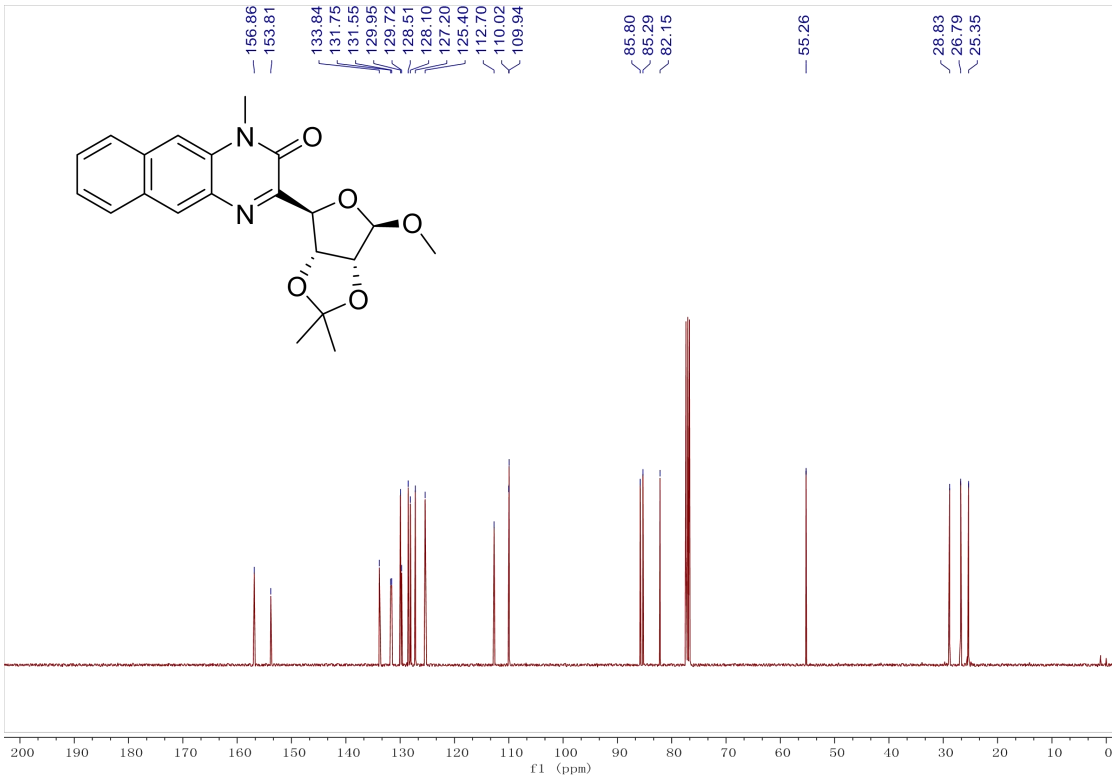
S41. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3da**



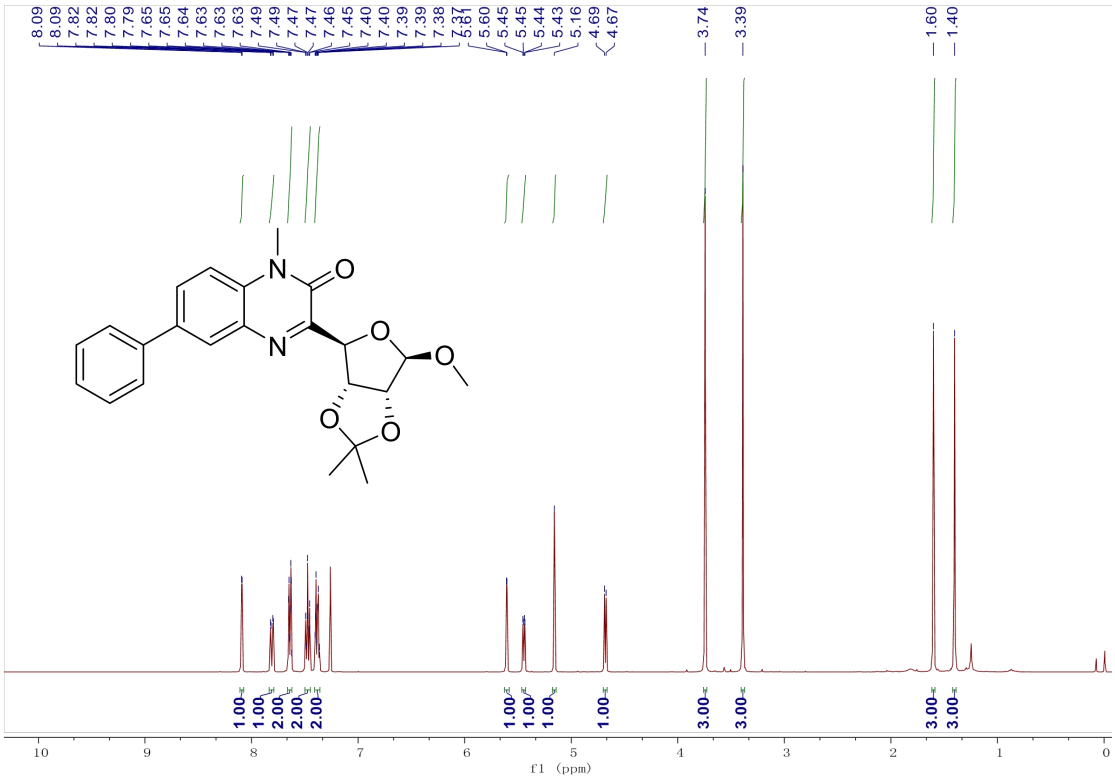
S42. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3da**



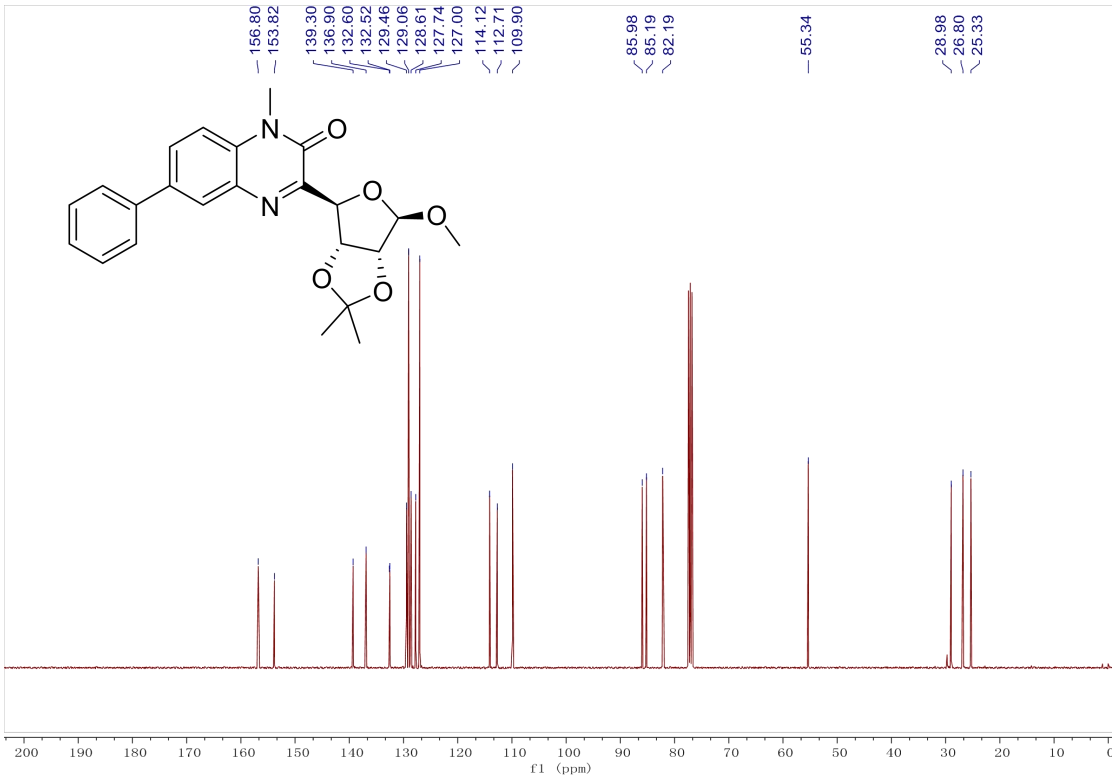
S43. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3ea**



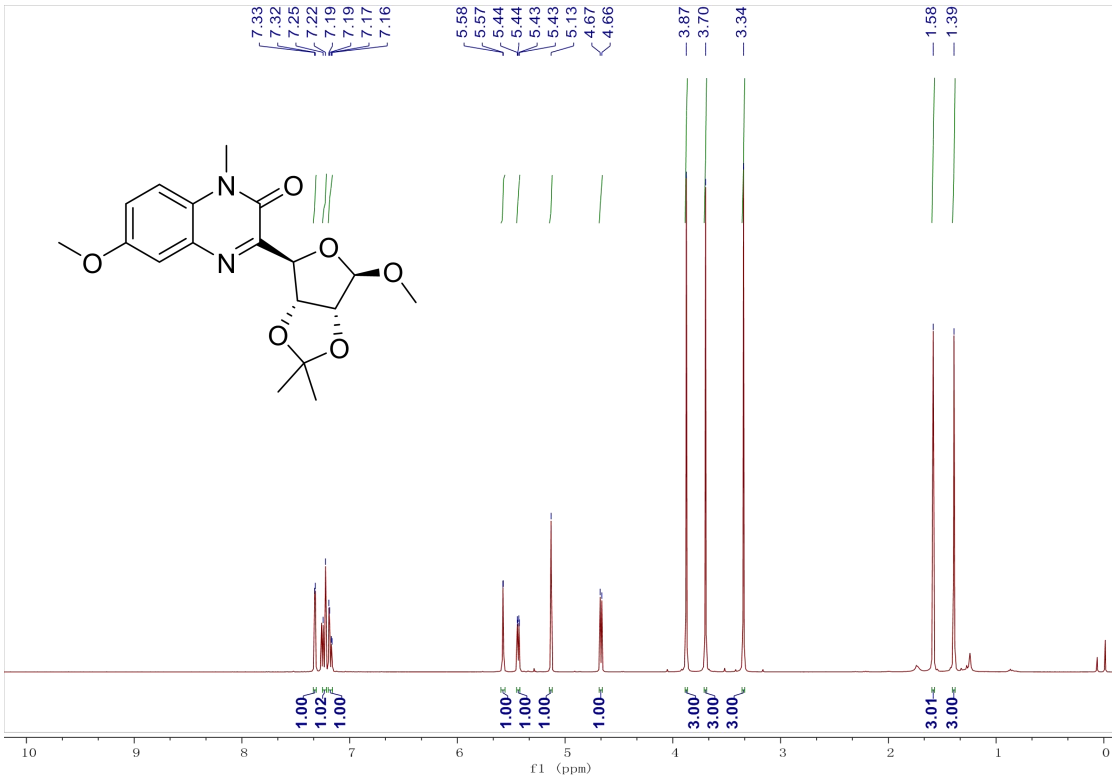
S44. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3ea**



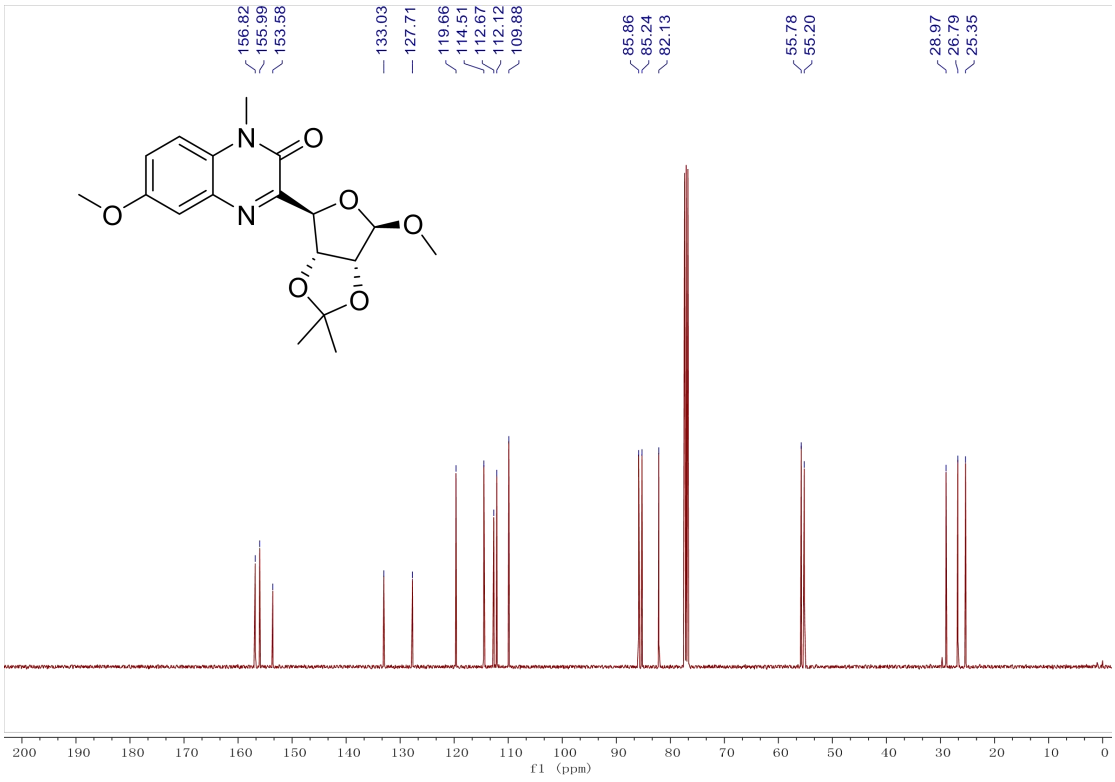
S45. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3fa**



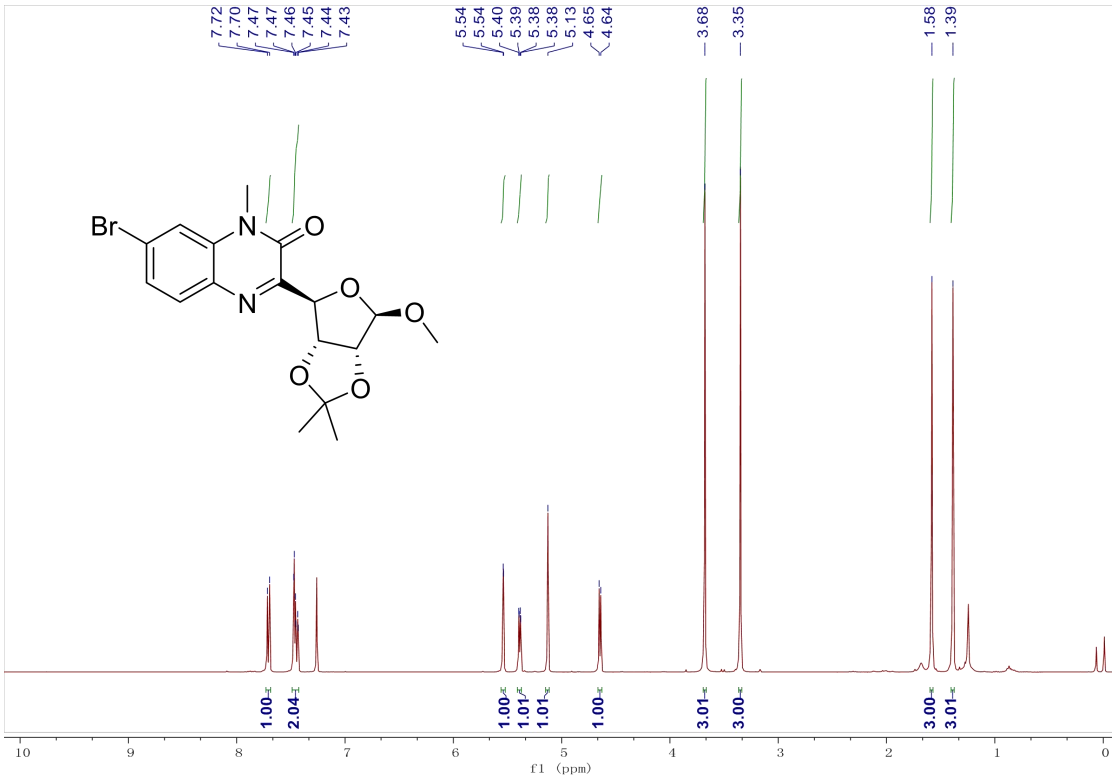
S46. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3fa**



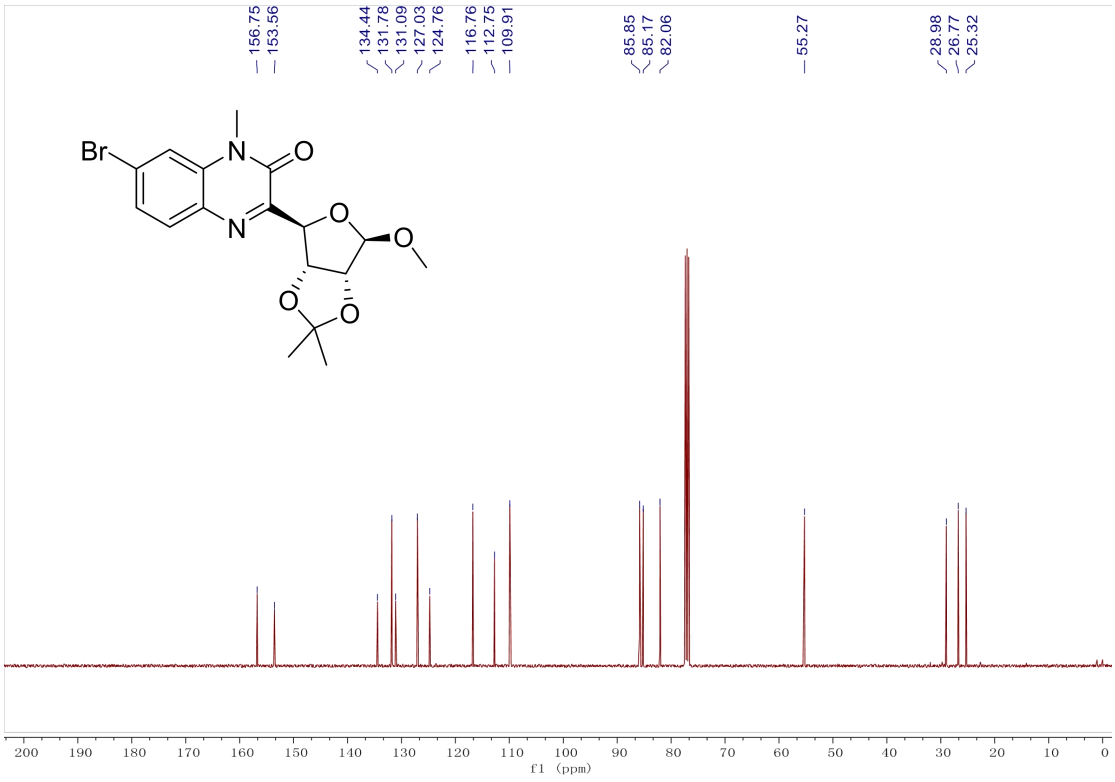
S47. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3ga**



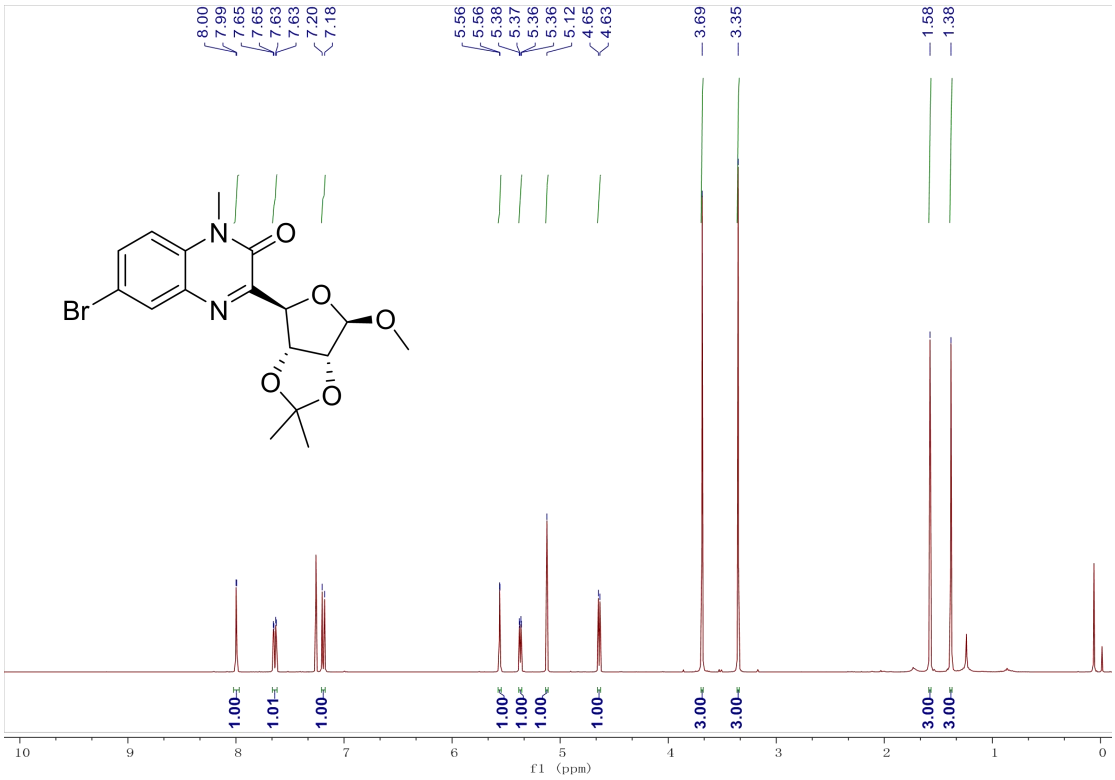
S48. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3ga**



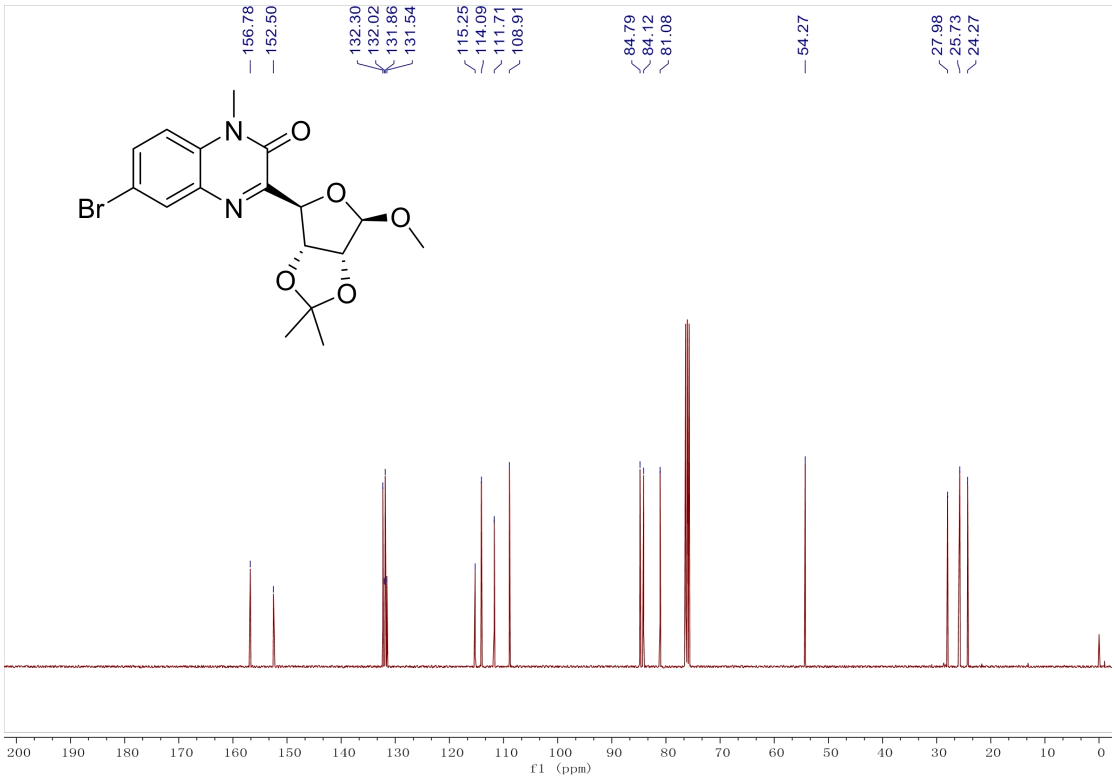
S49. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3ha**



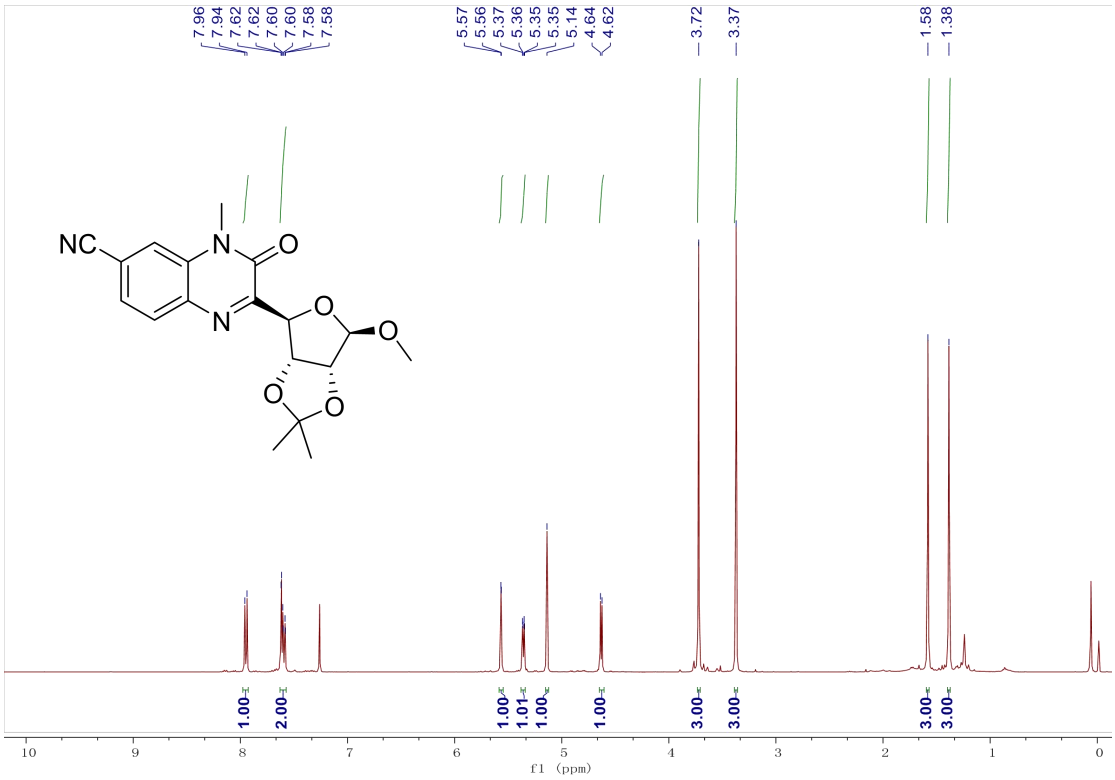
S50. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3ha**



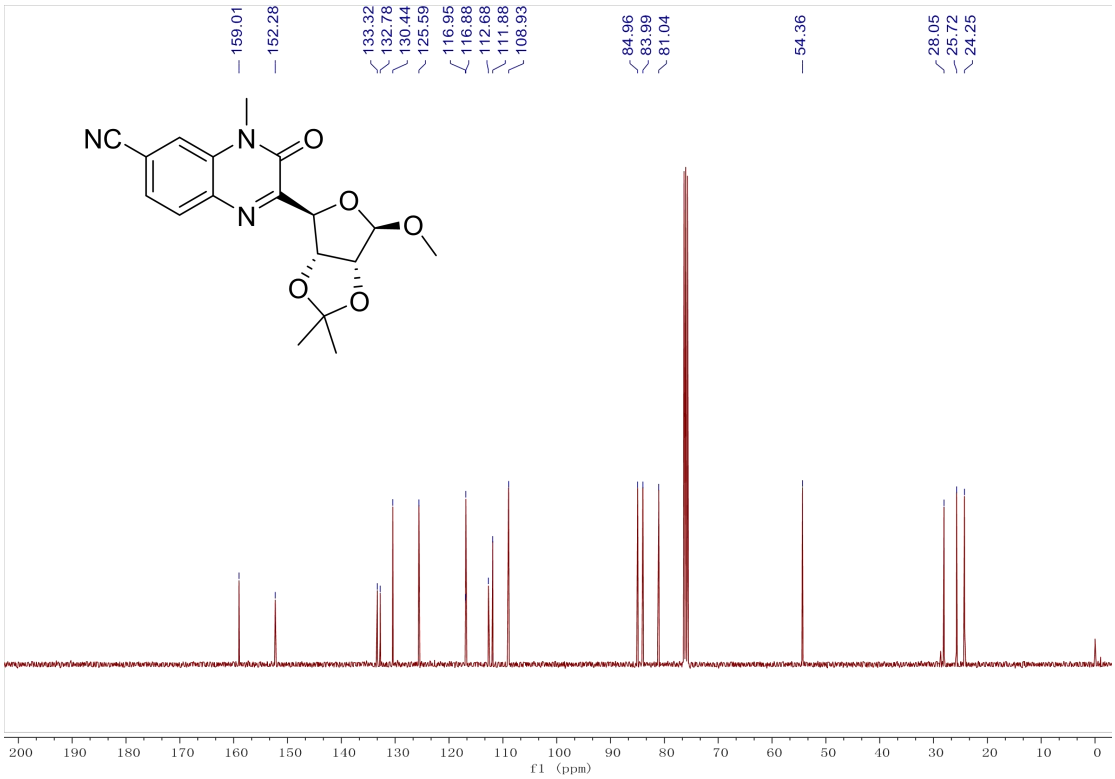
S51. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3ia**



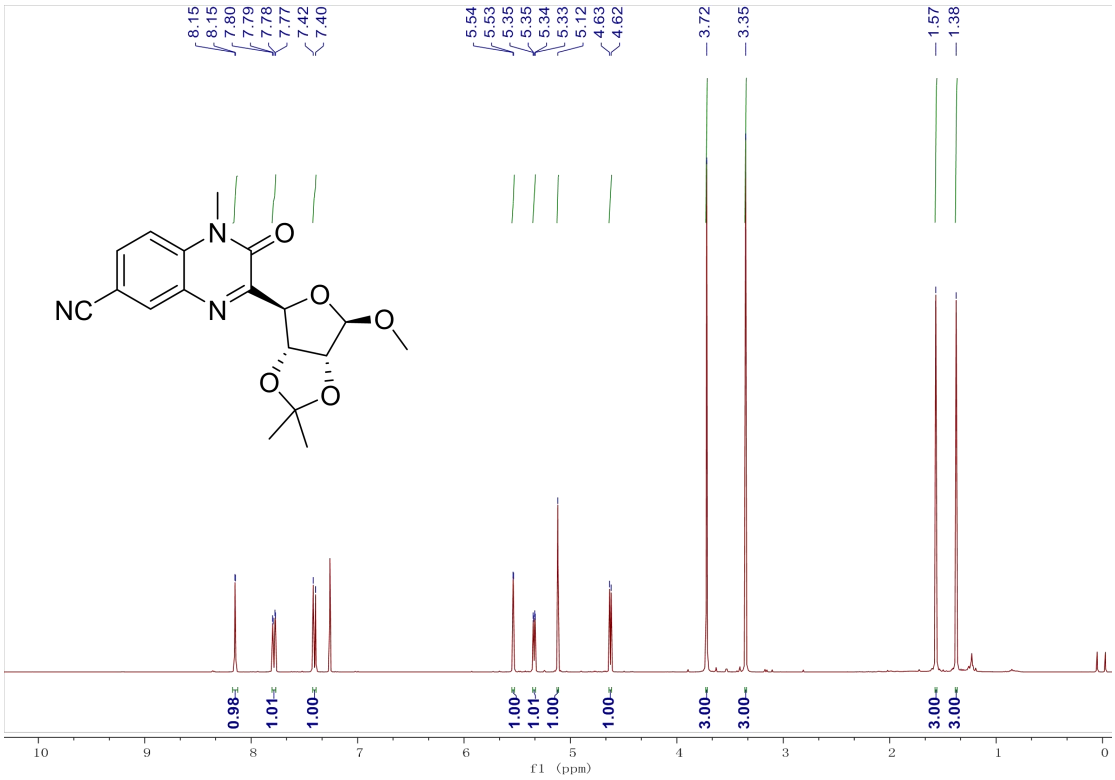
S52. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3ia**



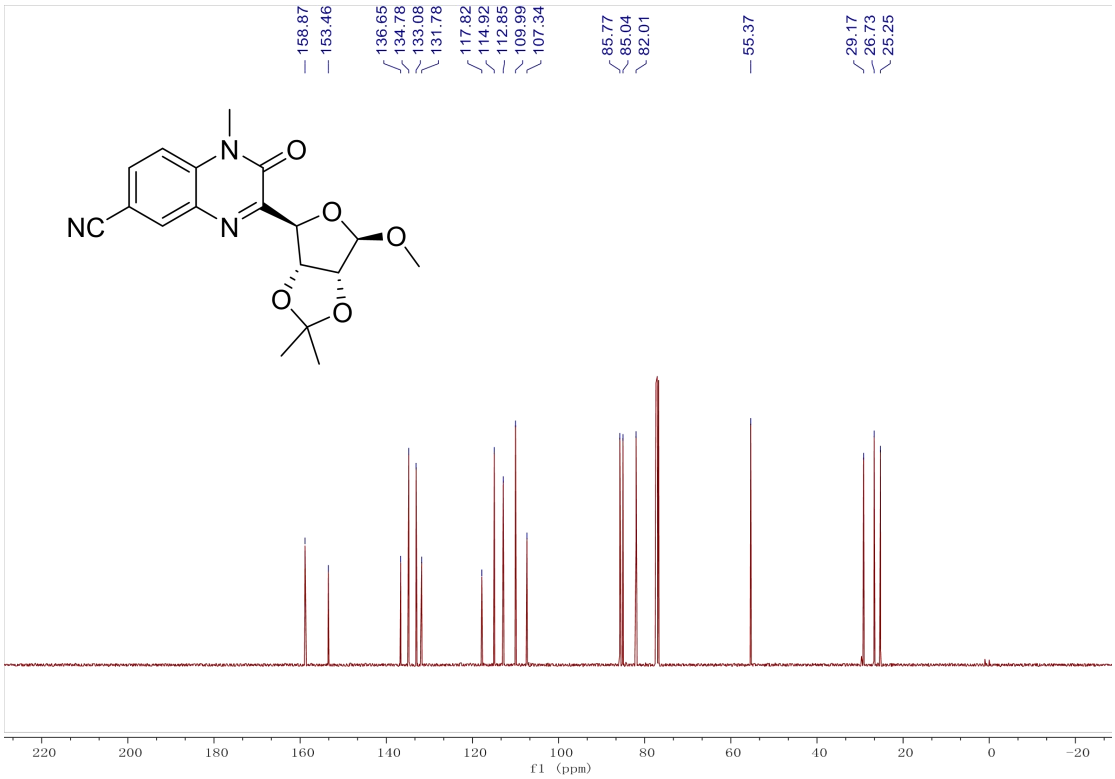
S53. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3ja**



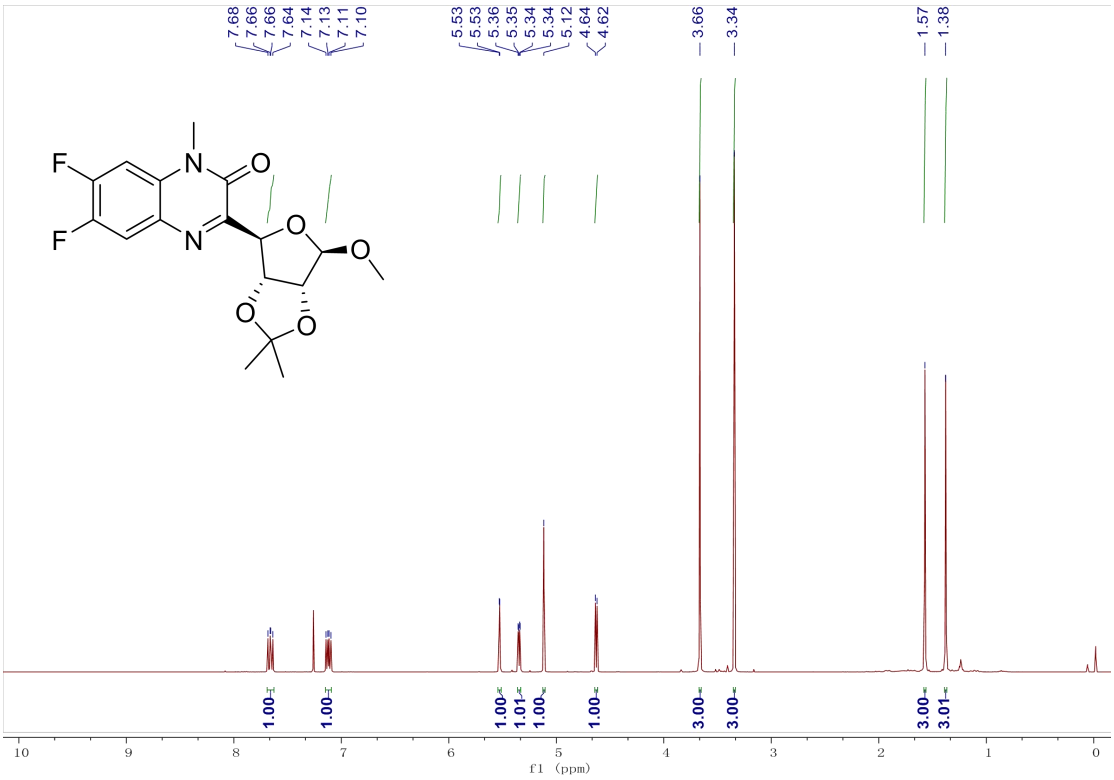
S54. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3ja**



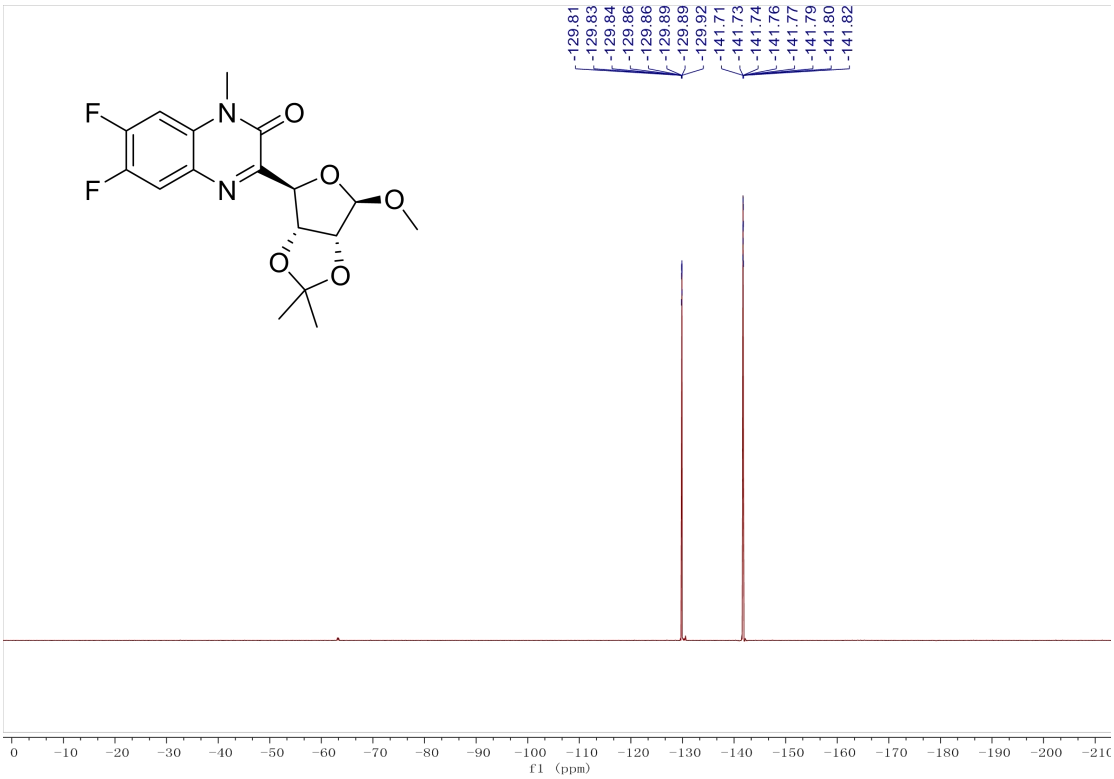
S55. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3ka**



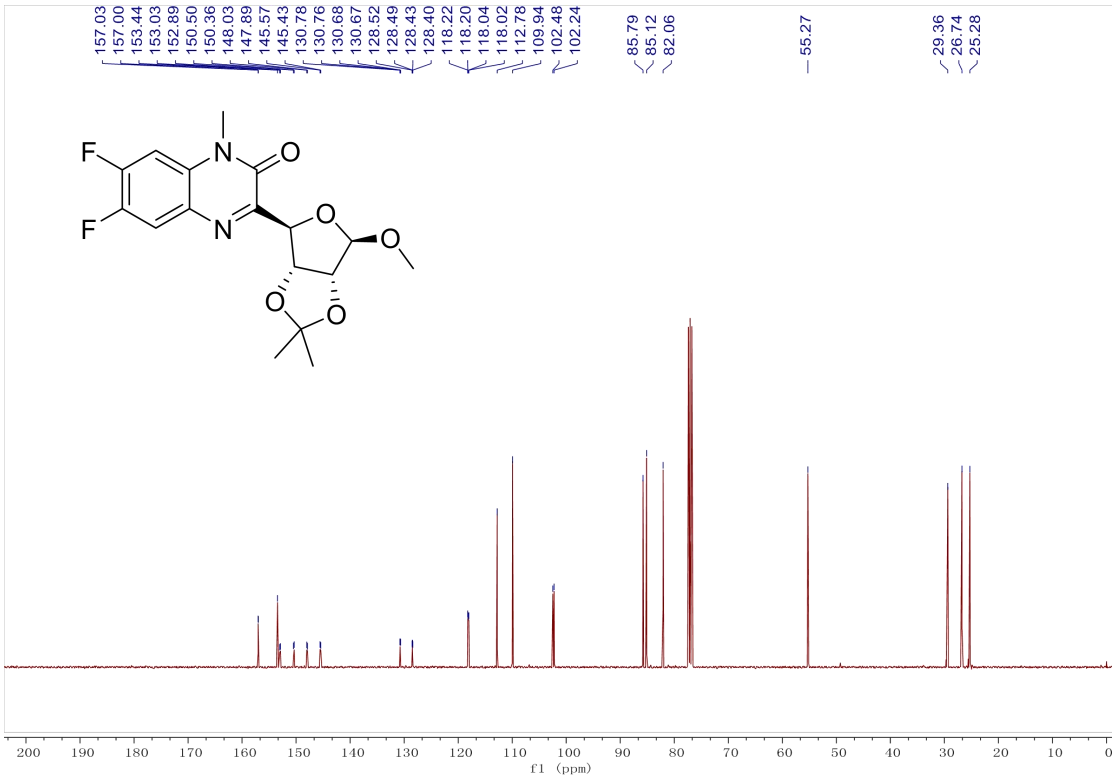
S56. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3ka**



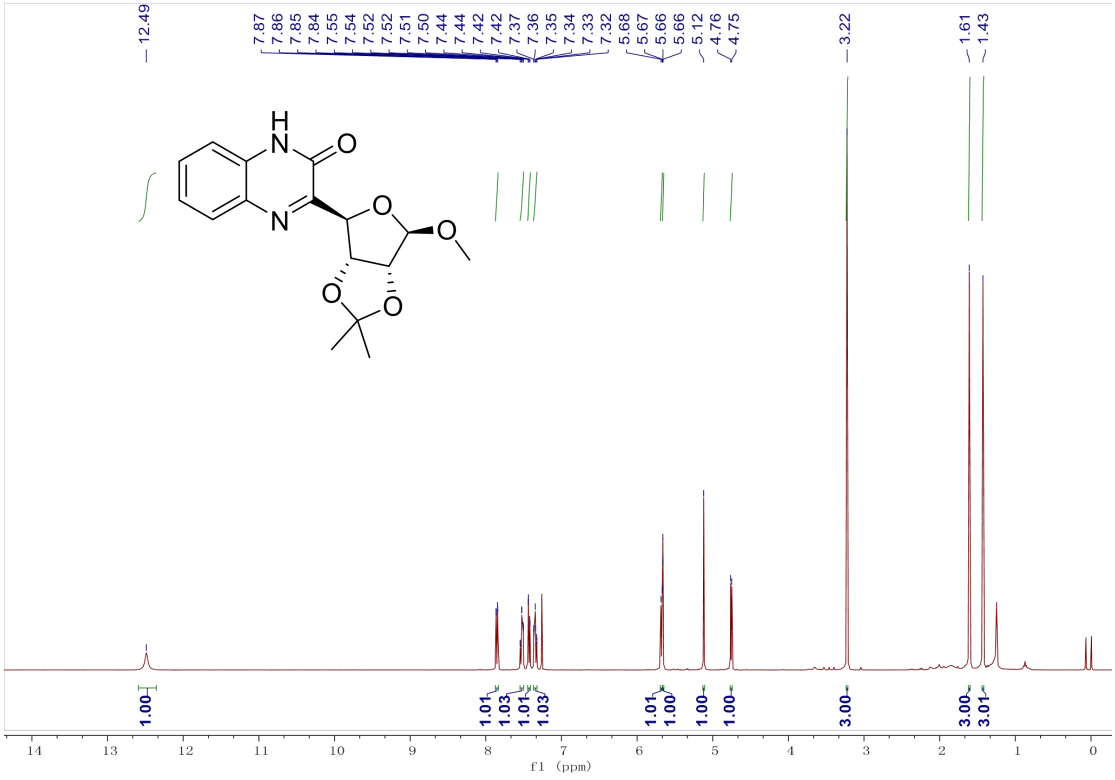
S57. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3la**



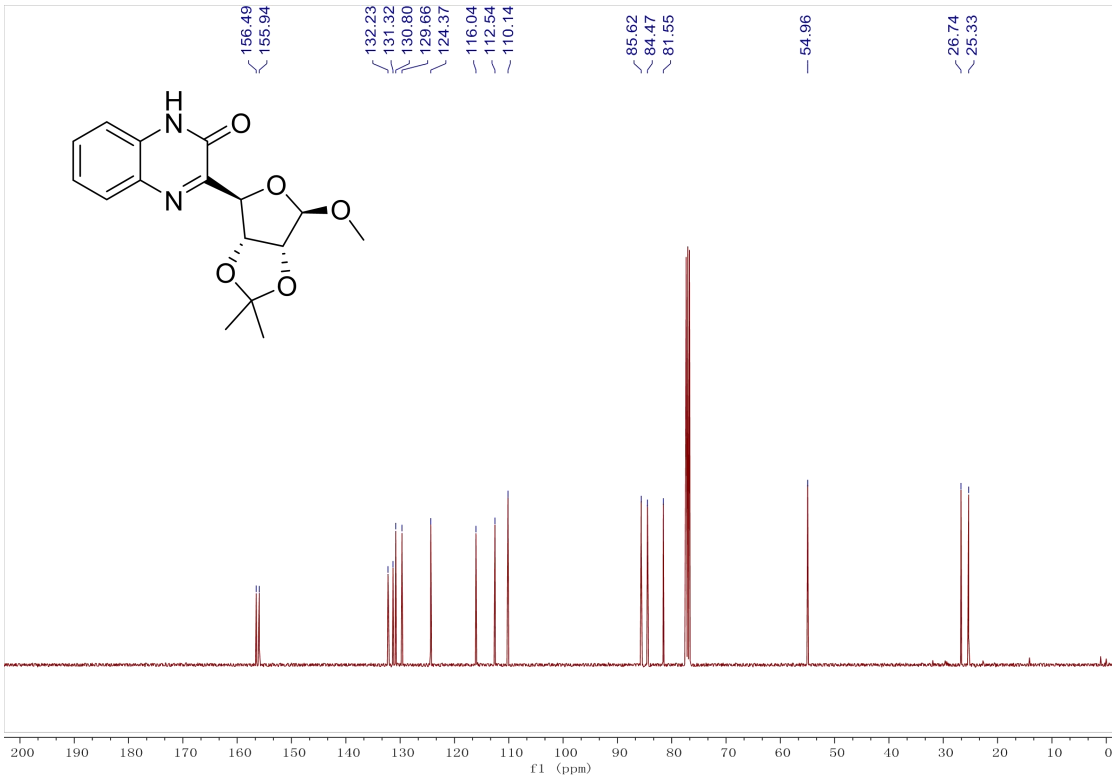
S58. ^{19}F NMR spectra (376 MHz, $CDCl_3$) of compound **3la**



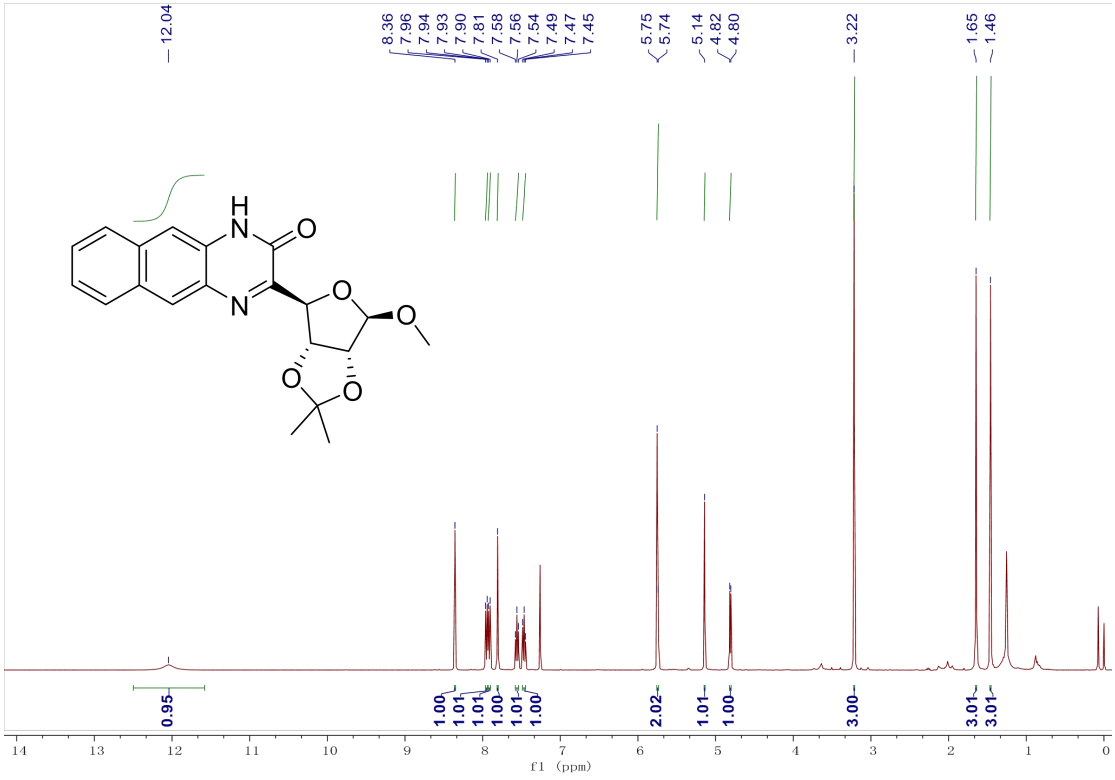
S59. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3la**



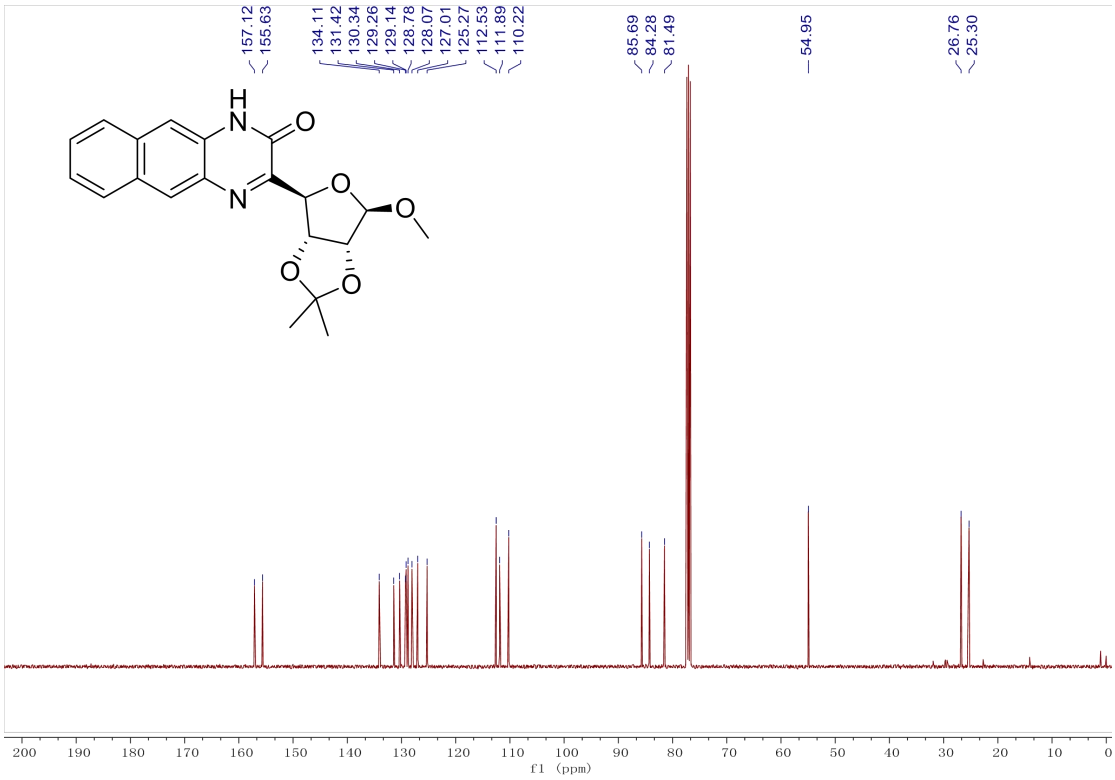
S60. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3ma**



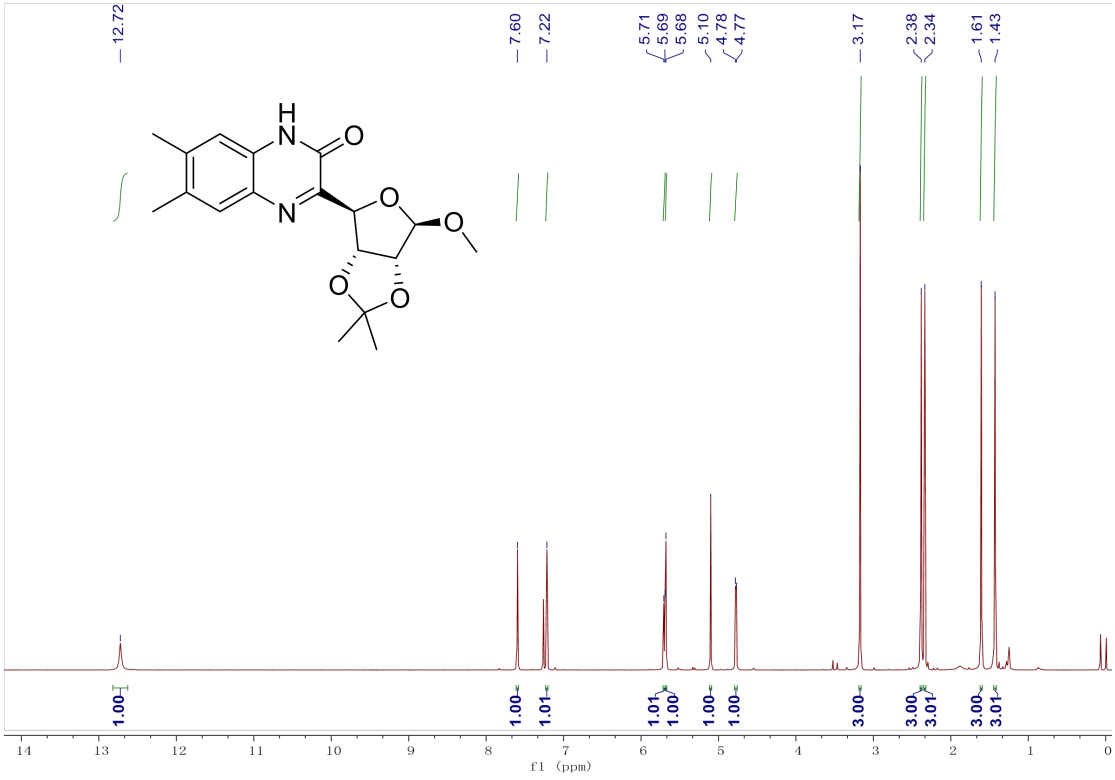
S61. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3ma**



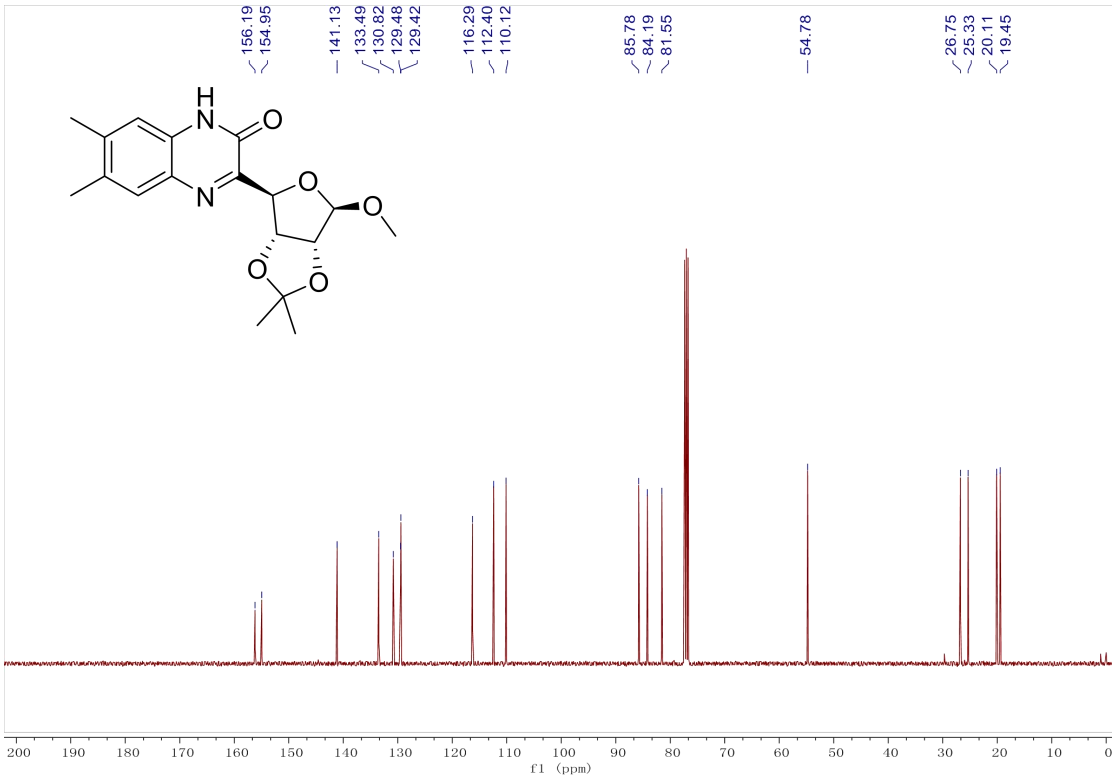
S62. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3na**



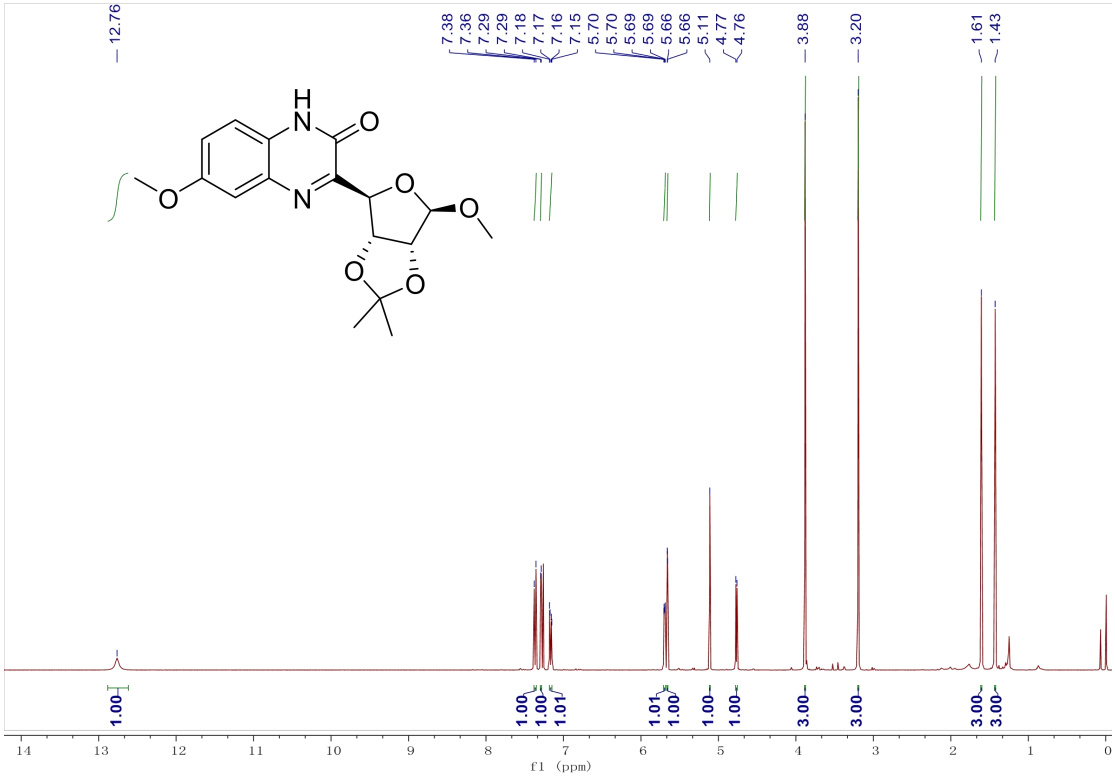
S63. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3na**



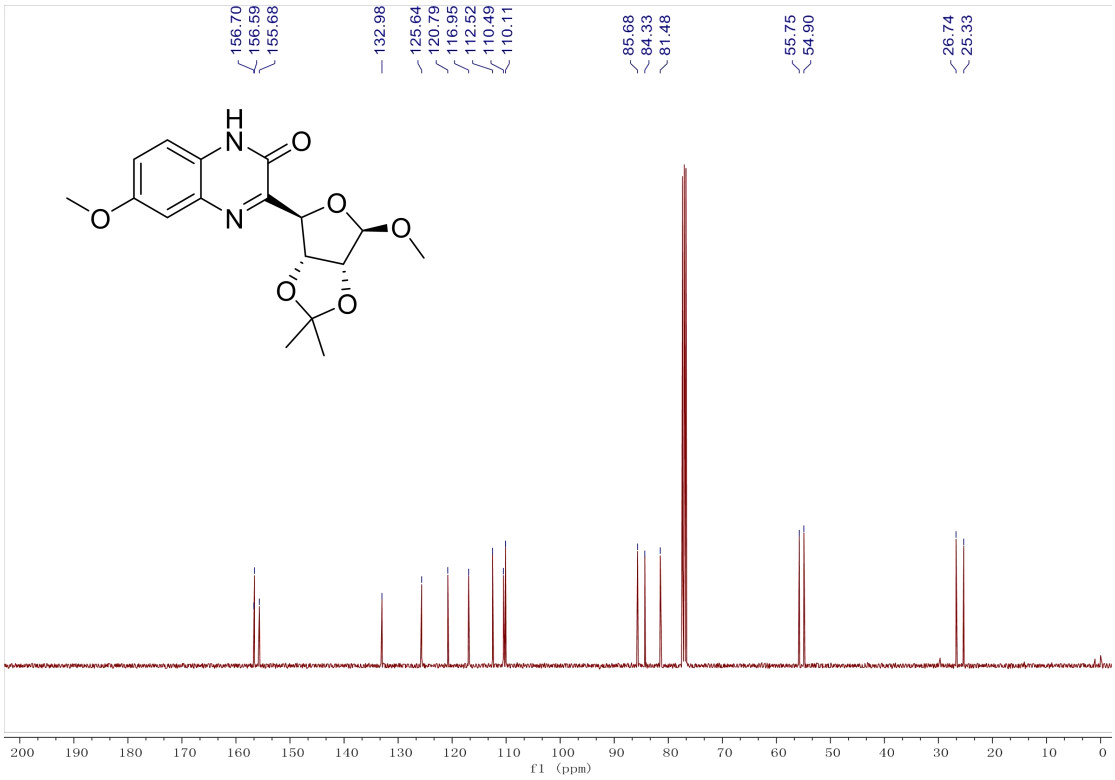
S64. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3oa**



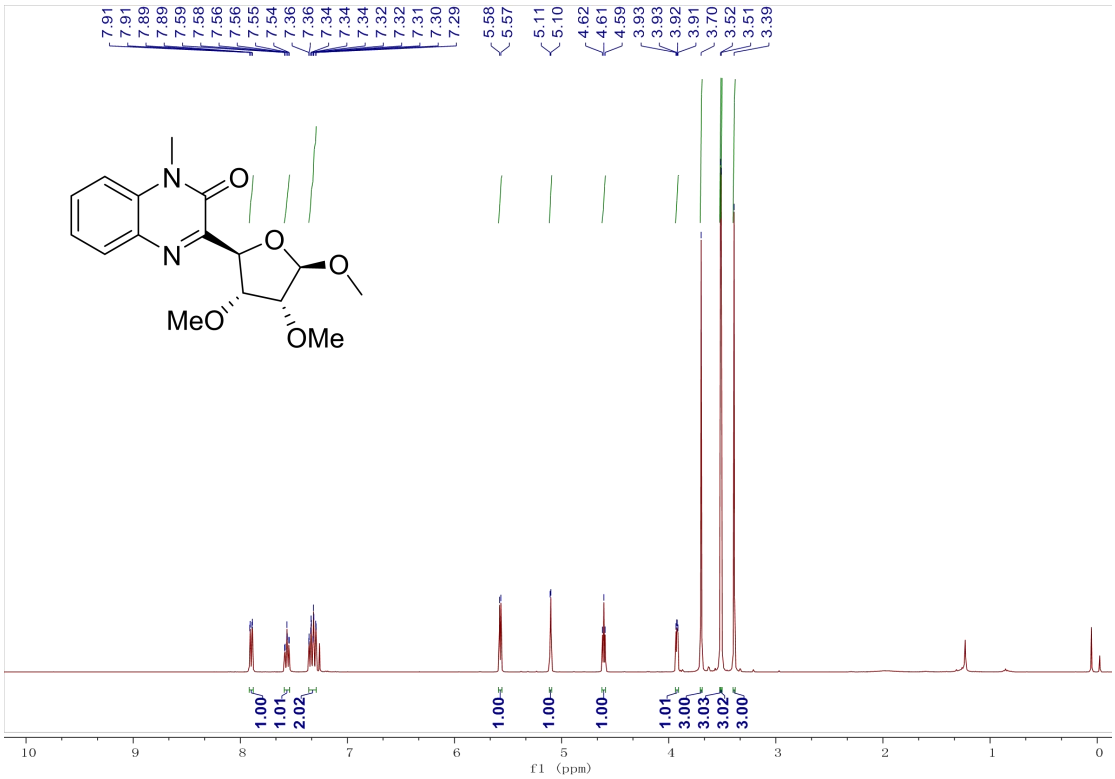
S65. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3oa**



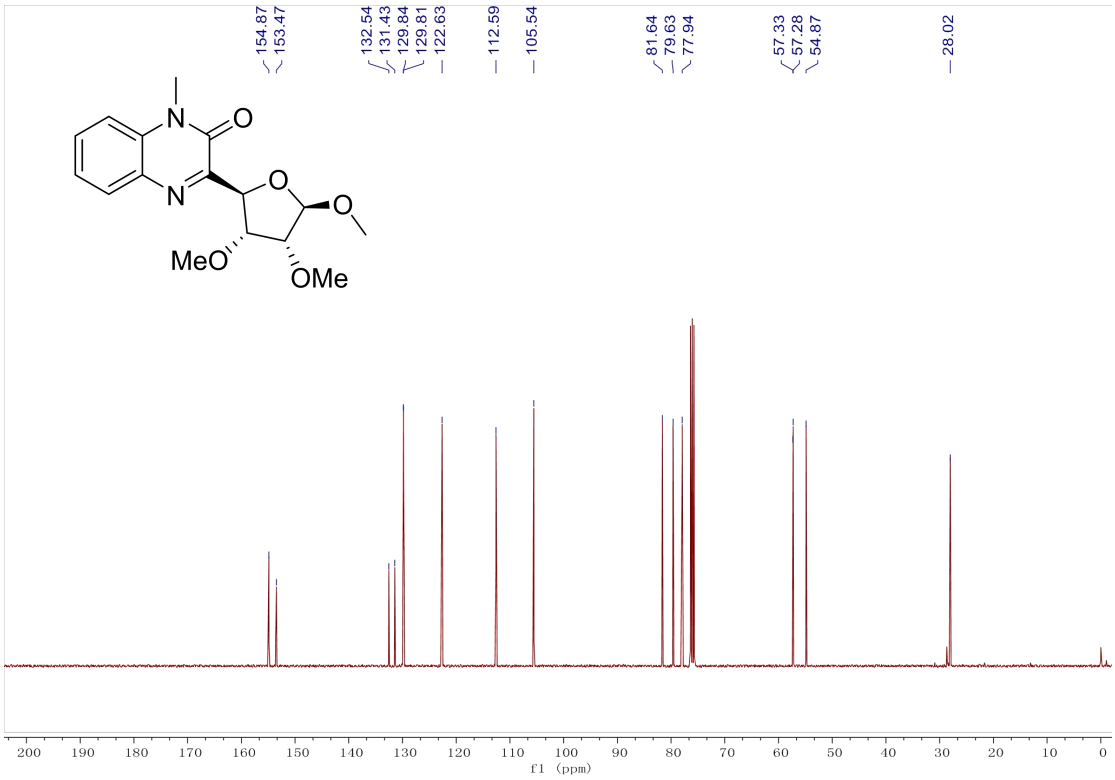
S66. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3pa**



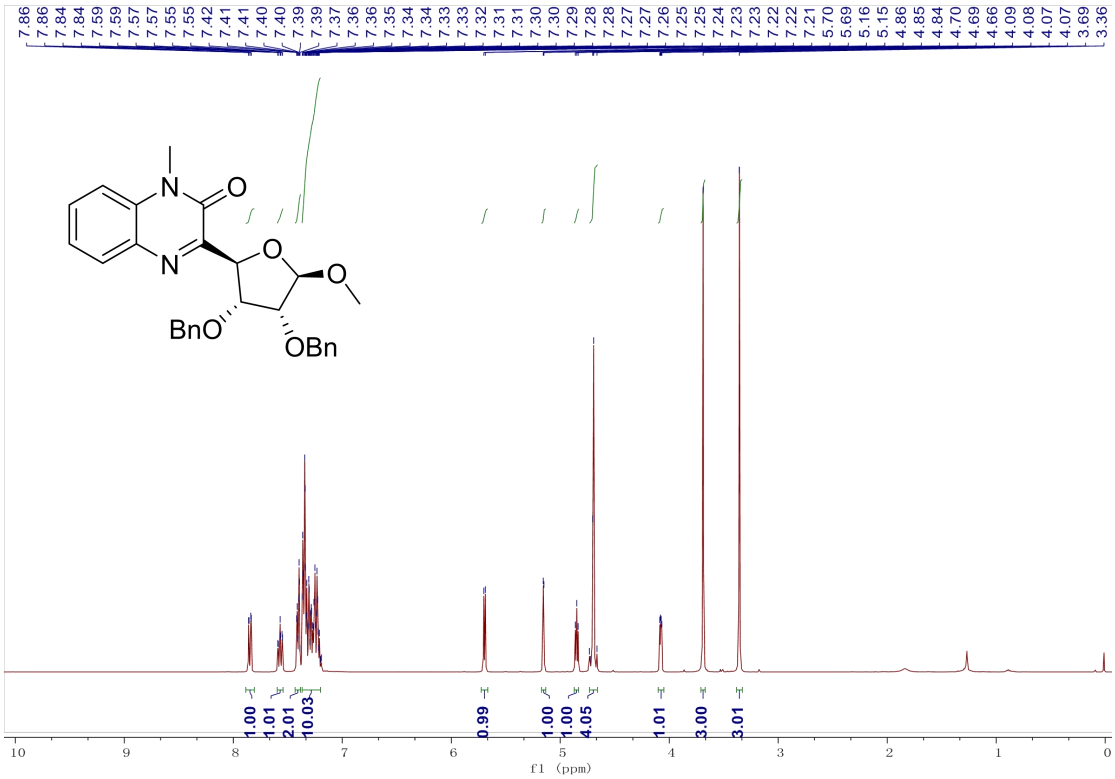
S67. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **3pa**



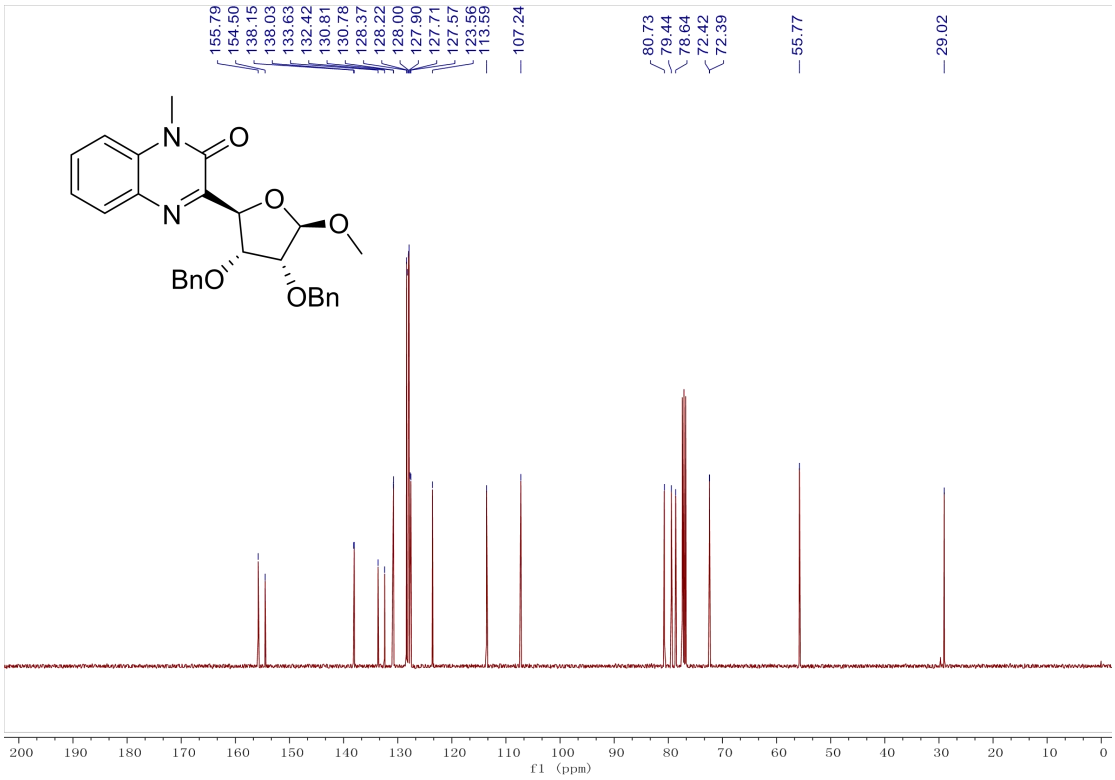
S68. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4aa**



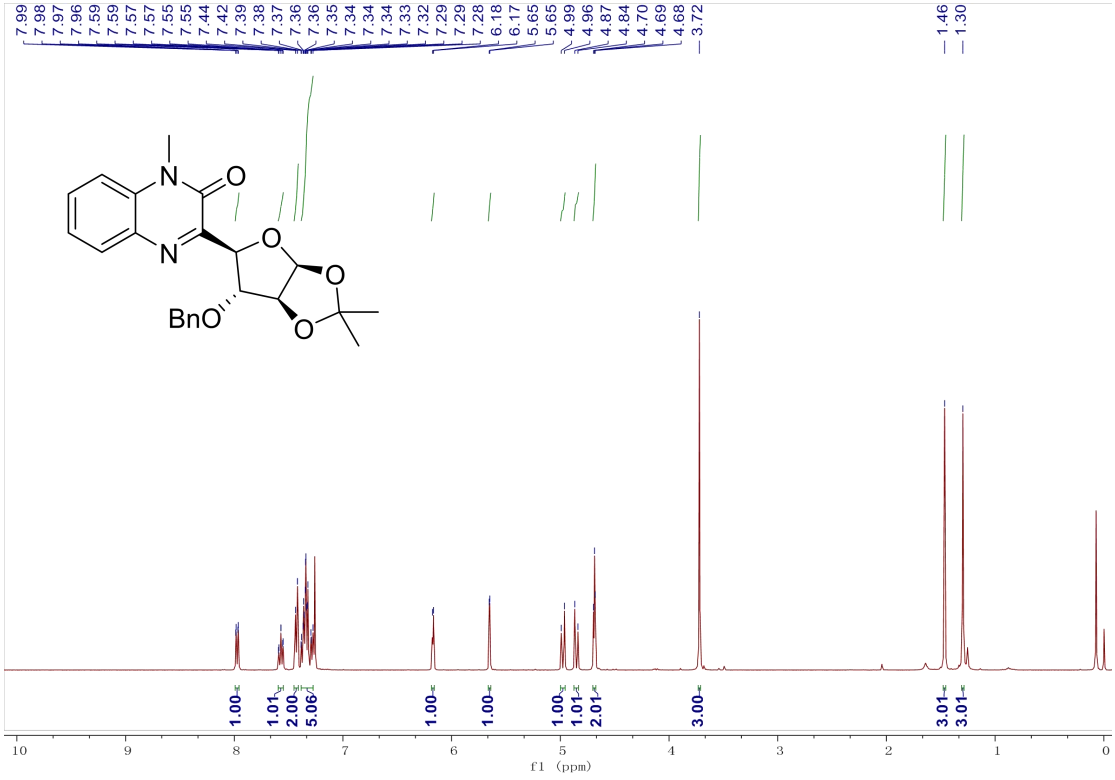
S69. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **4aa**



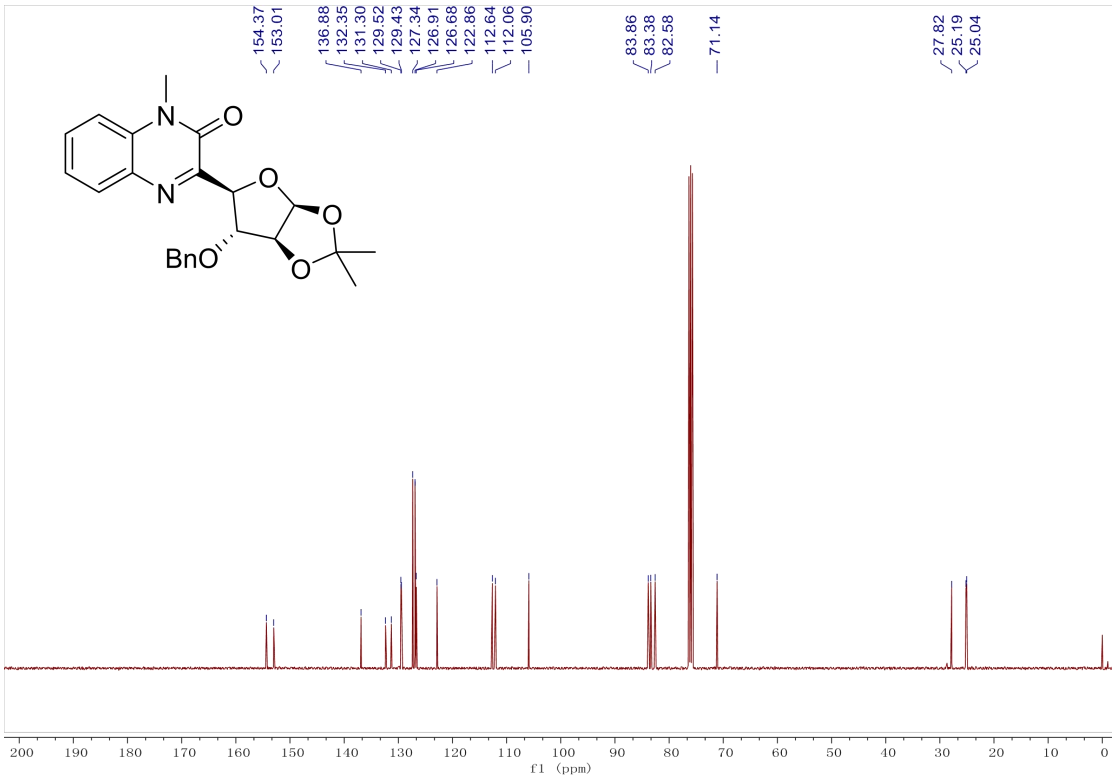
S70. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4ab**



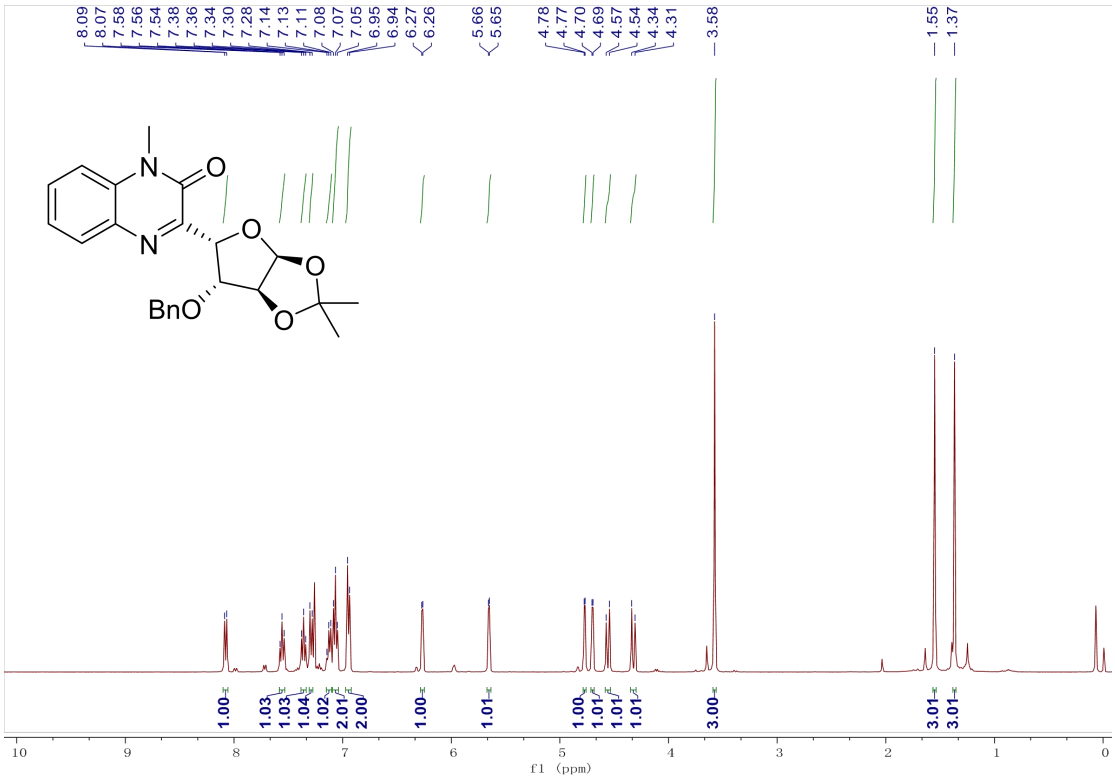
S71. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **4ab**



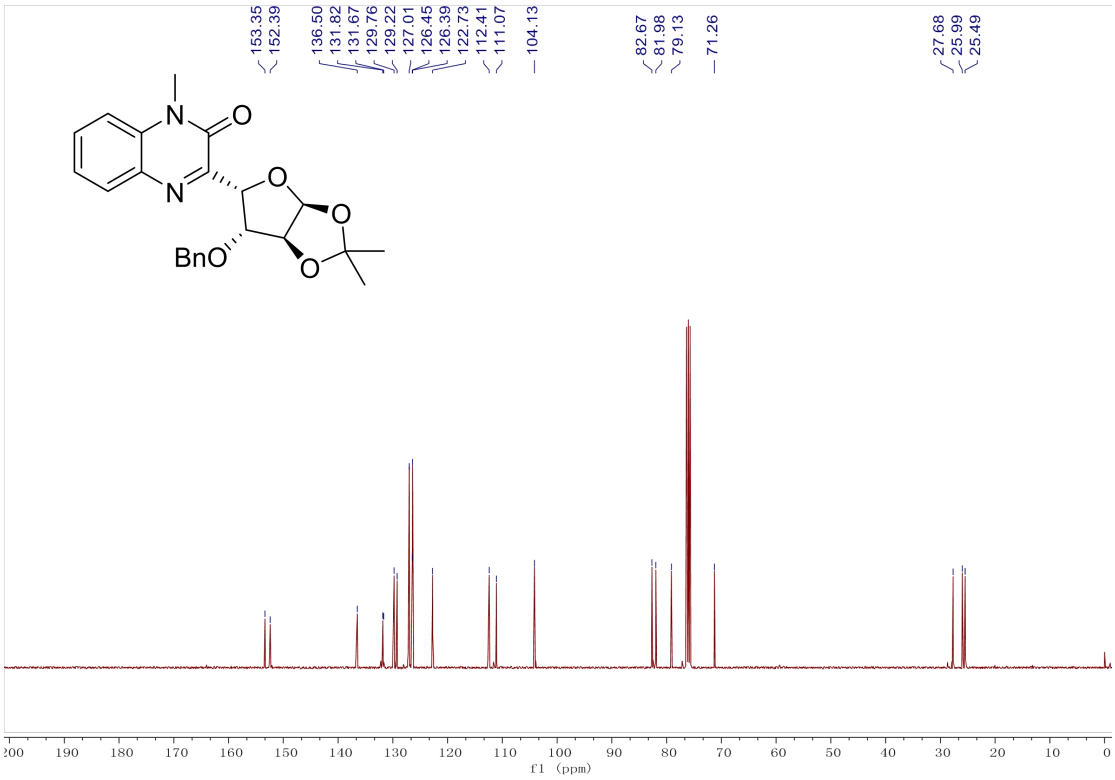
S72. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4ac**



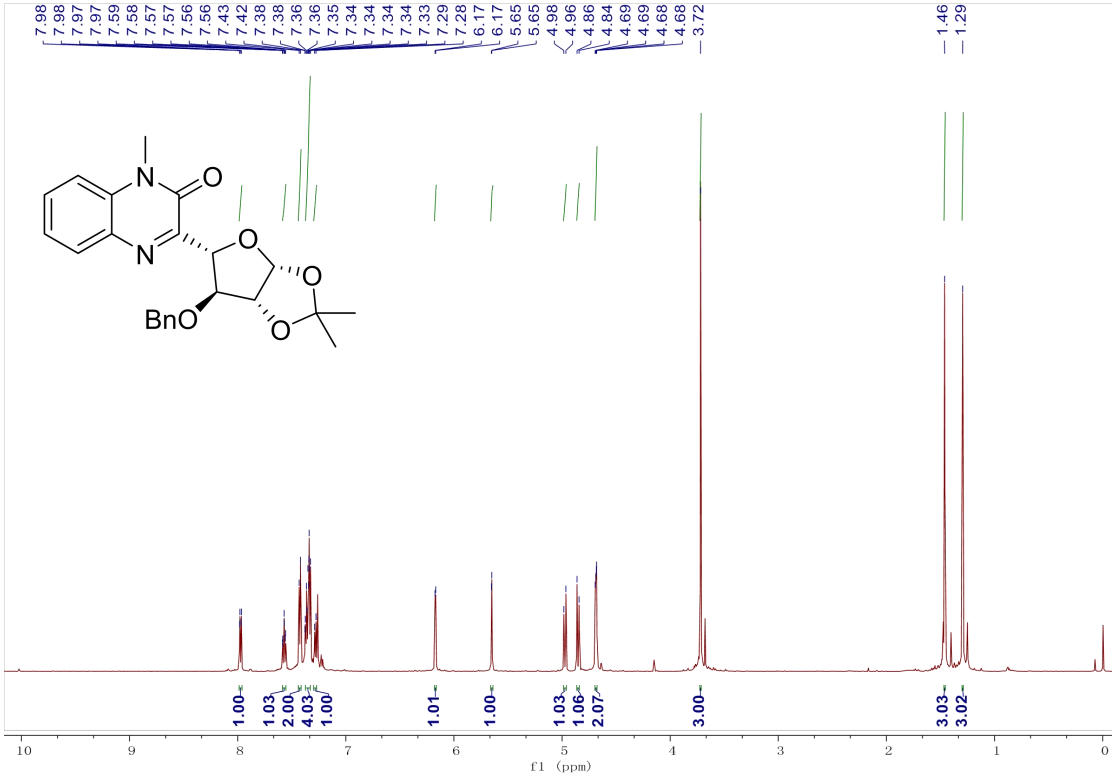
S73. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **4ac**



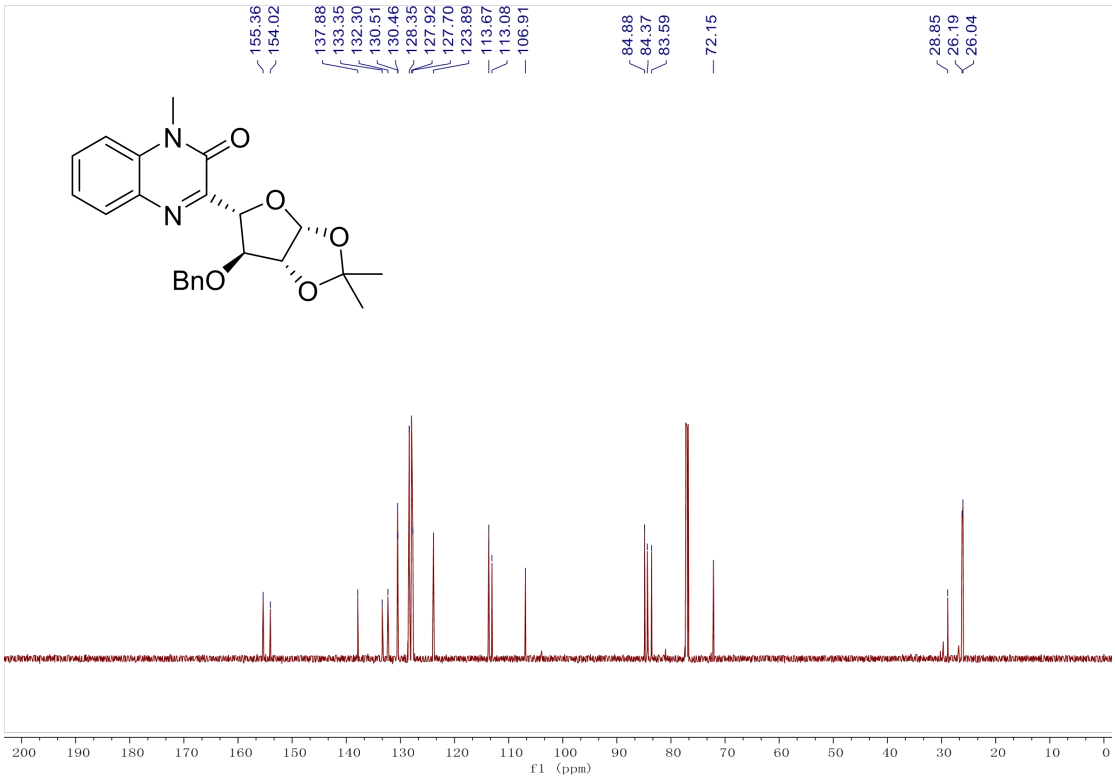
S74. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4ac'**



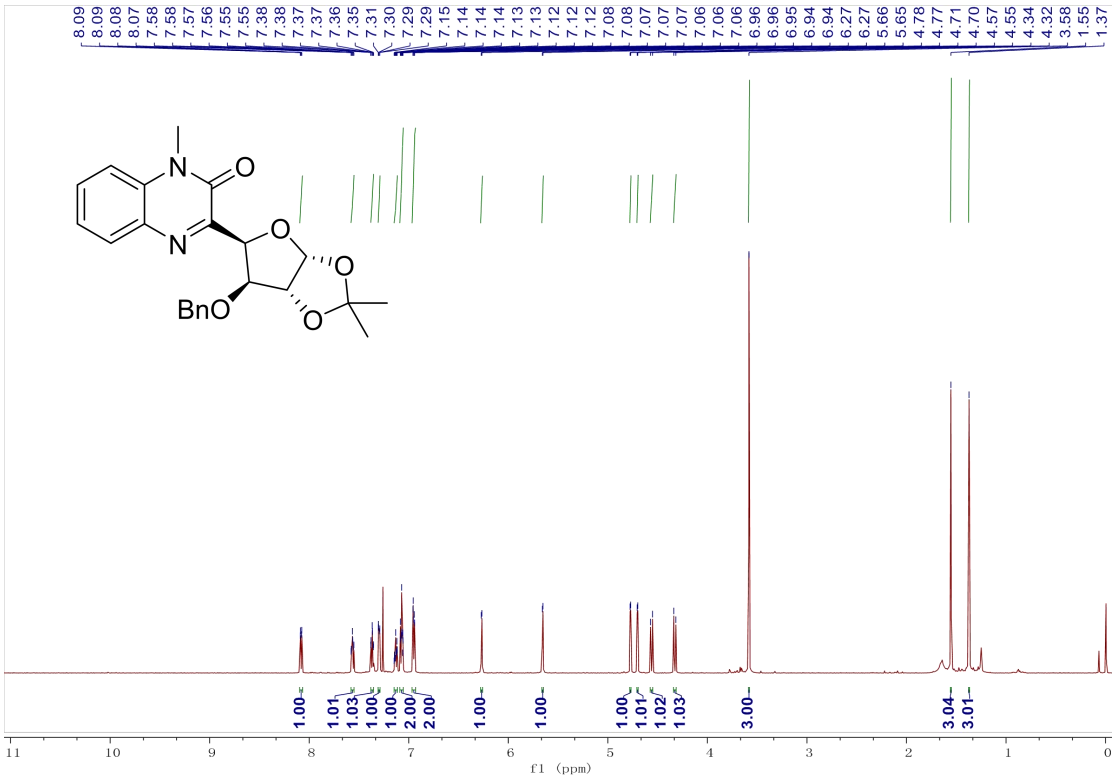
S75. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **4ac'**



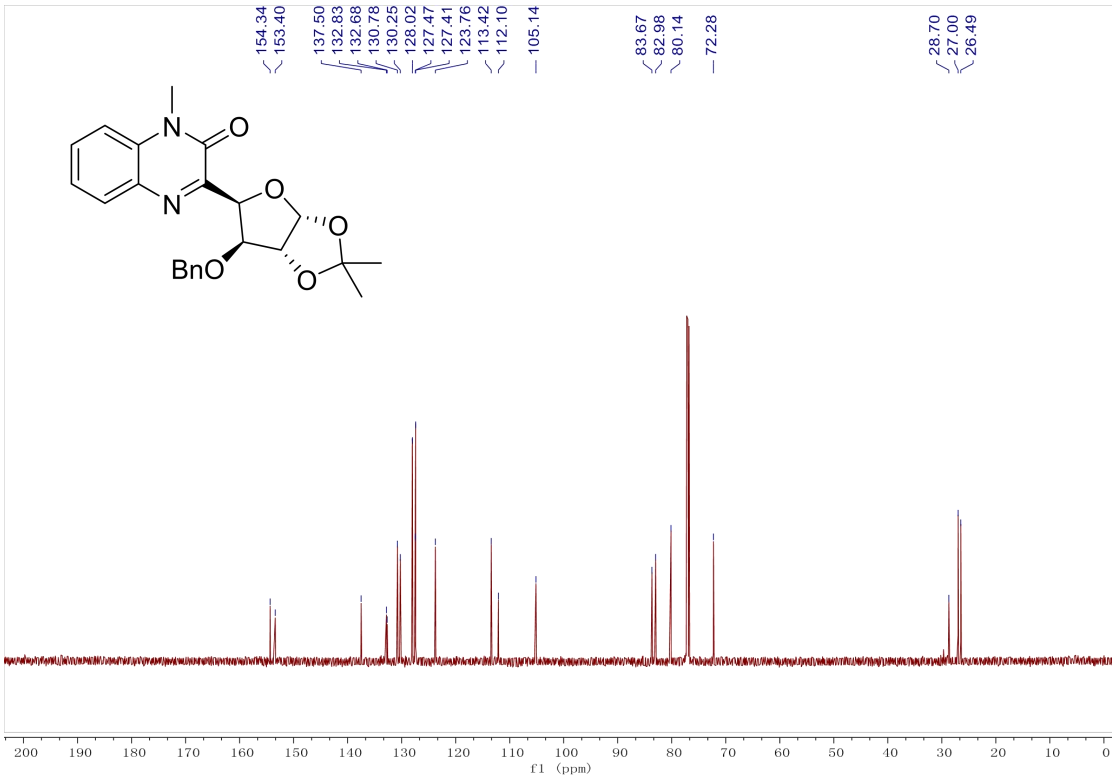
S76. ^{1}H NMR spectra (600 MHz, $CDCl_3$) of compound **4ad**



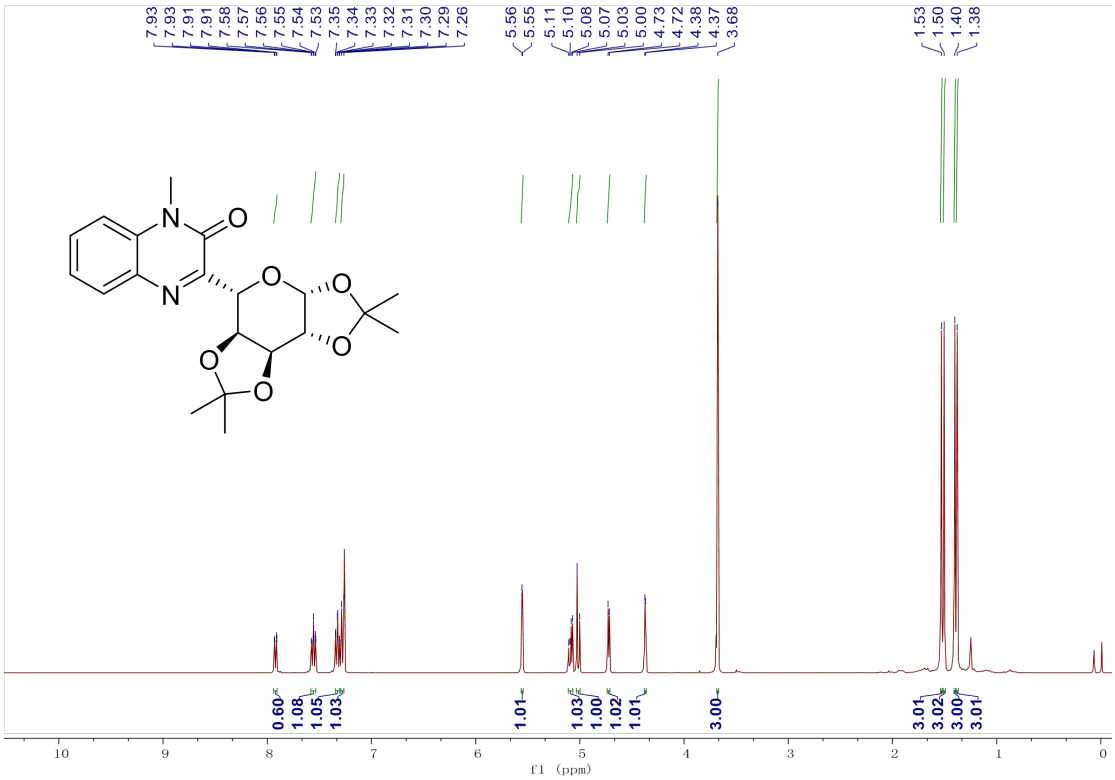
S77. ^{13}C NMR spectra (150 MHz, $CDCl_3$) of compound **4ad**



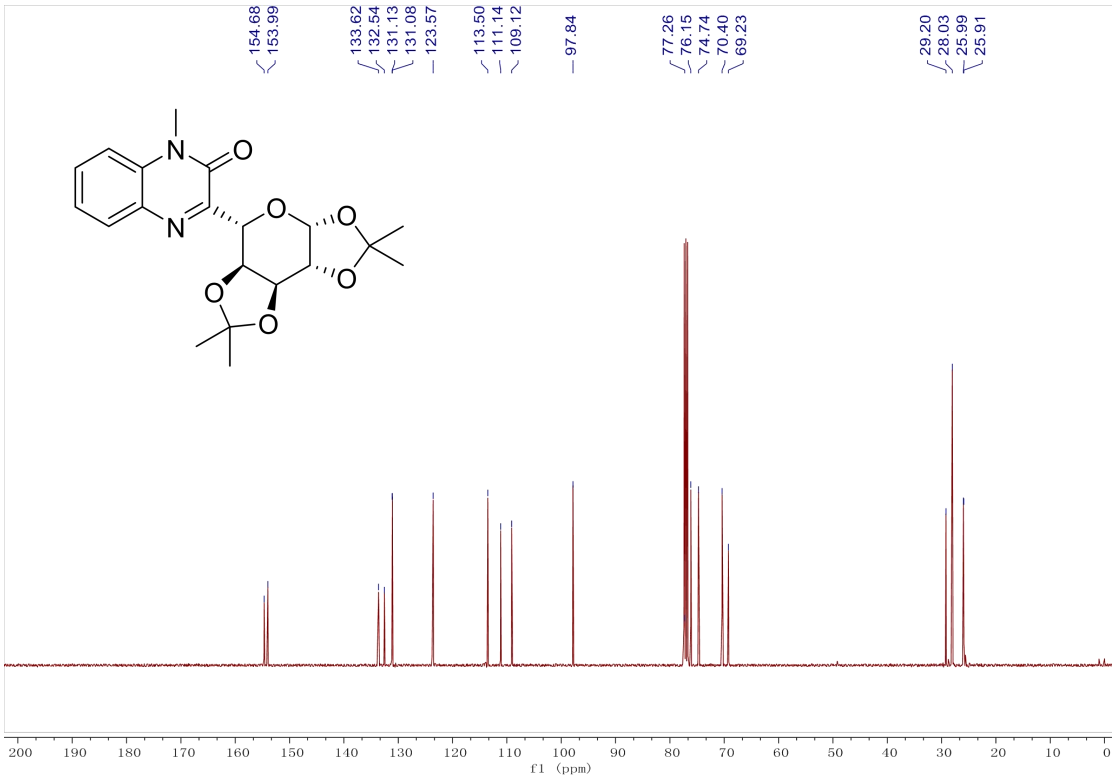
S78. ^{1}H NMR spectra (600 MHz, $CDCl_3$) of compound **4ad'**



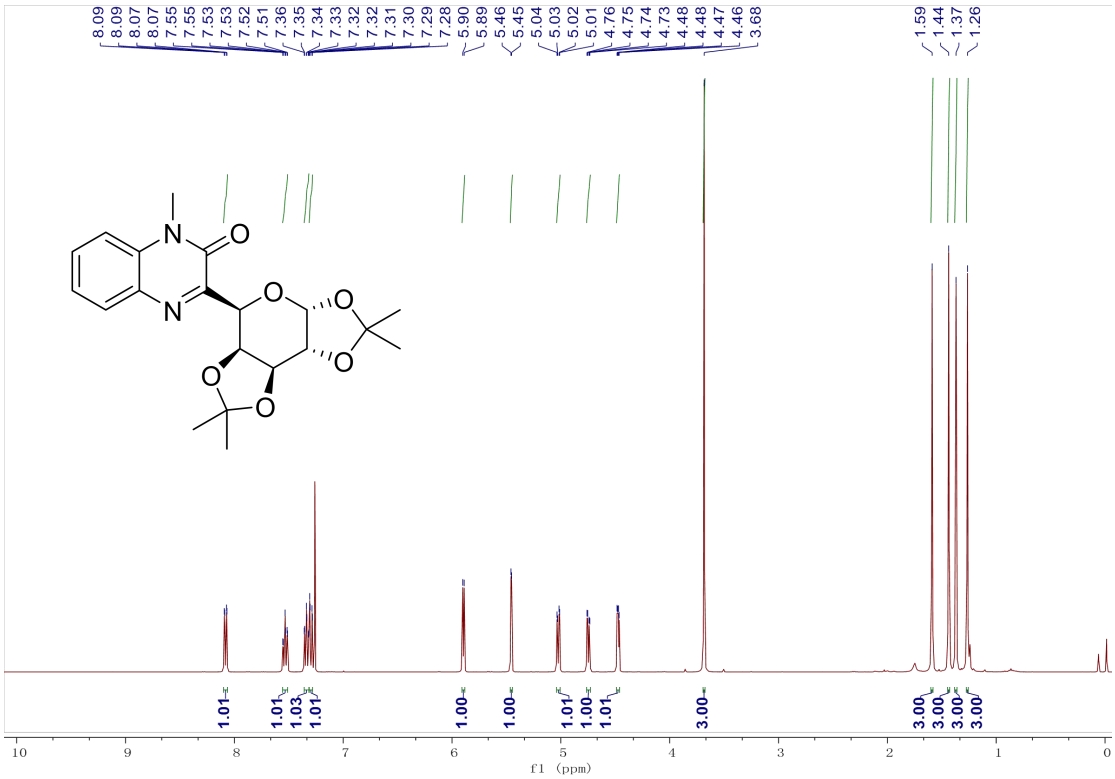
S79. ^{13}C NMR spectra (150 MHz, $CDCl_3$) of compound **4ad'**



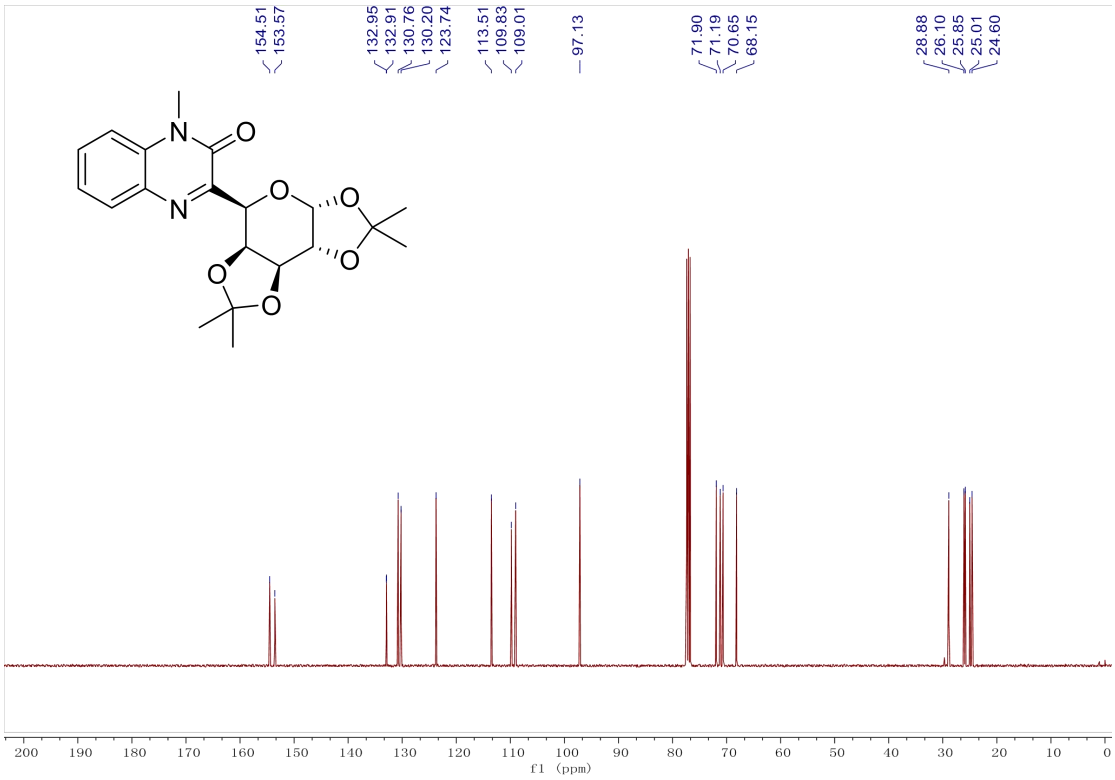
S80. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4ae**



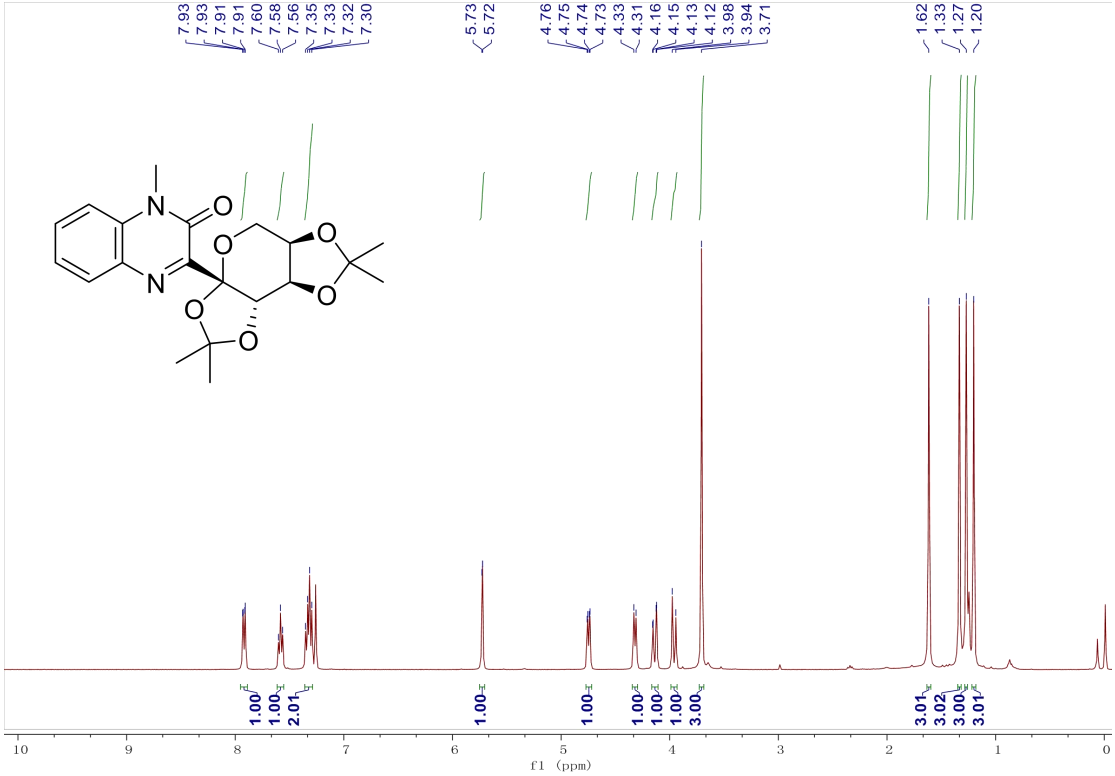
S81. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **4ae**



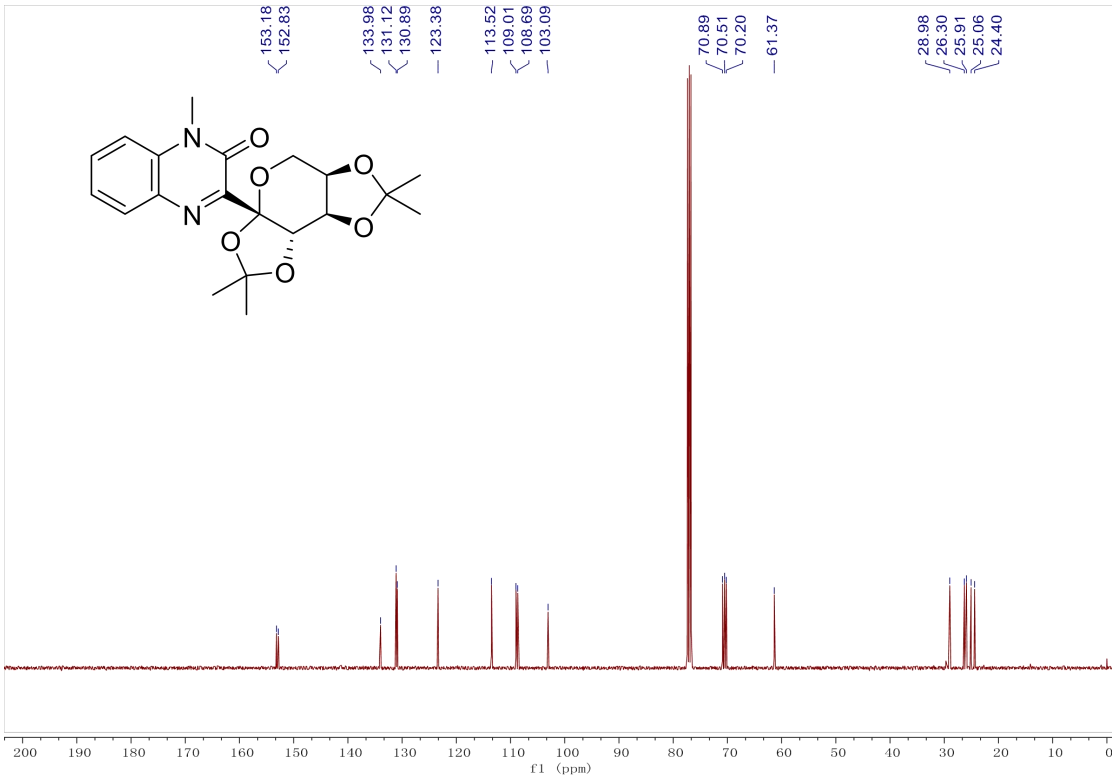
S82. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4ae'**



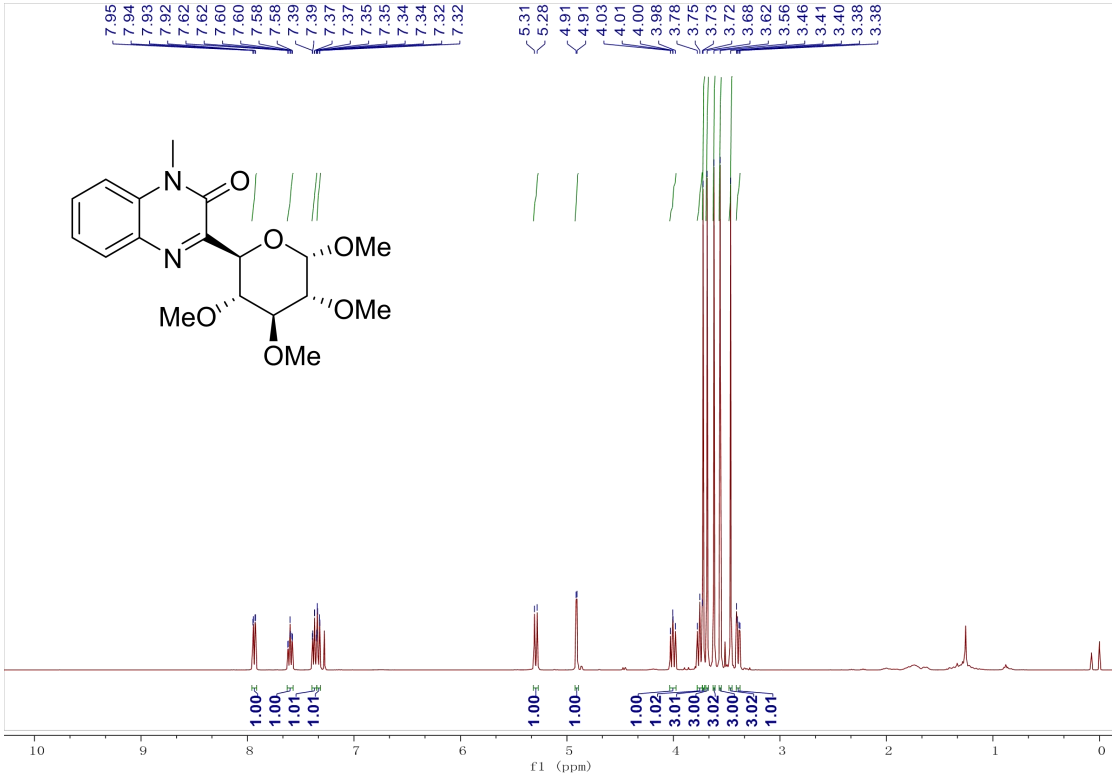
S83. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **4ae'**



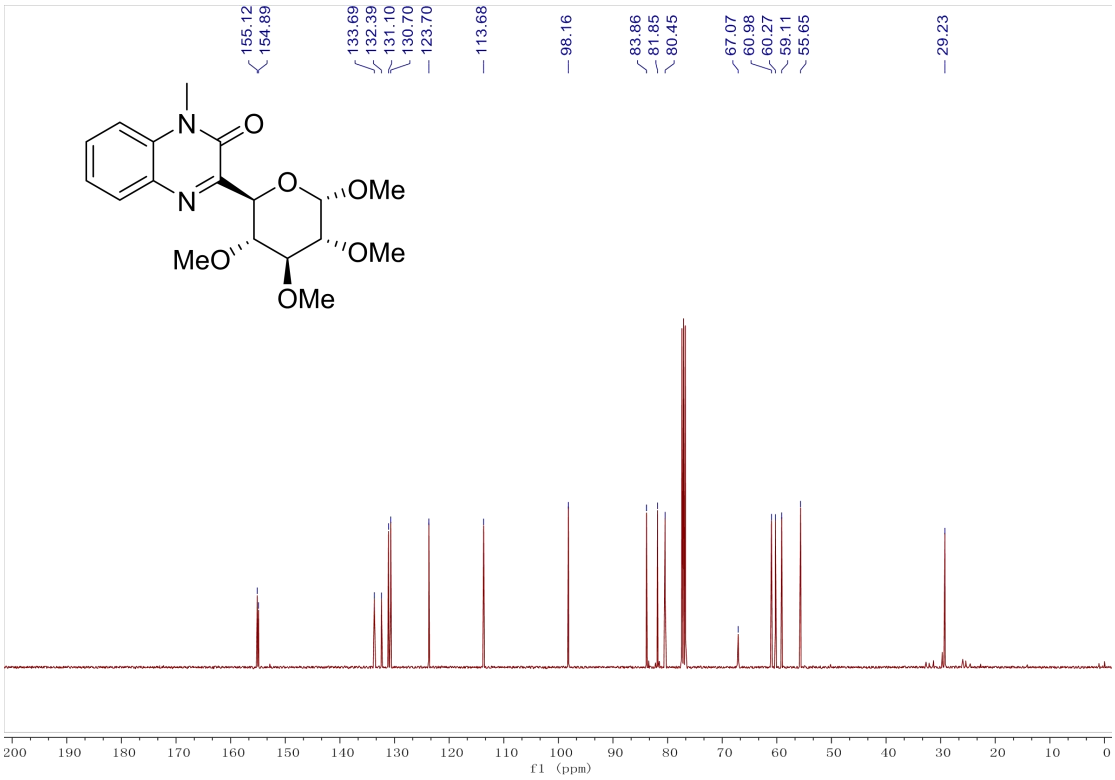
S84. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4af**



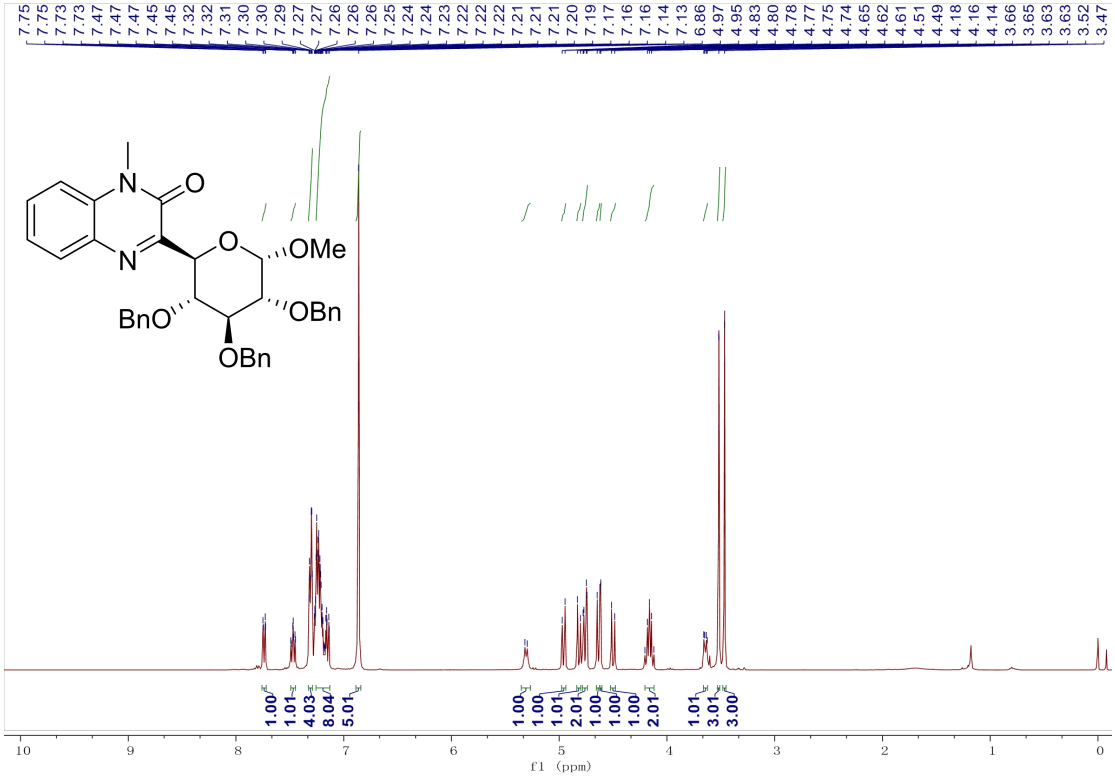
S85. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **4af**



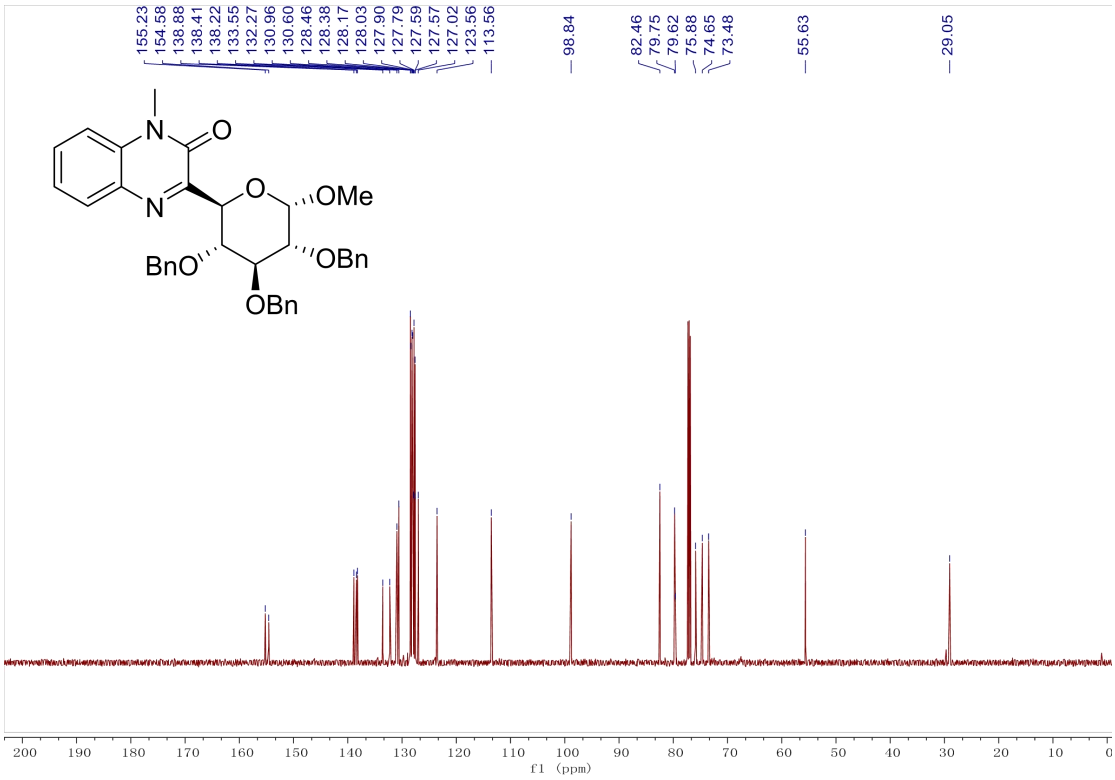
S86. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4ag**



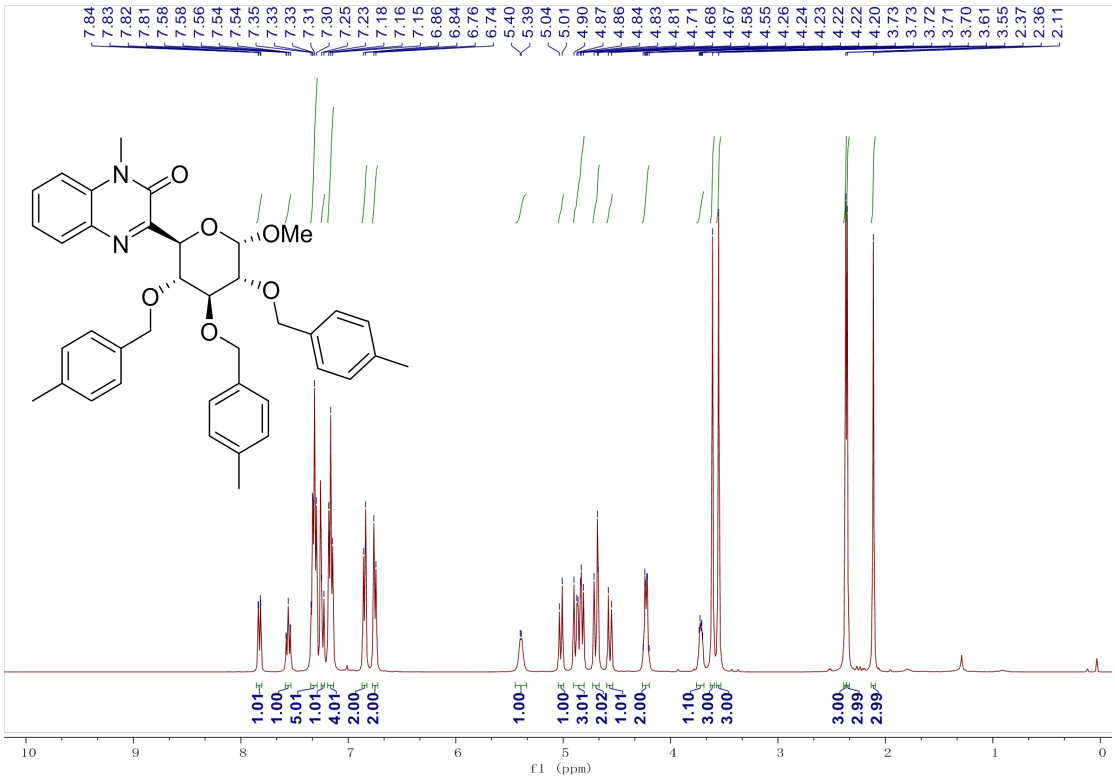
S87. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **4ag**



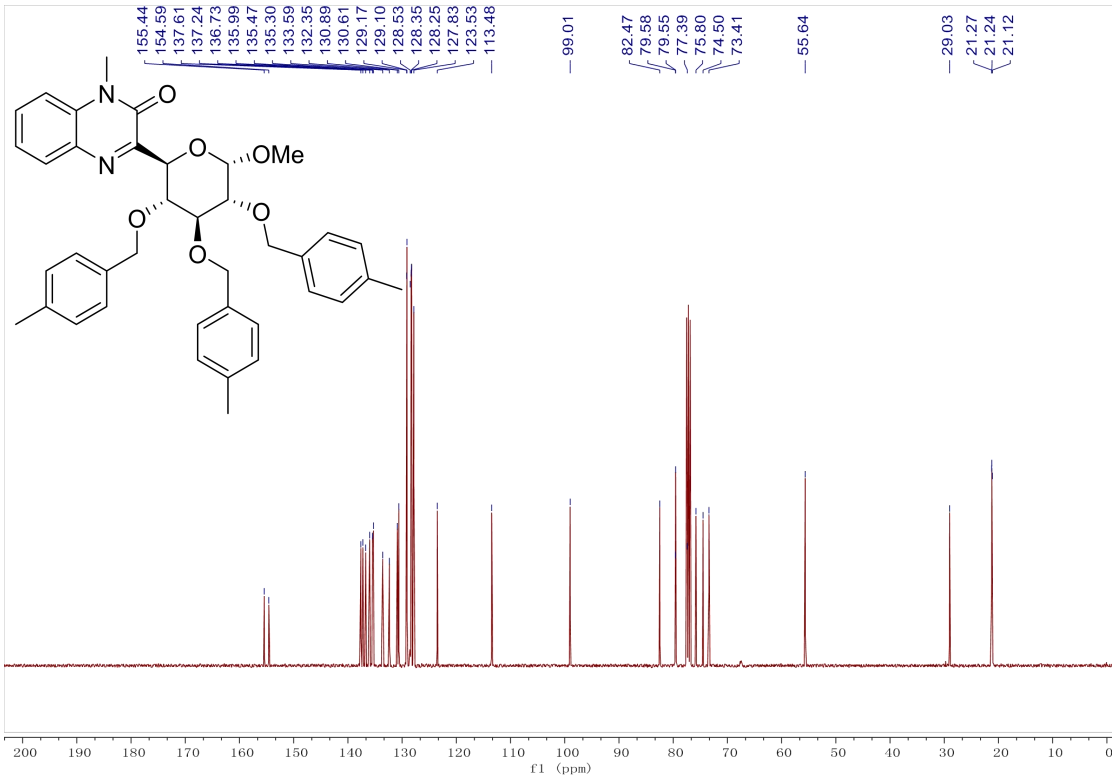
S88. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4ah**



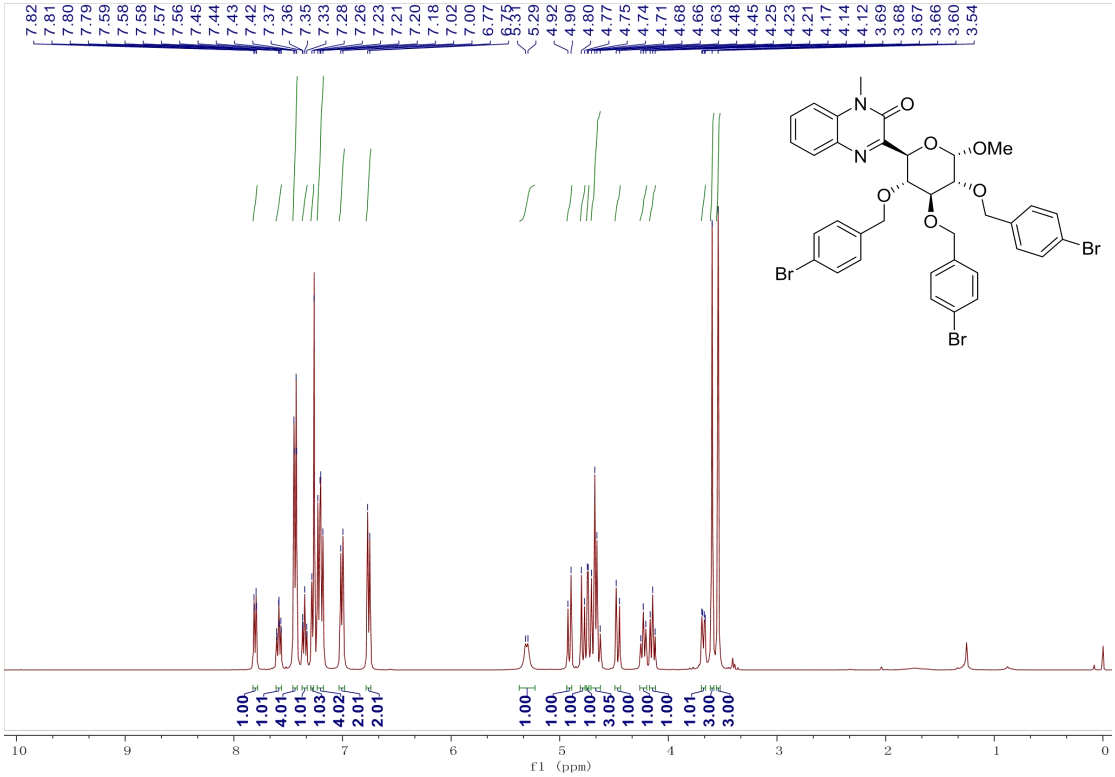
S89. ^{13}C NMR spectra (150 MHz, $CDCl_3$) of compound **4ah**



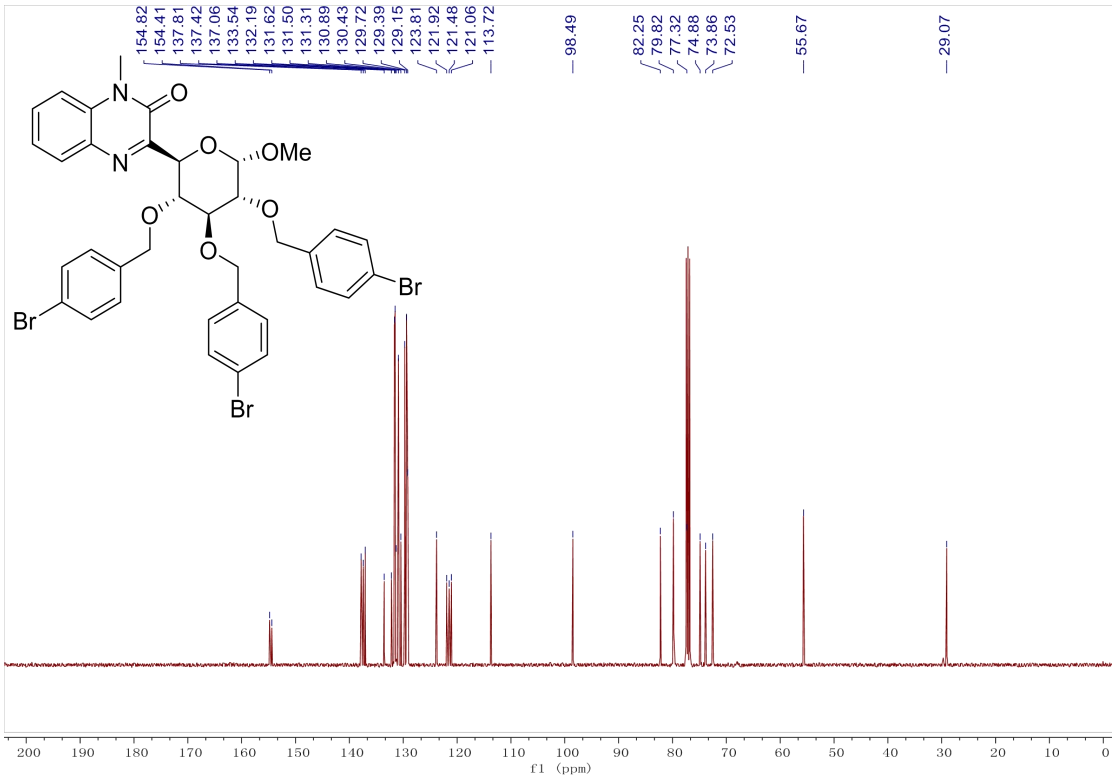
S90. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4ai**



S91. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **4ai**



S92. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4aj**



S93. ^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **4aj**