Concise synthesis of 3-*C*-glycosyl isocoumarins and 2- glycosyl-4*H*-chromen-4-ones

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Contents

1. General Information

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

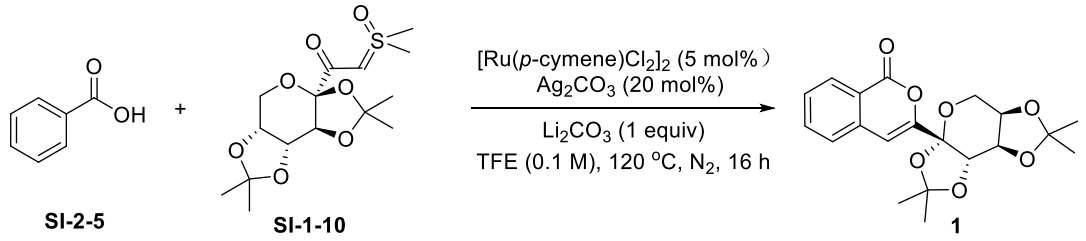
Proton NMR (^{1}H) were recorded at 300/400/500/600 MHz, and Carbon NMR (^{13}C) at 75/101/126/151 MHz NMR spectrometer unless otherwise stated. The following abbreviations are used for the multiplicities: s: singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s: broad singlet for proton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

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

Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. Visualization was accomplished with short wave UV light, or $KMnO_4$ staining solutions followed by heating. Flash column chromatography was performed using silica gel (300-400 mesh) with solvents distilled prior to use.

2. Optimization Data

Table S1. Reaction of Benzoic acid **SI-2-1** with carbonyl sulfoxonium ylides glycogen anomeric **SI-1-10**.

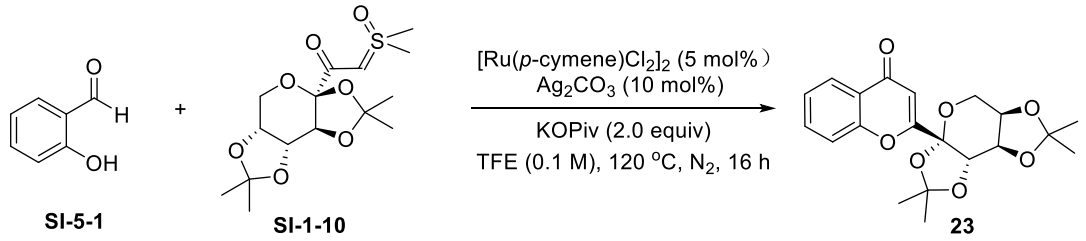


SI-2-5 + **SI-1-10** → **1**

Entry	Deviation from standard conditions	Yield of **1**(%)[b]
1	None	78
2	$RuCl_3·H_2O$ instead of $[Ru(p\text{-cymene})Cl_2]_2$	0
3	AgOTf instead of Ag_2CO_3	76
4	$AgSbF_6$ instead of Ag_2CO_3	52
5	NaOAc (1.0 equiv) instead of Li_2CO_3 (1.0 equiv)	67
6	NEt_3 (1.0 equiv) instead of Li_2CO_3 (1.0 equiv)	56
7	K_2CO_3 (1.0 equiv) instead of Li_2CO_3 (1.0 equiv)	60
8	DCM instead of TFE	61
9	1,4-dioxane instead of TFE	0
10	Without$[Ru(p\text{-cymene})Cl_2]_2$	-
11	Without Ag_2CO_3	32
12	Without $[Ru(p\text{-cymene})Cl_2]_2$ and $AgSbF_6$	-

Reaction conditions: [a] **SI-2-1** (0.2 mmol, 1.0 equiv.), **SI-1-10** (0.3 mmol, 1.5 equiv.), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %), Ag_2CO_3 (20 mol %), Li_2CO_3 (0.2 mmol, 1.0 equiv.), TFE (0.1 M) 120 °C, N_2, 16 h. [b] Isolated yields.

Table S2. Reaction of Salicylaldehyde **SI-5-1** with carbonyl sulfoxonium ylides glycogen anomeric **SI-1-10**.



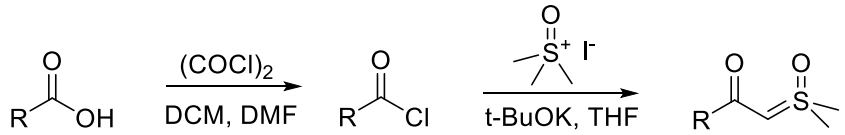
SI-5-1 + **SI-1-10** → **23**

Entry	Deviation from standard conditions	Yield of **23**(%)[b]
1	None	84
2	$RuCl_3·H_2O$ instead of $[Ru(p\text{-cymene})Cl_2]_2$	0
3	AgOAc instead of Ag_2CO_3	70
4	AgOTf instead of Ag_2CO_3	36
5	PivOH (2.0 equiv) instead of KOPiv (2.0 equiv)	24
6	NaOAc (2.0 equiv) instead of KOPiv (2.0 equiv)	0
7	K_2CO_3 (2.0 equiv) instead of KOPiv (2.0 equiv)	<10
8	n-Hexane instead of TFE	37
9	DCE instead of TFE	24
10	Without$[Ru(p\text{-cymene})Cl_2]_2$	-
11	Without Ag_2CO_3	79
12	Without $[Ru(p\text{-cymene})Cl_2]_2$ and Ag_2CO_3	-

Reaction conditions: [a] **SI-5-1** (0.2 mmol, 1.0 equiv.), **SI-1-10** (0.3 mmol, 1.5 equiv.) $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %), Ag_2CO_3 (10 mol %), KOPiv (0.4 mmol, 2.0 equiv.), TFE (0.1 M), 120 °C, N_2, 16 h. [b] Isolated yields.

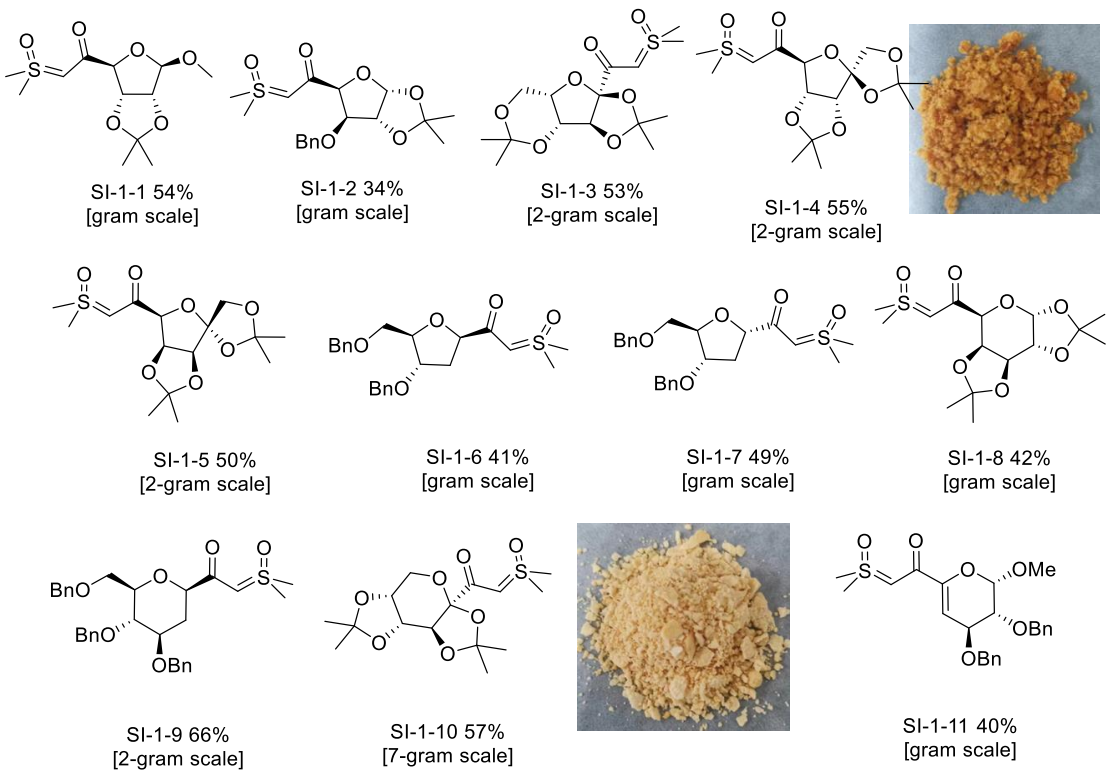
3. Synthesis of Starting Materials

3.1 Synthesis of Carbonyl sulfoxonium ylides glycogen anomeric (General procedure 1) [1]

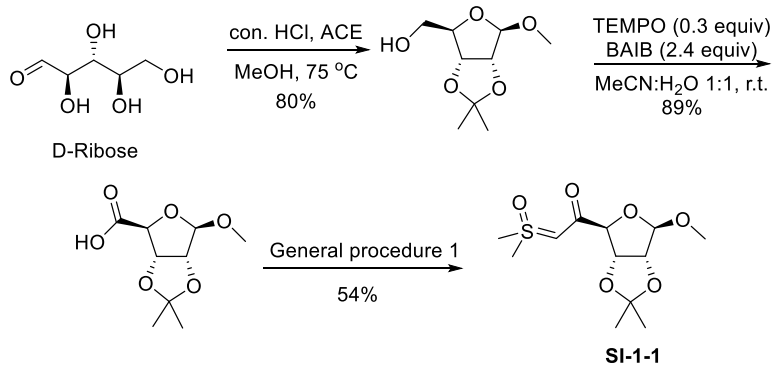


Step-I: To a stirred solution of a carboxylic acid (5 mmol) and DMF (2 drops) in CH_2Cl_2 (25 mL), $(COCl)_2$ (10 mmol, 0.9 mL) was added dropwise. The reaction was allowed to stir at room temperature 2 h. Evaporation of the reaction mixture gave a residue which was dissolved in THF (20 mL). The resulting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

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

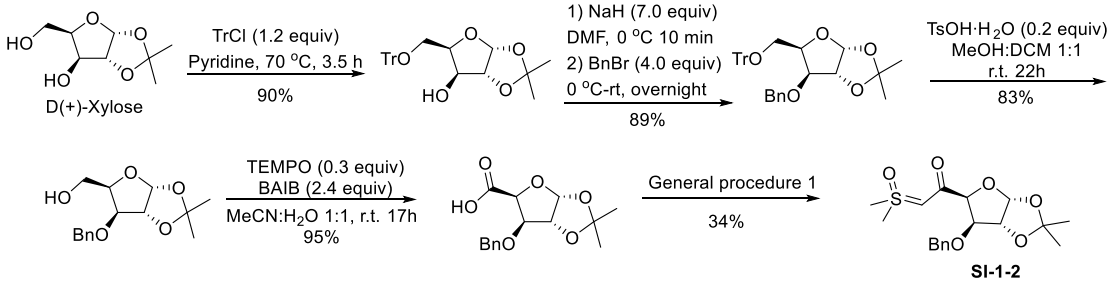


Synthesis of compound SI-1-1 [2-3]



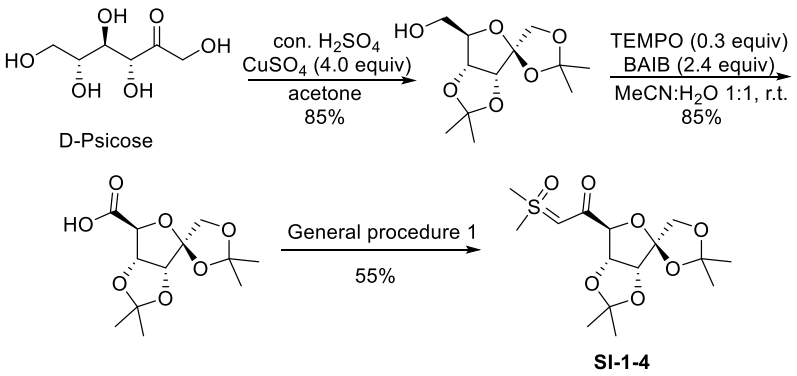
2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-((3a*S*,4*S*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)ethan-1-one (SI-1-1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.11 (dd, *J* = 6.1, 1.6 Hz, 1H), 5.01 (s, 1H), 4.78 (s, 1H), 4.54 – 4.46 (m, 2H), 3.42 (s, 3H), 3.39 (s, 6H), 1.48 (s, 3H), 1.31 (s, 3H). Spectroscopic data in accordance with literature.[1]

Synthesis of compound SI-1-2 [4-6]



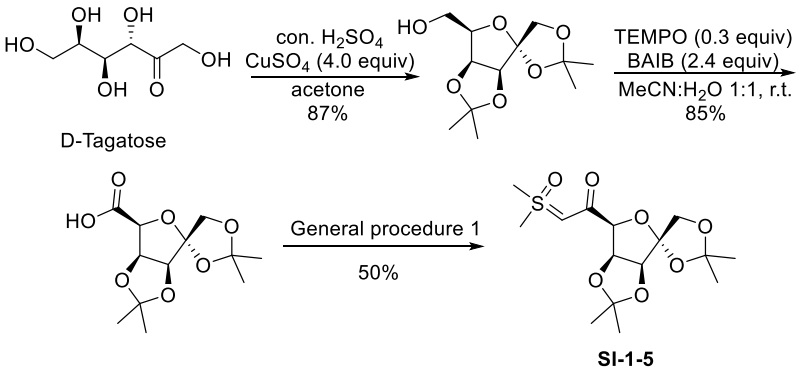
1-((3a*R*,5*S*,6*R*,6a*R*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)ethan-1-one (SI-1-2): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 4H), 7.27 – 7.25 (m, 1H), 6.01 (d, *J* = 3.6 Hz, 1H), 5.05 (s, 1H), 4.63 (s, 2H), 4.62 (d, *J* = 3.2 Hz, 1H), 4.58 (d, *J* = 3.6 Hz, 1H), 4.32 (d, *J* = 3.2 Hz, 1H), 3.36 (s, 3H), 3.32 (s, 3H), 1.47 (s, 3H), 1.31 (s, 3H). Spectroscopic data in accordance with literature.[1]

Synthesis of compound SI-1-4



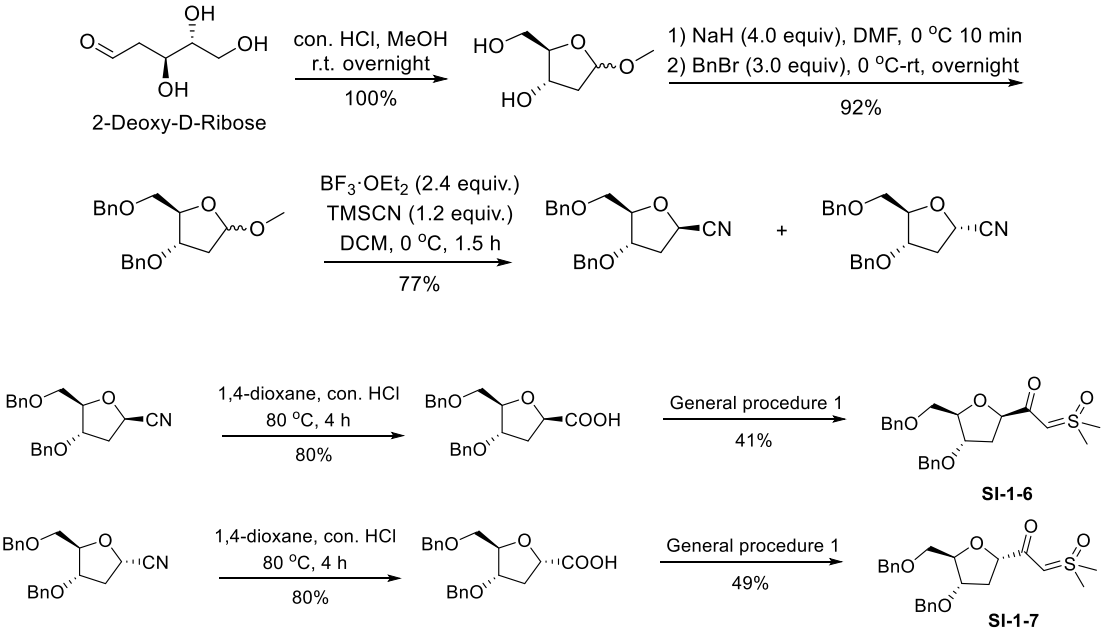
2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-((3a*R*,4*S*,6*S*,6a*R*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)ethan-1-one (SI-1-4): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.11 (dd, *J* = 6.0, 1.7 Hz, 1H), 4.95 (s, 1H), 4.56 (d, *J* = 5.9 Hz, 1H), 4.40 (d, *J* = 1.7 Hz, 1H), 4.35 (d, *J* = 9.8 Hz, 1H), 4.07 (d, *J* = 9.8 Hz, 1H), 3.42 (s, 3H), 3.38 (s, 3H), 1.54 (s, 3H), 1.45 (s, 3H), 1.38 (s, 3H), 1.31 (s, 3H). Spectroscopic data in accordance with literature.[1]

Synthesis of compound SI-1-5 [7]



2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-((3a*S*,4*R*,6*S*,6a*S*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)ethan-1-one (SI-1-5): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.07 – 4.99 (m, 1H), 4.82 (s, 1H), 4.61 – 4.54 (m, 1H), 4.37 – 4.25 (m, 2H), 4.11 (dd, J = 9.7, 2.0 Hz, 1H), 3.45 (s, 3H), 3.40 (s, 3H), 1.47 (s, 3H), 1.39 (s, 6H), 1.29 (s, 3H). Spectroscopic data in accordance with literature.[1]

Synthesis of compound SI-1-6 and **SI-1-7** [8-10]

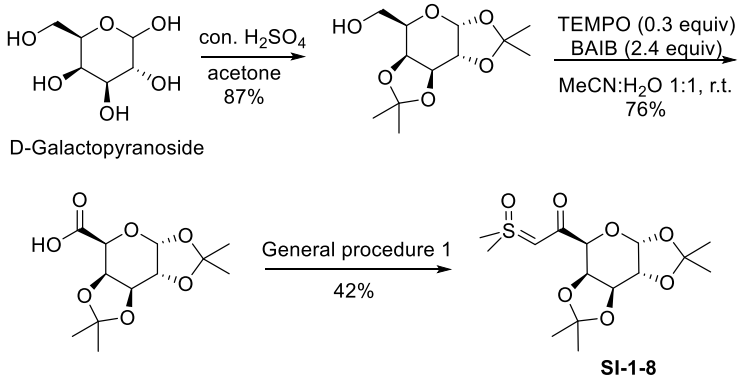


1-((2*R*,4*S*,5*R*)-4-(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-2-yl)-2-

(dimethyl(oxo)-λ^6-sulfaneylidene)ethan-1-one (SI-1-6): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 - 7.23 (m, 10H), 4.95 (s, 1H), 4.54 (d, *J* = 4.5 Hz, 3H), 4.50 – 4.40 (m, 2H), 4.21 (q, *J* = 4.5 Hz, 1H), 4.07 (dt, *J* = 6.2, 3.1 Hz, 1H), 3.64-3.49 (m, 2H), 3.36 (s, 3H), 3.24 (s, 3H), 2.42-2.32 (m, 1H), 2.10-1.98 (m, 1H). Spectroscopic data in accordance with literature.[1]

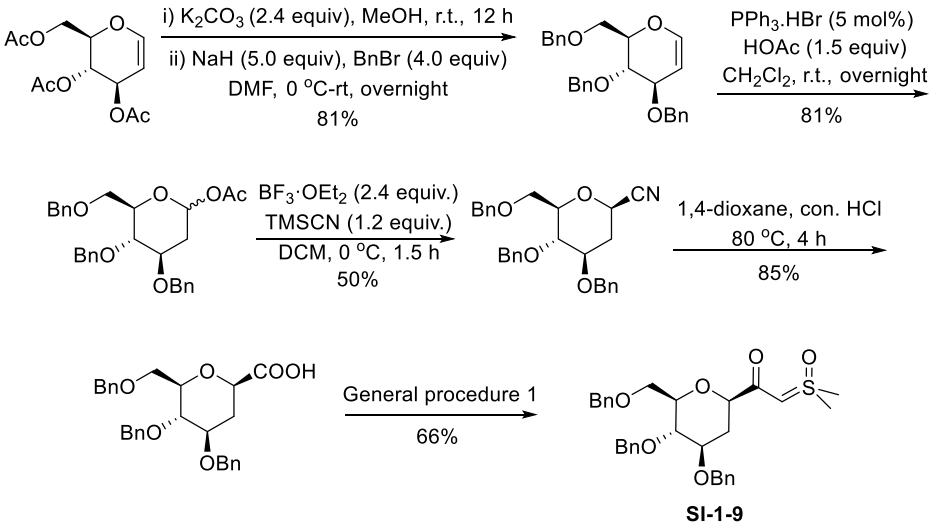
1-((2*S*,4*S*,5*R*)-4-(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-2-yl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)ethan-1-one (SI-1-7): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 10H), 4.98 (s, 1H), 4.56 (s, 2H), 4.47 (s, 1H), 4.40 (d, *J* = 11.1 Hz, 2H), 4.32 – 4.27 (m, 1H), 4.05 (q, *J* = 4.3 Hz, 1H), 3.55 – 3.48 (m, 2H), 3.31 (s, 3H), 3.20 (s, 3H), 2.36 (t, *J* = 6.0 Hz, 2H). Spectroscopic data in accordance with literature.[1]

Synthesis of compound SI-1-8 [11-12]



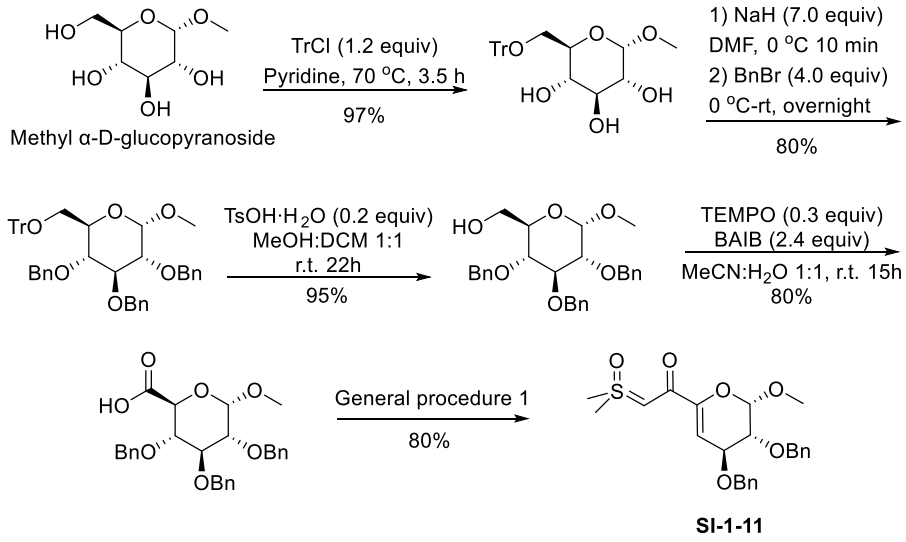
2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-((3a*R*,5*S*,5a*R*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)ethan-1-one (SI-1-8): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.60 (d, *J* = 5.0 Hz, 1H), 4.96 (s, 1H), 4.69 – 4.61 (m, 2H), 4.33 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.15 (d, *J* = 2.2 Hz, 1H), 3.42 (s, 6H), 1.51 (s, 3H), 1.42 (s, 3H), 1.32 (s, 6H). Spectroscopic data in accordance with literature.[1]

Synthesis of compound SI-1-9 [13-15]

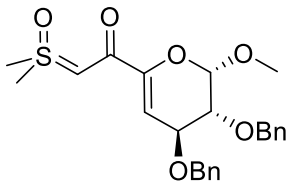


1-((2*R*,4*R*,5*S*,6*R*)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)ethan-1-one (SI-1-9): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (dt, *J* = 17.5, 5.7 Hz, 13H), 7.20 (d, *J* = 6.6 Hz, 2H), 5.00 – 4.86 (m, 2H), 4.73 (d, *J* = 11.6 Hz, 1H), 4.64 – 4.51 (m, 4H), 3.80 – 3.64 (m, 4H), 3.47 (d, *J* = 7.9 Hz, 2H), 3.40 (d, *J* = 3.6 Hz, 6H), 1.48 (q, *J* = 12.0 Hz, 1H), 1.27 (d, *J* = 8.8 Hz, 1H). Spectroscopic data in accordance with literature.[1]

Synthesis of compound SI-1-11



1-((2*S*,3*R*,4*S*)-3,4-bis(benzyloxy)-2-methoxy-3,4-dihydro-2*H*-pyran-6-yl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)ethan-1-one (SI-1-11)



Prepared according to the general procedure **1**. Purification by flash column (DCM/MeOH = 100/1-100/3) afforded **SI-1-11** (3.56 g, 80% yield) as yellow oil.

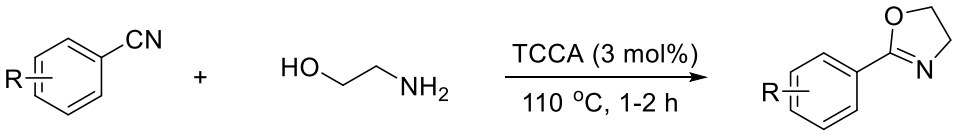
TLC: R*f* = 0.7 (DCM/MeOH = 20/1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (m, 9H), 7.30 – 7.28 (m, 1H), 5.94 (d, *J* = 3.1 Hz, 1H), 4.94 (s, 1H), 4.88 (d, *J* = 2.4 Hz, 1H), 4.80 (d, *J* = 12.2 Hz, 1H), 4.74 (d, *J* = 12.2 Hz, 1H), 4.67 (d, *J* = 11.7 Hz, 1H), 4.60 (d, *J* = 11.7 Hz, 1H), 4.28 (dd, *J* = 6.8, 3.1 Hz, 1H), 3.76 (dd, *J* = 6.8, 2.4 Hz, 1H), 3.51 (s, 3H), 3.44 (s, 6H).

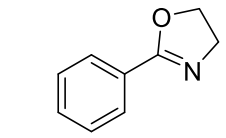
^{13}C NMR (126 MHz, $CDCl_3$): δ 175.80, 148.14, 138.40, 138.28, 128.54, 128.53, 128.20, 127.96, 127.92, 127.78, 101.90, 100.06, 75.91, 73.33, 73.27, 71.21, 69.32, 56.94, 42.30, 42.26.

HRMS (ESI): m/z calculated for $C_{31}H_{37}O_7S^+$ $[M+H]^+$, 445.1679; found, 445.1680.

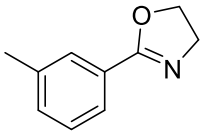
3.2 General procedure for the conversion of nitriles to 2-oxazoline [16]:



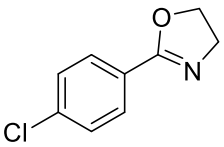
A mixture of a nitrile (l mmol), 2-aminoethanol (6 mmol) and TCCA (0.03 mmol) was stirred at 110 ℃ for an appropriate time. The reaction was performed under solvent-free conditions. After completion of the reaction, monitored by TLC (eluent: n-hexane: Ethyl acetate, 2:1), the reaction mixture was cooled to room temperature and the crude product was purified by column chromatography to afford the pure products in high yields.



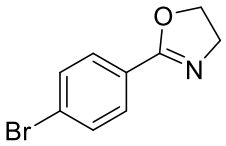
SI-3-1



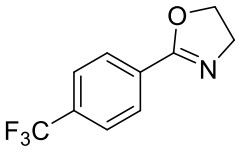
SI-3-2



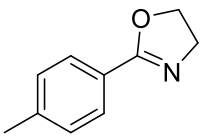
SI-3-3



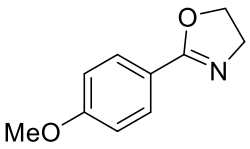
SI-3-4



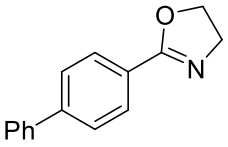
SI-3-5



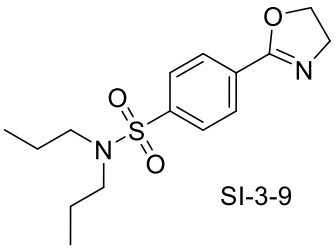
SI-3-6



SI-3-7

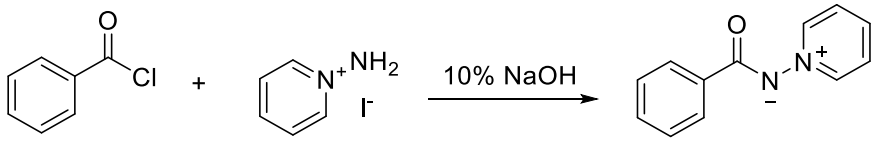


SI-3-8



SI-3-9

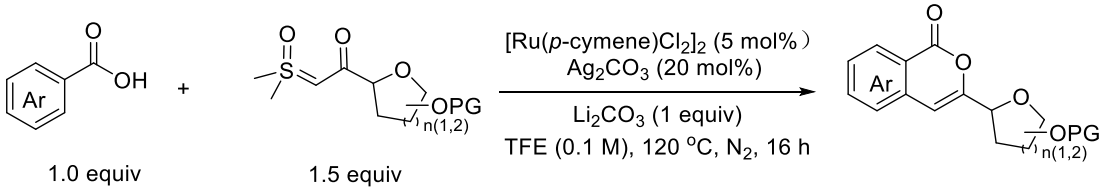
3.3 Synthesis of *N*-substituted iminopyridinium ylides [17]:



N-Aminopyridinium iodide (1.0 equiv) was added to an aqueous solution of 10% aq. NaOH at 0 ^{o}C and stirred for 10 min. Acid chloride (2.0 equiv) was added at this temperature and the mixture stirred overnight at room temperature. The resulting suspension was then extracted with CH_2Cl_2 (3 times) and the organic layer dried over Na_2SO_4. Evaporation of the solvent under reduced pressure afforded the desired ylides which, if necessary, were purified by recrystallisation.

4. General procedure for the ruthenium-catalyzed C–H functionalization

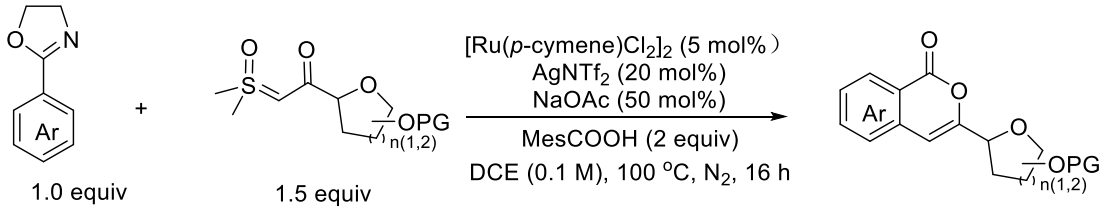
4.1 Procedure for the annulation of Benzoic acid with carbonyl sulfoxonium ylides glycogen anomeric (General procedure 2)



1.0 equiv 1.5 equiv

A Schlenk tube (15 mL) equipped with a magnetic stir bar and a Teflon-lined screwed cap was charged with substituted Benzoic acid **SI-2** (0.1 mmol), carbonyl sulfoxonium ylides glycogen anomeric **SI-1** (0.15 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (3.1 mg, 5 mol %), Ag_2CO_3 (5.5 mg, 20 mol %), Li_2CO_3 (7.4 mg, 0.1 mmol, 1.0 equiv) and TFE (1 mL, 0.1 M). The vial was then sealed and heated at 120 °C for 16 h under N_2. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the product.

4.2 Procedure for the annulation of oxazoline with carbonyl sulfoxonium ylides glycogen anomeric (General procedure 3)

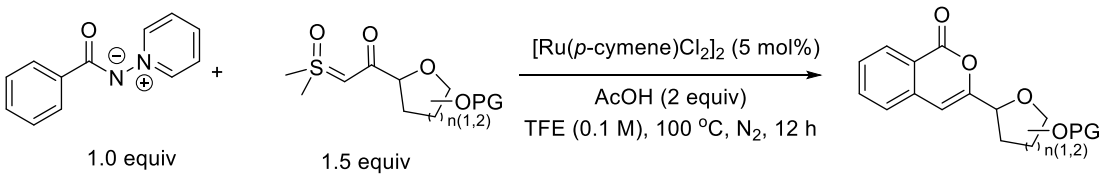


1.0 equiv 1.5 equiv

A Schlenk tube (15 mL) equipped with a magnetic stir bar and a Teflon-lined screwed cap was charged with substituted oxazoline **SI-3** (0.1 mmol), carbonyl sulfoxonium ylides glycogen anomeric **SI-1** (0.15 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (3.1 mg, 5 mol %), $AgNTf_2$ (7.8 mg, 20 mol %), NaOAc (4.1 mg, 50 mol %), MesCOOH (32.8 mg, 0.2 mmol, 2.0 equiv) and DCE (1 mL, 0.1 M). The vial was then sealed and heated at 100 °C for 16 h under N_2. After that, the solvent was removed under reduced pressure

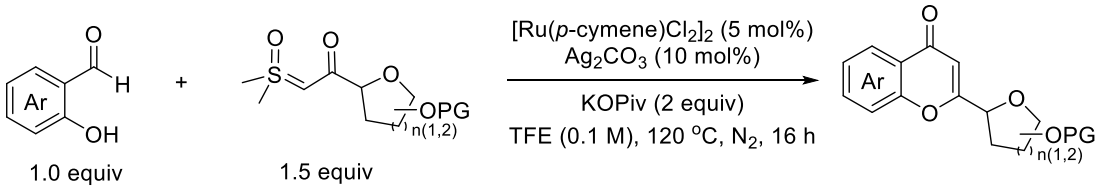
and the residue was purified by silica gel chromatography using PE/EA to afford the product.

4.3 Procedure for the annulation of benzoyl(pyridin-1-ium-1-yl)amide with carbonyl sulfoxonium ylides glycogen anomeric (General procedure 4)



A Schlenk tube (15 mL) equipped with a magnetic stir bar and a Teflon-lined screwed cap was charged with the benzoyl(pyridin-1-ium-1-yl)amide **SI-4-1** (0.1 mmol), carbonyl sulfoxonium ylides glycogen anomeric **SI-1** (0.15 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (3.1 mg, 5 mol %), CH_3COOH (12 mg, 0.2 mmol, 2.0 equiv) in TFE (1 mL, 0.1 M) was stirred at 100 °C for 12 h under an ambient atmosphere of N_2 in an oil bath. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 20:1 (v/v) to give the corresponding product.

4.4 Procedure for the annulation of 2-hydroxybenzaldehyde with carbonyl sulfoxonium ylides glycogen anomeric (General procedure 5)

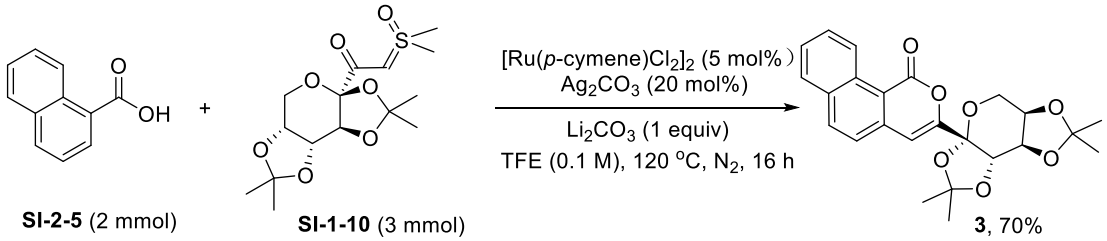


A Schlenk tube (15 mL) equipped with a magnetic stir bar and a Teflon-lined screwed cap was charged with substituted salicylaldehyde **SI-5** (0.2 mmol), carbonyl sulfoxonium ylides glycogen anomeric **SI-1** (0.3 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (6.1 mg,

5 mol %), Ag_2CO_3 (5.6 mg, 10 mol %), KOPiv (56.1 mg, 0.4 mmol, 2.0 equiv) and TFE (2 mL, 0.1 M). The vial was then sealed and heated at 120 °C for 16 h under N_2. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the product.

5 Experimental procedure for scale-up reaction

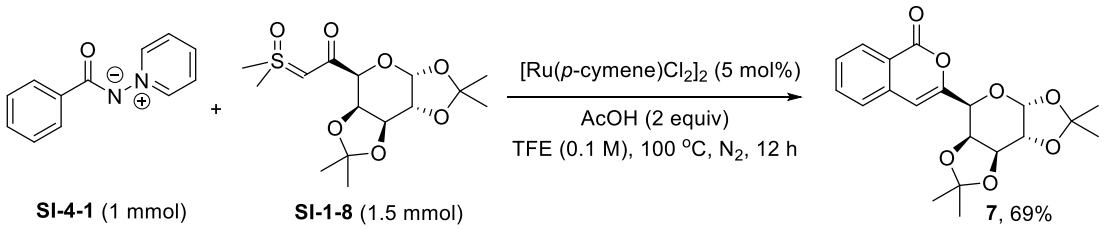
5.1 Gram-Scale Preparation of 3



SI-2-5 (2 mmol) **SI-1-10** (3 mmol) **3**, 70%

A Schlenk tube (100 mL) equipped with a magnetic stir bar and a Teflon-lined screwed cap was charged with substituted 1-naphthoic acid **SI-2-5** (344.4 mg, 2.0 mmol, 1.0 equiv), carbonyl sulfoxonium ylides glycogen anomeric **SI-1-10** (1045 mg, 3.0 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (61.2 mg, 5 mol %), Ag_2CO_3 (55.2 mg, 20 mol %), Li_2CO_3 (147.8 mg, 2.0 mmol, 1.0 equiv) and TFE (20 mL, 0.1 M). The vial was then sealed and heated at 120 °C for 16 h under N_2. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the product **3** (596.0 mg, 70% yield) as yellow oil.

5.2 Gram-Scale Preparation of 7

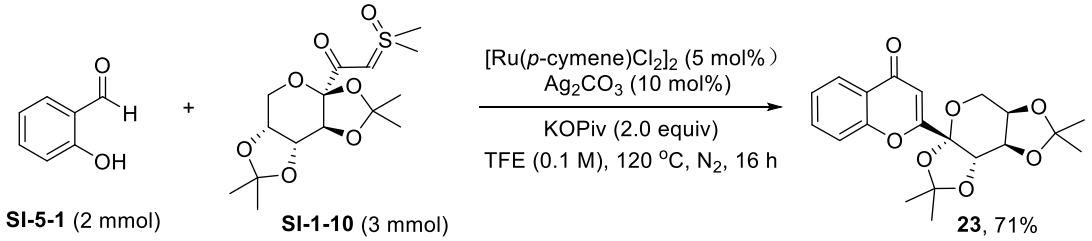


SI-4-1 (1 mmol) **SI-1-8** (1.5 mmol) **7**, 69%

A Schlenk tube (100 mL) equipped with a magnetic stir bar and a Teflon-lined screwed cap was charged with the benzoyl(pyridin-1-ium-1-yl)amide **SI-4-1** (198.2 mg, 1.0 mmol, 1.0 equiv), carbonyl sulfoxonium ylides glycogen anomeric **SI-1-8** (522.6 mg, 1.5 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (30.6 mg, 5 mol %), CH_3COOH (114 uL, 2 mmol, 2.0 equiv) in TFE (10 mL, 0.1 M) was stirred at 100 ℃ for 12 h under an ambient atmosphere of N_2 in an oil bath. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum

ether/ethyl acetate 20:1 (v/v) to give the corresponding product **7** (257 mg, 69% yield) as yellow oil.

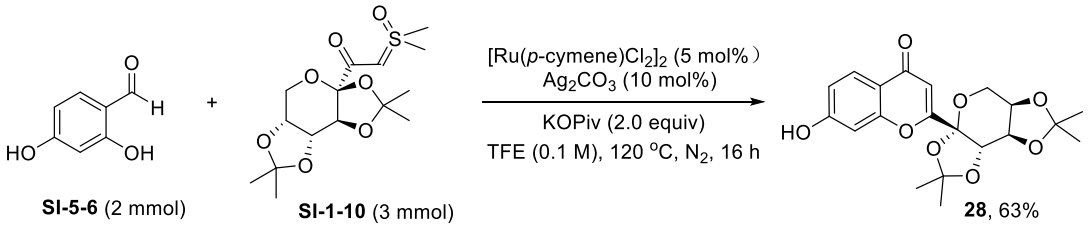
5.3 Gram-Scale Preparation of 23



SI-5-1 (2 mmol) **SI-1-10** (3 mmol) **23**, 71%

A Schlenk tube (100 mL) equipped with a magnetic stir bar and a Teflon-lined screwed cap was charged with substituted salicylaldehyde **SI-5-1** (199 uL, 2.0 mmol, 1.0 equiv), carbonyl sulfoxonium ylides glycogen anomeric **SI-1-10** (1045 mg, 3.0 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (61.2 mg, 5 mol %), Ag_2CO_3 (55.2 mg, 10 mol %), KOPiv (560.9 mg, 4.0 mmol, 2.0 equiv) and TFE (20 mL, 0.1 M). The vial was then sealed and heated at 120 °C for 16 h under N_2. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the product **23** (528.2 mg, 71% yield) as yellow oil.

5.4 Gram-Scale Preparation of 28



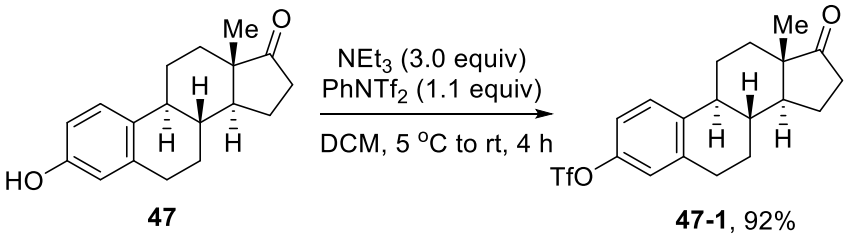
SI-5-6 (2 mmol) **SI-1-10** (3 mmol) **28**, 63%

A Schlenk tube (100 mL) equipped with a magnetic stir bar and a Teflon-lined screwed cap was charged with substituted salicylaldehyde **SI-5-6** (276.2 mg, 2.0 mmol, 1.0 equiv), carbonyl sulfoxonium ylides glycogen anomeric **SI-1-10** (1045 mg, 3.0 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (61.2 mg, 5 mol %), Ag_2CO_3 (55.2 mg, 10 mol %), KOPiv (560.9 mg, 4.0 mmol, 2.0 equiv) and TFE (20 mL, 0.1 M). The vial was then sealed and heated at 120 °C for 16 h under N_2. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel

chromatography using PE/EA to afford the product **28** (489.4 mg, 63% yield) as yellow solid.

6 Late-stage modification of estron and proposed reaction mechanism

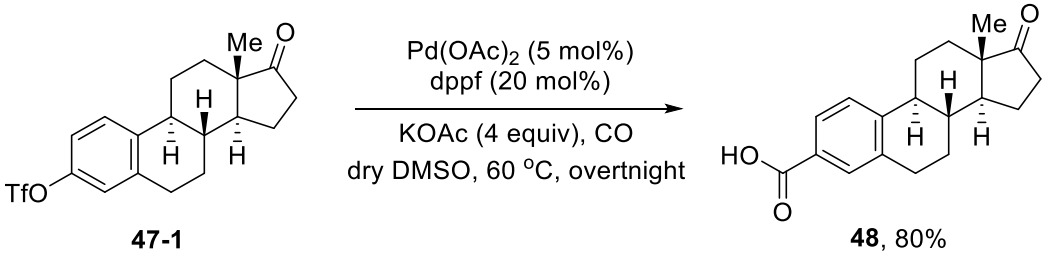
6.1 Transformations of 47 to 47-1 [18]



47 **47-1**, 92%

To a solution of estrone (2.7 g, 10.0 mmol, 1.0 equiv) and triethylamine (4.2 mL, 30.0 mmol, 3.0 equiv) in dichloromethane at 5 °C was charged dropwise a solution of 1,1,1-trifluoro-*N*-phenyl-*N*-((trifluoromethyl)sulfonyl)methanesulfonamide (3.9 g, 11.0 mmol, 1.1 equiv) in dichloromethane and the resulting mixture was stirred at rt for 4 h and then concentrated. The residue was purified by silica gel column chromatography to give pure product **47-1** (3.7 g, 92%) as white solid.

6.2 Transformations of 47-1 to 48 [19]

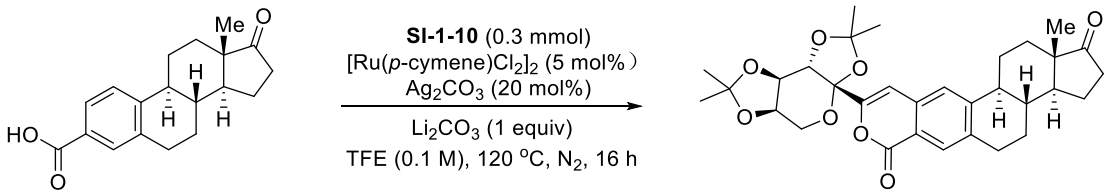


47-1 **48**, 80%

47-1 (805 mg, 2.0 mmol, 1.0 equiv), $Pd(OAc)_2$ (22.7 mg, 5 mol %), 1,1′-bis(diphenylphosphino) ferrocene (222 mg, 20 mol %), and potassium acetate (0.79 g, 8.0 mmol, 4 equiv) were added to the crude compound in DMSO (20 mL). The reaction mixture was stirred at 60 ℃ under a balloon of CO overnight. The mixture was then cooled to room temperature, quenched with 1 M HCl (pH < 3), and extracted with EtOAc (30 mL × 3). The combined organic phase was washed with brine, dried over sodium sulfate, filtered, and evaporated under reduced pressure to afford the corresponding crude carboxylic acid. The crude carboxylic acid was purified by

column chromatography on silica gel to obtain the corresponding acid **48** as a yellow oil (0.48 g, 80%).

6.3 Transformations of 48 to 49



48 (0.2 mmol) **49**, 60%

A Schlenk tube (10 mL) equipped with a magnetic stir bar and a Teflon-lined screwed cap was charged with substituted **48** (59.7 mg, 0.2 mmol, 1.0 equiv), carbonyl sulfoxonium ylides glycogen anomeric **SI-1-10** (104.5 mg, 0.3 mmol, 1.5 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (6.1 mg, 5 mol %), Ag_2CO_3 (5.5 mg, 20 mol %), Li_2CO_3 (14.8 mg, 0.2 mmol, 1.0 equiv) and TFE (2 mL, 0.1 M). The vial was then sealed and heated at 120 °C for 16 h under N_2. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the product **49** (65.7 mg, 60% yield) as white solid.

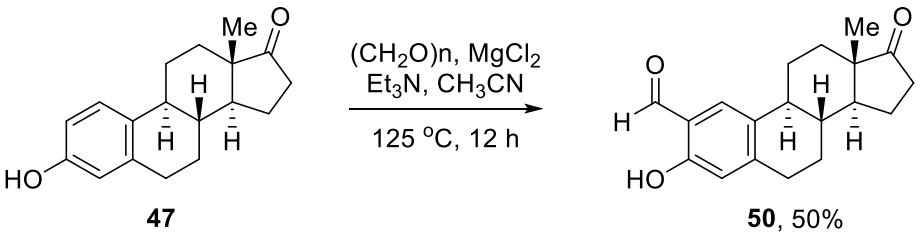
TLC: R*f* = 0.20 (Ethyl acetate/Petroleum Ether = 1/4)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.33 (s, 1H), 6.93 (s, 1H), 4.64 (d, *J* = 8.1 Hz, 2H), 4.30 (d, *J* = 7.7 Hz, 1H), 4.07 (dd, *J* = 13.1, 1.8 Hz, 1H), 3.96 (d, *J* = 13.0 Hz, 1H), 3.09 – 2.99 (m, 2H), 2.52 (dd, *J* = 19.0, 8.7 Hz, 1H), 2.49 – 2.43 (m, 1H), 2.41 – 2.35 (m, 1H), 2.20 – 2.14 (m, 1H), 2.11 – 2.05 (m, 2H), 2.01 (dt, *J* = 12.9, 3.2 Hz, 1H), 1.66 (s, 3H), 1.63 (t, *J* = 3.3 Hz, 2H), 1.60 (s, 3H), 1.56 – 1.47 (m, 4H), 1.38 (s, 3H), 1.31 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 162.03, 151.63, 148.15, 138.34, 134.42, 129.57, 123.00, 118.87, 109.95, 109.27, 104.97, 99.95, 72.33, 70.48, 70.12, 61.31, 50.79, 47.96, 44.83, 37.67, 35.92, 31.60, 29.30, 26.75, 26.29, 25.87, 25.61, 25.41, 24.01, 21.74, 13.93.

HRMS (ESI): m/z calculated for $C_{32}H_{38}NaO_8^+$ $[M+Na]^+$, 573.2459; found, 573.2459.

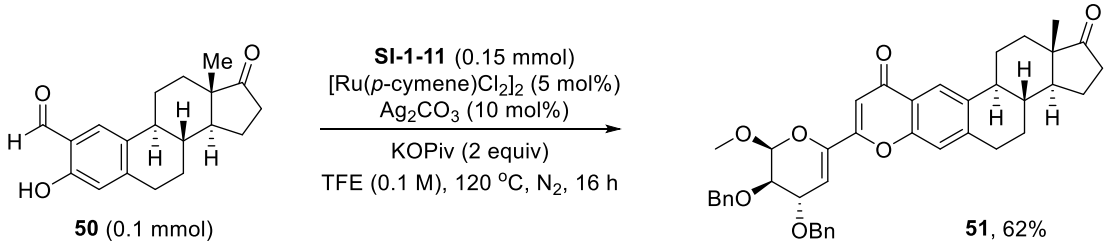
6.4 Transformations of 47 to 50 [20]



47 **50**, 50%

To a mixture of estrone (0.54 g, 2.0 mmol), paraformaldehyde (0.60 g, 20 mmol) and magnesium chloride (0.50 g, 5.2 mmol) was added acetonitrile (8 mL), followed by triethylamine (2.2 mL, 9.2 mmol) at room temperature. The sealed tube was heated at 125°C for 12 h. 6 N HCl (6 mL) was added slowly after cooling and the mixture extracted with diethyl ether (60 mL, 2 x 30 mL). The extracts were combined, washed with H_2O (2 x 50 mL), brine (30 mL), then dried over Na_2SO_4. Column chromatography (silica, PE : EA = 6:1) gave 1s as white solid (0.30 g, 50% yield).

6.5 Transformations of 50 to 51



50 (0.1 mmol) **51**, 62%

A Schlenk tube (15 mL) equipped with a magnetic stir bar and a Teflon-lined screwed cap was charged with substituted salicylaldehyde **50** (29.8 mg, 0.1 mmol), carbonyl sulfoxonium ylides glycogen anomeric **SI-1-11** (66.7 mg, 0.15 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (3.1 mg, 5 mol %), Ag_2CO_3 (2.8 mg, 10 mol %), KOPiv (28.0 mg, 0.2 mmol, 2.0 equiv) and TFE (1 mL, 0.1 M). The vial was then sealed and heated at 120 °C for 16 h under N_2. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the

product **51** (40.3 mg, 62% yield) as yellow oil.

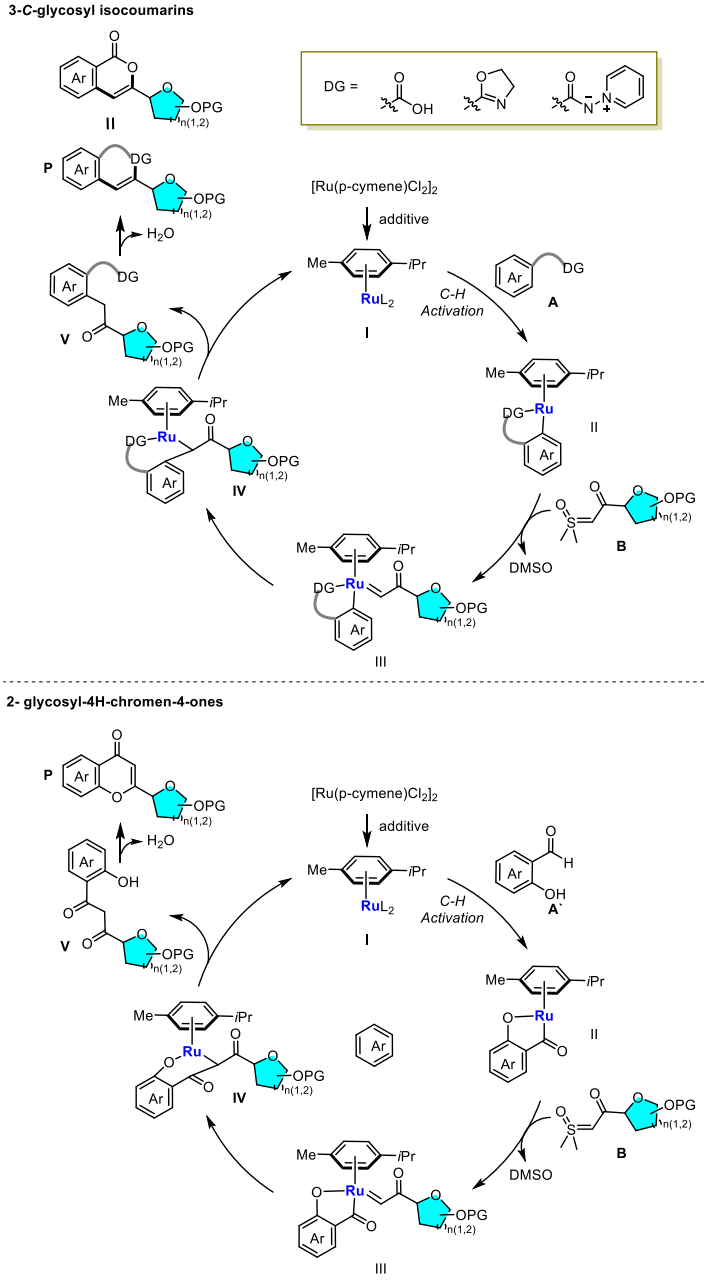
TLC: R*f* = 0.30 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 1.3 Hz, 1H), 7.39 – 7.35 (m, 7H), 7.34 – 7.30 (m, 3H), 7.18 (s, 1H), 6.62 (s, 1H), 6.04 (d, *J* = 3.3 Hz, 1H), 5.00 (d, *J* = 2.3 Hz, 1H), 4.80 (d, *J* = 4.7 Hz, 2H), 4.72 (d, *J* = 1.8 Hz, 2H), 4.39 (dd, *J* = 6.9, 3.3 Hz, 1H), 3.88 (dd, *J* = 6.9, 2.4 Hz, 1H), 3.54 (s, 3H), 3.07 – 2.98 (m, 2H), 2.62 – 2.56 (m, 1H), 2.52 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.39 – 2.29 (m, 1H), 2.20 – 2.11 (m, 1H), 2.08 – 1.98 (m, 3H), 1.70 – 1.62 (m, 2H), 1.58 – 1.45 (m, 4H), 0.92 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 156.89, 154.30, 144.54, 142.67, 138.16, 138.07, 137.89, 128.67, 128.65, 128.26, 128.20, 128.00, 127.95, 122.06, 117.27, 107.48, 104.66, 100.08, 75.81, 73.45, 73.30, 72.07, 57.20, 50.60, 48.02, 44.19, 37.92, 35.94, 31.47, 29.82, 26.19, 25.86, 21.72, 13.90.

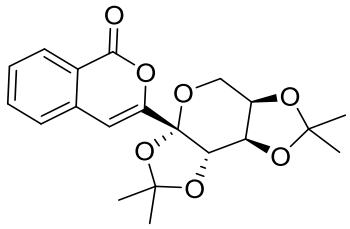
6.6 Proposed reaction mechanism

Based on literature[1,21,22], we propose a plausible mechanism for these reactions. Cyclometalation of A (or A`) forms a Ru-cyclic intermediate II. Coordination of sulfoxonium ylide glycol-reagents B occurs after subsequent a-elimination of DMSO, resulting in the formation of Ru-carbene species III. This species is then proposed to undergo migratory insertion of the Ru-C bond, leading to the formation of a six-membered Ru-cyclic intermediate IV. Protonolysis releases the acylmethylated intermediate V while regenerating the active catalyst. The intermediate V undergoes cyclization and dehydration to generate product P.



7 Spectra Data of substrates and products

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



Prepared from **SI-2-1** (0.1 mmol, 1.0 equiv) and **SI-1-10** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **1** (29.2 mg, 78% yield) as yellow oil.

Prepared from **SI-3-1** (0.1 mmol, 1.0 equiv) and **SI-1-10** (0.15 mmol, 1.5 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **1** (19.5 mg, 52% yield) as yellow oil.

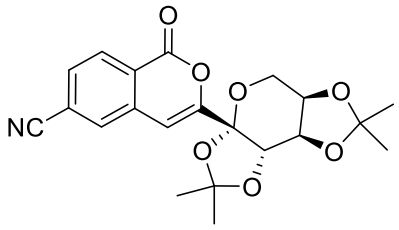
Prepared from **SI-4-1** (0.1 mmol, 1.0 equiv) and **SI-1-10** (0.15 mmol, 1.5 equiv) according to the general procedure **4**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **1** (13.1 mg, 35% yield) as yellow oil.
TLC: R*f* = 0.50 (Ethyl acetate/Petroleum Ether = 1/4)

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (d, *J* = 7.9 Hz, 1H), 7.70 (td, *J* = 7.6, 1.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 6.99 (s, 1H), 4.67 – 4.63 (m, 2H), 4.33 – 4.29 (m, 1H), 4.07 (dd, *J* = 13.0, 1.8 Hz, 1H), 3.96 (d, *J* = 13.0 Hz, 1H), 1.66 (s, 3H), 1.60 (s, 3H), 1.39 (s, 3H), 1.31 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 161.88, 152.49, 136.73, 134.98, 129.77, 128.81, 126.41, 121.08, 110.08, 109.27, 104.78, 99.85, 72.30, 70.43, 70.06, 61.30, 26.72, 25.77, 25.37, 23.97.

HRMS (ESI): m/z calculated for $C_{20}H_{22}NaO_7^+$ $[M+Na]^+$, 397.1258; found, 397.1258.

1-oxo-3-((3a*R*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)-1*H*-isochromene-6-carbonitrile (2)



Prepared from **SI-2-3** (0.1 mmol, 1.0 equiv) and **SI-1-10** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **2** (10.3 mg, 26% yield) as white solid.

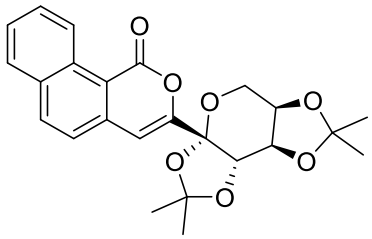
TLC: R*f* = 0.48 (Ethyl acetate/Petroleum Ether = 1/4)

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.37 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 8.6 Hz, 2H), 7.00 (s, 1H), 4.65 (dd, *J* = 10.3, 2.3 Hz, 2H), 4.31 (d, *J* = 7.9 Hz, 1H), 4.07 (d, *J* = 13.0 Hz, 1H), 3.97 (d, *J* = 13.0 Hz, 1H), 1.65 (s, 3H), 1.61 (s, 3H), 1.39 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 160.27, 154.82, 137.17, 131.08, 130.82, 130.42, 123.78, 118.60, 117.48, 110.44, 109.34, 103.49, 99.61, 72.39, 70.34, 69.97, 61.44, 26.70, 25.87, 25.30, 23.93.

HRMS (ESI): m/z calculated for $C_{21}H_{21}NNaO_7^+$ $[M+Na]^+$, 422.1210; found, 422.1210.

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



Prepared from **SI-2-5** (0.1 mmol, 1.0 equiv) and **SI-1-10** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **3** (33.2 mg, 78% yield) as yellow oil.

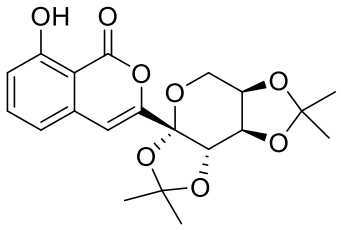
TLC: R*f* = 0.65 (Ethyl acetate/Petroleum Ether = 1/4)

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.70 (dd, *J* = 8.7, 1.1 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.91 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.79 – 7.74 (m, 1H), 7.65 – 7.61 (m, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.11 (s, 1H), 4.75 (d, *J* = 2.4 Hz, 1H), 4.67 (dd, *J* = 8.0, 2.5 Hz, 1H), 4.33 (dd, *J* = 8.0, 1.9 Hz, 1H), 4.10 (dd, *J* = 13.1, 1.8 Hz, 1H), 4.02 – 3.97 (m, 1H), 1.72 (s, 3H), 1.63 (s, 3H), 1.40 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 161.16, 154.12, 139.48, 136.60, 133.38, 131.70, 129.64, 128.81, 127.11, 126.70, 124.21, 114.60, 110.21, 109.31, 105.57, 99.84, 72.51, 70.44, 70.08, 61.35, 26.73, 25.79, 25.39, 23.98.

HRMS (ESI): m/z calculated for $C_{24}H_{24}NaO_7^+$ $[M+Na]^+$, 447.1414; found, 447.1415.

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



Prepared from **SI-2-6** (0.1 mmol, 1.0 equiv) and **SI-1-10** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl

acetate/Petroleum Ether = 1/10) afforded **4** (35.2 mg, 90% yield) as yellow oil.

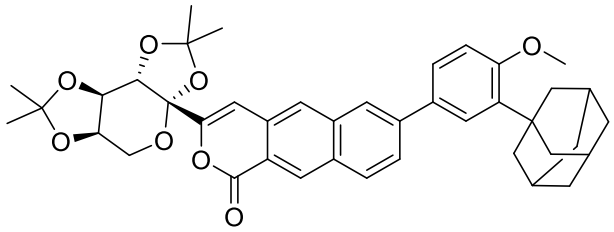
TLC: R*f* = 0.75 (Ethyl acetate/Petroleum Ether = 1/4)

^{1}H NMR (300 MHz, $CDCl_3$): δ 10.91 (s, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 4.3 Hz, 2H), 6.91 (d, *J* = 7.6 Hz, 1H), 4.64 (d, *J* = 8.6 Hz, 2H), 4.31 (d, *J* = 7.8 Hz, 1H), 4.07 (d, *J* = 13.0 Hz, 1H), 4.00 – 3.88 (m, 1H), 1.64 (s, 3H), 1.61 (s, 3H), 1.40 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 165.93, 161.78, 151.92, 137.55, 137.09, 116.89, 116.07, 110.14, 109.35, 106.60, 106.10, 99.74, 72.40, 70.39, 70.05, 61.36, 26.72, 25.78, 25.29, 23.97.

HRMS (ESI): m/z calculated for $C_{20}H_{22}NaO_8^+$ $[M+Na]^+$, 413.1207; found, 413.1219.

7-(3-(adamantan-1-yl)-4-methoxyphenyl)-3-((3a*R*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)-1*H*-benzo[*g*]isochromen-1-one (5)



Prepared from **SI-2-4** (0.1 mmol, 1.0 equiv) and **SI-1-10** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **5** (28.8 mg, 43% yield) as yellow solid.

TLC: R*f* = 0.50 (Ethyl acetate/Petroleum Ether = 1/4)

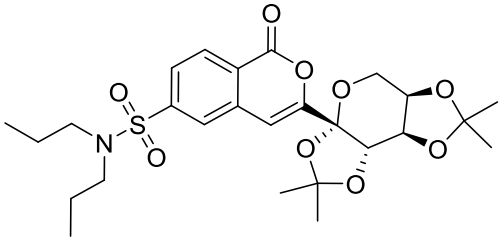
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.89 (s, 1H), 8.08 – 8.02 (m, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.11 (s, 1H), 7.01 (d, *J* = 8.5 Hz, 1H), 4.72 (d, *J* = 2.4 Hz, 1H), 4.68 (d, *J* = 8.1 Hz, 1H),

4.34 (d, *J* = 8.1 Hz, 1H), 4.11 (d, *J* = 13.0 Hz, 1H), 4.01 (d, *J* = 13.2 Hz, 1H), 3.91 (s, 3H), 2.18 (s, 6H), 2.11 (s, 3H), 1.81 (d, *J* = 3.1 Hz, 6H), 1.70 (s, 3H), 1.63 (s, 3H), 1.43 (s, 3H), 1.33 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 162.23, 159.30, 150.84, 142.61, 139.25, 137.11, 132.30, 131.83, 131.62, 130.19, 126.98, 126.14, 125.96, 124.91, 124.59, 118.90, 112.28, 110.02, 109.33, 105.04, 100.01, 72.24, 70.55, 70.16, 61.37, 55.32, 40.75, 37.38, 37.26, 29.24, 26.79, 26.30, 25.87, 25.46, 24.04.

HRMS (ESI): m/z calculated for $C_{41}H_{44}NaO_8^+$ $[M+Na]^+$, 687.2928; found, 687.2928.

1-oxo-*N*,*N*-dipropyl-3-((3a*R*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)-1*H*-isochromene-6-sulfonamide (6)



Prepared from **SI-2-2** (0.1 mmol, 1.0 equiv) and **SI-1-10** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **6** (25.1 mg, 47% yield) as white solid.

TLC: R*f* = 0.50 (Ethyl acetate/Petroleum Ether = 1/4)

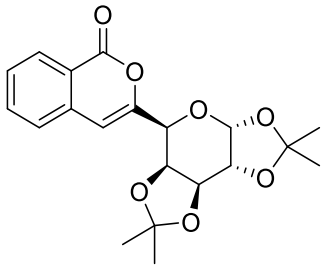
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 1.7 Hz, 1H), 7.86 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.06 (s, 1H), 4.65 (d, *J* = 4.1 Hz, 2H), 4.31 (d, *J* = 8.1 Hz, 1H), 4.10 – 4.04 (m, 1H), 3.97 (d, *J* = 13.0 Hz, 1H), 3.18 – 3.05 (m, 4H), 1.65 (s, 3H), 1.61 (s, 3H), 1.53 (q, *J* = 7.5 Hz, 4H), 1.38 (s, 3H), 1.32 (s, 3H), 0.86 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 160.60, 154.36, 146.54, 137.34, 131.03, 126.26,

125.02, 123.37, 110.35, 109.36, 104.27, 99.68, 72.40, 70.38, 70.00, 61.45, 49.95, 26.72, 25.84, 25.33, 23.98, 21.95, 11.27.

HRMS (ESI): m/z calculated for $C_{26}H_{36}NO_9S^+$ $[M+H]^+$, 538.2105; found, 538.2105.

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



Prepared from **SI-2-1** (0.1 mmol, 1.0 equiv) and **SI-1-8** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **7** (18.4 mg, 50% yield) as white solid.

Prepared from **SI-3-1** (0.1 mmol, 1.0 equiv) and **SI-1-8** (0.15 mmol, 1.5 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **7** (25.4 mg, 68% yield) as white solid.

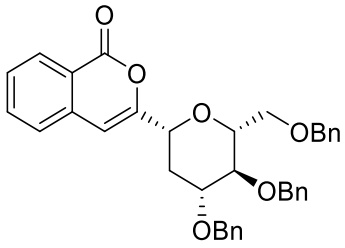
Prepared from **SI-4-1** (0.1 mmol, 1.0 equiv) and **SI-1-8** (0.15 mmol, 1.5 equiv) according to the general procedure **4**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **7** (23.6 mg, 63% yield) as white solid.
TLC: R*f* = 0.50 (Ethyl acetate/Petroleum Ether = 1/4)

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (d, *J* = 7.9 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 6.67 (s, 1H), 5.68 (d, *J* = 5.0 Hz, 1H), 4.72 (d, *J* = 6.4 Hz, 2H), 4.69 – 4.66 (m, 1H), 4.41 (dt, *J* = 4.5, 1.8 Hz, 1H), 1.59 (s, 3H), 1.41 (s, 3H), 1.37 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 162.37, 153.16, 137.37, 134.98, 129.73, 128.11, 125.98, 120.68, 109.87, 109.31, 103.40, 96.68, 71.27, 70.97, 70.81, 66.74, 26.25, 26.02, 25.00, 24.51.

HRMS (ESI): m/z calculated for $C_{20}H_{22}NaO_7^+$ $[M+Na]^+$, 397.1258; found, 397.1255.

3-((2*R*,4*R*,5*S*,6*R*)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-1*H*-isochromen-1-one (8)



Prepared from **SI-2-1** (0.1 mmol, 1.0 equiv) and **SI-1-9** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **8** (26.7 mg, 47% yield) as oil.

Prepared from **SI-3-1** (0.1 mmol, 1.0 equiv) and **SI-1-9** (0.15 mmol, 1.5 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **8** (15.3 mg, 27% yield) as oil.

Prepared from **SI-4-1** (0.1 mmol, 1.0 equiv) and **SI-1-9** (0.15 mmol, 1.5 equiv) according to the general procedure **4**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **8** (20.3 mg, 36% yield) as oil.

TLC: R*f* = 0.30 (Ethyl acetate/Petroleum Ether = 1/4)

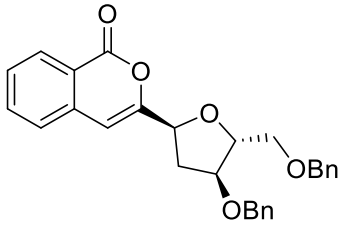
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.28 (d, *J* = 7.9 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.39 – 7.29 (m, 13H), 7.22 (d, *J* = 7.0 Hz, 2H), 6.64 (s, 1H), 4.95 (d, *J* = 10.7 Hz, 1H), 4.76 (d, *J* = 11.5 Hz, 1H), 4.68 – 4.58 (m, 4H), 4.27 (d, *J* = 11.6 Hz, 1H), 3.84 – 3.76 (m, 3H), 3.59 (d, *J* = 5.1 Hz, 2H),

2.71 (dt, *J* = 12.8, 3.2 Hz, 1H), 1.70 (q, *J* = 11.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 162.31, 155.53, 138.43, 138.33, 137.14, 135.08, 129.79, 128.61, 128.54, 128.52, 128.37, 128.15, 127.97, 127.87, 127.85, 127.82, 126.01, 120.71, 102.22, 80.65, 79.49, 77.97, 75.28, 73.59, 73.55, 71.52, 69.44, 35.32.

HRMS (ESI): m/z calculated for $C_{36}H_{34}KO_6^+$ $[M+K]^+$, 601.1987; found, 601.1987.

3-((2*S*,4*S*,5*R*)-4-(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-2-yl)-1*H*-isochromen-1-one (9)



Prepared from **SI-2-1** (0.1 mmol, 1.0 equiv) and **SI-1-7** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **9** (16.5 mg, 37% yield) as yellow oil.

Prepared from **SI-3-1** (0.1 mmol, 1.0 equiv) and **SI-1-7** (0.15 mmol, 1.5 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **9** (27.8 mg, 63% yield) as yellow oil.

Prepared from **SI-4-1** (0.1 mmol, 1.0 equiv) and **SI-1-7** (0.15 mmol, 1.5 equiv) according to the general procedure **4**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **9** (20.2 mg, 46% yield) as yellow oil.
TLC: R*f* = 0.40 (Ethyl acetate/Petroleum Ether = 1/4)

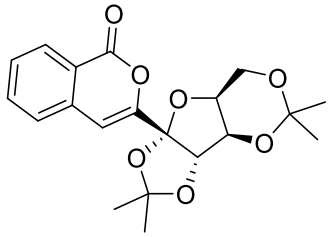
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.26 (d, *J* = 7.9 Hz, 1H), 7.69 (dd, *J* = 8.3, 6.9 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.33 –

7.29 (m, 3H), 7.21 – 7.17 (m, 3H), 7.17 – 7.14 (m, 2H), 6.66 (s, 1H), 4.99 – 4.95 (m, 1H), 4.62 – 4.55 (m, 2H), 4.48 (d, *J* = 11.9 Hz, 1H), 4.44 (s, 1H), 4.42 – 4.39 (m, 1H), 4.18 (dt, *J* = 6.9, 3.7 Hz, 1H), 3.62 – 3.57 (m, 2H), 2.58 – 2.52 (m, 1H), 2.39 (dt, *J* = 13.3, 4.6 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.60, 157.57, 138.12, 137.91, 137.40, 134.96, 129.75, 128.59, 128.45, 128.07, 127.88, 127.79, 127.77, 127.62, 125.90, 120.48, 101.67, 83.99, 80.22, 77.37, 77.16, 76.95, 76.69, 73.71, 71.48, 70.77, 36.67.

HRMS (ESI): m/z calculated for $C_{28}H_{26}NaO_5^+$ $[M+Na]^+$, 465.1672; found, 465.1682.

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



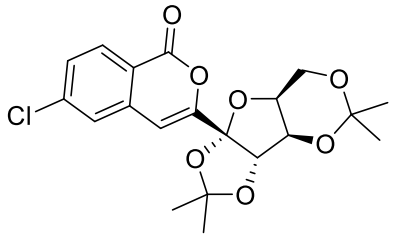
Prepared from **SI-3-1** (0.1 mmol, 1.0 equiv) and **SI-1-3** (0.15 mmol, 1.5 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **10** (26.8 mg, 72% yield) as yellow solid.
TLC: R*f* = 0.30 (Ethyl acetate/Petroleum Ether = 1/4)

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (d, *J* = 7.9 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.14 (s, 1H), 4.68 (s, 1H), 4.40 (d, *J* = 2.4 Hz, 1H), 4.27 (s, 1H), 4.23 – 4.13 (m, 2H), 1.63 (s, 3H), 1.58 (s, 3H), 1.42 (s, 3H), 1.23 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 162.08, 151.33, 136.87, 134.95, 129.80, 128.75, 126.45, 121.15, 114.12, 110.78, 105.45, 97.56, 86.98, 73.45, 72.91, 60.35, 29.05, 27.64, 26.40, 18.75.

HRMS (ESI): m/z calculated for $C_{20}H_{23}O_7^+$ $[M+H]^+$, 375.1438; found, 375.1438.

6-chloro-3-((3a*S*,3b*R*,7a*S*,8a*R*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)-1*H*-isochromen-1-one (11)



Prepared from **SI-3-3** (0.1 mmol, 1.0 equiv) and **SI-1-3** (0.15 mmol, 1.5 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **11** (19.9 mg, 49% yield) as white solid.

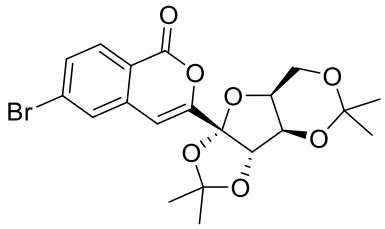
TLC: R*f* = 0.48 (Ethyl acetate/Petroleum Ether = 1/4)

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.4 Hz, 1H), 7.50 (t, *J* = 1.4 Hz, 1H), 7.46 (dt, *J* = 8.6, 1.5 Hz, 1H), 7.08 (s, 1H), 4.66 (s, 1H), 4.40 (d, *J* = 2.4 Hz, 1H), 4.27 (s, 1H), 4.21 – 4.12 (m, 2H), 1.62 (s, 3H), 1.58 (s, 3H), 1.42 (s, 3H), 1.23 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 161.28, 152.80, 141.68, 138.26, 131.48, 129.26, 125.98, 119.42, 114.31, 110.60, 104.58, 97.59, 87.04, 73.56, 72.84, 60.33, 29.13, 27.62, 26.35, 18.73.

HRMS (ESI): m/z calculated for $C_{20}H_{21}ClNaO_7^+$ $[M+Na]^+$, 431.0868; found, 431.0868.

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



Prepared from **SI-3-4** (0.1 mmol, 1.0 equiv) and **SI-1-3** (0.15 mmol, 1.5 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **12** (19.7 mg, 43% yield) as white solid.

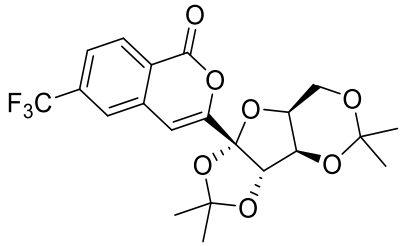
TLC: R*f* = 0.50 (Ethyl acetate/Petroleum Ether = 1/4)

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 1.7 Hz, 1H), 7.62 (dt, *J* = 8.5, 1.5 Hz, 1H), 7.07 (s, 1H), 4.66 (s, 1H), 4.40 (d, *J* = 2.4 Hz, 1H), 4.27 (s, 1H), 4.21 – 4.12 (m, 2H), 1.62 (s, 3H), 1.58 (s, 3H), 1.42 (s, 3H), 1.23 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 161.44, 152.78, 138.34, 132.13, 131.43, 130.42, 129.07, 119.79, 114.31, 110.59, 104.44, 97.59, 87.04, 73.56, 72.84, 60.33, 29.14, 27.61, 26.35, 18.73.

HRMS (ESI): m/z calculated for $C_{20}H_{21}BrNaO_7^+$ $[M+Na]^+$, 475.0363; found, 475.0363.

3-((3a*S*,3b*R*,7a*S*,8a*R*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)-6-(trifluoromethyl)-1*H*-isochromen-1-one (13)



Prepared from **SI-3-5** (0.1 mmol, 1.0 equiv) and **SI-1-3** (0.15 mmol, 1.5 equiv) according to the general procedure **3**. Purification by flash column (Ethyl

acetate/Petroleum Ether = 1/10) afforded **13** (26.4 mg, 60% yield) as white solid.

TLC: R*f* = 0.55 (Ethyl acetate/Petroleum Ether = 1/4)

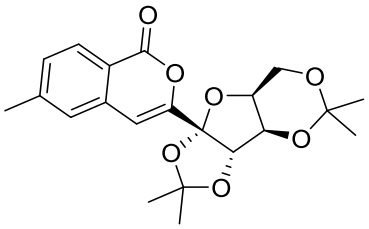
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.41 (d, *J* = 8.3 Hz, 1H), 7.78 (s, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.21 (s, 1H), 4.68 (s, 1H), 4.42 (d, *J* = 2.4 Hz, 1H), 4.29 (s, 1H), 4.23 – 4.13 (m, 2H), 1.63 (s, 3H), 1.59 (s, 3H), 1.43 (s, 3H), 1.23 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 160.92, 153.02, 137.23, 136.51 (q, *J* = 33.2 Hz), 130.81, 125.07 (q, J = 3.3 Hz), 123.46 (q, J = 282.3 Hz), 123.56(q, *J* = 4.0 Hz), 122.28, 114.40, 110.53, 104.89, 97.62, 87.10, 73.62, 72.86, 60.35, 29.13, 27.61, 26.34, 18.72.

^{19}F NMR (376 MHz, $CDCl_3$): δ -63.42.

HRMS (ESI): m/z calculated for $C_{21}H_{21}F_3NaO_7^+$ $[M+Na]^+$, 465.1132; found, 465.1131.

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



Prepared from **SI-3-6** (0.1 mmol, 1.0 equiv) and **SI-1-3** (0.15 mmol, 1.5 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **14** (30.6 mg, 79% yield) as white solid.

TLC: R*f* = 0.35 (Ethyl acetate/Petroleum Ether = 1/4)

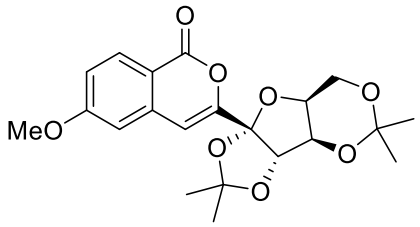
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H),

7.29 (s, 1H), 7.08 (s, 1H), 4.67 (s, 1H), 4.39 (d, *J* = 2.3 Hz, 1H), 4.27 (t, *J* = 1.9 Hz, 1H), 4.22 – 4.11 (m, 2H), 2.46 (s, 3H), 1.63 (s, 3H), 1.58 (s, 3H), 1.42 (s, 3H), 1.23 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 162.16, 151.30, 146.05, 136.96, 130.11, 129.74, 126.48, 118.70, 114.05, 110.81, 105.42, 97.52, 86.93, 73.41, 72.89, 60.35, 29.07, 27.63, 26.39, 22.07, 18.74.

HRMS (ESI): m/z calculated for $C_{21}H_{24}NaO_7^+$ $[M+Na]^+$, 411.1414; found, 411.1414.

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



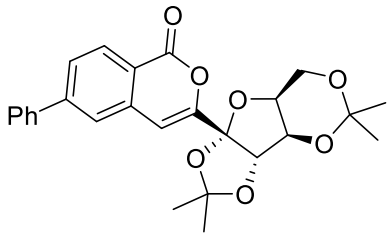
Prepared from **SI-3-7** (0.1 mmol, 1.0 equiv) and **SI-1-3** (0.15 mmol, 1.5 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **15** (21.7 mg, 54% yield) as yellow oil.
TLC: R*f* = 0.30 (Ethyl acetate/Petroleum Ether = 1/4)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.22 – 8.17 (m, 1H), 7.08 (s, 1H), 7.04 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.88 (d, *J* = 2.3 Hz, 1H), 4.68 (s, 1H), 4.40 (d, *J* = 2.8 Hz, 1H), 4.27 (s, 1H), 4.20 (d, *J* = 13.6 Hz, 1H), 4.15 (dd, *J* = 13.6, 2.2 Hz, 1H), 3.90 (d, *J* = 1.9 Hz, 3H), 1.63 (s, 3H), 1.58 (s, 3H), 1.42 (s, 3H), 1.24 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 164.87, 161.87, 151.92, 139.27, 131.98, 117.17, 114.24, 114.15, 110.81, 108.44, 105.47, 97.55, 86.95, 77.37, 77.16, 76.95, 73.43, 72.89, 60.41, 55.84, 29.11, 27.66, 26.42, 18.75.

HRMS (ESI): m/z calculated for $C_{21}H_{25}O_8^+$ $[M+H]^+$, 405.1544; found, 405.1544.

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



Prepared from **SI-3-8** (0.1 mmol, 1.0 equiv) and **SI-1-3** (0.15 mmol, 1.5 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **16** (19.0 mg, 42% yield) as white solid.

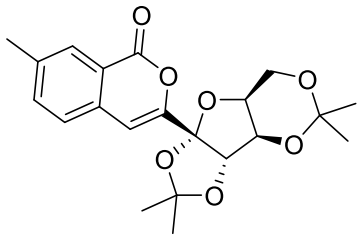
TLC: R*f* = 0.50 (Ethyl acetate/Petroleum Ether = 1/4)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 8.2 Hz, 1H), 7.75 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.70 (d, *J* = 1.8 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.52 – 7.47 (m, 2H), 7.46 – 7.40 (m, 1H), 7.21 (s, 1H), 4.70 (s, 1H), 4.42 (d, *J* = 2.5 Hz, 1H), 4.29 (q, *J* = 1.9 Hz, 1H), 4.22 (d, *J* = 13.6 Hz, 1H), 4.16 (dd, *J* = 13.6, 2.1 Hz, 1H), 1.65 (s, 3H), 1.60 (s, 3H), 1.43 (s, 3H), 1.25 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 162.01, 151.67, 147.75, 139.47, 137.35, 130.39, 129.20, 128.84, 127.73, 127.58, 124.61, 119.82, 114.15, 110.78, 105.62, 97.56, 86.97, 73.45, 72.90, 60.37, 29.13, 27.65, 26.40, 18.74.

HRMS (ESI): m/z calculated for $C_{26}H_{26}NaO_7^+$ $[M+Na]^+$, 473.1571; found, 473.1576.

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



Prepared from **SI-3-2** (0.1 mmol, 1.0 equiv) and **SI-1-3** (0.15 mmol, 1.5 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **17** (18.5 mg, 48% yield) as white solid.

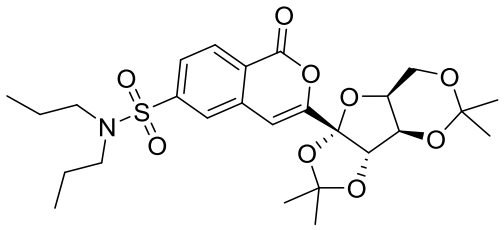
TLC: R*f* = 0.30 (Ethyl acetate/Petroleum Ether = 1/4)

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 5.7 Hz, 1H), 7.11 (d, *J* = 3.3 Hz, 1H), 4.67 (d, *J* = 3.2 Hz, 1H), 4.39 (d, *J* = 2.8 Hz, 1H), 4.27 (s, 1H), 4.22 – 4.13 (m, 2H), 2.46 (s, 3H), 1.63 (s, 3H), 1.58 (s, 3H), 1.42 (s, 3H), 1.22 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 162.29, 150.43, 139.09, 136.22, 134.39, 129.52, 126.38, 121.03, 114.02, 110.84, 105.39, 97.53, 86.90, 73.40, 72.91, 60.36, 29.03, 27.64, 26.42, 21.54, 18.75.

HRMS (ESI): m/z calculated for $C_{21}H_{24}NaO_7^+$ $[M+Na]^+$, 411.1414; found, 411.1414.

1-oxo-*N*,*N*-dipropyl-3-((3a*S*,3b*R*,7a*S*,8a*R*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)-1*H*-isochromene-6-sulfonamide (18)



Prepared from **SI-3-9** (0.1 mmol, 1.0 equiv) and **SI-1-3** (0.15 mmol, 1.5 equiv) according to the general procedure **3**. Purification by flash column (Ethyl

acetate/Petroleum Ether = 1/10) afforded **18** (24.6 mg, 46% yield) as white solid.

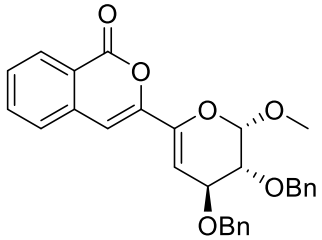
TLC: R*f* = 0.25 (Ethyl acetate/Petroleum Ether = 1/4)

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.39 (d, *J* = 8.2 Hz, 1H), 7.96 (s, 1H), 7.89 – 7.83 (m, 1H), 7.22 (s, 1H), 4.67 (s, 1H), 4.42 (d, *J* = 2.3 Hz, 1H), 4.29 (s, 1H), 4.23 – 4.13 (m, 2H), 3.12 (td, *J* = 7.1, 2.0 Hz, 4H), 1.62 (s, 3H), 1.58 (s, 3H), 1.54 (q, *J* = 7.6 Hz, 4H), 1.43 (s, 3H), 1.22 (s, 3H), 0.86 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 160.84, 146.48, 137.45, 131.05, 126.23, 125.07, 123.40, 114.45, 110.52, 105.02, 97.64, 87.10, 73.64, 72.85, 60.33, 50.00, 29.10, 27.61, 26.34, 21.99, 18.73, 11.27, 1.17.

HRMS (ESI): m/z calculated for $C_{26}H_{35}NNaO_9S^+$ $[M+Na]^+$, 560.1925; found, 560.1923.

3-((2*S*,3*S*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)-1*H*-isochromen-1-one (19)



Prepared from **SI-3-1** (0.1 mmol, 1.0 equiv) and **SI-1-11** (0.15 mmol, 1.5 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **19** (19.2 mg, 41% yield) as yellow oil.

TLC: R*f* = 0.50 (Ethyl acetate/Petroleum Ether = 1/4)

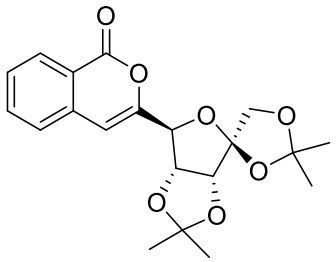
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.28 (d, *J* = 7.9 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.36 (q, *J* = 5.6, 4.3 Hz, 8H), 7.31 (dd, *J* = 8.8, 4.6 Hz, 2H), 6.84 (s, 1H), 6.02 (d, *J* = 3.5 Hz, 1H), 4.98 (d, *J* = 2.3 Hz,

1H), 4.83 (d, *J* = 12.3 Hz, 1H), 4.78 (d, *J* = 12.3 Hz, 1H), 4.74 – 4.70 (m, 1H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.35 (dd, *J* = 6.6, 3.4 Hz, 1H), 3.85 (dd, *J* = 6.6, 2.3 Hz, 1H), 3.57 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 161.63, 147.89, 142.26, 138.18, 138.16, 136.92, 135.05, 129.98, 128.75, 128.61, 128.22, 128.07, 127.97, 127.91, 127.12, 126.52, 121.36, 102.60, 101.98, 100.20, 77.41, 77.16, 76.91, 75.85, 73.44, 73.13, 71.52, 57.15.

HRMS (ESI): m/z calculated for $C_{29}H_{27}O_6^+$ $[M+Na]^+$, 471.1802; found, 471.1804.

3-((3a*R*,4*S*,6*S*,6a*R*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)-1*H*-isochromen-1-one (20)



Prepared from **SI-3-1** (0.1 mmol, 1.0 equiv) and **SI-1-4** (0.15 mmol, 1.5 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **20** (13.0 mg, 35% yield) as white solid.

Prepared from **SI-4-1** (0.1 mmol, 1.0 equiv) and **SI-1-4** (0.15 mmol, 1.5 equiv) according to the general procedure **4**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **20** (15.9 mg, 42% yield) as white solid.

TLC: R*f* = 0.50 (Ethyl acetate/Petroleum Ether = 1/4)

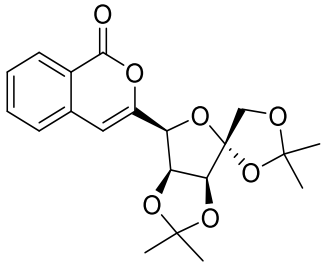
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 6.78 (s, 1H), 5.12 (d, *J* = 5.8 Hz, 1H), 4.97 (s, 1H), 4.67 (d, *J* = 6.0 Hz, 1H), 4.42 (d, *J* = 9.9 Hz, 1H), 4.17 (d, *J* = 10.0

Hz, 1H), 1.58 (s, 3H), 1.51 (s, 3H), 1.40 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.05, 154.47, 136.91, 135.02, 129.87, 128.51, 125.97, 120.62, 114.90, 113.32, 112.25, 103.97, 85.33, 84.07, 83.30, 70.35, 26.68, 26.62, 26.25, 25.23.

HRMS (ESI): m/z calculated for $C_{20}H_{22}NaO_7^+$ $[M+Na]^+$, 397.1258; found, 397.1268.

3-((3a*S*,4*R*,6*S*,6a*S*)-2,2,2',2'-tetramethyldihydro-6*H*-spiro[furo[3,4-*d*][1,3]dioxole-4,4'-[1,3]dioxolan]-6-yl)-1*H*-isochromen-1-one (21)



Prepared from **SI-3-1** (0.1 mmol, 1.0 equiv) and **SI-1-5** (0.15 mmol, 1.5 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **21** (3.1 mg, 8% yield) as white solid.

Prepared from **SI-4-1** (0.1 mmol, 1.0 equiv) and **SI-1-5** (0.15 mmol, 1.5 equiv) according to the general procedure **4**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **21** (15.9 mg, 42% yield) as white solid.

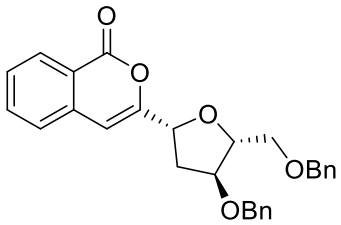
TLC: R*f* = 0.50 (Ethyl acetate/Petroleum Ether = 1/4)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.27 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.70 (td, *J* = 7.6, 1.3 Hz, 1H), 7.49 (td, *J* = 7.6, 1.2 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 6.61 (s, 1H), 5.07 (dd, *J* = 5.7, 4.0 Hz, 1H), 4.82 (dd, *J* = 4.0, 1.2 Hz, 1H), 4.70 (d, *J* = 5.7 Hz, 1H), 4.34 (d, *J* = 9.8 Hz, 1H), 4.21 (d, *J* = 9.8 Hz, 1H), 1.50 (s, 3H), 1.43 (s, 3H), 1.32 (s, 3H), 1.27 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.23, 152.09, 137.15, 134.97, 129.82, 128.21, 125.81, 120.82, 113.45, 112.41, 112.00, 103.64, 85.04, 80.44, 77.65, 77.37, 77.16, 76.95, 69.58, 26.66, 26.51, 26.06, 25.08.

HRMS (ESI): m/z calculated for $C_{20}H_{22}NaO_7^+$ $[M+Na]^+$, 397.1258; found, 397.1268.

3-((2*R*,4*S*,5*R*)-4-(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-2-yl)-1*H*-isochromen-1-one (22)



Prepared from **SI-3-1** (0.1 mmol, 1.0 equiv) and **SI-1-6** (0.15 mmol, 1.5 equiv) according to the general procedure **3**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **22** (22.1 mg, 50% yield) as yellow oil.

Prepared from **SI-4-1** (0.1 mmol, 1.0 equiv) and **SI-1-6** (0.15 mmol, 1.5 equiv) according to the general procedure **4**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **22** (14.3 mg, 32% yield) as yellow oil.
TLC: R*f* = 0.45 (Ethyl acetate/Petroleum Ether = 1/4)

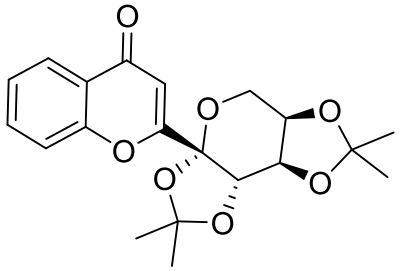
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.36 – 7.28 (m, 11H), 6.61 (s, 1H), 4.95 (dd, *J* = 9.1, 6.3 Hz, 1H), 4.62 – 4.53 (m, 4H), 4.29 (d, *J* = 6.7 Hz, 1H), 4.23 – 4.15 (m, 1H), 3.68 – 3.57 (m, 2H), 2.48 – 2.38 (m, 1H), 2.28 – 2.17 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 162.47, 156.18, 138.18, 137.93, 137.07, 134.95, 129.76, 128.64, 128.61, 128.54, 128.35, 128.10, 128.06, 127.93, 127.86, 127.80, 125.91, 120.88, 118.28, 111.37, 103.07, 83.95, 80.52, 73.60, 71.41, 70.73, 64.23,

36.82.

HRMS (ESI): m/z calculated for $C_{28}H_{26}NaO_5^+$ $[M+Na]^+$, 465.1672; found, 465.1672.

2-((3a*R*,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)-4*H*-chromen-4-one (23)



Prepared from **SI-5-1** (0.2 mmol, 1.0 equiv) and **SI-1-10** (0.3 mmol, 1.5 equiv) according to the general procedure **5**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **23** (63.2 mg, 84% yield) as yellow oil.

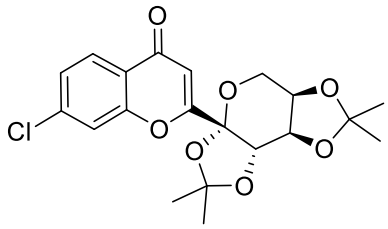
TLC: R*f* = 0.50 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (300 MHz, Chloroform-*d*): δ 8.20 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.48 – 7.35 (m, 2H), 6.84 (s, 1H), 4.66 (d, *J* = 3.0 Hz, 2H), 4.31 (d, *J* = 8.2 Hz, 1H), 4.01 (q, *J* = 13.1 Hz, 2H), 1.64 (s, 3H), 1.62 (s, 3H), 1.46 (s, 3H), 1.33 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 178.58, 163.66, 156.40, 133.96, 126.04, 125.45, 124.15, 118.04, 110.55, 110.24, 109.57, 100.32, 72.77, 70.28, 70.02, 61.57, 26.60, 26.01, 25.18, 24.09.

HRMS (ESI): m/z calculated for $C_{20}H_{22}NaO_7^+$ $[M+Na]^+$, 397.1258; found, 397.1267.

7-chloro-2-((3a*R*,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)-4*H*-chromen-4-one (24)



Prepared from **SI-5-2** (0.2 mmol, 1.0 equiv) and **SI-1-10** (0.3 mmol, 1.5 equiv) according to the general procedure **5**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **24** (73.3 mg, 90% yield) as yellow oil.

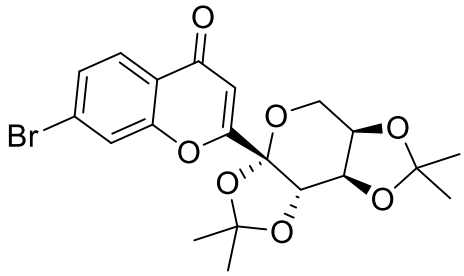
TLC: R*f* = 0.55 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.5 Hz, 1H), 7.45 (d, *J* = 1.9 Hz, 1H), 7.37 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.82 (s, 1H), 4.65 (dd, *J* = 8.0, 2.5 Hz, 1H), 4.62 (d, *J* = 2.5 Hz, 1H), 4.31 (d, *J* = 7.9 Hz, 1H), 4.04 (dd, *J* = 13.0, 1.9 Hz, 1H), 3.95 (dd, *J* = 13.1, 0.9 Hz, 1H), 1.63 (s, 3H), 1.60 (s, 3H), 1.44 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 177.64, 163.86, 156.47, 140.04, 127.43, 126.32, 122.69, 118.11, 110.86, 110.34, 109.58, 100.17, 72.76, 70.24, 69.97, 61.62, 26.58, 25.99, 25.21, 24.06.

HRMS (ESI): m/z calculated for $C_{20}H_{21}ClNaO_7^+$ $[M+Na]^+$, 431.0868; found, 431.0874.

7-bromo-2-((3a*R*,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)-4*H*-chromen-4-one (25)



Prepared from **SI-5-3** (0.2 mmol, 1.0 equiv) and **SI-1-10** (0.3 mmol, 1.5 equiv) according to the general procedure **5**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **25** (68.4 mg, 75% yield) as yellow oil.

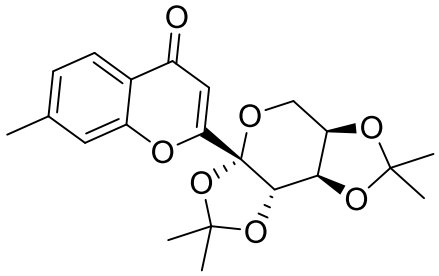
TLC: R*f* = 0.50 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.5 Hz, 1H), 7.62 (d, *J* = 1.8 Hz, 1H), 7.52 (dt, *J* = 8.6, 1.3 Hz, 1H), 6.82 (s, 1H), 4.65 (dd, *J* = 8.0, 2.5 Hz, 1H), 4.61 (d, *J* = 2.4 Hz, 1H), 4.31 (d, *J* = 8.0 Hz, 1H), 4.04 (dd, *J* = 13.1, 1.9 Hz, 1H), 3.95 (d, *J* = 13.0 Hz, 1H), 1.63 (s, 3H), 1.61 (s, 3H), 1.44 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 177.77, 163.73, 156.37, 129.10, 128.20, 127.43, 123.00, 121.16, 110.86, 110.35, 109.54, 100.09, 72.69, 70.19, 69.89, 61.57, 26.57, 25.96, 25.21, 24.03.

HRMS (ESI): m/z calculated for $C_{20}H_{22}BrO_7^+$ $[M+H]^+$, 453.0543; found, 453.0553.

7-methyl-2-((3a*R*,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)-4*H*-chromen-4-one (26)



Prepared from **SI-5-4** (0.2 mmol, 1.0 equiv) and **SI-1-10** (0.3 mmol, 1.5 equiv) according to the general procedure **5**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **26** (73.7 mg, 95% yield) as yellow oil.

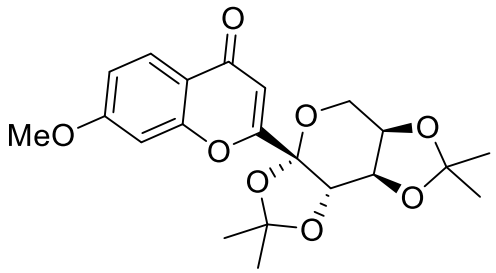
TLC: R*f* = 0.40 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.79 (s, 1H), 4.64 (d, *J* = 6.6 Hz, 2H), 4.32 – 4.27 (m, 1H), 4.04 (dd, *J* = 13.0, 1.9 Hz, 1H), 3.95 (dd, *J* = 13.0, 1.0 Hz, 1H), 2.47 (s, 3H), 1.62 (s, 3H), 1.62 (s, 3H), 1.44 (s, 3H), 1.31 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 178.45, 163.32, 156.54, 145.29, 126.90, 125.76, 121.91, 117.74, 110.47, 110.16, 109.55, 100.31, 72.75, 70.30, 70.04, 61.56, 26.59, 25.98, 25.22, 24.09, 21.91.

HRMS (ESI): m/z calculated for $C_{21}H_{25}O_7^+$ $[M+H]^+$, 389.1595; found, 389.1605.

7-methoxy-2-((3a*R*,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)-4*H*-chromen-4-one (27)



Prepared from **SI-5-5** (0.2 mmol, 1.0 equiv) and **SI-1-10** (0.3 mmol, 1.5 equiv) according to the general procedure **5**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **27** (70.5 mg, 87% yield) as yellow oil.

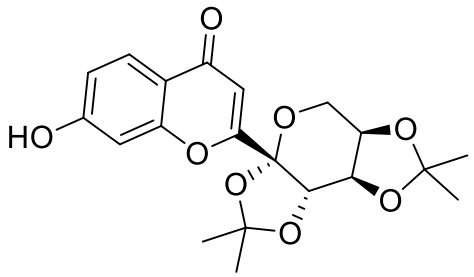
TLC: R*f* = 0.25 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.9 Hz, 1H), 6.96 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.81 (d, *J* = 2.4 Hz, 1H), 6.75 (s, 1H), 4.64 (d, *J* = 8.5 Hz, 2H), 4.30 (d, *J* = 7.8 Hz, 1H), 4.03 (dd, *J* = 13.1, 1.8 Hz, 1H), 3.94 (d, *J* = 13.0 Hz, 1H), 3.88 (s, 3H), 1.62 (s, 3H), 1.59 (s, 3H), 1.45 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 177.95, 164.30, 163.16, 158.07, 127.34, 117.96, 114.44, 110.37, 110.08, 109.48, 100.46, 100.26, 72.66, 70.21, 69.94, 61.47, 55.94, 26.54, 25.95, 25.18, 24.04.

HRMS (ESI): m/z calculated for $C_{21}H_{25}O_8^+$ $[M+H]^+$, 405.1544; found, 405.1554.

7-hydroxy-2-((3a*R*,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)-4*H*-chromen-4-one (28)



Prepared from **SI-5-6** (0.2 mmol, 1.0 equiv) and **SI-1-10** (0.3 mmol, 1.5 equiv) according to the general procedure **5**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/5) afforded **28** (54.4 mg, 70% yield) as yellow solid.

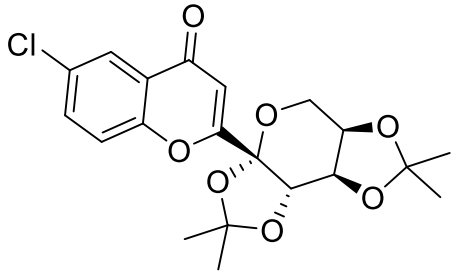
TLC: R*f* = 0.30 (Ethyl acetate/Petroleum Ether = 1/1)

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.50 (s, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.00 (dd, *J* = 8.9, 2.2 Hz, 1H), 6.92 (d, *J* = 2.2 Hz, 1H), 6.81 (s, 1H), 4.64 (d, *J* = 8.0 Hz, 2H), 4.30 (d, *J* = 7.8 Hz, 1H), 4.03 (d, *J* = 13.0 Hz, 1H), 3.94 (d, *J* = 13.0 Hz, 1H), 1.61 (s, 3H), 1.57 (s, 3H), 1.41 (s, 3H), 1.30 (s, 3H).

^{13}C NMR (75 MHz, CD_3OD): δ 180.09, 165.77, 165.17, 159.73, 128.02, 117.29, 116.71, 111.43, 110.36, 110.35, 103.29, 101.32, 74.08, 71.46, 71.13, 26.65, 26.14, 25.32, 24.03.

HRMS (ESI): m/z calculated for $C_{20}H_{23}O_8^+$ $[M+H]^+$, 391.1387; found, 391.1396.

6-chloro-2-((3a*R*,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)-4*H*-chromen-4-one (29)



Prepared from **SI-5-7** (0.2 mmol, 1.0 equiv) and **SI-1-10** (0.3 mmol, 1.5 equiv)

according to the general procedure **5**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **29** (64.1 mg, 78% yield) as yellow oil.

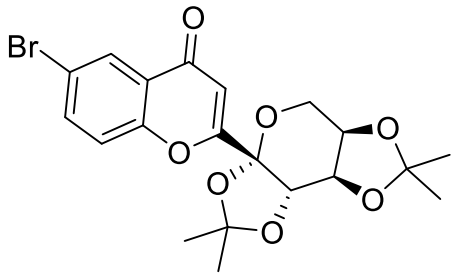
TLC: R*f* = 0.50 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 2.5 Hz, 1H), 7.61 (dd, J = 8.9, 2.6 Hz, 1H), 7.40 (d, J = 8.9 Hz, 1H), 6.83 (s, 1H), 4.65 (dd, J = 8.0, 2.5 Hz, 1H), 4.62 (d, J = 2.5 Hz, 1H), 4.31 (d, J = 8.0 Hz, 1H), 4.07 – 4.01 (m, 1H), 3.96 (d, J = 13.0 Hz, 1H), 1.63 (s, 3H), 1.60 (s, 3H), 1.45 (s, 3H), 1.33 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 177.33, 163.98, 154.68, 134.18, 131.46, 125.46, 125.06, 119.75, 110.49, 110.32, 109.54, 100.20, 72.76, 70.19, 69.91, 61.57, 26.56, 25.98, 25.15, 24.03.

HRMS (ESI): m/z calculated for $C_{20}H_{22}ClO_7^+$ $[M+H]^+$, 409.1049; found, 409.1059.

6-bromo-2-((3a*R*,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)-4*H*-chromen-4-one (30)



Prepared from **SI-5-8** (0.2 mmol, 1.0 equiv) and **SI-1-10** (0.3 mmol, 1.5 equiv) according to the general procedure **5**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **30** (65.4 mg, 72% yield) as yellow oil.

TLC: R*f* = 0.55 (Ethyl acetate/Petroleum Ether = 1/2)

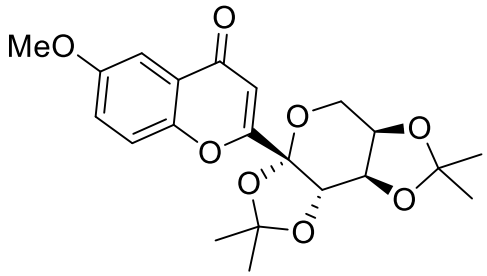
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 2.4 Hz, 1H), 7.74 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.34 (d, *J* = 8.9 Hz, 1H), 6.84 (s, 1H), 4.65 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.62 (d, *J* =

2.5 Hz, 1H), 4.31 (dd, *J* = 8.0, 1.7 Hz, 1H), 4.04 (dd, *J* = 13.1, 1.8 Hz, 1H), 3.96 (d, *J* = 13.0 Hz, 1H), 1.63 (s, 3H), 1.59 (s, 3H), 1.45 (s, 3H), 1.33 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 177.16, 164.03, 155.17, 136.93, 128.72, 125.49, 119.97, 118.92, 110.63, 110.33, 109.58, 100.25, 72.81, 70.24, 69.98, 61.62, 26.58, 26.00, 25.18, 24.06.

HRMS (ESI): m/z calculated for $C_{20}H_{21}BrNaO_7^+$ $[M+Na]^+$, 475.0363; found, 475.0370.

6-methoxy-2-((3a*R*,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)-4*H*-chromen-4-one (31)



Prepared from **SI-5-9** (0.2 mmol, 1.0 equiv) and **SI-1-10** (0.3 mmol, 1.5 equiv) according to the general procedure **5**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **31** (60.6 mg, 75% yield) as yellow oil.

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

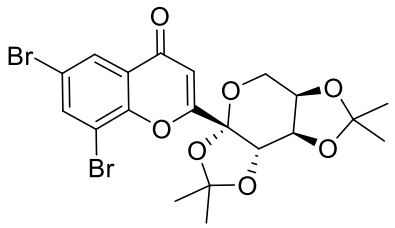
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 3.1 Hz, 1H), 7.37 (d, *J* = 9.1 Hz, 1H), 7.24 (d, *J* = 3.0 Hz, 1H), 6.82 (s, 1H), 4.65 (d, *J* = 7.8 Hz, 2H), 4.31 (d, *J* = 7.8 Hz, 1H), 4.04 (dd, *J* = 13.0, 1.9 Hz, 1H), 3.95 (d, *J* = 13.1 Hz, 1H), 3.88 (s, 3H), 1.63 (s, 3H), 1.60 (s, 3H), 1.45 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 178.49, 163.42, 157.15, 151.18, 124.67, 124.10, 119.43, 110.17, 109.65, 109.50, 104.96, 100.32, 72.77, 70.22, 69.96, 61.51, 56.06,

26.55, 25.97, 25.13, 24.05.

HRMS (ESI): m/z calculated for $C_{21}H_{25}O_8^+$ $[M+H]^+$, 405.1544; found, 405.1551.

6,8-dibromo-2-((3a*R*,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)-4*H*-chromen-4-one (32)



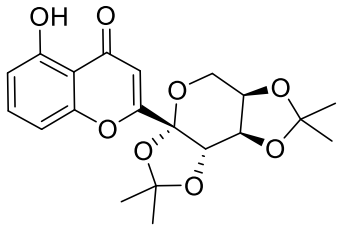
Prepared from **SI-5-10** (0.2 mmol, 1.0 equiv) and **SI-1-10** (0.3 mmol, 1.5 equiv) according to the general procedure **5**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **32** (58.8 mg, 55% yield) as yellow oil.
TLC: R*f* = 0.75 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, *J* = 2.4 Hz, 1H), 8.01 (d, *J* = 2.4 Hz, 1H), 6.94 (s, 1H), 4.82 (d, *J* = 2.6 Hz, 1H), 4.68 (dd, *J* = 8.0, 2.6 Hz, 1H), 4.34 – 4.28 (m, 1H), 4.12 (dd, *J* = 13.0, 1.8 Hz, 1H), 3.99 (dd, *J* = 12.8, 0.9 Hz, 1H), 1.75 (s, 3H), 1.63 (s, 3H), 1.33 (s, 3H), 1.30 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 176.42, 164.11, 152.26, 139.82, 128.21, 126.44, 118.81, 112.90, 111.21, 111.18, 109.66, 99.35, 72.68, 70.37, 69.79, 61.88, 26.86, 26.25, 25.83, 24.03.

HRMS (ESI): m/z calculated for $C_{20}H_{20}Br_2NaO_7^+$ $[M+H]^+$, 552.9468; found, 552.9478.

5-hydroxy-2-((3a*R*,*5aR*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)-4*H*-chromen-4-one (33)



Prepared from **SI-5-11** (0.2 mmol, 1.0 equiv) and **SI-1-10** (0.3 mmol, 1.5 equiv) according to the general procedure **5**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/4) afforded **33** (73.4 mg, 94% yield) as yellow oil.

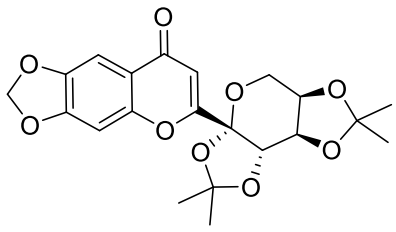
TLC: R*f* = 0.80 (Ethyl acetate/Petroleum Ether = 1/1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 12.40 (s, 1H), 7.51 (t, *J* = 8.3 Hz, 1H), 6.87 (dd, *J* = 8.4, 0.9 Hz, 1H), 6.79 (dd, *J* = 8.3, 0.8 Hz, 1H), 6.76 (s, 1H), 4.65 (dd, *J* = 8.0, 2.5 Hz, 1H), 4.62 (d, *J* = 2.5 Hz, 1H), 4.30 (dd, *J* = 8.0, 1.7 Hz, 1H), 4.03 (dd, *J* = 13.1, 1.9 Hz, 1H), 3.95 (d, *J* = 12.6 Hz, 1H), 1.62 (s, 3H), 1.60 (s, 3H), 1.45 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 183.97, 164.96, 161.04, 156.59, 135.62, 111.65, 111.09, 110.44, 109.53, 109.27, 106.97, 100.06, 72.77, 70.19, 69.91, 61.57, 26.56, 25.96, 25.11, 24.02.

HRMS (ESI): m/z calculated for $C_{20}H_{23}O_8^+$ $[M+H]^+$, 391.1387; found, 391.1394.

6-((3a*R*,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)-8*H*-[1,3]dioxolo[4,5-*g*]chromen-8-one (34)



Prepared from **SI-5-12** (0.2 mmol, 1.0 equiv) and **SI-1-10** (0.3 mmol, 1.5 equiv) according to the general procedure **5**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **34** (80.2 mg, 96% yield) as yellow oil.

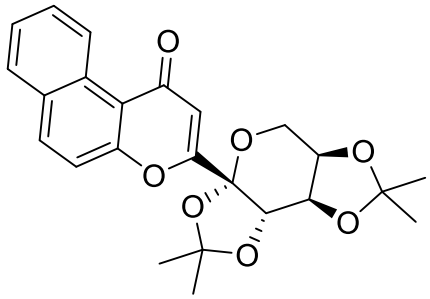
TLC: R*f* = 0.50 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (s, 1H), 6.81 (s, 1H), 6.75 (s, 1H), 6.08 (s, 2H), 4.64 (dd, *J* = 8.0, 2.5 Hz, 1H), 4.60 (d, *J* = 2.4 Hz, 1H), 4.30 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.02 (dd, *J* = 13.0, 1.9 Hz, 1H), 3.94 (dd, *J* = 13.0, 0.9 Hz, 1H), 1.62 (s, 3H), 1.57 (s, 3H), 1.45 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 177.47, 162.96, 153.64, 152.98, 146.42, 119.20, 110.09, 109.92, 109.54, 102.60, 102.55, 100.34, 97.94, 72.79, 70.27, 70.04, 61.55, 26.55, 26.02, 25.15, 24.08.

HRMS (ESI): m/z calculated for $C_{21}H_{23}O_9^+$ $[M+H]^+$, 419.1337; found, 419.1347.

3-((3a*R*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)-1*H*-benzo[*f*]chromen-1-one (35)



Prepared from **SI-5-13** (0.2 mmol, 1.0 equiv) and **SI-1-10** (0.3 mmol, 1.5 equiv) according to the general procedure **5**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **35** (67.7 mg, 80% yield) as yellow oil.

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

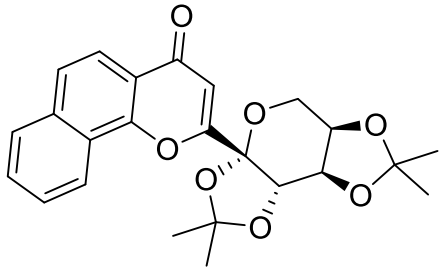
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.02 (d, *J* = 8.6 Hz, 1H), 8.08 (d, *J* = 9.1 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.75 (dd, *J* = 8.8, 6.9 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 9.0 Hz, 1H), 6.97 (s, 1H), 4.68 (d, *J* = 7.8 Hz, 2H), 4.33 (d, *J* = 7.8 Hz, 1H),

4.07 (dd, *J* = 13.1, 1.8 Hz, 1H), 3.99 (d, *J* = 13.0 Hz, 1H), 1.66 (s, 6H), 1.49 (s, 3H), 1.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 180.38, 161.03, 157.58, 135.71, 130.71, 130.58, 129.49, 128.28, 127.22, 126.83, 117.43, 113.52, 110.21, 109.55, 100.18, 72.78, 70.26, 69.98, 61.54, 26.59, 26.02, 25.22, 24.06.

HRMS (ESI): m/z calculated for $C_{24}H_{25}O_7^+$ $[M+H]^+$, 425.1595; found, 425.1604.

2-((3a*R*,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)-4*H*-benzo[*h*]chromen-4-one (36)



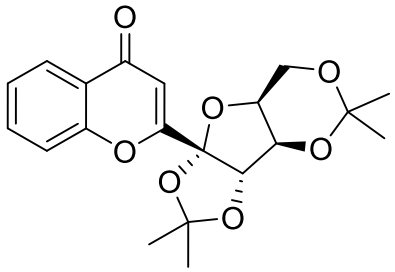
Prepared from **SI-5-14** (0.2 mmol, 1.0 equiv) and **SI-1-10** (0.3 mmol, 1.5 equiv) according to the general procedure **5**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **36** (80.7 mg, 95% yield) as yellow oil.
TLC: R*f* = 0.35 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, *J* = 8.1 Hz, 1H), 8.15 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.73 – 7.63 (m, 2H), 7.03 (s, 1H), 4.88 (s, 1H), 4.73 (d, *J* = 8.1 Hz, 1H), 4.35 (d, *J* = 8.0 Hz, 1H), 4.13 (d, *J* = 12.8 Hz, 1H), 4.00 (d, *J* = 13.0 Hz, 1H), 1.68 (s, 6H), 1.43 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 178.34, 163.24, 154.08, 136.25, 129.40, 128.37, 127.16, 125.67, 124.33, 122.85, 120.98, 120.70, 112.22, 110.27, 109.66, 100.41, 77.58, 77.16, 76.74, 72.81, 70.25, 70.14, 61.87, 26.60, 26.04, 25.79, 24.15.

HRMS (ESI): m/z calculated for $C_{24}H_{25}O_7^+$ $[M+H]^+$, 425.1595; found, 425.1604.

2-((3a*S*,3b*R*,7a*S*,8a*R*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)-4*H*-chromen-4-one (37)



Prepared from **SI-5-1** (0.2 mmol, 1.0 equiv) and **SI-1-3** (0.3 mmol, 1.5 equiv) according to the general procedure **5**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **37** (43.0 mg, 57% yield) as yellow solid.

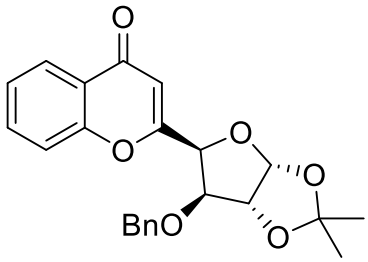
TLC: R*f* = 0.30 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (dd, J = 8.0, 1.6 Hz, 1H), 7.75 – 7.62 (m, 1H), 7.50 – 7.34 (m, 2H), 6.99 (s, 1H), 4.72 (s, 1H), 4.42 (d, J = 2.3 Hz, 1H), 4.29 (d, J = 2.2 Hz, 1H), 4.23 – 4.09 (m, 2H), 1.62 (s, 3H), 1.60 (s, 3H), 1.43 (s, 3H), 1.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 178.62, 162.62, 156.43, 133.88, 125.98, 125.36, 124.19, 118.16, 114.24, 111.06, 110.85, 97.76, 87.89, 73.92, 73.04, 60.11, 28.99, 27.47, 26.24, 18.84.

HRMS (ESI): m/z calculated for $C_{20}H_{23}O_7^+$ $[M+H]^+$, 375.1438; found, 375.1448.

2-((3a*R*,5*S*,6*S*,6a*R*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)-4*H*-chromen-4-one (38)



Prepared from **SI-5-1** (0.2 mmol, 1.0 equiv) and **SI-1-2** (0.3 mmol, 1.5 equiv) according to the general procedure **5**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **38** (66.4 mg, 84% yield) as yellow oil.

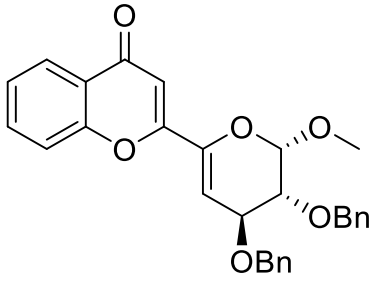
TLC: R*f* = 0.38 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.65 (td, *J* = 7.9, 7.1, 1.6 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 2H), 7.00 (d, *J* = 7.5 Hz, 2H), 6.61 (s, 1H), 6.11 (d, *J* = 3.6 Hz, 1H), 5.08 (d, *J* = 3.4 Hz, 1H), 4.72 (d, *J* = 3.6 Hz, 1H), 4.57 (d, *J* = 12.3 Hz, 1H), 4.36 (d, *J* = 12.3 Hz, 1H), 4.30 (d, *J* = 3.4 Hz, 1H), 1.54 (s, 3H), 1.37 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 177.82, 163.73, 155.98, 136.73, 133.61, 128.52, 128.16, 127.91, 126.09, 125.28, 124.38, 117.99, 112.67, 110.30, 105.54, 82.56, 81.63, 78.90, 72.24, 27.10, 26.42.

HRMS (ESI): m/z calculated for $C_{23}H_{23}O_6^+$ $[M+H]^+$, 395.1489; found, 395.1499.

2-((2*S*,3*R*,4*S*)-3,4-bis(benzyloxy)-2-methoxy-3,4-dihydro-2*H*-pyran-6-yl)-4*H*-chromen-4-one (39)



Prepared from **SI-5-1** (0.2 mmol, 1.0 equiv) and **SI-1-11** (0.3 mmol, 1.5 equiv)

according to the general procedure **5**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **39** (71.0 mg, 75% yield) as yellow oil.

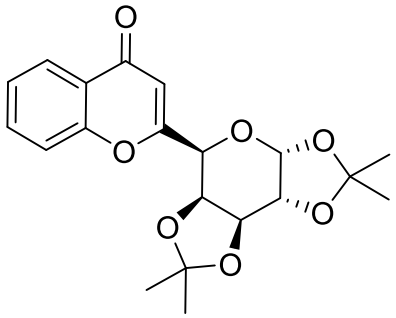
TLC: R*f* = 0.40 (Ethyl acetate/Petroleum Ether = 1/2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 7.9 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 4.0 Hz, 8H), 7.33 (dd, *J* = 7.5, 3.5 Hz, 3H), 6.67 (s, 1H), 6.08 (d, *J* = 3.3 Hz, 1H), 5.01 (d, *J* = 2.3 Hz, 1H), 4.86 – 4.79 (m, 2H), 4.73 (d, *J* = 4.7 Hz, 2H), 4.40 (dd, *J* = 7.0, 3.3 Hz, 1H), 3.89 (dd, *J* = 7.1, 2.4 Hz, 1H), 3.54 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 178.64, 157.26, 156.01, 142.44, 138.17, 137.92, 134.08, 128.66, 128.64, 128.23, 128.17, 128.00, 127.96, 125.84, 125.30, 124.09, 118.04, 107.69, 105.18, 100.11, 75.91, 73.44, 73.36, 72.19, 57.15.

HRMS (ESI): m/z calculated for $C_{29}H_{27}O_6^+$ $[M+H]^+$, 471.1802; found, 471.1812.

2-((3a*R*,5*S*,5a*R*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)-4*H*-chromen-4-one (40)



Prepared from **SI-5-1** (0.2 mmol, 1.0 equiv) and **SI-1-8** (0.3 mmol, 1.5 equiv) according to the general procedure **5**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **40** (35.5 mg, 47% yield) as yellow oil.

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

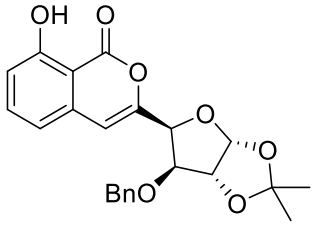
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.64 (dd, *J* = 8.7, 7.2

Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 6.55 (s, 1H), 5.69 (d, *J* = 4.9 Hz, 1H), 4.78 – 4.73 (m, 2H), 4.66 (dd, *J* = 7.8, 2.2 Hz, 1H), 4.45 (dd, *J* = 5.1, 2.6 Hz, 1H), 1.57 (s, 3H), 1.39 (s, 3H), 1.38 (s, 3H), 1.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 178.11, 164.71, 156.21, 133.58, 126.01, 125.17, 124.41, 118.04, 110.35, 109.95, 109.35, 96.70, 71.65, 70.98, 70.69, 67.34, 26.22, 26.03, 24.93, 24.82.

HRMS (ESI): m/z calculated for $C_{20}H_{23}O_7^+$ $[M+H]^+$, 375.1438; found, 375.1446.

3-((3a*R*,5*S*,6*S*,6a*R*)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)-8-hydroxy-1*H*-isochromen-1-one (43)



Prepared from **SI-2-6** (0.1 mmol, 1.0 equiv) and **SI-1-2** (0.15 mmol, 1.5 equiv) according to the general procedure **2**. Purification by flash column (Ethyl acetate/Petroleum Ether = 1/10) afforded **43** (26.1 mg, 64% yield) as yellow oil.
TLC: R*f* = 0.65 (Ethyl acetate/Petroleum Ether = 1/4)

^{1}H NMR (300 MHz, $CDCl_3$): δ 10.88 (d, *J* = 1.9 Hz, 1H), 7.60 (t, *J* = 8.2 Hz, 1H), 7.41 – 7.28 (m, 1H), 7.20 (d, *J* = 4.3 Hz, 2H), 7.12 – 7.07 (m, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 3.7 Hz, 1H), 6.08 (d, *J* = 4.0 Hz, 1H), 5.02 (s, 1H), 4.68 (d, *J* = 4.0 Hz, 1H), 4.59 (dd, *J* = 12.5, 5.5 Hz, 1H), 4.43 (dd, *J* = 12.1, 3.3 Hz, 1H), 4.33 – 4.25 (m, 1H), 1.52 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 165.79, 161.78, 151.41, 137.68, 137.44, 136.94, 128.60, 128.24, 127.83, 116.37, 115.41, 112.69, 106.24, 105.29, 105.27, 82.94, 81.93, 78.44, 72.84, 27.08, 26.46.

HRMS (ESI): m/z calculated for $C_{23}H_{22}NaO_7^+$ $[M+Na]^+$, 433.1258; found, 433.1269.

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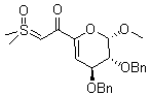
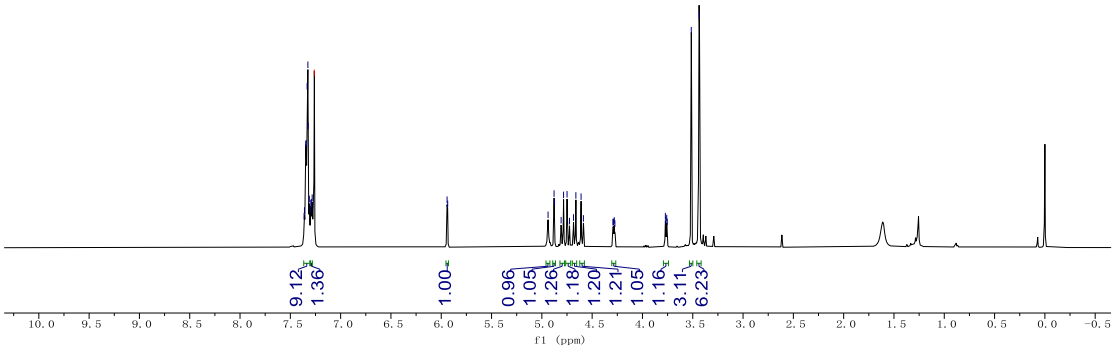
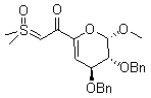
9 NMR Spectra of Substrates and Products

^{1}H NMR (500 MHz, $CDCl_3$) Spectra of compound SI-1-11

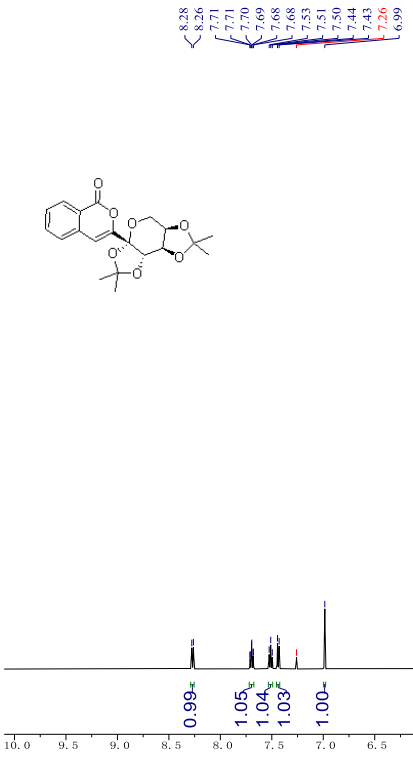




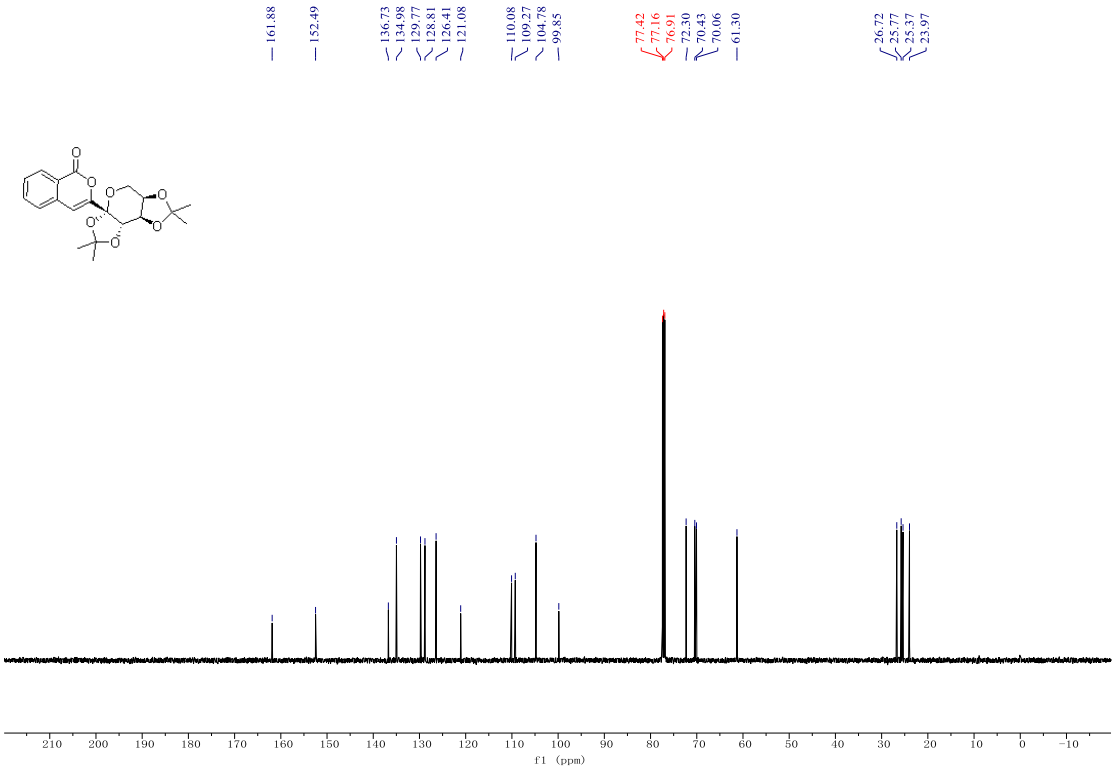
^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound SI-1-11



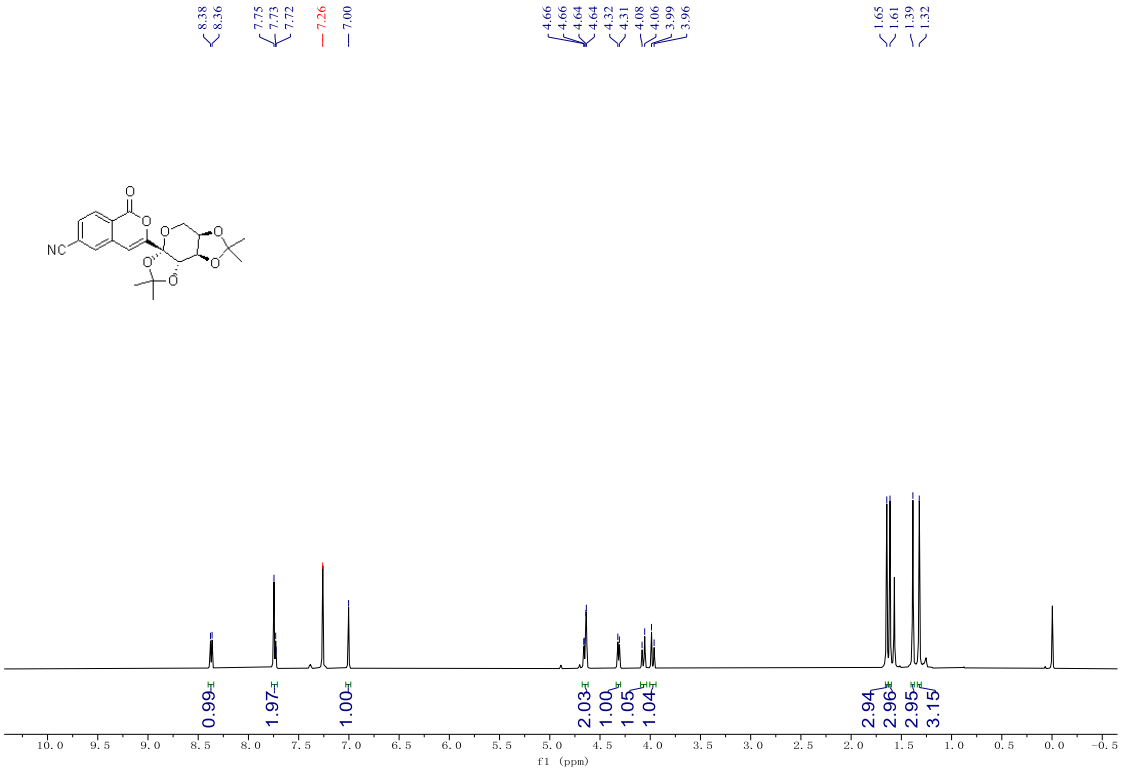
^{1}H NMR (500 MHz, $CDCl_3$) Spectra of compound 1



^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound 1



^{1}H NMR (500 MHz, $CDCl_3$) Spectra of compound 2



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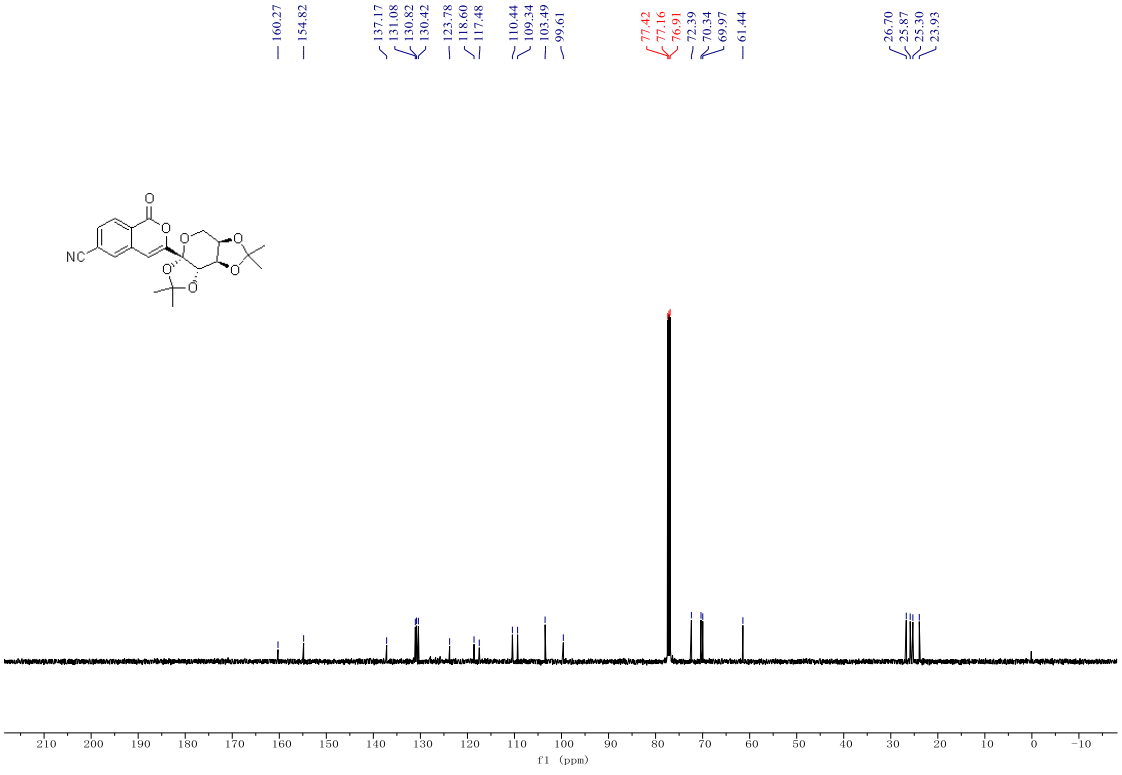
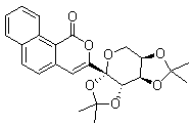
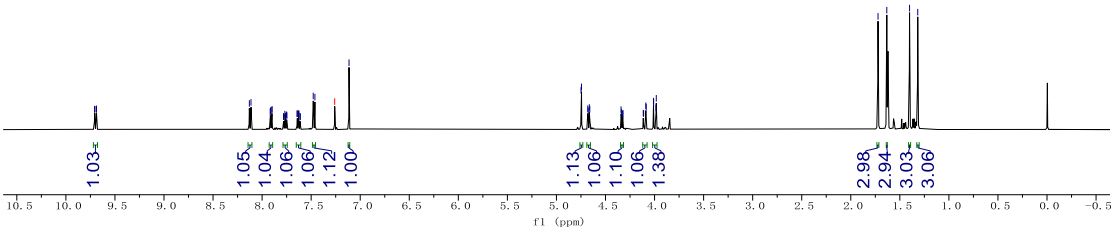
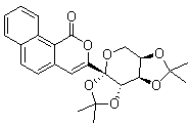


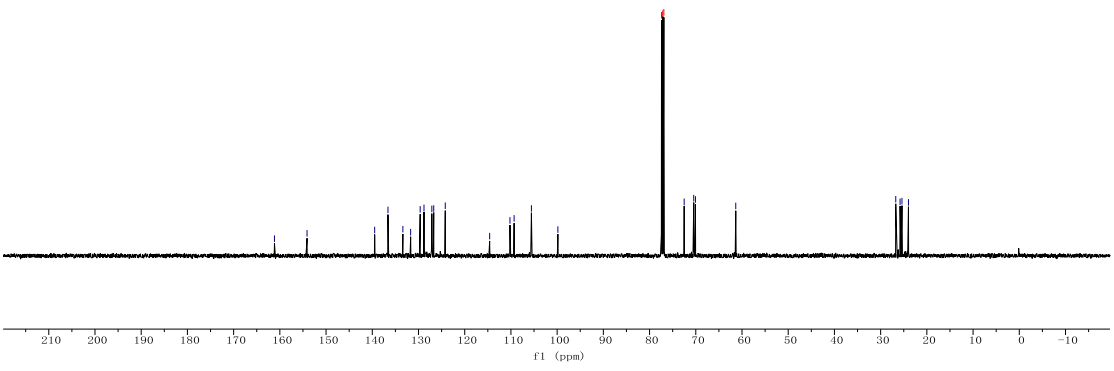
^{1}H NMR (500 MHz, $CDCl_3$) Spectra of compound 3



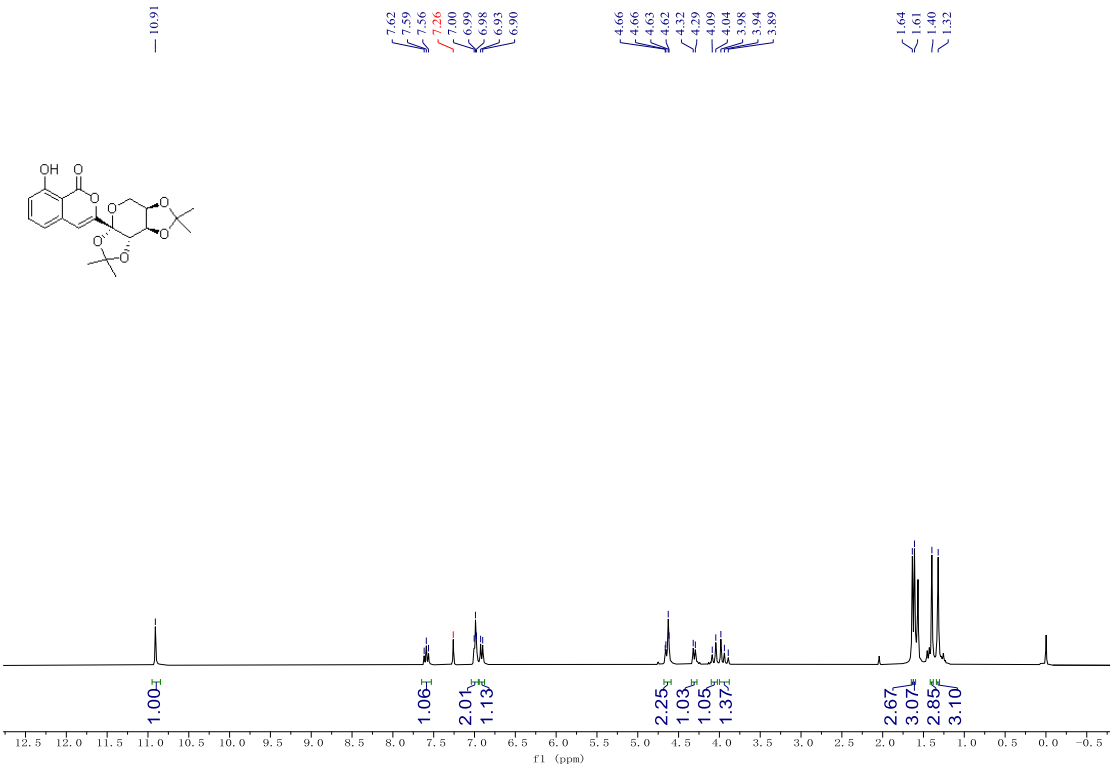


^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound 3

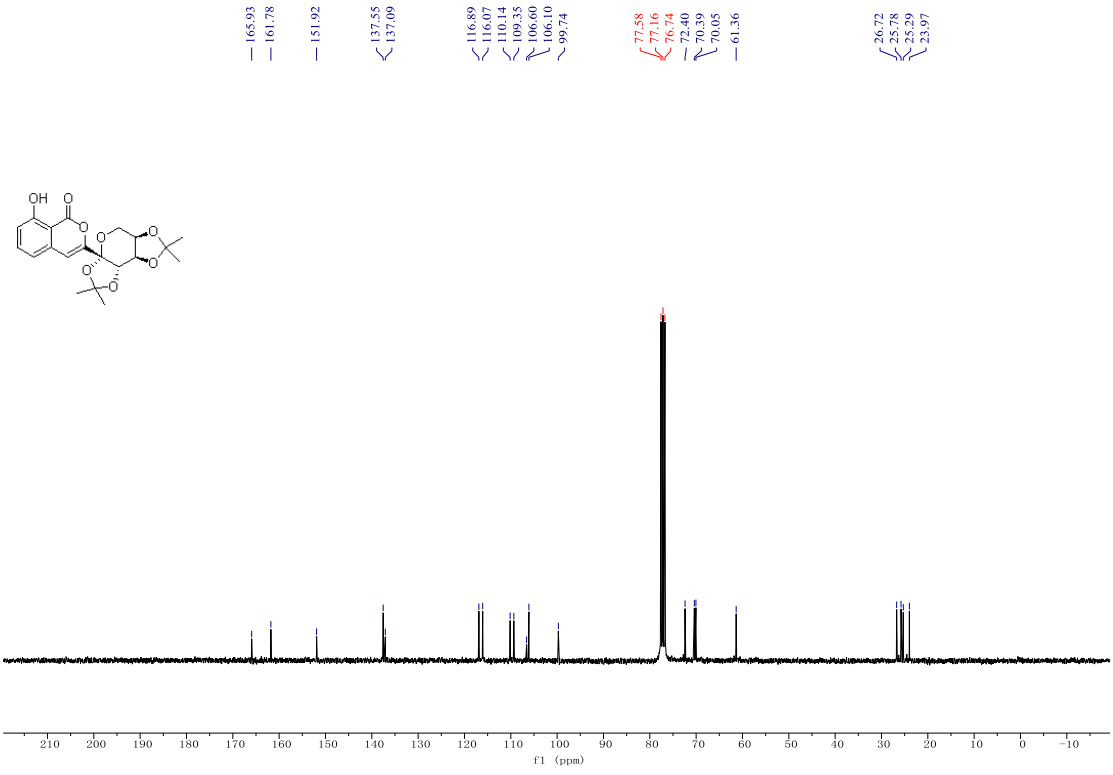




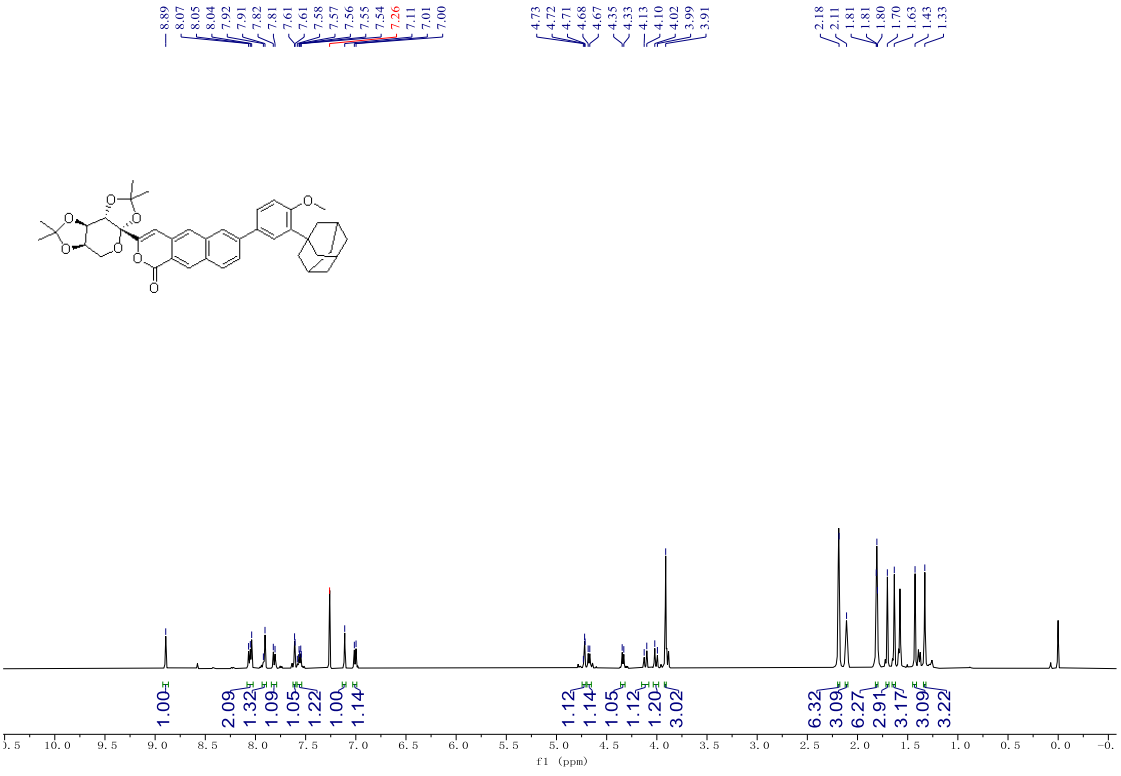
^{1}H NMR (300 MHz, $CDCl_3$) Spectra of compound 4



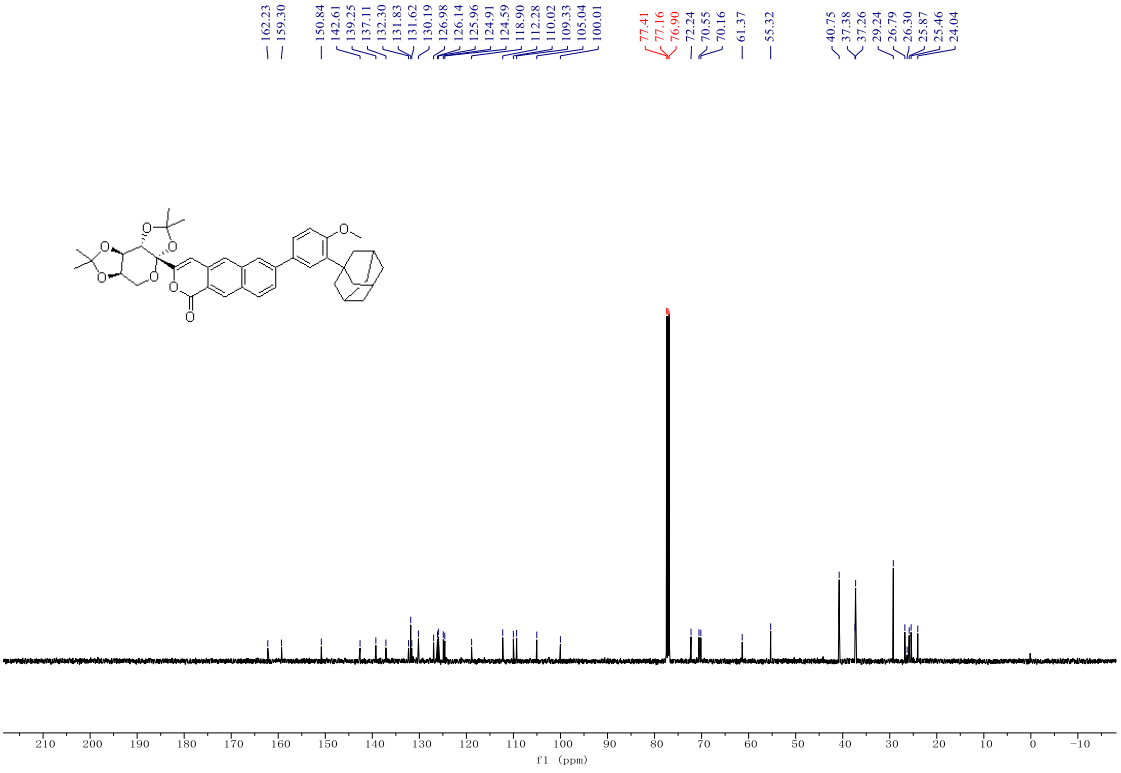
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 4



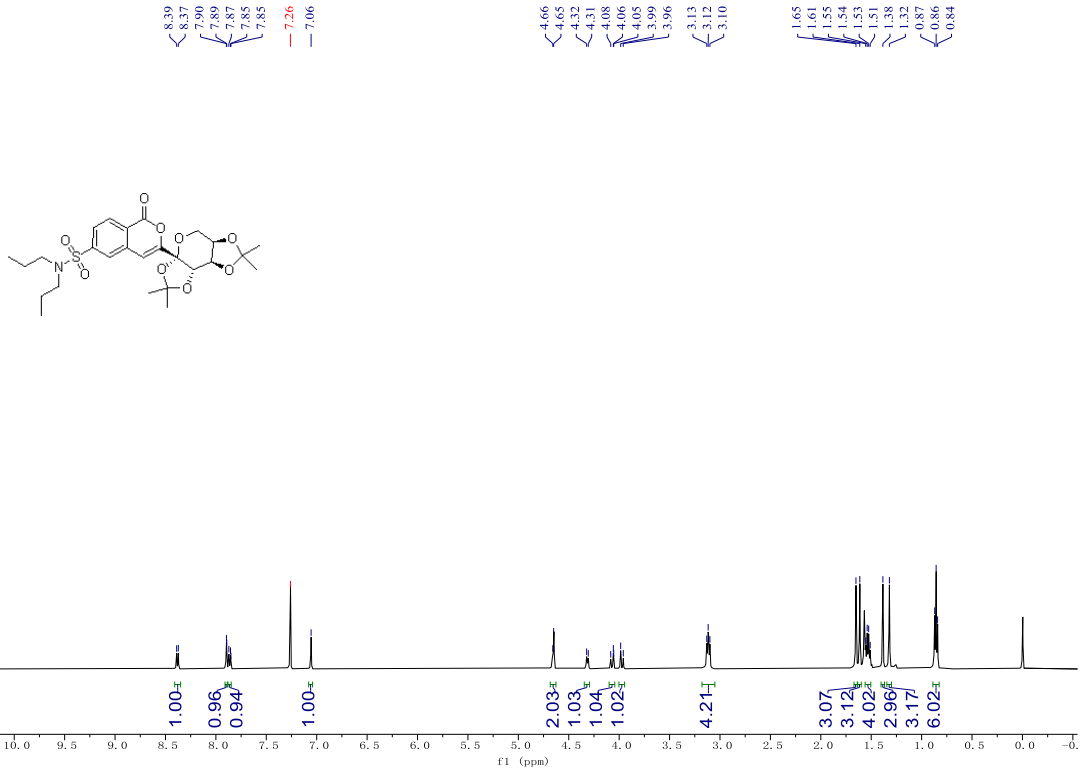
^{1}H NMR (500 MHz, $CDCl_3$) Spectra of compound 5



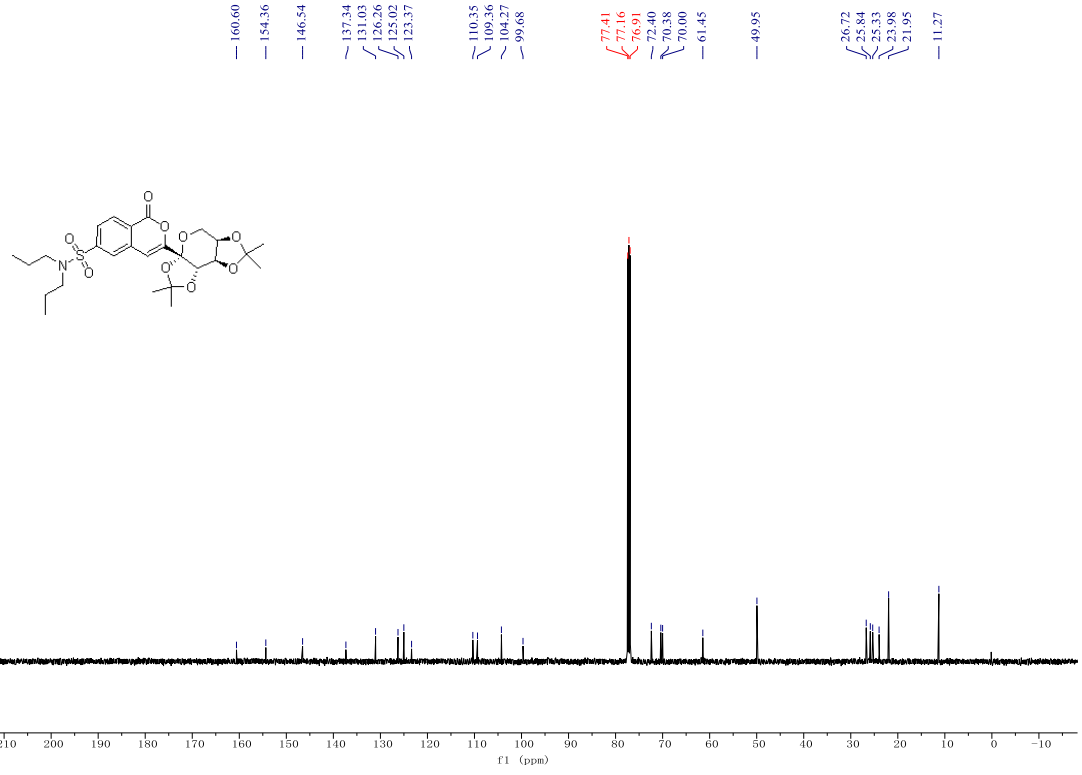
^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound 5



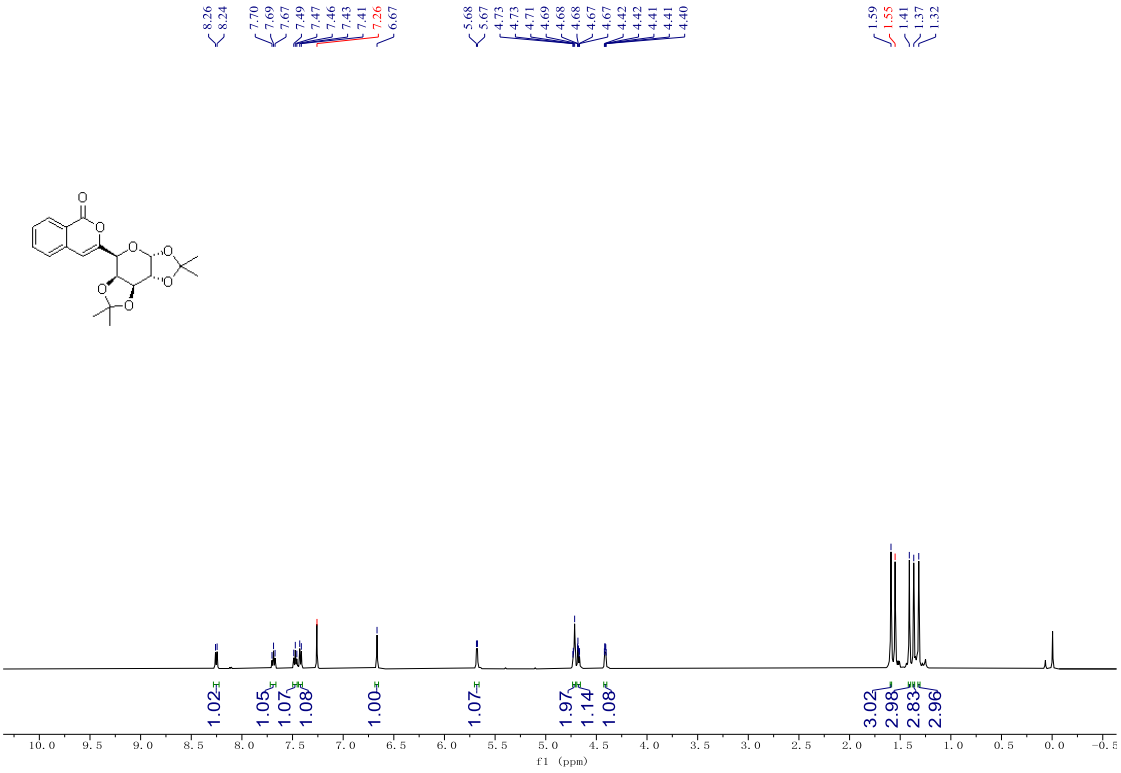
^{1}H NMR (500 MHz, $CDCl_3$) Spectra of compound 6



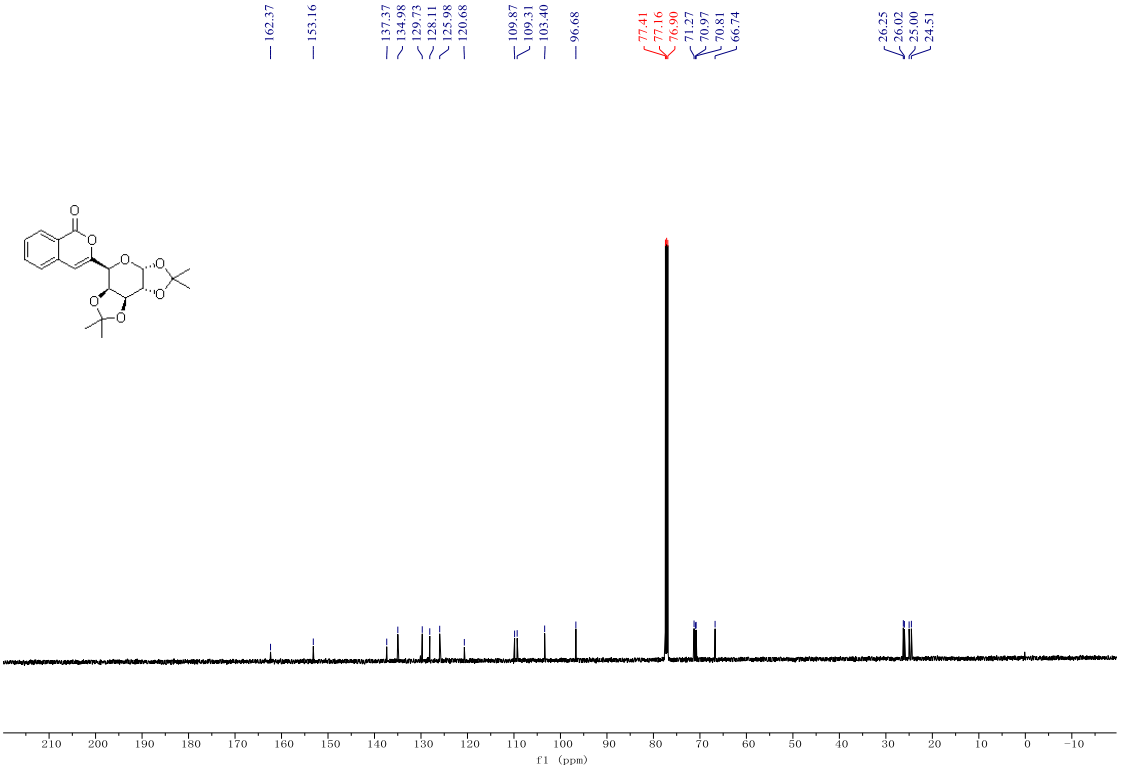
^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound 6



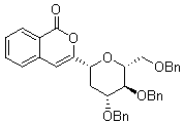
^{1}H NMR (500 MHz, $CDCl_3$) Spectra of compound 7

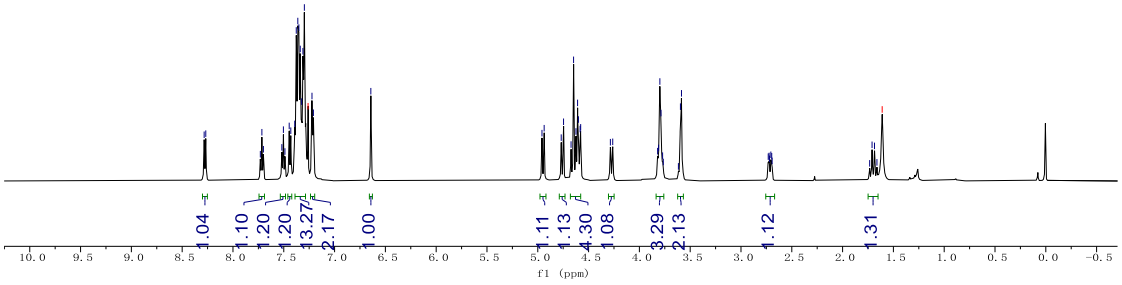


^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound 7

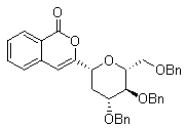


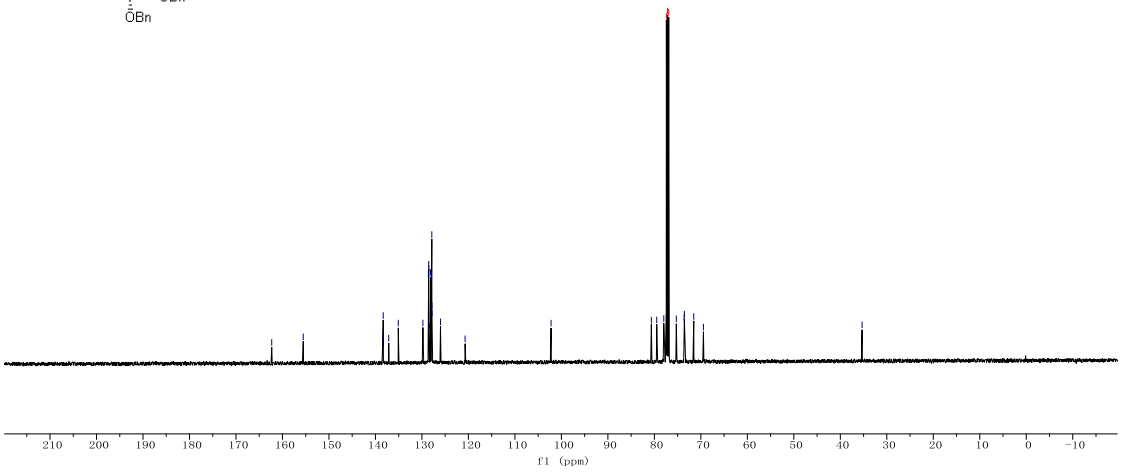
^{1}H NMR (500 MHz, $CDCl_3$) Spectra of compound 8



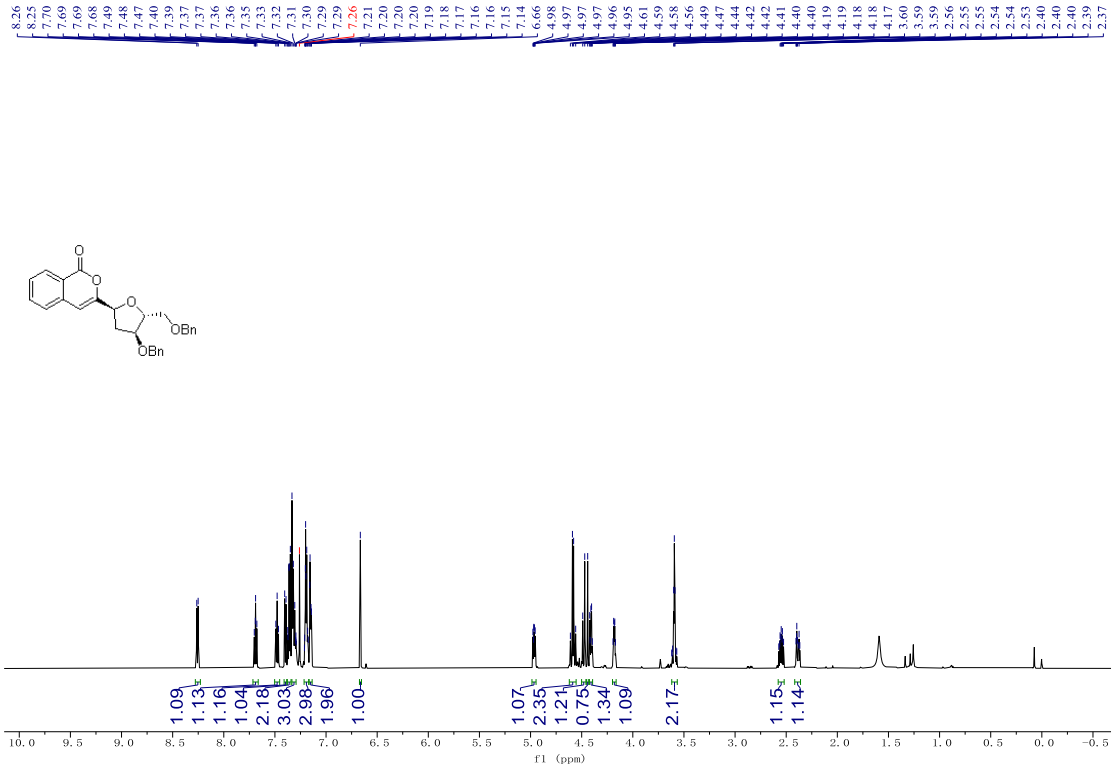


^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound 8

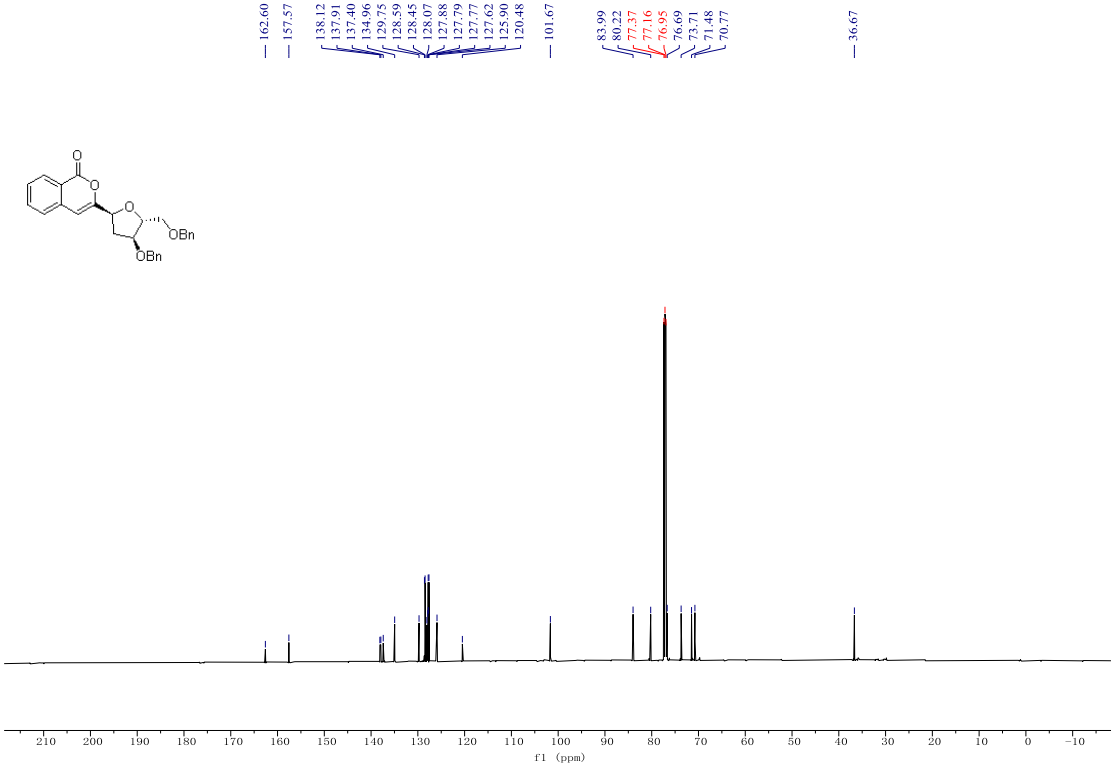




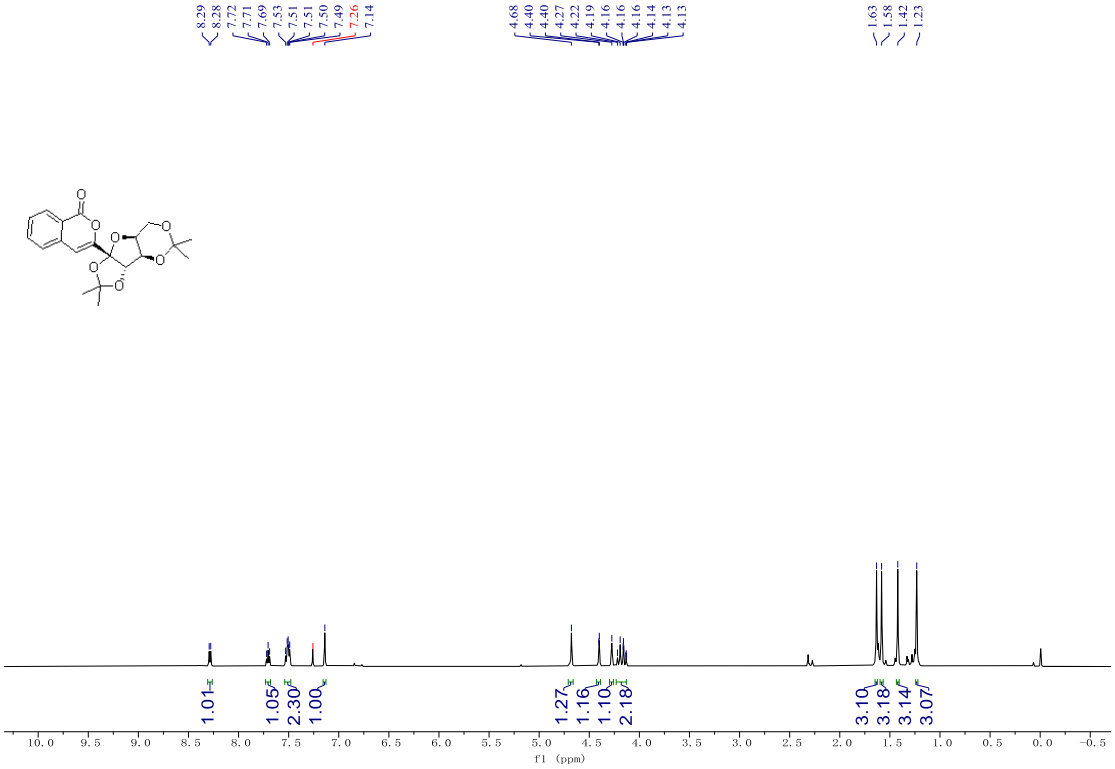
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of compound 9



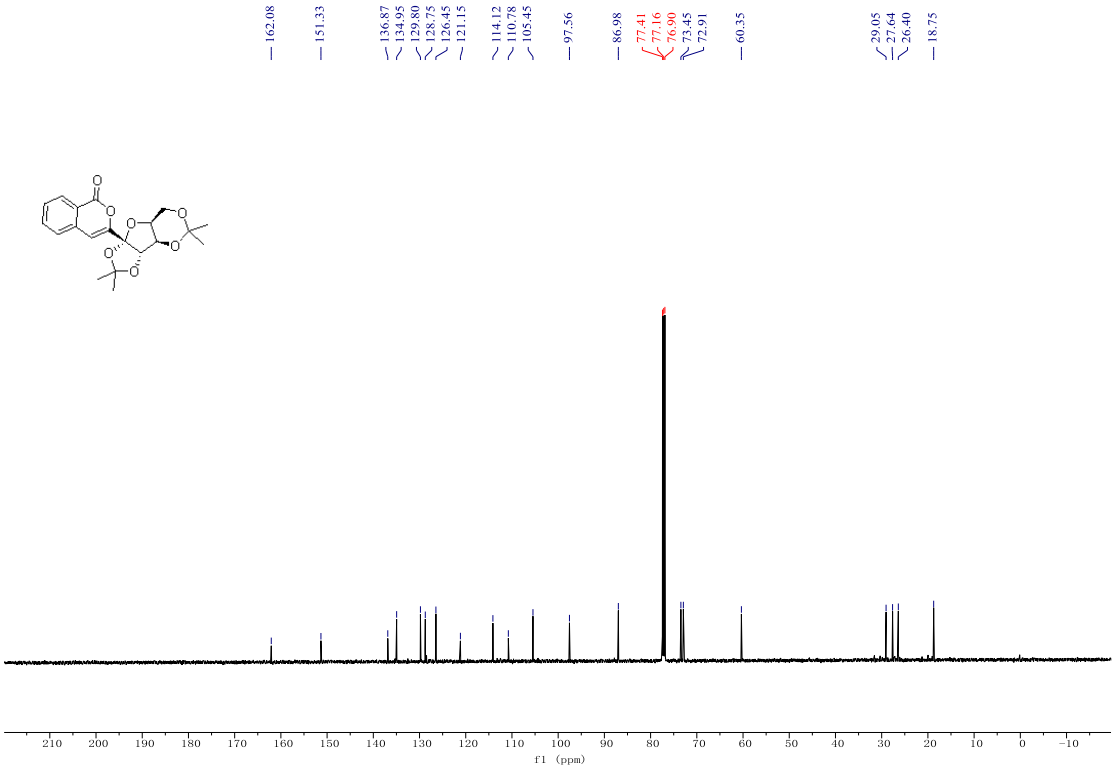
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of compound 9



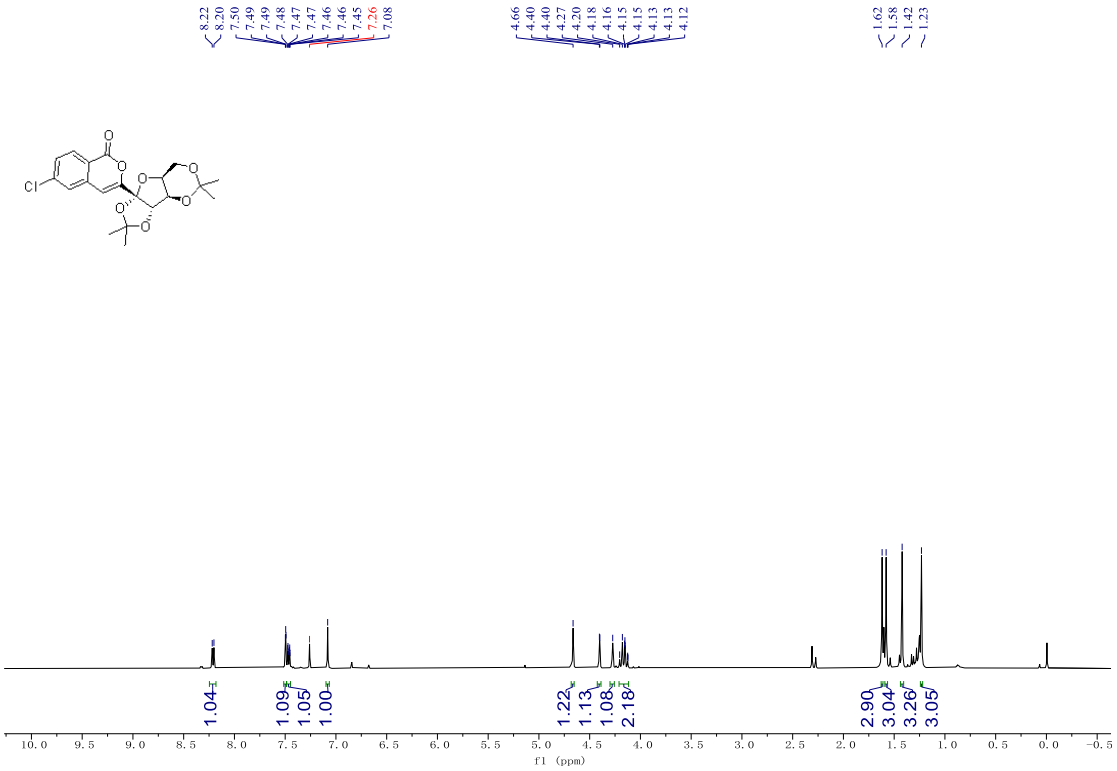
^{1}H NMR (500 MHz, $CDCl_3$) Spectra of compound 10



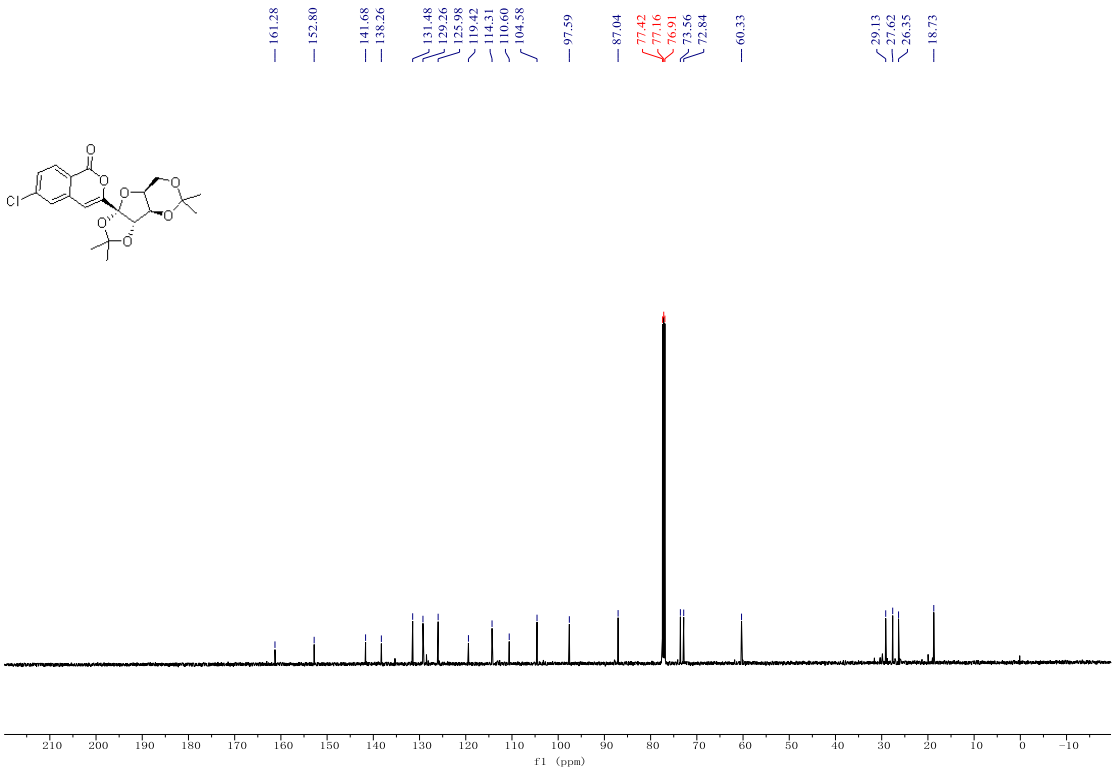
^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound 10



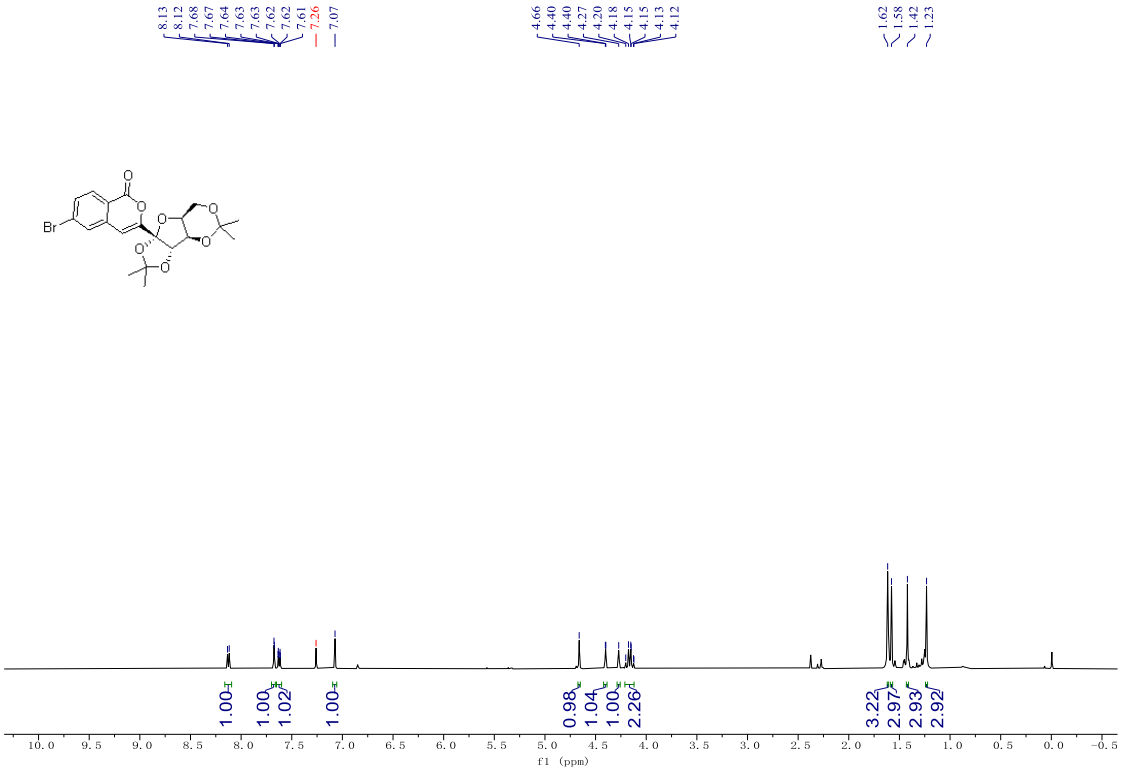
^{1}H NMR (500 MHz, $CDCl_3$) Spectra of compound 11



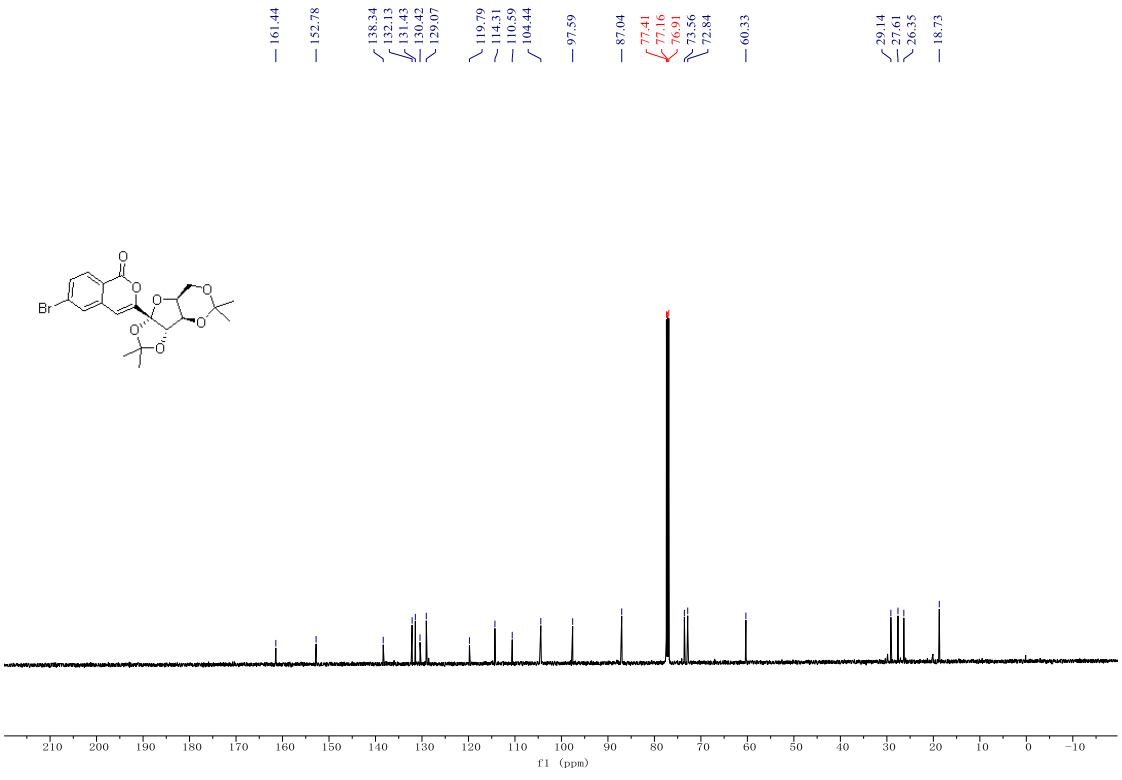
^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound 11



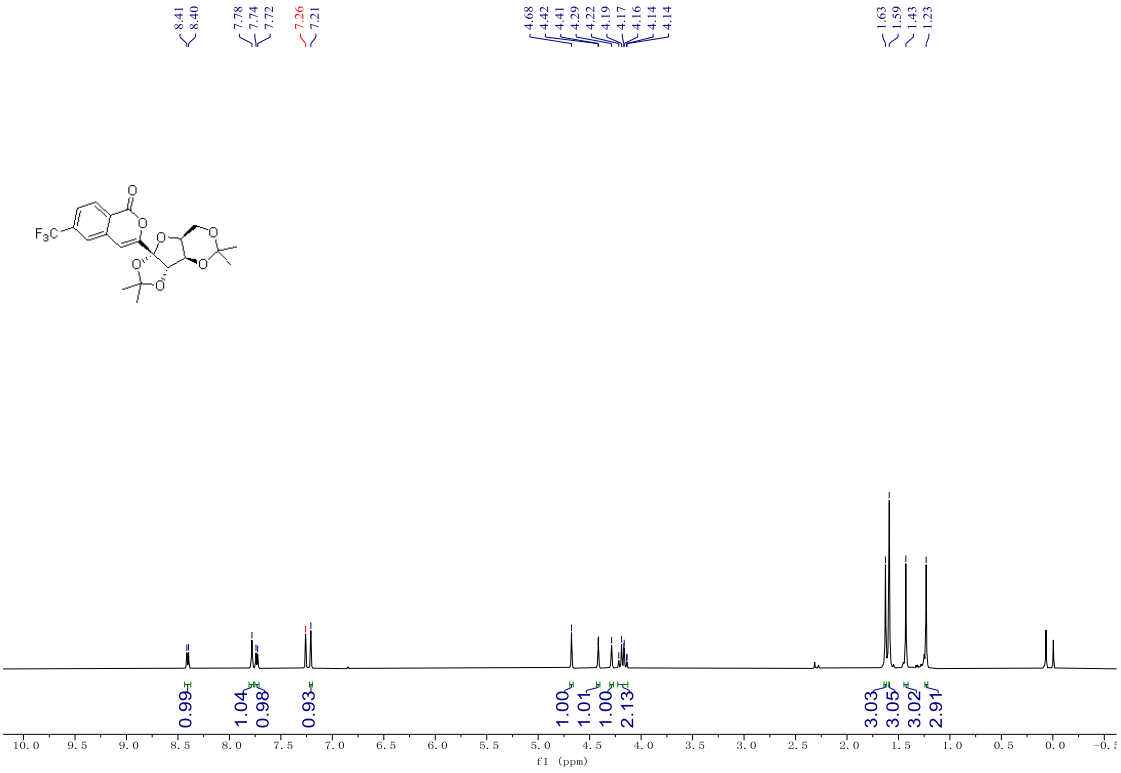
^{1}H NMR (500 MHz, $CDCl_3$) Spectra of compound 12



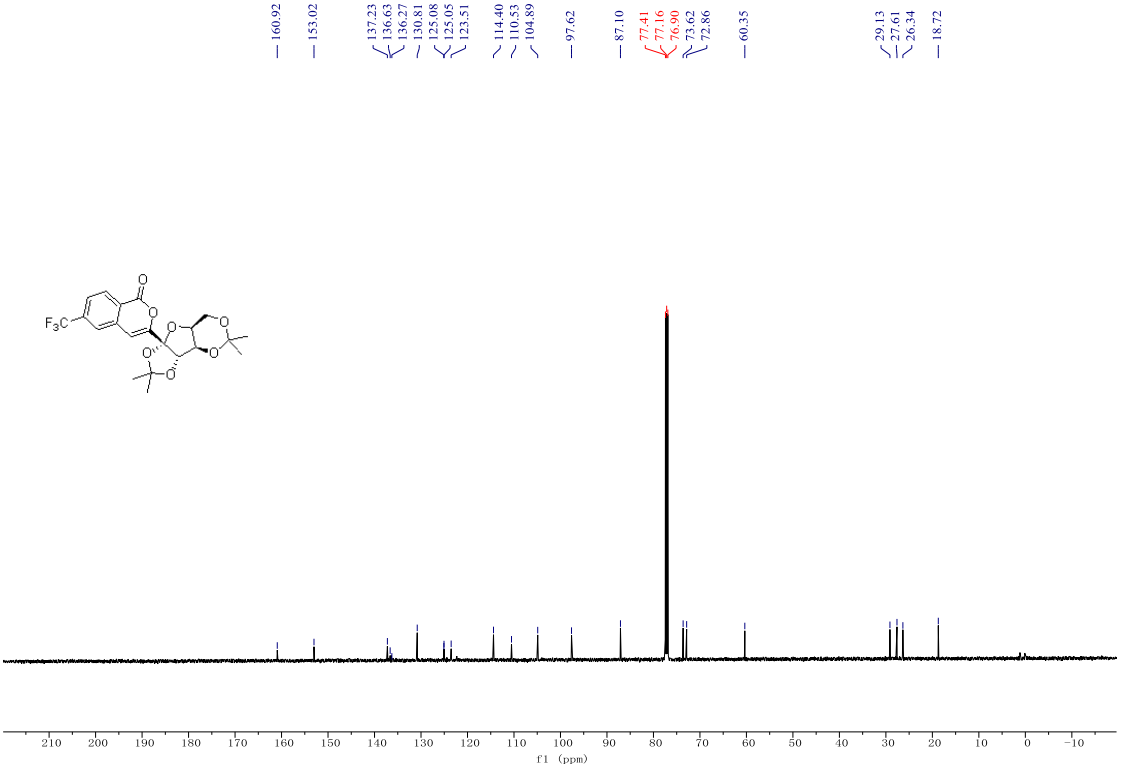
^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound 12



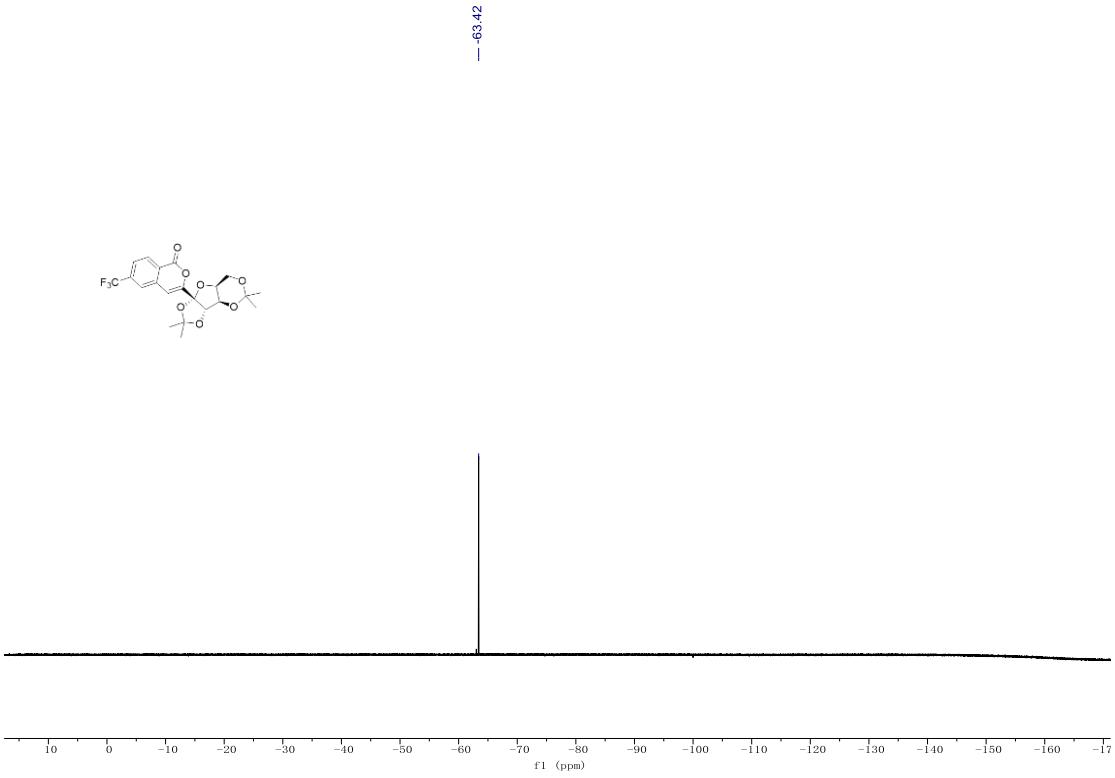
^{1}H NMR (500 MHz, $CDCl_3$) Spectra of compound 13



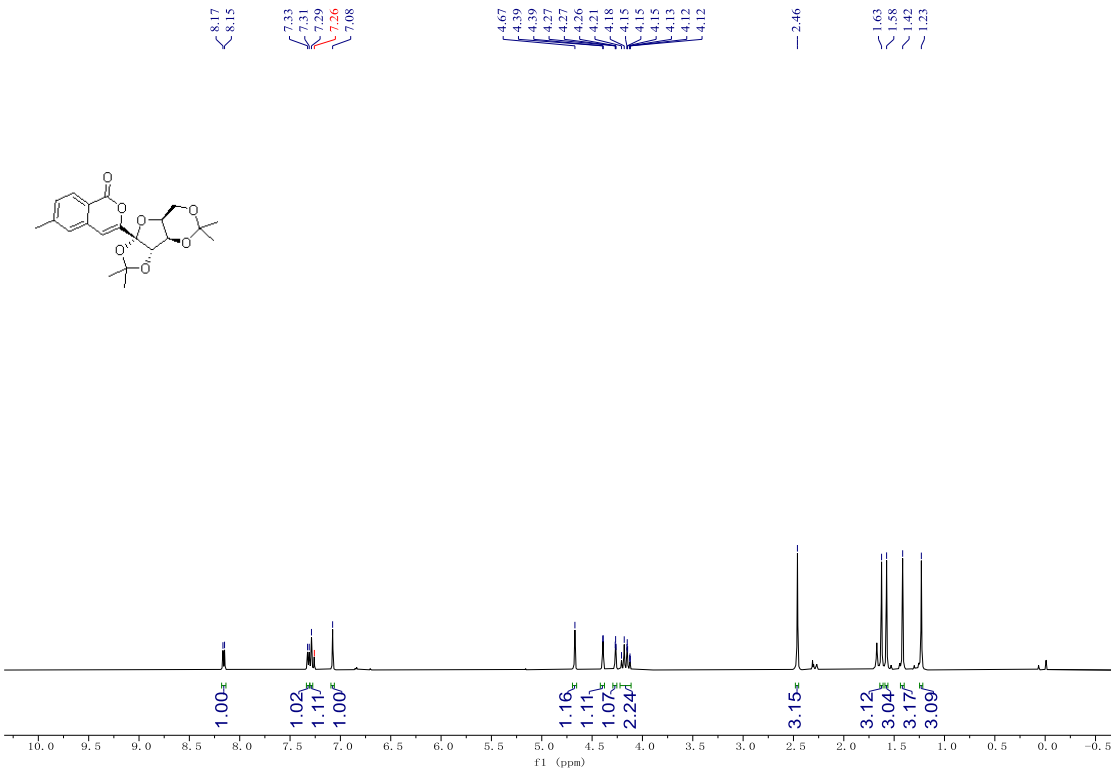
^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound 13



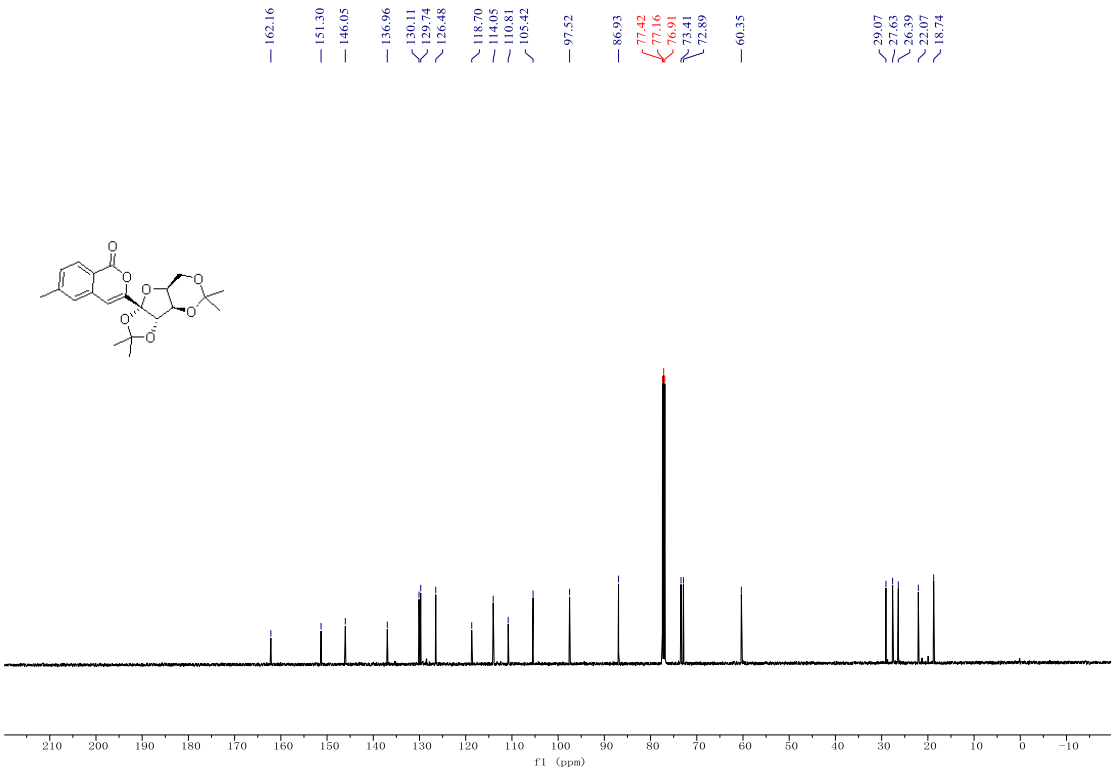
^{19}F NMR (376 MHz, $CDCl_3$) Spectra of compound 13



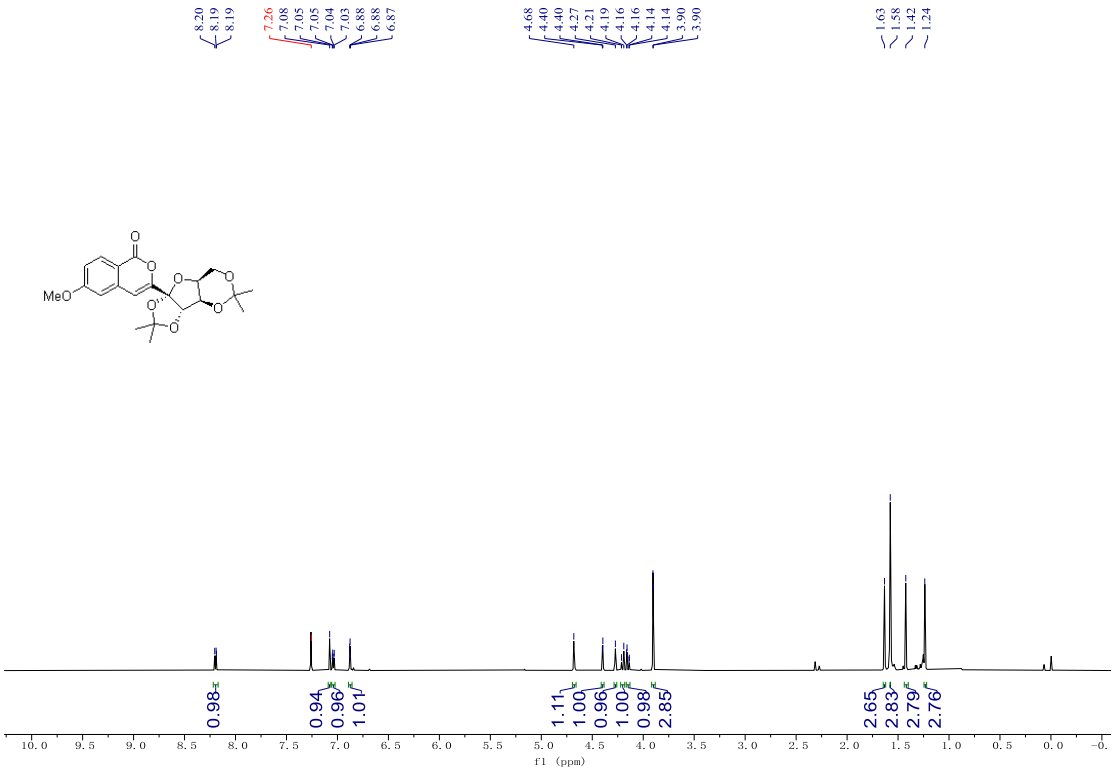
^{1}H NMR (500 MHz, $CDCl_3$) Spectra of compound 14



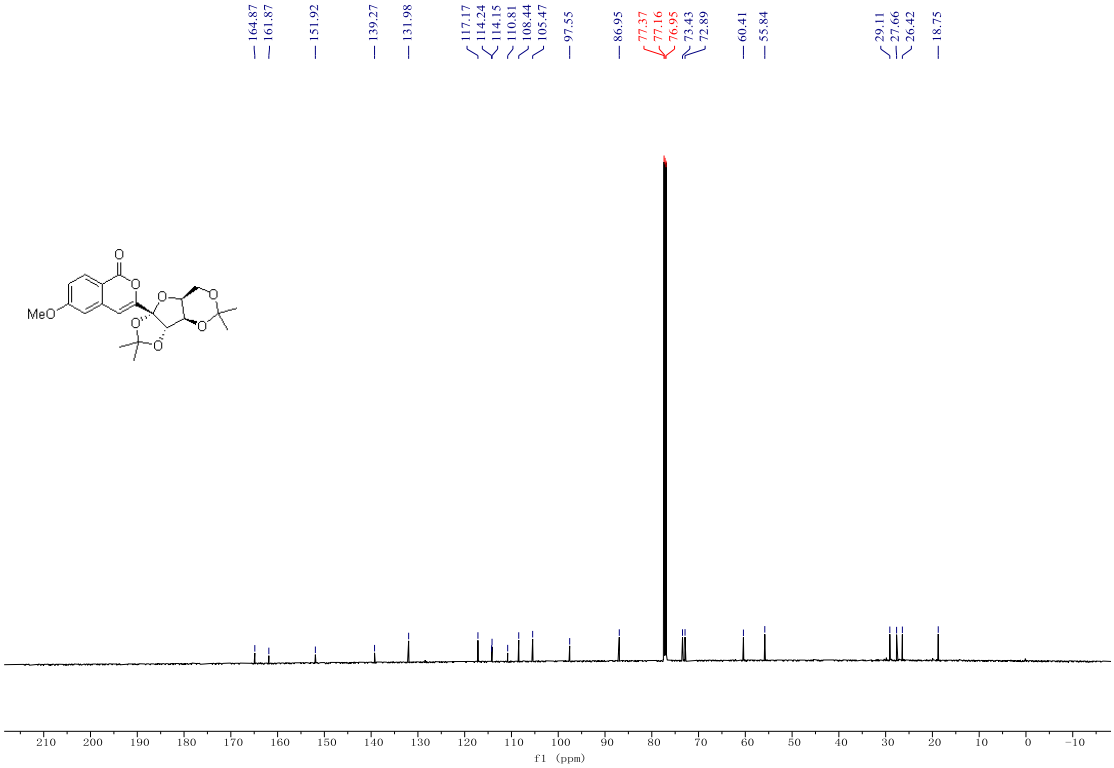
^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound 14



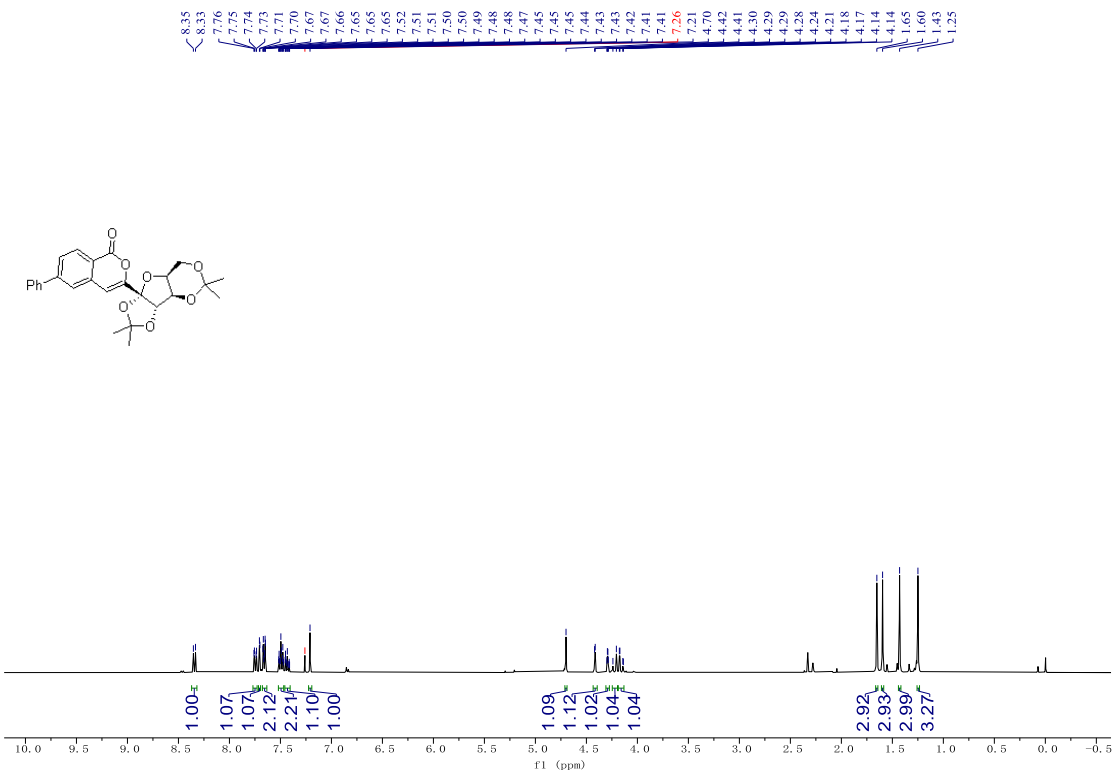
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of compound 15



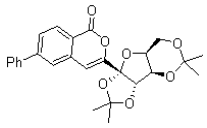
^{13}C NMR (151 MHz, $CDCl_3$) Spectra of compound 15



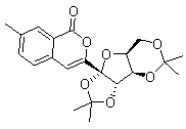
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 16



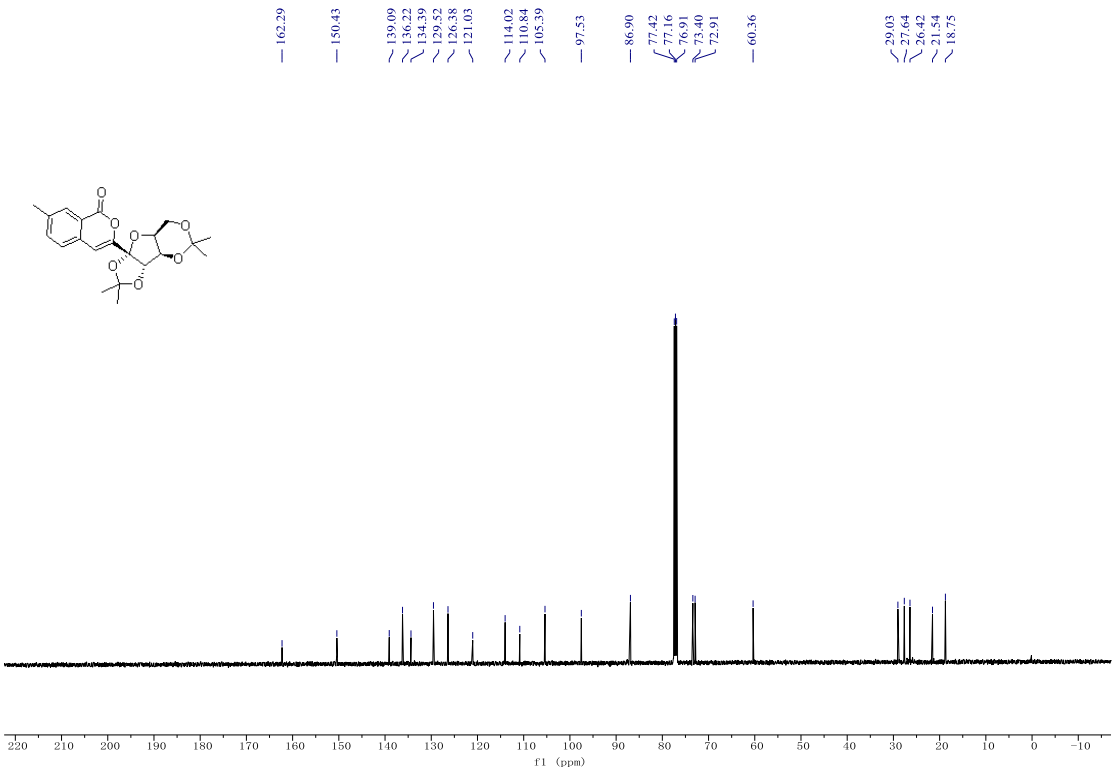
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 16



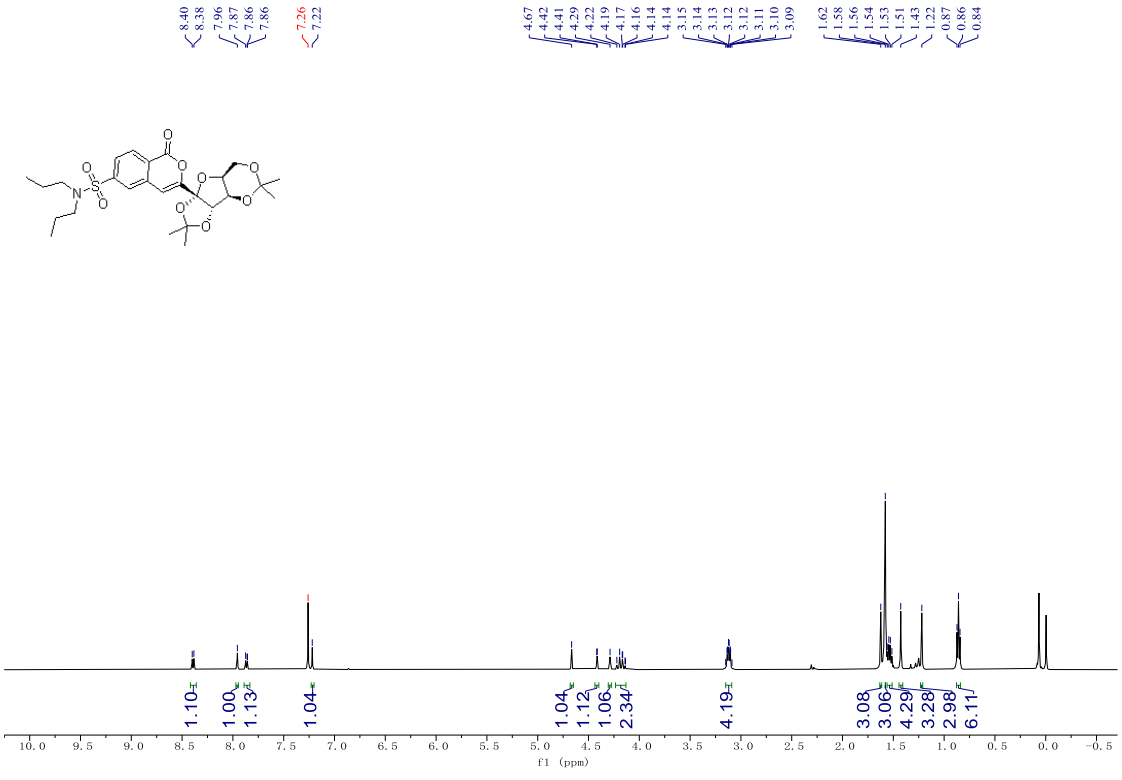
^{1}H NMR (500 MHz, $CDCl_3$) Spectra of compound 17



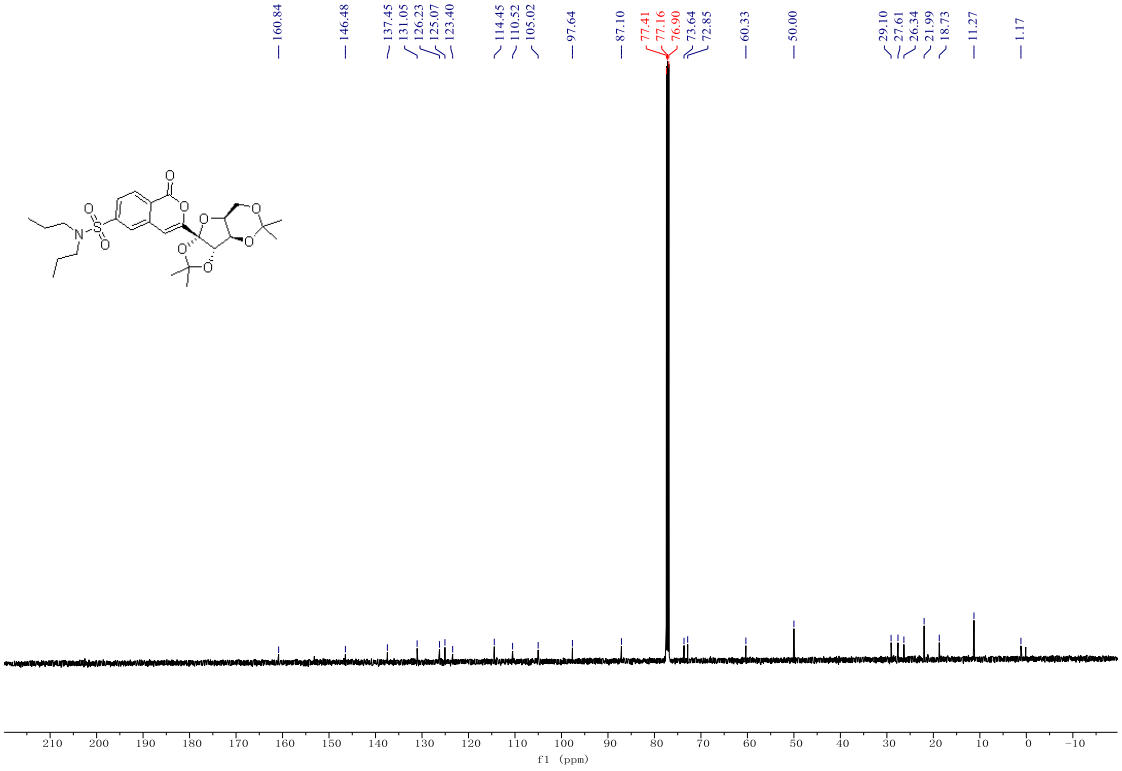
^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound 17



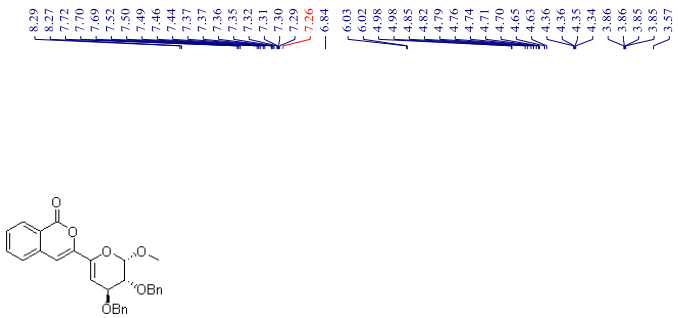
^{1}H NMR (500 MHz, $CDCl_3$) Spectra of compound 18

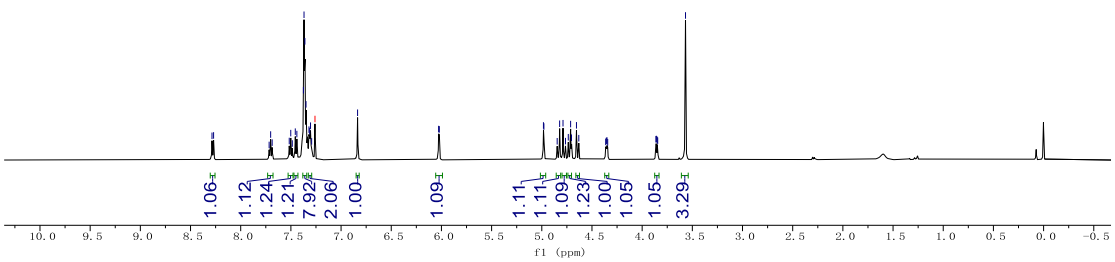


^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound 18

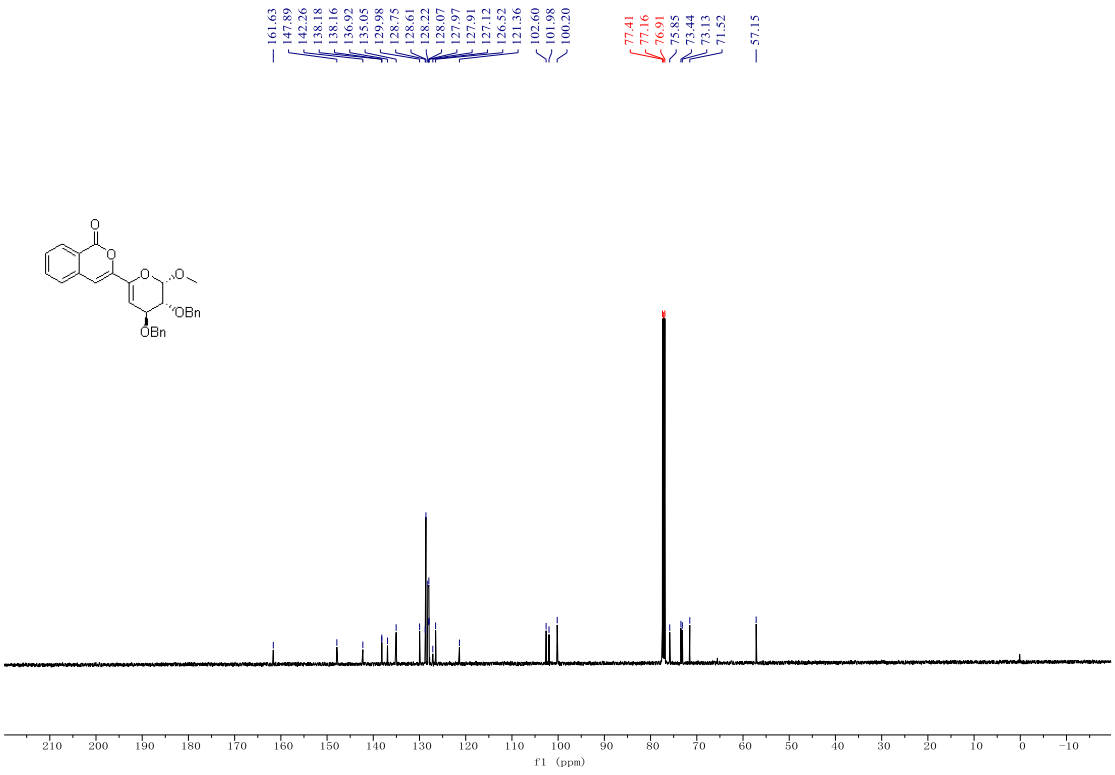


^{1}H NMR (500 MHz, $CDCl_3$) Spectra of compound 19

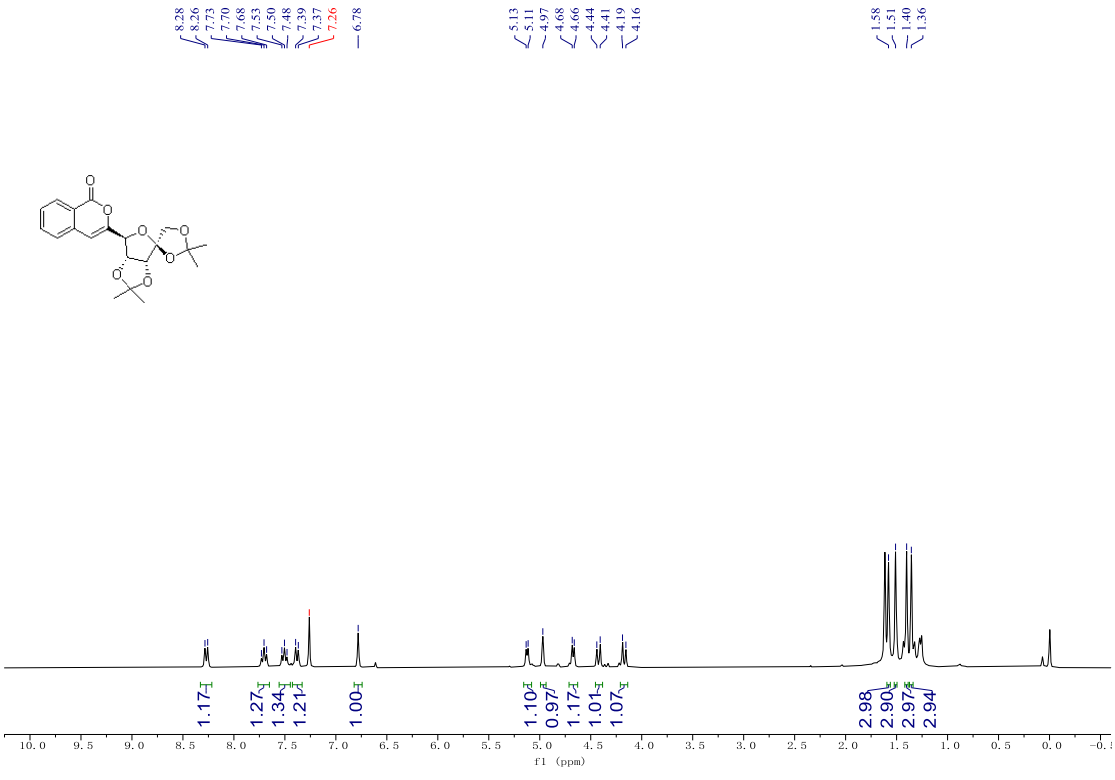




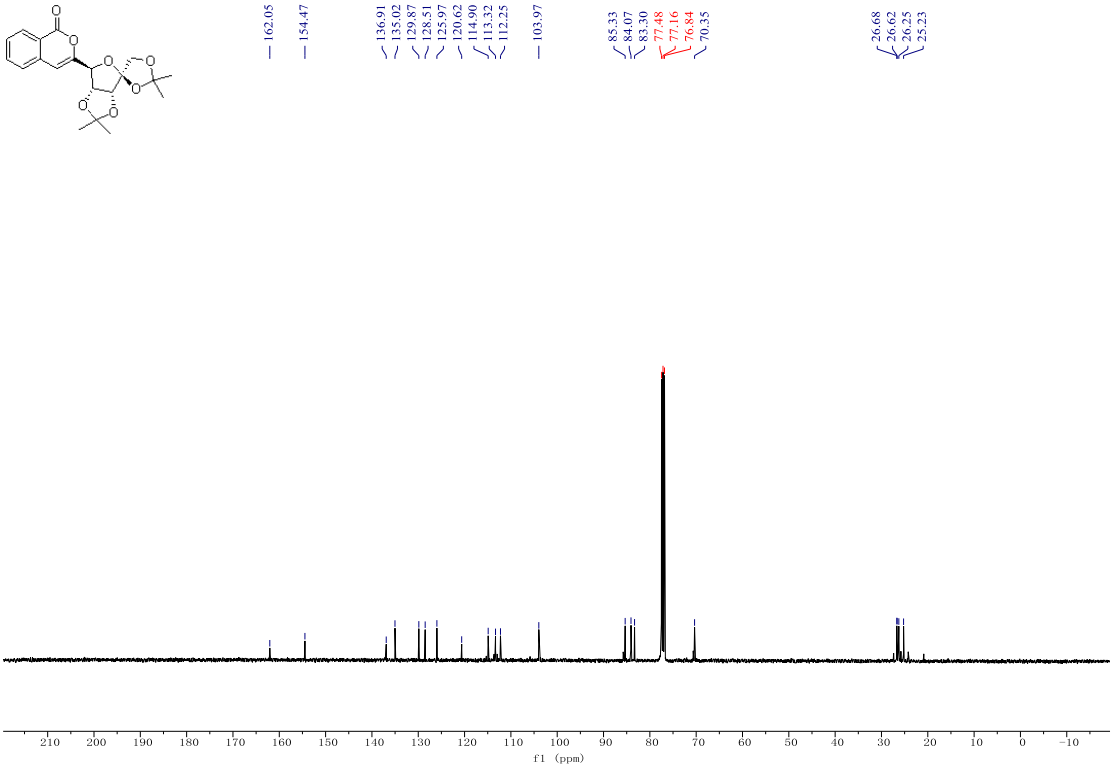
^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound 19



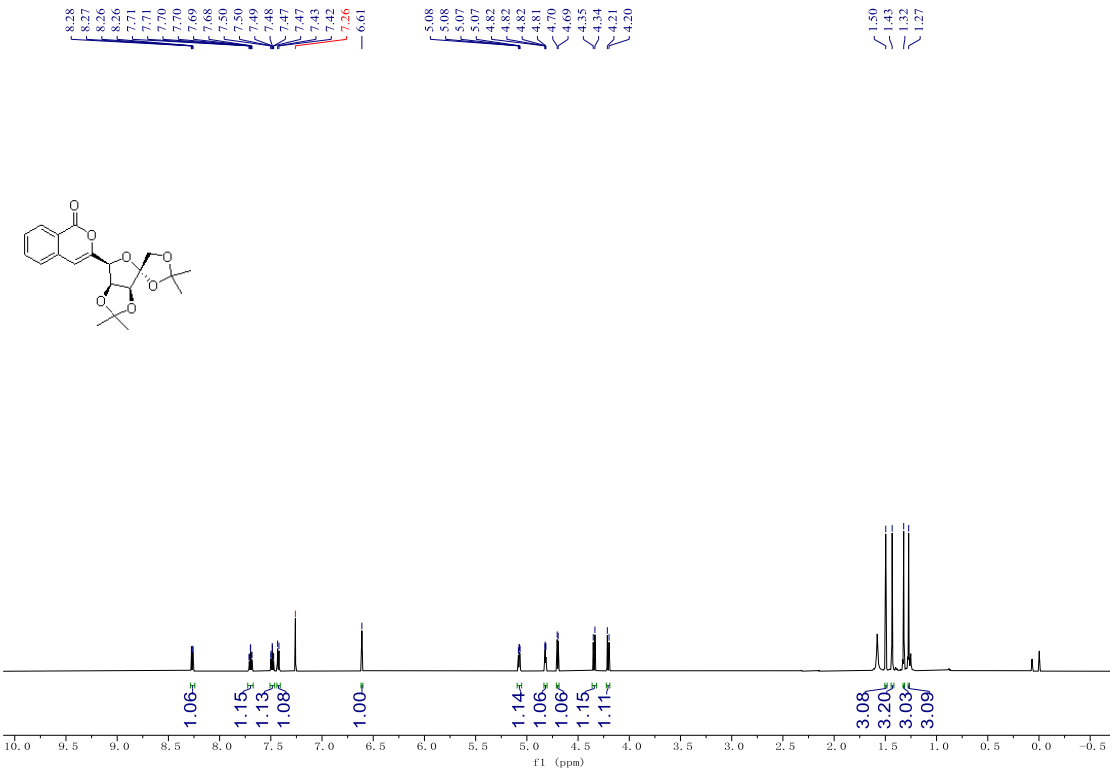
^{1}H NMR (300 MHz, $CDCl_3$) Spectra of compound 20



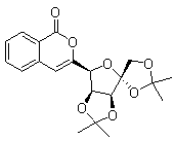
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of compound 20



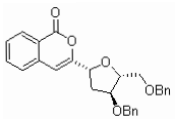
^{1}H NMR (600 MHz, $CDCl_3$) Spectra of compound 21

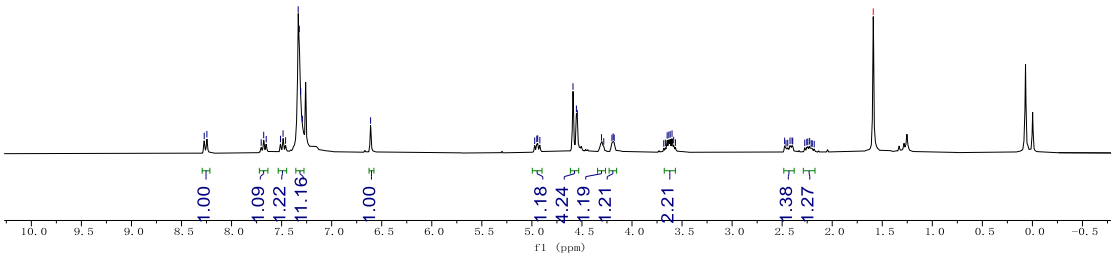


^{13}C NMR (151 MHz, $CDCl_3$) Spectra of compound 21

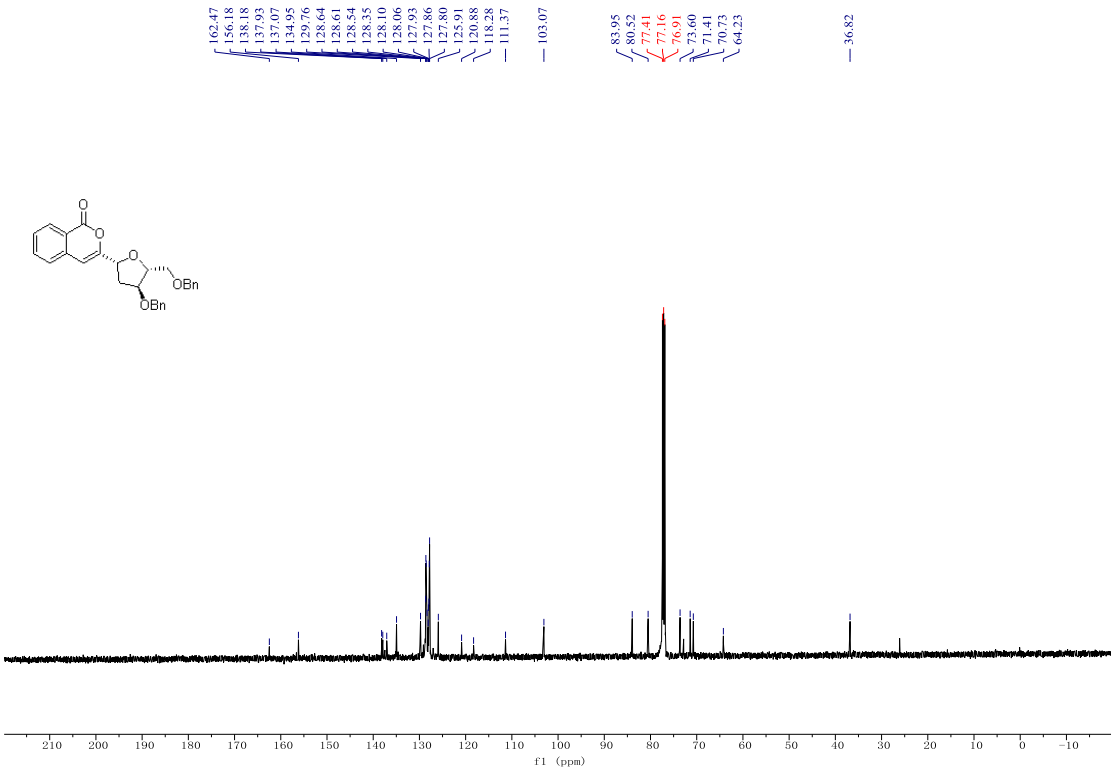


^{1}H NMR (300 MHz, $CDCl_3$) Spectra of compound 22

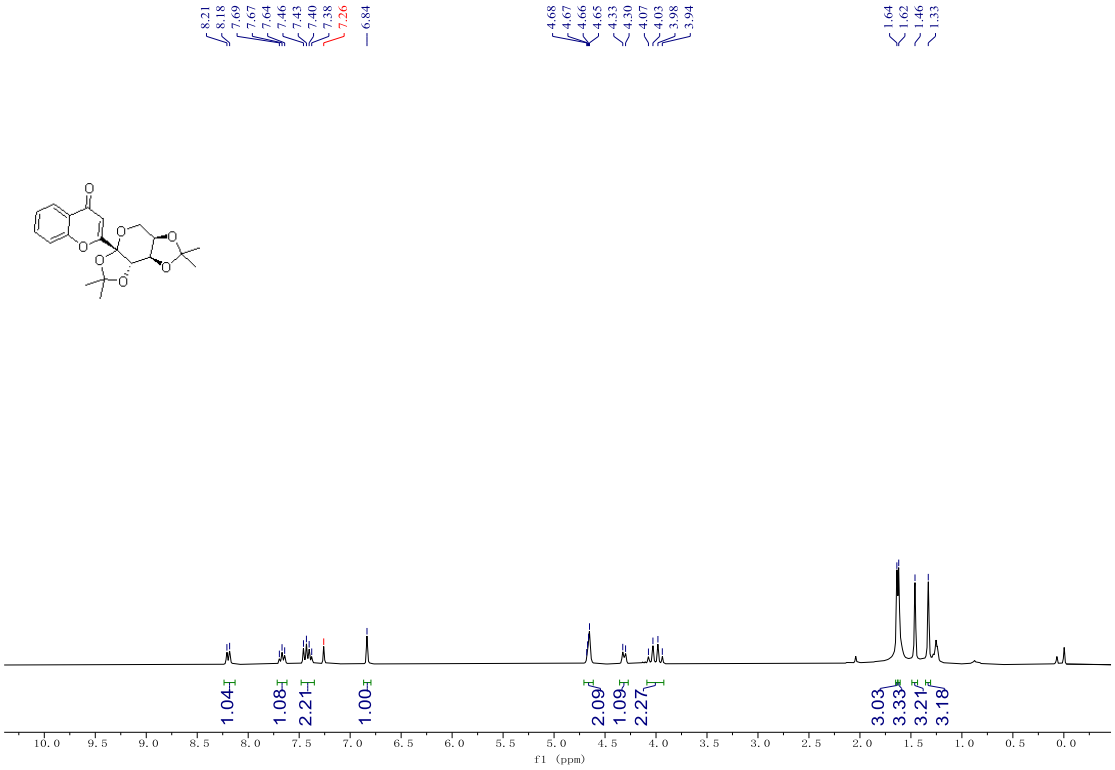




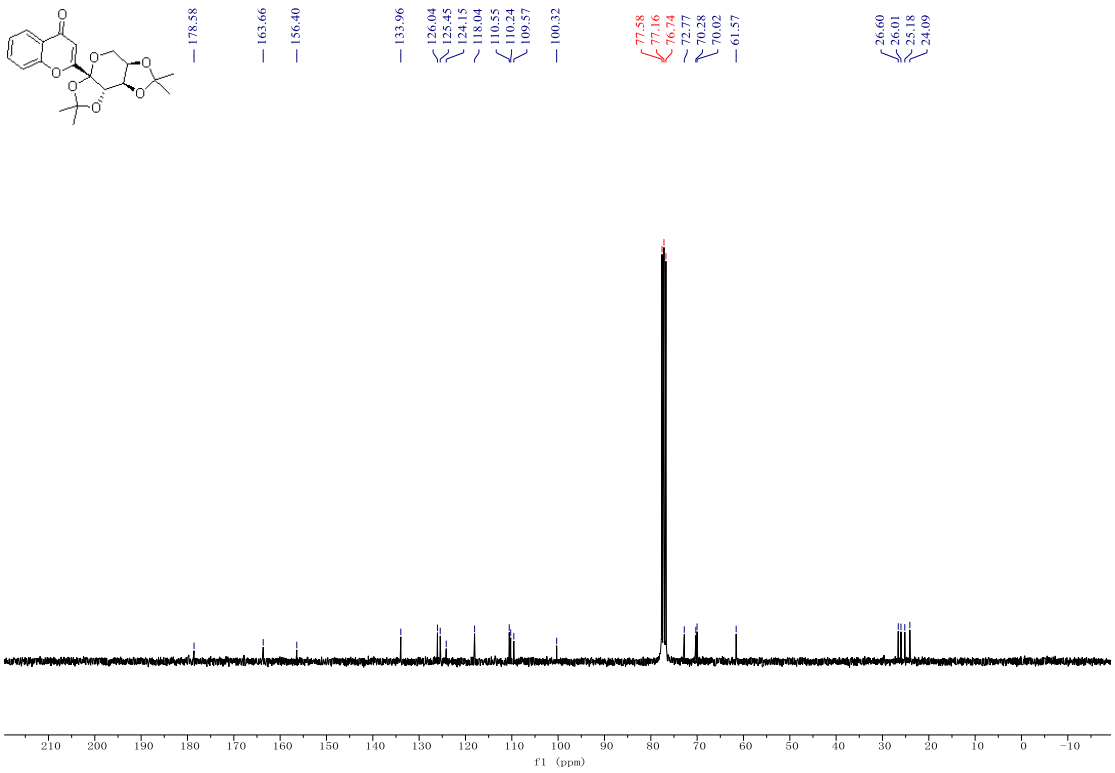
^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound 22



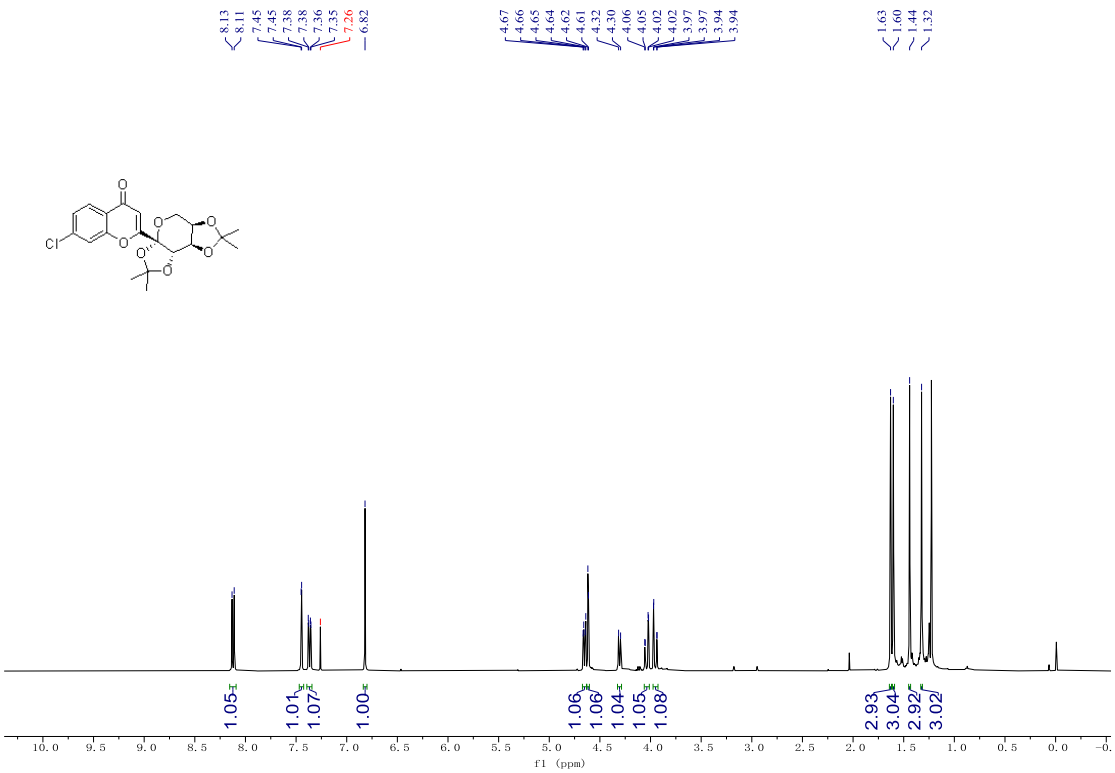
^{1}H NMR (300 MHz, $CDCl_3$) Spectra of compound 23



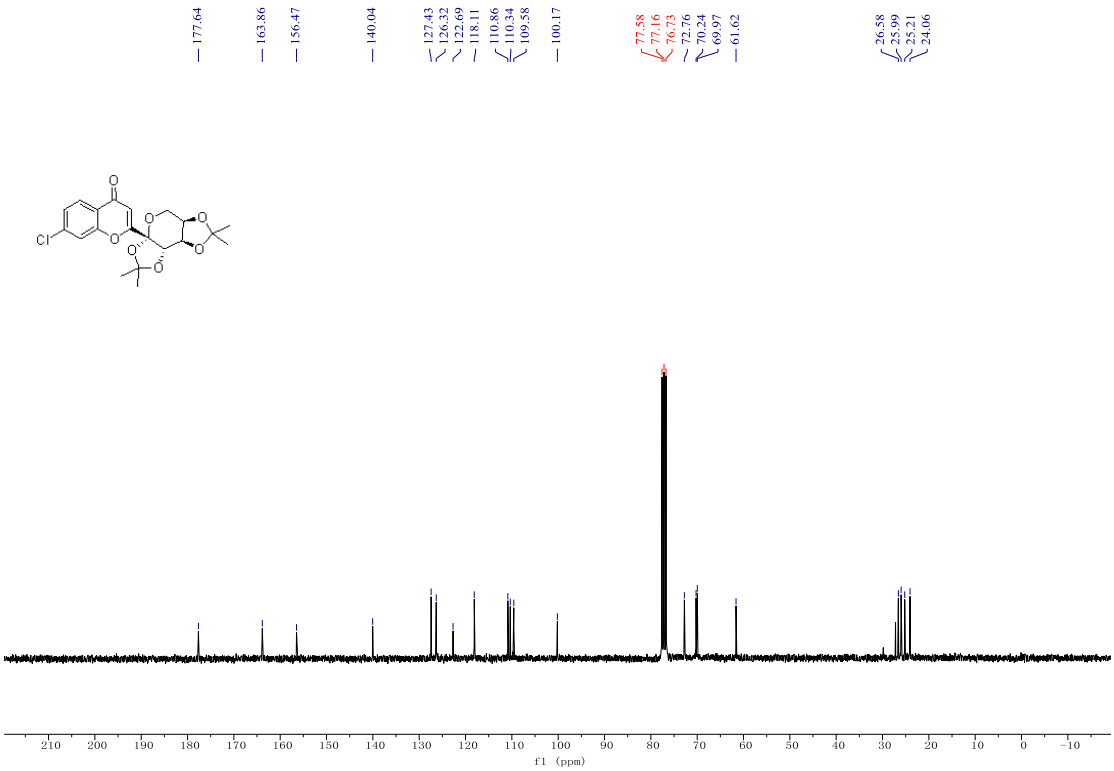
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 23



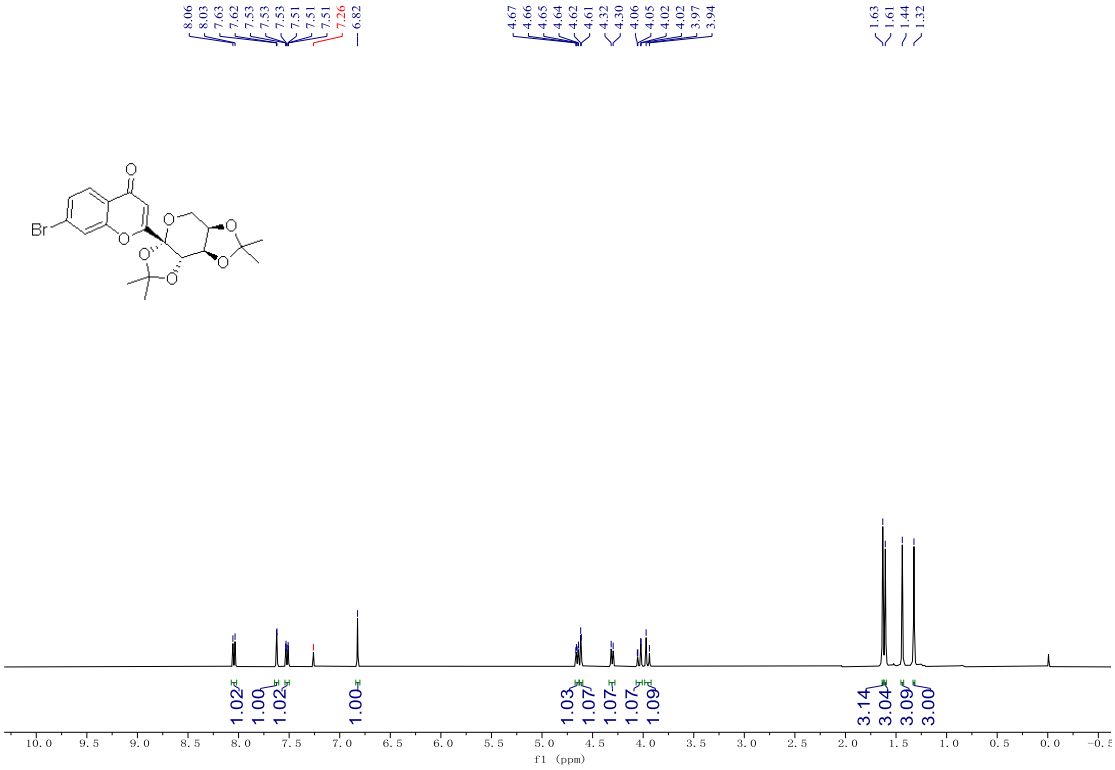
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 24



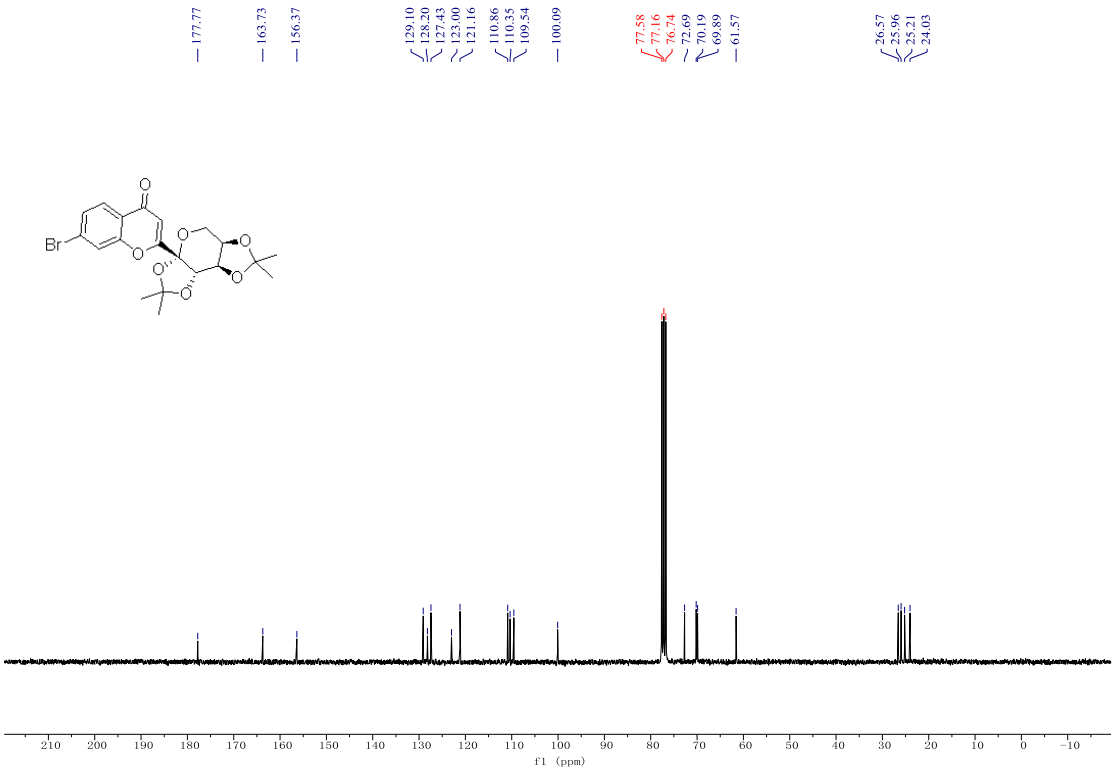
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 24



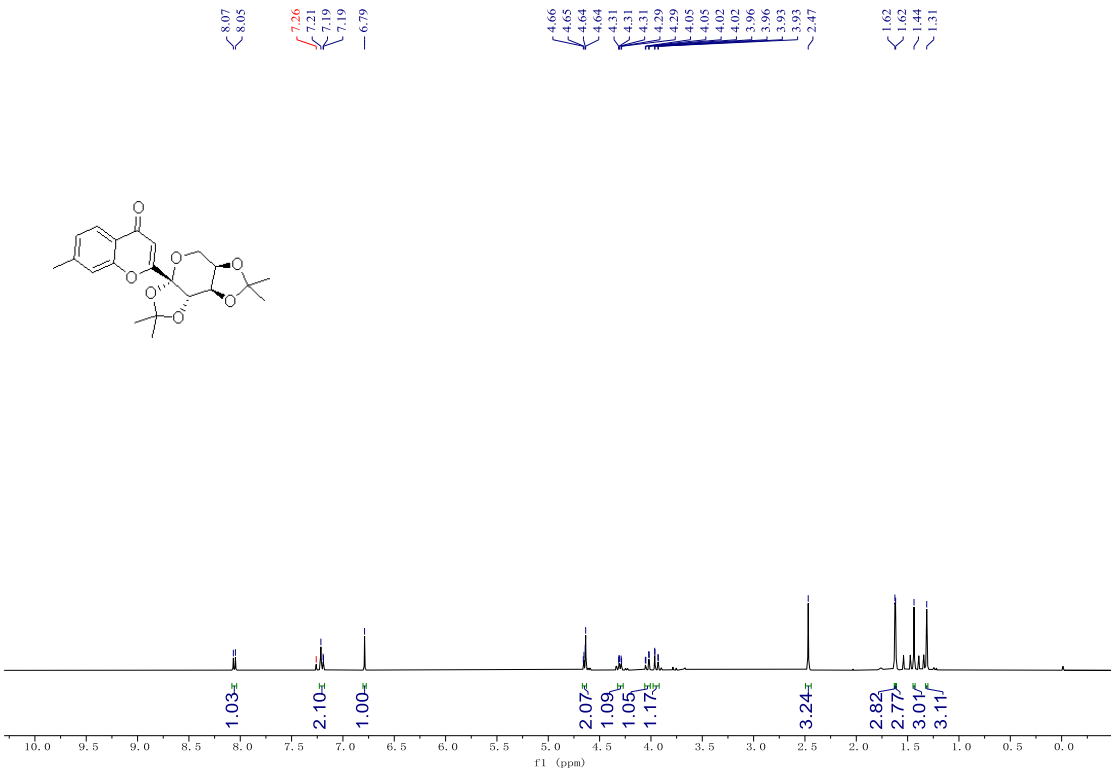
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 25



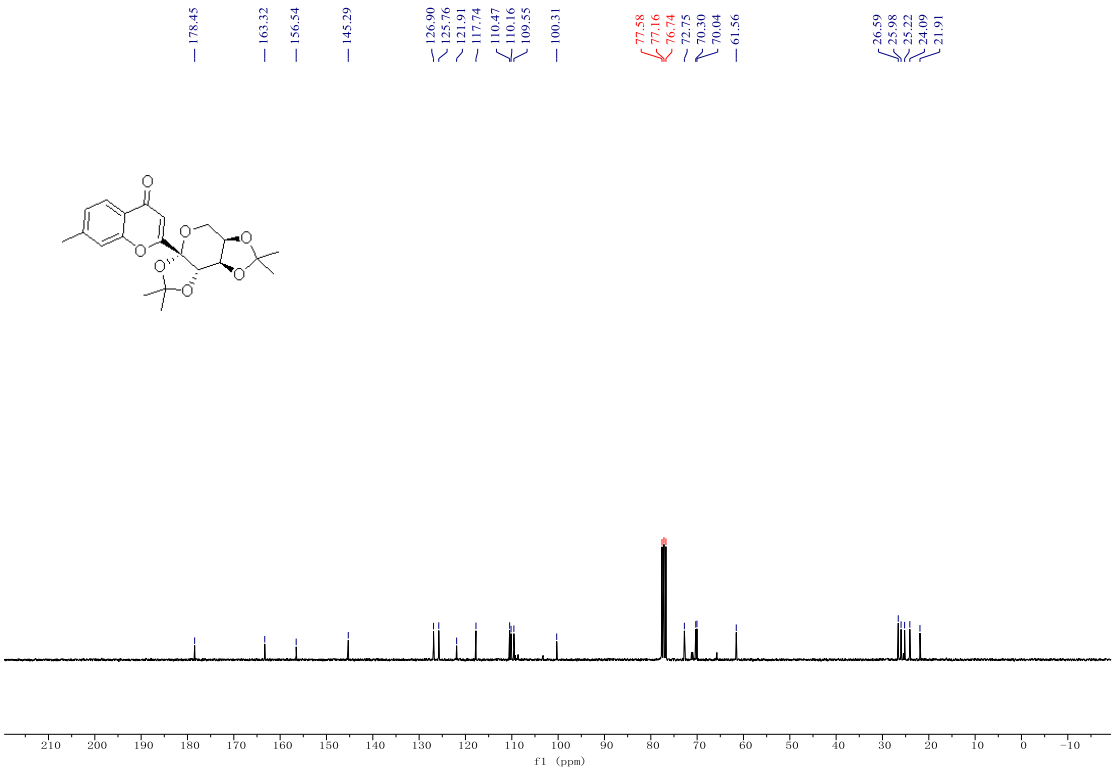
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 25



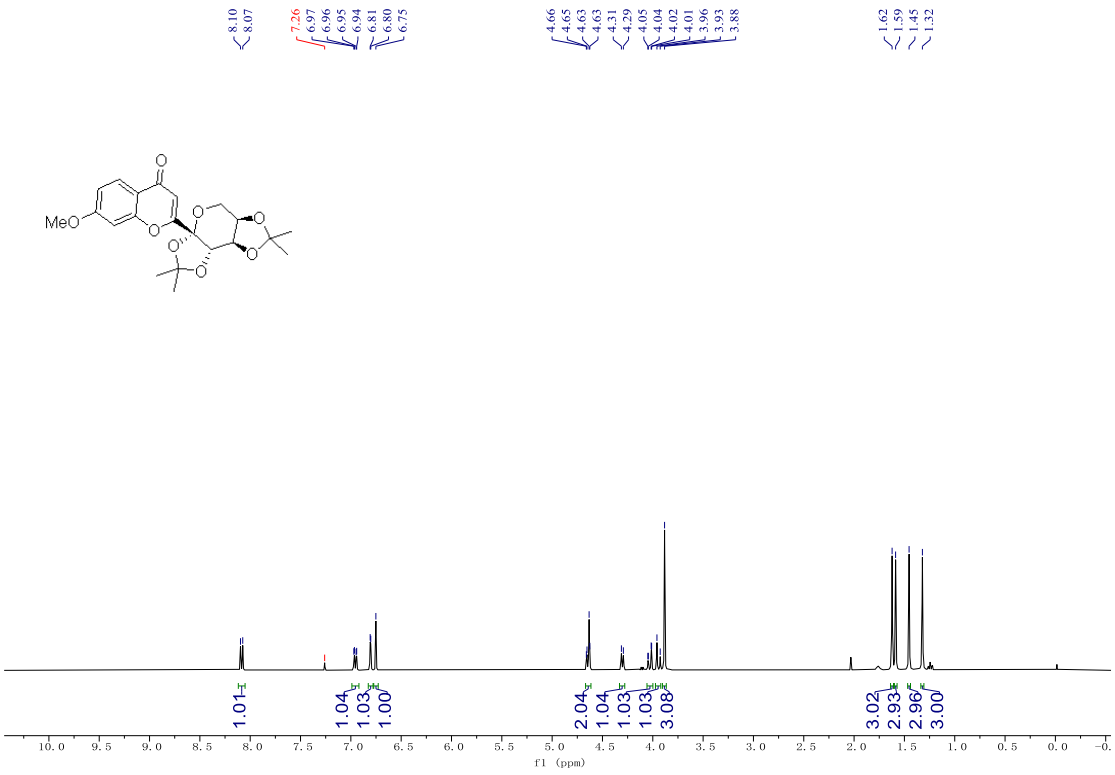
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 26



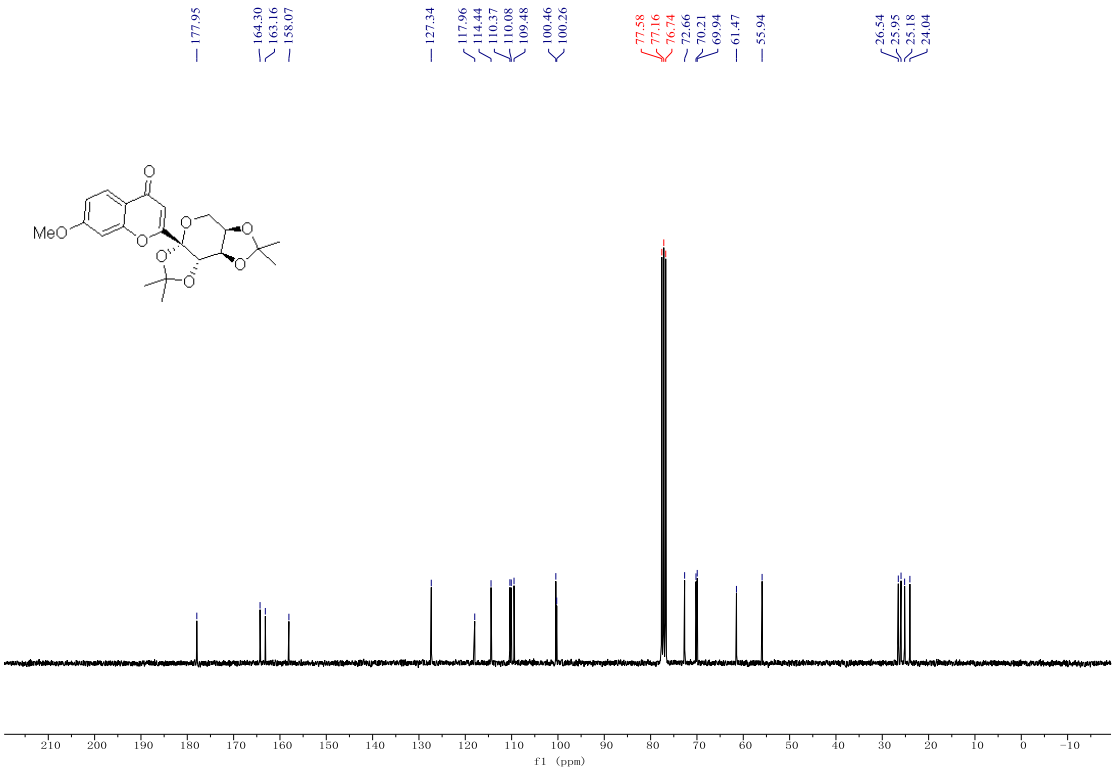
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 26



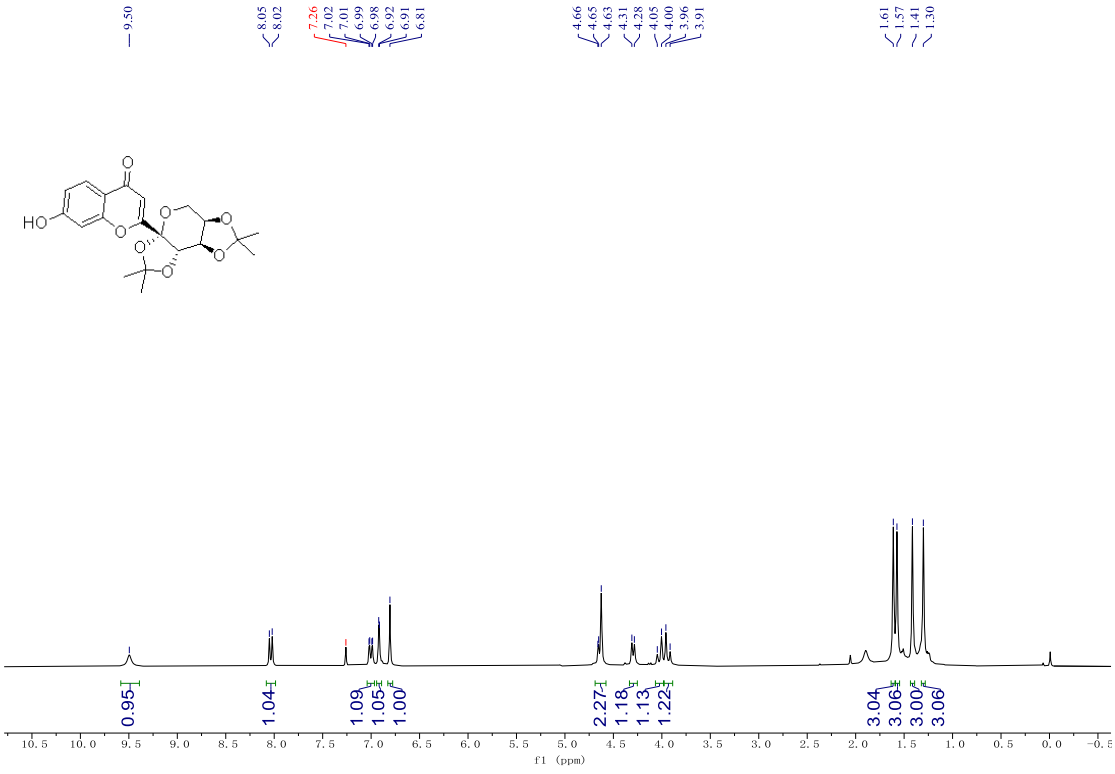
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 27



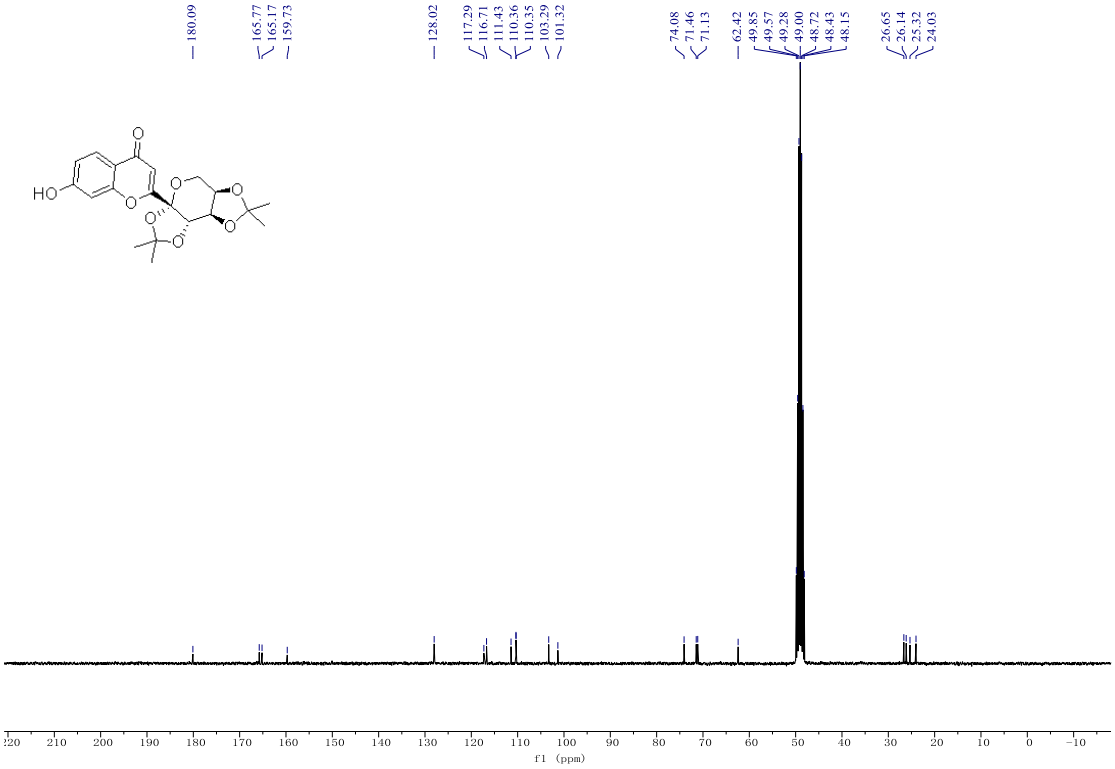
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 27



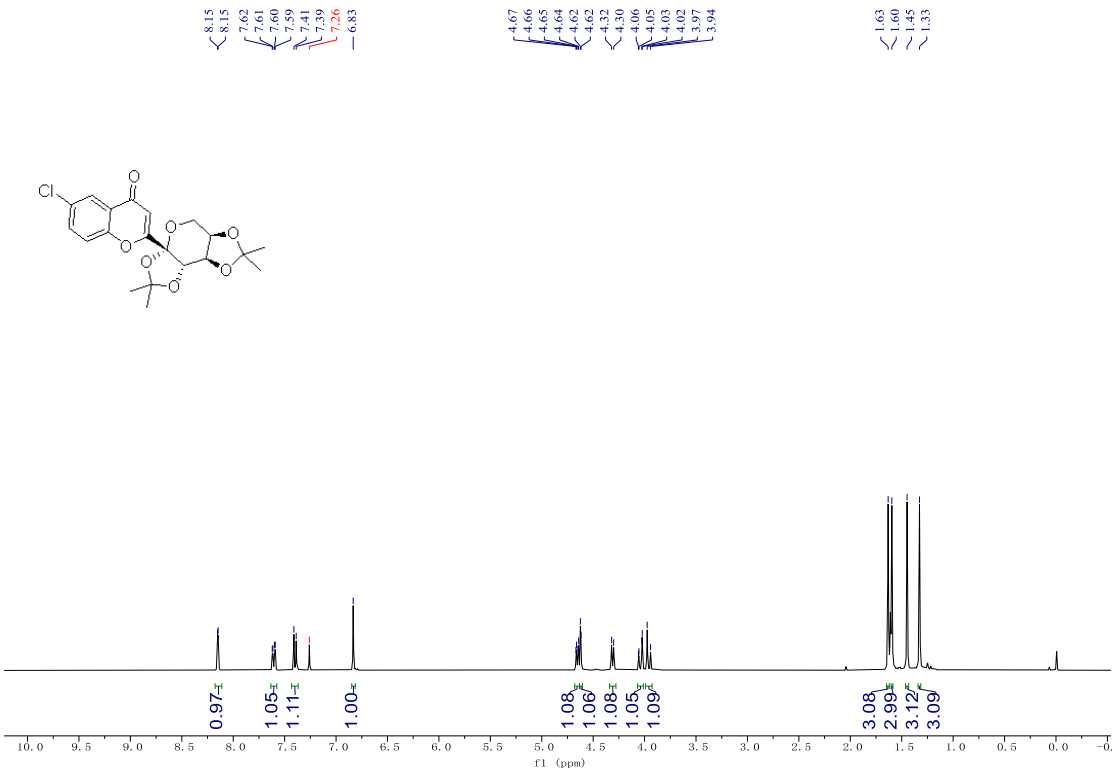
^{1}H NMR (300 MHz, $CDCl_3$) Spectra of compound 28



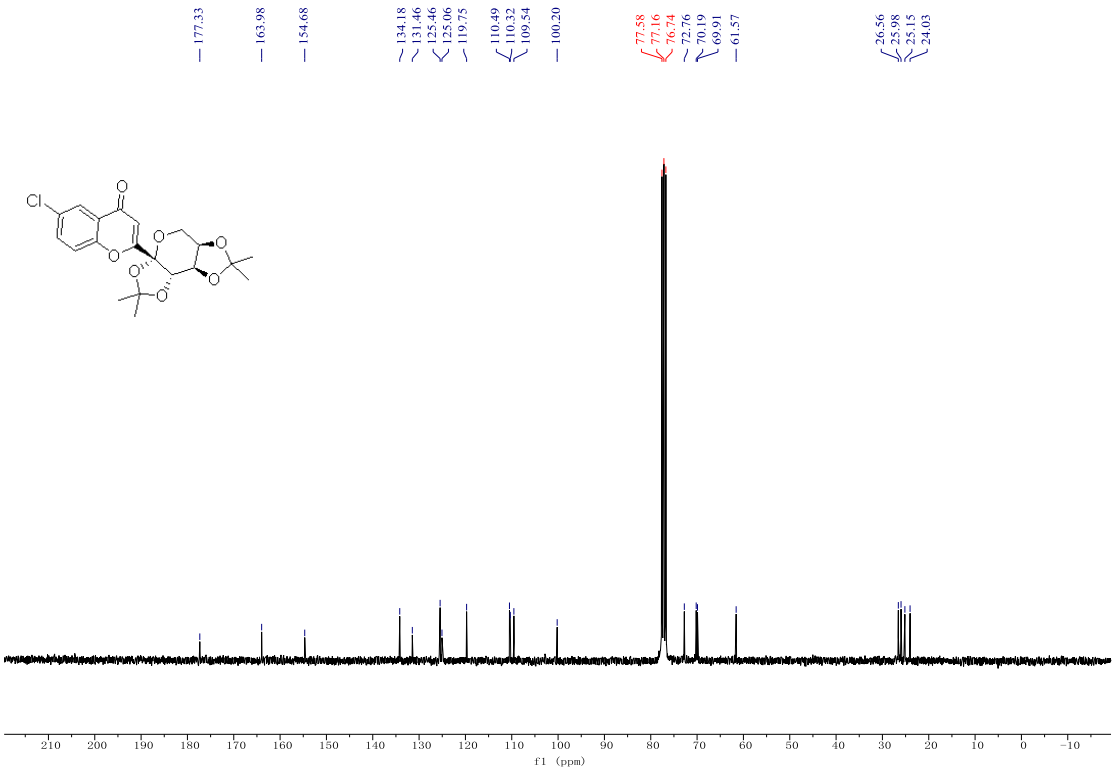
^{13}C NMR (75 MHz, CD_3OD) Spectra of compound 28



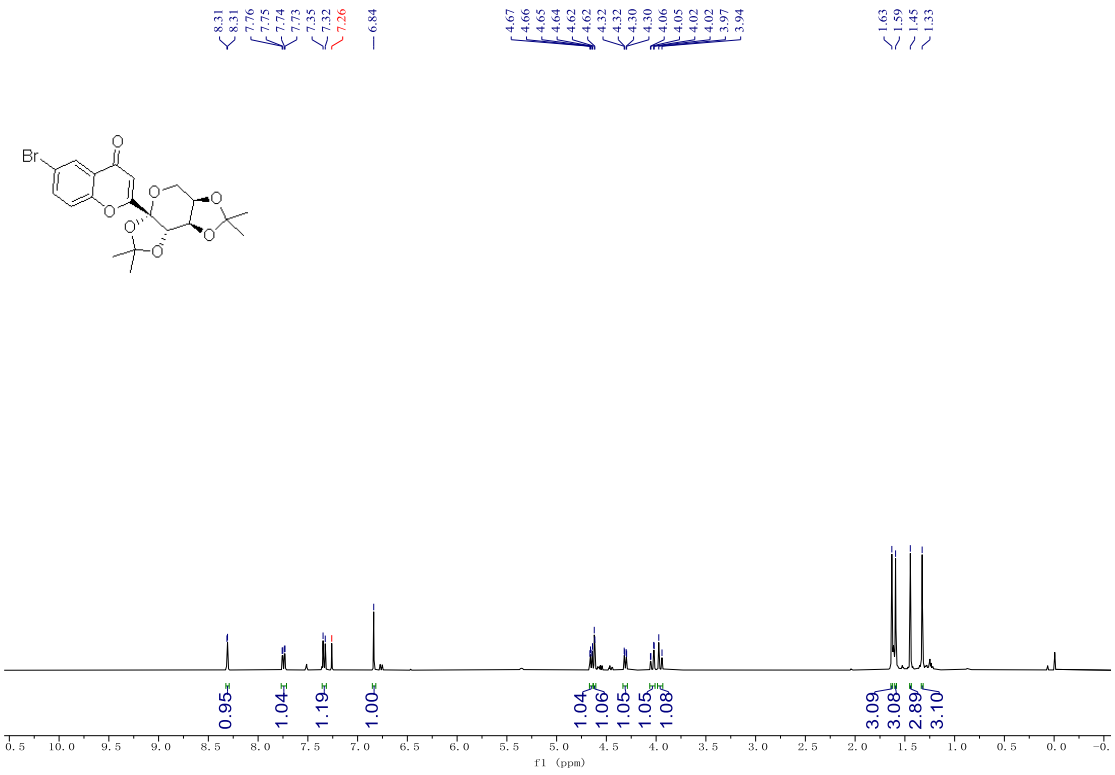
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 29



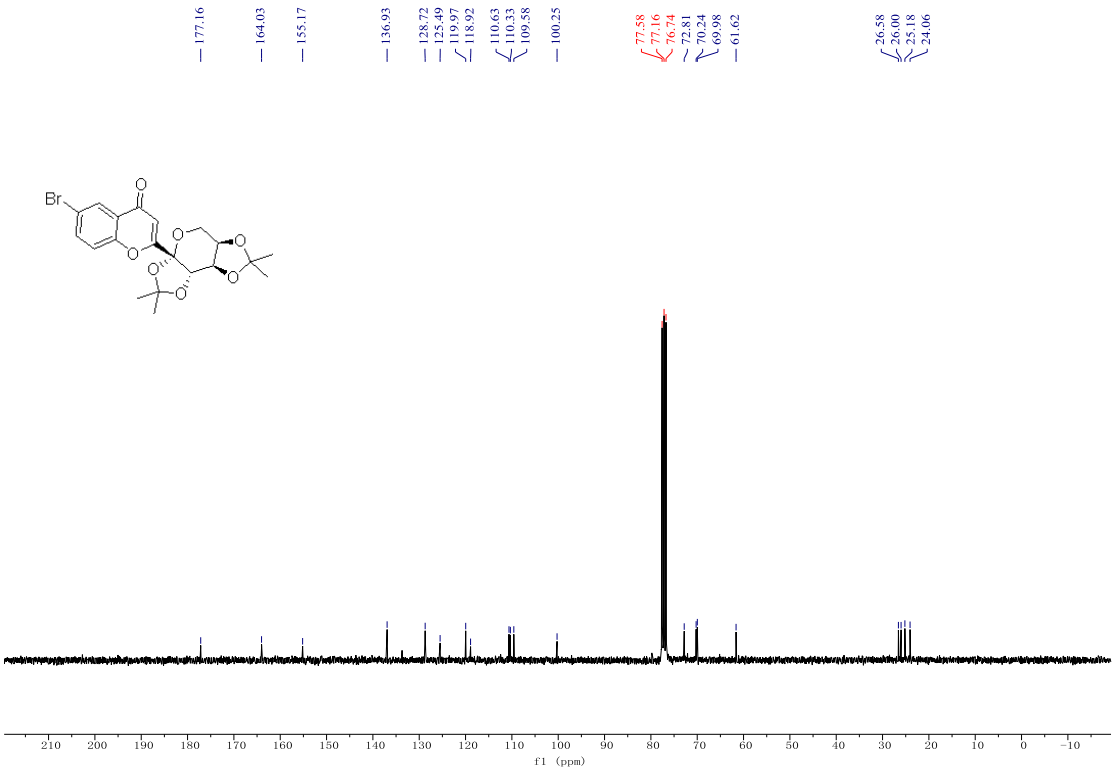
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 29



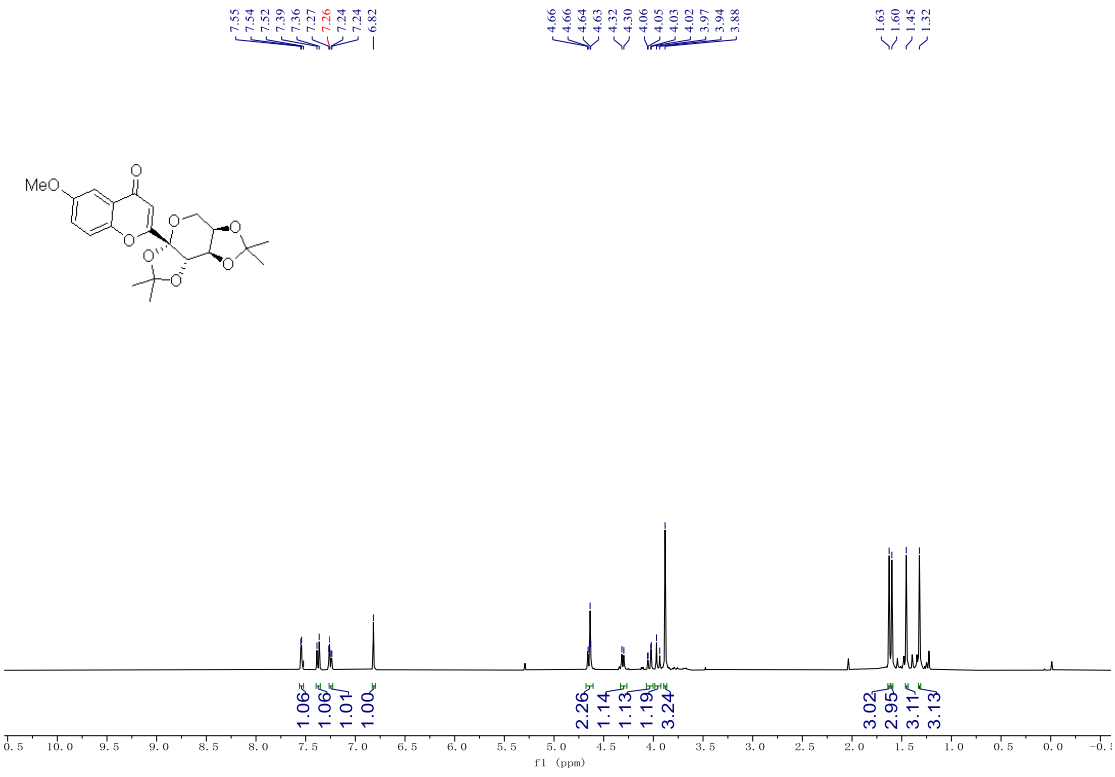
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 30



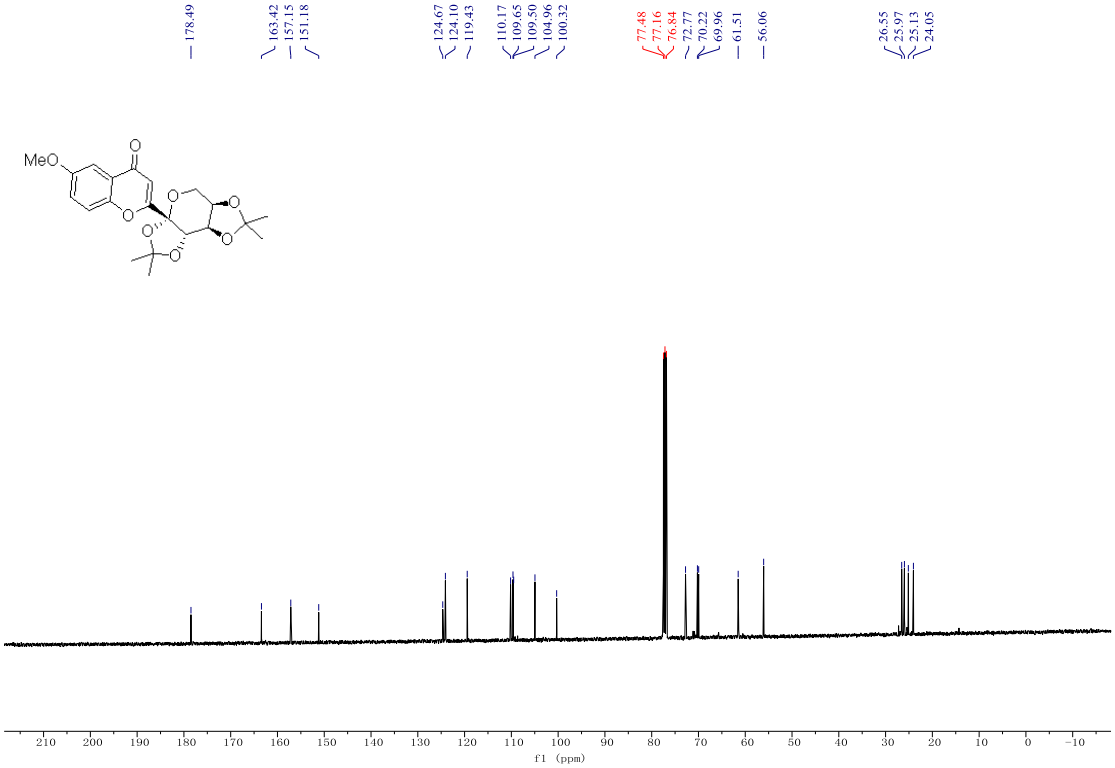
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 30



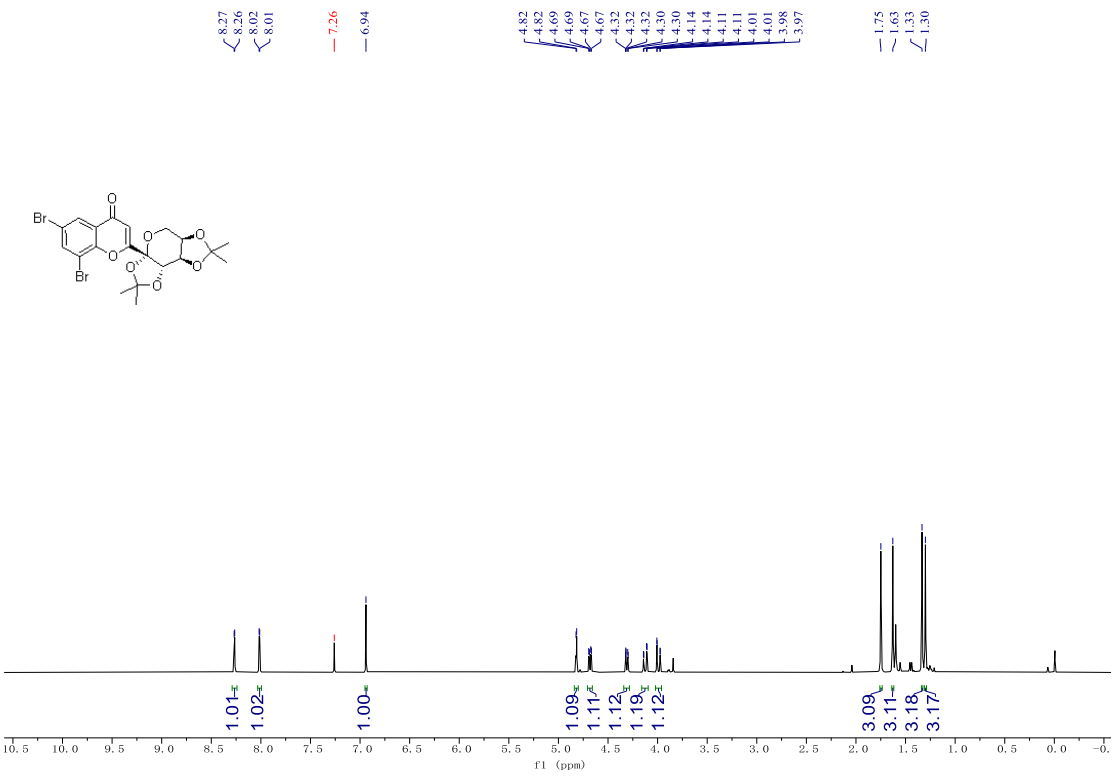
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 31



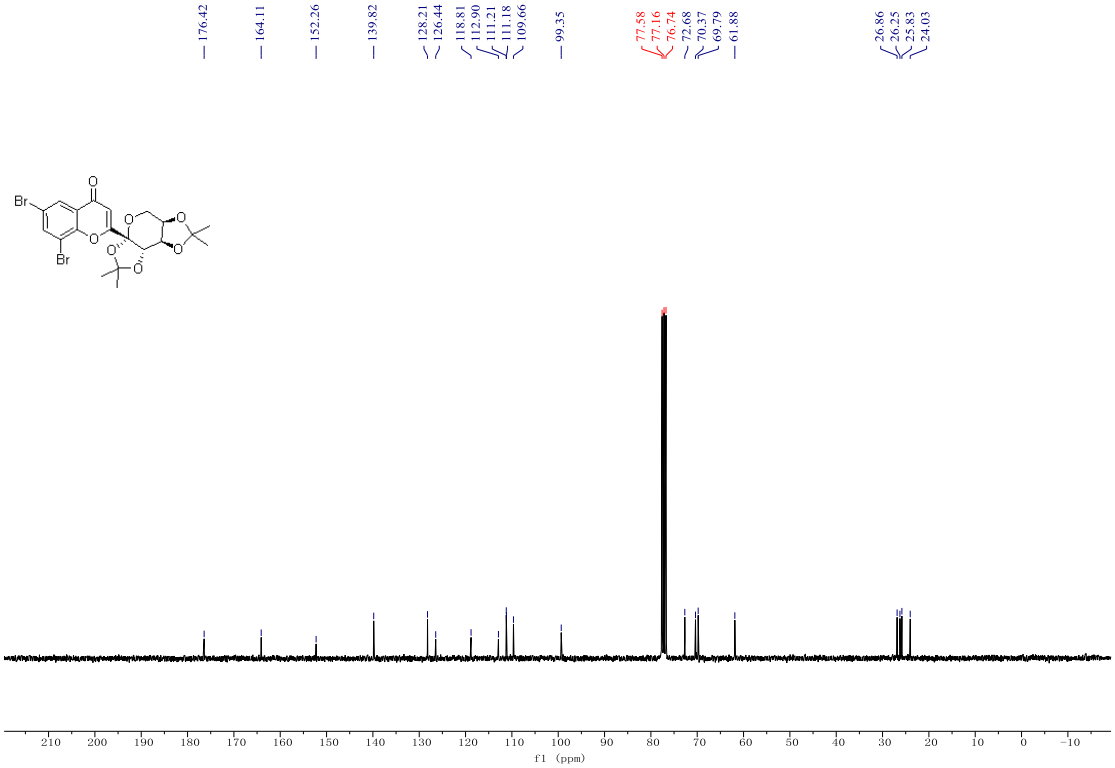
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of compound 31



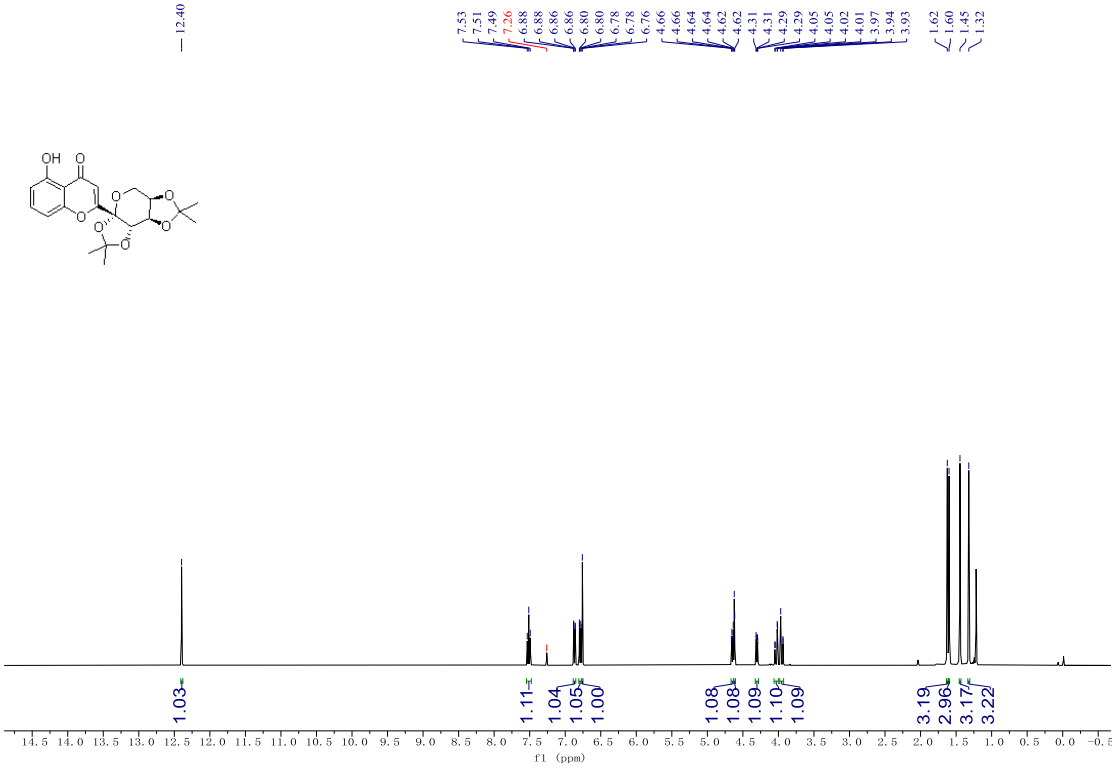
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 32



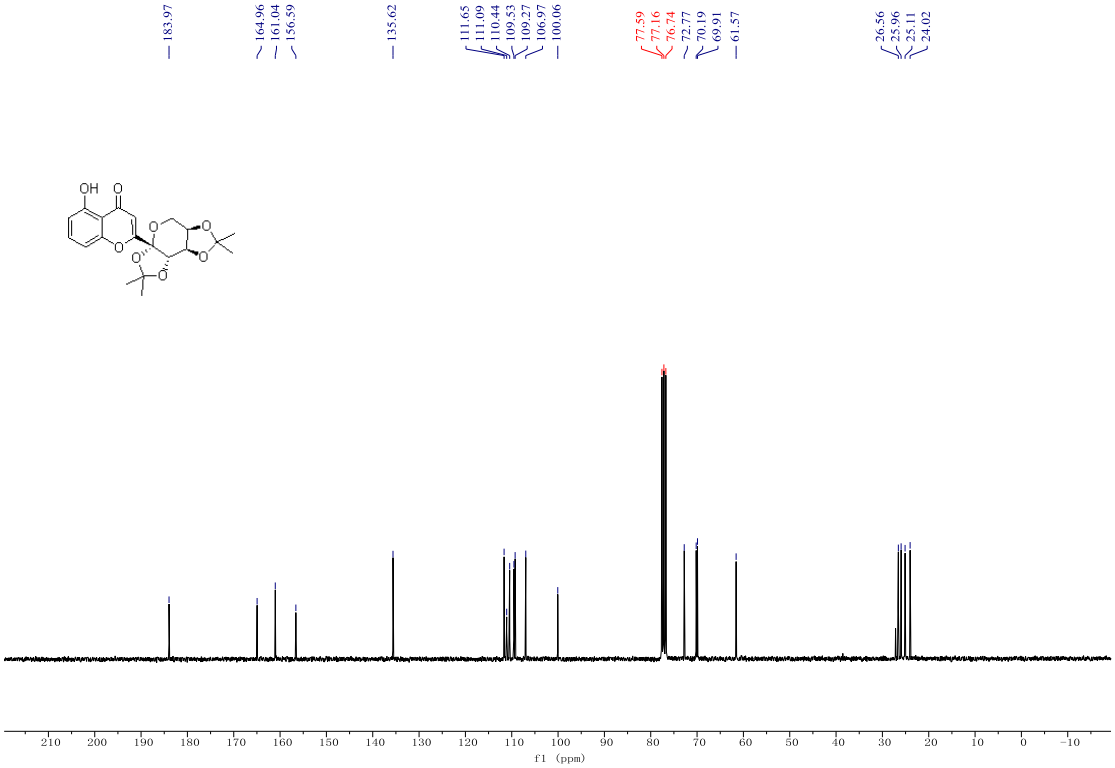
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of compound 32



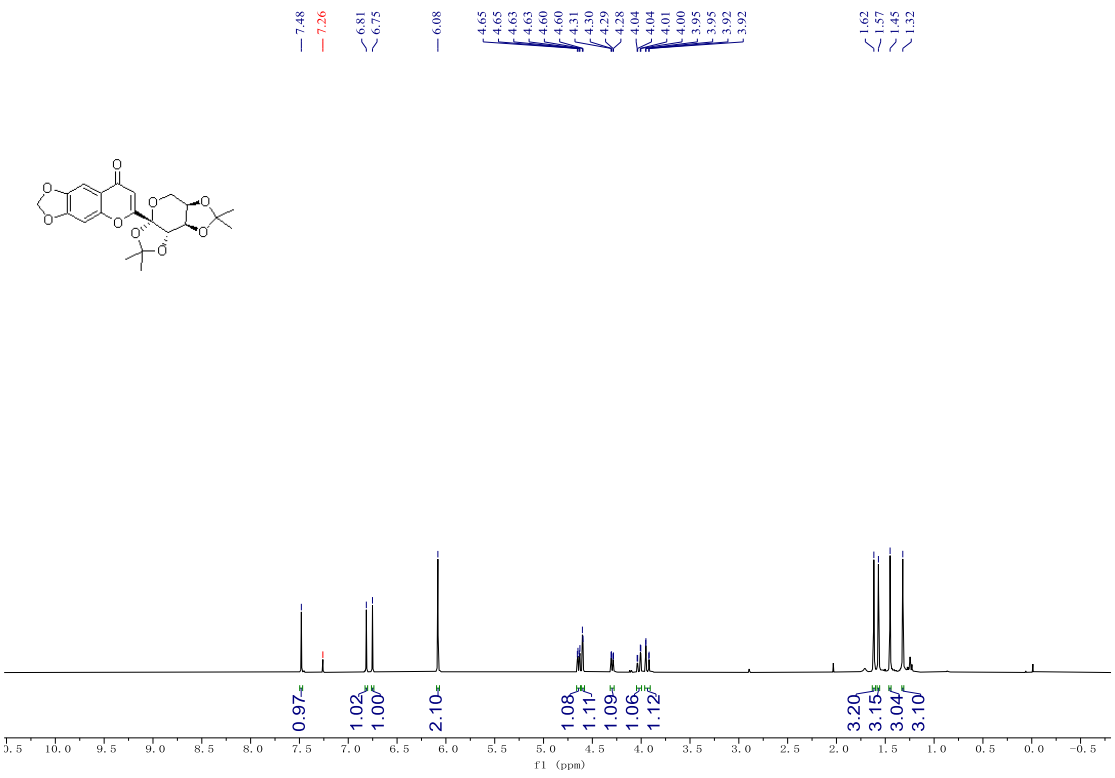
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 33



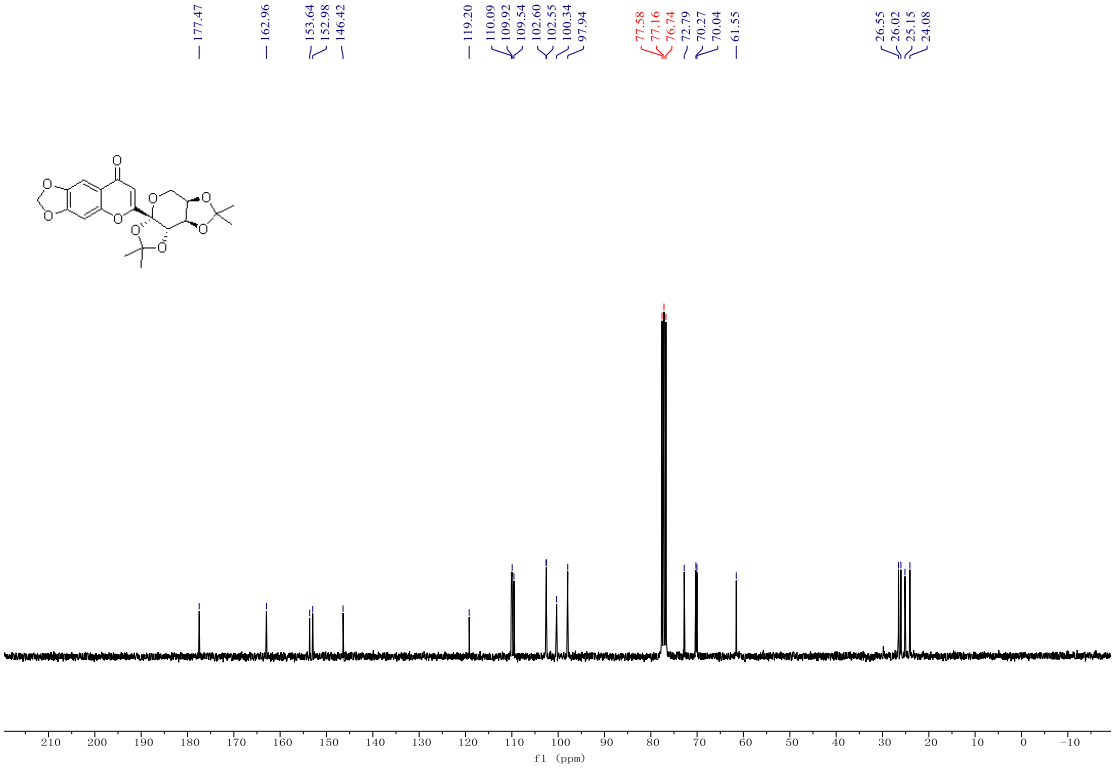
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 33



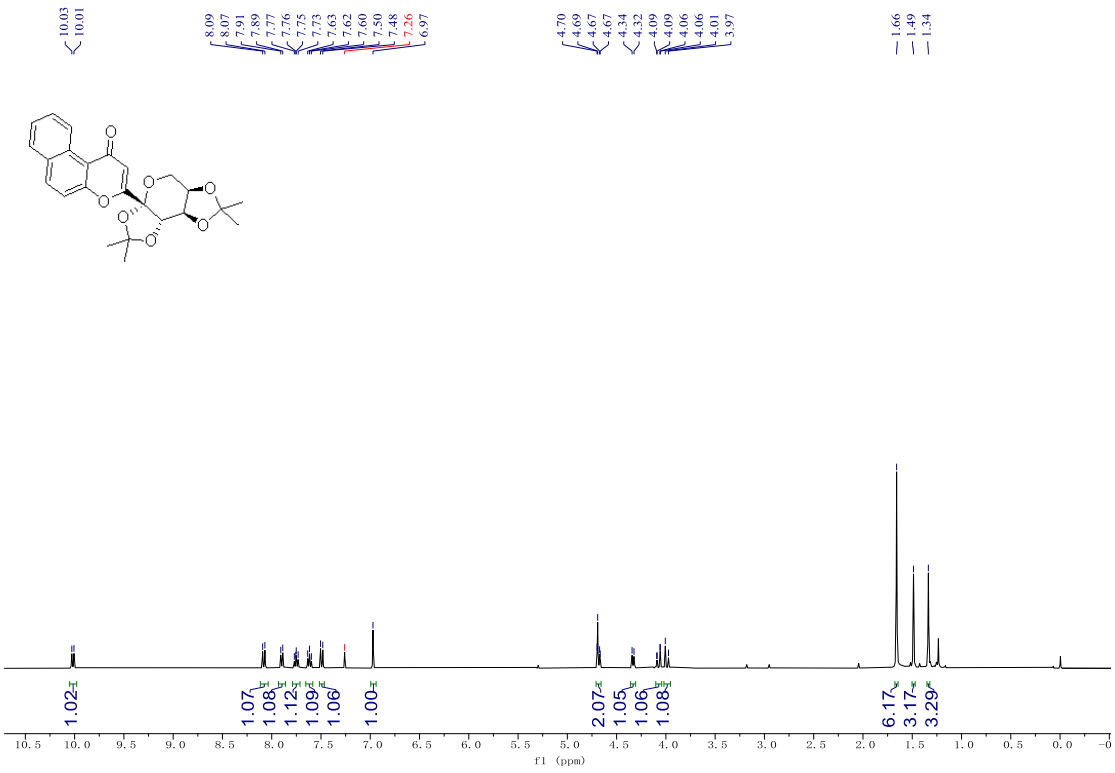
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 34



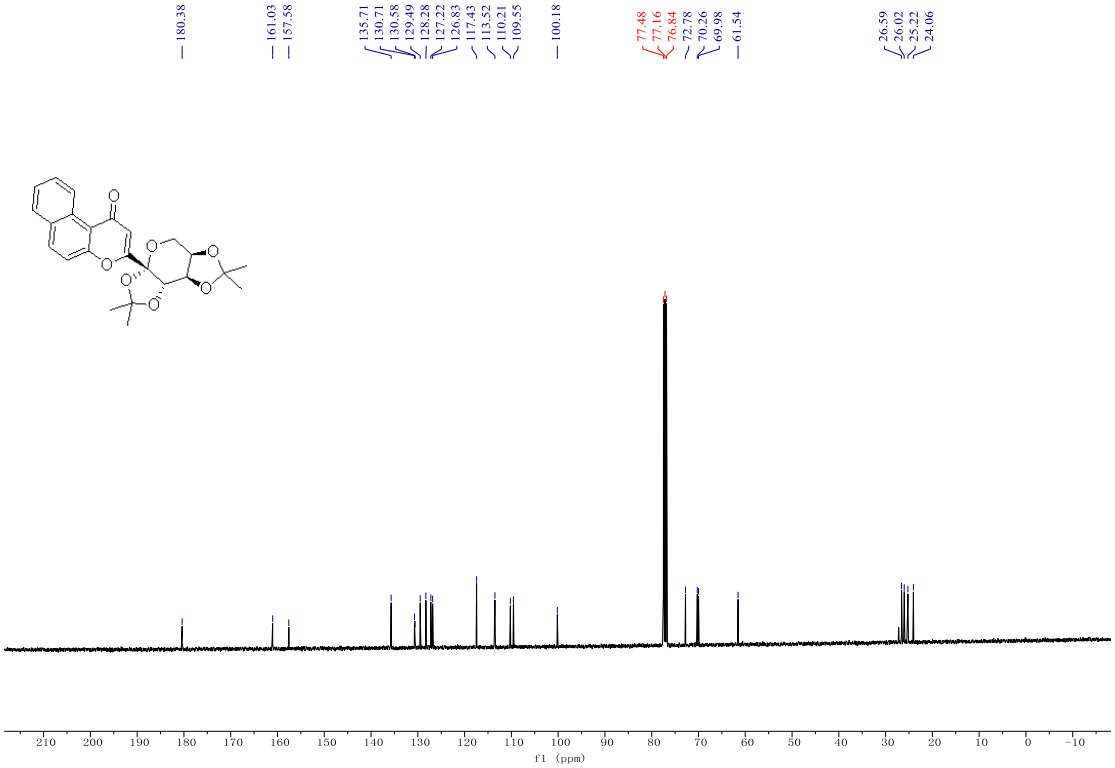
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 34



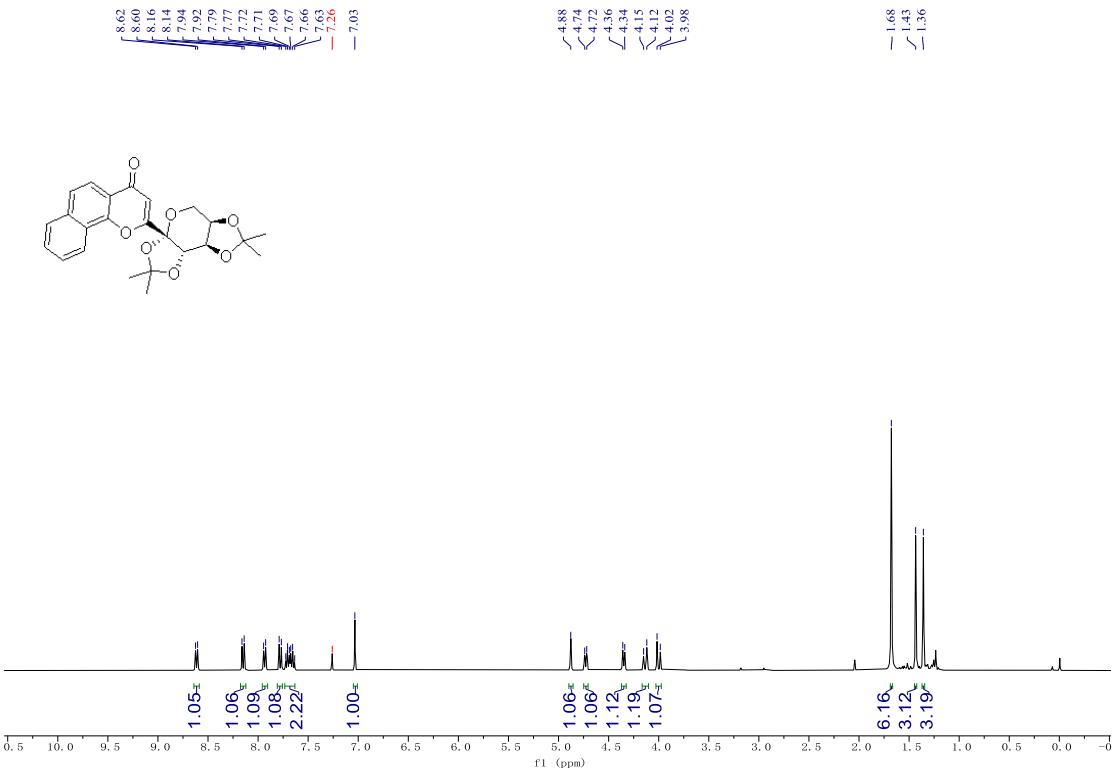
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 35



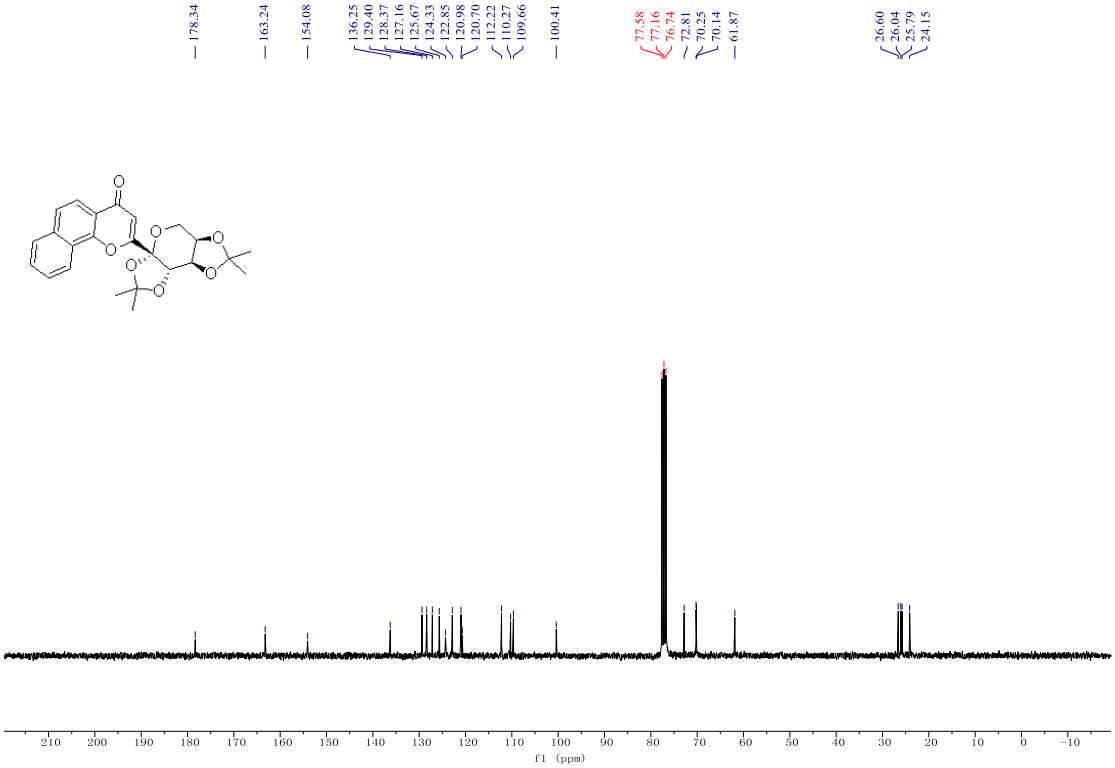
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of compound 35



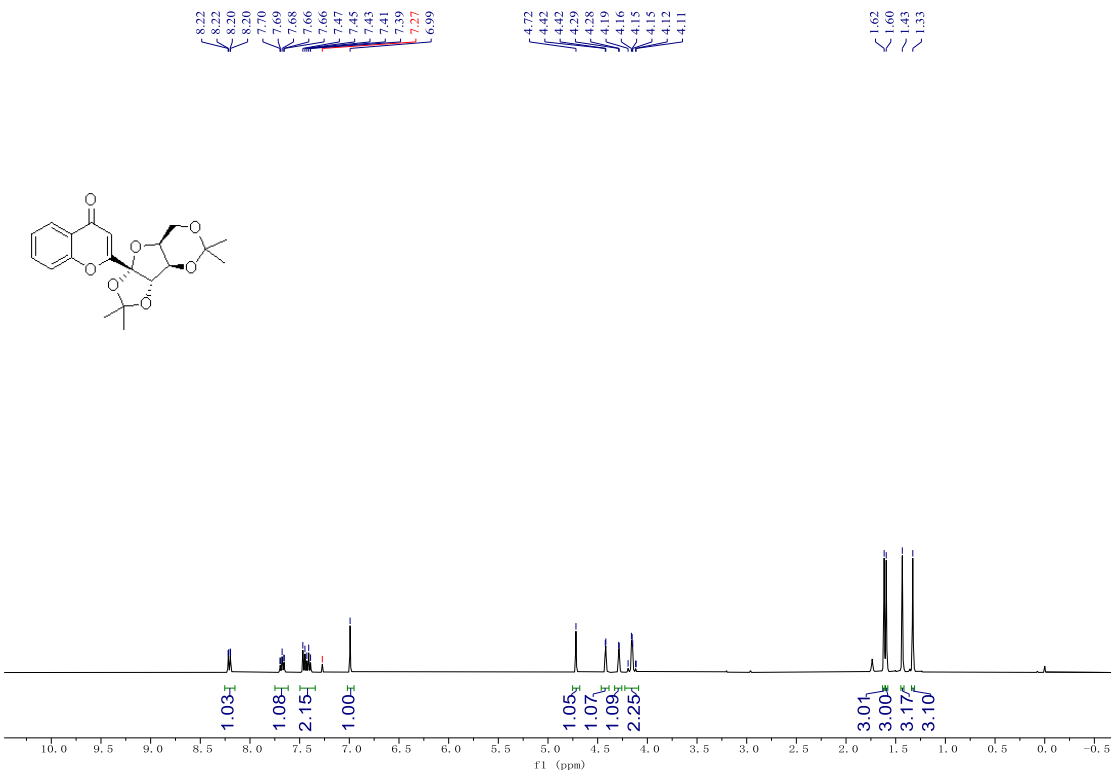
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 36



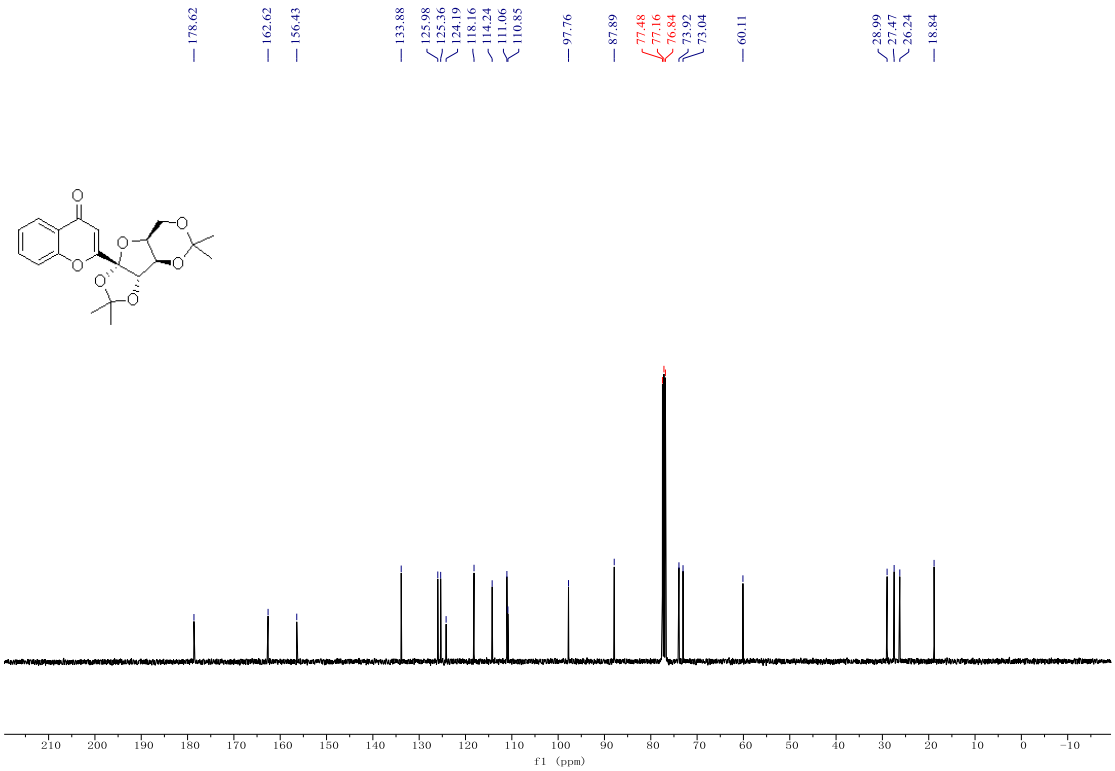
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 36



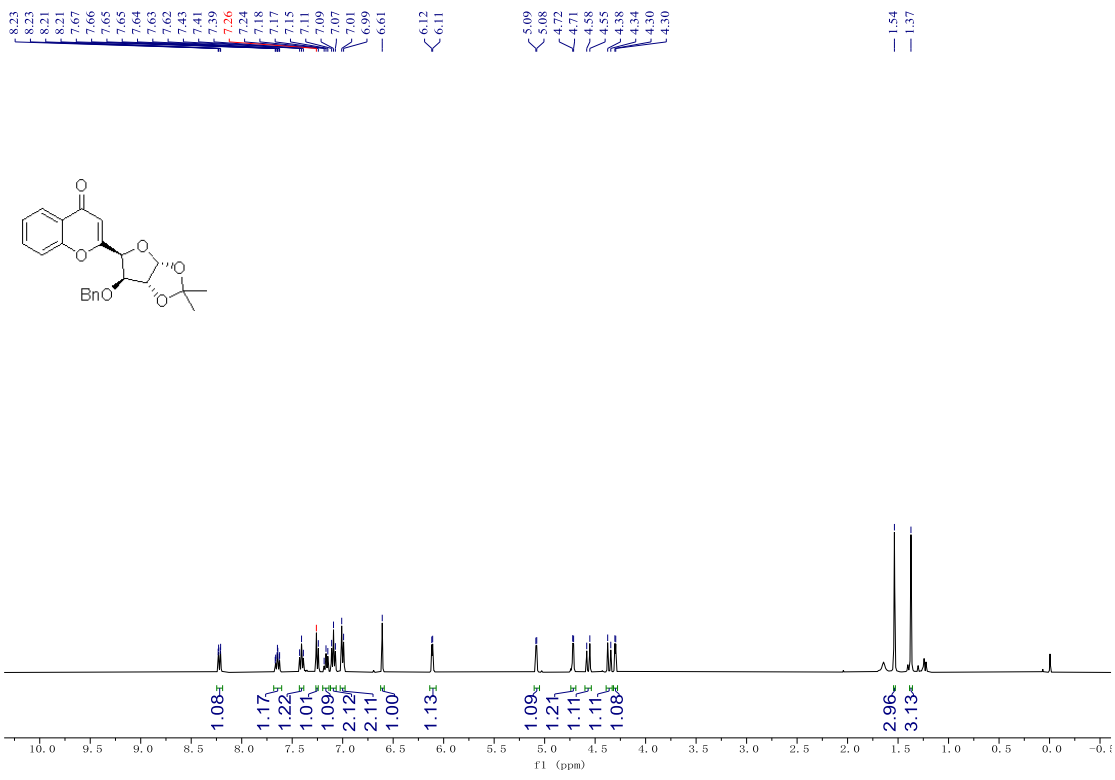
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 37



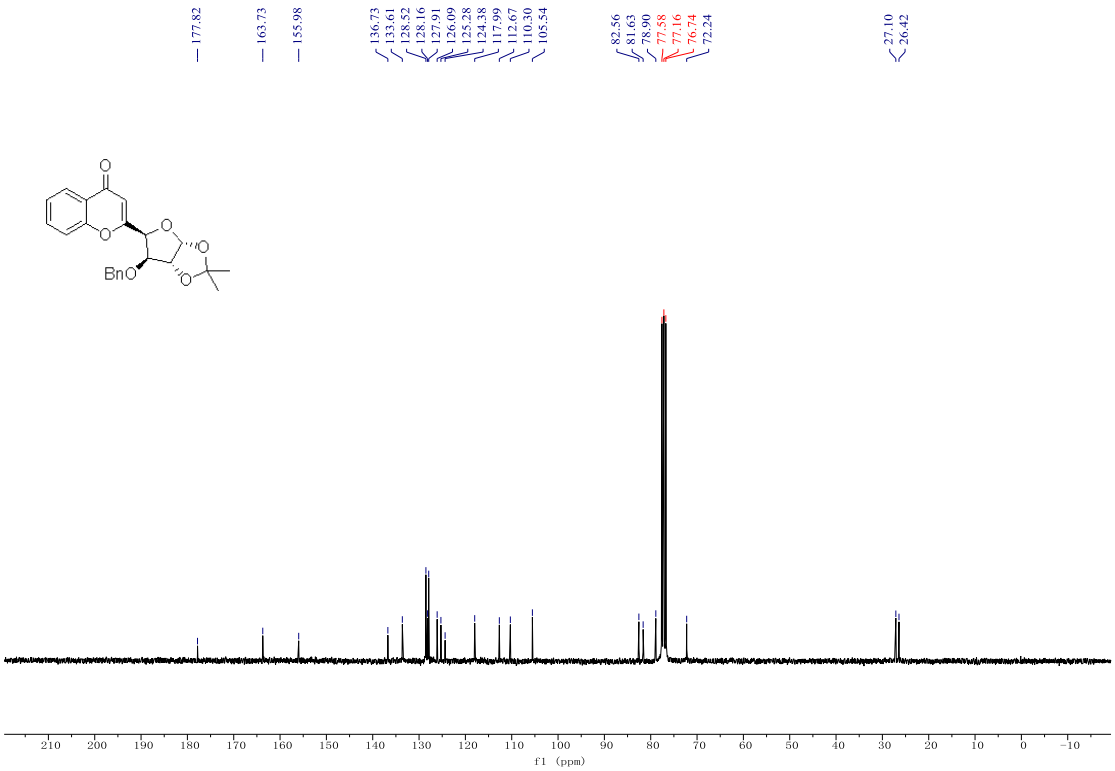
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of compound 37



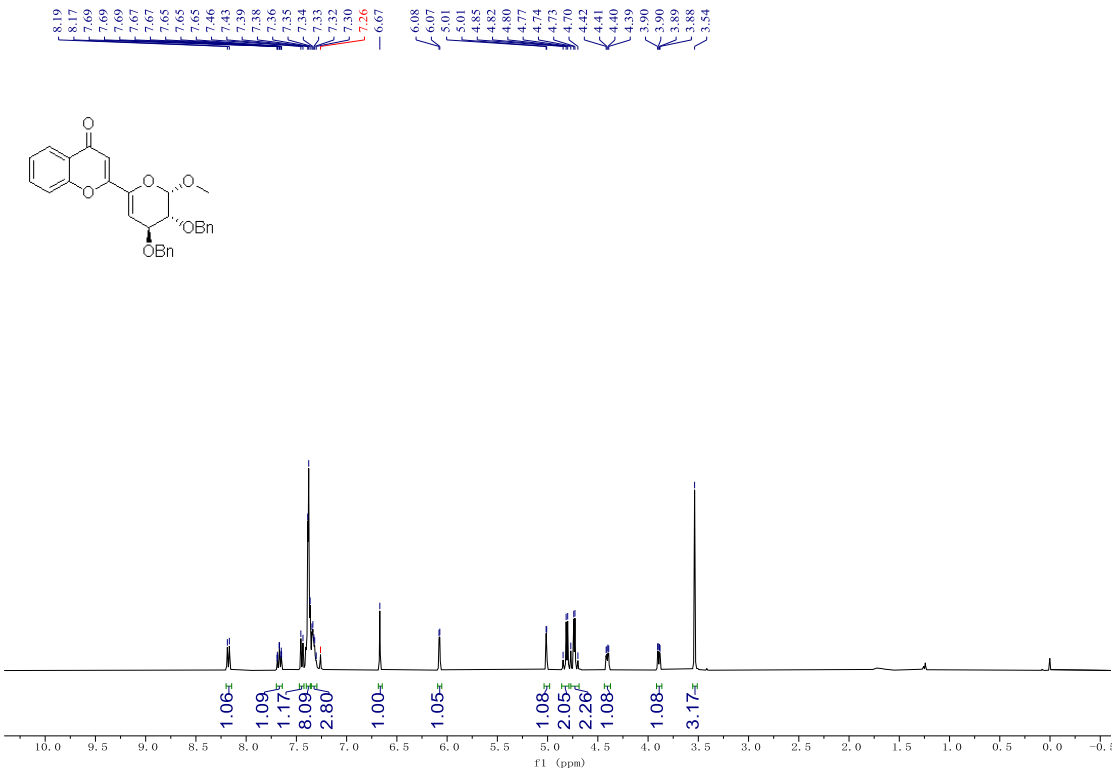
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 38



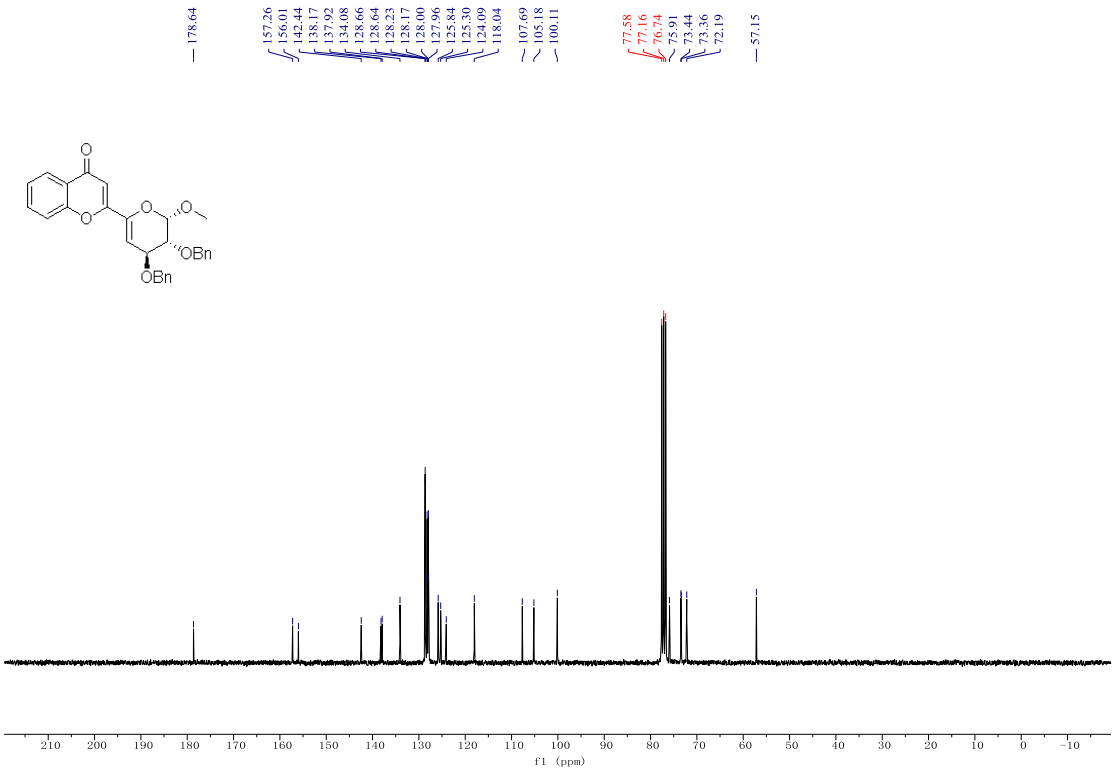
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 38



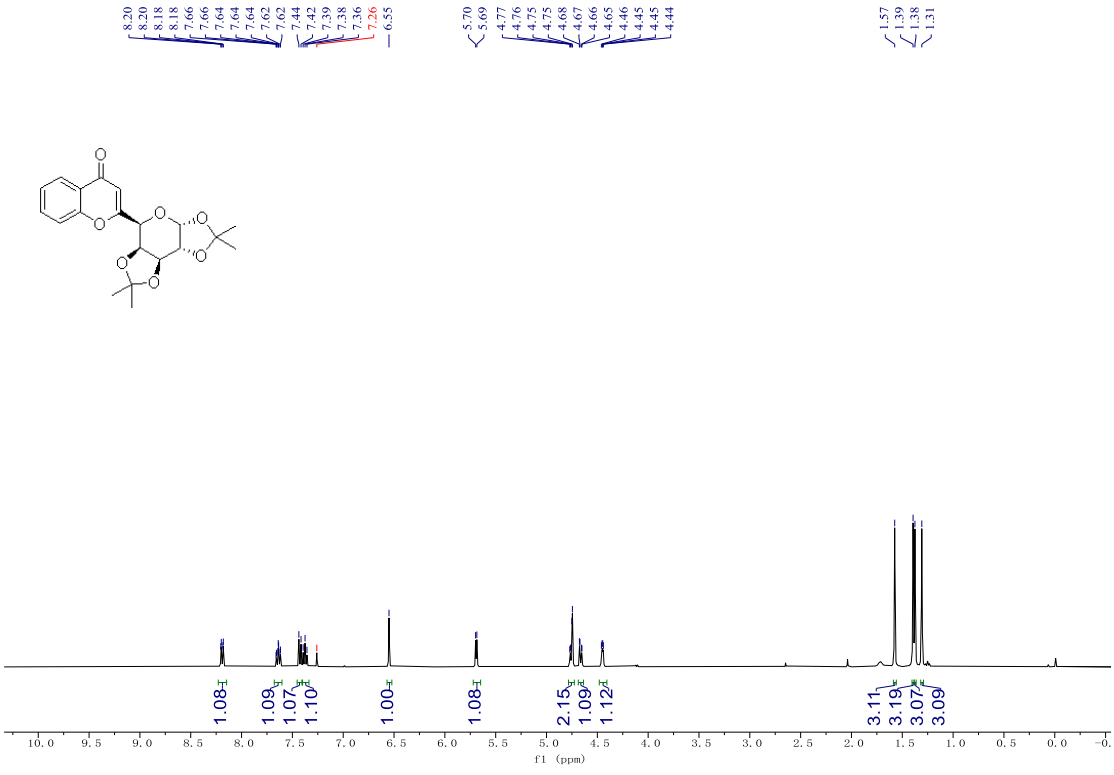
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 39



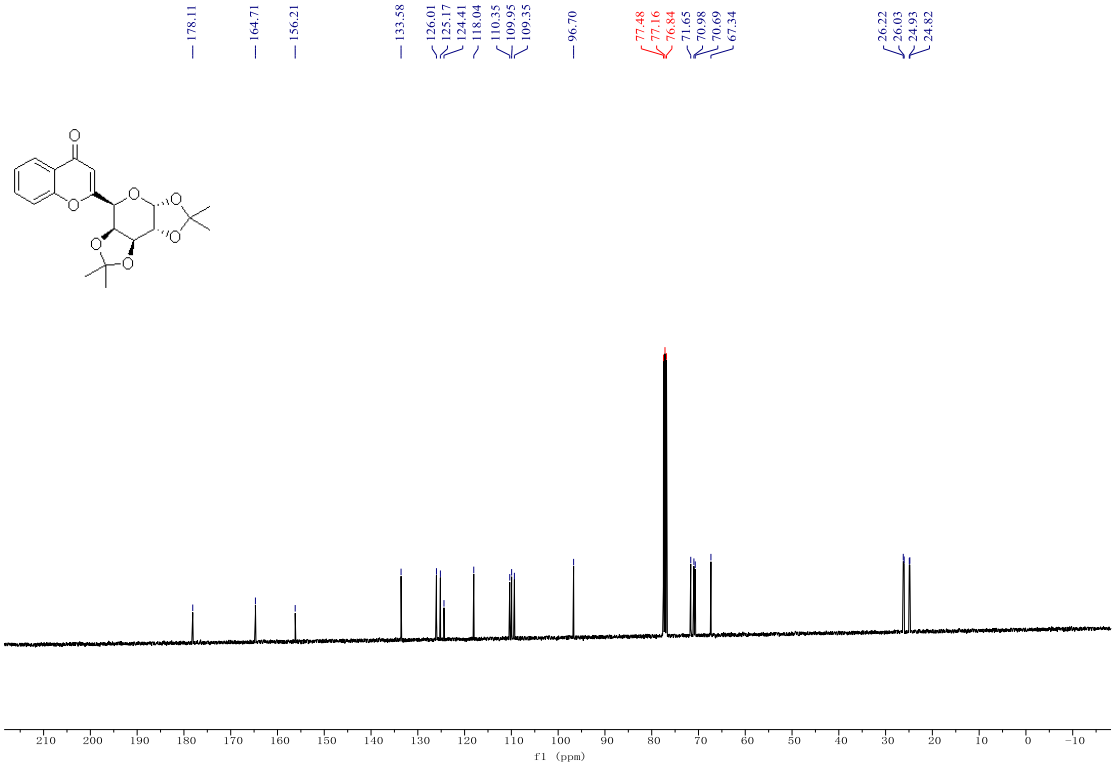
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 39



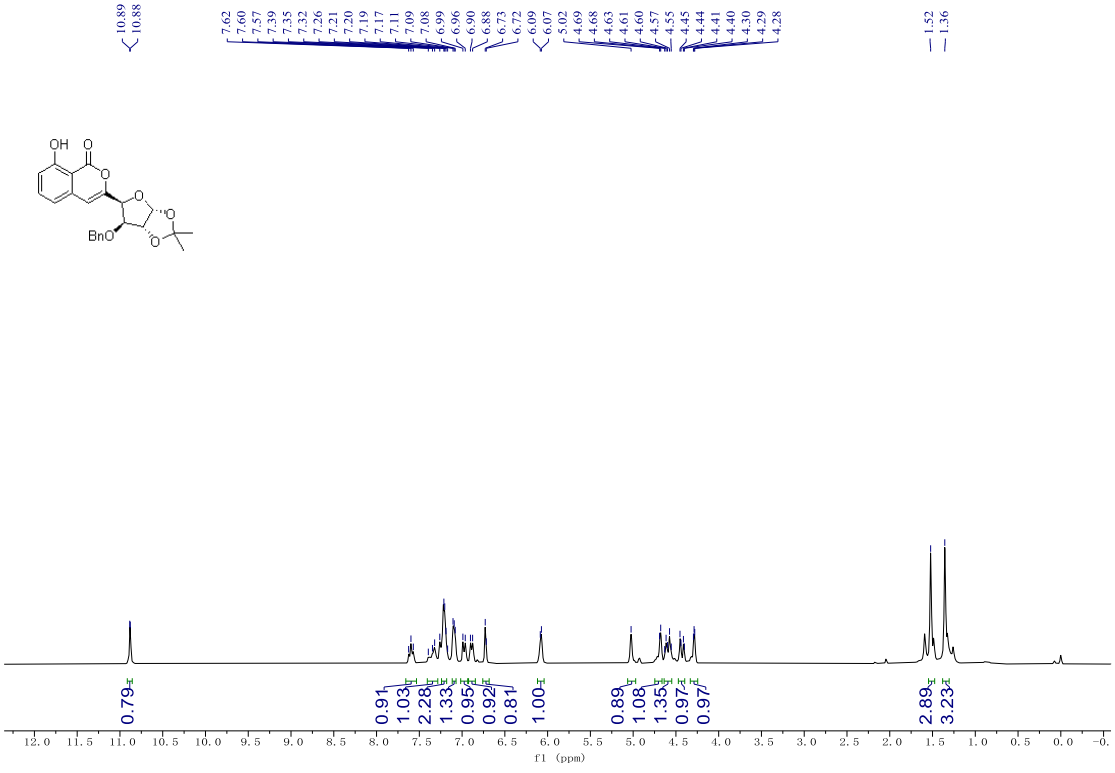
^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 40



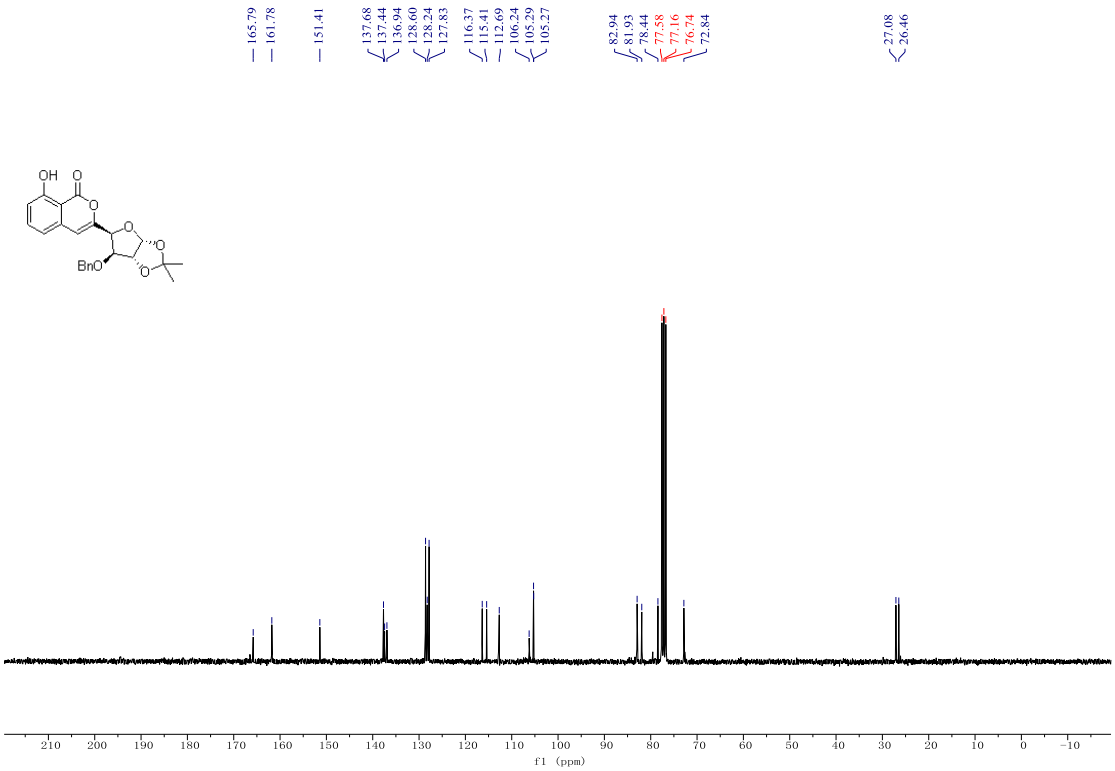
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of compound 40



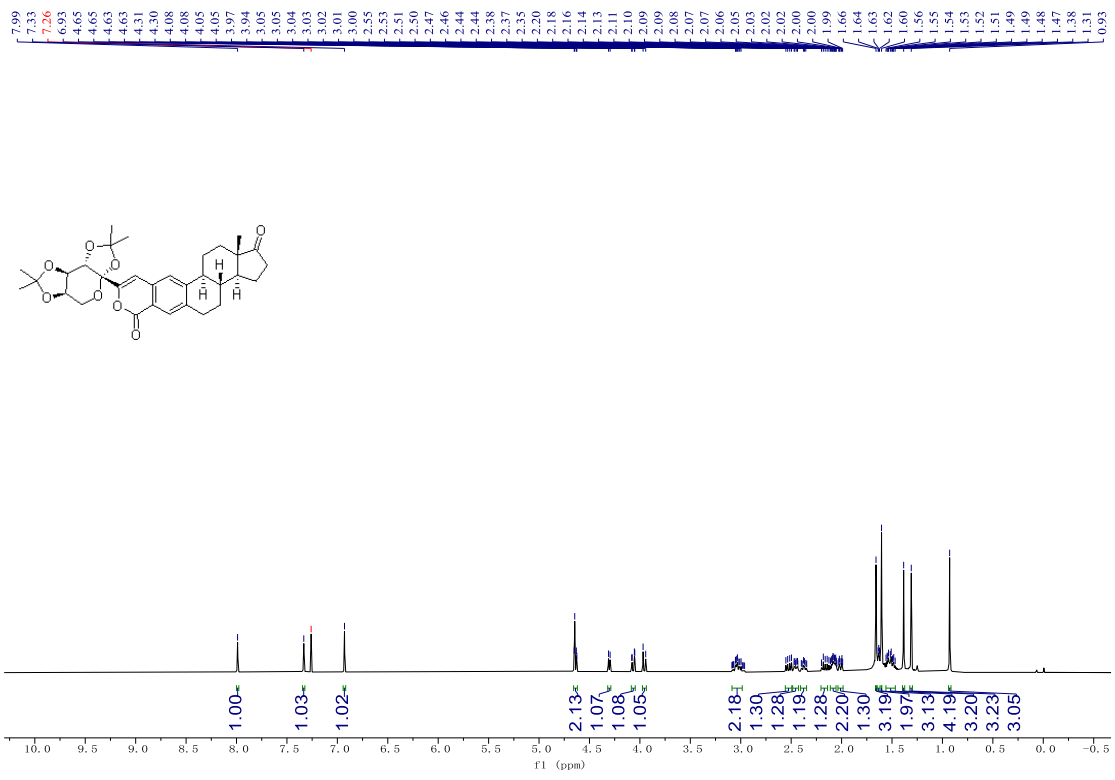
^{1}H NMR (300 MHz, $CDCl_3$) Spectra of compound 43



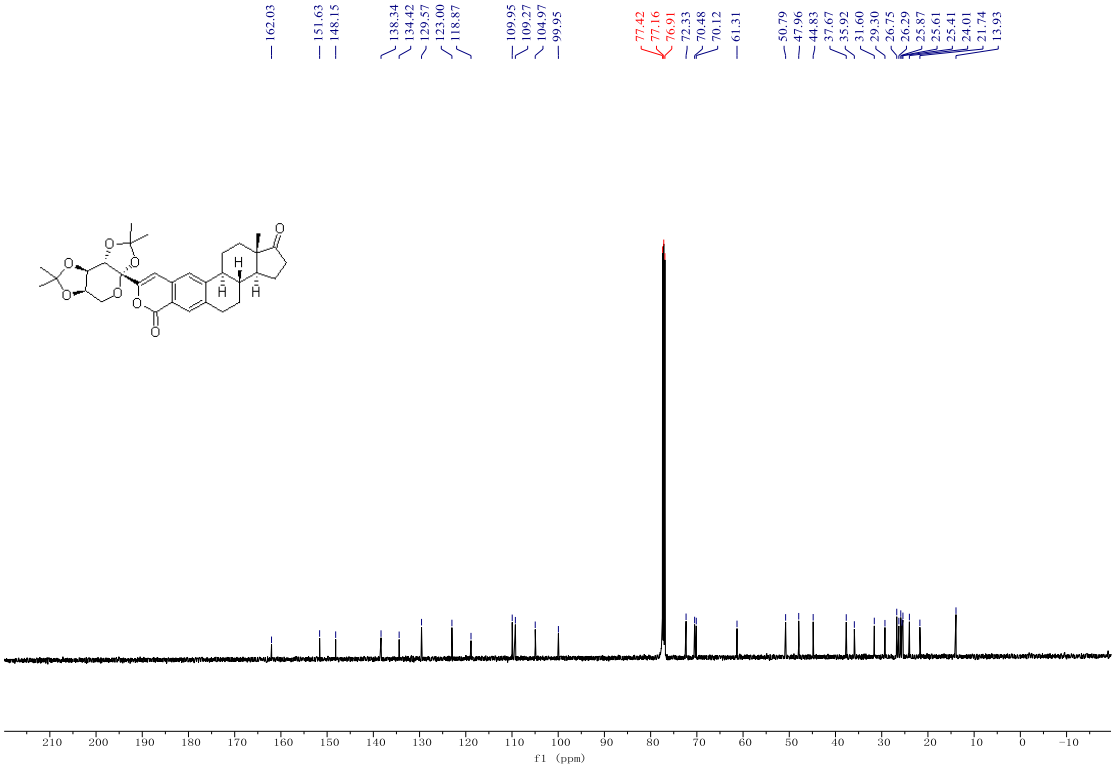
^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 43



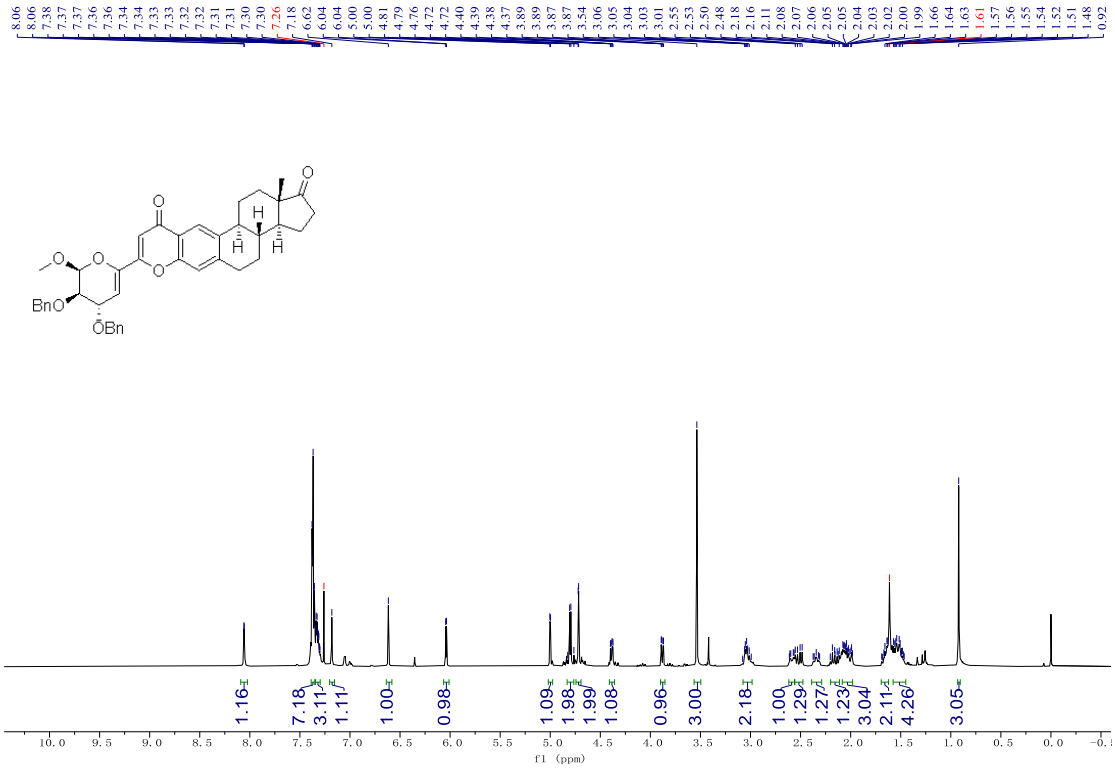
^{1}H NMR (500 MHz, $CDCl_3$) Spectra of compound 49



^{13}C NMR (126 MHz, $CDCl_3$) Spectra of compound 49



^{1}H NMR (400 MHz, $CDCl_3$) Spectra of compound 51



^{13}C NMR (75 MHz, $CDCl_3$) Spectra of compound 51