Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Rh(III)-Catalyzed Multi-site-selectivity C–H Bond Functionalization: Condition-Controlled Synthesis of Diversified Fused Polycyclic Benzimidazole Derivatives

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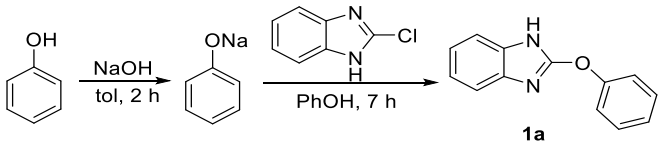
1. General methods

NMR data were obtained for ^{1}H at 400 MHz or 600 MHz, and for ^{13}C at 100 MHz or 151 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution. ESI HRMS was recorded on a Waters SYNAPT G2 and Water XEVO G2 Q-ToF. UV detection was monitored at 220 nm. TLC was performed on glass-backed silica plates. Column chromatography was performed on silica gel (200-300 mesh), eluting with ethyl acetate and petroleum ether. 2-Phenoxy benzimidazoles and 4-hydroxy-2-alkynoates were prepared according to the literature procedures.

2. General procedure for the synthesis of reaction substrates

2.1 General procedure for the synthesis of 2-phenoxy benzimidazoles

Procedure 1:

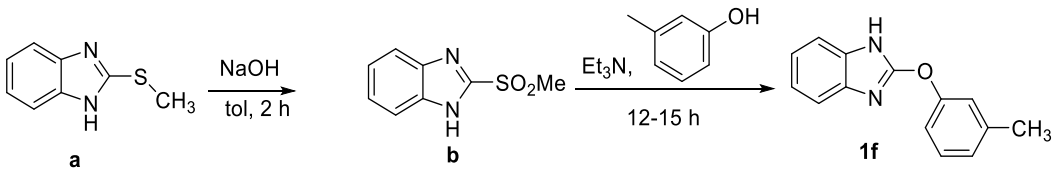


1a

Phenol (1 equiv), NaOH (1.1 equiv), and toluene (1.3 equiv) were added into the flask at 100-120 °C. The water produced by the reaction was continuously steamed with a water separator. When no water was distilled out, toluene was removed by vacuum distillation to obtain crude sodium phenate. The crude sodium phenolate was added to the organic ketone and stirred to dissolve. After filtering out the insoluble sodium hydroxide, the solution was cooled and crystallized in ice water to precipitate sodium phenol, which was separated by suction filtration and dried in a drying oven at 65 °C for 2 hours to obtain the product sodium phenoxide.

After 10.0 g (0.066 mol) of 2-chlorobenzimidazole and 10.0 g (0.086 mol) of sodium phenoxide in 150 g of phenol had been heated at 150 ℃ for 7 h, the reaction mixture was steam distilled and the residue was filtered and washed with 1% aqueous NaOH solution and water. The precipitate was then recrystallized from ethanol to give an analytical sample of 2-phenoxy benzimidazole[1].

Procedure 2:



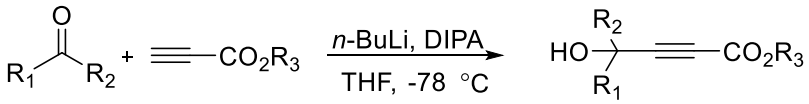
a **b** **1f**

To a solution of compound **a** (384 mg, 2 mmol) in C_2H_5OH (12 mL) was added ammonium molybdate tetrahydrate (494 mg, 0.4 mmol) and 30% H_2O_2 (613 μL, 6 mmol) at 0 °C. Then, the mixture was stirred for 2 h at room temperature. 10% of sodium thiosulfate was then added to the solution. The mixture was extracted with ethyl acetate, washed with brine, dried over Na_2SO_4. After filtration, the organic solvent was removed in vacuo, purification by silica gel column chromatography (hexane/ethyl acetate) gave the title compound **b** (872 mg, 89% yield) as a white solid[2].

Benzimidazole **b** (19.6 mg, 0.1 mmol), substituted phenol (54.0 mg, 0.5 mmol), and triethylamine (50.5 mg, 0.5 mmol) were placed in a vial with a stir bar. The vial was capped and put into a preheated oil bath (120 °C) with stirring. The reaction was monitored by LCMS. Upon

completion of the reaction (after 15 h), the residue was purified by preparative reverse phase liquid chromatography to give the desired product **1f** (10.9 mg, 49% yield)[3].

2.2 General procedure for synthesis of 4-hydroxy-2-alkynoates



A solution of *n*-butyllithium in hexanes (1.6 M, 33.0 mmol) was added dropwise to a solution of freshly distilled diisopropylamine (33.0 mmol) in dried THF (30 mL) at 0 °C. The solution was stirred for 1 h at 0 °C, then cooled to -78 °C. Propargyl ester (31.3 mmol) in dried THF (10 mL) was then added dropwise to the reaction mixture. After 1 h at the same temperature, ketone (62.6 mmol) was added, and the resulting mixture was stirred at -78 °C for 3 h. The reaction was quenched with saturated NH_4Cl solution, and the mixture was extracted four times with Et_2O. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and then the solvents were evaporated to dryness. The oily residue was purified by flash silica gel column chromatography (hexanes/EtOAc) to get propargylic alcohol[4].

References:

[1] Ishida, S.; Fukushima, Y.; Sekiguchi, S.; Matsui, K. *Bulletin of the chemical society of Japan*. **1975**, 48, 956-959.

[2] Toda, N.; Asano, S.; Barbas III, C. F. *Angew. Chem. Int. Ed*. **2013**, 52, 12592-12596.

[3] Lan, P.; Romero, F. A.; Malcolm, T. S.; Stevens, B. D. Wodka, D.; Makara, G. M. *Tetrahedron Letters*. **2008**, 49, 1910–1914.

[4] Liao, G.; Song, H.; Yin, X. S.; Shi, B. F. Expeditious Synthesis of Pyrano[2,3,4-de]quinolines via Rh(III)-Catalyzed Cascade C–H Activation/Annulation/Lactonization of Quinolin-4-ol with Alkynes. *Chem. Commun.* **2017**, 53, 7824-7827.

3. Screening reaction conditions

Many other conditions cannot increase the yield of products (Table S1, S2, S3).

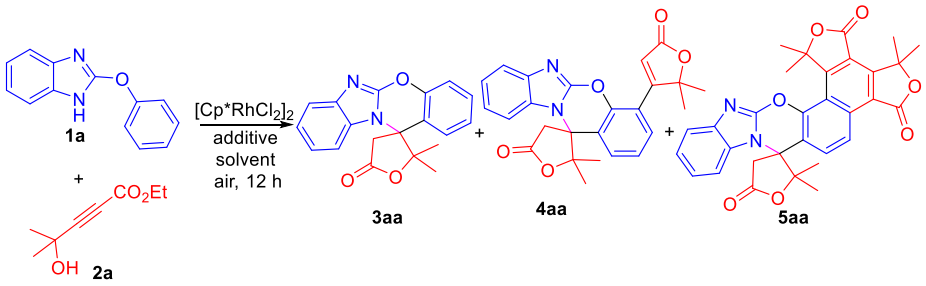


Table S1. Additional reaction conditions for the product 3aa[a]

Entry	1a:2a	Additive/ equiv	Solvent	Temp./°C	Yield[b]/%		
					3aa	4aa	5aa
1	3:1	$AgSbF_6$/0.2+K_3PO_4/1.0	DCE	100	31	trace	trace
2	3:1	$AgSbF_6$/0.2+NaOAc/1.0	DCE	100	40	/	trace
3	3:1	$AgSbF_6$/0.2+K_2CO_3/1.0	DCE	100	29	/	trace
4	3:1	$AgSbF_6$/0.2+HOAc/1.0	DCE	100	trace	10	trace
5	3:1	$AgSbF_6$/0.2+1-AdCOOH/1.0	DCE	100	63	trace	trace
6	3:1	$AgSbF_6$/0.2+1-AdCOOH/1.0+NaOAc/1.5	DCE	100	83	trace	trace

7	3:1	$AgSbF_6$/0.2+HOAc/1.0+NaOAc/1.5	DCE	100	78	trace	trace
8	2.5:1	$AgSbF_6$/0.2+HOAc/1.0+NaOAc/1.5	DCE	100	61	13	trace
9[c]	2.5:1	AgOTf/0.3+HOAc/1.0+NaOAc/1.5	DCE	100	95	trace	trace
10	2.5:1	AgOTf/0.3+HOAc/1.0+NaOAc/1.5	TFE	100	/	trace	/
11	2.5:1	AgOTf/0.3+HOAc/1.0+NaOAc/1.5	THF	100	/	/	/
12	2.5:1	AgOTf/0.3+HOAc/1.0+NaOAc/1.5	toluene	100	mess	/	/
13[d]	2.5:1	AgOTf/0.3+HOAc/1.0+NaOAc/1.5	DCE	60	27	/	/
14[d]	2.5:1	AgOTf/0.3+HOAc/1.0+NaOAc/1.5	DCE	80	55	/	/

[a]Reaction conditions unless otherwise specified: **1a** (3.0 equiv), **2a** (0.03 mmol), 5 mol % of $[Cp^*RhCl_2]_2$, 0.3 mL of DCE, 12 h under air atmosphere. [b]Isolated yield. [c]1.0 mL of DCE. [d]**1a** (2.5 equiv), **2a** (0.1 mmol).

Table S2. Additional reaction conditions for the product 4aa[a]

Entry	1a:2a	Additive/ equiv	Solvent	Temp./℃	Yield[b]/%		
					3aa	4aa	5aa
1[c]	1:3	$AgSbF_6$/0.2+ $Cu(OAc)_2·H_2O$/2.2	DCE	100	trace	/	trace
2[d]	1:3	$AgSbF_6$/0.2+ $Cu(OAc)_2·H_2O$/2.2	DCE	100	/	/	trace
3	1:3	AgTFA/0.2+ $Zn(OAc)_2·2H_2O$/1.5	DCE	100	trace	44	trace
4	1:3	$AgBF_4$/0.2+ $Zn(OAc)_2·2H_2O$/1.5	DCE	100	trace	48	trace
5	1:3	$AgSO_3CH_3$/0.2+ $Zn(OAc)_2·2H_2O$/1.5	DCE	100	trace	70	trace
6	1:3	$AgNTf_2$/0.2+ $Zn(OAc)_2·2H_2O$/1.5	DCE	80	13	45	trace
7	1:3	$AgNTf_2$/0.2+ $Zn(OAc)_2·2H_2O$/1.5	DCE	120	trace	30	trace
8	1:3	$AgNTf_2$/0.2+ $Zn(OAc)_2·2H_2O$/1.5	toluene	100	<10	31	/
9	1:3	$AgNTf_2$/0.2+ $Zn(OAc)_2·2H_2O$/1.5	CH3CN	100	trace	trace	/

[a]Reaction conditions unless otherwise specified: **1a** (0.1 mmol), **2a** (3.0 equiv), 5 mol % of $[Cp^*RhCl_2]_2$, 1.2 mL of DCE, 12 h under air atmosphere. [b] Isolated yield. [c]$[RuCl_2(p\text{-cymene})]_2$ (5 mol %). [d]$[Cp^*IrCl_2]_2$ (5 mol %).

Table S3. Additional reaction conditions for the product 5aa[a]

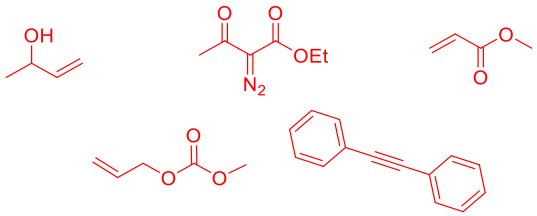
Entry	1a:2a	Additive/ equiv	Solvent	Temp./℃	Yield[b]/%		
					3aa	4aa	5aa
1	1:8	$AgBF_4$/0.5+$Cu(OAc)_2·H_2O$/2.2+NaOAc/2	DCE	100	/	/	42
2	1:6	$AgBF_4$/0.5+$Cu(OAc)_2·H_2O$/2.2+NaOAc/2	DCE	100	/	/	30
3	1:4	$AgBF_4$/0.5+$Cu(OAc)_2·H_2O$/2.2+NaOAc/2	DCE	100	/	/	27
4	1:10	$AgNTf_2$/0.3+$Cu(OAc)_2·H_2O$/2.2+NaOAc/2	DCE	100	/	/	32
5	1:10	$AgSbF_6$/0.3+ $Cu(OAc)_2·H_2O$/2.2+NaOAc/2	DCE	100	/	/	23
6	1:10	$AgSO_3CH_3$/0.3+$Cu(OAc)_2·H_2O$/2.2+NaOAc/2	DCE	100	/	/	34
7	1:10	$AgBF_4$/0.5+$Cu(OAc)_2·H_2O$/2.2+CsOAc/2	DCE	100	/	/	32
8	1:10	$AgBF_4$/0.5+$Cu(OAc)_2·H_2O$/2.2+KOAc/2	DCE	100	/	/	49
9	1:10	$Cu(OAc)_2·H_2O$/2.2+$NaBF_4$/2	DCE	100	/	/	31
10	1:10	$AgBF_4$/0.5+NaOAc/2	DCE	100	/	/	22
11	1:10	$AgBF_4$/0.5+AgOAc/2.2+NaOAc/2	DCE	100	/	/	34
12	1:10	$AgBF_4$/0.5+$AgCO_3$/2.2+NaOAc/2	DCE	100	/	/	21
13	1:10	$AgBF_4$/0.5+$Cu(acac)_2$ /2.2+NaOAc/2	DCE	100	/	/	45
14	1:10	$AgBF_4$/0.5+$Cu(OAc)_2·H_2O$/2.2+NaOAc/2	tol	100	/	/	36
15	1:10	$AgBF_4$/0.5+$Cu(OAc)_2·H_2O$/2.2+NaOAc/2	CH3CN	100	/	/	51
16	1:10	$AgBF_4$/0.5+$Cu(OAc)_2·H_2O$/2.2+NaOAc/2	DCE	80	/	/	52
17	1:10	$AgBF_4$/0.5+$Cu(OAc)_2·H_2O$/2.2+NaOAc/2	DCE	120	/	/	30

[a]Reaction conditions unless otherwise specified: **1a** (0.1 mmol), **2a** (10.0 equiv), 5 mol % of $[Cp^*RhCl_2]_2$, 1.2 mL of DCE, 12 h under Ar atmosphere. [b] Isolated yield.

4. The scope of substrates

Some coupling partners can't react with 2-phenoxy-1*H*-benzo[*d*]imidazole **1a**, giving no products unfortunately (Scheme S1).

Scheme S1. Unreacted coupling partners



5. General procedure for synthesis of diversified fused polycyclic benzimidazole derivatives

5.1 General procedure for the synthesis of 3aa

4-hydroxy-2-alkynoate **2a** (0.05 mmol, 7.8 mg), 2-phenoxy-1*H*-benzo[*d*]imidazole **1a** (2.5 equiv, 26.3 mg), $[Cp^*RhCl_2]_2$ (5.0 mol %, 1.6 mg), AgOTf (0.3 equiv, 3.9 mg), acetic acid (1.0 equiv, 6 μL) and sodium acetate (1.5 equiv, 6.2 mg) were stirred in DCE (0.5 mL) at 100 °C for 12 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (2:1) to give the product **3aa** as a white solid (15.2 mg, 95%).

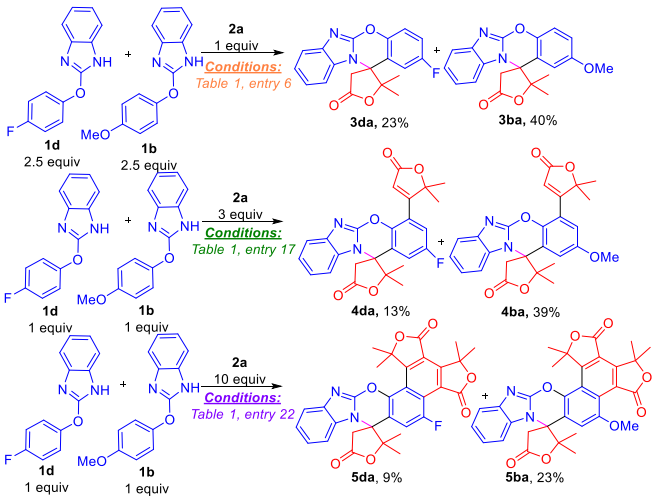
5.2 General procedure for the synthesis of 4aa

2-phenoxy-1*H*-benzo[*d*]imidazole **1a** (0.1 mmol, 21.0 mg), 4-hydroxy-2-alkynoate **2a** (3.0 equiv, 46.8 mg), $[Cp^*RhCl_2]_2$ (5.0 mol %, 3.1 mg), $AgNTf_2$ (0.3 equiv, 11.6 mg) and zinc acetate dihydrate (1.0 equiv, 21.9 mg) were stirred in DCE (1.0 mL) at 100 °C for 12 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:1) to give the product **4aa** as a white solid (34.8 mg, 81%).

5.3 General procedure for the synthesis of 5aa

2-phenoxy-1*H*-benzo[*d*]imidazole **1a** (0.1 mmol, 21.0 mg), 4-hydroxy-2-alkynoate **2a** (10.0 equiv, 156.0 mg), $[Cp^*RhCl_2]_2$ (5.0 mol %, 3.1 mg), $AgBF_4$ (0.3 equiv, 5.8 mg), sodium acetate (2.0 equiv, 16.4 mg) and cupric acetate monohydrate (2.2 equiv, 43.9 mg) were stirred in DCE (1.0 mL) at 100 °C for 12 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (2.5:1) to give the product **5aa** as a white solid (30.1 mg, 56%).

6. Intermolecular competition experiments



Following the general procedure for the synthesis of diversified fused polycyclic benzimidazole derivatives:

(1) 4-hydroxy-2-alkynoate **2a** (0.1 mmol, 15.6 mg), 2-(4-fluorophenoxy)-*1H*-benzo[*d*]imidazole **1d** (2.5 equiv, 28.5 mg), 2-(4-methoxyphenoxy)-*1H*-benzo[*d*]imidazole **1b** (2.5 equiv, 30.0 mg), $[Cp^*RhCl_2]_2$ (5.0 mol %, 3.1 mg), AgOTf (0.3 equiv, 3.9 mg), acetic acid (1.0 equiv, 6 μL) and sodium acetate (1.5 equiv, 6.2 mg) were stirred in DCE (0.5 mL) at 100 °C for 12 h. After consumption of substrates **2a**, using vacuum-rotary and evaporation procedure to remove DCE, and the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (2:1) to give the product **3da** (7.8 mg, 23%) and **3ba** (13.9 mg, 40%).

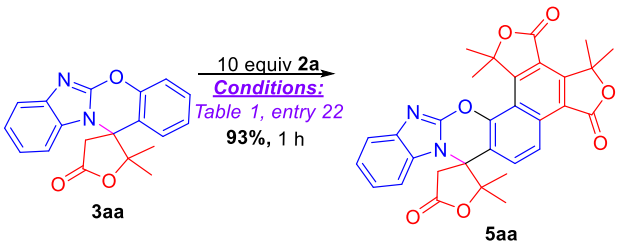
(2) 2-(4-fluorophenoxy)-*1H*-benzo[*d*]imidazole **1d** (0.05 mmol, 11.4 mg), 2-(4-methoxyphenoxy)-*1H*-benzo[*d*]imidazole **1b** (0.05 mmol, 12.0 mg), 4-hydroxy-2-alkynoate **2a** (3.0 equiv, 46.8 mg), $[Cp^*RhCl_2]_2$ (5.0 mol %, 3.1 mg), $AgNTf_2$ (0.3 equiv, 11.6 mg) and zinc acetate dihydrate (1.0 equiv, 21.9 mg) were stirred in DCE (0.5 mL) at 100 °C for 12 h. After consumption of substrates **1a**, using vacuum-rotary and evaporation procedure to remove DCE, and the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:1) to give the product **4da** (6.0 mg, 13%) and **4ba** (17.9 mg, 39%).

(3) 2-(4-fluorophenoxy)-*1H*-benzo[*d*]imidazole **1d** (0.05 mmol, 11.4 mg), 2-(4-methoxyphenoxy)-*1H*-benzo[*d*]imidazole **1b** (0.05 mmol, 12.0 mg), 4-hydroxy-2-alkynoate **2a** (10.0 equiv, 156.0 mg), $[Cp^*RhCl_2]_2$ (5.0 mol %, 3.1 mg), $AgBF_4$ (0.3 equiv, 5.8 mg), sodium acetate (2.0 equiv, 16.4 mg) and cupric acetate monohydrate (2.2 equiv, 43.9 mg) were stirred in DCE (1.0 mL) at 100 °C for 12 h. After consumption of substrates **1a**, using vacuum-rotary and evaporation procedure to remove DCE, and the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:1) to give the product **5da** (5.1 mg, 9%) and **5ba** (13.1 mg, 23%).

In conclusions, three groups of intermolecular competition experiments imply that electron-rich substituents were more appropriate for the cascade cyclization.

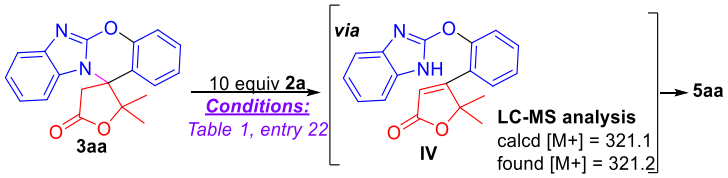
7. Mechanistic study

7.1 Experiments conducted to identify the reaction intermediates IV



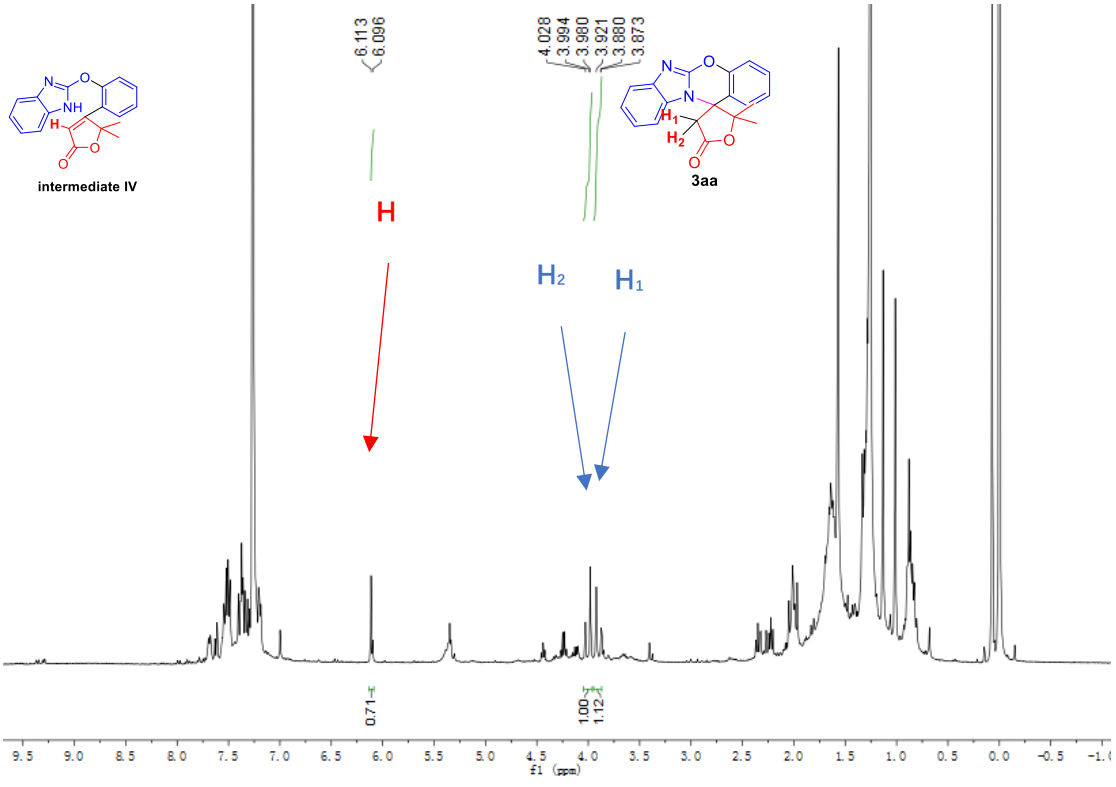
Under reaction conditions (Table 1, entry 26), the product **3aa** can be almost completely converted to **5aa** with 93% yield within 1 h. During the reaction process, through TLC thin-layer chromatography, crude NMR, and LC-MS analysis, it was confirmed that **3aa** can be underwent retro-Michael addition to generate ring-opened alkenyl intermediates **IV**.

We have conducted detail mechanistic studies by analyzing the crude reaction mixture of control experiments by LC-MS analysis. The LC-MS spectra are provided below. The characteristic signals indicate the presence of the important intermediate or the fragment of the intermediates. The presence of a sharp signal at m/z 321.2 indicates the formation of intermediate **IV** (Figure S1).



a. Identification of intermediate IV by crude NMR analysis

The reaction of conversion from **3aa** to **5aa** was quenched in 10 minutes. The target product was simply separated by thin-layer chromatography and sent it for crude NMR analysis.



b. Identification of intermediate IV by LC-MS analysis.

Sample I：the crude reaction mixture (10 min）

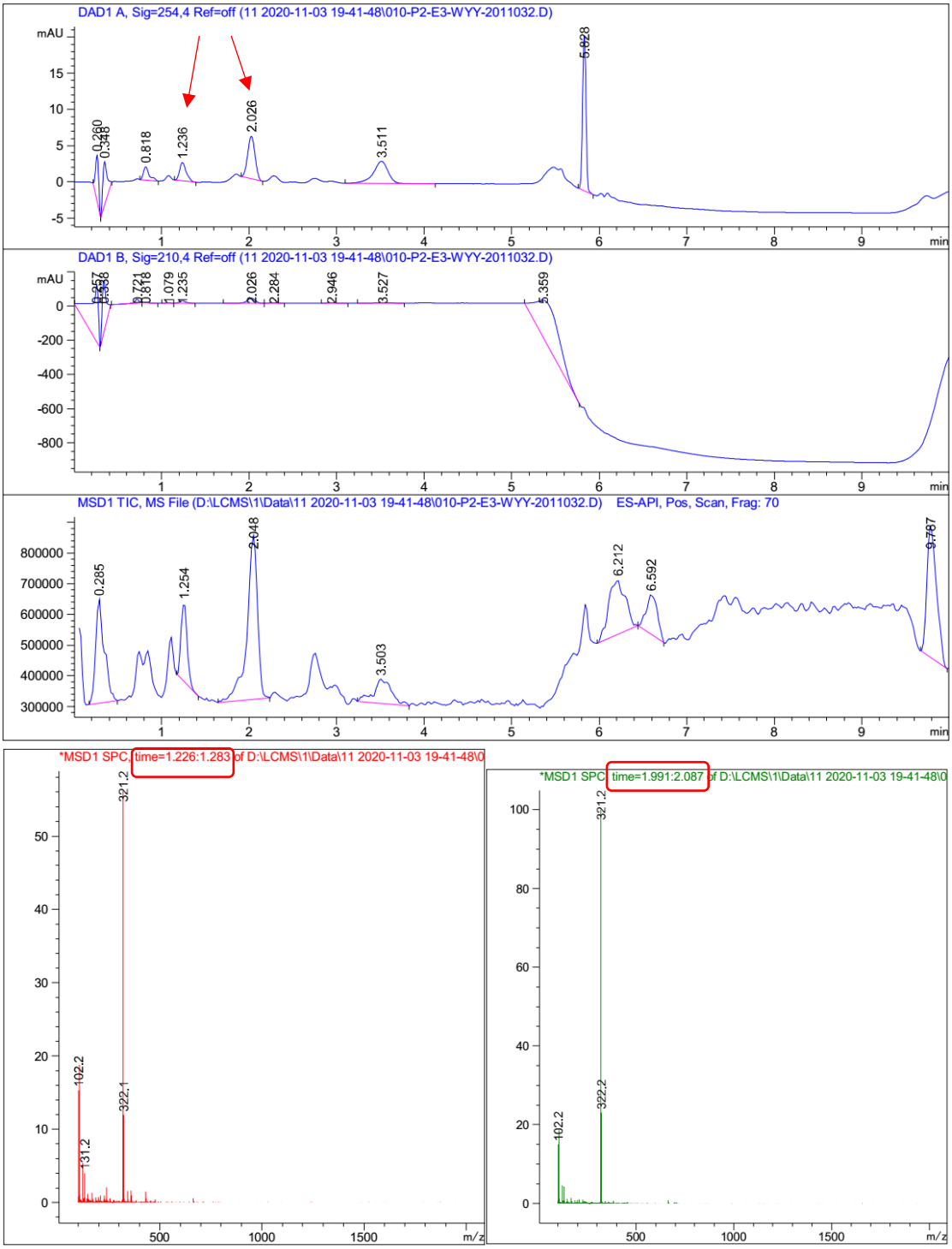


Figure S1. LC-MS analysis of sample I

Sample II：Add standard product **3aa** to the crude reaction mixture (10 minutes)

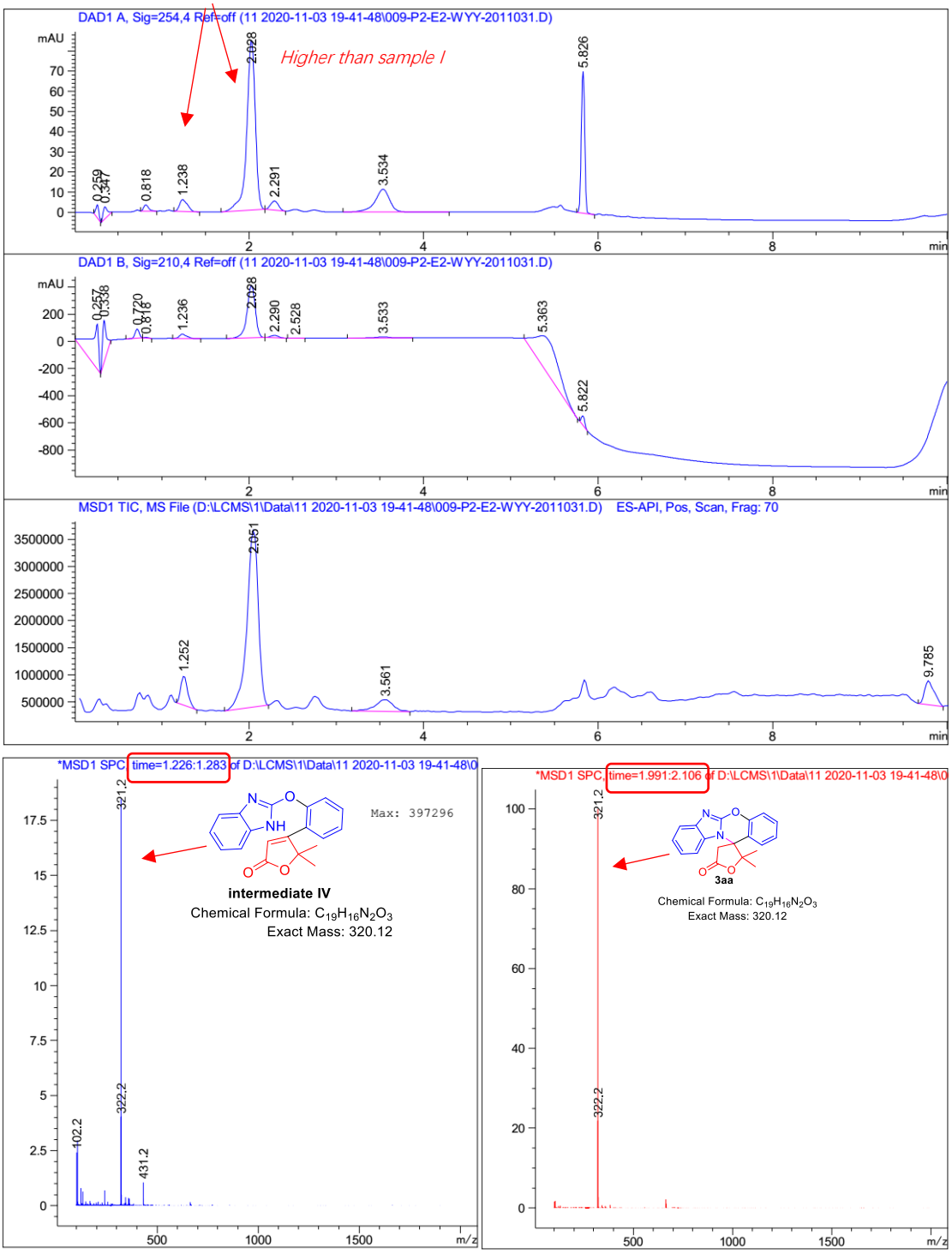


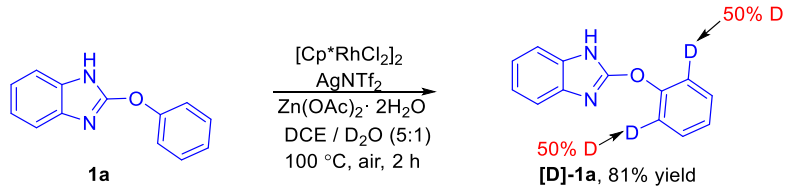
Figure S2. LC-MS analysis of sample II

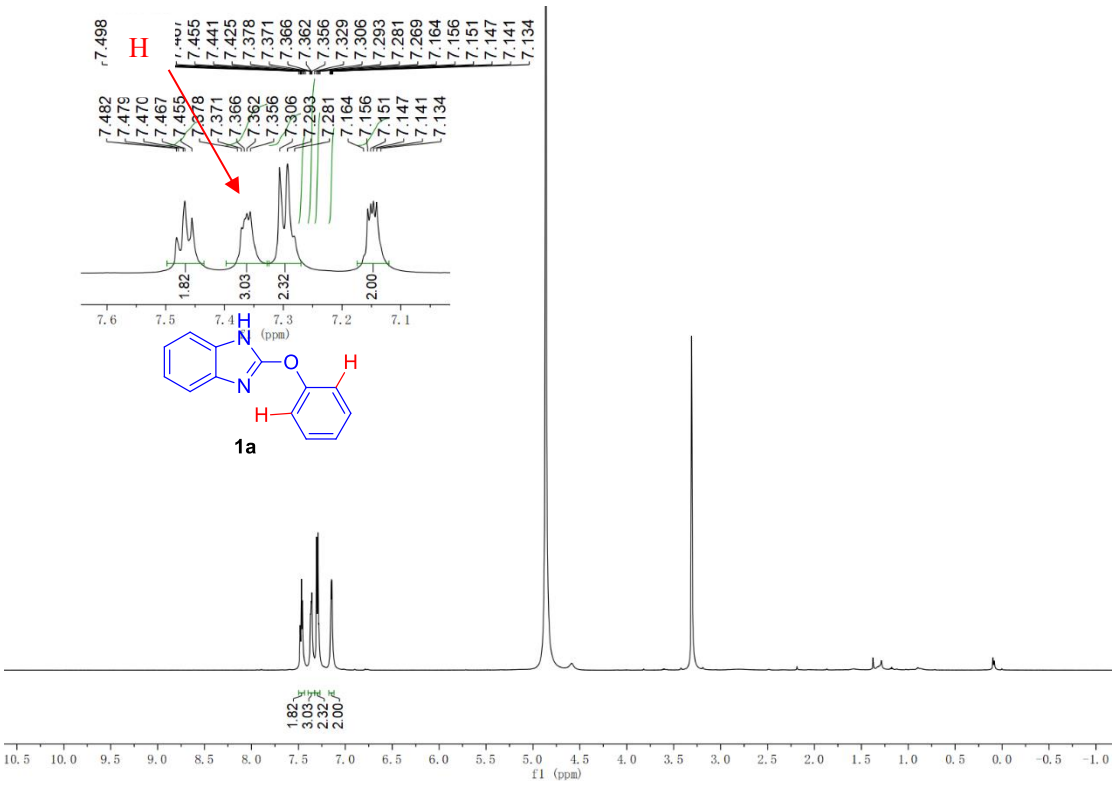
The appearance times of the ion peaks of the two samples are basically the same, and the addition of the standard product **3aa** in the sample II makes the second ion abundance significantly increased, indicating that the peak that appears later is **3aa**, and the peak that appears first is intermediate **IV**.

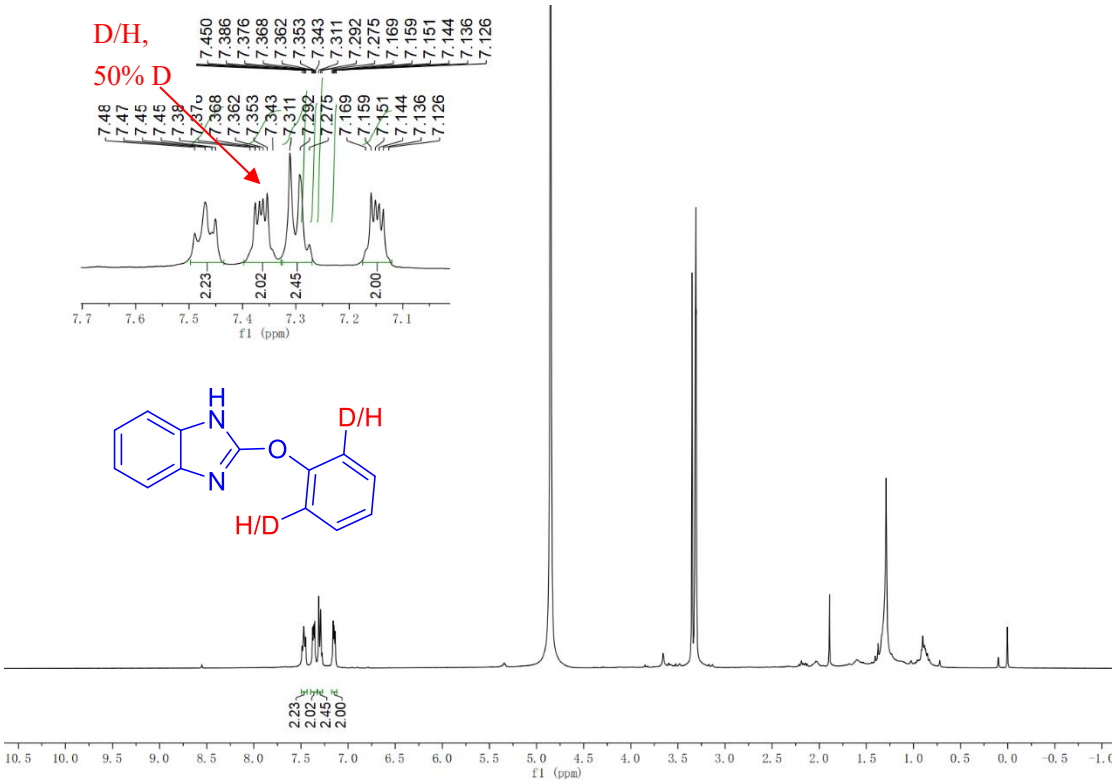
7.2 Deuterium-labeling experiment

2-phenoxy benzimidazole **1a** (0.05 mmol, 10.5 mg), $[Cp^*RhCl_2]_2$ (5.0 mol %, 1.5 mg), $AgNTf_2$ (5.8 mg, 30 mol%) and $Zn(OAc)_2 \cdot 2H_2O$ (11.0 mg, 1 equiv.) were stirred in DCE:D_2O (5:1) at 100

°C for 2 h. After completion, the mixture was purified by flash chromatography eluting giving the product **[D]-1a** as a white solid (8.5 mg, 81%). The deuterium rate (81% at *ortho*-positions of phenyl group) was obtained from ^{1}H NMR, which indicated the possibility of the C-H activation via the *ortho*-positions of phenyl group.



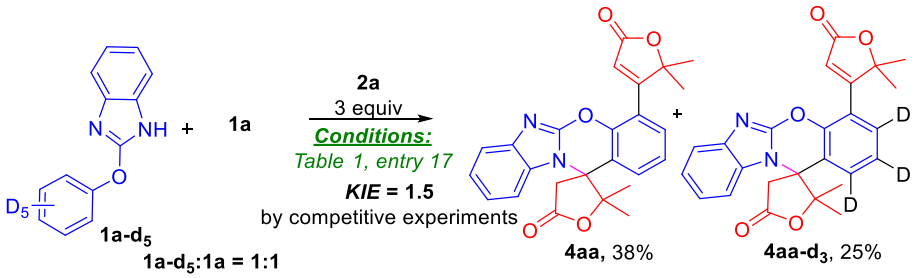


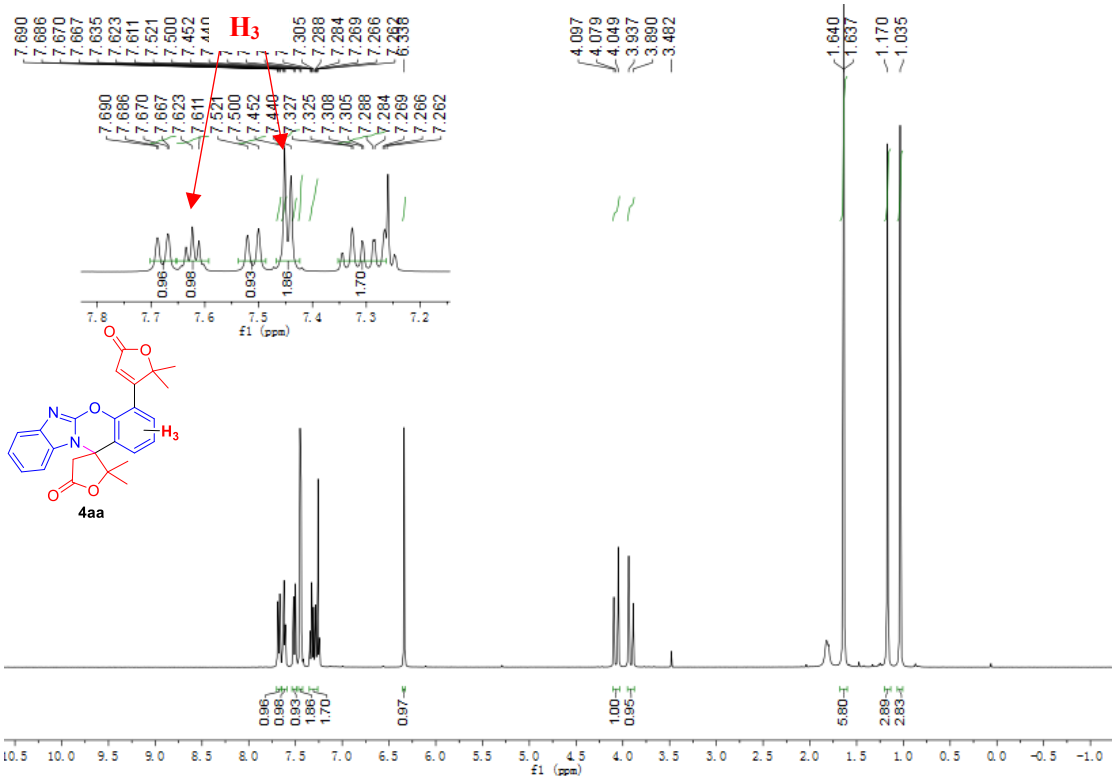


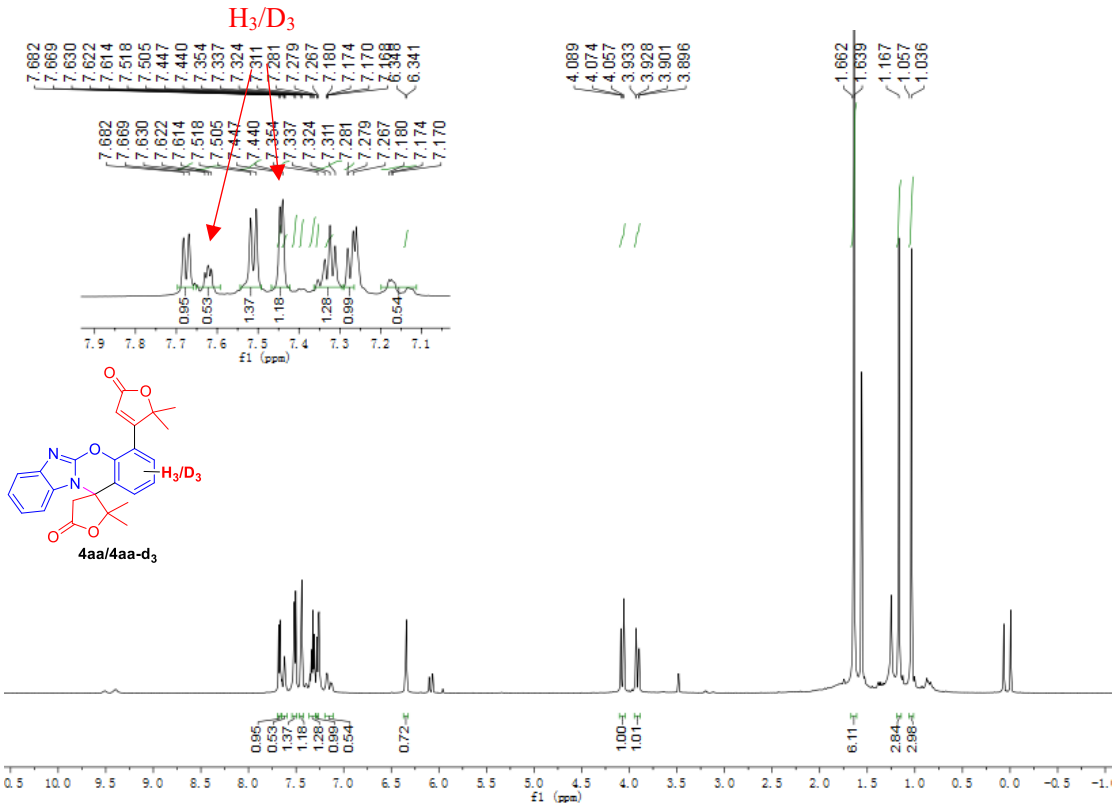
7.3 Kinetic isotope experiments

(1) Competitive Kinetic isotope experiments

To a flask charged with 2-phenoxy benzimidazole **1a** (0.05 mmol) and **1a**-d_5 (0.05 mmol), propargyl alcohol **2a** (0.3 mmol), $[Cp^*RhCl_2]_2$ (3 mg, 5 mol%), $AgNTf_2$ (11.6 mg, 30 mol%) and $Zn(OAc)_2 \cdot 2H_2O$ (21.9 mg, 1 equiv.) were stirred in DCE (1.0 mL). The reaction mixture was stirred at 100 °C for 12 h under air atmosphere. After cooled to room temperature, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:1) to give the product **4aa** /**4aa-d$_3$** as a white solid (27.5 mg, 64%). The ratio of two products was determined by ^{1}H NMR to give kinetic isotopic effect (KIE) k_H/k_D = 1.5, and thus indicated that the first C–H bond cleavage might not be involved in the rate-determining step.



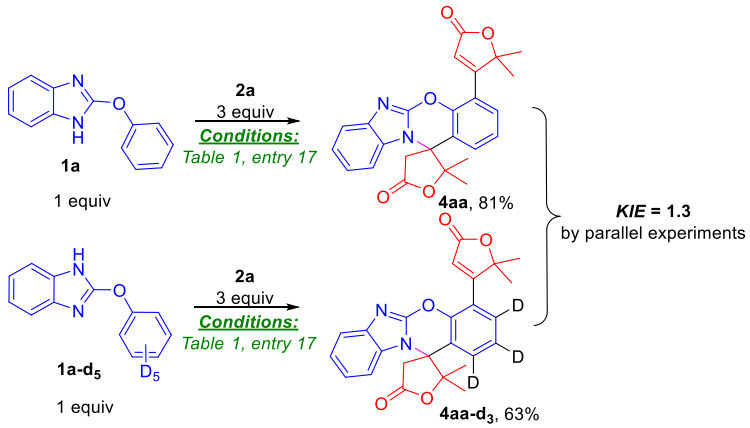




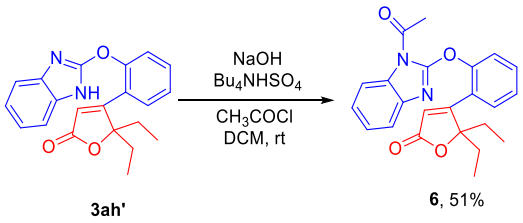
(2) Parallel Kinetic isotope experiments

To a flask charged with 2-phenoxy benzimidazole **1a** or **1a**-d_5 (0.1 mmol), propargyl alcohol **2a** (0.3 mmol), $[Cp^*RhCl_2]_2$ (3 mg, 5 mol%), $AgNTf_2$ (11.6 mg, 30 mol%) and $Zn(OAc)_2{\cdot}2H_2O$ (21.9 mg, 1 equiv.) were stirred in DCE (1.0 mL). The reaction mixture was stirred at 100 °C for 12 h under air atmosphere. After cooled to room temperature, the reaction mixture was purified by flash

chromatography eluting with ethyl acetate and petroleum ether (1:1) to give the product **4aa /4aa-d_3** as a white solid. The ratio of two products was determined by yieleds to give kinetic isotopic effect (KIE) k_H/k_D = 1.3, and thus indicated that the first C−H bond cleavage might not be involved in the rate-determining step.

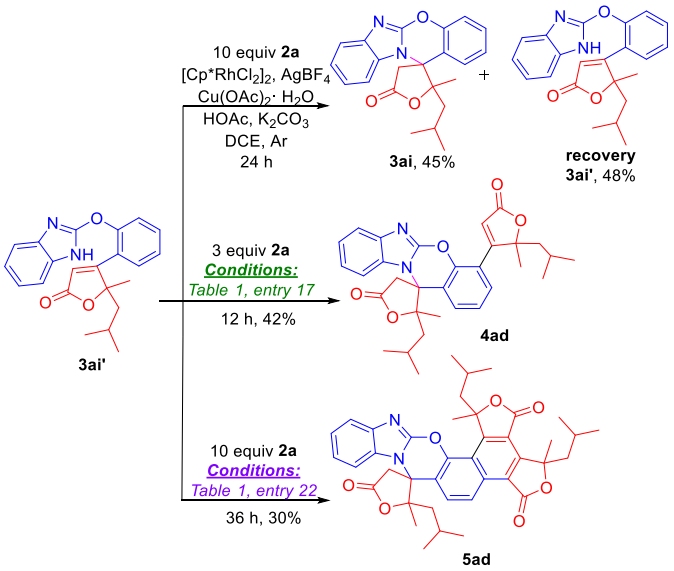


7.4 Procedure synthesis of compound 6 to verify the presence of N-H active hydrogen



NaOH (0.5 mmol, 2.5 equiv) and Bu_4NHSO_4 (12 mol %) were added to a solution of compound **3ah'** (0.2 mmol, 1 equiv) in DCM (1.0 mL), then CH_3COCl (0.3 mmol, 1.5 equiv) in DCM (1.0 mL) was added into the mixture solution and stirred at room temperature for 8 h. Upon completion, the mixture was concentrated and the residue was purified by chromatography on silica gel eluting with ethyl acetate and petroleum ether (1:2) to obtain compound **6** as white solid (39.8 mg, 51%).

7.5 Study of the ring-opened alkenyl product



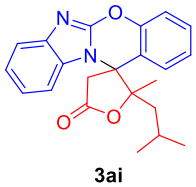
To further prove the existence of alkenyl intermediate, a series of conversion reactions from **3ai'** were conducted (Scheme 5). Fortunately, three different cyclization products were isolated respectively.

4-(2-((1*H*-benzo[*d*]imidazol-2-yl)oxy)phenyl)-5-isobutyl-5-methylfuran-2(5*H*)-one **3ai'** (0.1 mmol, 36.2 mg), 4-hydroxy-2-alkynoate **2a** (10.0 equiv, 156.0 mg), $[Cp^*RhCl_2]_2$ (5.0 mol %, 3.1 mg), $AgBF_4$ (0.3 equiv, 5.8 mg), acetic acid (1.0 equiv, 6 μL), potassium carbonate (2.0 equiv, 27.6 mg) and cupric acetate monohydrate (2.2 equiv, 43.9 mg) were stirred in DCE (1.0 mL) at 100 °C for 24 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (2:1) to give the product **3ai** as a white solid (16.3 mg, 45%). The two products **3ai** and **3ai'** are similar in polarity and difficult to separate. The spectrum is attached below.

4-(2-((1*H*-benzo[*d*]imidazol-2-yl)oxy)phenyl)-5-isobutyl-5-methylfuran-2(5*H*)-one **3ai'** (0.1 mmol, 36.2 mg), 4-hydroxy-2-alkynoate **2a** (3.0 equiv, 46.8 mg), $[Cp^*RhCl_2]_2$ (5.0 mol %, 3.1 mg), $AgNTf_2$ (0.3 equiv, 11.6 mg) and zinc acetate dihydrate (1.0 equiv, 21.9 mg) were stirred in DCE (1.0 mL) at 100 °C for 12 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:1) to give the product **4ad** as a white solid (21.6 mg, 42%).

4-(2-((1*H*-benzo[*d*]imidazol-2-yl)oxy)phenyl)-5-isobutyl-5-methylfuran-2(5*H*)-one **3ai'** (0.1 mmol, 36.2 mg), 4-hydroxy-2-alkynoate **2a** (10.0 equiv, 156.0 mg), $[Cp^*RhCl_2]_2$ (5.0 mol %, 3.1 mg), $AgBF_4$ (0.3 equiv, 5.8 mg), sodium acetate (2.0 equiv, 16.4 mg) and cupric acetate monohydrate (2.2 equiv, 43.9 mg) were stirred in DCE (1.0 mL) at 100 °C for 36 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (2.5:1) to give the product **5ad** as a yellow solid (19.9 mg, 30%).

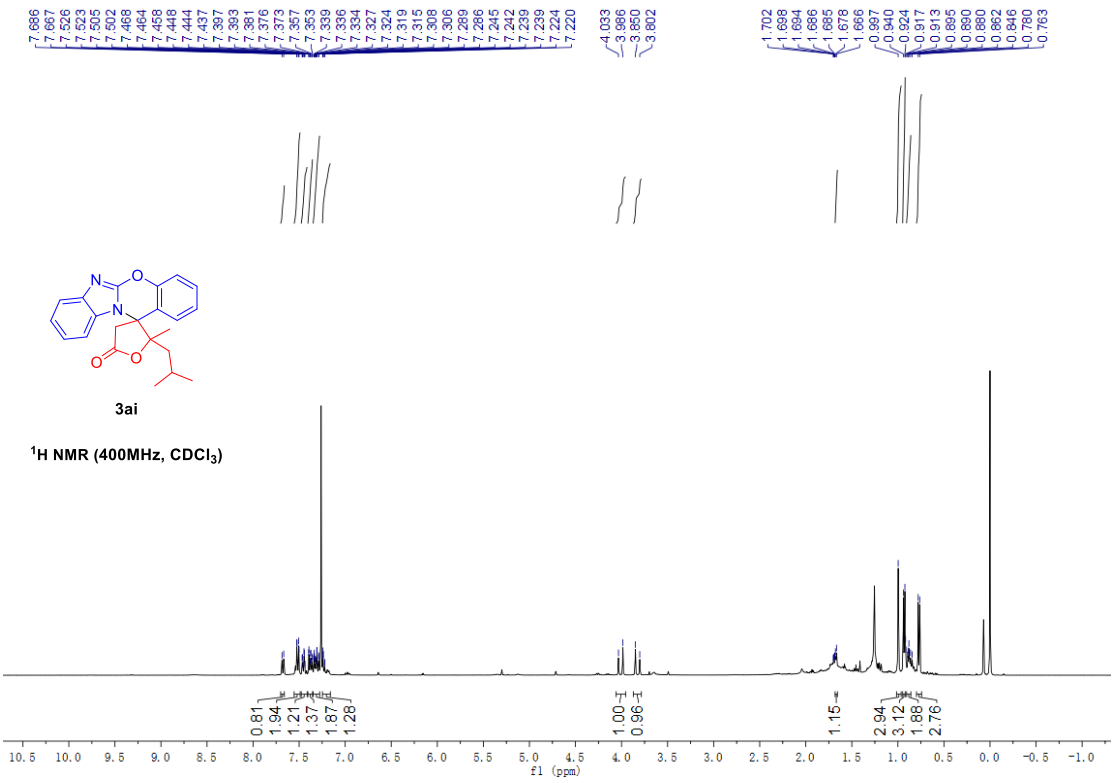
2'-isobutyl-2'-methyl-2'*H*-spiro[benzo[*e*]benzo[4,5]imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-5'(4'*H*)-one (3ai)

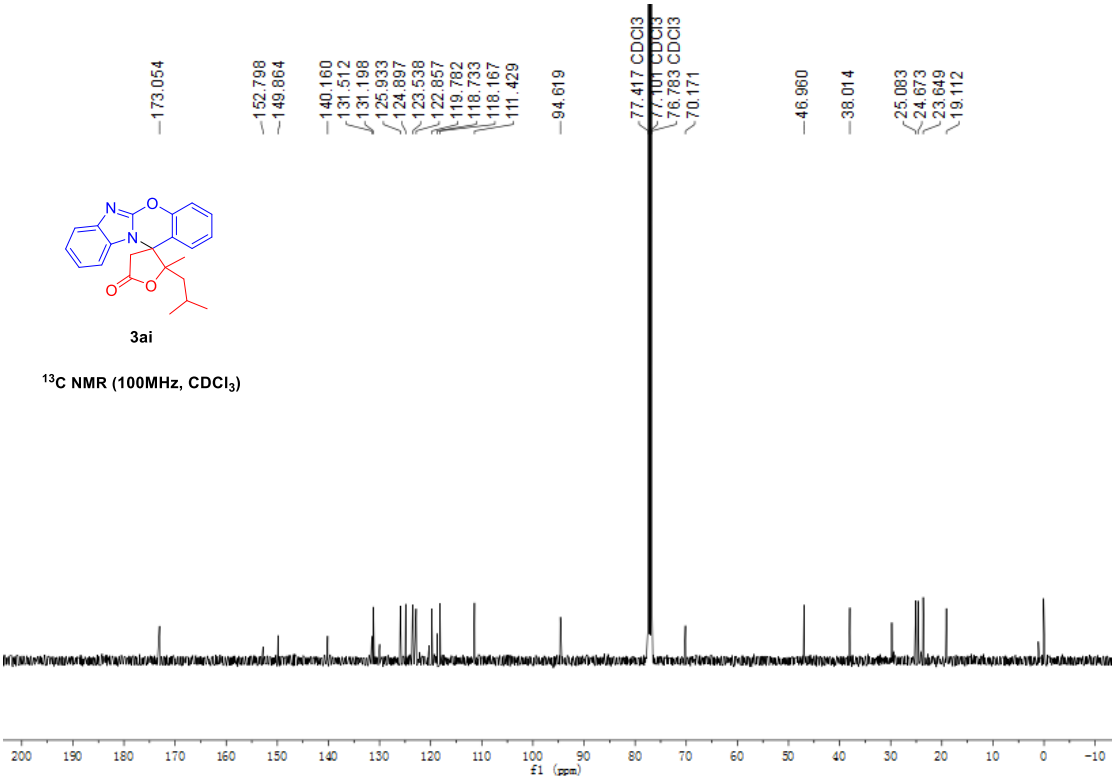


3ai

45% yield; light yellow solid; mp = 154.1-156.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.4 Hz, 1H), 7.51 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.45 (dt, *J* = 8.7, 2.2 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.35 – 7.28 (m, 2H), 7.25 – 7.16 (m, 1H), 4.01 (d, *J* = 19.1 Hz, 1H), 3.83 (d, *J* = 19.0 Hz, 1H), 1.67 (d, *J* = 4.6 Hz, 1H), 1.00 (s, 3H), 0.93 (d, *J*

= 6.4 Hz, 3H), 0.88 (t, *J* = 5.5 Hz, 2H), 0.77 (d, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.05, 152.80, 149.86, 140.16, 131.51, 131.20, 125.93, 124.90, 123.54, 122.86, 119.78, 118.73, 118.17, 111.43, 94.62, 70.17, 46.96, 38.01, 25.08, 24.67, 23.65, 19.11 ppm. $C_{22}H_{22}N_2O_3$+H 363.1709, found 363.1705.





8. X-ray Data of Compound 3aa, 4aa, 5aa and sample preparation

8.1 Sample preparation and crystal measurement

Single crystals suitable for X-ray diffraction experiment were obtained by slow evaporation of DCM/ methanol (10:1, V/V) solution, DCM/ petroleum ether (1:10, V/V) solution, DCM/ methanol (5:1, V/V) solution containing the corresponding compound **3aa**, **4aa**, **5aa**, respectively. The crystal was kept at 293.15 K during data collection with an Xcalibur Eos Gemini diffractometer using graphitemonochromatized enhance X-ray source Mo-Kα (λ=0.71073 Å) radiation for **3aa**. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation.

8.2 X-ray data of compound 3aa

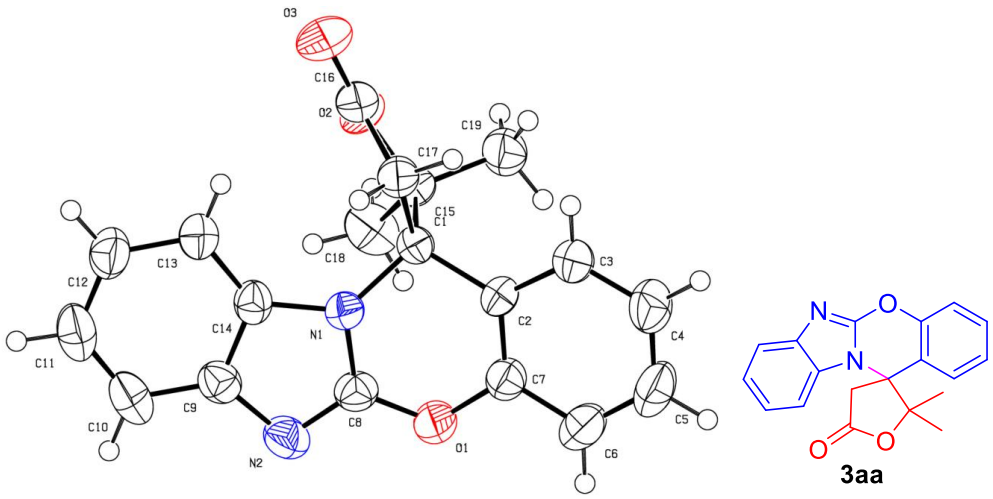


Figure S3. X-ray structure of 3aa. ORTEP plots for molecular structure of 3aa with the probability at 50% level.

CCDC 2027113 contains the crystal data and supplementary crystallographic data as following:

X-ray data of compound 3aa ($C_{19}H_{16}N_2O_3$): CCDC 2027113

Table S4. Crystal data and structure refinement.

Empirical formula	$C_{19}H_{16}N_2O_3$
Formula weight	320.34
Temperature/K	293.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.8130(9)
b/Å	10.0583(12)
c/Å	15.7918(15)
α/°	90
β/°	92.027(9)
γ/°	90
Volume/Å^3	1716.4(3)
Z	4
ρ_{calc}g/cm^3	1.240
μ/mm^{-1}	0.085
F(000)	672.0
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.05 to 52.742
Index ranges	-13 ≤ h ≤ 13, -12 ≤ k ≤ 8, -13 ≤ l ≤ 19
Reflections collected	7295
Independent reflections	3507 [R_{int} = 0.0248, R_{sigma} = 0.0528]
Data/restraints/parameters	3507/0/219
Goodness-of-fit on F^2	1.009
Final R indexes [I>=2σ (I)]	R_1 = 0.0548, wR_2 = 0.1368
Final R indexes [all data]	R_1 = 0.0935, wR_2 = 0.1501
Largest diff. peak/hole / e Å-3	0.20/-0.20

Table S5. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	7959.5(13)	-41.5(15)	4734.8(11)	54.1(5)
O2	6329.4(15)	3643.7(17)	3032.7(10)	58.1(5)
O3	4688.0(18)	4818(2)	3383.5(15)	87.1(7)
N1	6192.3(15)	1081.3(18)	4202.0(11)	38.5(4)
N2	6325.9(17)	-1150(2)	4104.1(13)	51.7(5)
C1	6753.8(17)	2416(2)	4301.4(13)	36.3(5)
C2	7719.4(18)	2293(2)	5019.7(13)	37.2(5)

C3	8097(2)	3359(2)	5510.9(15)	49.7(6)
C4	9046(2)	3246(3)	6104.9(16)	62.0(7)
C5	9618(2)	2041(3)	6231.1(16)	66.0(8)
C6	9240(2)	960(3)	5775.3(16)	58.1(7)
C7	8291.7(19)	1111(2)	5174.4(14)	43.5(6)
C8	6841(2)	-50(2)	4353.0(14)	43.4(6)
C9	5218(2)	-736(2)	3722.5(14)	45.1(6)
C10	4318(2)	-1509(3)	3329.8(16)	57.5(7)
C11	3290(2)	-866(3)	2988.4(16)	61.0(7)
C12	3170(2)	505(3)	3035.4(16)	61.3(7)
C13	4070(2)	1296(3)	3431.9(16)	52.6(6)
C14	5101.4(19)	649(2)	3767.1(13)	41.3(5)
C15	7329.5(19)	2886(2)	3440.5(13)	41.9(5)
C16	5496(2)	4062(3)	3588.1(18)	57.2(7)
C17	5770(2)	3470(2)	4432.0(15)	47.1(6)
C18	7635(3)	1781(3)	2841.2(16)	63.1(7)
C19	8400(2)	3834(3)	3570.8(16)	56.2(7)

Table S6. Bond Lengths.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C7	1.392(3)	C2	C7	1.358(3)
O1	C8	1.332(3)	C3	C4	1.370(3)
O2	C15	1.455(3)	C4	C5	1.372(4)
O2	C16	1.347(3)	C5	C6	1.358(4)
O3	C16	1.194(3)	C6	C7	1.381(3)
N1	C1	1.479(3)	C9	C10	1.376(3)
N1	C8	1.353(3)	C9	C14	1.400(3)
N1	C14	1.412(3)	C10	C11	1.379(3)
N2	C8	1.294(3)	C11	C12	1.388(4)
N2	C9	1.386(3)	C12	C13	1.388(3)
C1	C2	1.519(3)	C13	C14	1.381(3)
C1	C15	1.587(3)	C15	C18	1.504(3)
C1	C17	1.522(3)	C15	C19	1.509(3)
C2	C3	1.377(3)	C16	C17	1.480(3)

Table S7. Bond Angles.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	O1	C7	116.42(17)	N2	C8	O1	121.1(2)
C16	O2	C15	112.30(18)	N2	C8	N1	116.8(2)
C8	N1	C1	122.39(17)	N2	C9	C14	110.8(2)
C8	N1	C14	104.22(18)	C10	C9	N2	127.8(2)
C14	N1	C1	131.58(18)	C10	C9	C14	121.4(2)

C8	N2	C9	103.34(19)	C9	C10	C11	117.3(2)
N1	C1	C2	105.89(17)	C10	C11	C12	121.4(2)
N1	C1	C15	110.57(16)	C11	C12	C13	121.9(2)
N1	C1	C17	111.14(16)	C14	C13	C12	116.5(2)
C2	C1	C15	112.57(15)	C9	C14	N1	104.80(19)
C2	C1	C17	114.89(18)	C13	C14	N1	133.7(2)
C17	C1	C15	101.88(17)	C13	C14	C9	121.5(2)
C3	C2	C1	122.6(2)	O2	C15	C1	103.13(15)
C7	C2	C1	120.2(2)	O2	C15	C18	106.57(19)
C7	C2	C3	117.1(2)	O2	C15	C19	106.47(18)
C4	C3	C2	121.4(2)	C18	C15	C1	114.89(19)
C3	C4	C5	119.7(3)	C18	C15	C19	111.62(19)
C6	C5	C4	120.3(2)	C19	C15	C1	113.19(17)
C5	C6	C7	118.6(3)	O2	C16	C17	110.1(2)
C2	C7	O1	122.1(2)	O3	C16	O2	121.5(3)
C2	C7	C6	122.9(2)	O3	C16	C17	128.4(3)
C6	C7	O1	115.1(2)	C16	C17	C1	106.07(19)
O1	C8	N1	122.1(2)				

8.3 X-ray data of compound 4aa

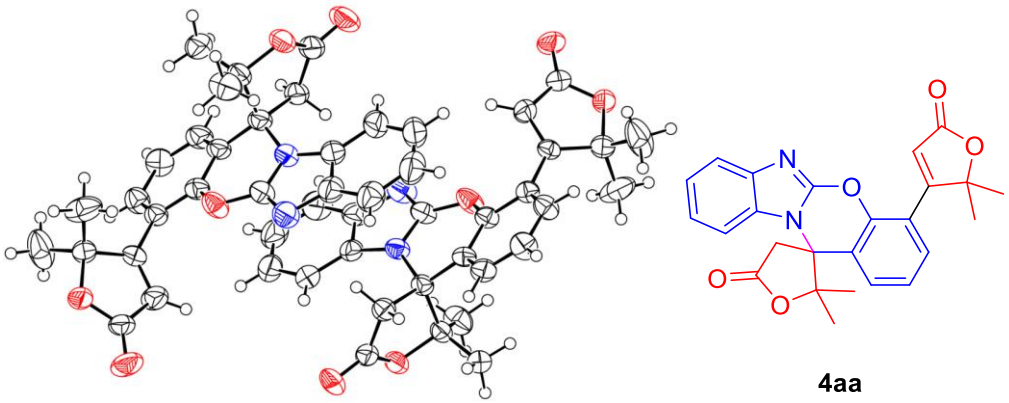


Figure S4. X-ray structure of 4aa. ORTEP plots for molecular structure of 4aa with the probability at 50% level.

CCDC 2027134 contains the crystal data and supplementary crystallographic data as following:

X-ray data of compound 4aa ($C_{25}H_{22}N_2O_5$): CCDC 2027134

Table S8. Crystal data and structure refinement.

Empirical formula	$C_{25}H_{22}N_2O_5$
Formula weight	430.44
Temperature/K	293.15
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	17.9537(5)
b/Å	13.2164(4)

c/Å	18.0414(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4280.9(2)
Z	8
ρ_{calc}g/cm^3	1.336
μ/mm^{-1}	0.094
F(000)	1808.0
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.166 to 52.744
Index ranges	-21 ≤ h ≤ 22, -16 ≤ k ≤ 16, -22 ≤ l ≤ 15
Reflections collected	18272
Independent reflections	7278 [R_{int} = 0.0235, R_{sigma} = 0.0372]
Data/restraints/parameters	7278/1/585
Goodness-of-fit on F^2	1.014
Final R indexes [I>=2σ (I)]	R_1 = 0.0429, wR_2 = 0.0860
Final R indexes [all data]	R_1 = 0.0653, wR_2 = 0.0951
Largest diff. peak/hole / e Å^{-3}	0.14/-0.18
Flack parameter	0.5(4)

Table S9. Bond Lengths.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C7	1.389(4)	O6	C32	1.391(4)
O1	C8	1.343(4)	O6	C33	1.344(4)
O2	C15	1.465(4)	O7	C40	1.468(4)
O2	C16	1.348(4)	O7	C41	1.345(4)
O3	C16	1.197(4)	O8	C41	1.192(4)
O4	C21	1.470(3)	O9	C46	1.460(3)
O4	C22	1.340(3)	O9	C47	1.334(4)
O5	C22	1.206(3)	O10	C47	1.207(4)
N1	C8	1.287(4)	N3	C33	1.290(4)
N1	C9	1.398(4)	N3	C34	1.393(4)
N2	C1	1.486(4)	N4	C26	1.474(4)
N2	C8	1.364(4)	N4	C33	1.366(4)
N2	C14	1.420(4)	N4	C39	1.409(4)
C1	C2	1.522(4)	C26	C27	1.517(5)
C1	C15	1.577(4)	C26	C40	1.584(5)
C1	C17	1.531(4)	C26	C42	1.524(4)
C2	C3	1.388(4)	C27	C28	1.385(5)
C2	C7	1.381(4)	C27	C32	1.383(4)

C3	C4	1.372(5)	C28	C29	1.374(5)
C4	C5	1.382(5)	C29	C30	1.383(5)
C5	C6	1.382(4)	C30	C31	1.386(5)
C6	C7	1.389(4)	C31	C32	1.394(5)
C6	C20	1.483(4)	C31	C45	1.482(4)
C9	C10	1.388(5)	C34	C35	1.388(5)
C9	C14	1.394(4)	C34	C39	1.399(5)
C10	C11	1.372(5)	C35	C36	1.368(6)
C11	C12	1.376(6)	C36	C37	1.379(6)
C12	C13	1.378(5)	C37	C38	1.375(6)
C13	C14	1.382(4)	C38	C39	1.397(5)
C15	C18	1.514(5)	C40	C43	1.511(5)
C15	C19	1.500(5)	C40	C44	1.513(5)
C16	C17	1.501(5)	C41	C42	1.502(5)
C20	C21	1.507(4)	C45	C46	1.504(4)
C20	C23	1.317(4)	C45	C48	1.314(4)
C21	C24	1.505(6)	C46	C49	1.509(6)
C21	C25	1.502(6)	C46	C50	1.490(6)
C22	C23	1.451(4)	C47	C48	1.444(4)

Table S10. Bond Angles.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	O1	C7	117.7(2)	C33	O6	C32	117.5(3)
C16	O2	C15	110.8(3)	C41	O7	C40	110.5(3)
C22	O4	C21	110.2(2)	C47	O9	C46	110.1(2)
C8	N1	C9	102.6(3)	C33	N3	C34	103.0(3)
C8	N2	C1	121.5(2)	C33	N4	C26	121.5(3)
C8	N2	C14	103.6(2)	C33	N4	C39	103.9(3)
C14	N2	C1	132.1(2)	C39	N4	C26	132.2(3)
N2	C1	C2	106.2(2)	N4	C26	C27	106.8(2)
N2	C1	C15	110.6(2)	N4	C26	C40	110.6(3)
N2	C1	C17	109.5(2)	N4	C26	C42	110.2(3)
C2	C1	C15	113.1(2)	C27	C26	C40	112.3(3)
C2	C1	C17	116.5(3)	C27	C26	C42	116.3(3)
C17	C1	C15	100.9(2)	C42	C26	C40	100.7(2)
C3	C2	C1	123.0(3)	C28	C27	C26	123.7(3)
C7	C2	C1	119.9(3)	C32	C27	C26	119.4(3)
C7	C2	C3	116.9(3)	C32	C27	C28	116.8(3)
C4	C3	C2	120.8(3)	C29	C28	C27	121.4(3)
C3	C4	C5	120.7(3)	C28	C29	C30	120.5(4)
C4	C5	C6	120.6(3)	C29	C30	C31	120.3(4)
C5	C6	C7	117.0(3)	C30	C31	C32	117.4(3)
C5	C6	C20	123.1(3)	C30	C31	C45	122.8(3)
C7	C6	C20	119.9(3)	C32	C31	C45	119.9(3)

O1	C7	C6	115.1(2)	O6	C32	C31	115.4(3)
C2	C7	O1	120.9(3)	C27	C32	O6	121.0(3)
C2	C7	C6	124.0(3)	C27	C32	C31	123.6(3)
O1	C8	N2	121.3(3)	O6	C33	N4	121.3(3)
N1	C8	O1	121.0(3)	N3	C33	O6	121.7(3)
N1	C8	N2	117.6(3)	N3	C33	N4	117.1(3)
C10	C9	N1	127.7(3)	N3	C34	C39	111.0(3)
C10	C9	C14	120.9(3)	C35	C34	N3	128.6(4)
C14	C9	N1	111.4(3)	C35	C34	C39	120.4(4)
C11	C10	C9	118.0(4)	C36	C35	C34	118.6(4)
C10	C11	C12	120.8(4)	C35	C36	C37	120.9(4)
C11	C12	C13	122.1(4)	C38	C37	C36	122.1(4)
C12	C13	C14	117.5(3)	C37	C38	C39	117.4(4)
C9	C14	N2	104.8(3)	C34	C39	N4	105.1(3)
C13	C14	N2	134.5(3)	C38	C39	N4	134.4(4)
C13	C14	C9	120.6(3)	C38	C39	C34	120.5(4)
O2	C15	C1	102.4(2)	O7	C40	C26	102.7(2)
O2	C15	C18	106.2(2)	O7	C40	C43	106.5(3)
O2	C15	C19	108.1(3)	O7	C40	C44	106.4(3)
C18	C15	C1	112.3(3)	C43	C40	C26	113.1(3)
C19	C15	C1	115.1(3)	C43	C40	C44	111.7(3)
C19	C15	C18	111.8(3)	C44	C40	C26	115.3(3)
O2	C16	C17	109.9(3)	O7	C41	C42	110.2(3)
O3	C16	O2	121.3(3)	O8	C41	O7	121.3(4)
O3	C16	C17	128.9(3)	O8	C41	C42	128.5(4)
C16	C17	C1	104.8(3)	C41	C42	C26	105.1(3)
C6	C20	C21	123.4(2)	C31	C45	C46	122.5(3)
C23	C20	C6	127.6(3)	C48	C45	C31	128.6(3)
C23	C20	C21	108.8(3)	C48	C45	C46	108.6(3)
O4	C21	C20	102.6(2)	O9	C46	C45	102.7(2)
O4	C21	C24	105.9(3)	O9	C46	C49	108.2(3)
O4	C21	C25	108.2(3)	O9	C46	C50	107.0(3)
C24	C21	C20	115.4(4)	C45	C46	C49	111.0(3)
C25	C21	C20	112.0(3)	C50	C46	C45	115.6(3)
C25	C21	C24	111.9(4)	C50	C46	C49	111.5(3)
O4	C22	C23	108.1(2)	O9	C47	C48	108.3(3)
O5	C22	O4	121.3(3)	O10	C47	O9	121.1(3)
O5	C22	C23	130.6(3)	O10	C47	C48	130.6(3)
C20	C23	C22	110.2(3)	C45	C48	C47	110.1(3)

8.4 X-ray data of compound 5aa

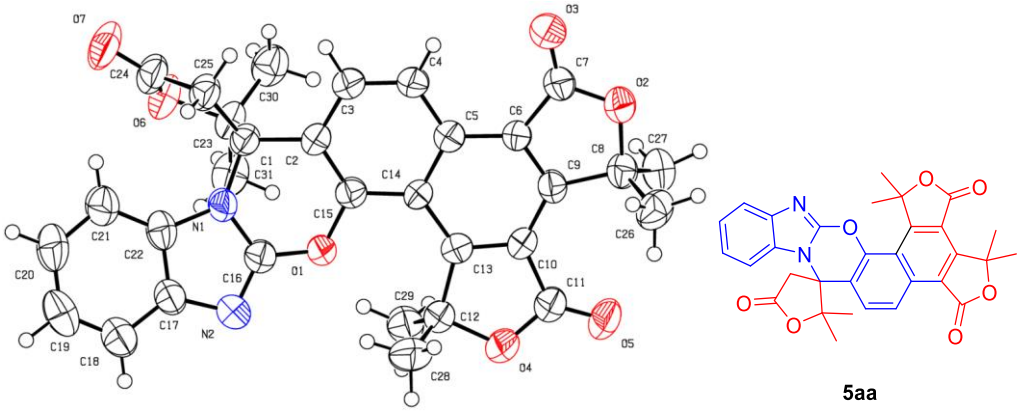


Figure S5. X-ray structure of 5aa. ORTEP plots for molecular structure of 5aa with the probability at 50% level.

CCDC 2006648 contains the crystal data and supplementary crystallographic data as following:

X-ray data of compound 5aa ($C_{31}H_{26}N_2O_7$): CCDC 2006648

Table S11. Crystal data and structure refinement.

Empirical formula	$C_{31}H_{26}N_2O_7$
Formula weight	538.54
Temperature/K	293.15
Crystal system	trigonal
Space group	R-3
a/Å	18.0539(9)
b/Å	18.0539(9)
c/Å	44.372(2)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	12525.0(14)
Z	18
ρ_{calc}g/cm^3	1.285
μ/mm^{-1}	0.092
F(000)	5076.0
Crystal size/mm^3	0.35 × 0.25 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.376 to 52.734
Index ranges	-14 ≤ h ≤ 22, -22 ≤ k ≤ 21, -53 ≤ l ≤ 55
Reflections collected	29204
Independent reflections	5706 [R_{int} = 0.0560, R_{sigma} = 0.0731]
Data/restraints/parameters	5706/0/367
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0673, wR_2 = 0.1637
Final R indexes [all data]	R_1 = 0.1290, wR_2 = 0.1945
Largest diff. peak/hole / e Å^{-3}	0.18/-0.18

Table S12. Bond Lengths.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C15	1.388(3)	C5	C14	1.434(4)
O1	C16	1.338(3)	C6	C7	1.473(4)
O2	C7	1.355(4)	C6	C9	1.349(4)
O2	C8	1.473(3)	C8	C9	1.514(4)
O3	C7	1.202(3)	C8	C26	1.514(4)
O4	C11	1.346(4)	C8	C27	1.501(4)
O4	C12	1.477(3)	C9	C10	1.403(4)
O5	C11	1.198(4)	C10	C11	1.470(4)
O6	C23	1.477(3)	C10	C13	1.379(4)
O6	C24	1.351(4)	C12	C13	1.531(4)
O7	C24	1.189(4)	C12	C28	1.516(4)
N1	C1	1.480(3)	C12	C29	1.513(4)
N1	C16	1.358(4)	C13	C14	1.438(4)
N1	C22	1.415(4)	C14	C15	1.414(4)
N2	C16	1.301(4)	C17	C18	1.376(4)
N2	C17	1.396(4)	C17	C22	1.415(4)
C1	C2	1.520(4)	C18	C19	1.349(5)
C1	C23	1.581(4)	C19	C20	1.393(5)
C1	C25	1.511(4)	C20	C21	1.378(4)
C2	C3	1.412(4)	C21	C22	1.379(4)
C2	C15	1.364(4)	C23	C30	1.507(4)
C3	C4	1.356(4)	C23	C31	1.513(4)
C4	C5	1.410(4)	C24	C25	1.500(4)
C5	C6	1.421(4)			

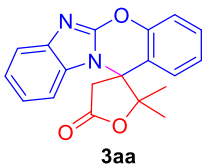
Table S13. Bond Angles.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C16	O1	C15	118.1(2)	O5	C11	O4	122.3(3)
C7	O2	C8	112.0(2)	O5	C11	C10	130.0(3)
C11	O4	C12	112.7(2)	O4	C12	C13	101.9(2)
C24	O6	C23	110.6(2)	O4	C12	C28	104.5(2)
C16	N1	C1	121.5(2)	O4	C12	C29	104.6(2)
C16	N1	C22	104.7(2)	C28	C12	C13	113.9(3)
C22	N1	C1	132.4(2)	C29	C12	C13	116.3(2)
C16	N2	C17	103.0(2)	C29	C12	C28	113.7(3)
N1	C1	C2	106.6(2)	C10	C13	C12	108.4(2)
N1	C1	C23	111.3(2)	C10	C13	C14	120.4(2)
N1	C1	C25	109.5(2)	C14	C13	C12	131.3(3)
C2	C1	C23	110.7(2)	C5	C14	C13	118.1(2)
C25	C1	C2	117.4(2)	C15	C14	C5	115.8(2)
C25	C1	C23	101.3(2)	C15	C14	C13	126.1(2)

C3	C2	C1	122.2(2)	O1	C15	C14	115.1(2)
C15	C2	C1	120.1(2)	C2	C15	O1	120.6(3)
C15	C2	C3	117.6(3)	C2	C15	C14	124.3(3)
C4	C3	C2	121.3(3)	O1	C16	N1	121.6(3)
C3	C4	C5	121.0(3)	N2	C16	O1	121.5(3)
C4	C5	C6	122.3(3)	N2	C16	N1	116.9(3)
C4	C5	C14	119.7(3)	N2	C17	C22	110.9(2)
C6	C5	C14	118.0(2)	C18	C17	N2	128.8(3)
C5	C6	C7	128.3(3)	C18	C17	C22	120.2(3)
C9	C6	C5	123.0(2)	C19	C18	C17	119.6(4)
C9	C6	C7	108.7(3)	C18	C19	C20	120.3(3)
O2	C7	C6	107.5(3)	C21	C20	C19	121.9(3)
O3	C7	O2	121.8(3)	C20	C21	C22	117.7(3)
O3	C7	C6	130.7(3)	N1	C22	C17	104.4(3)
O2	C8	C9	101.6(2)	C21	C22	N1	135.4(3)
O2	C8	C26	107.1(2)	C21	C22	C17	120.2(3)
O2	C8	C27	106.9(2)	O6	C23	C1	102.4(2)
C26	C8	C9	112.9(3)	O6	C23	C30	106.5(2)
C27	C8	C9	114.9(2)	O6	C23	C31	106.9(2)
C27	C8	C26	112.4(3)	C30	C23	C1	113.5(2)
C6	C9	C8	110.2(2)	C30	C23	C31	111.1(3)
C6	C9	C10	119.4(3)	C31	C23	C1	115.3(2)
C10	C9	C8	130.3(3)	O6	C24	C25	109.7(3)
C9	C10	C11	129.5(3)	O7	C24	O6	121.5(3)
C13	C10	C9	121.1(3)	O7	C24	C25	128.8(3)
C13	C10	C11	109.4(3)	C24	C25	C1	105.8(2)
O4	C11	C10	107.7(3)				

9. Characterization data

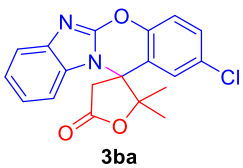
2',2'-dimethyl-2'*H*-spiro[benzo[*e*]benzo[4,5]imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-5'(4'*H*)-one (3aa)



3aa

95% yield; white solid; mp = 226.0-228.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.47 (m, 3H), 7.40 – 7.37 (m, 1H), 7.32 (dt, *J* = 19.4, 7.9 Hz, 2H), 7.23 (d, *J* = 7.3 Hz, 1H), 3.99 (d, *J* = 19.2 Hz, 1H), 3.90 (d, *J* = 19.2 Hz, 1H), 1.13 (s, 3H), 1.00 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.99, 152.43, 149.61, 140.06, 131.32, 131.14, 125.66, 124.82, 123.49, 122.79, 119.69, 118.37, 118.11, 111.16, 92.25, 69.21, 38.39, 27.02, 22.38 ppm. ESI HRMS: calcd. for $C_{19}H_{16}N_2O_3$+H 321.1239, found 321.1241.

2-chloro-2',2'-dimethyl-2'*H*-spiro[benzo[*e*]benzo[4,5]imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-5'(4'*H*)-one (3ba)

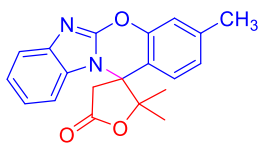


3ba

92% yield; white solid; mp = 243.6-247.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.44 – 7.39 (m, 3H), 7.25 (ddd, *J* = 13.7, 7.8, 1.2 Hz, 2H), 7.21 – 7.15 (m, 1H), 3.92 (d, *J* = 19.3 Hz, 1H), 3.75 (d, *J* = 19.2 Hz,

1H), 1.10 (s, 3H), 0.92 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.40, 152.01, 148.21, 140.00, 131.24, 131.21, 130.32, 125.72, 123.69, 123.05, 120.12, 119.84, 119.49, 111.15, 91.97, 69.12, 38.38, 27.06, 22.32 ppm. ESI HRMS: calcd. for $C_{19}H_{15}ClN_2O_3$+H 355.0849, found 355.0855.

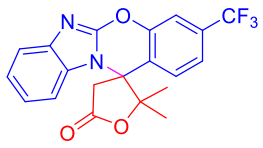
2',2',3-trimethyl-2'*H*-spiro[benzo[*e*]benzo[4,5]imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-5'(4'*H*)-one (3ca)



3ca

86% yield; white solid; mp = 204.8-207.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.23 (td, *J* = 7.8, 1.4 Hz, 1H), 7.20 – 7.16 (m, 1H), 7.12 (dd, *J* = 8.1, 1.8 Hz, 1H), 3.95 (d, *J* = 19.2 Hz, 1H), 3.85 (d, *J* = 19.3 Hz, 1H), 2.44 (s, 3H), 1.12 (s, 3H), 0.98 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.14, 152.57, 149.42, 141.96, 140.05, 131.33, 125.67, 125.39, 123.41, 122.70, 119.61, 118.27, 115.28, 111.15, 92.31, 69.09, 38.43, 27.06, 22.30, 21.08 ppm. ESI HRMS: calcd. for $C_{20}H_{18}N_2O_3$+Na 357.1215, found 357.1210.

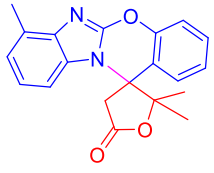
2',2'-dimethyl-3-(trifluoromethyl)-2'*H*-spiro[benzo[*e*]benzo[4,5]imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-5'(4'*H*)-one (3da)



3da

56% yield; white solid; mp = 198.9-200.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 1H), 7.65 (d, *J* = 5.8 Hz, 2H), 7.63 – 7.59 (m, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.37 – 7.27 (m, 2H), 4.05 (d, *J* = 19.2 Hz, 1H), 3.89 (d, *J* = 19.2 Hz, 1H), 1.15 (s, 3H), 1.03 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.37, 151.65, 149.81, 139.96, 133.82, 133.48, 131.17, 129.41, 126.79, 123.83, 123.23, 121.67 (q, $J_{C\text{-}F}$= 258 Hz), 119.99, 115.59 (q, *J* = 4.0 Hz), 111.19, 91.94, 69.20, 38.51, 26.96, 22.43 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.08 ppm. ESI HRMS: calcd. for $C_{20}H_{18}N_2O_3$+Na 357.1215, found 357.1210.

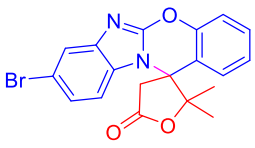
2',2',7-trimethyl-2'*H*-spiro[benzo[*e*]benzo[4,5]imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-5'(4'*H*)-one (3ga)



3ga

50% yield; light yellow solid; mp = 220.1-227.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H), 7.40 – 7.30 (m, 3H), 7.18 – 7.10 (m, 2H), 4.01 (d, *J* = 19.2 Hz, 1H), 3.87 (d, *J* = 19.2 Hz, 1H), 2.61 (s, 3H), 1.13 (s, 3H), 1.03 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.03, 151.79, 149.69, 138.96, 131.11, 130.89, 129.50, 125.64, 124.76, 124.05, 122.64, 118.52, 118.06, 108.72, 92.23, 69.13, 38.34, 27.01, 22.53, 16.56 ppm. ESI HRMS: calcd. for $C_{20}H_{18}N_2O_3$+H 335.1396, found 335.1397.

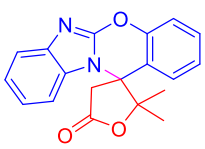
8-bromo-2',2'-dimethyl-2'*H*-spiro[benzo[*e*]benzo[4,5]imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-5'(4'*H*)-one (3ha)



3ha

51% yield; white solid; mp = 234.7-236.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.42 (dt, *J* = 16.0, 6.4 Hz, 3H), 7.33 (d, *J* = 14.5 Hz, 1H), 7.29 (d, *J* = 3.4 Hz, 1H), 7.17 (s, 1H), 3.81 (d, *J* = 3.1 Hz, 2H), 1.04 (s, 3H), 0.90 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.74, 153.04, 149.39, 141.52, 131.33, 130.28, 125.69, 125.06, 122.53, 118.18, 117.91, 116.51, 112.34, 92.17, 69.44, 38.34, 27.02, 22.52, 22.21 ppm. ESI HRMS: calcd. for $C_{19}H_{15}BrN_2O_3$+H 399.0344, found 399.0356.

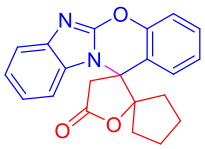
2',2'-dimethyl-2'*H*-spiro[benzo[*e*]benzo[4,5]imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-5'(4'*H*)-one (3ab)



3ab

81% yield; white solid; mp = 226.0-228.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.47 (m, 3H), 7.40 – 7.37 (m, 1H), 7.32 (dt, *J* = 19.4, 7.9 Hz, 2H), 7.23 (d, *J* = 7.3 Hz, 1H), 3.99 (d, *J* = 19.2 Hz, 1H), 3.90 (d, *J* = 19.2 Hz, 1H), 1.13 (s, 3H), 1.00 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.99, 152.43, 149.61, 140.06, 131.32, 131.14, 125.66, 124.82, 123.49, 122.79, 119.69, 118.37, 118.11, 111.16, 92.25, 69.21, 38.39, 27.02, 22.38 ppm. ESI HRMS: calcd. for $C_{19}H_{16}N_2O_3$+H 321.1239, found 321.1241.

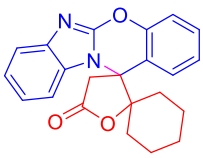
dispiro[benzo[*e*]benzo[4,5]imidazo[2,1-*b*][1,3]oxazine-12,3'-furan-2',1''-cyclopentan]-5'(4'*H*)-one (3ac)



3ac

73% yield; yellow solid; mp = 200.7-213.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 9.3 Hz, 2H), 7.32 (dt, *J* = 19.8, 8.1 Hz, 3H), 7.23 (d, *J* = 7.9 Hz, 1H), 4.15 (d, *J* = 19.3 Hz, 1H), 3.75 (d, *J* = 19.3 Hz, 1H), 1.81 – 1.64 (m, 2H), 1.62 – 1.46 (m, 3H), 1.37 (dt, *J* = 14.0, 9.5 Hz, 1H), 1.29 – 1.18 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.87, 151.57, 148.80, 140.05, 131.23, 130.93, 125.71, 124.97, 123.42, 122.56, 119.63, 119.30, 117.91, 111.49, 103.54, 67.25, 40.40, 37.41, 33.91, 22.78, 22.08 ppm. ESI HRMS: calcd. for $C_{21}H_{18}N_2O_3$+H 347.1396, found 347.1393.

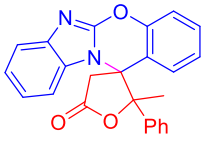
4-(2,2-dimethyl-5-oxo-2,5-dihydrofuran-3-yl)-2-methoxy-2',2'-dimethyl-2'*H*-spiro[benzo[*e*]benzo [4,5]imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-5'(4'*H*)-one (3ad)



3ad

65% yield; white solid; mp = 203.3-207.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.9 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.45 (d, J = 7.9 Hz, 1H), 7.38 (d, J = 8.2 Hz, 1H), 7.31 (q, J = 7.6 Hz, 2H), 7.23 (d, J = 7.7 Hz, 1H), 3.97 (d, J = 19.2 Hz, 1H), 3.87 (d, J = 19.2 Hz, 1H), 1.64 – 1.49 (m, 4H), 1.44 (tt, J = 7.9, 3.7 Hz, 2H), 1.19 – 1.07 (m, 1H), 1.00 (dd, J = 13.5, 3.3 Hz, 1H), 0.85 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.11, 152.54, 149.62, 140.00, 131.54, 131.02, 125.85, 124.74, 123.40, 122.74, 119.61, 118.44, 118.09, 111.23, 93.13, 69.66, 38.16, 35.46, 30.15, 24.13, 22.20, 21.66 ppm. ESI HRMS: calcd. for $C_{22}H_{20}N_2O_3$+H 361.1552, found 361.1548.

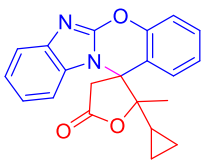
2'-methyl-2'-phenyl-2'*H*-spiro[benzo[*e*]benzo[4,5]imidazo[2,1-*b*][1,3]oxazine -12,3'-furan]-5'(4'*H*)-one (3ae)



3ae

55% yield; white solid; mp = 225.7-230.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.8 Hz, 1H), 7.61 (d, J = 8.2 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.34 (dp, J = 16.1, 8.4, 7.4 Hz, 3H), 7.24 – 7.15 (m, 3H), 7.12 (d, J = 8.0 Hz, 2H), 6.77 (t, J = 7.6 Hz, 1H), 6.40 (d, J = 8.0 Hz, 1H), 4.04 (d, J = 19.2 Hz, 1H), 3.74 (d, J = 19.2 Hz, 1H), 1.41 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.02, 149.10, 139.46, 130.49, 129.98, 129.81, 128.30, 128.27, 125.86, 125.64, 124.16, 123.65, 122.89, 122.26, 120.23, 119.77, 118.63, 117.13, 111.37, 95.24, 38.67, 22.67 ppm. ESI HRMS: calcd. for $C_{24}H_{18}N_2O_3$+H 405.1215, found 405.1209.

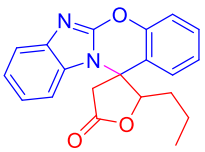
2'-cyclopropyl-2'-methyl-2'*H*-spiro[benzo[*e*]benzo[4,5]imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-5'(4'*H*)-one (3af)



3af

85% yield; white solid; mp = 175.6-192.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.50 (q, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.37 (t, *J* = 8.2 Hz, 1H), 7.30 (dd, *J* = 8.9, 6.2 Hz, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 4.06 – 3.85 (m, 2H), 1.07 – 0.94 (m, 3H), 0.51 (tdd, *J* = 11.8, 7.2, 5.2 Hz, 2H), 0.46 – 0.40 (m, 2H), 0.30 (ddt, *J* = 13.8, 9.3, 6.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl3) δ 173.93, 149.70, 140.16, 131.17, 130.02, 126.42, 124.50, 123.64, 122.92, 120.33, 119.77, 118.31, 118.00, 111.16, 92.55, 70.26, 39.59, 21.05, 19.73, 3.26, 1.84 ppm. ESI HRMS: calcd. for $C_{21}H_{18}N_2O_3$+H 347.1396, found 347.1373.

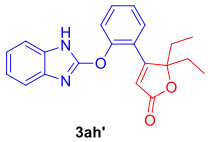
2'-propyl-2'*H*-spiro[benzo[*e*]benzo[4,5]imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-5'(4'*H*)-one (3ag)



3ag

34% yield; yellow solid; mp = 118.7-122.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.27 (m, 1H), 7.21 (m, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.15 – 7.08 (m, 1H), 4.71 (t, *J* = 6.4 Hz, 1H), 3.71 (d, *J* = 19.7 Hz, 1H), 3.55 (d, *J* = 19.7 Hz, 1H), 1.38 – 1.10 (m, 4H), 0.63 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.36, 150.14, 148.00, 139.78, 130.85, 130.78, 125.61, 125.55, 123.60, 122.78, 119.52, 119.16, 117.74, 111.24, 92.40, 65.97, 44.10, 30.15, 19.50, 13.51 ppm. ESI HRMS: calcd. for $C_{20}H_{18}N_2O_3$+Na 357.1215, found 357.1219.

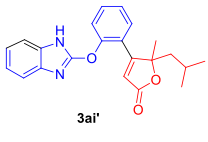
4-(2-((1*H*-benzo[*d*]imidazol-2-yl)oxy)phenyl)-5,5-diethylfuran-2(5*H*)-one (3ah')



3ah'

45% yield; white solid; mp = 158.6-160.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.18 (p, *J* = 5.2, 4.7 Hz, 2H), 6.39 (s, 1H), 2.05 (dq, *J* = 14.8, 7.4 Hz, 2H), 1.91 (dq, *J* = 14.7, 7.3 Hz, 2H), 0.83 (t, *J* = 7.3 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.80, 163.57, 155.57, 151.05, 140.42, 131.99, 131.60, 127.80, 125.93, 123.30, 122.69, 122.21, 122.12, 121.86, 118.49, 110.21, 94.49, 29.95, 29.71, 7.36, 1.03 ppm. ESI HRMS: calcd. for $C_{21}H_{20}N_2O_3$+H 349.1552, found 349.1555.

4-(2-((1*H*-benzo[*d*]imidazol-2-yl)oxy)phenyl)-5-isobutyl-5-methylfuran-2(5*H*)-one (3ai')

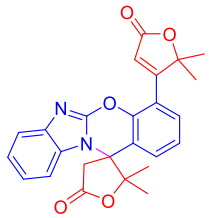


3ai'

57% yield; light yellow solid; mp = 226.0-228.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.67 (s, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.43 – 7.30 (m, 3H), 7.17 (dt, *J* = 6.0, 3.7 Hz, 2H), 6.25 (s, 1H), 1.84 (dd, *J* = 14.4, 6.1 Hz, 1H), 1.72 (dp, *J* = 12.0, 5.9 Hz, 1H), 1.62 (dd, *J* = 14.5, 5.8 Hz, 1H), 1.57 (s, 3H), 0.88 (d, *J* = 6.5 Hz, 3H), 0.85 (d, *J* = 6.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.33, 167.86, 155.61, 150.74, 131.97, 131.43, 129.90, 128.45, 125.77, 125.69, 123.64, 122.49, 122.15, 122.04, 120.20, 120.12, 91.79, 45.95, 24.44, 24.40, 24.12, 23.85 ppm. ESI HRMS: calcd. for $C_{22}H_{22}N_2O_3$+Na 385.1528, found 385.1516.

4-(2,2-dimethyl-5-oxo-2,5-dihydrofuran-3-yl)-2',2'-dimethyl-2'*H*-spiro[benzo[e]benzo[4,5] imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-5'(4'*H*)-one (4aa)

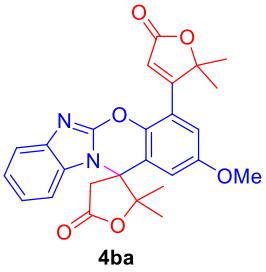
81% yield; white solid; mp = 247.3-248.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.32 (ddd, *J* = 16.1, 7.9, 1.3 Hz, 1H), 7.26 (d, *J* = 7.2 Hz, 1H), 6.35 (s, 1H), 4.08 (d, *J* = 19.1 Hz, 1H), 3.93 (d, *J* = 19.1 Hz, 1H), 1.65 (s,



4aa

6H), 1.18 (s, 3H), 1.04 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.44, 170.64, 166.35, 151.45, 146.72, 139.95, 131.18, 130.42, 127.13, 124.64, 123.83, 123.25, 121.81, 121.26, 120.17, 120.01, 111.22, 91.92, 88.32, 69.24, 38.42, 26.82, 25.59, 22.69 ppm. ESI HRMS: calcd. for $C_{25}H_{22}N_2O_5$+Na 453.1426, found 453.1433.

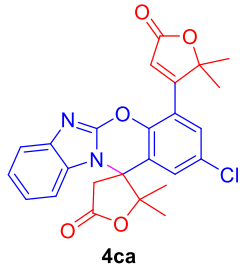
4-(2,2-dimethyl-5-oxo-2,5-dihydrofuran-3-yl)-2-methoxy-2',2'-dimethyl-2'*H*-spiro[benzo[*e*]benzo [4,5]imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-5'(4'*H*)-one (4ba)



4ba

76% yield; white solid; mp = 241.9-248.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 2.8 Hz, 1H), 6.91 (d, *J* = 2.6 Hz, 1H), 6.31 (s, 1H), 4.07 (d, *J* = 19.4 Hz, 1H), 3.89 – 3.82 (m, 1H), 1.64 (s, 6H), 1.20 (s, 3H), 1.03 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.40, 170.58, 166.43, 155.84, 151.89, 140.38, 140.01, 131.15, 123.77, 123.11, 122.52, 121.32, 121.27, 119.91, 115.26, 112.62, 111.17, 91.91, 88.31, 69.32, 56.19, 38.37, 26.85, 25.61, 25.59, 22.77 ppm. ESI HRMS: calcd. for $C_{26}H_{24}N_2O_6$+H 461.1713, found 461.1713.

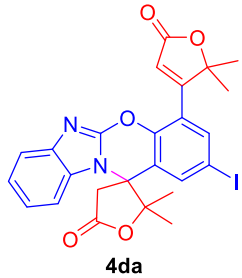
2-chloro-4-(2,2-dimethyl-5-oxo-2,5-dihydrofuran-3-yl)-2',2'-dimethyl-2'H-spiro[benzo[*e*]benzo [4,5]imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-5'(4'*H*)-one (4ca)



4ca

58% yield; white solid; mp = 277.9-282.1 °C. ^{1}H NMR (400 MHz, CDCl3) δ 7.70 – 7.66 (m, 1H), 7.57 (d, *J* = 2.3 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.41 (d, *J* = 2.2 Hz, 1H), 7.37 – 7.27 (m, 2H), 6.34 (s, 1H), 4.08 (d, *J* = 19.1 Hz, 1H), 3.82 (d, *J* = 19.1 Hz, 1H), 1.66 – 1.62 (m, 6H), 1.22 (s, 3H), 1.03 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.76, 170.06, 164.87, 151.08, 145.36, 139.91, 131.08, 130.35, 130.14, 126.91, 124.03, 123.51, 123.41, 122.00, 121.91, 120.18, 111.21, 91.64, 88.14, 69.17, 38.40, 26.87, 25.56, 25.56, 22.67 ppm. ESI HRMS: calcd. for $C_{25}H_{21}ClN_2O_5$+Na 487.1037, found 487.1037.

4-(2,2-dimethyl-5-oxo-2,5-dihydrofuran-3-yl)-2-iodo-2',2'-dimethyl-2'*H*-spiro[benzo[*e*]benzo[4,5] imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-5'(4'*H*)-one (4da)

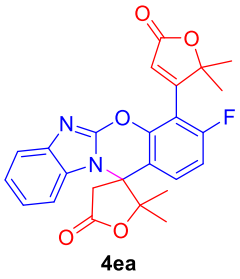


4da

44% yield; white solid; mp = 286.4-288.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.61 (q, *J* = 4.3, 3.8 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.35 – 7.28 (m, 1H), 6.34 (s, 1H), 4.08 (d, *J* = 19.1 Hz, 1H), 3.91 (d, *J* = 19.1 Hz, 1H), 1.64 (s, 6H), 1.17 (s, 3H), 1.04 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 170.6, 166.3, 151.4, 146.7, 140.0, 131.2, 130.4, 127.1, 124.6, 123.8, 123.3, 121.8, 121.3, 120.2, 120.0, 111.2, 91.9, 88.3, 77.2, 69.2, 38.4, 26.8, 25.6, 22.7 ppm. ESI HRMS: calcd. for $C_{25}H_{21}IN_2O_5$+H 557.0573, found 557.0575.

4-(2,2-dimethyl-5-oxo-2,5-dihydrofuran-3-yl)-3-fluoro-2',2'-dimethyl-2'*H*-spiro[benzo[*e*]benzo [4,5]imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-5'(4'*H*)-one (4ea)

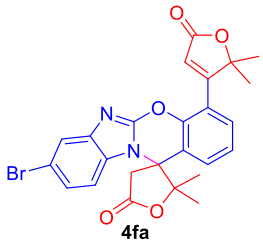
35% yield; white solid; mp = 210.4-211.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 1H), 7.61 (dd, *J* = 9.0, 5.5 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.31 (dd, *J* = 6.8, 1.4 Hz, 1H), 7.24 – 7.19 (m, 1H), 6.21 (s, 1H), 4.08 (d, *J* = 19.1 Hz, 1H), 3.86 (d, *J* = 19.1 Hz, 1H), 1.65 – 1.57 (m, 6H), 1.19 (s, 3H), 1.03 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.21, 170.06, 161.94, 159.42(d,



4ea

J_{C-F} = 255 Hz), 151.15, 147.27(d, J_{C-F} = 7.1 Hz), 139.83, 131.12, 128.05(d, J_{C-F} = 10.1 Hz), 123.94, 123.46, 123.39, 120.15, 115.85(d, J_{C-F} = 3.6 Hz), 112.5(d, J_{C-F} = 23.1 Hz), 111.27, 110.65(d, J_{C-F} = 22.2 Hz), 91.82, 89.05, 69.11, 38.51, 26.81, 25.50, 25.33, 22.61 ppm. ^{19}F NMR (376 MHz, CDCl3) δ -105.75 ppm. ESI HRMS: calcd. for $C_{25}H_{21}FN_2O_5$ +H 449.1513, found 449.1505.

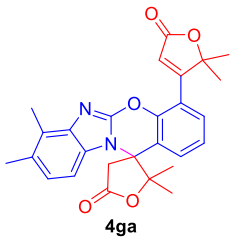
8-bromo-4-(2,2-dimethyl-5-oxo-2,5-dihydrofuran-3-yl)-2',2'-dimethyl-2'*H*-spiro [benzo[*e*]benzo [4,5]imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-5'(4'*H*)-one (4fa)



4fa

68% yield; white solid; mp = 222.5-225.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 1.6 Hz, 1H), 7.61 (p, *J* = 3.7 Hz, 1H), 7.46 (d, *J* = 4.8 Hz, 2H), 7.37 (d, *J* = 1.3 Hz, 2H), 6.33 (s, 1H), 3.98 (d, *J* = 19.3 Hz, 1H), 3.91 (d, *J* = 19.2 Hz, 1H), 1.63 (s, 6H), 1.17 (s, 3H), 1.01 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.16, 170.52, 166.12, 152.07, 146.51, 141.40, 130.58, 130.14, 127.12, 126.18, 124.86, 122.87, 121.95, 121.37, 119.73, 116.84, 112.40, 91.83, 88.27, 77.23, 69.47, 38.37, 26.83, 25.56, 22.51 ppm. ESI HRMS: calcd. for $C_{25}H_{21}BrN_2O_5$+H 509.0712, found 509.0715.

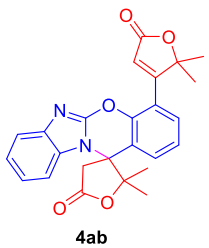
4-(2,2-dimethyl-5-oxo-2,5-dihydrofuran-3-yl)-2',2',8,9-tetramethyl-2'*H*-spiro[benzo[*e*]benzo[4,5] imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-5'(4'*H*)-one (4ga)



4ga

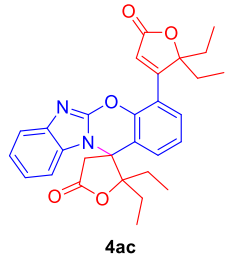
72% yield; white solid; mp = 244.1-250.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 5.9, 3.7 Hz, 1H), 7.45 – 7.39 (m, 3H), 7.28 (s, 1H), 6.33 (s, 1H), 4.13 – 3.82 (m, 2H), 2.34 (d, *J* = 8.6 Hz, 6H), 1.63 (s, 6H), 1.15 (s, 3H), 1.03 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.62, 170.69, 166.43, 150.94, 146.85, 138.28, 132.68, 132.09, 130.29, 129.52, 127.14, 124.46, 121.68, 121.16, 120.32, 120.13, 111.66, 91.97, 88.32, 77.25, 68.99, 38.45, 26.76, 25.60, 22.73, 20.81, 20.05 ppm. ESI HRMS: calcd. for $C_{27}H_{26}N_2O_5$+H 459.1920, found 459.1924.

4-(2,2-dimethyl-5-oxo-2,5-dihydrofuran-3-yl)-2',2'-dimethyl-2'*H*-spiro[benzo[*e*]benzo[4,5] imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-5'(4'*H*)-one (4ab)



4ab

80% yield; white solid; mp = 241.9-248.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.62 (q, *J* = 4.2, 3.7 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.45 (d, *J* = 4.7 Hz, 2H), 7.35 – 7.26 (m, 2H), 6.34 (s, 1H), 4.07 (d, *J* = 19.0 Hz, 1H), 3.91 (d, *J* = 19.1 Hz, 1H), 1.64 (d, *J* = 1.0 Hz, 6H), 1.17 (s, 3H), 1.04 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.42, 170.62, 166.32, 151.41, 146.70, 139.83, 131.14, 130.45, 127.15, 124.68, 123.87, 123.29, 121.83, 121.30, 120.15, 119.99, 111.25, 91.91, 88.31, 69.27, 38.46, 26.84, 25.62, 25.60, 22.70 ppm. ESI HRMS: calcd. for $C_{25}H_{22}N_2O_5$+H 431.1607, found 431.1601.



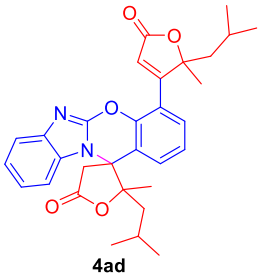
4ac

4-(5,5-diethyl-2-oxo-2,5-dihydrofuran-3-yl)-5',5'-diethyl-4',5'-dihydro-2'*H*-spiro[benzo[*e*]benzo [4,5]imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-2'-one (4ac)

42% yield; white solid; mp = 166.4-172.3 °C. ^{1}H NMR (400 MHz, CDCl3) δ 7.70 (d, *J* = 7.9 Hz, 1H), 7.63 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.37 – 7.27 (m, 2H), 6.64 (s, 1H), 4.04 (d, *J* = 19.3 Hz,

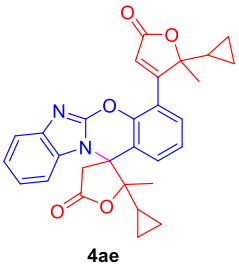
1H), 3.89 (s, 1H), 2.11 – 2.03 (m, 2H), 1.90 (ddq, *J* = 14.8, 12.5, 7.4 Hz, 2H), 1.76 – 1.64 (m, 1H), 1.47 – 1.37 (m, 1H), 1.28 (d, *J* = 2.6 Hz, 1H), 0.93 (td, *J* = 7.4, 2.3 Hz, 6H), 0.89 – 0.82 (m, 1H), 0.68 (t, *J* = 7.4 Hz, 3H), 0.47 (t, *J* = 7.3 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.50, 171.26, 160.73, 151.12, 147.50, 140.01, 131.25, 129.44, 127.44, 124.74, 124.14, 123.80, 123.25, 121.57, 120.43, 120.06, 111.34, 96.75, 93.61, 69.26, 39.35, 30.02, 29.84, 28.07, 24.35, 7.80, 7.64, 7.58, 7.49 ppm. ESI HRMS: calcd. for $C_{29}H_{30}N_2O_5$+H 487.2233, found 487.2235.

5'-isobutyl-4-(5-isobutyl-5-methyl-2-oxo-2,5-dihydrofuran-3-yl)-5'-methyl-4',5'-dihydro-2'*H*-spiro[benzo[*e*]benzo[4,5]imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-2'-one (4ad)


4ad

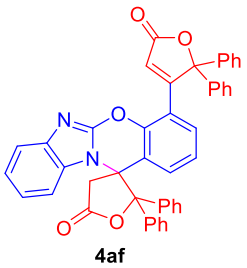
77% yield; white solid; mp = 264.0-266.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.45 – 7.24 (m, 4H), 6.40 (s, 1H), 4.25 (d, *J* = 19.1 Hz, 1H), 3.73 (d, *J* = 19.0 Hz, 1H), 2.17 – 1.97 (m, 9H), 1.76 (q, *J* = 15.5, 13.0 Hz, 9H), 1.68 – 1.60 (m, 2H), 1.60 – 1.52 (m, 2H), 1.45 – 1.32 (m, 1H), 1.26 (dt, *J* = 13.2, 9.5 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.28, 170.80, 163.59, 150.60, 146.04, 139.96, 131.11, 130.53, 127.08, 124.68, 123.75, 122.99, 122.13, 121.55, 121.12, 120.01, 111.60, 103.13, 98.27, 67.19, 40.46, 37.22, 36.87, 36.81, 34.32, 24.58, 24.46, 22.69, 22.22 ppm. ESI HRMS: calcd. for $C_{31}H_{34}N_2O_5$+H 515.2546, found 515.2550.

2'-cyclopropyl-4-(2-cyclopropyl-2-methyl-5-oxo-2,5-dihydrofuran-3-yl)-2'-methyl-2'*H*-spiro[benzo[*e*]benzo[4,5]imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-5'(4'*H*)-one (4ae)


4ae

94% yield; yellow solid; mp = 178.9-191.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 8.4, 2.6 Hz, 1H), 7.67 (dd, *J* = 8.2, 4.3 Hz, 1H), 7.58 (dt, *J* = 15.3, 6.8 Hz, 1H), 7.51 – 7.37 (m, 2H), 7.35 – 7.21 (m, 2H), 6.29 (d, *J* = 2.7 Hz, 1H), 4.15 – 3.84 (m, 2H), 1.62 (d, *J* = 13.0 Hz, 3H), 1.14 – 1.05 (m, 3H), 0.99 (d, *J* = 3.7 Hz, 2H), 0.70 (dp, *J* = 12.4, 7.0, 5.9 Hz, 1H), 0.62 (ddd, *J* = 13.6, 6.8, 3.1 Hz, 1H), 0.53 (dt, *J* = 14.9, 4.5 Hz, 2H), 0.46 (dp, *J* = 14.2, 4.6 Hz, 2H), 0.32 (dtt, *J* = 12.5, 8.7, 5.0 Hz, 1H), 0.17 – -0.04 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.30, 172.65, 171.00, 166.56, 146.73, 140.01, 132.03, 131.18, 130.56 (d, *J* = 4.0 Hz), 127.72, 126.93, 124.48 (d, *J* = 123.2 Hz), 123.96 (d, *J* = 20.2 Hz), 123.30 (d, *J* = 59.6 Hz), 120.72 (dd, *J* = 3.4, 14.7 Hz), 119.88 (t, *J* = 12.9 Hz), 111.11, 92.26, 88.49, 70.20, 38.88(d, *J* = 144.4 Hz), 23.18 (m, *J* = 5.5, 8.3 MHz), 21.14 (d, *J* = 5.5 Hz), 19.64 (d, *J* = 3.4 Hz), 17.89 (d, *J* = 7.1 Hz), 15.69, 3.20(m, *J* = 9.7, 11.4 MHz), 1.87, 1.09 ppm. ESI HRMS: calcd. for $C_{29}H_{26}N_2O_5$+H 483.1920, found 483.1922.

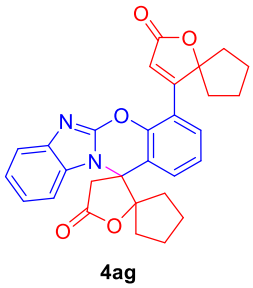
4-(5-oxo-2,2-diphenyl-2,5-dihydrofuran-3-yl)-2',2'-diphenyl-2'*H*-spiro[benzo[*e*]benzo[4,5] imidazo[2,1-*b*][1,3]oxazine-12,3'-furan]-5'(4'*H*)-one (4af)


4af

51% yield; white solid; mp = 280.4-290.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 6H), 7.37 (s, 5H), 7.17 (dd, *J* = 7.5, 2.3 Hz, 3H), 7.14 – 7.08 (m, 3H), 7.07 – 7.03 (m, 2H), 6.98 – 6.93 (m, 4H), 6.92 – 6.85 (m, 3H), 6.64 (t, *J* = 7.9 Hz, 1H), 6.58 (dd, *J* = 8.2, 1.6 Hz, 1H), 4.14 (d, *J* = 19.5 Hz, 1H), 3.56 (d, *J* = 19.5 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.80, 171.13, 160.92, 149.64, 146.30, 139.23, 138.99, 137.63, 137.37, 137.22, 130.48, 130.43, 129.31, 129.05, 128.79, 128.70, 128.52, 128.42, 128.36, 128.30, 128.14,

127.84, 127.80, 125.87, 124.81, 123.27, 123.10, 122.47, 122.40, 120.72, 119.97, 119.25, 111.56, 96.25, 94.09, 77.23, 71.20, 41.59 ppm. ESI HRMS: calcd. for $C_{45}H_{30}N_2O_5$+H 679.2233, found 679.2230.

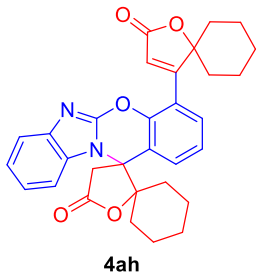
4-(2-oxo-1-oxaspiro[4.4]non-3-en-4-yl)dispiro[benzo[*e*]benzo[4,5]imidazo[2,1-*b*][1,3]oxazine-12,3'-furan-2',1''-cyclopentan]-5'(4'*H*)-one (4ag)



4ag

89% yield; light yellow solid; mp = 233.8-236.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.53 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.37 – 7.33 (m, 1H), 7.31 (d, *J* = 9.0 Hz, 1H), 6.40 (s, 1H), 4.26 (d, *J* = 19.2 Hz, 1H), 3.71 (d, *J* = 19.2 Hz, 1H), 2.04 (d, *J* = 10.9 Hz, 6H), 1.75 (q, *J* = 10.5 Hz, 4H), 1.60 (dd, *J* = 16.1, 8.7 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.28, 170.83, 163.58, 150.57, 146.02, 139.96, 131.12, 130.53, 127.01, 124.66, 123.76, 123.01, 122.13, 121.56, 121.13, 120.04, 111.61, 103.14, 98.28, 67.14, 40.42, 37.19, 36.85, 36.79, 34.34, 24.57, 24.45, 22.66, 22.21 ppm. ESI HRMS: calcd. for $C_{29}H_{26}N_2O_5$+Na 505.1739, found 505.1734.

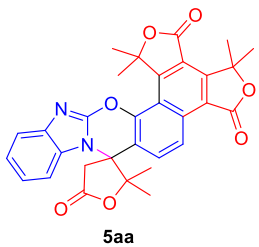
4-(2-oxo-1-oxaspiro[4.5]dec-3-en-4-yl)dispiro[benzo[*e*]benzo[4,5]imidazo[2,1-*b*][1,3]oxazine-12,3'-furan-2',1''-cyclohexan]-5'(4'*H*)-one (4ah)



4ah

85% yield; light yellow solid; mp = 272.4-275.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.29 – 7.23 (m, 1H), 6.20 (s, 1H), 4.05 (d, *J* = 19.1 Hz, 1H), 3.89 (d, *J* = 19.1 Hz, 1H), 1.99 (d, *J* = 13.9 Hz, 1H), 1.94 – 1.86 (m, 1H), 1.82 (ddt, *J* = 12.9, 6.7, 3.4 Hz, 1H), 1.78 – 1.66 (m, 4H), 1.65 – 1.54 (m, 5H), 1.46 (h, *J* = 3.2 Hz, 2H), 1.06 (dd, *J* = 8.5, 4.9 Hz, 3H), 0.91 – 0.83 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.57, 170.94, 167.45, 151.61, 146.31, 139.94, 131.42, 130.41, 127.03, 124.42, 123.68, 123.12, 122.27, 121.20, 119.98, 119.92, 111.31, 92.87, 90.14, 69.70, 38.25, 35.31, 33.98, 33.83, 30.58, 29.70, 24.46, 24.21, 22.11, 22.09, 21.72 ppm. ESI HRMS: calcd. for $C_{31}H_{30}N_2O_5$+Na 533.2052, found 533.2050.

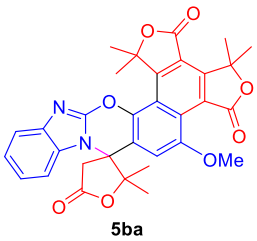
2',2',3,3,6,6-hexamethyl-2'*H*-spiro[benzo[4,5]imidazo[2,1-*b*]difuro[3',4':5,6;3'',4'':7,8]naphtho[2,1-*e*][1,3]oxazine-9,3'-furan]-1,4,5'(3*H*,4'*H*,6*H*)-trione (5aa)



5aa

56% yield; white solid; mp = 345.1-347.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (d, *J* = 9.0 Hz, 1H), 8.00 (d, *J* = 8.9 Hz, 1H), 7.78 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.36 (ddd, *J* = 13.9, 7.8, 1.2 Hz, 2H), 4.11 (s, 2H), 2.32 (s, 3H), 2.27 (s, 3H), 1.99 (d, *J* = 3.2 Hz, 6H), 1.19 (s, 3H), 1.06 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.29, 168.26, 1 66.57, 159.88, 154.79, 150.77, 145.42, 140.10, 134.03, 131.01, 127.87, 124.23, 123.81, 122.62, 121.83, 120.64, 120.29, 118.99, 117.19, 111.45, 92.10, 91.41, 86.42, 69.66, 38.65, 27.24, 27.08, 27.03, 25.48, 25.46, 22.51 ppm. ESI HRMS: calcd. for $C_{31}H_{26}N_2O_7$+H 539.1818, found 539.1625.

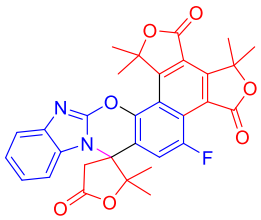
7-methoxy-2',2',3,3,6,6-hexamethyl-2'*H*-spiro[benzo[4,5]imidazo[2,1-*b*]difuro[3',4':5,6;3'',4'':7,8]naphtho[2,1-*e*][1,3]oxazine-9,3'-furan]-1,4,5'(3*H*,4'*H*,6*H*)-trione (5ba)



5ba

33% yield; light green yellow solid; mp = 318.3-320.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.41 – 7.29 (m, 2H), 7.21 (s, 1H), 4.15 (d, *J* = 8.8 Hz, 4H), 4.02 (d, *J* = 19.1 Hz, 1H), 2.27 (d, *J* = 2.3 Hz, 6H), 1.97 (d, *J* = 9.8 Hz, 6H), 1.21 (s, 3H), 1.08 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.14, 166.31, 165.06, 159.49, 155.63, 154.48, 151.16, 140.18, 138.85, 130.92, 126.28, 124.36, 124.06, 123.52, 121.02, 120.86, 120.18, 117.41, 111.33, 107.22, 92.08, 91.19, 84.09, 69.43, 57.13, 38.27, 27.23, 27.18, 26.87, 25.78, 25.53, 22.74 ppm. ESI HRMS: calcd. for $C_{32}H_{28}N_2O_8$+Na 591.1743, found 591.1742.

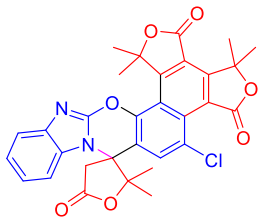
7-fluoro-2',2',3,3,6,6-hexamethyl-2'*H*-spiro[benzo[4,5]imidazo[2,1-*b*]difuro[3',4':5,6;3'',4'':7,8]naphtho[2,1-*e*][1,3]oxazine-9,3'-furan]-1,4,5'(3*H*,4'*H*,6*H*)-trione (5ca)



5ca

37% yield; yellow solid; mp = 388.3-390.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.75 (m, 1H), 7.71 (d, *J* = 11.1 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.43 – 7.31 (m, 2H), 4.10 (d, *J* = 19.2 Hz, 1H), 3.97 (d, *J* = 19.1 Hz, 1H), 2.29 (d, *J* = 9.8 Hz, 6H), 1.99 (d, *J* = 7.0 Hz, 6H), 1.23 (s, 3H), 1.05 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.74, 165.85, 164.74, 159.87, 156.76, 155.52 (d, $J_{C\text{-}F}$ = 264 Hz), 150.60, 141.67 (d, $J_{C\text{-}F}$ = 3.9 Hz), 140.01, 130.74, 124.29, 123.89, 123.36 (d, $J_{C\text{-}F}$ = 20.3 Hz), 123.12 (d, $J_{C\text{-}F}$ = 7.1 Hz), 121.68, 120.90 (d, $J_{C\text{-}F}$ = 5.9 Hz), 120.29, 117.60 (d, $J_{C\text{-}F}$ = 7.0 Hz), 113.76 (d, $J_{C\text{-}F}$ = 27.3 Hz), 111.32, 91.81, 91.37, 85.05, 69.39, 38.57, 27.25, 27.09, 27.03, 25.58, 25.47, 22.36 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -100.24 ppm. ESI HRMS: calcd. for $C_{31}H_{25}FN_2O_7$+H 557.1724, found 557.1721.

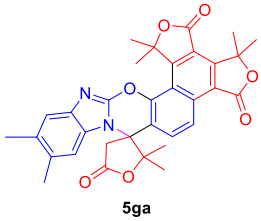
7-chloro-2',2',3,3,6,6-hexamethyl-2'*H*-spiro[benzo[4,5]imidazo[2,1-*b*]difuro[3',4':5,6;3'',4'':7,8]naphtho[2,1-*e*][1,3]oxazine-9,3'-furan]-1,4,5'(3*H*,4'*H*,6*H*)-trione (5da)



5da

65% yield; yellow solid; mp = 374.3-376.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 4.07 (s, 2H), 2.32 (d, *J* = 8.7 Hz, 3H), 2.26 (d, *J* = 17.4 Hz, 3H), 2.03 (s, 3H), 1.98 (d, *J* = 11.5 Hz, 4H), 1.21 (d, *J* = 10.9 Hz, 3H), 1.04 (d, *J* = 20.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.75, 165.81, 164.56, 160.23, 157.00, 150.36, 144.17, 139.97, 132.34, 130.85, 129.88, 128.58, 127.82, 124.31, 123.96, 121.38, 121.28, 120.35, 117.17, 111.35, 91.83, 91.46, 84.87, 69.37, 38.25, 27.27, 27.07, 25.87, 25.37, 22.44, 22.24 ppm. ESI HRMS: calcd. for $C_{31}H_{25}ClN_2O_7$+H 573.1429, found 573.1428.

2',2',3,3,6,6,12,13-octamethyl-2'*H*-spiro[benzo[4,5]imidazo[2,1-*b*]difuro[3',4':5,6;3'', 4'':7,8]naphtha[2,1-*e*][1,3]oxazine-9,3'-furan]-1,4,5'(3*H*,4'*H*,6*H*)-trione (5ga)

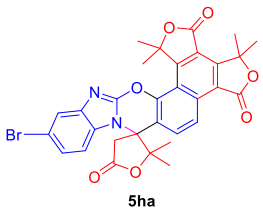


5ga

37% yield; white solid; mp = 342.6-352.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (d, *J* = 8.9 Hz, 1H), 7.98 (dd, *J* = 9.0, 1.9 Hz, 1H), 7.53 (s, 1H), 7.35 (s, 1H), 4.07 (s, 2H), 2.39 (s, 3H), 2.37 (s, 3H), 2.31 (s, 3H), 2.25 (s, 3H), 1.98 (d, *J* = 2.3 Hz, 6H), 1.17 (s, 3H), 1.06 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.39, 168.22, 166.55, 159.88, 154.63, 150.18, 145.47, 138.37, 133.91, 133.08, 132.69, 129.28, 127.88, 122.50, 121.54, 120.45, 120.35, 118.95, 117.27, 111.74, 92.07,

91.38, 86.31, 69.34, 38.61, 27.16, 26.96, 25.39, 22.47, 20.85, 20.13 ppm. ESI HRMS: calcd. for $C_{33}H_{30}N_2O_7$+H 567.2131, found 567.2125.

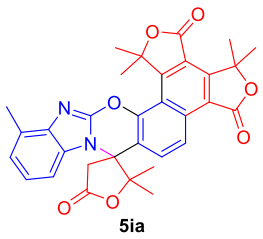
13-bromo-2',2',3,3,6,6-hexamethyl-2'*H*-spiro[benzo[4,5]imidazo[2,1-*b*]difuro[3',4':5,6; 3'',4'':7,8]naphtho[2,1-*e*][1,3]oxazine-9,3'-furan]-1,4,5'(3*H*,4'*H*,6*H*)-trione (5ha)



5ha

31% yield; brown solid; mp = 199.1-201.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (d, *J* = 9.0 Hz, 1H), 8.02 (dd, *J* = 9.1, 3.7 Hz, 1H), 7.92 – 7.61 (m, 1H), 7.52 – 7.39 (m, 2H), 4.16 (dd, *J* = 19.3, 7.2 Hz, 1H), 4.01 (dd, *J* = 19.2, 7.8 Hz, 1H), 2.32 – 2.22 (m, 6H), 1.98 (d, *J* = 4.0 Hz, 6H), 1.20 (d, *J* = 3.7 Hz, 3H), 1.05 (d, *J* = 14.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.07, 168.15, 166.43, 159.71, 154.80, 151.30, 145.14, 141.44, 134.01, 129.91, 127.79, 126.65, 123.11, 122.58, 121.99, 120.70, 118.88, 117.14, 116.76, 112.58, 91.97, 91.27, 86.39, 69.85, 38.52, 27.13, 26.95, 25.40, 25.37, 22.53, 22.28 ppm. ESI HRMS: calcd. for $C_{31}H_{25}BrN_2O_7$+H 617.0923, found 617.0916.

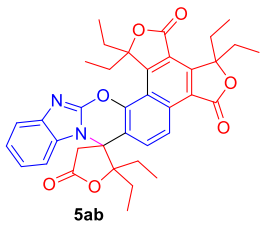
2',2',3,3,6,6,14-heptamethyl-2'*H*-spiro[benzo[4,5]imidazo[2,1-*b*]difuro[3',4':5,6;3'', 4'':7,8]naphtho[2,1-*e*][1,3]oxazine-9,3'-furan]-1,4,5'(3*H*,4'*H*,6*H*)-trione (5ia)



5ia

64% yield; yellow solid; mp = 334.5-336.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34 (d, *J* = 8.9 Hz, 1H), 7.99 (d, *J* = 9.0 Hz, 1H), 7.43 – 7.36 (m, 1H), 7.25 – 7.15 (m, 2H), 4.11 (dd, *J* = 13.7, 6.9 Hz, 2H), 2.65 (s, 3H), 2.33 (s, 3H), 2.28 (s, 3H), 2.00 (d, *J* = 3.1 Hz, 6H), 1.19 (s, 3H), 1.07 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.30, 168.23, 166.61, 159.98, 154.65, 150.03, 145.57, 139.27, 133.92, 130.63, 130.29, 127.83, 124.52, 123.41, 122.50, 121.55, 120.45, 118.98, 117.38, 108.76, 92.00, 91.51, 86.31, 69.44, 38.51, 27.06, 26.96, 25.42, 25.39, 22.61, 16.57 ppm. ESI HRMS: calcd. for $C_{32}H_{28}N_2O_7$+H 553.1975, found 553.1971.

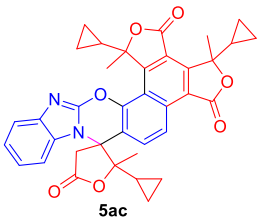
2',2',3,3,6,6-hexaethyl-2'*H*-spiro[benzo[4,5]imidazo[2,1-*b*]difuro[3',4':5,6;3'',4'':7,8] naphtho[2,1-*e*][1,3]oxazine-9,3'-furan]-1,4,5'(3*H*,4'*H*,6*H*)-trione (5ab)



5ab

16% yield; yellow solid; mp = 281.8-310.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (d, *J* = 8.9 Hz, 1H), 8.00 (d, *J* = 9.0 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 4.09 (d, *J* = 19.5 Hz, 1H), 4.04 (d, *J* = 19.5 Hz, 1H), 3.14 (dq, *J* = 14.9, 7.4 Hz, 1H), 3.00 (dq, *J* = 14.9, 7.4 Hz, 1H), 2.71 – 2.51 (m, 4H), 2.40 (ddq, *J* = 14.4, 10.3, 7.2 Hz, 2H), 1.75 (dq, *J* = 14.8, 7.4 Hz, 1H), 1.50 (dq, *J* = 15.1, 7.6 Hz, 1H), 1.40 (dq, *J* = 14.6, 7.2 Hz, 1H), 1.19 (dt, *J* = 14.5, 7.3 Hz, 1H), 0.67 (dt, *J* = 11.2, 7.4 Hz, 9H), 0.62 (dq, *J* = 7.6, 4.1 Hz, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.37, 169.02, 167.37, 156.08, 151.75, 150.15, 145.73, 140.13, 133.35, 131.16, 128.20, 124.53, 124.17, 123.76, 123.53, 121.64, 120.32, 119.37, 117.17, 111.73, 97.83, 96.99, 92.36, 69.58, 40.19, 31.39, 31.27, 29.79, 29.52, 29.47, 28.55, 24.28, 8.26, 8.08, 7.93, 7.84, 7.67 ppm. ESI HRMS: calcd. for $C_{37}H_{38}N_2O_7$+H 623.2757, found 623.2754.

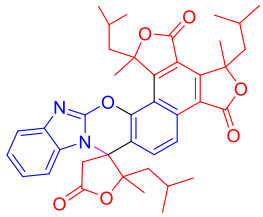
2',3,6-tricyclopropyl-2',3,6-trimethyl-2'*H*-spiro[benzo[4,5]imidazo[2,1-*b*]difuro[3',4':5,6;3'',4'':7,8]naphtha[2,1-*e*][1,3]oxazine-9,3'-furan]-1,4,5'(3*H*,4'*H*,6*H*)-trione (5ac)



5ac

76% yield; green solid; mp = 167.5-182.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 – 9.24 (m, 1H), 8.18 – 7.96 (m, 1H), 7.78 (dq, *J* = 10.1, 5.2, 4.7 Hz, 1H), 7.61 – 7.50 (m, 1H), 7.34 (dtd, *J* = 18.3, 7.5, 3.1 Hz, 2H), 4.16 – 3.95 (m, 2H), 2.64 – 2.52 (m, 1H), 2.39 (dt, *J* = 6.4, 3.0 Hz, 3H), 2.16 (q, *J* = 6.4, 5.8 Hz, 1H), 2.05 (d, *J* = 4.4 Hz, 3H), 1.25 (s, 3H), 1.08 (d, *J* = 5.4 Hz, 1H), 1.06 – 1.01 (m, 2H), 0.94 – 0.75 (m, 2H), 0.65 (ddt, *J* = 25.2, 9.2, 3.8 Hz, 2H), 0.54 – 0.33 (m, 1H), 0.33 – 0.21 (m, 2H), 0.14 (dh, *J* = 9.5, 5.9 Hz, 2H), 0.07 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.45, 168.59, 167.00, 159.95, 154.66, 151.25, 145.69, 140.12, 134.12, 131.34 (m, *J* = 8.1, 70.5, 3.4 Hz), 128.15 (d, *J* = 72.9 Hz), 124.16, 123.95, 123.72, 123.53, 121.63 (m, *J* = 46.0, 50.0 Hz), 120.28, 117.59, 116.97, 111.37 (m, *J* = 7.1, 8.1 Hz), 92.67 (m, *J* = 77.0 Hz), 90.99 (m, *J* = 9.8, 28.2, 6.4 Hz), 85.89, 70.48, 39.12 (m, *J* = 130.1 Hz), 26.17, 25.85, 24.14, 20.50 (d, *J* = 153.5 Hz), 18.13 (d, *J* = 80.8 Hz), 15.34, 3.96, 3.60, 2.49, 1.93, 1.70, 0.78 ppm. ESI HRMS: calcd. for $C_{37}H_{32}N_2O_7$+H 617.2288, found 617.2292.

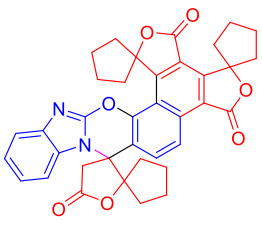
2',3,6-triisobutyl-2',3,6-trimethyl-2'*H*-spiro[benzo[4,5]imidazo[2,1-*b*]difuro[3',4':5,6; 3'',4'':7,8]naphtho[2,1-*e*][1,3]oxazine-9,3'-furan]-1,4,5'(3*H*,4'*H*,6*H*)-trione (5ad)



5ad

30% yield; yellow solid; mp = 221.2-223.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.35 (dd, *J* = 8.9, 4.0 Hz, 1H), 7.97 (dd, *J* = 46.9, 9.0 Hz, 1H), 7.79 (t, *J* = 7.9 Hz, 1H), 7.58 (dd, *J* = 32.2, 8.3 Hz, 1H), 7.38 (q, *J* = 7.3 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 4.12 (dd, *J* = 41.7, 19.2 Hz, 1H), 3.99 (dd, *J* = 19.2, 5.8 Hz, 1H), 2.97 (ddd, *J* = 15.4, 6.6, 2.9 Hz, 1H), 2.53 (ddt, *J* = 34.8, 15.4, 5.5 Hz, 2H), 2.32 (ddd, *J* = 21.0, 15.0, 5.5 Hz, 1H), 2.25 (d, *J* = 3.3 Hz, 3H), 1.95 (s, 3H), 1.52 – 1.35 (m, 2H), 1.33 – 1.26 (m, 3H), 1.19 (s, 2H), 1.07 (s, 1H), 0.93 (dd, *J* = 13.4, 6.7 Hz, 3H), 0.87 (dd, *J* = 6.7, 2.8 Hz, 3H), 0.74 (dd, *J* = 16.6, 6.5 Hz, 3H), 0.66 (dd, *J* = 21.7, 6.8 Hz, 6H), 0.51 (dd, *J* = 21.8, 6.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.72, 168.54, 166.80, 158.34, 153.94, 150.67, 145.55, 140.00, 133.51, 130.96, 128.07, 124.07, 123.72, 123.21, 122.08, 121.49, 120.23, 119.58, 117.84, 111.36, 94.36, 93.99, 88.97, 77.34, 77.23, 77.02, 76.71, 70.67, 47.37, 46.84, 45.53, 42.41, 38.20, 27.77, 25.52, 25.37, 24.97, 24.72, 24.31, 24.07, 23.87, 23.69, 22.49, 19.32 ppm. ESI HRMS: calcd. for $C_{40}H_{44}N_2O_7$+H 665.3227, found 665.3233.

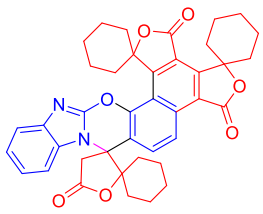
2',3,6-tricyclopentane-2'*H*-spiro[benzo[4,5]imidazo[2,1-*b*]difuro[3',4':5, 6;3'',4'': 7,8]naphtha[2,1-*e*][1,3]oxazine-9,3'-furan]-1,4,5'(3*H*,4'*H*,6*H*)-trione (5ae)



5ae, 72%

72% yield; yellow solid; mp = 236.9-243.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34 (d, *J* = 9.0 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.31 (m, 2H), 4.25 (d, *J* = 19.4 Hz, 1H), 3.89 (d, *J* = 19.4 Hz, 1H), 3.21 – 2.94 (m, 2H), 2.83 (ddd, *J* = 20.3, 11.9, 7.1 Hz, 2H), 2.74 – 2.25 (m, 4H), 2.24 – 2.01 (m, 8H), 1.99 (d, *J* = 5.3 Hz, 1H), 1.89 – 1.65 (m, 1H), 1.45 – 1.36 (m, 1H), 1.23 – 1.11 (m, 1H), 0.95 – 0.76 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.06, 168.30, 166.61, 157.51, 152.23, 149.82, 144.88, 140.20, 133.82, 130.98, 129.93, 127.70, 123.87, 123.36, 123.27, 121.80, 121.67, 120.36, 119.08, 117.92, 111.63, 103.12, 101.45, 96.03, 67.57, 40.61, 40.08, 39.95, 37.98, 37.89, 37.51, 34.25, 25.95, 25.77, 25.39(d, *J* = 2.2 Hz), 22.86, 22.03 ppm. ESI HRMS: calcd. for $C_{37}H_{32}N_2O_7$+Na 639.2107, found 639.2099.

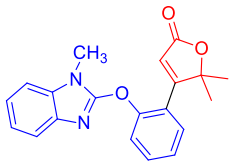
2',3,6-cyclohexane-2'*H*-spiro[benzo[4,5]imidazo[2,1-*b*]difuro[3',4':5, 6;3'',4'': 7,8]naphtha[2,1-*e*][1,3]oxazine-9,3'-furan]-1,4,5'(3*H*,4'*H*,6*H*)-trione (5af)



5af, 70%

70% yield; light yellow solid; mp = 354.5-357.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (d, *J* = 9.0 Hz, 1H), 7.91 (d, *J* = 9.1 Hz, 1H), 7.76 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.35 (dtd, *J* = 22.3, 7.5, 1.3 Hz, 2H), 4.12 – 4.00 (m, 2H), 3.30 – 3.14 (m, 2H), 2.89 (ddt, *J* = 18.0, 12.2, 5.4 Hz, 2H), 2.31 (dq, *J* = 12.0, 6.9, 6.0 Hz, 1H), 2.02 (ddd, *J* = 15.9, 9.4, 4.1 Hz, 4H), 1.94 – 1.82 (m, 6H), 1.75 – 1.58 (m, 5H), 1.55 (s, 4H), 1.50 (td, *J* = 7.2, 6.6, 3.4 Hz, 1H), 1.43 (s, 1H), 1.09 (t, *J* = 6.6 Hz, 2H), 0.86 (d, *J* = 6.7 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.39, 168.53, 166.71, 160.18, 154.86, 150.83, 145.43, 140.25, 134.15, 131.19, 127.79, 123.87, 123.53, 122.55, 121.57, 121.07, 120.36, 119.23, 117.29, 111.40, 93.37, 93.13, 88.23, 69.97, 38.59, 35.56, 34.28, 33.42, 33.38, 30.40, 29.71, 24.14, 24.05, 23.31, 23.00, 22.96, 22.37, 22.34, 22.13, 21.56 ppm. ESI HRMS: calcd. for $C_{40}H_{38}N_2O_7$+Na 681.2577, found 681.2574.

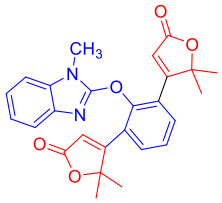
5,5-dimethyl-4-(2-((1-methyl-1*H*-benzo[*d*]imidazol-2-yl)oxy)phenyl)furan-2(5*H*)-one (3')



3'

73% yield; white solid; mp = 121.7-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 3H), 7.36 (d, *J* = 3.7 Hz, 2H), 7.22 (dd, *J* = 10.5, 4.4 Hz, 4H), 6.08 (s, 1H), 3.68 (s, 3H), 1.57 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.24, 168.80, 155.32, 150.44, 139.33, 133.97, 131.31, 128.66, 125.86, 123.89, 122.19, 122.16, 121.90, 119.53, 118.64, 108.56, 88.66, 28.59, 25.50 ppm. ESI HRMS: calcd. for $C_{20}H_{18}N_2O_3$+H 335.1396, found 335.1393.

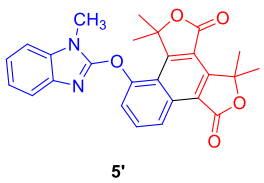
4,4'-(2-((1-methyl-1*H*-benzo[*d*]imidazol-2-yl)oxy)-1,3-phenylene)bis(5,5-dimethylfuran-2(5*H*)-one) (4')



4'

38% yield; light yellow solid; mp = 250.4-252.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (q, *J* = 5.3 Hz, 3H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.22 – 7.13 (m, 3H), 5.99 (s, 2H), 3.62 (s, 3H), 1.55 (s, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.57, 167.52, 155.38, 147.02, 138.76, 133.95, 130.07, 127.32, 126.91, 122.44, 122.26, 120.14, 118.46, 108.78, 88.46, 28.52, 25.56 ppm. ESI HRMS: calcd. for $C_{26}H_{24}N_2O_5$+H 445.1763, found 445.1765.

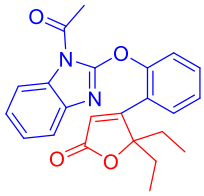
3,3,6,6-tetramethyl-7-((1-methyl-1*H*-benzo[*d*]imidazol-2-yl)oxy)naphtho[1,2-*c*:3,4-*c'*]difuran-1,4(3*H*,6*H*)-dione (5')



5'

25% yield; white solid; mp = 206.4-210.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (d, *J* = 8.3 Hz, 1H), 7.87 (t, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.47 – 7.23 (m, 4H), 3.88 (s, 3H), 2.04 (s, 6H), 1.97 (s, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.63, 166.95, 159.24, 154.21, 153.11, 150.80, 139.46, 134.16, 134.00, 132.01, 122.85, 122.71, 122.62, 122.36, 120.41, 119.42, 118.94, 118.81, 109.05, 90.07, 85.66, 29.17, 27.09, 25.44 ppm. ESI HRMS: calcd. for $C_{26}H_{22}N_2O_5$+Na 465.1426, found 465.1417.

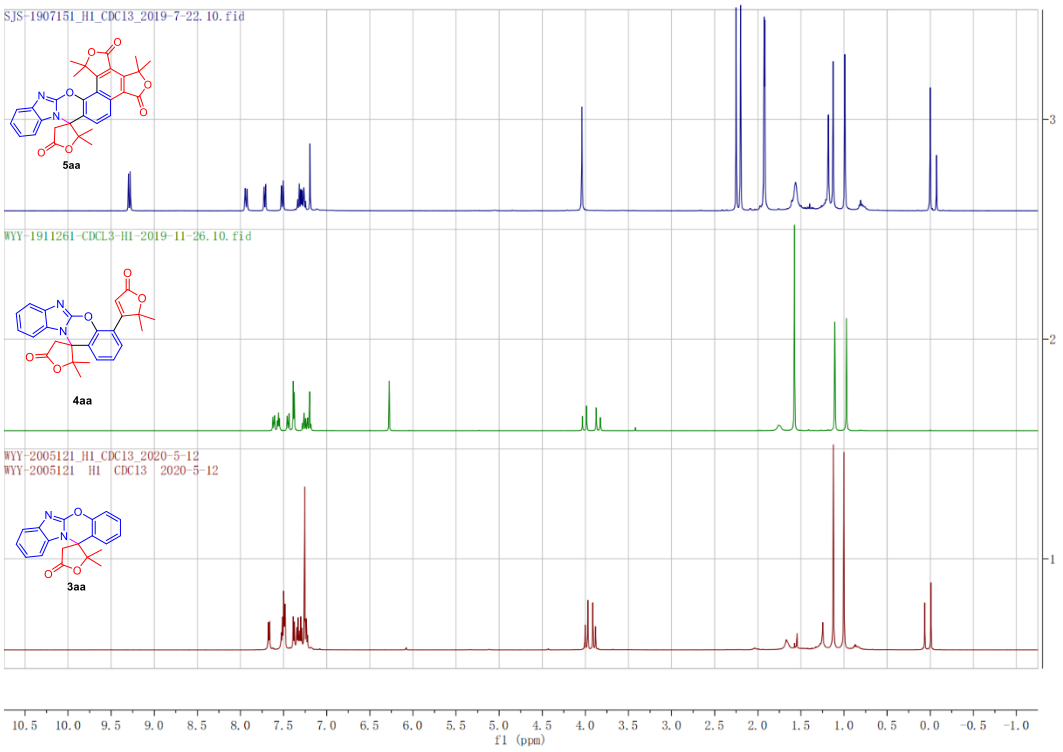
4-(2-((1-acetyl-1*H*-benzo[*d*]imidazol-2-yl)oxy)phenyl)-5,5-diethylfuran-2(5*H*)-one(6)

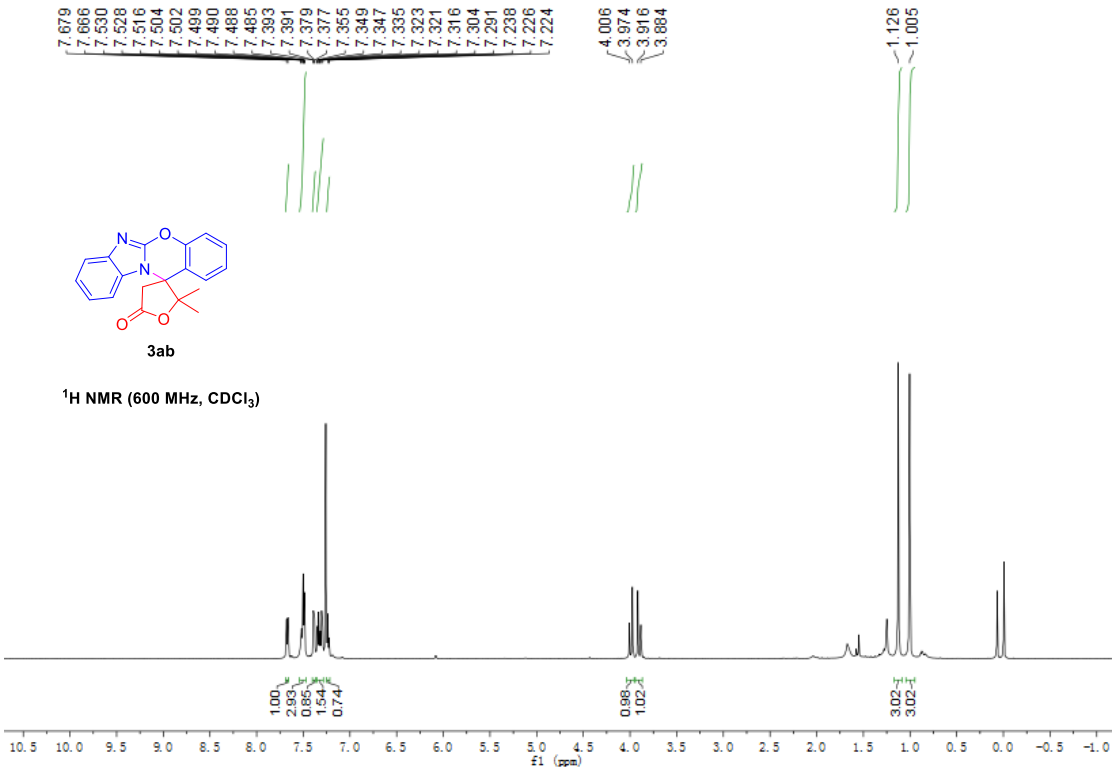


6

51% yield; light yellow solid; mp = 210.4-212.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.18 (m, 1H), 7.65 – 7.54 (m, 1H), 7.48 – 7.39 (m, 4H), 7.31 (td, *J* = 6.6, 5.6, 3.7 Hz, 2H), 6.28 (s, 1H), 2.74 (s, 3H), 2.07 (dd, *J* = 14.5, 7.2 Hz, 2H), 1.91 (dd, *J* = 14.6, 7.4 Hz, 2H), 0.86 (d, *J* = 7.5 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.66, 167.71, 163.31, 154.14, 150.71, 138.86, 132.09, 131.79, 128.14, 127.08, 125.26, 124.55, 124.24, 123.10, 121.87, 118.66, 115.93, 94.02, 30.01, 29.85, 26.32, 7.55, 7.45 ppm. ESI HRMS: calcd. for $C_{23}H_{22}N_2O_4$+H 391.1658, found 391.1652.

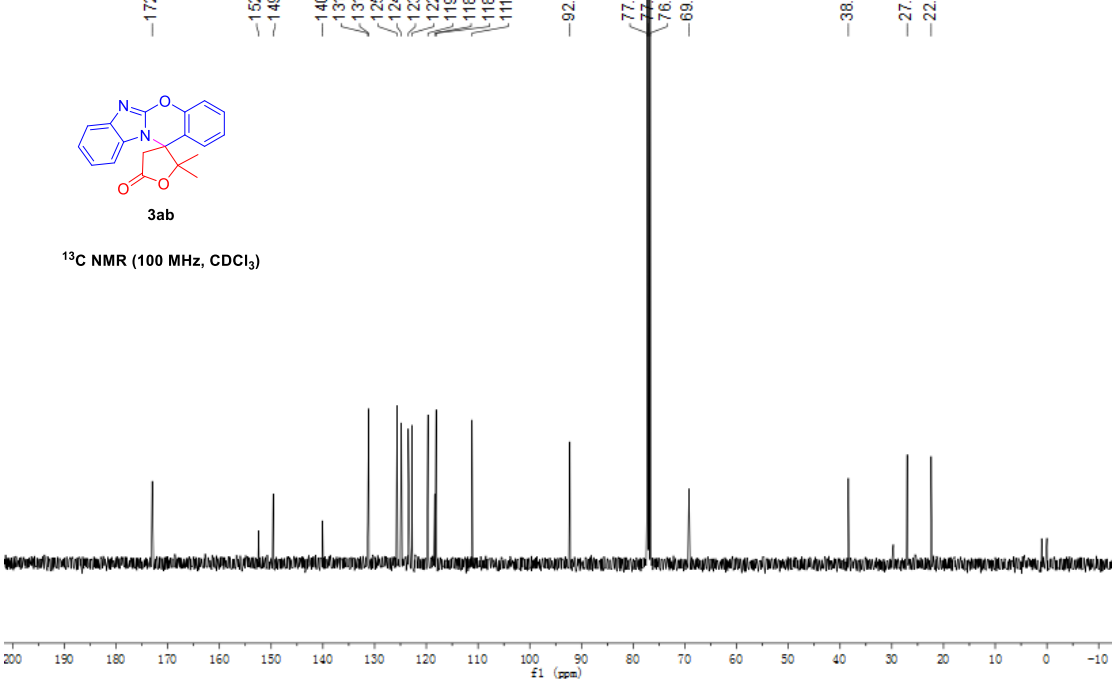
10. ^{1}H and ^{13}C NMR spectra.





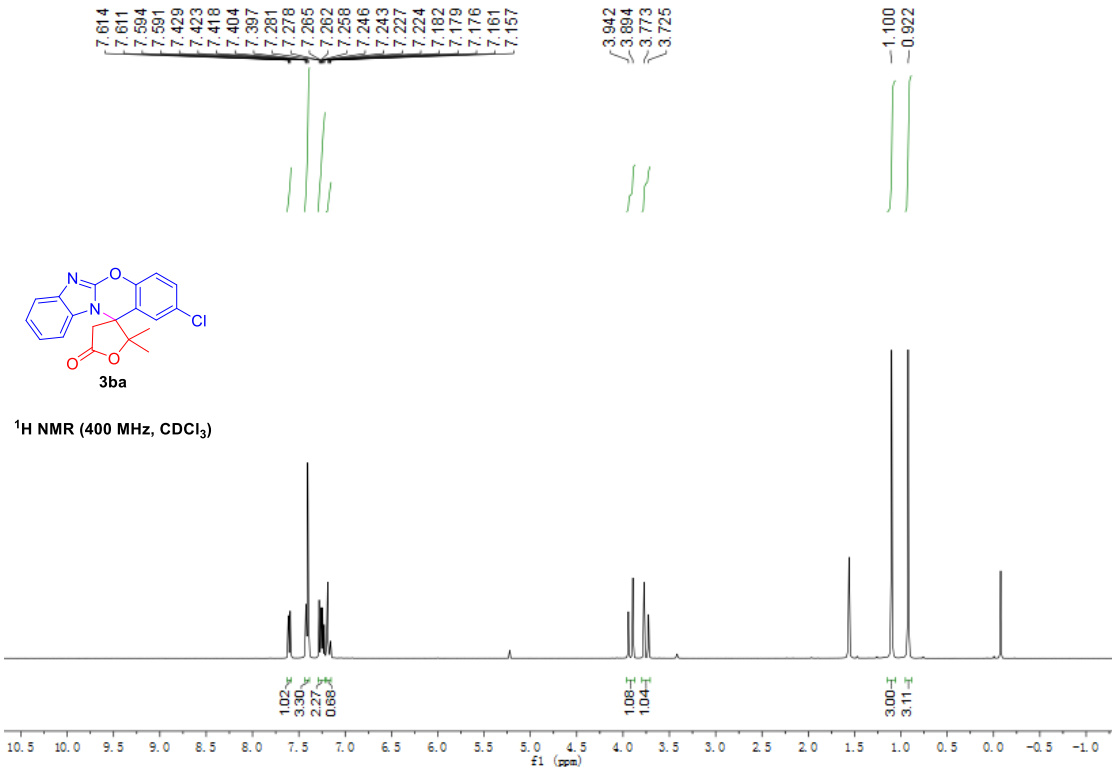
3ab

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



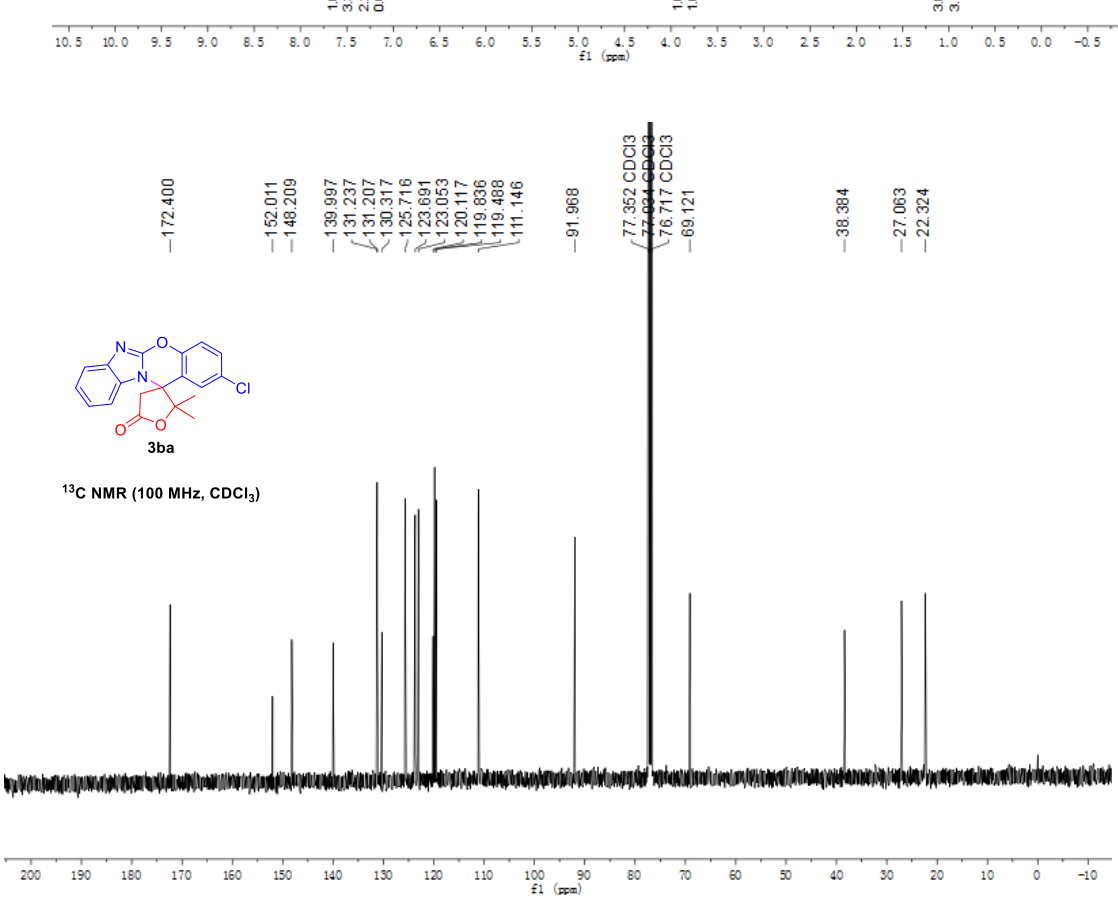
3ab

^{13}C NMR (100 MHz, $CDCl_3$)



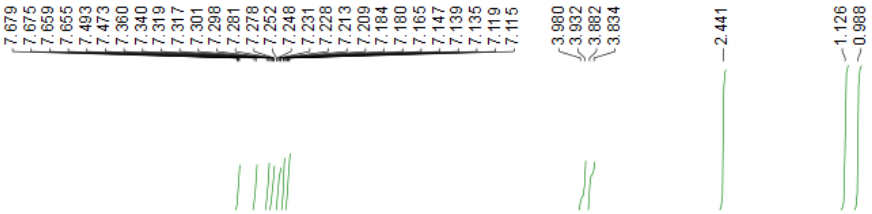
3ba

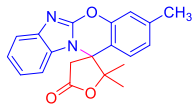
^{1}H NMR (400 MHz, $CDCl_3$)



3ba

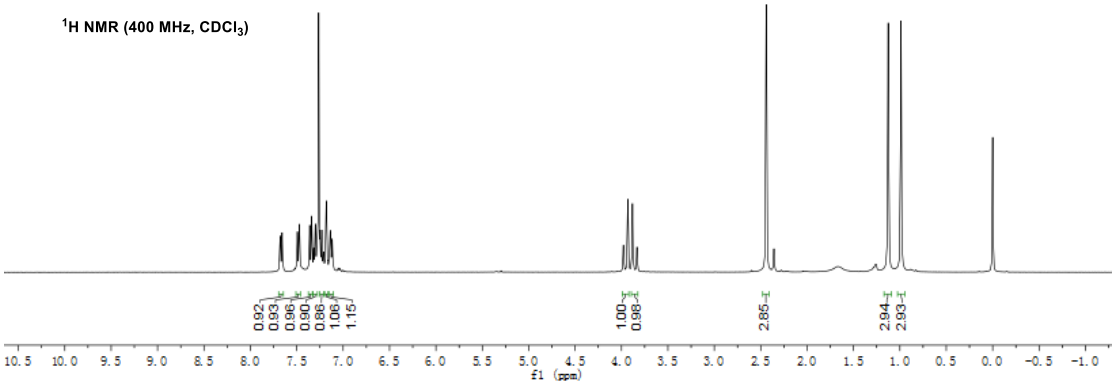
^{13}C NMR (100 MHz, $CDCl_3$)

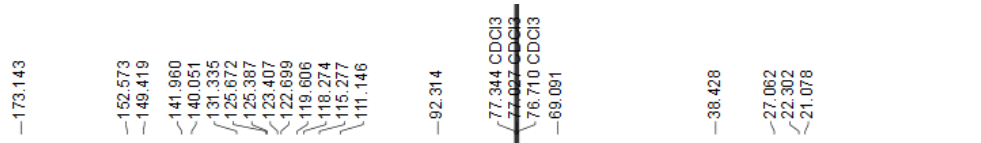


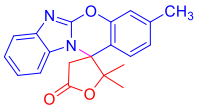


3ca

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

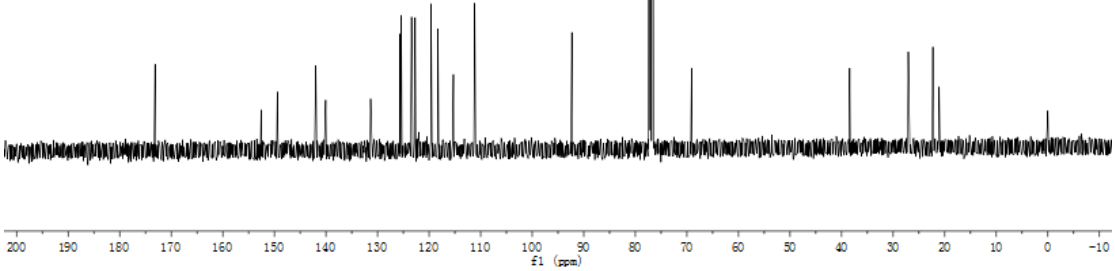


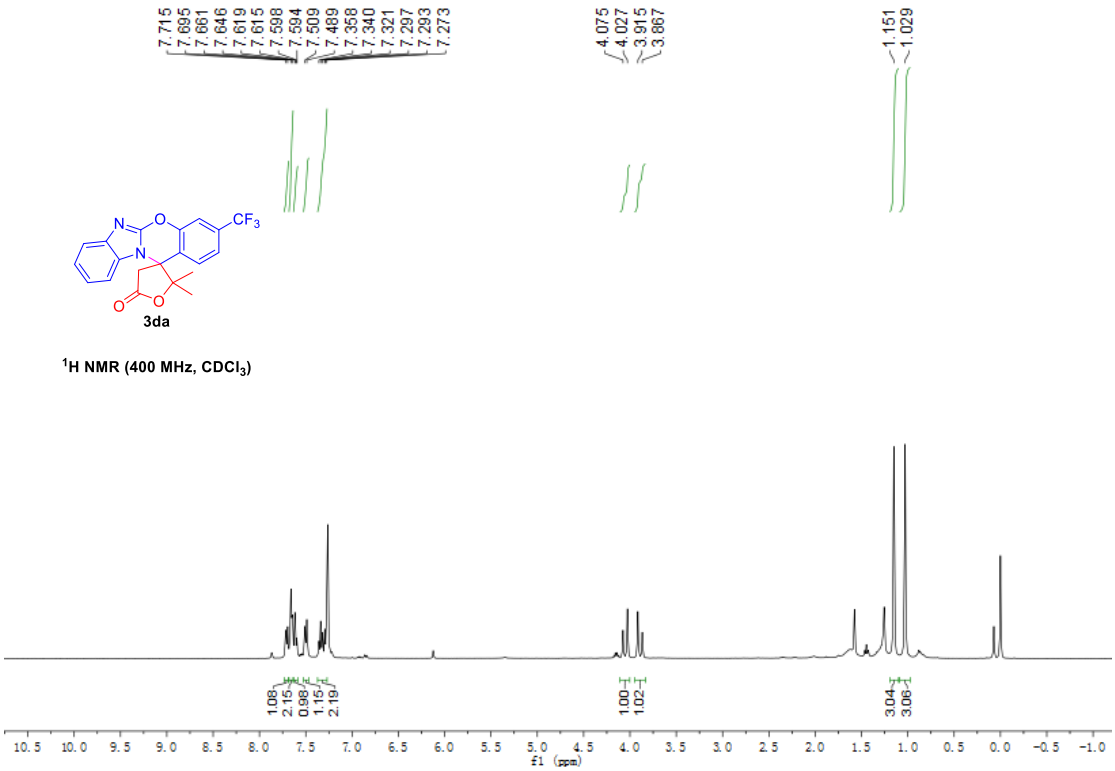




3ca

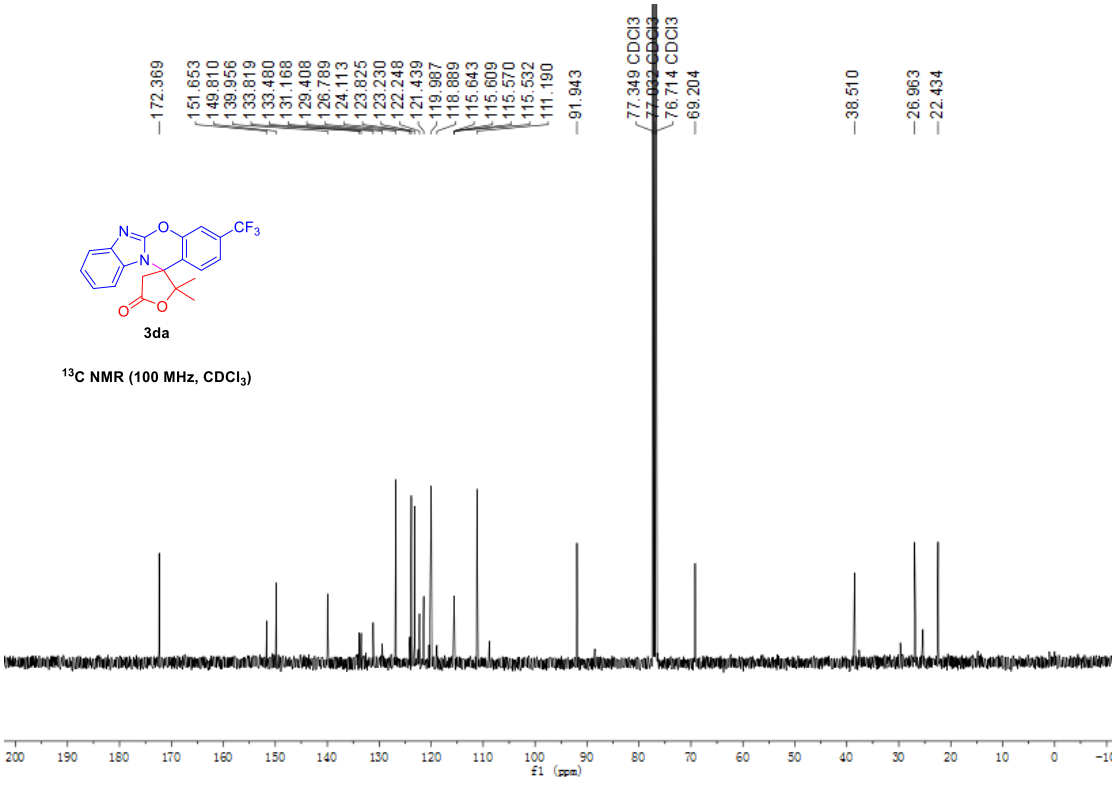
^{13}C NMR (100 MHz, $CDCl_3$)





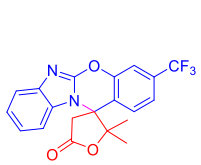
3da

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



3da

^{13}C NMR (100 MHz, $CDCl_3$)

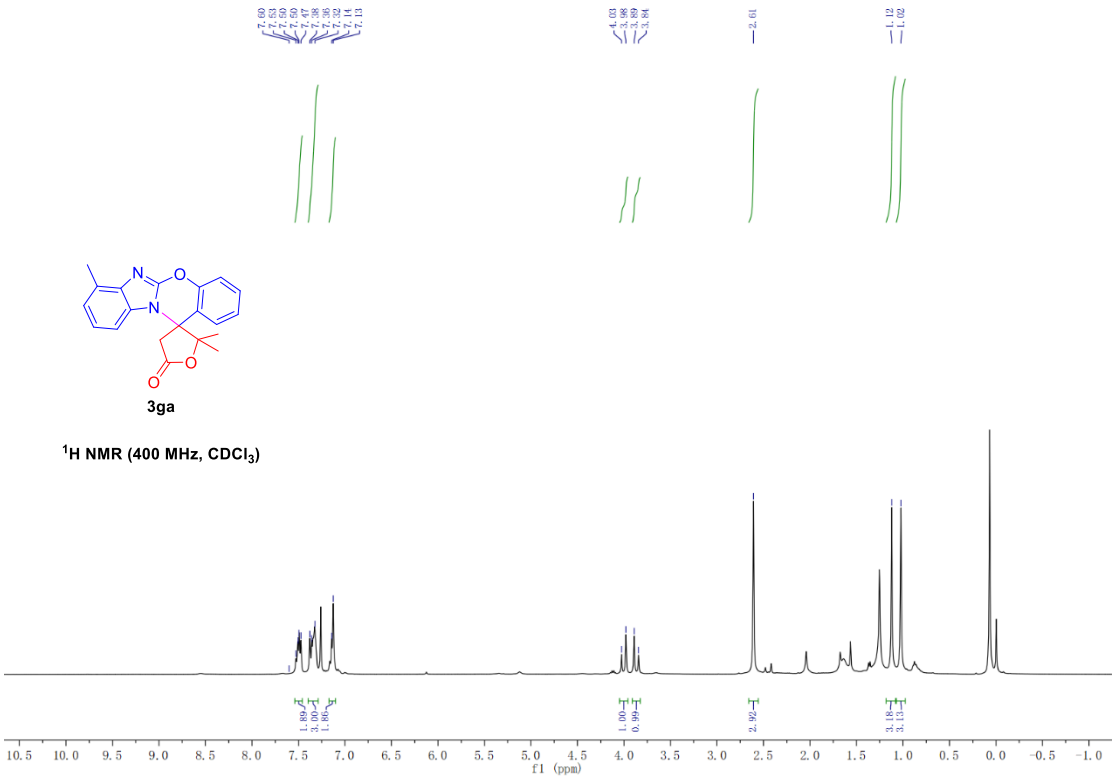


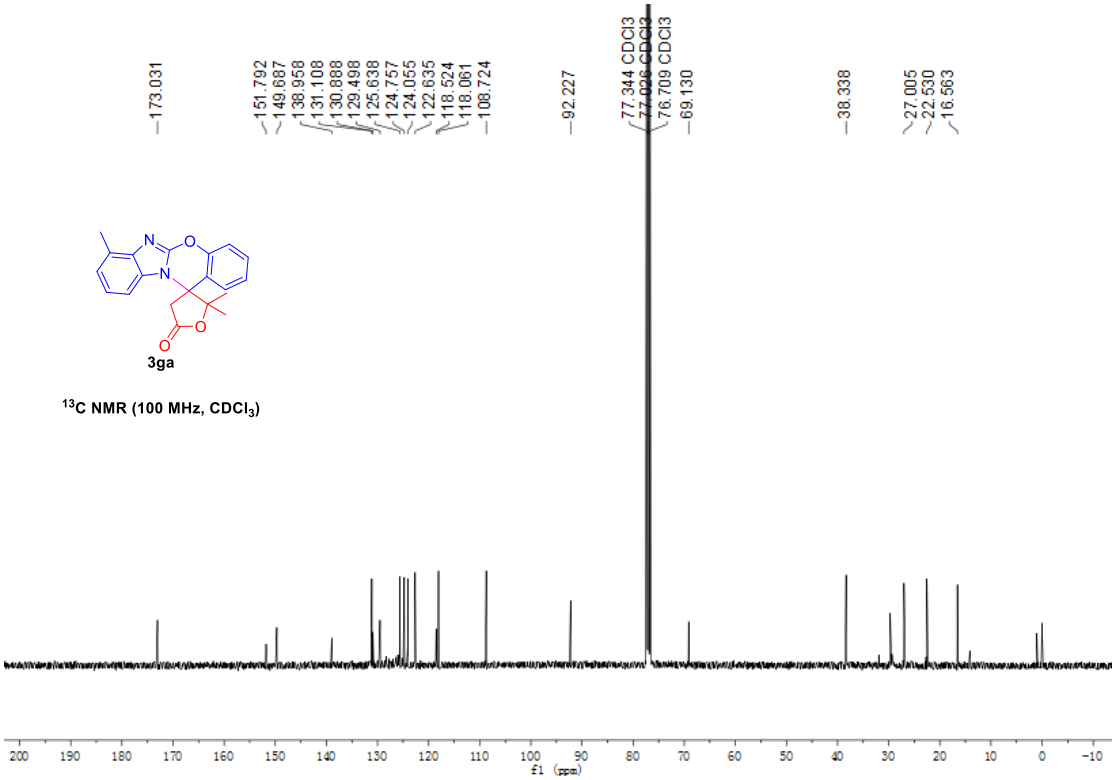
3da

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

3ga

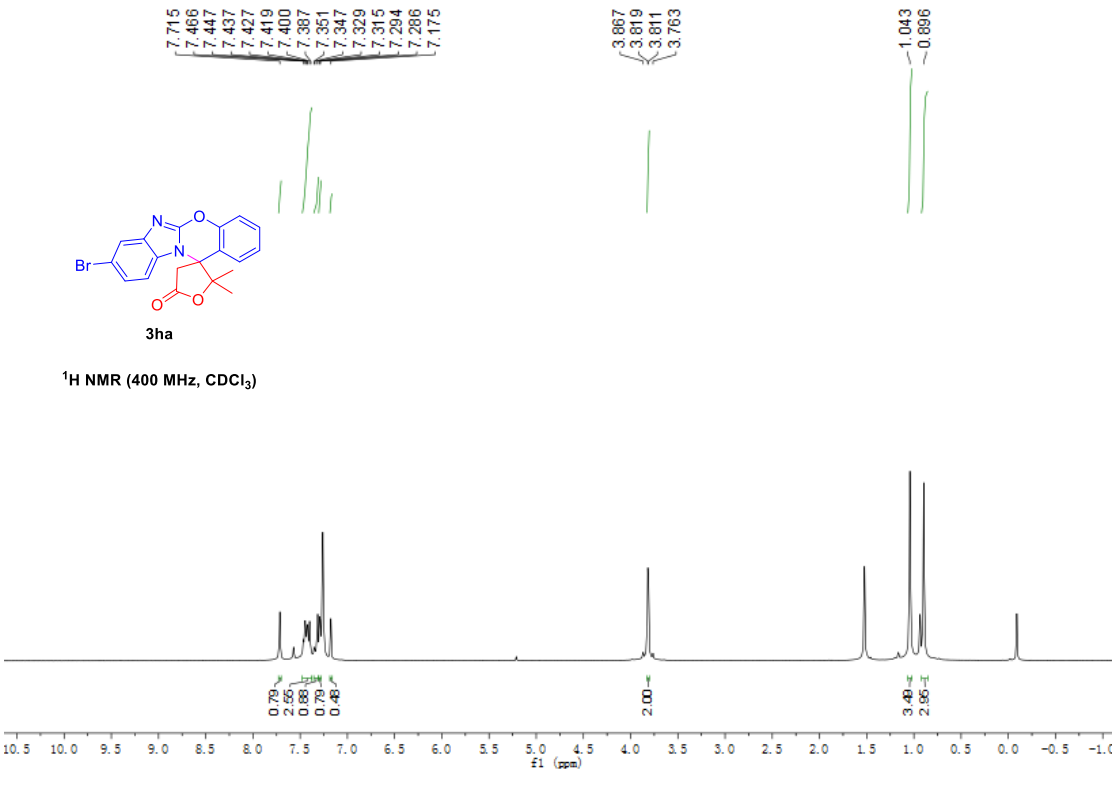
^{1}H NMR (400 MHz, $CDCl_3$)





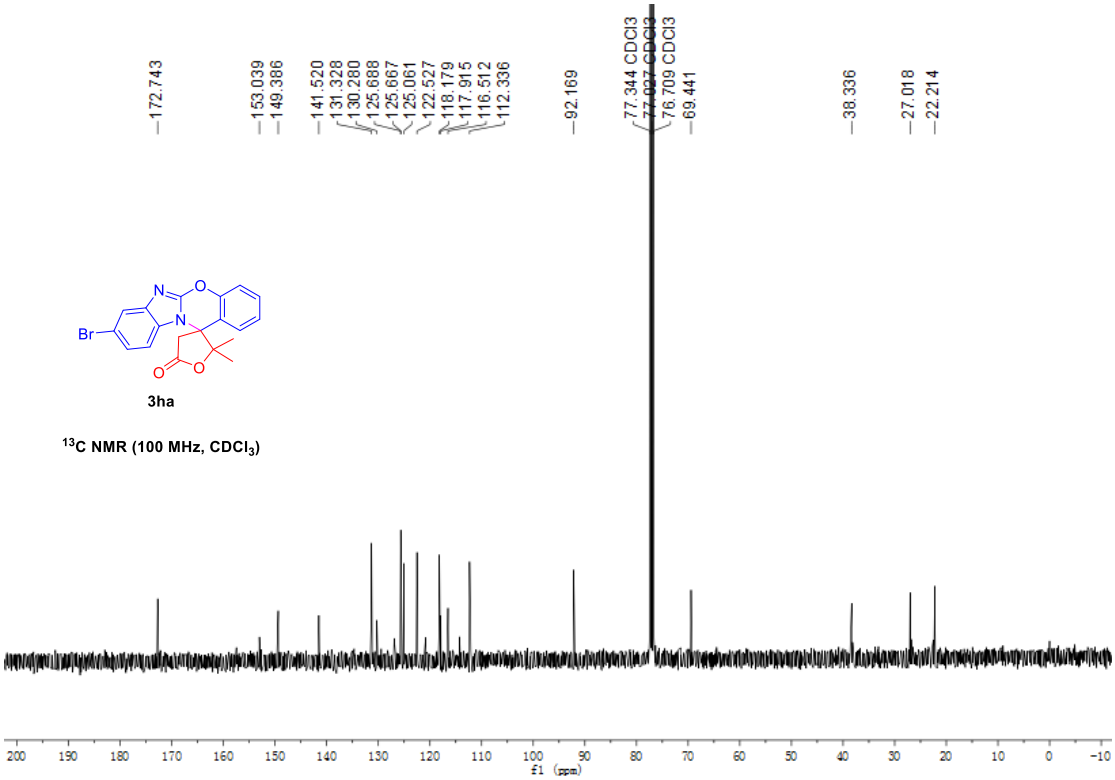
3ga

^{13}C NMR (100 MHz, $CDCl_3$)



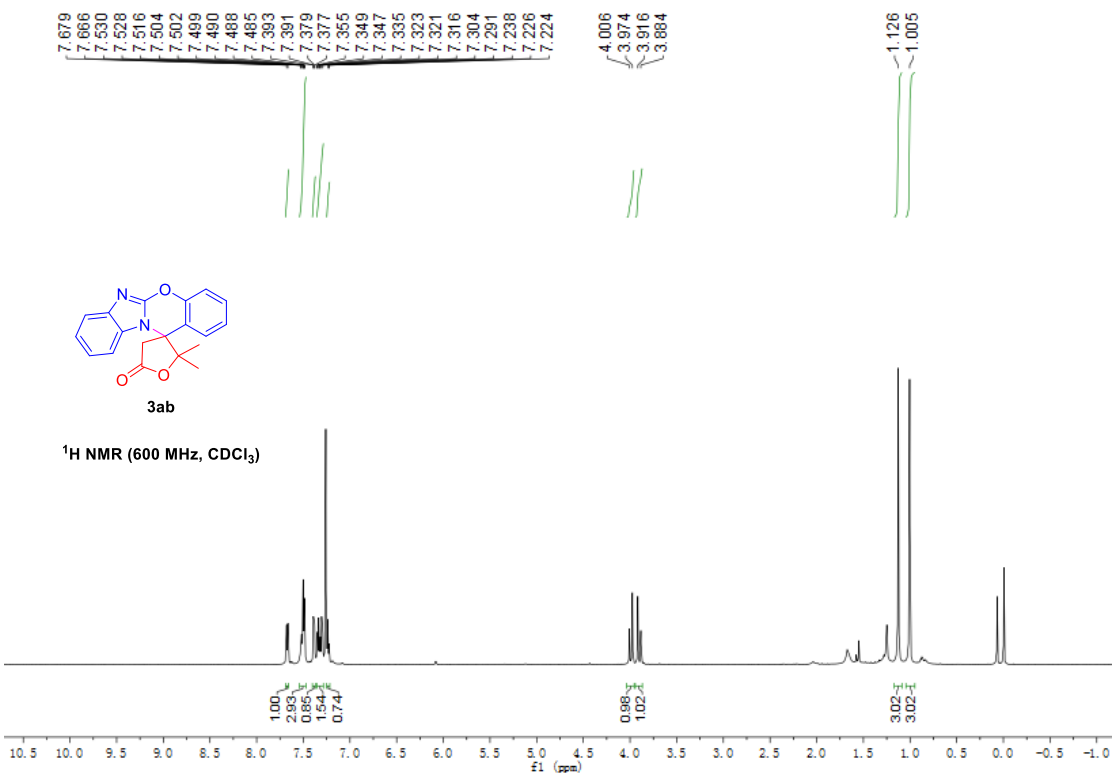
3ha

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



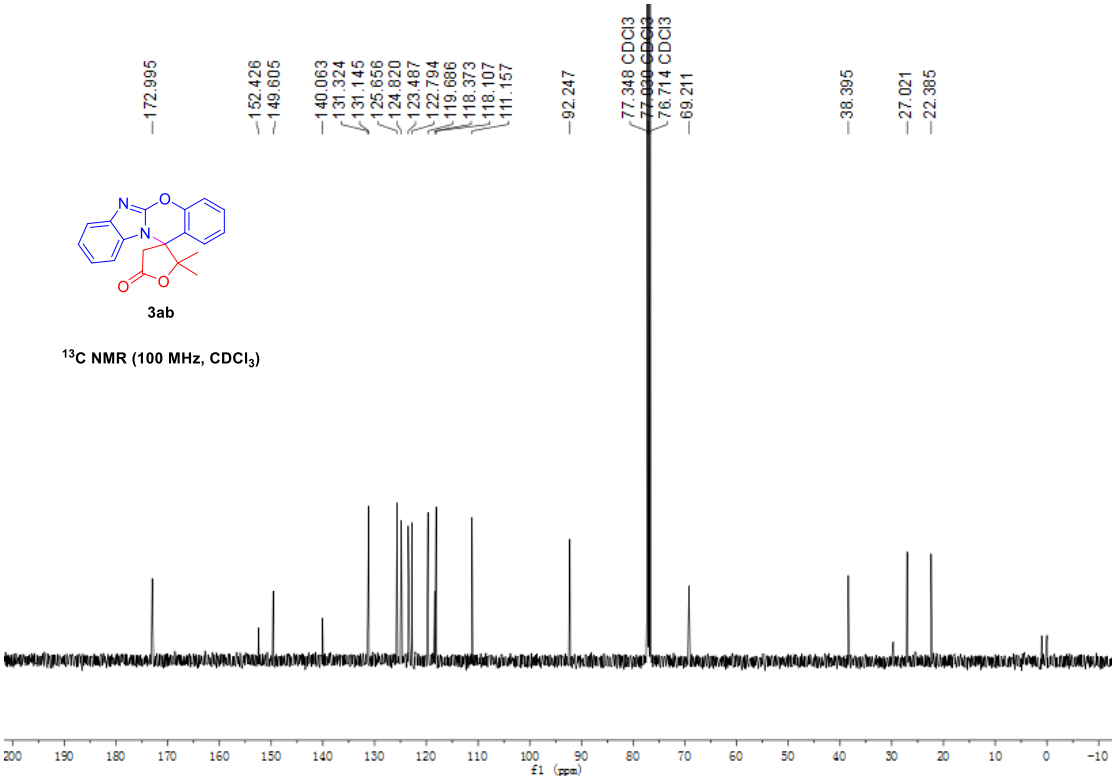
3ha

^{13}C NMR (100 MHz, $CDCl_3$)



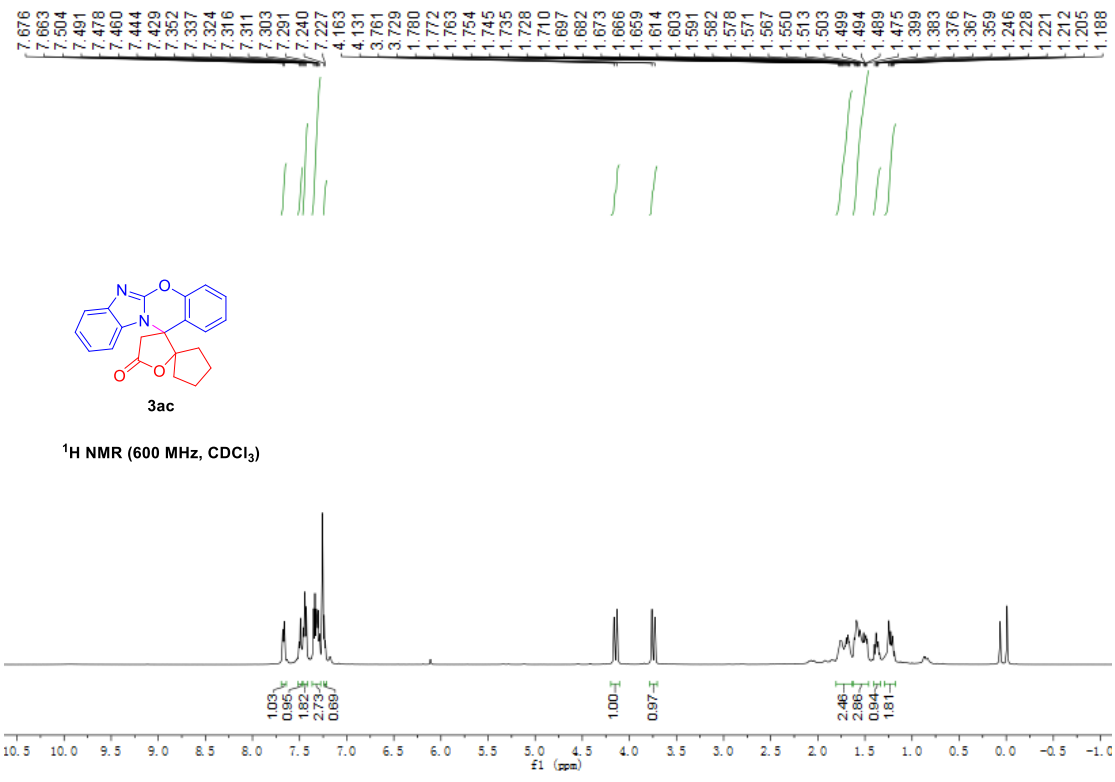
3ab

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



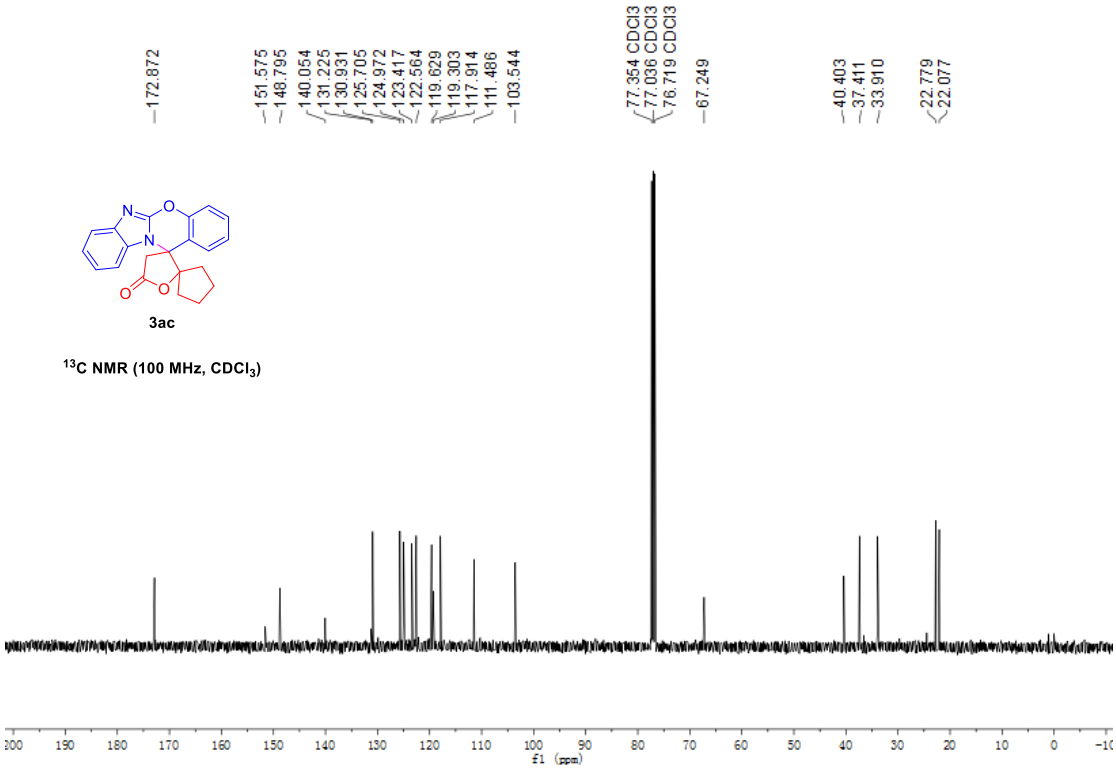
3ab

^{13}C NMR (100 MHz, $CDCl_3$)



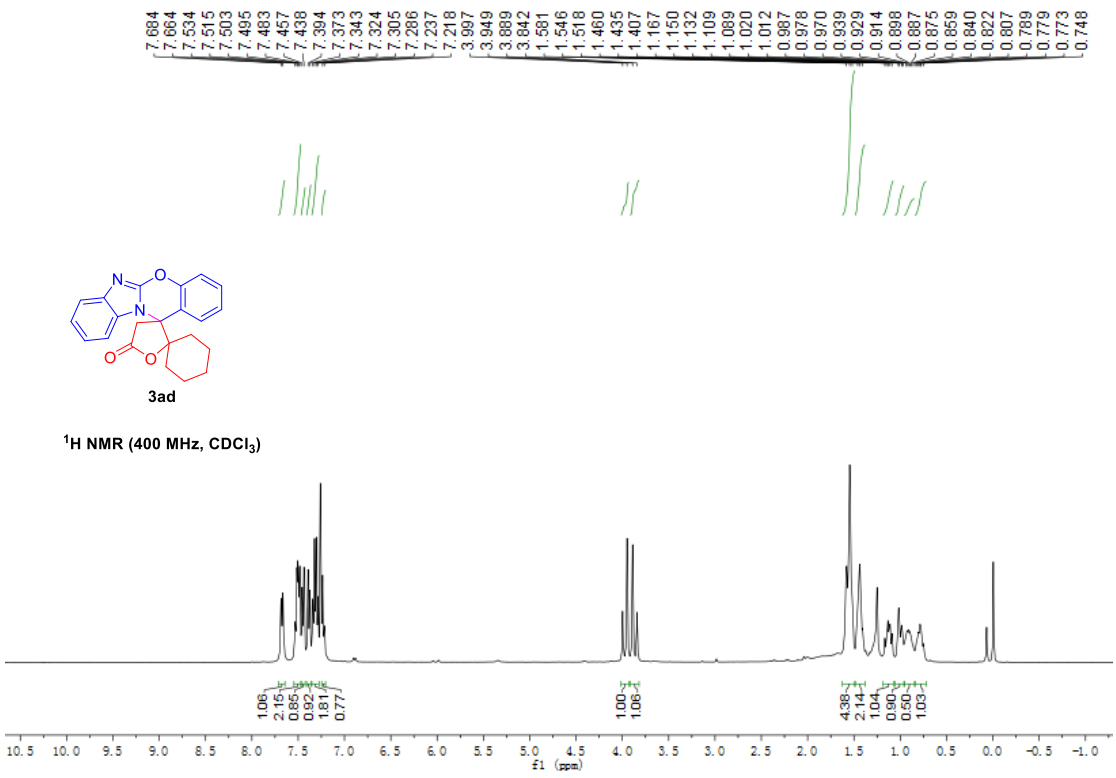
3ac

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



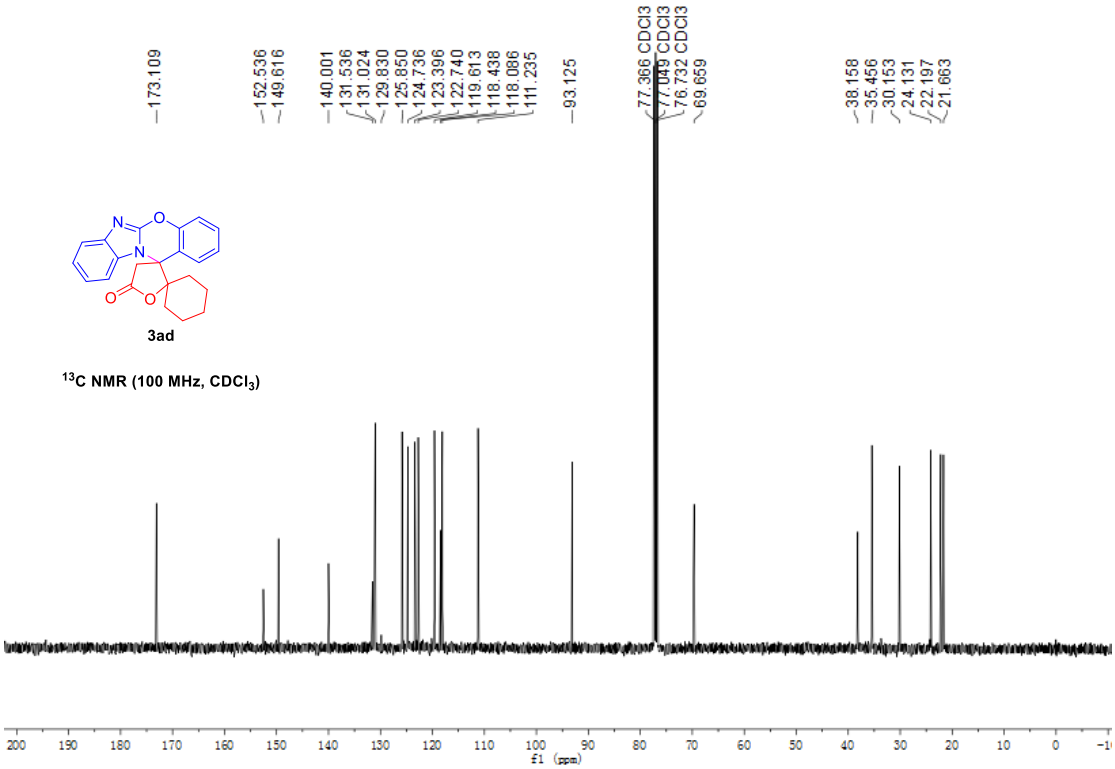
3ac

^{13}C NMR (100 MHz, $CDCl_3$)



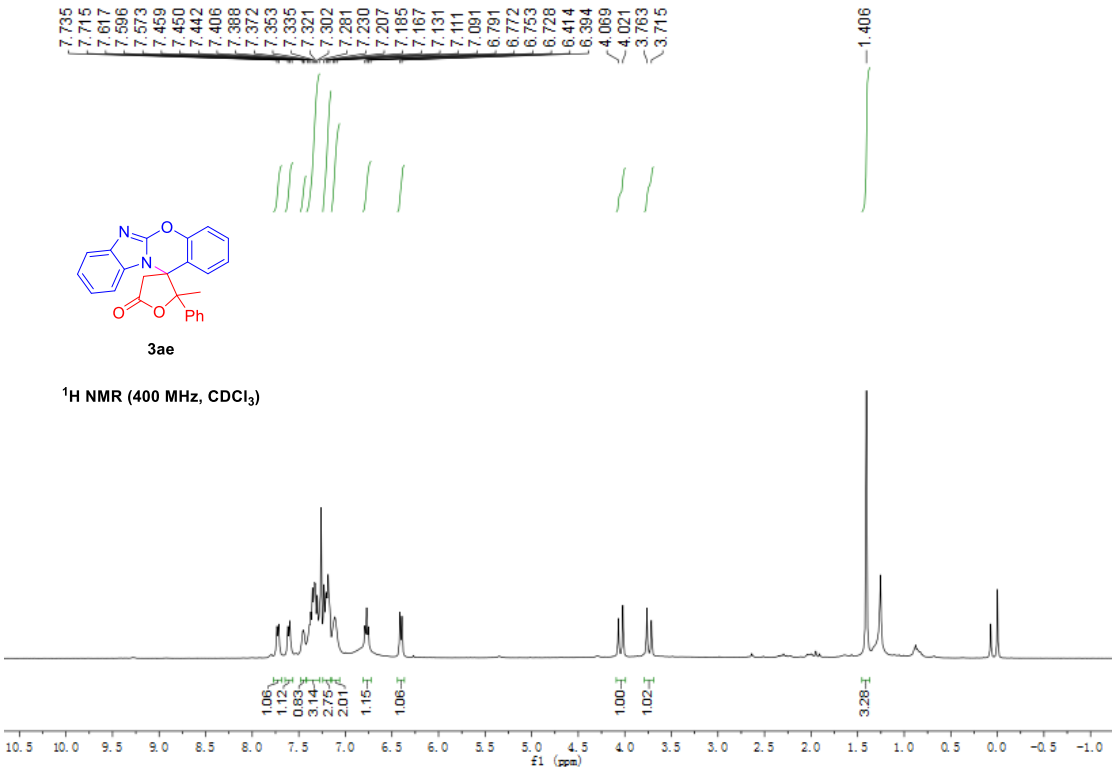
3ad

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



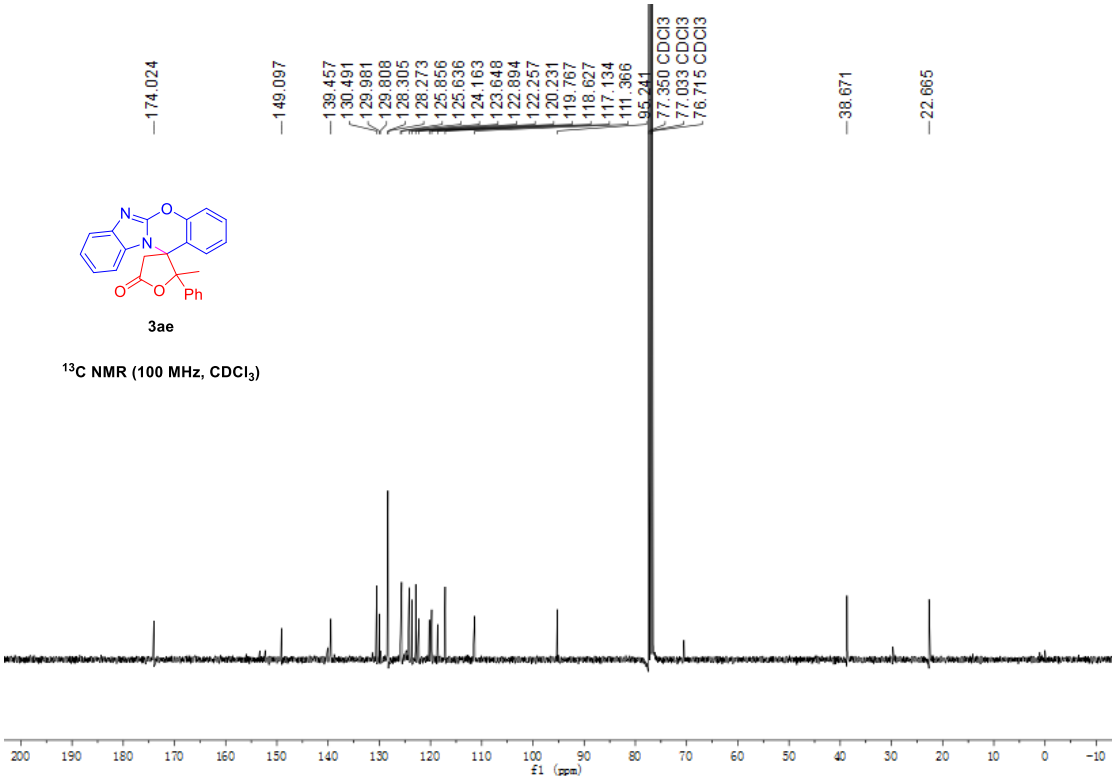
3ad

^{13}C NMR (100 MHz, $CDCl_3$)



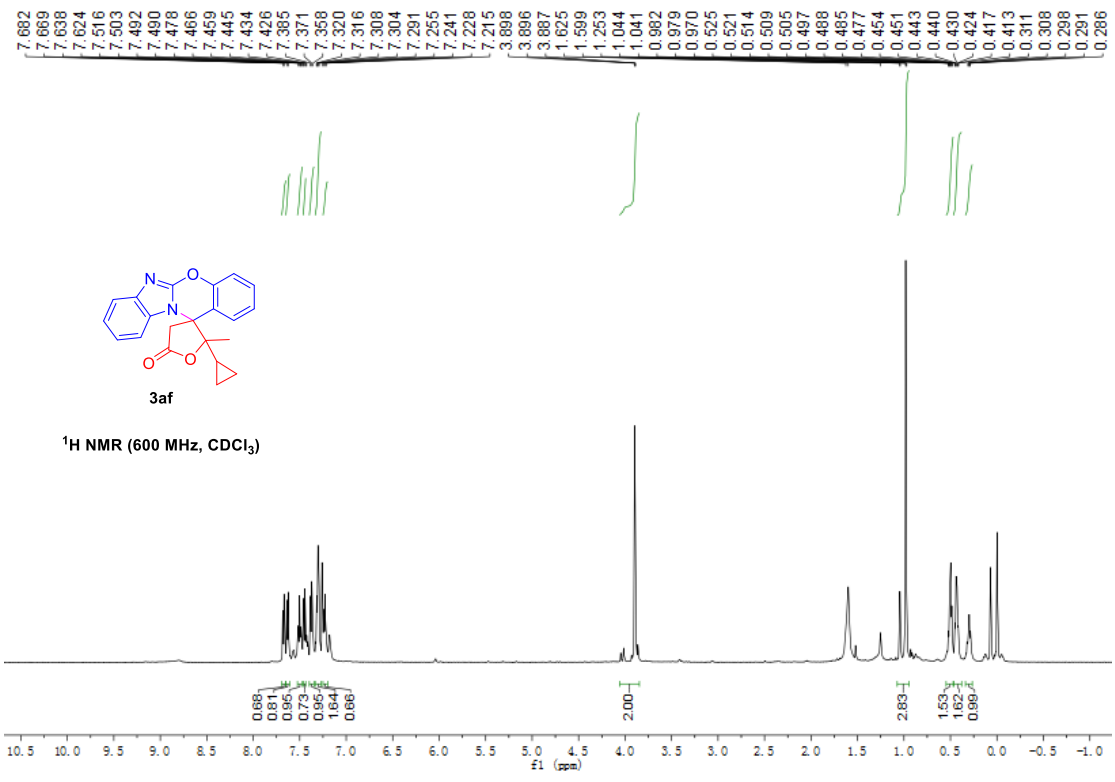
3ae

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



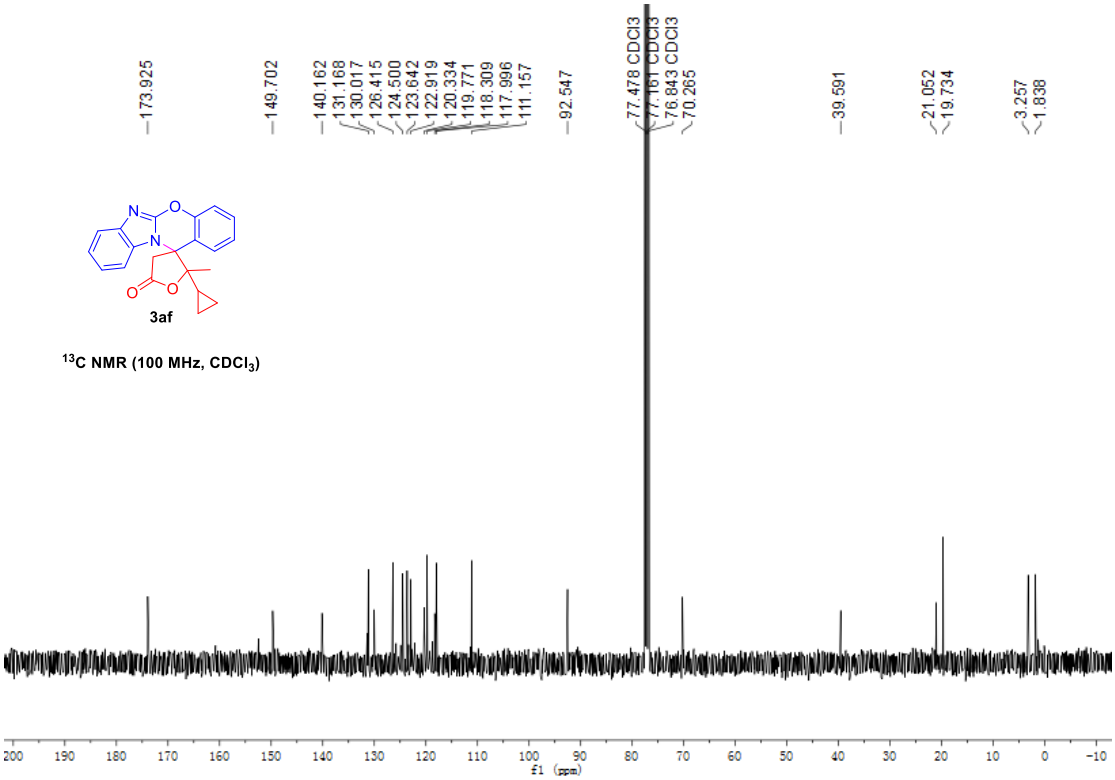
3ae

^{13}C NMR (100 MHz, $CDCl_3$)



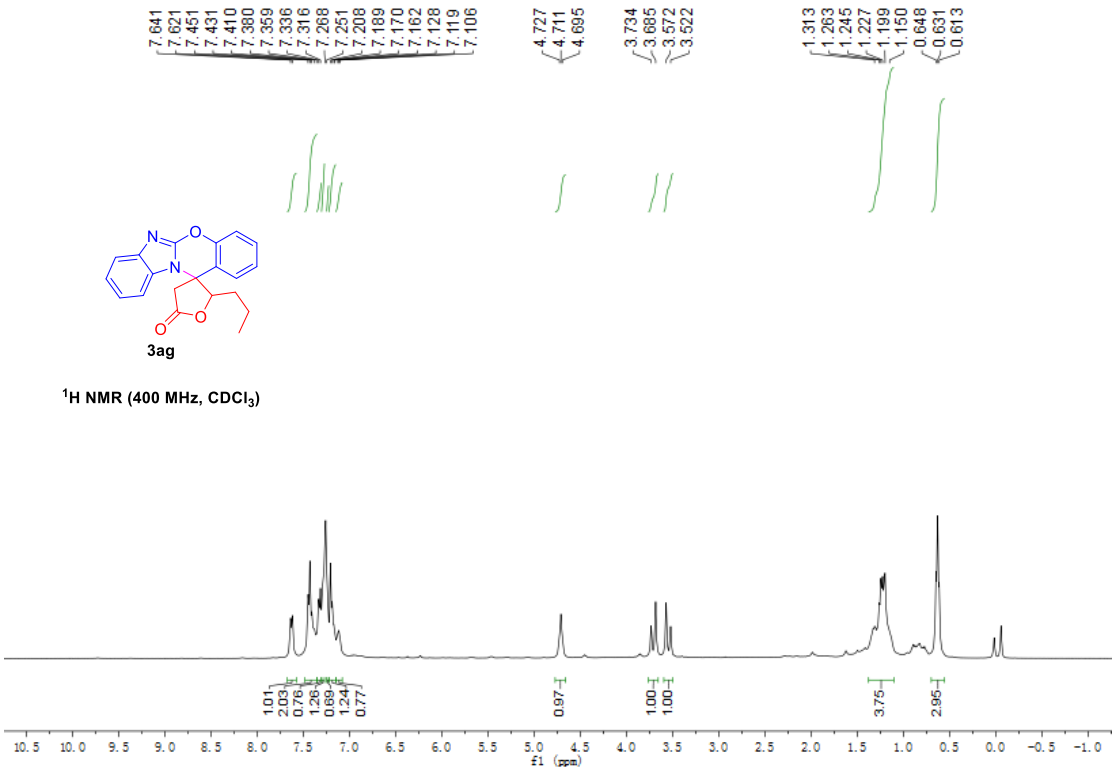
3af

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



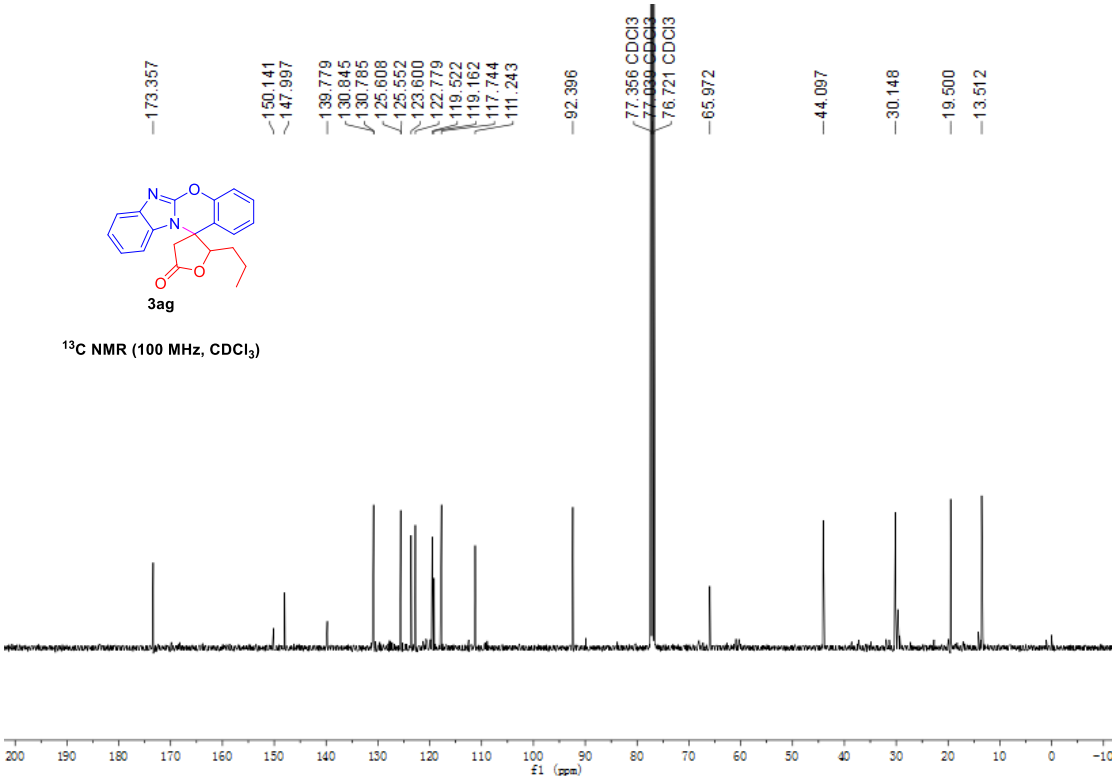
3af

^{13}C NMR (100 MHz, $CDCl_3$)



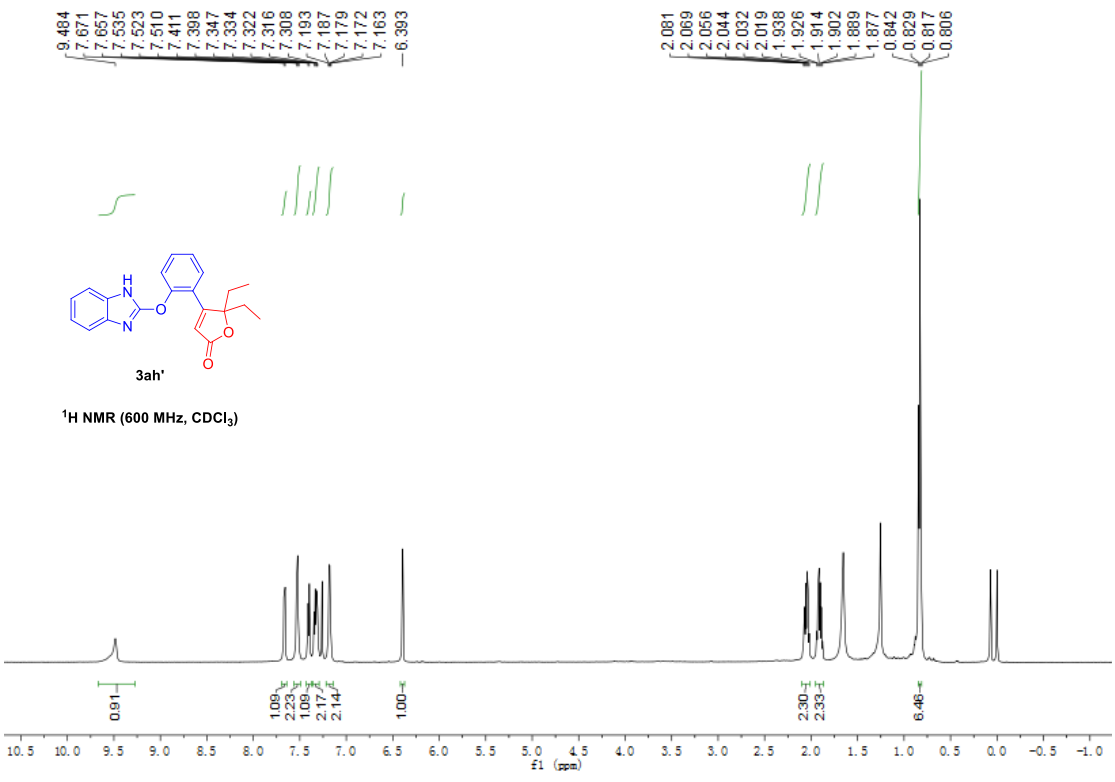
3ag

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



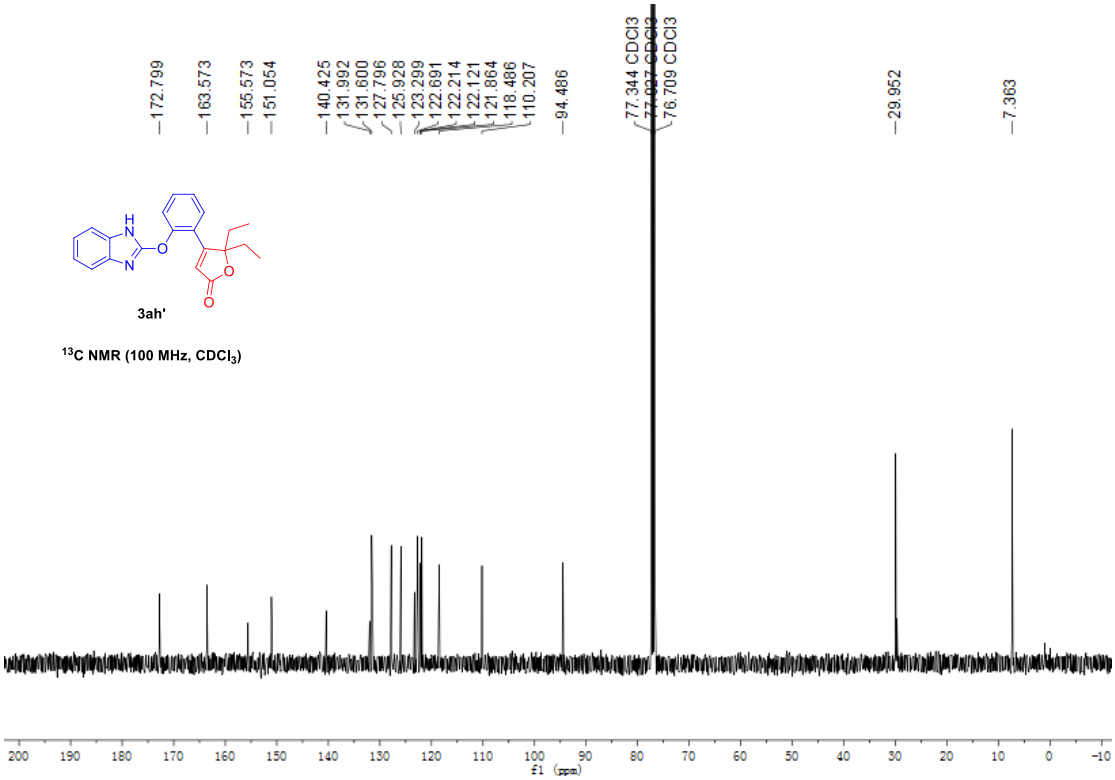
3ag

^{13}C NMR (100 MHz, $CDCl_3$)



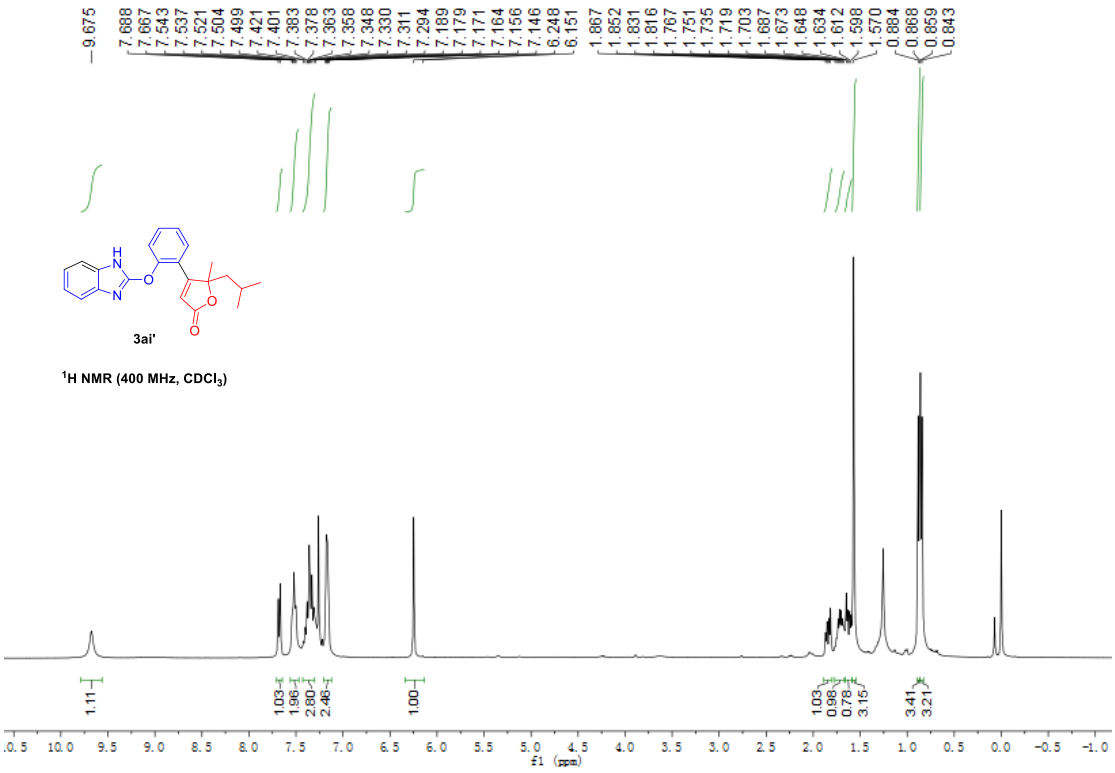
3ah'

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



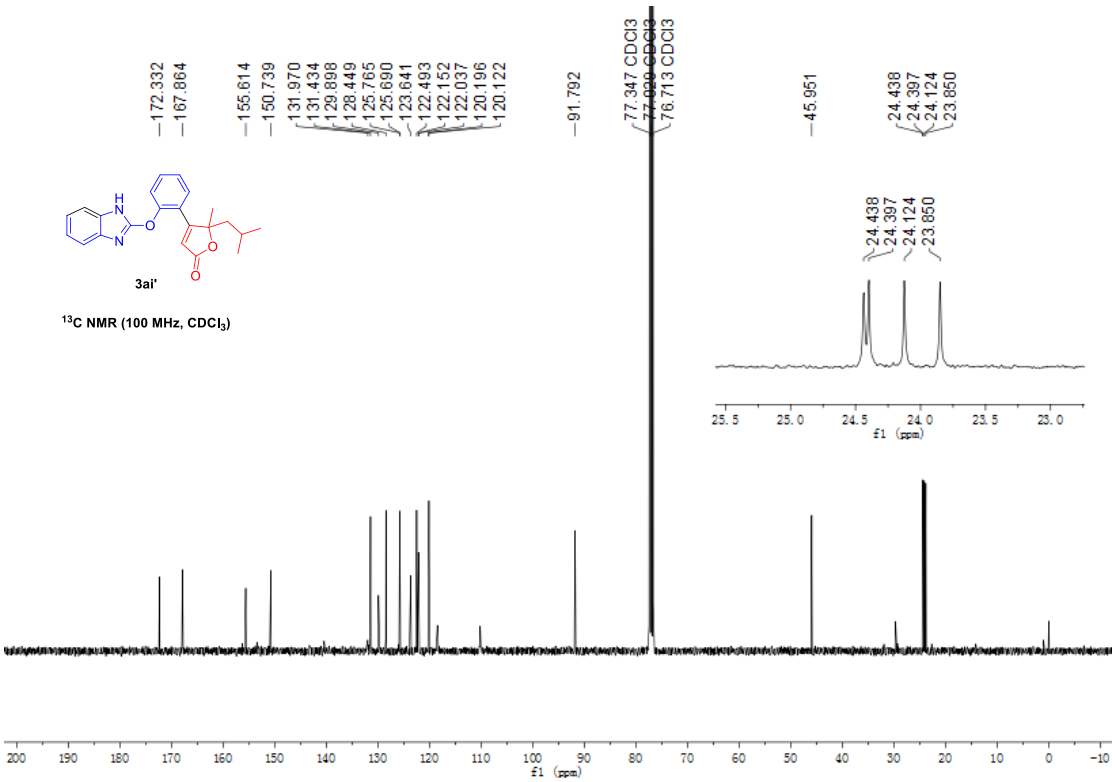
3ah'

^{13}C NMR (100 MHz, $CDCl_3$)



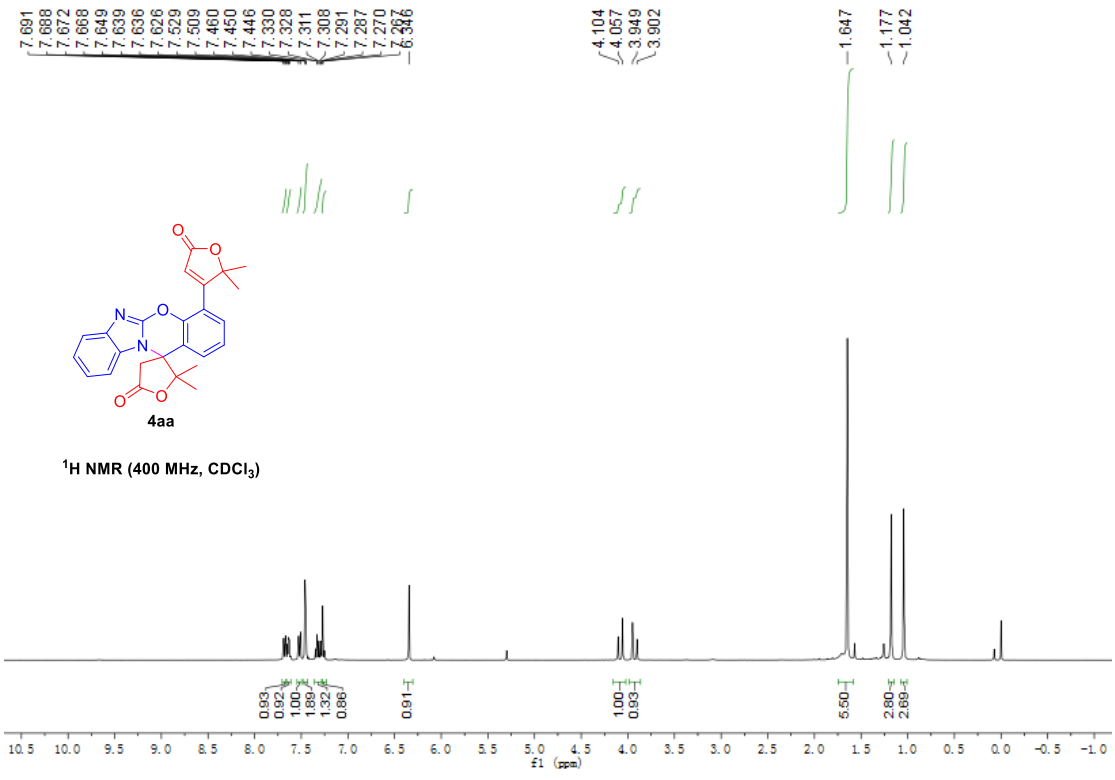
3ai'

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



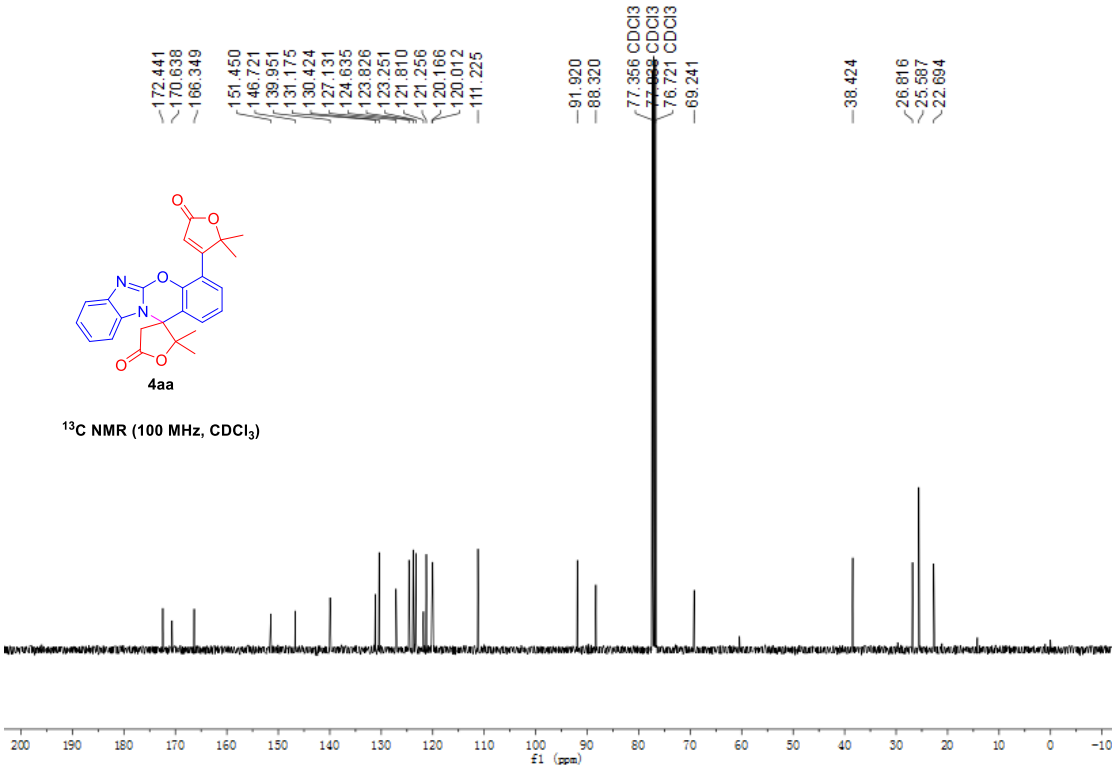
3ai'

^{13}C NMR (100 MHz, $CDCl_3$)



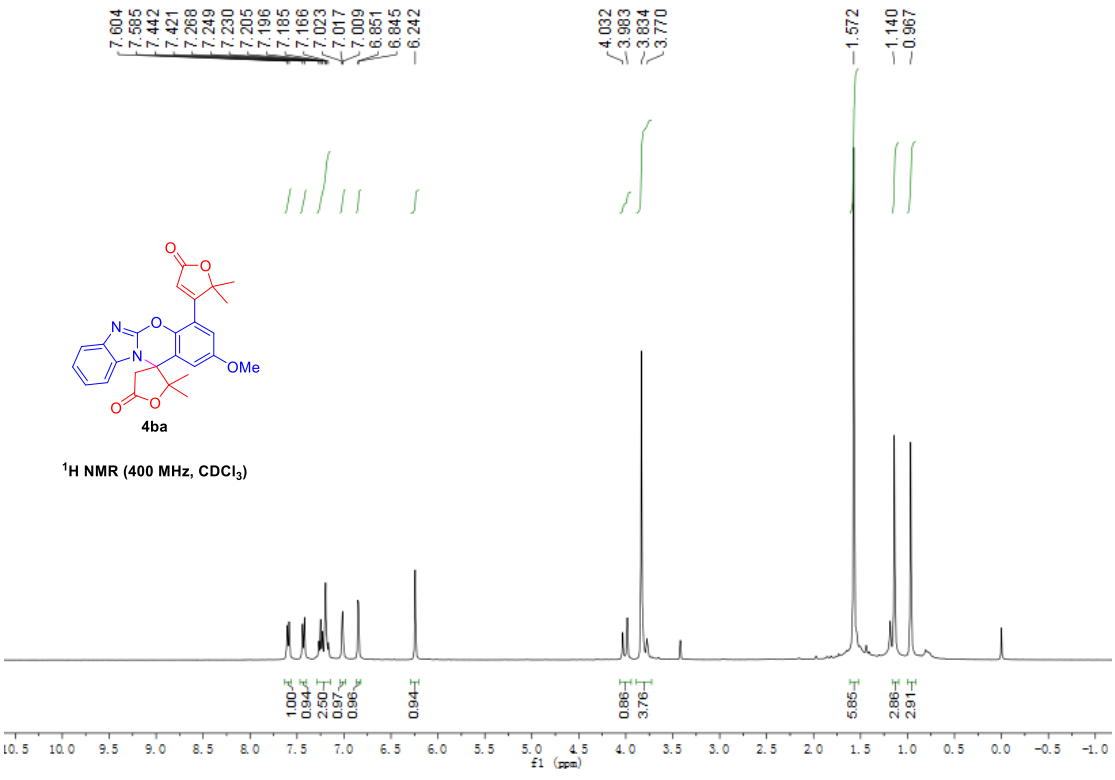
4aa

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



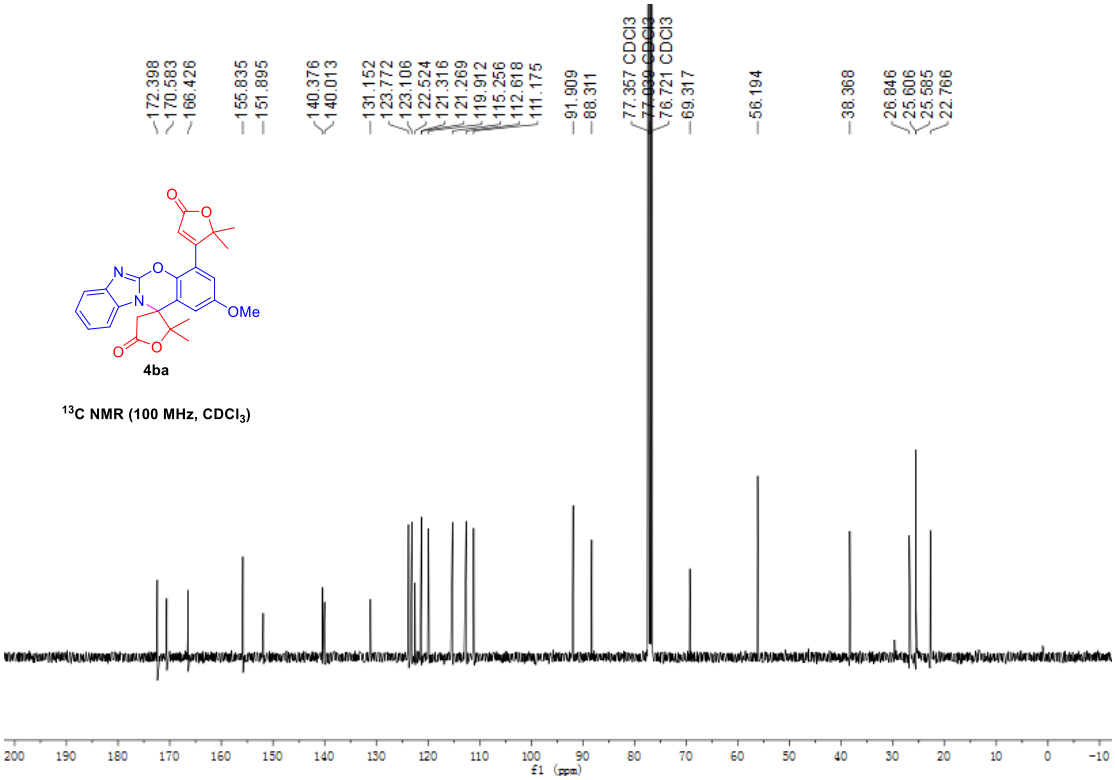
4aa

^{13}C NMR (100 MHz, $CDCl_3$)



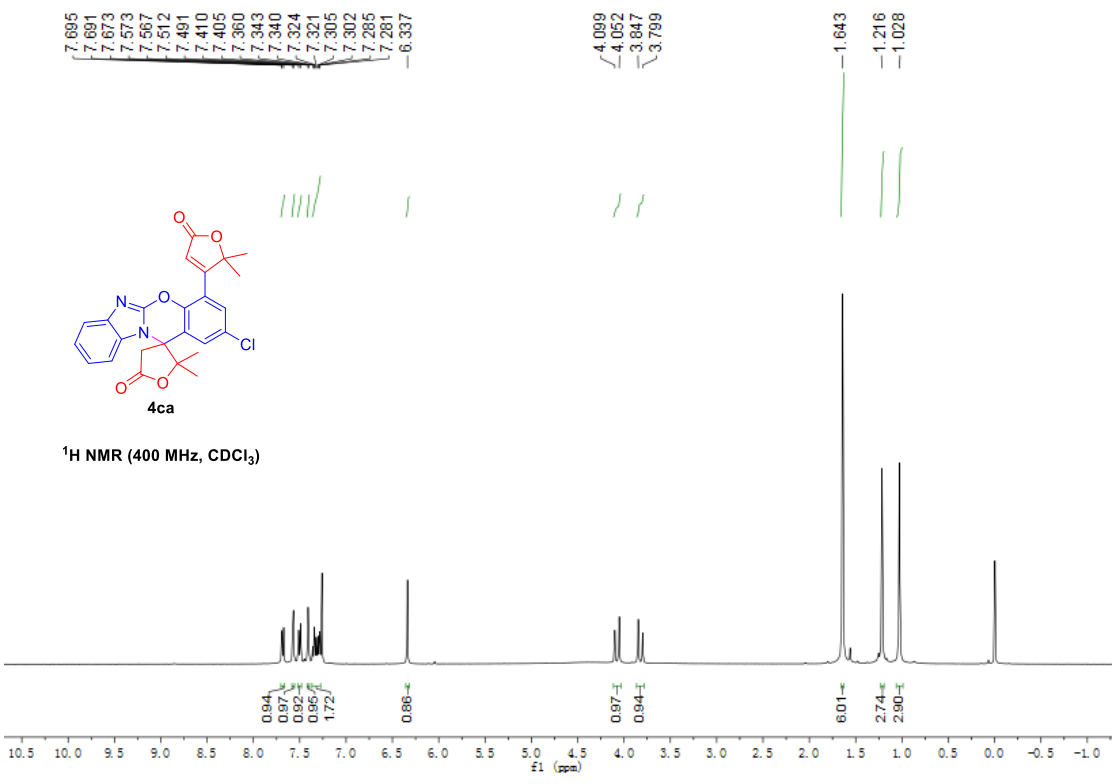
4ba

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



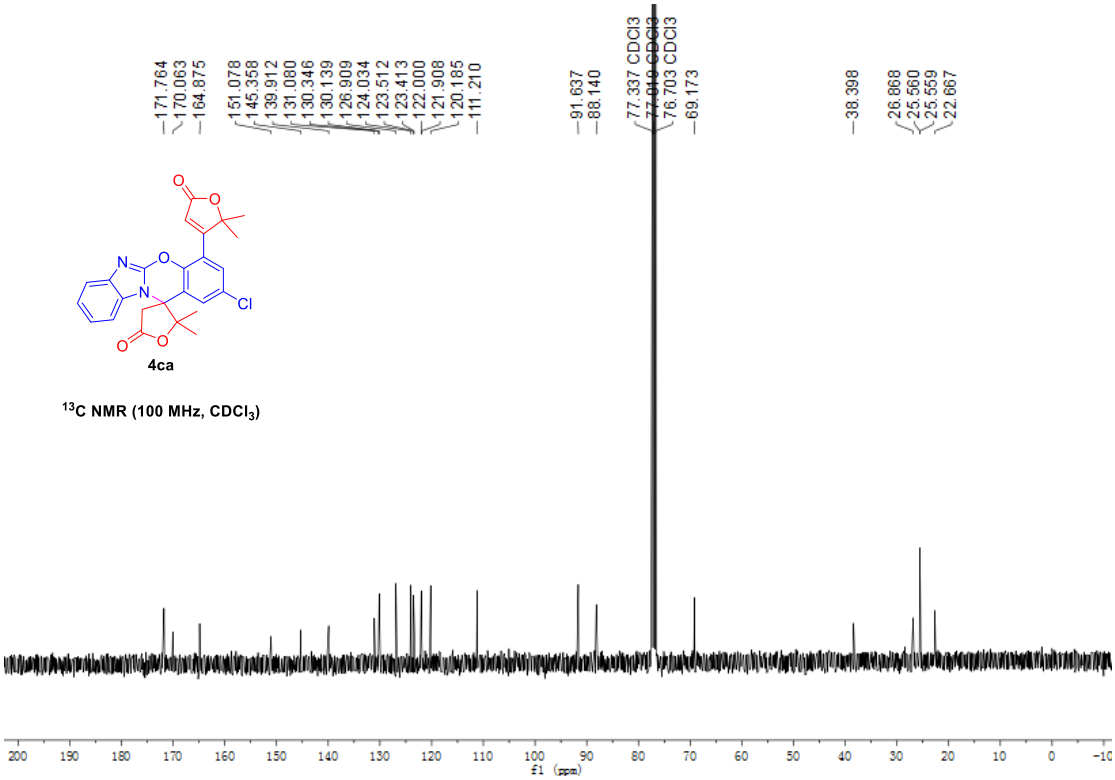
4ba

^{13}C NMR (100 MHz, $CDCl_3$)



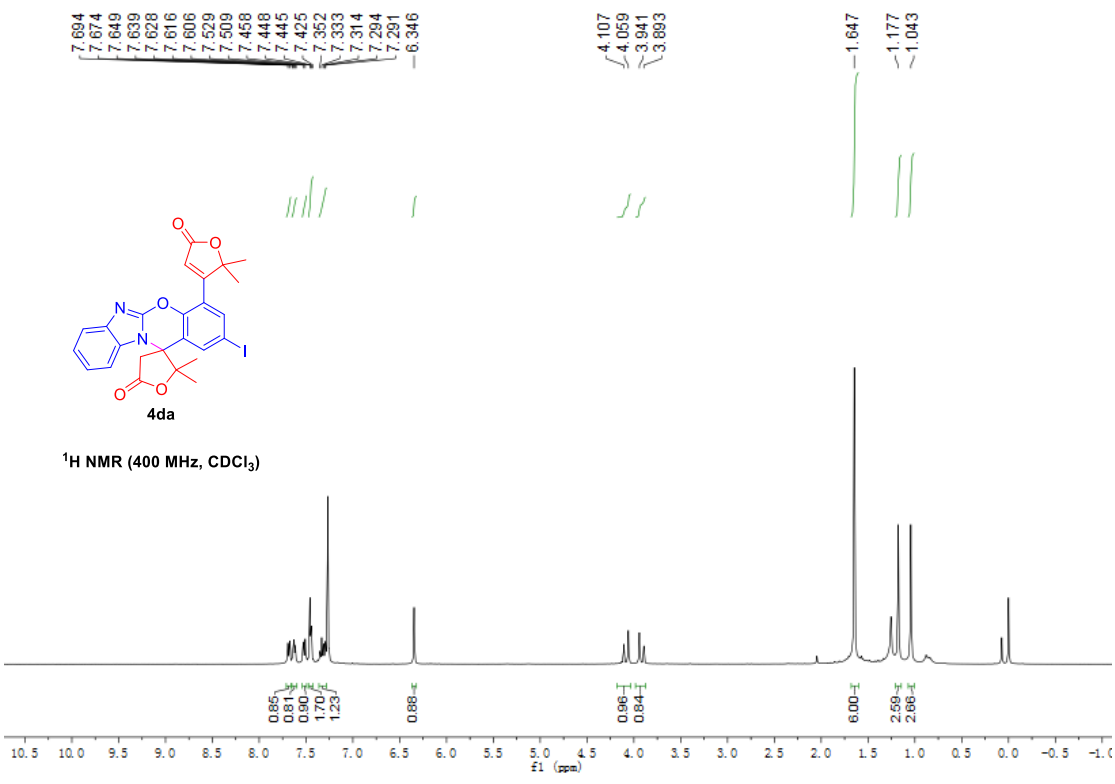
4ca

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



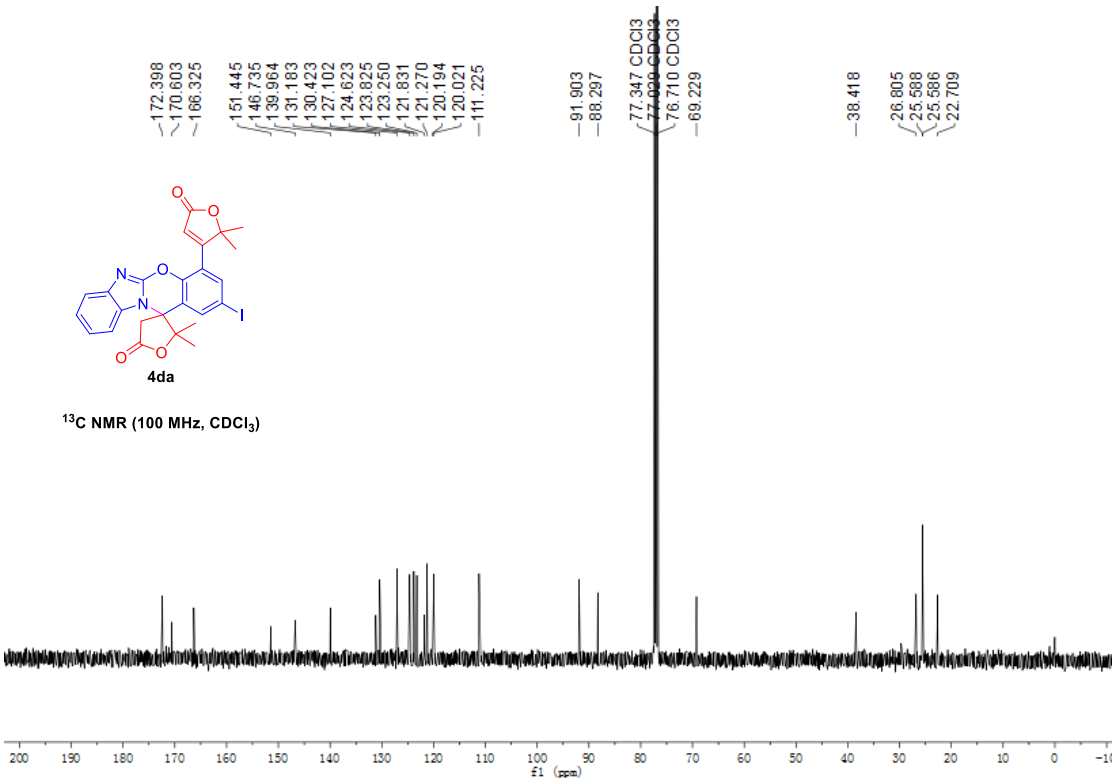
4ca

^{13}C NMR (100 MHz, $CDCl_3$)



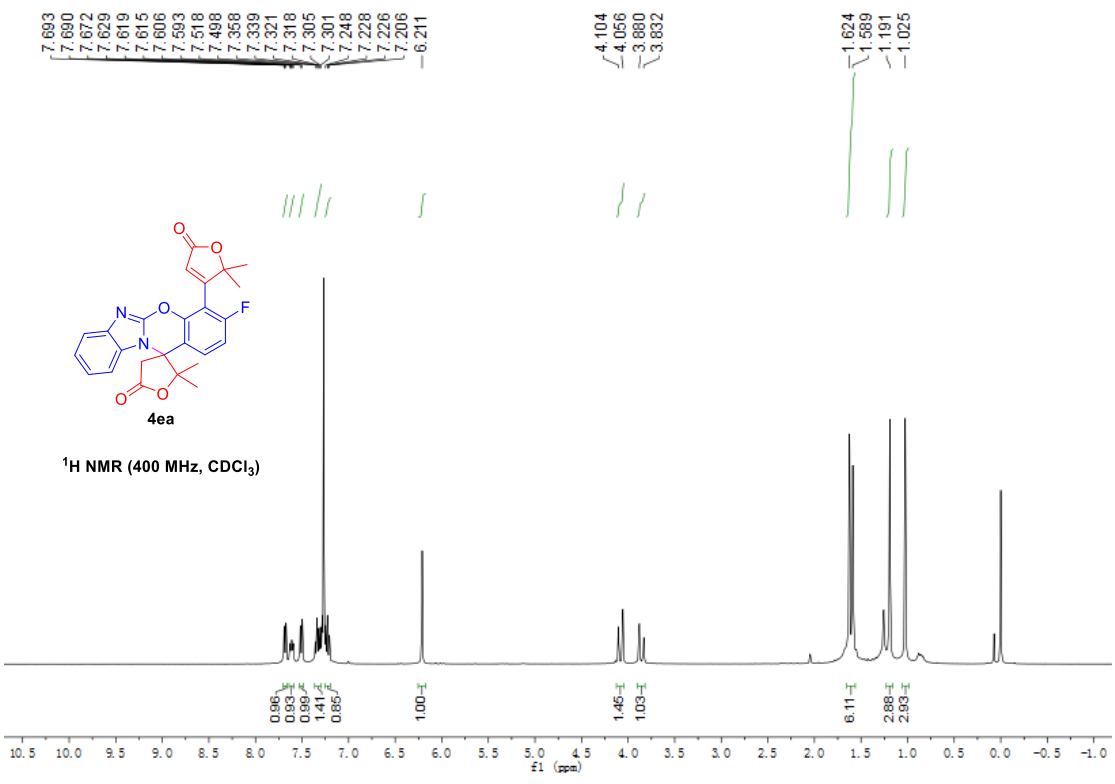
4da

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



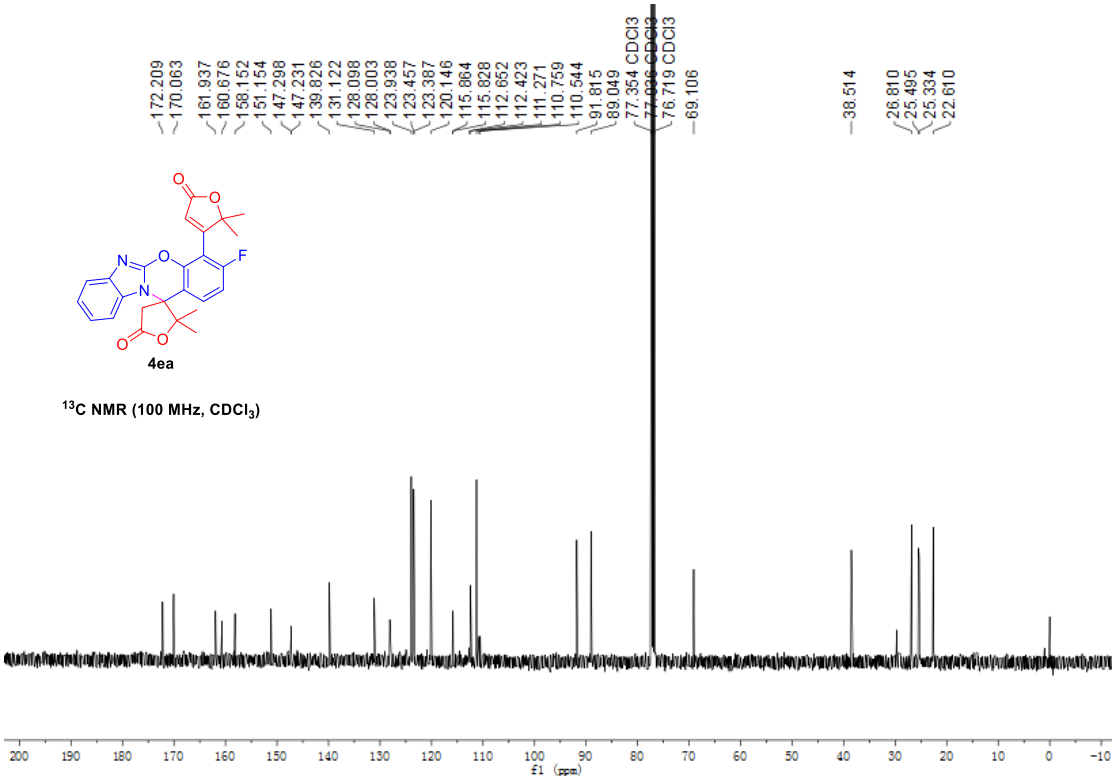
4da

^{13}C NMR (100 MHz, $CDCl_3$)



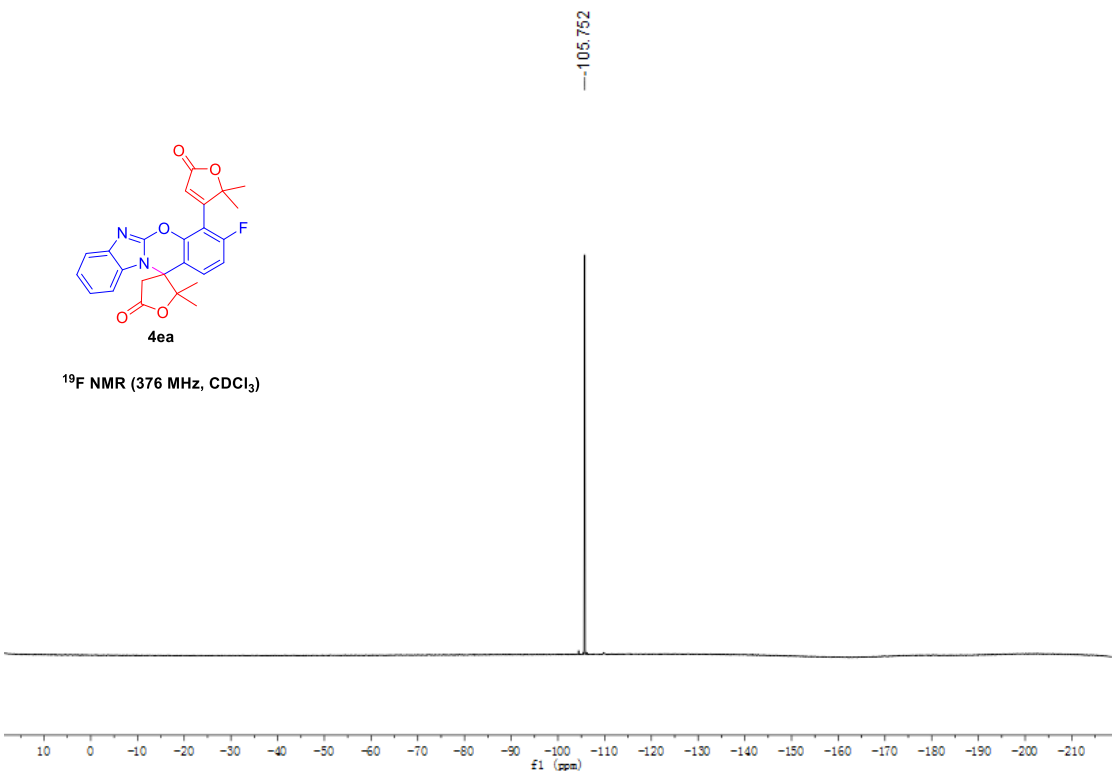
4ea

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



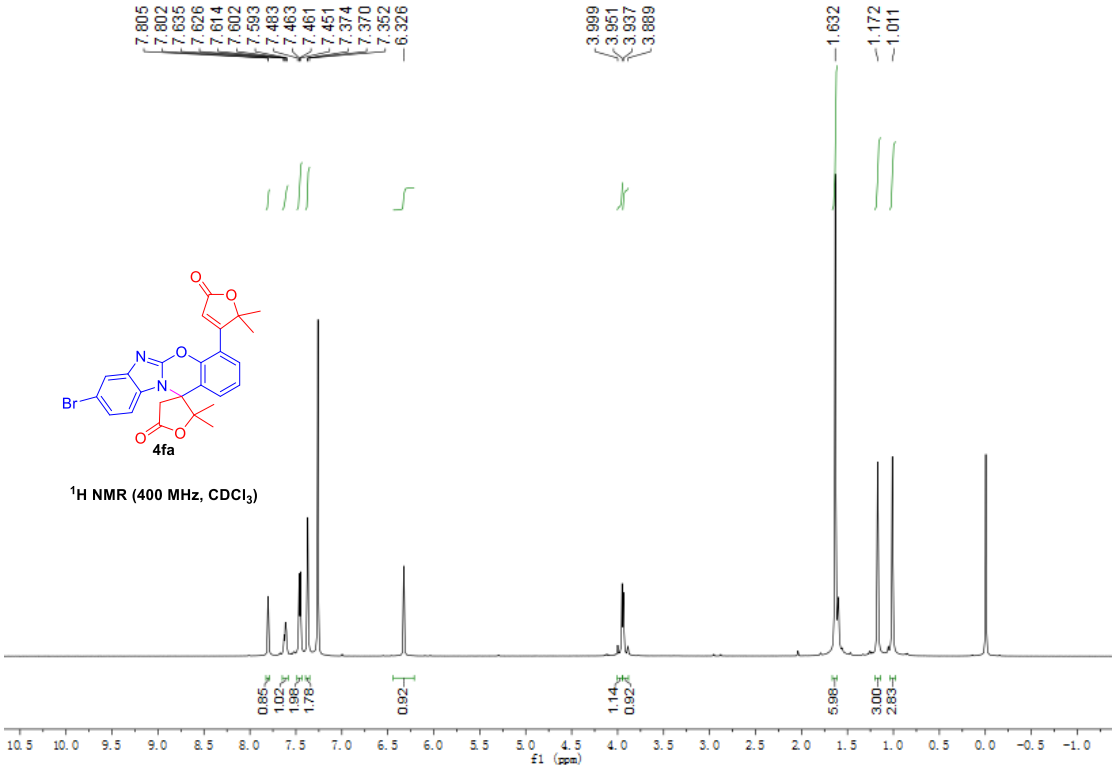
4ea

^{13}C NMR (100 MHz, $CDCl_3$)

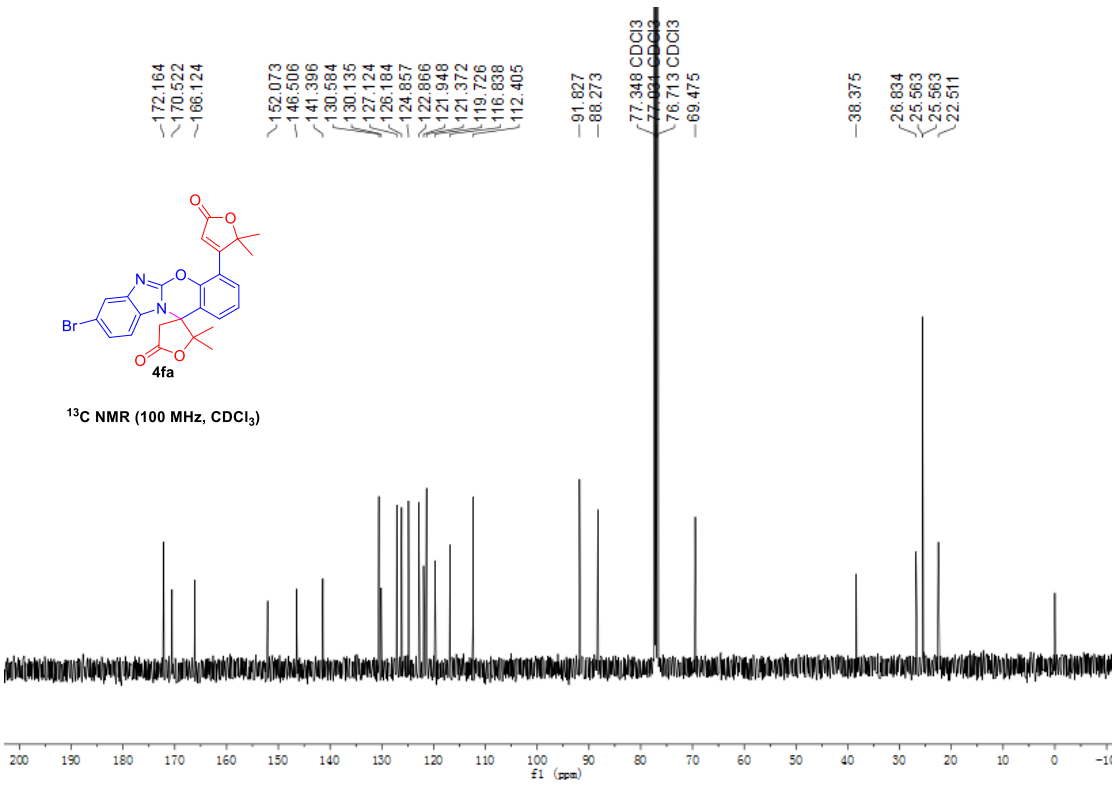


4ea

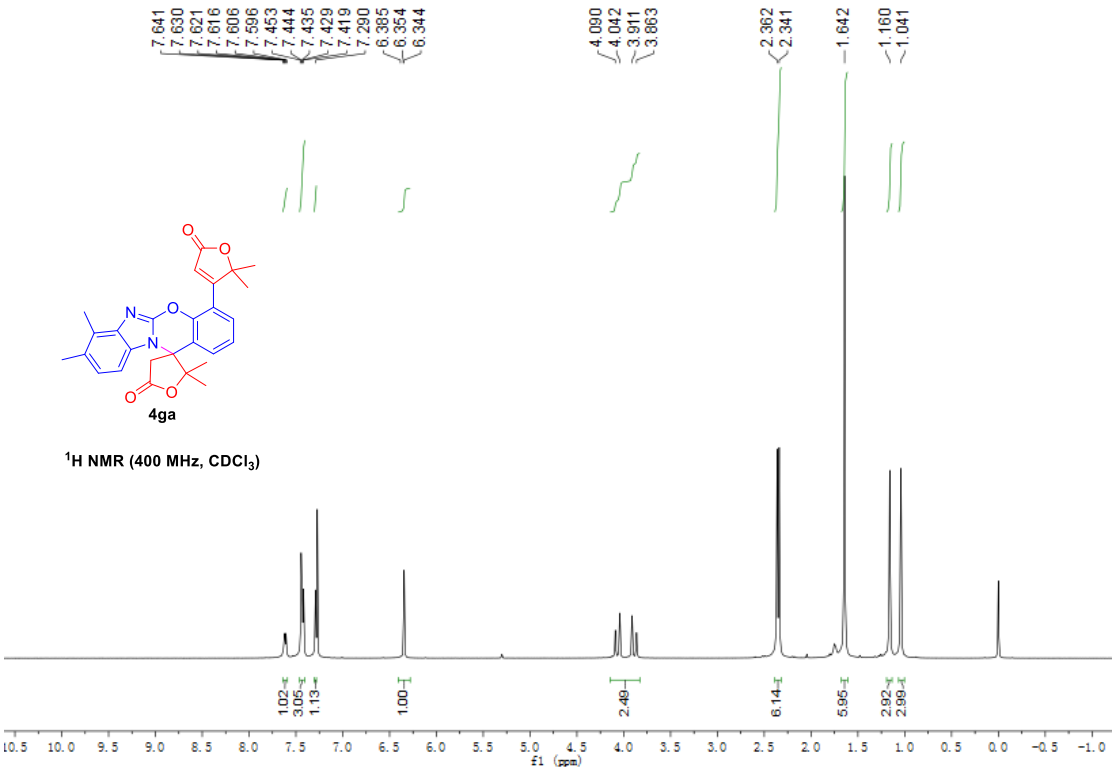
^{19}F NMR (376 MHz, $CDCl_3$)



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

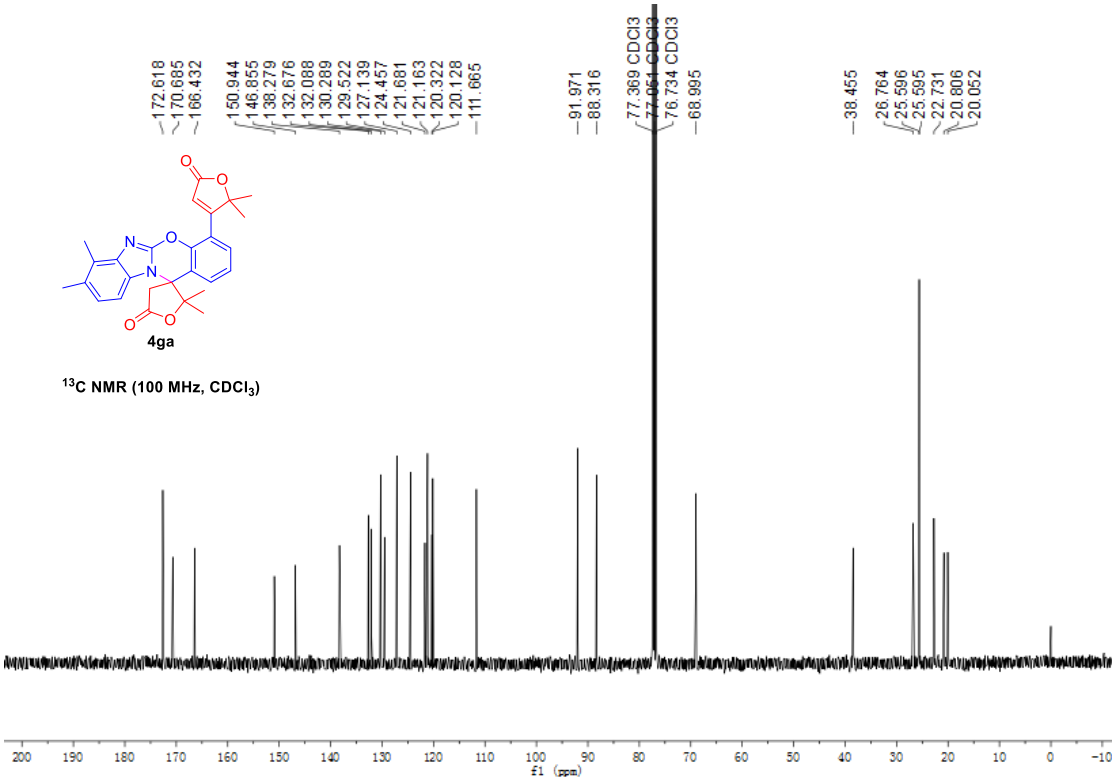


^{13}C NMR (100 MHz, $CDCl_3$)



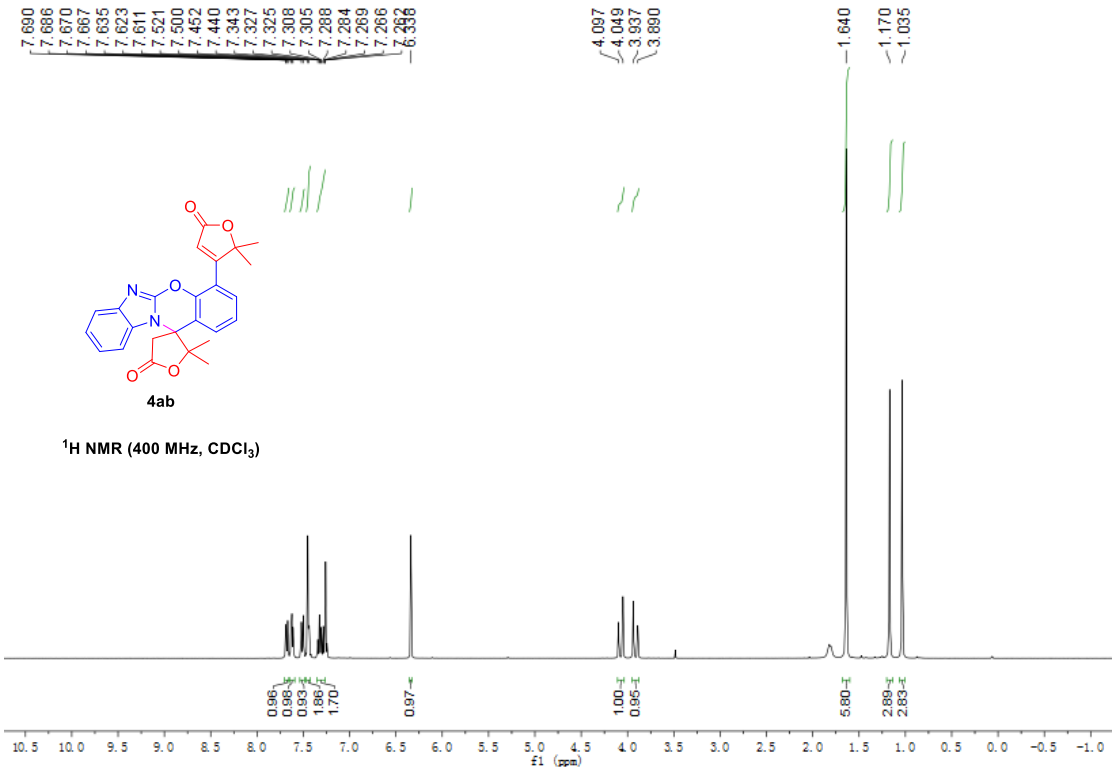
4ga

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



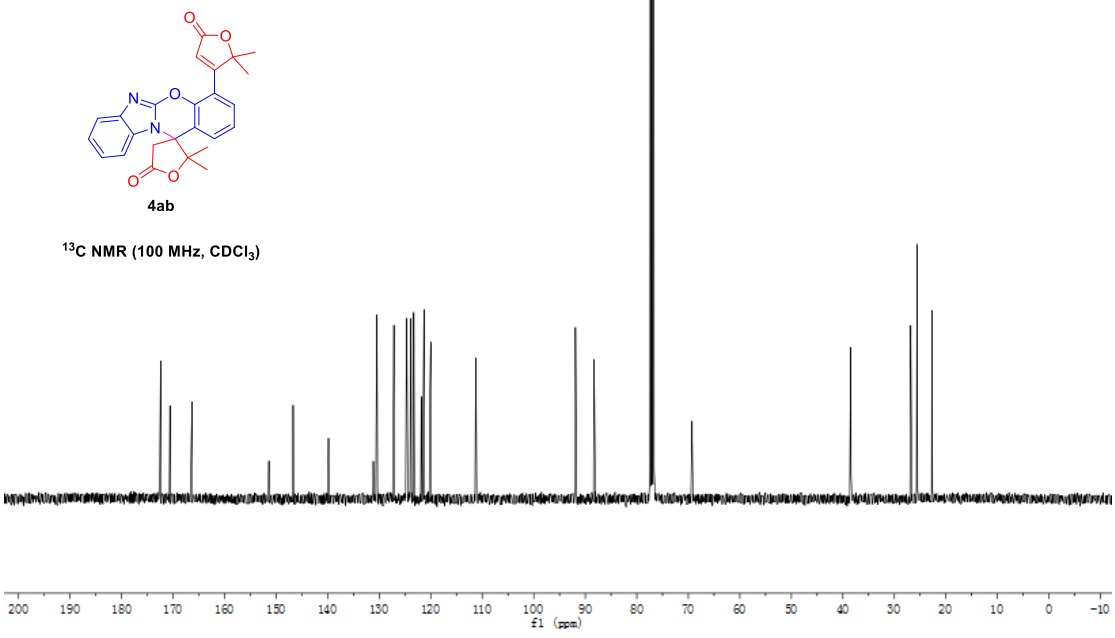
4ga

^{13}C NMR (100 MHz, $CDCl_3$)



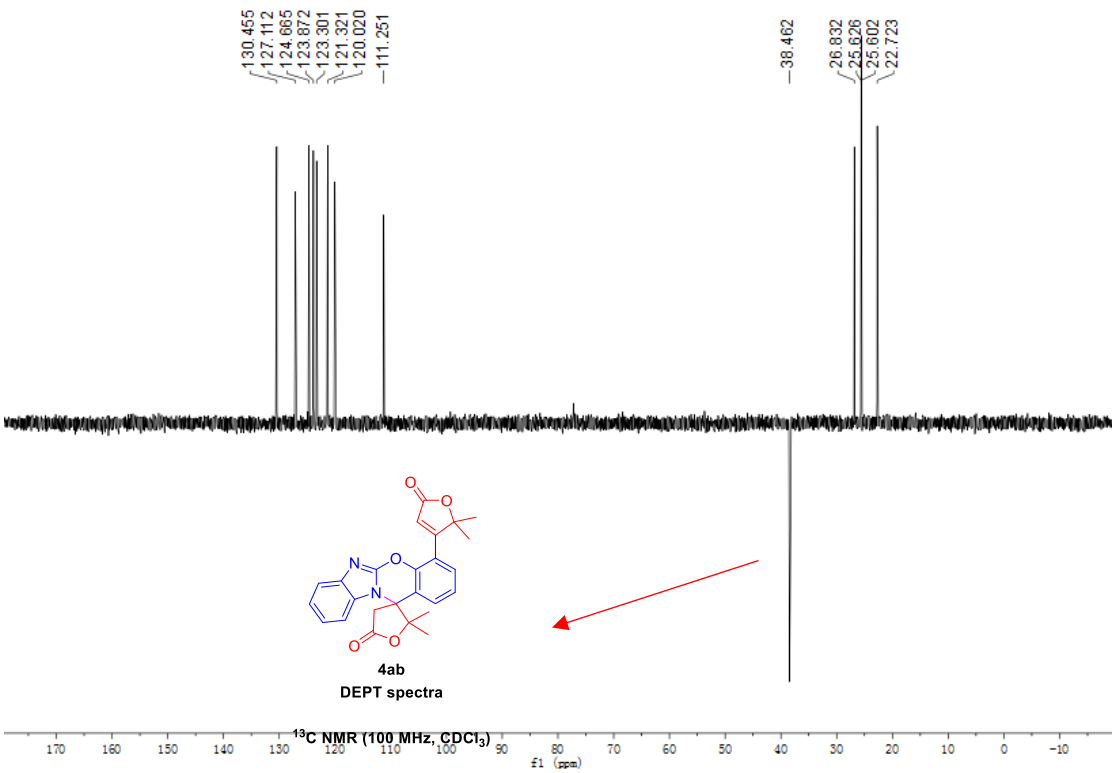
4ab

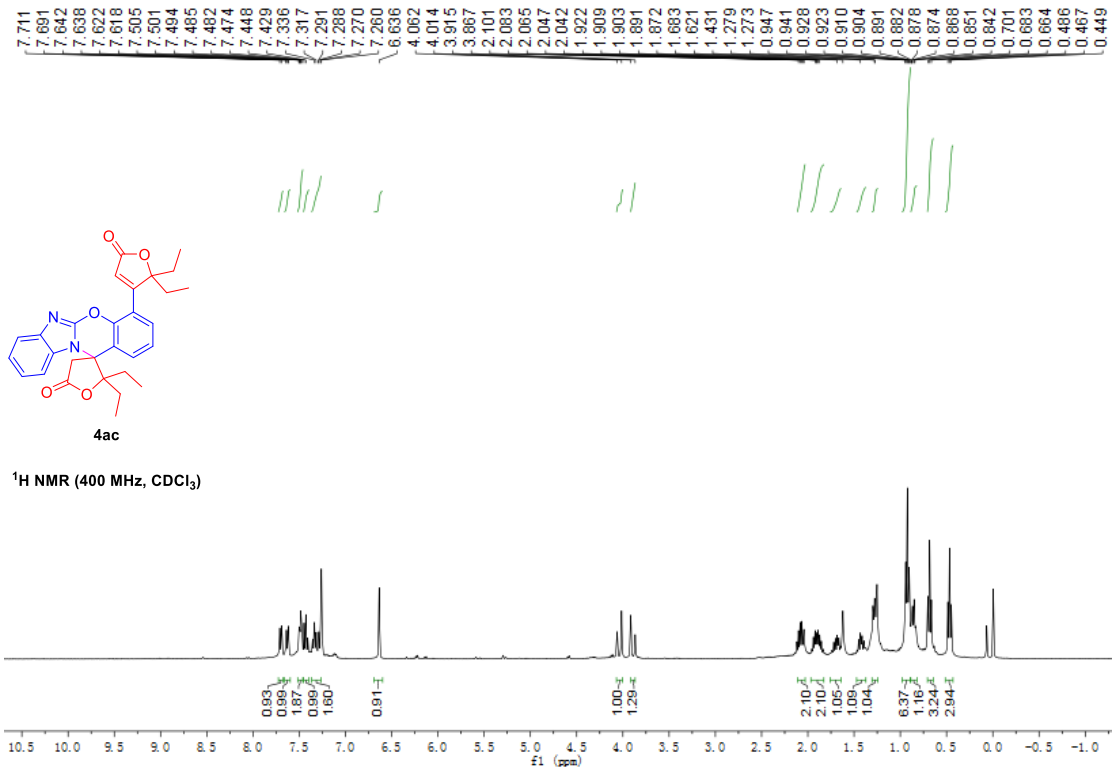
^{1}H NMR (400 MHz, $CDCl_3$)

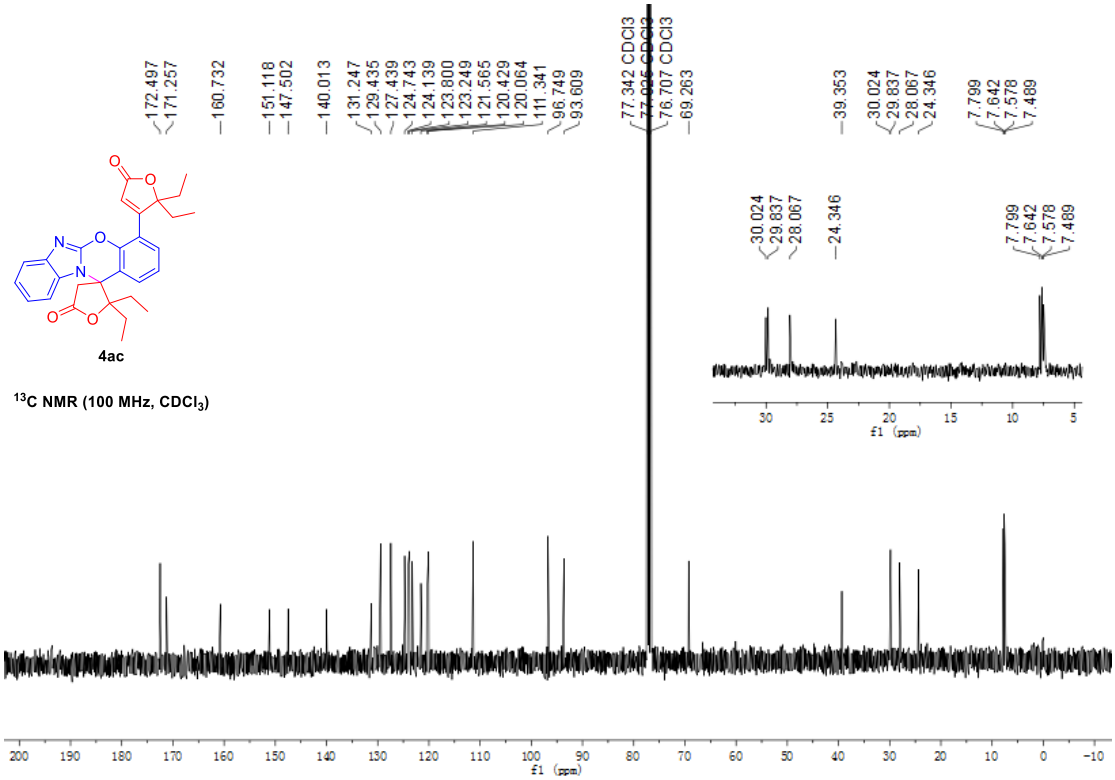


4ab

^{13}C NMR (100 MHz, $CDCl_3$)

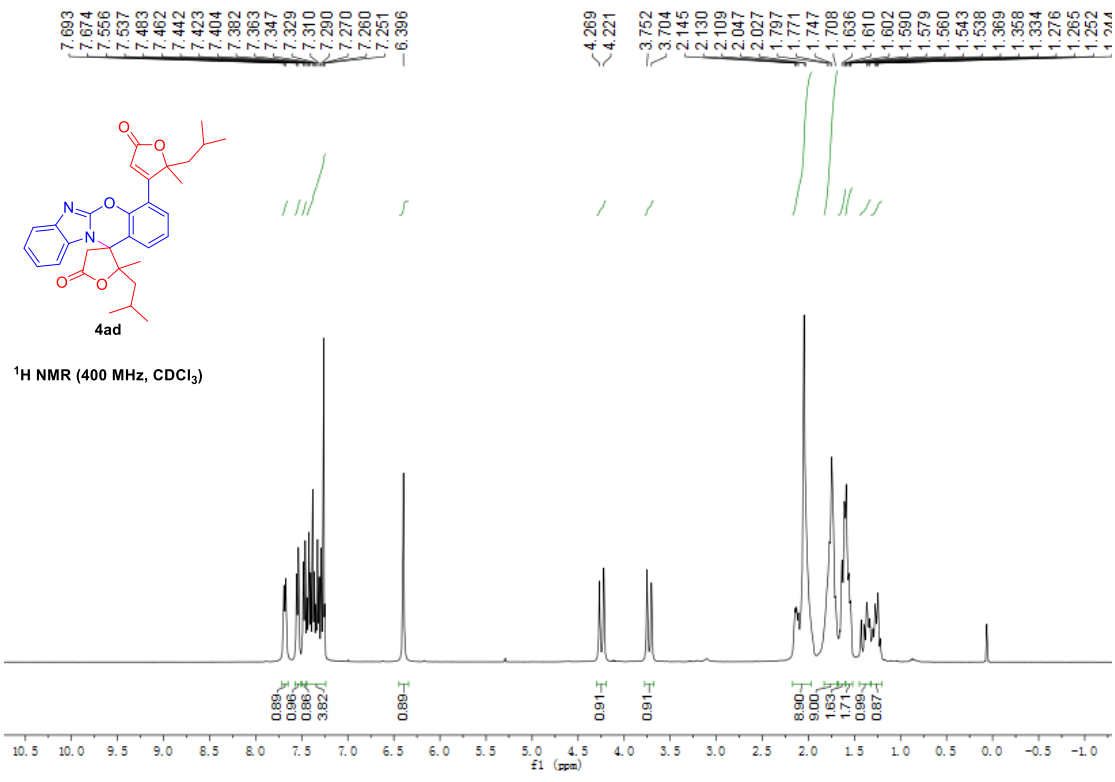

130.455
127.112
124.665
123.872
123.301
121.321
120.020
111.251
38.462
26.832
25.626
25.602
22.723
4ab
DEPT spectra
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.711
7.691
7.642
7.638
7.622
7.618
7.505
7.501
7.494
7.485
7.482
7.474
7.448
7.429
7.336
7.317
7.291
7.288
7.270
7.260
6.636
4.062
4.014
3.915
3.867
2.101
2.083
2.065
2.047
2.042
1.922
1.909
1.903
1.891
1.872
1.683
1.621
1.431
1.279
1.273
0.947
0.941
0.928
0.923
0.910
0.904
0.891
0.882
0.878
0.874
0.868
0.851
0.842
0.701
0.683
0.664
0.486
0.467
0.449
4ac
1H NMR (400 MHz, CDCl3)
0.93
0.99
1.87
0.99
1.60
0.91
1.00
1.29
2.10
2.10
1.05
1.09
1.04
6.37
1.16
3.24
2.94
f1 (ppm)



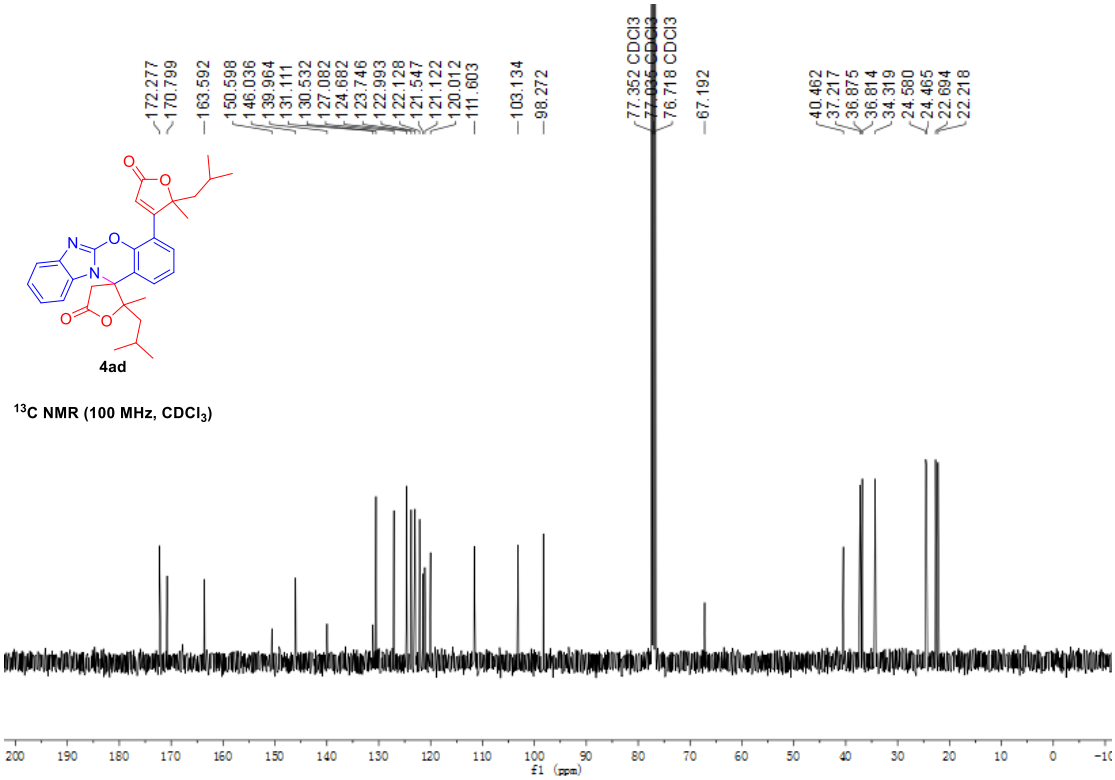
4ac

^{13}C NMR (100 MHz, $CDCl_3$)



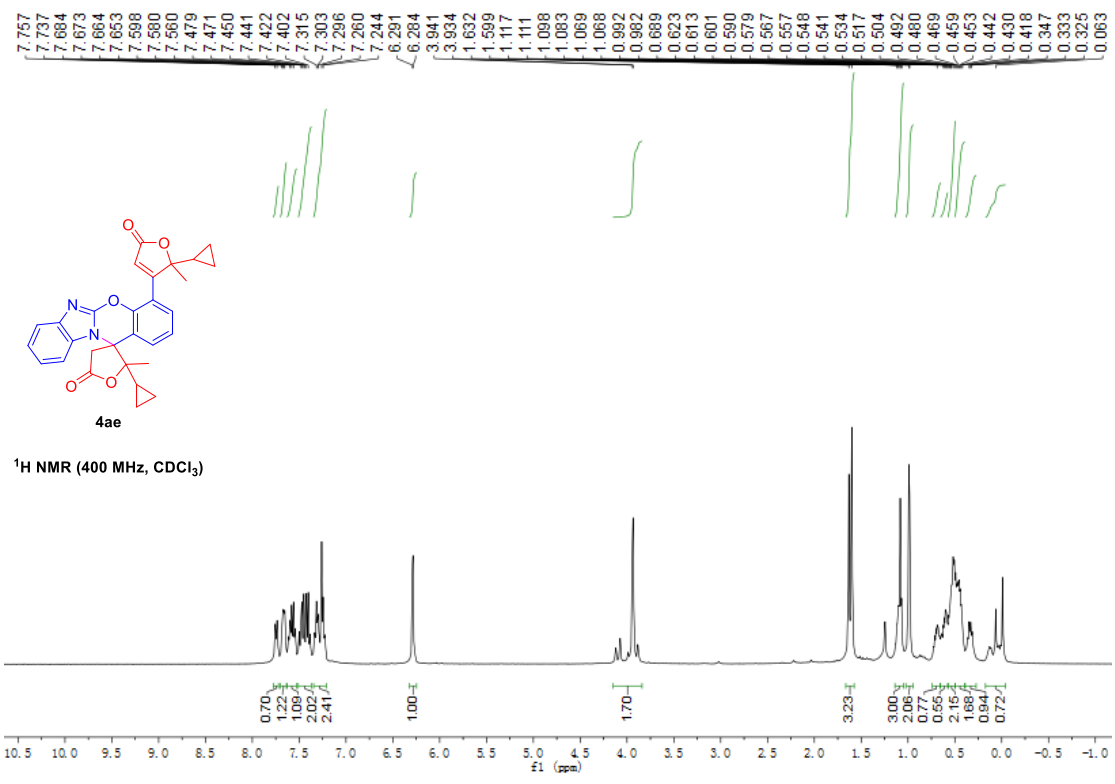
4ad

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



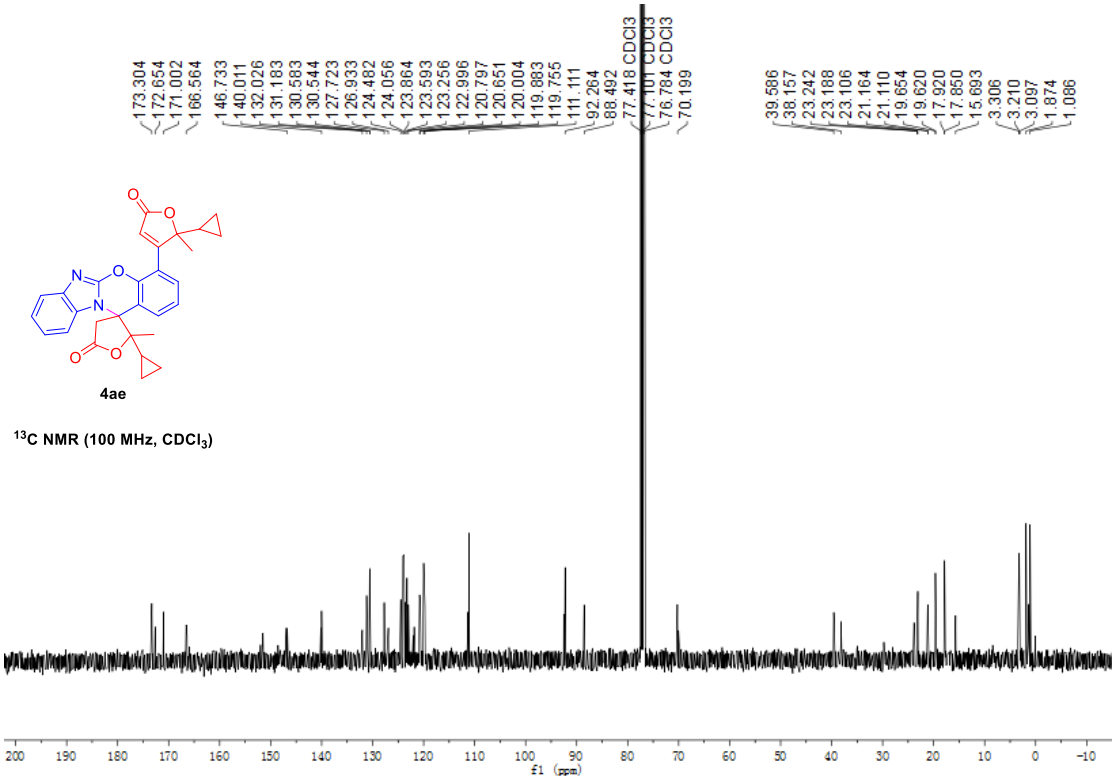
4ad

^{13}C NMR (100 MHz, $CDCl_3$)



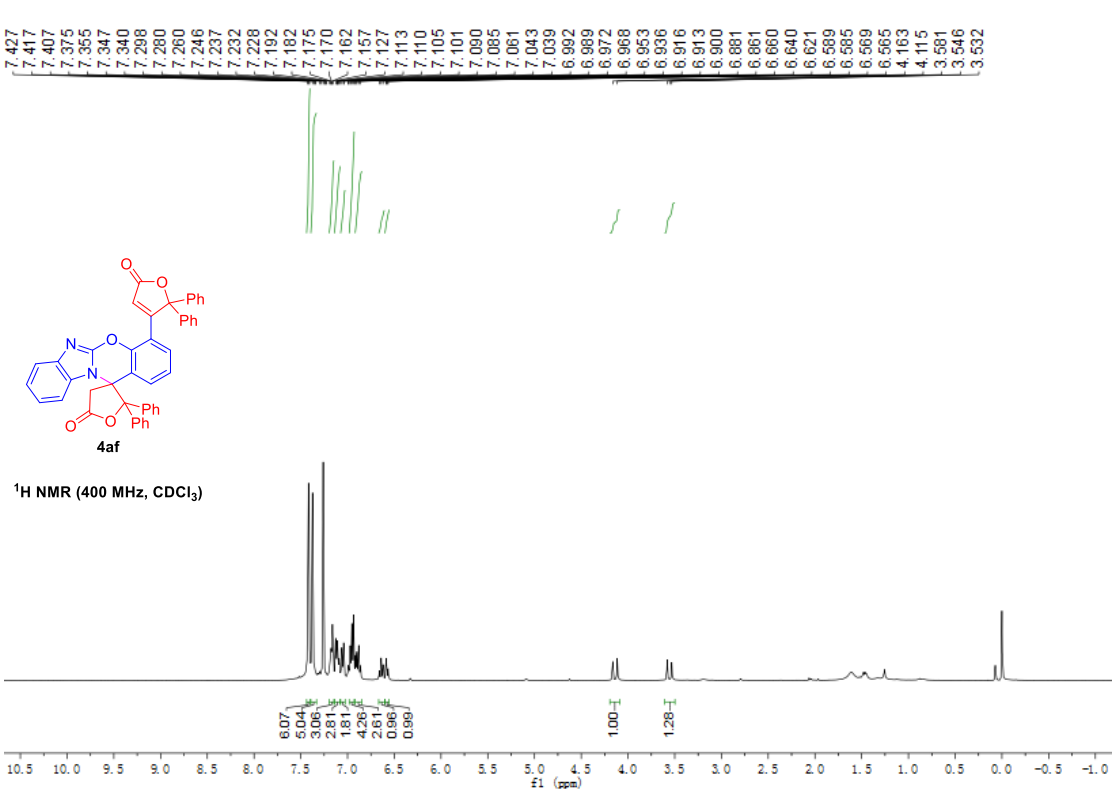
4ae

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



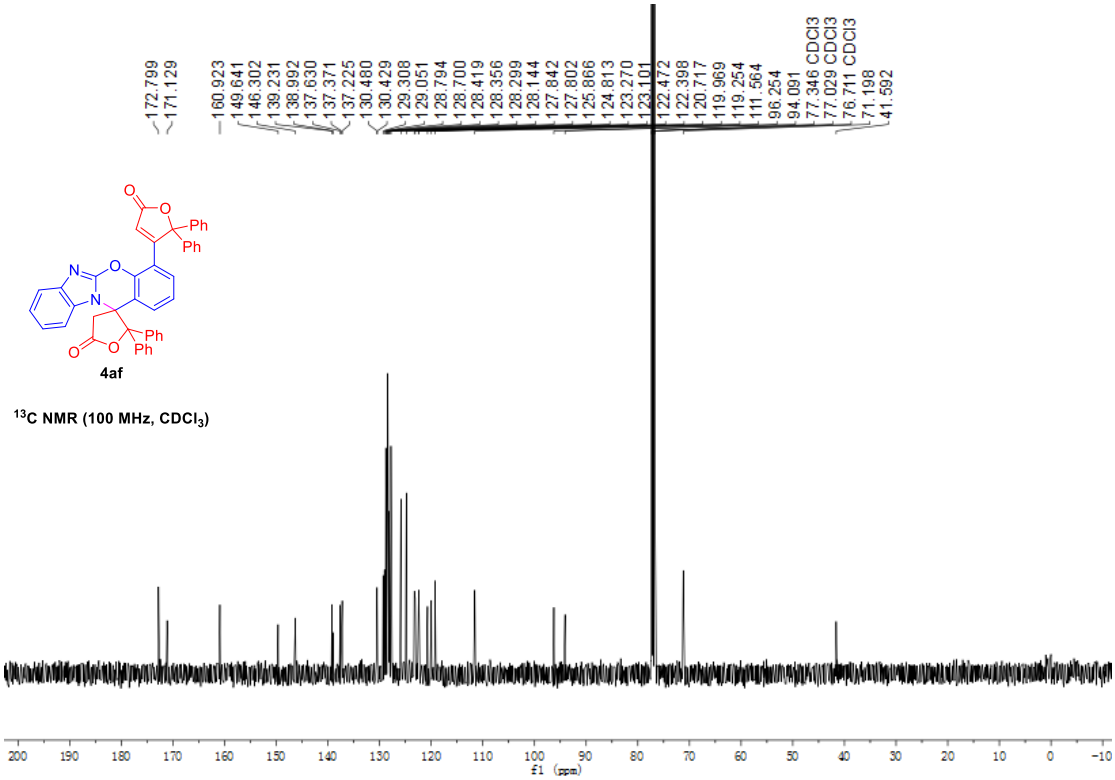
4ae

^{13}C NMR (100 MHz, $CDCl_3$)



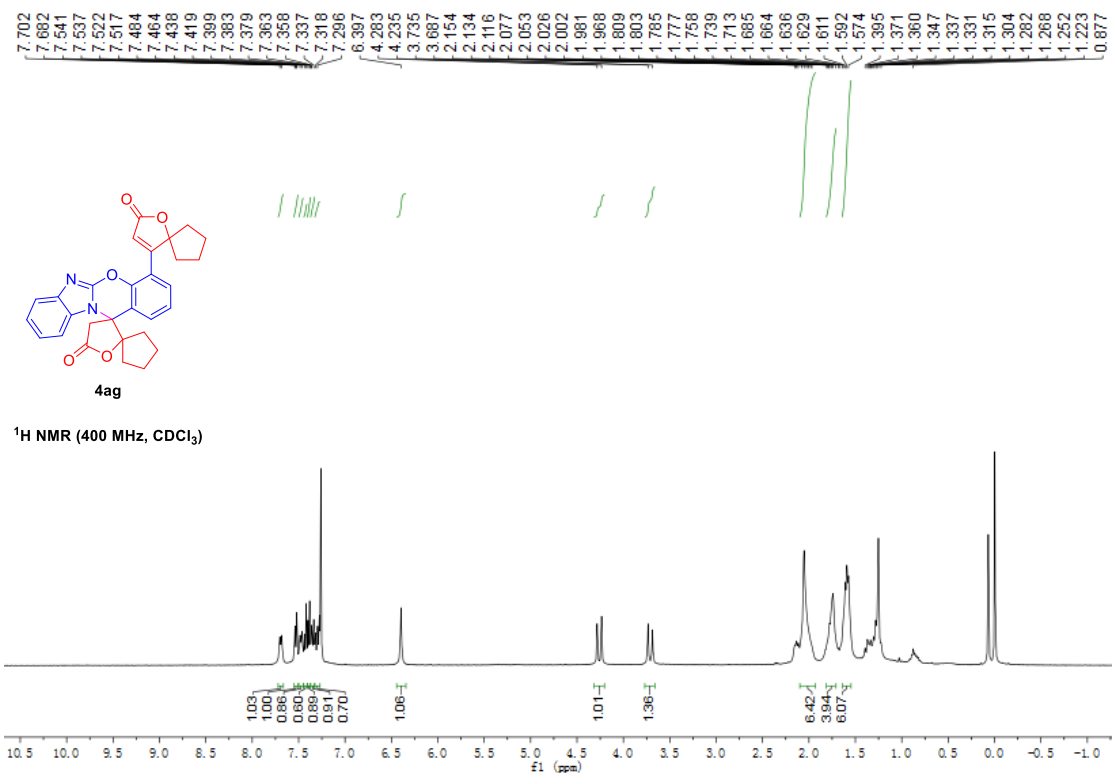
4af

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



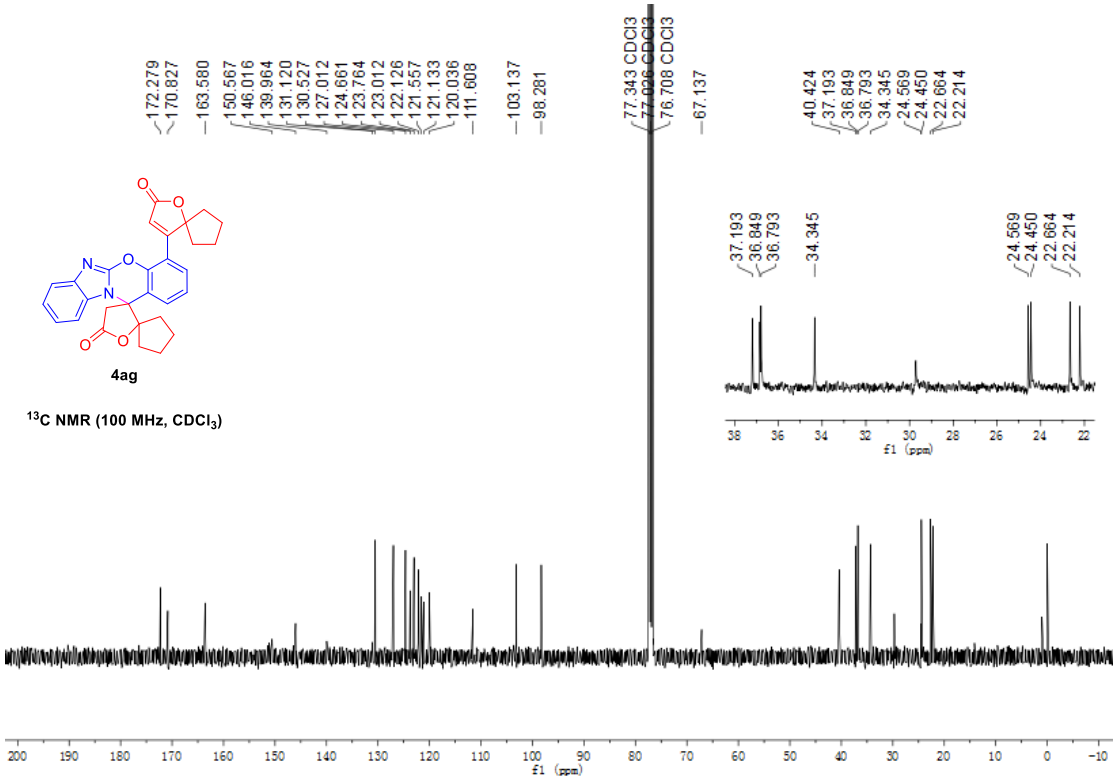
4af

^{13}C NMR (100 MHz, $CDCl_3$)



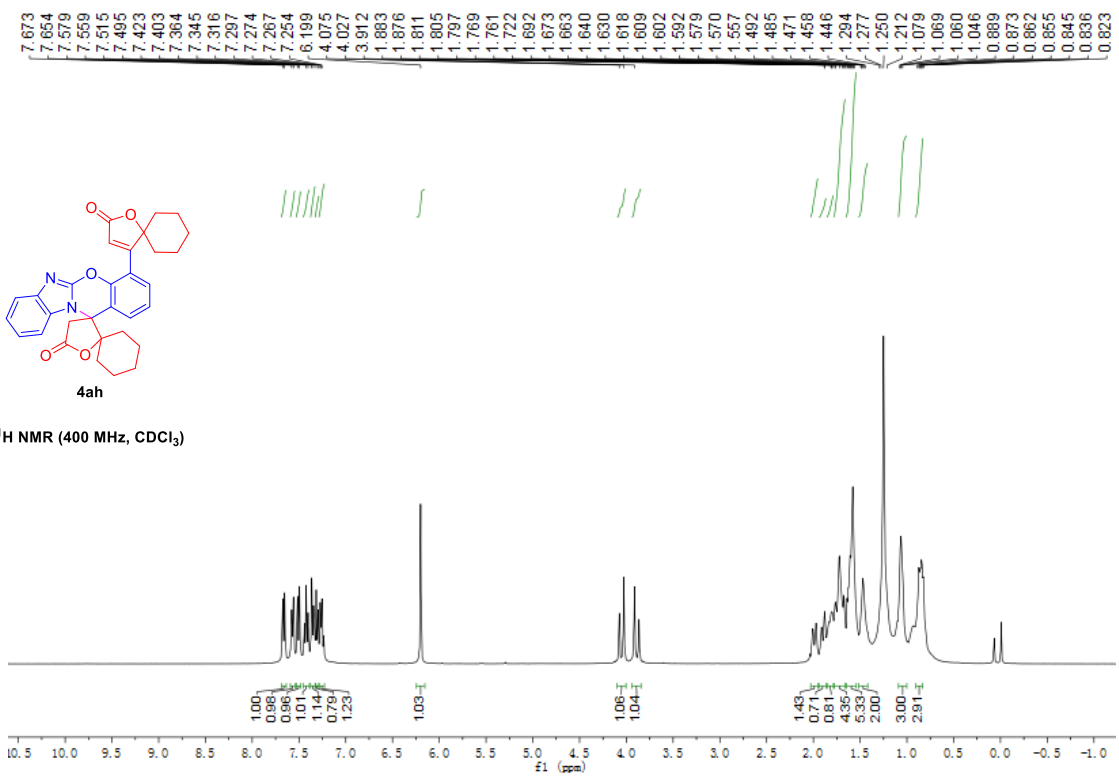
4ag

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



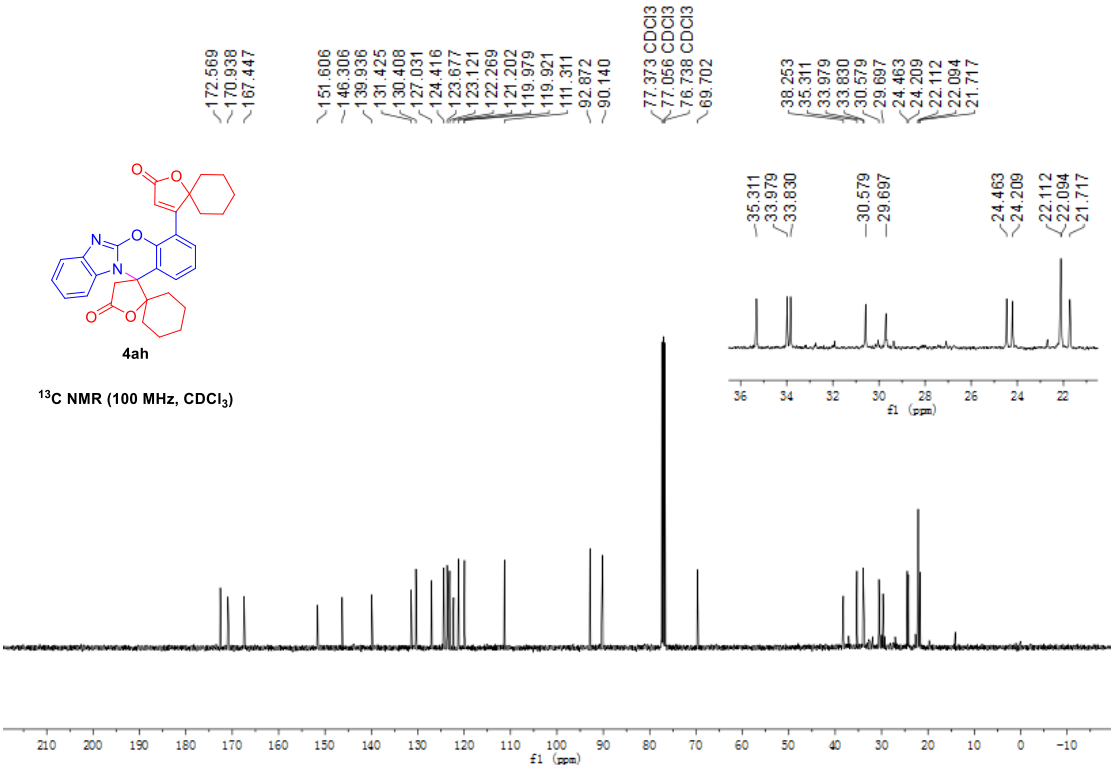
4ag

^{13}C NMR (100 MHz, $CDCl_3$)



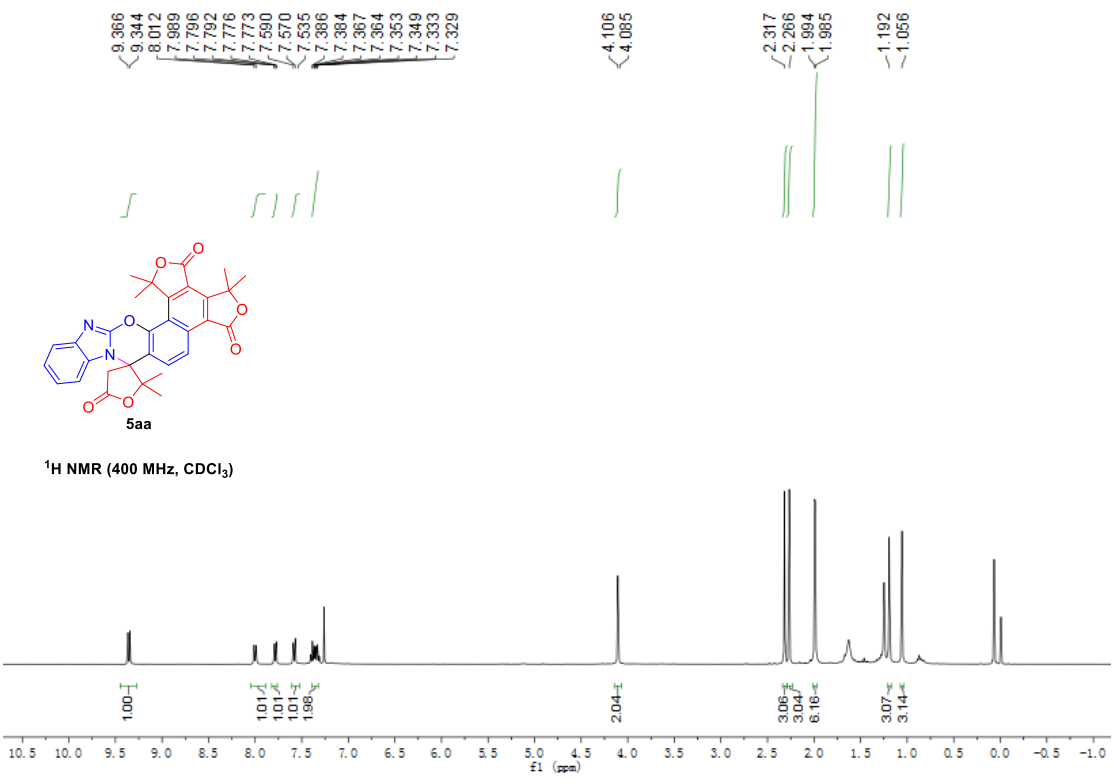
4ah

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



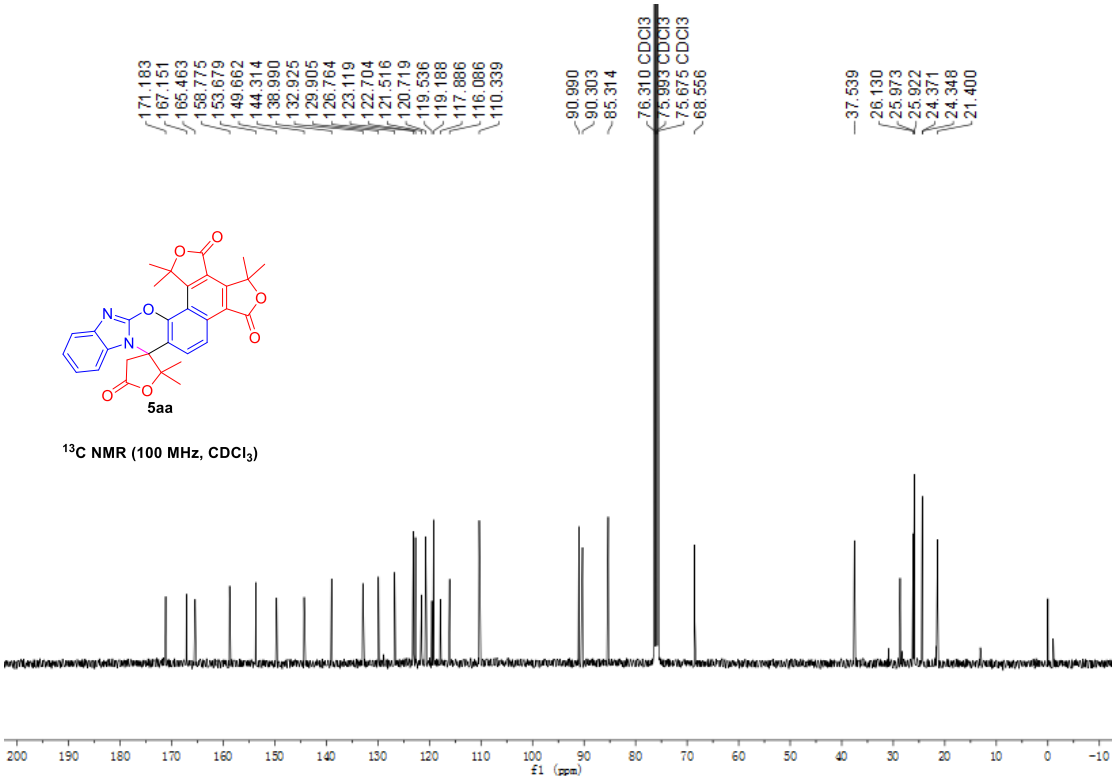
4ah

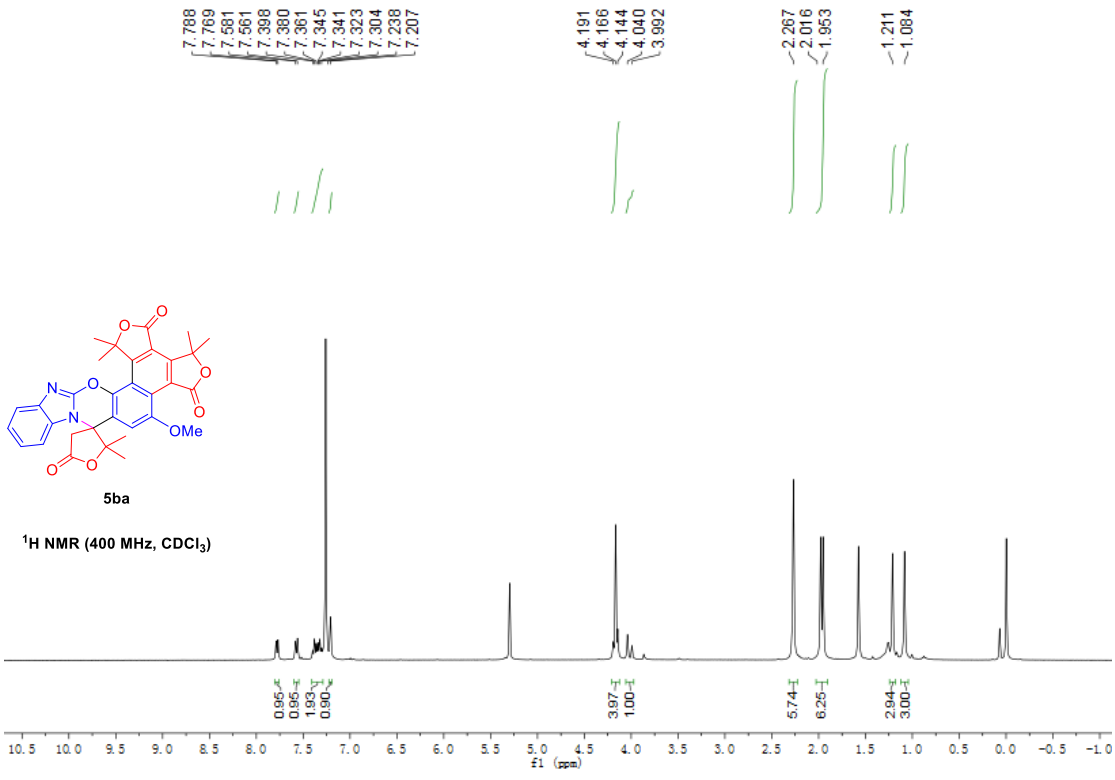
^{13}C NMR (100 MHz, $CDCl_3$)

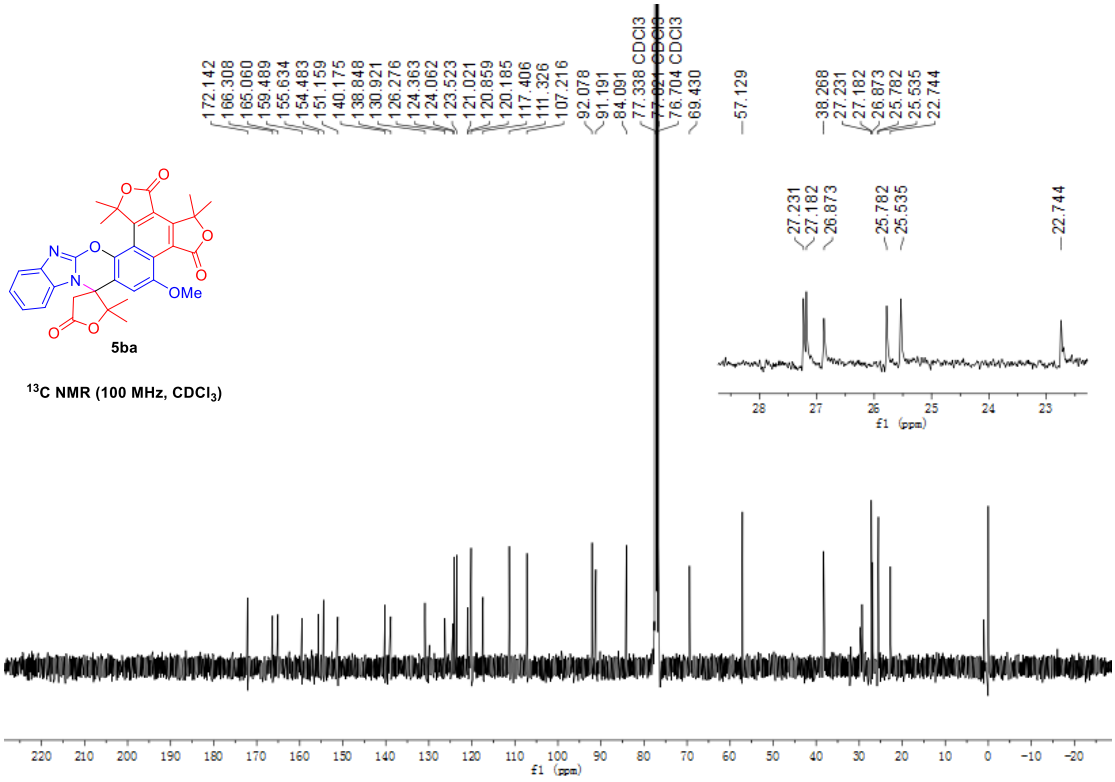


5aa

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

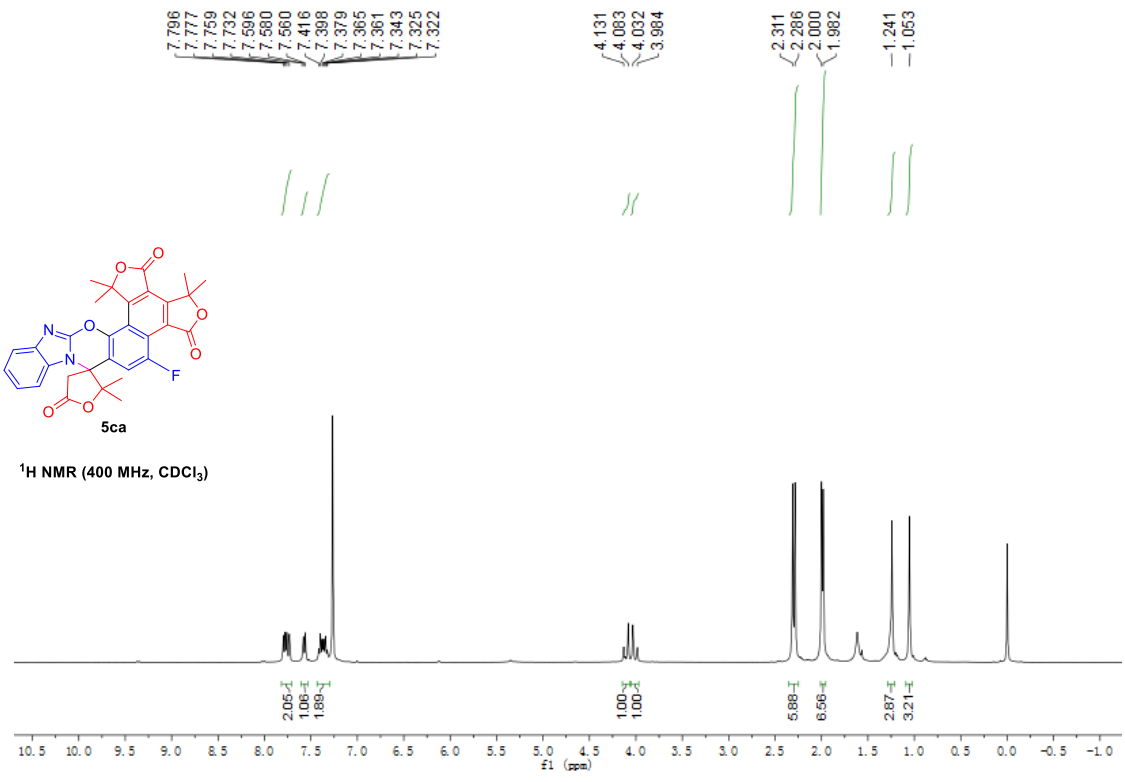

171.183
167.151
165.463
158.775
153.679
149.662
144.314
138.990
132.925
129.905
126.764
123.119
122.704
121.516
120.719
119.536
119.188
117.886
116.086
110.339
90.990
90.303
85.314
76.310 CDCl3
75.993 CDCl3
75.675 CDCl3
68.556
37.539
26.130
25.973
25.922
24.371
24.348
21.400
O
O
O
O
O
N
O
N
O
O
5aa
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.788
7.769
7.581
7.561
7.398
7.380
7.361
7.345
7.341
7.323
7.304
7.238
7.207
4.191
4.166
4.144
4.040
3.992
2.267
2.016
1.953
1.211
1.084
O
O
O
O
O
N
O
N
O
OMe
O
5ba
1H NMR (400 MHz, CDCl3)
0.95
0.95
1.93
0.90
3.97
1.00
5.74
6.25
2.94
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



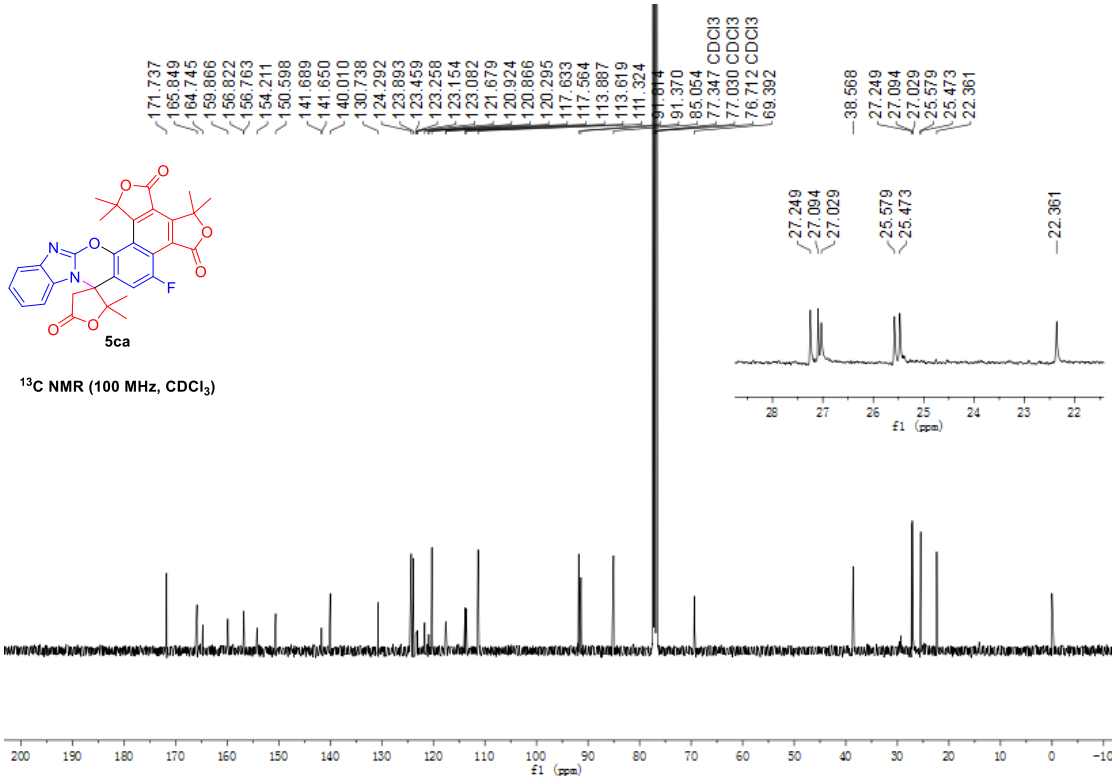
5ba

^{13}C NMR (100 MHz, $CDCl_3$)



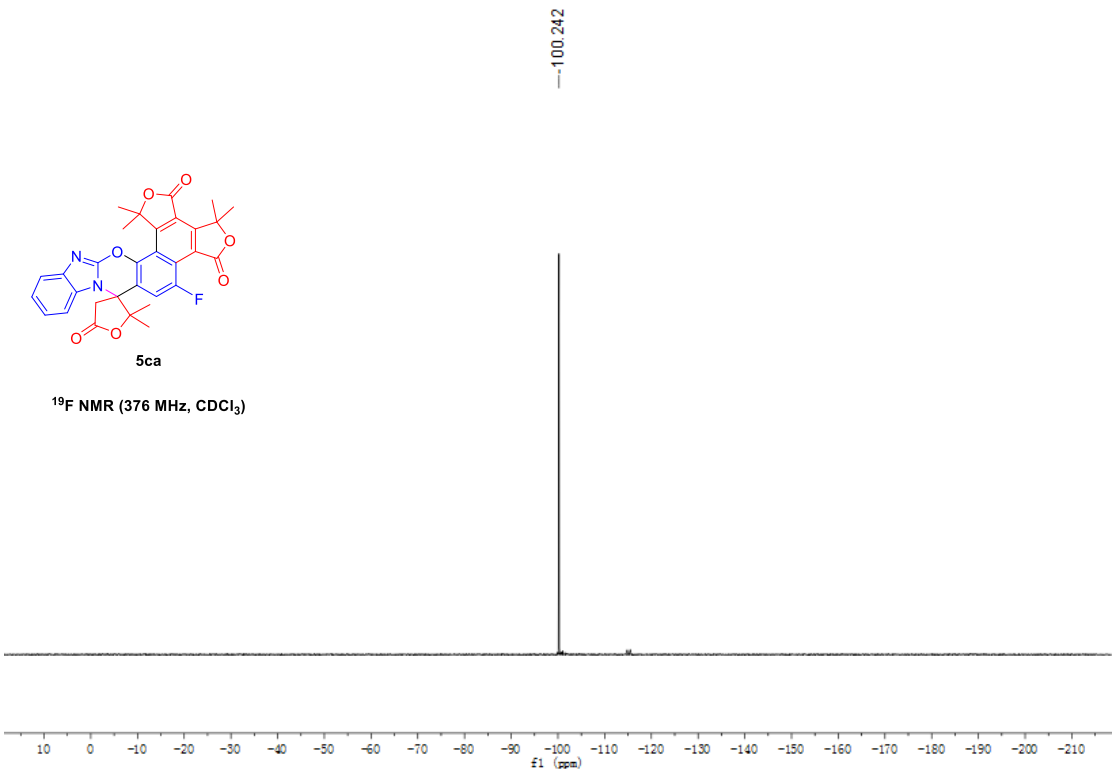
5ca

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



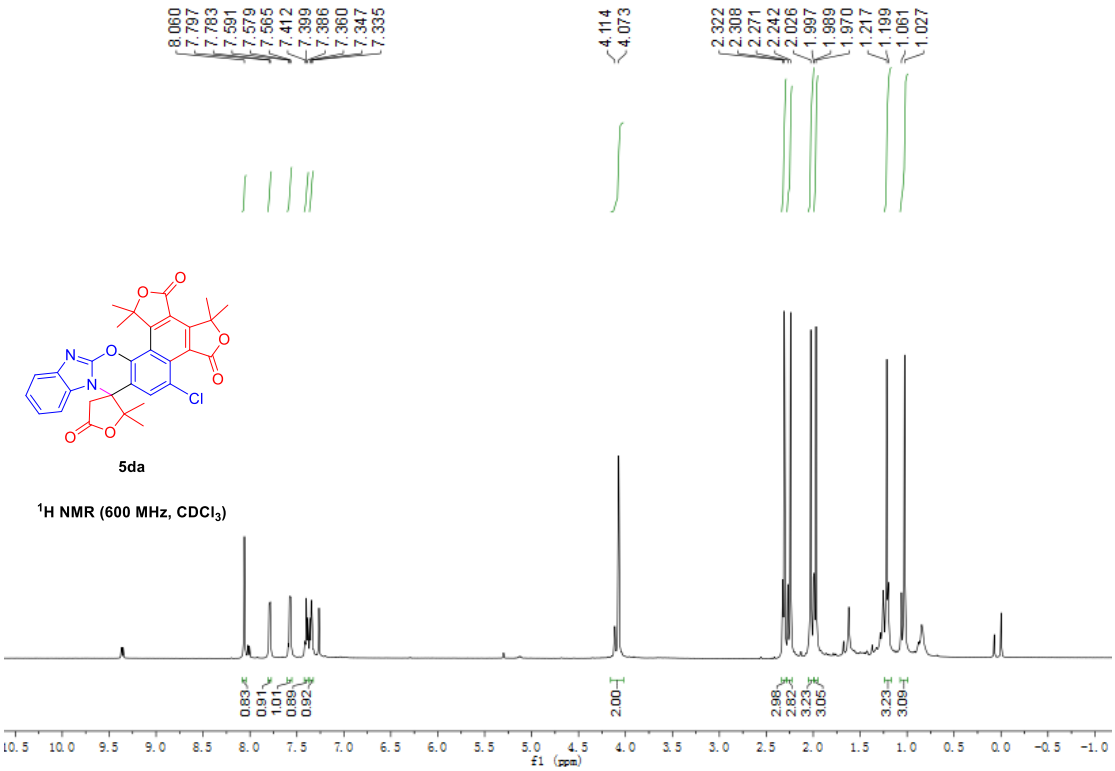
5ca

^{13}C NMR (100 MHz, $CDCl_3$)



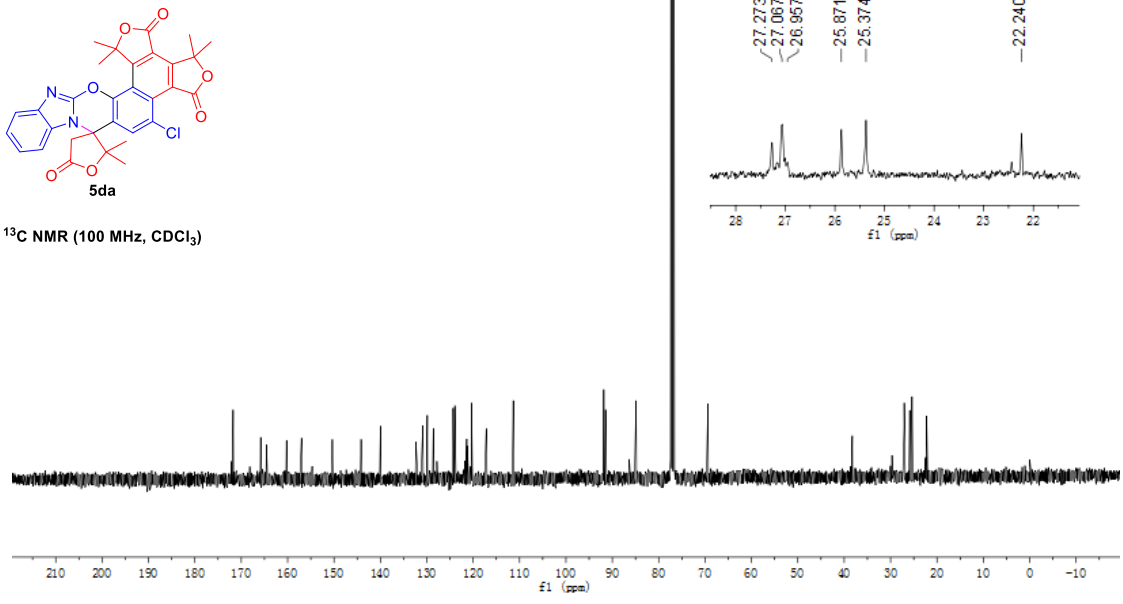
5ca

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



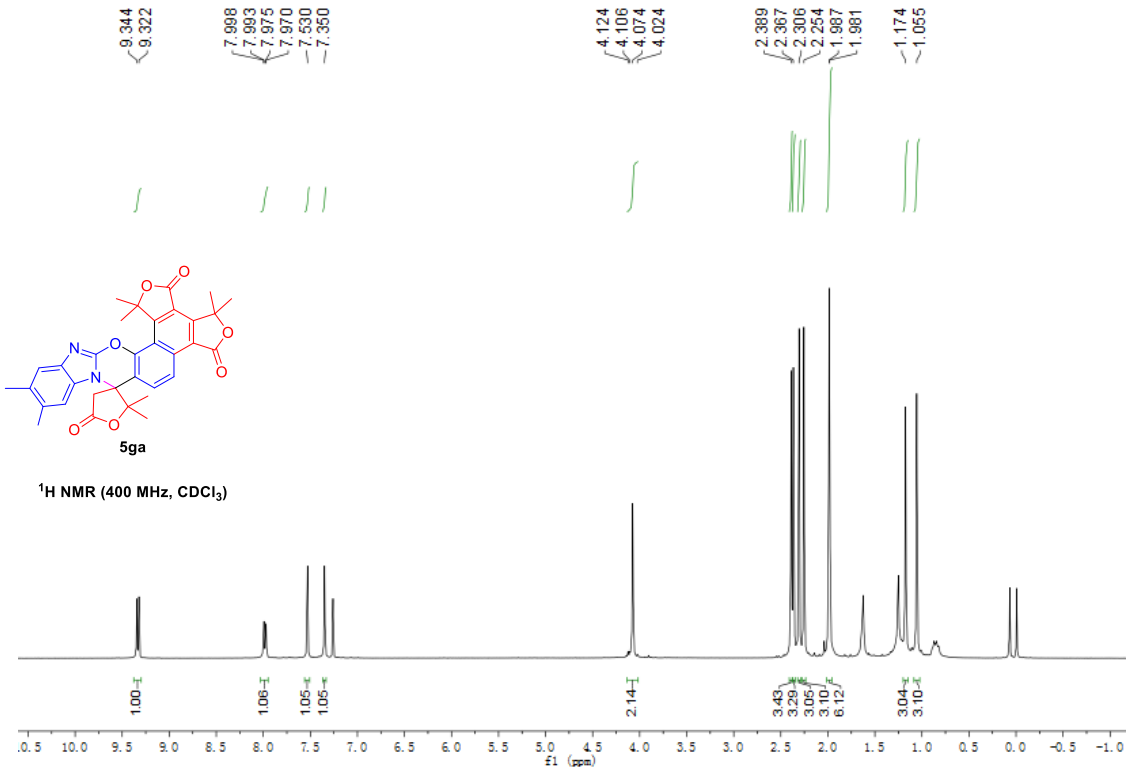
5da

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



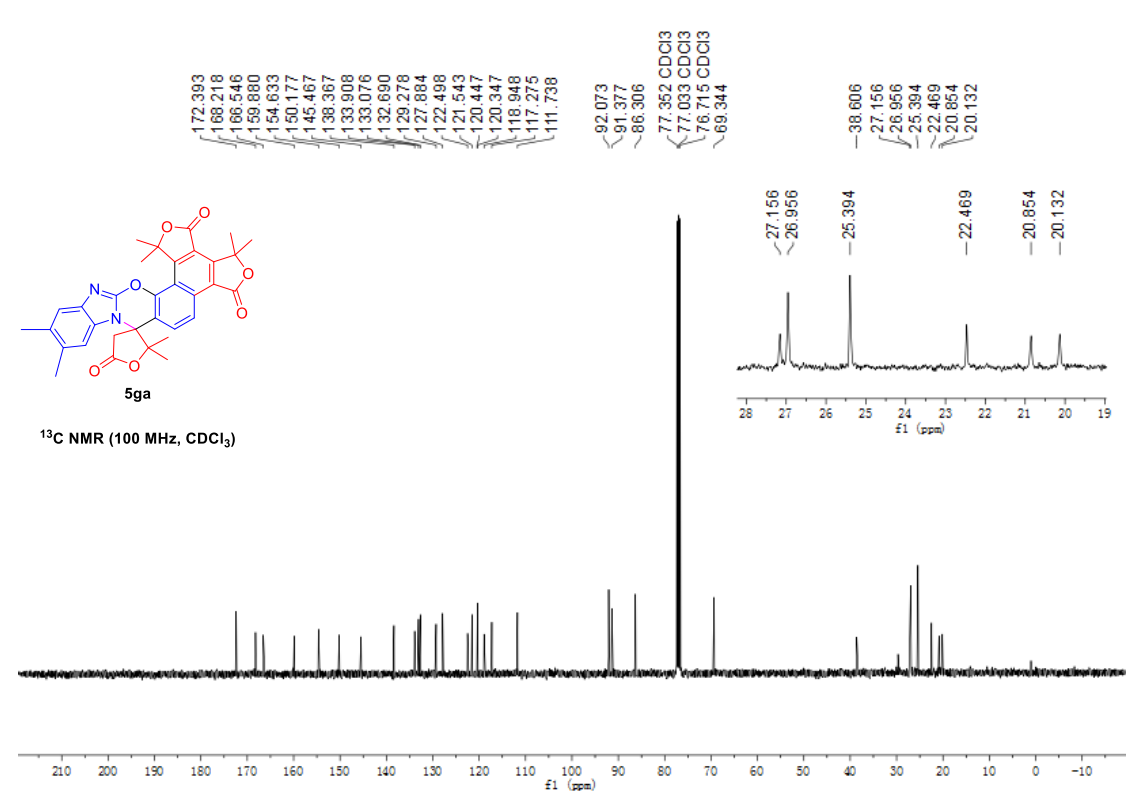
5da

^{13}C NMR (100 MHz, $CDCl_3$)



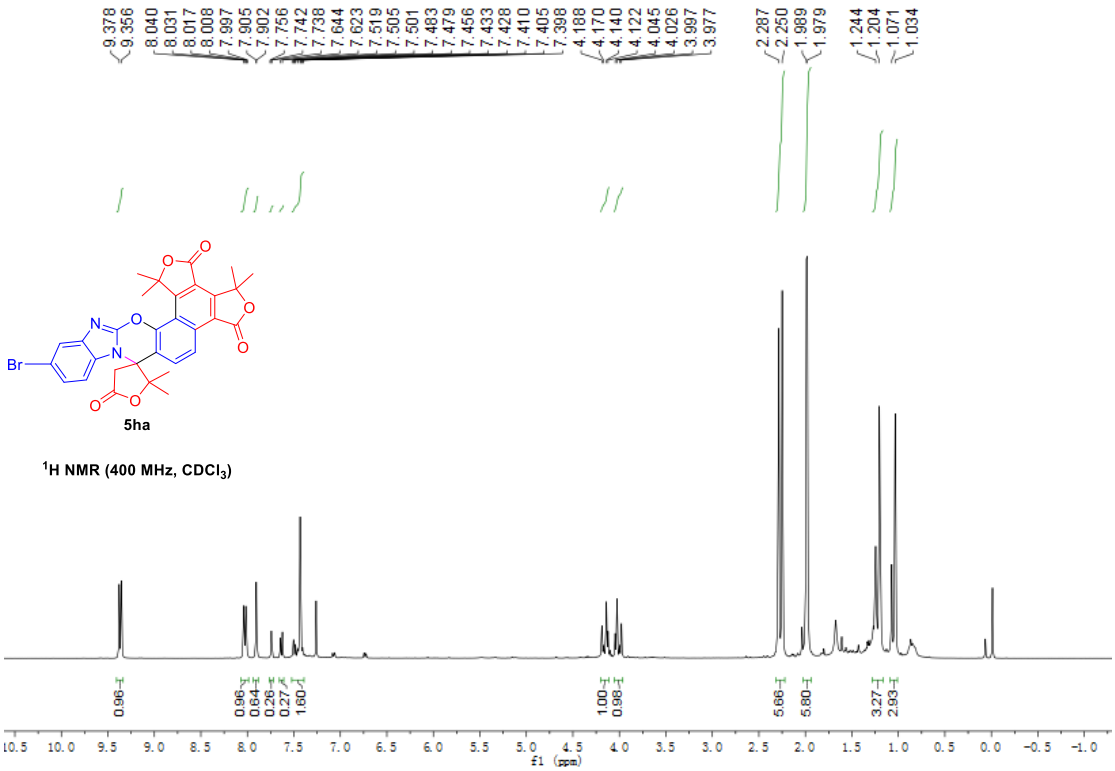
5ga

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



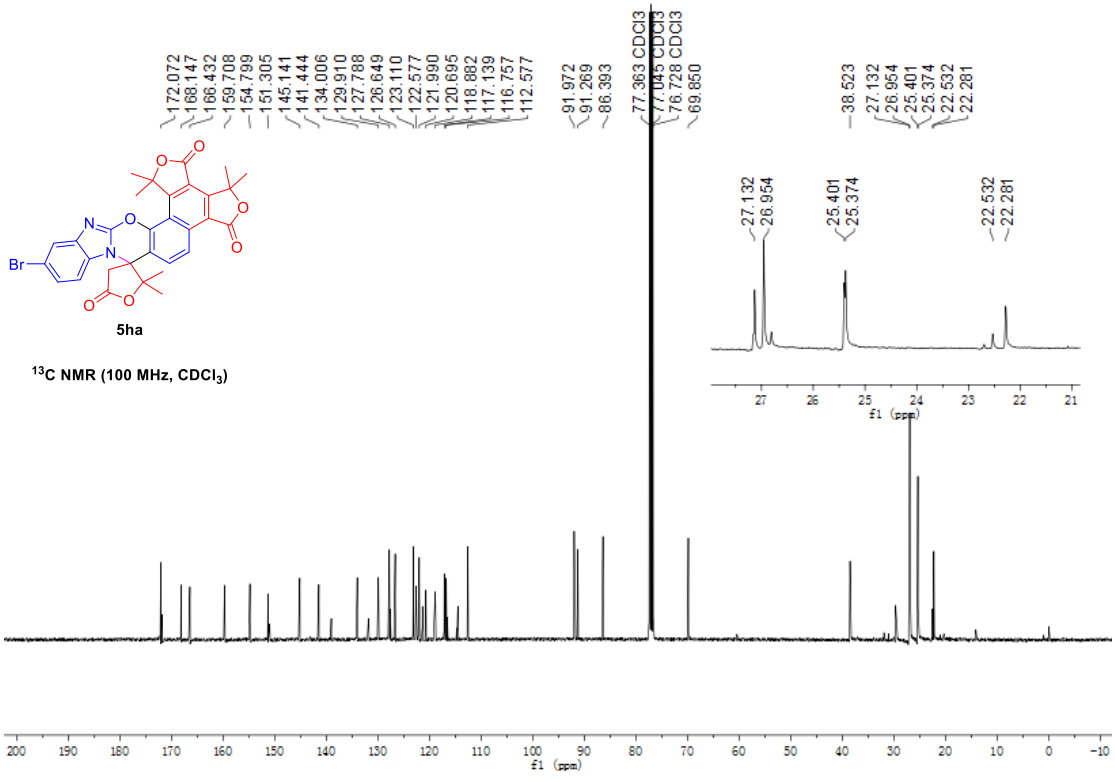
5ga

^{13}C NMR (100 MHz, $CDCl_3$)



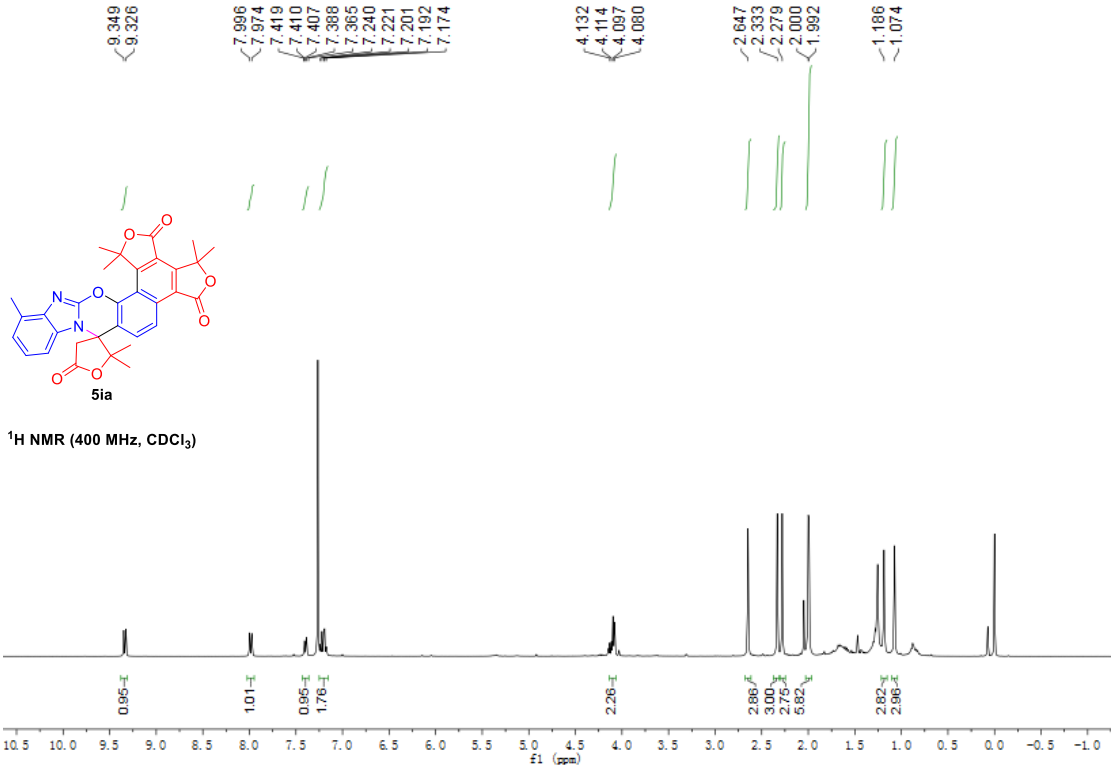
5ha

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



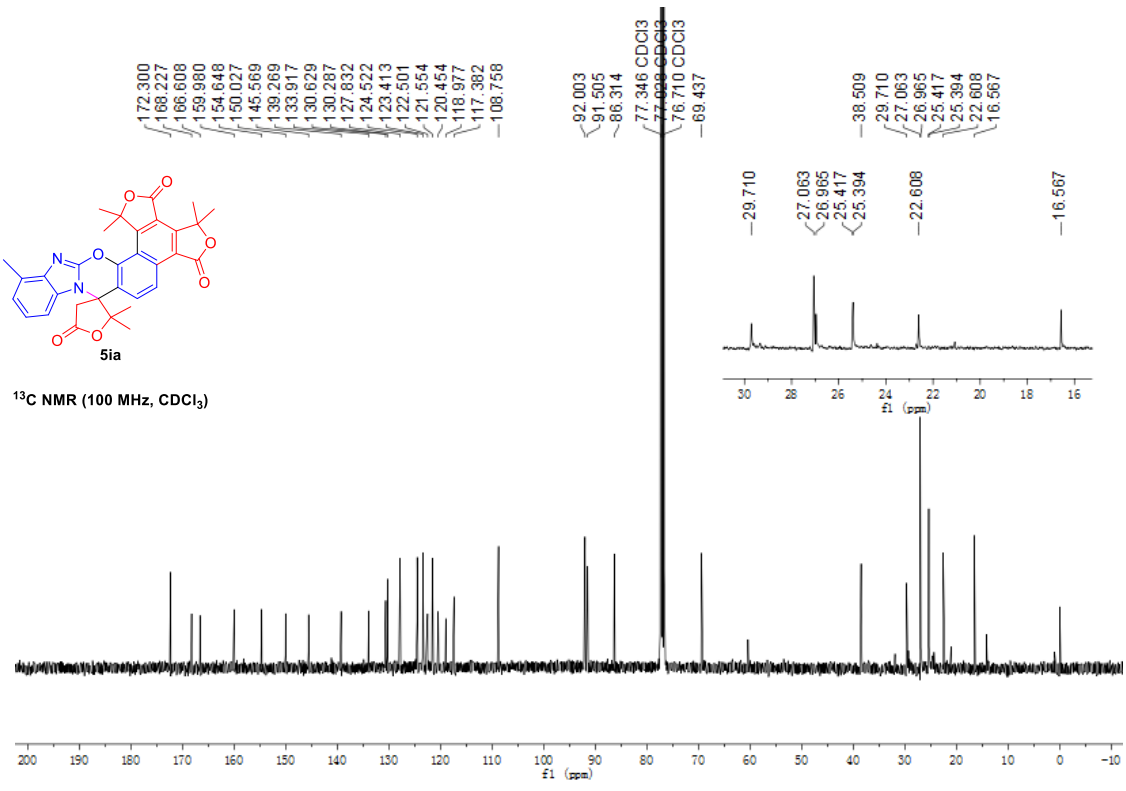
5ha

^{13}C NMR (100 MHz, $CDCl_3$)



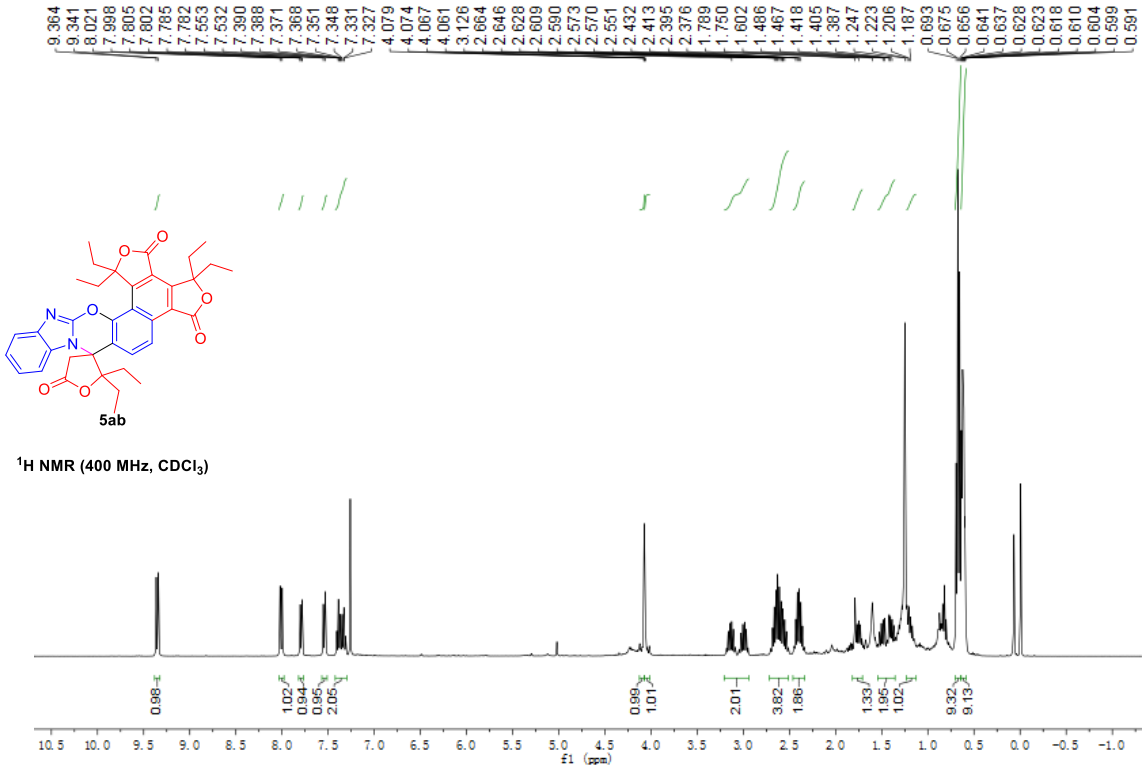
5ia

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



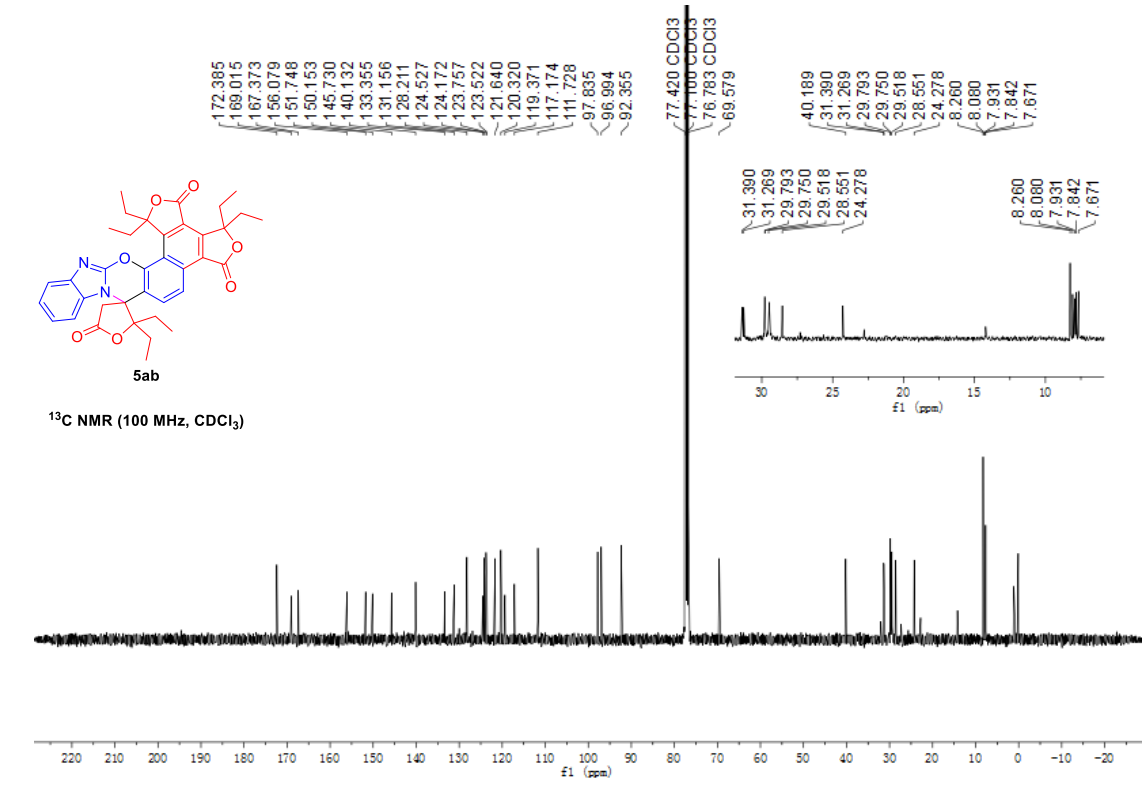
5ia

^{13}C NMR (100 MHz, $CDCl_3$)



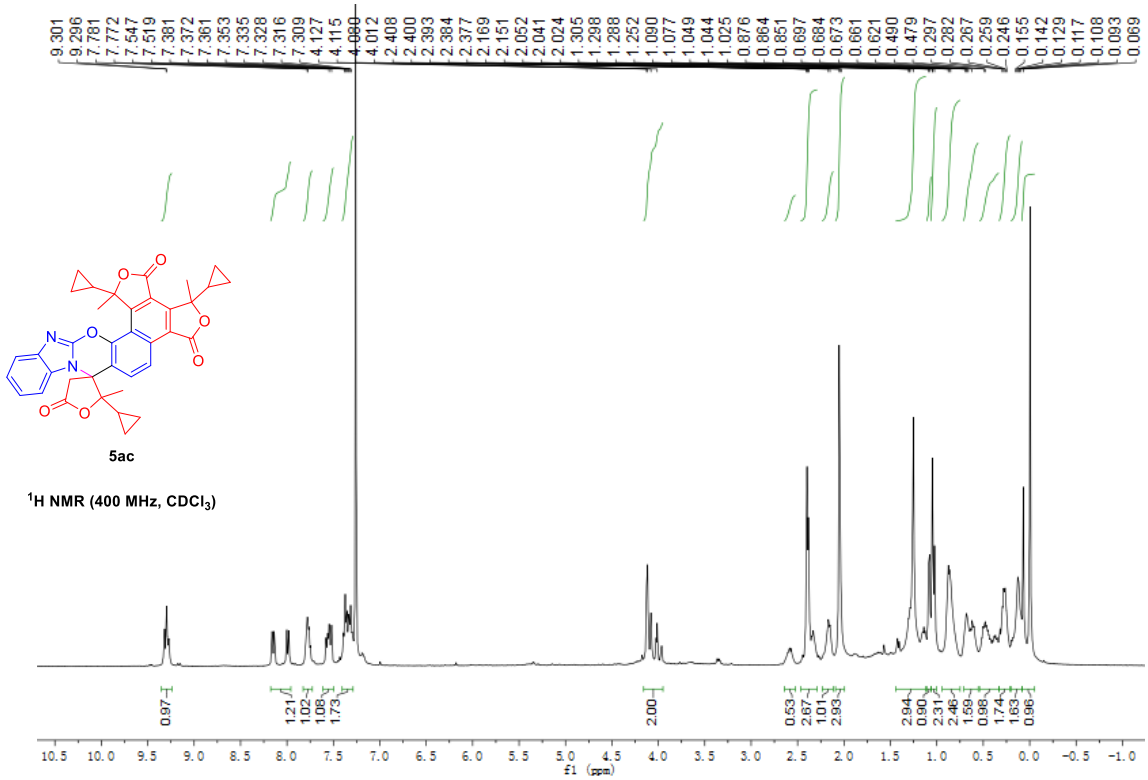
5ab

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



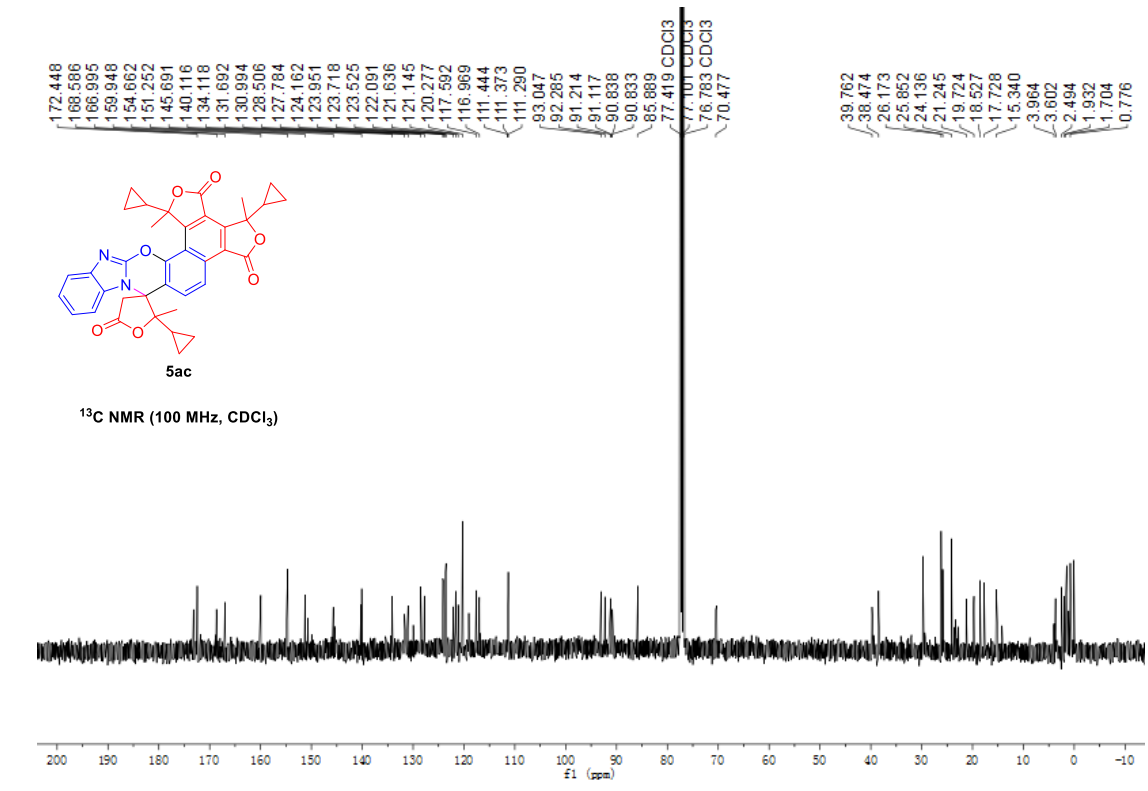
5ab

^{13}C NMR (100 MHz, $CDCl_3$)



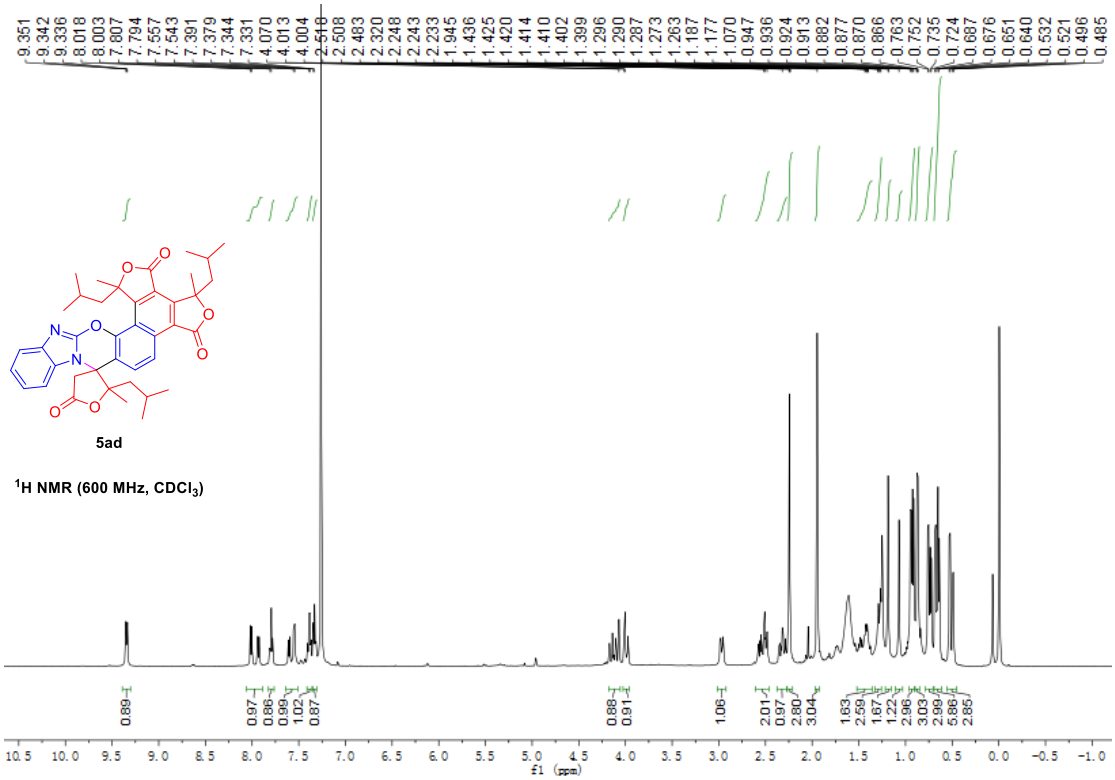
5ac

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



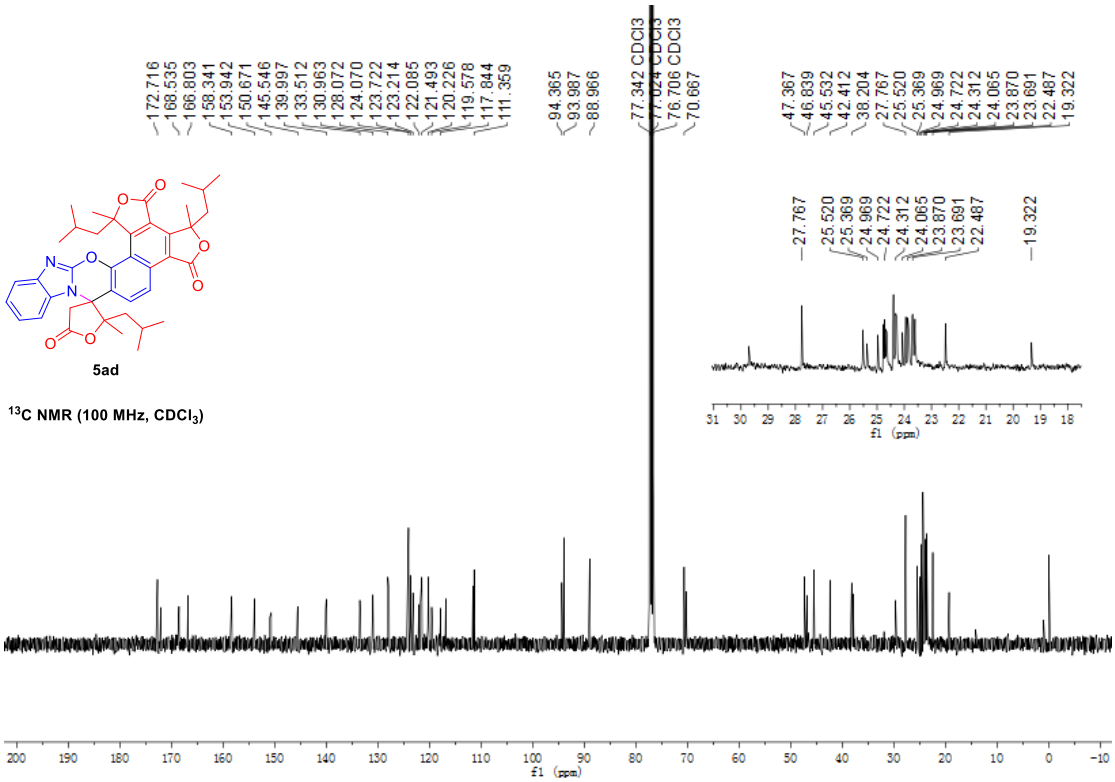
5ac

^{13}C NMR (100 MHz, $CDCl_3$)



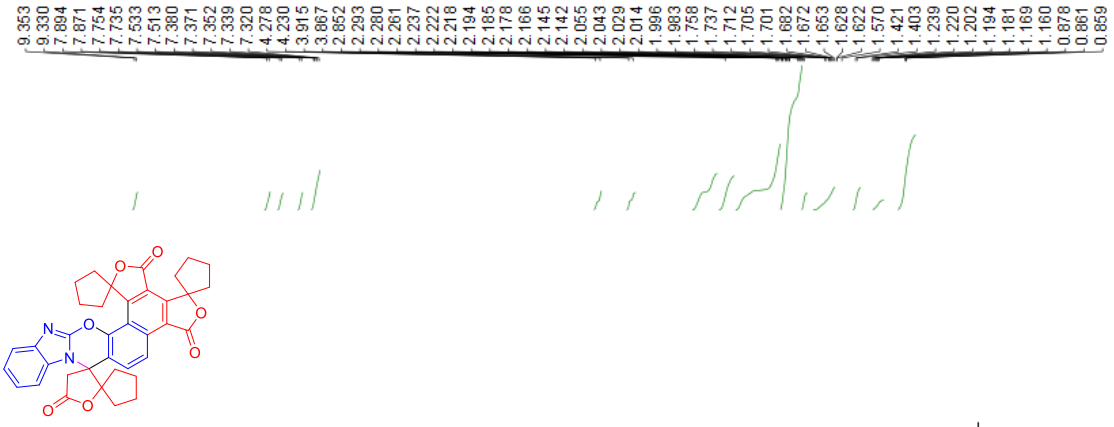
5ad

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



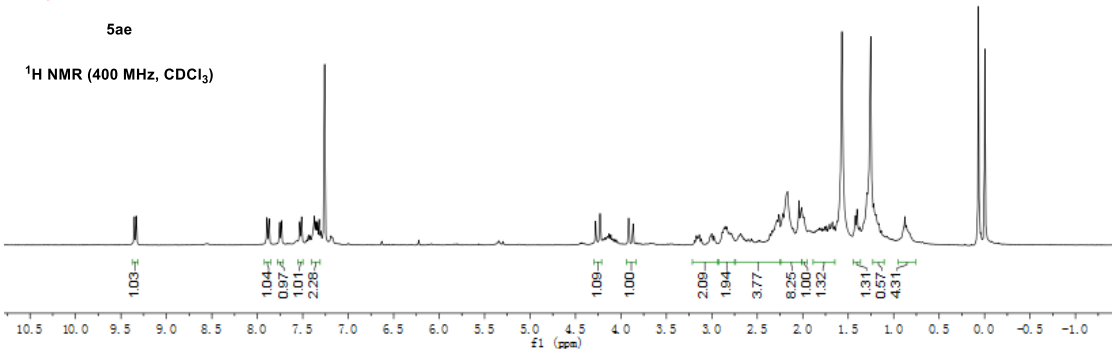
5ad

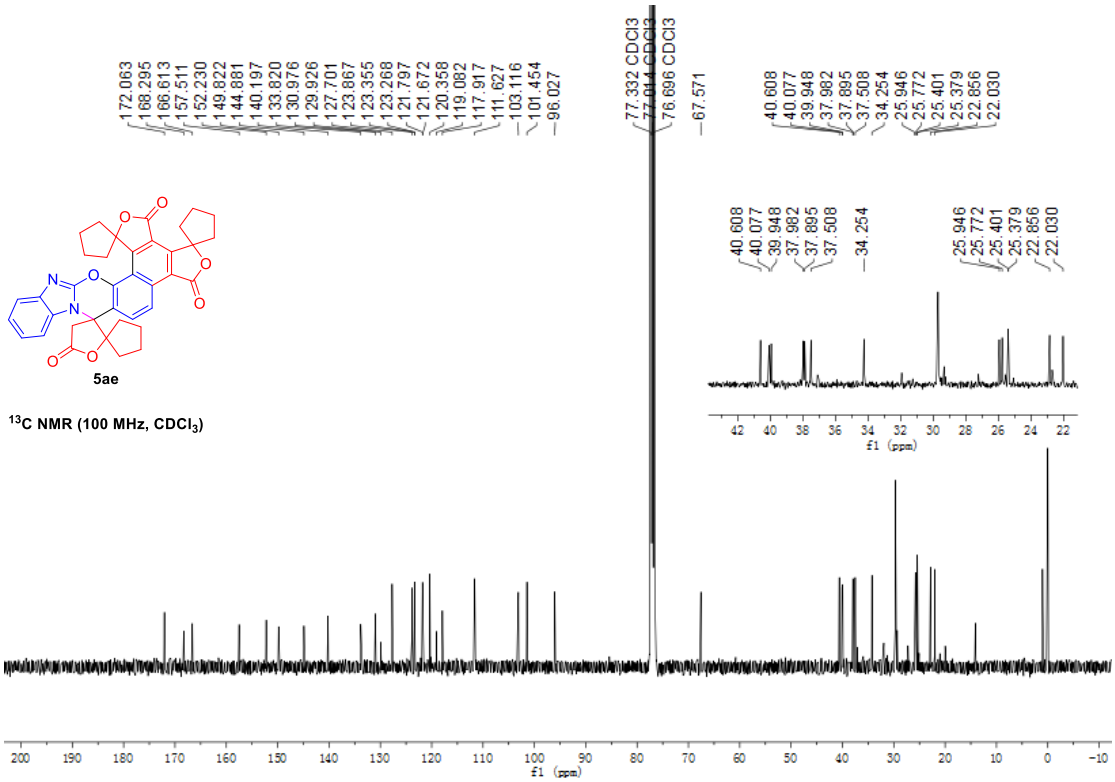
^{13}C NMR (100 MHz, $CDCl_3$)



5ae

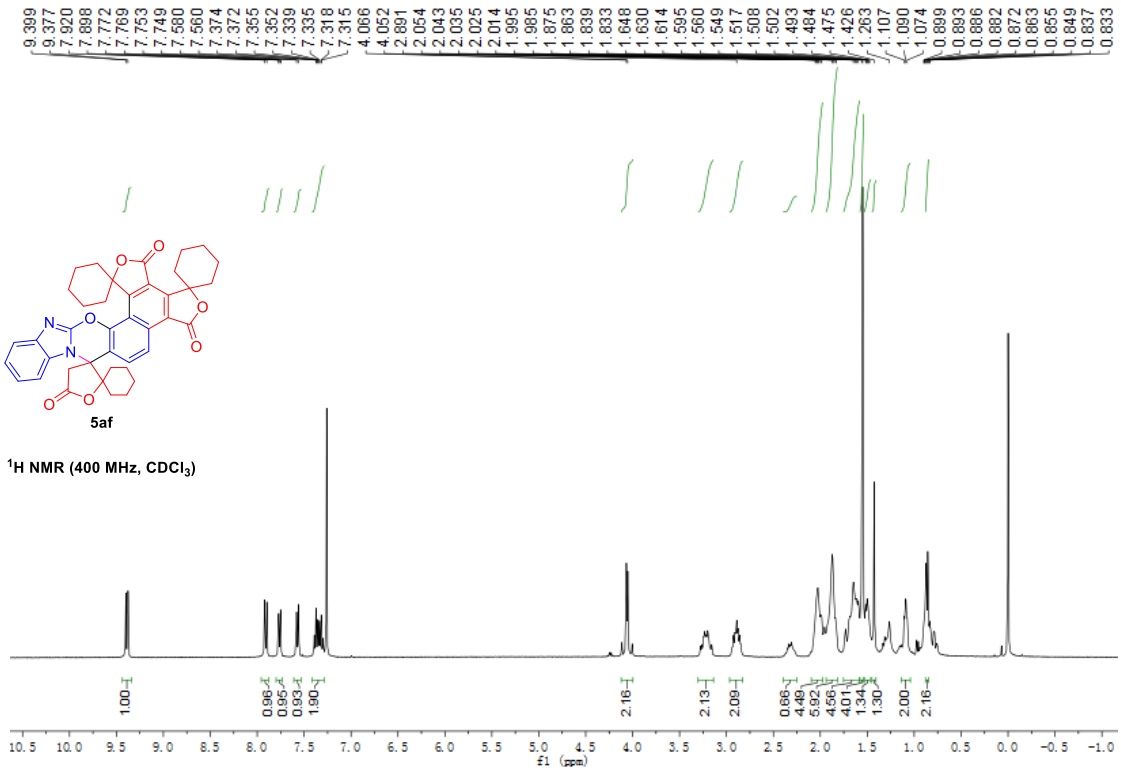
^{1}H NMR (400 MHz, $CDCl_3$)





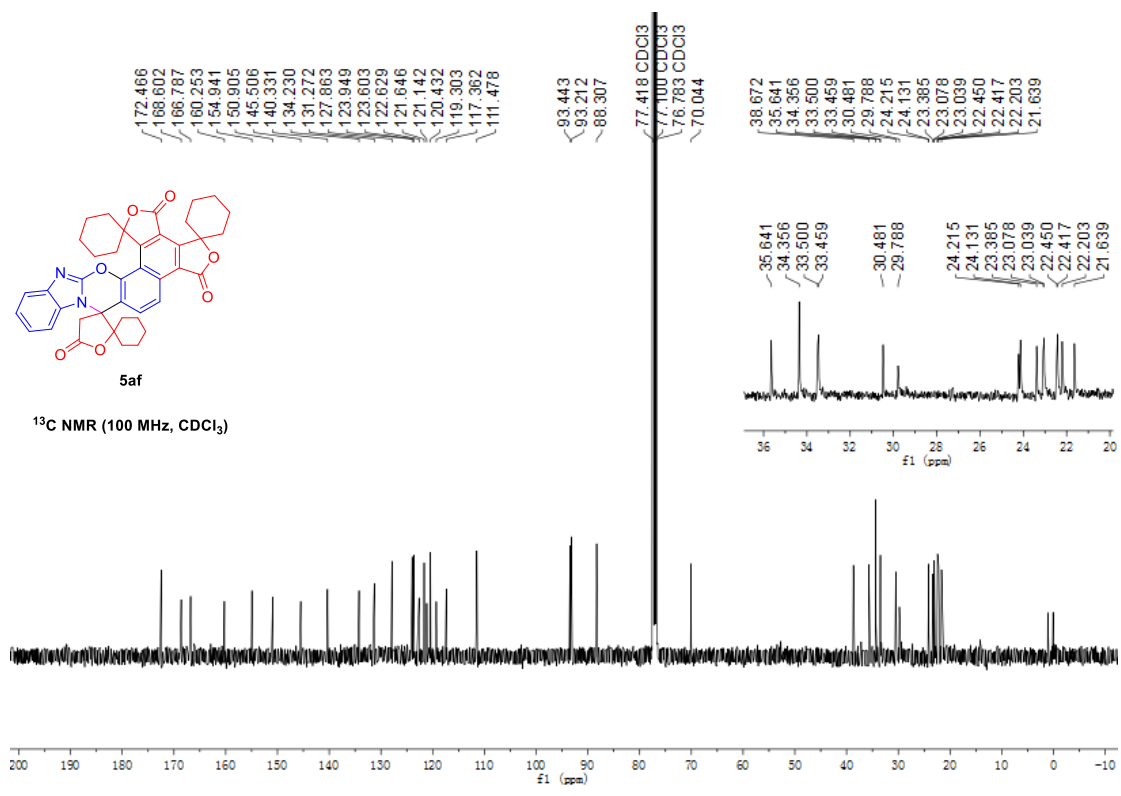
5ae

^{13}C NMR (100 MHz, $CDCl_3$)



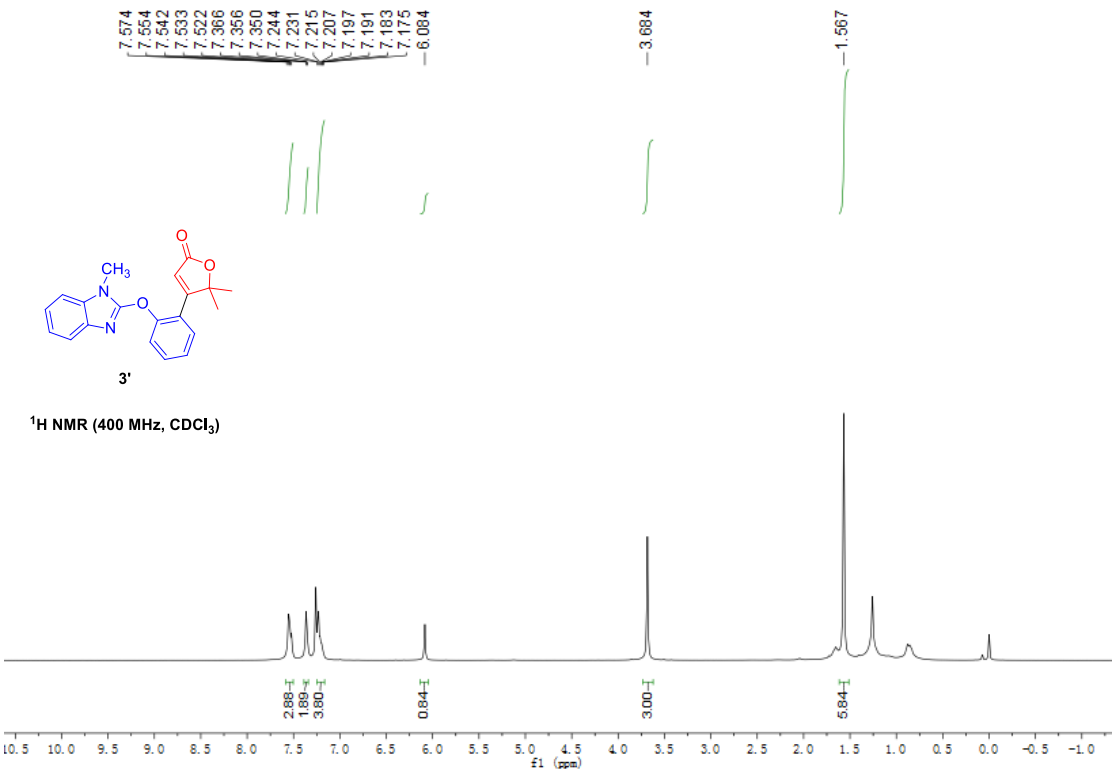
5af

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



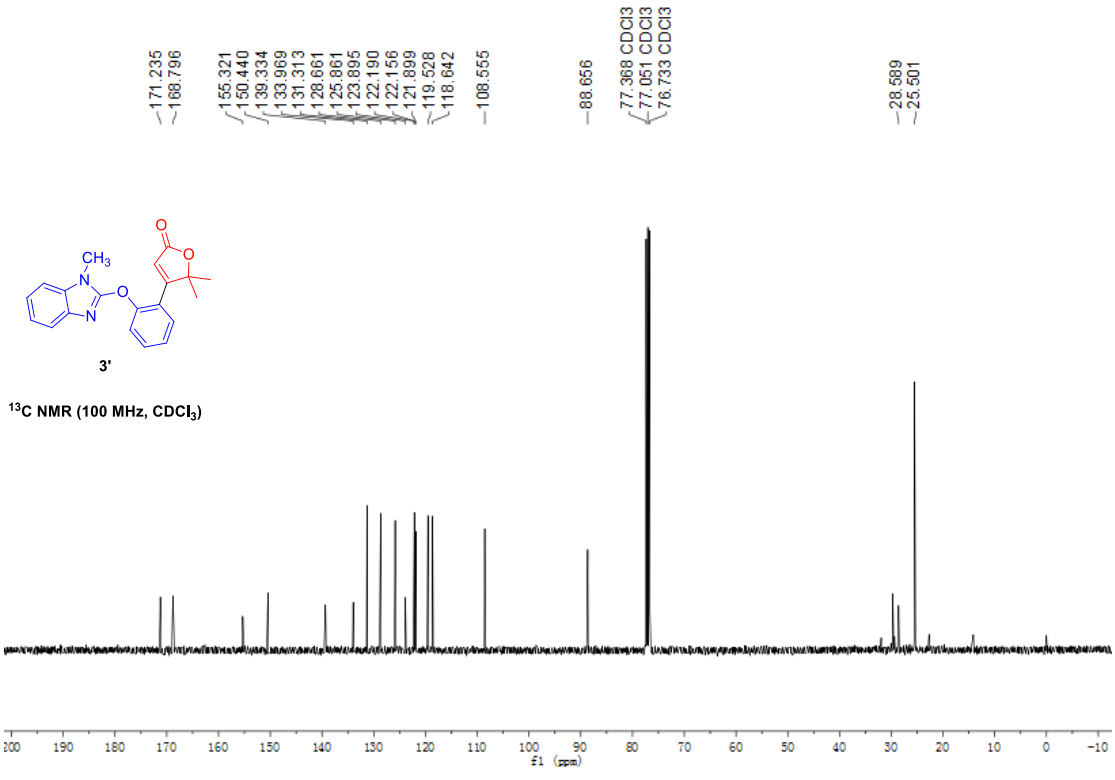
5af

^{13}C NMR (100 MHz, $CDCl_3$)



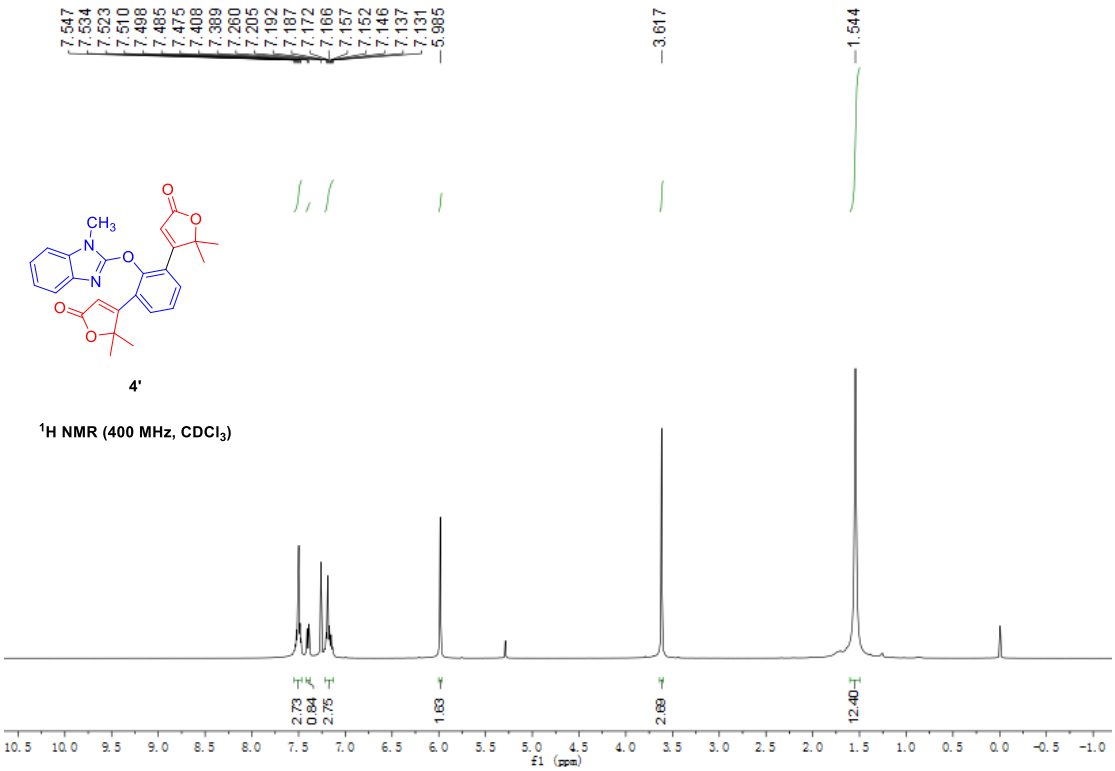
3'

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



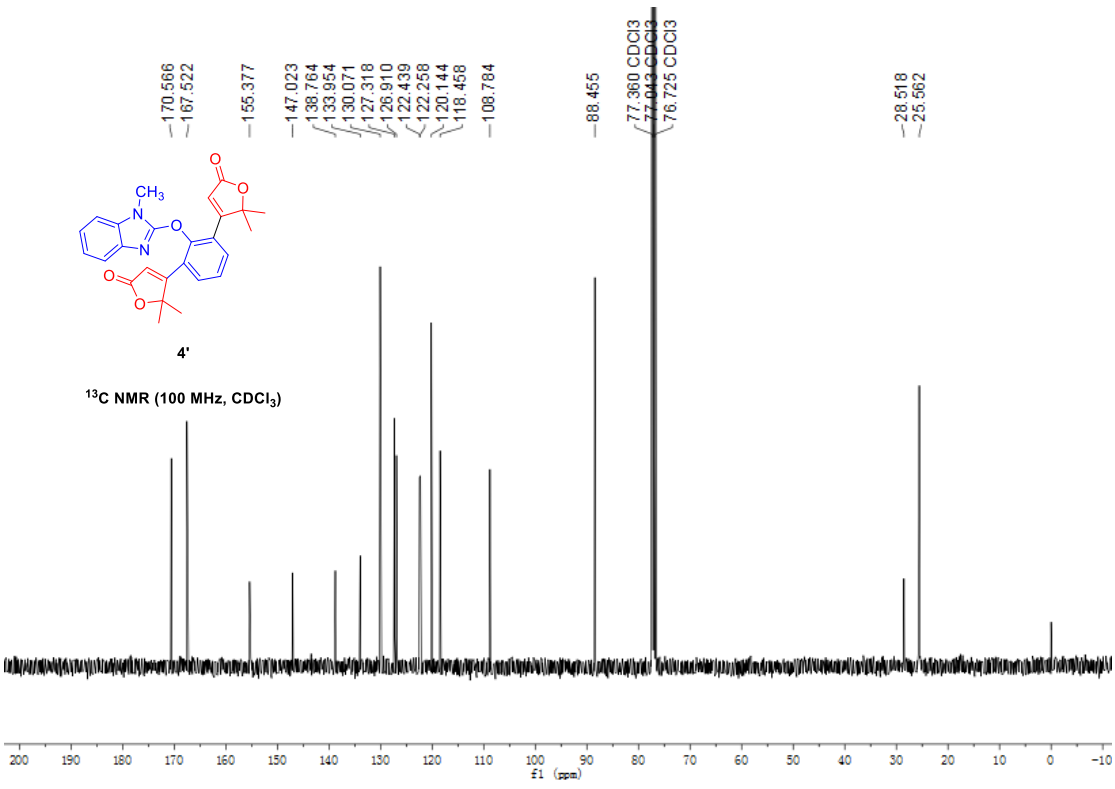
3'

^{13}C NMR (100 MHz, $CDCl_3$)



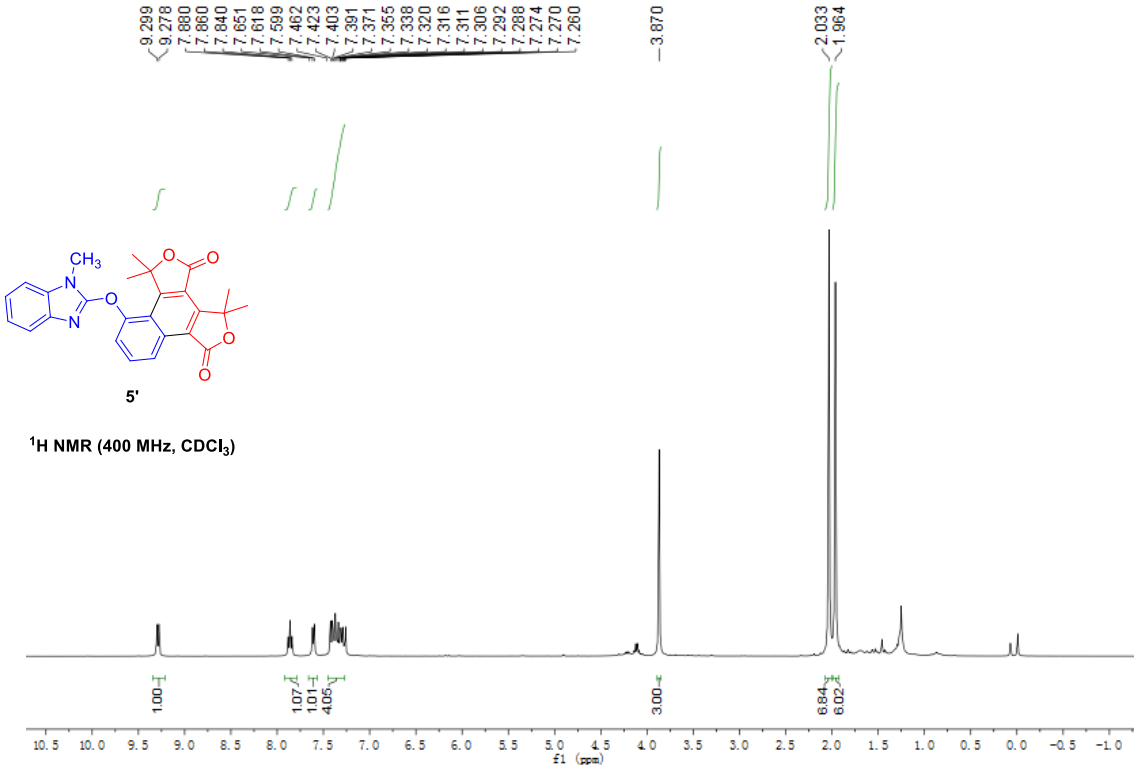
4'

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



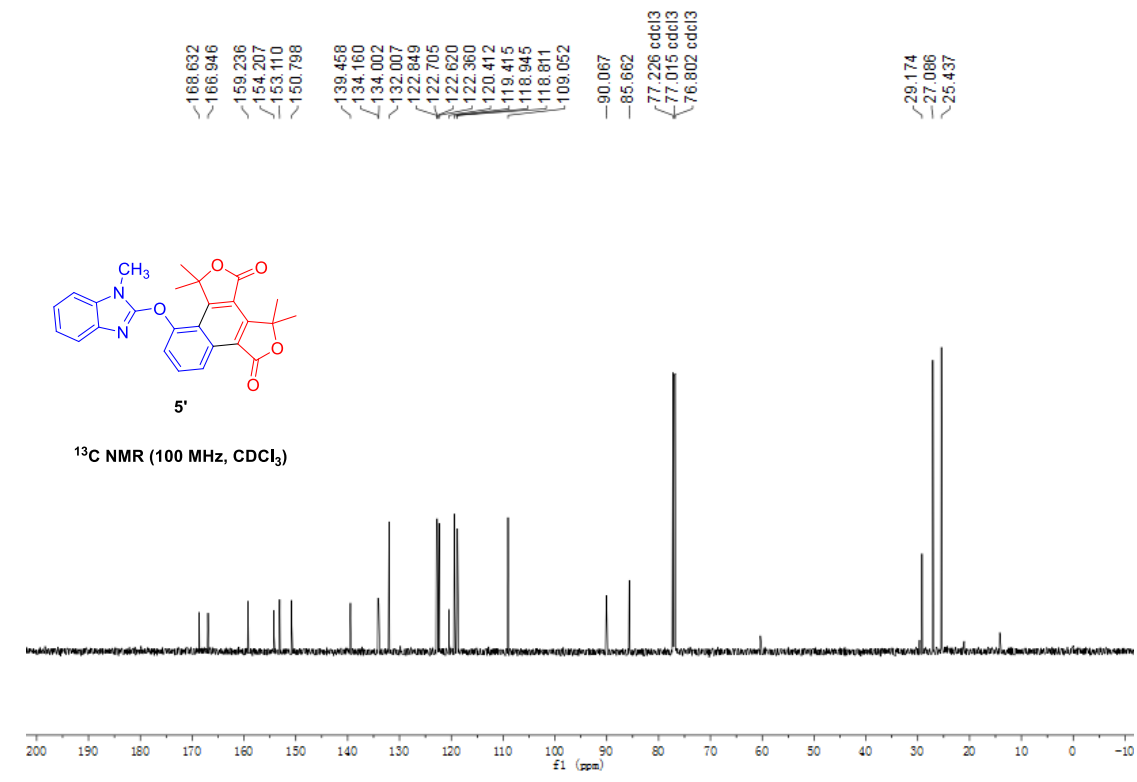
4'

^{13}C NMR (100 MHz, $CDCl_3$)



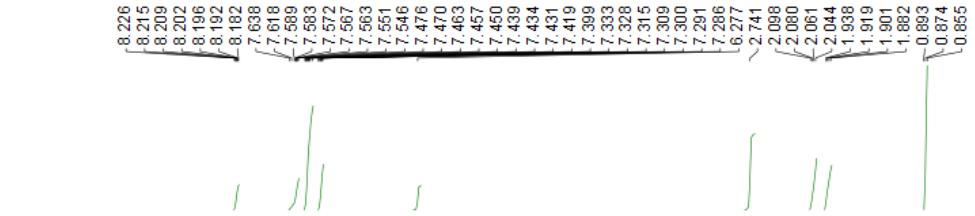
5'

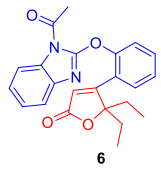
^{1}H NMR (400 MHz, $CDCl_3$)



5'

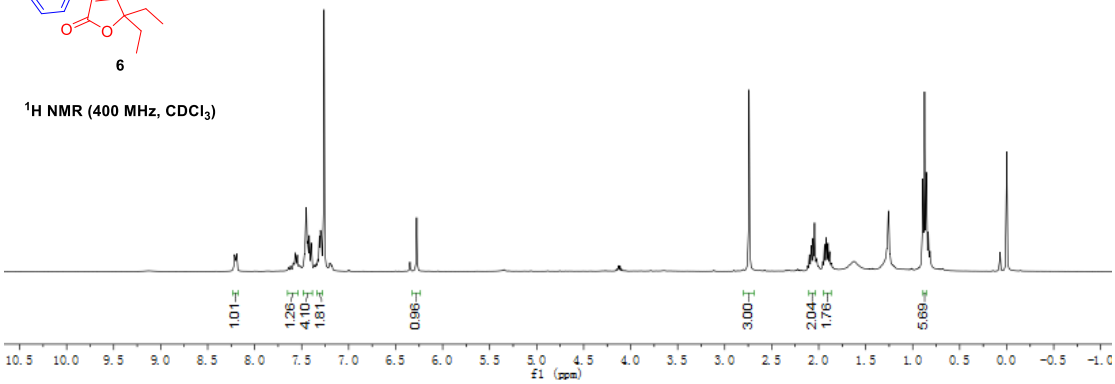
^{13}C NMR (100 MHz, $CDCl_3$)

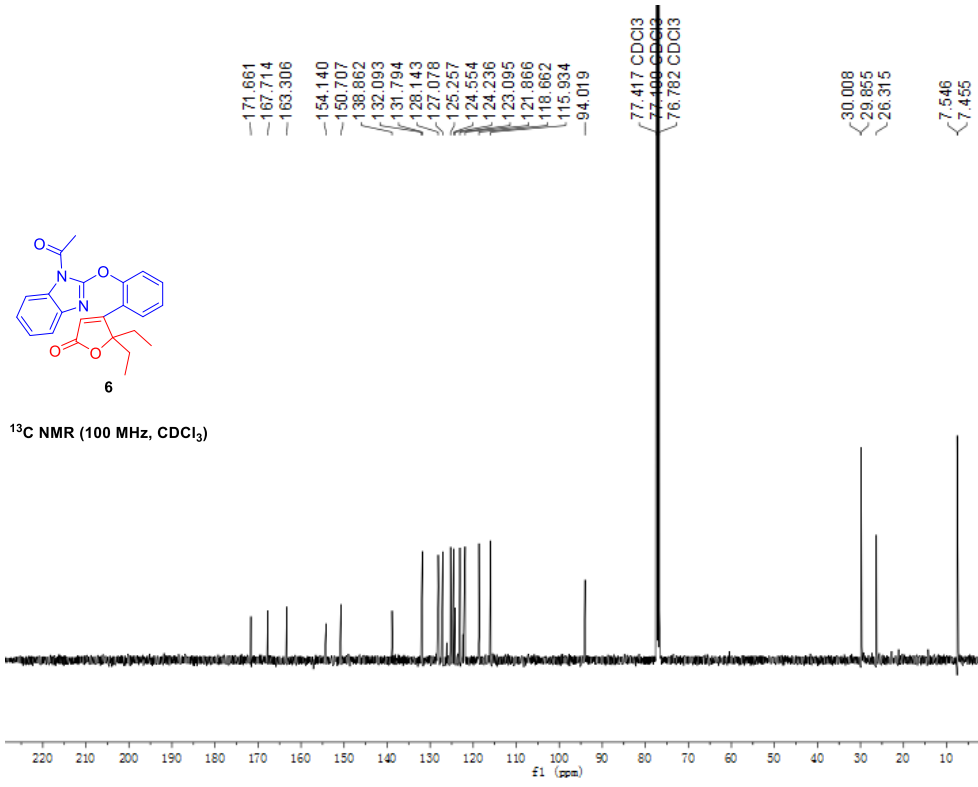




6

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





6

^{13}C NMR (100 MHz, $CDCl_3$)