Supporting Information

Construction of Cyclobutane-fused Tetracyclic Skeletons via Substrate-dependent EnT-enabled Dearomative [2+2] Cycloaddition of Benzofurans (Benzothiophenes)/Maleimides

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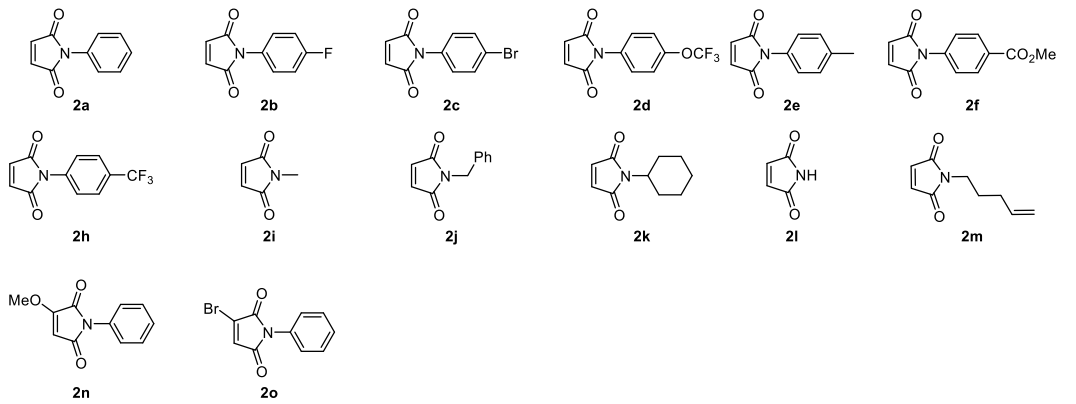
1.Materials and Methods

^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were recorded on Bruker AVANCE III 600 instrument, and chemical shifts were reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard in $CDCl_3$ solution and DMSO-d_6 solution. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, dd = double doublet, m = multiplet, br (broad), or a combination of them, and coupling constants (*J*) are reported in hertz (Hz). High-resolution mass spectra were obtained with a waters G2-xs qtof by ESI on a TOF mass analyzer. Melting points were measured on a melting point apparatus and are uncorrected. UV detection was monitored at 254 nm. Photochemical reactions were carried with 20 W 450 nm Blue LEDs, and 30 W 390 nm LEDs. For light-promoted reactions, the material of the irradiation vessel was borosilicate glass purchased from Synthware.Column chromatography was performed on silica gel (200-300 mesh) eluting with ethyl acetate (EtOAc), petroleum ether (PE), and dichloromethane (DCM). TLC was performed on glass-backed silica plates. UV light and I_2 were used to visualize products or starting materials. Unless otherwise specified, all reagents were obtained from commercial suppliers and used without further purification. All experiments were performed under an atmosphere of argon atmosphere.

2.Preparation of Substrates

2a, **2i**, **2j**, **2l** were purchased from Titan and Bide, **2b**-**2h**, **2k**, **2m-2o** were synthesized according to the literature procedures.[1-4]

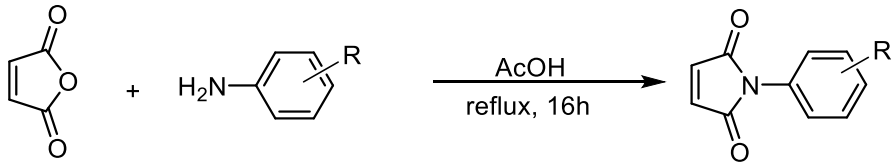
Table S1 List of maleimides



General Method for the Synthesis of Substituted Maleimides

Method A

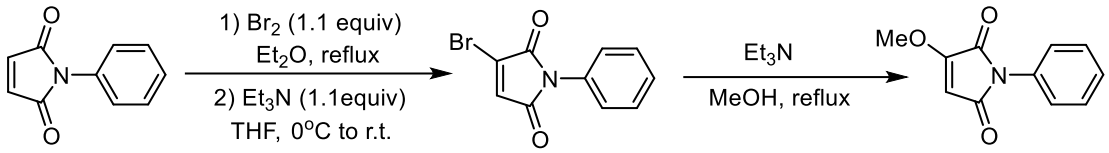
The *N*-Phenylmaleimides were prepared from maleic anhydride and amine according to the reported procedure[1].



To a solution of maleic anhydride (981 mg, 10.00 mmol) in glacial acetic acid (6 mL), amine (4.00 mmol) was added and the reaction mixture was refluxed for 16 h. Subsequently, the solvent was removed in vacuo, the residue was dissolved in CH_2Cl_2 (15 mL) and the organic layer was washed with aq. $NaHCO_3$ 10% (2 x 25 mL), aq. HCl 1N (2 x 25 mL) and saturated aq. NaCl (20 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuo. The crude reaction mixture was further purified by column chromatography on silica gel (Pet. Ether/ EtOAc 5:1), to obtain the desired product.

Method B

2n, 2o were prepared according to the reported procedure[2,3].



Step 1

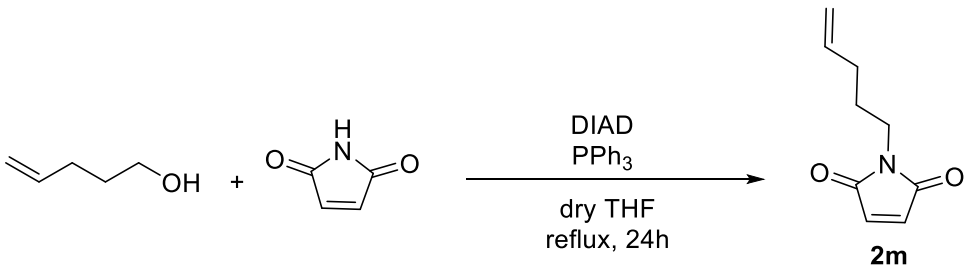
Bromine (0.3 mL, 5 mmol) was added to a magnetically stirred slurry of *N*-phenylmaleimide (865mg, 5.5 mmol.) in diethyl ether (14 mL). The ensuing mixture was heated at reflux for 1 h , then cooled to 0 °C and triethylamine (0.76 mL, 5.5 mmol) was added. The reaction mixture was then stirred for a further 2 h at 0 °C before being warmed to room temperature and diluted with ethyl acetate (10 mL) and water (10 mL). The separated aqueous layer was extracted with ethyl acetate (3×10 mL) and the combined organic phases were washed with water (1×10 mL) and brine (1×10 mL), then dried over $MgSO_4$ and filtered, finally concentrated under reduced pressure to obtain a white-solid product (769mg, 61 %).

Step 2

To a solution of 2-Bromo-*N*-phenylmaleimide (1.0 g, 3.97 mmol) in MeOH (10 mL) was added a solution of Et_3N (0.61 mL, 4.37 mmol) in MeOH (5 mL), and the reaction mixture was refluxed for 1 h. Concentration of the mixture in vacuo followed by silica gel column chromatographic purification of the residue using petroleum ether–EtOAc (8:2) as eluent and gave a white-solid product (604mg, 75 %).

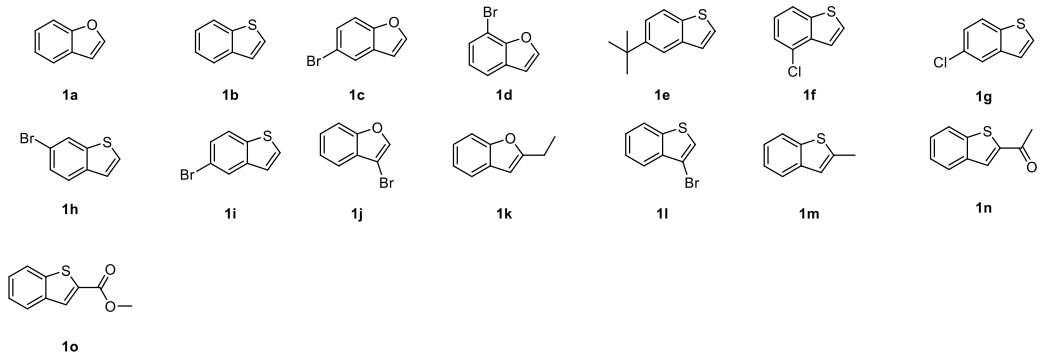
Method C

2m were prepared according to the reported procedure[4].



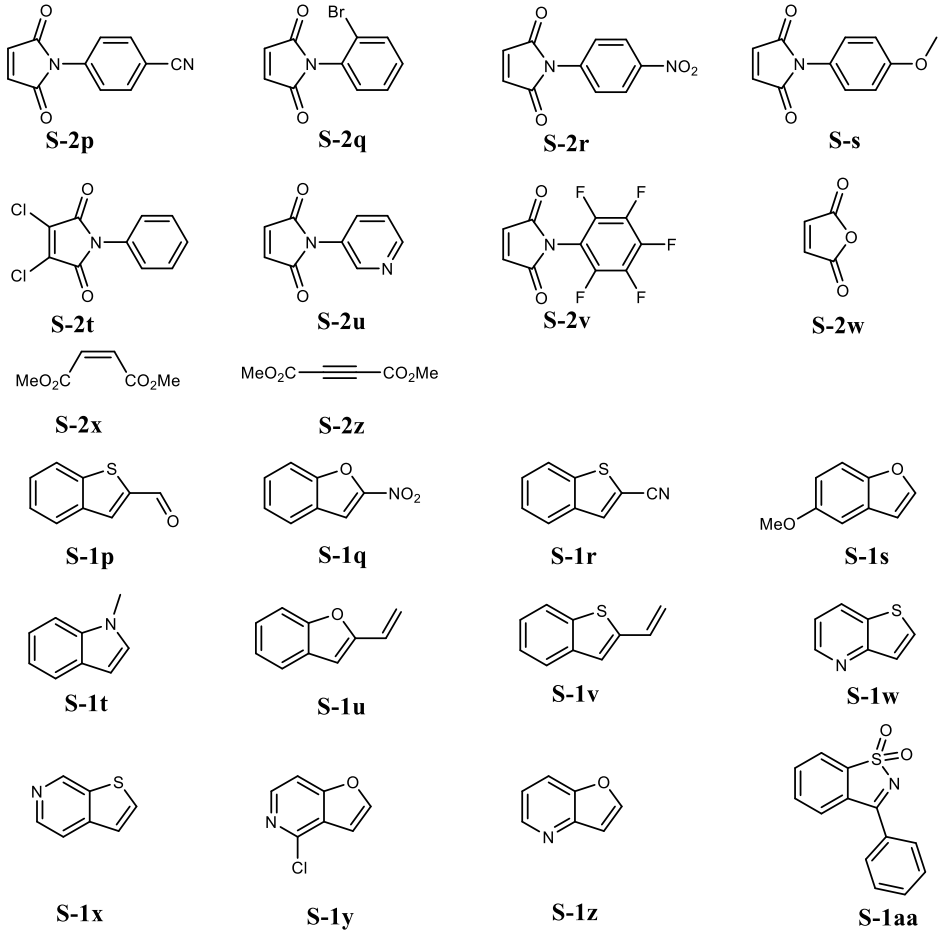
The maleimide (485 mg,5.0 mmol) and PPh_3 (1.31 g, 5.0 mmol) were added in dry THF (20.0 mL) and dissolved in a 100 mL round bottom flask equipped with a magnetic stirring bar. Then, pent-4-en-1-ol(1.00 ml, 5.0 mmol) and diisopropylazodicarboxylate (DIAD) (0.50 mL, 5.0 mmol)were added. The flask was equipped with a condenser and the mixture was stirred for 24 h under reflux.The solvent was evaporated under reduced pressure. The residue was purified by column chromatography.(420mg, 49 %)

Table S2 List of derivatives of Benzothiophenes and Benzofurans



1b-1o were purchased from Titan and Bide.

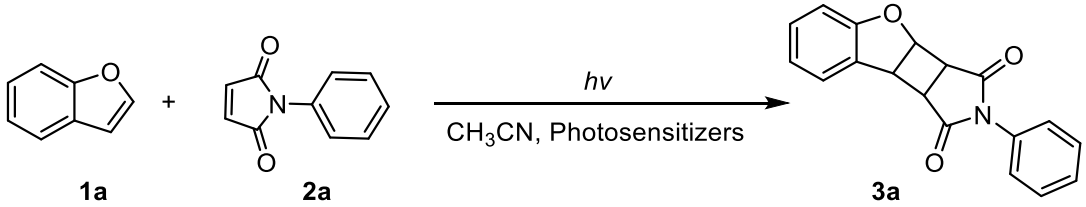
Table S3 List of unsuccessful substrates



However, when moving to examine other *N*-substituted maleimides such as *N*-(*4*-nitrophenyl) maleimide, *N*-(pentafluorophenyl)maleimi-de, *N*-heteroarylmaleimides and *N*-alkyl substituted maleimides, these substrates were proved to be incompatible with this reaction which limited the application of catalytic systems to a certain extent. This table showcased substrates incompatible with our reaction protocol.

3.Optimization of the Reaction Conditions

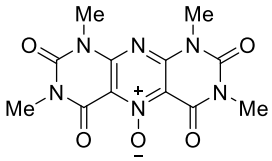
Table S4 Photosensitizer Screening



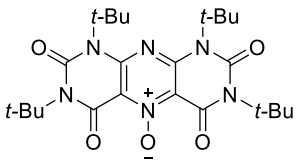
Entry[a]	Photosensitizers	Yield(%)[d]	d.r.
1	MePPTNO	0	-
2	EosinY	0	-
3	BuPPTNO	0	-

4	*t*-BuPPTNO	0	-
5	4CzIPN	0	-
6[b]	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	22	5.5:1
7[b]	$Ru(bpy)_3Cl\cdot 6H_2O$	0	-
8[b]	$Ru(bpy)_3(PF_6)_2$	0	-
9[c]	Thioxanthone	40	3.4:1

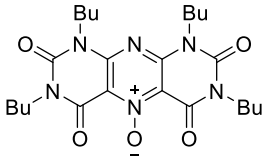
[a]benzofuran **1a** (0.20 mmol), *N*-phenylmaleimide **2a** (0.20 mmol), and photosensitizer (5 mol%) in solvent (2 mL),irradiated with 450 nm LEDs under argon atmosphere at room temperature for 24 h. [b]Photosensitizer (1 mol%), irradiated with 450 nm LEDs. [c]Photosensitizer (30 mol%), irradiated with 390 nm LEDs. [d]Yield was determined by column chromatography.



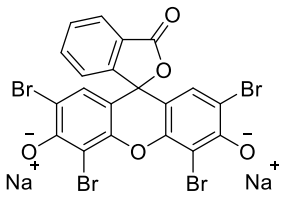
MePPTNO



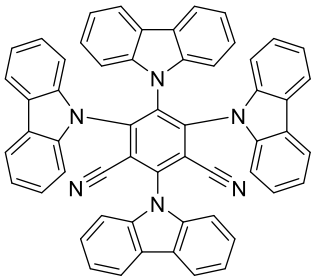
***t*-BuPPTNO**



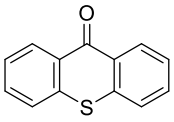
BuPPTNO



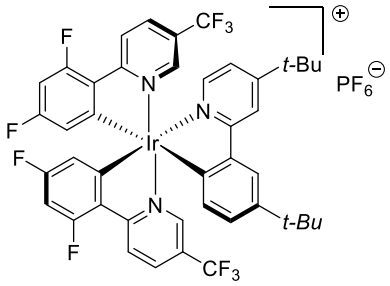
EosinY



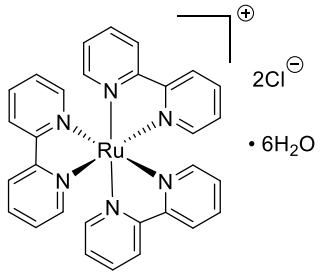
4CzIPN



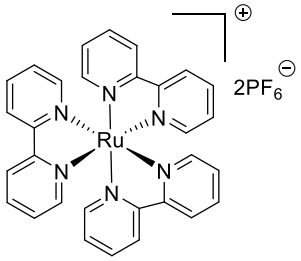
Thioxanthone



$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$

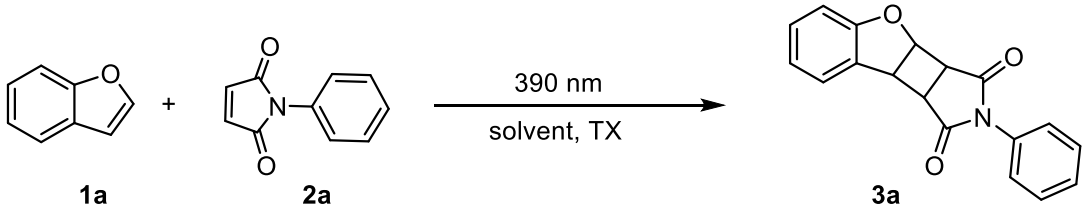


$Ru(bpy)_3Cl_2\cdot 6H_2O$



$Ru(bpy)_3(PF_6)_2$

Table S5 Solvent Screening



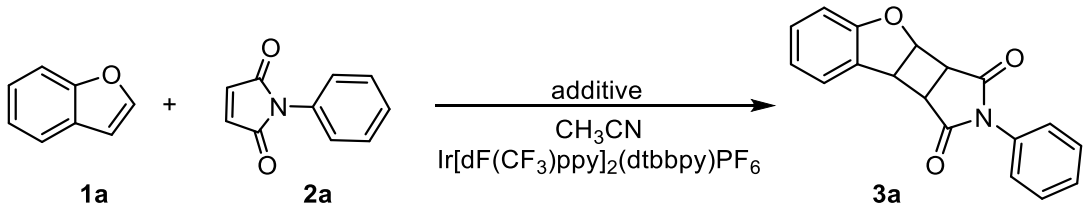
1a **2a** **3a**

Entry[a]	Solvent	Yield(%)[c]	d.r.
1	MeCN	40	3.4:1
2	DCM	44	3:1

3	DCE	44	6:1
4	THF	0	-
5	DMSO	20	2:1
6	DMF	10	2:1
7	1,4-Dioxane	0	-
8	CF_3CH_2OH	48	2.5:1

[a]benzofuran **1a** (0.20 mmol), *N*-phenylmaleimide **2a** (0.20 mmol), and photosensitizer (30 mol%) in solvent (2 mL), irradiated with 390 nm LEDs under argon atmosphere at room temperature for 24 h. [b]Yield was determined by column chromatography.

Table S6 Addtive Screening

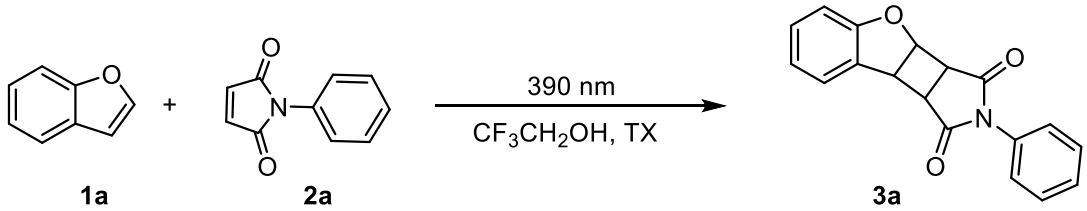


1a **2a** **3a**

Entry[a]	Additive	Yield(%)	d.r.
1	Na_2HPO_4	n.r	-
2	Cs_2CO_3	0	-
3	PivONa	n.r	-
4	2,6-Lutidine	n.r	-
5	$FeCl_3$	n.r	-
6[b]	TFA	19	2:1
7	AcOH	0	-

[a]benzofuran **1a** (0.20 mmol), *N*-phenylmaleimide **2a** (0.20 mmol), additive (0.20 mmol) and photosensitizer (1 mol%) in solvent(2 mL),irradiated with 450 nm LEDs under argon atmosphere at room temperature for 24 h. [b]Yield was determined by ^{1}H-NMR, using internal standard (CH_2Br_2).

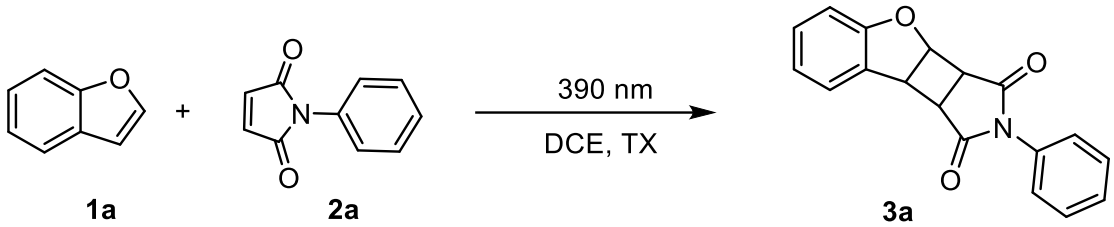
Table S7 Ratio of substrate and Volume of solvent Screening



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

Entry[a]	Ratio of substrate **(1a**:**2a)**	Volume of solvent	Yield(%)[c]	d.r.
1[b]	0.20 mmol: 0.20 mmol	2ml	0	-
2	0.20 mmol: 0.20 mmol	2ml	48	2.5:1
3[d]	0.20 mmol: 0.20 mmol	4ml	60	2:1
4	0.40 mmol: 0.20 mmol	4ml	84	1.1:1

[a]benzofurans **1a**, *N*-phenylmaleimide **2a** and photosensitizer (30 mol%) in CF_3CH_2OH, irradiated with 390 nm LEDs under argon atmosphere at room temperature for 24 h. [b]photosensitizer (5 mol%). [c]Yield was determined by column chromatography. [d]Yield was determined by ^{1}H-NMR, using internal standard (CH_2Br_2).

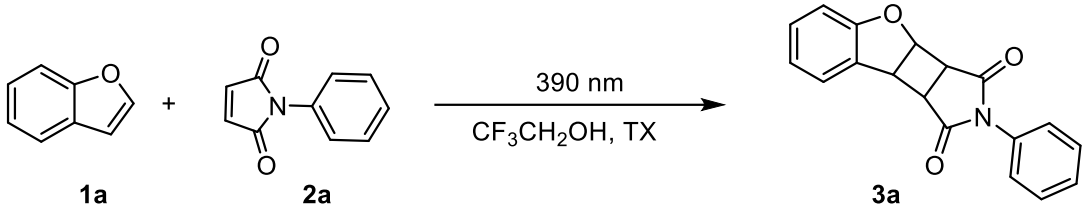


1a **2a** **3a**

Entry[a]	Ratio of substrate (1a : 2a)	Solvent volume (mL)	Yield(%)[b]	d.r.
1	**(0.20 mmol) : (0.20mmol)**	4	49	6.8:1
2	**(0.40 mmol) : (0.20mmol)**	4	59	8.3:1

[a]benzofurans **1a**, *N*-phenylmaleimide **2a** and photosensitizer (30 mol%) in DCE, irradiated with 390 nm LEDs under argon atmosphere at room temperature for 24 h. [b]Yield was determined by column chromatography.

Table S8 Control experiment



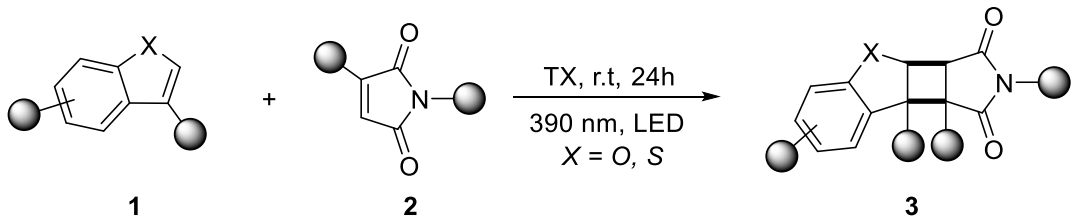
1a **2a** **3a**

Entry	Variation from above	Yield(%)	d.r.
1	no light	n.r	-
2	no photosensitizer	n.r	-
3	Air instead of Ar	n.r	-

Reaction condition: benzofuran **1a** (0.40 mmol), *N*-phenylmaleimide **2a** (0.20 mmol) and photosensitizer (30 mol%) in CF_3CH_2OH (4 ml), irradiated with 390 nm LEDs under argon atmosphere at room temperature for 24 h.

4. Photosensitized Cycloadditions

4.1 General Procedures for [2+2] cycloaddition of Benzofuran or Benzothiophene Derivatives with Maleimides



1 2 3

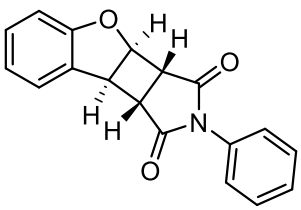
An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the substrate **1** (0.4 mmol) and substrate **2** (0.2 mmol), TX (30 mol %).The Schlenk tube was then connected to a vacuum line where it was evacuated and back-filled with argon for 3 times, then add trifluoroethanol. Finally, the reaction mixture was placed at a distance of 2 ~ 3 cm from 390 nm LED and stirred at room temperature 24 h. Then, the mixture was concentrated in vacuo and purified by silica gel flash chromatography (petroleum ether/ethyl acetate 10/1 ~ 1/1 or petroleum ether /DCM 1/1) to afford the corresponding product.

4.2 Reactor Set-Ups

Figure S1. Reaction set up with a 30 W 390 nm LEDs (distance app. 2.0 cm from the bulb, left: model reaction; right: gram-scale reaction)

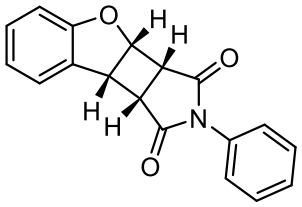
5. Characterization of compounds

(3a*R*,3b*R*,8b*S*,8c*R*)-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzofuro[2',3':3,4]cycobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3a)



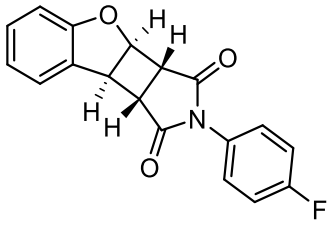
Yield: 24mg (41 %); white solid; R_f= 0.5 (petroleum ether / dichloromethane, 1:1); mp 276 °C.
^{1}H NMR (600 MHz, DMSO-d_6) δ 7.47 – 7.42 (m, 2H), 7.40 – 7.35 (m, 1H), 7.35 – 7.30 (m, 3H), 7.19 –7.17 (m, 1H), 6.94 – 6.86 (m, 2H), 5.40 (dd, *J* = 6.4, 2.2 Hz, 1H), 4.29 – 4.23 (m, 1H), 3.58 (m, 1H), 3.35 (dd, *J* = 6.9, 2.5 Hz, 1H).
^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 176.5, 175.2, 160.3, 132.9, 129.9, 129.3, 128.9, 128.4, 127.7, 126.3, 122.3, 110.9, 82.4, 49.1, 46.4, 46.2.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{13}NO_3Na^+$: 314.0793; Found: 314.0798.

(3a*R*,3b*S*,8b*R*,8c*R*)-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzofuro[2',3':3,4]cycobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3a')



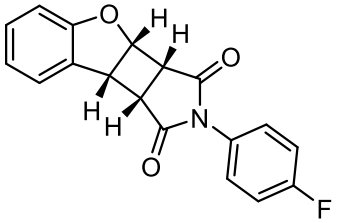
Yield: 25mg (43 %); white solid; R_f= 0.3 (petroleum ether / dichloromethane, 1:1); mp 193 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 3H), 7.24 (m, 2H), 6.96 – 6.89 (m, 2H), 6.53 – 6.46 (m, 2H), 5.56 (m, 1H), 4.68 – 4.63 (m, 1H), 3.87 (m, 1H), 3.82 (m, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 175.4, 172.9, 161.8, 131.6, 130.1, 129.1, 128.8, 126.8, 126.49, 124.5, 122.1, 110.7, 77.4, 46.0, 45.4, 42.3.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{13}NO_3Na^+$: 314.0793; Found: 314.0798.

(3a*R*,3b*R*,8b*S*,8c*R*)-2-(4-fluorophenyl)-3a,3b,8b,8c-tetrahydro-1*H*-benzofuro[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3b)



Yield: 34 mg (55 %); white solid; R_f= 0.5 (petroleum ether / dichloromethane, 1:1); mp 269–271 °C.
^{1}H NMR (600 MHz, DMSO-d_6) δ 7.46 – 7.42 (m, 3H), 7.40 – 7.37 (m, 2H), 7.27 (t, J = 7.8 Hz, 1H), 7.03 – 6.94 (m, 2H), 5.51 (d, *J* = 4.2 Hz, 1H), 4.33 (d, *J* = 6.4 Hz, 1H), 3.66 (d, *J* = 6.2 Hz, 1H)., 3.42 (dd, *J* = 6.8, 2.4 Hz, 1H).
^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 176.5, 175.2, 162.9, 161.2, 160.3, 129.9 (d, *J* = 9.5 Hz), 129.1 (d, *J* = 3.0 Hz), 128.4, 126.2, 122.3, 116.3 (d, *J* = 22.8 Hz), 110.9, 82.4, 49.1, 46.4, 46.2.
^{19}F NMR (565 MHz, DMSO-d_6) δ -112.98 – -113.04 (m).
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{13}NO_3FNa^+$: 332.0706; Found: 332.0706.

(3a*R*,3b*S*,8b*R*,8c*R*)-2-(4-fluorophenyl)-3a,3b,8b,8c-tetrahydro-1*H*-benzofuro[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3b')



Yield: 25 mg (18 %); white solid; R_f= 0.3 (petroleum ether / dichloromethane, 1:1); mp 208–210 °C.

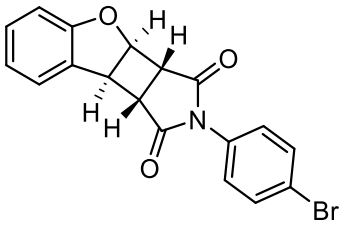
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 – 7.25 (m, 2H), 7.00 – 6.88 (m, 4H), 6.50 – 6.40 (m, 2H), 5.56 (t, *J* = 7.4 Hz, 1H), 4.66 (t, *J* = 6.8 Hz, 1H), 3.88 – 3.86 (m, 1H), 3.83 –3.81 (m, 1H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 175.3, 172.8, 163.2, 161.7, 130.2, 128.4 (d, *J* = 8.9 Hz), 127.4 (d, *J* = 3.2 Hz), 126.8, 124.4, 122.1, 116.1 (d, *J* = 22.8 Hz), 110.7, 46.0, 45.4, 42.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -107.7 – -124.1 (m).

HRMS (ESI): m/z: $[M + H]^+$ Calcd. for $C_{18}H_{14}NO_3F^+$: 310.0879; Found: 310.0880.

(3a*R*,3b*R*,8b*S*,8c*R*)-2-(4-bromophenyl)-3a,3b,8b,8c-tetrahydro-1*H*-benzofuro[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3c)



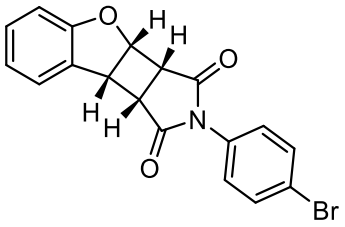
Yield: 28.8 mg (39 %); white solid; R_f= 0.5 (petroleum ether / dichloromethane, 1:1); mp 250°C.

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.76 – 7.74 (m, 2H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.38 – 7.36 (m, 2H), 7.28 – 7.25 (m, 1H), 6.79 – 7.01 (m, 2H), 5.50 (dd, *J* = 6.4, 2.3 Hz, 1H), 4.30 (dd, *J* = 4.8, 1.6 Hz, 1H), 3.67 – 3.65 (m, 1H), 3.40 (dd, *J* = 6.9, 2.5 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 176.2, 175.0, 160.3, 132.4, 132.2, 129.9, 129.8, 128.4, 126.2, 122.3, 122.0, 110.9, 82.4, 49.1, 46.4, 46.2.

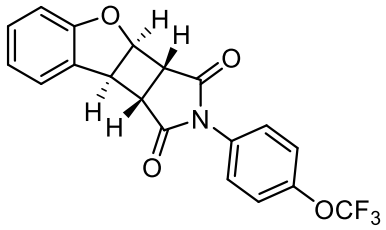
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{12}NO_3BrNa^+$: 391.9898; Found: 391.9899.

(3a*R*,3b*S*,8b*R*,8c*R*)-2-(4-bromophenyl)-3a,3b,8b,8c-tetrahydro-1*H*-benzofuro[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3c')



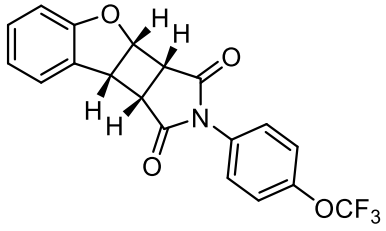
Yield: 23.9 mg (32 %); white solid; R_f= 0.4 (petroleum ether / dichloromethane, 1:1); mp 178°C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.22 – 7.24 (m, 2H), 6.96 – 6.87 (m, 2H), 6.42 – 6.34 (m, 2H), 5.59 – 5.56 (m, 1H), 4.71 – 4.64 (m, 1H), 3.90 – 3.87 (m, 1H), 3.85 – 3.82 (m, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 175.0, 172.4, 161.7, 132.3, 130.5, 130.2, 128.0, 126.8, 124.3, 122.8, 122.1, 110.7, 77.4, 46.0, 45.5, 42.3.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{12}NO_3BrNa^+$: 391.9898; Found: 391.9906.

(3a*R*,3b*R*,8b*S*,8c*R*)-2-(4-(trifluoromethoxy)phenyl)-3a,3b,8b,8c-tetrahydro-1*H*-benzofuro[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3d)



Yield: 26mg (35 %); white solid; R_f= 0.4 (petroleum ether / dichloromethane, 1:1); mp 223 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.37 – 7.36 (m, 2H), 7.29 –7.27 (m, 1H), 7.03 –7.01 (m, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 5.36 (dd, *J* = 6.4, 2.1 Hz, 1H), 4.38 (d, *J* = 6.3 Hz, 1H), 3.75 – 3.73 (m, 1H), 3.50 (dd, *J* = 6.8, 2.5 Hz, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 175.7, 174.2, 160.0, 149.0, 130.1, 130.0, 127.8, 126.9, 125.6, 122.3, 121.7, 120.4 (d, *J* = 258.7 Hz), 111.0, 82.5, 48.8, 47.2, 46.0.
^{19}F NMR (565 MHz, DMSO-d_6) δ -56.85.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{19}H_{12}NO_4F_3Na^+$: 398.0616; Found: 398.0620.

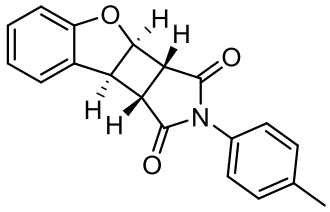
(3a*R*,3b*S*,8b*R*,8c*R*)-2-(4-(trifluoromethoxy)phenyl)-3a,3b,8b,8c-tetrahydro-1*H*-benzofuro[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3d')



Yield: 10 mg (13 %); white solid; R_f= 0.4 (petroleum ether / dichloromethane, 1:1); mp 182 °C.

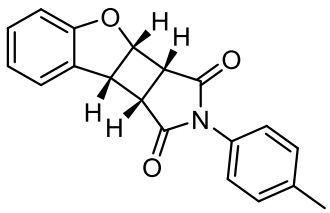
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 6.98 – 6.96 (m, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.58 – 6.55 (m, 2H), 5.60 (t, *J* = 7.4 Hz, 1H)., 4.70(t, *J* = 8.9 Hz, 1H)., 3.93 – 3.90 (m, 1H), 3.87 – 3.85 (m, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 175.0, 172.4, 161.8, 149.0, 130.2, 130.0, 128.0, 126.8, 124.4, 122.1, 121.4, 120.3 (d, *J* = 258.0 Hz), 110.7, 77.4, 46.0, 45.5, 42.3.
^{19}F NMR (565 MHz, $CDCl_3$) δ -57.88.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{19}H_{12}NO_4F_3Na^+$: 398.0616; Found: 398.0624.

(3a*R*,3b*R*,8b*S*,8c*R*)-2-(p-tolyl)-3a,3b,8b,8c-tetrahydro-1*H*-benzofuro[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3e)



Yield: 15.3mg (25 %); white solid; R_f= 0.5 (petroleum ether / dichloromethane, 1:1); mp 250 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, J = 7.5 Hz, 1H), 7.33 – 7.30 (m, 2H), 7.27 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.23 – 7.20 (m, 2H),7.02 – 6.99 (M, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 5.36 (dd, *J* = 6.4, 2.1 Hz, 1H), (d, *J* = 6.4 Hz, 1H), 3.72 – 3.70 (m, 1H), 3.50 – 3.46 (m, 1H), 2.41 (s, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 176.1, 174.6, 160.1, 139.1, 130.0, 130.0, 129.1, 127.1, 126.2, 125.6, 122.2, 111.0, 82.6, 48.8, 47.2, 46.0, 21.3.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{19}H_{15}NO_3Na^+$: 328.0950; Found: 328.0951.

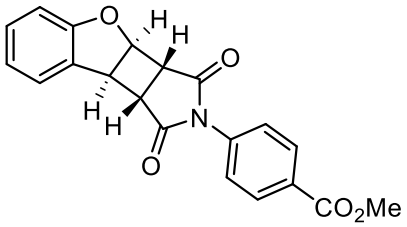
(3a*R*,3b*S*,8b*R*,8c*R*)-2-(p-tolyl)-3a,3b,8b,8c-tetrahydro-1*H*-benzofuro[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3e')



Yield: 20.1mg (33 %); pale yellow solid; R_f= 0.3 (petroleum ether / dichloromethane, 1:1); mp 184 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 2H), 7.08 (d, *J*= 8.1 Hz, 2H), 6.95 – 6.86 (m, 2H), 6.40 – 6.35 (m, 2H), 5.54 (t, *J* = 7.5 Hz, 1H), 4.64 (t, *J* = 6.9 Hz, 1H)., 3.86– 3.83 (m, 1H), 3.80– 3.78 (m, 1H), 2.28 (s, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 175.5, 173.0, 161.8, 138.9, 130.1, 129.8, 128.9, 126.8, 126.2, 124.5, 122.0, 110.7, 46.0, 45.4, 42.3, 21.2.

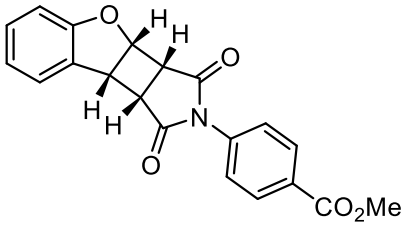
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{19}H_{15}NO_3Na^+$: 328.0950; Found: 328.0958.

methyl 4-((3a*R*,3b*R*,8b*S*,8c*R*)-1,3-dioxo-1,3,3a,3b,8b,8c-hexahydro-2*H*-benzofuro[2',3':3,4]cyclobuta[1,2-c]pyrrol-2-yl)benzoate (3f)



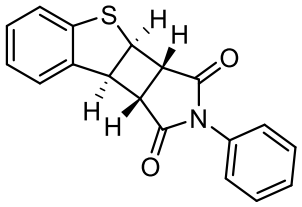
Yield: 8mg (10 %); white solid; R_f= 0.5 (petroleum ether / ethyl acetate, 5:1); mp 248 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 5.37 (dd, *J* = 6.3, 2.1 Hz, 1H), 4.38 (d, *J* = 5.5 Hz, 1H), 3.95 (s, 3H), 3.74 (d, *J* = 6.8 Hz, 1H)., 3.51 (dd, *J* = 6.8, 2.5 Hz, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ175.5, 174.0, 166.1, 160.0, 135.7, 130.6, 130.3, 130.0, 126.9, 126.1, 125.6, 122.3, 111.0, 82.5, 52.4, 48.8, 47.3, 46.0.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{20}H_{15}NO_5Na^+$: 372.0850; Found: 372.0848.

methyl 4-((3a*R*,3b*S*,8b*R*,8c*R*)-1,3-dioxo-1,3,3a,3b,8b,8c-hexahydro-2*H*-benzofuro[2',3':3,4]cyclobuta[1,2-c]pyrrol-2-yl)benzoate (3f')



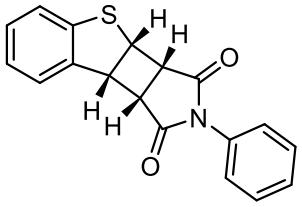
Yield: 17mg (23 %); white solid; R_f= 0.5 (petroleum ether / ethyl acetate, 5:1); mp 182 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.19 – 7.14 (m, 2H), 6.89 – 6.81 (m, 2H), 6.55 (d, *J* = 8.4 Hz, 2H), 5.52 (t, *J* = 7.4 Hz, 1H), 4.62 (t, *J* = 7.8 Hz, 1H), 3.85 – 3.81 (m, 4H), 3.80 – 3.76 (m, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 174.9, 172.3, 166.1, 161.7, 135.6, 130.4, 130.2, 126.8, 126.3, 124.3, 122.1, 110.8, 52.3, 46.1, 45.5, 42.4.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{20}H_{15}NO_5Na^+$: 372.0855; Found: 372.0848.

(3a*S*,3b*R*,8b*S*,8c*R*)-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3g)



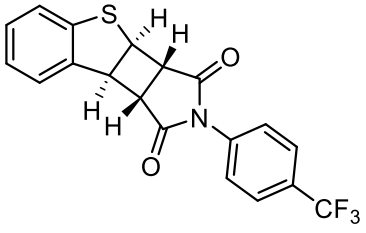
Yield: 22mg (35 %); white solid; R_f= 0.5 (petroleum ether / ethyl acetate,5:1); mp 188 °C
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (t, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.38 – 7.32 (m, 3H), 7.27 – 7.23 (m, 2H), 7.16 – 7.14 (m, 1H), 4.62 (dd, *J* = 8.2, 3.1 Hz, 1H), 4.54 (dd, *J* = 8.1, 3.6 Hz, 1H), 3.69 (dd, *J* = 6.3, 3.0 Hz, 1H), 3.53 (dd, *J* = 6.9, 3.2 Hz, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ176.0, 175.6, 141.5, 138.6, 131.8, 129.3, 129.2, 128.9, 126.4, 125.5, 125.2, 122.1, 52.9, 50.0, 48.2, 47.8.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{13}NO_2SNa^+$: 330.0565; Found: 330.0567.

(3a*S*,3b*S*,8b*R*,8c*R*)-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3g')



Yield: 31mg (51 %); pale yellow solid; R_f= 0.5 (petroleum ether / ethyl acetate,2:1); mp 178 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 3H), 7.15 – 7.08 (m, 3H), 6.99 (t, *J* = 7.0 Hz, 1H), 6.55 –6.53 (m, 2H), 4.88 (t, *J* = 9.1 Hz, 2H), 4.81 (t, *J* = 9.0 Hz, 2H), 3.88 (dd, *J* = 9.1, 6.8 Hz, 1H), 3.76 – 3.73 (m, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ175.1, 174.5, 143.3, 135.9, 131.7, 129.2, 129.1, 128.8, 126.7, 126.5, 125.0, 122.0, 51.0, 45.8, 45.3, 44.7.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{13}NO_2SNa^+$: 330.0565; Found: 330.0571.

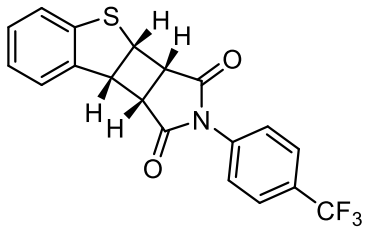
(3a*S*,3b*R*,8b*S*,8c*R*)-2-(4-(trifluoromethyl)phenyl)-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3h)



Yield: 30mg (40 %); white solid; R_f= 0.5 (petroleum ether / ethyl acetate, 5:1); mp 202 °C.

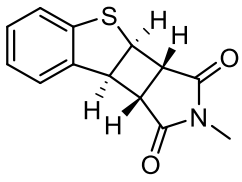
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.5 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.5, 1H), 7.21 – 7.16 (m, 2H), 7.10 – 7.07 (m, 1H), 4.57–4.55 (m, 1H), 4.49–4.47 (m, 1H), 3.65–3.63 (m, 1H), 3.49–3.47 (m, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 175.6, 175.1, 141.4, 138.4, 134.8, 130.8 (d, *J* = 32.9 Hz), 129.3, 126.6, 126.4 (q, *J* = 3.7 Hz), 125.6, 125.2, 123.6 (d, *J* = 272.5 Hz), 52.9, 50.0, 48.1, 47.8.
^{19}F NMR (565 MHz, $CDCl_3$) δ -62.76. 50.0.,48.0,47.8.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{19}H_{12}NO_2F_3SNa^+$: 398.0439; Found: 398.0429.

(3a*S*,3b*S*,8b*R*,8c*R*)-2-(4-(trifluoromethyl)phenyl)-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3h')



Yield: 12mg (16 %); yellow solid; R_f= 0.5 (petroleum ether / ethyl acetate, 2:1); mp 176 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.16 – 7.08 (m, 3H), 7.02 – 6.99 (m, 1H), 6.72 (d, *J* = 7.9 Hz, 2H), 4.94 (t, *J* = 9.1 Hz, 1H), 4.86 (t, *J* = 8.7 Hz, 1H), 3.96– 3.93 (m, 1H), 3.82– 3.79 (m, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 174.6, 173.9, 143.2, 135.7, 134.7, 130.7 (d, *J* = 32.7 Hz), 129.3, 126.8, 126.8, 126.2 (q, *J* = 3.8 Hz), 125.1, 123.6 (d, *J* = 272.4 Hz), 122.02, 51.1, 45.9, 45.4, 44.7.
^{19}F NMR (565 MHz, $CDCl_3$) δ -62.84.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{19}H_{12}NO_2F_3SNa^+$: 398.0439; Found: 398.0447.

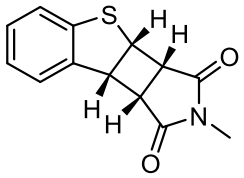
(3a*S*,3b*R*,8b*S*,8c*R*)-2-methyl-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno-[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3i)



Yield: 16mg (33 %); white solid; R_f= 0.5 (petroleum ether / ethyl acetate, 5:1); mp 194 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.14 – 7.11 (m, 1H), 4.47 (dd, *J* = 8.2, 3.1 Hz, 1H), 4.38 – 4.36 (m, 1H), 3.55 –3.53 (m, 1H), 3.38 (dd, *J* = 6.8, 3.2 Hz, 1H)., 3.10 (s, 3H).

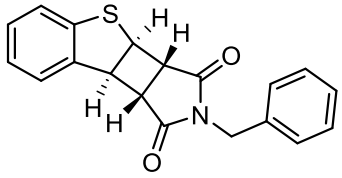
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 177.1, 176.6, 141.5, 138.7, 129.1, 125.4, 125.1, 122.1, 52.54, 50.1, 48.2, 47.5, 25.4.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{13}H_{11}NO_2SNa^+$: 268.0408; Found: 268.0417.

(3a*S*,3b*S*,8b*R*,8c*R*)-2-methyl-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3i')



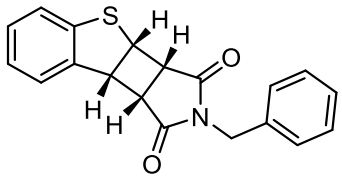
Yield: 10mg (20 %); pale yellow solid; R_f= 0.5 (petroleum ether / ethyl acetate, 2:1); mp 144 °C.
^1H NMR (600 MHz, $CDCl_3$) δ 7.14 – 7.11 (m, 3H), 7.04 – 7.00 (m, 1H), 4.88 (t, *J* = 9.2 Hz, 1H), 4.82 (t, *J* = 9.0 Hz, 1H), 3.86 – 3.80 (m, 1H), 3.72 – 3.67 (m, 1H), 2.67 (s, 3H).
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 175.9, 175.5, 142.9, 135.8, 129.0, 126.3, 124.8, 121.8, 50.6, 45.6, 45.4, 44.4, 24.5.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{13}H_{11}NO_2SNa^+$: 268.0408; Found: 268.0414.

(3a*S*,3b*R*,8b*S*,8c*R*)-2-benzyl-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3j)



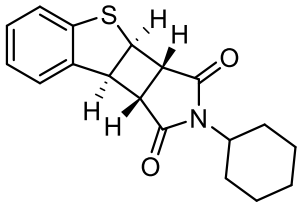
Yield: 31mg (48 %); white solid; R_f= 0.5 (petroleum ether / ethyl acetate, 10:1); mp 196 °C.
^1H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.29 – 7.19 (m, 4H), 7.17 – 7.10 (m, 2H), 7.05 – 7.03 (m, 1H), 4.67 (s, 2H), 4.34 (dd, *J* = 8.1, 3.1 Hz, 1H), 4.24 – 4.22 (m, 1H), 3.46 – 3.44 (m, 1H), 3.29 – 3.27 (m, 1H).
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 176.7, 176.2, 141.5, 138.7, 135.6, 129.1, 128.8, 128.7, 128.2, 125.4, 125.1, 122.1, 52.6, 50.0, 48.2, 47.5, 42.8.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{19}H_{15}N_2SNa^+$: 344.0721; Found: 344.0728.

(3a*S*,3b*S*,8b*R*,8c*R*)-2-benzyl-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3j')



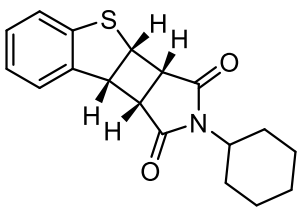
Yield: 5mg (8 %); pale yellow solid; R_f= 0.5 (petroleum ether / ethyl acetate, 2:1); mp 180 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 –7.07 (m, 3H), 7.02 (d, *J* = 7.5 Hz, 1H), 7.01 – 6.97 (m, 2H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.87 (t, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 4.79 (t, *J* = 9.2 Hz, 1H), 4.72 (t, *J* = 9.0 Hz, 1H), 4.36 – 4.28 (m, 2H), 3.74– 3.72 (m, 1H), 3.62 (t, *J* = 7.9 Hz, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 175.7, 175.3, 143.0, 135.34, 135.2, 129.0, 128.7, 128.5, 127.5, 126.1, 124.6, 121.8, 50.5, 45.4, 45.0, 44.4, 42.5.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{19}H_{15}N_2SNa^+$: 344.0721; Found: 344.0729.

(3a*S*,3b*R*,8b*S*,8c*R*)-2-cyclohexyl-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3k)



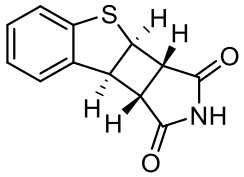
Yield: 30mg (52 %); white solid; R_f= 0.4 (petroleum ether / ethyl acetate, 5:1); mp 130 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.6 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.13 – 7.10 (m, 1H), 4.42 (dd, *J* = 8.1, 3.1 Hz, 1H), 4.32 (dd, *J* = 8.0, 3.5 Hz, 1H), 4.06 – 3.99 (m, 1H), 3.44 – 3.42 (m, 1H), 3.27 (dd, *J* = 6.8, 3.1 Hz, 1H), 2.26 – 2.16 (m, 2H), 1.87 (d, *J* = 13.3 Hz, 1H), 1.72 – 1.67 (m, 1H), 1.67 – 1.62 (m, 2H), 1.39 –1.31 (m, 2H), 1.30 – 1.21 (m, 2H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 177.3, 176.8, 141.6, 138.9, 129.0, 125.3, 125.1, 122.0, 52.8, 52.1, 49.6, 47.8, 28.7, 28.6, 25.8, 25.0.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{19}NO_2SNa^+$: 336.1034; Found: 336.1038.

(3a*S*,3b*S*,8b*R*,8c*R*)-2-cyclohexyl-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3k')



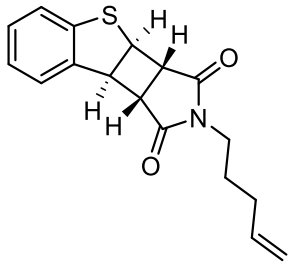
Yield: 5mg (9 %); white solid; R_f= 0.5 (petroleum ether / ethyl acetate, 2:1); mp 176 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 – 7.07 (m, 3H), 7.03 –7.02 (m, 1H), 4.87 (t, *J* = 9.1 Hz, 1H), 4.80 (t, *J* = 9.0 Hz, 1H), 3.75 – 3.68 (m, 2H), 3.61 – 3.59 (m, 1H), 1.95 –1.88 (m, 1H), 1.71 – 1.62 (m, 3H), 1.55 – 1.50 (m, 1H), 1.18 – 1.02 (m, 4H), 0.93 (d, *J* = 11.5 Hz, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 176.1, 175.5, 143.5, 135.8, 128.9, 126.6, 124.7, 121.7, 51.8, 50.8, 45.0, 44.7, 44.4, 28.2, 27.6, 25.7, 25.7, 24.9.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{19}NO_2SNa^+$: 336.1034; Found: 336.1042.

(3a*S*,3b*R*,8b*S*,8c*R*)-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3l)



Yield: 26mg (56 %); white solid; R_f= 0.5 (petroleum ether / ethyl acetate, 2:1); mp 190 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.29 – 7.20 (m, 4H), 7.13 (t, *J* = 7.3 Hz, 1H), 4.56 (dd, *J* = 8.1, 3.2 Hz, 1H), 4.49 (dd, *J* = 8.1, 3.6 Hz, 1H), 3.56 (dd, *J* = 7.0, 3.7 Hz, 1H), 3.41 (dd, *J* = 6.7, 3.2 Hz, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 176.0, 176.3, 141.3, 138.6, 129.2, 125.5, 125.1, 122.1, 52.6, 51.5, 49.6, 47.5.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{12}H_9NO_2SNa^+$: 254.0252; Found: 254.0249.

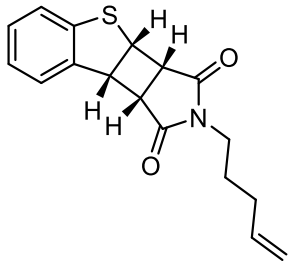
(3a*S*,3b*R*,8b*S*,8c*R*)-2-(pent-4-en-1-yl)-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3m)



Yield: 20mg (34 %); colorless oil; R_f= 0.5 (petroleum ether / ethyl acetate, 10:1).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.13 –7.11 (m, 1H), 5.86 – 5.78 (m, 1H), 5.09 – 5.05 (m, 1H), 5.02 –5.00 (m, 1H), 4.45 (dd, *J* = 8.2, 3.2 Hz, 1H), 4.35 (dd, *J* = 8.1, 3.6 Hz, 1H), 3.60–3.59 (m, 2H), 3.52 –3.50 (m, 1H), 3.34 (dd, *J* = 6.7, 3.2 Hz, 1H), 2.15 – 2.07 (m, 2H), 1.77 – 1.72 (m, 2H).

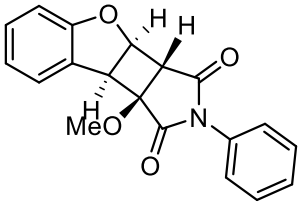
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 177.0, 176.6, 141.5, 138.8, 137.1, 129.1, 125.4, 125.1, 122.0, 115.6, 52.6, 49.9, 48.1, 47.6, 38.8, 31.0, 26.7.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{17}H_{17}NO_2SNa^+$: 322.0878; Found: 322.0880.

(3a*S*,3b*S*,8b*R*,8c*R*)-2-(pent-4-en-1-yl)-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3m')



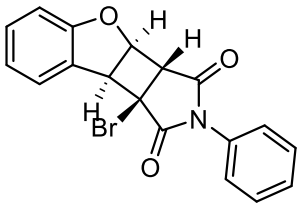
Yield: 10mg (17 %); colorless oil; R_f= 0.5 (petroleum ether / ethyl acetate, 2:1).
^1H NMR (600 MHz, $CDCl_3$) δ 7.16 – 7.06 (m, 3H), 7.03 – 7.01 (m, 1H), 5.67 – 5.60 (m, 1H), 4.96 – 4.87 (m, 3H), 4.82 (t, *J* = 9.0 Hz, 1H), 3.82 – 3.79 (m, 1H), 3.68 – 3.65 (m, 1H), 3.32 – 3.18 (m, 2H), 1.81 – 1.78 (m, 2H), 1.16 –1.09 (m, 1H), 0.98 – 0.92 (m, 1H).
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ175.9, 175.3, 143.4, 137.3, 135.7, 129.0, 126.5, 124.8, 121.8, 115.0, 50.7, 45.5, 45.1, 44.3, 38.4, 30.8, 26.1.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{17}H_{17}NO_2SNa^+$: 322.0878; Found: 322.0886.

(3a*S*,3b*R*,8b*S*,8c*R*)-3a-methoxy-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzofuro[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3n)



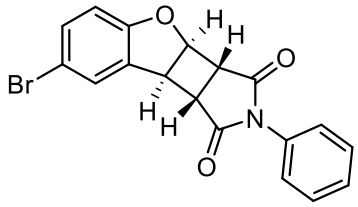
Yield: 44mg (68 %); white solid; R_f= 0.5 (petroleum ether / ethyl acetate, 5:1); mp 196 °C.
^1H NMR (600 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 2H), 7.50 – 7.46 (m, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.37 –7.35 (m, 2H), 7.32 – 7.29 (m, 1H), 7.05 –7.03 (m, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 5.11 (dd, *J* = 6.1, 2.1 Hz, 1H), 4.59 (d, *J* = 6.0 Hz, 1H), 3.60 (dd, *J* = 1.9, 1.4 Hz, 1H), 3.38 (s, 3H).
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 175.3, 172.4, 160.4, 131.3, 130.0, 129.4, 129.1, 128.2, 126.30, 122.5, 121.8, 110.9, 77.3, 53.3, 52.0, 51.0.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{19}H_{15}NO_4Na^+$: 344.0899 ; Found: 344.0904.

(3a*S*,3b*R*,8b*S*,8c*S*)-3a-bromo-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzofuro[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3o)



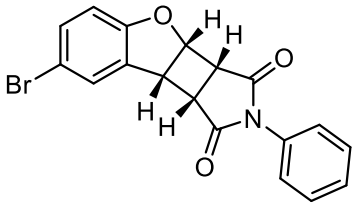
Yield: 43mg (58 %); white solid; R_f= 0.5 (petroleum ether / ethyl acetate, 10:1); mp 160 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.48 – 7.44 (m, 1H), 7.41 – 7.32 (m, 4H), 7.09 – 7.07 (m, 1H), 7.00 (d, J = 8.1 Hz, 3H), 5.34 (dd, *J* = 5.9, 2.3 Hz, 1H), 4.55 (d, *J* = 5.2 Hz, 1H), 3.80 (dd, *J* = 2.3, 1.5 Hz, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 173.6, 171.3, 160.3, 131.3, 130.7, 129.4, 129.3, 128.2, 126.3, 124.2, 122.0, 111.2, 80.4, 58.5, 53.0, 53.0.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{12}NO_3BrNa^+$: 391.9898; Found: 391.9903.

(3a*R*,3b*R*,8b*S*,8c*R*)-7-bromo-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzofuro[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3aa)



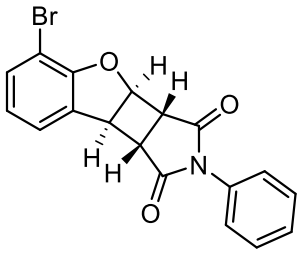
Yield: 22mg (31 %); white solid; R_f= 0.4 (petroleum ether / dichloromethane, 1:1); mp 212 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 3H), 7.45 – 7.42 (m, 1H), 7.38 – 7.33 (m, 3H), 6.83 (d, *J* = 8.5 Hz, 1H), 5.37 (dd, *J* = 6.3, 2.1 Hz, 1H), 4.34 (d, *J* = 6.4 Hz, 1H), 3.72 –3.70 (m, 1H), 3.48 (dd, *J* = 6.8, 2.5 Hz, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ175.5, 174.1, 159.3, 132.8, 131.6, 129.4, 129.3, 129.0, 128.5, 126.3, 113.9, 112.5, 83.2, 48.7, 47.0, 45.9.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{12}NO_3BrNa^+$: 391.9898; Found: 391.9895.

(3a*R*,3b*S*,8b*R*,8c*R*)-7-bromo-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzofuro[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3aa')



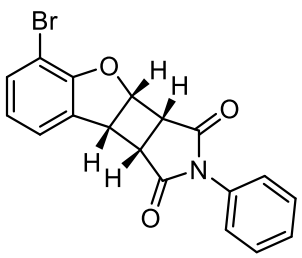
Yield: 32mg (43 %); white solid; R_f = 0.5 (petroleum ether / ethyl acetate,2:1); mp 202 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 5H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.60 – 6.58 (m, 2H), 5.57 (t, *J* = 7.4 Hz, 1H), 4.62 (t, *J* = 7.9 Hz, 1H), 3.89 –3.86 (m, 1H), 3.82 – 3.80 (m, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ174.9, 172.5, 161.0, 133.0, 131.5, 129.6, 129.2, 129.0, 126.9, 126.3, 113.8, 112.2, 78.2, 46.0, 45.2, 42.3.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{12}NO_3BrNa^+$: 391.9898; Found: 391.9901.

(3a*R*,3b*R*,8b*S*,8c*R*)-5-bromo-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzofuro[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3ab)



Yield: 7mg (10 %); white solid; R_f = 0.5 (petroleum ether / dichloromethane, 1:1); mp 238 °C.
^{1}H NMR (600 MHz, DMSO-d_6) δ 7.55 – 7.52 (m, 1H), 7.50 – 7.42 (m, 3H), 7.40 – 7.38 (m, 2H), 6.95 (t, *J* = 7.7 Hz, 4H), 5.60 (dd, *J* = 6.4, 2.2 Hz, 1H), 4.45 (d, *J* = 6.3 Hz, 1H), 3.76 – 3.74 (m, 1H), 3.48 (dd, *J* = 7.0, 2.6 Hz, 1H).
^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ176.2, 174.9, 157.6, 132.9, 132.7, 130.2, 129.3, 129.0, 127.6, 125.6, 124.0, 102.9, 82.8, 49.0, 47.2, 46.3.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{12}NO_3BrNa^+$: 391.9898; Found: 391.9902.

(3a*R*,3b*S*,8b*R*,8c*R*)-5-bromo-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzofuro[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3ab')



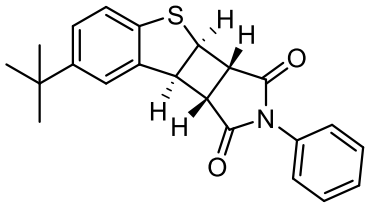
Yield: 30mg (41 %); white solid; R_f = 0.3 (petroleum ether / dichloromethane, 1:1); mp 256 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.44 (d, J = 7.0 Hz, 1H), 7.37 – 7.33 (m, 3H), 7.14 –7.13 (m, 1H), 6.85 (t, J = 7.7 Hz, 1H), 6.55 – 6.53 (m, 2H), 5.69 –5.66 (m, 1H), 4.79 – 4.73 (m, 1H), 3.97 –3.94 (m, 1H), 3.88 – 3.85 (m, 1H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 175.74, 173.29, 159.13, 132.67, 132.64, 129.28, 128.91, 127.92, 127.05, 126.33, 123.51, 102.46, 78.53, 46.52, 45.57, 43.28.

HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{12}NO_3BrNa^+$: 391.9898; Found: 391.9902.

(3a*S*,3b*R*,8b*S*,8c*R*)-7-(tert-butyl)-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3ac)



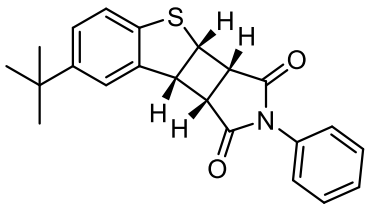
Yield: 13mg (18 %); white solid; R_f= 0.5 (petroleum ether / ethyl acetate, 5:1); mp 149 °C

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.46 – 7.43 (m, 1H), 7.38 – 7.35 (m, 3H), 7.30 (dd, J = 8.3, 1.4 Hz, 1H), 7.16 (d, J = 8.3 Hz, 1H), 4.60 (dd, J = 8.3, 3.0 Hz, 1H), 4.55 – 4.53 (m, 1H), 3.70 –3.68 (m, 1H), 3.56 –3.54 (m, 1H), 1.32 (s, 12H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ176.3, 175.7, 149.2, 138.6, 138.0, 131.8, 129.3, 128.9, 126.6, 126.4, 122.2, 121.6, 53.0, 50.1, 48.2, 48.2, 34.6, 31.5.

HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{22}H_{21}NO_2SNa^+$: 386.1191; Found: 386.1196.

(3a*S*,3b*S*,8b*R*,8c*R*)-7-(tert-butyl)-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3ac')

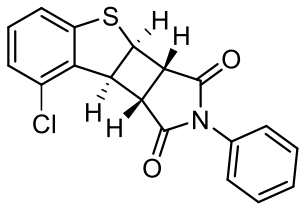


Yield: 27mg (37 %); white solid; R_f= 0.5 (petroleum ether / ethyl acetate, 5:1); mp 116 °C.

^{1}H NMR (600 MHz,$CDCl_3$) δ 7.28 – 7.25 (m, 5H), 7.23 (dd, J = 2.0, 0.9 Hz, 1H), 7.11 (d, J = 8.2 Hz, 1H), 6.49 – 6.47 (m, 2H), 4.95 (t, J = 8.5 Hz, 1H), 4.89 (t, J = 8.9 Hz, 1H), 4.01 – 3.98 (m, 1H), 3.81 – 3.78 (m, 1H), 1.25 (s, 12H).

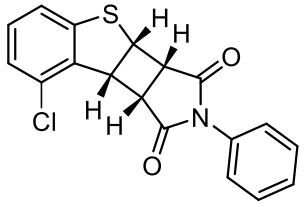
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ175.2, 174.3, 148.4, 139.8, 136.0, 131.7, 129.0, 128.7, 126.6, 126.4, 124.1, 121.7, 51.4, 45.9, 45.4, 45.0, 34.5, 31.3, 28.4.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{22}H_{21}NO_2SNa^+$: 386.1191; Found: 386.1198.

(3a*S*,3b*R*,8b*S*,8c*R*)-8-chloro-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3ad)



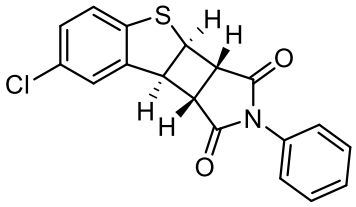
Yield: 14mg (21 %); white solid; R_f= 0.5 (petroleum ether / dichloromethane, 1:1); mp 192 °C.
^1H NMR (600 MHz, $CDCl_3$) δ 7.55 –7.53 (m, 2H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.40 – 7.38 (m, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 2H), 4.74 (dd, *J* = 8.2, 3.1 Hz, 1H), 4.57 (dd, *J* = 8.2, 3.6 Hz, 1H), 3.76 – 3.74 (m, 1H), 3.63 (dd, *J* = 6.7, 3.1 Hz, 1H).
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ175.4, 175.2, 143.5, 136.4, 131.9, 131.8, 130.8, 129.3, 128.9, 126.3, 125.6, 120.4, 52.9, 50.1, 47.1, 46.9.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{12}NO_2SClNa^+$: 364.0175; Found: 364.0179.

(3a*S*,3b*S*,8b*R*,8c*R*)-8-chloro-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3ad')



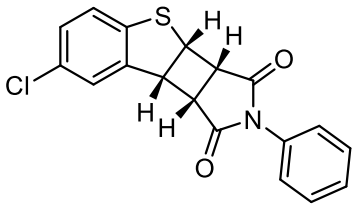
Yield: 42mg (62 %); white solid; R_f= 0.5 (petroleum ether / ethyl acetate, 2:1); mp 188 °C.
^1H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 3H), 7.14 – 7.11 (m, 1H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.86 (d, *J* = 7.3 Hz, 2H), 5.10 (t, *J* = 9.3 Hz, 1H), 4.92 (t, *J* = 8.8 Hz, 1H), 4.03 – 3.98 (m, 1H), 3.93 – 3.91 (m, 1H).
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ174.5, 174.4, 145.2, 134.7, 132.6, 131.8, 130.8, 129.1, 128.7, 126.4, 125.5, 119.7, 50.6, 45.8, 45.1, 44.5.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{12}NO_2SClNa^+$: 364.0175; Found: 364.0183.

(3a*S*,3b*R*,8b*S*,8c*R*)-7-chloro-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3ae)



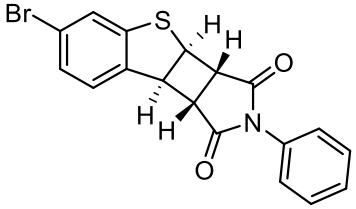
Yield: 16mg (23 %); white solid; R_f= 0.5 (petroleum ether / ethyl acetate, 2:1); mp 221 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.46 – 7.43 (m, 1H), 7.37 – 7.34 (m, 2H), 7.32 (d, *J* = 2.1 Hz, 1H), 7.23 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 4.59 –4.56 (m, 2H), 3.70 (dd, *J* = 6.9, 2.5 Hz, 1H), 3.53 (dd, *J* = 6.9, 2.3 Hz, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ175.6, 175.3, 140.5, 140.1, 131.7, 131.2, 129.4, 129.3, 129.0, 126.3, 125.4, 123.0, 52.6, 50.0, 48.4, 48.0.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{12}NO_2SClNa^+$: 364.0175; Found: 364.0183.

(3a*S*,3b*S*,8b*R*,8c*R*)-7-chloro-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3ae')



Yield: 25mg (37 %); white solid; R_f= 0.5 (petroleum ether / ethyl acetate, 5:1); mp 194 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 –7.31 (m, 3H), 7.19 – 7.15 (m, 2H), 7.10 – 7.08 (m, 1H), 6.76 – 6.73 (m, 2H), 4.97 – 4.92 (m, 2H), 3.99 – 3.96 (m, 1H), 3.88 – 3.85 (m, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ174.6, 174.2, 142.0, 137.8, 131.6, 130.8, 129.3, 129.2, 128.9, 126.8, 126.3, 122.6, 50.7, 45.7, 45.5, 45.2.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{12}NO_2SClNa^+$: 364.0175; Found: 364.0182.

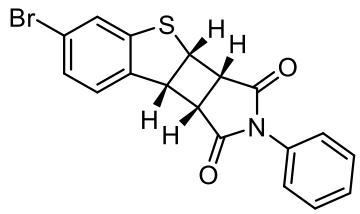
(3a*R*,3b*R*,8b*S*,8c*R*)-6-bromo-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzofuro[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3af)



Yield: 17mg (19 %); white solid; R_f= 0.5 (petroleum ether / ethyl acetate, 5:1); mp 224 °C.

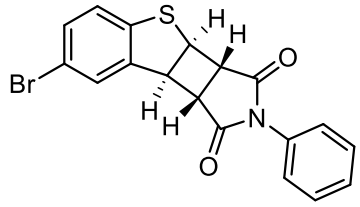
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 2H), 7.48 – 7.45 (m, 1H), 7.40 – 7.35 (m, 3H), 7.30 – 7.27 (m, 2H), 7.21 (d, *J* = 8.1 Hz, 1H), 4.59 – 4.56 (m, 2H), 3.73 – 3.71 (m, 1H), 3.54 – 3.52 (m, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ175.6, 175.2, 144.0, 137.7, 131.7, 129.3, 128.9, 128.5, 126.3, 126.2, 124.9, 123.0, 52.4, 50.0, 48.4, 48.1.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{12}NO_2SBrNa^+$: 407.9670; Found: 407.9666.

(3a*R*,3b*S*,8b*R*,8c*R*)-6-bromo-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzofuro[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3af')



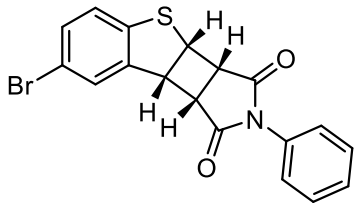
Yield: 45mg (56 %); white solid; R_f= 0.4 (petroleum ether / ethyl acetate, 2:1); mp 220 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 4H), 7.18 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.71 – 6.68 (m, 2H), 4.94 – 4.88 (m, 2H), 3.98 – 3.95 (m, 1H), 3.86 – 3.83 (m, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ174.8, 174.1, 145.8, 135.0, 131.5, 129.3, 128.9, 128.2, 127.7, 126.4, 124.6, 123.1, 50.4, 45.7, 45.4, 45.2.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{12}NO_2SBrNa^+$: 407.9670; Found: 407.9679.

(3a*S*,3b*R*,8b*S*,8c*R*)-7-bromo-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3ag)



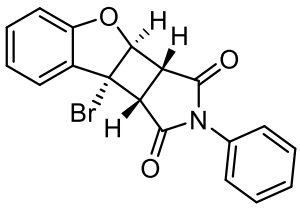
Yield: 14mg (18 %); white solid; R_f= 0.5 (petroleum ether / dichloromethane, 1:1); mp 252 °C.
^{1}H NMR (600 MHz, DMSO-d_6) δ 7.56 – 7.52 (m, 2H), 7.47 – 7.44 (m, 3H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 1H), 4.80 (dd, *J* = 8.1, 3.9 Hz, 1H), 4.64 (d, *J* = 8.0 Hz, 1H), 3.62 –3.60 (m, 1H), 3.55 – 3.53 (m, 1H).
^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ176.3, 175.9, 142.7, 141.4, 132.9, 132.0, 129.3, 129.0, 128.5, 127.7, 124.3, 118.0, 52.0, 50.5, 48.5, 47.7.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{12}NO_2SBrNa^+$: 407.9670; Found: 407.9666.

(3a*S*,3b*S*,8b*R*,8c*R*)-7-bromo-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3ag')



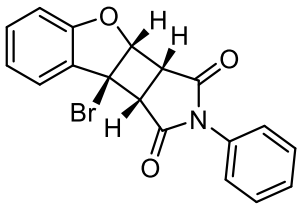
Yield: 36mg (47 %); white solid; R_f = 0.5 (petroleum ether / ethyl acetate, 2:1); mp 206 °C
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 5H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.75 – 6.73 (m, 2H), 4.96 – 4.92 (m, 2H), 3.99 – 3.96 (m, 1H), 3.88 – 3.85 (m, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ174.6, 174.2, 142.7, 138.1, 132.1, 131.6, 129.6, 129.2, 128.9, 126.3, 123.0, 118.2, 50.6, 45.7, 45.4, 45.2.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{12}NO_2SBrNa^+$: 407.9670; Found: 407.9671.

(3a*R*,3b*S*,8b*R*,8c*R*)-8b-bromo-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzofuro[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3ah)



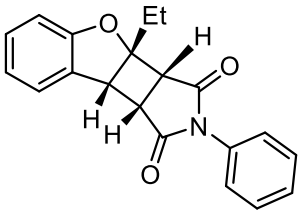
Yield: 30mg (41 %); white solid; R_f = 0.4 (petroleum ether / dichloromethane, 1:1); mp 222 °C.
^{1}H NMR (600 MHz, DMSO-d_6) δ 7.65 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.57 –7.54 (m, 2H), 7.50 – 7.46 (m, 2H), 7.43 – 7.37 (m, 3H), 7.18 –7.16 (m, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 5.89 (d, *J* = 2.0 Hz, 1H), 4.01 (d, *J* = 6.6 Hz, 1H), 3.55 (dd, *J* = 6.7, 2.7 Hz, 1H).
^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ174.0, 172.7, 158.2, 132.7, 132.1, 130.2, 129.5, 129.2, 127.6, 126.8, 123.7, 112.0, 88.3, 57.3, 52.1, 46.3.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{12}NO_3BrNa^+$: 391.9898; Found: 391.9891.

(3a*R*,3b*R*,8b*S*,8c*R*)-8b-bromo-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzofuro[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3ah')



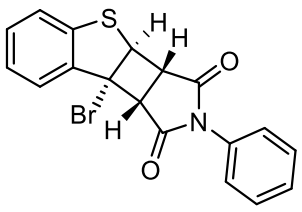
Yield: 10mg (13 %); white solid; R_f= 0.3 (petroleum ether / dichloromethane, 1:1); mp 198 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.23 – 7.20 (m, 3H), 7.02 – 6.99 (m, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.39 – 6.37 (m, 2H), 5.53 (dd, *J* = 8.5, 1.0 Hz, 1H), 4.10 (dd, *J* = 7.7, 1.0 Hz, 1H), 3.96 –3.93 (m, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ172.4, 171.1, 160.1, 132.2, 131.1, 129.1, 129.0, 127.2, 126.3, 126.2, 123.3, 111.7, 85.0, 56.1, 53.5, 43.2.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{12}NO_3BrNa^+$: 391.9898; Found: 391.9900.

(3a*R*,3b*S*,8b*R*,8c*R*)-3b-ethyl-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzofuro[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3ai)



Yield: 32mg (50 %); white solid; R_f= 0.5 (petroleum ether / ethyl acetate, 2:1); mp 181 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.27 (m, 3H), 7.24 – 7.19 (m, 2H), 6.92 – 6.85 (m, 2H), 6.53 – 6.51 (m, 2H), 4.29 (d, *J* = 8.7 Hz, 1H), 3.71 (dd, *J* = 8.7, 7.0 Hz, 1H), 3.59 (dd, *J* = 7.0, 2.0 Hz, 1H), 2.19 –2.13 (m, 1H), 2.10 –2.04 (m, 1H), 1.11 (t, *J* = 7.3 Hz, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ175.5, 173.0, 161.8, 131.6, 130.0, 129.0, 128.7, 126.8, 126.5, 125.0, 121.7, 110.3, 89.5, 49.5, 47.4, 40.9, 30.2, 7.2.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{20}H_{17}NO_3Na^+$: 342.1113; Found: 342.1106.

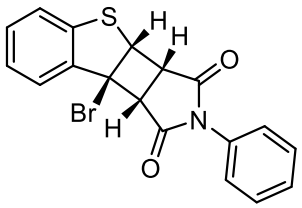
(3a*S*,3b*S*,8b*R*,8c*R*)-8b-bromo-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3aj)



Yield: 50mg (65 %); white solid; R_f = 0.4 (petroleum ether / dichloromethane, 1:1); mp 232°C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 7.4 Hz, 2H), 7.37 – 7.34 (m, 1H), 7.31 – 7.25 (m, 2H), 4.66 (d, *J* = 3.9 Hz, 1H), 3.97 (d, *J* = 6.7 Hz, 1H), 3.53 (dd, *J* = 6.6, 4.1 Hz, 1H).

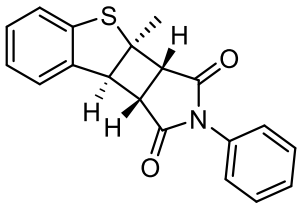
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ174.4, 171.7, 140.8, 139.0, 131.7, 130.7, 129.3, 129.1, 126.6, 126.5, 126.4, 122.4, 63.7, 58.2, 54.7, 46.8.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{12}NO_2SBrNa^+$: 407.9670; Found: 407.9677.

(3a*S*,3b*R*,8b*S*,8c*R*)-8b-bromo-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3aj')



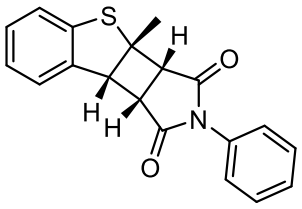
Yield: 14mg (18 %); white solid; R_f= 0.6 (petroleum ether / dichloromethane, 1:1); mp 172 °C.
^1H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.8 Hz, 1H), 7.32 – 7.28 (m, 4H), 7.21 – 7.17 (m, 2H), 6.52 – 6.49 (m, 2H), 5.02 (dd, *J* = 9.9, 0.8 Hz, 1H), 4.42 (dd, *J* = 7.6, 0.8 Hz, 1H), 3.99 (dd, *J* = 9.9, 7.6 Hz, 1H).
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ:72.4, 172.2, 141.5, 137.5, 131.1, 131.0, 129.1, 129.0, 128.3, 126.3, 126.0, 122.3, 57.5, 55.7, 42.9.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{18}H_{12}NO_2SBrNa^+$: 407.9670; Found: 407.9677.

(3a*S*,3b*R*,8b*S*,8c*R*)-3b-methyl-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3ak)



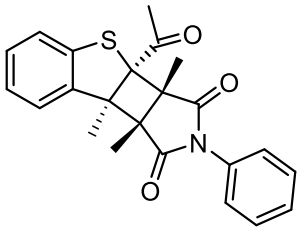
Yield: 15mg (22 %); white solid; R_f= 0.5 (petroleum ether / ethyl acetate, 2:1); mp 174 °C.
^1H NMR (600 MHz, $CDCl_3$) δ 7.53 –7.51 (m, 2H), 7.45 – 7.43 (m, 1H), 7.35 – 7.33 (m, 2H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 4.10 (d, *J* = 3.9 Hz, 1H), 3.90 (d, *J* = 7.0 Hz, 1H), 3.44 (dd, *J* = 7.0, 3.8 Hz, 1H), 1.76 (s, 3H).
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ176.4, 174.3, 142.0, 138.4, 131.8, 129.4, 129.1, 129.0, 126.4, 125.2, 125.2, 121.5, 58.4, 52.9, 45.1, 25.5.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{19}H_{15}NO_2SNa^+$: 344.0721; Found: 344.0728.

(3a*S*,3b*S*,8b*R*,8c*R*)-3b-methyl-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3ak')



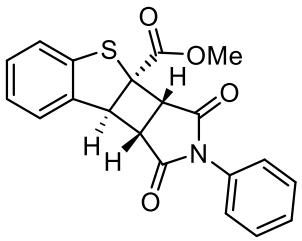
Yield: 27mg (43 %); white solid; R_f= 0.5 (petroleum ether / ethyl acetate, 10:1); mp 158 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 3H), 7.21 – 7.16 (m, 2H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.06 –7.04 (m, 1H), 6.68 – 6.66 (m, 2H), 4.45 (d, *J* = 9.4 Hz, 1H), 3.93 (dd, *J* = 9.4, 6.9 Hz, 1H), 3.54 (dd, *J* = 6.9, 1.5 Hz, 1H), 1.99 (s, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ175.1, 174.4, 143.6, 136.0, 131.7, 129.1, 129.1, 128.7, 126.7, 126.5, 124.9, 121.5, 57.3, 57.1, 52.2, 42.7, 29.1.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{19}H_{15}NO_2SNa^+$: 344.0721; Found: 344.0728.

(3a*S*,3b*R*,8b*S*,8c*R*)-3b-acetyl-3a,8b,8c-trimethyl-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3al)



Yield: 42mg (60 %); white solid; R_f= 0.5 (petroleum ether / ethyl acetate, 10:1); mp 209 °C.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 2H), 7.45 – 7.42 (m, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.27 (m, 3H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.19 –7.16 (m, 1H), 4.88 (d, *J* = 4.2 Hz, 1H), 3.99 (dd, *J* = 7.0, 1.3 Hz, 1H), 3.52 (dd, *J* = 6.9, 4.2 Hz, 1H), 2.42 (s, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 01.9, 175.2, 173.6, 140.1, 137.7, 131.6, 129.4, 129.3, 129.1, 126.7, 126.1, 125.3, 121.7, 67.6, 52.8, 52.4, 44.6, 29.7, 27.6.
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{20}H_{15}NO_3SNa^+$: 372.0670; Found: 372.0676.

methyl (3a*S*,3b*R*,8b*S*,8c*R*)-1,3-dioxo-2-phenyl-1,2,3,3a,8b,8c-hexahydro-3bH-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-3b-carboxylate (3am)



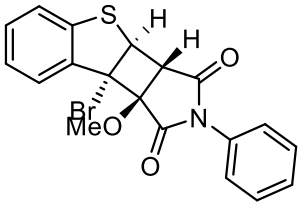
Yield: 59mg (81 %); white solid; R_f= 0.5 (petroleum ether / dichloromethane, 1:1); mp 208 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 2H), 7.46 –7.43 (m, 1H), 7.34 – 7.31 (m, 3H), 7.28 – 7.25 (m, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.17 –7.15 (m, 1H), 4.88 (d, *J* = 4.0 Hz, 1H), 3.97 (dd, *J* = 7.0, 1.2 Hz, 1H), 3.80 (s, 3H), 3.50 (dd, *J* = 7.0, 4.1 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ175.2, 173.3, 169.5, 140.8, 137.2, 131.8, 129.4, 129.3, 129.1, 126.6, 125.7, 125.0, 121.5, 54.6, 53.7, 52.5, 45.3.

HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{20}H_{15}NO_4SNa^+$: 388.0619; Found: 388.0625.

(3a*R*,3b*R*,8b*S*,8c*R*)-8b-bromo-3a-methoxy-2-phenyl-3a,3b,8b,8c-tetrahydro-1*H*-benzo[4',5']thieno[2',3':3,4]cyclobuta[1,2-c]pyrrole-1,3(2*H*)-dione (3an)



Yield: 61mg (73 %); white solid; R_f= 0.3 (petroleum ether / ethyl acetate, 10:1); mp 188 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.2 Hz, 1H), 7.56 –7.53 (m , 2H), 7.49 – 7.46 (m, 1H), 7.39 – 7.37 (m, 2H), 7.35 –7.32 (m, 1H), 7.26 – 7.22 (m, 2H), 4.28 (d, *J* = 4.2 Hz, 1H), 3.41 (d, *J* = 4.3 Hz, 1H), 3.32 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 172.5, 171.4, 139.7, 135.8, 131.3, 130.8, 130.3, 129.4, 129.3, 126.4, 125.5, 122.2, 86.2, 66.7, 54.0, 53.5, 50.8.

HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{19}H_{14}NO_3SBrNa^+$: 437.9775; Found: 437.9773.

6.Mechanistic studies

6.1 Stern-Volmer quenching studies

Stern-Volmer luminescence quenching studies were carried out using a 7.5×10^{-3} M solution of photocatalyst and variable concentrations of substrate(ranging from 0 to 0.125 M) in CF_3CH_2OH at room temperature under an argon atmosphere and were conducted on a Fluorescence spectrophotomer (SHIMADZU, RF-5301pc). The solutions were irradiated at 390 nm and the luminescence measured at 445 nm. Linear regression of I_0/I against concentration was performed in Origin. (I_0 = emission intensity of the photocatalyst in isolation at the specified wavelength; I = observed intensity as a function of the quencher concentration).

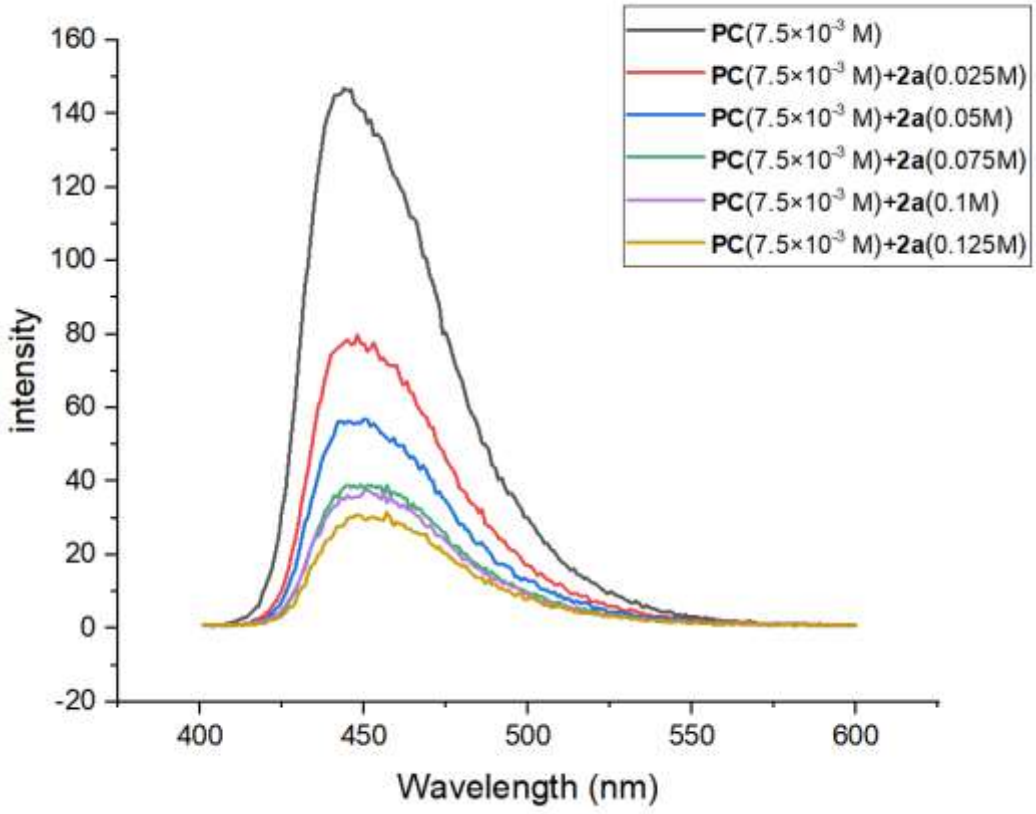


Figure S2. Luminescence quenching of *N*-Phenylmaleimide (**2a**) in CF_3CH_2OH.

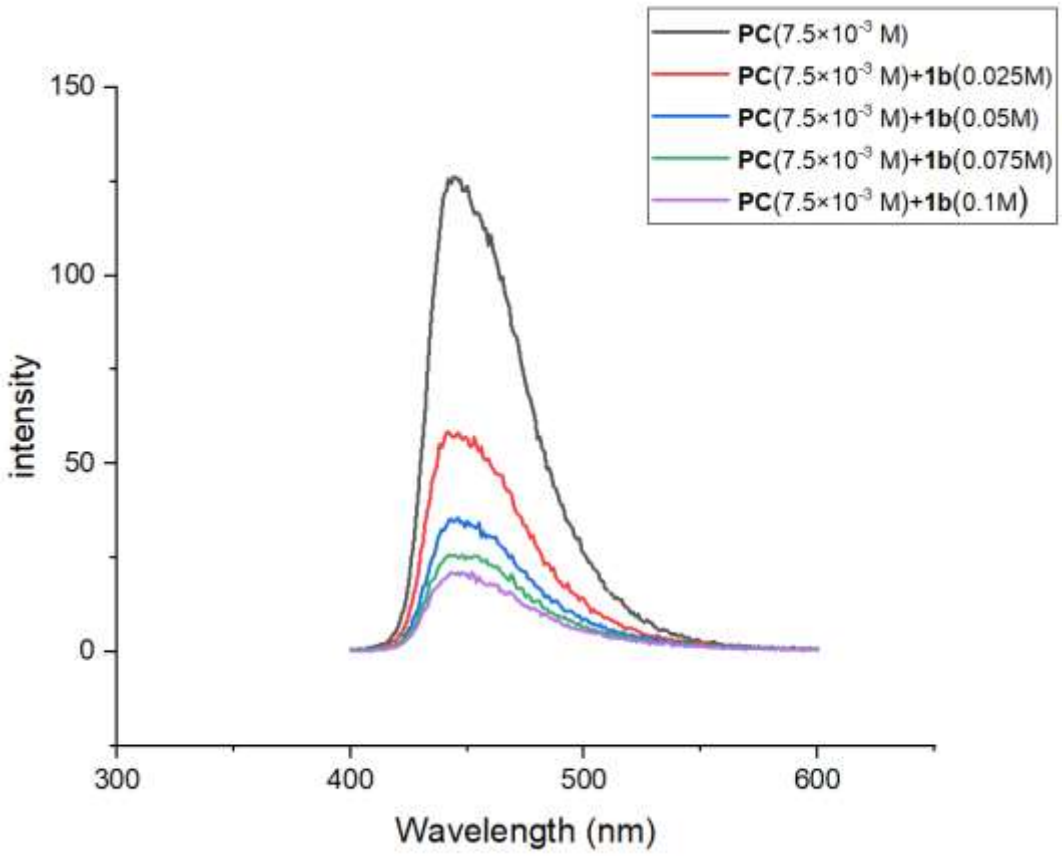


Figure S3. Luminescence quenching of Benzothiophene (**1b**) in CF_3CH_2OH.

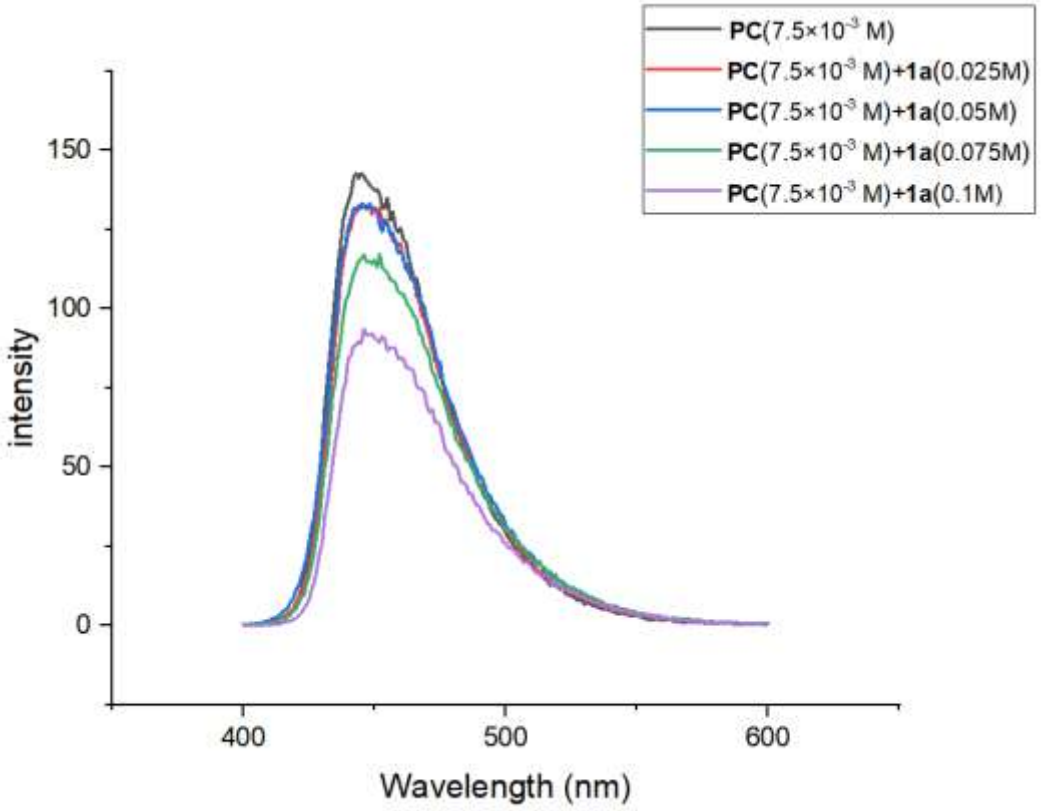


Figure S4. Luminescence quenching of Benzofuran (**1a**) in CF_3CH_2OH.

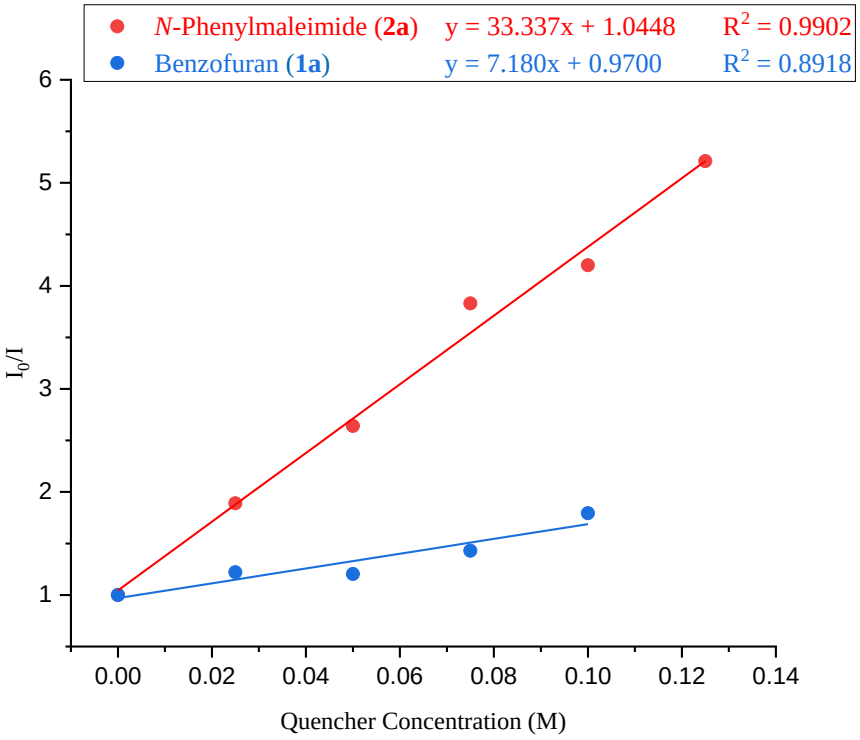


Figure S5. The luminescence quenching and corresponding Stern–Volmer plots of Thioxanthen-9-one (7.5×10^{-3} M) by *N*-Phenylmaleimide (**2a**) and Benzofuran (**1a**) in deoxygenated CF_3CH_2OH, respectively.

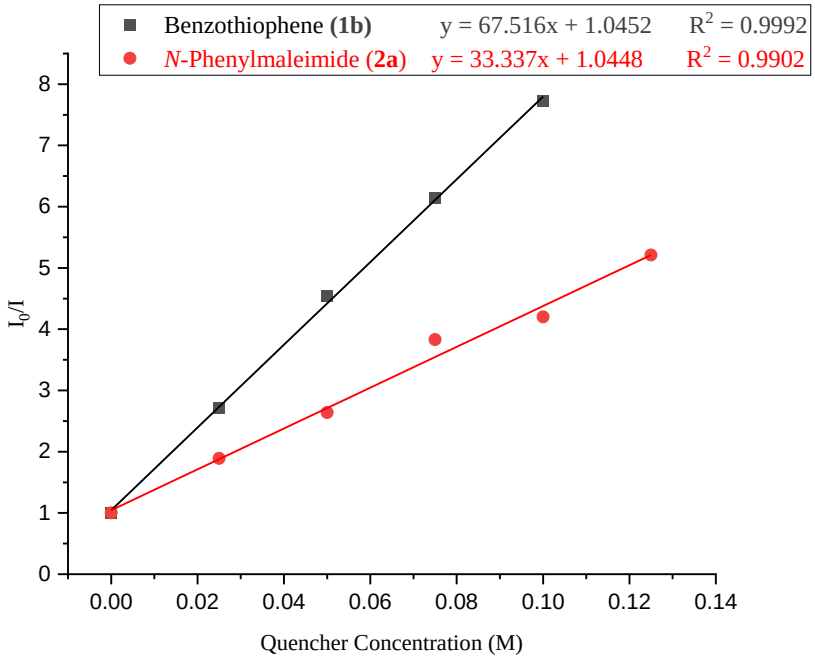


Figure S6. The luminescence quenching and corresponding Stern–Volmer plots of

Thioxanthen-9-one (7.5×10^{-3} M) by *N*-Phenylmaleimide (**2a**) and Benzothiophene (**1b**) in deoxygenated CF_3CH_2OH, respectively.

6.2 UV -Vis absorption

UV/vis absorption spectroscopy measurements were performed on a SHIMADZU UV-2600 spectrophotometer, equipped with a temperature control unit at 25 ℃. The samples were measured in fluorescence quartz cuvettes The reaction substrates and photosensitizer were measured as following concentration (in CF_3CH_2OH).

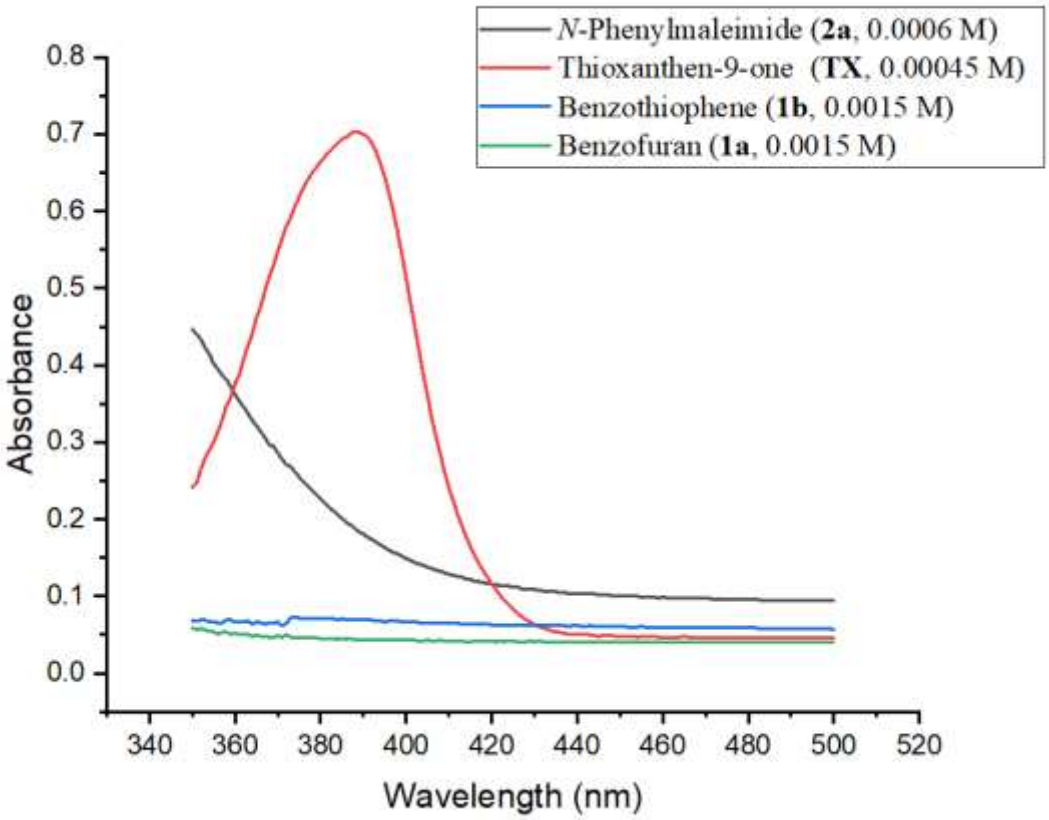
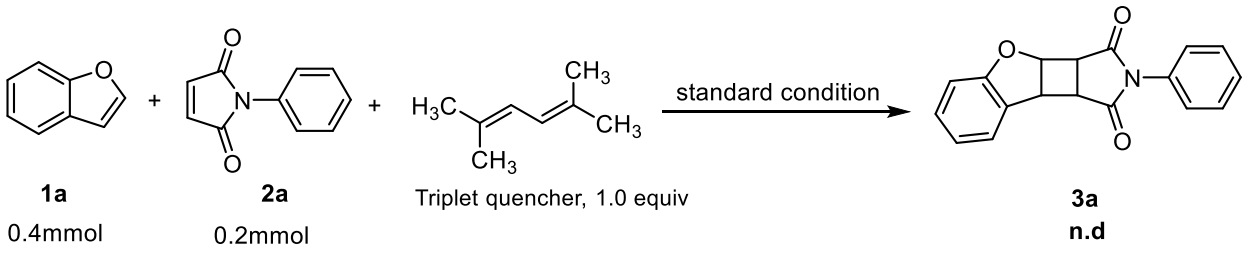


Figure S7.UV-Vis absorption of photosensitizer and substrates.

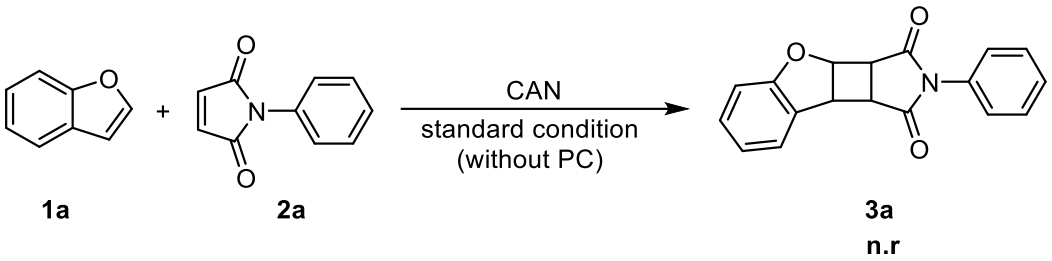
6.3 Control experiment with triplet quencher



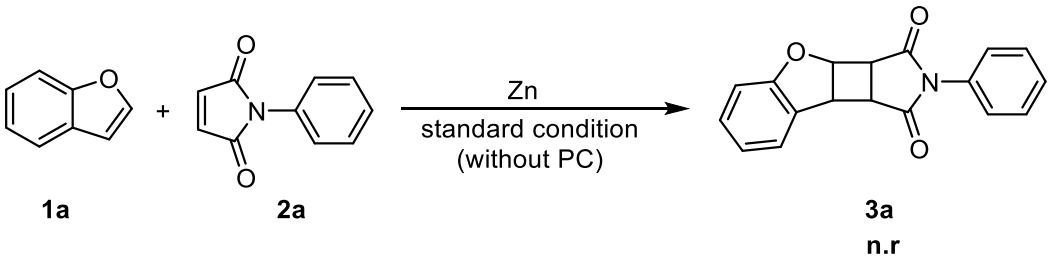
Triplet quencher: Reactions were conducted in the oven-dried Schlenk tube (10 mL) containing a stirring bar. **1a** (0.4mmol), **2a** (0.2 mmol) and triplet quencher (1.0 equiv) and CF_3CH_2OH (4.0 mL) were combined under Ar atmosphere. The resulting mixture was stirred at room temperature for 24 h. No target product was detected after the reaction was completed by TLC analysis.

6.4 SET reagent experiment

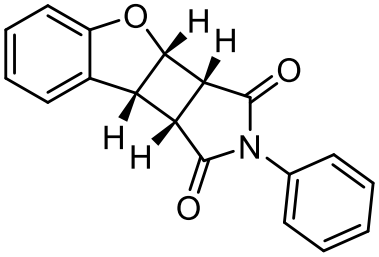
Electron transfer reagent: Reactions were conducted in the vial (10 mL) sealed with rubber septa. **1a** (0.4 mmol), **2a** (0.2 mmol) and CAN (1.0 equiv) and CF_3CH_2OH (4.0 mL) were combined under Ar atmosphere. The resulting mixture was stirred at room temperature for 24 h. No target product was detected after the reaction was completed by TLC analysis.



Electron transfer reagent: Reactions were conducted in the vial (10 mL) sealed with rubber septa. **1a** (0.4 mmol), **2a** (0.2 mmol) and Zn (1.0 equiv) and CF_3CH_2OH (4.0 mL) were combined under Ar atmosphere. The resulting mixture was stirred at room temperature for 24 h. No target product was detected after the reaction was completed by TLC analysis.



7.X-Ray Crystallographic Data



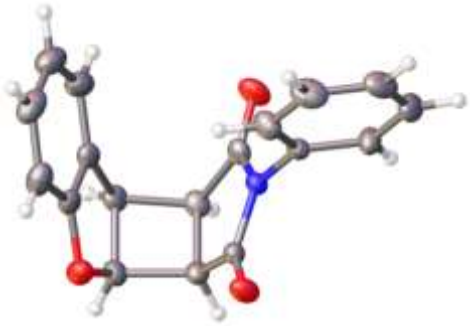


Table 9 Crystal data and structure refinement for **3a'**

Identification code	3a'
Empirical formula	$C_{18}H_{13}NO_3$
Formula weight	291.29
Temperature/K	292.37(10)
Crystal system	orthorhombic

Space group	Pbca
a/Å	11.24800(10)
b/Å	11.9893(2)
c/Å	21.1722(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2855.19(6)
Z	8
ρ_{calc}g/cm^3	1.355
μ/mm^{-1}	0.760
F(000)	1216.0
Crystal size/mm^3	0.43 × 0.32 × 0.31
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	11.478 to 143.638
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 10, -26 ≤ l ≤ 26
Reflections collected	14004
Independent reflections	2758 [R_{int} = 0.0285, R_{sigma} = 0.0177]
Data/restraints/parameters	2758/0/199
Goodness-of-fit on F^2	1.074
Final R indexes [I>=2σ (I)]	R_1 = 0.0572, wR_2 = 0.1571
Final R indexes [all data]	R_1 = 0.0597, wR_2 = 0.1599
Largest diff. peak/hole / e Å^{-3}	0.56/-0.25

Table 10 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å2×10^3) for **3a'**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*Z*	U(eq)
O1	1638.1(13)	2252.5(13)	7134.3(7)	50.9(4)
O2	5529.8(14)	1363.7(13)	6101.8(8)	54.1(4)
O3	3933.2(14)	3805.6(12)	7517.6(7)	50.6(4)
N1	4832.0(12)	2777.8(12)	6737.9(7)	31.5(4)
C1	1732.0(17)	2282.3(16)	6486.4(9)	40.5(4)
C2	1111(2)	3055(2)	6115.3(13)	56.8(6)
C3	1280(3)	2978(2)	5463.8(13)	62.4(7)

C4	1996(3)	2179(2)	5211.5(12)	64.1(7)
C5	2588(2)	1421(2)	5582.7(11)	55.8(6)
C6	2445.2(18)	1474.7(16)	6226.6(9)	40.2(4)
C7	2921.0(18)	747.7(16)	6760.1(10)	42.2(5)
C8	2451.3(18)	1410.5(17)	7333.9(10)	42.8(5)
C9	3742.3(17)	1776.8(17)	7496.4(9)	38.3(4)
C10	4224.8(17)	968.9(16)	6990.7(10)	40.5(4)
C11	4955.3(15)	1668.5(16)	6551.1(9)	36.5(4)
C12	4140.1(15)	2917.1(15)	7277.2(8)	34.0(4)
C13	5431.5(16)	3682.6(14)	6429.0(8)	32.4(4)
C14	4808.6(19)	4408.8(18)	6051.3(11)	48.4(5)
C15	5409(3)	5286(2)	5768.8(12)	63.1(7)
C16	6616(2)	5414.0(19)	5859.6(11)	58.4(6)
C17	7228(2)	4676(2)	6226.7(11)	56.9(6)
C18	6634.6(18)	3813.9(19)	6522.3(10)	46.9(5)

Table 11 Anisotropic Displacement Parameters ($Å2\times10^3$) for **3a'**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
O1	43.6(8)	63.0(10)	46.0(8)	-11.1(7)	0.5(6)	7.7(7)
O2	53.3(9)	44.9(8)	64.1(10)	-4.8(7)	21.6(8)	11.0(7)
O3	57.2(9)	41.6(8)	52.9(8)	-11.2(7)	16.9(7)	-5.7(6)
N1	29.9(7)	30.9(8)	33.8(7)	2.1(6)	2.8(6)	-0.1(6)
C1	40.9(10)	38.6(10)	41.9(10)	-7.6(8)	-2.2(8)	-8.1(8)
C2	55.7(13)	42.9(12)	72.0(15)	-8.1(11)	-14.2(11)	0.2(10)
C3	80.0(17)	46.6(13)	60.6(14)	13.0(11)	-25.2(13)	-13.1(12)
C4	83.3(18)	63.4(15)	45.6(12)	2.6(11)	-5.4(12)	-21.3(13)
C5	64.9(14)	55.9(13)	46.4(11)	-10.3(10)	6.6(11)	-12.3(11)
C6	40.1(10)	33.8(9)	46.7(10)	-7.3(8)	0.9(8)	-7.4(7)
C7	46.5(11)	30.3(9)	49.9(11)	0.9(8)	3.3(8)	-9.0(8)
C8	39.3(10)	42.8(11)	46.2(10)	4.8(8)	3.2(8)	-5.5(8)
C9	39.3(10)	41.8(11)	33.9(9)	6.9(8)	0.1(7)	-4.6(8)
C10	41.8(10)	29.5(9)	50.3(11)	7.5(8)	1.6(8)	3.8(7)
C11	30.2(8)	32.6(9)	46.7(10)	2.4(8)	1.0(8)	7.1(7)
C12	30.7(8)	37.2(10)	34.1(8)	-0.9(7)	0.9(7)	-2.1(7)
C13	35.1(9)	30.7(9)	31.5(8)	1.4(7)	3.1(7)	-1.4(7)
C14	43.6(10)	44.6(11)	56.9(12)	13.3(10)	5.0(9)	10.1(9)
C15	84.1(18)	43.3(12)	61.9(14)	19.9(11)	12.6(13)	15.5(12)
C16	79.9(17)	39.7(11)	55.7(13)	2.5(10)	22.2(12)	-15.4(11)
C17	54.6(13)	62.5(14)	53.7(12)	2.7(11)	1.9(10)	-27.1(11)
C18	40.6(10)	56.7(12)	43.4(10)	11.4(9)	-6.7(8)	-11.3(9)

Table 12 Bond Lengths for **3a'**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C1	1.376(2)	C6	C7	1.524(3)
O1	C8	1.426(3)	C7	C8	1.545(3)
O2	C11	1.207(2)	C7	C10	1.568(3)
O3	C12	1.203(2)	C8	C9	1.556(3)
N1	C11	1.394(2)	C9	C10	1.542(3)
N1	C12	1.392(2)	C9	C12	1.511(3)
N1	C13	1.435(2)	C10	C11	1.498(3)
C1	C2	1.401(3)	C13	C14	1.374(3)
C1	C6	1.372(3)	C13	C18	1.377(3)
C2	C3	1.395(4)	C14	C15	1.386(3)
C3	C4	1.361(4)	C15	C16	1.379(4)
C4	C5	1.374(4)	C16	C17	1.364(4)
C5	C6	1.374(3)	C17	C18	1.381(3)

Table 13 Bond Angles for **3a'**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	O1	C8	105.33(15)	C10	C9	C8	89.87(15)
C11	N1	C13	123.03(15)	C12	C9	C8	117.63(16)
C12	N1	C11	113.75(15)	C12	C9	C10	104.52(14)
C12	N1	C13	123.09(14)	C9	C10	C7	89.61(14)
O1	C1	C2	122.54(19)	C11	C10	C7	114.47(16)
C6	C1	O1	115.21(18)	C11	C10	C9	105.82(15)
C6	C1	C2	122.2(2)	O2	C11	N1	124.45(18)
C3	C2	C1	116.3(2)	O2	C11	C10	127.87(18)
C4	C3	C2	121.0(2)	N1	C11	C10	107.65(15)
C3	C4	C5	121.9(2)	O3	C12	N1	124.15(17)
C4	C5	C6	118.7(2)	O3	C12	C9	127.85(17)
C1	C6	C5	119.9(2)	N1	C12	C9	107.99(15)
C1	C6	C7	108.17(17)	C14	C13	N1	120.30(17)
C5	C6	C7	131.9(2)	C14	C13	C18	120.81(18)
C6	C7	C8	99.71(16)	C18	C13	N1	118.89(16)
C6	C7	C10	117.54(15)	C13	C14	C15	118.9(2)
C8	C7	C10	89.32(15)	C16	C15	C14	120.2(2)
O1	C8	C7	110.52(16)	C17	C16	C15	120.3(2)
O1	C8	C9	117.67(16)	C16	C17	C18	120.0(2)
C7	C8	C9	89.99(15)	C13	C18	C17	119.7(2)

Table 14 Torsion Angles for **3a'**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C1	C2	C3	-179.2(2)	C8	C7	C10	C11	-115.58(17)
O1	C1	C6	C5	179.20(18)	C8	C9	C10	C7	8.28(14)
O1	C1	C6	C7	0.9(2)	C8	C9	C10	C11	123.66(16)
O1	C8	C9	C10	-121.71(18)	C8	C9	C12	O3	80.0(3)
O1	C8	C9	C12	-15.3(3)	C8	C9	C12	N1	-101.18(18)
N1	C13	C14	C15	178.83(19)	C9	C10	C11	O2	177.0(2)
N1	C13	C18	C17	179.69(19)	C9	C10	C11	N1	-4.9(2)
C1	O1	C8	C7	-10.1(2)	C10	C7	C8	O1	127.99(16)
C1	O1	C8	C9	91.25(19)	C10	C7	C8	C9	8.27(14)
C1	C2	C3	C4	1.2(4)	C10	C9	C12	O3	177.62(19)
C1	C6	C7	C8	-6.51(19)	C10	C9	C12	N1	-3.55(19)
C1	C6	C7	C10	-100.8(2)	C11	N1	C12	O3	179.42(18)
C2	C1	C6	C5	1.4(3)	C11	N1	C12	C9	0.5(2)
C2	C1	C6	C7	-176.83(18)	C11	N1	C13	C14	107.3(2)
C2	C3	C4	C5	-0.5(4)	C11	N1	C13	C18	-73.3(2)
C3	C4	C5	C6	0.2(4)	C12	N1	C11	O2	-179.00(18)
C4	C5	C6	C1	-0.7(3)	C12	N1	C11	C10	2.9(2)
C4	C5	C6	C7	177.1(2)	C12	N1	C13	C14	-77.3(2)
C5	C6	C7	C8	175.5(2)	C12	N1	C13	C18	102.2(2)
C5	C6	C7	C10	81.2(3)	C12	C9	C10	C7	-110.31(15)
C6	C1	C2	C3	-1.6(3)	C12	C9	C10	C11	5.07(19)
C6	C7	C8	O1	10.14(19)	C13	N1	C11	O2	-3.2(3)
C6	C7	C8	C9	-109.58(15)	C13	N1	C11	C10	178.68(15)
C6	C7	C10	C9	92.26(18)	C13	N1	C12	O3	3.6(3)
C6	C7	C10	C11	-15.0(2)	C13	N1	C12	C9	-175.28(15)
C7	C8	C9	C10	-8.41(14)	C13	C14	C15	C16	1.0(4)
C7	C8	C9	C12	97.96(18)	C14	C13	C18	C17	-0.9(3)
C7	C10	C11	O2	-86.0(2)	C14	C15	C16	C17	0.2(4)
C7	C10	C11	N1	92.04(19)	C15	C16	C17	C18	-1.7(4)
C8	O1	C1	C2	-176.50(18)	C16	C17	C18	C13	2.0(3)
C8	O1	C1	C6	5.8(2)	C18	C13	C14	C15	-0.6(3)

C8	C7	C10	C9	-8.34(14)

Table 15 Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3a'.

Atom	x	y	z	U(eq)
H2	613	3588	6293	68
H3	898	3481	5198	75
H4	2087	2145	4775	77
H5	3076	882	5402	67
H7	2683	-38	6744	51
H8	2110	923	7658	51
H9	3989	1593	7928	46
H10	4635	312	7159	49
H14	3997	4313	5986	58
H15	4997	5791	5517	76
H16	7014	6006	5670	70
H17	8045	4754	6278	68
H18	7046	3324	6783	56

8.References

[1] I. Triandafillidi; N. F. Nikitas; P. L. Gkizis; N. Spiliopoulou; C. G. Kokotos. *ChemSusChem* **2022**, *15*, e202102441.

[2] N. F. Nikitas; M. A. Theodoropoulou; C. G. Kokotos. *Eur. J. Org. Chem*. **2021**, *2021*, 1168-1175.

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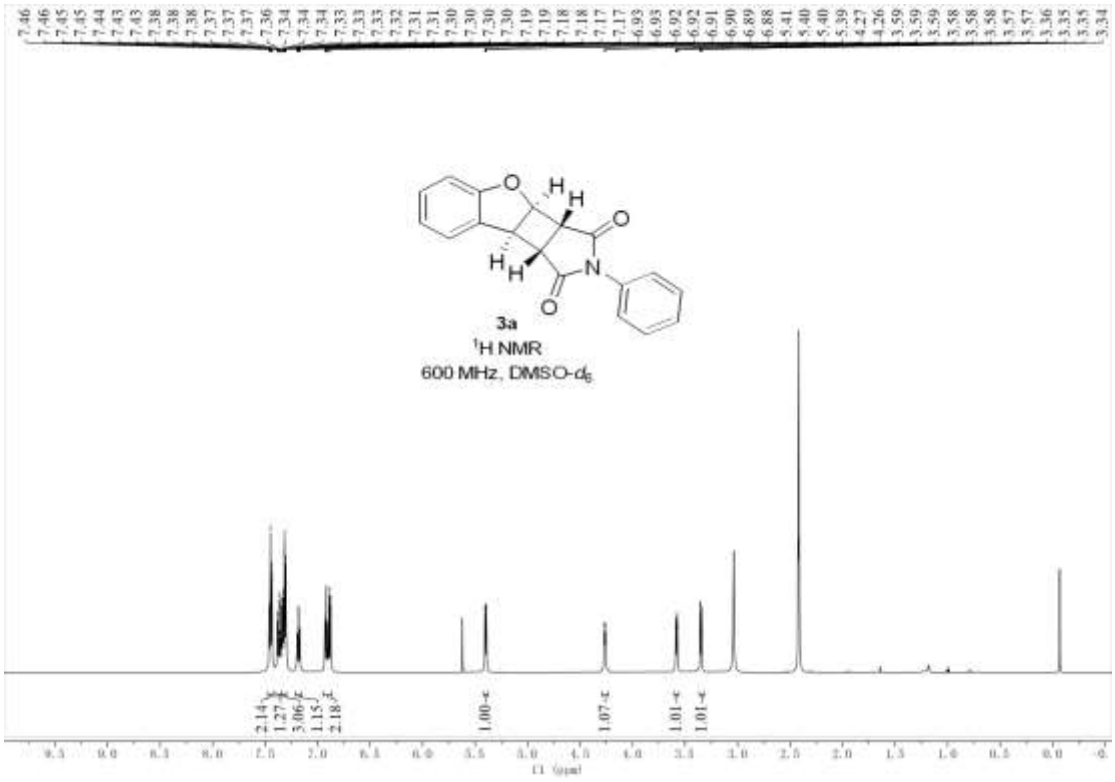
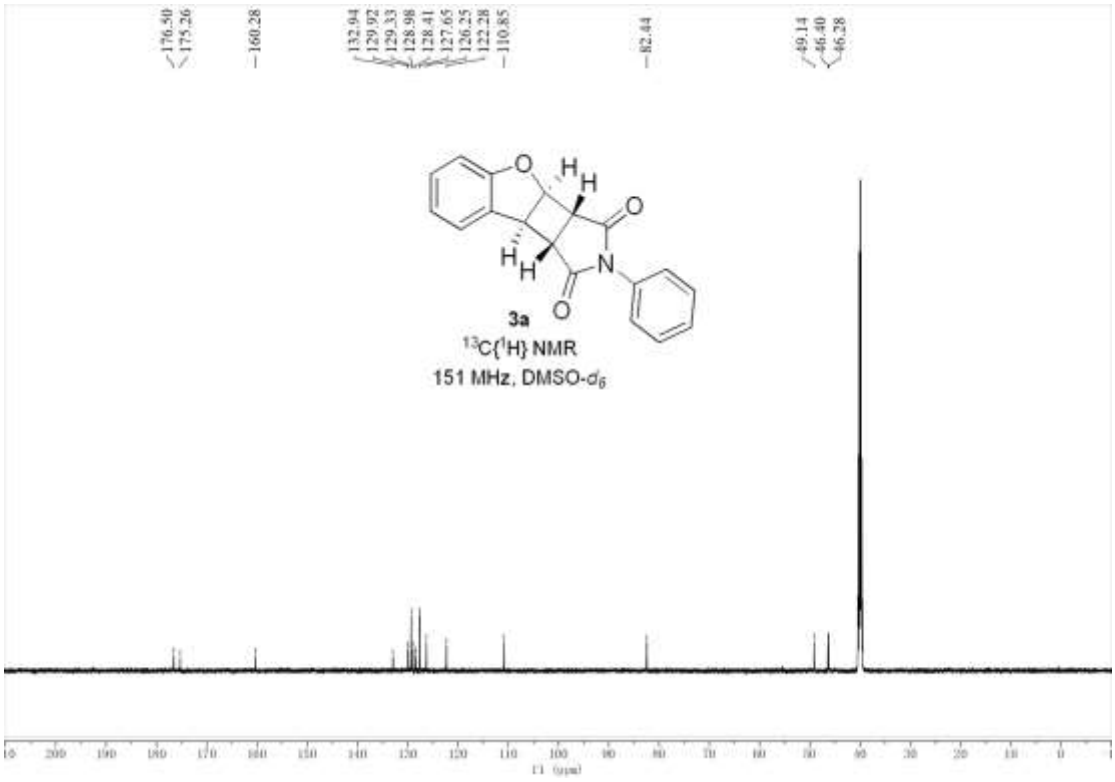
9.^{1}H and ^{13}C NMR Spectra

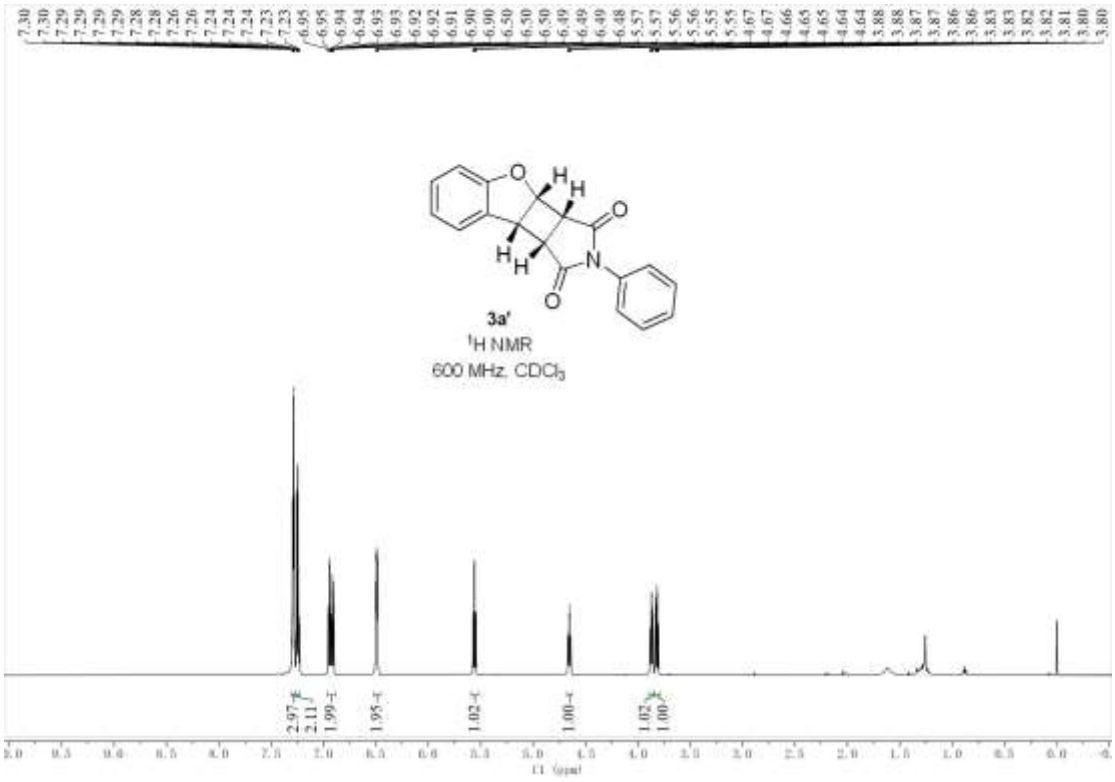
^{1}H NMR Spectrum of 3a



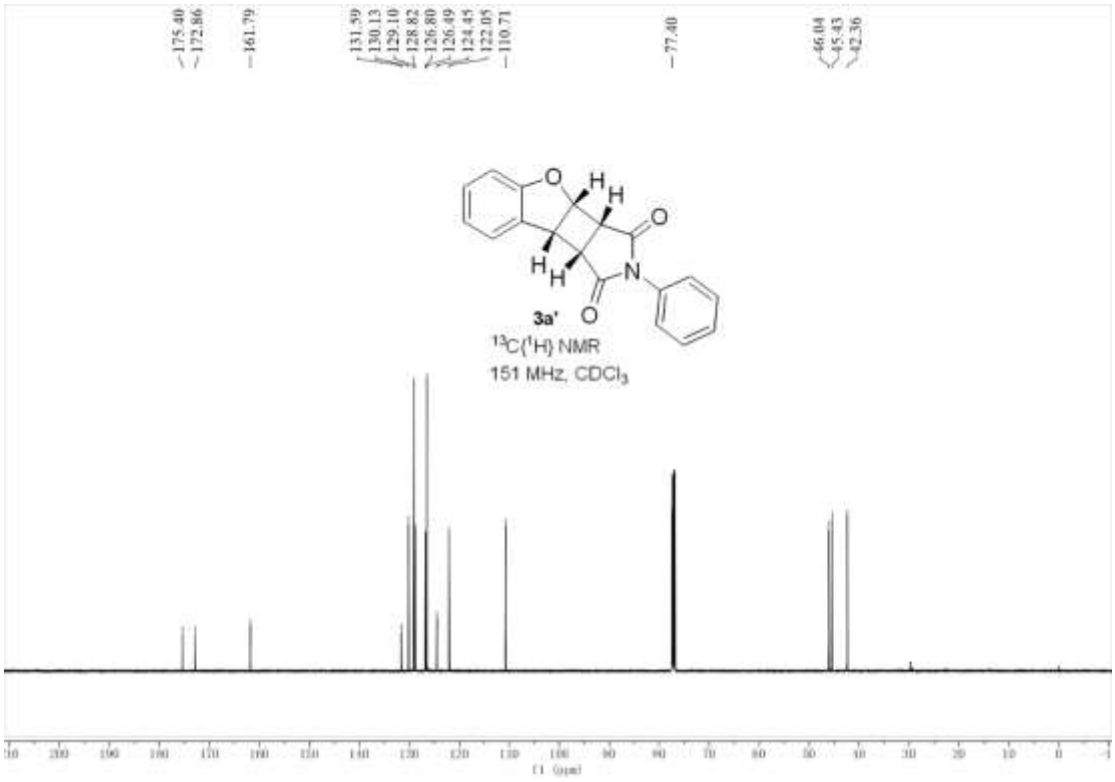
^{13}C{^{1}H} NMR Spectrum of 3a



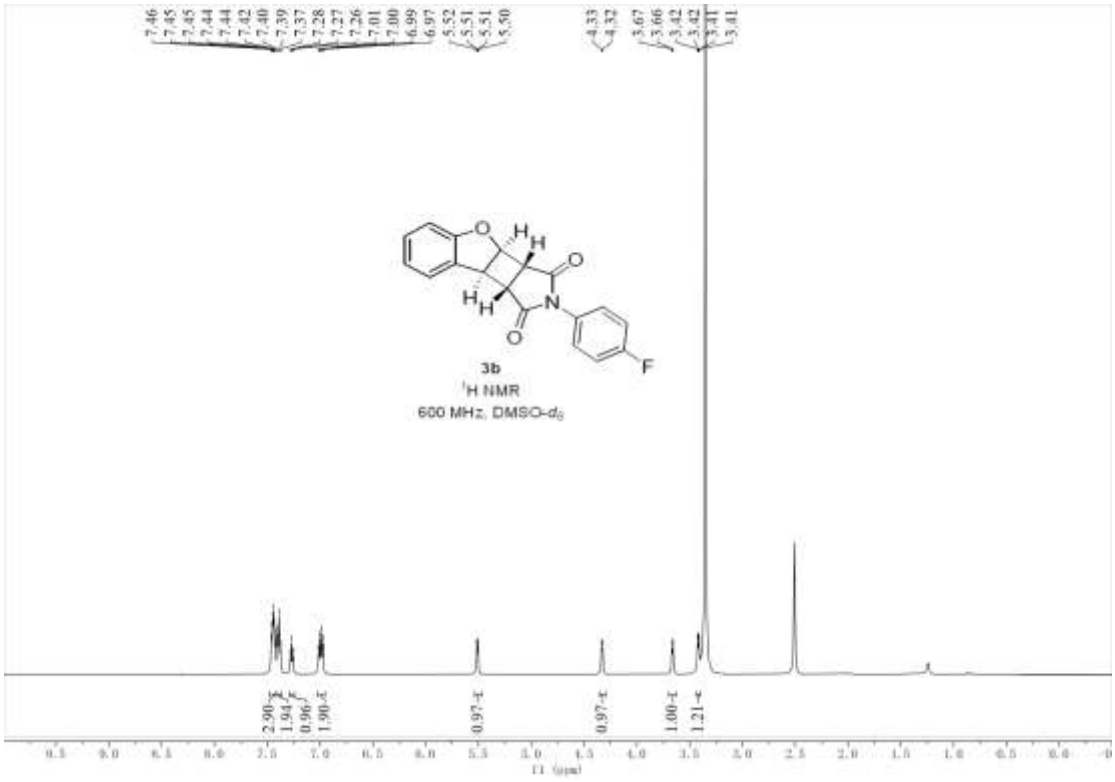
^{1}H NMR Spectrum of 3a'



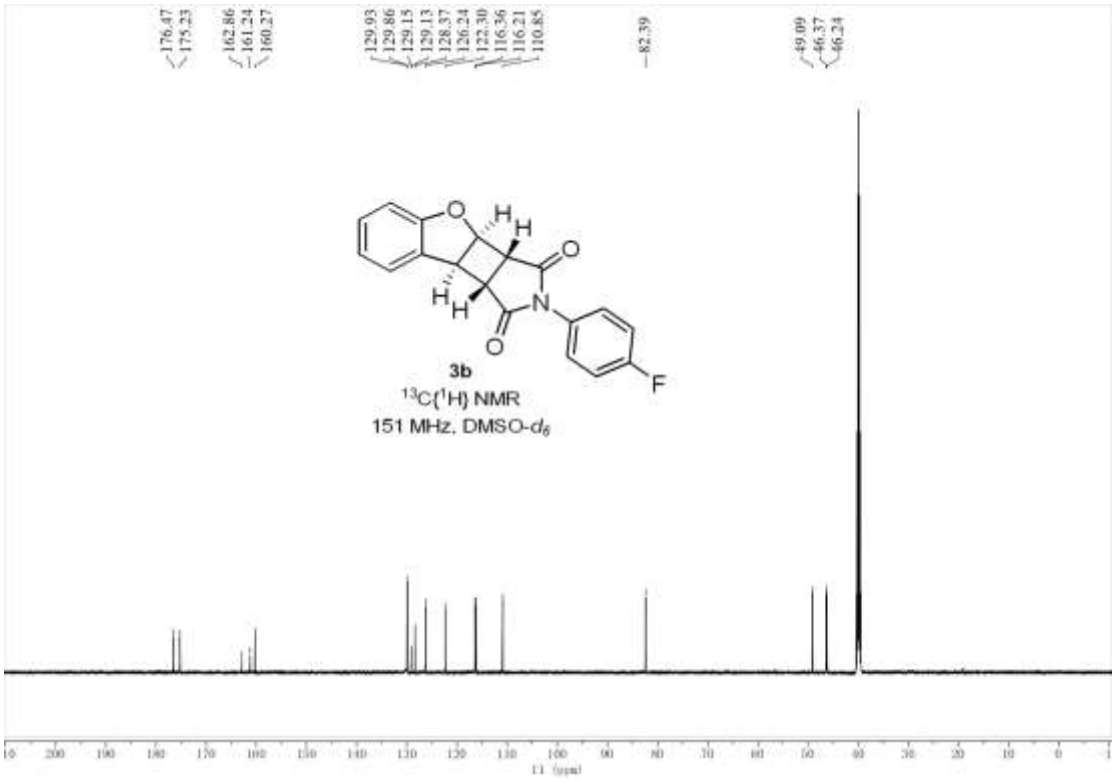
^{13}C{^{1}H} NMR Spectrum of 3a'



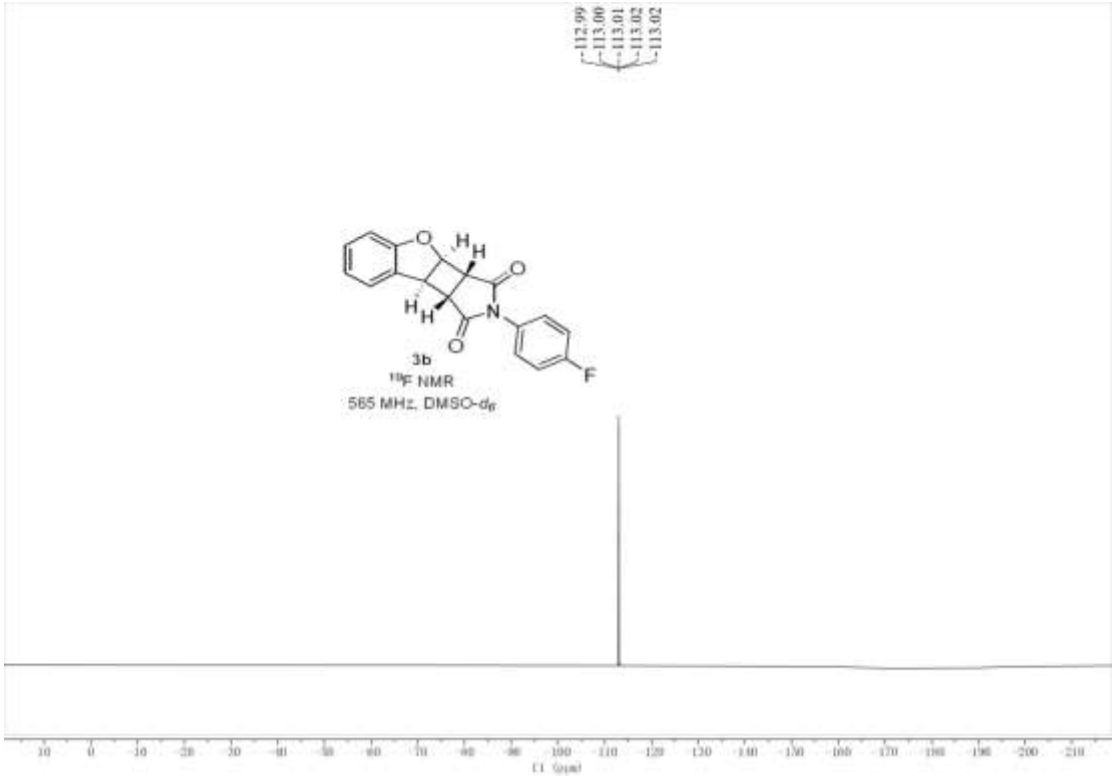
^{1}H NMR Spectrum of 3b



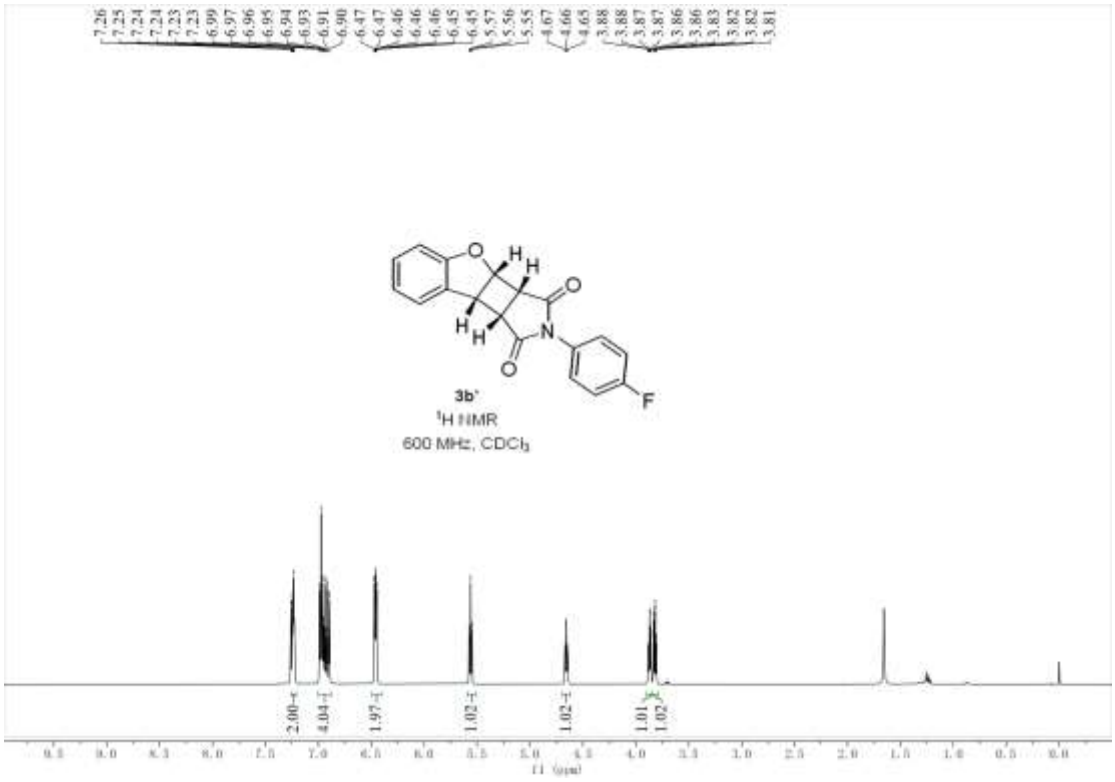
^{13}C{^{1}H} NMR Spectrum of 3b



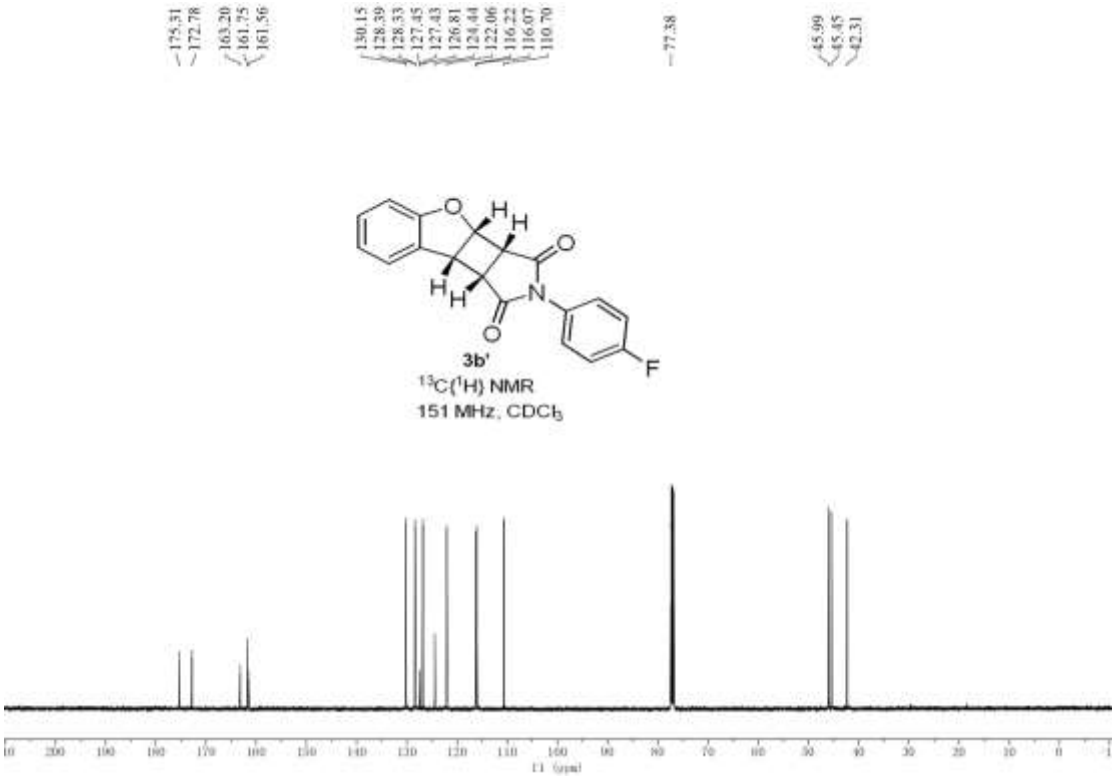
^{19}F NMR Spectrum of 3b



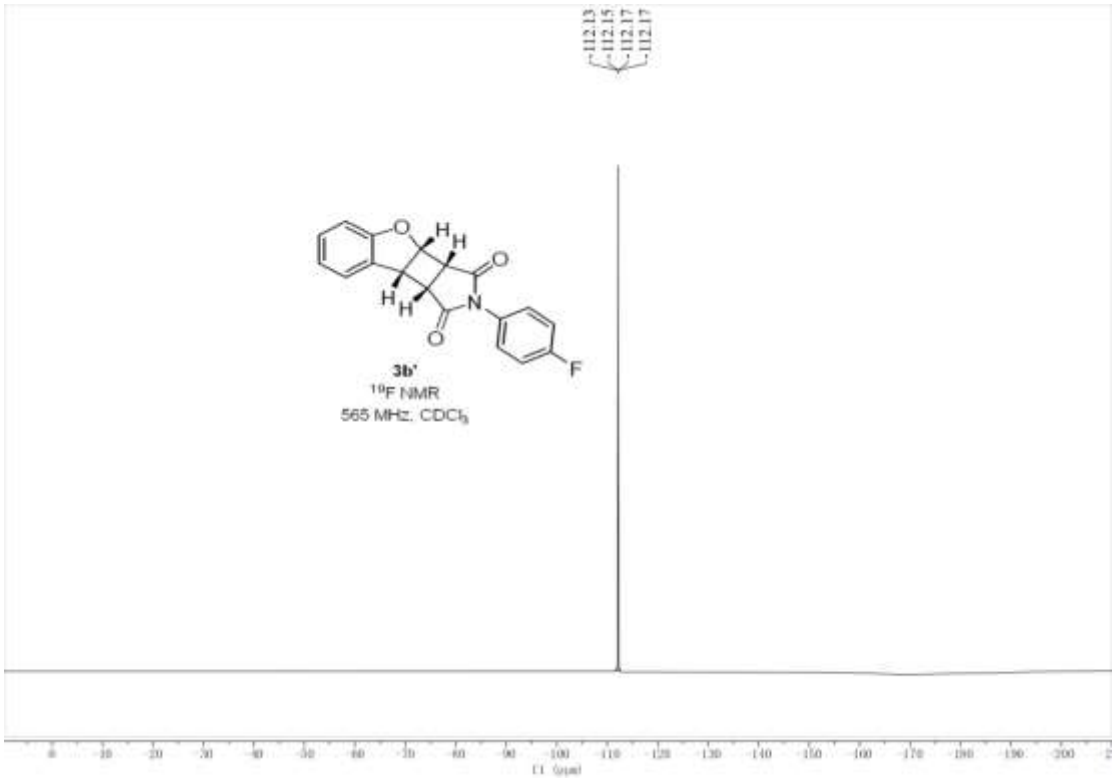
^{1}H NMR Spectrum of 3b'



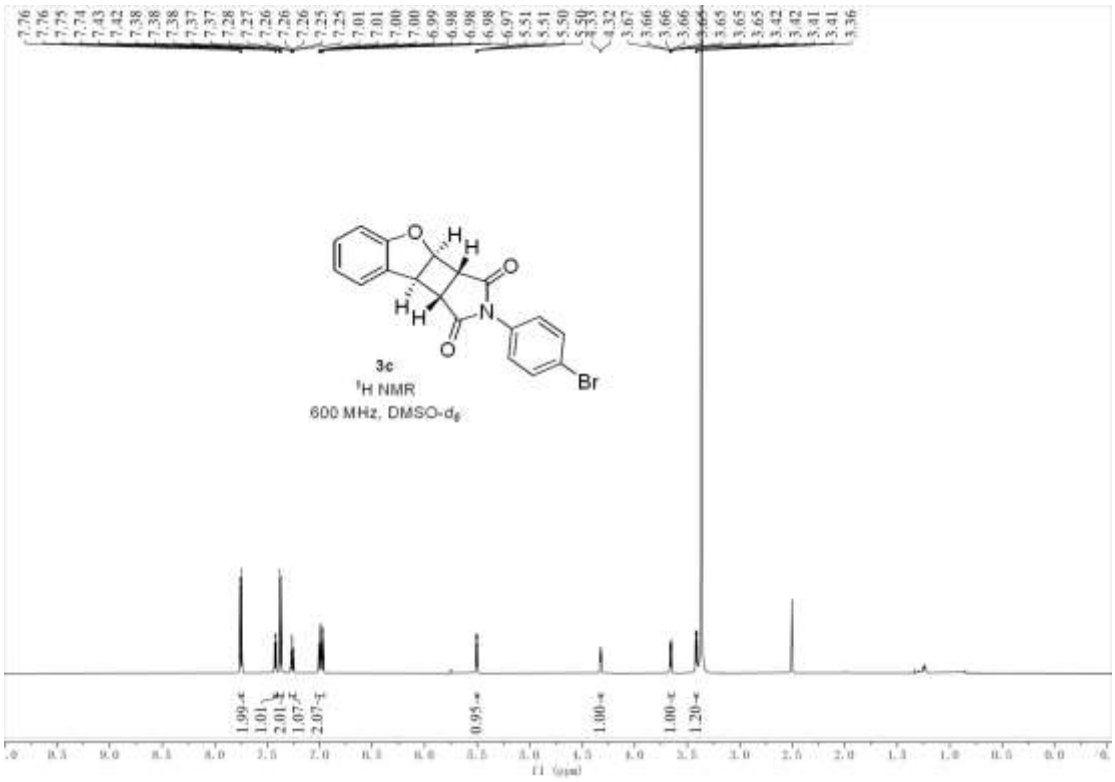
$^{13}C\{^{1}H\}$ NMR Spectrum of 3b'



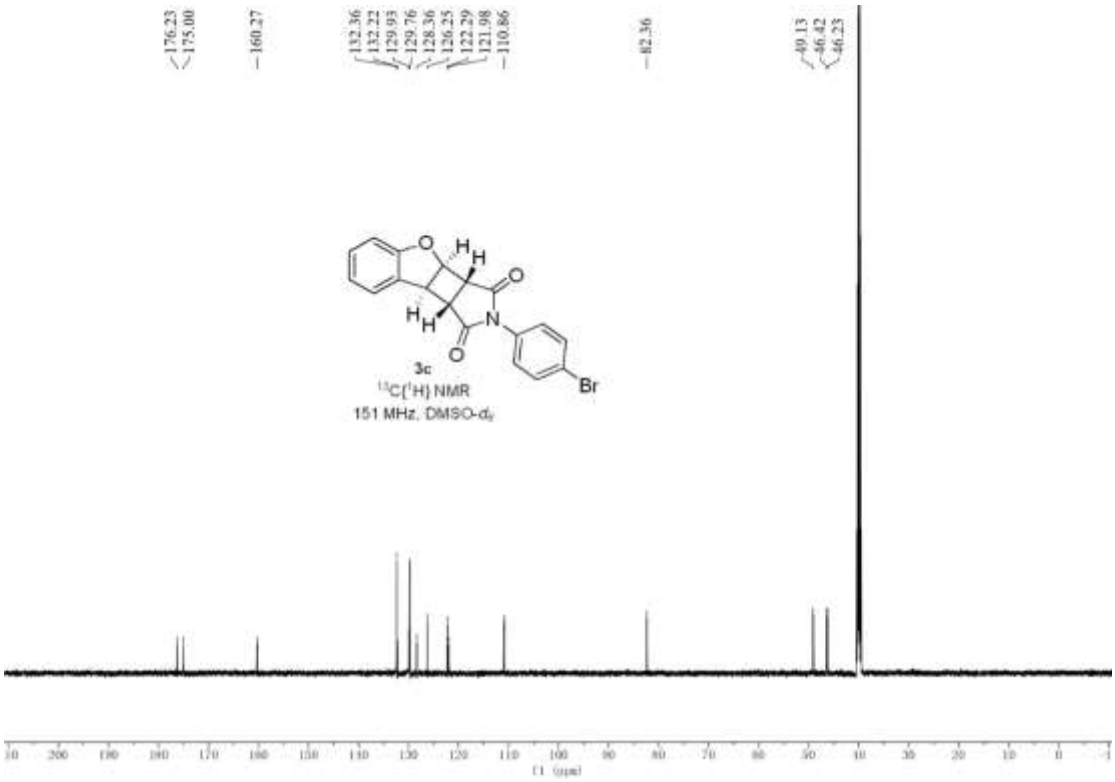
^{19}F NMR Spectrum of 3b'



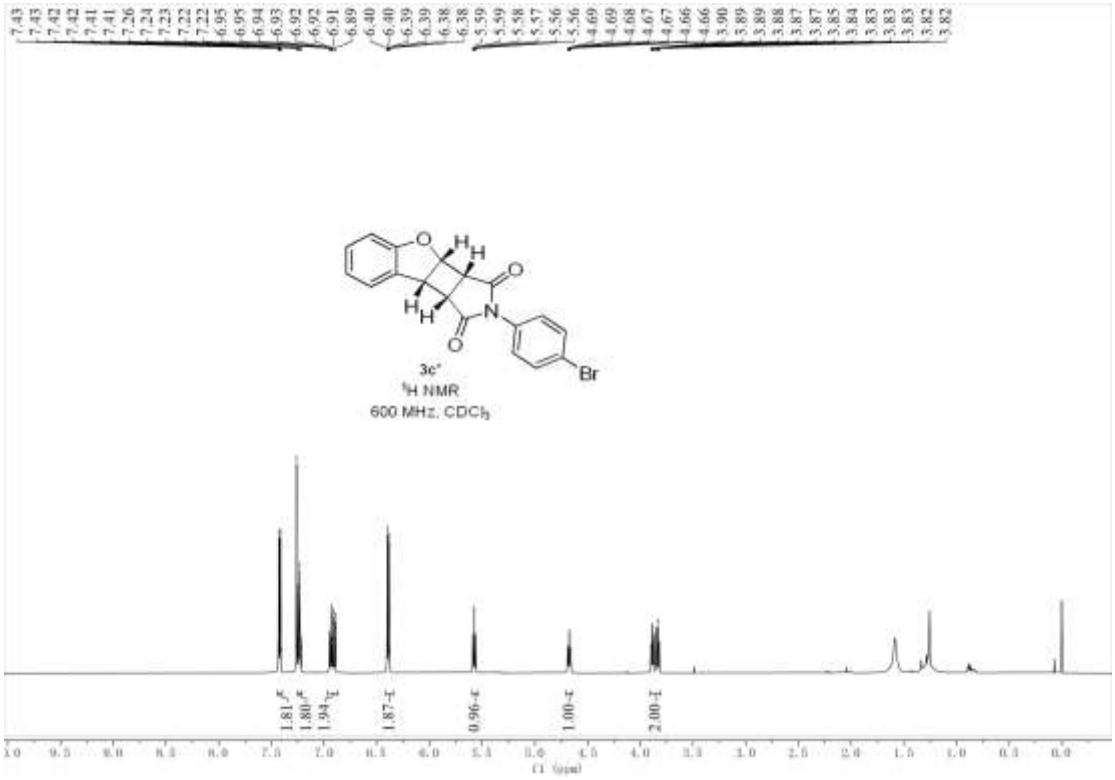
^{1}H NMR Spectrum of 3c



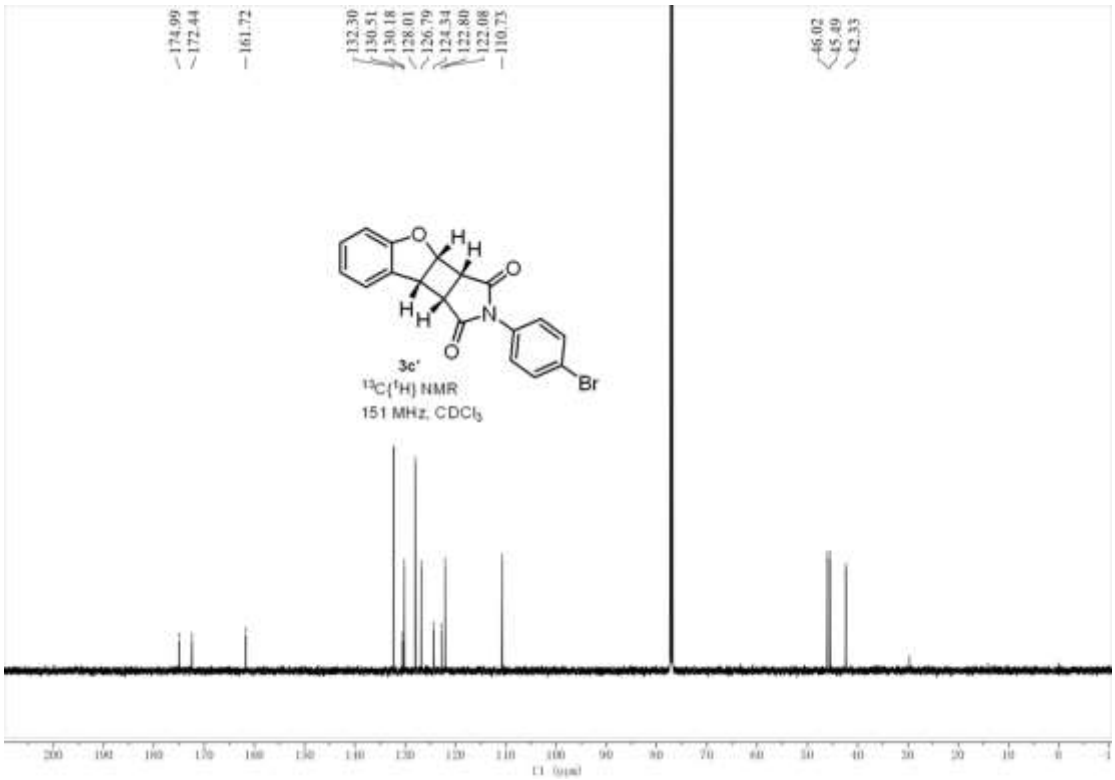
^{13}C{^{1}H} NMR Spectrum of 3c



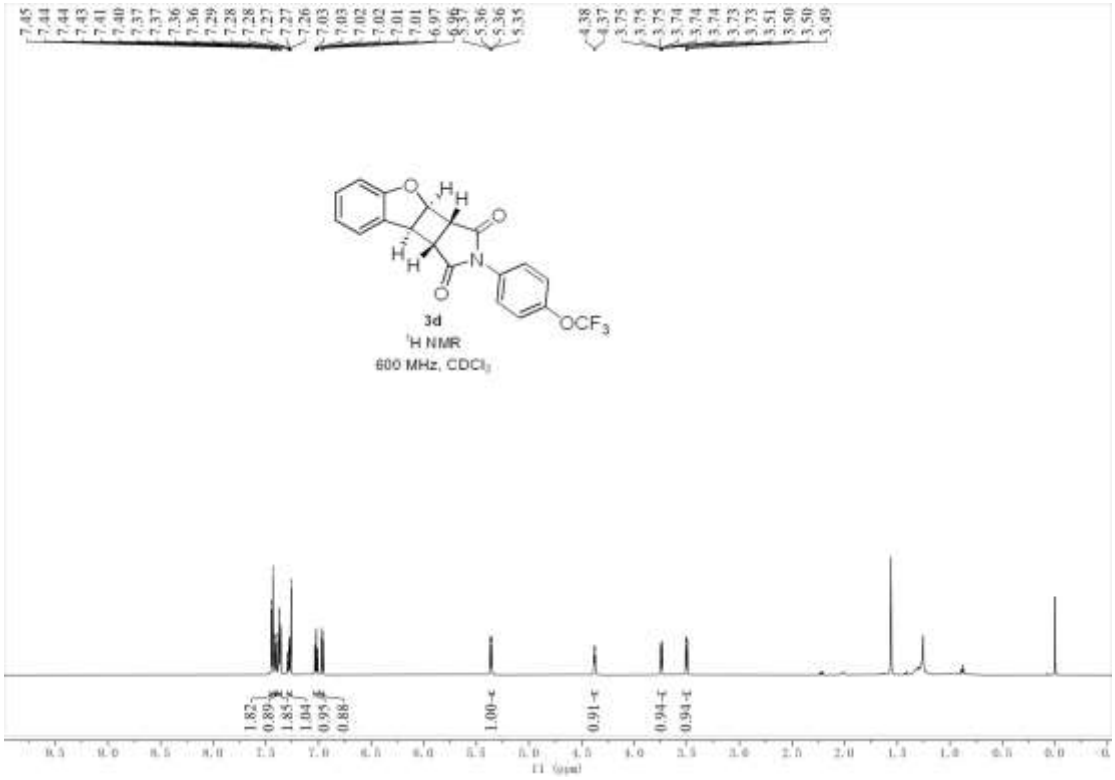
^{1}H NMR Spectrum of 3c'



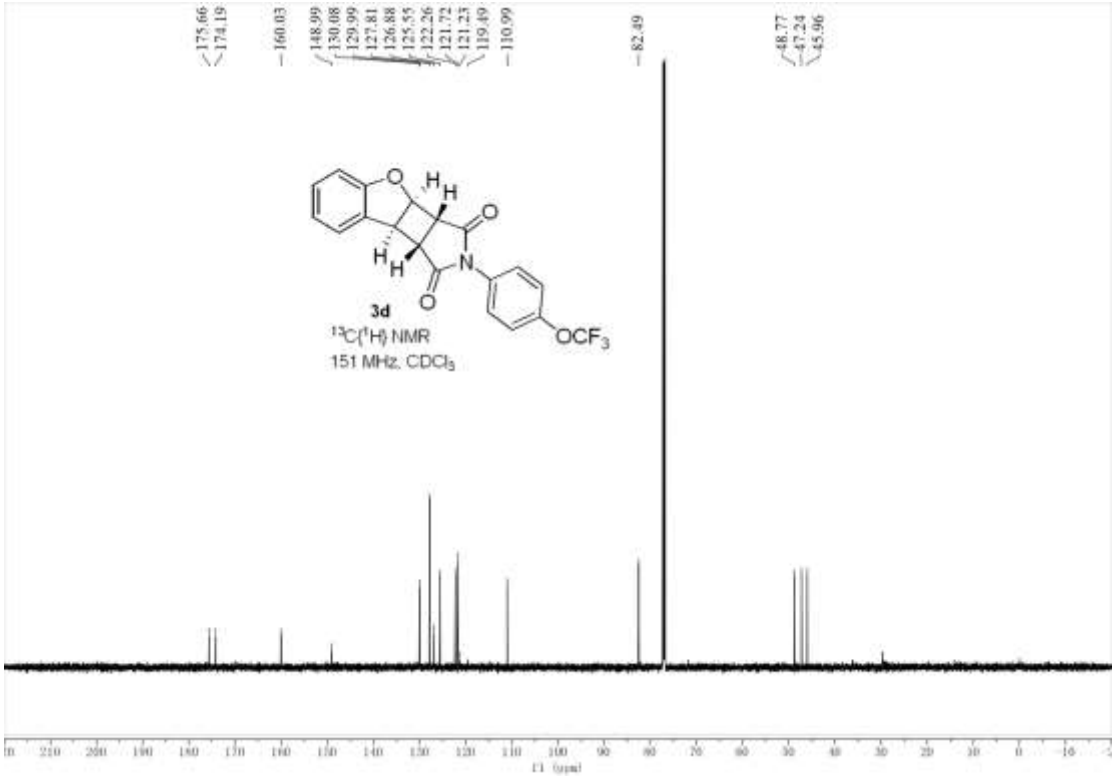
^{13}C{^{1}H} NMR Spectrum of 3c'



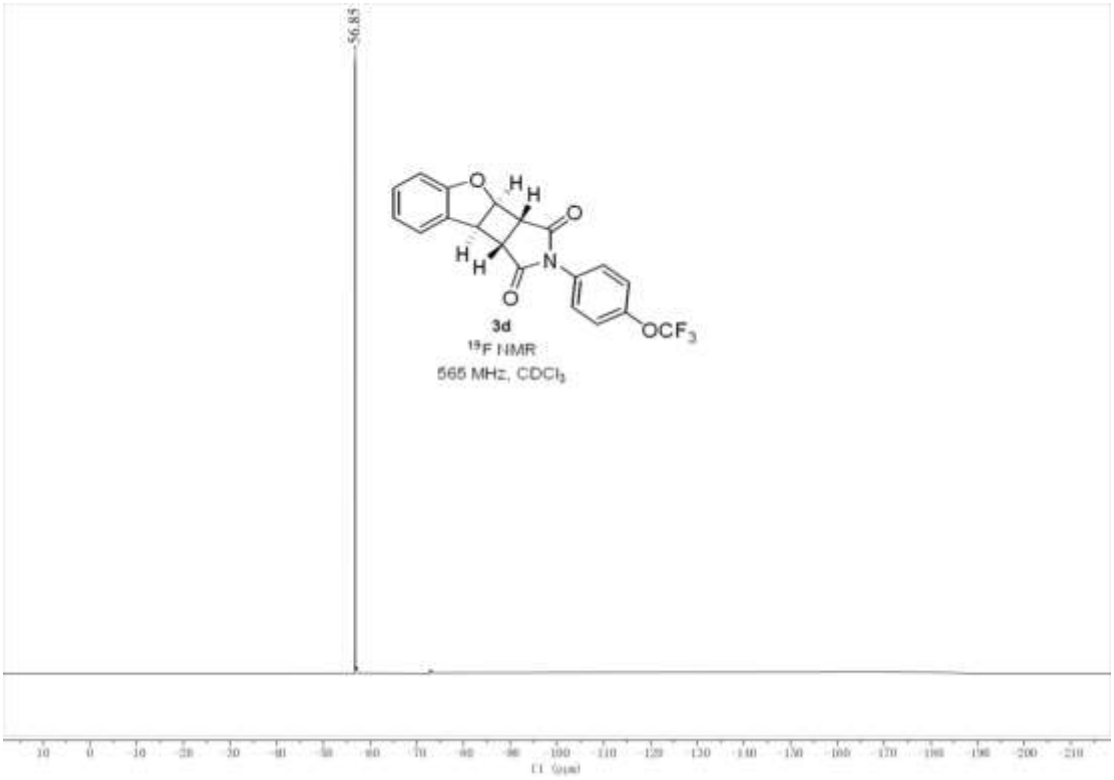
^{1}H NMR Spectrum of 3d



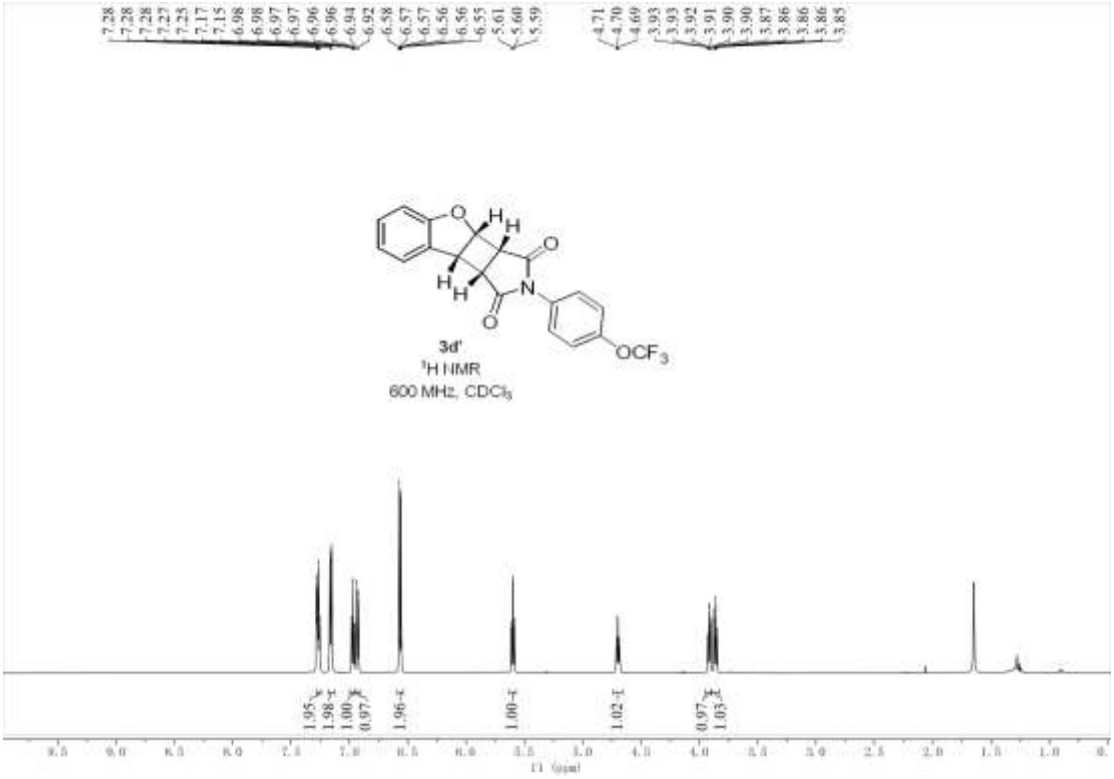
^{13}C{^{1}H} NMR Spectrum of 3d



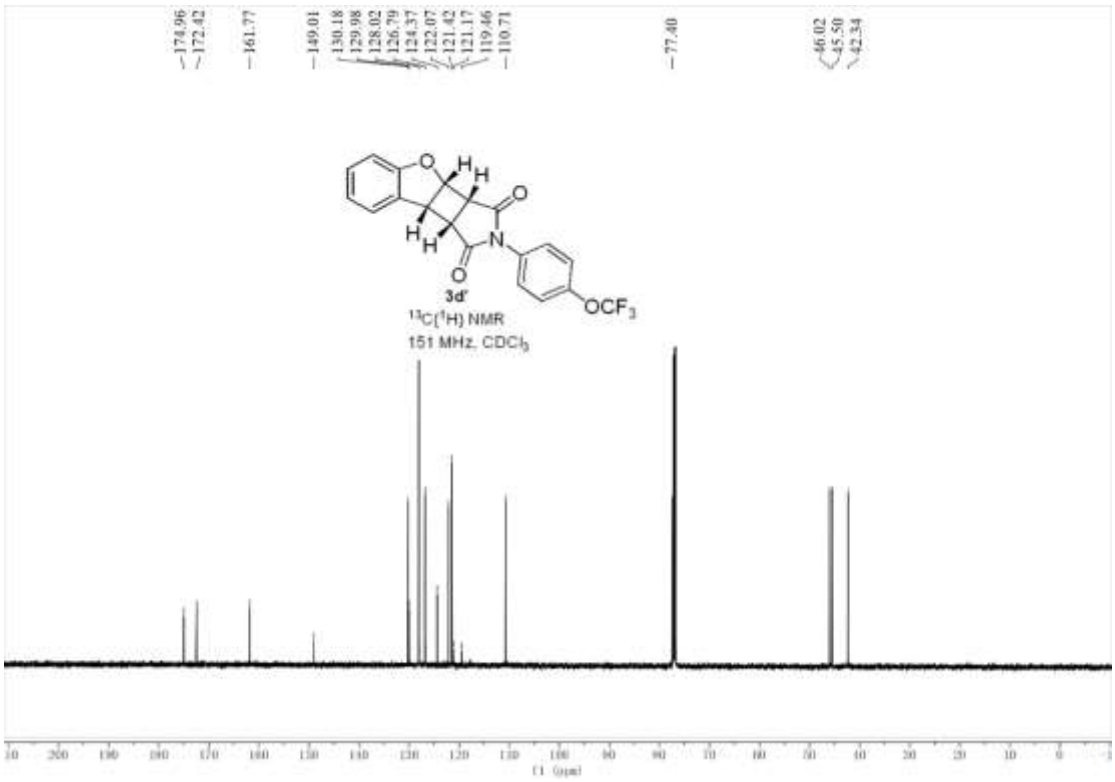
^{19}F NMR Spectrum of 3d



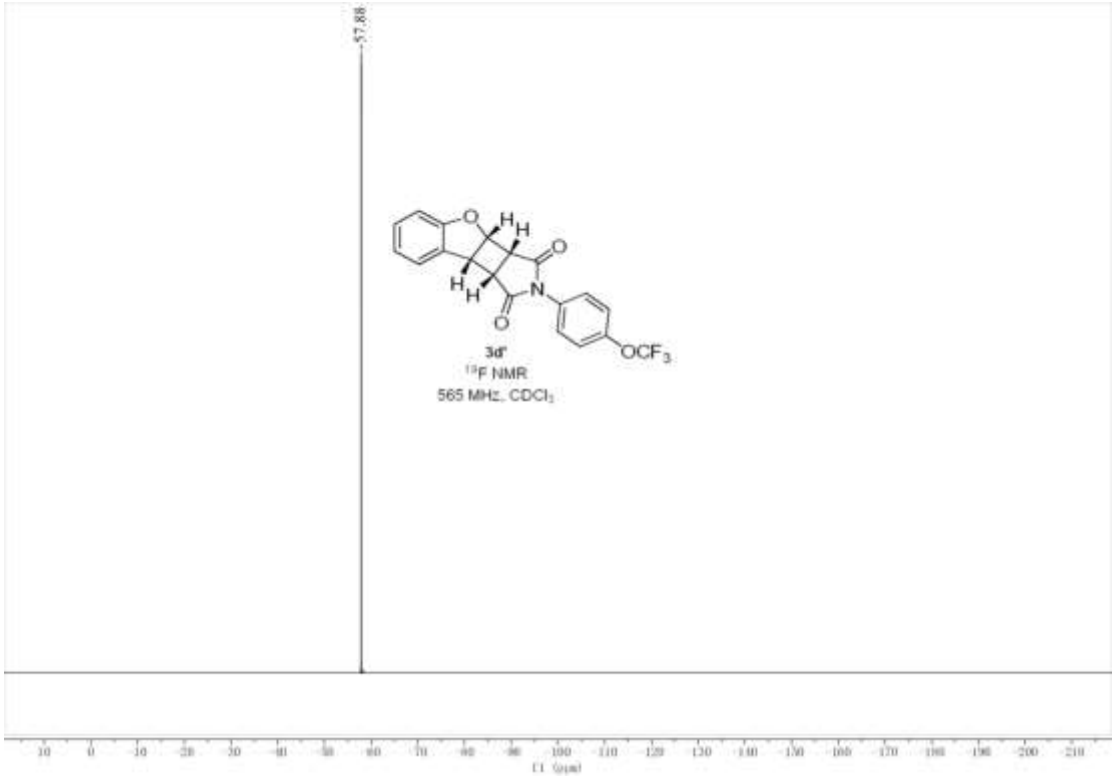
^{1}H NMR Spectrum of 3d'



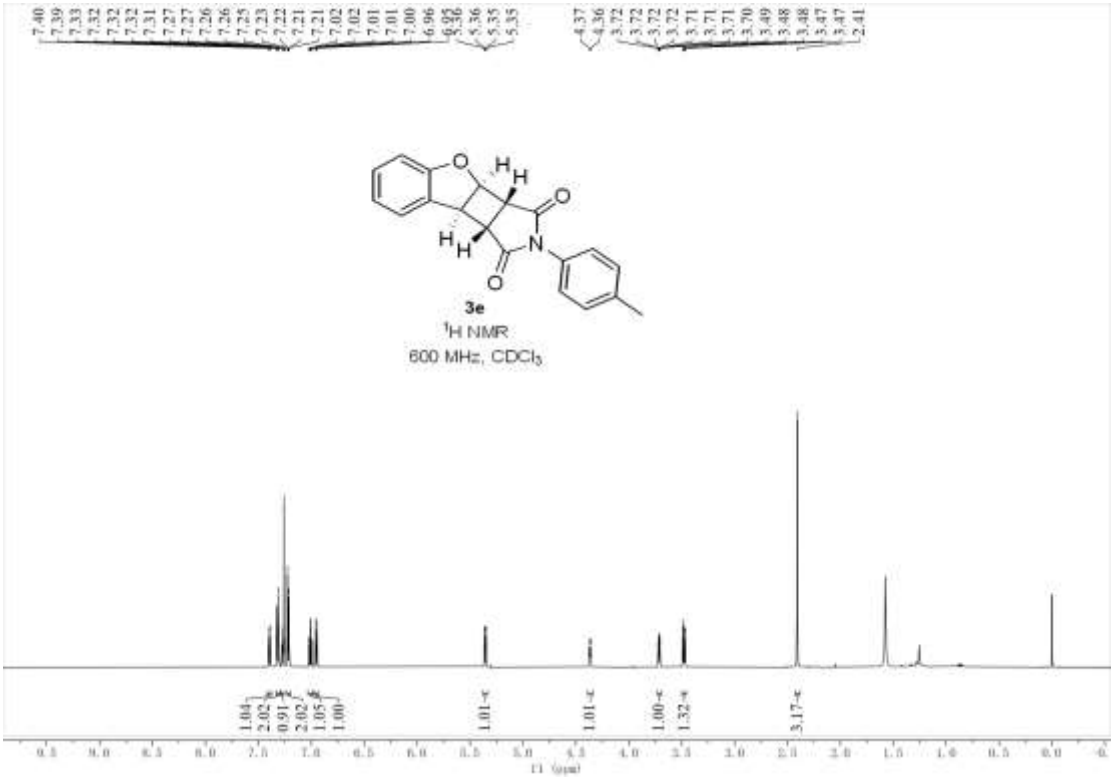
^{13}C{^{1}H} NMR Spectrum of 3d'



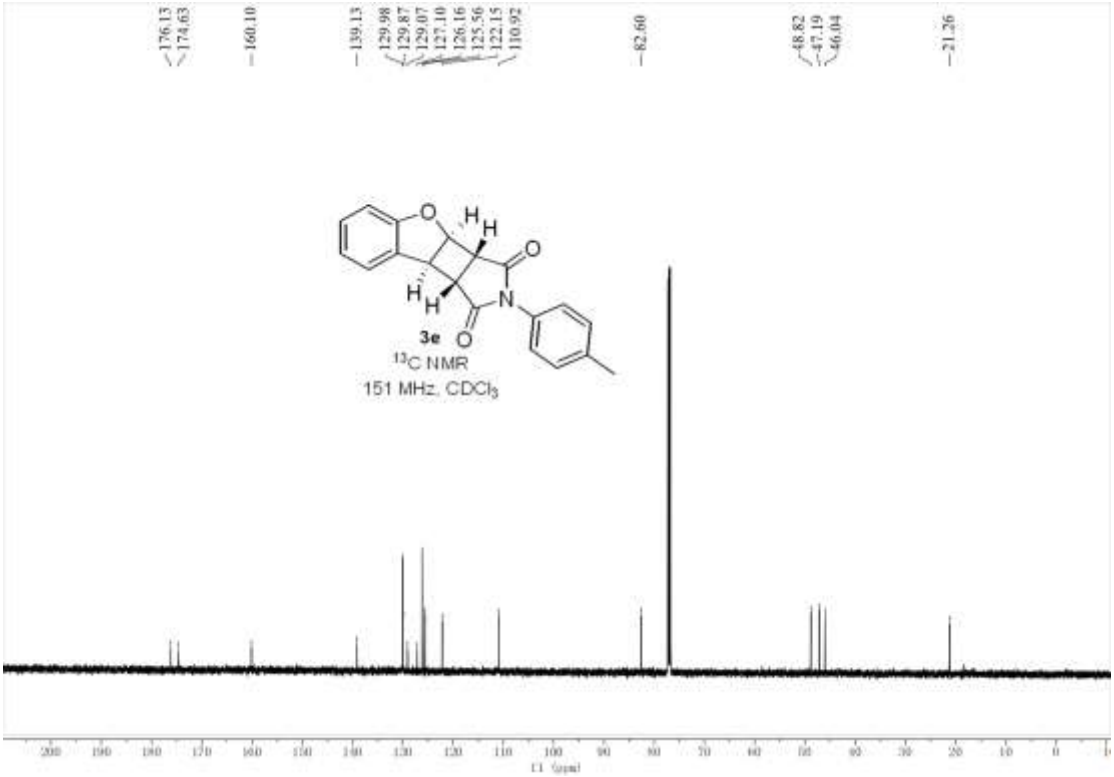
^{19}F NMR Spectrum of 3d'



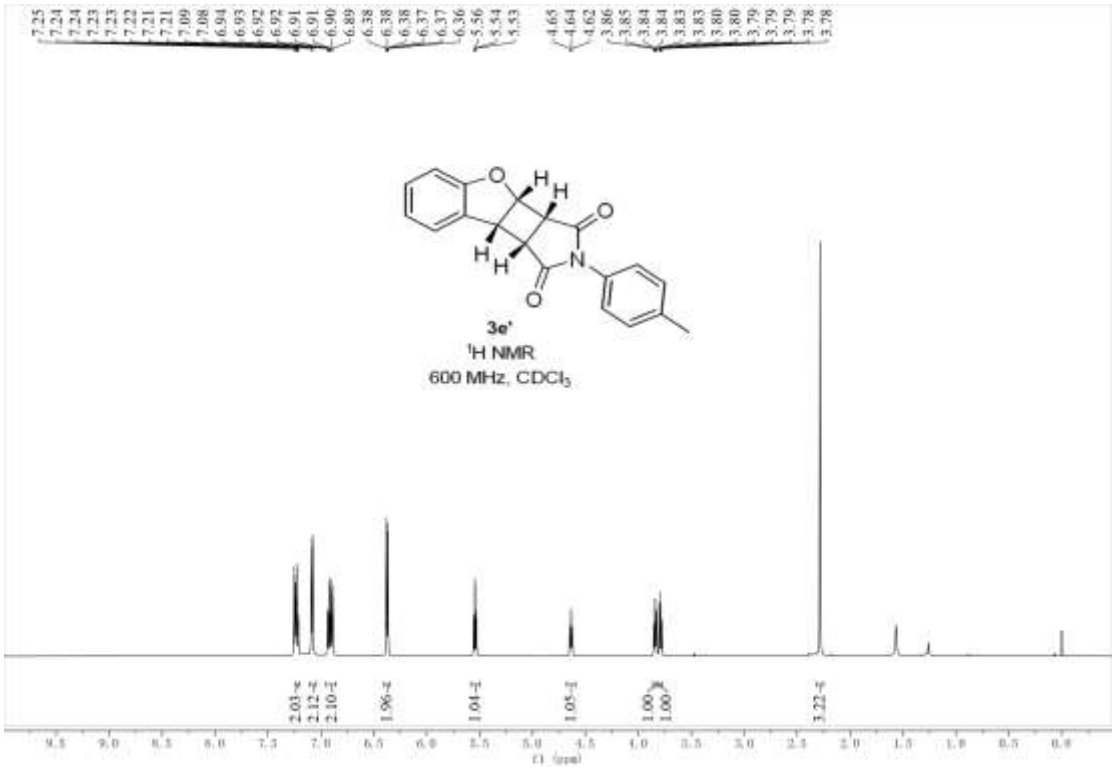
^{1}H NMR Spectrum of 3e



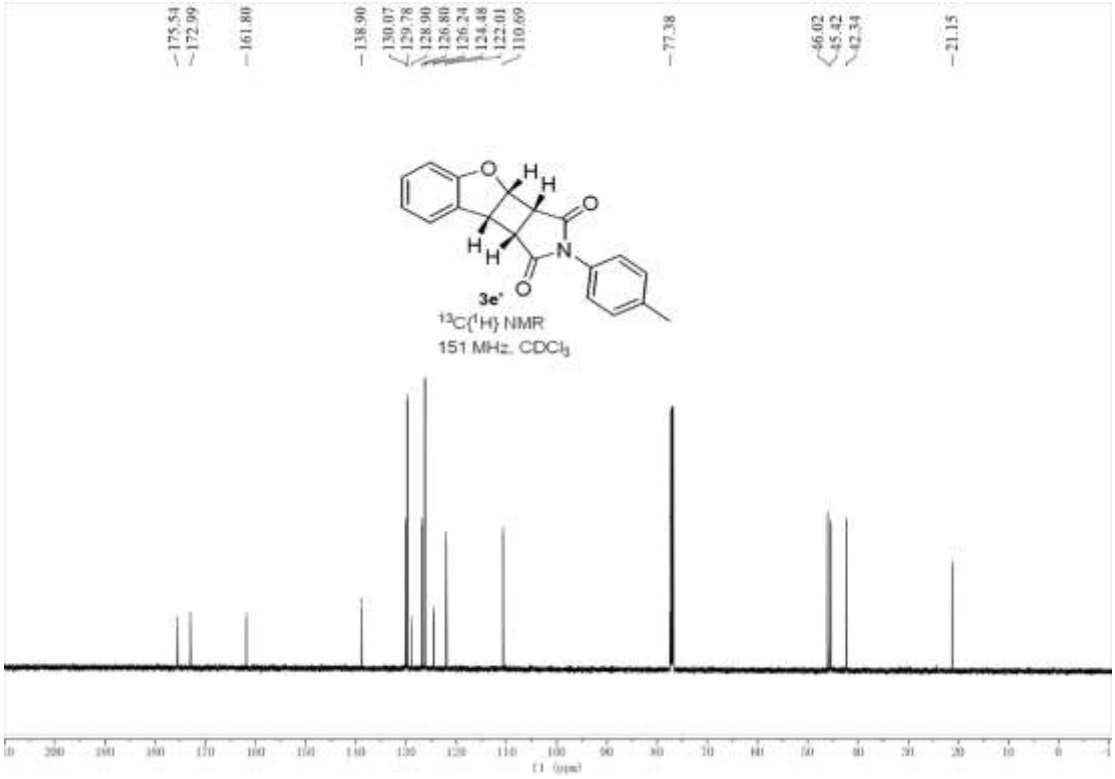
$^{13}C\{^1H\}$ NMR Spectrum of 3e



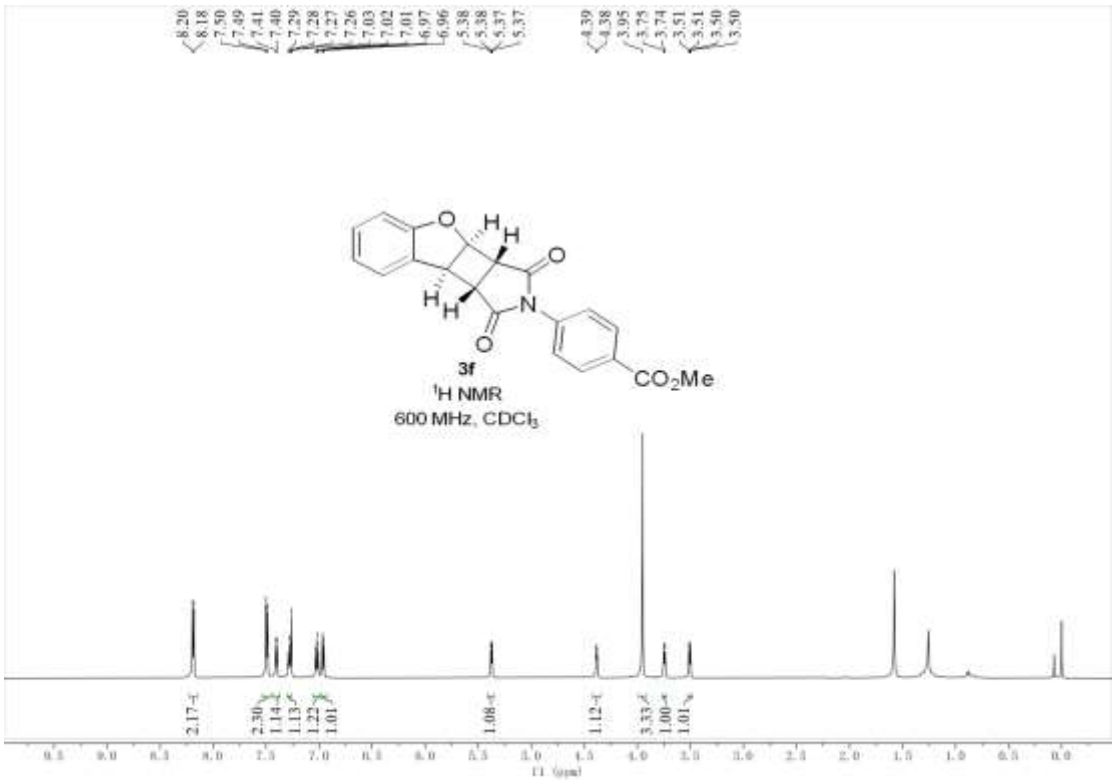
^{1}H NMR Spectrum of 3e'



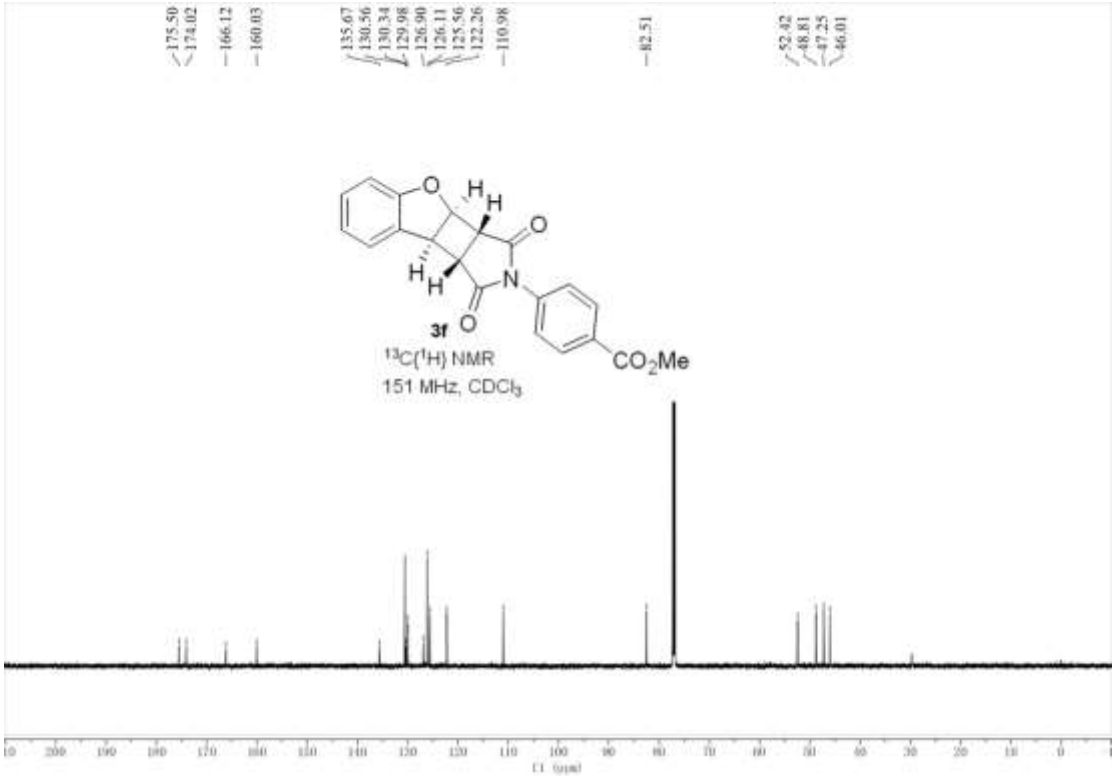
^{13}C{^{1}H} NMR Spectrum of 3e'



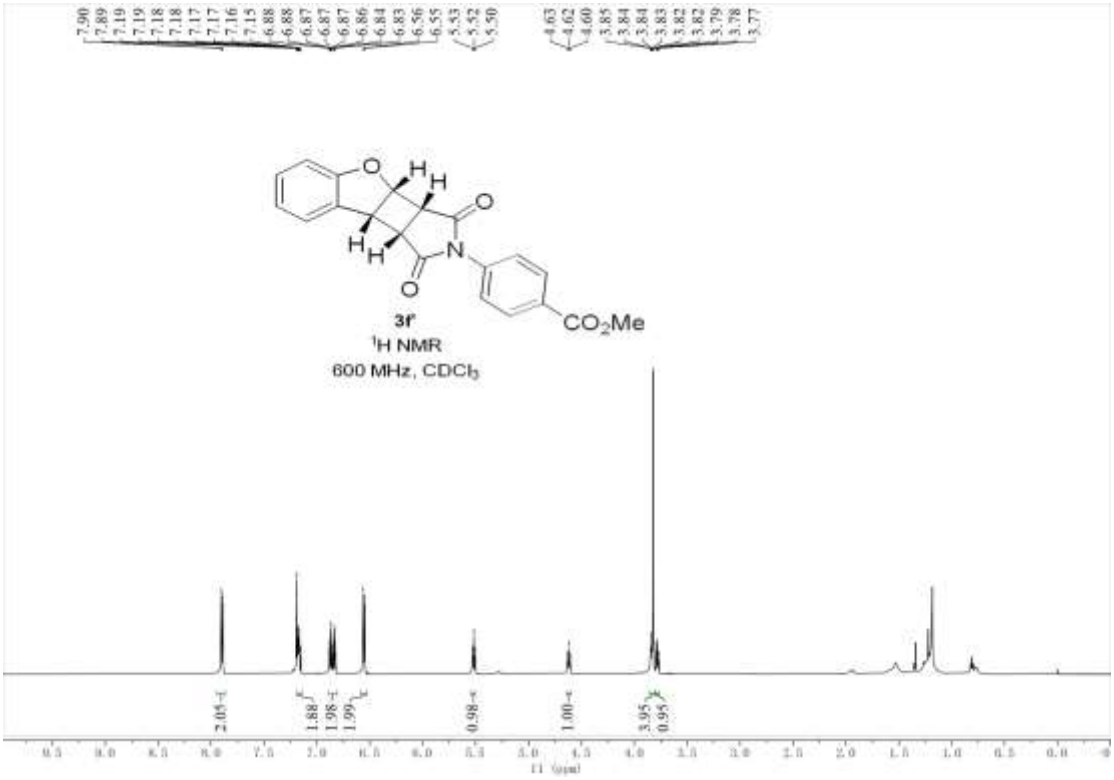
^{1}H NMR Spectrum of 3f



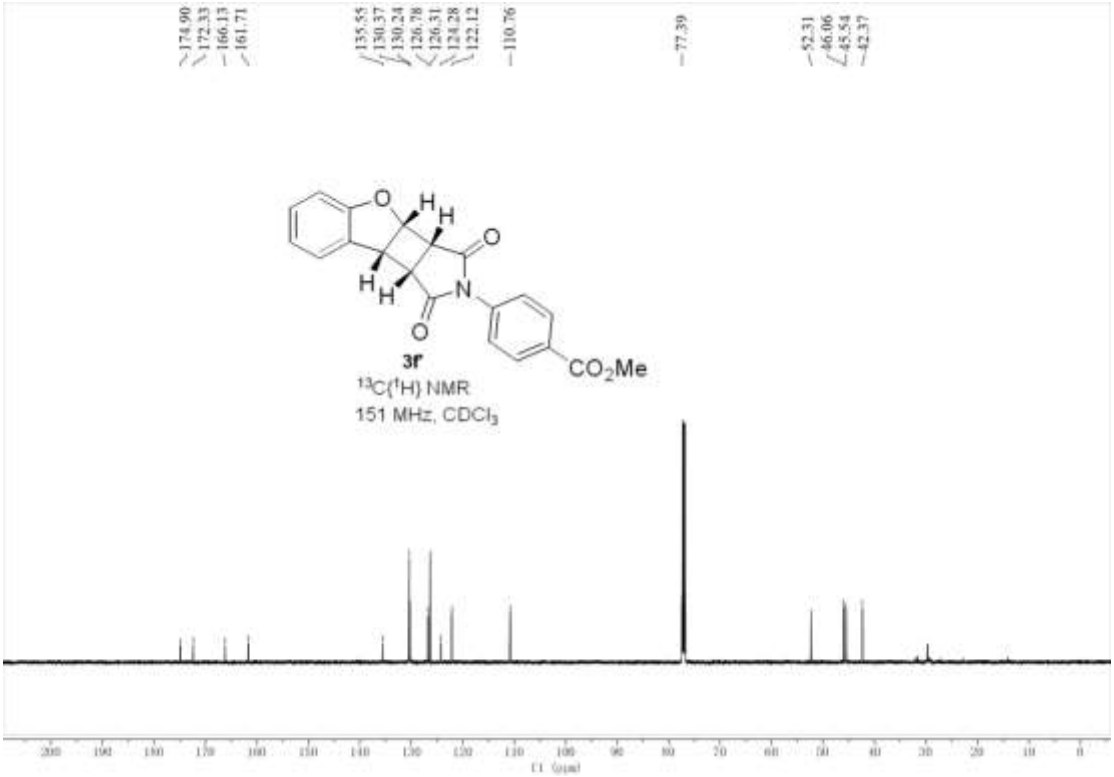
^{13}C {^{1}H} NMR Spectrum of 3f



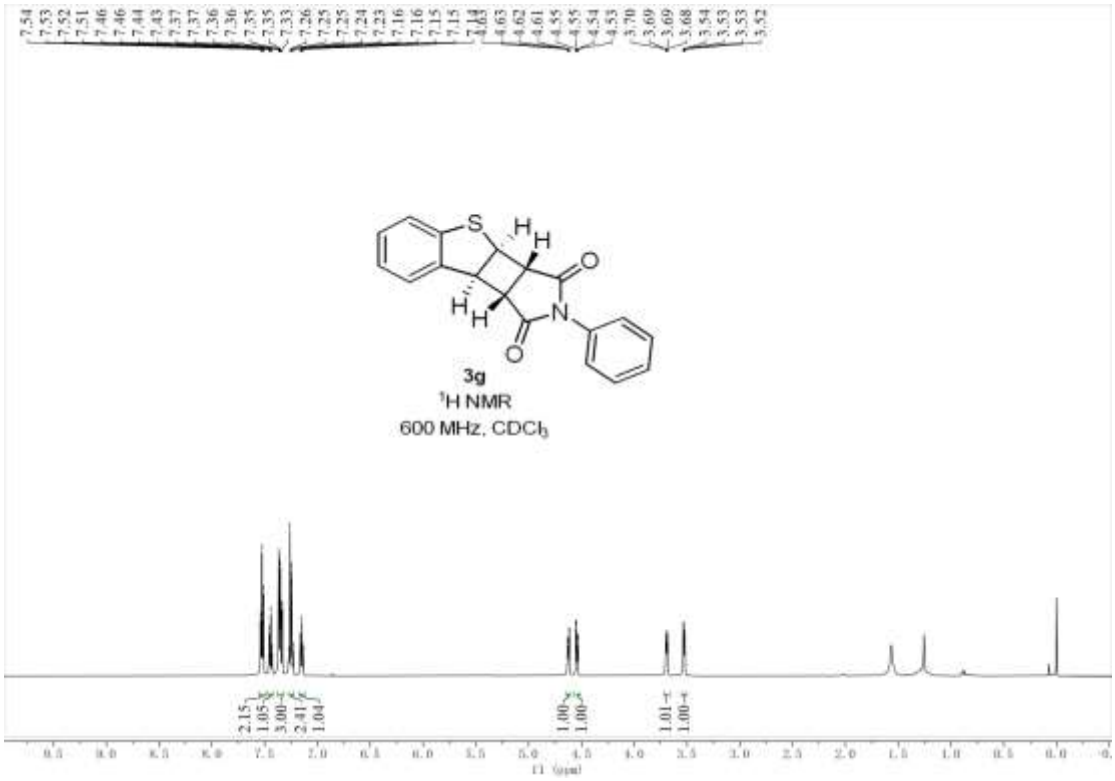
^{1}H NMR Spectrum of 3f'



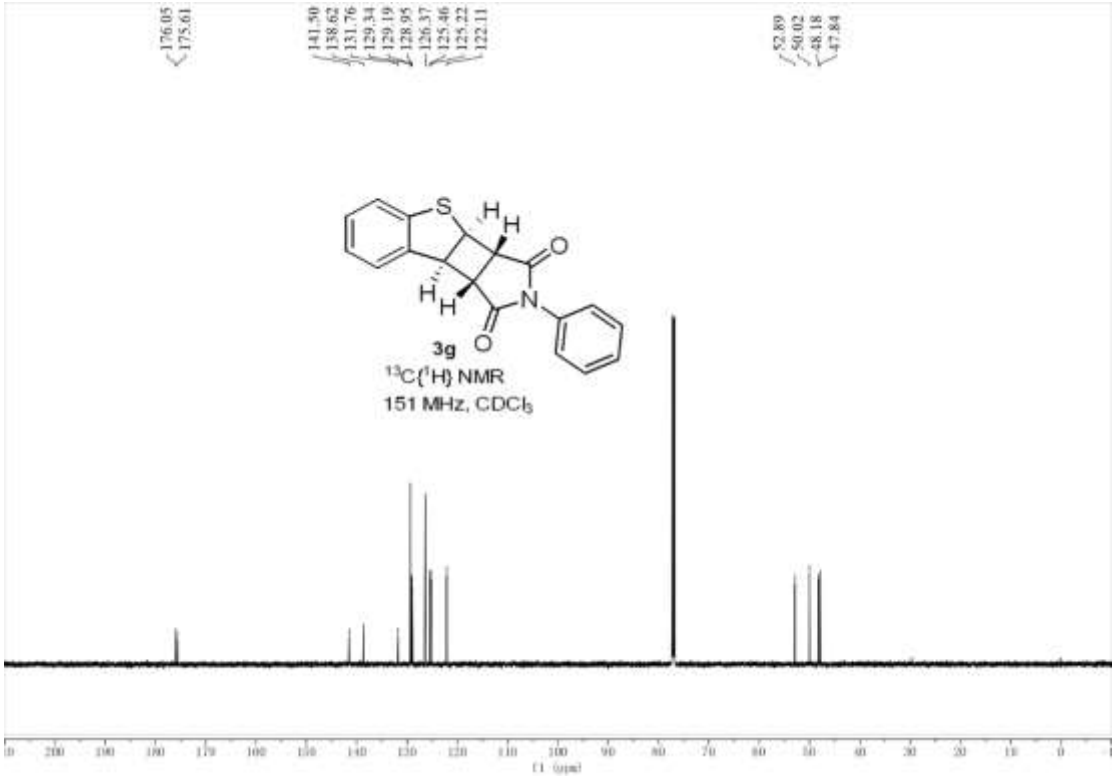
^{13}C{^{1}H} NMR Spectrum of 3f'



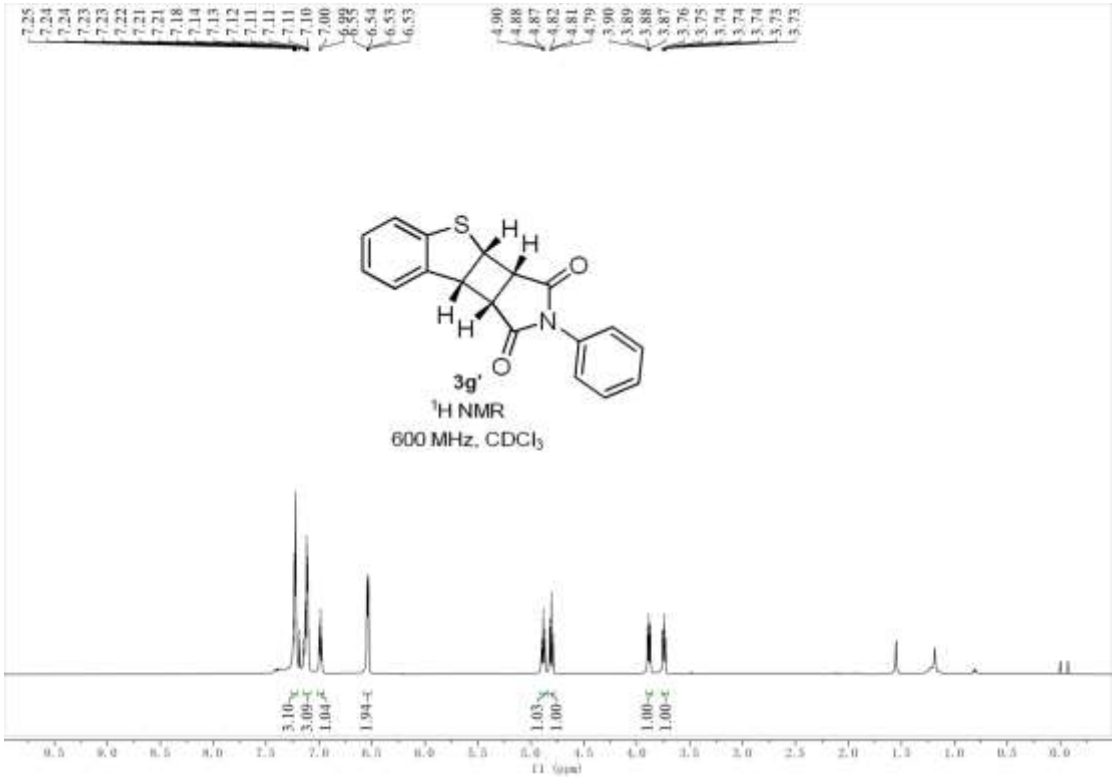
^{1}H NMR Spectrum of 3g



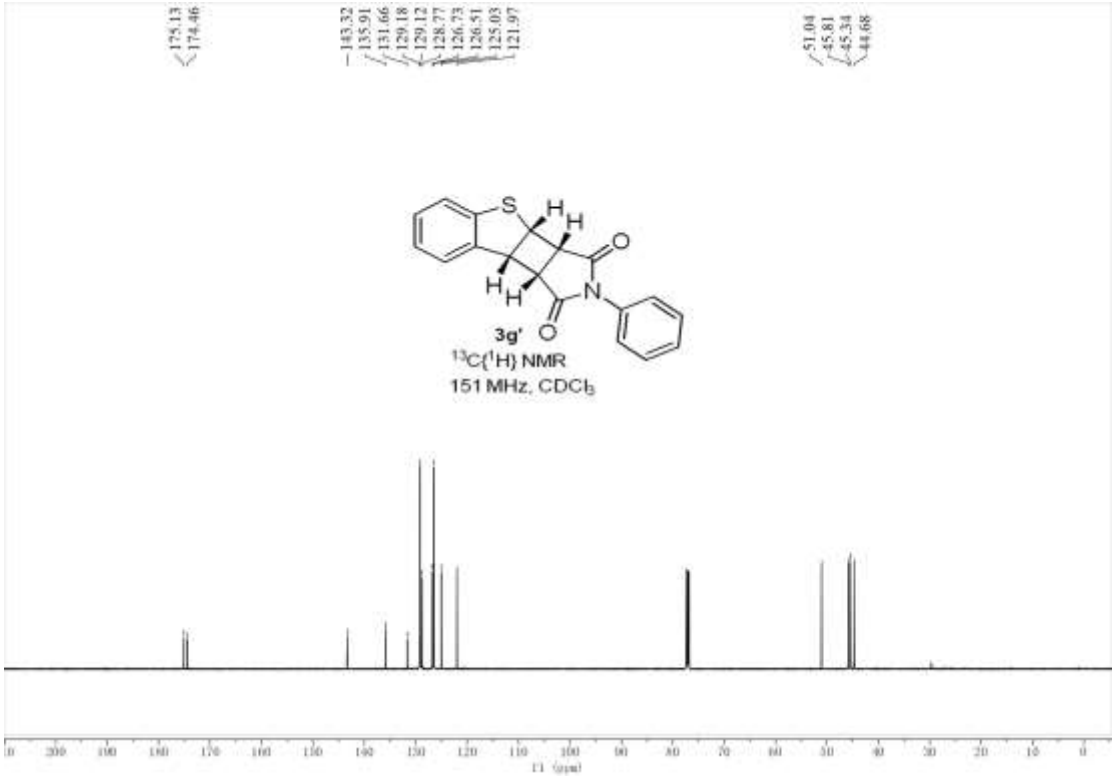
^{13}C{^{1}H} NMR Spectrum of 3g



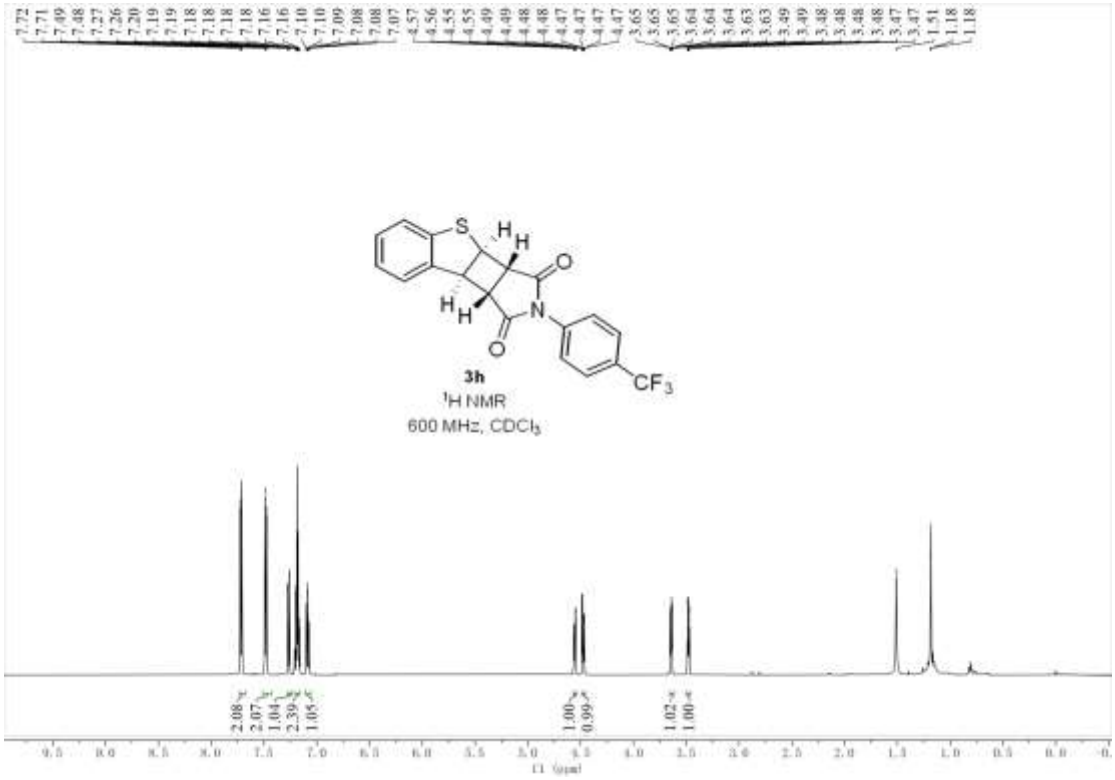
^{1}H NMR Spectrum of 3g'



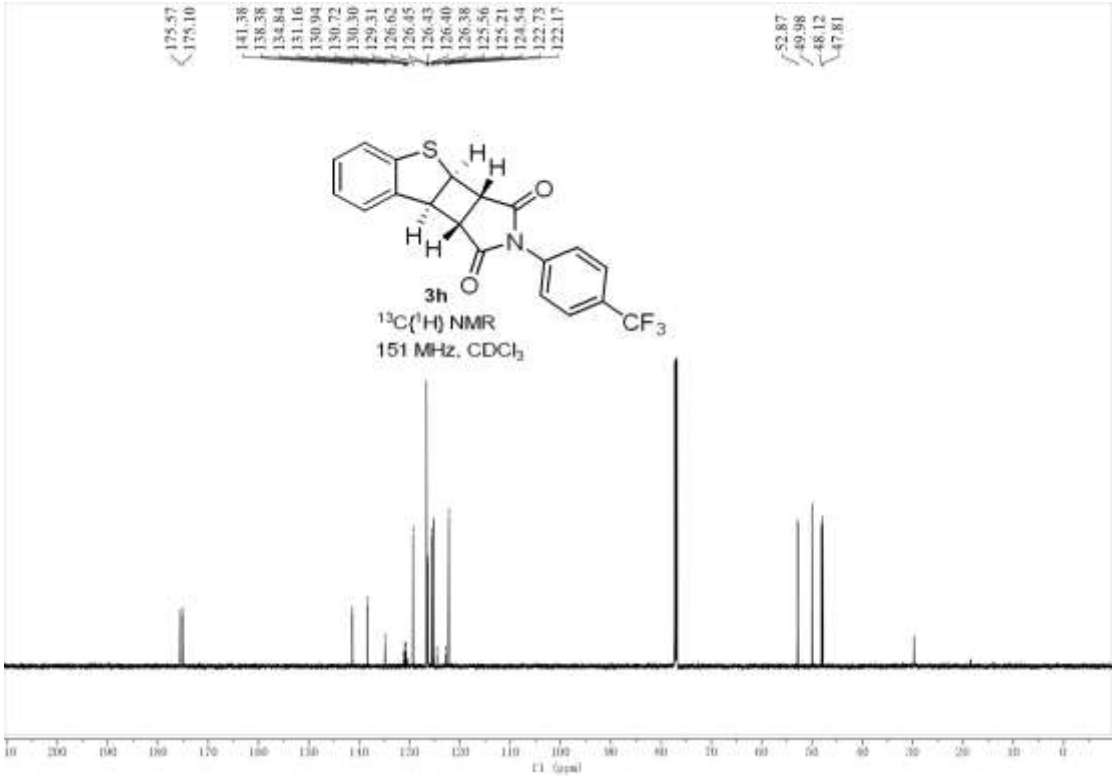
^{13}C{^{1}H} NMR Spectrum of 3g'



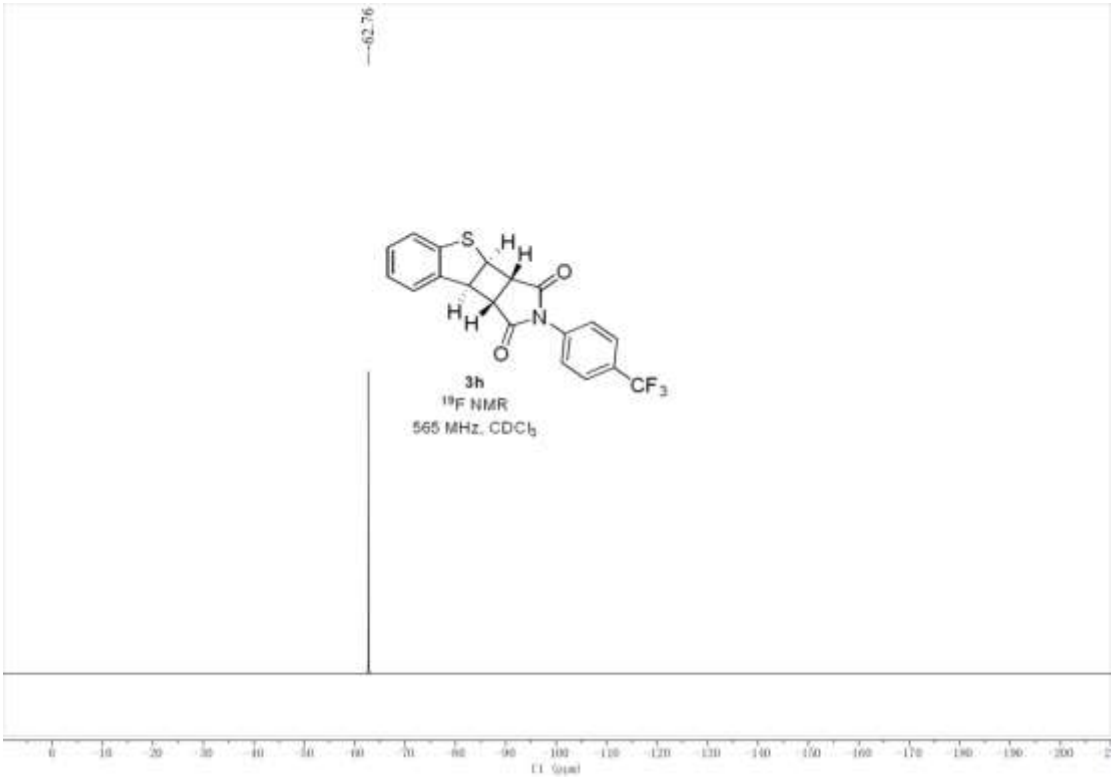
^{1}H NMR Spectrum of 3h



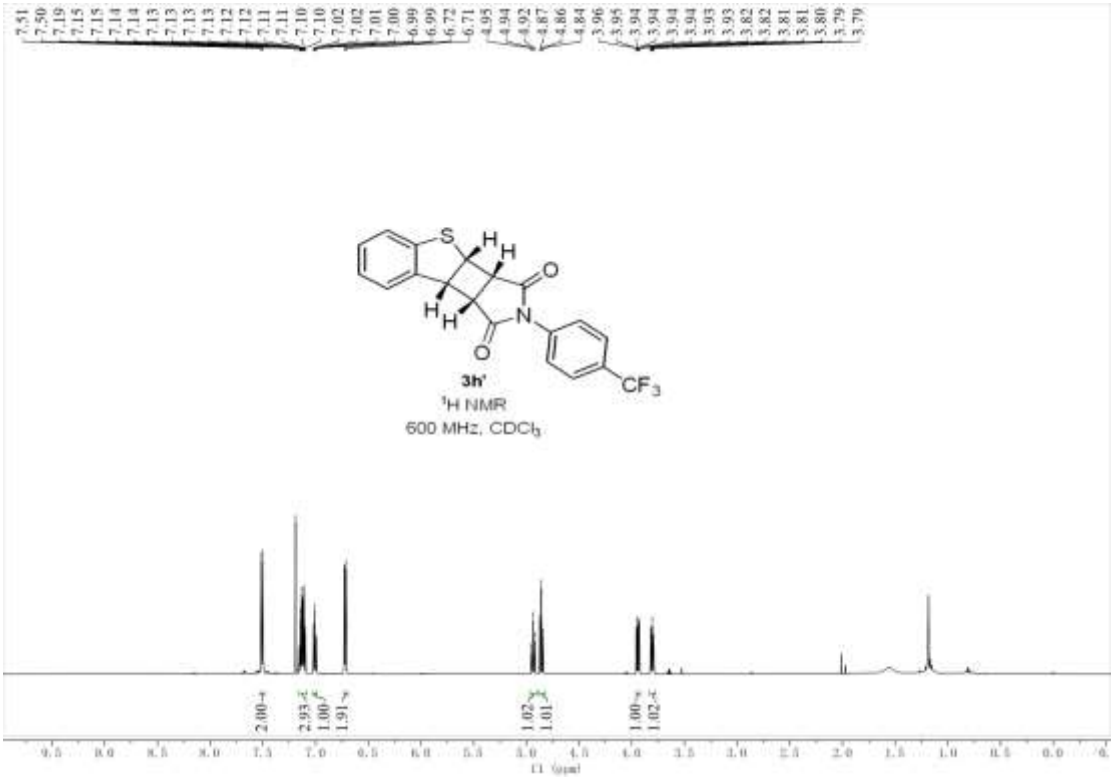
^{13}C{^{1}H} NMR Spectrum of 3h



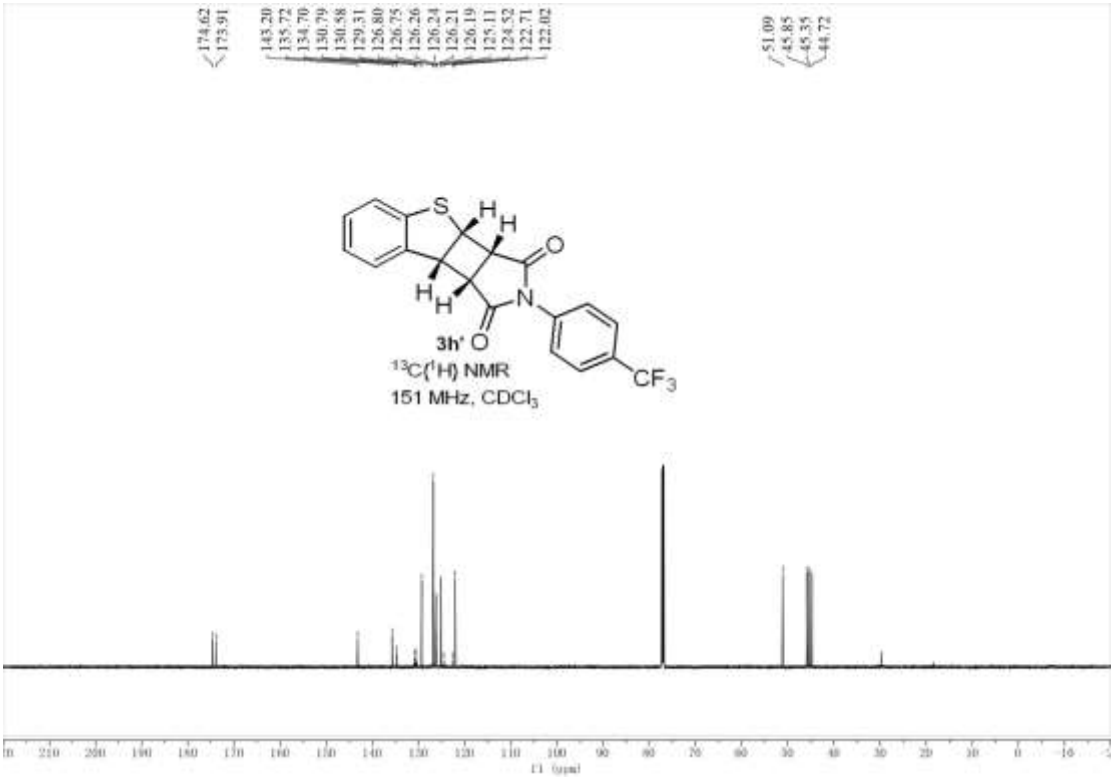
^{19}F NMR Spectrum of 3h



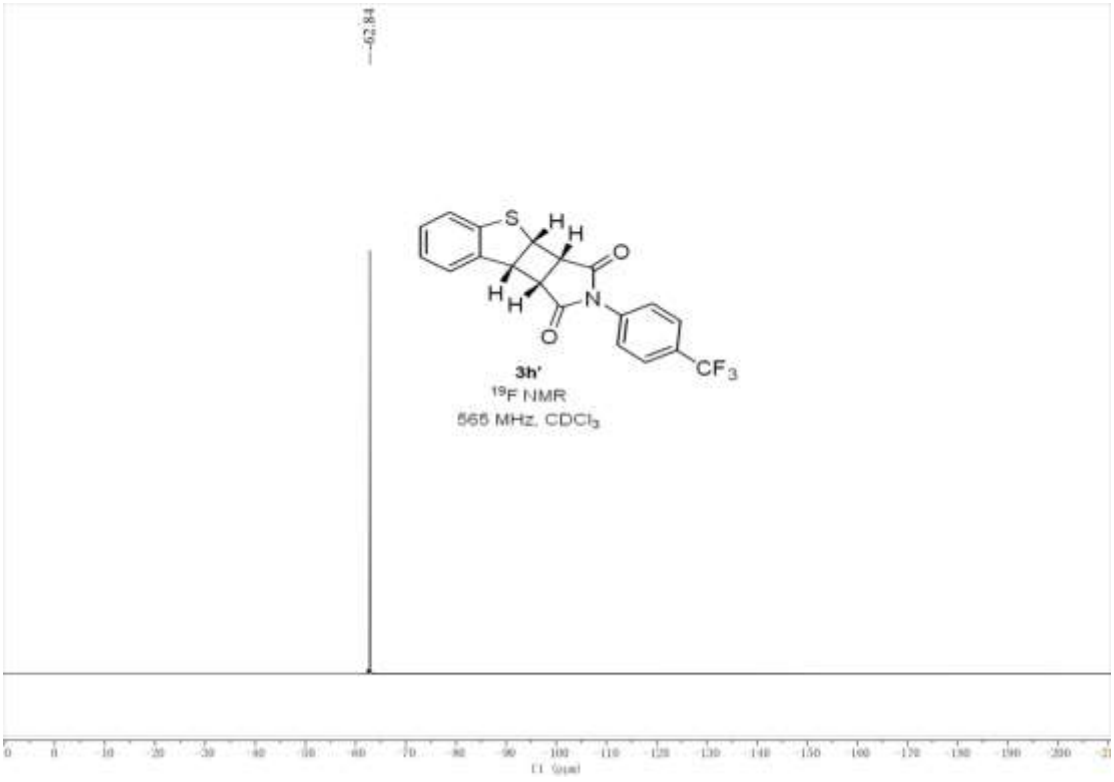
^{1}H NMR Spectrum of 3h'



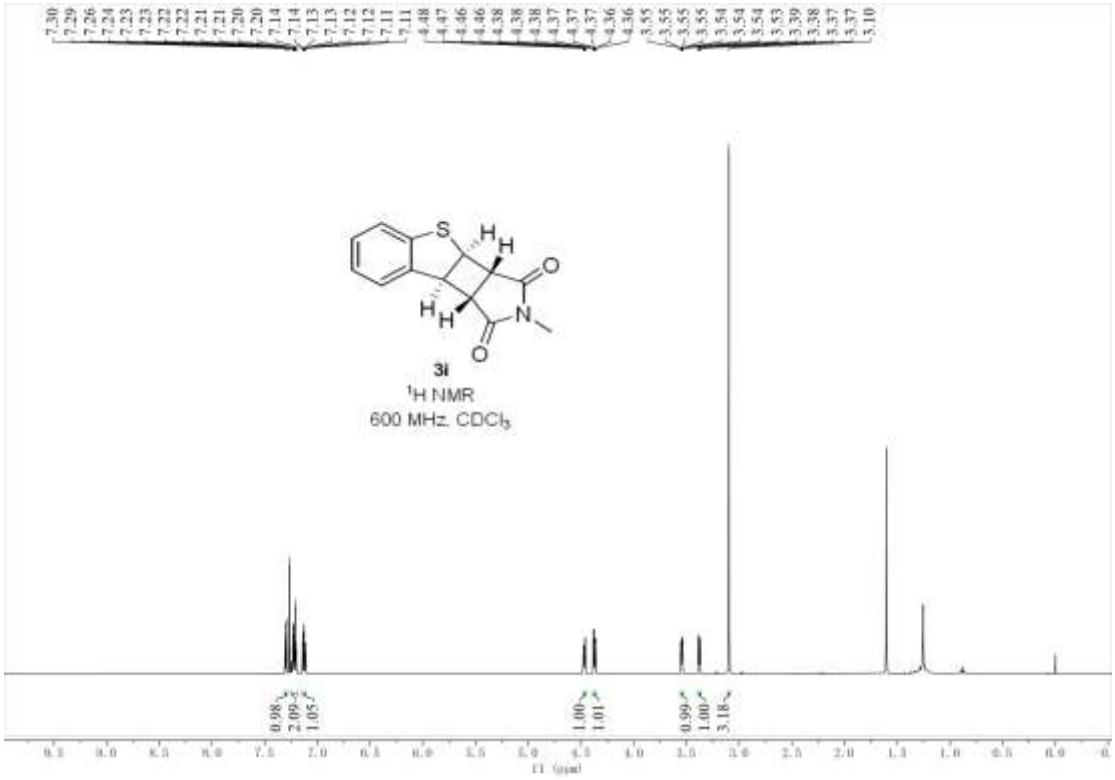
^{13}C{^{1}H} NMR Spectrum of 3h'



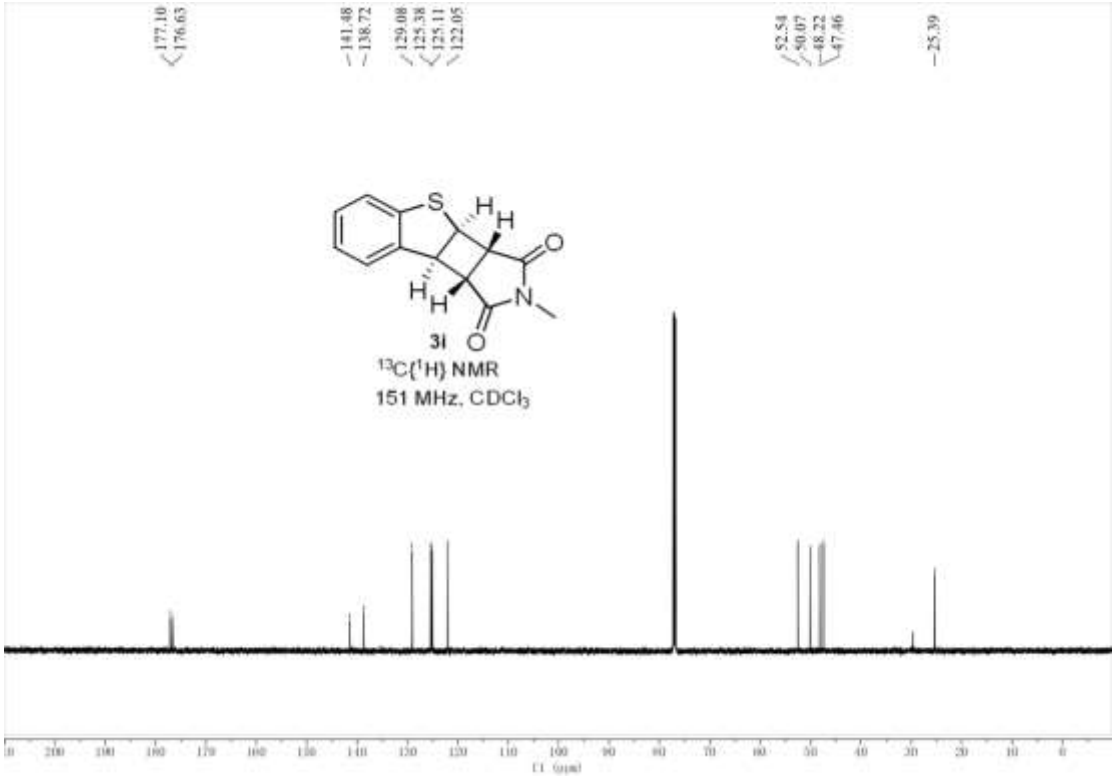
^{19}F NMR Spectrum of 3h'



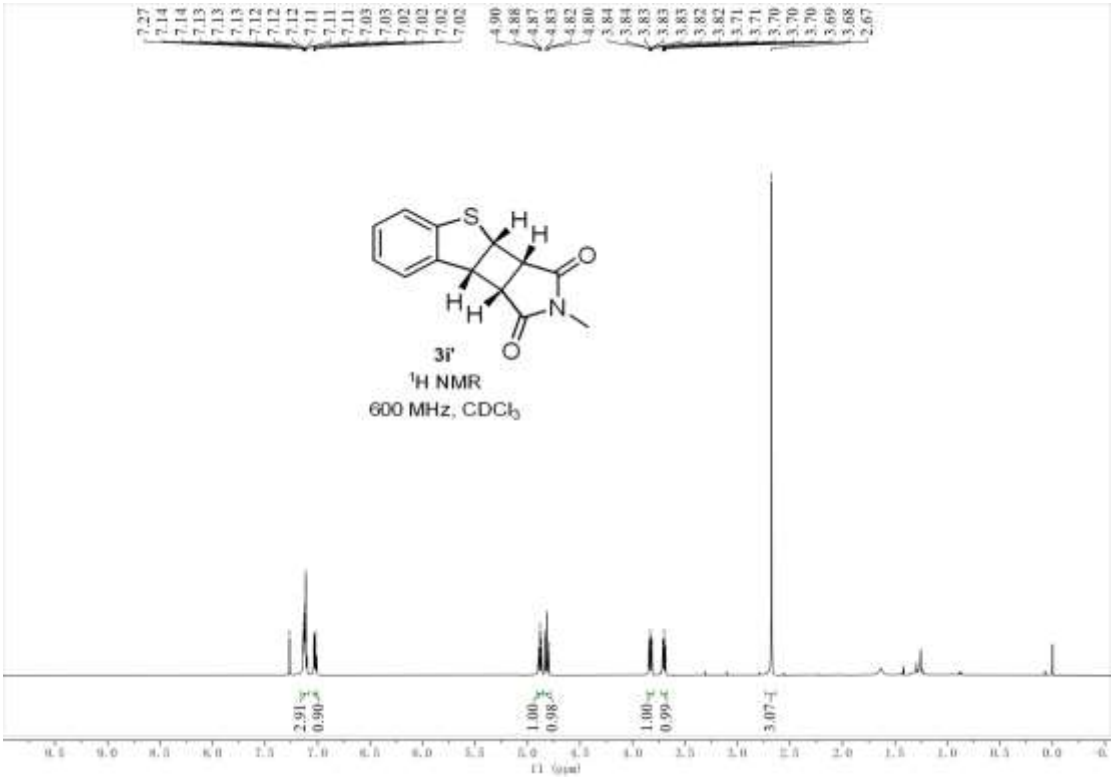
^{1}H NMR Spectrum of 3i



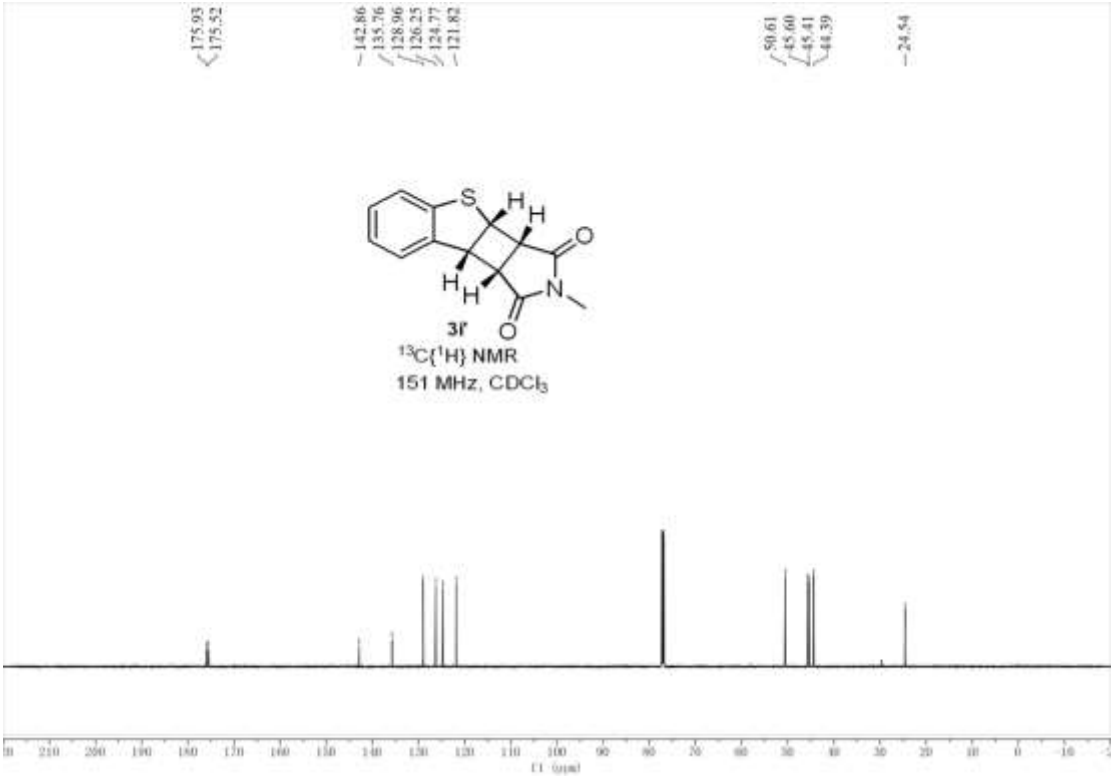
^{13}C{^{1}H} NMR Spectrum of 3i



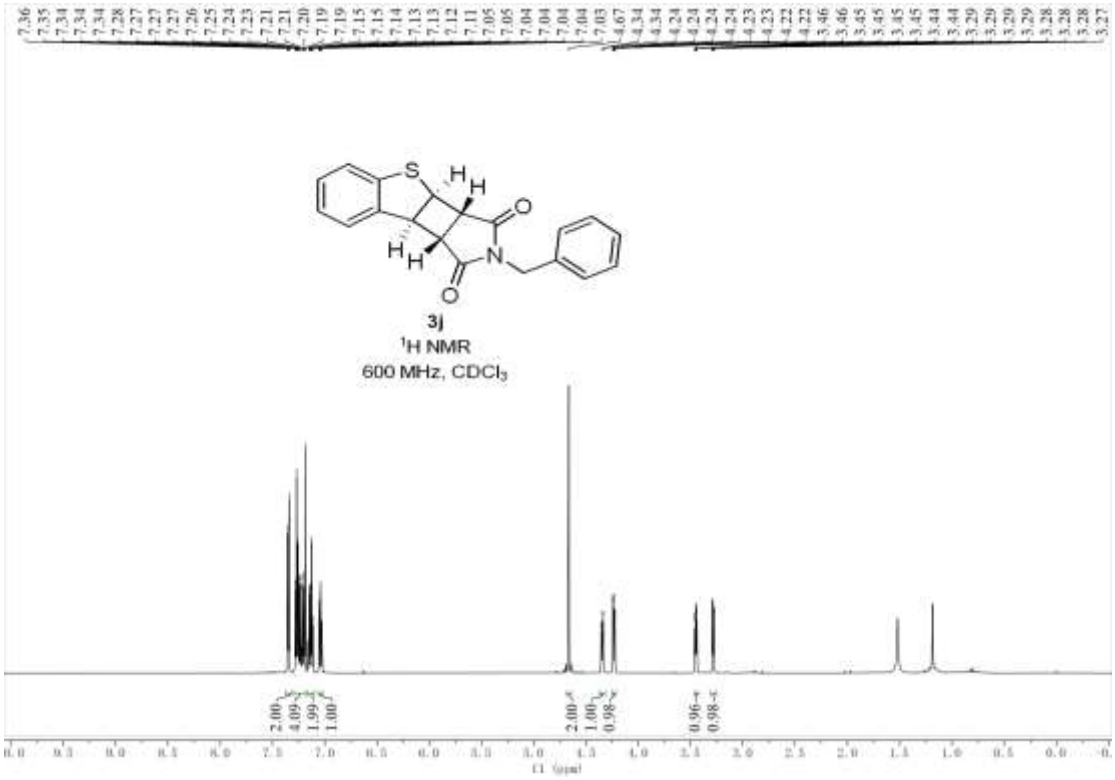
^{1}H NMR Spectrum of 3i'



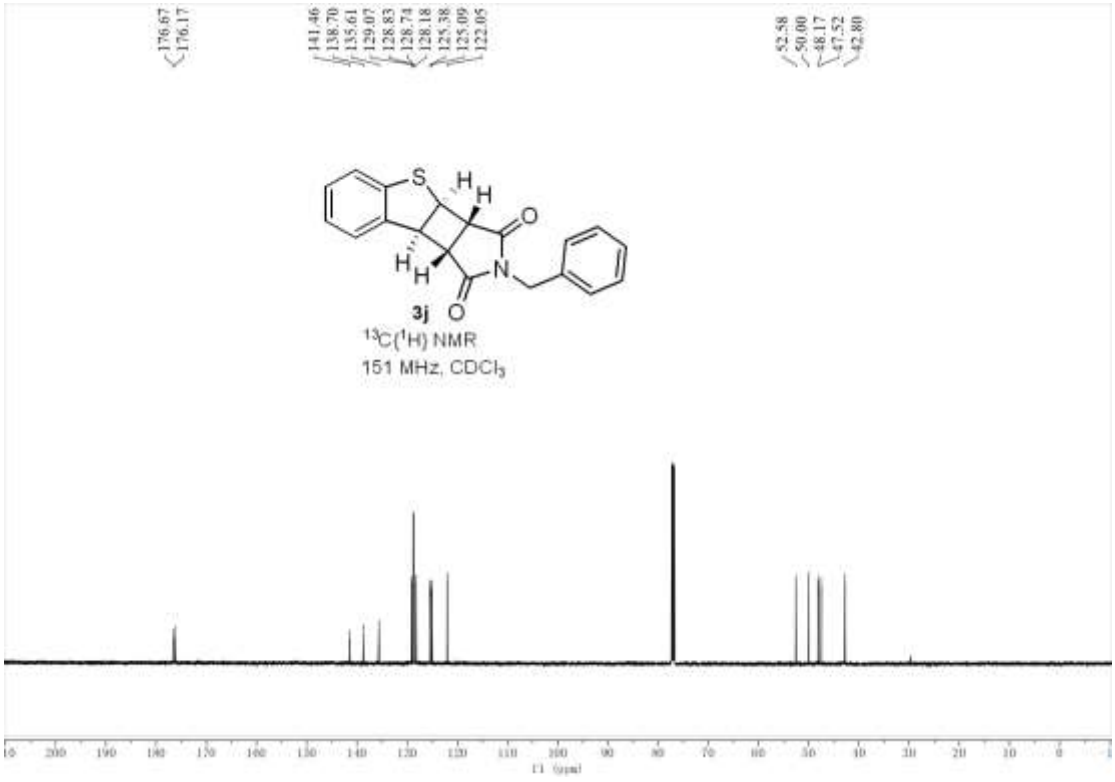
^{13}C{^{1}H} NMR Spectrum of 3i'



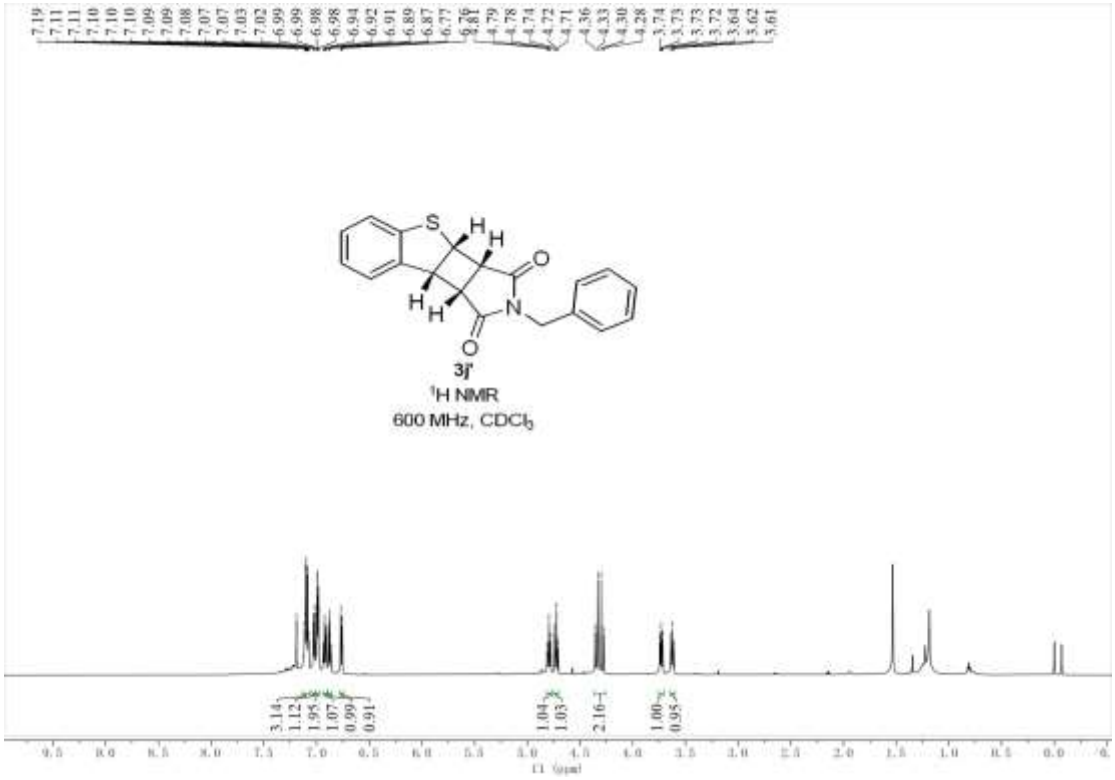
^{1}H NMR Spectrum of 3j



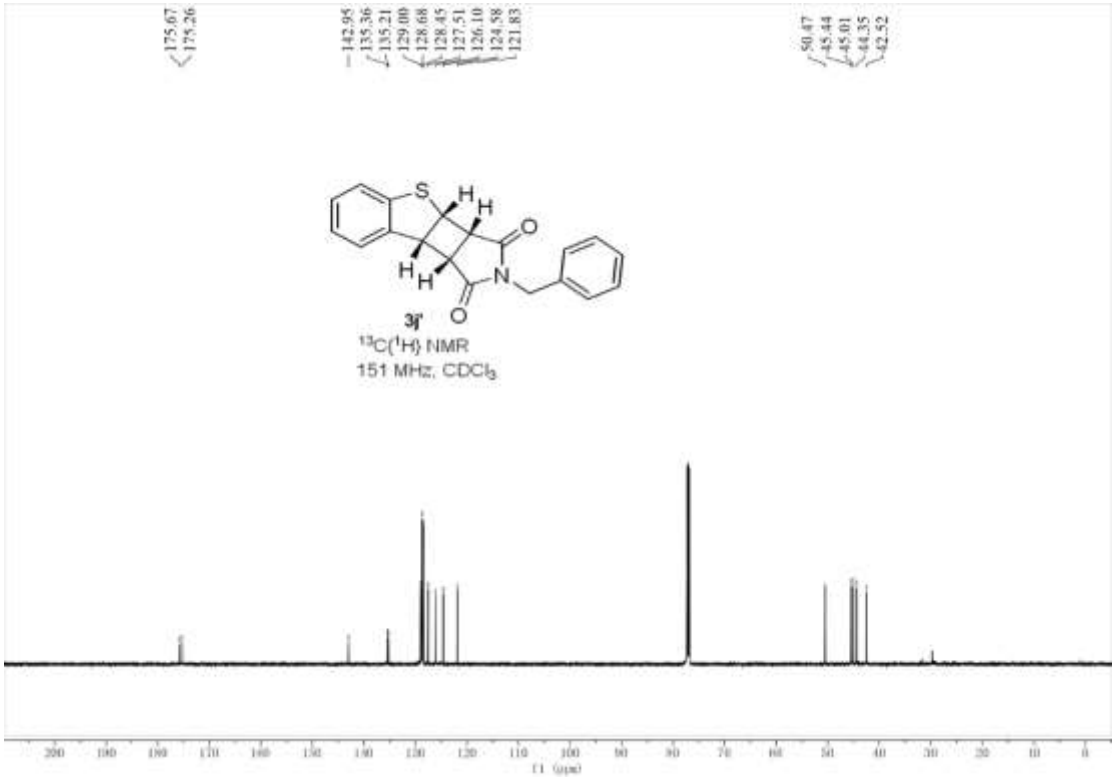
$^{13}C\{^{1}H\}$ NMR Spectrum of 3j



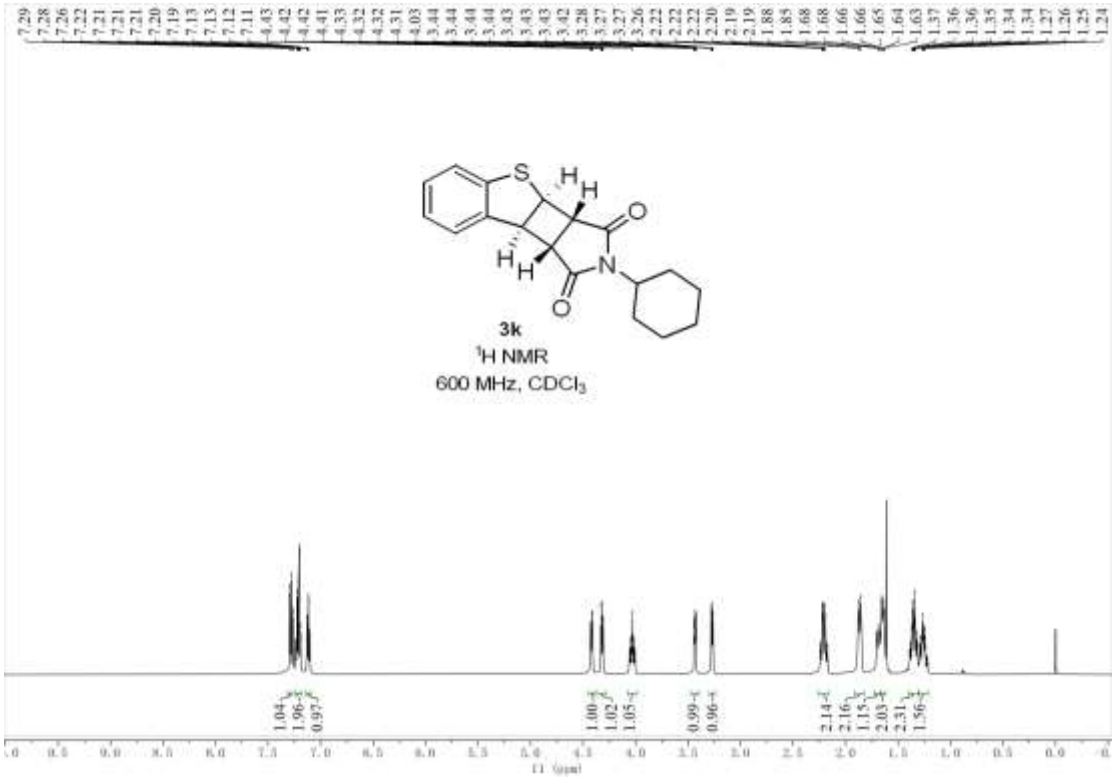
^{1}H NMR Spectrum of 3j'



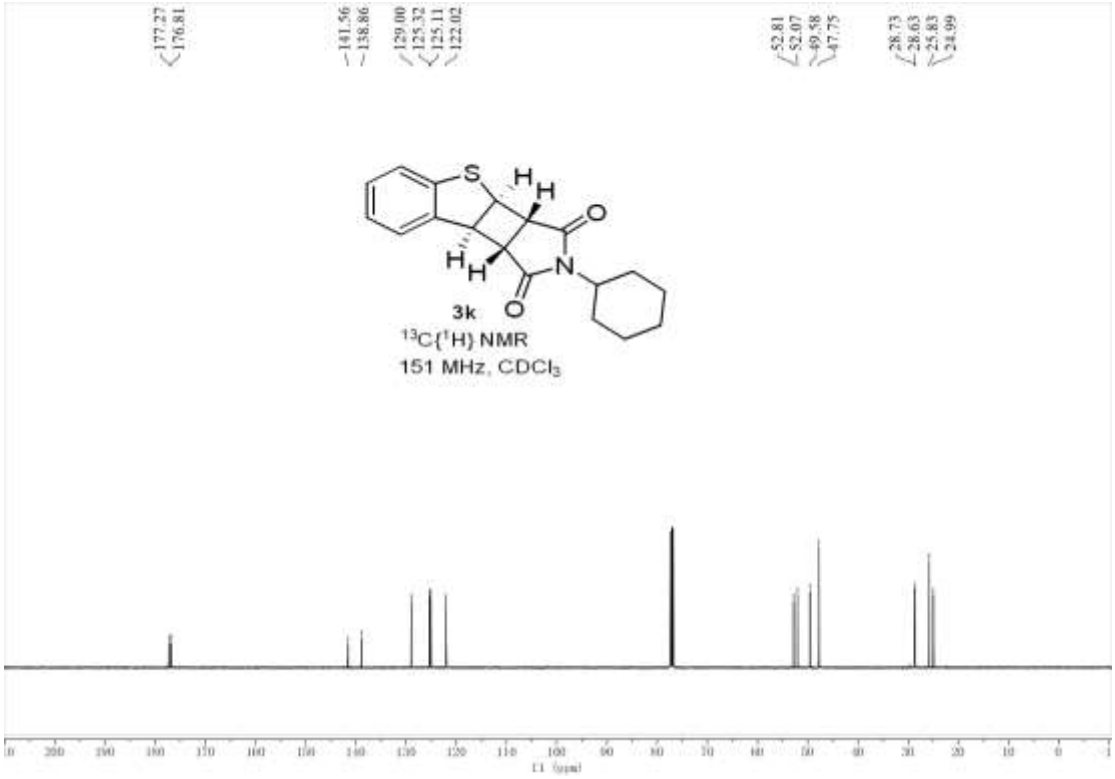
$^{13}C\{^{1}H\}$ NMR Spectrum of 3j'



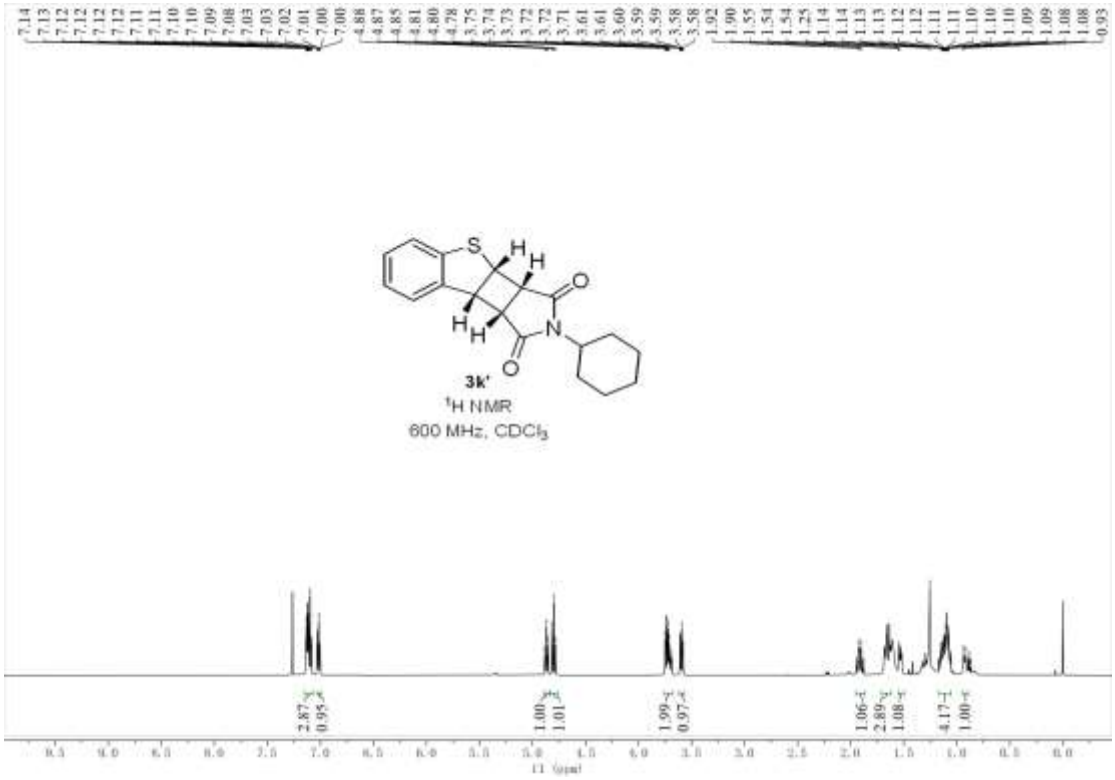
^{1}H NMR Spectrum of 3k



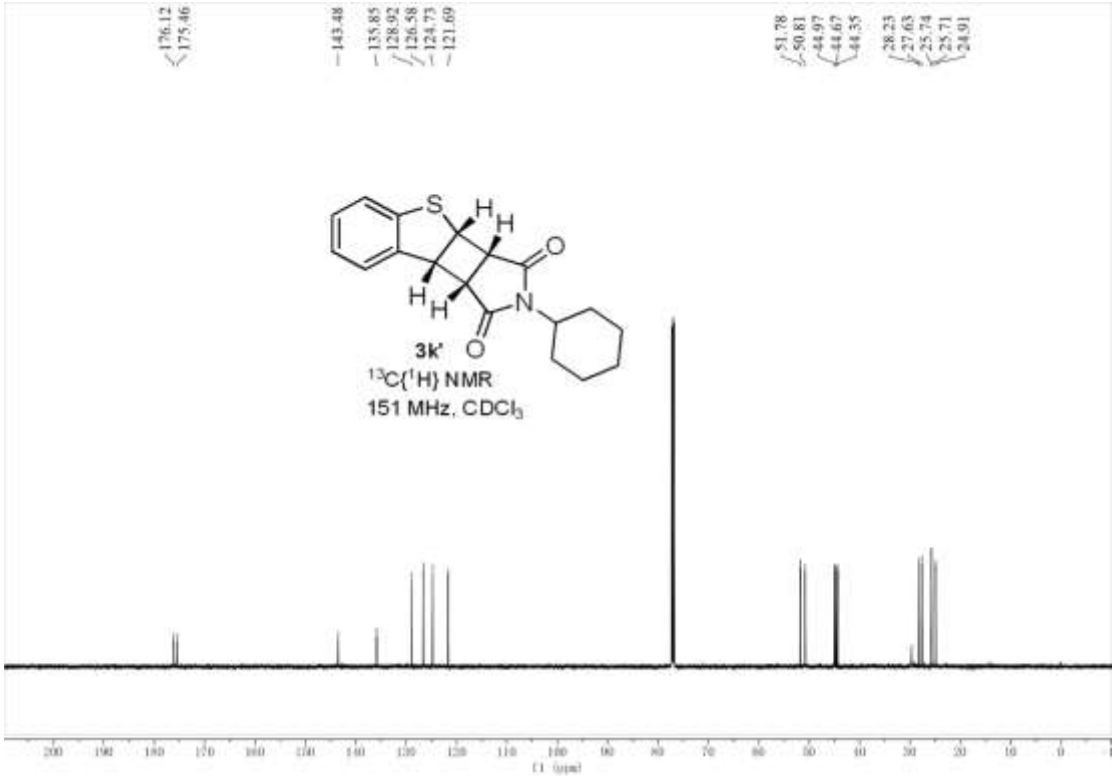
^{13}C{^{1}H} NMR Spectrum of 3k



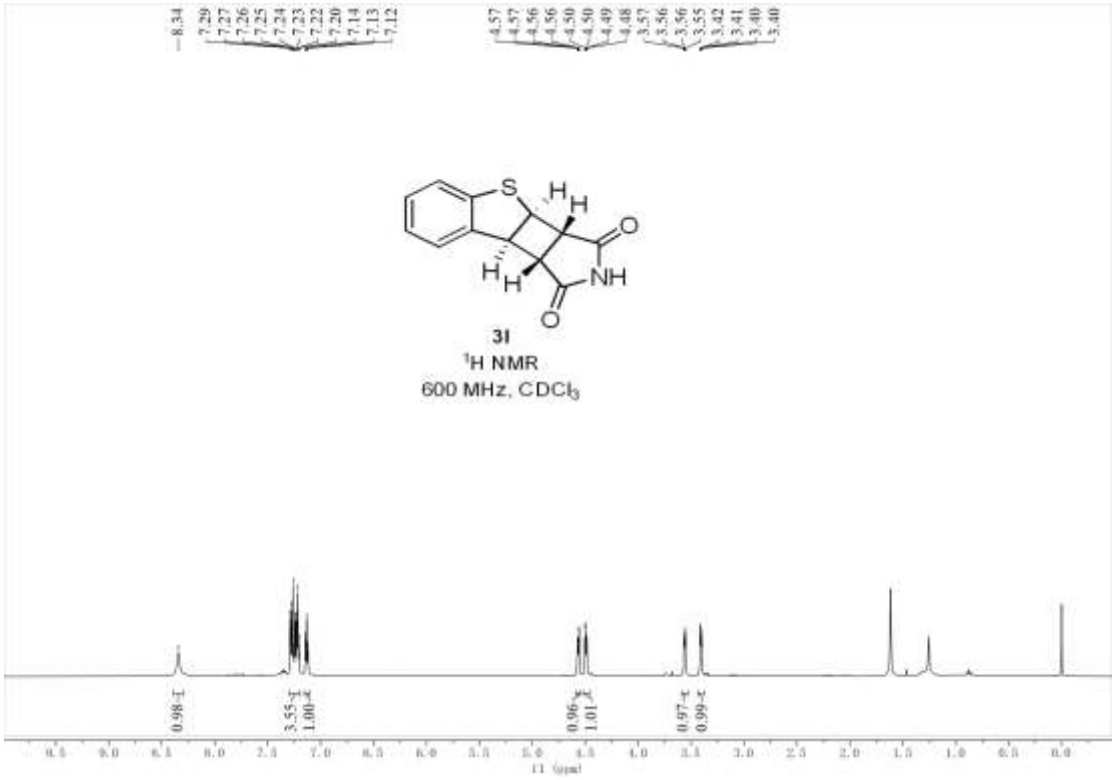
^{1}H NMR Spectrum of 3k'



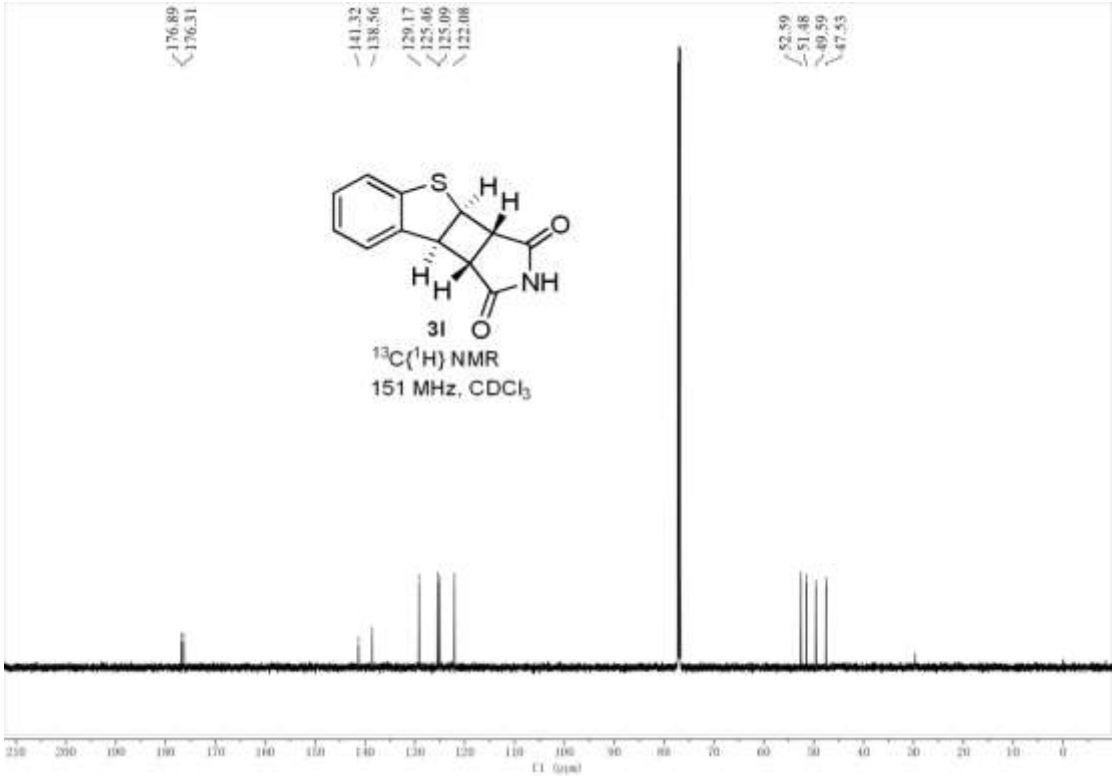
^{13}C{^{1}H} NMR Spectrum of 3k'



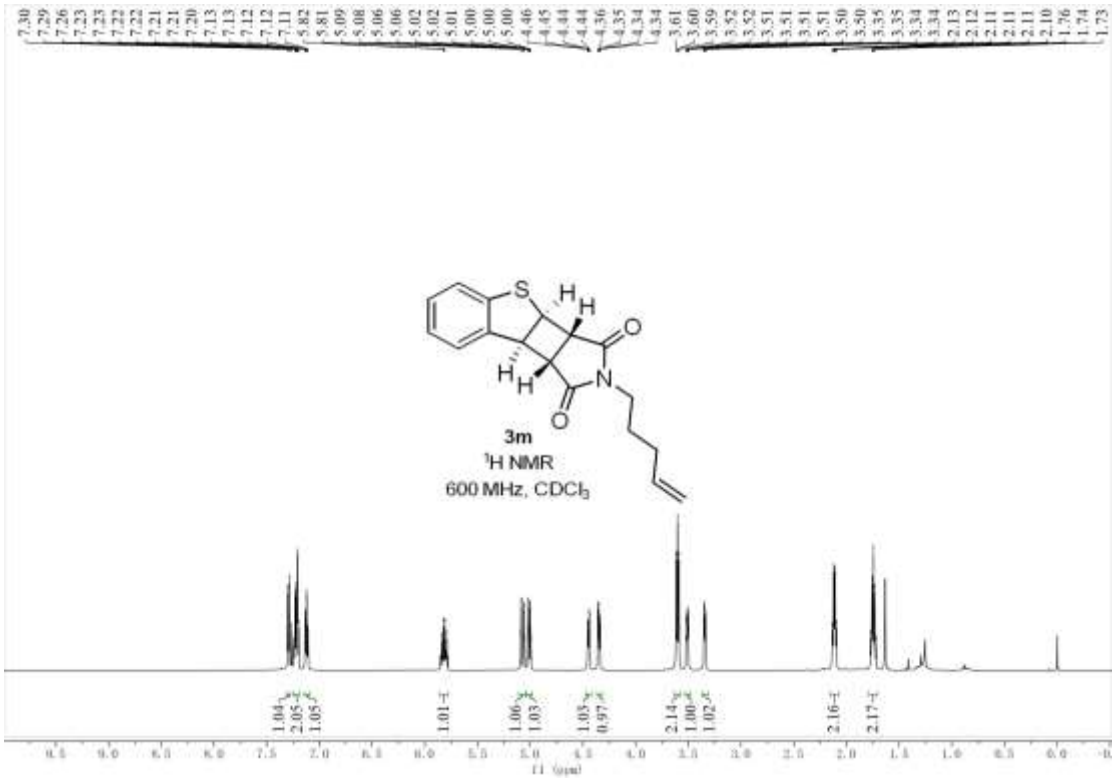
^{1}H NMR Spectrum of 3l



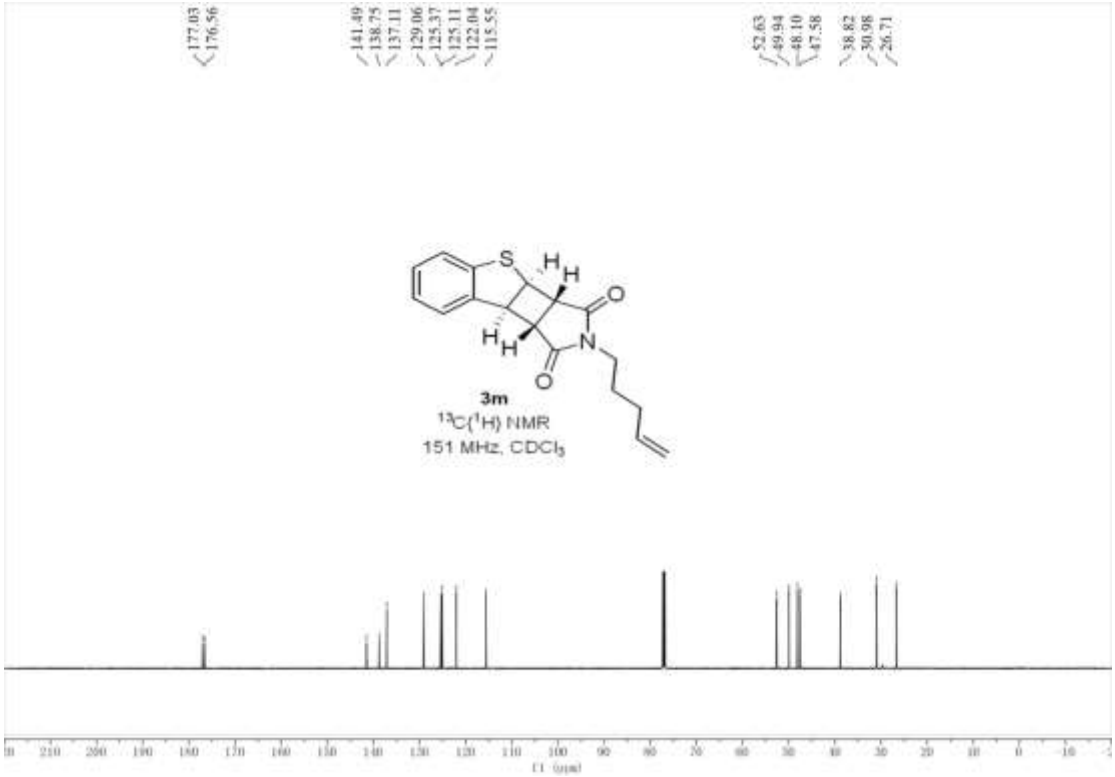
$^{13}C\{^{1}H\}$ NMR Spectrum of 3l



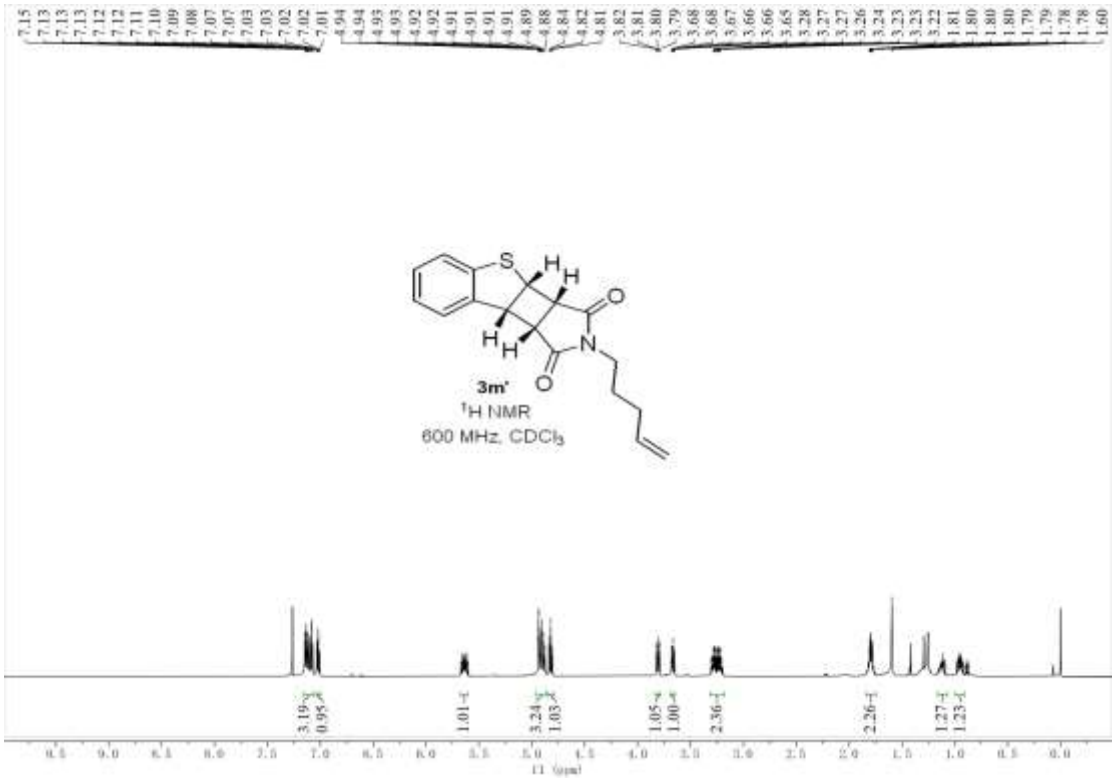
^{1}H NMR Spectrum of 3m



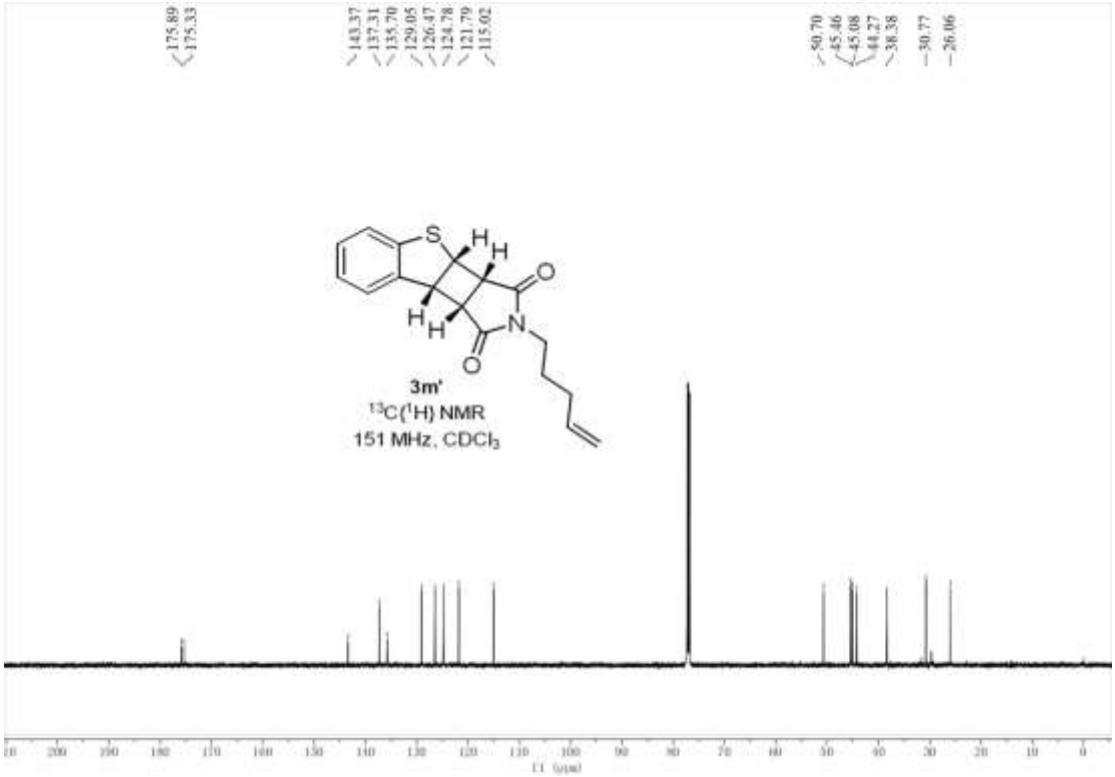
^{13}C{^{1}H} NMR Spectrum of 3m



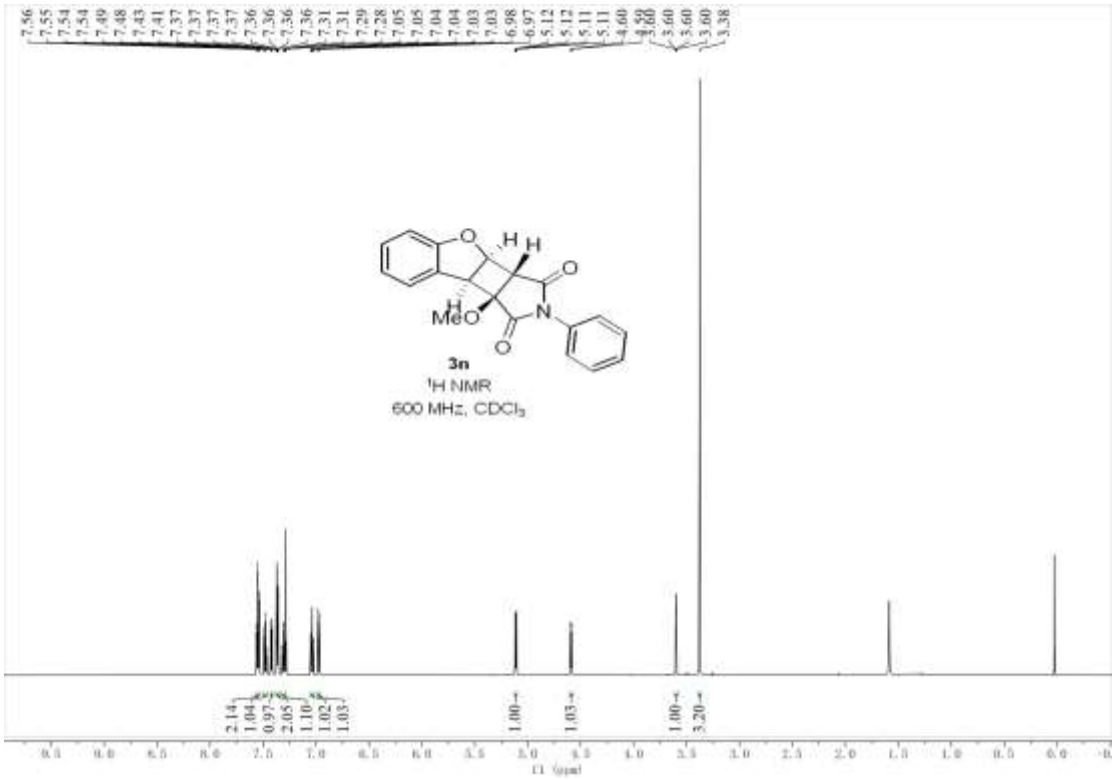
^{1}H NMR Spectrum of 3m'



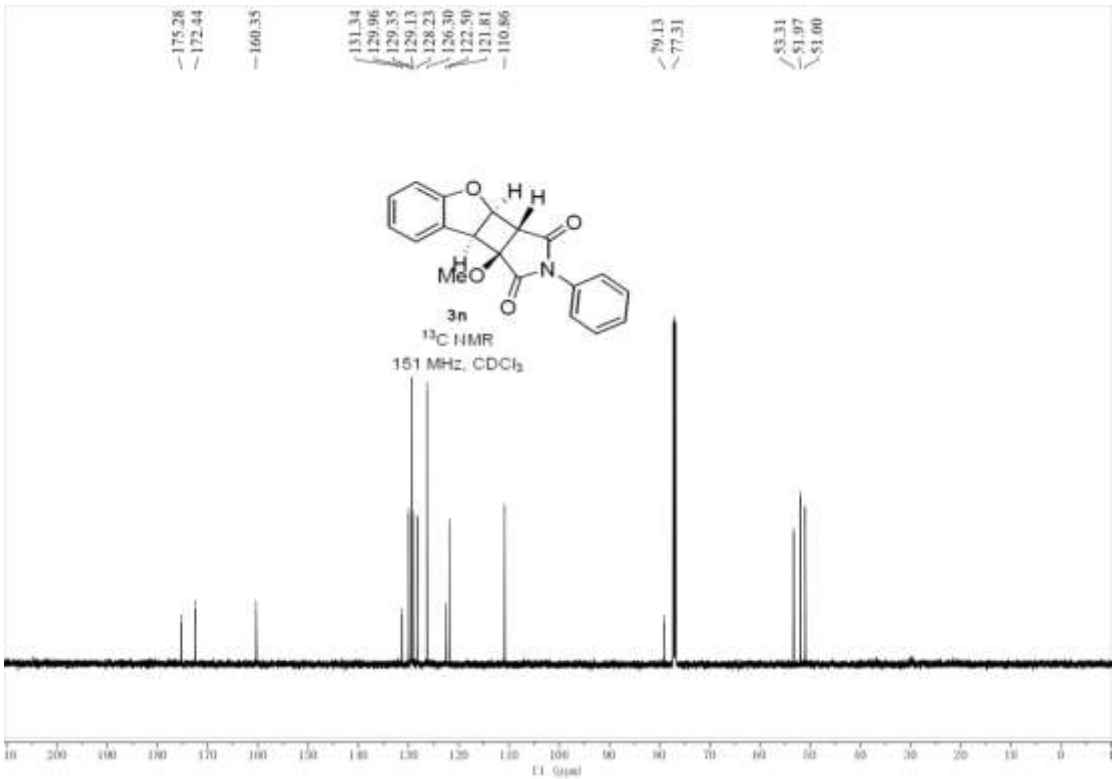
^{13}C{^{1}H} NMR Spectrum of 3m'



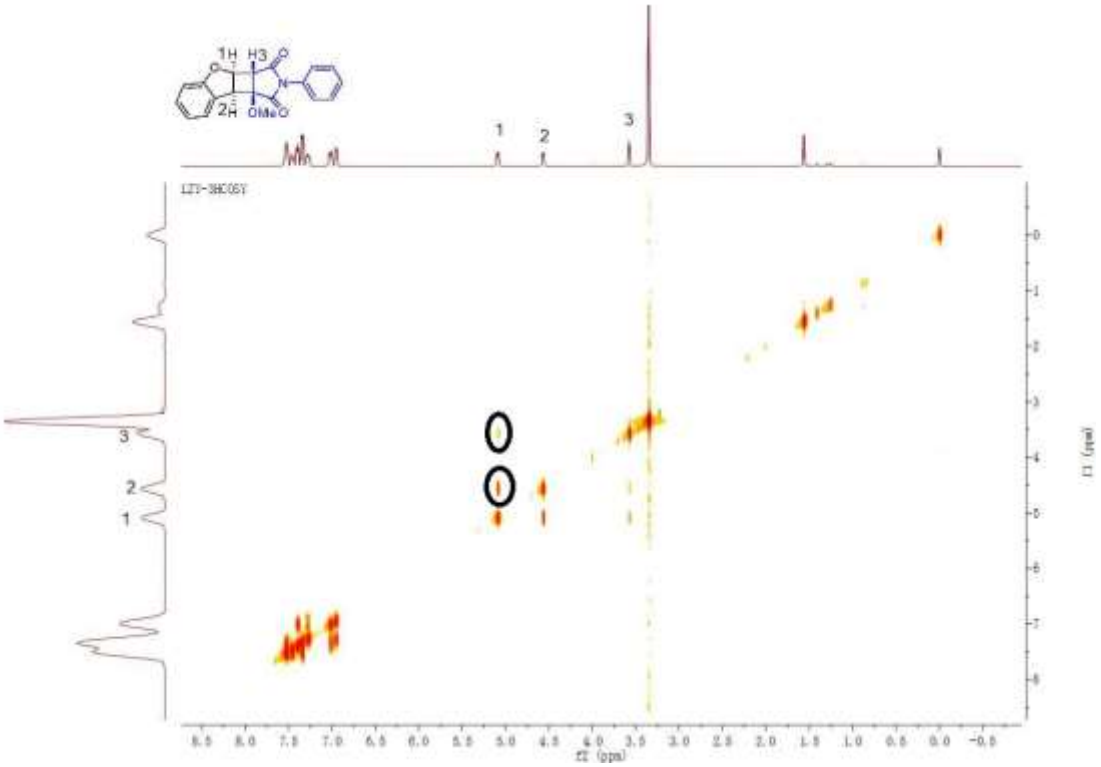
^{1}H NMR Spectrum of 3n



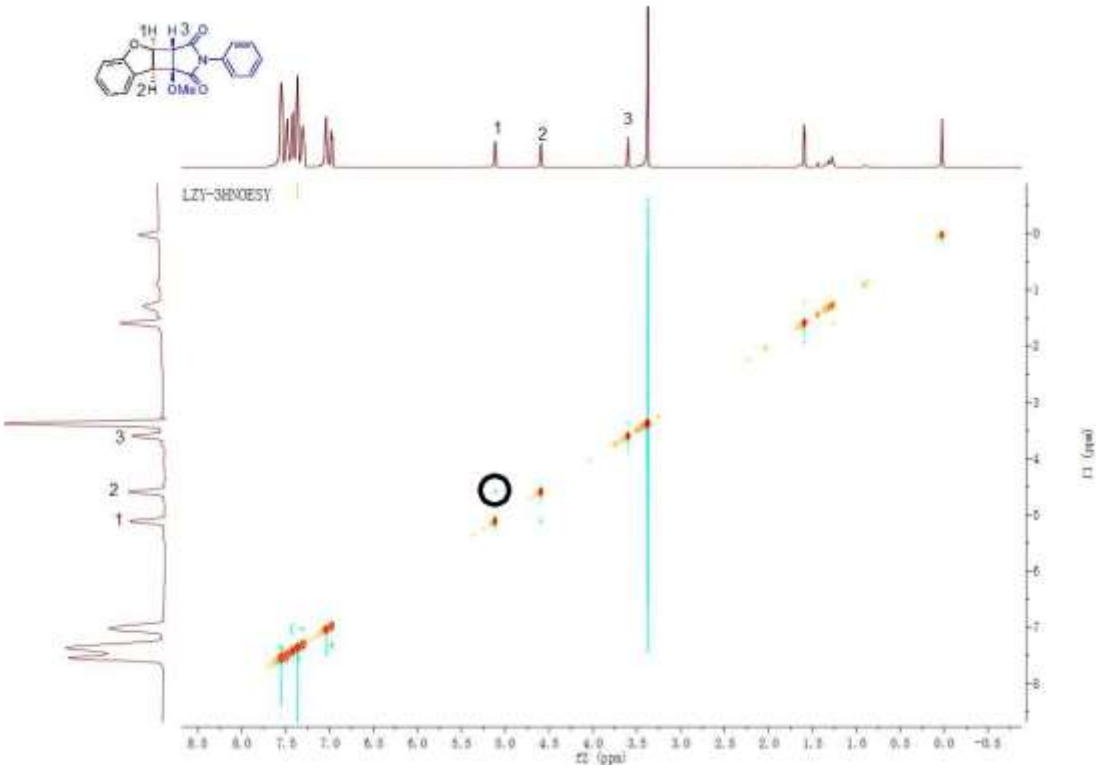
^{13}C{^{1}H} NMR Spectrum of 3n



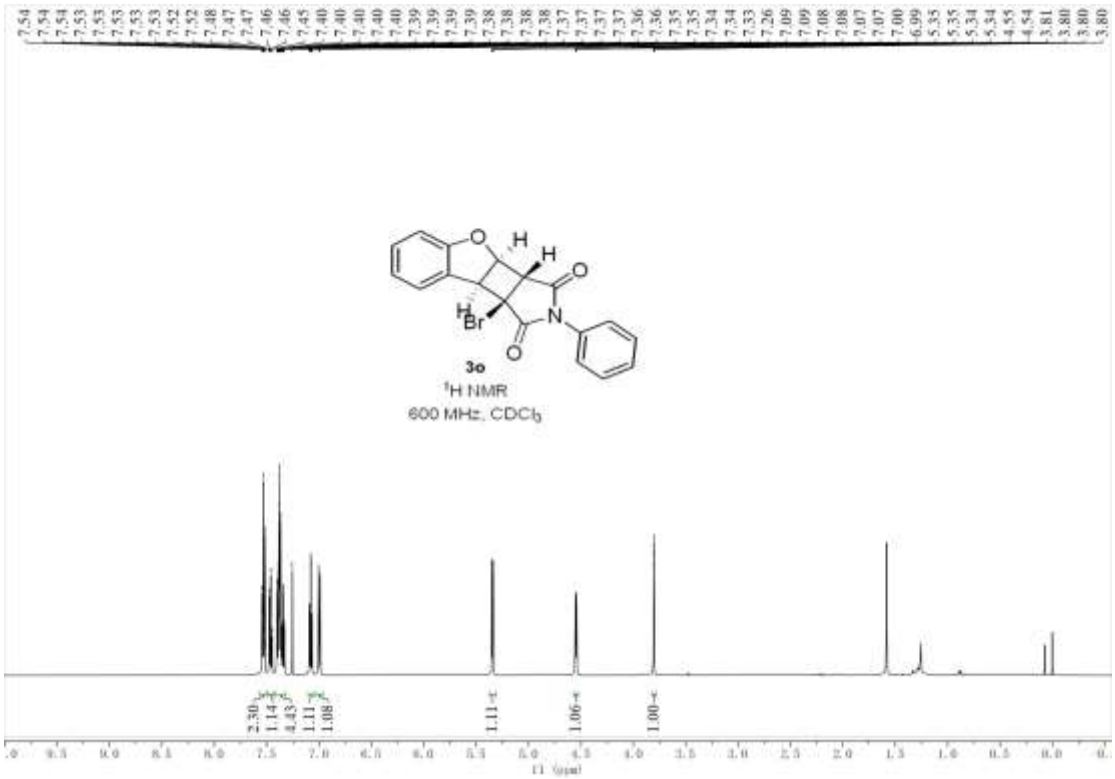
COSY (400 MHZ, $CDCl_3$) of 3n



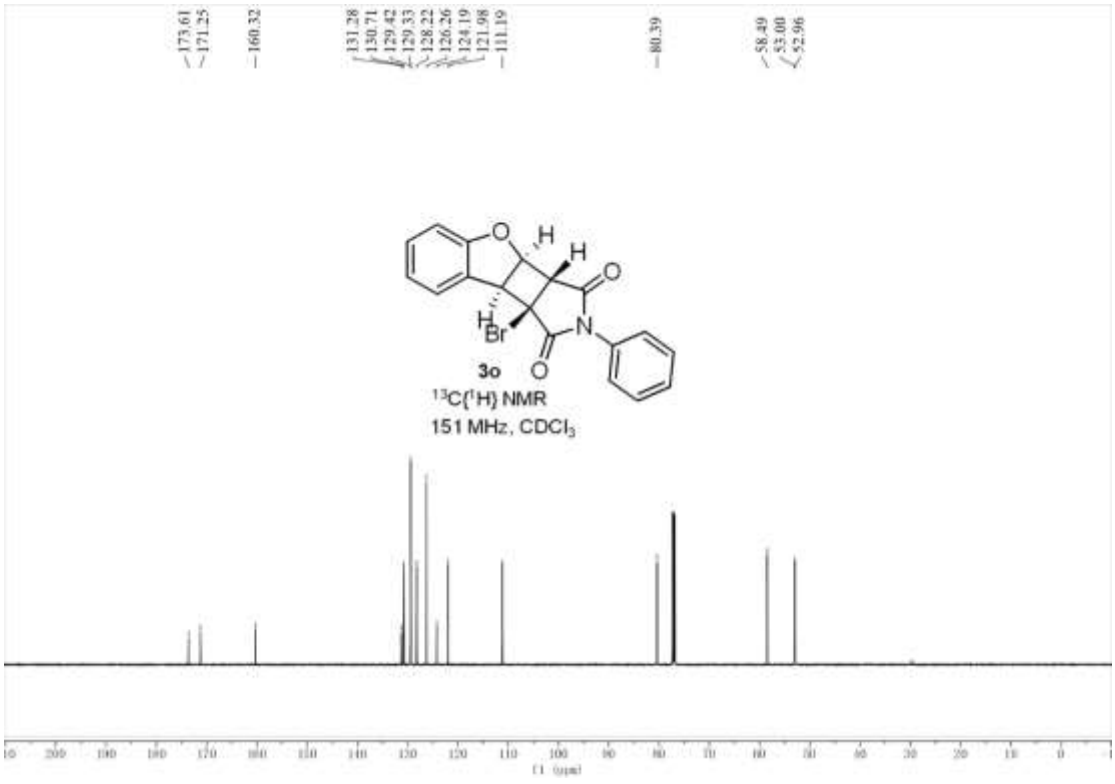
NOESY (400 MHZ, $CDCl_3$) of 3n



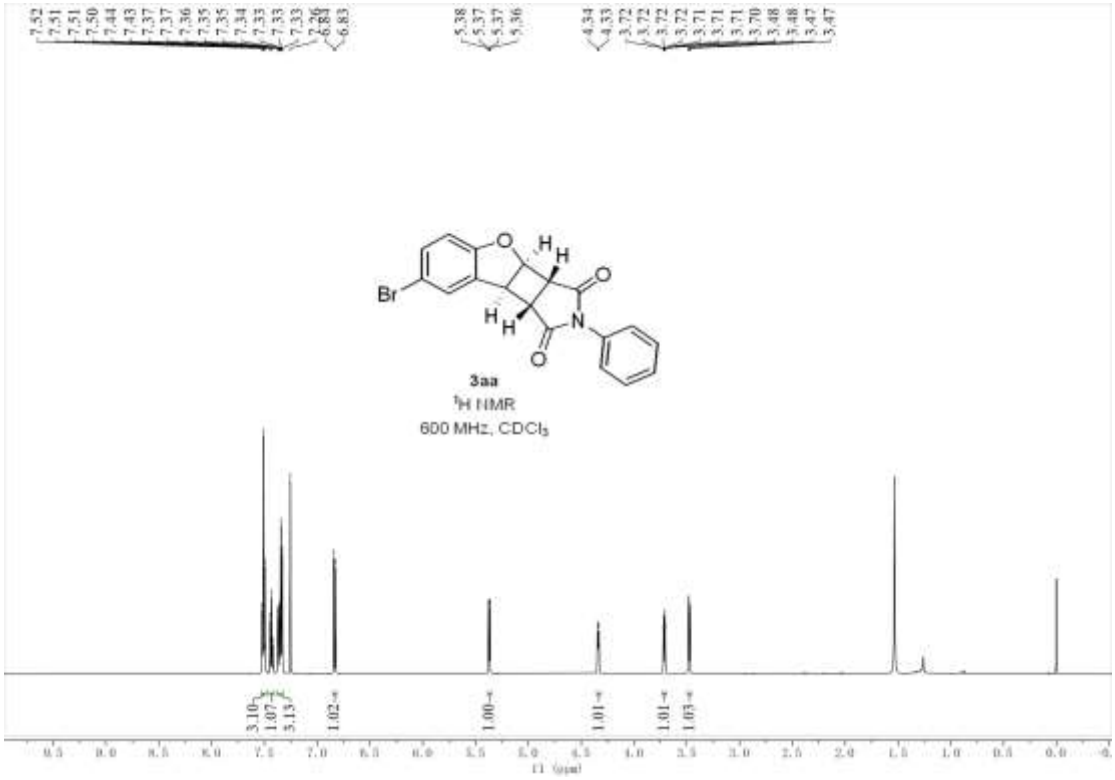
^{1}H NMR Spectrum of 3o



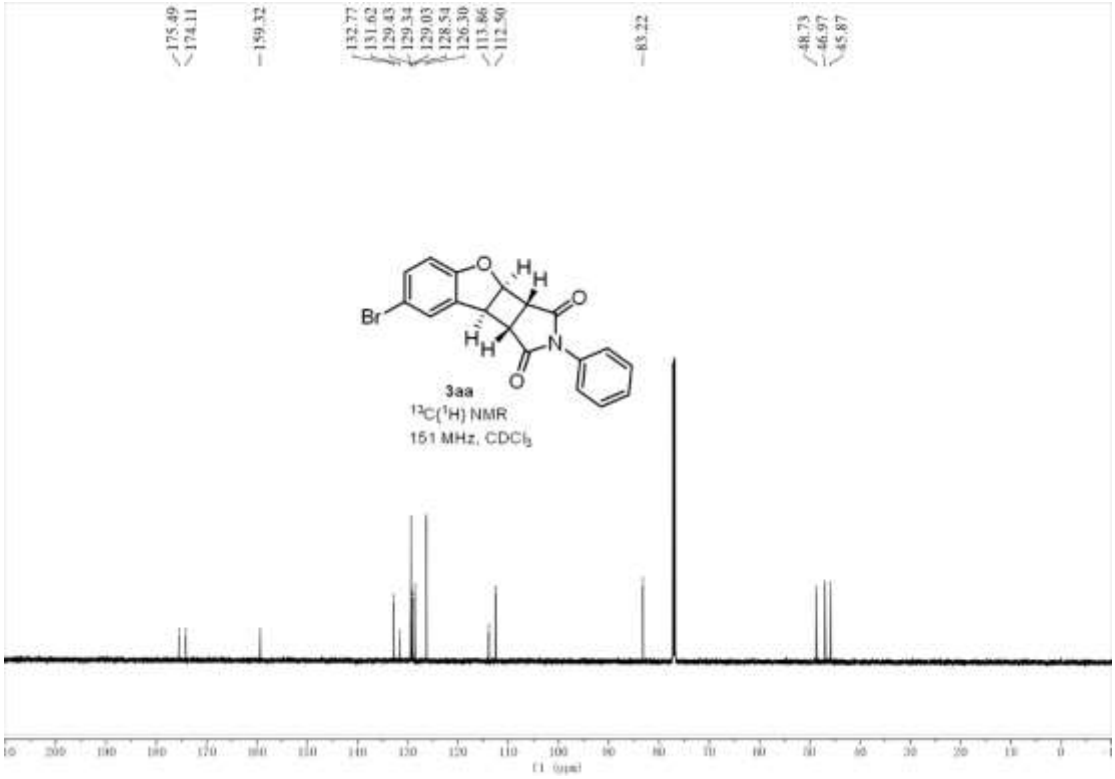
^{13}C{^{1}H} NMR Spectrum of 3o



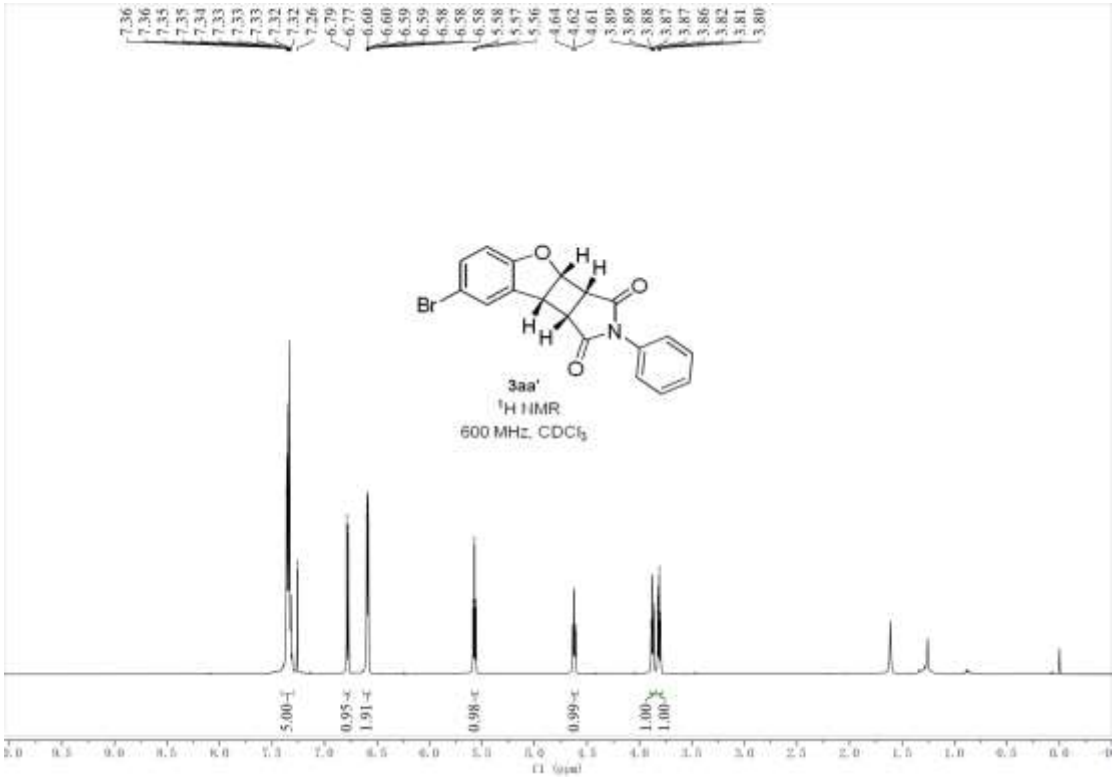
^{1}H NMR Spectrum of 3aa



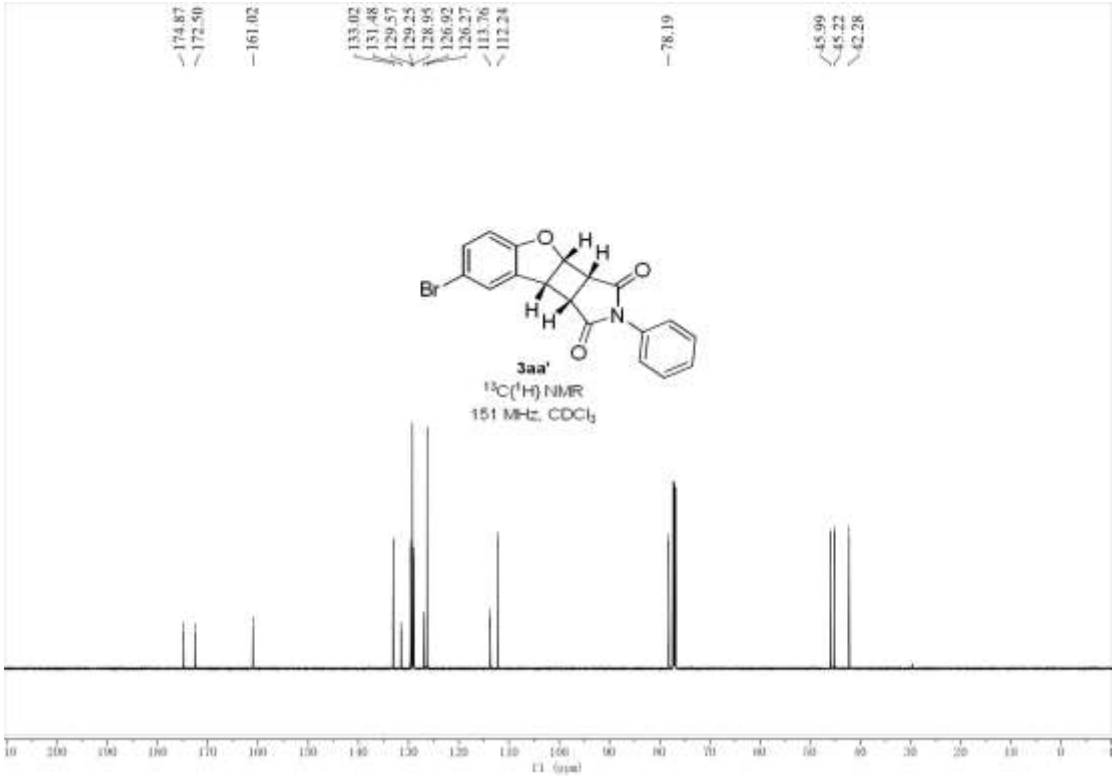
^{13}C{^{1}H} NMR Spectrum of 3aa



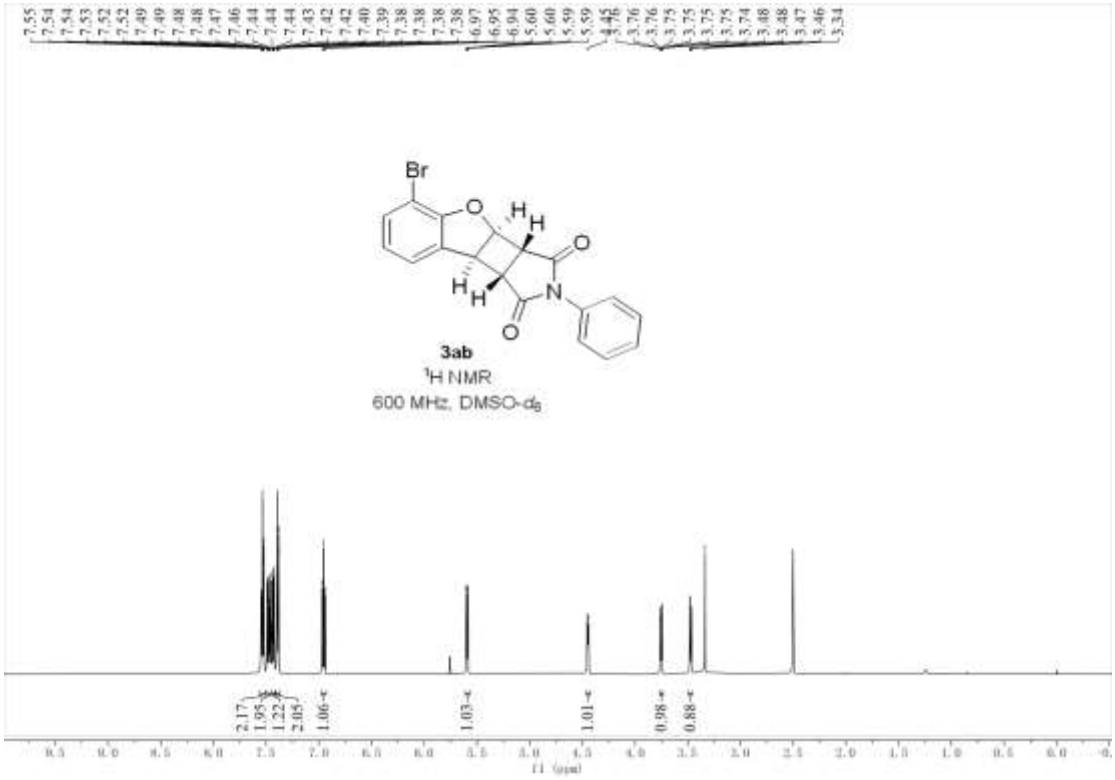
^{1}H NMR Spectrum of 3aa'



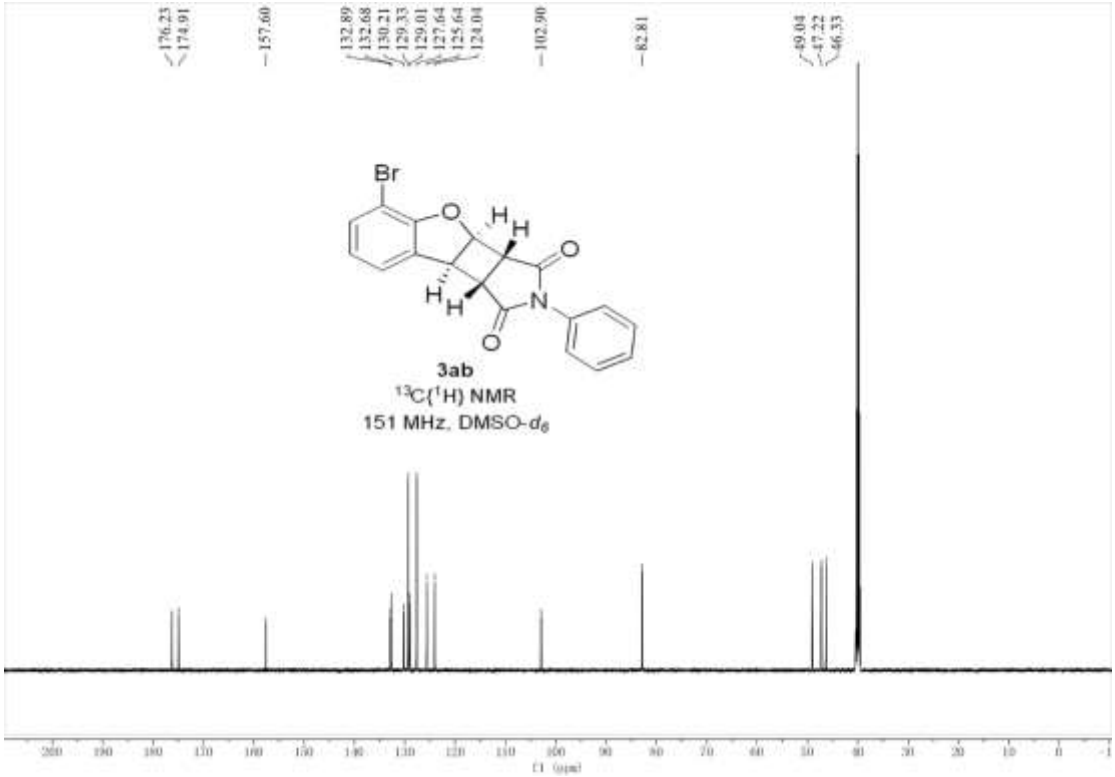
^{13}C{^{1}H} NMR Spectrum of 3aa'



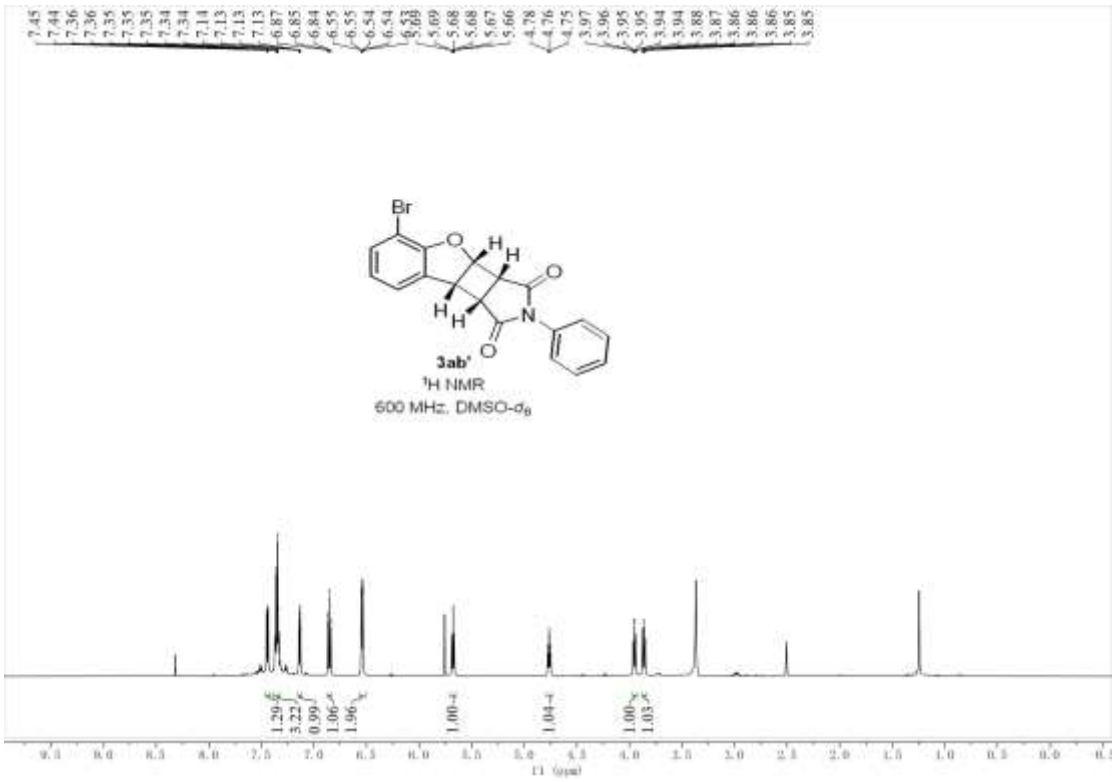
^{1}H NMR Spectrum of 3ab



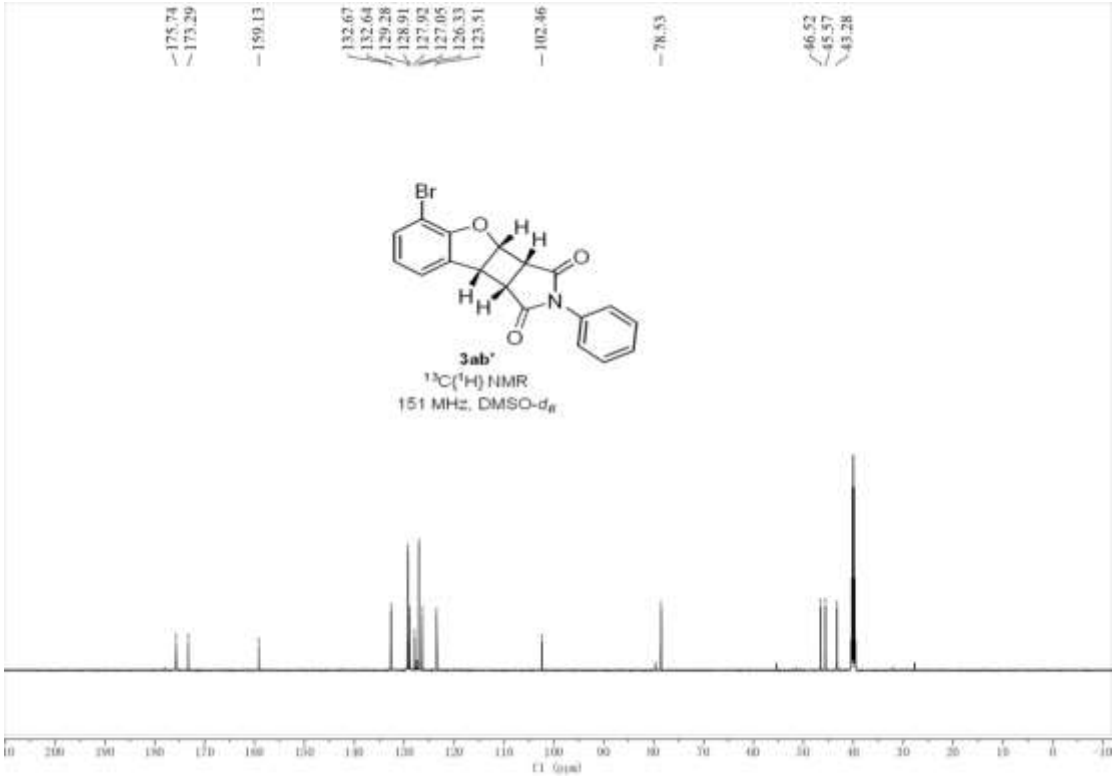
$^{13}C\{^{1}H\}$ NMR Spectrum of 3ab



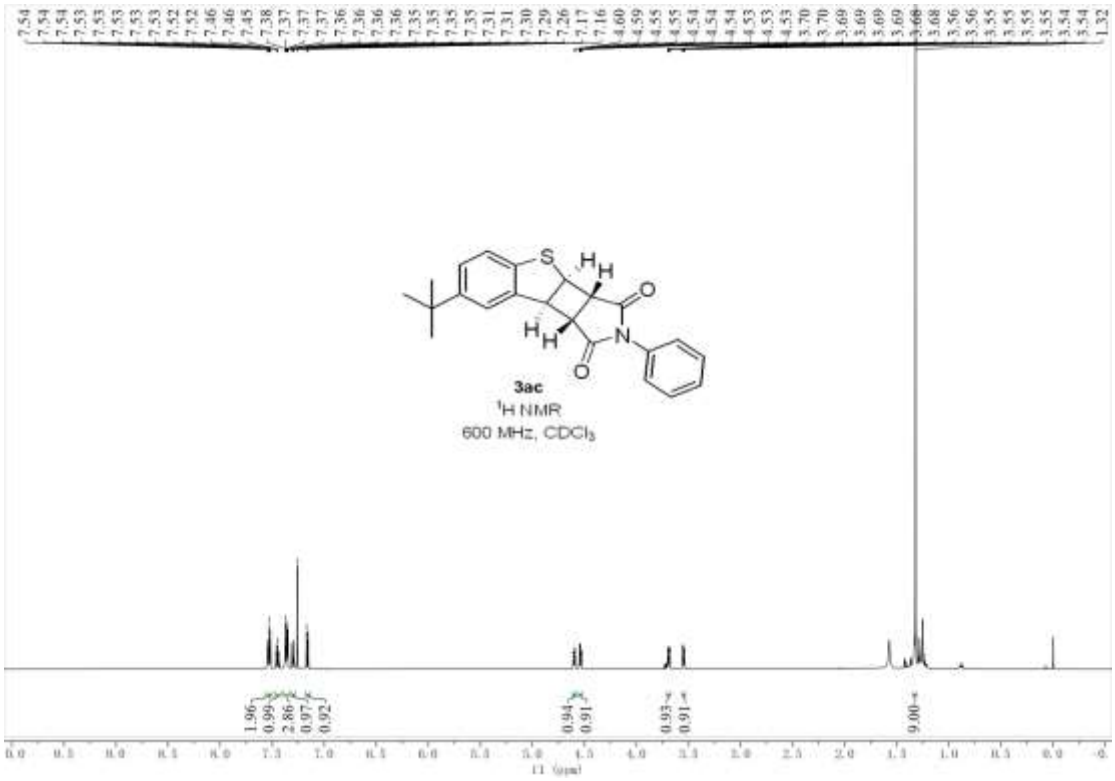
^{1}H NMR Spectrum of 3ab'



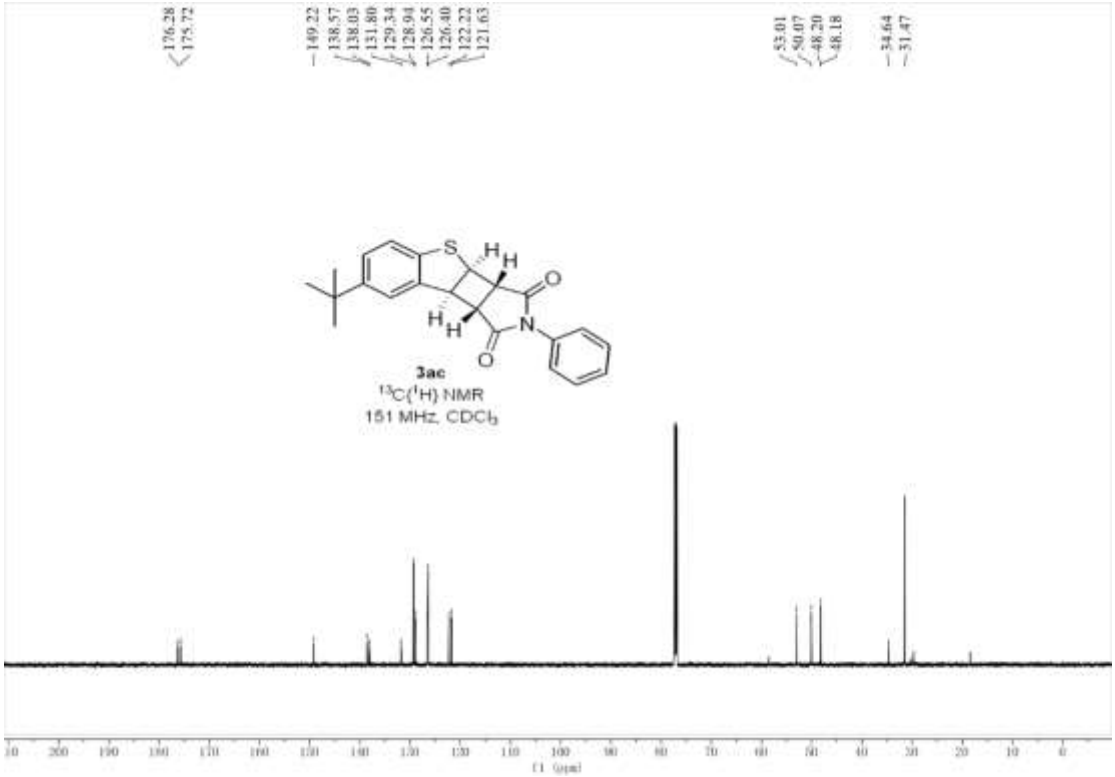
^{13}C{^{1}H} NMR Spectrum of 3ab'



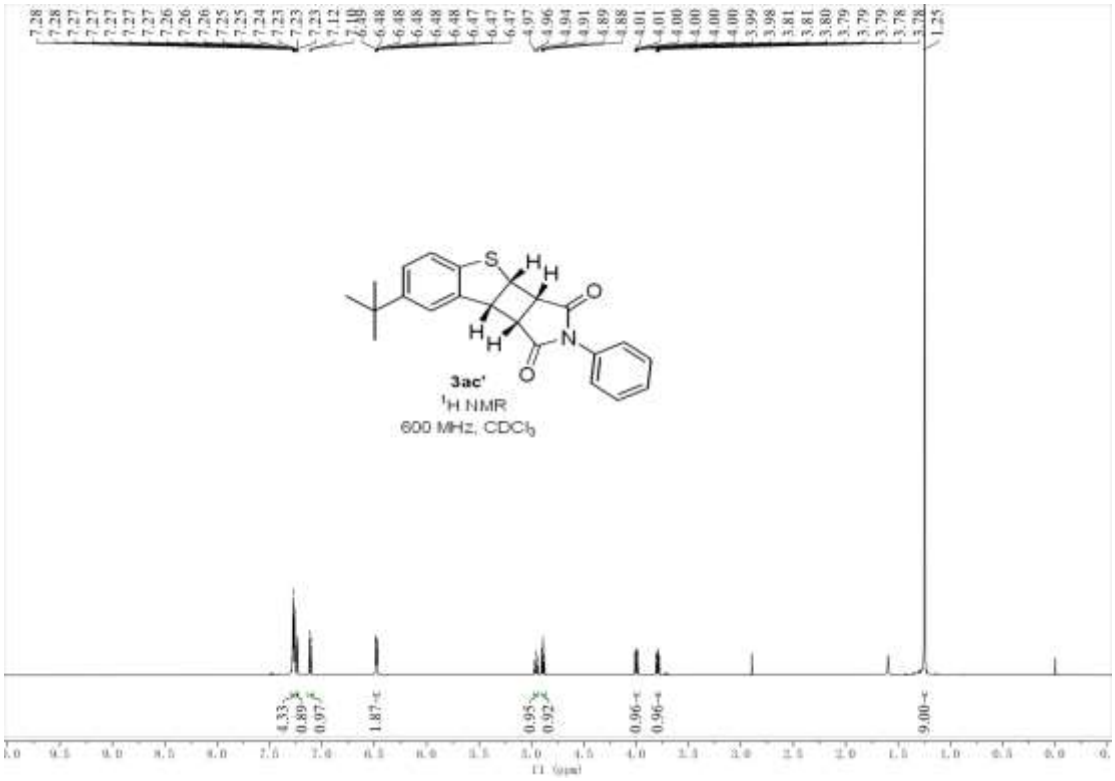
^{1}H NMR Spectrum of 3ac



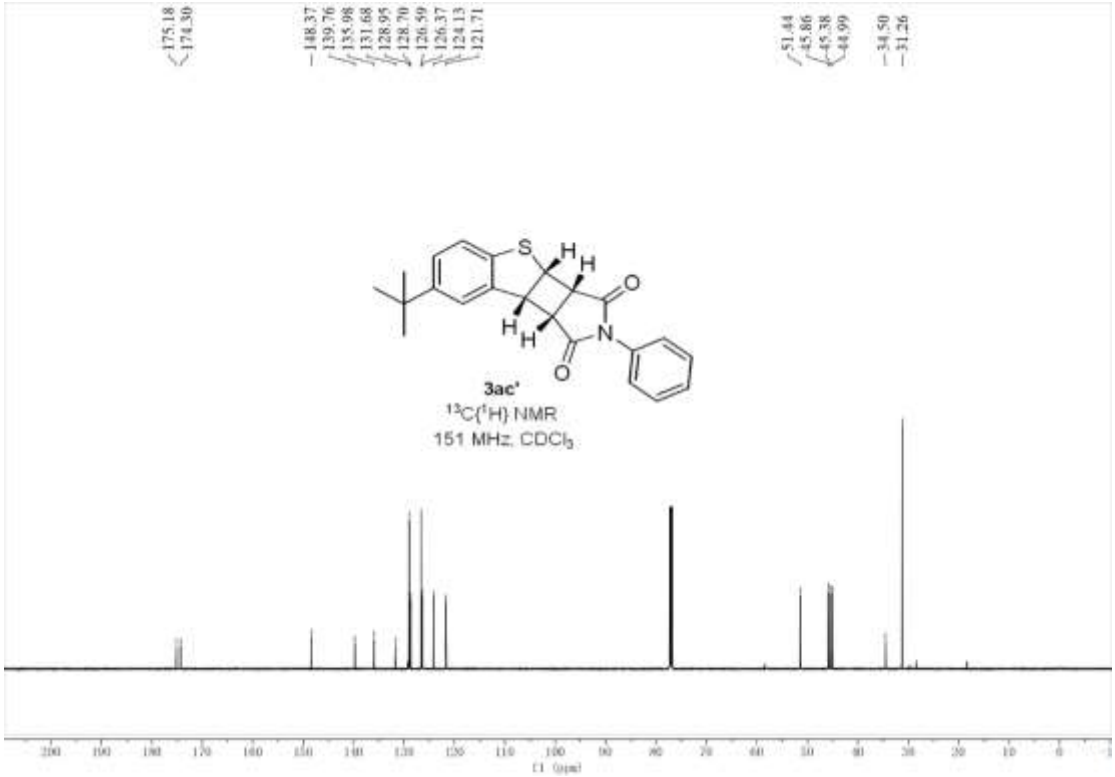
^{13}C{^{1}H} NMR Spectrum of 3ac



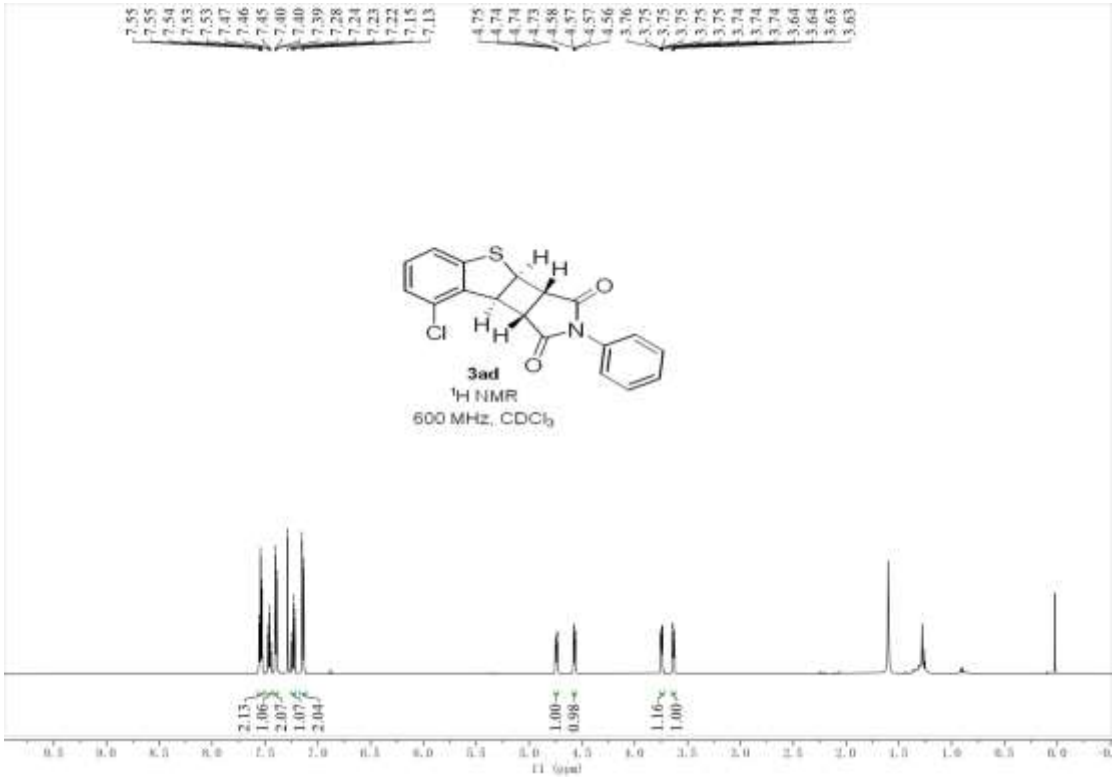
^{1}H NMR Spectrum of 3ac'



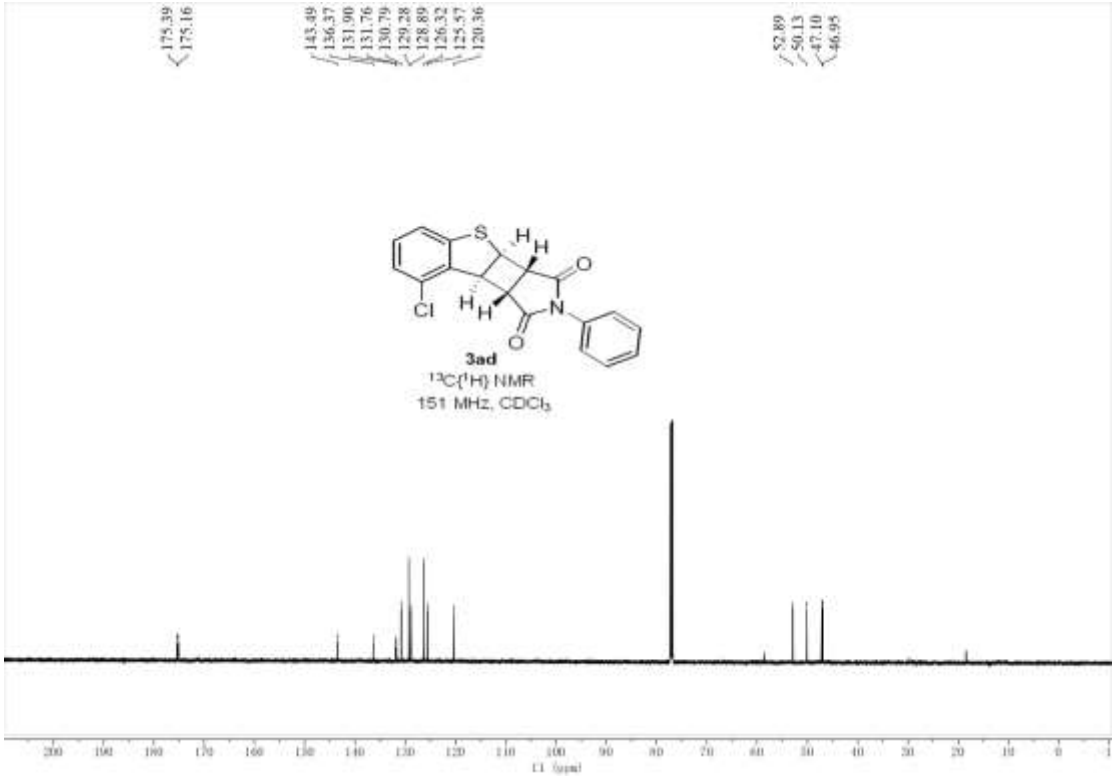
^{13}C{^{1}H} NMR Spectrum of 3ac'



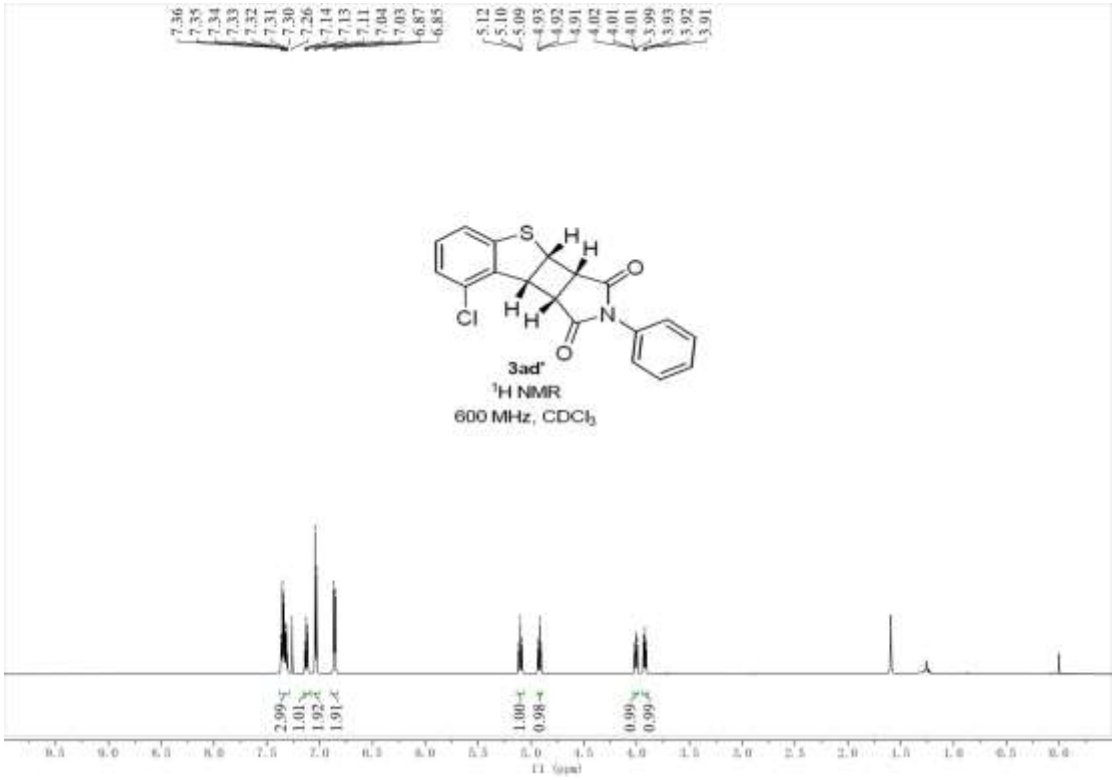
^{1}H NMR Spectrum of 3ad



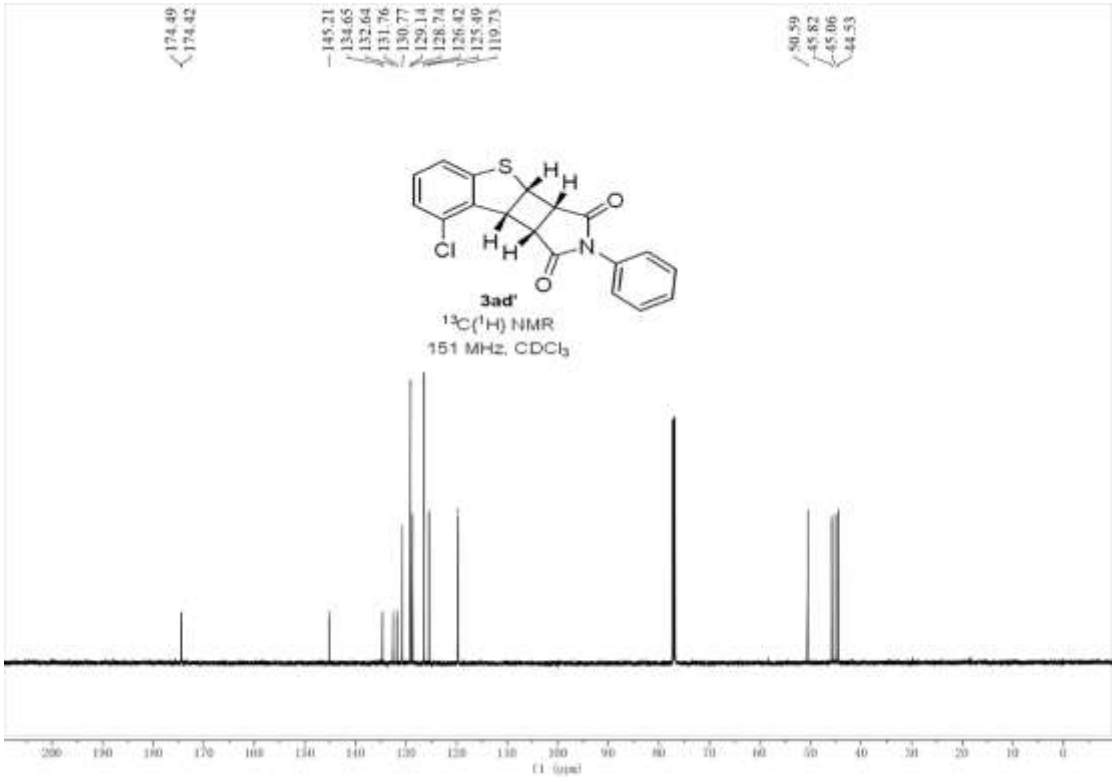
$^{13}C\{^{1}H\}$ NMR Spectrum of 3ad



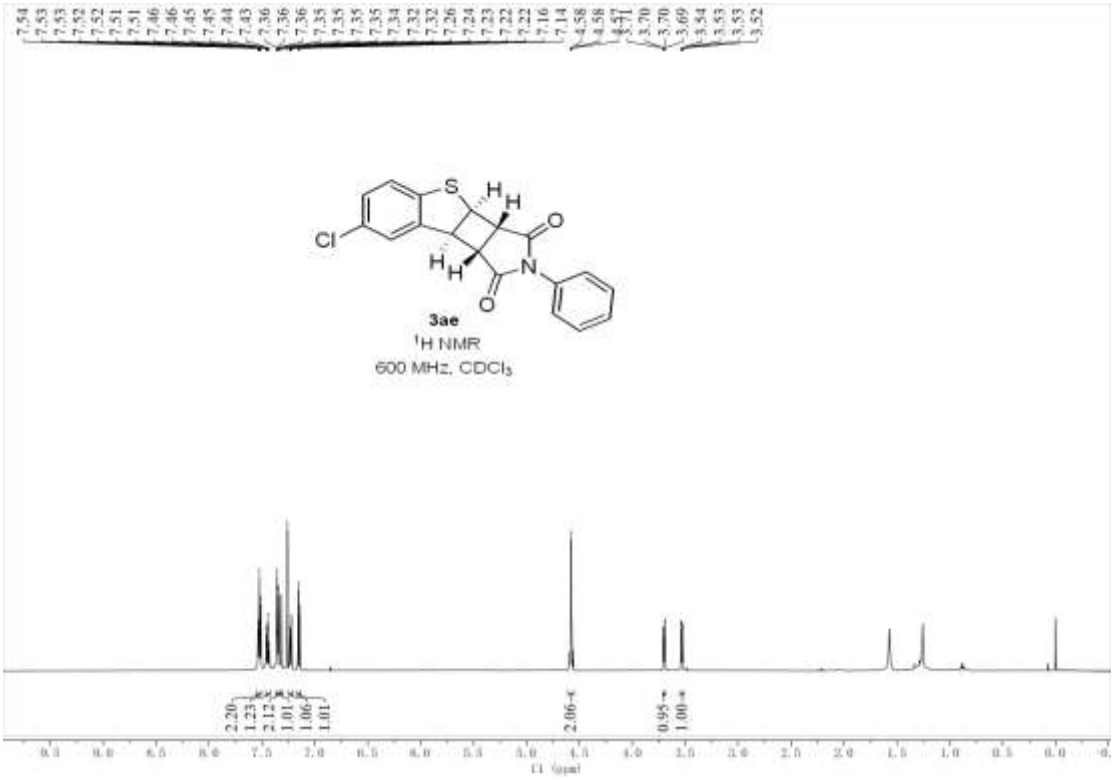
^{1}H NMR Spectrum of 3ad'



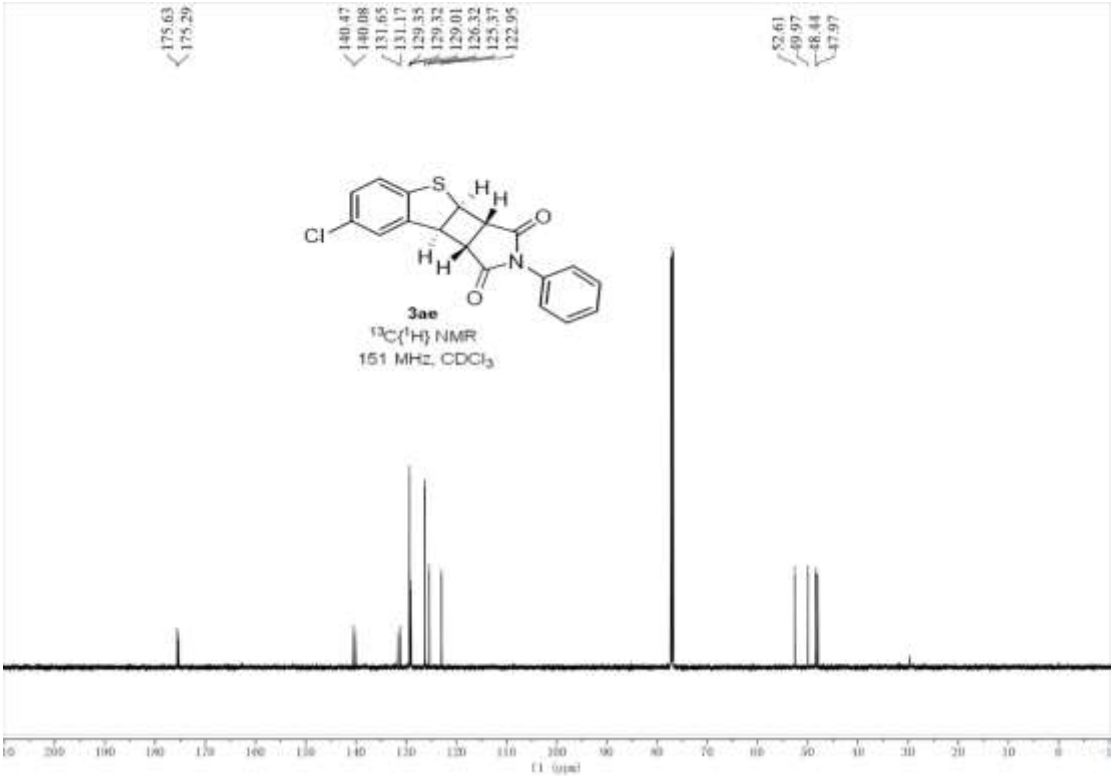
^{13}C{^{1}H} NMR Spectrum of 3ad'



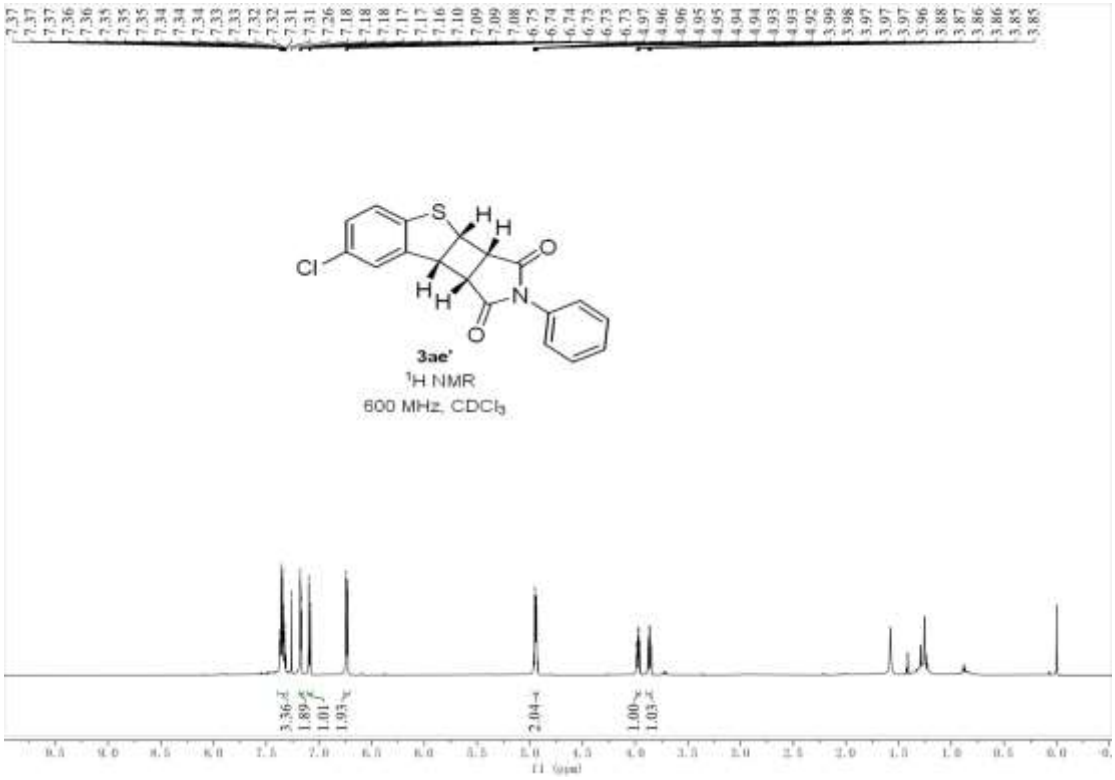
^{1}H NMR Spectrum of 3ae



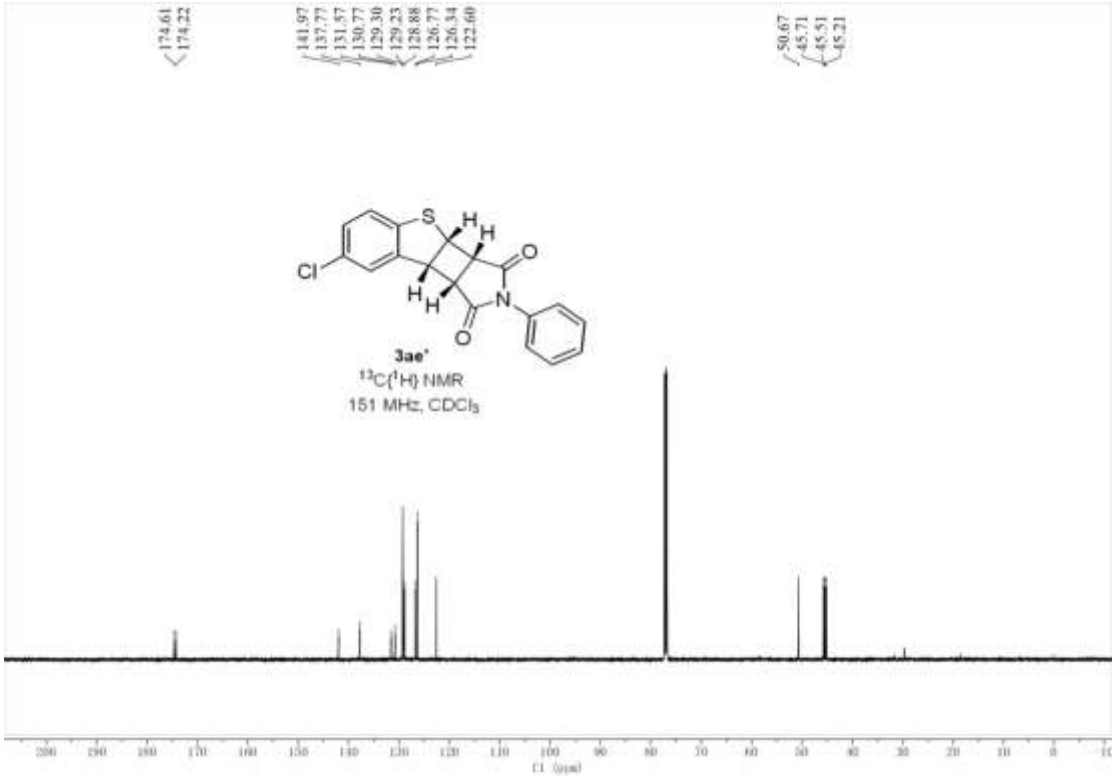
^{13}C{^{1}H} NMR Spectrum of 3ae



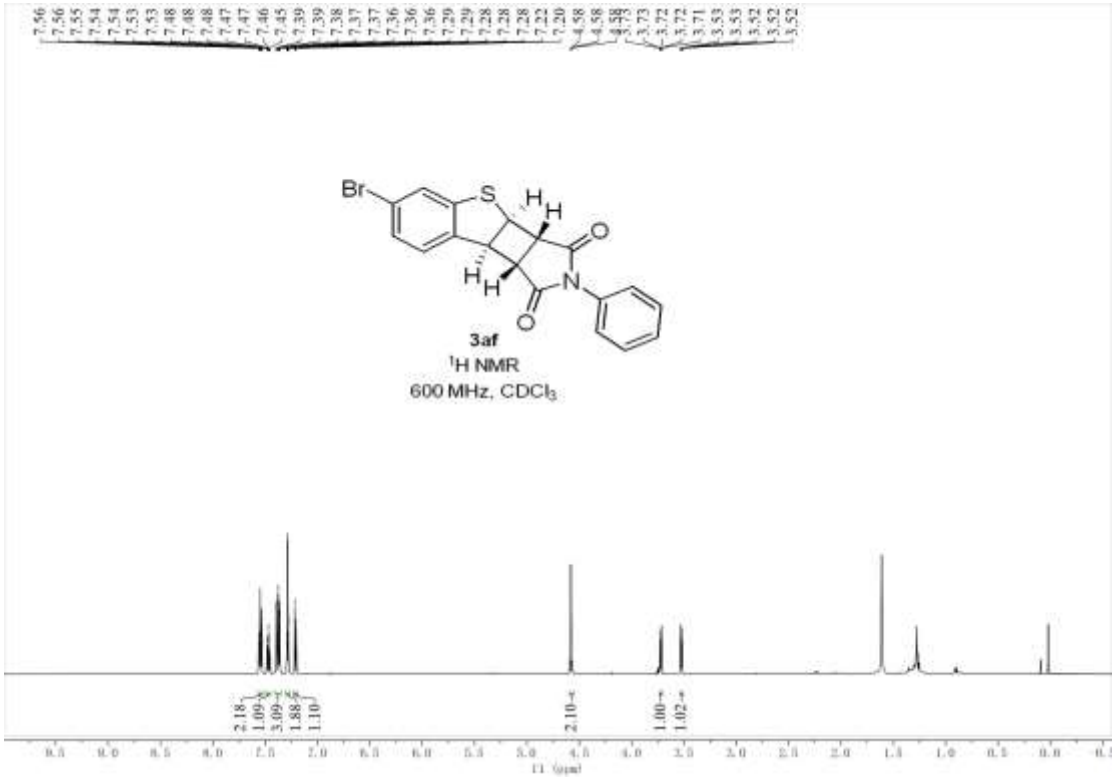
^{1}H NMR Spectrum of 3ae'



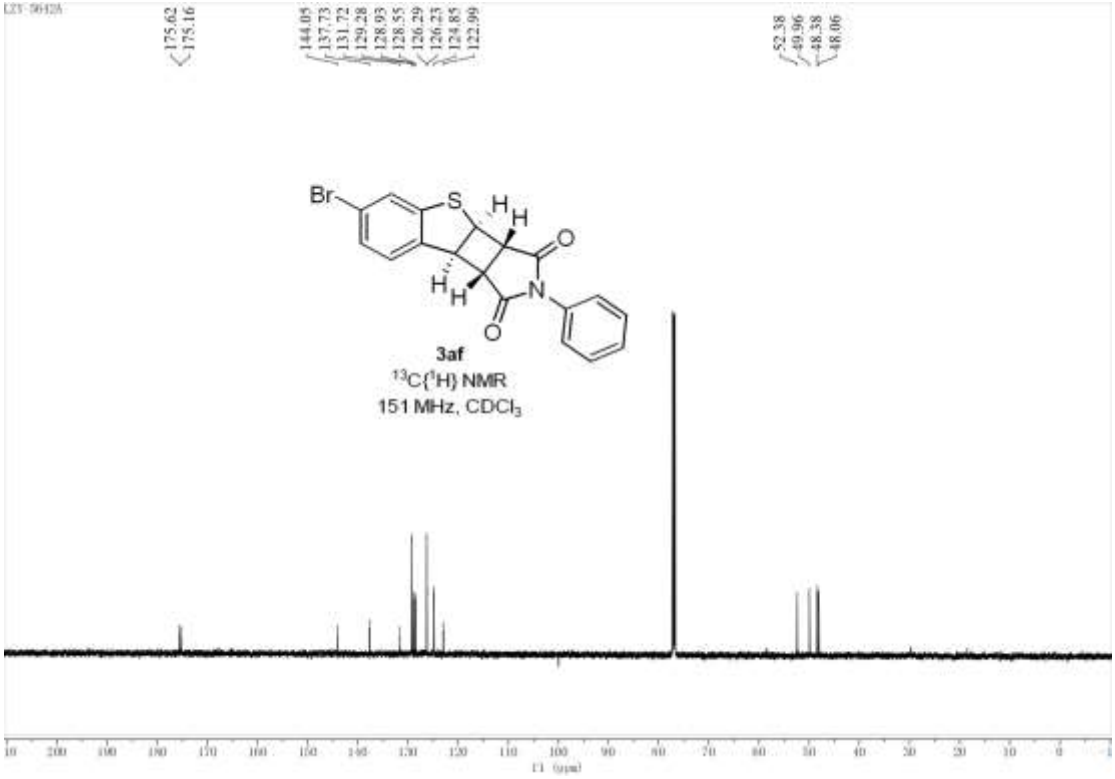
^{13}C{^{1}H} NMR Spectrum of 3ae'



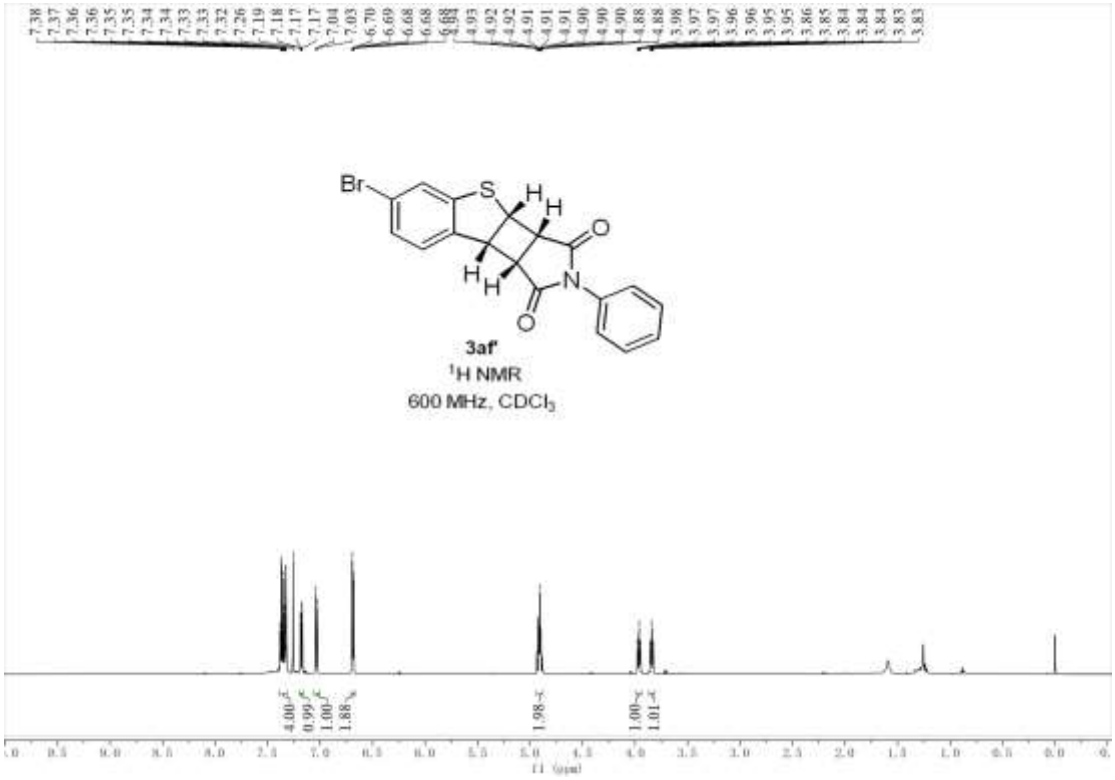
^{1}H NMR Spectrum of 3af



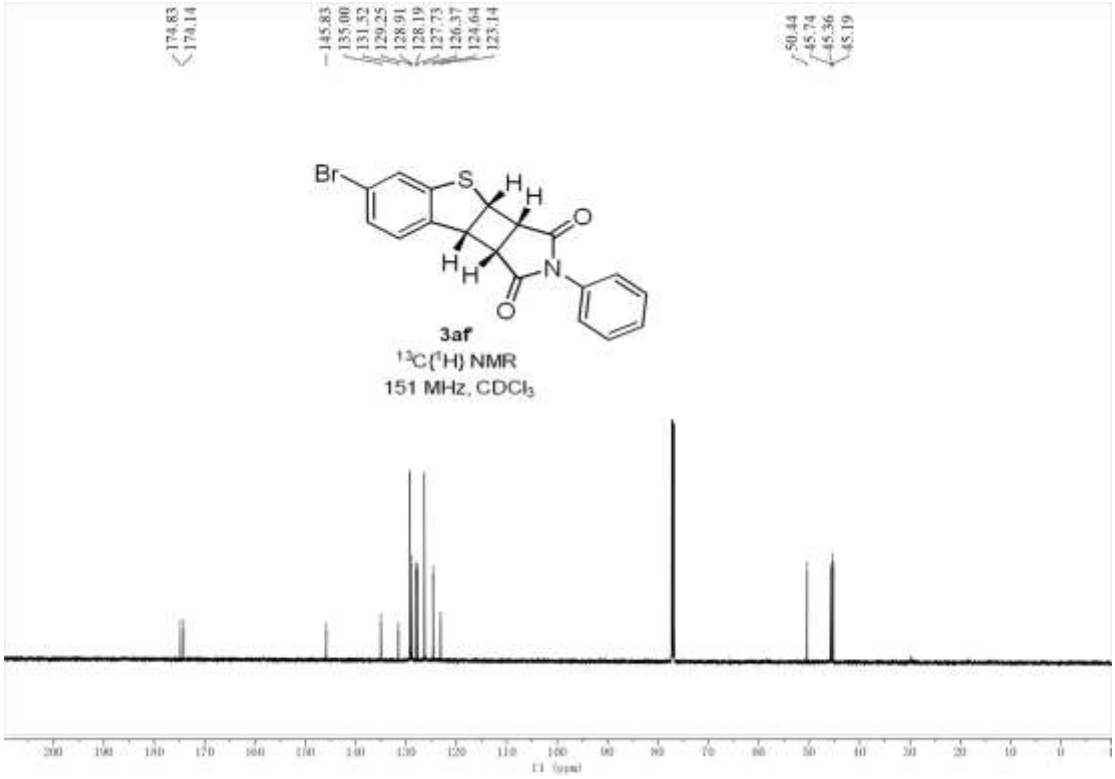
^{13}C{^{1}H} NMR Spectrum of 3af



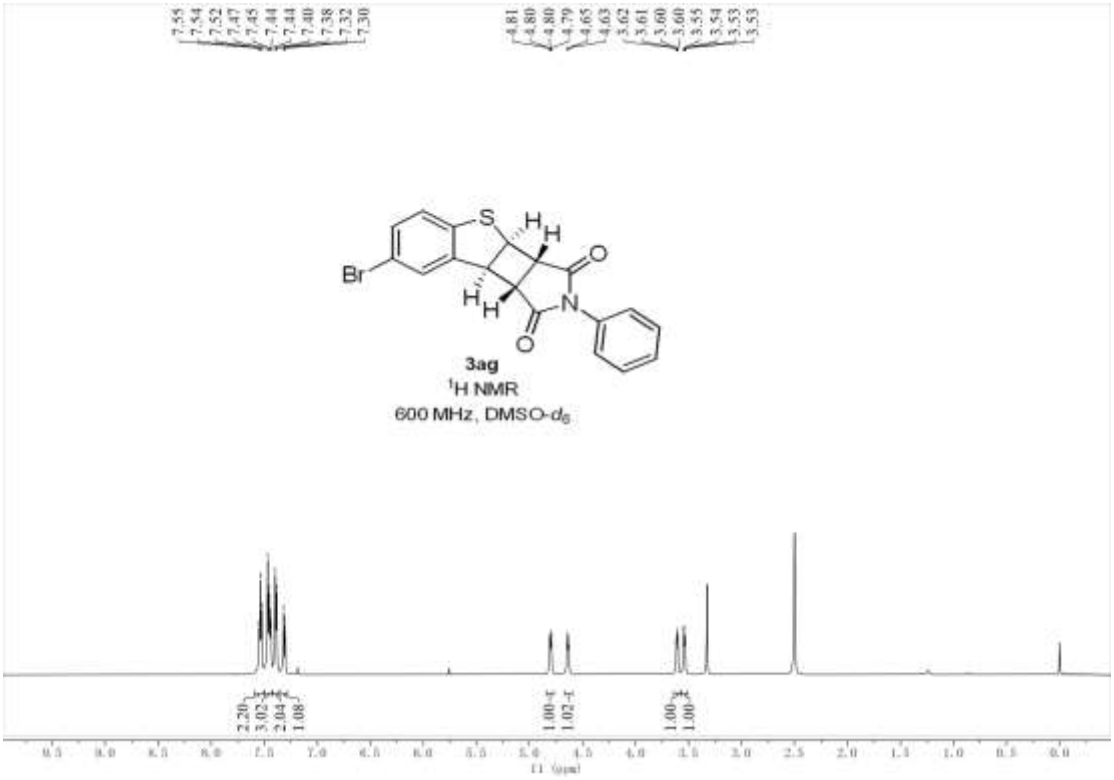
^{1}H NMR Spectrum of 3af'



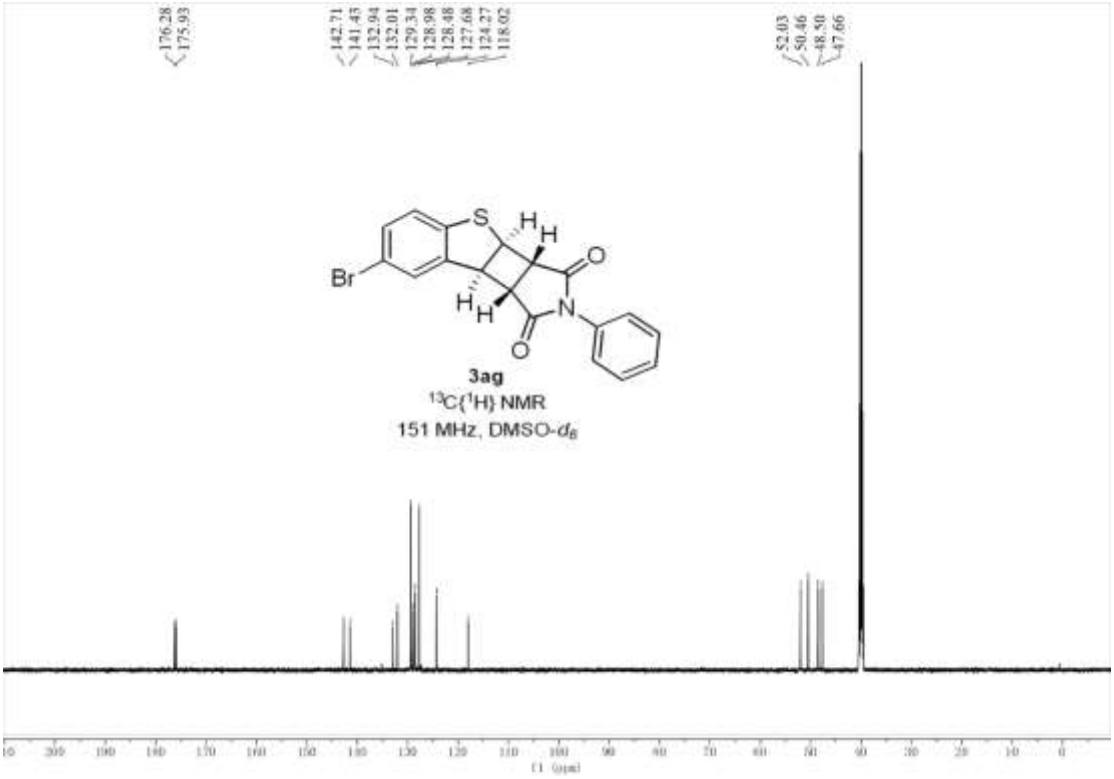
^{13}C{^{1}H} NMR Spectrum of 3af'



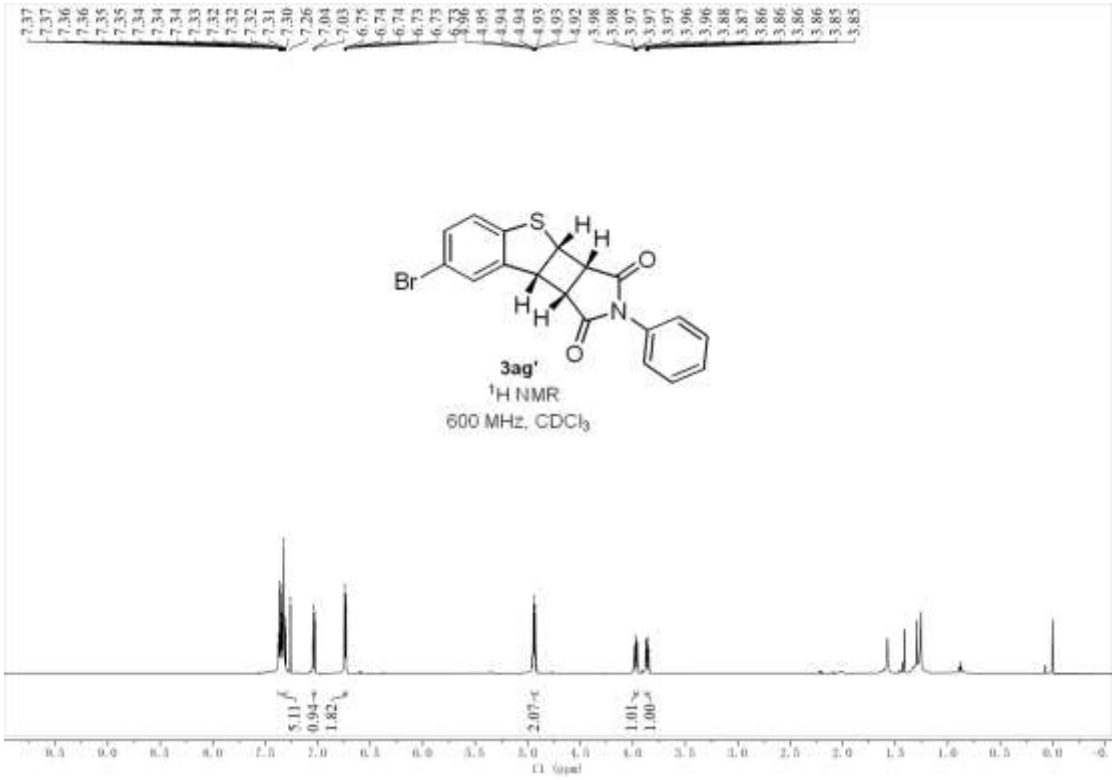
^{1}H NMR Spectrum of 3ag



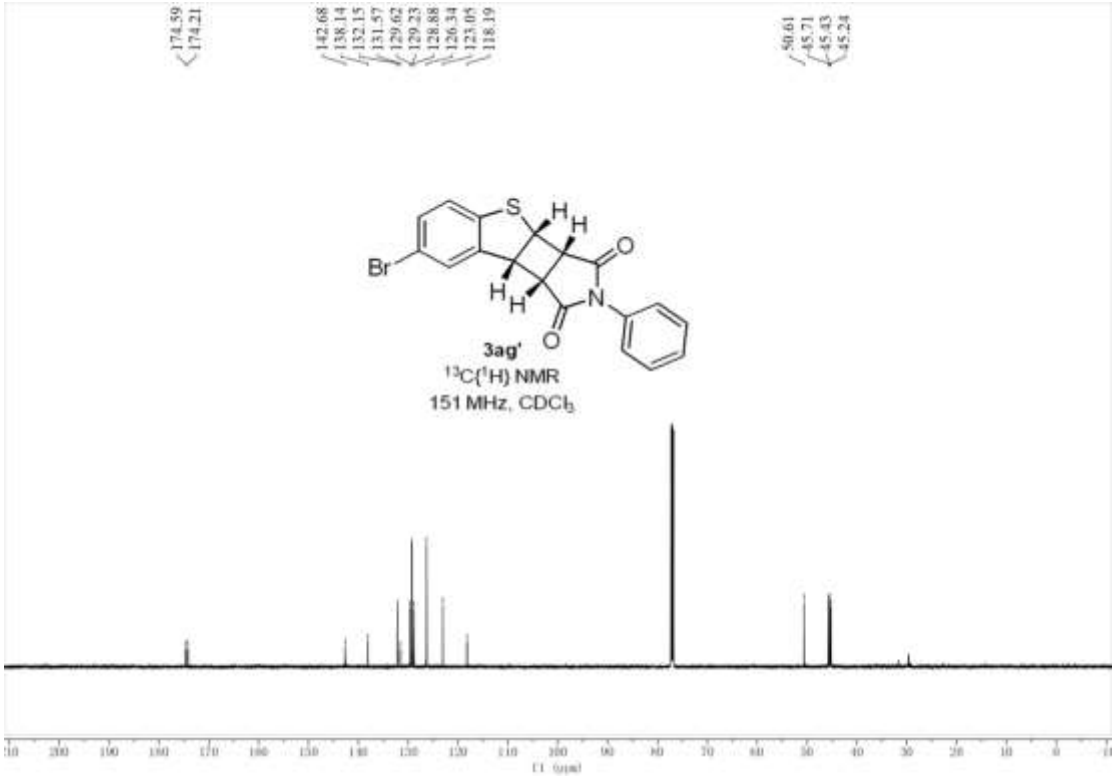
$^{13}C\{^{1}H\}$ NMR Spectrum of 3ag



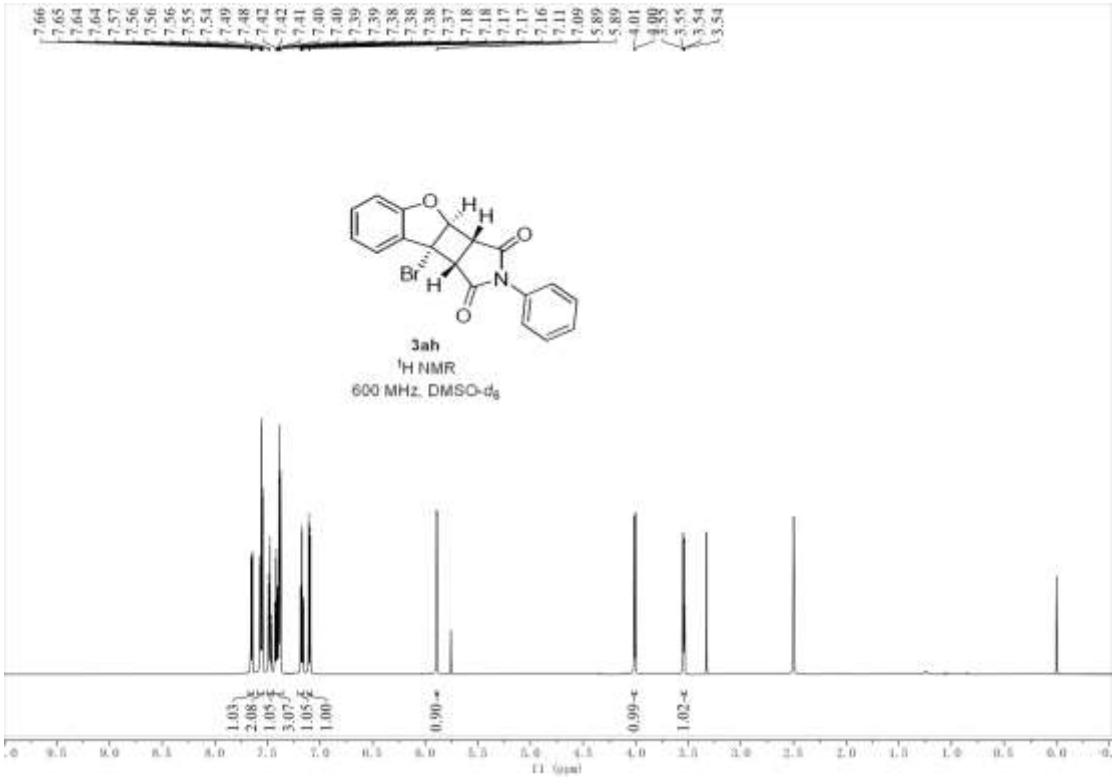
^{1}H NMR Spectrum of 3ag'



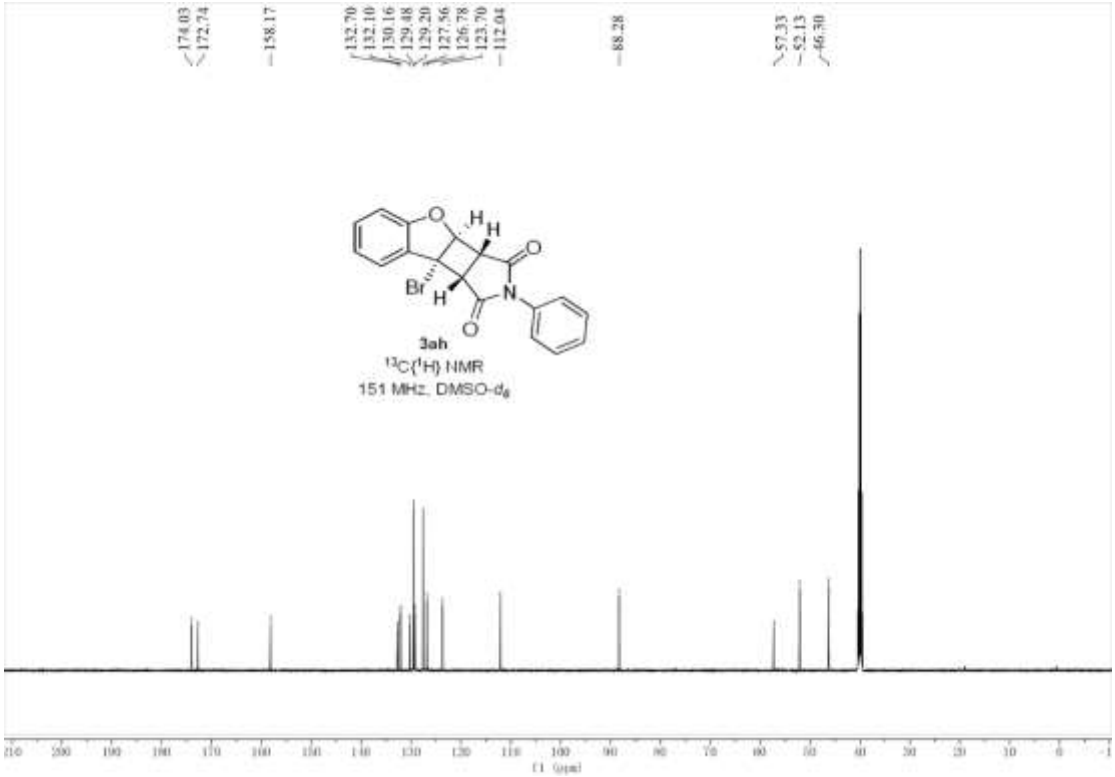
$^{13}C\{^{1}H\}$ NMR Spectrum of 3ag'



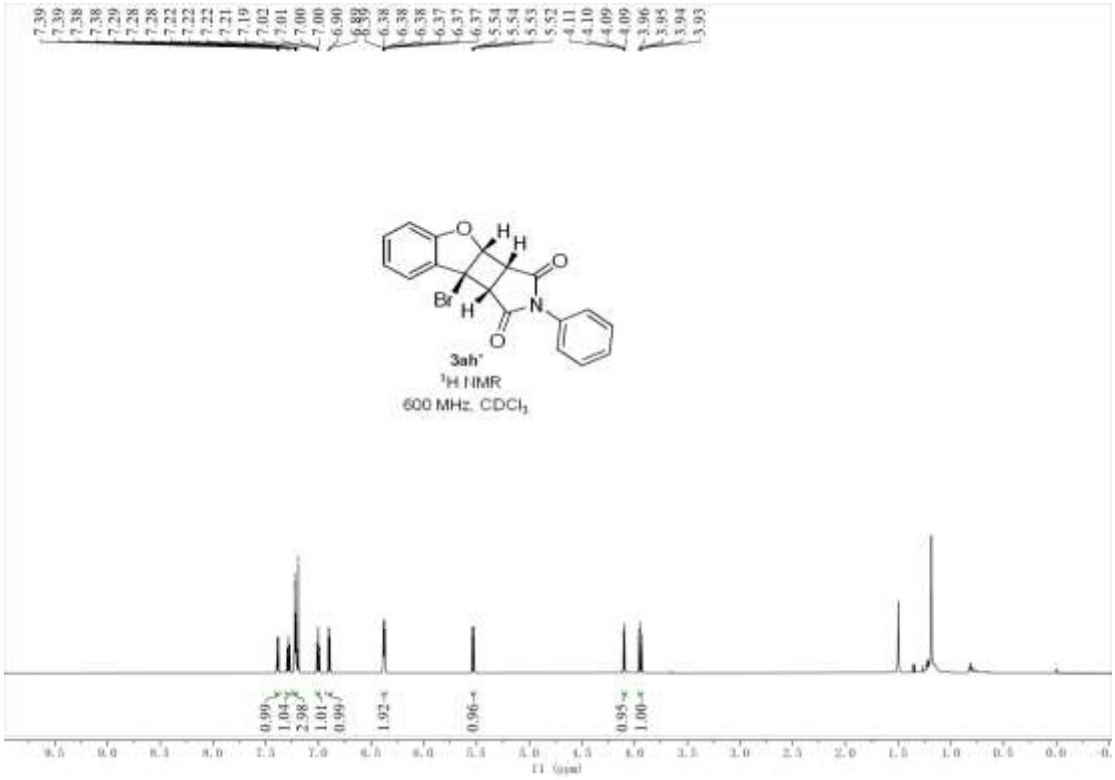
^{1}H NMR Spectrum of 3ah



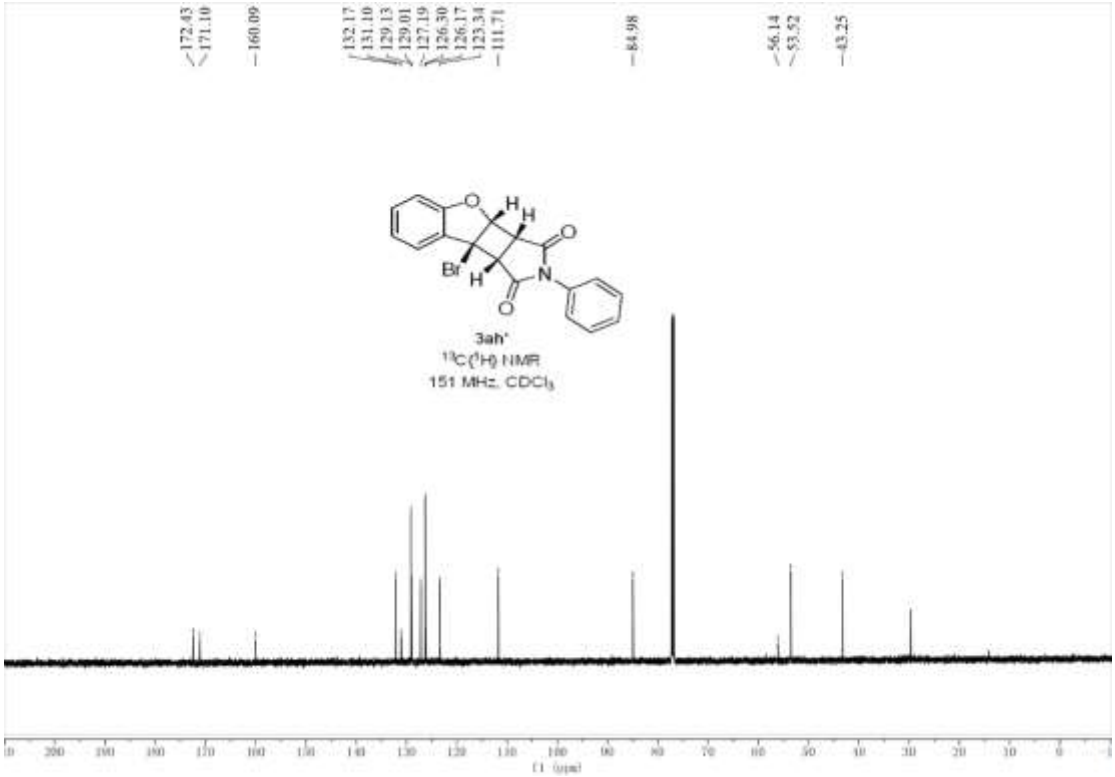
$^{13}C\{^{1}H\}$ NMR Spectrum of 3ah



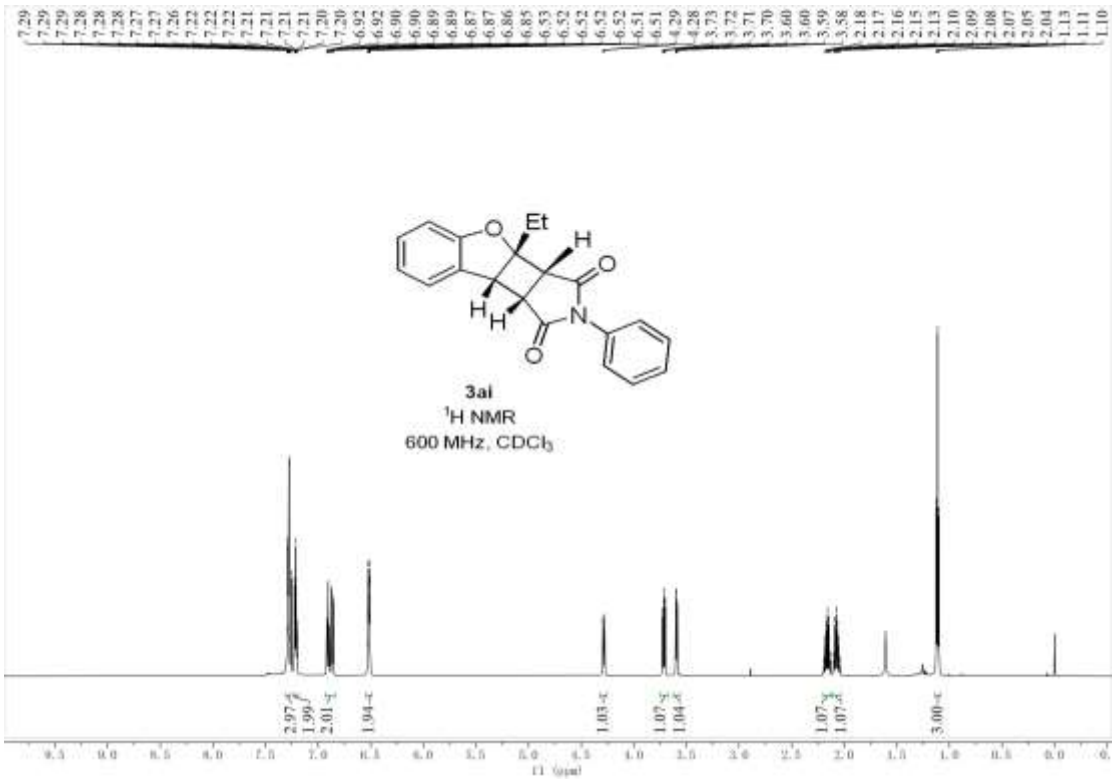
^{1}H NMR Spectrum of 3ah'



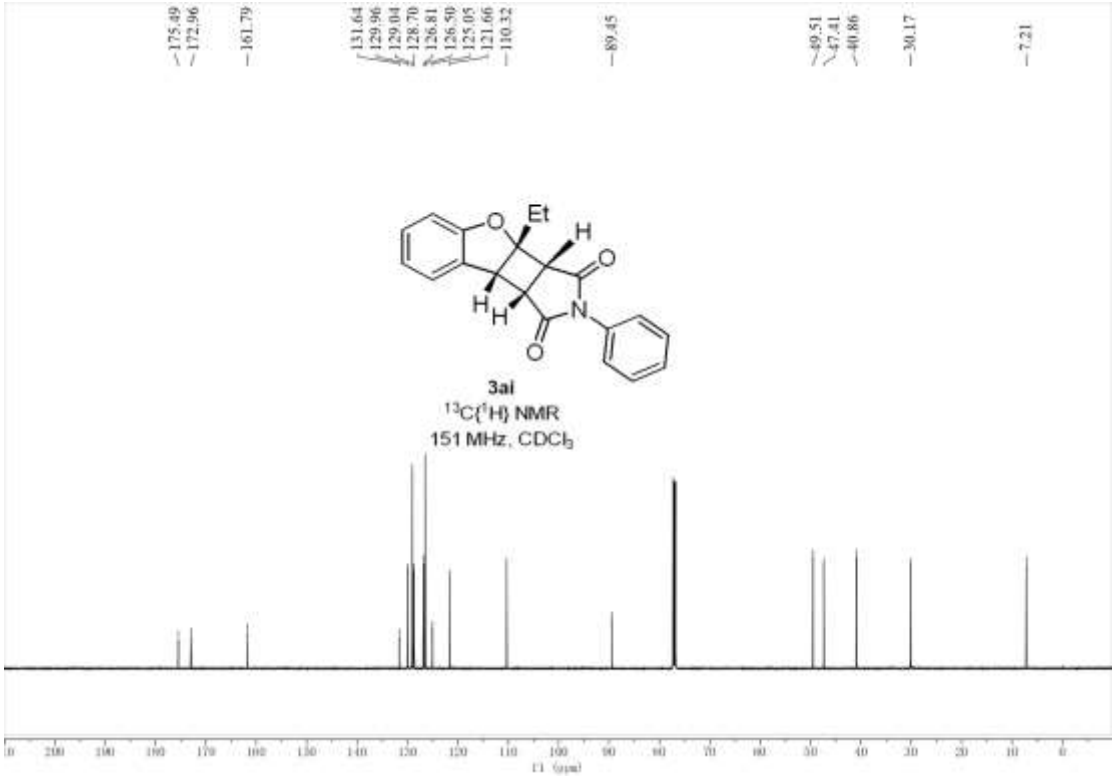
$^{13}C\{^1H\}$ NMR Spectrum of 3ah'



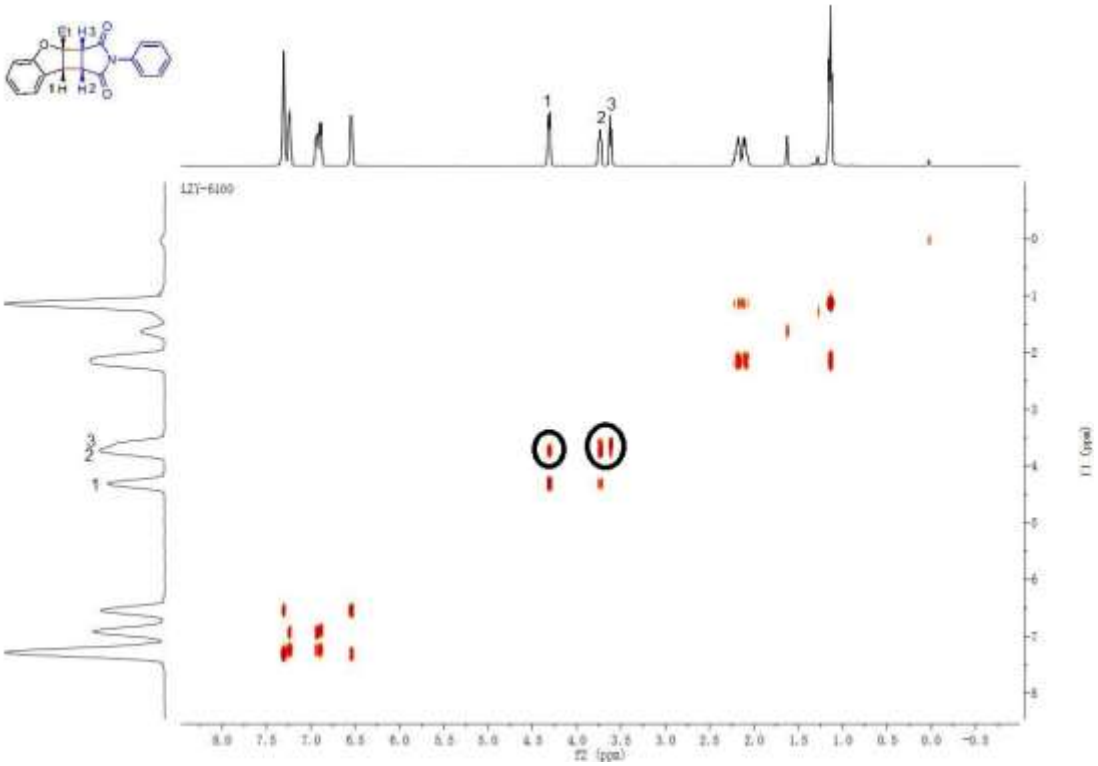
^{1}H NMR Spectrum of 3ai



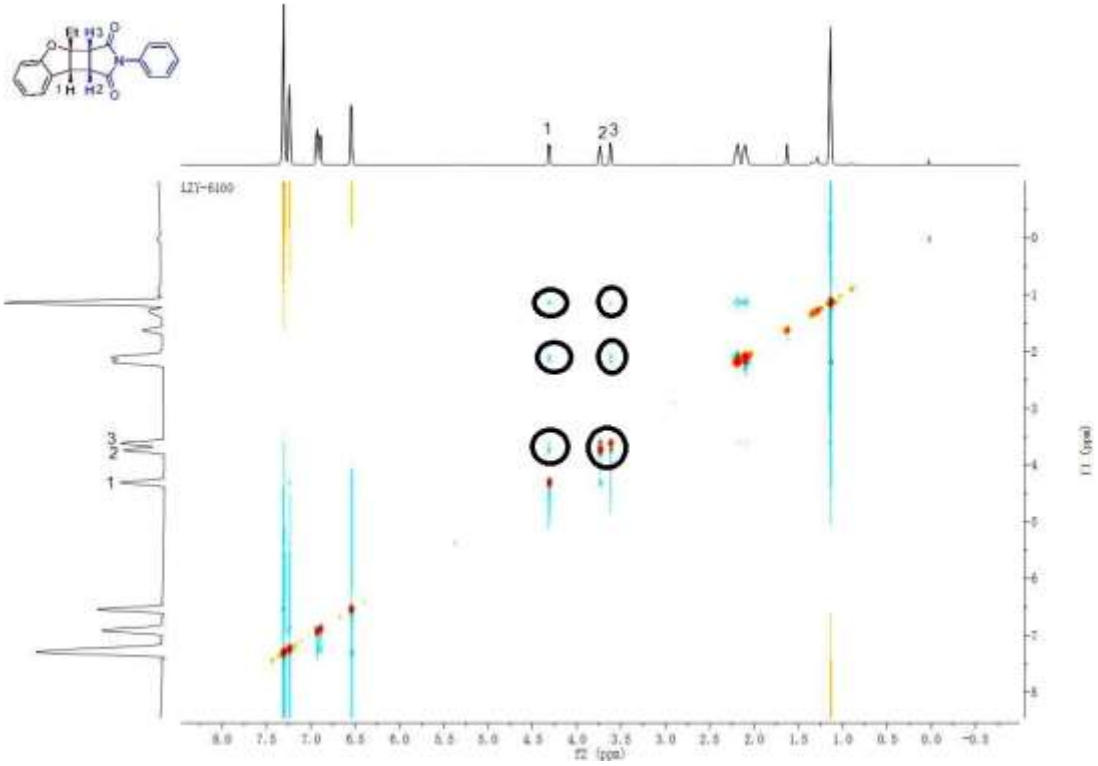
$^{13}C\{^{1}H\}$ NMR Spectrum of 3ai



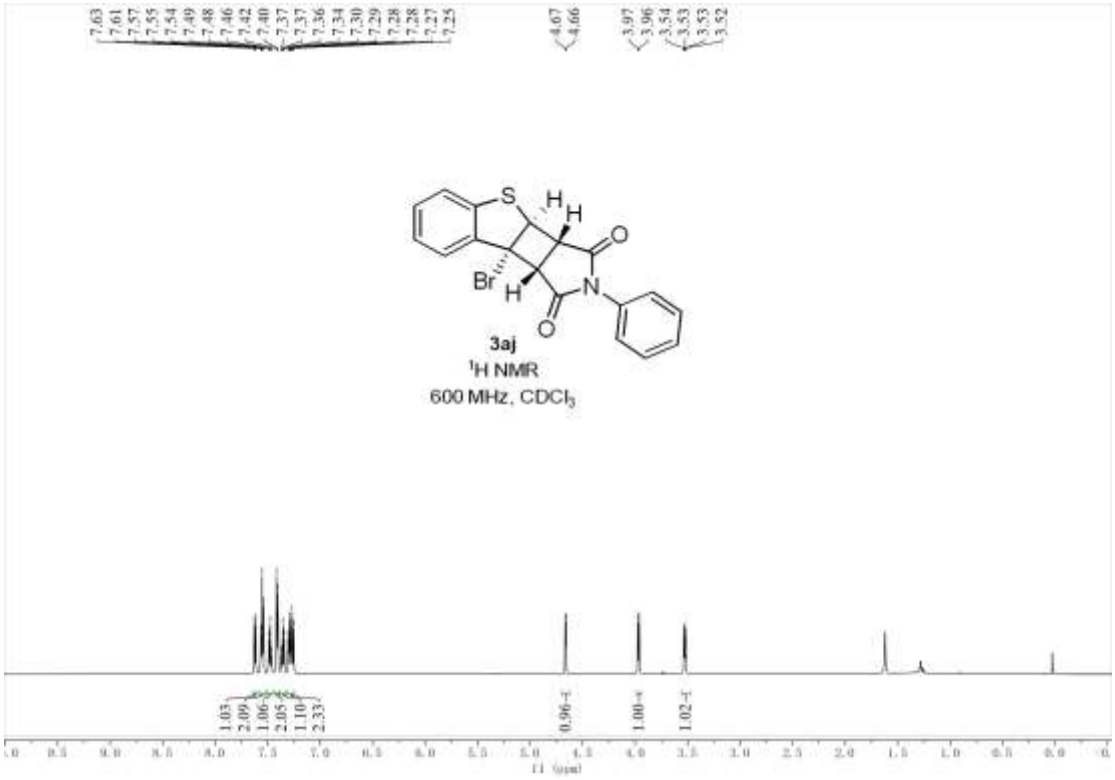
COSY (400HMZ, $CDCl_3$) of 3ai



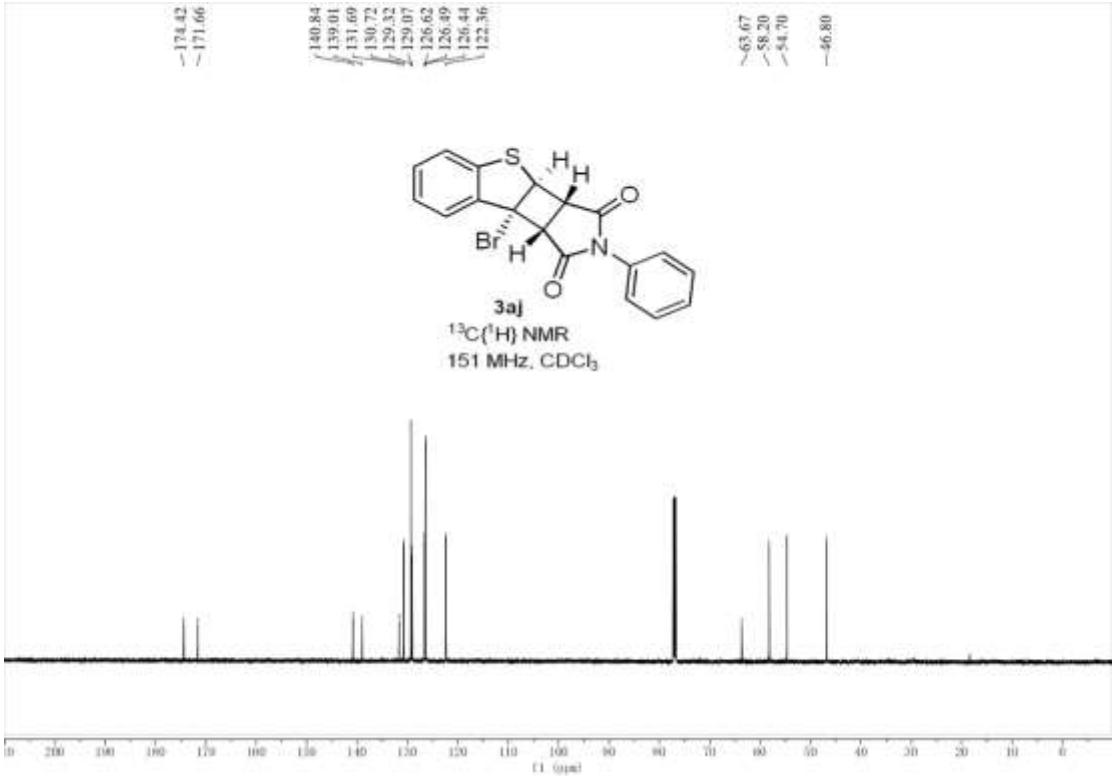
NOESY (400HMZ, $CDCl_3$) of 3ai



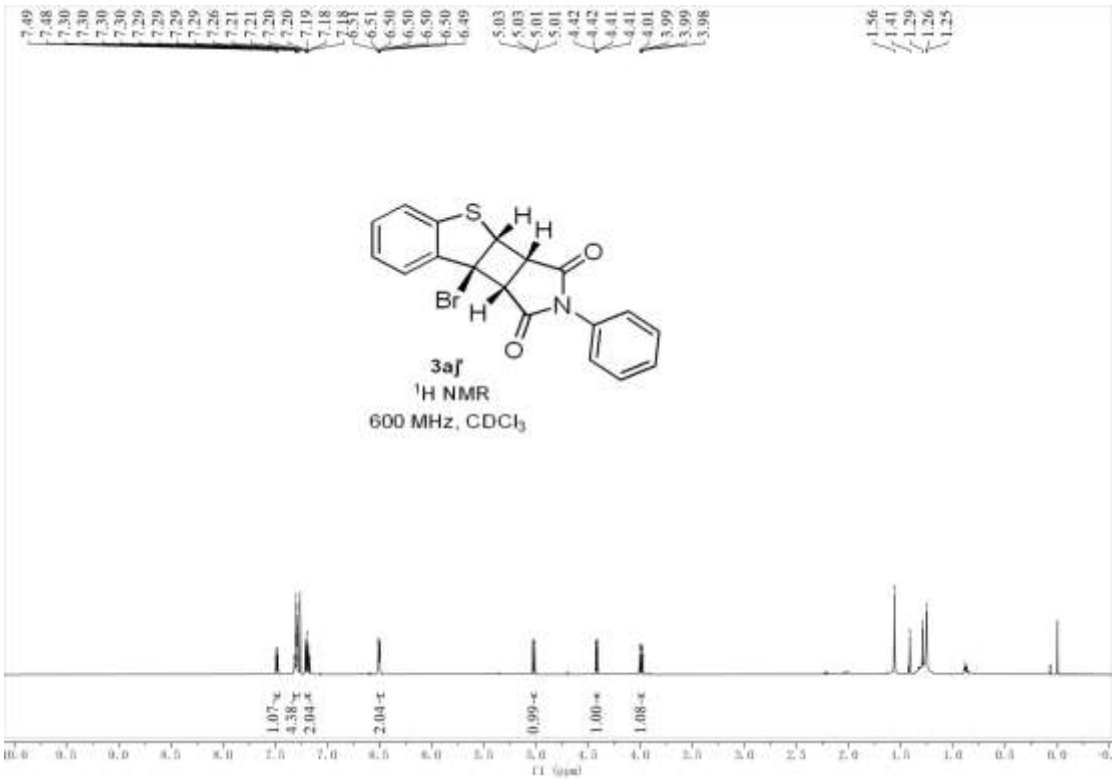
^{1}H NMR Spectrum of 3aj



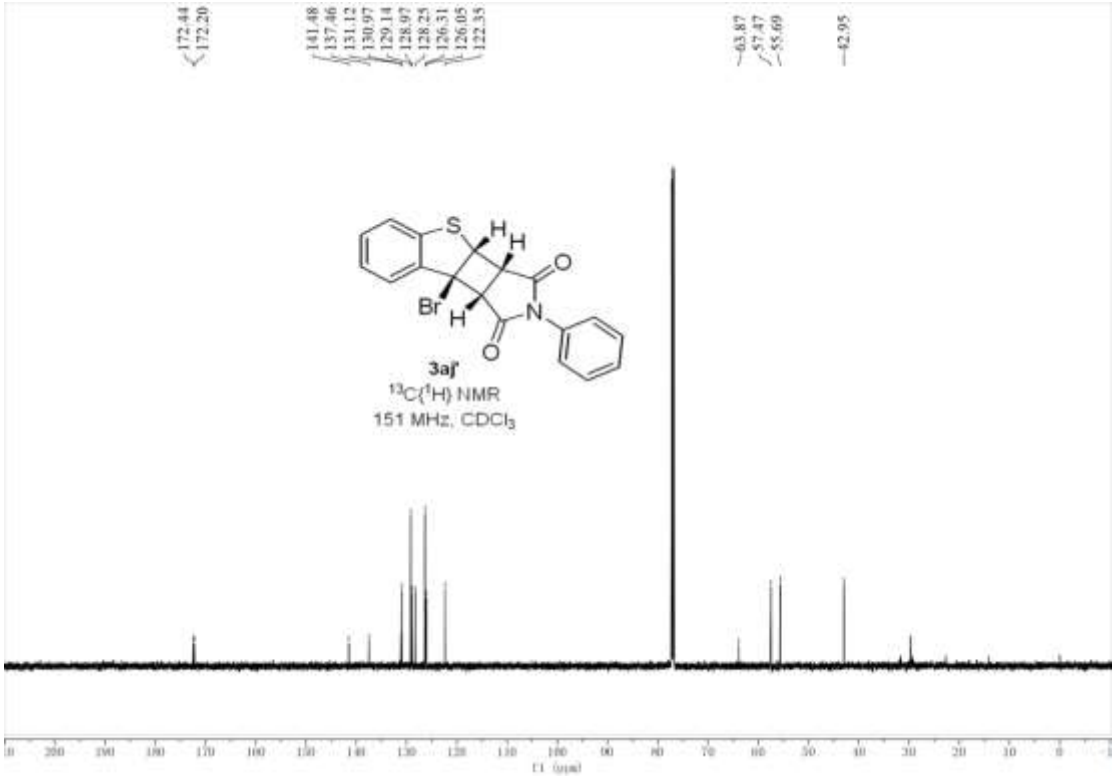
$^{13}C\{^1H\}$ NMR Spectrum of 3aj



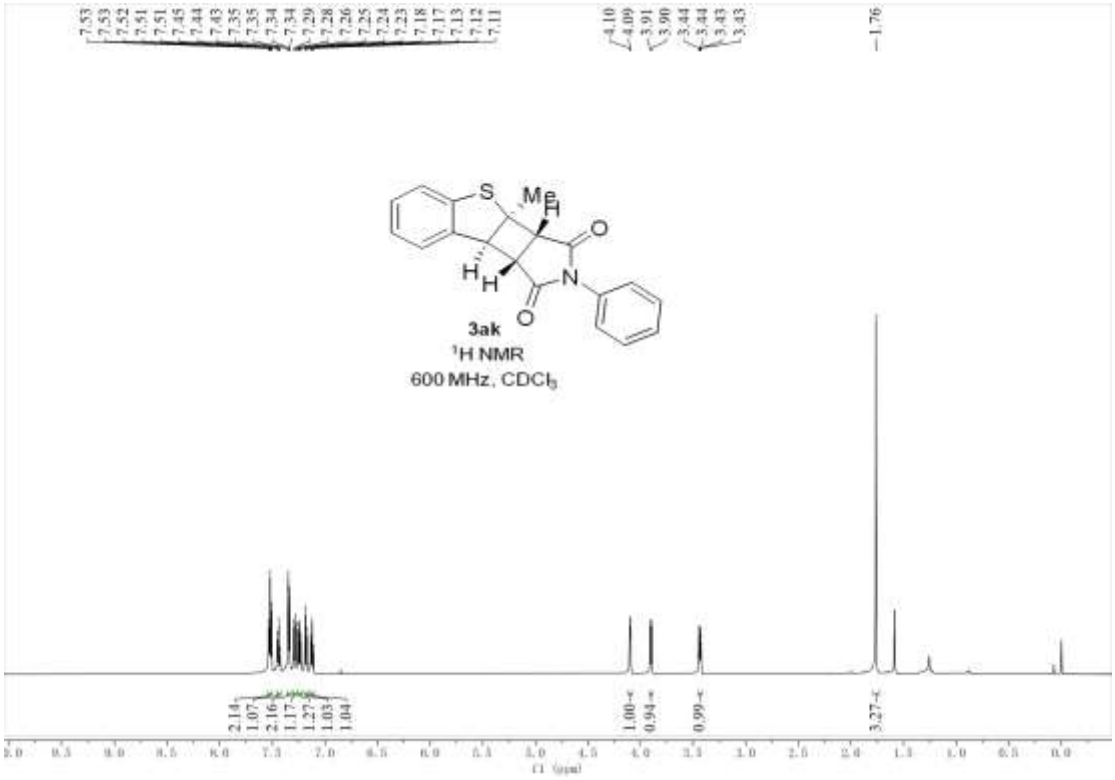
^{1}H NMR Spectrum of 3aj'



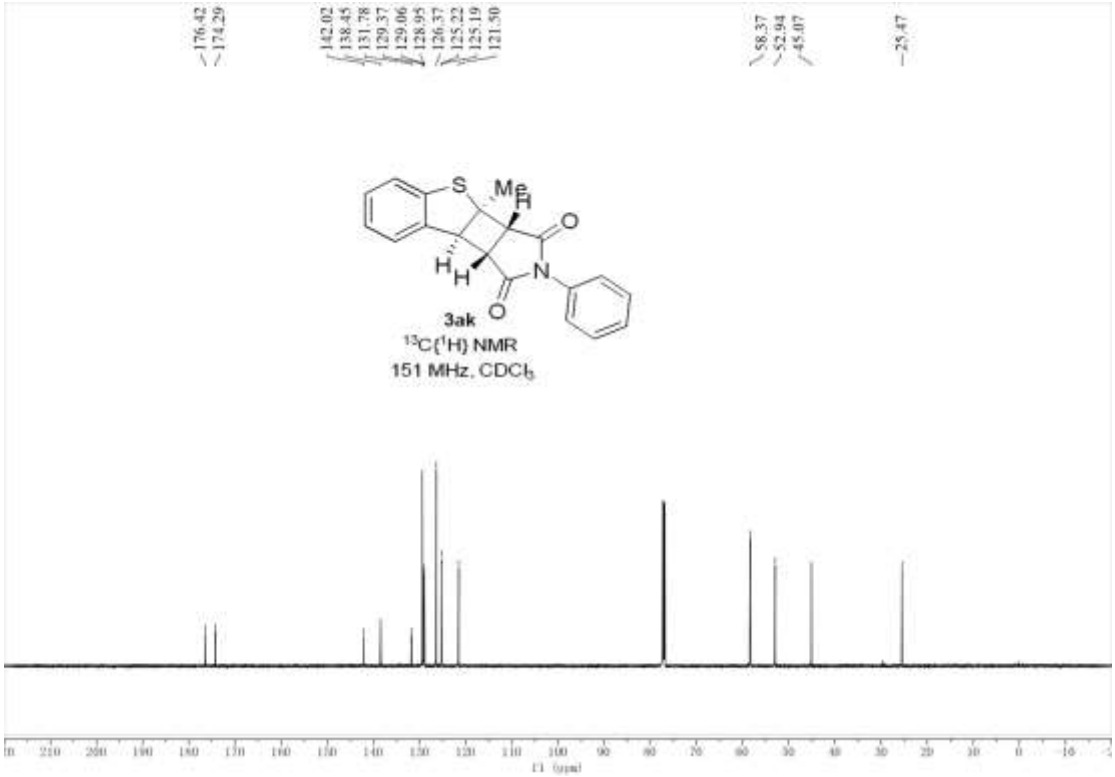
$^{13}C\{^{1}H\}$ NMR Spectrum of 3aj'



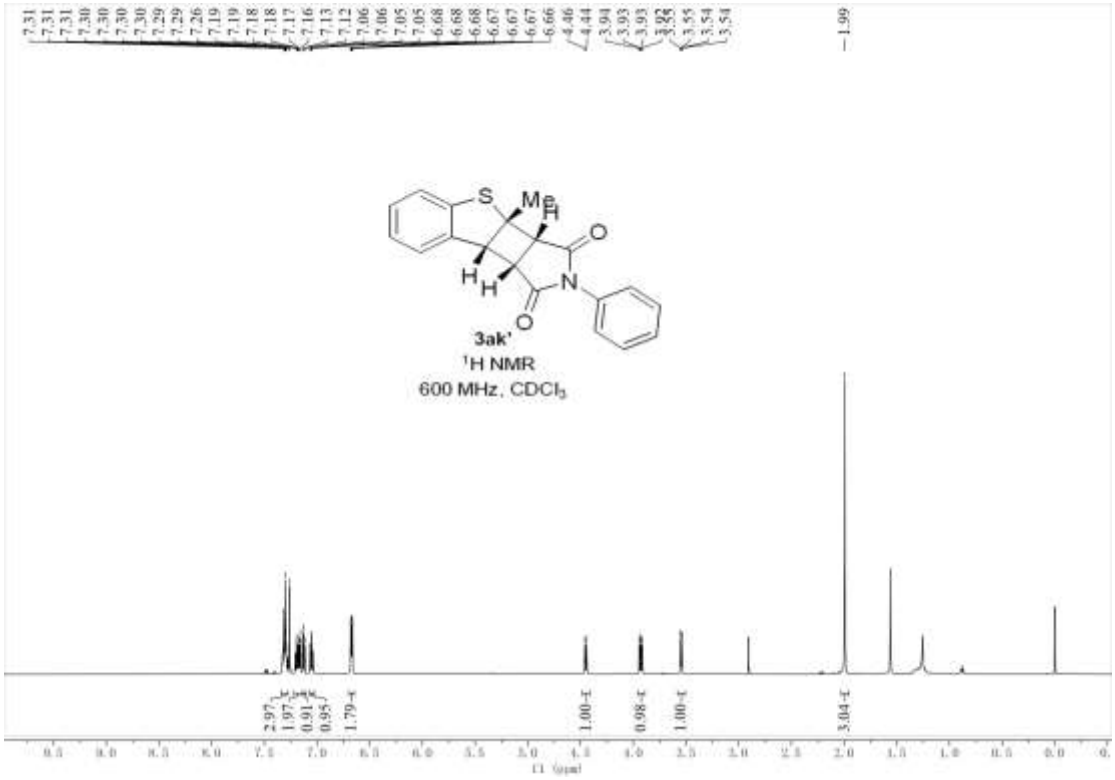
^{1}H NMR Spectrum of 3ak



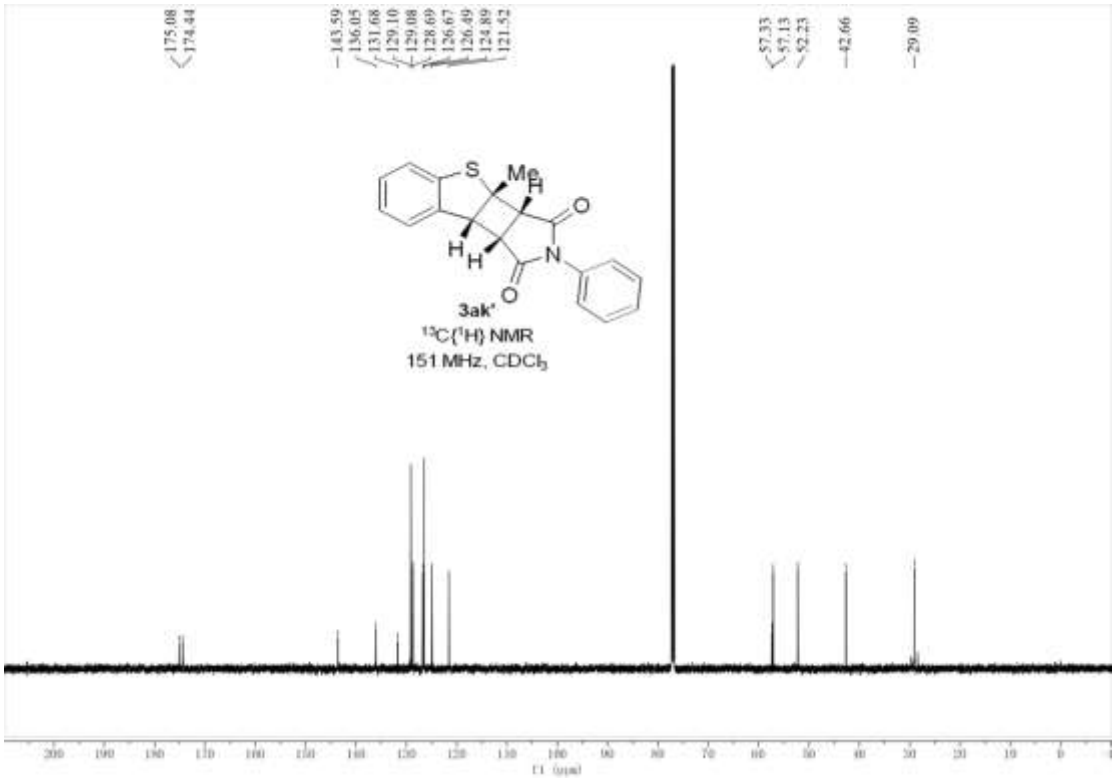
$^{13}C\{^{1}H\}$ NMR Spectrum of 3ak



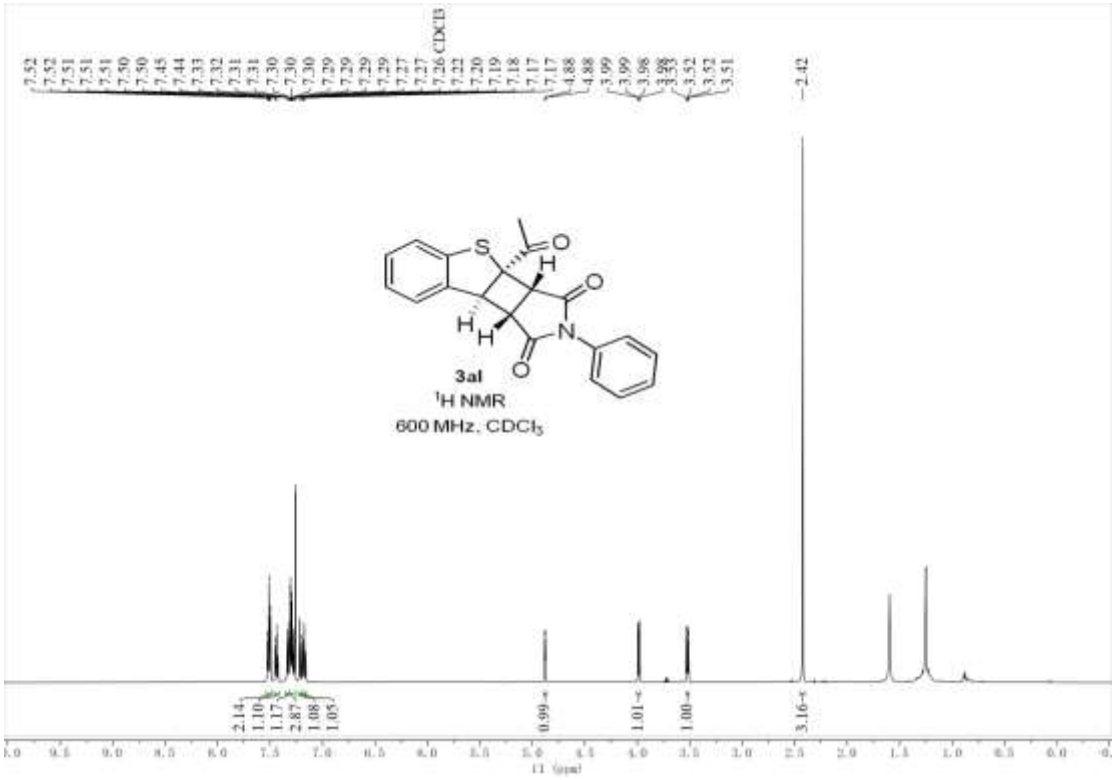
^{1}H NMR Spectrum of 3ak'



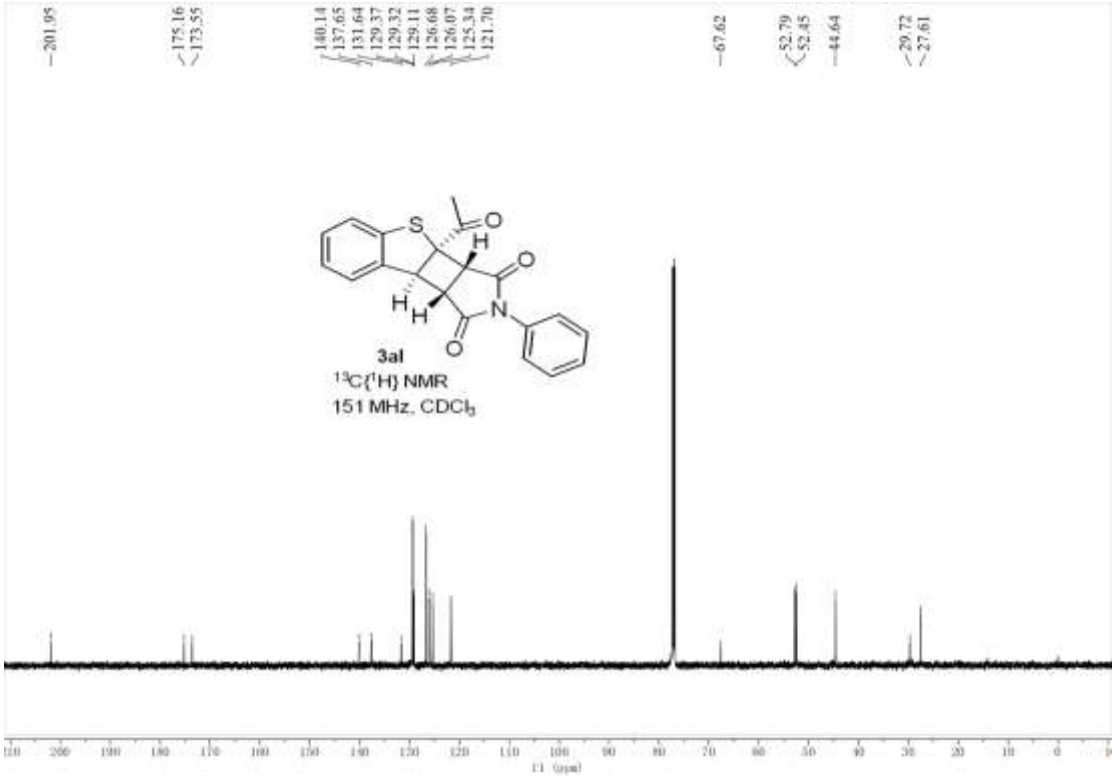
^{13}C{^{1}H} NMR Spectrum of 3ak'



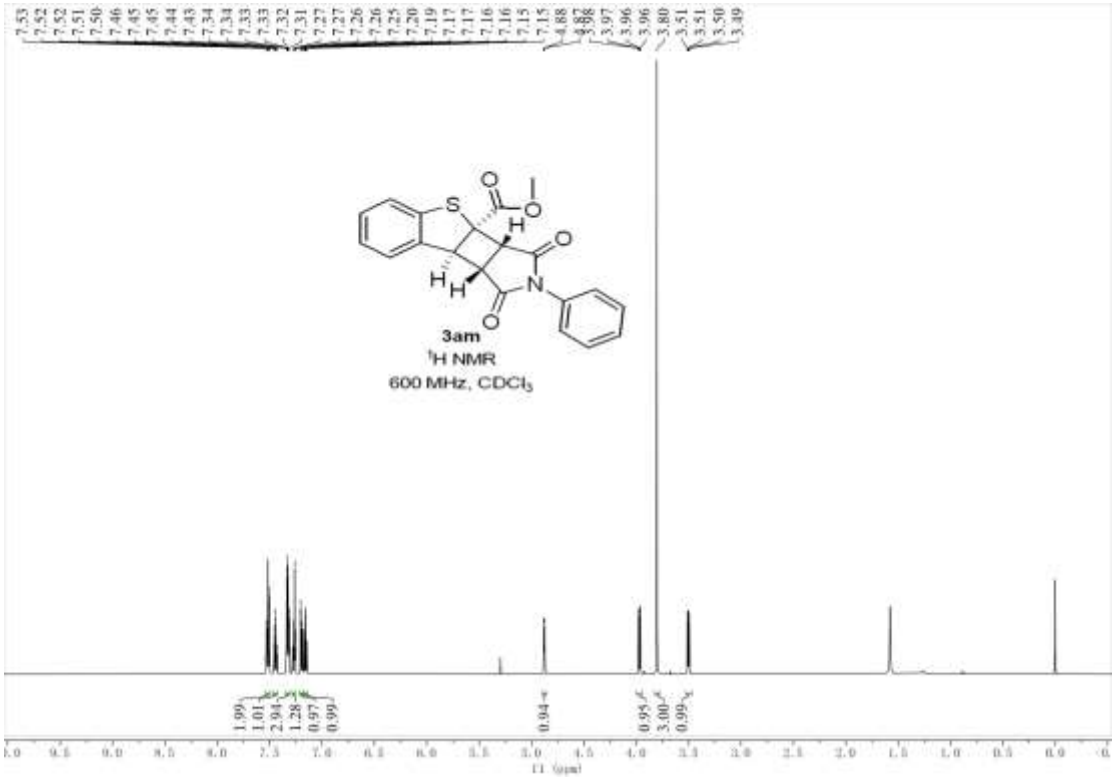
^{1}H NMR Spectrum of 3al



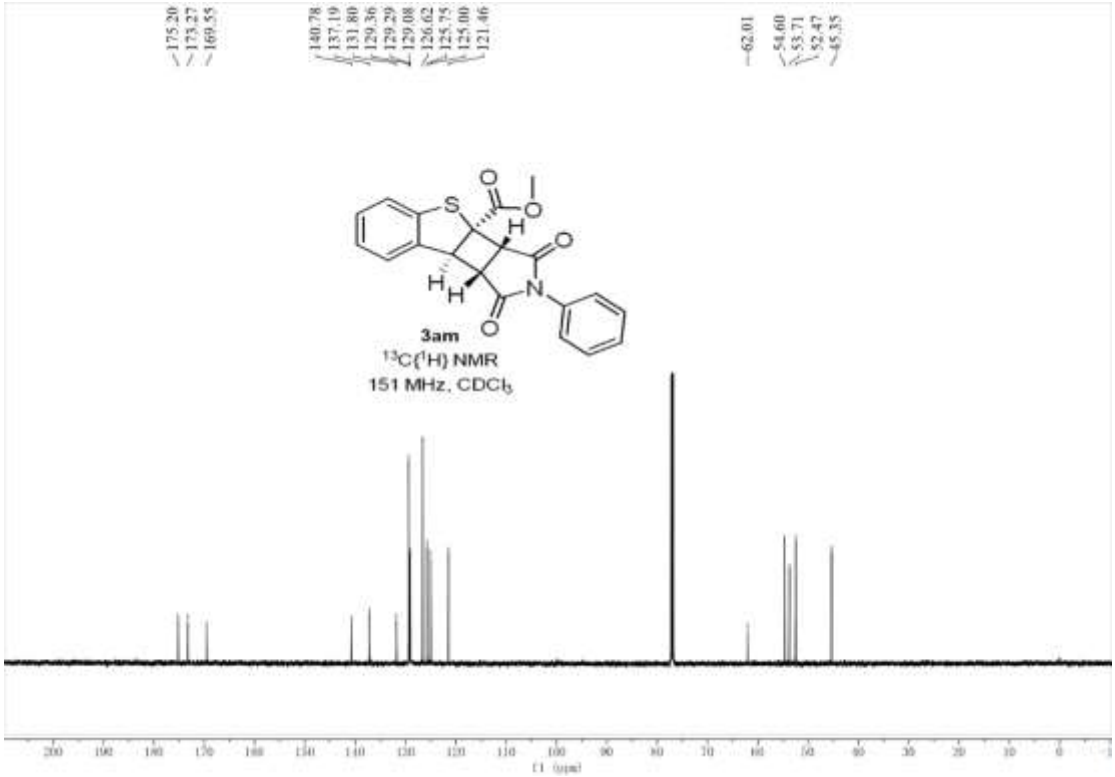
$^{13}C\{^{1}H\}$ NMR Spectrum of 3al



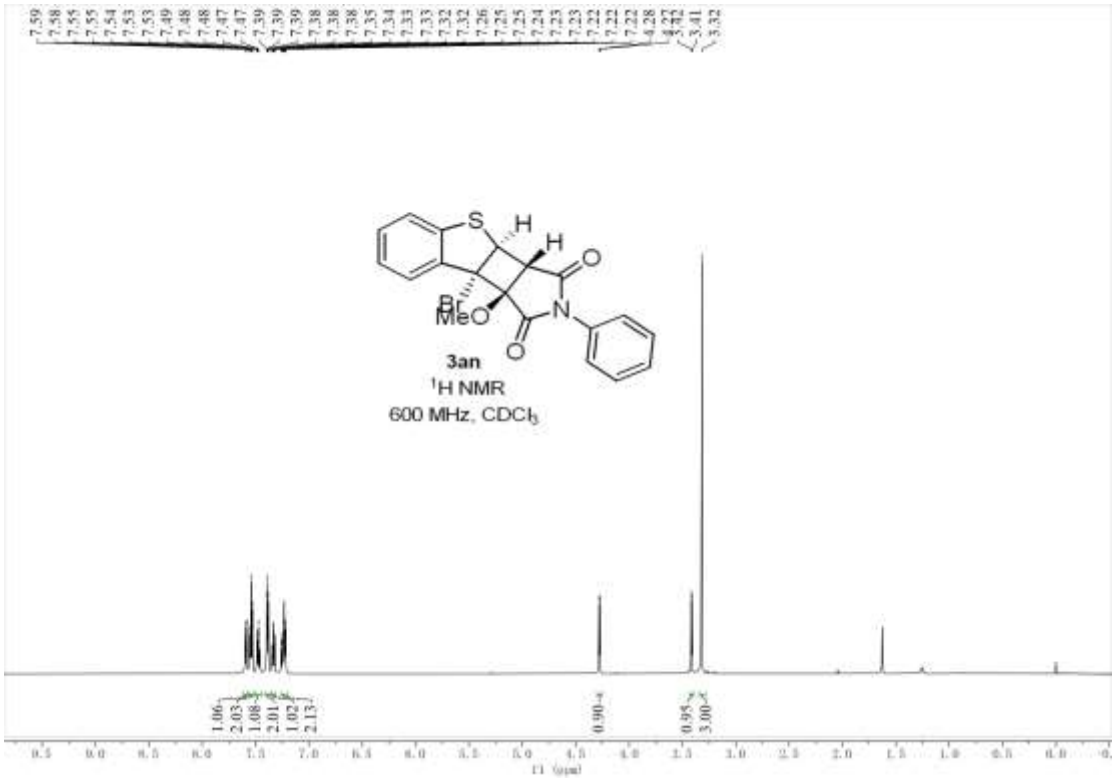
^{1}H NMR Spectrum of 3am



^{13}C{^{1}H} NMR Spectrum of 3am



^{1}H NMR Spectrum of 3an



^{13}C{^{1}H} NMR Spectrum of 3an