

**Copper-Catalysed Decarboxylative Alkynylation-Cyclization**  
**Reaction of Propargylic Cyclic Carbonates with Nitrile Imines to**  
**Access Tetrasubstituted Pyrazoles**

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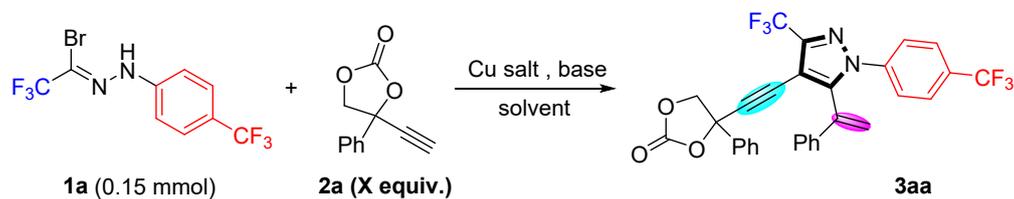
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## 1. General Methods

All chemicals were purchased from Energy chemical company, Bide Pharmatech Ltd. and so forth. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. For chromatography, 200 mesh silica gel was employed.  $^1\text{H}$  NMR and  $^{13}\text{C}\{^1\text{H}\}$  NMR were recorded on a Bruker ADVANCE (400 MHz or 500 MHz) spectrometer at room temperature. The chemical shifts ( $\delta$ ) and coupling constants (J) were expressed in ppm and Hz respectively.  $^1\text{H}$  NMR spectra were referenced to the solvent residual peak (TMS,  $\delta$  0 ppm) and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were referenced to the solvent residual peak ( $\text{CDCl}_3$ ,  $\delta$  77.0 ppm). The following abbreviations are used to illuminate the diversities:  $\delta$ , chemical shift; J, coupling constant; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. HRMS was obtained on Waters Xevo G2-XS QToF with ESI source.

## 2. Reaction Conditions Optimization of Copper-Catalysed Decarboxylative Alkynylation-Cyclization Reaction of Propargylic Cyclic Carbonates with Nitrile Imines



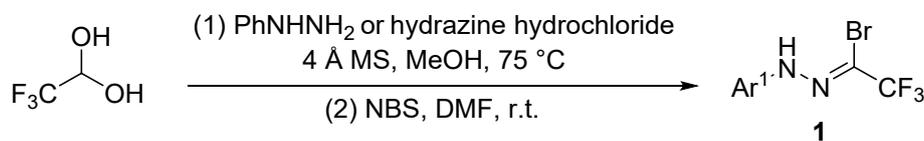
entry	X	Cu salt	base	ligand	solvent	Yield (%)
1 <sup>a</sup>	2.2	CuI	K <sub>2</sub> CO <sub>3</sub>	—	THF	51
2 <sup>a</sup>	2.2	CuI	DIPEA	—	THF	56
3 <sup>a</sup>	2.2	CuI	Na <sub>2</sub> CO <sub>3</sub>	—	THF	38
4 <sup>a</sup>	2.2	CuI	NaHCO <sub>3</sub>	—	THF	18
5 <sup>a</sup>	2.2	CuI	NaOAc	—	THF	16
6 <sup>b</sup>	2.2	CuI	DIPEA + K <sub>2</sub> CO <sub>3</sub>	—	THF	81
7 <sup>c</sup>	3	CuI	DIPEA + K <sub>2</sub> CO <sub>3</sub>	—	THF	86
8 <sup>d</sup>	3	CuI	DIPEA + K <sub>2</sub> CO <sub>3</sub>	—	THF	92
9 <sup>c</sup>	3	CuI	DIPEA + K <sub>2</sub> CO <sub>3</sub>	—	dioxane	72
10 <sup>c</sup>	3	CuI	DIPEA + K <sub>2</sub> CO <sub>3</sub>	—	Et <sub>3</sub> N	35
11 <sup>c</sup>	3	CuI	DIPEA + K <sub>2</sub> CO <sub>3</sub>	—	CH <sub>3</sub> CN	43
12 <sup>c</sup>	3	CuI	DIPEA + K <sub>2</sub> CO <sub>3</sub>	—	CH <sub>3</sub> OH	trace
13 <sup>c</sup>	3	CuI	DIPEA + K <sub>2</sub> CO <sub>3</sub>	—	toluene	51
14 <sup>d</sup>	3	CuBr	DIPEA + K <sub>2</sub> CO <sub>3</sub>	—	THF	29
15 <sup>d</sup>	3	Cu(OAc) <sub>2</sub>	DIPEA + K <sub>2</sub> CO <sub>3</sub>	—	THF	59
16 <sup>d</sup>	3	CuOTf <sub>2</sub>	DIPEA + K <sub>2</sub> CO <sub>3</sub>	—	THF	80
17 <sup>e</sup>	3	CuI	DIPEA + K <sub>2</sub> CO <sub>3</sub>	Tripyridine	THF	60
18 <sup>e</sup>	3	CuI	DIPEA + K <sub>2</sub> CO <sub>3</sub>	DTBBPY	THF	67
19 <sup>e</sup>	3	CuI	DIPEA + K <sub>2</sub> CO <sub>3</sub>	1,10-phen	THF	75
20 <sup>f</sup>	3	CuI	DIPEA + K <sub>2</sub> CO <sub>3</sub>	—	THF	70
21 <sup>g</sup>	3	CuI	DIPEA + K <sub>2</sub> CO <sub>3</sub>	—	THF	82
22 <sup>h</sup>	3	CuI	DIPEA + K <sub>2</sub> CO <sub>3</sub>	—	THF	70
23	3	—	DIPEA + K <sub>2</sub> CO <sub>3</sub>	—	THF	N.D.

<sup>a</sup> **1a**, **2a**, CuI (10 mol%), base (0.5 mmol), THF (2 ml), rt, Ar, 12 h. <sup>b</sup> **1a**, **2a**, CuI (10 mol%), DIPEA (0.35 mmol), K<sub>2</sub>CO<sub>3</sub> (0.15 mmol), THF (2 ml), rt, air, 12 h. <sup>c</sup> **1a**, **2a**, CuI (10 mol%), DIPEA (0.35 mmol), K<sub>2</sub>CO<sub>3</sub> (0.15 mmol), solvent (2 ml), rt, air, 12 h. <sup>d</sup> **1a**, **2a**, catalyst (10 mol%), DIPEA (0.35 mmol), K<sub>2</sub>CO<sub>3</sub> (0.15 mmol), dry THF (2 ml), rt, air, 12 h. <sup>e</sup> **1a**, **2a**, CuI (10 mol%), ligand (12 mol%), DIPEA (0.35 mmol), K<sub>2</sub>CO<sub>3</sub> (0.15 mmol), dry THF (2 ml), rt, air, 12 h. <sup>f</sup> **1a**, **2a**, CuI (10 mol%), DIPEA (0.35 mmol), K<sub>2</sub>CO<sub>3</sub> (0.15 mmol), dry THF (2 ml), 50 °C, air, 12 h. <sup>g</sup> **1a**, **2a**, CuI (10 mol%), DIPEA (0.35 mmol), K<sub>2</sub>CO<sub>3</sub> (0.15 mmol), dry THF (2 ml), 0 °C, air, 12 h. <sup>h</sup> **1a**, **2a**, CuI (5 mol%), DIPEA (0.35 mmol), K<sub>2</sub>CO<sub>3</sub> (0.15 mmol), dry THF (2 ml), 0 °C, air, 12 h.

### Scheme S1 Reaction Conditions Optimization

### 3. General Procedure for Preparation of Nitrile Imine Precursors

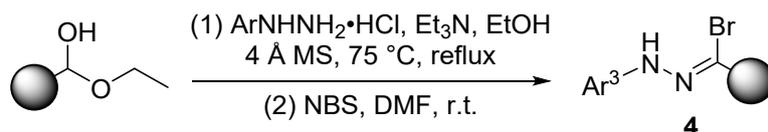
#### 3.1 Synthesis Procedure of CF<sub>3</sub>-Substituted Nitrile Imine Precursors **1**<sup>1</sup>



**Step 1:** A mixture of the phenylhydrazine or hydrazine hydrochloride (10.0 mmol, 1.0 equiv), 2,2,2-trifluoro-1,1-ethanediol (3.48 g, 30.0 mmol, 3 equiv), and freshly activated 4 Å molecular sieves in MeOH (15 mL) was heated at 75 °C overnight in a closed ampoule. Upon completion, the resulting mixture was cooled to room temperature, diluted with DCM (15 mL), and filtered through Celite. The solvent was removed under reduced pressure to afford the intermediate, which was used directly in the next step without further purification.

**Step 2:** To a solution of the crude intermediate from Step 1 in DMF (15 mL) was added NBS (1.96 g, 11 mmol, 1.1 equiv). The resulting mixture was stirred at room temperature and monitored by TLC. After completion, the reaction was quenched with saturated NaCl solution and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether) to afford the desired compounds.

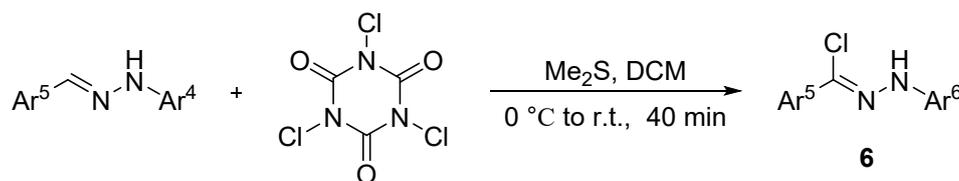
#### 3.2 Synthesis Procedure of CF<sub>2</sub>H or Cl-Substituted Nitrile Imine Precursors **4**<sup>2</sup>



**Step 1:** A mixture of hydrazine hydrochloride (2.5 mmol, 1.0 equiv), triethylamine (253 mg, 2.5 mmol, 1.0 equiv), difluoroacetaldehyde ethyl hemiacetal (473 mg, 3.75 mmol, 1.5 equiv), and freshly activated 4 Å molecular sieves in MeOH (8 mL) was heated overnight at 75 °C in a closed ampoule. The reaction progress was monitored by TLC. Upon completion, the solvent was removed under reduced pressure to afford the crude intermediate, which was used directly in the next step without further purification.

**Step 2:** To a solution of the crude product from Step 1 in DMF (8 mL) was added NBS (490 mg, 2.75 mmol, 1.1 equiv). The resulting mixture was stirred at room temperature and monitored by TLC. After completion, the reaction was quenched with saturated NaCl solution and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether) to afford the desired compounds **4**.

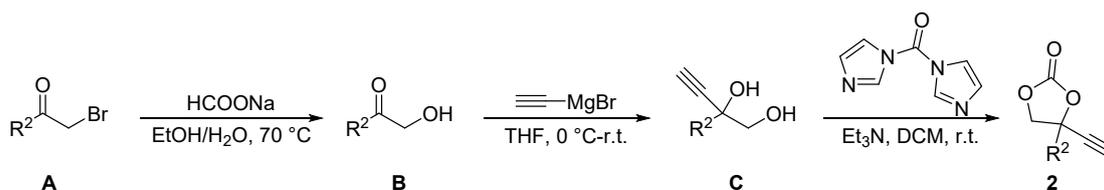
### 3.3 Synthesis Procedure of Ar-Substituted Nitrile Imine Precursors **6**<sup>3</sup>



To a 25 mL round-bottom flask cooled in an ice bath were sequentially

added trichloroisocyanuric acid (1.94 g, 8.33 mmol, 1.0 equiv), DCM (15 mL), and dimethyl sulfide (620 mg, 10 mmol, 1.2 equiv). The mixture was stirred for 20 minutes, during which a large amount of white cloudy precipitate formed. A solution of hydrazone (10 mmol, 1.2 equiv) in DCM (8 mL) was then added, and stirring was continued for 5 minutes. The reaction flask was subsequently allowed to warm to room temperature and stirred for an additional 15 minutes. The reaction progress was monitored by TLC. Upon completion, the mixture was quenched with saturated NaCl solution and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using petroleum ether as the eluent to afford the desired compounds **6**.

#### 4. General Procedure for Preparation of Propargylic Cyclic Carbonates<sup>4</sup>



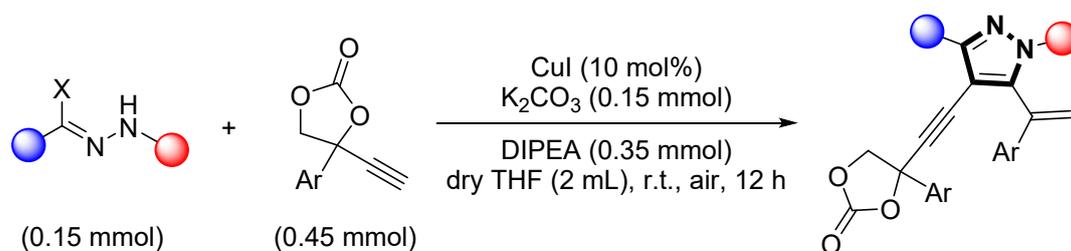
To a mixture of sodium formate (13.9g, 204 mmol, 6.8 equiv), ethanol (80 mL), and water (40 mL) was added compound **A** (30 mmol). The reaction mixture was stirred at 70 °C for 12 h in an oil bath. After concentration under reduced pressure, the residue was diluted with ethyl acetate (100 mL) and water (50 mL). The aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried

over anhydrous sodium sulfate and concentrated under vacuum to afford crude product **B**.

A solution of **B** in THF (50 mL) was cooled to 0 °C in an ice-water bath, and ethynylmagnesium bromide (0.5 M in THF, 180 mL) was added dropwise. The mixture was stirred at room temperature for 12 h. The reaction was quenched with saturated ammonium chloride solution, and the aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure to give crude product **C**.

To a solution of **C** in DCM (40 mL) were sequentially added triethylamine (3.04 g, 30 mmol) and 1,1'-carbonyldiimidazole (4.86 g, 30 mmol). The resulting mixture was stirred at room temperature for 12 h. After concentration under reduced pressure, the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) to afford substrate **2**.

## 5. General Procedure of the Copper-Catalysed Decarboxylative Alkynylation-Cyclization Reaction of Propargylic Cyclic Carbonates with Nitrile Imines

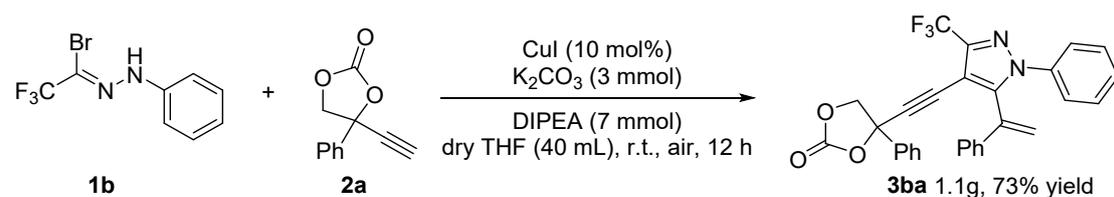


To an over-dried 25 mL Schlenk tube equipped with a stir bar were

added CuI (2.86 mg, 0.015 mmol, 10 mol%), dry THF (2 mL), Nitrile imine precursor (0.15 mmol, 1.0 equiv), propargyl carbonate (0.45 mmol, 3.0 equiv), DIPEA (45 mg, 0.35 mmol, 2.33 equiv), and K<sub>2</sub>CO<sub>3</sub> (21 mg, 0.15 mmol, 1.0 equiv) sequentially. The reaction mixture was then stirred at room temperature for 12 hours under air. After completion of the reaction, the solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel to afford the title compound.

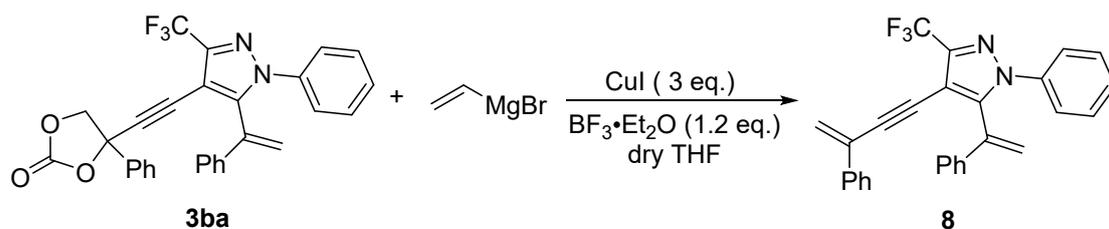
## 6. Scale-up and Synthetic Transformation Experiments

### 1. Scale-up Experiment

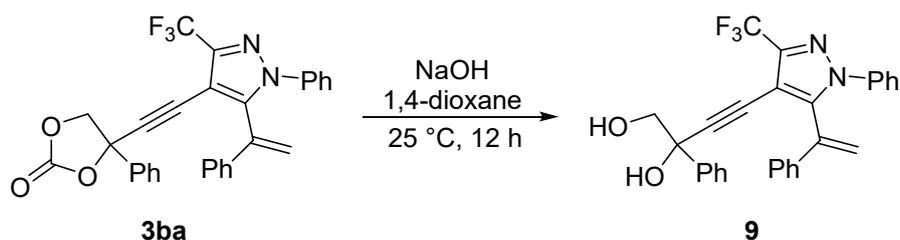


To an over-dried 100 mL Schlenk tube equipped with a stir bar were added sequentially CuI (57.2 mg, 0.3 mmol, 10 mol%), dry THF (40 mL), **1b** (801 mg, 3 mmol, 1.0 equiv), **2a** (1.69 g, 9 mmol, 3.0 equiv), DIPEA (903 mg, 7 mmol, 2.33 equiv), and K<sub>2</sub>CO<sub>3</sub> (414.6 mg, 3 mmol, 1.0 equiv). The reaction mixture was then stirred at room temperature for 12 hours under air. After completion of the reaction, the solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) to afford the title compound **3ba** as a white solid (1.1 g, 73% yield).

### 2. Synthetic Transformation Experiments



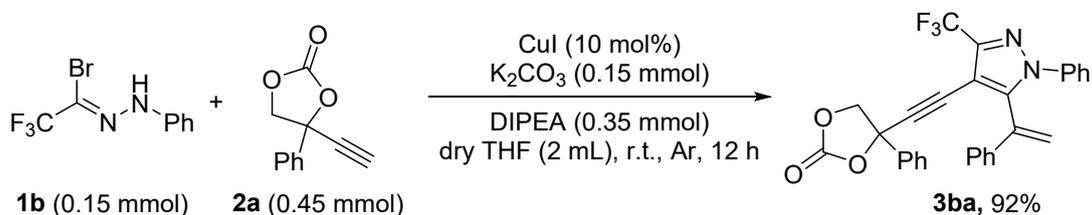
To an over-dried 25 mL Schlenk tube equipped with a stir bar were added CuI (114 mg, 0.6 mmol, 3.0 equiv), after degassed and nitrogen backfilling for three times, dry THF (1 mL) was added. Then, vinylmagnesium bromide (1.0 M in THF, 1.2 mL, 6.0 equiv) and  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (0.3 mL, 1.2 equiv) were added at  $-78^\circ\text{C}$ . After that, **3ba** (100 mg, 0.2 mmol) in dry THF (1 mL) was added and the mixture was allowed to warm to  $25^\circ\text{C}$  for 12 h. To the reaction mixture was added saturated  $\text{NH}_4\text{Cl}$  solution (2.0 mL) and extracted with EA (10.0 mL  $\times$  3). The organic layer was dried over  $\text{Na}_2\text{SO}_4$  and evaporated in vacuo. Purification by column chromatography (hexane/EtOAc: 10/1) yielded **8** (70 mg, 80%) as colorless oil.



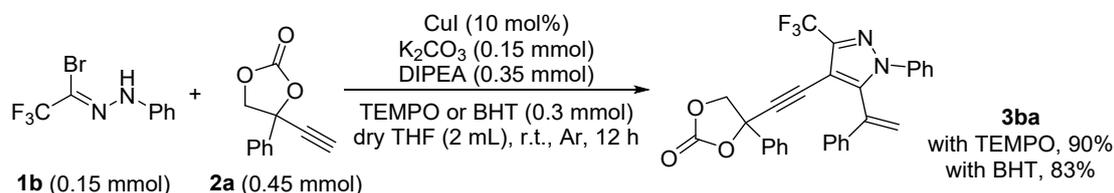
To an over-dried 25 mL Schlenk tube equipped with a stir bar were added **3ba** (100 mg, 0.2 mmol) and 1, 4-dioxane (2 mL), followed by NaOH (1 M, 2 mL). The resulting solution was allowed to stir for 12 h at  $25^\circ\text{C}$ . The mixture was transferred into a round bottom flask with DCM (20 mL), and concentrated in vacuo. Purification by column

chromatography on silica gel (EtOAc: 100%) afforded the desired products **9** (85 mg, 90%) as white solid.

## 7. Reaction Mechanism Probing

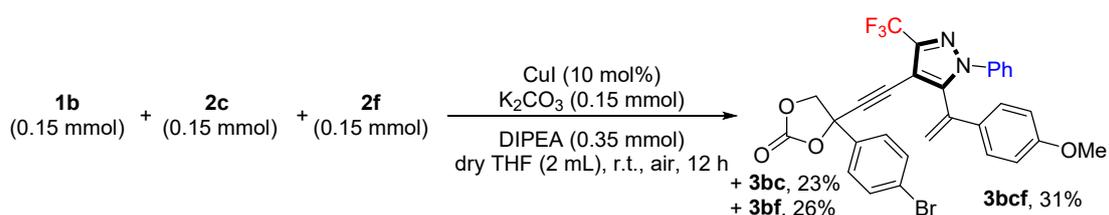


To an over-dried 25 mL Schlenk tube equipped with a stir bar were added  $\text{CuI}$  (2.86 mg, 0.015 mmol, 10 mol%), **1b** (40 mg, 0.15 mmol, 1.0 equiv), **2a** (84.6 mg, 0.45 mmol, 3.0 equiv),  $\text{DIPEA}$  (45 mg, 0.35 mmol, 2.33 equiv), and  $\text{K}_2\text{CO}_3$  (21 mg, 0.15 mmol, 1.0 equiv) sequentially, after degassed and nitrogen backfilling for three times, THF (2 mL) was added. The reaction mixture was then stirred at room temperature for 12 hours. After completion of the reaction (monitored by TLC), the solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) to afford the title compound **3**.



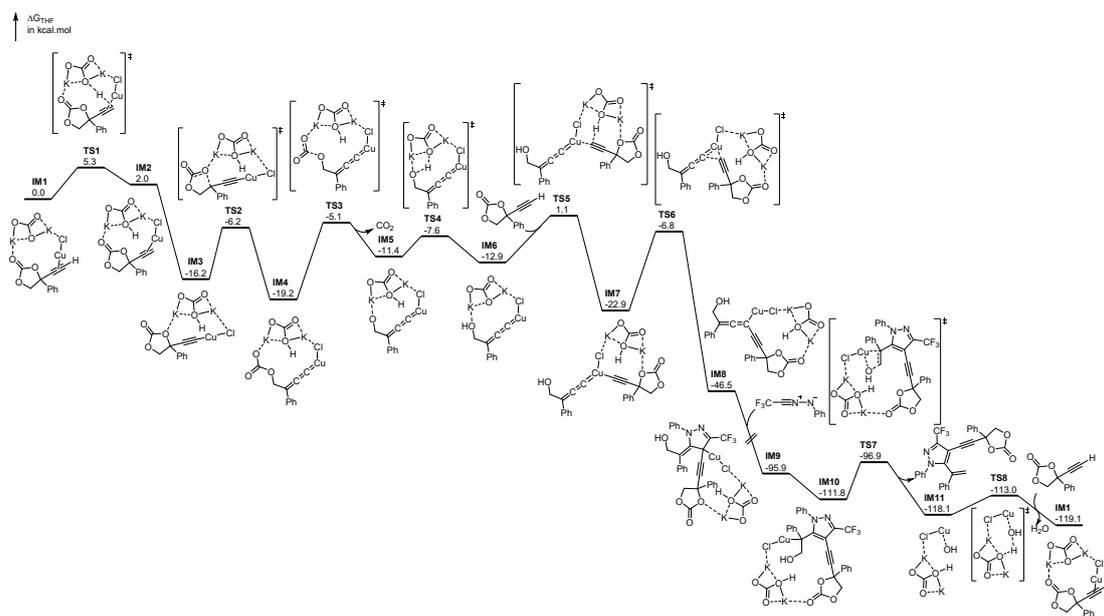
To an over-dried 25 mL Schlenk tube equipped with a stir bar were added  $\text{CuI}$  (2.86 mg, 0.015 mmol, 10 mol%), THF (2 mL), **1b** (40 mg, 0.15 mmol, 1.0 equiv), **2a** (84.6 mg, 0.45 mmol, 3.0 equiv), TEMPO or BHT (0.3 mmol, 2.0 equiv),  $\text{DIPEA}$  (45 mg, 0.35 mmol, 2.33 equiv), and

$\text{K}_2\text{CO}_3$  (21 mg, 0.15 mmol, 1.0 equiv) sequentially. The reaction mixture was then stirred at room temperature for 12 hours under Ar. After completion of the reaction (monitored by TLC), the solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) to afford the title compound.



To an over-dried 25 mL Schlenk tube equipped with a stir bar were added CuI (2.86 mg, 0.015 mmol, 10 mol%), THF (2 mL), **1b** (40 mg, 0.15 mmol, 1.0 equiv), **2c** (32.7 mg, 0.15 mmol, 1.0 equiv), **2f** (40 mg, 0.15 mmol, 1.0 equiv), DIPEA (45 mg, 0.35 mmol, 2.33 equiv), and  $\text{K}_2\text{CO}_3$  (21 mg, 0.15 mmol, 1.0 equiv) sequentially. The reaction mixture was then stirred at room temperature for 12 hours under Ar. After completion of the reaction (monitored by TLC), the solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10 :1) to afford the products.

## 8. Theoretical Calculations



**Scheme S2.** Gibbs Free Energy Profile

All calculations were performed using density functional theory (DFT). Geometries were optimized in the gas phase at the B3LYP-GD3BJ<sup>5</sup>/BSI level with Gaussian 09 software<sup>6</sup>. The BSI basis set combines SDD<sup>7</sup> for Cu and 6-31G(d) for nonmetal atoms. Subsequent single-point calculations were carried out with the M06<sup>8</sup> functional using the SMD<sup>9</sup> solvation model, applying the SDD basis set for palladium and the 6-311++G(d,p)<sup>10</sup> basis set for all other atoms.

### Cartesian Coordinates (Å) of Optimized Structures.

#### CO<sub>2</sub>

C	0.00000000	0.00060100	0.00000000
O	1.15674800	0.03541400	0.00000000
O	-1.15674800	-0.03586400	0.00000000

**CuCl**

Cu	0.00000000	0.00000000	0.76264600
Cl	0.00000000	0.00000000	-1.30098400

**H<sub>2</sub>O**

O	0.00000000	0.11974000	0.00000000
H	0.76167300	-0.47904800	0.00000000
H	-0.76167300	-0.47887100	0.00000000

**IM1**

Cu	0.70304000	-1.14652300	0.70453800
Cl	0.40360300	-2.63661900	-0.95948400
C	-1.20357300	0.52996000	-1.54716600
C	-1.74536900	0.66946200	-0.12488700
H	-0.63275500	-0.38894000	-1.71815800
H	-2.01073900	0.64524200	-2.28252500
C	-0.74905700	2.58320500	-0.74359800
O	-0.21391800	3.65026200	-0.59341200
O	-0.32895300	1.66596900	-1.63246100
O	-1.79265100	2.12591700	-0.03651800
C	-3.09946600	0.04932900	0.06671600

C	-3.18467100	-1.34484700	0.06413900
C	-4.24833900	0.82510200	0.18924400
C	-4.42592900	-1.95679800	0.18678400
H	-2.27948600	-1.94792600	-0.03945500
C	-5.48666400	0.20277800	0.31787300
H	-4.17160200	1.91016300	0.19370000
C	-5.57765200	-1.18488700	0.31589300
H	-4.49075500	-3.04324000	0.18373200
H	-6.38455800	0.80947400	0.42203900
H	-6.54840600	-1.66738500	0.41647800
C	-0.72928100	0.25025700	0.86788100
C	0.11124900	0.42868800	1.76561200
H	0.90703200	0.72154800	2.44746000
C	2.95981800	0.14673600	0.92420300
O	3.37801600	0.35194300	-0.28224700
O	2.81780200	1.09346100	1.75553600
O	2.61109900	-1.09097500	1.25125000
K	3.40969100	-2.14530300	-0.94625500
K	2.42527100	2.74878900	-0.16621700

## **IM2**

Cu	0.76804000	-1.04217700	0.56096800
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Cl	0.83695600	-2.45231600	-1.17027600
C	-1.36828800	0.48902700	-1.53193100
C	-1.86006200	0.58813700	-0.08828800
H	-0.71340700	-0.36853800	-1.71851700
H	-2.20694500	0.51379600	-2.24068300
C	-1.12700100	2.59740700	-0.78091600
O	-0.69260900	3.71538200	-0.66437900
O	-0.61756300	1.70993300	-1.66226500
O	-2.08880000	2.04701700	-0.04144400
C	-3.14391500	-0.15567400	0.15172400
C	-3.10413900	-1.44046500	0.69146100
C	-4.36404200	0.39361700	-0.24390200
C	-4.27928800	-2.17051600	0.83340000
H	-2.14916300	-1.86425400	1.00184500
C	-5.53707500	-0.33465600	-0.08744400
H	-4.39491900	1.40116000	-0.65591000
C	-5.49659000	-1.61891000	0.44840200
H	-4.24027300	-3.17355100	1.25428000
H	-6.48811800	0.10487000	-0.38351300
H	-6.41650300	-2.18882700	0.56848500
C	-0.76345600	0.31841700	0.86189800
C	0.12995700	0.44247300	1.74516400

H	2.15536300	0.70207300	2.45758200
C	3.22572500	0.18383100	0.98662500
O	3.72467000	0.66214800	-0.06103800
O	2.91271300	1.09243400	1.95852700
O	2.92936800	-1.02302500	1.19879300
K	3.73277100	-1.79441000	-1.14453800
K	1.77982700	2.60485900	0.07087200

### **IM3**

Cu	-2.39737300	-0.93123200	-1.10450600
Cl	-4.52216800	-0.69618900	-1.00534900
C	2.88904700	-1.77046000	-1.46271400
C	2.08874500	-0.71008700	-0.69199700
H	2.47296700	-1.97420800	-2.45172900
H	3.95523900	-1.52169800	-1.53959700
C	2.38956500	-2.57677100	0.58231100
O	2.14789200	-3.31975700	1.49477800
O	2.74227800	-2.94152800	-0.65423800
O	2.29655500	-1.23485100	0.67774700
C	2.64162800	0.69416700	-0.73447200
C	1.81742900	1.77390200	-1.05111500
C	3.97278700	0.92785200	-0.38083700

C	2.31858300	3.07219900	-1.01330200
H	0.77056900	1.59620900	-1.29381000
C	4.47397700	2.22309000	-0.35257300
H	4.61624100	0.09633600	-0.09328400
C	3.64705500	3.29868900	-0.66832800
H	1.65652000	3.90517500	-1.24241100
H	5.51127400	2.39456600	-0.07059100
H	4.03854500	4.31401400	-0.63684200
C	0.66138700	-0.81765900	-0.95596200
C	-0.55622000	-0.93103600	-1.06925300
H	1.02696300	1.93644100	1.27701700
C	-0.84548800	1.61321600	1.44328200
O	-1.67823800	0.80389000	1.92622800
O	0.46797300	1.31251100	1.77044500
O	-1.04588700	2.59843800	0.71310600
K	-3.53498700	1.82063800	0.38500400
K	-0.15360100	-1.31738100	2.02963400

#### **IM4**

Cu	-1.39376900	-1.99220300	-0.32657100
Cl	-2.63007100	-2.84047300	1.32838500
C	2.14464600	1.44141400	1.17752900

C	2.35416200	0.18096800	0.38385000
H	2.81168200	1.42229000	2.05323400
H	2.42558600	2.29912800	0.54557900
C	-0.01845300	2.39628400	0.85338700
O	-1.14998500	2.52069300	1.36202200
O	0.84061000	1.60792400	1.64927100
O	0.42079000	2.82415100	-0.22458900
C	3.70110600	-0.17323000	-0.04209300
C	3.93341600	-1.39996800	-0.68873700
C	4.78717500	0.69096800	0.17970200
C	5.20919300	-1.75144000	-1.09455500
H	3.09119400	-2.06896000	-0.86007000
C	6.06272000	0.33700100	-0.23284600
H	4.63537500	1.65186700	0.66728800
C	6.27707300	-0.88416700	-0.86782100
H	5.37536200	-2.70583800	-1.58989900
H	6.89461100	1.01668400	-0.05962100
H	7.28010700	-1.16079900	-1.18791800
C	1.28979000	-0.59523000	0.08955200
C	0.29174100	-1.30285500	-0.22063700
H	-3.41283200	0.15045200	-3.28854300
C	-2.88750800	-0.07698800	-1.48011700

O	-2.70349800	0.52832800	-0.40858600
O	-3.33099100	0.73086100	-2.51520000
O	-2.69428300	-1.27866500	-1.76723300
K	-1.80539000	0.05633600	2.02410000
K	-2.08419300	2.93388700	-1.10308900

### **IM5**

Cu	-1.76835800	-1.42544000	-0.68154200
Cl	-2.53204300	-2.65344800	1.00278700
C	1.71414500	1.37304300	1.33113800
C	2.05182100	0.33511200	0.26360500
H	2.24152400	0.96018400	2.23802600
H	2.37209900	2.24900200	1.06217400
O	0.43152200	1.66480600	1.51185900
C	3.42744300	-0.03557100	-0.04629800
C	3.68792700	-1.01053200	-1.02455600
C	4.51483200	0.55951900	0.61765400
C	4.98890600	-1.37745400	-1.32987400
H	2.84538200	-1.47588400	-1.53495400
C	5.81451800	0.18913900	0.31099900
H	4.34027300	1.31445800	1.38168000
C	6.05550900	-0.77848900	-0.66327500

H	5.17373400	-2.13545200	-2.08847300
H	6.64696800	0.65577000	0.83423800
H	7.07799100	-1.06681700	-0.90129000
C	0.99844000	-0.25115100	-0.36472300
C	-0.04902600	-0.78604200	-0.81914200
H	-3.35341000	1.55290100	-2.69219800
C	-3.10403900	0.91065700	-0.92616500
O	-2.77997400	1.25992200	0.22553800
O	-3.11040900	1.95956400	-1.84485200
O	-3.35117500	-0.21910300	-1.39627700
K	-1.49041500	0.00454300	2.14422600
K	-0.78011200	2.74815900	-0.44150000

## IM6

Cu	1.75663500	-0.59514300	-1.01393200
Cl	3.49115900	-1.96405800	-1.09831600
C	-2.41599500	2.16981100	0.02541900
C	-2.24704100	0.72662600	-0.38869800
H	-3.12669900	2.64796300	-0.67088500
H	-2.90445300	2.17896300	1.01651500
O	-1.24490700	2.90691700	0.03232200
C	-3.32136600	-0.23034400	-0.17462600

C	-3.12489300	-1.58789600	-0.48658500
C	-4.57192400	0.17290600	0.32583100
C	-4.14083300	-2.50854900	-0.29771200
H	-2.15585000	-1.89992200	-0.87328700
C	-5.59004300	-0.75097600	0.50380900
H	-4.75556200	1.21646000	0.57342700
C	-5.37671300	-2.09271700	0.19618900
H	-3.97196600	-3.55649000	-0.53706900
H	-6.55447500	-0.42484100	0.88800400
H	-6.17617500	-2.81702000	0.34250400
C	-1.07411800	0.35212400	-0.95204900
C	0.05134900	-0.01575900	-1.38454200
H	-0.65343500	2.53501100	0.75938000
C	1.17712000	0.83824300	1.45937200
O	2.16575600	0.66656800	0.55401000
O	0.67311100	2.01533100	1.52036200
O	0.84237100	-0.13257300	2.17858600
K	3.02191600	-1.44260700	1.85459700
K	1.41611600	2.74141000	-0.83690600

## IM7

Cu	-0.35559500	-0.79460800	-1.27838200
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Cl	0.41767500	-2.94177600	-1.79171900
C	-3.94334000	0.79191500	2.08514500
C	-3.95488400	0.88619400	0.57713000
H	-3.93638000	1.81905400	2.48563900
H	-4.91133000	0.35378500	2.40079000
O	-2.86947400	0.12021700	2.63717400
C	-5.01971500	1.62696000	-0.08914100
C	-5.02694800	1.73935800	-1.49043700
C	-6.04900000	2.24482200	0.64148900
C	-6.02739600	2.44475100	-2.13701300
H	-4.22706800	1.26372000	-2.05662900
C	-7.04995100	2.95019300	-0.00999000
H	-6.07232800	2.17574700	1.72725000
C	-7.04242100	3.05221900	-1.39880200
H	-6.01785600	2.52458800	-3.22226100
H	-7.84066800	3.42370600	0.56862300
H	-7.82900400	3.60695000	-1.90734800
C	-2.96877200	0.28005300	-0.11302500
C	-2.02327000	-0.29709700	-0.71973800
H	-2.86917800	-0.83863000	2.36889600
C	-0.93650100	-2.31295600	1.98057400
O	-0.17261300	-3.27034000	1.74680200

O	-0.30683200	-1.12512200	2.25283900
O	-2.19640700	-2.32755600	1.92407100
K	-1.86136000	-3.92345600	-0.17224400
K	1.99340400	-2.05294000	0.84240800
C	4.74317300	0.75347400	-1.67280900
C	3.73768600	1.04734200	-0.54574600
H	4.31406300	0.89729800	-2.66695000
H	5.66722700	1.33666500	-1.56270100
C	4.70867500	-0.99571100	-0.25710400
O	4.80702900	-2.10751400	0.19078900
O	5.04493500	-0.63072200	-1.49768000
O	4.19701700	0.04051800	0.43340500
C	3.89011200	2.42391600	0.05085700
C	2.87715900	3.36896100	-0.09019900
C	5.06958100	2.77090200	0.71402400
C	3.04545700	4.65368100	0.41747400
H	1.95502600	3.08217500	-0.59416700
C	5.23138900	4.05026800	1.22896000
H	5.85595900	2.02768000	0.84559700
C	4.22027300	4.99652300	1.07678800
H	2.24919300	5.38697900	0.30131500
H	6.14957200	4.30975900	1.75326900

H	4.34909700	6.00048200	1.47806900
C	2.38143600	0.66502200	-0.90932200
C	1.27232900	0.20086000	-1.16041000
H	-0.97304500	-0.41037400	2.30836700

### **IM8**

Cu	0.94819000	2.01026600	-1.04848800
Cl	0.66724200	4.13288400	-1.28506500
C	2.71687000	-1.47704800	1.87450800
C	2.80963700	-1.28910400	0.37095200
H	2.60518900	-2.55207000	2.08970700
H	3.66824000	-1.16664000	2.34484100
O	1.63300300	-0.83161700	2.48416900
C	3.90767800	-1.95079600	-0.35832700
C	4.06821500	-1.76395300	-1.73988200
C	4.82396300	-2.77842200	0.30318600
C	5.09867900	-2.38194100	-2.42973100
H	3.36521300	-1.11914100	-2.26804500
C	5.85917000	-3.39774900	-0.39136100
H	4.73589000	-2.94866500	1.37516400
C	6.00342600	-3.20482600	-1.75941000
H	5.20010700	-2.21895400	-3.50205100

H	6.55735700	-4.03715900	0.14752100
H	6.81380500	-3.68914400	-2.30177800
C	1.88213400	-0.57730200	-0.23834700
C	0.92835800	0.12438900	-0.79764800
H	1.79529800	0.14081100	2.52116300
C	0.00200800	1.87198800	2.15265900
O	-0.67274500	2.90851200	1.94285700
O	-0.67670800	0.70166900	1.96001200
O	1.21816100	1.82580700	2.47193200
K	1.52190900	4.28296000	1.61669200
K	-2.20497600	2.04392100	0.00588200
C	-3.44506100	-1.92134800	-2.22648100
C	-2.79058500	-1.46816700	-0.91386400
H	-2.72829800	-2.35362300	-2.92832700
H	-4.27993700	-2.61371200	-2.06108400
C	-4.06835400	0.20453100	-1.80635600
O	-4.45467500	1.33365500	-1.93992500
O	-3.95166400	-0.70416100	-2.77977500
O	-3.65301900	-0.30008400	-0.62621100
C	-2.90921100	-2.43403200	0.24306200
C	-1.78883400	-2.83261400	0.97057500
C	-4.17159600	-2.90534700	0.61468000

C	-1.92816400	-3.70167900	2.04793900
H	-0.80424200	-2.45410000	0.69837500
C	-4.30849800	-3.77102400	1.69125600
H	-5.05956200	-2.57176500	0.07728000
C	-3.18450500	-4.17406800	2.40854500
H	-1.04544900	-4.00035500	2.61025800
H	-5.29694100	-4.12781700	1.97510200
H	-3.29200300	-4.85210900	3.25341200
C	-1.44939700	-0.94727200	-1.11207700
C	-0.32098100	-0.49463600	-1.02598200
H	-0.04553900	-0.05074500	2.01995700

### **IM9**

Cu	-0.02117700	0.93950700	-0.96412400
Cl	-0.02975800	2.81330200	-2.02651900
C	0.62450800	-1.27303200	2.57990100
C	1.60352900	-1.57210200	1.48457900
H	-0.40351800	-1.49658600	2.26760500
H	0.84667000	-1.91031700	3.44874000
O	0.65608000	0.09189500	3.01026700
C	2.94666400	-2.02596600	1.88868400
C	3.65671800	-2.99335600	1.16205100

C	3.55742700	-1.48945500	3.03237600
C	4.94203100	-3.36581800	1.52914400
H	3.19067400	-3.44979800	0.28923100
C	4.84240400	-1.86774000	3.40467500
H	3.02119500	-0.74696500	3.62505700
C	5.54762300	-2.79812400	2.64791500
H	5.47368900	-4.11175500	0.93965300
H	5.29672400	-1.42543800	4.29060500
H	6.55776200	-3.08785400	2.93317200
C	1.25756900	-1.31415100	0.19103800
C	-0.03820800	-0.98782700	-0.43168800
H	1.40713400	0.54295200	2.56450000
C	0.96499600	2.77945000	1.45149700
O	0.98390500	3.92086200	0.94279800
O	-0.26838100	2.35996200	1.88485400
O	1.93108200	1.97606200	1.53633200
K	2.83654800	2.92665200	-0.74503600
K	-1.59500200	4.05738900	0.36300300
C	-4.14793700	0.58002500	-0.69879400
C	-3.89516100	-0.35523400	0.49811600
H	-3.58316300	0.29663400	-1.59050100
H	-5.22029900	0.67133900	-0.92048400

C	-3.73867000	1.82140700	1.13723000
O	-3.55884900	2.80115600	1.80909200
O	-3.67048600	1.83762100	-0.21171400
O	-4.02608300	0.60151500	1.59276900
C	-4.93981900	-1.43554500	0.61147300
C	-4.75177600	-2.61992600	-0.10054100
C	-6.11839900	-1.23245500	1.32680700
C	-5.73922100	-3.59808000	-0.09336700
H	-3.82602200	-2.77124100	-0.65685100
C	-7.09719000	-2.22038900	1.34170100
H	-6.25956300	-0.31097600	1.88840900
C	-6.91136000	-3.40193800	0.63065700
H	-5.58704700	-4.52094500	-0.65006400
H	-8.00921000	-2.06544200	1.91561200
H	-7.67992900	-4.17282000	0.64378600
C	-2.51663000	-0.82635300	0.42765600
C	-1.34316500	-0.93795500	0.12057400
H	-0.18524800	1.46671900	2.30805100
C	0.18124100	-1.40171000	-1.82214300
N	1.42380100	-1.61071800	-2.11709900
C	-0.88692100	-1.59530800	-2.84903800
F	-1.65750500	-0.49428900	-2.96810400

F	-1.70980600	-2.59569500	-2.49734600
F	-0.39387500	-1.87259500	-4.04550100
N	2.11958800	-1.41677200	-0.93525100
C	3.43483400	-0.93283400	-1.05111400
C	3.95294600	-0.03212000	-0.11253000
C	4.23545600	-1.36001400	-2.11448500
C	5.27063900	0.40233700	-0.22409800
H	3.33160200	0.30087400	0.71687900
C	5.54262200	-0.90300300	-2.22190300
H	3.81840700	-2.04902700	-2.84469300
C	6.07467100	-0.02691400	-1.27770800
H	5.67339400	1.06617800	0.54212500
H	6.15890400	-1.25059300	-3.04977600
H	7.10874800	0.30427700	-1.35418100

### **IM10**

Cu	-2.06550400	1.69145700	0.04536800
Cl	-2.27559100	3.40972200	1.31300500
C	-0.21428800	0.50504500	-1.62133900
C	-1.52832100	0.08550400	-0.96835700
H	0.45843200	-0.34830500	-1.81344700
H	-0.45477000	0.94748100	-2.59951300

O	0.49384200	1.47958900	-0.83179000
C	-2.52603100	-0.33701000	-2.01402800
C	-2.74436300	-1.68476100	-2.31557300
C	-3.24796500	0.61708100	-2.74201100
C	-3.68597800	-2.06767900	-3.26550200
H	-2.18103500	-2.44974000	-1.77788000
C	-4.17268900	0.24278300	-3.70810700
H	-3.09411200	1.67521100	-2.51319900
C	-4.40714900	-1.10603900	-3.96408700
H	-3.85340200	-3.12609800	-3.46119500
H	-4.72916000	1.00735900	-4.24881500
H	-5.14723000	-1.40415100	-4.70491600
C	-1.37215800	-0.83458900	0.17386100
C	-0.21234400	-1.23733500	0.86688400
H	3.40712100	3.50131800	-0.87727100
C	2.32561200	3.28935400	0.70621100
O	1.41242100	3.83050100	1.36814300
O	2.87273200	2.18352600	0.91496700
O	2.67086400	3.97669300	-0.43911400
K	-0.06999200	4.29857000	-0.68913800
K	0.47965200	1.53757300	2.20122300
C	4.67972100	-0.16686400	0.75941200

C	3.65870600	-0.72520700	-0.26383400
H	4.18540800	0.25551900	1.63998700
H	5.43278000	-0.90779400	1.04203200
C	4.52282900	1.28865500	-0.94353100
O	4.66351000	2.29279900	-1.58705200
O	5.31493700	0.88664700	0.05001600
O	3.57123800	0.36712200	-1.20819200
C	4.17733400	-1.97243100	-0.95496300
C	3.88724100	-3.22490700	-0.41287000
C	5.01108300	-1.87671900	-2.06752600
C	4.42842200	-4.37237200	-0.98027600
H	3.22388700	-3.29939000	0.44976000
C	5.54518900	-3.02869000	-2.63603400
H	5.23049300	-0.90520700	-2.50658200
C	5.25791000	-4.27678100	-2.09377600
H	4.19325300	-5.34609100	-0.55423700
H	6.18745900	-2.94717100	-3.51115500
H	5.67641600	-5.17626000	-2.54193600
C	2.32311500	-0.91399200	0.28568400
C	1.14654800	-1.06822600	0.53276400
C	-0.68588200	-1.95605100	1.99155400
N	-1.99280900	-2.05866500	2.01495600

C	0.17125200	-2.42373700	3.11067200
F	1.17508000	-3.19613800	2.68093500
F	-0.49783500	-3.08225900	4.04132300
F	0.75181800	-1.34701200	3.70486200
N	-2.40710100	-1.38649300	0.91002700
C	-3.80329000	-1.45487900	0.60677500
C	-4.55860500	-0.30768100	0.39730200
C	-4.38717100	-2.71623300	0.52530400
C	-5.89853700	-0.42898100	0.04764700
H	-4.10094900	0.67804100	0.49813800
C	-5.73117900	-2.82804500	0.19505400
H	-3.77476500	-3.59572400	0.71438300
C	-6.48482900	-1.68574200	-0.06057700
H	-6.48555000	0.46934900	-0.13332300
H	-6.18828800	-3.81336100	0.12520400
H	-7.53413500	-1.77487900	-0.33601900
H	1.44561800	1.26457700	-0.83156300

### **IM11**

Cu	1.29003200	-0.72387900	-0.54423400
Cl	0.49991700	-1.71168300	1.20768800
O	1.73779200	0.37149000	-1.90957000

H	0.61800000	1.64455600	-1.40189700
C	-1.11686700	1.32902900	-0.61589000
O	-1.64001400	1.29342200	0.53858700
O	-1.50200600	0.72475000	-1.63040400
O	0.05311300	2.05481500	-0.68454200
K	0.59396100	1.43658900	1.81254000
K	-2.26317100	-1.20221900	-0.13906500
H	2.69759500	0.46353400	-1.95928400

**K<sub>2</sub>CO<sub>3</sub>**

C	0.00005900	-0.79494600	0.00000000
O	0.00000000	0.54401200	0.00000000
O	1.12189000	-1.40292600	0.00000000
O	-1.12171600	-1.40303200	0.00000000
K	-2.47578900	0.60157500	0.00000000
K	2.47569800	0.60185900	0.00000000

**Product**

C	-0.95242400	-1.72793900	-1.86587500
C	-1.73441300	-1.19593600	-0.91446100
H	-0.20108800	-1.13970100	-2.38753900
H	-1.02857900	-2.78038000	-2.13065800

C	-2.78444700	-1.98228400	-0.22706600
C	-3.05345700	-1.79222200	1.13159300
C	-3.54365700	-2.91676500	-0.93743900
C	-4.06081600	-2.51209900	1.76048700
H	-2.46774000	-1.06887300	1.69968100
C	-4.54765300	-3.64031500	-0.30825000
H	-3.36644100	-3.04379300	-2.00554000
C	-4.81331100	-3.43607300	1.04227800
H	-4.25996400	-2.34868300	2.81803600
H	-5.13732000	-4.35521700	-0.87949400
H	-5.60919000	-3.99282400	1.53352200
C	-1.49985700	0.19496900	-0.50640900
C	-0.28418100	0.83977800	-0.29693700
C	4.37812300	1.15130300	-0.87924000
C	3.63500200	-0.17037300	-0.57733500
H	3.73501700	1.86358600	-1.41356700
H	4.78865200	1.61803400	0.02083100
C	5.13747100	-0.46113500	-2.27124500
O	5.77485200	-1.01167100	-3.11169500
O	5.43926000	0.73336400	-1.72004600
O	4.00089300	-0.95680800	-1.71996100
C	4.13698400	-0.82099900	0.70204900

C	3.74672400	-0.27385700	1.92585400
C	5.01161700	-1.90219700	0.67420800
C	4.23449100	-0.80217300	3.11259700
H	3.04927200	0.56530600	1.94151000
C	5.49651300	-2.43054000	1.86801200
H	5.30671500	-2.34217000	-0.27618500
C	5.11222300	-1.88340000	3.08559000
H	3.92516600	-0.37110100	4.06298800
H	6.17888300	-3.27808500	1.84043300
H	5.49359600	-2.29966200	4.01626100
C	2.19921000	0.05625200	-0.54902400
C	1.03310000	0.35820000	-0.44196200
C	-0.64274900	2.13096000	0.15313100
N	-1.94887500	2.29552000	0.21916800
C	0.31207400	3.20533300	0.55068200
F	1.07139100	2.80502800	1.58375600
F	-0.30817800	4.32205600	0.90581500
F	1.15270700	3.49266300	-0.45272300
N	-2.46336900	1.12053000	-0.19388200
C	-3.87933900	0.98576100	-0.26591500
C	-4.46461300	0.35188100	-1.35574800
C	-4.65112200	1.47804300	0.78152400

C	-5.84172600	0.16934000	-1.37246300
H	-3.84349100	-0.00165900	-2.17691800
C	-6.02819500	1.30733700	0.74379600
H	-4.16065400	1.98121600	1.61148900
C	-6.62413500	0.64259600	-0.32458100
H	-6.30398800	-0.34019300	-2.21546500
H	-6.63849200	1.68589800	1.56130400
H	-7.70259300	0.49848800	-0.34281300

**2a**

C	1.13245500	0.05269600	1.41635000
C	0.53240300	0.38873600	0.03813400
H	1.18802200	0.91674400	2.08401800
H	0.57246200	-0.76211800	1.89627700
C	2.46445900	-0.81654400	-0.18287900
O	3.36873500	-1.39091900	-0.69780500
O	2.44073100	-0.38991100	1.10047600
O	1.29596400	-0.50080800	-0.79873100
C	-0.94033300	0.05860300	-0.04536500
C	-1.89964000	1.05031500	0.14377400
C	-1.34180200	-1.26475400	-0.23010200
C	-3.25112200	0.72212500	0.15006400

H	-1.58583200	2.08468300	0.27696500
C	-2.69269300	-1.58739100	-0.23220300
H	-0.59265500	-2.03732600	-0.39351100
C	-3.65026100	-0.59574500	-0.03923700
H	-3.99426100	1.50368700	0.29668000
H	-2.99879300	-2.61993900	-0.38966600
H	-4.70829400	-0.85131300	-0.04124700
C	0.84399400	1.76830500	-0.34296900
C	1.11951900	2.90811200	-0.62106500
H	1.37402900	3.91193700	-0.88806300

**Nitrile imine**

C	-3.94980700	-0.45251800	0.15347500
C	-2.78938000	-1.21163900	0.10146200
C	-1.55630100	-0.57756600	-0.04792200
C	-1.48063400	0.81480100	-0.13046400
C	-2.64817500	1.56328300	-0.07778800
C	-3.88350900	0.93527400	0.06130600
H	-4.91251300	-0.94737400	0.26621300
H	-2.81108900	-2.29741100	0.16813600
H	-0.51211500	1.30569800	-0.22049300
H	-2.59196800	2.64843000	-0.14089700

H	-4.79427600	1.52921200	0.10437900
N	-0.42446800	-1.43040000	-0.10079200
N	0.65238900	-0.89801700	-0.35364700
C	1.70145600	-0.48399700	-0.77112200
C	2.79977400	0.14592200	0.01476400
F	3.15313100	-0.60341500	1.05881900
F	3.88045900	0.33961000	-0.73037700
F	2.39596400	1.33702800	0.46949900

**TS1**

Cu	0.69426500	-1.19110300	0.61950200
Cl	0.65074900	-2.60862100	-1.11681400
C	-1.28992200	0.44613100	-1.53209400
C	-1.79997700	0.60484500	-0.09967700
H	-0.72740700	-0.47773900	-1.70505800
H	-2.11000000	0.55964100	-2.25390600
C	-0.82416500	2.51131900	-0.77458700
O	-0.28491700	3.58304400	-0.65623500
O	-0.40990600	1.57728600	-1.64994200
O	-1.85465500	2.07213600	-0.04757100
C	-3.15779400	0.00030400	0.11396200
C	-3.24420500	-1.35313600	0.44134800

C	-4.31778000	0.74262400	-0.09931300
C	-4.48993500	-1.95877500	0.55648900
H	-2.33275800	-1.93012600	0.60306700
C	-5.56125600	0.13355300	0.02993100
H	-4.24537100	1.79951800	-0.34869800
C	-5.64963600	-1.21650200	0.35500200
H	-4.55201000	-3.01526200	0.81064500
H	-6.46594400	0.71958600	-0.12292600
H	-6.62471100	-1.69065400	0.45357900
C	-0.75764200	0.21283300	0.87156400
C	0.13104500	0.39349600	1.73571900
H	1.33185300	0.70486300	2.12670300
C	2.99250000	0.15360700	1.03597300
O	3.64538200	0.52825700	0.00702800
O	2.55227200	1.05239600	1.88456500
O	2.67542700	-1.08492900	1.21993400
K	3.59866200	-1.90864400	-1.01989100
K	2.28311300	2.77029700	-0.05438600

## TS2

Cu	-2.01827600	-1.75105600	-0.62507500
Cl	-3.91697600	-2.07302400	0.37854900

C	1.64642200	-0.98323700	2.06105800
C	1.94237300	-0.79687500	0.58363600
H	1.44552100	-2.03800100	2.27626200
H	2.47835700	-0.63514800	2.68718400
C	0.41669500	0.88160900	1.63470500
O	-0.55939100	1.62160000	1.74208800
O	0.47201600	-0.25724900	2.36964500
O	1.42679600	1.05391300	0.85517000
C	3.32977600	-0.68800000	0.10926500
C	3.67656500	-1.27344900	-1.11363400
C	4.31439700	-0.02619400	0.85482600
C	4.98522800	-1.21565200	-1.57389600
H	2.90394900	-1.78430100	-1.68715300
C	5.61899700	0.03692300	0.38921700
H	4.04798200	0.47268400	1.78490900
C	5.95800000	-0.56264900	-0.82285300
H	5.24662700	-1.68319200	-2.52111600
H	6.37666300	0.55797200	0.97150500
H	6.98454600	-0.51725300	-1.18256200
C	0.93440000	-1.27671400	-0.24803900
C	-0.18350300	-1.58148700	-0.69928700
H	-0.61648000	0.36410100	-2.39819600

C	-1.94600100	1.40535200	-1.51243400
O	-2.13826900	2.50398900	-0.94620700
O	-0.70578700	1.29829600	-2.14152600
O	-2.67625100	0.39814800	-1.52552200
K	-3.18184500	0.84242500	1.05061200
K	0.31544700	3.09535600	-0.47395800

### **TS3**

Cu	1.68820000	-2.09198800	0.24824800
Cl	2.72313900	-2.63440800	-1.59721800
C	-1.44251600	1.09911000	-0.85907500
C	-1.97794300	-0.14317200	-0.16245500
H	-1.84073900	1.00644000	-1.90227600
H	-2.03653900	1.95526900	-0.43473700
C	0.46959400	3.25432300	-1.10523700
O	1.27624100	3.10676400	-1.95134700
O	-0.11492900	1.28319500	-0.78785900
O	-0.19488100	3.81686600	-0.30145100
C	-3.40354600	-0.43388600	-0.12097800
C	-3.85723200	-1.61504000	0.49158700
C	-4.34788300	0.44119700	-0.68636500
C	-5.20946800	-1.91151700	0.53821600

H	-3.12325300	-2.29576200	0.92170100
C	-5.69977800	0.14043800	-0.63899400
H	-4.02250500	1.35984100	-1.17067600
C	-6.13355000	-1.03434600	-0.02663900
H	-5.54686800	-2.83092300	1.01223900
H	-6.42139800	0.82342500	-1.08266900
H	-7.19633900	-1.26742500	0.00781000
C	-1.04769700	-0.97399200	0.37045800
C	-0.04072700	-1.67069700	0.67478000
H	2.06283800	-0.69397500	2.97348000
C	2.58631000	0.41310300	1.51401300
O	2.49944500	1.56208300	1.04808300
O	1.95683200	0.24362000	2.74502000
O	3.10281100	-0.60785800	1.00243800
K	2.32783600	0.49100900	-1.49451100
K	0.05617000	1.97031800	1.79207500

#### **TS4**

Cu	1.78118800	-0.95269000	-0.99942000
Cl	3.65685900	-2.01325200	-0.84555600
C	-2.22878400	2.05872200	-0.04438700
C	-2.25435700	0.57836800	-0.35099100

H	-3.05752200	2.49683400	-0.64977900
H	-2.59944200	2.12858000	1.00724400
O	-1.05900900	2.68784800	-0.24362900
C	-3.43549200	-0.23472200	-0.11717800
C	-3.40662400	-1.61112800	-0.40299700
C	-4.61960000	0.32693800	0.39342100
C	-4.52333900	-2.40042400	-0.18370400
H	-2.48742300	-2.04380100	-0.79565600
C	-5.73552500	-0.46497000	0.60767800
H	-4.66450900	1.38849200	0.62733300
C	-5.68966300	-1.82874900	0.32093300
H	-4.48705300	-3.46500800	-0.40555700
H	-6.64648000	-0.02068400	1.00351300
H	-6.56800100	-2.44841600	0.49377300
C	-1.10213000	0.03148000	-0.82889500
C	0.03757900	-0.40301300	-1.10730000
H	-0.21209700	2.46354600	0.69552100
C	1.29966000	1.15461300	1.35607300
O	2.26156200	0.89896800	0.52187300
O	0.76395200	2.37588400	1.26816700
O	0.90591300	0.33189200	2.20928300
K	3.08401400	-1.05918200	2.00464900

K 1.33029000 2.51993500 -1.29518600

**TS5**

Cu -0.14422000 -0.04891200 -0.72645600

Cl 0.88324500 -1.90882900 -1.62358600

C -3.95751300 0.64201700 1.91105600

C -4.12255300 0.94346500 0.43300500

H -4.52999900 1.40195300 2.47004000

H -4.49601600 -0.31988600 2.07448900

O -2.67557500 0.63056100 2.37854000

C -5.42094500 1.28815600 -0.12291900

C -5.53070300 1.60926700 -1.48756400

C -6.58008400 1.30427000 0.67209800

C -6.75675900 1.94207700 -2.03764500

H -4.62984700 1.59527000 -2.10023200

C -7.80763700 1.62912200 0.11582300

H -6.52353600 1.05466500 1.72954200

C -7.89807300 1.95149500 -1.23681000

H -6.82745500 2.19534800 -3.09351500

H -8.69931800 1.63490300 0.73938800

H -8.86293200 2.21186600 -1.66860700

C -3.01203500 0.82740600 -0.33196000

C	-1.88426400	0.59265500	-0.83504700
H	-2.21925800	-0.20519400	2.06027600
C	-0.61085200	-2.09107900	1.85072000
O	-0.21303800	-3.26856800	1.57099000
O	0.17196800	-1.29350300	2.53771200
O	-1.72714800	-1.63593500	1.39381100
K	-1.63548400	-3.26961400	-0.58040300
K	2.24362700	-2.43828200	1.22575500
C	3.03187300	0.76683700	-1.95259700
C	3.10305100	0.84852500	-0.40434100
H	2.01290800	0.56710600	-2.30674200
H	3.43717100	1.66117300	-2.43492000
C	4.08745200	-1.09649600	-1.21571400
O	4.55874000	-2.19651700	-1.20115000
O	3.84841700	-0.34712900	-2.29707800
O	3.74565000	-0.43045900	-0.09077200
C	4.00340700	1.96205500	0.09336700
C	3.58809300	2.86168500	1.07111300
C	5.29044600	2.07488600	-0.44156400
C	4.44739100	3.86710100	1.50673300
H	2.58798100	2.77253600	1.49207700
C	6.14701600	3.07460200	-0.00304100

H	5.62930400	1.37323900	-1.20497200
C	5.72546900	3.97542500	0.97293800
H	4.11152900	4.56602500	2.27063700
H	7.14772700	3.15145800	-0.42448700
H	6.39667100	4.76112400	1.31561100
C	1.80193400	0.80737200	0.26182600
C	0.87530000	0.61007700	1.05517800
H	0.28534700	-0.11614400	1.90357900

### **TS6**

Cu	1.91957000	-1.27720000	-1.54452700
Cl	4.08436300	-1.10256900	-1.70196300
C	-2.11697000	-1.67551200	1.85250800
C	-2.00338100	-1.75177700	0.34759600
H	-2.91506600	-0.95931600	2.10081200
H	-2.45274400	-2.65875300	2.23670600
O	-0.97592400	-1.24079000	2.52479200
C	-3.23862100	-1.77692200	-0.44680700
C	-3.20264200	-1.47186100	-1.81685900
C	-4.48362800	-2.03408000	0.14477300
C	-4.36995800	-1.41323400	-2.56204400
H	-2.23830400	-1.25779200	-2.27927200

C	-5.65237900	-1.98285100	-0.60682600
H	-4.54524500	-2.28079000	1.20384900
C	-5.60275700	-1.66636700	-1.96061800
H	-4.32069800	-1.16493500	-3.62132100
H	-6.60852600	-2.19115100	-0.12886300
H	-6.51903200	-1.61948600	-2.54679200
C	-0.80940300	-1.76541600	-0.24560400
C	0.30650100	-1.88689700	-0.86661400
H	-0.20354100	-1.84506900	2.40313600
C	2.09835100	-0.84285600	2.10613000
O	3.30212500	-0.63001400	1.82668500
O	1.30558500	0.27443500	2.10747300
O	1.57170900	-1.96414100	2.31878700
K	3.40430400	-3.00040900	0.72423900
K	3.10478800	1.42424100	0.25158500
C	-0.74365200	3.53886000	-1.45082300
C	-0.49316600	2.43294500	-0.41924600
H	-1.04863500	3.16120300	-2.42987400
H	-1.46207100	4.28104900	-1.07846100
C	1.26931900	3.84995800	-0.49671200
O	2.40889800	4.18124200	-0.30992900
O	0.54193900	4.14940400	-1.57795300

O	0.57315300	3.06780900	0.35220600
C	-1.67753200	2.11352400	0.45326700
C	-2.86899300	1.74350900	-0.17300500
C	-1.59392000	2.12433500	1.84320100
C	-3.98594500	1.42110000	0.58600200
H	-2.91680300	1.67934100	-1.26169200
C	-2.71553800	1.79912300	2.60079100
H	-0.65419900	2.37994300	2.32935000
C	-3.91178200	1.45629200	1.97693800
H	-4.90752100	1.12214400	0.08849700
H	-2.64626400	1.80210400	3.68696400
H	-4.78541400	1.20091200	2.57500500
C	0.07390600	1.21330000	-0.98111000
C	0.59919600	0.13915700	-1.25742500
H	0.36772100	-0.00927400	2.20438800

### **TS7**

Cu	-0.93425400	-1.84755100	-0.26432400
Cl	-1.96052400	-2.12239800	-2.10086400
C	-0.60645500	-0.23253300	2.12494000
C	-1.76887400	0.22226200	1.45508900
H	0.28484500	0.39738400	2.11851900

H	-0.78426000	-0.69398100	3.09588100
O	0.14575400	-1.60754600	1.32165200
C	-3.07545000	-0.16899200	2.03756600
C	-3.99213400	0.79036800	2.48623300
C	-3.40794500	-1.51874800	2.21327700
C	-5.21134200	0.41805000	3.03704000
H	-3.74080500	1.84626500	2.38210300
C	-4.61798600	-1.89739000	2.78584300
H	-2.70958100	-2.28212700	1.85992000
C	-5.53142000	-0.92897700	3.18954200
H	-5.91549800	1.18660000	3.35391000
H	-4.85599300	-2.95478200	2.89901300
H	-6.48690800	-1.22110700	3.62251500
C	-1.61447300	0.98710000	0.26290800
C	-0.41092500	1.35721000	-0.41201200
H	4.15820000	-3.08088800	0.06695800
C	2.63142200	-2.72346900	-1.06714500
O	1.43914300	-3.07816100	-1.25874400
O	3.26645500	-1.82239700	-1.64187100
O	3.25151100	-3.43397100	-0.05530200
K	0.93725600	-4.19402100	1.01165700
K	0.88949000	-1.01935100	-2.81543800

C	4.41342500	0.98262000	-0.87665100
C	3.52338900	0.81329000	0.37897000
H	3.87703500	0.71327300	-1.79415500
H	4.84282000	1.98544000	-0.95455500
C	5.03844400	-0.88865800	0.19141200
O	5.59912900	-1.92752000	0.41718000
O	5.45729600	0.04396600	-0.66637300
O	3.92144100	-0.49602900	0.83242100
C	3.85350000	1.84768200	1.44430400
C	3.32888200	3.13592000	1.31658100
C	4.72069900	1.55782800	2.49430000
C	3.66829400	4.12187700	2.23317600
H	2.64393900	3.35957900	0.49719900
C	5.05347000	2.54839500	3.41518100
H	5.12739500	0.55479900	2.60563300
C	4.53067200	3.82944400	3.28740400
H	3.25178500	5.12206900	2.12762700
H	5.72628700	2.31160200	4.23767100
H	4.79190300	4.60127800	4.00930500
C	2.10781200	0.80577300	0.03799500
C	0.92905600	1.08297600	-0.11602500
C	-0.84040400	2.07897700	-1.55478400

N	-2.14209100	2.16802100	-1.64698600
C	0.05222400	2.66978200	-2.58275700
F	1.00986200	3.42749800	-2.03555500
F	-0.58817000	3.38856700	-3.48609400
F	0.71815300	1.68285900	-3.26125700
N	-2.60939300	1.49169600	-0.55872100
C	-4.02690400	1.33345200	-0.48774400
C	-4.59844000	0.07121300	-0.60365800
C	-4.81413400	2.47003000	-0.33774600
C	-5.97970300	-0.05281100	-0.50976000
H	-3.95937200	-0.79606000	-0.76708700
C	-6.19519600	2.33744200	-0.26171700
H	-4.33142400	3.44408500	-0.27763500
C	-6.77741200	1.07447000	-0.33434500
H	-6.43327300	-1.03980500	-0.58047500
H	-6.81784500	3.22213000	-0.13967900
H	-7.85885600	0.96940400	-0.26281100
H	0.96711300	-1.21391400	0.96199600

### **TS8**

Cu	0.94444100	-1.16118300	0.07192900
Cl	-0.42138500	-1.10441100	1.75547500

O	2.31311800	-0.74024900	-1.20185600
H	1.82740700	0.27192500	-1.33906100
C	-0.18405100	0.95752300	-1.23588500
O	-1.09016900	1.67518500	-0.67640000
O	-0.43839300	-0.17393800	-1.76358900
O	1.07386700	1.35556300	-1.14066800
K	0.50012800	2.05551400	1.28559100
K	-2.55181300	-0.47150800	-0.45103700
H	3.16628400	-0.59637500	-0.77109300

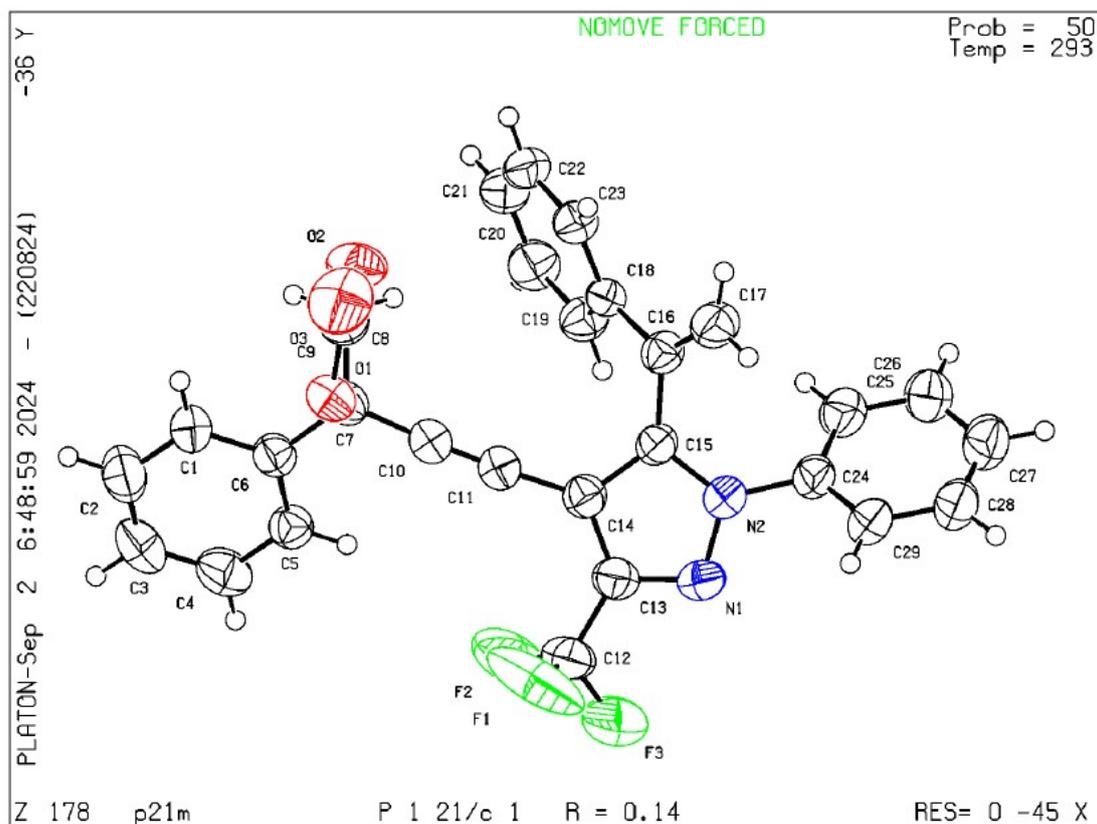
## 9. Crystal Data

The data were collected on a Agilent Gemini E diffractometer (Mo, 50kV 40mA) instrument using Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 296 K and reduced by CrysAlisPro (Rigaku). The crystal structures were solved and refined using the SHELXTL software package. Refinements were performed with SHELXL-2013 using fullmatrix least-squares calculations on F<sup>2</sup>, with anisotropic displacement parameters for all the nonhydrogen atoms. The crystallographic data have already been deposited at the Cambridge Crystallographic Data Centre.

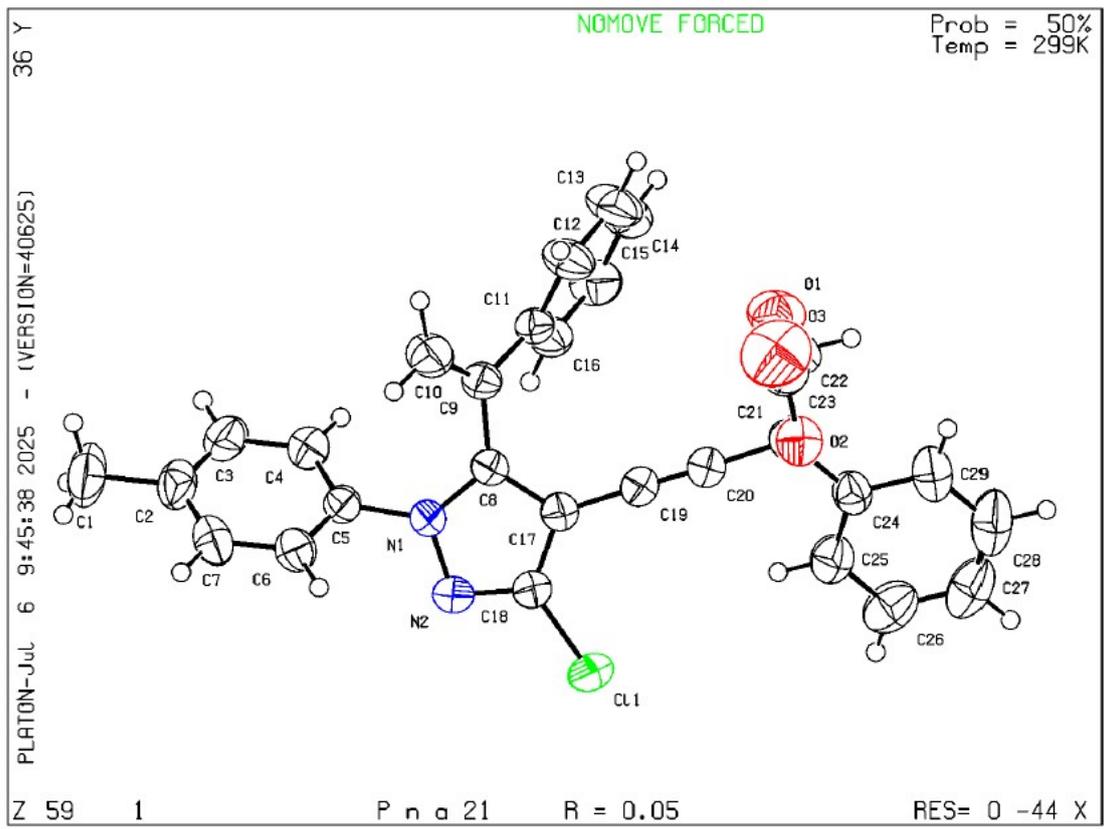
### 1. Crystal Data of **3ba**

Single crystals of **3ba** were obtained by recrystallization from hexane/CHCl<sub>3</sub>. The details of crystal data collection and refinement of **3ba** are summarized in the following Table. CCDC 2384304 contains the

supplementary crystallographic data for this paper. Thermal ellipsoids are drawn at 50% probability level.









## 10. Characterization Data

*p*-tolylcarbonohydrazonic bromide chloride (**4b**). Purified by column chromatography (PE), red oily liquid (107 mg, 17%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.43 (s, 1H), 7.09 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.3 Hz, 2H), 2.30 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ 140.7 (s), 131.2 (s), 130.0 (s), 113.5 (s), 109.6 (s), 20.7 (s).

(4-ethylphenyl)carbonohydrazonic bromide chloride (**4c**). Purified by column chromatography (PE), red oily liquid (99 mg, 15%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.41 (s, 1H), 7.10 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.5 Hz, 2H), 2.58 (q, J = 7.6 Hz, 2H), 1.20 (t, J = 7.6 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ 140.8 (s), 137.7 (s), 128.8 (s), 113.5 (s), 109.6 (s), 28.2 (s), 15.9 (s).

(4-(tert-butyl)phenyl)carbonohydrazonic bromide chloride (**4d**). Purified by column chromatography (PE), red oily liquid (113 mg, 16%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.46 (s, 1H), 7.30 (d, J = 8.6 Hz, 2H), 6.98 (d, J = 8.6 Hz, 2H), 1.29 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ 144.7 (s), 140.5 (s), 126.3 (s), 113.2 (s), 109.7 (s), 34.3 (s), 31.6 (s).

(4-fluorophenyl)carbonohydrazonic bromide chloride (**4e**). Purified by column chromatography (PE), red oily liquid (120 mg, 19%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43 (s, 1H), 7.00 (s, 2H), 6.98 (d, J = 0.9 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 158.2 (d, J = 239.7 Hz), 139.2 (d, J = 2.2 Hz), 116.1 (d, J = 22.8 Hz), 114.6 (d, J = 7.6 Hz), 110.5 (s). <sup>19</sup>F NMR

(376 MHz, CDCl<sub>3</sub>)  $\delta$  -122.60 (s).

***4-phenyl-4-((5-(1-phenylvinyl)-3-(trifluoromethyl)-1-(4-(trifluoromethyl)phenyl)-1H-pyrazol-4-yl)ethynyl)-1,3-dioxolan-2-one (3aa)***. Purified by column chromatography (PE/EA = 8:1), yellow solid (69 mg, 92%), mp 91.2 - 91.5 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.55 (q, J = 8.9 Hz, 4H), 7.46 (dd, J = 6.9, 2.9 Hz, 2H), 7.42 – 7.39 (m, 3H), 7.27 (dd, J = 7.3, 4.2 Hz, 3H), 7.22 – 7.18 (m, 2H), 6.00 (s, 1H), 5.55 (s, 1H), 4.50 (d, J = 8.5 Hz, 1H), 4.44 (d, J = 8.5 Hz, 1H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  153.5 (s), 147.8 (s), 144.5 (q, J = 37.9 Hz), 141.1 (s), 136.8 (s), 136.7 (s), 136.2 (s), 130.8 (q, J = 33.0 Hz), 129.8 (s), 129.1 (s), 128.9 (s), 126.5 (s), 126.3 (q, J = 3.5 Hz), 125.2 (s), 124.7 (s), 122.6 (s), 122.3 (s), 120.4 (q, J = 270.3 Hz), 102.5 (s), 91.3 (s), 79.8 (s), 78.5 (s), 77.2 (s). **<sup>19</sup>F NMR** (471 MHz, CDCl<sub>3</sub>)  $\delta$  -62.37 (s), -62.79 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>30</sub>H<sub>19</sub>F<sub>6</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 569.1294, found: 569.1298.

***4-phenyl-4-((1-phenyl-5-(1-phenylvinyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-1,3-dioxolan-2-one (3ba)***. Purified by column chromatography (PE/EA = 8:1), white solid (69 mg, 92%), mp 111.2 - 111.9 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 (d, J = 3.4 Hz, 2H), 7.35 – 7.27 (m, 5H), 7.22 (d, J = 5.2 Hz, 3H), 7.17 (s, 3H), 7.14 (d, J = 3.0 Hz, 2H), 5.86 (s, 1H), 5.40 (s, 1H), 4.36 (q, J = 8.4 Hz, 2H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  153.7 (s), 147.7 (s), 143.9 (q, J = 37.6 Hz), 138.5 (s),

137.4 (s), 137.0 (s), 136.5 (s), 129.9 (s), 129.2 (s), 129.0 (s), 128.9 (s), 128.8 (s), 126.7 (s), 125.3 (s), 124.8 (s), 122.4 (s), 120.7 (dd, J = 541.2, 270.4 Hz), 101.8 (s), 91.0 (s), 80.0 (s), 79.1 (s), 77.3 (s). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -62.17 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>29</sub>H<sub>20</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 501.1421, found: 501.1425.

***4-phenyl-4-((5-(1-phenylvinyl)-1-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-1,3-dioxolan-2-one (3ca)***. Purified by column chromatography (PE/EA = 8:1), white solid (64.2 mg, 83%), mp 41.5 - 42.1 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.38 – 7.35 (m, 2H), 7.33 (d, J = 2.1 Hz, 4H), 7.19 (dd, J = 4.9, 2.6 Hz, 4H), 7.16 (d, J = 3.0 Hz, 2H), 7.01 (dd, J = 7.9, 1.0 Hz, 1H), 6.97 (d, J = 8.0 Hz, 1H), 5.69 (s, 1H), 5.36 (s, 1H), 4.31 (s, 2H), 2.25 (s, 3H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (126 MHz, CDCl<sub>3</sub>) δ 152.5 (s), 148.2 (s), 142.9 (q, J = 37.0 Hz), 141.1 (s), 136.7 (s), 135.9 (s), 135.0 (s), 134.1 (s), 132.8 (s), 128.7 (s), 128.0 (s), 127.7 (s), 127.4 (s), 126.1 (s), 124.2 (s), 121.4 (s), 120.3 (s), 119.5 (q, J = 270.8 Hz), 99.5 (s), 90.0 (s), 78.7 (s), 77.9 (s), 76.1 (s), 19.9 (s). **<sup>19</sup>F NMR** (471 MHz, CDCl<sub>3</sub>) δ -62.25 (d, J = 3.4 Hz). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>30</sub>H<sub>22</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 515.1577, found: 515.1561.

***4-((1-(4-methoxyphenyl)-5-(1-phenylvinyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (3da)***. Purified by column chromatography (PE/EA = 8:1), white solid (66 mg, 83%), mp 39.8 - 40.1 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.37 (dd, J = 6.9, 3.0 Hz,

2H), 7.32 (q, J = 3.3 Hz, 3H), 7.19 (dd, J = 6.0, 2.9 Hz, 5H), 7.13 (dd, J = 6.6, 3.1 Hz, 2H), 6.74 – 6.70 (m, 2H), 5.84 (s, 1H), 5.38 (s, 1H), 4.35 (q, J = 8.4 Hz, 2H), 3.69 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.9 (s), 153.7 (s), 147.6 (s), 143.6 (dd, J = 75.2, 37.7 Hz), 137.5 (s), 137.0 (s), 136.5 (s), 131.6 (s), 129.9 (s), 129.2 (s), 128.9 (s), 128.8 (s), 126.7 (s), 126.2 (s), 125.3 (s), 122.4 (s), 120.7 (q, J = 270.6 Hz), 114.3 (s), 101.3 (s), 90.8 (s), 80.0 (s), 79.2 (s), 77.3 (s), 55.6 (s).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.10 (s). HRMS (ESI, m/z):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{30}\text{H}_{22}\text{F}_3\text{N}_2\text{O}_4^+$ : 531.1526, found: 531.1530.

***4-((1-(4-fluorophenyl)-5-(1-phenylvinyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (3ea)***. Purified by column chromatography (PE/EA = 8:1), white solid (77 mg, 99%), mp 104.0 - 104.4 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 – 7.45 (m, 2H), 7.42 – 7.39 (m, 3H), 7.34 (dd, J = 8.8, 4.6 Hz, 2H), 7.26 (d, J = 3.4 Hz, 3H), 7.19 – 7.16 (m, 2H), 6.98 (t, J = 8.4 Hz, 2H), 5.95 (s, 1H), 5.52 (s, 1H), 4.50 (d, J = 8.5 Hz, 1H), 4.44 (d, J = 8.4 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.5 (d, J = 250.0 Hz), 153.6 (s), 147.8 (s), 144.0 (q, J = 37.6 Hz), 137.2 (s), 136.9 (s), 136.4 (s), 134.7 (d, J = 3.2 Hz), 129.9 (s), 129.2 (s), 129.1 (s), 128.9 (s), 126.7 (d, J = 9.0 Hz), 126.7 (s), 125.3 (s), 122.6 (s), 120.6 (q, J = 270.6 Hz), 116.2 (d, J = 23.2 Hz), 101.9 (s), 91.0 (s), 80.0 (s), 78.9 (s), 77.3 (s).  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.24 (s), -111.35 (s). HRMS (ESI, m/z):  $[\text{M} + \text{H}]^+$ , calcd. for

$C_{29}H_{19}F_4N_2O_3^+$ : 519.1326, found: 519.1311.

***4-((1-(4-chlorophenyl)-5-(1-phenylvinyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (3fa)***. Purified by column chromatography (PE/EA = 8:1), white solid (56.8 mg, 71%), mp 96.4 - 97.1 °C.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.47 – 7.44 (m, 2H), 7.42 – 7.38 (m, 3H), 7.33 (d,  $J$  = 8.7 Hz, 2H), 7.27 (d,  $J$  = 9.0 Hz, 5H), 7.21 – 7.17 (m, 2H), 5.97 (s, 1H), 5.51 (s, 1H), 4.49 (d,  $J$  = 8.5 Hz, 1H), 4.43 (d,  $J$  = 8.4 Hz, 1H).  $^{13}C\{^1H\}$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  153.6 (s), 147.7 (s), 144.2 (q,  $J$  = 37.7 Hz), 137.1 (s), 137.0 (s), 136.9 (s), 136.3 (s), 134.9 (s), 129.9 (s), 129.4 (s), 129.2 (s), 129.1 (s), 128.9 (s), 126.6 (s), 125.9 (s), 125.3 (s), 122.6 (s), 120.6 (q,  $J$  = 270.9 Hz), 102.1 (s), 91.2 (s), 79.9 (s), 78.8 (s), 77.3 (s).  $^{19}F$  NMR (471 MHz,  $CDCl_3$ )  $\delta$  -62.26 (d,  $J$  = 4.9 Hz). HRMS (ESI,  $m/z$ ):  $[M + Na]^+$ , calcd. for  $C_{29}H_{18}ClF_3N_2NaO_3^+$ : 557.0850, found: 557.0840.

***4-((1-(4-bromophenyl)-5-(1-phenylvinyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (3ga)***. Purified by column chromatography (PE/EA = 8:1), white solid (80 mg, 92%), mp 118.7 - 119.5 °C.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.37 (dd,  $J$  = 7.1, 3.5 Hz, 3H), 7.33 (t,  $J$  = 5.6 Hz, 4H), 7.20 (dd,  $J$  = 8.7, 5.5 Hz, 5H), 7.12 (dd,  $J$  = 6.1, 2.5 Hz, 2H), 5.90 (s, 1H), 5.43 (s, 1H), 4.41 (d,  $J$  = 8.4 Hz, 1H), 4.35 (d,  $J$  = 8.4 Hz, 1H).  $^{13}C\{^1H\}$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  153.6 (s), 147.7 (s), 144.2 (q,  $J$  = 37.6 Hz), 137.6 (s), 137.1 (s), 136.9 (s), 136.3 (s), 132.4

(s), 129.9 (s), 129.2 (s), 129.2 (s), 129.0 (s), 126.7 (s), 126.1 (s), 125.3 (s), 122.9 (s), 122.6 (s), 120.6 (dd, J = 541.7, 271.4 Hz), 102.2 (s), 91.2 (s), 79.9 (s), 78.8 (s), 77.3 (s). **<sup>19</sup>F NMR** (471 MHz, CDCl<sub>3</sub>) δ -62.28 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>29</sub>H<sub>19</sub>BrF<sub>3</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 579.0526, found: 579.0513.

**4-((1-(4-iodophenyl)-5-(1-phenylvinyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (3ha)**. Purified by column chromatography (PE/EA = 8:1), white solid (70 mg, 75%), mp 126.2 - 126.9 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.56 (d, J = 8.5 Hz, 2H), 7.40 – 7.35 (m, 3H), 7.33 (d, J = 5.2 Hz, 3H), 7.23 – 7.20 (m, 3H), 7.15 – 7.11 (m, 2H), 7.07 (d, J = 8.5 Hz, 2H), 5.90 (s, 1H), 5.42 (s, 1H), 4.37 (dd, J = 18.2, 8.4 Hz, 2H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>) δ 153.6 (s), 147.6 (s), 144.2 (dd, J = 75.3, 37.6 Hz), 138.3 (s), 138.2 (s), 137.1 (s), 136.8 (s), 136.3 (s), 129.9 (s), 129.2 (s), 129.2 (s), 129.0 (s), 126.6 (s), 126.2 (s), 125.3 (s), 122.6 (s), 120.5 (dd, J = 541.5, 271.1 Hz), 102.2 (s), 94.4 (s), 91.2 (s), 79.9 (s), 78.8 (s), 77.3 (s). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -62.27 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>29</sub>H<sub>19</sub>F<sub>3</sub>IN<sub>2</sub>O<sub>3</sub><sup>+</sup>: 627.0387, found: 627.0391.

**4-(4-((2-oxo-4-phenyl-1,3-dioxolan-4-yl)ethynyl)-5-(1-phenylvinyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzotrile (3ia)**. Purified by column chromatography (PE/EA = 8:1), yellow solid (48 mg, 61%), mp 52.6 - 53.4 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.60 – 7.55 (m, 4H), 7.47 (dd, J =

6.8, 3.0 Hz, 2H), 7.43 – 7.40 (m, 3H), 7.26 (dd, J = 4.8, 1.7 Hz, 3H), 7.17 (dd, J = 6.7, 2.9 Hz, 2H), 6.04 (s, 1H), 5.62 (s, 1H), 4.55 (d, J = 8.5 Hz, 1H), 4.46 (d, J = 8.5 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.5 (s), 147.8 (s), 144.8 (q, J = 38.0 Hz), 141.7 (s), 136.7 (s), 136.6 (s), 136.1 (s), 133.1 (s), 130.0 (s), 129.3 (s), 129.2 (s), 129.0 (s), 126.6 (s), 125.2 (s), 124.8 (s), 122.8 (s), 120.4 (q, J = 270.7 Hz), 117.7 (s), 112.5 (s), 103.0 (s), 91.6 (s), 79.9 (s), 78.3 (s), 77.2 (s).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.42 (s). HRMS (ESI, m/z):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{30}\text{H}_{19}\text{F}_3\text{N}_3\text{O}_3^+$ : 526.1373, found: 526.1358.

*4-((1-(3-methoxyphenyl)-5-(1-phenylvinyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (3ja)*. Purified by column chromatography (PE/EA = 8:1), white solid (56 mg, 70%), mp 130.2-131.0 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (s, 1H), 7.51 – 7.47 (m, 2H), 7.46 – 7.37 (m, 4H), 7.31 – 7.21 (m, 4H), 7.19 – 7.16 (m, 2H), 6.59 (s, 1H), 5.81 (s, 1H), 5.56 (s, 1H), 4.48 (dd, J = 27.2, 8.4 Hz, 2H), 3.66 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.5 (s), 153.6 (s), 149.5 (s), 144.4 (q, J = 37.4 Hz), 137.8 (s), 137.3 (s), 136.9 (s), 136.6 (s), 135.9 (s), 129.9 (s), 129.2 (s), 128.9 (s), 128.6 (s), 127.2 (s), 125.3 (s), 123.0 (s), 120.5 (q, J = 270.9 Hz), 114.4 (s), 112.6 (s), 112.3 (s), 101.0 (s), 91.1 (s), 79.9 (s), 78.7 (s), 77.2 (s), 56.6 (s).  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.31 (s). HRMS (ESI, m/z):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{30}\text{H}_{22}\text{F}_3\text{N}_2\text{O}_4^+$ : 531.1526, found: 531.1544.

***4-phenyl-4-((5-(1-phenylvinyl)-3-(trifluoromethyl)-1-(3-(trifluoromethyl)phenyl)-1H-pyrazol-4-yl)ethynyl)-1,3-dioxolan-2-one (3ka)***. Purified by column chromatography (PE/EA = 8:1), white solid (69 mg, 81%), mp 86.3 - 87.1 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.35 (s, 2H), 7.33 – 7.27 (m, 5H), 7.19 (d, J = 13.5 Hz, 5H), 7.13 (s, 2H), 5.70 (s, 1H), 5.27 (s, 1H), 4.33 – 4.27 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ 153.6 (s), 149.5 (s), 144.6 (q, J = 38.1 Hz), 143.9 (s), 137.3 (s), 137.0 (s), 136.3 (s), 131.3 (s), 130.8 (s), 129.9 (s), 129.4 (s), 129.2 (s), 128.9 (s), 128.6 (s), 127.2 (s), 127.1 (s), 125.3 (s), 122.0 (s), 120.7 (s), 120.5 (q, J = 270.5 Hz), 120.2 (q, J = 260.6 Hz), 101.0 (s), 91.4 (s), 79.9 (s), 78.8 (s), 77.2 (s). <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -57.36 (s), -62.40 (s). HRMS (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>30</sub>H<sub>19</sub>F<sub>6</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 569.1294, found: 569.1292.

***4-((1-(3-fluorophenyl)-5-(1-phenylvinyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (3la)***. Purified by column chromatography (PE/EA = 8:1), yellow solid (74 mg, 95%), mp 83.3 - 83.9 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.48 – 7.44 (m, 2H), 7.42 – 7.39 (m, 3H), 7.28 – 7.25 (m, 4H), 7.21 – 7.17 (m, 3H), 7.15 (d, J = 9.1 Hz, 1H), 6.98 (td, J = 8.2, 1.2 Hz, 1H), 5.98 (s, 1H), 5.56 (s, 1H), 4.48 (dd, J = 33.7, 8.4 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ 162.5 (d, J = 248.9 Hz), 153.6 (s), 147.8 (s), 144.3 (q, J = 37.7 Hz), 139.7 (d, J = 10.1 Hz), 137.1 (s), 136.9 (s), 136.3 (s), 130.5 (d, J = 8.9 Hz), 129.9 (s), 129.2

(s), 129.1 (s), 128.9 (s), 126.7 (s), 125.3 (s), 122.6 (s), 120.6 (q,  $J = 270.4$  Hz), 120.3 (d,  $J = 3.0$  Hz), 116.0 (d,  $J = 21.1$  Hz), 112.4 (d,  $J = 25.5$  Hz), 102.3 (s), 91.2 (s), 80.0 (s), 78.8 (s), 77.3 (s).  **$^{19}\text{F}$  NMR** (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.31 (s), -110.51 (s). **HRMS** (ESI,  $m/z$ ):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{29}\text{H}_{19}\text{F}_4\text{N}_2\text{O}_3^+$ : 519.1326, found: 519.1323.

***4-((1-(3-chlorophenyl)-5-(1-phenylvinyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (3ma)***. Purified by column chromatography (PE/EA = 8:1), white solid (61 mg, 76%), mp 106.9 - 107.1 °C.  **$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 – 7.45 (m, 2H), 7.41 (d,  $J = 1.4$  Hz, 4H), 7.28 – 7.17 (m, 8H), 5.98 (s, 1H), 5.57 (s, 1H), 4.52 (d,  $J = 8.5$  Hz, 1H), 4.45 (d,  $J = 8.4$  Hz, 1H).  **$^{13}\text{C}\{^1\text{H}\}$  NMR** (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.6 (s), 147.7 (s), 144.3 (q,  $J = 37.6$  Hz), 139.4 (s), 137.1 (s), 136.9 (s), 136.3 (s), 134.9 (s), 130.1 (s), 129.9 (s), 129.2 (s), 129.1 (s), 128.9 (s), 126.7 (s), 125.3 (s), 125.0 (s), 122.7 (s), 120.6 (q,  $J = 270.5$  Hz), 102.2 (s), 91.2 (s), 80.0 (s), 78.8 (s), 77.3 (s).  **$^{19}\text{F}$  NMR** (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.30 (s). **HRMS** (ESI,  $m/z$ ):  $[\text{M} + \text{Na}]^+$ , calcd. for  $\text{C}_{29}\text{H}_{18}\text{ClF}_3\text{N}_2\text{NaO}_3^+$ : 557.0850, found: 557.0855.

***4-((1-(3-bromophenyl)-5-(1-phenylvinyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (3na)***. Purified by column chromatography (PE/EA = 8:1), white solid (61 mg, 70%), mp 118.5 - 119.1 °C.  **$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (s, 1H), 7.40 (dd,  $J = 6.5, 2.6$  Hz, 2H), 7.33 (dd,  $J = 9.9, 6.1$  Hz, 4H), 7.23 (d,  $J = 8.1$  Hz, 1H),

7.20 – 7.18 (m, 3H), 7.10 (dd,  $J = 6.5, 2.5$  Hz, 2H), 7.06 (t,  $J = 8.1$  Hz, 1H), 5.90 (s, 1H), 5.51 (s, 1H), 4.45 (d,  $J = 8.5$  Hz, 1H), 4.38 (d,  $J = 8.4$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.6 (s), 147.8 (s), 144.3 (q,  $J = 37.6$  Hz), 139.5 (s), 137.1 (s), 136.9 (s), 136.3 (s), 132.0 (s), 130.3 (s), 129.9 (s), 129.2 (s), 129.1 (s), 128.9 (s), 127.8 (s), 126.7 (s), 125.3 (s), 123.2 (s), 122.8 (s), 122.6 (s), 120.6 (dd,  $J = 541.3, 270.6$  Hz), 102.2 (s), 91.2 (s), 78.0 (s), 78.8 (s), 77.3 (s).  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.31 (s). HRMS (ESI,  $m/z$ ):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{29}\text{H}_{19}\text{BrF}_3\text{N}_2\text{O}_3^+$ : 579.0526, found: 579.0532.

*3-(4-((2-oxo-4-phenyl-1,3-dioxolan-4-yl)ethynyl)-5-(1-phenylvinyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzotrile (3oa)*. Purified by column chromatography (PE/EA = 8:1), yellow solid (66 mg, 84%), mp 46.1-47.0 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (d,  $J = 1.5$  Hz, 1H), 7.66 – 7.63 (m, 1H), 7.54 (d,  $J = 7.8$  Hz, 1H), 7.49 (dt,  $J = 7.7, 3.4$  Hz, 2H), 7.43 – 7.39 (m, 4H), 7.26 – 7.24 (m, 3H), 7.16 (dt,  $J = 4.5, 3.3$  Hz, 2H), 6.03 (s, 1H), 5.65 (s, 1H), 4.53 (dd,  $J = 50.0, 8.5$  Hz, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.6 (s), 147.8 (s), 144.7 (q,  $J = 37.8$  Hz), 139.1 (s), 136.7 (s), 136.0 (s), 132.2 (s), 130.2 (s), 130.0 (s), 129.3 (s), 129.2 (s), 129.0 (s), 128.6 (s), 127.8 (s), 126.7 (s), 125.2 (s), 123.1 (s), 120.4 (q,  $J = 270.6$  Hz), 117.3 (s), 113.4 (s), 102.8 (s), 91.5 (s), 79.9 (s), 78.4 (s), 77.3 (s).  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.41 (s). HRMS (ESI,  $m/z$ ):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{30}\text{H}_{19}\text{F}_3\text{N}_3\text{O}_3^+$ : 526.1373, found: 526.1371.

***4-phenyl-4-((5-(1-phenylvinyl)-1-(2-(trifluoromethoxy)phenyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-1,3-dioxolan-2-one (3pa).***

Purified by column chromatography (PE/EA = 8:1), yellow solid (76 mg, 87%), mp 107.1-107.8 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.65 (s, 1H), 7.57 (d, J = 8.1 Hz, 1H), 7.52 – 7.48 (m, 3H), 7.43 – 7.38 (m, 4H), 7.21 (dd, J = 6.6, 3.4 Hz, 3H), 7.15 – 7.11 (m, 2H), 5.99 (s, 1H), 5.65 (s, 1H), 4.53 (dd, J = 56.0, 8.5 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ 153.6 (s), 147.9 (s), 144.5 (q, J = 37.8 Hz), 138.9 (s), 136.9 (s), 136.8 (s), 136.3 (s), 131.6 (q, J = 33.3 Hz), 130.0 (s), 129.9 (s), 129.2 (s), 129.1 (s), 128.9 (s), 127.7 (s), 126.7 (s), 125.5 (dd, J = 7.0, 3.3 Hz), 125.3 (s), 123.3 (q, J = 272.6 Hz), 122.9 (s), 121.7 (dd, J = 7.6, 3.7 Hz), 119.5 (s), 102.5 (s), 91.2 (s), 80.0 (s), 78.7 (s), 77.3 (s). <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -62.33 (s), -62.97 (s). HRMS (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>30</sub>H<sub>19</sub>F<sub>6</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup>: 585.1244, found: 585.1241.

***4-((1-(2-methoxyphenyl)-5-(1-phenylvinyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (3qa).*** Purified by column chromatography (PE/EA = 8:1), yellow solid (60 mg, 75%), mp 123.2 - 124.1 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.39 (s, 5H), 7.34 – 7.27 (m, 6H), 7.22 (d, J = 8.3 Hz, 1H), 7.13 (dd, J = 8.4, 1.8 Hz, 1H), 6.99 (d, J = 1.7 Hz, 1H), 5.71 (s, 1H), 5.25 (s, 1H), 4.34 (d, J = 8.4 Hz, 1H), 4.25 (d, J = 8.3 Hz, 1H), 3.60 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ 154.3 (s), 153.6 (s), 149.6 (s), 144.1 (q, J = 37.3 Hz), 137.6 (s), 137.1 (s), 136.8

(s), 129.8 (s), 129.7 (s), 129.2 (s), 128.8 (s), 128.5 (s), 127.2 (s), 126.7 (s), 125.3 (s), 124.7 (s), 124.1 (s), 120.7 (s), 120.6 (q,  $J = 270.5$  Hz), 115.7 (s), 100.5 (s), 91.3 (s), 79.9 (s), 79.0 (s), 77.2 (s), 55.8 (s).  **$^{19}\text{F}$  NMR** (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.23 (s). **HRMS** (ESI,  $m/z$ ):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{30}\text{H}_{22}\text{F}_3\text{N}_2\text{O}_4^+$ : 531.1526, found: 531.1541.

***4-((1-(2-chlorophenyl)-5-(1-phenylvinyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (3ra)***. Purified by column chromatography (PE/EA = 8:1), white solid (60 mg, 75%), mp 91.5 - 91.7 °C.  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (s, 3H), 7.40 (d,  $J = 13.2$  Hz, 4H), 7.35 – 7.30 (m, 2H), 7.25 (d,  $J = 9.6$  Hz, 5H), 5.77 (s, 1H), 5.43 (s, 1H), 4.42 – 4.37 (m, 2H).  **$^{13}\text{C}\{^1\text{H}\}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.7 (s), 149.5 (s), 144.3 (q,  $J = 38.0$  Hz), 137.6 (s), 136.9 (s), 136.2 (s), 136.1 (s), 131.9 (s), 131.3 (s), 130.5 (s), 129.9 (s), 129.5 (s), 129.2 (s), 128.9 (s), 128.6 (s), 127.5 (s), 127.2 (s), 125.3 (s), 122.4 (s), 120.6 (dd,  $J = 504.7, 234.6$  Hz), 100.7 (s), 91.3 (s), 79.9 (s), 78.9 (s), 77.3 (s).  **$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.31 (s). **HRMS** (ESI,  $m/z$ ):  $[\text{M} + \text{Na}]^+$ , calcd. for  $\text{C}_{29}\text{H}_{18}\text{ClF}_3\text{N}_2\text{NaO}_3^+$ : 557.0850, found: 557.0855.

***4-((1-(2-bromophenyl)-5-(1-phenylvinyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (3sa)***. Purified by column chromatography (PE/EA = 8:1), white solid (59.6 mg, 69%), mp 71.0 - 71.6 °C.  **$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 – 7.47 (m, 1H), 7.43 – 7.35 (m, 2H), 7.36 – 7.31 (m, 3H), 7.24 – 7.09 (m, 8H), 5.70 (d,  $J = 1.1$

Hz, 1H), 5.40 (d,  $J = 1.1$  Hz, 1H), 4.34 (s, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.6 (s), 149.4 (s), 144.2 (q,  $J = 37.9$  Hz), 137.8 (s), 137.7 (s), 137.0 (s), 136.1 (s), 133.7 (s), 131.4 (s), 129.9 (s), 129.7 (s), 129.2 (s), 128.9 (s), 128.6 (s), 128.1 (s), 127.2 (s), 125.3 (s), 122.7 (s), 121.9 (s), 120.6 (dd,  $J = 541.3, 270.5$  Hz), 100.8 (s), 91.2 (s), 79.9 (s), 79.0 (s), 77.2 (s).  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.27 (d,  $J = 4.3$  Hz). HRMS (ESI,  $m/z$ ):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{29}\text{H}_{19}\text{BrF}_3\text{N}_2\text{O}_3^+$ : 579.0526, found: 579.0532.

*4-((1-(3,5-dimethylphenyl)-5-(1-phenylvinyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (3ta)*. Purified by column chromatography (PE/EA = 8:1), yellow solid (71.5 mg, 90%), mp 35.3 - 36.1 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 – 7.43 (m, 3H), 7.42 – 7.39 (m, 3H), 7.29 – 7.24 (m, 4H), 7.21 – 7.18 (m, 2H), 7.08 (s, 2H), 5.93 (s, 1H), 5.51 (s, 1H), 4.48 (d,  $J = 8.3$  Hz, 1H), 4.43 (d,  $J = 8.4$  Hz, 1H), 2.32 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.7 (s), 147.6 (s), 143.9 (q,  $J = 36.2$  Hz), 139.5 (s), 137.5 (s), 136.9 (s), 136.8 (s), 136.5 (s), 129.9 (s), 129.2 (s), 129.0 (s), 128.8 (s), 128.0 (s), 126.7 (s), 125.3 (s), 124.0 (s), 122.6 (s), 120.6 (dd,  $J = 541.3, 270.1$  Hz), 101.8 (s), 91.0 (s), 80.0 (s), 79.0 (s), 77.3 (s), 24.0 (s).  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.21 (s). HRMS (ESI,  $m/z$ ):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{31}\text{H}_{24}\text{F}_3\text{N}_2\text{O}_3^+$ : 529.1734, found: 529.1731.

*4-((1-(2,4-difluorophenyl)-5-(1-phenylvinyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (3ua)*. Purified by

column chromatography (PE/EA = 8:1), white solid (63 mg, 78%), mp 116.7 - 117.3 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.44 (dd, J = 6.8, 3.0 Hz, 2H), 7.42 – 7.39 (m, 3H), 7.37 – 7.33 (m, 1H), 7.29 – 7.26 (m, 3H), 7.20 (dd, J = 6.3, 2.5 Hz, 2H), 6.83 (ddd, J = 18.1, 13.6, 5.1 Hz, 2H), 5.82 (s, 1H), 5.44 (s, 1H), 4.40 (s, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ 163.3 (dd, J = 254.0, 11.1 Hz), 156.9 (dd, J = 256.6, 12.8 Hz), 153.6 (s), 149.7 (s), 144.7 (q, J = 37.7 Hz), 137.4 (s), 136.9 (s), 136.2 (s), 129.9 (s), 129.7 (d, J = 10.2 Hz), 129.2 (s), 129.0 (s), 128.7 (s), 127.0 (s), 125.3 (s), 123.1 (dd, J = 12.1, 4.1 Hz), 122.1 (s), 120.5 (q, J = 270.8 Hz), 112.1 (dd, J = 22.7, 3.7 Hz), 105.2 (dd, J = 26.6, 23.2 Hz), 101.2 (s), 91.4 (s), 79.9 (s), 78.6 (s), 77.2 (s). <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -62.42 (s), -105.31 (d, J = 8.8 Hz), -114.98 (d, J = 8.7 Hz). HRMS (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>29</sub>H<sub>18</sub>F<sub>5</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 537.1232, found: 537.1229.

***4-((1-(naphthalen-1-yl)-5-(1-phenylvinyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (3va)***. Purified by column chromatography (PE/EA = 8:1), white solid (60.5 mg, 73%), mp 52.1 - 53.1 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.26 – 8.18 (m, 1H), 7.59 (dddd, J = 15.0, 11.5, 6.9, 2.7 Hz, 3H), 7.50 – 7.45 (m, 2H), 7.44 – 7.18 (m, 5H), 7.10 (ddd, J = 8.3, 6.2, 3.6 Hz, 4H), 7.02 (dd, J = 7.8, 1.4 Hz, 2H), 5.64 (s, 1H), 5.41 (d, J = 3.0 Hz, 1H), 4.47 (dd, J = 22.1, 8.5 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 153.6 (s), 150.1 (s), 144.3 (q, J = 37.6 Hz), 137.4 (s), 136.8 (s), 136.1 (s), 134.4 (s), 132.4 (s), 130.6 (s),

129.9 (s), 129.1 (s), 128.6 (s), 128.6 (s), 128.6 (s), 128.4 (s), 128.4 (s), 127.7 (s), 126.8 (s), 125.7 (s), 125.2 (s), 123.1 (s), 122.4 (s), 120.6 (q, J = 270.6 Hz), 100.8 (s), 91.2 (s), 79.9 (s), 78.9 (s), 77.2 (s). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -62.08 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>33</sub>H<sub>22</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 551.1577, found: 551.1568.

**4-((1-phenyl-5-(1-(p-tolyl)vinyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-4-(p-tolyl)-1,3-dioxolan-2-one (3bb).** Purified by column chromatography (PE/EA = 8:1), white solid (70 mg, 88%), mp 103.6 - 104.2 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.42 – 7.37 (m, 2H), 7.32 (ddd, J = 7.1, 6.5, 1.6 Hz, 5H), 7.19 (d, J = 8.2 Hz, 2H), 7.15 – 7.11 (m, 2H), 7.08 (d, J = 7.7 Hz, 2H), 5.90 (d, J = 1.9 Hz, 1H), 5.39 (d, J = 2.2 Hz, 1H), 4.41 (d, J = 2.0 Hz, 2H), 2.37 (s, 3H), 2.31 (s, 3H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>) δ 153.8 (s), 147.9 (s), 143.9 (dd, J = 74.3, 39.1 Hz), 140.0 (s), 139.0 (s), 138.6 (s), 136.3 (s), 134.5 (s), 134.0 (s), 129.8 (s), 129.5 (s), 129.2 (s), 129.0 (s), 126.6 (s), 125.4 (s), 124.8 (s), 121.5 (s), 118.1 (dd, J = 537.0, 269.3 Hz), 101.8 (s), 91.0 (s), 80.1 (s), 79.0 (s), 77.3 (s), 21.3 (s). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -62.18 (s). **HRMS** (ESI, m/z): [M + Na]<sup>+</sup>, calcd. for C<sub>31</sub>H<sub>23</sub>F<sub>3</sub>N<sub>2</sub>NaO<sub>3</sub><sup>+</sup>: 551.1553, found: 551.1569.

**4-(4-methoxyphenyl)-4-((5-(1-(4-methoxyphenyl)vinyl)-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-1,3-dioxolan-2-one (3bc).** Purified by column chromatography (PE/EA = 8:1), white solid (75 mg, 89%), mp 153.6 - 154.4 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.39 (dd, J =

12.9, 5.8 Hz, 4H), 7.34 – 7.29 (m, 3H), 7.17 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 8.7 Hz, 2H), 5.84 (s, 1H), 5.33 (s, 1H), 4.48 – 4.43 (m, 2H), 3.82 (s, 3H), 3.78 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.7 (s), 160.2 (s), 153.7 (s), 147.9 (s), 143.8 (q, J = 37.6 Hz), 138.5 (s), 135.8 (s), 129.8 (s), 129.2 (s), 129.0 (s), 128.5 (s), 128.0 (s), 127.2 (s), 124.7 (d, J = 4.7 Hz), 120.7 (dd, J = 540.4, 269.9 Hz), 120.4 (s), 114.4 (s), 114.2 (s), 101.7 (s), 91.0 (s), 80.1 (s), 79.1 (s), 77.3 (s), 55.5 (s), 55.4 (s).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.15 (s). HRMS (ESI, m/z):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{31}\text{H}_{24}\text{F}_3\text{N}_2\text{O}_5^+$ : 561.1632, found: 561.1650.

*4-([1,1'-biphenyl]-4-yl)-4-((5-(1-([1,1'-biphenyl]-4-yl)vinyl)-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-1,3-dioxolan-2-one (3bd).*

Purified by column chromatography (PE/EA = 8:1), white solid (80 mg, 95%), mp 149.3 - 150.2 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 – 7.51 (m, 6H), 7.47 (d, J = 7.2 Hz, 3H), 7.42 (dd, J = 13.3, 6.2 Hz, 7H), 7.38 – 7.31 (m, 7H), 6.00 (s, 1H), 5.47 (d, J = 6.3 Hz, 1H), 4.47 (dd, J = 21.4, 8.5 Hz, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.7 (s), 147.6 (s), 144.0 (q, J = 37.4 Hz), 142.8 (s), 141.7 (s), 140.1 (s), 139.8 (s), 138.5 (s), 136.2 (s), 135.9 (s), 135.6 (s), 129.3 (s), 129.1 (s), 129.1 (s), 129.0 (s), 128.0 (s), 127.9 (s), 127.8 (s), 127.5 (s), 127.2 (s), 127.1 (s), 127.1 (s), 125.9 (s), 124.8 (s), 122.3 (s), 120.7 (dd, J = 541.5, 270.9 Hz), 101.7 (s), 91.0 (s), 80.0 (s), 79.2 (s), 77.3 (s).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.06 (s). HRMS (ESI, m/z):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{41}\text{H}_{28}\text{F}_3\text{N}_2\text{O}_3^+$ : 653.2047,

found: 653.2032.

***4-(4-fluorophenyl)-4-((5-(1-(4-fluorophenyl)vinyl)-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-1,3-dioxolan-2-one (3be).***

Purified by column chromatography (PE/EA = 8:1), white solid (58.4 mg, 73%), mp 128.2 - 128.9 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.47 (dd, J = 8.6, 5.0 Hz, 2H), 7.36 – 7.29 (m, 5H), 7.17 – 7.08 (m, 4H), 6.92 (t, J = 8.5 Hz, 2H), 5.89 (s, 1H), 5.52 (s, 1H), 4.58 (d, J = 8.5 Hz, 1H), 4.45 (d, J = 8.5 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 164.4 (d, J = 55.0 Hz), 161.9 (d, J = 54.2 Hz), 153.3 (s), 147.3 (s), 143.9 (q, J = 38.0 Hz), 138.3 (s), 135.3 (s), 133.3 (d, J = 3.2 Hz), 132.6 (d, J = 3.3 Hz), 129.2 (s), 129.1 (s), 128.4 (d, J = 8.3 Hz), 127.4 (d, J = 8.7 Hz), 124.6 (d, J = 10.1 Hz), 122.2 (s), 124.6 – 116.3 (m), 116.2 (d, J = 22.1 Hz), 115.7 (d, J = 21.9 Hz), 101.5 (s), 90.6 (s), 79.5 (s), 79.1 (s), 77.2 (s). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.19 (s), -110.87 (s), -112.06 (s). HRMS (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>29</sub>H<sub>18</sub>F<sub>5</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 537.1232, found: 537.1219.

***4-(4-bromophenyl)-4-((5-(1-(4-bromophenyl)vinyl)-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-1,3-dioxolan-2-one (3bf).***

Purified by column chromatography (PE/EA = 8:1), pale yellow oil (70 mg, 71%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.52 (m, 2H), 7.38 – 7.28 (m, 8H), 7.25 (s, 1H), 7.03 (d, J = 8.4 Hz, 2H), 5.94 (d, J = 15.4 Hz, 1H), 5.51 (s, 1H), 4.54 (d, J = 8.4 Hz, 1H), 4.41 (d, J = 8.4 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*) δ 153.3, 147.01, 144.2,

143.8, 138.3, 136.1, 135.9, 135.4, 132.4, 131.9, 129.3, 129.2, 128.1, 126.9, 125.1 (q,  $J = 208.1$  Hz), 124.7, 123.1, 122.9, 101.6, 90.6, 79.4, 79.2, 77.3.  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -62.09. HRMS (ESI,  $m/z$ ):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{29}\text{H}_{18}\text{Br}_2\text{F}_3\text{N}_2\text{O}_3^+$ : 656.9631, found: 656.9622.

**4-((1-phenyl-3-(trifluoromethyl)-5-(1-(4-(trifluoromethyl)phenyl)vinyl)-1H-pyrazol-4-yl)ethynyl)-4-(4-(trifluoromethyl)phenyl)-1,3-dioxolan-2-one (3bg)**. Purified by column chromatography (PE/EA = 8:1), white solid (91 mg, 95%), mp 46.6 - 46.8 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (d,  $J = 8.4$  Hz, 2H), 7.50 (d,  $J = 8.3$  Hz, 2H), 7.40 (d,  $J = 8.3$  Hz, 2H), 7.29 – 7.14 (m, 7H), 5.94 (s, 1H), 5.57 (s, 1H), 4.50 (d,  $J = 8.5$  Hz, 1H), 4.34 (d,  $J = 8.6$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  151.98 (s), 145.68 (s), 144.41 – 141.65 (m), 139.54 (s), 137.07 (s), 134.19 (s), 131.85 – 130.40 (m), 129.66 (q,  $J = 32.7$  Hz), 128.23 (s), 128.20 (s), 126.66 (d,  $J = 16.5$  Hz), 125.89 (s), 125.16 (q,  $J = 3.6$  Hz), 124.78 – 124.54 (m), 124.52 (s), 124.26 – 123.70 (m), 123.65 (s), 123.41 (s), 121.16 (t,  $J = 17.2$  Hz), 120.76 (s), 100.39 (s), 89.38 (s), 78.18 (s), 78.05 (s), 75.82 (s).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.22 (s), -62.80 (s), -62.92 (s). HRMS (ESI,  $m/z$ ):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{31}\text{H}_{18}\text{F}_9\text{N}_2\text{O}_3^+$ : 637.1168, found: 637.1183.

**4-((1-phenyl-5-(1-(*m*-tolyl)vinyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-4-(*m*-tolyl)-1,3-dioxolan-2-one (3bh)**. Purified by column chromatography (PE/EA = 8:1), white solid (71 mg, 89%), mp 71.3 - 72.0

°C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.37 (d, J = 8.1 Hz, 2H), 7.34 – 7.28 (m, 5H), 7.27 – 7.20 (m, 3H), 7.14 (t, J = 7.9 Hz, 1H), 7.06 (d, J = 7.5 Hz, 1H), 7.00 (d, J = 6.1 Hz, 2H), 5.92 (s, 1H), 5.46 (s, 1H), 4.42 (s, 2H), 2.36 (s, 3H), 2.27 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ 153.7 (s), 147.7 (s), 143.8 (dd, J = 75.3, 37.7 Hz), 139.0 (s), 138.5 (s), 138.4 (s), 137.2 (s), 136.8 (s), 136.4 (s), 130.5 (s), 129.5 (s), 129.0 (s), 129.0 (s), 128.9 (s), 128.6 (s), 127.2 (s), 125.9 (s), 124.7 (s), 123.8 (s), 122.3 (s), 122.1 (s), 120.7 (dd, J = 528.6, 247.1 Hz), 101.7 (s), 90.9 (s), 79.9 (s), 78.9 (s), 77.3 (s), 21.4 (s), 21.3 (s). <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -62.15 (s). HRMS (ESI, m/z): [M + Na]<sup>+</sup>, calcd. for C<sub>31</sub>H<sub>23</sub>F<sub>3</sub>N<sub>2</sub>NaO<sub>3</sub><sup>+</sup>: 551.1553, found: 551.1569.

***4-(3-fluorophenyl)-4-((5-(1-(3-fluorophenyl)vinyl)-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-1,3-dioxolan-2-one (3bi).***  
Purified by column chromatography (PE/EA = 8:1), white solid (71.5 mg, 89%), mp 104.8 - 105.2 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.40 (td, J = 8.1, 5.8 Hz, 1H), 7.37 – 7.30 (m, 5H), 7.26 – 7.18 (m, 3H), 7.12 (td, J = 8.2, 2.1 Hz, 1H), 6.95 – 6.86 (m, 3H), 5.97 (s, 1H), 5.58 (s, 1H), 4.59 (d, J = 8.5 Hz, 1H), 4.44 (d, J = 8.5 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ 163.8 (d, J = 8.1 Hz), 161.9 (d, J = 6.5 Hz), 153.1 (s), 146.9 (s), 144.0 (q, J = 37.8 Hz), 139.3 (d, J = 1.8 Hz), 139.3 (d, J = 2.4 Hz), 138.3 (s), 135.4 (d, J = 2.0 Hz), 130.9 (d, J = 8.2 Hz), 130.3 (d, J = 8.5 Hz), 129.2 (s), 129.1 (s), 124.7 (s), 123.4 (s), 122.4 (d, J = 2.7 Hz), 120.7 (d, J = 3.2

Hz), 120.5 (q, J = 270.3 Hz), 116.9 (d, J = 21.0 Hz), 115.8 (d, J = 21.2 Hz), 113.5 (d, J = 22.8 Hz), 112.7 (d, J = 24.1 Hz), 101.5 (s), 90.5 (s), 79.1 (d, J = 2.2 Hz), 79.0 (s), 77.0 (s). **<sup>19</sup>F NMR** (471 MHz, CDCl<sub>3</sub>) δ -62.21 (s), -110.51 (s), -112.36 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>29</sub>H<sub>18</sub>F<sub>5</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 537.1232, found: 537.1219.

***4-(3-bromophenyl)-4-((5-(1-(3-bromophenyl)vinyl)-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-1,3-dioxolan-2-one (3bj).***

Purified by column chromatography (PE/EA = 8:1), yellow solid (89 mg, 90%), mp 42.5 - 43.3 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.67 (s, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.34 - 7.28 (m, 8H), 7.10 (dd, J = 8.3, 5.7 Hz, 2H), 5.96 (s, 1H), 5.59 (s, 1H), 4.52 (dd, J = 57.3, 8.5 Hz, 2H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>) δ 153.2 (s), 146.9 (s), 144.0 (q, J = 37.7 Hz), 139.2 (s), 139.1 (s), 138.3 (s), 135.1 (s), 133.1 (s), 131.8 (s), 130.8 (s), 130.3 (s), 129.6 (s), 129.3 (s), 128.5 (s), 125.4 (s), 124.8 (s), 123.8 (s), 123.7 (s), 123.2 (s), 122.8 (s), 120.5 (q, J = 270.5 Hz), 101.6 (s), 90.5 (s), 79.3 (s), 79.0 (s), 77.0 (s). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -62.12 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>29</sub>H<sub>18</sub>Br<sub>2</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 656.9631, found: 656.9615.

***4-((1-phenyl-5-(1-(o-tolyl)vinyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-4-(o-tolyl)-1,3-dioxolan-2-one (3bk).*** Purified by column chromatography (PE/EA = 8:1), yellow solid (73 mg, 92%), mp 69.3 - 69.5 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.54 (d, J = 7.8 Hz, 1H), 7.31 (t, J

= 7.4 Hz, 1H), 7.28 – 7.23 (m, 5H), 7.18 (d, J = 6.9 Hz, 2H), 7.02 (t, J = 7.4 Hz, 1H), 6.91 (t, J = 7.7 Hz, 2H), 6.82 (d, J = 7.6 Hz, 1H), 5.74 (s, 1H), 5.58 (s, 1H), 4.81 (d, J = 8.2 Hz, 1H), 4.55 (d, J = 8.2 Hz, 1H), 2.42 (s, 3H), 1.97 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.3 (s), 148.6 (s), 143.8 (q, J = 37.5 Hz), 138.5 (s), 137.6 (s), 136.1 (s), 135.5 (s), 135.3 (s), 134.3 (s), 132.4 (s), 130.5 (s), 129.8 (s), 129.5 (s), 129.3 (s), 129.0 (s), 128.3 (s), 126.5 (s), 125.8 (s), 125.6 (s), 125.3 (s), 124.3 (s), 120.6 (q, J = 270.5 Hz), 100.8 (s), 91.2 (s), 79.3 (s), 78.0 (s), 75.9 (s), 20.3 (s), 20.1 (s).  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.31 (s). HRMS (ESI, m/z):  $[\text{M} + \text{Na}]^+$ , calcd. for  $\text{C}_{31}\text{H}_{23}\text{F}_3\text{N}_2\text{NaO}_3^+$ : 551.1553, found: 551.1569.

**4-((1-phenyl-5-(1-(o-tolyl)vinyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-4-(o-tolyl)-1,3-dioxolan-2-one (3bl).** Purified by column chromatography (PE/EA = 8:1), white solid (69 mg, 70%), mp 121.1 - 121.3 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (dd, J = 7.7, 1.4 Hz, 1H), 7.46 (dd, J = 7.8, 1.6 Hz, 2H), 7.41 – 7.36 (m, 1H), 7.32 (dt, J = 11.7, 4.1 Hz, 3H), 7.26 – 7.21 (m, 1H), 7.15 (dd, J = 7.5, 1.5 Hz, 1H), 7.00 – 6.92 (m, 2H), 6.86 (t, J = 7.4 Hz, 1H), 6.75 (d, J = 8.2 Hz, 1H), 5.73 (s, 1H), 5.40 (s, 1H), 4.51 (dd, J = 22.0, 8.2 Hz, 2H), 3.86 (s, 3H), 3.64 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.7 (s), 156.5 (s), 154.2 (s), 148.4 (s), 143.5 (q, J = 37.0 Hz), 138.9 (s), 134.3 (s), 131.3 (s), 130.4 (s), 130.3 (s), 129.0 (s), 128.8 (s), 127.6 (s), 127.2 (s), 125.5 (s), 125.2 (s), 124.5 (s), 121.0 (s), 120.8 (q, J = 269.9 Hz), 120.7 (s), 111.5 (s), 111.1 (s), 100.1 (s),

91.5 (s), 78.6 (s), 78.2 (s), 76.1 (s), 55.7 (s), 55.6 (s).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.32 (d,  $J = 2.0$  Hz). HRMS (ESI,  $m/z$ ):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{31}\text{H}_{24}\text{F}_3\text{N}_2\text{O}_5^+$ : 561.1632, found: 561.1650.

***4-(2-chlorophenyl)-4-((5-(1-(2-chlorophenyl)vinyl)-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-1,3-dioxolan-2-one (3bm).***

Purified by column chromatography (PE/EA = 8:1), white solid (73 mg, 86%), mp 122.3 - 123.0 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 – 7.68 (m, 1H), 7.47 – 7.44 (m, 1H), 7.38 – 7.34 (m, 4H), 7.30 – 7.27 (m, 3H), 7.16 (d,  $J = 7.7$  Hz, 1H), 7.11 – 7.06 (m, 1H), 7.04 (d,  $J = 4.4$  Hz, 2H), 5.71 (s, 1H), 5.70 (s, 1H), 4.89 (d,  $J = 8.7$  Hz, 1H), 4.65 (d,  $J = 8.7$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.1 (s), 147.0 (s), 144.1 (dd,  $J = 74.9, 37.4$  Hz), 138.6 (s), 136.7 (s), 135.4 (s), 134.4 (s), 132.4 (s), 131.5 (s), 131.2 (s), 130.8 (s), 129.9 (s), 129.8 (s), 129.2 (s), 129.1 (s), 127.5 (s), 126.9 (s), 126.6 (s), 125.7 (s), 120.6 (q,  $J = 270.5$  Hz), 101.0 (s), 90.6 (s), 78.2 (s), 77.9 (s), 75.9 (s).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.33 (s). HRMS (ESI,  $m/z$ ):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{29}\text{H}_{18}\text{Cl}_2\text{F}_3\text{N}_2\text{O}_3^+$ : 569.0641, found: 569.0650.

***4-((1-phenyl-5-(1-(thiophen-2-yl)vinyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-4-(thiophen-2-yl)-1,3-dioxolan-2-one (3bn).***

Purified by column chromatography (PE/EA = 8:1), white solid (30 mg, 39%), mp 132.1 - 132.8 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 – 7.43 (m, 2H), 7.42 (d,  $J = 5.1$  Hz, 1H), 7.40 – 7.34 (m, 3H), 7.23 (d,  $J = 4.1$  Hz,

2H), 7.03 – 6.99 (m, 1H), 6.93 – 6.89 (m, 1H), 6.81 (d, J = 3.5 Hz, 1H), 5.92 (s, 1H), 5.31 (s, 1H), 4.60 (dd, J = 35.0, 8.7 Hz, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.0 (s), 146.9 (s), 144.0 (q, J = 37.7 Hz), 140.9 (s), 139.6 (s), 138.5 (s), 130.3 (s), 129.3 (s), 129.2 (s), 128.5 (s), 128.1 (s), 127.9 (s), 127.5 (s), 126.9 (s), 126.5 (s), 124.4 (s), 120.7 (s), 120.6 (dd, J = 541.0, 270.6 Hz), 101.6 (s), 90.4 (s), 78.3 (s), 77.1 (s).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.12 (s). **HRMS** (ESI, m/z):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{25}\text{H}_{16}\text{F}_3\text{N}_2\text{O}_3\text{S}_2^+$ : 513.0549, found: 513.0541.

**4-((3-(difluoromethyl)-1-phenyl-5-(1-phenylvinyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (5aa).** Purified by column chromatography (PE/EA = 8:1), white solid (59 mg, 82%), mp 146.6 - 147.3 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (dt, J = 7.4, 3.3 Hz, 2H), 7.42 – 7.34 (m, 5H), 7.31 – 7.20 (m, 8H), 6.81 (t, J = 53.8 Hz, 1H), 5.92 (s, 1H), 5.47 (s, 1H), 4.45 (dd, J = 21.8, 8.4 Hz, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.8 (s), 147.9 (t, J = 28.2 Hz), 147.4 (s), 138.7 (s), 137.6 (s), 137.2 (s), 136.7 (s), 129.8 (s), 129.2 (s), 128.8 (s), 128.7 (s), 126.8 (s), 125.4 (s), 124.7 (s), 122.1 (s), 110.9 (t, J = 235.9 Hz), 101.3 (s), 90.5 (s), 80.1 (s), 80.0 (s), 77.4 (s).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -113.48 (d, J = 10.0 Hz). **HRMS** (ESI, m/z):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{29}\text{H}_{21}\text{F}_2\text{N}_2\text{O}_3^+$ : 483.1515, found: 483.1516.

**4-((3-chloro-5-(1-phenylvinyl)-1-(p-tolyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (5ba).** Purified by column chromatography

(PE/EA = 8:1), yellow solid (49 mg, 68%), mp 132.6 - 133.3 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 – 7.43 (m, 3H), 7.42 – 7.36 (m, 3H), 7.29 – 7.21 (m, 6H), 7.07 (d,  $J = 8.0$  Hz, 2H), 5.87 (s, 1H), 5.40 (s, 1H), 4.42 (dd,  $J = 15.9, 8.4$  Hz, 2H), 2.29 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.8 (s), 146.9 (s), 143.1 (s), 138.6 (s), 137.5 (s), 137.2 (s), 136.9 (s), 136.3 (s), 129.8 (s), 129.6 (s), 129.1 (s), 128.8 (s), 128.7 (s), 126.8 (s), 125.4 (s), 124.4 (s), 121.8 (s), 102.7 (s), 90.9 (s), 80.3 (s), 80.1 (s), 77.5 (s), 21.2 (s). HRMS (ESI,  $m/z$ ):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{29}\text{H}_{22}\text{ClN}_2\text{O}_3^+$ : 481.1313, found: 481.1314.

*4-((3-chloro-1-(4-ethylphenyl)-5-(1-phenylvinyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (5ca)*. Purified by column chromatography (PE/EA = 8:1), yellow solid (32 mg, 43%), mp 108.6 - 109.2 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 – 7.44 (m, 2H), 7.39 (d,  $J = 6.0$  Hz, 3H), 7.24 (d,  $J = 8.8$  Hz, 7H), 7.09 (d,  $J = 8.2$  Hz, 2H), 5.87 (s, 1H), 5.42 (s, 1H), 4.43 (q,  $J = 8.4$  Hz, 2H), 2.59 (q,  $J = 7.6$  Hz, 2H), 1.17 (t,  $J = 7.6$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.7 (s), 146.8 (s), 144.8 (s), 142.9 (s), 137.5 (s), 137.1 (s), 136.8 (s), 136.3 (s), 129.7 (s), 129.0 (s), 128.7 (s), 128.6 (s), 128.4 (s), 126.7 (s), 125.3 (s), 124.4 (s), 102.5 (s), 100.0 (s), 90.8 (s), 80.2 (s), 80.0 (s), 77.3 (s), 28.4 (s), 15.4 (s). HRMS (ESI,  $m/z$ ):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{30}\text{H}_{24}\text{ClN}_2\text{O}_3^+$ : 495.1470, found: 495.1466.

*4-((1-(4-(tert-butyl)phenyl)-3-chloro-5-(1-phenylvinyl)-1H-pyrazol-4-*

*yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (5da)*. Purified by column chromatography (PE/EA = 8:1), yellow solid (32.2 mg, 41%), mp 158.5 - 159.1 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.49 – 7.45 (m, 2H), 7.39 (d, J = 5.9 Hz, 3H), 7.25 (d, J = 2.0 Hz, 9H), 5.87 (s, 1H), 5.43 (s, 1H), 4.43 (q, J = 8.4 Hz, 2H), 1.25 (s, 9H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>) δ 153.8 (s), 151.8 (s), 147.0 (s), 143.1 (s), 137.7 (s), 137.2 (s), 137.0 (s), 136.2 (s), 129.8 (s), 129.2 (s), 128.7 (s), 128.7 (s), 126.9 (s), 126.0 (s), 125.4 (s), 124.3 (s), 121.9 (s), 102.6 (s), 90.9 (s), 80.4 (s), 80.2 (s), 77.4 (s), 34.8 (s), 31.3 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>32</sub>H<sub>28</sub>ClN<sub>2</sub>O<sub>3</sub><sup>+</sup>: 523.1783, found: 523.1779.

*4-((3-chloro-1-(4-fluorophenyl)-5-(1-phenylvinyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (5ea)*. Purified by column chromatography (PE/EA = 8:1), yellow liquid (49 mg, 68%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.51 – 7.47 (m, 2H), 7.40 (d, J = 5.5 Hz, 3H), 7.31 (dd, J = 8.4, 4.7 Hz, 2H), 7.26 (s, 3H), 7.20 (d, J = 4.8 Hz, 2H), 6.95 (t, J = 8.4 Hz, 2H), 5.91 (s, 1H), 5.49 (s, 1H), 4.48 (dd, J = 30.2, 8.4 Hz, 2H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>) δ 162.1 (d, J = 249.4 Hz), 153.7 (s), 147.1 (s), 143.4 (s), 137.3 (s), 137.1 (s), 136.8 (s), 134.9 (d, J = 3.3 Hz), 129.9 (s), 129.2 (s), 129.0 (s), 128.8 (s), 126.7 (s), 126.5 (d, J = 8.8 Hz), 125.4 (s), 122.1 (s), 116.0 (d, J = 23.2 Hz), 103.1 (s), 91.0 (s), 80.1 (s), 80.0 (s), 77.5 (s). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -112.16 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>28</sub>H<sub>19</sub>ClFN<sub>2</sub>O<sub>3</sub><sup>+</sup>: 485.1063, found:

485.1059.

**4-((1-(3-bromophenyl)-3-(difluoromethyl)-5-(1-phenylvinyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (5fa).** Purified by column chromatography (PE/EA = 8:1), yellow solid (50 mg, 59%), mp 48.2 - 48.5 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.56 (s, 1H), 7.50 (dd, J = 6.4, 3.0 Hz, 2H), 7.42 – 7.35 (m, 4H), 7.31 – 7.28 (m, 1H), 7.27 – 7.24 (m, 3H), 7.18 (dd, J = 6.6, 2.8 Hz, 2H), 7.12 (t, J = 8.1 Hz, 1H), 6.80 (t, J = 53.8 Hz, 1H), 5.96 (s, 1H), 5.57 (s, 1H), 4.54 (d, J = 8.4 Hz, 1H), 4.45 (d, J = 8.4 Hz, 1H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>) δ 153.7 (s), 148.3 (t, J = 28.3 Hz), 147.5 (s), 139.7 (s), 137.3 (s), 137.1 (s), 136.5 (s), 131.6 (s), 130.3 (s), 129.8 (s), 129.2 (s), 128.9 (s), 128.8 (s), 127.6 (s), 126.7 (s), 125.4 (s), 123.0 (s), 122.5 (s), 122.4 (s), 110.7 (t, J = 236.2 Hz), 101.8 (s), 90.7 (s), 80.1 (s), 79.7 (s), 77.4 (s). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -113.72 (d, J = 8.0 Hz). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>29</sub>H<sub>20</sub>BrF<sub>2</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 561.0620, found: 561.0627.

**4-((3-(difluoromethyl)-5-(1-phenylvinyl)-1-(o-tolyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (5ga).** Purified by column chromatography (PE/EA = 8:1), yellow liquid (33.5 mg, 45%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.50 (dd, J = 6.5, 2.6 Hz, 2H), 7.44 – 7.39 (m, 3H), 7.29 – 7.21 (m, 5H), 7.16 (d, J = 6.0 Hz, 2H), 7.11 (t, J = 7.6 Hz, 1H), 7.05 (d, J = 7.6 Hz, 1H), 6.78 (t, J = 53.9 Hz, 1H), 5.72 (s, 1H), 5.38 (s, 1H), 4.43 (q, J = 8.4 Hz, 2H), 2.07 (s, 3H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz,

CDCl<sub>3</sub>) δ 153.8 (s), 148.7 (s), 147.8 (t, J = 28.1 Hz), 138.2 (s), 137.7 (s), 137.3 (s), 136.7 (s), 135.2 (s), 131.2 (s), 129.8 (s), 129.8 (s), 129.2 (s), 128.7 (s), 128.5 (s), 127.6 (s), 127.0 (s), 126.6 (s), 125.4 (s), 122.0 (s), 110.9 (t, J = 235.8 Hz), 100.0 (s), 90.5 (s), 80.2 (s), 80.1 (s), 77.4 (s), 17.9 (s). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -113.38 (d, J = 18.8 Hz). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>30</sub>H<sub>23</sub>F<sub>2</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 497.1671, found: 497.1667.

***4-((1-(2-bromophenyl)-3-(difluoromethyl)-5-(1-phenylvinyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (5ha)***. Purified by column chromatography (PE/EA = 8:1), yellow solid (49 mg, 58%), mp 43.6 - 44.5 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.59 – 7.56 (m, 1H), 7.50 – 7.47 (m, 2H), 7.42 – 7.39 (m, 3H), 7.26 – 7.19 (m, 8H), 6.80 (t, J = 53.8 Hz, 1H), 5.75 (s, 1H), 5.46 (s, 1H), 4.45 – 4.39 (m, 2H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>) δ 153.8 (s), 149.1 (s), 148.2 (t, J = 28.6 Hz), 137.9 (s), 137.2 (s), 136.3 (s), 133.7 (s), 131.2 (s), 129.8 (s), 129.7 (s), 129.2 (s), 128.7 (s), 128.5 (s), 128.1 (s), 127.2 (s), 125.4 (s), 122.3 (s), 121.8 (s), 110.8 (t, J = 236.2 Hz), 100.3 (s), 90.7 (s), 80.1 (s), 79.9 (s), 77.4 (s). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -113.65 (d, J = 47.4 Hz). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>29</sub>H<sub>20</sub>BrF<sub>2</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 561.0620, found: 561.0627.

***4-((3-(difluoromethyl)-1-(naphthalen-2-yl)-5-(1-phenylvinyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (5ia)***. Purified by column chromatography (PE/EA = 8:1), yellow solid (46.3 mg, 58%), mp 49.9 - 50.2 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.27 – 8.21 (m, 1H), 7.67 –

7.51 (m, 5H), 7.47 – 7.38 (m, 5H), 7.09 (dt, J = 18.0, 6.9 Hz, 6H), 6.84 (t, J = 53.7 Hz, 1H), 5.64 (s, 1H), 5.41 (d, J = 2.6 Hz, 1H), 4.49 (dd, J = 27.5, 8.4 Hz, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.8 (s), 150.0 (s), 148.4 (t, J = 28.7 Hz), 137.7 (s), 137.2 (s), 136.5 (s), 134.2 (s), 134.0 (s), 132.5 (s), 131.2 (s), 130.7 (s), 129.9 (s), 129.2 (s), 128.8 (s), 128.6 (s), 128.4 (s), 128.1 (s), 127.8 (s), 126.9 (s), 125.4 (s), 125.0 (s), 123.3 (s), 122.1 (s), 110.9 (t, J = 236.2 Hz), 100.4 (s), 90.8 (s), 80.1 (s), 79.9 (s), 77.4 (s).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -113.45 (d, J = 14.8 Hz). HRMS (ESI, m/z):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{33}\text{H}_{23}\text{F}_2\text{N}_2\text{O}_3^+$ : 533.1671, found: 533.1676.

*4-((3-(difluoromethyl)-5-(1-(4-methoxyphenyl)vinyl)-1-phenyl-1H-pyrazol-4-yl)ethynyl)-4-(4-methoxyphenyl)-1,3-dioxolan-2-one* (5ac). Purified by column chromatography (PE/EA = 8:1), yellow liquid (40.7 mg, 50%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (t, J = 8.3 Hz, 4H), 7.26 – 7.20 (m, 3H), 7.09 (d, J = 8.5 Hz, 2H), 6.94 – 6.84 (m, 1H), 6.81 (d, J = 8.7 Hz, 2H), 6.73 – 6.70 (m, 2H), 5.74 (s, 1H), 5.25 (s, 1H), 4.38 (q, J = 8.4 Hz, 2H), 3.74 (s, 3H), 3.70 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.7 (s), 160.1 (s), 153.9 (s), 147.9 (t, J = 28.2 Hz), 147.7 (s), 138.8 (s), 136.1 (s), 130.1 (s), 129.1 (s), 128.8 (s), 128.7 (s), 128.0 (s), 127.3 (s), 124.6 (s), 120.1 (s), 114.4 (s), 114.1 (s), 110.9 (t, J = 235.9 Hz), 101.3 (s), 90.6 (s), 80.3 (s), 80.0 (s), 77.4 (s), 55.5 (s), 55.4 (s).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -113.46 (d, J = 9.5 Hz). HRMS (ESI, m/z):  $[\text{M} + \text{H}]^+$ , calcd. for

$C_{31}H_{25}F_2N_2O_5^+$ : 543.1726, found: 543.1707.

***4-((3-(difluoromethyl)-5-(1-(3-fluorophenyl)vinyl)-1-phenyl-1H-pyrazol-4-yl)ethynyl)-4-(3-fluorophenyl)-1,3-dioxolan-2-one (5ah).***

Purified by column chromatography (PE/EA = 8:1), white solid (45 mg, 58%). mp 125.6 - 126.4 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.40 (dd, J = 13.8, 7.9 Hz, 1H), 7.34 – 7.16 (m, 8H), 7.11 (t, J = 8.2 Hz, 1H), 6.96 – 6.67 (m, 4H), 5.95 (s, 1H), 5.57 (s, 1H), 4.52 (dd, J = 65.7, 8.5 Hz, 2H).  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  164.2 (d, J = 7.5 Hz), 161.7 (d, J = 5.9 Hz), 153.4 (s), 148.1 (t, J = 28.7 Hz), 146.8 (s), 139.7 (s), 139.6 (d, J = 1.2 Hz), 138.6 (s), 135.7 (d, J = 2.3 Hz), 131.0 (d, J = 8.2 Hz), 130.3 (d, J = 8.5 Hz), 129.2 (s), 128.9 (s), 124.6 (s), 123.1 (s), 122.5 (d, J = 2.8 Hz), 120.9 (d, J = 3.0 Hz), 116.9 (d, J = 21.2 Hz), 115.7 (d, J = 21.3 Hz), 113.6 (d, J = 22.7 Hz), 112.9 (d, J = 24.0 Hz), 110.9 (t, J = 235.9 Hz), 101.2 (s), 90.1 (s), 80.1 (s), 79.4 (s), 77.2 (s).  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  -110.65 (s), -112.54 (s), -113.40 (s). HRMS (ESI, m/z):  $[M + H]^+$ , calcd. for  $C_{29}H_{19}F_4N_2O_3^+$ : 519.1326, found: 519.1320.

***4-((1,3-diphenyl-5-(1-phenylvinyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (7aa).*** Purified by column chromatography (PE/EA = 8:1), yellow solid (63.6 mg, 83%), mp 45.6 - 45.9 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.00 (d, J = 7.7 Hz, 2H), 7.39 (d, J = 7.5 Hz, 2H), 7.32 (dt, J = 12.1, 6.5 Hz, 9H), 7.21 (ddd, J = 12.0, 8.0, 1.5 Hz, 7H), 5.85 (s, 1H), 5.38 (s, 1H), 4.30 (s, 2H).  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$

153.8 (s), 152.7 (s), 147.3 (s), 139.3 (s), 138.0 (s), 137.4 (s), 137.2 (s), 131.9 (s), 129.7 (s), 129.1 (s), 129.0 (s), 128.9 (s), 128.7 (s), 128.7 (s), 128.1 (s), 127.1 (s), 126.8 (s), 125.4 (s), 124.7 (s), 121.3 (s), 101.1 (s), 90.1 (s), 83.7 (s), 80.4 (s), 77.2 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>34</sub>H<sub>25</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 509.1860, found: 509.1845.

**4-phenyl-4-((3-phenyl-5-(1-phenylvinyl)-1-(p-tolyl)-1H-pyrazol-4-yl)ethynyl)-1,3-dioxolan-2-one (7ab).** Purified by column chromatography (PE/EA = 8:1), yellow solid (63.6 mg, 81%), mp 153.1 - 154.3 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.07 (dd, J = 7.6, 1.9 Hz, 2H), 7.43 – 7.33 (m, 12H), 7.31 – 7.27 (m, 3H), 7.10 (d, J = 8.3 Hz, 2H), 5.91 (s, 1H), 5.41 (s, 1H), 4.38 – 4.33 (m, 2H), 2.30 (s, 3H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>) δ 153.8 (s), 152.4 (s), 147.3 (s), 138.2 (s), 138.1 (s), 137.4 (s), 137.3 (s), 136.9 (s), 132.0 (s), 129.7 (s), 129.6 (s), 129.1 (s), 128.9 (s), 128.7 (s), 128.6 (s), 127.1 (s), 126.8 (s), 125.4 (s), 124.5 (s), 121.2 (s), 100.8 (s), 90.0 (s), 83.8 (s), 80.4 (s), 77.2 (s), 21.2 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>35</sub>H<sub>27</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 523.2016, found: 523.2003.

**4-((1-(4-fluorophenyl)-3-phenyl-5-(1-phenylvinyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (7ac).** Purified by column chromatography (PE/EA = 8:1), white solid (69 mg, 87%), mp 149.9 - 150.2 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.06 (dd, J = 7.2, 2.2 Hz, 2H), 7.42 (ddt, J = 13.7, 8.8, 4.4 Hz, 10H), 7.29 (d, J = 6.7 Hz, 5H), 6.98 (t, J = 8.5 Hz, 2H), 5.94 (s, 1H), 5.49 (s, 1H), 4.45 – 4.38 (m, 2H). **<sup>13</sup>C{<sup>1</sup>H}**

**NMR** (101 MHz, CDCl<sub>3</sub>) δ 162.0 (d, J = 248.6 Hz), 153.8 (s), 152.8 (s), 147.4 (s), 137.9 (s), 137.3 (s), 137.2 (s), 135.5 (d, J = 3.1 Hz), 131.8 (s), 129.7 (s), 129.1 (s), 129.0 (s), 128.8 (s), 128.7 (s), 127.1 (s), 126.7 (s), 126.5 (d, J = 8.7 Hz), 125.4 (s), 121.4 (s), 115.9 (d, J = 23.0 Hz), 101.3 (s), 90.1 (s), 83.5 (s), 80.4 (s), 77.2 (s). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -112.96 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>34</sub>H<sub>24</sub>FN<sub>2</sub>O<sub>3</sub><sup>+</sup>: 527.1765, found: 527.1749.

**4-((1-(4-chlorophenyl)-3-phenyl-5-(1-phenylvinyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (7ad)**. Purified by column chromatography (PE/EA = 8:1), white solid (60 mg, 74%), mp 150.9 - 151.4 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.06 (dd, J = 6.2, 2.5 Hz, 2H), 7.44 – 7.37 (m, 10H), 7.27 (dd, J = 14.4, 5.6 Hz, 7H), 5.96 (s, 1H), 5.49 (s, 1H), 4.43 – 4.38 (m, 2H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>) δ 153.8 (s), 152.9 (s), 147.3 (s), 137.8 (s), 137.8 (s), 137.3 (s), 137.2 (s), 133.8 (s), 131.7 (s), 129.7 (s), 129.2 (s), 129.1 (s), 128.9 (s), 128.8 (s), 128.7 (s), 127.1 (s), 126.7 (s), 125.7 (s), 125.4 (s), 121.5 (s), 101.6 (s), 90.3 (s), 83.4 (s), 80.4 (s), 77.2 (s). **HRMS** (ESI, m/z): [M + Na]<sup>+</sup>, calcd. for C<sub>34</sub>H<sub>23</sub>ClN<sub>2</sub>NaO<sub>3</sub><sup>+</sup>: 565.1289, found: 565.1298.

**4-((1-(4-bromophenyl)-3-phenyl-5-(1-phenylvinyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (7ae)**. Purified by column chromatography (PE/EA = 8:1), white solid (65 mg, 74%), mp 149.6 - 150.1 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.08 – 8.03 (m, 2H), 7.44 – 7.36

(m, 11H), 7.35 (t, J = 2.2 Hz, 1H), 7.29 (d, J = 7.8 Hz, 5H), 5.96 (s, 1H), 5.48 (s, 1H), 4.40 (s, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.8 (s), 152.9 (s), 147.3 (s), 138.3 (s), 137.7 (s), 137.3 (s), 137.2 (s), 132.1 (s), 131.7 (s), 129.7 (s), 129.1 (s), 128.9 (s), 128.8 (s), 128.7 (s), 127.1 (s), 126.7 (s), 125.9 (s), 125.3 (s), 121.7 (s), 121.5 (s), 101.7 (s), 90.3 (s), 83.3 (s), 80.4 (s), 77.2 (s). HRMS (ESI, m/z):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{34}\text{H}_{24}\text{BrN}_2\text{O}_3^+$ : 587.0965, found: 587.0964.

***4-phenyl-4-((3-phenyl-5-(1-phenylvinyl)-1-(m-tolyl)-1H-pyrazol-4-yl)ethynyl)-1,3-dioxolan-2-one (7af).*** Purified by column chromatography (PE/EA = 8:1), white solid (77.6 mg, 99%), mp 86.7 - 87.5 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 – 8.03 (m, 2H), 7.47 – 7.32 (m, 10H), 7.31 – 7.27 (m, 5H), 7.22 (dd, J = 11.1, 5.0 Hz, 2H), 5.93 (d, J = 12.6 Hz, 1H), 5.47 (d, J = 9.8 Hz, 1H), 4.39 (d, J = 6.3 Hz, 2H), 2.31 (d, J = 4.6 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.8 (s), 152.8 (s), 147.3 (s), 137.9 (s), 137.7 (s), 137.4 (s), 137.2 (s), 137.1 (s), 133.9 (s), 131.7 (s), 129.7 (s), 129.4 (s), 129.1 (s), 129.0 (s), 128.8 (s), 128.7 (s), 127.1 (s), 126.8 (s), 126.7 (s), 125.3 (s), 123.0 (s), 121.4 (s), 101.4 (s), 90.2 (s), 83.5 (s), 80.4 (s), 77.2 (s), 20.2 (s). HRMS (ESI, m/z):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{35}\text{H}_{27}\text{N}_2\text{O}_3^+$ : 523.2016, found: 523.2003.

***4-((1-(3-fluorophenyl)-3-phenyl-5-(1-phenylvinyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (7ag).*** Purified by column chromatography (PE/EA = 8:1), white solid (77.5 mg, 98%), mp 100.6 -

101.1 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.07 (d, J = 2.6 Hz, 2H), 7.41 (dd, J = 22.4, 8.0 Hz, 8H), 7.26 (dd, J = 16.1, 8.4 Hz, 8H), 6.94 (t, J = 7.6 Hz, 1H), 6.00 (d, J = 11.8 Hz, 1H), 5.55 (d, J = 8.7 Hz, 1H), 4.42 (q, J = 8.2 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 162.5 (d, J = 247.7 Hz), 153.8 (s), 152.9 (s), 147.4 (s), 140.5 (d, J = 9.9 Hz), 137.7 (s), 137.3 (s), 137.1 (s), 131.6 (s), 130.2 (d, J = 9.0 Hz), 129.8 (s), 129.1 (s), 128.8 (s), 128.7 (s), 127.1 (s), 126.7 (s), 125.4 (s), 121.5 (s), 120.0 (d, J = 3.1 Hz), 115.0 (d, J = 21.1 Hz), 112.0 (d, J = 25.1 Hz), 101.8 (s), 90.3 (s), 83.3 (s), 80.4 (s), 77.2 (s). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -111.15 (d, J = 2.9 Hz). HRMS (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>34</sub>H<sub>24</sub>FN<sub>2</sub>O<sub>3</sub><sup>+</sup>: 527.1765, found: 527.1749.

*4-((1-(2-methoxyphenyl)-3-phenyl-5-(1-phenylvinyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (7ah)*. Purified by column chromatography (PE/EA = 8:1), yellow solid (50 mg, 62%), mp 63.8 - 64.7 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.04 (dd, J = 6.5, 2.9 Hz, 2H), 7.43 (dd, J = 6.9, 4.6 Hz, 3H), 7.37 (s, 6H), 7.35 (d, J = 2.0 Hz, 2H), 7.34 (s, 1H), 7.33 – 7.30 (m, 3H), 7.01 (t, J = 7.6 Hz, 1H), 6.87 (d, J = 8.3 Hz, 1H), 5.66 (s, 1H), 5.22 (s, 1H), 4.30 (d, J = 8.3 Hz, 1H), 4.15 (d, J = 8.3 Hz, 1H), 3.61 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 153.9 (s), 153.9 (s), 152.6 (s), 149.4 (s), 138.6 (s), 137.8 (s), 137.5 (s), 132.1 (s), 130.5 (s), 129.6 (s), 129.1 (s), 128.9 (s), 128.7 (s), 128.5 (s), 128.4 (s), 128.4 (s), 128.4 (s), 127.4 (s), 127.2 (s), 125.3 (s), 120.9 (s), 119.4 (s),

111.9 (s), 99.4 (s), 90.3 (s), 83.9 (s), 80.3 (s), 77.2 (s), 55.4 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>35</sub>H<sub>27</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup>: 539.1965, found: 539.1942.

**4-((1-(2-bromophenyl)-3-phenyl-5-(1-phenylvinyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (7ai).** Purified by column chromatography (PE/EA = 8:1), white solid (66.7 mg, 76%), mp 143.5 - 144.2 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.06 (s, 2H), 7.60 (d, J = 7.4 Hz, 1H), 7.45 – 7.27 (m, 16H), 5.76 (s, 1H), 5.45 (s, 1H), 4.35 (dd, J = 19.3, 8.1 Hz, 2H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>) δ 153.8 (s), 152.9 (s), 149.0 (s), 138.6 (s), 138.4 (s), 137.3 (s), 137.0 (s), 133.7 (s), 131.8 (s), 130.8 (s), 129.9 (s), 129.7 (s), 129.1 (s), 129.0 (s), 128.6 (s), 128.6 (s), 128.5 (s), 128.0 (s), 127.3 (s), 127.3 (s), 125.4 (s), 122.2 (s), 121.5 (s), 100.1 (s), 90.3 (s), 83.6 (s), 80.3 (s), 77.2 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>34</sub>H<sub>24</sub>BrN<sub>2</sub>O<sub>3</sub><sup>+</sup>: 587.0965, found: 587.0964.

**4-((3-(4-(methylthio)phenyl)-1-phenyl-5-(1-phenylvinyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (7aj).** Purified by column chromatography (PE/EA = 8:1), yellow solid (54 mg, 65%). mp 53.1 - 53.7 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.01 (d, J = 8.1 Hz, 2H), 7.43 (dd, J = 13.2, 8.0 Hz, 4H), 7.36 (d, J = 6.4 Hz, 3H), 7.30 – 7.23 (m, 10H), 5.91 (s, 1H), 5.44 (s, 1H), 4.38 (s, 2H), 2.48 (s, 3H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>) δ 153.7 (s), 152.0 (s), 147.3 (s), 139.5 (s), 139.2 (s), 137.9 (s), 137.3 (s), 137.1 (s), 129.6 (s), 129.0 (s), 128.9 (s), 128.6 (s), 128.6 (s), 128.5 (s), 128.0 (s), 127.3 (s), 126.7 (s), 126.1 (s), 125.3 (s), 124.5 (s),

121.2 (s), 100.9 (s), 90.2 (s), 83.6 (s), 80.3 (s), 77.1 (s), 15.5 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>35</sub>H<sub>27</sub>N<sub>2</sub>O<sub>3</sub>S<sup>+</sup>: 555.1737, found: 555.1719.

**4-(4-((2-oxo-4-phenyl-1,3-dioxolan-4-yl)ethynyl)-1-phenyl-5-(1-phenylvinyl)-1H-pyrazol-3-yl)benzotrile (7ak).** Purified by column chromatography (PE/EA = 8:1), yellow solid (62 mg, 78%), mp 66.7 - 67.2 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.20 (d, J = 8.3 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 7.7 Hz, 2H), 7.41 (d, J = 3.5 Hz, 5H), 7.34 (t, J = 4.6 Hz, 2H), 7.31 (s, 6H), 5.96 (s, 1H), 5.47 (s, 1H), 4.42 – 4.36 (m, 2H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>) δ 153.6 (s), 150.4 (s), 147.9 (s), 139.0 (s), 137.8 (s), 137.1 (s), 137.0 (s), 136.3 (s), 132.4 (s), 129.9 (s), 129.2 (s), 129.1 (s), 128.8 (s), 128.8 (s), 128.5 (s), 127.3 (s), 126.7 (s), 125.2 (s), 124.6 (s), 121.7 (s), 118.9 (s), 112.2 (s), 101.5 (s), 91.2 (s), 82.7 (s), 80.2 (s), 77.1 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>35</sub>H<sub>24</sub>N<sub>3</sub>O<sub>3</sub><sup>+</sup>: 534.1812, found: 534.1811.

**4-phenyl-4-((1-phenyl-5-(1-phenylvinyl)-3-(m-tolyl)-1H-pyrazol-4-yl)ethynyl)-1,3-dioxolan-2-one (7al).** Purified by column chromatography (PE/EA = 8:1), yellow solid (62.6 mg, 80%), mp 50.5 - 51.5 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.94 – 7.86 (m, 2H), 7.44 (ddd, J = 7.9, 6.9, 1.8 Hz, 4H), 7.37 (t, J = 5.8 Hz, 3H), 7.33 – 7.24 (m, 9H), 7.19 (d, J = 7.6 Hz, 1H), 5.94 (d, J = 13.6 Hz, 1H), 5.46 (d, J = 11.7 Hz, 1H), 4.38 (s, 2H), 2.34 (s, 3H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>) δ 153.8 (s),

152.8 (s), 147.4 (s), 139.3 (s), 138.4 (s), 138.1 (s), 137.4 (s), 137.3 (s), 131.8 (s), 129.7 (s), 129.7 (s), 129.1 (s), 129.0 (s), 128.7 (s), 128.6 (s), 128.6 (s), 128.1 (s), 127.7 (s), 126.8 (s), 125.4 (s), 124.7 (s), 124.2 (s), 121.3 (s), 101.1 (s), 90.1 (s), 83.7 (s), 80.4 (s), 77.3 (s), 21.5 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>35</sub>H<sub>27</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 523.2016, found: 523.2003.

**4-((3-(3-methoxyphenyl)-1-phenyl-5-(1-phenylvinyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (7am)**. Purified by column chromatography (PE/EA = 8:1), white solid (75.1 mg, 93%), mp 45.4 - 46.1 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.67 (dd, J = 9.7, 4.9 Hz, 2H), 7.47 (d, J = 7.7 Hz, 2H), 7.44 – 7.41 (m, 2H), 7.37 (t, J = 5.8 Hz, 3H), 7.34 – 7.30 (m, 4H), 7.28 (dd, J = 5.3, 1.9 Hz, 4H), 7.25 (dd, J = 6.3, 3.4 Hz, 1H), 6.93 (dd, J = 8.2, 2.4 Hz, 1H), 5.93 (s, 1H), 5.45 (s, 1H), 4.36 (s, 2H), 3.75 (s, 3H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>) δ 159.9 (s), 153.8 (s), 152.4 (s), 147.5 (s), 139.3 (s), 138.0 (s), 137.4 (s), 133.2 (s), 129.7 (s), 129.7 (s), 129.1 (s), 129.0 (s), 128.7 (s), 128.7 (s), 128.1 (s), 126.8 (s), 125.3 (s), 124.7 (s), 121.3 (s), 119.5 (s), 115.4 (s), 111.8 (s), 101.2 (s), 90.3 (s), 83.6 (s), 80.3 (s), 77.3 (s), 55.4 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>35</sub>H<sub>27</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup>: 539.1965, found: 539.1969.

**4-((3-(3-nitrophenyl)-1-phenyl-5-(1-phenylvinyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (7an)**. Purified by column chromatography (PE/EA = 8:1), yellow liquid (64 mg, 77%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.03 (s, 1H), 8.43 (d, J = 7.8 Hz, 1H), 8.22 (dd, J =

8.2, 1.2 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.46 (d, J = 7.6 Hz, 2H), 7.43 (dd, J = 7.5, 2.2 Hz, 2H), 7.38 (dd, J = 7.4, 2.2 Hz, 3H), 7.30 (dd, J = 11.1, 6.1 Hz, 8H), 5.96 (s, 1H), 5.49 (s, 1H), 4.51 (dd, J = 39.1, 8.5 Hz, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.7 (s), 150.0 (s), 148.5 (s), 148.0 (s), 139.0 (s), 137.8 (s), 137.1 (s), 133.7 (s), 132.7 (s), 129.8 (s), 129.7 (s), 129.2 (s), 129.1 (s), 128.8 (s), 128.5 (s), 126.7 (s), 125.2 (s), 124.6 (s), 123.4 (s), 121.7 (s), 121.7 (s), 101.4 (s), 91.2 (s), 82.5 (s), 80.2 (s), 77.1 (s). **HRMS** (ESI, m/z):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{34}\text{H}_{24}\text{N}_3\text{O}_5^+$ : 554.1710, found: 554.1708.

***4-phenyl-4-((1-phenyl-5-(1-phenylvinyl)-3-(o-tolyl)-1H-pyrazol-4-yl)ethynyl)-1,3-dioxolan-2-one (7ao)***. Purified by column chromatography (PE/EA = 8:1), yellow liquid (50 mg, 64%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (d, J = 7.5 Hz, 1H), 7.48 (d, J = 7.5 Hz, 2H), 7.34 (dd, J = 11.1, 5.1 Hz, 8H), 7.30 (d, J = 3.8 Hz, 6H), 7.28 (d, J = 2.1 Hz, 2H), 5.94 (s, 1H), 5.52 (s, 1H), 4.32 (dd, J = 20.9, 8.4 Hz, 2H), 2.52 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.6 (s), 153.8 (s), 146.0 (s), 139.4 (s), 138.1 (s), 137.5 (s), 137.3 (s), 137.2 (s), 131.2 (s), 130.8 (s), 130.3 (s), 129.6 (s), 129.0 (s), 128.9 (s), 128.9 (s), 128.7 (s), 128.6 (s), 127.9 (s), 126.8 (s), 125.6 (s), 125.5 (s), 124.5 (s), 121.2 (s), 103.5 (s), 89.5 (s), 83.5 (s), 80.3 (s), 77.3 (s), 20.8 (s). **HRMS** (ESI, m/z):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{35}\text{H}_{27}\text{N}_2\text{O}_3^+$ : 523.2016, found: 523.2003.

***4-((3-(2-fluorophenyl)-1-phenyl-5-(1-phenylvinyl)-1H-pyrazol-4-***

*yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (7ap)*. Purified by column chromatography (PE/EA = 8:1), white solid (66 mg, 84%), mp 113.3 - 113.7 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.79 (t, J = 7.4 Hz, 1H), 7.46 (d, J = 7.7 Hz, 2H), 7.40 (ddd, J = 12.6, 5.7, 4.0 Hz, 3H), 7.35 (t, J = 4.3 Hz, 2H), 7.33 – 7.26 (m, 8H), 7.26 – 7.21 (m, 2H), 7.21 – 7.16 (m, 1H), 5.94 (d, J = 13.1 Hz, 1H), 5.51 (d, J = 11.3 Hz, 1H), 4.40 – 4.35 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 160.2 (d, J = 251.6 Hz), 153.9 (s), 149.5 (d, J = 2.2 Hz), 146.5 (s), 139.2 (s), 138.0 (s), 137.3 (d, J = 8.3 Hz), 131.2 (d, J = 3.1 Hz), 130.9 (d, J = 8.2 Hz), 129.7 (s), 129.0 (d, J = 3.1 Hz), 128.7 (s), 128.7 (s), 128.2 (s), 126.8 (s), 125.5 (s), 124.7 (s), 124.3 (d, J = 3.4 Hz), 121.5 (s), 119.9 (d, J = 13.8 Hz), 116.3 (d, J = 21.7 Hz), 103.5 (s), 89.7 (s), 82.8 (s), 80.4 (s), 77.5 (s). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -112.36 (s). HRMS (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>34</sub>H<sub>24</sub>FN<sub>2</sub>O<sub>3</sub><sup>+</sup>: 527.1765, found: 527.1749.

*4-((3-(naphthalen-2-yl)-1-phenyl-5-(1-phenylvinyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (7aq)*. Purified by column chromatography (PE/EA = 8:1), white solid (70.3 mg, 84%), mp 63.2 - 63.8 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.63 (s, 1H), 8.20 (td, J = 9.1, 1.6 Hz, 1H), 7.86 (dd, J = 13.7, 7.8 Hz, 2H), 7.74 – 7.70 (m, 1H), 7.52 – 7.45 (m, 6H), 7.40 – 7.37 (m, 2H), 7.34 (dd, J = 6.8, 3.4 Hz, 4H), 7.32 – 7.28 (m, 4H), 7.27 (dd, J = 7.3, 4.6 Hz, 1H), 5.97 (d, J = 13.3 Hz, 1H), 5.50 (d, J = 11.2 Hz, 1H), 4.43 – 4.37 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

$\delta$  153.9 (s), 152.5 (s), 147.6 (s), 139.4 (s), 138.1 (s), 137.5 (s), 137.4 (s), 133.6 (s), 133.4 (s), 129.7 (s), 129.4 (s), 129.2 (s), 129.1 (s), 128.8 (s), 128.7 (s), 128.7 (s), 128.4 (s), 128.2 (s), 127.8 (s), 126.8 (s), 126.6 (s), 126.4 (s), 126.4 (s), 125.4 (s), 124.8 (s), 121.4 (s), 101.3 (s), 90.4 (s), 83.8 (s), 80.5 (s), 77.3 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>38</sub>H<sub>27</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 559.2016, found: 559.2014.

**4-phenyl-4-((1-phenyl-5-(1-phenylvinyl)-3-(thiophen-2-yl)-1H-pyrazol-4-yl)ethynyl)-1,3-dioxolan-2-one (7ar)**. Purified by column chromatography (PE/EA = 8:1), yellow solid (70 mg, 91%), mp 119.6 - 120.0 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.73 (dd, J = 3.6, 0.8 Hz, 1H), 7.47 – 7.41 (m, 4H), 7.40 – 7.35 (m, 3H), 7.33 – 7.23 (m, 9H), 7.05 (dd, J = 5.0, 3.8 Hz, 1H), 5.93 (d, J = 13.5 Hz, 1H), 5.46 (d, J = 11.6 Hz, 1H), 4.44 (dd, J = 26.7, 8.4 Hz, 2H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  153.8 (s), 148.2 (s), 147.1 (s), 139.1 (s), 137.9 (s), 137.2 (s), 134.2 (s), 129.7 (s), 129.1 (s), 129.0 (s), 128.7 (s), 128.7 (s), 128.2 (s), 127.6 (s), 126.8 (s), 126.1 (s), 125.3 (s), 124.7 (s), 121.3 (s), 100.5 (s), 90.9 (s), 83.0 (s), 80.4 (s), 77.2 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>32</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub>S<sup>+</sup>: 515.1424, found: 515.1414.

**4-((3-(benzo[b]thiophen-2-yl)-1-phenyl-5-(1-phenylvinyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (7as)**. Purified by column chromatography (PE/EA = 8:1), yellow solid (76.3 mg, 90%), mp 74.7 - 75.6 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.71 (dd, J = 13.1, 8.3 Hz,

1H), 8.15 – 8.06 (m, 1H), 7.89 (d,  $J = 7.6$  Hz, 1H), 7.57 – 7.50 (m, 2H), 7.49 – 7.43 (m, 1H), 7.43 – 7.35 (m, 7H), 7.34 – 7.24 (m, 7H), 5.97 (d,  $J = 12.5$  Hz, 1H), 5.51 (d,  $J = 10.5$  Hz, 1H), 4.40 – 4.31 (m, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.8 (s), 149.1 (s), 146.6 (s), 140.2 (s), 139.4 (s), 138.0 (s), 137.4 (s), 137.4 (s), 137.3 (s), 129.8 (s), 129.2 (s), 129.0 (s), 128.7 (s), 128.7 (s), 128.1 (s), 127.5 (s), 126.8 (s), 126.6 (s), 125.3 (s), 124.9 (s), 124.8 (s), 124.6 (s), 122.6 (s), 121.4 (s), 102.2 (s), 90.6 (s), 83.6 (s), 80.30(s). HRMS (ESI,  $m/z$ ):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{36}\text{H}_{25}\text{N}_2\text{O}_3\text{S}^+$ : 565.1580, found: 565.1568.

**4-((3-(3-(2-((3,7-dimethyloct-6-en-1-yl)oxy)acetyl)phenyl)-1-phenyl-5-(1-phenylvinyl)-1H-pyrazol-4-yl)ethynyl)-4-phenyl-1,3-dioxolan-2-one (7at).** Purified by column chromatography (PE/EA = 8:1), pale yellow oil (55 mg, 52%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.40 (s, 1H), 8.17 (d,  $J = 7.9$  Hz, 1H), 7.59 (d,  $J = 7.6$  Hz, 1H), 7.46 (d,  $J = 7.7$  Hz, 2H), 7.43 (d,  $J = 7.8$  Hz, 1H), 7.38 (m, 5H), 7.34 – 7.26 (m, 8H), 6.16 (d,  $J = 6.9$  Hz, 1H), 5.95 (s, 1H), 5.47 (s, 1H), 4.60 (d,  $J = 8.5$  Hz, 1H), 4.41 (d,  $J = 8.5$  Hz, 1H), 4.18 (t,  $J = 11.6$  Hz, 1H), 3.47 (d,  $J = 7.8$  Hz, 1H), 2.07 – 1.91 (m, 2H), 1.82 (dd,  $J = 25.5, 12.0$  Hz, 4H), 1.53 (d,  $J = 11.5$  Hz, 3H), 1.34 – 1.14 (m, 6H), 1.07 – 0.81 (m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.19 (s), 154.39 (s), 153.97 (s), 151.59 (s), 147.39 (s), 139.17 (s), 137.85 (s), 137.38 (s), 137.28 (s), 136.59 (s), 132.52 (s), 129.77 (s), 129.13 (s), 129.04 (s), 129.01 (s), 128.71 (s), 128.67 (s),

128.66 (s), 128.22 (s), 126.84 (s), 126.72 (s) , 125.85 (s), 125.44 (s), 124.60 (s), 121.34 (s), 101.19 (s), 90.29 (s), 83.36 (s), 80.89 (s), 77.31 (s), 56.91 (s), 49.90 (s), 32.31(s) , 32.14 (s), 31.01 (s), 30.61 (s), 26.28 (s), 25.40 (s), 25.37 (s), 24.76(s) , 24.73 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>46</sub>H<sub>45</sub>N<sub>2</sub>O<sub>5</sub><sup>+</sup>: 705.3323, found: 705.3317.

***1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 3-(4-((2-oxo-4-phenyl-1,3-dioxolan-4-yl)ethynyl)-1-phenyl-5-(1-phenylvinyl)-1H-pyrazol-3-yl)benzoate (7au)***. Purified by column chromatography (PE/EA = 8:1), pale yellow oil (92 mg, 89%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.83 (s, 1H), 8.25 (d, *J* = 7.6 Hz, 1H), 8.09 (d, *J* = 7.6 Hz, 1H), 7.49 (dd, *J* = 15.8, 7.8 Hz, 3H), 7.43 (d, *J* = 6.8 Hz, 2H), 7.35 (d, *J* = 6.7 Hz, 3H), 7.33 – 7.24 (m, 8H), 5.93 (s, 1H), 5.49 (s, 1H), 5.23 – 5.02 (m, 1H), 4.62 (dd, *J* = 8.0, 6.0 Hz, 1H), 4.45 (d, *J* = 8.5 Hz, 1H), 2.46 (dt, *J* = 13.3, 10.2 Hz, 1H), 2.27 – 2.03 (m, 1H), 1.90 – 1.69 (m, 2H), 1.40 (t, *J* = 12.6 Hz, 1H), 1.29 (dd, *J* = 18.4, 6.9 Hz, 1H), 1.17 – 1.06 (m, 1H), 0.97 (s, 3H), 0.91 (d, *J* = 4.8 Hz, 6H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>) δ 166.62 (s), 166.60 (s), 153.86 (s), 151.80 (s), 147.45 (d, *J* = 2.0 Hz), 139.13 (s), 137.83 (s), 137.21 (s), 137.19 (s), 132.34 (s), 131.34 (s), 131.30 (s), 129.63 (s), 129.58 (s), 129.02 (s), 128.95 (s), 128.73 (s), 128.63 (s), 128.60 (s), 128.36 (s), 128.13 (s), 126.69 (s), 125.36 (s), 125.35 (s), 124.51 (s), 121.42 (s), 101.42 (s), 90.29 (s), 83.08 (s), 80.76 (d, *J* = 5.4 Hz), 80.33 (s), 77.35 (s), 49.16 (d, *J* = 3.7 Hz), 47.96 (s), 44.97 (s), 36.90 (d, *J* = 2.5 Hz),

28.12 (s), 27.44 (s), 19.80 (s), 19.01 (s), 13.74 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>45</sub>H<sub>41</sub>N<sub>2</sub>O<sub>5</sub><sup>+</sup>: 689.3010, found: 689.3016.

**4-([1,1'-biphenyl]-4-yl)-4-((5-(1-([1,1'-biphenyl]-4-yl)vinyl)-3-phenyl-1-(p-tolyl)-1H-pyrazol-4-yl)ethynyl)-1,3-dioxolan-2-one (7bd)**. Purified by column chromatography (PE/EA = 8:1), white solid (55 mg, 54%), mp 163.4 - 164.2 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.15 – 8.11 (m, 2H), 7.59 (d, J = 8.2 Hz, 4H), 7.52 (d, J = 8.4 Hz, 2H), 7.49 – 7.41 (m, 14H), 7.40 – 7.37 (m, 3H), 7.15 (d, J = 8.2 Hz, 2H), 6.01 (s, 1H), 5.44 (s, 1H), 4.45 – 4.40 (m, 2H), 2.34 (s, 3H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>) δ 153.9 (s), 152.5 (s), 147.2 (s), 142.6 (s), 141.4 (s), 140.2 (s), 139.9 (s), 138.2 (s), 137.0 (s), 137.0 (s), 136.9 (s), 135.9 (s), 132.0 (s), 129.7 (s), 129.1 (s), 129.0 (s), 128.9 (s), 128.7 (s), 128.0 (s), 127.8 (s), 127.7 (s), 127.4 (s), 127.2 (s), 127.1 (s), 127.1 (s), 126.0 (s), 124.5 (s), 121.2 (s), 100.9 (s), 90.1 (s), 83.9 (s), 80.5 (s), 77.3 (s), 21.2 (s). **HRMS** (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>47</sub>H<sub>35</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 675.2642, found: 675.2650.

**4-(2-chlorophenyl)-4-((5-(1-(2-chlorophenyl)vinyl)-3-(3-methoxyphenyl)-1-phenyl-1H-pyrazol-4-yl)ethynyl)-1,3-dioxolan-2-one (7ml)**. Purified by column chromatography (PE/EA = 8:1), yellow solid (69 mg, 75%), mp 48.3 - 48.9 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.76 – 7.70 (m, 1H), 7.59 (dd, J = 4.0, 1.6 Hz, 2H), 7.48 – 7.43 (m, 3H), 7.40 – 7.36 (m, 2H), 7.30 (dd, J = 13.3, 5.6 Hz, 3H), 7.24 – 7.19 (m, 2H), 7.14 – 7.05 (m, 3H), 6.90 (dd, J = 8.0, 1.9 Hz, 1H), 5.75 (d, J = 5.0 Hz, 2H),

4.77 (dd, J = 89.1, 8.7 Hz, 2H), 3.77 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.7 (s), 153.1 (s), 152.6 (s), 146.9 (s), 139.4 (s), 137.3 (s), 135.8 (s), 135.1 (s), 133.2 (s), 132.6 (s), 131.4 (s), 131.1 (s), 130.7 (s), 130.6 (s), 129.9 (s), 129.4 (s), 129.4 (s), 128.9 (s), 128.4 (s), 127.5 (s), 126.7 (s), 126.6 (s), 125.7 (s), 125.6 (s), 119.6 (s), 115.1 (s), 111.9 (s), 100.4 (s), 89.6 (s), 82.6 (s), 78.6 (s), 75.9 (s), 55.3 (s). HRMS (ESI, m/z):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{35}\text{H}_{25}\text{Cl}_2\text{N}_2\text{O}_4^+$ : 607.1186, found: 607.1172.

***4-((3-(benzo[b]thiophen-2-yl)-5-(1-(4-bromophenyl)vinyl)-1-phenyl-1H-pyrazol-4-yl)ethynyl)-4-(4-bromophenyl)-1,3-dioxolan-2-one (7so).***  
Purified by column chromatography (PE/EA = 8:1), yellow solid (98 mg, 91%), mp 81.8 - 82.5 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.66 (d, J = 7.6 Hz, 1H), 8.07 (s, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.50 (dd, J = 7.8, 5.6 Hz, 4H), 7.43 (dd, J = 7.4, 5.9 Hz, 3H), 7.40 (s, 1H), 7.35 (t, J = 7.3 Hz, 2H), 7.31 (d, J = 7.1 Hz, 1H), 7.24 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 5.96 (s, 1H), 5.55 (s, 1H), 4.40 (dd, J = 27.3, 8.5 Hz, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.4 (s), 149.3 (s), 146.1 (s), 140.2 (s), 139.2 (s), 137.3 (s), 136.8 (s), 136.4 (s), 136.2 (s), 132.4 (s), 131.9 (s), 129.2 (s), 128.3 (s), 127.4 (s), 126.9 (s), 126.7 (s), 125.1 (s), 125.0 (s), 124.8 (s), 124.5 (s), 124.2 (s), 122.9 (s), 122.7 (s), 121.9 (s), 102.2 (s), 90.2 (s), 83.8 (s), 79.8 (s), 76.9 (s). HRMS (ESI, m/z):  $[\text{M} + \text{H}]^+$ , calcd. for  $\text{C}_{36}\text{H}_{23}\text{Br}_2\text{N}_2\text{O}_3\text{S}^+$ : 720.9791, found: 720.9787.

***1-(4-fluorophenyl)-4-(3-phenylbut-3-en-1-yn-1-yl)-5-(1-phenylvinyl)-***

**3-(trifluoromethyl)-1H-pyrazole (8).** Purified by column chromatography (PE), white liquid (70 mg, 80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.48 – 7.44 (m, 2H), 7.30 (d, J = 7.7 Hz, 2H), 7.22 (d, J = 5.8 Hz, 3H), 7.18 (d, J = 6.8 Hz, 3H), 7.15 (s, 5H), 5.90 (s, 1H), 5.84 (s, 1H), 5.55 (s, 1H), 5.46 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 146.3 (s), 143.5 (q, J = 58.4, 21.2 Hz), 138.9 (s), 137.6 (s), 137.0 (s), 136.7 (s), 130.4 (s), 129.0 (s), 128.7 (s), 128.6 (s), 128.5 (s), 128.4 (s), 126.8 (s), 126.1 (s), 124.8 (s), 121.0 (q, J = 270.5 Hz), 104.2 (s), 94.6 (s), 78.9 (s). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.18 (s). HRMS (ESI, m/z): [M + H]<sup>+</sup>, calcd. for C<sub>28</sub>H<sub>20</sub>F<sub>3</sub>N<sub>2</sub><sup>+</sup>: 441.1573, found: 441.1567.

**2-phenyl-4-(1-phenyl-5-(1-phenylvinyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)but-3-yne-1,2-diol (9).** Purified by column chromatography (PE/EA = 8:1), white solid (85 mg, 90%). mp 152.1 - 152.3 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49 (dd, J = 7.7, 1.6 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.32 – 7.21 (m, 11H), 5.92 (s, 1H), 5.48 (s, 1H), 3.55 (ddd, J = 19.9, 11.2, 7.4 Hz, 2H), 3.06 (s, 1H), 1.96 (dd, J = 8.6, 6.0 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 146.7 (s), 143.6 (q, J = 37.3 Hz), 140.1 (s), 138.7 (s), 137.6 (s), 136.6 (s), 129.1 (s), 128.8 (s), 128.8 (s), 128.8 (s), 128.4 (s), 128.4 (s), 126.7 (s), 125.9 (s), 124.8 (s), 120.9 (q, J = 270.4 Hz), 103.0 (s), 95.7 (s), 75.1 (s), 74.4 (s), 72.3 (s). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.06 (s). HRMS (ESI, m/z): [M + Na]<sup>+</sup>, calcd. for C<sub>28</sub>H<sub>22</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>: 497.1447, found: 497.1464.

***4-(4-bromophenyl)-4-((5-(1-(4-methoxyphenyl)vinyl)-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-4-yl)ethynyl)-1,3-dioxolan-2-one (3bcf).***

Purified by column chromatography (PE/EA = 8:1), pale yellow oil (28 mg, 31%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.37 (m, 2H), 7.35 (d, *J* = 2.1 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.25 (s, 1H), 7.05 (dd, *J* = 8.6, 1.7 Hz, 2H), 6.90 (dd, *J* = 8.9, 2.0 Hz, 2H), 5.95 (d, *J* = 15.3 Hz, 1H), 5.53 (s, 1H), 4.54 – 4.44 (m, 2H), 3.82 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*) δ 160.8, 153.7, 146.9, 138.4, 136.2, 135.4, 132.5, 132.1, 131.9, 129.3, 128.2, 127.1, 125.96, 125.6 (q, *J* = 236.3 Hz), 124.7, 122.9, 114.4, 101.9, 91.3, 80.1, 78.7, 77.2, 55.6. <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -62.08. HRMS (ESI, *m/z*): [M + H]<sup>+</sup>, calcd. for C<sub>30</sub>H<sub>21</sub>BrF<sub>3</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup>: 609.0631, found: 609.0624.

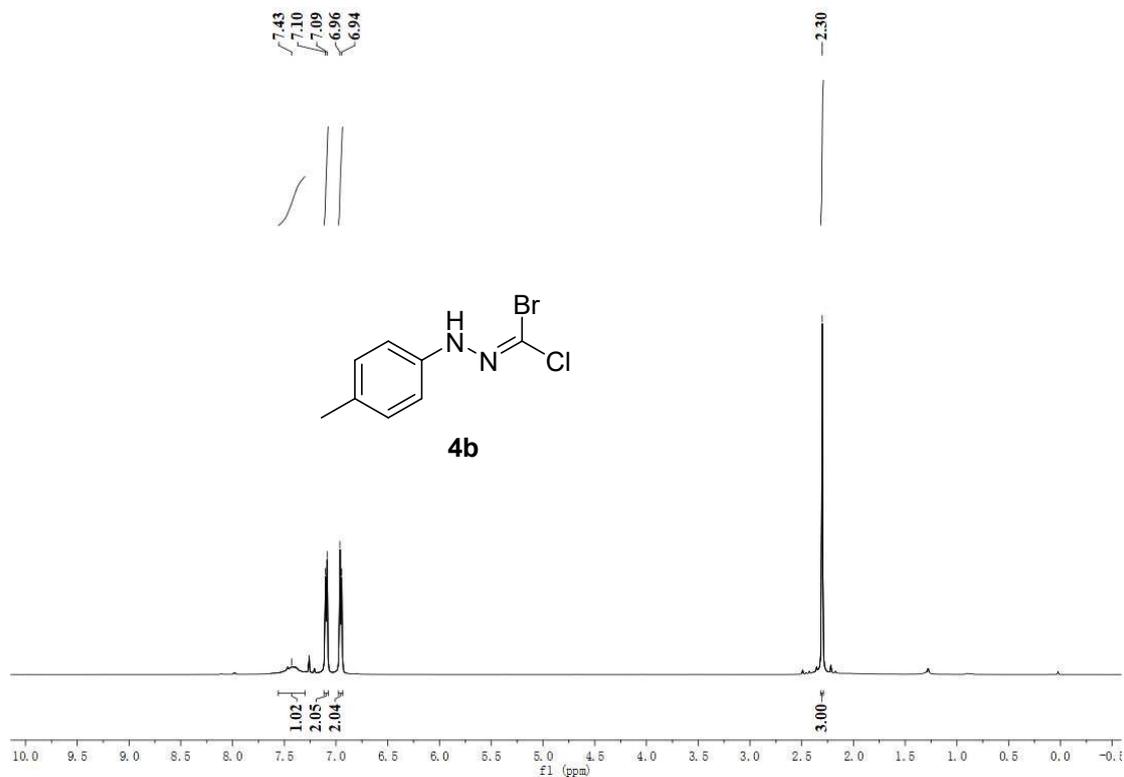
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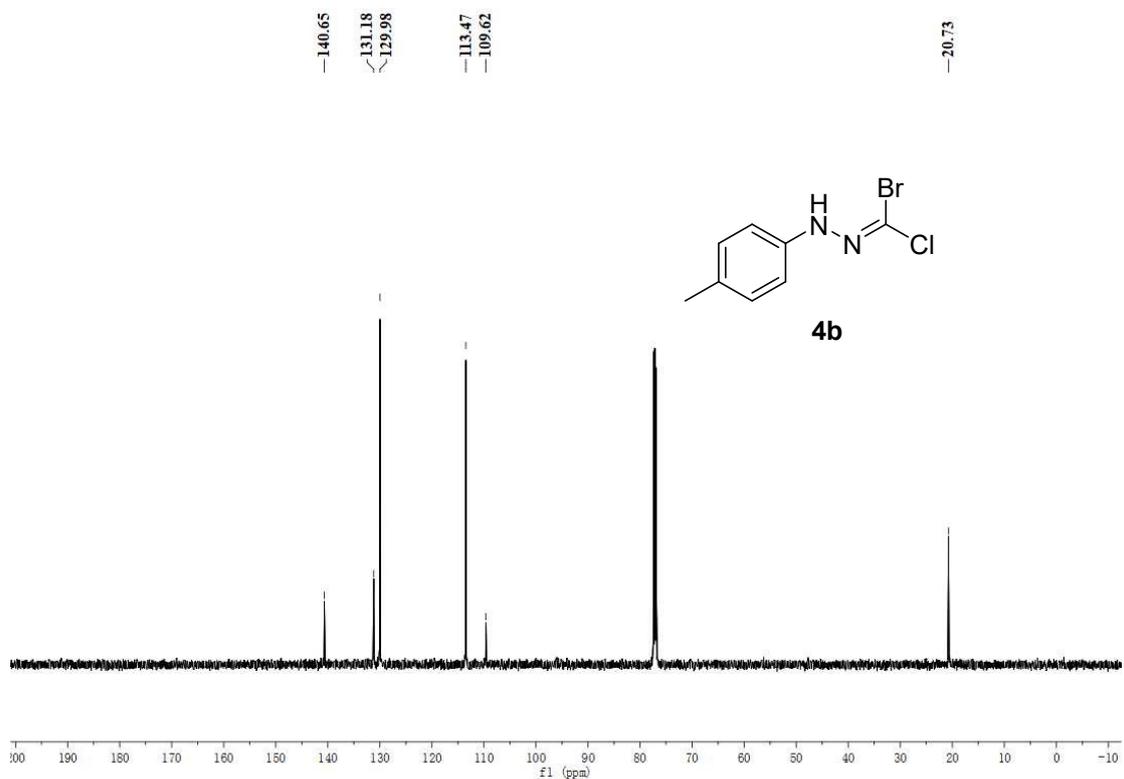
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## 11. NMR Spectra

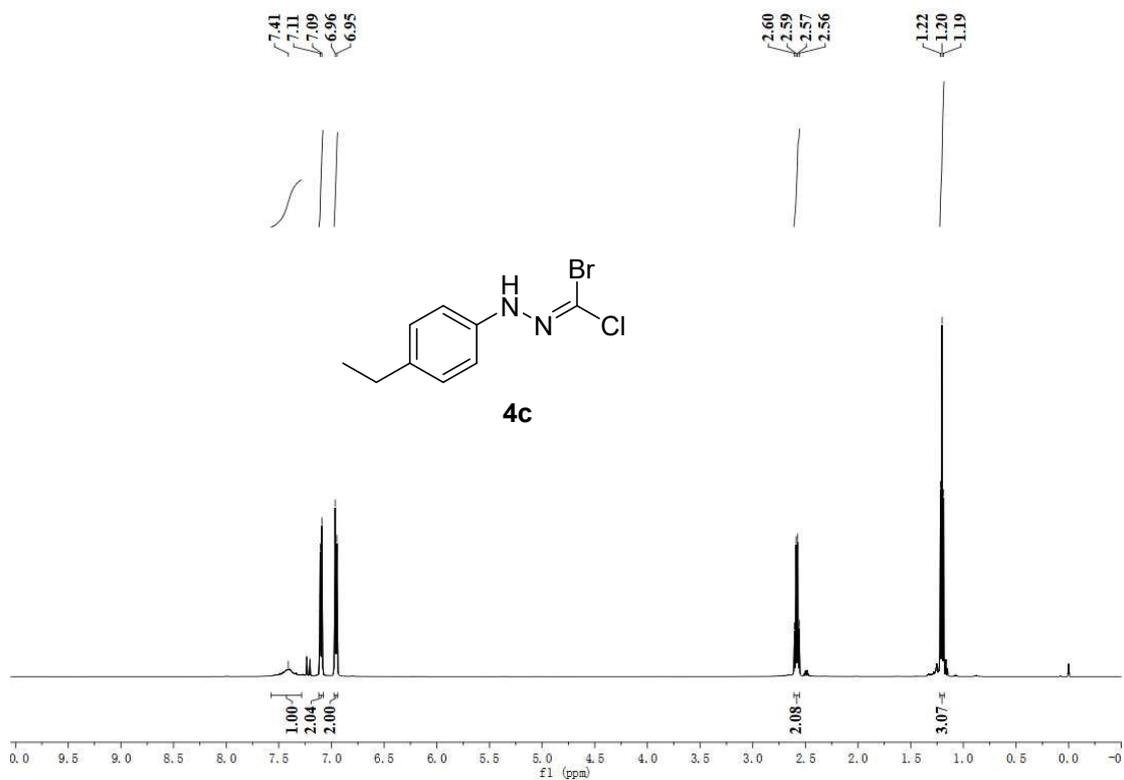
### $^1\text{H}$ NMR of 4b (500 MHz, $\text{CDCl}_3$ )



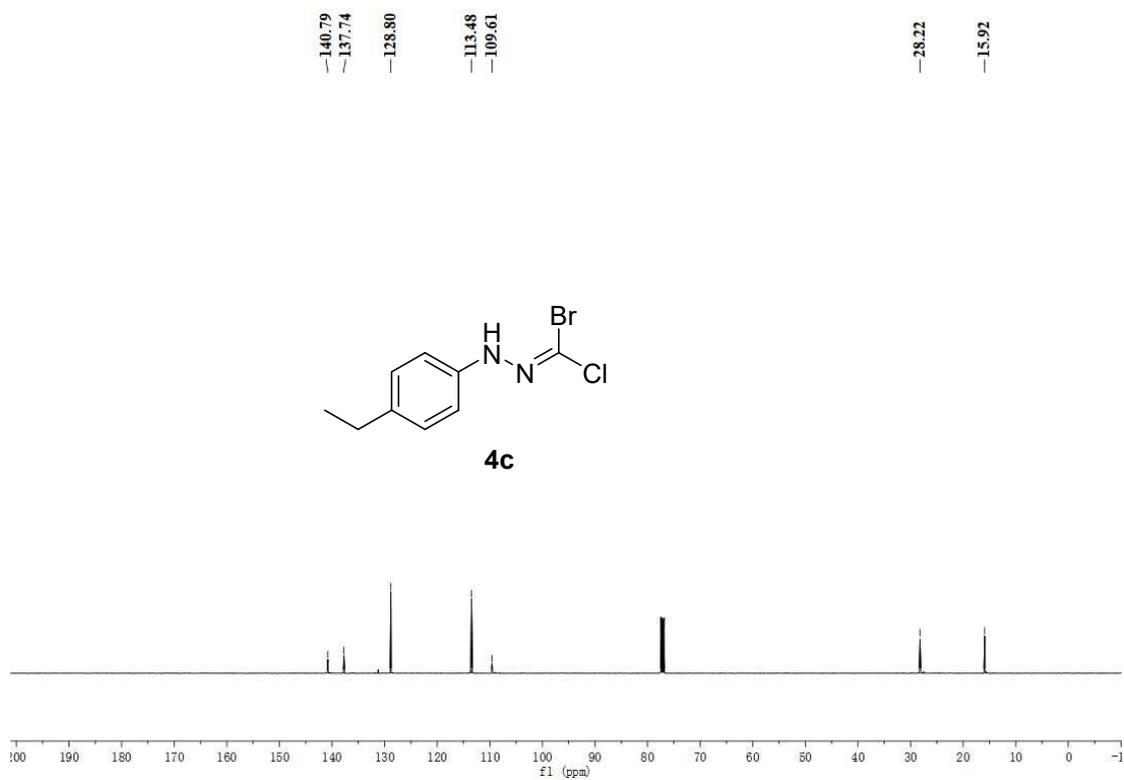
### $^{13}\text{C}\{^1\text{H}\}$ NMR of 4b (126 MHz, $\text{CDCl}_3$ )



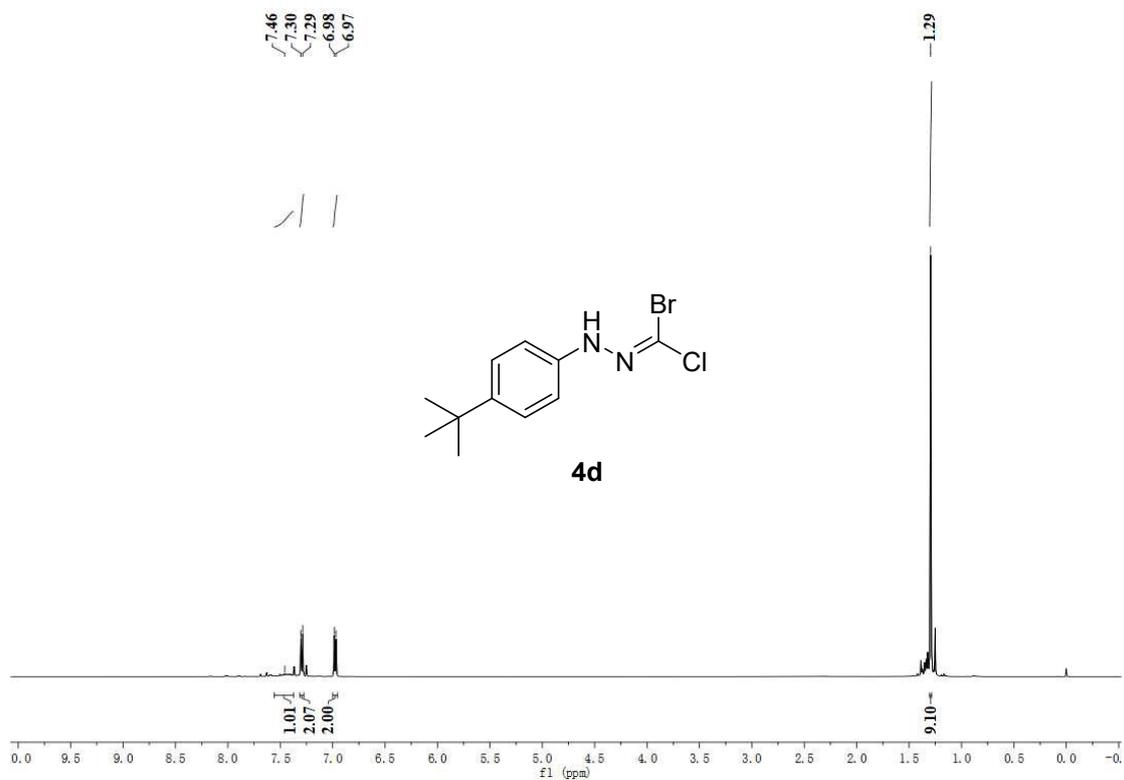
**<sup>1</sup>H NMR of 4c (500 MHz, CDCl<sub>3</sub>)**



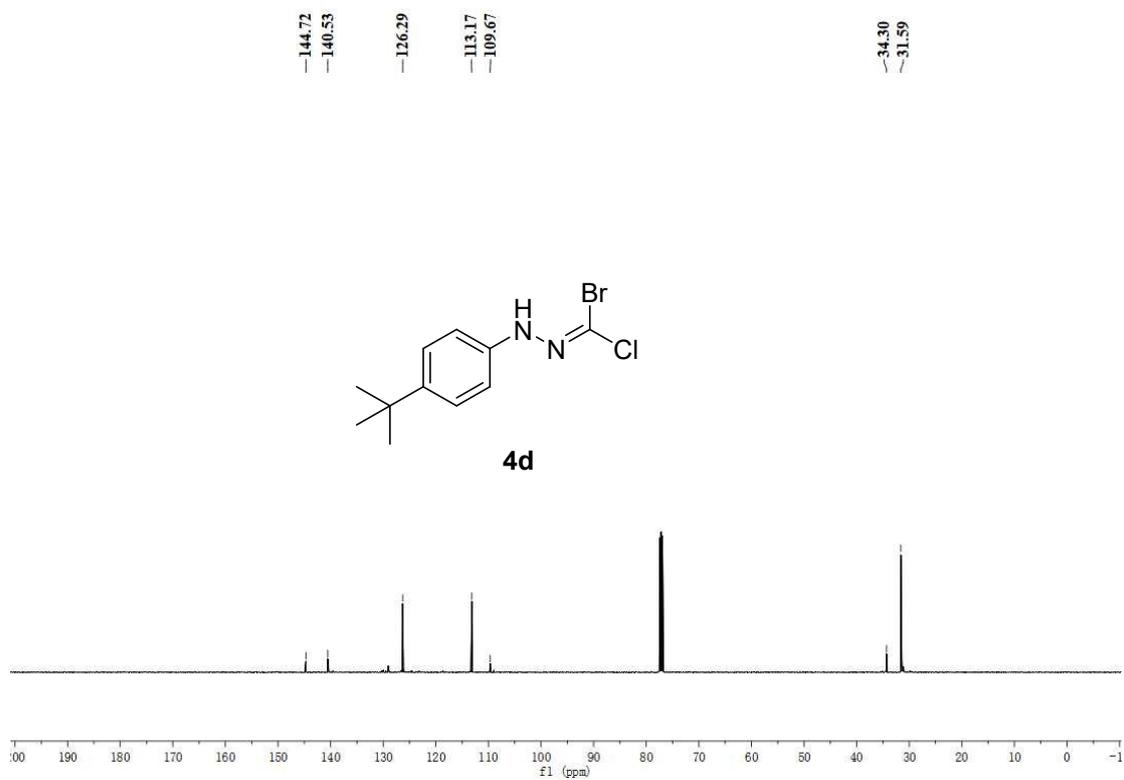
**<sup>13</sup>C{<sup>1</sup>H} NMR of 4c (126 MHz, CDCl<sub>3</sub>)**



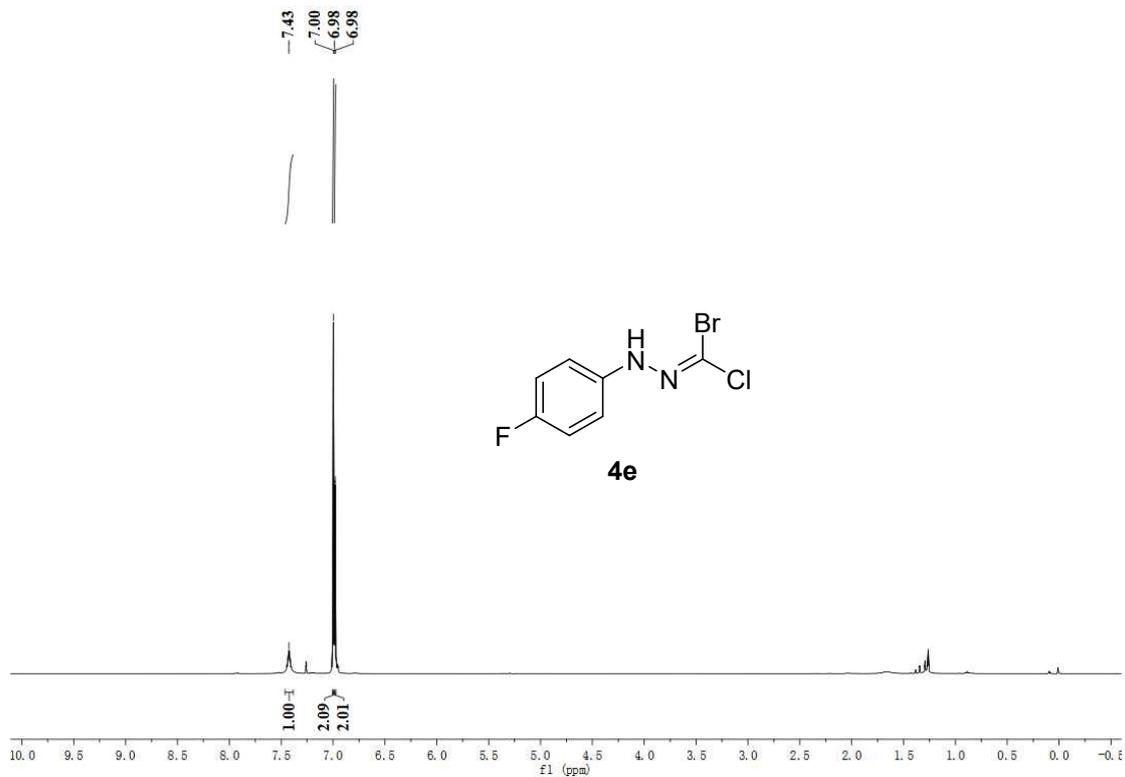
**<sup>1</sup>H NMR of 4d (500 MHz, CDCl<sub>3</sub>)**



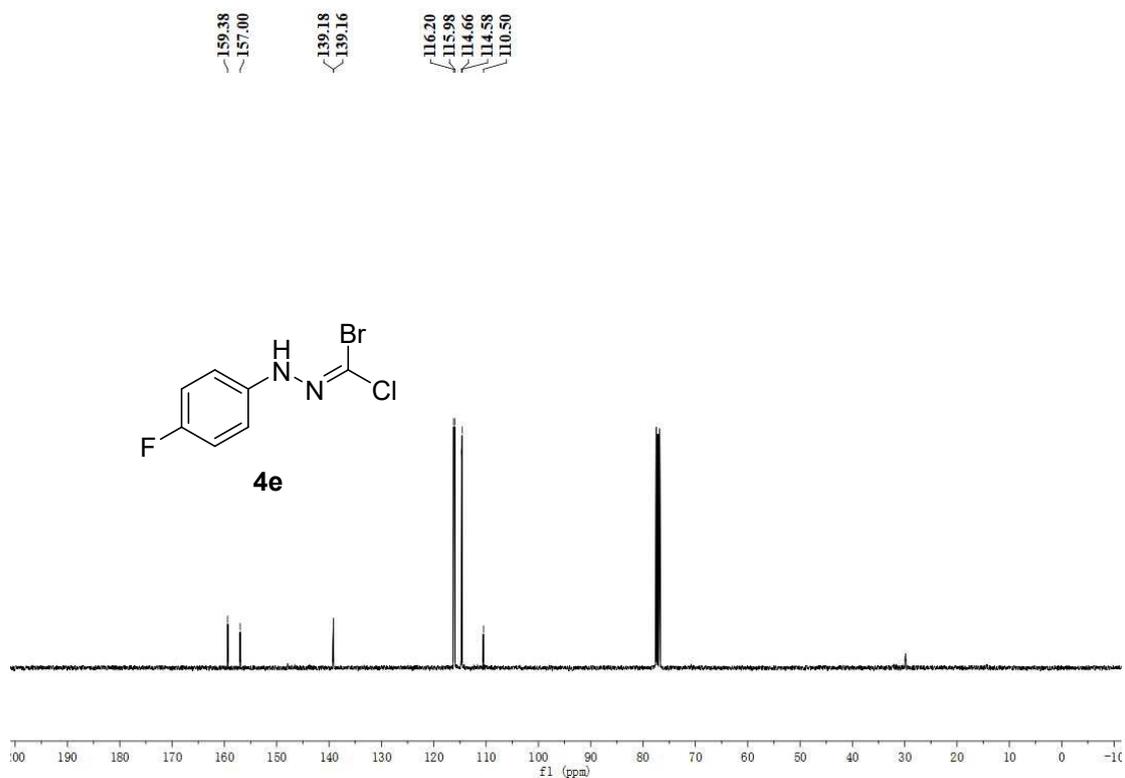
**<sup>13</sup>C{<sup>1</sup>H} NMR of 4d (126 MHz, CDCl<sub>3</sub>)**



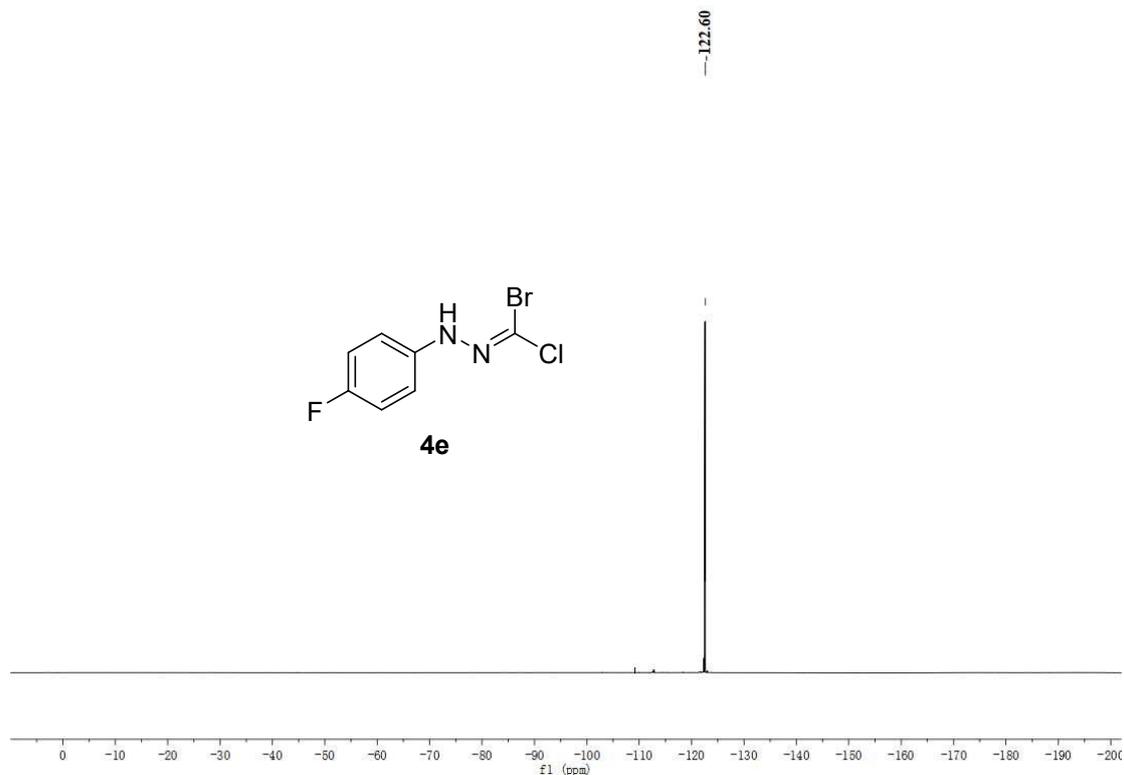
**<sup>1</sup>H NMR of 4e (400 MHz, CDCl<sub>3</sub>)**



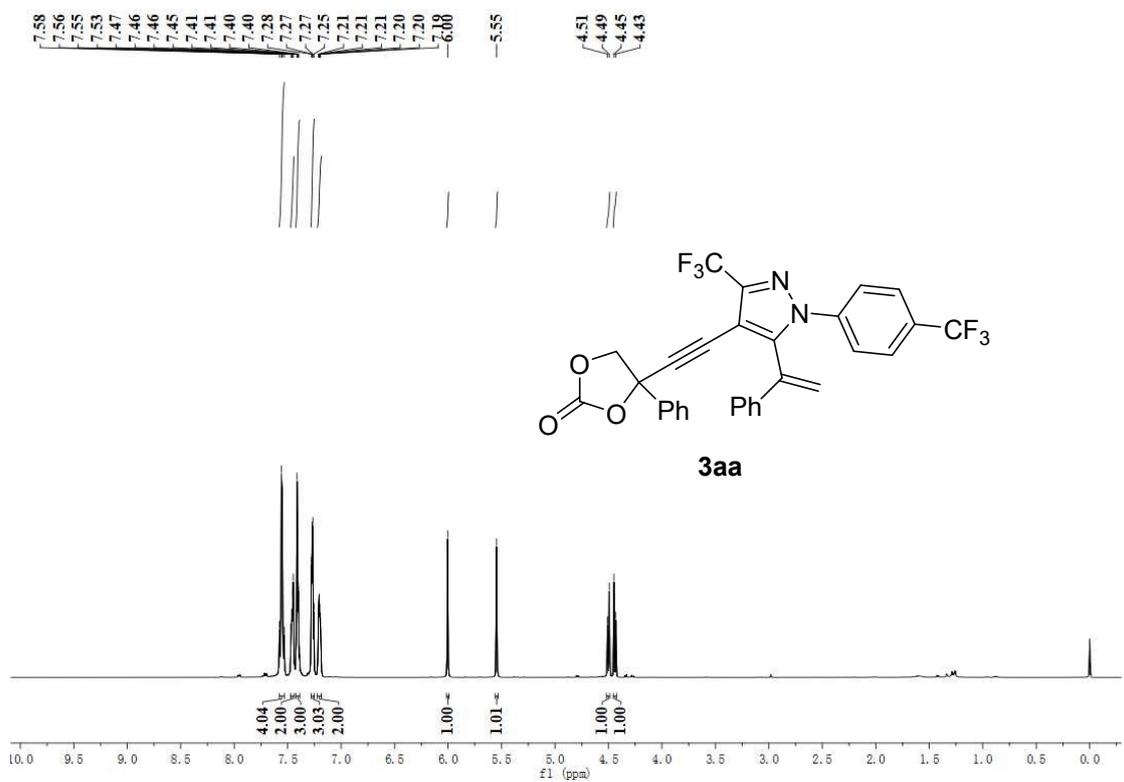
**<sup>13</sup>C{<sup>1</sup>H} NMR of 4e (101 MHz, CDCl<sub>3</sub>)**



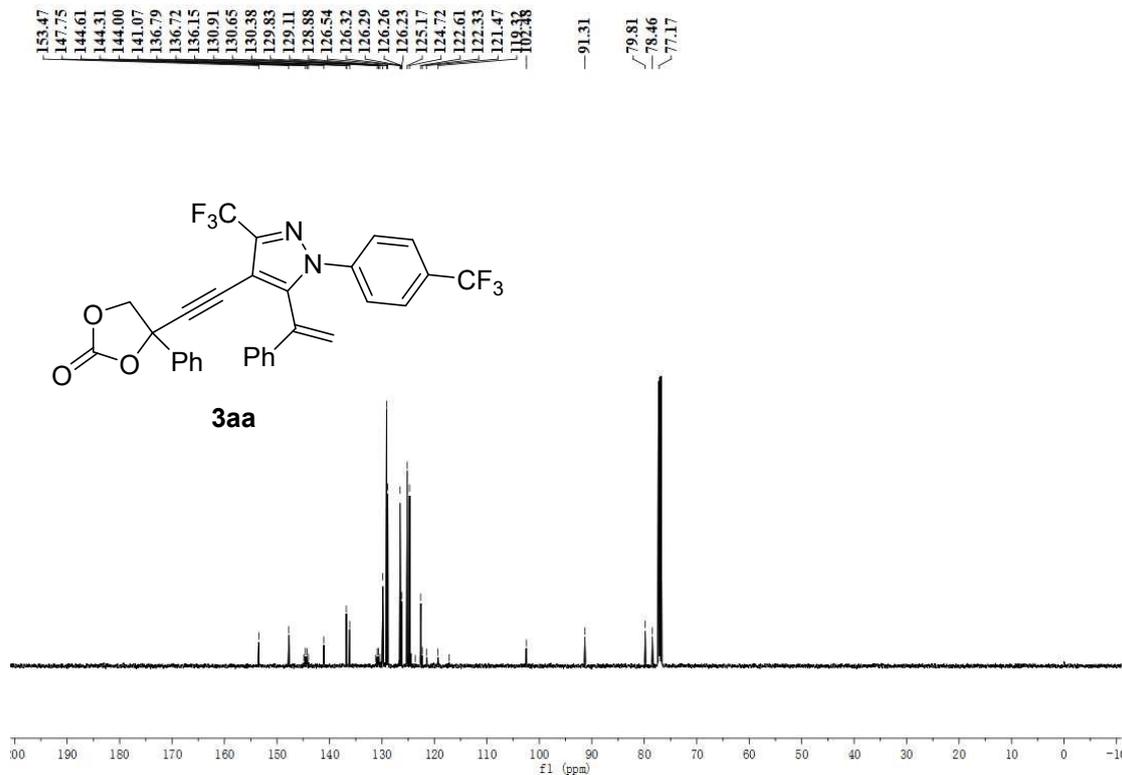
**<sup>19</sup>F NMR of 4e (471 MHz, CDCl<sub>3</sub>)**



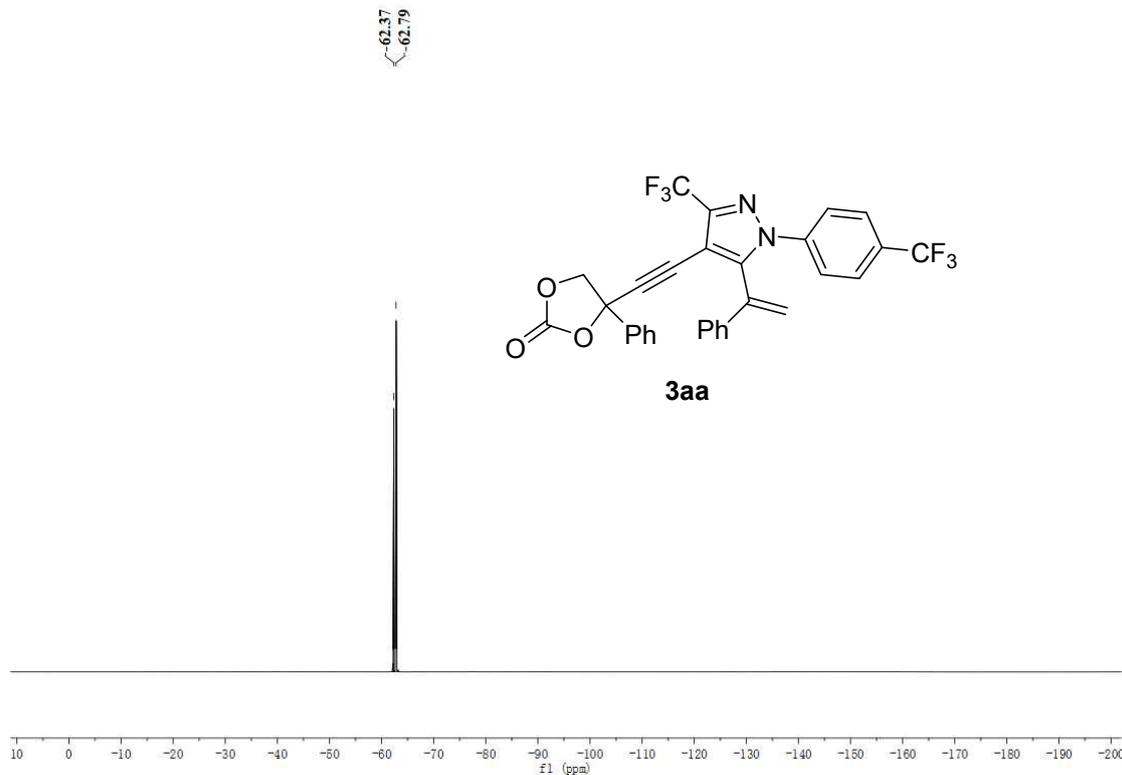
**<sup>1</sup>H NMR of 3aa (500 MHz, CDCl<sub>3</sub>)**



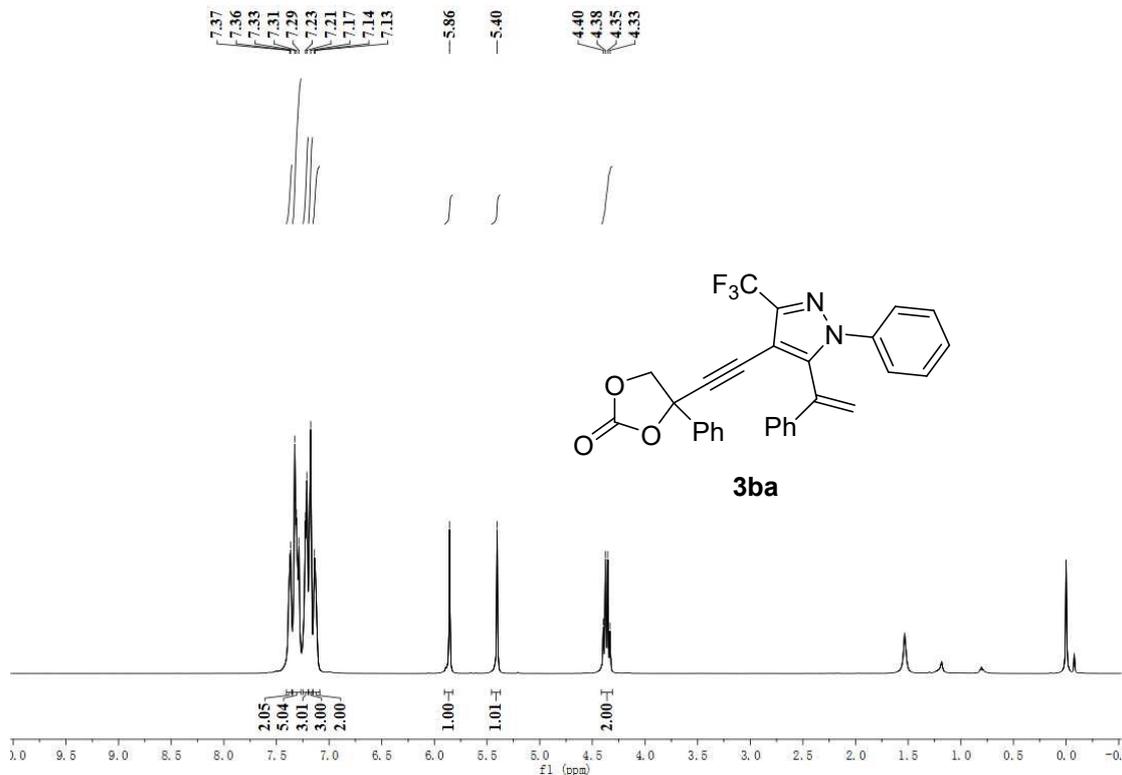
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 3aa (126 MHz,  $\text{CDCl}_3$ )**



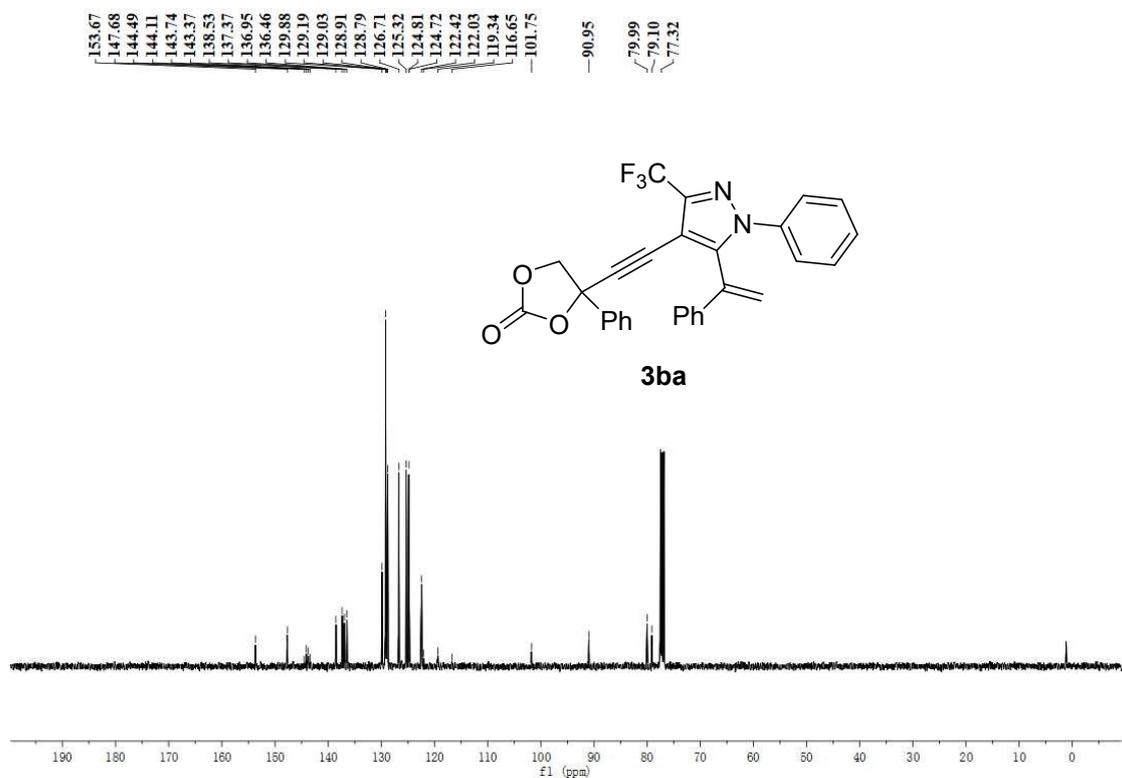
**$^{19}\text{F}$  NMR of 3aa (471 MHz,  $\text{CDCl}_3$ )**



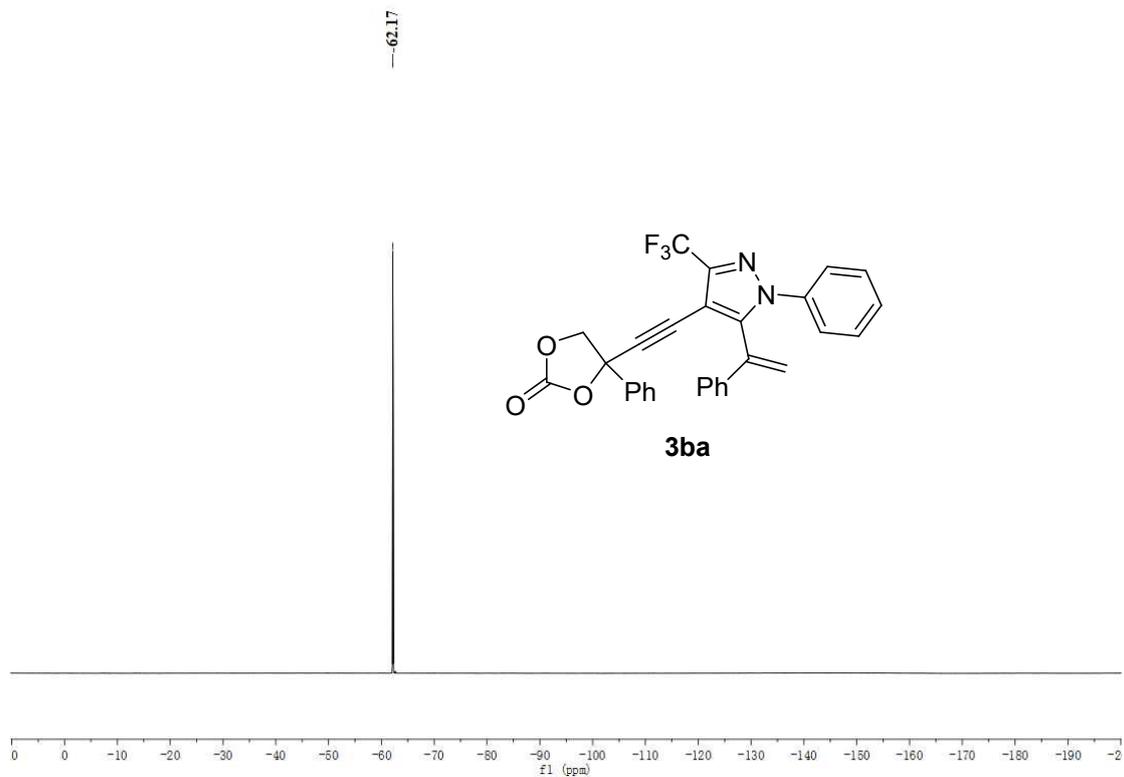
**<sup>1</sup>H NMR of 3ba (400 MHz, CDCl<sub>3</sub>)**



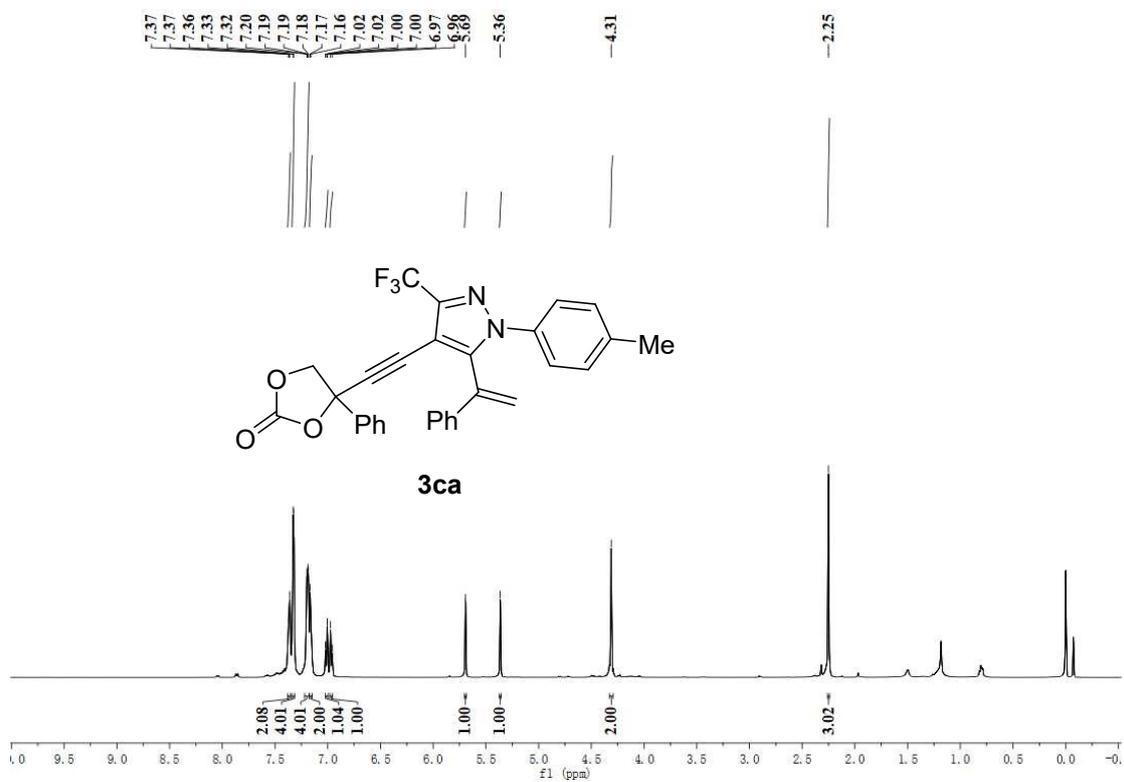
**<sup>13</sup>C{<sup>1</sup>H} NMR of 3ba (101 MHz, CDCl<sub>3</sub>)**



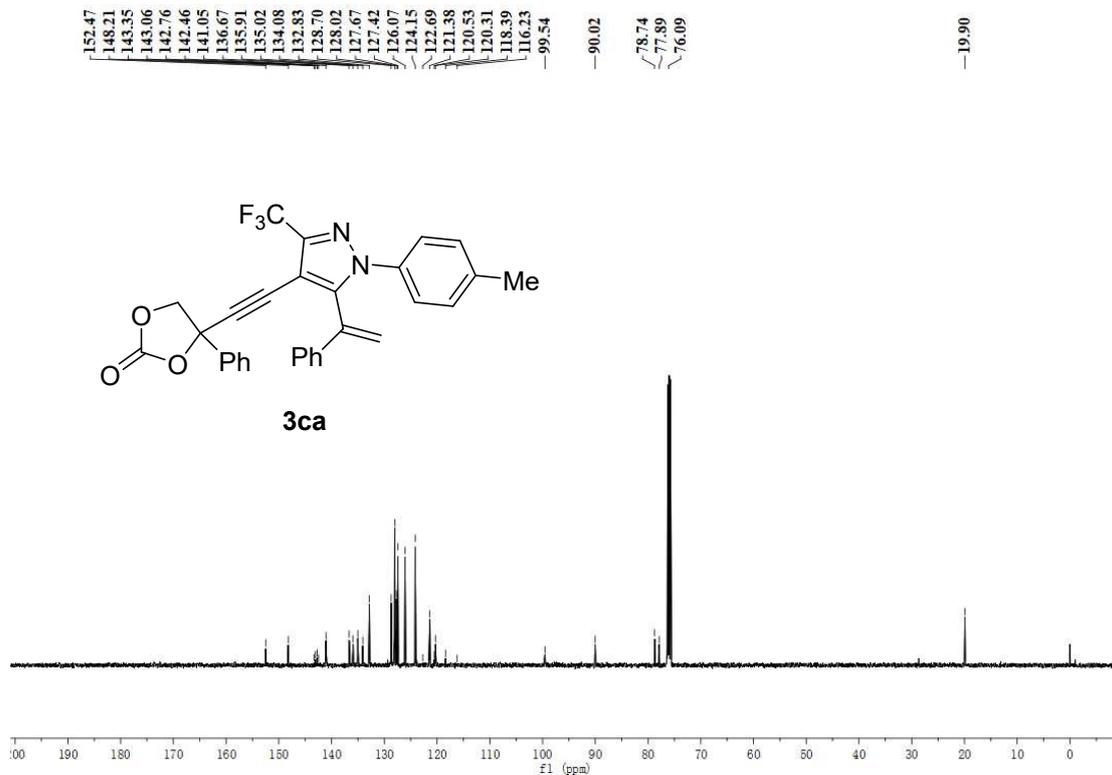
**<sup>19</sup>F NMR of 3ba (376 MHz, CDCl<sub>3</sub>)**



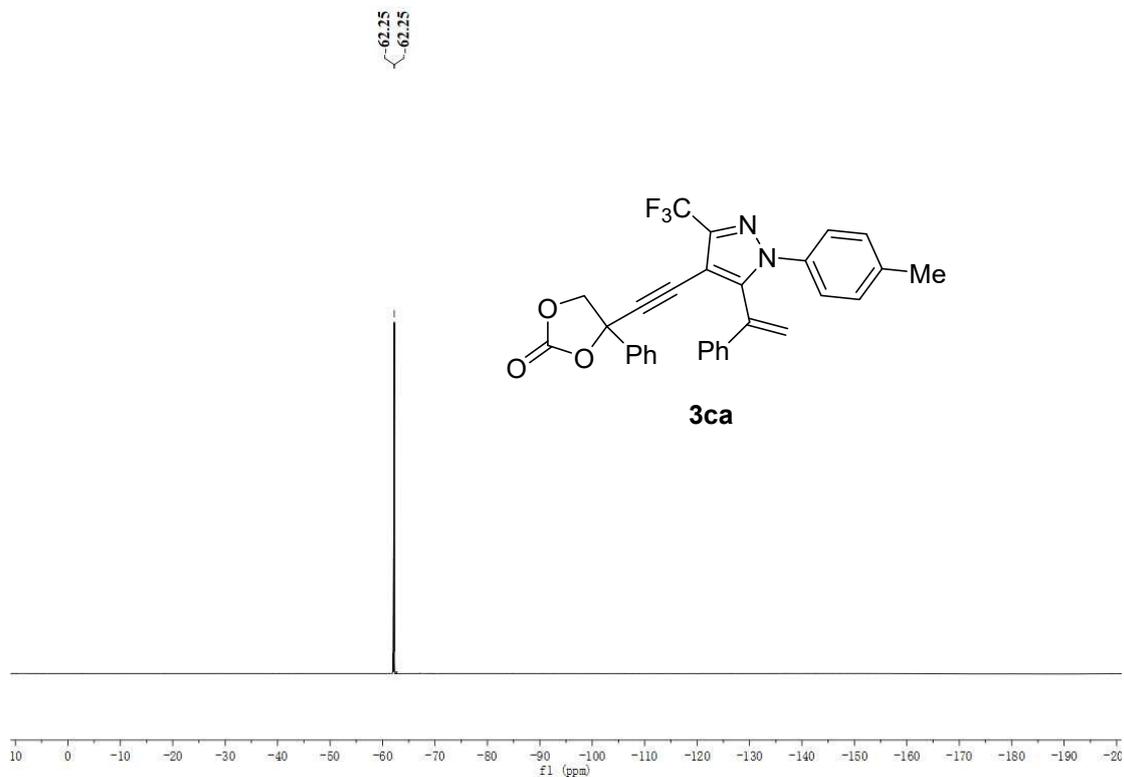
**<sup>1</sup>H NMR of 3ca (500 MHz, CDCl<sub>3</sub>)**



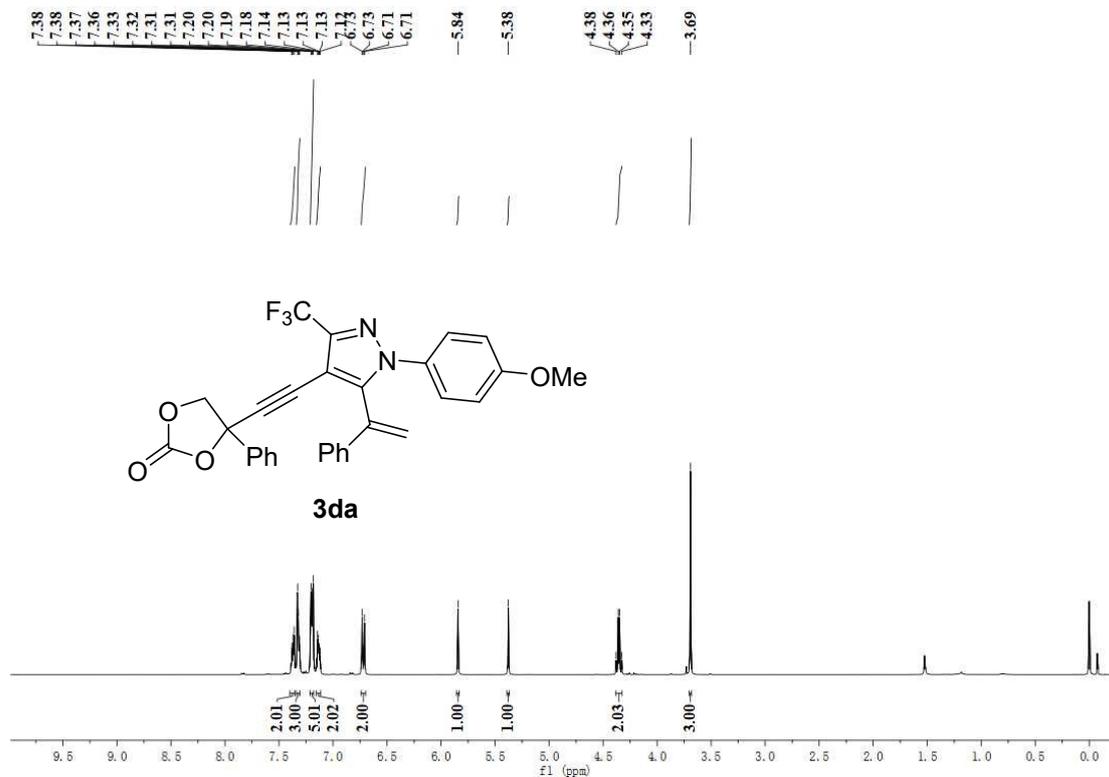
$^{13}\text{C}\{^1\text{H}\}$  NMR of 3ca (126 MHz,  $\text{CDCl}_3$ )



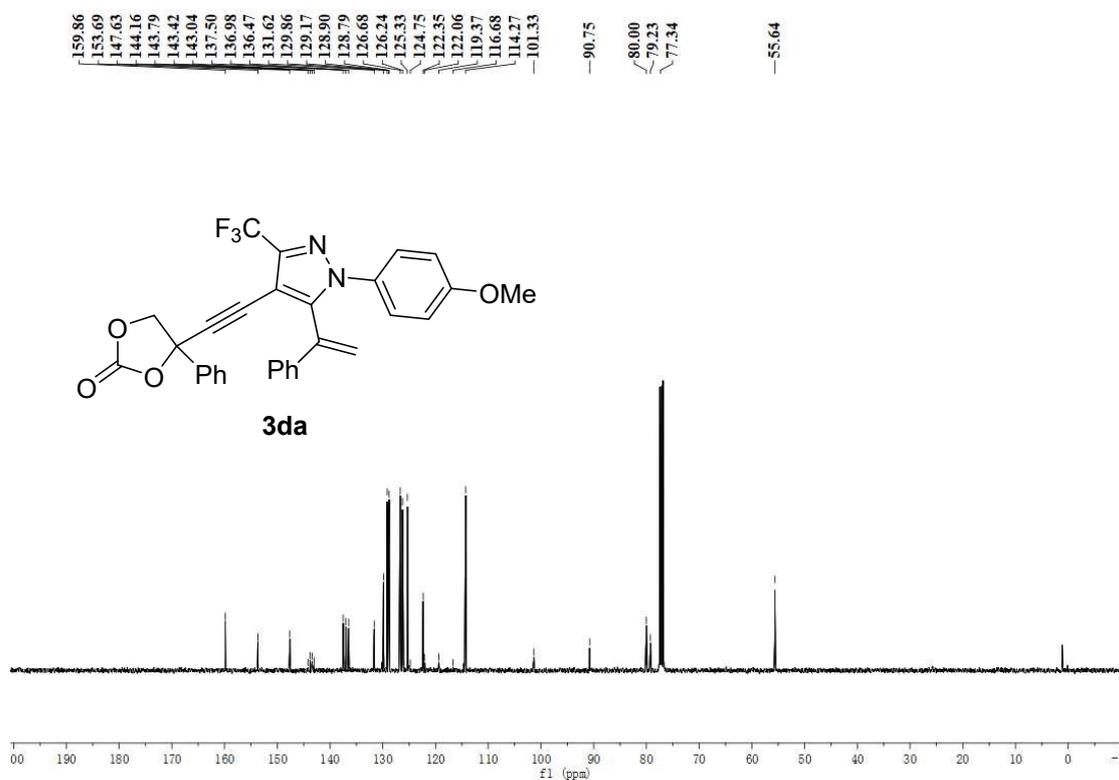
$^{19}\text{F}$  NMR of 3ca (471 MHz,  $\text{CDCl}_3$ )



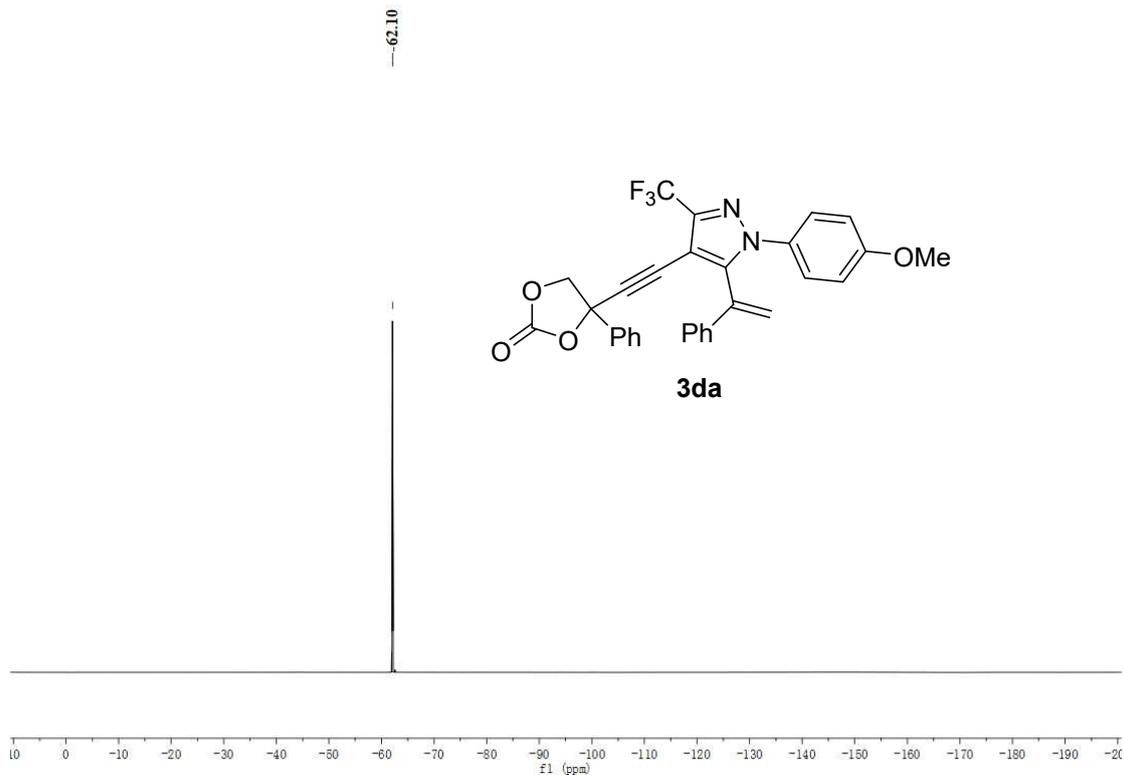
**<sup>1</sup>H NMR of 3da (400 MHz, CDCl<sub>3</sub>)**



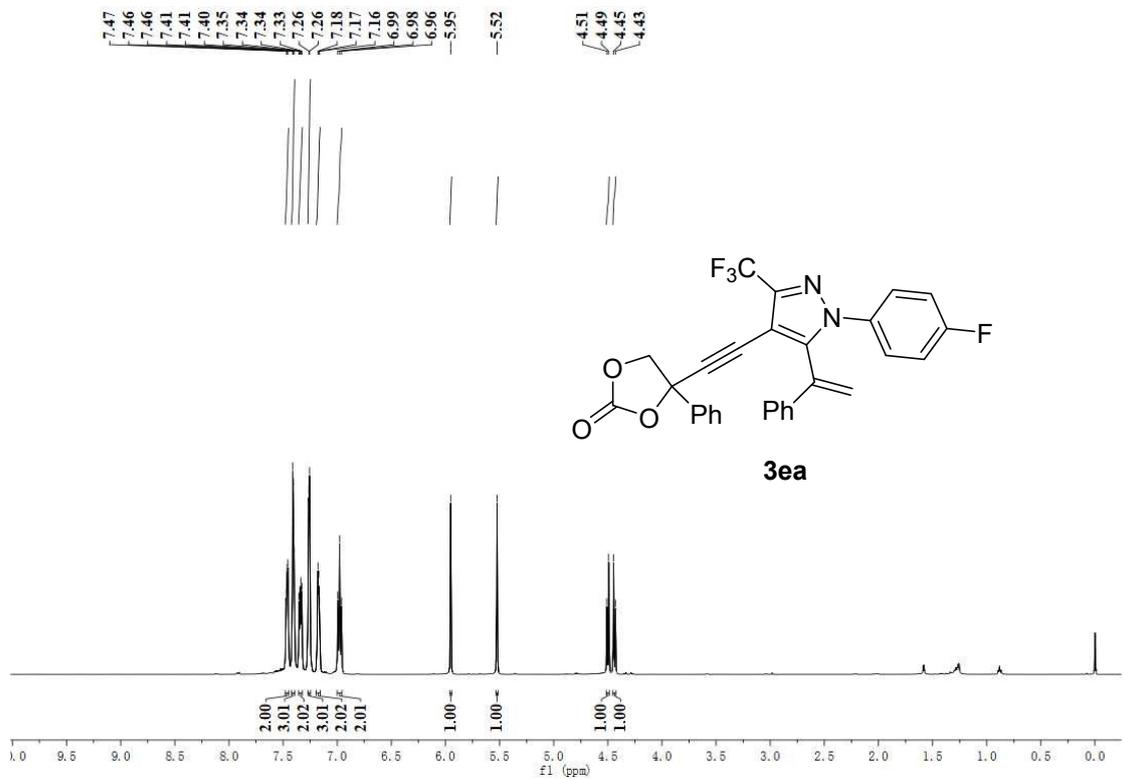
**<sup>13</sup>C{<sup>1</sup>H} NMR of 3da (101 MHz, CDCl<sub>3</sub>)**



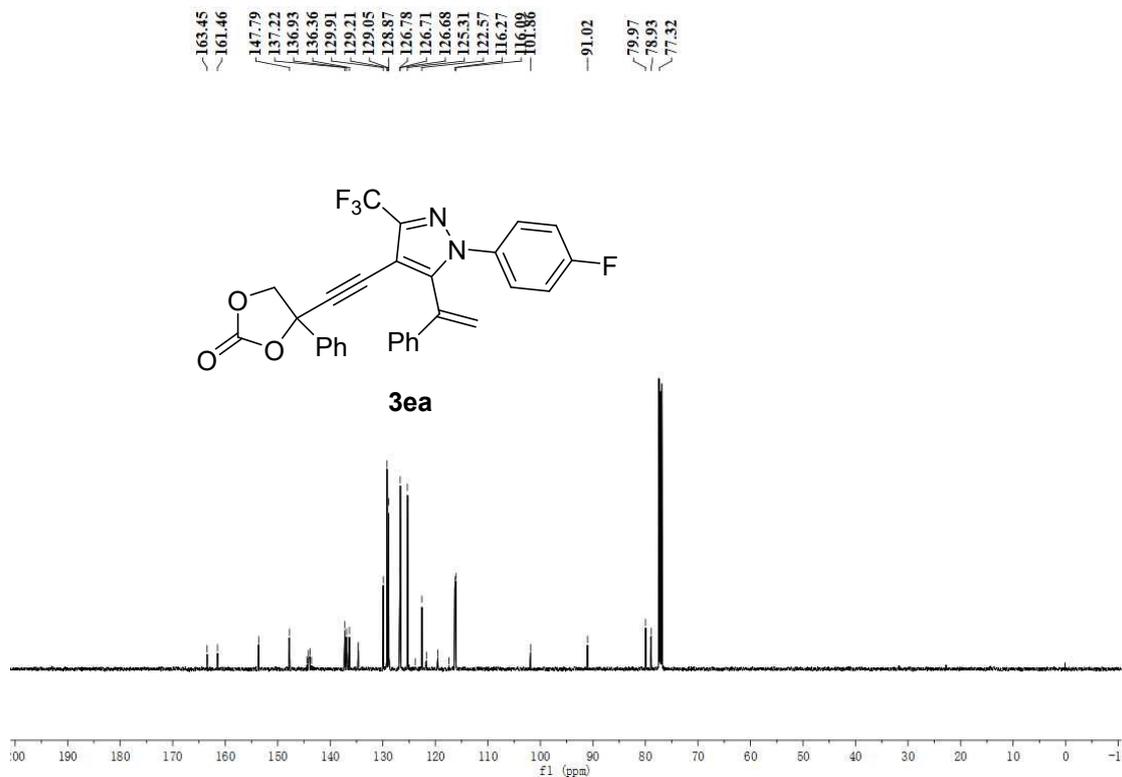
**<sup>19</sup>F NMR of 3da (376 MHz, CDCl<sub>3</sub>)**



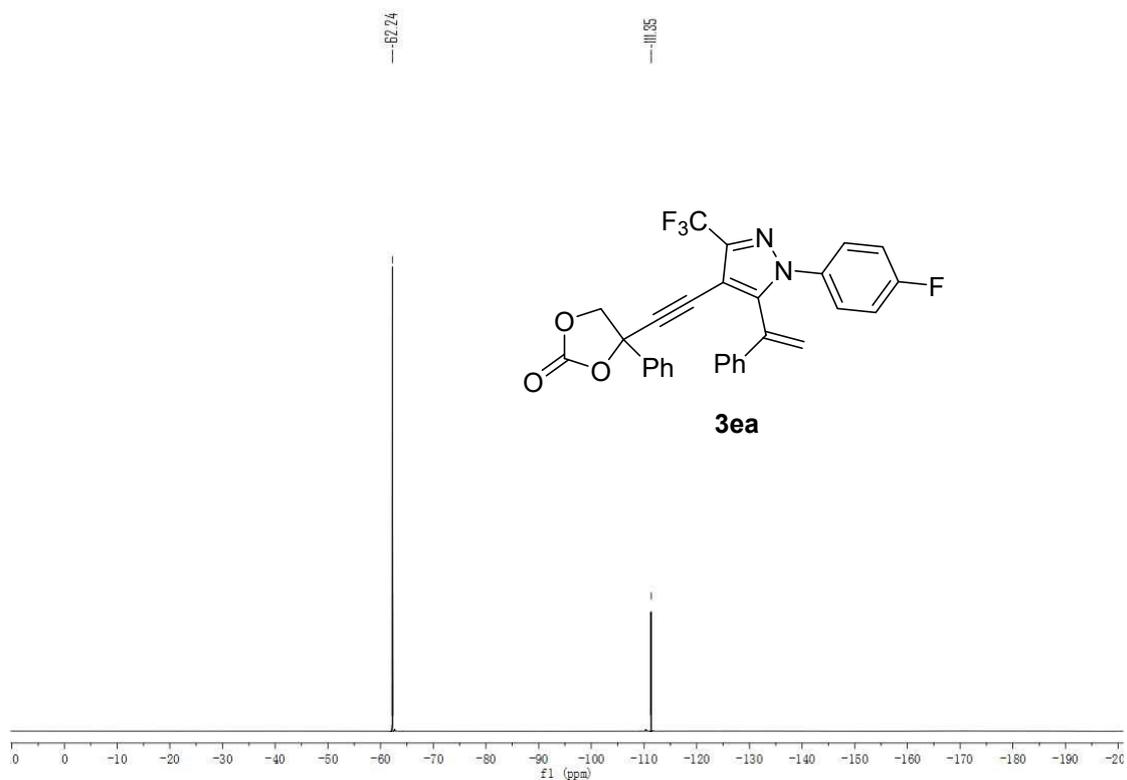
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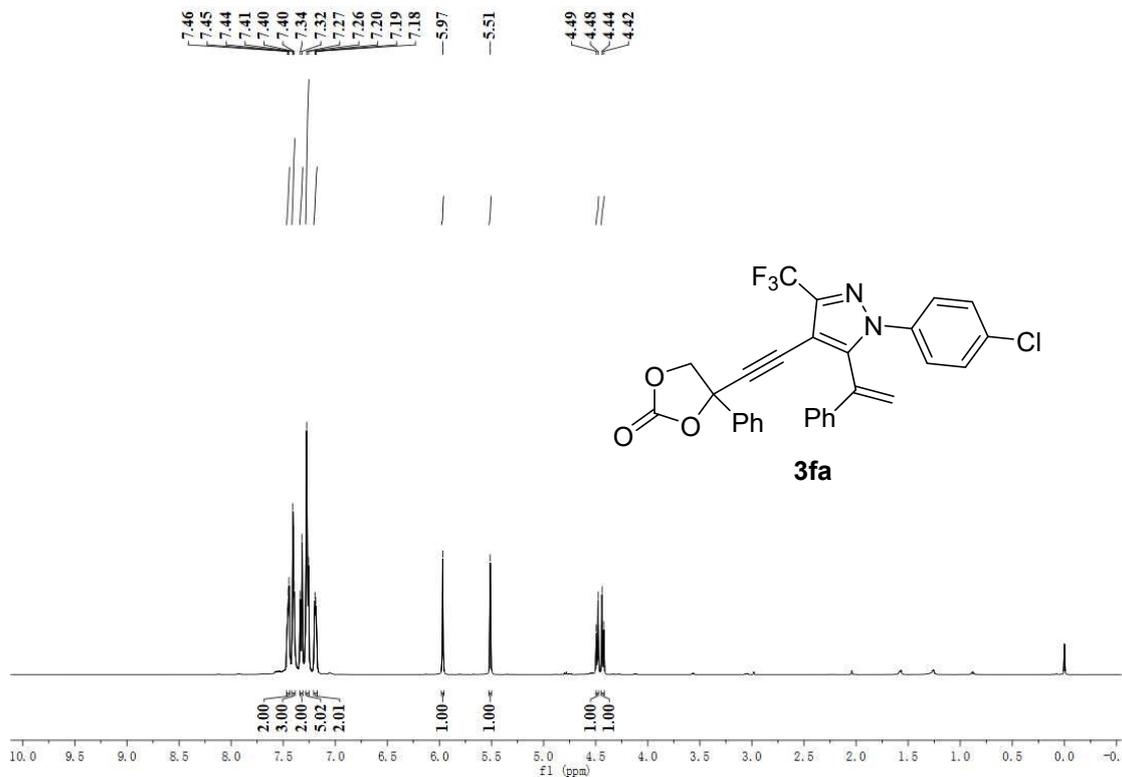
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 3ea (126 MHz,  $\text{CDCl}_3$ )**



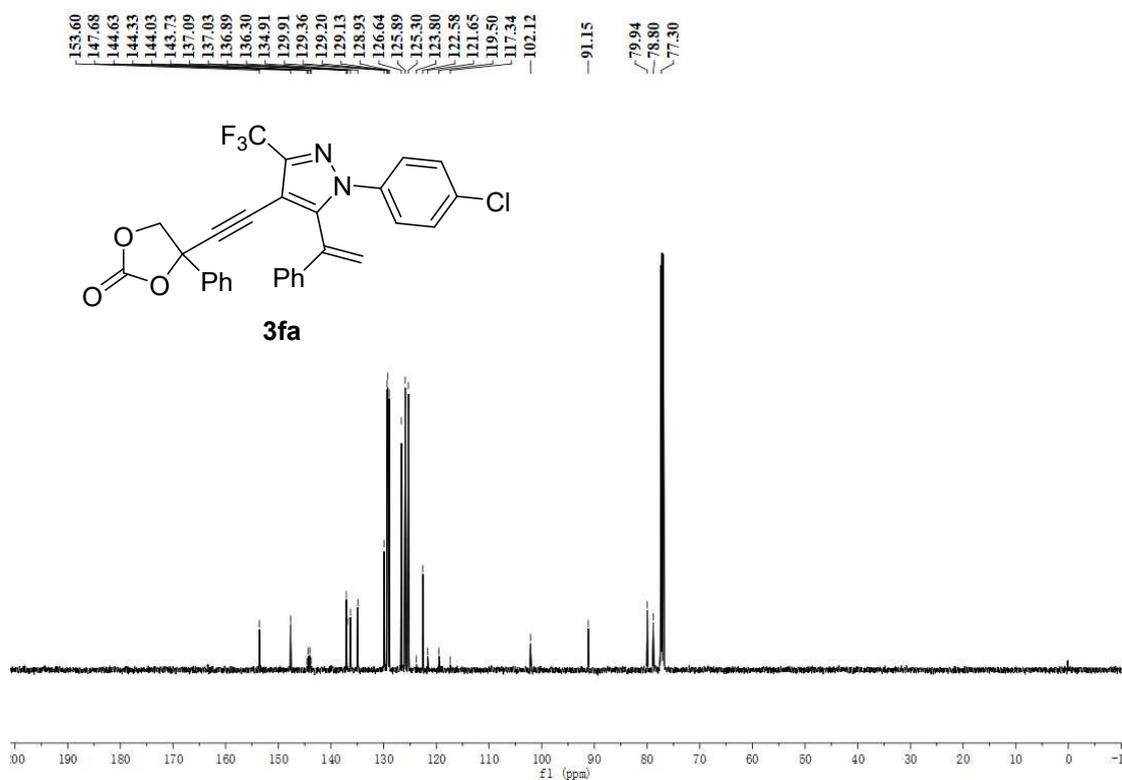
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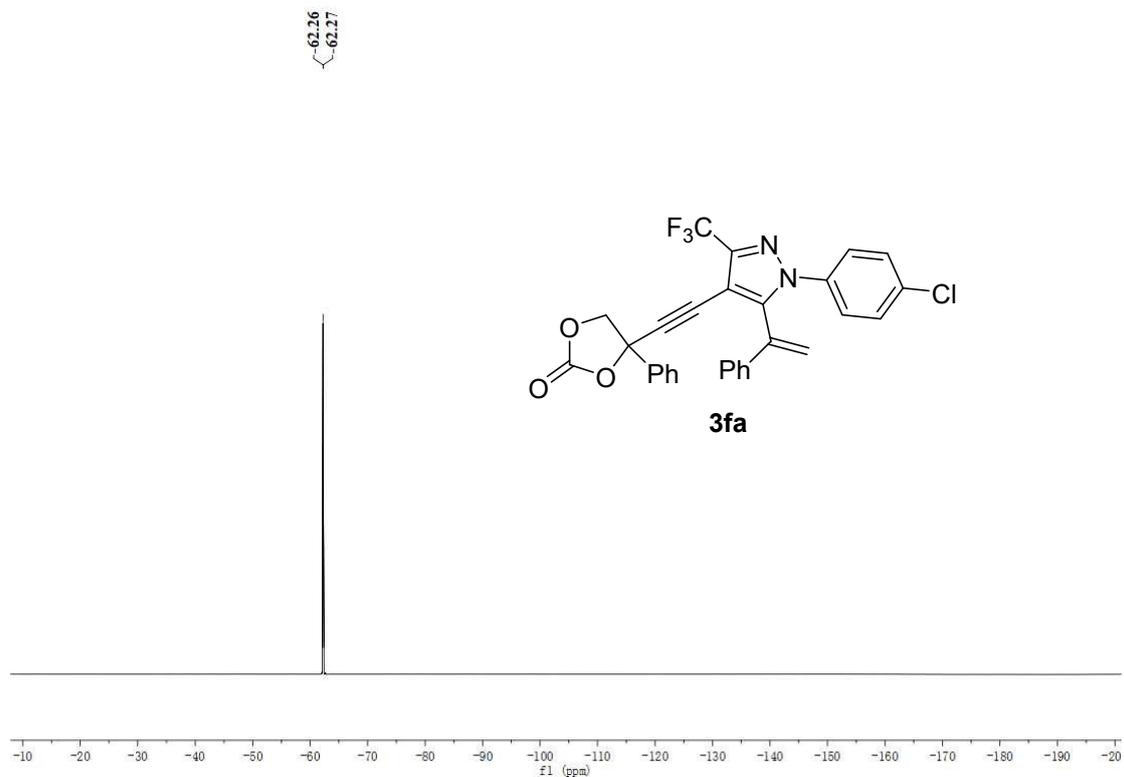
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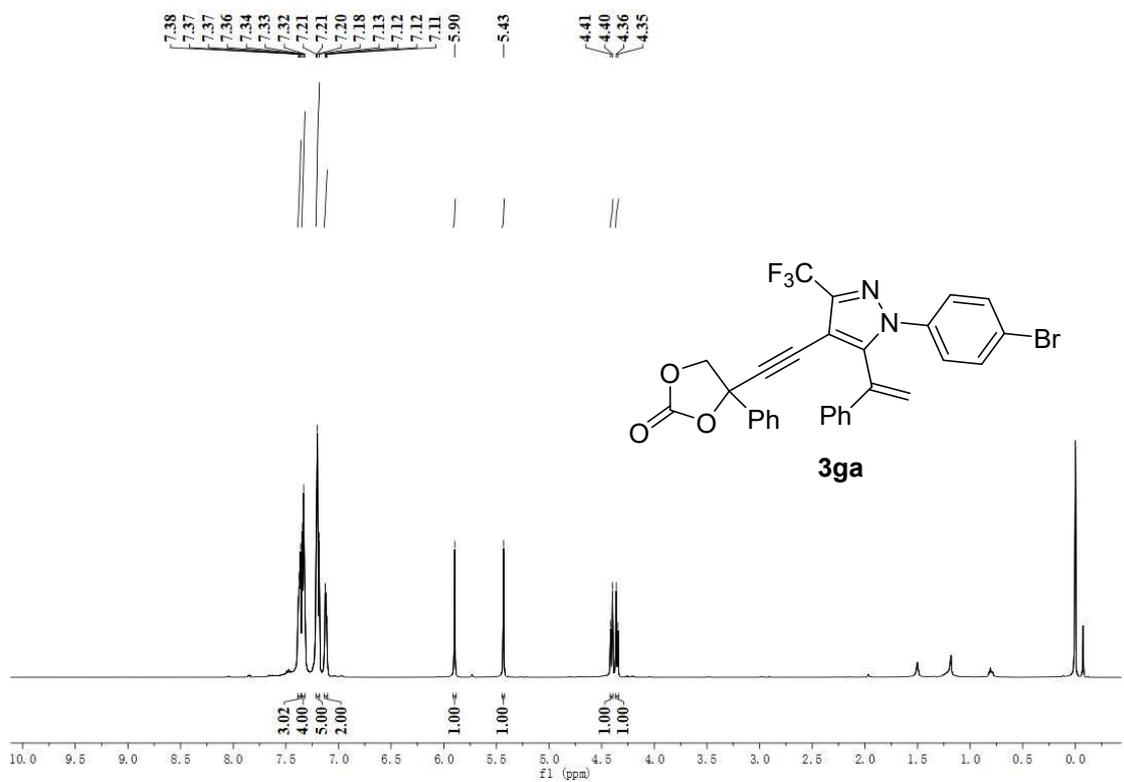
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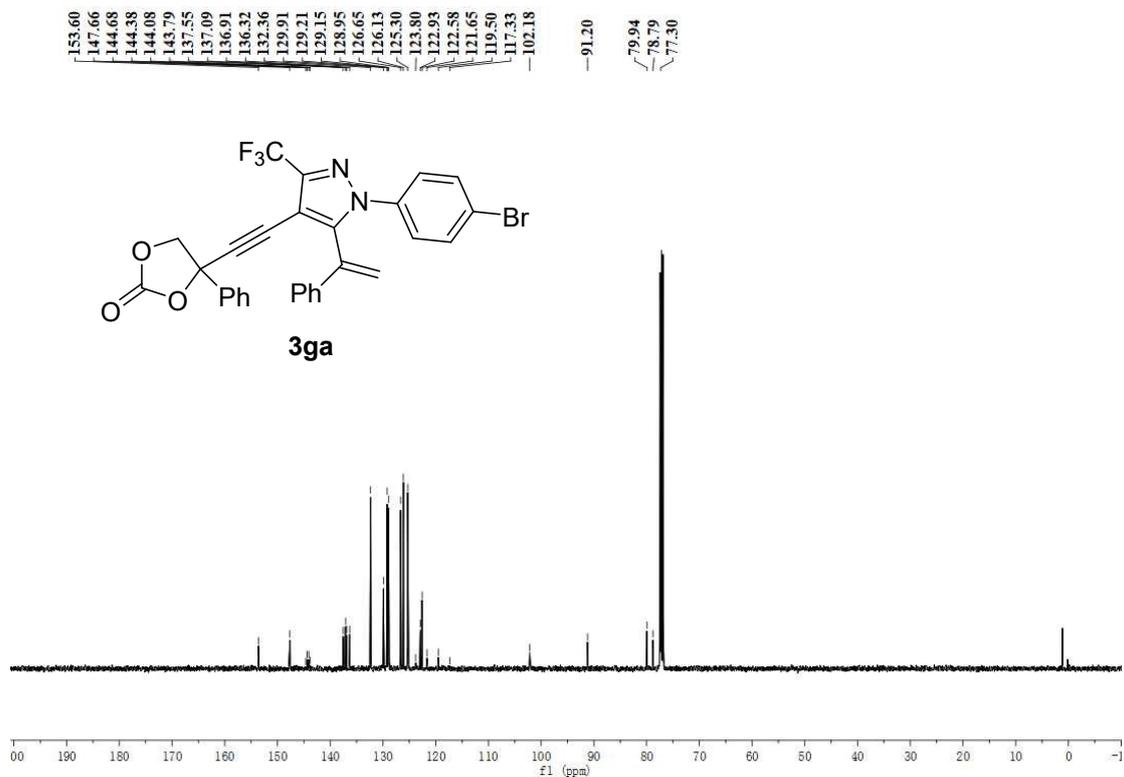
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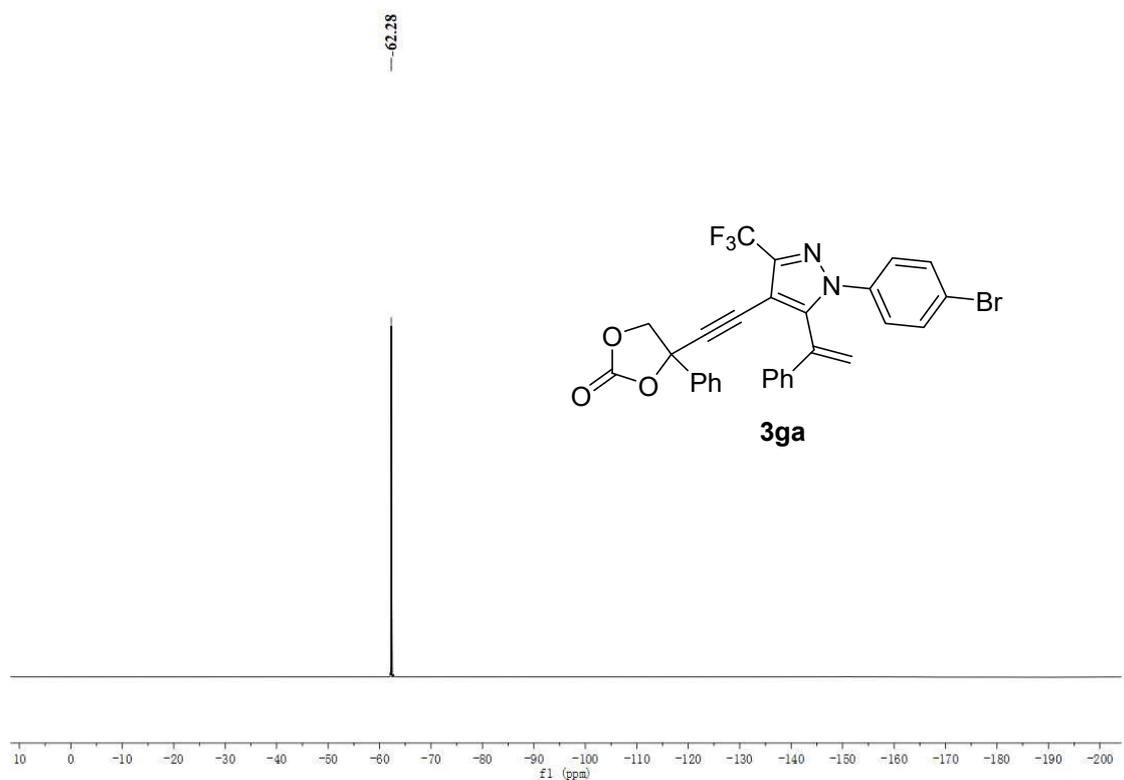
**<sup>1</sup>H NMR of 3ga (500 MHz, CDCl<sub>3</sub>)**



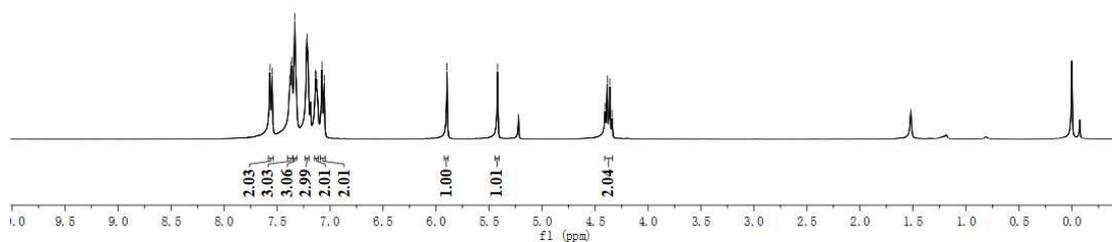
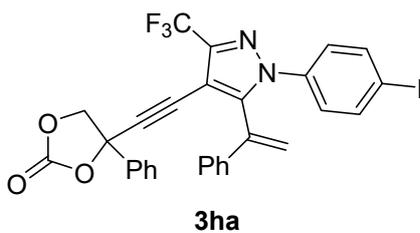
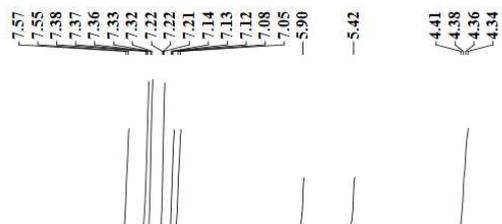
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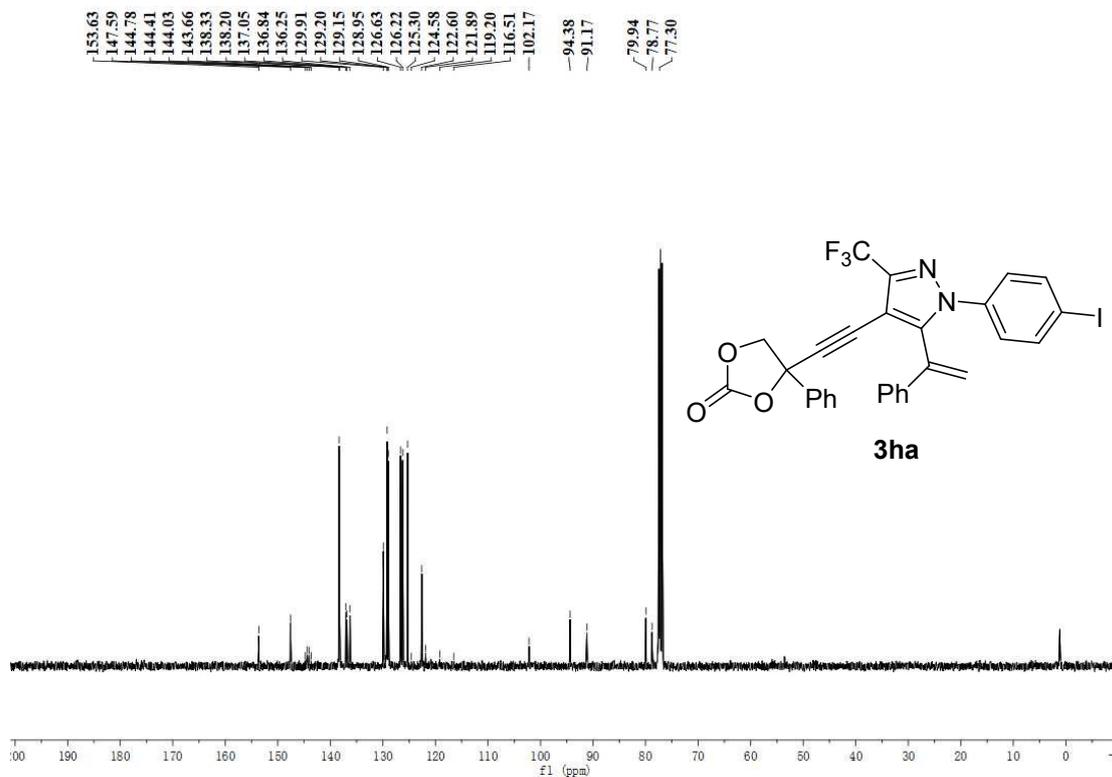
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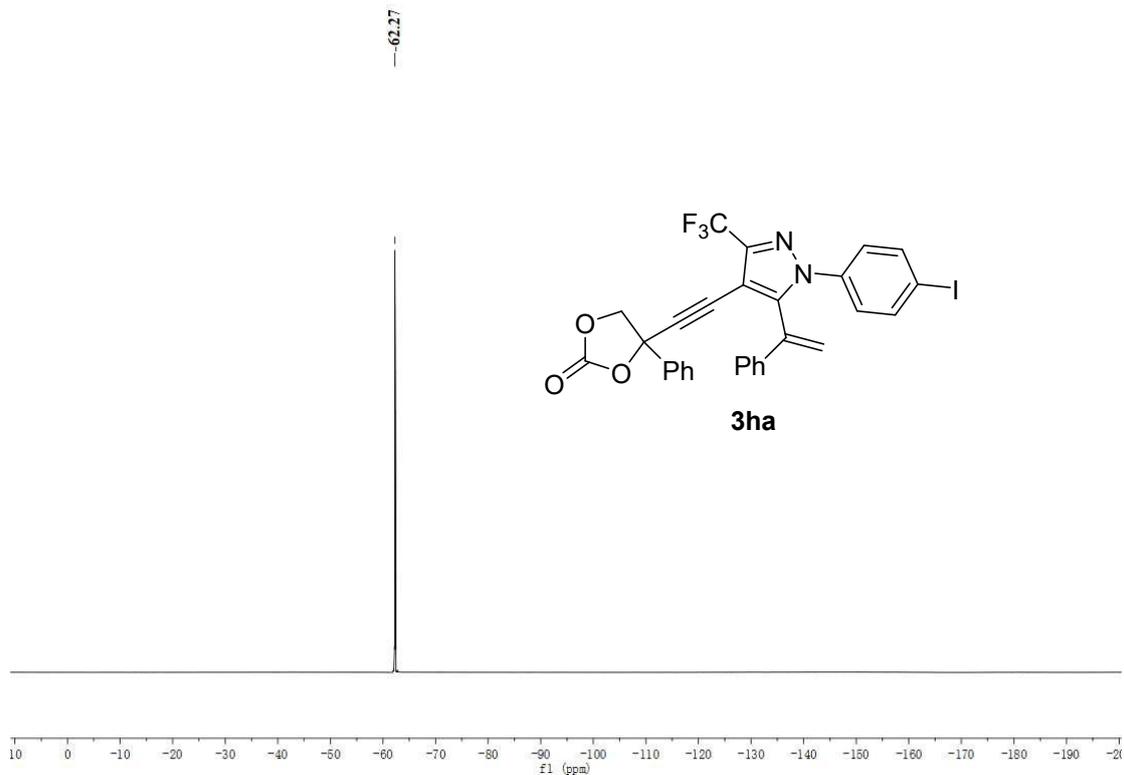
**$^1\text{H}$  NMR of 3ha (400 MHz,  $\text{CDCl}_3$ )**



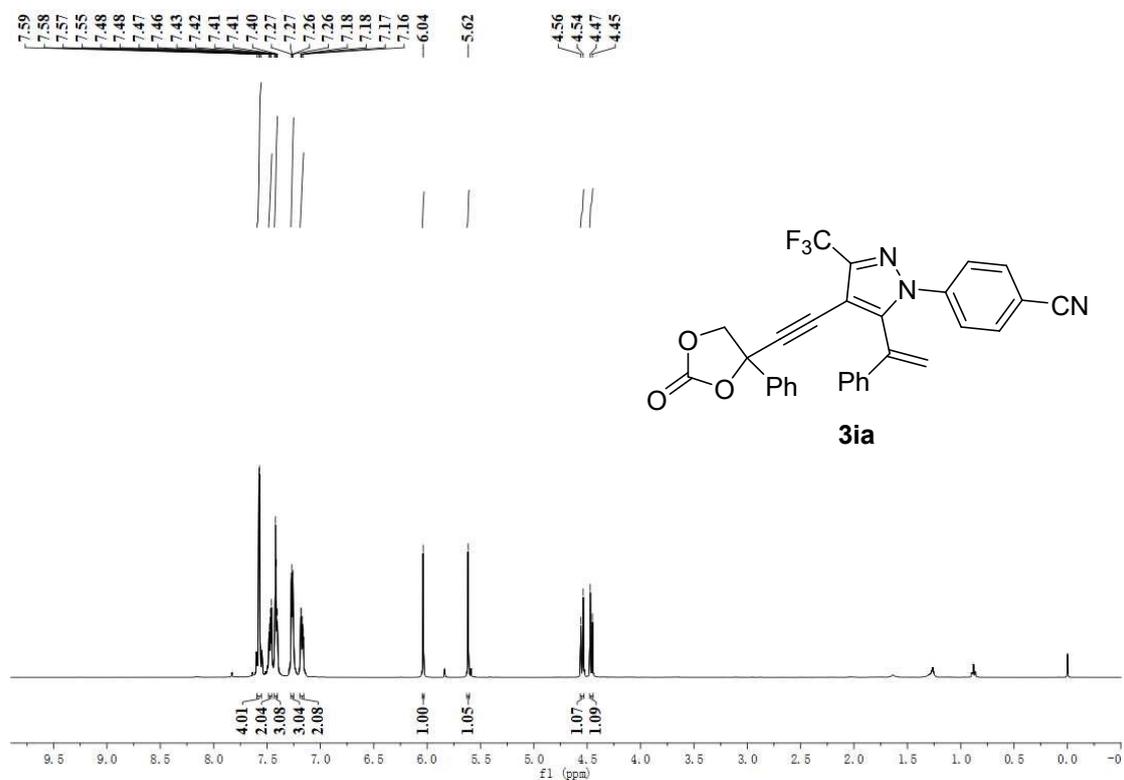
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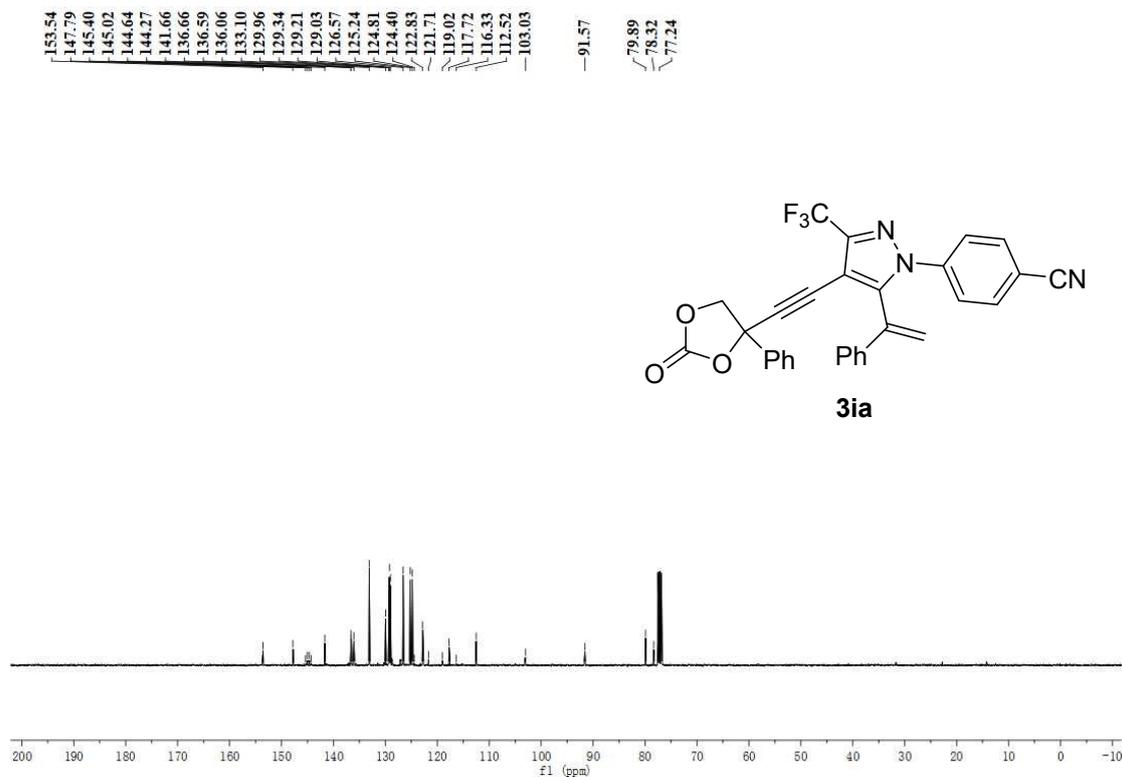
**<sup>19</sup>F NMR of 3ha (376 MHz, CDCl<sub>3</sub>)**



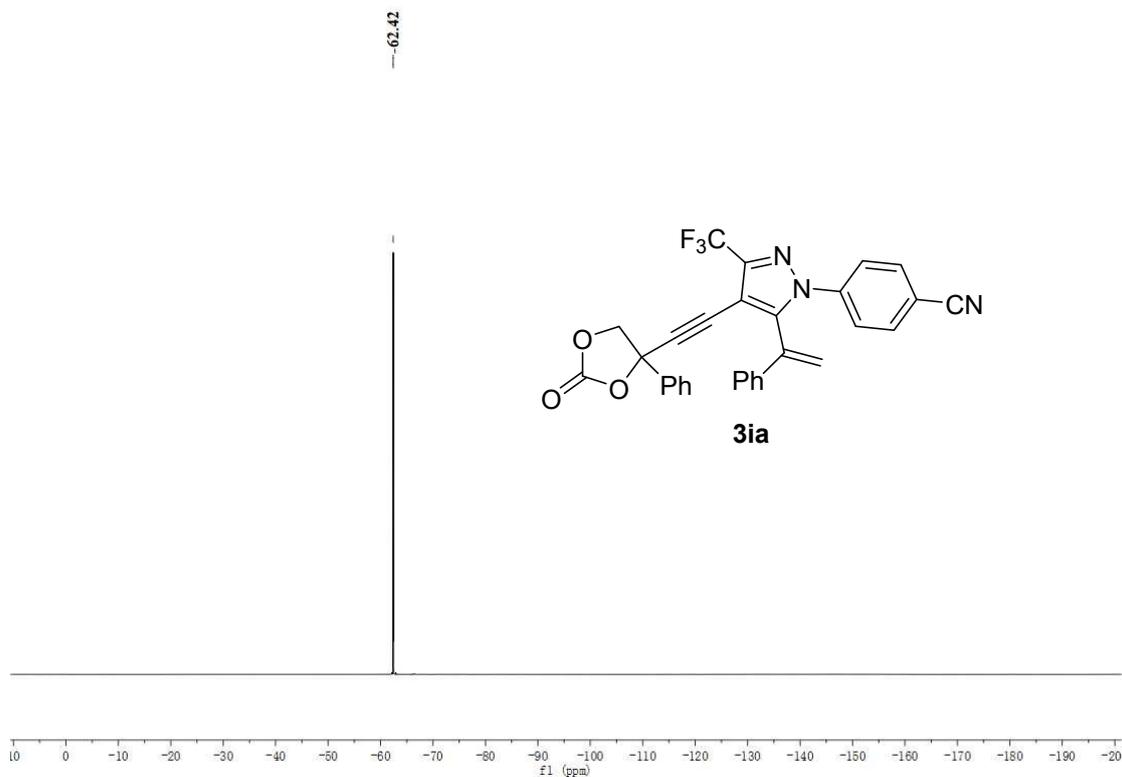
**<sup>1</sup>H NMR of 3ia (400 MHz, CDCl<sub>3</sub>)**



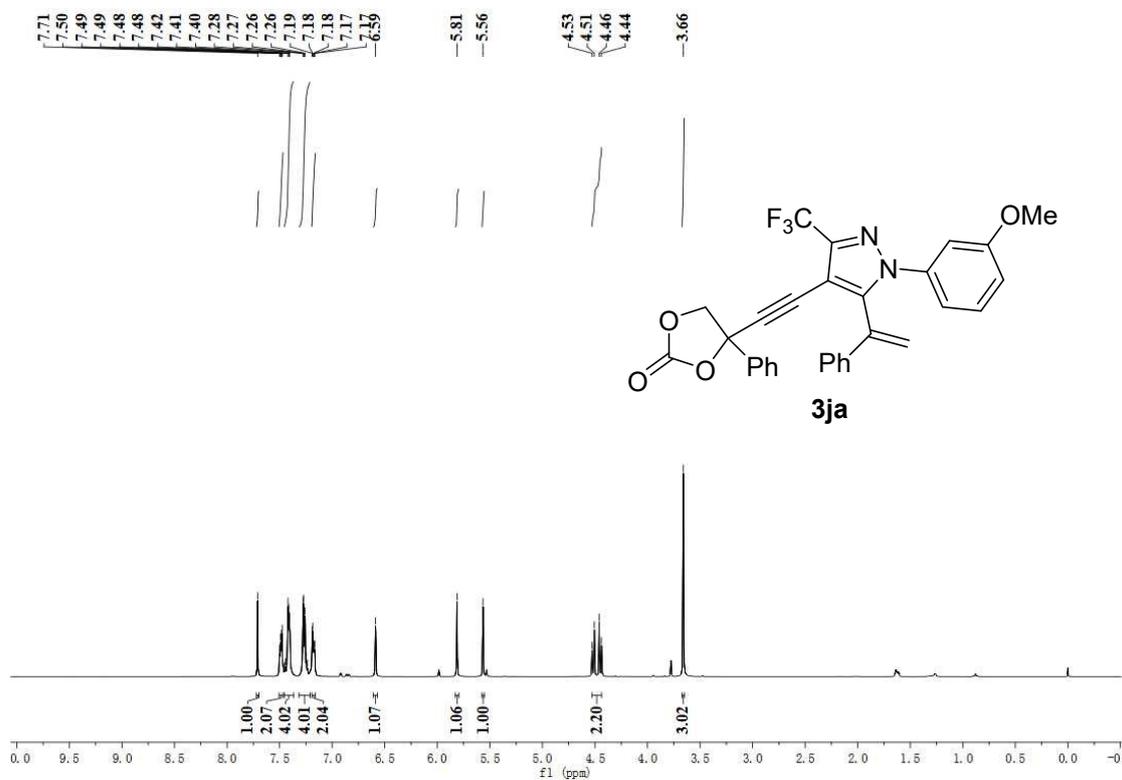
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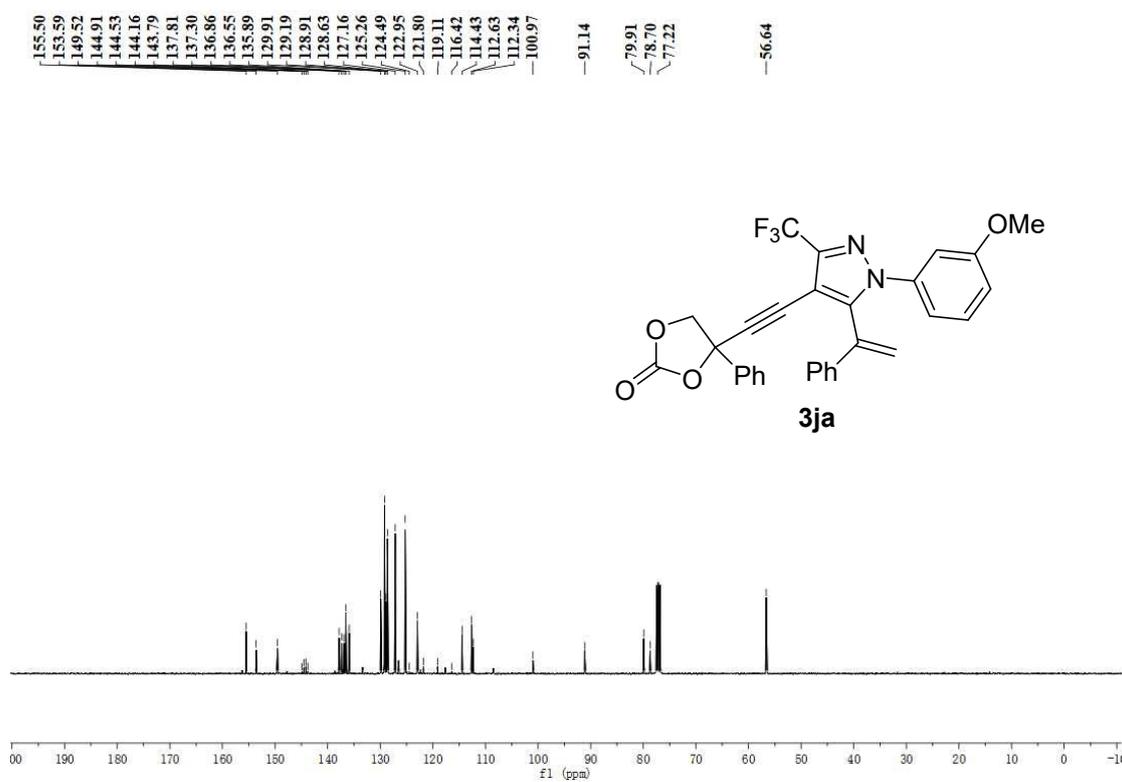
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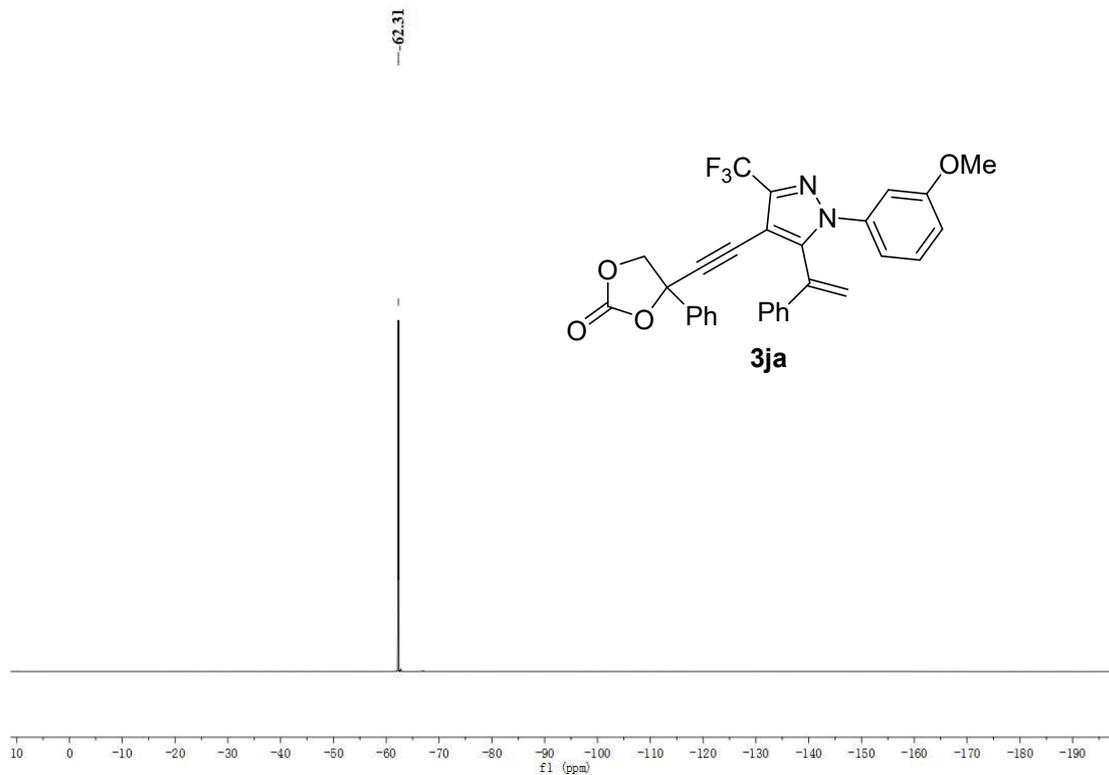
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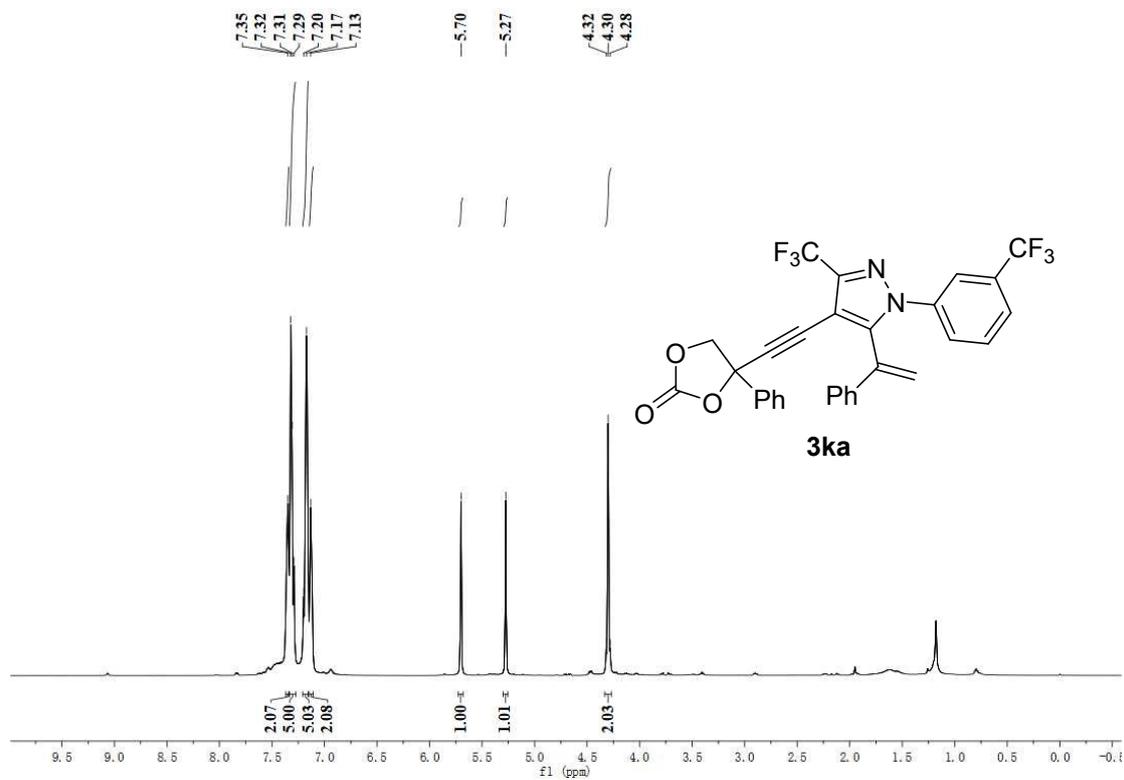
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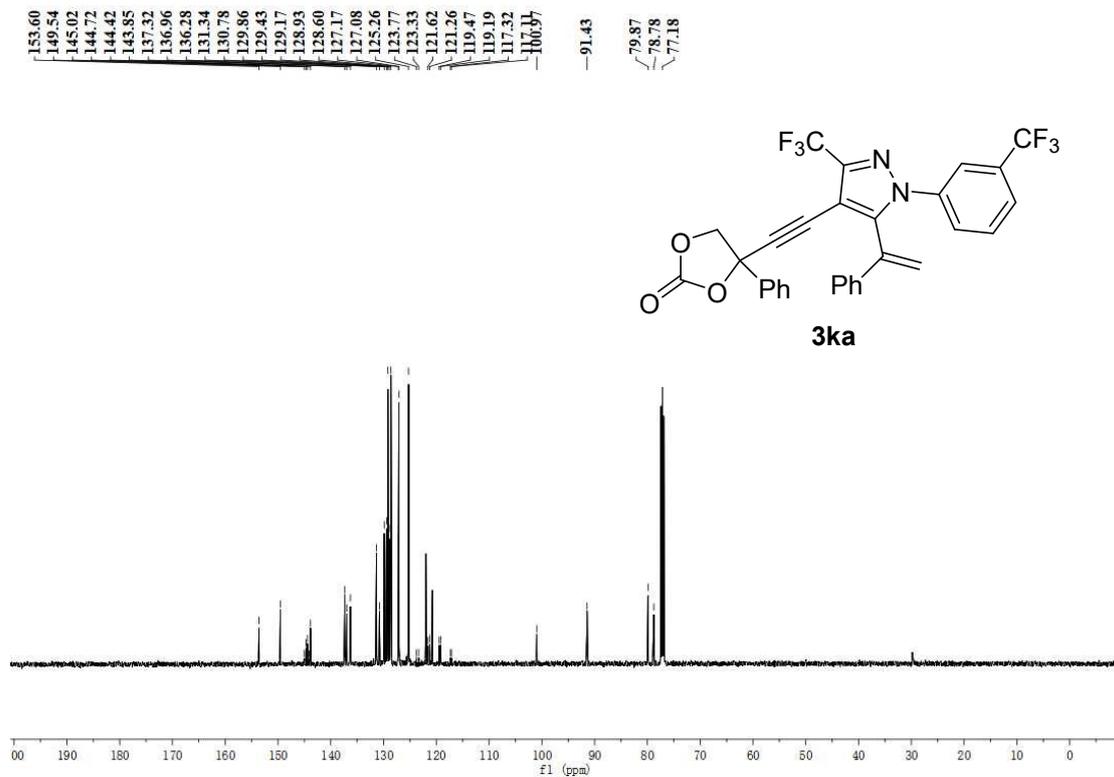
**<sup>19</sup>F NMR of 3ja (376 MHz, CDCl<sub>3</sub>)**



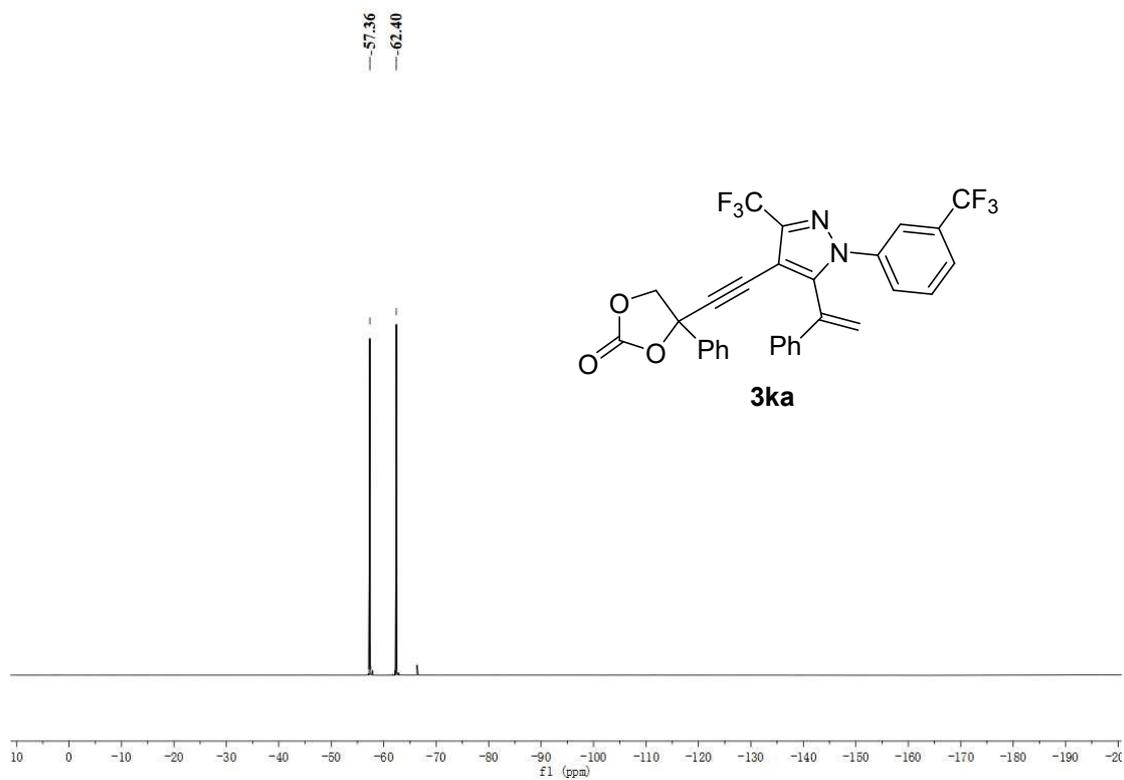
**<sup>1</sup>H NMR of 3ka (500 MHz, CDCl<sub>3</sub>)**



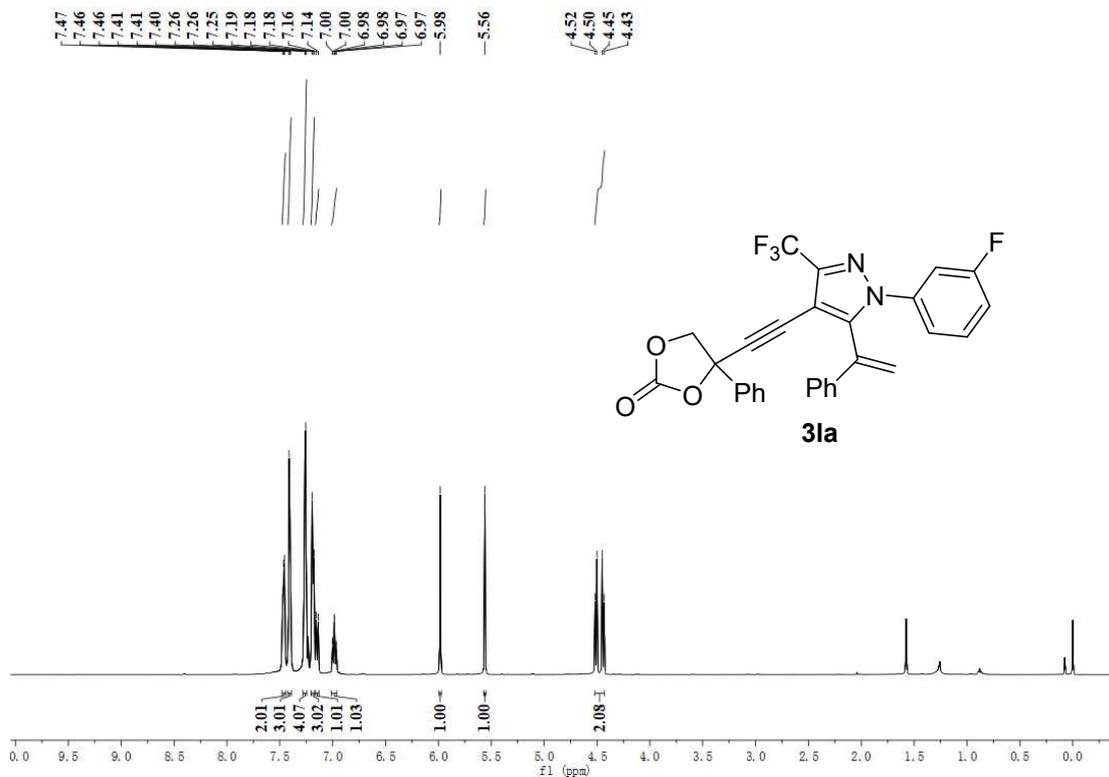
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 3ka (126 MHz,  $\text{CDCl}_3$ )**



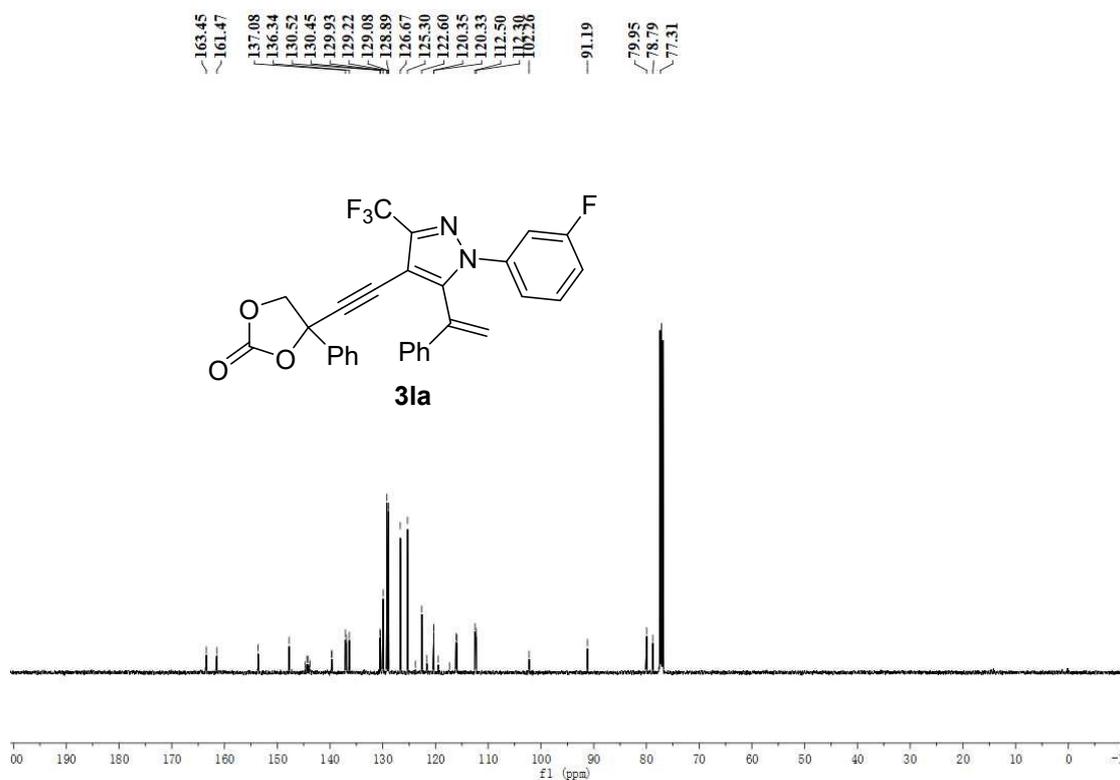
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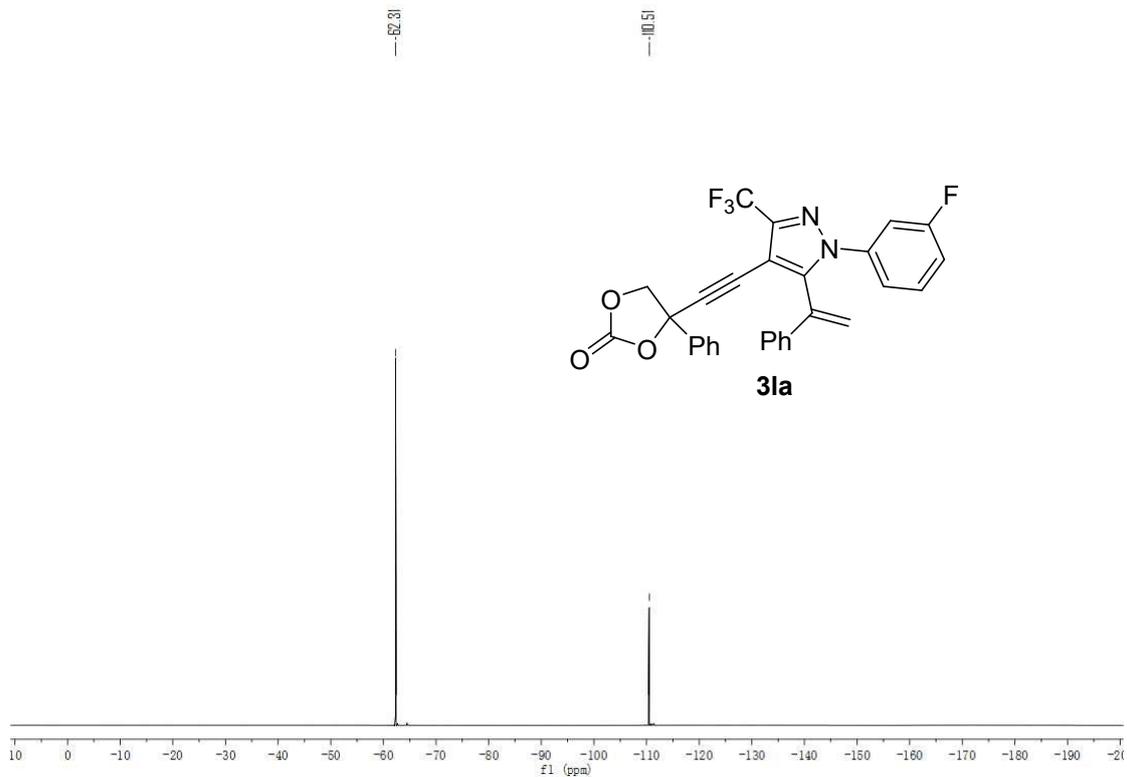
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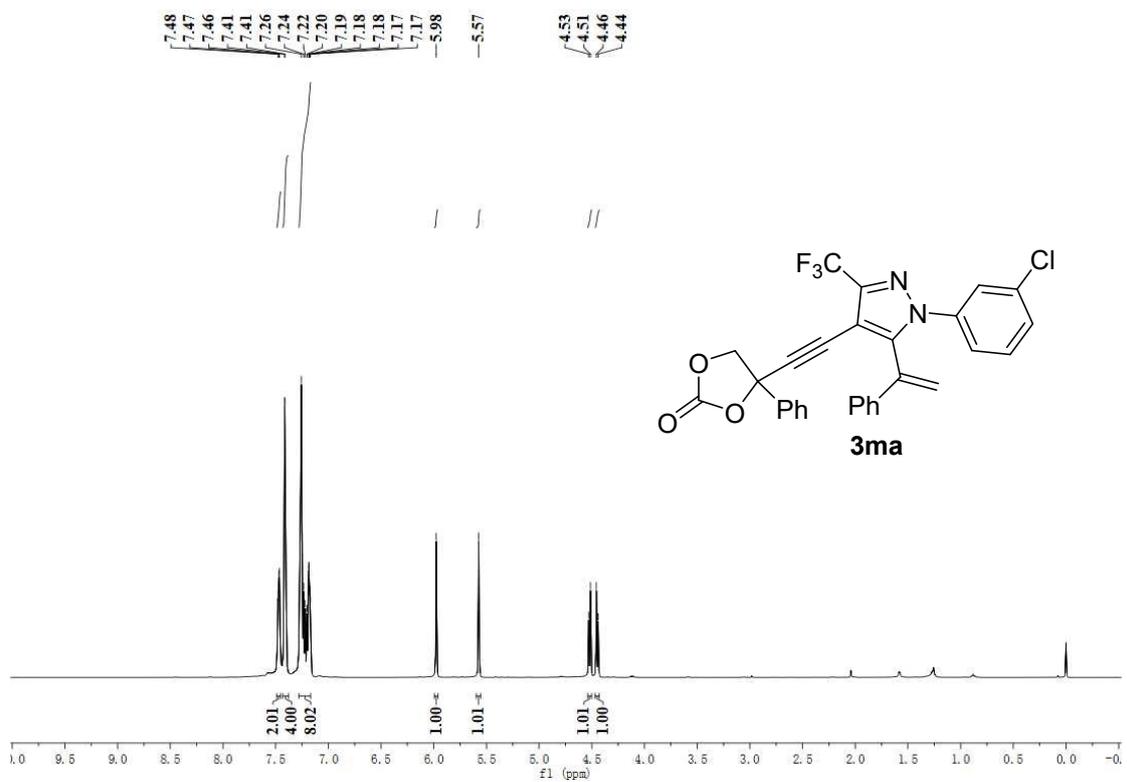
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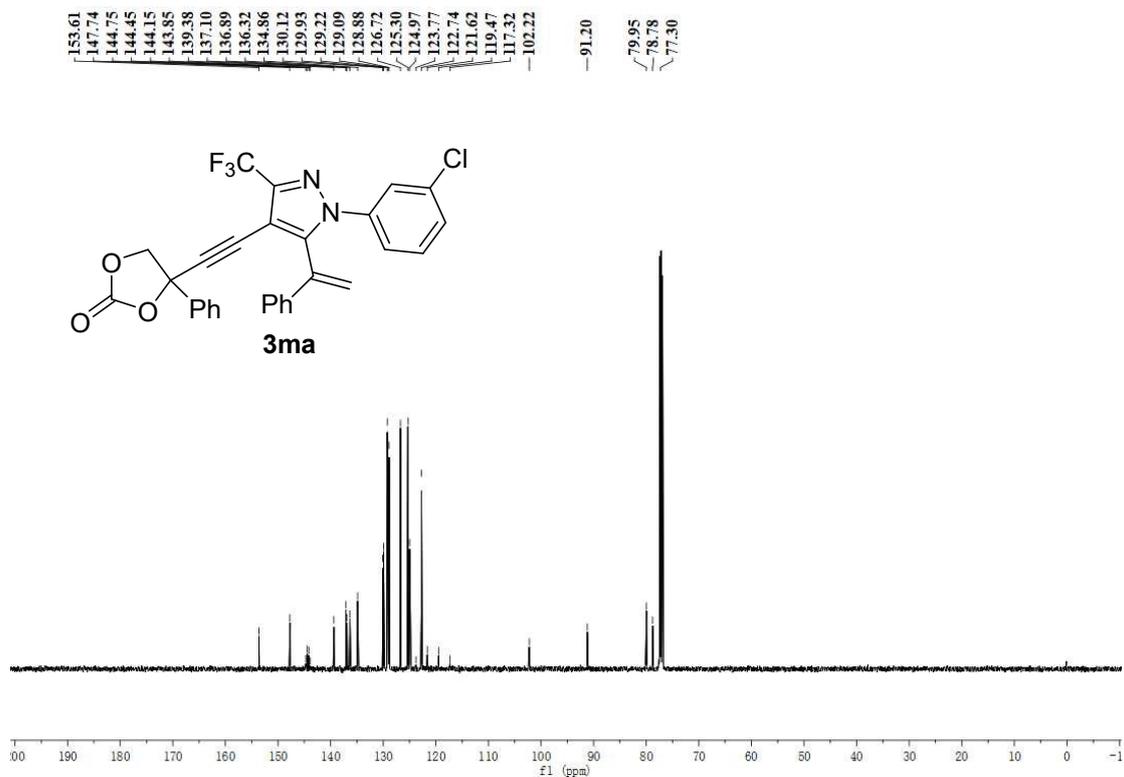
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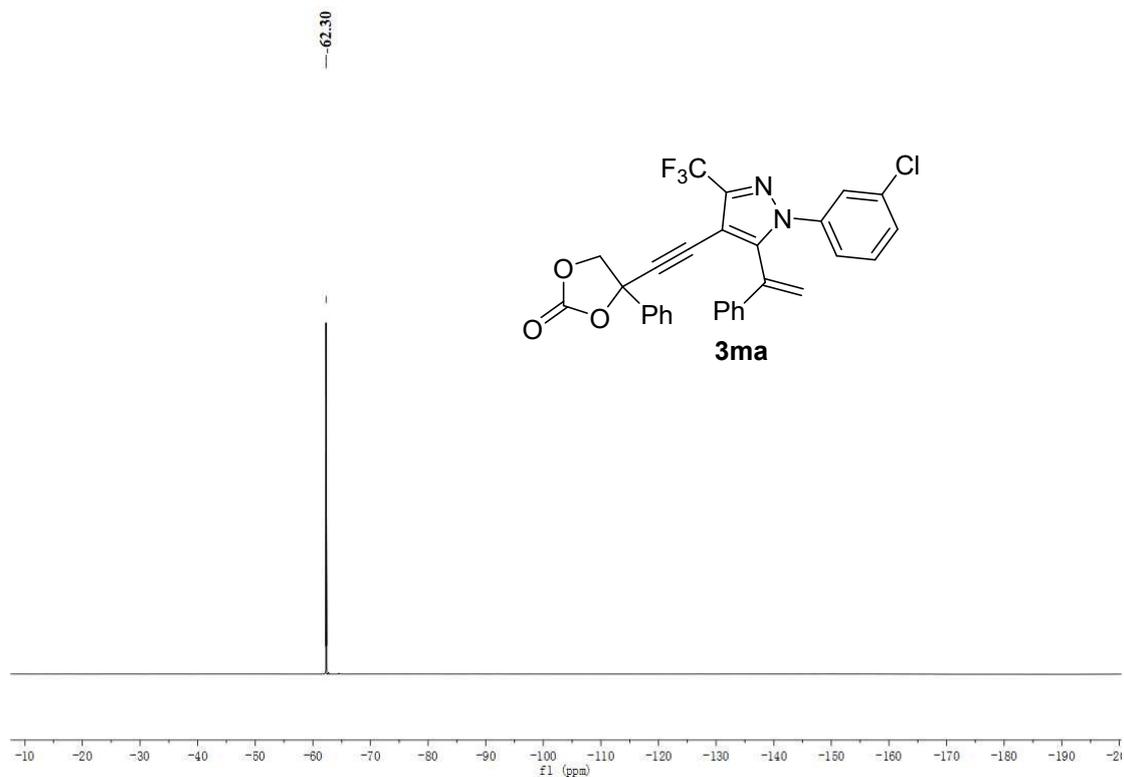
**<sup>1</sup>H NMR of 3ma (500 MHz, CDCl<sub>3</sub>)**



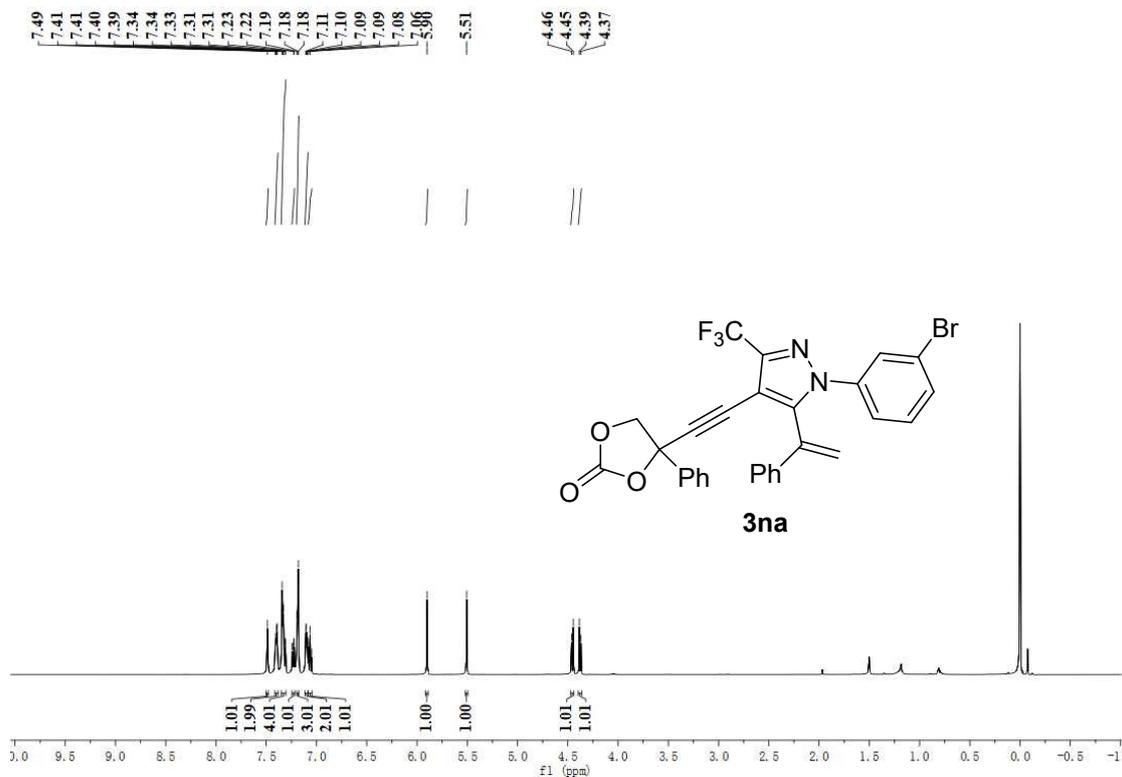
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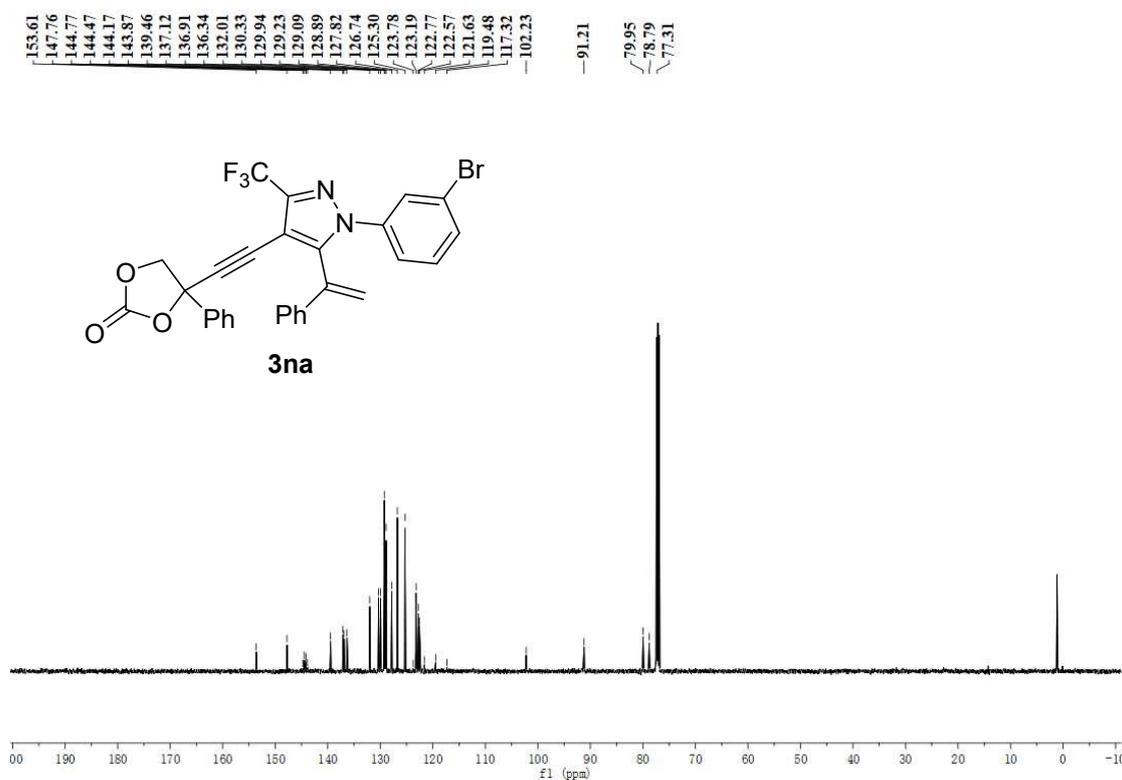
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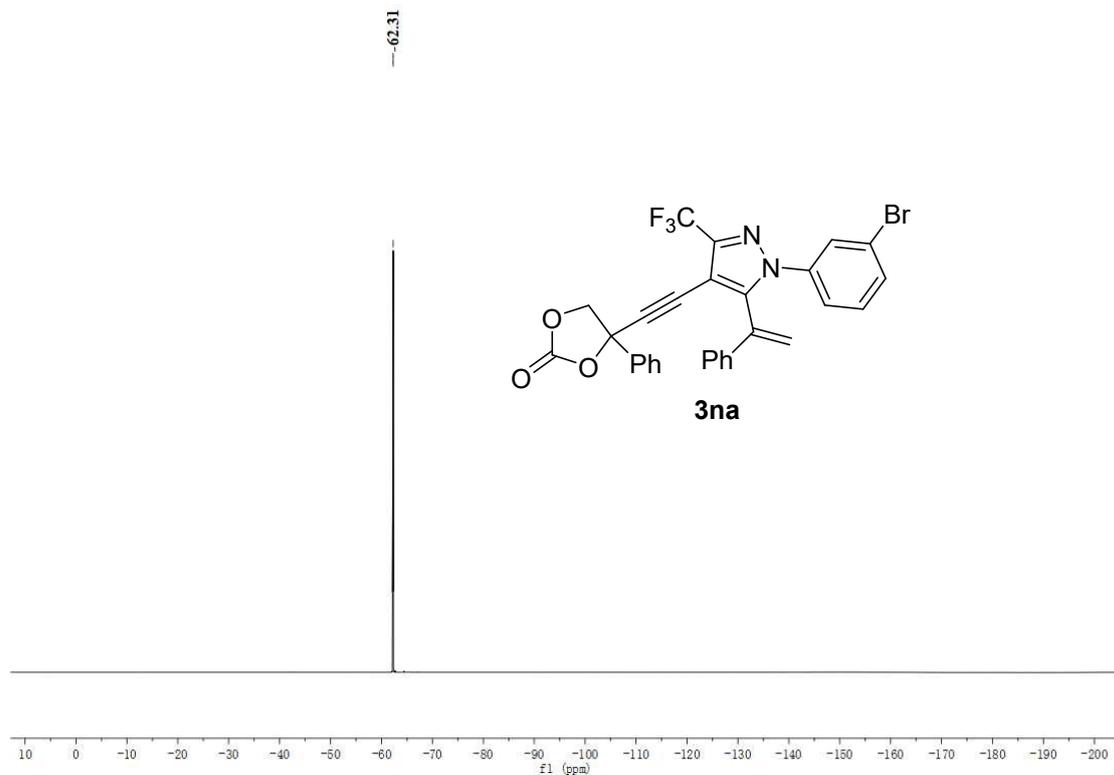
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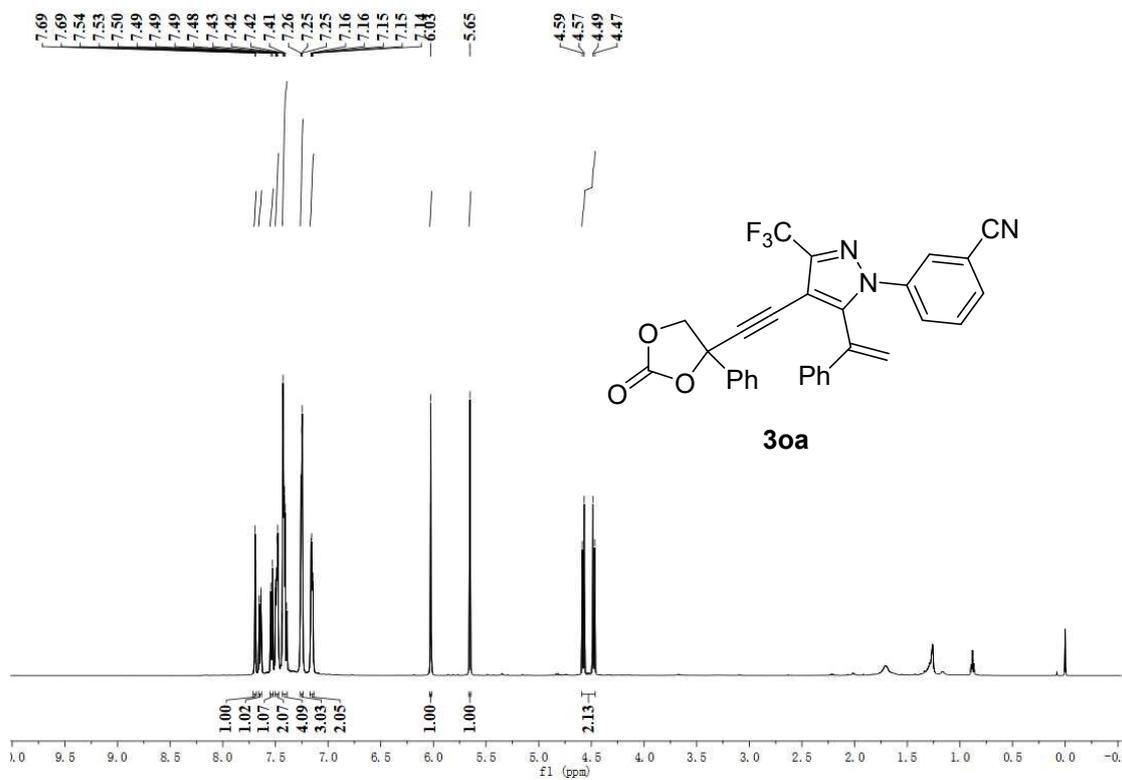
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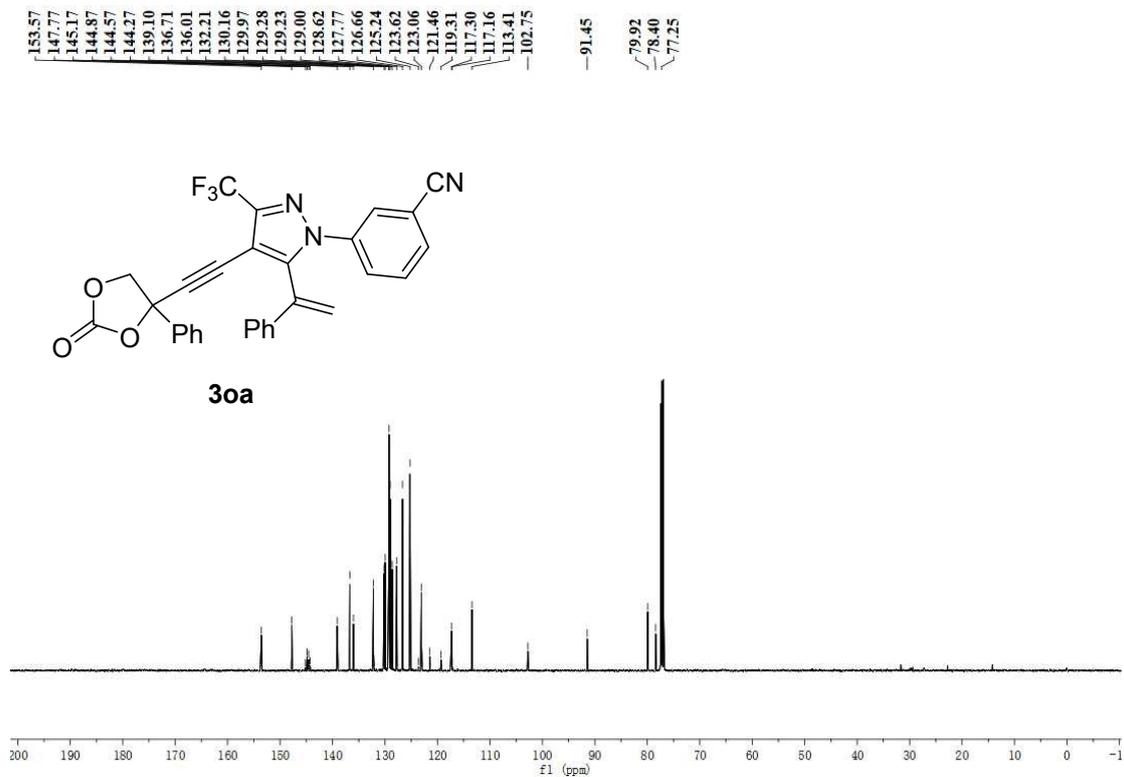
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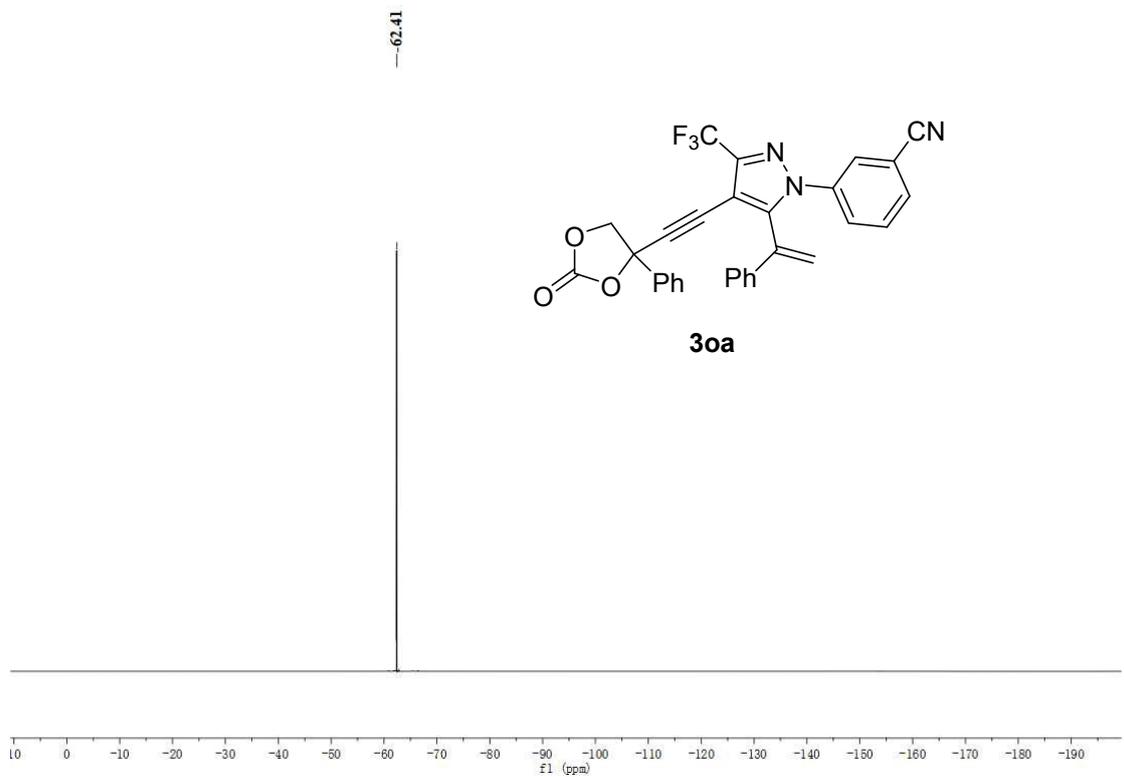
**<sup>1</sup>H NMR of 3oa (500 MHz, CDCl<sub>3</sub>)**



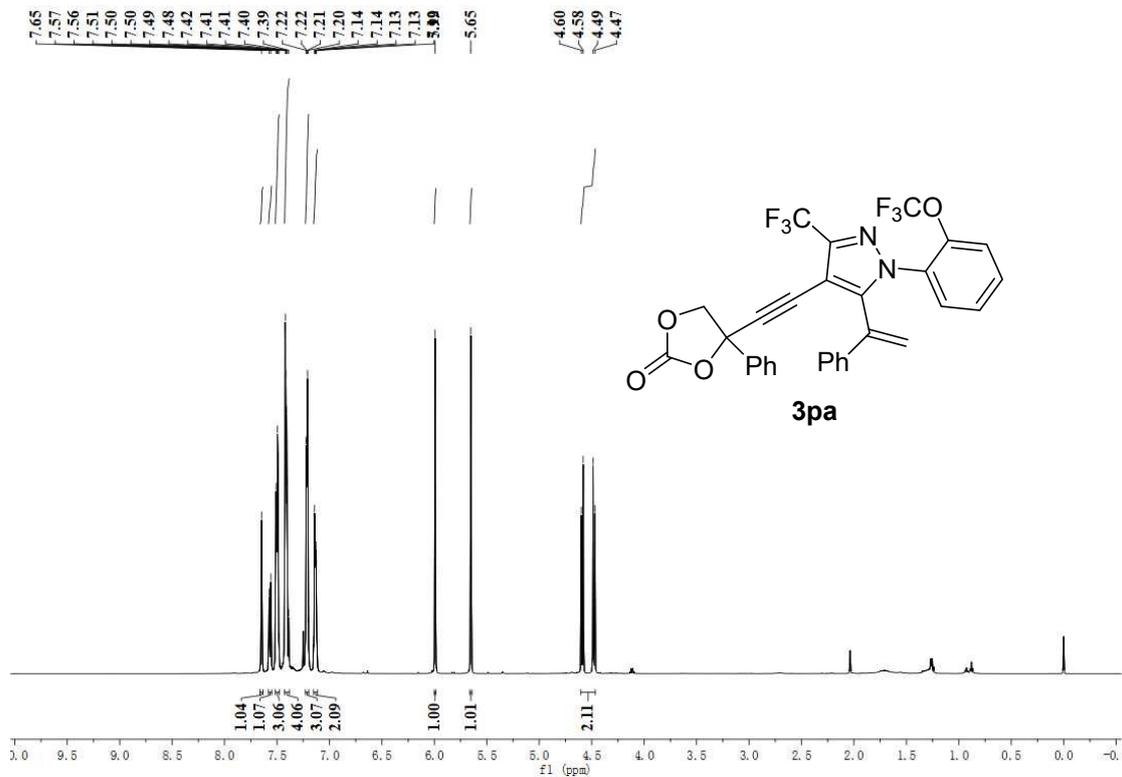
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 3a (126 MHz,  $\text{CDCl}_3$ )**



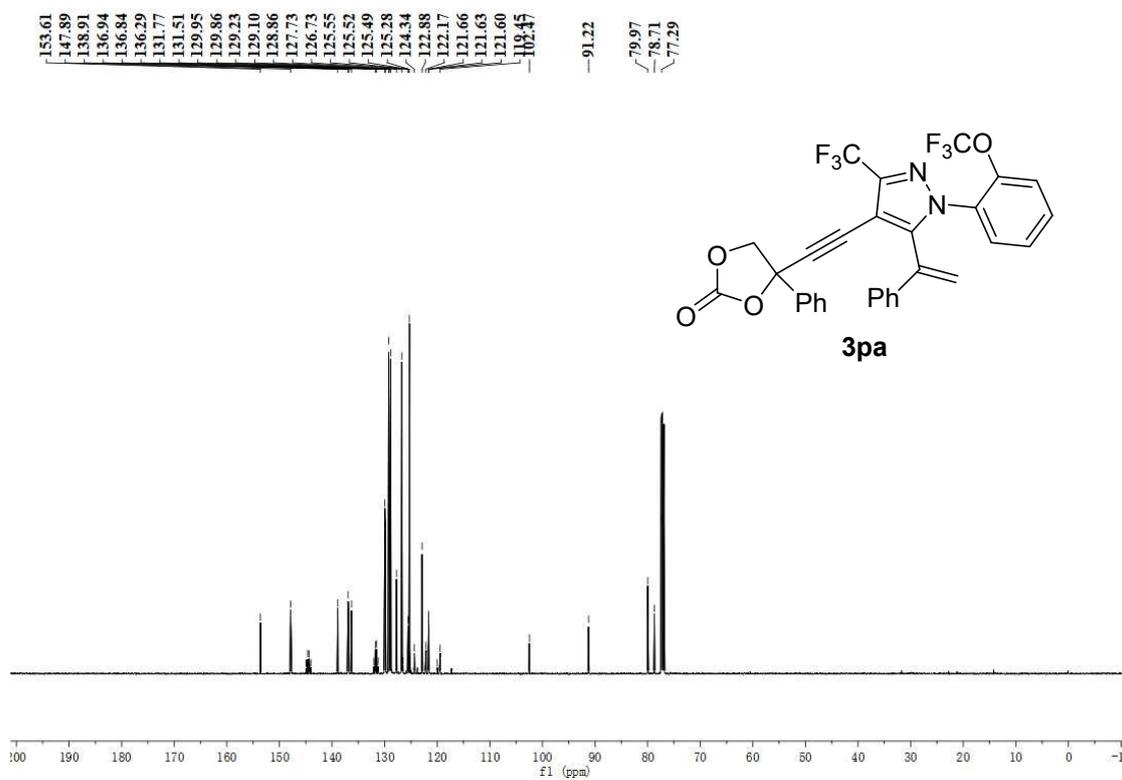
**$^{19}\text{F}$  NMR of 3a (471 MHz,  $\text{CDCl}_3$ )**



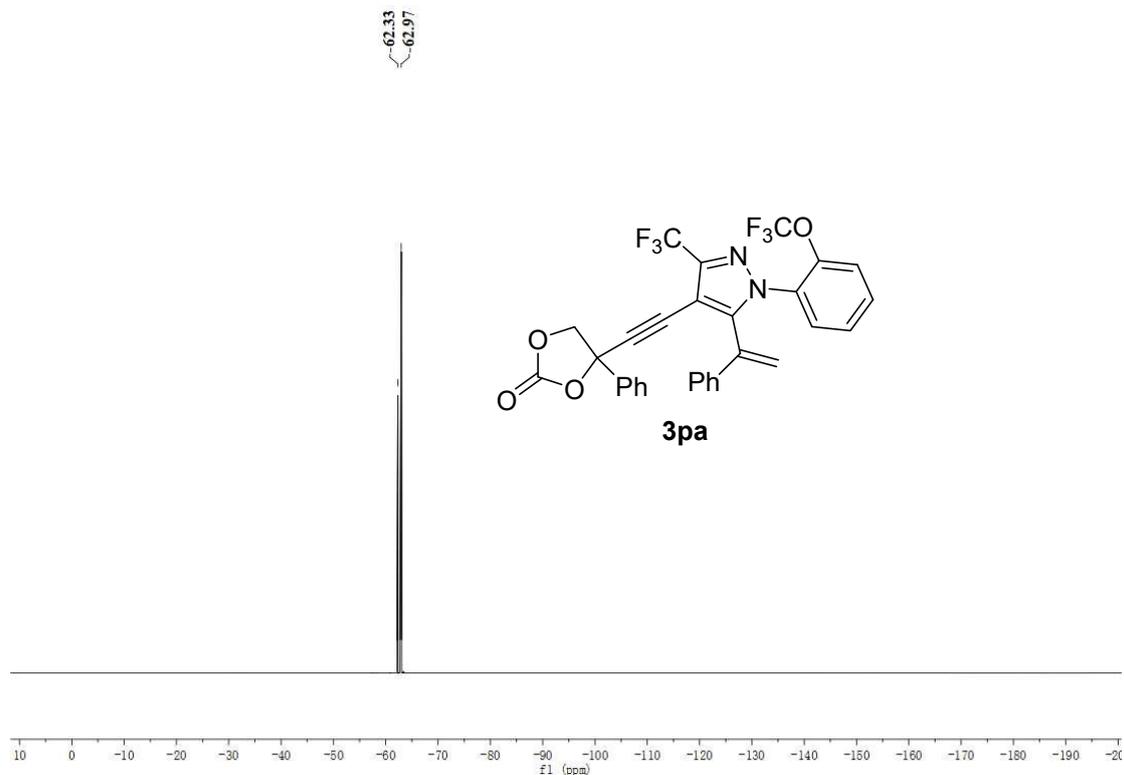
**<sup>1</sup>H NMR of 3pa (500 MHz, CDCl<sub>3</sub>)**



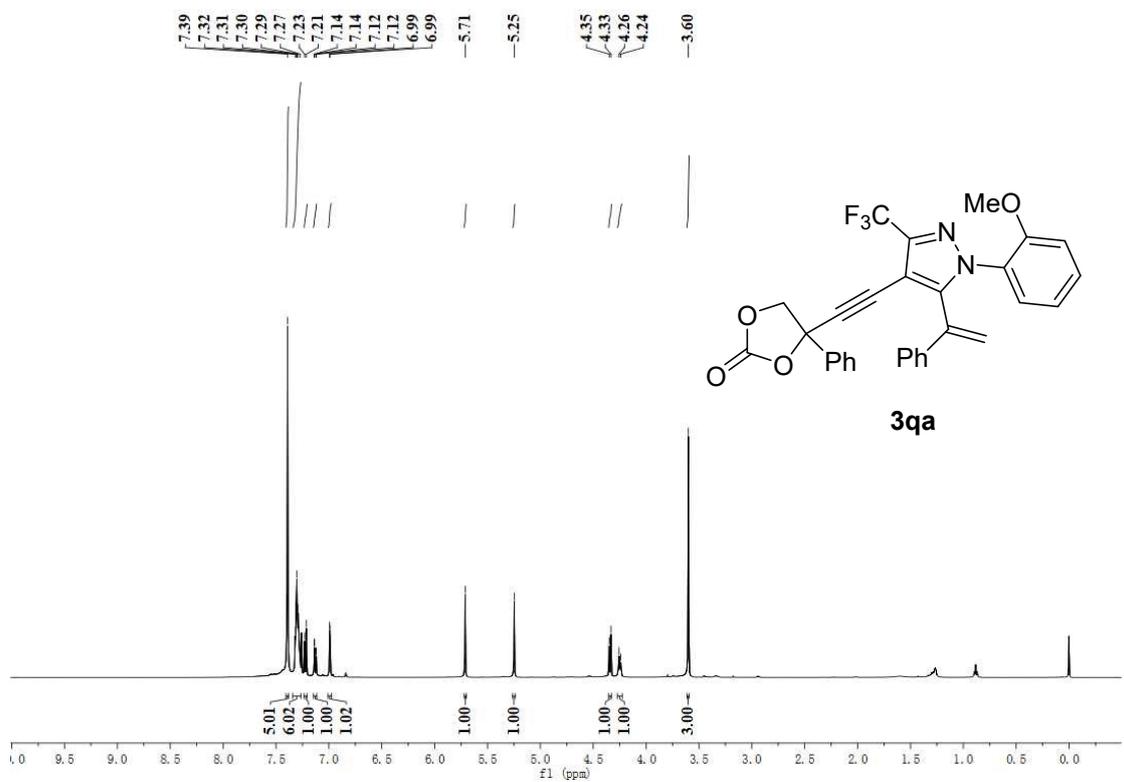
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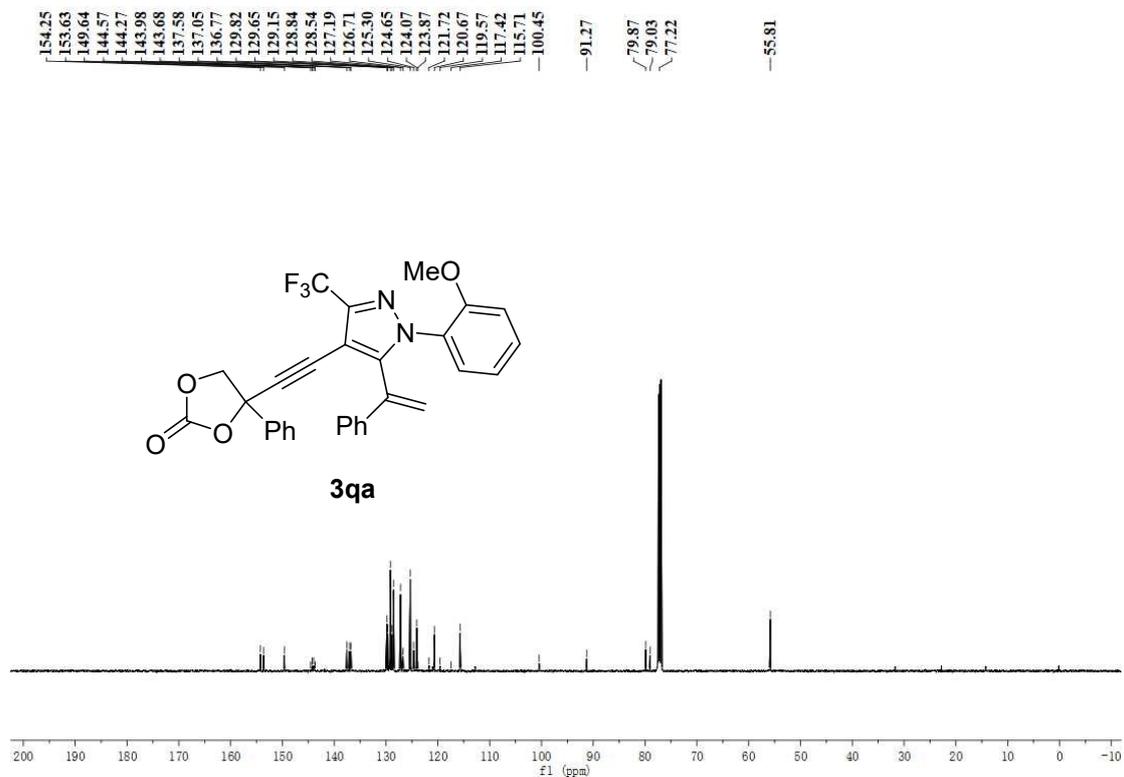
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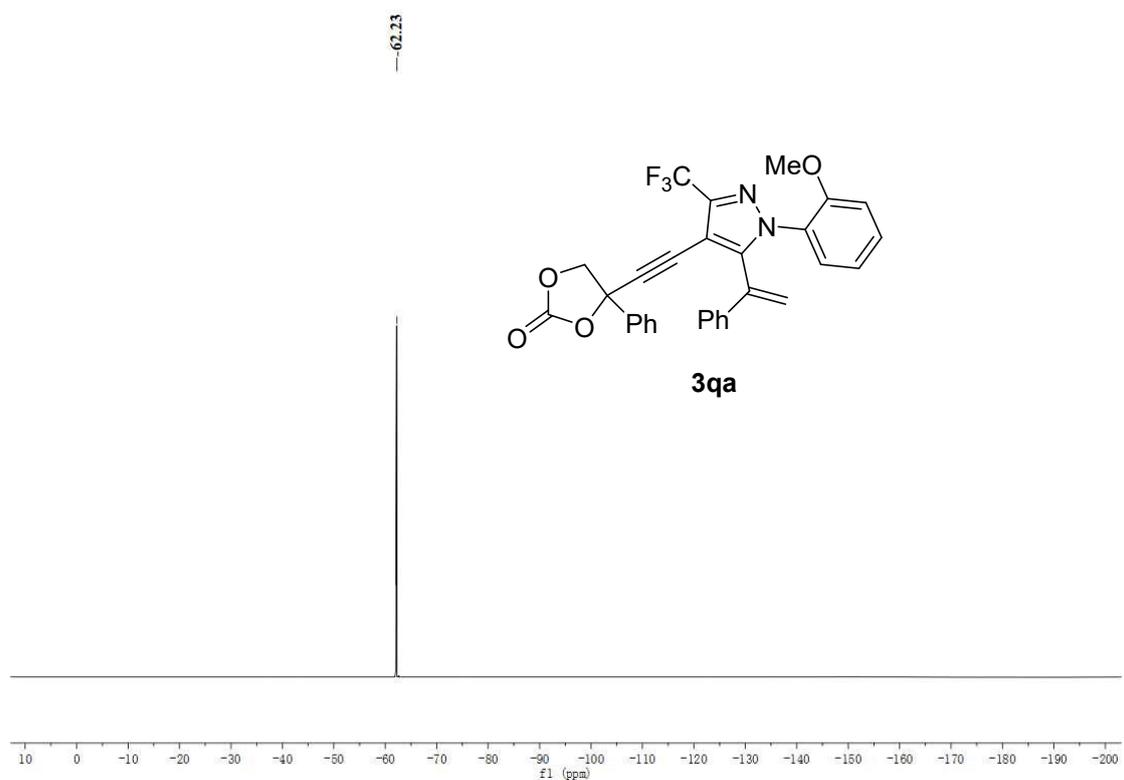
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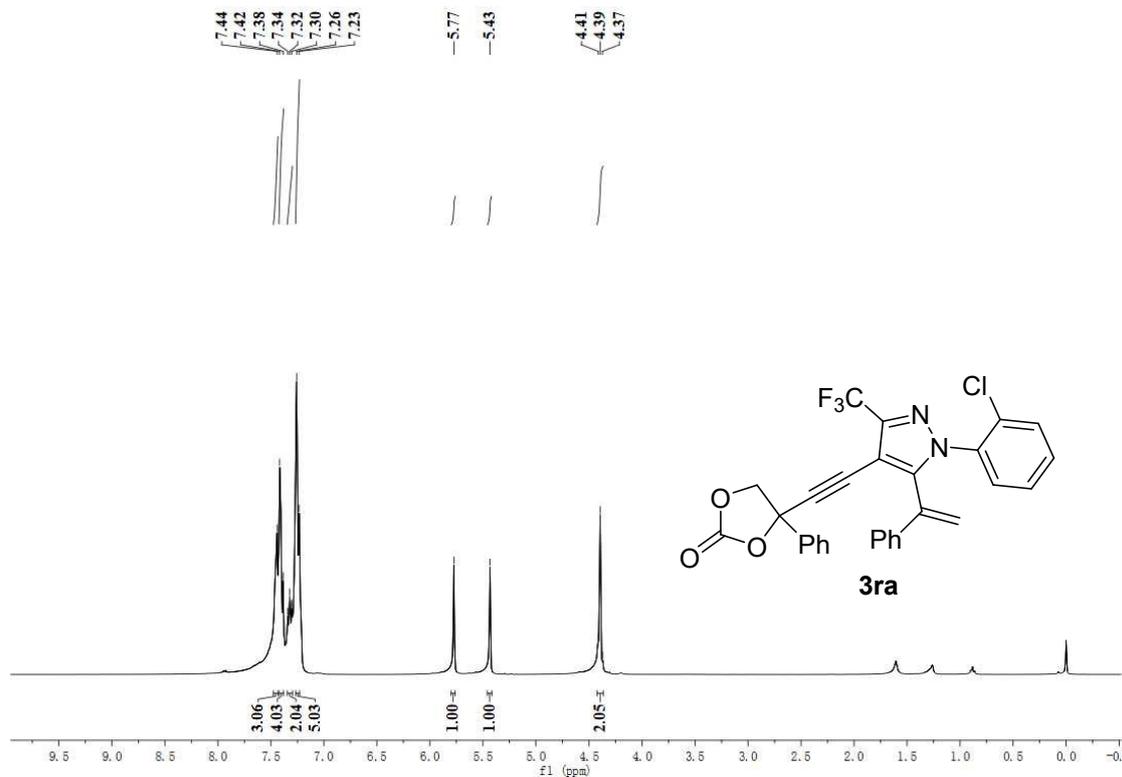
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 3qa (126 MHz,  $\text{CDCl}_3$ )**



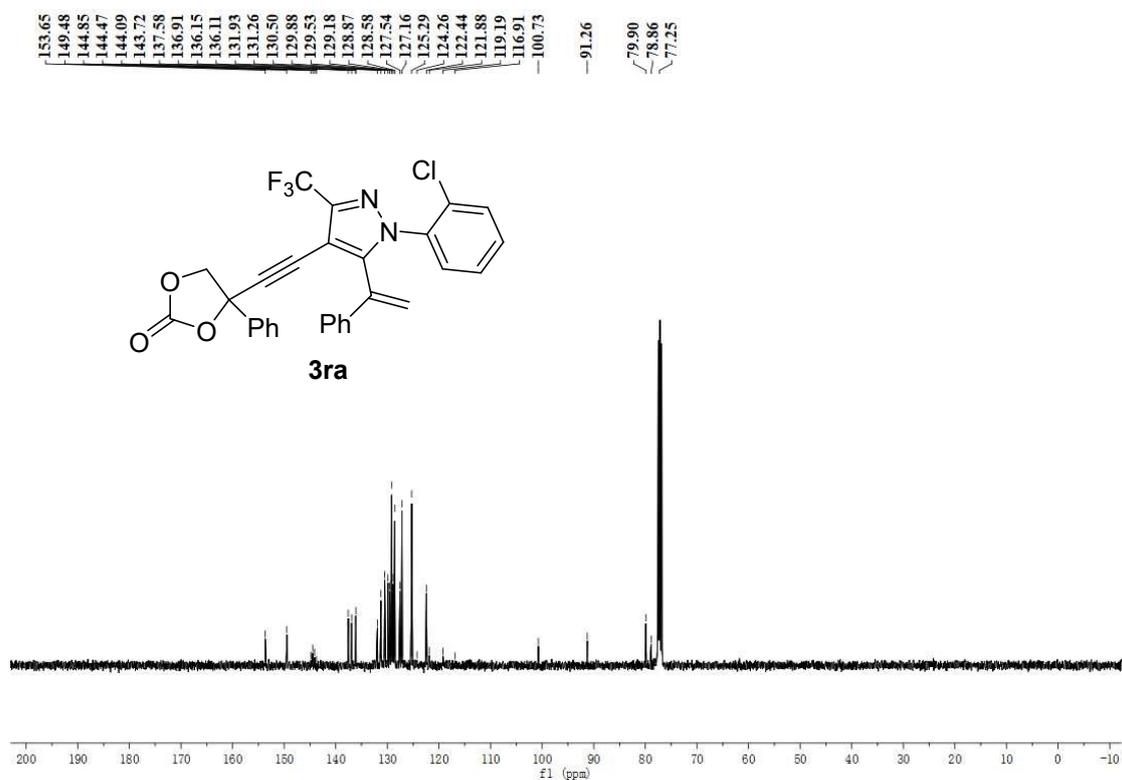
**$^{19}\text{F}$  NMR of 3qa (471 MHz,  $\text{CDCl}_3$ )**



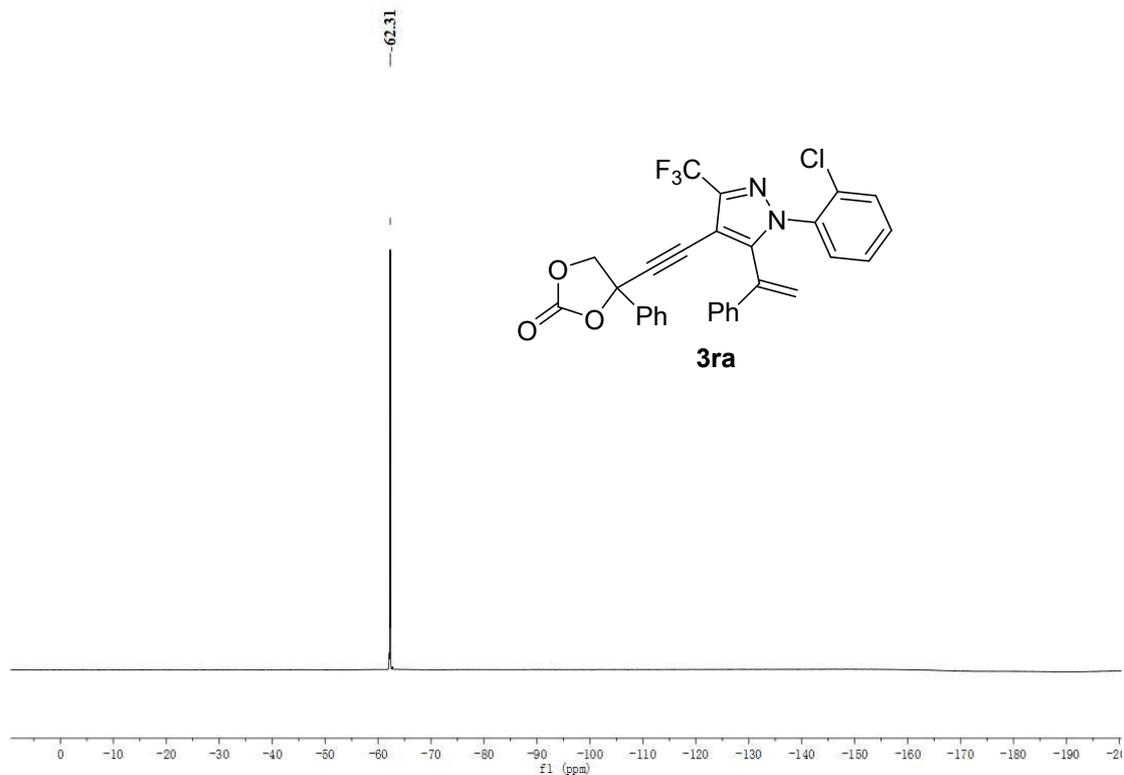
**<sup>1</sup>H NMR of 3ra (400 MHz, CDCl<sub>3</sub>)**



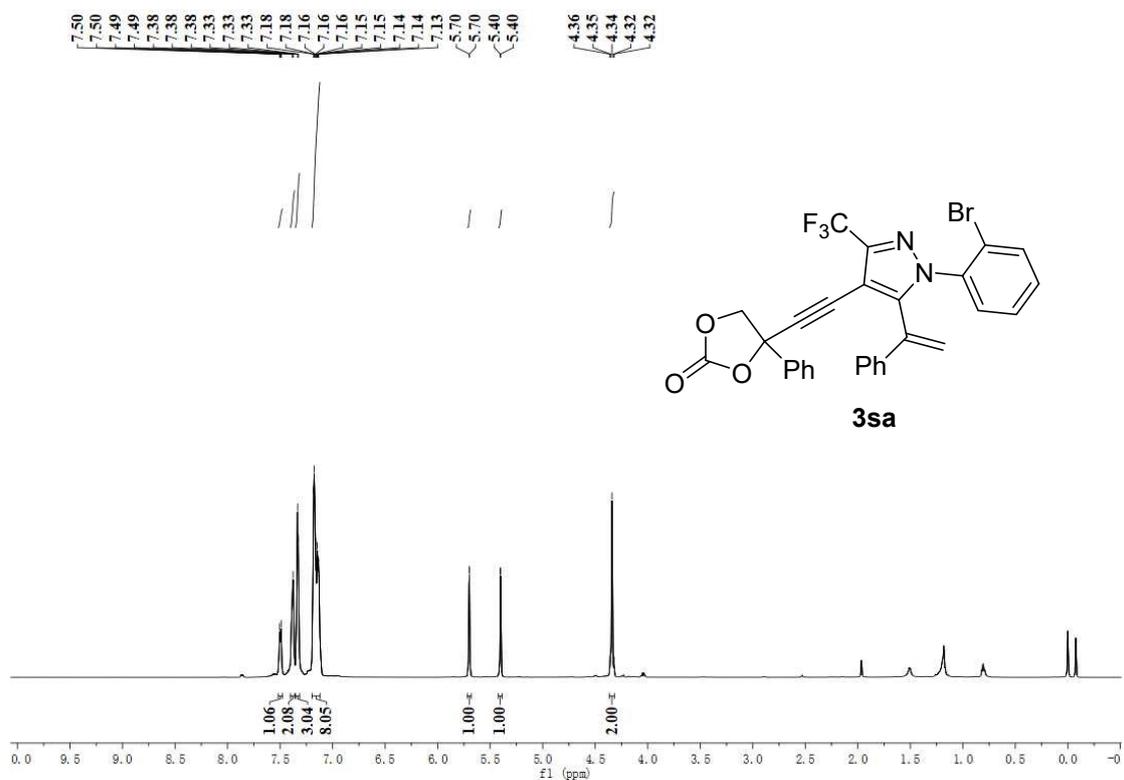
**<sup>13</sup>C{<sup>1</sup>H} NMR of 3ra (101 MHz, CDCl<sub>3</sub>)**



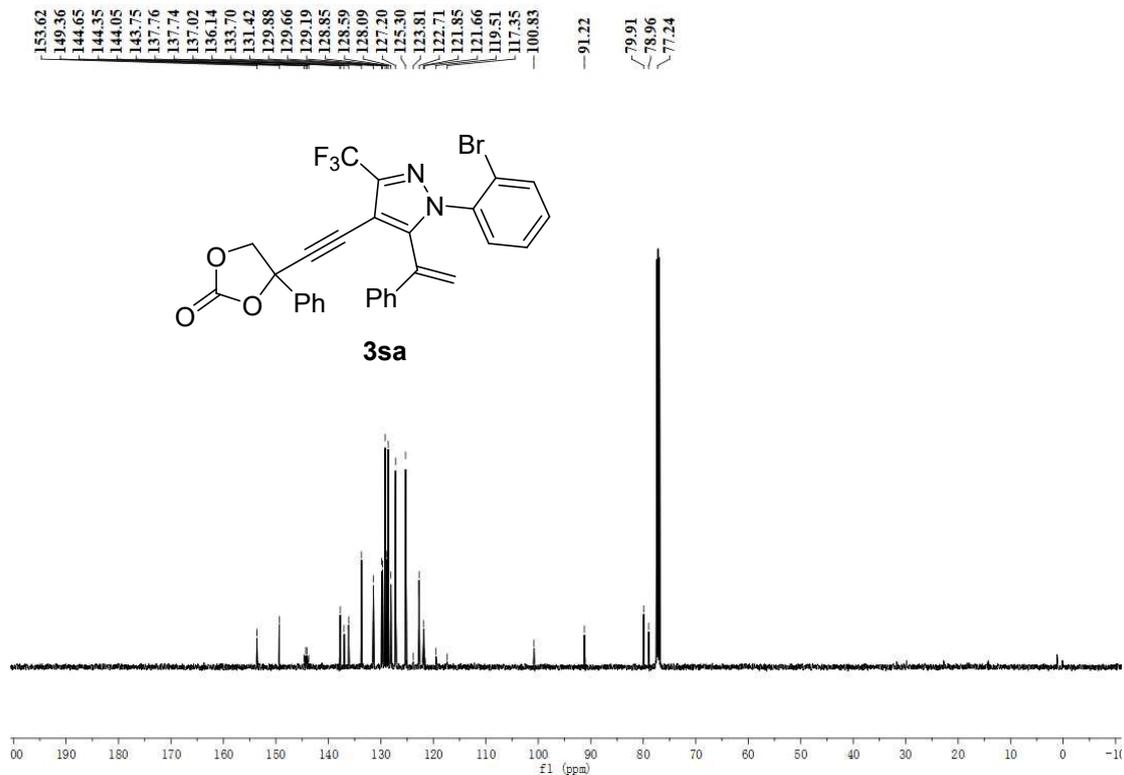
**<sup>19</sup>F NMR of 3ra (376 MHz, CDCl<sub>3</sub>)**



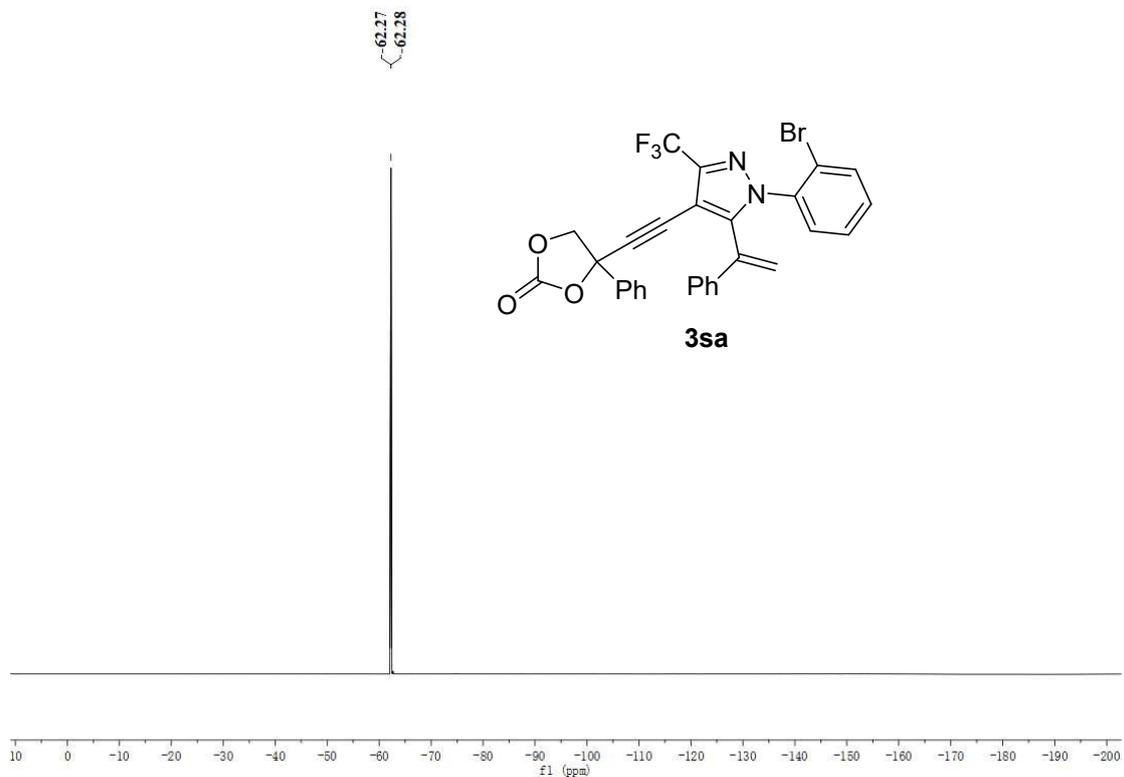
**<sup>1</sup>H NMR of 3sa (500 MHz, CDCl<sub>3</sub>)**



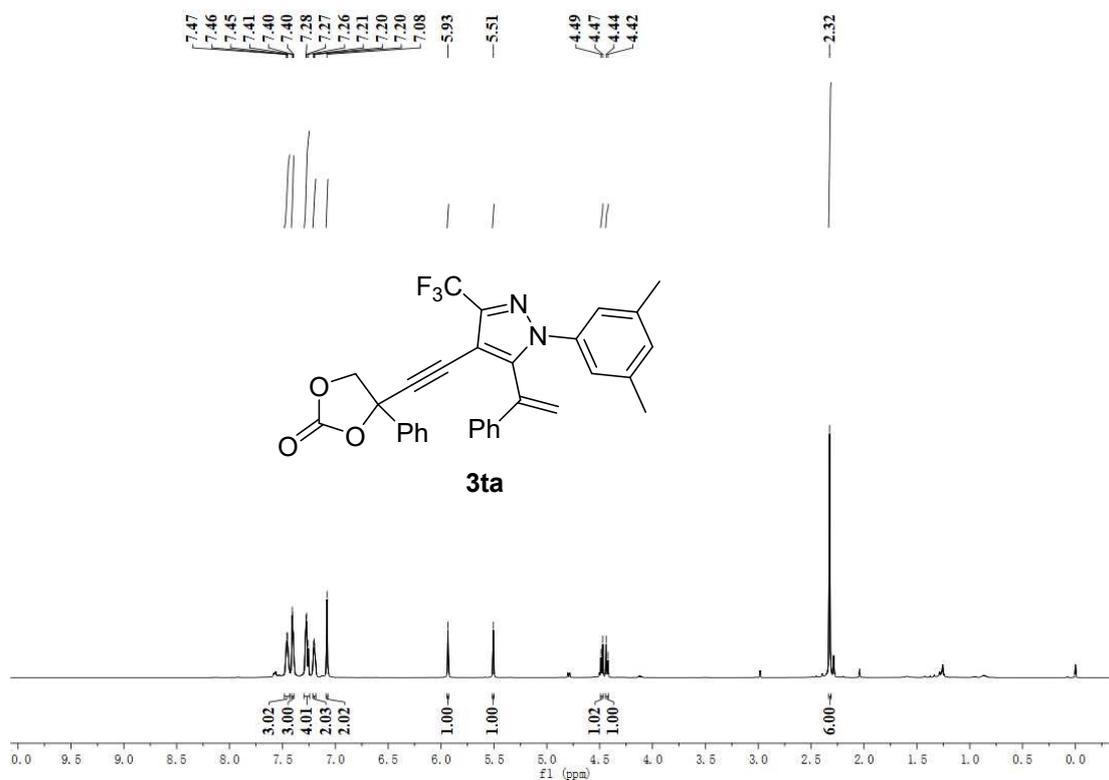
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 3sa (126 MHz,  $\text{CDCl}_3$ )**



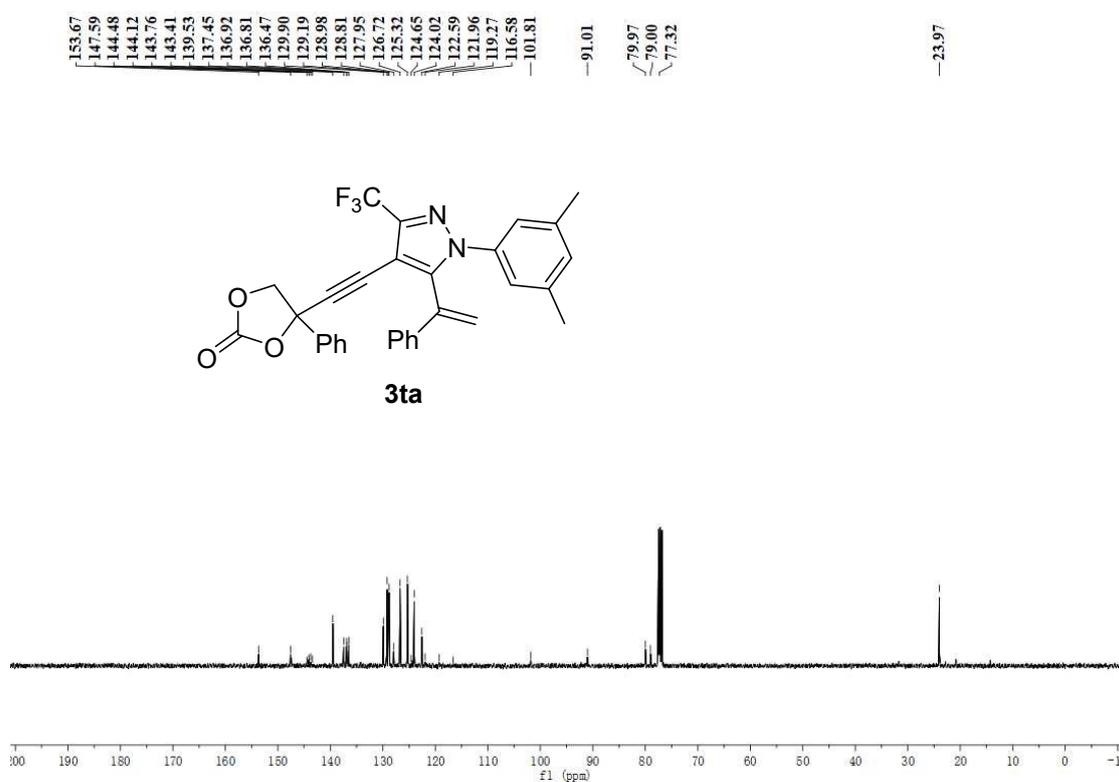
**$^{19}\text{F}$  NMR of 3sa (471 MHz,  $\text{CDCl}_3$ )**



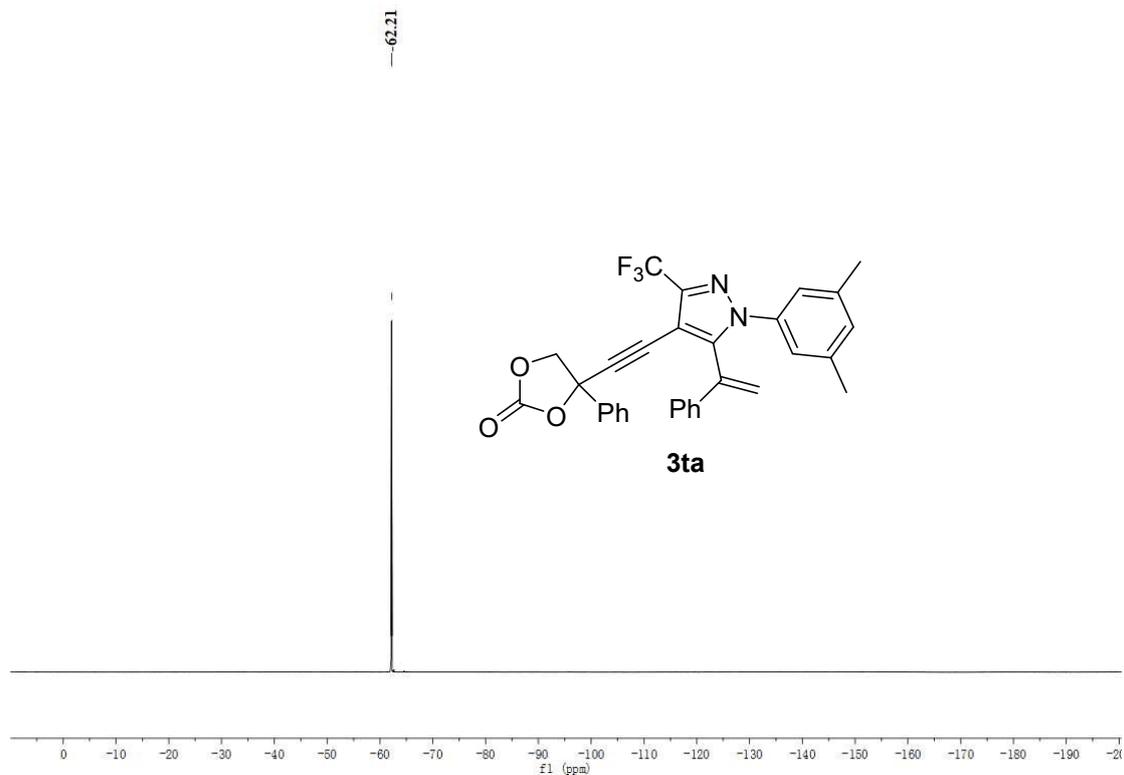
**<sup>1</sup>H NMR of 3ta (500 MHz, CDCl<sub>3</sub>)**



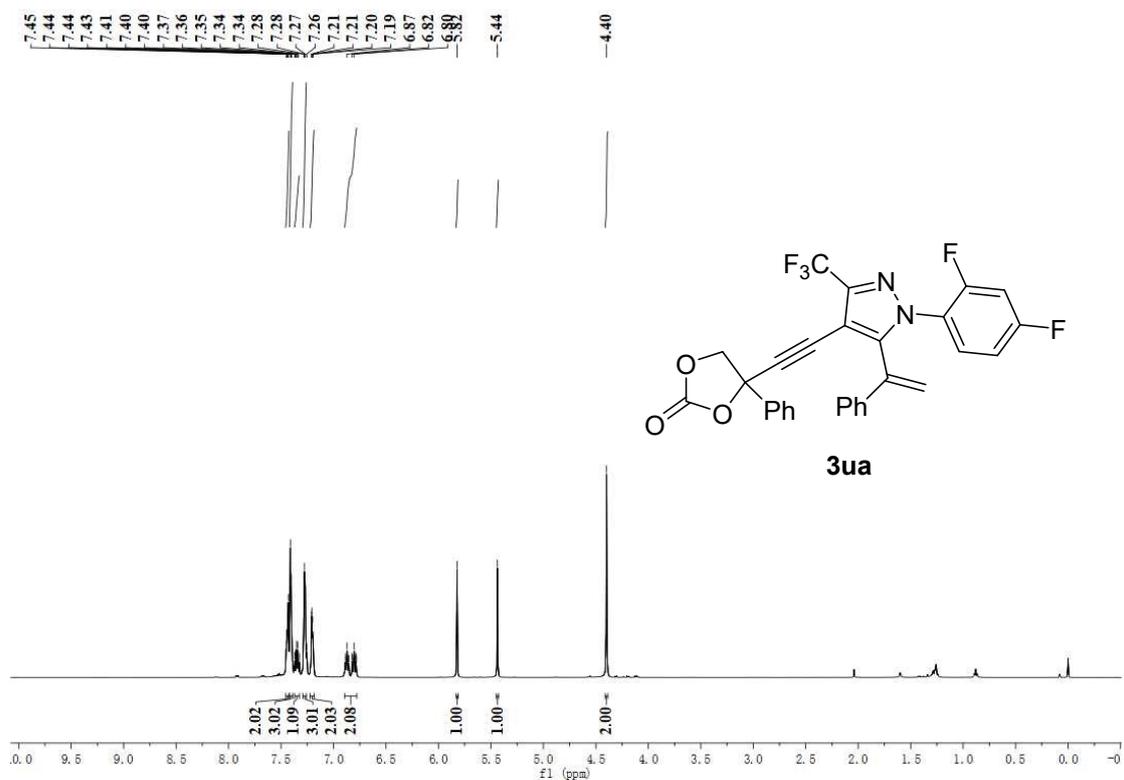
**<sup>13</sup>C{<sup>1</sup>H} NMR of 3ta (126 MHz, CDCl<sub>3</sub>)**



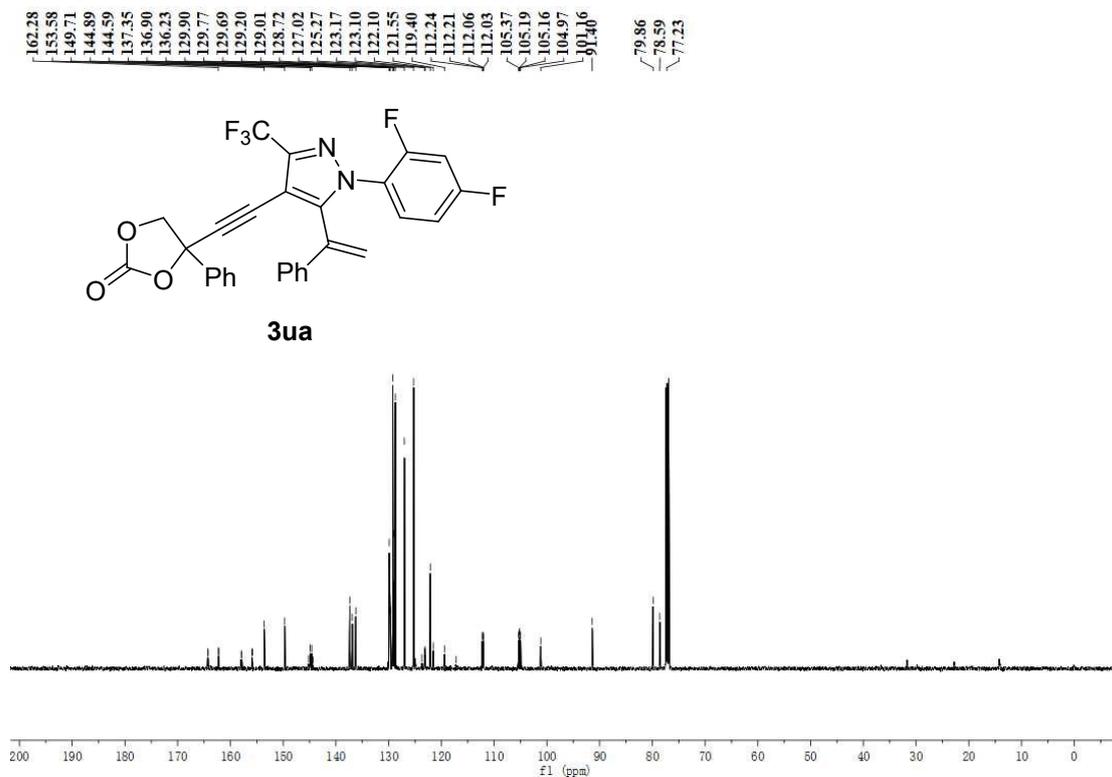
**<sup>19</sup>F NMR of 3ta (471 MHz, CDCl<sub>3</sub>)**



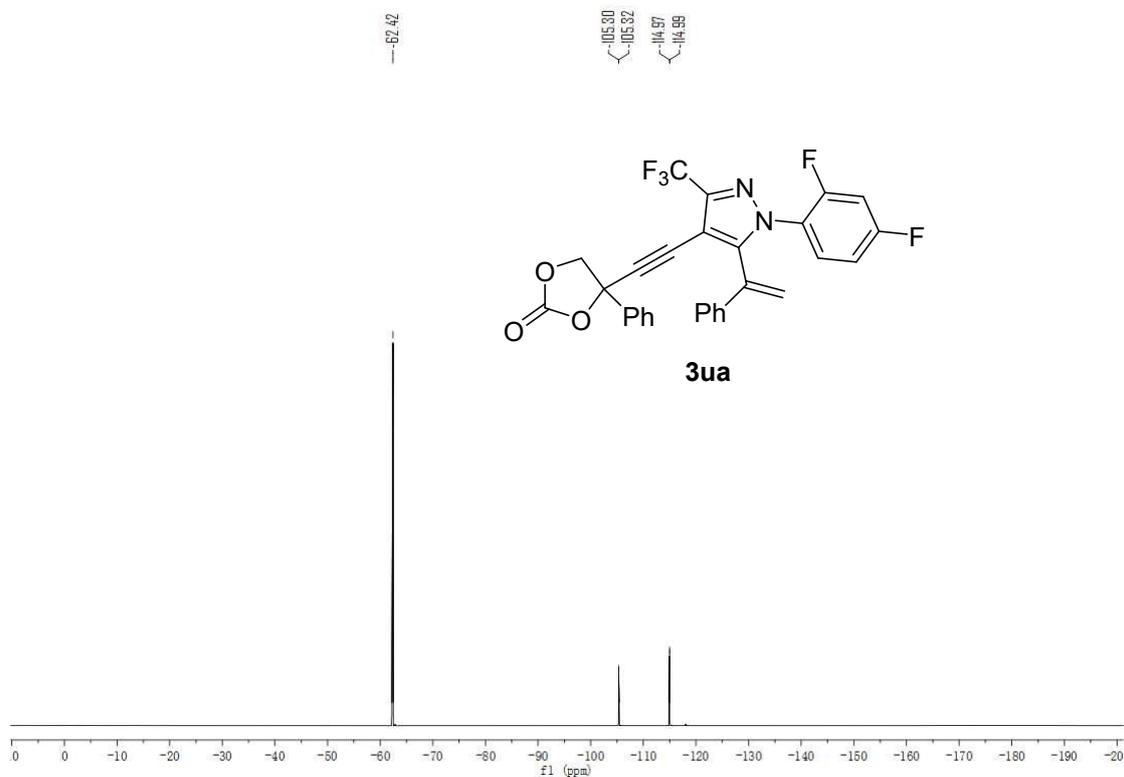
**<sup>1</sup>H NMR of 3ua (500 MHz, CDCl<sub>3</sub>)**



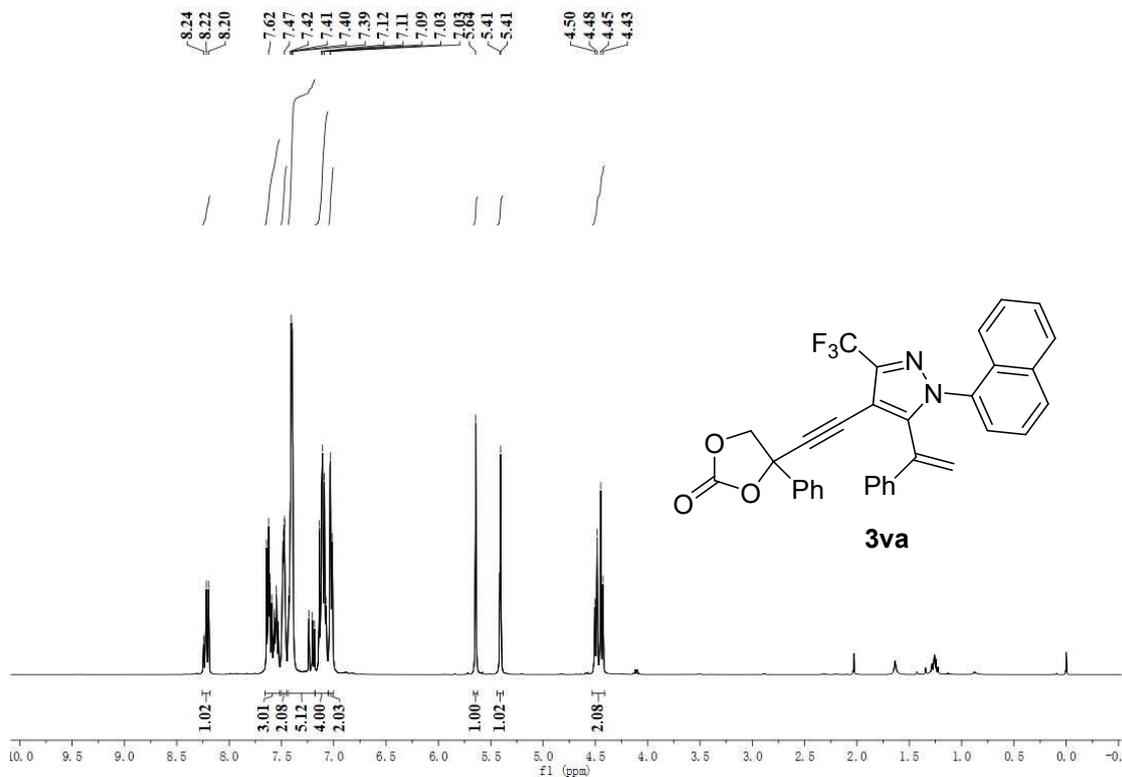
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 3ua (126 MHz,  $\text{CDCl}_3$ )**



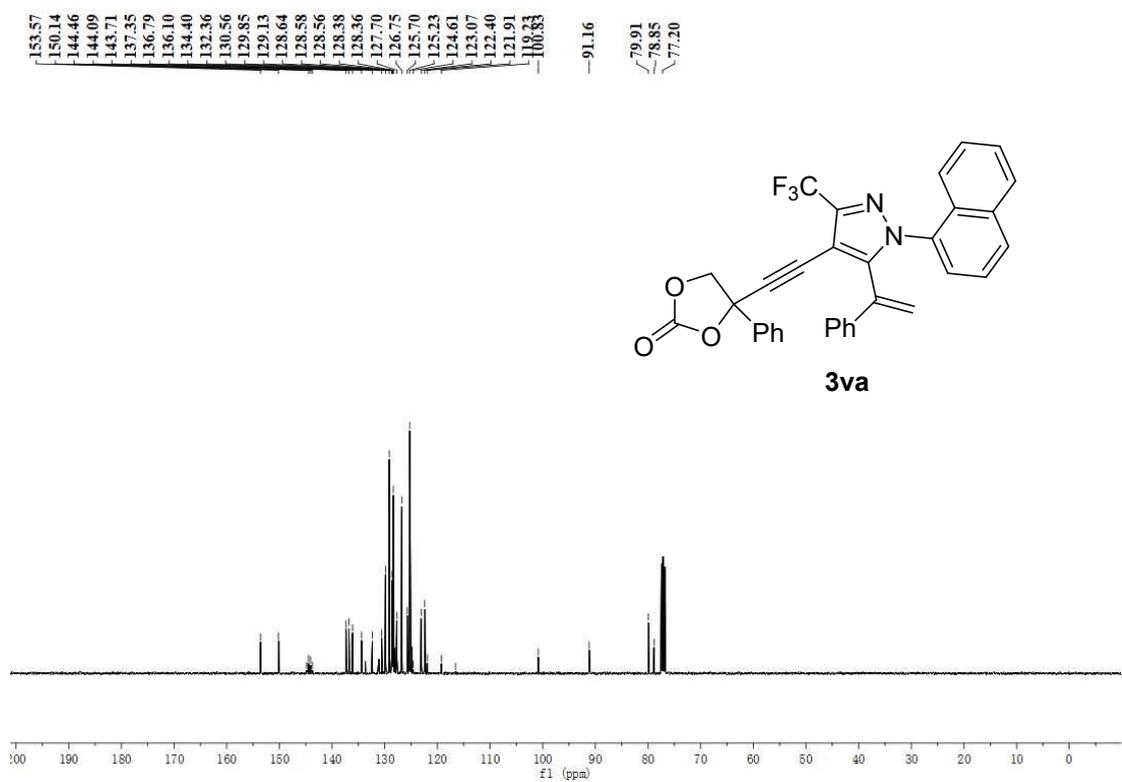
**$^{19}\text{F}$  NMR of 3ua (471 MHz,  $\text{CDCl}_3$ )**



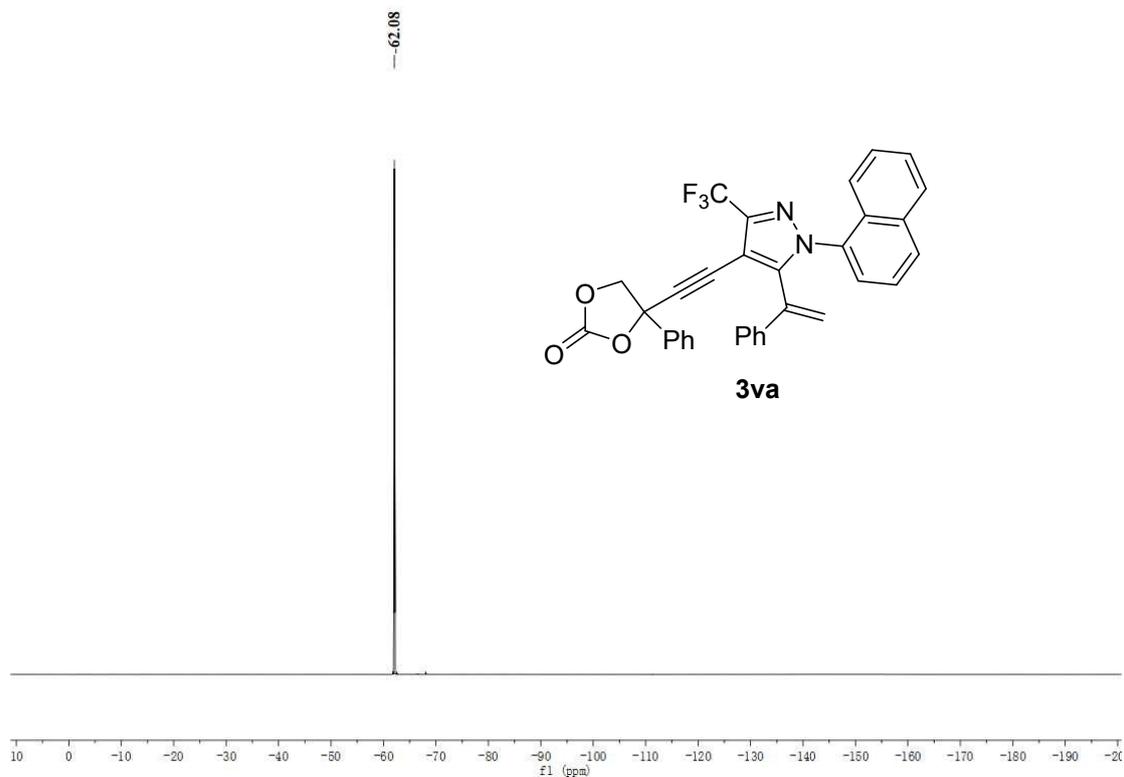
**<sup>1</sup>H NMR of 3va (400 MHz, CDCl<sub>3</sub>)**



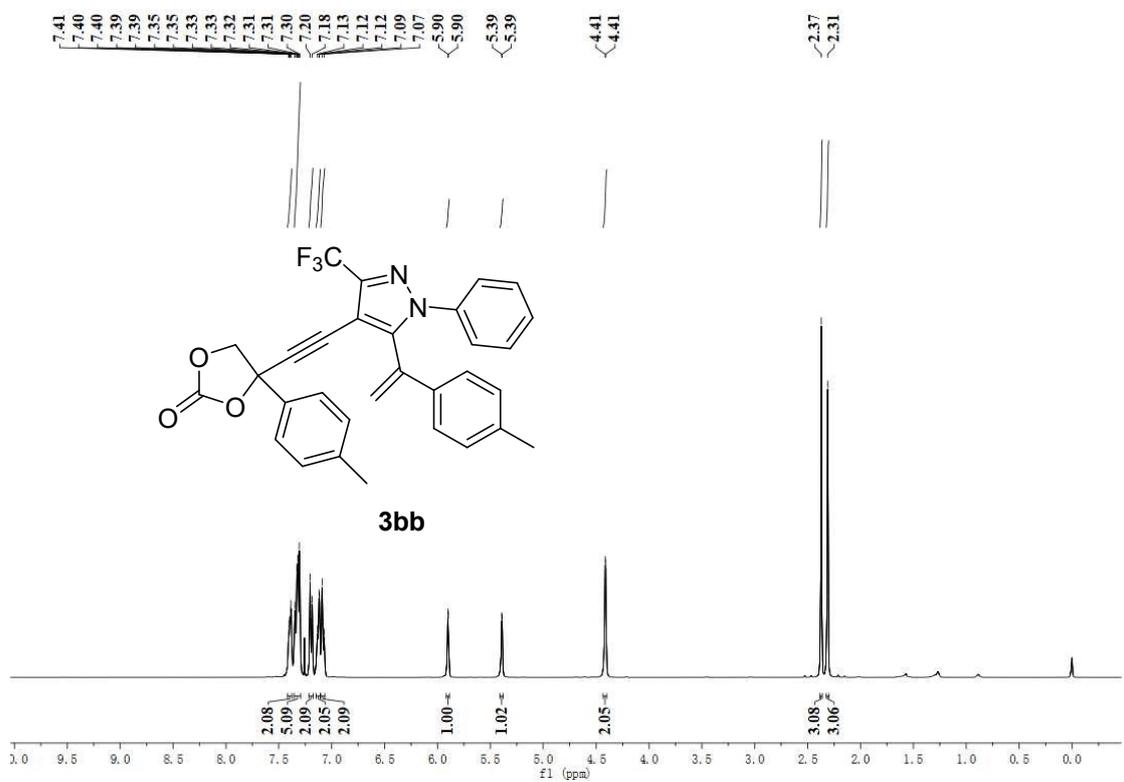
**<sup>13</sup>C{<sup>1</sup>H} NMR of 3va (101 MHz, CDCl<sub>3</sub>)**



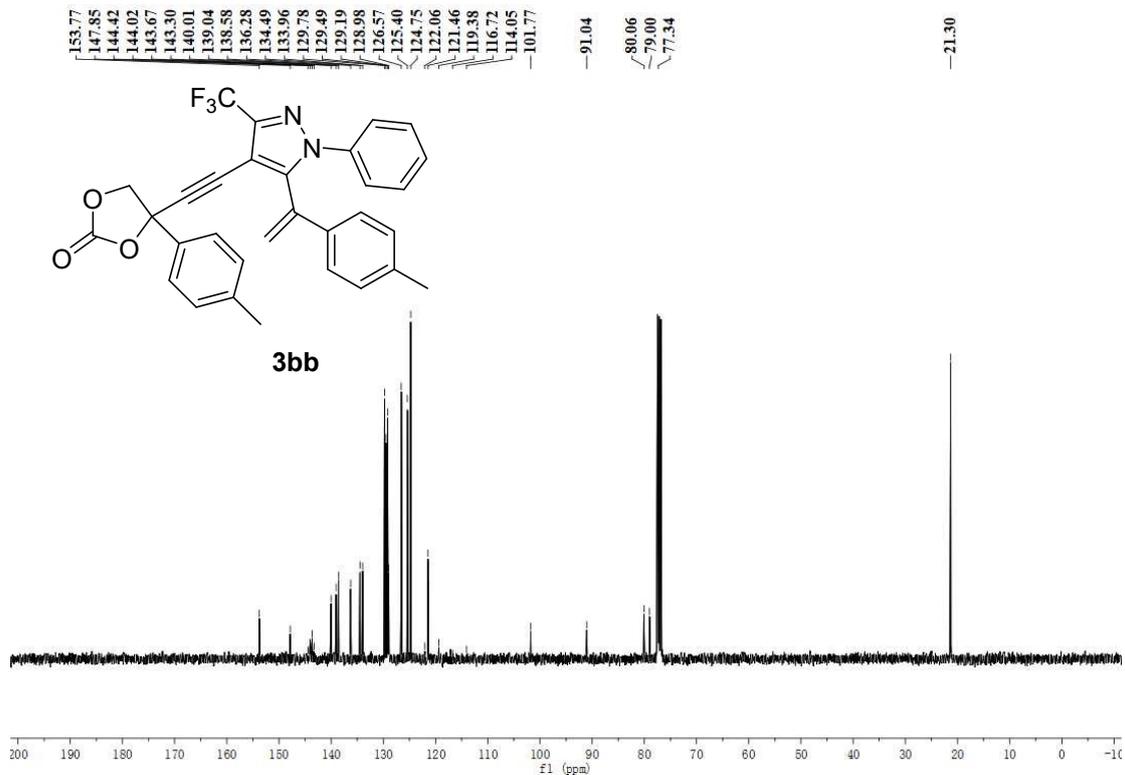
**<sup>19</sup>F NMR of 3va (376 MHz, CDCl<sub>3</sub>)**



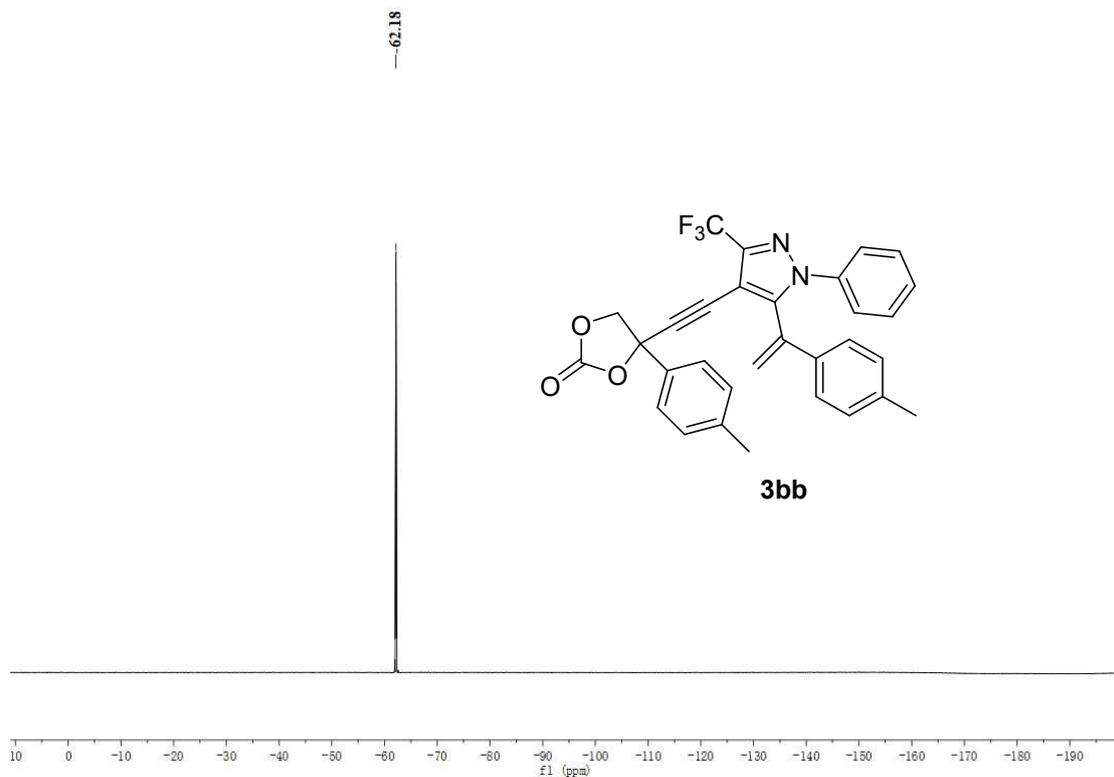
**<sup>1</sup>H NMR of 3bb (400 MHz, CDCl<sub>3</sub>)**



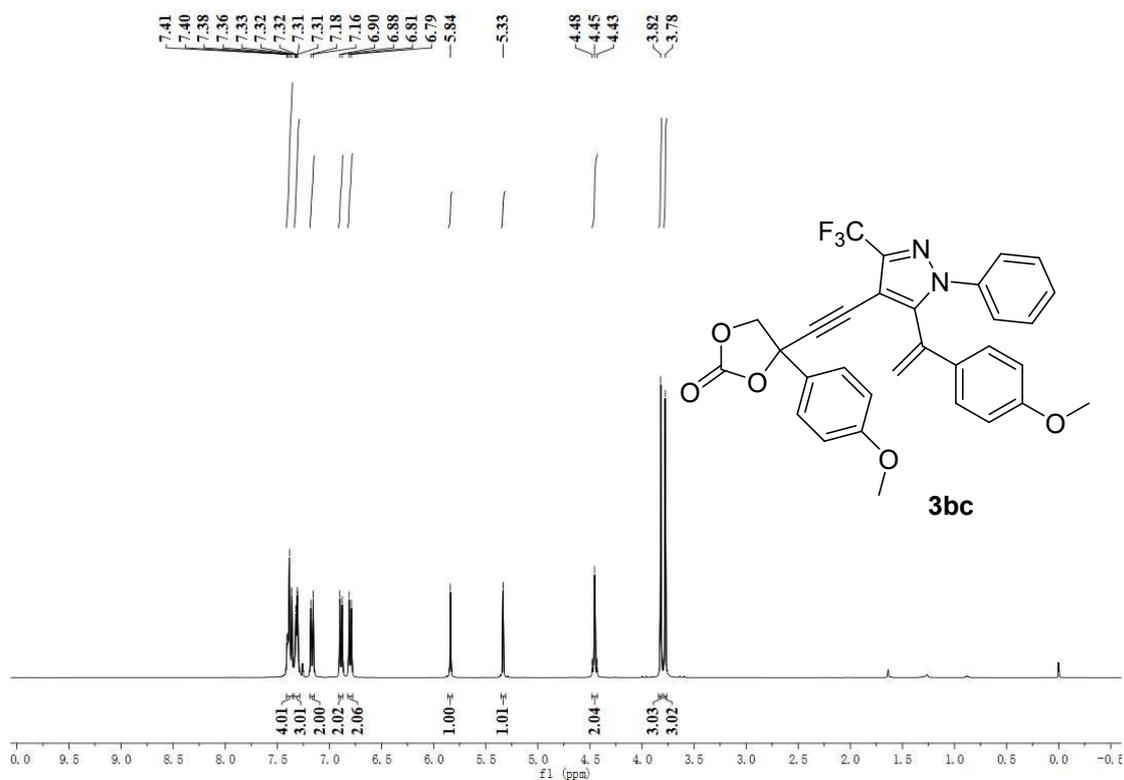
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 3bb (101 MHz,  $\text{CDCl}_3$ )**



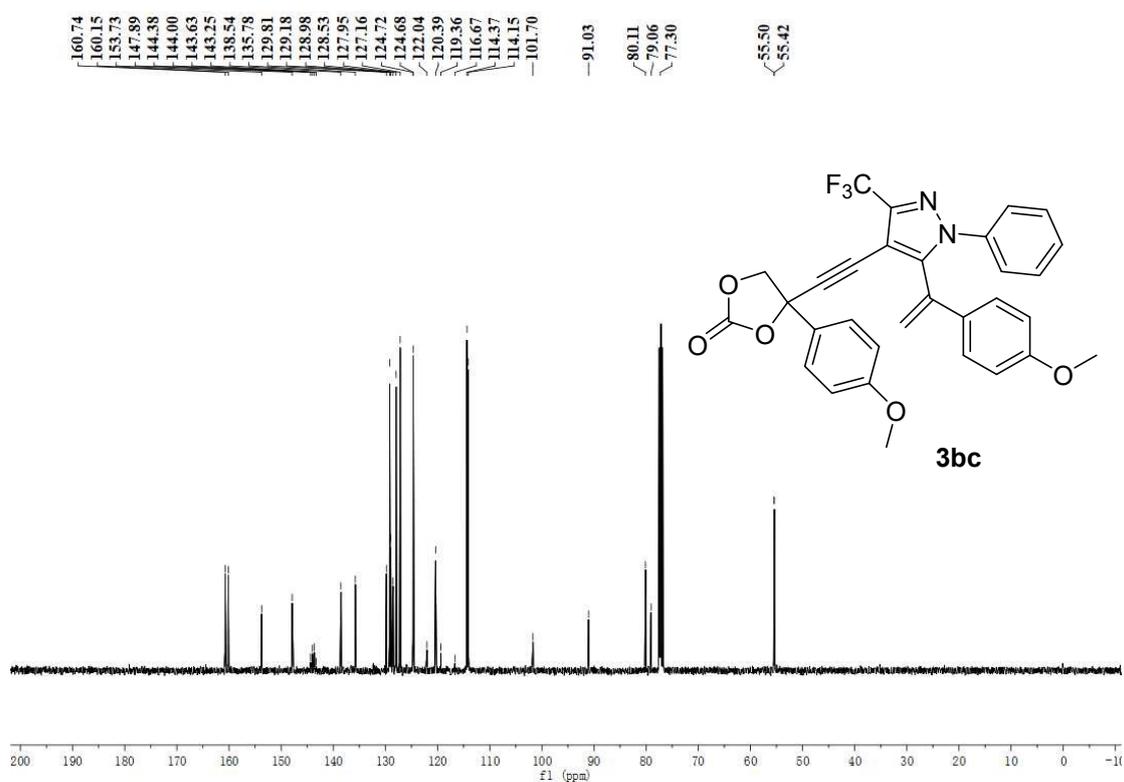
**$^{19}\text{F}$  NMR of 3bb (376 MHz,  $\text{CDCl}_3$ )**



**<sup>1</sup>H NMR of 3bc (400 MHz, CDCl<sub>3</sub>)**



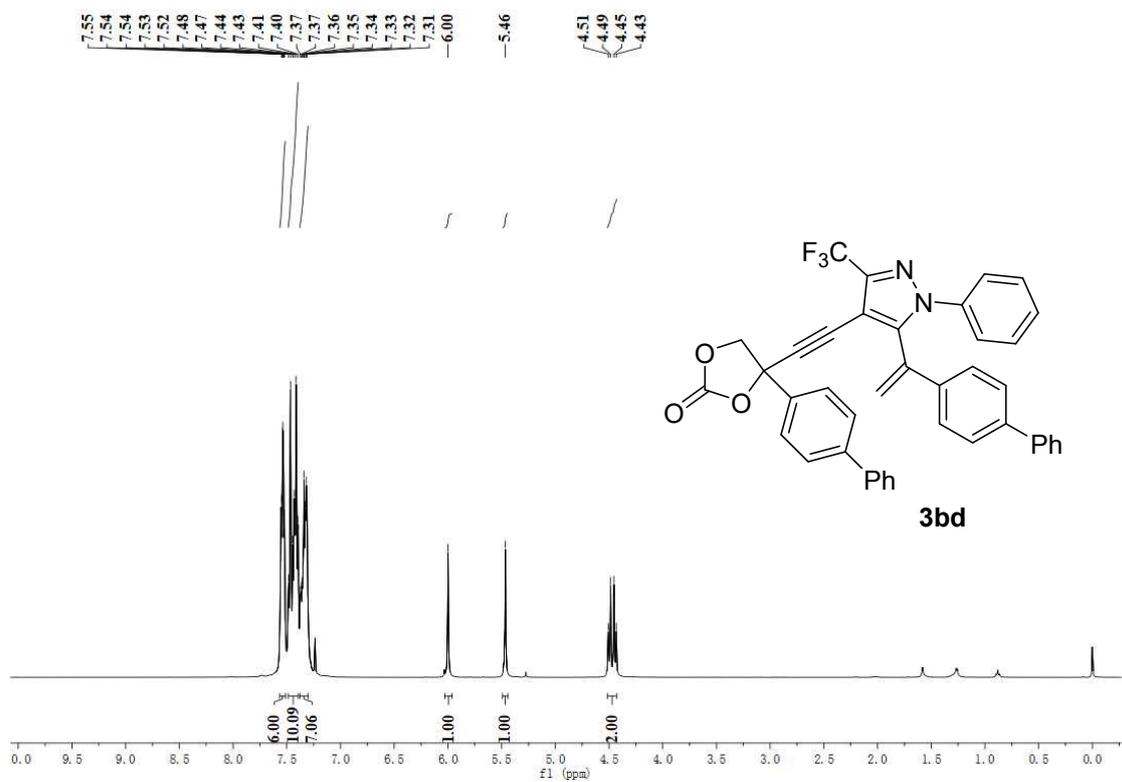
**<sup>13</sup>C{<sup>1</sup>H} NMR of 3bc (101 MHz, CDCl<sub>3</sub>)**



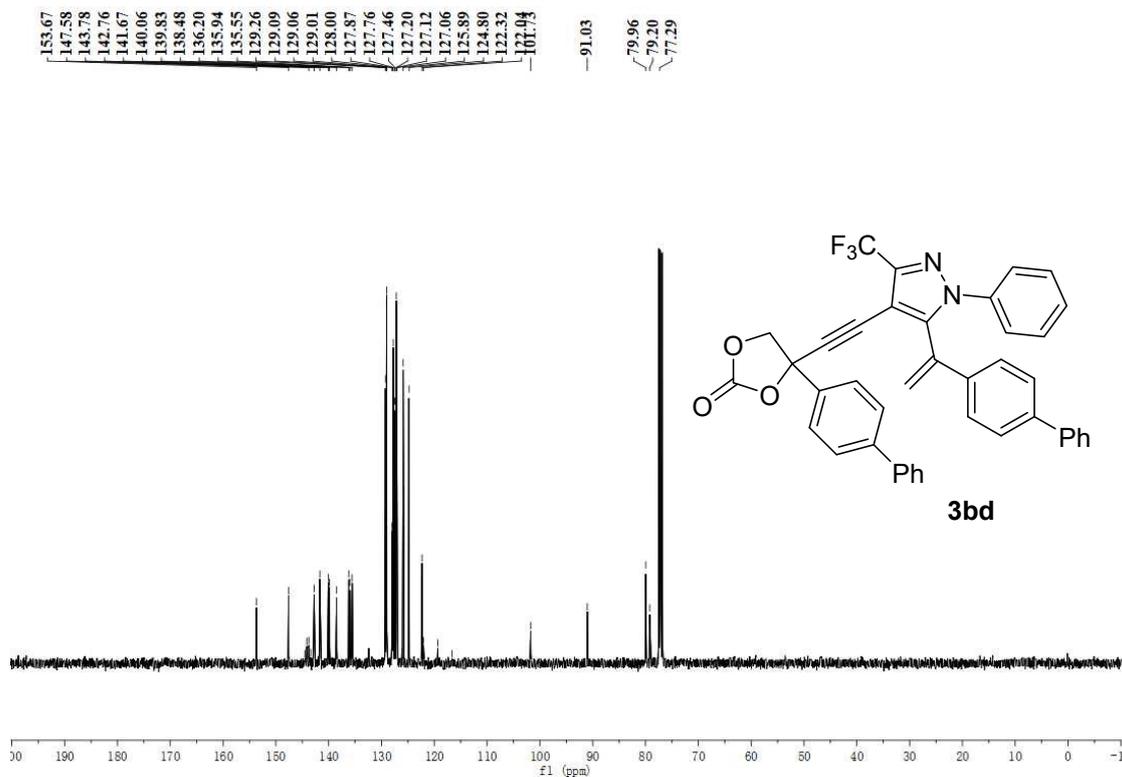
**<sup>19</sup>F NMR of 3bc (376 MHz, CDCl<sub>3</sub>)**



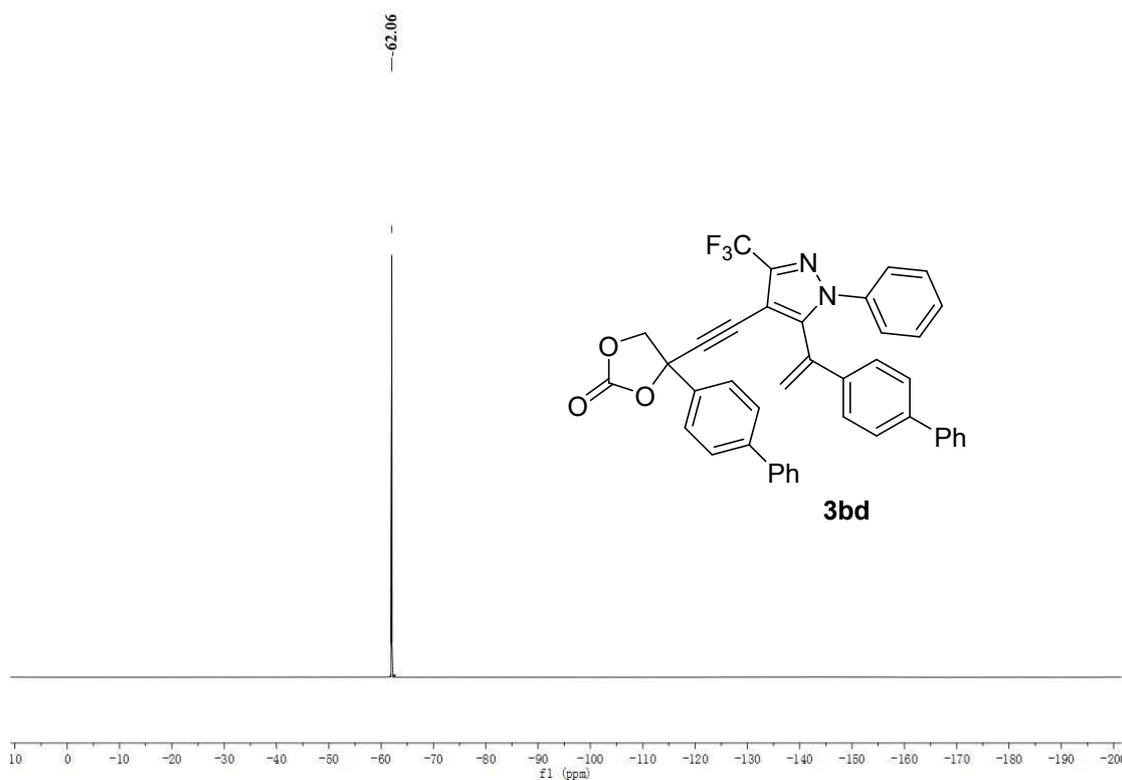
**<sup>1</sup>H NMR of 3bd (400 MHz, CDCl<sub>3</sub>)**



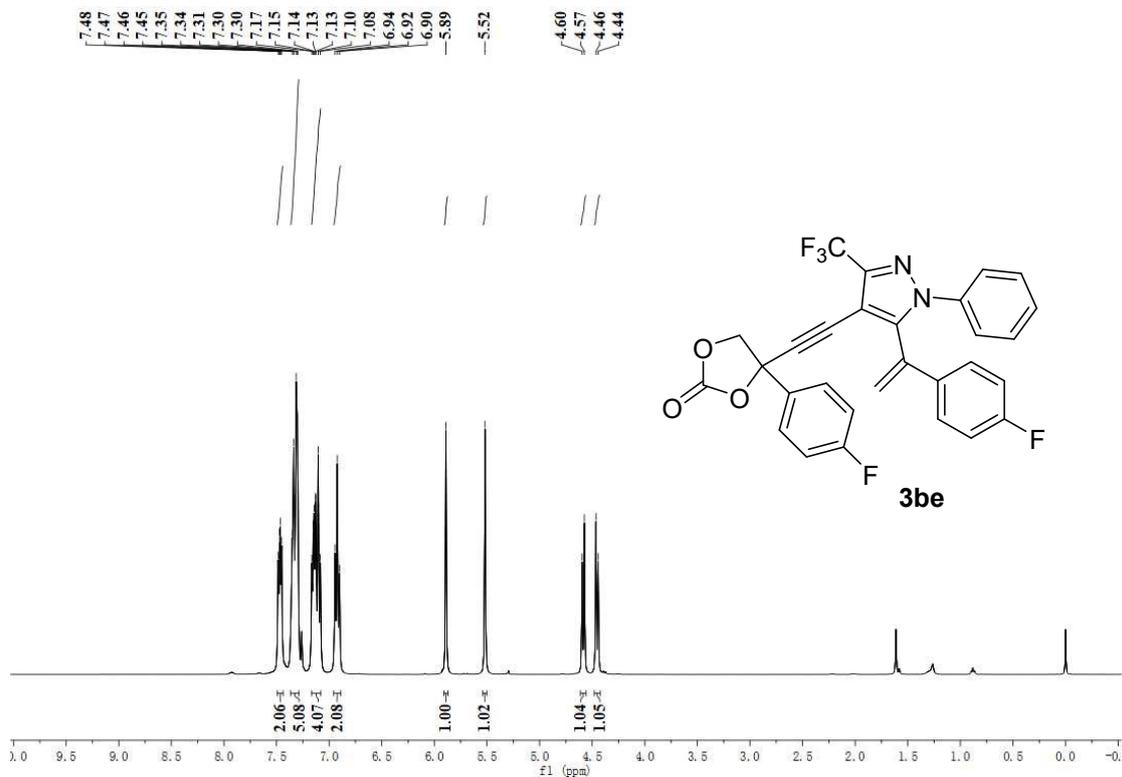
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 3bd (101 MHz,  $\text{CDCl}_3$ )**



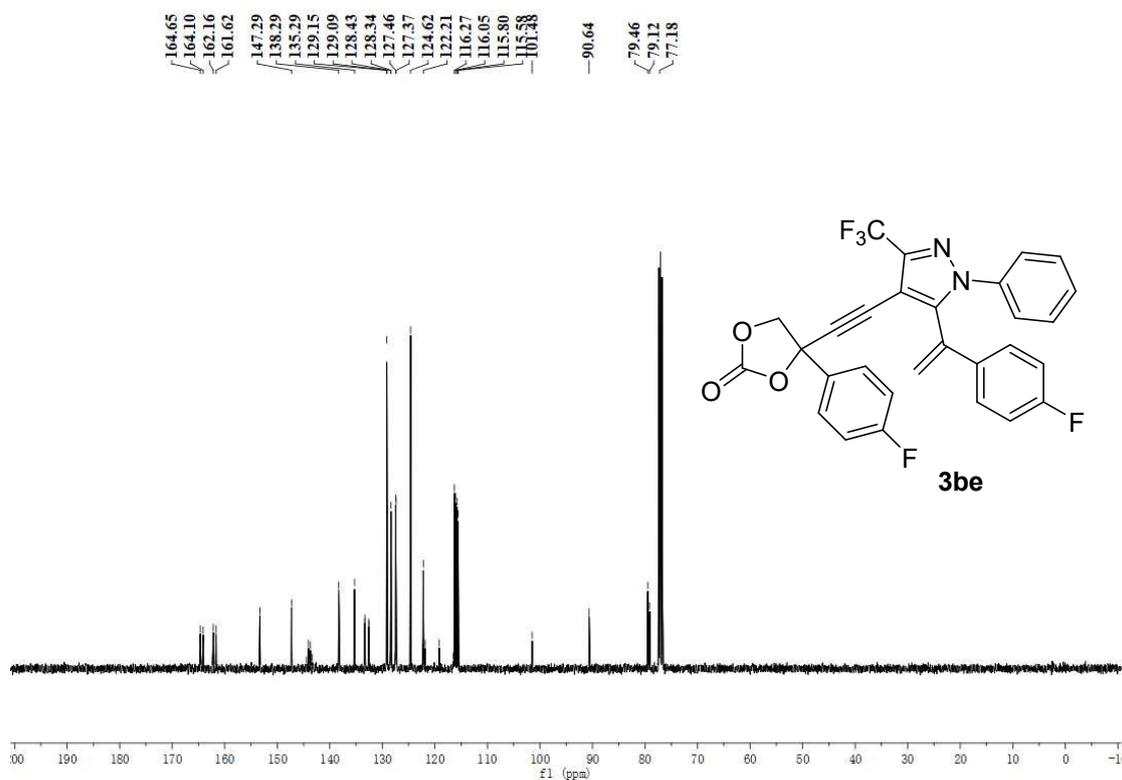
**$^{19}\text{F}$  NMR of 3bd (376 MHz,  $\text{CDCl}_3$ )**



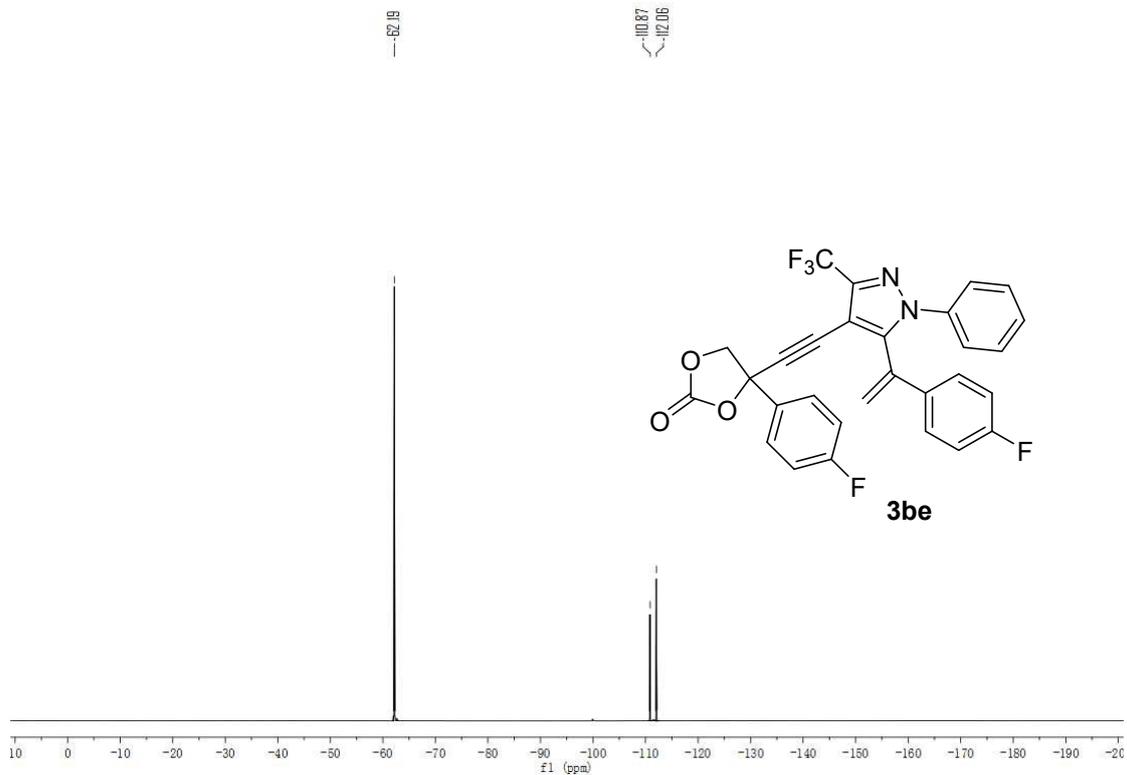
**<sup>1</sup>H NMR of 3be (400 MHz, CDCl<sub>3</sub>)**



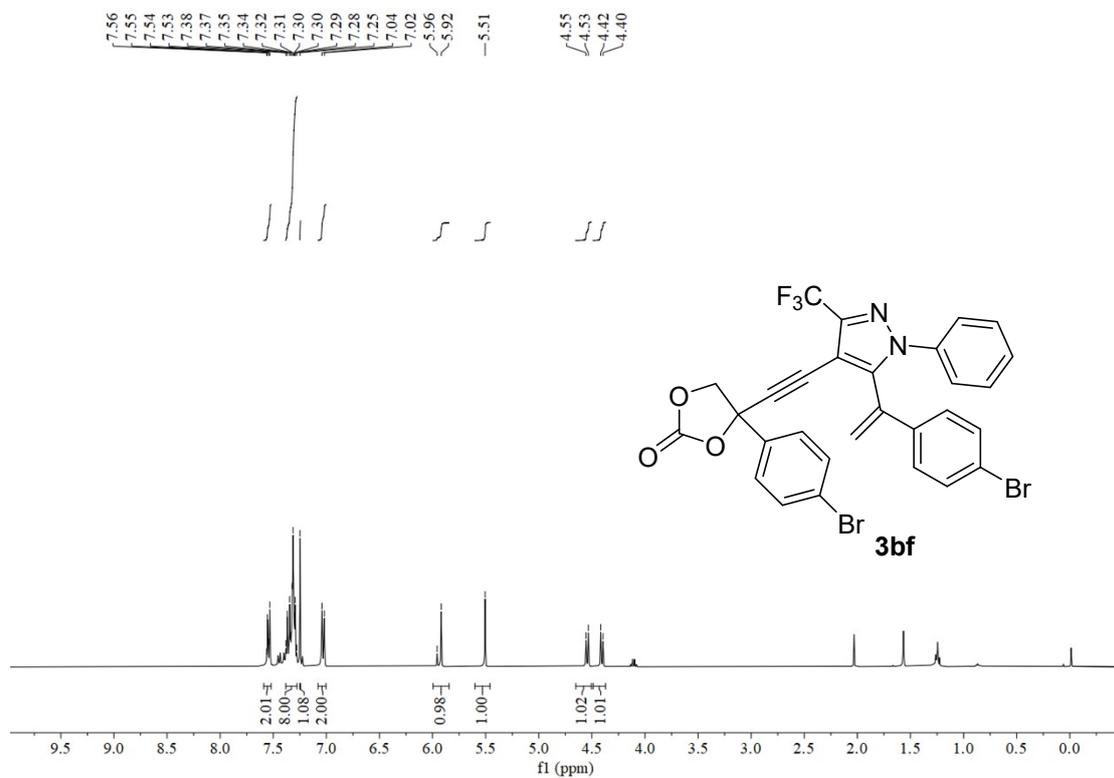
**<sup>13</sup>C{<sup>1</sup>H} NMR of 3be (101 MHz, CDCl<sub>3</sub>)**



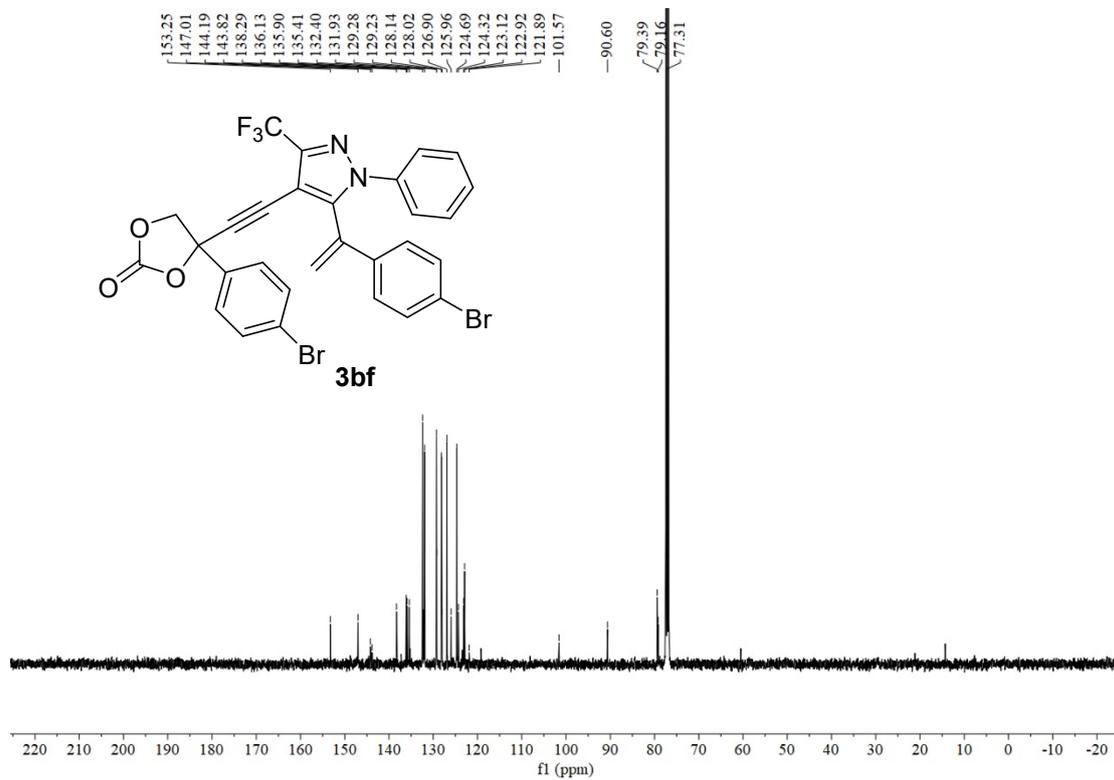
**<sup>19</sup>F NMR of 3be (376 MHz, CDCl<sub>3</sub>)**



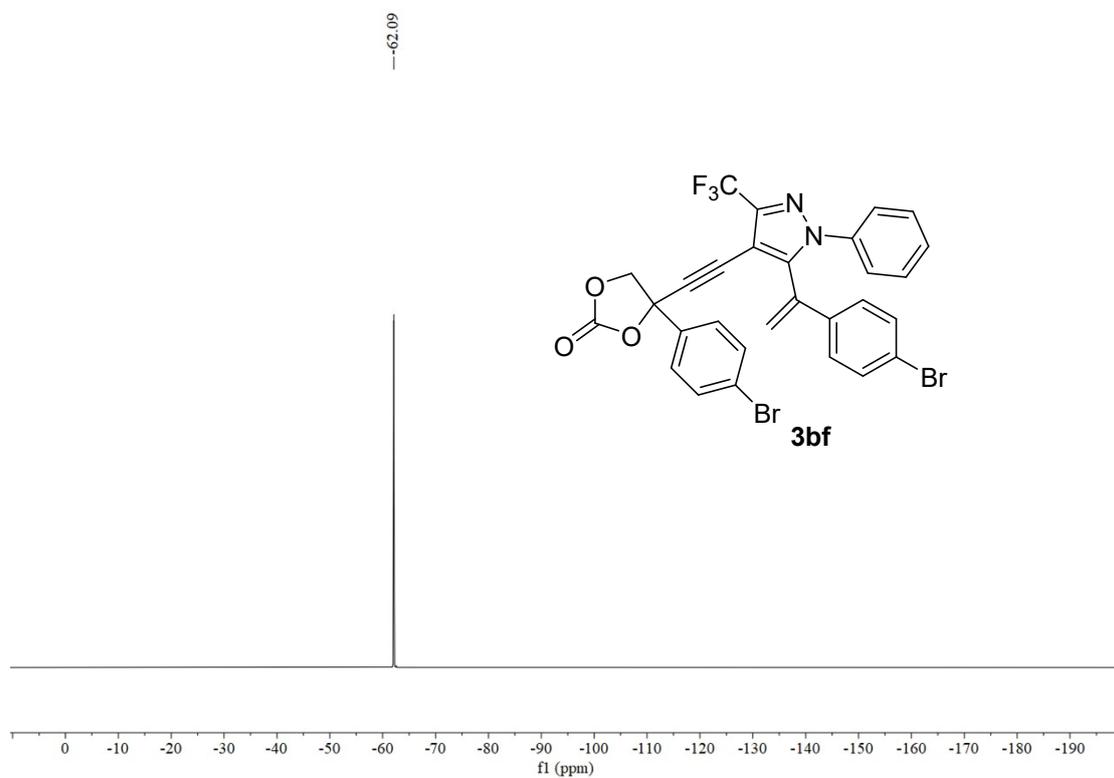
**<sup>1</sup>H NMR of 3bf (400 MHz, CDCl<sub>3</sub>)**



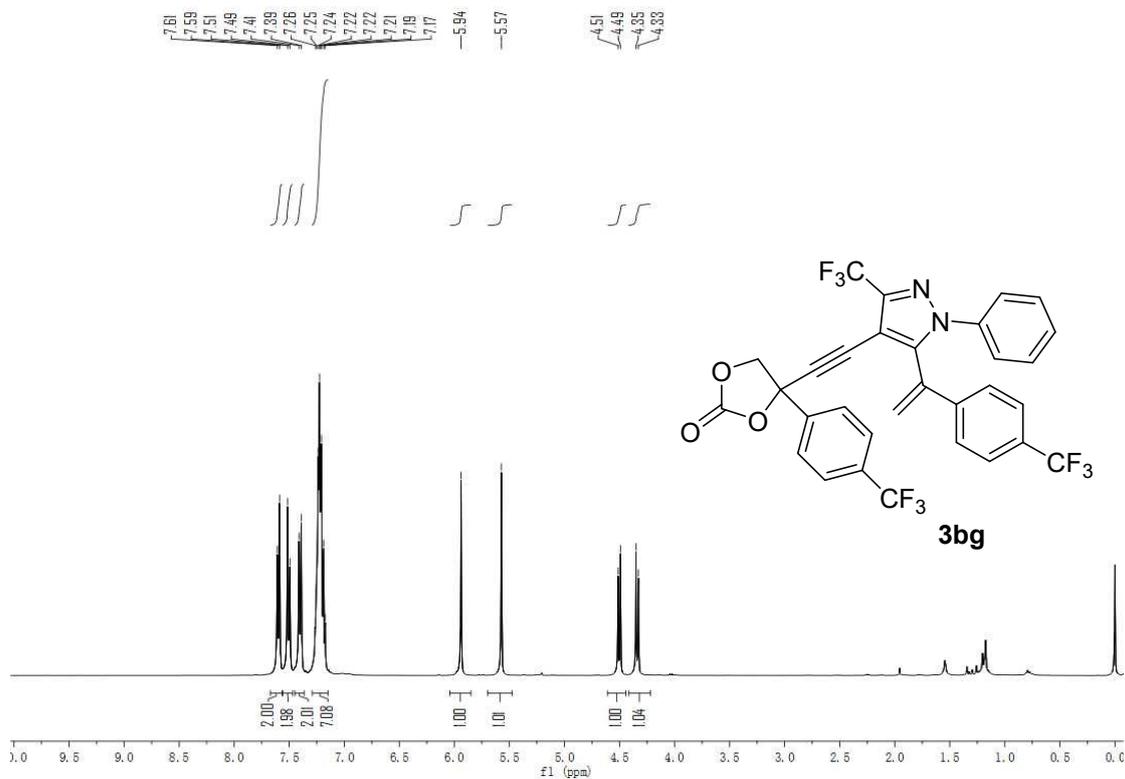
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 3bf (101 MHz,  $\text{CDCl}_3$ )**



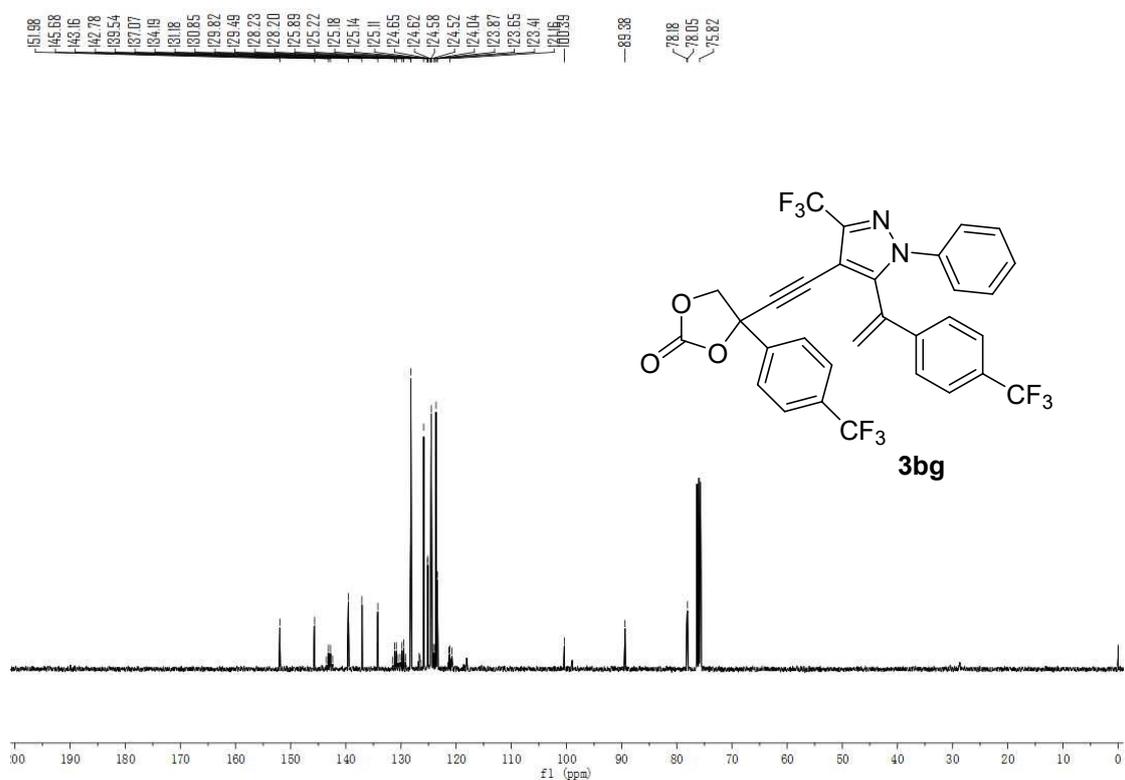
**$^{19}\text{F}$  NMR of 3bf (376 MHz,  $\text{CDCl}_3$ )**



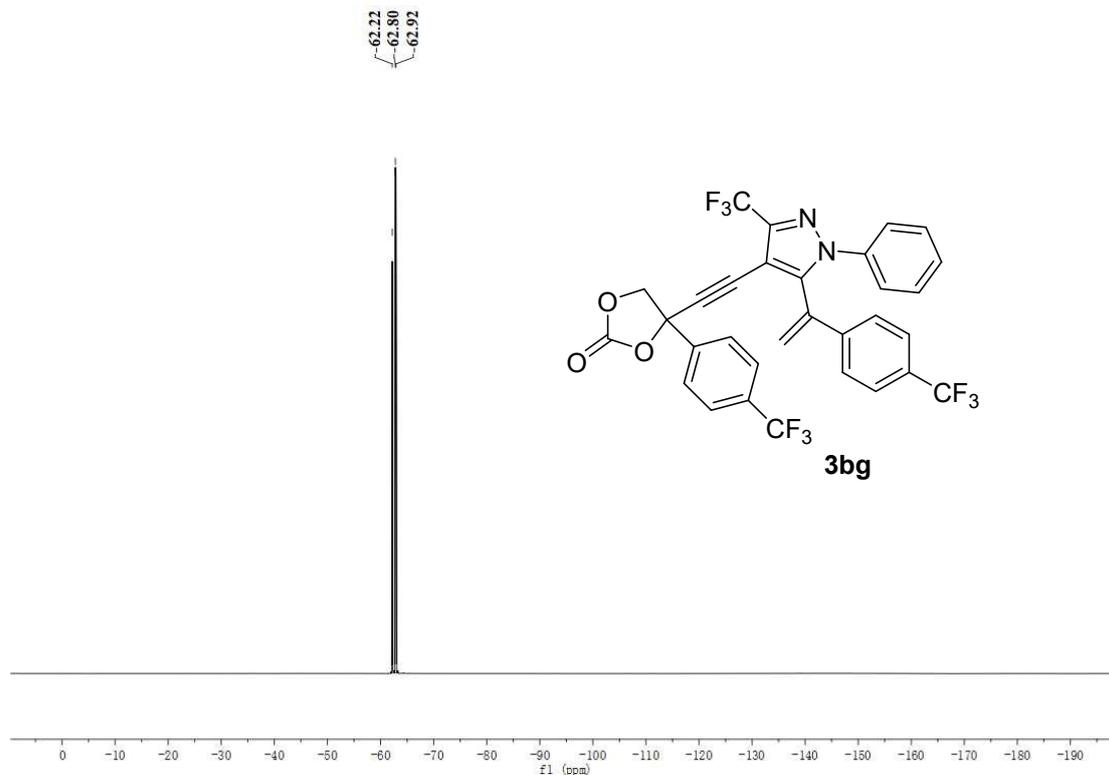
**<sup>1</sup>H NMR of 3bg (400 MHz, CDCl<sub>3</sub>)**



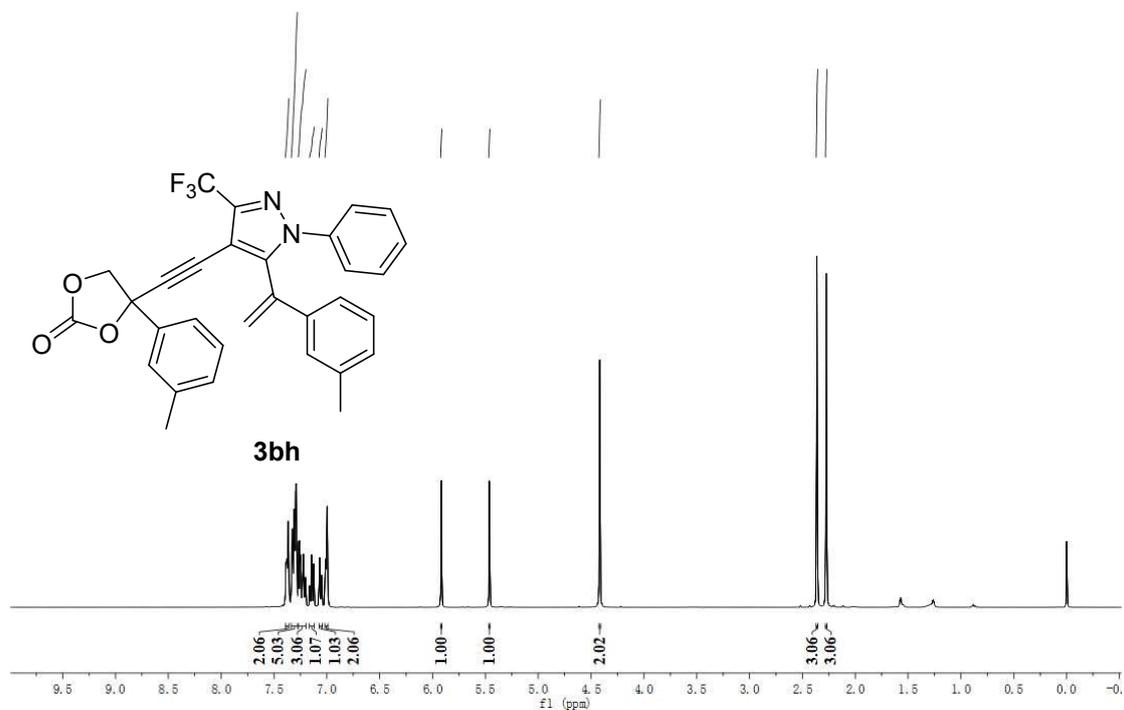
**<sup>13</sup>C{<sup>1</sup>H} NMR of 3bg (101 MHz, CDCl<sub>3</sub>)**



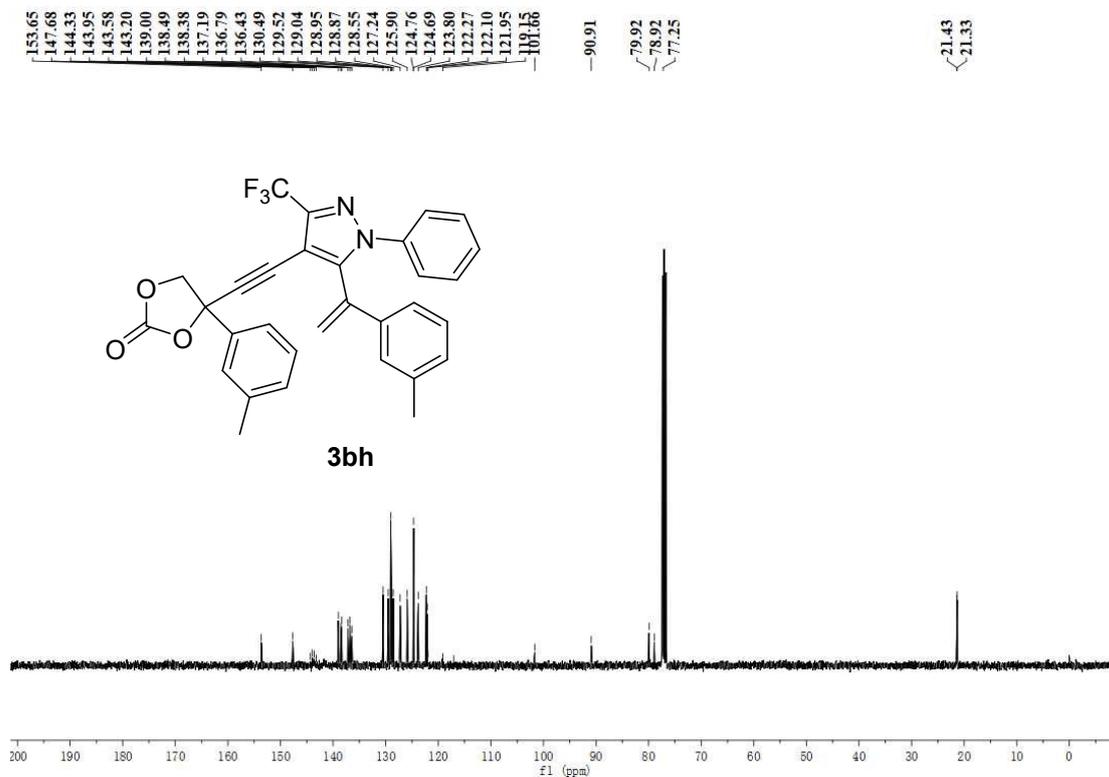
**<sup>19</sup>F NMR of 3bg (376 MHz, CDCl<sub>3</sub>)**



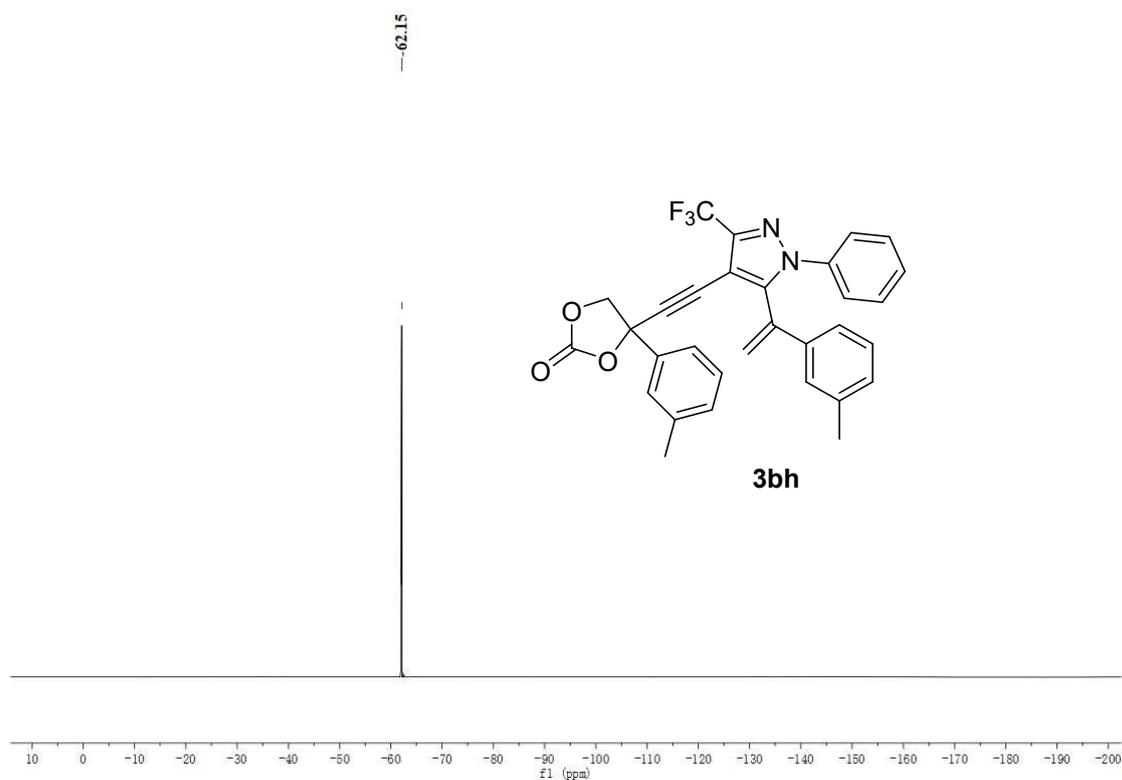
**<sup>1</sup>H NMR of 3bh (500 MHz, CDCl<sub>3</sub>)**



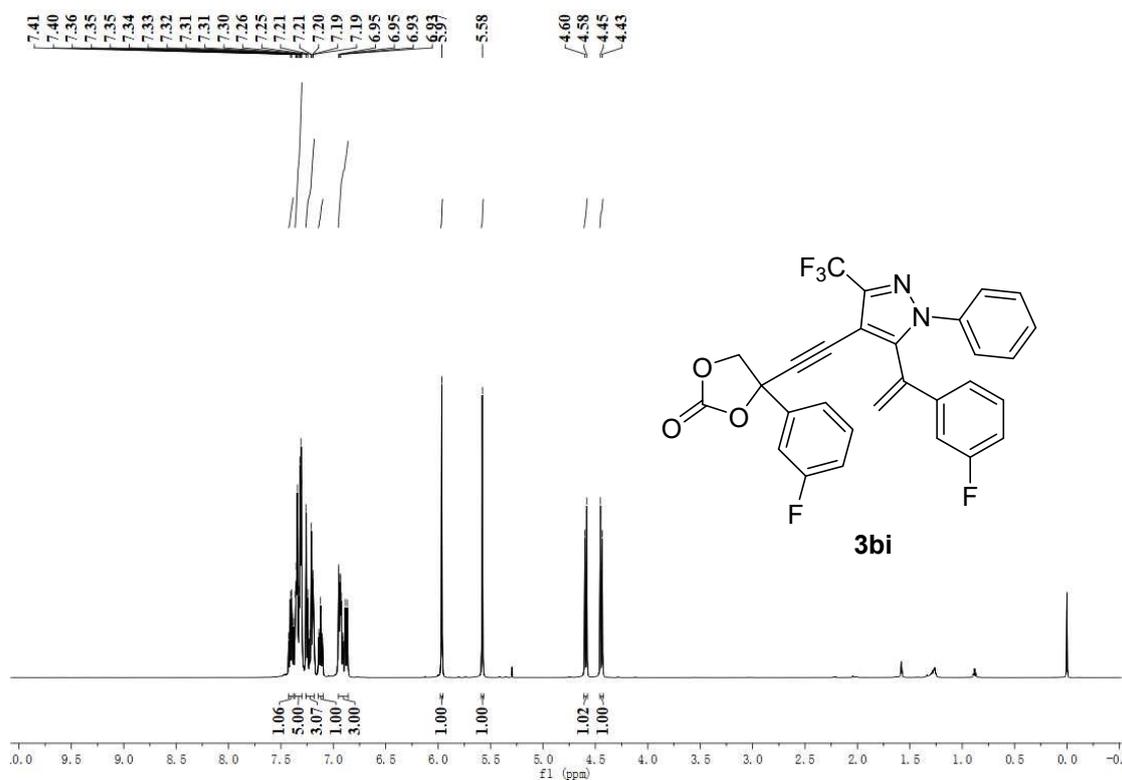
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 3bh (126 MHz,  $\text{CDCl}_3$ )**



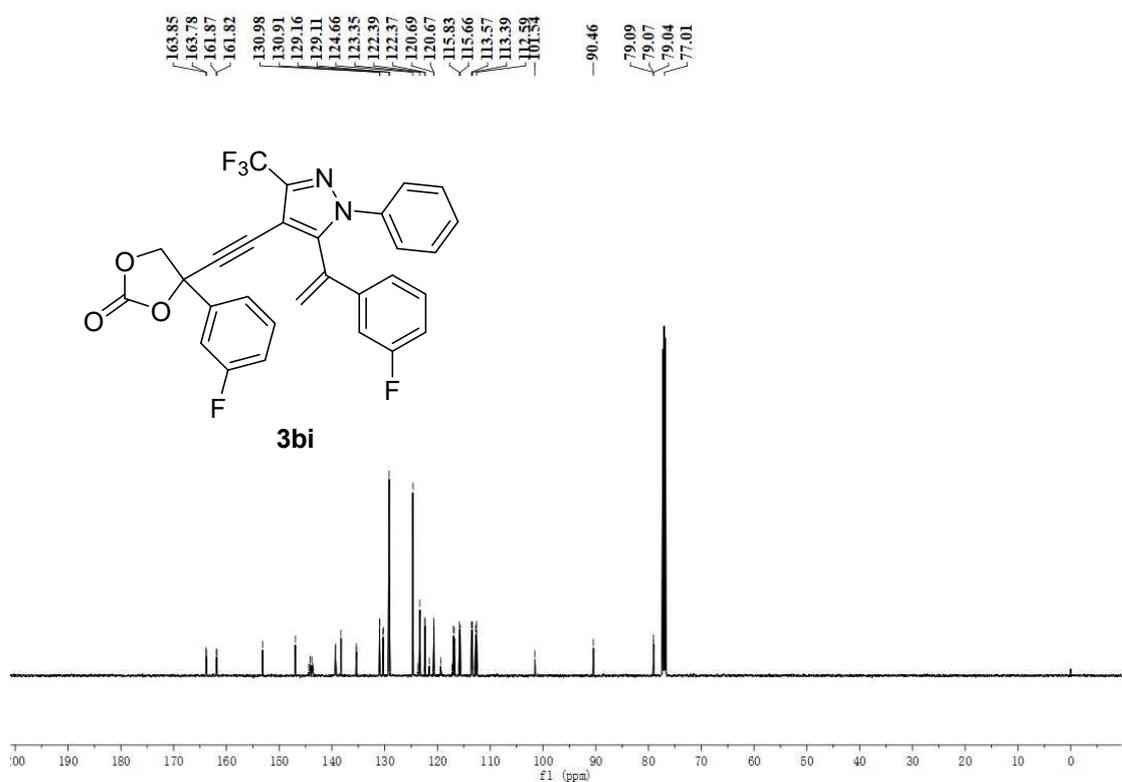
**$^{19}\text{F}$  NMR of 3bh (471 MHz,  $\text{CDCl}_3$ )**



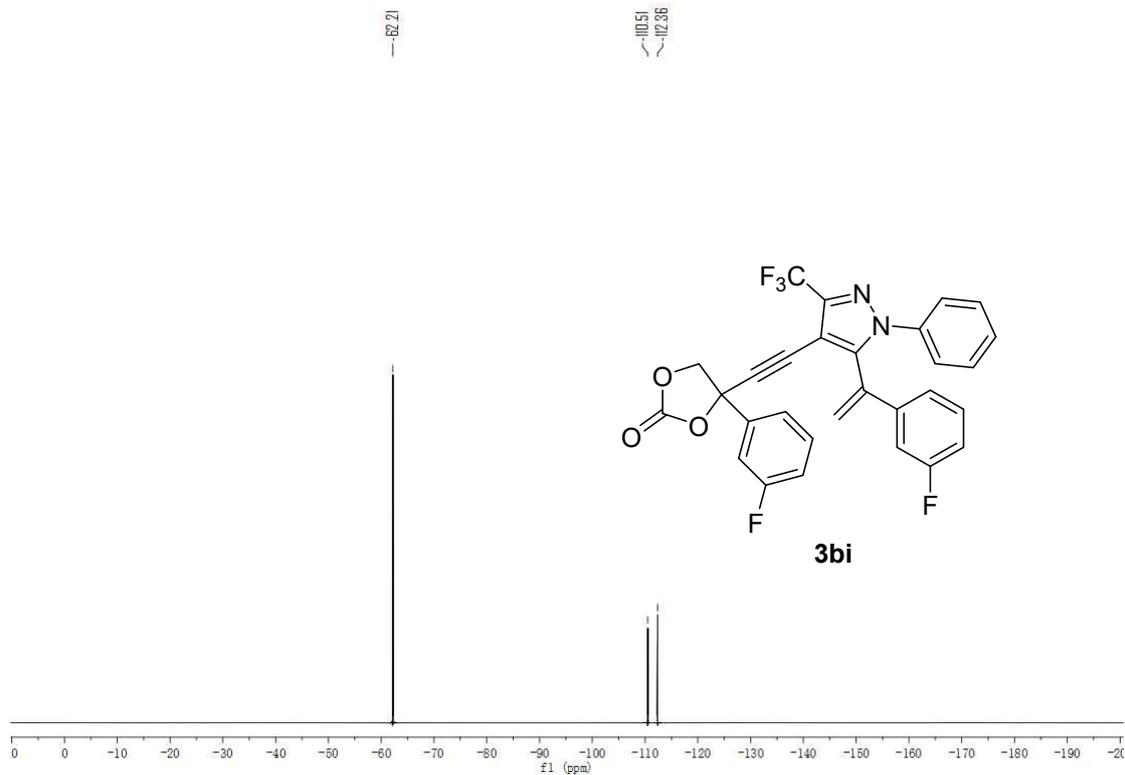
**<sup>1</sup>H NMR of 3bi (500 MHz, CDCl<sub>3</sub>)**



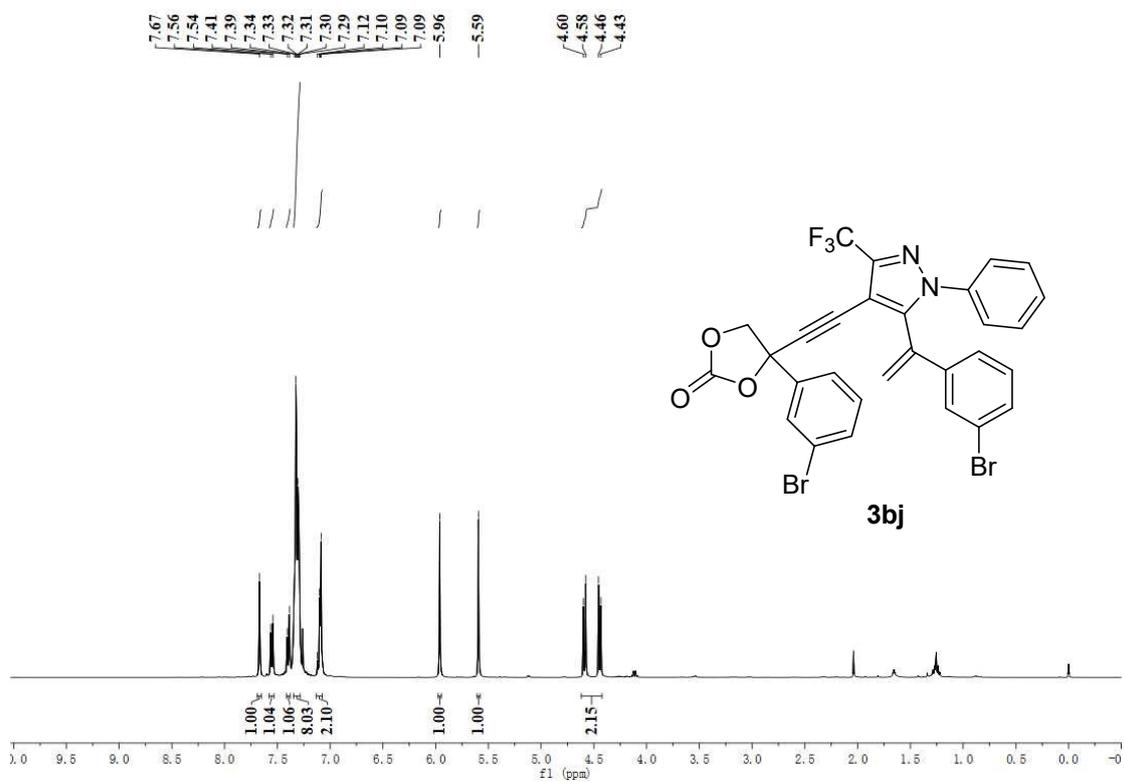
**<sup>13</sup>C{<sup>1</sup>H} NMR of 3bi (126 MHz, CDCl<sub>3</sub>)**



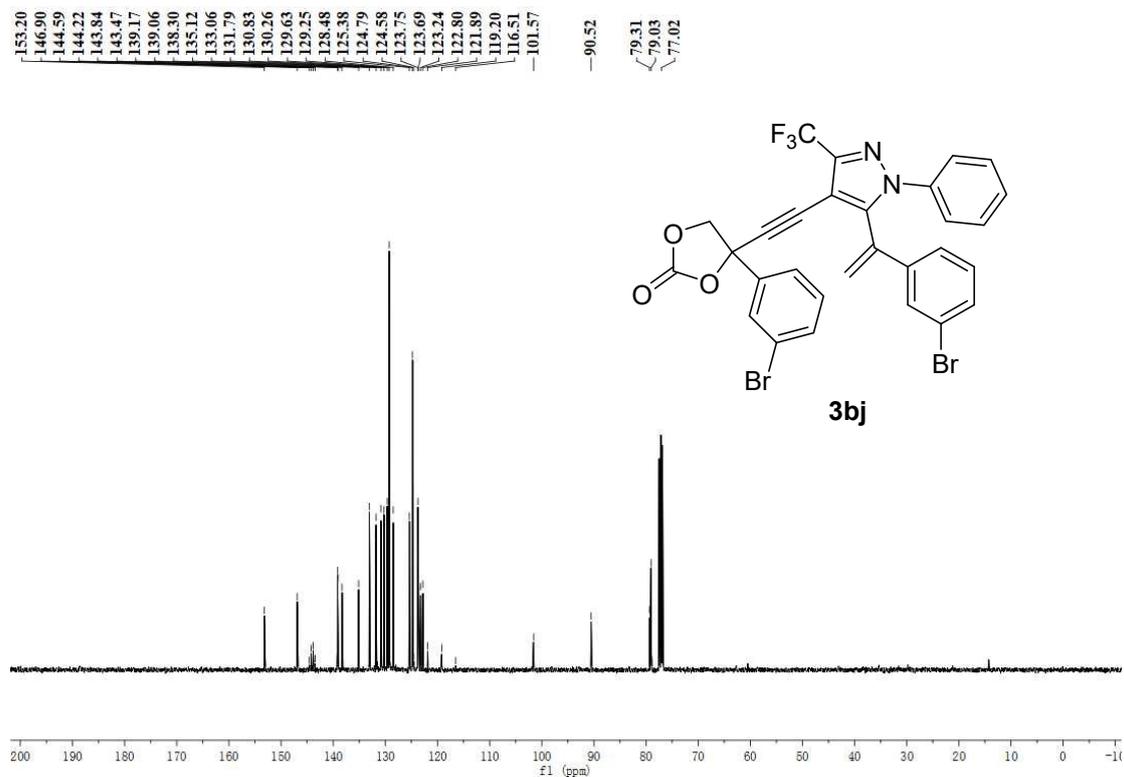
**<sup>19</sup>F NMR of 3bi (471 MHz, CDCl<sub>3</sub>)**



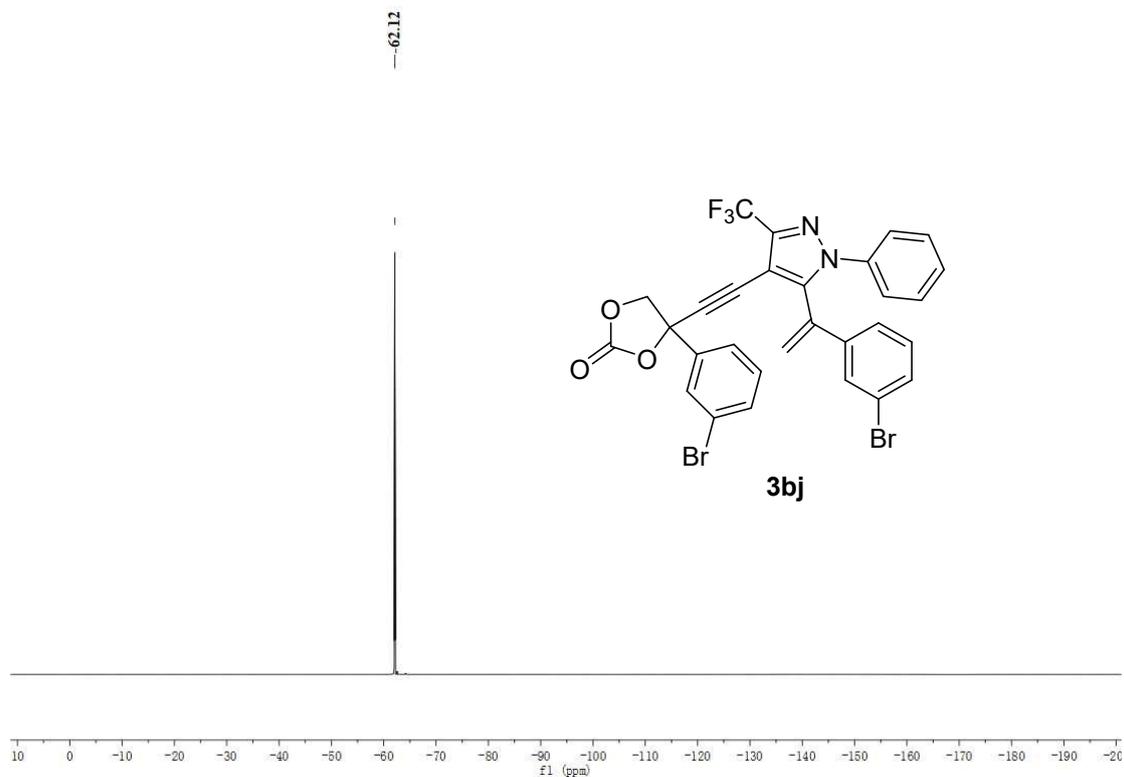
**<sup>1</sup>H NMR of 3bj (400 MHz, CDCl<sub>3</sub>)**



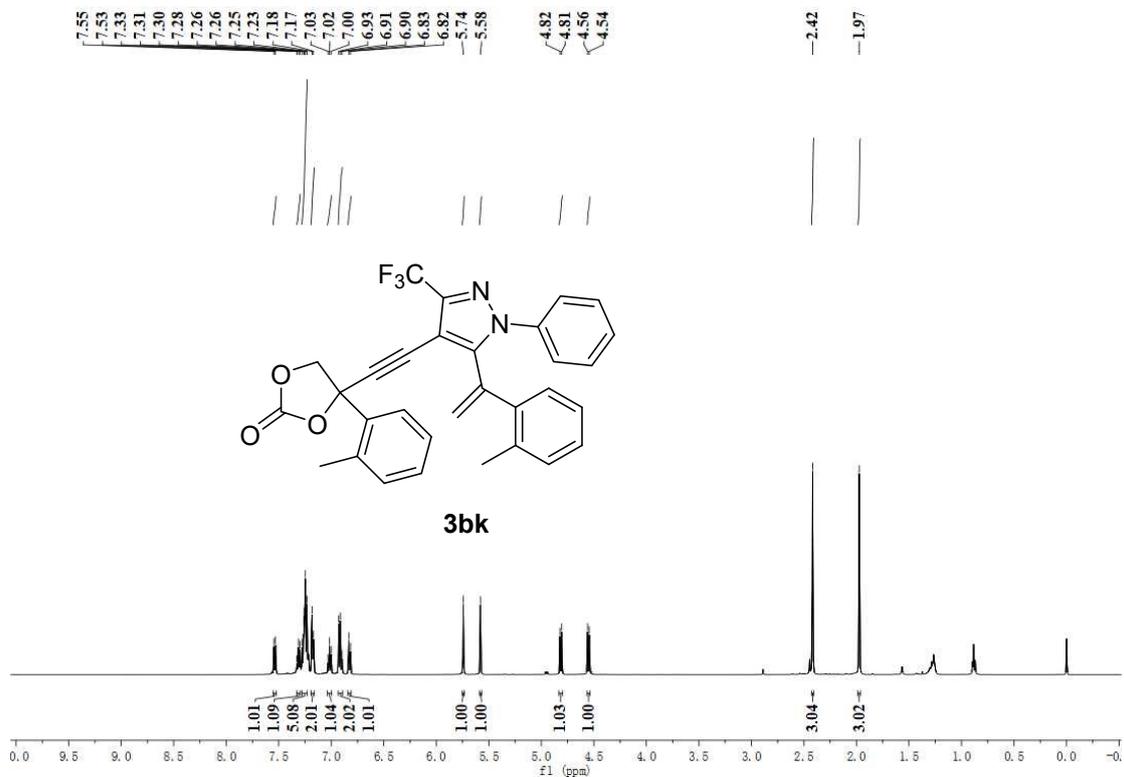
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 3bj (101 MHz,  $\text{CDCl}_3$ )**



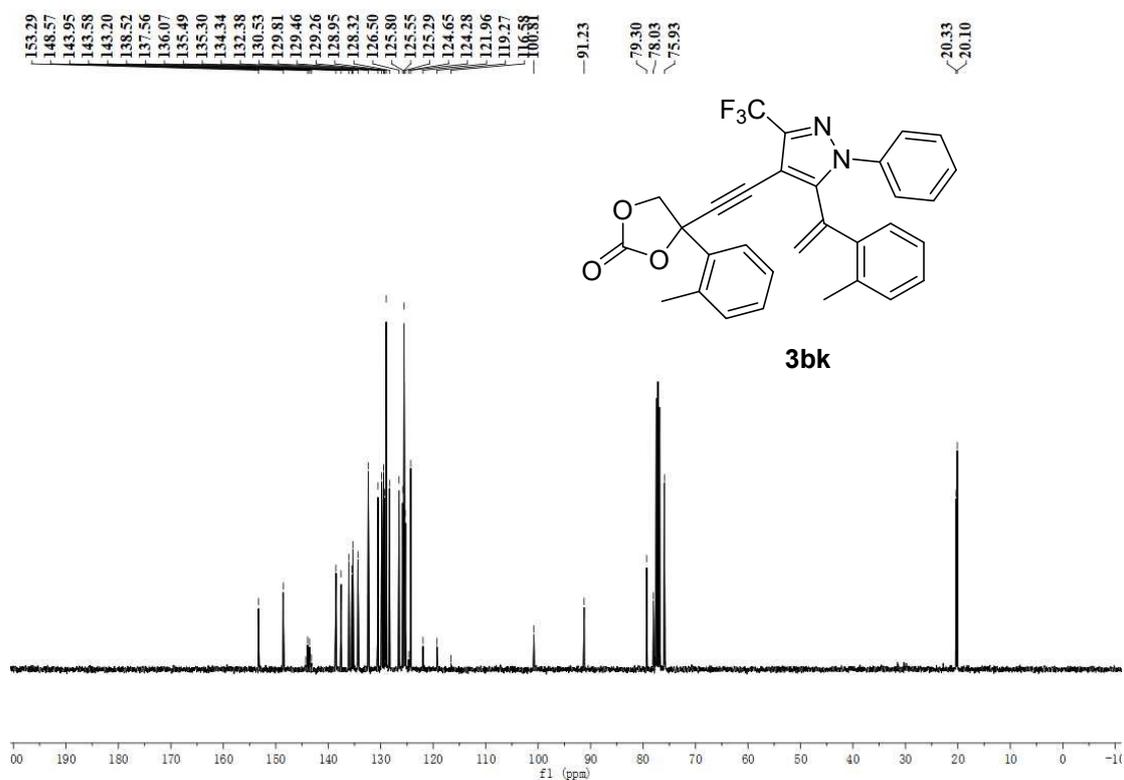
**$^{19}\text{F}$  NMR of 3bj (376 MHz,  $\text{CDCl}_3$ )**



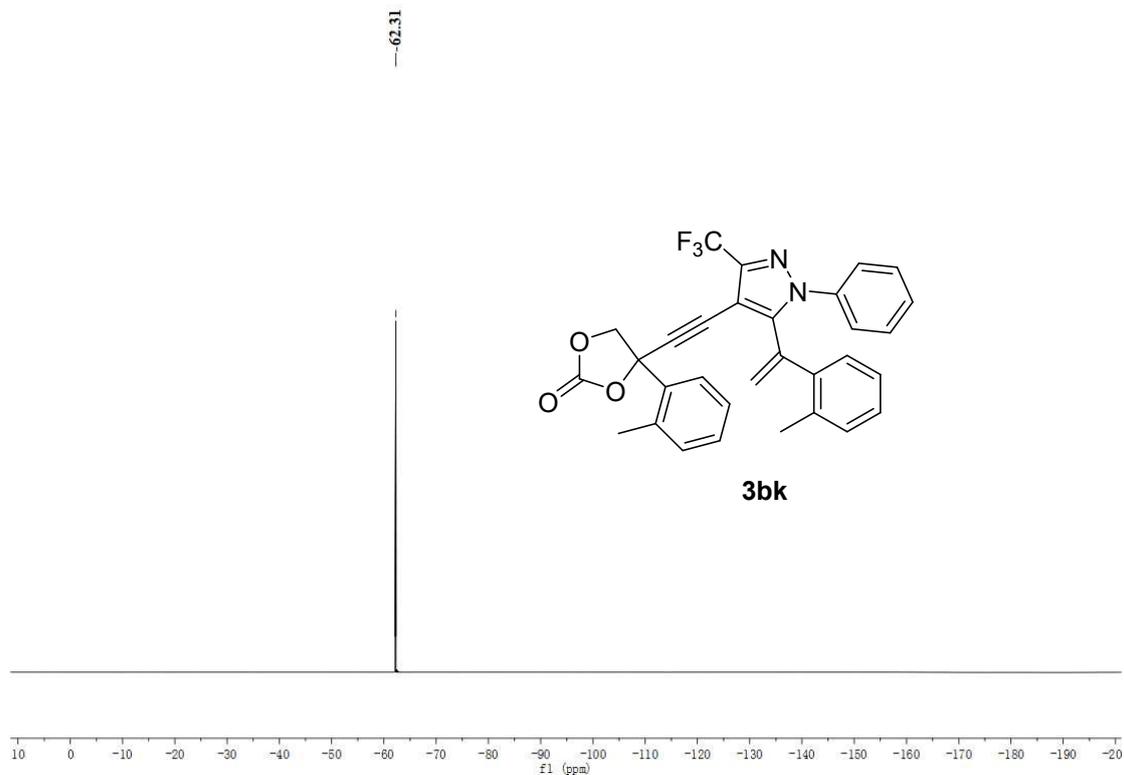
**<sup>1</sup>H NMR of 3bk (500 MHz, CDCl<sub>3</sub>)**



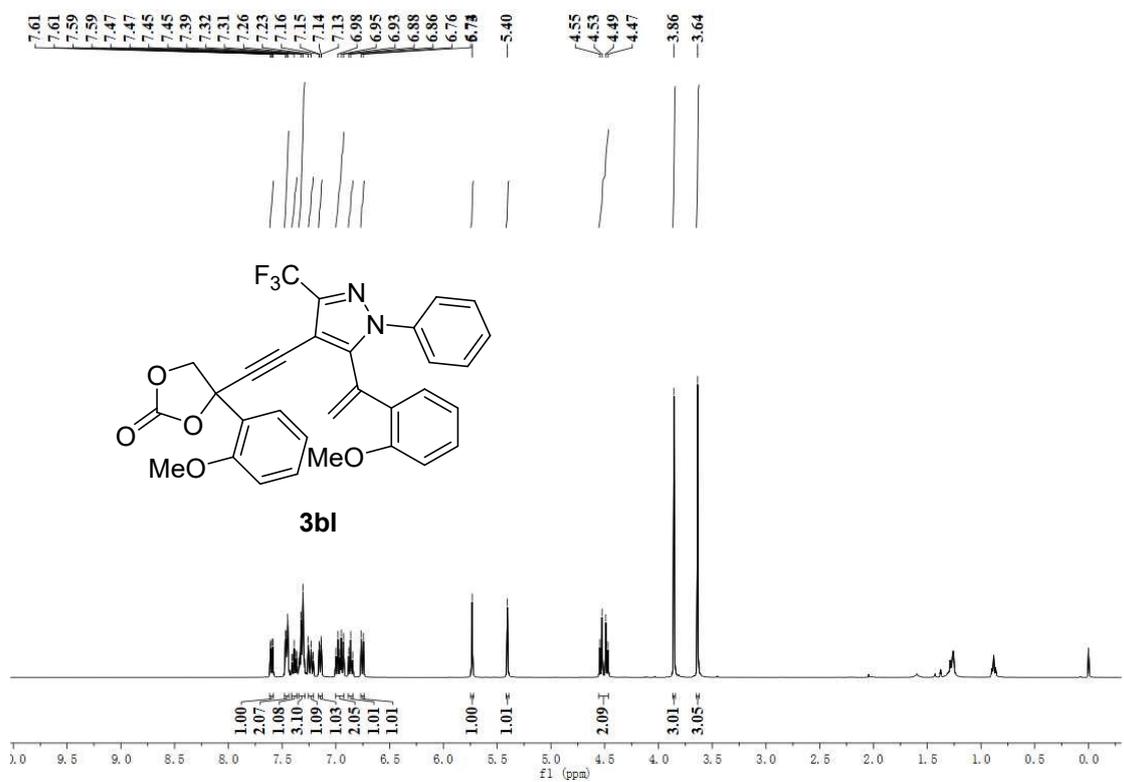
**<sup>13</sup>C{<sup>1</sup>H} NMR of 3bk (126 MHz, CDCl<sub>3</sub>)**



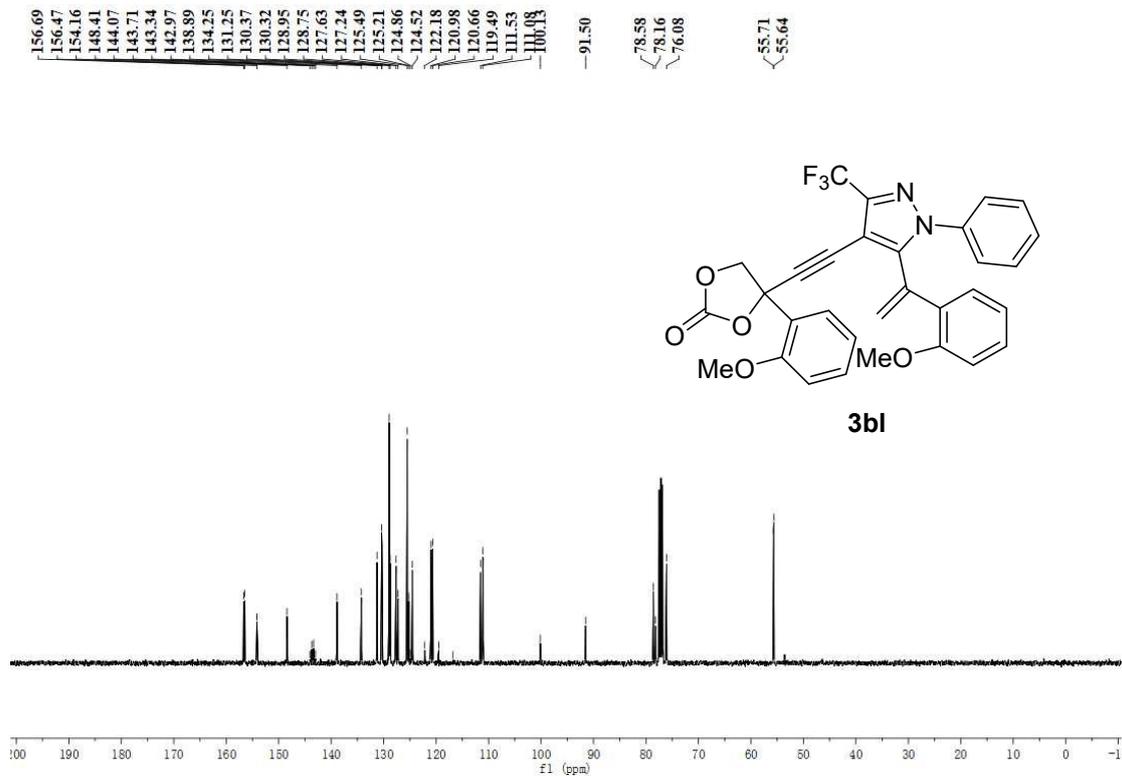
**<sup>19</sup>F NMR of 3bk (471 MHz, CDCl<sub>3</sub>)**



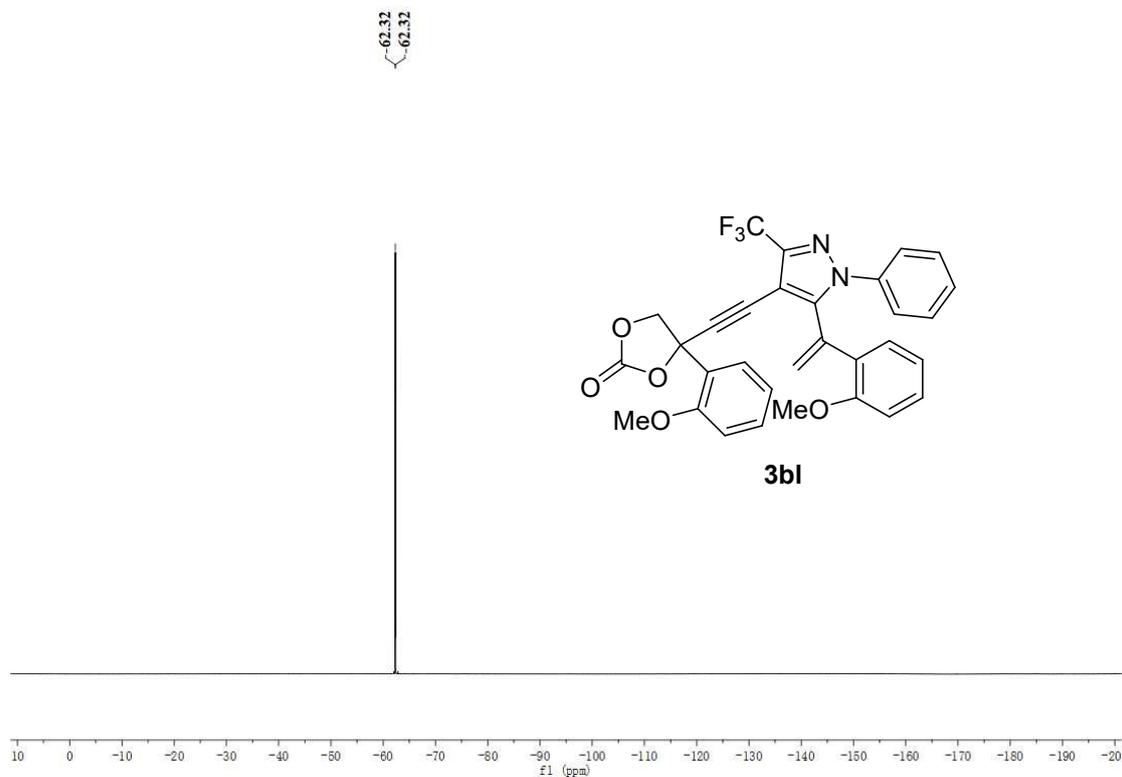
**<sup>1</sup>H NMR of 3bl (400 MHz, CDCl<sub>3</sub>)**



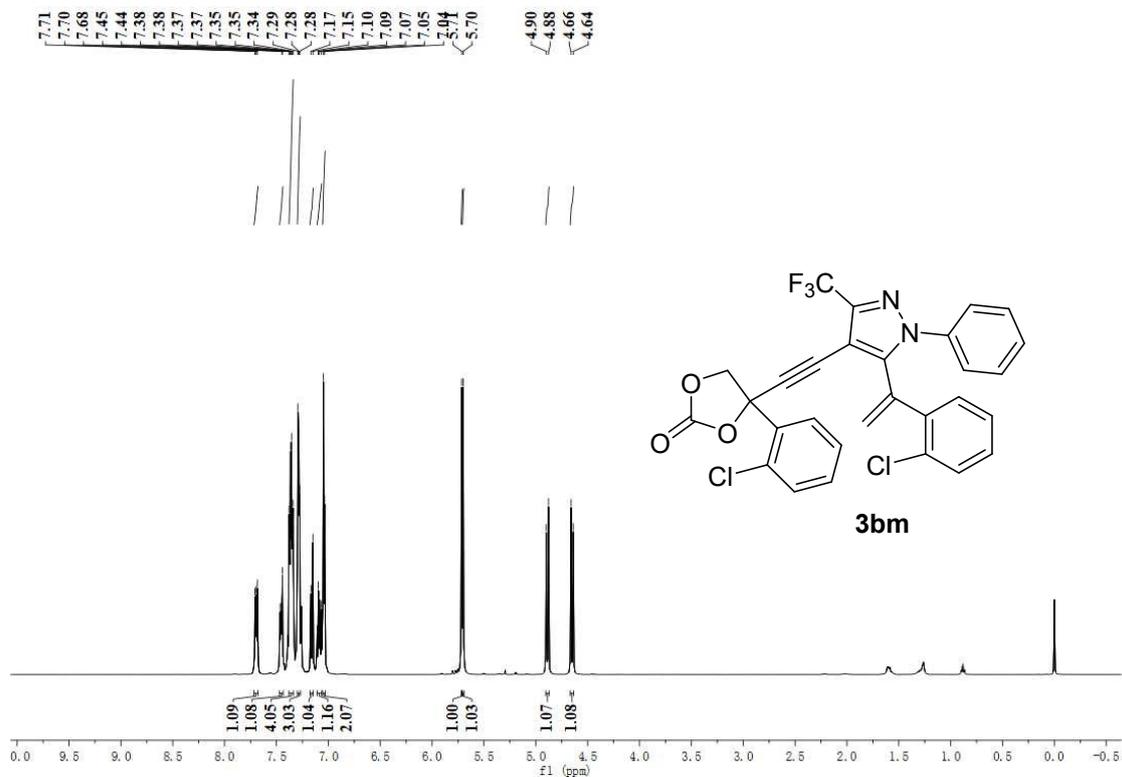
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 3bl (101 MHz,  $\text{CDCl}_3$ )**



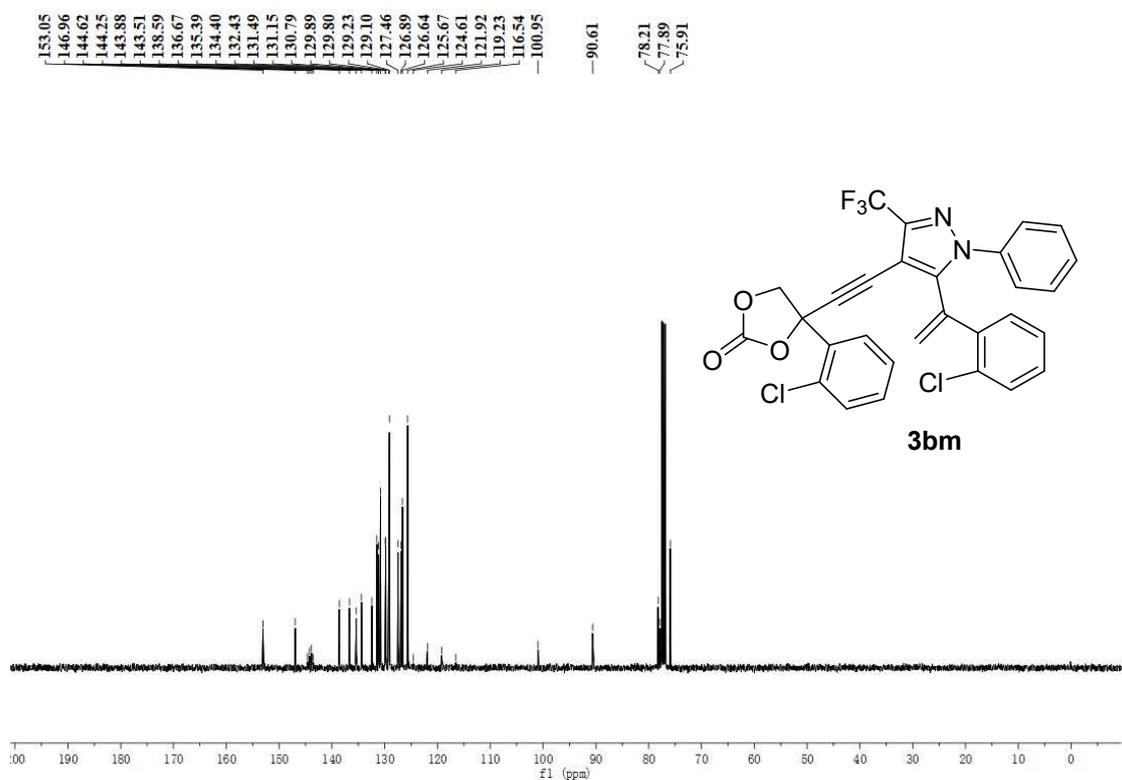
**$^{19}\text{F}$  NMR of 3bl (376 MHz,  $\text{CDCl}_3$ )**



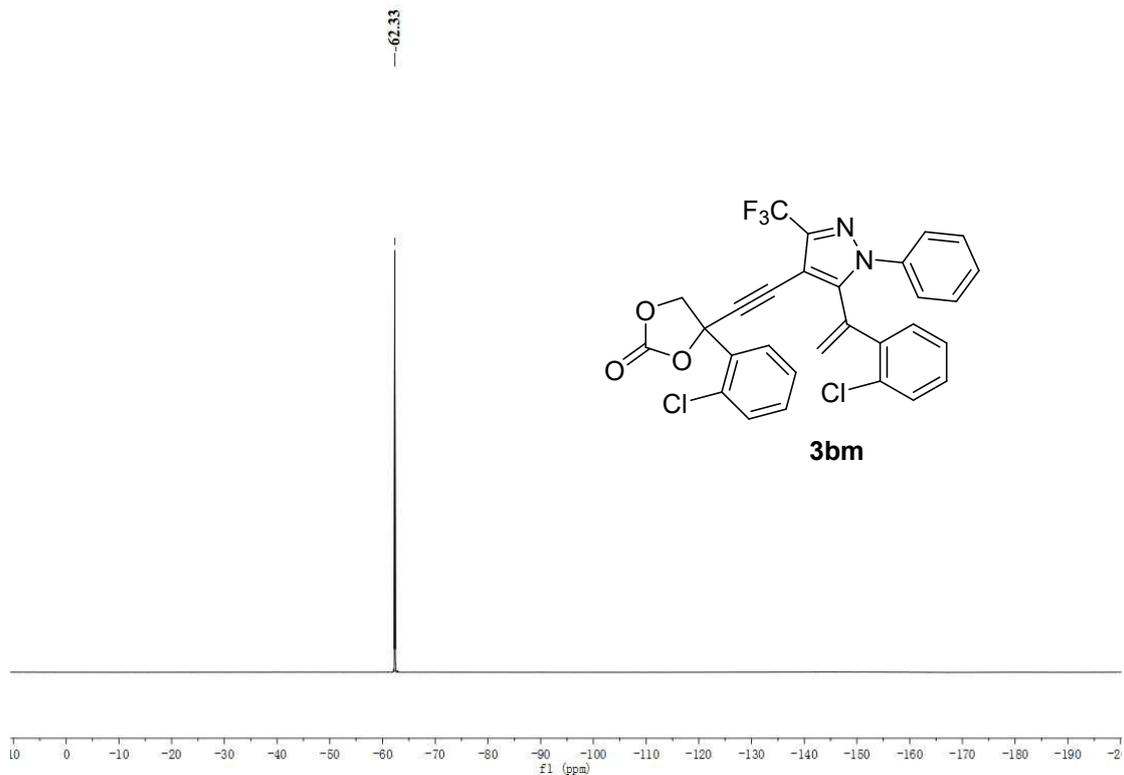
**<sup>1</sup>H NMR of 3bm (400 MHz, CDCl<sub>3</sub>)**



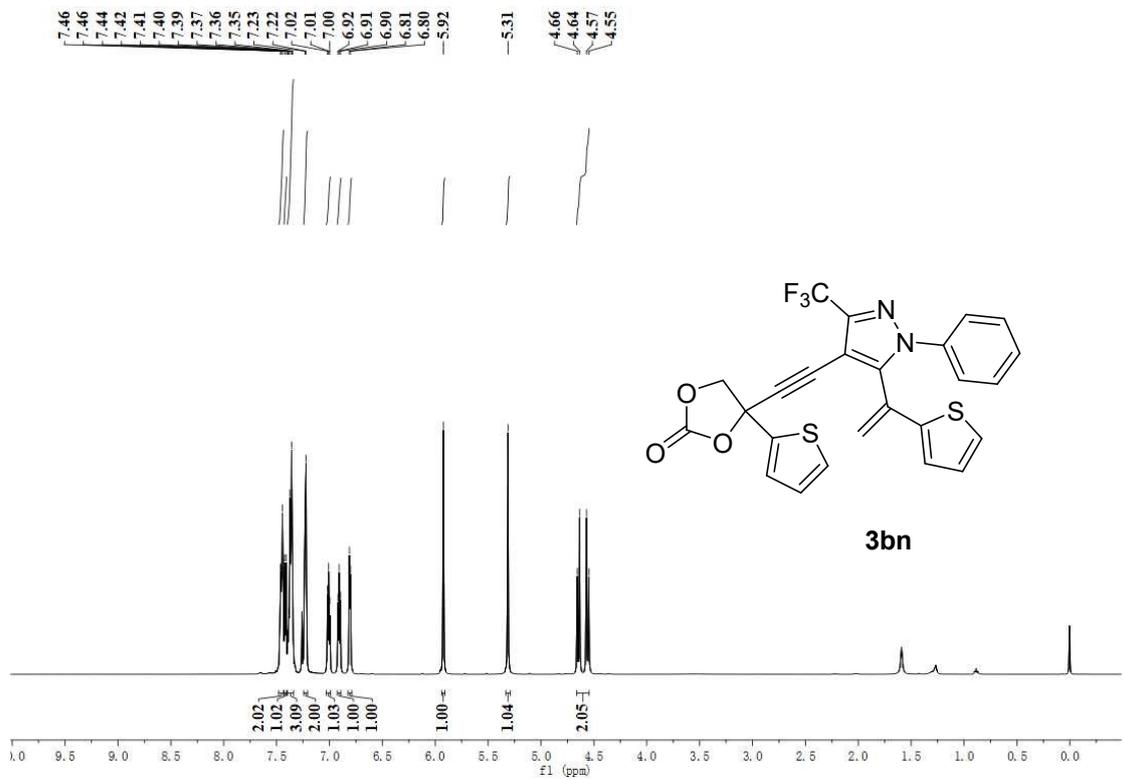
**<sup>13</sup>C{<sup>1</sup>H} NMR of 3bm (101 MHz, CDCl<sub>3</sub>)**



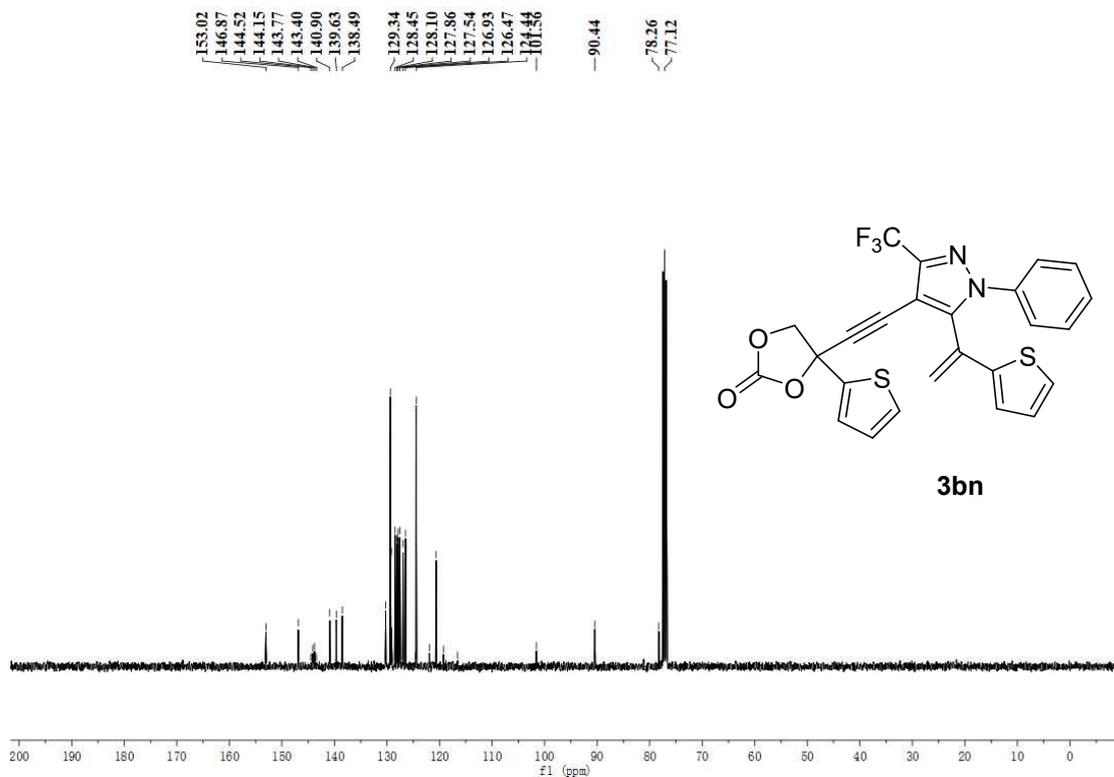
**<sup>19</sup>F NMR of 3bm (376 MHz, CDCl<sub>3</sub>)**



**<sup>1</sup>H NMR of 3bn (400 MHz, CDCl<sub>3</sub>)**



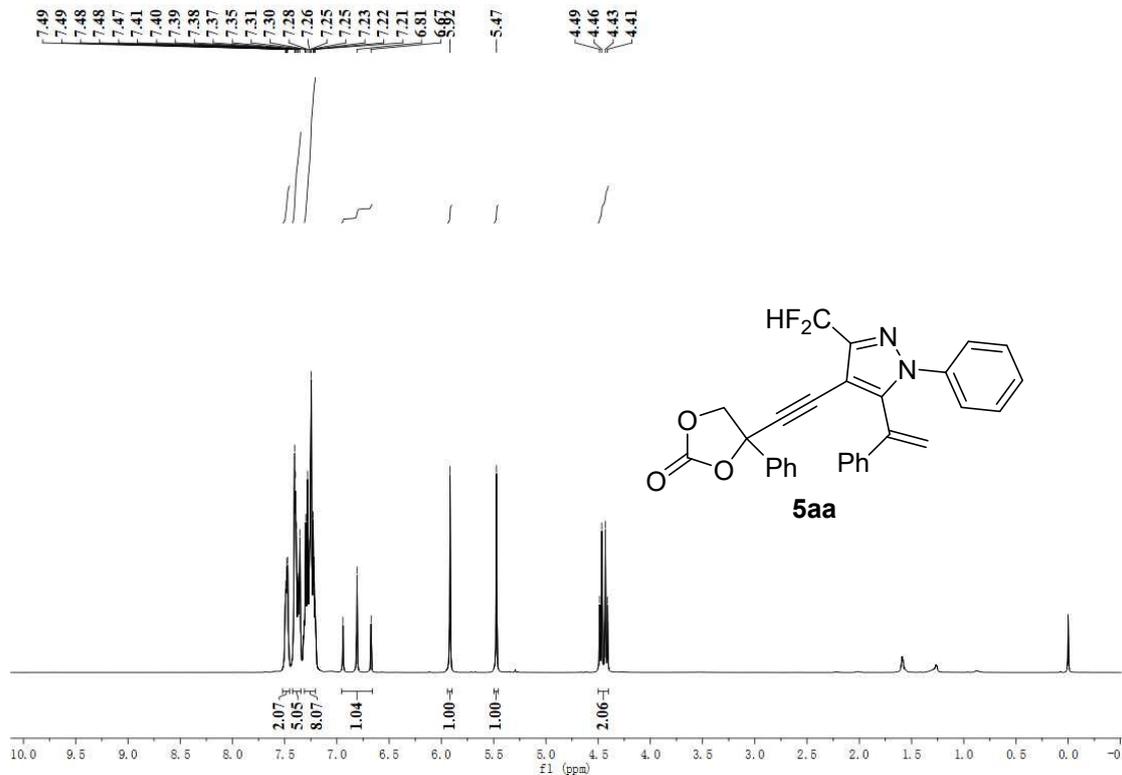
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 3bn (101 MHz,  $\text{CDCl}_3$ )**



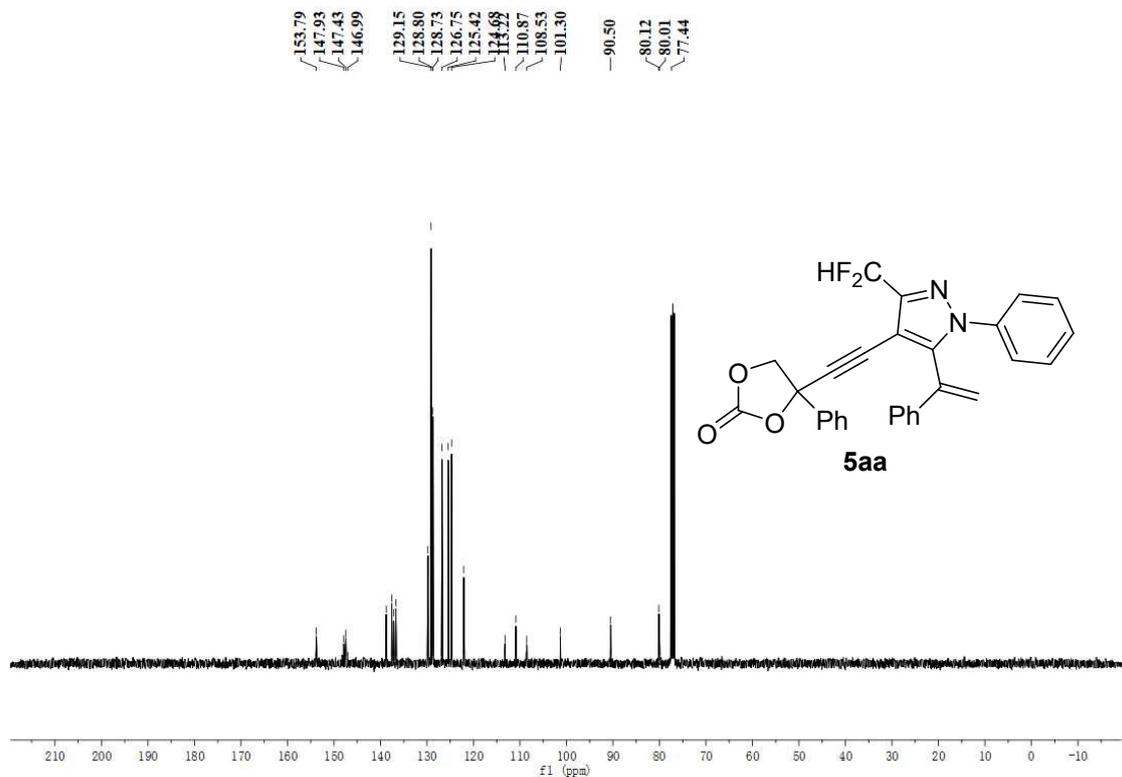
**$^{19}\text{F}$  NMR of 3bn (376 MHz,  $\text{CDCl}_3$ )**



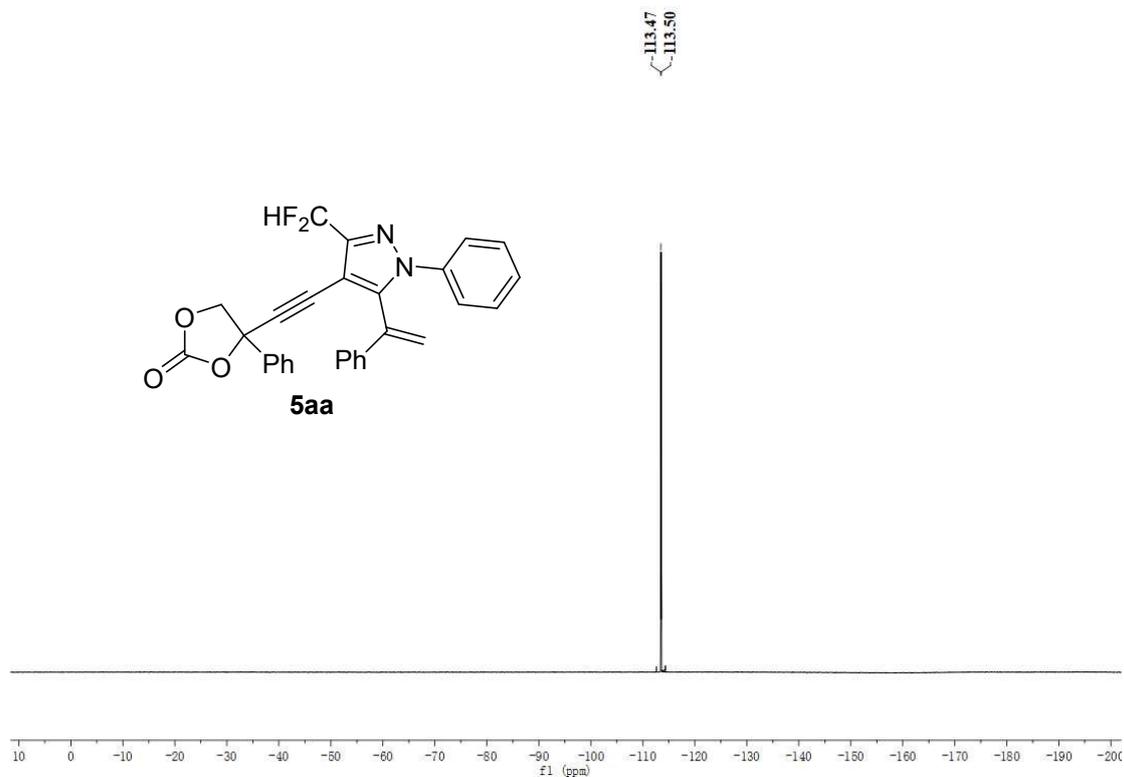
**<sup>1</sup>H NMR of 5aa (400 MHz, CDCl<sub>3</sub>)**



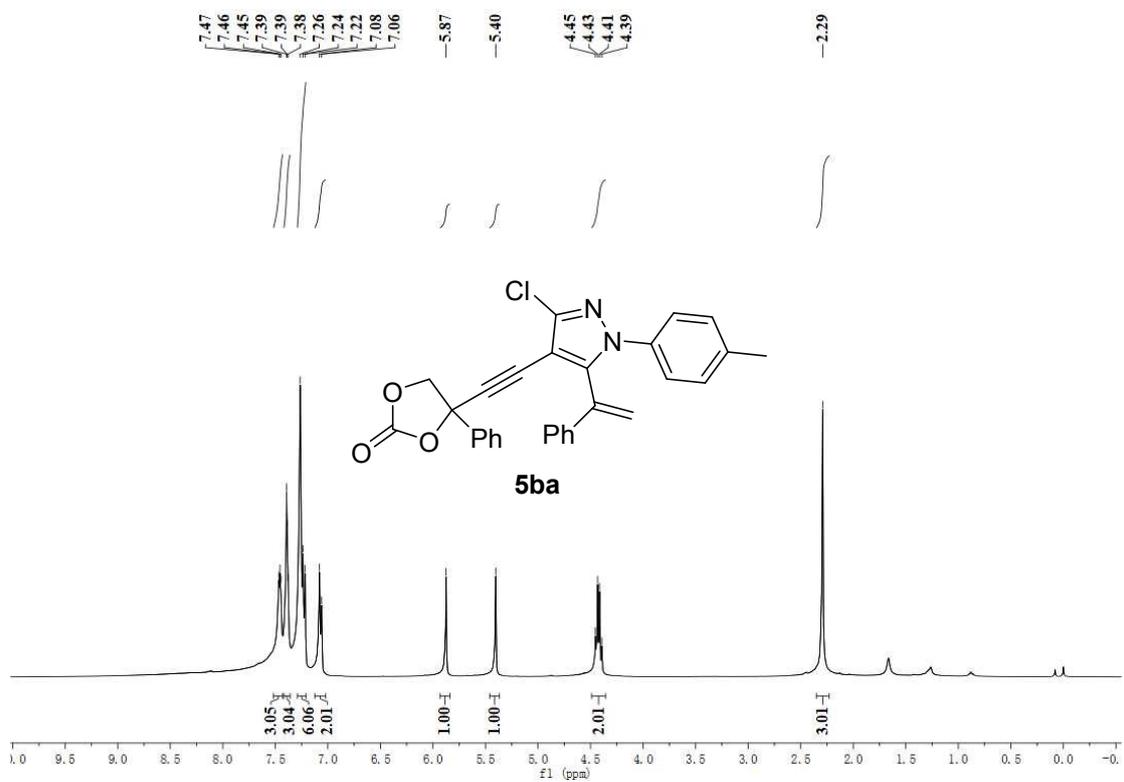
**<sup>13</sup>C{<sup>1</sup>H} NMR of 5aa (101 MHz, CDCl<sub>3</sub>)**



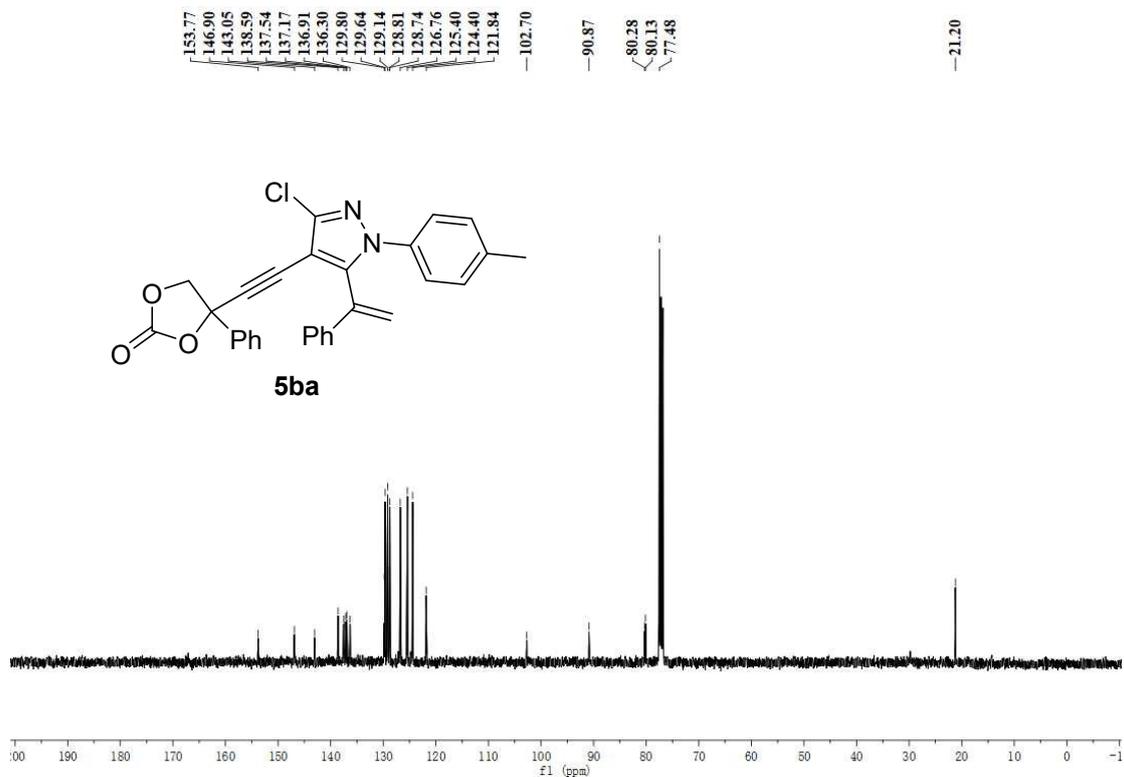
**<sup>19</sup>F NMR of 5aa (376 MHz, CDCl<sub>3</sub>)**



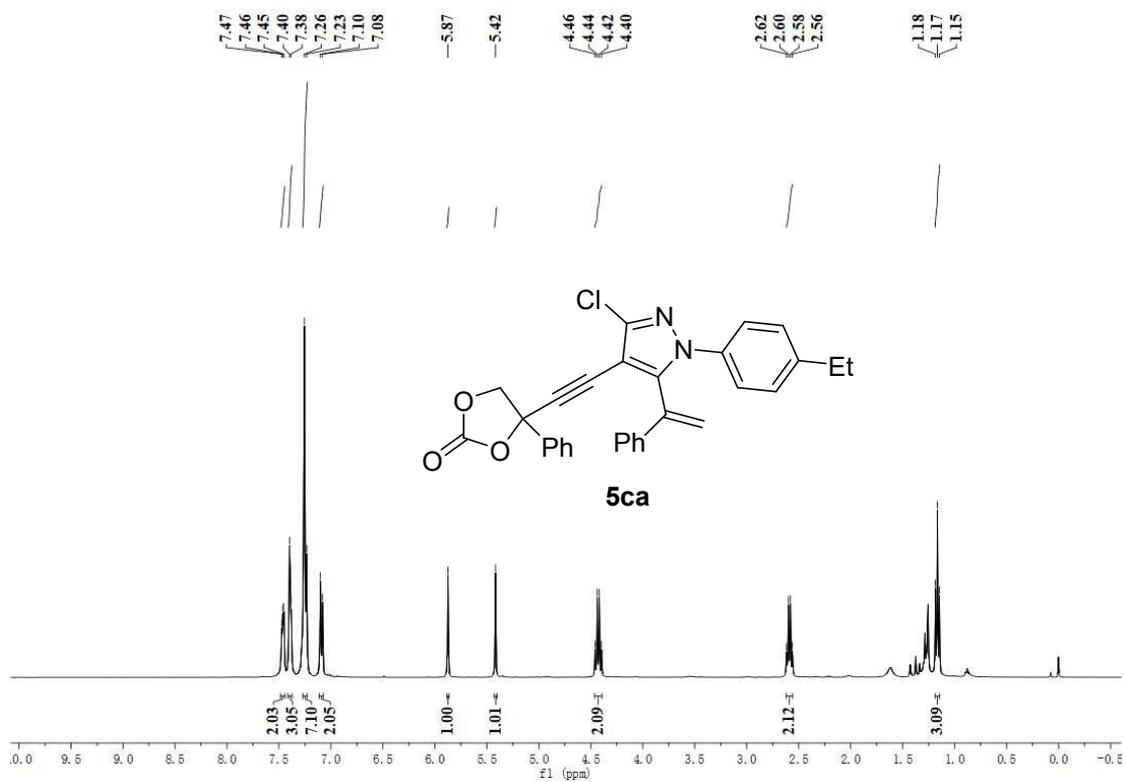
**<sup>1</sup>H NMR of 5ba (400 MHz, CDCl<sub>3</sub>)**



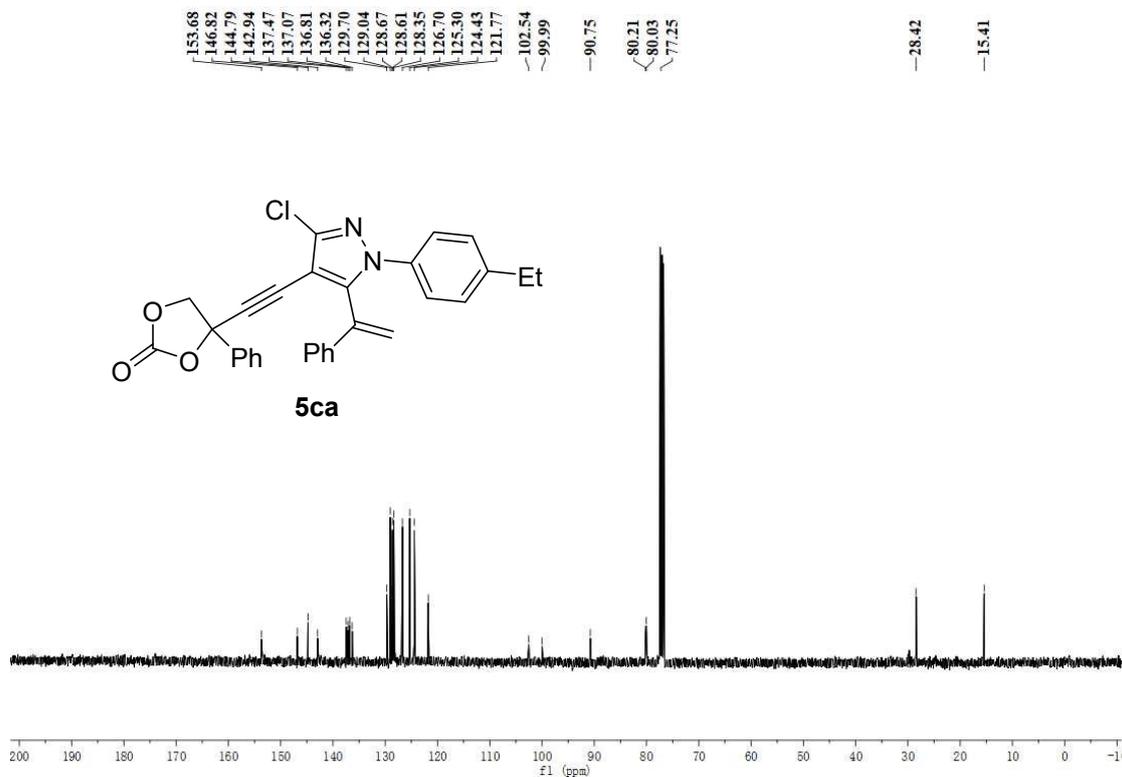
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 5ba (101 MHz,  $\text{CDCl}_3$ )**



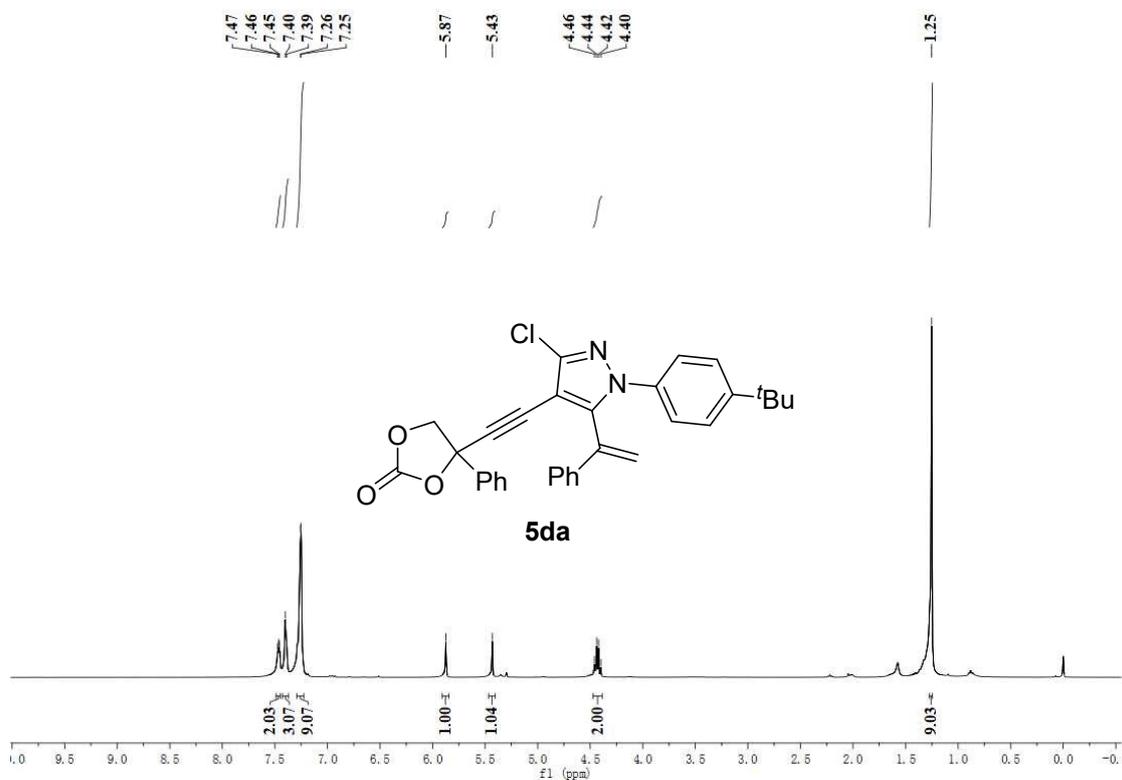
**$^1\text{H}$  NMR of 5ca (400 MHz,  $\text{CDCl}_3$ )**



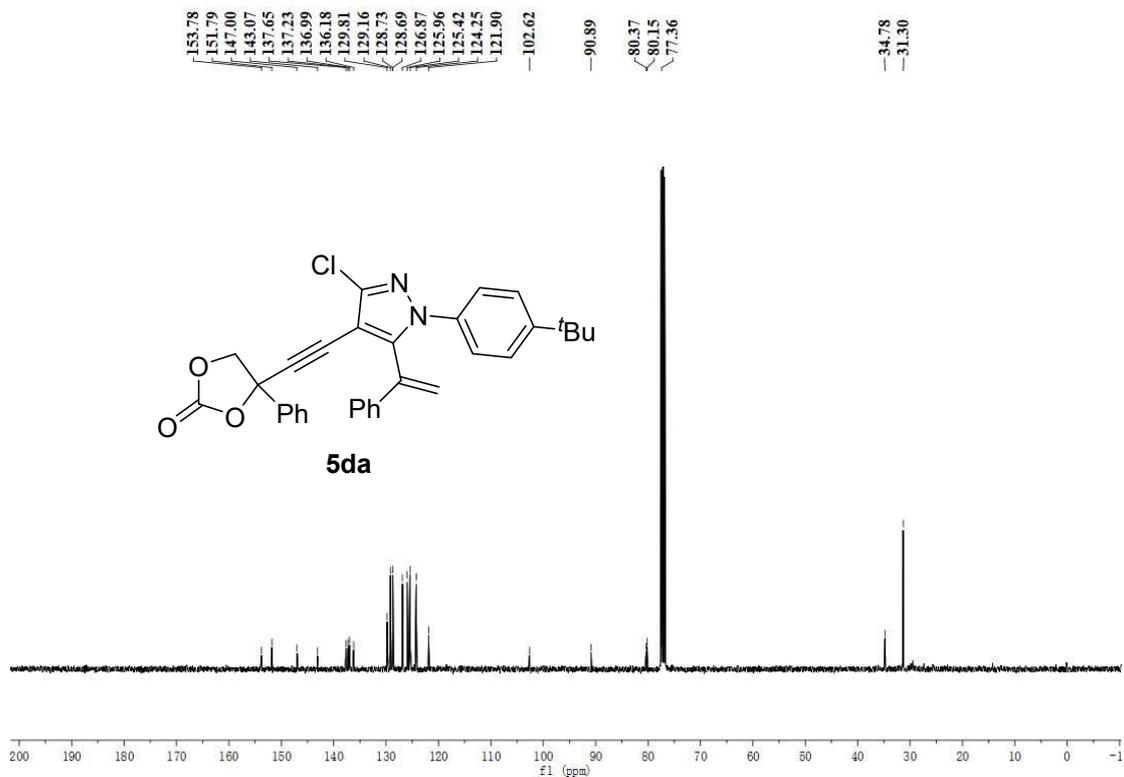
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 5ca (101 MHz,  $\text{CDCl}_3$ )**



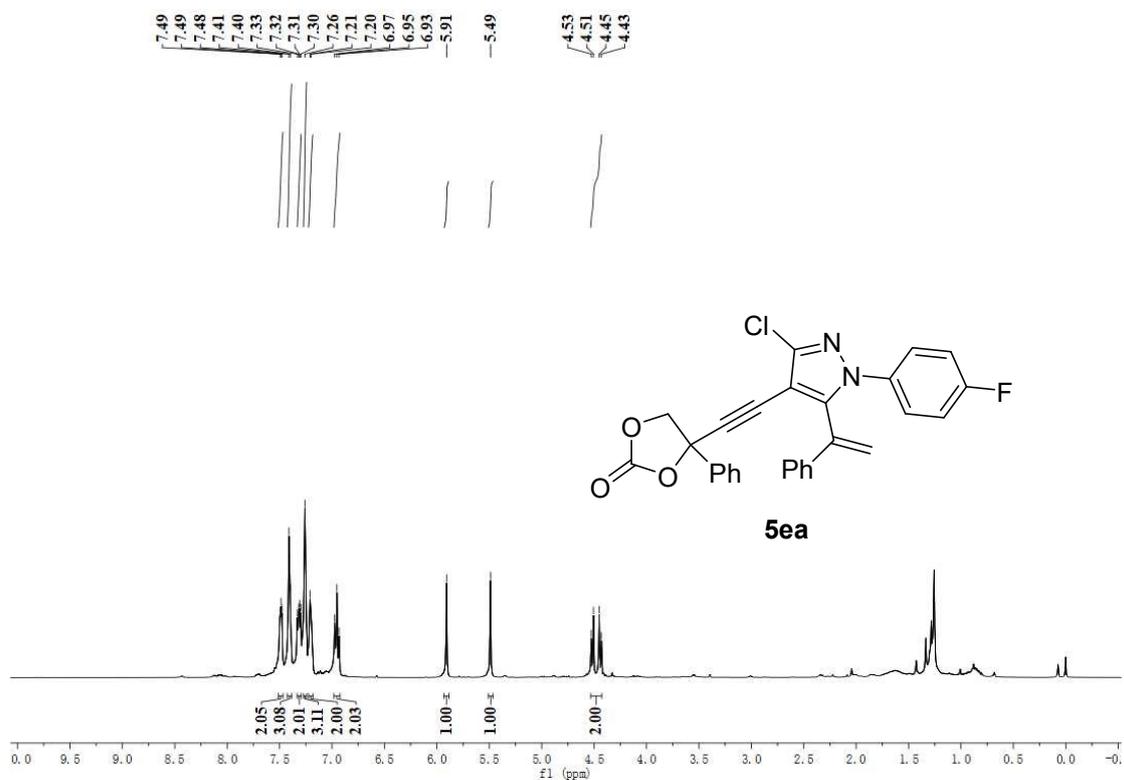
**$^1\text{H}$  NMR of 5da (400 MHz,  $\text{CDCl}_3$ )**



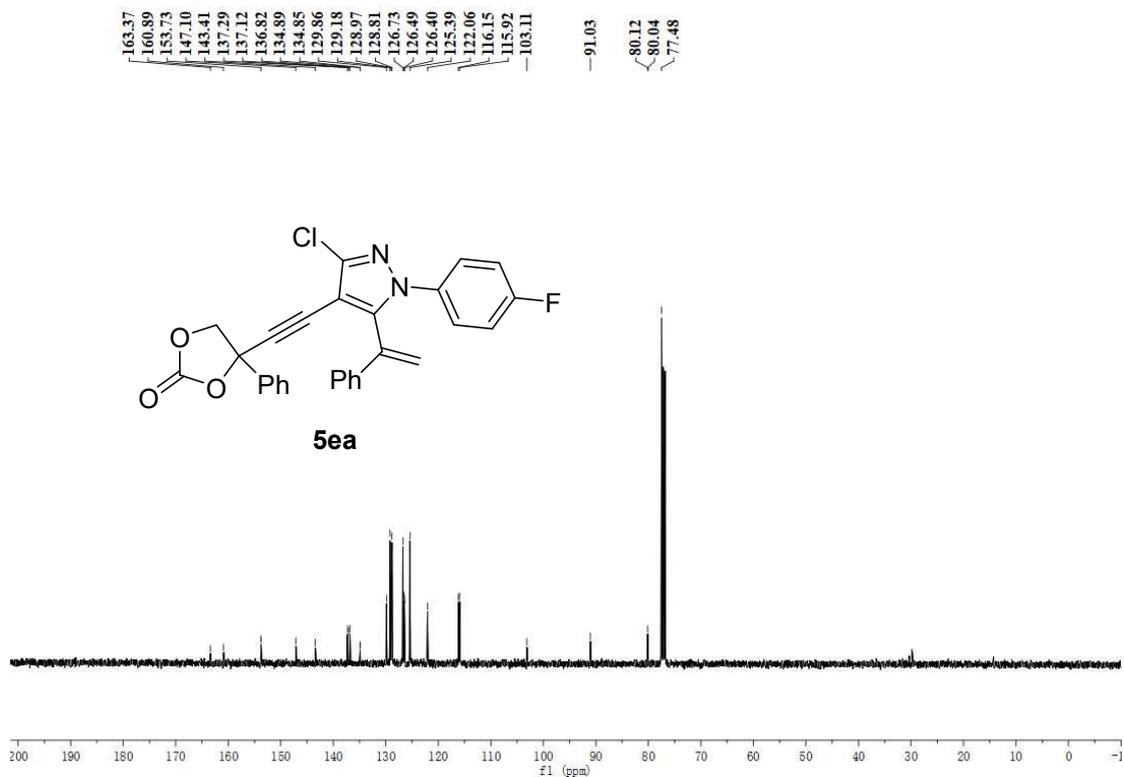
$^{13}\text{C}\{^1\text{H}\}$  NMR of 5da (101 MHz,  $\text{CDCl}_3$ )



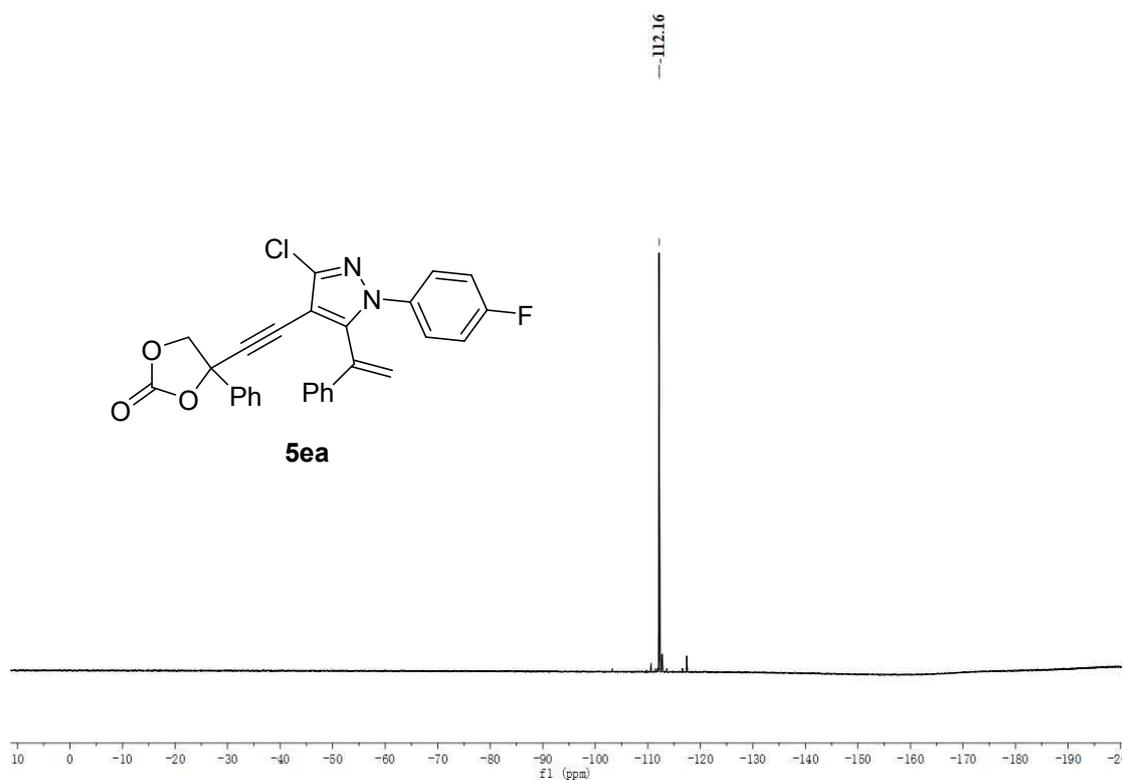
$^1\text{H}$  NMR of 5ea (400 MHz,  $\text{CDCl}_3$ )



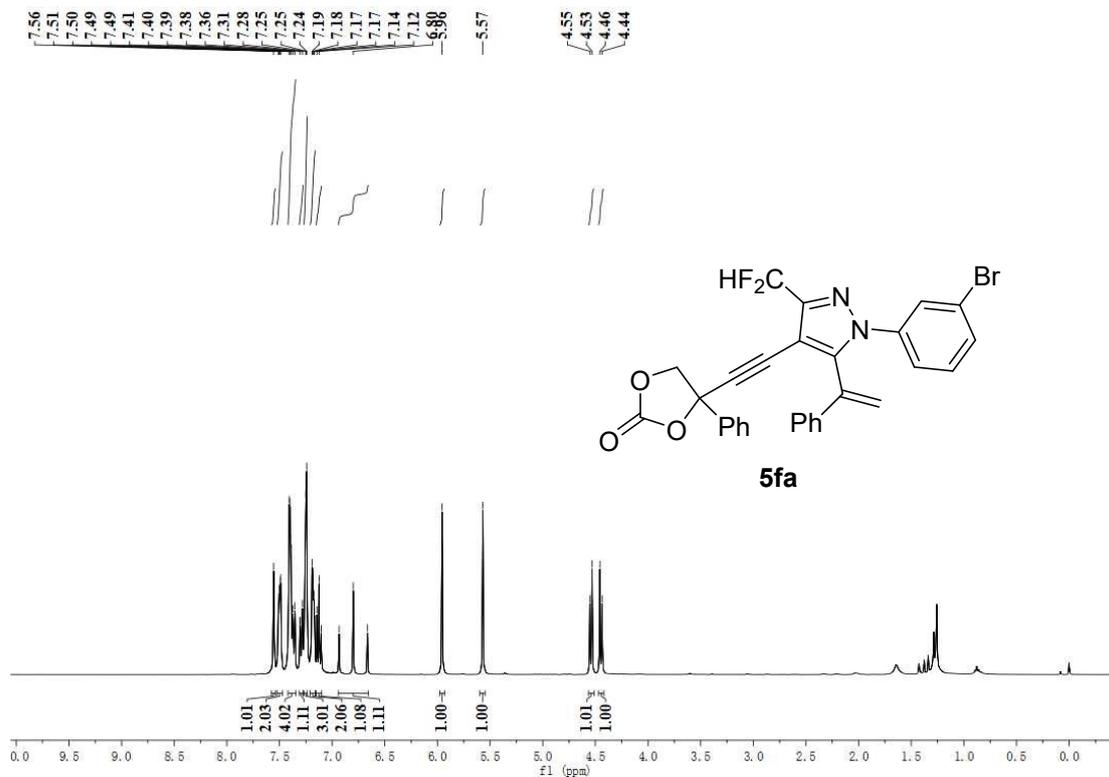
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 5ea (101 MHz,  $\text{CDCl}_3$ )**



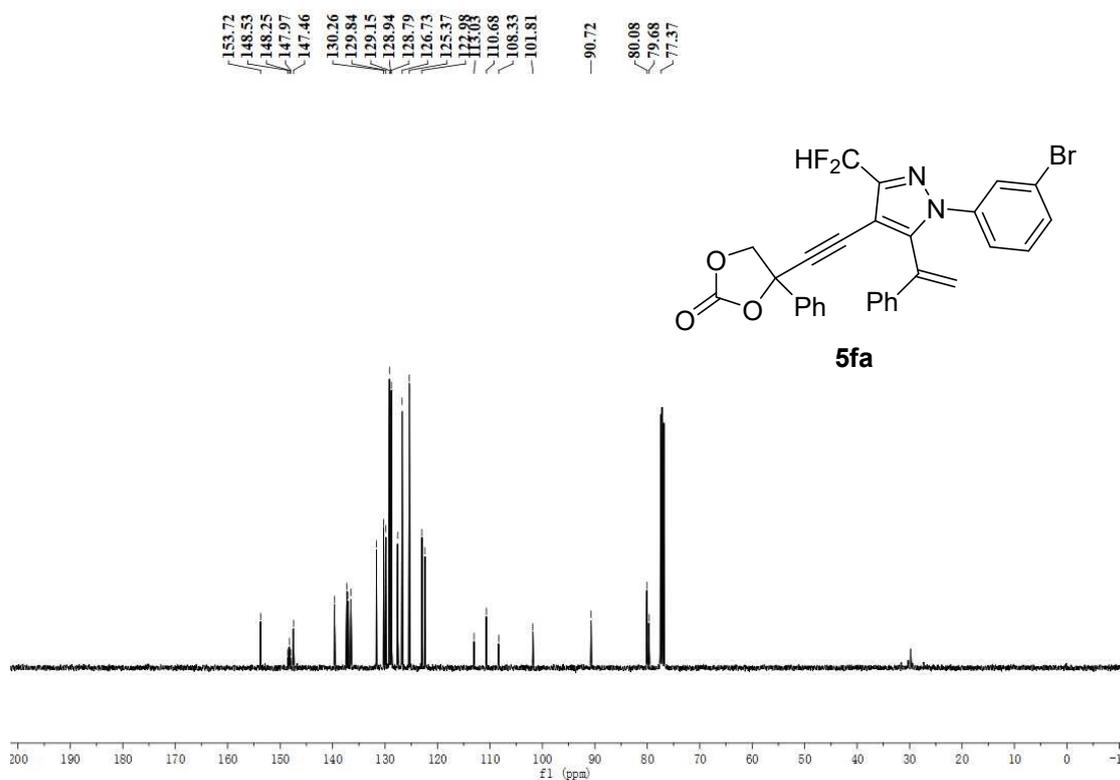
**$^{19}\text{F}$  NMR of 5ea (376 MHz,  $\text{CDCl}_3$ )**



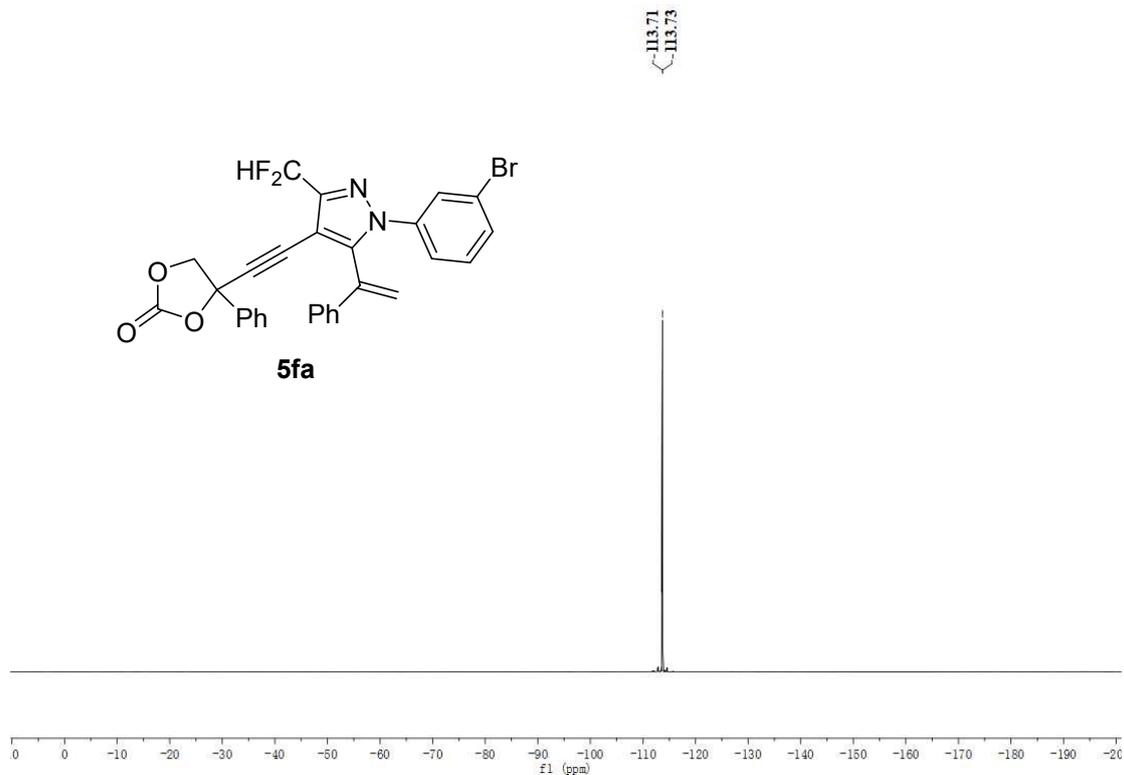
**<sup>1</sup>H NMR of 5fa (400 MHz, CDCl<sub>3</sub>)**



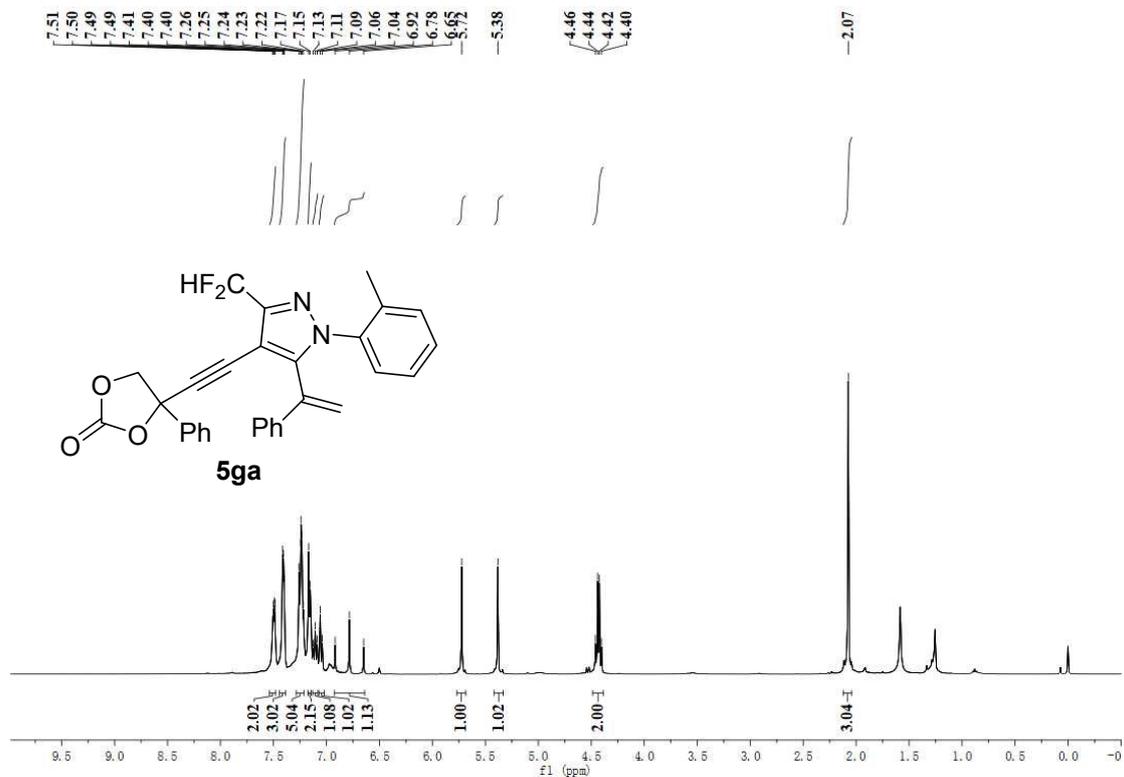
**<sup>13</sup>C{<sup>1</sup>H} NMR of 5fa (101 MHz, CDCl<sub>3</sub>)**



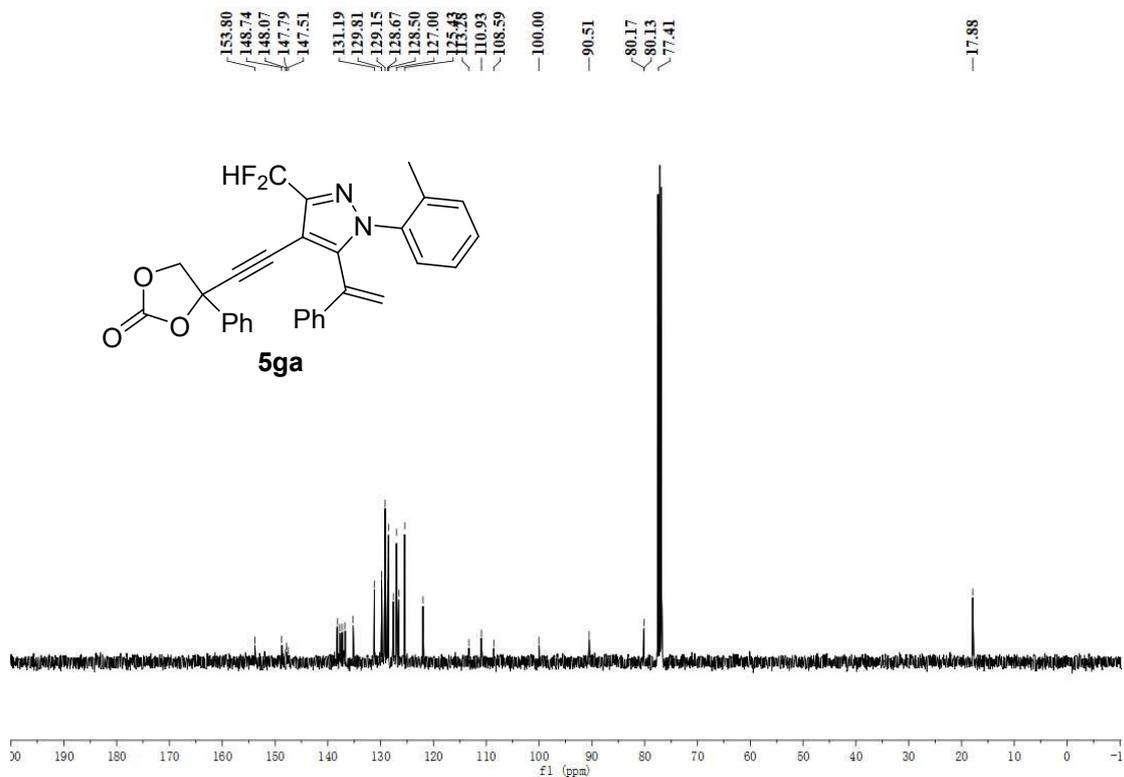
**<sup>19</sup>F NMR of 5fa (376 MHz, CDCl<sub>3</sub>)**



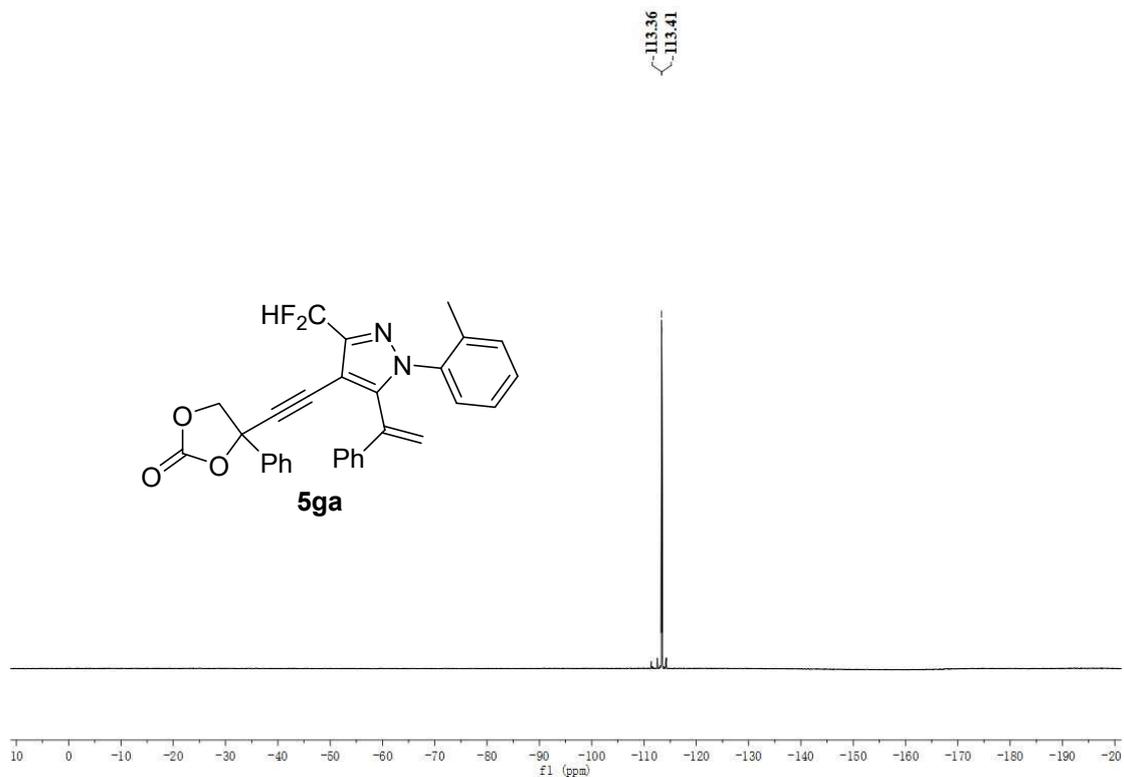
**<sup>1</sup>H NMR of 5ga (400 MHz, CDCl<sub>3</sub>)**



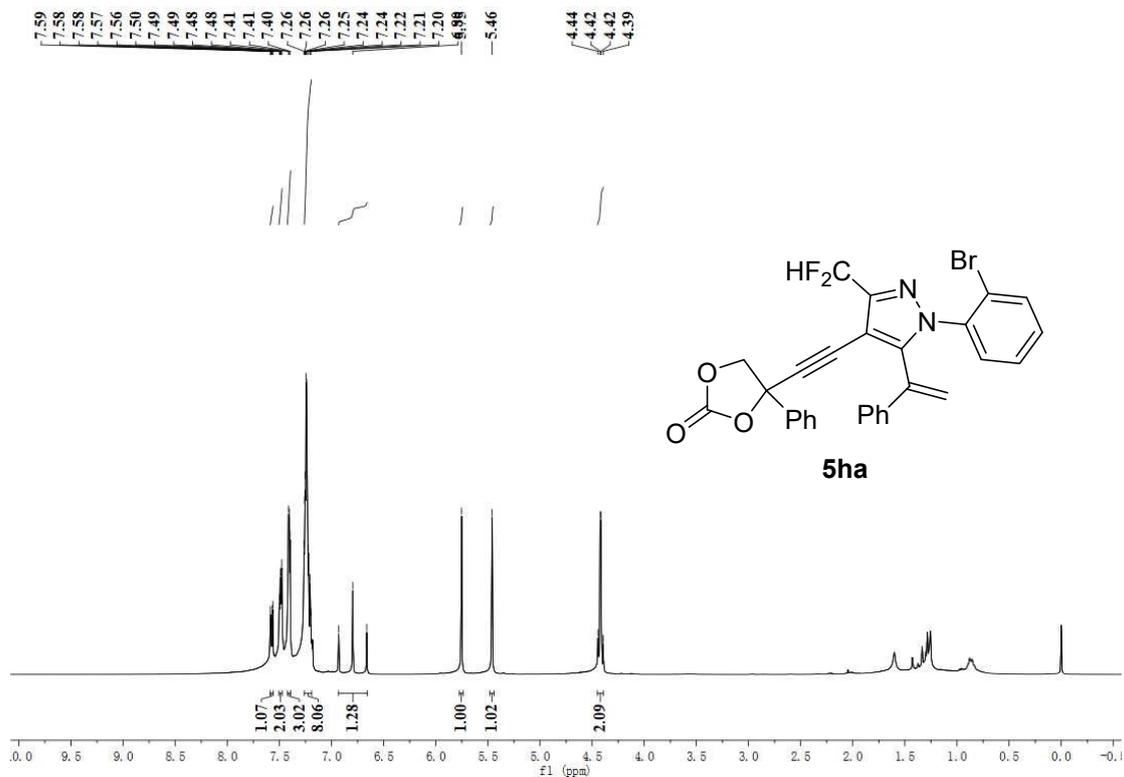
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 5ga (101 MHz,  $\text{CDCl}_3$ )**



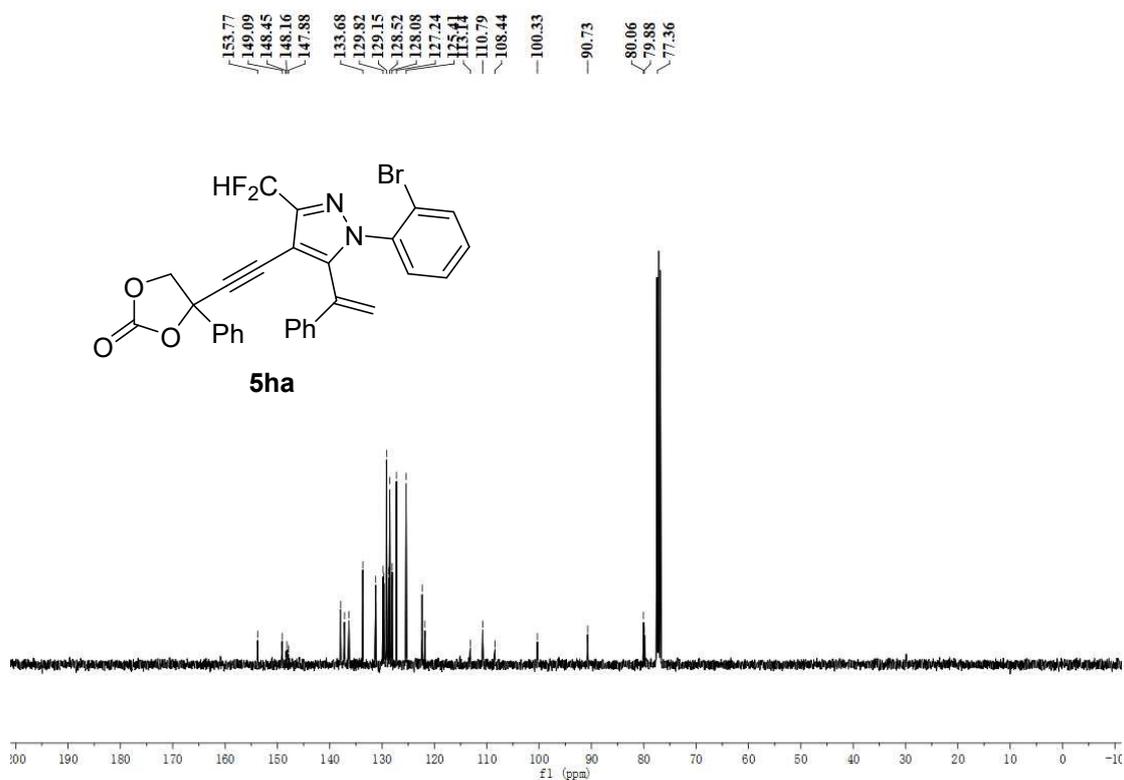
**$^{19}\text{F}$  NMR of 5ga (376 MHz,  $\text{CDCl}_3$ )**



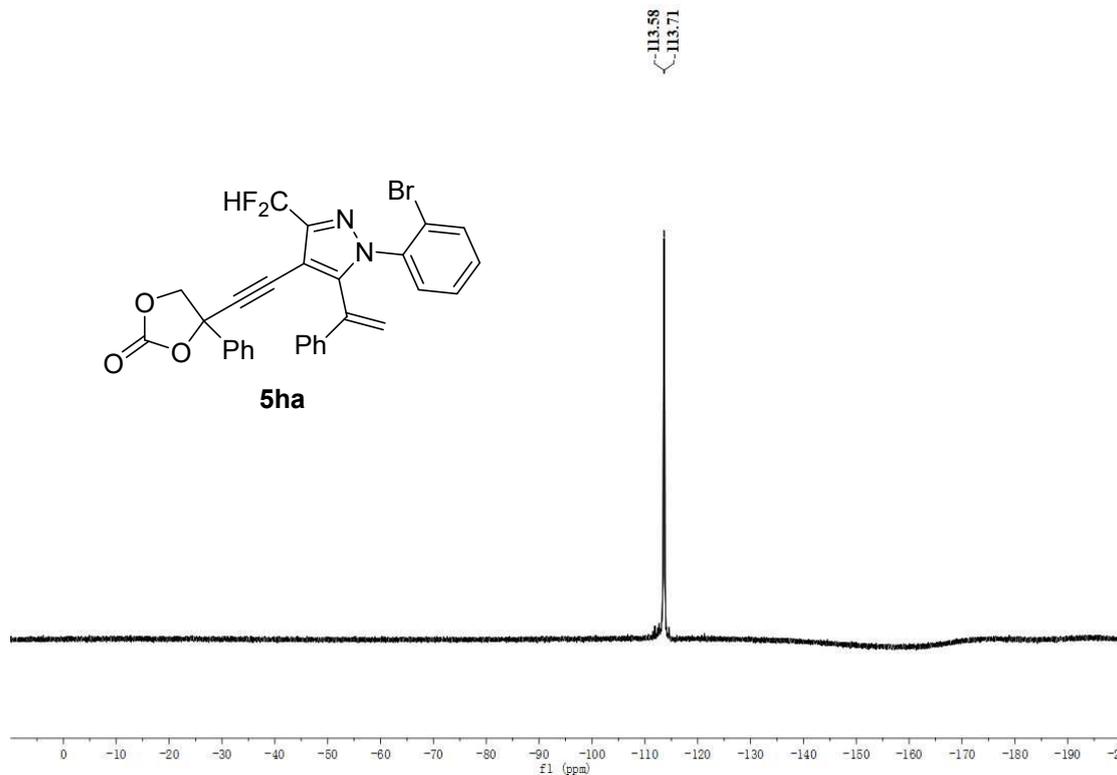
**<sup>1</sup>H NMR of 5ha (400 MHz, CDCl<sub>3</sub>)**



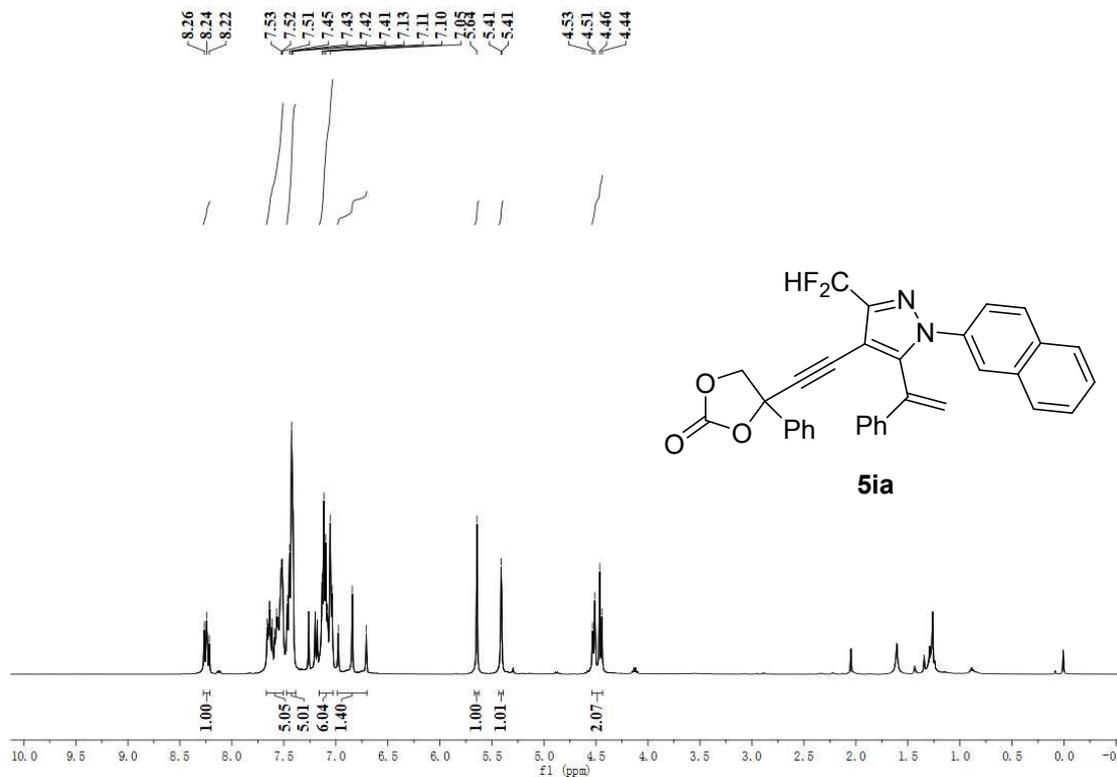
**<sup>13</sup>C{<sup>1</sup>H} NMR of 5ha (101 MHz, CDCl<sub>3</sub>)**



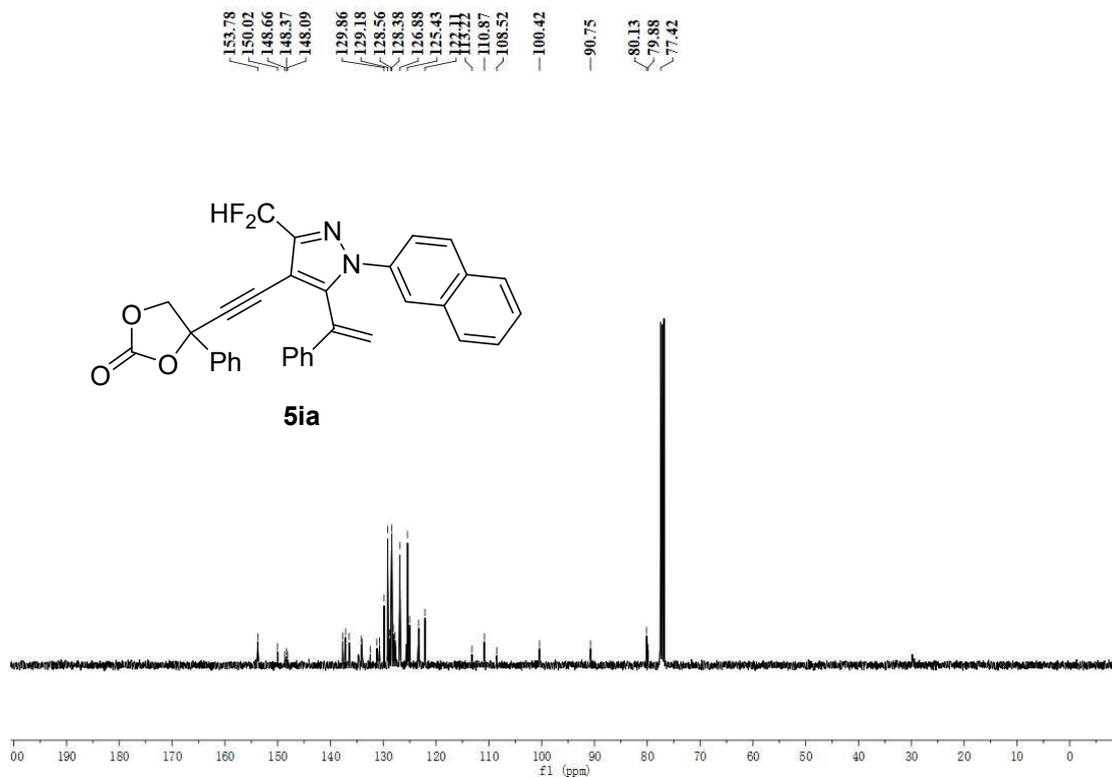
**<sup>19</sup>F NMR of 5ha (376 MHz, CDCl<sub>3</sub>)**



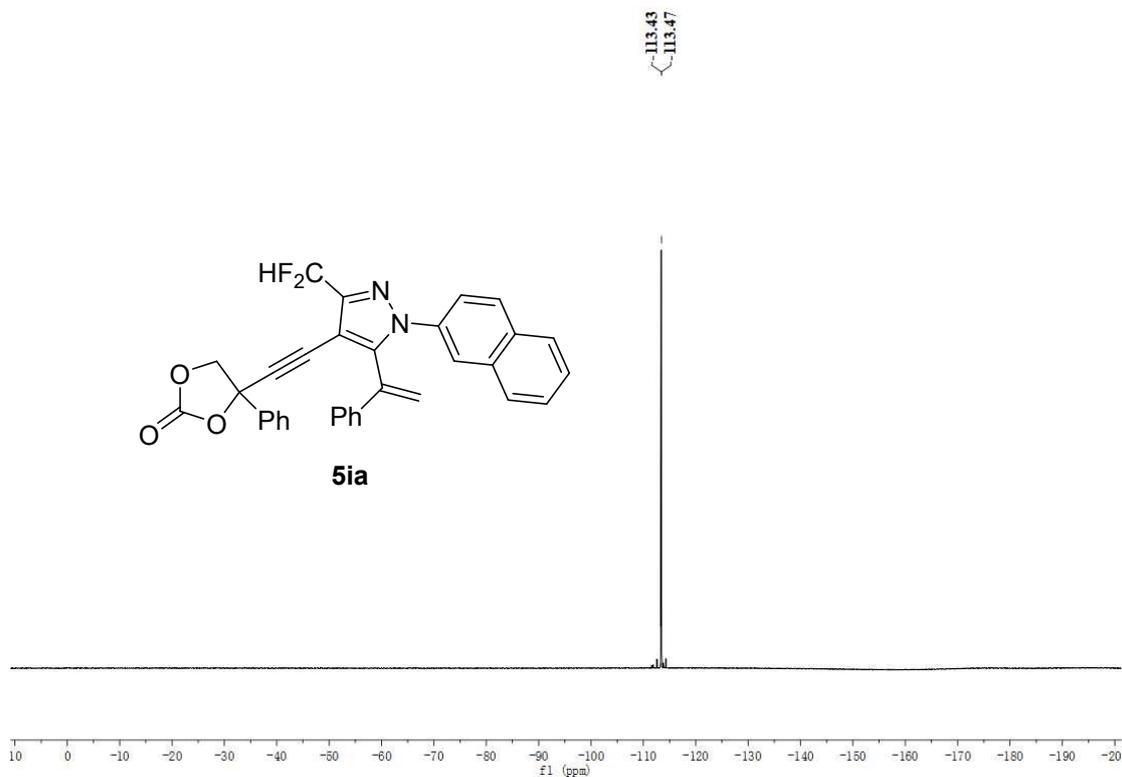
**<sup>1</sup>H NMR of 5ia (400 MHz, CDCl<sub>3</sub>)**



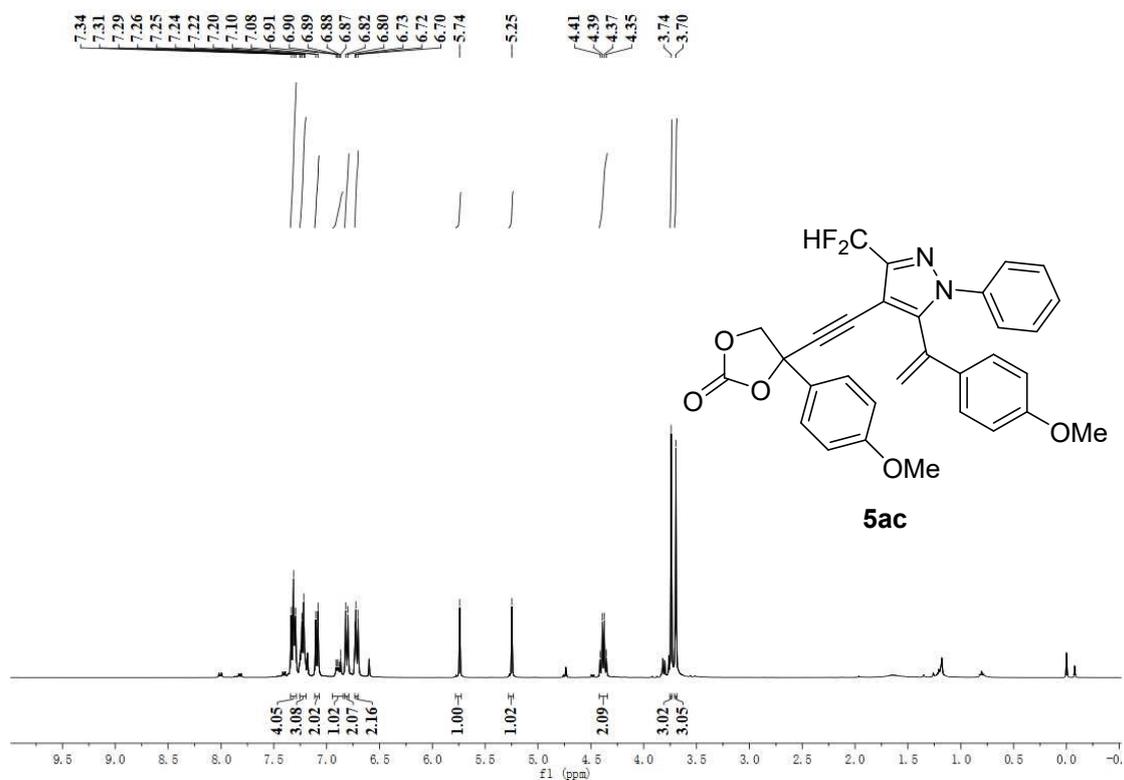
$^{13}\text{C}\{^1\text{H}\}$  NMR of **5ia** (101 MHz,  $\text{CDCl}_3$ )



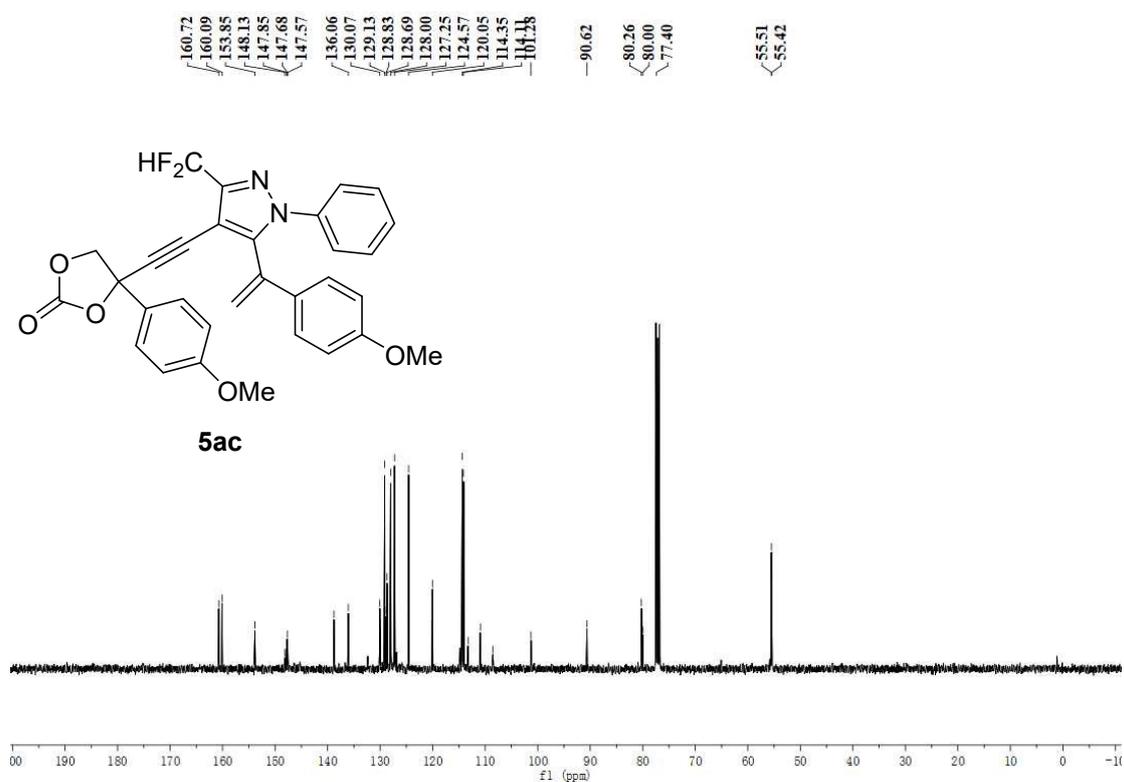
$^{19}\text{F}$  NMR of **5ia** (376 MHz,  $\text{CDCl}_3$ )



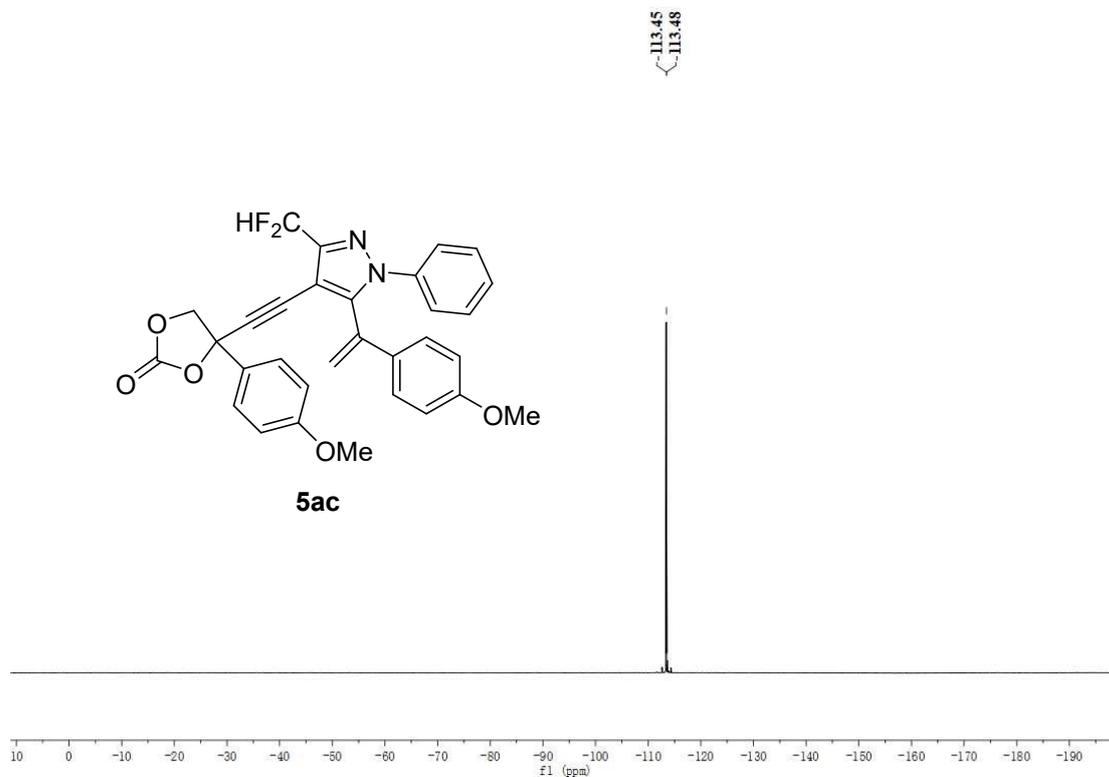
**<sup>1</sup>H NMR of 5ac (400 MHz, CDCl<sub>3</sub>)**



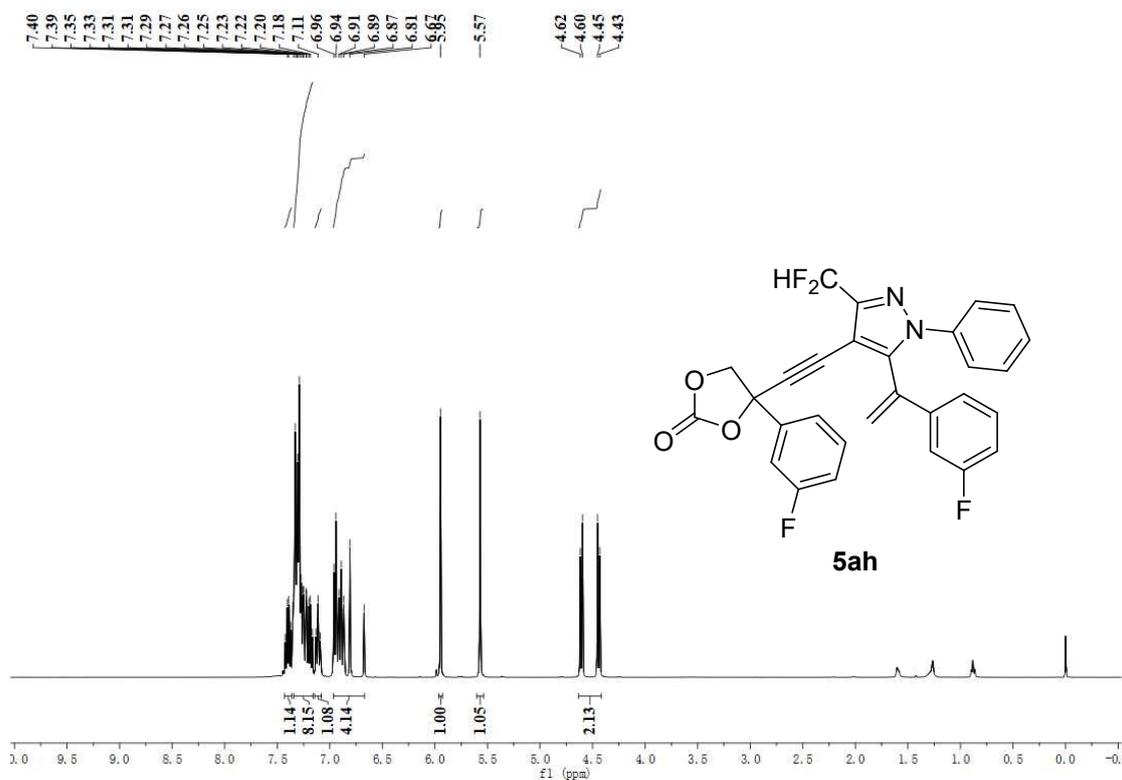
**<sup>13</sup>C{<sup>1</sup>H} NMR of 5ac (101 MHz, CDCl<sub>3</sub>)**



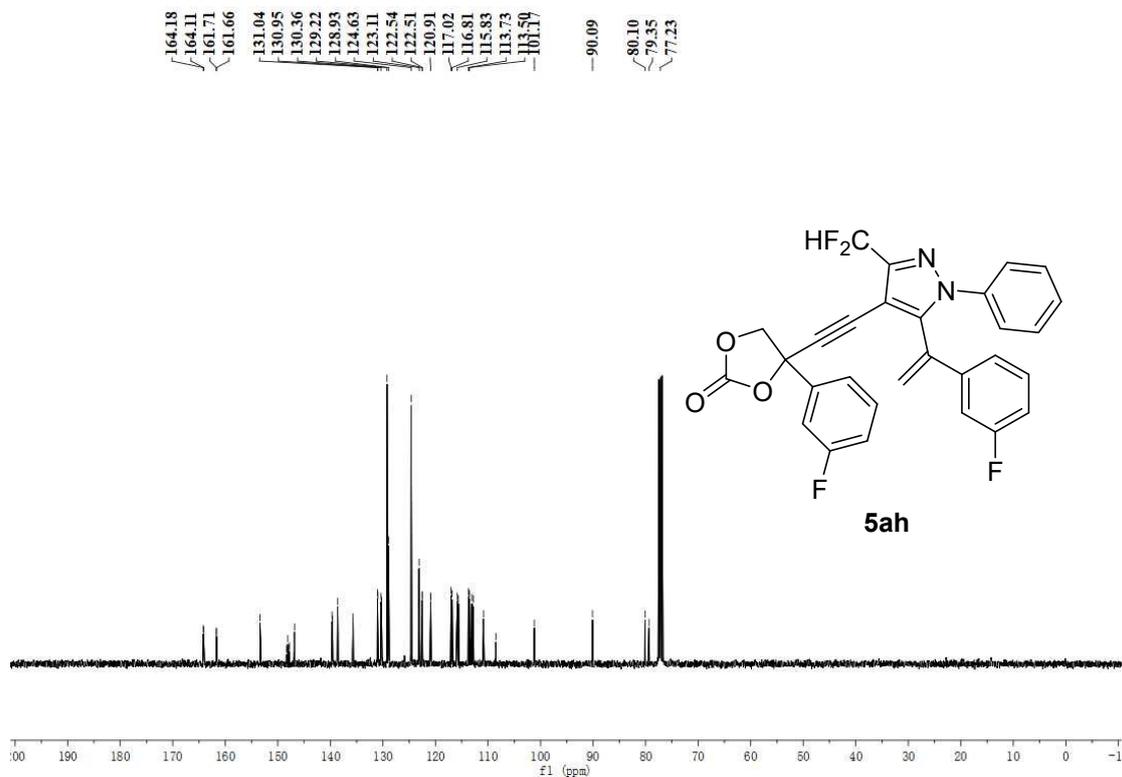
**<sup>19</sup>F NMR of 5ac (376 MHz, CDCl<sub>3</sub>)**



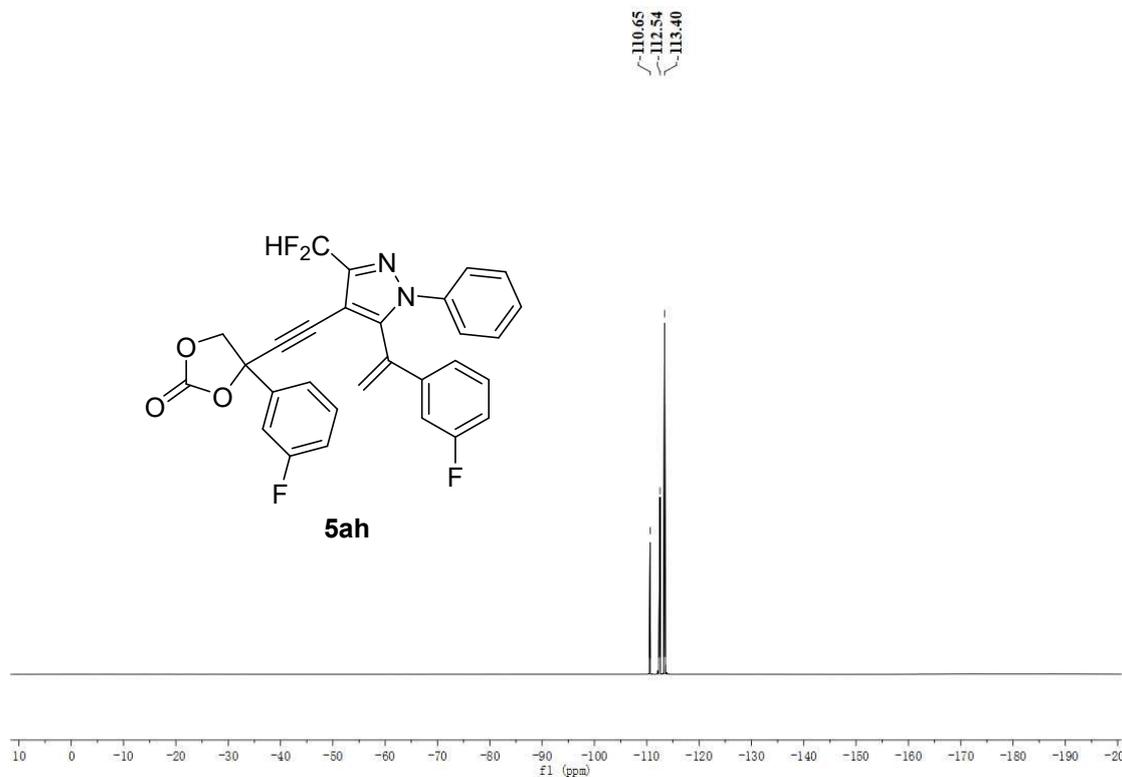
**<sup>1</sup>H NMR of 5ah (400 MHz, CDCl<sub>3</sub>)**



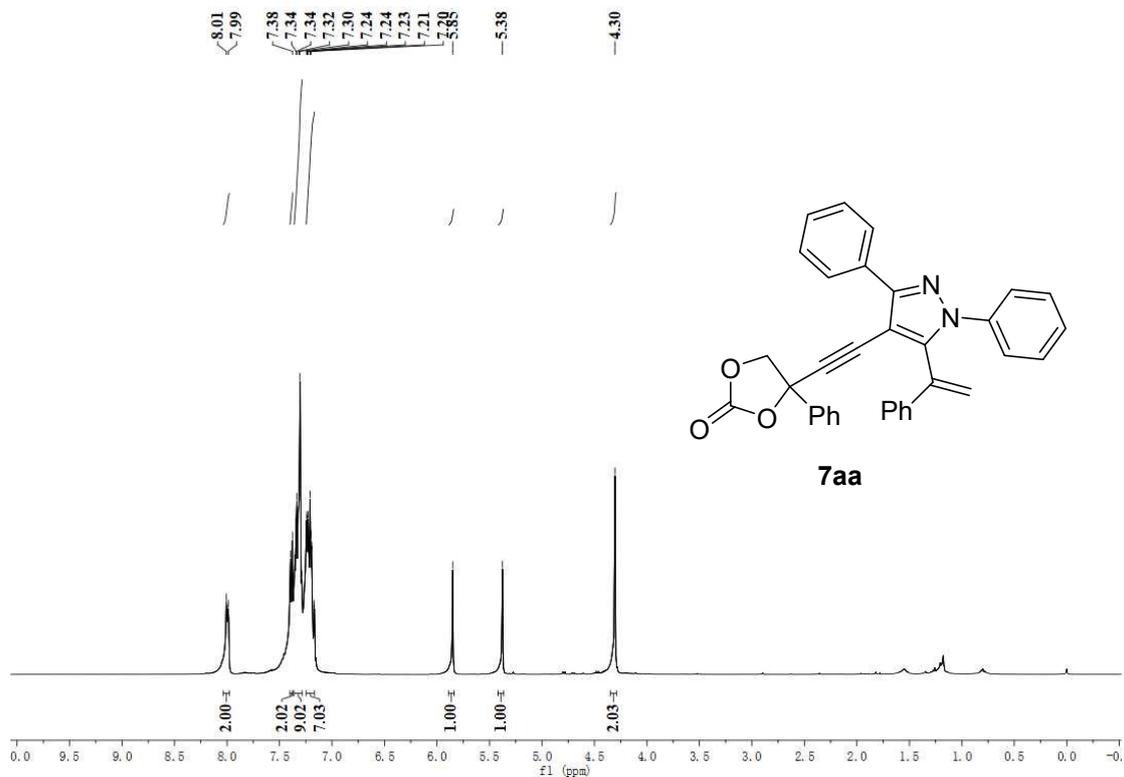
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 5ah (101 MHz,  $\text{CDCl}_3$ )**



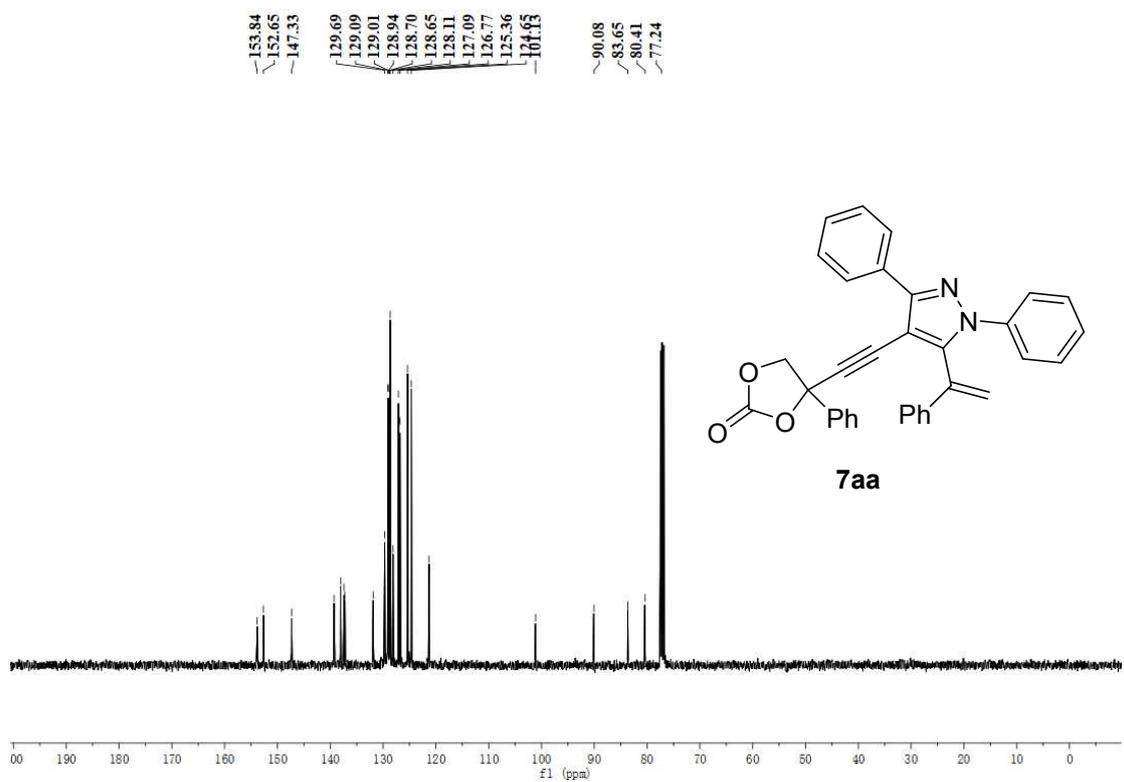
**$^{19}\text{F}$  NMR of 5ah (376 MHz,  $\text{CDCl}_3$ )**



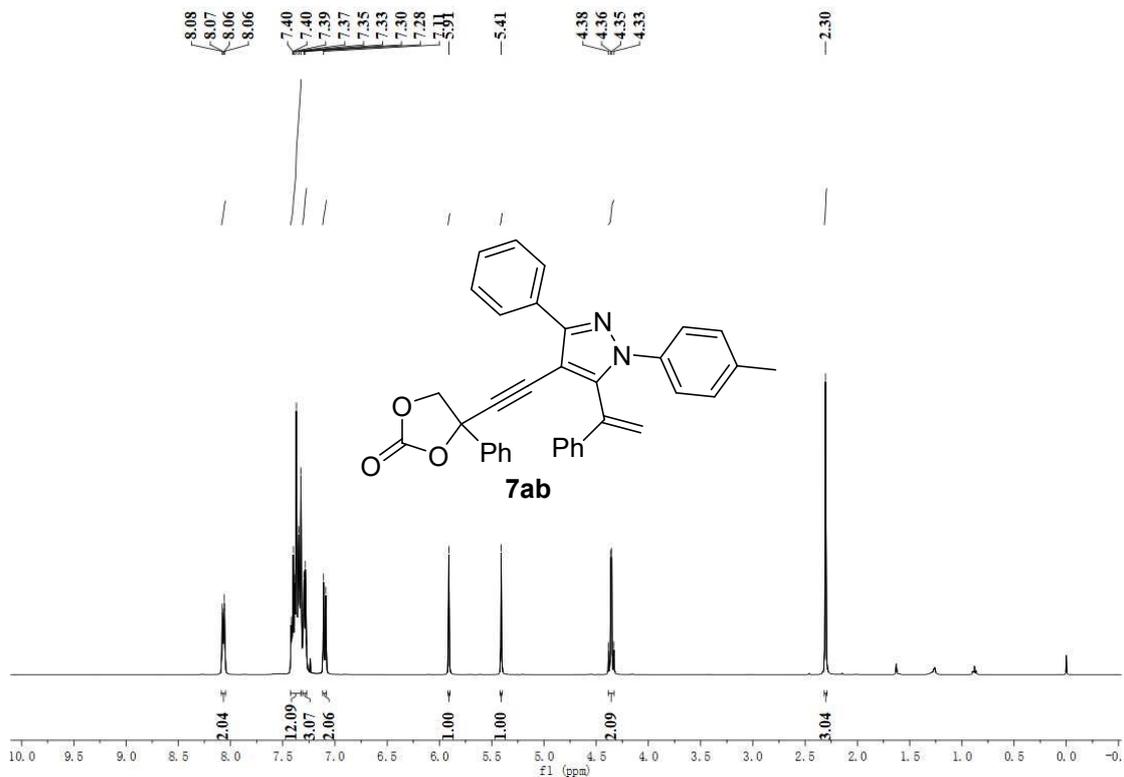
**$^1\text{H}$  NMR of 7aa (400 MHz,  $\text{CDCl}_3$ )**



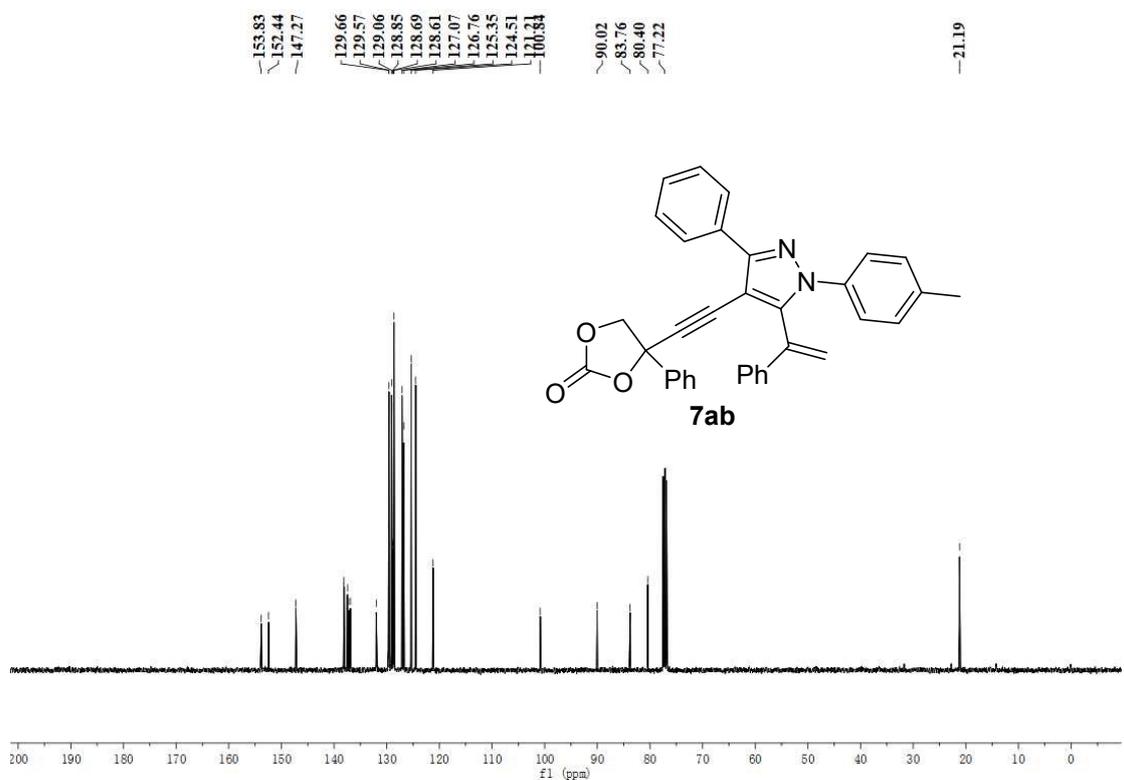
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 7aa (101 MHz,  $\text{CDCl}_3$ )**



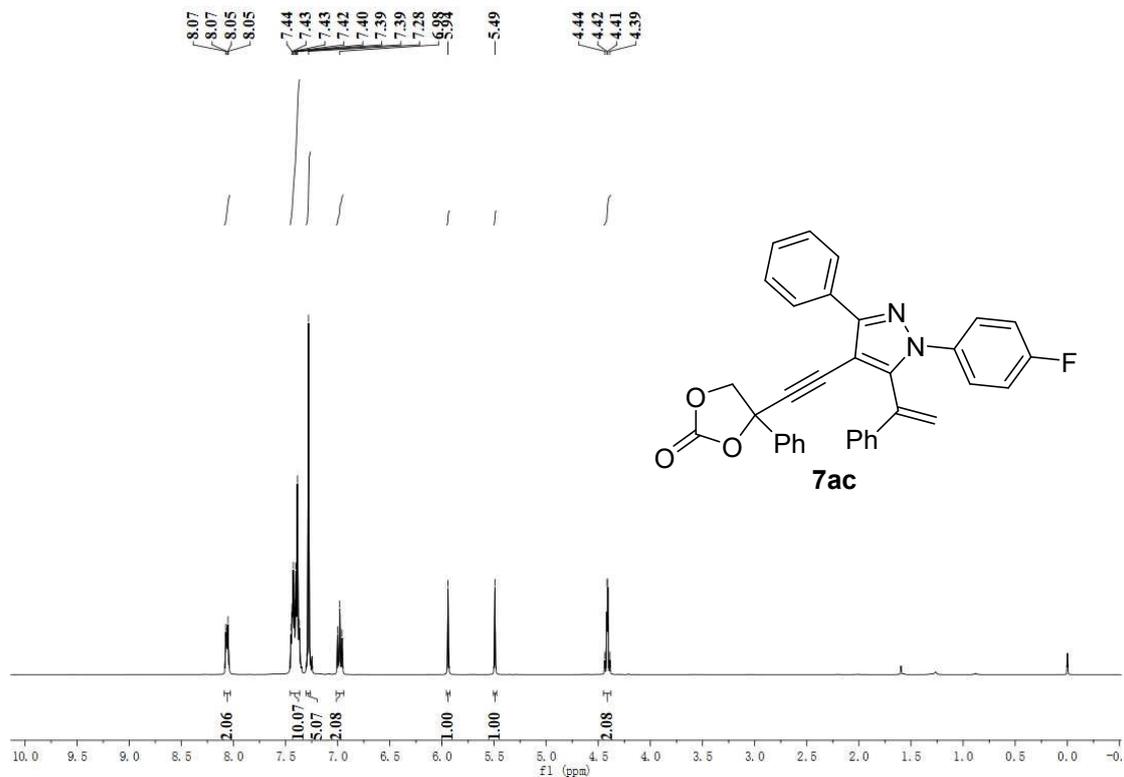
**<sup>1</sup>H NMR of 7ab (400 MHz, CDCl<sub>3</sub>)**



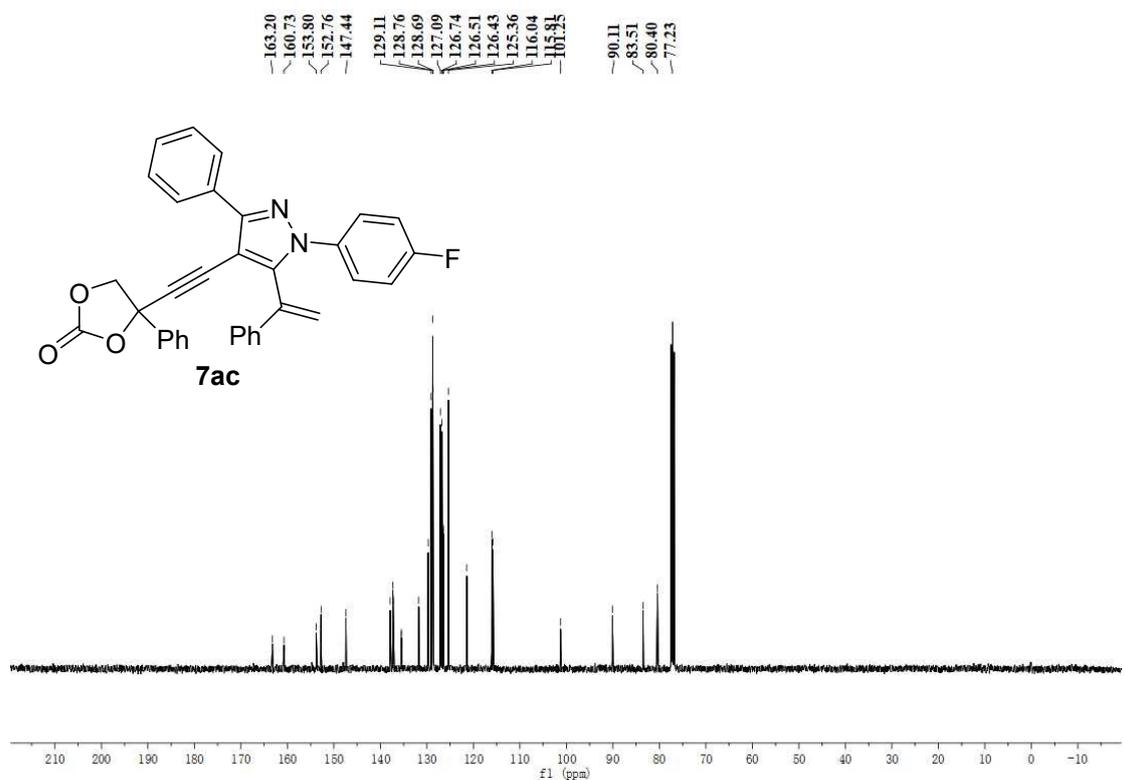
**<sup>13</sup>C{<sup>1</sup>H} NMR of 7ab (101 MHz, CDCl<sub>3</sub>)**



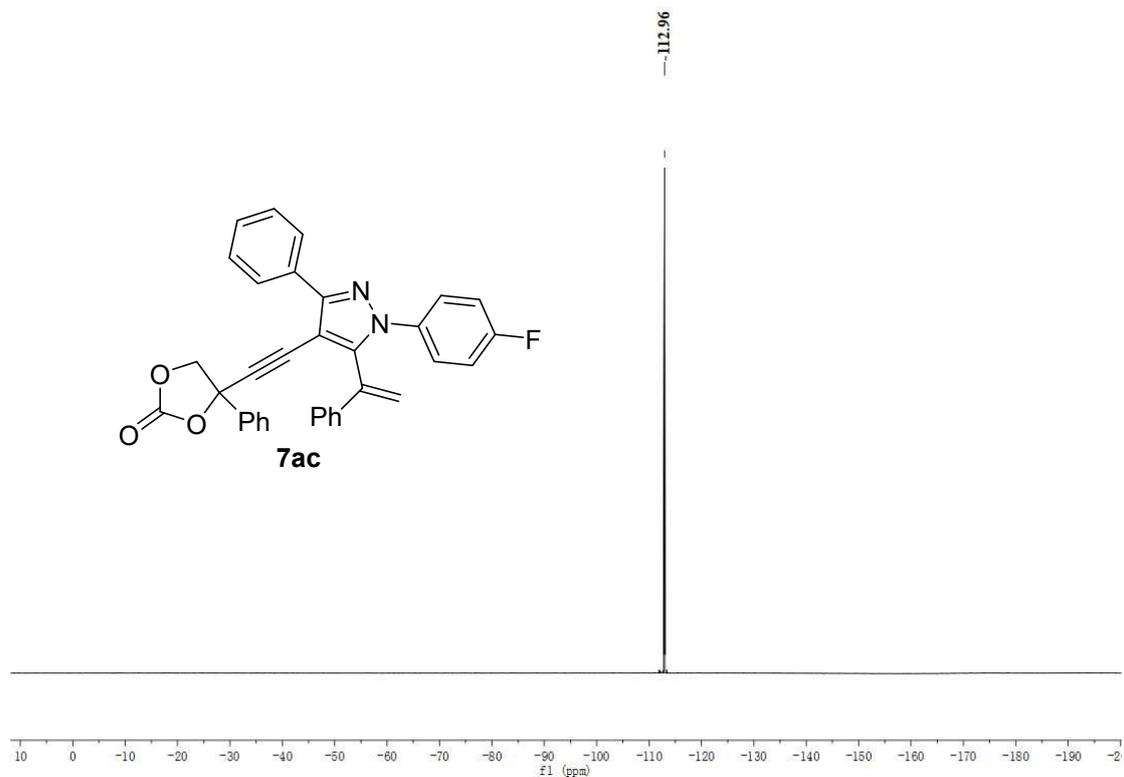
**$^1\text{H}$  NMR of 7ac (400 MHz,  $\text{CDCl}_3$ )**



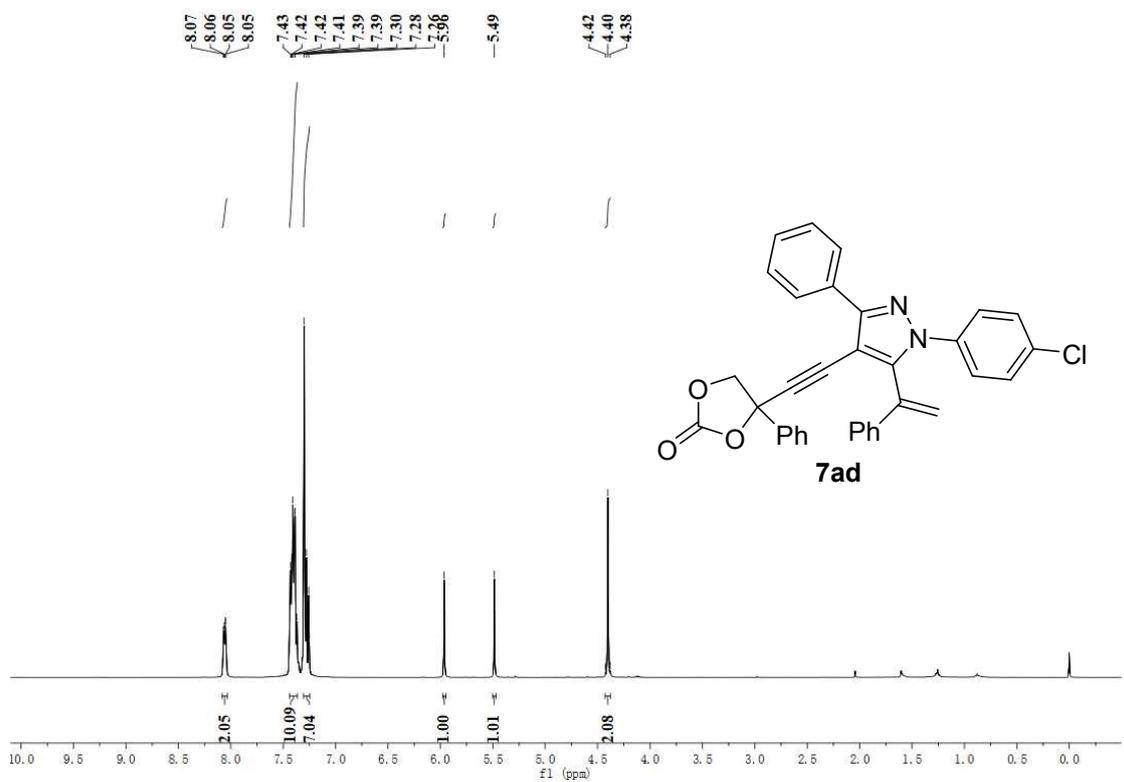
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 7ac (101 MHz,  $\text{CDCl}_3$ )**



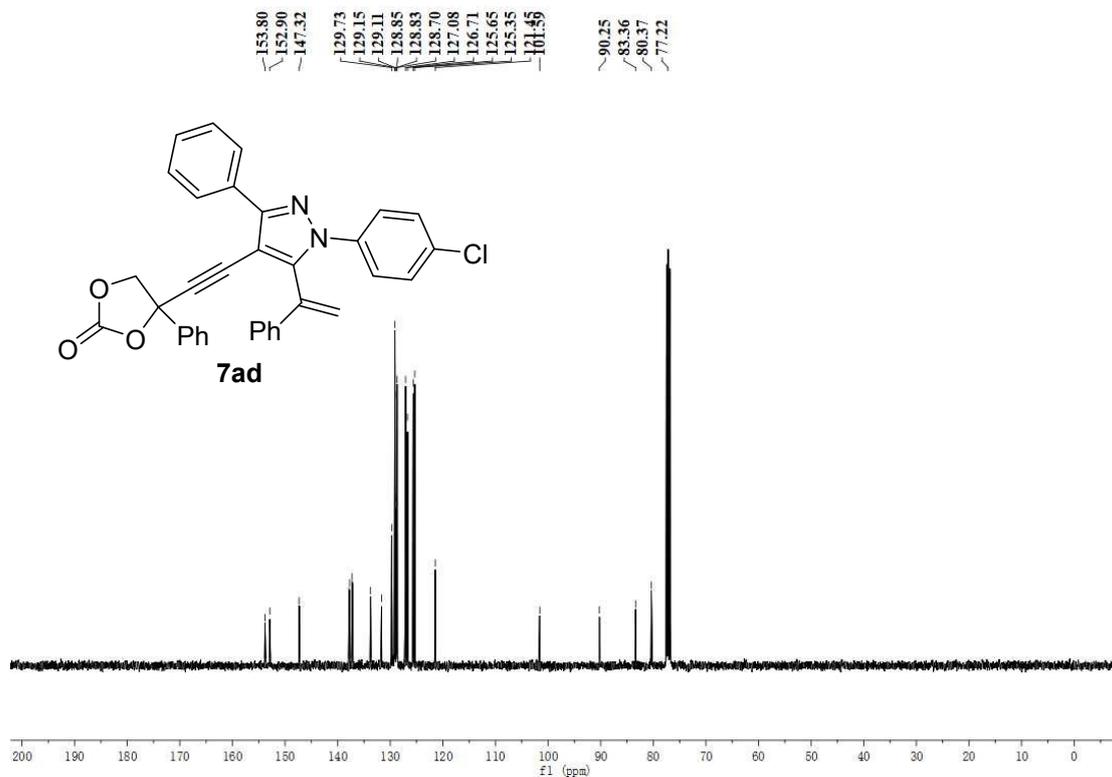
**$^{19}\text{F}$  NMR of 7ac (376 MHz,  $\text{CDCl}_3$ )**



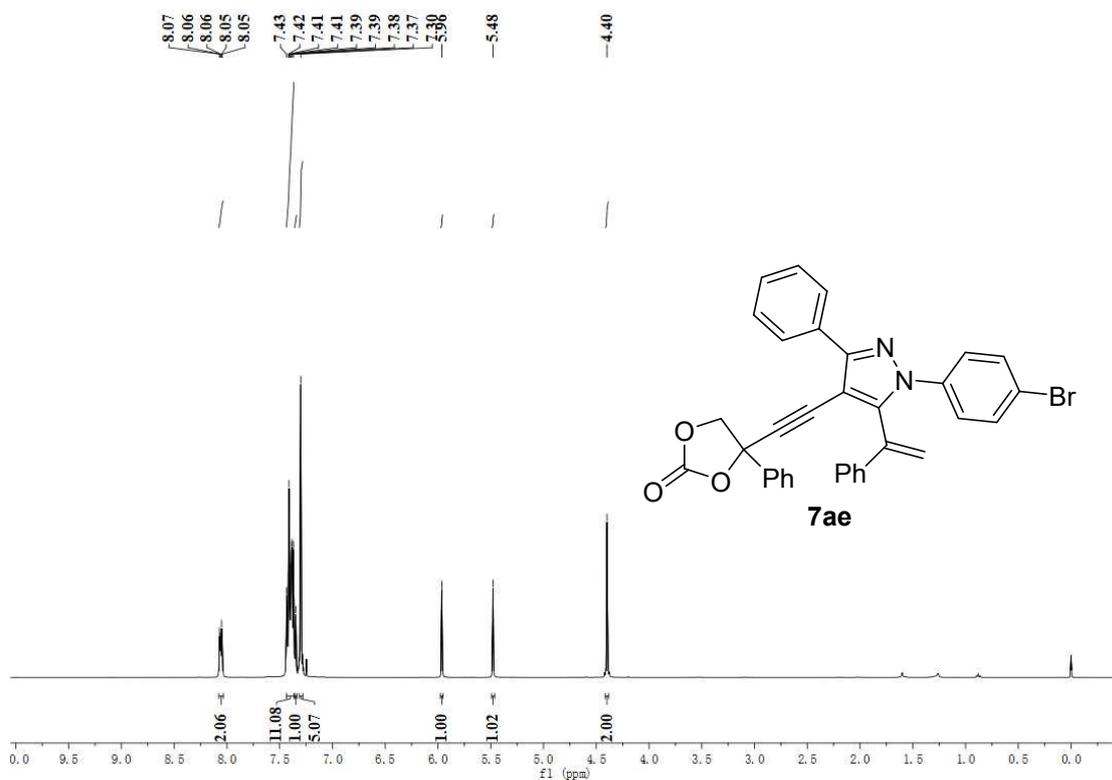
**$^1\text{H}$  NMR of 7ad (400 MHz,  $\text{CDCl}_3$ )**



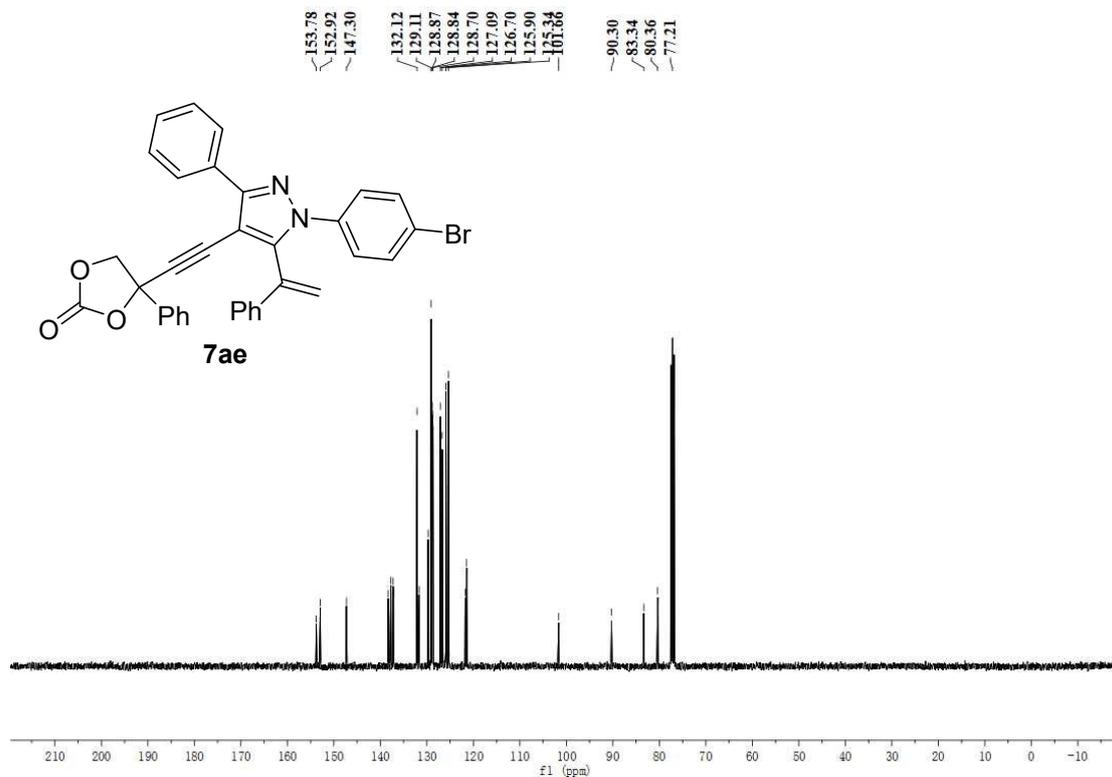
$^{13}\text{C}\{^1\text{H}\}$  NMR of 7ad (101 MHz,  $\text{CDCl}_3$ )



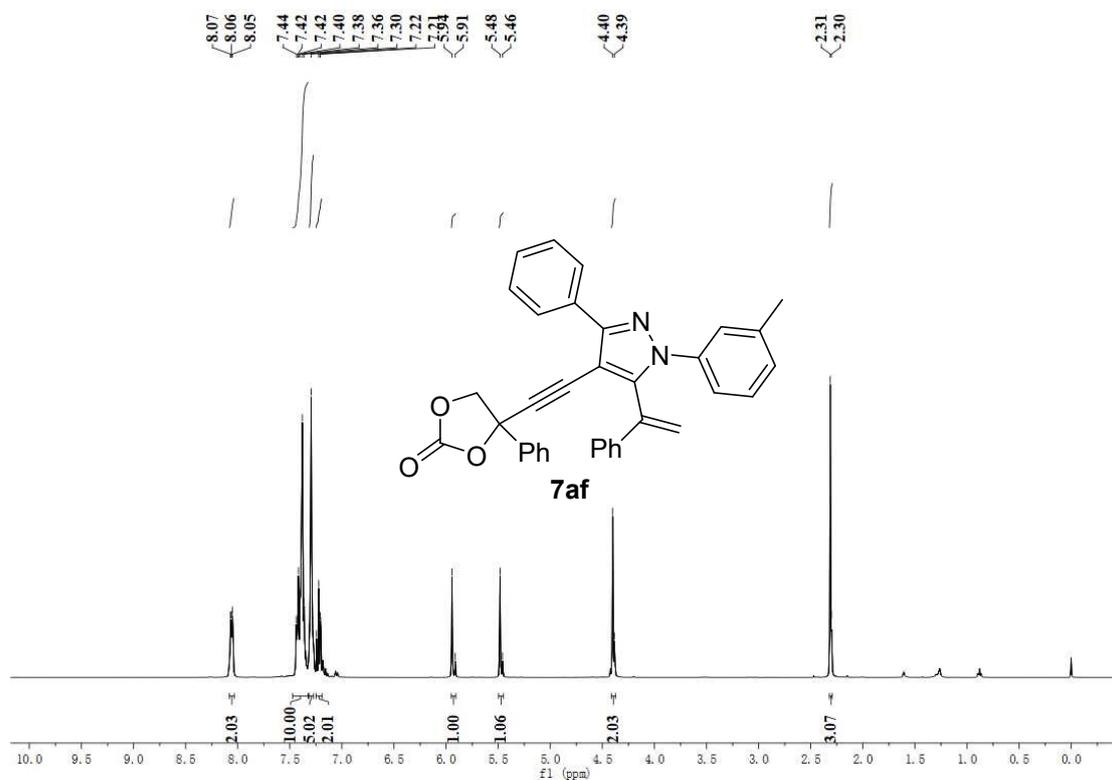
$^1\text{H}$  NMR of 7ae (400 MHz,  $\text{CDCl}_3$ )



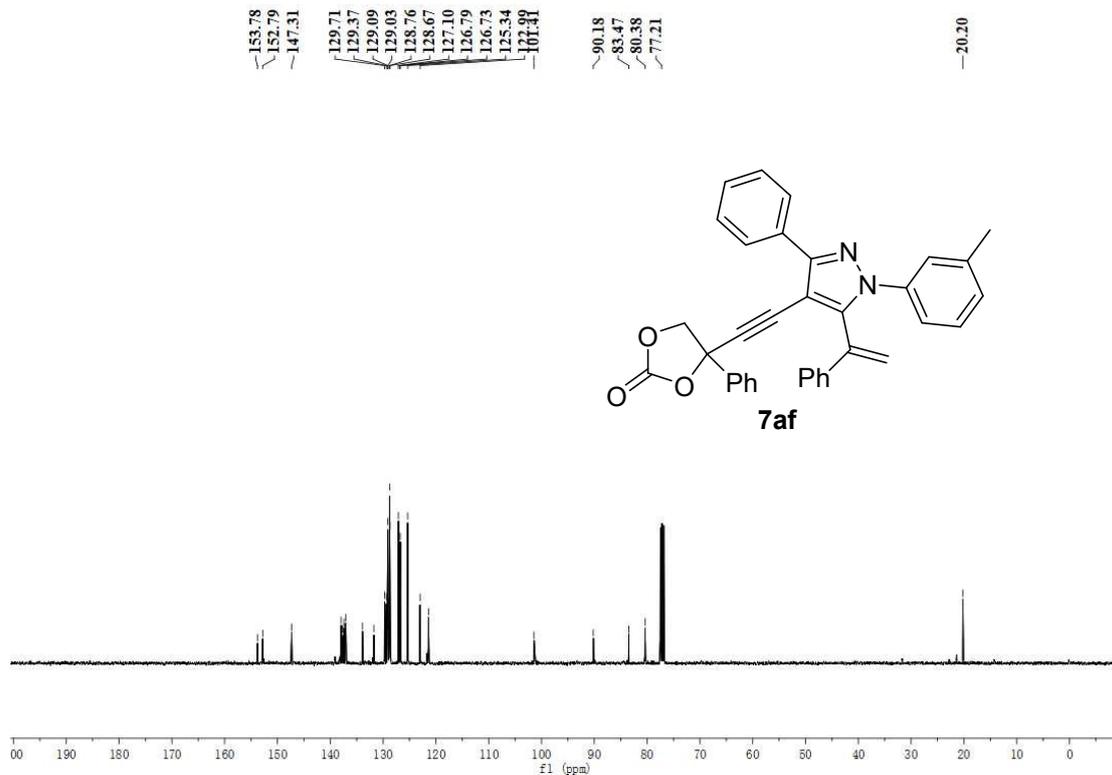
$^{13}\text{C}\{^1\text{H}\}$  NMR of 7ae (101 MHz,  $\text{CDCl}_3$ )



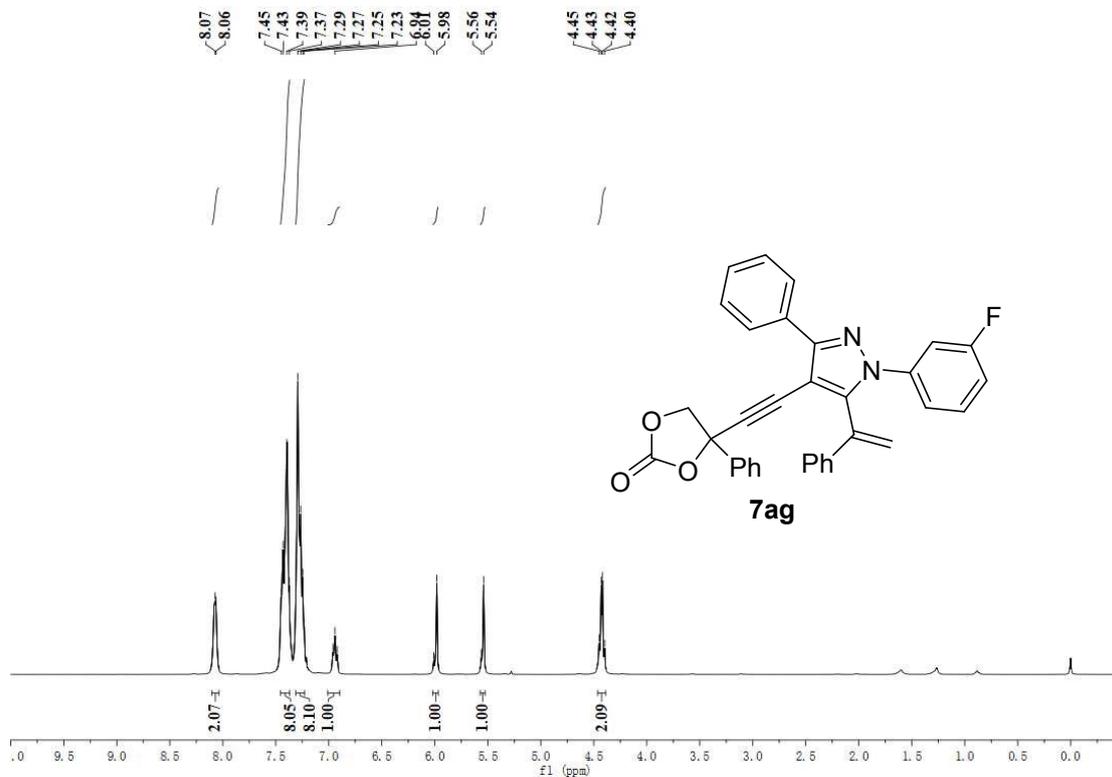
$^1\text{H}$  NMR of 7af (400 MHz,  $\text{CDCl}_3$ )



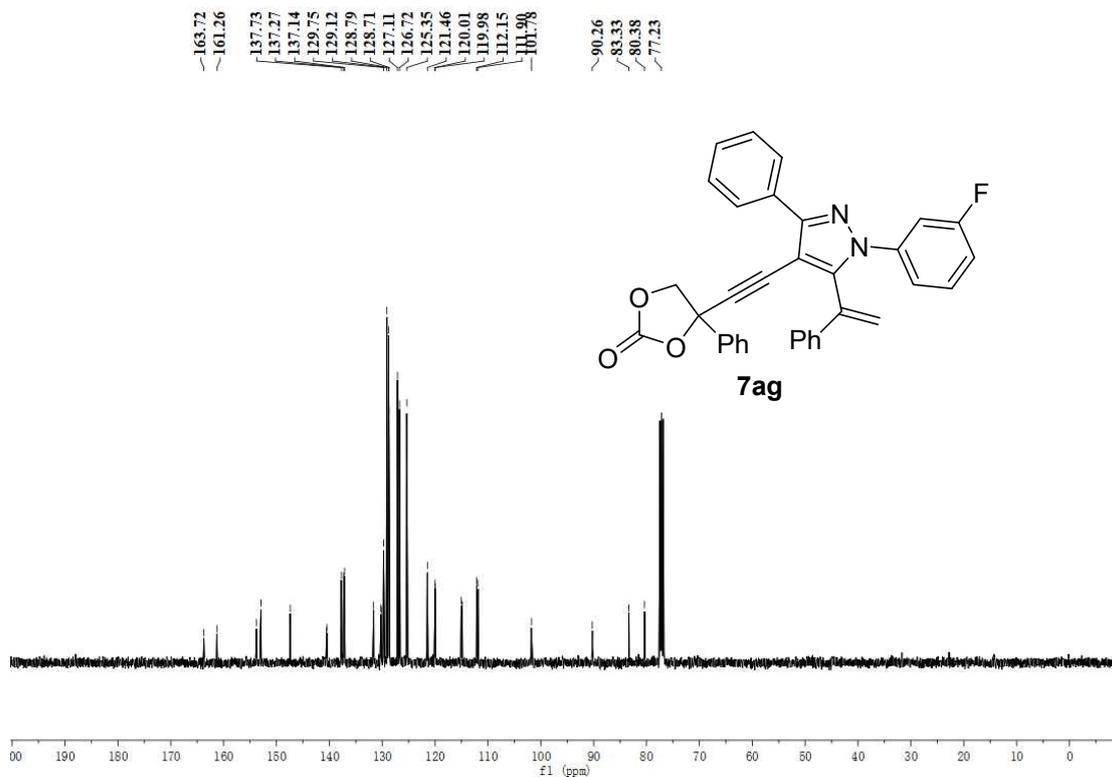
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 7af (101 MHz,  $\text{CDCl}_3$ )**



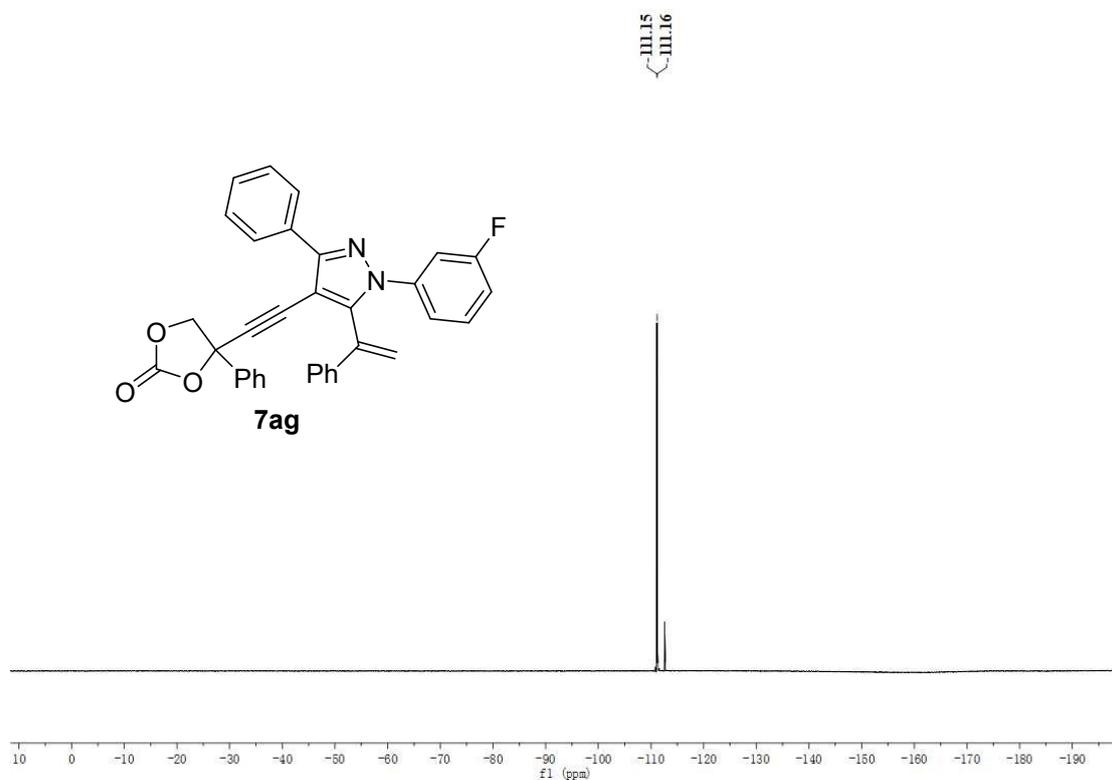
**$^1\text{H}$  NMR of 7ag (400 MHz,  $\text{CDCl}_3$ )**



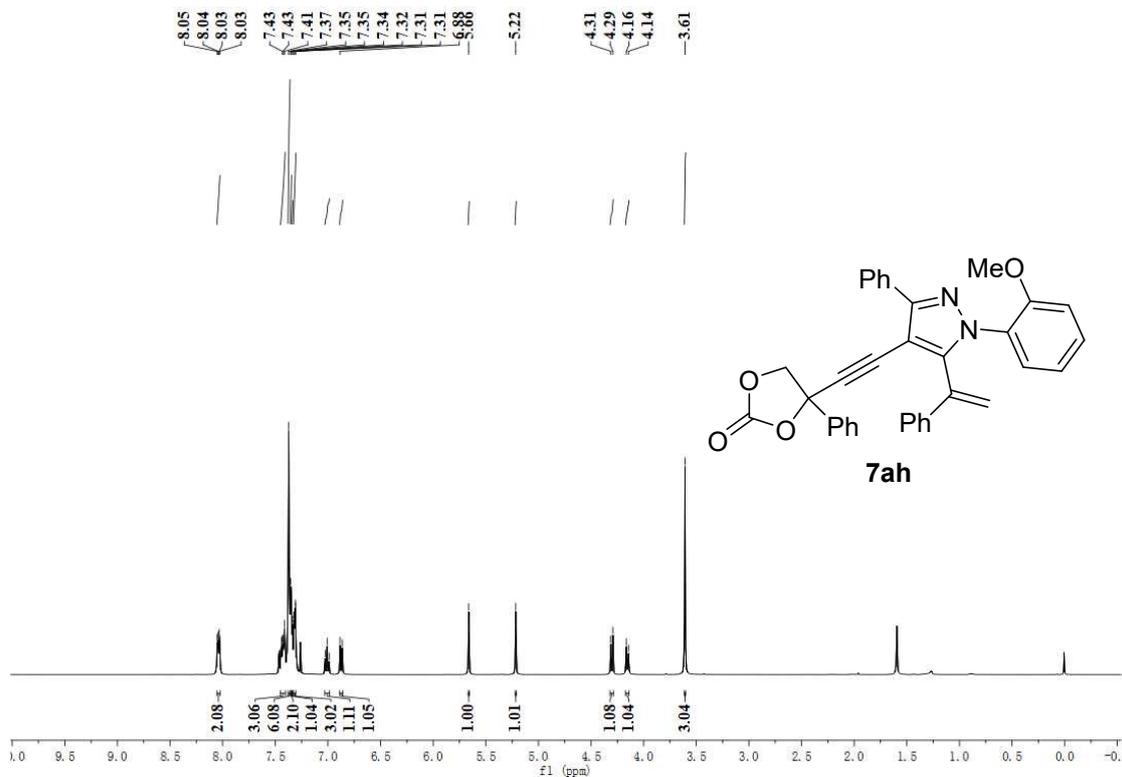
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 7ag (101 MHz,  $\text{CDCl}_3$ )**



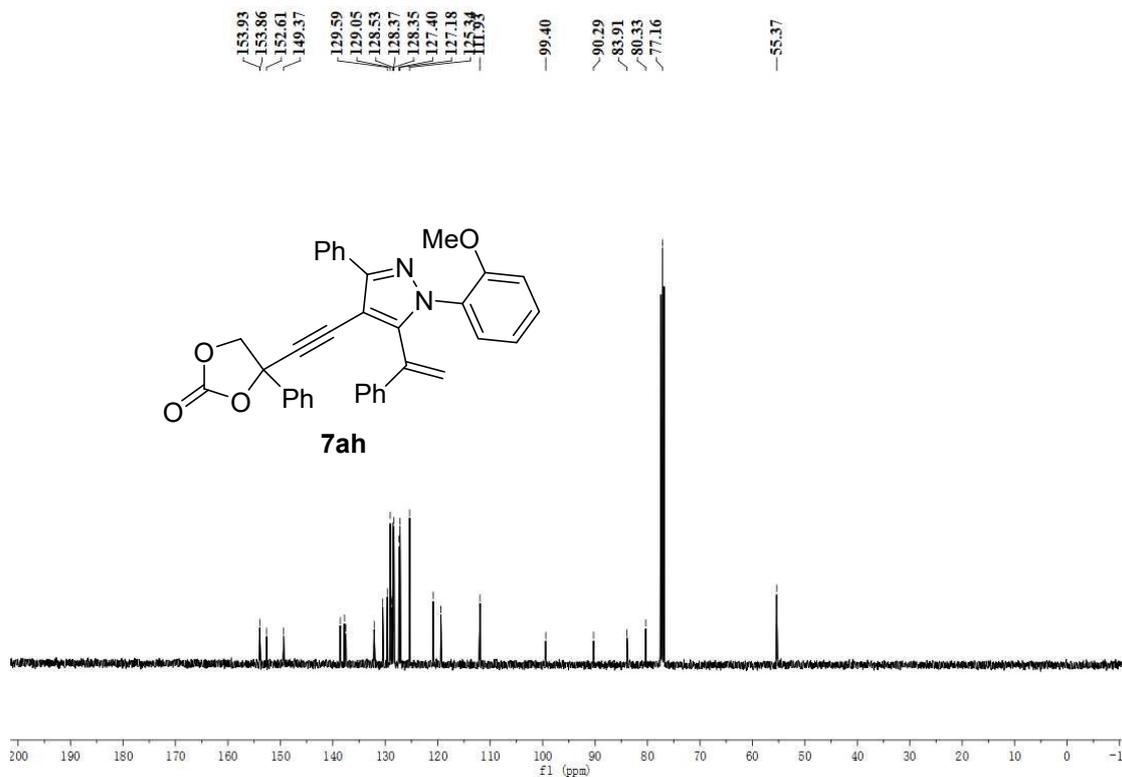
**$^{19}\text{F}$  NMR of 7ag (376 MHz,  $\text{CDCl}_3$ )**



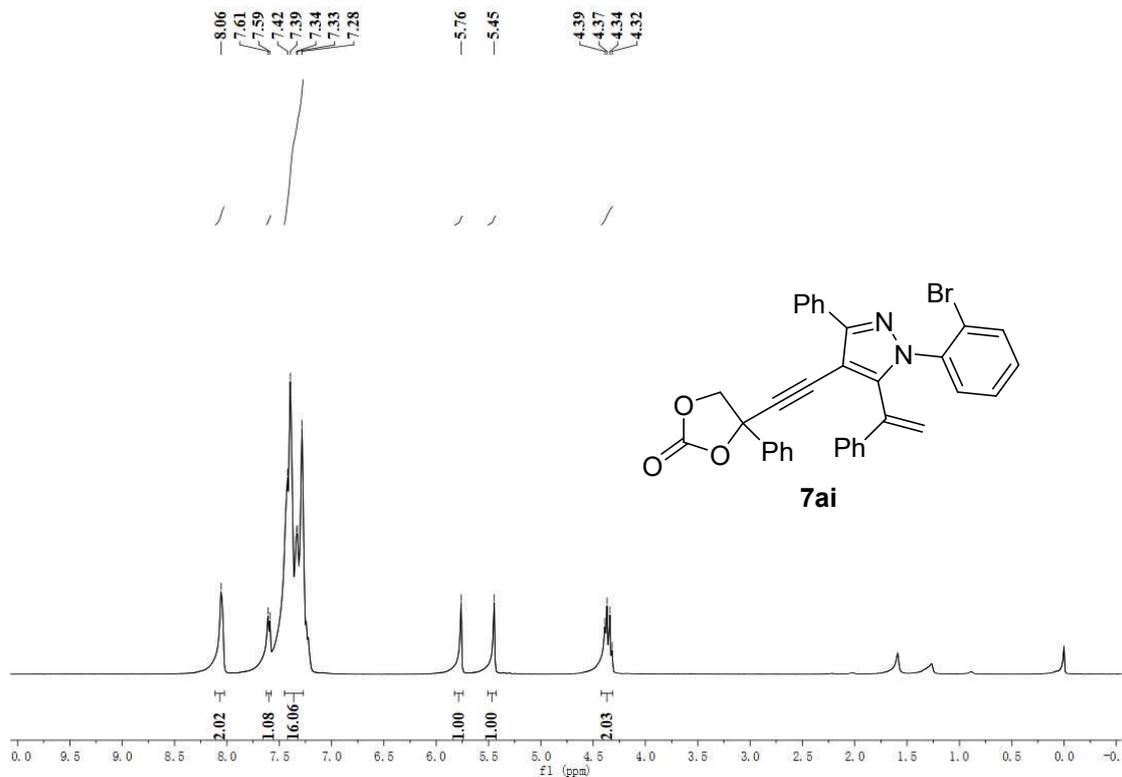
**<sup>1</sup>H NMR of 7ah (400 MHz, CDCl<sub>3</sub>)**



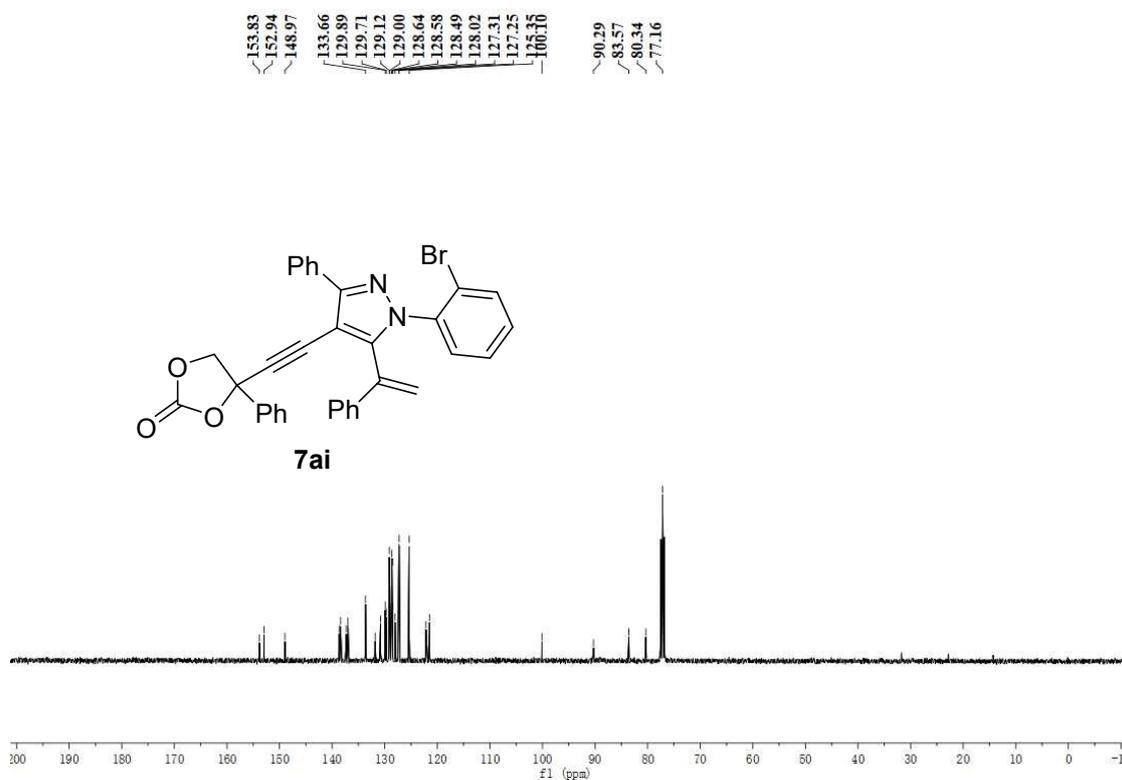
**<sup>13</sup>C{<sup>1</sup>H} NMR of 7ah (101 MHz, CDCl<sub>3</sub>)**



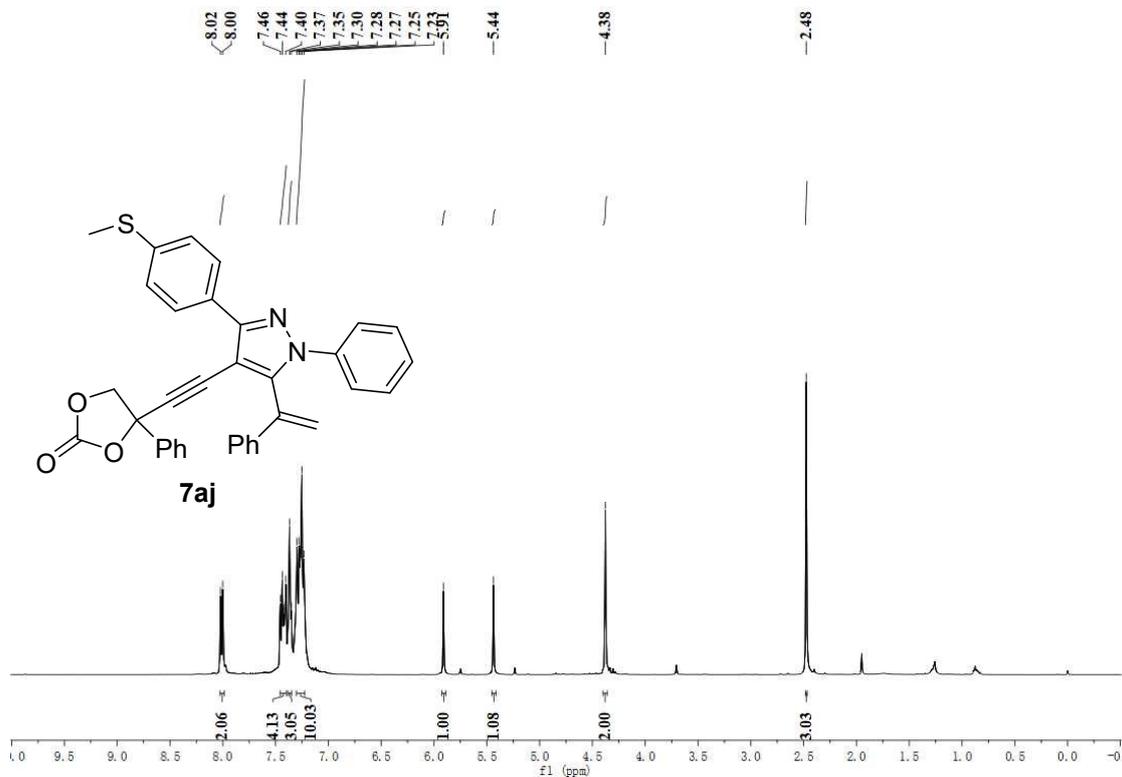
**<sup>1</sup>H NMR of 7ai (400 MHz, CDCl<sub>3</sub>)**



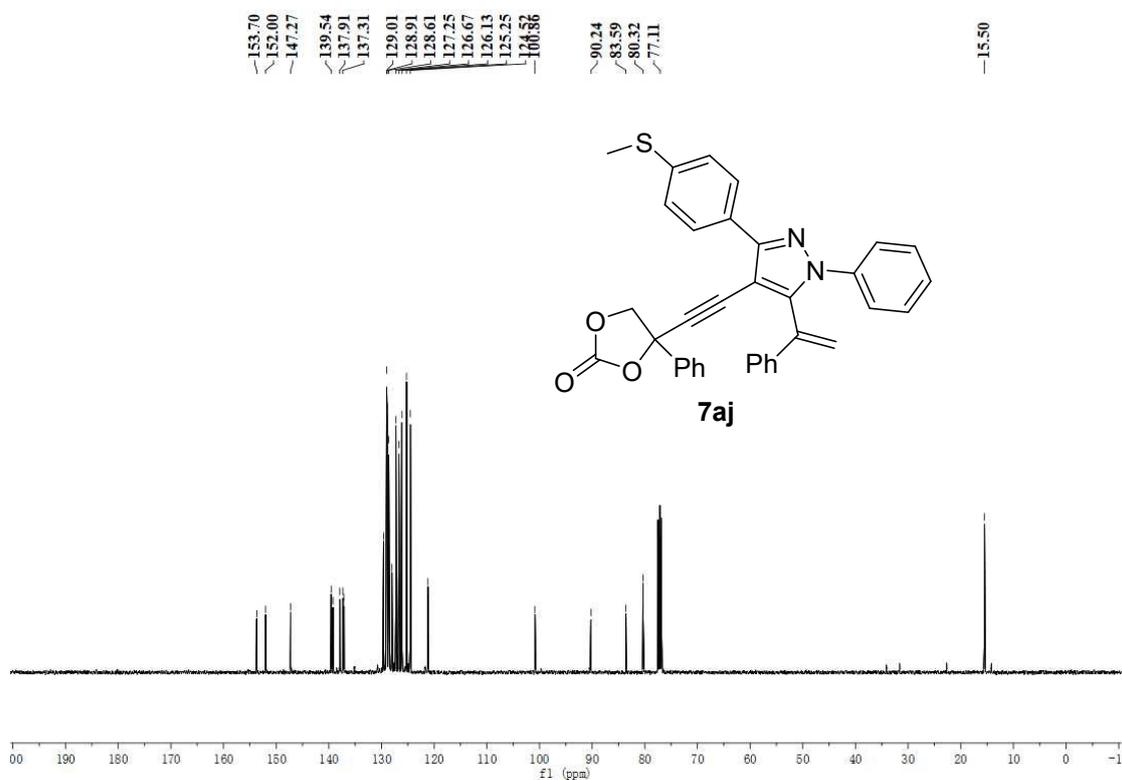
**<sup>13</sup>C{<sup>1</sup>H} NMR of 7ai (101 MHz, CDCl<sub>3</sub>)**



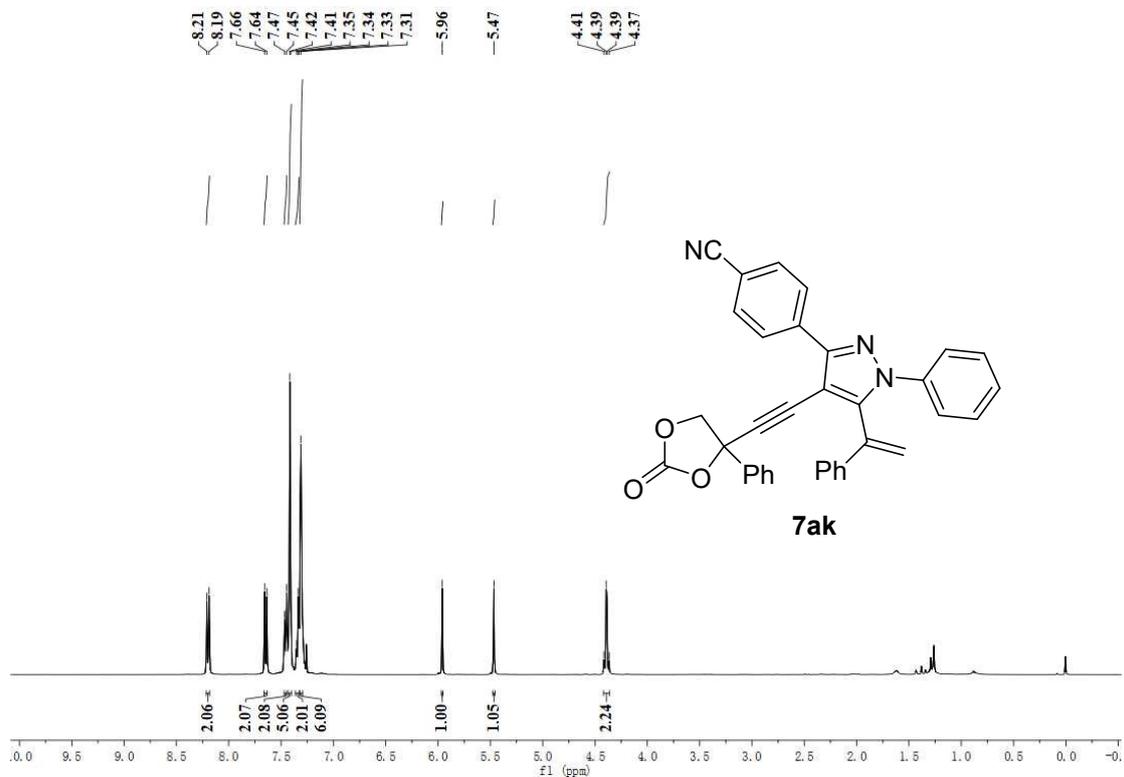
**<sup>1</sup>H NMR of 7aj (400 MHz, CDCl<sub>3</sub>)**



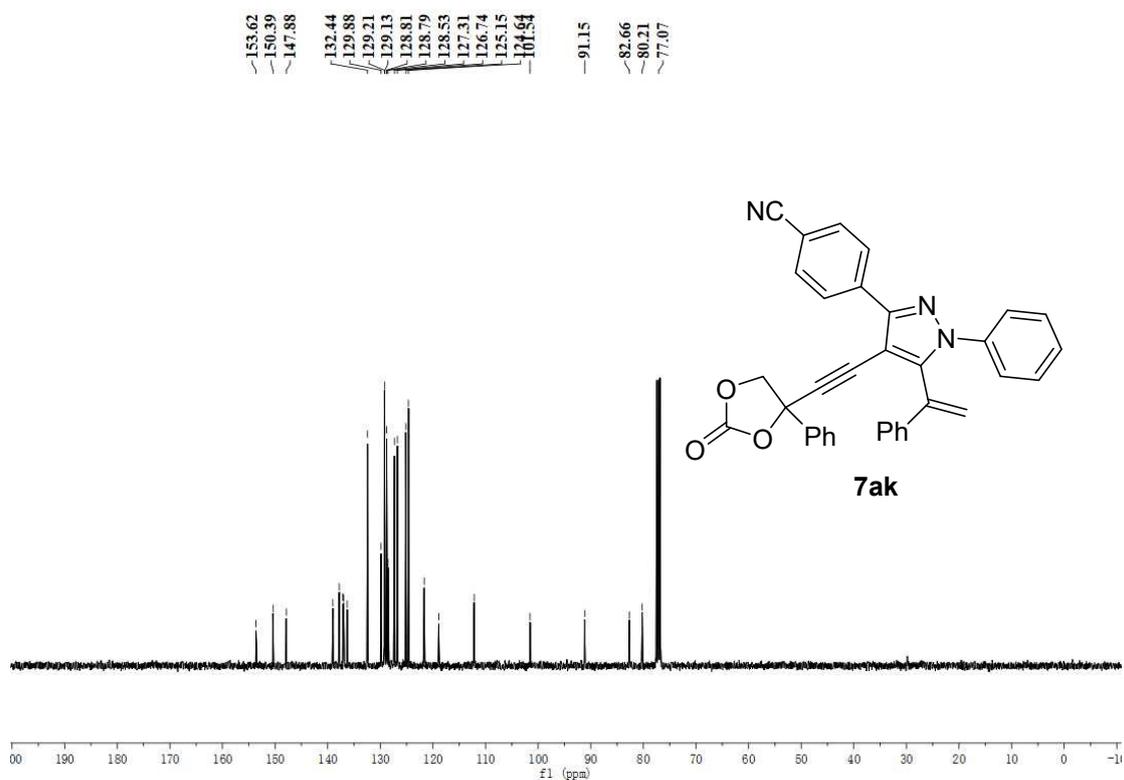
**<sup>13</sup>C{<sup>1</sup>H} NMR of 7aj (101 MHz, CDCl<sub>3</sub>)**



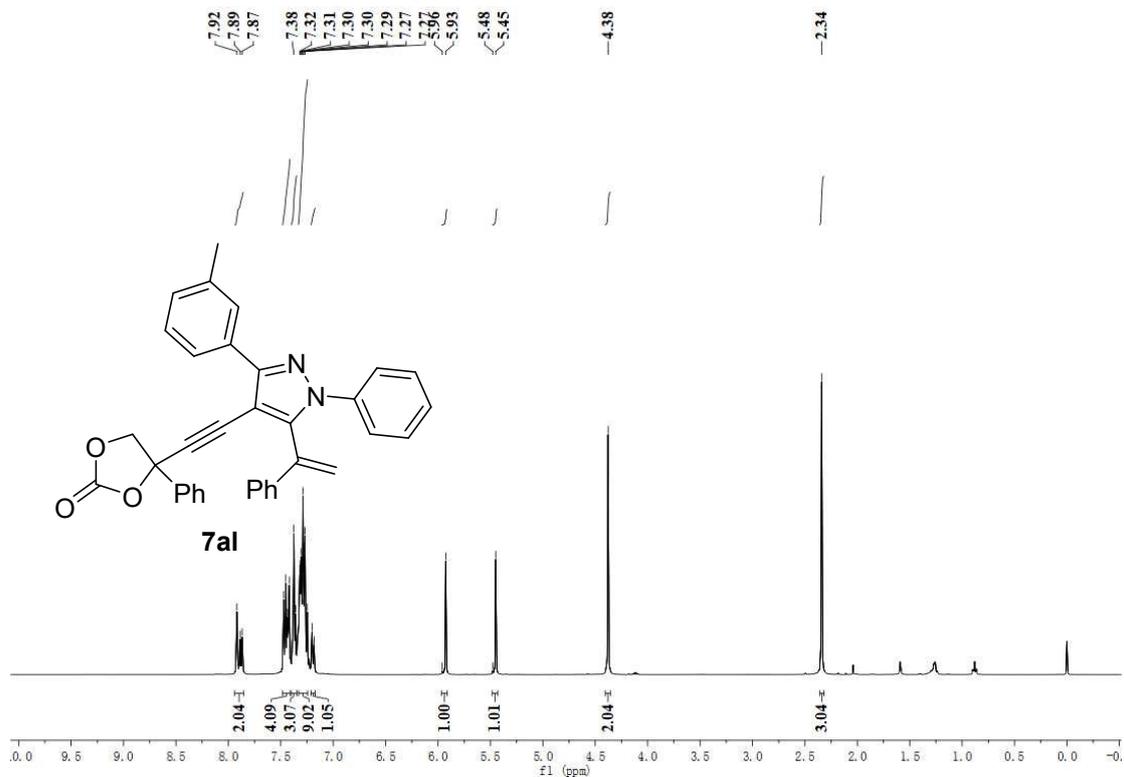
**<sup>1</sup>H NMR of 7ak (400 MHz, CDCl<sub>3</sub>)**



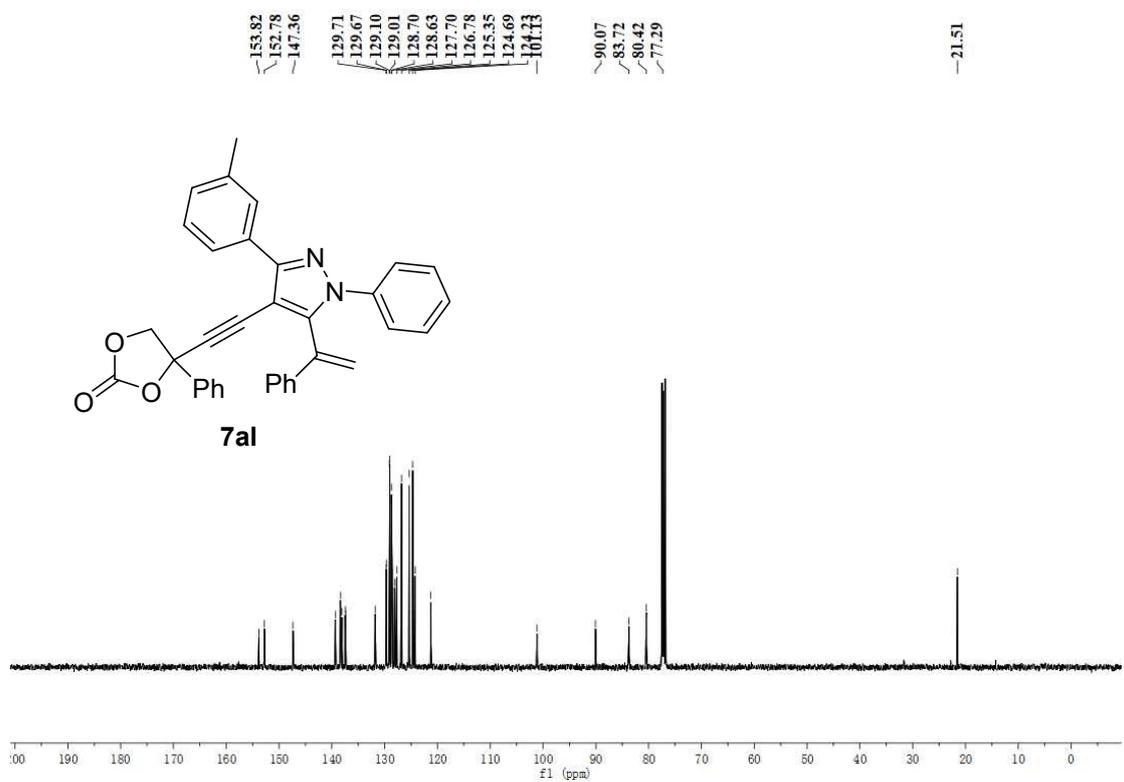
**<sup>13</sup>C{<sup>1</sup>H} NMR of 7ak (101 MHz, CDCl<sub>3</sub>)**



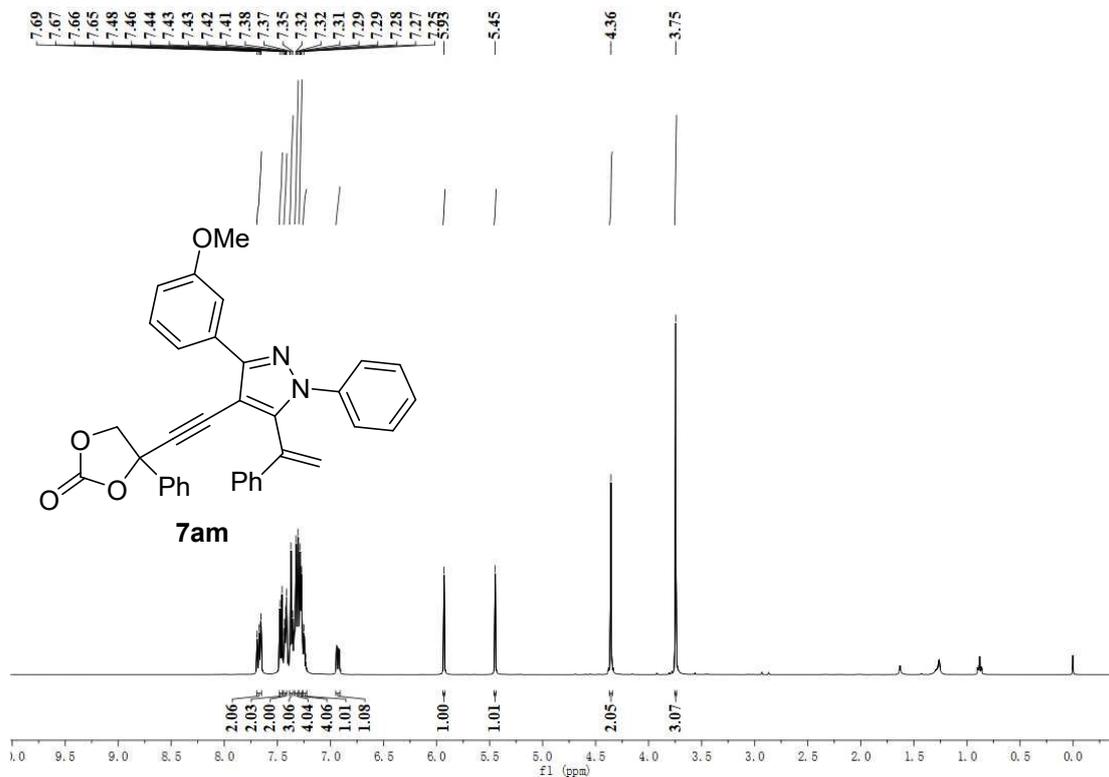
**<sup>1</sup>H NMR of 7al (400 MHz, CDCl<sub>3</sub>)**



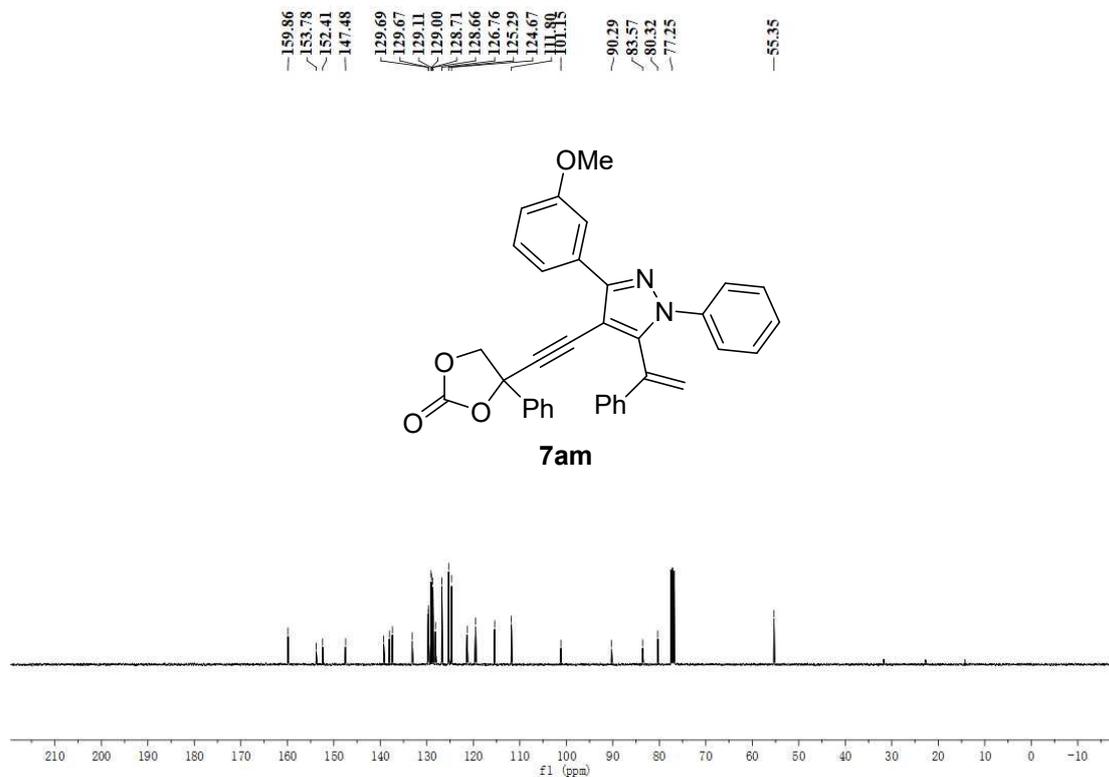
**<sup>13</sup>C{<sup>1</sup>H} NMR of 7al (101 MHz, CDCl<sub>3</sub>)**



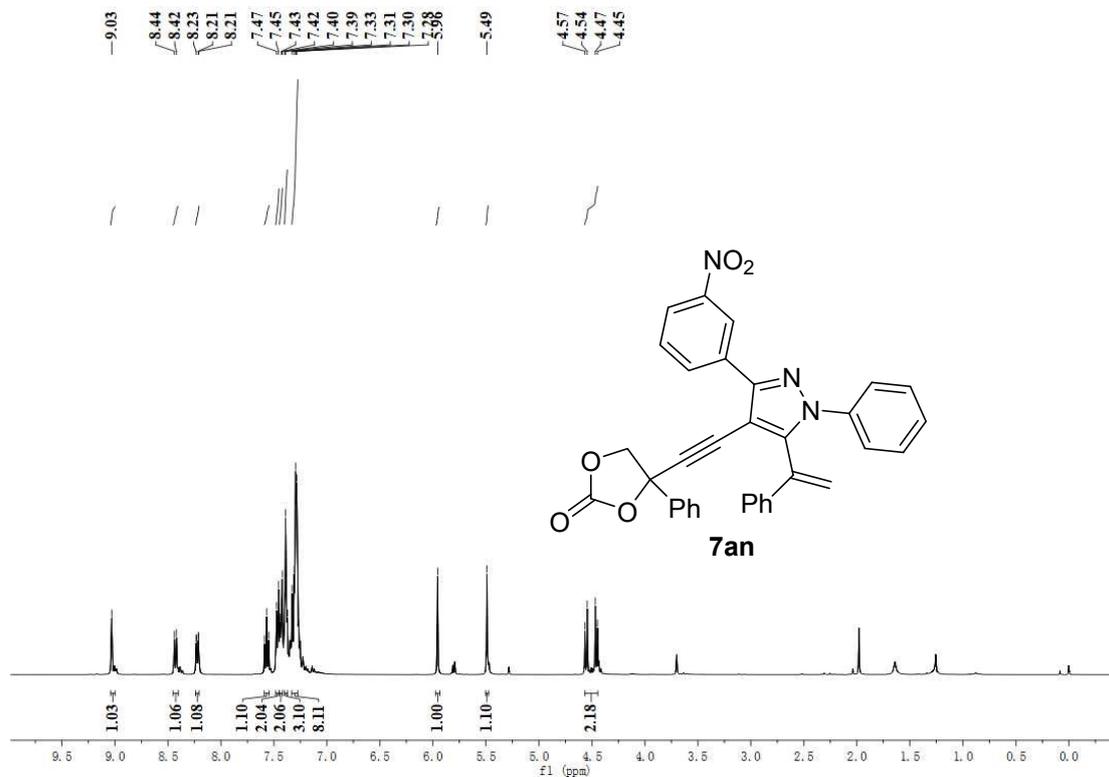
**<sup>1</sup>H NMR of 7am (400 MHz, CDCl<sub>3</sub>)**



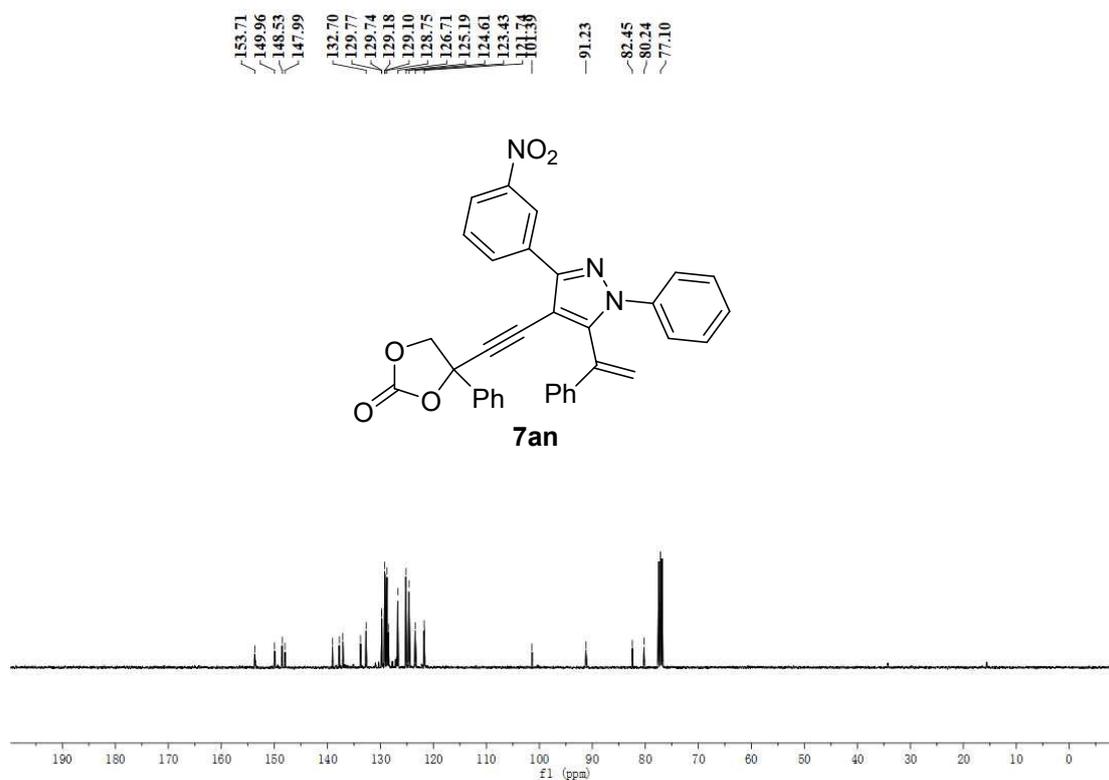
**<sup>13</sup>C{<sup>1</sup>H} NMR of 7am (101 MHz, CDCl<sub>3</sub>)**



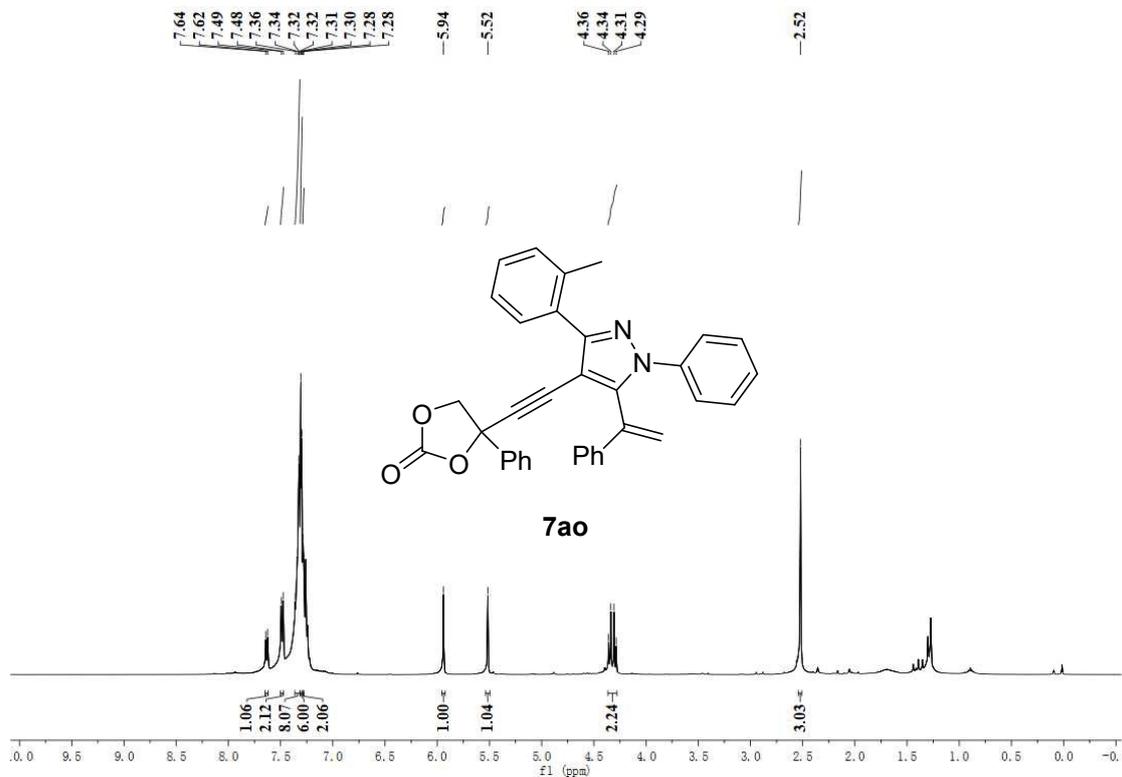
**<sup>1</sup>H NMR of 7an (400 MHz, CDCl<sub>3</sub>)**



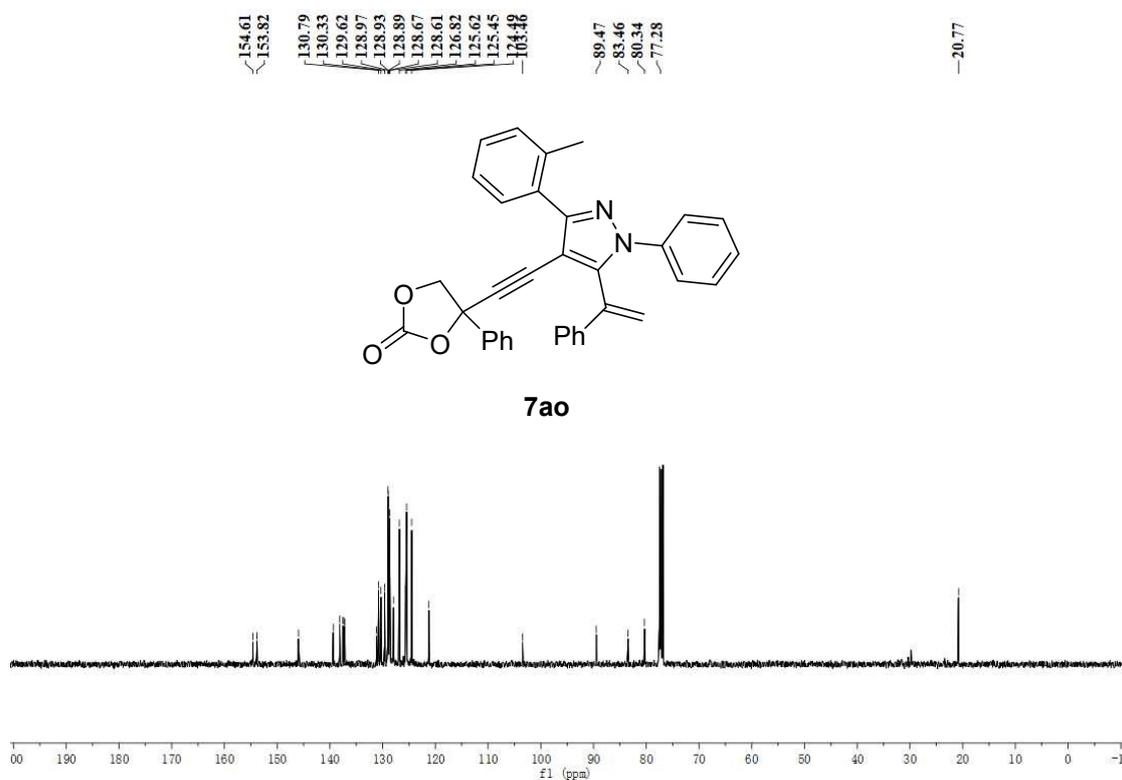
**<sup>13</sup>C{<sup>1</sup>H} NMR of 7an (101 MHz, CDCl<sub>3</sub>)**



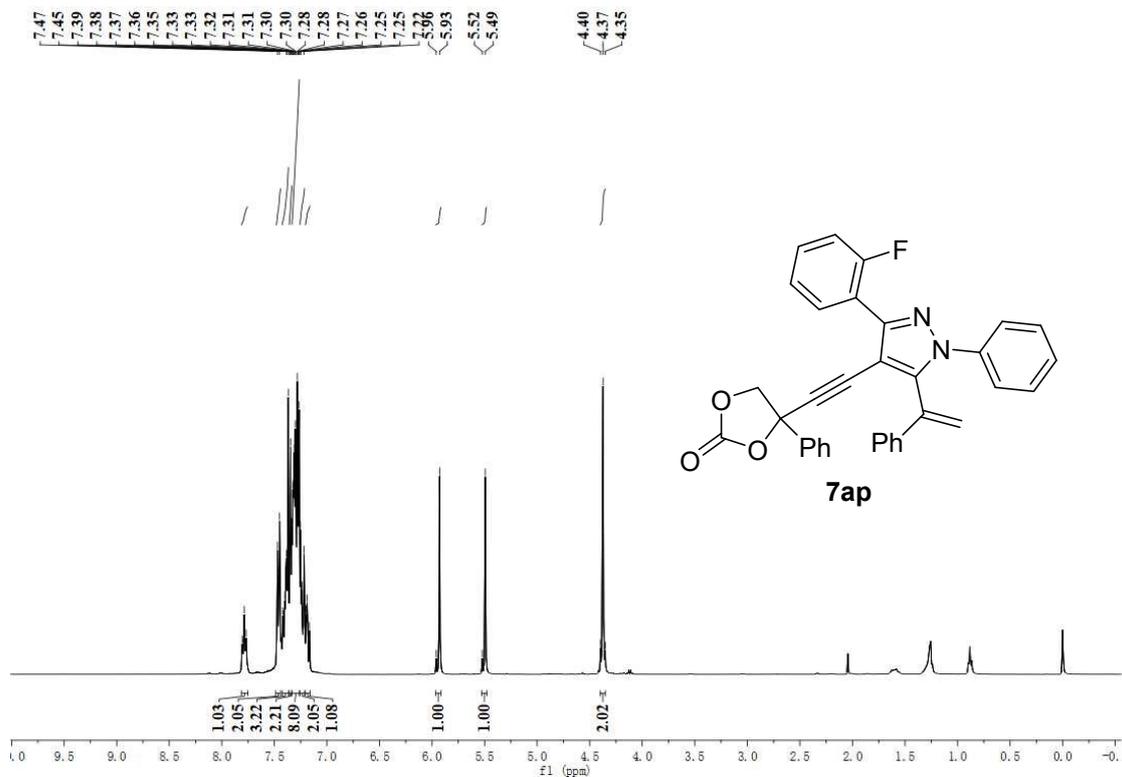
**<sup>1</sup>H NMR of 7ao (400 MHz, CDCl<sub>3</sub>)**



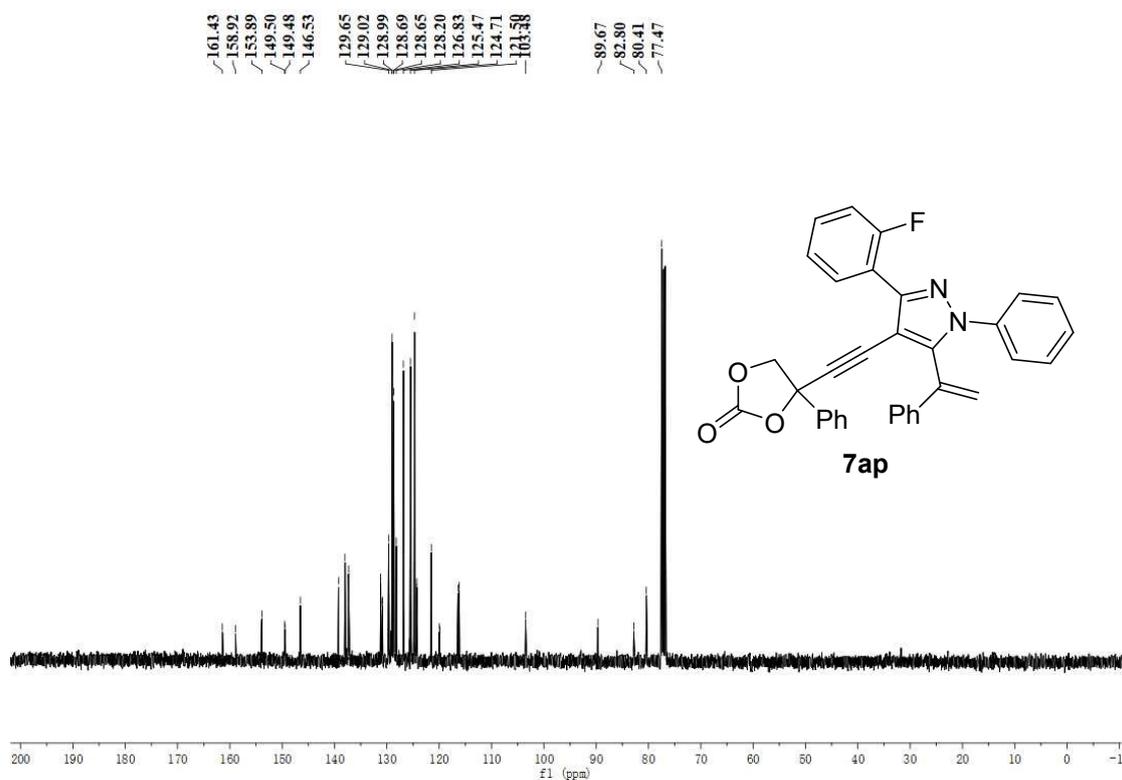
**<sup>13</sup>C{<sup>1</sup>H} NMR of 7ao (101 MHz, CDCl<sub>3</sub>)**



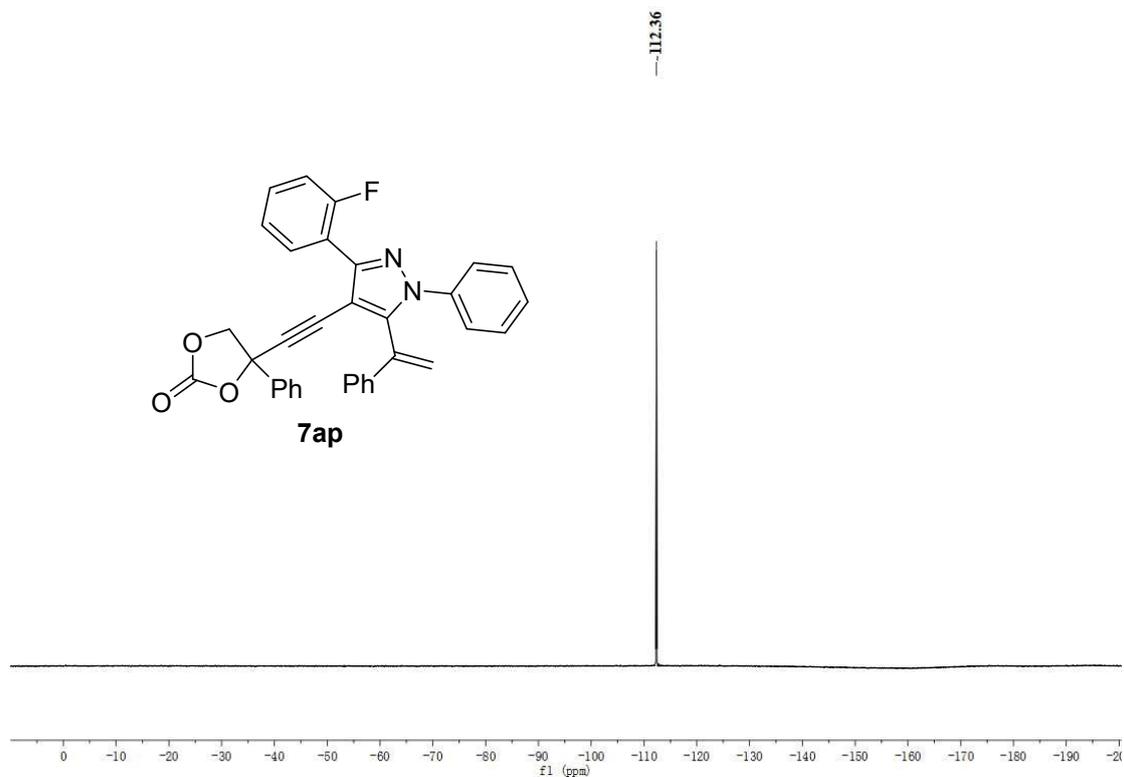
**$^1\text{H}$  NMR of 7ap (400 MHz,  $\text{CDCl}_3$ )**



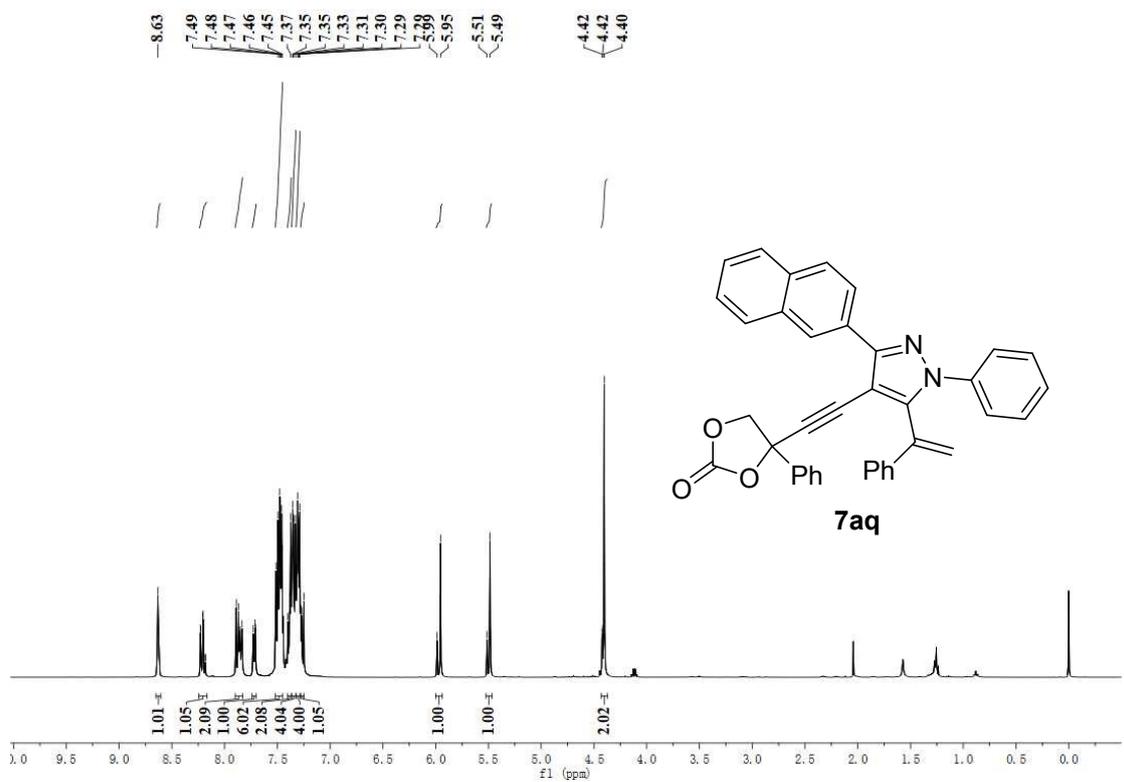
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 7ap (101 MHz,  $\text{CDCl}_3$ )**



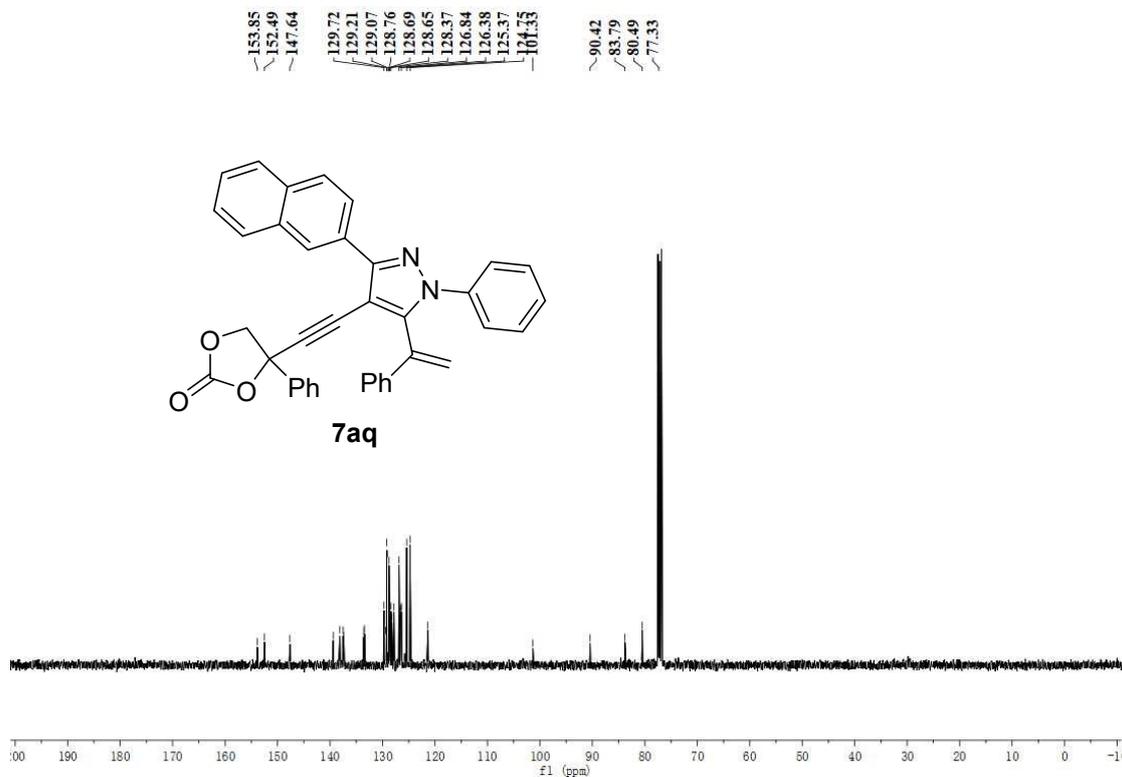
**$^{19}\text{F}$  NMR of 7ap (376 MHz,  $\text{CDCl}_3$ )**



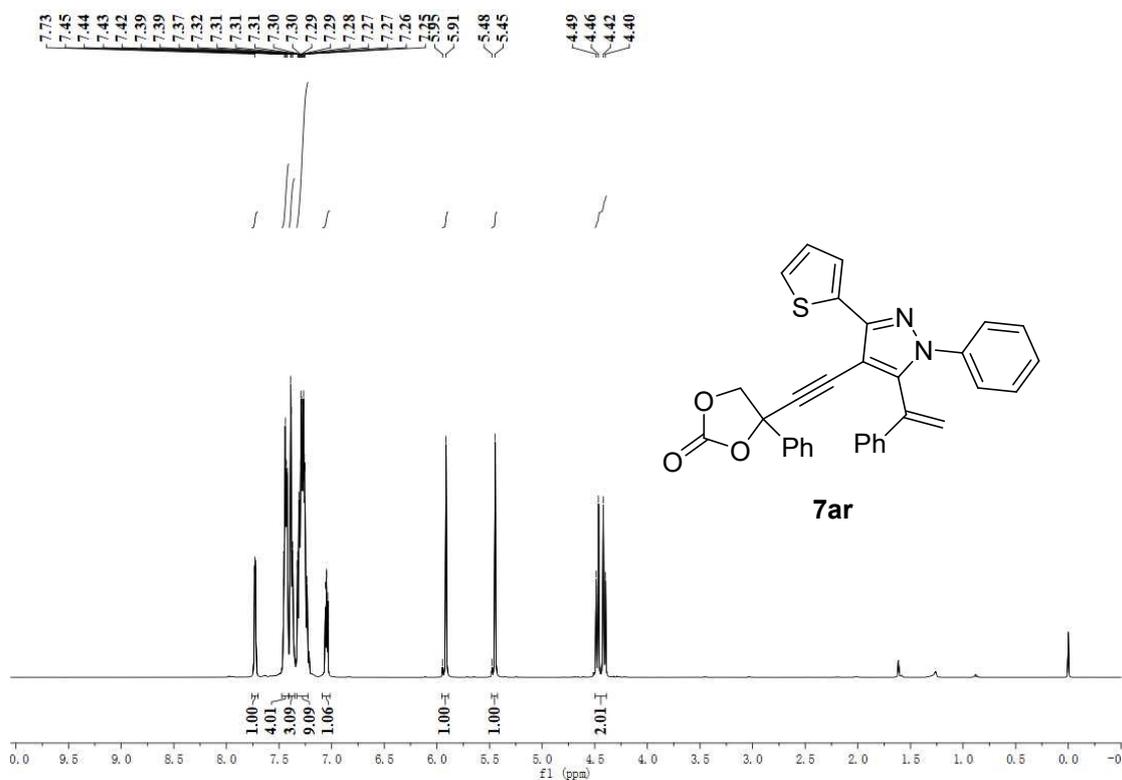
**$^1\text{H}$  NMR of 7aq (400 MHz,  $\text{CDCl}_3$ )**



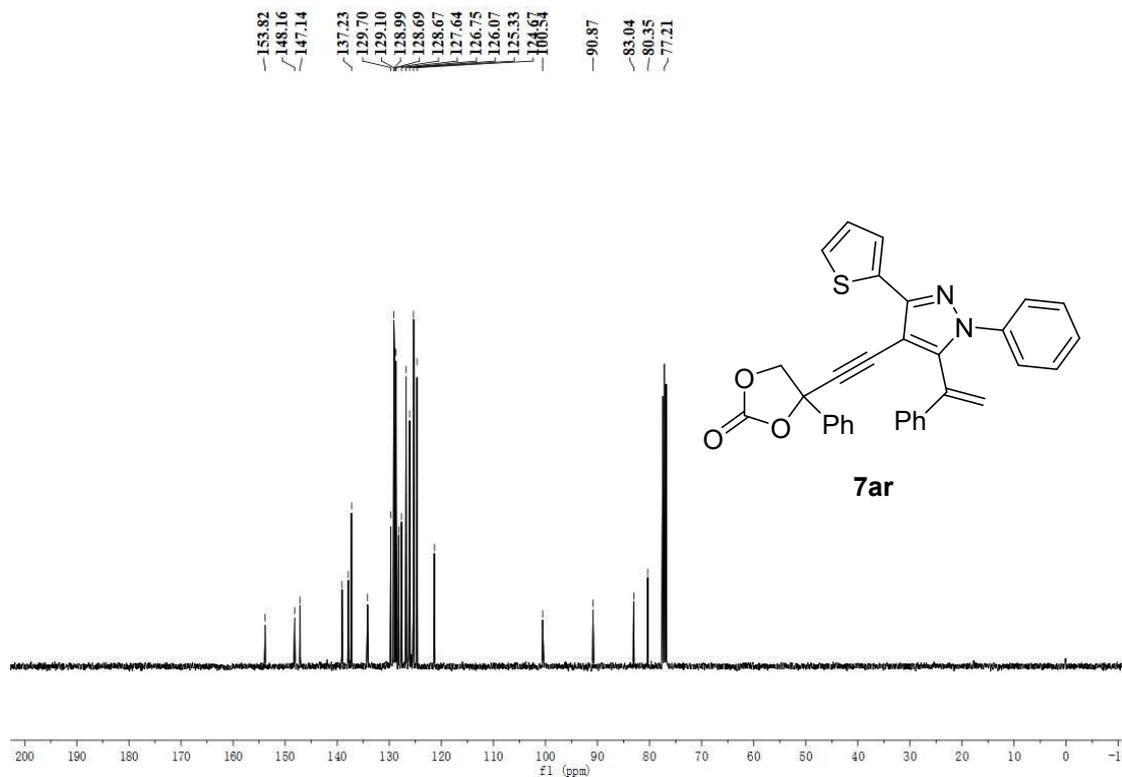
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 7aq (101 MHz,  $\text{CDCl}_3$ )**



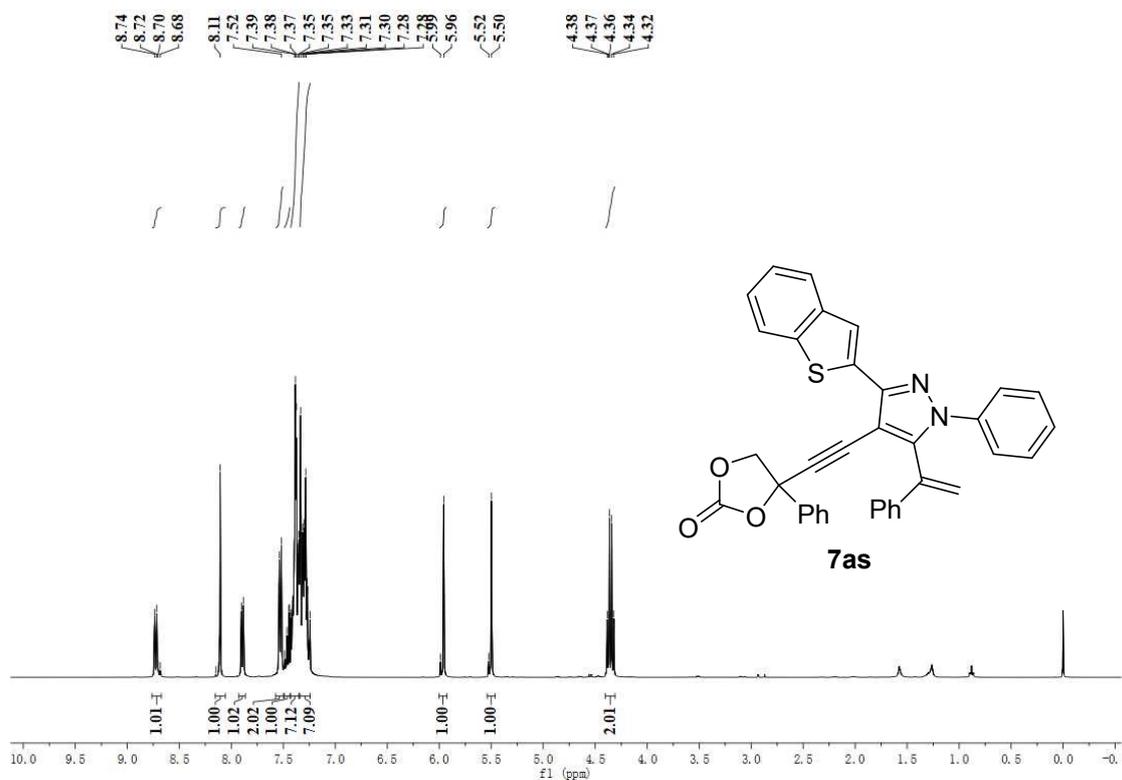
**$^1\text{H}$  NMR of 7ar (400 MHz,  $\text{CDCl}_3$ )**



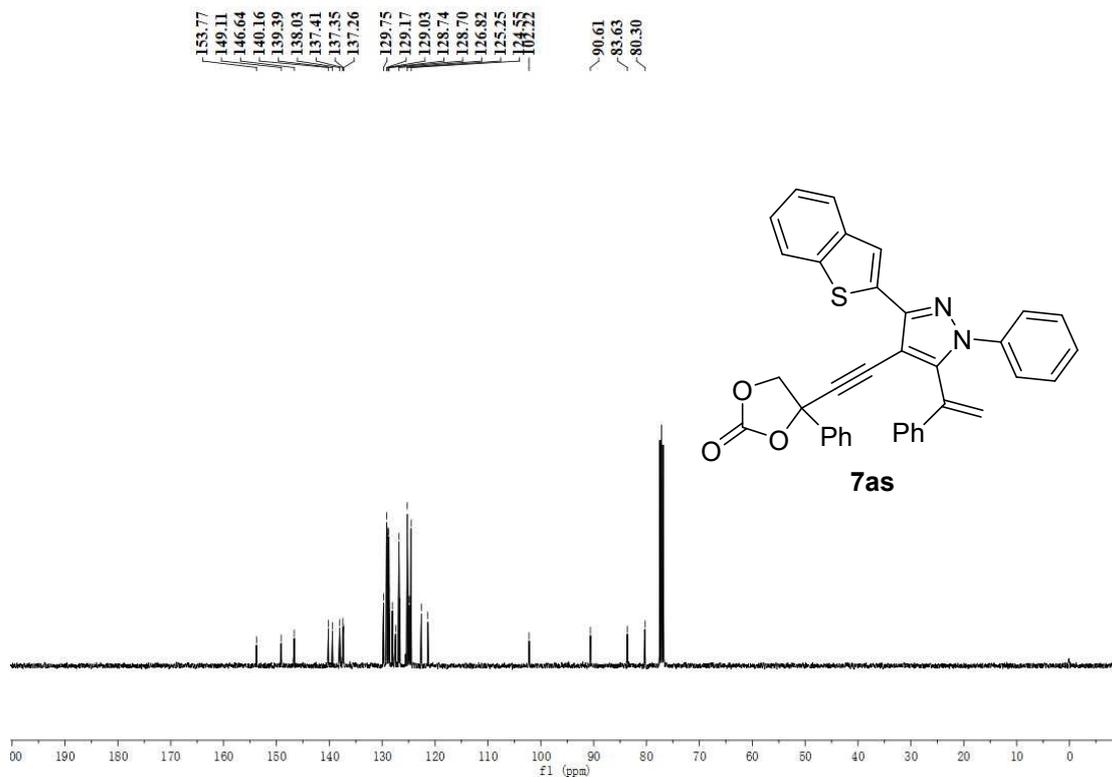
$^{13}\text{C}\{^1\text{H}\}$  NMR of 7ar (101 MHz,  $\text{CDCl}_3$ )



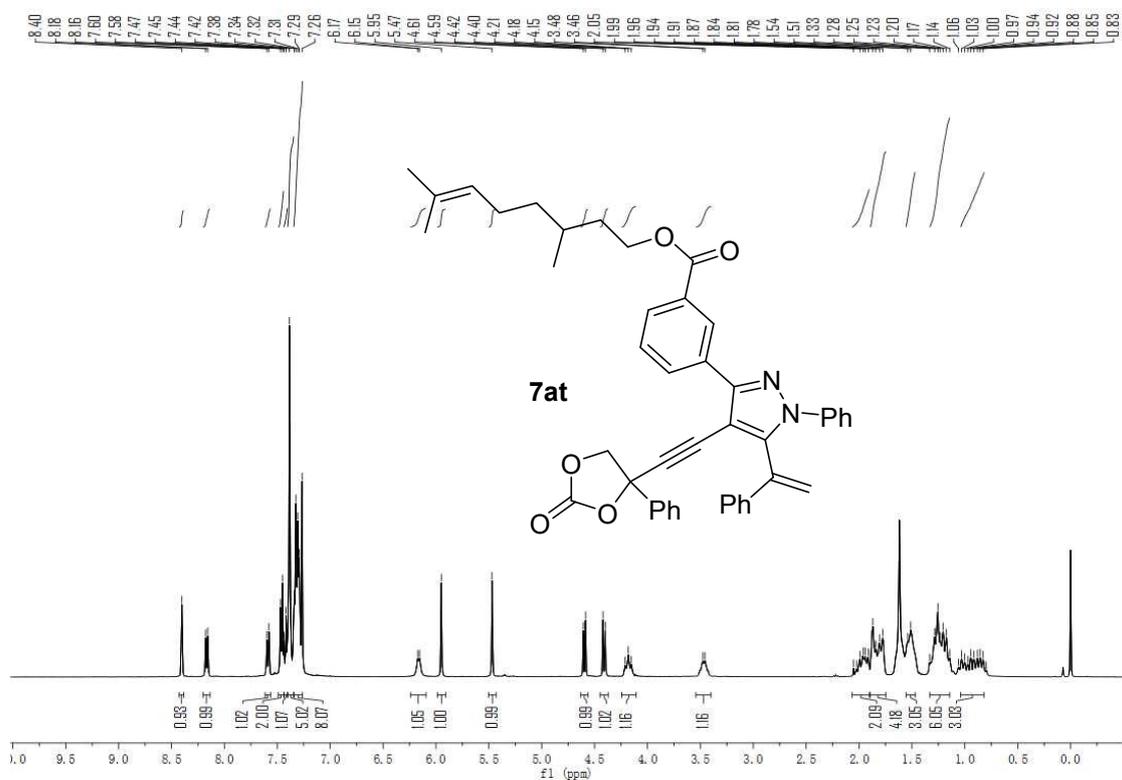
$^1\text{H}$  NMR of 7as (400 MHz,  $\text{CDCl}_3$ )



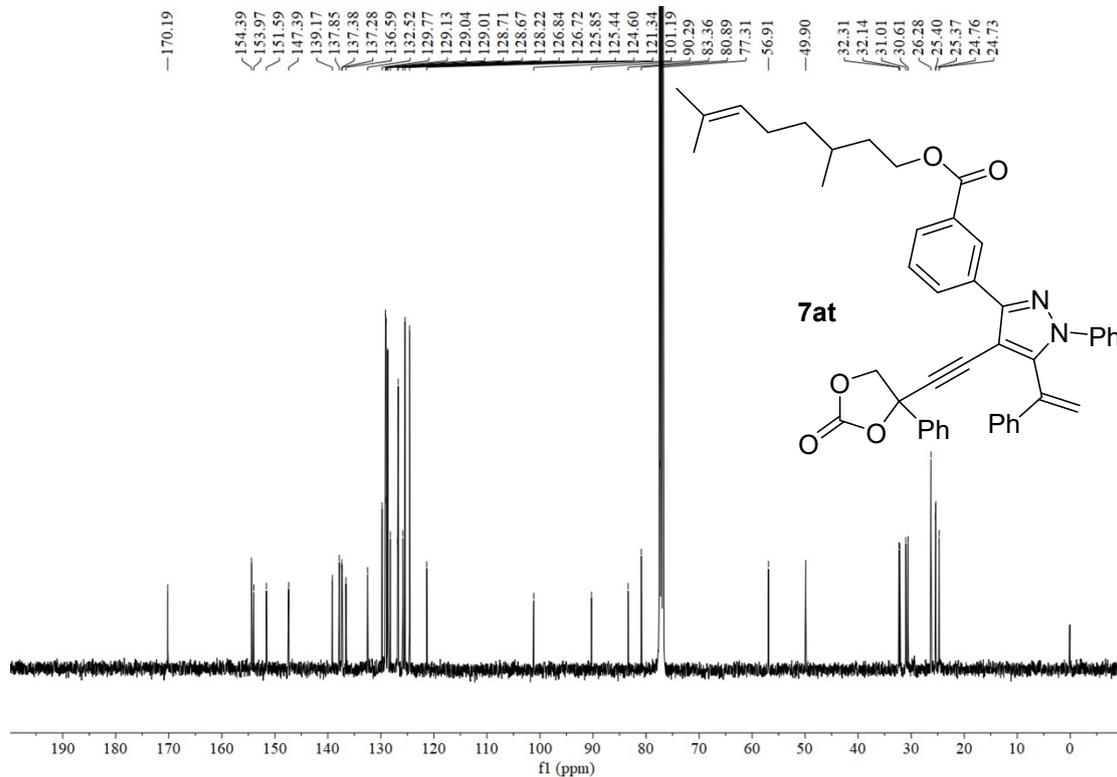
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 7as (101 MHz,  $\text{CDCl}_3$ )**



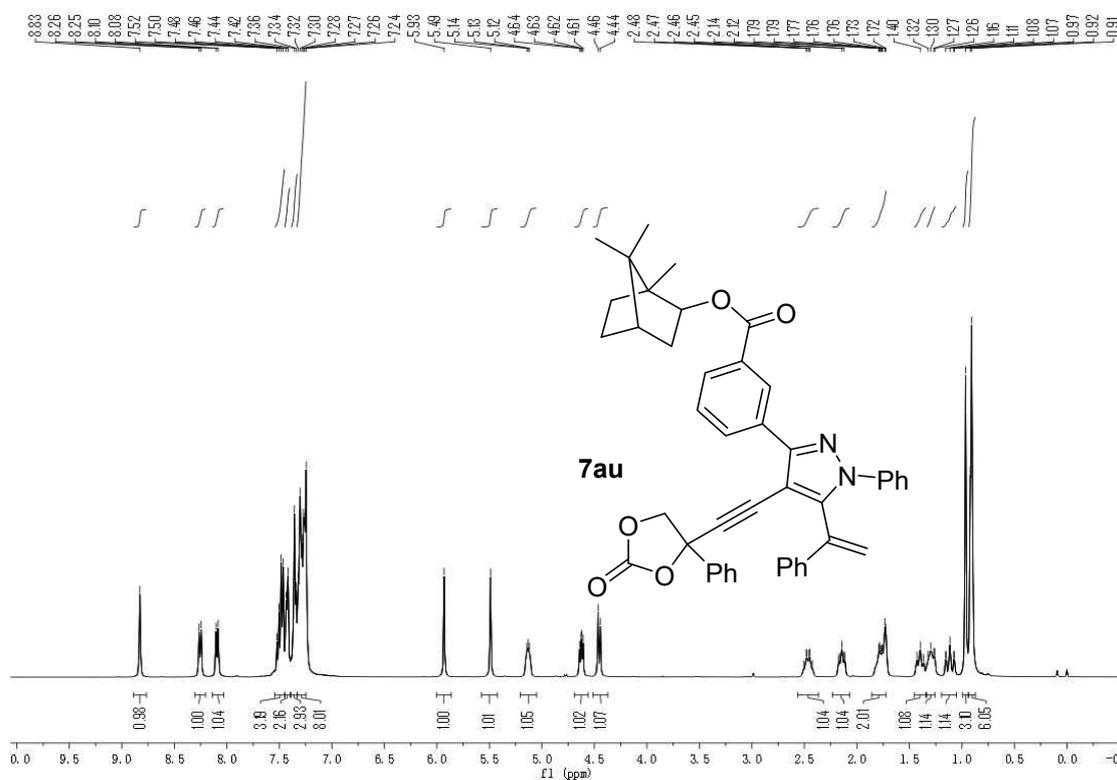
**$^1\text{H}$  NMR of 7at (400 MHz,  $\text{CDCl}_3$ )**



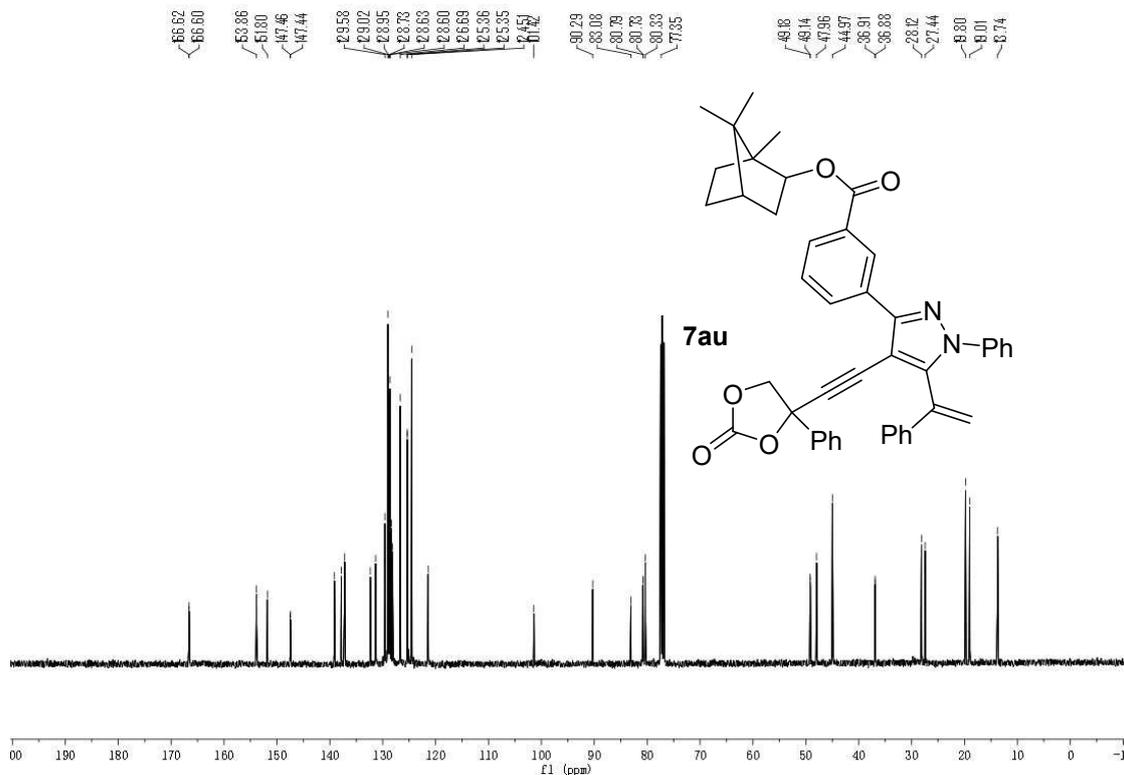
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 7at (101 MHz,  $\text{CDCl}_3$ )**



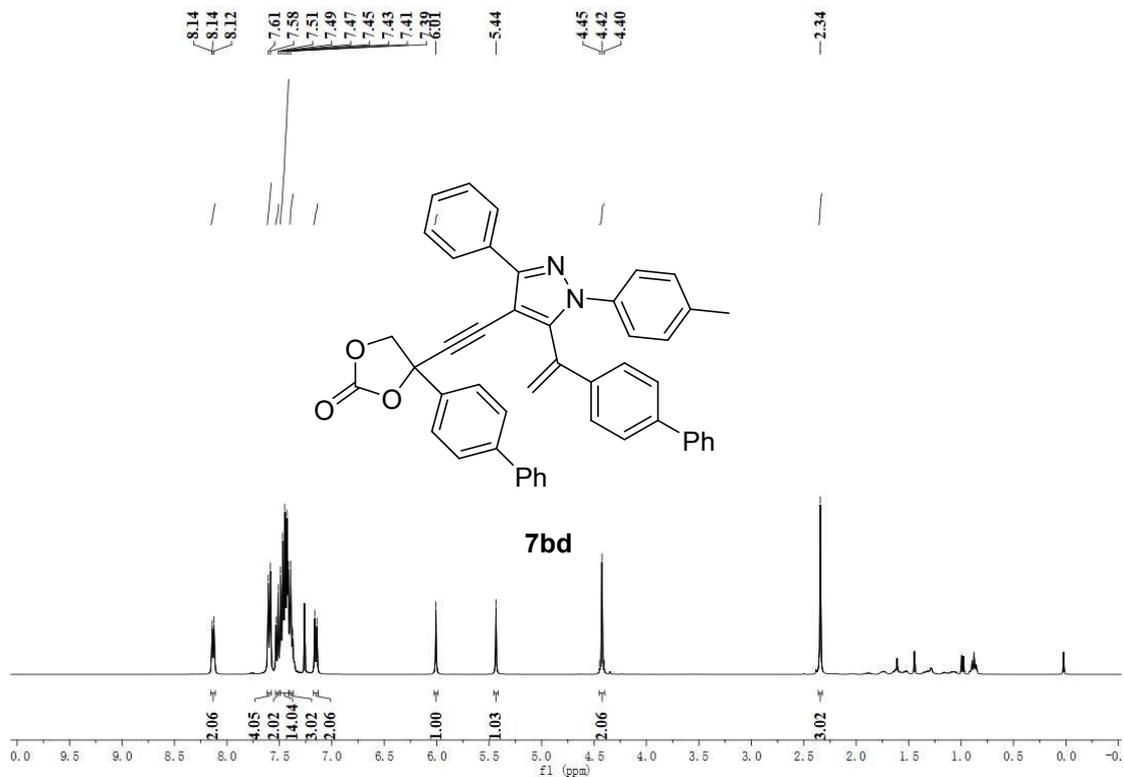
**$^1\text{H}$  NMR of 7au (400 MHz,  $\text{CDCl}_3$ )**



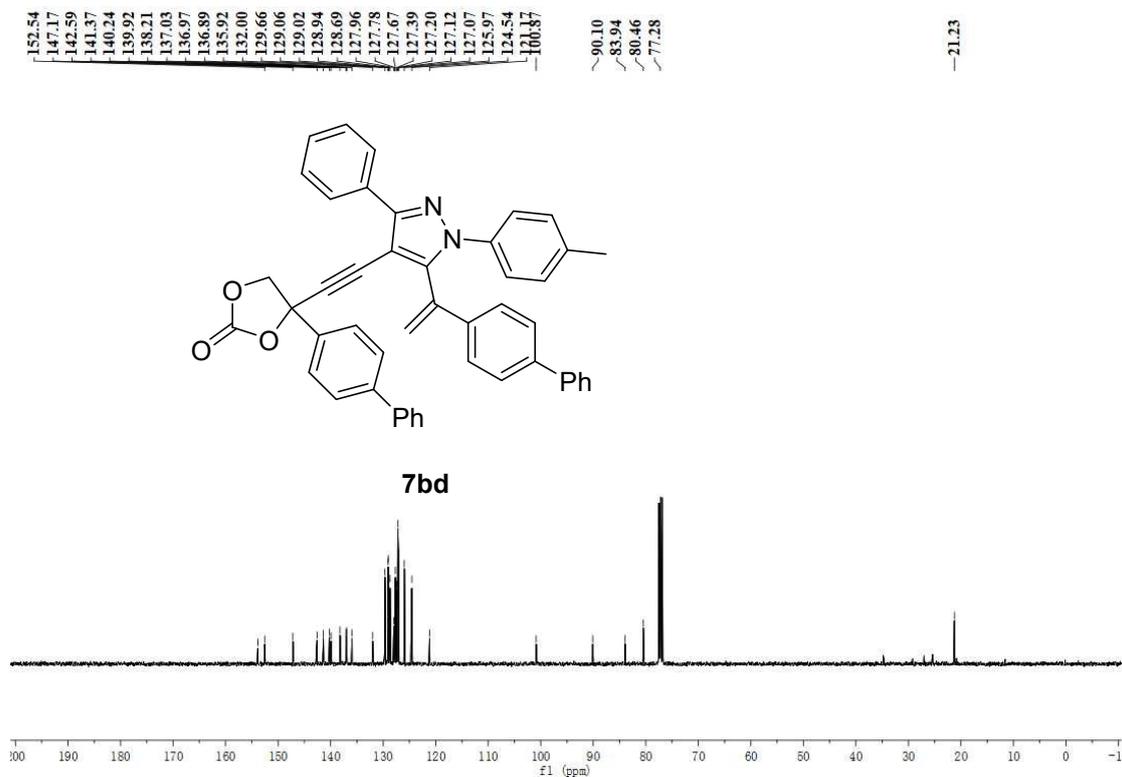
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 7au (101 MHz,  $\text{CDCl}_3$ )**



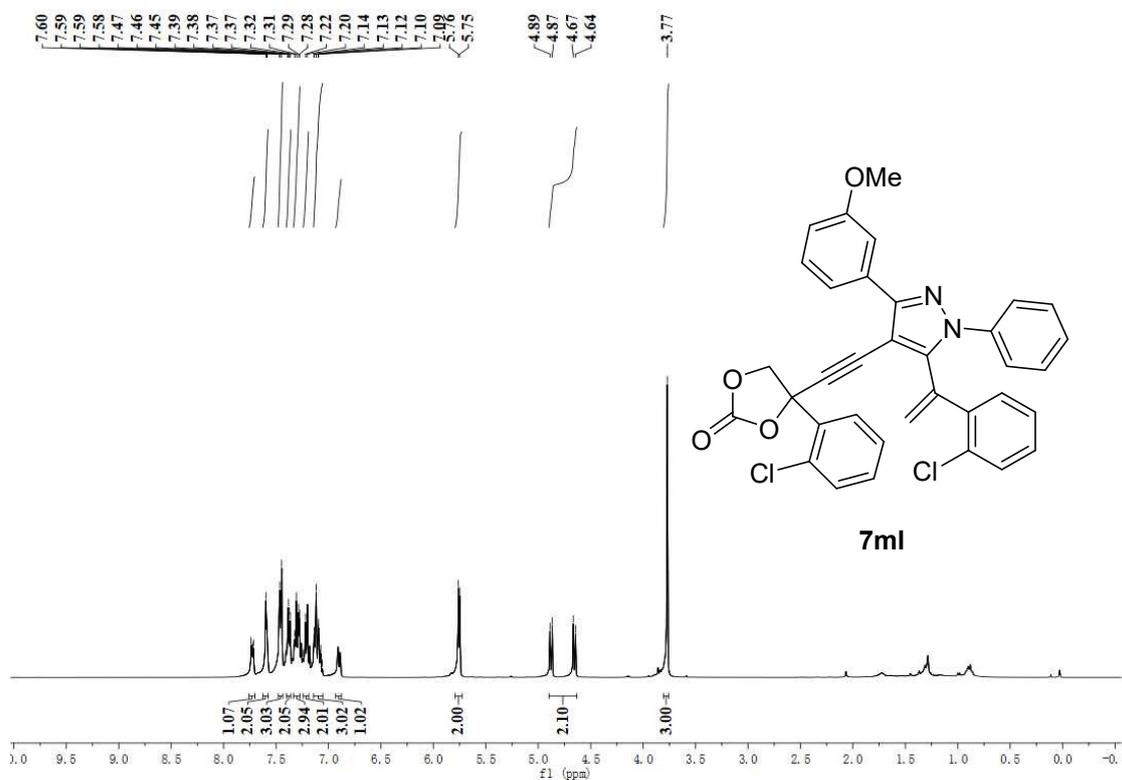
**$^1\text{H}$  NMR of 7bd (400 MHz,  $\text{CDCl}_3$ )**



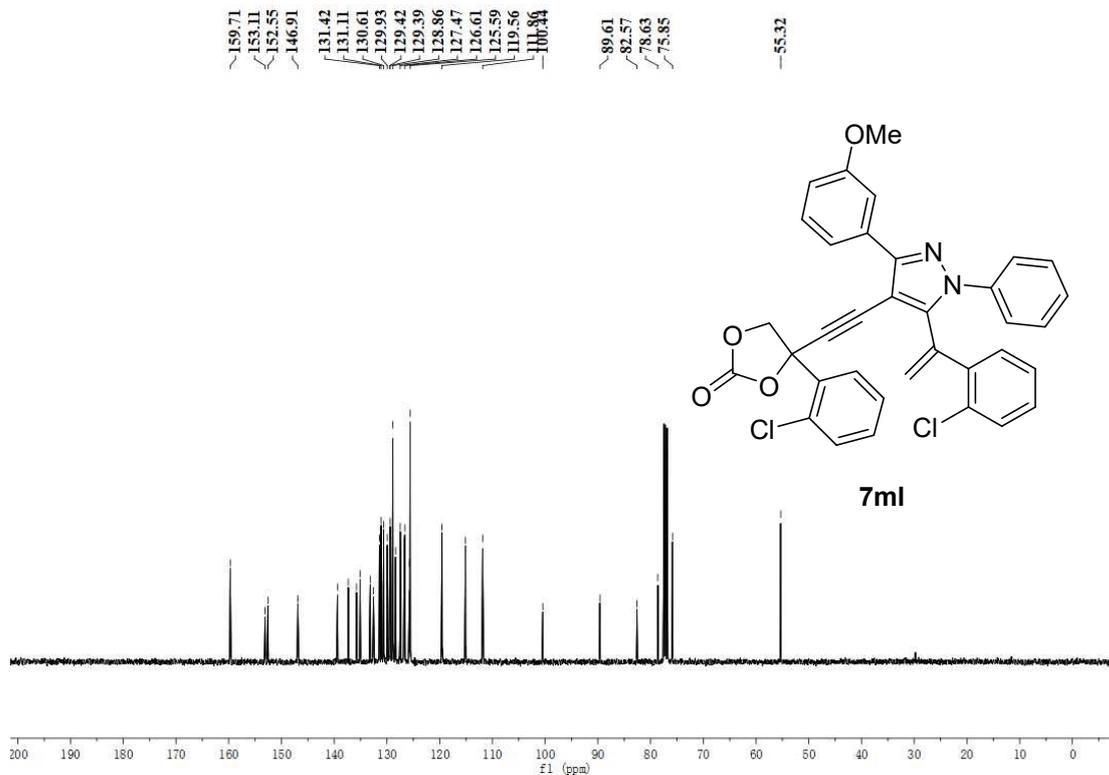
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 7bd (101 MHz,  $\text{CDCl}_3$ )**



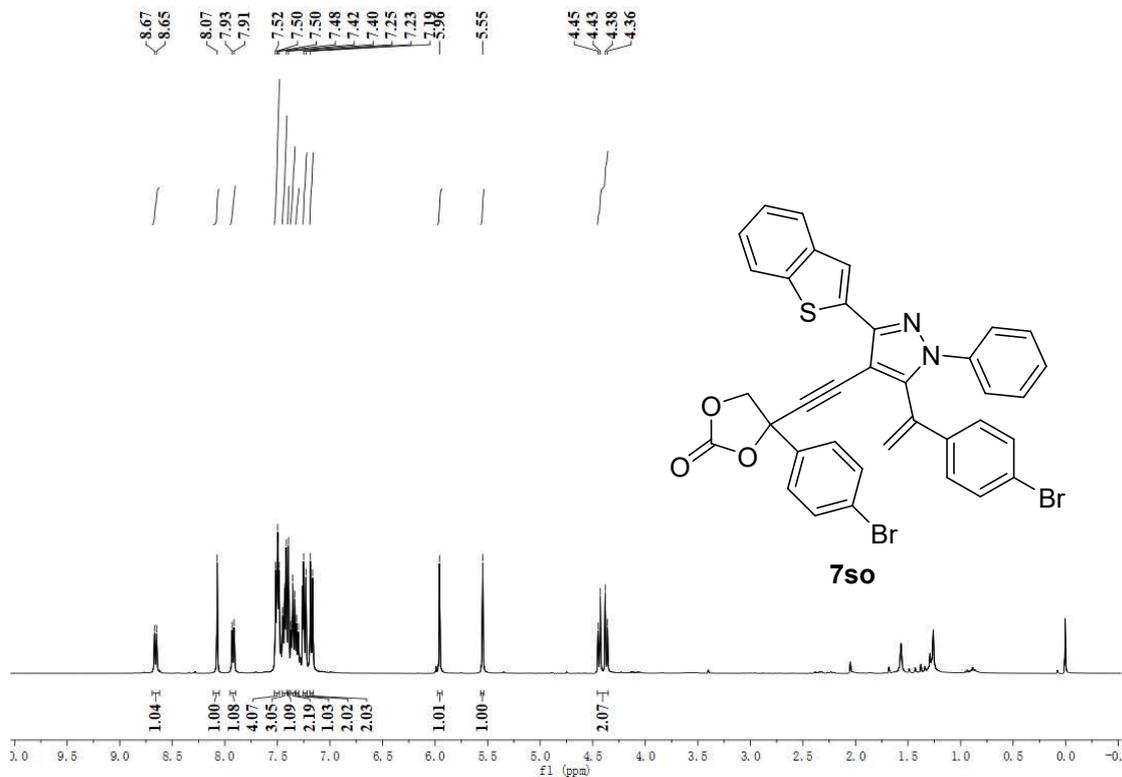
**$^1\text{H}$  NMR of 7ml (400 MHz,  $\text{CDCl}_3$ )**



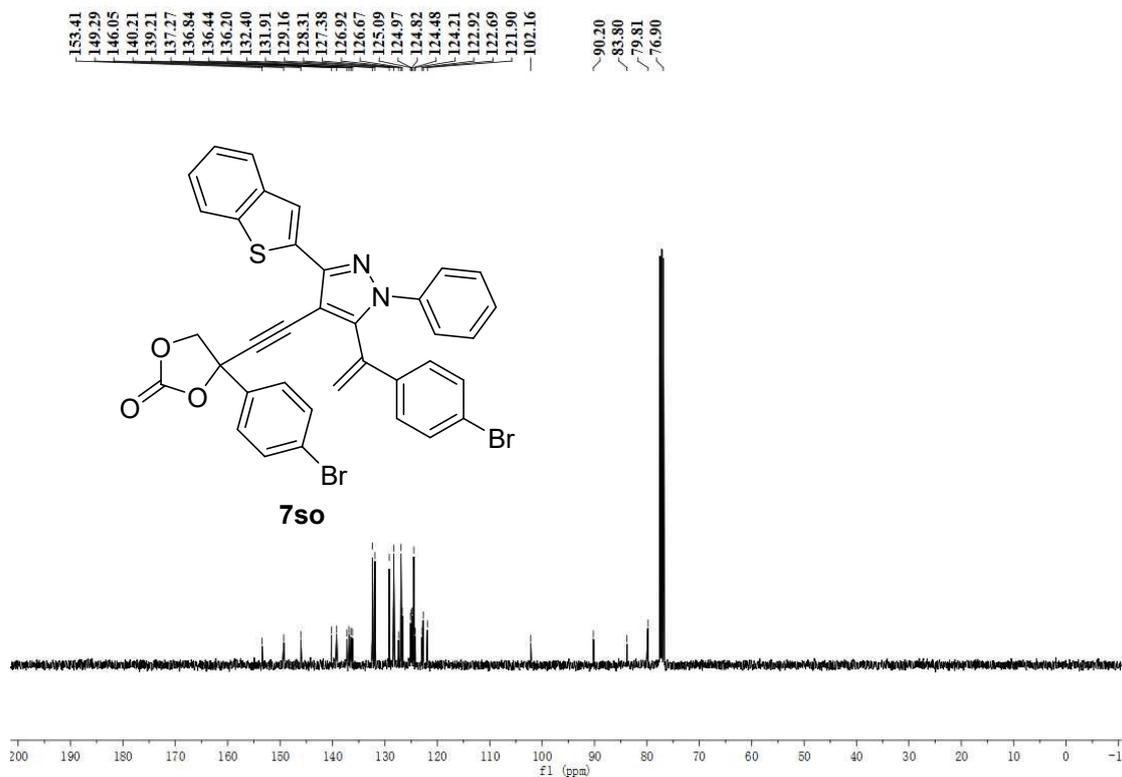
$^{13}\text{C}\{^1\text{H}\}$  NMR of 7ml (101 MHz,  $\text{CDCl}_3$ )



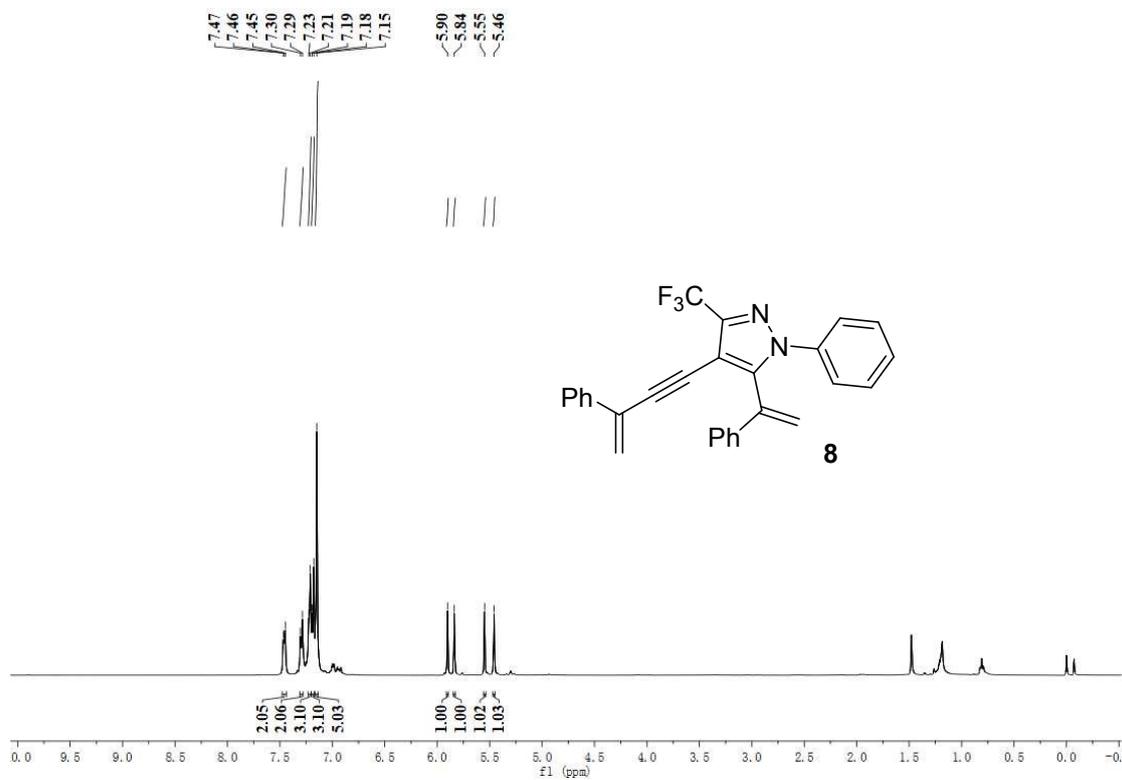
$^1\text{H}$  NMR of 7so (400 MHz,  $\text{CDCl}_3$ )



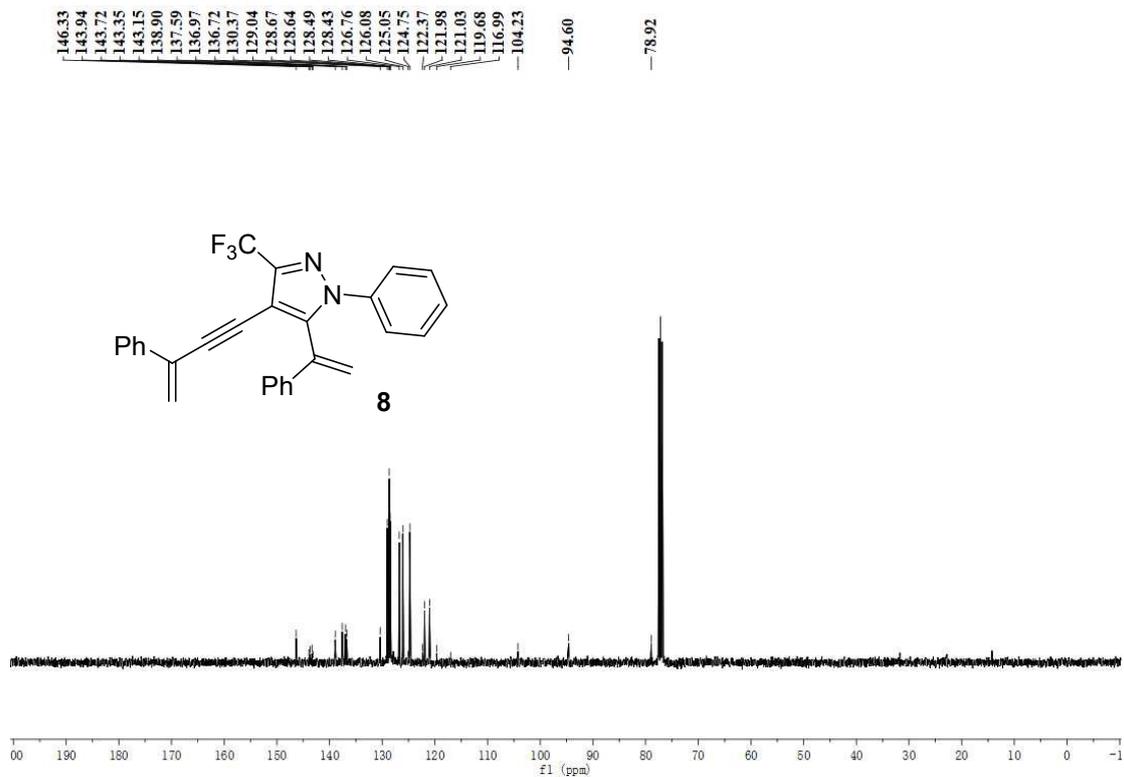
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 7so (101 MHz,  $\text{CDCl}_3$ )**



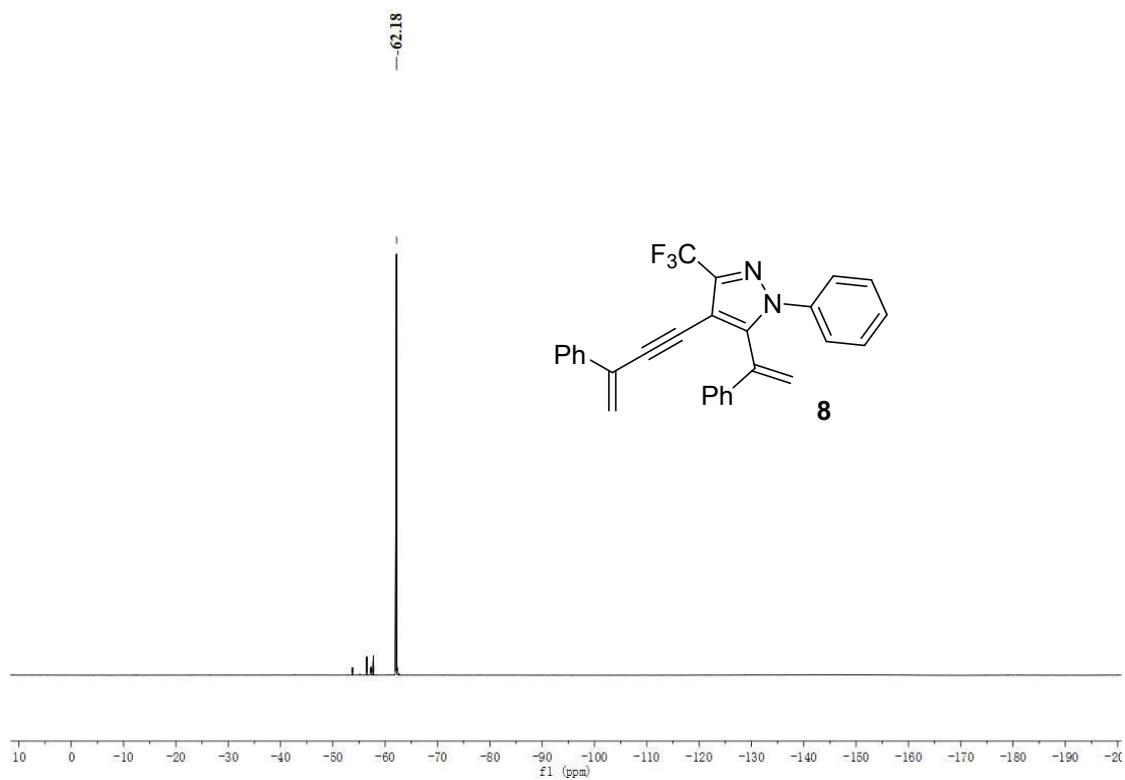
**$^1\text{H}$  NMR of 8 (400 MHz,  $\text{CDCl}_3$ )**



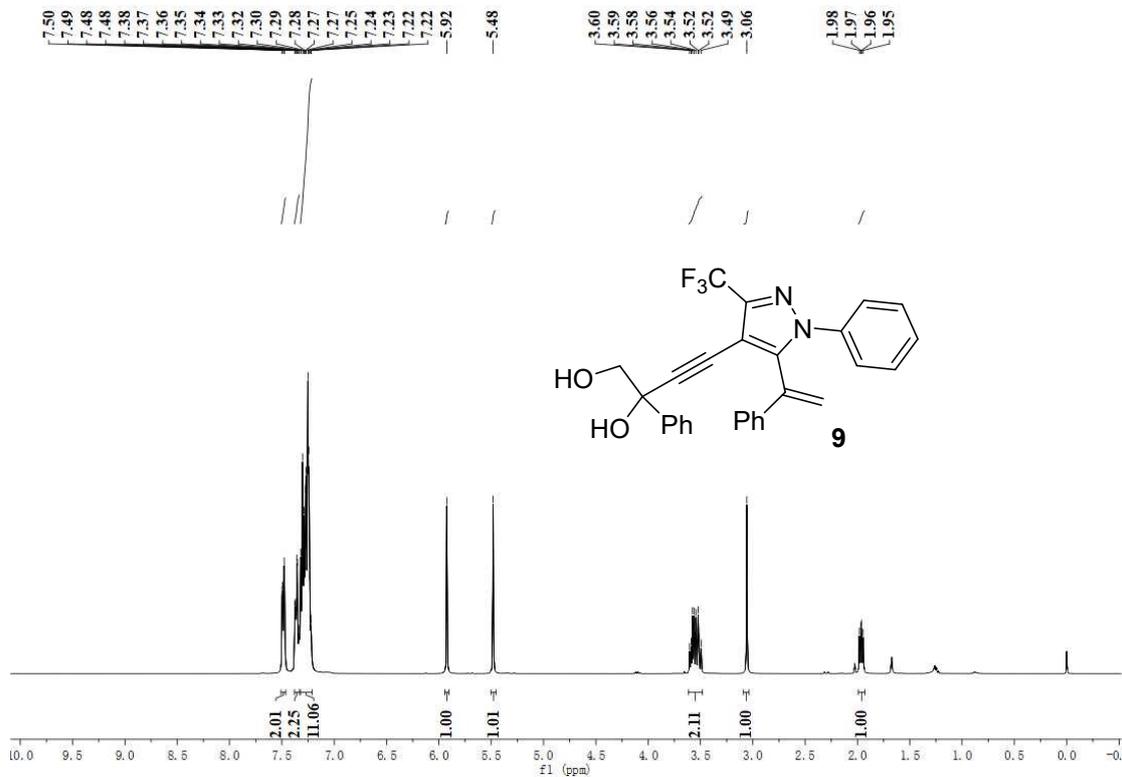
**$^{13}\text{C}\{^1\text{H}\}$  NMR of 8 (101 MHz,  $\text{CDCl}_3$ )**



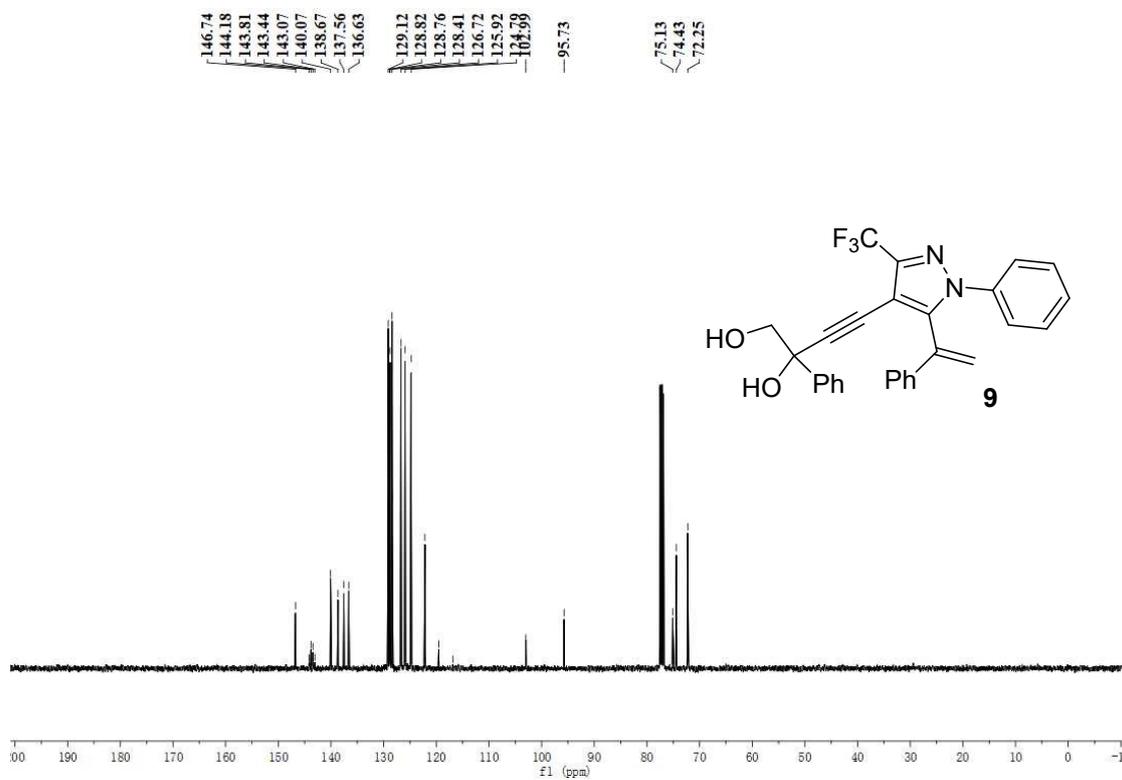
**$^{19}\text{F}$  NMR of 8 (376 MHz,  $\text{CDCl}_3$ )**



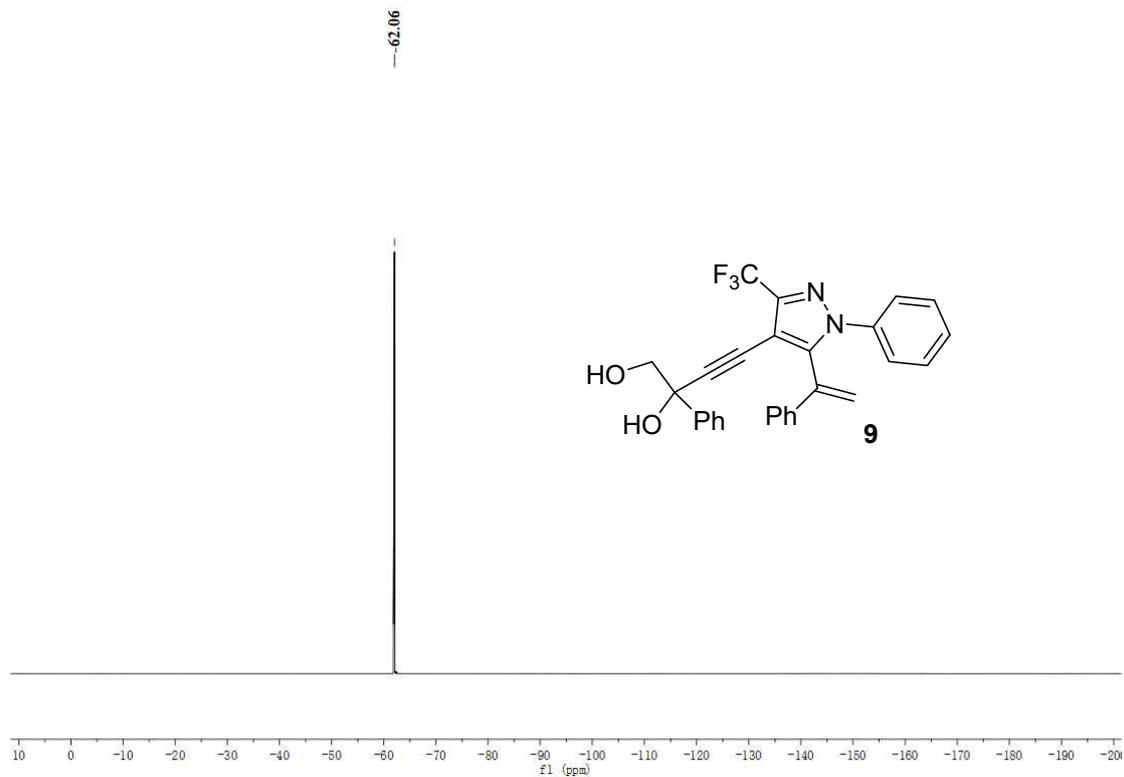
**<sup>1</sup>H NMR of 9 (400 MHz, CDCl<sub>3</sub>)**



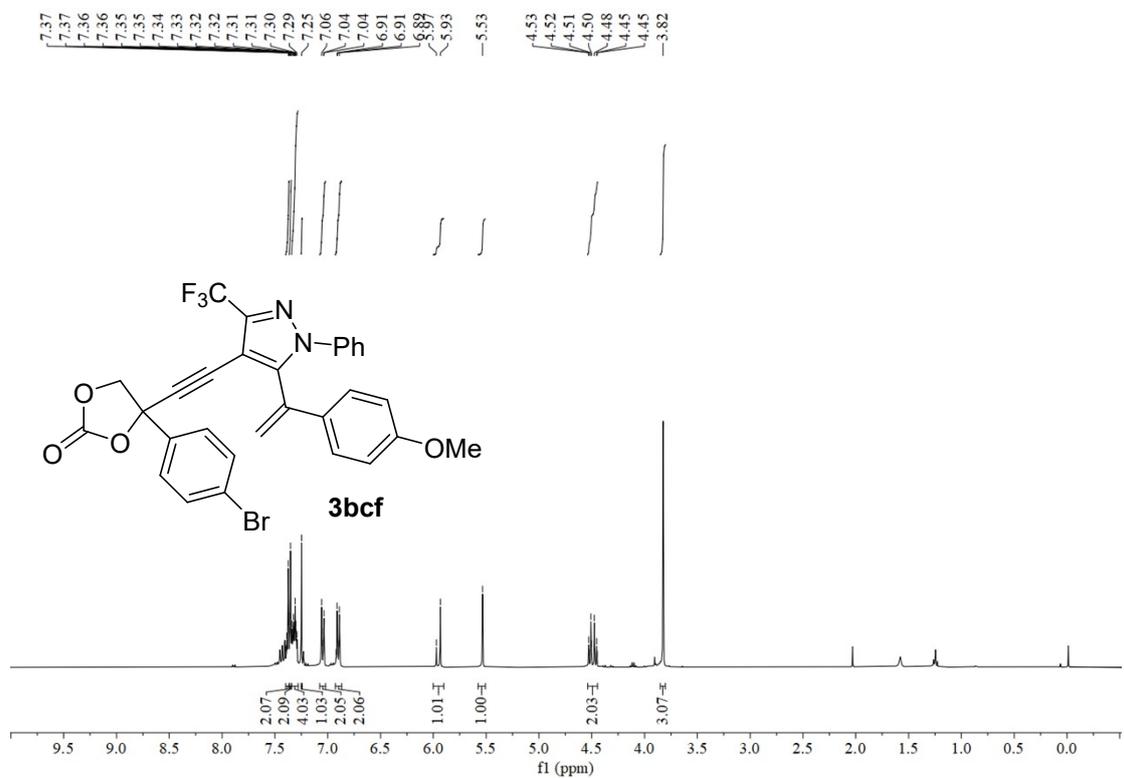
**<sup>13</sup>C{<sup>1</sup>H} NMR of 9 (101 MHz, CDCl<sub>3</sub>)**



**<sup>19</sup>F NMR of 9 (376 MHz, CDCl<sub>3</sub>)**



**<sup>1</sup>H NMR of 3bcf (400 MHz, CDCl<sub>3</sub>)**



$^{13}\text{C}\{^1\text{H}\}$  NMR of **3bcf** (101 MHz,  $\text{CDCl}_3$ )

