Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

A Cascade Indazolone-directed Ir(III)- and Rh(III)-Catalyzed C(sp^2)-H Functionalization/[4+2] Annulation of 1-arylindazolones with Sulfoxonium Ylides to Access Chemical Divergent 8*H*-indazolo [1,2-a]cinnolines

Yi-Chuan Zheng,[a] Bing Shu,[b] Yao-Fu Zeng,[d] Shao-Yong Chen,[a] Jia-Lin Song,[a] Yan-Zhi Liu,[a] Lin Xiao,[a] Xu-Ge Liu,*[c] Xuanxuan Zhang,*[a] Shang-Shi Zhang*[a]

[a]*Guangdong Provincial Key Laboratory of Advanced Drug Delivery Systems, Center for Drug Research and Development, Guangdong Pharmaceutical University, Guangzhou, 510006, P. R. China.*

[b]*School of Pharmacy, Guangdong Pharmaceutical University, Guangzhou, 510006, P. R. China.*

[c]*School of Pharmacy, Henan University, Kaifeng, Henan 475004, P. R. China.*

[d]*School of Pharmaceutical Science, Hunan Provincial Key Laboratory of Tumor Microenvironment Responsive Drug Research, Hengyang Medical School, University of South China, Hengyang, Hunan, 421001, P. R. China.*

*Email: zhangshangshi@gdpu.edu.cn

*Email: phil2424123@163.com

*Email: liuxg7@henu.edu.cn

Supporting Information

1. General information

Unless otherwise noted, all reactions were carried out at room temperature under an atmosphere of nitrogen with flame-dried glassware. If reaction was not conducted at room temperature, reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The dry solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under nitrogen: THF (Na-benzophenone), 1,2-dichloroethane (CaH_2), dichloromethane (CaH_2). Anhydrous CF_3CH_2OH, CH_3CN, DMF and MeOH were purchased from Acros Organics and stored under nitrogen atmosphere. Commercially available chemicals were obtained from commercial suppliers and used without further purification unless otherwise stated.

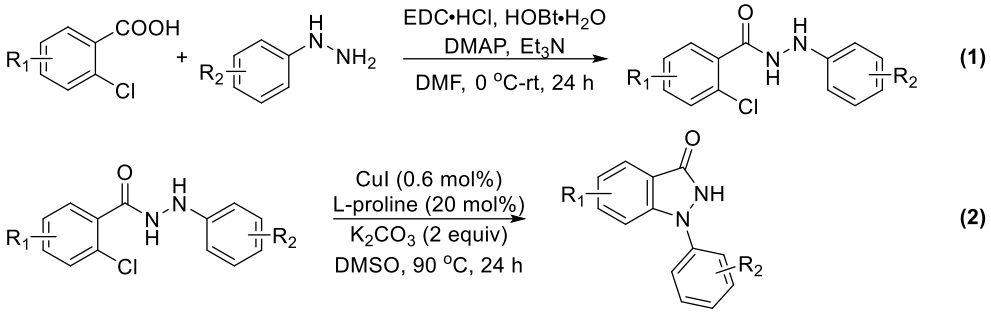
Proton NMR (^1H) were recorded at 400 MHz, and Carbon NMR (^{13}C) at 101 MHz NMR spectrometer unless otherwise stated. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br s: broad singlet for proton spectra. Coupling constants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

High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI and ESI mode unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. Visualization was accomplished with short wave UV light, or KMnO4 staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use.

No attempts were made to optimize yields for substrate synthesis.

2. Synthesis of 1-phenyl-1,2-dihydro-3*H*-indazol-3-one derivatives



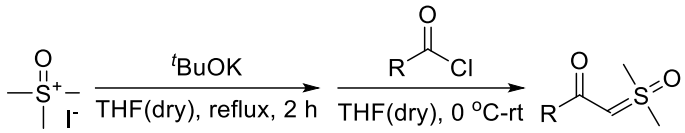
Experimental procedure for the synthesis of 2-chloro-*N*-phenylbenzohydrazide derivatives:

According to a previous reference,[1] to an oven-dried round bottom flask charged with 2-chlorobenzoic acids (10.0 mmol, 100 mol %) in DMF (20 mL) were added EDC·HCl (2.1 g, 11.0 mmol, 110 mol %), HOBt·H_2O (1.49 g, 11.0 mmol, 110 mol %), 4-(dimethylamino)pyridine (DMAP, 61.1 mg, 0.5 mmol, 5 mol %), and phenylhydrazines (10.0 mmol, 100 mol %) at 0 ^oC under N_2 atmosphere. The reaction mixture was allowed to stir for 24 h at room temperature. The reaction mixture was diluted with EtOAc (50 mL) and poured into saturated NH_4Cl solution. Extractive workup with EtOAc and purification by column chromatography afforded acid hydrzide as a white solid.

Experimental procedure for the synthesis of 1-phenyl-1,2-dihydro-3*H*-indazol-3-one derivatives:

According to a previous reference,[1] a mixture of 2-chloro-*N*'-phenylbenzohydrazides (5.25 mmol), CuI (5 mg, 0.026 mmol, 0.5 mol%), L-proline (120 mg, 1.05 mmol, 20 mol%), and K_2CO_3 (1.45 g, 10.5 mmol) in DMSO (15 mL) was stirred at 90 ^oC for 24 h under nitrogen atmosphere. After cooling, the mixture was treated with sat. $NaHCO_3$ aq. (100 mL) and the mixture was extracted eight times with ethyl acetate (30 mL × 8). The combined organic layer was washed with water (50 mL × 3) and brine (50 mL) and dried over magnesium sulfate. After filtration, solvent was evaporated in vacuo to afford a crude product which was recrystallized to provide pure1-phenyl-1,2-dihydro-3H-indazol-3-one derivatives.

3. Synthesis of sulfoxonium ylides

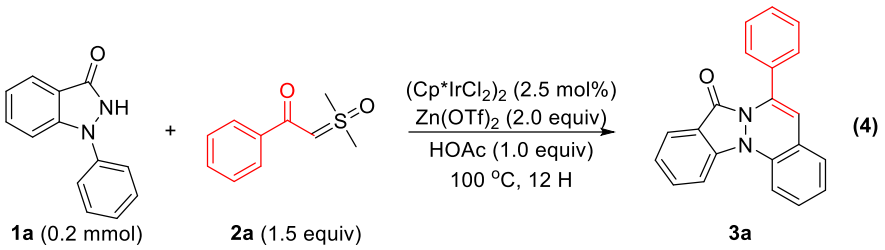


(3)

All the sulfoxonium ylides were synthesized according to literature.[2] In a 125 mL flame-dried round bottom flask attached to a reflux condenser, under argon atmosphere, 3.0 g of potassium tertbutoxide (27.2 mmol, 4.0 equiv) and 27.0 mL of anhydrous THF were added. Then, 4.48 g of trimethylsulfoxonium iodide (20.4 mmol; 3.0 equiv) was added in one portion. The suspension was heated at reflux for 2 hours. After this time, the mixture was cooled at 0 °C, followed by slow addition of the appropriate benzoyl chloride (6.8 mmol, 1.0 equiv). The reaction mixture temperature was naturally increased to room temperature and this mixture stirred for additional 3 hours. Then, the solvent was removed on a rotary evaporator. After that, 70 mL of water was added and the product extracted with a 3:1 CH_2Cl_2 : *i*-PrOH mixture (20 mL × 8). The organic phase was washed with water (10 mL × 8), dried over Na_2SO_4, and the solvent was removed on a rotary evaporator. The crude material was purified by solubilization in the minimal amount of hot AcOEt (10-15 mL), followed by slow addition of 15 mL of hexanes. The solid was filtered and washed with two portions of a 2:1 mixture of hexanes:AcOEt (2 x 10mL), furnishing the respective sulfoxonium ylides.

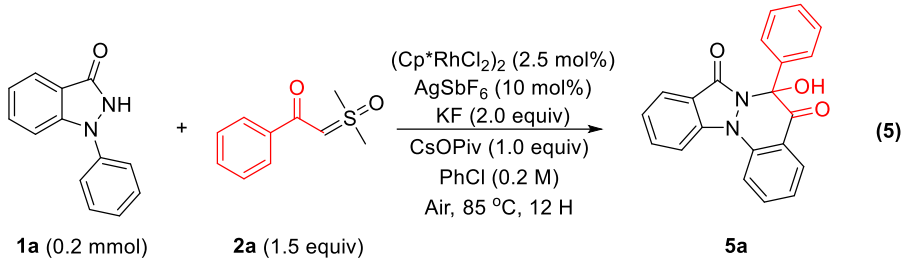
4. General procedure for the product

(1) General procedure A



To a Schlenk tube, 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.0 mg, 0.2 mmol), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol, 1.5 equiv), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol, 2.5 mmol%), HOAc (12.0 mg, 0.2 mmol, 1.0 equiv) and $Zn(OTf)_2$ (145.4 mg, 0.4 mmol, 2.0 equiv) were added. The resulting mixture was stirred at 100 °C (oil bath) for 12 h. The reaction mixture was cooled to room temperature and quenched with saturated sodium chloride. The mixture was diluted with DCM and water. The organic phase was separated and the aqueous layer was extracted with DCM for two times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. After that, the resulting mixture was purified by silica gel chromatography using a mixture of petroleum ether/ethyl acetate as an eluent to get the products **3** and **4**.

(2) General procedure B

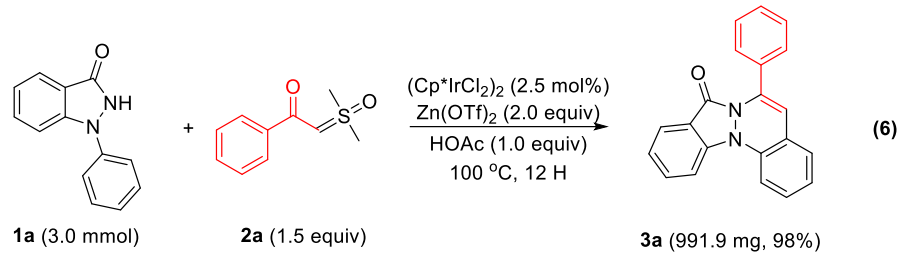


To a Schlenk tube, 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.0 mg, 0.2 mmol), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol, 1.5 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mmol%), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10.0 mmol%), CsOPiv (46.8 mg, 0.2 mmol, 1.0 equiv), KF (23.2 mg, 0.4 mmol, 2.0 equiv) and PhCl (1.0 mL, 0.2 M) were added. The resulting mixture was stirred at 85 °C (oil bath) for 12 h. The reaction mixture was cooled to room temperature and quenched with saturated sodium chloride. The mixture was diluted with DCM and water. The organic phase was separated and the aqueous layer

was extracted with DCM for two times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. After that, the resulting mixture was purified by silica gel chromatography using a mixture of petroleum ether/ethyl acetate as an eluent to get the products **5**.

5. Synthetic application of the product

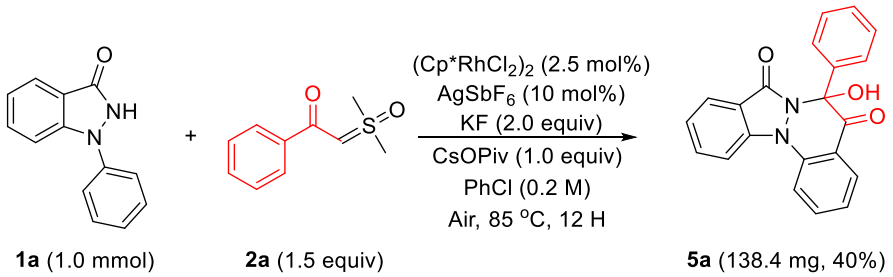
Gram- Scale Synthesis



(6)

According to the general procedure A, to a Schlenk tube, 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (630.7 mg, 3.0 mmol), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (883.1 mg, 1.5 equiv), $[Cp^*IrCl_2]_2$ (59.8 mg, 2.5 mmol%), HOAc (180.2 mg, 1.0 equiv) and $Zn(OTf)_2$ (2181.1 mg, 2.0 equiv) were added. The resulting mixture was stirred at 100 °C (oil bath) for 12 h. The reaction mixture was cooled to room temperature and quenched with saturated sodium chloride. The mixture was diluted with DCM and water. The organic phase was separated and the aqueous layer was extracted with DCM for two times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. After that, the resulting mixture was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4:1) to get the product **3a** as a yellow solid (991.9 mg, 98% yield).

The larger-scale Synthesis



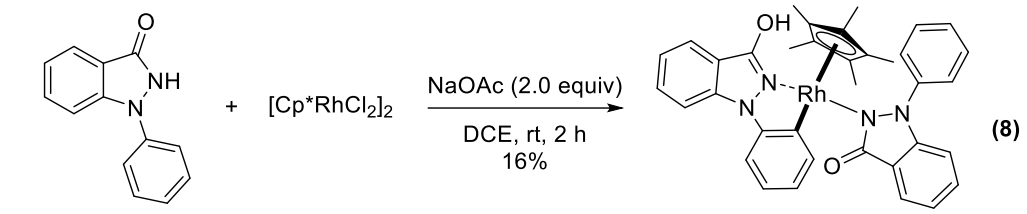
(7)

According to the general procedure B, to a Schlenk tube, 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (210.2 mg, 1.0 mmol), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (294.0 mg, 1.5 equiv), $[Cp^*RhCl_2]_2$ (15.3 mg, 2.5 mmol%), $AgSbF_6$ (34.3 mg, 10.0 mmol%), CsOPiv (234.0 mg, 1.0 equiv), KF (116.2 mg, 2.0 equiv) and PhCl (10.0 mL, 0.2 M) were added. The resulting mixture was stirred at 85 °C (oil bath) for 12 h.

The reaction mixture was cooled to room temperature and quenched with saturated sodium chloride. The mixture was diluted with DCM and water. The organic phase was separated and the aqueous layer was extracted with DCM for two times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. After that, the resulting mixture was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1) to get the product **5a** as a yellow solid (138.4 mg, 40% yield).

6. Mechanistic studies

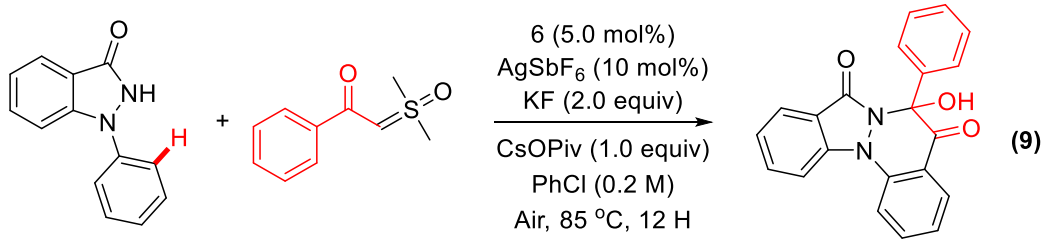
(1) Preparation of Rhodium Complex 6



1a (42.0 mg,0.2 mmol) 0.5 equiv **6**

Preparation of **Rhodium complex 6** was carried out according to the reported procedure[1]: To an oven-dried sealed tube charged with 1-phenyl-1*H*-indazol-3-ol (**1a**) (42.1 mg, 0.2 mmol, 100 mol %), [RhCp*Cl_2]$_2$ (61.8 mg, 0.1 mmol, 50 mol %), and NaOAc (32.8 mg, 0.4 mmol, 200 mol %) was added DCE (3.5 mL) under air atmosphere at room temperature. The reaction mixture was allowed to stir at room temperature for 2 h. The reaction mixture was diluted with EtOAc (5 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (CH_2Cl_2/MeOH = 100:1) to afford a dark brown solid, which was further recrystallized by CH_2Cl_2/pentane (1:5) to give **Rhodium complex 6** as a red solid (18 mg, 16%).

(2) Mechanistic experiments with Rhodium Complex 6

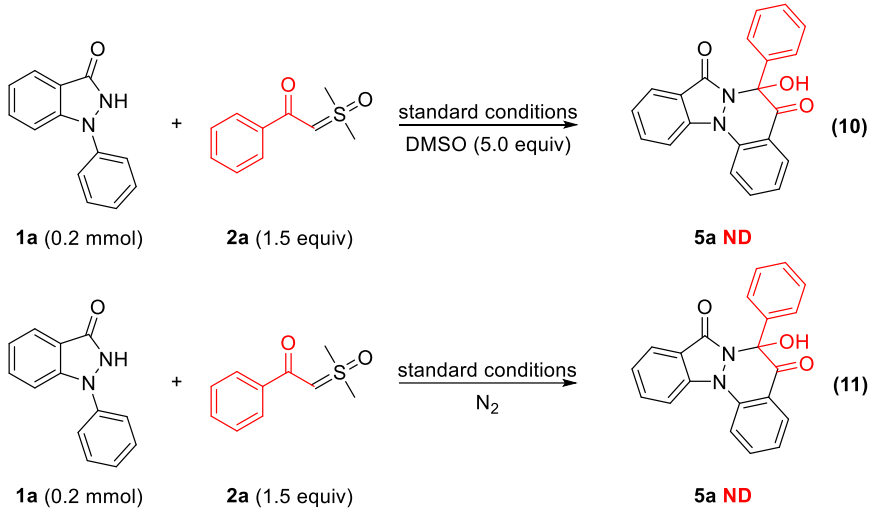


1a (42.0 mg,0.2 mmol) **2a (1.5 equiv)** **5a** (47.9 mg, 70%)

According to the general procedure B, to a Schlenk tube, 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.0 mg, 0.2 mmol), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol, 1.5 equiv), **Rhodium complex 6** (6.1 mg, 0.005 mmol, 2.5 mmol%), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10.0 mmol%), CsOPiv (46.8 mg, 0.2 mmol, 1.0 equiv), KF (23.2 mg, 0.4 mmol, 2.0 equiv) and PhCl (1.0 mL, 0.2 M) were added. The resulting mixture was stirred at 85 °C (oil bath) for 12 h. The reaction mixture was cooled to room temperature and quenched with saturated sodium chloride. The mixture was diluted with DCM and water. The organic phase was separated and the aqueous layer was extracted with DCM for

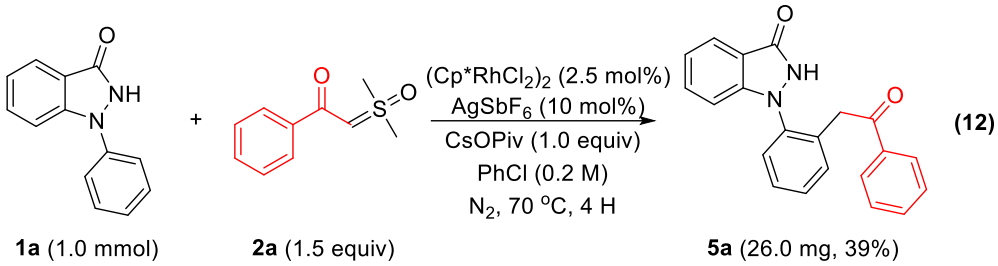
two times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. After that, the resulting mixture was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1) to get the product **5a** as a yellow solid (47.9 mg, 70% yield).

(3) Control experiment



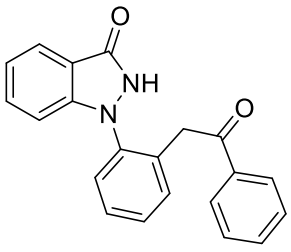
In order to discuss the oxygen source in this oxidizing reaction, we designed two control experiments as follow. According to the general procedure B, to a Schlenk tube, 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.0 mg, 0.2 mmol), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol, 1.5 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mmol%), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10.0 mmol%), CsOPiv (46.8 mg, 0.2 mmol, 1.0 equiv), KF (23.2 mg, 0.4 mmol, 2.0 equiv), DMSO (78.1 mg, 77 μL, 5.0) and PhCl (1.0 mL, 0.2 M) were added. The resulting mixture was stirred at 85 ^oC (oil bath) for 12 h. It was remarkable that we cannot detected the desired product **5a** in the resulting mixture by TLC. (**Formula 9**) Same results also occurred when we using the standard condition according to procedure B, in contrast, under the N_2 atmosphere. (**Formula 10**) To a Schlenk tube, 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.0 mg, 0.2 mmol), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol, 1.5 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mmol%), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10.0 mmol%), CsOPiv (46.8 mg, 0.2 mmol, 1.0 equiv), KF (23.2 mg, 0.4 mmol, 2.0 equiv) and PhCl (1.0 mL, 0.2 M) were added. The resulting mixture was stirred at 85 ^oC (oil bath) under N_2 atmosphere for 12 h.

(4) Synthesis of the intermediate V



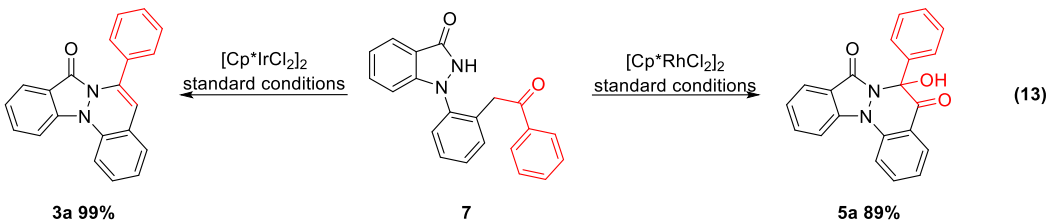
To a Schlenk tube, 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.0 mg, 0.2 mmol), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol, 1.5 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mmol%), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10.0 mmol%), CsOPiv (46.8 mg, 0.2 mmol, 1.0 equiv) and PhCl (1.0 mL, 0.2 M) were added. The resulting mixture was stirred at 70 °C (oil bath) for 4 h under the N_2 atmosphere. The reaction mixture was cooled to room temperature and quenched with saturated sodium chloride. The mixture was diluted with DCM and water. The organic phase was separated and the aqueous layer was extracted with DCM for two times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. After that, the resulting mixture was purified by silica gel chromatography using a mixture of petroleum ether/ethyl acetate (4:1) as an eluent to get the products **7** as a yellow solid (26.0 mg, 39% yield).

1-(2-(2-oxo-2-phenylethyl)phenyl)-1,2-dihydro-3H-indazol-3-one (7)



^{1}H NMR (400 MHz, DMSO) δ 7.63 (d, *J* = 7.4 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.38 – 7.36 (m, 1H), 7.34 (s, 1H), 7.32 (d, *J* = 2.3 Hz, 1H), 7.28 (d, *J* = 3.6 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.16 – 7.12 (m, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 4.37 (s, 2H). **^{13}C NMR** (101 MHz, DMSO) δ 196.8, 138.4, 136.5, 133.0, 132.7, 132.5, 128.7, 128.6, 128.1, 127.9, 127.8, 127.6, 126.4, 120.7, 120.2, 119.7, 109.8, 41.4. **HRMS (ESI)** m/z calcd. for $C_{21}H_{16}N_2O_2Na^+$ $[M+Na]^+$: 351.1109, found: 351.1112.

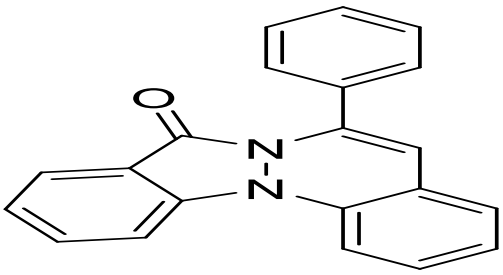
(5) Mechanistic experiments with Intermediate V



According to the general procedure A, to a Schlenk tube, 1-(2-(2-oxo-2-phenylethyl)phenyl)-1,2-dihydro-3*H*-indazol-3-one **7** (32.8 mg, 0.1 mmol), $[Cp^*IrCl_2]_2$ (2.0 mg, 2.5 mmol%), HOAc (6.0 mg, 1.0 equiv) and $Zn(OTf)_2$ (72.7 mg, 2.0 equiv) were added. The resulting mixture was stirred at 100 ^oC (oil bath) for 12 h. The reaction mixture was cooled to room temperature and quenched with saturated sodium chloride. The mixture was diluted with DCM and water. The organic phase was separated and the aqueous layer was extracted with DCM for two times. The combined organic layer was dried over anhydrous Na2SO4 and concentrated under reduced pressure. After that, the resulting mixture was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4:1) to get the product **3a** as a yellow solid (30.7 mg, 99% yield).

According to the general procedure B, to a Schlenk tube, 1-(2-(2-oxo-2-phenylethyl)phenyl)-1,2-dihydro-3*H*-indazol-3-one **7** (32.8 mg, 0.1 mmol), $[Cp^*RhCl_2]_2$ (1.5 mg, 2.5 mmol%), $AgSbF_6$ (3.4 mg, 10.0 mmol%), CsOPiv (23.4 mg, 1.0 equiv), KF (11.6 mg, 2.0 equiv) and PhCl (0.5 mL, 0.2 M) were added. The resulting mixture was stirred at 85 ^oC (oil bath) for 12 h. The reaction mixture was cooled to room temperature and quenched with saturated sodium chloride. The mixture was diluted with DCM and water. The organic phase was separated and the aqueous layer was extracted with DCM for two times. The combined organic layer was dried over anhydrous Na2SO4 and concentrated under reduced pressure. After that, the resulting mixture was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1) to get the product **5a** as a yellow solid (30.4 mg, 89% yield).

7. X-Ray crystal data for compound 3k



X-ray-quality crystal was obtained by slow diffusion of Petroleum ether into a dilute dichloromethane solution of **3k** at room temperature under air. Thermal ellipsoids drawn at the 50 % probability level. Crystal data were obtained on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer using Mo Kα radiation (λ = 0.71073 Å). The crystal was kept at 199.99(10) K during data collection.

Table 1 Crystal data and structure refinement for 3k(d-243).

Identification code	d-243
Empirical formula	$C_{21}H_{13}ClN_2O$
Formula weight	344.78
Temperature/K	199.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.5768(6)
b/Å	8.3055(3)
c/Å	15.5210(7)
α/°	90
β/°	94.117(4)
γ/°	90
Volume/Å^3	1617.09(12)
Z	4
ρ_{calc}g/cm^3	1.416
μ/mm^{-1}	0.247
F(000)	712.0
Crystal size/mm^3	0.15 × 0.13 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.262 to 49.986
Index ranges	$-13 \le h \le 14$, $-8 \le k \le 9$, $-18 \le l \le 15$
Reflections collected	7003
Independent reflections	2838 [R_{int} = 0.0186, R_{sigma} = 0.0252]
Data/restraints/parameters	2838/0/226

Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0363, wR_2 = 0.0956
Final R indexes [all data]	R_1 = 0.0422, wR_2 = 0.1004
Largest diff. peak/hole / e $Å^{-3}$	0.58/-0.30

Crystal structure determination of 3k

Crystal Data for $C_{21}H_{13}ClN_2O$ (*M* =344.78 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 12.5768(6) Å, *b* = 8.3055(3) Å, *c* = 15.5210(7) Å, *β* = 94.117(4)°, *V* = 1617.09(12) $Å^3$, *Z* = 4, *T* = 199.99(10) K, μ(Mo Kα) = 0.247 mm^{-1}, *Dcalc* = 1.416 g/cm^3, 7003 reflections measured (5.262° ≤ 2Θ ≤ 49.986°), 2838 unique (R_{int} = 0.0186, R_{sigma} = 0.0252) which were used in all calculations. The final R_1 was 0.0363 (I > 2σ(I)) and wR_2 was 0.1004 (all data).

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å²×10^3) for 3k. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	426.1(4)	6392.7(6)	4383.1(3)	31.66(16)
O1	1952.2(11)	3713.6(16)	3225.8(8)	30.7(3)
N1	3004.0(12)	4664.6(18)	5306.1(9)	25.3(4)
N2	2764.2(12)	5016.9(18)	4416.6(9)	23.7(3)
C1	3894.9(15)	5481(2)	5706.1(11)	25.5(4)
C2	4510.6(15)	4851(3)	6402.3(12)	31.6(5)
C3	5295.5(16)	5804(3)	6823.8(13)	38.5(5)
C4	5467.7(16)	7356(3)	6557.1(14)	39.5(5)
C5	4869.8(16)	7967(3)	5848.5(14)	36.4(5)
C6	4084.4(14)	7044(2)	5404.2(12)	27.8(4)
C7	3438.0(15)	7630(2)	4656.8(12)	29.4(4)
C8	2800.1(14)	6650(2)	4176.7(12)	24.8(4)
C9	2078.2(15)	7180(2)	3434.7(12)	24.7(4)
C10	974.1(14)	7095(2)	3457.4(11)	24.9(4)
C11	290.6(16)	7597(2)	2775.0(13)	32.6(5)
C12	715.2(18)	8222(3)	2050.5(13)	39.0(5)
C13	1801.7(18)	8360(3)	2016.1(14)	41.0(5)
C14	2480.3(16)	7842(2)	2702.5(13)	33.4(5)
C15	2246.5(14)	3729(2)	3995.3(12)	23.9(4)
C16	2141.8(14)	2532(2)	4663.6(11)	24.2(4)
C17	2614.7(14)	3126(2)	5440.8(11)	23.9(4)
C18	2564.0(16)	2258(2)	6207.4(12)	30.9(4)
C19	2037.5(17)	800(2)	6161.0(13)	35.8(5)

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

Atom	*x*	*y*	*z*	U(eq)
C20	1565.1(18)	203(2)	5385.5(13)	36.6(5)
C21	1605.9(16)	1062(2)	4632.2(13)	30.8(4)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3k. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	30.4(3)	37.8(3)	27.7(3)	1.3(2)	8.21(19)	-4.0(2)
O1	35.6(8)	35.6(8)	19.9(7)	-1.9(6)	-6.0(6)	-0.9(6)
N1	29.0(9)	28.4(8)	17.6(7)	0.1(6)	-3.9(6)	-1.4(7)
N2	26.1(8)	26.6(8)	17.7(7)	1.0(6)	-3.0(6)	-0.6(6)
C1	21.4(9)	34.4(10)	20.7(9)	-6.7(8)	1.5(7)	2.0(8)
C2	28.3(11)	40.5(11)	25.6(10)	-2.8(9)	-0.7(8)	5.4(9)
C3	26.3(11)	60.0(14)	28.3(11)	-4.7(10)	-5.3(8)	6.1(10)
C4	25.5(11)	56.3(14)	35.7(11)	-13.0(10)	-3.4(9)	-6.9(10)
C5	29.2(11)	40.4(12)	39.3(12)	-6.1(10)	0.2(9)	-7.0(9)
C6	20.8(10)	33.0(10)	29.5(10)	-4.7(9)	1.6(8)	-0.2(8)
C7	25.8(10)	27.0(10)	35.2(11)	1.7(8)	1.4(8)	-2.7(8)
C8	22.4(9)	26.3(9)	26.1(10)	1.4(8)	3.7(7)	-0.1(7)
C9	25.9(10)	21.8(9)	26.3(9)	1.6(8)	0.5(7)	0.4(7)
C10	26.6(10)	23.5(9)	24.8(9)	1.2(8)	3.2(7)	0.5(8)
C11	25.0(10)	35.1(11)	37.1(11)	2.5(9)	-2.2(8)	4.5(8)
C12	41.6(13)	41.7(12)	32.7(11)	13.5(10)	-4.3(9)	7.4(10)
C13	43.8(13)	45.0(12)	34.8(12)	18.7(10)	8.1(10)	1.3(10)
C14	28.1(11)	35.6(11)	37.1(11)	9.3(9)	5.2(9)	-2.1(9)
C15	19.8(9)	26.4(9)	25.3(10)	-4.5(8)	0.3(7)	2.7(7)
C16	24.0(10)	25.1(9)	23.4(9)	-2.5(8)	1.0(7)	4.6(7)
C17	24.3(9)	24.8(9)	22.5(9)	-2.1(8)	1.4(7)	4.1(7)
C18	37.6(11)	31.8(10)	23.1(10)	0.0(8)	0.7(8)	3.0(9)
C19	46.6(13)	30.4(11)	31.1(11)	6.4(9)	6.9(9)	3.7(9)
C20	46.3(13)	23.0(10)	41.0(12)	-1.2(9)	7.4(10)	-2.9(9)
C21	35.7(11)	27.5(10)	29.1(10)	-6.6(8)	1.8(8)	1.4(8)

Table 4 Bond Lengths for 3k.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C10	1.7384(18)	C8	C9	1.481(2)
O1	C15	1.225(2)	C9	C10	1.393(3)
N1	N2	1.4224(19)	C9	C14	1.390(3)
N1	C1	1.414(2)	C10	C11	1.380(3)

Table 4 Bond Lengths for 3k.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C17	1.390(2)	C11	C12	1.380(3)
N2	C8	1.408(2)	C12	C13	1.376(3)
N2	C15	1.391(2)	C13	C14	1.385(3)
C1	C2	1.386(3)	C15	C16	1.450(3)
C1	C6	1.406(3)	C16	C17	1.396(2)
C2	C3	1.392(3)	C16	C21	1.394(3)
C3	C4	1.376(3)	C17	C18	1.397(3)
C4	C5	1.383(3)	C18	C19	1.379(3)
C5	C6	1.393(3)	C19	C20	1.395(3)
C6	C7	1.452(3)	C20	C21	1.374(3)
C7	C8	1.332(3)			

Table 5 Bond Angles for 3k.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	N2	115.69(14)	C14	C9	C10	117.55(17)
C17	N1	N2	106.42(13)	C9	C10	Cl1	119.54(14)
C17	N1	C1	130.64(15)	C11	C10	Cl1	118.27(15)
C8	N2	N1	116.50(14)	C11	C10	C9	122.16(17)
C15	N2	N1	110.96(14)	C10	C11	C12	118.87(19)
C15	N2	C8	129.74(15)	C13	C12	C11	120.41(19)
C2	C1	N1	122.82(17)	C12	C13	C14	120.20(19)
C2	C1	C6	120.64(18)	C13	C14	C9	120.77(19)
C6	C1	N1	116.37(16)	O1	C15	N2	124.41(17)
C1	C2	C3	119.3(2)	O1	C15	C16	130.83(17)
C4	C3	C2	120.88(19)	N2	C15	C16	104.75(15)
C3	C4	C5	119.63(19)	C17	C16	C15	108.73(16)
C4	C5	C6	121.2(2)	C21	C16	C15	130.11(17)
C1	C6	C7	118.48(17)	C21	C16	C17	120.97(17)
C5	C6	C1	118.30(18)	N1	C17	C16	109.13(15)
C5	C6	C7	123.20(18)	N1	C17	C18	129.87(17)
C8	C7	C6	121.51(18)	C18	C17	C16	120.74(17)
N2	C8	C9	117.53(15)	C19	C18	C17	117.37(18)
C7	C8	N2	118.01(17)	C18	C19	C20	122.04(19)
C7	C8	C9	124.36(17)	C21	C20	C19	120.66(19)
C10	C9	C8	121.44(16)	C20	C21	C16	118.22(18)
C14	C9	C8	120.96(17)				

Table 6 Torsion Angles for 3k.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cl1	C10	C11	C12	177.25(16)	C6	C7	C8	N2	0.3(3)
O1	C15	C16	C17	179.82(19)	C6	C7	C8	C9	176.66(17)
O1	C15	C16	C21	-5.2(3)	C7	C8	C9	C10	-113.8(2)
N1	N2	C8	C7	27.0(2)	C7	C8	C9	C14	63.7(3)
N1	N2	C8	C9	-149.67(15)	C8	N2	C15	O1	20.1(3)
N1	N2	C15	O1	-179.86(17)	C8	N2	C15	C16	-158.81(17)
N1	N2	C15	C16	1.20(19)	C8	C9	C10	Cl1	1.4(2)
N1	C1	C2	C3	-172.52(17)	C8	C9	C10	C11	179.41(17)
N1	C1	C6	C5	172.19(17)	C8	C9	C14	C13	-178.91(18)
N1	C1	C6	C7	-6.5(2)	C9	C10	C11	C12	-0.8(3)
N1	C17	C18	C19	173.78(19)	C10	C9	C14	C13	-1.4(3)
N2	N1	C1	C2	-151.77(17)	C10	C11	C12	C13	-0.8(3)
N2	N1	C1	C6	33.1(2)	C11	C12	C13	C14	1.3(3)
N2	N1	C17	C16	-0.25(19)	C12	C13	C14	C9	-0.2(3)
N2	N1	C17	C18	-174.23(19)	C14	C9	C10	Cl1	-176.12(14)
N2	C8	C9	C10	62.7(2)	C14	C9	C10	C11	1.9(3)
N2	C8	C9	C14	-119.94(19)	C15	N2	C8	C7	-173.93(18)
N2	C15	C16	C17	-1.33(19)	C15	N2	C8	C9	9.4(3)
N2	C15	C16	C21	173.62(18)	C15	C16	C17	N1	1.0(2)
C1	N1	N2	C8	-44.2(2)	C15	C16	C17	C18	175.62(17)
C1	N1	N2	C15	152.92(15)	C15	C16	C21	C20	-175.13(19)
C1	N1	C17	C16	-148.32(18)	C16	C17	C18	C19	0.4(3)
C1	N1	C17	C18	37.7(3)	C17	N1	N2	C8	162.28(15)
C1	C2	C3	C4	-0.1(3)	C17	N1	N2	C15	-0.63(19)
C1	C6	C7	C8	-10.8(3)	C17	N1	C1	C2	-6.0(3)
C2	C1	C6	C5	-3.1(3)	C17	N1	C1	C6	178.80(17)
C2	C1	C6	C7	178.19(17)	C17	C16	C21	C20	-0.7(3)
C2	C3	C4	C5	-1.5(3)	C17	C18	C19	C20	-0.3(3)
C3	C4	C5	C6	0.8(3)	C18	C19	C20	C21	-0.3(3)
C4	C5	C6	C1	1.5(3)	C19	C20	C21	C16	0.8(3)
C4	C5	C6	C7	-179.89(19)	C21	C16	C17	N1	-174.51(16)
C5	C6	C7	C8	170.57(19)	C21	C16	C17	C18	0.1(3)
C6	C1	C2	C3	2.5(3)					

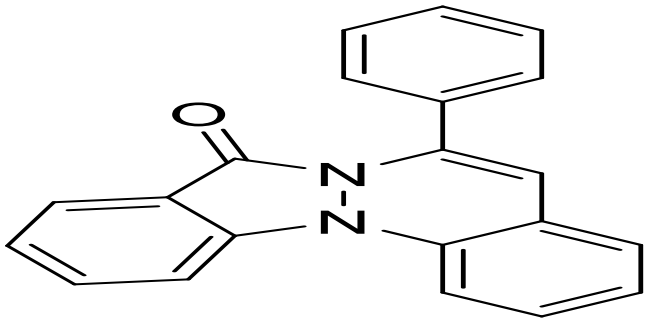
Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3k.

Atom	*x*	*y*	*z*	U(eq)
H2	4400.28	3802.25	6585.88	38
H3	5709.08	5386.3	7292.09	46

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3k.

Atom	*x*	*y*	*z*	U(eq)
H4	5983.3	7991.17	6851.6	47
H5	4994.21	9011.91	5665.53	44
H7	3470.02	8713.17	4509.88	35
H11	-443.69	7515.8	2802.72	39
H12	264.21	8552.28	1582.65	47
H13	2081.18	8803.16	1530.57	49
H14	3213.54	7937.01	2673.06	40
H18	2872.99	2647.11	6728.61	37
H19	1996.25	197.06	6662.35	43
H20	1219.02	-787.15	5378.21	44
H21	1284.5	673.58	4115.22	37

8. X-Ray crystal data for compound 5a



X-ray-quality crystal was obtained by slow diffusion of Petroleum ether into a dilute dichloromethane solution of **5a** at room temperature under air. Thermal ellipsoids drawn at the 50 % probability level. Crystal data were obtained on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer using Mo Kα radiation (λ = 0.71073 Å). The crystal was kept at 179.99(10) K during data collection.

Table 1 Crystal data and structure refinement for 5a(d-40f).

Identification code	d-40f
Empirical formula	$C_{21}H_{14}N_2O_3$
Formula weight	342.34
Temperature/K	179.99(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.3638(11)
b/Å	7.4704(7)
c/Å	15.0035(10)
α/°	90
β/°	94.451(7)
γ/°	90
Volume/Å^3	1605.1(2)
Z	4
ρ_{calc}g/cm^3	1.417
μ/mm^{-1}	0.096
F(000)	712.0
Crystal size/mm^3	0.14 × 0.12 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.088 to 49.99
Index ranges	$-14 \le h \le 17$, $-6 \le k \le 8$, $-17 \le l \le 17$

Reflections collected	7251
Independent reflections	2824 [R_{int} = 0.0380, R_{sigma} = 0.0446]
Data/restraints/parameters	2824/0/237
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0460, wR_2 = 0.1137
Final R indexes [all data]	R_1 = 0.0601, wR_2 = 0.1249
Largest diff. peak/hole / e Å^{-3}	0.19/-0.25

Crystal structure determination of 5a

Crystal Data for $C_{21}H_{14}N_2O_3$ (*M* =342.34 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 14.3638(11) Å, *b* = 7.4704(7) Å, *c* = 15.0035(10) Å, *β* = 94.451(7)°, *V* = 1605.1(2) Å^3, *Z* = 4, *T* = 179.99(10) K, μ(Mo Kα) = 0.096 mm^{-1}, *Dcalc* = 1.417 g/cm^3, 7251 reflections measured (4.088° ≤ 2Θ ≤ 49.99°), 2824 unique (R_{int} = 0.0380, R_{sigma} = 0.0446) which were used in all calculations. The final R_1 was 0.0460 (I > 2σ(I)) and wR_2 was 0.1249 (all data).

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 5a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O2	3490.2(9)	3844.8(16)	5229.7(8)	31.7(3)
O1	1620.9(9)	4490(2)	4817.3(8)	40.3(4)
O3	5013.9(9)	6559(2)	5782.5(9)	41.8(4)
N1	3110.9(10)	6040(2)	7041.3(9)	28.8(4)
N2	3523.4(10)	6302(2)	6225.6(9)	31.0(4)
C16	3206.3(11)	6857(3)	4625.5(11)	26.9(4)
C15	3110.0(12)	5525(2)	5383.2(11)	27.6(4)
C1	1614.6(12)	5885(2)	6224.0(11)	27.5(4)
C14	2051.8(12)	5228(3)	5438.4(11)	28.8(4)
C6	2145.6(12)	6245(2)	7030.1(11)	26.2(4)
C17	3170.9(12)	6220(3)	3755.3(11)	30.2(5)
C13	4480.8(13)	6500(3)	6380.5(12)	30.3(4)
C7	3816.7(13)	6277(2)	7722.5(11)	29.2(4)
C8	4656.1(13)	6550(3)	7345.9(12)	31.1(5)
C5	1691.3(13)	6724(3)	7782.3(12)	32.8(5)
C18	3203.4(13)	7399(3)	3049.3(12)	34.9(5)
C21	3251.8(14)	8686(3)	4771.1(13)	37.2(5)
C2	648.1(12)	6038(3)	6189.2(12)	33.8(5)
C19	3259.9(14)	9208(3)	3199.7(13)	39.7(5)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 5a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C12	3787.1(15)	6190(3)	8652.1(12)	37.3(5)
C4	730.8(14)	6842(3)	7725.4(13)	39.8(5)
C9	5491.6(14)	6733(3)	7871.6(13)	39.4(5)
C3	206.7(13)	6518(3)	6926.7(13)	40.6(5)
C20	3279.0(15)	9860(3)	4058.2(14)	45.9(5)
C11	4616.6(16)	6421(3)	9160.1(13)	44.4(6)
C10	5458.4(16)	6681(3)	8785.3(13)	45.0(6)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 5a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	32.3(7)	34.6(8)	29.4(7)	-0.2(5)	9.6(6)	0.9(6)
O1	32.6(7)	61.4(10)	26.8(7)	-10.6(7)	2.1(6)	-10.9(7)
O3	25.8(7)	61.5(10)	39.1(8)	-6.4(7)	9.5(6)	-3.4(7)
N1	25.3(8)	43.3(10)	18.1(7)	-2.3(6)	3.7(6)	2.4(7)
N2	23.4(8)	49.9(10)	20.0(7)	-3.7(7)	4.5(6)	-3.0(7)
C16	18.3(8)	37.0(11)	25.8(9)	-2.6(8)	3.9(7)	-2.3(8)
C15	26.8(9)	36.0(11)	20.1(8)	-4.2(8)	2.9(7)	-0.5(9)
C1	27.2(9)	30.8(10)	24.6(9)	-0.5(8)	3.5(8)	-2.6(8)
C14	28.4(9)	34.2(10)	23.8(9)	1.3(8)	1.8(8)	-2.7(8)
C6	25.6(9)	27.7(10)	25.9(9)	-0.5(7)	5.8(8)	-0.7(8)
C17	30.3(10)	33.8(11)	26.7(9)	-2.6(8)	2.5(8)	-3.1(8)
C13	22.8(9)	36.6(11)	31.6(10)	-5.2(8)	2.8(8)	0.1(8)
C7	31.0(10)	30.2(10)	25.3(9)	-3.4(8)	-3.6(8)	3.2(8)
C8	27.9(10)	32.1(10)	32.6(10)	-2.8(8)	-2.5(8)	3.0(8)
C5	33.7(10)	38.3(11)	27.0(9)	-5.0(8)	6.5(8)	-1.7(9)
C18	31.1(10)	47.7(12)	26.1(9)	2.1(9)	4.4(8)	-5.6(9)
C21	40.0(11)	38.5(12)	33.2(10)	-6.4(9)	3.5(9)	-0.8(9)
C2	25.1(10)	43.0(12)	33.4(10)	-3.5(9)	3.4(8)	-2.4(9)
C19	35.7(11)	45.2(13)	38.6(11)	13.6(9)	4.9(9)	-1.7(10)
C12	43.2(12)	41.1(12)	26.9(10)	0.4(8)	-1.4(9)	5.3(9)
C4	35.2(11)	48.7(13)	37.5(11)	-8.6(9)	16.6(9)	-1.9(10)
C9	32.4(11)	40.2(12)	43.6(11)	-4.5(9)	-9.2(9)	1.1(9)
C3	24.1(10)	50.8(13)	47.8(12)	-8.6(10)	9.0(9)	-2.3(9)
C20	53.8(13)	32.3(11)	51.9(13)	3.5(10)	6.6(11)	-0.7(10)
C11	56.6(14)	45.4(13)	28.8(10)	-2.4(9)	-12.9(10)	8.7(11)
C10	45.6(12)	44.2(13)	41.8(12)	-5.9(10)	-19.2(10)	4.8(11)

Table 4 Bond Lengths for 5a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O2	C15	1.395(2)	C6	C5	1.393(2)
O1	C14	1.211(2)	C17	C18	1.381(3)
O3	C13	1.225(2)	C13	C8	1.451(2)
N1	N2	1.414(2)	C7	C8	1.386(3)
N1	C6	1.394(2)	C7	C12	1.400(3)
N1	C7	1.394(2)	C8	C9	1.391(3)
N2	C15	1.473(2)	C5	C4	1.378(3)
N2	C13	1.385(2)	C18	C19	1.372(3)
C16	C15	1.526(2)	C21	C20	1.386(3)
C16	C17	1.387(2)	C2	C3	1.365(3)
C16	C21	1.384(3)	C19	C20	1.375(3)
C15	C14	1.545(2)	C12	C11	1.375(3)
C1	C14	1.463(2)	C4	C3	1.386(3)
C1	C6	1.405(2)	C9	C10	1.376(3)
C1	C2	1.390(2)	C11	C10	1.386(3)

Table 5 Bond Angles for 5a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	N1	N2	117.23(13)	C5	C6	C1	119.30(17)
C6	N1	C7	131.38(15)	C18	C17	C16	120.12(18)
C7	N1	N2	106.69(14)	O3	C13	N2	123.37(16)
N1	N2	C15	121.31(14)	O3	C13	C8	131.33(17)
C13	N2	N1	110.30(14)	N2	C13	C8	105.27(15)
C13	N2	C15	121.00(14)	N1	C7	C12	130.39(18)
C17	C16	C15	118.59(17)	C8	C7	N1	109.03(15)
C21	C16	C15	122.17(16)	C8	C7	C12	120.50(17)
C21	C16	C17	119.04(17)	C7	C8	C13	108.31(15)
O2	C15	N2	111.06(14)	C7	C8	C9	121.54(17)
O2	C15	C16	113.88(14)	C9	C8	C13	130.07(18)
O2	C15	C14	106.22(14)	C4	C5	C6	119.72(17)
N2	C15	C16	109.15(15)	C19	C18	C17	120.49(18)
N2	C15	C14	110.08(14)	C16	C21	C20	120.43(18)
C16	C15	C14	106.27(13)	C3	C2	C1	121.09(17)
C6	C1	C14	121.31(16)	C18	C19	C20	119.97(19)
C2	C1	C14	119.17(15)	C11	C12	C7	117.0(2)
C2	C1	C6	119.37(17)	C5	C4	C3	121.08(18)
O1	C14	C15	118.06(15)	C10	C9	C8	117.8(2)

Table 5 Bond Angles for 5a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	C14	C1	123.17(16)	C2	C3	C4	119.43(18)
C1	C14	C15	118.75(15)	C19	C20	C21	119.9(2)
N1	C6	C1	117.53(15)	C12	C11	C10	122.58(19)
C5	C6	N1	123.13(16)	C9	C10	C11	120.46(19)

Table 6 Torsion Angles for 5a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O2	C15	C14	O1	-55.1(2)	C6	N1	C7	C8	-158.40(19)
O2	C15	C14	C1	126.32(16)	C6	N1	C7	C12	24.9(3)
O3	C13	C8	C7	-174.6(2)	C6	C1	C14	O1	161.06(18)
O3	C13	C8	C9	2.2(4)	C6	C1	C14	C15	-20.4(3)
N1	N2	C15	O2	-91.95(18)	C6	C1	C2	C3	-0.5(3)
N1	N2	C15	C16	141.68(15)	C6	C5	C4	C3	-0.9(3)
N1	N2	C15	C14	25.4(2)	C17	C16	C15	O2	33.2(2)
N1	N2	C13	O3	172.14(18)	C17	C16	C15	N2	157.94(15)
N1	N2	C13	C8	-6.1(2)	C17	C16	C15	C14	-83.39(19)
N1	C6	C5	C4	-177.83(18)	C17	C16	C21	C20	-1.2(3)
N1	C7	C8	C13	0.5(2)	C17	C18	C19	C20	-0.4(3)
N1	C7	C8	C9	-176.62(17)	C13	N2	C15	O2	55.1(2)
N1	C7	C12	C11	177.57(19)	C13	N2	C15	C16	-71.3(2)
N2	N1	C6	C1	28.3(2)	C13	N2	C15	C14	172.46(16)
N2	N1	C6	C5	-154.01(17)	C13	C8	C9	C10	-178.0(2)
N2	N1	C7	C8	-4.14(19)	C7	N1	N2	C15	156.69(16)
N2	N1	C7	C12	179.17(18)	C7	N1	N2	C13	6.49(19)
N2	C15	C14	O1	-175.41(17)	C7	N1	C6	C1	-179.57(18)
N2	C15	C14	C1	6.0(2)	C7	N1	C6	C5	-1.9(3)
N2	C13	C8	C7	3.4(2)	C7	C8	C9	C10	-1.6(3)
N2	C13	C8	C9	-179.80(19)	C7	C12	C11	C10	-1.7(3)
C16	C15	C14	O1	66.5(2)	C8	C7	C12	C11	1.2(3)
C16	C15	C14	C1	-112.07(17)	C8	C9	C10	C11	1.1(3)
C16	C17	C18	C19	-0.8(3)	C5	C4	C3	C2	1.4(3)
C16	C21	C20	C19	0.1(3)	C18	C19	C20	C21	0.7(3)
C15	N2	C13	O3	21.8(3)	C21	C16	C15	O2	-152.11(17)
C15	N2	C13	C8	-156.38(16)	C21	C16	C15	N2	-27.4(2)
C15	C16	C17	C18	176.39(15)	C21	C16	C15	C14	91.31(19)
C15	C16	C21	C20	-175.85(17)	C21	C16	C17	C18	1.5(3)
C1	C6	C5	C4	-0.2(3)	C2	C1	C14	O1	-14.5(3)
C1	C2	C3	C4	-0.6(3)	C2	C1	C14	C15	164.02(17)

Table 6 Torsion Angles for 5a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C14	C1	C6	N1	3.1(3)	C2	C1	C6	N1	178.68(17)
C14	C1	C6	C5	-174.62(17)	C2	C1	C6	C5	0.9(3)
C14	C1	C2	C3	175.12(19)	C12	C7	C8	C13	177.54(17)
C6	N1	N2	C15	-44.8(2)	C12	C7	C8	C9	0.5(3)
C6	N1	N2	C13	164.99(16)	C12	C11	C10	C9	0.6(3)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 5a.

Atom	*x*	*y*	*z*	U(eq)
H2	3965.52	3963.85	4966.19	48
H17	3125.23	4995.7	3646.93	36
H5	2034.56	6962.19	8320.45	39
H18	3186.93	6963.1	2467.64	42
H21	3264.14	9129.45	5351.03	45
H2A	296.16	5808.88	5654.73	41
H19	3285.19	9993.93	2721.39	48
H12	3230.99	5985.74	8914.23	45
H4	429.6	7144.72	8231.11	48
H9	6054.53	6886.17	7613.86	47
H3	-440.05	6627.12	6893.52	49
H20	3310.22	11086.96	4160.43	55
H11	4612.95	6402.37	9779.65	53
H10	6004.53	6820.57	9154.01	54

Experimental

Single crystals of $C_{21}H_{14}N_2O_3$ were **[5a]**. A suitable crystal was selected and **[5a]** on a **SuperNova, Dual, Cu at zero, AtlasS2** diffractometer. The crystal was kept at 179.99(10) K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

3. Sheldrick, G.M. (2015). Acta Cryst. C71,

2. a Aromatic/amide H refined with riding coordinates:

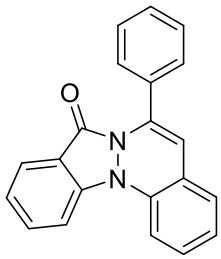
C17(H17), C5(H5), C18(H18), C21(H21), C2(H2A), C19(H19), C12(H12), C4(H4), C9(H9), C3(H3), C20(H20), C11(H11), C10(H10)

2. b Idealised tetrahedral OH refined as rotating group:

O2(H2)

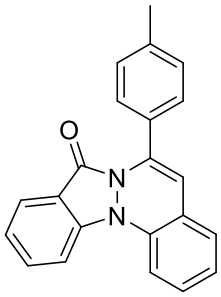
9. Product characterization

6-phenyl-8*H*-indazolo[1,2-a]cinnolin-8-one (3a)



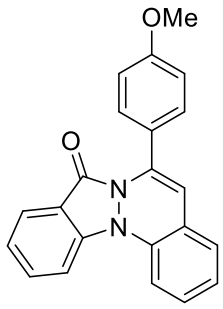
The reaction was performed according to general procedure A with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.0 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.2), the desired product **3a** was obtained as a yellow solid (56.7 mg, 91 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.42 (dd, *J* = 8.6, 5.5 Hz, 5H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.22 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.0, 140.0, 138.5, 137.5, 132.3, 132.1, 129.1, 129.0, 128.0, 128.0, 127.2, 124.5, 124.3, 123.4, 123.2, 118.7, 114.3, 112.7, 111.1. **HRMS (ESI)** m/z calcd. for $C_{21}H_{15}N_2O^+$ $[M+H]^+$: 311.1184, found: 311.1187.

6-(p-tolyl)-8*H*-indazolo[1,2-a]cinnolin-8-one (3b)



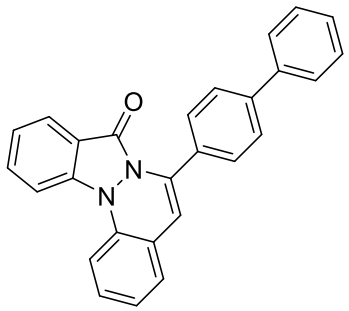
The reaction was performed according to general procedure A with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.1 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(p-tolyl)ethan-1-one **2b** (63.1mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 5:1, R_f = 0.2), the desired product **3b** was obtained as a yellow solid (60.8 mg, 94 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.30 (dd, *J* = 14.1, 6.9 Hz, 3H), 7.24 (d, *J* = 4.6 Hz, 1H), 7.22 (d, *J* = 4.2 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.03 (s, 1H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.3, 139.0, 137.7, 137.5, 136.9, 132.8, 132.4, 129.7, 129.3, 129.2, 128.9, 127.0, 125.8, 124.6, 124.3, 123.4, 122.6, 117.7, 113.4, 111.6, 111.4, 19.6. **HRMS (ESI)** m/z calcd. for $C_{22}H_{17}N_2O^+$ $[M+H]^+$: 325.1341, found: 325.1342.

6-(4-methoxyphenyl)-8*H*-indazolo[1,2-a]cinnolin-8-one (3c)



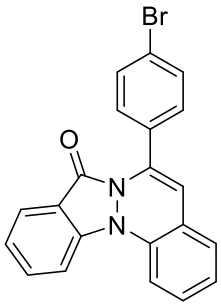
The reaction was performed according to general procedure A with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.0 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(4-methoxyphenyl)ethan-1-one **2c** (67.9 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.2), the desired product **3c** was obtained as a yellow solid (60.8 mg, 94 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 7.3 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.19 (s, 1H), 3.84 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.4, 156.1, 140.1, 138.5, 137.4, 132.3, 129.4, 128.7, 127.0, 124.6, 124.5, 124.4, 123.7, 123.3, 118.9, 114.5, 113.5, 111.6, 111.1, 55.5. **HRMS (ESI)** m/z calcd. for $C_{22}H_{17}N_2O_2^+$ $[M+H]^+$: 341.1290, found: 341.1292.

6-([1,1'-biphenyl]-4-yl)-8*H*-indazolo[1,2-a]cinnolin-8-one (3d)



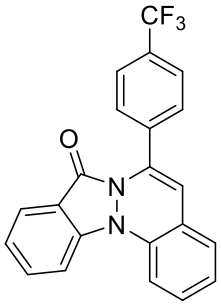
The reaction was performed according to general procedure A with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (41.8 mg, 0.2 mmol) and 1-([1,1'-biphenyl]-4-yl)-2-(dimethyl(oxo)-λ^6-sulfanylidene)ethan-1-one **2d** (81.7 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, R_f = 0.2), the desired product **3d** was obtained as a yellow solid (70.8 mg, 92 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.57 (dd, *J* = 7.4, 5.1 Hz, 5H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 6.1 Hz, 1H), 7.28 (d, *J* = 4.7 Hz, 1H), 7.22 – 7.17 (m, 2H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.23 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.2, 142.0, 140.8, 140.2, 138.7, 137.2, 132.4, 131.1, 129.1, 128.9, 128.4, 127.6, 127.3, 127.3, 126.8, 124.6, 124.4, 123.5, 123.4, 118.9, 114.5, 112.9, 111.2. **HRMS (ESI)** m/z calcd. for $C_{27}H_{19}N_2O^+$ $[M+H]^+$: 387.1497, found: 387.1500.

6-(4-bromophenyl)-8*H*-indazolo[1,2-a]cinnolin-8-one (3e)



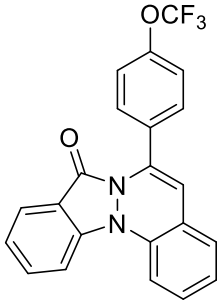
The reaction was performed according to general procedure A with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.0 mg, 0.2 mmol) and 1-(4-bromophenyl)-2-(dimethyl(oxo)-λ^6-sulfanylidene)ethan-1-one **2e** (82.5 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 5:1, R_f = 0.2), the desired product **3e** was obtained as a yellow solid (69.1 mg, 89 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.77 (t, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.24 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.24 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.0, 140.1, 138.5, 136.4, 132.4, 131.2, 131.0, 129.4, 129.2, 127.3, 124.5, 124.4, 123.3, 123.1, 118.5, 114.3, 113.0, 111.1. **HRMS (ESI)** m/z calcd. for $C_{21}H_{14}BrN_2O^+$ $[M+H]^+$: 389.0290, found: 389.0292.

6-(4-(trifluoromethyl)phenyl)-8*H*-indazolo[1,2-a]cinnolin-8-one (3f)



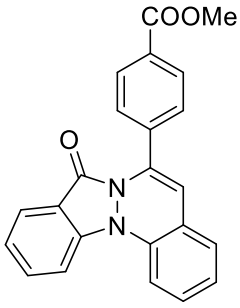
The reaction was performed according to general procedure A with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (41.9 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(4-(trifluoromethyl)phenyl)ethan-1-one **2f** (79.3 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, R_f = 0.2), the desired product **3f** was obtained as a yellow solid (74.5 mg, 98 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 6.7 Hz, 3H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.25 (d, *J* = 8.6 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.27 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.0, 140.2, 138.6, 136.0, 135.7, 132.6, 130.9 (d, *J* = 32.6 Hz), 129.7, 128.2, 127.6, 125.5, 125.0 (q, *J* = 3.7 Hz), 124.5 (d, *J* = 6.3 Hz), 123.5, 122.9, 122.8, 118.5, 114.4, 114.1, 111.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.62. **HRMS (ESI)** m/z calcd. for $C_{22}H_{14}F_3N_2O^+$ $[M+H]^+$: 379.1058, found: 379.1060.

6-(4-(trifluoromethoxy)phenyl)-8*H*-indazolo[1,2-a]cinnolin-8-one (3g)



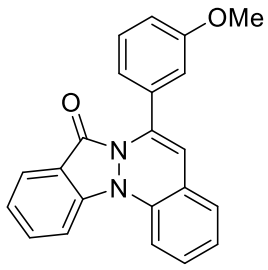
The reaction was performed according to general procedure A with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.1 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(4-(trifluoromethoxy)phenyl)ethan-1-one **2g** (84.1 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 6:1, R_f = 0.2), the desired product **3g** was obtained as a yellow solid (35.7 mg, 45 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 6.2 Hz, 3H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.25 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.1, 149.8, 140.2, 138.6, 136.2, 132.5, 130.8, 129.5, 129.4, 127.4, 124.6, 124.5, 123.5, 123.2, 120.4, 118.6, 114.4, 113.3, 111.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.60. **HRMS (ESI)** m/z calcd. for $C_{22}H_{14}F_3N_2O_2^+$ $[M+H]^+$: 395.1007, found: 395.1010.

methyl 4-(8-oxo-8*H*-indazolo[1,2-a]cinnolin-6-yl)benzoate (3h)



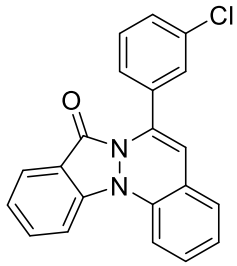
The reaction was performed according to general procedure A with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.0 mg, 0.2 mmol) and methyl 4-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)benzoate **2h** (76.3 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.2), the desired product **3h** was obtained as a yellow solid (66.4 mg, 90 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.2 Hz, 2H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.29 (dd, *J* = 13.6, 7.6 Hz, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.32 (s, 1H), 3.93 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 156.1, 140.2, 138.7, 136.5, 136.4, 132.5, 130.5, 129.6, 129.3, 127.8, 127.6, 124.6, 124.5, 123.5, 123.0, 118.6, 114.4, 114.1, 111.2, 52.3. **HRMS (ESI)** m/z calcd. for $C_{23}H_{17}N_2O_3^+$ $[M+H]^+$: 369.1239, found: 369.1240.

6-(3-methoxyphenyl)-8*H*-indazolo[1,2-a]cinnolin-8-one (3i)



The reaction was performed according to general procedure A with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.1 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(3-methoxyphenyl)ethan-1-one **2i** (67.9 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.2), the desired product **3i** was obtained as a yellow solid (62.7 mg, 92 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.77 (t, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.37 – 7.32 (m, 1H), 7.28 (t, *J* = 8.7 Hz, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 7.03 (d, *J* = 2.3 Hz, 1H), 6.98 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.27 (s, 1H), 3.86 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.3, 156.0, 140.2, 138.7, 137.4, 133.6, 132.3, 129.1, 129.0, 127.2, 124.6, 124.4, 123.4, 123.3, 120.6, 118.9, 114.7, 114.4, 113.7, 112.8, 111.1, 55.4. **HRMS (ESI)** m/z calcd. for $C_{22}H_{17}N_2O_2^+$ $[M+H]^+$: 341.1290, found: 341.1293.

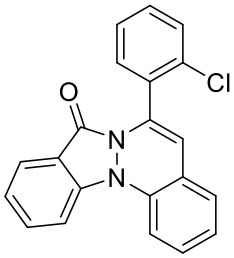
6-(3-chlorophenyl)-8*H*-indazolo[1,2-a]cinnolin-8-one (3j)



The reaction was performed according to general procedure A with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.0 mg, 0.2 mmol) and 1-(3-chlorophenyl)-2-(dimethyl(oxo)-λ^6-sulfanylidene)ethan-1-one **2j** (69.2 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, R_f = 0.2), the desired product **3j** was obtained as a yellow solid (63.0 mg, 91 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.42 (s, 1H), 7.36 – 7.30 (m, 2H), 7.28 (d, *J* = 8.7 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.21 (dd, *J* = 8.8, 6.5 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.19 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.0, 140.2, 138.7, 136.1, 134.1, 133.9, 132.5, 129.4, 129.2, 129.1, 127.9, 127.4, 126.4, 124.6, 124.5, 123.5, 123.1, 118.6, 114.4, 113.6, 111.2. **HRMS (ESI)** m/z calcd. for $C_{21}H_{14}ClN_2O^+$ $[M+H]^+$: 345.0795, found: 345.0796.

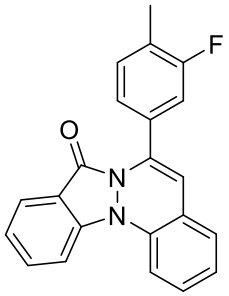
6-(2-chlorophenyl)-8*H*-indazolo[1,2-a]cinnolin-8-one (3k)

The reaction was performed according to general procedure A with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.2 mg, 0.2 mmol) and



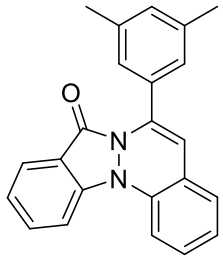
1-(2-chlorophenyl)-2-(dimethyl(oxo)-λ^6-sulfanylidene)ethan-1-one **2k** (69.2 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.2), the desired product **3k** was obtained as a yellow solid (57.2 mg, 83 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.44 (dd, *J* = 6.6, 2.3 Hz, 1H), 7.37 – 7.27 (m, 3H), 7.23 (dd, *J* = 13.1, 7.3 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.02 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.5, 139.1, 138.0, 135.2, 133.7, 132.5, 132.1, 130.7, 130.5, 129.4, 129.2, 127.3, 126.9, 124.7, 124.3, 123.0, 122.7, 117.7, 113.3, 112.8, 111.4. **HRMS (ESI)** m/z calcd. for $C_{21}H_{14}ClN_2O^+$ $[M+H]^+$: 345.0795, found: 345.0796.

6-(3-fluoro-4-methylphenyl)-8*H*-indazolo[1,2-a]cinnolin-8-one (3l)



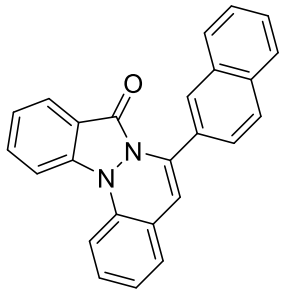
The reaction was performed according to general procedure A with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.2 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(3-fluoro-4-methylphenyl)ethan-1-one **2l** (68.5 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, R_f = 0.2), the desired product **3l** was obtained as a yellow solid (58.4 mg, 85 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.8 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.82 (t, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.31 (dt, *J* = 15.0, 7.3 Hz, 3H), 7.19 (s, 1H), 7.17 (dd, *J* = 8.5, 5.8 Hz, 2H), 6.29 (s, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.8 (d, *J* = 244.6 Hz), 156.0, 140.2, 138.7, 136.4, 132.4, 131.5 (d, *J* = 8.3 Hz), 131.0 (d, *J* = 5.5 Hz), 129.2, 127.3, 126.0 (d, *J* = 17.3 Hz), 124.6, 124.4, 123.5 (d, *J* = 3.3 Hz), 123.4, 123.3, 118.8, 114.6 (d, *J* = 24.0 Hz), 114.5, 112.9, 111.1, 14.71 (d, *J* = 3.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.44. **HRMS (ESI)** m/z calcd. for $C_{22}H_{16}FN_2O^+$ $[M+H]^+$: 343.1247, found: 343.1247

6-(3,5-dimethylphenyl)-8*H*-indazolo[1,2-a]cinnolin-8-one (3m)



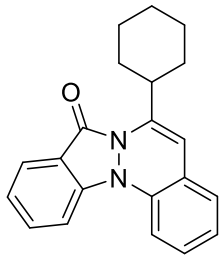
The reaction was performed according to general procedure A with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (41.9 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(3,5-dimethylphenyl)ethan-1-one **2m** (67.3 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, R_f = 0.2), the desired product **3m** was obtained as a yellow solid (31.6 mg, 47 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 8.2 Hz, 2H), 7.15 – 7.10 (m, 2H), 7.09 (d, *J* = 8.3 Hz, 3H), 6.24 (s, 1H), 2.39 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.0, 140.2, 138.7, 137.9, 137.5, 132.2, 131.1, 128.8, 127.1, 125.8, 124.6, 124.4, 123.7, 123.3, 119.0, 114.5, 112.5, 111.1, 21.5. **HRMS (ESI)** m/z calcd. for $C_{23}H_{19}N_2O^+$ $[M+H]^+$: 339.1497, found: 339.1496.

6-(naphthalen-2-yl)-8*H*-indazolo[1,2-a]cinnolin-8-one (3n)



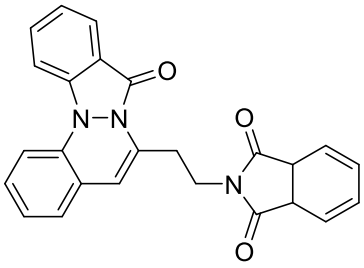
The reaction was performed according to general procedure A with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.1 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(naphthalen-2-yl)ethan-1-one **2n** (73.9 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, R_f = 0.2), the desired product **3n** was obtained as a yellow solid (67.2 mg, 93 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 1H), 8.01 (s, 1H), 7.90 – 7.83 (m, 4H), 7.79 – 7.74 (m, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 3H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.34 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.2, 140.1, 138.59, 137.53, 133.72, 133.08, 132.35, 130.11, 129.05, 128.52, 127.83, 127.23, 127.22, 126.99, 126.72, 126.37, 125.79, 124.64, 124.41, 123.49, 123.30, 118.73, 114.38, 113.05, 111.17. **HRMS (ESI)** m/z calcd. for $C_{25}H_{17}N_2O^+$ $[M+H]^+$: 361.1341, found: 361.1345.

6-cyclohexyl-8*H*-indazolo[1,2-a]cinnolin-8-one (3o)



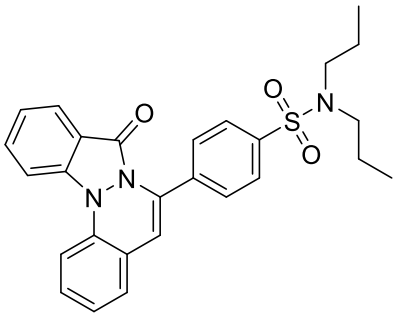
The reaction was performed according to general procedure A with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.0 mg, 0.2 mmol) and 1-cyclohexyl-2-(dimethyl(oxo)-λ^6-sulfanylidene)ethan-1-one **2o** (60.7 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 16:1, R_f = 0.2), the desired product **3o** was obtained as a yellow solid (47.2 mg, 75 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 6.9 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 5.94 (s, 1H), 3.89 (t, *J* = 11.5 Hz, 1H), 2.11 (d, *J* = 11.8 Hz, 2H), 1.81 (dd, *J* = 18.7, 16.1 Hz, 3H), 1.58 – 1.44 (m, 2H), 1.35 – 1.17 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.7, 146.1, 138.5, 136.9, 132.2, 128.0, 126.2, 124.4, 124.2, 123.4, 122.4, 118.0, 113.3, 111.3, 105.3, 36.6, 32.6, 26.5, 26.4. **HRMS (ESI)** m/z calcd. for $C_{21}H_{21}N_2O^+$ $[M+H]^+$: 317.1654, found: 317.1656.

2-(2-(8-oxo-8*H*-indazolo[1,2-a]cinnolin-6-yl)ethyl)-3a,7a-dihydro-1*H*-isoindole-1,3(2*H*)-dione (3p)



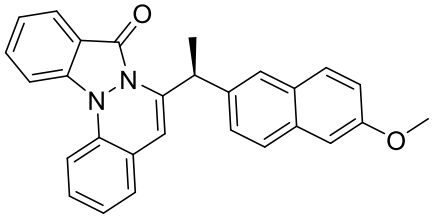
The reaction was performed according to general procedure A with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (41.9 mg, 0.2 mmol) and 2-(4-(dimethyl(oxo)-λ^6-sulfanylidene)-3-oxobutyl)isoindole-1,3-dione **2p** (88.0 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 3:1, R_f = 0.2), the desired product **3p** was obtained as a yellow solid (53.6 mg, 65 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.74 – 7.68 (m, 3H), 7.64 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.3 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 6.7 Hz, 1H), 5.70 (s, 1H), 4.17 (t, *J* = 6.1 Hz, 2H), 3.48 (t, *J* = 6.1 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.3, 156.6, 138.4, 136.9, 136.2, 133.9, 132.4, 132.1, 128.5, 126.0, 124.5, 124.1, 123.3, 122.8, 122.3, 117.4, 113.0, 111.5, 110.1, 37.3, 30.8. **HRMS (ESI)** m/z calcd. for $C_{25}H_{19}N_3O_3Na^+$ $[M+Na]^+$: 432.1324, found: 432.1322.

4-(8-oxo-8*H*-indazolo[1,2-a]cinnolin-6-yl)-*N*,*N*-dipropylbenzenesulfonamide (3q)



The reaction was performed according to general procedure A with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.0 mg, 0.2 mmol) and 4-(2-(dimethyl(oxo)-λ^6-sulfanylidene)acetyl)-N,N-dipropyl benzenesulfonamide **2q** (107.9 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.2), the desired product **3q** was obtained as a yellow solid (89.5 mg, 94 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 9.8 Hz, 1H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.30 (dd, *J* = 15.3, 7.5 Hz, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.32 (s, 1H), 3.14 – 3.08 (m, 4H), 1.66 – 1.55 (m, 4H), 0.90 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.1, 140.2, 140.1, 138.6, 136.0, 135.7, 132.6, 129.8, 128.4, 127.7, 126.7, 124.6, 124.5, 123.6, 122.8, 118.4, 114.7, 114.5, 111.3, 50.6, 22.5, 11.3. **HRMS (ESI)** m/z calcd. for $C_{27}H_{28}N_3O_3S^+$ $[M+H]^+$: 474.1851, found: 474.1856.

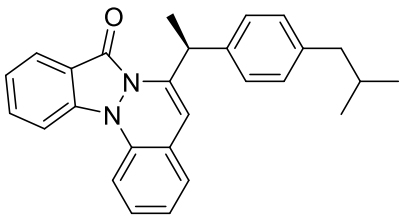
6-(1-(6-methoxynaphthalen-2-yl)ethyl)-8*H*-indazolo[1,2-a]cinnolin-8-one (3r)



The reaction was performed according to general procedure A with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.1 mg, 0.2 mmol) and (S)-1-(dimethyl(oxo)-λ^6-sulfanylidene)-3-(6-methoxynaph thalen-2-yl)butan-2-one **2r** (91.3 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.2), the desired product **3r** was obtained as a yellow solid (59.0 mg, 70 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.9 Hz, 1H), 7.97 (s, 1H), 7.87 (t, *J* = 8.3 Hz, 3H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.28 (dd, *J* = 7.4, 4.3 Hz, 3H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.17 (s, 1H), 5.91 (q, *J* = 7.0 Hz, 1H), 4.04 (s, 3H), 1.86 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.5, 156.8, 144.3, 138.8, 138.7, 137.2, 133.6, 132.2, 129.4, 129.0, 128.5, 127.6, 127.1, 126.6, 126.1, 124.3, 124.2, 123.0, 122.5, 118.7, 118.1, 113.4, 111.1, 108.3, 105.6, 55.4, 37.8, 20.8. **HRMS (ESI)** m/z calcd. for $C_{27}H_{28}N_3O_3S^+$ $[M+H]^+$: 474.1851, found: 474.1856. **HRMS (ESI)** m/z calcd. for

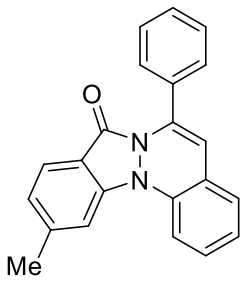
$C_{28}H_{23}N_2O_2^+$ $[M+H]^+$: 419.1760, found: 419.1759.

6-(1-(4-isobutylphenyl)ethyl)-8*H*-indazolo[1,2-a]cinnolin-8-one (3s)



The reaction was performed according to general procedure A with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.0 mg, 0.2 mmol) and (R)-1-(dimethyl(oxo)-λ^6-sulfanylidene)-3-(4-isobutylphenyl)butan-2-one **2s** (44.2 mg, 0.3 mmol). However, this product will be detected by TLC until the temperature rises to 120°C. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 16:1, R_f = 0.2), the desired product **3s** was obtained as a yellow oil (58.4 mg, 74 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.9 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.89 (t, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.33 – 7.27 (m, 3H), 6.18 (s, 1H), 5.81 (q, *J* = 7.0 Hz, 1H), 2.65 (d, *J* = 7.2 Hz, 2H), 2.06 (dt, *J* = 13.5, 6.7 Hz, 1H), 1.84 (d, *J* = 7.1 Hz, 3H), 1.11 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.8, 144.6, 140.7, 140.1, 138.7, 137.1, 132.1, 129.3, 128.4, 127.8, 126.6, 124.4, 124.2, 123.1, 122.5, 118.1, 113.4, 111.1, 108.1, 45.2, 37.5, 30.2, 22.5, 21.0. **HRMS (ESI)** m/z calcd. for $C_{27}H_{27}N_2O^+$ $[M+H]^+$: 395.2123, found: 395.2123.

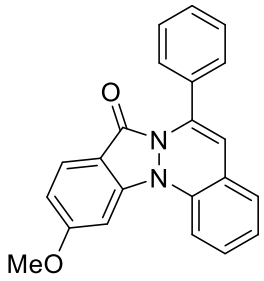
11-methyl-6-phenyl-8*H*-indazolo[1,2-a]cinnolin-8-one (4a)



The reaction was performed according to general procedure A with 6-methyl-1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1b** (44.9 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, R_f = 0.2), the desired product **4a** was obtained as a yellow solid (43.0 mg, 66 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.63 (s, 1H), 7.48 – 7.39 (m, 5H), 7.30 – 7.26 (m, 1H), 7.24 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.22 (s, 1H), 2.62 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.1, 143.5, 140.7, 138.7, 137.7, 132.3, 129.2, 128.9, 128.0, 128.0, 127.1, 125.0, 124.3, 124.2, 123.7, 116.6, 114.3, 112.5, 111.2, 22.8. **HRMS**

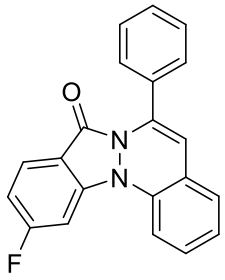
(ESI) m/z calcd. for $C_{22}H_{17}N_2O^+$ $[M+H]^+$: 325.1341, found: 325.1345.

11-methoxy-6-phenyl-8*H*-indazolo[1,2-a]cinnolin-8-one (4b)



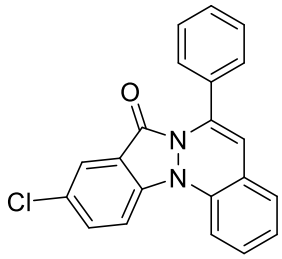
The reaction was performed according to general procedure A with 6-methoxy-1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1c** (48.3 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.2), the desired product **4b** was obtained as a yellow solid (55.6 mg, 82 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.7 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.48 (d, *J* = 9.5 Hz, 5H), 7.28 (dd, *J* = 11.4, 5.4 Hz, 3H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 6.21 (s, 1H), 4.02 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.7, 155.9, 141.7, 138.4, 137.9, 132.3, 129.1, 128.7, 128.0, 128.0, 127.1, 125.7, 124.4, 123.9, 112.2, 112.1, 112.0, 110.9, 98.0, 56.1. **HRMS (ESI)** m/z calcd. for $C_{22}H_{17}N_2O_2^+$ $[M+H]^+$: 341.1290, found: 341.1294.

11-fluoro-6-phenyl-8*H*-indazolo[1,2-a]cinnolin-8-one (4c)



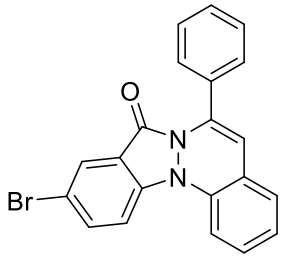
The reaction was performed according to general procedure A with 6-fluoro-1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1d** (45.8 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, R_f = 0.2), the desired product **4c** was obtained as a yellow solid (64.1 mg, 98 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.4, 5.7 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 9.5 Hz, 1H), 7.43 (s, 5H), 7.32 – 7.27 (m, 1H), 7.25 (d, *J* = 5.5 Hz, 1H), 7.16 – 7.11 (m, 1H), 7.11 – 7.05 (m, 1H), 6.20 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.9, 164.4, 155.3, 140.5, 140.3, 137.8, 137.6, 132.0, 129.3, 129.0, 128.0, 127.3, 126.7, 126.6, 124.8, 123.5, 114.9, 112.4, 112.2, 111.9, 111.0, 101.3, 101.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.51. **HRMS (ESI)** m/z calcd. for $C_{21}H_{14}FN_2O^+$ $[M+H]^+$: 329.1090, found: 329.1093.

10-chloro-6-phenyl-8*H*-indazolo[1,2-a]cinnolin-8-one (4d)



The reaction was performed according to general procedure A with 5-chloro-1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1e** (48.9 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.2), the desired product **4d** was obtained as a yellow solid (43.6 mg, 63 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 2.1 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.70 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.43 (s, 5H), 7.29 (s, 1H), 7.27 (s, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.26 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.8, 138.2, 138.1, 137.4, 132.6, 131.9, 129.4, 129.2, 128.9, 128.1, 128.0, 127.4, 124.7, 124.1, 123.3, 120.0, 115.6, 113.0, 111.2. **HRMS (ESI)** m/z calcd. for $C_{21}H_{14}ClN_2O^+$ $[M+H]^+$: 345.1090, found: 345.1093.

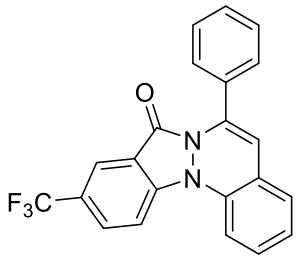
10-bromo-6-phenyl-8*H*-indazolo[1,2-a]cinnolin-8-one (4e)



The reaction was performed according to general procedure A with 5-bromo-1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1f** (57.8 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.2), the desired product **4e** was obtained as a yellow solid (40.6 mg, 52 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 1.1 Hz, 1H), 7.78 (dd, *J* = 8.8, 1.1 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.39 (s, 5H), 7.23 (d, *J* = 7.2 Hz, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.20 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.5, 138.4, 137.9, 137.3, 135.2, 131.8, 129.3, 129.2, 128.0, 127.9, 127.4, 127.2, 124.7, 123.2, 120.3, 116.0, 115.8, 112.9, 111.1. **HRMS (ESI)** m/z calcd. for $C_{21}H_{14}BrN_2O^+$ $[M+H]^+$: 389.0290, found: 389.0285.

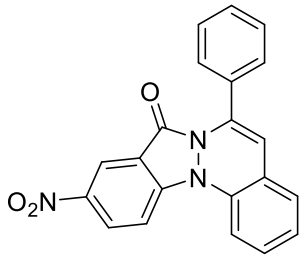
6-phenyl-10-(trifluoromethyl)-8*H*-indazolo[1,2-a]cinnolin-8-one (4f)

The reaction was performed according to general procedure A with 1-phenyl-5-(trifluoromethyl)-1,2-dihydro-3*H*-indazol-3-one **1g** (55.5 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol). After



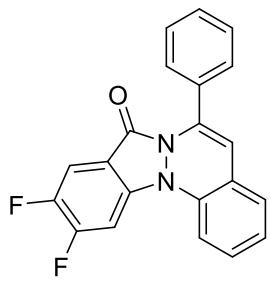
purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.2), the desired product **4f** was obtained as a yellow solid (48.5 mg, 64 % yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.97 (s, 2H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.44 (s, 5H), 7.34 – 7.30 (m, 1H), 7.29 (d, *J* = 6.3 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 6.25 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.93, 140.69, 137.39 (d, *J* = 8.2 Hz), 131.75, 129.45, 129.24, 129.00 (dd, *J* = 6.4, 3.2 Hz), 128.07, 127.51, 125.41 (d, *J* = 5.1 Hz), 125.14, 125.12 (d, *J* = 4.1 Hz), 123.30, 122.62 (dd, *J* = 8.0, 3.8 Hz), 118.19, 114.44, 112.69, 111.40. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -61.54. **HRMS (ESI)** m/z calcd. for $C_{22}H_{14}F_3N_2O^+$ $[M+H]^+$: 379.1058, found: 379.1060.

10-nitro-6-phenyl-8*H*-indazolo[1,2-a]cinnolin-8-one (4g)



The reaction was performed according to general procedure A with 5-nitro-1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1h** (51.0 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, R_f = 0.2), the desired product **4g** was obtained as a red solid (35.7 mg, 50 % yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 1.9 Hz, 1H), 8.61 (dd, *J* = 9.2, 1.9 Hz, 1H), 7.98 (d, *J* = 9.2 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.45 (s, 5H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 7.3 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 6.22 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.4, 142.7, 140.7, 137.4, 136.3, 131.6, 129.6, 129.4, 128.2, 128.1, 127.7, 127.3, 125.9, 123.3, 121.9, 117.8, 113.6, 112.3, 111.9. **HRMS (ESI)** m/z calcd. for $C_{21}H_{14}N_3O_3^+$ $[M+H]^+$: 356.1035, found: 356.1040.

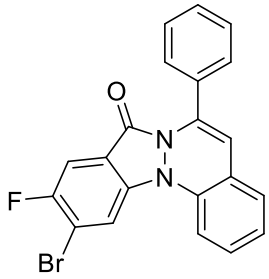
10,11-difluoro-6-phenyl-8*H*-indazolo[1,2-a]cinnolin-8-one (4h)



The reaction was performed according to general procedure A with 5,6-difluoro-1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1i** (49.2 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol). After purification by silica gel chromatography

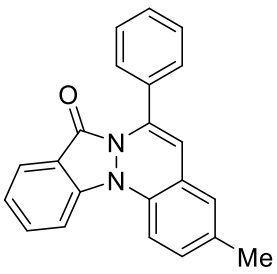
(petroleum ether/ethyl acetate = 8:1, R_f = 0.2), the desired product **4h** was obtained as a yellow solid (51.7 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (t, *J* = 8.2 Hz, 1H), 7.67 (dd, *J* = 10.0, 6.0 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.44 (s, 5H), 7.33 – 7.26 (m, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.25 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.8, 154.8, 149.1, 148.9, 146.6, 146.5, 137.8, 137.4, 135.8, 135.7, 131.8, 129.4, 129.2, 128.1, 128.0, 127.5, 125.0, 123.3, 114.5, 114.5, 114.4, 114.4, 112.8, 112.0, 112.0, 111.8, 111.8, 110.8, 103.5, 103.2.(extra signals due to C−F coupling); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -126.66, -140.23. **HRMS (ESI)** m/z calcd. for $C_{21}H_{13}F_2N_2O^+$ $[M+H]^+$: 347.0996, found: 347.0995.

11-bromo-10-fluoro-6-phenyl-8*H*-indazolo[1,2-a]cinnolin-8-one (4i)



The reaction was performed according to general procedure A with 6-bromo-5-fluoro-1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1j** (61.4 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.2), the desired product **4i** was obtained as a yellow solid (57.0 mg, 70 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 5.0 Hz, 1H), 7.69 (d, *J* = 6.9 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.43 (s, 5H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.26 (s, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.5, 154.7, 154.7 (d, *J* = 3.8 Hz), 154.7, 154.0, 137.9, 137.3, 136.4, 131.7, 129.4, 129.4 (d, *J* = 10.8 Hz), 129.3, 128.1, 127.9, 127.5, 124.9, 123.2, 119.2, 119.0 (d, *J* = 7.9 Hz), 115.4 (d, *J* = 24.3 Hz), 115.5, 115.3, 113.1, 110.9, 110.6, 110.5 (d, *J* = 25.2 Hz), 110.3, 77.5, 77.2, 76.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.57. **HRMS (ESI)** m/z calcd. for $C_{21}H_{13}BrFN_2O^+$ $[M+H]^+$: 407.0195, found: 407.0190.

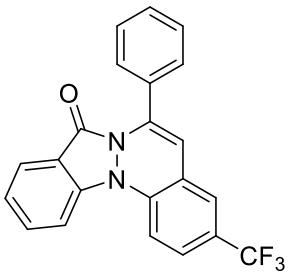
3-methyl-6-phenyl-8*H*-indazolo[1,2-a]cinnolin-8-one (4j)



The reaction was performed according to general procedure A with 1-(p-tolyl)-1,2-dihydro-3*H*-indazol-3-one **1k** (44.7 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum

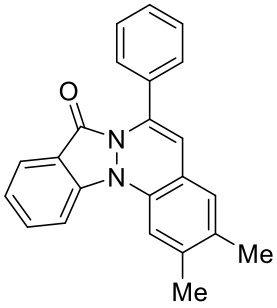
ether/ethyl acetate = 8:1, R_f = 0.2), the desired product **4j** was obtained as a yellow solid (33.1 mg, 51 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.44 (d, *J* = 5.3 Hz, 5H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.05 (s, 2H), 6.19 (s, 1H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.0, 140.1, 137.3, 136.2, 133.9, 132.2, 132.2, 129.3, 129.1, 128.0, 127.9, 127.7, 124.5, 123.2, 123.0, 118.5, 114.2, 112.9, 111.0, 20.7. **HRMS (ESI)** m/z calcd. for $C_{22}H_{17}N_2O^+$ $[M+H]^+$: 325.1341, found: 325.1341.

6-phenyl-3-(trifluoromethyl)-8*H*-indazolo[1,2-a]cinnolin-8-one (4k)



The reaction was performed according to general procedure A with 1-(4-(trifluoromethyl)phenyl)-1,2-dihydro-3*H*-indazol-3-one **1l** (55.6 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.2), the desired product **4k** was obtained as a yellow solid (69.6 mg, 92 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.82 – 7.77 (m, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.49 (d, *J* = 8.8 Hz, 1H), 7.44 (s, 6H), 7.41 (d, *J* = 7.7 Hz, 1H), 6.21 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.9, 140.9, 139.8, 139.0, 132.8, 131.6, 129.6, 128.1, 128.0, 126.6, 126.2, 126.0, 126.0, 125.9, 125.9, 125.2, 124.8, 124.1, 123.9, 123.8, 123.8, 123.7, 122.5, 119.0, 114.3, 111.4, 111.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.38. **HRMS (ESI)** m/z calcd. for $C_{22}H_{14}F_3N_2O^+$ $[M+H]^+$: 379.1058, found: 379.1057.

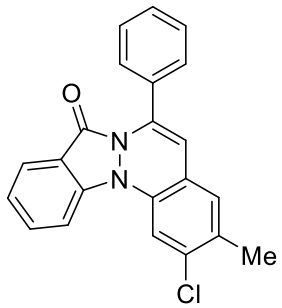
2,3-dimethyl-6-phenyl-8*H*-indazolo[1,2-a]cinnolin-8-one (4l)



The reaction was performed according to general procedure A with 1-(3,4-dimethylphenyl)-1,2-dihydro-3*H*-indazol-3-one **1m** (47.7 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.2), the desired product **4l** was obtained as a yellow solid (66.1 mg, 98 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.42 (dt, *J* = 7.1, 4.3 Hz, 6H), 7.36 (t, *J*

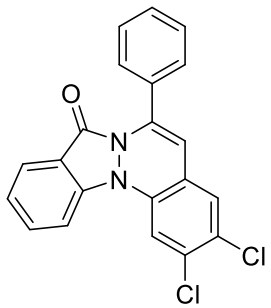
= 7.5 Hz, 1H), 7.02 (s, 1H), 6.21 (s, 1H), 2.31 (s, 3H), 2.24 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.0, 140.1, 137.8, 136.5, 132.5, 132.4, 132.1, 128.9, 128.3, 128.0, 127.9, 124.5, 122.9, 120.8, 118.6, 114.3, 112.9, 112.3, 20.5, 19.1. **HRMS (ESI)** m/z calcd. for $C_{23}H_{19}N_2O^+$ $[M+H]^+$: 339.1497, found: 339.1499.

2-chloro-3-methyl-6-phenyl-8*H*-indazolo[1,2-a]cinnolin-8-one (4m)



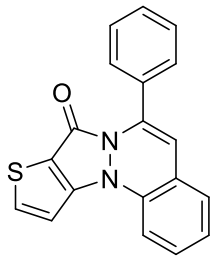
The reaction was performed according to general procedure A with 1-(3-chloro-4-methylphenyl)-1,2-dihydro-3*H*-indazol-3-one **1n** (51.9 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene) -1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.2), the desired product **4m** was obtained as a yellow oil (57.0 mg, 79 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 3.8 Hz, 2H), 7.56 (s, 1H), 7.41 (s, 5H), 7.38 (dd, *J* = 7.9, 4.0 Hz, 2H), 7.03 (s, 1H), 6.13 (s, 1H), 2.30 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.0, 140.0, 137.6, 137.3, 134.0, 132.6, 131.9, 131.8, 129.2, 129.0, 128.0, 127.9, 124.6, 123.6, 122.1, 118.8, 114.2, 111.9, 111.8, 19.4. **HRMS (ESI)** m/z calcd. for $C_{22}H_{16}ClN_2O^+$ $[M+H]^+$: 359.0951, found: 359.0952.

2,3-dichloro-6-phenyl-8*H*-indazolo[1,2-a]cinnolin-8-one (4n)



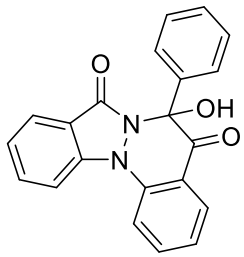
The reaction was performed according to general procedure A with 1-(3,4-dichlorophenyl)-1,2-dihydro-3*H*-indazol-3-one **1o** (56.2 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.2), the desired product **4n** was obtained as a yellow oil (45.2 mg, 60 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 1H), 7.84 – 7.79 (m, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.65 (s, 1H), 7.43 (s, 6H), 7.26 (s, 1H), 6.11 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.1, 140.0, 139.0, 137.8, 133.0, 131.9, 131.5, 129.7, 128.2, 128.0, 127.8, 127.7, 124.9, 124.1, 123.9, 119.0, 114.2, 113.0, 110.6. **HRMS (ESI)** m/z calcd. for $C_{21}H_{13}Cl_2N_2O^+$ $[M+H]^+$: 379.0405, found: 379.0407.

6-phenyl-8*H*-thieno[2',3':4,5]pyrazolo[1,2-a]cinnolin-8-one (4o)



The reaction was performed according to general procedure A with 1-phenyl-1,2-dihydro-3*H*-thieno[3,2-c]pyrazol-3-one **1p** (43.2 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, R_f = 0.2), the desired product **4o** was obtained as a yellow oil (48.3 mg, 76 % yield). **^{1}H NMR** (400 MHz, DMSO) δ 8.28 (d, *J* = 5.2 Hz, 1H), 7.93 (d, *J* = 5.3 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.45 – 7.34 (m, 7H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.41 (s, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 151.9, 146.3, 138.7, 136.2, 136.0, 132.2, 129.6, 128.7, 127.7, 127.6, 127.4, 124.3, 121.1, 114.8, 112.9, 111.8, 111.3. **HRMS (ESI)** m/z calcd. for $C_{19}H_{13}N_2OS^+$ $[M+H]^+$: 317.0749, found: 317.0750.

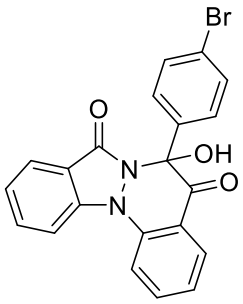
6-hydroxy-6-phenyl-8*H*-indazolo[1,2-a]cinnoline-5,8(6*H*)-dione (5a)



The reaction was performed according to general procedure B with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.0 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.2), the desired product **5a** was obtained as a yellow solid (52.4 mg, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.37 – 7.21 (m, 6H), 7.15 (t, *J* = 7.2 Hz, 1H), 6.95 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.6, 164.5, 141.1, 139.7, 138.3, 136.4, 134.3, 130.3, 129.7, 129.1, 125.7, 125.1, 123.7, 117.9, 117.3, 113.1, 112.9, 91.4. **HRMS (ESI)** m/z calcd. for $C_{21}H_{15}N_2O_3^+$ $[M+H]^+$: 343.1083, found: 343.1076.

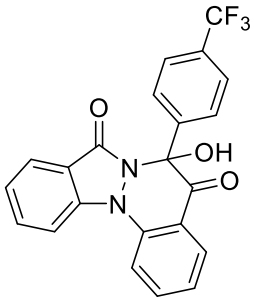
6-(4-bromophenyl)-6-hydroxy-8*H*-indazolo[1,2-a]cinnoline-5,8(6*H*)-dione (5b)

The reaction was performed according to general procedure B with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.0 mg, 0.2 mmol) and 1-(4-bromophenyl)-2-(dimethyl(oxo)-λ^6-sulfanylidene)ethan-1-one **2e** (76.3 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.2), the



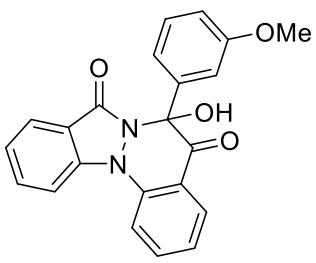
desired product **5b** was obtained as a yellow oil (25.3 mg, 30% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 – 8.04 (m, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.79 (t, *J* = 7.7 Hz, 1H), 7.74 – 7.69 (m, 1H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 6.87 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.3, 164.5, 141.3, 139.9, 137.5, 136.6, 134.4, 132.2, 130.4, 127.5, 125.2, 124.2, 123.9, 123.9, 117.9, 117.3, 113.2, 112.9, 90.8. **HRMS (ESI)** m/z calcd. for $C_{21}H_{14}BrN_2O_3^+$ $[M+H]^+$: 421.0188, found: 421.0190.

6-hydroxy-6-(4-(trifluoromethyl)phenyl)-8*H*-indazolo[1,2-a]cinnoline-5,8(6*H*)-dione (5c)



The reaction was performed according to general procedure B with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (41.9 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(4-(trifluoromethyl)phenyl)ethan-1-one **2f** (79.3 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.2), the desired product **5c** was obtained as a yellow oil (27.9 mg, 34% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.80 (t, *J* = 8.0 Hz, 1H), 7.73 (t, *J* = 7.4 Hz, 1H), 7.59 – 7.53 (m, 4H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 6.86 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.24, 164.48, 142.25, 141.47, 139.98, 136.76, 136.09, 134.54, 130.47, 126.95, 126.36, 126.05 (dd), 125.21, 123.99 (d), 123.86, 122.46, 117.55 (d), 113.08 (d), 110.70, 90.55. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.88. **HRMS (ESI)** m/z calcd. for $C_{22}H_{14}F_3N_2O_3^+$ $[M+H]^+$: 411.0957, found: 411.0954.

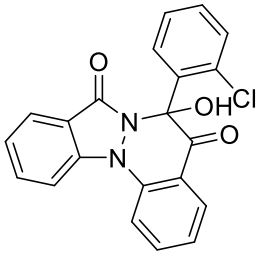
6-hydroxy-6-(3-methoxyphenyl)-8*H*-indazolo[1,2-a]cinnoline-5,8(6*H*)-dione (5d)



The reaction was performed according to general procedure B with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.0 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(3-methoxyphenyl)ethan-1-one **2i** (67.9 mg, 0.3 mmol). After

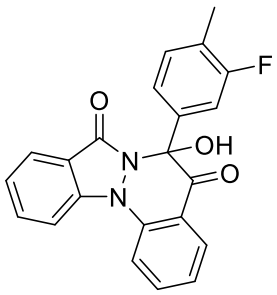
purification by silica gel chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.2), the desired product **5d** was obtained as a yellow oil (36.3 mg, 49% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.9 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.90 (d, *J* = 8.6 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.77 (t, *J* = 7.9 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.17 (dt, *J* = 12.0, 7.8 Hz, 2H), 7.03 (s, 1H), 6.99 (s, 1H), 6.82 (dd, *J* = 11.1, 5.0 Hz, 2H), 3.72 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.4, 164.4, 160.1, 141.0, 139.9, 139.6, 136.4, 134.3, 130.3, 130.0, 125.0, 123.7, 123.6, 117.9, 117.6, 117.2, 115.4, 113.0, 112.9, 111.5, 91.2, 55.4. **HRMS (ESI)** m/z calcd. for $C_{22}H_{17}N_2O_4^+$ $[M+H]^+$: 373.1188, found: 373.1180.

6-(2-chlorophenyl)-6-hydroxy-8*H*-indazolo[1,2-a]cinnoline-5,8(6*H*)-dione (5e)



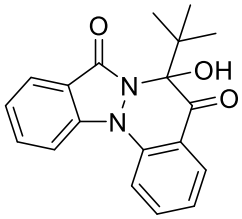
The reaction was performed according to general procedure B with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (41.9 mg, 0.2 mmol) and 1-(2-chlorophenyl)-2-(dimethyl(oxo)-λ^6-sulfanylidene)ethan-1-one **2k** (69.2 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.2), the desired product **5e** was obtained as a yellow oil (21.4 mg, 28% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.76 – 7.67 (m, 3H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 13.9 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.22 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.3, 162.3, 141.2, 139.9, 136.1, 135.5, 133.9, 131.2, 130.4, 130.2, 130.1, 129.9, 126.9, 125.0, 123.5, 123.0, 118.1, 117.6, 112.9, 87.4. **HRMS (ESI)** m/z calcd. for $C_{21}H_{13}ClN_2O_3Na^+$ $[M+Na]^+$: 399.0512, found: 399.0518.

6-(3-fluoro-4-methylphenyl)-6-hydroxy-8*H*-indazolo[1,2-a]cinnoline-5,8(6*H*)-dione (5f)



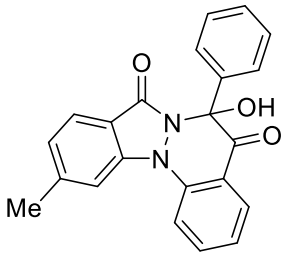
The reaction was performed according to general procedure B with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.0 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-(3-fluoro-4-methylphenyl)ethan-1-one **2l** (68.5 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, R_f = 0.2), the desired product **5f** was obtained as a yellow oil (24.4 mg, 33% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.9 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.13 – 7.02 (m, 3H), 6.88 (s, 1H), 2.19 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.3, 164.4, 161.5 (d, *J* = 246.0 Hz), 141.2, 139.8, 138.1 (d, *J* = 6.8 Hz), 136.5, 134.4, 132.1 (d, *J* = 5.3 Hz), 130.4, 126.9, 126.7 (d, *J* = 0.5 Hz), 125.2, 123.8 (d, *J* = 8.0 Hz), 121.0 (d, *J* = 3.5 Hz), 117.9, 117.3, 113.2, 112.9, 112.7, 90.6, 14.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.56. **HRMS (ESI)** m/z calcd. for $C_{22}H_{16}FN_2O_3^+$ $[M+H]^+$: 375.1145, found: 375.1139.

6-(tert-butyl)-6-hydroxy-8*H*-indazolo[1,2-a]cinnoline-5,8(6*H*)-dione (5g)



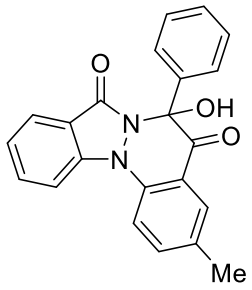
The reaction was performed according to general procedure B with 1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1a** (42.0 mg, 0.2 mmol) and 1-(dimethyl(oxo)-λ^6-sulfanylidene)-3,3-dimethylbutan-2-one **2t** (52.9 mg, 0.3 mmol). However, this product will be detected by TLC until the temperature rises to 120^{o}C. After purification by silica gel chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.2), the desired product **5g** was obtained as a yellow oil (34.8 mg, 57% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.9 Hz, 1H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.60 (dd, *J* = 8.0, 6.0 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.24 – 7.18 (m, 3H), 0.90 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.1, 158.1, 141.0, 135.8, 133.6, 129.7, 128.9, 126.6, 126.3, 125.1, 122.9, 116.2, 112.3, 112.1, 79.2, 41.9, 25.1. **HRMS (ESI)** m/z calcd. for $C_{21}H_{21}N_2O_3^+$ $[M+H]^+$: 349.1552, found: 349.1554.

6-hydroxy-11-methyl-6-phenyl-8*H*-indazolo[1,2-a]cinnoline-5,8(6*H*)-dione (5h)



The reaction was performed according to general procedure B with 6-methyl-1-phenyl-1,2-dihydro-3*H*-indazol-3-one **1b** (44.8 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.2), the desired product **5h** was obtained as a yellow oil (43.6 mg, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.8 Hz, 1H), 7.95 (dd, *J* = 8.2, 3.4 Hz, 2H), 7.83 – 7.77 (m, 2H), 7.48 – 7.42 (m, 2H), 7.37 (dd, *J* = 6.7, 3.0 Hz, 3H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.12 (s, 1H), 2.71 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.7, 164.8, 145.7, 141.7, 139.9, 138.4, 136.3, 130.3, 129.68, 129.0, 125.7, 125.4, 124.7, 123.6, 117.3, 115.7, 113.1, 112.9, 91.4, 23.0. **HRMS (ESI)** m/z calcd. for $C_{22}H_{17}N_2O_3^+$ $[M+H]^+$: 357.1239, found: 357.1232.

6-hydroxy-3-methyl-6-phenyl-8*H*-indazolo[1,2-a]cinnoline-5,8(6*H*)-dione (5i)

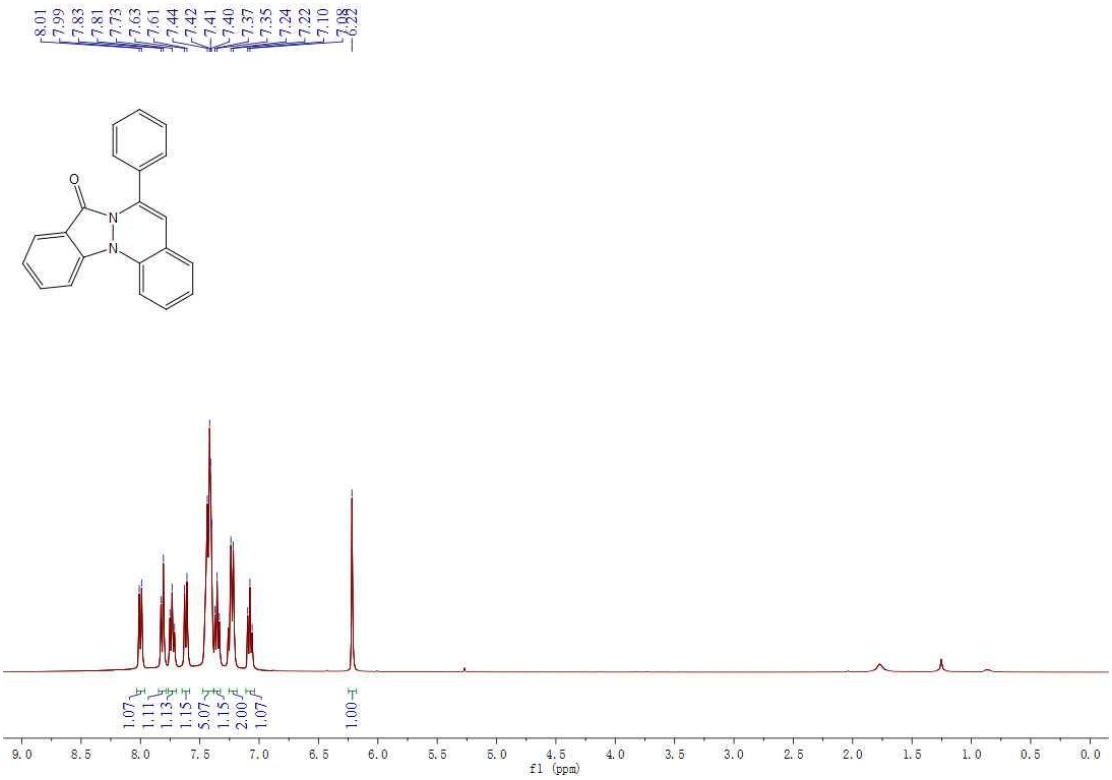


The reaction was performed according to general procedure B with 1-(p-tolyl)-1,2-dihydro-3*H*-indazol-3-one **1k** (44.9 mg, 0.2 mmol) and 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **2a** (58.9 mg, 0.3 mmol). After purification by silica gel chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.2), the desired product **5i** was obtained as a yellow oil (46.3 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.9 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.85 (s, 1H), 7.79 – 7.73 (m, 2H), 7.49 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.38 – 7.27 (m, 6H), 7.01 (s, 1H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.7, 164.2, 140.9, 138.3, 137.6, 137.2, 134.1, 133.5, 130.0, 129.6, 129.0, 125.6, 124.9, 123.3, 117.6, 117.1, 112.8, 112.7, 91.2, 20.5. **HRMS (ESI)** m/z calcd. for $C_{22}H_{17}N_2O_3^+$ $[M+H]^+$: 357.1239, found: 357.1246.

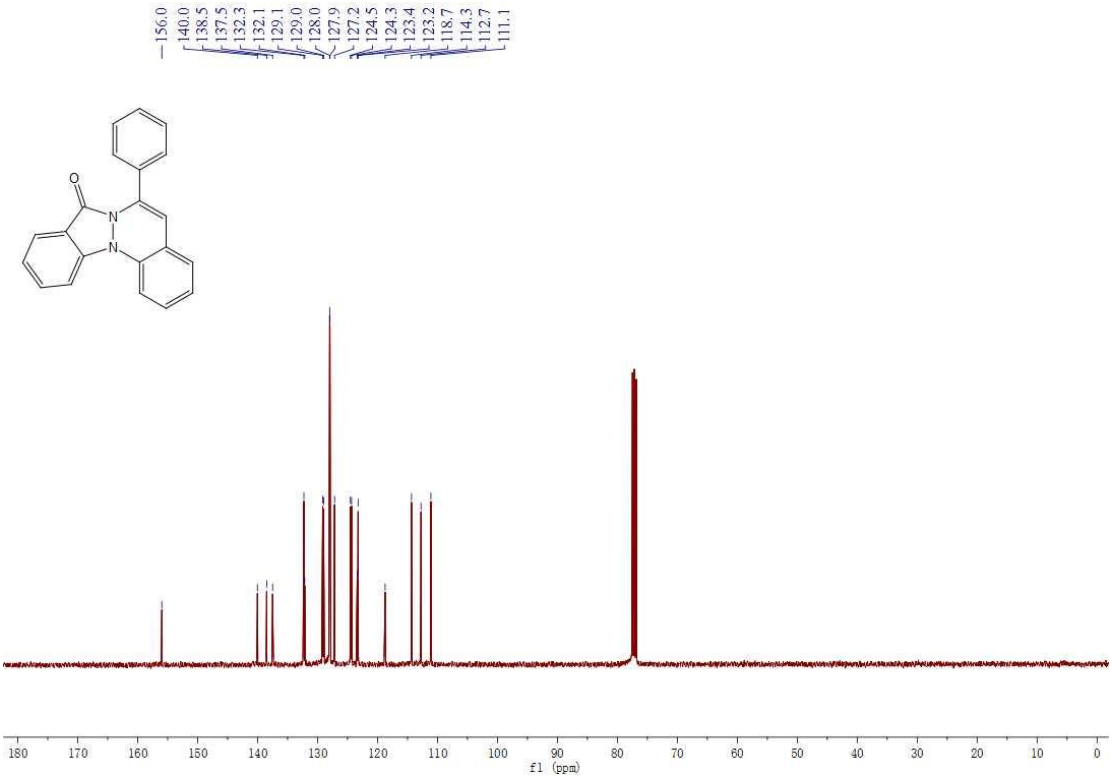
10. Copies of product NMR spectra

3a

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

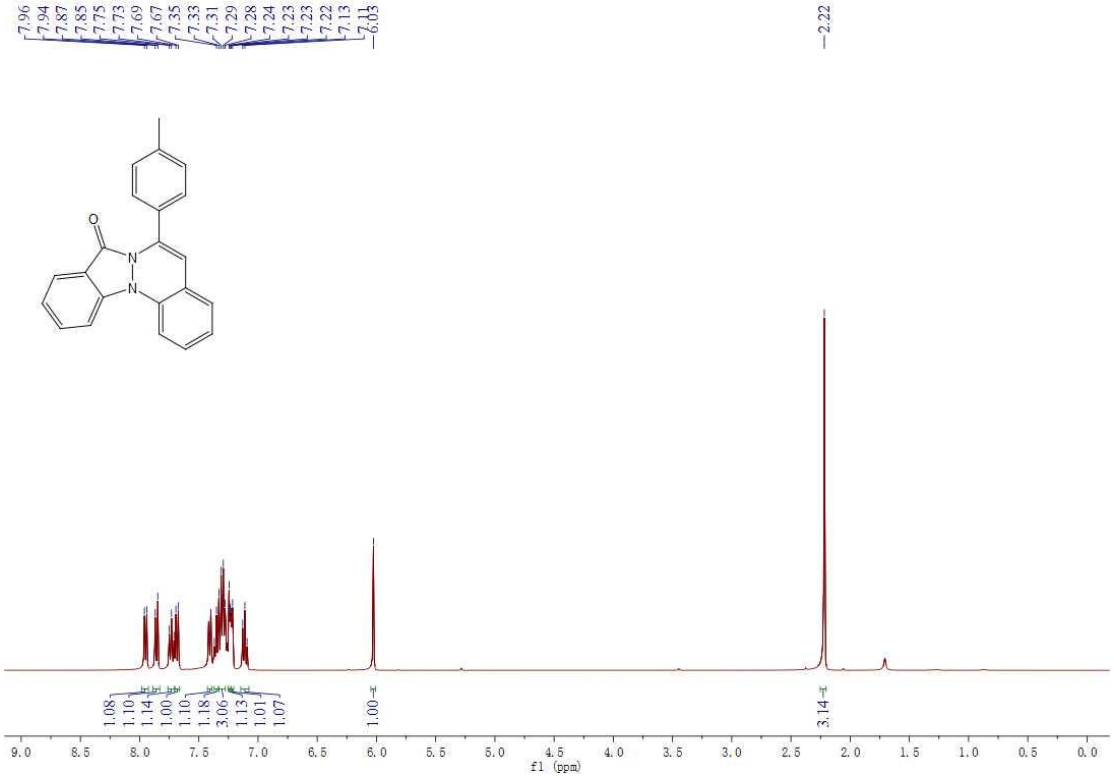


^{13}C NMR (101 MHz, $CDCl_3$)

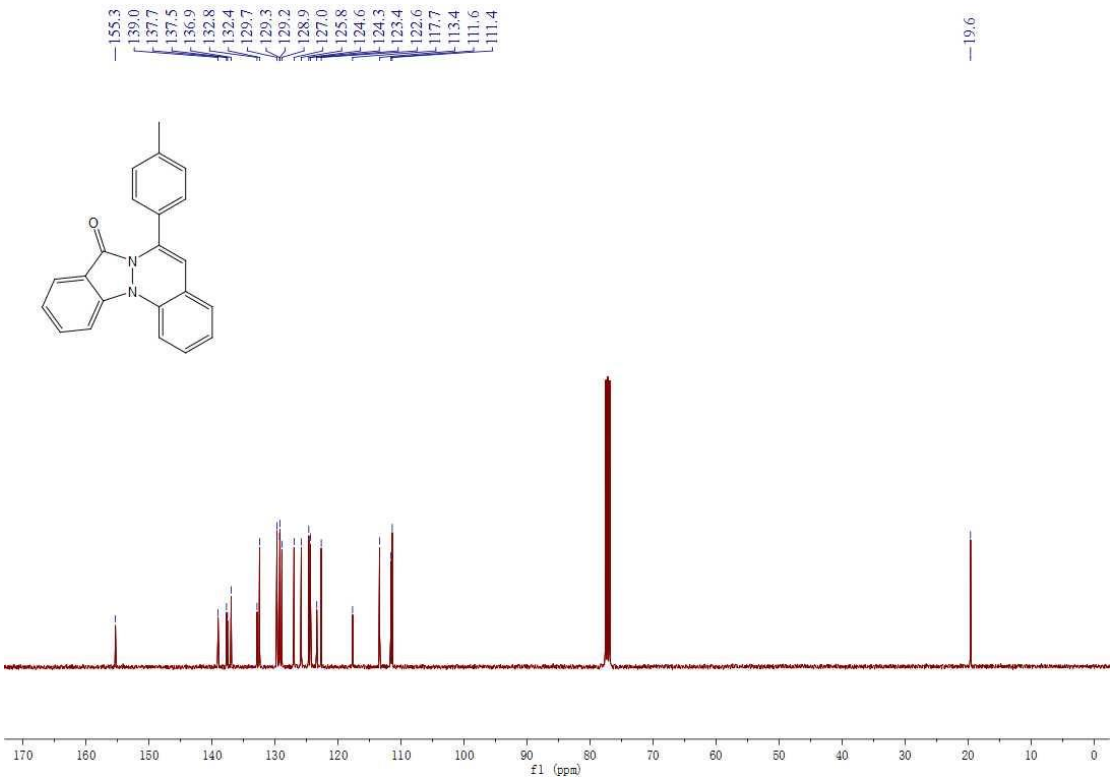


3b

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

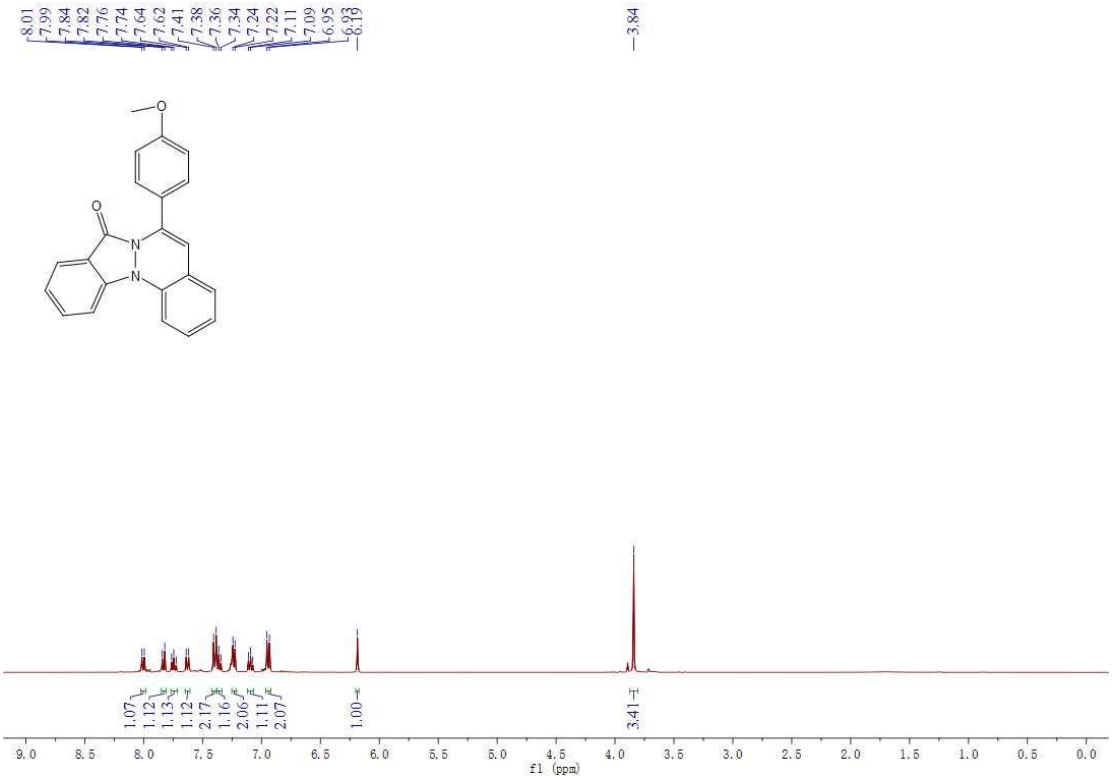


^{13}C NMR (101 MHz, $CDCl_3$)

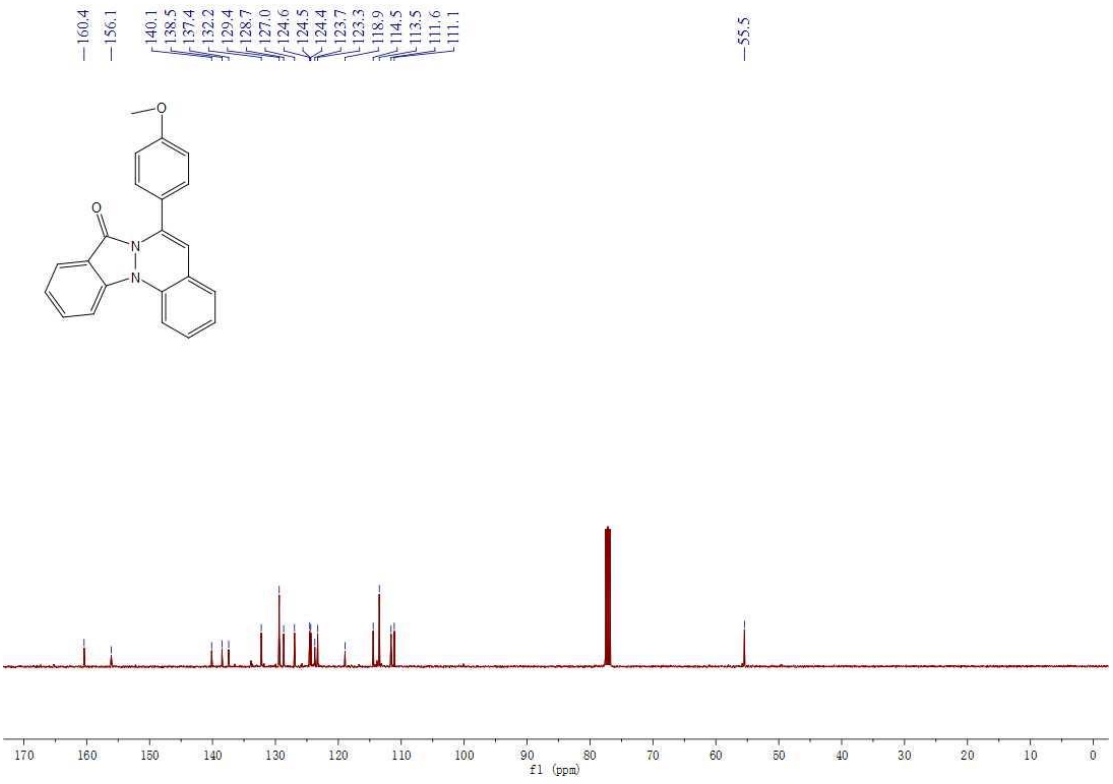


3c

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

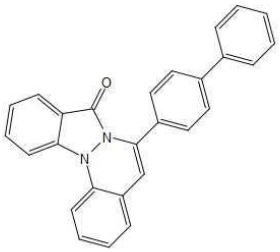


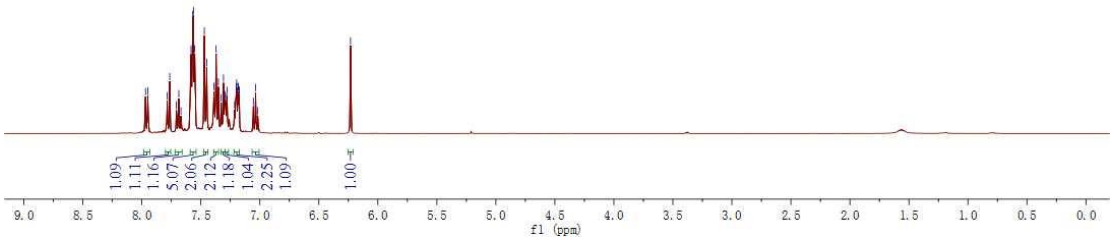
^{13}C NMR (101 MHz, $CDCl_3$)



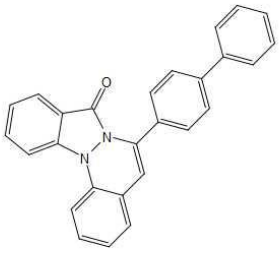
3d

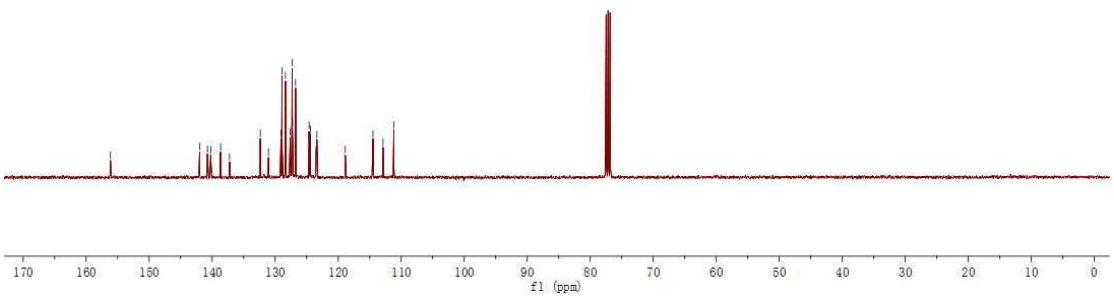
^{1}H NMR (400 MHz, $CDCl_3$)





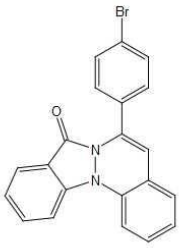
^{13}C NMR (101 MHz, $CDCl_3$)

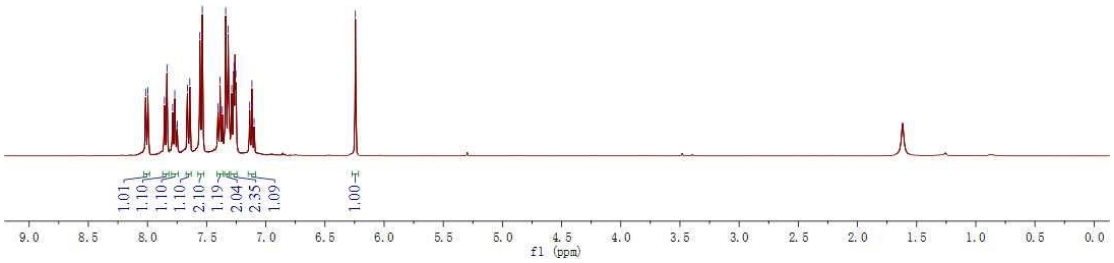




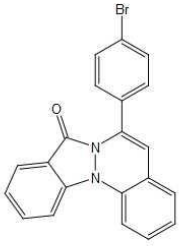
3e

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



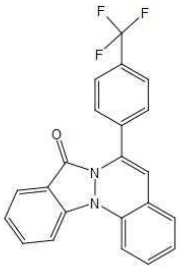


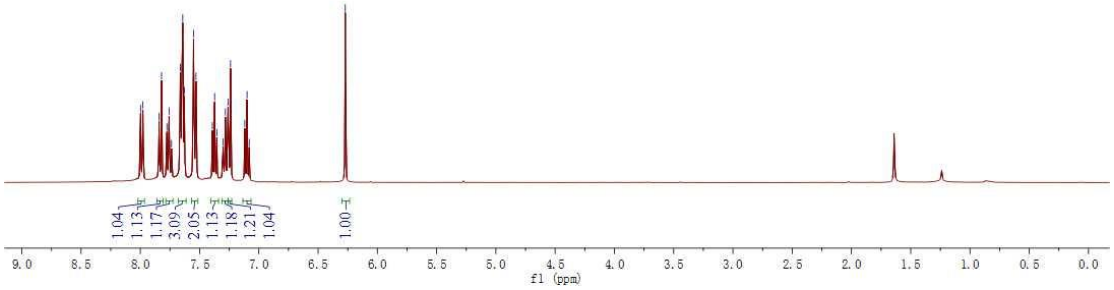
^{13}C NMR (101 MHz, $CDCl_3$)



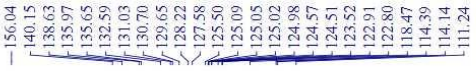
3f

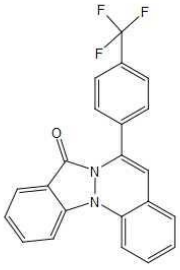
^{1}H NMR (400 MHz, $CDCl_3$)

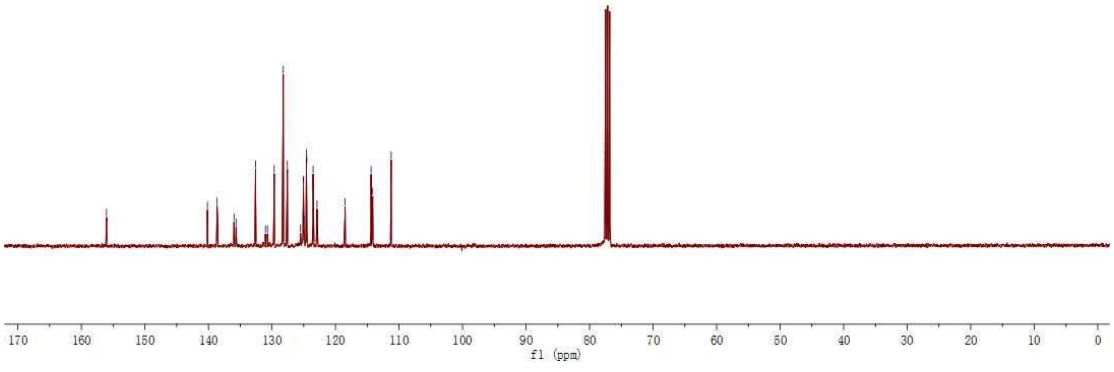




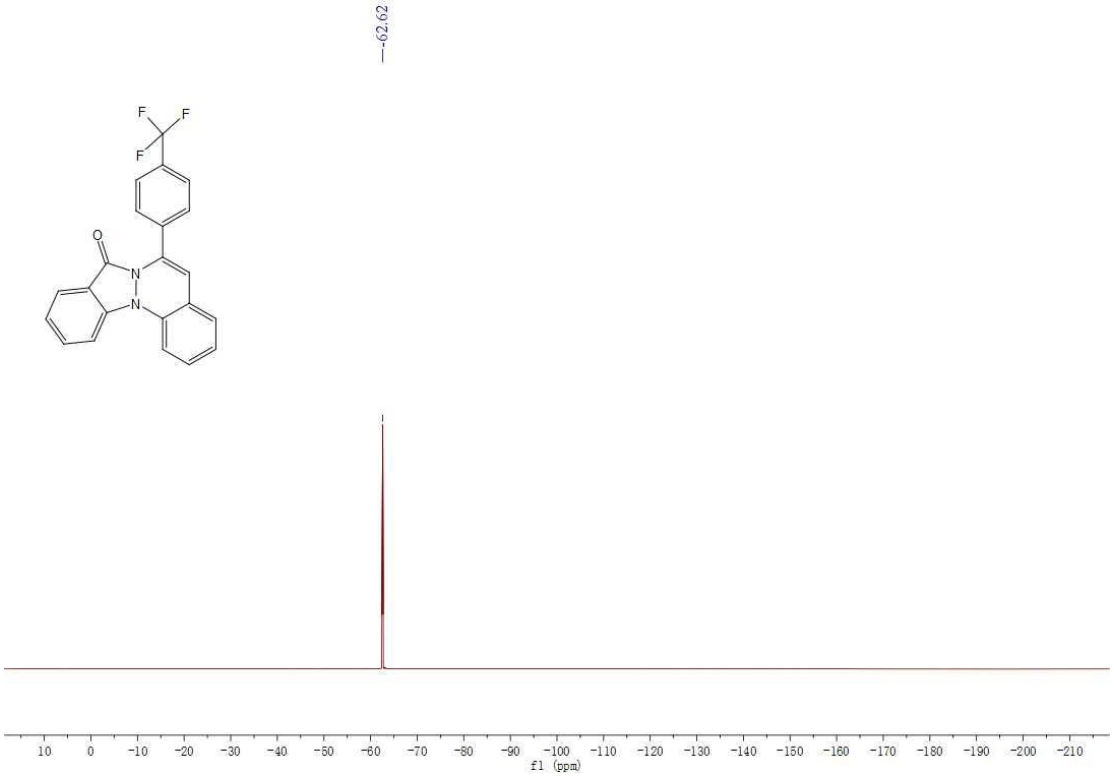
^{13}C NMR (101 MHz, $CDCl_3$)





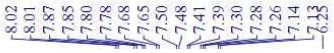


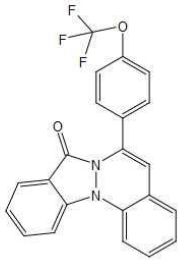
^{19}F NMR (376 MHz, $CDCl_3$)

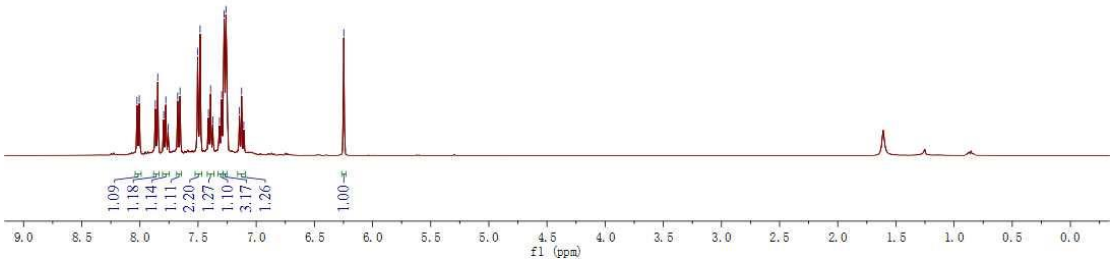


3g

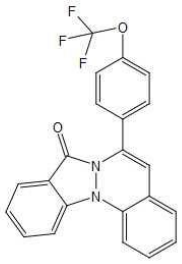
^{1}H NMR (400 MHz, $CDCl_3$)

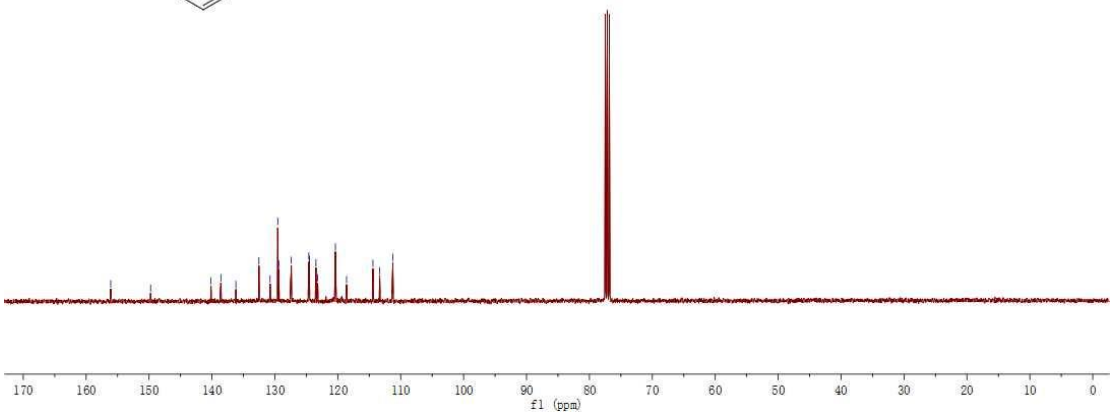




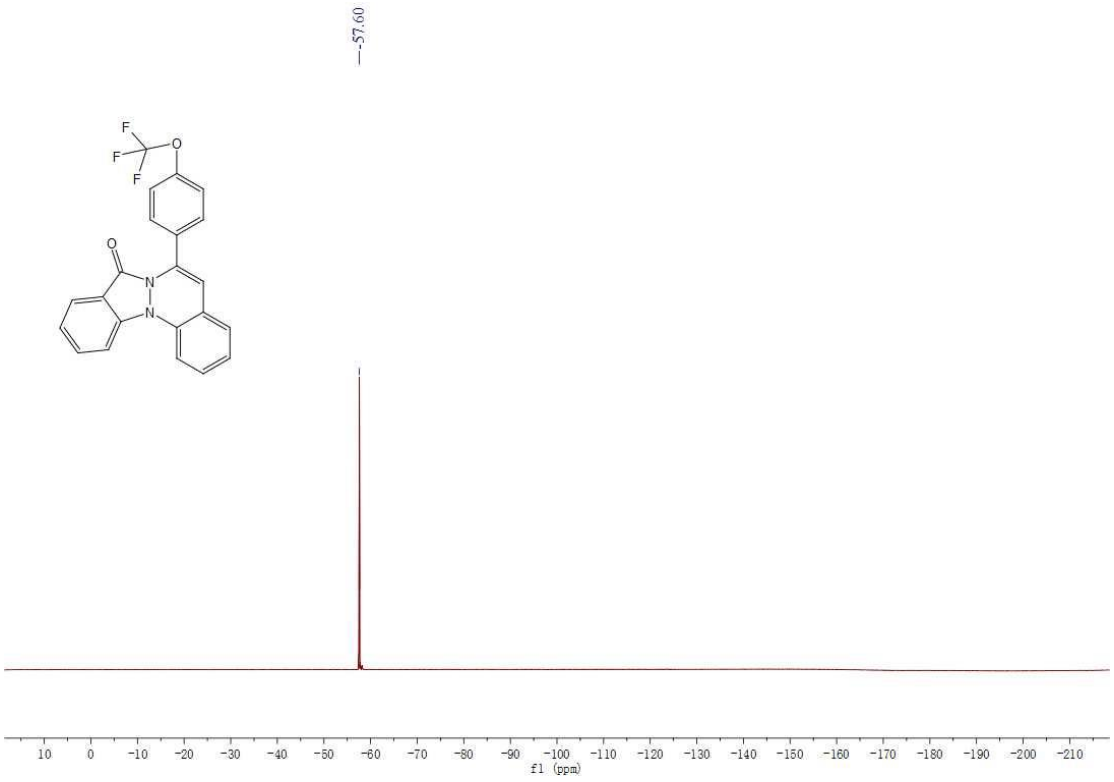


^{13}C NMR (101 MHz, $CDCl_3$)



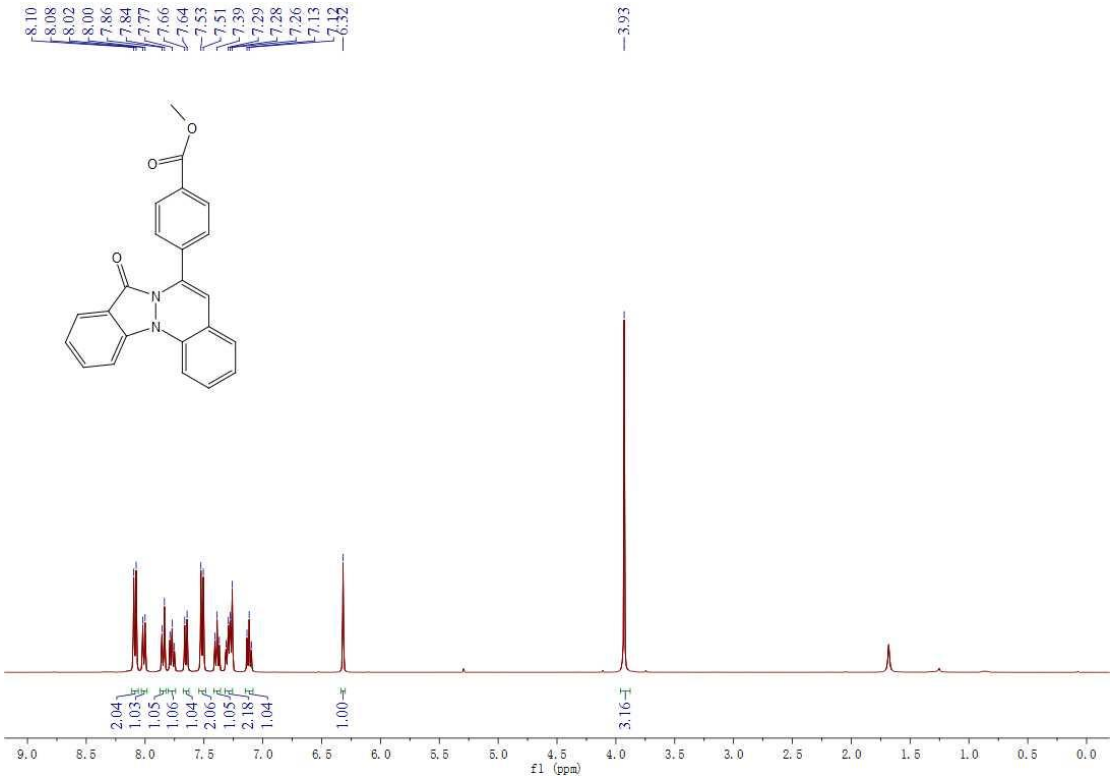


^{19}F NMR (376 MHz, $CDCl_3$)

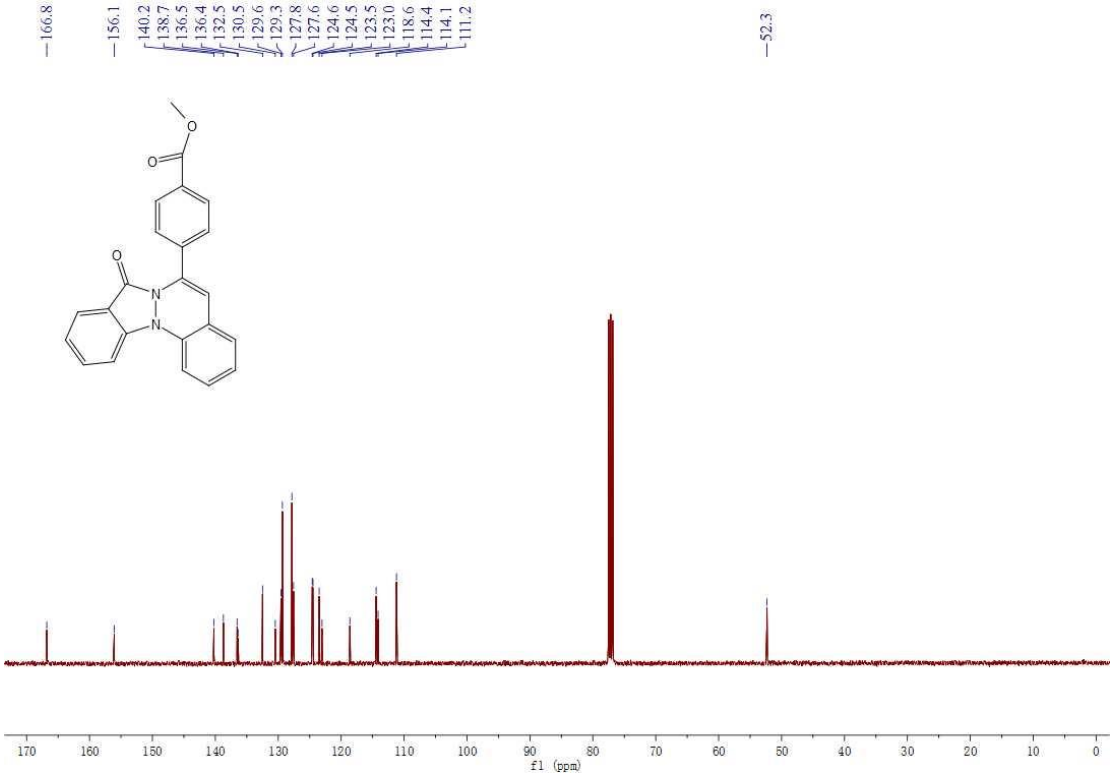


3h

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

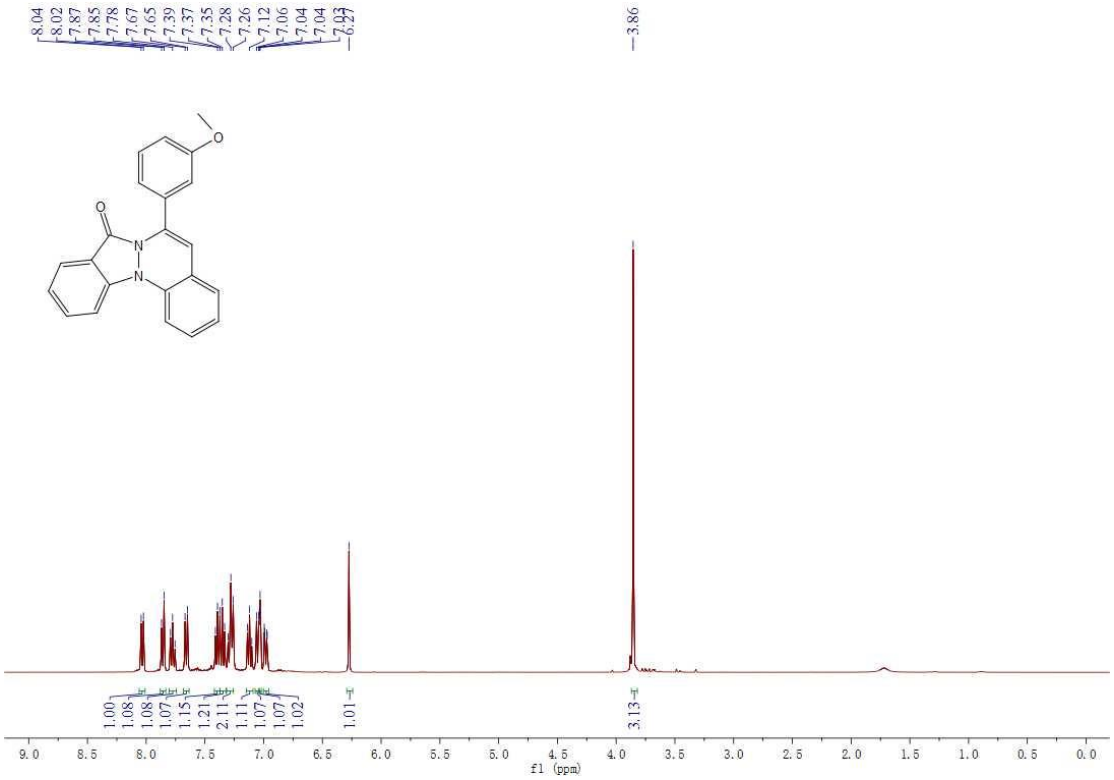


^{13}C NMR (101 MHz, $CDCl_3$)

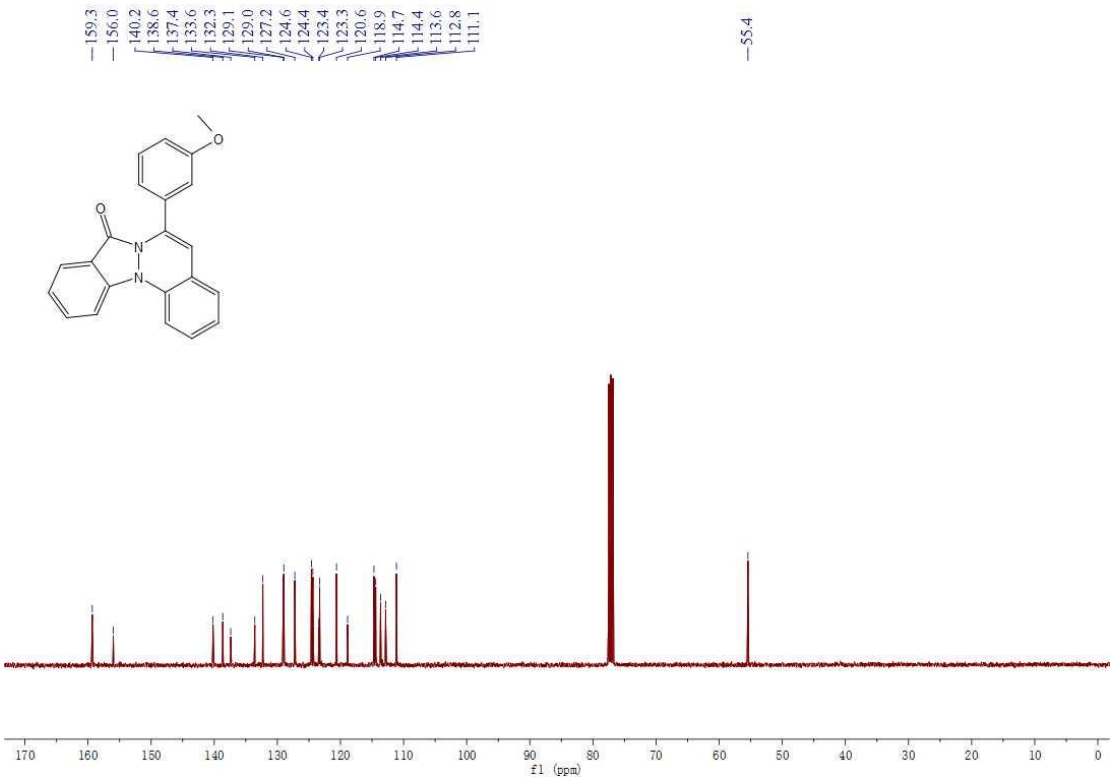


3i

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

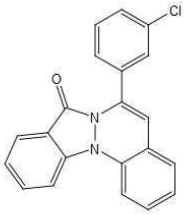


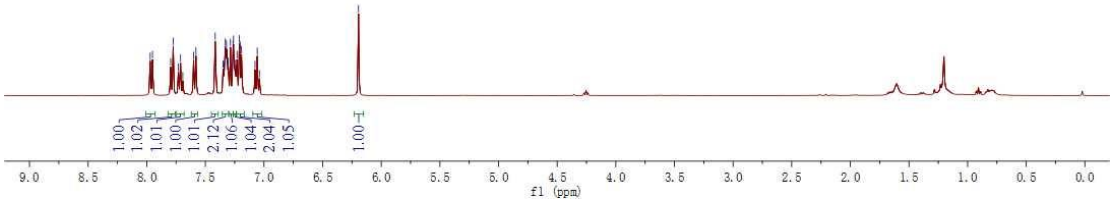
^{13}C NMR (101 MHz, $CDCl_3$)



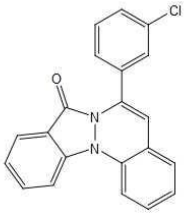
3j

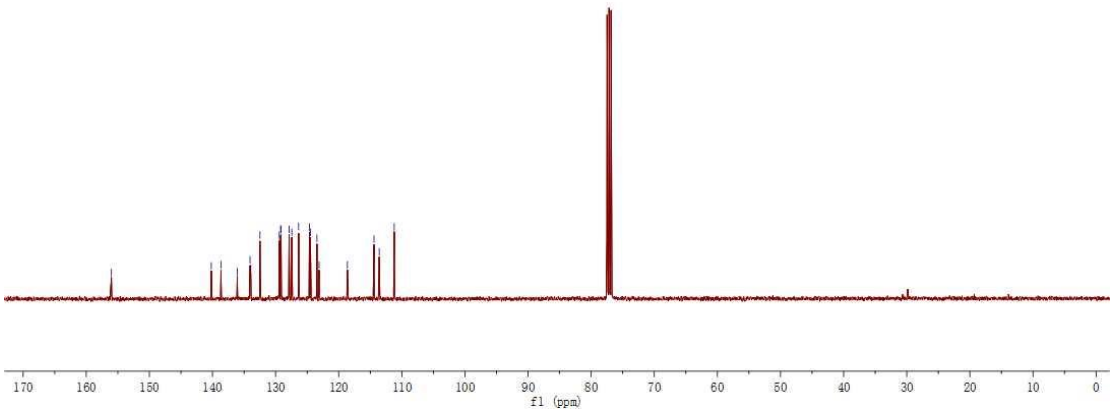
^{1}H NMR (400 MHz, $CDCl_3$)





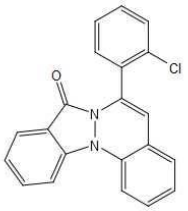
^{13}C NMR (101 MHz, $CDCl_3$)

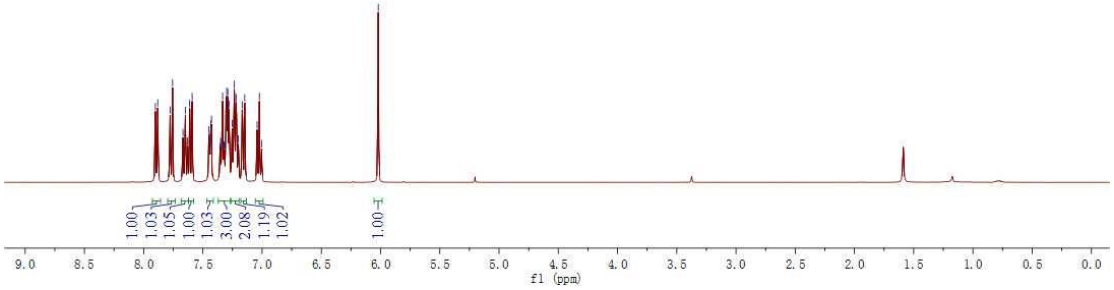




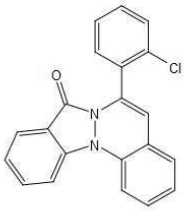
3k

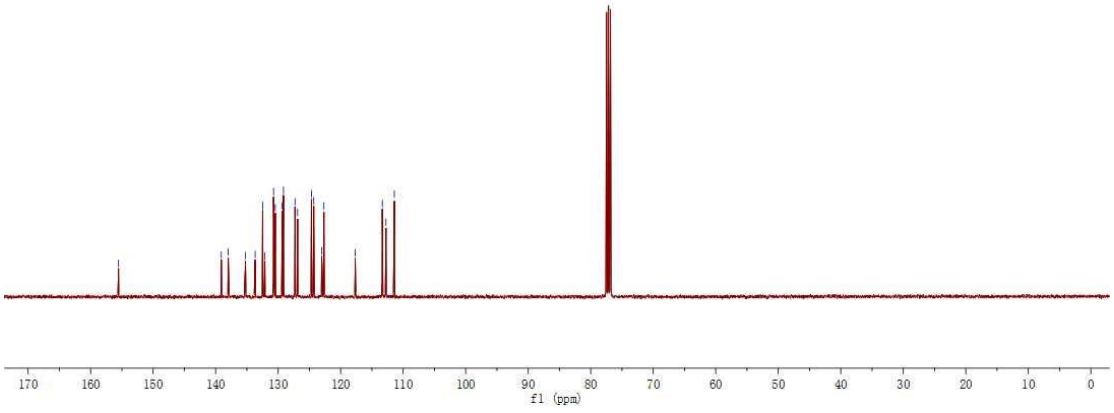
^{1}H NMR (400 MHz, $CDCl_3$)





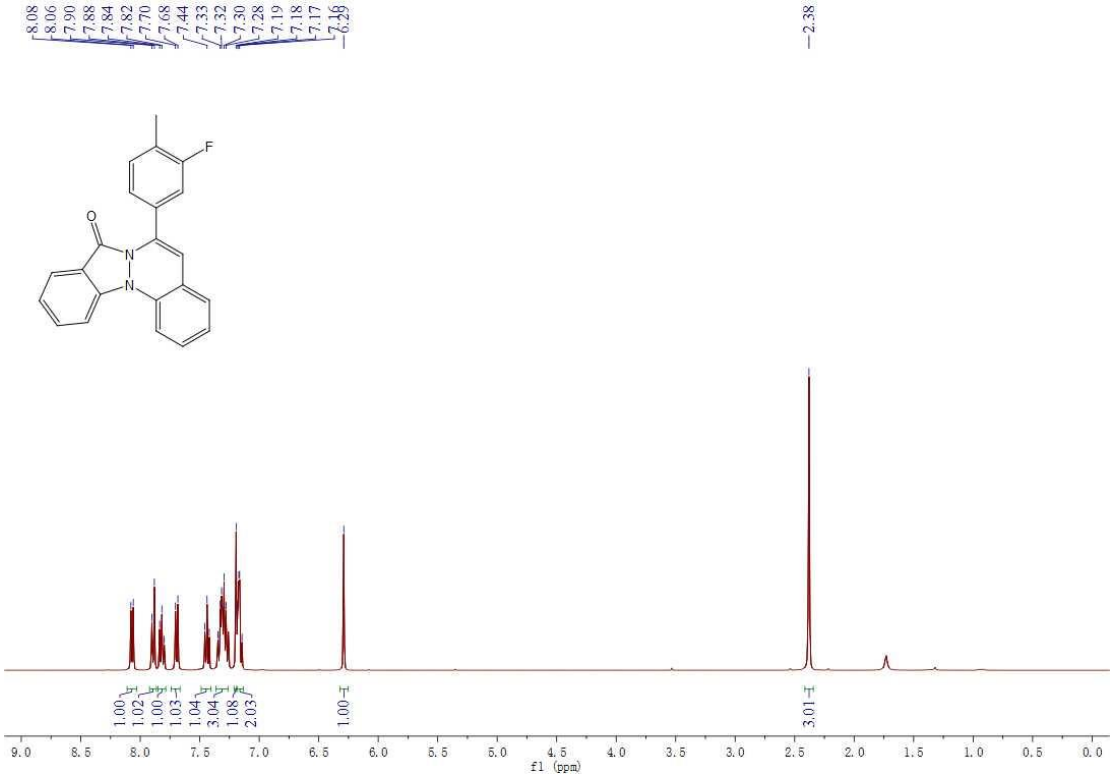
^{13}C NMR (101 MHz, $CDCl_3$)



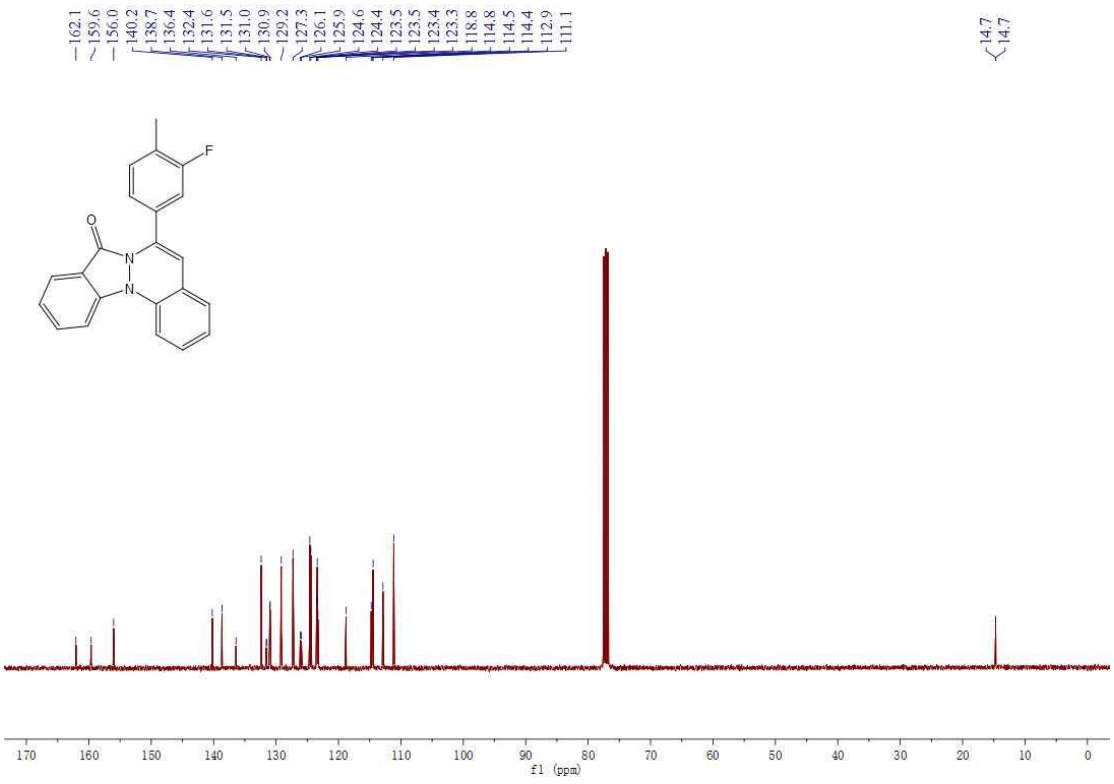


3l

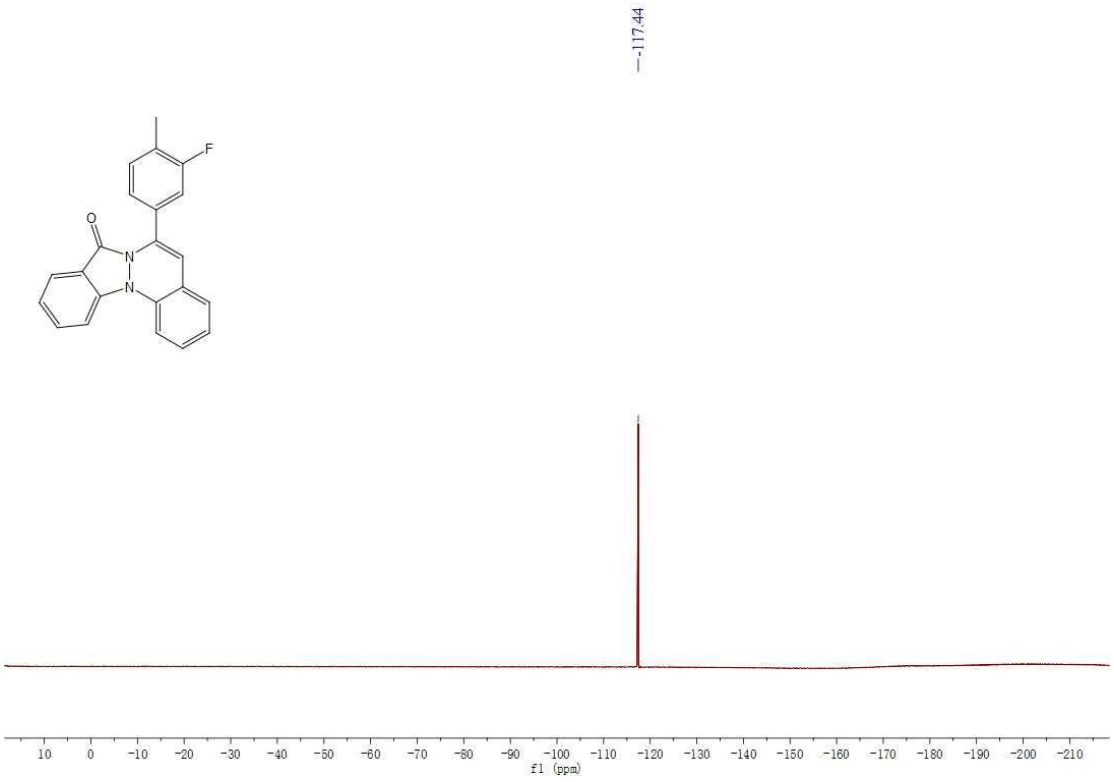
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

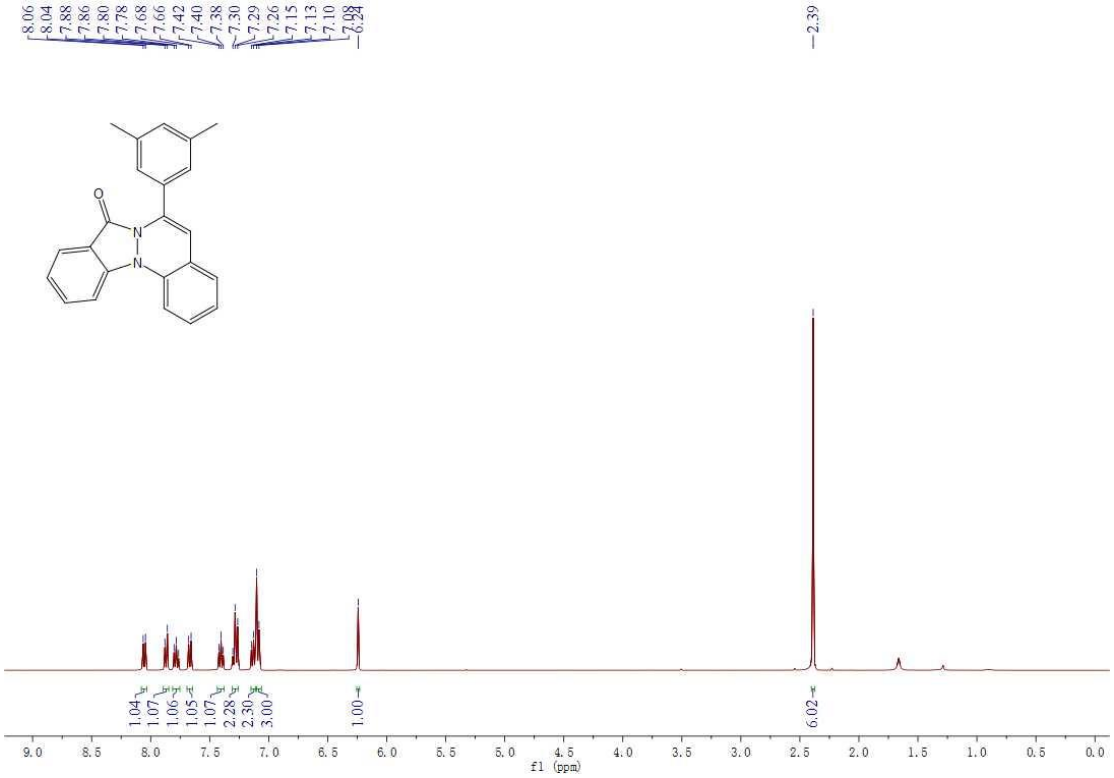


^{19}F NMR (376 MHz, $CDCl_3$)

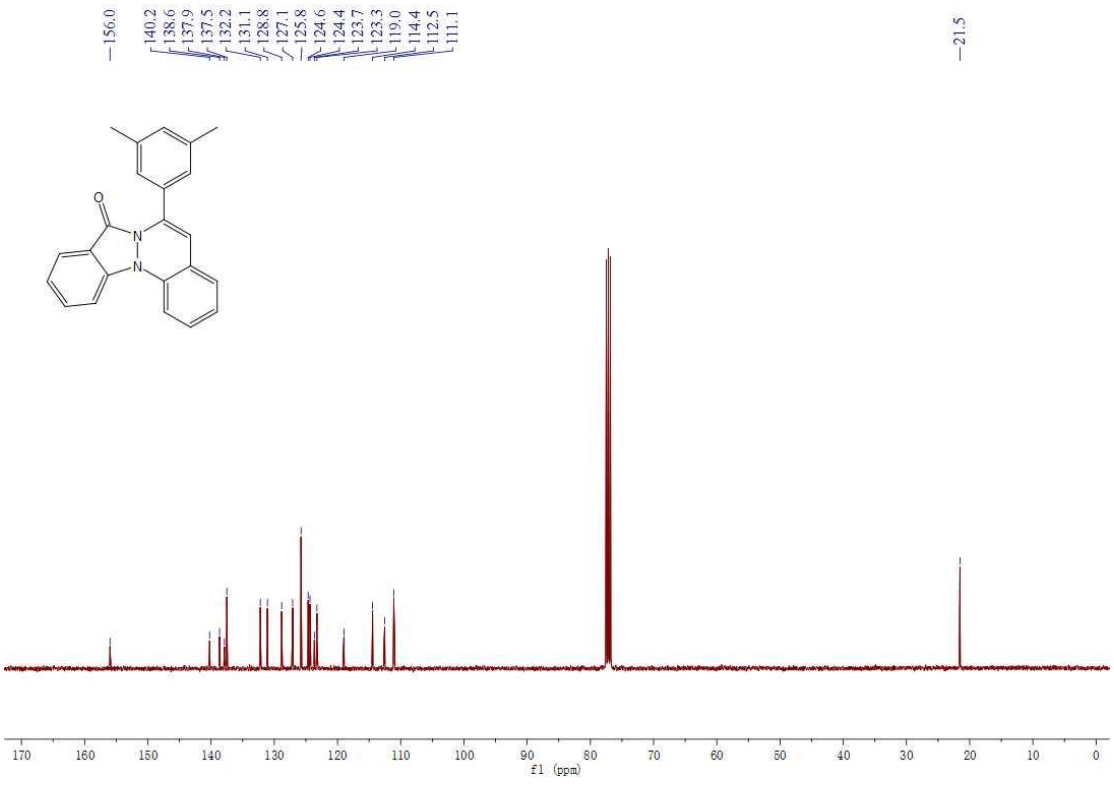


3m

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

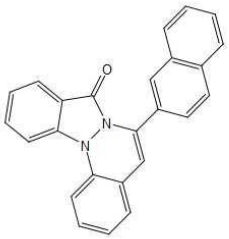


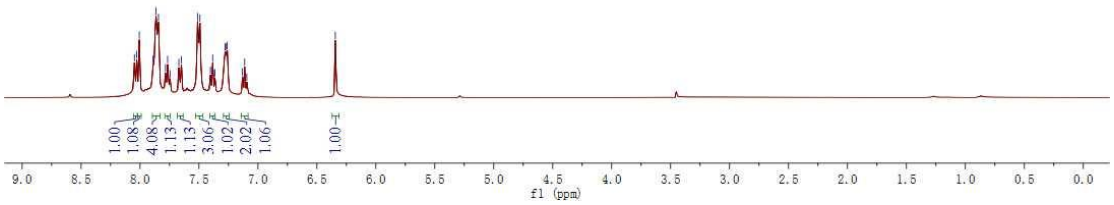
^{13}C NMR (101 MHz, $CDCl_3$)



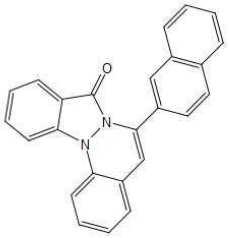
3n

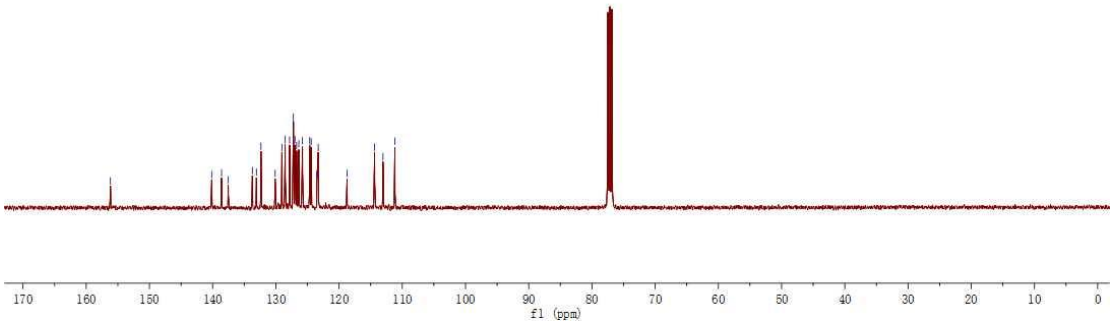
^{1}H NMR (400 MHz, $CDCl_3$)





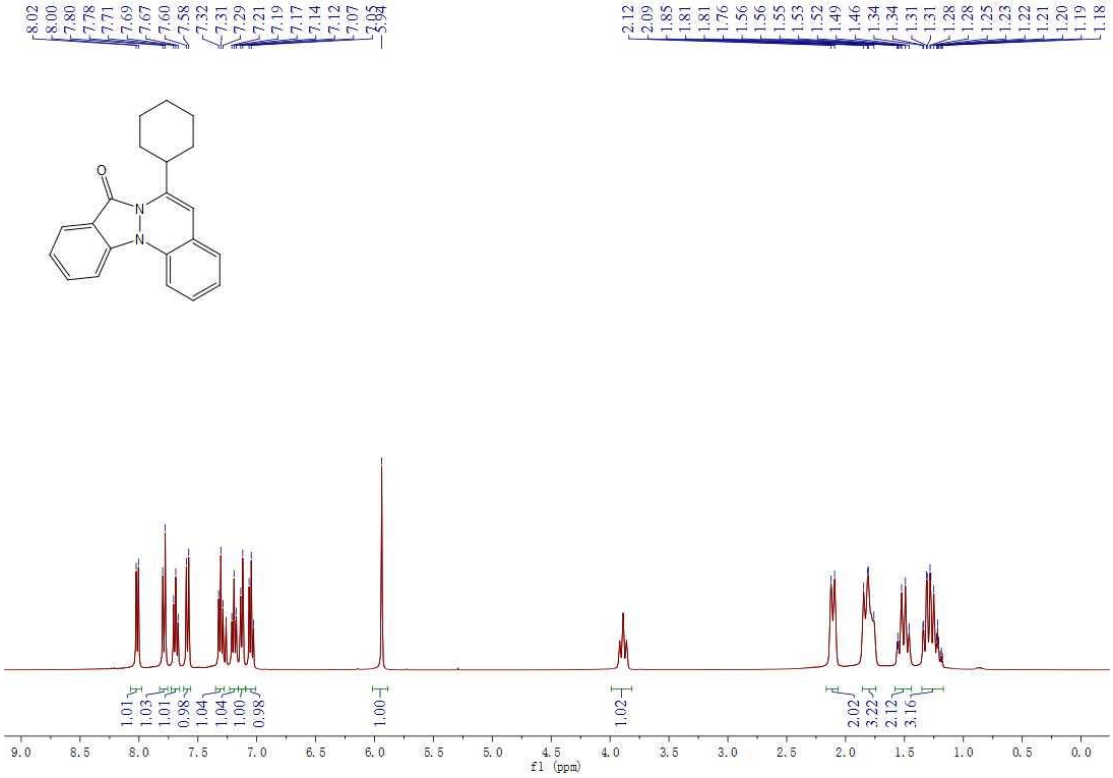
^{13}C NMR (101 MHz, $CDCl_3$)



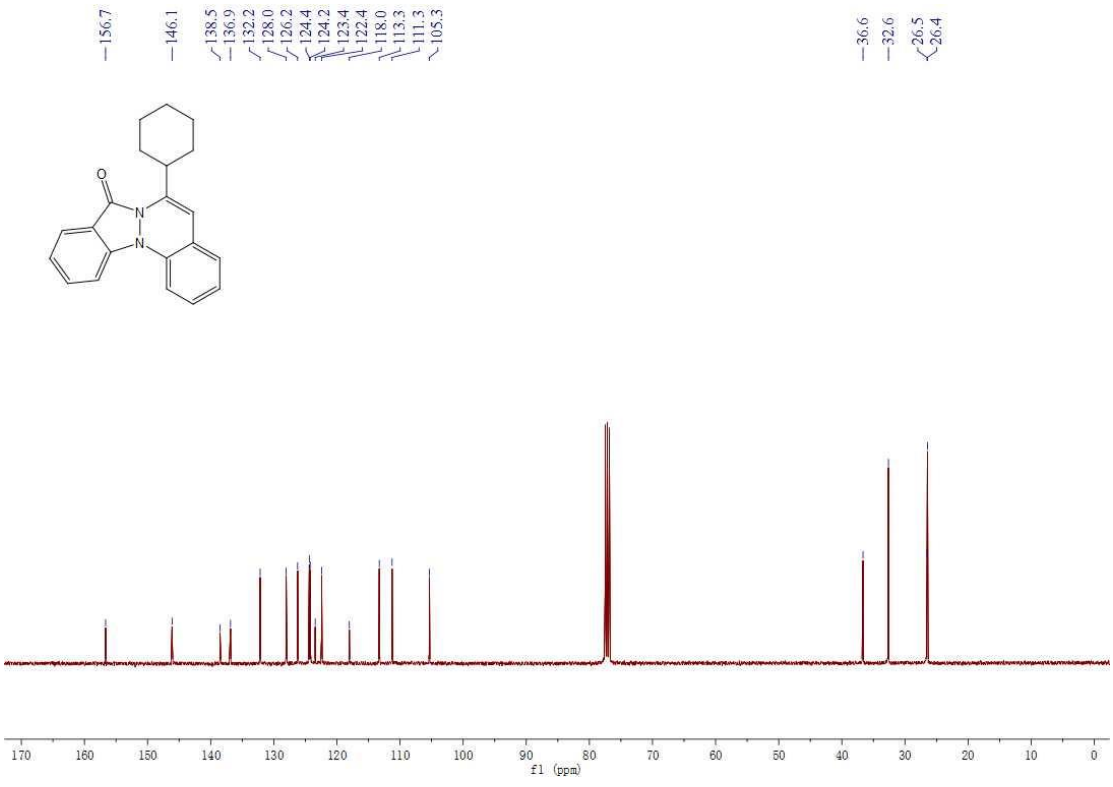


3o

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

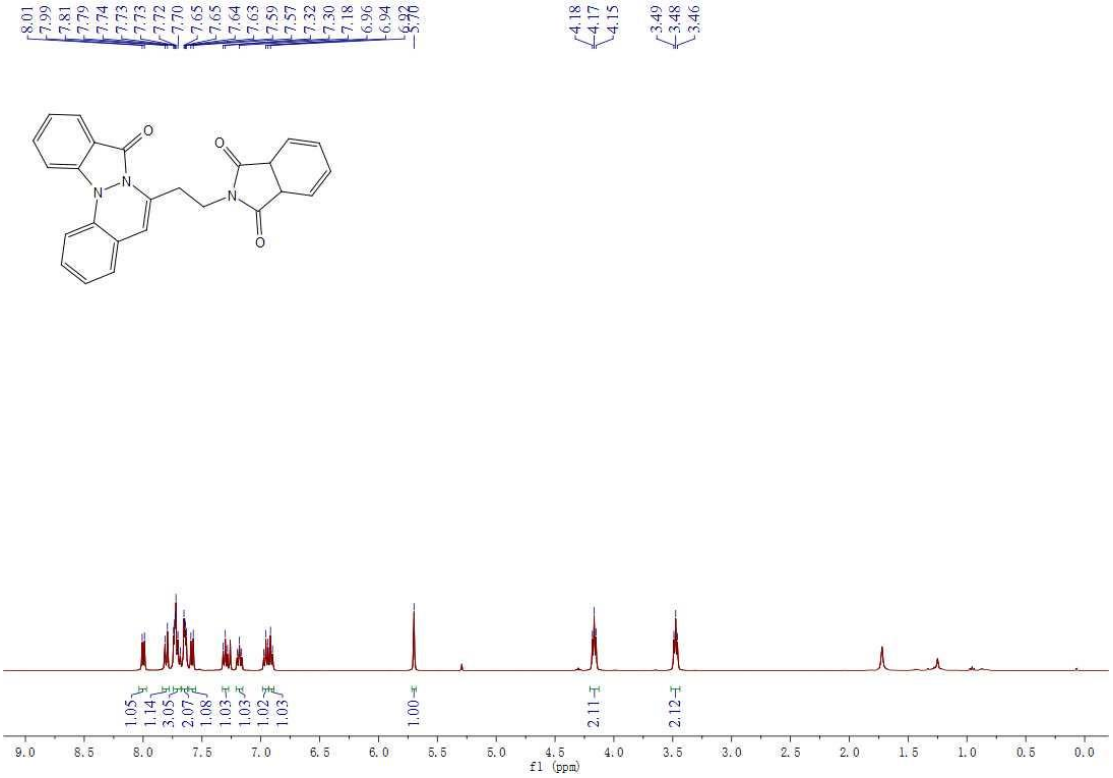


^{13}C NMR (101 MHz, $CDCl_3$)

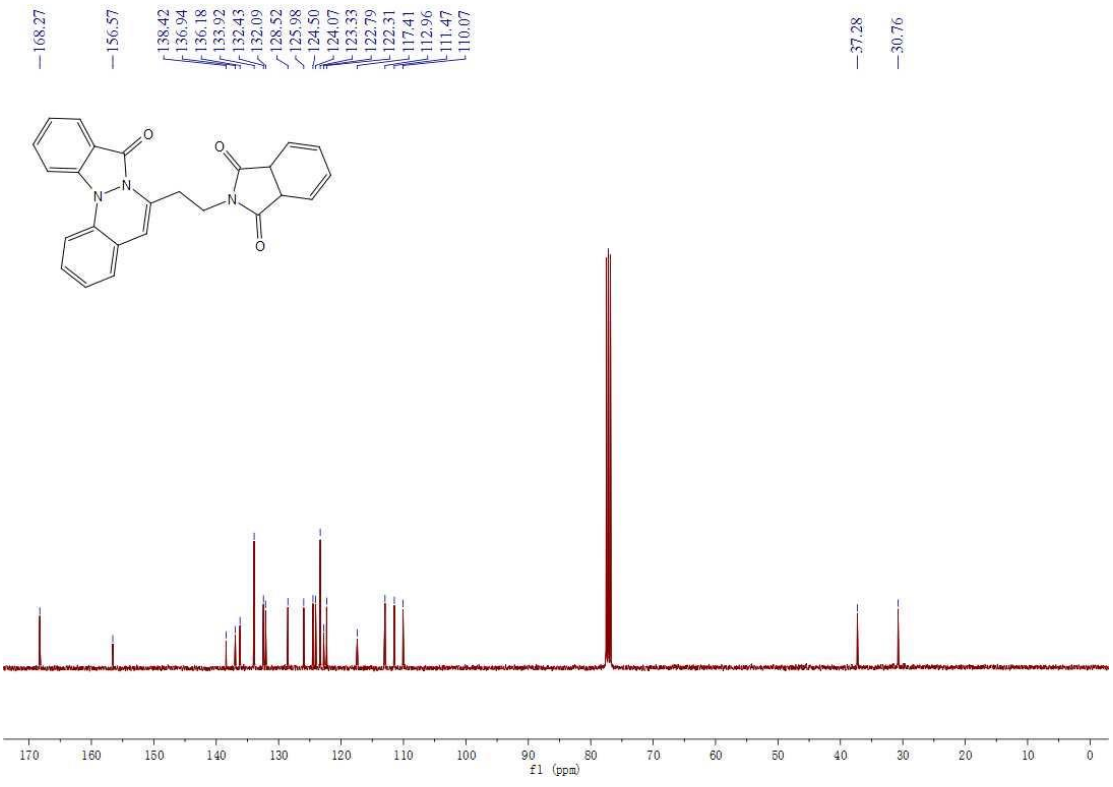


3p

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

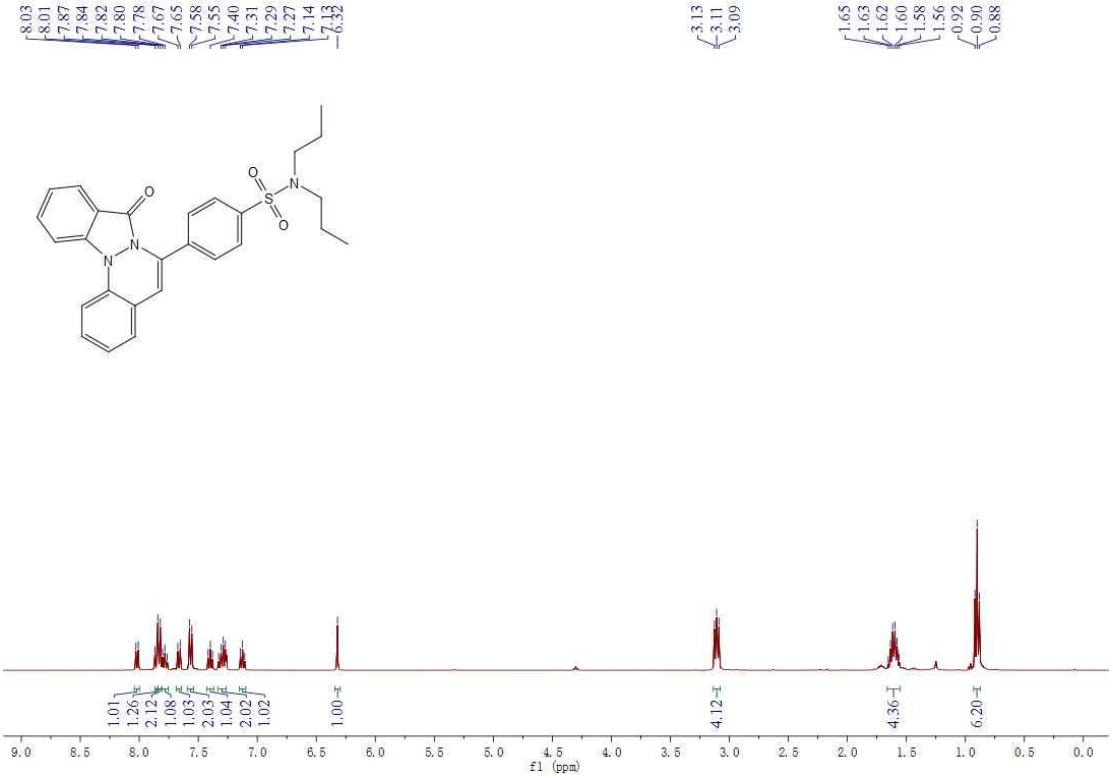


^{13}C NMR (101 MHz, $CDCl_3$)

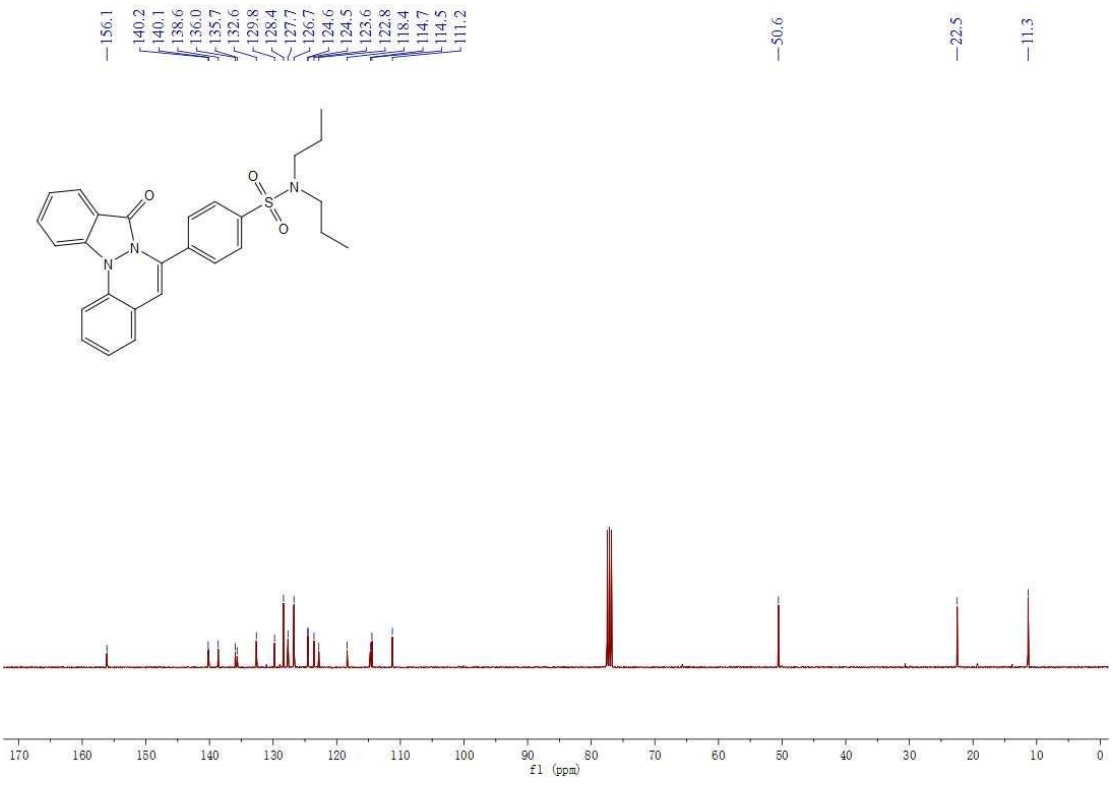


3q

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

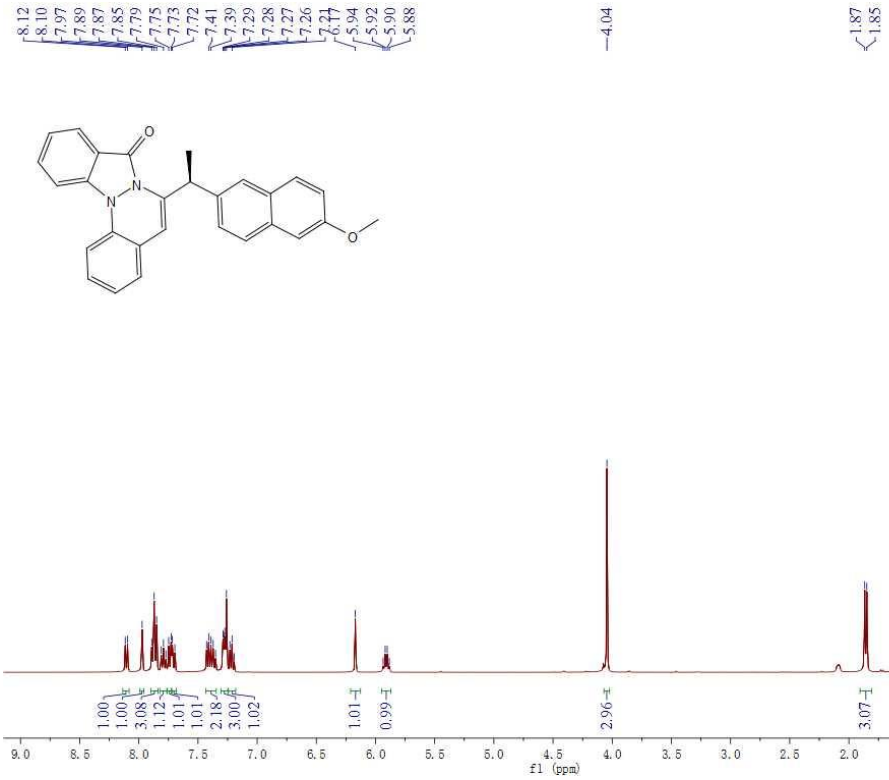


^{13}C NMR (101 MHz, $CDCl_3$)

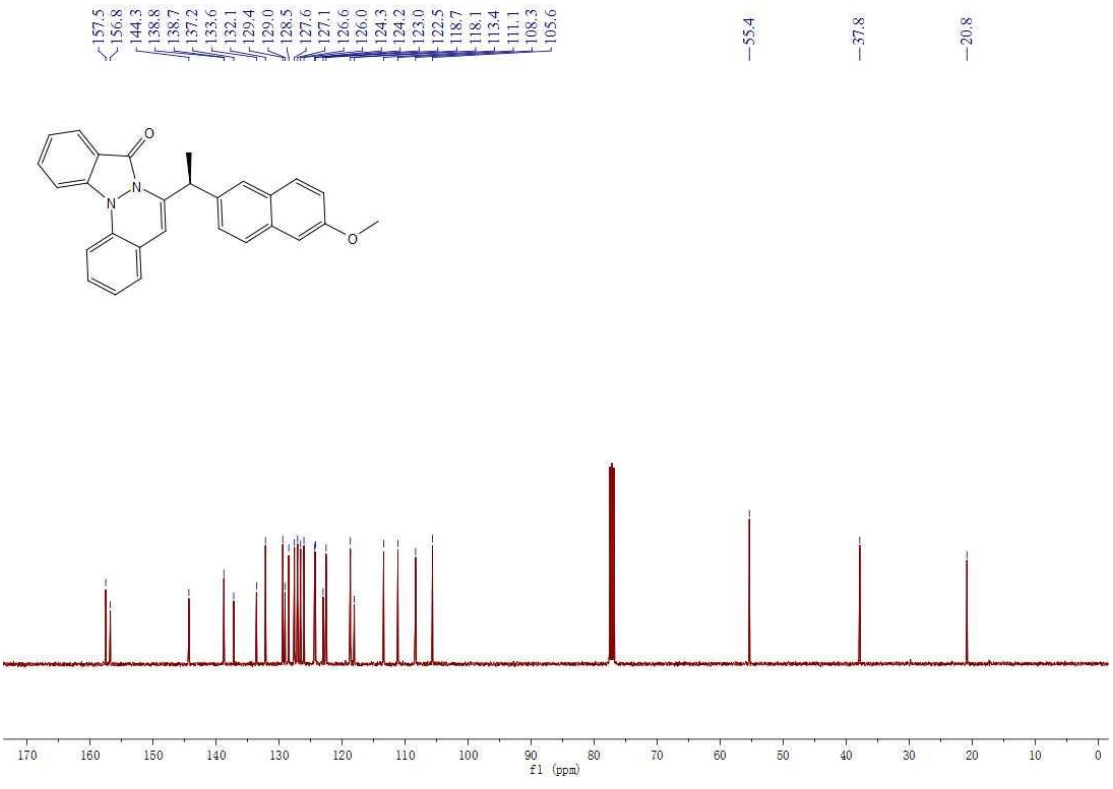


3r

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

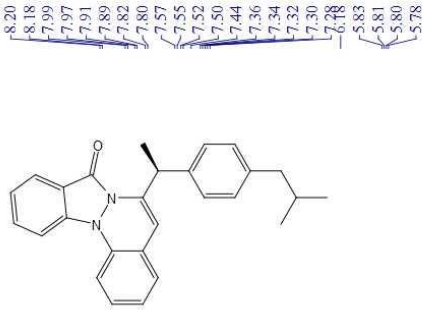


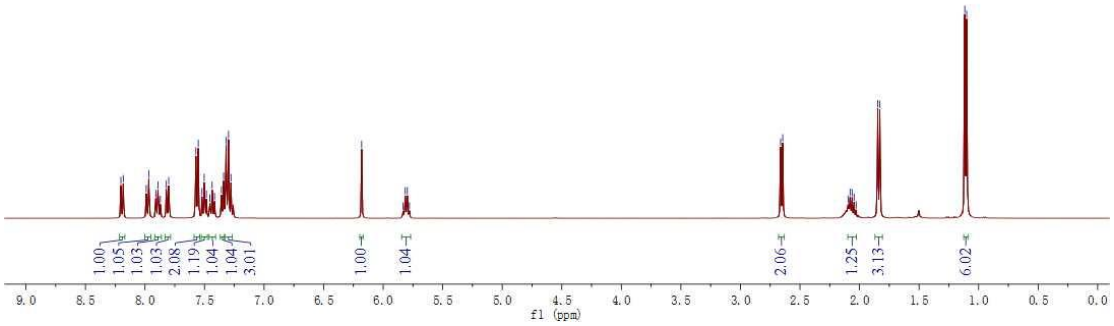
^{13}C NMR (101 MHz, $CDCl_3$)



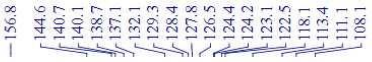
3s

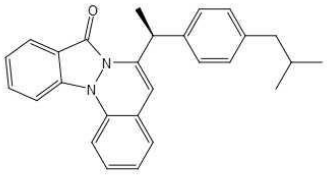
^{1}H NMR (400 MHz, $CDCl_3$)

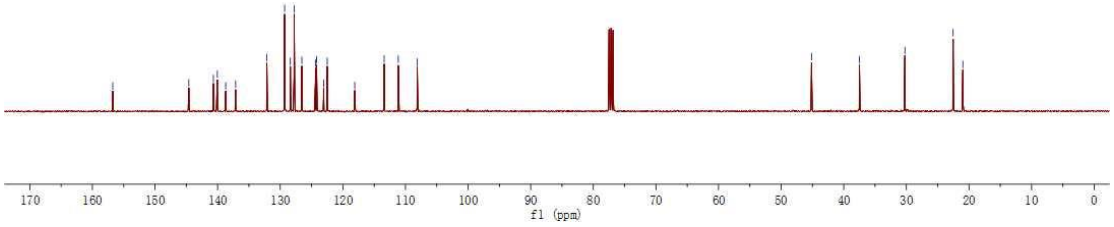




^{13}C NMR (101 MHz, $CDCl_3$)

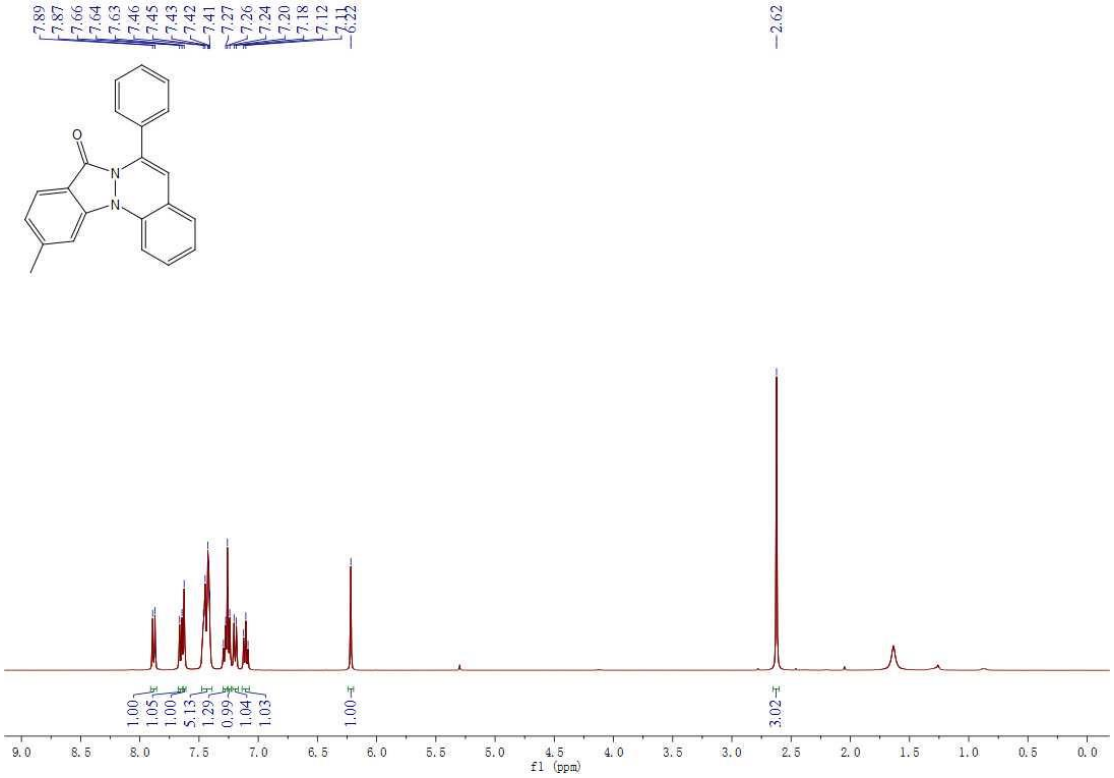




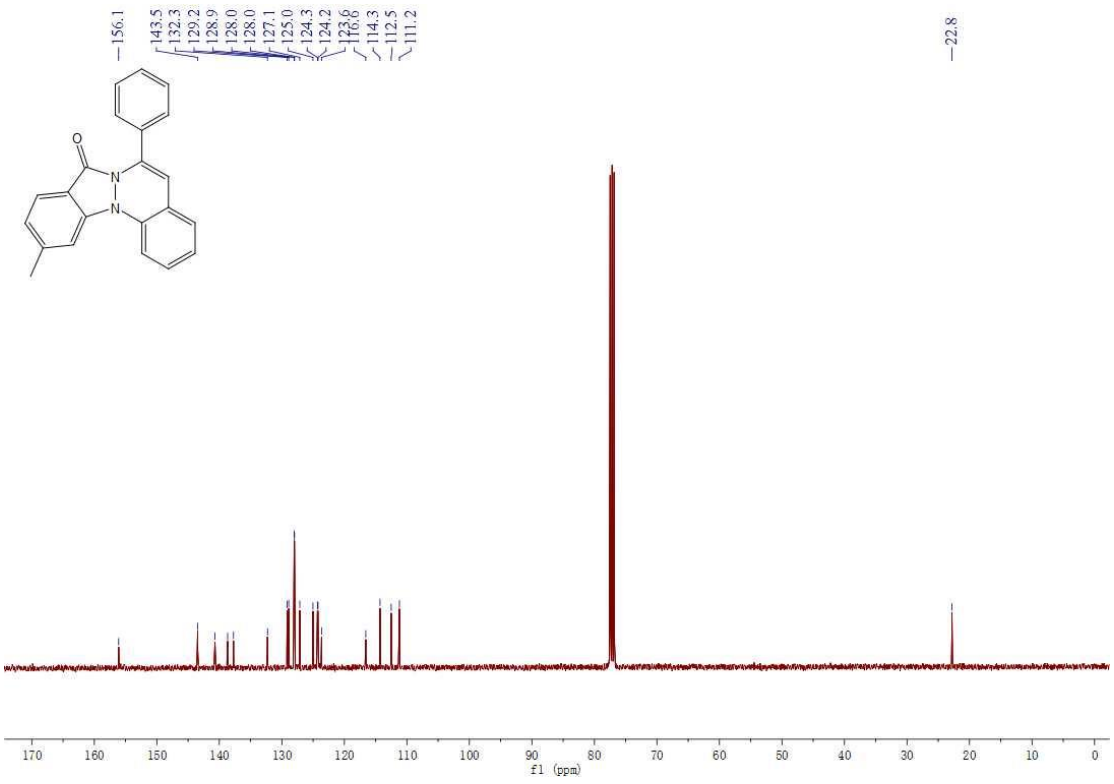


4a

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

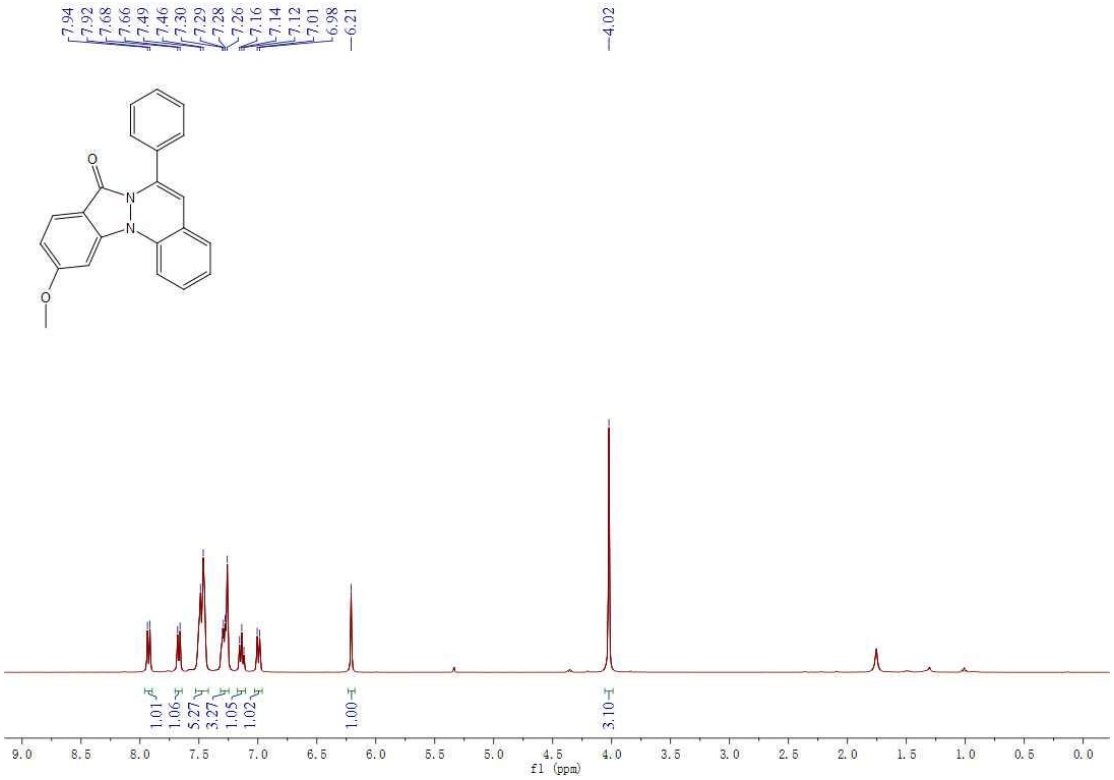


^{13}C NMR (101 MHz, $CDCl_3$)

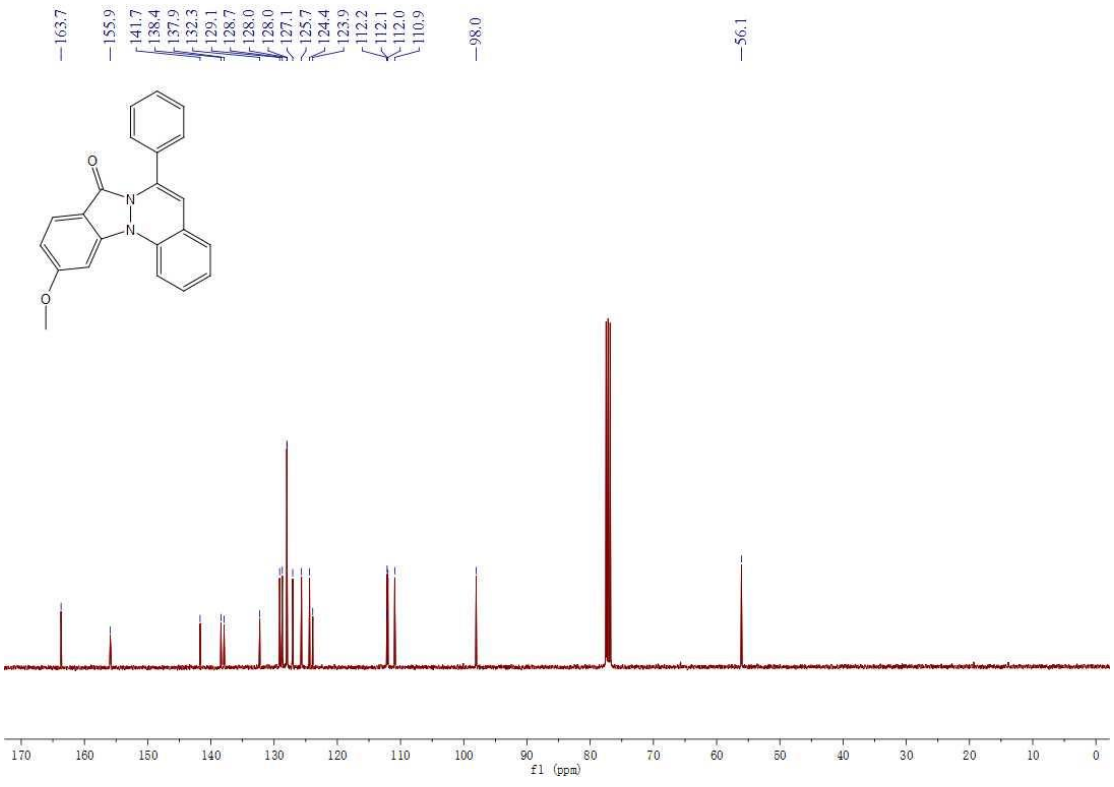


4b

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

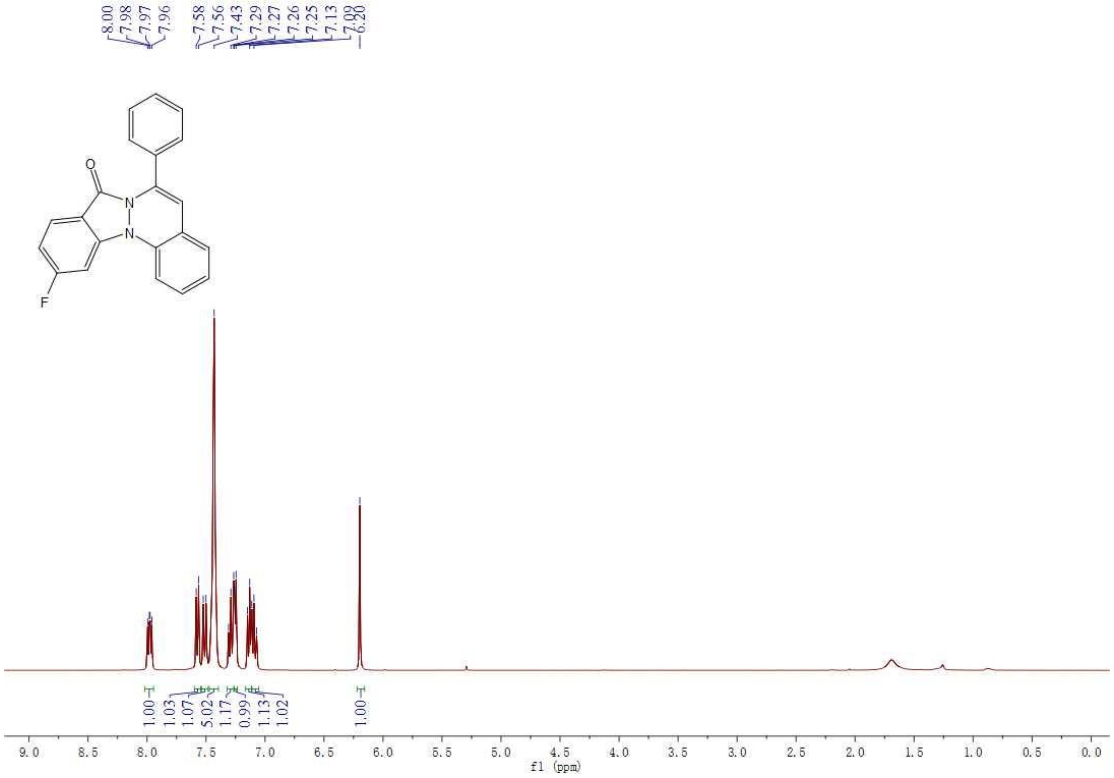


^{13}C NMR (101 MHz, $CDCl_3$)

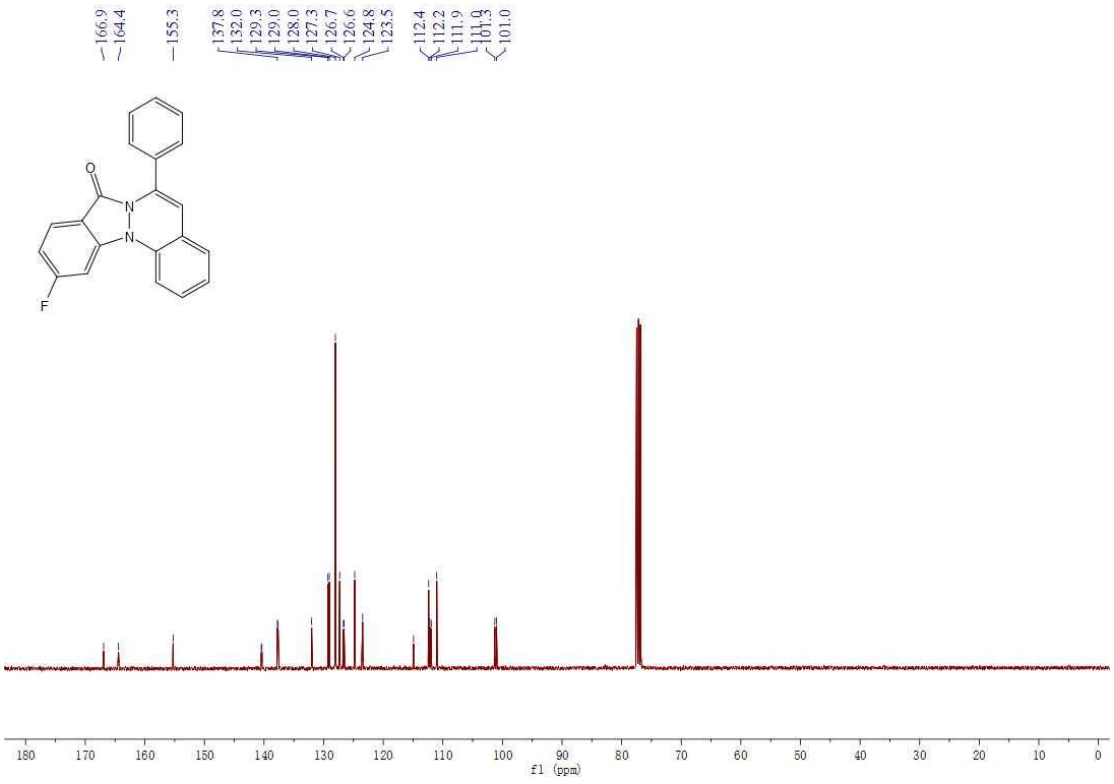


4c

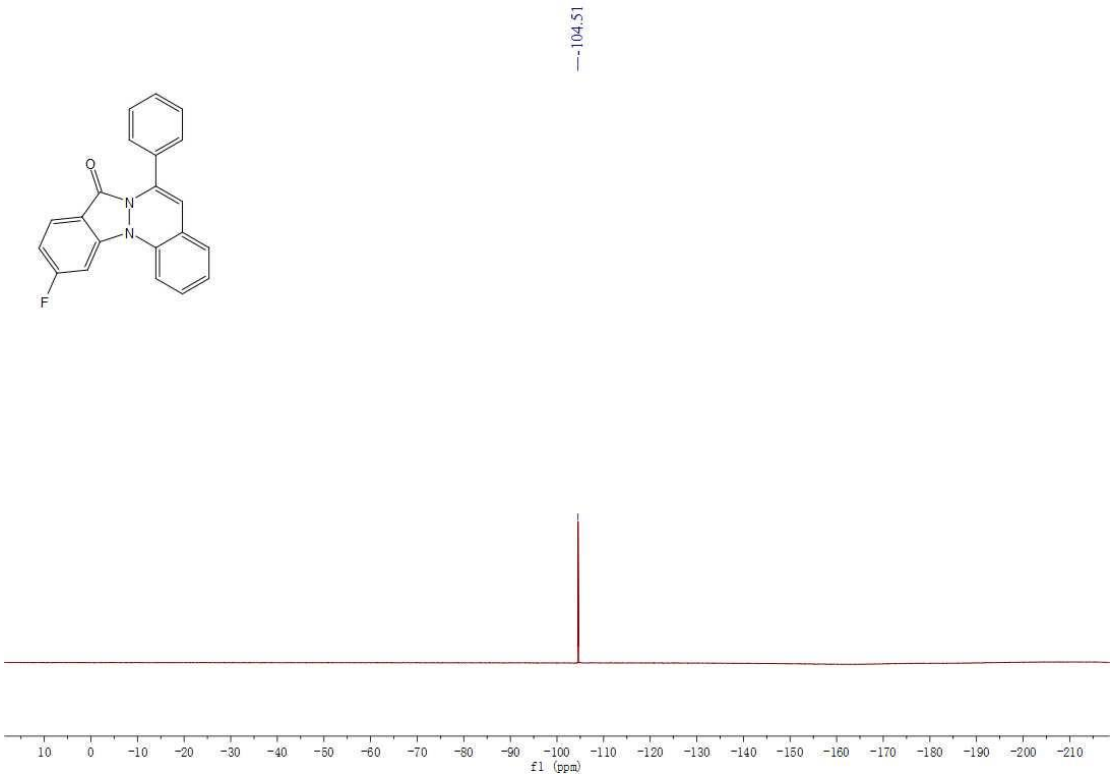
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

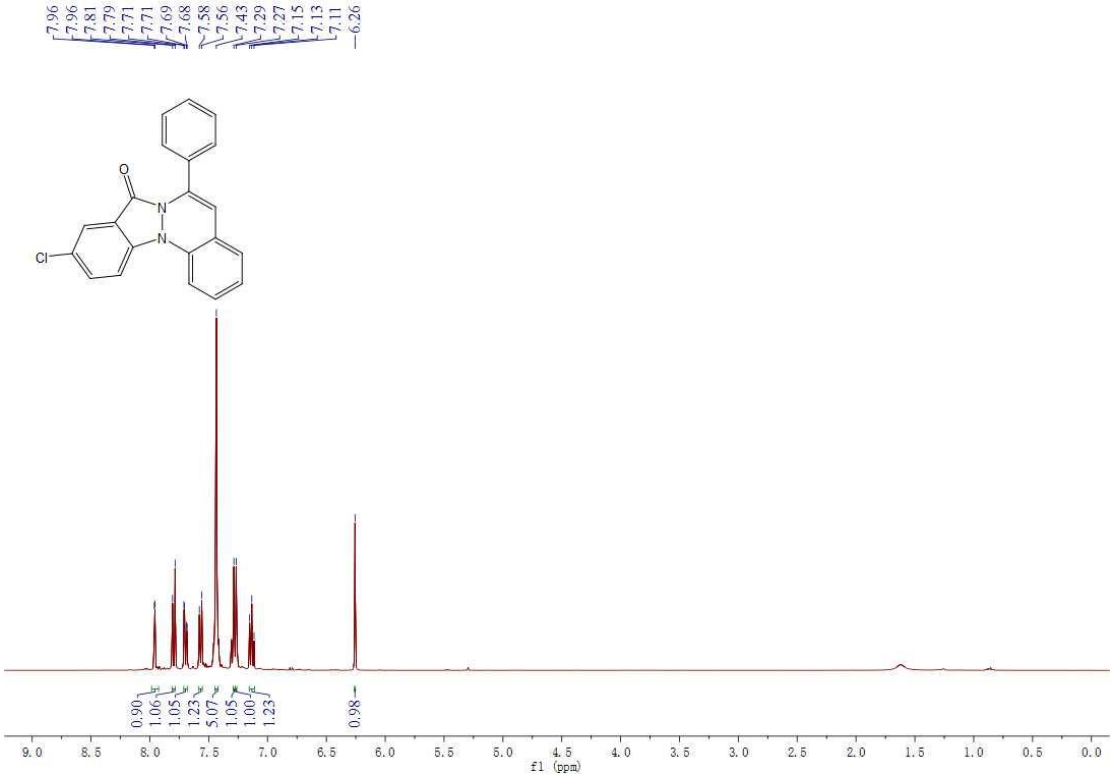


^{19}F NMR (376 MHz, $CDCl_3$)

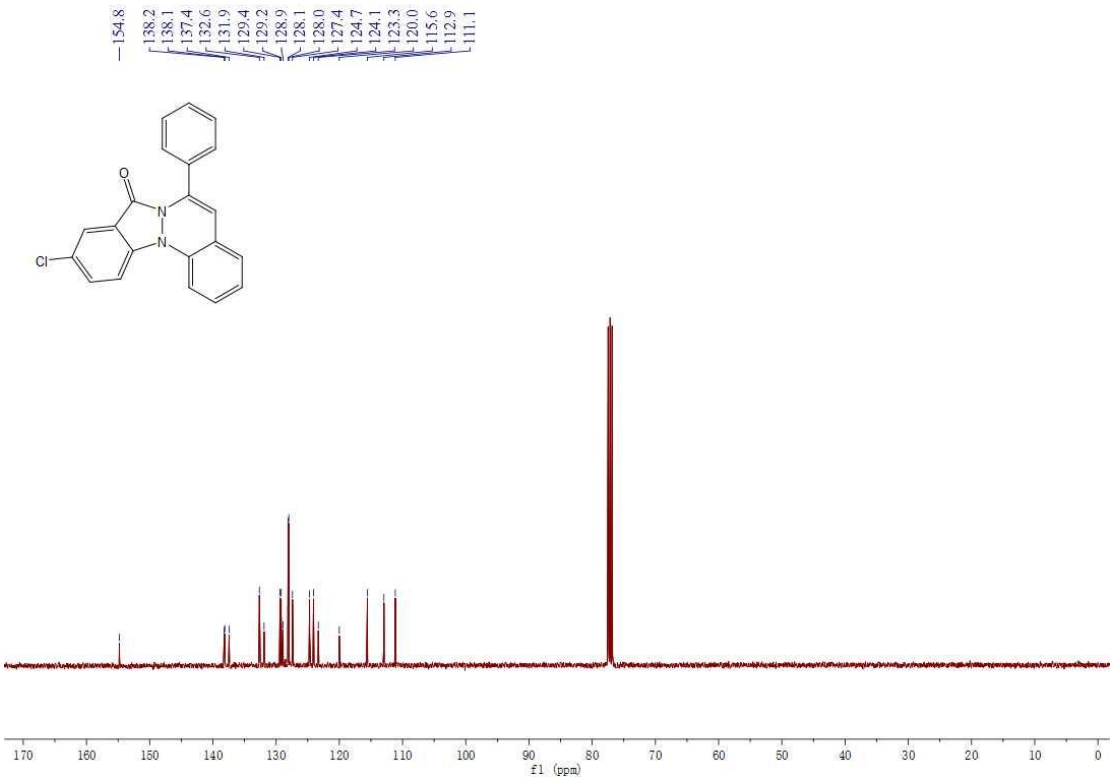


4d

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

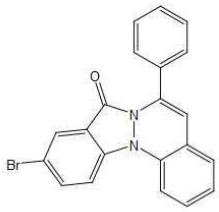


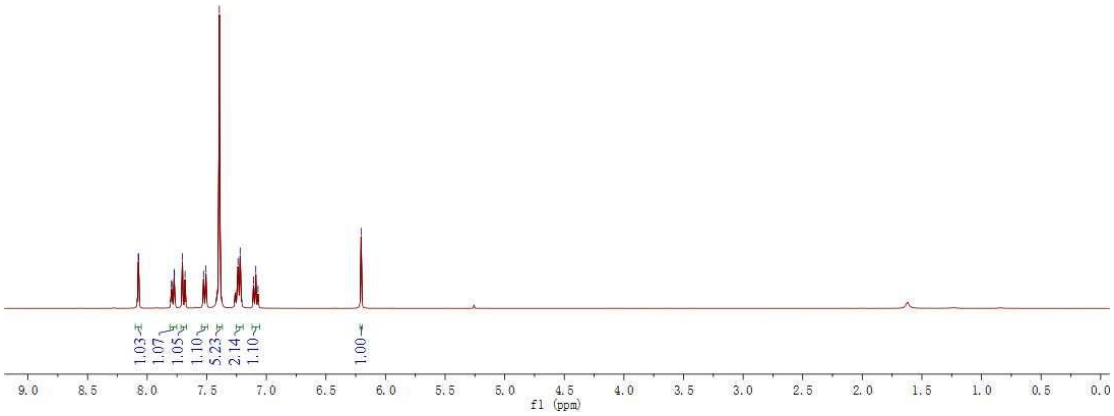
^{13}C NMR (101 MHz, $CDCl_3$)



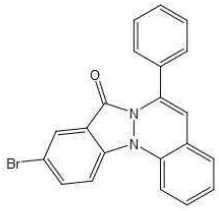
4e

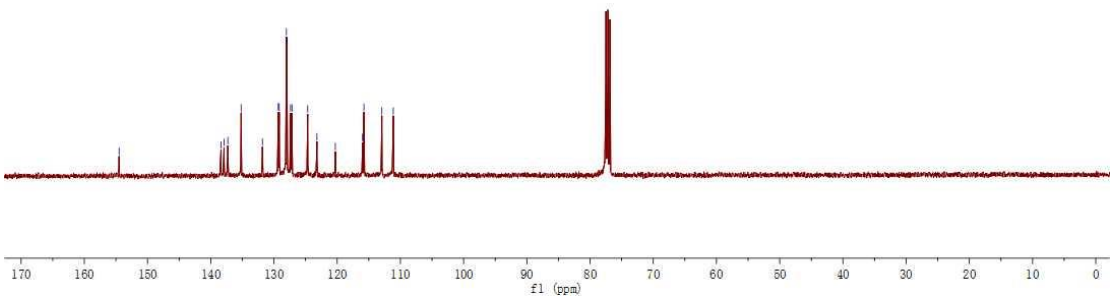
^{1}H NMR (400 MHz, $CDCl_3$)





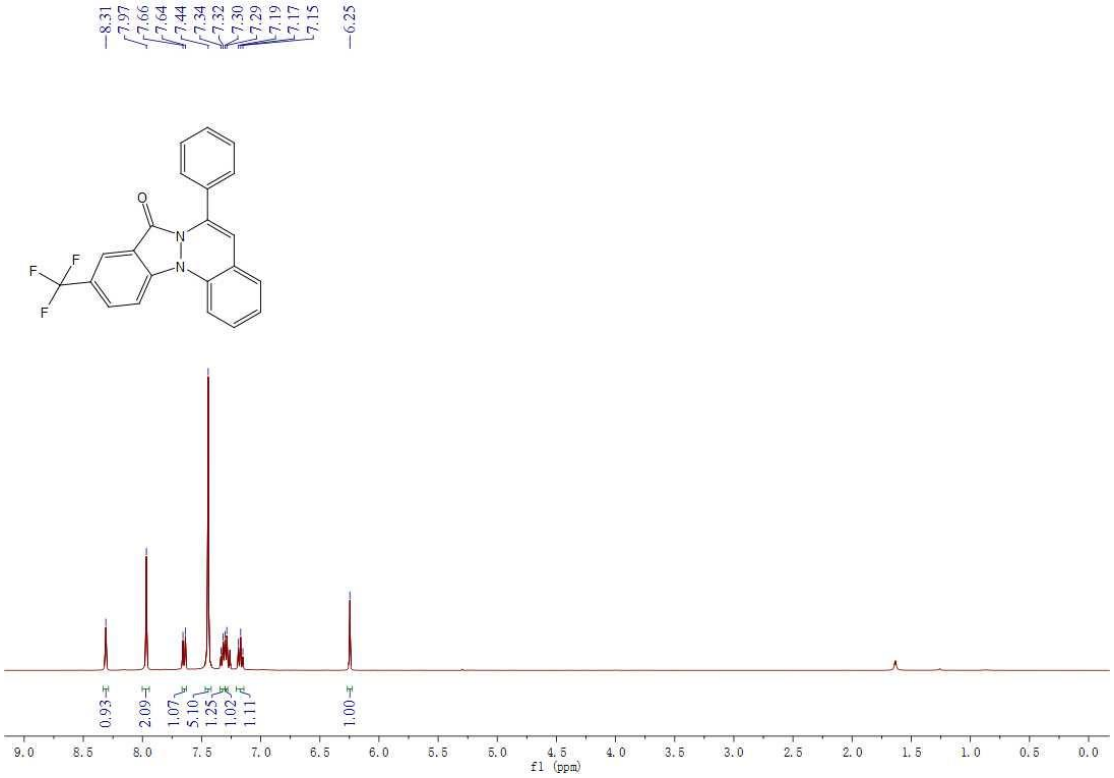
^{13}C NMR (101 MHz, $CDCl_3$)



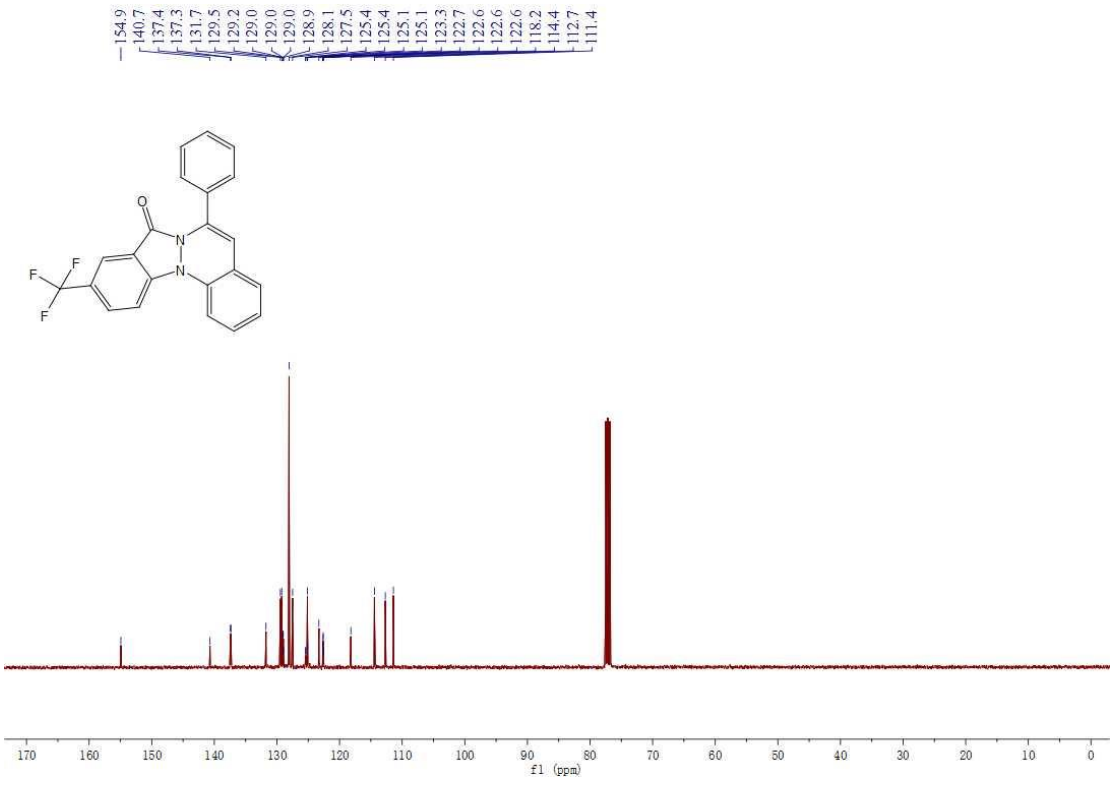


4f

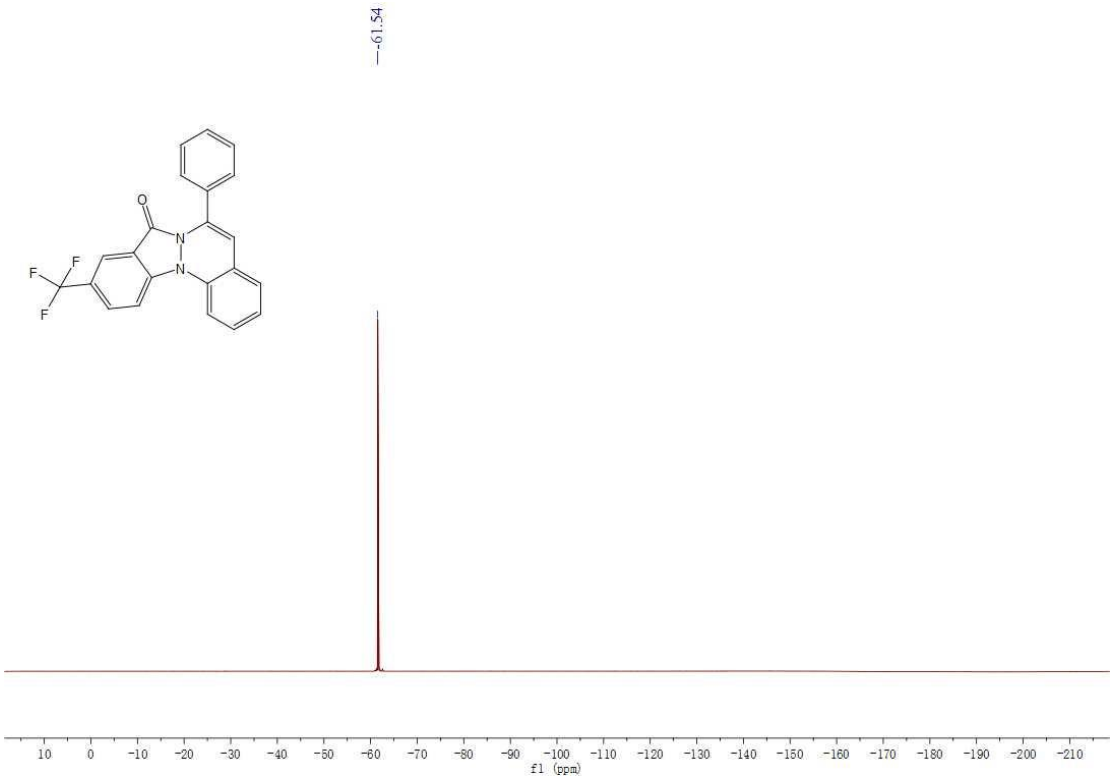
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

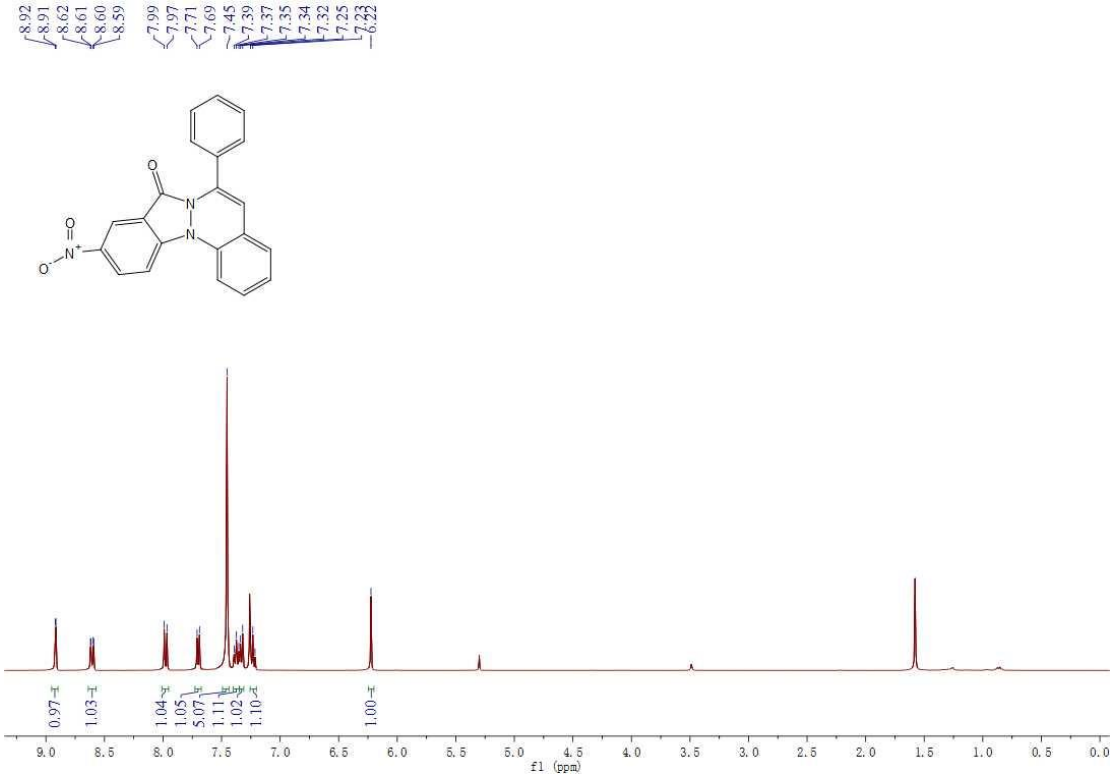


^{19}F NMR (376 MHz, $CDCl_3$)

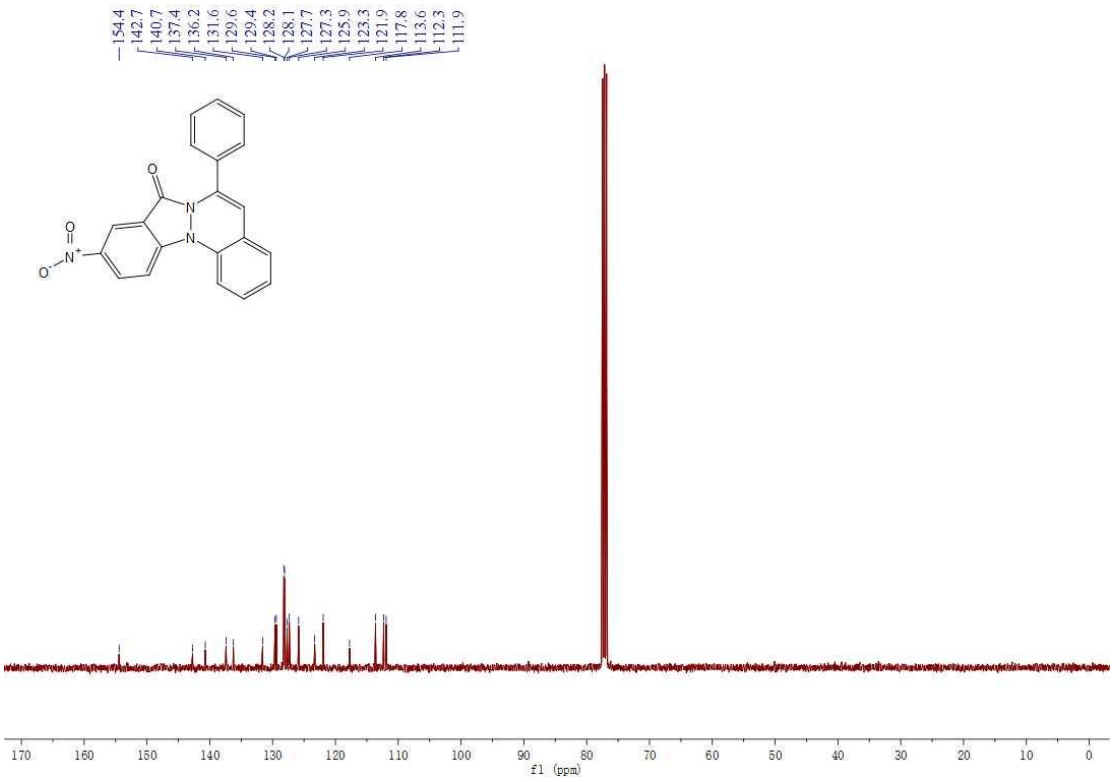


4g

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

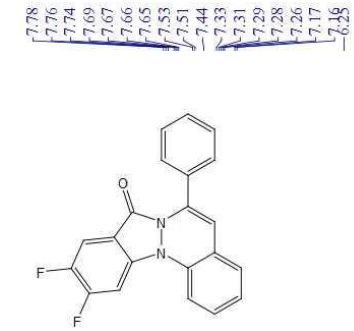


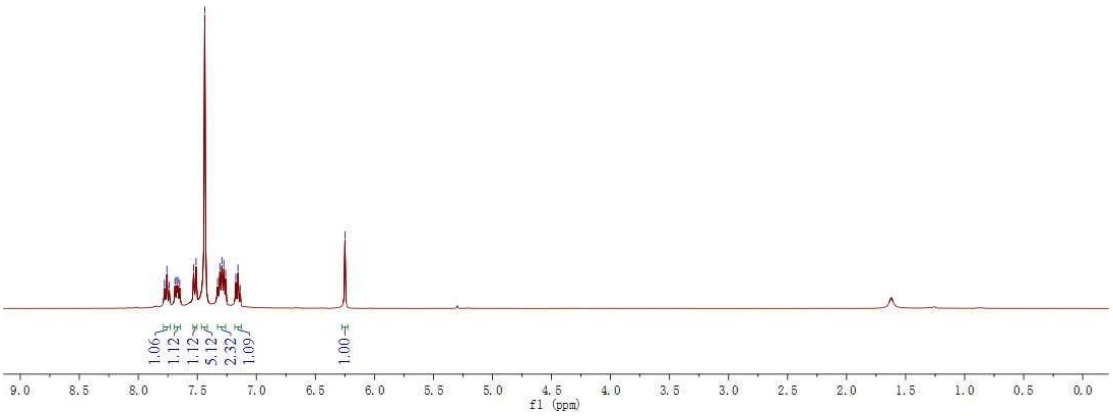
^{13}C NMR (101 MHz, $CDCl_3$)



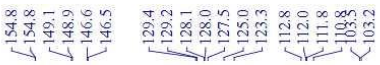
4h

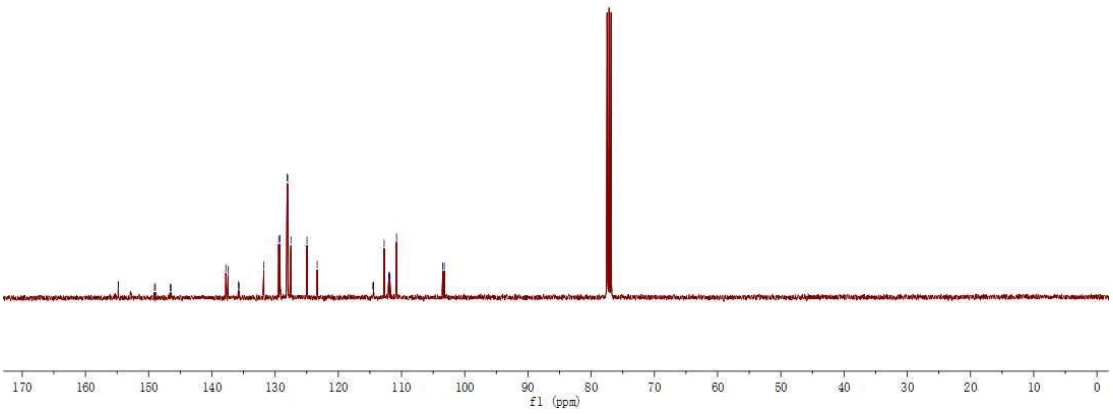
^{1}H NMR (400 MHz, $CDCl_3$)



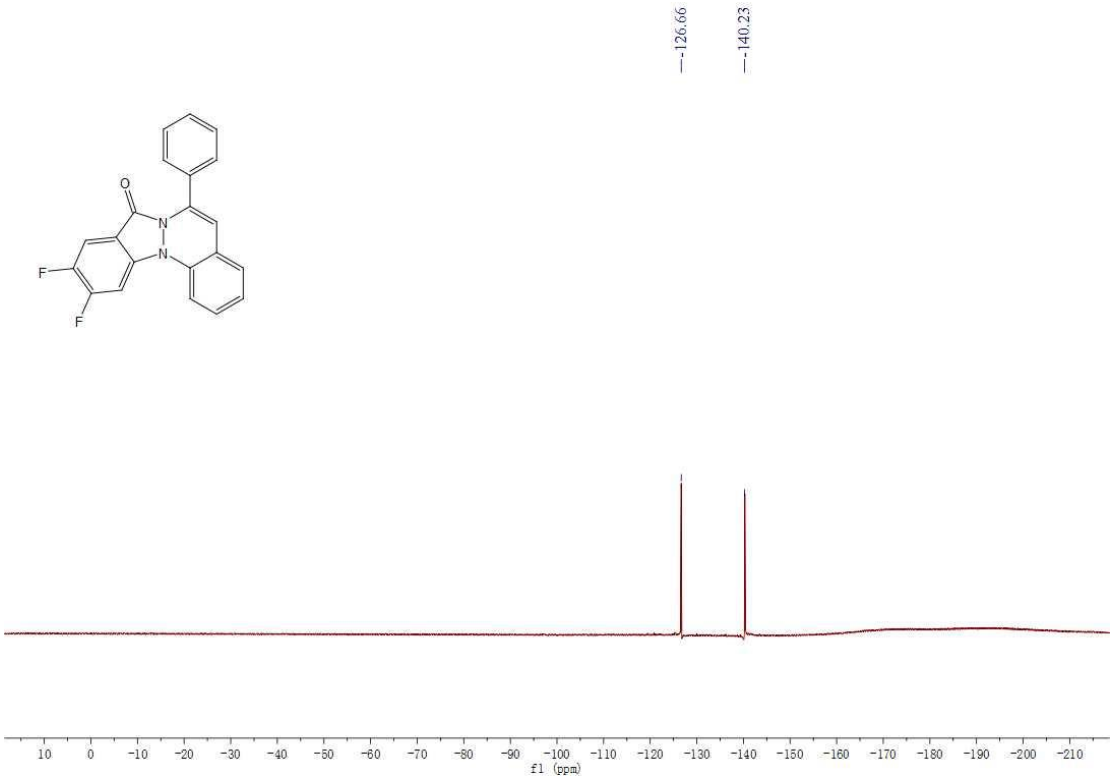


^{13}C NMR (101 MHz, $CDCl_3$)



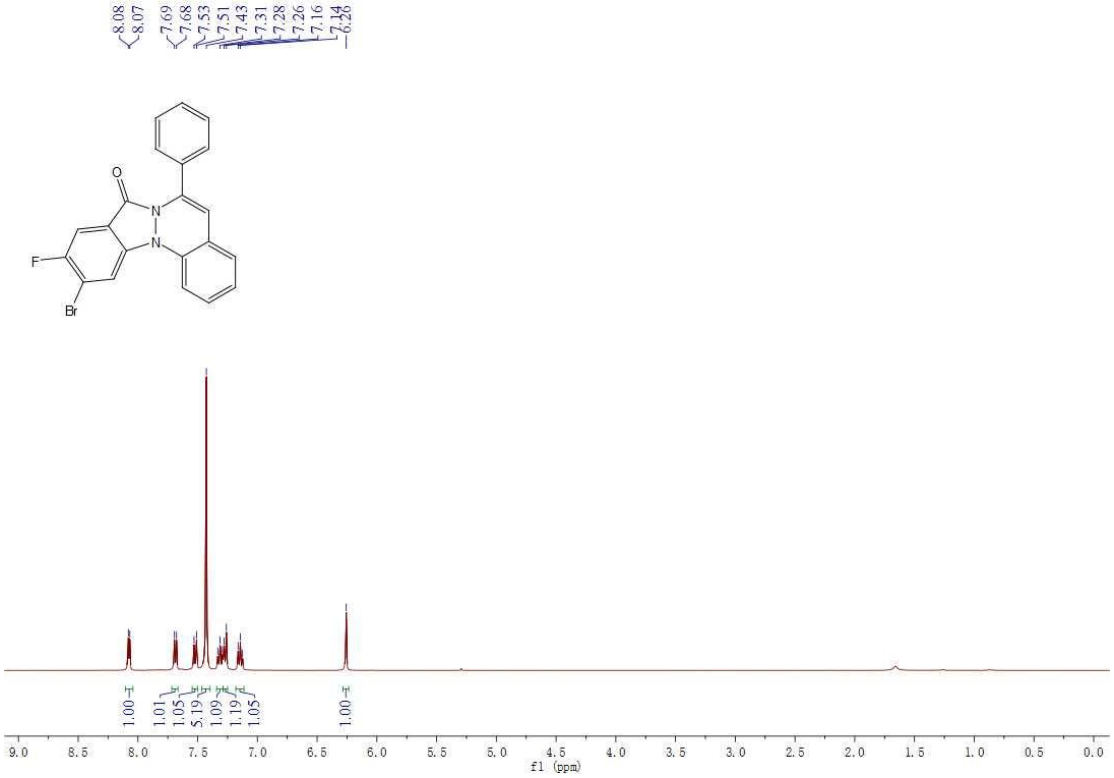


^{19}F NMR (376 MHz, $CDCl_3$)

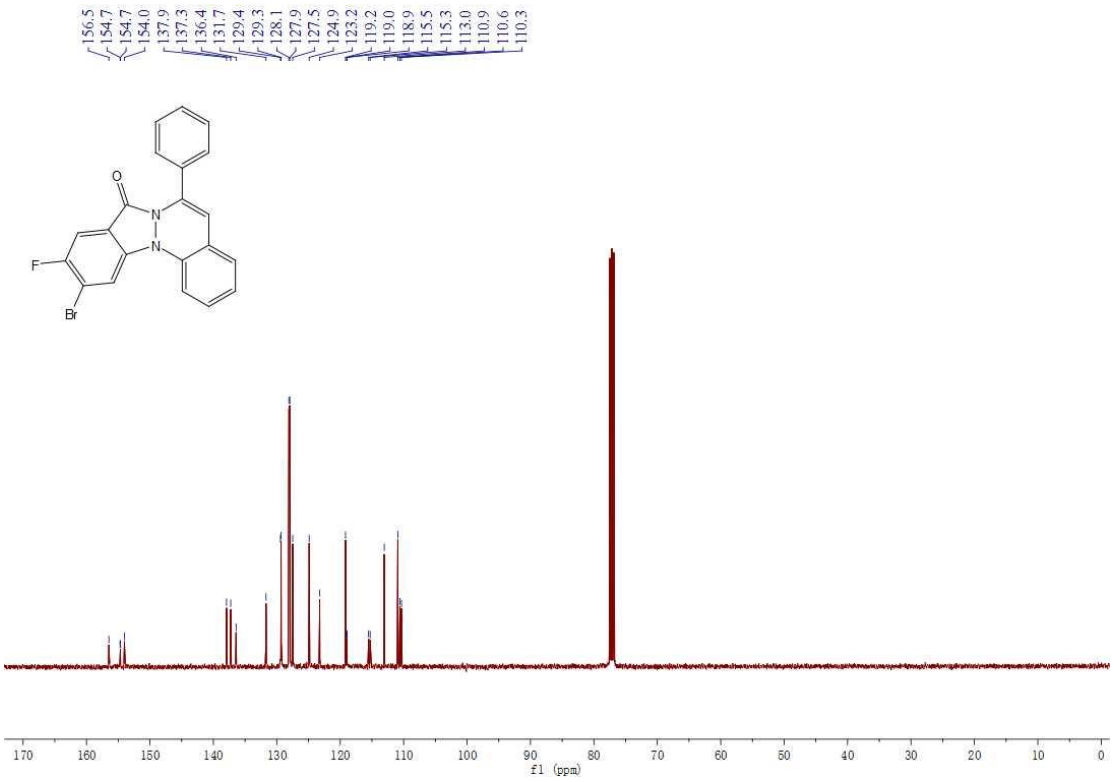


4i

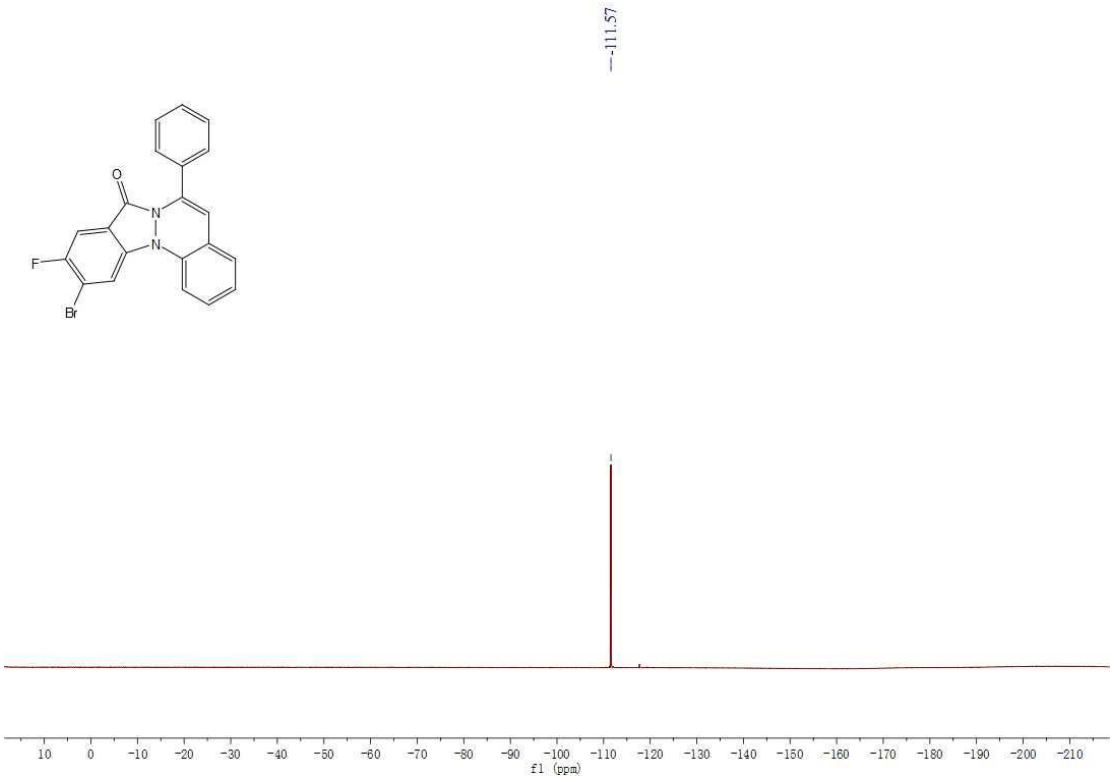
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

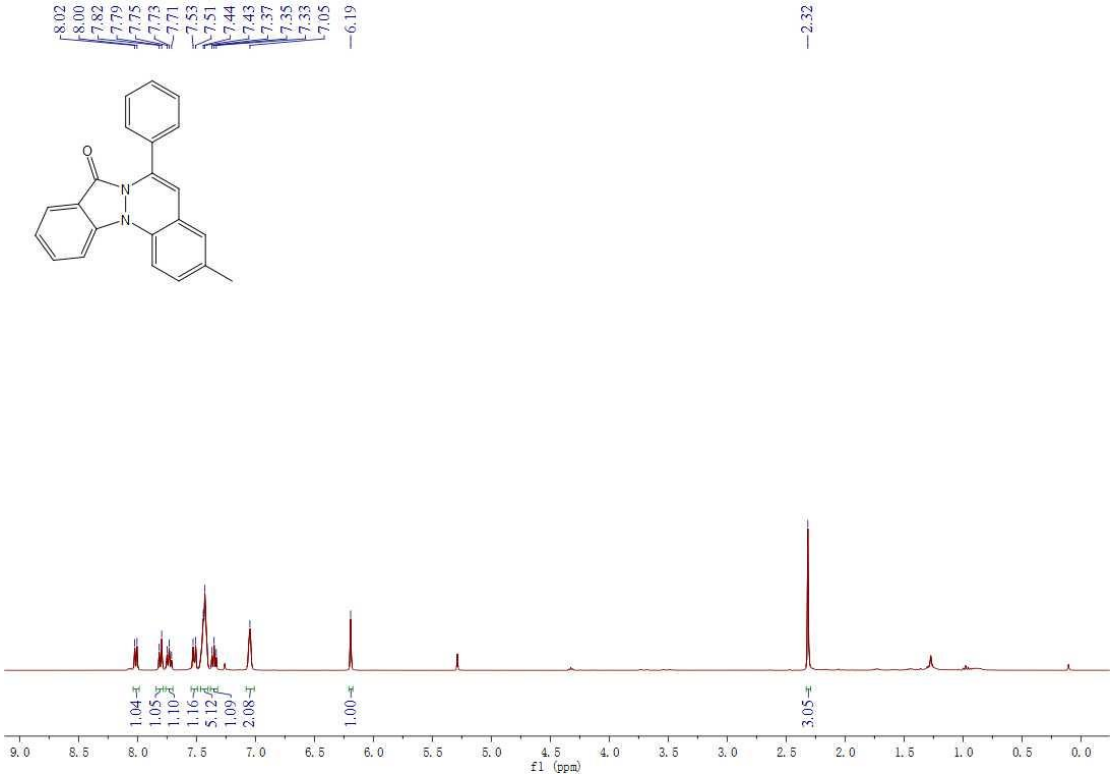


^{19}F NMR (376 MHz, $CDCl_3$)

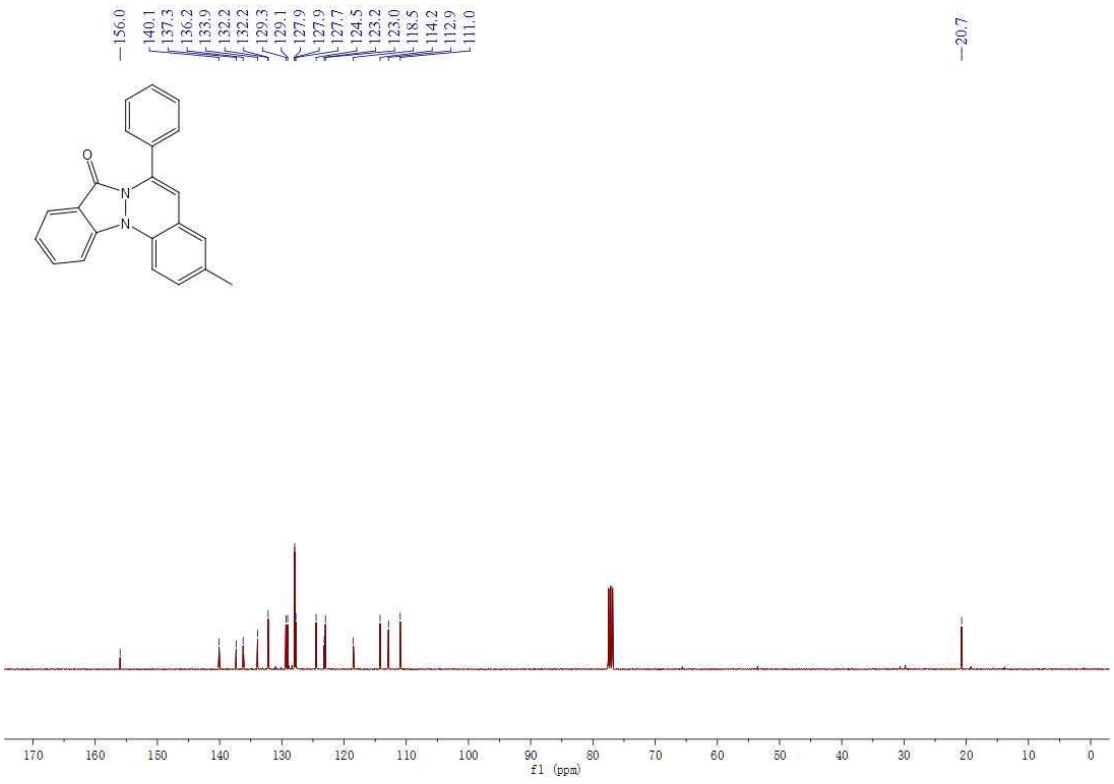


4j

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

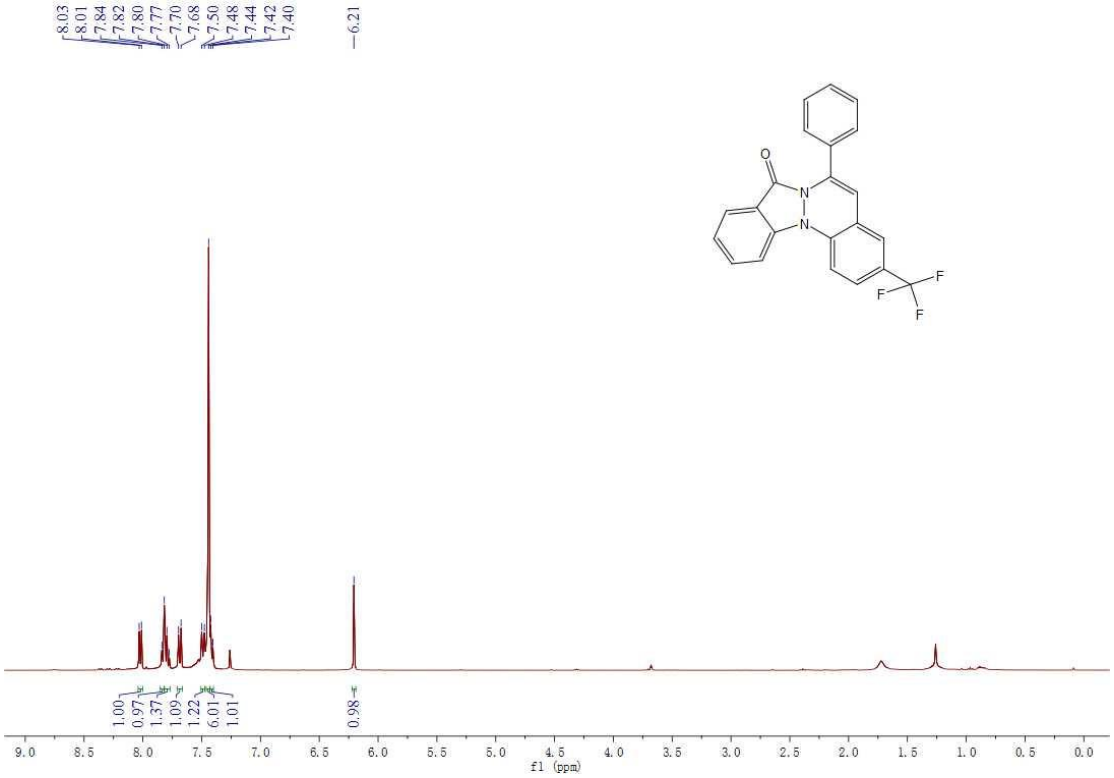


^{13}C NMR (101 MHz, $CDCl_3$)

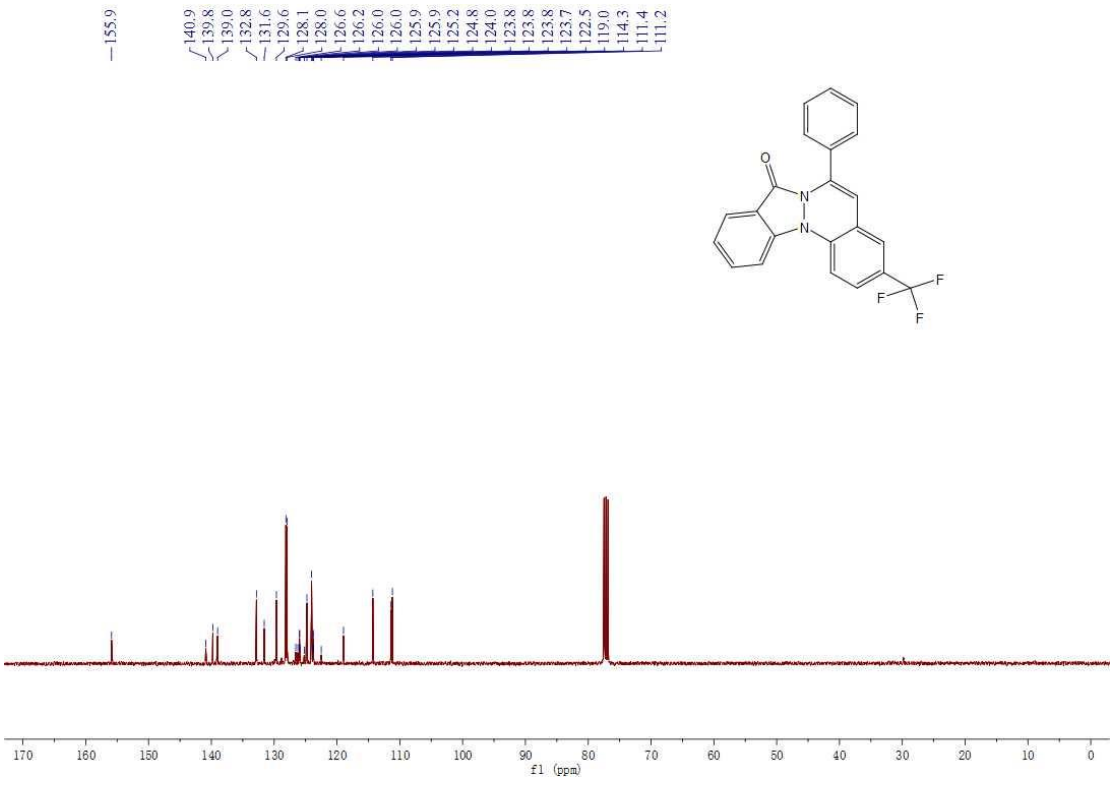


4k

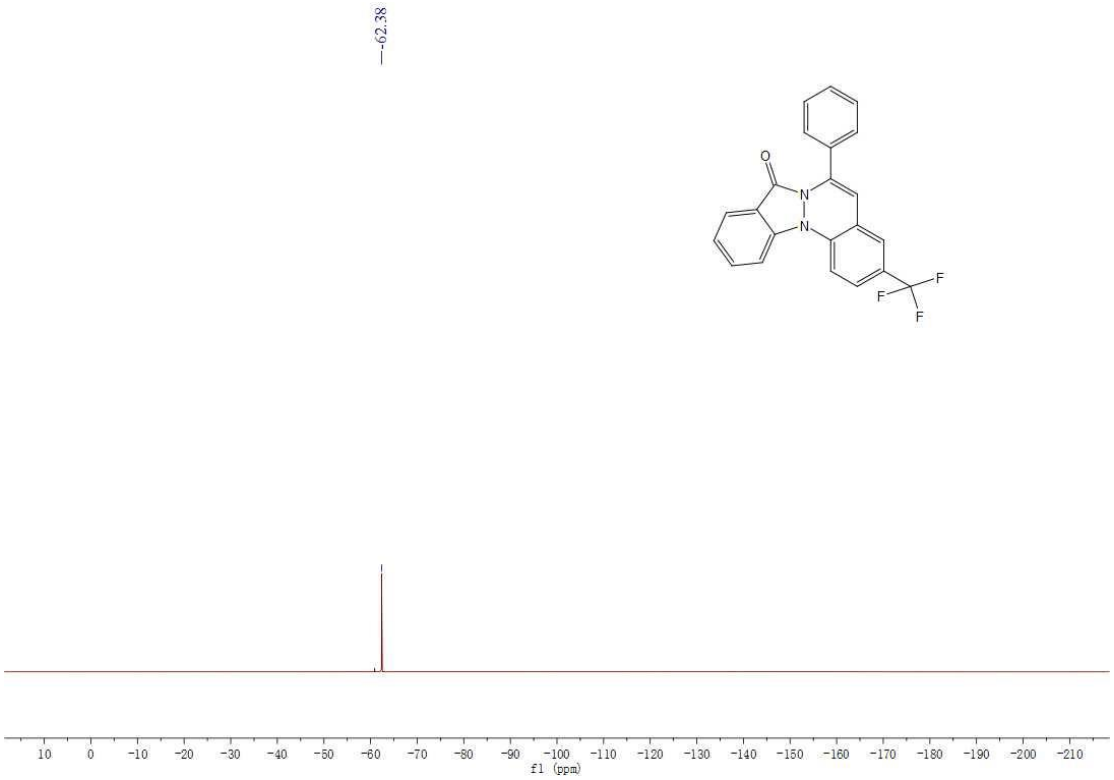
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

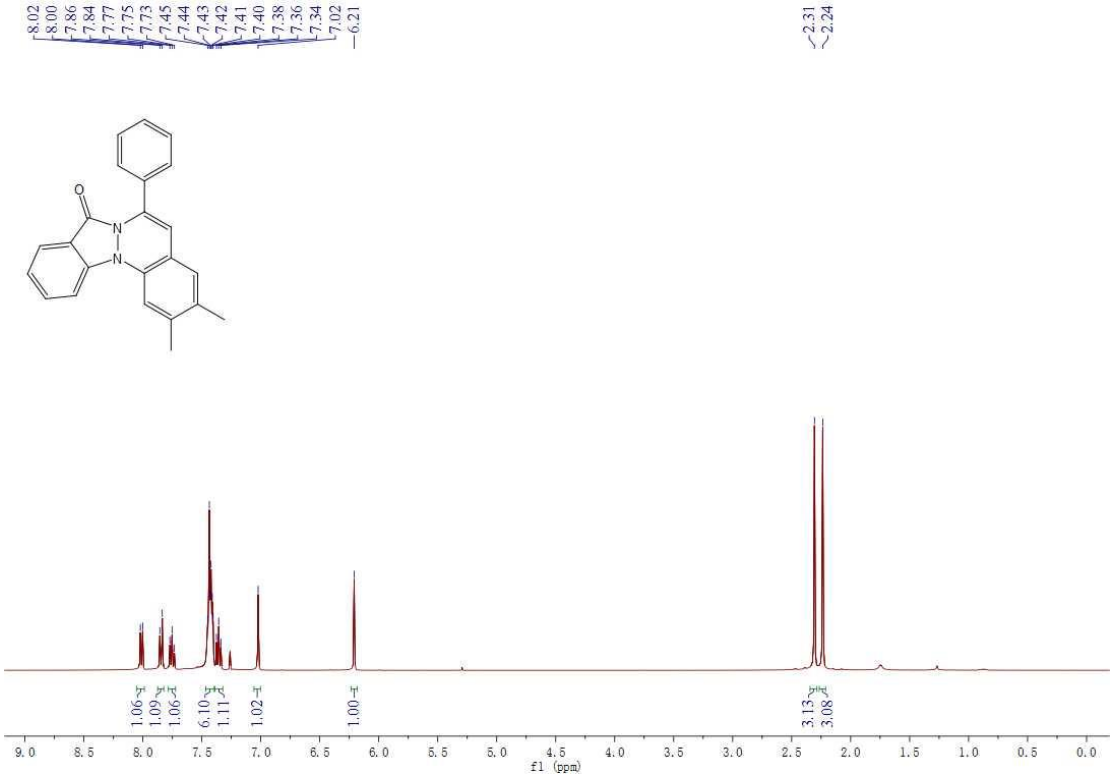


^{19}F NMR (376 MHz, $CDCl_3$)

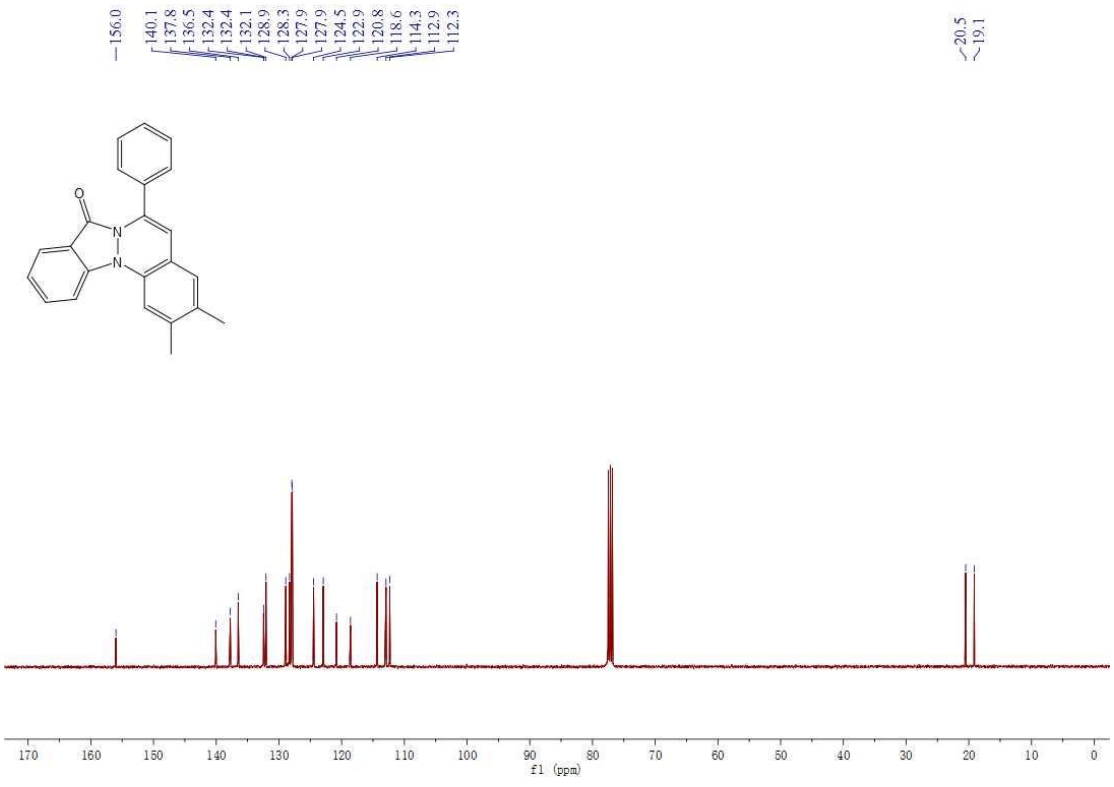


4l

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

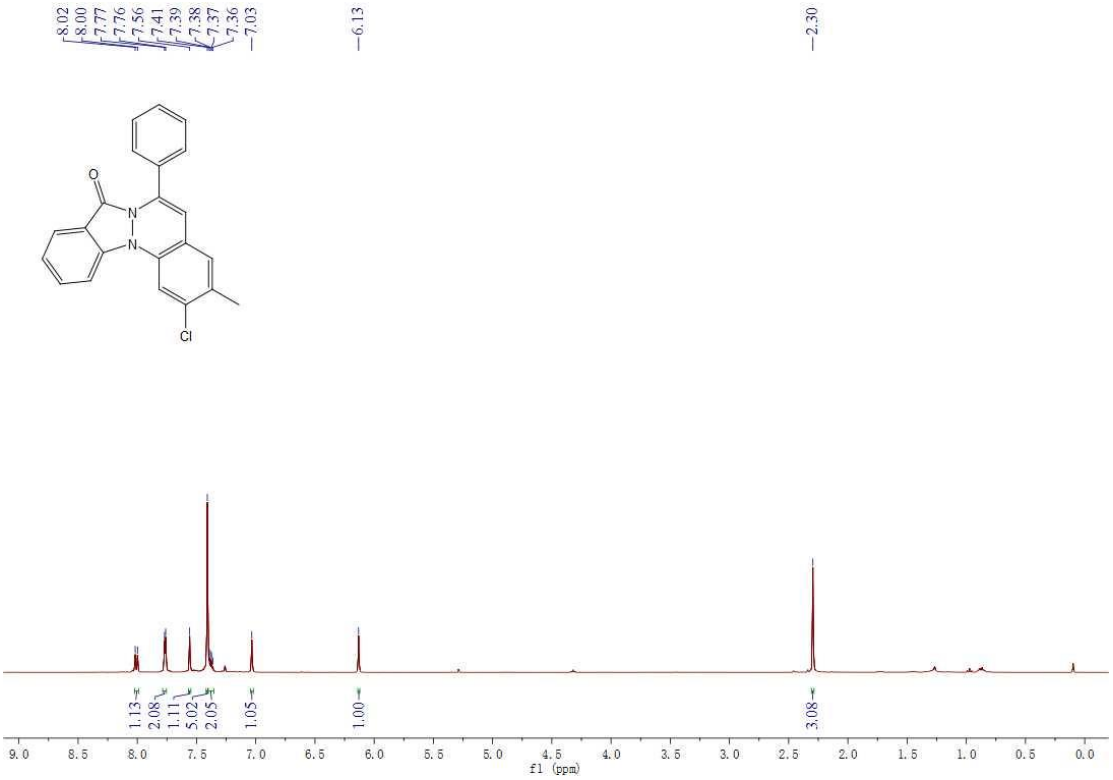


^{13}C NMR (101 MHz, $CDCl_3$)

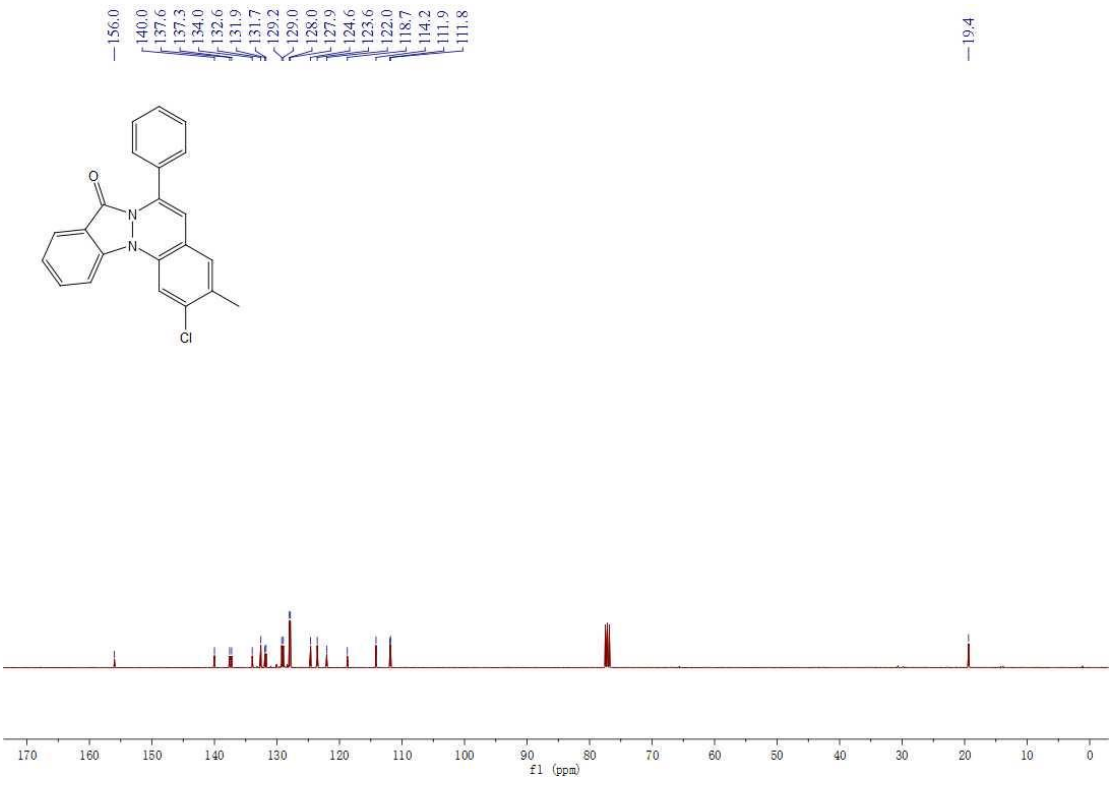


4m

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

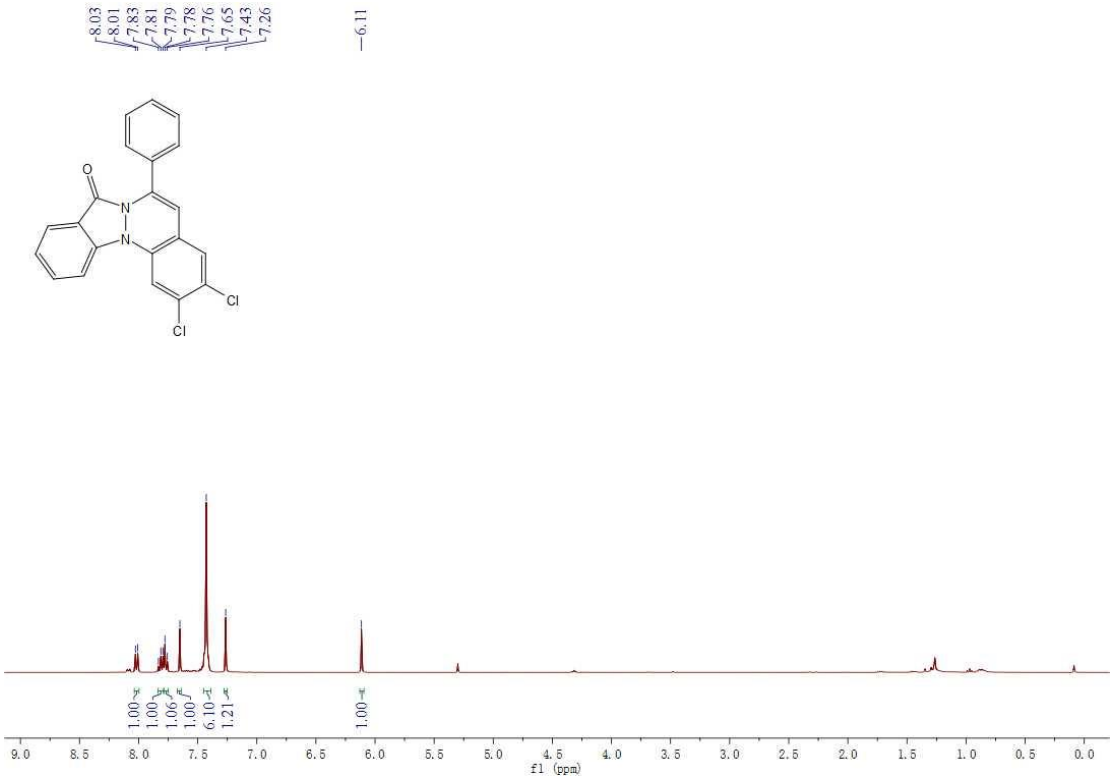


^{13}C NMR (101 MHz, $CDCl_3$)

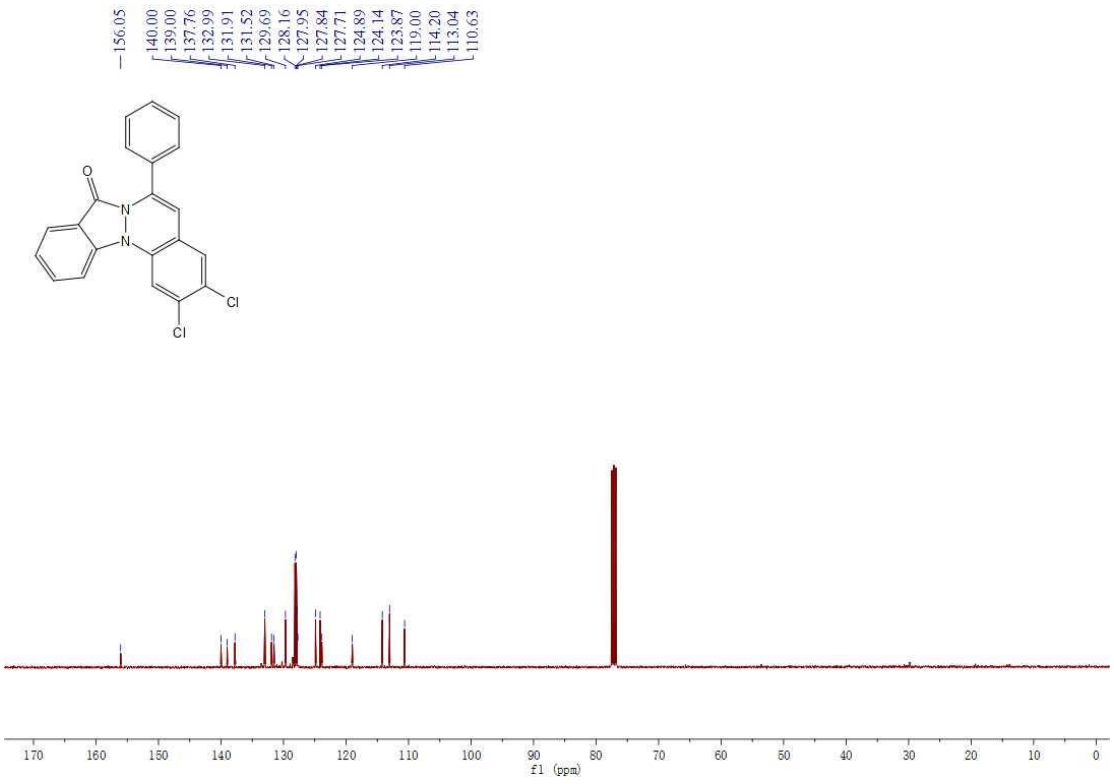


4n

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

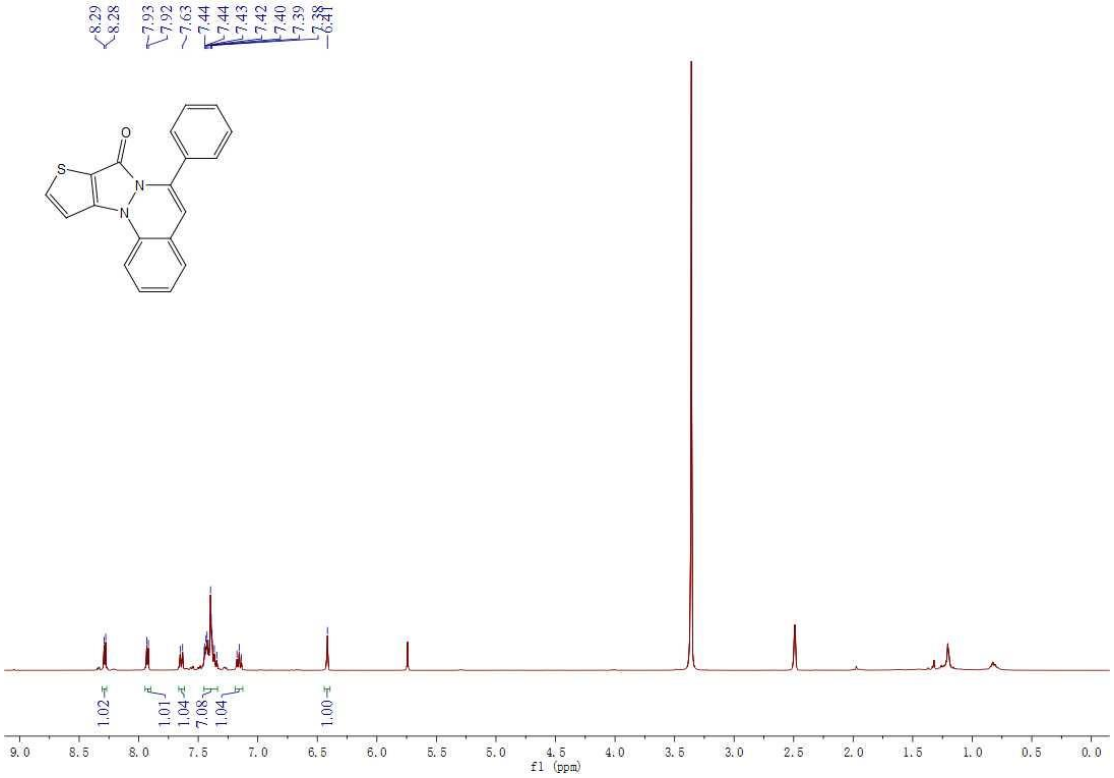


^{13}C NMR (101 MHz, $CDCl_3$)

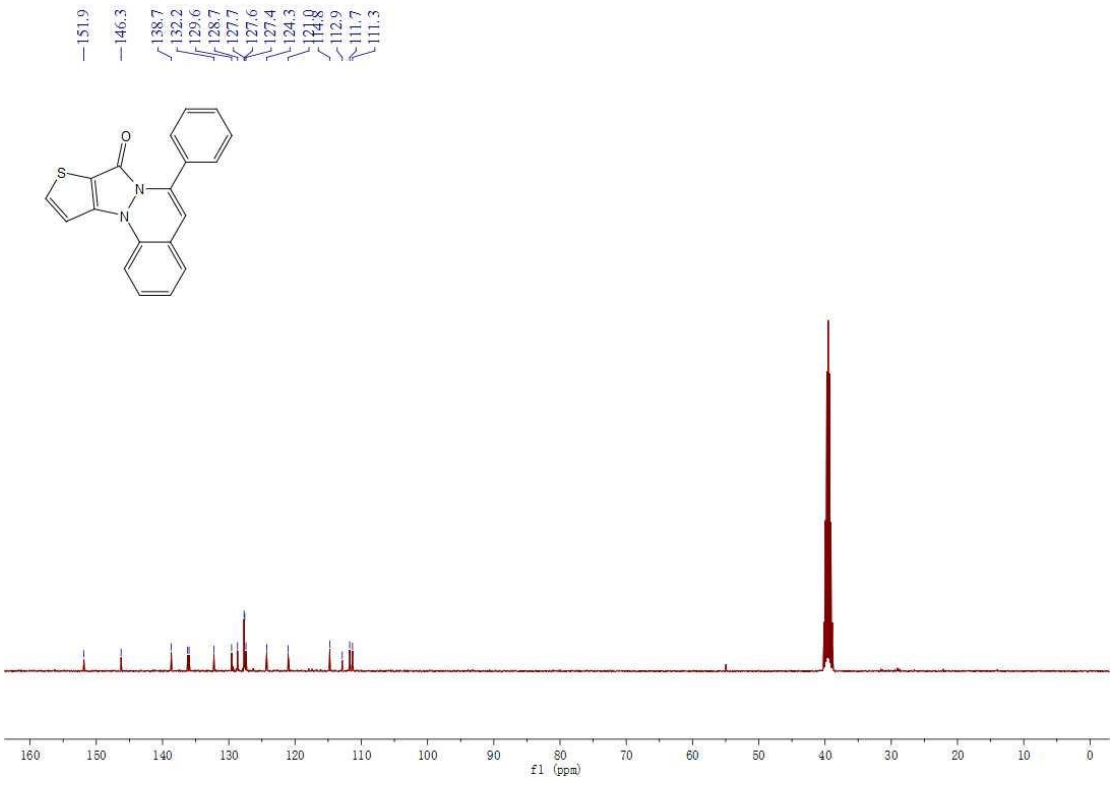


4o

^{1}H NMR (400 MHz, DMSO)

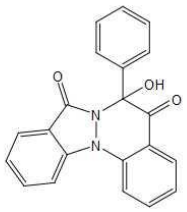


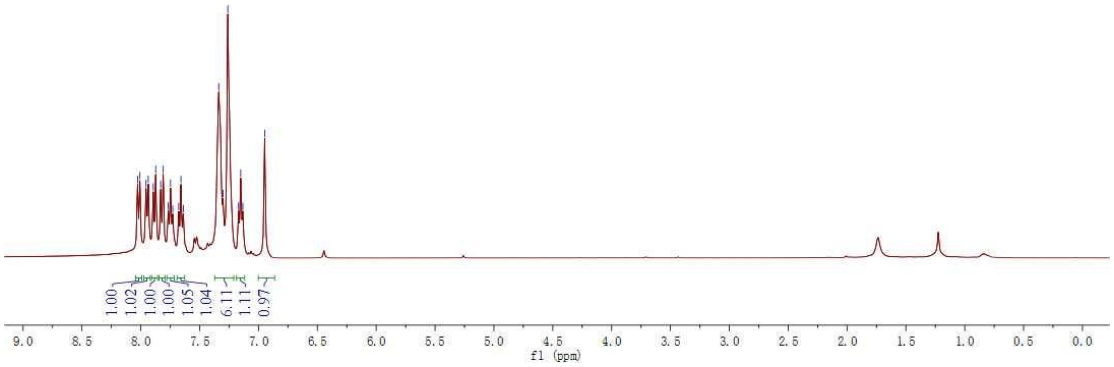
^{13}C NMR (101 MHz, DMSO)



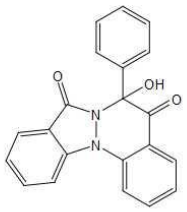
5a

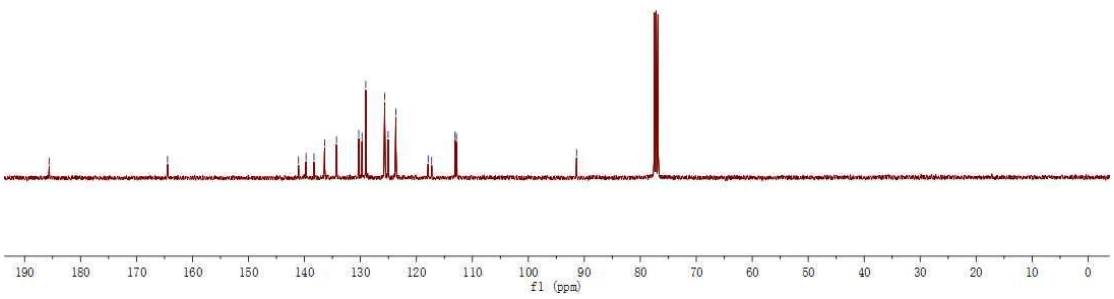
^{1}H NMR (400 MHz, $CDCl_3$)





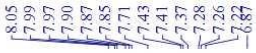
^{13}C NMR (101 MHz, $CDCl_3$)

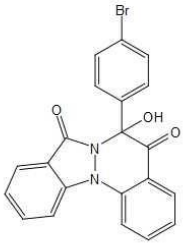


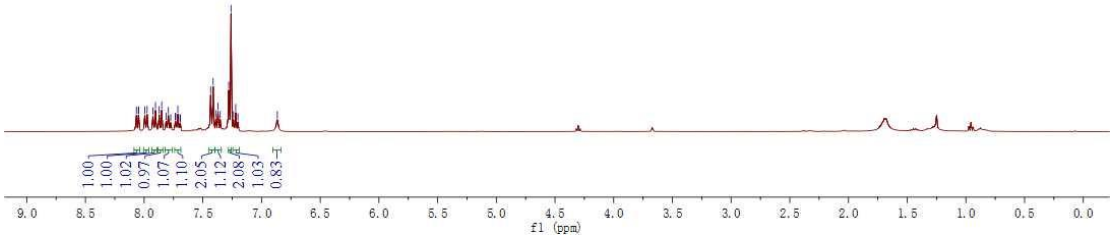


5b

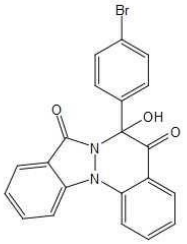
^{1}H NMR (400 MHz, $CDCl_3$)





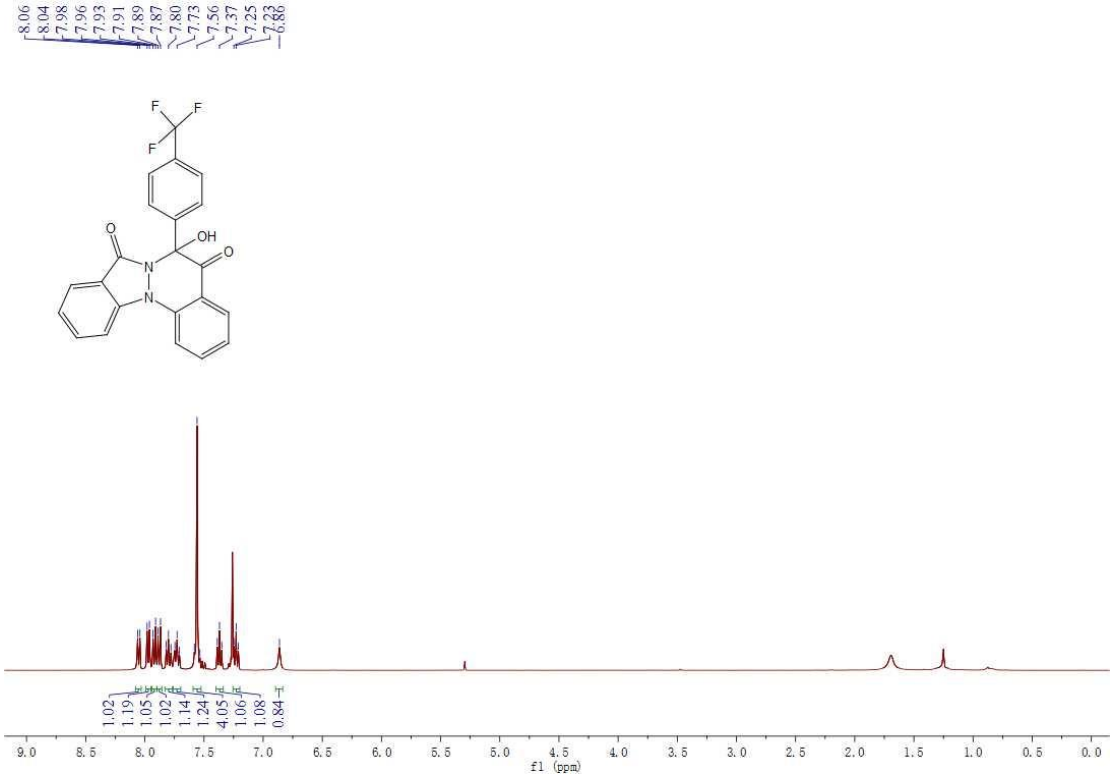


^{13}C NMR (101 MHz, $CDCl_3$)

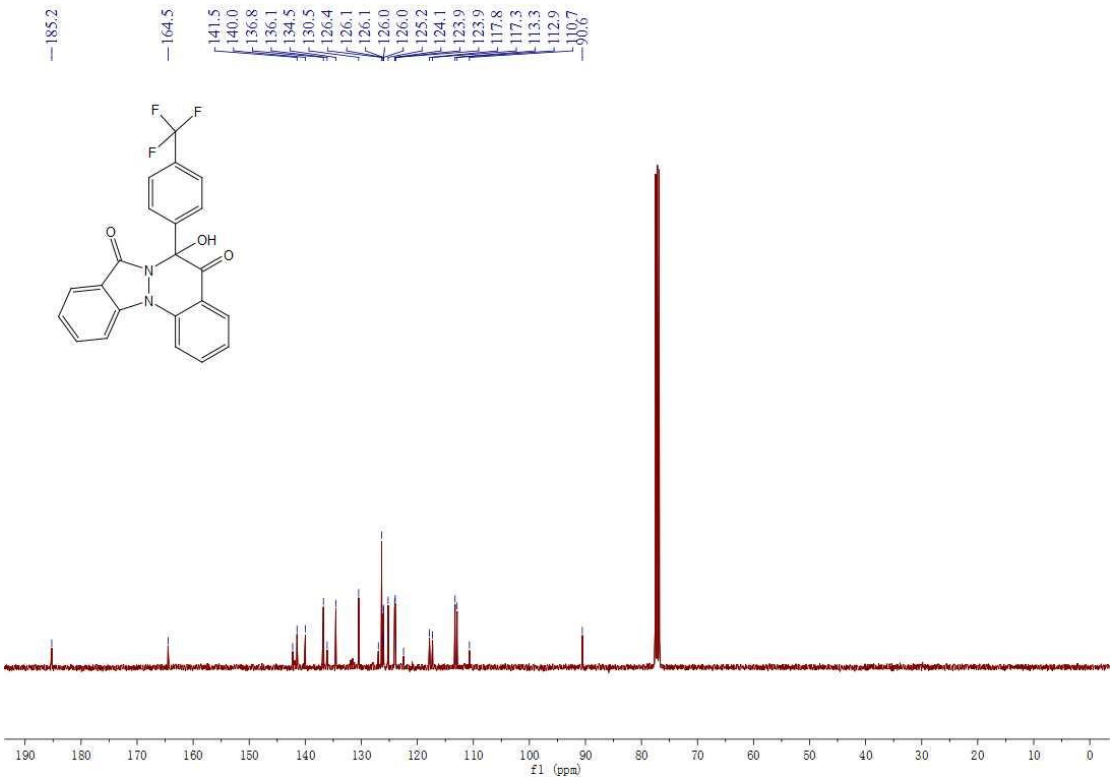


5c

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



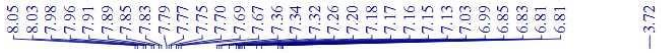
^{13}C NMR (101 MHz, $CDCl_3$)

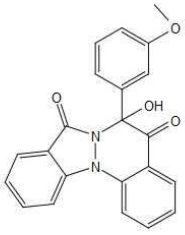


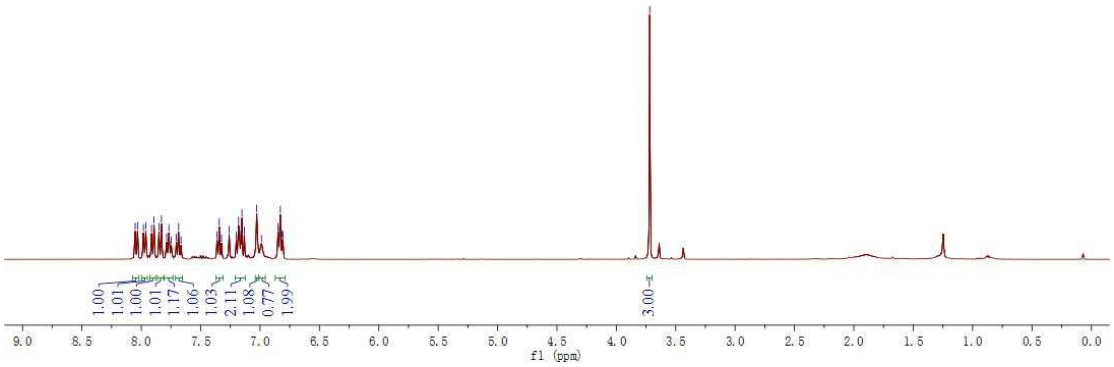
^{19}F NMR (376 MHz, $CDCl_3$)

5d

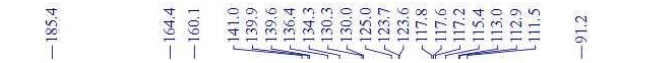
^{1}H NMR (400 MHz, $CDCl_3$)

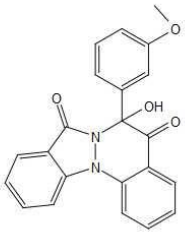


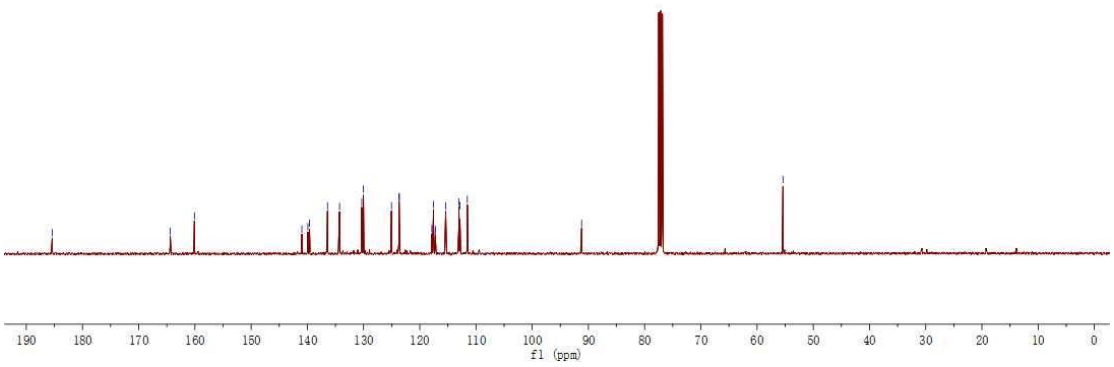




^{13}C NMR (101 MHz, $CDCl_3$)

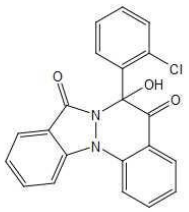


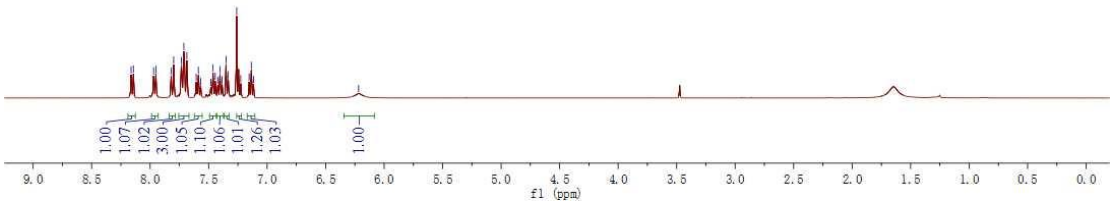




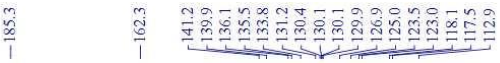
5e

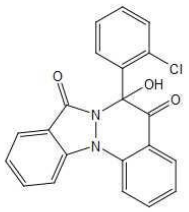
^{1}H NMR (400 MHz, $CDCl_3$)





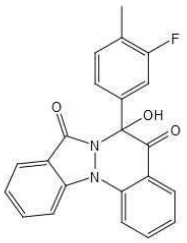
^{13}C NMR (101 MHz, $CDCl_3$)

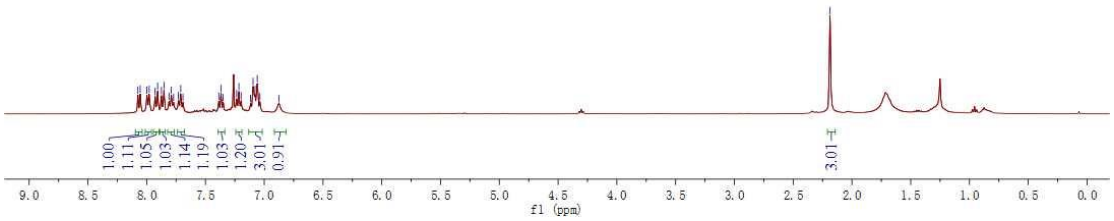




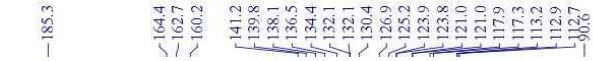
5f

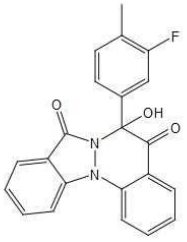
^{1}H NMR (400 MHz, $CDCl_3$)



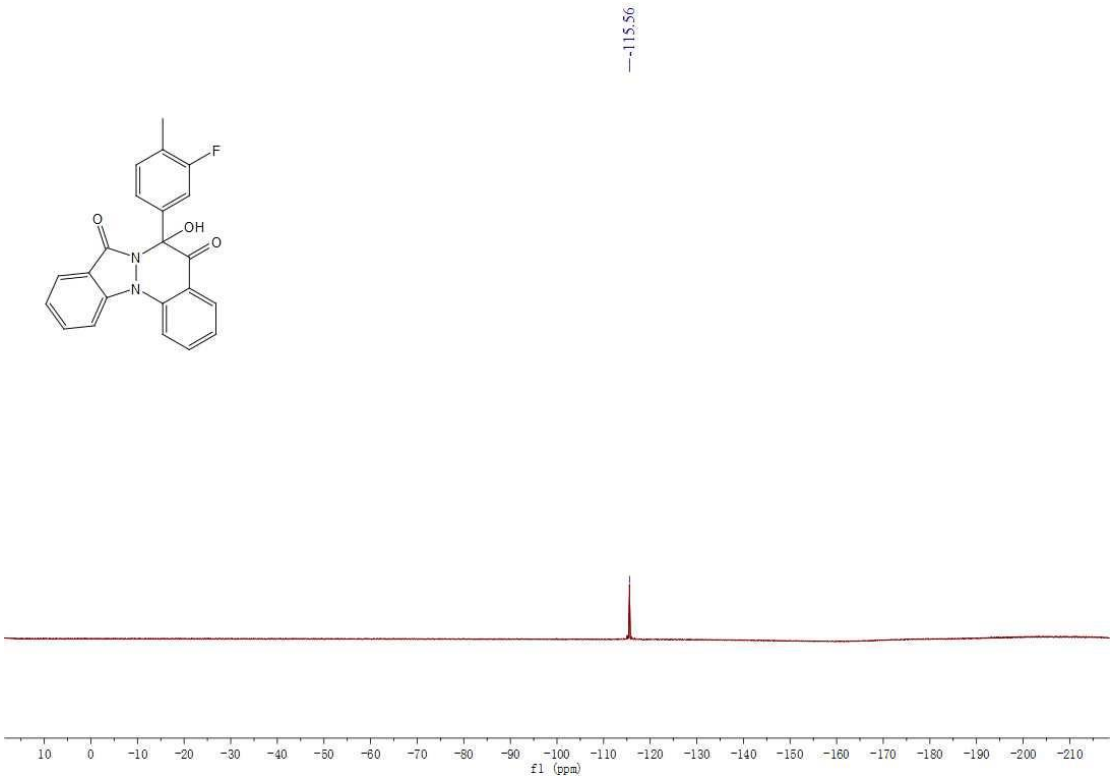


^{13}C NMR (101 MHz, $CDCl_3$)



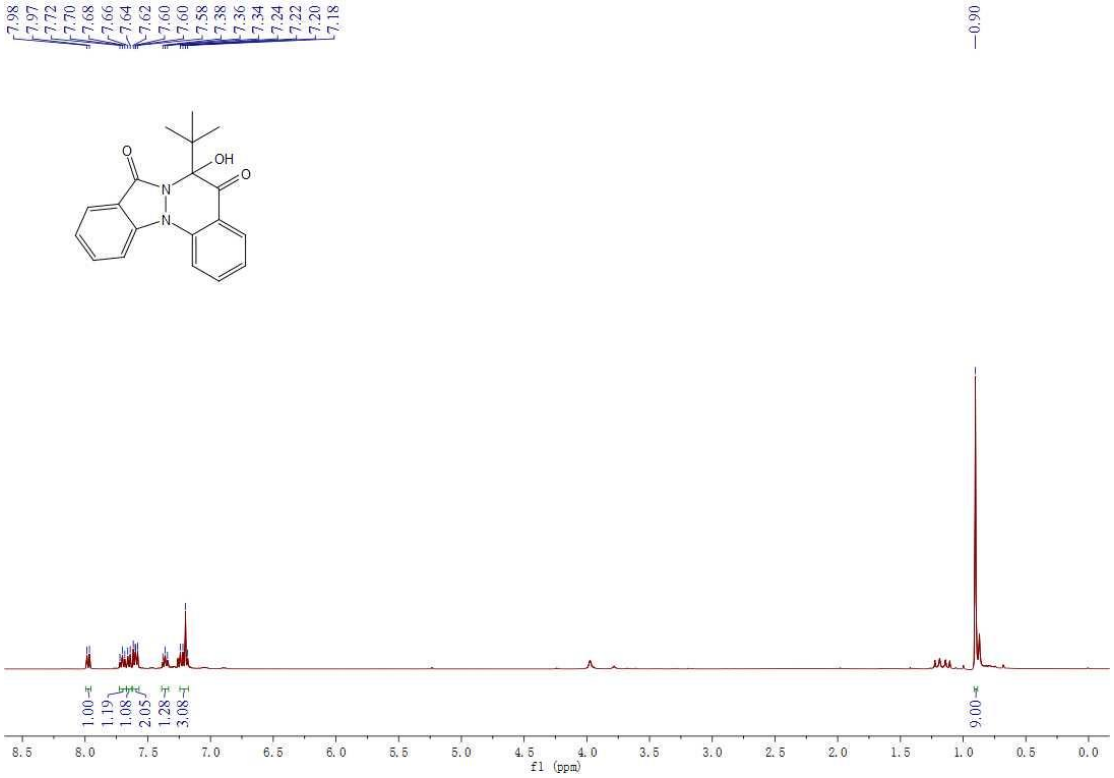


^{19}F NMR (376 MHz, $CDCl_3$)

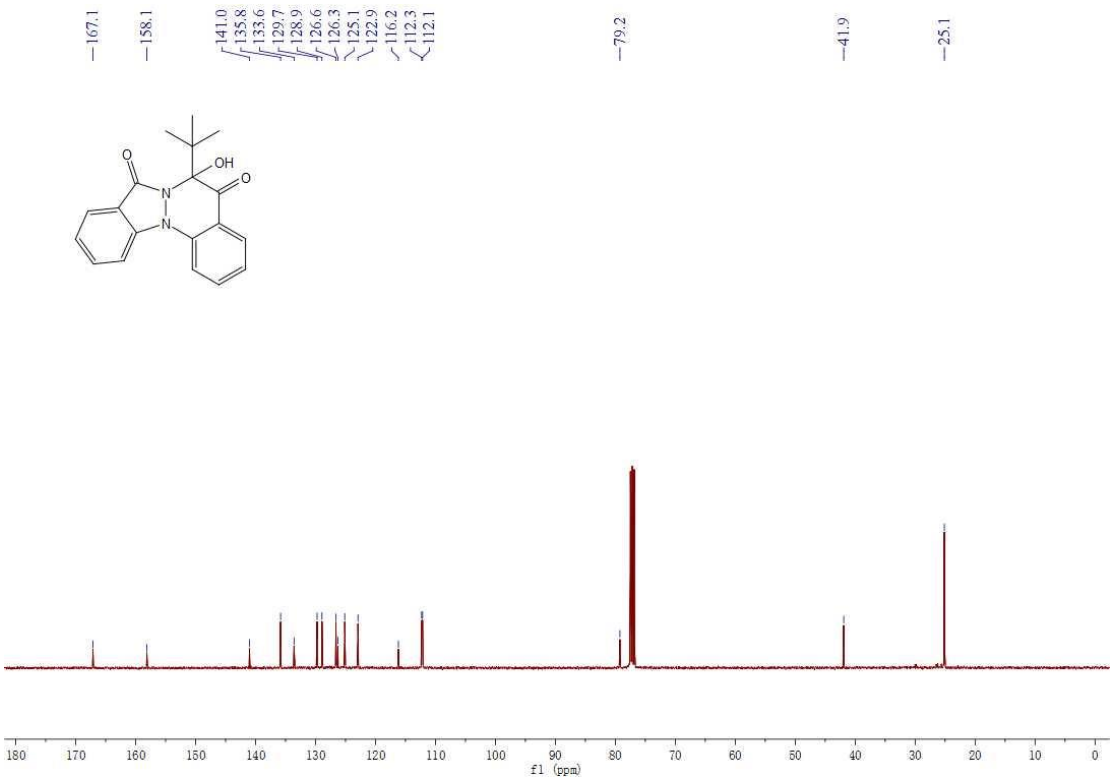


5g

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

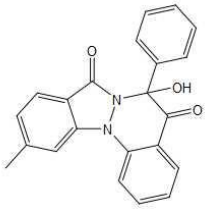


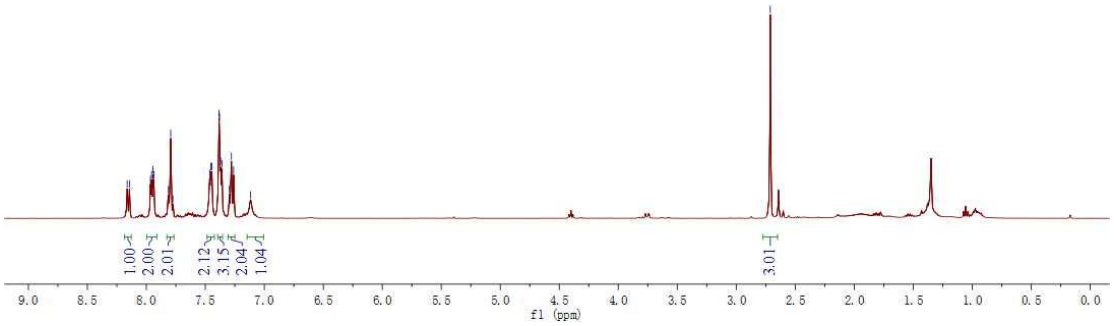
^{13}C NMR (101 MHz, $CDCl_3$)



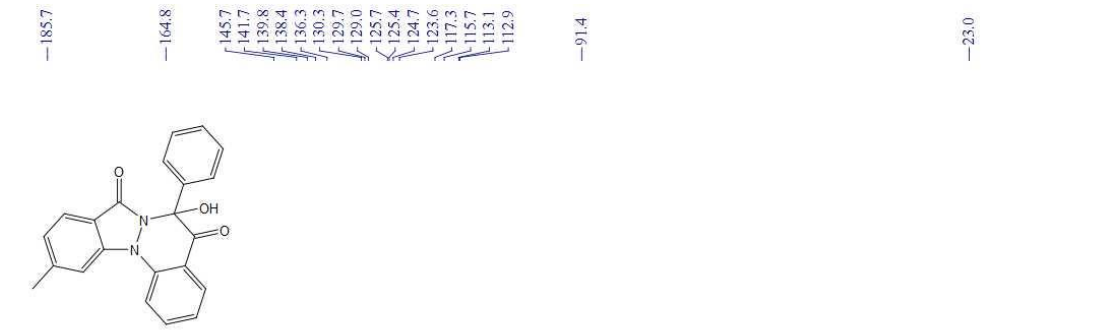
5h

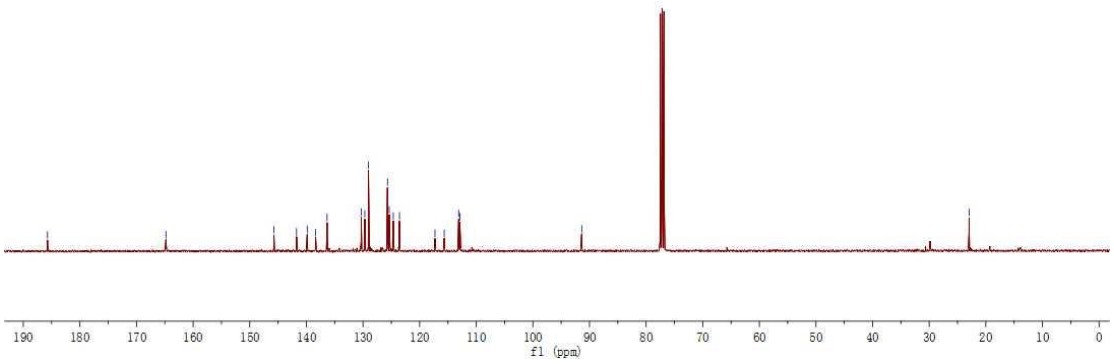
^{1}H NMR (400 MHz, $CDCl_3$)





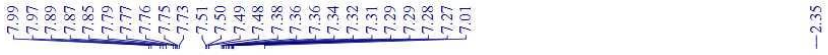
^{13}C NMR (101 MHz, $CDCl_3$)

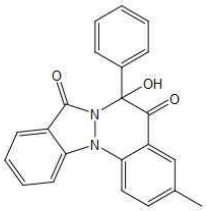


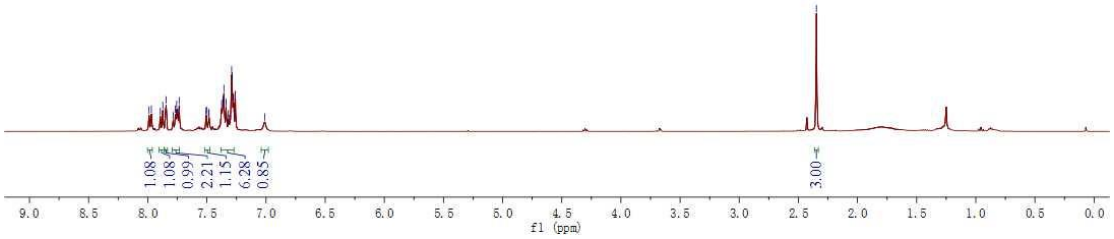


5i

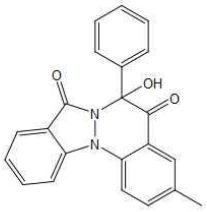
^{1}H NMR (400 MHz, $CDCl_3$)





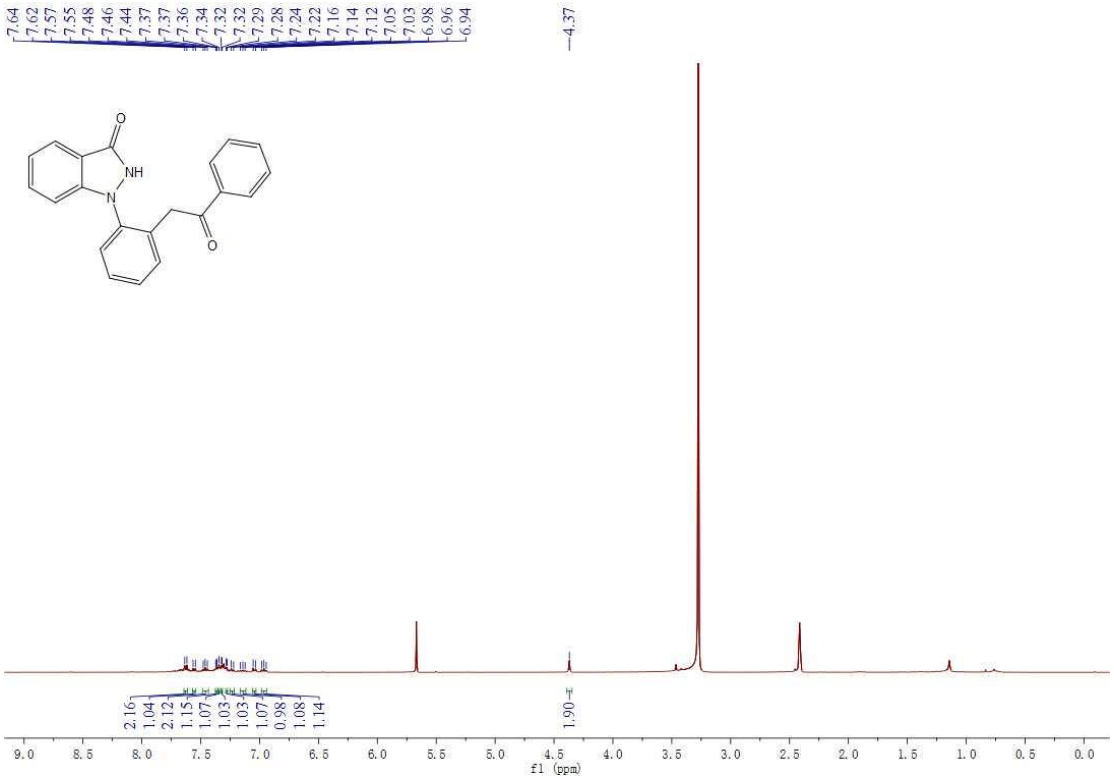


^{13}C NMR (101 MHz, $CDCl_3$)

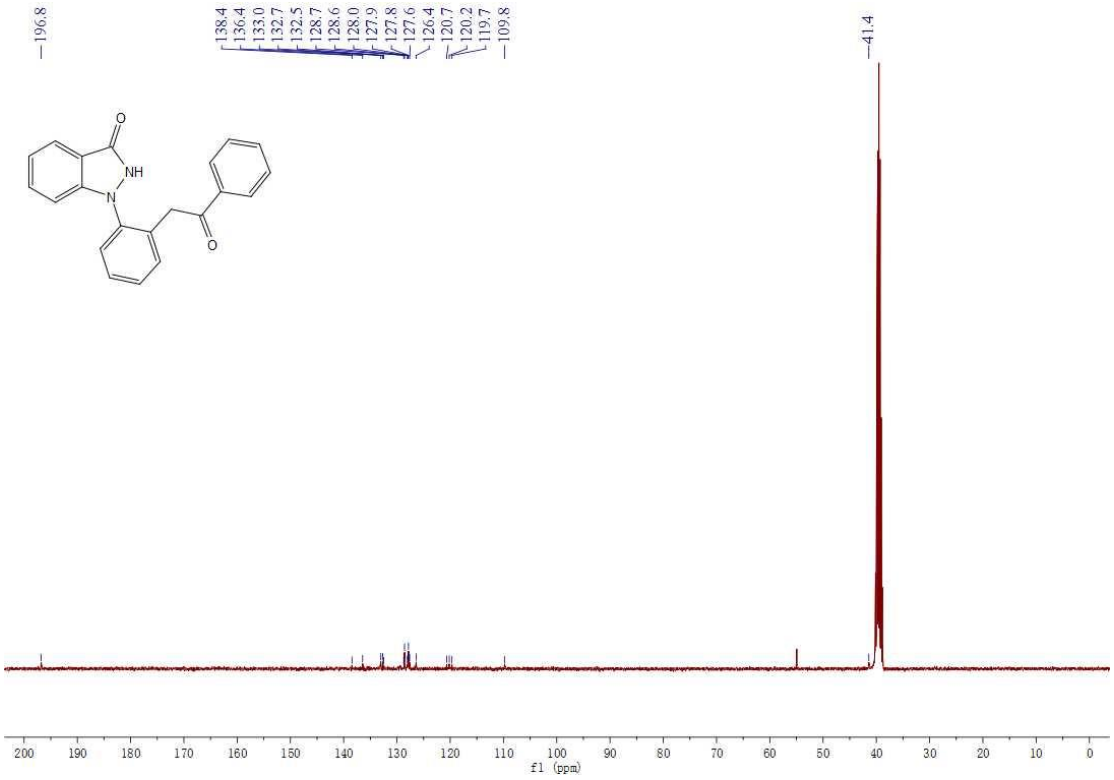


7

^{1}H NMR (400 MHz, DMSO)



^{13}C NMR (101 MHz, DMSO)



11. References

[1] J. Y. Kang, W. An, S. Kim, N. Y. Kwon, T. Jeong, P. Ghosh, H. S. Kim, N. K. Mishra, I. S. Kim. *Chem. Commun.*, **2021**, *57*, 10947-10950.

[2] M. Barday, C. Janot, N. R. Halcovitch, J. Muir, C. Aïssa. *Angew. Chem. Int. Ed.*, **2017**, *56*, 13117-13121.