Ru(II)-catalyzed regioselective [4 + 1] redox-neutral spirocyclization of aryl amidines with diazopyrazolones: direct access to spiro[indole-3,4'-pyrazol]-5'-ones

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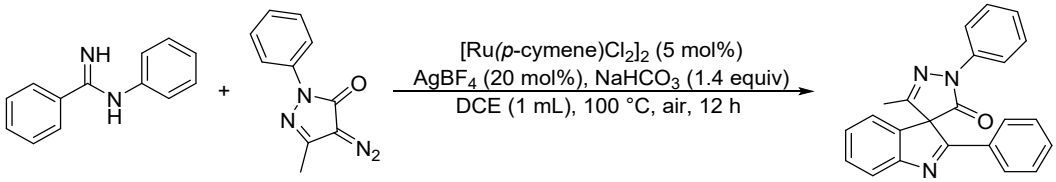
General information

All manipulations were conducted under air atmosphere. Unless otherwise stated, all commercial materials and solvents were used directly without further purification. Commercially available chemicals were obtained from Energy Chemical, Admas, J&K. ^{1} H and ^{13}C NMR spectra were measured on a 400 MHz Bruker spectrometer (^{1}H 400MHz, ^{13}C 100MHz, ^{19}F NMR 376 MHz), using $CDCl_3$ (spectra were referenced to the solvent peaks ^{1}H: residual $CDCl_3$ = 7.26 ppm, ^{13}C: $CDCl_3$ = 77.0 ppm). High-resolution mass spectra (HRMS) were equipped with an ESI source and a TOF detector. Column chromatography was performed on silica gel (70-230 mesh ASTM) using the reported eluent. Thin-layer chromatography (TLC) was carried out on 4×5 cm plates with a layer thickness of 0.2 mm (silica gel 60 F254). Starting materials N-aryl amidines[1] and diazopyrazolones[2] were prepared according to the literatures.

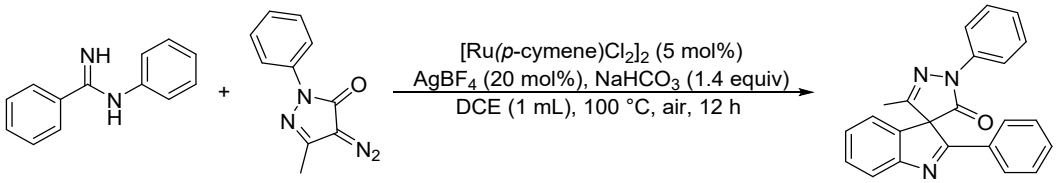
General catalytic procedure



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

To a tube changed with N-aryl amidine **1a** (0.1 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5.0 mol %), $AgBF_4$ (20 mol %), $NaHCO_3$ (1.4 equiv), diazopyrazolone **2a** (0.12 mmol) were added sequentially and dissolved in dichloroethane (1.0 mL) under air atmosphere. The mixture was stirred at 100 ℃ for 12 h. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using ethyl acetate /petroleum ether (1: 25~1: 15) as eluent to afford the desired product **3aa**.

The scale-up reaction procedure

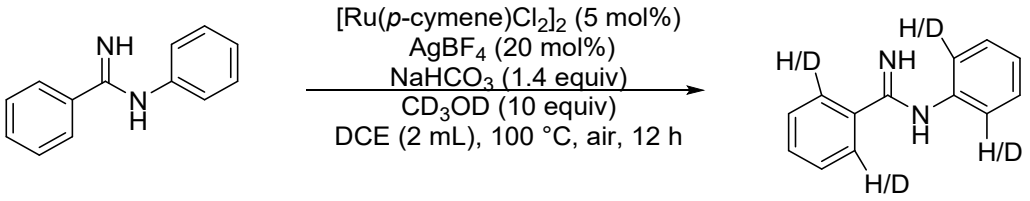


1a **2a** **3aa**

To a tube charged with N-phenylbenzamidine **1a** (5.5 mmol, 1.08 g), $[RuCl_2(p\text{-cymene})]_2$ (5.0 mol%, 168 mg), $AgBF_4$ (20 mol%, 213.4 mg), $NaHCO_3$ (1.4 equiv, 646 mg), diazopyrazolones **2a** (6.6 mmol, 1.28g), were added sequentially and dissolved in dichloroethane (55.0 mL) under air atmosphere. The mixture was stirred at 100 ℃ for 12 h in oil bath. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using ethyl acetate (EA)/petroleum ether (PE) (1: 30~1: 10) as eluent to afford the desired product **3aa** (67 %, 1.29 g).

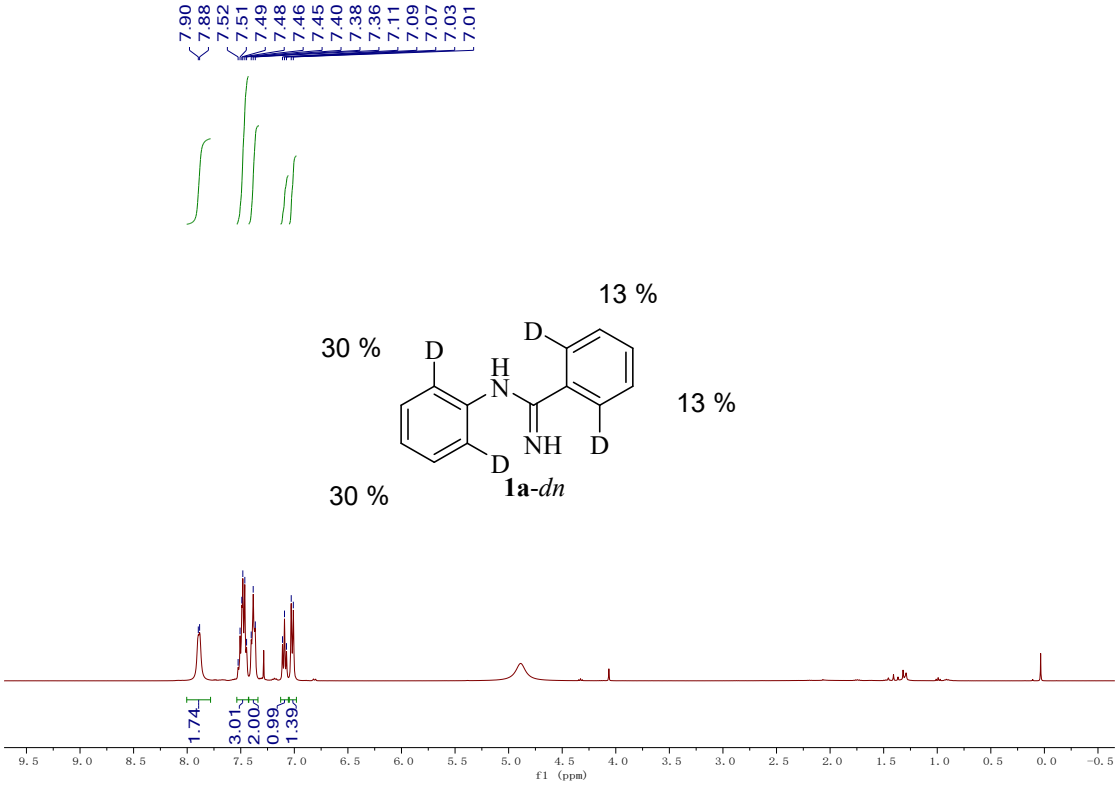
Mechanism studies

1. H/D exchange

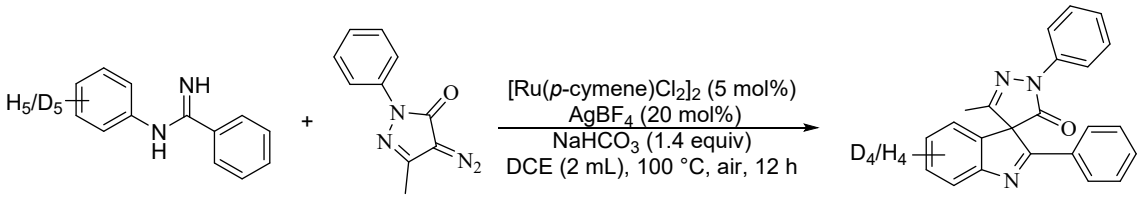


1a **1a-*dn***

To a tube charged with N-phenylbenzamidine **1a** (0.2 mmol, 39.3 mg), $[RuCl_2(p\text{-cymene})]_2$ (5 mol %, 6.1 mg), $AgBF_4$ (20 mol %, 7.8 mg), $NaHCO_3$ (1.4 equiv, 23.5 mg) and CD_3OD (10 equiv, 72 mg), were added sequentially and dissolved in dichloroethane (2.0 mL) under air atmosphere. The mixture was stirred at 100 ℃ in oil bath for 12 h. After cooled to room temperature, the solvent was removed under the reduced pressure and the residue was purified by silica gel chromatography using ethyl acetate /petroleum ether (1: 20~1: 10) as eluent to afford the desired product of **1a** and **1a-*dn***. Based on ^1H NMR spectrum of the mixture, the deuteration ratio was determined to be 30% and 13 %.

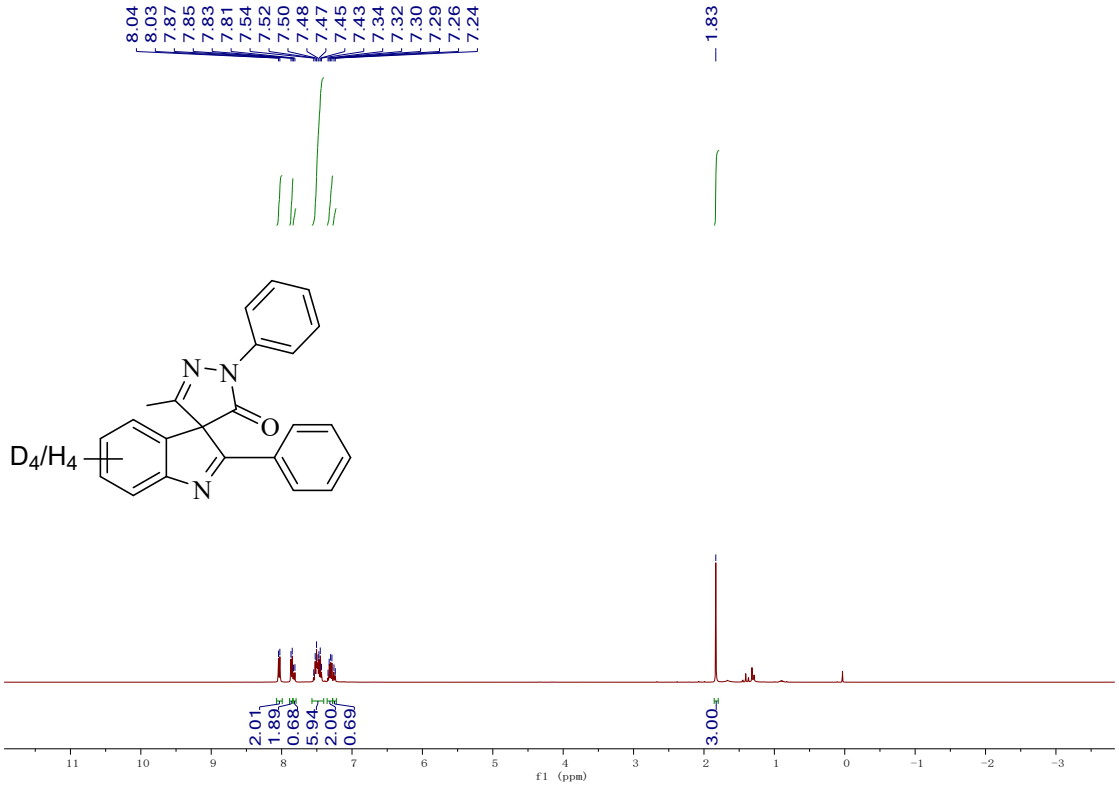


2. Kinetic isotope effect study

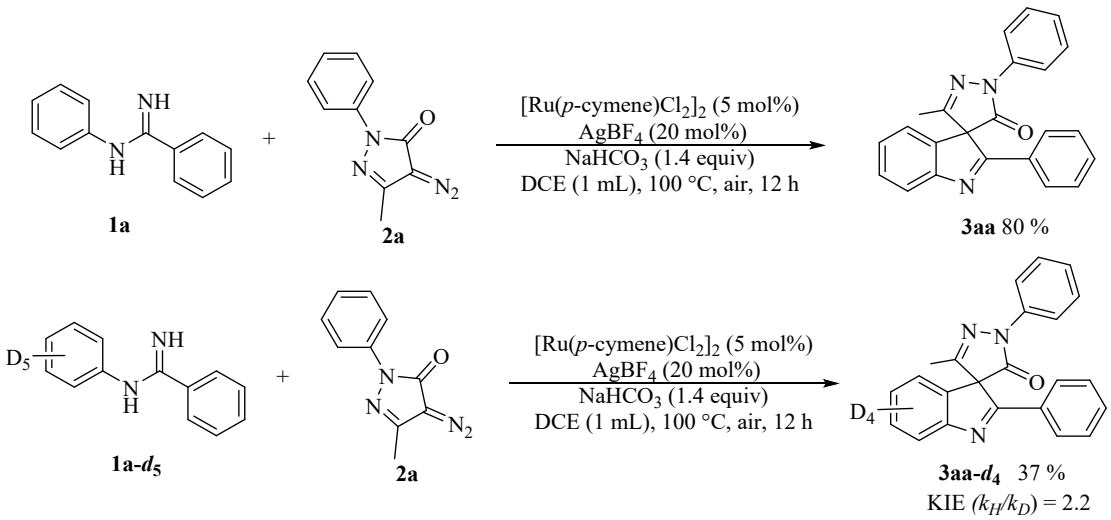


1a/1a-*d*5 **2a** **3aa/3aa-d_4**

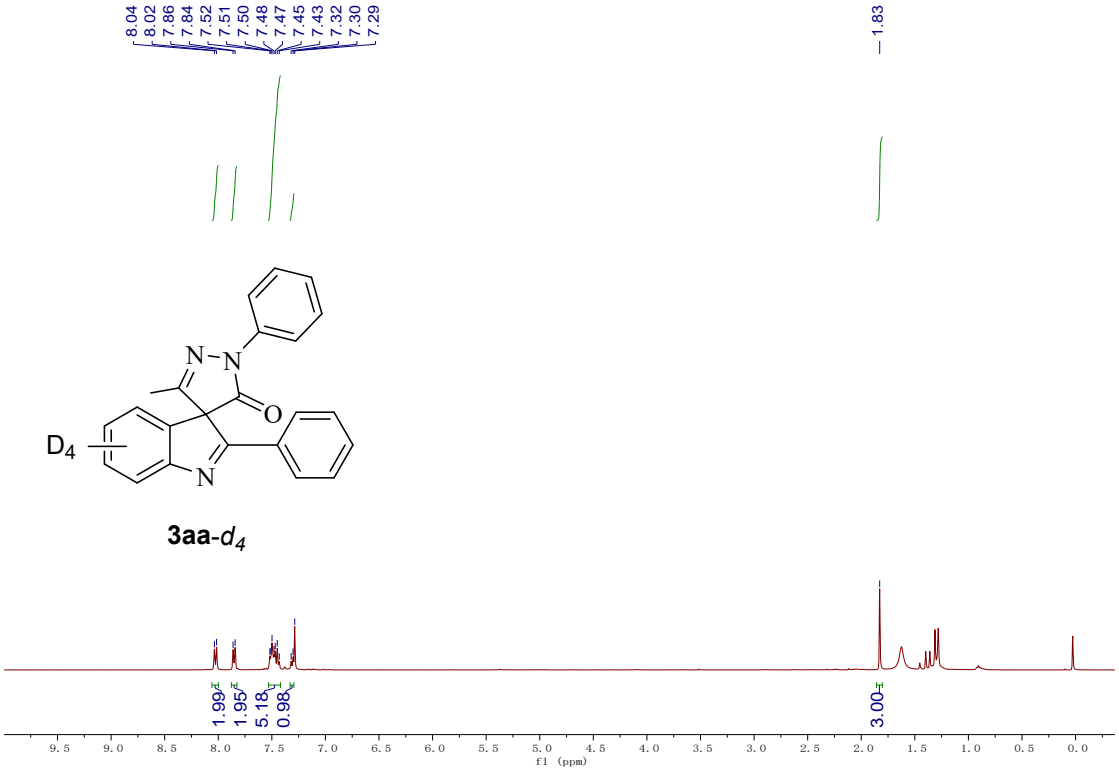
To a tube charged with N-phenylbenzamidine **1a** (0.2 mmol, 39.3 mg), N-phenylbenzamidine **1a-*d5*** (0.2 mmol, 43.8 mg), $[RuCl_2(p\text{-cymene})]_2$ (5 mol %, 6.1 mg), $AgBF_4$ (20 mol %, 7.76 mg), $NaHCO_3$ (1.4 equiv, 23.5 mg), diazopyrazolones **2a** (0.24 mmol, 48 mg), were added sequentially and dissolved in dichloroethane (2.0 mL) under air atmosphere. The mixture was stirred at 100 °C for 12 h. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using ethyl acetate /petroleum ether (1: 25~1: 15) as eluent to afford the desired product of **3aa** and **3aa**-*d4*. Based on the ^{1}H NMR spectrum of the mixture, the ratio of **3aa** to **3aa**-*d*4 was determined to be 16:9. Accordingly, the intermolecular KIE (k_H/k_D) was calculated to be 2.2.



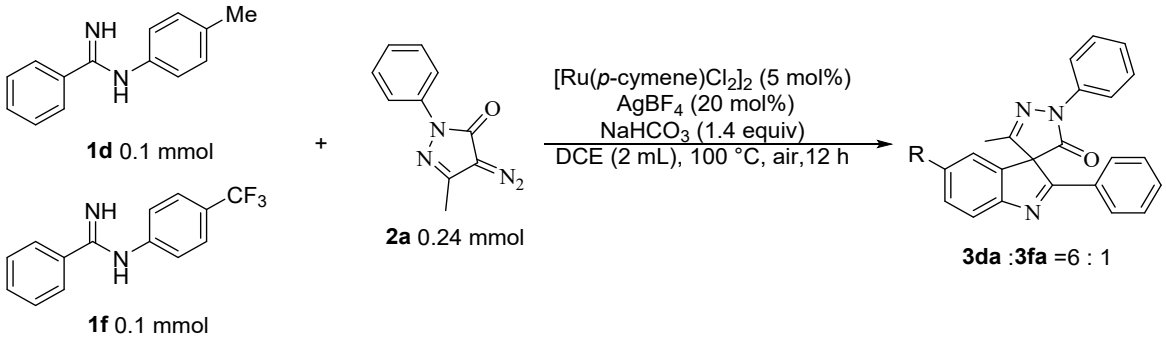
3. Parallel kinetic isotope effect



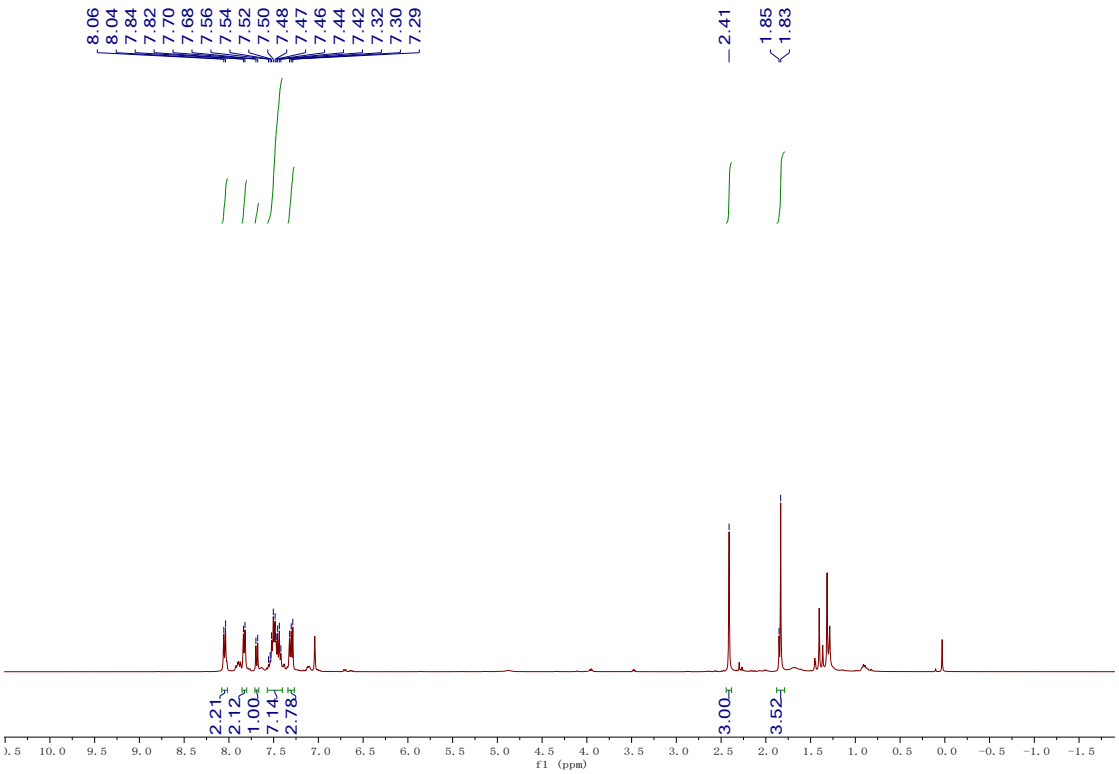
To the tube separately charged with N-phenylbenzamidine **1a** (0.2 mmol, 39.3 mg), N-phenylbenzamidine **1a-*d5*** (0.2 mmol, 43.8 mg), then $[RuCl_2(p\text{-cymene})]_2$ (5 mol %, 6.1 mg), $AgBF_4$ (20 mol %, 7.76 mg), $NaHCO_3$ (1.4 equiv, 23.5 mg), diazopyrazolones **2a** (0.24 mmol, 48 mg) were added sequentially and dissolved in dichloroethane (2.0 mL) under air atmosphere. These reactions were stirred at 100 °C for 12 h. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using ethyl acetate /petroleum ether (1: 25~1: 15) as eluent to afford the desired product of **3aa** and**3aa-*d4***. **3aa** and **3aa-*d4*** was obtained in 80 % and 37 % yield. Accordingly, the parallel kinetic isotope (k_H/k_D) was calculated to be 2.2.



4. Competitive Reaction



To a tube charged with N-phenylbenzamidine (**1d**, 21.0 mg, 0.10 mmol), (**1f**, 26.4 mg, 0.10 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol %, 6.1 mg), $AgBF_4$ (20 mol %, 7.76 mg), $NaHCO_3$ (1.4 equiv, 23.5 mg), diazopyrazolones **2a** (0.24 mmol, 48 mg), were added sequentially and dissolved in dichloroethane (2.0 mL) under air atmosphere. The mixture was stirred at 100 ℃ in oil bath for 12 h. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using ethyl acetate /petroleum ether (1: 25~1: 15) as eluent to afford the desired product of **3da** and **3fa**. Based on the 1H NMR spectrum of the mixture, the ratio of **3da** to **3fa** was determined to be 6:1.



5. X-ray Crystallographic data of 3aa

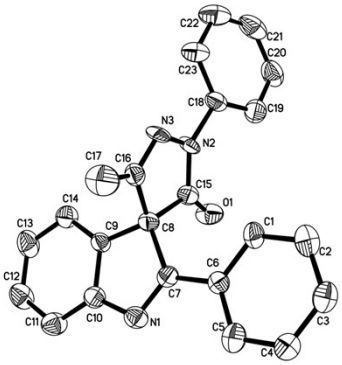


Figure S1. X-ray molecular structure of 3aa with the probability at 50% level.

The single crystal of compound **3aa** was prepared by the slow evaporation from the solution of DCM and methanol with the compounds **3aa** at room temperature. The structures of **3aa** were determined by the X-ray diffraction. Further information can be found in the CIF file. These crystals were deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC **2192315**. ORTEP view of complex Ellipsoids are represented at the 50% probability level.

Table 1 Crystal data and structure refinement for 3aa.

Empirical formula	$C_{23}H_{17}N_3O$
Formula weight	351.39
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.8882(10)
b/Å	9.6114(14)
c/Å	17.595(3)
α/°	90
β/°	98.512(10)
γ/°	90
Volume/Å^3	1821.0(4)
Z	4
ρ_{calc}g/cm^3	1.282
μ/mm^{-1}	0.080
F(000)	736.0
Crystal size/mm^3	0.17 × 0.12 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.998 to 52.744
Index ranges	$-13 \le h \le 11$, $-6 \le k \le 12$, $-21 \le l \le 21$
Reflections collected	7901
Independent reflections	3708 [R_{int} = 0.0427, R_{sigma} = 0.0834]
Data/restraints/parameters	3708/13/262
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0804, wR_2 = 0.1429

Final R indexes [all data]	$R_1 = 0.1773$, $wR_2 = 0.1885$
Largest diff. peak/hole / e Å^{-3}	0.14/-0.19

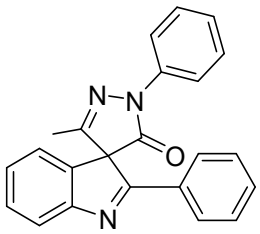
References

(1) Ren, J.; Huang, Y. Z.; Pi, C.; Cui, X. L.; Wu, Y. J. Rhodium(III)-catalyzed [4+2] annulation of N-arylbenzamidines with 1,4,2-dioxazol-5-ones: Easy access to 4-aminoquinazolines via highly selective C- H bond activation. *Chin. Chem. Lett.* **2021**, *32*, 2592-2596.

(2) Fang, F. F.; Hu, S. L.; Li, C. P.; Wang, Q.; Wang, R.; Han, X.; Zhou, Y.; Liu, H. Catalytic System-Controlled Divergent Reaction Strategies for the Construction of Diversified Spiropyrazolone Skeletons from Pyrazolidinones and Diazopyrazolones. *Angew. Chem.-Int. Edit.* **2021**, *60*, 21327-21333.

Characterization data for products

3'-methyl-1',2-diphenylspiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3aa)



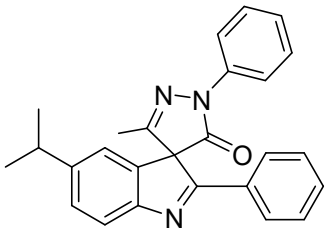
White solid. 28.1 mg, Yield: 80 %, mp 180-182 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.6 Hz, 2H), 7.86 (d, J = 7.0 Hz, 2H), 7.82 (d, J = 7.8 Hz, 1H), 7.57 – 7.41 (m, 6H), 7.31 (q, J = 7.3 Hz, 2H), 7.25 (d, J = 7.5 Hz, 1H), 1.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 168.5, 159.1, 157.2, 138.0, 134.7, 132.1, 131.9, 130.3, 129.4, 129.1, 127.5, 127.3, 125.7, 121.8, 121.7, 119.0, 74.9, 27.0, 14.2.

HRMS (ESI) *m/z* Calcd for $C_{23}H_{17}N_3O$ $[M+H]^+$ 352.1444, found 352.1445.

5-chloro-3'-methyl-1',2-diphenylspiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3ba)



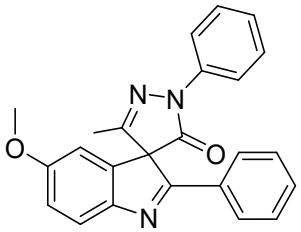
White oil. 27.9 mg, Yield: 71 %, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.4 Hz, 2H), 7.86 (d, *J* = 6.8 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.56 - 7.36 (m, 6H), 7.36 - 7.26 (m, 1H), 7.09 (d, *J* = 1.7 Hz, 1H), 3.08 - 2.85 (m, 1H), 1.84 (s, 3H), 1.28 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 168.7, 159.4, 155.3, 148.8, 138.1, 134.9, 132.1, 131.8, 129.4, 129.2, 128.3, 127.3, 125.7, 121.5, 119.7, 119.0, 74.9, 34.3, 24.3, 24.1, 14.2.

HRMS (ESI) *m/z* Calcd for $C_{26}H_{23}N_3O$ $[M+H]^+$ 394.1914, found 394.1916.

5-isopropyl-3'-methyl-1',2-diphenylspiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3ca)



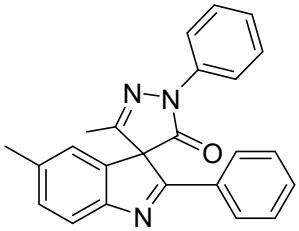
White solid. 27.8 mg,Yield: 73 %, mp 135-136 ℃. column chromatography eluent, PE/EtOAc = 25:1 → 15:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.7 Hz, 2H), 7.81 (d, *J* = 6.7 Hz, 2H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.55 - 7.38 (m, 5H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.03 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.78 (d, *J* = 2.5 Hz, 1H), 3.83 (s, 3H), 1.85 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 167.6, 159.4, 159.3, 150.8, 138.0, 136.3, 132.1, 131.6, 129.4, 129.2, 127.1, 125.7, 122.3, 119.0, 115.3, 107.9, 75.0, 55.9, 14.2.

HRMS (ESI) *m/z* Calcd for $C_{24}H_{19}N_3O_2$ $[M+H]^+$ 382.1550, found 382.1552.

5-fluoro-3'-methyl-1',2-diphenylspiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3da)



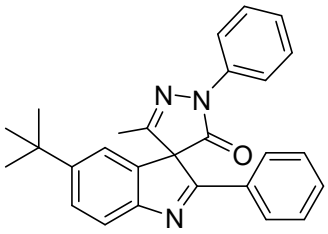
White solid. 37.8 mg, Yield: 88 %, mp 140-142 ℃. column chromatography eluent, PE/EtOAc = 25:1 → 15:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.5 Hz, 2H), 7.77 (dd, *J* = 17.9, 8.0 Hz, 3H), 7.55 - 7.44 (m, 3H), 7.33 - 7.20 (m, 5H), 2.40 (s, 3H), 1.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 168.6, 159.2, 157.4, 142.8, 138.0, 134.6, 130.2, 130.2, 129.2, 129.1, 127.5, 127.0, 125.7, 121.6, 121.6, 119.0, 74.8, 27.9, 14.2.

HRMS (ESI) *m/z* Calcd for $C_{24}H_{19}N_3O$ $[M+H]^+$ 366.1601, found 366.1598.

5-methoxy-3'-methyl-1',2-diphenylspiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3ea)



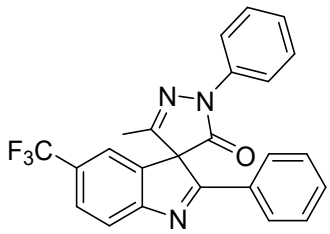
White solid. 26.5 mg, Yield: 65 %, mp 129-130 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.8 Hz, 3H), 7.85 (d, *J* = 7.0 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.60 - 7.39 (m, 6H), 7.36 - 7.26 (m, 1H), 7.21 (d, *J* = 1.9 Hz, 1H), 1.84 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (100MHz, $CDCl_3$) 169.1, 168.7, 159.4, 154.9, 151.2, 138.08, 134.6, 132.1, 131.8, 129.4, 129.2, 127.4, 127.3, 125.7, 121.1, 119.1, 118.4, 75.0, 35.2, 31.6, 14.2.

HRMS (ESI) *m/z* Calcd for $C_{27}H_{25}N_3O$ $[M+H]^+$: 408.2070, found 408.2071.

7-bromo-3'-methyl-1',2-diphenylspiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3fa)



White soild. 19.3 mg, Yield: 50 %, mp 151-152 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 10:1

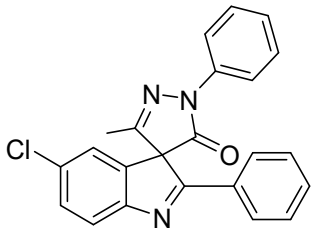
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 1.9 Hz, 1H), 8.06 – 8.00 (m, 1H), 7.95 (d, J = 8.1 Hz, 2H), 7.86 (d, J = 7.8 Hz, 1H), 7.74 (d, J = 8.1 Hz, 2H), 7.57 (t, J = 7.7 Hz, 1H), 7.43 (t, 3H), 7.27 (s, 1H), 1.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 167.9, 159.0, 156.8, 138.9, 134.9, 133.2 (q, J = 33.2 Hz),132.8, 131.3, 129.6, 129.2, , 126.4 (q, J = 3.7 Hz), 127.8, 126.0,124.7 (q, J = 272.7 Hz), 121.9, 118.9, (q, J = 3.4 Hz), 74.9, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.63.

HRMS (ESI) *m/z* Calcd for $C_{24}H_{16}F_3N_3O$ $[M+H]^+$ 386.1055, found 386.1057.

3'-methyl-1',2-diphenyl-5-(trifluoromethyl)spiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3ga)



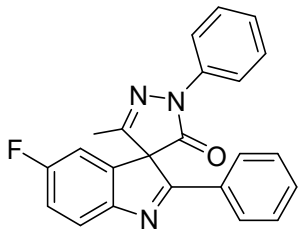
Yellow solid. 15.4 mg, Yield: 40 %, mp 155-156 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

^{1}H NMR (400 MH z, $CDCl_3$) δ 8.02 (d, *J* = 7.5 Hz, 2H), 7.84 (d, *J* = 7.1 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.56 - 7.41 (m, 6H), 7.36 - 7.26 (m, 1H), 7.23 (d, *J* = 2.1 Hz, 1H), 1.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 167.8, 158.4, 155.7, 137.8, 136.1, 132.9, 132.4, 131.6, 130.5, 129.5, 129.2, 127.5, 125.9, 122.6, 122.2, 119.1, 74.8, 14.2.

HRMS (ESI) *m/z* Calcd for $C_{23}H_{16}ClN_3O$ $[M+H]^+$ 386.1055, found 386.1057.

3',7-dimethyl-1',2-diphenylspiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3ha)



White soild. 16.6 mg, Yield: 45 %, mp 171-178 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

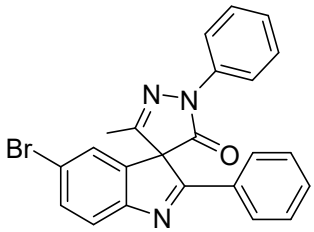
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23(s, 1H), 8.04 (d, *J* = 9.42 Hz, 1H), 7.8 (d, *J* = 7.0 Hz, 2H), 7.8 (d, *J* = 7.6 Hz, 1H), 7.54 - 7.43 (m, 6H), 7.32 - 7.29 (t, 2H), 7.26 (d, *J* = 2.1 Hz, 1H), 1.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4 (d, J = 3.7 Hz), 167.9, 161.8 (d, J = 248.1 Hz), 158.9, 153.4, 138.9, 136.0 (d, J = 9.4 Hz), 132.2, 131.6, 130.5, 129.5, 127.1, 127.2, 122.8, 122.7(d, J = 9.4 Hz), 117.4, 117.3, 117.1, 109.7 (q, J = 25.8 Hz), 75.1, 14.3

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.13.

HRMS(ESI)m/z Calcd for $C_{23}H_{16}FN_3O$ $[M+H]^+$ 370.1350, found 370.1349.

5-bromo-3'-methyl-1',2-diphenylspiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3ia)



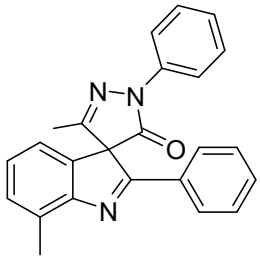
White solid. 19.3 mg, Yield: 45 %, mp 188-190 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.4 Hz, 2H), 7.84 (d, *J* = 7.2 Hz, 2H), 7.72 - 7.62 (m, 2H), 7.56 - 7.41 (m, 5H), 7.38 (s, 1H), 7.36 - 7.26 (m, 1H), 1.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 167.8, 158.8, 156.1, 138.9, 136.2, 133.6, 132.5, 131.4, 130.5, 129.6, 128.7, 127.5, 125.1., 123.1, 122.9, 121.7, 120.7, 117.1, 74.7, 14.3.

HRMS (ESI) *m/z* Calcd for $C_{23}H_{16}BrN_3O$ $[M+H]^+$ 386.1055, found 386.1057.

3',6-dimethyl-1',2-diphenylspiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3ja)



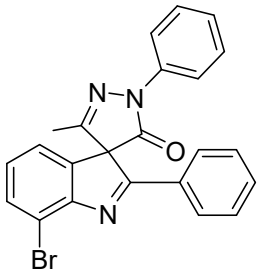
White solid. 15.3 mg, Yield: 42 %, mp 139-140 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

^{1}H NMR (400 MHz, $CDCl_3$) 8.03 (d, *J* = 7.5 Hz, 2H), 7.87 (d, *J* = 6.8 Hz, 2H), 7.54 – 7.40 (m, 5H), 7.35 – 7.25 (m, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 2.74 (s, 3H), 1.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) 169.9, 167.8, 158.8, 156.1, 138.9, 136.2, 133.6, 132.5, 131.4, 130.5, 129.6, 128.7, 127.5, 124.9, 123.1, 122.9, 121.7, 120.7, 117.1, 14.3.

HRMS (ESI) m/z Calcd for $C_{24}H_{19}N_3O$ $[M+H]^+$: 366.1601, found 366.1599.

6-bromo-3'-methyl-1',2-diphenylspiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3ka)



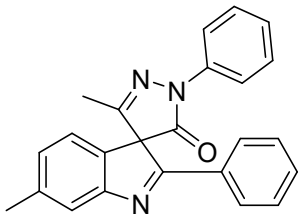
White solid. 19.3 mg, Yield: 45 %, mp 130-131 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.4 Hz, 2H), 7.89 (d, *J* = 6.8 Hz, 2H), 7.54 (dd, *J* = 13.8, 7.4 Hz, 4H), 7.47 - 7.41 (m, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 6.97 (t, *J* = 7.9 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 2.16 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 162.3, 153.3, 138.0, 134.0, 133.5, 132.9, 131.5, 129.0, 128.9, 126.6, 125.4, 125.0, 124.5, 118.9, 116.4, 110.3, 72.7, 14.2.

HRMS (ESI) m/z Calcd for $C_{23}H_{16}BrN_3O$ $[M+H]^+$ 430.0550, found 430.0551.

3',6-dimethyl-1',2-diphenylspiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3la)



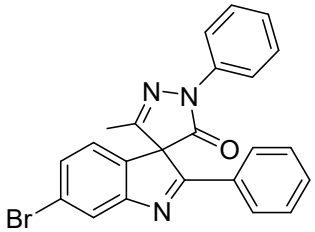
White solid. 31.03 mg, Yield: 85 %, mp 134-136 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.5 Hz, 2H), 7.87 (d, *J* = 6.8 Hz, 2H), 7.54 – 7.40 (m, 5H), 7.30 (td, *J* = 7.5, 3.4 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 2.74 (s, 3H), 1.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 168.7, 159.3, 157.5, 140.6, 138.1, 132.0, 132.0 131.8, 129.4, 129.1, 127.9, 127.4, 125.7, 122.5, 121.3, 119.0, 74.6, 21.7, 14.2.

HRMS (ESI) m/z Calcd for $C_{24}H_{19}N_3O$ $[M+H]^+$ 366.1601, found :366.1598.

6-bromo-3'-methyl-1',2-diphenylspiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3ma)



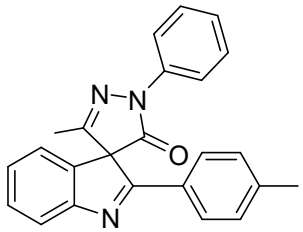
White solid. 18.5 mg, Yield: 43 %, mp 152-154 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.1 Hz, 2H), 7.97 (s, 1H), 7.85 (d, *J* = 7.4 Hz, 2H), 7.49 (dd, *J* = 19.4, 8.8 Hz, 6H), 7.31 (t, *J* = 8.7 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 1.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 167.8, 158.6, 158.4, 137.8, 133.5, 132.5, 131.5, 130.0, 129.5, 129.2, 127.6, 125.9, 125.2, 123.9, 122.8, 119.0, 74.6, 14.3.

HRMS (ESI) m/z Calcd for $C_{23}H_{16}BrN_3O$ $[M+H]^+$: 430.0550, found : 430.0547.

3'-methyl-1'-phenyl-2-(p-tolyl)spiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3na)



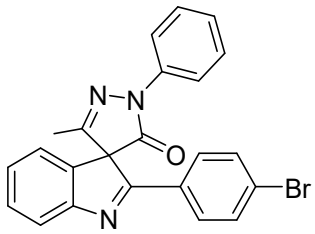
White solid. 25.6 mg, Yield: 70 %, mp 152-153 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.6 Hz, 2H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.55 - 7.45 (m, 3H), 7.34 - 7.20 (m, 5H), 2.40 (s, 3H), 1.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 168.6, 159.2, 157.4, 142.8, 138.0, 134.6, 130.2, 130.2, 129.2, 129.1, 127.5, 127.0, 125.7, 121.6, 121.6, 119.0, 74.8, 21.6, 14.2.

HRMS (ESI) m/z Calcd for $C_{24}H_{19}N_3O$ $[M+H]^+$ 366.1601, found : 366.1604.

2-(4-bromophenyl)-3'-methyl-1'-phenylspiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3oa)



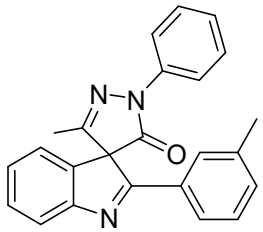
White solid. 28.3 mg, Yield: 66%, mp 188-190 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.5 Hz, 2H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.52 (dd, *J* = 18.3, 8.2 Hz, 3H), 7.38 - 7.26 (m, 3H), 7.25 (d, *J* = 6.9 Hz, 3H), 1.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 168.2, 158.8, 157.3, 137.9, 134.6, 132.7, 130.8, 130.4, 129.2, 128.8, 127.5, 126.9, 125.9, 122.0, 121.7, 119.0, 74.8, 14.2.

HRMS (ESI) m/z Calcd for $C_{23}H_{16}N_3O$ $[M+H]^+$ 430.0550, found 430.0548.

3'-methyl-1'-phenyl-2-(m-tolyl)spiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3pa)



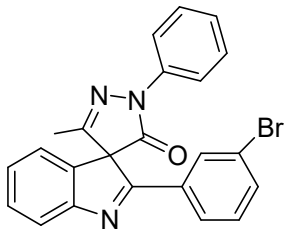
White solid. 24.8 mg, Yield: 68%, mp 148-149 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.5 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.51 (q, *J* = 8.7 Hz, 4H), 7.36 – 7.26 (m, 4H), 7.25 (d, *J* = 6.6 Hz, 1H), 2.38 (s, 3H), 1.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 168.6, 159.2, 157.2, 139.2, 138.0, 134.7, 133.0, 131.8, 130.2, 129.3, 129.1, 128.1, 127.2, 125.8, 124.5, 121.7, 119.1, 21.4, 14.2.

HRMS (ESI) m/z Calcd for $C_{24}H_{19}N_3O$ $[M+H]^+$: 366.1601, found 366.1603.

2-(3-bromophenyl)-3'-methyl-1'-phenylspiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3qa)



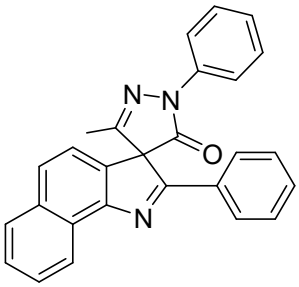
White solid. 14.2 mg, Yield: 33%, mp 187-189 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.1 Hz, 2H), 7.97 (s, 1H), 7.85 (d, *J* = 7.4 Hz, 2H), 7.49 (dd, *J* = 19.4, 8.8 Hz, 6H), 7.31 (t, *J* = 8.7 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 1.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 167.8, 158.6, 158.4, 137.8, 133.5, 132.5, 131.5, 130.0, 129.5, 129.2, 127.6, 125.9, 125.2, 123.9, 122.8, 119.0, 74.6, 14.3.

HRMS (ESI) m/z Calcd for $C_{23}H_{16}BrN_3O$ $[M+H]^+$ 430.0550, found 430.0548.

3'-methyl-1',2-diphenylspiro[benzo[g]indole-3,4'-pyrazol]-5'(1'*H*)-one (3ra)



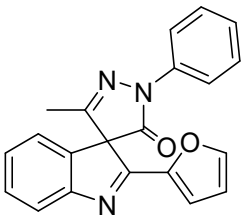
White solid. 30.1 mg, Yield: 75%, mp 146-148 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 9.5 Hz, 1H), 8.07 (d, *J* = 7.4 Hz, 2H), 7.97 (t, *J* = 7.9 Hz, 3H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.56 – 7.44 (m, 5H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 5.7 Hz, 1H), 1.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 168.2, 159.0, 154.1, 138.1, 134.7, 132.2, 131.9, 130.8, 129.4, 129.2, 128.2, 127.9, 127.5, 127.4, 127.2, 127.0, 125.7, 123.9, 119.1, 118.3, 76.0, 14.3.

HRMS (ESI) m/z Calcd for $C_{27}H_{19}N_3O$ $[M+H]^+$ 402.1601, found 402.1602.

2-(furan-2-yl)-3'-methyl-1'-phenylspiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3sa)



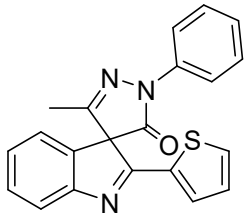
White solid. 28.3 mg, Yield: 83 %, mp 132-134 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 - 7.97 (m, 2H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 1.7 Hz, 1H), 7.50 (m, *J* = 8.7, 7.4, 1.5 Hz, 3H), 7.34 - 7.23 (m, 3H), 7.03 (d, *J* = 3.6 Hz, 1H), 6.56 (dd, *J* = 3.6, 1.8 Hz, 1H), 1.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 160.0, 157.9, 157.6, 147.4, 146.7, 138.0, 133.4, 130.4, 129.1, 127.2, 125.7, 122.0, 121.8, 119.0, 115.0, 113.1, 74.4, 14.1.

HRMS (ESI) m/z Calcd for $C_{21}H_{15}N_3O_2$ $[M+Na]^+$ 364.1056, found 364.1056.

3'-methyl-1'-phenyl-2-(thiophen-2-yl)spiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3ta)



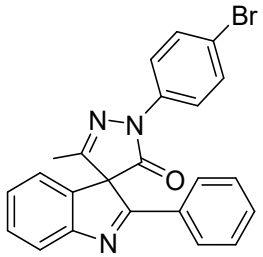
White solid. 24.3 mg, Yield: 68 %, mp 217-219 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 13:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 - 8.01 (m, 2H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.57 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.54 - 7.46 (m, 3H), 7.34 - 7.27 (m, 2H), 7.27 - 7.22 (m, 2H), 7.08 (dd, *J* = 5.0, 3.9 Hz, 1H), 1.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 163.9, 159.0, 157.4, 137.9, 136.1, 134.2, 131.8, 130.4, 129.3, 129.2, 128.8, 127.1, 125.7, 121.9, 121.5, 119.0, 74.9, 14.2.

HRMS (ESI) *m/z* Calcd for $C_{21}H_{15}N_3OS$ $[M+H]^+$ 358.1009, found 358.1007.

1'-(4-bromophenyl)-3'-methyl-2-phenylspiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3ab)



White solid. 28.3 mg, Yield: 66 %, mp 160-162 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

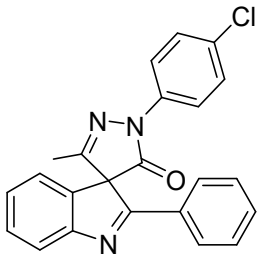
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 - 7.97 (m, 2H), 7.87 - 7.80 (m, 3H), 7.52 (q, *J* = 7.4 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 8.7 Hz, 2H), 1.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 168.2, 158.8, 157.0, 137.9, 134.6, 132.7, 130.7,

130.4, 129.18, 128.8, 127.5, 126.9, 125.9, 121.9, 121.7, 119.0, 74.8, 14.2.

HRMS (ESI) m/z Calcd for $C_{23}H_{16}BrN_3O$ $[M+H]^+$ 430.0550, found 430.0548

1'-(4-chlorophenyl)-3'-methyl-2-phenylspiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3ac)



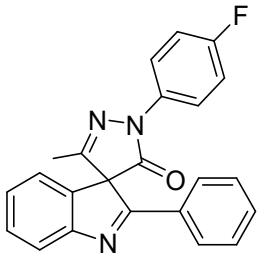
White solid. 32.8 mg, Yield: 85 %, mp 152-154 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

^{1}H NMR (400 MHz, $CDCl_3$) 8.01 (d, *J* = 8.9 Hz, 2H), 7.83 (d, *J* = 8.9 Hz, 3H), 7.52 (q, *J* = 7.4 Hz, 2H), 7.45 (dd, *J* = 8.1, 5.8 Hz, 4H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 1H), 1.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 168.4, 159.5, 157.2, 136.5, 134.5, 132.2, 131.8, 130.8, 130.4, 129.5, 129.2, 127.4, 127.3, 121.9, 121.6, 120.1, 74.8, 14.2.

HRMS (ESI) m/z Calcd for $C_{23}H_{16}ClN_3O$ $[M+H]^+$ 430.0550, found 430.0548

1'-(4-fluorophenyl)-3'-methyl-2-phenylspiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3ad)



White solid. 23.3 mg, Yield:63 %, mp 168-170 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 - 7.97 (m, 2H), 7.87 - 7.80 (m, 3H), 7.52 (q, *J* = 7.4 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 8.7 Hz, 2H), 1.83 (s, 3H).

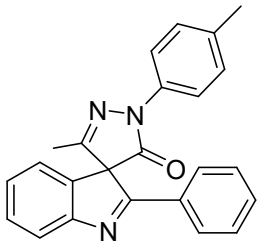
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 168.4, 160.3 (d, *J* = 244.2 Hz), 159.3, 157.2,

134.6, 134.1 (d, *J* = 2.8 Hz), 134.1, 131.9, 130.3, 129.4, 127.4, 127.3, 121.9, 121.6, 120.8, 120.8, 115.9 (d, *J* = 22.9 Hz), 74.8, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.09.

HRMS (ESI) m/z Calcd for $C_{23}H_{16}FN_3O$ $[M+H]^+$:370.1350, found 370.1349

3'-methyl-2-phenyl-1'-(p-tolyl)spiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3ae)



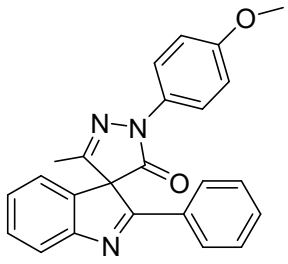
White solid. 31.3 mg, Yield: 85 %, mp 155-156 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.87 (d, *J* = 7.2 Hz, 2H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.49 (m, *J* = 23.0, 7.1 Hz, 4H), 7.31 (d, *J* = 8.0 Hz, 3H), 7.25 (d, *J* = 7.4 Hz, 1H), 2.43 (s, 3H), 1.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 168.3, 158.9, 157.2, 135.6, 135.5, 134.8, 132.1, 131.9, 130.2, 129.7, 129.4, 127.5, 127.2, 121.8, 121.7, 119.1, 74.9, 21.0, 14.2.

HRMS (ESI) m/z Calcd for $C_{24}H_{19}N_3O$ $[M+H]^+$ 366.1601, found 366.1603.

1'-(4-methoxyphenyl)-3'-methyl-2-phenylspiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3af)



White solid. 25.2 mg, Yield: 68 %, mp 135-136 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

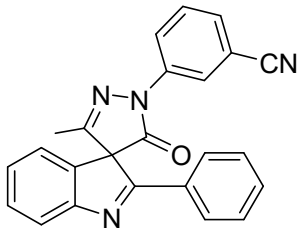
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 9.1 Hz, 2H), 7.86 (d, *J* = 7.2 Hz, 2H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.45 (t, J = 7.3 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 9.2 Hz, 1H), 7.02 (d, *J* = 9.1 Hz, 2H), 3.87 (s, 3H), 1.81 (s, 3H).

^{13}C NMR (100 MHz, CDCl3) δ 169.9, 168.2, 158.9, 157.5, 157.2, 134.7, 132.0, 131.9,

131.3, 130.2, 129.4, 127.5, 127.2, 121.8 121.7, 120.9, 114.3, 74.7, 55.6, 14.2.

HRMS (ESI) m/z Calcd for $C_{24}H_{19}N_3O_2$ $[M+H]^+$ 382.1550, found 382.1548

3-(3'-methyl-5'-oxo-2-phenylspiro[indole-3,4'-pyrazol]-1'(5'*H*)-yl)benzonitrile (3ag)



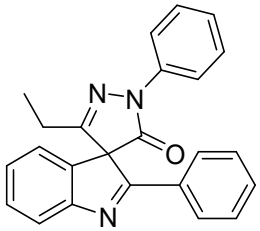
White solid. 24.4 mg, Yield: 64 %, mp 193-194 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 13.2 Hz, 2H), 7.82 (t, J = 8.0 Hz, 3H), 7.56 (dd, J = 18.6, 8.0 Hz, 4H), 7.53 – 7.41 (m, 2H), 7.33 (t, J = 7.7 Hz, 1H), 7.23 (d, J = 7.5 Hz, 1H), 1.85 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.29, 168.73, 160.18, 157.17, 138.60, 134.30, 132.25, 131.71, 130.55, 130.11, 129.52, 128.77, 127.40, 127.35, 122.44, 122.01, 121.77, 121.59, 118.33, 113.30, 74.76, 14.25.

HRMS (ESI) m/z Calcd for $C_{24}H_{16}N_4O$ $[M+H]^+$ 377.1396, found 377.1400

3'-ethyl-1',2-diphenylspiro[indole-3,4'-pyrazol]-5'(1'*H*)-one (3ah)



White solid. 15.3 mg, Yield: 42 %, mp 138-140 ℃, column chromatography eluent, PE/EtOAc = 25:1 → 15:1

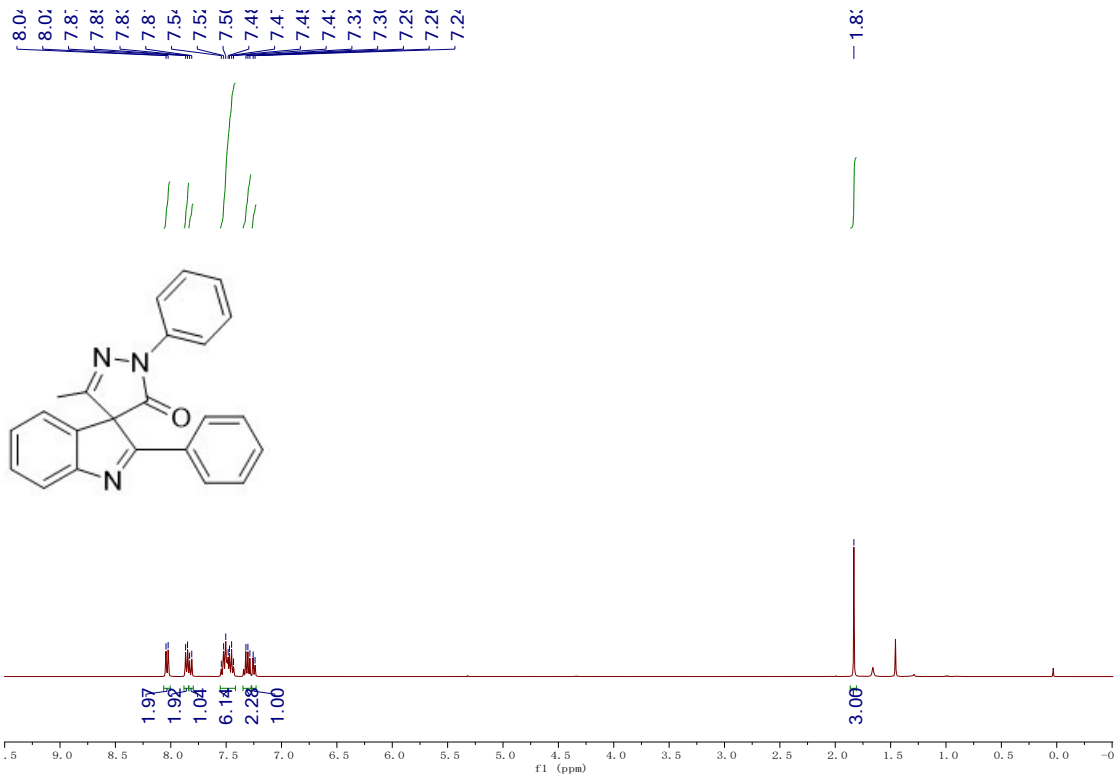
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.4 Hz, 2H), 7.86 (d, *J* = 6.9 Hz, 2H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.56 – 7.46 (m, 4H), 7.45 (t, *J* = 7.3 Hz, 2H), 7.35 – 7.26 (m, 2H), 7.25 (d, *J* = 7.5 Hz, 1H), 2.13 (dd, *J* = 7.4, 3.5 Hz, 2H), 1.05 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 168.5, 163.2, 157.1, 138.1, 135.1, 132.1, 132.0, 130.2, 129.4, 129.1, 127.5, 127.2, 125.7, 121.8, 121.7, 119.1, 74.7, 22.4, 9.9.

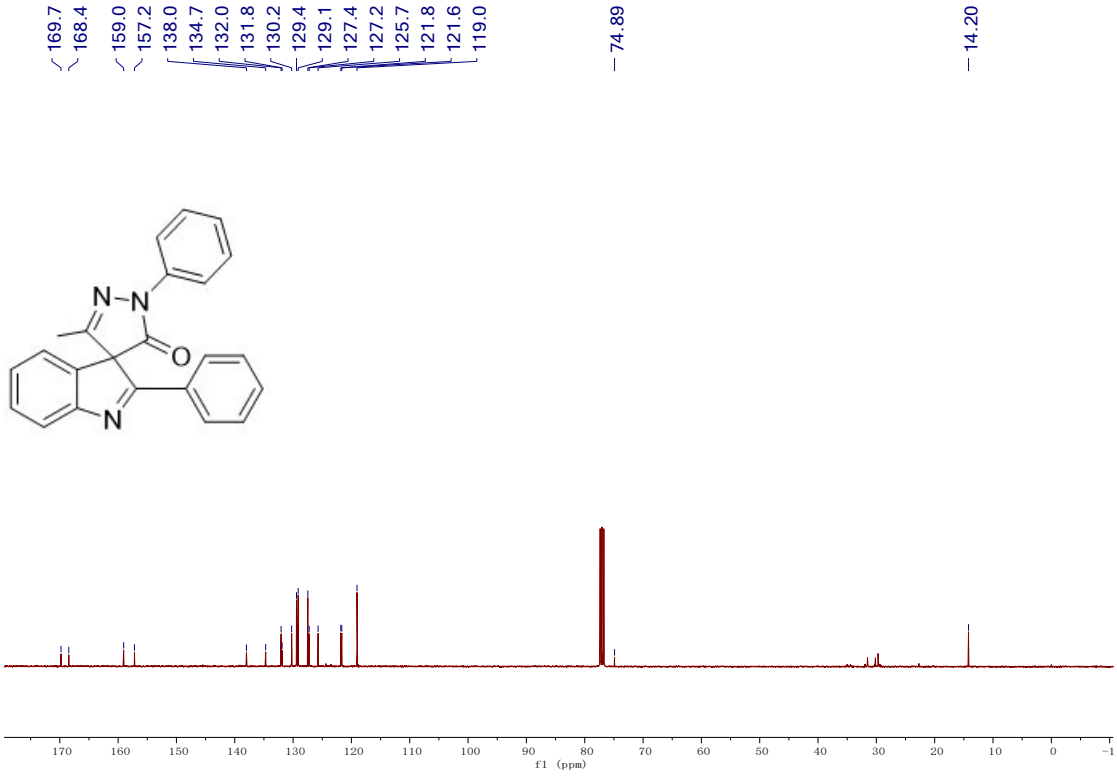
HRMS (ESI) m/z Calcd for $C_{24}H_{19}N_3O$ $[M+H]^+$ 366.1601, found 366.1600

NMR spectra of products

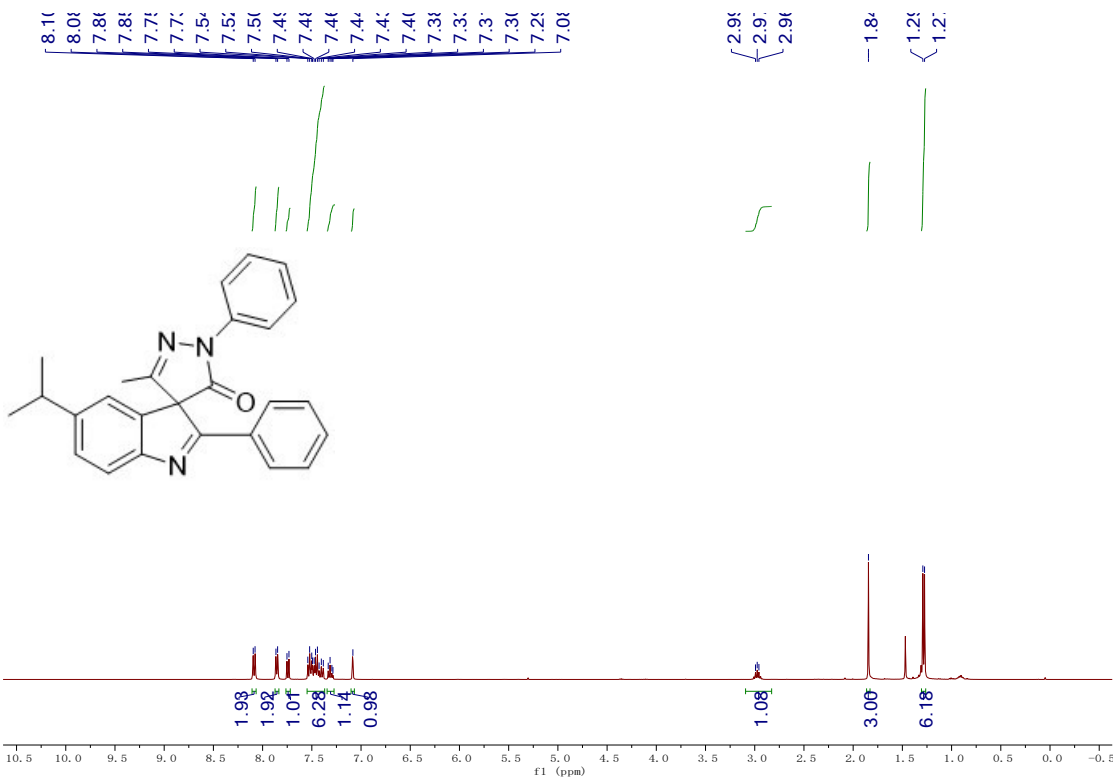
^{1}H NMR($CDCl_3$) spectrum of **3aa**



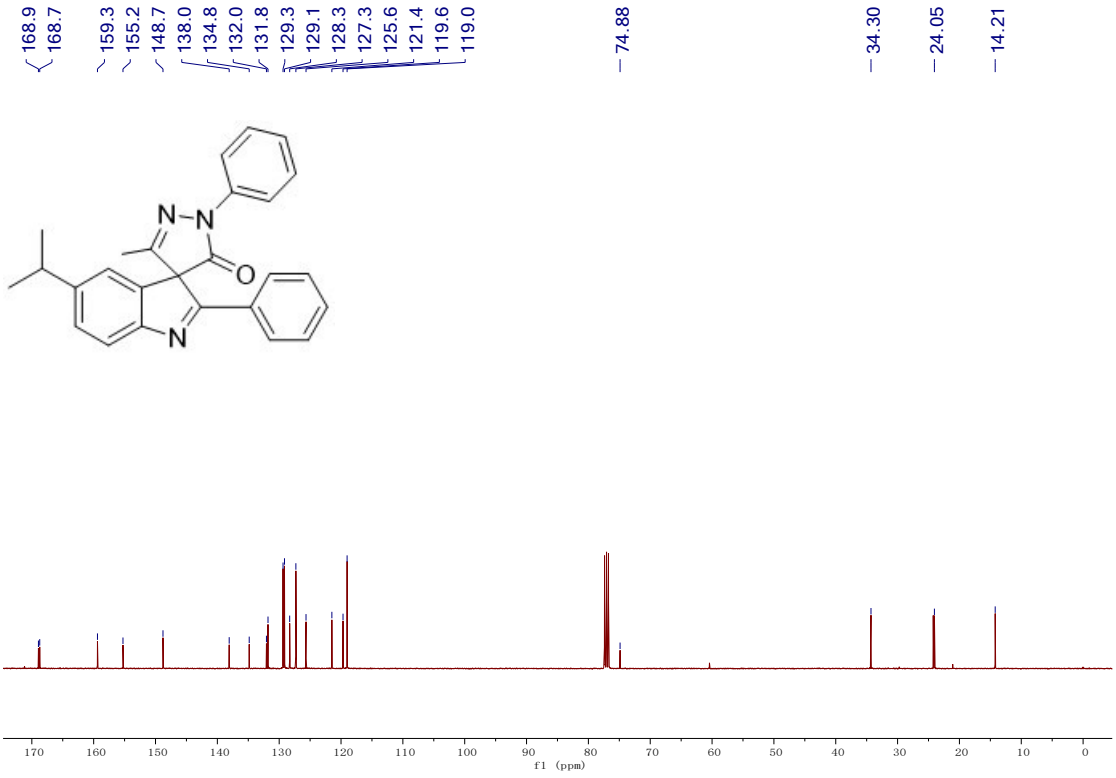
^{13}C NMR($CDCl_3$) spectrum of **3aa**



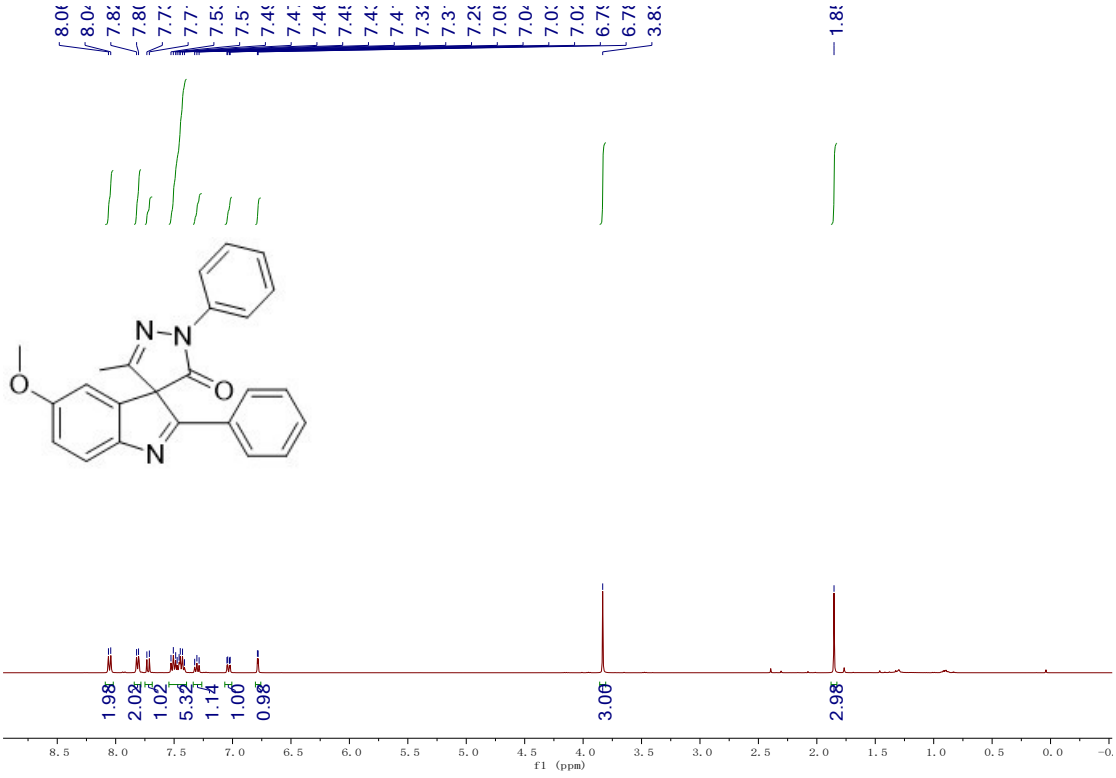
^{1}H NMR($CDCl_3$) spectrum of **3ba**



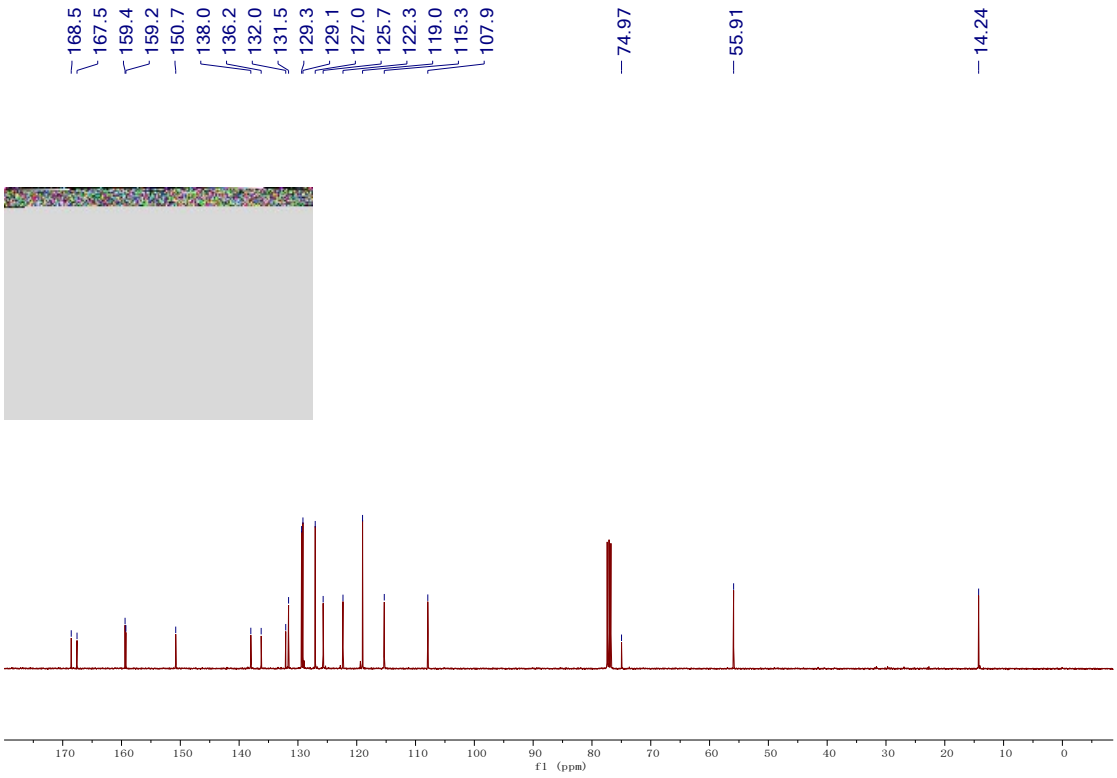
^{13}C NMR($CDCl_3$) spectrum of **3ba**



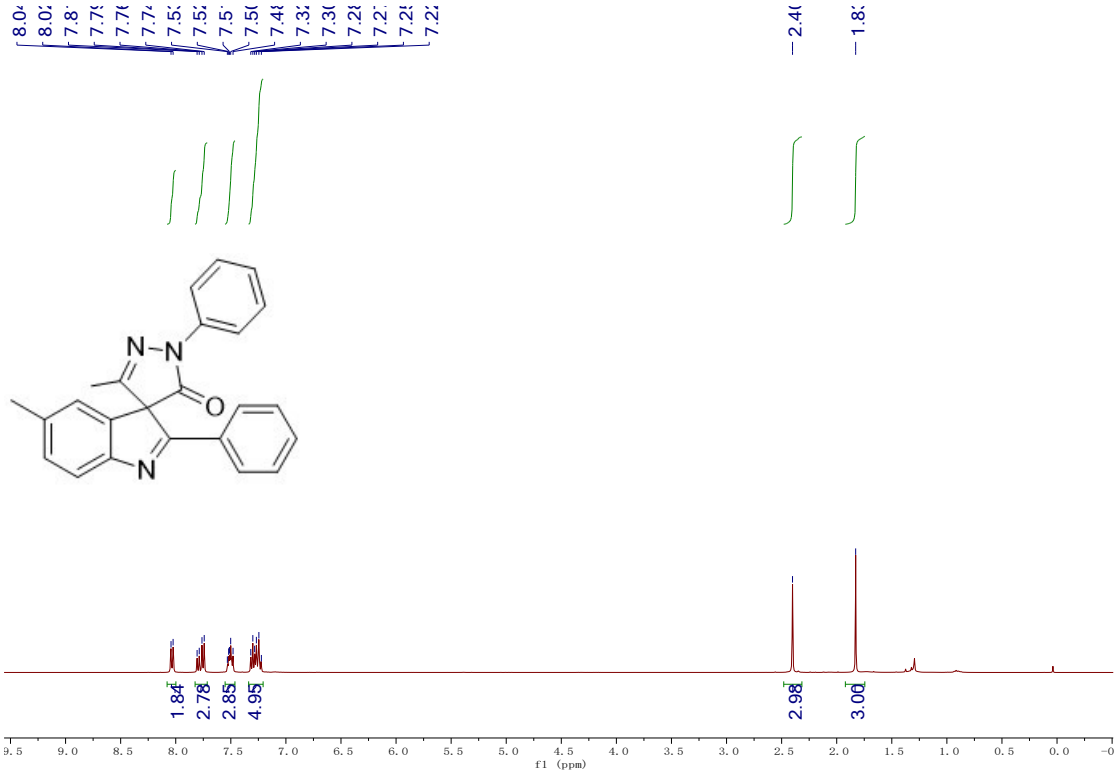
^{1}H NMR($CDCl_3$) spectrum of **3ca**



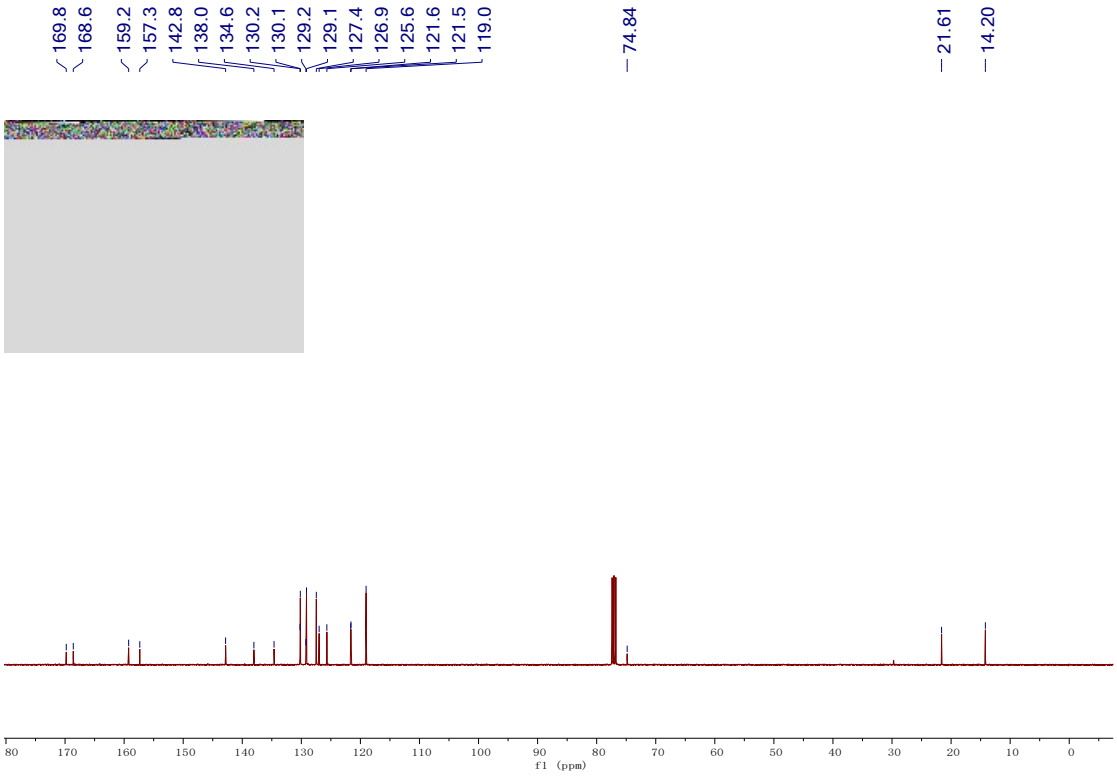
^{13}C NMR($CDCl_3$) spectrum of **3ca**



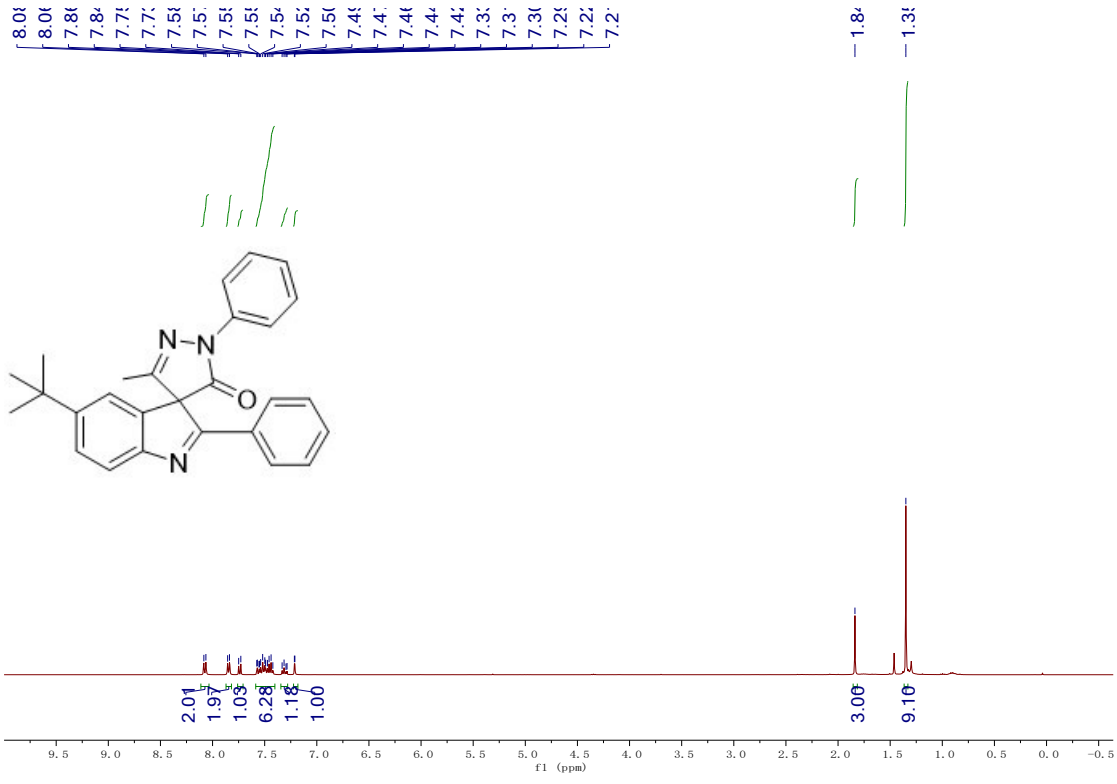
^{1}H NMR($CDCl_3$) spectrum of **3da**



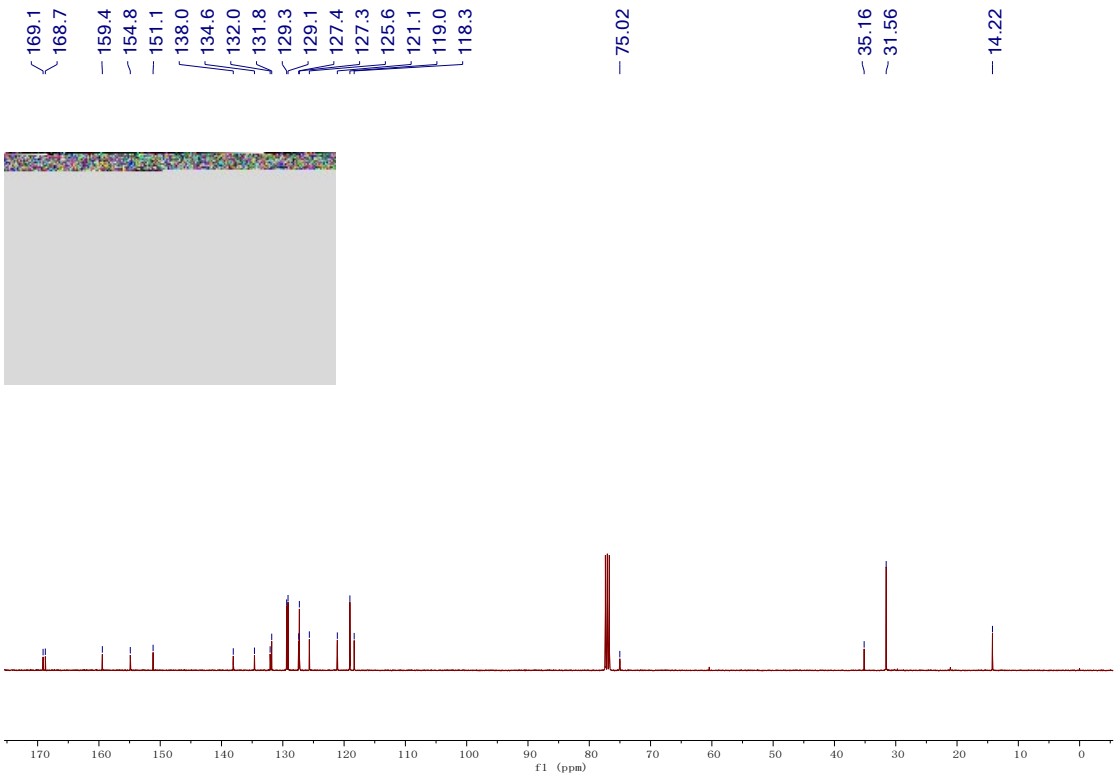
^{13}C NMR($CDCl_3$) spectrum of **3da**



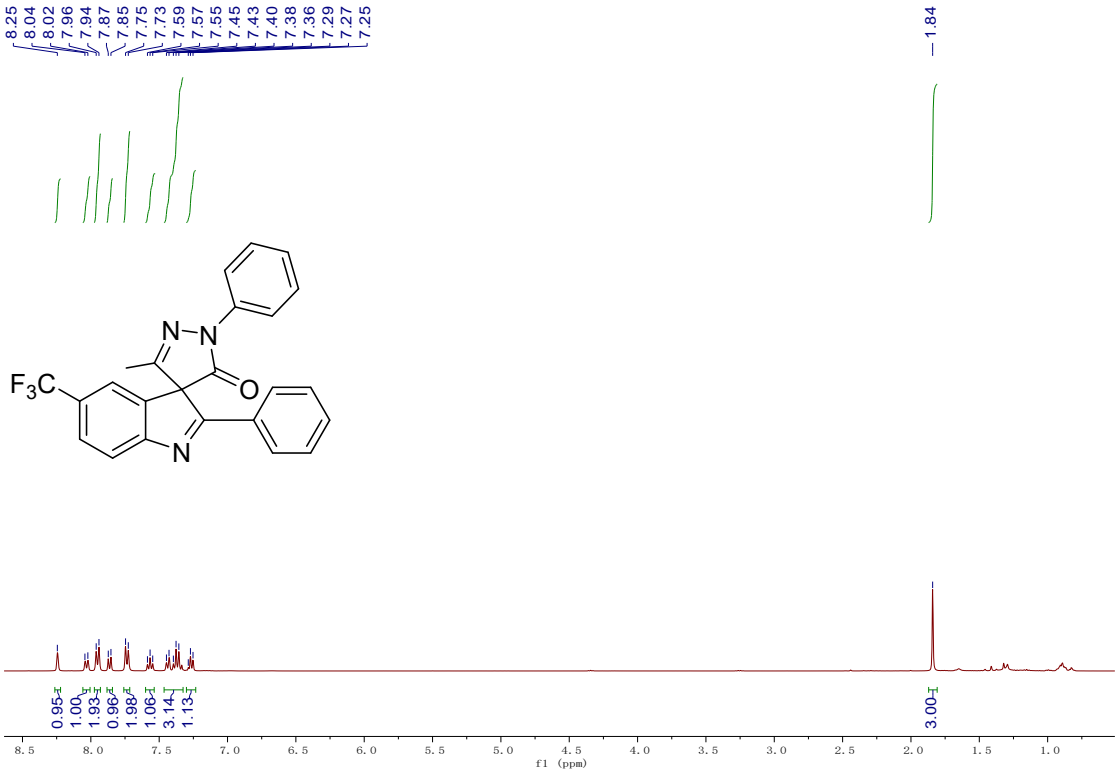
^{1}H NMR($CDCl_3$) spectrum of **3ea**



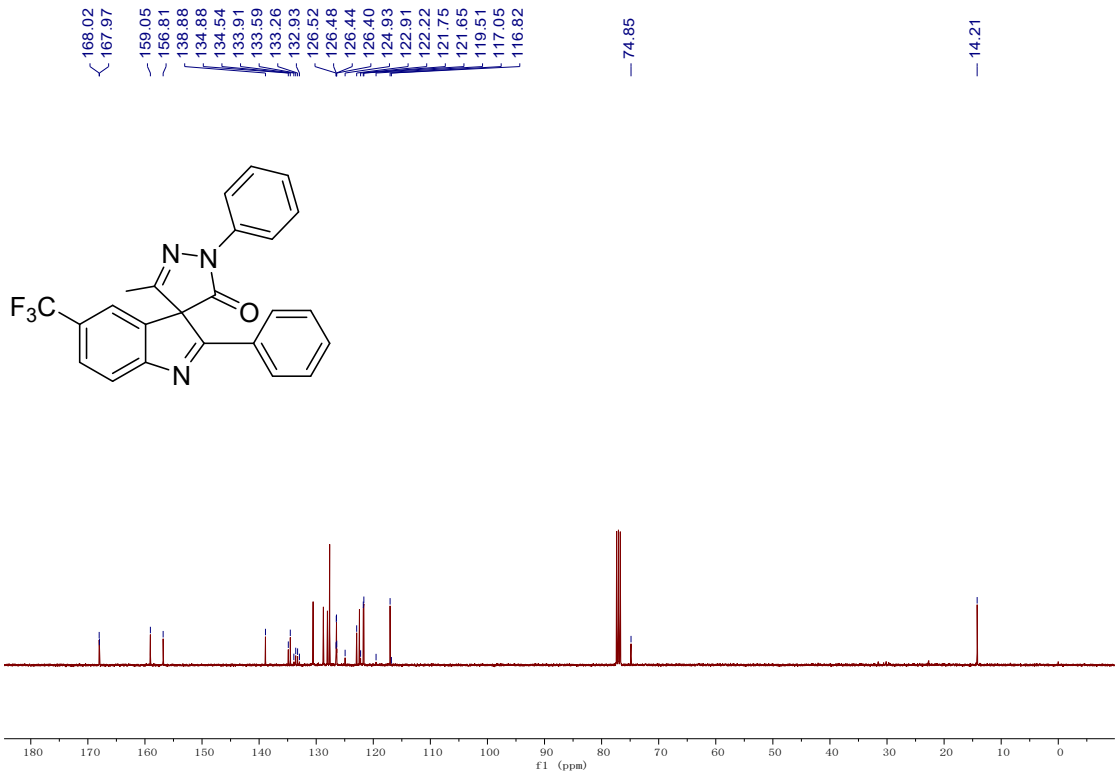
^{13}C NMR($CDCl_3$) spectrum of **3ea**



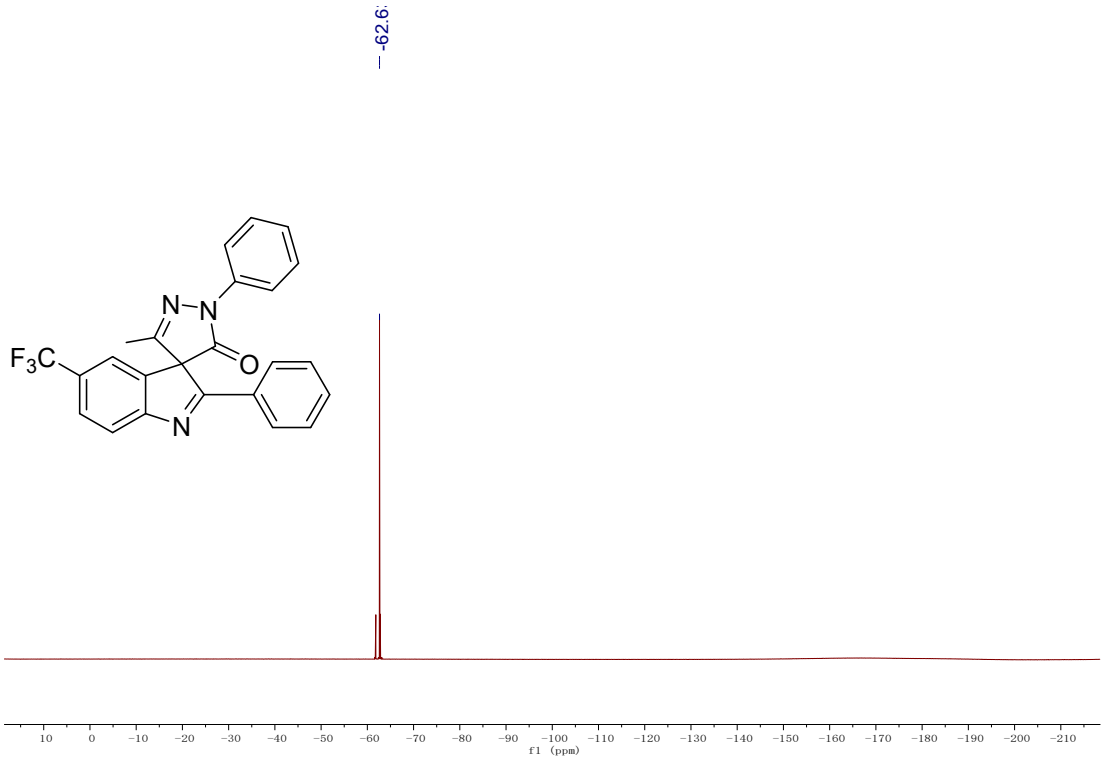
^{1}H NMR($CDCl_3$) spectrum of **3fa**



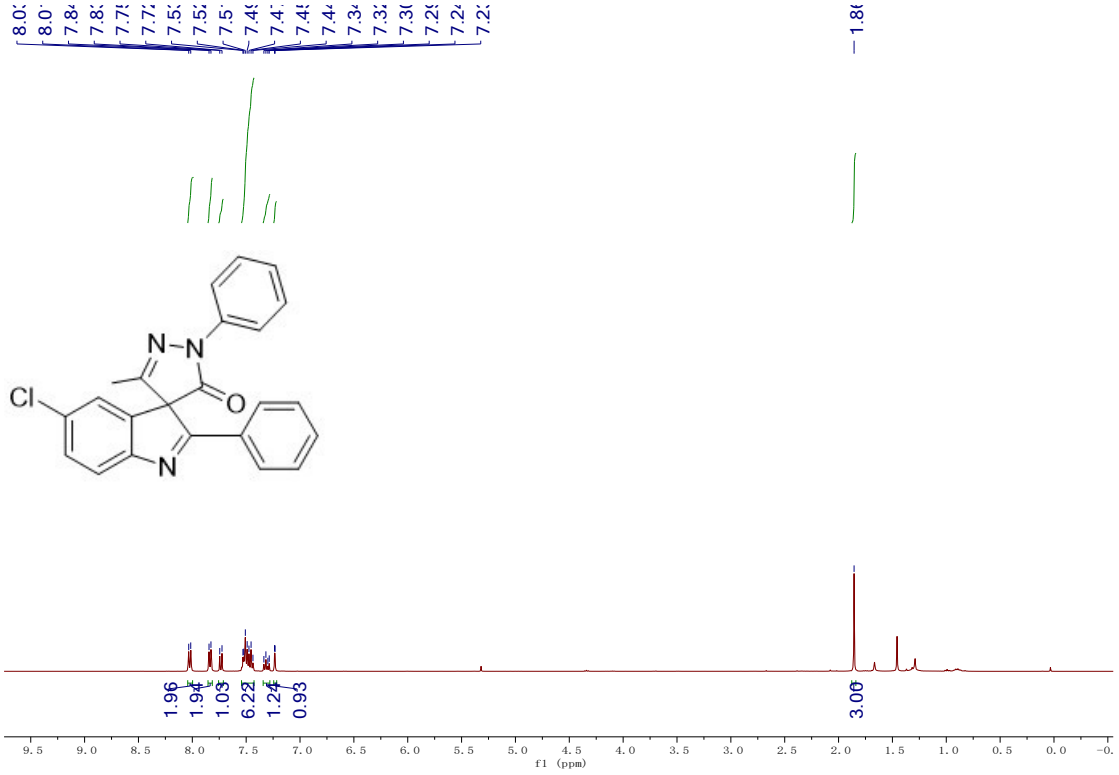
^{13}C NMR($CDCl_3$) spectrum of **3fa**



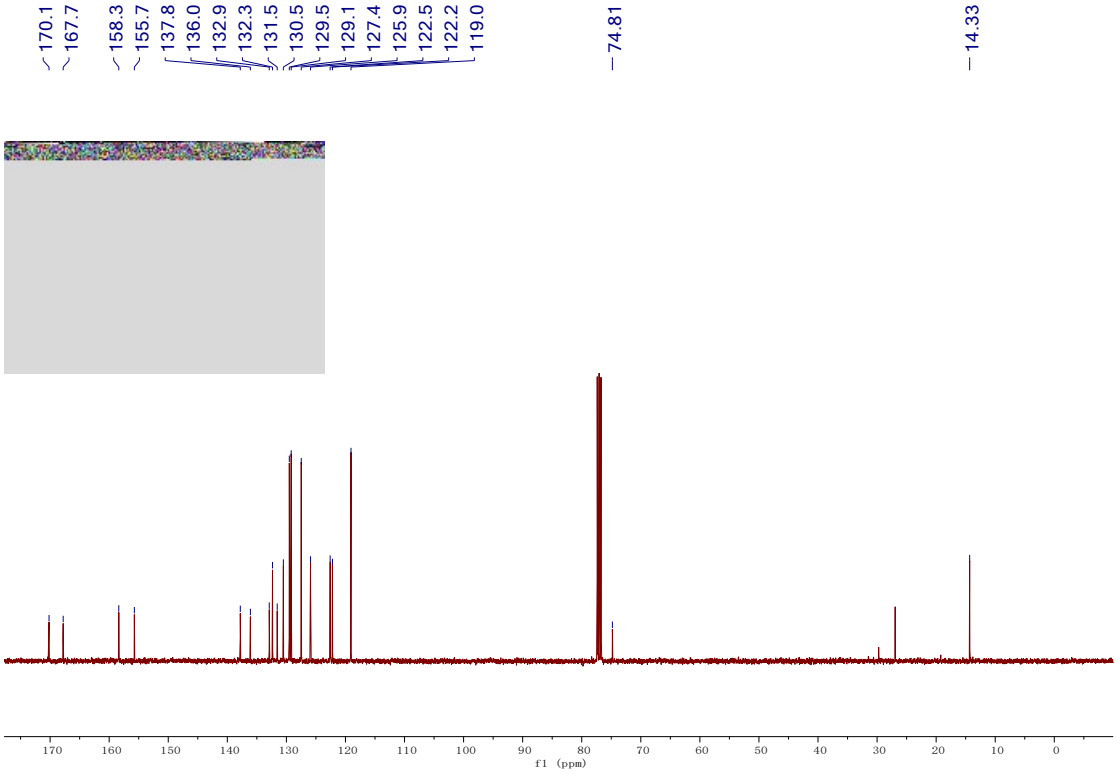
^{19}F NMR ($CDCl_3$) spectrum of **3fa**



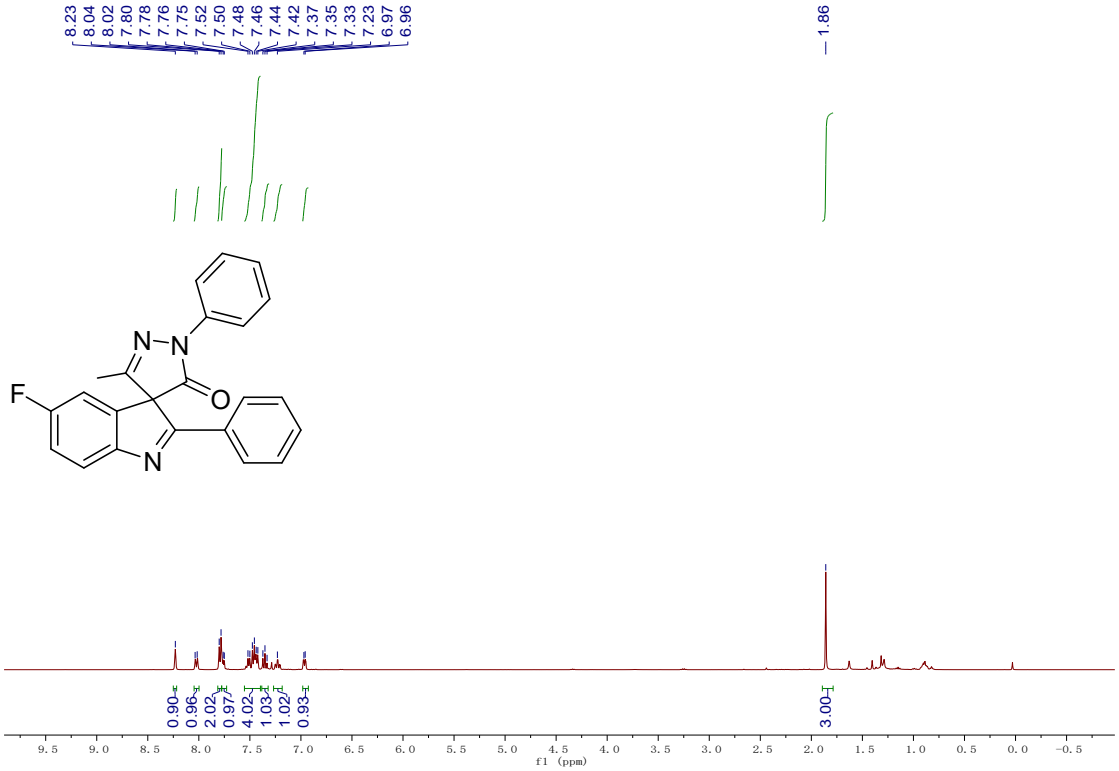
^{1}H NMR($CDCl_3$) spectrum of **3ga**



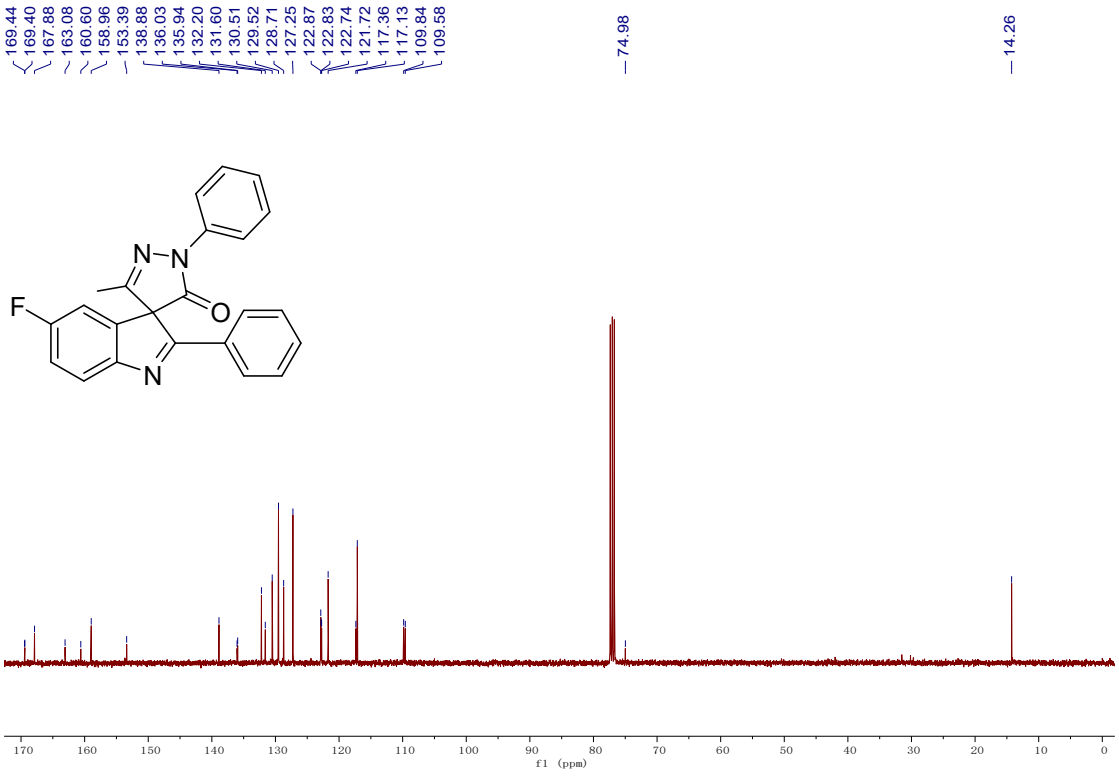
^{13}C NMR($CDCl_3$) spectrum of **3ga**



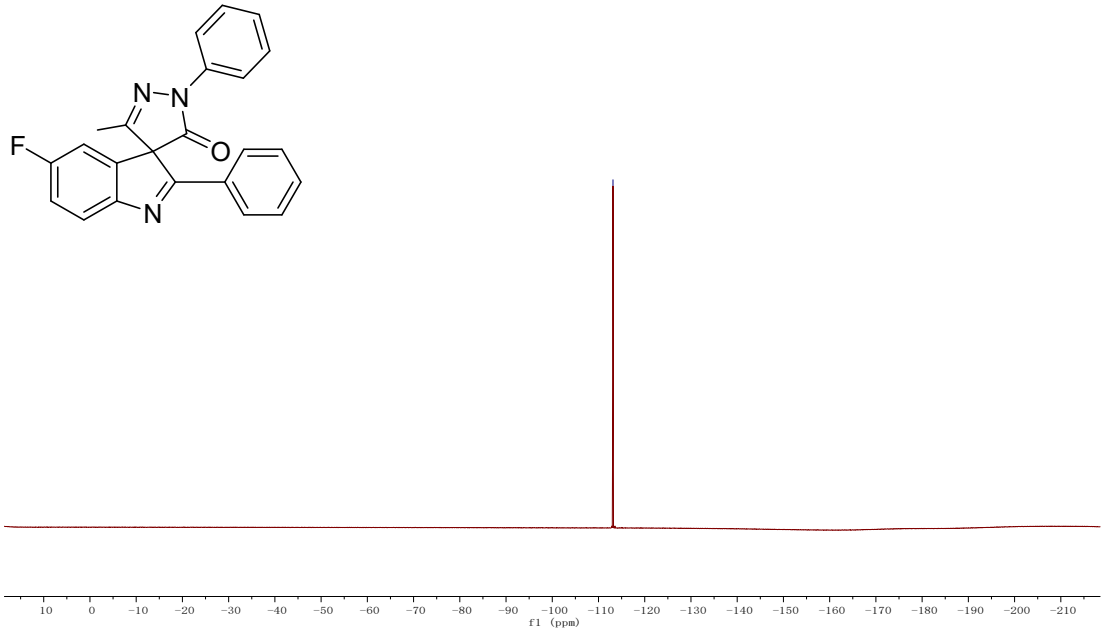
^{1}H NMR($CDCl_3$) spectrum of **3ha**



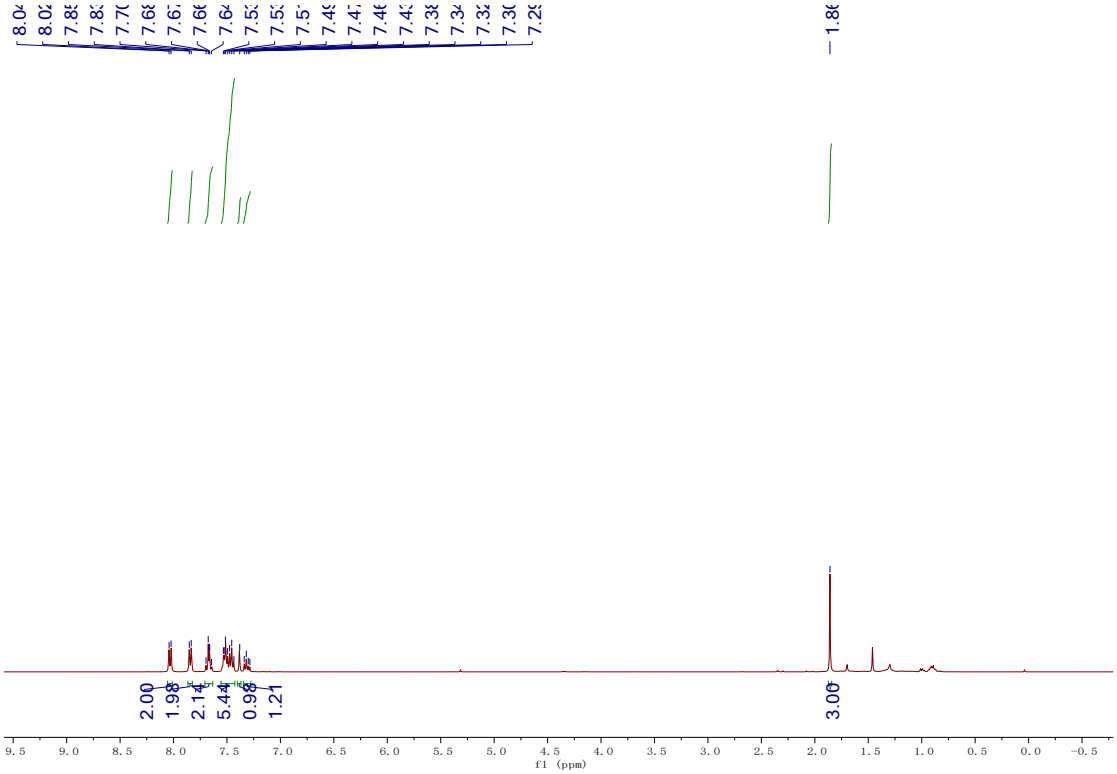
^{13}C NMR($CDCl_3$) spectrum of **3ha**



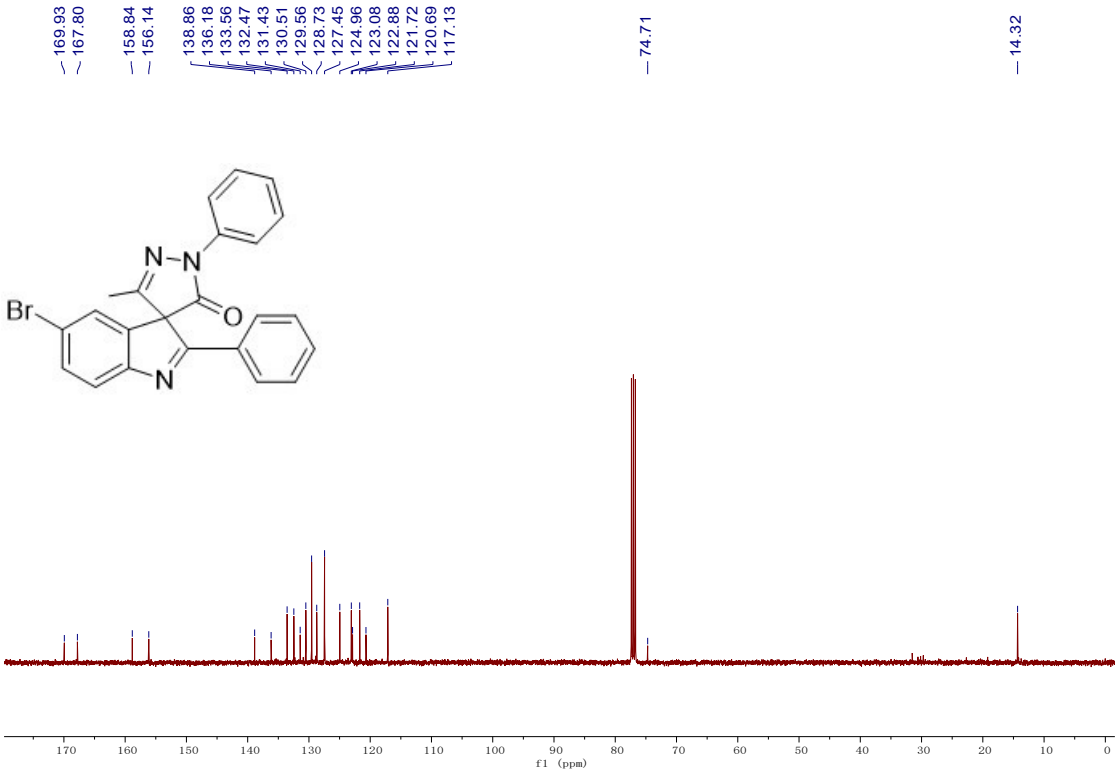
^{19}F NMR ($CDCl_3$) spectrum of **3ha**



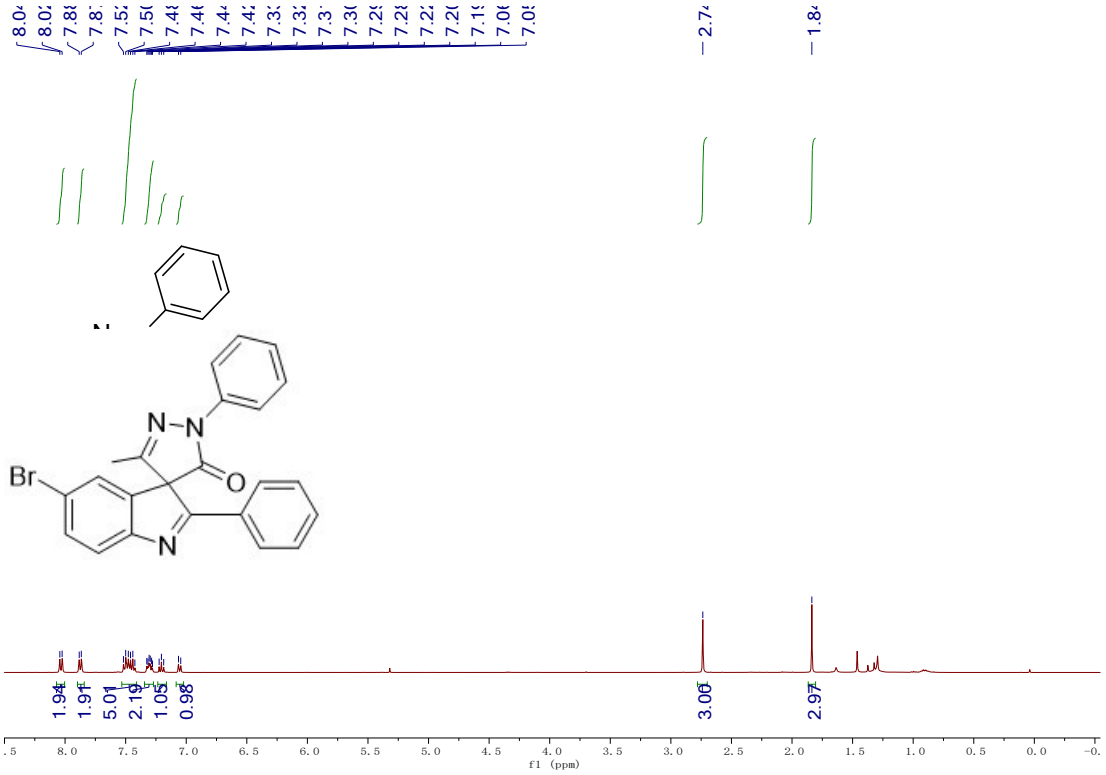
^{1}H NMR($CDCl_3$) spectrum of **3ia**



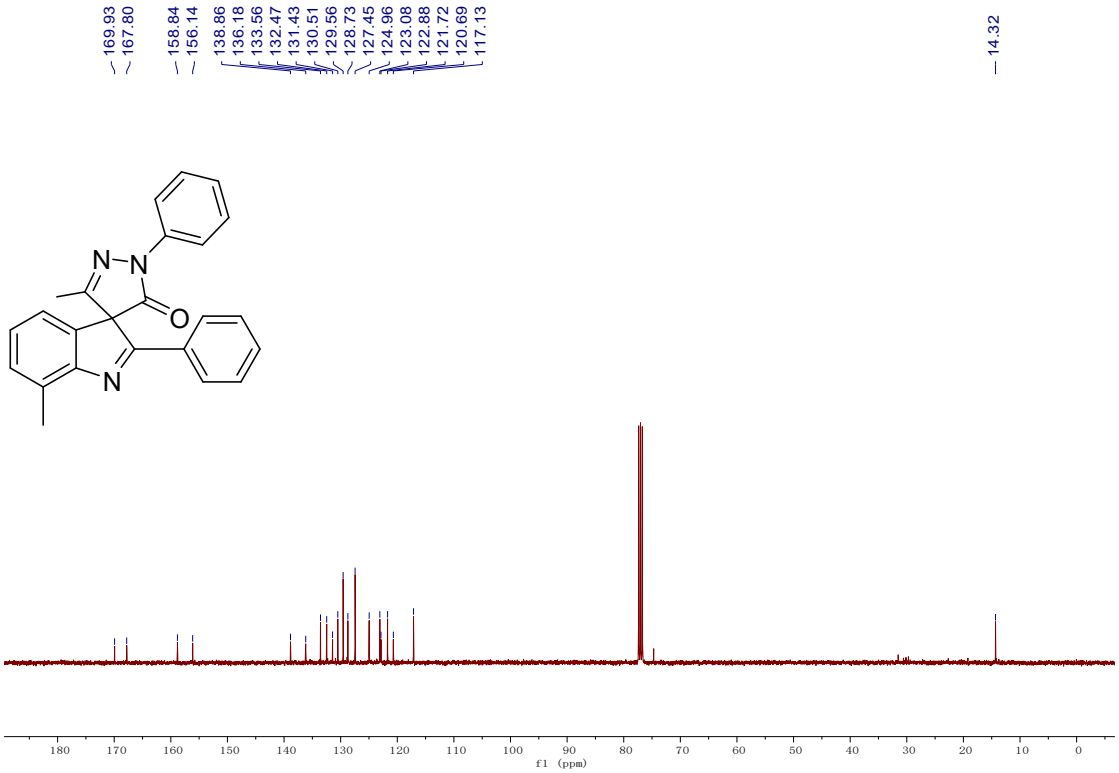
^{13}C NMR($CDCl_3$) spectrum of **3ia**



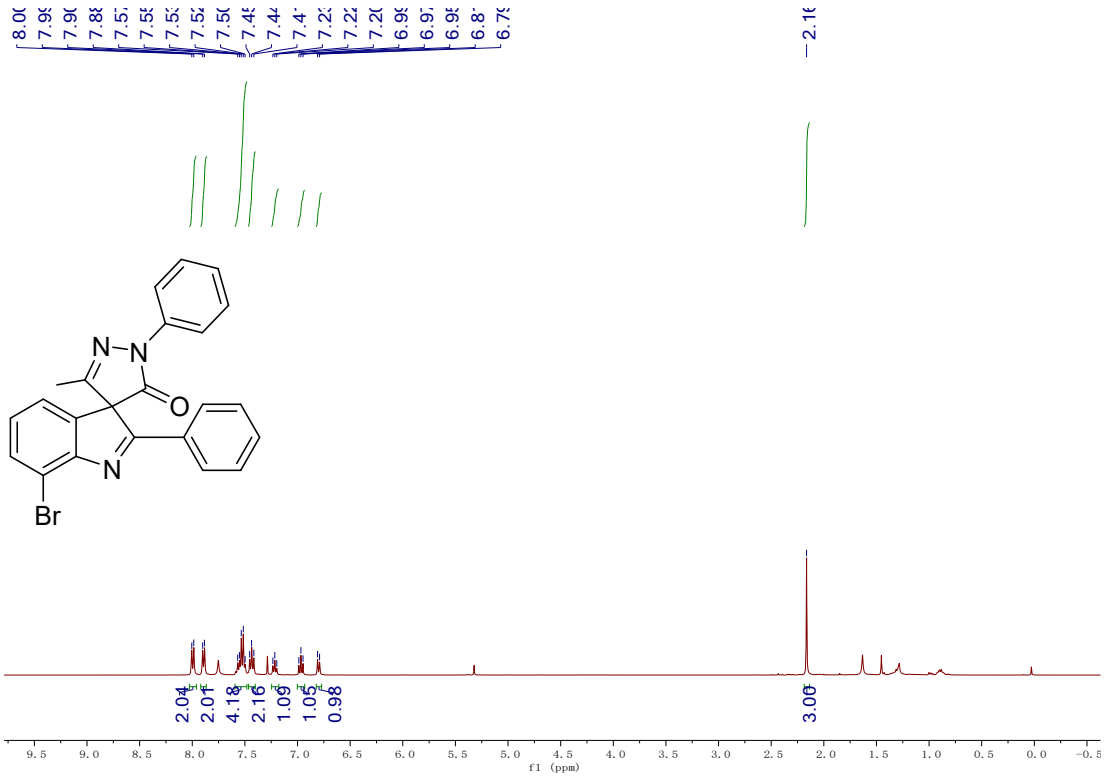
^{1}H NMR($CDCl_3$) spectrum of **3ja**



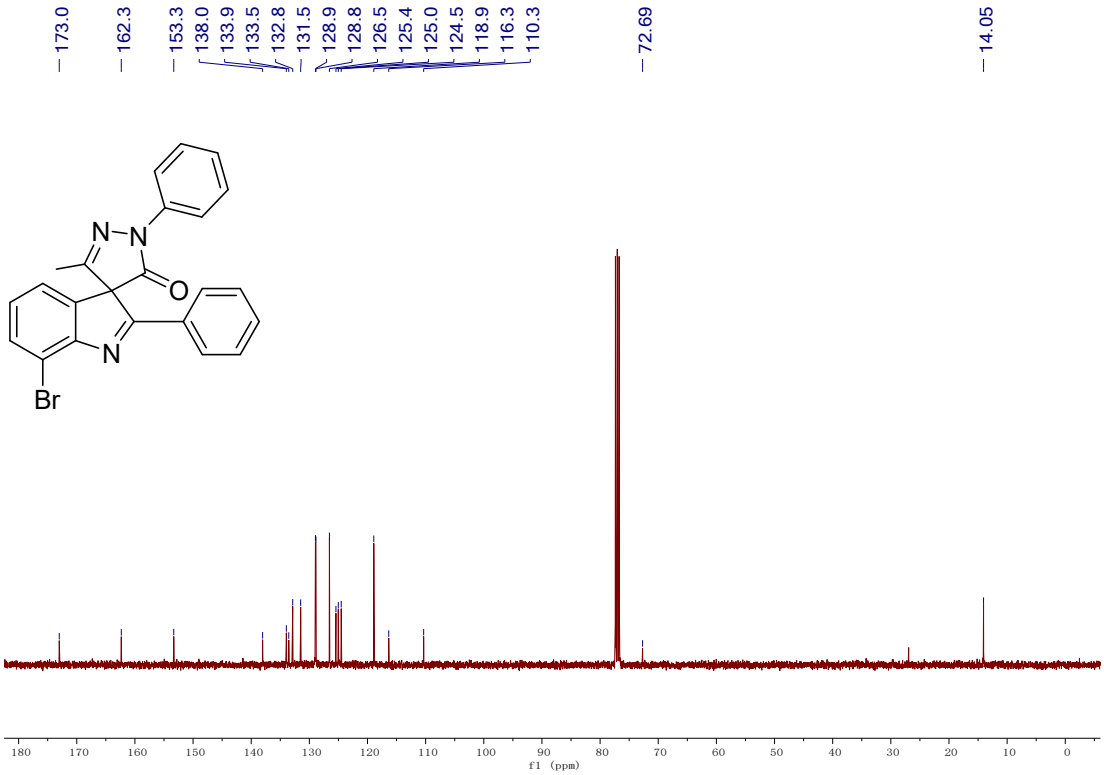
^{13}C NMR($CDCl_3$) spectrum of **3ja**



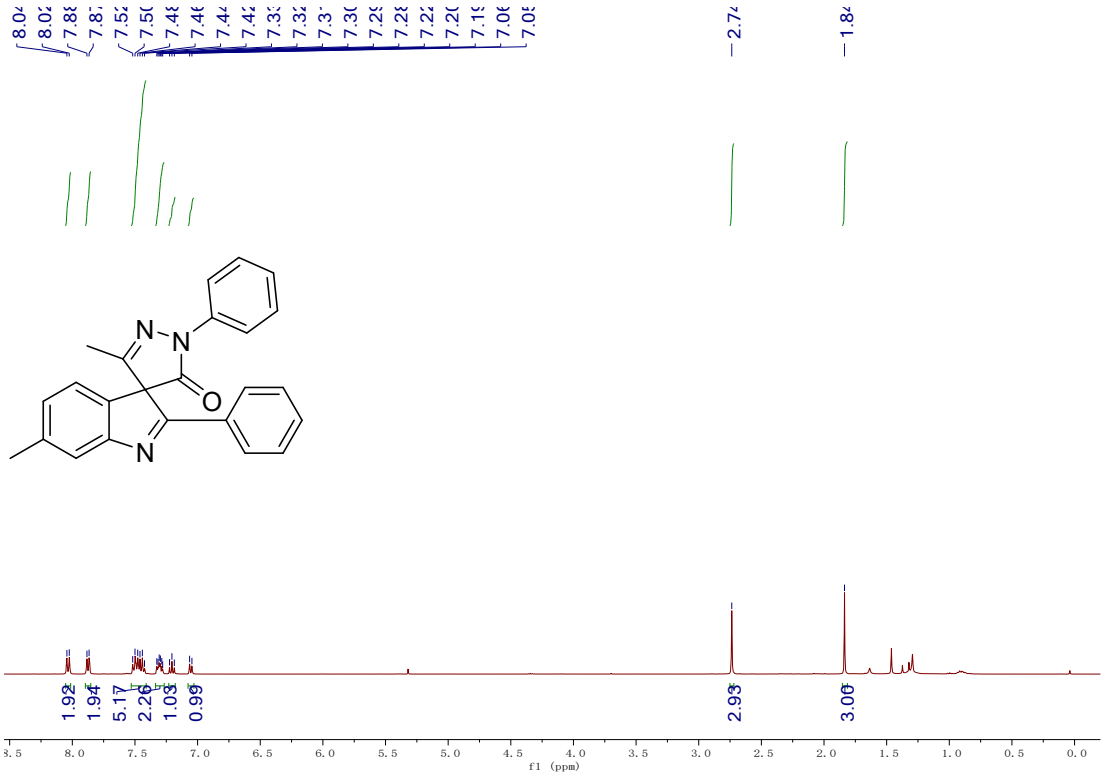
^{1}H NMR(CD Cl_3) spectrum of **3ka**



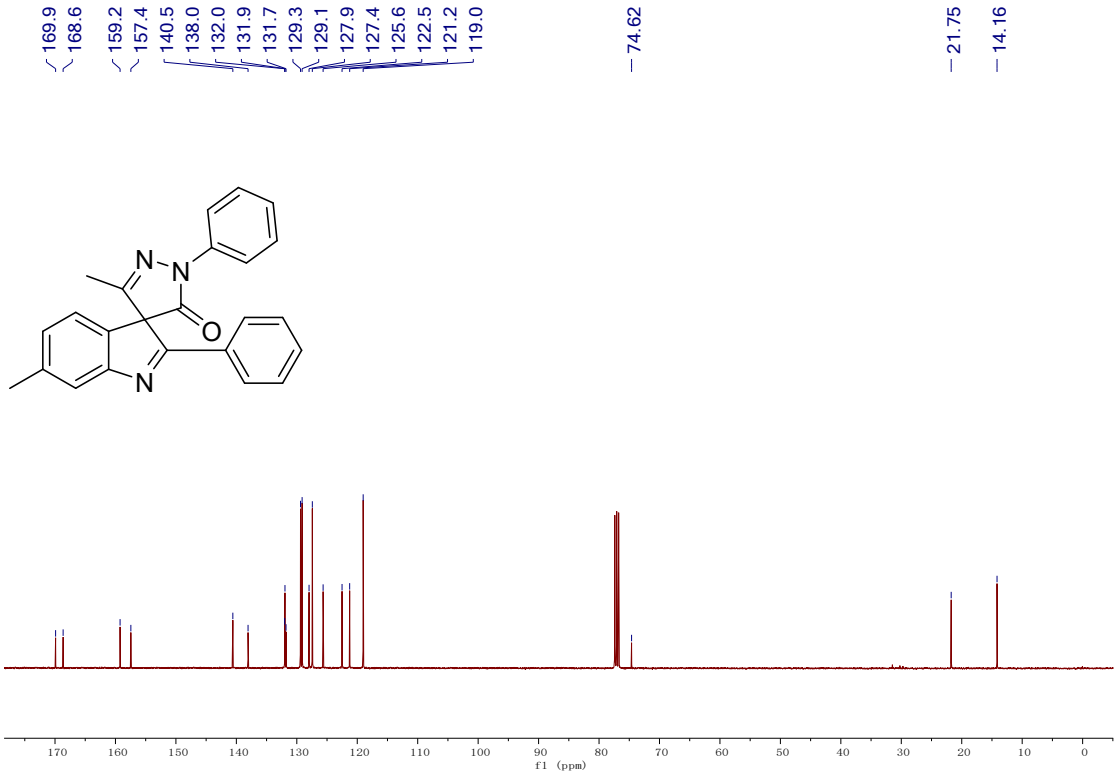
^{13}C NMR($CDCl_3$) spectrum of **3ka**



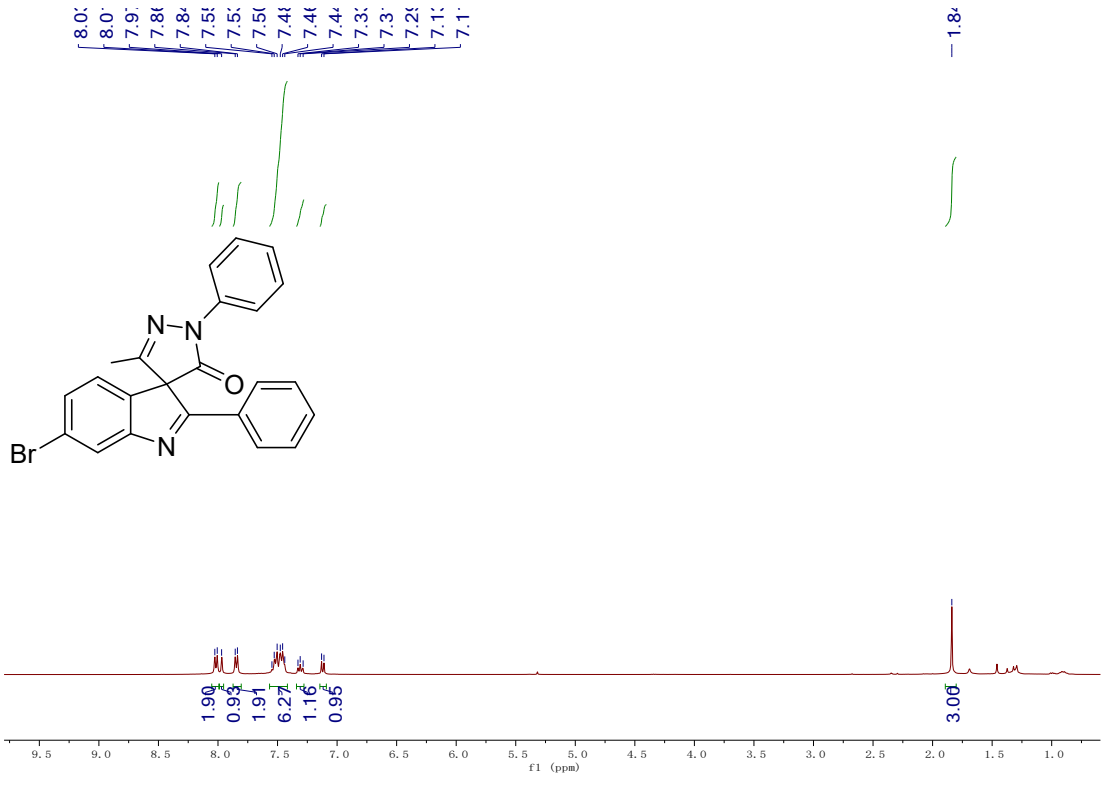
^{1}H NMR(CD Cl_3) spectrum of 3**la**



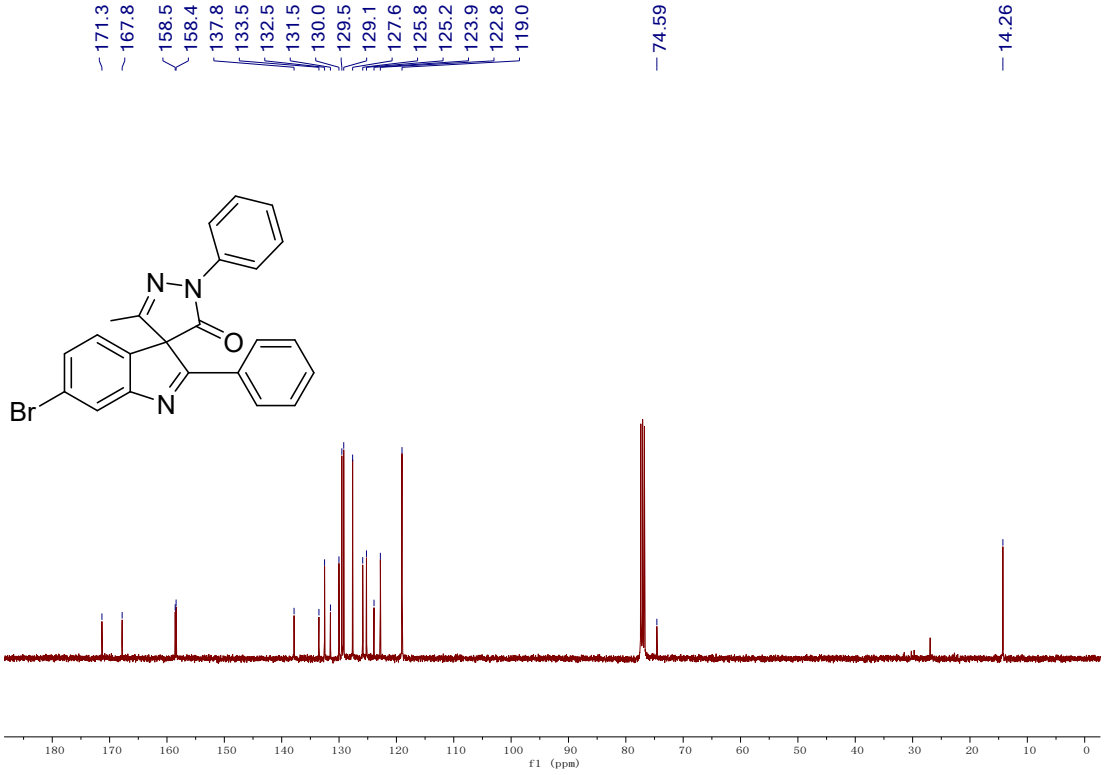
^{13}C NMR($CDCl_3$) spectrum of **3la**



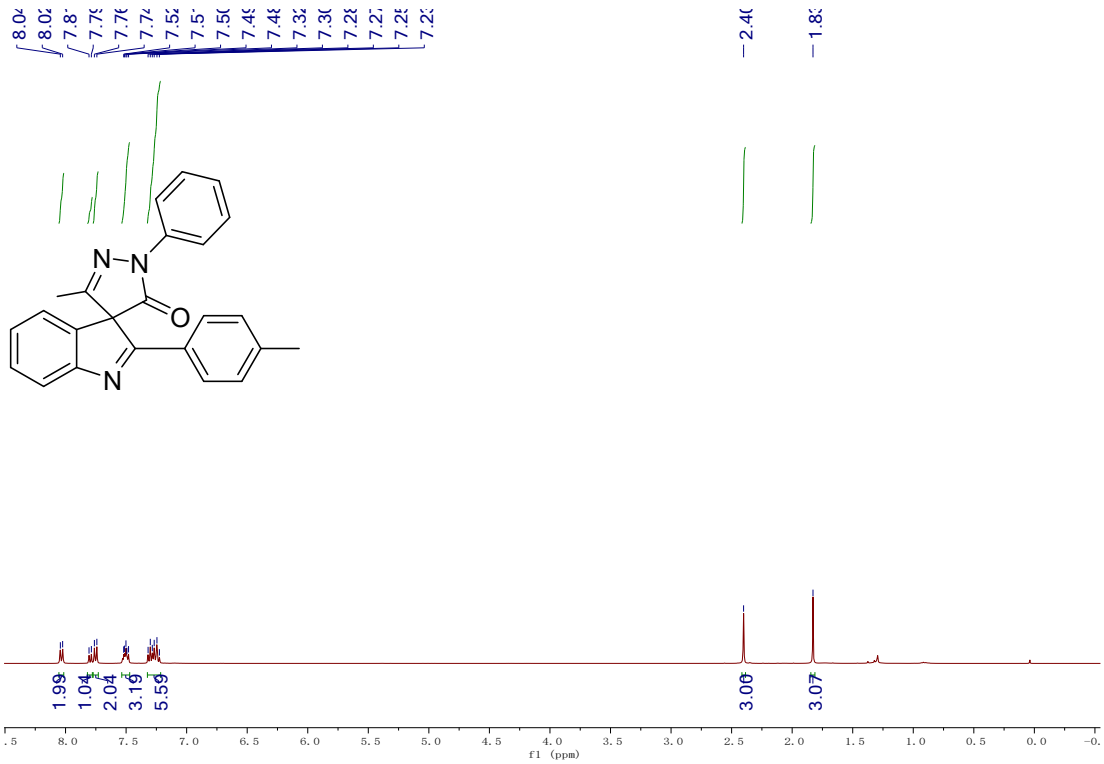
^{1}H NMR($CDCl_3$) spectrum of **3ma**



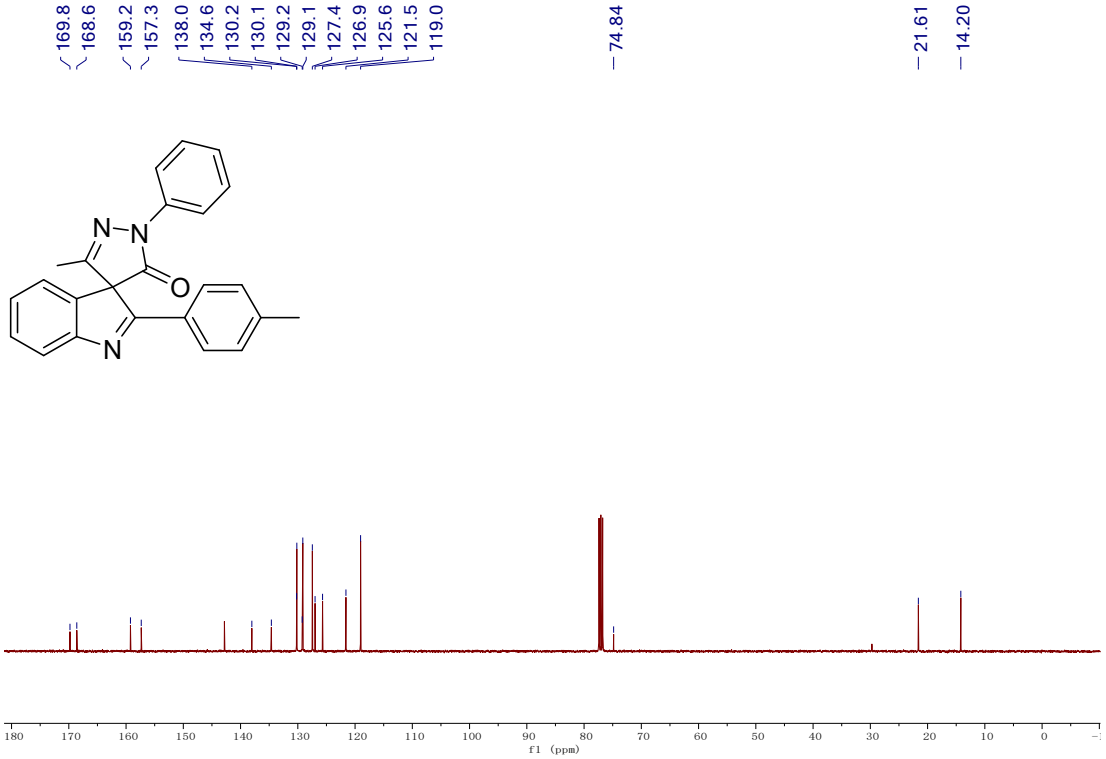
^{13}C NMR($CDCl_3$) spectrum of **3ma**



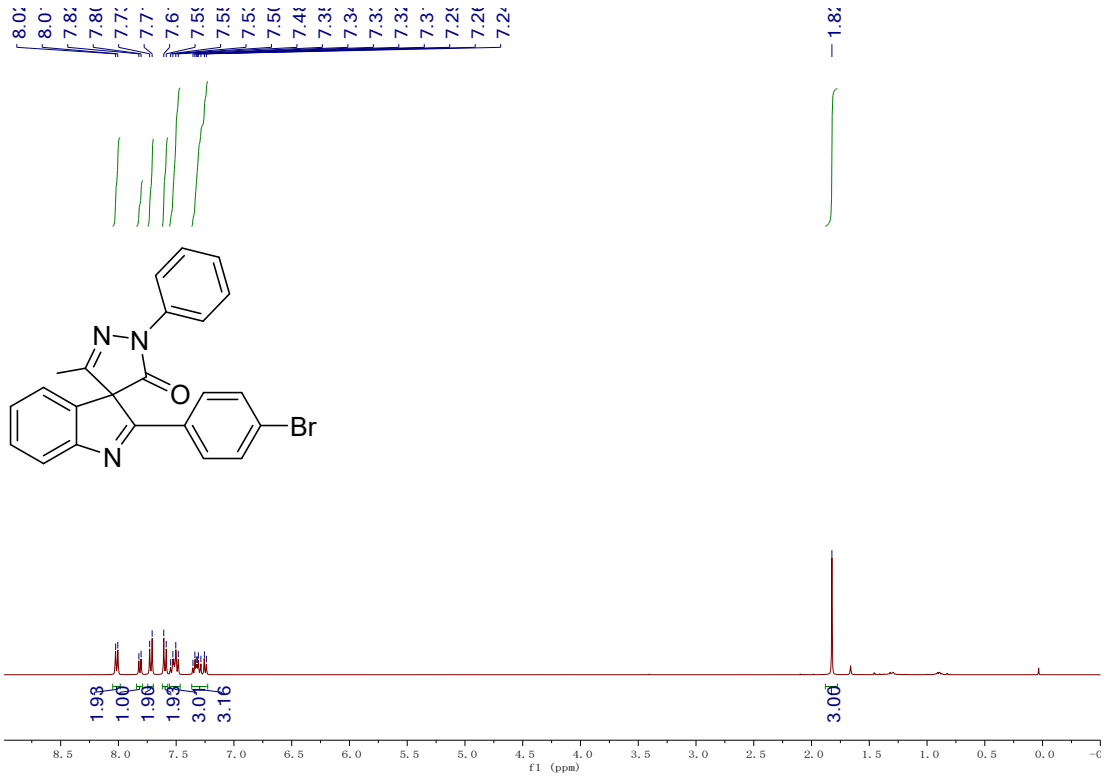
^{1}H NMR ($CDCl_3$) spectrum of **3na**



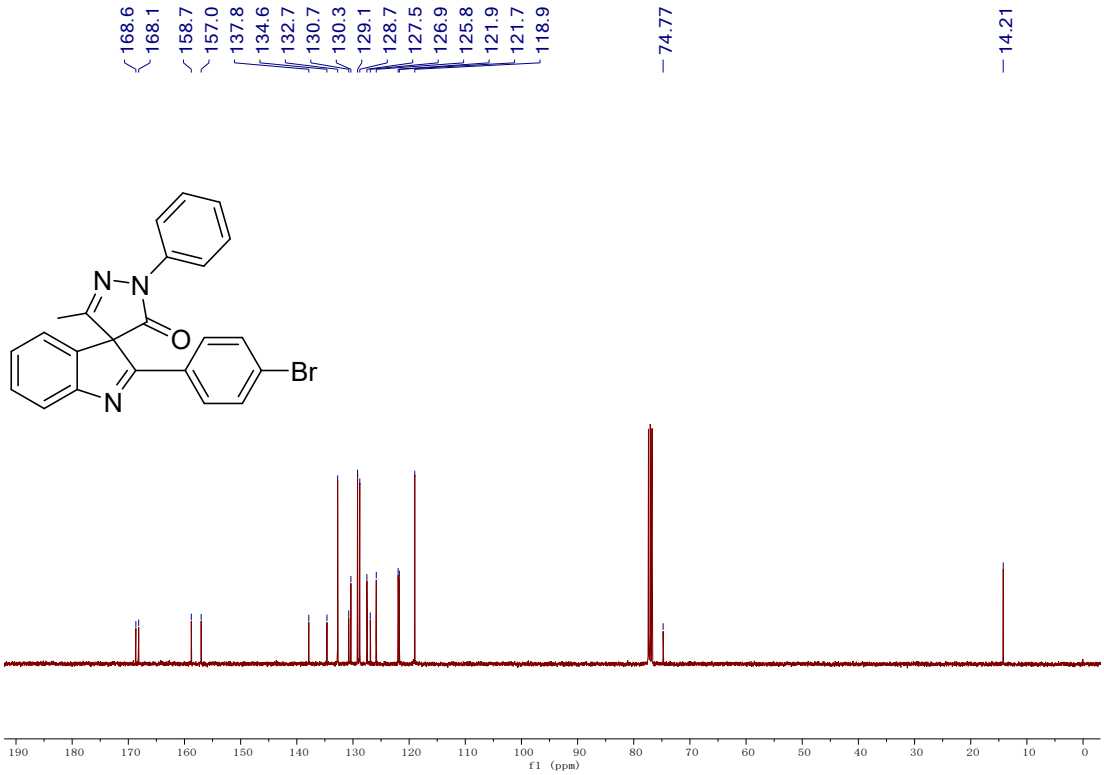
^{13}C NMR($CDCl_3$) spectrum of **3na**



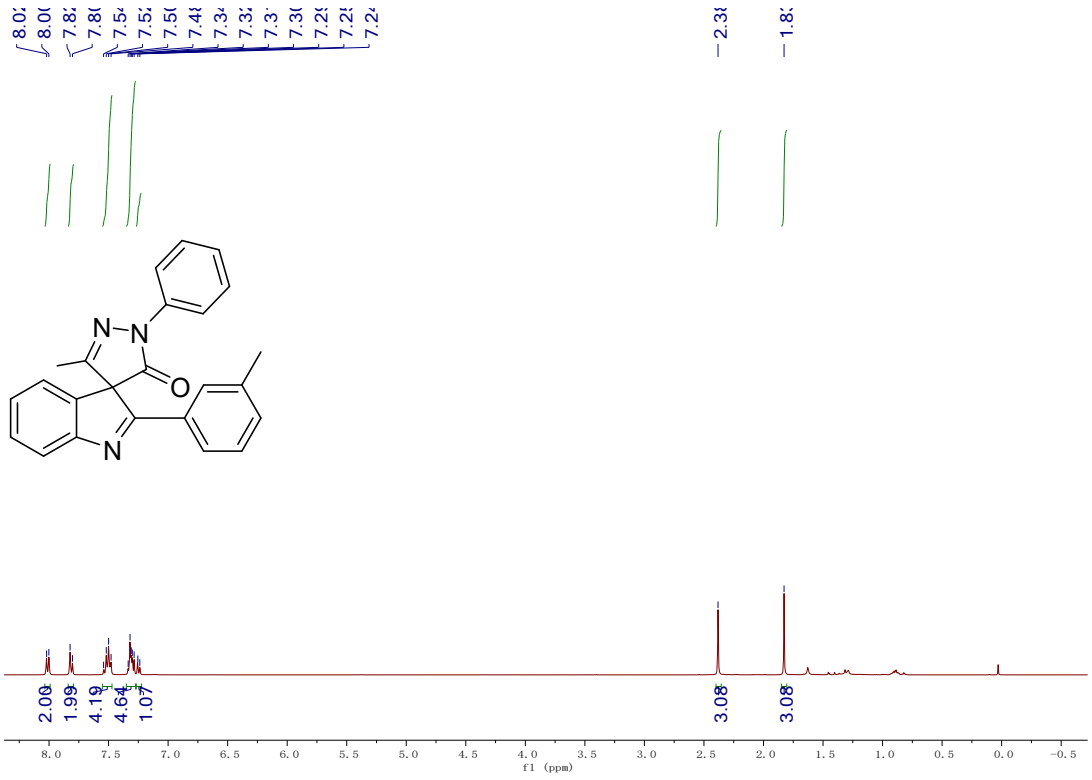
^{1}H NMR(CD Cl_3) spectrum of **3oa**



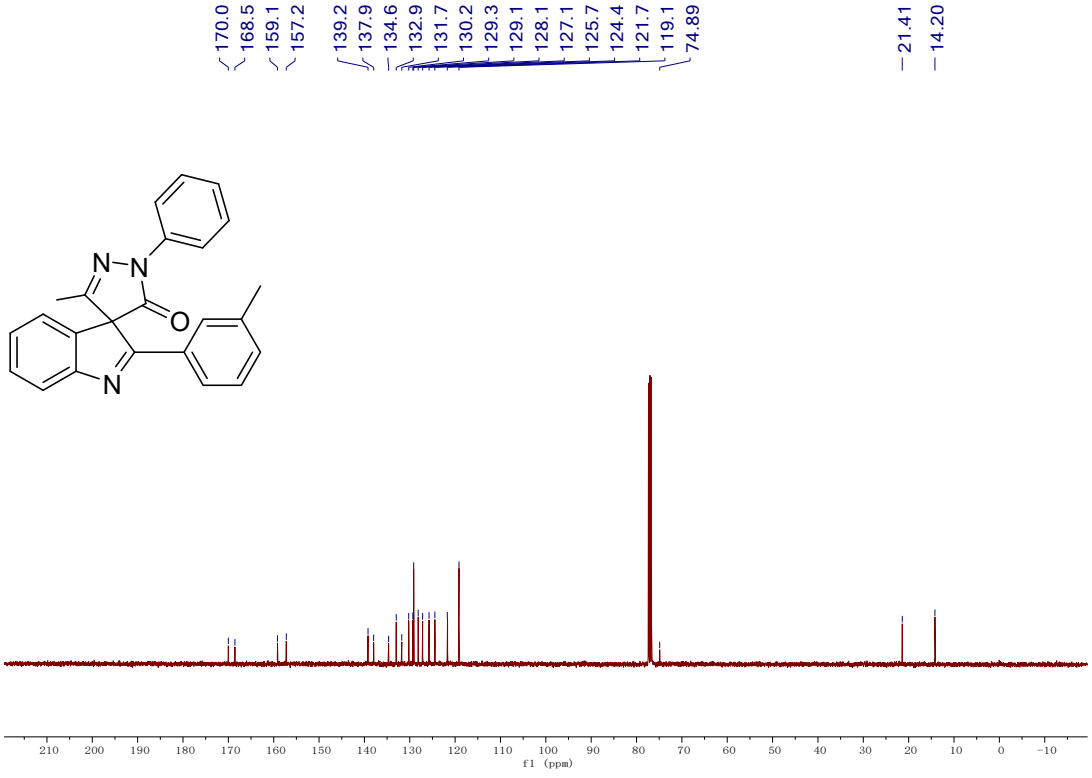
^{13}C NMR($CDCl_3$) spectrum of **3oa**



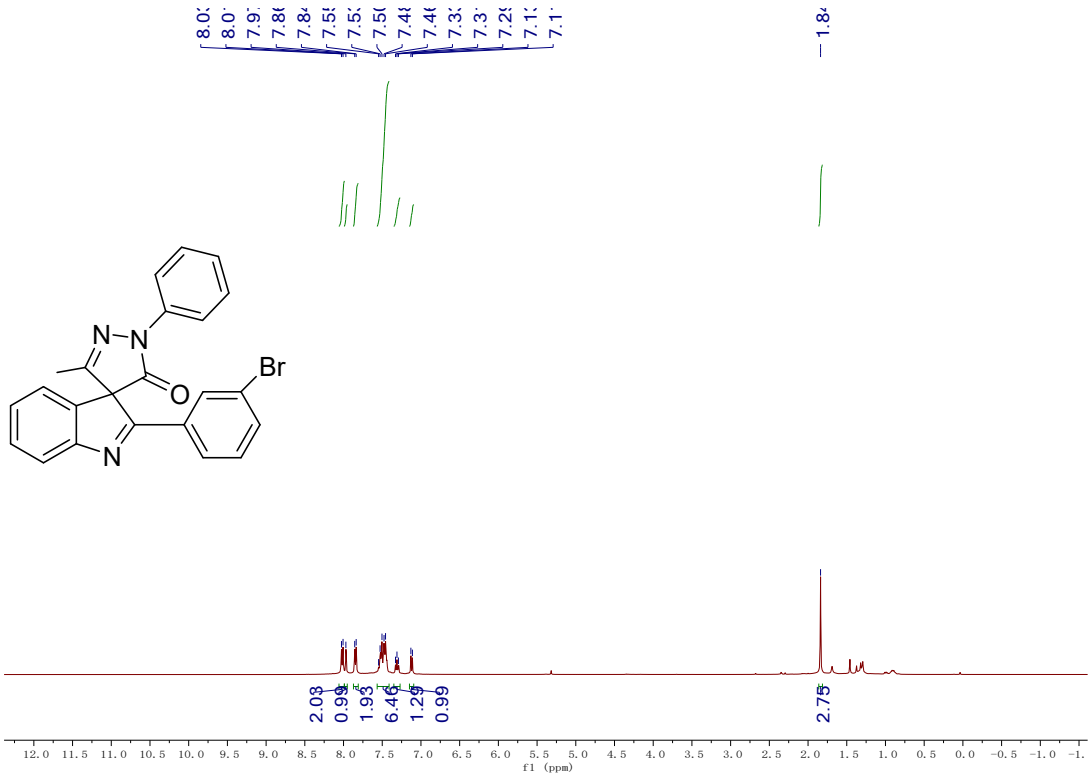
^{1}H NMR($CDCl_3$) spectrum of **3pa**



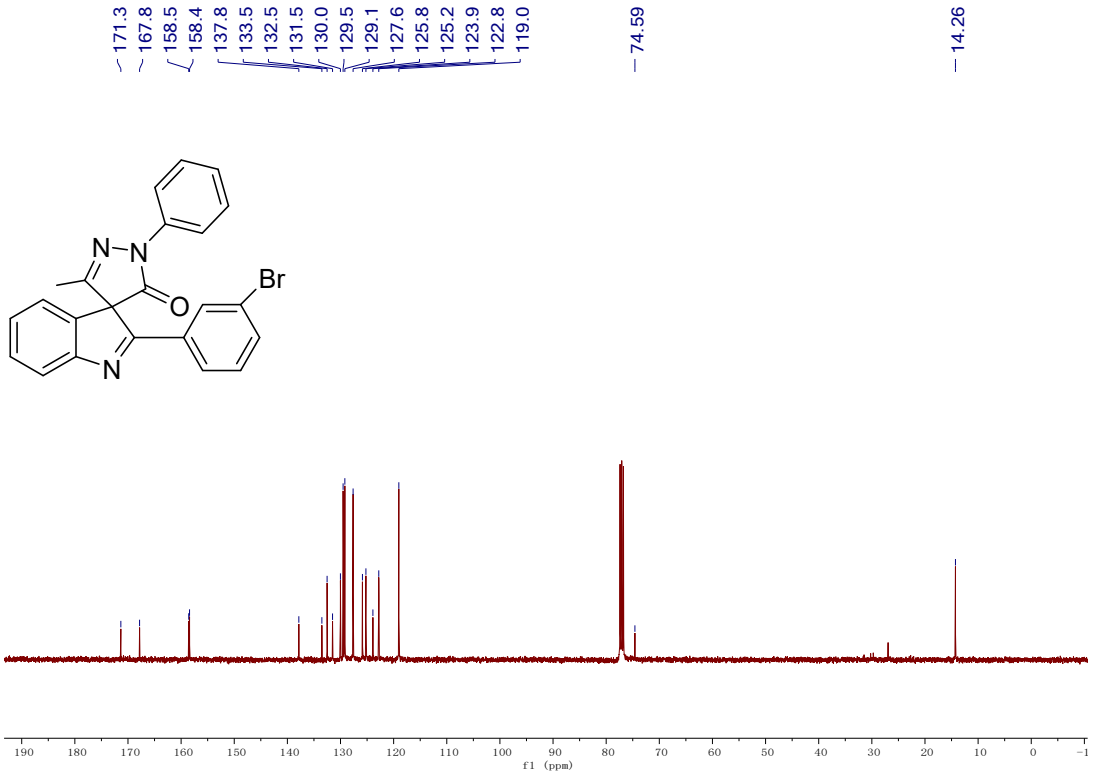
^{13}C NMR($CDCl_3$) spectrum of **3pa**



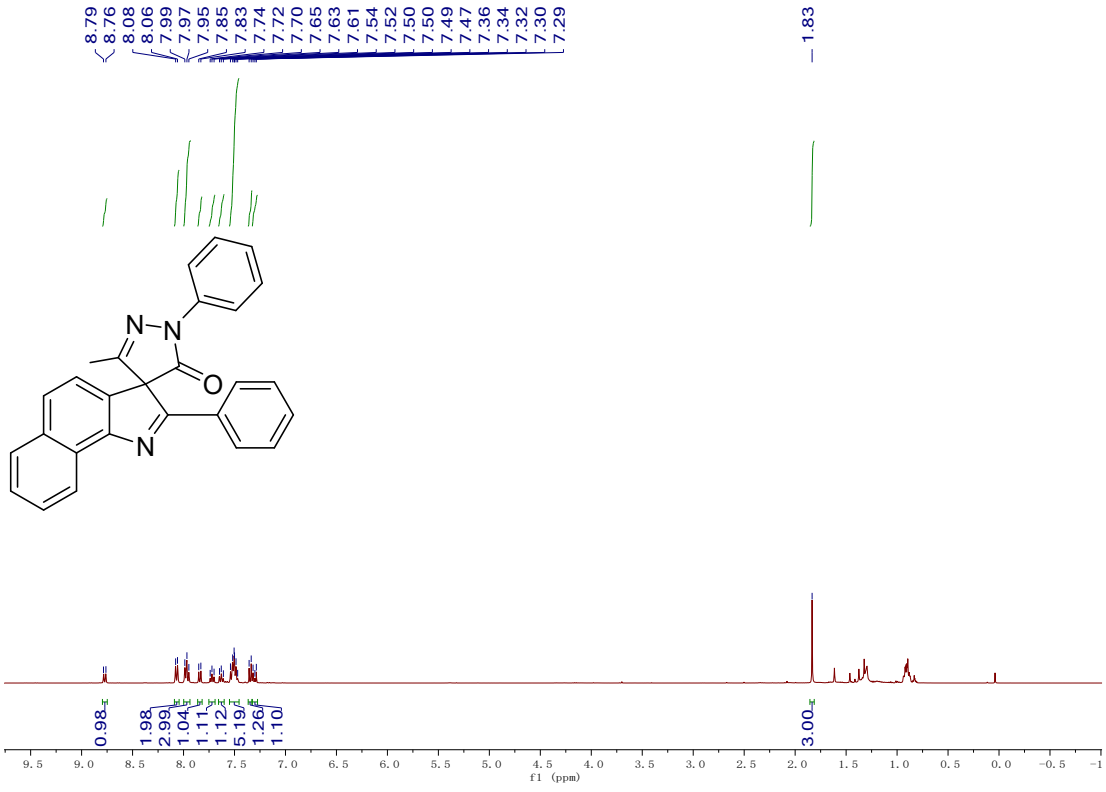
^{1}H NMR(CD Cl_3) spectrum of **3qa**



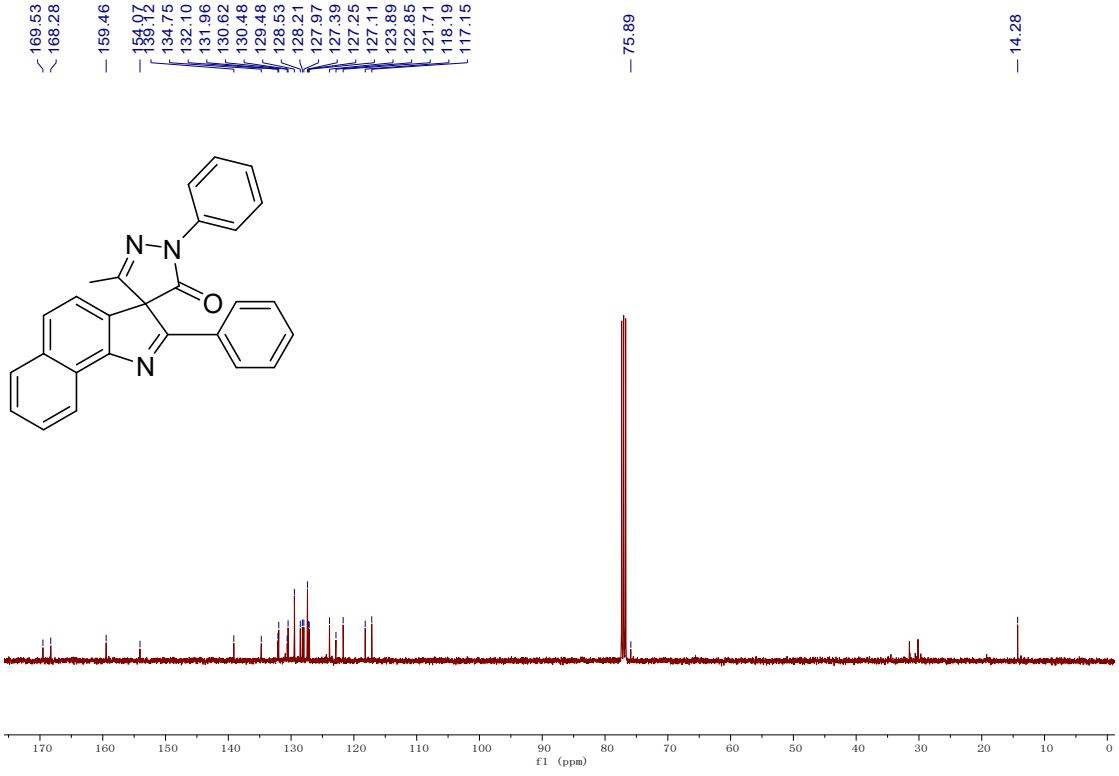
^{13}C NMR($CDCl_3$) spectrum of **3qa**



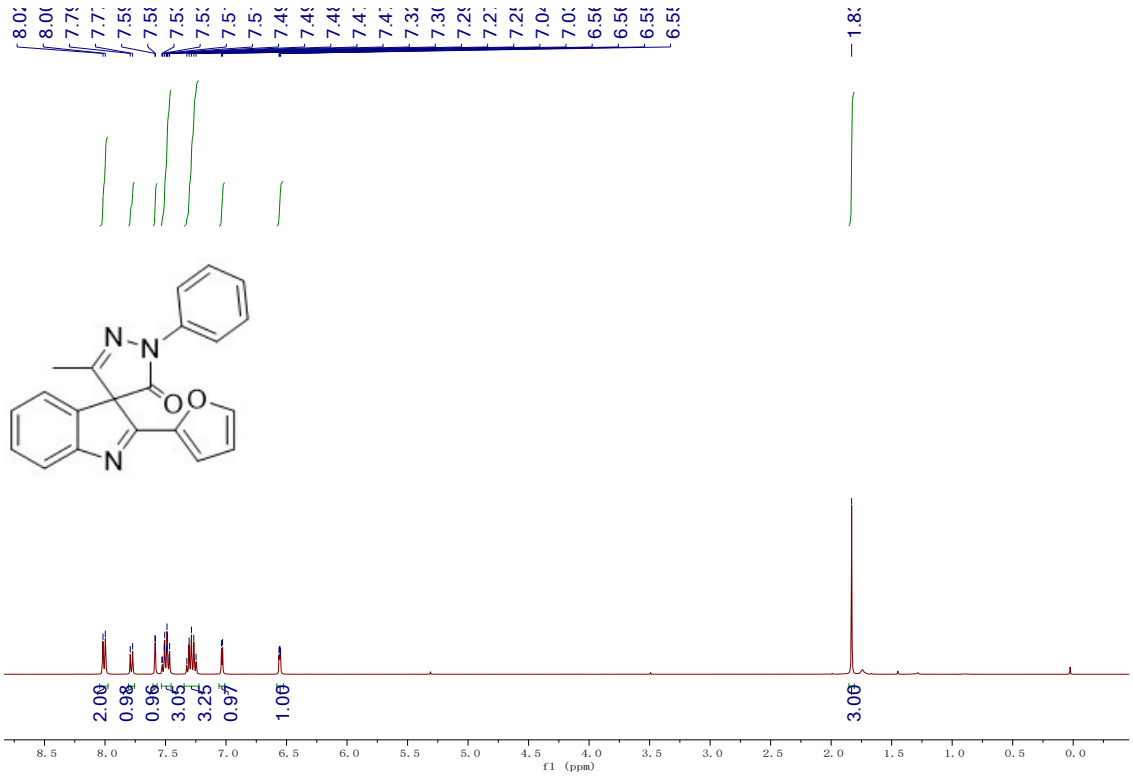
^{1}H NMR(CD Cl_3) spectrum of **3ra**



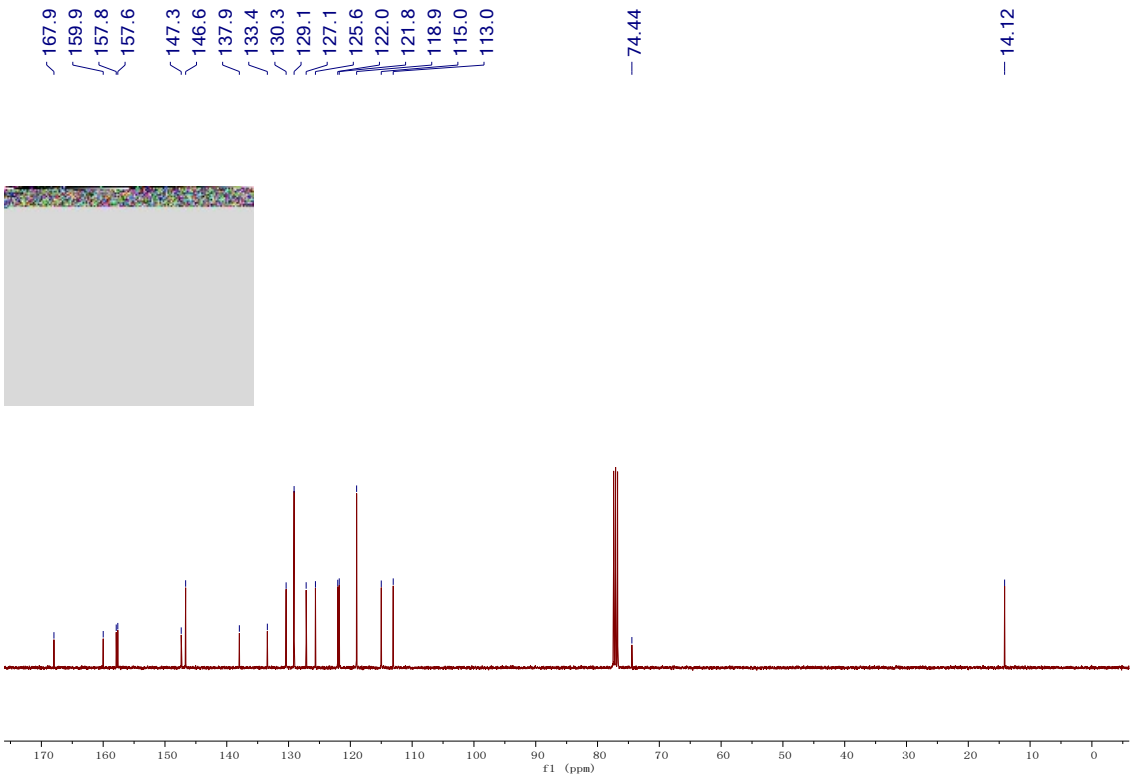
^{13}C NMR($CDCl_3$) spectrum of **3ra**



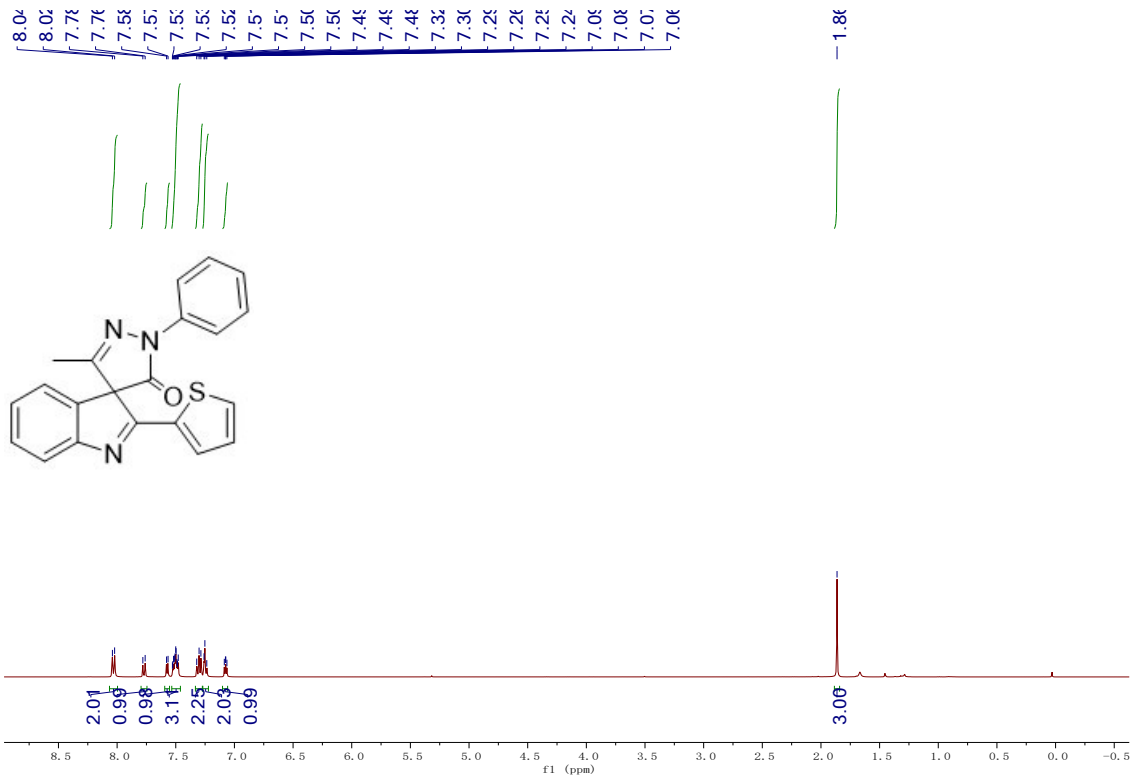
^{1}H NMR ($CDCl_3$) spectrum of **3sa**



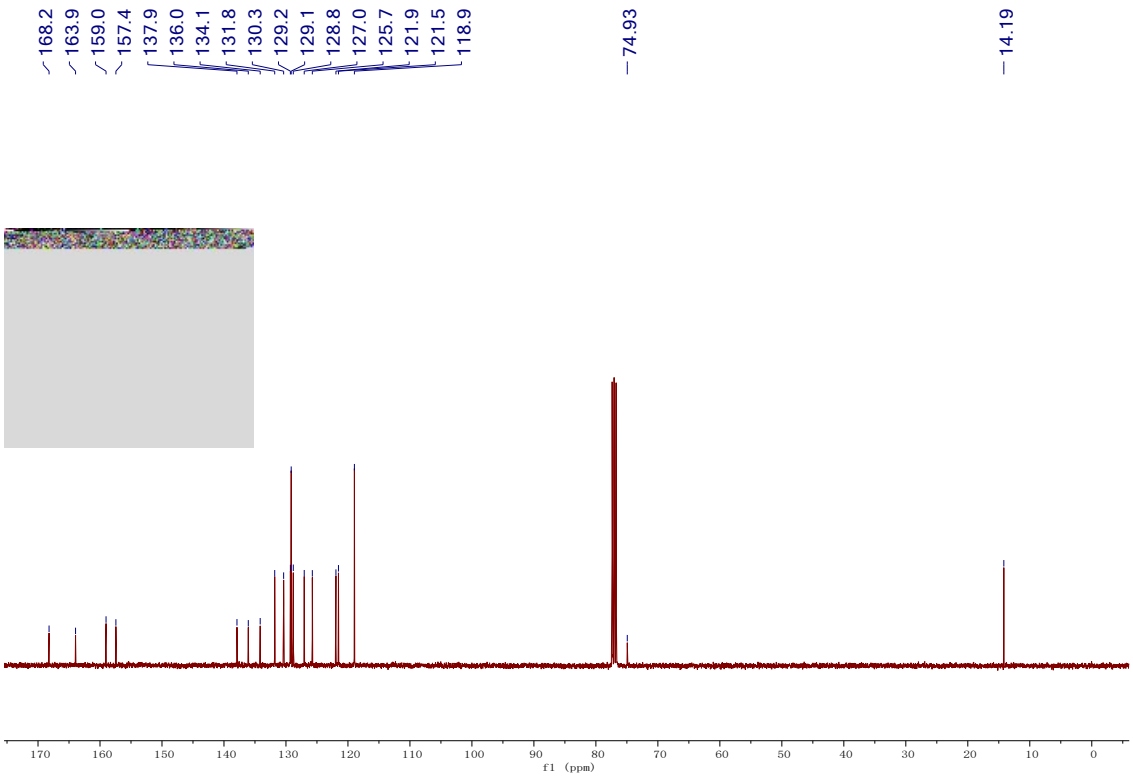
^{13}C NMR($CDCl_3$) spectrum of **3sa**



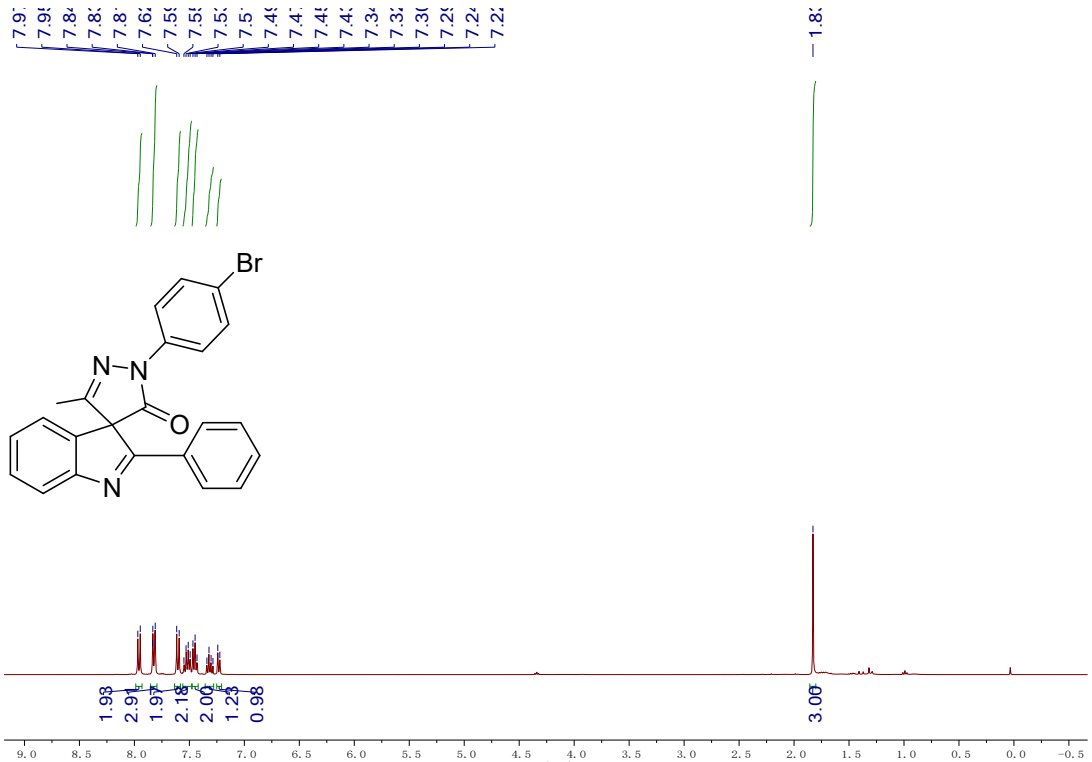
^{1}H NMR($CDCl_3$) spectrum of **3ta**



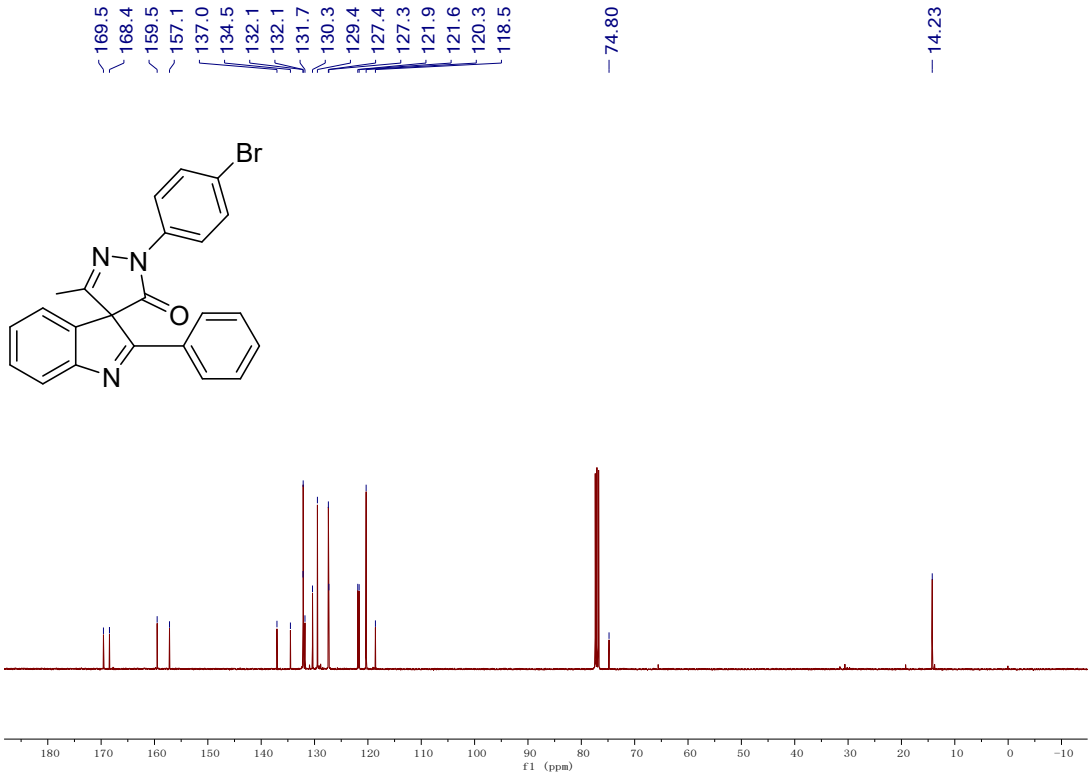
^{13}C NMR($CDCl_3$) spectrum of **3ta**



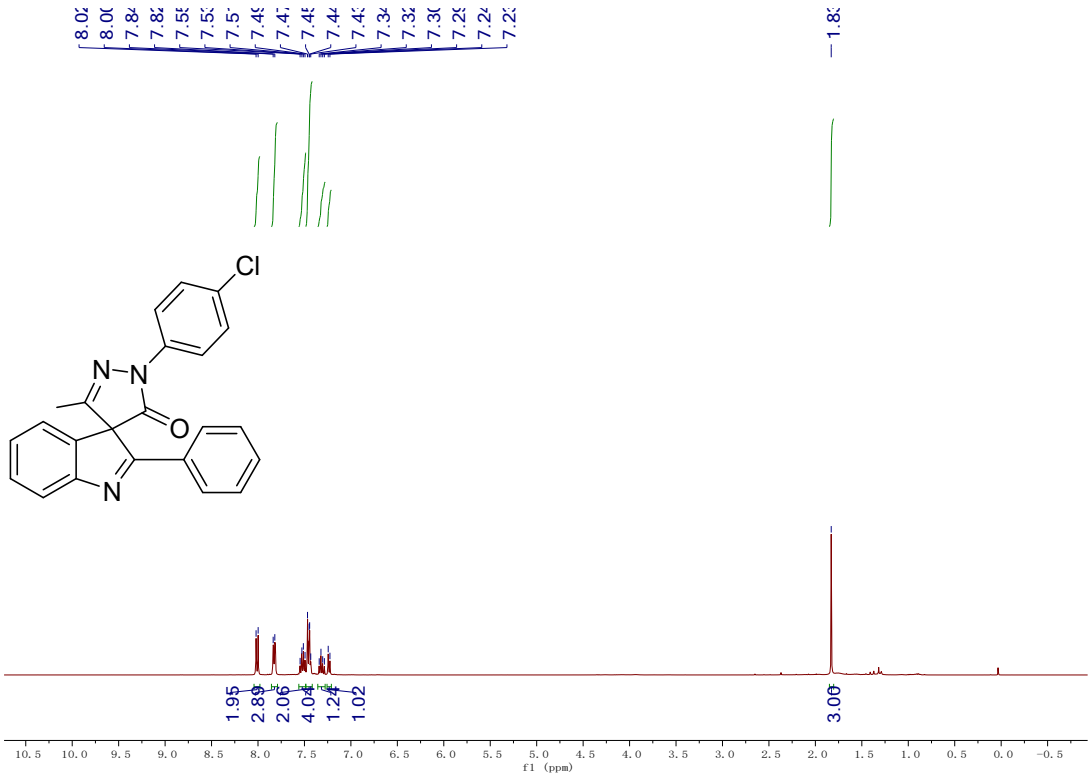
^{1}H NMR($CDCl_3$) spectrum of **3ab**



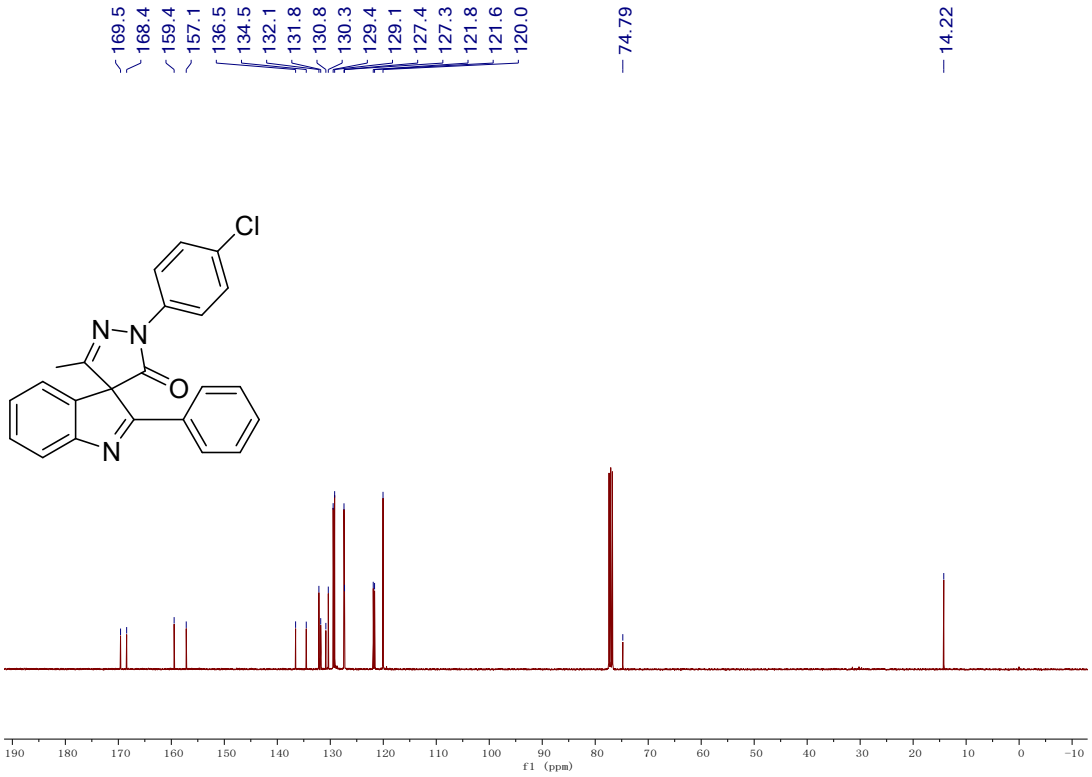
^{13}C NMR($CDCl_3$) spectrum of **3ab**



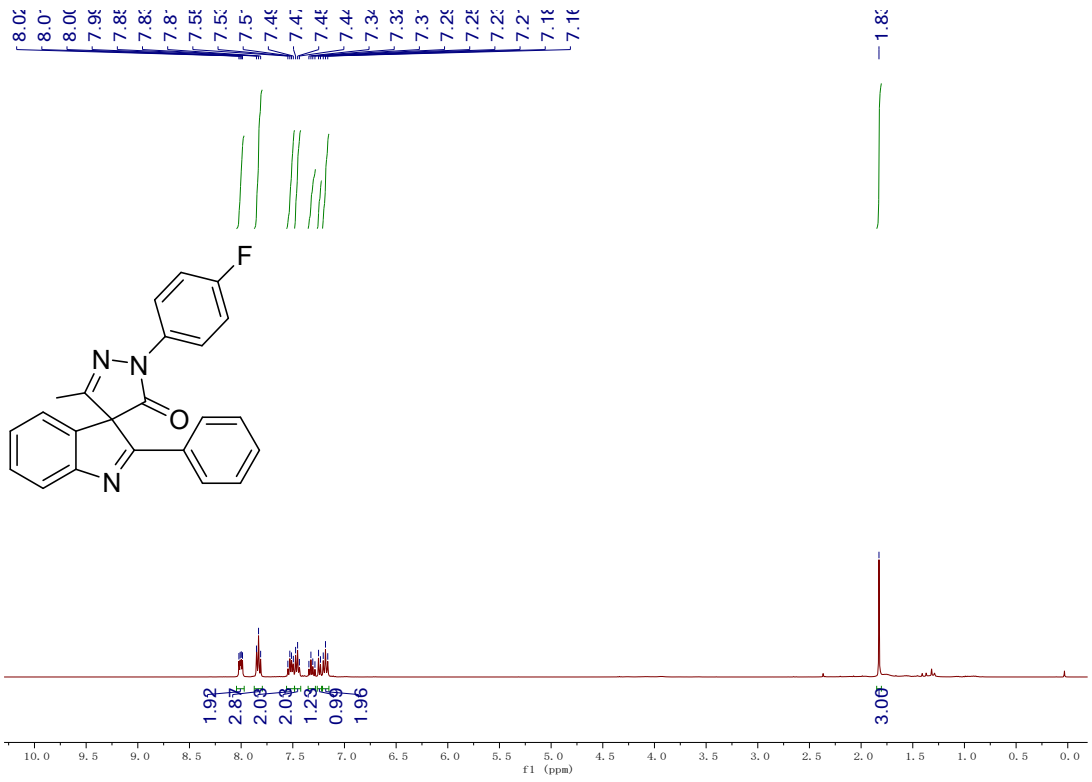
^{1}H NMR($CDCl_3$) spectrum of **3ac**



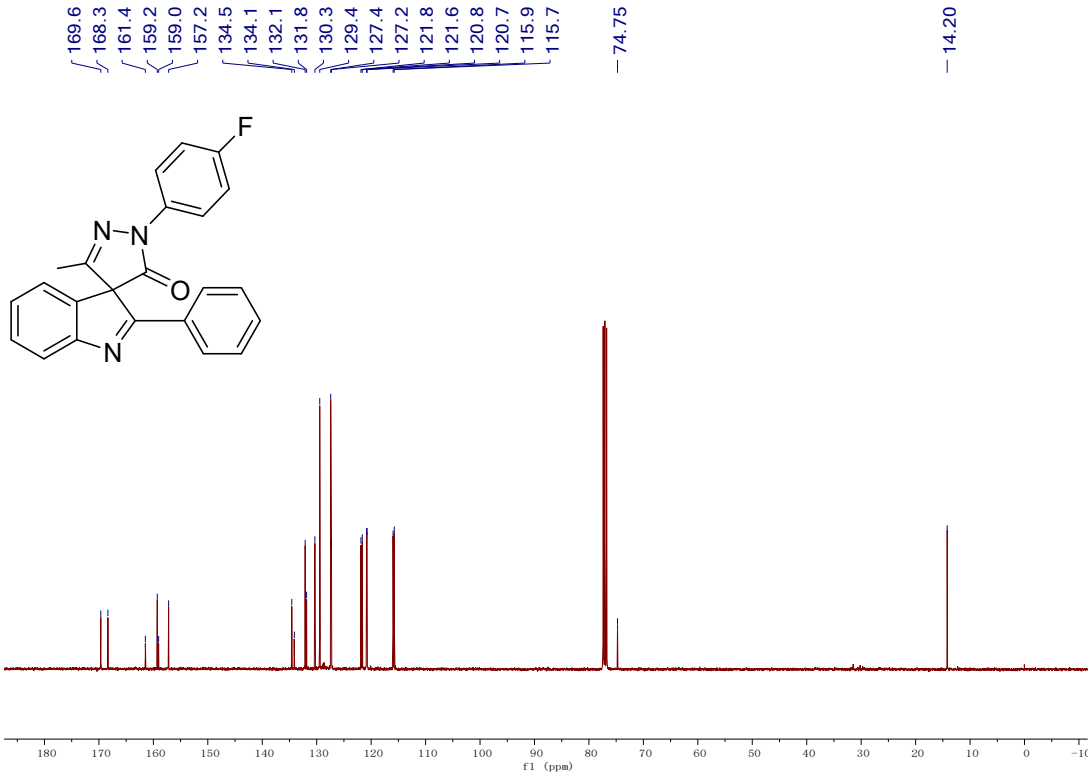
^{13}C NMR($CDCl_3$) spectrum of **3ac**



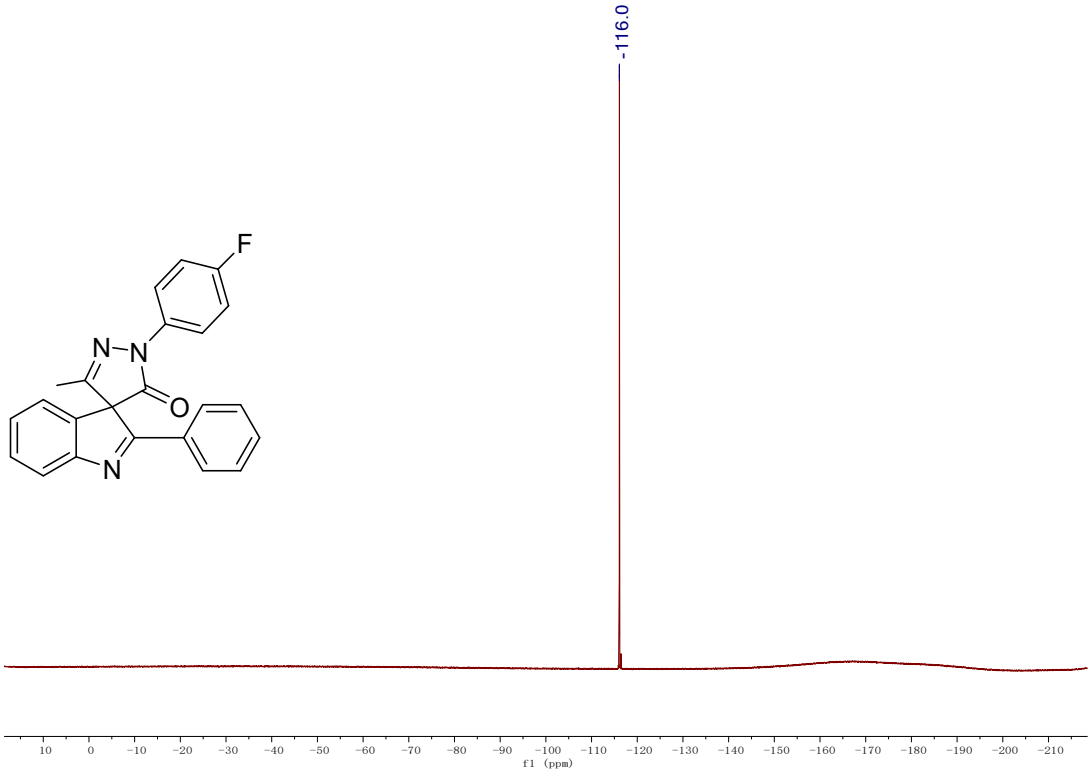
^{1}H NMR($CDCl_3$) spectrum of **3ad**



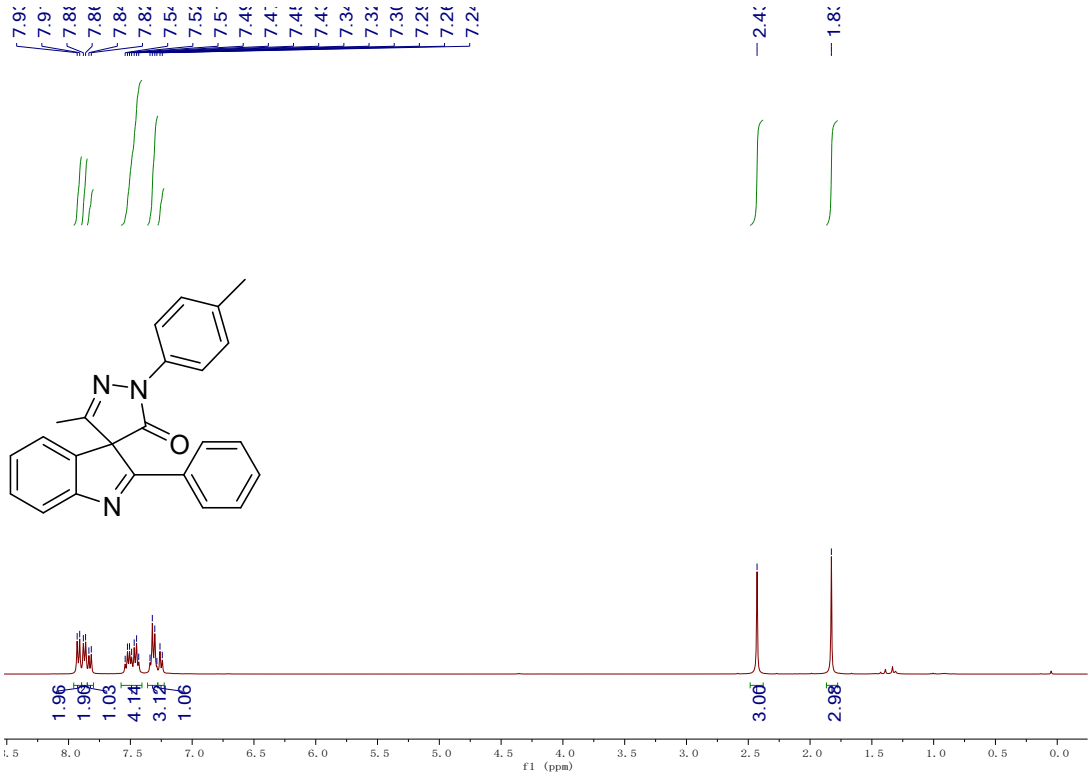
^{13}C NMR($CDCl_3$) spectrum of **3ad**



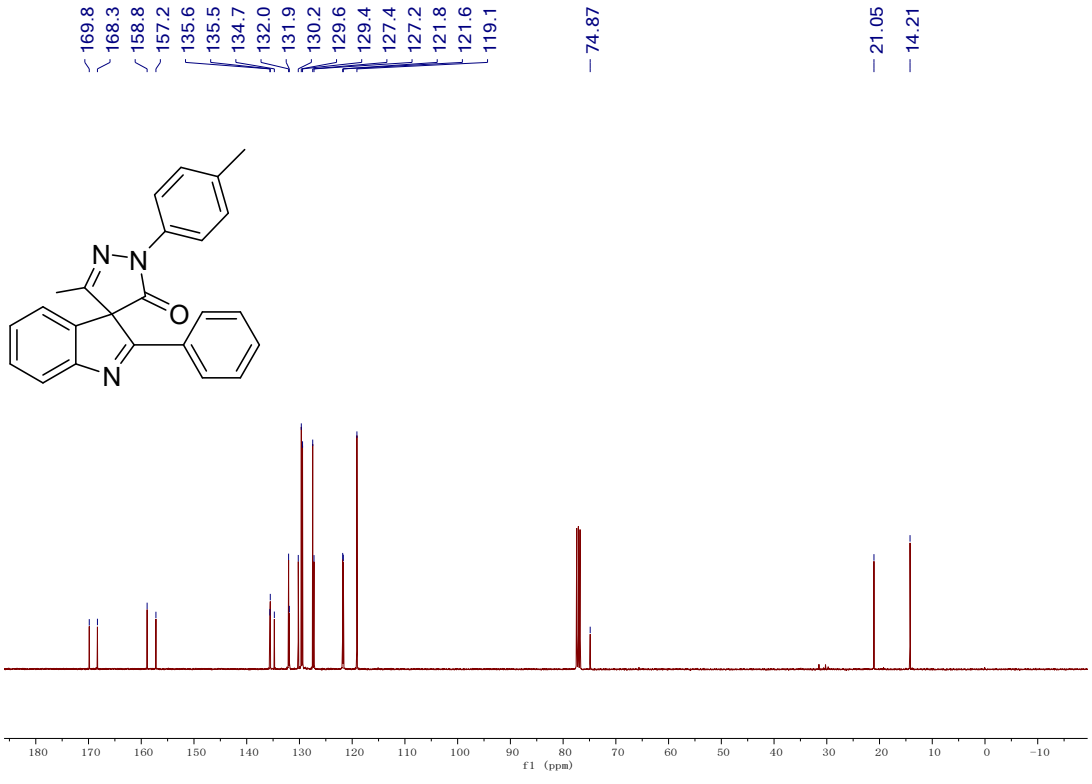
^{19}F NMR($CDCl_3$) spectrum of **3ad**



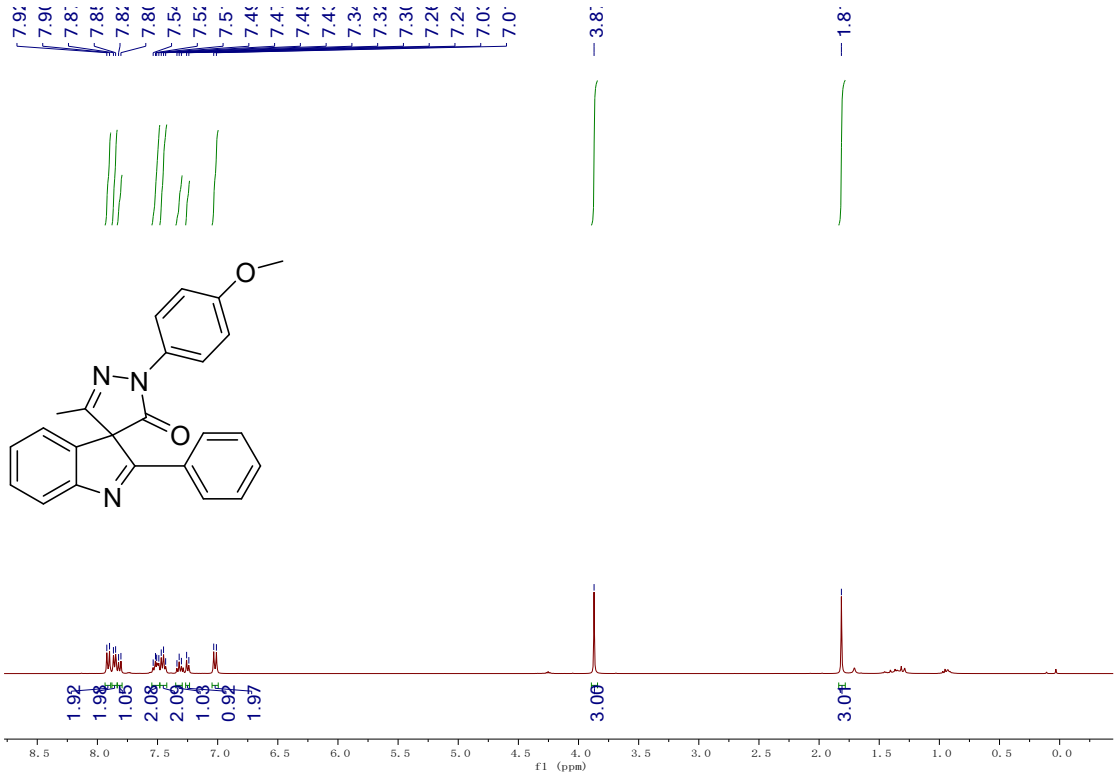
^{1}H NMR($CDCl_3$) spectrum of **3ae**



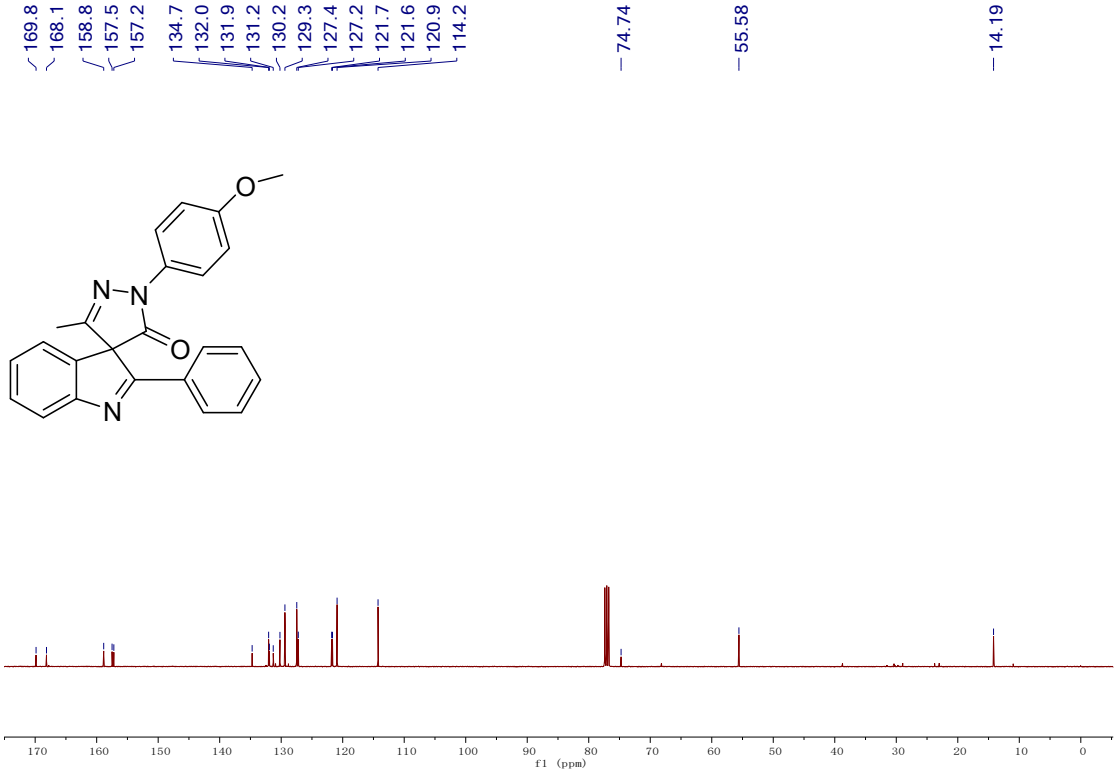
^{13}C NMR($CDCl_3$) spectrum of **3ae**



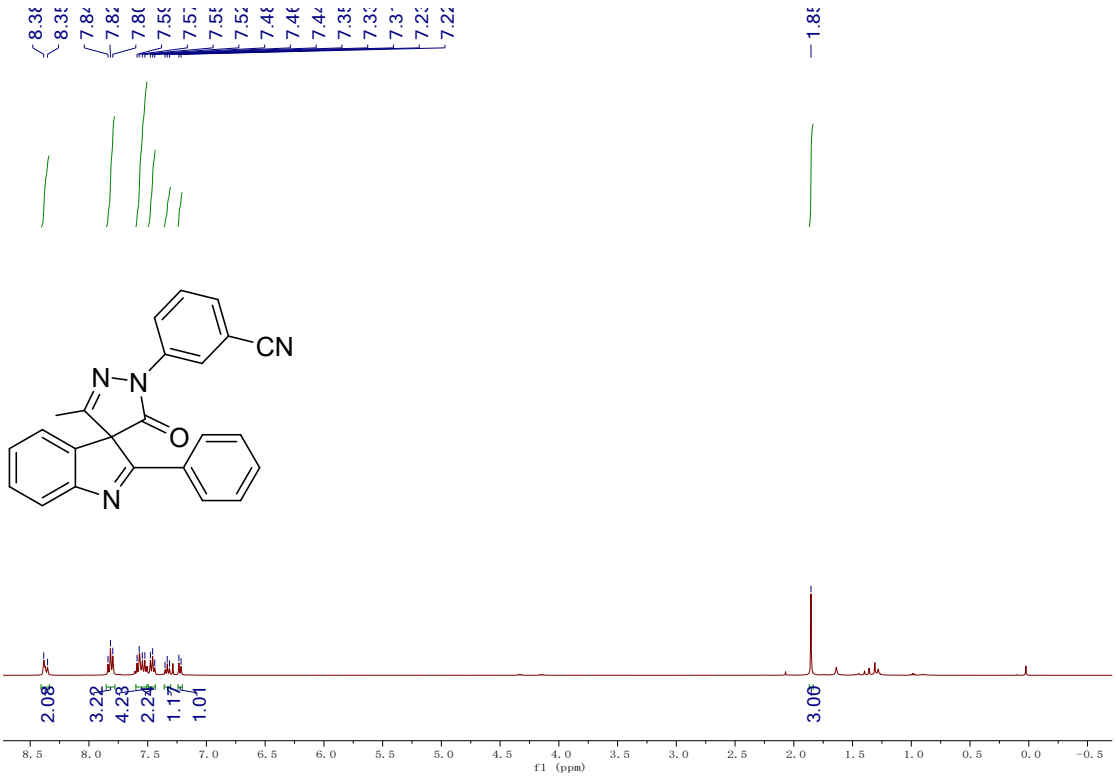
^{1}H NMR($CDCl_3$) spectrum of **3af**



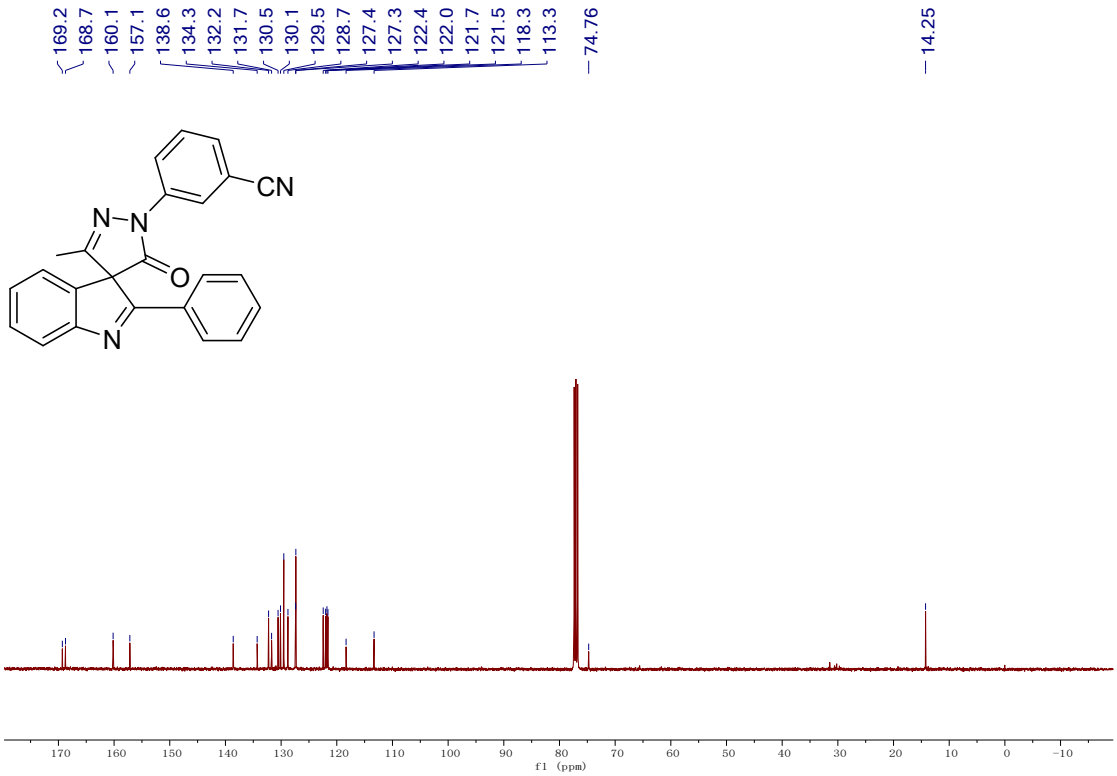
^{13}C NMR($CDCl_3$) spectrum of **3af**



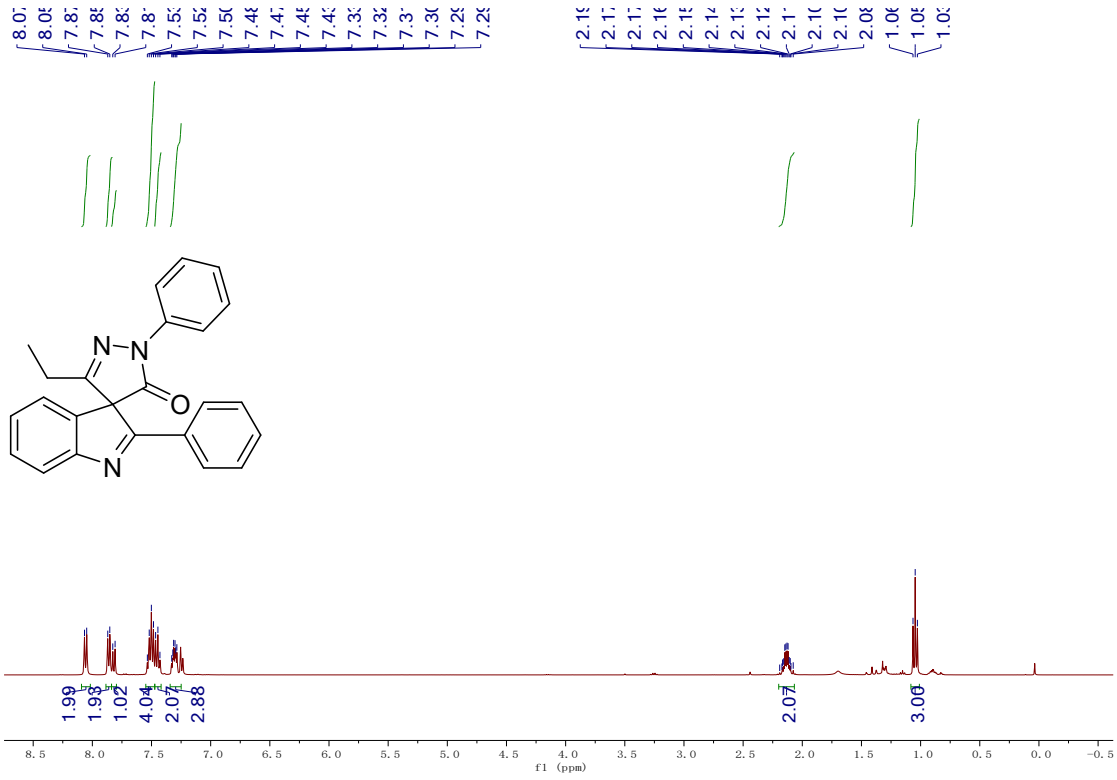
^{1}H NMR($CDCl_3$) spectrum of **3ag**



^{13}C NMR($CDCl_3$) spectrum of **3ag**



^{1}H NMR($CDCl_3$) spectrum of **3ah**



^{13}C NMR ($CDCl_3$) spectrum of **3ah**