

Supporting Information for

**α -Amidino Rhodium Carbenes: Key Intermediates for
the Preparation of (*E*)-2-Aminomethylene-3-oxoindoles
and Pyranoindoles**

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General Information

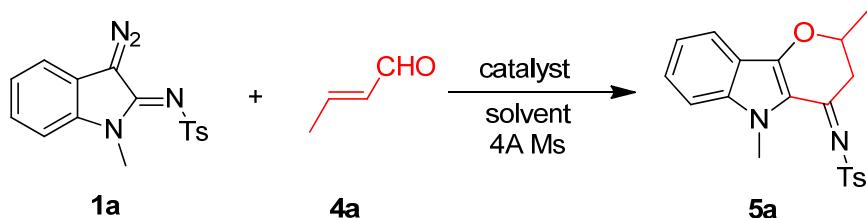
¹H NMR spectra were obtained on 600 or 400 MHz in CDCl₃. The chemical shifts were quoted in parts per million (ppm) referenced to 0.0 ppm for tetramethylsilane (TMS) as an internal standard. ¹³C NMR spectra were recorded on 150 or 100 MHz in CDCl₃. The chemical shifts were reported in ppm referenced to the internal solvent signals (77.00 ppm for CDCl₃). The following abbreviations were used to describe peak patterns where appropriate: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants J were reported in hertz unit (Hz). Infrared spectra were obtained on an FTIR spectrometer. High-resolution mass spectra (HRMS) data were obtained by using EI, MALDI-TOF, or ESI ionization. Melting points were measured with SGW X-4 micro melting point apparatus. Flash column chromatography was performed employing 300-400 mesh silica gel. Thin layer chromatography (TLC) was performed on silica gel HSGF254.

1,2-Dichloroethane was dried by distillation over CaH₂. Toluene was distilled from Na. Chloroform was distilled from phosphorous pentoxide. Rh₂(Oct)₄, Rh₂(TFA)₄, Rh₂(HFB)₄, Rh₂(OAc)₄, Cu(OTf)₂, AgOTf, Rh₂(S-DOSP)₄, Rh₂(esp)₂, aromatic aldehyde, α,β -unsaturated aldehyde, NaH were used as received from the commercial sources. The 3-diazoindolin-2-imines and its analogues were prepared according to the published methods.^{1,2}

References

1. Xing, Y. P.; Sheng, G. R.; Wang, J.; Lu, P.; Wang, Y. G. *Org. Lett.* **2014**, 16, 1244.
2. Sheng, G. R.; Huang, K.; Chi, Z. H.; Ding, H. L.; Xing, Y. P.; Lu, P.; Wang, Y. G. *Org. Lett.* **2014**, 16, 5096.

Table S1 Optimization of Reaction Conditions



entry	catalyst	temp (°C)	time (h)	solvent	yields ^b (%)
1	Rh ₂ (TFA) ₄	60	3	Toluene	34
2	Rh ₂ (HFD) ₄	60	3	Toluene	trace
3	Rh ₂ (s-DOSP) ₄	60	3	Toluene	trace
4	Rh ₂ (OAc) ₄	60	3	Toluene	18
5	Rh ₂ (Oct) ₄	60	3	Toluene	trace
6	Rh ₂ (esp) ₄	60	3	Toluene	trace
7	Cu(OTf) ₂	60	3	Toluene	trace
8	AgOTf	60	3	Toluene	trace
9	Rh ₂ (HFB) ₄	rt	3	Toluene	21
10	Rh ₂ (HFB) ₄	40	3	Toluene	27
11	Rh ₂ (HFB) ₄	120	3	Toluene	31
12	Rh ₂ (HFB) ₄	60	2	Toluene	29
13	Rh ₂ (HFB) ₄	60	4	Toluene	33
14	Rh ₂ (HFB) ₄	60	3	DCE	25
15	Rh ₂ (HFB) ₄	60	3	CHCl ₃	22
16	Rh ₂ (HFB) ₄	60	3	DCM	31
17	Rh ₂ (HFB) ₄	60	3	CH ₃ CN	trace
18	Rh ₂ (HFB) ₄	60	3	DMSO	trace
19	Rh ₂ (HFB) ₄	60	3	Toluene	19 ^c
20	Rh ₂ (HFB) ₄	60	3	Toluene	30 ^d

^aReaction conditions: **1a** (0.20 mmol), **4a** (0.30 mmol), catalyst (0.005 mmol), solvent (2 mL), 4 Å MS (20 mg). ^bIsolated yields. ^cWithout 4 Å MS. ^d**4a** (0.60 mmol).

General Procedure for the Synthesis of 3

To an oven-dried Heavy-wall Pressure Vessel equipped with a magnetic stirring bar were added **1** (0.2 mmol), **2** (0.9 mmol), Rh₂(HFB)₄ (0.005 mmol), 4 Å MS (20 mg) and dry DCM (2 mL) under air atmosphere. Then the mixture was stirred at 100 °C for 4 h until the reaction was completed (monitored by TLC). After the reaction mixture was cooled to room temperature, the solvent was removed in vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 4:1) to give pure product **3**.

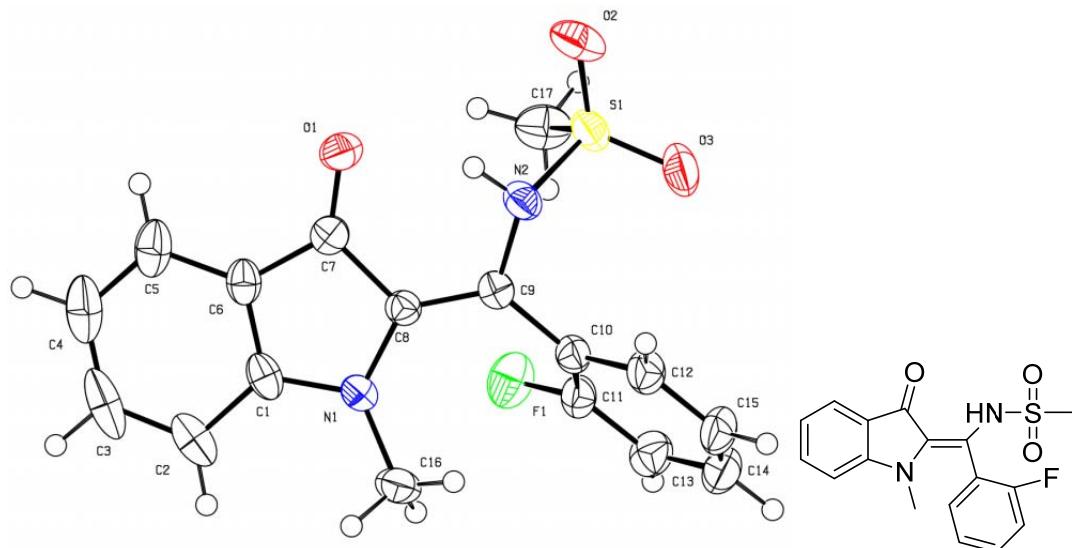
General Procedure for the Synthesis of 5

To an oven-dried flask equipped with a magnetic stirring bar were added **1** (0.2 mmol), **4** (0.3 mmol), Rh₂(TFA)₄ (0.005 mmol), 4 Å MS (20 mg) and dry toluene (2 mL) under air atmosphere. Then the mixture was stirred at 60 °C for 3 h. After the reaction completed, the reaction mixture was cooled to room temperature. The solvent was removed in vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 5:1) to give the product **5**.

General Procedure for the Synthesis of 6

To an oven-dried flask equipped with a magnetic stirring bar were added **1** (0.2 mmol), NaH (0.6 mmol) and dry THF (2 mL) under air atmosphere. Then the mixture was stirred at reflux temperature for 12 h. After the reaction completed, the reaction mixture was cooled to room temperature. The solvent was removed in vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 4:1) to give the product **6**.

The ORTEP diagram and Crystal Parameters of 3t



Bond precision: C-C = 0.0044 Å

Wavelength=0.71073

Cell: a=11.9912(7) b=15.1463(7) c=9.4590(6)
 alpha=90 beta=111.614(7) gamma=90

Temperature: 170 K

	Calculated	Reported
Volume	1597.17(17)	1597.18(15)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C17 H15 F N2 O3 S	C17 H15 F N2 O3 S
Sum formula	C17 H15 F N2 O3 S	C17 H15 F N2 O3 S
Mr	346.37	346.37
Dx, g cm-3	1.441	1.440
Z	4	4
Mu (mm-1)	0.232	0.232
F000	720.0	720.0
F000'	720.86	
h, k, lmax	14, 18, 11	14, 18, 11
Nref	2936	2926
Tmin, Tmax	0.905, 0.928	0.788, 1.000
Tmin'	0.905	

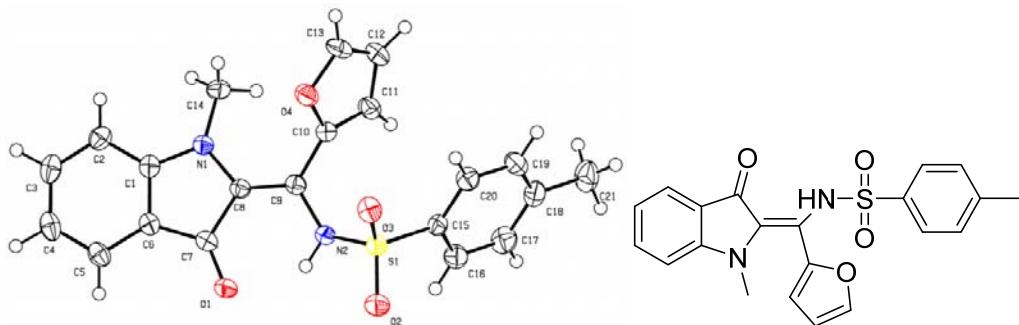
Correction method= # Reported T Limits: Tmin=0.788 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 25.350

R(reflections)= 0.0514(2290) wR2(reflections)= 0.1483(2926)

S = 1.052 Npar= 223

The ORTEP diagram and Crystal Parameters of 3o



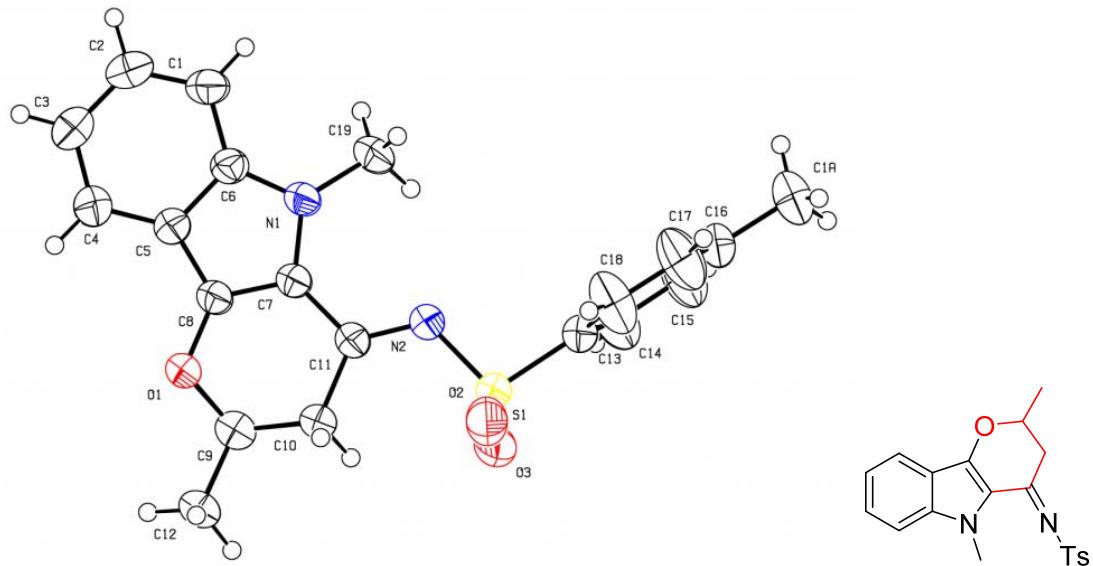
Cell: $a=7.3603(3)$ $b=7.5430(4)$ $c=17.2163(9)$
 $\alpha=87.384(5)$ $\beta=86.032(4)$ $\gamma=74.912(5)$
 Temperature: 170 K

	Calculated	Reported
Volume	920.29(8)	920.29(8)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C ₂₁ H ₁₈ N ₂ O ₄ S	C ₂₁ H ₁₈ N ₂ O ₄ S
Sum formula	C ₂₁ H ₁₈ N ₂ O ₄ S	C ₂₁ H ₁₈ N ₂ O ₄ S
Mr	394.43	394.43
Dx, g cm ⁻³	1.423	1.423
Z	2	2
μ (mm ⁻¹)	0.207	0.207
F000	412.0	412.0
F000'	412.44	
h, k, lmax	8, 9, 20	8, 9, 20
Nref	3351	3336
Tmin, Tmax	0.917, 0.959	0.707, 1.000
Tmin'	0.917	

Correction method= # Reported T Limits: Tmin=0.707 Tmax=1.000
 AbsCorr = MULTI-SCAN

Data completeness= 0.996 Theta(max)= 25.350
 R(reflections)= 0.0422(2763) wR2(reflections)= 0.1145(3336)
 S = 1.052 Npar= 259

The ORTEP diagram and Crystal Parameters of 5a



Bond precision: C-C = 0.0046 Å

Wavelength=0.71073

Cell: $a=5.5675(5)$ $b=8.6310(6)$ $c=19.5676(16)$
 $\alpha=77.417(6)$ $\beta=83.698(7)$ $\gamma=82.645(6)$

Temperature: 293 K

	Calculated	Reported
Volume	906.89(13)	906.89(12)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C ₂₀ H ₂₀ N ₂ O ₃ S	C ₂₀ H ₂₀ N ₂ O ₃ S
Sum formula	C ₂₀ H ₂₀ N ₂ O ₃ S	C ₂₀ H ₂₀ N ₂ O ₃ S
Mr	368.44	368.44
Dx, g cm ⁻³	1.349	1.349
Z	2	2
μ (mm ⁻¹)	0.201	0.201
F000	388.0	388.0
F000'	388.41	
h, k, lmax	6, 10, 23	6, 10, 23
Nref	3328	3317
Tmin, Tmax	0.914, 0.930	0.988, 1.000
Tmin'	0.914	

Correction method= # Reported T Limits: Tmin=0.988 Tmax=1.000
 AbsCorr = MULTI-SCAN

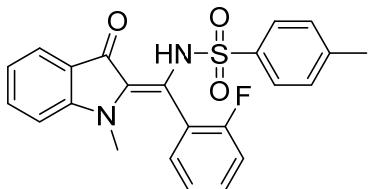
Data completeness= 0.997 Theta(max)= 25.350

R(reflections)= 0.0545(2428) wR2(reflections)= 0.1507(3317)

S = 1.026 Npar= 238

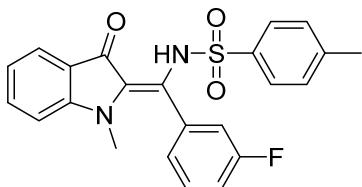
Analysis Data of Products

(E)-N-((2-fluorophenyl)(1-methyl-3-oxoindolin-2-ylidene)methyl)methylbenzenesulfonamide (**3a**):



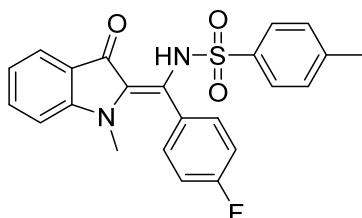
Red solid (56.5 mg, 67%); M.p. 164 – 165 °C ; ¹H NMR (400 MHz, CDCl₃) δ 12.25 (s, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.52 – 7.42 (m, 4H), 7.29 – 7.23 (m, 1H), 7.18 (dd, *J* = 11.8, 7.8 Hz, 3H), 7.06 (t, *J* = 8.9 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 2.65 (s, 3H), 2.37 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 184.3 , 160.3 (d, *J* = 251.5 Hz), 152.9 , 143.9 , 136.8 , 135.7 , 132.8 (d, *J* = 2.1 Hz), 132.6 (d, *J* = 8.2 Hz), 129.9 , 129.4 , 127.5 , 125.6 , 124.6 , 123.6 (d, *J* = 3.6 Hz), 120.2 , 119.3 , 118.8 (d, *J* = 15.2 Hz), 115.5 (d, *J* = 21.1 Hz), 109.6 , 32.0 , 21.6 ; IR (film): 3063, 2949, 2924, 2845, 1926, 1619, 1345, 1201, 1185, 1107 cm⁻¹; HRMS (MALDI-TOF): calcd for C₂₃H₁₉FN₂O₃S+H⁺ ([M+H]⁺): 423.1173, Found: 423.1151.

(E)-N-((3-fluorophenyl)(1-methyl-3-oxoindolin-2-ylidene)methyl)-4-methylbenzenesulfonamide (**3b**):



Red solid (52.3 mg, 62%); M.p. 145 – 146 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.06 (s, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.51-7.32 (m, 4H), 7.16 (d, *J* = 7.7 Hz, 3H), 7.09 (d, *J* = 7.4 Hz, 1H), 6.98 – 6.83 (m, 3H), 2.62 (s, 3H), 2.37 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 184.5 , 161.9 (d, *J* = 248.1 Hz), 153.3 , 144.1 , 136.7 , 135.7 , 135.0 , 132.8 (d, *J* = 8.1 Hz), 129.5 , 129.5 , 127.7 , 127.0 (d, *J* = 3.1 Hz), 125.4 , 124.5 , 120.5 , 119.6 , 118.0 (d, *J* = 22.8 Hz), 117.4 (d, *J* = 21.0 Hz), 110.1 , 33.6 , 21.6 ; IR (film): 3067, 2921, 1867, 1748, 1620, 1573, 1185, 1086, 899, 716 cm⁻¹; HRMS (MALDI-TOF): calcd for C₂₃H₁₉FN₂O₃S+H⁺ ([M+H]⁺): 423.1173, Found: 423.1170.

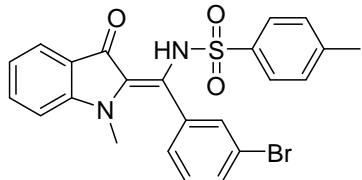
(E)-N-((4-fluorophenyl)(1-methyl-3-oxoindolin-2-ylidene)methyl)-4-methylbenzenesulfonamide (**3c**):



Red solid (51.5 mg, 61%); M.p. 163-164 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.11 (s, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.50-7.44 (m, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.22 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.11 – 7.05 (m, 2H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 2.61 (s, 3H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 184.5 , 161.9 (d, *J* = 248.1 Hz), 153.3 , 144.1 , 136.7 , 135.7 , 135.0 , 132.8 (d, *J* = 8.1 Hz), 129.5 , 129.5 , 127.7 , 127.0 (d, *J* = 3.1 Hz), 125.4 , 124.5 , 120.5 , 119.6 , 118.0 (d, *J* = 22.8 Hz), 117.4 (d, *J* = 21.0 Hz), 110.1 , 33.6 , 21.6 ; IR (film): 3067, 2921, 1867, 1748, 1620, 1573, 1185, 1086, 899, 716 cm⁻¹; HRMS (MALDI-TOF): calcd for C₂₃H₁₉FN₂O₃S+H⁺ ([M+H]⁺): 423.1173, Found: 423.1151.

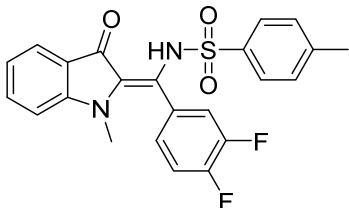
NMR (100 MHz, CDCl₃) δ 184.1, 163.8 (d, *J* = 251.9 Hz), 153.2, 144.0, 136.7, 136.2, 135.5, 133.1 (d, *J* = 8.6 Hz), 129.4, 127.6, 126.7 (d, *J* = 3.4 Hz), 126.2, 124.5, 120.6, 119.5, 115.1 (d, *J* = 21.9 Hz), 110.1, 33.7, 21.6; IR (film): 3065, 2944, 2836, 2795, 1909, 1649, 1505, 1487, 1345, 1085 cm⁻¹; HRMS (ESI): calcd for C₂₃H₁₉FN₂O₃S-H⁺ (M-H⁺): 421.1028, Found: 421.1028.

(*E*)-N-((3-bromophenyl)(1-methyl-3-oxoindolin-2-ylidene)methyl)-4-methylbenzenesulfonamide (**3d**):



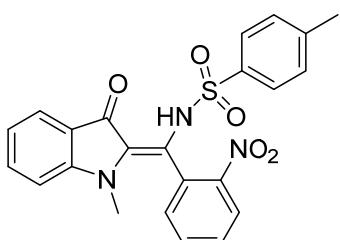
Red solid (51.1 mg, 53%); M.p. 185-186 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.11 (s, 1H), 7.79-7.73 (m, 1H), 7.62-7.54 (m, 1H), 7.51-7.45 (m, 1H), 7.42 – 7.34 (m, 3H), 7.32-7.25 (m, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.12 (t, *J* = 1.8 Hz, 1H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 2.62 (s, 3H), 2.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 184.6, 153.3, 144.2, 136.7, 135.7, 134.7, 133.4, 133.2, 132.6, 129.9, 129.5, 129.4, 127.7, 125.3, 124.6, 121.8, 120.5, 119.5, 110.0, 33.7, 21.6; IR (film): 3061, 2942, 2851, 1905, 1649, 1618, 1486, 1342, 1204, 1043 cm⁻¹; HRMS (ESI): calcd for C₂₃H₁₉BrN₂O₃S+H⁺ ([M+H]⁺): 483.0373, Found: 483.037.

(*E*)-N-((3,4-difluorophenyl)(1-methyl-3-oxoindolin-2-ylidene)methyl)-4-methylbenzenesulfonamide (**3e**):



Red solid (48.4 mg, 55%); M.p. 197-198 °C; ¹H NMR (400 MHz, CDCl₃) δ 11.94 (s, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.52 – 7.42 (m, 3H), 7.24-7.15 (m, 3H), 7.10 – 7.02 (m, 2H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 2.65 (s, 2H), 2.37 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 184.8, 153.5, 151.4 (dd, J_{C,F}= 253.0 Hz, J_{C,F}= 12.0 Hz), 149.7 (dd, J_{C,F}= 250.0 Hz, J_{C,F}= 13.0 Hz), 144.3, 136.6, 135.9, 133.6, 129.5, 127.9 – 127.7 (m), 127.6, 125.7, 124.6, 120.6, 120.2 (d, *J* = 18.5 Hz), 119.8, 117.0 (d, *J* = 17.7 Hz), 110.1, 33.8, 21.6; IR(film): 3060, 2930, 2845, 1867, 1747, 1614, 1557, 1486, 1085, 747 cm⁻¹; HRMS (ESI): calcd for C₂₃H₁₈F₂N₂O₃S+H⁺ ([M+H]⁺): 441.1079, Found: 441.1083.

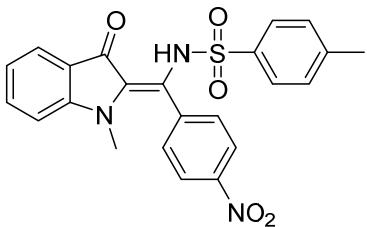
(*E*)-4-methyl-N-((1-methyl-3-oxoindolin-2-ylidene)(2-nitrophenyl)methyl)benzenesulfonamide (**3f**):



Red solid(26.9 mg, 30%); M.p. 191-192 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.26 (s, 1H), 8.22 (d, *J* =

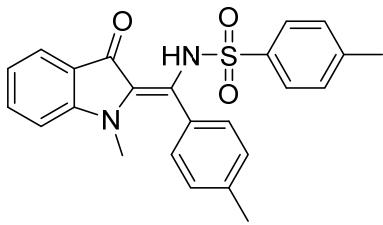
8.1 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.66–7.59 (m, 1H), 7.50–7.41 (m, 3H), 7.17 (t, J = 7.7 Hz, 3H), 6.97 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 8.4 Hz, 1H), 2.67 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.5, 150.7, 148.3, 144.1, 139.6, 137.2, 134.7, 133.0, 132.6, 131.5, 129.6, 127.3, 126.6, 124.7, 124.0, 123.3, 119.7, 119.6, 109.9, 32.4, 21.6; IR (film): 3064, 2924, 1740, 1571, 1530, 1347, 1204, 1202, 883, 789 cm^{-1} ; HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{19}\text{N}_3\text{O}_5\text{S}-\text{H}^+$ ($\text{M}-\text{H}^+$): 448.0973, Found: 448.0972.

(*E*)-4-methyl-*N*-((1-methyl-3-oxoindolin-2-ylidene)(4-nitrophenyl)methyl)benzenesulfonamide (**3g**):



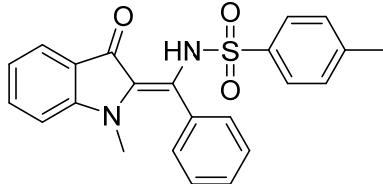
Red solid (44.9 mg, 50%); M.p. 235–236 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 11.79 (s, 1H), 8.26 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 7.7 Hz, 1H), 7.56–7.47 (m, 3H), 7.44 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 6.97 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 8.3 Hz, 1H), 2.61 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 185.5, 153.8, 148.5, 144.4, 137.9, 136.4, 136.2, 132.1, 131.9, 129.6, 127.6, 126.5, 124.8, 122.9, 120.5, 120.1, 110.1, 34.3, 21.6; IR(film): 3104, 3065, 2924, 2857, 1741, 1618, 1520, 1485, 1342, 1098 cm^{-1} ; HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{19}\text{N}_3\text{O}_5\text{S}+\text{H}^+$ ($[\text{M}+\text{H}]^+$): 450.1118, Found: 450.1121.

(*E*)-4-methyl-*N*-((1-methyl-3-oxoindolin-2-ylidene)(*p*-tolyl)methyl)benzenesulfonamide (**3h**):



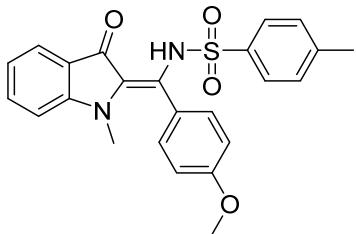
Red solid (31.8 mg, 38%); M.p. 206–207 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 12.15 (s, 1H), 7.79 – 7.72 (m, 1H), 7.49 – 7.39 (m, 3H), 7.22 – 7.11 (m, 6H), 6.92 (t, J = 7.4 Hz, 1H), 6.86 (d, J = 8.3 Hz, 1H), 2.61 (s, 3H), 2.43 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 183.3, 152.8, 143.8, 140.8, 138.7, 136.9, 135.07 (s), 130.9, 129.3, 128.5, 127.9, 127.7, 125.1, 124.3, 120.5, 119.2, 110.0, 33.5, 21.7, 21.6; IR (film): 3059, 3024, 2946, 2922, 1913, 1618, 1508, 1436, 1344, 1043 cm^{-1} ; HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_3\text{S}-\text{H}^+$ ($\text{M}-\text{H}^+$): 417.1278, Found: 417.1275.

(*E*)-4-methyl-*N*-((1-methyl-3-oxoindolin-2-ylidene)(phenyl)methyl)benzenesulfonamide (**3i**):



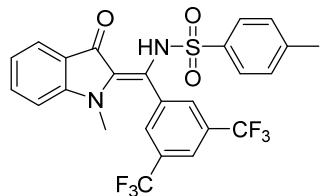
Red solid (41.2 mg, 51%); M.p. 168-169 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.23 (s, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.42-7.33 (m, 4H), 7.24 (d, *J* = 7.5 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 2.58 (s, 3H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 183.7, 152.9, 143.8, 138.1, 136.9, 135.3, 131.0, 130.7, 130.4, 129.4, 127.8, 127.7, 125.1, 124.4, 120.5, 119.3, 110.0, 33.4, 21.6; IR (film): 3061, 2949, 2860, 1722, 1617, 1487, 1345, 1204, 1099, 1043 cm⁻¹; HRMS (ESI): calcd for C₂₃H₂₀N₂O₃S-H⁺ (M-H⁺): 403.1122, Found: 403.1119.

(E)-N-((4-methoxyphenyl)(1-methyl-3-oxoindolin-2-ylidene)methyl)-4-methylbenzenesulfonamide (**3j**):



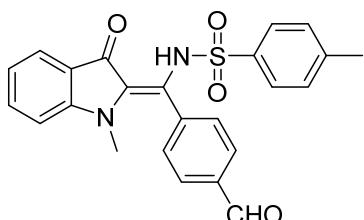
Red solid (24.3 mg, 28%); M.p. 154-155 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.09 (s, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.38 (m, 3H), 7.20 (d, *J* = 8.7 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.96-6.84 (m, 4H), 3.89 (s, 3H), 2.64 (s, 3H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 161.3, 152.8, 143.8, 138.7, 136.8, 135.0, 132.7, 129.3, 127.7, 125.2, 124.3, 122.8, 120.7, 119.3, 113.2, 110.1, 55.4, 33.6, 21.6; IR (film): 3059, 2961, 2830, 2113, 1737, 1603, 1545, 1427, 1210, 1085 cm⁻¹; HRMS (ESI): calcd for C₂₄H₂₂N₂O₄S-H⁺ (M-H⁺): 433.1228, Found: 433.1223.

(E)-N-((3,5-bis(trifluoromethyl)phenyl)(1-methyl-3-oxoindolin-2-ylidene)methyl)-4-methylbenzenesulfonamide (**3k**):



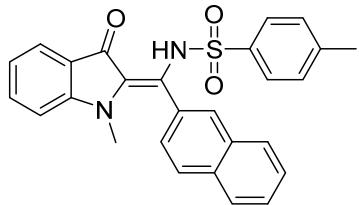
Red solid (56.2 mg, 52%); M.p. 189-190 °C; ¹H NMR (400 MHz, CDCl₃) δ 11.87 (s, 1H), 7.95 (s, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.69 (s, 2H), 7.52 (t, *J* = 1.4 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 2.57 (s, 3H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 185.8, 153.8, 144.6, 136.4, 136.3, 133.2, 131.5-131.0 (m), 130.3, 129.7, 127.5, 126.4, 124.9, 124.2, 123.71 – 123.48 (m), 121.5, 120.5, 120.1, 110.0, 34.1, 21.5; IR (film): 3044, 2967, 2917, 1929, 1685, 1479, 1281, 1172, 1086, 864 cm⁻¹; HRMS (ESI): calcd for C₂₅H₁₈F₆N₂O₃S-H⁺ (M-H⁺): 539.0870, Found: 539.0867.

(E)-N-((4-formylphenyl)(1-methyl-3-oxoindolin-2-ylidene)methyl)-4-methylbenzenesulfonamide (**3i**):



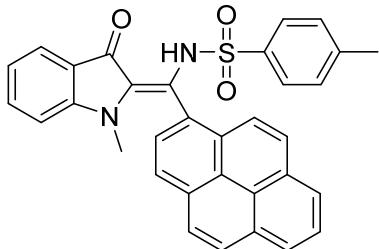
Red solid (52.7 mg, 61%); M.p. 170-171⁰C; ¹H NMR (400 MHz, CDCl₃) δ 11.93 (s, 1H), 10.10 (s, 1H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.51-7.45 (m, 3H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 2.59 (s, 3H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 191.5, 185.0, 153.5, 144.2, 137.1, 136.6, 135.9, 134.0, 131.8, 129.5, 128.8, 127.6, 126.0, 124.6, 120.5, 119.8, 110.1, 34.0, 21.6; IR (film): 3387, 2952, 2923, 2851, 2113, 1739, 1612, 1383, 1158, 1085 cm⁻¹; HRMS (ESI): calcd for C₂₄H₂₀N₂O₄S-H⁺ (M-H⁺): 431.1071, Found: 431.1068.

(E)-4-methyl-N-((1-methyl-3-oxoindolin-2-ylidene)(naphthalen-2-yl)methyl)benzenesulfonamide (**3m**):



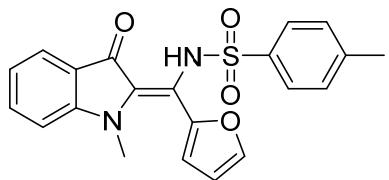
Red solid (43.6 mg, 48%); M.p. 182-183⁰C; ¹H NMR (400 MHz, CDCl₃) δ 12.21 (s, 1H), 7.94-7.82 (m, 2H), 7.81-7.69 (m, 2H), 7.63 – 7.52 (m, 3H), 7.50 – 7.43 (m, 2H), 7.35 – 7.30 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 2.55 (s, 3H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 184.1, 153.1, 143.8, 137.4, 136.9, 135.4, 133.8, 132.1, 131.1, 129.3, 128.5, 128.2, 128.0, 127.8, 127.7, 127.7, 127.4, 126.8, 125.6, 124.5, 120.6, 119.4, 110.0, 33.7, 21.6; IR (film): 3056, 2936, 1908, 1650, 1617, 1485, 1341, 1184, 1085, 740 cm⁻¹; HRMS (ESI): calcd for C₂₇H₂₂N₂O₃S-H⁺ (M-H⁺): 453.1278, Found: 453.1280.

(E)-4-methyl-N-((1-methyl-3-oxoindolin-2-ylidene)(pyren-1-yl)methyl)benzenesulfonamide (**3n**):



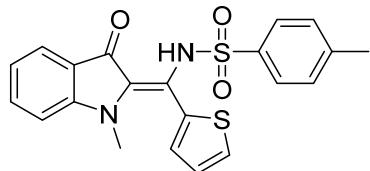
Red solid (65.5 mg, 62%); M.p. 139-140⁰C; ¹H NMR (400 MHz, CDCl₃) δ 12.82 (s, 1H), 8.27 (d, *J* = 7.5 Hz, 1H), 8.22 – 8.10 (m, 4H), 8.08 – 8.01 (m, 2H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.79 (d, *J* = 9.2 Hz, 1H), 7.53 (d, *J* = 9.2 Hz, 1H), 7.47-7.39 (m, 1H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 2H), 2.16 (s, 3H), 1.89 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 183.6, 152.6, 143.4, 136.4, 136.3, 135.4, 132.7, 131.1, 130.5, 130.1, 129.4, 129.0, 128.8, 128.6, 127.4, 127.3, 126.4, 126.1, 125.9, 125.6, 124.6, 124.2, 124.1, 124.1, 123.9, 123.7, 120.4, 119.2, 109.7, 32.1, 21.0; IR (film): 3047, 2941, 1921, 1742, 1614, 1486, 1323, 1197, 1043, 848 cm⁻¹; HRMS (ESI): calcd for C₃₃H₂₄N₂O₃S+H⁺ ([M+H]⁺): 529.1580, Found: 529.1577.

(E)-N-(furan-2-yl(1-methyl-3-oxoindolin-2-ylidene)methyl)-4-methylbenzenesulfonamide (**3o**):



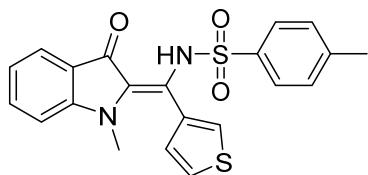
Red solid (56.8 mg, 72%); M.p. 162-163 °C; ¹H NMR (400 MHz, CDCl₃) δ 11.42 (s, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.59 (s, 1H), 7.55-7.41 (m, 3H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.97 – 6.85 (m, 2H), 6.82 (d, *J* = 3.5 Hz, 1H), 6.61 (s, 1H), 2.79 (s, 3H), 2.35 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 187.5, 155.8, 147.4, 146.6, 145.5, 138.8, 138.4, 132.1, 130.2, 128.7, 127.1, 126.7, 123.1, 122.3, 120.6, 114.9, 112.6, 35.2, 24.3; IR (film): 3063, 2944, 1920, 1619, 1485, 1469, 1202, 1102, 1043, 885 cm⁻¹; HRMS (ESI): calcd for C₂₁H₁₈N₂O₄S-H⁺ (M-H⁺): 393.0915, Found: 393.0915.

(E)-4-methyl-N-((1-methyl-3-oxoindolin-2-ylidene)(thiophen-2-yl)methyl)benzenesulfonamide (**3p**):



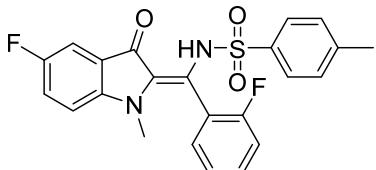
Red solid (45.1 mg, 55%); M.p. 173-174 °C; ¹H NMR (400 MHz, CDCl₃) δ 11.77 (s, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.61-7.56 (m, 2.1 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.10 (dd, *J* = 5.0, 2.8 Hz, 2H), 6.97 – 6.86 (m, 2H), 2.73 (s, 3H), 2.35 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 186.4, 155.8, 146.5, 139.1, 138.1, 135.6, 134.1, 133.3, 132.0, 130.4, 129.4, 129.0, 127.1, 123.2, 122.3, 112.8, 35.6, 24.2; IR (film): 3067, 2925, 2253, 1777, 1616, 1485, 1336, 1185, 1085, 884 cm⁻¹; HRMS (ESI): calcd for C₂₁H₁₈N₂O₃S₂-H⁺ (M-H⁺): 409.0686, Found: 409.0681.

(E)-4-methyl-N-((1-methyl-3-oxoindolin-2-ylidene)(thiophen-3-yl)methyl)benzenesulfonamide (**3q**):



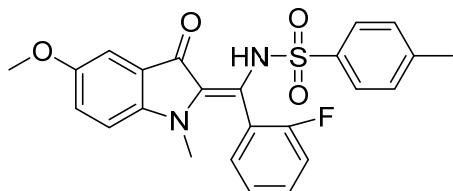
Red solid (35.3 mg, 43%); M.p. 167-168 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.16 (s, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.43 (m, 1H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.35-7.31 (m, 1H), 7.29 – 7.26 (m, 1H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.08-7.04 (m, 1H), 6.96 – 6.87 (m, 2H), 2.67 (s, 3H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 183.2, 152.8, 143.8, 136.7, 135.2, 133.7, 130.70 (s), 130.0, 129.8, 129.4, 127.6, 125.4, 125.3, 124.3, 120.5, 119.4, 110.2, 33.1, 21.6; IR (film): 3106, 2924, 2253, 1914, 1644, 1486, 1184, 1099, 909 cm⁻¹; HRMS (ESI): calcd for C₂₁H₁₈N₂O₃S₂-H⁺ (M-H⁺): 409.0686, Found: 409.0689.

(E)-N-((5-fluoro-1-methyl-3-oxoindolin-2-ylidene)(2-fluorophenyl)methyl)-4-methylbenzenesulfonamide (**3r**):



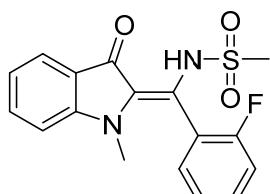
Red solid (71.3 mg, 81%); M.p. 180-181 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.23 (s, 1H), 7.54 – 7.46 (m, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.36 (m, 1H), 7.28-7.13 (m, 5H), 7.07 (t, *J* = 8.9 Hz, 1H), 6.85-6.79 (m, 1H), 2.65 (s, 3H), 2.37 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 181.9, 160.1 (d, *J* = 251.5 Hz), 156.8 (d, *J* = 239.8 Hz), 148.9, 144.0, 136.9, 133.2, 132.8 (d, *J* = 8.2 Hz), 132.6 (d, *J* = 2.0 Hz), 129.5, 127.5, 125.7, 123.7 (d, *J* = 3.0 Hz), 123.5 (d, *J* = 25.8 Hz), 120.1 (d, *J* = 8.2 Hz), 118.7 (d, *J* = 19.4 Hz), 115.6 (d, *J* = 21.0 Hz), 110.9 (d, *J* = 8.0 Hz), 109.2 (d, *J* = 23.2 Hz), 32.3, 21.6; IR (film): 3062, 2970, 2923, 2244, 1616, 1493, 1165, 1085, 881, 734 cm⁻¹; HRMS (ESI): calcd for C₂₃H₁₈F₂N₂O₃S-H⁺ (M-H⁺): 439.0933, Found: 439.0939.

(E)-N-((2-fluorophenyl)(5-methoxy-1-methyl-3-oxoindolin-2-ylidene)methyl)-4-methylbenzenesulfonamide (**3s**):



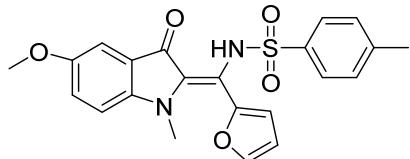
Red solid (59.7 mg, 66%); M.p. 156-157 °C; ¹H NMR (400 MHz, CDCl₃) δ 12.30 (s, 1H), 7.52 – 7.42 (m, 3H), 7.29 – 7.03 (m, 7H), 6.80 (d, *J* = 8.9 Hz, 1H), 3.80 (s, 3H), 2.62 (s, 3H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 182.6, 160.2 (d, *J* = 251.6 Hz), 153.6, 148.5, 143.9, 136.9, 132.7, 132.6, 132.6, 132.1, 129.5, 127.5, 126.2 (d, *J* = 7.8 Hz), 123.6 (d, *J* = 3.5 Hz), 120.0, 118.9 (d, *J* = 15.2 Hz), 115.5 (d, *J* = 21.1 Hz), 111.2, 104.4, 55.9, 32.4, 21.6; IR (film): 3062, 2945, 2839, 2247, 1644, 1615, 1495, 1337, 1281, 1165 cm⁻¹; HRMS (ESI): calcd for C₂₄H₂₁FN₂O₄S-H⁺ (M-H⁺): 451.1133, Found: 451.1130.

(E)-N-((2-fluorophenyl)(1-methyl-3-oxoindolin-2-ylidene)methyl)methanesulfonamide (**3t**):



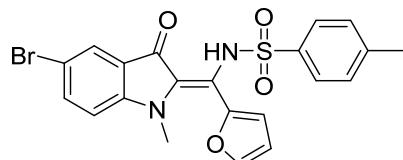
Red solid (38.1 mg, 55%); M.p. 177-178 °C; ¹H NMR (400 MHz, CDCl₃) δ 11.69 (s, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.66 – 7.43 (m, 3H), 7.37 – 7.16 (m, 2H), 7.00-6.89 (m, 2H), 2.97 (s, 3H), 2.77 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 184.2, 160.1(d, *J* = 249.3 Hz), 153.1, 136.0, 132.7(d, *J* = 8.3 Hz), 132.6 (d, *J* = 1.9 Hz), 129.4, 126.2, 124.6, 124.2 (d, *J* = 3.5 Hz), 120.1, 119.8 (d, *J* = 15.2 Hz), 119.6, 115.8 (d, *J* = 21.1 Hz), 109.8, 41.9, 32.0; IR (film): 3064, 3006, 2933, 2848, 1735, 1620, 1487, 1344, 1201, 1044 cm⁻¹; HRMS (ESI): calcd for C₁₇H₁₅FN₂O₃S-H⁺ (M-H⁺): 345.0715, Found: 345.0728.

(E)-N-(furan-2-yl(5-methoxy-1-methyl-3-oxoindolin-2-ylidene)methyl)-4-methylbenzenesulfonamide (**3u**):



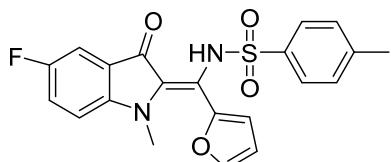
Purple solid (43.3mg, 51%); M.p. 197-198 °C; ¹H NMR (600 MHz, CDCl₃) δ 11.41 (s, 1H), 7.60 (s, 1H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.10 (m, 2H), 6.92-6.81 (m, 2H), 6.64 – 6.60 (m, 1H), 3.80 (s, 3H), 2.77 (s, 3H), 2.35 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 183.2, 153.8, 148.8, 144.9, 143.9, 143.0, 136.2, 129.4, 127.5, 126.7, 125.9, 120.4, 118.3, 112.3, 111.5, 104.4, 55.8, 33.1, 21.6; IR (film): 3405, 2924, 1734, 1646, 1605, 1494, 1336, 1280, 1185, 884 cm⁻¹; HRMS (ESI): calcd for C₂₂H₂₀N₂O₅S-H⁺ (M-H⁺): 423.1020, Found: 423.1017.

(E)-N-((5-bromo-1-methyl-3-oxoindolin-2-ylidene)(furan-2-yl)methyl)-4-methylbenzenesulfonamide (**3v**):



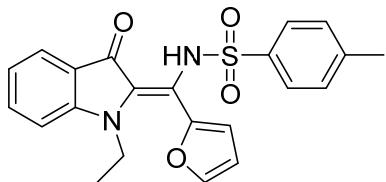
Red solid (69.9 mg, 74%); M.p. 179-180 °C; ¹H NMR (400 MHz, CDCl₃) δ 11.29 (s, 1H), 7.77 (d, *J* = 1.9 Hz, 1H), 7.60 (d, *J* = 1.1 Hz, 1H), 7.54 – 7.46 (m, 3H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 3.1 Hz, 1H), 6.79 (d, *J* = 8.7 Hz, 1H), 6.65-6.61 (m, 1H), 2.79 (s, 3H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.0, 145.2, 144.1, 142.6, 137.7, 136.2, 129.5, 127.6, 126.7, 125.4, 121.8, 118.7, 112.5, 112.2, 111.7, 32.6, 21.6; IR (film): 3128, 3036, 2920, 2836, 1867, 1747, 1595, 1471, 1302, 1026 cm⁻¹; HRMS (ESI): calcd for C₂₁H₁₇BrN₂O₄S-H⁺ (M-H⁺): 471.0020, Found: 471.0017.

(E)-N-((5-fluoro-1-methyl-3-oxoindolin-2-ylidene)(furan-2-yl)methyl)-4-methylbenzenesulfonamide (**3w**):



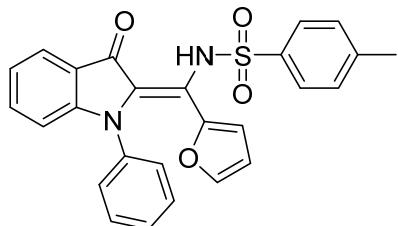
Red solid (68.4 mg, 83%); M.p. 164-165 °C; ¹H NMR (400 MHz, CDCl₃) δ 11.28 (s, 1H), 7.60 (d, *J* = 1.4 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.35-7.30 (m, 1H), 7.25 – 7.15 (m, 3H), 6.92 – 6.84 (m, 2H), 6.65-6.60 (m, 1H), 2.80 (s, 3H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 157.0 (d, *J* = 240.1 Hz), 149.0, 145.2, 144.1, 142.8, 136.3, 129.5, 127.5, 126.3, 126.1, 123.3 (d, *J* = 25.7 Hz), 120.4 (d, *J* = 8.1 Hz), 118.8 (s), 112.5 (s), 111.4 (d, *J* = 7.9 Hz), 109.1 (d, *J* = 23.3 Hz), 32.9, 21.6; IR (film): 3131, 3062, 2923, 2119, 1747, 1650, 1492, 1340, 1165, 1039 cm⁻¹; HRMS (ESI): calcd for C₂₁H₁₇FN₂O₄S-H⁺ (M-H⁺): 411.0820, Found: 411.0813.

(E)-N-((1-ethyl-3-oxoindolin-2-ylidene)(furan-2-yl)methyl)-4-methylbenzenesulfonamide (**3x**):



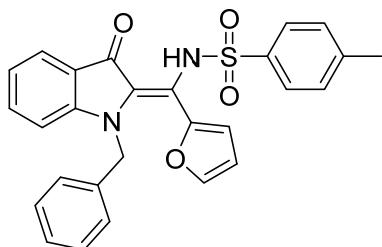
Red solid (58.8 mg, 72%); M.p. 148–149 °C; ¹H NMR (400 MHz, CDCl₃) δ 11.68 (s, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.58 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 1.0 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.98 – 6.88 (m, 2H), 6.81 (d, *J* = 3.4 Hz, 1H), 6.62–6.58 (m, 1H), 3.17 (q, *J* = 7.0 Hz, 2H), 2.35 (s, 3H), 0.83 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 185.3, 152.5, 144.7, 143.9, 142.8, 136.3, 135.7, 129.5, 127.6, 124.9, 124.6, 124.5, 121.3, 119.8, 117.6, 112.2, 110.7, 39.4, 21.6, 12.4; IR (film): 2959, 2925, 2866, 2112, 1736, 1611, 1482, 1346, 1162, 1045 cm⁻¹; HRMS (ESI): calcd for C₂₂H₂₀N₂O₄S-H⁺ (M-H⁺): 407.1071, Found: 407.1061.

(E)-N-(furan-2-yl(3-oxo-1-phenylindolin-2-ylidene)methyl)-4-methylbenzenesulfonamide (**3y**):



Red solid (42.0 mg, 46%); M.p. 136–137 °C; ¹H NMR (400 MHz, CDCl₃) δ 11.67 (s, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.42 – 7.34 (m, 1H), 7.17 (t, *J* = 7.2 Hz, 4H), 7.13 – 7.07 (m, 1H), 7.03 – 6.90 (m, 5H), 6.52 (d, *J* = 3.5 Hz, 1H), 6.13–6.08 (m, 1H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 184.5, 152.1, 144.9, 143.9, 1412.0, 138.1, 136.2, 135.4, 129.4, 128.9, 127.6, 126.6, 126.5, 126.0, 124.4, 123.9, 120.9, 120.7, 118.6, 111.5, 110.9, 21.6; IR (film): 3135, 3036, 2917, 2102, 1899, 1614, 1497, 1365, 1198, 1183 cm⁻¹; HRMS (ESI): calcd for C₂₆H₂₀N₂O₄S-H⁺ (M-H⁺): 455.1071, Found: 455.1070.

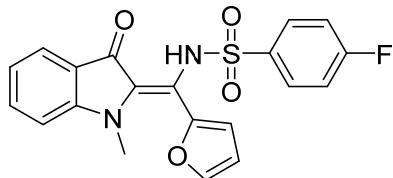
(E)-N-((1-benzyl-3-oxoindolin-2-ylidene)(furan-2-yl)methyl)-4-methylbenzenesulfonamide (**3z**):



Red solid (69.6 mg, 74%); M.p. 158–159 °C; ¹H NMR (400 MHz, CDCl₃) δ 11.59 (s, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.37 (m, 1H), 7.32 (d, *J* = 1.1 Hz, 1H), 7.22 – 7.15 (m, 5H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.85 – 6.75 (m, 3H), 6.65 (d, *J* = 3.4 Hz, 1H), 6.48–6.43 (m, 1H), 4.37 (s, 2H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 184.0, 152.0, 143.8, 142.9, 141.5, 135.4, 135.2,

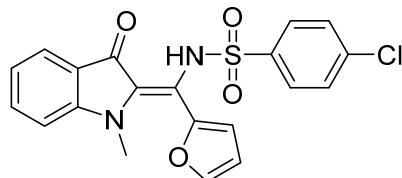
134.7, 128.4, 127.4, 126.6, 126.3, 125.0, 124.1, 124.0, 123.5, 120.0, 119.1, 117.0, 111.1, 110.1, 47.7, 20.6; IR (film): 3030, 2956, 2924, 2855, 2114, 1737, 1614, 1482, 1349, 1104 cm⁻¹; HRMS (ESI): calcd for C₂₇H₂₂N₂O₄S-H⁺ (M-H⁺): 469.1228, Found: 469.1237.

(E)-4-fluoro-N-(furan-2-yl(1-methyl-3-oxoindolin-2-ylidene)methyl)benzenesulfonamide (**3A**):



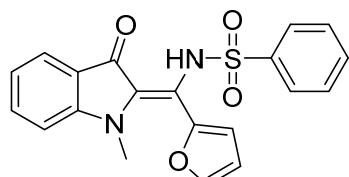
Purple solid (62.1 mg, 78%); M.p. 168–169 °C; ¹H NMR (400 MHz, CDCl₃) δ 11.36 (s, 1H), 7.70 – 7.62 (m, 3H), 7.59 (d, J = 1.1 Hz, 1H), 7.51–7.46 (m, 1H), 7.09 – 7.03 (m, 2H), 6.93 – 6.88 (m, 2H), 6.85–6.80 (m, 1H), 6.64–6.59 (m, 1H), 2.81 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 184.9, 165.2 (d, J = 255.4 Hz), 153.3, 144.9, 142.9, 136.0, 135.1, 130.5 (d, J = 9.5 Hz), 126.3, 124.5, 123.4, 120.3, 119.8, 118.0, 116.0 (d, J = 22.7 Hz), 112.4, 110.0, 32.5; IR (film): 3105, 3070, 2942, 2857, 1896, 1651, 1485, 1345, 1203, 1101 cm⁻¹; HRMS (ESI): calcd for C₂₀H₁₅FN₂O₄S-H⁺ (M-H⁺): 397.0664, Found: 397.0660.

(E)-4-chloro-N-(furan-2-yl(1-methyl-3-oxoindolin-2-ylidene)methyl)benzenesulfonamide (**3B**):



Red solid (62.9 mg, 76%); M.p. 130–131 °C; ¹H NMR (400 MHz, CDCl₃) δ 11.39 (s, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.61 – 7.55 (m, 3H), 7.49 (t, J = 7.4 Hz, 1H), 7.36 (d, J = 8.3 Hz, 2H), 6.98 – 6.87 (m, 2H), 6.82 (d, J = 3.4 Hz, 1H), 6.65–6.59 (m, 1H), 2.81 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 184.8, 153.3, 144.9, 142.8, 139.6, 137.6, 136.0, 129.1, 129.1, 126.3, 124.6, 123.4, 120.3, 119.8, 118.0, 112.4, 110.0, 32.5; IR (film): 3121, 3092, 1922, 1867, 1698, 1584, 1484, 1294, 1088, 827 cm⁻¹; HRMS (MALDI-TOF): calcd for C₂₀H₁₅ClN₂O₄S+H⁺ ([M+H]⁺): 415.0514, Found: 415.0540.

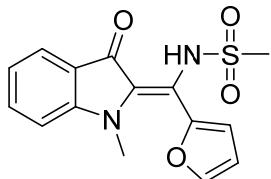
(E)-N-(furan-2-yl(1-methyl-3-oxoindolin-2-ylidene)methyl)benzenesulfonamide (**3C**):



Red solid (54.0 mg, 71%); M.p. 157–158 °C; ¹H NMR (400 MHz, CDCl₃) δ 11.45 (s, 1H), 7.71–7.62 (m, 3H), 7.59 – 7.55 (m, 1H), 7.48 (q, J = 7.3 Hz, 2H), 7.39 (t, J = 7.7 Hz, 2H), 6.96 – 6.86 (m, 2H), 6.80 (d, J = 3.4 Hz, 1H), 6.63–6.58 (m, 1H), 2.79 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 184.7, 153.2, 144.8, 142.9, 139.1, 135.8, 133.1, 128.8, 127.6, 126.1, 124.5, 124.0, 120.4, 119.7, 118.0, 112.3, 110.0,

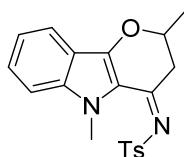
32.5; IR (film): 3143, 3064, 2940, 2842, 2110, 1619, 1484, 1343, 1202, 1086 cm⁻¹; HRMS (ESI): calcd for C₂₀H₁₆N₂O₄S-H⁺ (M-H⁺): 379.0758 , Found: 379.0747.

(E)-N-(furan-2-yl(1-methyl-3-oxoindolin-2-ylidene)methyl)methanesulfonamide (**3D**):



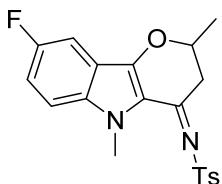
Red solid (43.3 mg, 68%); M.p. 158-159 °C; ¹H NMR (400 MHz, CDCl₃) δ 10.82 (s, 1H), 7.76- 7.72(m, 1H), 7.71 – 7.68 (m, 1H), 7.56 – 7.50 (m, 1H), 7.00 – 6.95 (m, 2H), 6.91 (d, J = 3.5 Hz, 1H), 6.92-6.87 (m, 1H), 3.05 (s, 3H), 2.95 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 153.4, 145.1, 143.9, 135.9, 126.3, 124.5, 123.9, 120.6, 120.0, 117.7, 112.5, 110.2, 41.5, 33.1; IR (film): 3139, 3122, 3003, 2930, 1868, 1649, 1487, 1298, 1187, 1042 cm⁻¹; HRMS (ESI): calcd for C₁₅H₁₄N₂O₄S-H⁺ (M-H⁺): 317.0602, Found: 317.0594.

N-(2,5-dimethyl-2,3-dihydropyrano[3,2-*b*]indol-4(5*H*)-ylidene)-4-methylbenzenesulfonamide (**5a**):



Yellow solid (25.0 mg, 34%); M.p. 190-191 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 8.1 Hz, 1H), 7.42-7.36 (m, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.6 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 4.68-4.55 (m, 1H), 3.83 (s, 3H), 3.76 (dd, J = 17.9, 3.2 Hz, 1H), 3.10-3.00 (m, 1H), 2.44 (s, 3H), 1.60 (d, J = 6.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.6, 152.7, 143.0, 141.0, 139.6, 129.4, 129.3, 126.7, 120.5, 119.7, 117.2, 115.3, 110.0, 76.1, 37.7, 32.1, 21.6, 20.4; IR (film): 3041, 2976, 2899, 1614, 1556, 1404, 1379, 1297, 1085, 931 cm⁻¹; HRMS (EI): calcd for C₂₀H₂₀N₂O₃S ([M]⁺): 368.1195, Found: 368.1195.

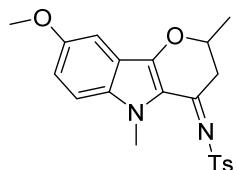
N-(8-fluoro-2,5-dimethyl-2,3-dihydropyrano[3,2-*b*]indol-4(5*H*)-ylidene)-4-methylbenzenesulfonamide (**5b**):



Yellow solid (18.5 mg, 24%); M.p. 200-201 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.29-7.24 (m, 1H), 7.19-7.11 (m, 2H), 4.65-4.55 (m, 1H), 3.81 (s, 3H), 3.76 (dd, J = 17.9, 3.1 Hz, 1H), 3.11-2.99 (m, 1H), 2.44 (s, 3H), 1.60 (d, J = 6.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.8, 157.1 (d, J = 238.4 Hz), 151.9 (d, J = 5.9 Hz), 143.2, 139.4, 137.5, 129.5, 126.7, 118.4(d,J = 27.0 Hz), 118.4, 114.9 (d, J = 10.0 Hz), 111.2 (d, J = 9.0 Hz), 104.6 (d, J = 24.1 Hz), 76.1,

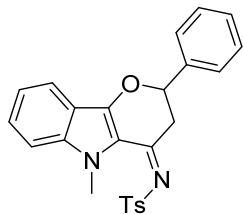
37.7, 32.3, 21.6, 20.4; IR (film): 3012, 2921, 2892, 1741, 1688, 1537, 1296, 1183, 1150, 1084 cm⁻¹; HRMS (EI): calcd for C₂₀H₁₉FN₂O₃S ([M]⁺): 386.1100, Found: 386.1100.

N-(8-methoxy-2,5-dimethyl-2,3-dihydropyrano[3,2-*b*]indol-4(5*H*)-ylidene)-4-methylbenzenesulfonamide (**5c**):



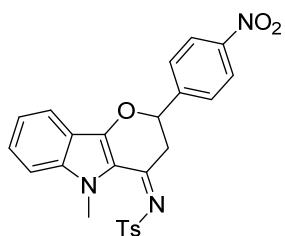
Yellow solid (28.7 mg, 36%); M.p. 197-198°C; ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.12 – 7.04 (m, 2H), 6.96 (d, *J* = 1.9 Hz, 1H), 4.67-4.54 (m, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.75 (dd, *J* = 17.9, 3.1 Hz, 1H), 3.12-2.98 (m, 1H), 2.44 (s, 3H), 1.60 (d, *J* = 6.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.5, 153.8, 151.9, 143.0, 139.6, 137.0, 129.4, 126.6, 121.8, 117.8, 114.9, 111.2, 99.2, 76.0, 55.7, 37.8, 32.2, 21.6, 20.4; IR (film): 3027, 2929, 2941, 2893, 1893, 1530, 1301, 1180, 1086, 893 cm⁻¹; HRMS (EI): calcd for C₂₁H₂₂N₂O₄S ([M]⁺): 398.1300, Found: 398.1306.

4-methyl-*N*-(5-methyl-2-phenyl-2,3-dihydropyrano[3,2-*b*]indol-4(5*H*)-ylidene)benzenesulfonamide (**5d**):



Yellow solid (19.8 mg, 23%); M.p. 195-196 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 6.8 Hz, 2H), 7.48 – 7.37 (m, 4H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 5.51 (dd, *J* = 13.4, 3.3 Hz, 1H), 3.97 (dd, *J* = 18.0, 3.4 Hz, 1H), 3.87 (s, 3H), 3.53-3.40 (m, 1H), 2.44 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 152.3, 143.1, 141.0, 139.5, 138.0, 129.5, 129.4, 129.0, 128.8, 126.7, 126.6, 120.6, 119.9, 117.3, 115.4, 110.0, 81.2, 37.7, 32.2, 21.6; IR (film): 3065, 3027, 2908, 1610, 1551, 1298, 1243, 1148, 1086, 955 cm⁻¹; HRMS (EI): calcd for C₂₅H₂₂N₂O₃S ([M]⁺): 430.1351, Found: 430.1348.

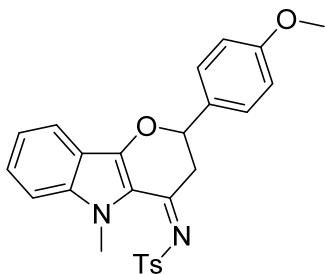
4-methyl-*N*-(5-methyl-2-(4-nitrophenyl)-2,3-dihydropyrano[3,2-*b*]indol-4(5*H*)-ylidene)benzenesulfonamide (**5e**):



Yellow solid (20.9 mg, 22%); M.p. 193-194 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.7 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.89 – 6.77 (m, 2H), 6.26 (d, *J* = 8.2 Hz, 1H), 5.48-5.43 (m, 1H), 4.77 (s, 1H), 2.44 (s, 3H), 2.25 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 197.7, 159.8, 147.4, 144.4, 143.1, 139.0,

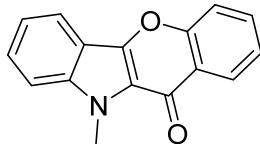
136.7, 131.6, 129.7, 128.7, 127.4, 124.9, 123.3, 118.9, 118.5, 107.6, 106.2, 87.7, 58.5, 29.0, 21.7; IR (film): 3104, 2925, 2833, 2256, 1714, 1614, 1520, 1346, 1164, 998 cm⁻¹; HRMS (EI): calcd for C₂₅H₂₁N₃O₅S ([M]⁺): 475.1202, Found: 475.1206.

N-(2-(4-methoxyphenyl)-5-methyl-2,3-dihydropyrano[3,2-*b*]indol-4(5*H*)-ylidene)-4-methylbenzenesulfonamide (**5f**):



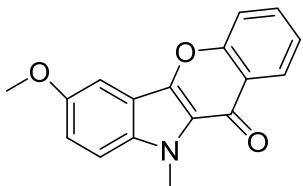
Yellow solid (24.8 mg, 27%); M.p. 227-228 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.67-7.57 (m, 3H), 7.44 – 7.34 (m, 1H), 7.32 – 7.23 (m, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.79-6.72 (m, 2H), 6.69 – 6.63 (m, 2H), 6.23 (d, *J* = 8.3 Hz, 1H), 5.43 (dd, *J* = 4.5, 2.1 Hz, 1H), 4.66 (t, *J* = 2.4 Hz, 1H), 3.71 (s, 3H), 2.42 (s, 3H), 2.14 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 198.5, 159.8, 159.0, 144.0, 138.5, 137.0, 130.2, 129.6, 129.0, 127.4, 127.2, 124.8, 118.8, 117.7, 113.4, 108.1, 107.3, 87.7, 58.2, 55.2, 28.9, 21.6; IR (film): 2964, 2928, 2839, 2259, 1869, 1714, 1613, 1514, 1487, 1040 cm⁻¹; HRMS (EI): calcd for C₂₆H₂₄N₂O₄S ([M]⁺): 460.1457, Found: 460.1459.

10-methylchromeno[3,2-*b*]indol-11(10*H*)-one (**6a**):



White solid (46.8 mg, 94%); M.p. 192-193 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, *J* = 8.0 Hz, 1H), 7.90 (dd, *J* = 8.1, 0.7 Hz, 1H), 7.66 – 7.50 (m, 2H), 7.46-7.40 (m, 1H), 7.37 – 7.29 (m, 2H), 7.19-7.12 (m, 1H), 4.18 (d, *J* = 0.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.5, 155.4, 144.7, 138.4, 132.6, 128.1, 126.0, 124.3, 123.7, 120.5, 120.2, 120.0, 118.0, 114.8, 110.1, 31.3; IR (film): 1642, 1606, 1503, 1458, 1378, 1299, 1252, 956, 920, 754 cm⁻¹; HRMS(ESI): calcd for C₁₆H₁₁NO₂+H⁺ ([M+H]⁺): 250.0863, Found: 250.0858.

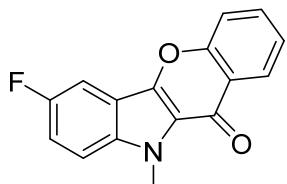
7-methoxy-10-methylchromeno[3,2-*b*]indol-11(10*H*)-one (**6b**):



White solid (50.8 mg, 91%); M.p. 190-191 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.40 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.70-7.63 (m, 1H), 7.62-7.57 (m, 1H), 7.43-7.37 (m, 1H), 7.32-7.28 (m, 2H), 7.18-7.13 (m, 1H), 4.22 (s, 3H), 3.91 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.4, 155.3, 154.2, 144.1, 134.1, 132.5, 126.1, 124.1, 123.6, 120.8, 120.0, 117.9, 114.4, 111.2, 99.4, 55.8, 31.3; IR (film): 1866, 1747, 1646,

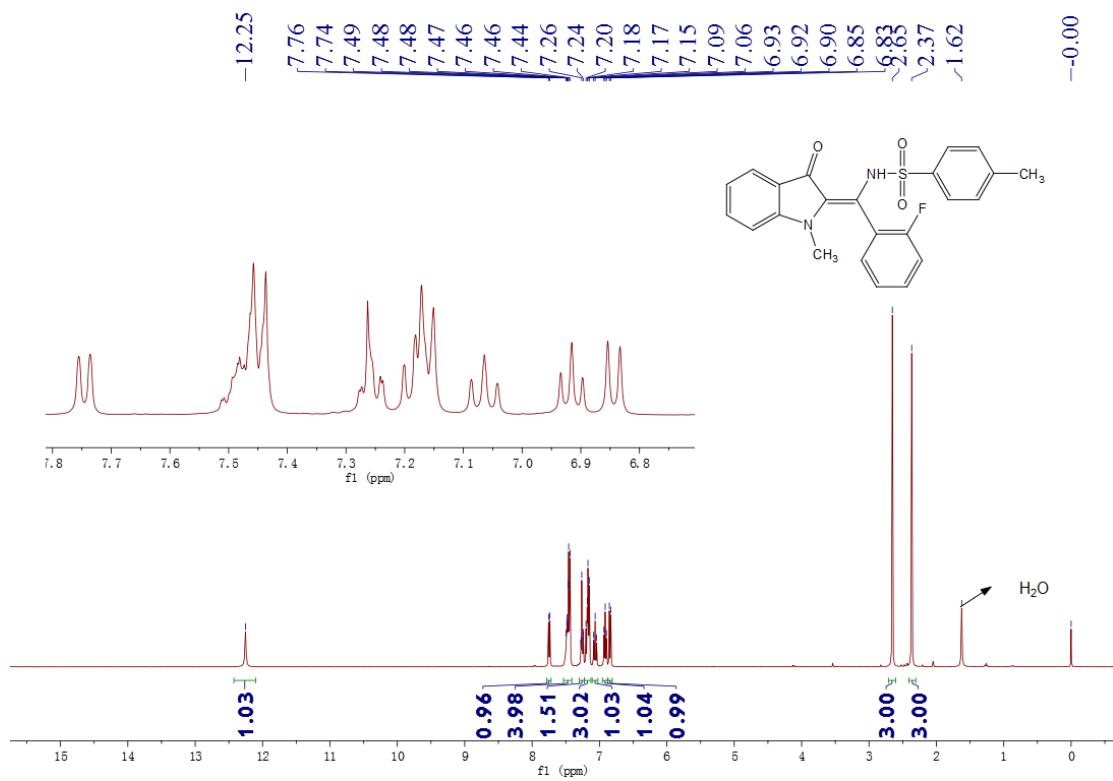
1556, 1516, 1417, 1309, 1259, 1205, 1052 cm⁻¹; HRMS(ESI): calcd for C₁₇H₁₃NO₃+H⁺ ([M+H]⁺): 280.0968, Found: 280.0965.

7-fluoro-10-methylchromeno[3,2-*b*]indol-11(10*H*)-one (**6c**):

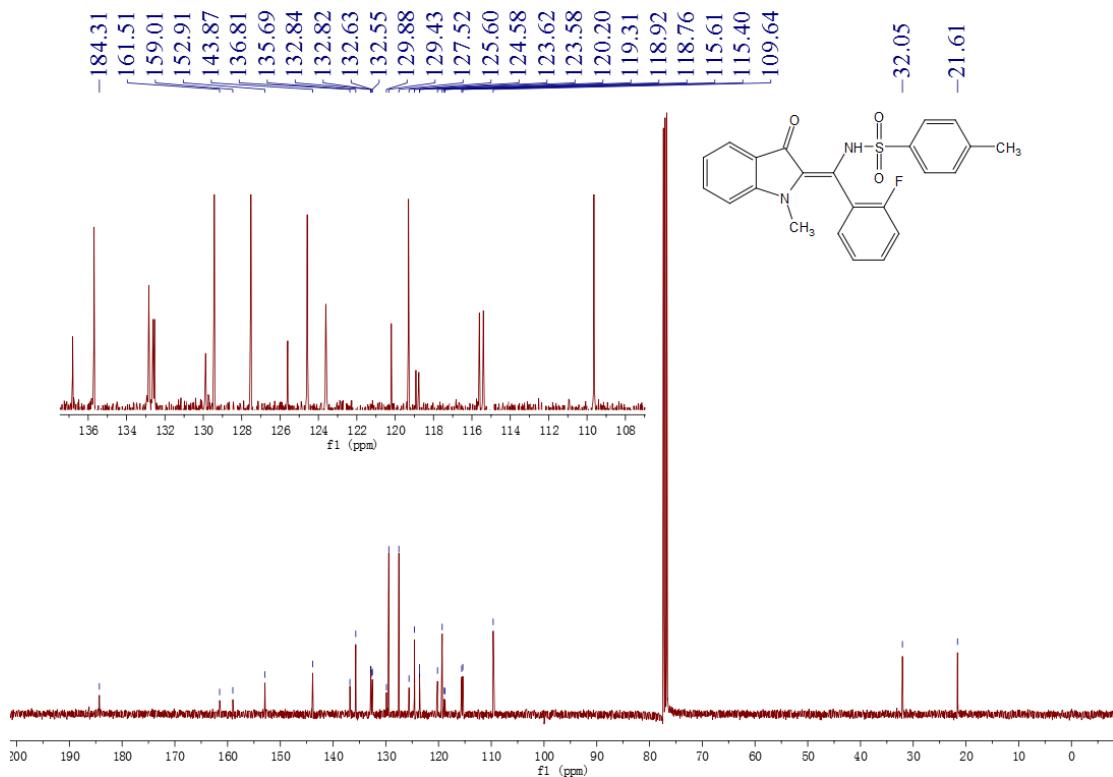


White solid (47.0 mg, 88%); M.p. 224-225 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.40 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.73-7.66 (m, 1H), 7.65 – 7.56 (m, 2H), 7.46 – 7.33 (m, 2H), 7.30-7.21 (m, 1H), 4.25 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.6, 157.5 (d, *J* = 238.4 Hz), 155.4, 144.2, 135.0, 132.9, 126.1, 124.1, 123.8, 121.6, 118.1, 117.2 (d, *J* = 27.0 Hz), 114.5 (d, *J* = 10.3 Hz), 111.4 (d, *J* = 9.2 Hz), 104.5 (d, *J* = 24.7 Hz), 31.5; IR (film): 1643, 1503, 1459, 1378, 1300, 1134, 1109, 1025, 953, 738 cm⁻¹; HRMS (ESI): calcd for C₁₆H₁₀FNO₂+H⁺ ([M+H]⁺): 268.0768, Found: 268.0774.

Copies of ^1H & ^{13}C NMR Spectra

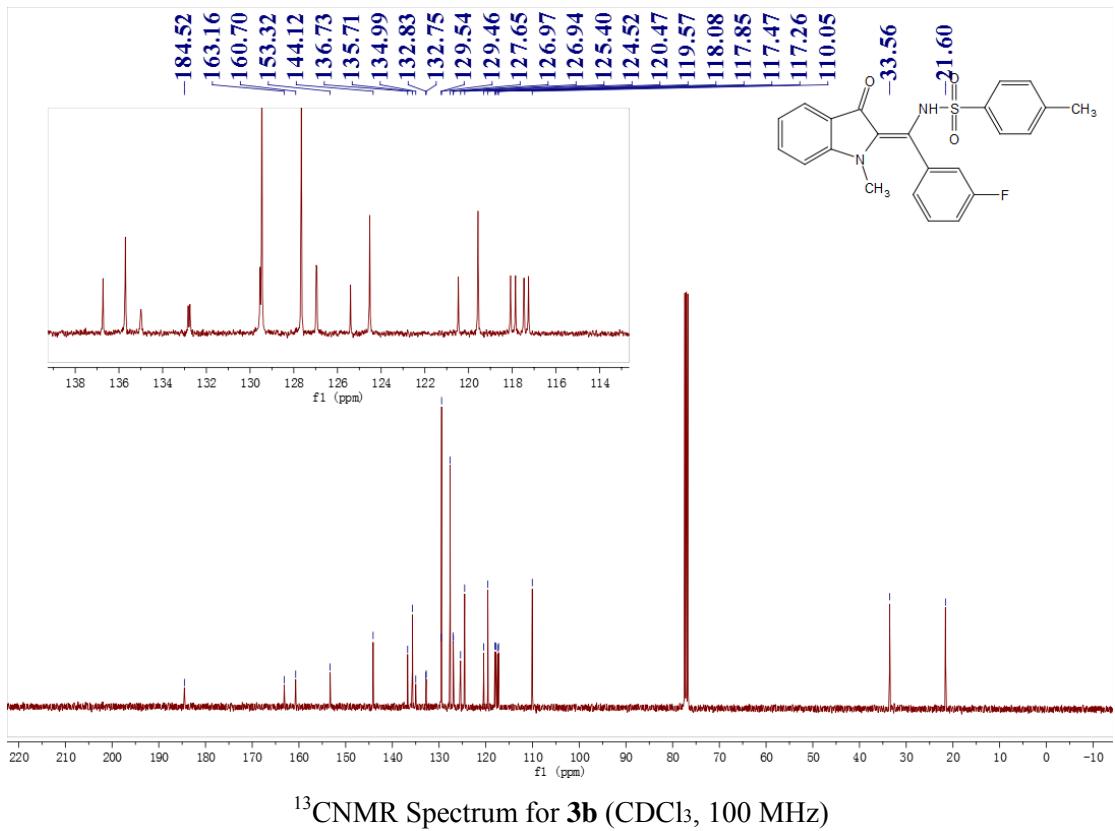
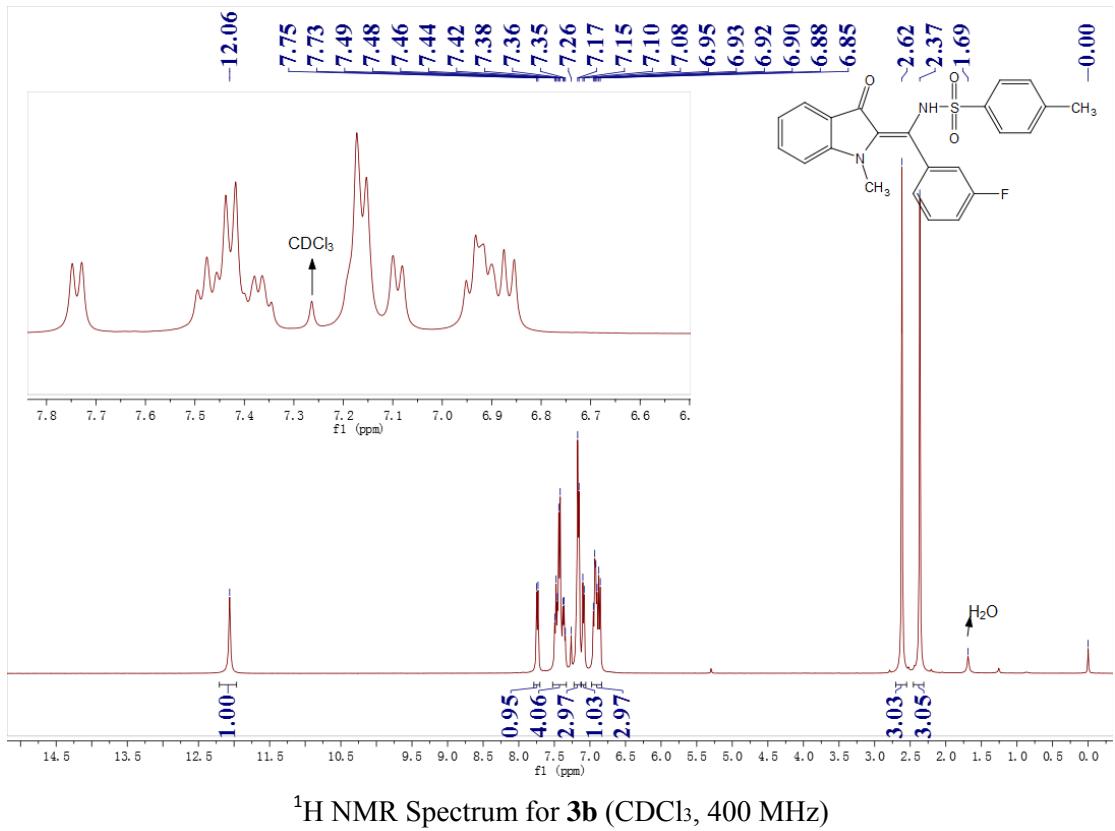


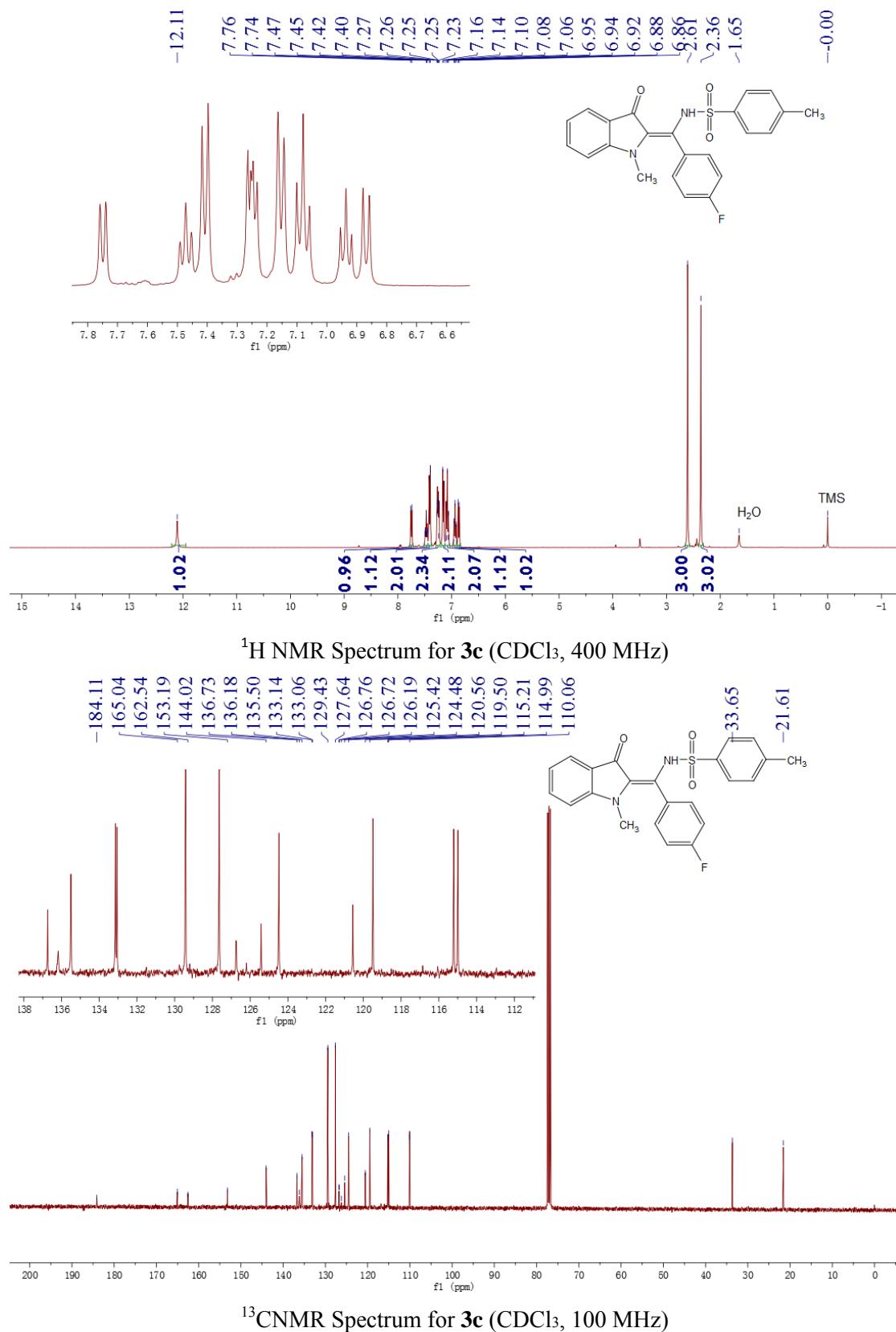
¹H NMR Spectrum for **3a** (CDCl₃, 400 MHz)

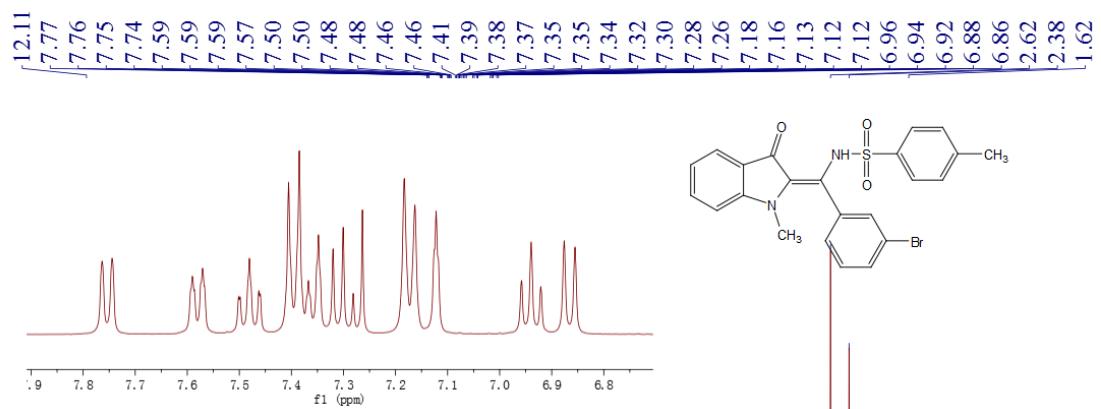


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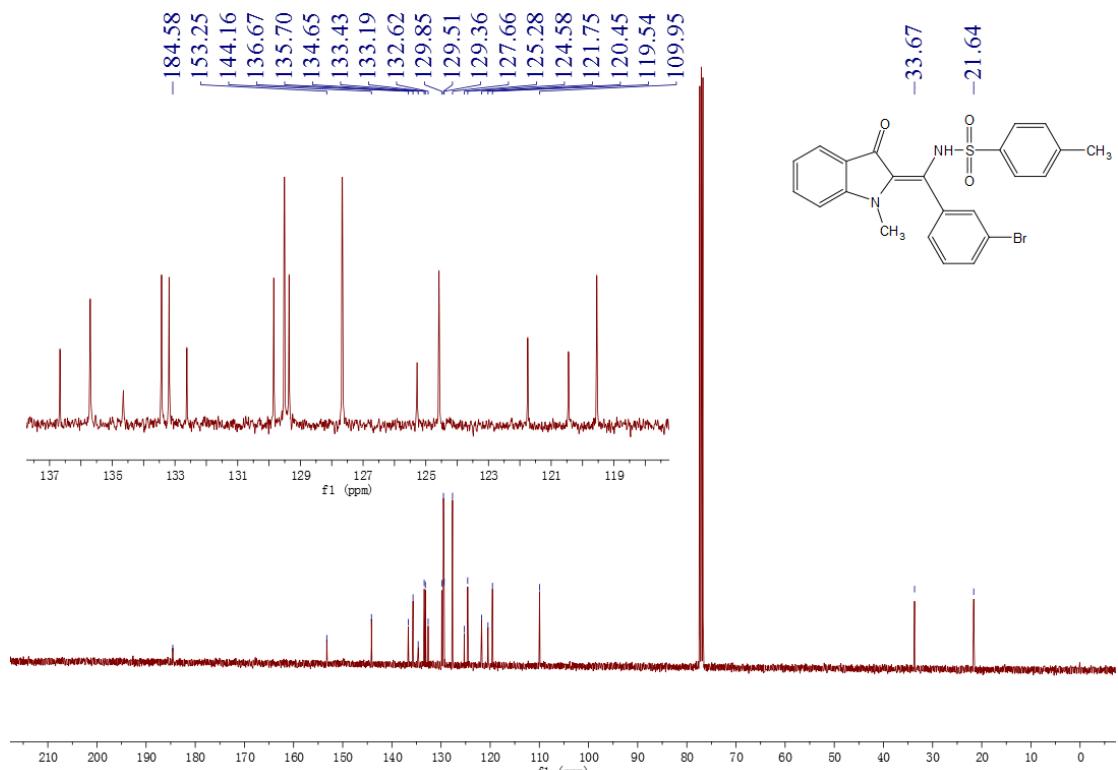
¹³CNMR Spectrum for **3a** (CDCl₃, 100 MHz)



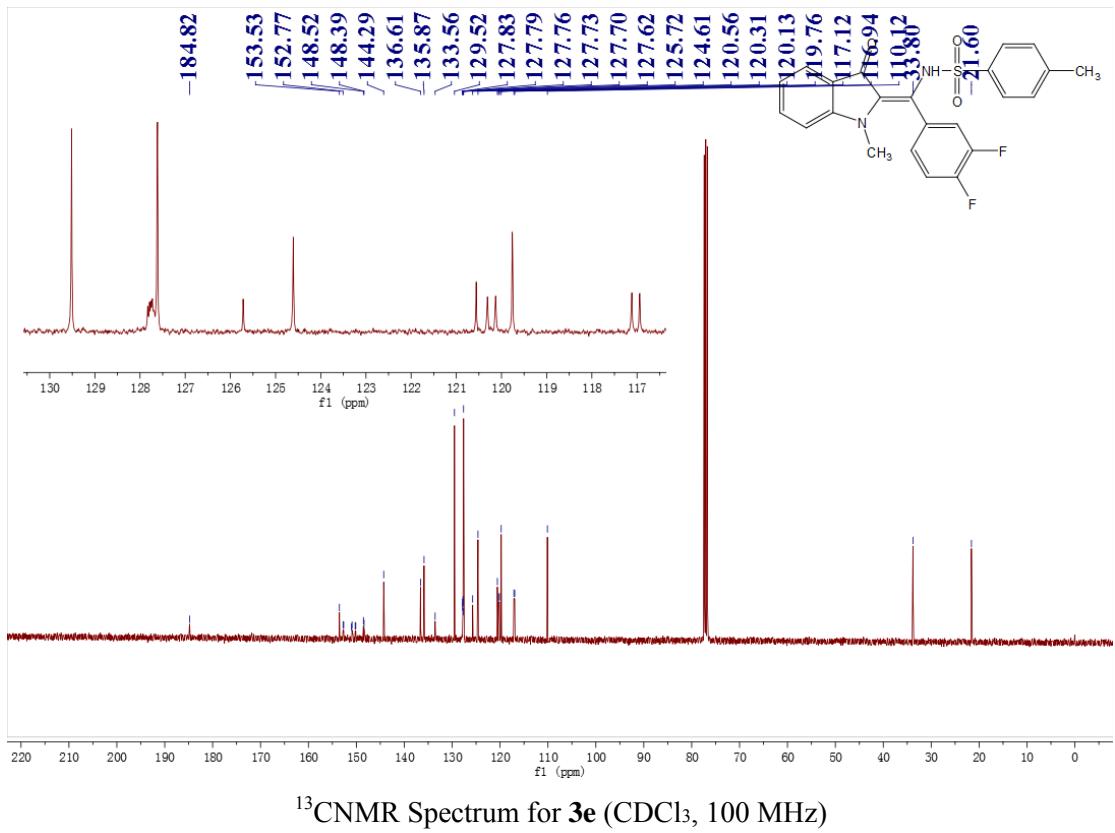
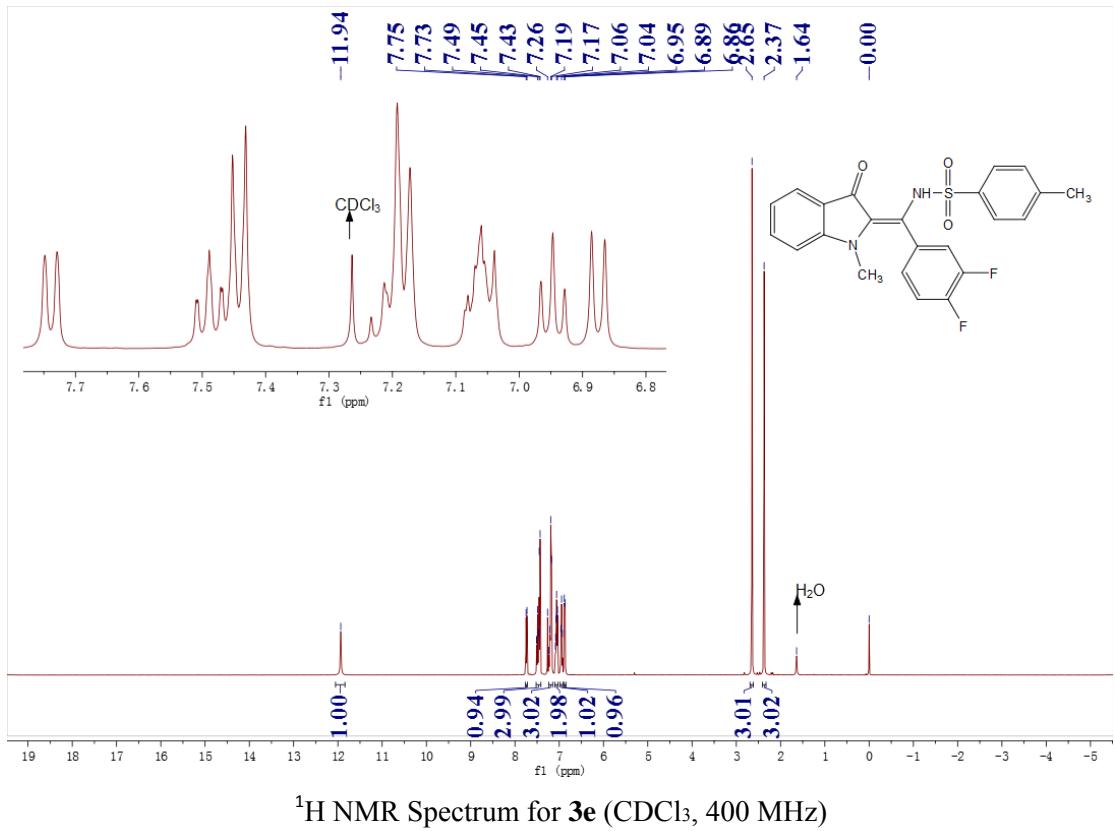


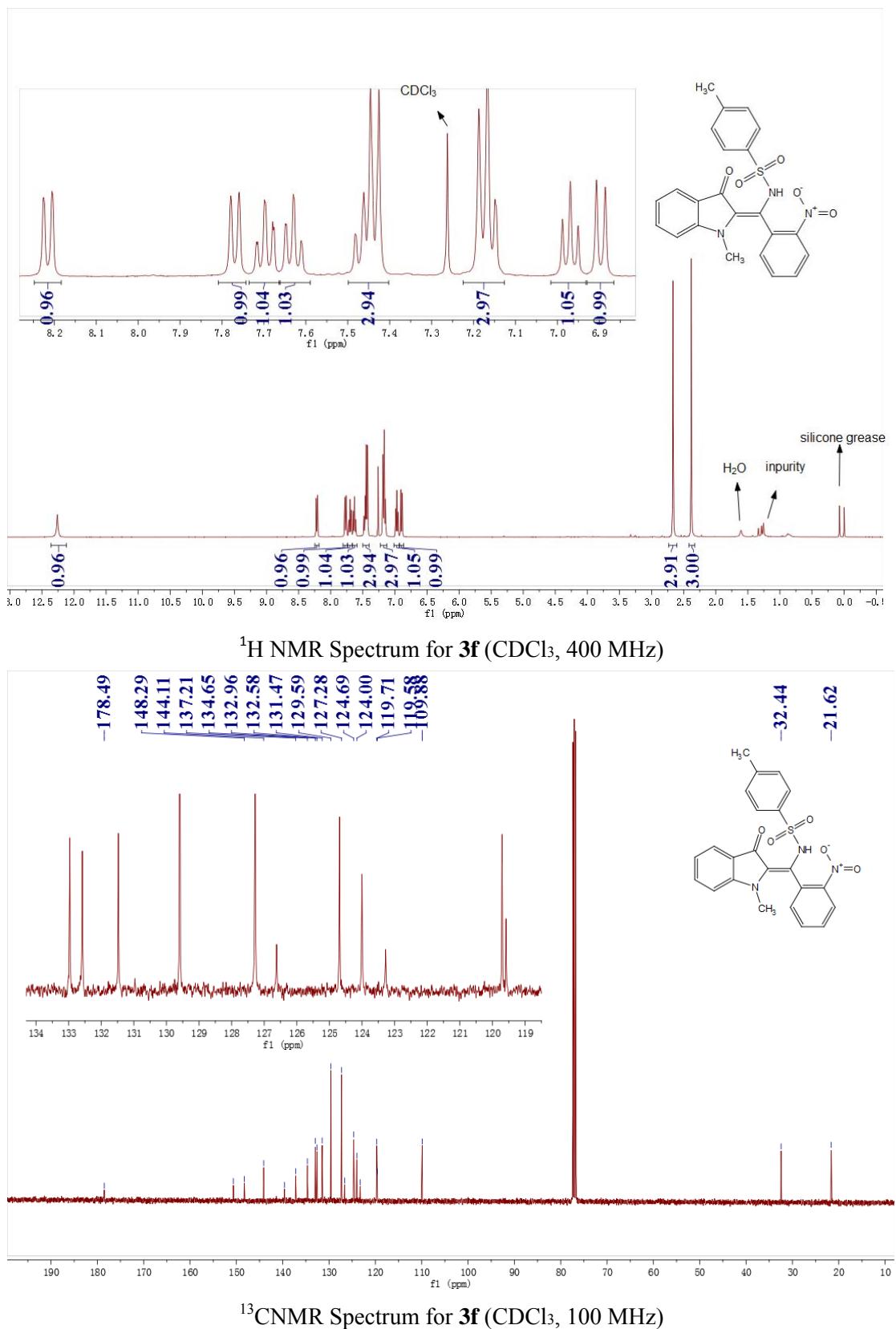


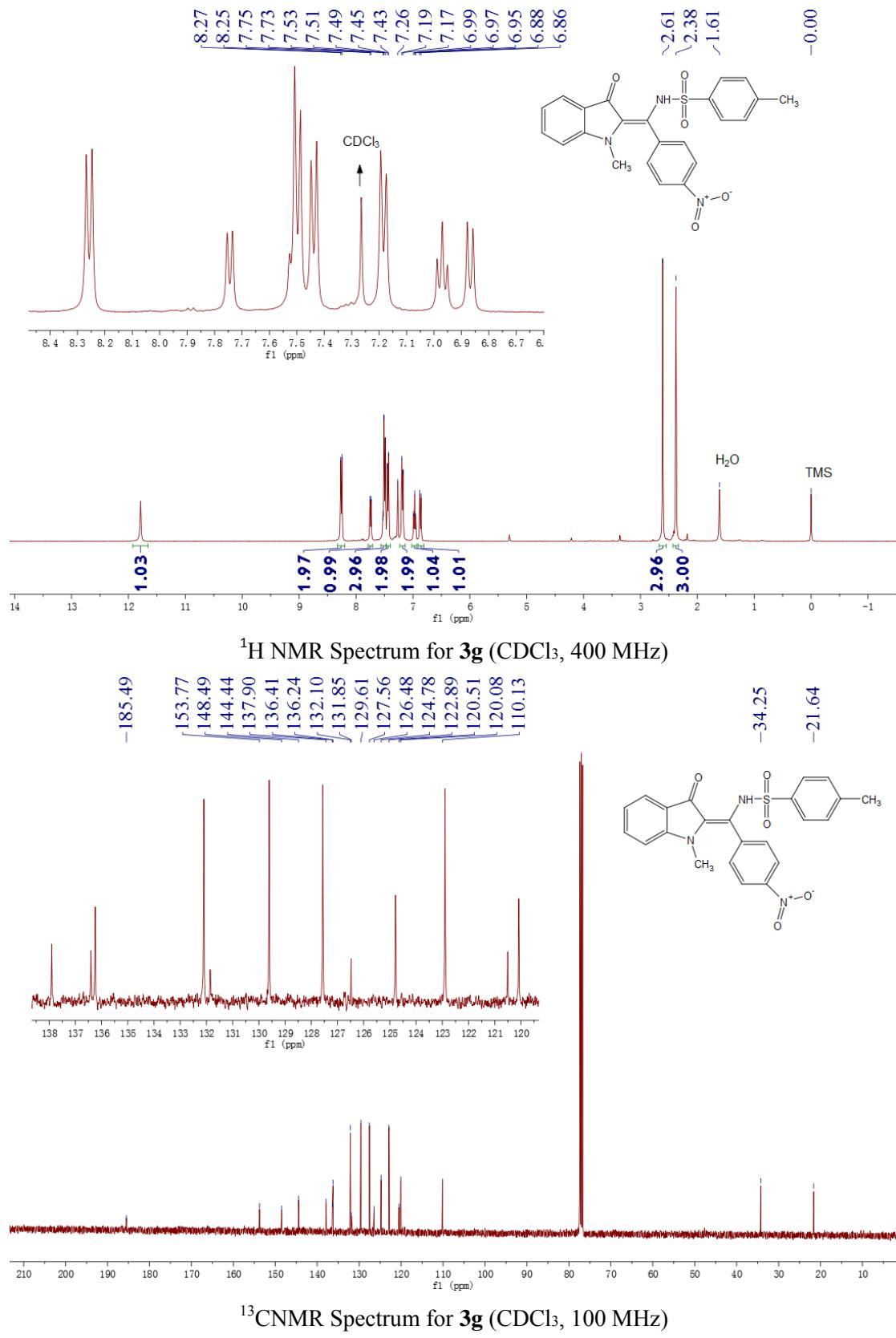
¹H NMR Spectrum for **3d** (CDCl₃, 400 MHz)

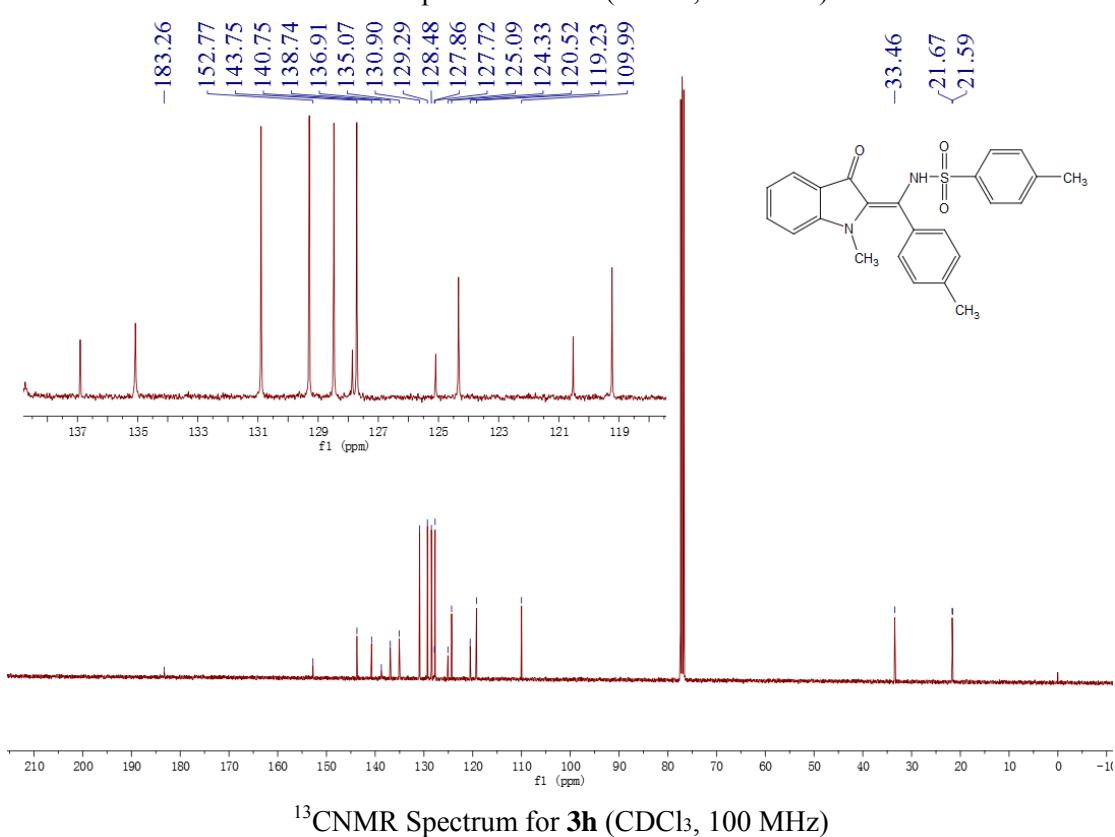
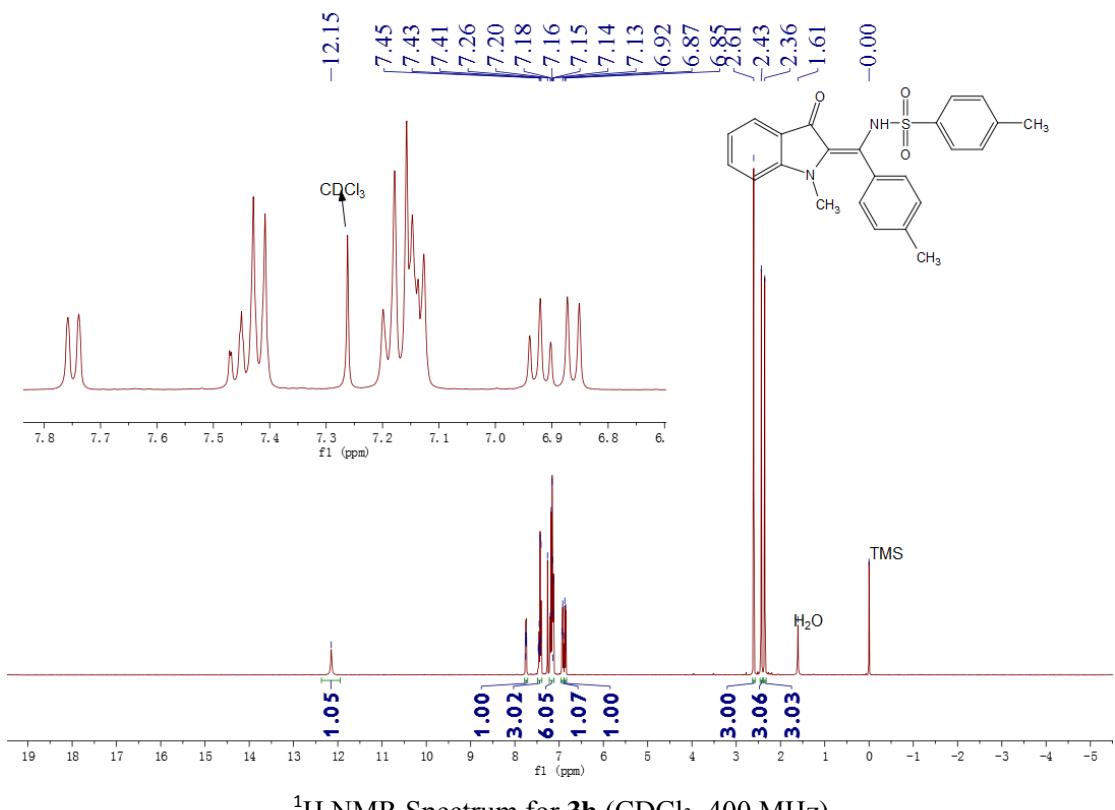


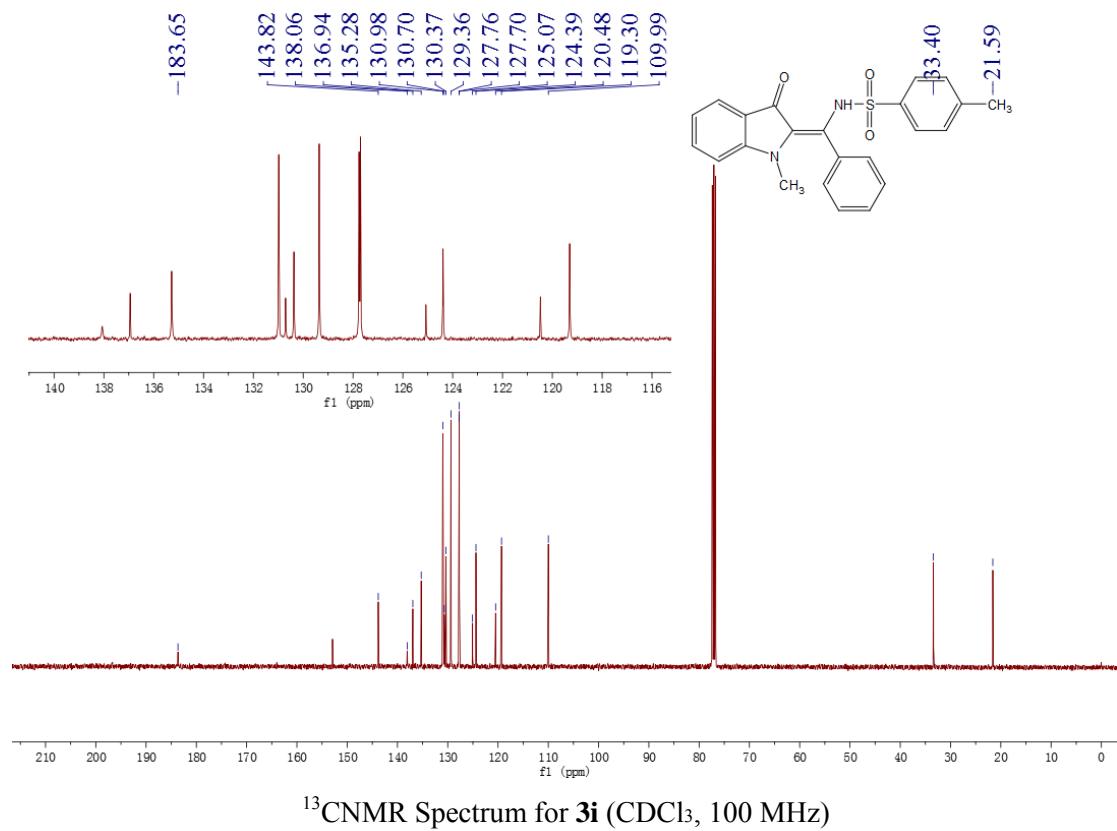
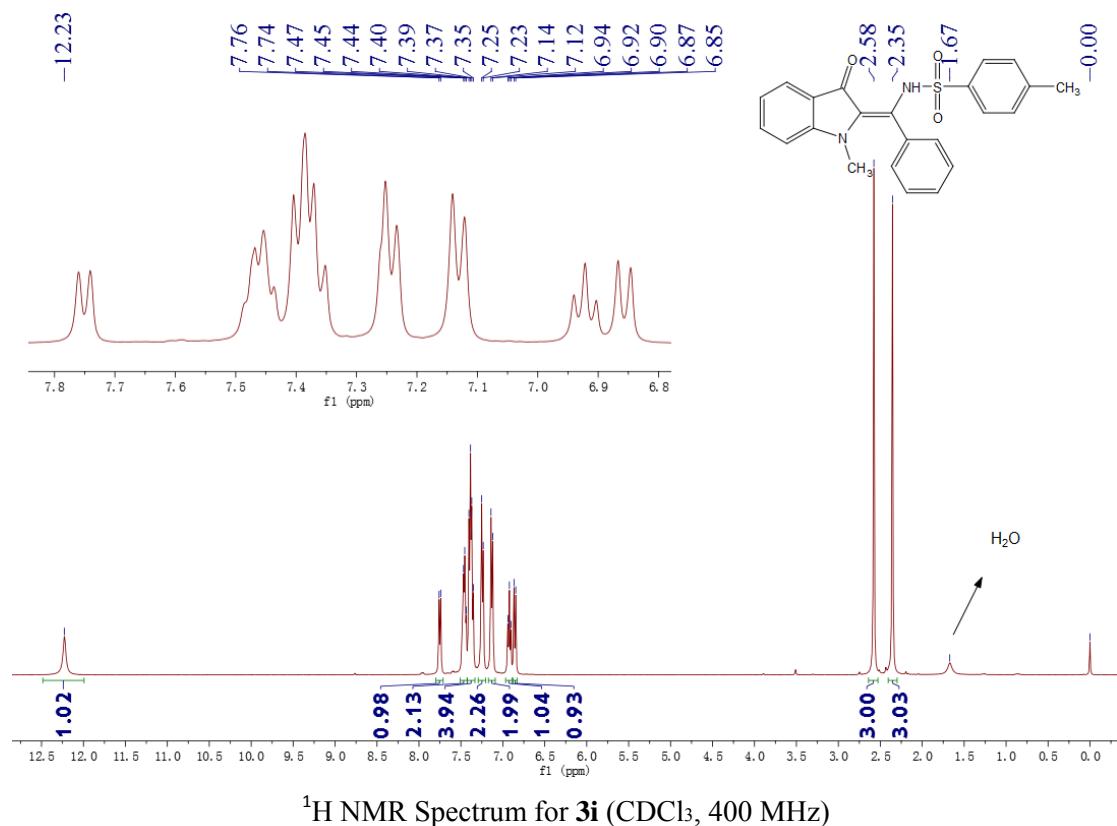
¹³C NMR Spectrum for **3d** (CDCl₃, 100 MHz)

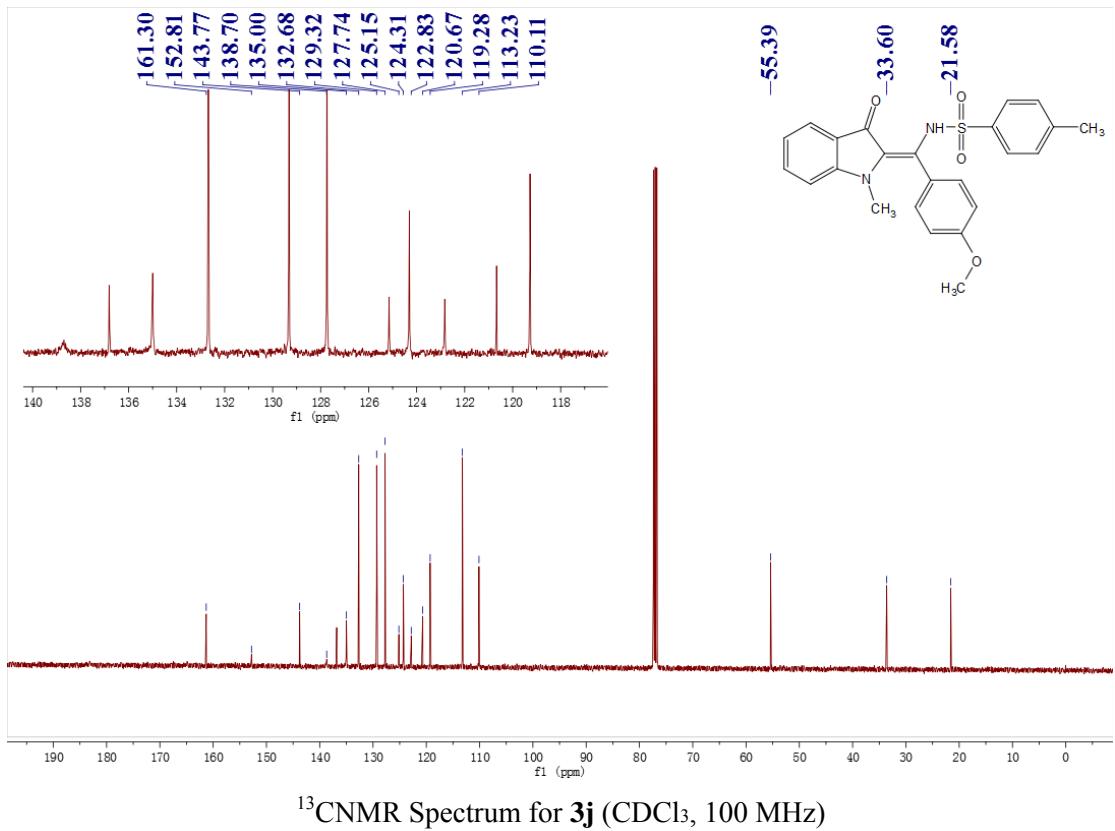
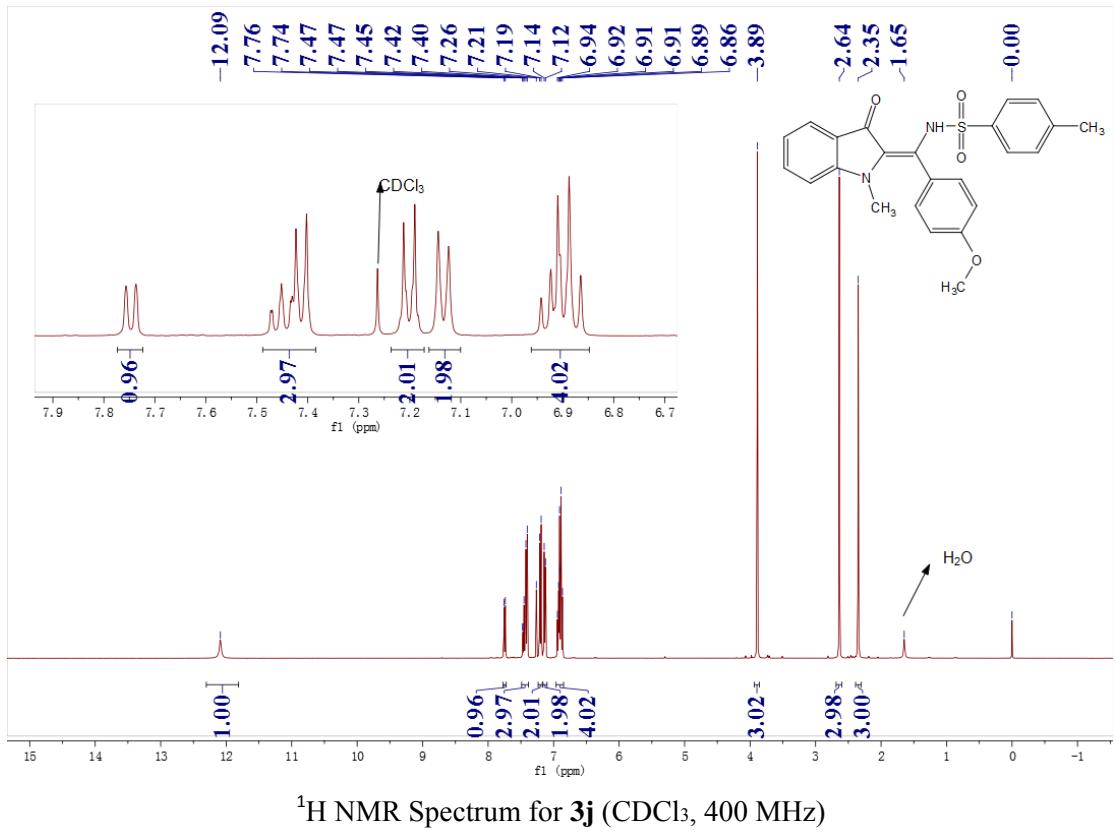


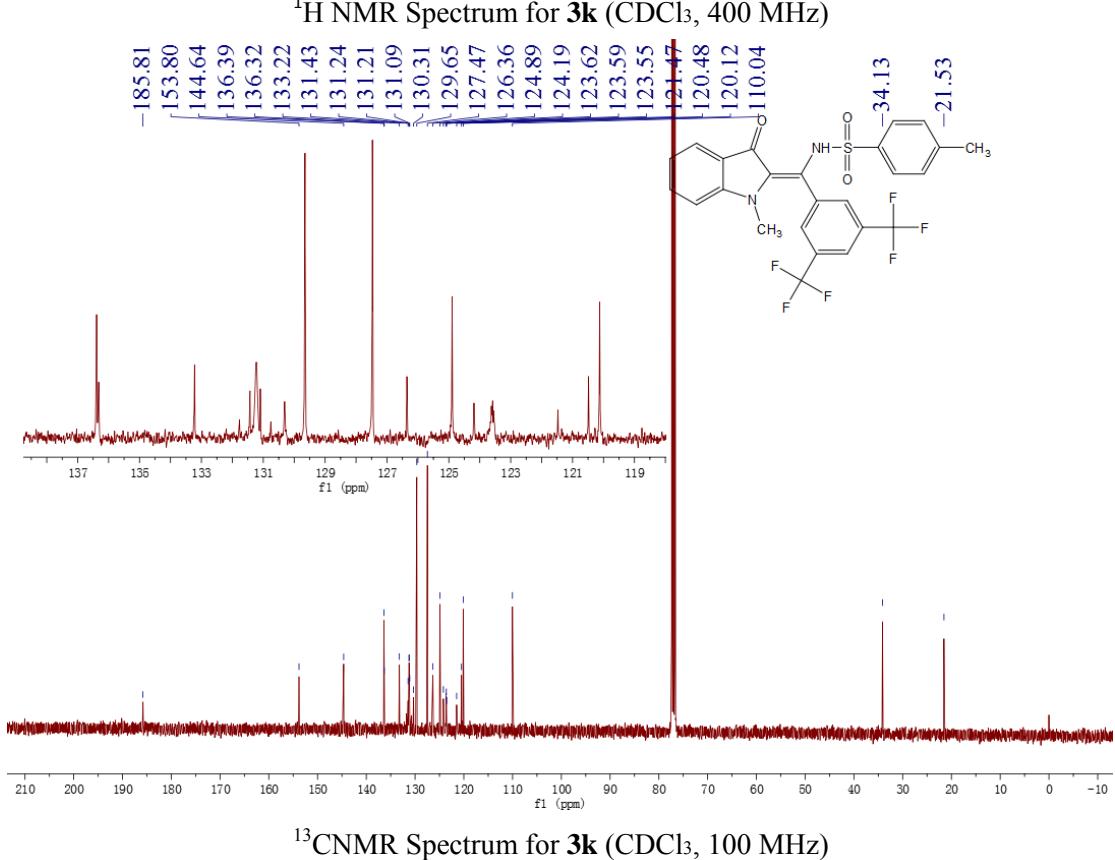
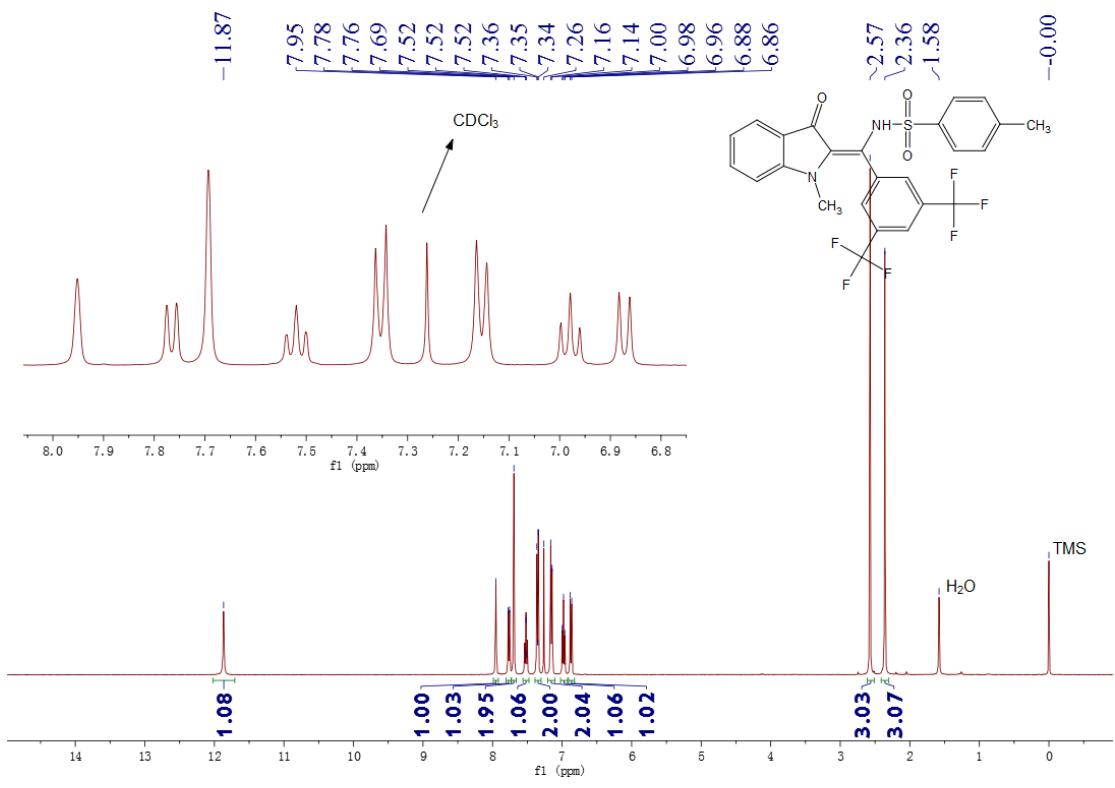


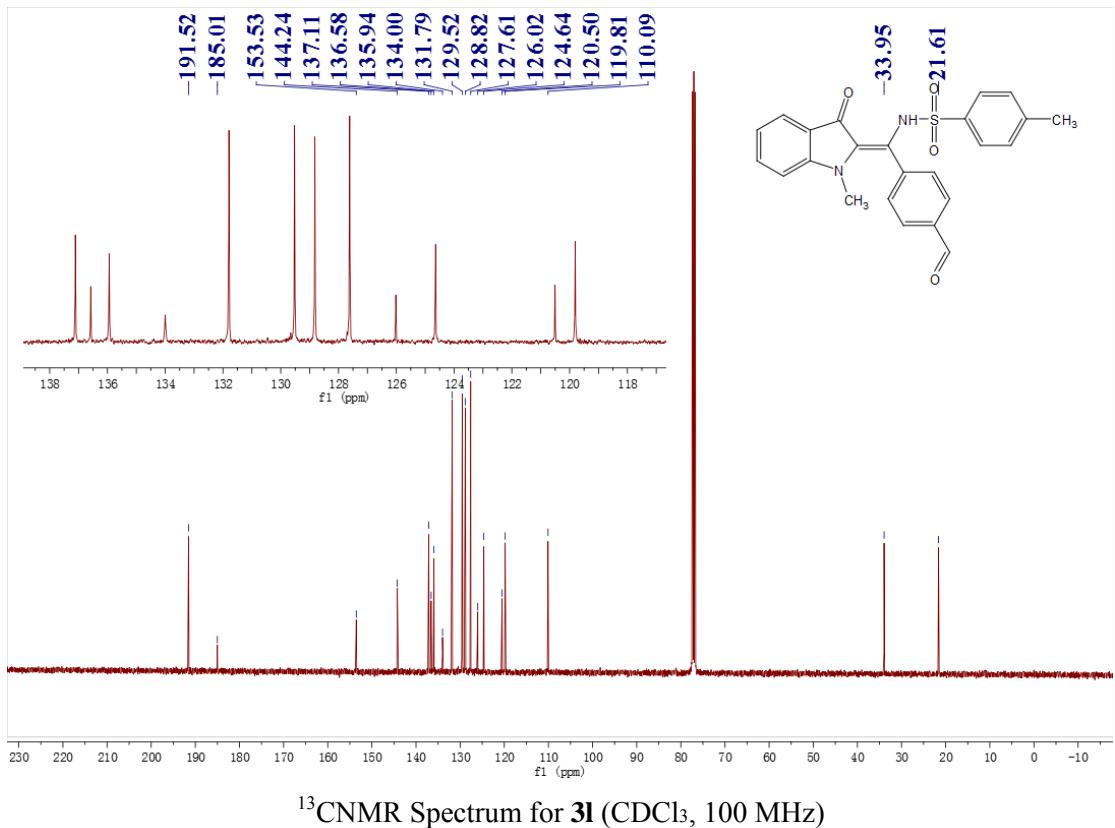
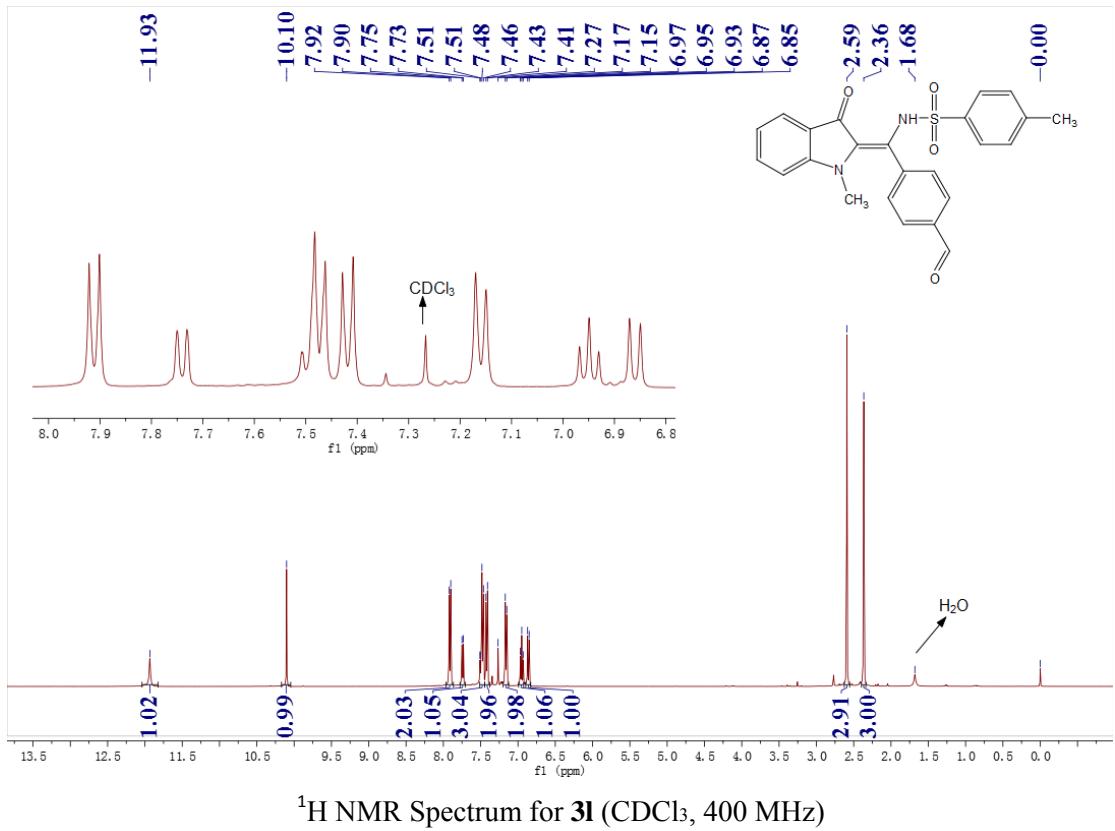


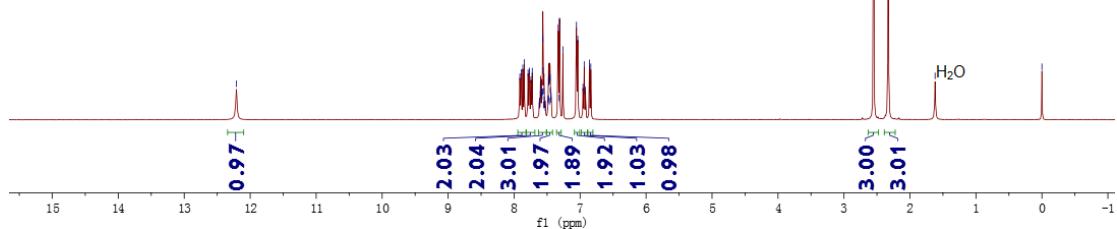
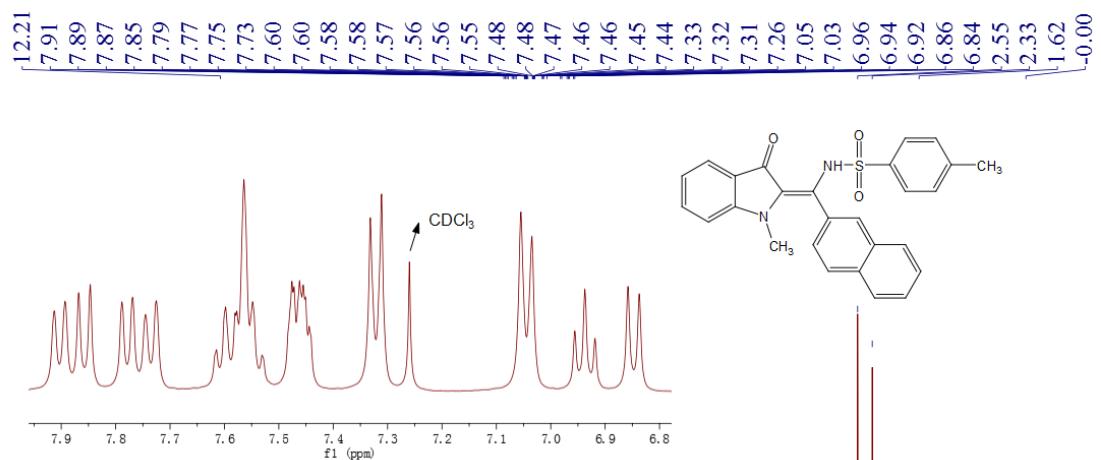




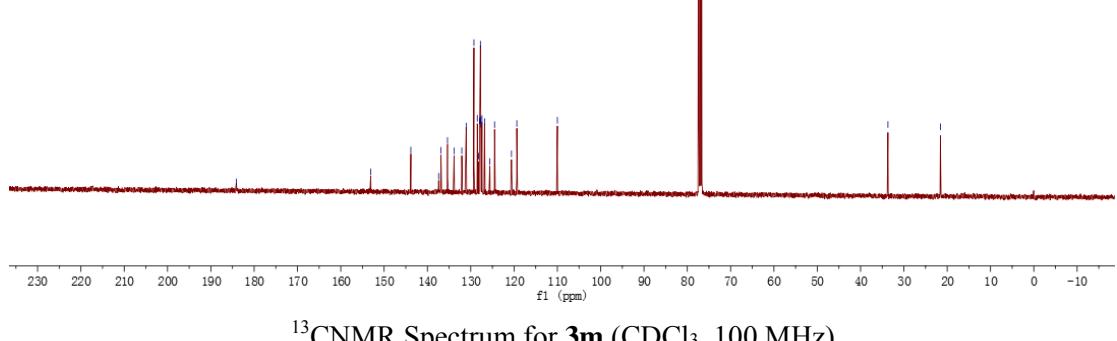
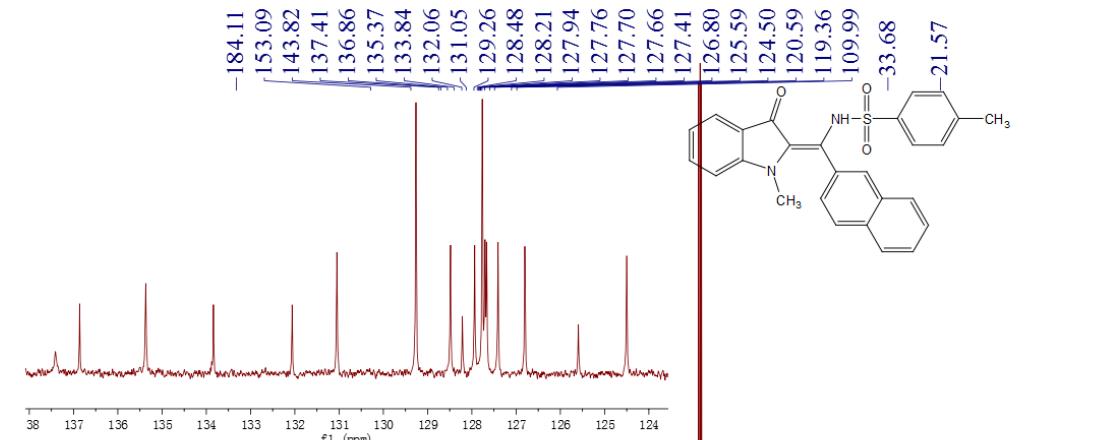




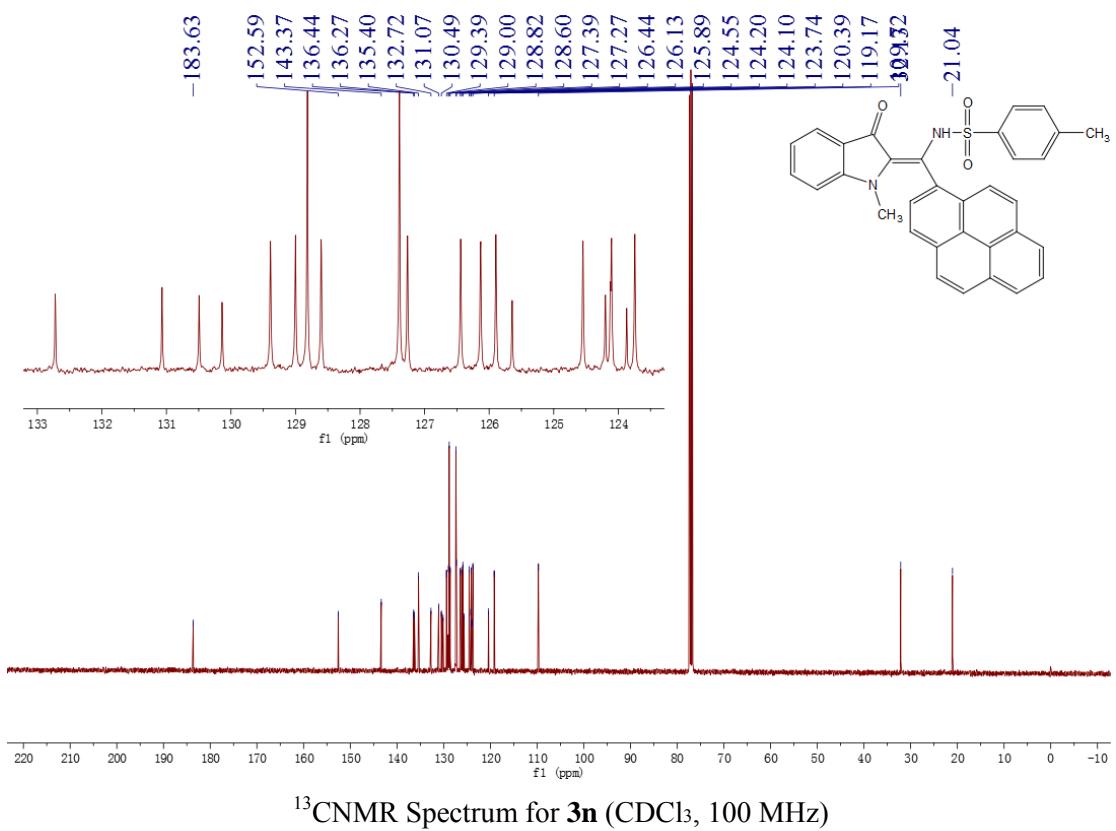
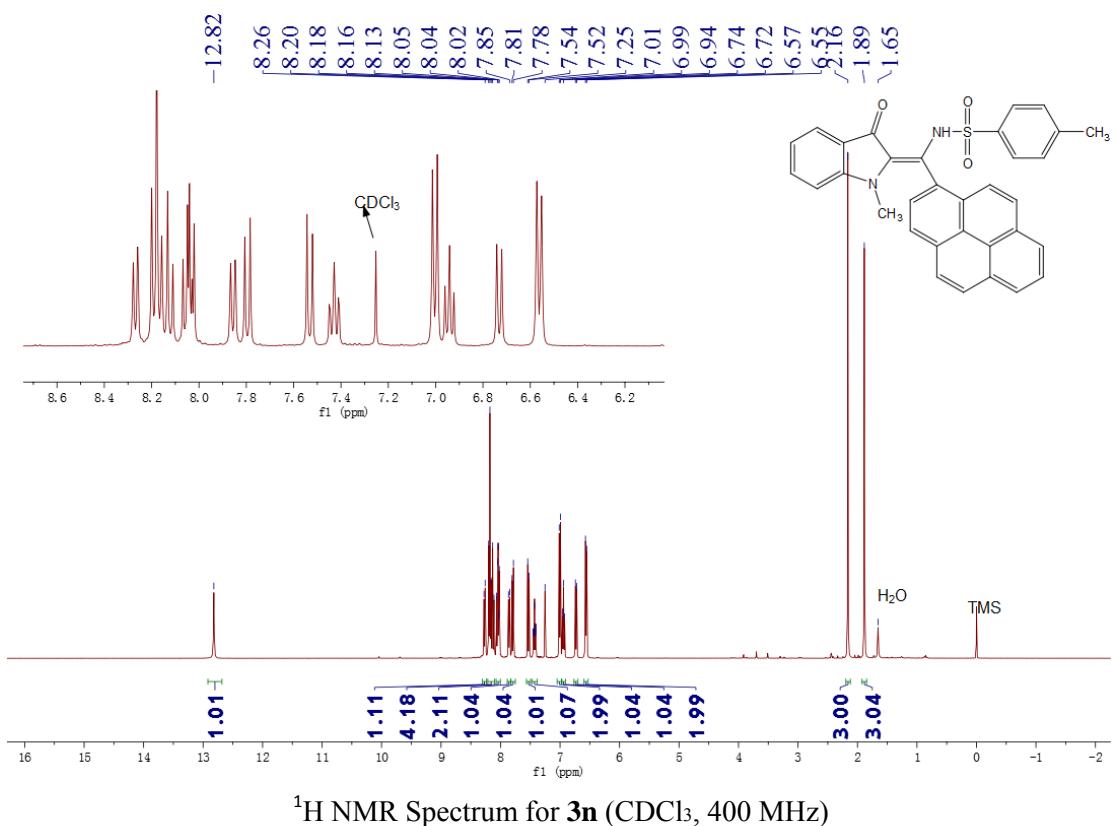


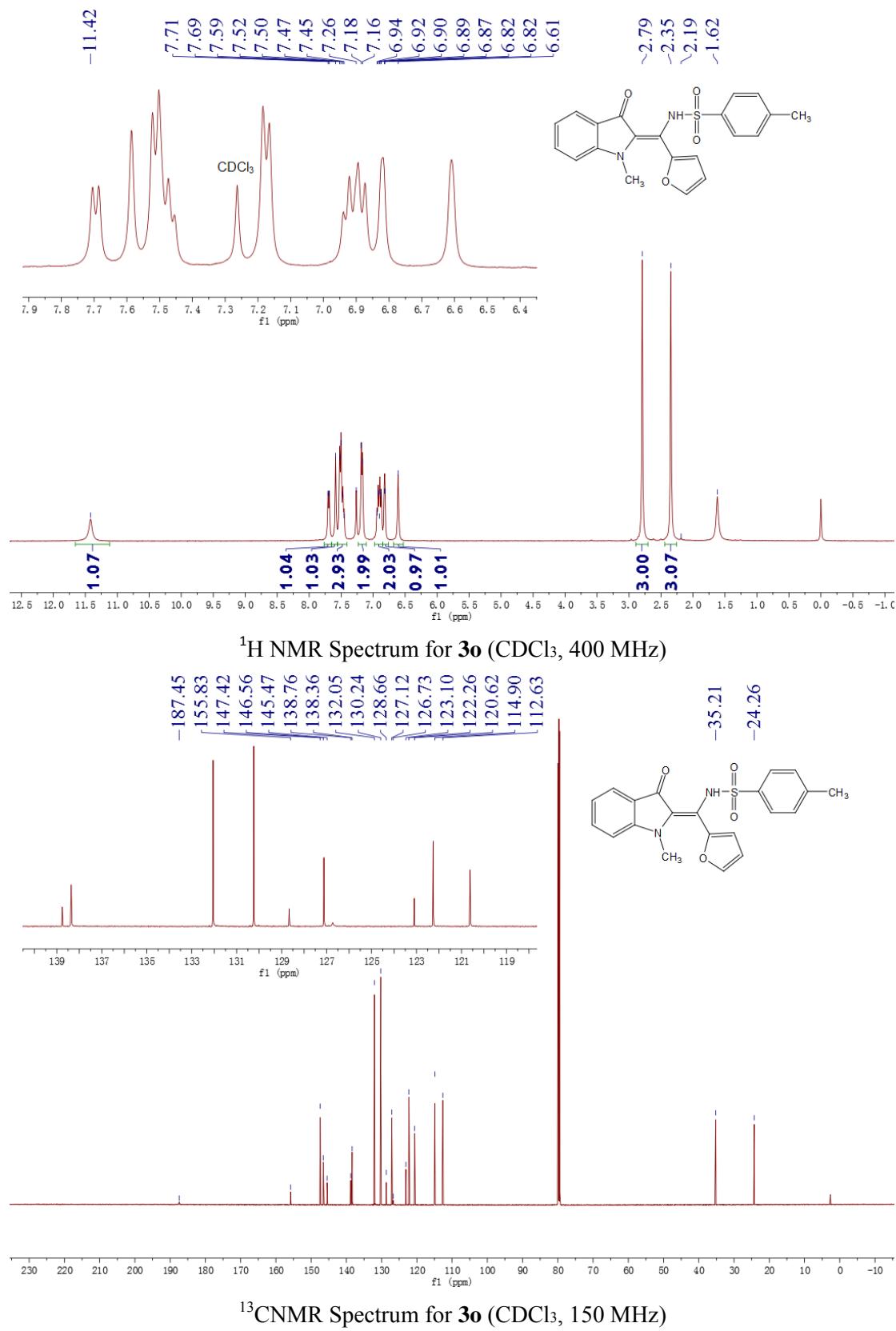


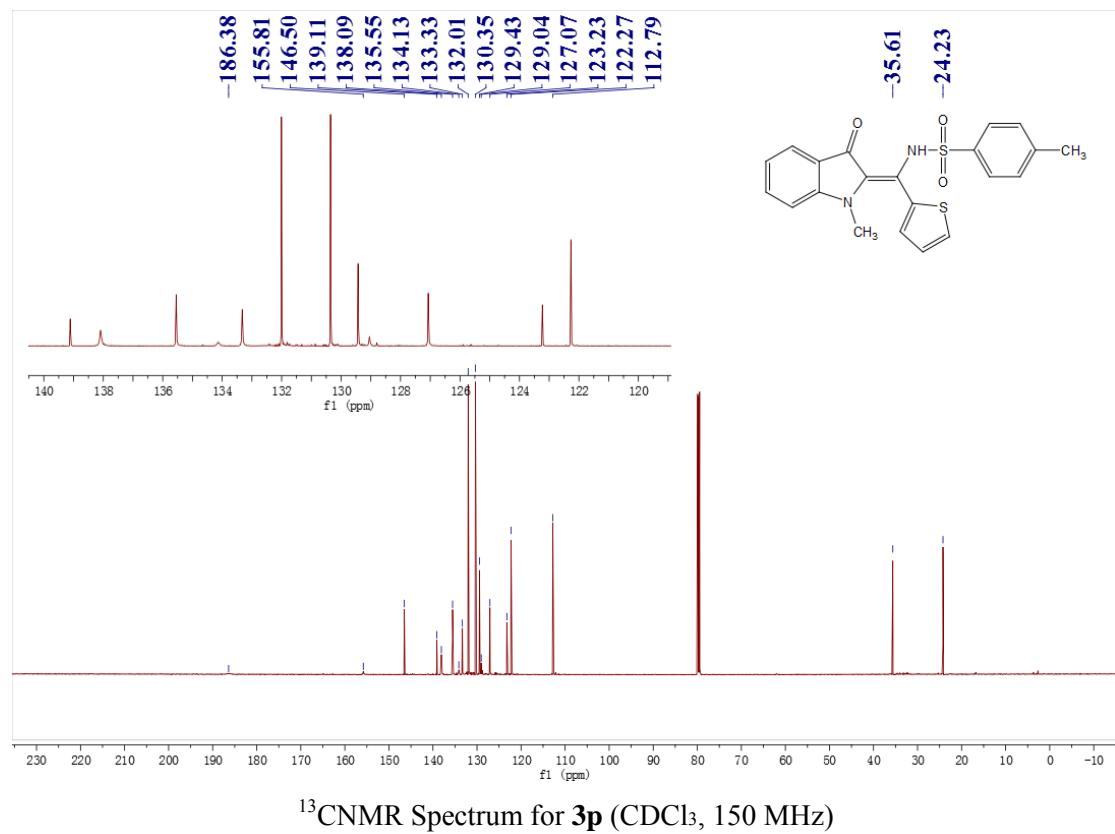
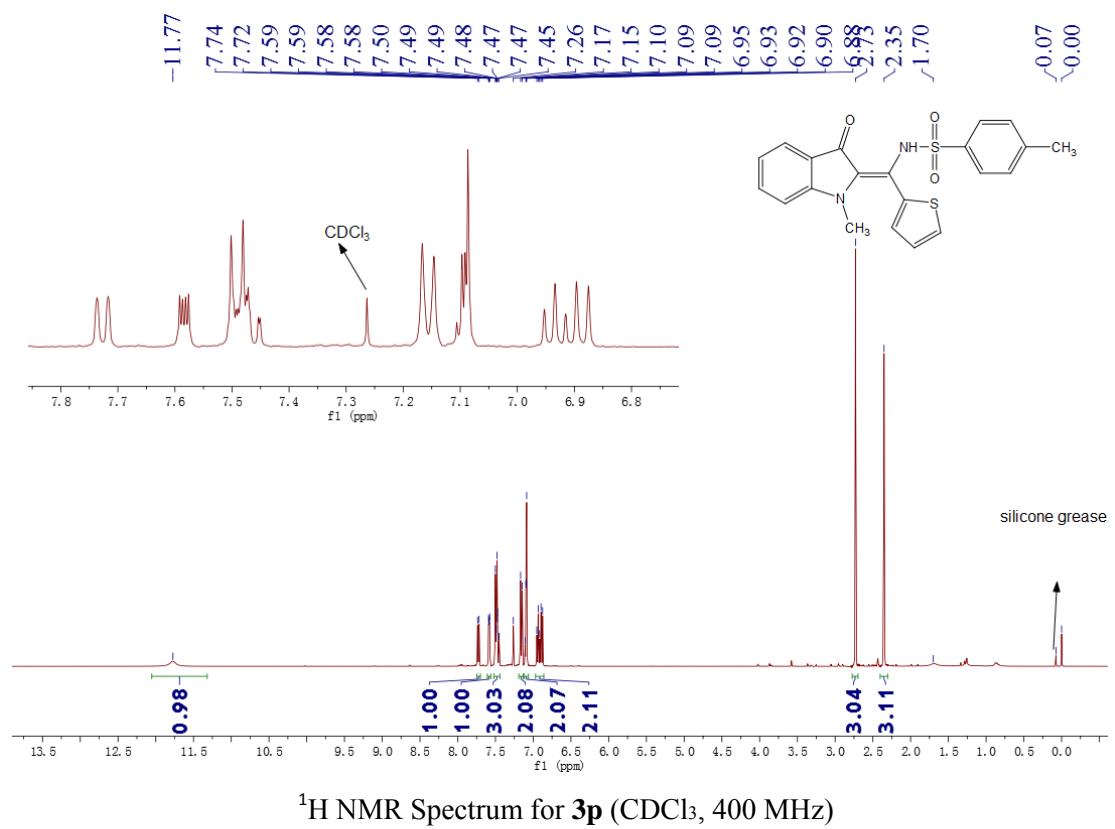
¹H NMR Spectrum for **3m** (CDCl_3 , 400 MHz)

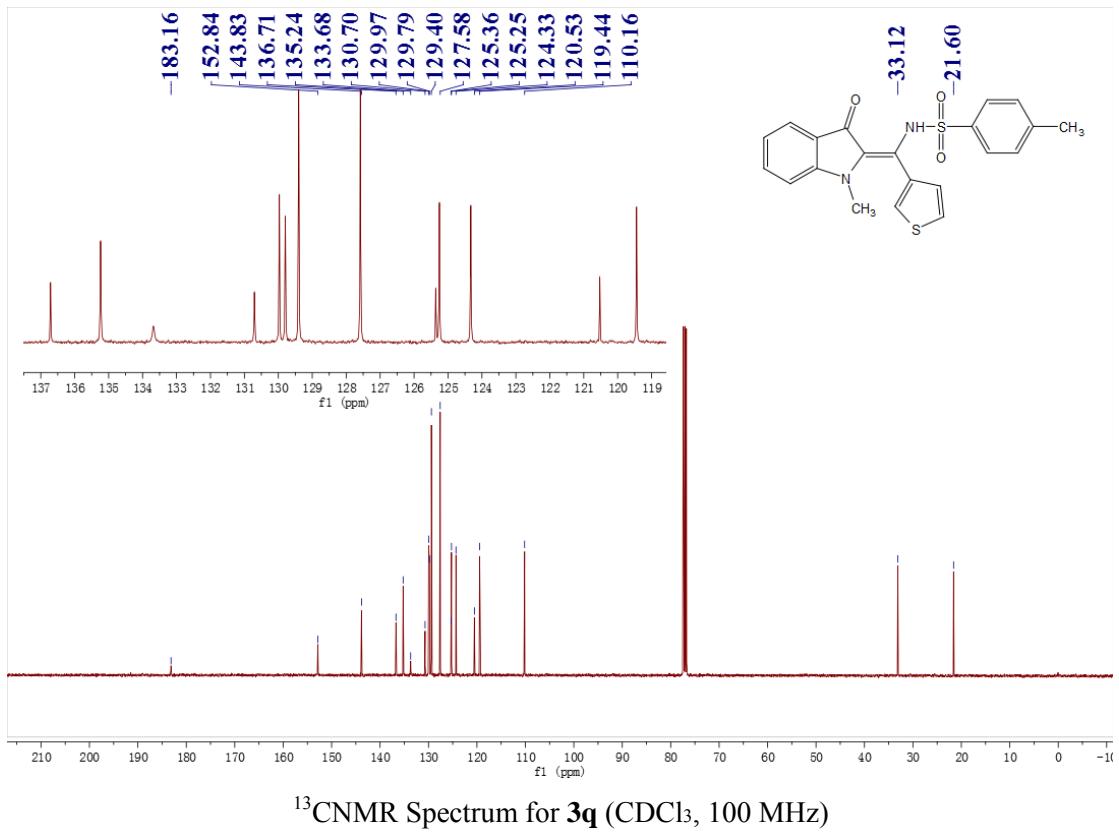
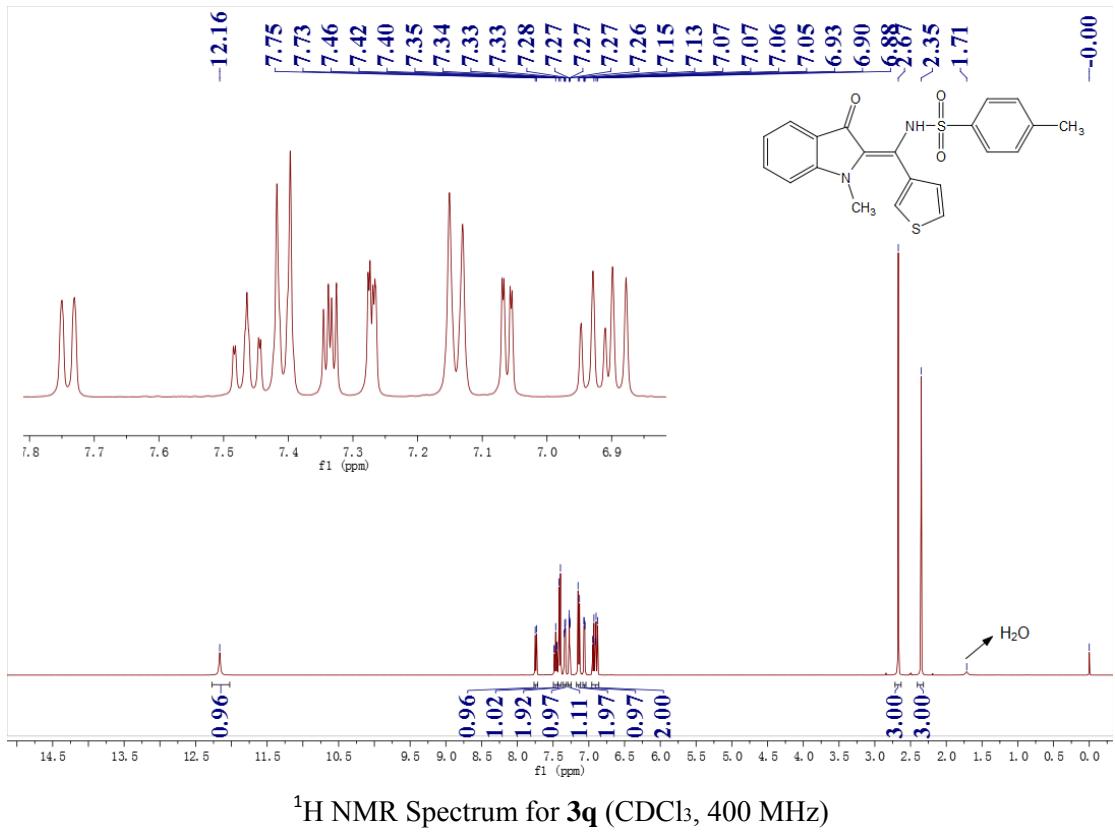


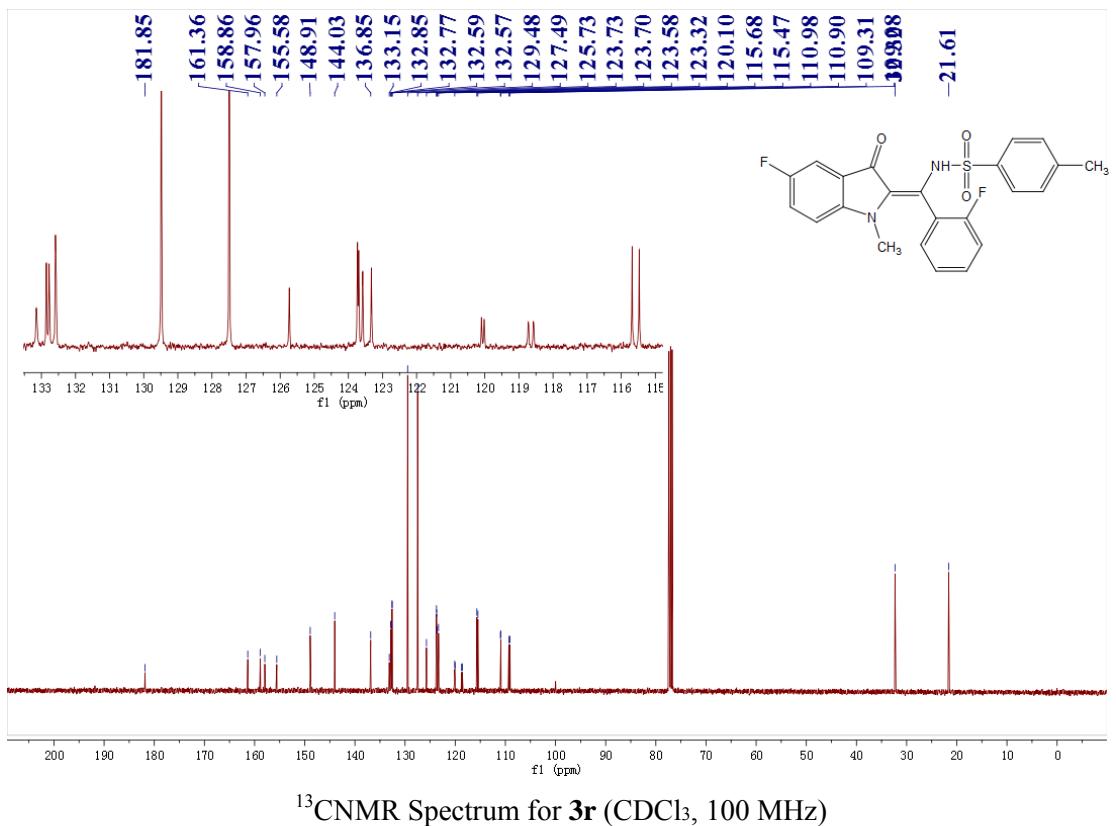
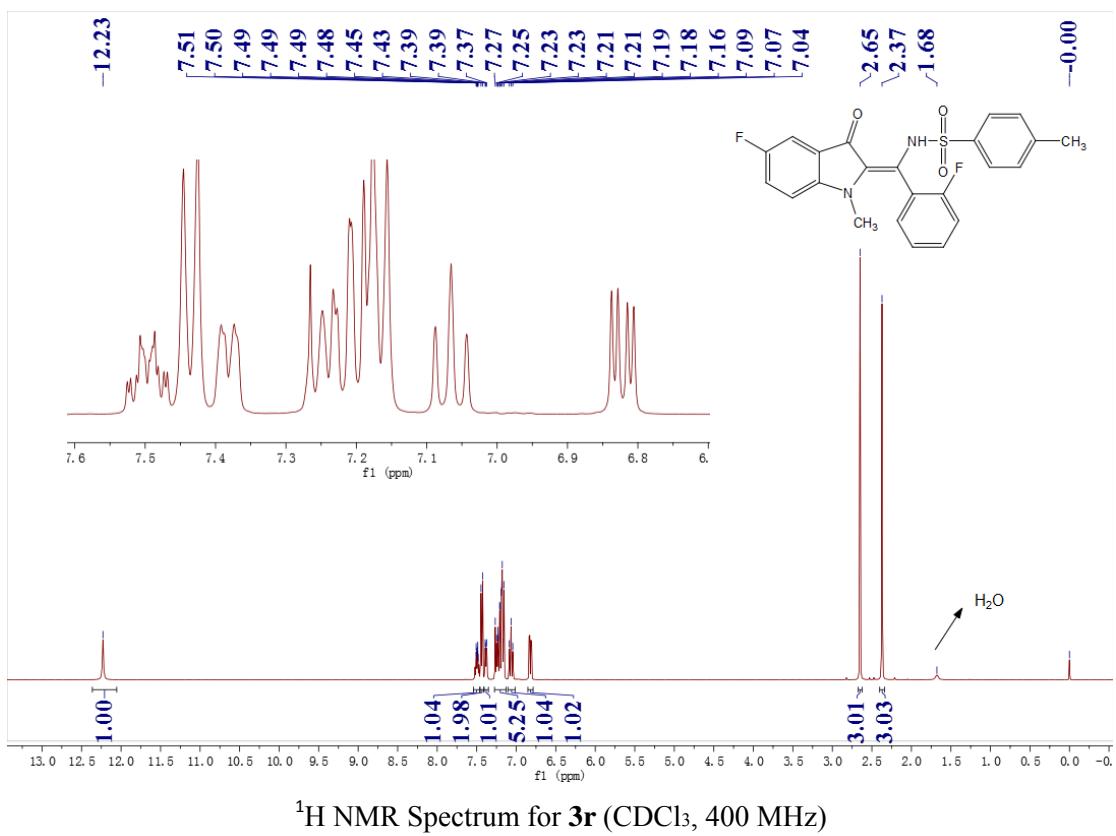
¹³C NMR Spectrum for **3m** (CDCl_3 , 100 MHz)

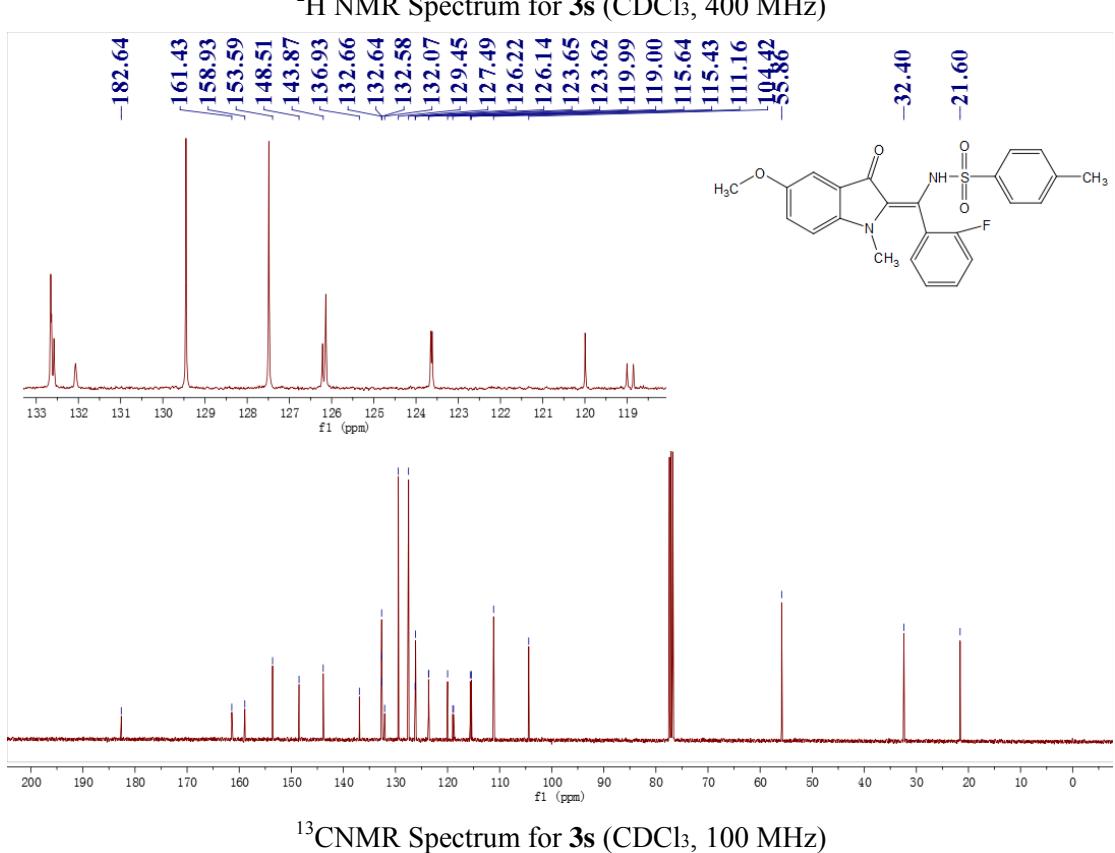
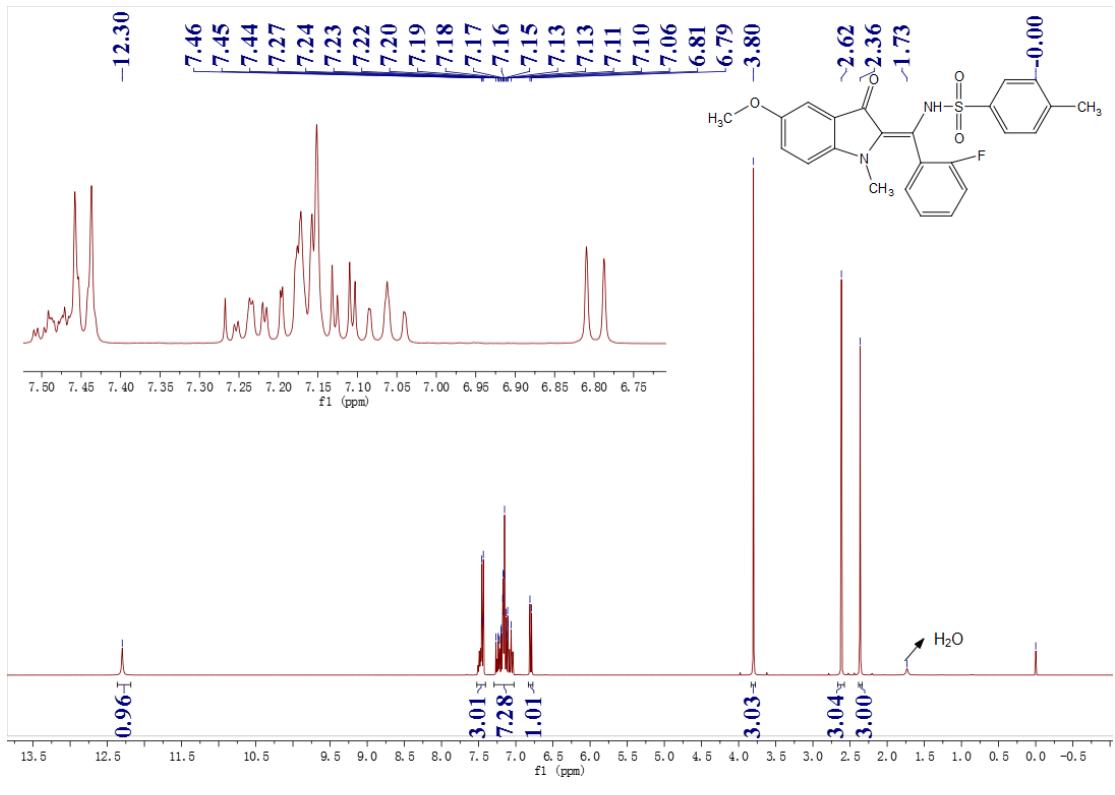


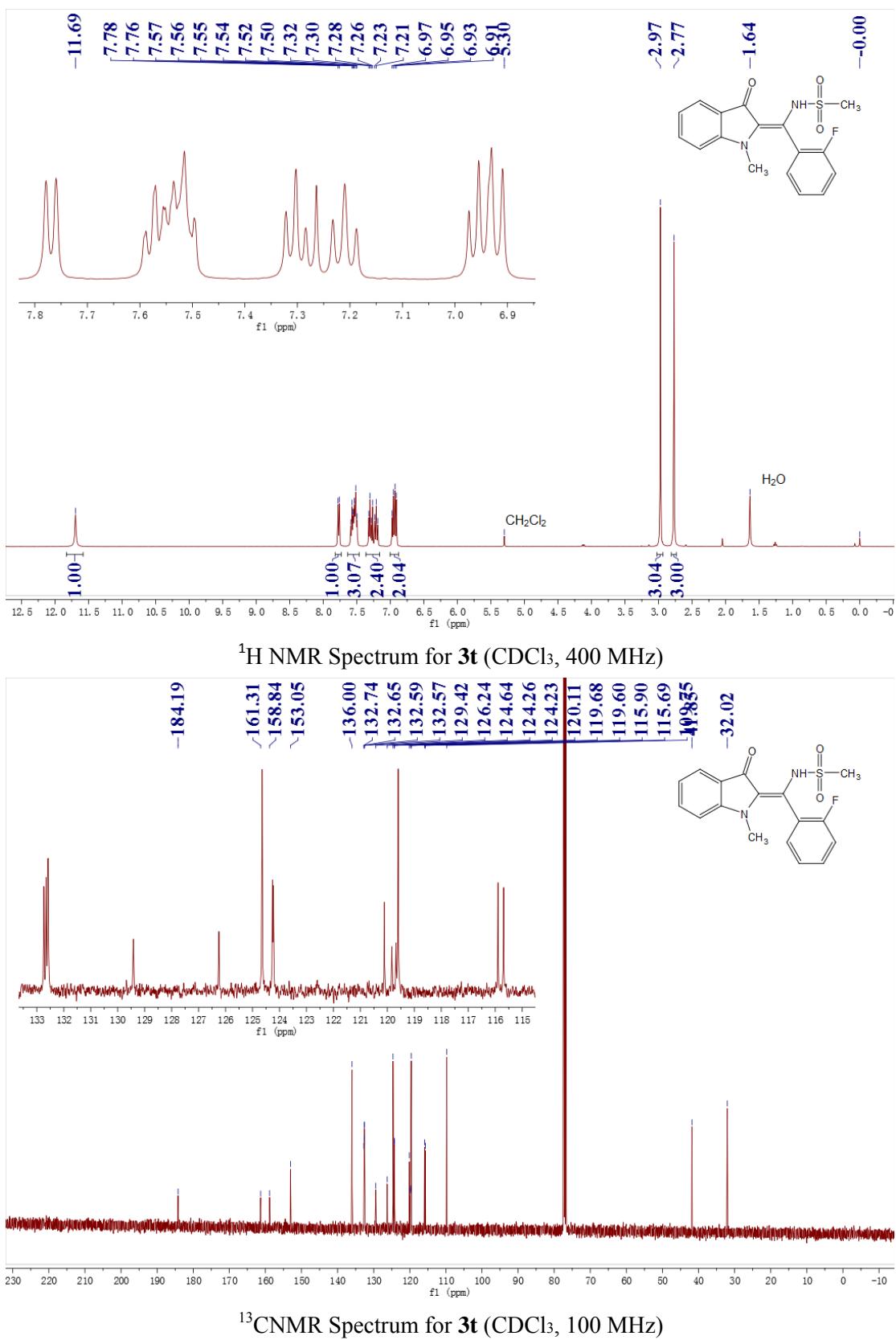


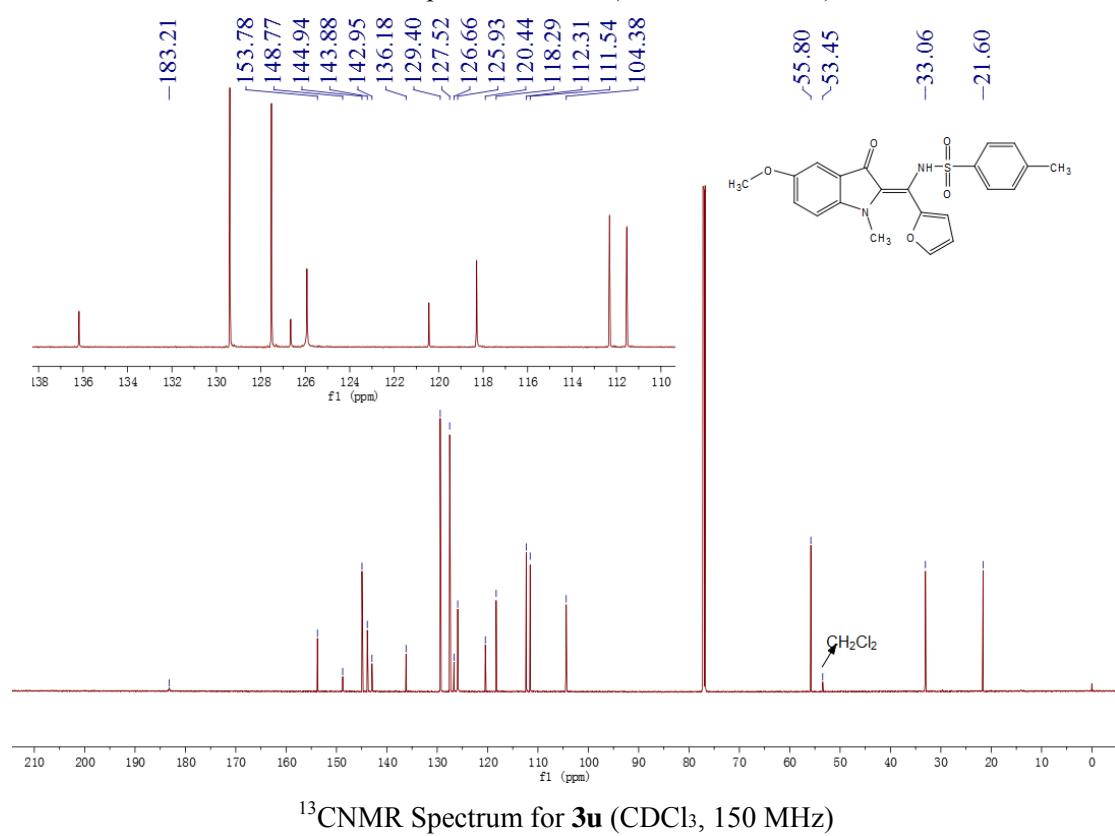
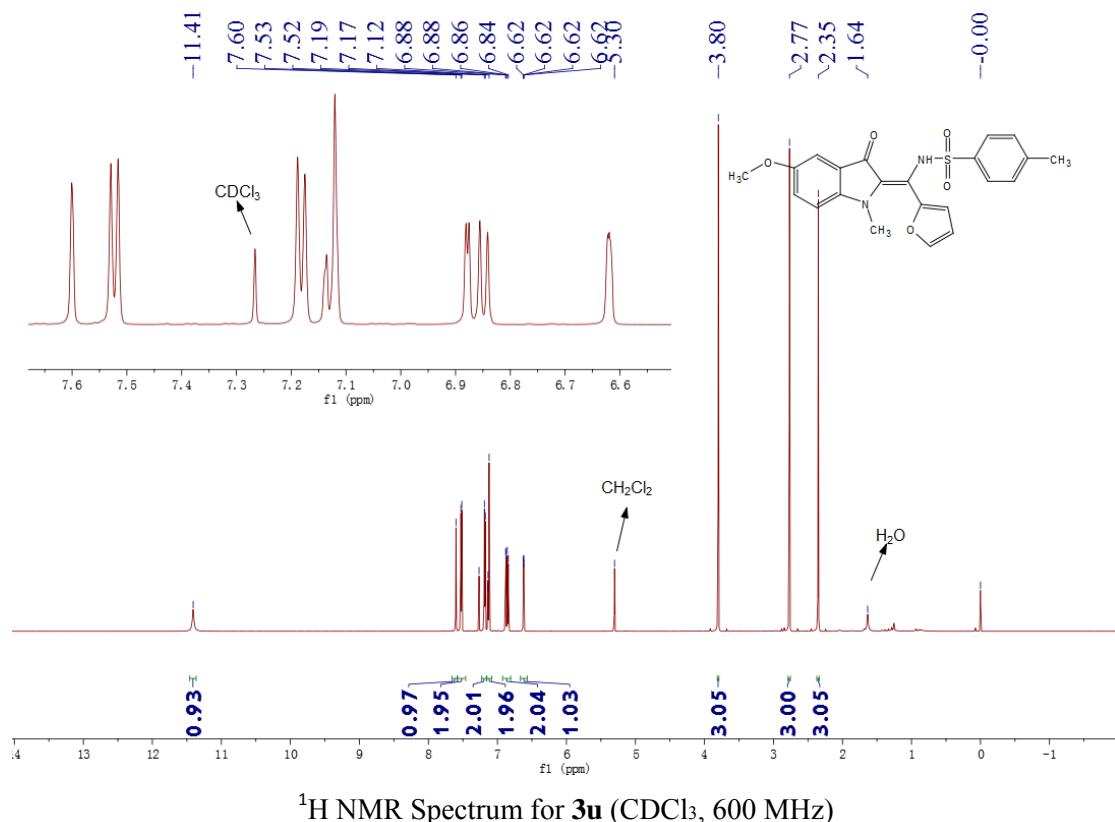


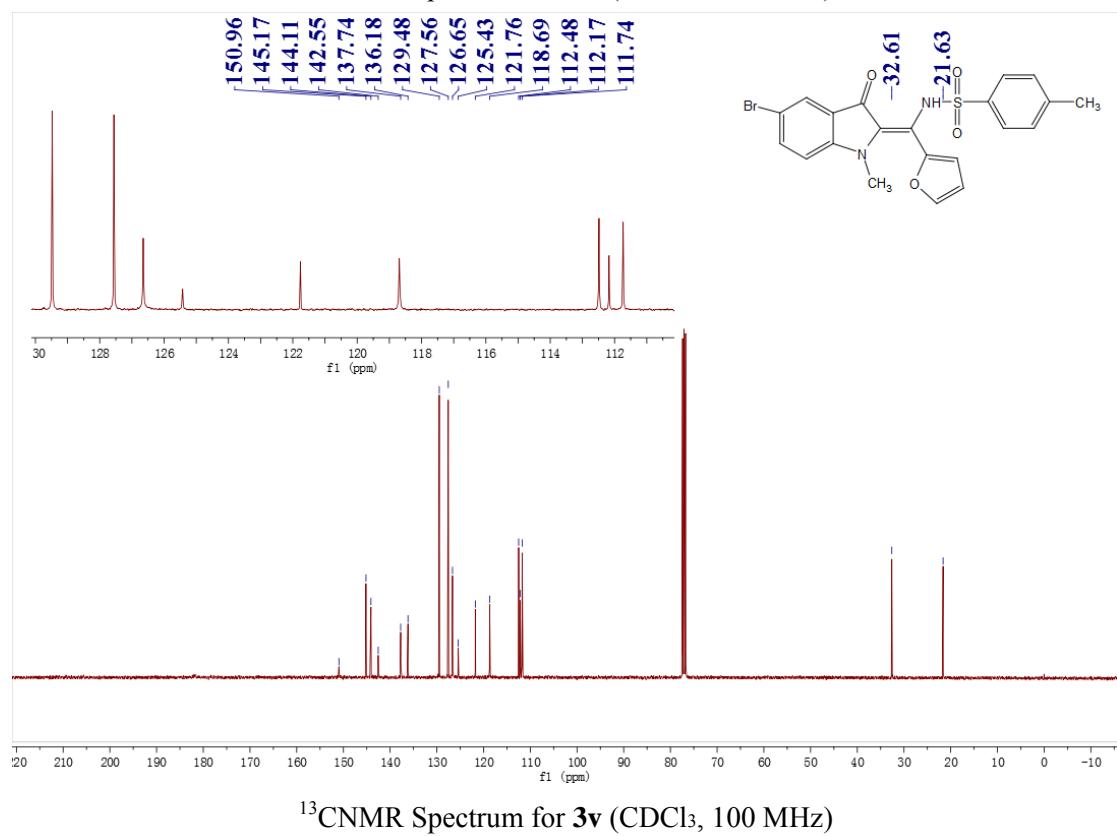
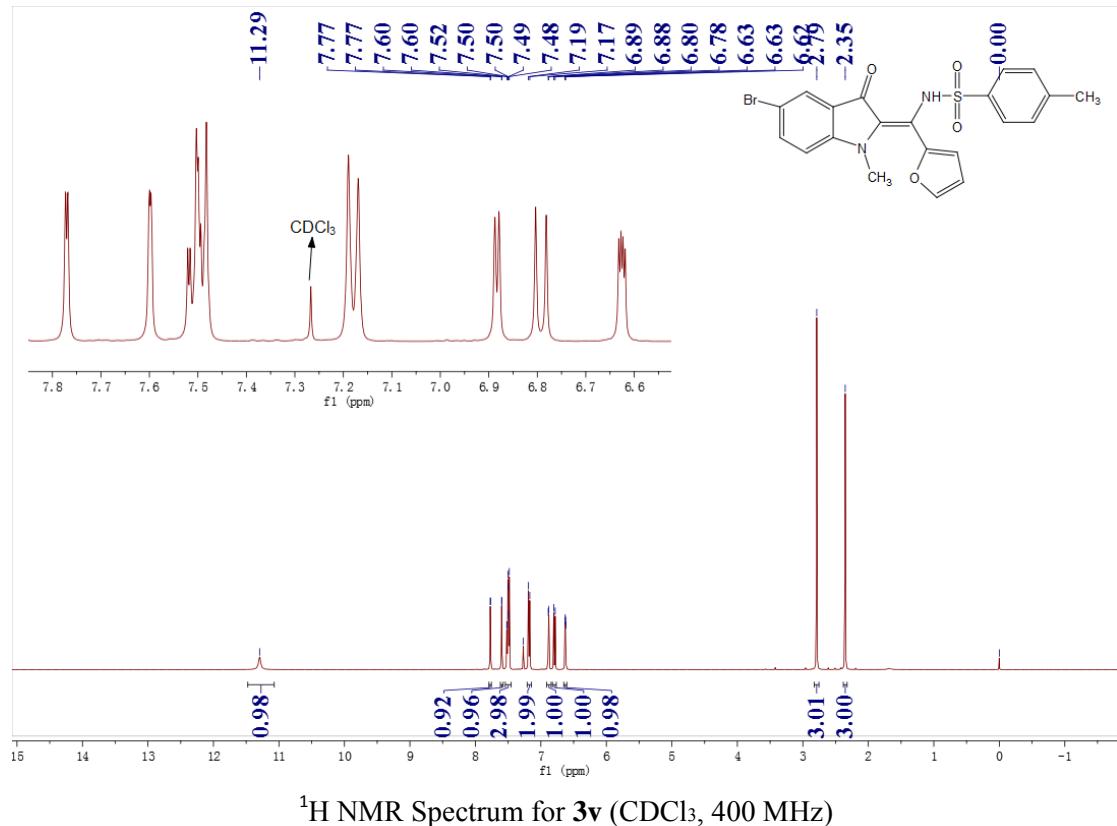


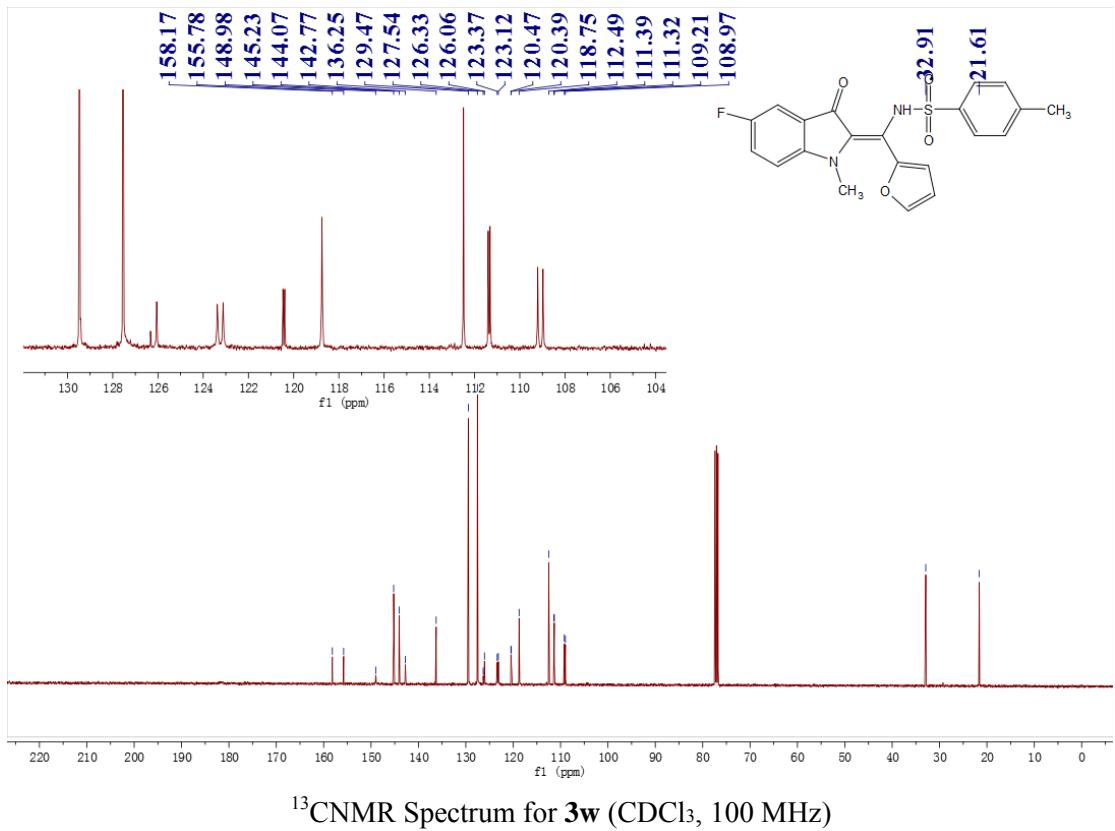
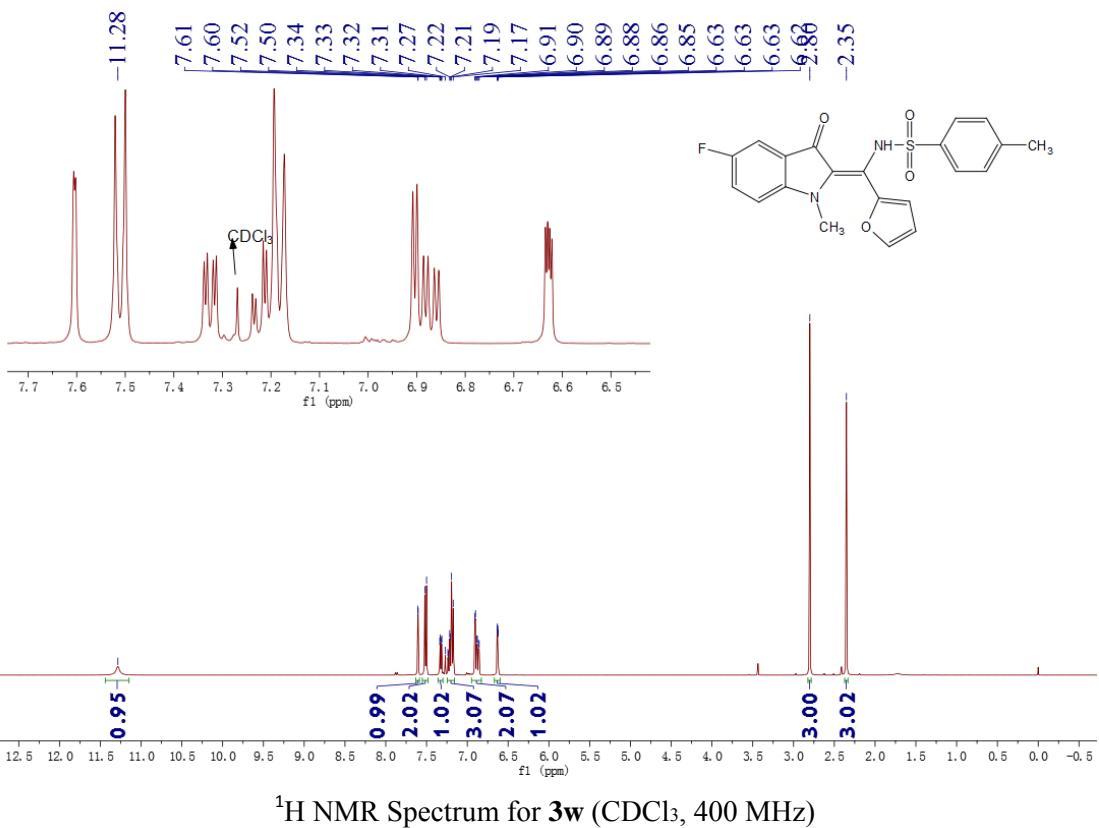


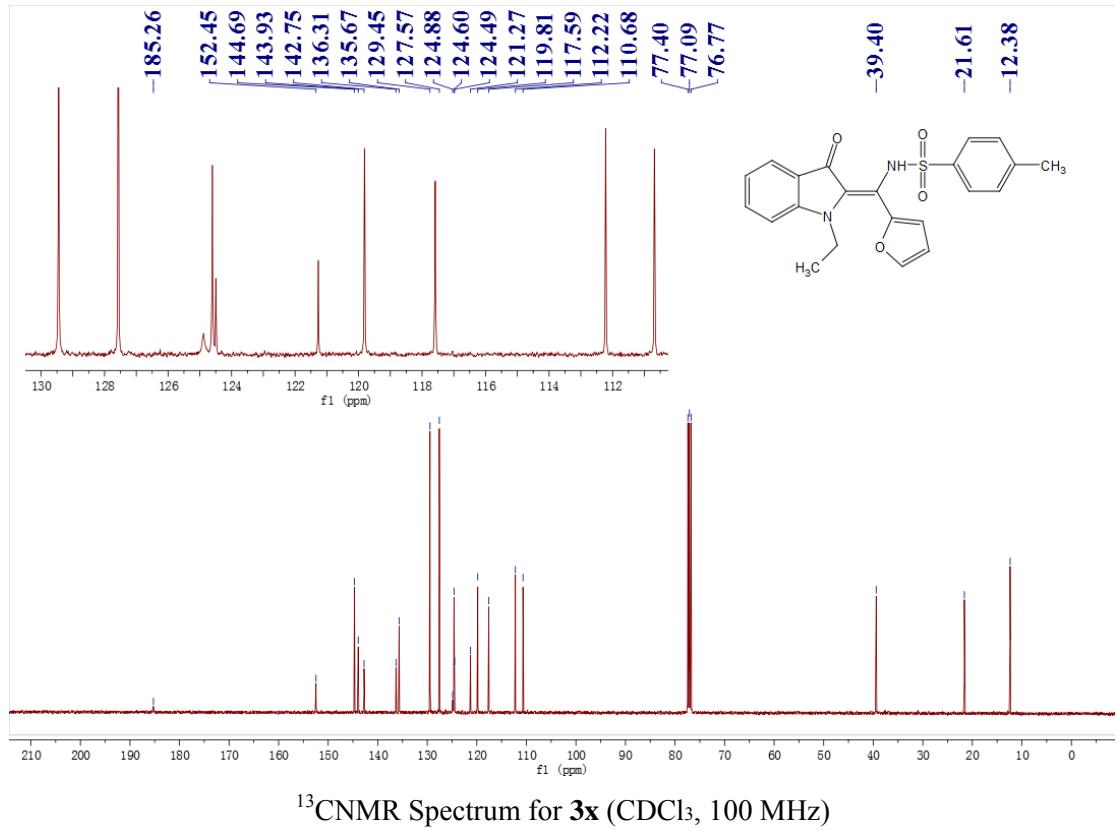
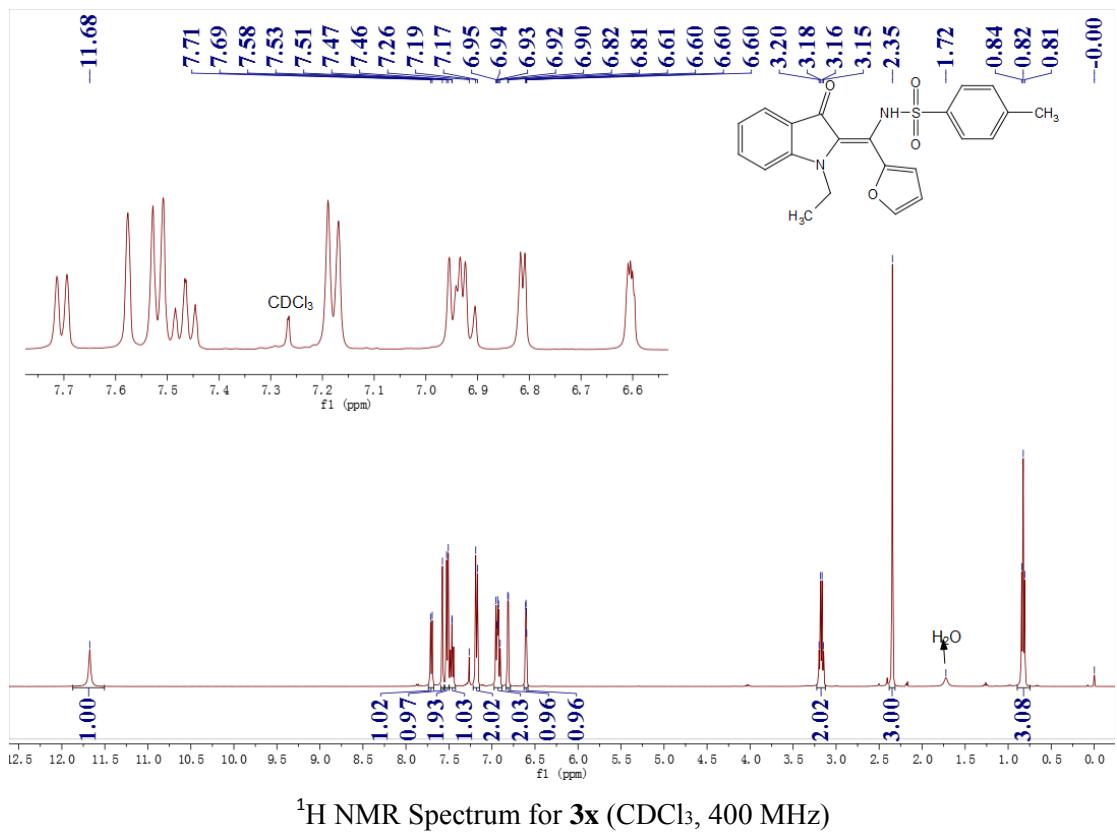


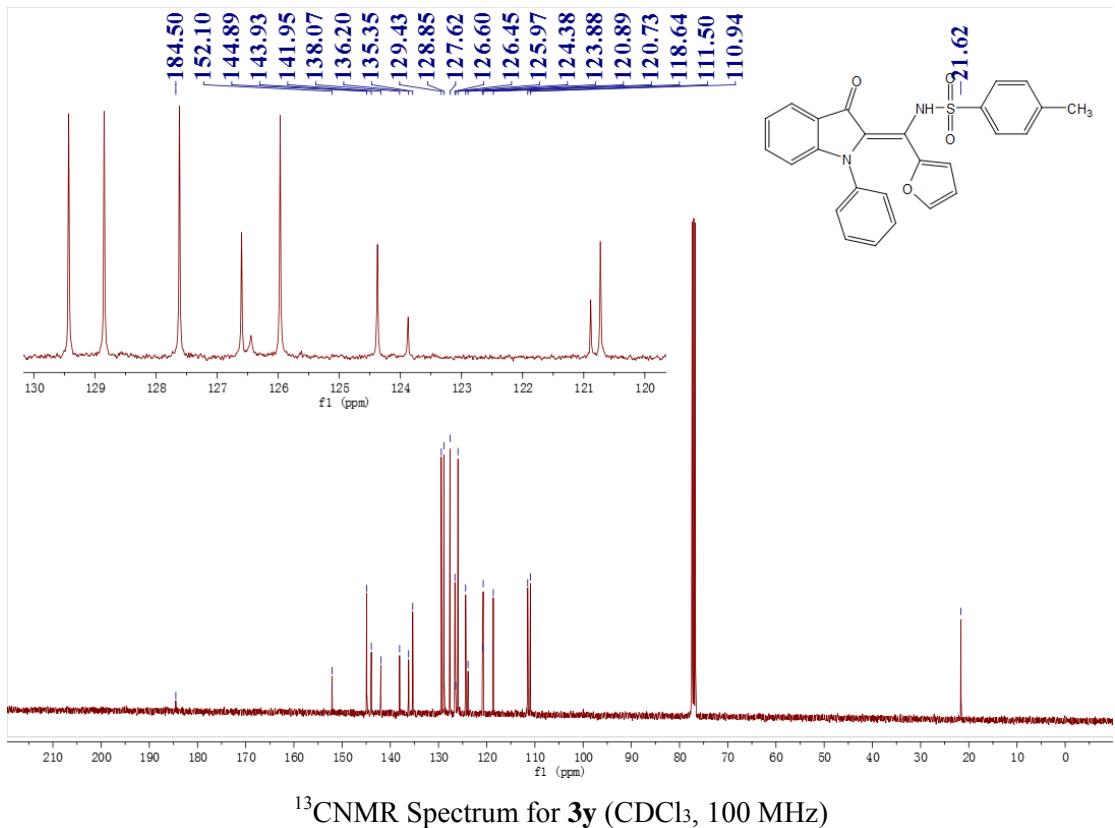
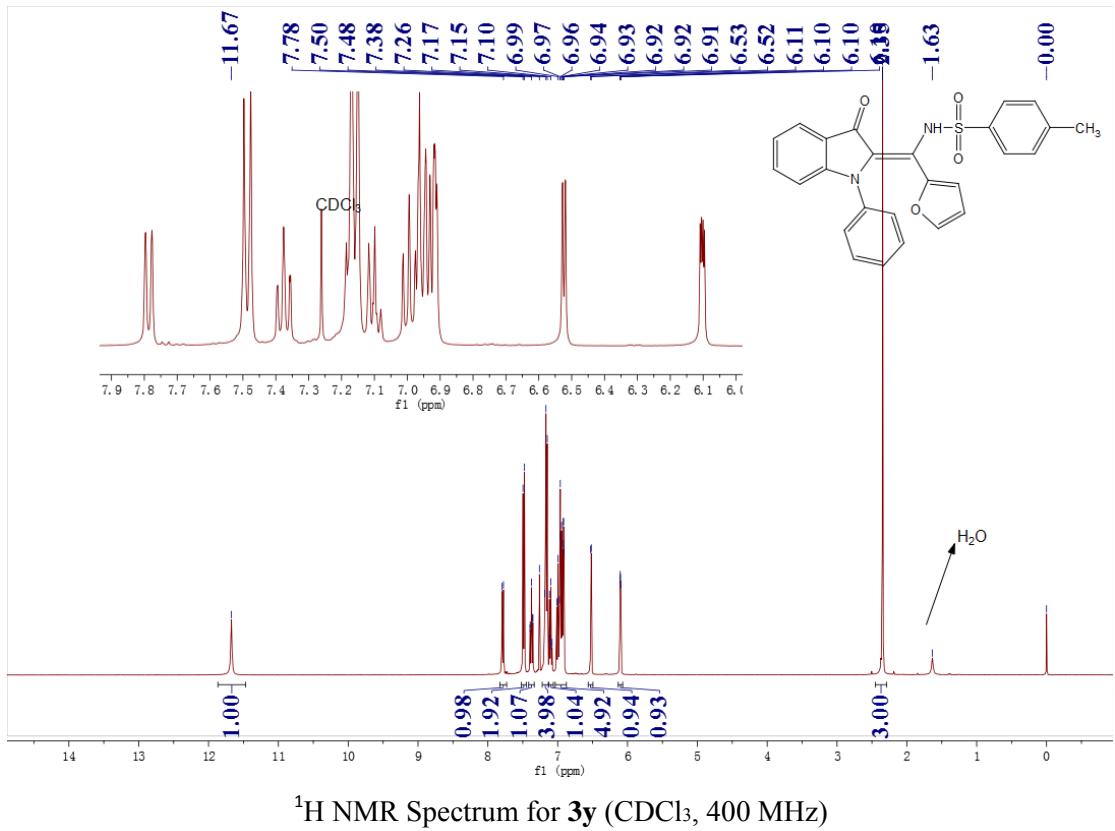


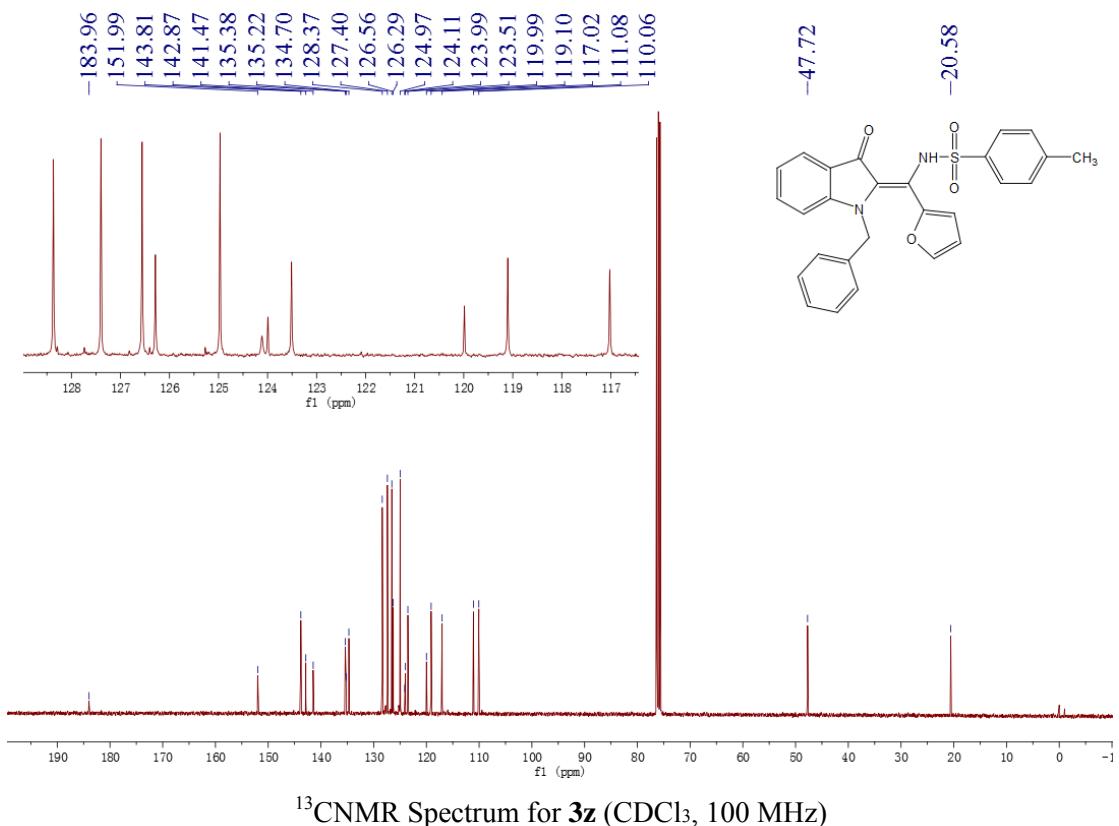
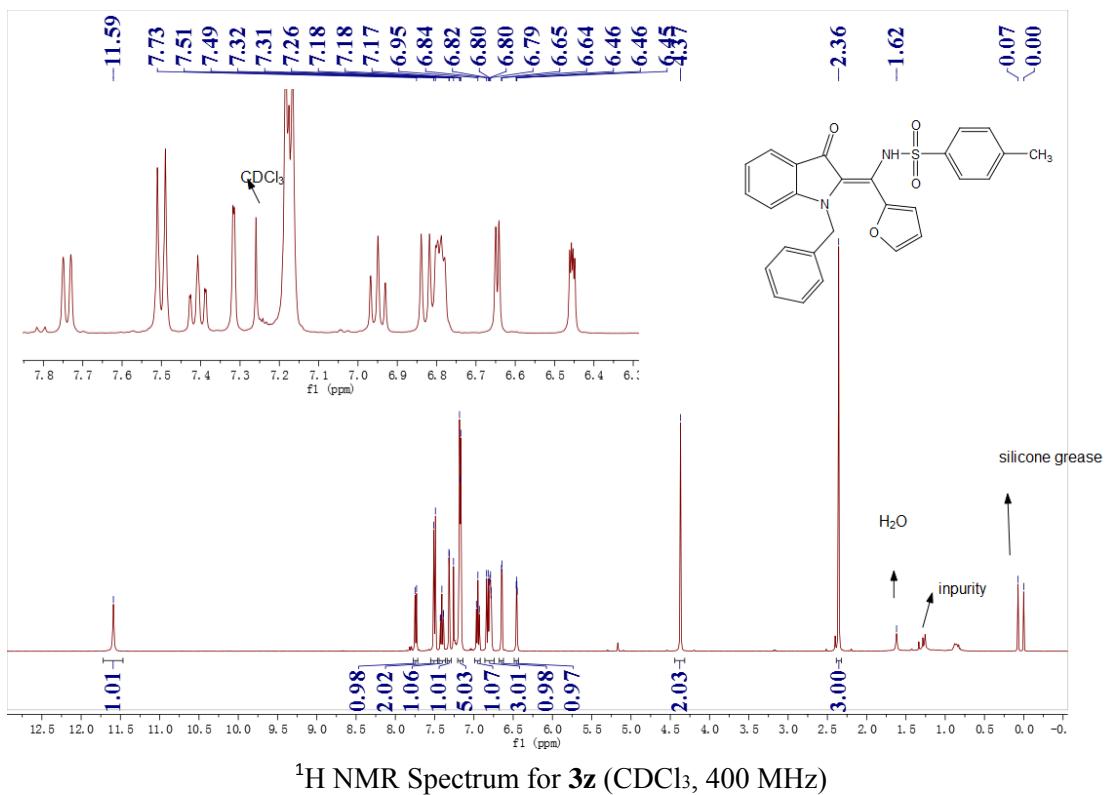


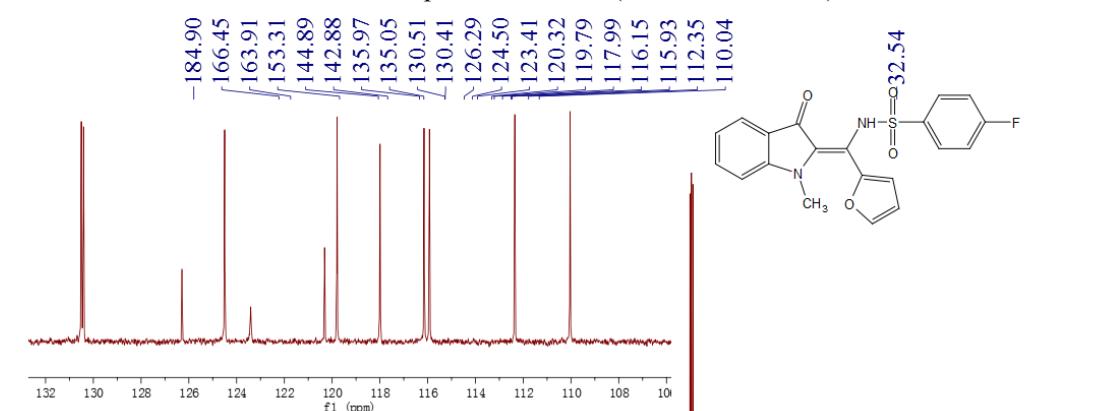
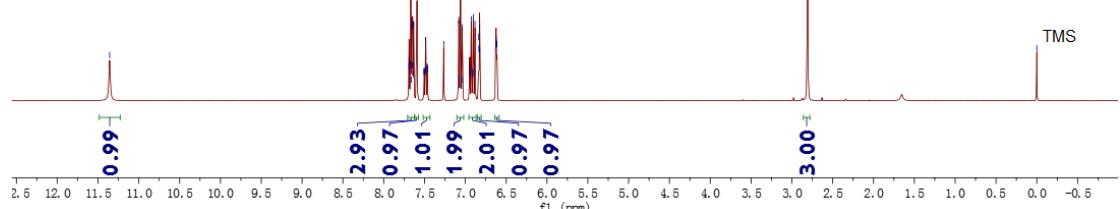
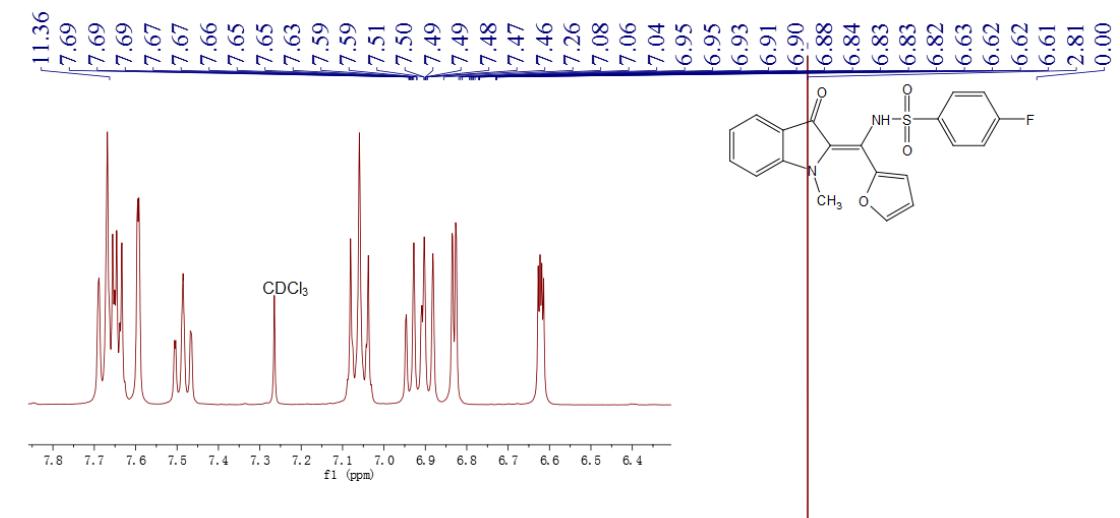


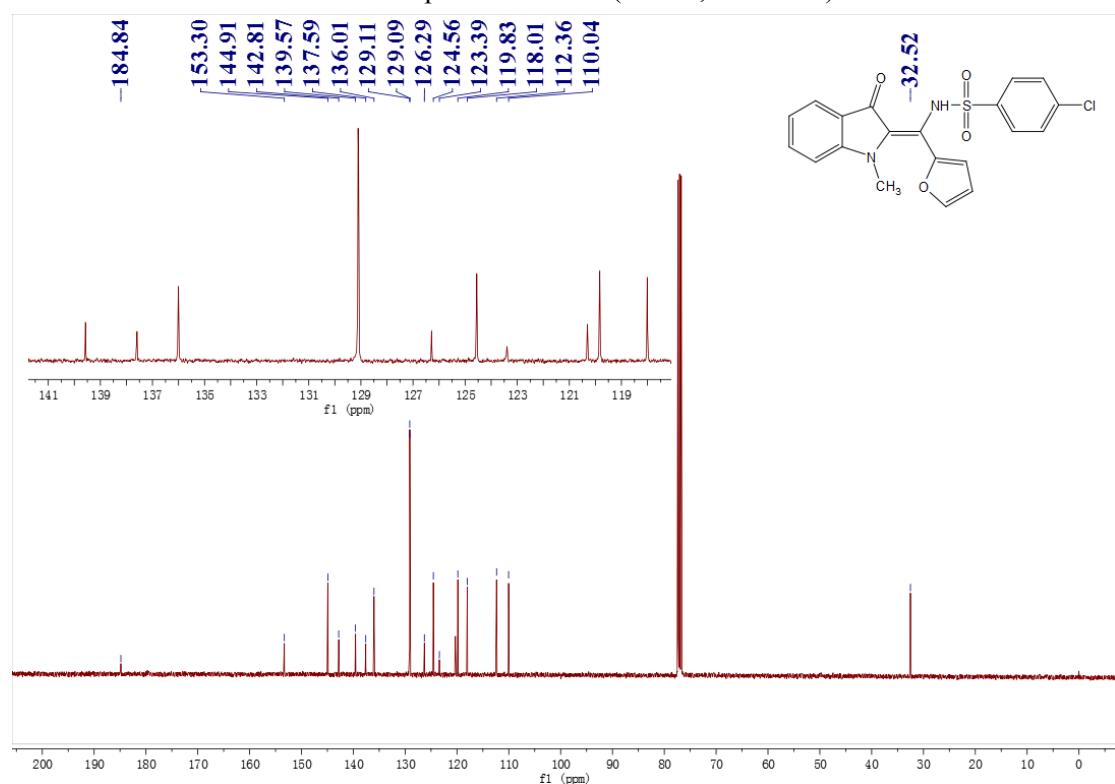
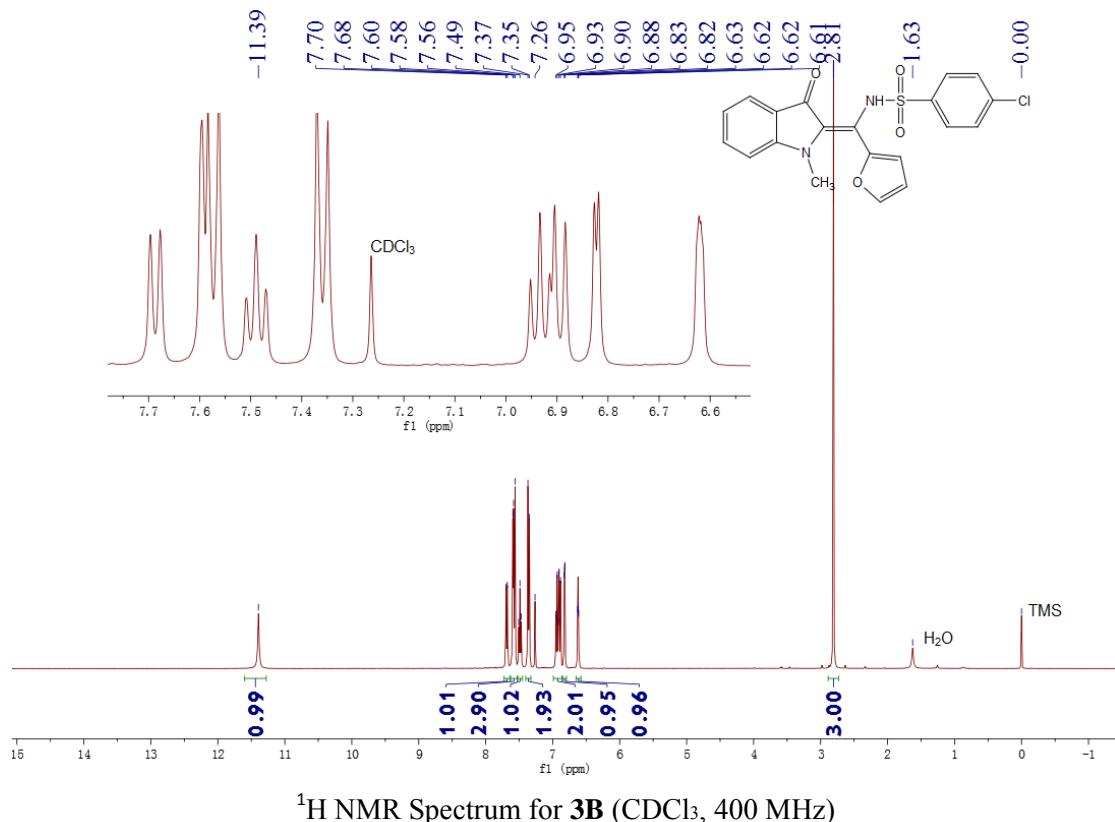




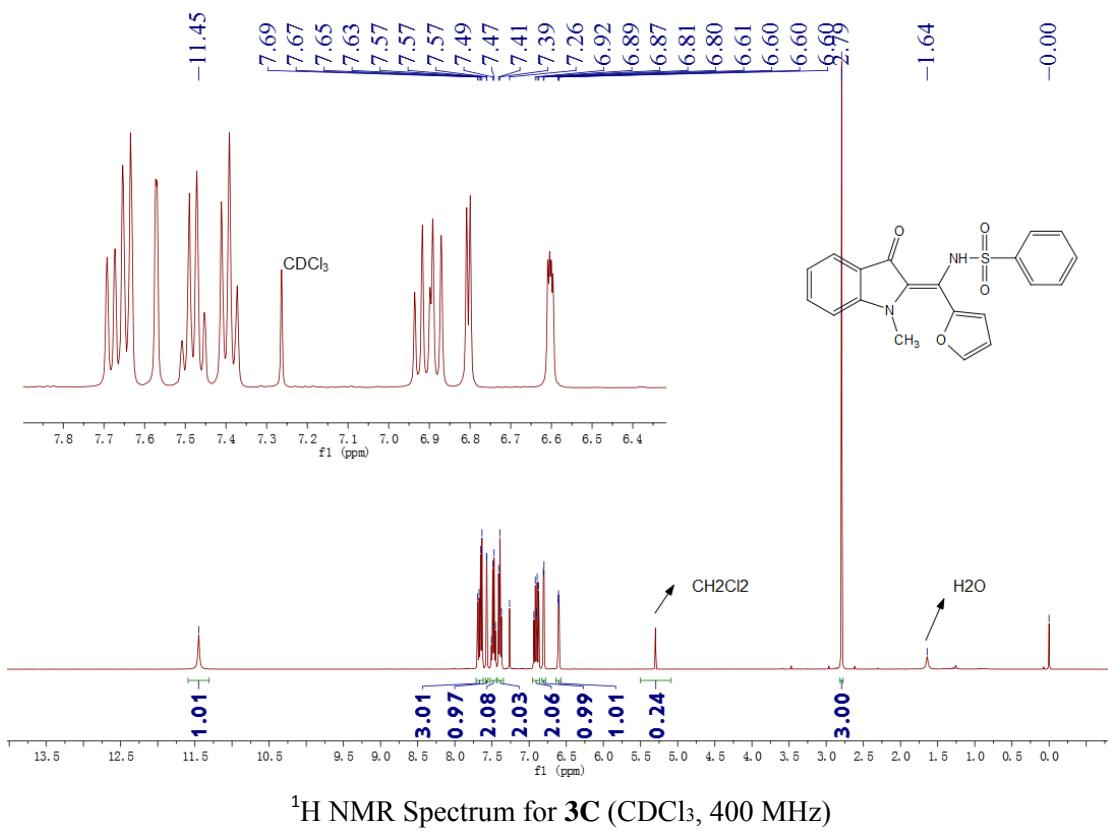




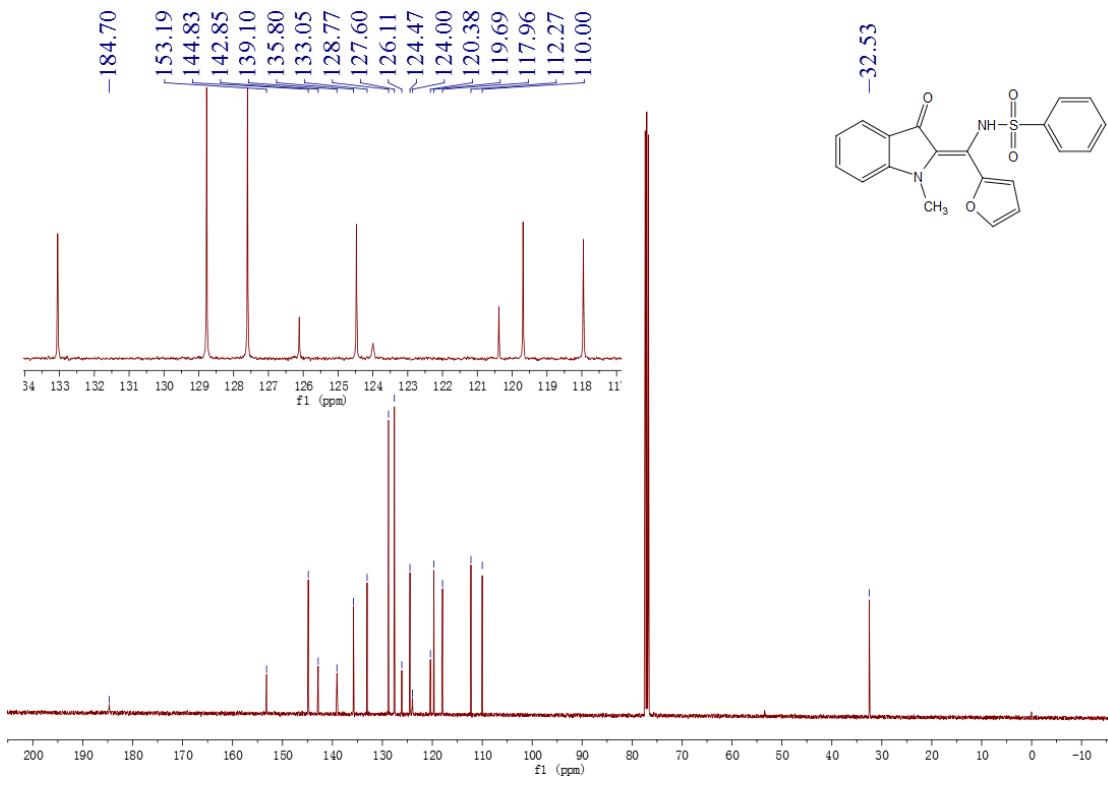




¹³CNMR Spectrum for **3B** (CDCl₃, 100 MHz)



¹H NMR Spectrum for **3C** (CDCl₃, 400 MHz)



¹³CNMR Spectrum for **3C** (CDCl₃, 100 MHz)

