

**Electronic supporting information (ESI) for:**

**Multicomponent synthesis of pyrrolo[2,1-a]isoindolylidene-malononitrile  
(PIYM) fluorophores and their photophysical properties**

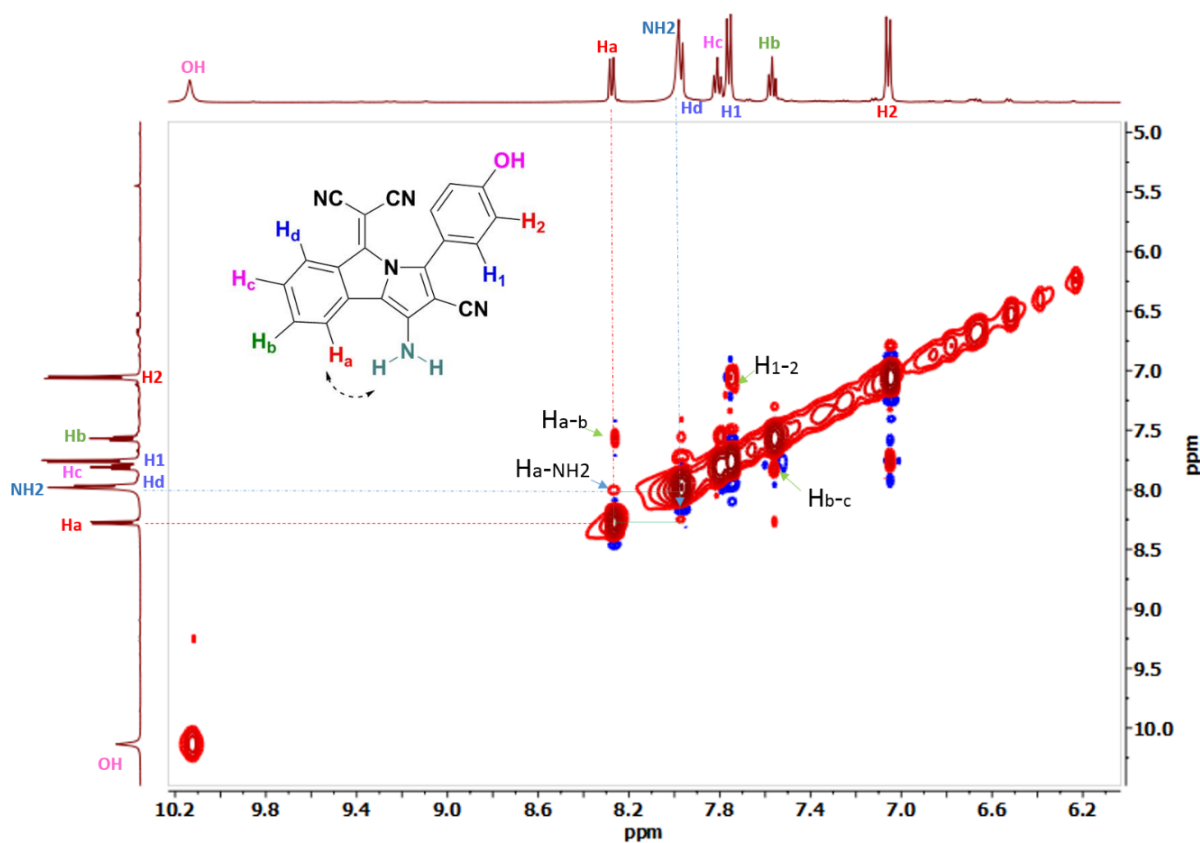
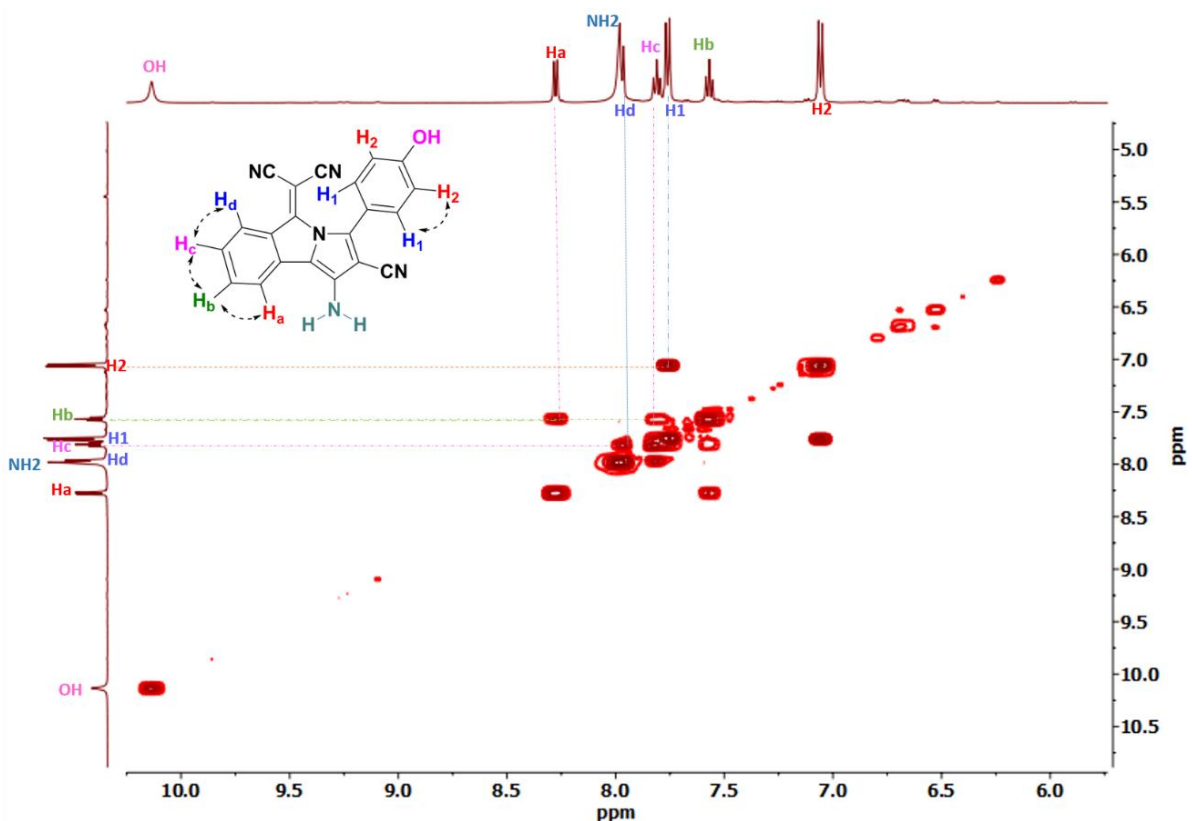
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# 1. 2D NMR characterization of PIYM fluorophore 5l



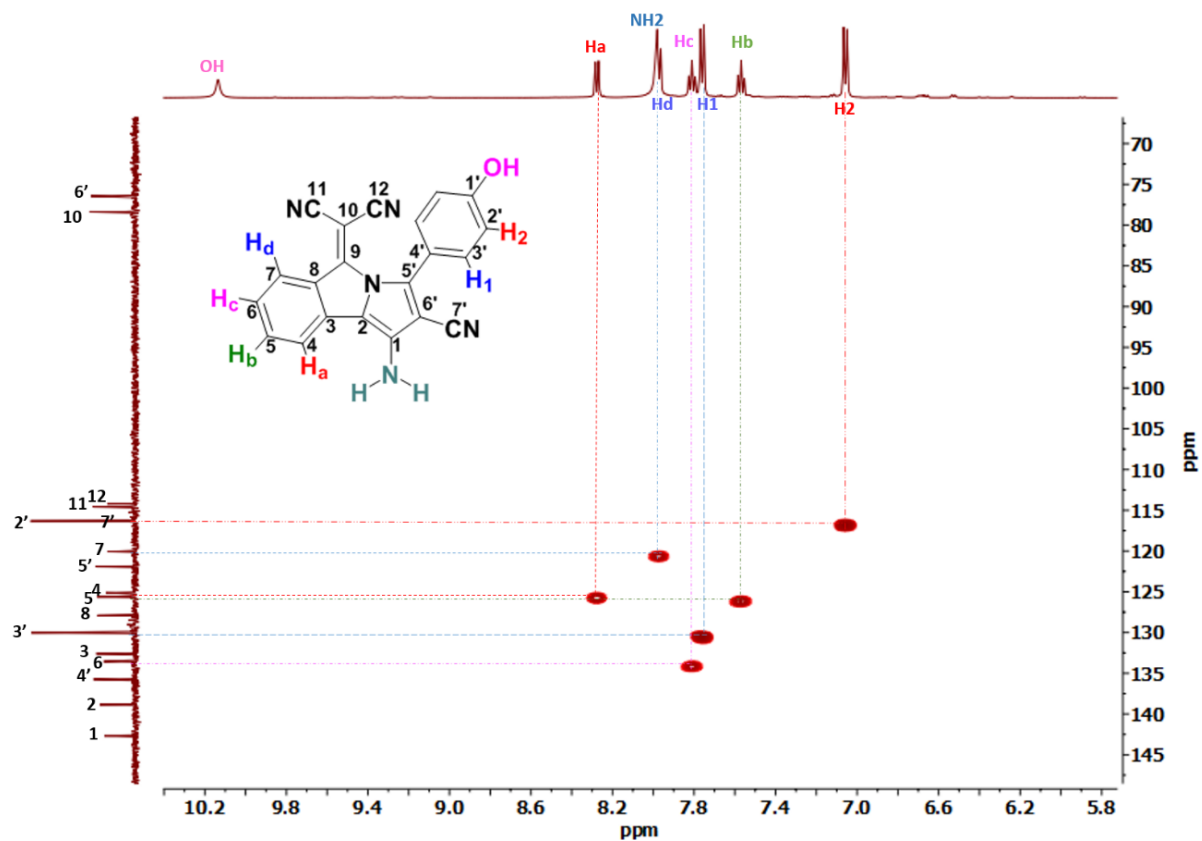


Fig. S3 HSQC (C-H) spectra of 5l in DMSO- $d_6$

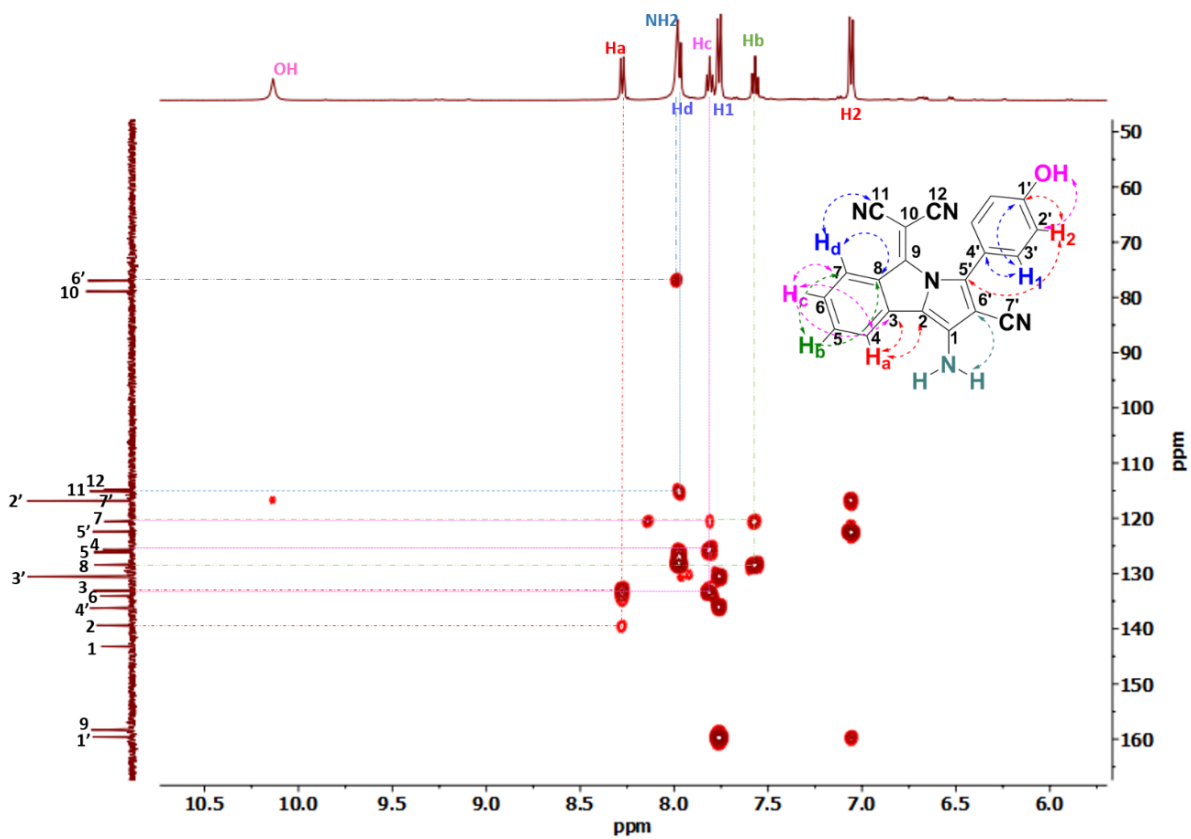
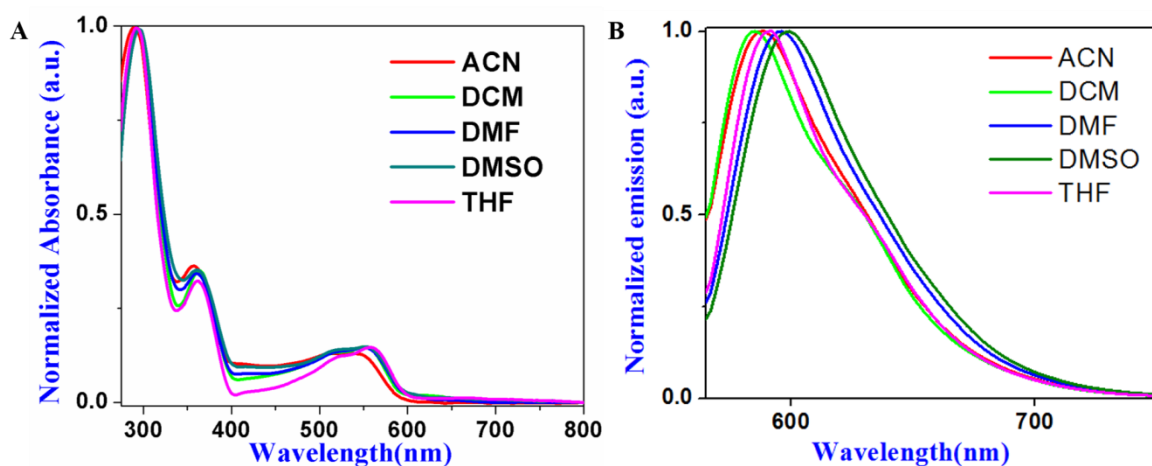


Fig. S4 HMBC (C-H) spectra of 5l in DMSO- $d_6$

## 2. Photophysical and electrochemical data

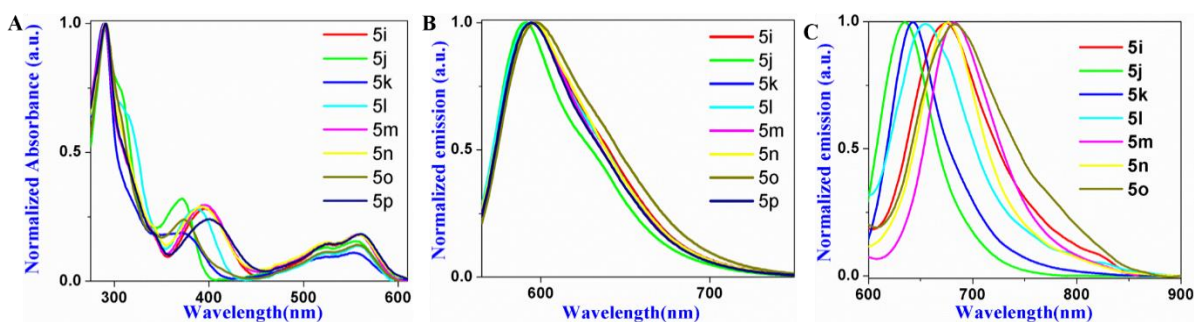


**Fig. S5** UV-vis (A) and emission spectra (B) of **5a** measured in different solvents at 2.5  $\mu\text{M}$ .

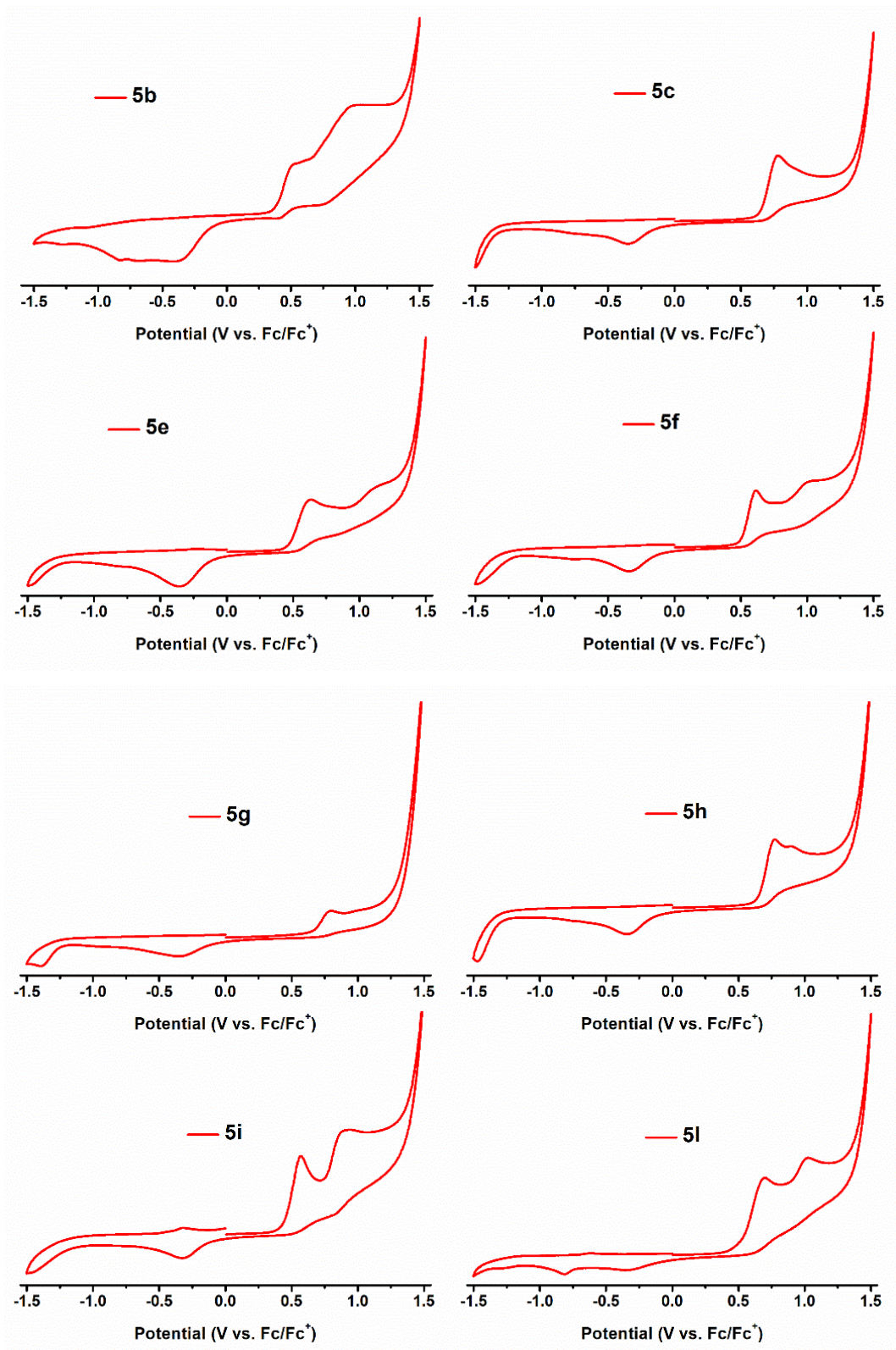
**Table S1** UV-vis and emission data of **5a** measured in different solvents at 2.5  $\mu\text{M}$ .

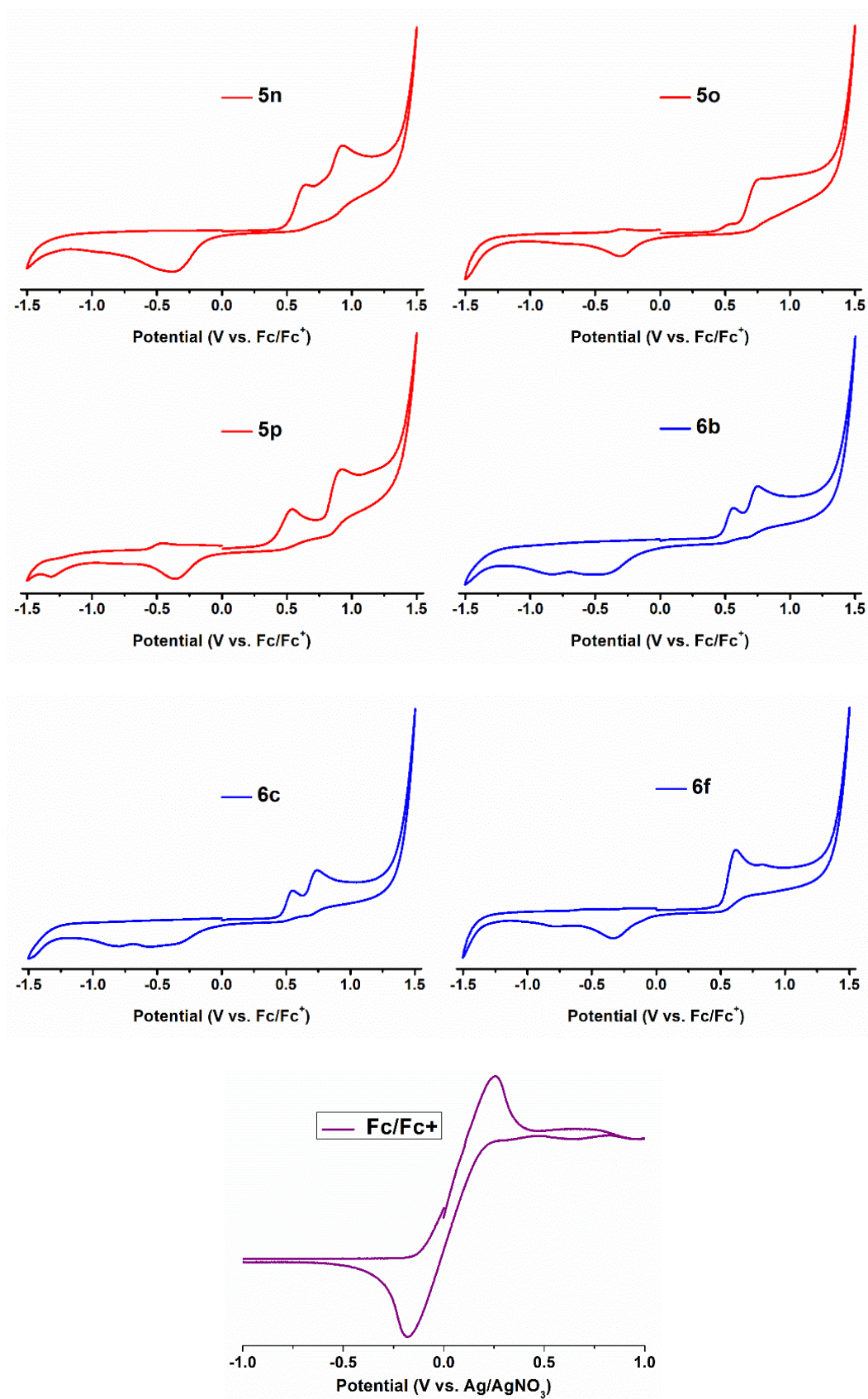
Compound	Solvent	$\lambda_{\text{abs}}^{\text{a,b}}$ (nm)	$\lambda_{\text{em}}$ (nm)
<b>5a</b>	DCM	367, 555	585
	ACN	364, 551	589
	THF	370, 561	592
	DMF	368, 555	596
	DMSO	370, 561	599

<sup>a,b</sup>Absorption maxima of the corresponding two absorption bands.

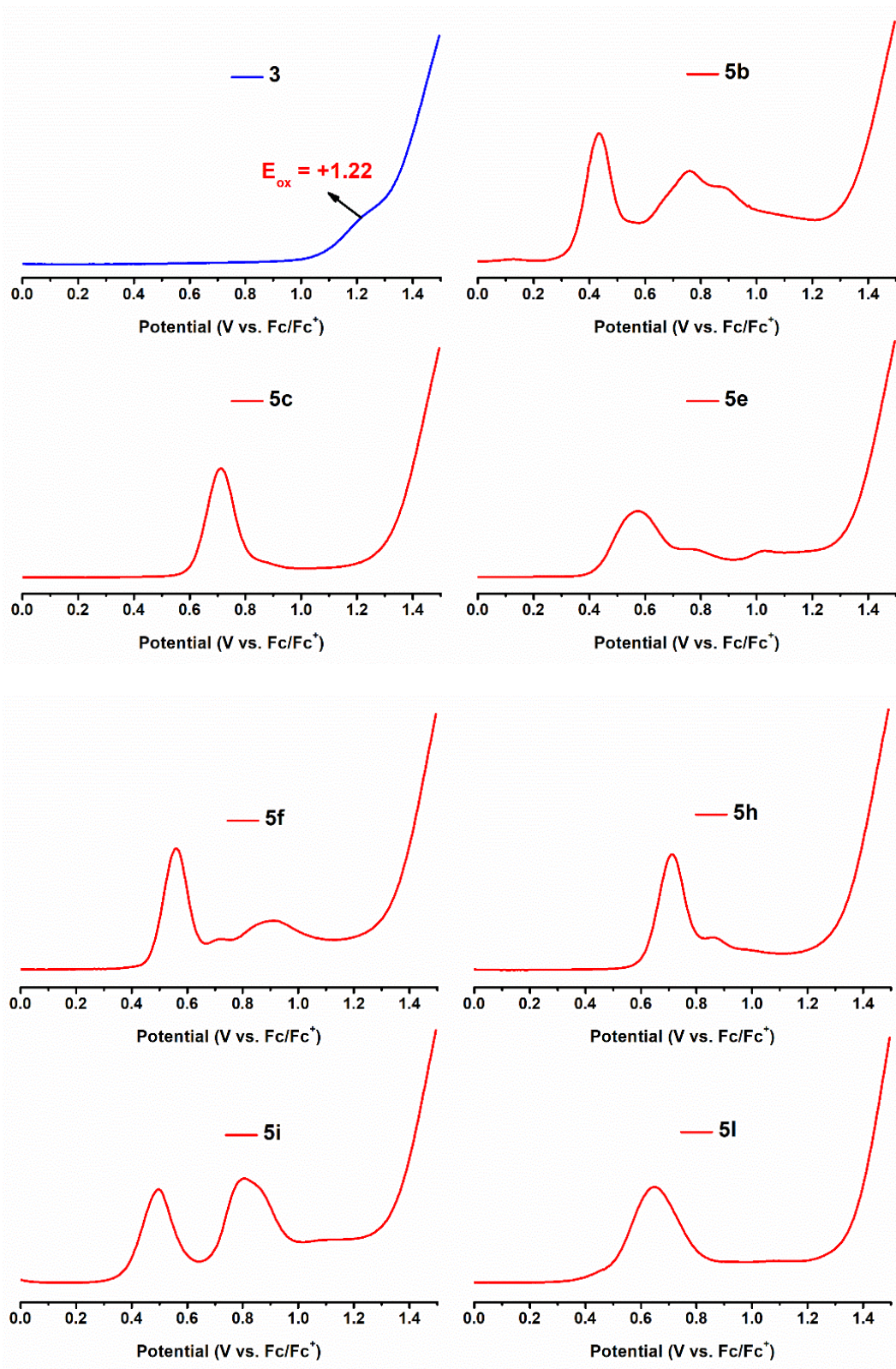


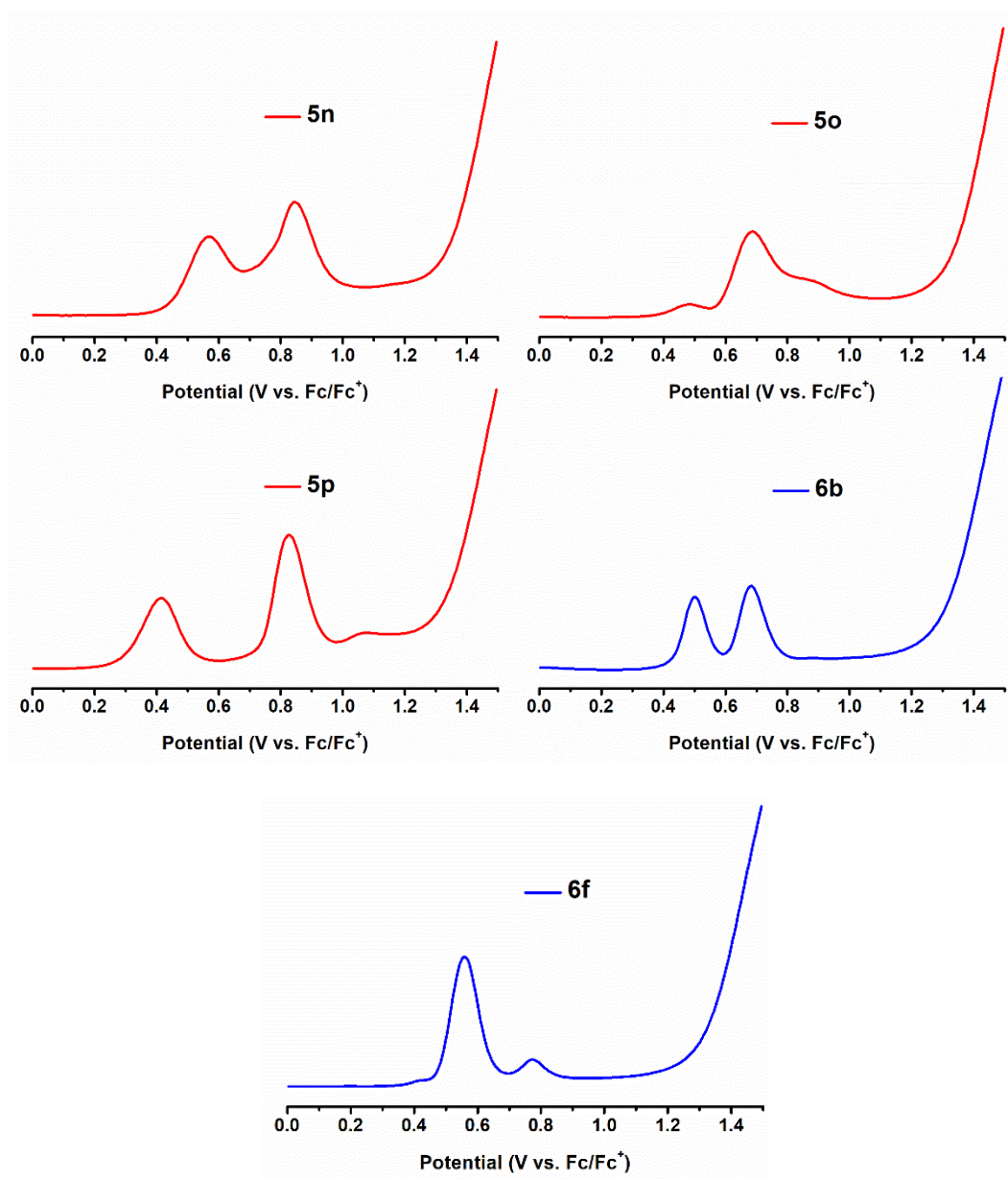
**Fig. S6** UV-vis (A), emission spectra in DMF (B), and solid-state emission spectra (C) of compounds **5i–p**.





**Fig. S7** Cyclic voltammograms of selected PIYM fluorophores and ferrocene reference.





**Fig. S8** Differential pulse voltammograms of selected PIYM fluorophores.

**Table S2** Photophysical and electrochemical properties of rest of the PIYM fluorophores

S.No.	Compd	$\lambda_{\text{abs}}^{\text{a,b}}$ (nm)	$\lambda_{\text{em}}$ (nm)	$\lambda_{\text{em}}(\text{solid})$ (nm)	$E_{\text{ox}}$ (eV)	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$E_{\text{g}}(\text{opt})$ (eV)
1	5i	392, 558	595	676	0.57	-5.01	-2.92	2.09
2	5j	373, 555	592	645	-	-	-	2.09
3	5k	372, 554	594	641	-	-	-	2.09
4	5l	387, 558	597	652	0.70	-5.14	-3.05	2.09

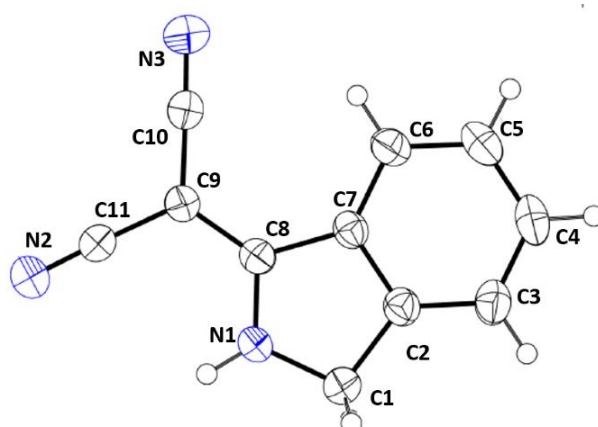


5	5m	397, 560	595	682	-	-	-	2.08
6	5n	400, 561	595	677	0.64	-5.08	-3.01	2.07
7	5o	387, 558	597	681	0.76	-5.20	-3.12	2.08
8	5p	397, 558	595	-	0.55	-4.99	-2.93	2.06
9	6c	383, 560	605	657	0.54	-4.98	-2.97	2.01
10	6d	376, 581	618	649	-	-	-	2.00
11	6e	370, 577	617	672	-	-	-	2.01
12	6f	370, 570	629	684	0.62	-5.06	-3.11	1.95
13	6g	375, 578	615	643	-	-	-	2.01

<sup>a,b</sup>Absorption maxima of the corresponding two absorption bands.

### 3. Single crystal X-ray diffraction

Single crystals of compound **3** was obtained by crystallization of dimethylformamide solution. Data collection was performed with a **Xcalibur, Eos** diffractometer. The crystal was kept at 298 K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL [1–3] refinement package using Least Squares minimization. Details for data collection and structure refinement are summarized in **Table S1**. CCDC-1969167 (for **3**), contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



**Fig. S9** Molecular structure of compound **3** presented using thermal ellipsoids of the 50% probability.

**Table S3** Crystal data and structure refinement for compound **3**.

	<b>Compound 3</b>
Empirical formula	C <sub>11</sub> H <sub>7</sub> N <sub>3</sub>
Formula weight	181.20
Temperature/K	298(2)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	3.9218(3)
b/Å	15.5165(11)
c/Å	14.5798(11)
α/°	90
β/°	95.477(7)
γ/°	90
Volume/Å <sup>3</sup>	883.18(11)
Z	4
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.363
μ/mm <sup>-1</sup>	0.086
F(000)	376.0
Crystal size/mm <sup>3</sup>	0.72 × 0.4 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	6.198 to 58.422
Index ranges	-5 ≤ h ≤ 5, -20 ≤ k ≤ 19, -18 ≤ l ≤ 19
Reflections collected	9532
Independent reflections	2161 [R <sub>int</sub> = 0.0280, R <sub>sigma</sub> = 0.0215]
Data/restraints/parameters	2161/0/127
Goodness-of-fit on F <sup>2</sup>	1.257
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0744, wR <sub>2</sub> = 0.2012
Final R indexes [all data]	R <sub>1</sub> = 0.0845, wR <sub>2</sub> = 0.2065
Largest diff. peak/hole / e Å <sup>-3</sup>	0.29/-0.30

#### 4. Cartesian coordinates for the optimized structure

5a

E = -1080.52718319 a.u., Number of negative frequencies = 0

0 1

C	-4.80857000	-0.57895200	0.44147400
C	-4.88337600	0.81847000	0.36777900
C	-3.73730000	1.59164700	0.18371600
C	-2.50328400	0.94533300	0.08096700
C	-2.42438400	-0.47583600	0.14085300
C	-3.58454000	-1.23774800	0.32069900
C	-1.16597100	1.44003200	-0.07635200
N	-0.29486500	0.32931200	-0.07787800
C	-1.02461600	-0.86814700	-0.09250000
C	-0.40629200	2.58499300	-0.18522800
C	0.97692100	2.14871200	-0.20592800
C	1.03041000	0.75924800	-0.09880300
C	-0.54611700	-2.11866900	-0.44736500
C	0.70155500	-2.36242100	-1.09108300
N	1.66686400	-2.62368900	-1.68854600
C	-1.37063500	-3.27657200	-0.32313000
N	-2.01626800	-4.24046600	-0.21488500
C	2.06467300	3.05431300	-0.18601200
N	2.89656200	3.87086400	-0.17455900
H	-5.71300800	-1.16045200	0.59008200
H	-5.84887000	1.30897100	0.45483100
H	-3.81181600	2.67331600	0.11944700
H	-3.54751000	-2.31818700	0.37408500
C	2.21633700	-0.05142800	0.19460100

C	2.20975800	-0.95633400	1.27132100
C	3.40201000	0.14219900	-0.53195900
C	3.36469500	-1.65796300	1.60446100
H	1.30484900	-1.09493100	1.85605400
C	4.55354000	-0.56546300	-0.19447500
H	3.41365700	0.82994600	-1.37127100
C	4.53852600	-1.46652300	0.87147900
H	3.34963100	-2.35155700	2.44029800
H	5.46190300	-0.41617500	-0.77056700
H	5.43747000	-2.01860100	1.13038400
N	-0.80454400	3.89377100	-0.28328700
H	-0.08991500	4.58980900	-0.10885600
H	-1.71067100	4.13597200	0.09252000

**6a**

E = -1156.99138138 a.u., Number of negative frequencies = 0

0 1

C	-4.97906000	-0.24864900	0.38342700
C	-4.91754400	1.15125900	0.32153000
C	-3.70261500	1.81081700	0.14744300
C	-2.53561500	1.04800200	0.03866000
C	-2.59223800	-0.37490500	0.10301700
C	-3.82388400	-1.02123700	0.27073200
C	-1.16116600	1.41098900	-0.11771000
N	-0.39890600	0.22811500	-0.11588300
C	-1.23293700	-0.89845000	-0.10296700
C	-0.29666500	2.48639000	-0.17040700
C	1.05456800	1.93631400	-0.12642000
C	0.96300700	0.54781100	-0.07316200
C	-0.87365700	-2.20990300	-0.38799200

C	0.33052200	-2.61953200	-1.02780700
N	1.24409700	-3.03236100	-1.62227700
C	-1.79958500	-3.27735100	-0.19247000
N	-2.52451800	-4.17483300	-0.02586900
H	-5.93652400	-0.74082200	0.52304900
H	-5.83127200	1.73211600	0.41349400
H	-3.66693000	2.89562700	0.11240000
H	-3.89242900	-2.09988700	0.32534800
C	2.03279400	-0.44112800	0.16965000
C	3.09913600	-0.59309600	-0.73201800
C	2.02041200	-1.20587000	1.34894400
C	4.13123300	-1.48936100	-0.45686800
H	3.10216500	-0.02298500	-1.65595800
C	3.05169300	-2.10498500	1.61601500
H	1.20571800	-1.08656700	2.05757800
C	4.10965600	-2.24703600	0.71567800
H	4.94276000	-1.60839200	-1.16879200
H	3.03057600	-2.69048200	2.53072700
H	4.91080500	-2.95037100	0.92387100
N	-0.59186400	3.81549900	-0.17301400
H	0.20135500	4.41542500	-0.38508400
H	-1.50511100	4.10618800	-0.48908400
C	2.23047000	2.84409800	-0.06700100
O	2.10810500	4.04366300	-0.34982800
N	3.43075000	2.35103200	0.33765600
H	4.21153100	2.99194000	0.33009900
H	3.59447100	1.37168800	0.51506100

## 6. Lifetime data

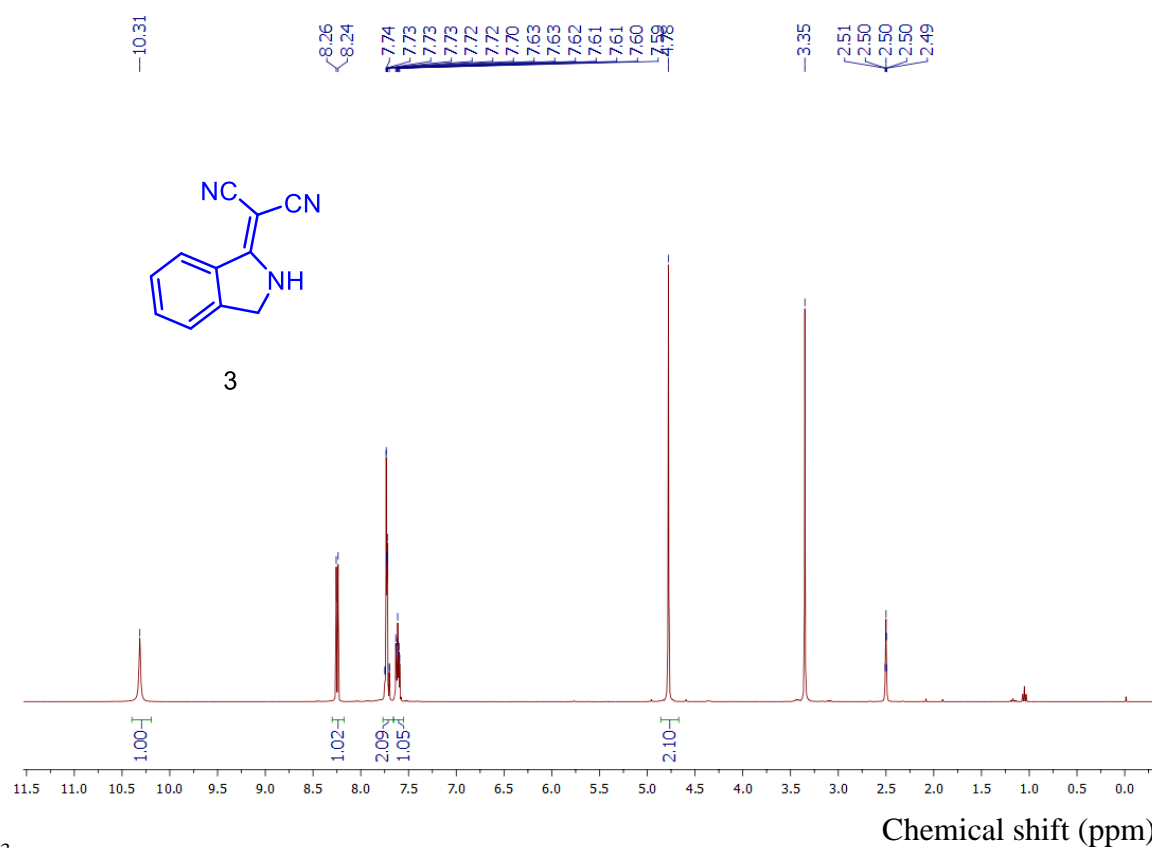
**Table S4** CHISQ values of the data obtained for lifetime fitting.

<b>S.No.</b>	<b>Compd</b>	<b>CHISQ value</b>	<b>Degrees of freedom</b>
1	5a	1.034984/1.504469*	981/869*
2	5b	1.173358	885
3	5c	1.130323	981
4	5d	1.123169	981
5	5e	1.194393	981
6	5f	1.24269	981
7	5g	1.169749	981
8	5h	1.267221	981
9	6a	1.696128	1000
10	6b	1.469595	1000

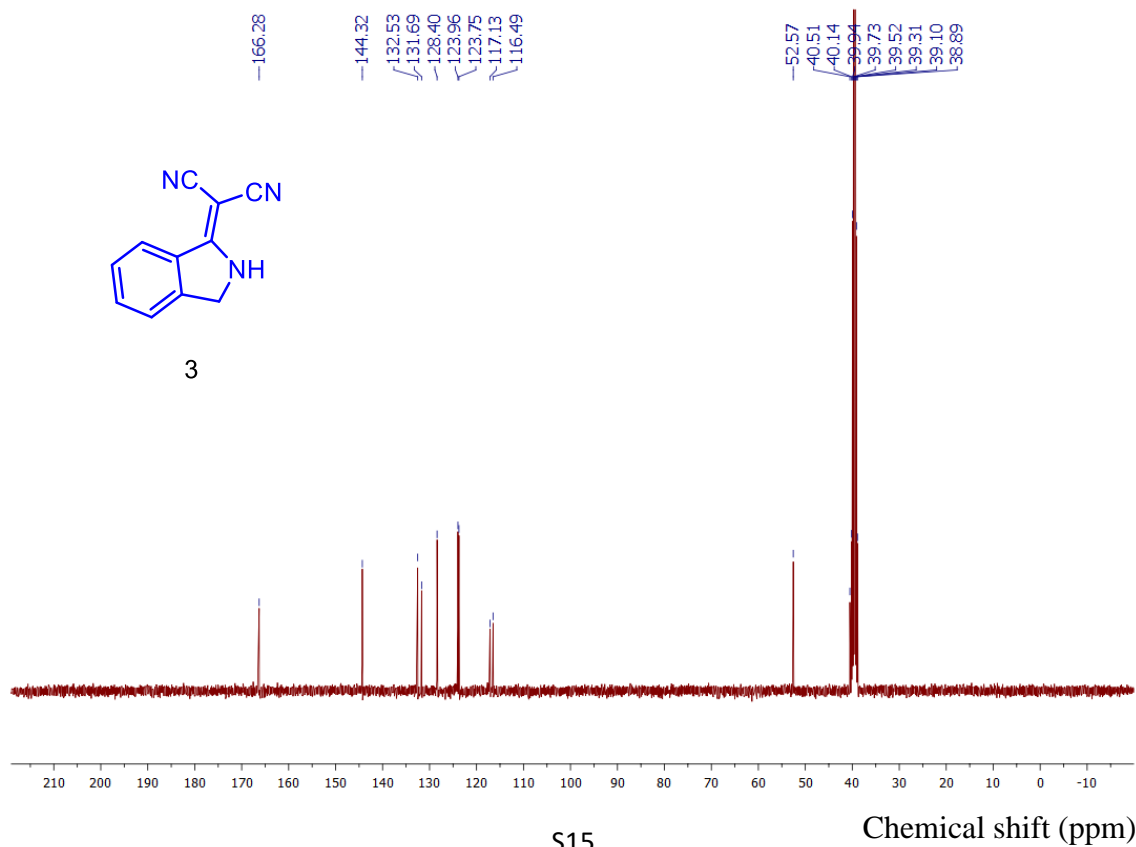
\*Obtained in solid-state.

## 7. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

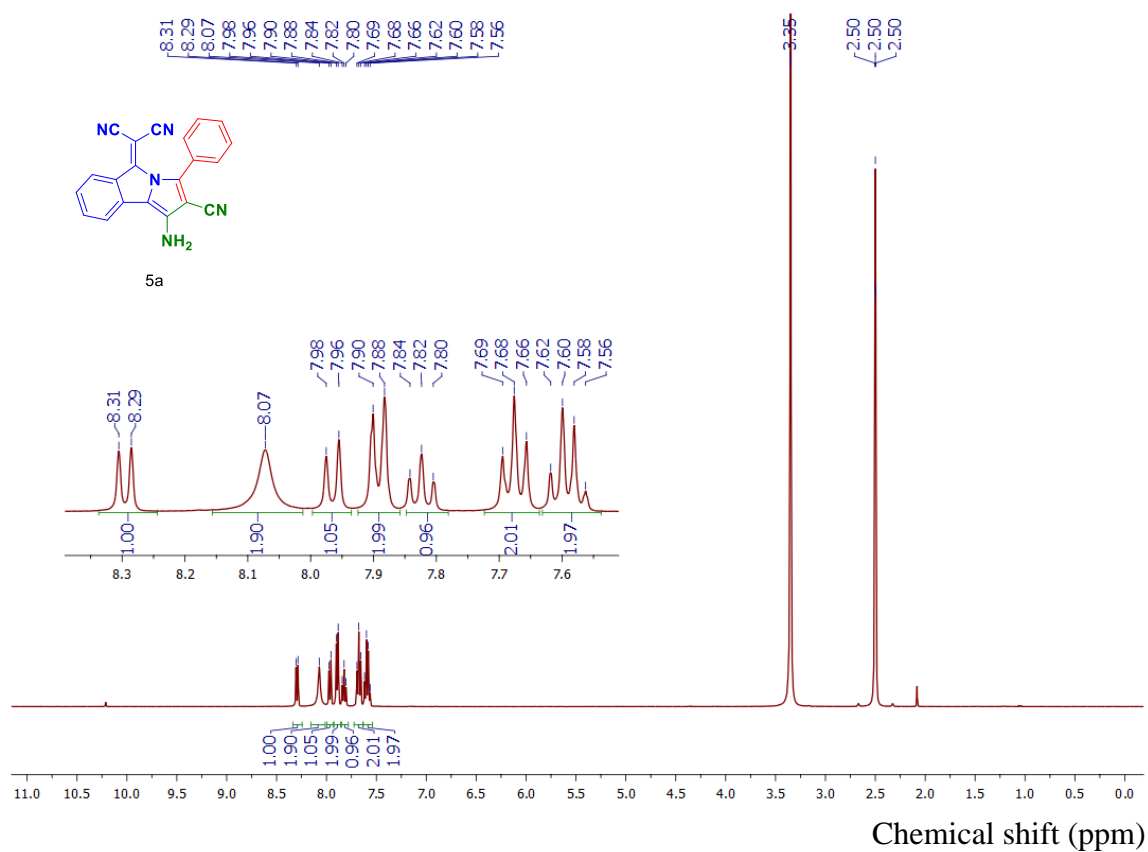
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) spectra of **3**



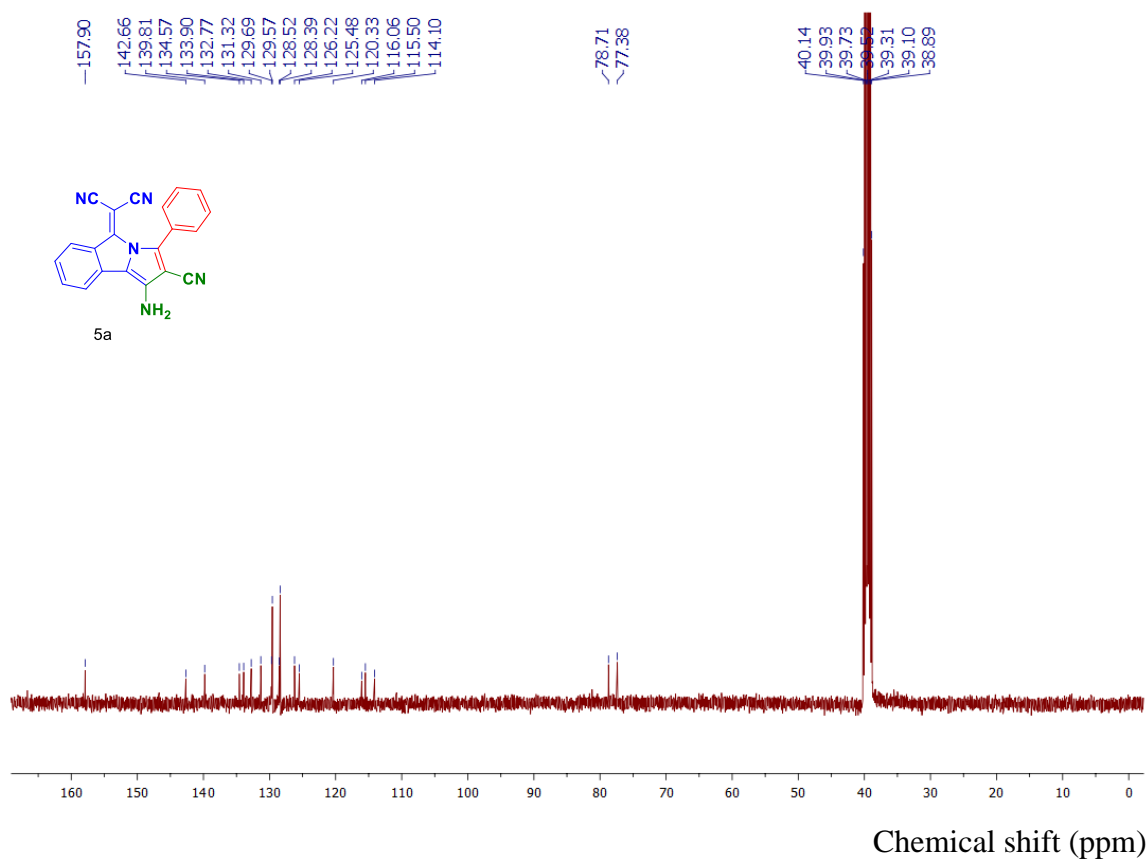
$^{13}\text{C}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) spectra of **3**



<sup>1</sup>H NMR Spectra of **5a** (400 MHz, DMSO-*d*<sub>6</sub>)

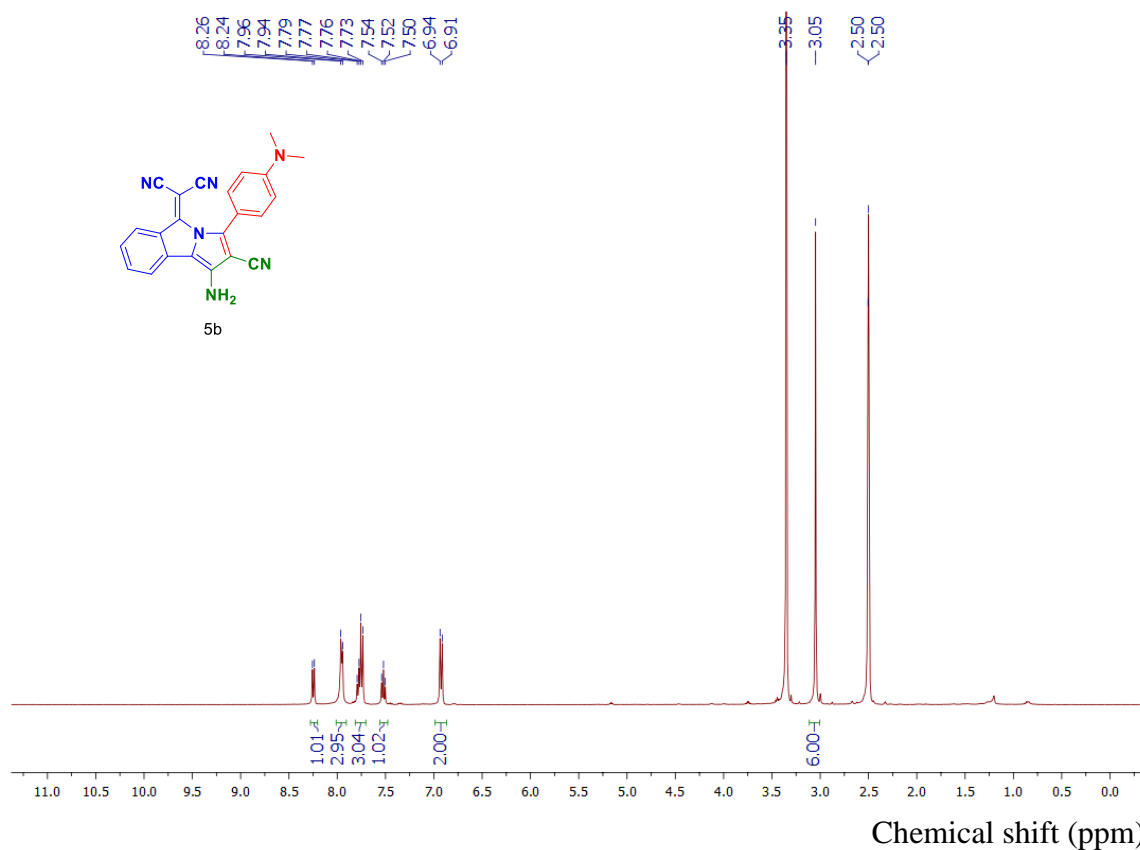


<sup>13</sup>C NMR Spectra of **5a** (400 MHz, DMSO-*d*<sub>6</sub>)

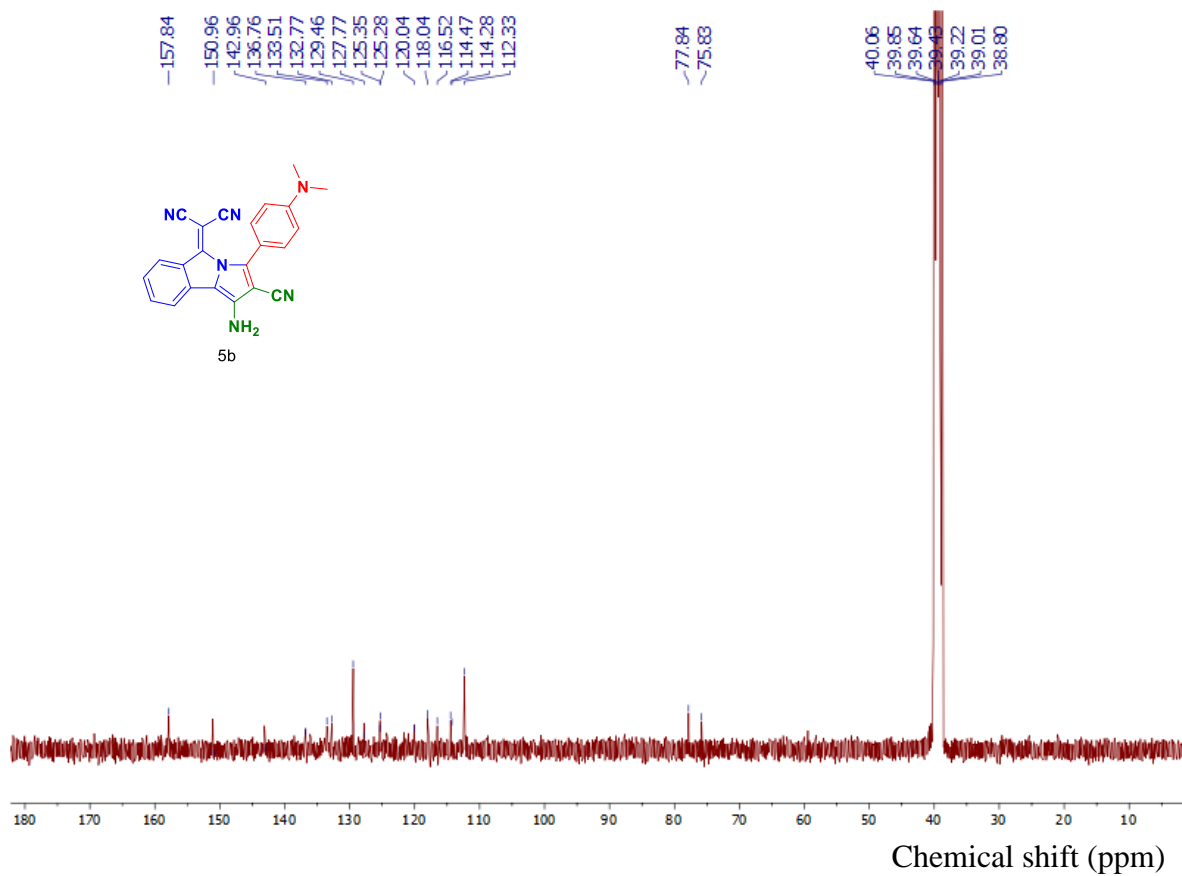




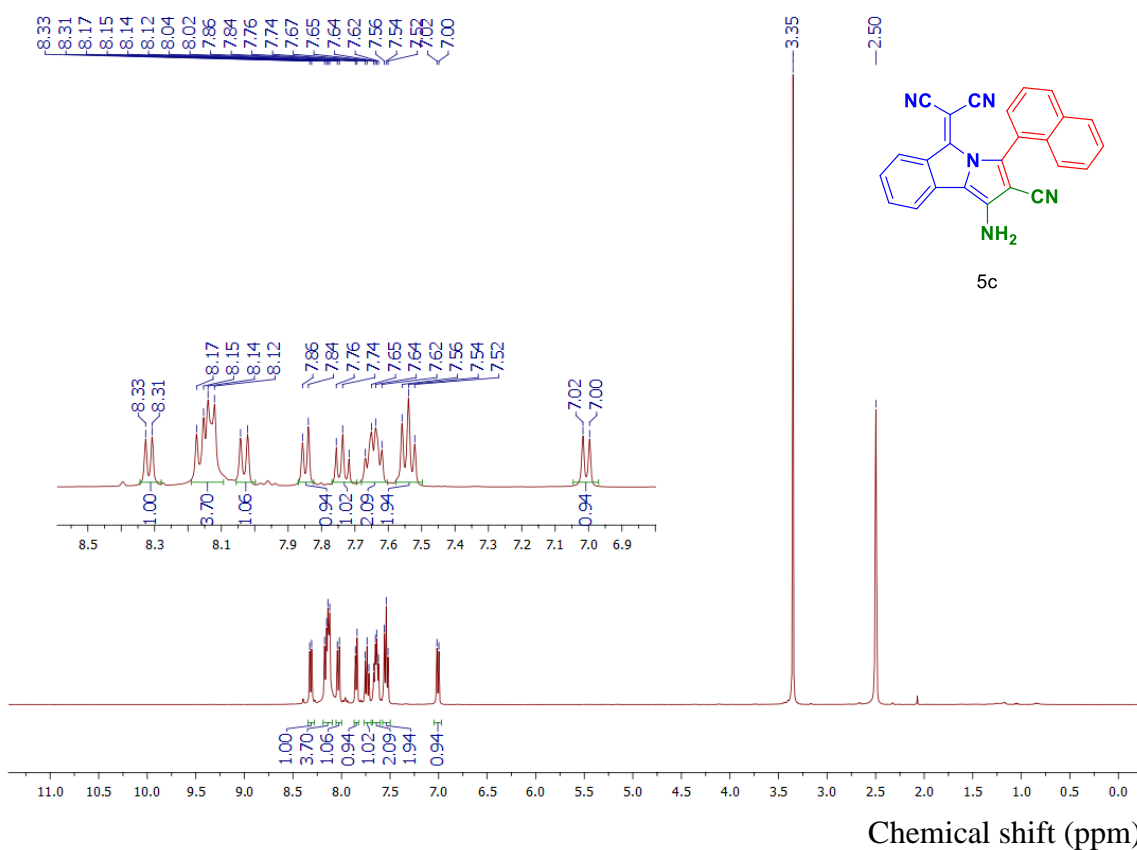
<sup>1</sup>H NMR Spectra of **5b** (400 MHz, DMSO-*d*<sub>6</sub>)



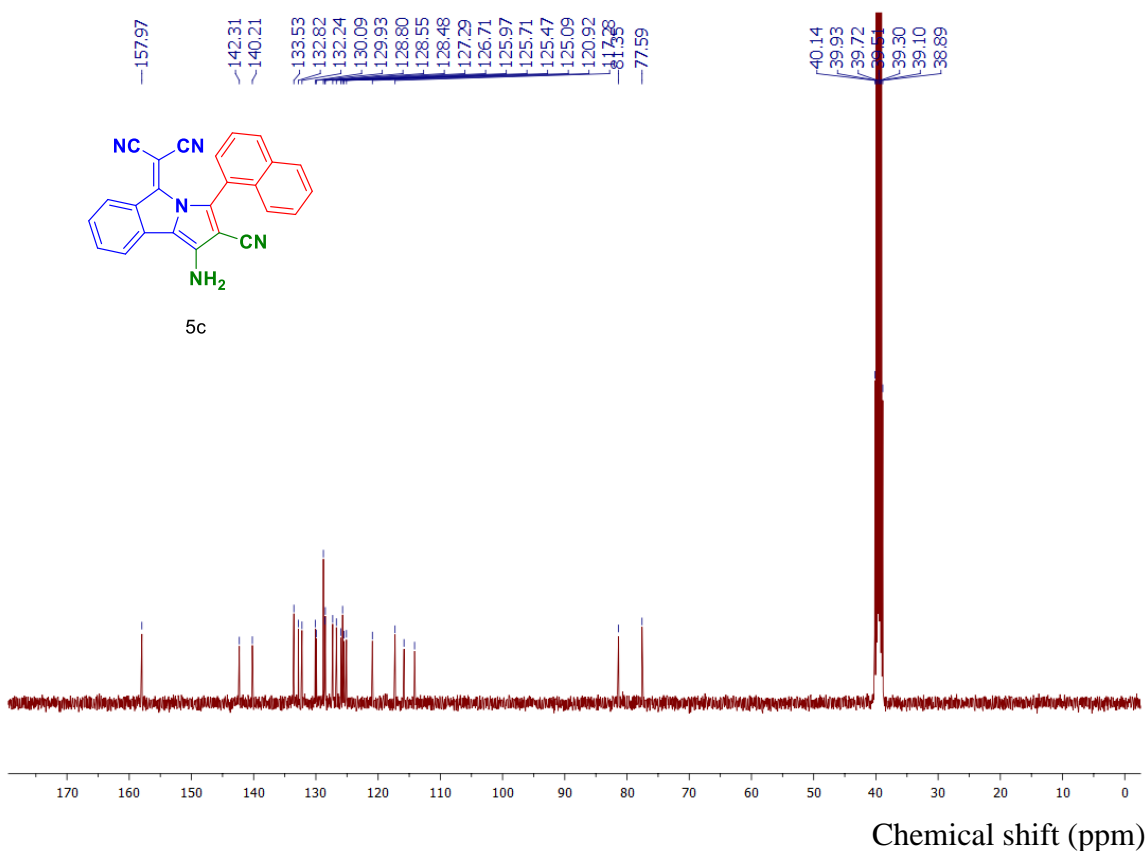
<sup>13</sup>C NMR Spectra of **5b** (400 MHz, DMSO-*d*<sub>6</sub>)



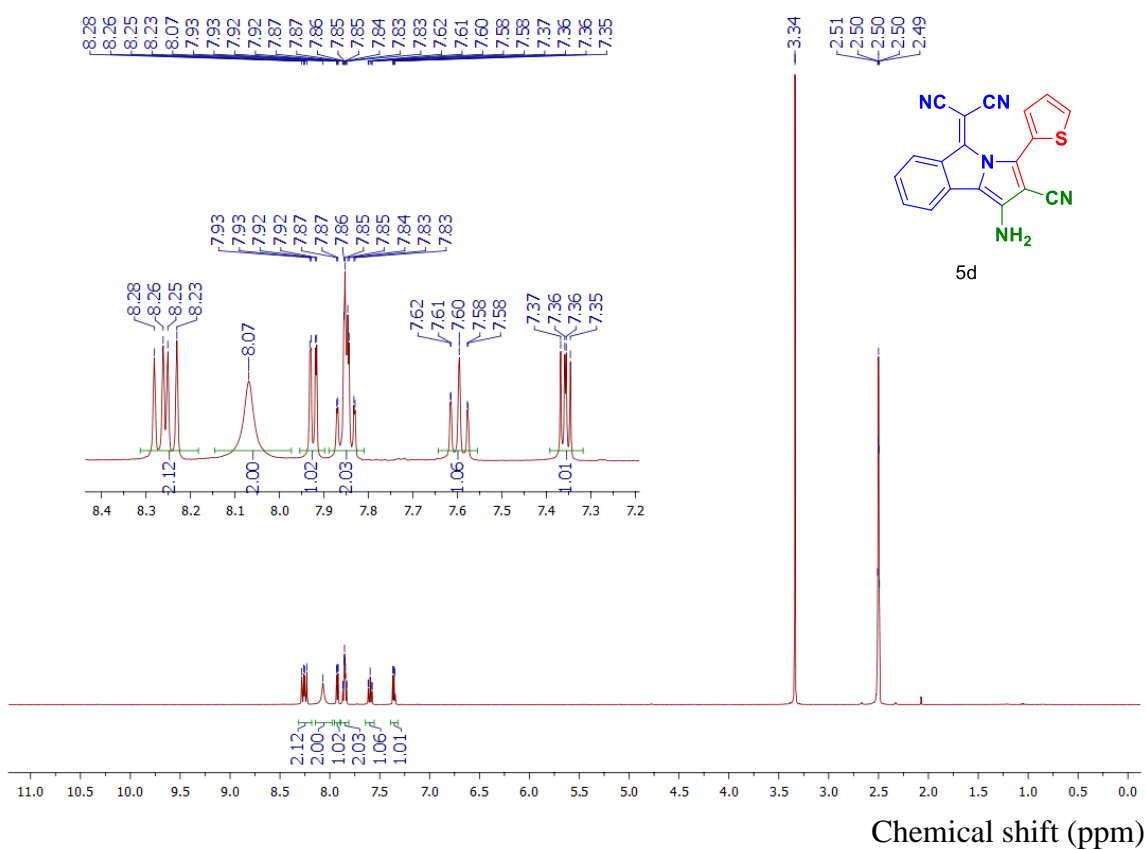
<sup>1</sup>H NMR Spectra of **5c** (400 MHz, DMSO-*d*<sub>6</sub>)



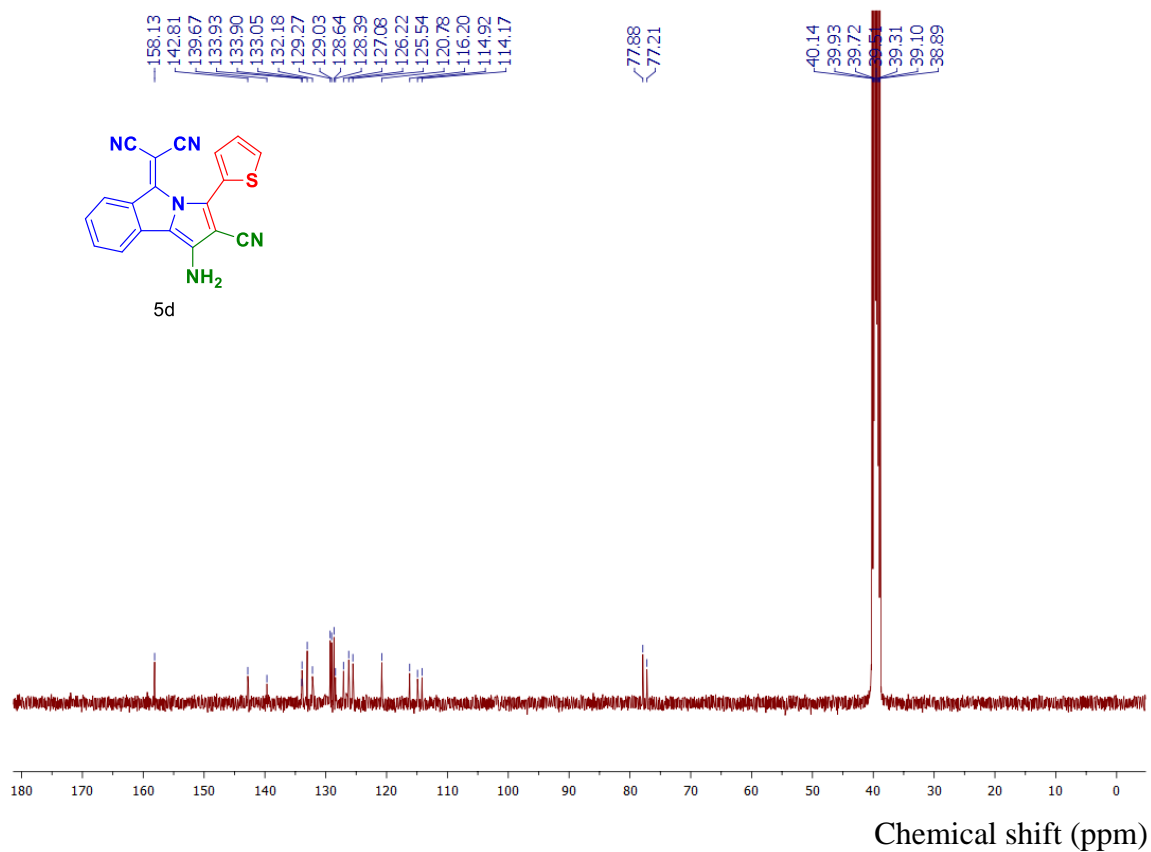
<sup>13</sup>C NMR Spectra of **5c** (400 MHz, DMSO-*d*<sub>6</sub>)



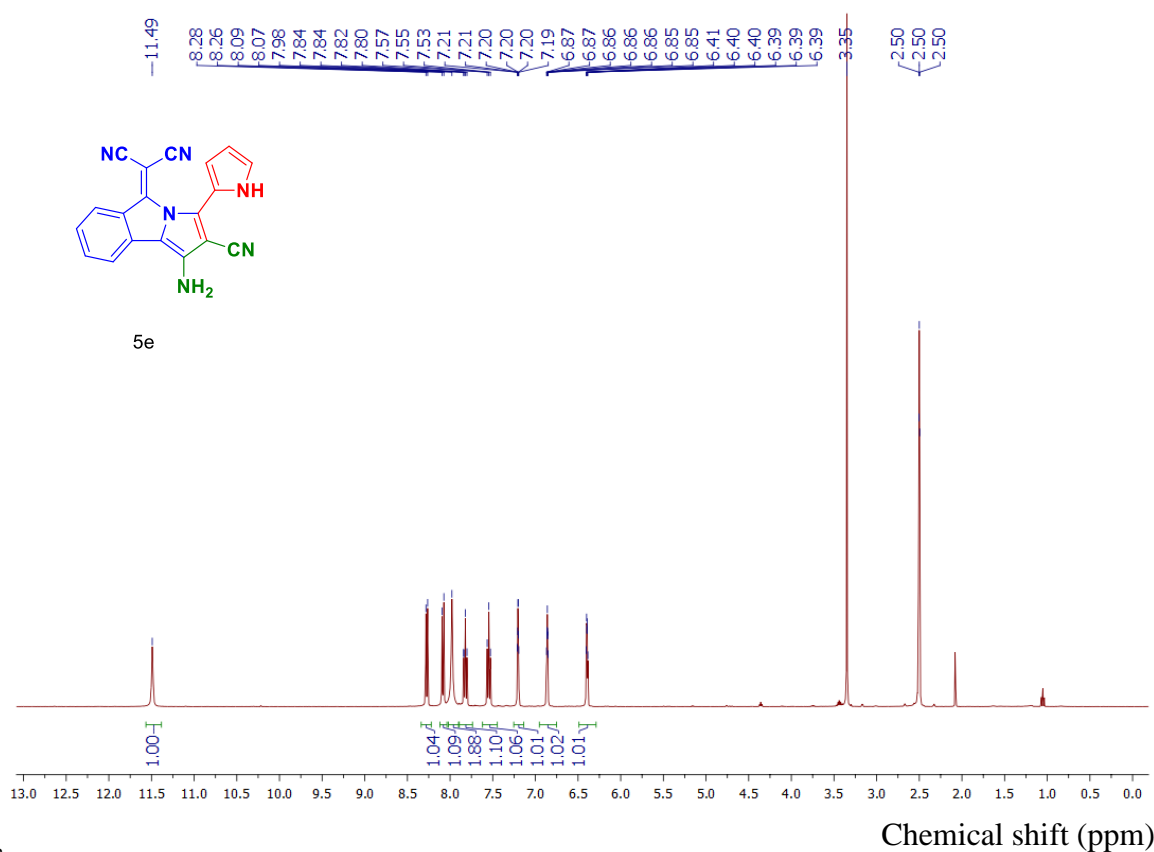
<sup>1</sup>H NMR Spectra of **5d** (400 MHz, DMSO-*d*<sub>6</sub>)



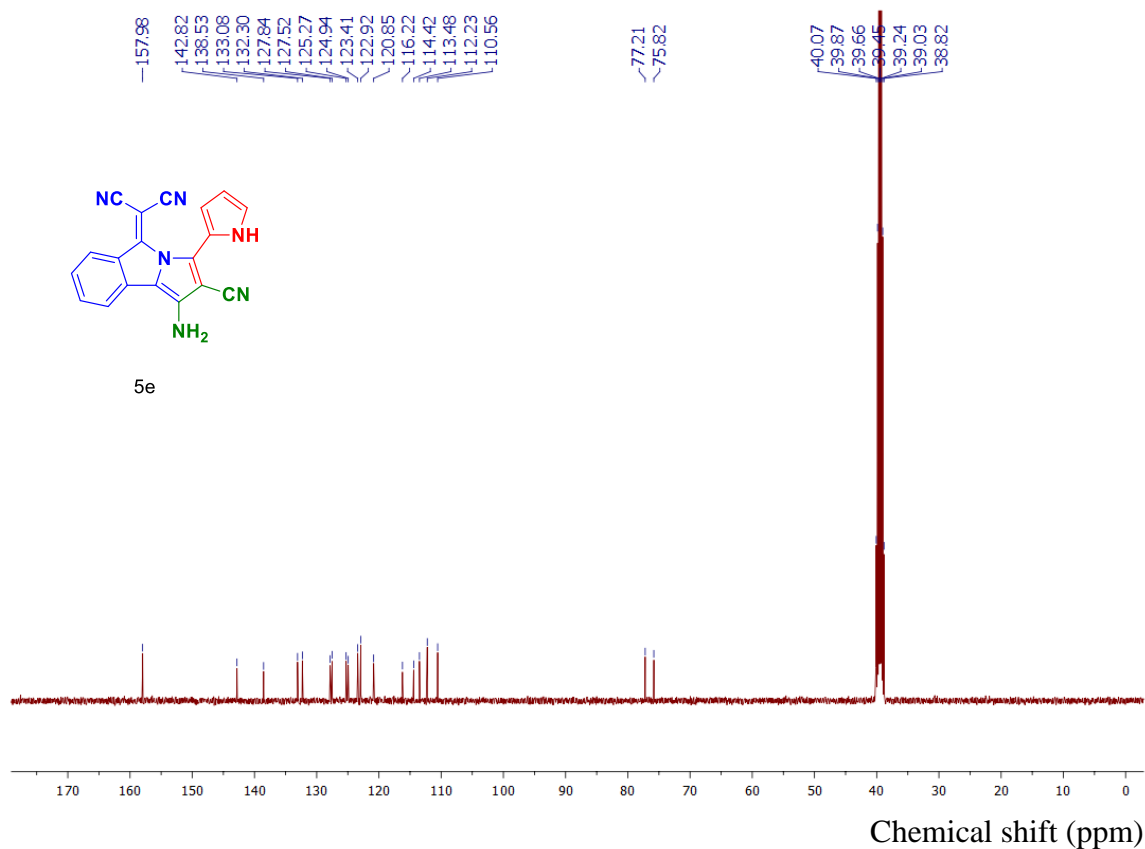
<sup>13</sup>C NMR Spectra of **5d** (400 MHz, DMSO-*d*<sub>6</sub>)



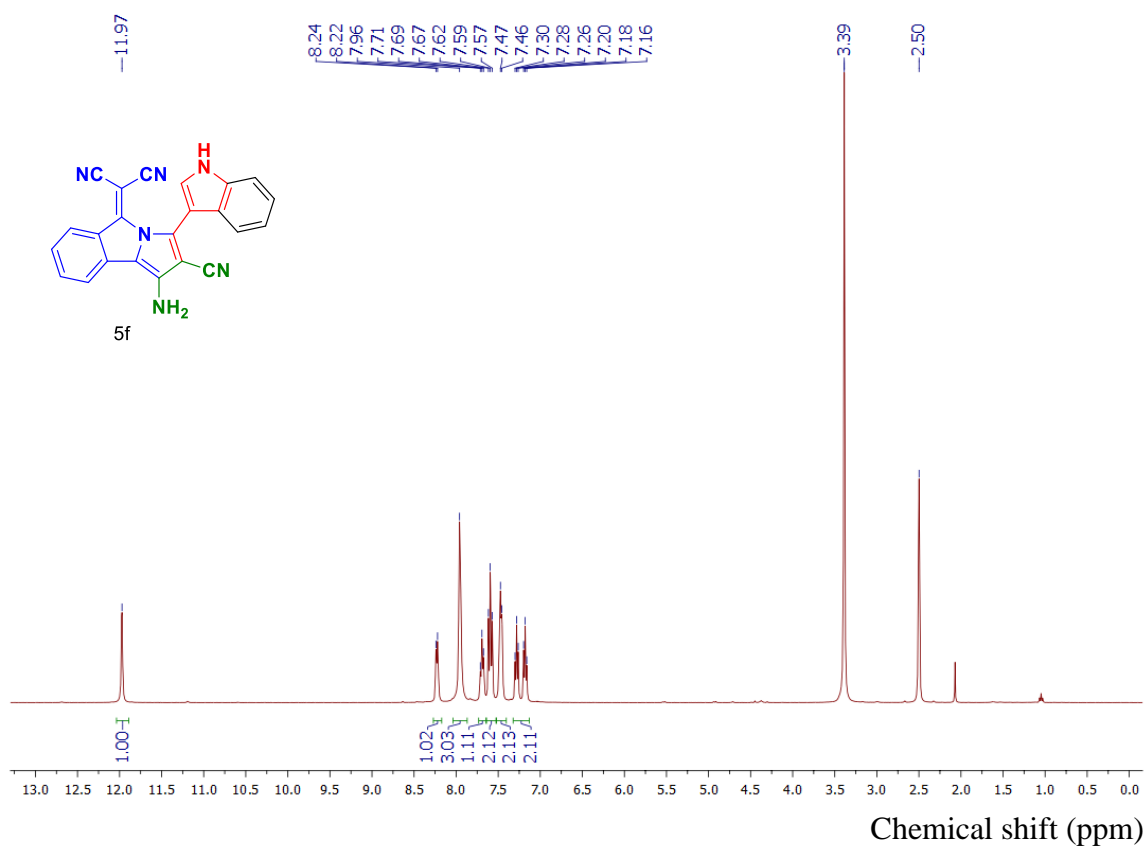
<sup>1</sup>H NMR Spectra of **5e** (400 MHz, DMSO-*d*<sub>6</sub>)



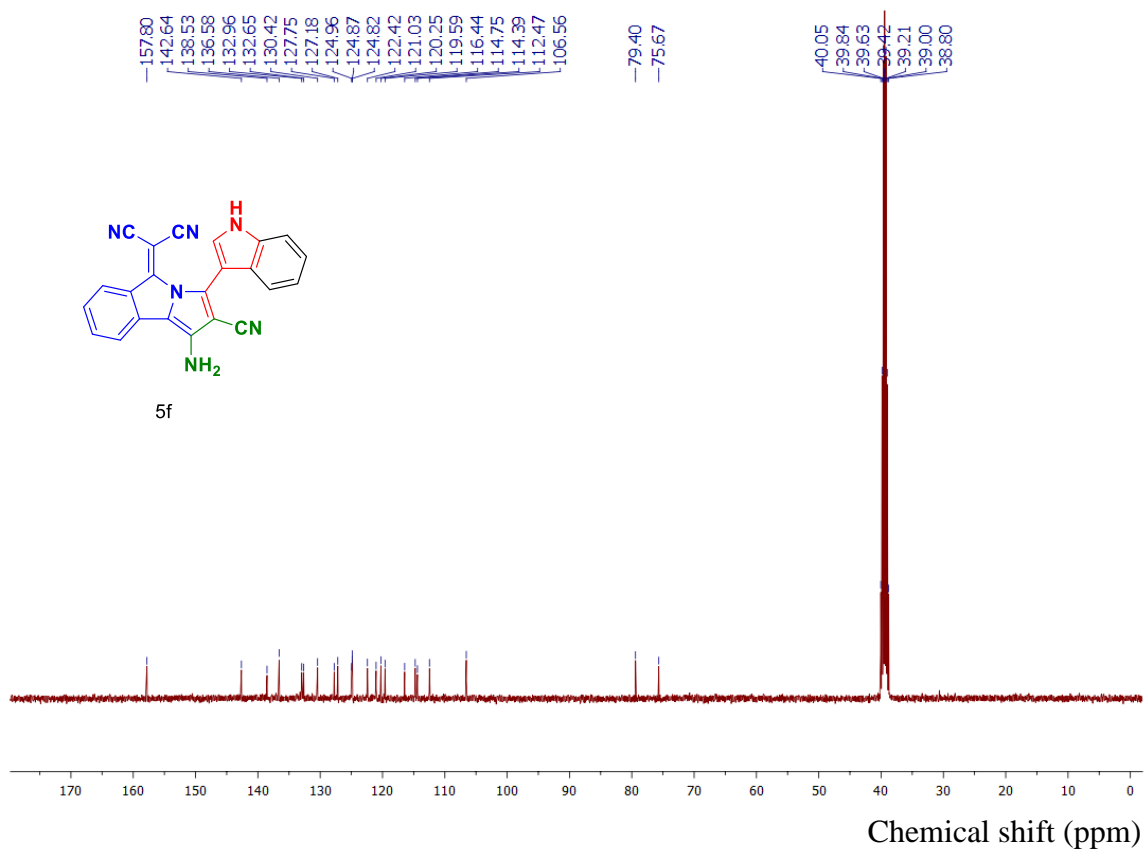
<sup>13</sup>C NMR Spectra of **5e** (400 MHz, DMSO-*d*<sub>6</sub>)



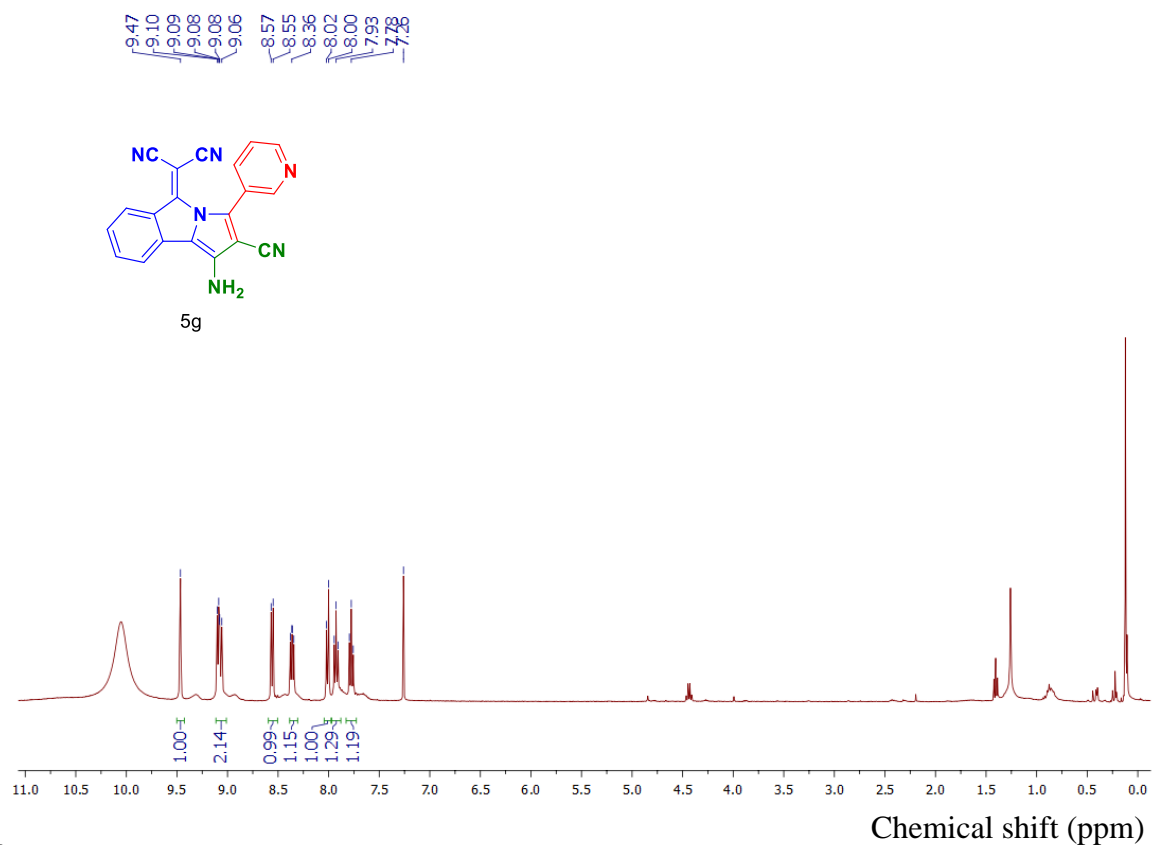
$^1\text{H}$  NMR Spectra of **5f** (400 MHz,  $\text{DMSO-}d_6$ )



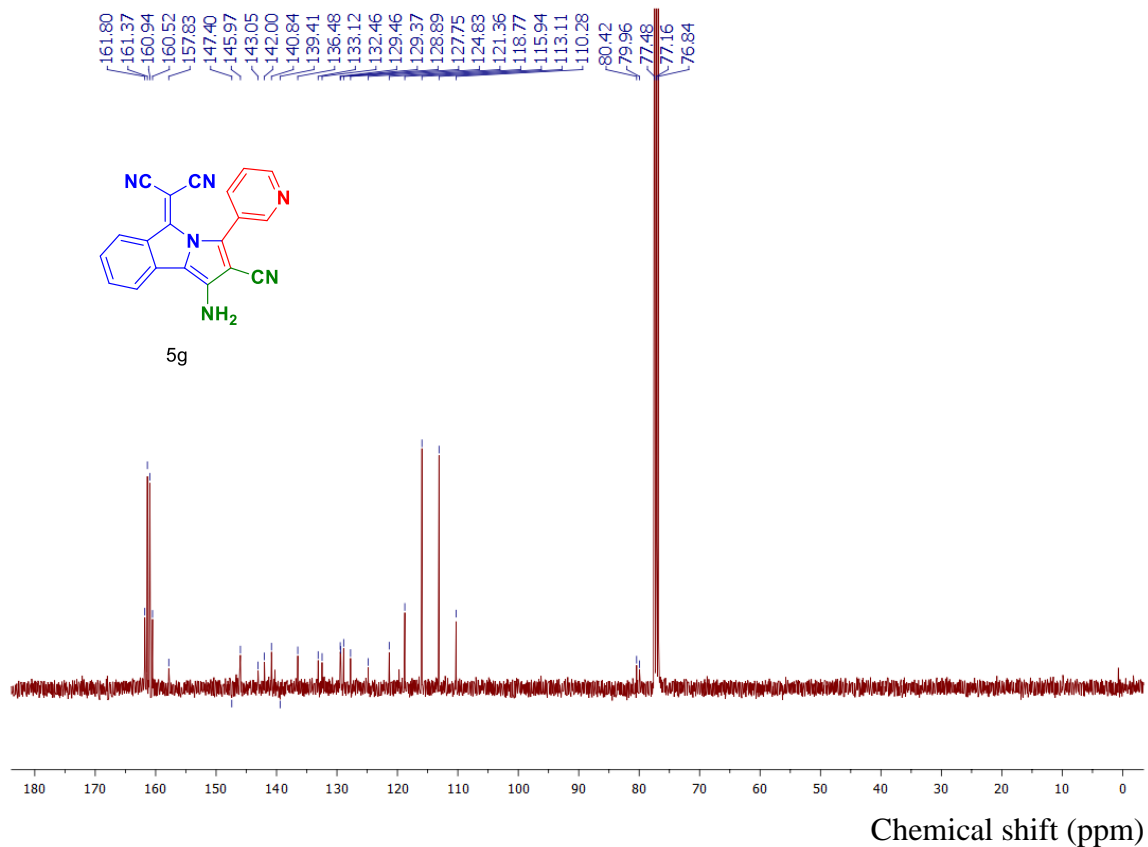
$^{13}\text{C}$  NMR Spectra of **5f** (400 MHz,  $\text{DMSO-}d_6$ )



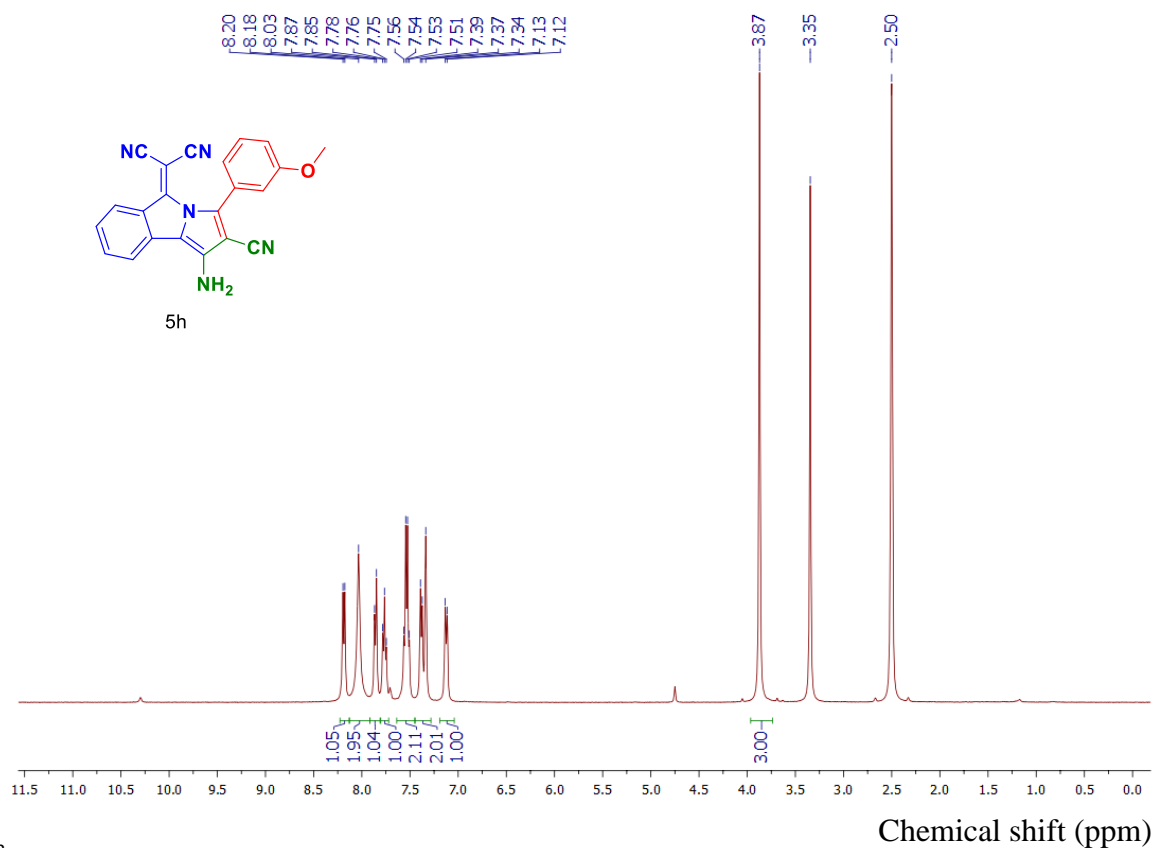
<sup>1</sup>H NMR Spectra of **5g** (400 MHz, CDCl<sub>3</sub>/CF<sub>3</sub>COOD)



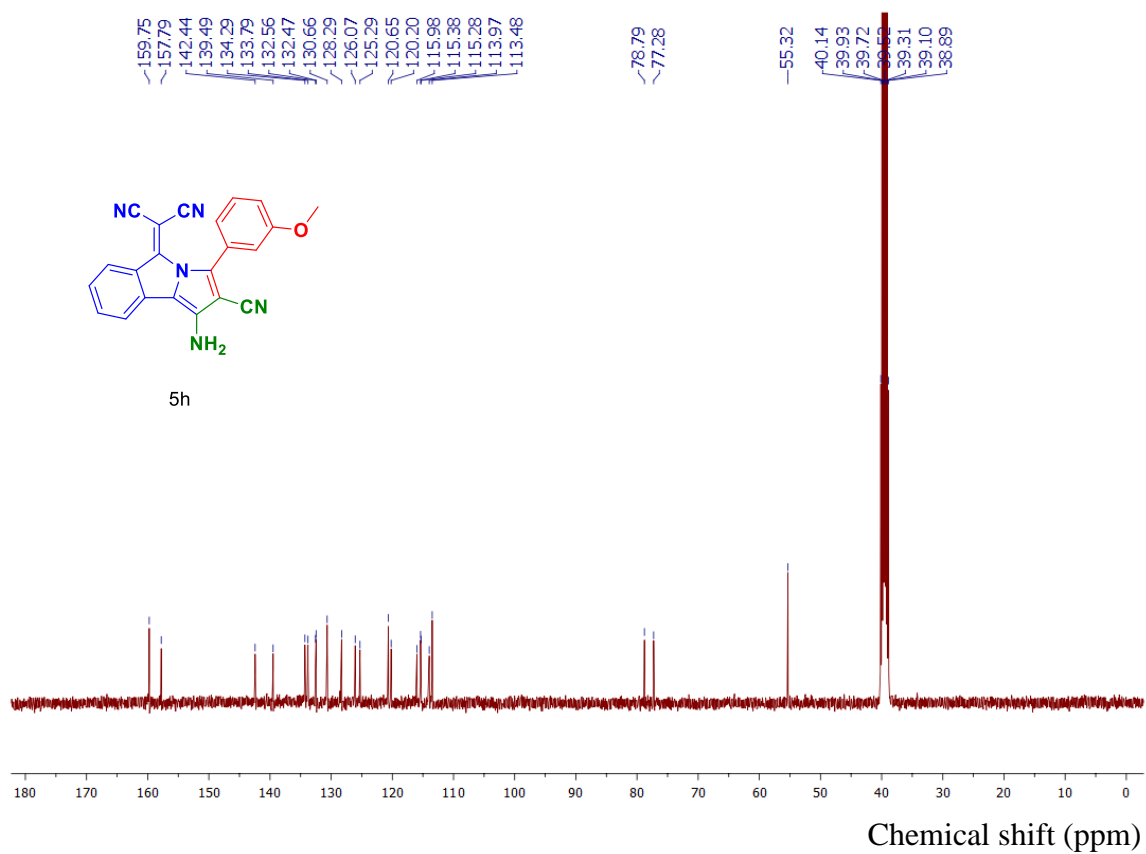
<sup>13</sup>C NMR Spectra of **5g** (400 MHz, CDCl<sub>3</sub>/CF<sub>3</sub>COOD)



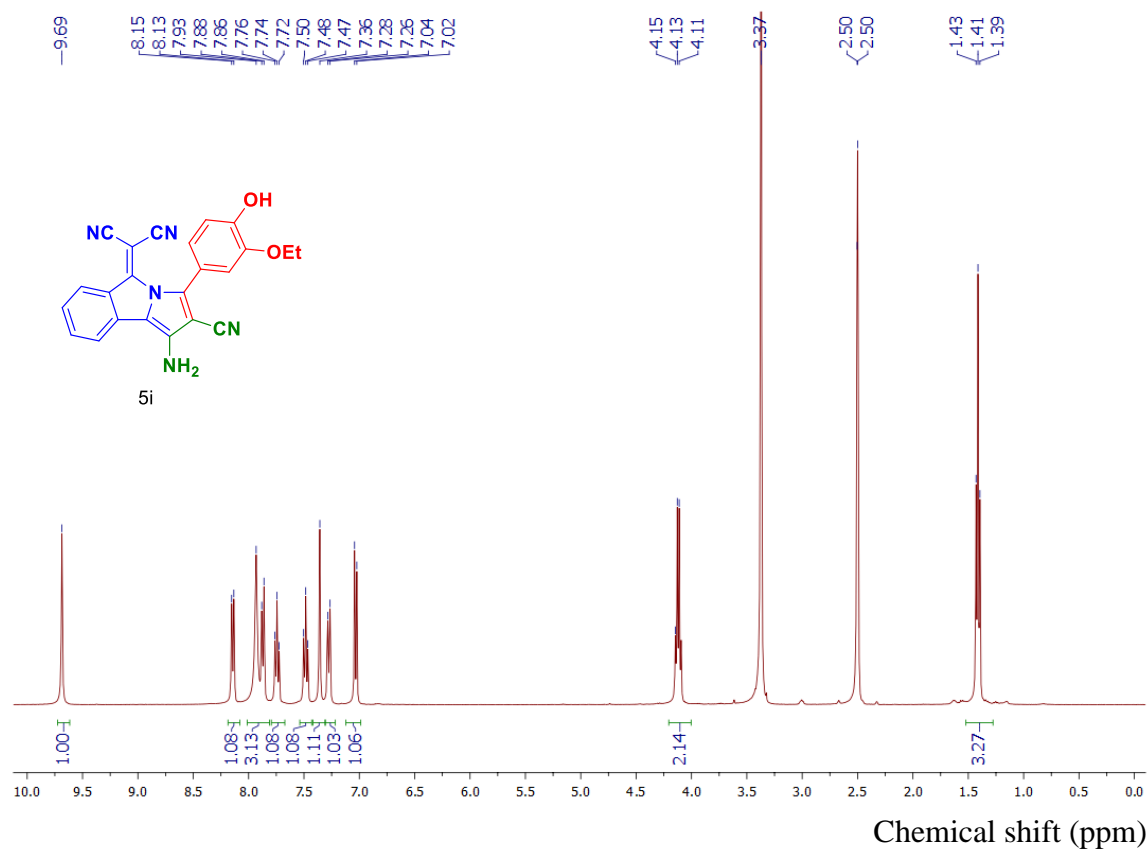
<sup>1</sup>H NMR Spectra of **5h** (400 MHz, DMSO-*d*<sub>6</sub>)



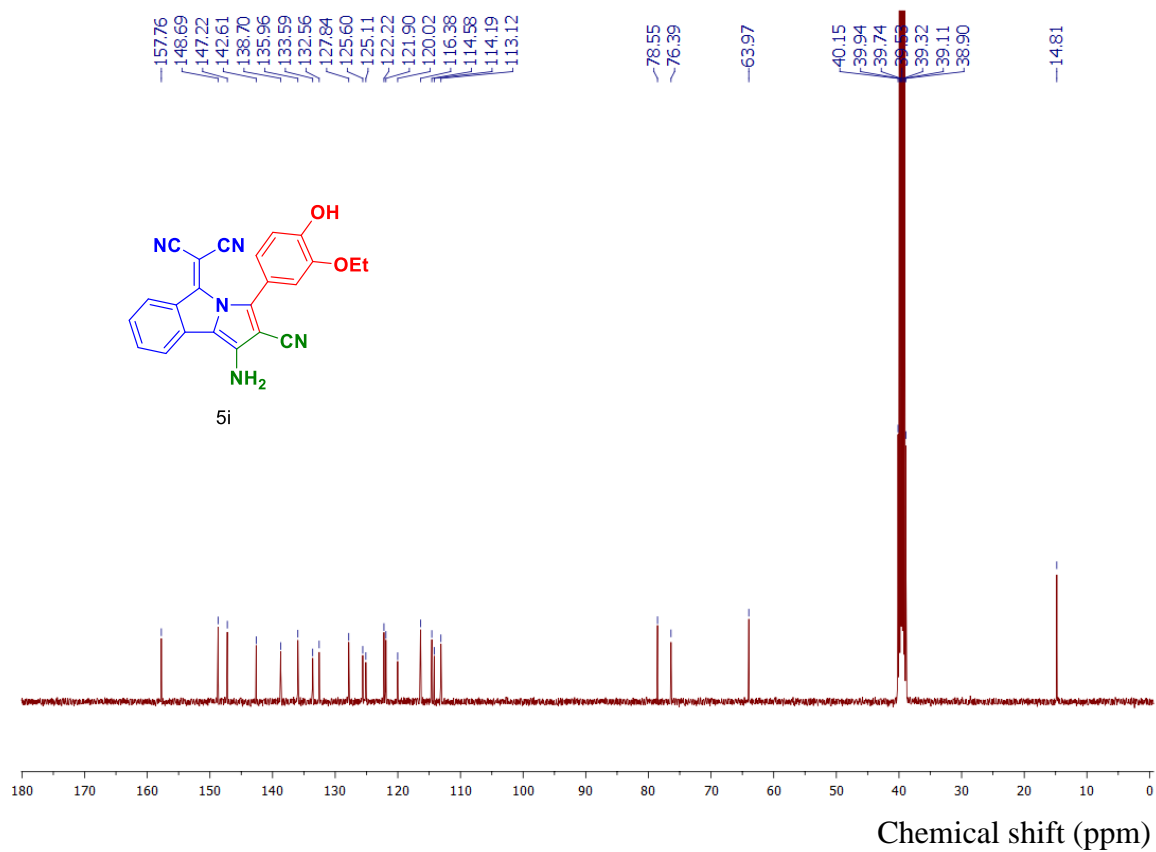
<sup>13</sup>C NMR Spectra of **5h** (400 MHz, DMSO-*d*<sub>6</sub>)



<sup>1</sup>H NMR Spectra of **5i** (400 MHz, DMSO-*d*<sub>6</sub>)

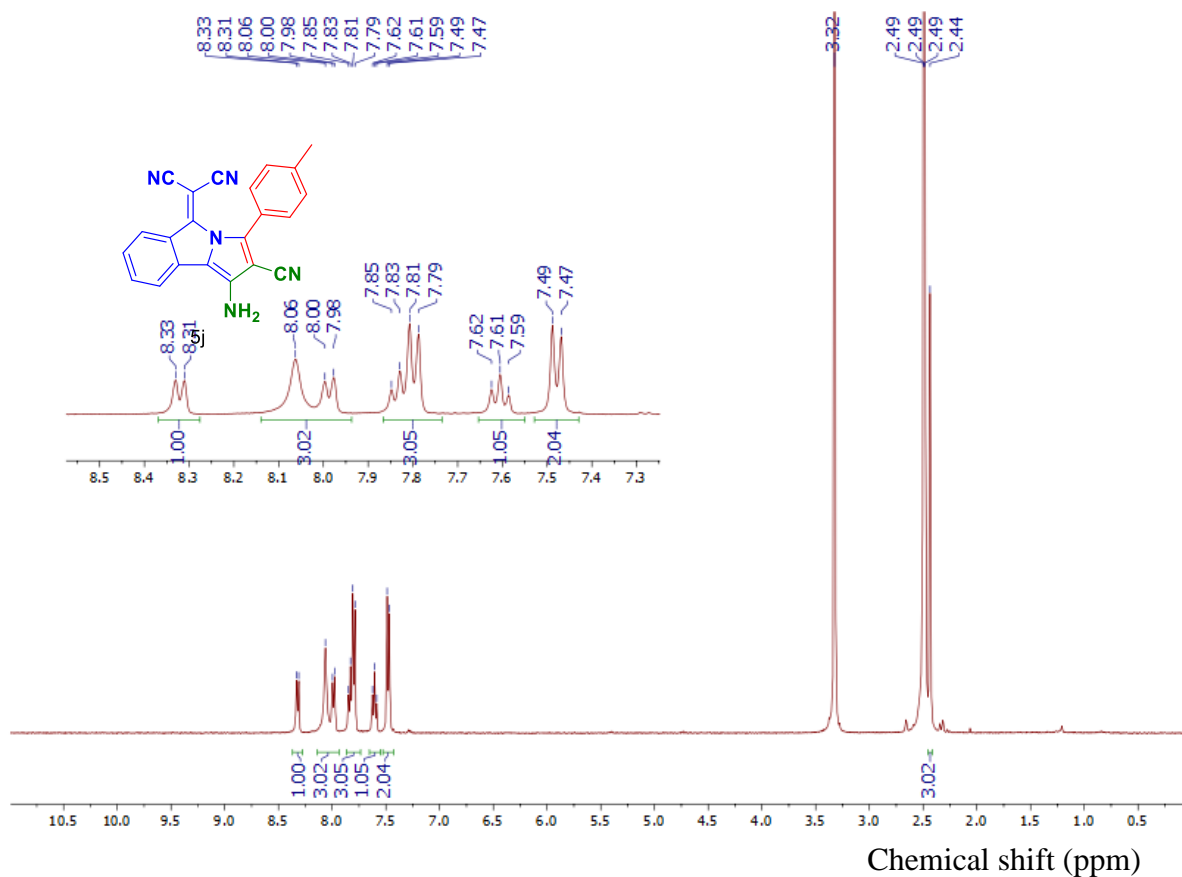


<sup>13</sup>C NMR Spectra of **5i** (400 MHz, DMSO-*d*<sub>6</sub>)

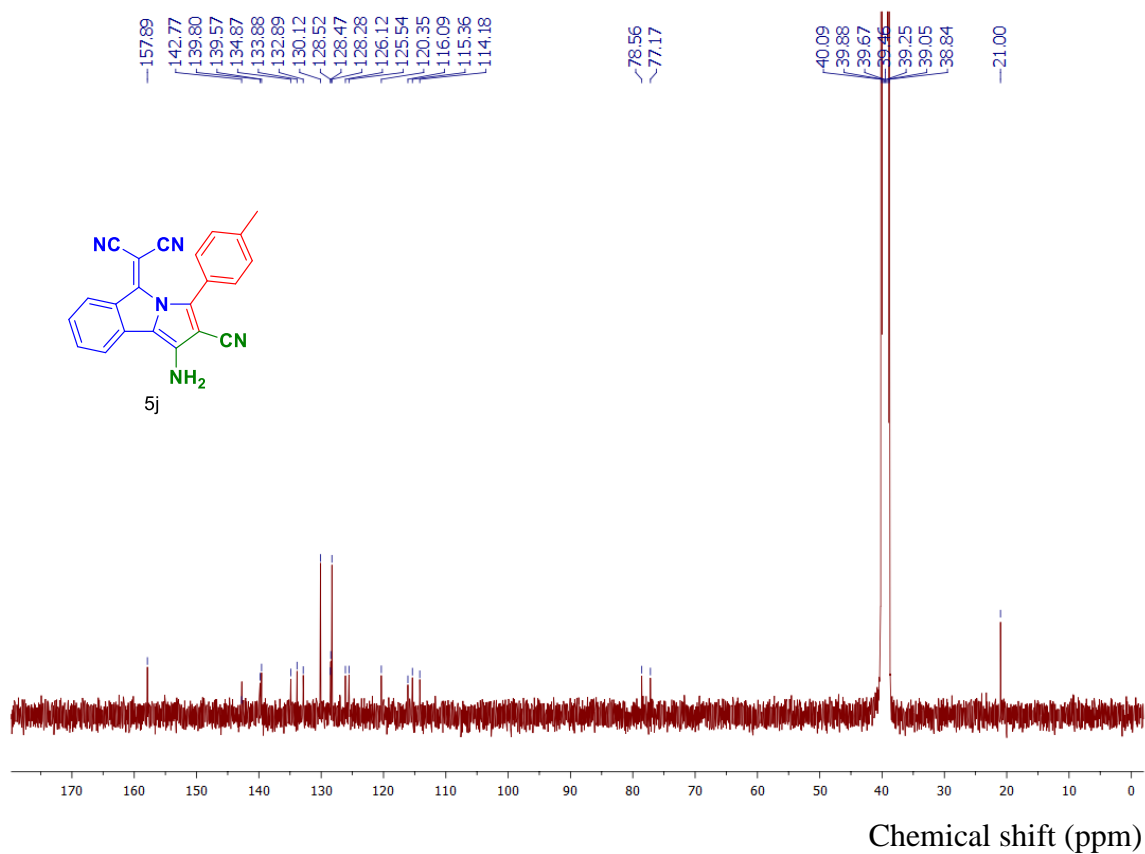




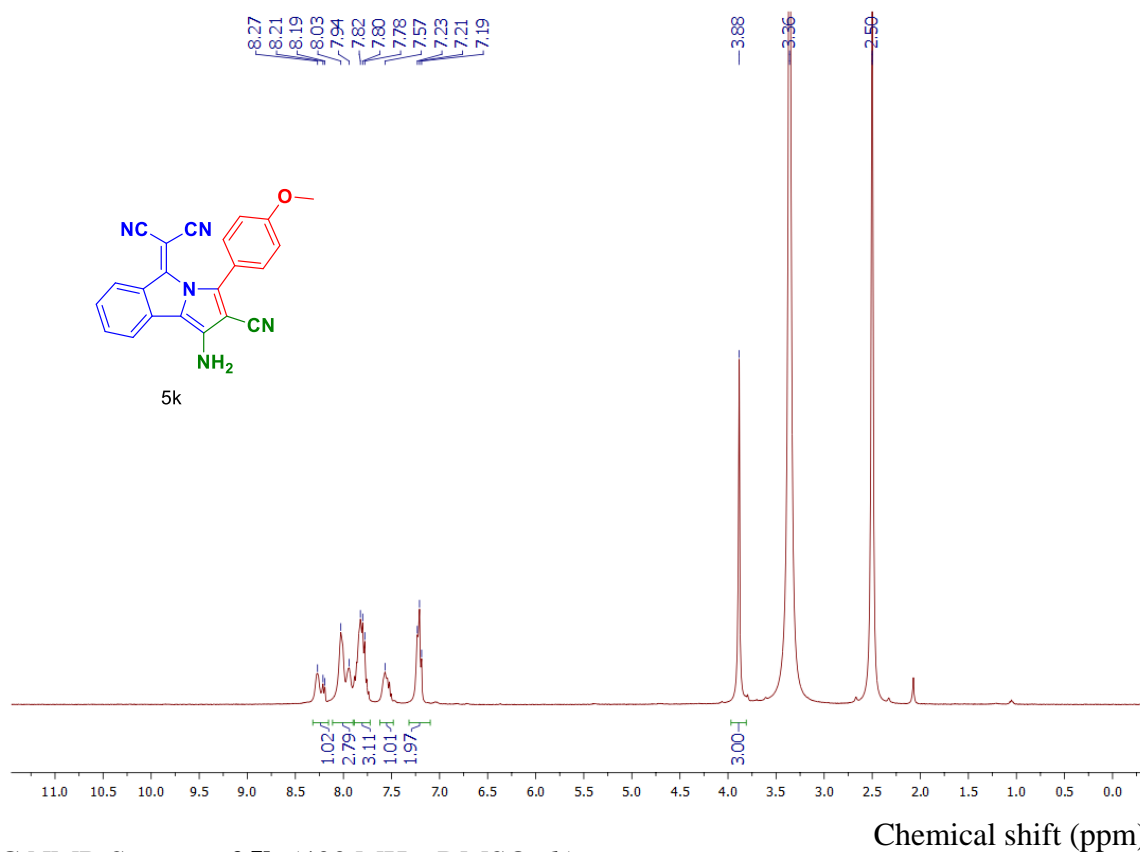
<sup>1</sup>H NMR Spectra of **5j** (400 MHz, DMSO-*d*<sub>6</sub>)



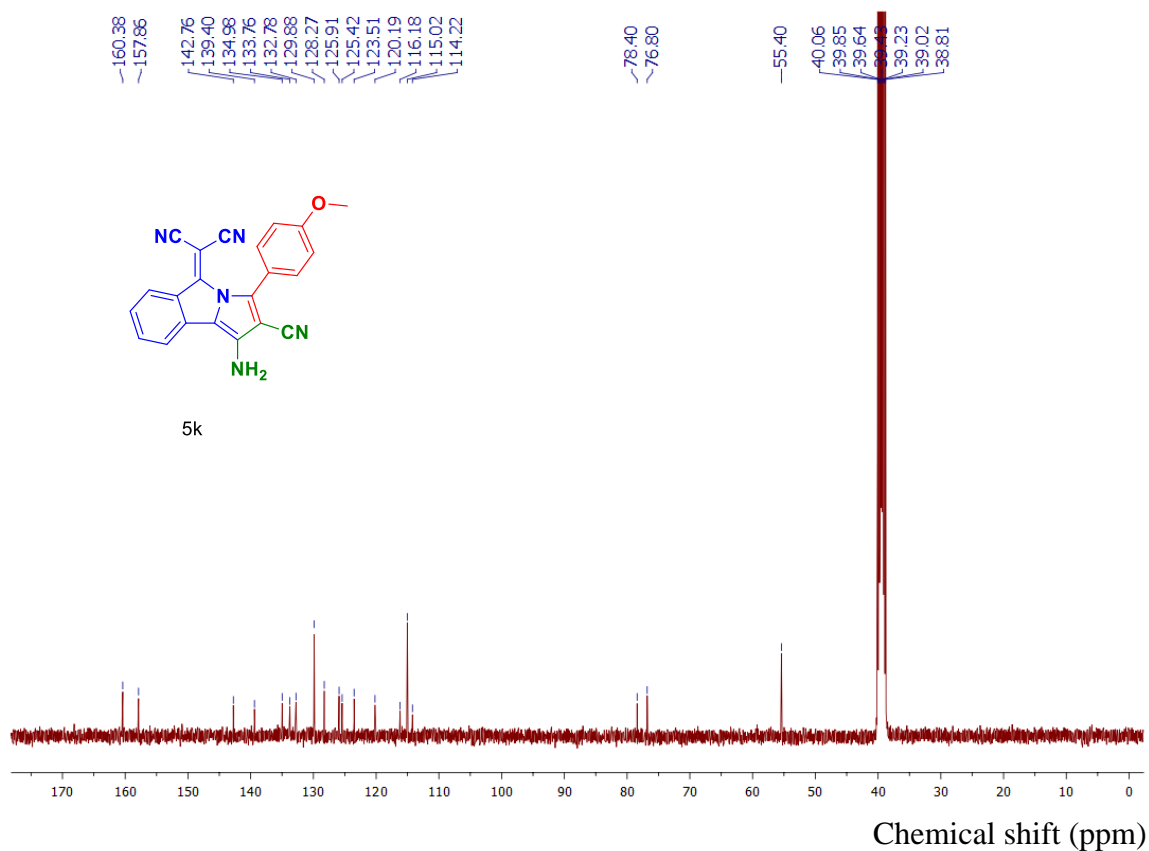
<sup>13</sup>C NMR Spectra of **5j** (400 MHz, DMSO-*d*<sub>6</sub>)



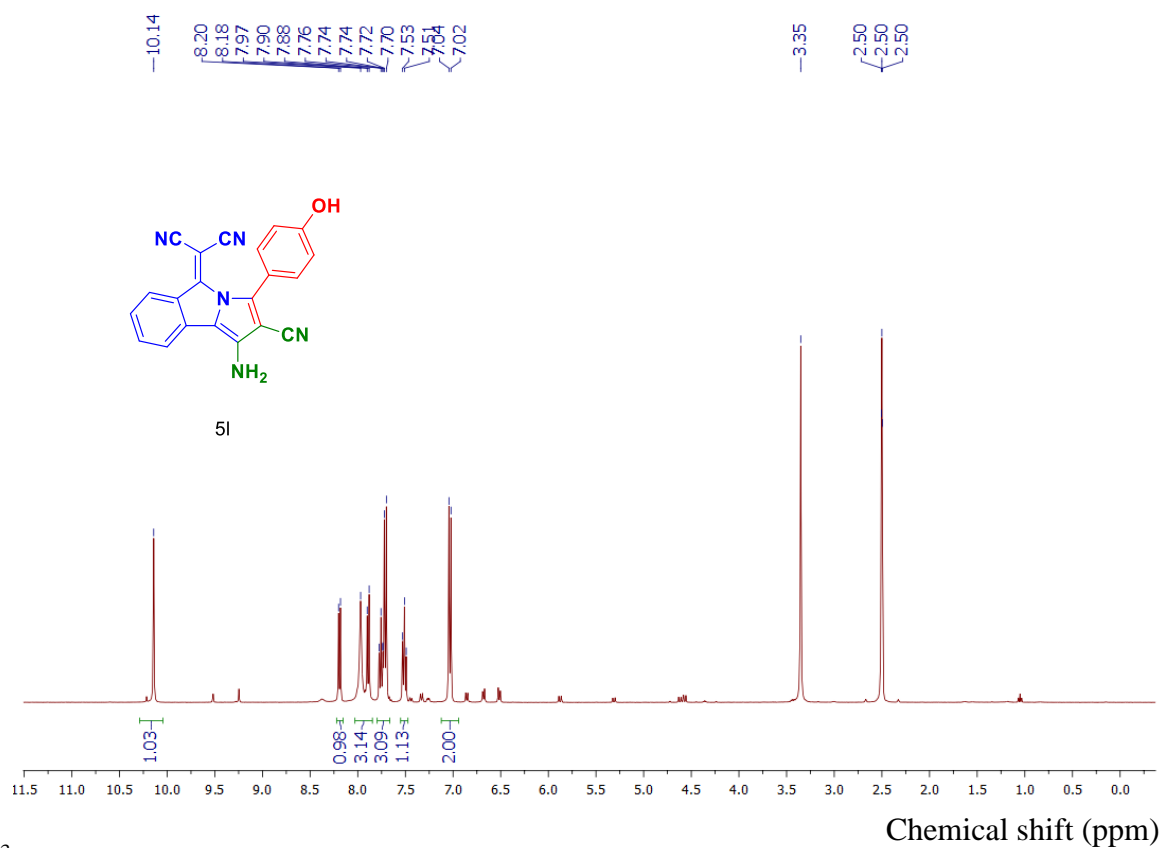
<sup>1</sup>H NMR Spectra of **5k** (400 MHz, DMSO-*d*<sub>6</sub>)



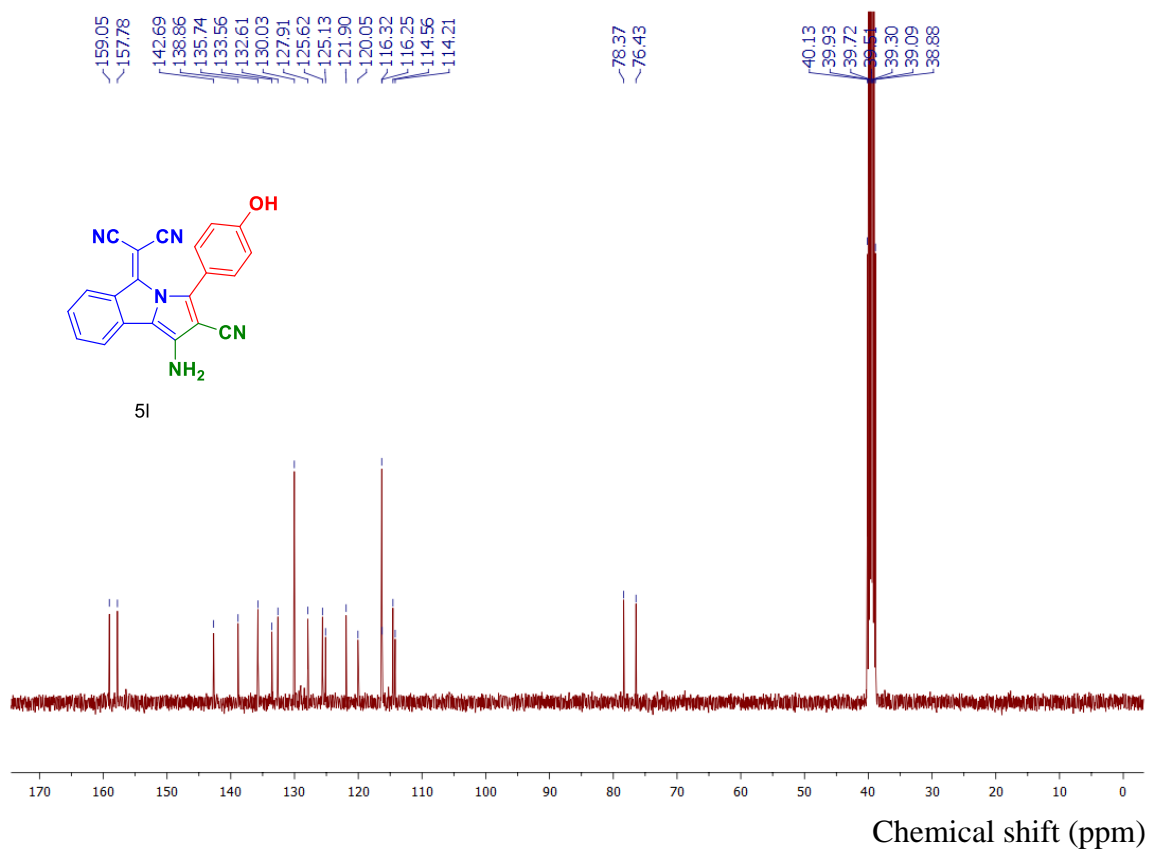
<sup>13</sup>C NMR Spectra of **5k** (400 MHz, DMSO-*d*<sub>6</sub>)



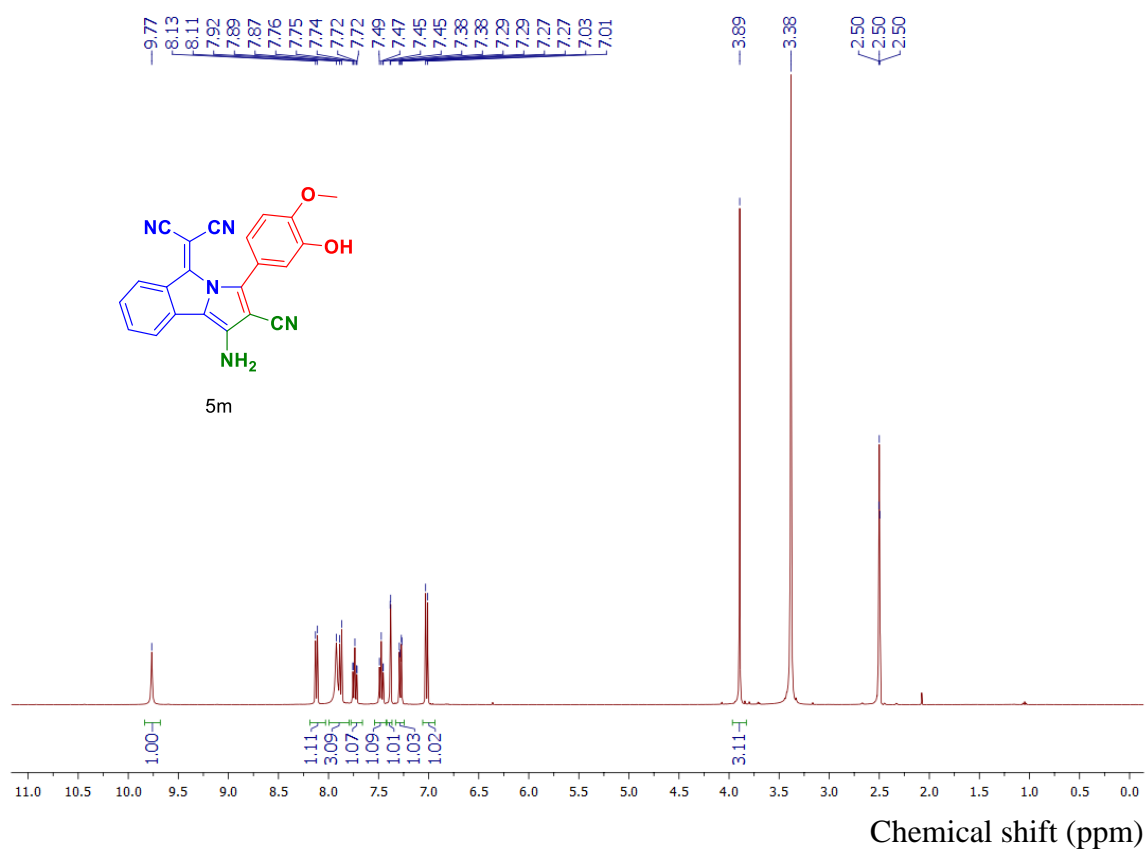
<sup>1</sup>H NMR Spectra of **5l** (400 MHz, DMSO-*d*<sub>6</sub>)



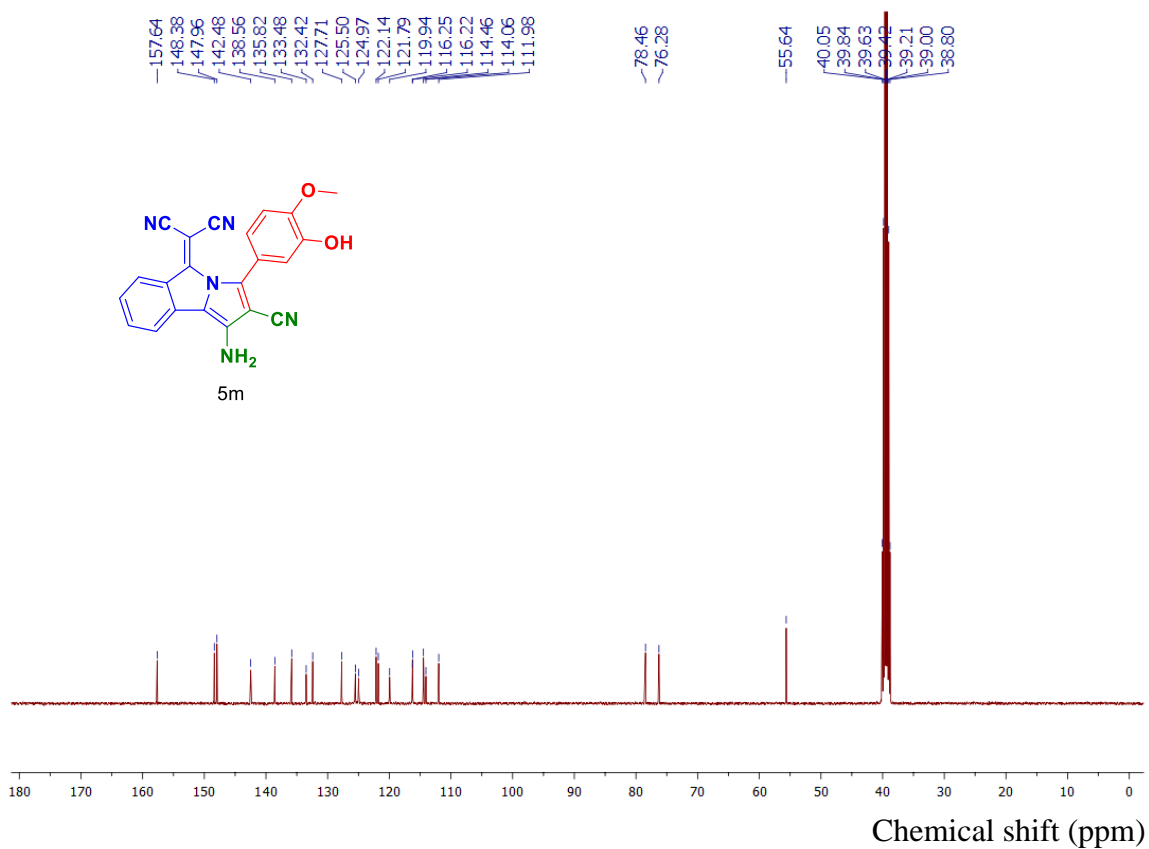
<sup>13</sup>C NMR Spectra of **5l** (400 MHz, DMSO-*d*<sub>6</sub>)



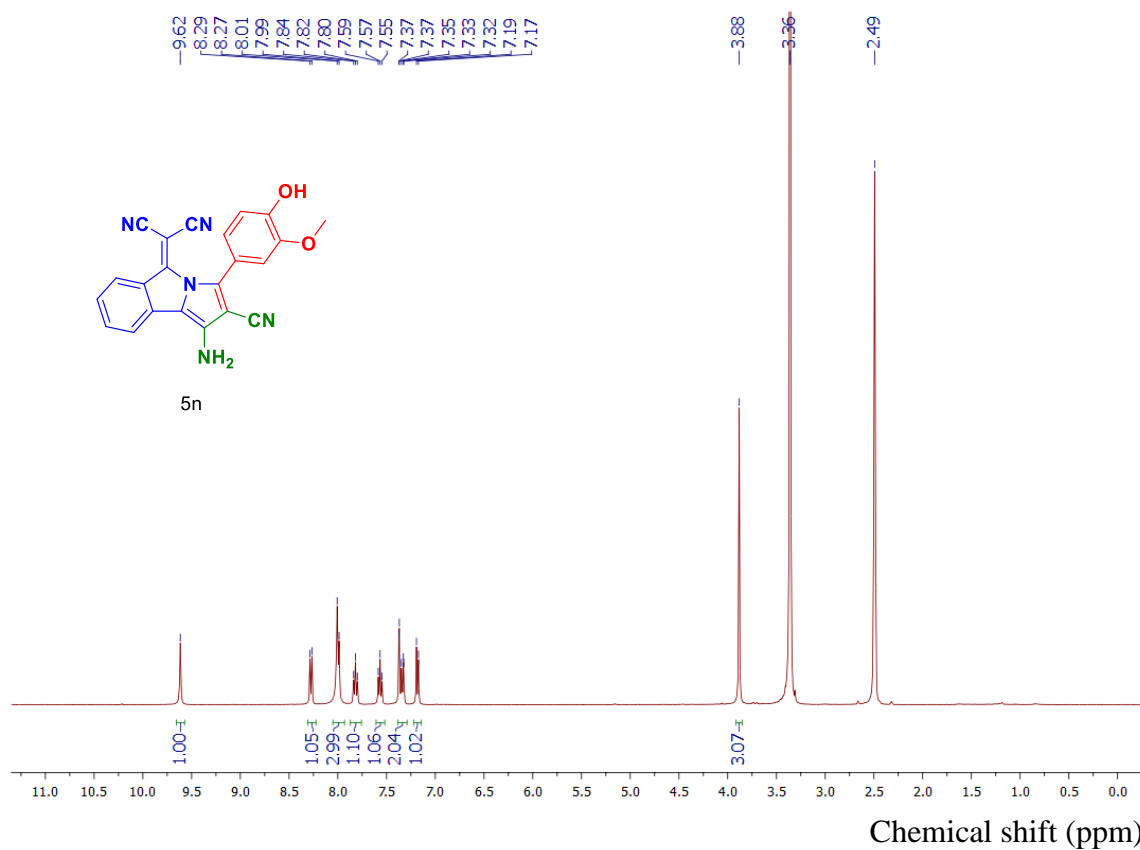
<sup>1</sup>H NMR Spectra of **5m** (400 MHz, DMSO-*d*<sub>6</sub>)



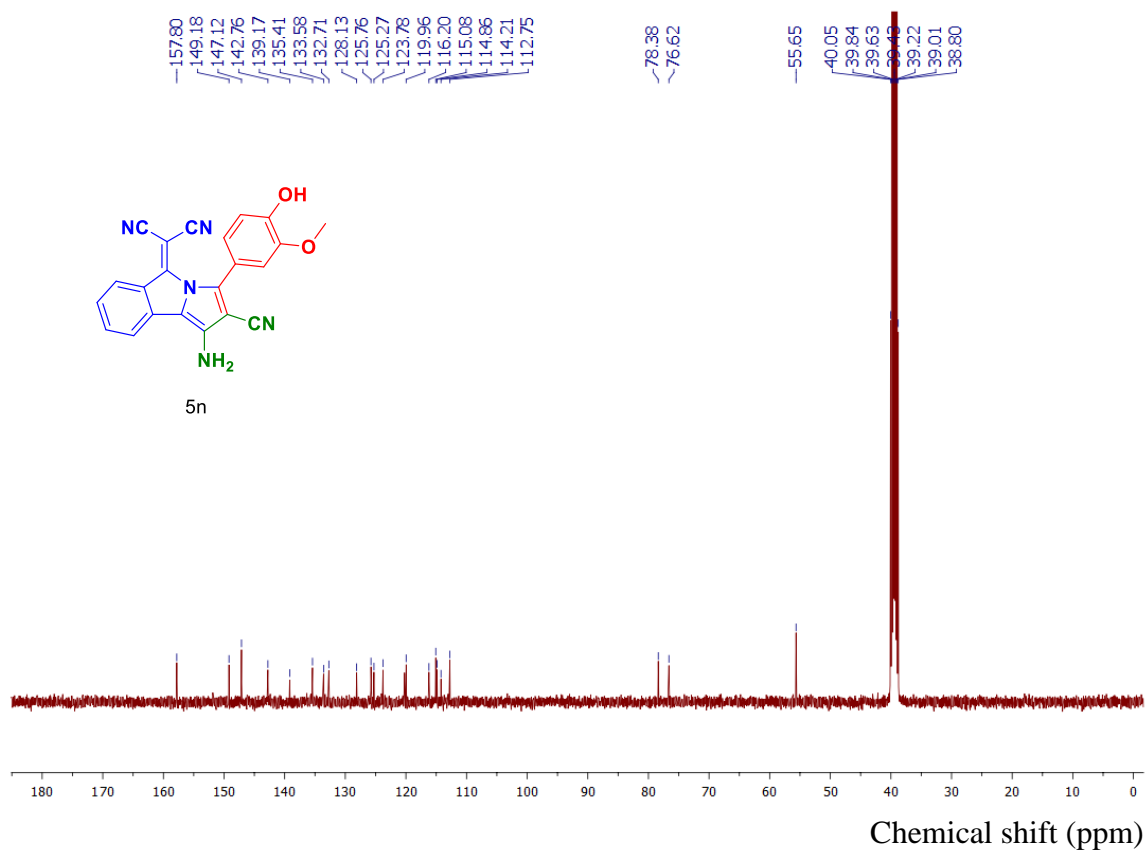
<sup>13</sup>C NMR Spectra of **5m** (400 MHz, DMSO-*d*<sub>6</sub>)



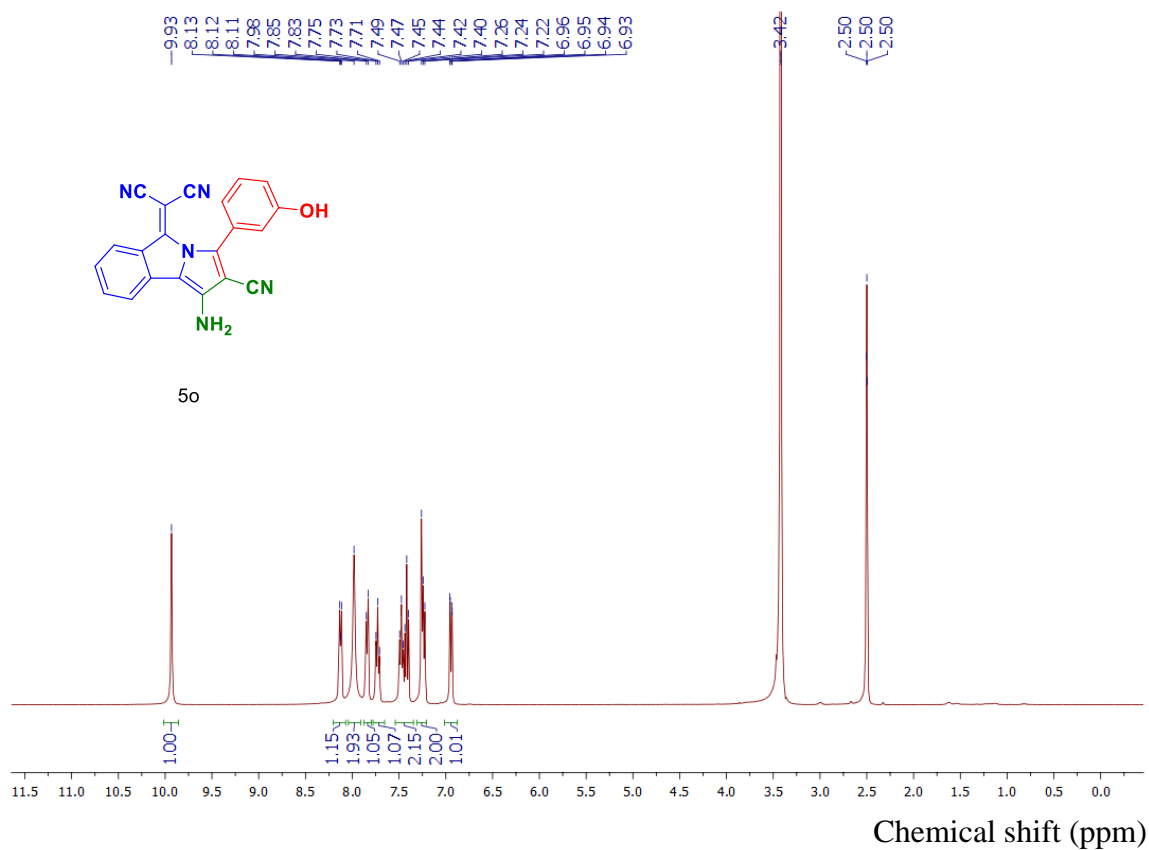
$^1\text{H}$  NMR Spectra of **5n** (400 MHz,  $\text{DMSO-}d_6$ )



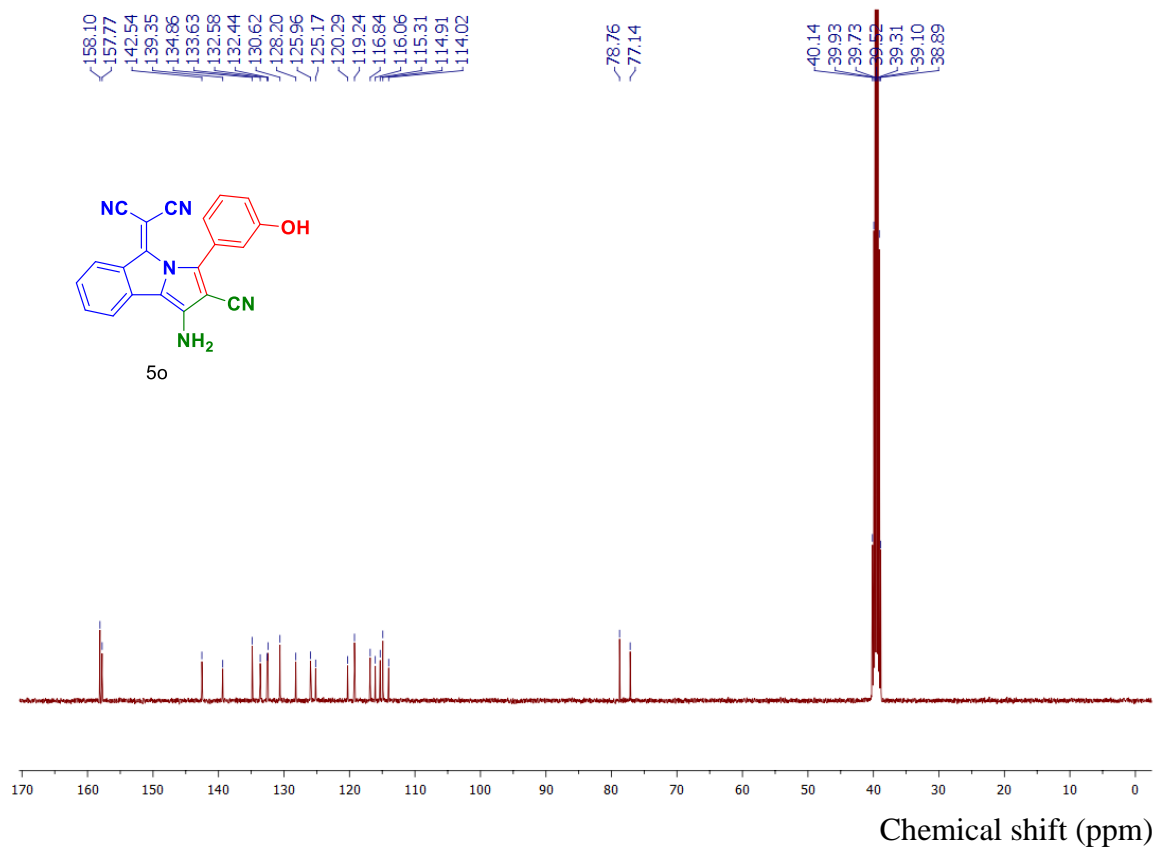
$^{13}\text{C}$  NMR Spectra of **5n** (400 MHz,  $\text{DMSO-}d_6$ )



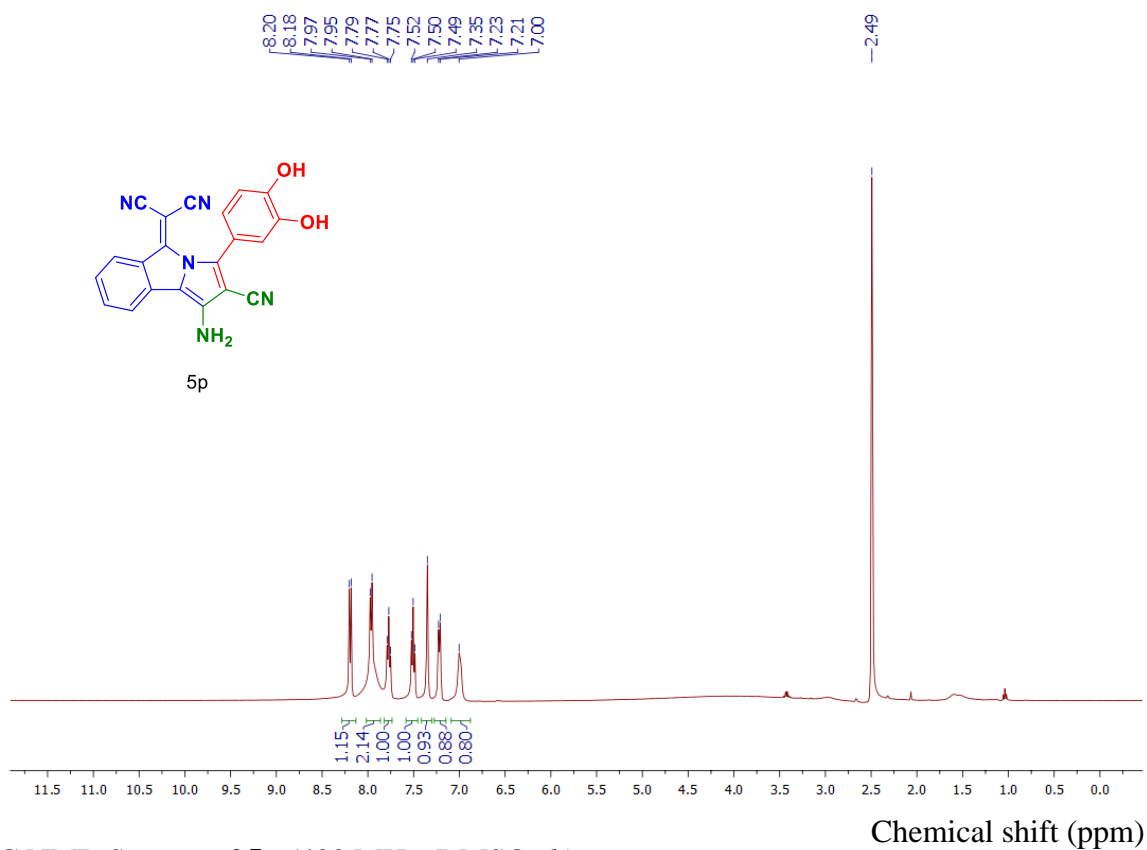
<sup>1</sup>H NMR Spectra of **5o** (400 MHz, DMSO-*d*<sub>6</sub>)



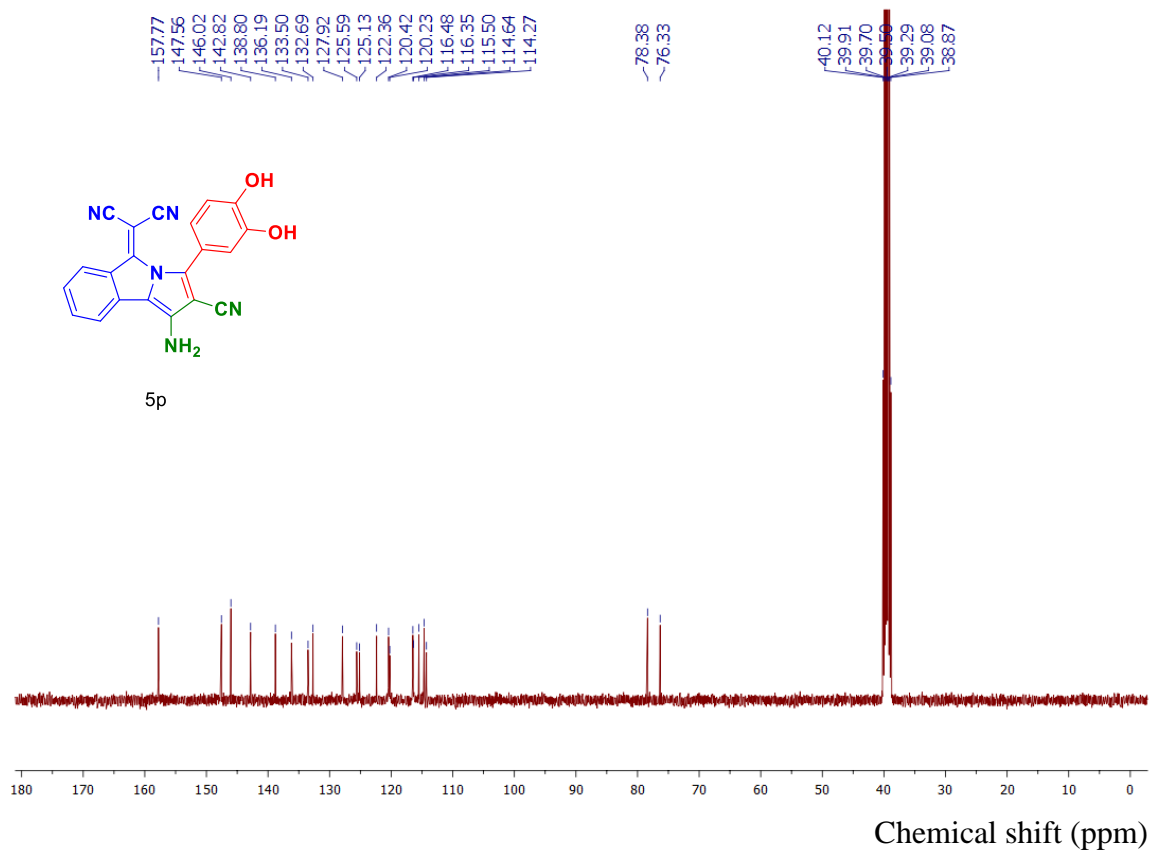
<sup>13</sup>C NMR Spectra of **5o** (400 MHz, DMSO-*d*<sub>6</sub>)



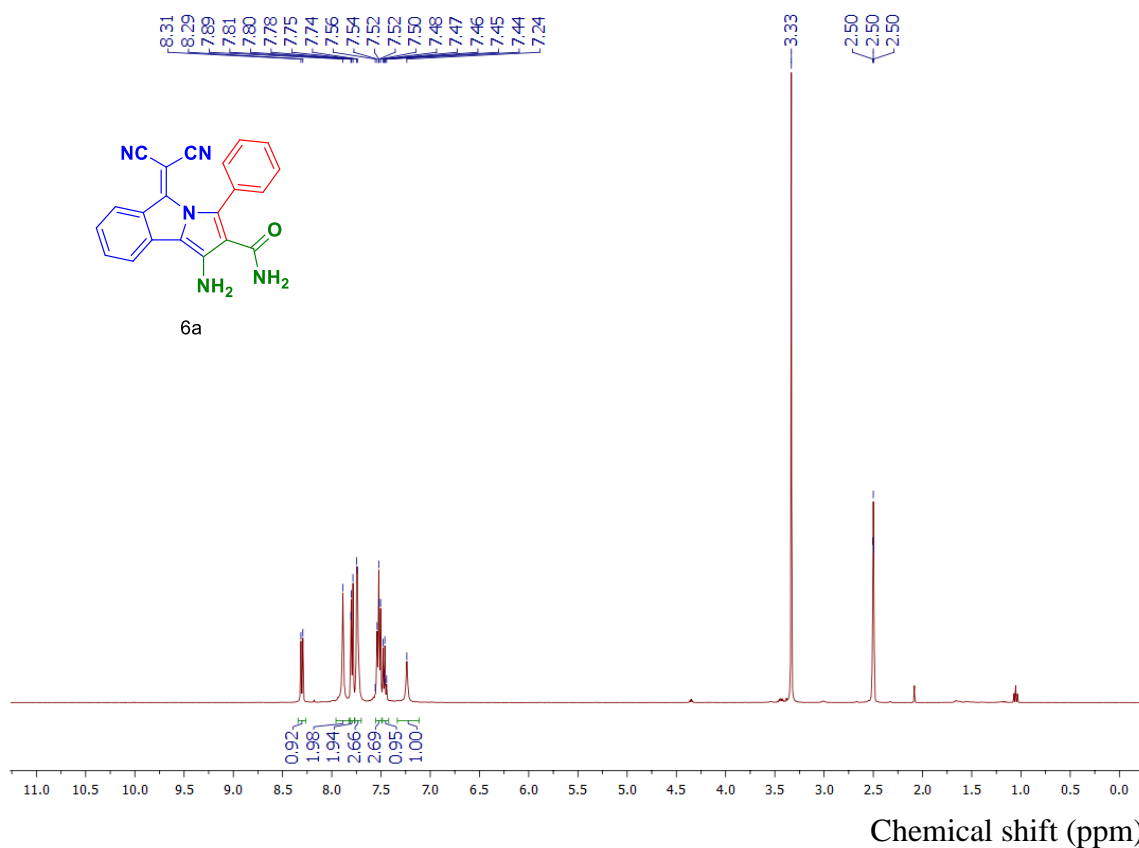
<sup>1</sup>H NMR Spectra of **5p** (400 MHz, DMSO-*d*<sub>6</sub>)



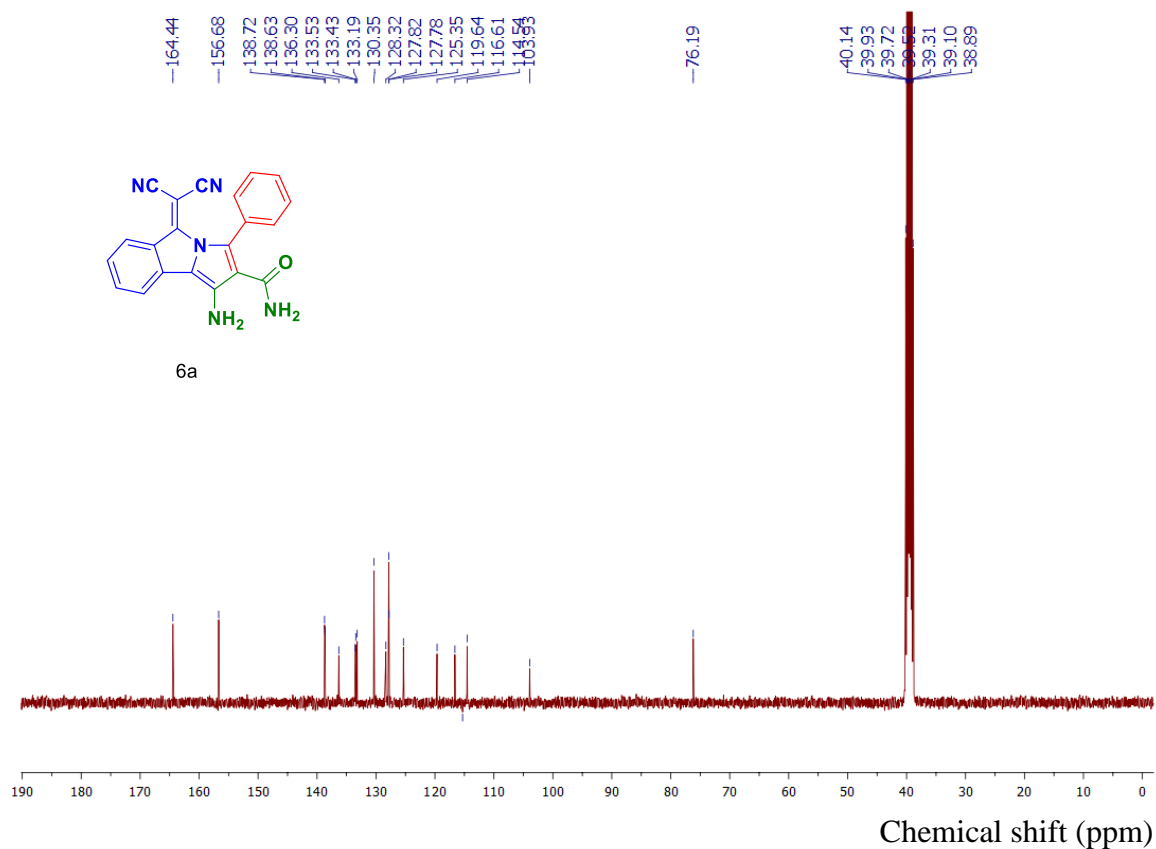
<sup>13</sup>C NMR Spectra of **5p** (400 MHz, DMSO-*d*<sub>6</sub>)



<sup>1</sup>H NMR Spectra of **6a** (400 MHz, DMSO-*d*<sub>6</sub>)

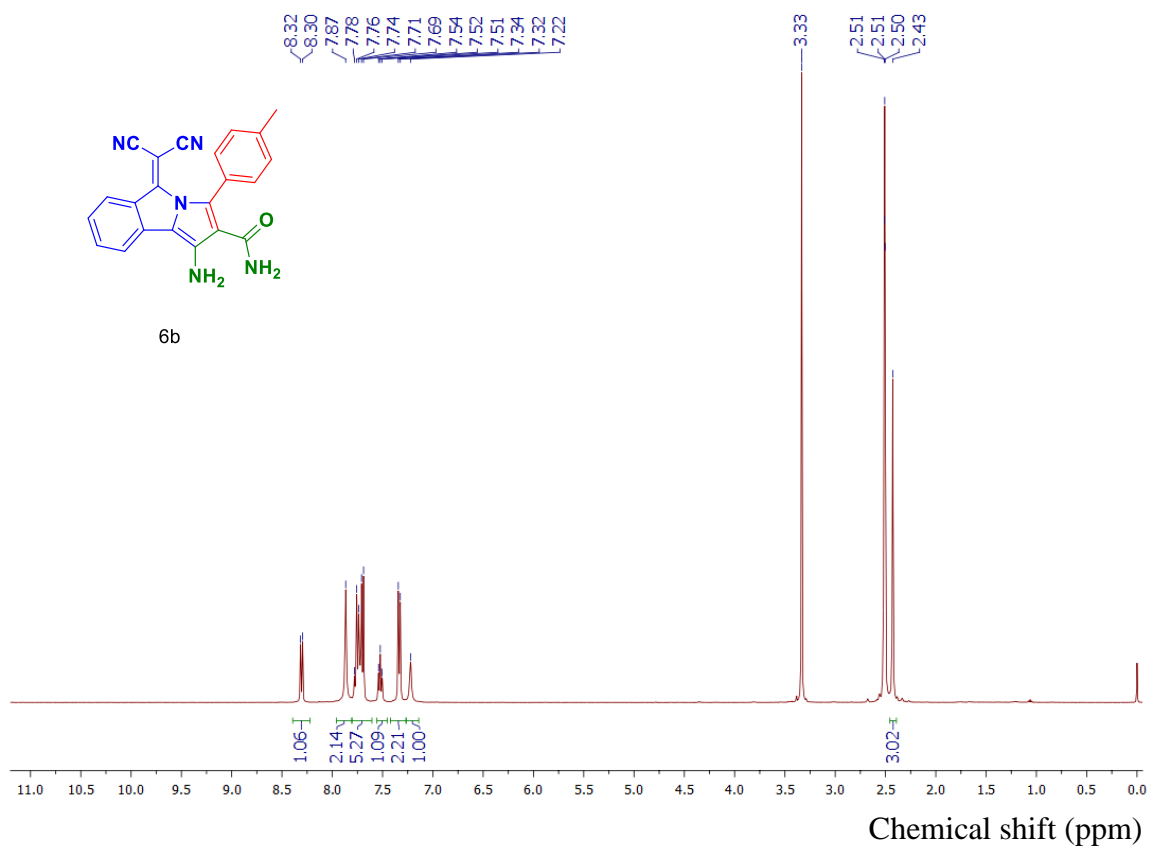


<sup>13</sup>C NMR Spectra of **6a** (400 MHz, DMSO-*d*<sub>6</sub>)

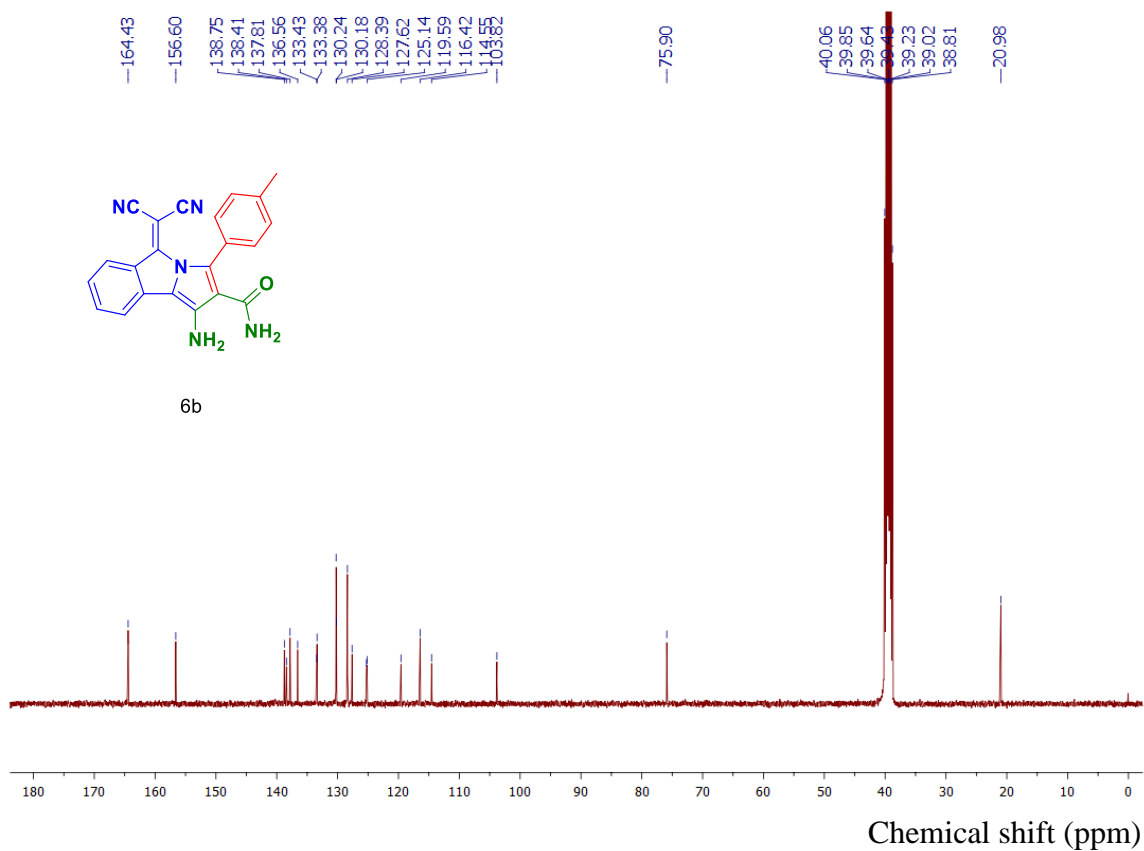




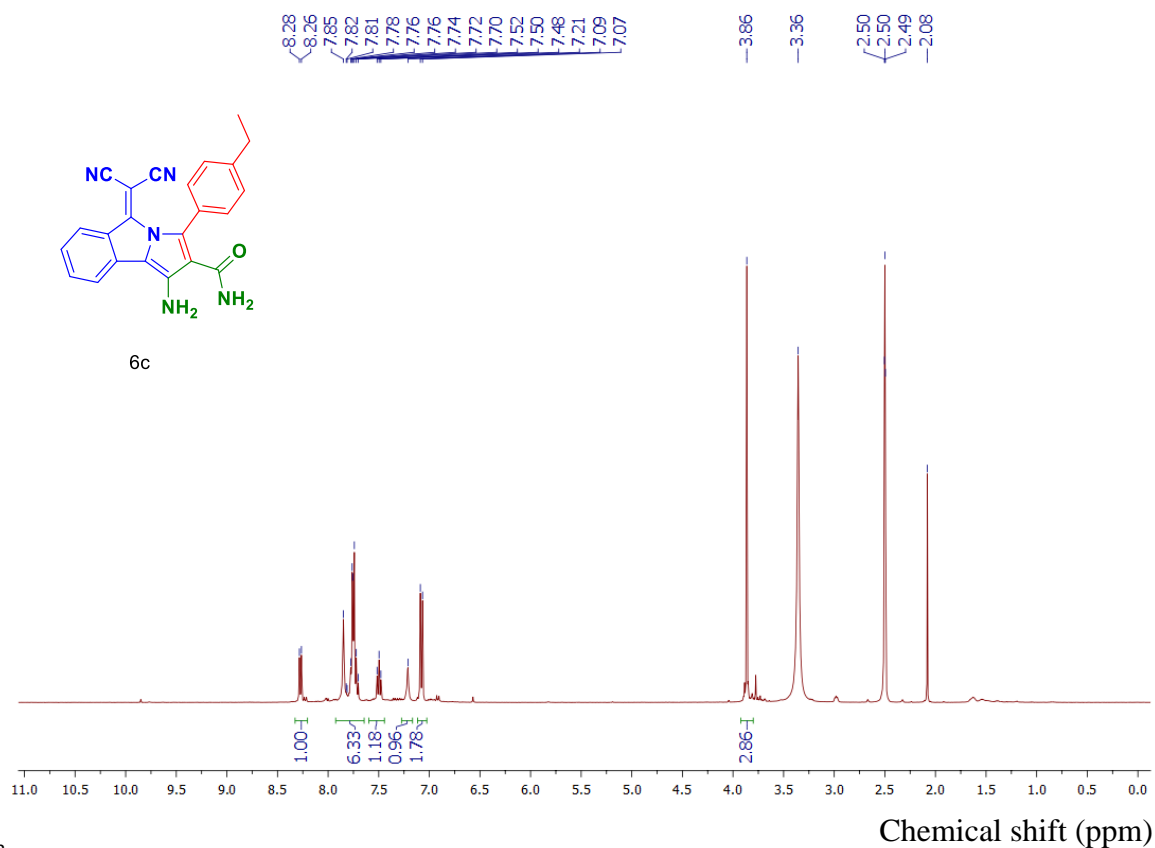
<sup>1</sup>H NMR Spectra of **6b** (400 MHz, DMSO-*d*<sub>6</sub>)



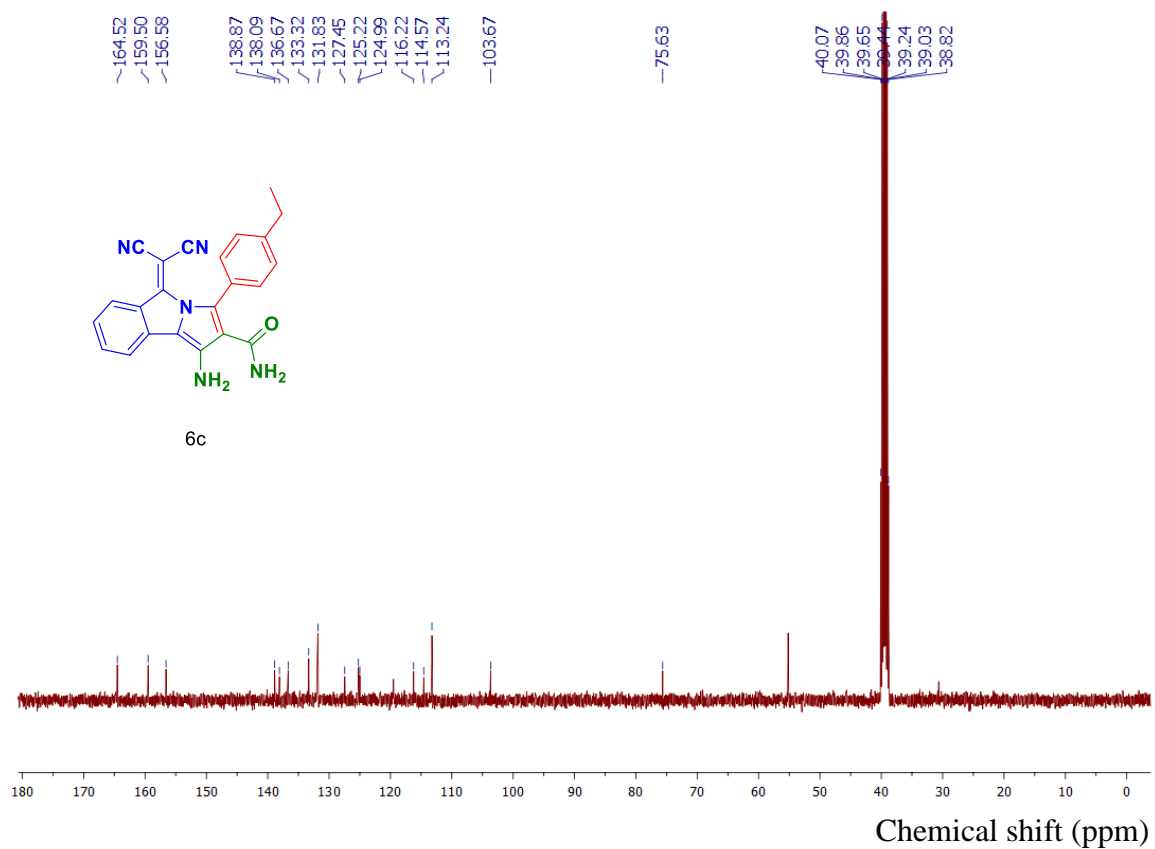
<sup>13</sup>C NMR Spectra of **6b** (400 MHz, DMSO-*d*<sub>6</sub>)



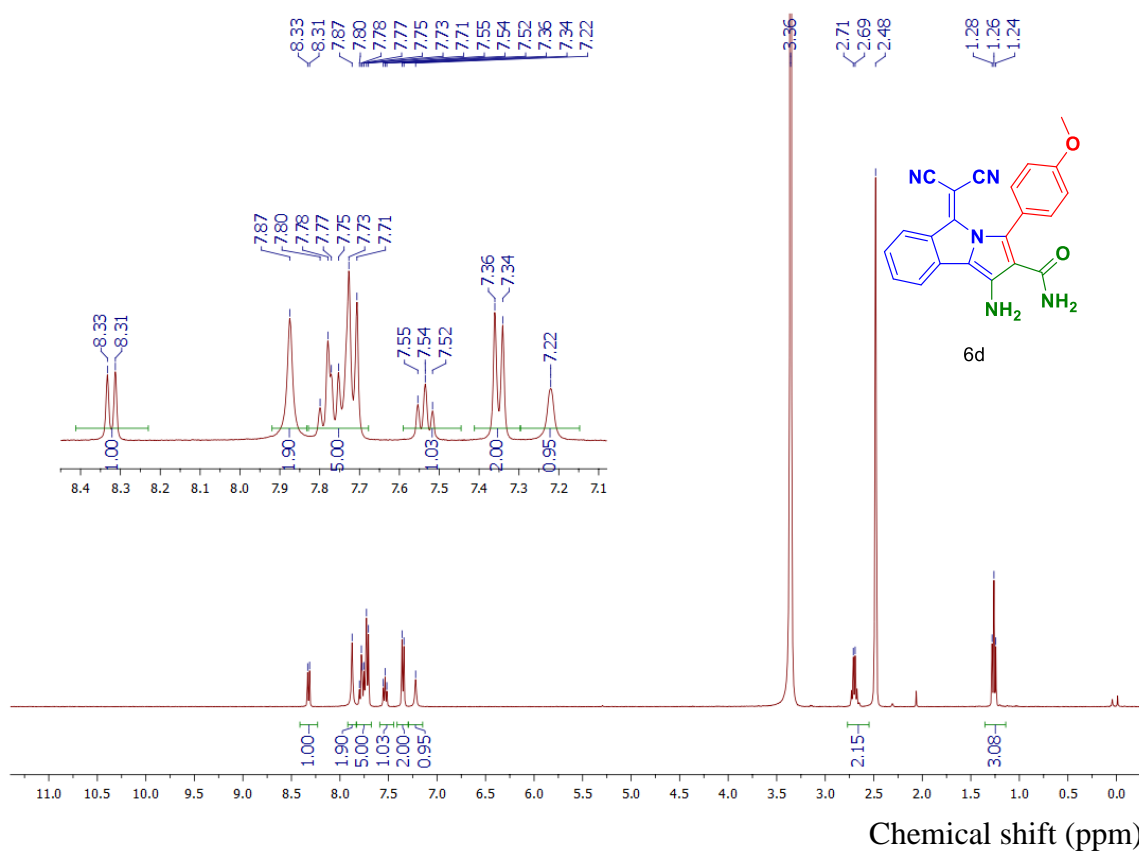
<sup>1</sup>H NMR Spectra of **6c** (400 MHz, DMSO-*d*<sub>6</sub>)



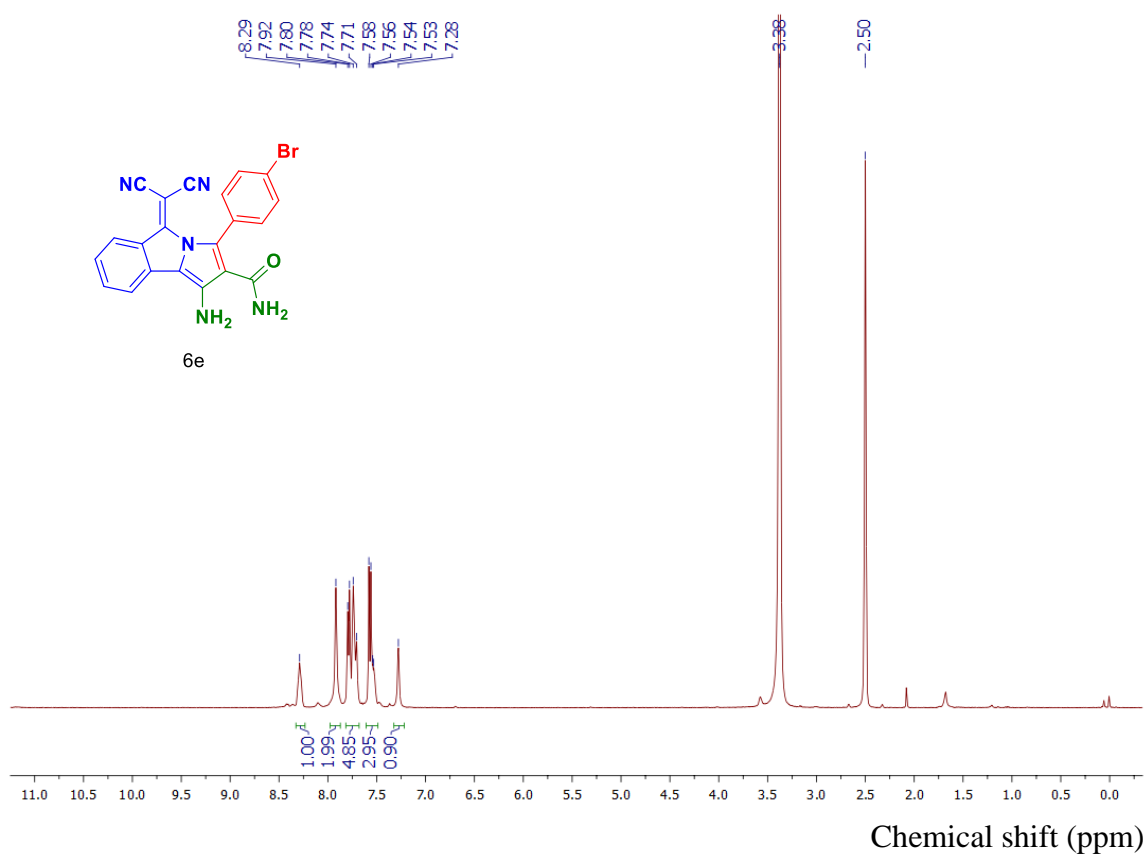
<sup>13</sup>C NMR Spectra of **6c** (400 MHz, DMSO-*d*<sub>6</sub>)



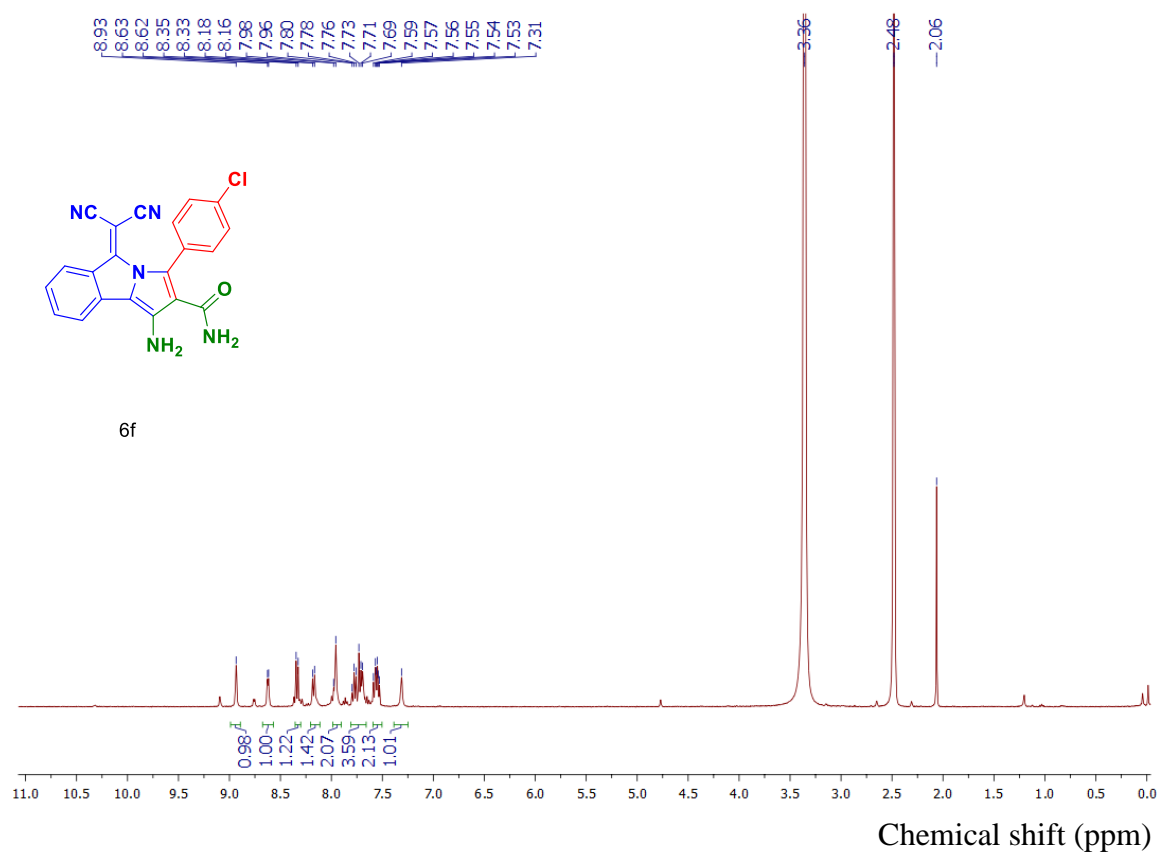
$^1\text{H}$  NMR Spectra of **6d** (400 MHz,  $\text{DMSO-}d_6$ )



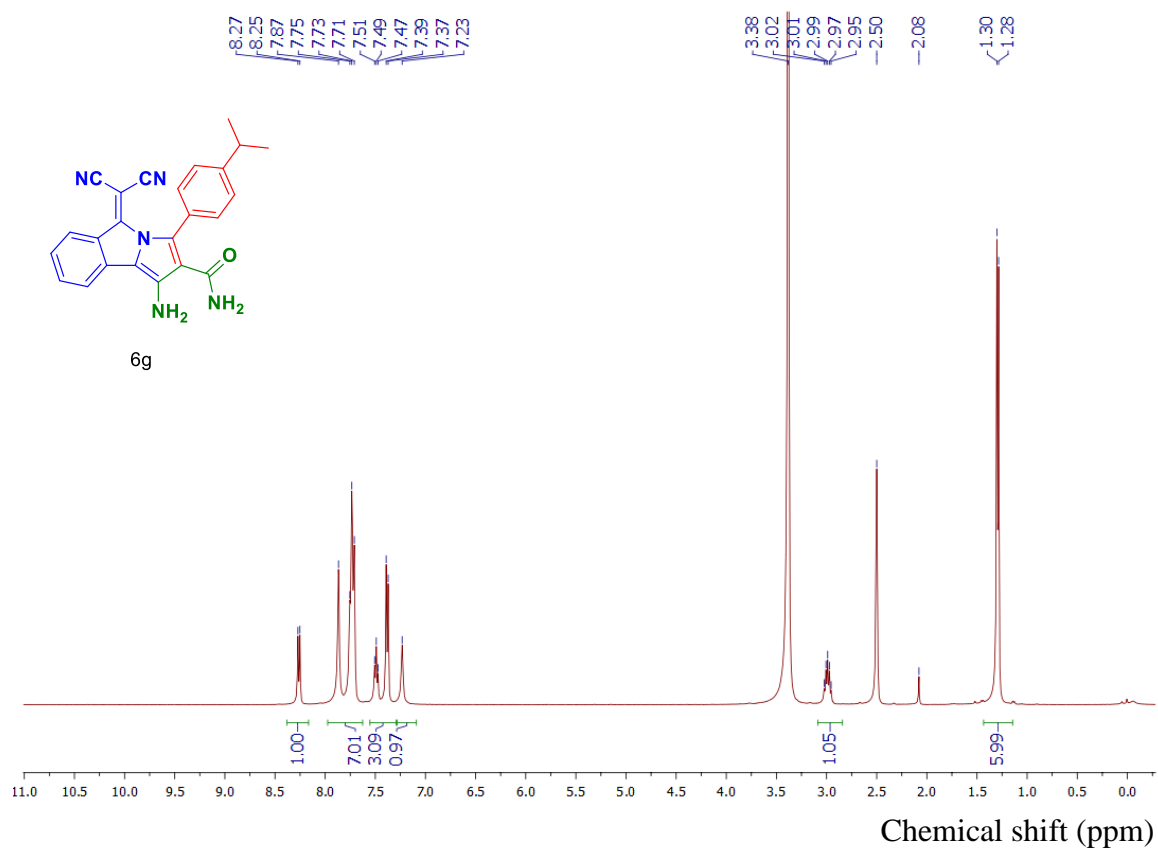
$^1\text{H}$  NMR Spectra of **6e** (400 MHz,  $\text{DMSO-}d_6$ )



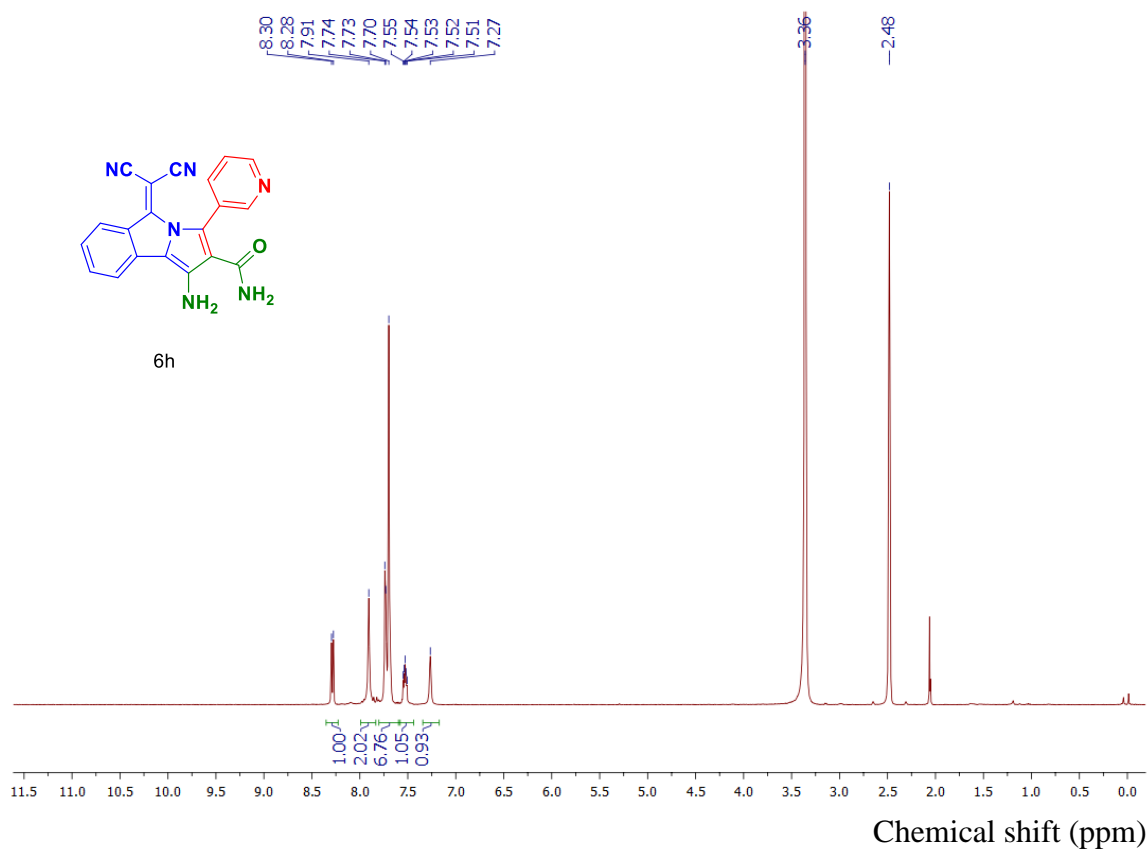
<sup>1</sup>H NMR Spectra of **6f** (400 MHz, DMSO-*d*<sub>6</sub>)



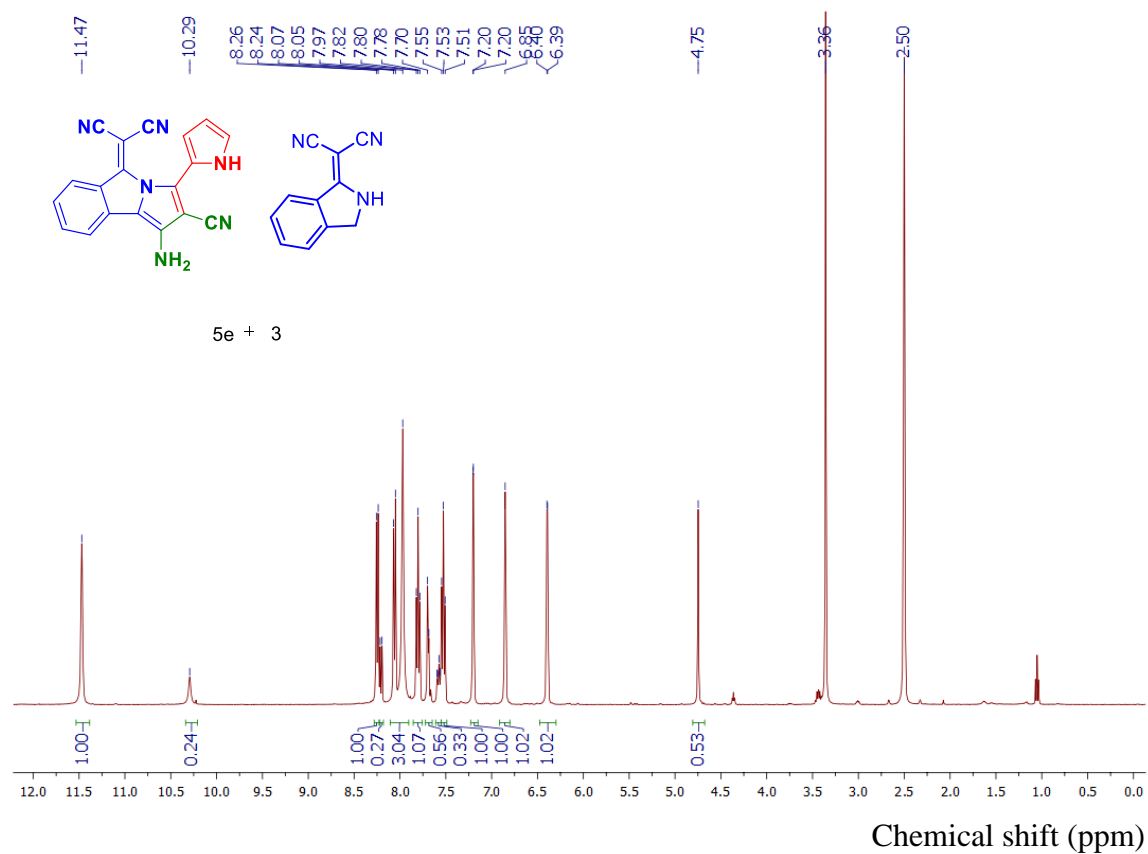
<sup>1</sup>H NMR Spectra of **6g** (400 MHz, DMSO-*d*<sub>6</sub>)



$^1\text{H}$  NMR Spectra of **6h** (400 MHz,  $\text{DMSO-}d_6$ )



$^1\text{H}$  NMR Spectra of **5e+3** (400 MHz,  $\text{DMSO-}d_6$ )



## 7. References

- [1] Sheldrick, G. M. *SHELX-97 - A Program for Crystal Structure Solution and Refinement*; University of Gottingen: Germany, 1997.
- [2] Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112–122.
- [3] Farrugia, L. J. ORTEP-3 for Windows - a Version of ORTEPIII with a Graphical User Interface. *J. Appl. Crystallogr.* **1997**, *30*, 565.