

Supporting Information

Synthesis of Fluorescent Heterocycles via a Knoevenagel/ [4+1]- cycloaddition cascade using Acetyl Cyanide

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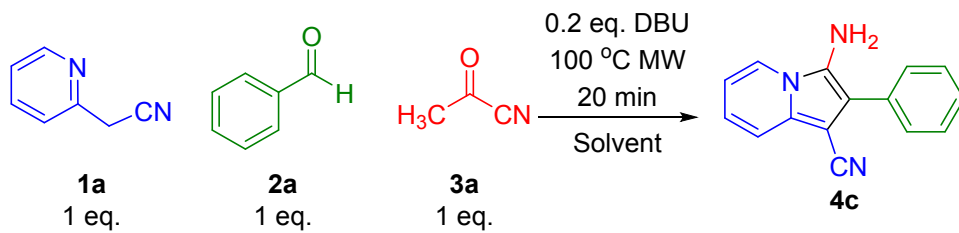
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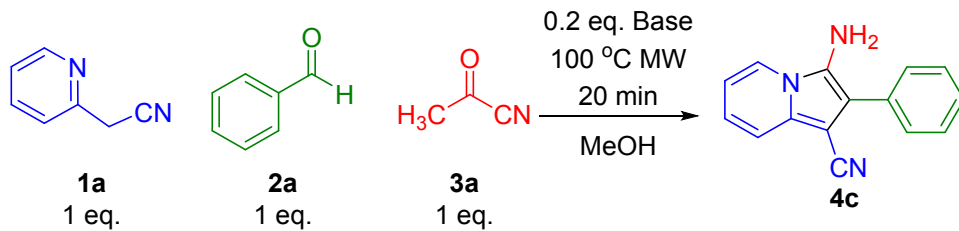
Table S1. Solvent optimization



Entry ^[a]	Solvent	Yield 4c ^[b] [%]
1	<i>n</i> -BuOH	82
2	TFE	13
3	MeOH	95
4	EtOH	87
5	<i>t</i> -BuOH	nr
6	2-EtO-EtOH	12
7	<i>i</i> -PrOH	46
8	THF	71
9	DCE	nr
10	DMF	91
11	Dioxane	60
12	DMSO	84
13	1,2-DME	57

^[a] Scale: 0.25 mmol ^[b] Reported % yields are 'Area under the Curve' of desired product (A%) as judged by LC/MS at UV 254 nm. nr = no reaction

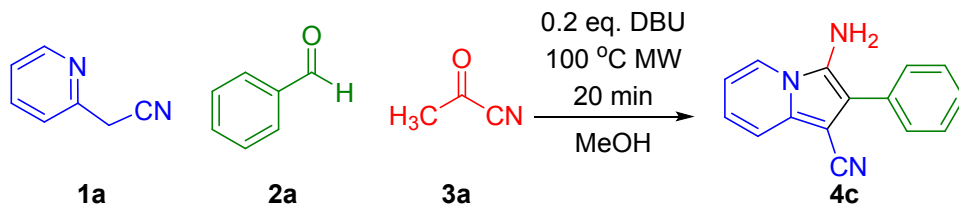
Table S2. Base optimization



Entry ^[a]	Base	Yield 4c ^[b] [%]
1	DBU	95
2	TEA	nr
3	DIPEA	nr
4	DIPA	1
5	Cs ₂ CO ₃	64
6	K ₂ CO ₃	67
7	KOAc	nr
8	NaH	nr
9	CsOH	90

^[a] Scale: 0.25 mmol ^[b] Reported % yields are 'Area under the Curve' of desired product (A%) as judged by LC/MS at UV 254 nm. nr = no reaction.

Table S3. Stoichiometry optimization.



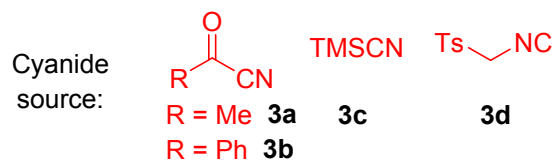
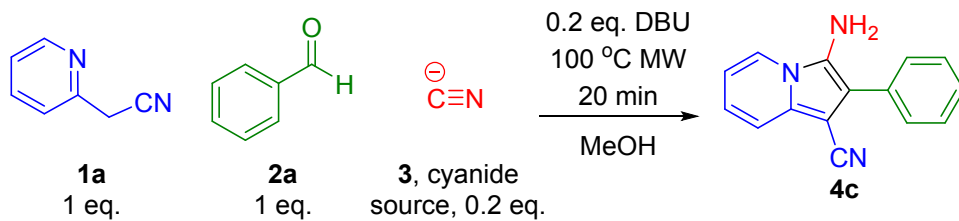
Entry ^[a]	1a eq.	2a eq.	3a eq.	DBU eq.	Yield 4c ^[b] [%]
1	1	1	1	0.2	95
2	1	1	1	0.5	94
3	1	1	1	1	93
4	1	1	1.3	0.2	92
5	1	1	2	0.2	90
6	1	1.3	1	0.2	78
7	1.3	1	1	0.2	87

^[a] Scale: 0.25 mmol, ^[b]

‘Area under the Curve’ of desired product (A%) as judged by LC/MS at UV 254 nm

Reported % yields are

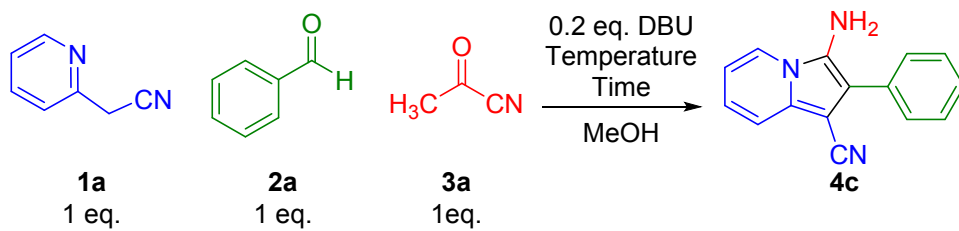
Table S4. Cyanide source optimization.



Entry ^[a]	Cyanide source	Yield 4c ^[b] [%]
1	3a	95
2	3b	90
3	3c	84
4	3d	13

^[a] Scale: 0.25 mmol, ^[b] Reported % yields are 'Area under the Curve' of desired product (A%) as judged by LC/MS at UV 254 nm

Table S5. Temperature optimization.



Entry ^[a]	Temperature	Time	Yield 4c ^[b] [%]
1	80 °C MW	20 min.	12
2	100 °C MW	20 min.	95
3	120 °C MW	20 min.	97
4	RT	overnight	82

^[a] Scale: 0.25 mmol, ^[b] Reported % yields are 'Area under the Curve' of desired product (A%) as judged by LC/MS at UV 254 nm

General procedure

All reagents and solvents were acquired from commercially available suppliers and used without further purification. The products were purified using an automated flash chromatography apparatus. Low resolution mass spectra were obtained using positive ESI methods in a mass spectrometer. High resolution mass spectra were obtained using positive ESI method for all the compounds, obtained in an Ion Cyclotron Resonance (ICR) spectrometer. ^1H and ^{13}C NMR spectra were obtained on a Bruker NMR spectrometer at 400 and 100 MHz respectively. The data is reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet). Coupling constant are reported in Hertz (Hz) and were automatically generated using known NMR analyzer software (Mestrenova). All microwave irradiation experiments were carried out in a Biotage Initiator, operating at a frequency of 2.45GHz with continuous irradiation power from 0 to 300W with utilization of the standard absorbance level of 220W maximum power using an external sensor of temperature. The reactions were carried out in 5 mL microwave vials, sealed with Teflon septum and placed in the microwave cavity at the specified temperature without the use of inert conditions. Absorbance spectra were measured with an Agilent 8453 UV-vis spectrophotometer. Fluorescence spectra were measured with a QuantaMaster 400 Steady State Spectrofluorometer and PTRI fluorescence spectrophotometer. Quantum yield was calculated using coumarine 151¹ and rhodamine² in absolute ethanol.

References:

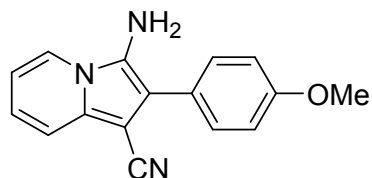
1. *The Journal of Physical Chemistry*, **2001**, *105*, 1097-1106
2. *Chemical Physics letters*, **1996**, *260*, 115-118

General procedure for the preparation of compound 4a-4q

The corresponding 2-cyanomethyl pyridine (**1**, 1 eq., 0.5 mmol) was placed in a 5 mL microwave vial equipped with a magnetic stir bar. Subsequently, anhydrous MeOH (1 mL) was added followed by the addition of the corresponding aldehyde (**2**, 1 eq., 0.5 mmol) and DBU (0.2 eq., 0.1 mmol). Then, acetyl cyanide (**3**, 1 eq. 0.5 mmol) was added slowly through the wall of the vial (note: if acetyl cyanide is not added slowly the solvent mixture will splash outside of the vial). The reaction was heated via microwave irradiation for 20 minutes at 120 °C. After reaction completion (monitored by TLC and LC/MS), the solvent was removed *in vacuo* and the crude product was purified using a silica column by flash chromatography (0-30% AcOEt/Hexane) to afford title compounds, **4a-4q**.

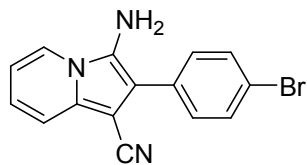
Analytical data of compound 4a-4q

3-amino-2-(4-methoxyphenyl) indolizine-1-carbonitrile (4a)



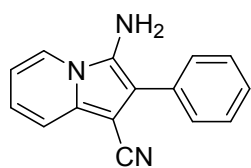
Brown solid, 76 mg, 58% yield, m.p. 144-146 °C, ¹H NMR (400 MHz, DMSO-d₆) δ 8.23 – 8.21 (m, 1H), 7.58 – 7.57 (m, 2H), 7.56 – 7.55 (m, 1H), 7.08 – 7.06 (m, 2H), 7.00 – 6.97 (m, 1H), 6.88 – 6.86 (m, 1H), 5.14 (s, 2H), 3.81 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆) δ 148.6, 123.0, 120.0, 117.9, 115.1, 112.8, 110.5, 107.9, 106.7, 104.6, 102.5, 102.4, 67.6, 45.5; [M+H]⁺ = 264; HRMS (ESI) m/z calculated for C₁₆H₁₄N₃O [M+H]⁺ = 264.11314; found 264.11327; λ_{ex} = 292, 393 nm; λ_{em} = 497 nm.

3-amino-2-(4-bromophenyl) indolizine-1-carbonitrile (4b)



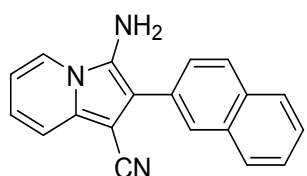
Light brown solid, 98 mg, 63%, m.p. 164-166 °C, ¹H NMR (400 MHz, DMSO-d₆) δ 8.25 – 8.23 (m, 1H), 7.69 – 7.67 (m, 2H), 7.59 – 7.57 (m, 2H), 7.01 (d, *J* = 8.9 Hz, 1H), 7.03 – 6.99 (m, 1H), 6.90 – 6.86 (m, 1H), 5.35 (br s, 2H); ¹³C NMR (100 MHz, DMSO-d₆) δ 133.0, 131.9, 131.7, 130.4, 128.4, 122.6, 120.7, 119.9, 117.3, 116.6, 112.4, 110.1, 77.0; [M]⁺ = 312, 314; HRMS (ESI) m/z calculated for C₁₅H₁₁BrN₃ [M+H]⁺ = 312.01309; found 312.01321, 314.01116; λ_{ex} = 282, 398 nm; λ_{em} = 493 nm.

3-amino-2-phenylindolizine-1-carbonitrile (4c)



Dark brown solid, 86 mg, 74% yield, m.p. 128-130 °C, ¹H NMR (400 MHz, DMSO-d₆) δ 8.27 – 8.25 (m, 1H), 7.68 – 7.51 (m, 6H), 7.02 – 6.85 (m, 2H), 5.29 (s, 2H); ¹³C NMR (100 MHz, DMSO-d₆) δ 132.9, 132.7, 128.8, 128.5, 126.7, 122.5, 120.4, 117.5, 116.6, 112.2, 111.6, 77.3; [M+H]⁺ = 234; HRMS (ESI) m/z calculated for C₁₅H₁₂N₃ [M+H]⁺ = 234.10257; found 234.10277; λ_{ex} = 287, 398 nm; λ_{em} = 496 nm.

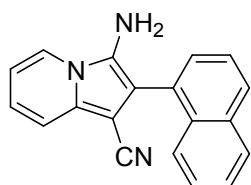
3-amino-2-(naphthalen-2-yl) indolizine-1-carbonitrile (4d)



Brown solid, 79 mg, 56% yield, m.p. 146-148 °C, ¹H NMR (400 MHz, DMSO-d₆) δ 8.30 – 8.27 (m, 1H), 8.14 – 8.13 (m, 1H), 8.04 – 8.02 (m, 1H), 7.96 – 7.95 (m, 2H), 7.83 – 7.80 (m, 1H), 7.58 – 7.50 (m, 3H), 7.04 – 7.00 (m, 1H), 6.92 – 6.88 (m, 1H), 5.43 (s, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ 149.5, 137.4,

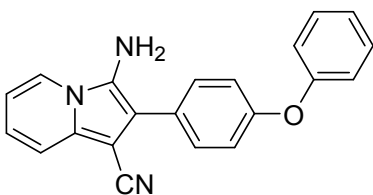
128.1, 127.9, 127.5, 127.0, 126.7, 126.3, 126.0, 122.6, 120.5, 116.6, 112.3, 112.2, 77.5; $[M+H]^+ = 284$; HRMS (ESI) m/z calculated for $C_{19}H_{13}N_3Na$ $[M+Na]^+ = 306.10017$; found 306.10019; $\lambda_{ex} = 292, 398$ nm; $\lambda_{em} = 505$ nm.

3-amino-2-(naphthalen-1-yl) indolizine-1-carbonitrile (4e)



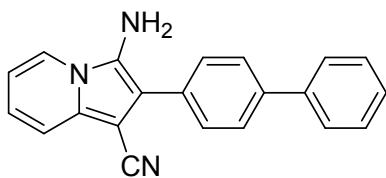
Brown solid, 96 mg, 67%, 142-144 °C, 1H NMR (400 MHz, DMSO- d_6) δ 8.25 – 8.23 (m, 1H), 8.04 – 7.99 (m, 2H), 7.74 – 7.72 (m, 1H), 7.66 – 7.62 (m, 1H), 7.59 – 7.49 (m, 4H), 7.06 – 7.02 (m, 1H), 6.94 – 6.90 (m, 1H), 5.08 (s, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 133.5, 132.4, 131.5, 129.8, 129.2, 128.9, 128.3, 128.0, 126.0, 125.8, 125.6, 122.5, 120.2, 117.2, 116.6, 112.2, 109.7, 79.8; $[M+H]^+ = 284$; HRMS (ESI) m/z calculated for $C_{19}H_{13}N_3Na$ $[M+Na]^+ = 306.10017$; found 306.10013; $\lambda_{ex} = 297, 397$ nm; $\lambda_{em} = 512$ nm.

3-amino-2-(4-phenoxyphenyl) indolizine-1-carbonitrile (4f)



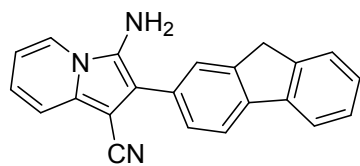
Brown oil, 71 mg, 43%, 1H NMR (400 MHz, DMSO- d_6) δ 8.24 – 8.22 (m, 1H), 7.66 – 7.62 (m, 2H), 7.52 – 7.50 (m, 1H), 7.44 – 7.40 (m, 3H), 7.18 – 7.07 (m, 5H), 7.02 – 6.97 (m, 1H), 6.89 – 6.85 (m, 1H), 5.24 (s, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 156.5, 155.6, 151.3, 149.5, 137.4, 132.8, 130.2, 130.1, 128.0, 127.7, 122.5, 120.4, 118.9, 118.8, 117.5, 116.5, 112.3, 111.2, 77.2; $[M+H]^+ = 326$; HRMS (ESI) m/z calculated for $C_{21}H_{15}N_3O$ $[M+H]^+ = 326.12879$, found 326.12877; $\lambda_{ex} = 300, 400$ nm; $\lambda_{em} = 494$ nm.

2-([1,1'-biphenyl]-4-yl)-3-aminoindolizine-1-carbonitrile (4g)



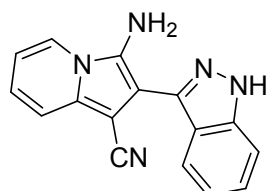
Beige solid, 85 mg, 55% yield, 160-62 °C, 1H NMR (400 MHz, DMSO- d_6) δ 8.27 – 8.25 (m, 1H), 7.82 – 7.72 (m, 6H), 7.55 – 7.47 (m, 3H), 7.40 – 7.36 (m, 1H), 7.03 – 6.99 (m, 1H), 6.90 – 6.87 (m, 1H), 5.36 (s, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 139.7, 138.4, 133.0, 131.8, 129.0, 128.9, 128.4, 127.5, 127.0, 126.5, 122.5, 120.5, 117.6, 116.6, 112.3, 111.0, 77.1; $[M+H]^+ = 310$; HRMS (ESI) m/z calculated for $C_{21}H_{15}N_3$ $[M+H]^+ = 310.13387$, found 310.131387; $\lambda_{ex} = 292, 398$ nm; $\lambda_{em} = 496$ nm.

3-amino-2-(9H-fluoren-2-yl)indolizine-1-carbonitrile (4h)



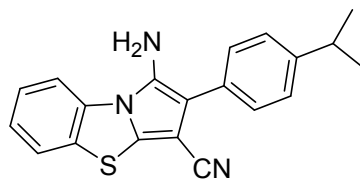
Brown solid, 113 mg, 70% yield, m.p. 156-158 °C, ^1H NMR (400 MHz, DMSO- d_6) δ 8.26 – 8.24 (m, 1H), 8.02 – 8.00 (m, 1H), 7.94– 7.92 (m, 1H), 7.85– 7.81(m, 1H), 7.66 – 7.52 (m, 3H), 7.42 – 7.30 (m, 2H), 7.01– 6.98 (m, 1H), 6.90 – 6.86 (m, 1H), 5.35 (s, 2H), 3.99 (s, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 143.5, 143.1, 140.8, 139.7, 137.4, 132.9, 131.1, 128.3, 127.2, 126.83, 126.79, 125.2, 122.5, 120.35, 120.30 120.0, 117.6, 116.6, 112.3, 111.8, 77.3, 36.5; $[\text{M} + \text{H}]^+ = 322$; HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{14}\text{N}_3$ $[\text{M} - \text{H}]^+ = 320.11822$, found 320.11847; $\lambda_{\text{ex}} = 300, 398 \text{ nm}$; $\lambda_{\text{em}} = 490 \text{ nm}$.

3-amino-2-(1H-indazol-3-yl)indolizine-1-carbonitrile (4i)



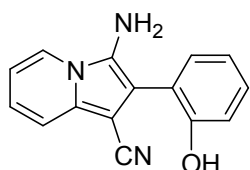
Brown solid, 61 mg, 44% yield, m.p. 140-142 °C, ^1H NMR (400 MHz, DMSO- d_6) δ 13.32 (s, 1H), 8.22 – 8.20 (m, 1 H), 8.07 –8.05 (m, 1H), 7.62 –7.57 (m, 2H), 7.44 –7.40 (m, 1H), 7.20 –7.17 (m, 1H), 7.04 –7.00 (m, 1H), 6.93 –6.89 (m, 1H), 5.67 (s, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 144.6, 141.0, 137.8, 133.0, 130.1, 126.4, 122.5, 121.3, 121.0, 120.29, 120.27, 117.9, 116.7, 112.4, 110.4, 102.9, 90.9, 76.8; $[\text{M} + \text{H}]^+ = 274$; HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{12}\text{N}_5$ $[\text{M} + \text{H}]^+ = 274.10872$, found 274.10890; $\lambda_{\text{ex}} = 299, 399 \text{ nm}$; $\lambda_{\text{em}} = 493 \text{ nm}$.

1-amino-2-(4-isopropylphenyl)benzo[d]pyrrolo[2,1-b]thiazole-3-carbonitrile (4j)



Light brown solid, 102 mg, 62% yield, m.p. 186-188 °C, ^1H NMR (400 MHz, DMSO- d_6) δ 8.39 – 8.37 (m, 1H), 7.98 – 7.96 (m, 1H), 7.53 – 7.47 (m, 3H), 7.42 – 7.34 (m, 3H), 4.97 (s, 2H), 2.97 – (m, 1H), 1.26 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 146.8, 134.2, 131.0, 130.5, 129.9, 129.6, 128.2, 126.7, 126.2, 124.9, 124.3, 116.5, 115.2, 114.6, 80.3, 33.2, 23.9; $[\text{M} + \text{H}]^+ = 332$; HRMS (ESI) m/z calculated for $\text{C}_{20}\text{H}_{17}\text{N}_3\text{SNa}$ $[\text{M} + \text{Na}]^+ = 354.10354$; found 354.10373; $\lambda_{\text{ex}} = 313, 392 \text{ nm}$; $\lambda_{\text{em}} = 498 \text{ nm}$.

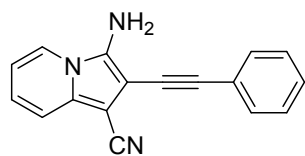
3-amino-2-(2-hydroxyphenyl)indolizine-1-carbonitrile (4k)



Brown solid, 36 mg, 29% yield, m.p. 180-182 °C, ^1H NMR (400 MHz, DMSO- d_6) δ 9.96 (s, 1H), 8.19 –8.17 (m, 1H), 7.52 –7.50 (m, 1H), 7.34 –7.32 (m, 1H), 7.24 –7.20 (m, 1H), 7.02 –6.84 (m, 4H), 4.98 (s, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 134.8, 113.2, 111.9, 109.1, 108.7, 102.7, 100.4, 99.85, 99.81, 98.0,

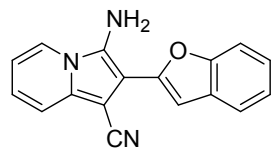
97.0, 96.6, 92.5, 90.5, 59.1; $[M + H]^+ = 250$; HRMS (ESI) m/z calculated for $C_{15}H_{11}N_3ONa$ $[M + Na]^+ = 272.07943$, found 272.07946; $\lambda_{ex} = 291, 392$ nm; $\lambda_{em} = 494$ nm.

3-amino-2-(phenylethynyl)indolizine-1-carbonitrile (4l)



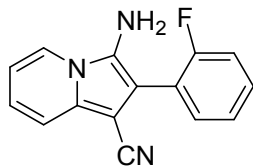
Dark brown solid, 44 mg, 35% yield, m.p. 158-160 °C, 1H NMR (400 MHz, DMSO- d_6) δ 8.41–8.39 (m, 1H), 7.77–7.74 (m, 1H), 7.56–7.49 (m, 1H), 7.38–7.30 (m, 3H), 7.26–7.23 (m, 2H), 7.10–7.07 (m, 1H), 4.51 (s, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 153.6, 137.2, 135.4, 132.6, 128.9, 128.2, 127.2, 125.9, 125.4, 123.8, 117.7, 115.3, 113.8, 113.4, 98.3, 81.9, 29.9; $[M + H]^+ = 258$; HRMS (ESI) m/z calculated for $C_{17}H_{12}N_3$ $[M + H]^+ = 258.10257$, found 258.10268; $\lambda_{ex} = 304, 348$ nm; $\lambda_{em} = 404$ nm.

3-amino-2-(benzofuran-2-yl)indolizine-1-carbonitrile (4m)



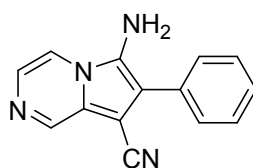
Brown oil, 40 mg, 29% yield, 1H NMR (400 MHz, DMSO- d_6) δ 8.26–8.24 (m, 1H), 7.67–7.61 (m, 2H), 7.53–7.50 (m, 1H), 7.31–7.23 (m, 2H), 7.20–7.19 (m, 1H), 7.04–6.99 (m, 1H), 6.90–6.86 (m, 1H), 6.09 (s, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 153.3, 150.4, 133.4, 130.5, 128.6, 123.8, 123.2, 122.5, 121.2, 120.5, 117.1, 116.7, 112.6, 111.0, 100.7, 98.3, 74.8; $[M + H]^+ = 274$; HRMS (ESI) m/z calculated for $C_{17}H_{12}N_3O$ $[M + H]^+ = 274.09749$; found 274.09763; $\lambda_{ex} = 294, 332, 373$ nm; $\lambda_{em} = 476$ nm.

3-amino-2-(2-fluorophenyl)indolizine-1-carbonitrile (4n)



Beige solid, 91 mg, 73% yield, m.p. 128-130 °C, 1H NMR (400 MHz, DMSO- d_6) δ 8.21–8.18 (m, 1H), 7.56–7.50 (m, 2H), 7.48–7.42 (m, 1H), 7.38–7.31 (m, 2H), 7.03–6.98 (m, 1H), 6.90–6.86 (m, 1H), 5.25 (s, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 161.1, 158.7, 133.0, 132.4, 130.0, 129.7, 125.1, 120.9, 120.4, 117.4, 117.1, 112.7, 105.5, 79.0; $[M + H]^+ = 252$; HRMS (ESI) m/z calculated for $C_{15}H_{11}FN_3$ $[M + H]^+ = 252.09315$; found 252.09333; $\lambda_{ex} = 280, 323, 383$ nm; $\lambda_{em} = 493$ nm.

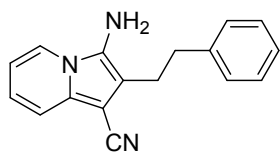
6-amino-7-phenylpyrrolo[1,2-a]pyrazine-8-carbonitrile (4o)



Light brown solid, 86 mg, 74% yield, m.p. 172-174 °C, 1H NMR (400 MHz, DMSO- d_6) δ 8.82 (s, 1H), 8.17–8.15 (m, 1H), 7.72–7.70 (m, 1H), 7.64–7.61 (m, 2H), 7.55–7.51 (m, 2H), 7.42–7.38 (m, 1H), 5.92 (s, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 142.2, 131.5, 130.9, 129.0, 128.9, 128.6, 127.5, 125.9, 115.7,

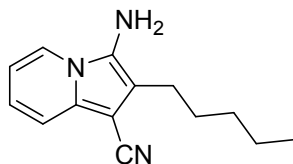
114.4, 112.8, 82.0; $[M+H]^+ = 235$; HRMS (ESI) m/z calculated for $C_{14}H_{11}N_4$ $[M+H]^+ = 235.09784$; found 235.09782; $\lambda_{ex} = 295$, 399 nm; $\lambda_{em} = 494$ nm.

3-amino-2-phenethylindolizine-1-carbonitril (4p)



Brown oil, 99 mg, 76% yield, 1H NMR (400 MHz, DMSO- d_6) δ 8.09– 8.06 (m, 1H), 7.45– 7.43 (m, 1H), 7.30– 7.26 (m, 4H), 7.20– 7.17 (m, 1H), 6.92– 7.88 (m, 1H), 6.80– 6.77 (m, 1H), 4.97 (s, 2H), 3.11 – 2.82 (m, 5H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 141.4, 131.8, 128.3, 128.2, 128.0, 125.9, 122.1, 119.3, 117.3, 116.2, 112.34, 112.31, 111.6, 78.2, 35.8, 26.1; $[M+H]^+ = 262$; HRMS (ESI) m/z calculated for $C_{17}H_{16}N_3$ $[M+H]^+ = 262.13387$; found 262.13402.

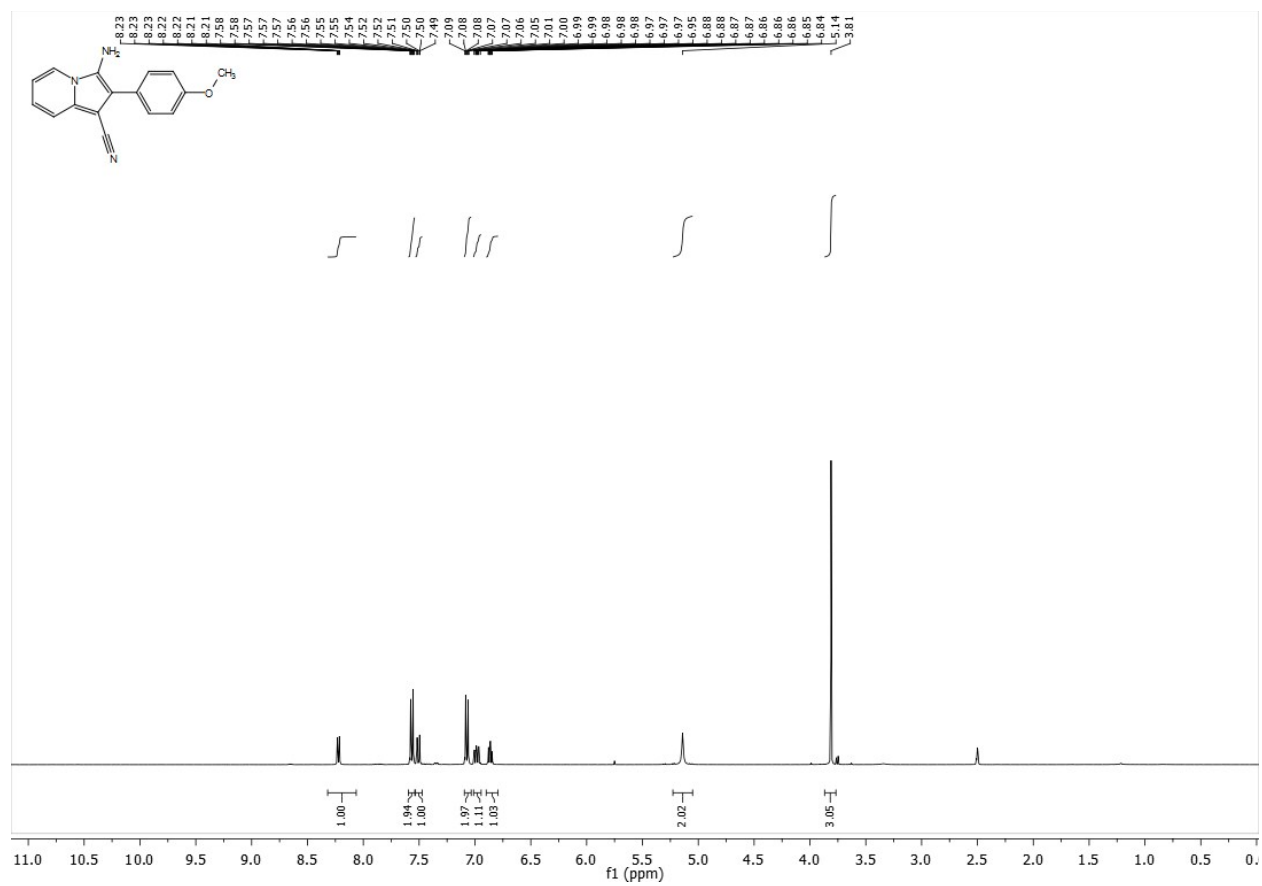
3-amino-2-pentylindolizine-1-carbonitrile (4q)



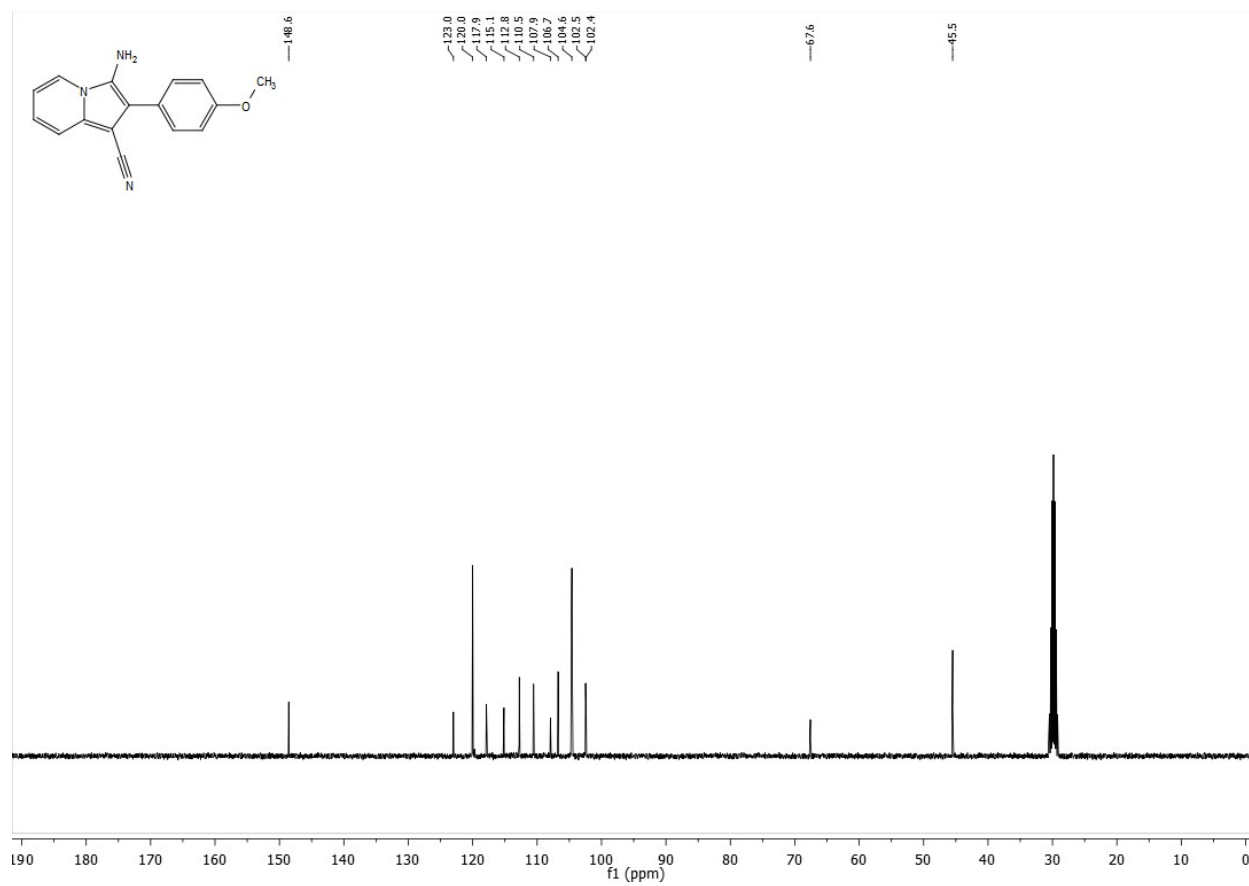
Brown oil, 91 mg, 80% yield, 1H NMR (400 MHz, DMSO- d_6) δ 8.06 – 8.04 (m, 1H), 7.43 – 7.40 (m, 1H), 6.91 – 6.87 (m, 1H), 6.79 – 6.76 (m, 1H), 4.91 (s, 2H), 2.65 (t, $J = 7.5$ Hz, 2H), 1.61 – 1.57 (m, 2H), 1.42 – 1.14 (m, 4H), 0.92 – 0.74 (m, 3H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 131.7, 127.9, 122.0, 119.2, 117.4, 116.1, 113.3, 111.5, 30.9, 29.5, 23.8, 22.0, 13.9; $[M+H]^+ = 228$; HRMS (ESI) m/z calculated for $C_{14}H_{18}N_3$ $[M+H]^+ = 228.14952$; found 228.14971.

NMR spectra for compounds 4a-4q

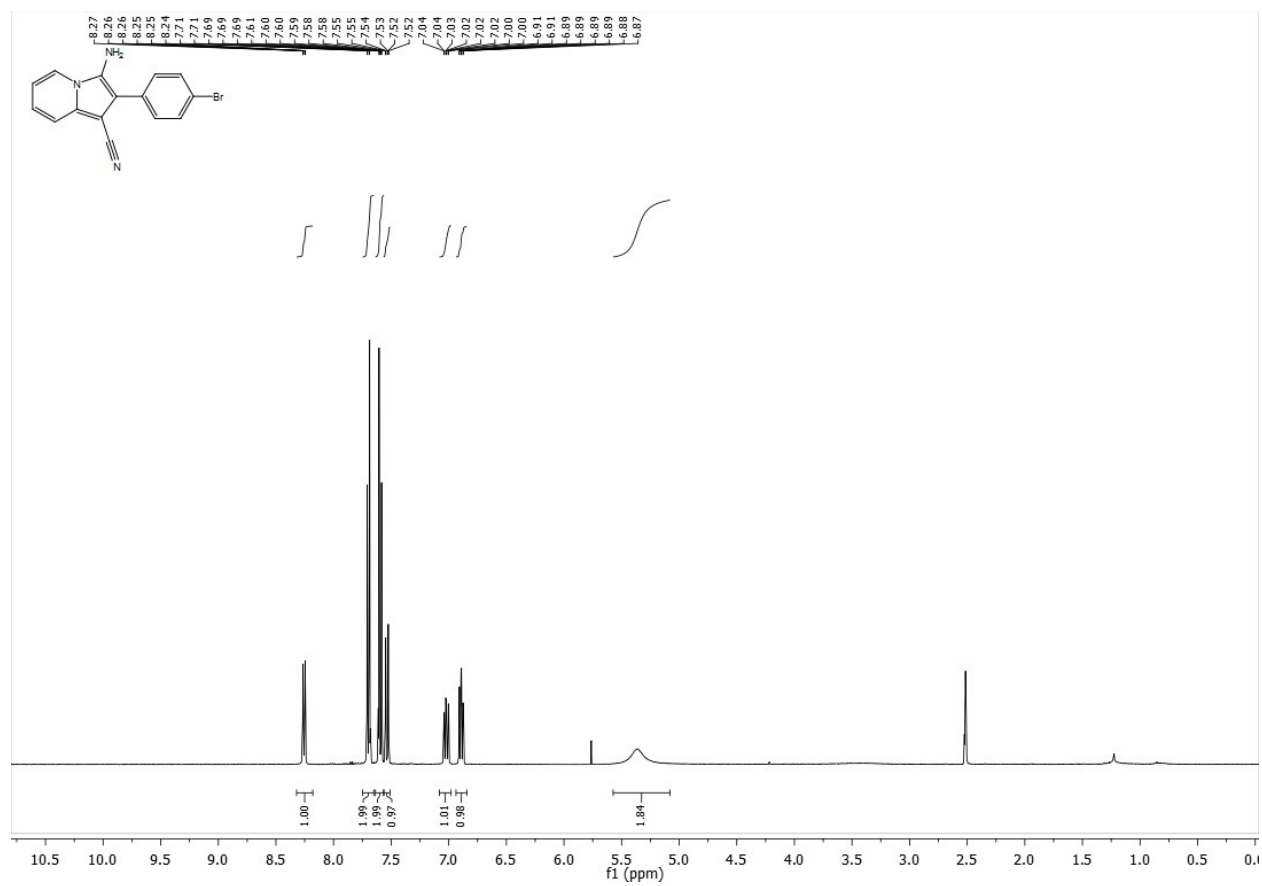
1H NMR for compound **4a** (400 MHz, DMSO- d_6)



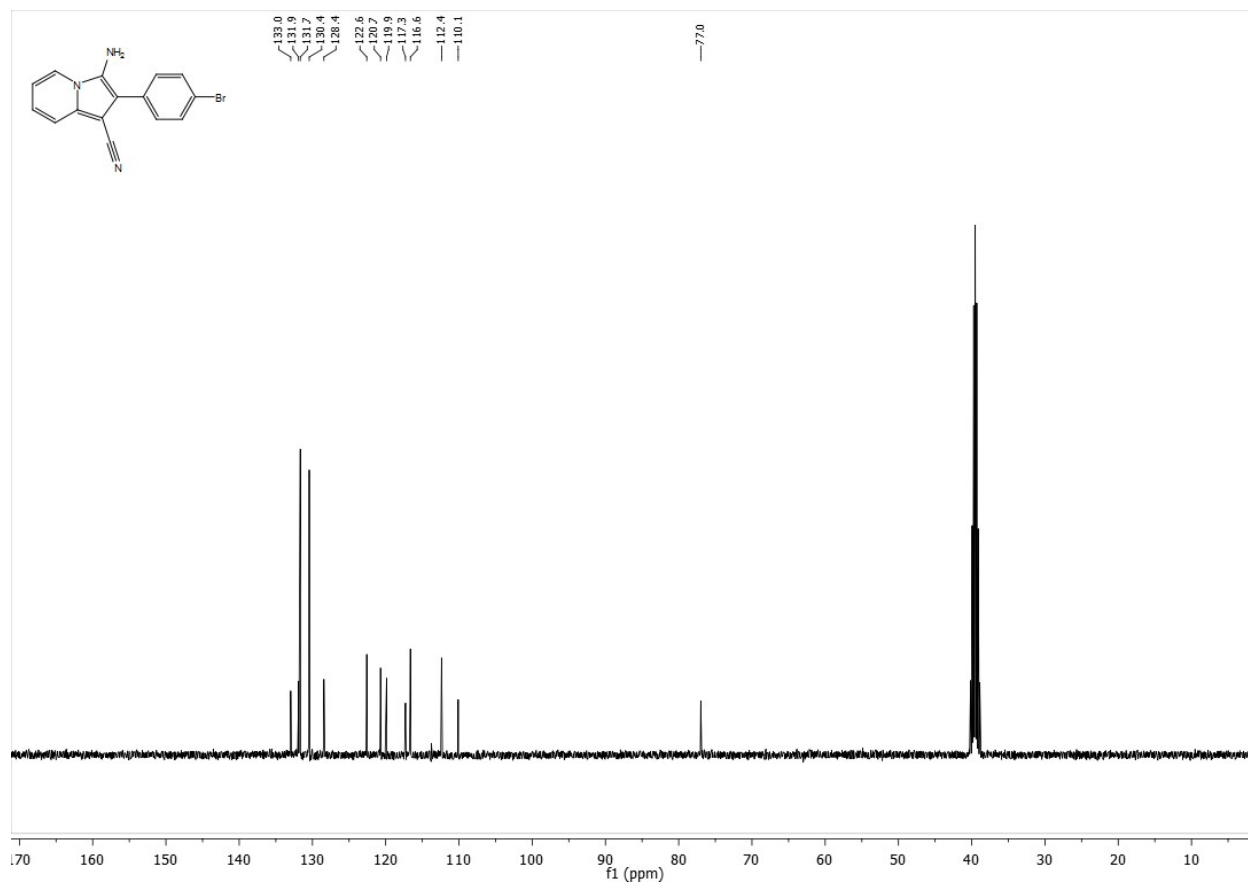
¹³C NMR for compound **4a** (100 MHz, DMSO-d₆)



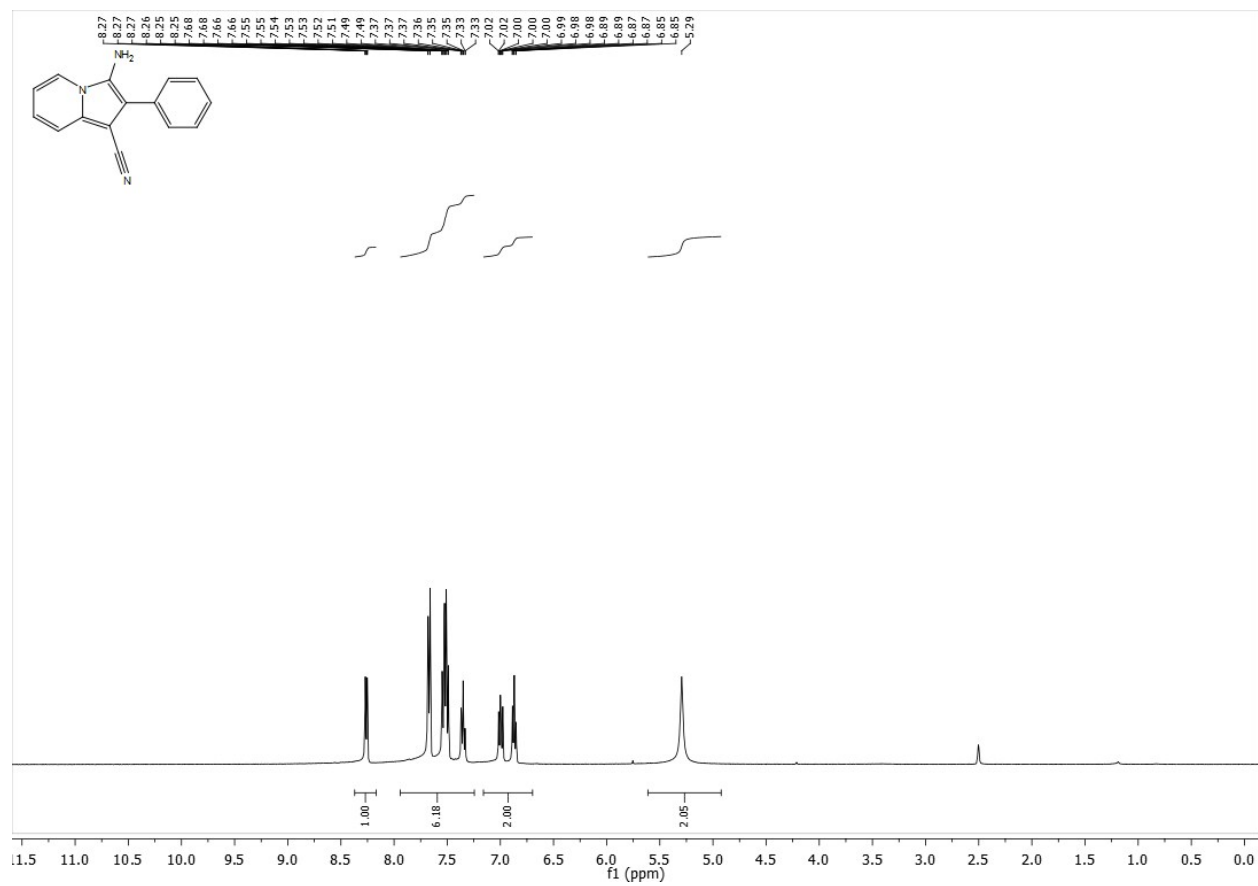
¹H NMR for compound **4b** (400 MHz, DMSO-d₆)



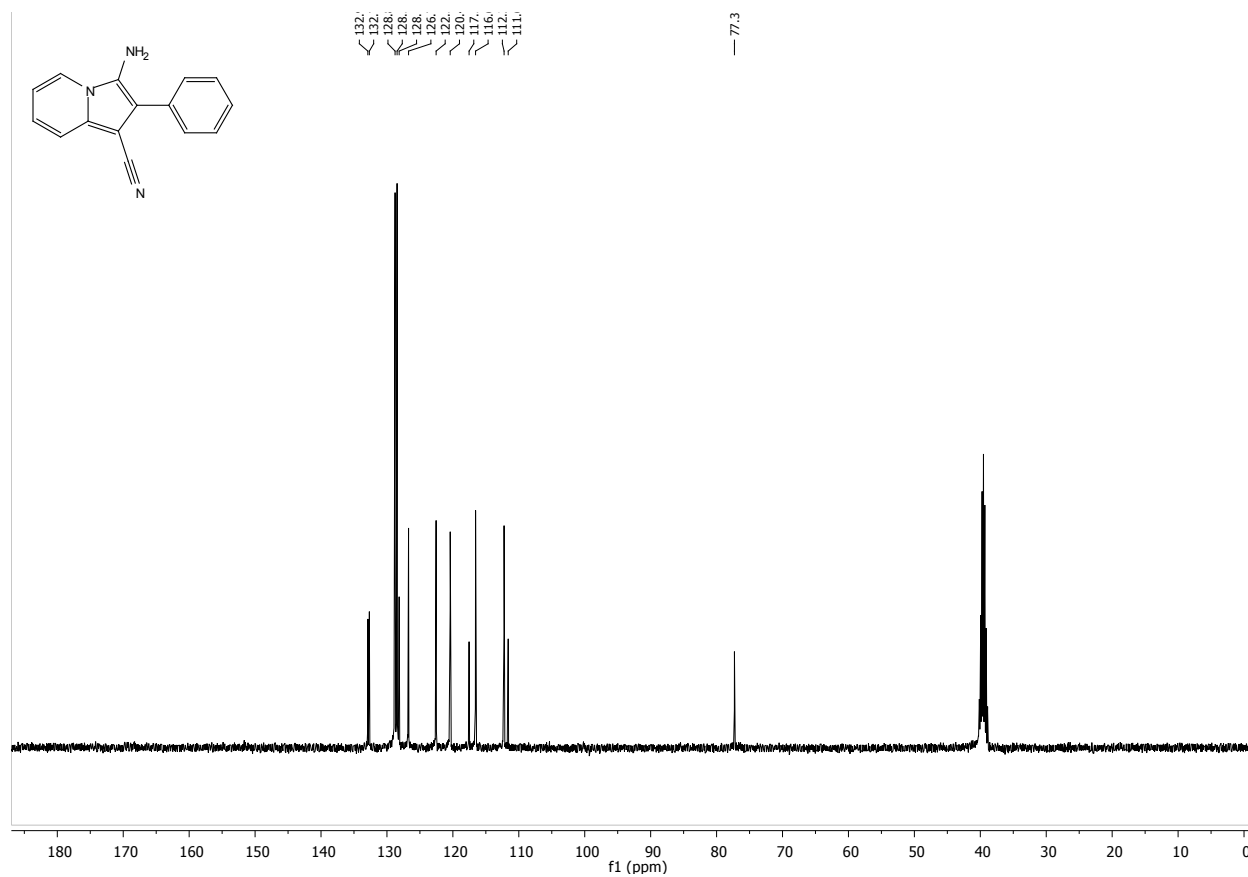
¹³C NMR for compound **4b** (100 MHz, DMSO-d₆)



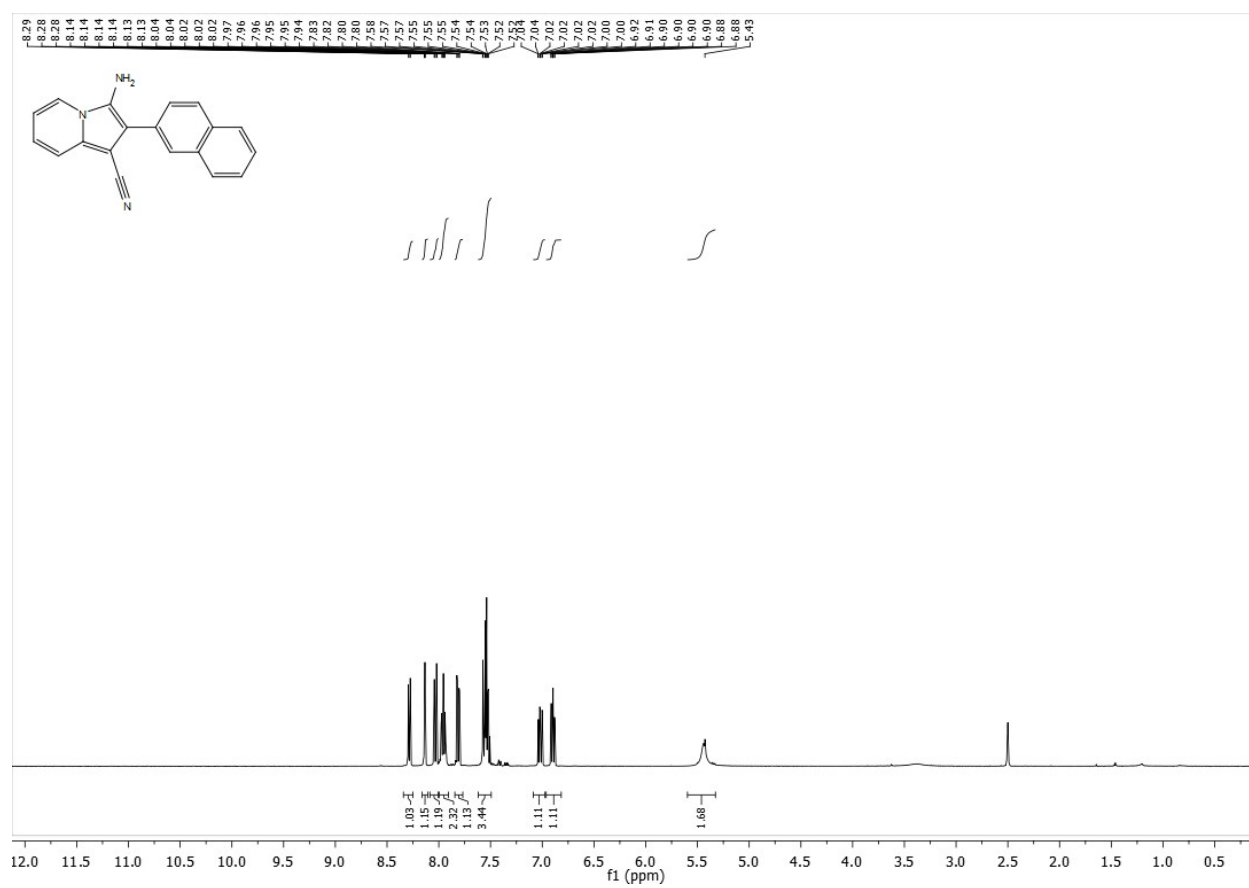
^1H NMR for compound **4c** (400 MHz, DMSO-d_6)



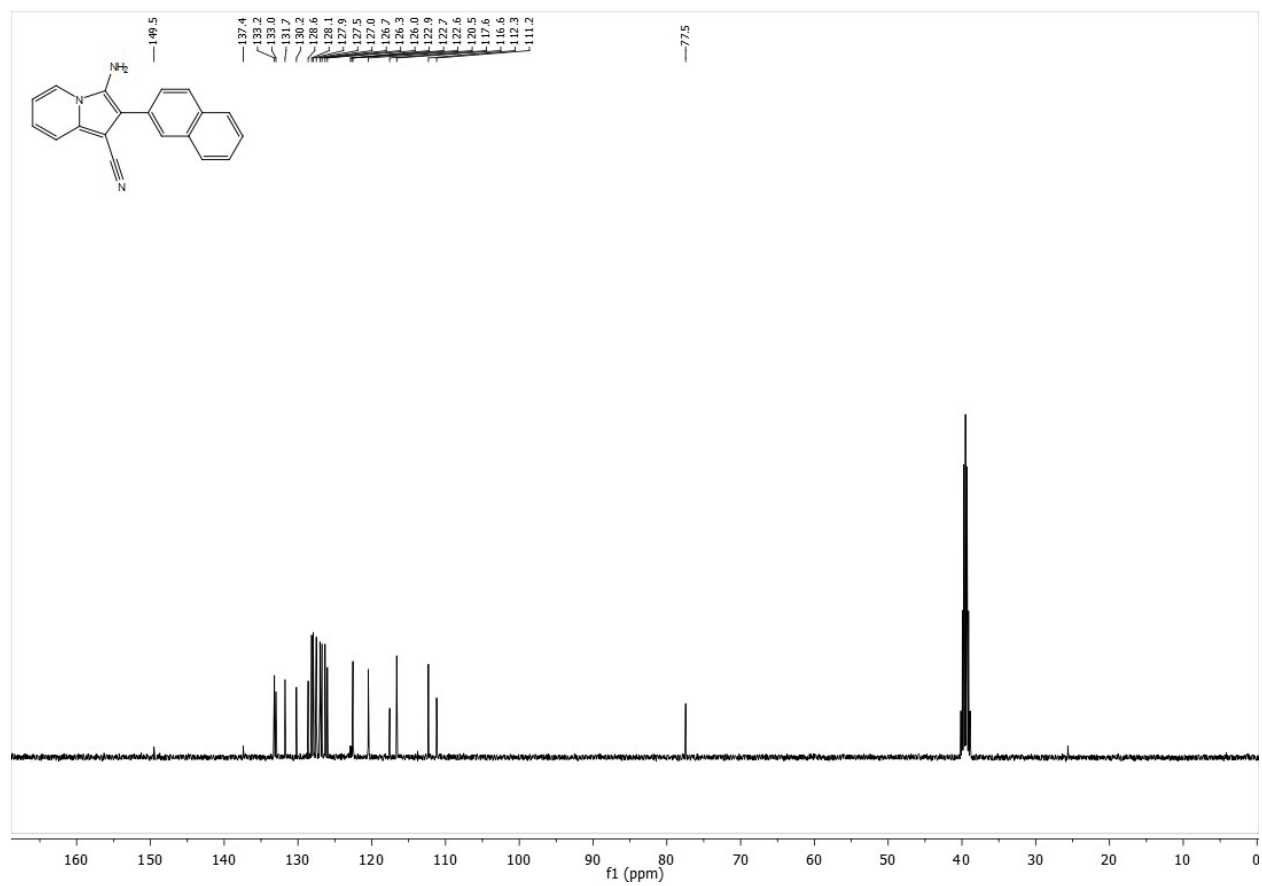
¹³C NMR for compound **4c** (100 MHz, DMSO-d₆)



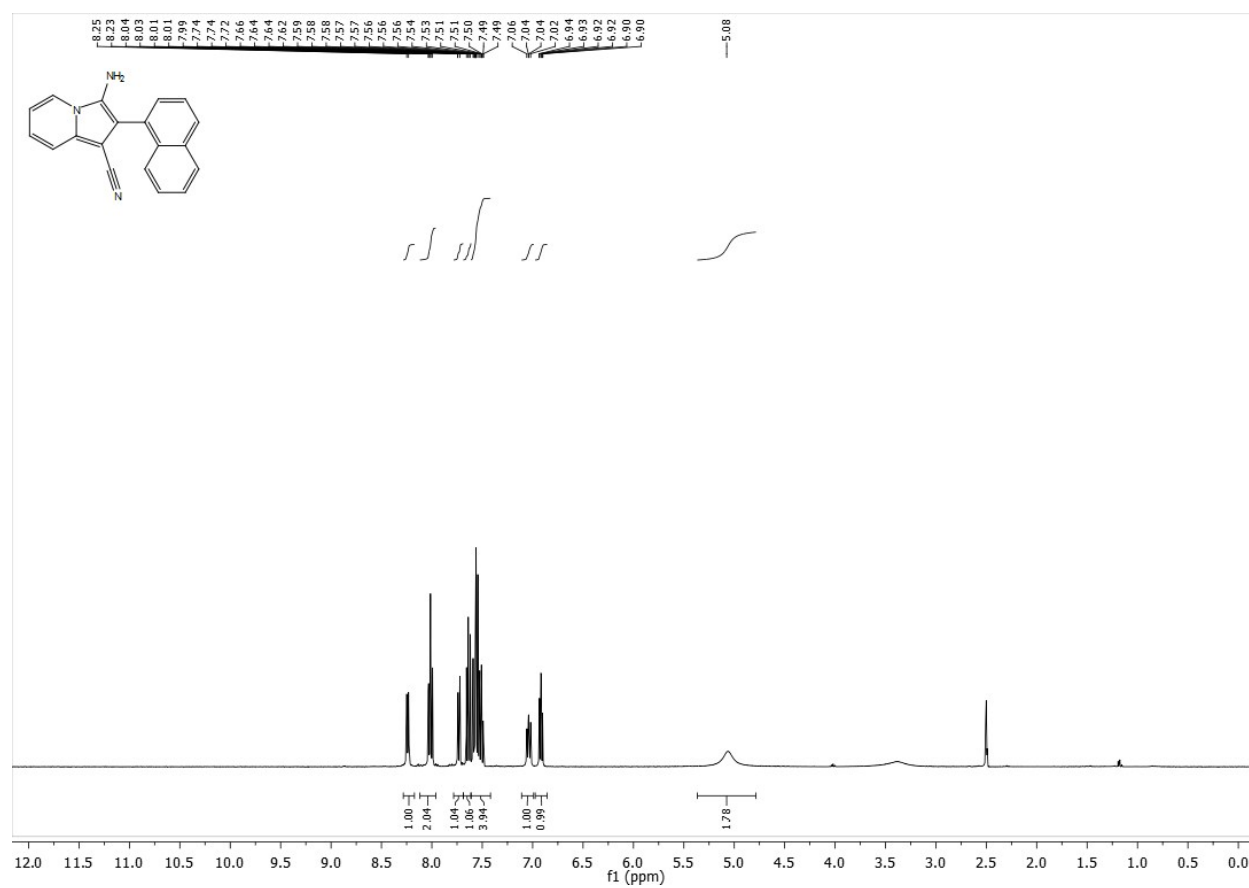
¹H NMR for compound **4d** (400 MHz, DMSO-d₆)



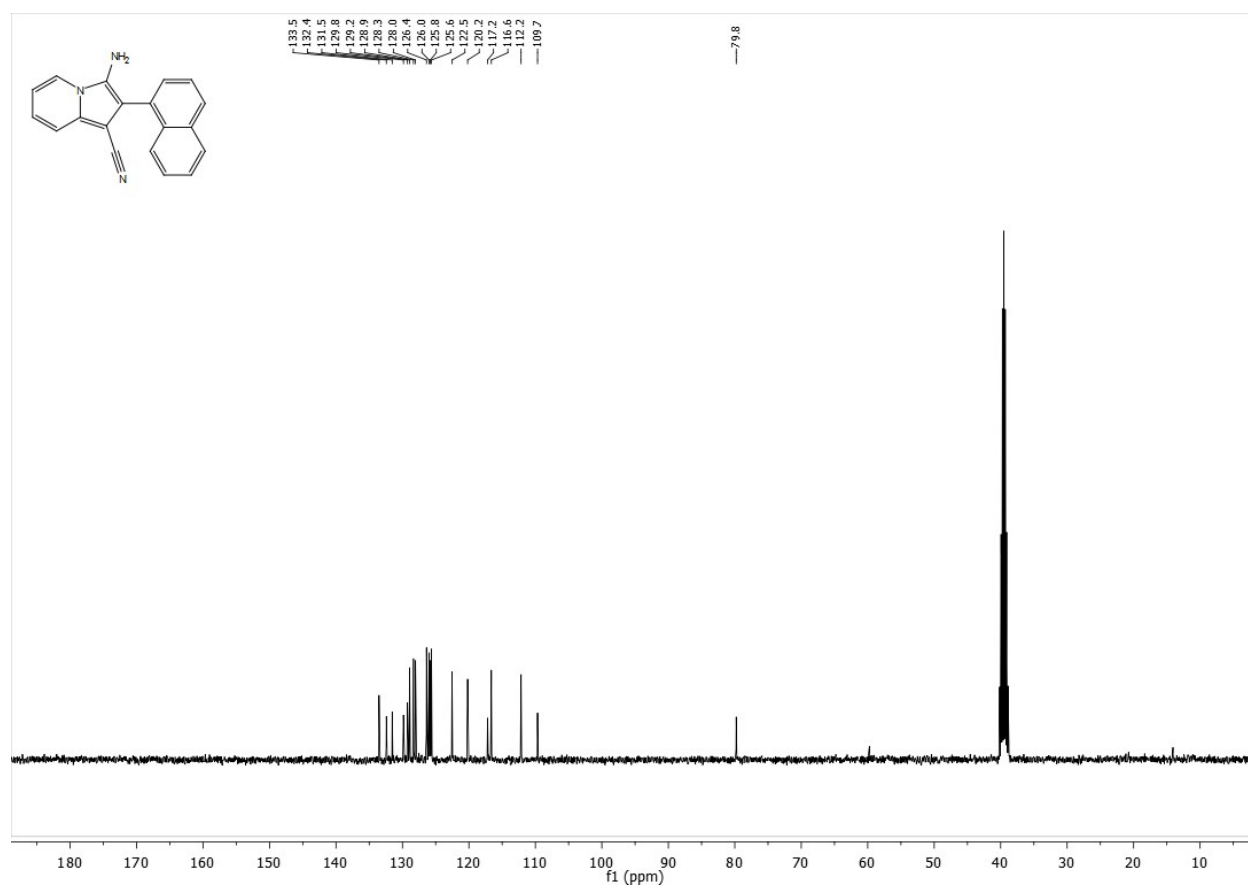
¹³C NMR for compound **4d** (100 MHz, DMSO-d₆)



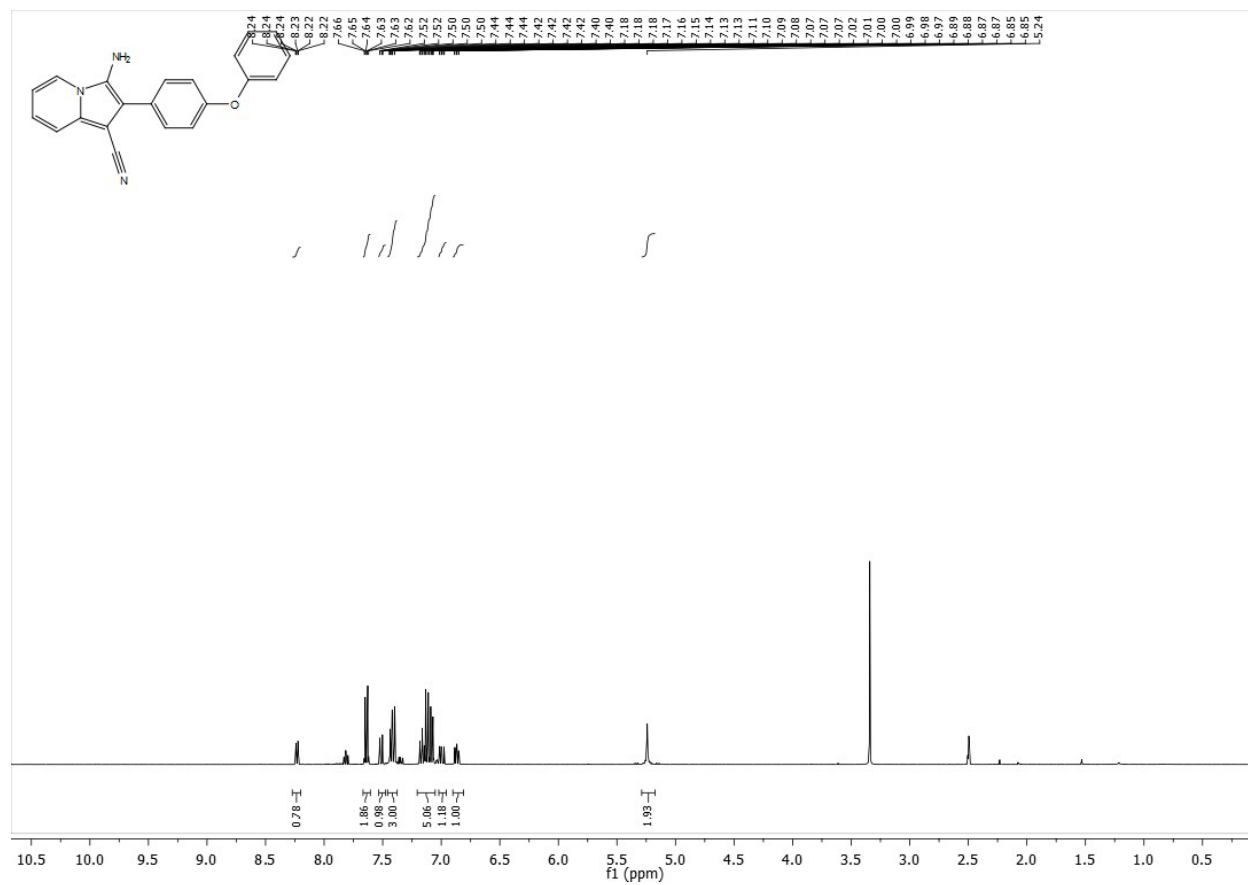
^1H NMR for compound **4e** (400 MHz, DMSO- d_6)



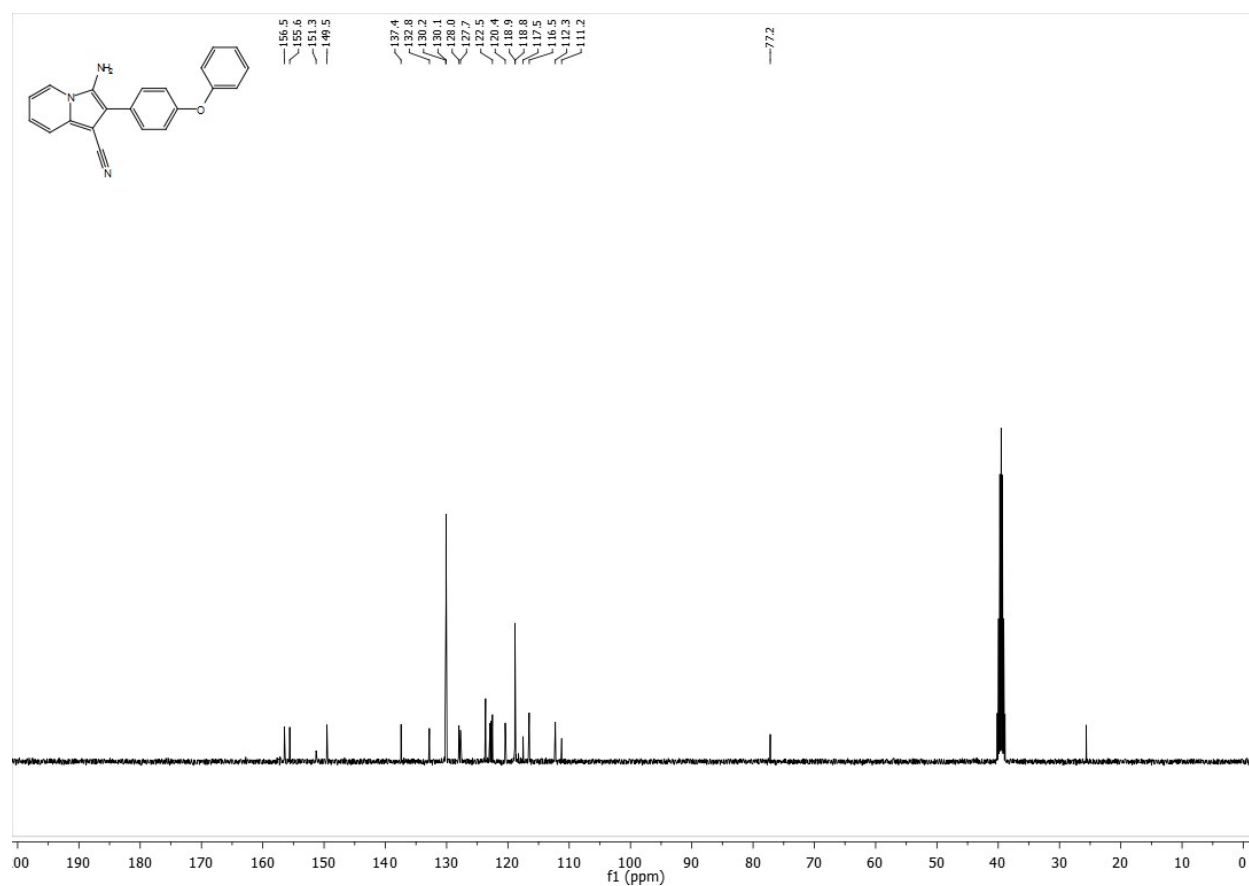
^{13}C NMR for compound **4e** (100 MHz, DMSO- d_6)



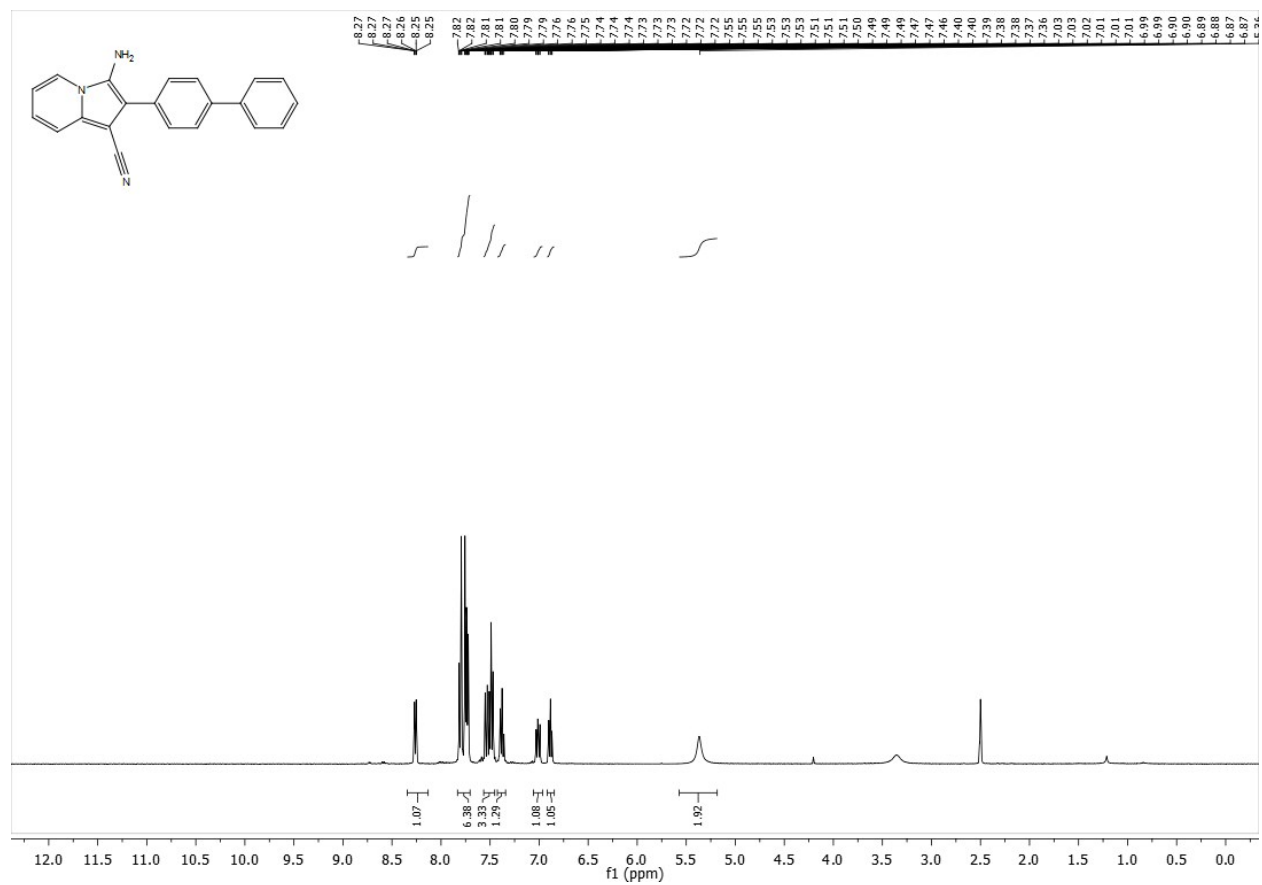
^1H NMR for compound **4f** (400 MHz, DMSO- d_6)



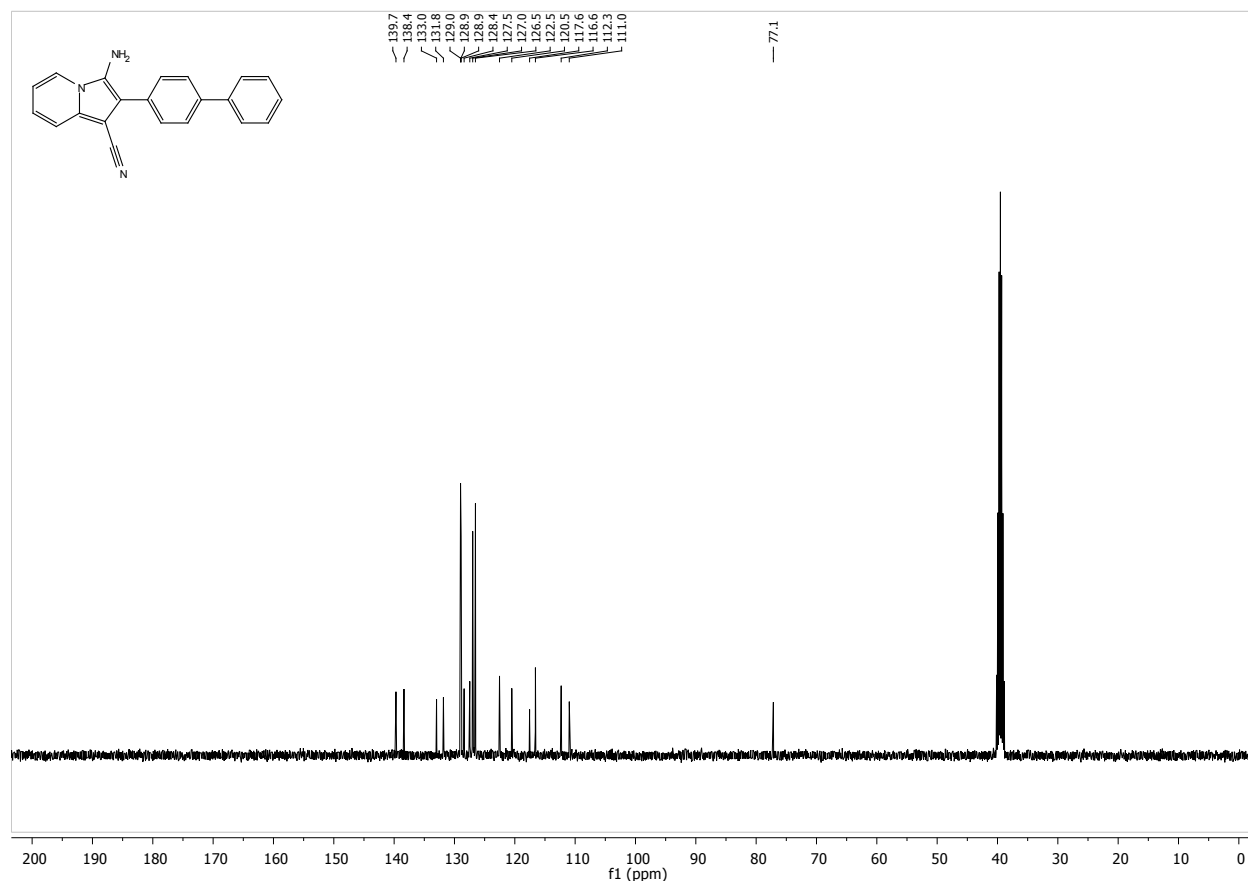
^{13}C NMR for compound **4f** (100 MHz, DMSO- d_6)



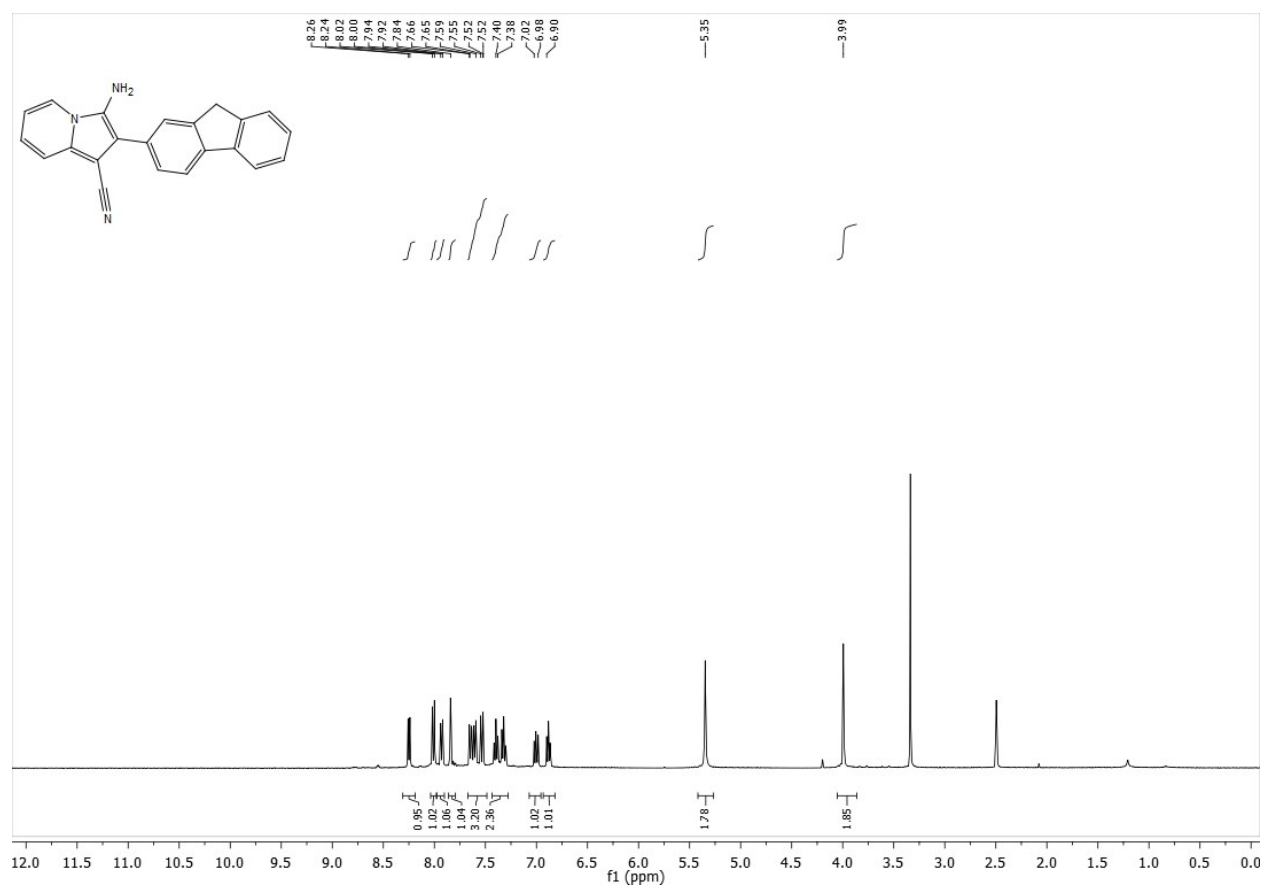
¹H NMR for compound **4g** (400 MHz, DMSO-d₆)



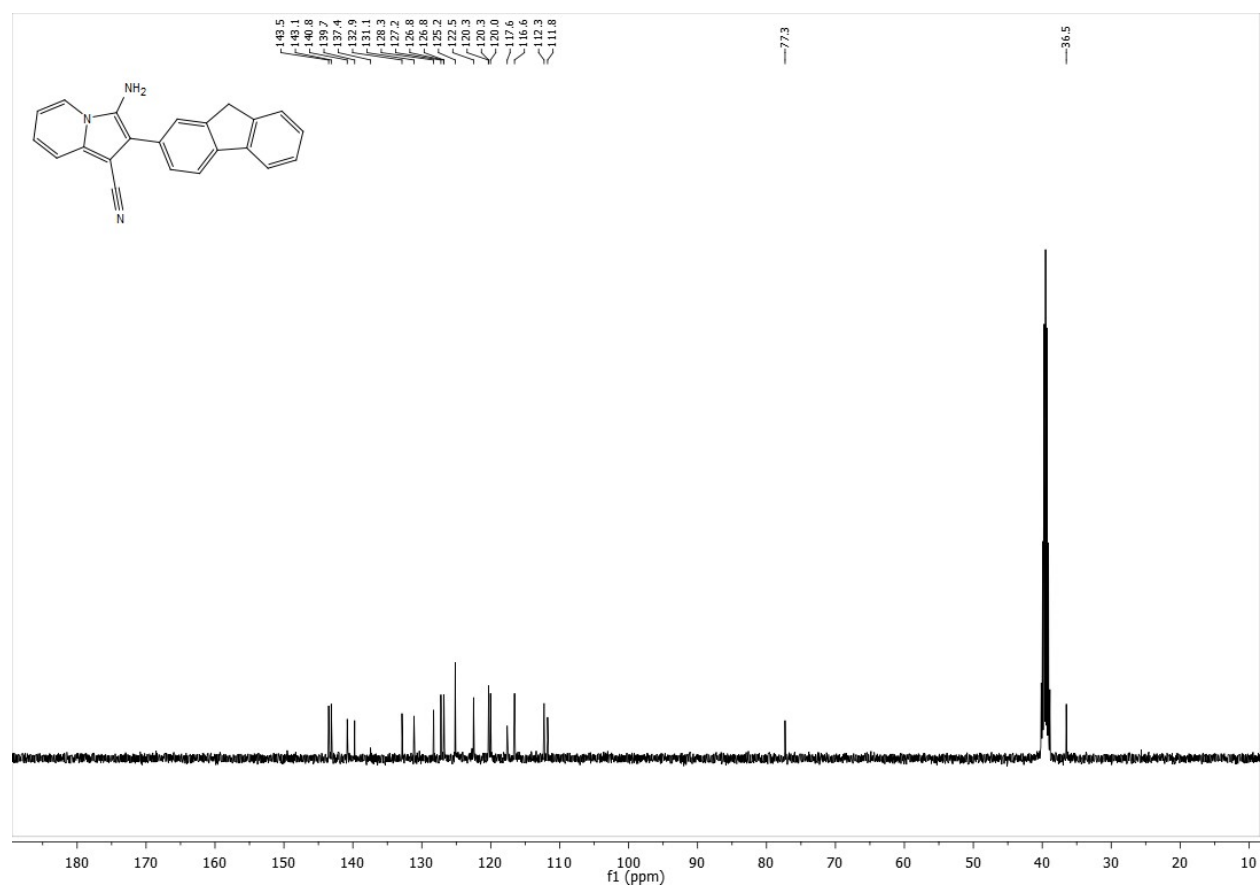
^{13}C NMR for compound **4g** (100 MHz, DMSO- d_6)



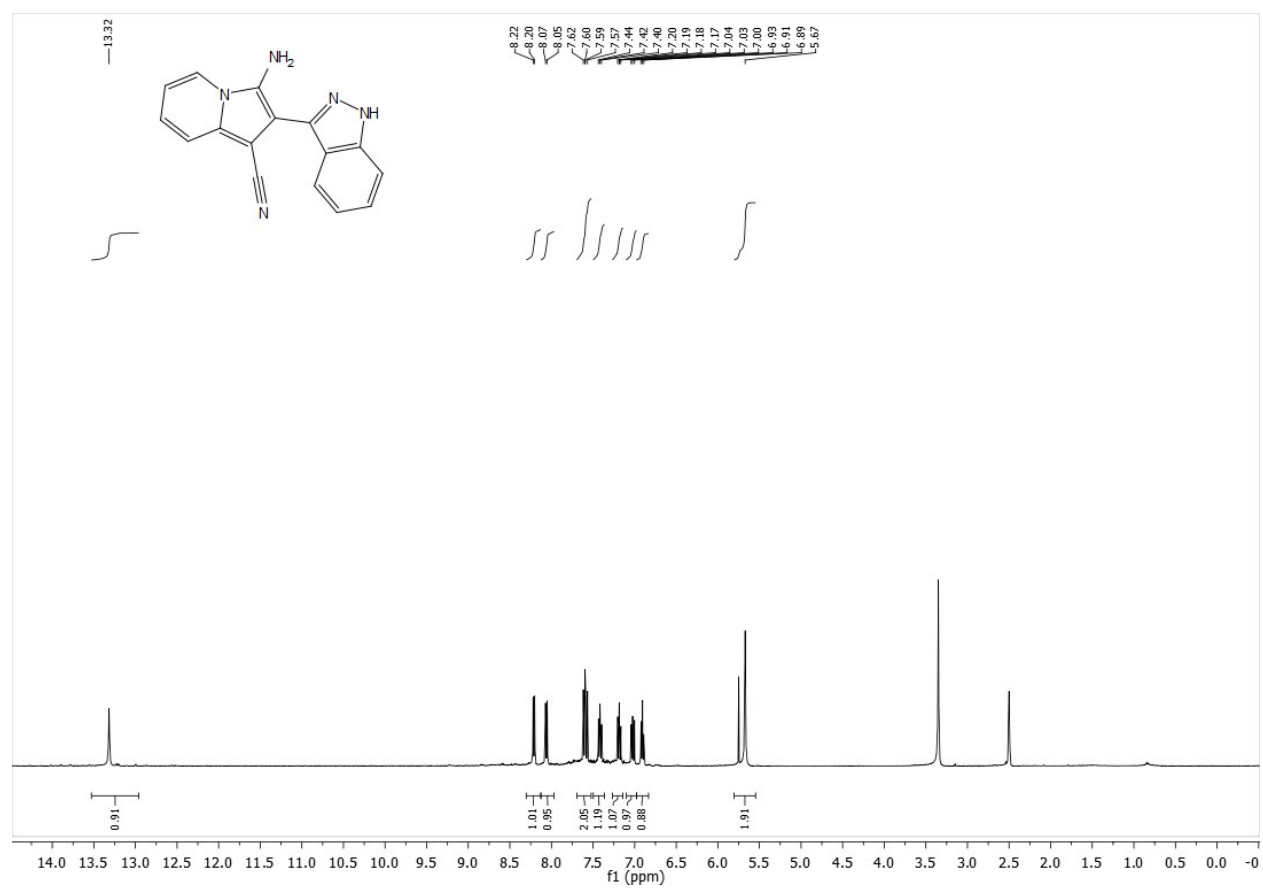
^1H NMR for compound **4h** (400 MHz, DMSO-d_6)



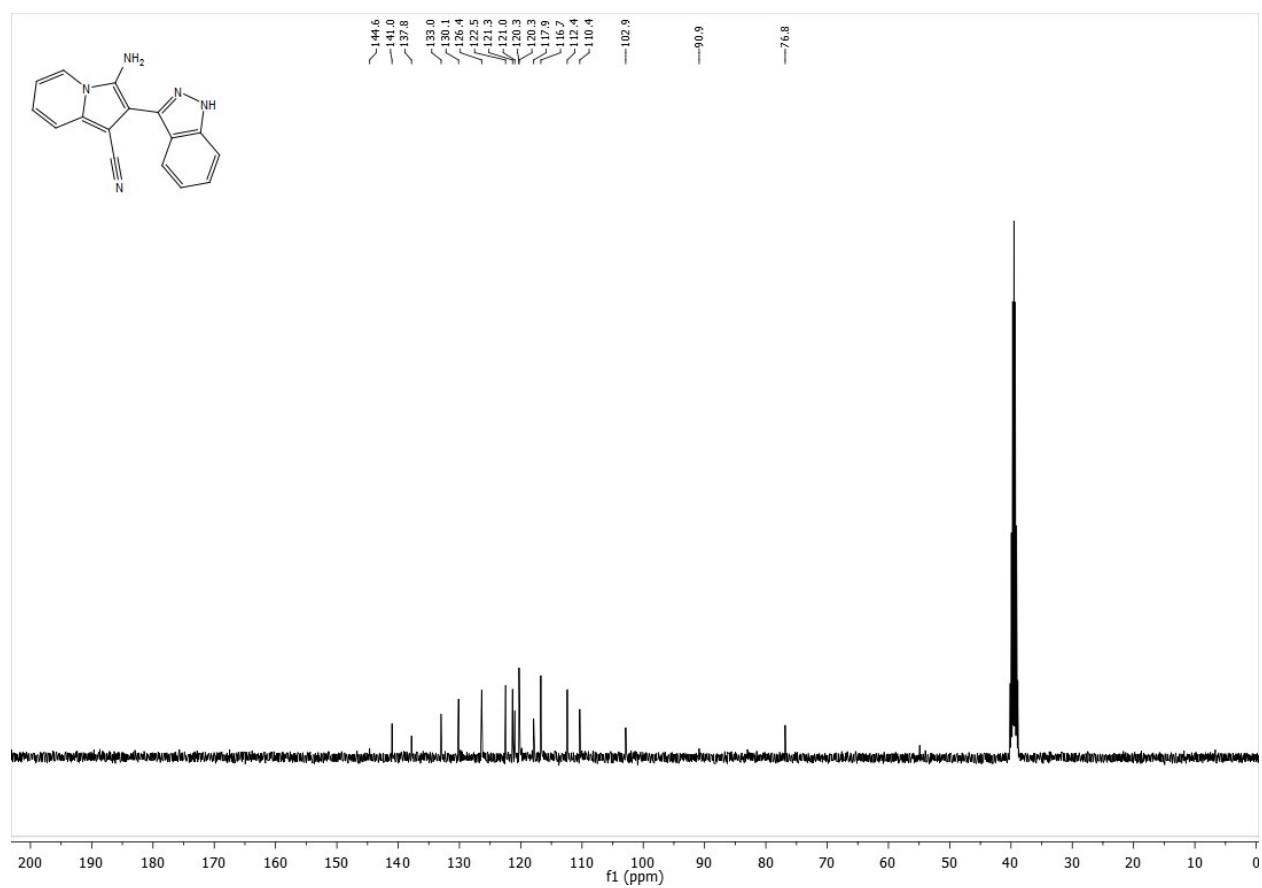
^{13}C NMR for compound **4h** (100 MHz, DMSO- d_6)



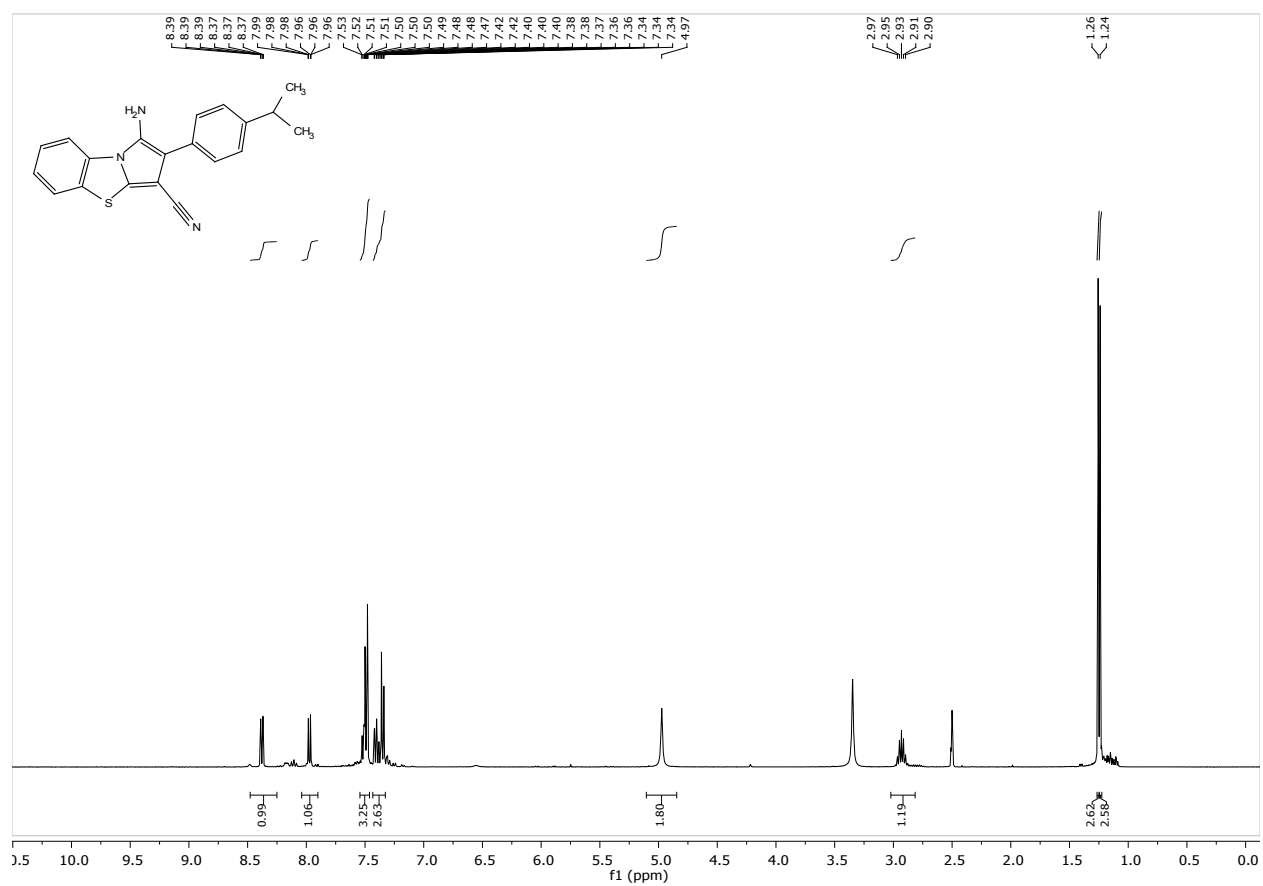
^1H NMR for compound **4i** (400 MHz, DMSO- d_6)



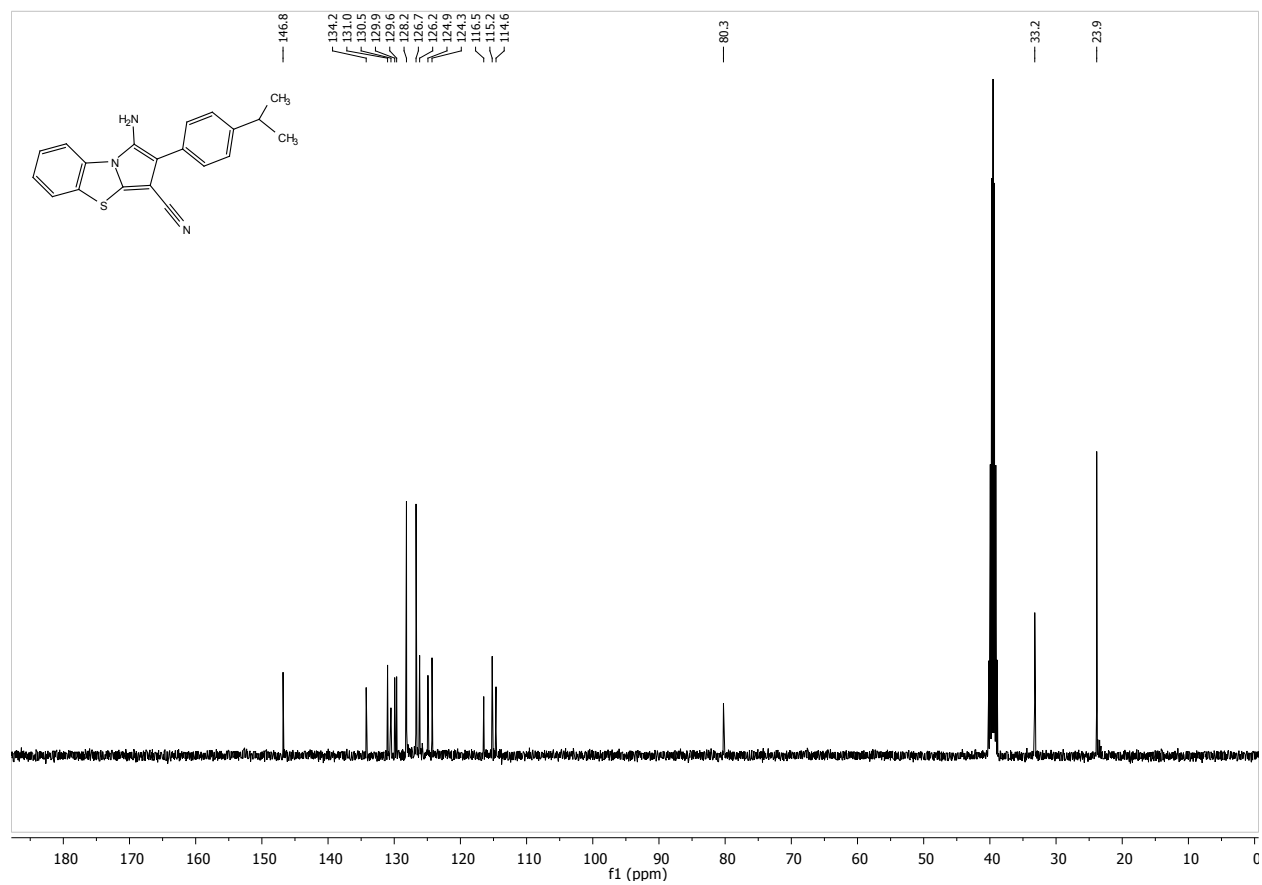
^1H NMR for compound **4i** (100 MHz, DMSO- d_6)



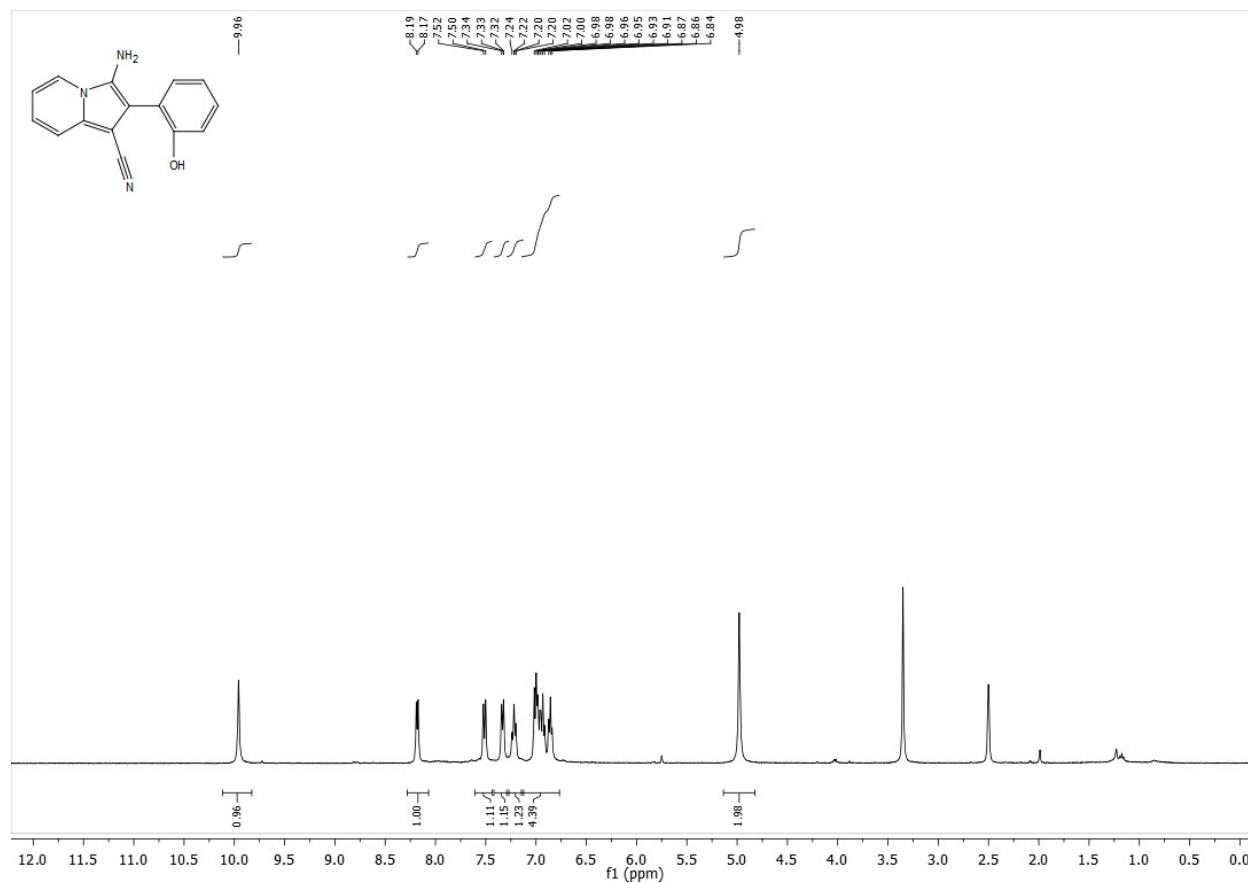
^1H NMR for compound **4j** (400 MHz, DMSO- d_6)



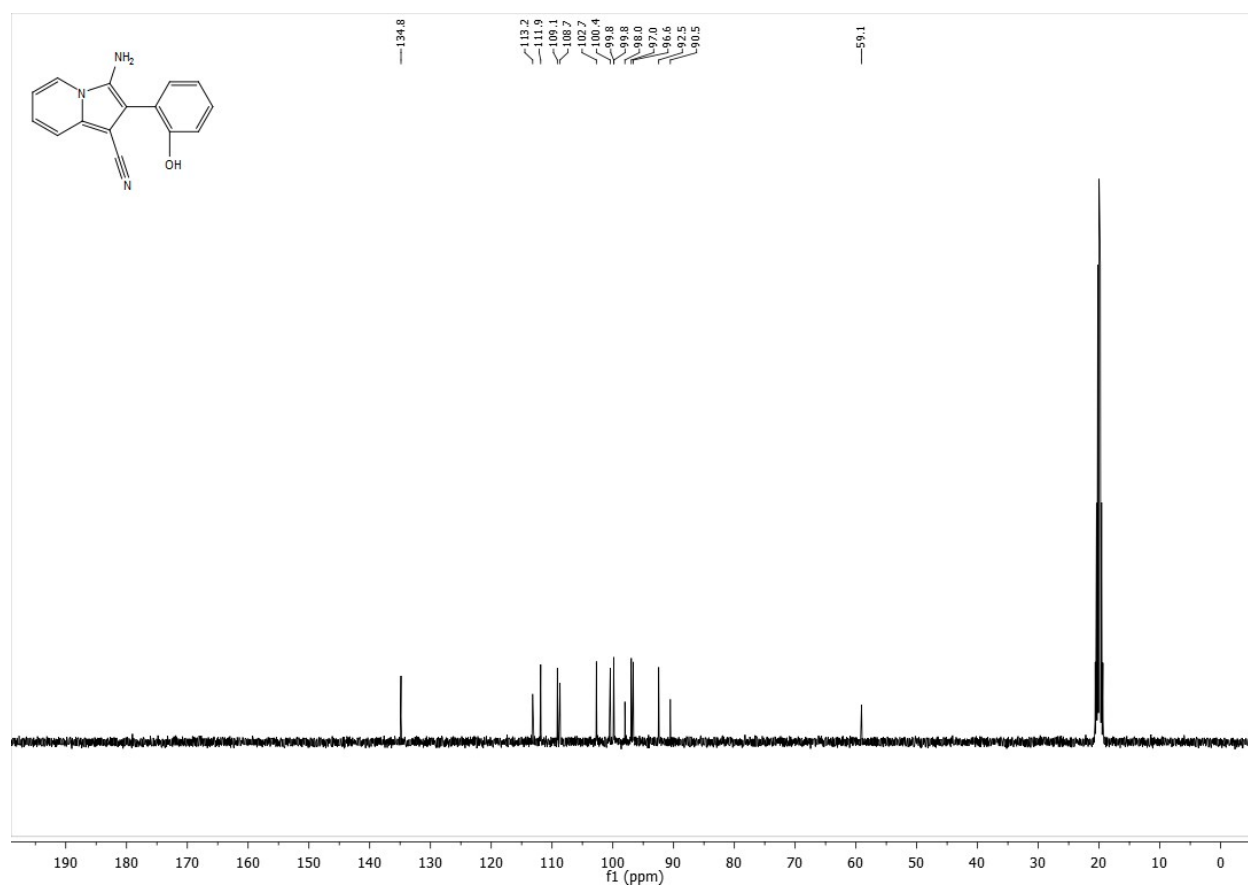
^{13}C NMR for compound **4j** (100 MHz, DMSO- d_6)



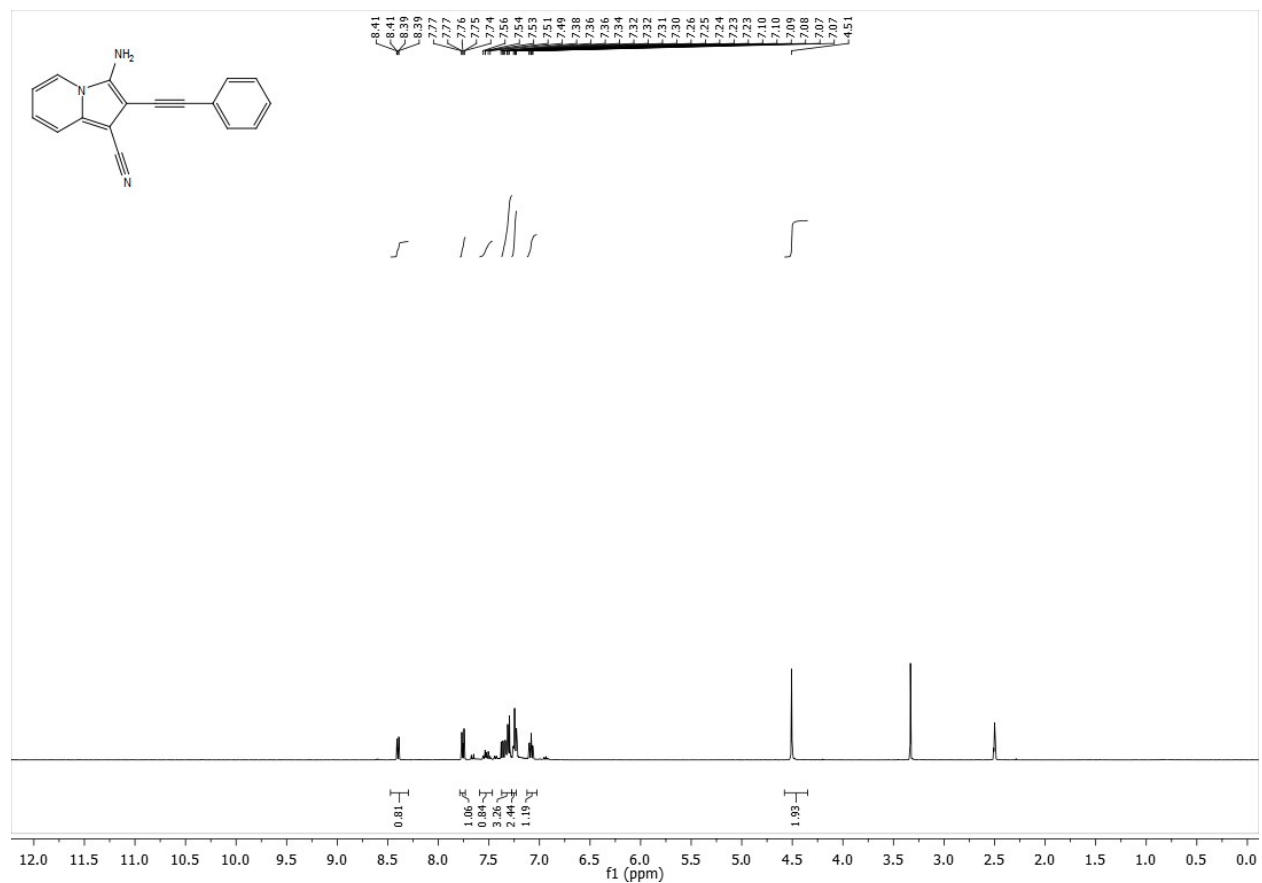
^1H NMR for compound **4k** (400 MHz, DMSO-d_6)



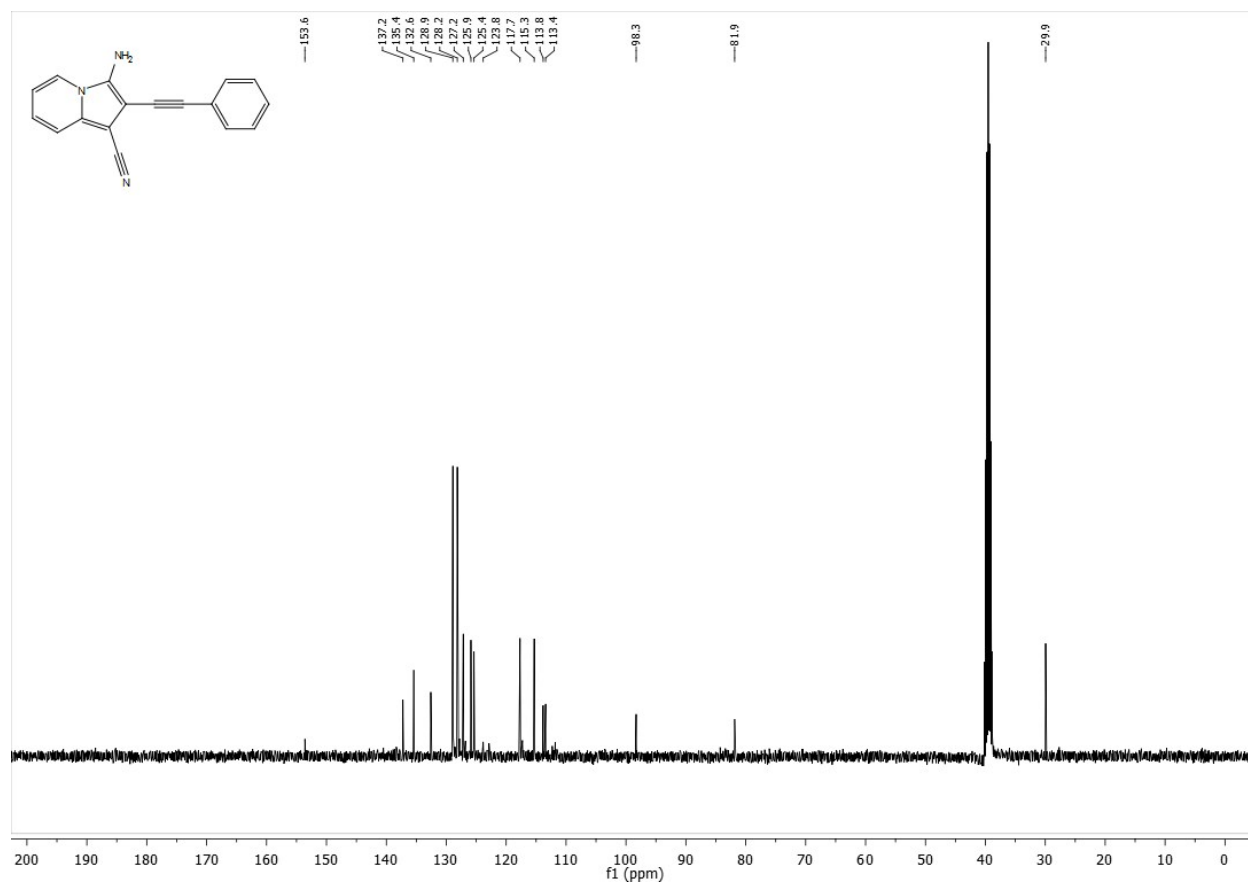
^{13}C NMR for compound **4k** (100 MHz, DMSO- d_6)



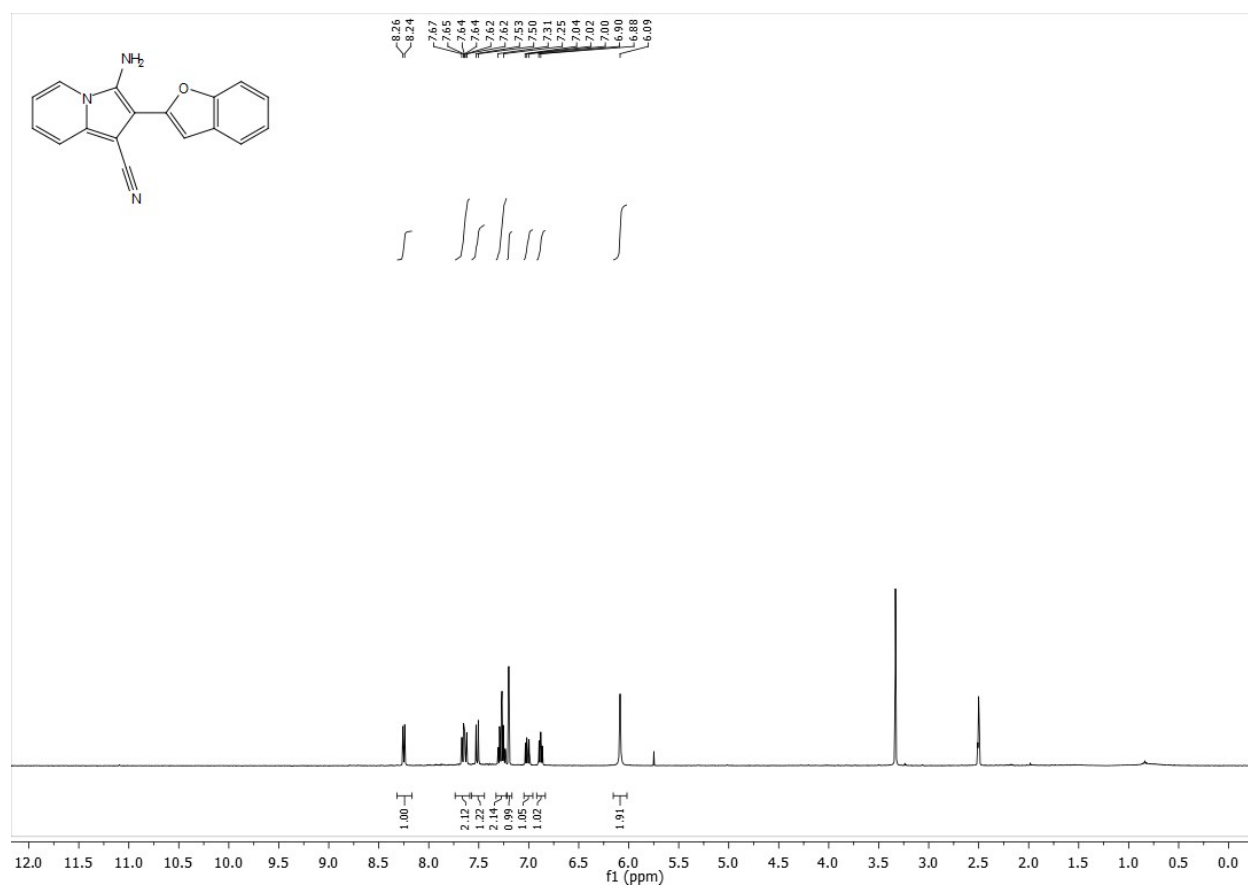
^1H NMR for compound **4l** (400 MHz, DMSO- d_6)



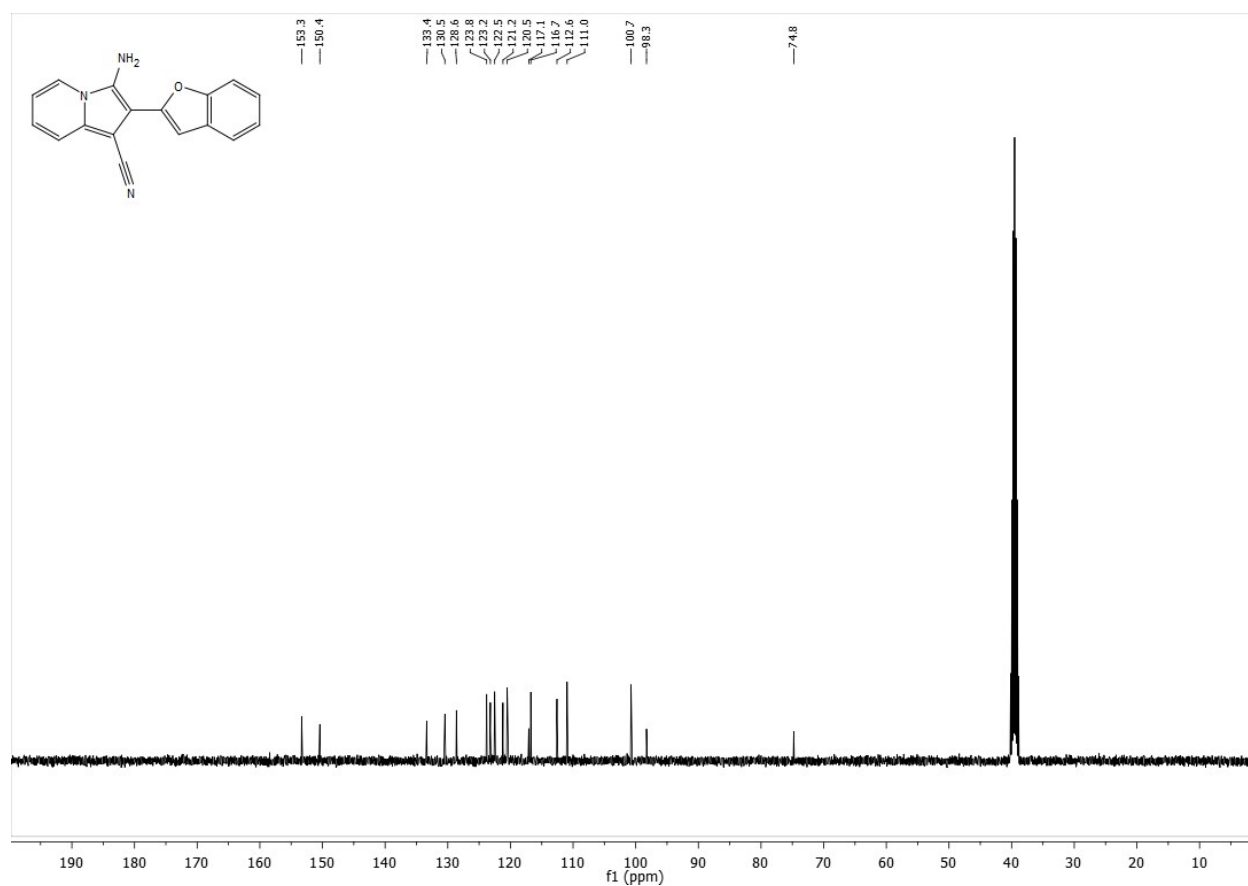
^{13}C NMR for compound **4l** (100 MHz, DMSO-d_6)



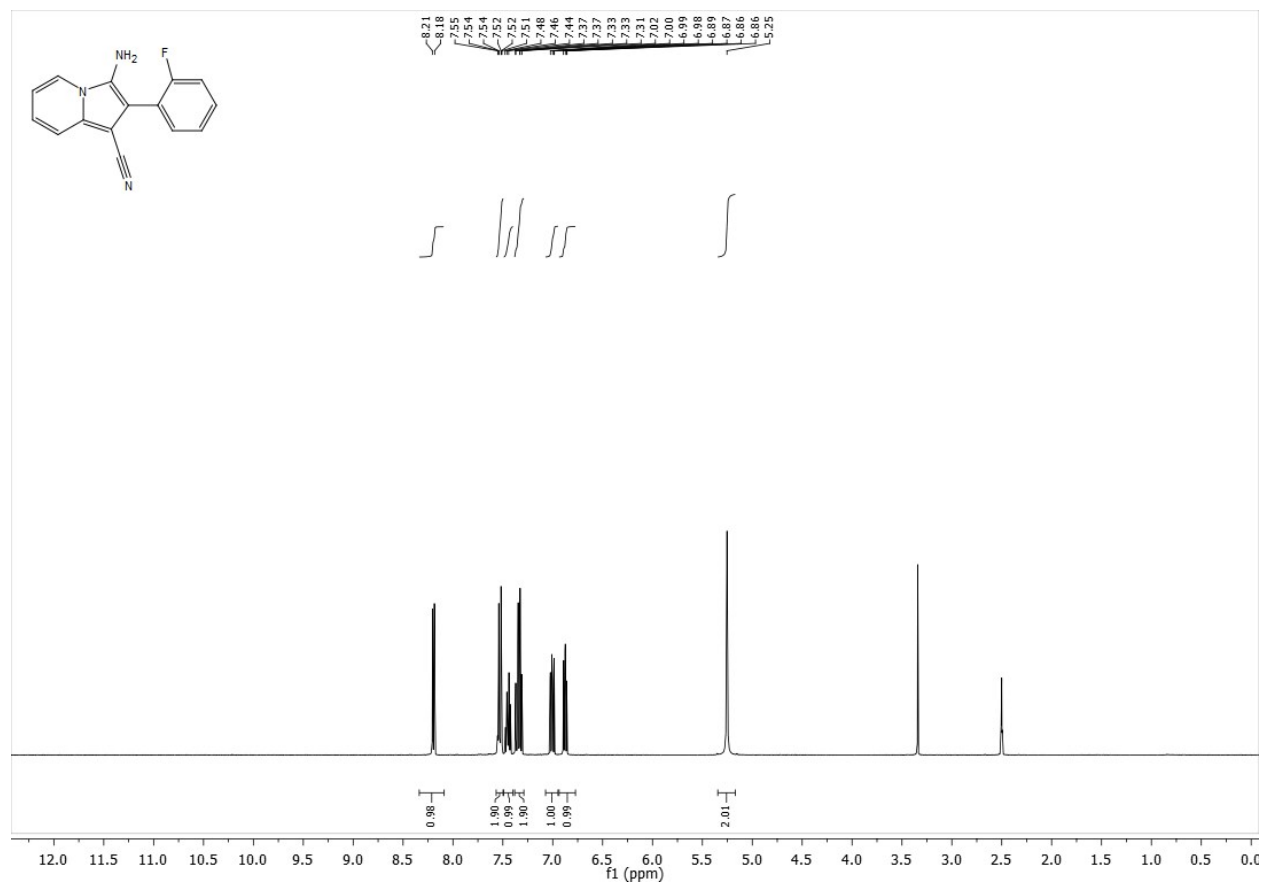
^1H NMR for compound **4m** (400 MHz, DMSO- d_6)



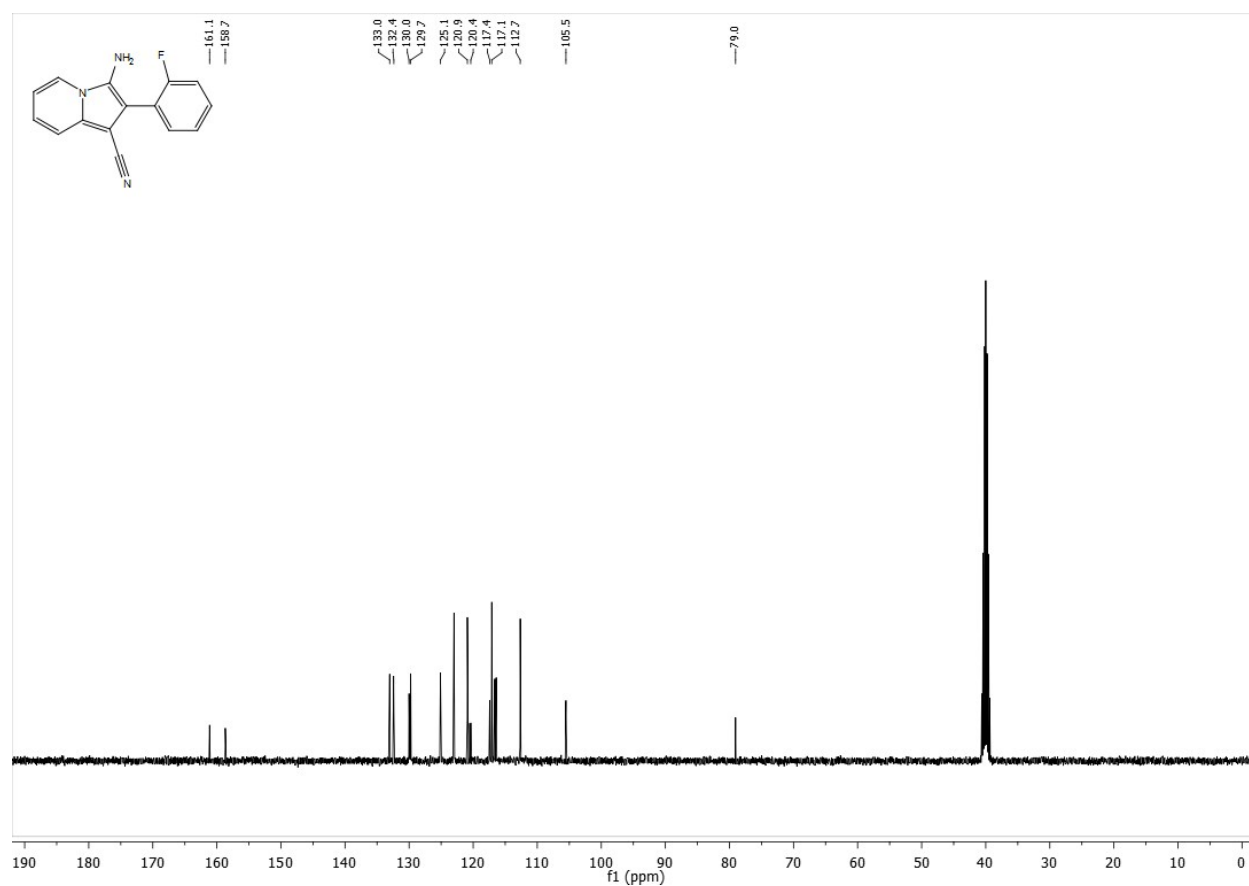
^{13}C NMR for compound **4m** (100 MHz, DMSO- d_6)



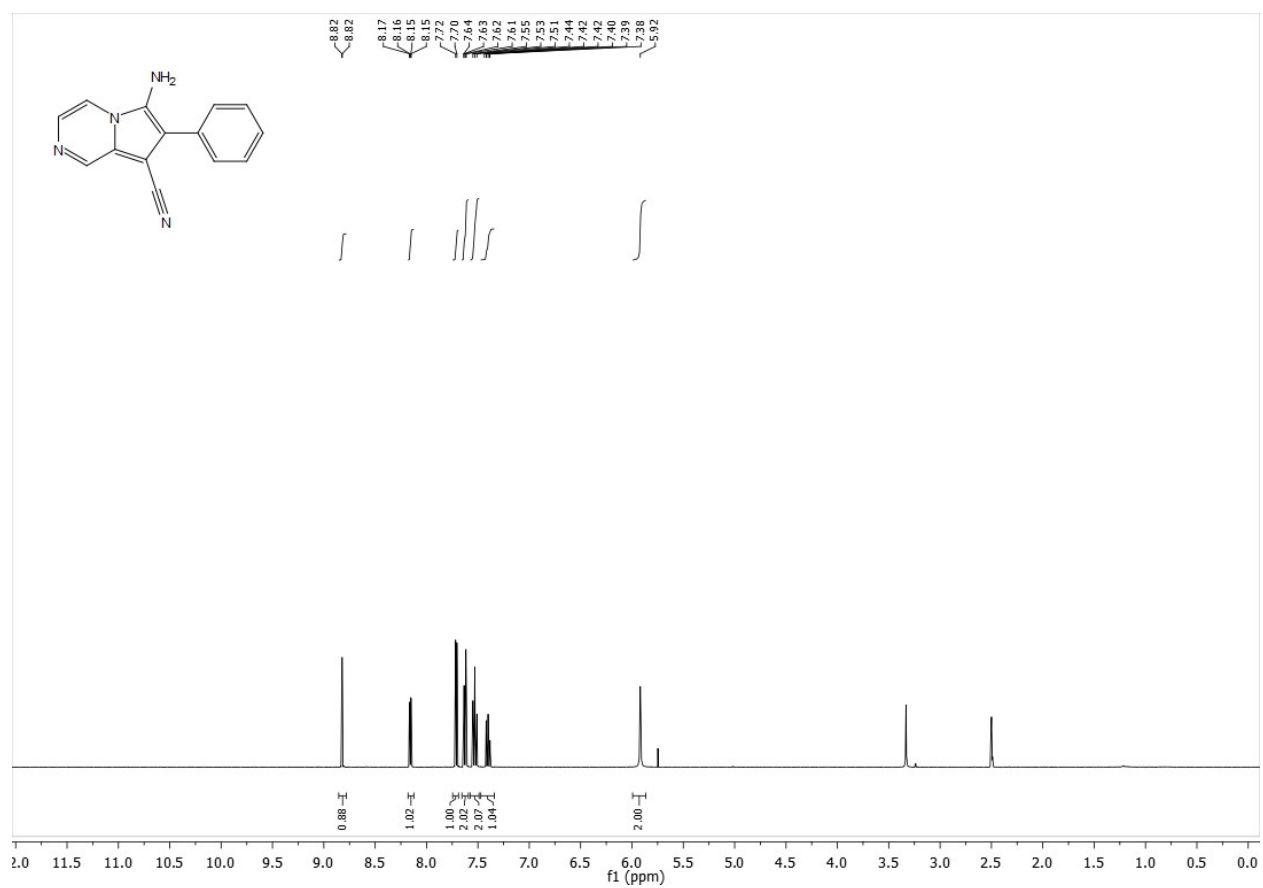
^1H NMR for compound **4n** (400 MHz, DMSO- d_6)



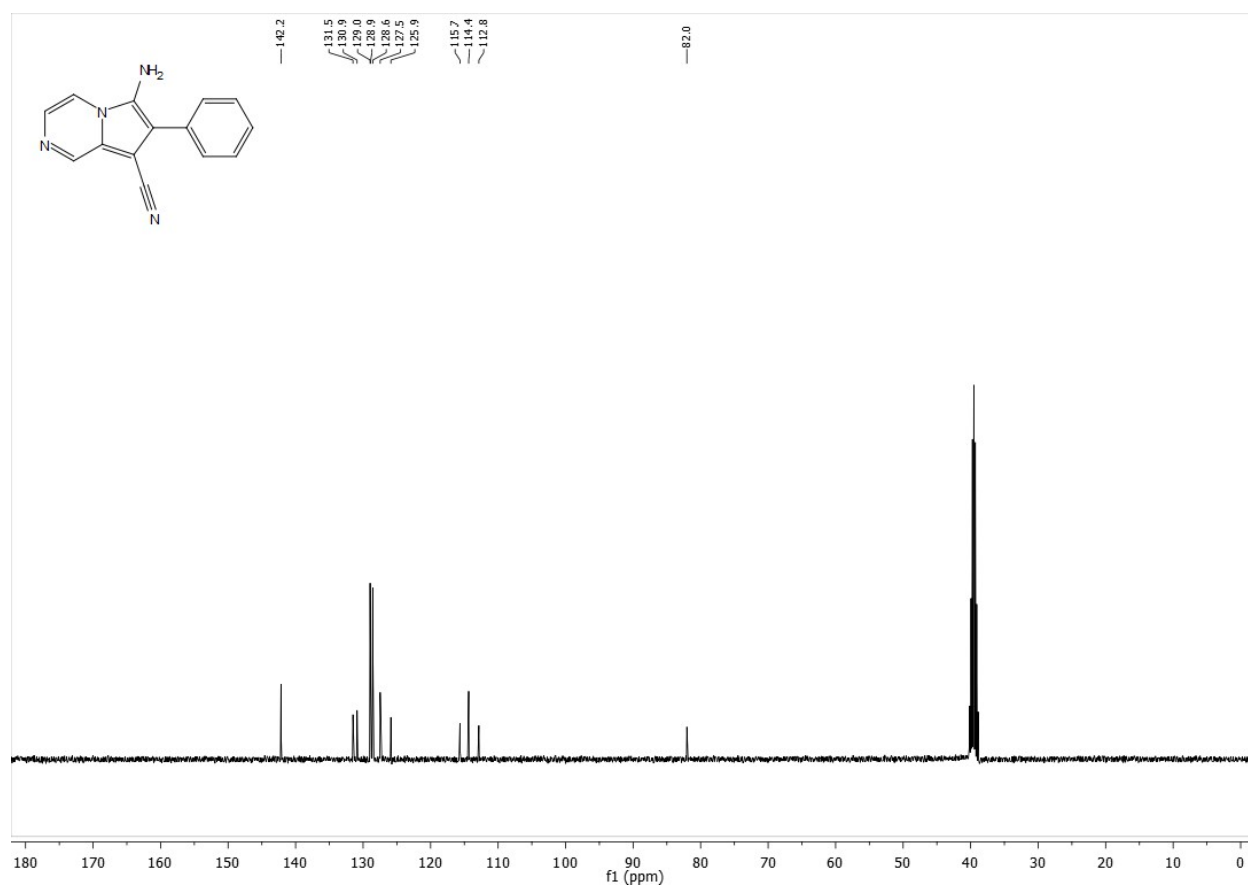
^{13}C NMR for compound **4n** (100 MHz, DMSO- d_6)



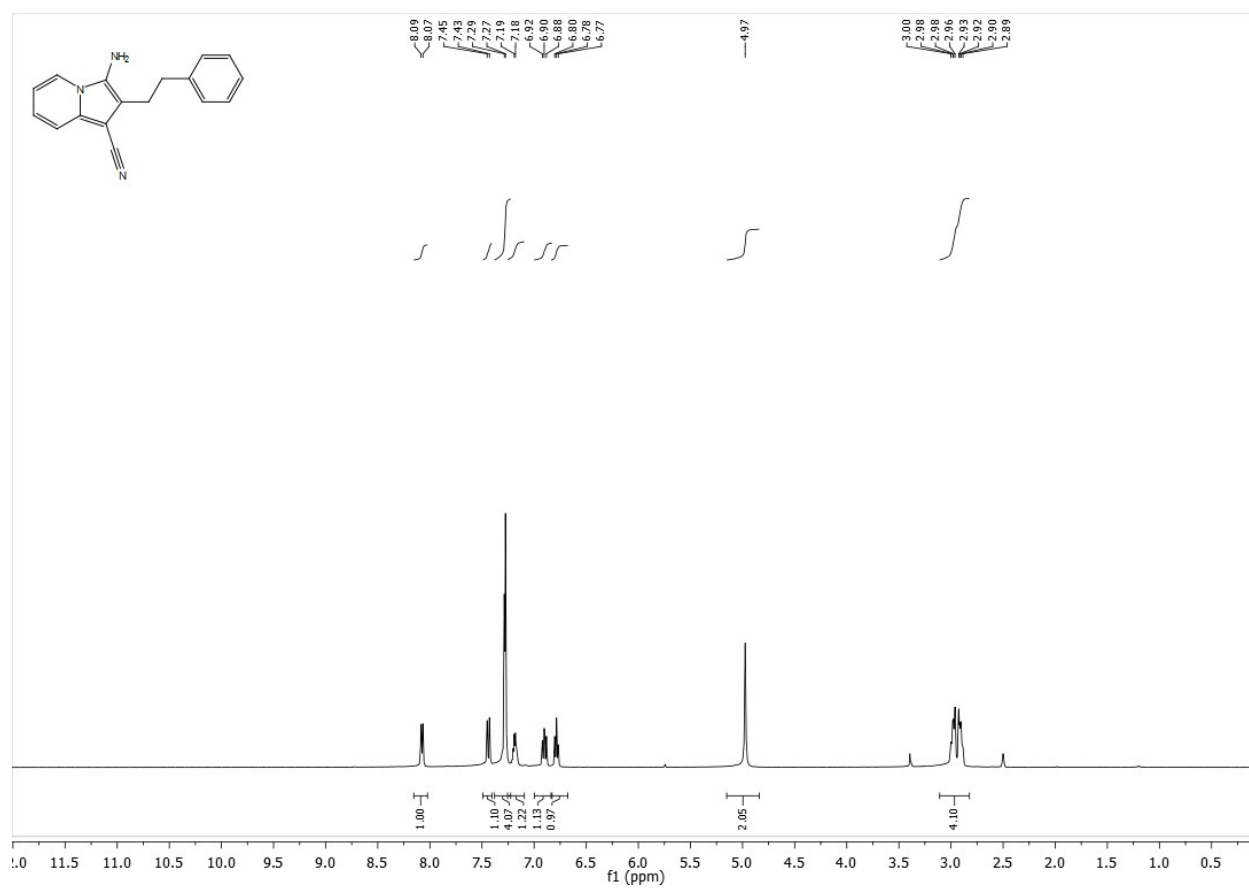
^1H NMR for compound **4o** (400 MHz, DMSO- d_6)



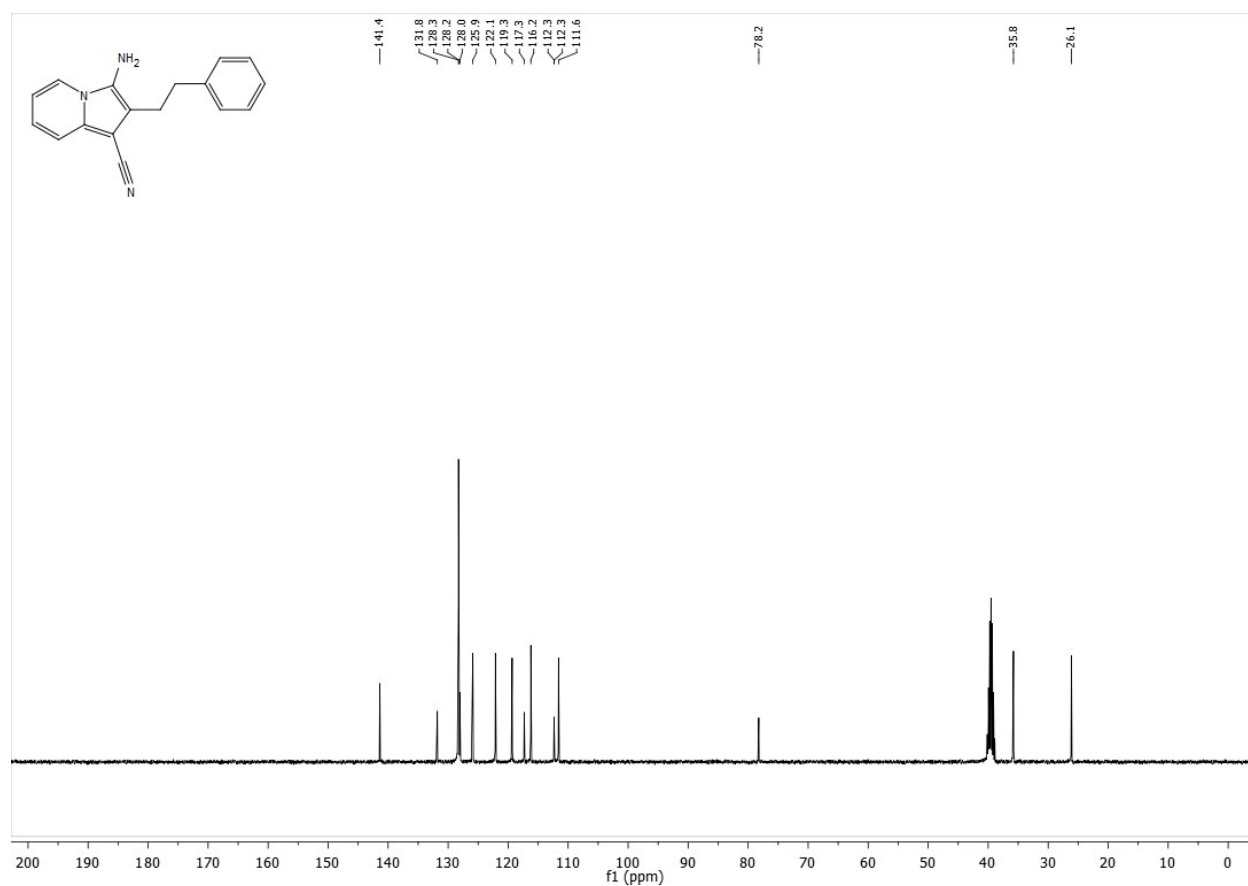
^{13}C NMR for compound **4o** (100 MHz, DMSO- d_6)



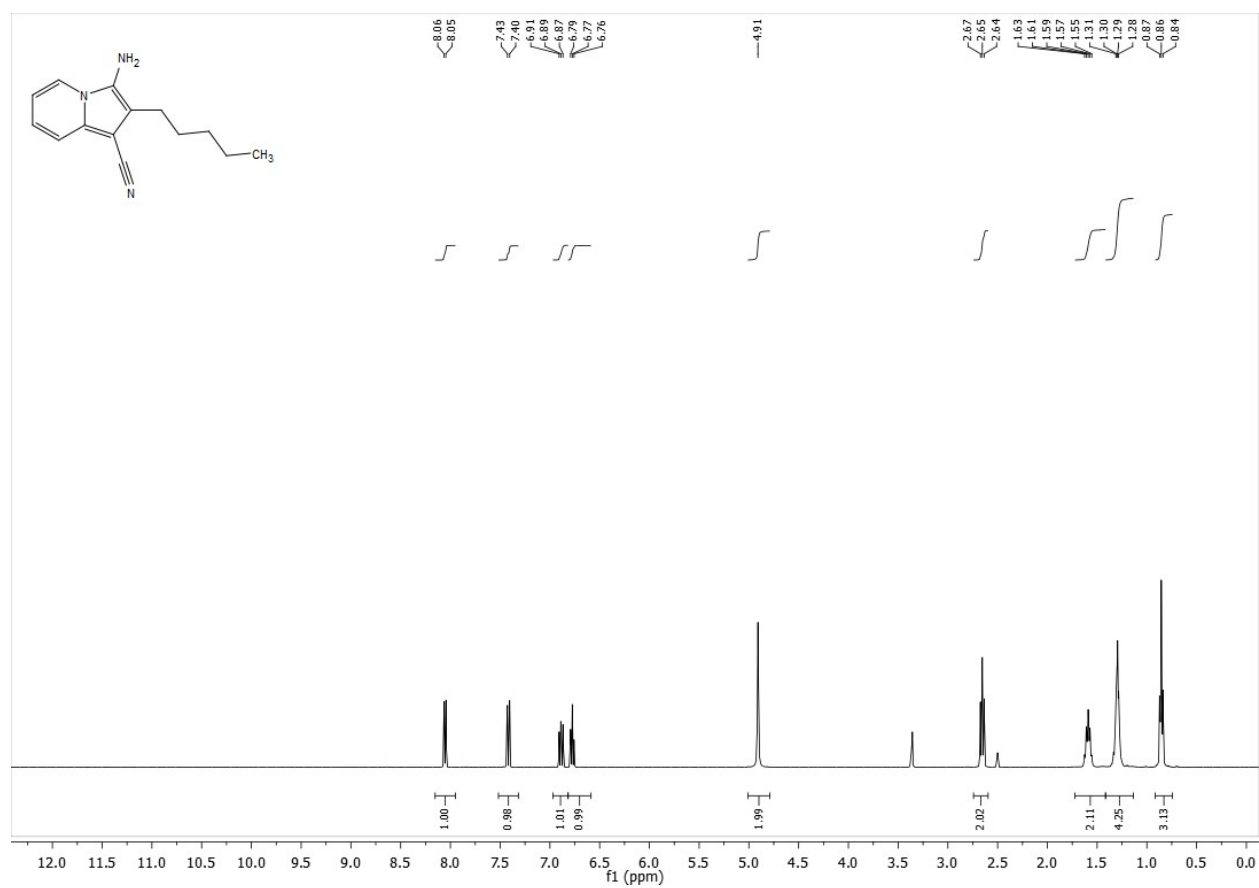
^1H NMR for compound **4p** (400 MHz, DMSO- d_6)



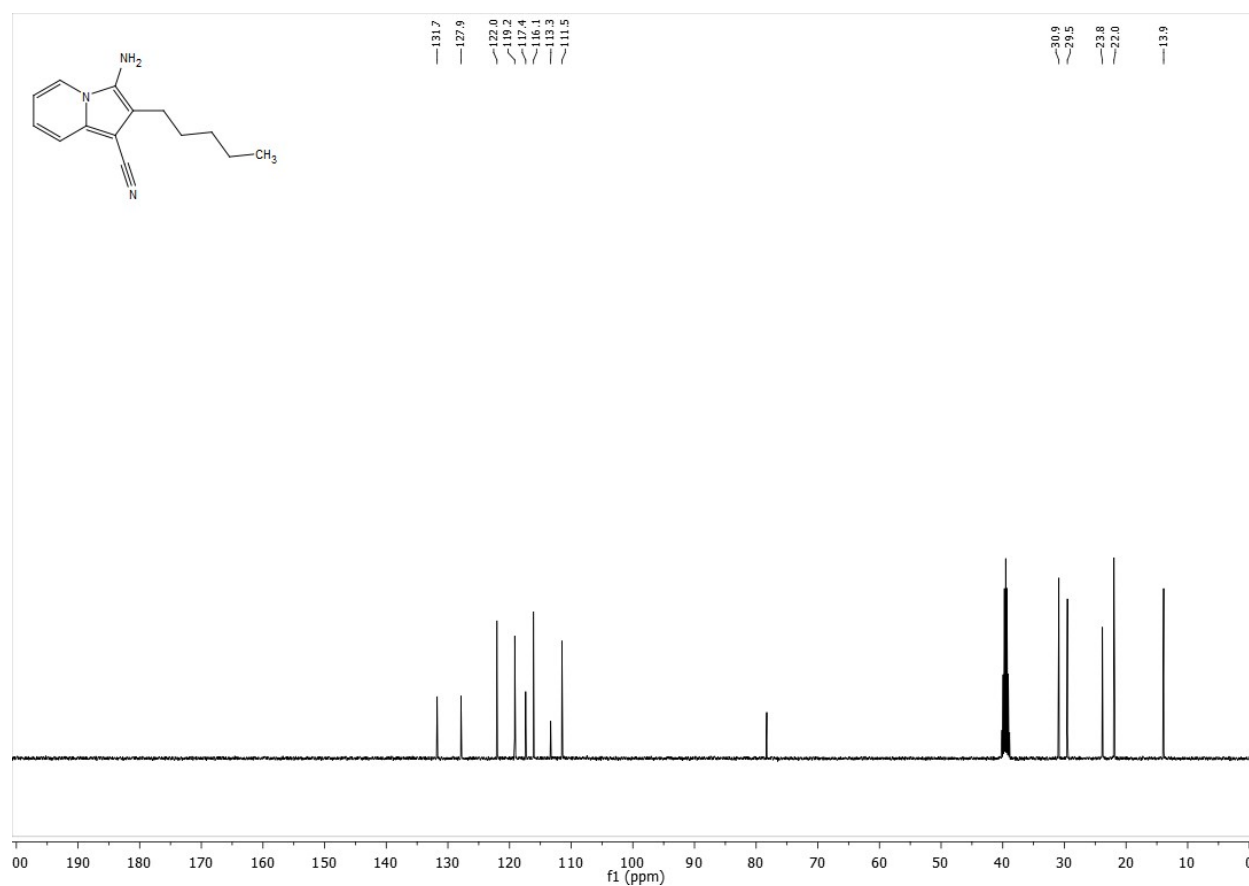
^{13}C NMR for compound **4p** (100 MHz, DMSO- d_6)



^1H NMR for compound **4q** (400 MHz, DMSO-d_6)

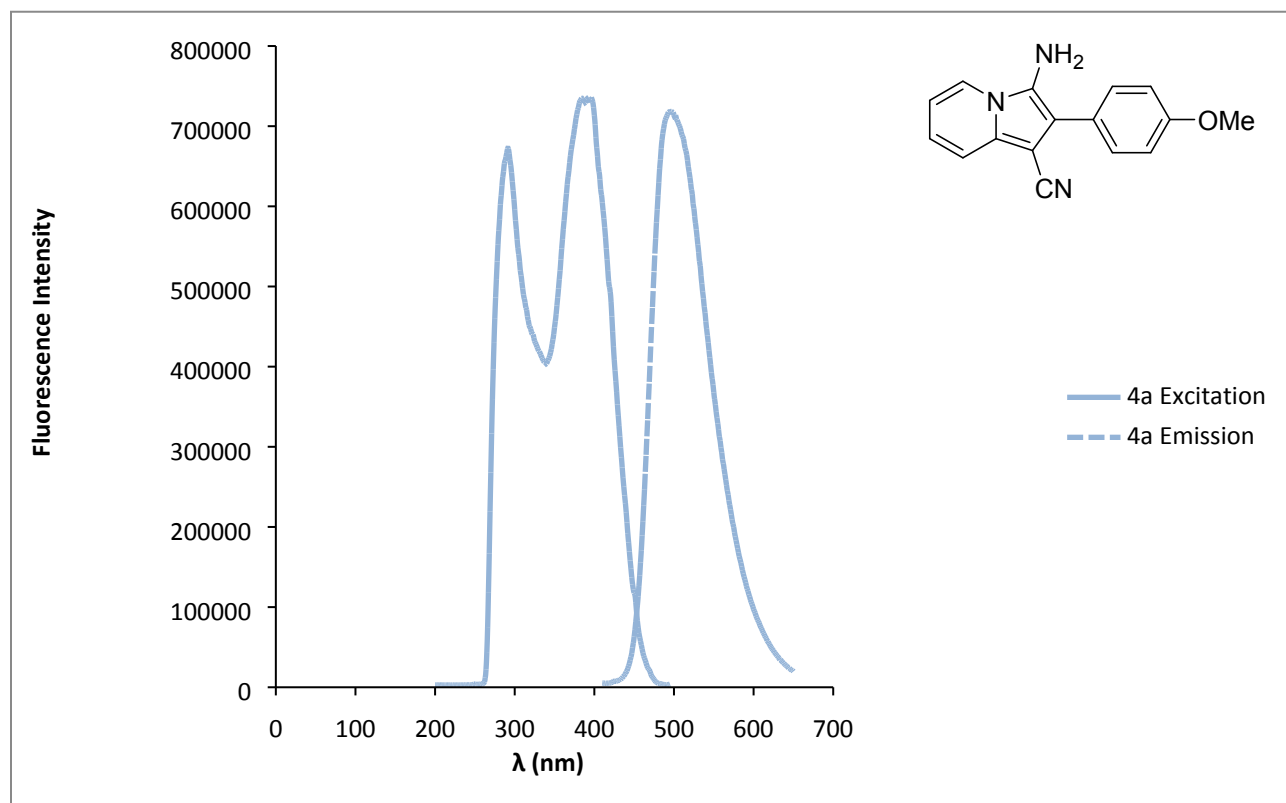


^{13}C NMR for compound **4q** (100 MHz, DMSO- d_6)

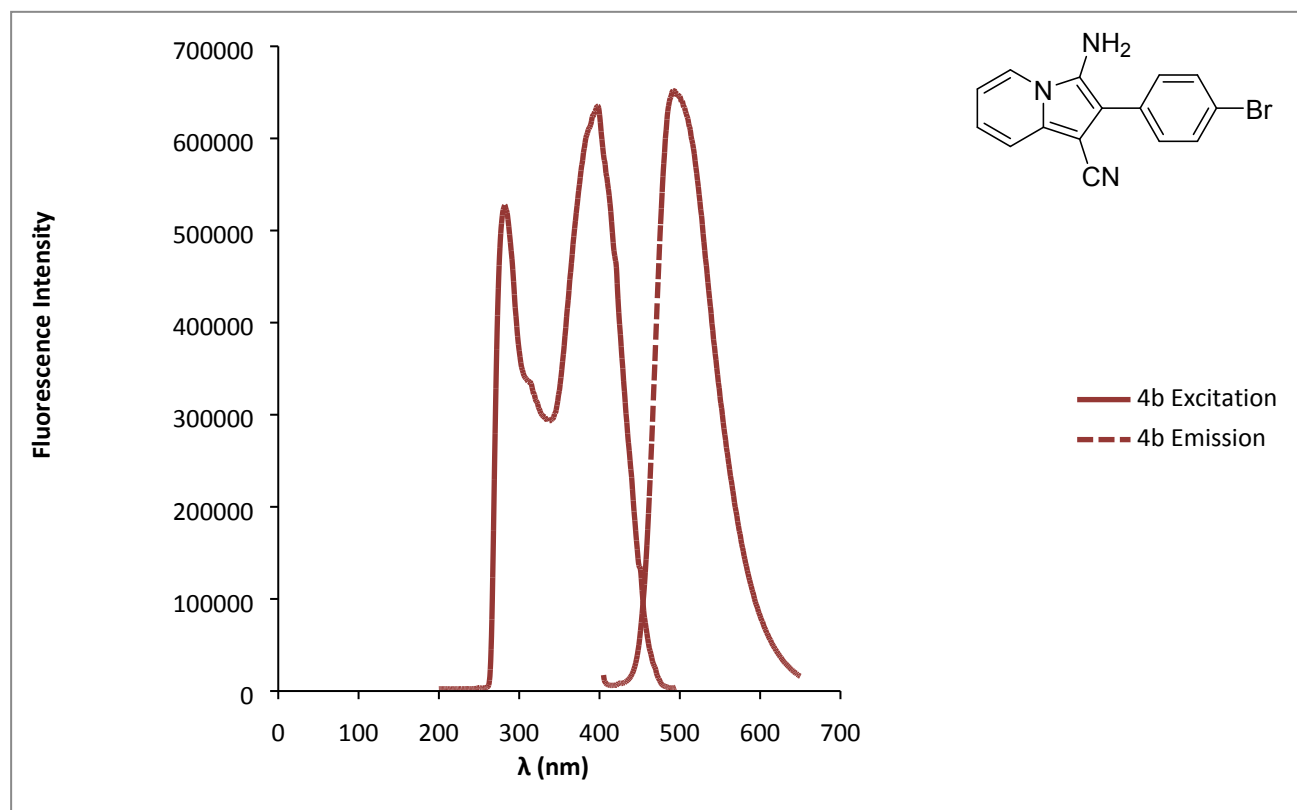


Fluorescent spectra for compounds 4a-4o

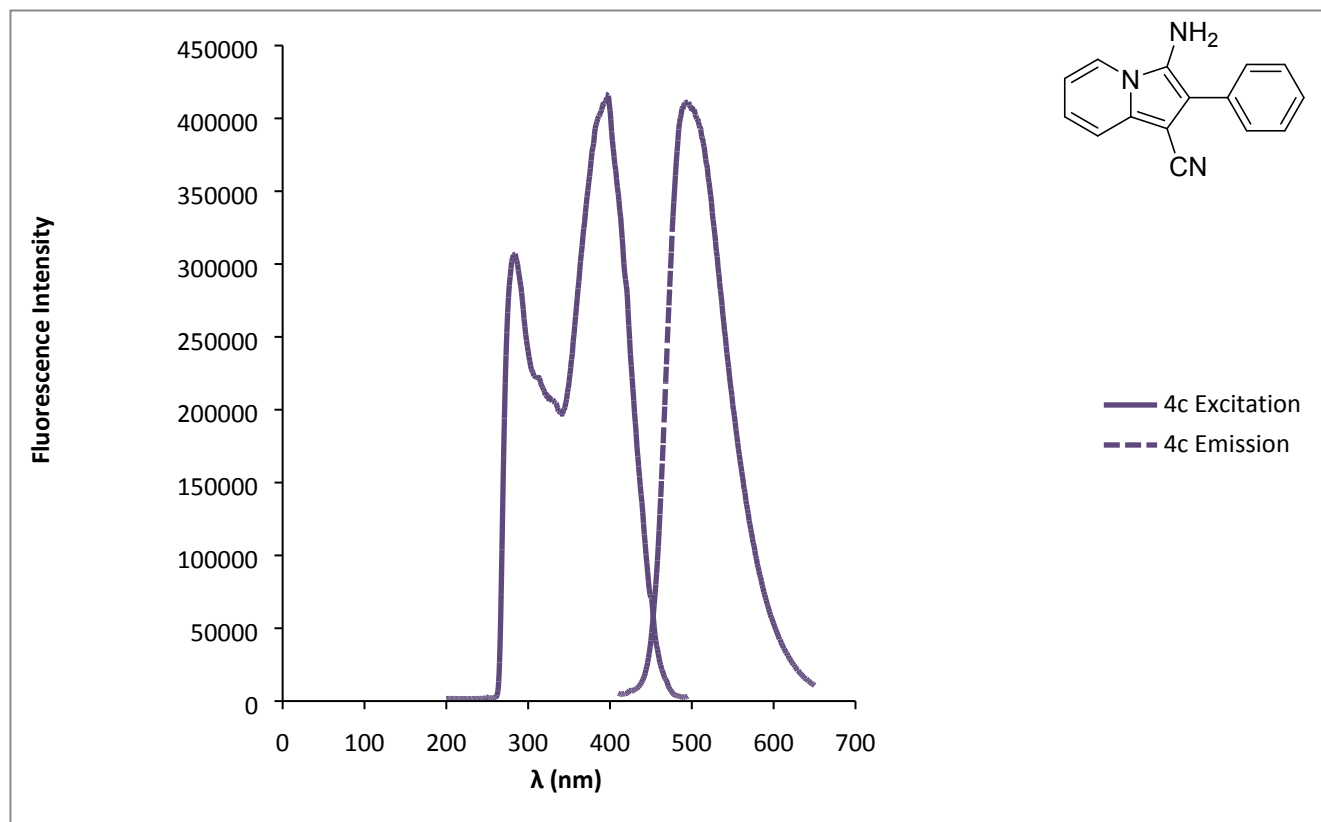
Fluorescent spectra for compound **4a** (10 μ M, DMF, λ_{ex} = 292, 393 nm; λ_{em} = 497 nm)



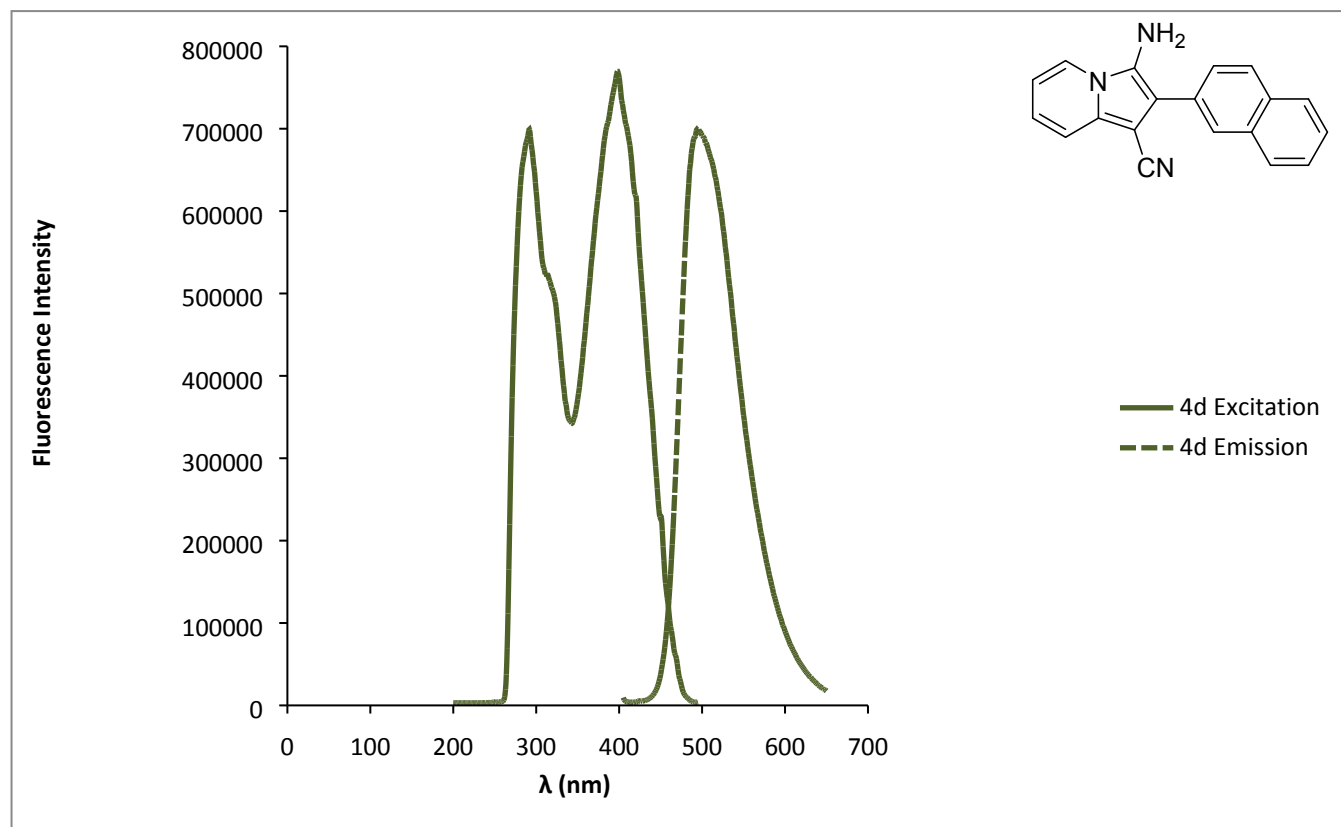
Fluorescent spectra for compound **4b** (10 μ M, DMF, λ_{ex} = 282, 398 nm; λ_{em} = 493 nm)



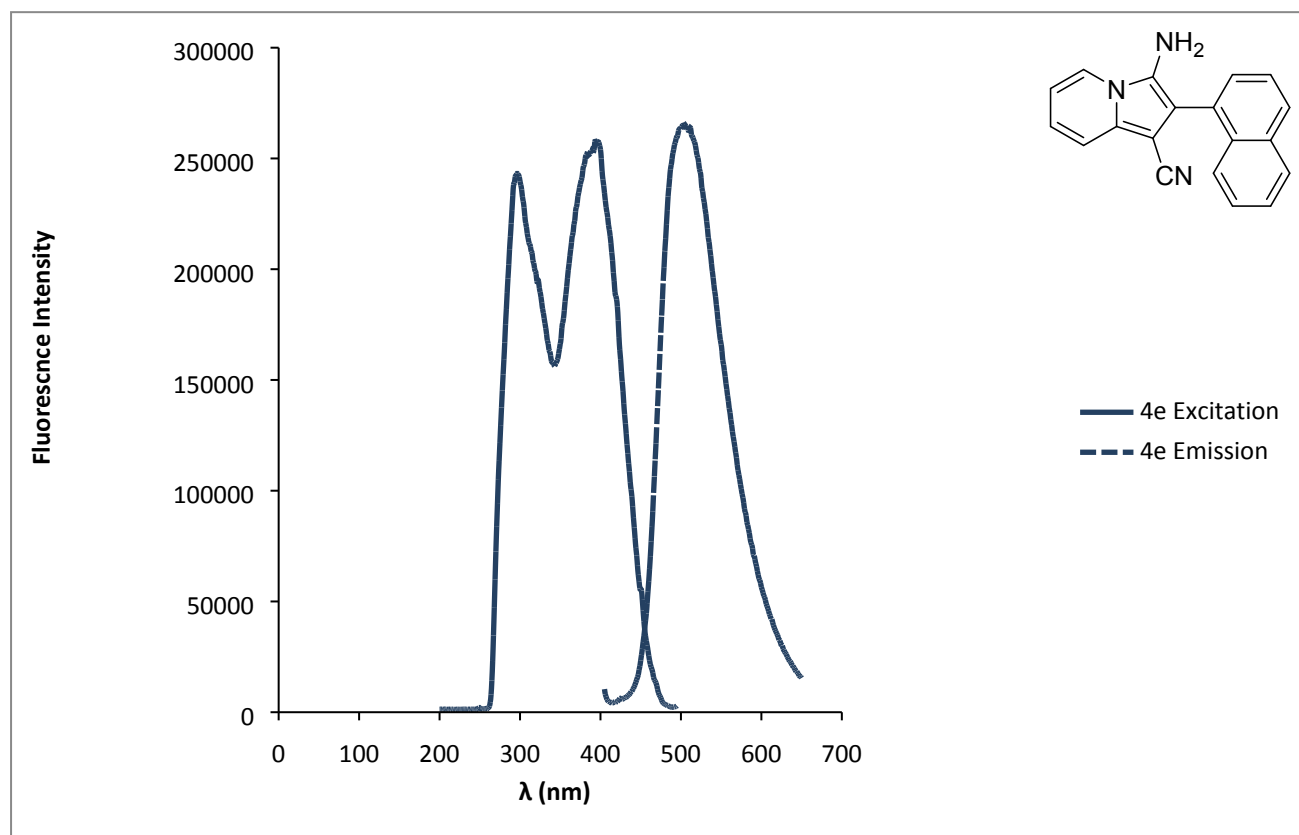
Fluorescent spectra for compound **4c** (10 μ M, DMF, λ_{ex} = 287, 398 nm; λ_{em} = 496 nm)



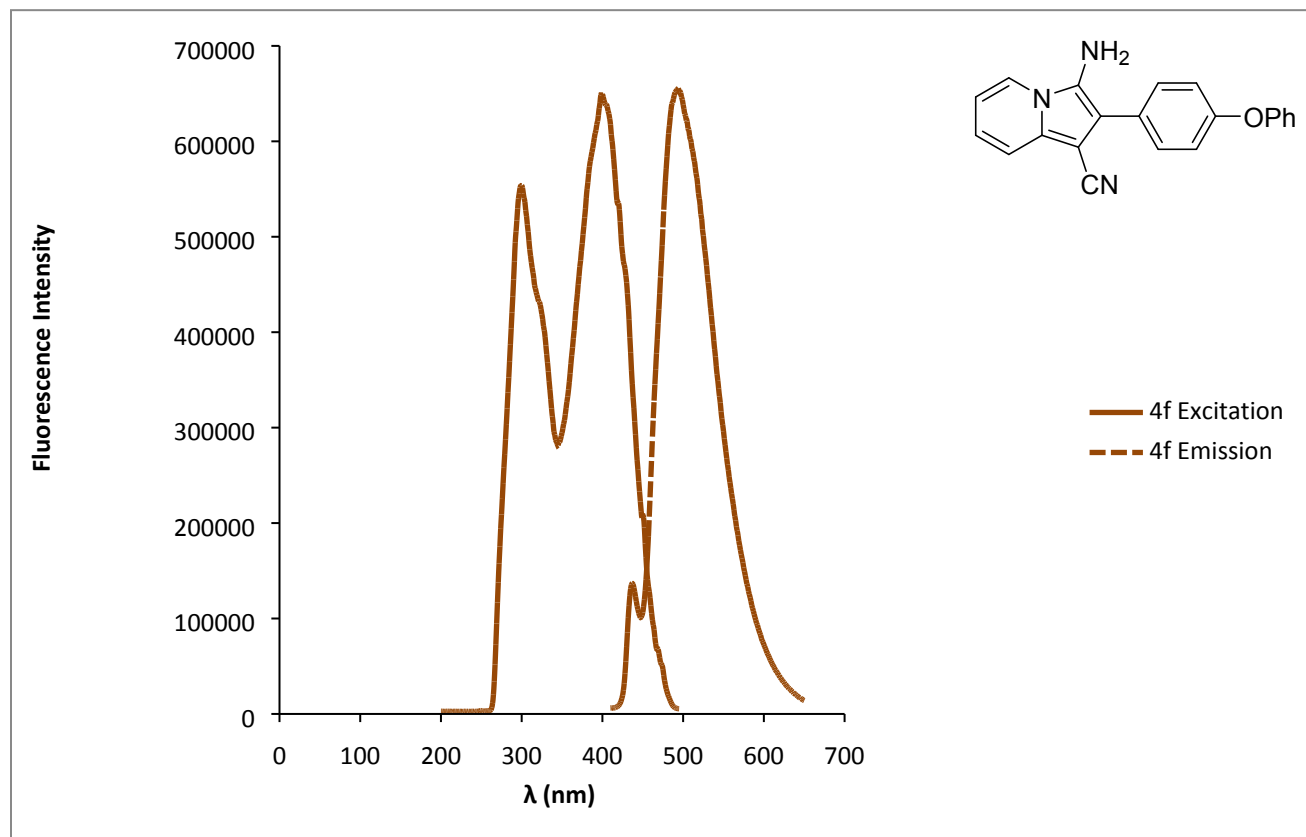
Fluorescent spectra for compound **4d** (10 μ M, DMF, λ_{ex} = 292, 398 nm; λ_{em} = 505 nm)



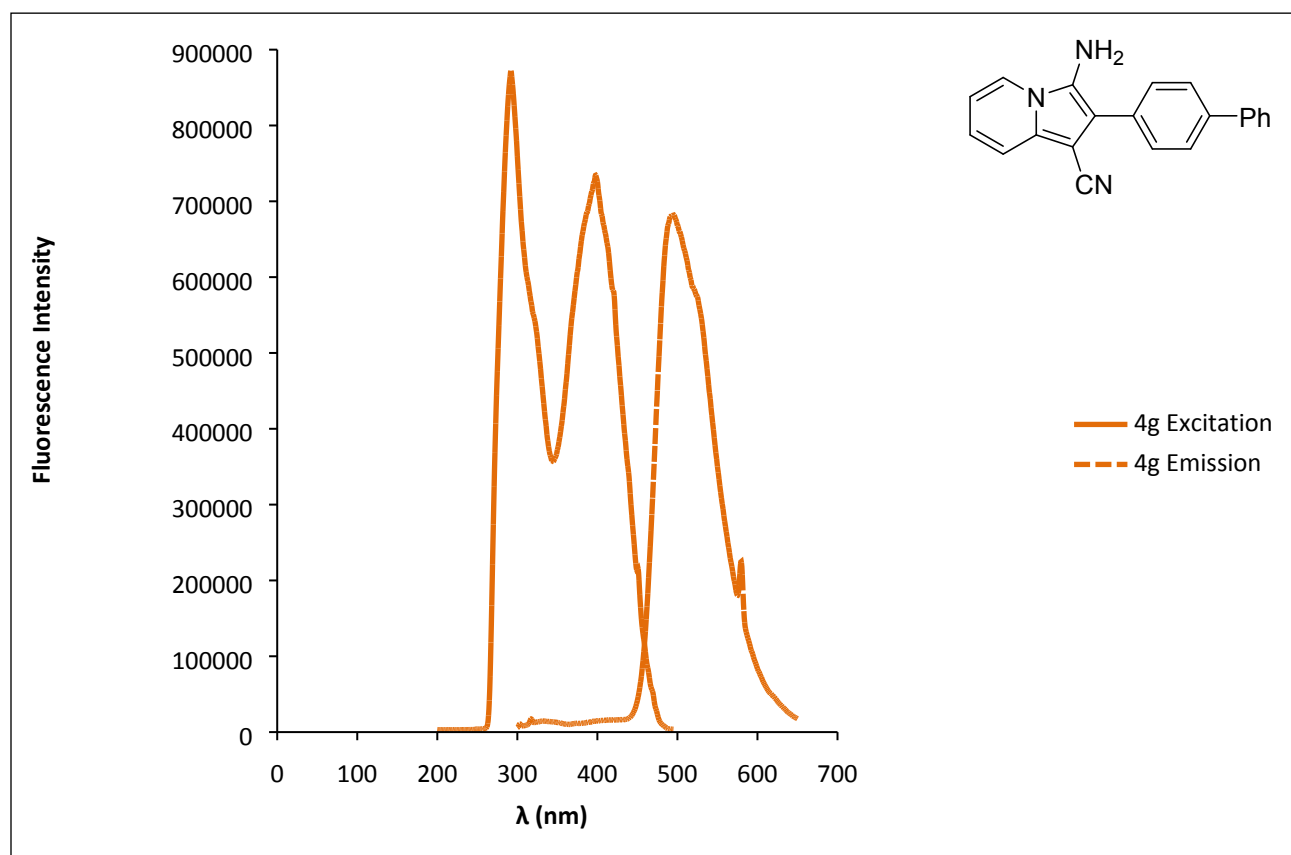
Fluorescent spectra for compound **4e** (10 μ M, DMF, λ_{ex} = 297, 397 nm; λ_{em} = 512 nm)



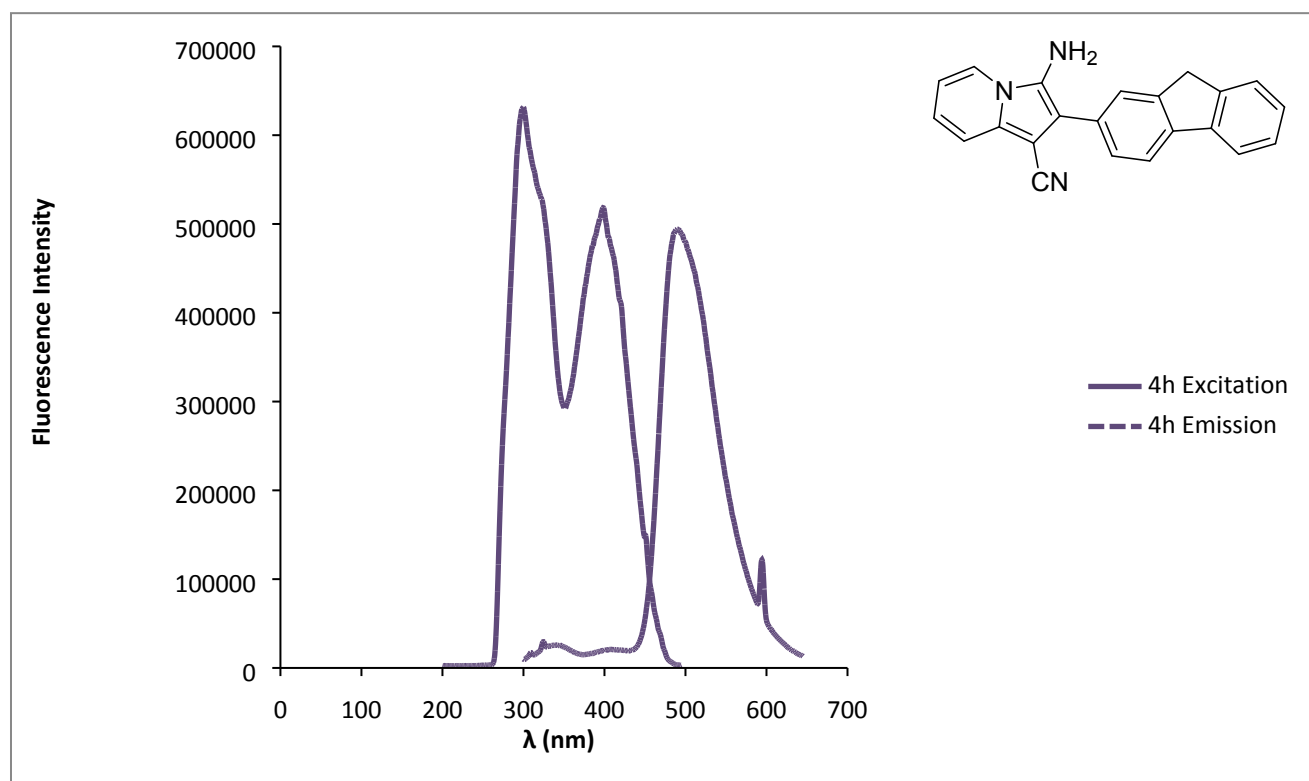
Fluorescent spectra for compound **4f** (10 μ M, DMF, λ_{ex} = 300, 400 nm; λ_{em} = 494 nm)



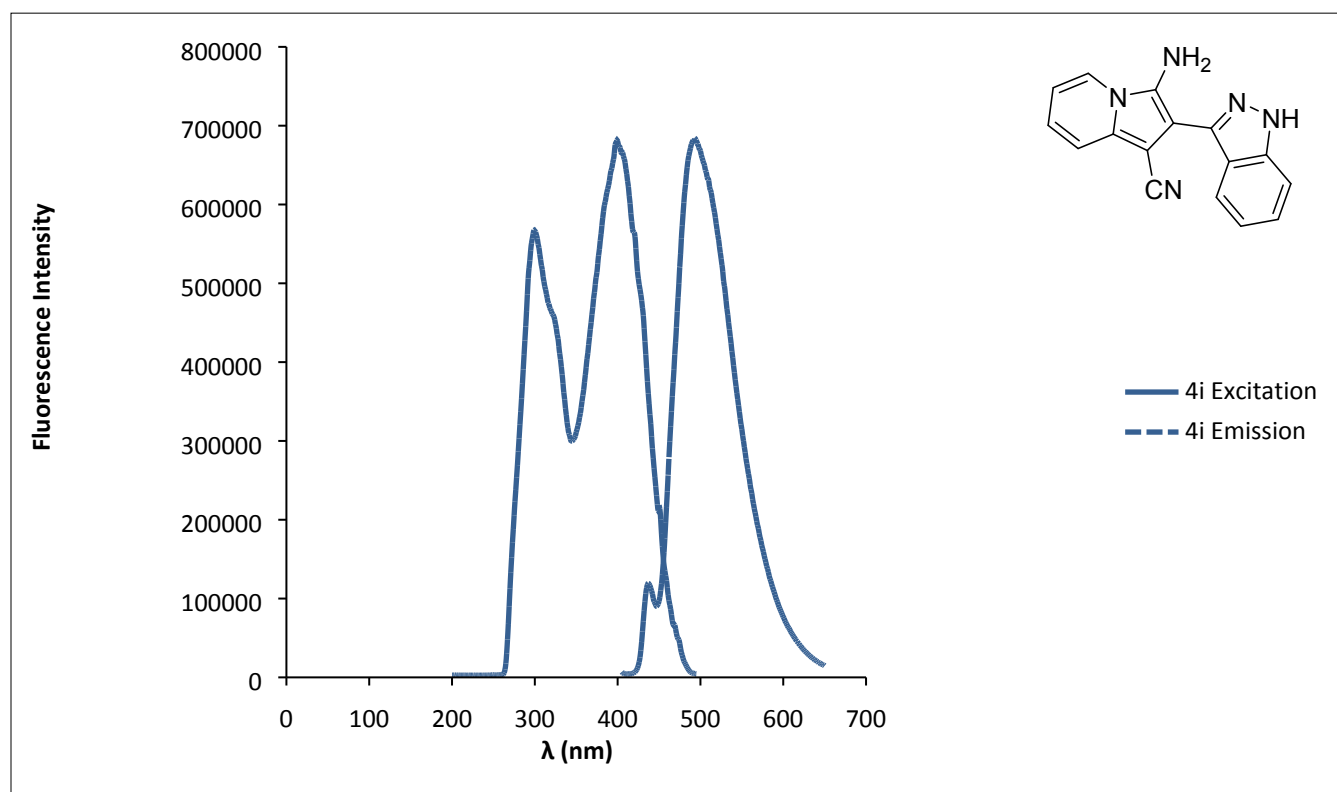
Fluorescent spectra for compound **4g** (10 μ M, DMF, λ_{ex} = 292, 398 nm; λ_{em} = 496 nm)



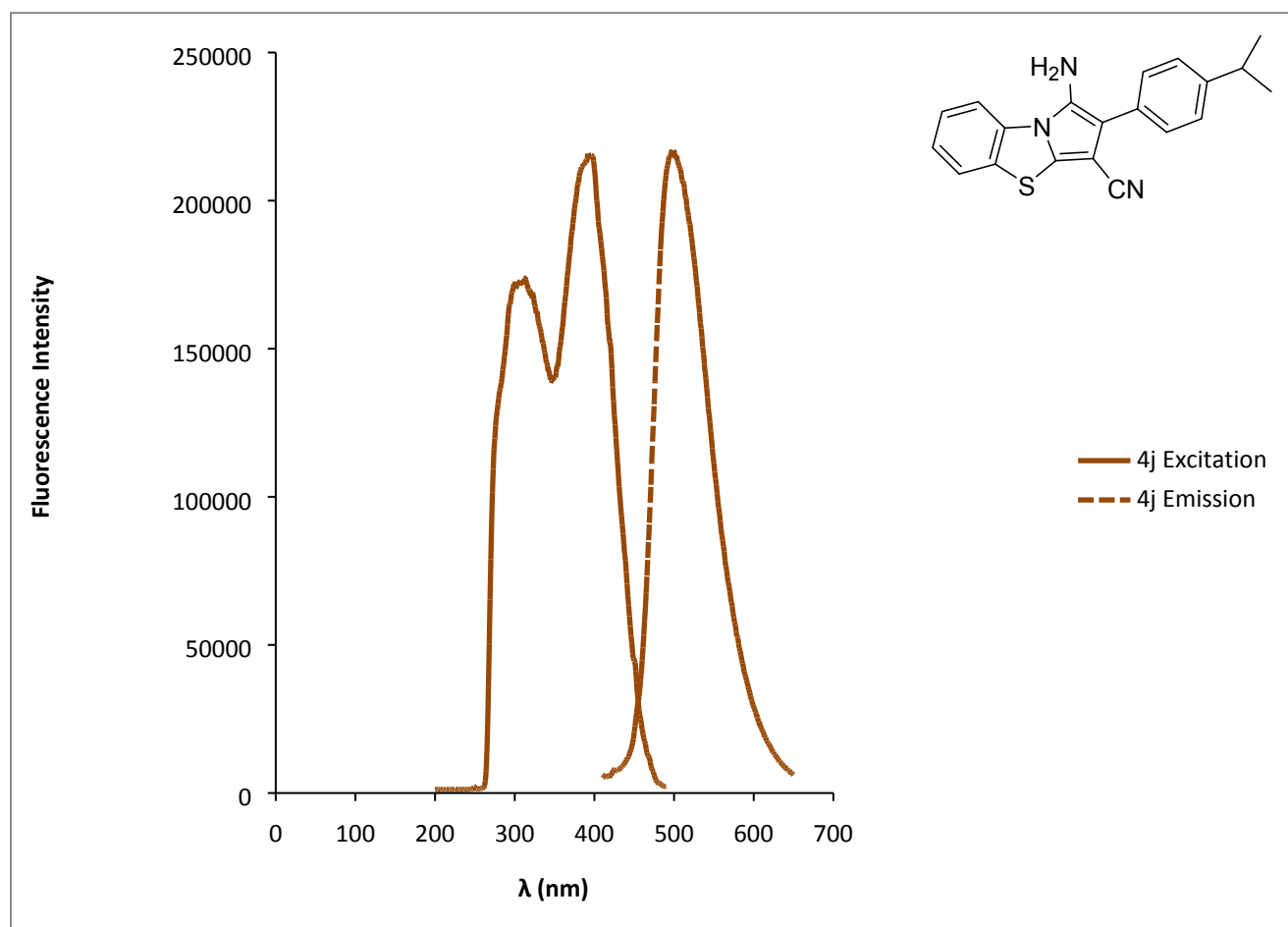
Fluorescent spectra for compound **4h** (10 μ M, DMF, λ_{ex} = 300, 398 nm; λ_{em} = 490 nm)



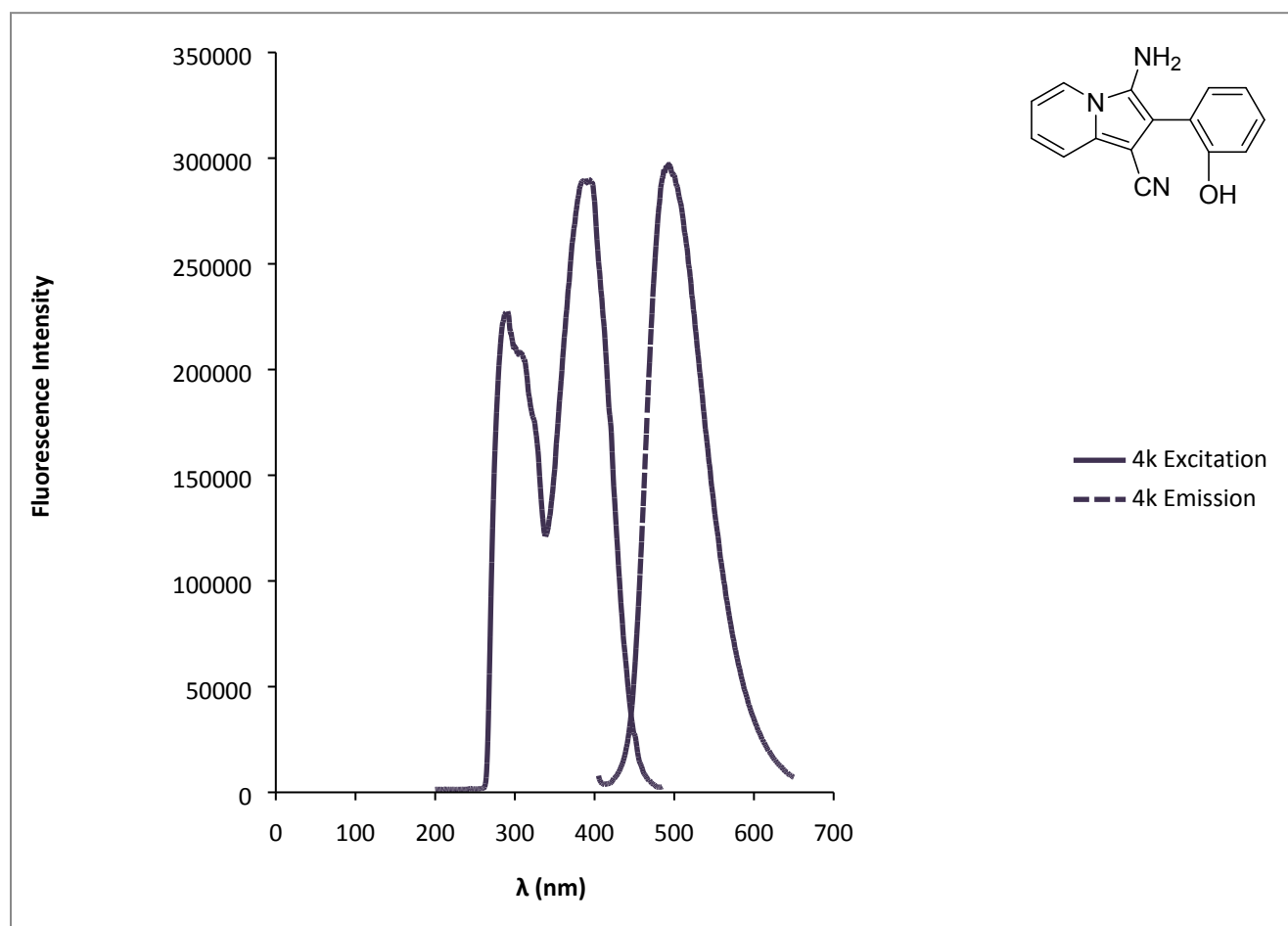
Fluorescent spectra for compound **4i** (10 μ M, DMF, λ_{ex} = 299, 399 nm; λ_{em} = 493 nm)



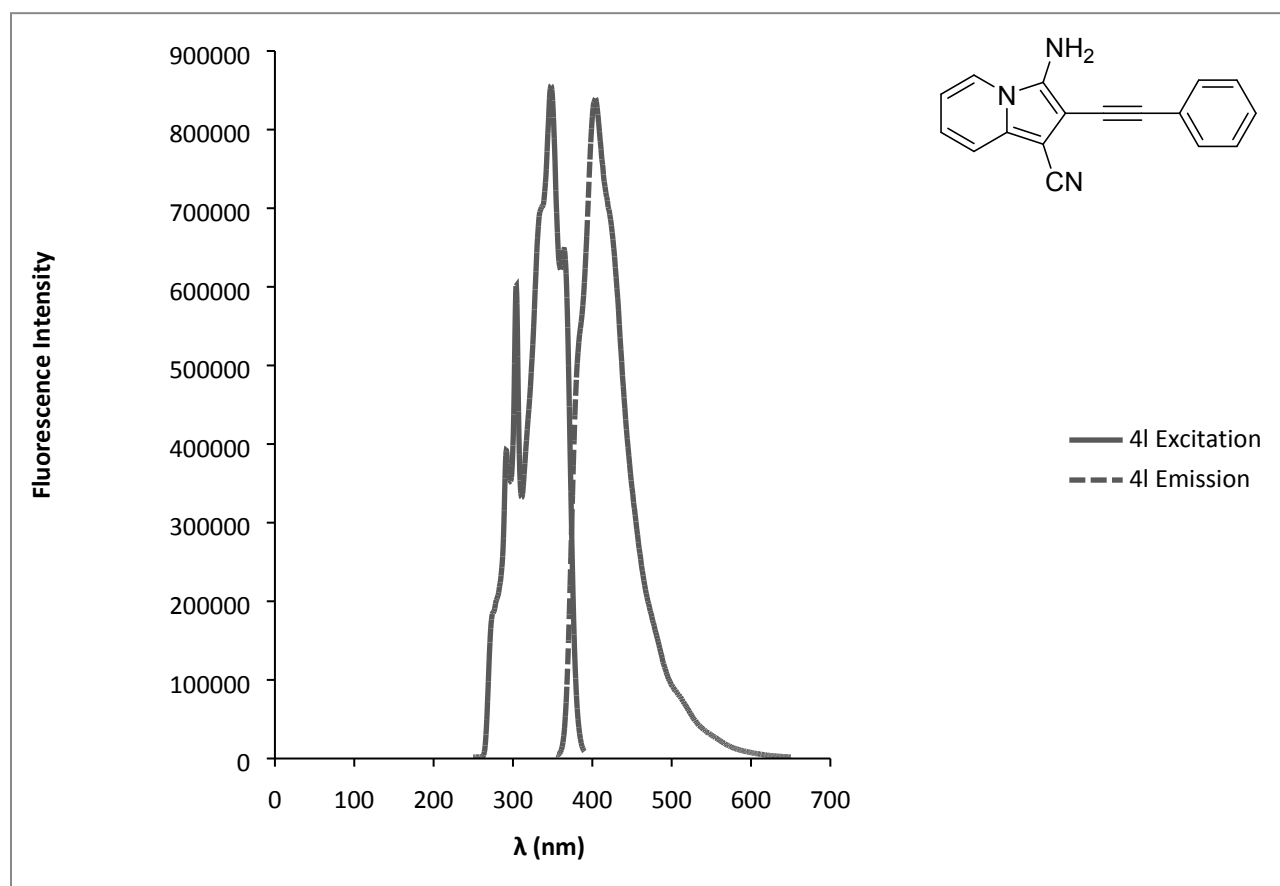
Fluorescent spectra for compound **4j** (10 μ M, DMF, λ_{ex} = 313, 392 nm; λ_{em} = 498 nm)



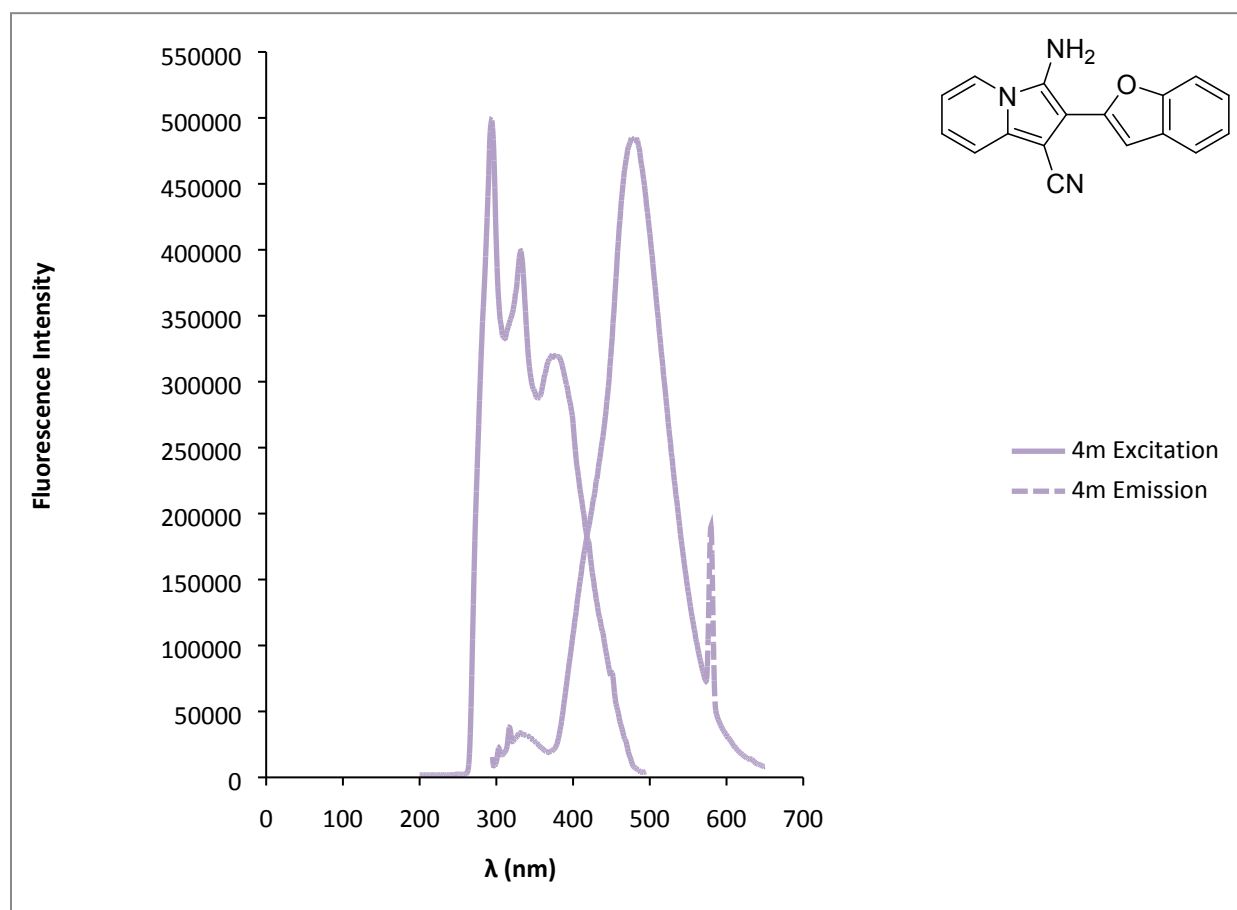
Fluorescent spectra for compound **4k** (10 μ M, DMF, λ_{ex} = 291, 392 nm; λ_{em} = 494 nm)



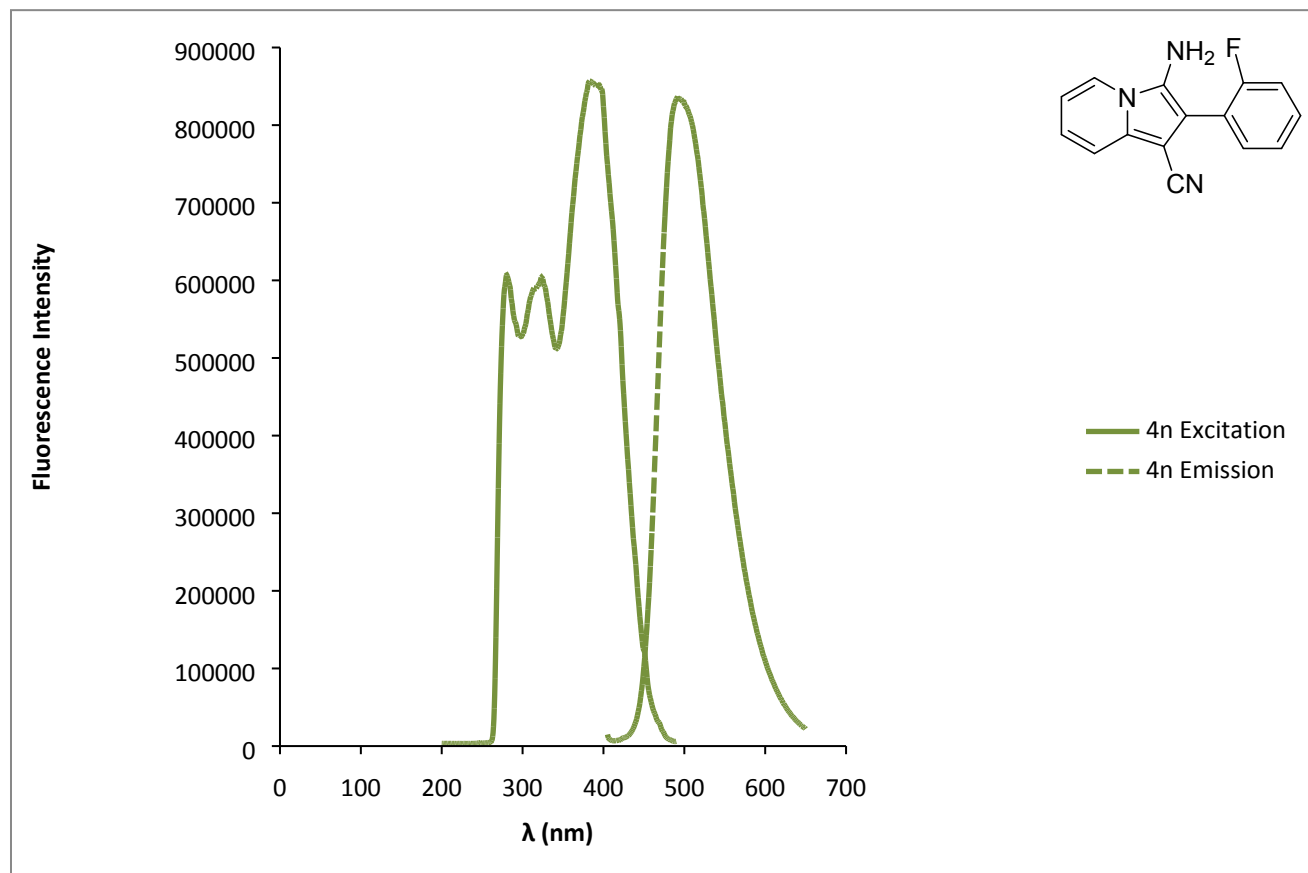
Fluorescent spectra for compound **4l** (10 μ M, DMF, λ_{ex} = 304, 348 nm; λ_{em} = 404 nm)



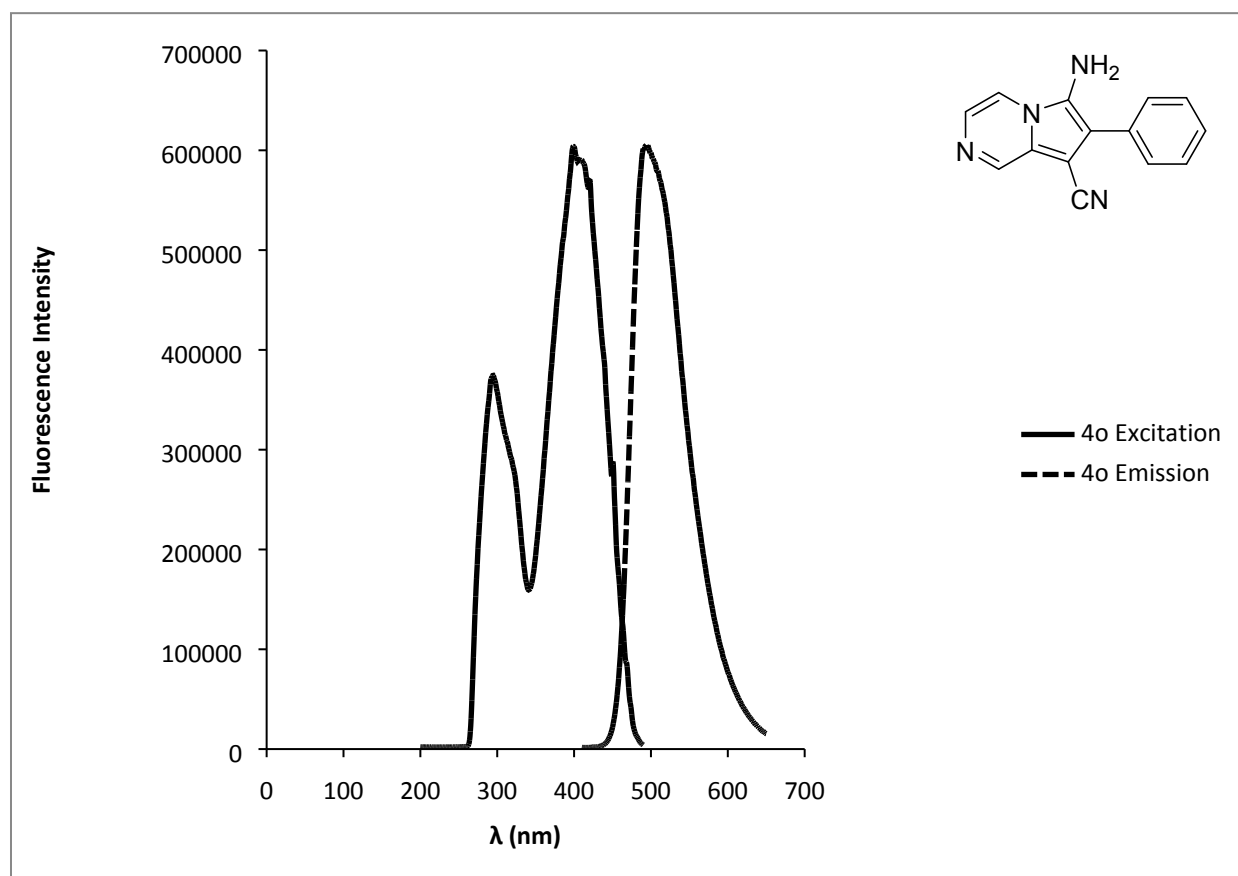
Fluorescent spectra for compound **4m** (10 μ M, DMF, λ_{ex} = 294, 332, 373 nm; λ_{em} = 476 nm)



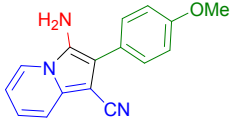
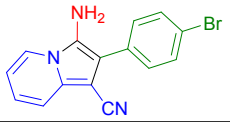
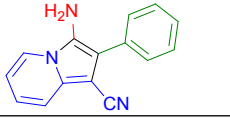
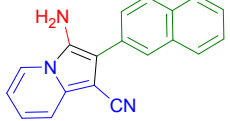
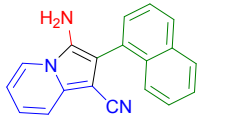
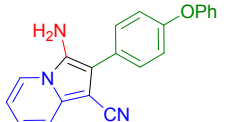
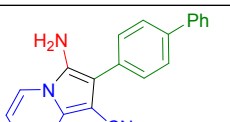
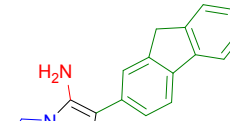
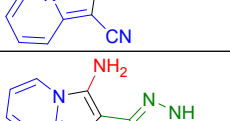
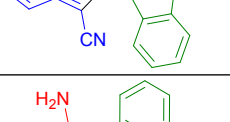
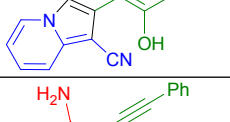
Fluorescent spectra for compound **4n** (10 μ M, DMF, λ_{ex} = 280, 323, 383 nm; λ_{em} = 493 nm)

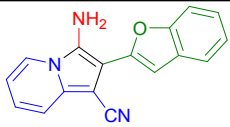
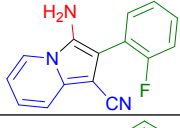
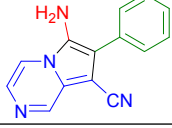


Fluorescent spectra for compound **4o** (10 μ M, DMF, λ_{ex} = 295, 399 nm; λ_{em} = 494 nm)



Data for Compounds 4a-4o

Compound Number	Structure	Quantum yield (ϕ_f) in DMF	Molar Absorptivity ($M^{-1}cm^{-1}$)	λ_{ex} (nm)	λ_{em} (nm)
4a		0.03	5525	292, 393	497
4b		0.01	6395	282, 398	493
4c		0.02	4128	287, 398	496
4d		0.02	8147	292, 398	505
4e		0.05	4920	297, 397	512
4f		0.05	3613	300, 400	494
4g		0.02	7634	292, 398	496
4h		0.10	4358	300, 398	490
4i		0.07	6096	299, 399	493
4k		0.03	4267	291, 392	494
4l		0.24	4938	304, 348	404

4m		0.06	7465	294, 332, 373	476
4n		0.09	6449	280, 323, 383	493
4o		0.22	8100	295, 399	494

(Reference coumarine 151 in ethanol)