Supporting Information

Sustainable photocatalytic C−H annulation of heteroarenes with sulfoxonium ylides: Synthesis and photophysical properties of fused imidazo[1,2-*a*]pyridine based molecules

Sravani Sana,[a] Srinivas Reddy Dannarm,[b] Ramya Tokala,[a] Sowmya Dastari,[a] Manda Sathish,[d] Rahul Kumar,[c] Rajesh Sonti,[b] Nagula Shankaraiah*[,a]

[a]*Department of Medicinal Chemistry,* [b]*Department of Pharmaceutical Analysis, National Institute of Pharmaceutical Education and Research (NIPER), Hyderabad 500 037, India*

[c]*Department of Pharmacology and Toxicology, National Institute of Pharmaceutical Education and Research (NIPER), Hyderabad 500 037, India*

[d]*Centro de Investigación de Estudios Avanzados del Maule (CIEAM), Vicerrectoría de Investigación y Postgrado, Universidad Católica del Maule, Talca-3460000, Chile*

*Corresponding author: Email: shankar@niperhyd.ac.in, shankarnbs@gmail.com

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1. Experimental Section

General methods

Commercially available reagents and solvents were used without further purification. Column chromatography was performed using silica gel 60-120 and 100-200 mesh. The NMR measurements were done on a Bruker AVANCE 500 MHz spectrometer using a standard library pulse programs on BBO and TXI probes with DMSO-d_6 as solvent at 30 ^{o}C. Unambiguous aromatic proton and carbon chemical shifts were assigned by using a combination of 2D HSQC and HSQC-TOCSY experiments. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (DMSO-d_6: δ = 2.50 ppm). ^{13}C NMR spectra were recorded on an NMR instrument operated at 125 MHz with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (DMSO-d_6: δ = 39.52 ppm and $CDCl_3$: δ = 77.16 ppm). The following abbreviations were used for ^{1}H NMR spectra to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). All 2D experiments were recorded in phase-sensitive mode using QF for COSY and Echo-Antiecho mode for HSQC and HSQC-TOCSY in the F1 dimension. HRMS was obtained in an ESI QTOF mass spectrometer. Thin-layer chromatography was performed on MERCK precoated silica gel 60F-254 (0.5 mm) aluminium plates and visualized under UV light at 254 nm. Experiments were performed on a JASCO V-650 spectrophotometer in a quartz cuvette with a 1 cm path length at an absorbance scan range from 400-700 nm. Spectro-fluorescence experiments were performed on the Perkin Elmer EnVision® Multimode Plate Reader using fluorescence intensity experiment.

General procedure for the synthesis of sulfoxonium ylides:

Under N_2, trimethylsulfoxonium iodide (3 mmol) was suspended in dry THF (55 mL) in a flame-dried 250 mL round bottom flask that was protected from light with aluminium foil. Potassium *tert*-butoxide (3 mmol) was added, and the mixture was stirred at reflux for 2 h. After cooling to 0 ^{o}C, substituted aroyl chlorides (**A-M**, 1 mmol) in THF (18 mL) were added drop-wise to the mixture. The mixture was stirred at 0 ^{o}C for another hour and then filtered at room temperature through a plug of celite before all volatiles were removed under vacuum. Purification by flash chromatography using 70-90% of ethyl acetate and hexane afforded the substituted phenyl sulfoxonium ylide derivatives **2a-m** (65-95%).

General experimental procedure for the synthesis of compounds 3a–aa:

Imidazo[1,2-*a*]pyridine (**1**, 0.2 mmol), phenyl sulfoxonium ylide (**2**, 0.3 mmol), $Ru(bpy)_3Cl_2$ (0.05 mol%), $AgNO_3$ (0.1 mol%), $K_2S_2O_8$ (3 mmol) and $CH_3CN:H_2O$ (1:1, 5.0 mL) were added to an oven-dried reaction vessel equipped with a magnetic stir bar, and the reaction vessel was irradiated using a 47W CFL bulb at room temperature under ambient air for 12 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to get the crude residue, which was purified by column chromatography on silica gel (60−120 mesh) using ethyl acetate/petroleum ether (10/90) as an eluent to afford the pure annulated products **3a**–**aa**.

Gram-scale reaction procedure (3b).

To demonstrate the scalability of this C-H annulation, a gram-scale synthesis was performed by using **1a** (1.5 g) and **2b** (1.8 g) under the optimized conditions, discussed in the general procedure. The reaction proceeded efficiently to give the desired product **3b** (1.96 g) in 82% yield.

General experimental procedure for the synthesis of compounds 5a-d, 7a, 9a.

4a-c, **6a**, **8a** (0.2 mmol), phenyl sulfoxonium ylide (**2**, 0.3 mmol), $Ru(bpy)_3Cl_2$ (0.05 mol%), $AgNO_3$ (0.1 mol%), $K_2S_2O_8$ (3 mmol) and $CH_3CN:H_2O$ (1:1, 5.0 mL) were added to an oven-dried reaction vessel equipped with a magnetic stir bar, and the reaction vessel was irradiated using a 47W CFL bulb at room temperature under ambient air for 12 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to get the crude residue, which was purified by column chromatography on silica gel (60−120 mesh) using petroleum ether and ethyl acetate/petroleum ether as an eluent to afford the pure annulated products.

Table S1. Detailed optimization reaction conditions for C-H activation/annulation

Entry	Catalyst	Ag Salt	Oxidant	Solvent	Yield (%)[b]
Oxidant Screening					
1	$Ru(bpy)_3Cl_2.6H_2O$	$AgNO_3$	TBHP (3 equiv.)	MeCN:Water	30
2	$Ru(bpy)_3Cl_2.6H_2O$	$AgNO_3$	O_2	MeCN:Water	N.R
3	$Ru(bpy)_3Cl_2.6H_2O$	$AgNO_3$	K_2CO_3 (3 equiv.)	MeCN:Water	traces
Ag Salt Screening					
4	$Ru(bpy)_3Cl_2.6H_2O$	AgOTf	$K_2S_2O_8$ (3 equiv.)	MeCN:Water	40
5	$Ru(bpy)_3Cl_2.6H_2O$	$AgNTf_2$	$K_2S_2O_8$ (3 equiv.)	MeCN:Water	25
6	$Ru(bpy)_3Cl_2.6H_2O$	$AgSbF_6$	$K_2S_2O_8$ (3 equiv.)	MeCN:Water	45
7	$Ru(bpy)_3Cl_2.6H_2O$	AgOAc	$K_2S_2O_8$ (3 equiv.)	MeCN:Water	10
8	$Ru(bpy)_3Cl_2.6H_2O$	$AgNO_3$	-	MeCN:Water	traces
9	$Ru(bpy)_3Cl_2.6H_2O$	-	$K_2S_2O_8$ (3 equiv.)	MeCN:Water	50
10	$Ru(bpy)_3Cl_2.6H_2O$	-	-	MeCN:Water	N.R
Other photocatalysts screening					
11	Eosin Y	$AgNO_3$	$K_2S_2O_8$ (3 equiv.)	MeCN:Water	N.R
12	$Mes^-Acr^+BF_4$	$AgNO_3$	$K_2S_2O_8$ (3 equiv.)	MeCN:Water	N.R
13	Rose Bengal	$AgNO_3$	$K_2S_2O_8$ (3 equiv.)	MeCN:Water	N.R
14	$Ru(bpy)_3(PF_6)_2$	$AgNO_3$	$K_2S_2O_8$ (3 equiv.)	MeCN:Water	40

[a]Reaction conditions: **1** (1 mmol), **2** (1.5 mmol), catalyst (5 mol%), $AgNO_3$ (0.1 mmol), $K_2S_2O_8$ (3 mmol), 47W CFL, 12 h, open air. [b]Isolated yields. [c]Reaction carried out under 47W CFL, rt, 12 h, open air.

2. Structural Confirmation

Structural Confirmation by Single Crystal XRD:

ORTEP diagram of **3n** compound with the atom-numbering. Displacement ellipsoids are drawn at the 35% probability level and H atoms are shown as small spheres of arbitrary radius. Hydrogen bonds are shown in dotted lines.

Crystal data for 3n: $C_{21}H_{12}Cl_1F_1N_2$, M = 346.78, Triclinic, space group P-1 (No.2), a = 7.6674(19)Å, b = 9.375(2)Å, c = 12.301(2)Å, α = 72.479(5)°, β = 83.153(6)°, γ = 75.425(6)°, V = 815.2(3)Å^3, Z = 2, D_c = 1.413 g/cm^3, F_{000} = 356, Bruker D8 QUEST PHOTON-100, Mo-Kα radiation, λ = 0.71073 Å, T = 293(2)K, $2\theta_{max}$ = 55°, μ= 0.250 mm^{-1}, 16983 reflections collected, 3719 unique (R_{int} = 0.0433), 226 parameters, $R1$ = 0.0412, $wR2$ = 0.1007, R indices based on 2970 reflections with I > 2σ(I) (refinement on F^2), Final $GooF$ = 1.054, largest difference hole and peak = -0.314 and 0.248 e.Å^{-3}. **CCDC 2072978** deposition number contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

Data collection and Structure solution details: Single crystal X-ray data were collected at room temperature on a Bruker D8 QUEST equipped with a four-circle kappa diffractometer and Photon 100 detector. An Iμs microfocus Mo source (λ = 0.71073Å) supplied the multi-mirror monochromated incident beam. A combination of Phi and Omega scans were used to collect the necessary data. Integration and scaling of intensity data were accomplished using SAINT program.[1] The structures were solved by Direct Methods using SHELXS97[2] and refinement was carried out by full-matrix least-squares technique using SHELXL-2014/7.[2-3] Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms, with C-H distances of 0.93--0.97 Å, and with U_{iso}(H) = 1.2U_{eq} (C) or 1.5U_{eq} for methyl atoms. **CCDC 2072978** deposition number contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

References:

S1. SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, U.S.A., 2001.

S2. Sheldrick, G. M. SHELXS97 and SHELXL Version 2014/7, http://shelx.uni-ac.gwdg.de/SHELX/index.php

S3. Muller, P, Herbst-Imer, R, Spek, A. L, Schneider, T. R, and Sawaya, M. R. Crystal Structure Refinement: A Crystallographer's Guide to SHELXL. Muller, P. Ed. Oxford University Press: Oxford, New York, 2006, 57–91.

S4. A. L. Spek, Structure validation in chemical crystallography *D. Acta Cryst*. *D65*, 2009, ***65***, 148-155.

Structural Confirmation by NMR Spectral assignment:

^{1}H NMR spectrum of **3a** showed well-resolved peaks for the aromatic ring protons. Ring specific proton assignments were carried out by the analysis of 2D COSY, HSQC and HSQC-TOCSY experiments (**Figure S1,2**).[S5,S6] Further, the 1D Homo-decoupling experiment resulted in the confirmation of ^4J coupling between C1 and D1 protons (**Figure S4**). The sel-ROESY experiment (**Figure S3**) on the C1 proton resonance provided ROEs to D1, D2 and E1 ring protons suggesting spatial proximity, thereby confirming the structure of **3a** as shown in **Scheme 1** in the manuscript.

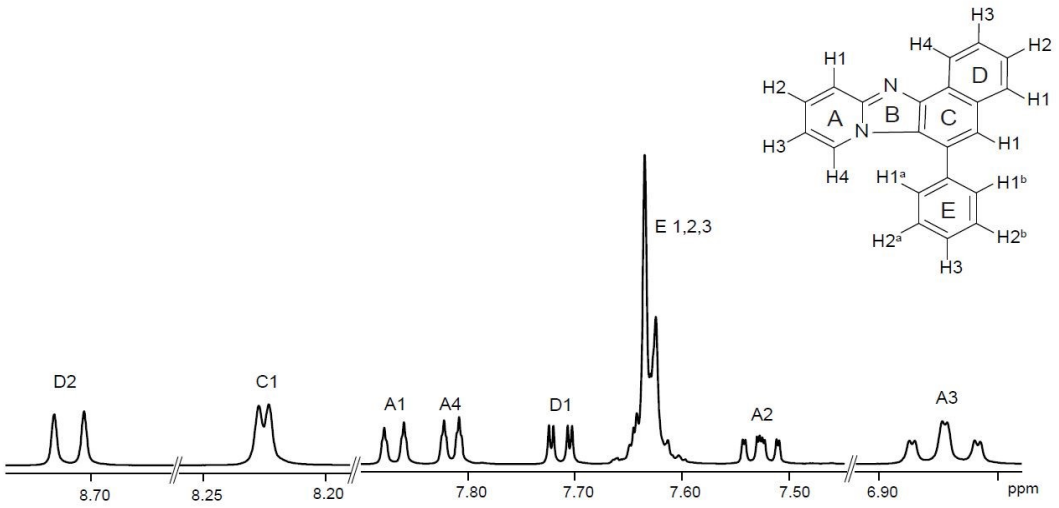


Figure S1. Partial 500 MHz 1D ^{1}H NMR spectrum of **3a** in DMSO-*d*$_6$

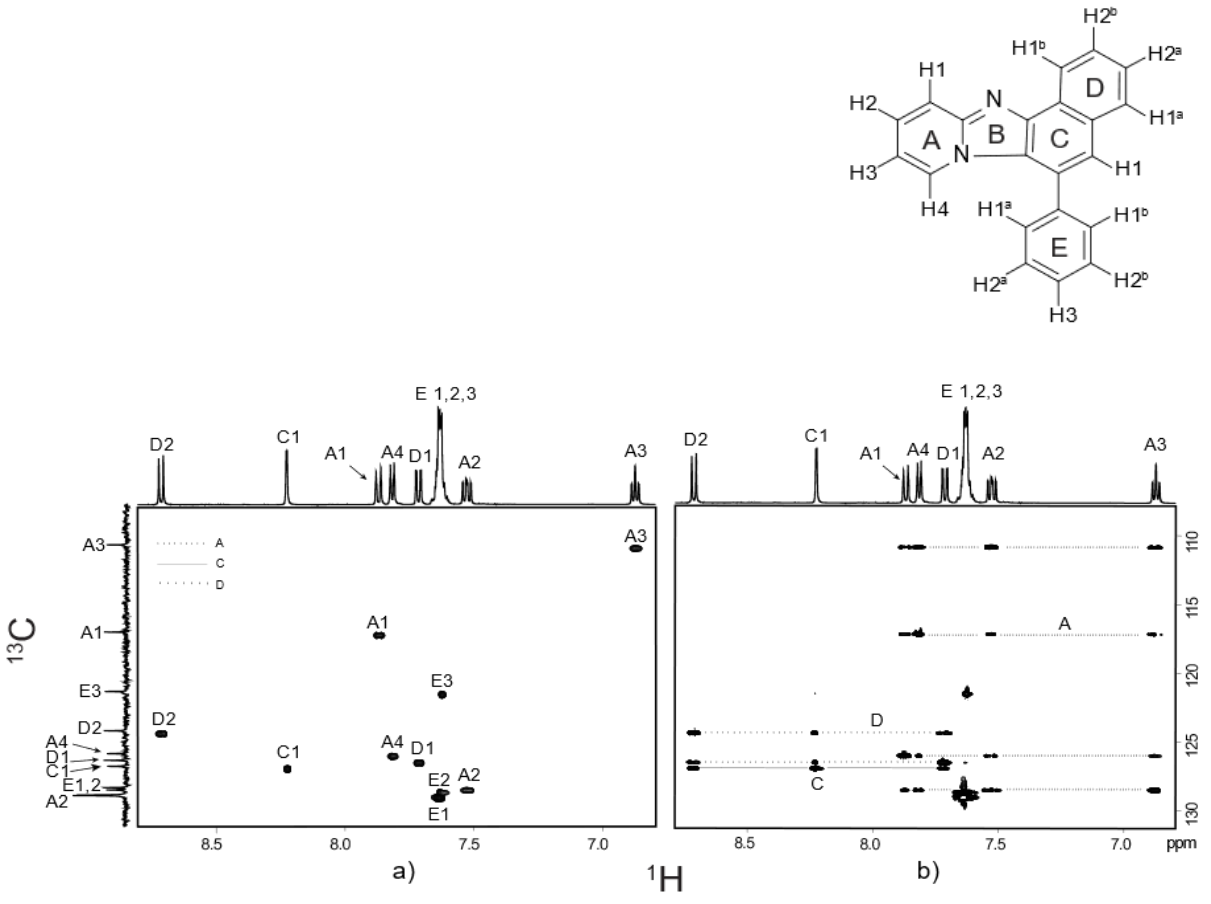


Figure S2. Partial 2D ^{1}H-^{13}C a) HSQC b) HSQC-TOCSY spectra of **3a** in DMSO-*d*$_6$ illustrating the assignment of aromatic ring systems.

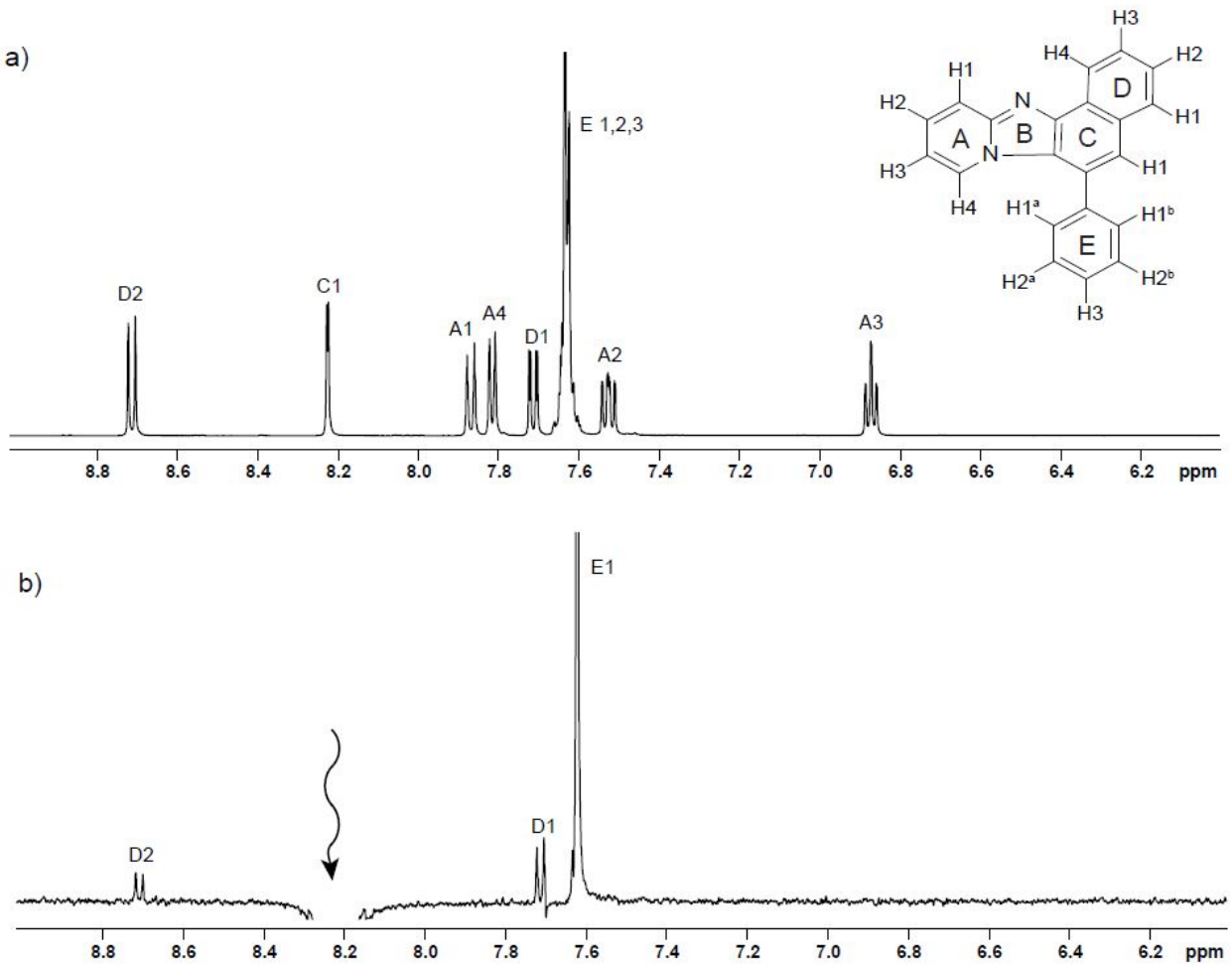


Figure S3. One dimensional 500 MHz NMR spectra. a) Partial ^{1}H NMR spectrum b) Partial ^{1}H NMR selective ROESY spectrum illustrating the irradiation of the C1 peak of **3a** in DMSO-d_6. Note the ROE peaks to D1, D2 and E1 protons.

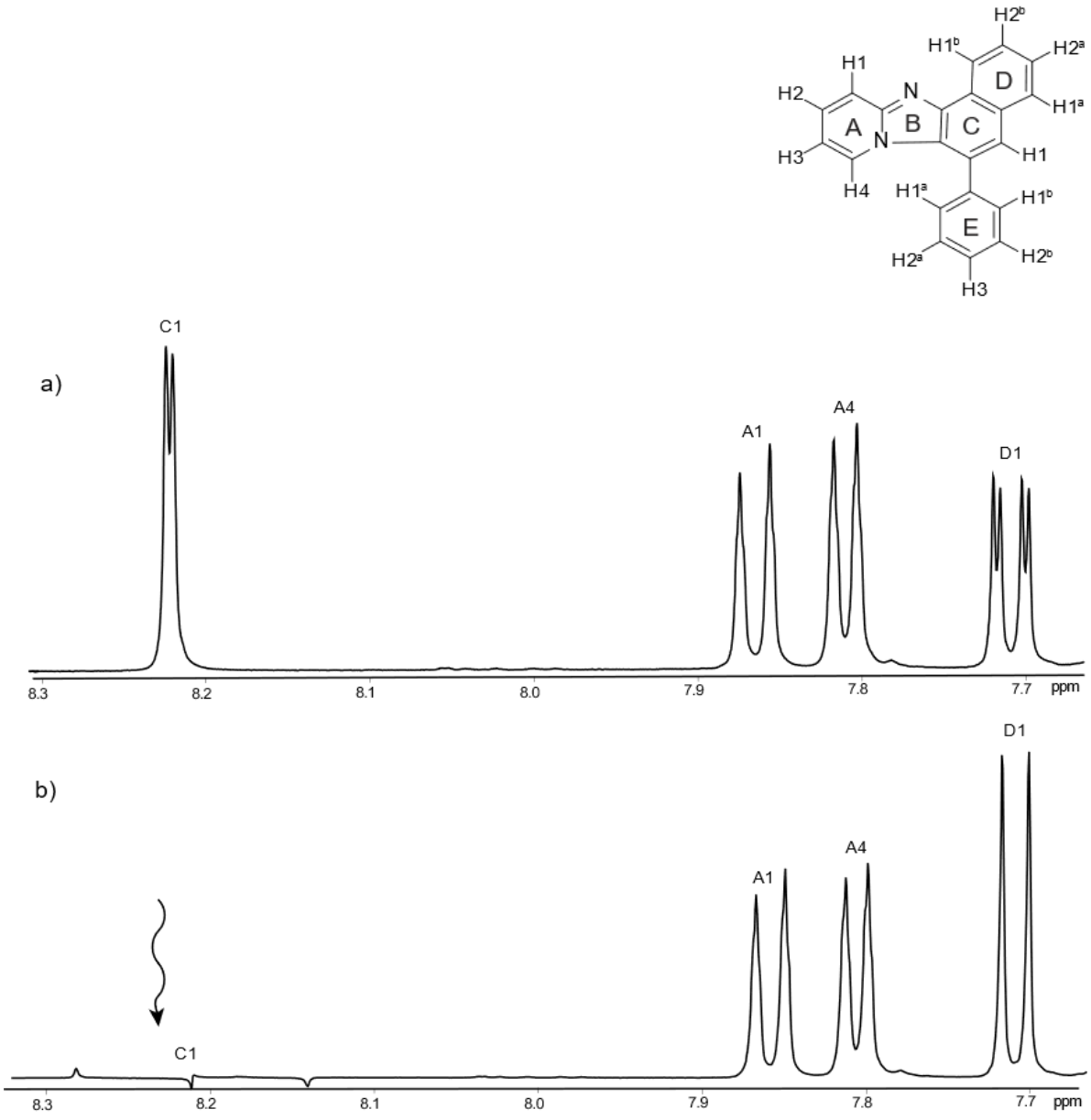
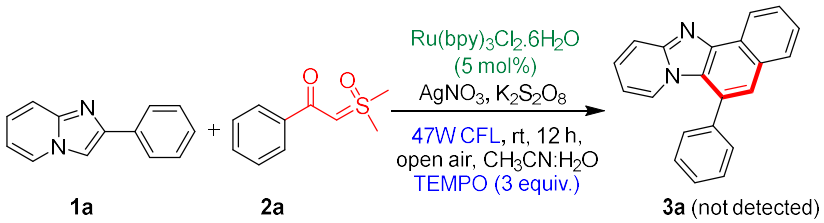


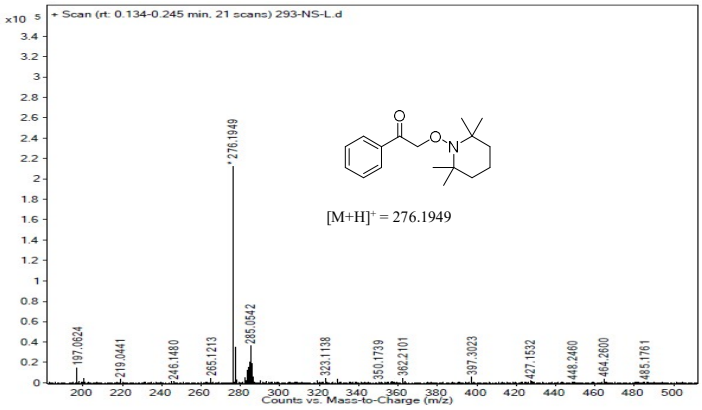
Figure S4. One dimensional 500 MHz NMR spectra a) Partial ^{1}H NMR spectrum (b) Homo decoupled spectrum saturating the C1 peak of **3a** in DMSO-d_6. Note the changes of the splitting on the D1 peak by saturation of the C1 peak.

3. The Mechanism Studies:

TEMPO Trapping Experiments:



Entry	TEMPO (equiv.)	**1a** recovered
1	1.5	20%
2	3	trace
3	5	trace



Control experiments were performed in the presence of above-mentioned equivalents of TEMPO, added separately to capture the sulfonyl radical species. The reaction mixtures were then analyzed through HRMS at different time intervals. In all reaction mixtures, anticipated product was not detected, signifying that the reaction might involve radical intermediates in reaction. The HRMS analysis indicated that TEMPO-trapped benzoylmethyl radical could be observed that should be generated from sulfoxonium ylide **2a**.

Luminescence quenching experiments and Stern-Volmer plots:

The $Ru(bpy)_3Cl_2.6H_2O$ fluorophore was excited at 470 nm and the emission intensity was observed from 600 to 800 nm in $MeCN/H_2O$ (1/1) as solvent using Perkin Elmer EnVision® Multimode Plate Reader. A distinctive quenching profile as exposed in **Figure S5** was observed and is in agreement with the literature reports.[S7,S8] The Stern-Volmer quenching constant was calculated using the Stern-Volmer equation: $F_o/F = 1 + K[Q]$ at 25 °C in $MeCN/H_2O$ (1/1) from the detected fluorescence data as represented in **Figure S6**. The results indicated a strong quenching of a photoexcited reaction with the quenching constant of $11.22 \times 10^4\ M^{-1}$. To validate the point of photoreaction as the major pathway of fluorescence quenching a parallel experiment of absorption study involving the UV-Visible monitoring of photoexcited $[Ru(bpy)_3]^{2+}$ oxidation

reaction by potassium persulfate was attempted and is as shown in **Figure S7**. From **Figure S7**, it is observed that initially there is only the broad absorbance band around λ 470 nm corresponding to the Ru(II)bpy complex. However, on addition of the cumulative concentration of potassium persulfate to the photoexcited $[Ru(bpy)_3]^{2+}$, there is a consecutive reduction in the absorbance band at λ 470 nm and an increase in the baseline from 600-750 nm was observed. The absorption studies thus specify a photo-redox reaction between photo potassium persulfate and excited $[Ru(bpy)_3]^{2+}$ resulting its single electron oxidation to $[Ru(bpy)_3]^{3+}$ and product of sulfate radical ion as per the projected mechanism under **Scheme 1** in the manuscript. Thus, both absorption and emission studies of the system are well in support of the radical mechanism of the reaction.

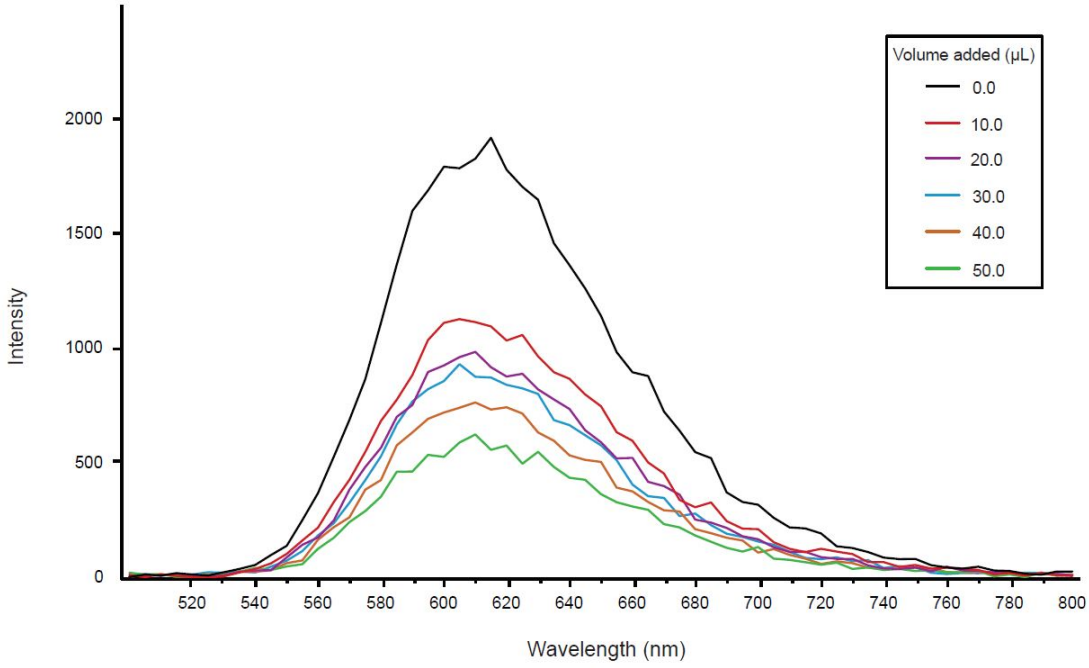


Figure S5. Fluorescence quenching of 200 µM $[Ru(bpy)_3]^{2+}$ upon addition of varying amounts of 5 mM $K_2S_2O_8$ (potassium persulfate). Inset shows the volume of persulfate added.

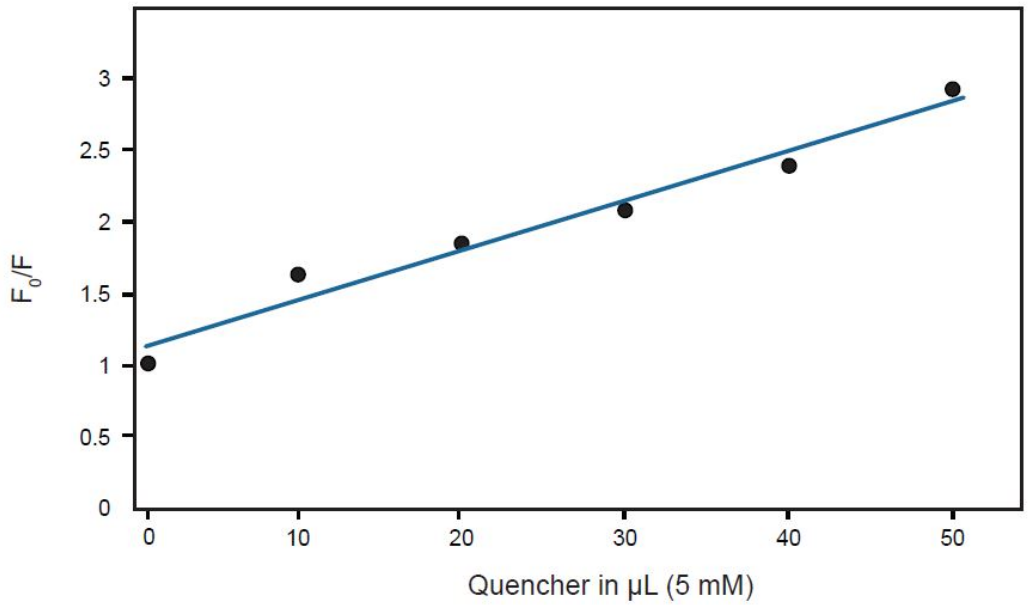


Figure S6. Stern-Volmer plot for $[Ru(bpy)3]^{2+}$ complex with quencher in MeCN: H_2O (1:1) at 25 °C.

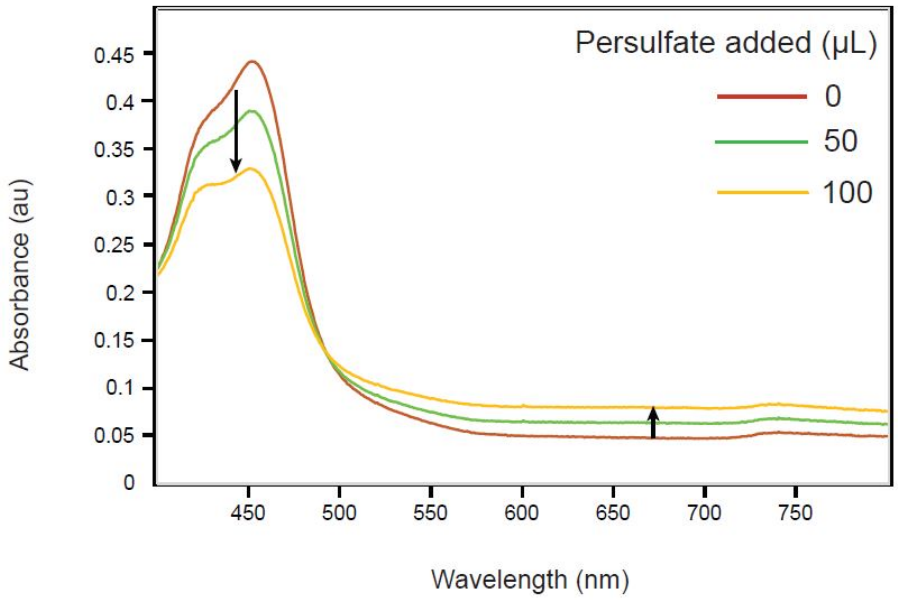


Figure S7. UV-Visible monitoring of 100 µM photoexcited $[Ru(bpy)_3]^{2+}$ oxidation upon addition of 5 mM $K_2S_2O_8$ (potassium persulfate). Inset shows the colour code with a volume of persulfate added. Note the single headed arrows indicating the decrease in absorption of the complex at 450 nm and an increase in the baseline from 600-750 nm with an increase in quencher concentration.

4. Photophysical properties

Fluorescence Quantum Yield Measurements. Quantum yields were determined using quinine sulfate ($\Phi = 0.55$ in 0.5 M H_2SO_4) as a standard. The sample absorbance was maintained < 0.1 to minimize internal absorption. Corrections were made to account for the differences in solvent refractive indexes.

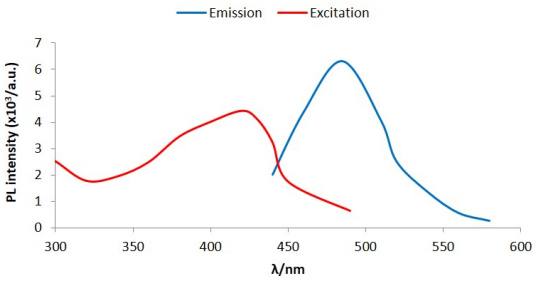


Figure S8. Excitation and Emission spectra of **3a**

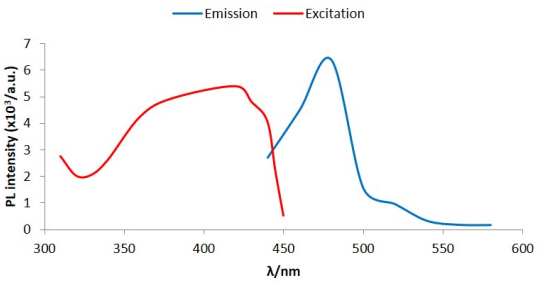


Figure S9. Excitation and Emission spectra of **3b**

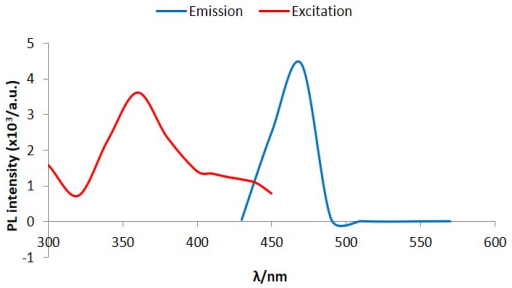


Figure S10. Excitation and Emission spectra of **3c**

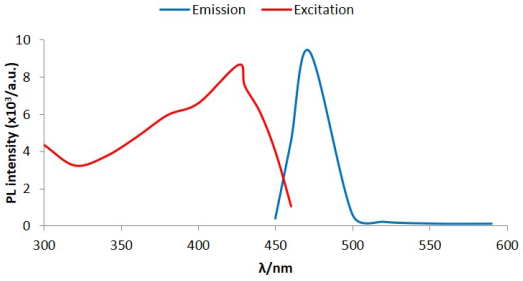


Figure S11. Excitation and Emission spectra of **3d**

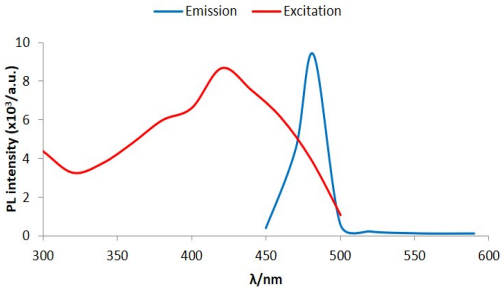


Figure S12. Excitation and Emission spectra of **3e**

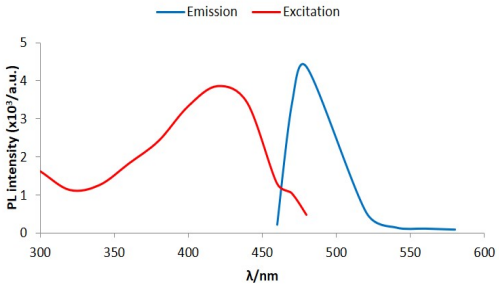


Figure S13. Excitation and Emission spectra of **3f**

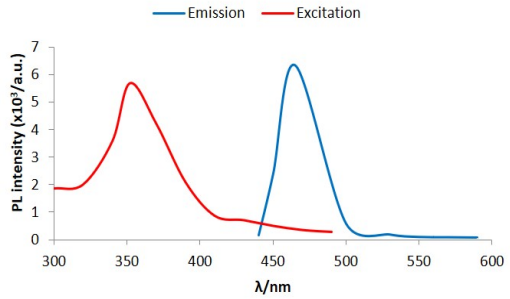


Figure S14. Excitation and Emission spectra of **3g**

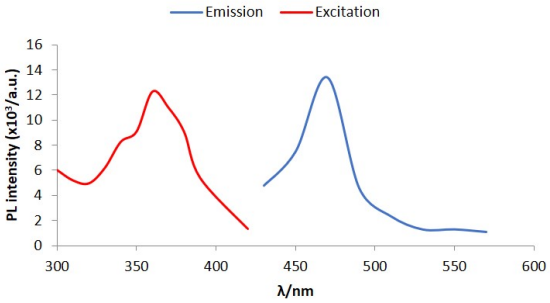


Figure S15. Excitation and Emission spectra of **3h**

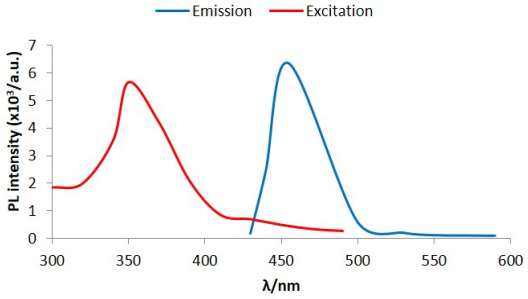


Figure S16. Excitation and Emission spectra of **3i**

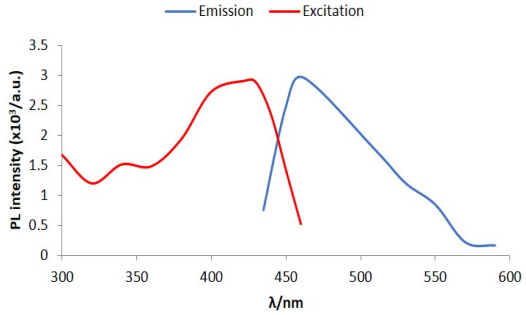


Figure S17. Excitation and Emission spectra of **3j**

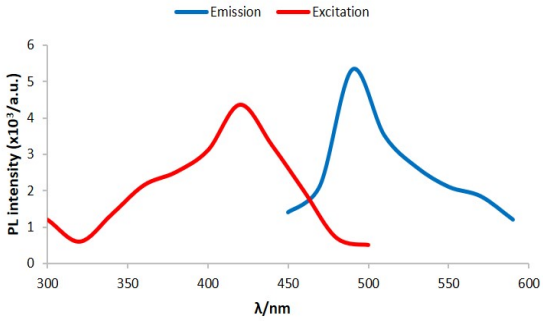


Figure S18. Excitation and Emission spectra of **3k**

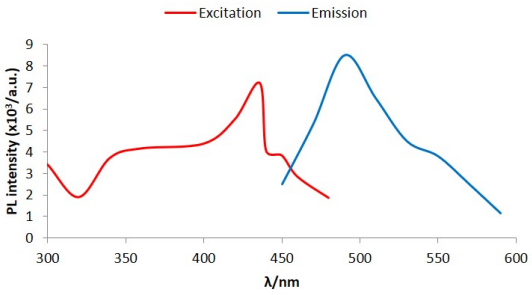


Figure S19. Excitation and Emission spectra of **3l**

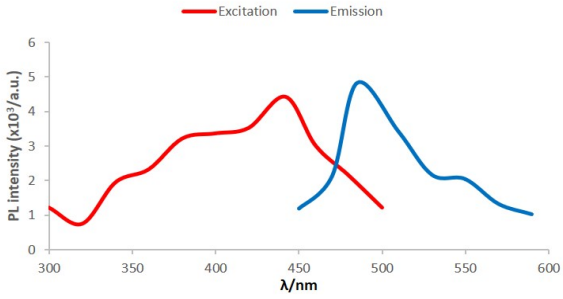


Figure S20. Excitation and Emission spectra of **3m**

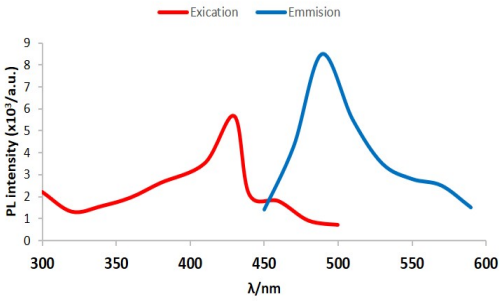


Figure S21. Excitation and Emission spectra of **3n**

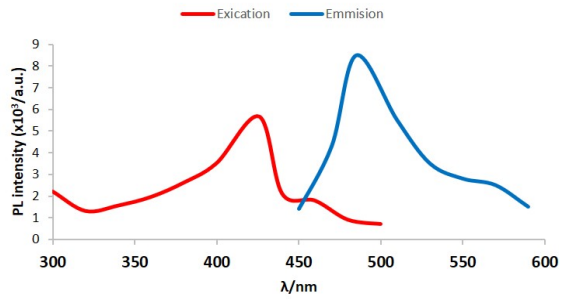


Figure S22. Excitation and Emission spectra of **3o**

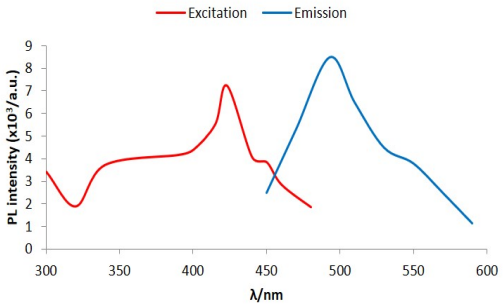


Figure S23. Excitation and Emission spectra of **3p**

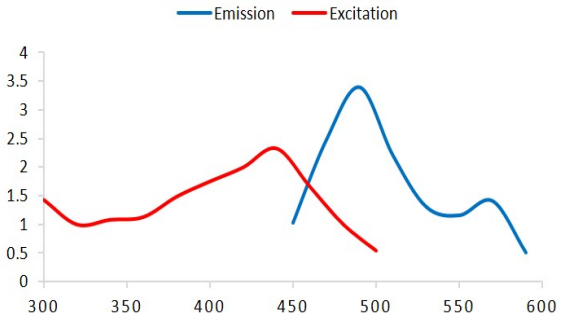


Figure S24. Excitation and Emission spectra of **3q**

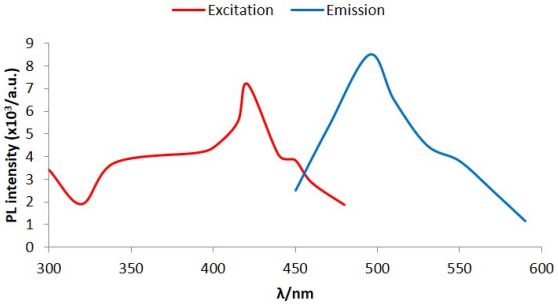


Figure S25. Excitation and Emission spectra of **3r**

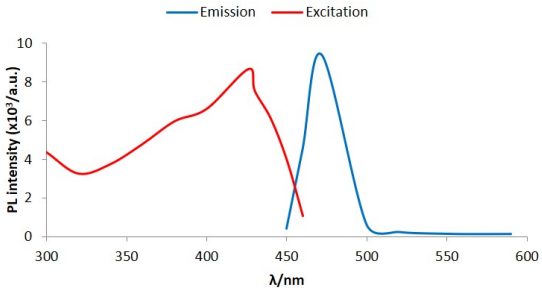


Figure S26. Excitation and Emission spectra of **3s**

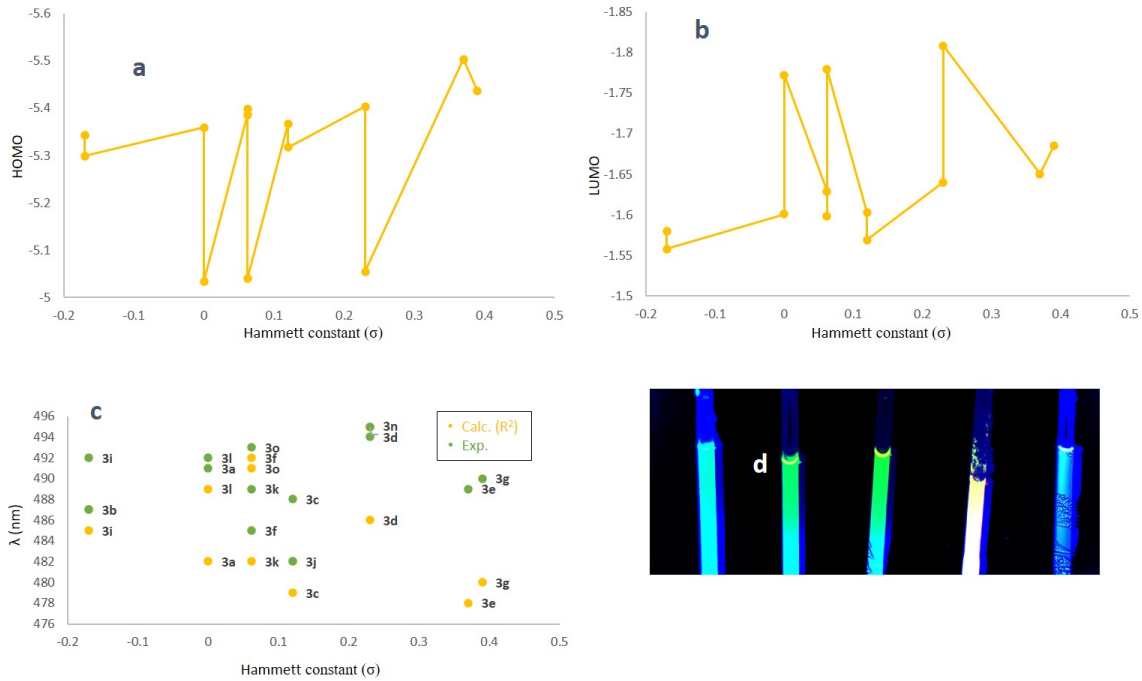


Figure S27. Effect of electronic nature on (**a**,**b**) Calculated HOMO and LUMO energies (**c**) Scatter plots of the emission wavelengths (**d**) Fluorescence images in CH_2Cl_2 irradiated at 365 nm for polycyclic imidazo[1,2-*a*]pyridine with various substituents.

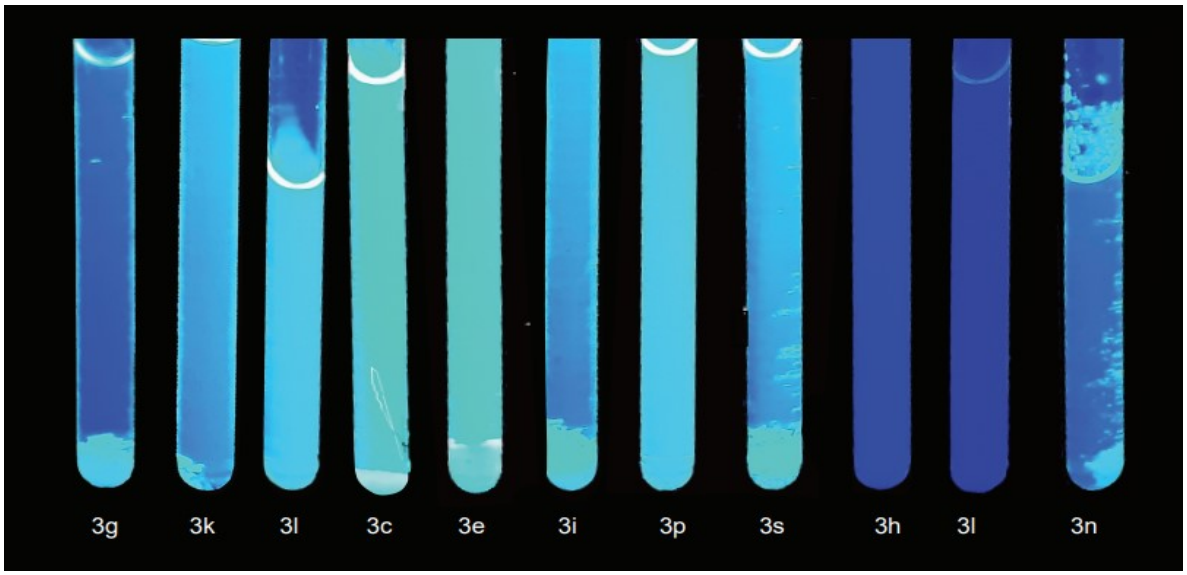
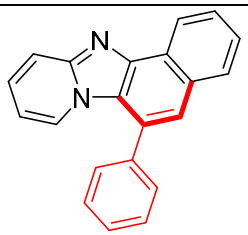
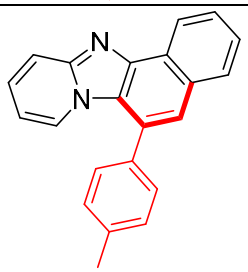


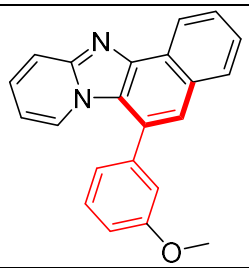
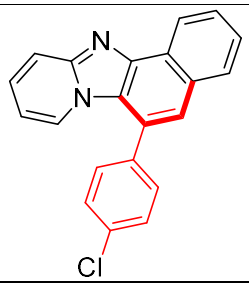
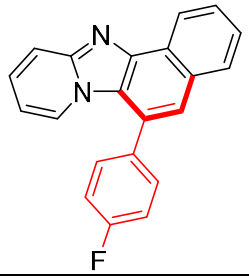
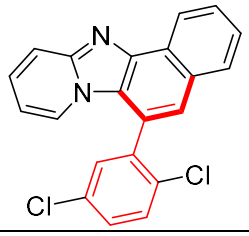
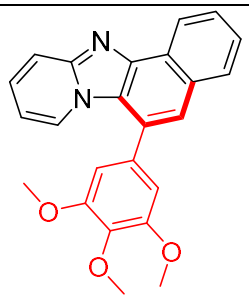
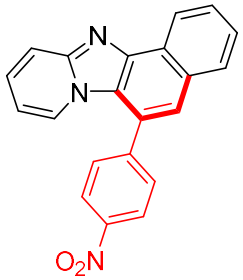
Figure S28. Fluorescence images in DMSO irradiated at 365 nm for polycyclic imidazo[1,2-*a*]pyridine with various substituents.

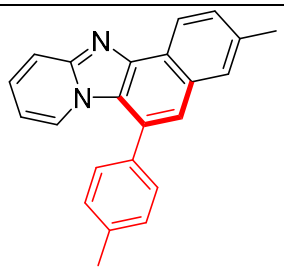
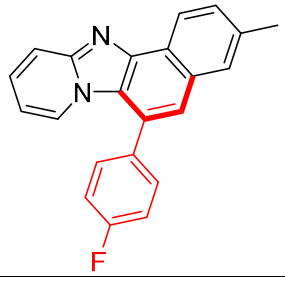
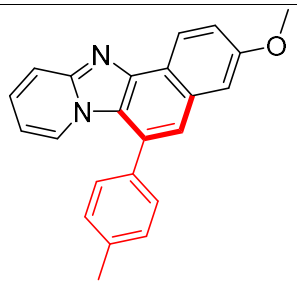
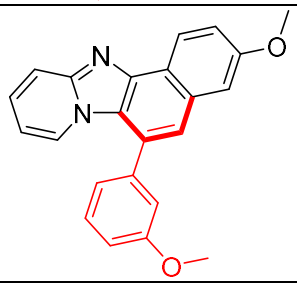
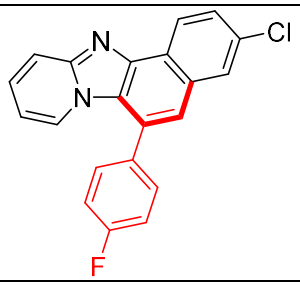
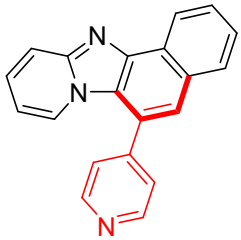
5. Computational Results

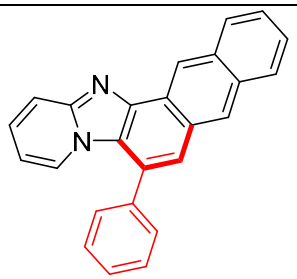
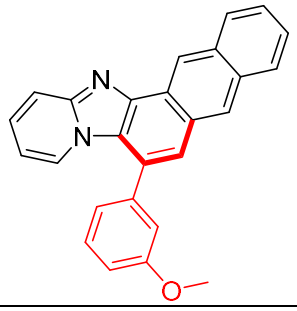
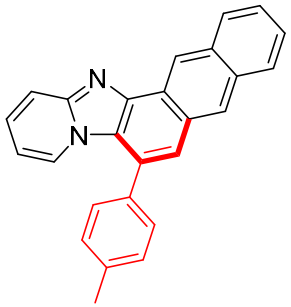
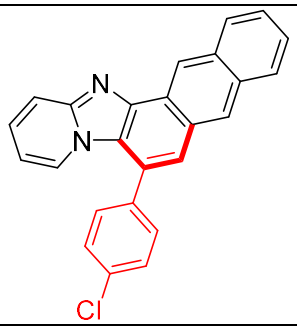
Computational Details All calculations were performed using density functional theory[S9] (DFT) as implemented in the Jaguar 9.1[S10] suite of *ab initio* quantum chemistry programs. The geometry optimizations were performed with the B3LYP[S11] hybrid exchange and correlation functional. The 6-31G** basis set was used for all atoms,[S12] which were represented by the Los Alamos LACVP basis set including relativistic effective core potential.[S13] The HOMO and LUMO energies of the optimized structures were reevaluated by single-point calculations using Dunning's correlation consistent triple-ζ basis set cc-pVTZ(-f) that includes a double set of polarization functions.[S14] Calculations for the solvent effect are conducted by a self-consistent reaction field (SCRF) approach,[S15] in which dichloromethane (CH_2Cl_2) is regarded as the continuum with the dielectric constant ε = 9.08. Furthermore, time-dependent DFT[S16] (TD-DFT) calculation with Tamm-Dancoff approximation[S17] (TDA) is used to optimize the structure of ground states and first excited states of the nature for emission parameter. The isosurface plots of MOs were obtained by using the Molden software.[S18]

Table S2. Photophysical properties in gas phase (isodensity value = 0.05 a.u.)

Cpd	Structure	Calc. (Gas-phase)			λ_{em} (nm)
		HOMO	LUMO	λem (nm)	
3a		-5.359	-1.601	482	475
3b		-5.342	-1.580	487	462

3c		-5.366	-1.603	482	472
3d		-5.403	-1.640	486	484
3f		-5.385	-1.629	492	485
3g		-5.436	-1.685	480	483
3h		-5.397	-1.599	465	476
3i		-5.499	-1.758	437	456

3j		-5.369	-1.588	479	462
3k		-5.347	-1.599	477	488
3l		-5.299	-1.558	487	492
3m		-5.317	-1.569	482	482
3n		-5.399	-1.598	482	489
3o		-5.334	-1.596	487	482

3p		-5.034	-1.772	489	492
3q		-5.070	-1.779	501	493
3r		-5.055	-1.808	495	495
3s		-5.040	-1.779	491	493

Cartesian Coordinates of All Structures Optimized in Gas-Phase

3a

C	-0.2366312395	5.3337189744	0.0005414065
C	0.9361534713	4.5928703086	0.0003090688
C	0.9012651274	3.1864160922	0.0000631371
N	-0.3558625229	2.5909779907	0.0000871240
C	-1.5320236394	3.2959078600	0.0001872731
C	-1.5083982123	4.7073480509	0.0004232211
C	-0.7055253532	1.2176587514	0.0001222144
C	-2.1349314505	1.2172059540	0.0000753993
N	-2.6279764530	2.4617913625	0.0000700793
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C	-4.2600916942	-0.0877192813	-0.0002199820
C	0.0502065816	0.0550484041	0.0002327381
C	-0.6740961247	-1.1673059083	0.0005626724
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C	3.6441286990	-0.0926587515	1.2071510895
C	2.2500517848	-0.0281698727	1.2090335263
H	-0.1828720407	6.4183263276	0.0008169341
H	1.9032422204	5.0823440618	0.0003320880
H	1.7582019315	2.5371483063	-0.0001144264
H	-2.4407208234	5.2517509410	0.0005394380
H	-2.1937118537	-3.3927878727	0.0010586951
H	-4.6667133203	-3.4747583396	0.0007195825
H	-5.9839082987	-1.3628216934	-0.0001896221
H	-4.8257113711	0.8382068862	-0.0006457088
H	-0.1057296047	-2.0923747310	0.0008755632
H	1.7053549395	-0.0008142009	-2.1485121729
H	4.1825454873	-0.1160066731	-2.1503311148
H	5.4270397883	-0.1713376235	-0.0005826011
H	4.1832680754	-0.1141097414	2.1495703584
H	1.7060300889	0.0010427768	2.1484270514

3b

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N	-0.3716768194	2.5638698000	-0.0002108944
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N	-2.6499008231	2.4845217780	0.000383614
C	-2.8564248361	-0.0119105274	0.0007249904
C	-2.0885731571	-1.2148102609	0.0004712306
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C	-0.6576121275	-1.1593605853	0.0022231414
C	1.5468233179	0.0065796289	0.0059980600
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H	6.3126043898	0.7572767210	-0.5174133411
H	6.2633385244	-1.0039356526	-0.5248449175

3c

C	-2.9895620160	2.7529046717	5.3146263332
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C	-4.9706666964	6.1109594990	-2.4813774367
C	-5.3301263956	6.7607581865	-1.2803669658
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C	-2.8425428728	2.4613367763	0.0095912743
C	-3.2093961052	3.0755732802	-1.1681198402
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C	-2.0227896326	-1.2451819374	-0.0947858932
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C	0.0454021731	-0.0023001802	-0.0497459459
C	-0.6770641094	1.1954057933	-0.0114285030
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C	2.1593822373	1.1172428821	-0.0174695863

H	-2.9559826210	2.7020907992	6.3981036629
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H	-5.8706559194	7.7019628362	-1.3177990027
H	-5.2647859965	6.6875990539	0.8714712156
H	-2.9426779337	2.6022672252	-2.1083707489
H	-3.8390337267	-0.0723122941	-0.0653885454
H	-2.5442571542	-2.1974401755	-0.1299875187
H	-0.0535591900	-2.1437388527	-0.1177720404
H	-0.1709782348	2.1529401295	0.0149608573
H	3.2073839044	0.8143976025	-0.0254176768
H	1.9572808741	1.6951689656	0.8933153758
H	1.9580466660	1.7467302197	-0.8933882953

3d

C	-0.2885926226	5.3218141004	0.0003409373
C	0.9123665203	4.5560919363	-0.0018068992
C	0.8611375175	3.1922953663	-0.0027028601
N	-0.3588850804	2.5582306231	-0.0014426087
C	-1.5775503749	3.2828686971	0.0006991364
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C	-0.7165957790	1.2123485810	-0.0016927413
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C	-2.8545852796	-0.0081255301	0.0007680633
C	-2.0932429014	-1.2148149589	-0.0009237268
C	-2.7888939921	-2.4501368212	-0.0005556171
C	-4.1682076406	-2.4858751846	0.0014132002
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C	-0.6619961289	-1.1650364346	-0.0029355339
C	1.5466997249	-0.0085531132	-0.0053233276
C	2.2621592867	-0.0337278701	-1.2109522095
C	3.6561206812	-0.0759477097	-1.2211048538
C	4.3426917639	-0.0945569828	-0.0089254045
C	3.6592778290	-0.0760484715	1.2050389755
C	2.2652926493	-0.0338449117	1.1984223561
Cl	6.1017086015	-0.1431465530	-0.0112665126
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H	1.8804288863	5.0427870535	-0.0027555585
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H	-2.4434662348	5.2456567842	0.0032039289
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H	4.2035618581	-0.0958792034	-2.1569043200
H	4.2090956759	-0.0960875046	2.1394369602
H	1.7267569181	-0.0217938993	2.1412508712

3f

C	-0.2810415080	5.3193779544	0.0003520334
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N	-0.3525728667	2.5558325752	-0.0009752070
C	-1.5709601357	3.2809852614	0.0004176151
C	-1.5017648348	4.6952315865	0.0009578560
C	-0.7105209025	1.2099616959	-0.0013384049
C	-2.1189998489	1.2183752389	0.0002115837
N	-2.6309259063	2.4854937994	0.0011010530
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C	-2.0867490919	-1.2165214942	-0.0004116616
C	-2.7833036391	-2.4514089608	0.0001527220
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C	-4.9054147140	-1.2857360804	0.0027924366
C	-4.2588221645	-0.0663026832	0.0023694675
C	0.0578010107	0.0124933986	-0.0027137715
C	-0.6552584943	-1.1670183771	-0.0021707162
C	1.5535723525	-0.0093918560	-0.0050346276
C	2.2680062747	-0.0341273391	-1.2121786747
C	3.6617495109	-0.0766488630	-1.2236314497
C	4.3368263691	-0.0963143679	-0.0095498685
C	3.6656213078	-0.0773825564	1.2066625836
C	2.2718626294	-0.0348578456	1.1997354644
F	5.6858836931	-0.1357205631	-0.0116475513
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H	1.7418328541	2.5549827202	-0.0026453364
H	-2.4359018917	5.2443238002	0.0018752803
H	-2.2103628001	-3.3747293568	-0.0006571301
H	-4.6811132017	-3.4408319946	0.0020614968
H	-5.9909175643	-1.3237267644	0.0040145440
H	-4.8131591335	0.8666183823	0.0032842781
H	-0.1097759703	-2.1063880340	-0.0032137526
H	1.7248200606	-0.0215095260	-2.1522351584
H	4.2241156461	-0.0972294647	-2.1508540772
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C	-1.5217421374	-4.6971020797	-0.0072361431
C	-0.7209427764	-1.2157829724	-0.0309502579
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C	-4.9119512993	1.2863070350	0.0577632710
C	-4.2664394169	0.0665886217	0.0401286772
C	0.0441055343	-0.0173807020	-0.0409988426
C	-0.6630299790	1.1649737207	-0.0163157468
C	1.5388429624	0.0078976180	-0.0436477788
C	2.2235777161	0.1129143103	1.1773775470
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H	-4.8185693776	-0.8673306461	0.0440142254
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C	-1.5638879478	3.2950894412	0.0015531851
C	-1.4787496950	4.7077296833	-0.0087254752
C	-0.7282189114	1.2145154815	0.0199272150
C	-2.1356526091	1.2377151203	0.0148532422
N	-2.6336002302	2.5104328866	0.0021465880
C	-2.8759043540	0.0159037089	0.0230905911
C	-2.1318600279	-1.2034070962	0.0386389375
C	-2.8364540540	-2.4260328702	0.0473049844
C	-4.2229988144	-2.4498635103	0.0398330873
C	-4.9545847025	-1.2387033743	0.0241601661
C	-4.2825621865	-0.0313840832	0.0162411767
C	0.0256673524	0.0073497175	0.0292715358
C	-0.6966822612	-1.1661170916	0.0405407240
C	1.5228286476	-0.0206066009	0.0172290755
C	2.2468287483	-0.0724497345	1.2118115800
C	3.6447878802	-0.1034768915	1.1767186074
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C	3.6053056411	-0.0378504683	-1.2354589209
C	2.2068754419	-0.0054613760	-1.2106268688
O	-4.8016047767	-3.6893888855	0.0490026646
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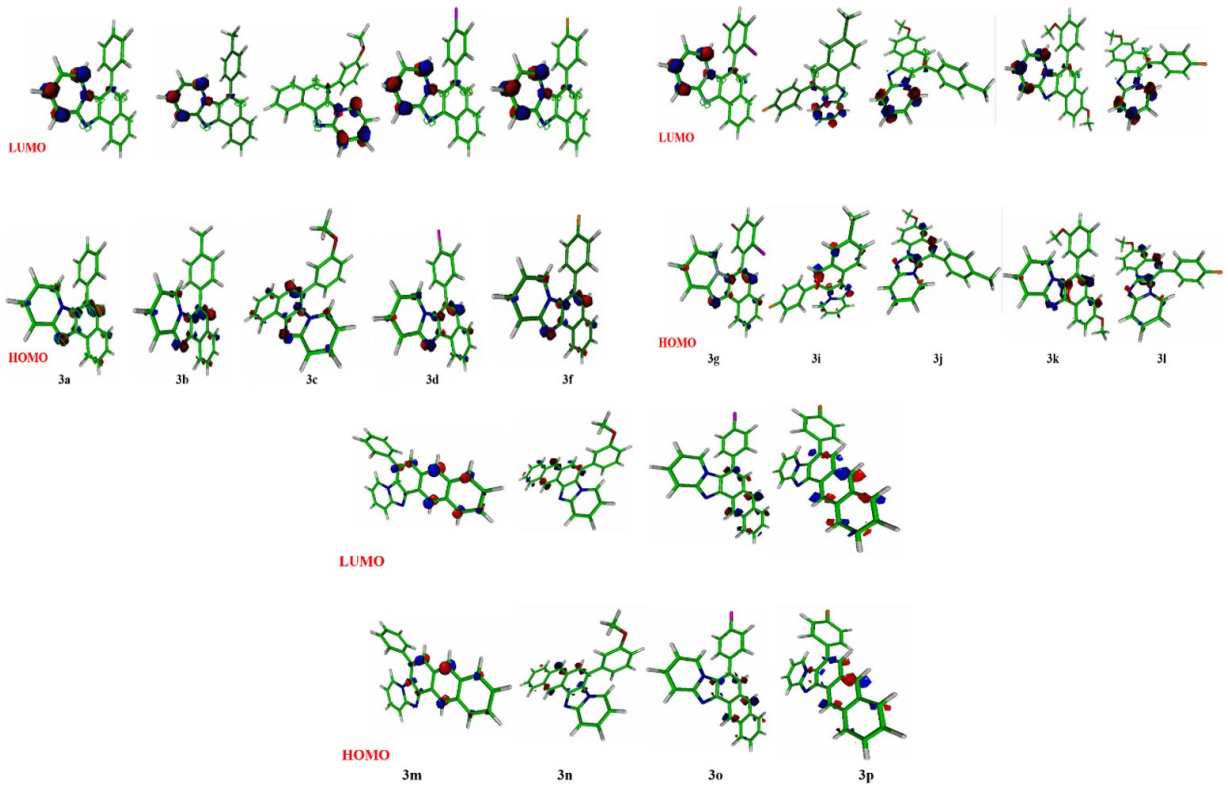

Figure S29. The iso-surface plots of MOs were obtained by using the Molden software.

6. Characterization data

6-Phenylnaphtho[1',2':4,5]imidazo[1,2-*a*]pyridine (3a).

White solid; yield 90%; mp:194-196 ºC; FT-IR (cm^{-1}): 3059, 1683, 1660, 1635, 1517, 1330, 1286; ^1H NMR (500 MHz, DMSO-d_6): δ 8.72 (d, J = 8.6 Hz, 1H), 8.24 (s, 1H), 8.03–7.89 (m, 2H), 7.90–7.84 (m, 2H), 7.84 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.73–7.61 (m, 3H), 7.61 (t, J = 7.7 Hz, 1H), 7.58–7.52 (m, 1H), 6.94 (t, J = 6.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 148.0, 141.4, 140.0, 132.3, 132.2, 132.0, 131.5, 131.3, 129.0, 128.8, 128.4, 127.6, 127.2, 126.7, 125.0, 124.5, 122.7, 122.5, 122.1, 118.1, 112.1; HRMS (ESI): *m/z* calculated for $C_{21}H_{15}N_2$ 295.1235 found 295.1242 $[M+H]^+$.

6-(*p*-Tolyl)naphtho[1',2':4,5]imidazo[1,2-*a*]pyridine (3b).

White solid; yield 93%; mp: 194-197 ºC; FT-IR (cm^{-1}): 3094, 2923, 1688, 1651, 1587, 1372, 1286; ^1H NMR (500 MHz, DMSO-d_6): δ 8.72 (d, J = 8.3 Hz, 1H), 8.24 (s, 1H), 7.89 (d, J = 9.6 Hz, 2H), 7.72 (d, J = 7.8 Hz, 1H), 7.61 (s, 1H), 7.54 (dd, J = 38.2, 32.3 Hz, 6H), 6.91 (s, 1H), 2.49 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 148.0, 141.4, 138.5, 134.7, 132.4, 131.2, 130.0, 129.4, 128.9, 127.4, 126.9,

126.7, 125.0, 124.3, 122.5, 122.2, 118.1, 111.9, 21.4; HRMS (ESI): *m/z* calculated for $C_{22}H_{17}N_2$ 309.1392 found 309.1389 $[M+H]^+$.

6-(3-Methoxyphenyl)naphtho[1',2':4,5]imidazo[1,2-*a*]pyridine (3c).

White solid; yield 90%; mp: 195-198 °C; FT-IR (cm^{-1}): 3057, 2922, 1684, 1633, 1589, 1514, 1286; ^1H NMR (500 MHz, DMSO-d_6): δ 8.71 (d, J = 8.7 Hz, 1H), 8.24 (d, J = 1.2 Hz, 1H), 7.95–7.84 (m, 2H), 7.72 (dd, J = 8.7, 1.6 Hz, 1H), 7.65 (s, 1H), 7.66–7.44 (m, 3H), 7.20 (dd, J = 12.2, 7.2 Hz, 3H), 6.92 (t, J = 6.8 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 160.1, 148.0, 141.3, 138.9, 132.4, 131.2, 130.6, 129.9, 128.9, 127.5, 127.0, 126.8, 125.0, 124.4, 122.3, 122.1, 121.7, 118.0, 114.9, 111.9, 55.8; HRMS (ESI): *m/z* calculated for $C_{22}H_{17}N_2O$ 325.1341 found 325.1344 $[M+H]^+$.

6-(4-Chlorophenyl)naphtho[1',2':4,5]imidazo[1,2-*a*]pyridine (3d).

White solid; yield 89%; mp: 199-200 °C; FT-IR (cm^{-1}): 3076, 2925, 2855, 1670, 1614, 1508, 1407, 1373, 1282; ^1H NMR (500 MHz, DMSO-d_6): δ 8.72 (d, J = 8.7 Hz, 1H), 8.25 (s, 1H), 7.88 (dd, J = 15.9, 8.1 Hz, 2H), 7.86–7.65 (m, 4H), 7.61 (d, J = 32.0 Hz, 1H), 7.58–7.53 (m, 1H), 7.49 (t, J = 8.8 Hz, 2H), 6.93 (t, J = 6.8 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.6, 158.4, 157.9, 150.6, 143.1, 141.0, 135.4, 135.2, 134.9, 133.9, 132.9, 131.4, 129.1, 128.9, 128.7, 127.1, 123.5, 123.3, 120.2, 119.3, 118.0, 114.6, 112.9; HRMS (ESI): *m/z* calculated for $C_{21}H_{14}ClN_2$ 329.0846 found 330.0738 $[M+2]^+$.

6-(3-Bromophenyl)naphtho[1',2':4,5]imidazo[1,2-*a*]pyridine (3e).

White solid; yield 85%; mp: 199-202 °C; FT-IR (cm^{-1}): 3060, 2919, 1681, 1622, 1508, 1366, 1334, 1289; ^1H NMR (500 MHz, DMSO-d_6): δ 8.72 (d, J = 8.7 Hz, 1H), 8.24 (s, 1H), 7.89 (d, J = 9.1 Hz, 1H), 7.83 (d, J = 6.9 Hz, 1H), 7.72 (d, J = 8.6 Hz, 1H), 7.64 (d, J = 5.6 Hz, 6H), 7.57–7.51 (m, 1H), 6.89 (t, J = 6.7 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 148.0, 141.3, 137.6, 132.4, 131.2, 130.0, 129.6, 129.5, 129.1, 128.9, 127.5, 127.0, 126.6, 125.0, 124.3, 122.4, 122.2, 118.1, 111.9; HRMS (ESI): *m/z* calculated for $C_{21}H_{15}BrN_2$ 374.0419 found 374.0413 $[M+2]^+$.

6-(4-Fluorophenyl)naphtho[1',2':4,5]imidazo[1,2-*a*]pyridine (3f).

White solid; yield 85%; mp: 194-198 °C; FT-IR (cm^{-1}): 3068, 2923, 1682, 1655, 1509, 1334, 1287; ^1H NMR (500 MHz, DMSO-d_6): δ 8.21 (d, J = 7.7 Hz, 1H), 8.13 (d, J = 7.8 Hz, 1H), 8.01 (d, J = 3.2 Hz,

1H), 7.88 (t, *J* = 7.3 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 3.2 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.85 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-*d*$_6$): *δ* 159.5, 159.1, 158.3, 150.9, 139.8, 138.8, 135.8, 134.5, 134.2, 133.6, 130.7, 129.4, 128.8, 128.7, 128.5, 128.3, 126.3, 123.4, 123.1, 121.0, 114.4; HRMS (ESI): *m/z* calculated for $C_{21}H_{14}FN_2$ 313.1141 found 313.1139 $[M+H]^+$.

6-(2,5-Dichlorophenyl)naphtho[1',2':4,5]imidazo[1,2-*a*]pyridine (3g).

Off-white solid; yield 79%; mp: 197-199 ºC; FT-IR (cm^{-1}): 3068, 2923, 1682, 1655, 1509, 1334, 1287; ^{1}H NMR (500 MHz, DMSO-*d*$_6$): *δ* 8.72 (d, *J* = 8.7 Hz, 1H), 8.24 (s, 1H), 7.95 (d, *J* = 6.9 Hz, 1H), 7.88 (dt, *J* = 28.3, 14.3 Hz, 3H), 7.81 (s, 2H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.70 (s, 1H), 7.61–7.54 (m, 1H), 6.98 (t, *J* = 6.6 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-*d*$_6$): *δ* 148.1, 141.4, 141.1, 135.1, 132.2, 131.3, 129.1, 128.8, 128.5, 128.2, 127.6, 127.5, 127.1, 126.9, 125.0, 124.7, 122.7, 122.0, 118.1, 112.2; HRMS (ESI): *m/z* calculated for $C_{21}H_{13}Cl_2N_2$ 363.0456 found 364.0438 $[M+2]^+$.

6-(3,4,5-Trimethoxyphenyl)naphtho[1',2':4,5]imidazo[1,2-*a*]pyridine (3h).

White solid; yield 84%; mp: 197-200 ºC; FT-IR (cm^{-1}): 3076, 2925, 2855, 1670, 1614, 1508, 1417, 1363, 1282; ^{1}H NMR (500 MHz, DMSO-*d*$_6$): *δ* 8.20 (d, *J* = 8.0 Hz, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 7.92 (s, 1H), 7.87 (t, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.18 (s, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.85 (t, *J* = 7.6 Hz, 1H), 6.49 (s, 1H) 3,54 (s, 9H); ^{13}C NMR (125 MHz, DMSO-*d*$_6$): *δ* 159.7, 152.7, 147.6, 147.2, 145.3, 137.4, 135.2, 135.0, 133.7, 127.2, 126.8, 126.6, 126.3, 119.8, 118.8, 115.7, 115.6, 103.5, 59.9, 55.7; HRMS (ESI): *m/z* calculated for $C_{24}H_{21}N_2O_3$ 385.1552 found 385.1554 $[M+H]^+$.

6-(4-Nitrophenyl)naphtho[1',2':4,5]imidazo[1,2-*a*]pyridine (3i).

Lemon-yellow solid; yield 65%; mp: 198-202 ºC; FT-IR (cm^{-1}): 3086, 2925, 1677, 1624, 1538, 1407, 1373, 1282; ^{1}H NMR (500 MHz, DMSO-*d*$_6$): *δ* 8.55 (s, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.98–7.90 (m, 3H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 8.2, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.13–7.08 (m, 1H), 7.04 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-*d*$_6$): *δ* 167.9, 156.2, 154.2, 154.2, 147.6, 134.4, 129.5, 129.5, 129.0, 126.8, 125.4, 125.3, 125.2, 124.3, 124.2, 123.9, 123.3, 123.3, 122.6, 122.5, 116.8, 116.6, 115.6; HRMS (ESI): *m/z* calculated for $C_{21}H_{14}N_3O_2$ 340.1086 found 340.1082 $[M+H]^+$.

3-Methyl-6-(*p*-tolyl)naphtho[1',2':4,5]imidazo[1,2-*a*]pyridine (3j).

Off-white solid; yield 92%; mp: 193-195 °C; FT-IR (cm^{-1}): 3068, 2923, 1682, 1655, 1509, 1334, 1287; ^1H NMR (500 MHz, DMSO-d_6): δ 8.61 (d, J = 8.2 Hz, 1H), 7.88 (dd, J = 18.7, 9.7 Hz, 3H), 7.55 (d, J = 8.2 Hz, 1H), 7.50 (dd, J = 14.4, 8.0 Hz, 4H), 7.44 (d, J = 7.6 Hz, 2H), 6.87 (t, J = 6.7 Hz, 1H), 2.55 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 147.6, 141.71, 138.2, 135.9, 135.1, 131.7, 130.0, 129.5, 128.6, 128.6, 128.2, 127.9, 126.5, 124.0, 122.8, 122.8, 121.8, 118.0, 111.4, 21.8, 21.4; HRMS (ESI): *m/z* calculated for $C_{23}H_{19}N_2$ 323.1548 found 323.1549 $[M+H]^+$.

6-(4-Fluorophenyl)-3-methylnaphtho[1',2':4,5]imidazo[1,2-*a*]pyridine (3k).

Off-white solid; yield 86%; mp: 195-198 °C; FT-IR (cm^{-1}): 3068, 2925, 1682, 1660, 1622, 1526, 1504, 1415, 1384, 1346; ^1H NMR (500 MHz, DMSO-d_6): δ 8.61 (d, J = 8.3 Hz, 1H), 7.85 (dd, J = 13.6, 5.1 Hz, 3H), 7.69 (dd, J = 8.4, 5.5 Hz, 2H), 7.56 (d, J = 8.2 Hz, 1H), 7.53–7.44 (m, 4H), 6.87 (t, J = 7.1 Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 163.6, 161.6, 147.7, 141.7, 136.0, 134.4, 134.4, 132.6, 132.5, 131.8, 131.7, 131.6, 128.8, 128.4, 127.9, 127.6, 126.6, 124.1, 123.1, 122.8, 121.8, 118.0, 116.4, 116.3, 116.1, 116.0, 111.7, 21.8; HRMS (ESI): *m/z* calculated for $C_{22}H_{16}FN_2$ 327.1298 found 327.1285 $[M+H]^+$.

3-Methoxy-6-(*p*-tolyl)naphtho[1',2':4,5]imidazo[1,2-*a*]pyridine (3l).

White solid; yield 94%; mp: 194-197 °C; FT-IR (cm^{-1}): 3066, 2924, 1687, 1658, 1628, 1585, 1533, 1503, 1411, 1380, 1285; ^1H NMR (500 MHz, DMSO-d_6): δ 8.59 (d, J = 8.9 Hz, 1H), 7.86 (d, J = 7.0 Hz, 1H), 7.73 (d, J = 9.0 Hz, 1H), 7.42 (d, J = 8.1 Hz, 3H), 7.40–7.33 (m, 4H), 7.26 (dd, J = 8.8, 2.0 Hz, 1H), 6.69 (t, J = 6.8 Hz, 1H), 3.90 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 158.2, 147.7, 141.9, 138.1, 135.0, 132.9, 129.8, 129.2, 128.9, 127.8, 126.6, 124.3, 122.5, 121.1, 120.6, 117.7, 117.6, 110.9, 107.9, 55.5, 21.4; HRMS (ESI): *m/z* calculated for $C_{23}H_{19}N_2O$ 339.1497 found 339.1492 $[M+H]^+$.

3-Methoxy-6-(3-methoxyphenyl)naphtho[1',2':4,5]imidazo[1,2-*a*]pyridine (3m).

White solid; yield 95%; mp: 198-200 °C; FT-IR (cm^{-1}): 2928, 1686, 1655, 1634, 1579, 1524, 1334, 1260; ^1H NMR (500 MHz, DMSO-d_6): 8.62 (d, J = 8.5 Hz, 1H), 7.87 (dd, J = 15.6, 7.6 Hz, 2H), 7.65–7.45 (m, 4H), 7.37 (d, J = 8.0 Hz, 1H), 7.19 (d, J = 9.2 Hz, 3H), 6.88 (s, 1H), 3.93 (s, 3H), 3.83 (d, J =

20.0 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 160.0, 158.2, 147.7, 139.4, 132.9, 130.6, 128.9, 128.3, 126.6, 124.4, 122.4, 121.7, 120.7, 118.1, 117.8, 114.9, 114.8, 111.4, 108.4, 55.8, 55.7; HRMS (ESI): *m/z* calculated for $C_{23}H_{19}N_2O_2$ 355.1447 found 355.1449 $[M+H]^+$.

3-Chloro-6-(4-fluorophenyl)naphtho[1',2':4,5]imidazo[1,2-*a*]pyridine (3n).

White solid; yield 87%; mp: 194-197 °C; FT-IR (cm^{-1}): 3055, 2921, 1679, 1662, 1634, 1607, 1518, 1419, 1344, 1285; ^{1}H NMR (500 MHz, DMSO-d_6): 8.61 (d, J = 8.9 Hz, 1H), 7.88 (d, J = 9.1 Hz, 1H), 7.88–7.83 (m, 2H), 7.81 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.66–7.50 (m, 4H), 7.50 (dd, J = 9.0, 6.9 Hz, 1H), 7.37 (dd, J = 8.9, 2.3 Hz, 1H), 6.88 (t, J = 6.8 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 158.3, 147.8, 141.9, 140.4, 132.8, 132.2, 131.8, 131.4, 128.8, 128.4, 127.4, 126.5, 124.4, 122.9, 122.7, 120.8, 120.7, 118.3, 117.9, 111.6, 108.5, 55.7; HRMS (ESI): *m/z* calculated for $C_{21}H_{13}ClFN_2$ 347.0751 found 348.0746 $[M+2]^+$.

6-(Pyridin-4-yl)naphtho[1',2':4,5]imidazo[1,2-*a*]pyridine (3o).

White solid; yield 81%; mp: 192-195 °C; FT-IR (cm^{-1}): 3085, 2821, 1689, 1666, 1637, 1528, 1415, 1354, 1295; ^{1}H NMR (500 MHz, DMSO-d_6): 8.56 (s, 1H), 8.08 (d, J = 8.0 Hz, 1H), 8.05–7.86 (m, 3H), 7.50 (d, J = 8.3 Hz, 1H), 7.41 (d, J = 7.7 Hz, 2H), 7.30 (d, J = 8.2 Hz, 1H), 7.20 (t, J = 7.7 Hz, 1H), 7.11 (t, J = 7.9 Hz, 1H), 7.05 (d, J = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 167.9, 156.2, 154.2, 154.2, 147.6, 134.4, 129.5, 129.0, 126.8, 125.3, 125.2, 124.2, 123.9, 123.3, 122.6, 122.53, 116.8, 116.6, 115.6; HRMS (ESI): *m/z* calculated for $C_{20}H_{14}N_3$ 296.1188 found 296.1192$[M+H]^+$.

6-Phenylanthra[1',2':4,5]imidazo[1,2-*a*]pyridine (3p).

Yellow solid; yield 93%; mp: 227-279 °C; FT-IR (cm^{-1}): 3075, 2852, 1686, 1654, 1598, 1313, 1286, 1230; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.34 (s, 1H), 8.74 (s, 1H), 8.31 (d, J = 7.9 Hz, 1H), 8.17 (d, J = 7.8 Hz, 1H), 7.98–7.91 (m, 2H), 7.85 (dd, J = 14.5, 7.5 Hz, 2H), 7.78 (s, 1H), 7.73 (d, J = 7.5 Hz, 1H), 7.72–7.54 (m, 4H), 7.55–7.51 (m, 1H), 6.96 (t, J = 6.8 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.3, 162.3, 141.2, 136.3, 134.9, 133.0, 130.3, 130.2, 128.6, 128.0, 127.7, 127.6, 127.3, 127.0, 122.2, 120.9, 117.1, 116.5, 115.9, 115.7, 111.4; HRMS (ESI): *m/z* calculated for $C_{25}H_{17}N_2$ 345.1392 found 345.1380 $[M+H]^+$.

6-(3-Methoxyphenyl)anthra[1',2':4,5]imidazo[1,2-*a*]pyridine (3q).

Yellow solid; yield 93%; mp: 234-236 °C; FT-IR (cm^{-1}): 3102, 2921, 1688, 1656, 1621, 1587, 1378, 1367, 1286; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.34 (s, 1H), 8.71 (s, 1H), 8.30 (d, J = 7.9 Hz, 1H), 8.15 (d, J = 7.8 Hz, 1H), 7.90 (dd, J = 17.1, 8.0 Hz, 2H), 7.74 (s, 1H), 7.63–7.55 (m, 3H), 7.52–7.48 (m, 1H), 7.28–7.22 (m, 2H), 7.19 (dd, J = 8.3, 2.0 Hz, 1H), 6.92 (t, J = 6.8 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 160.0, 147.3, 141.6, 139.3, 131.8, 131.7, 130.6, 130.2, 129.2, 128.8, 128.5, 127.8, 127.4, 126.4, 126.3, 126.1, 125.1, 123.5, 121.8, 121.3, 121.2, 118.0, 114.9, 114.8, 112.1, 55.8; HRMS (ESI): *m/z* calculated for $C_{26}H_{19}N_2O$ 375.1497 found 375.1507 $[M+H]^+$.

6-(*p*-Tolylphenyl)anthra[1',2':4,5]imidazo[1,2-*a*]pyridine (3r).

Yellow solid; yield 91%; mp: 232-234 °C; FT-IR (cm^{-1}): 3102, 2921, 1688, 1656, 1621, 1587, 1378, 1367, 1286; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.34 (s, 1H), 8.74 (s, 1H), 8.31 (d, J = 7.8 Hz, 1H), 8.17 (d, J = 7.7 Hz, 1H), 7.91 (dd, J = 13.2, 8.0 Hz, 2H), 7.77–7.69 (m, 5H), 7.65–7.58 (m, 2H), 7.55 – 7.50 (m, 1H), 6.96 (dd, J = 9.8, 3.9 Hz, 1H), 1.95 (S, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 172.4, 147.4, 141.7, 136.8, 133.8, 131.9, 131.8, 131.5, 130.1, 129.5, 128.8, 128.5, 128.1, 127.8, 127.5, 126.5, 126.4, 126.1, 125.1, 123.9, 121.4, 121.1, 118.08, 112.34, 21.5; HRMS (ESI): *m/z* calculated for $C_{25}H_{16}ClN_2$ 359.1548 found 359.1551 $[M+H]^+$.

6-(4-Fluorophenyl)anthra[1',2':4,5]imidazo[1,2-*a*]pyridine (3s).

Yellow solid; yield 89%; mp: 230-233 °C; FT-IR (cm^{-1}): 3095, 2918, 1687, 1857, 1616, 1586, 1511, 1371, 1287; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.35 (s, 1H), 8.75 (s, 1H), 8.31 (d, J = 7.7 Hz, 1H), 8.17 (d, J = 7.6 Hz, 1H), 7.93 (d, J = 9.0 Hz, 1H), 7.83 (d, J = 7.0 Hz, 1H), 7.75 (s, 1H), 7.70 (t, J = 6.8 Hz, 2H), 7.66 (dd, J = 6.7, 4.6 Hz, 2H), 7.62 (dd, J = 11.3, 4.2 Hz, 2H), 7.54–7.50 (m, 1H), 6.91 (t, J = 6.8 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 147.3, 141.7, 140.3, 132.2, 131.9, 131.5, 130.1, 128.8, 128.6, 127.9, 127.8, 127.6, 126.4, 126.3, 126.2, 125.2, 124.0, 122.7, 121.4, 121.0, 118.1, 112.3; HRMS (ESI): *m/z* calculated for $C_{25}H_{16}FN_2$ 363.1298 found 363.1295 $[M+H]^+$.

3-Fluoro-6-(4-methoxyphenyl)naphtho[1',2':4,5]imidazo[1,2-*a*]pyridine (3t).

Off-white solid; yield 78%; mp: 232-235 °C; FT-IR (cm^{-1}): 3112, 2912, 1689, 1666, 1631, 1578, 1387, 1376, 1268; ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.17 (s, 1H), 7.86 (dd, J = 14.5, 4.7 Hz, 2H), 7.64 (s, 1H), 7.54 (s, 1H), 7.48 (dd, J = 9.6, 2.5 Hz, 1H), 7.39 (dd, J = 11.7, 4.9 Hz, 1H), 7.23 (d, J = 9.1 Hz,

1H), 7.19 (d, *J* = 8.6 Hz, 2H), 7.15 (s, 1H), 6.84 (t, *J* = 6.8 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 163.0, 160.9, 159.9, 159.0, 146.6, 141.6, 136.9, 133.6, 133.3, 131.2, 130.7, 129.6, 129.3, 128.4, 126.4, 117.6, 114.9, 114.1, 111.7, 55.5; HRMS (ESI): *m/z* calculated for $C_{22}H_{16}FN_2O$ 343.1247 found 343.1251 $[M+H]^+$.

6-(4-Methoxyphenyl)naphtho[1',2':4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (3u).

Yellow solid; yield 76%; mp: 233-236 ^oC; FT-IR (cm^{-1}): 3012, 2932, 2865, 2245, 1678, 1665, 1644, 1596, 1389, 1378, 1297; ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.82 (t, *J* = 5.7 Hz, 1H), 8.59 (s, 1H), 8.15 (d, *J* = 8.4 Hz, 2H), 7.99–7.97 (m, 1H), 7.90 (s, 2H), 7.60 (s, 2H), 7.31–7.28 (m, 1H), 7.20 (d, *J* = 1.5 Hz, 1H), 6.94 (d, *J* = 1.1 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 160.0, 142.8, 138.9, 134.7, 133.2, 130.8, 128.8, 127.6, 126.5, 126.2, 126.1, 124.2, 123.1, 117.4, 114.9, 113.2, 112.2, 111.6, 55.7; HRMS (ESI): *m/z* calculated for $C_{23}H_{16}N_3O$ 350.1293 found 350.1289 $[M+H]^+$.

3,4-Dichloro-6-phenylnaphtho[1',2':4,5]imidazo[1,2-*a*]pyridine (3v).

White solid; yield 81%; mp: 231-234 ^oC; FT-IR (cm^{-1}): 3087, 2925, 1676, 1846, 1605, 1575, 1500, 1360, 1276; ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.80 (s, 1H), 8.48 (d, *J* = 6.0 Hz, 1H), 7.95 (s, 1H), 7.89 (d, *J* = 9.1 Hz, 1H), 7.82 (d, *J* = 7.0 Hz, 1H), 7.66 (d, *J* = 3.7 Hz, 5H), 7.51 (s, 1H), 6.91 (t, *J* = 6.7 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 148.1, 140.2, 137.1, 133.3, 130.8, 130.2, 129.7, 129.5, 129.3, 129.0, 126.7, 125.1, 124.1, 122.8, 121.8, 118.2, 112.2; HRMS (ESI): *m/z* calculated for $C_{21}H_{13}Cl_2N_2$ 363.0456 found 363.0447 $[M+H]^+$.

3-Bromo-10-methyl-6-phenylnaphtho[1',2':4,5]imidazo[1,2-*a*]pyridine (3w).

Off-white solid; yield 79%; mp: 235-238 ^oC; FT-IR (cm^{-1}): 3113, 2910, 1697, 1665, 1630, 1596, 1387, 1375, 1294; ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.61 (d, *J* = 8.7 Hz, 1H), 8.38 (d, *J* = 1.9 Hz, 1H), 7.81 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.69 (s, 1H), 7.64 (d, *J* = 2.8 Hz, 5H), 7.63 (d, *J* = 4.9 Hz, 1H), 7.59 (s, 1H), 6.73 (dd, *J* = 7.2, 1.6 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 148.5, 141.5, 139.8, 137.6, 132.7, 130.6, 129.8, 129.6, 129.5, 129.4, 129.1, 125.7, 125.1, 124.4, 122.3, 121.6, 119.6, 116.1, 114.4, 21.5; HRMS (ESI): *m/z* calculated for $C_{22}H_{16}BrN_2$ 387.0497 found 389.0441 $[M+2]^+$.

10-Chloro-6-(4-methoxyphenyl)naphtho[1',2':4,5]imidazo[1,2-*a*]pyridine (3x).

Off-white solid; yield 80%; mp: 229-231 °C; FT-IR (cm^{-1}): 3115, 2899, 1666, 1634, 1609, 1565, 1356, 1345, 1275; ^1H NMR (500 MHz, DMSO-d_6): δ 8.15 (s, 1H), 8.07 (d, J = 7.9 Hz, 1H), 7.86 (s, 1H), 7.71 (s, 1H), 7.62 (dd, J = 10.0, 7.2 Hz, 2H), 7.58 (d, J = 4.3 Hz, 1H), 7.55 (s, 1H), 7.45 (d, J = 9.6 Hz, 1H), 7.29 (d, J = 9.6 Hz, 1H), 7.23 (s, 1H), 7.14 (s, 1H), 3.91 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 163.0, 160.1, 144.4, 142.0, 130.9, 130.7, 130.5, 128.7, 127.9, 126.4, 125.1, 124.2, 118.9, 118.5, 117.8, 114.9, 114.1, 83.8, 55.9, 55.8; HRMS (ESI): *m/z* calculated for $C_{25}H_{16}ClN_2O$ 359.0951 found 359.0962 $[M+H]^+$.

5-Phenylthieno[2'',3'':5',6']benzo[1',2':4,5]imidazo[1,2-*a*]pyridine (3y).

Off-white solid; yield 68%; mp: 225-228 °C; FT-IR (cm^{-1}): 3064, 2903, 1653, 1696, 1595, 1427, 1351, 1268; ^1H NMR (500 MHz, DMSO-d_6): δ 8.74–8.72 (m, 1H), 8.36 (d, J = 8.0 Hz, 1H), 8.30 (d, J = 7.9 Hz, 1H), 7.99 (s, 2H), 7.95 (d, J = 6.3 Hz, 1H), 7.76 (s, 1H), 7.55 (s, 2H), 7.51 (s, 1H), 7.44 (s, 1H), 7.03 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 147.9, 145.0, 133.9, 131.6, 131.1, 131.0, 130.9, 130.1, 127.8, 127.1, 126.2, 122.0, 117.8, 115.3, 114.9; HRMS (ESI): *m/z* calculated for $C_{19}H_{13}N_2S$ 301.0799 found 301.0809 $[M+H]^+$.

6-Phenylbenzo[*d*]naphtho[1',2':4,5]imidazo[2,1-*b*]thiazole (5a).

White solid; yield 90%; mp: 196-199 °C; FT-IR (cm^{-1}): 3076, 2925, 1674, 1618, 1518, 1409, 1373, 1292; ^1H NMR (500 MHz, DMSO-d_6): δ 8.55–8.30 (m, 2H), 8.19–8.03 (m, 1H), 7.90–7.76 (m, 3H), 7.66 (d, J = 8.3 Hz, 2H), 7.61–7.57 (m, 1H), 7.26 (dd, J = 16.0, 7.6 Hz, 2H), 6.79–6.65 (m, 2H), 5.84 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 163.8, 147.9, 145.0, 133.9, 131.6, 131.2, 131.0, 130.8, 130.1, 128.1, 127.8, 127.4, 127.2, 126.3, 126.2, 122.3, 122.0, 117.8, 115.3, 114.9; HRMS (ESI): *m/z* calculated for $C_{23}H_{15}N_2S$ 351.0956 found 351.0960 $[M+H]^+$.

6-(*p*-Tolyl)benzo[*d*]naphtho[1',2':4,5]imidazo[2,1-*b*]thiazole (5b). White solid; yield 88%; mp: 194-196 °C; FT-IR (cm^{-1}): 3076, 2925, 2855, 1670, 1614, 1508, 1407, 1373, 1282; ^1H NMR (500 MHz, DMSO-d_6): δ 8.80 (d, J = 8.2 Hz, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.79–7.65 (m, 3H), 7.63 (t, J = 7.6 Hz, 1H), 7.53 (d, J = 7.5 Hz, 2H), 7.41 (d, J = 7.6 Hz, 2H), 7.24 (d, J = 15.4 Hz, 1H), 6.99 (t, J = 8.1 Hz, 1H), 6.01 (d, J = 8.4 Hz, 1H), 2.60 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): 198.3, 144.2, 143.0, 138.4, 137.5, 135.7, 134.0, 133.5, 132.5, 132.4, 129.8, 129.4, 129.3, 129.1, 128.5, 128.3, 125.4, 124.0,

123.6, 123.5, 118.6, 116.4, 21.7; HRMS (ESI): *m/z* calculated for $C_{24}H_{17}N_2S$ 365.1112 found 365.1113 $[M+H]^+$.

2-Methyl-6-(*p*-tolyl)benzo[d]naphtho[1',2':4,5]imidazo[2,1-b]thiazole (5c).

White solid; yield 89%; mp: 195-199 °C; FT-IR (cm^{-1}): 3076, 2935, 1670, 1614, 1508, 1407, 1383, 1288; ^1H NMR (500 MHz, DMSO-d_6): δ 8.09 (d, J = 7.9 Hz, 1H), 8.05 (s, 1H), 7.54 (d, J = 6.7 Hz, 2H), 7.41 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 7.4 Hz, 3H), 7.14 (t, J = 7.7 Hz, 1H), 6.88 (t, J = 8.0 Hz, 1H), 5.87 (d, J = 8.4 Hz, 1H), 5.34 (s, 1H), 2.51 (d, J = 16.8 Hz, 6H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 198.4, 144.4, 143.1, 138.5, 137.7, 135.8, 134.2, 133.7, 132.6, 132.5, 129.9, 129.5, 129.4, 129.2, 128.6, 128.5, 125.6, 124.1, 123.8, 123.6, 118.7, 116.5, 21.8, 21.5; HRMS (ESI): *m/z* calculated for $C_{25}H_{19}N_2S$ 379.1269 found 379.1266 $[M+H]^+$.

6-Isobutylbenzo[*d*]naphtho[1',2':4,5]imidazo[2,1-*b*]thiazole (5d).

White solid; yield 72%; mp: 183-185 °C; FT-IR (cm^{-1}): 2945, 1662, 1624, 1538, 1407, 1362, 1266; ^1H NMR (500 MHz, DMSO-d_6): δ 8.16 (d, J = 8.0, 2H), 7.81 (d, J = 7.0 Hz, 1H), 7.68 (d, J = 8.3, 1H), 7.47 (d, J = 7.1 Hz, 1H), 7.34–7.27 (m, 1H), 6.91–6.83 (m, 2H), 6.18 (t, J = 9.6 Hz, 1H), 1.82–1.78 (m, 1H), 1.68–1.60 (m, 1H), 1.27–1.22 (m, 1H), 0.95 (d, J = 6.5 Hz, 3H), 0.83 (d, J = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 159.5, 148.2, 147.4, 145.3, 135.1, 134.0, 127.5, 127.4, 126.8, 126.3, 120.6, 118.9, 116.4, 115.7, 61.0, 41.5, 24.0, 23.6, 21.8; HRMS (ESI): *m/z* calculated for $C_{27}H_{16}ClN_2S$ 331.1269 found 331.1275 $[M+H]^+$.

6-Phenylbenzo[e]pyrido[1,2-*a*]indole (7a).

White solid; yield 63%; mp: 195-197 °C; FT-IR (cm^{-1}): 3216, 2954, 1627, 1614, 1581, 1472, 1326, 1267; ^1H NMR (500 MHz, DMSO-d_6): δ 8.22 (dd, J = 6.9, 1.0 Hz, 1H), 7.97 (d, J = 1.2 Hz, 1H), 7.72 (d, J = 1.2 Hz, 1H), 7.70 (d, J = 1.2 Hz, 1H), 7.42–7.37 (m, 5H), 7.28–7.20 (m, 2H), 6.77 (s, 1H), 6.72–6.69 (m, 1H), 6.70–6.66 (m, 1H), 6.55–6.53 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 135.4, 134.0, 133.4, 129.3, 129.1, 128.7, 128.7, 126.9, 126.1, 126.0, 125.4, 125.3, 119.1, 118.7, 118.0, 110.9, 110.5, 110.3, 96.6; HRMS (ESI): *m/z* calculated for $C_{22}H_{16}N$ 294.1283 found 294.1298 $[M+H]^+$.

6-Phenyl-7a,11a-dihydroindolo[2,1-*a*]isoquinoline (9a).

White solid; yield 59%; mp: 182-185 ^{o}C; FT-IR (cm^{-1}): 2955, 1682, 1644, 1583, 1435, 1356, 1278; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18–8.14 (m, 1H), 7.75 (t, J = 9.8 Hz, 1H), 7.39 (d, J = 7.9 Hz, 2H), 7.38–7.30 (m, 3H), 7.29–7.17 (m, 2H), 7.17 (dd, J = 11.3, 4.0 Hz, 1H), 6.98 (dd, J = 11.4, 4.0 Hz, 1H), 6.92 (t, J = 7.5 Hz, 1H), 6.71 (t, J = 10.3 Hz, 1H), 6.60 (s, 1H), 6.48 (t, J = 10.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 135.3, 133.4, 129.2, 128.7, 128.6, 128.6, 128.4, 127.3, 127.1, 126.9, 126.1, 126.0, 119.0, 118.0, 110.8, 110.3, 96.6; HRMS (ESI): *m/z* calculated for $C_{22}H_{16}N$ 294.1283 found 294.1292 $[M+H]^+$.

7. References

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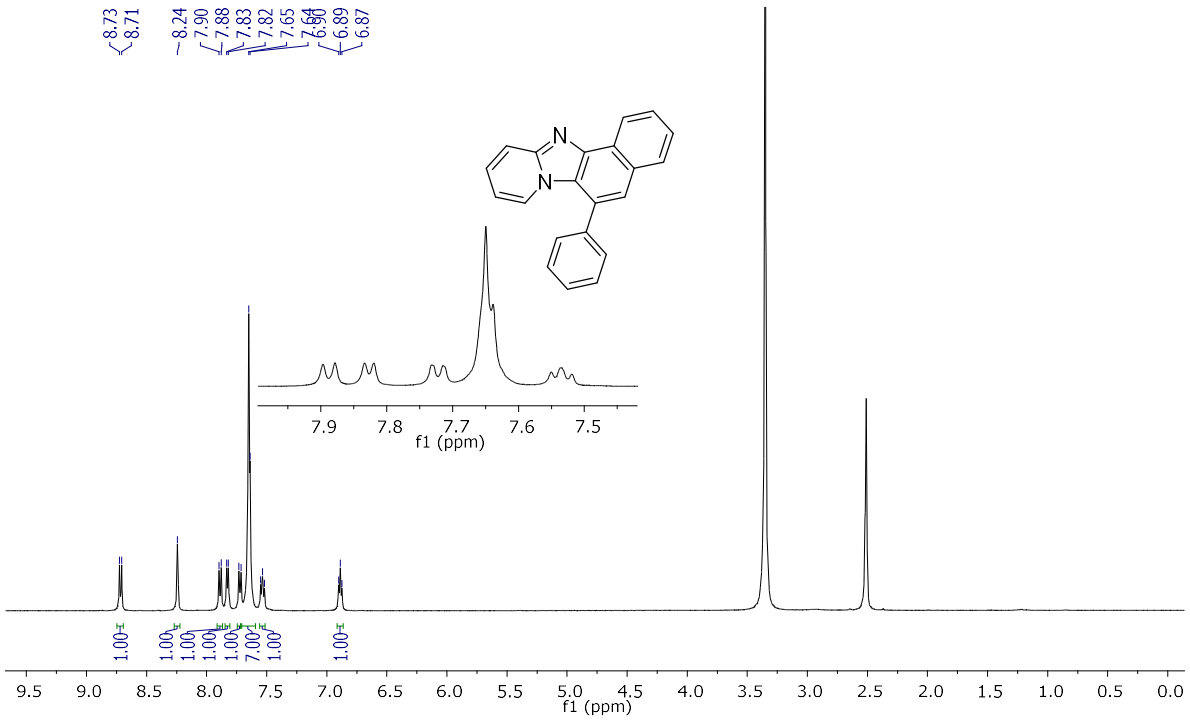
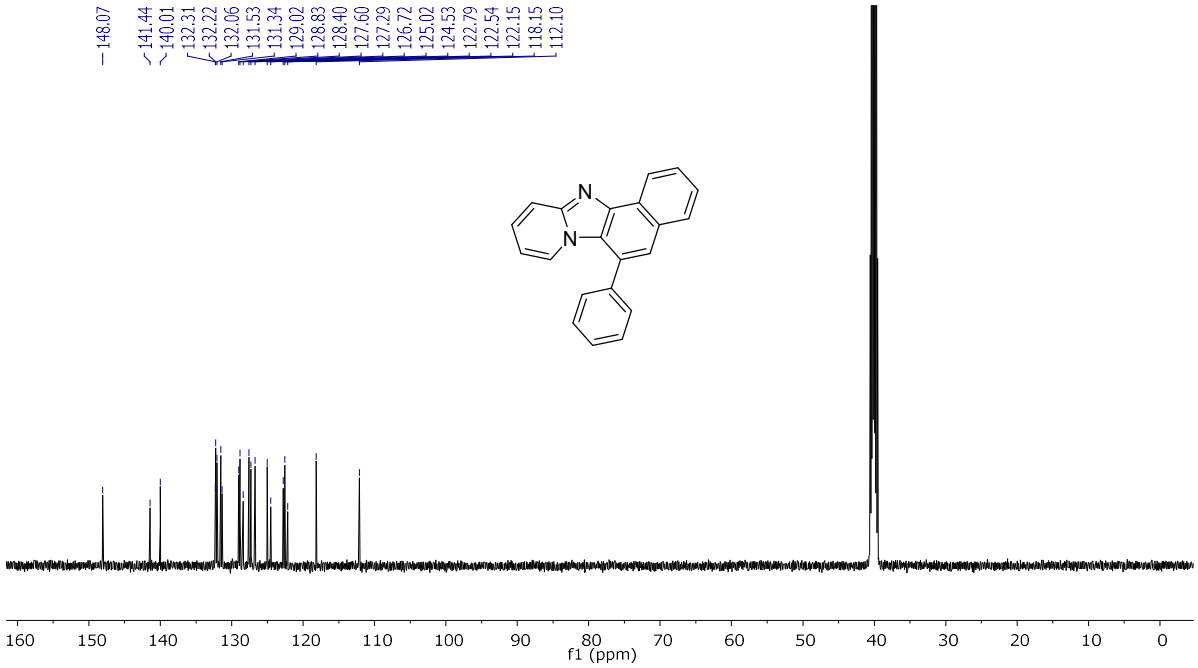
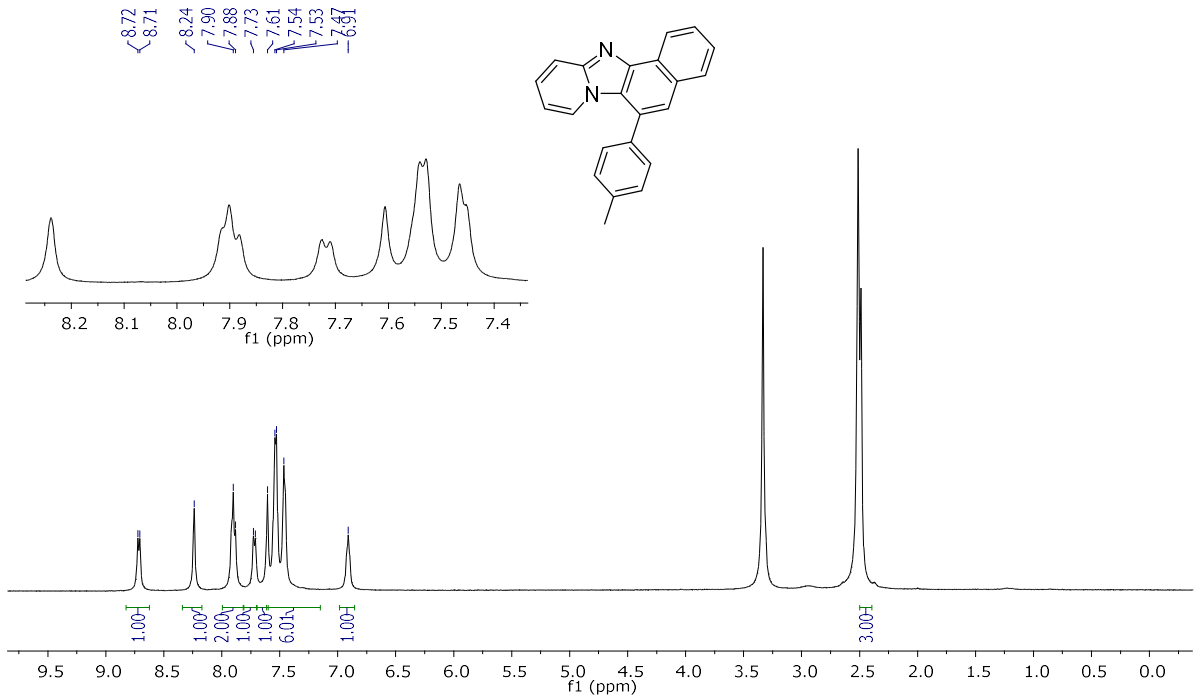
Copies of NMR spectra



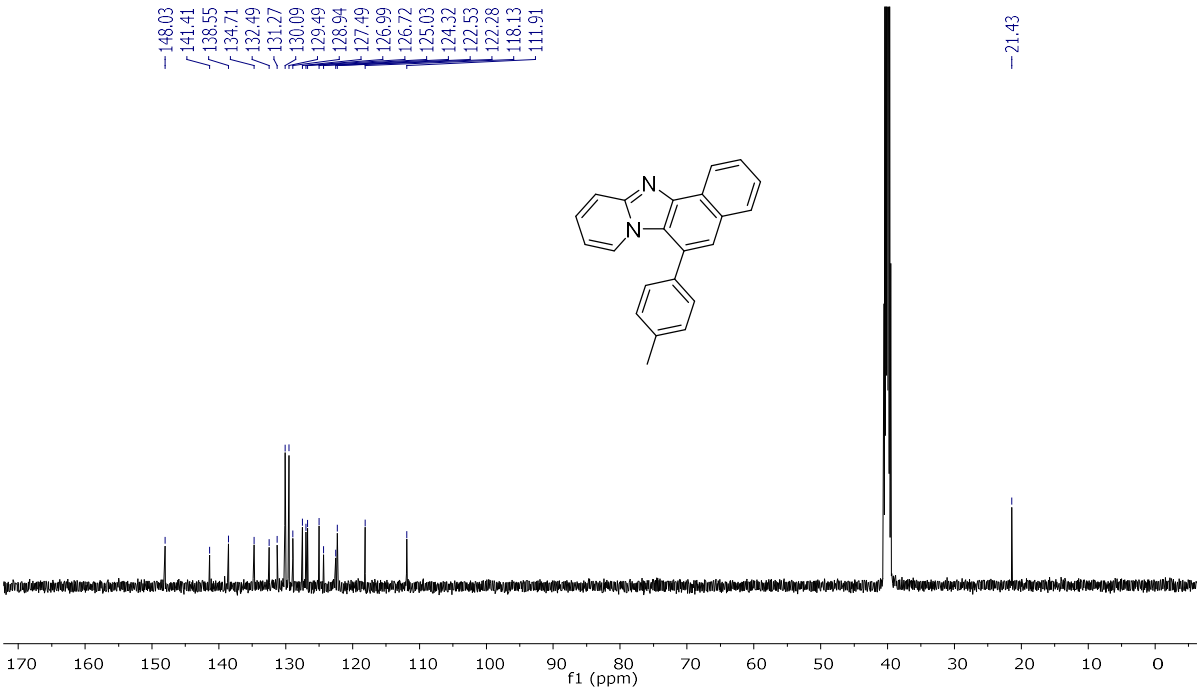
Compound **3a**: ^{1}H NMR (500 MHz, DMSO-d_6).



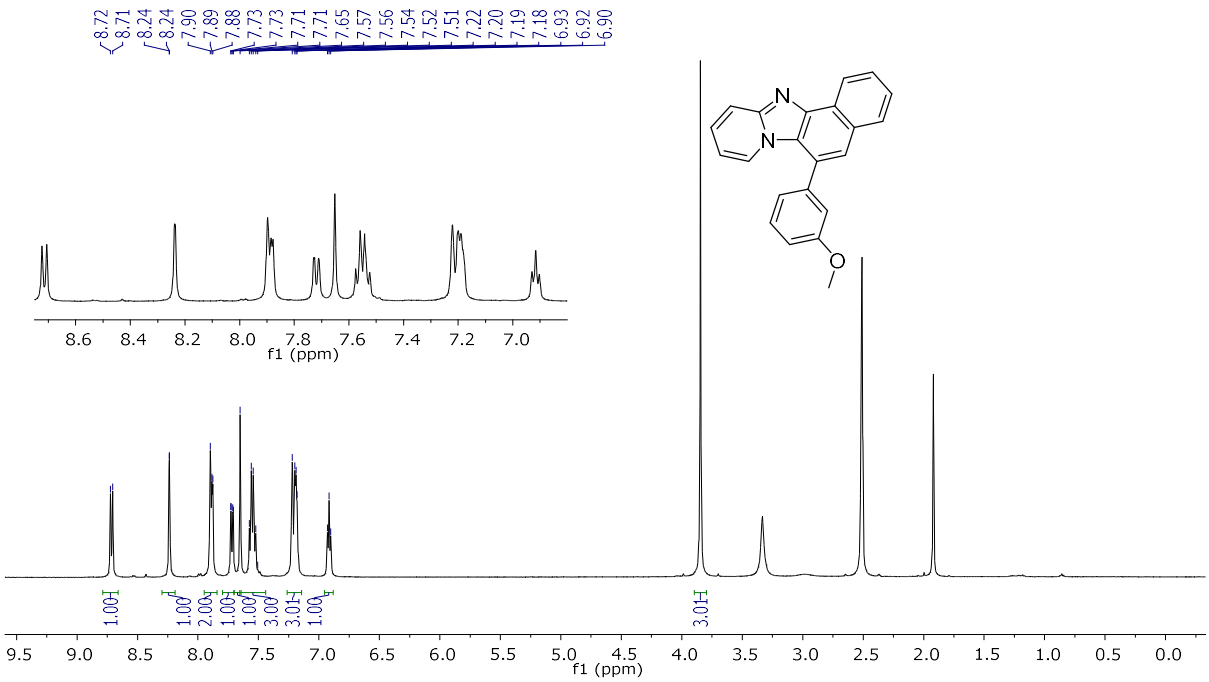
Compound **3a**: ^{13}C NMR (125 MHz, DMSO-d_6).



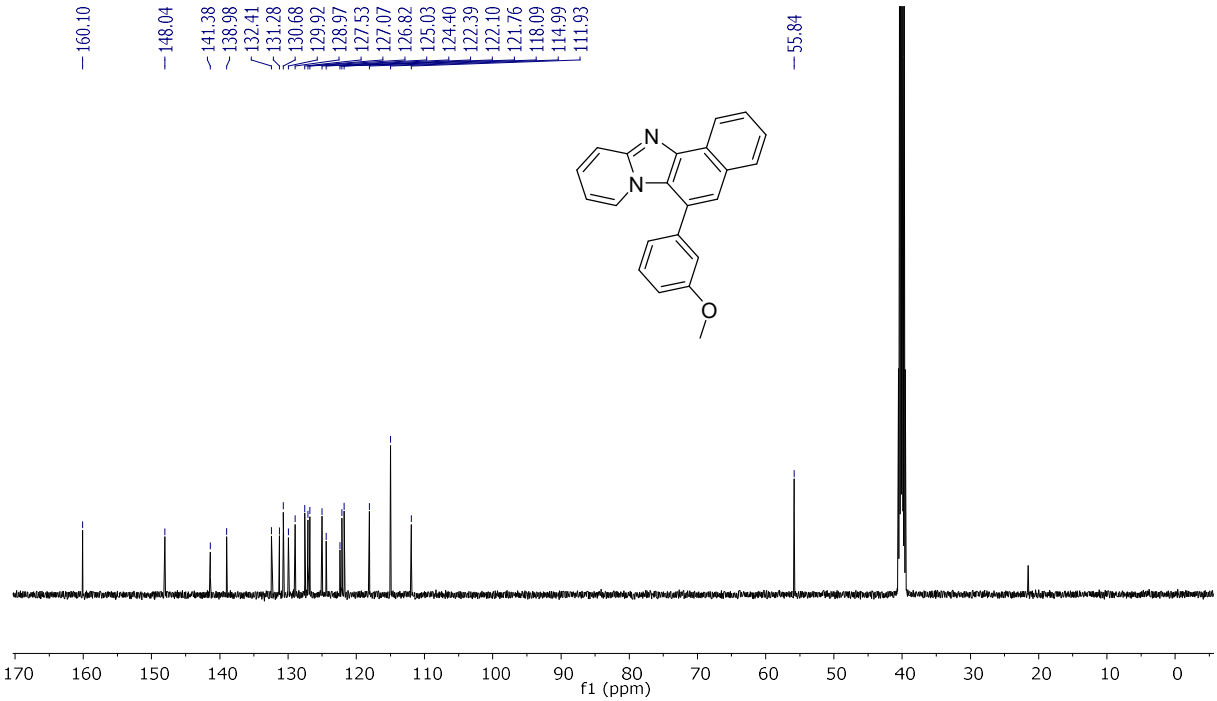
Compound **3b**: ^{1}H NMR (500 MHz, DMSO-d_6).



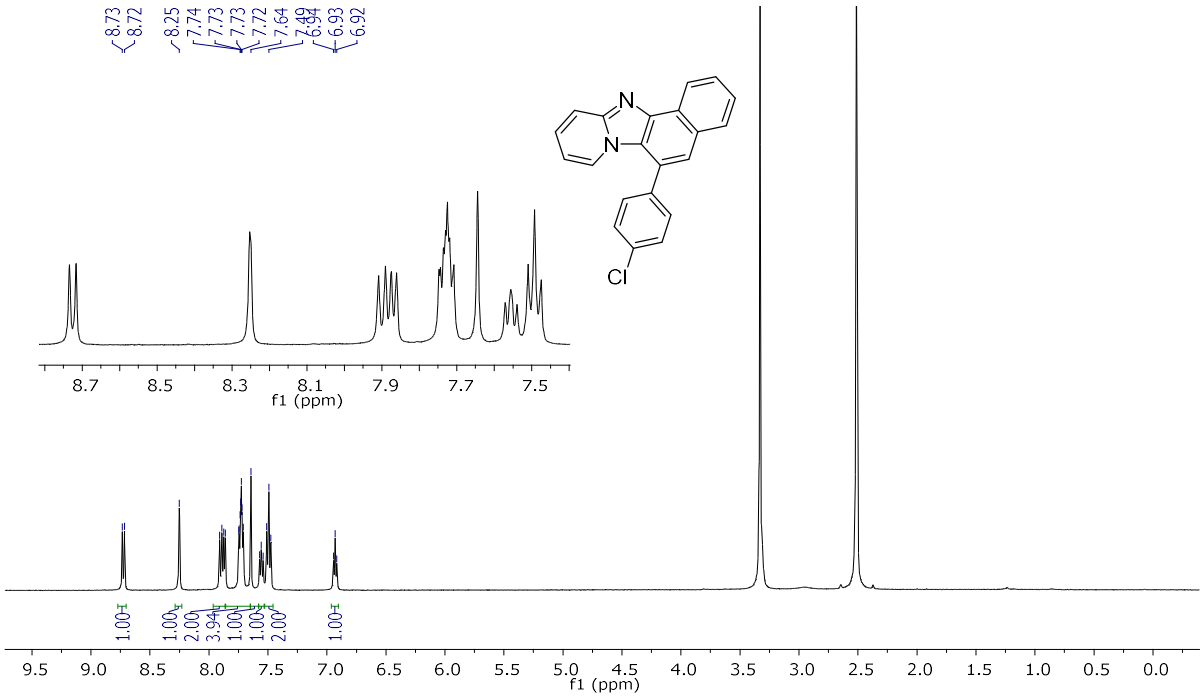
Compound **3b**: ^{13}C NMR (125 MHz, DMSO-d_6).



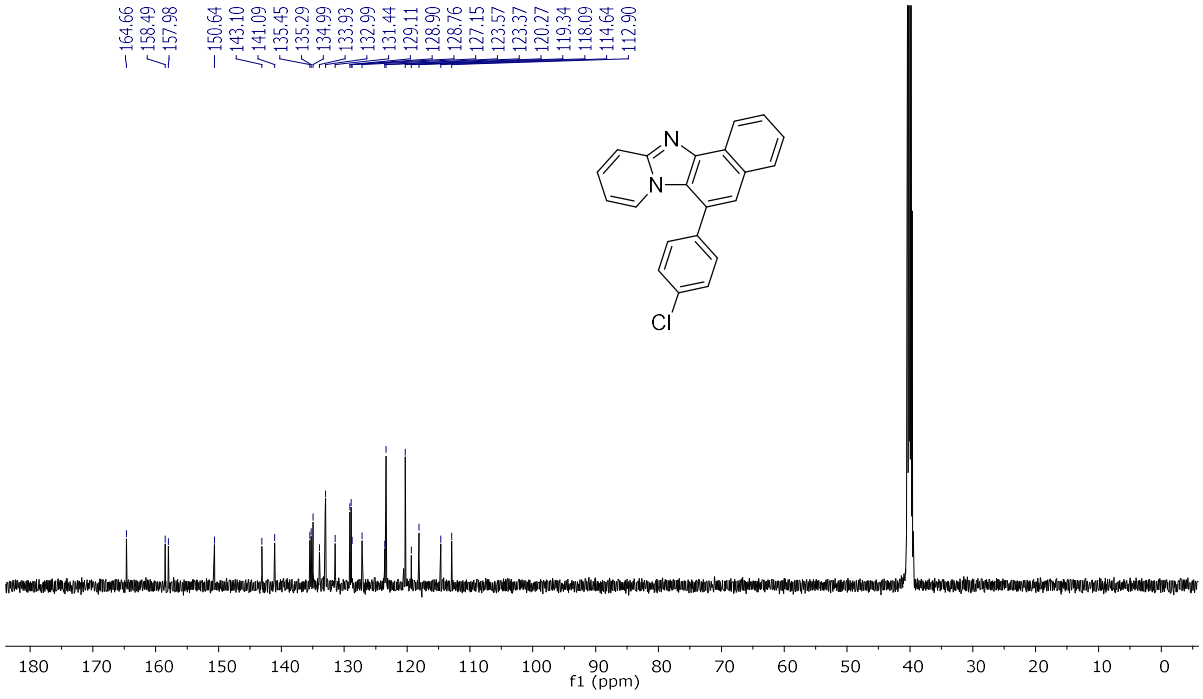
Compound **3c**: ^{1}H NMR (500 MHz, DMSO-d_6).



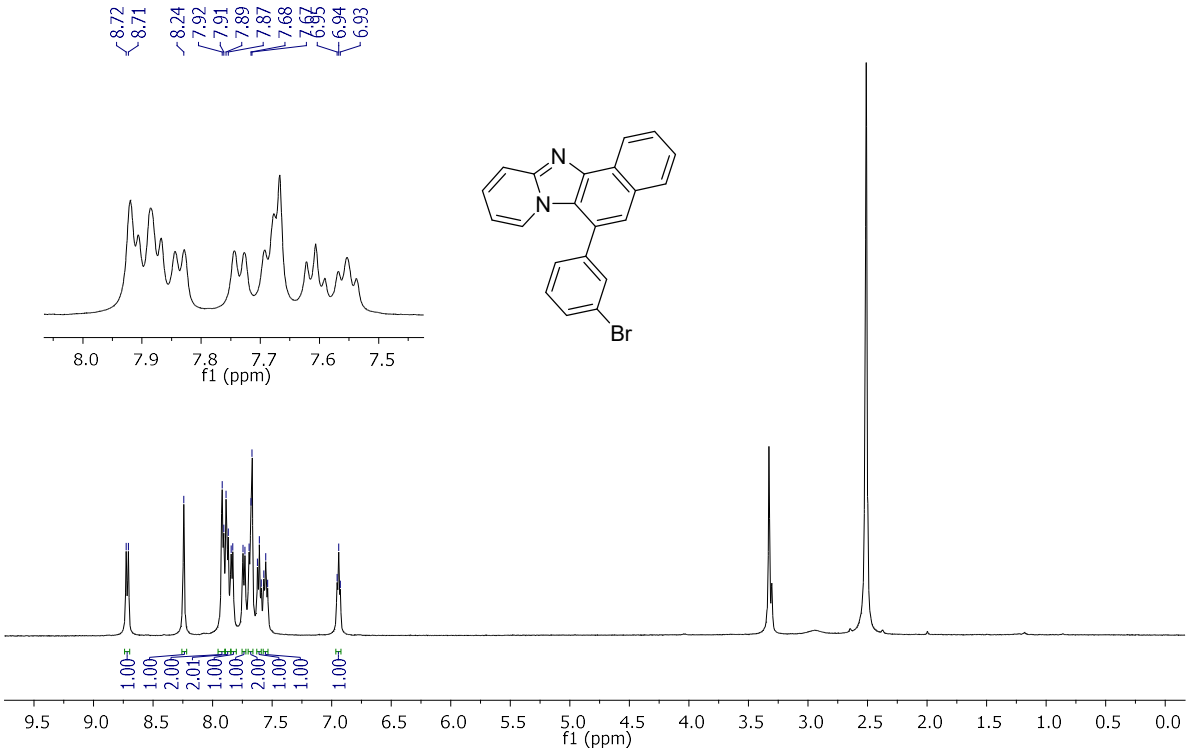
Compound **3c**: ^{13}C NMR (125 MHz, DMSO-d_6).



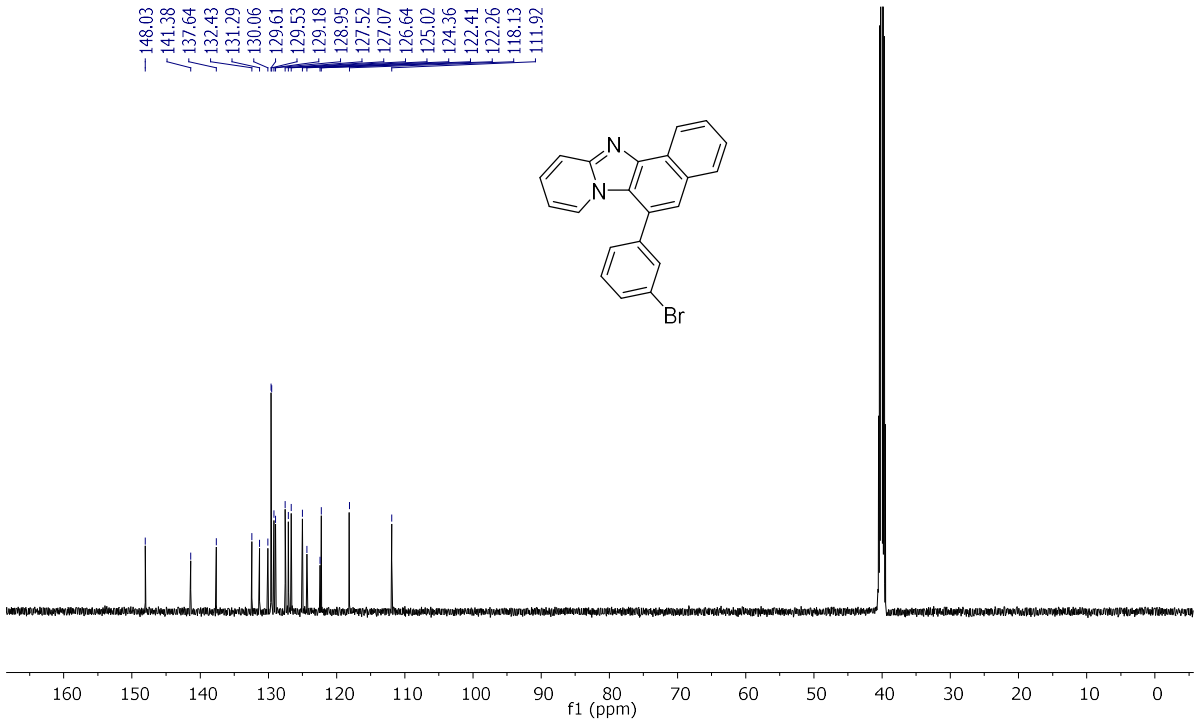
Compound **3d**: ^{1}H NMR (500 MHz, DMSO-d_6).



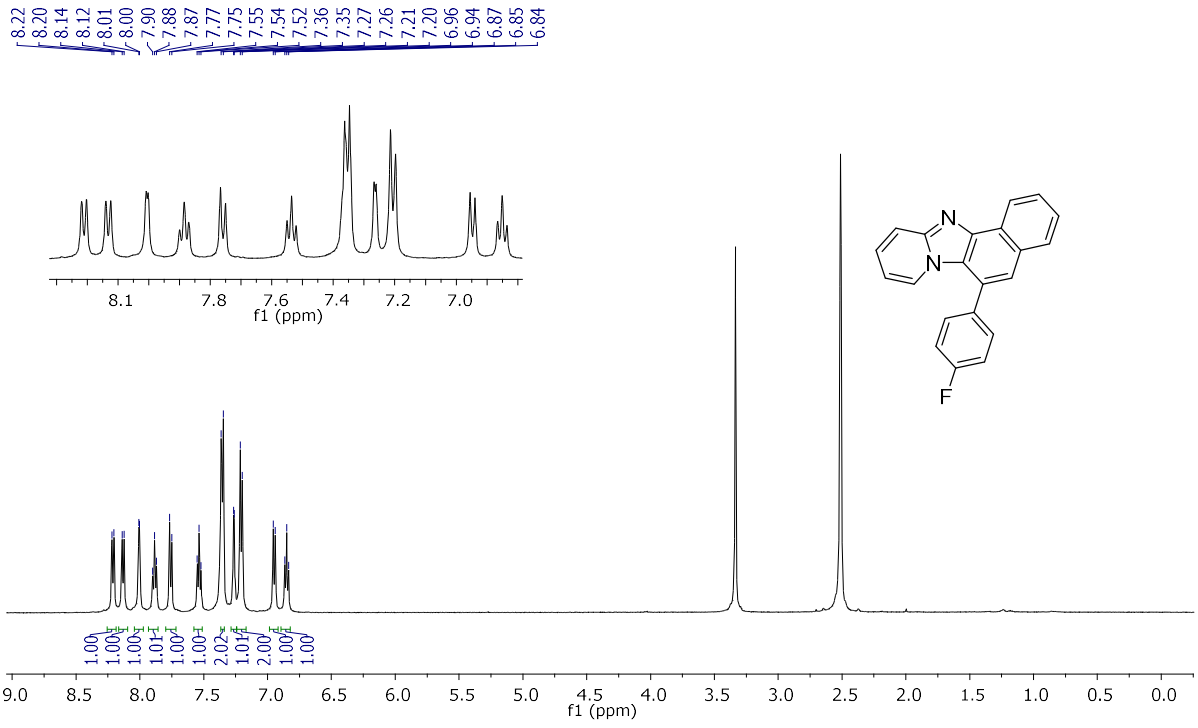
Compound **3d**: ^{13}C NMR (125 MHz, DMSO-d_6).



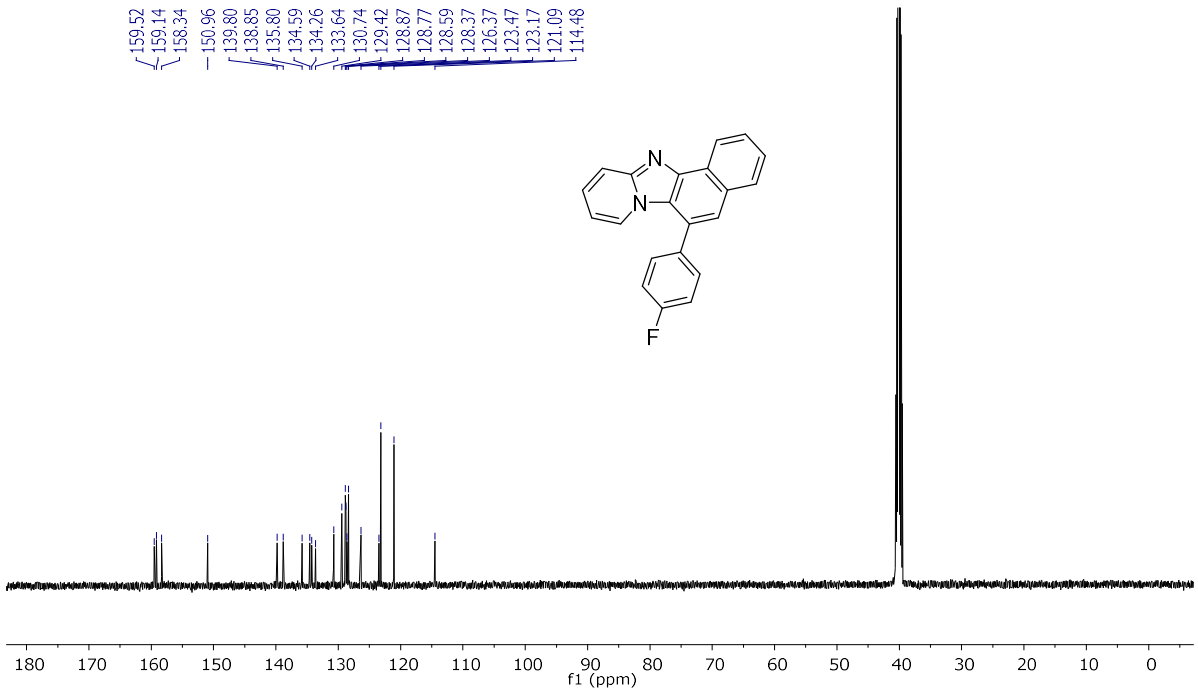
Compound **3e**: ^{1}H NMR (500 MHz, DMSO-d_6).



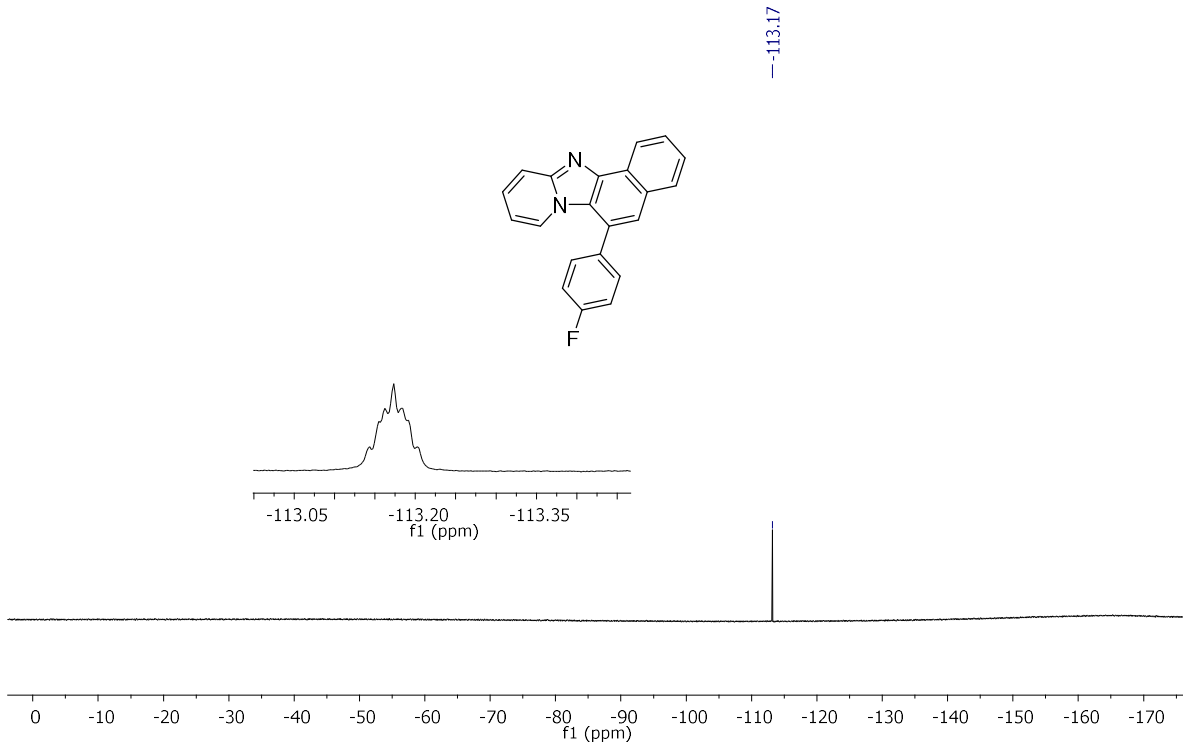
Compound **3e**: ^{13}C NMR (125 MHz, DMSO-d_6).



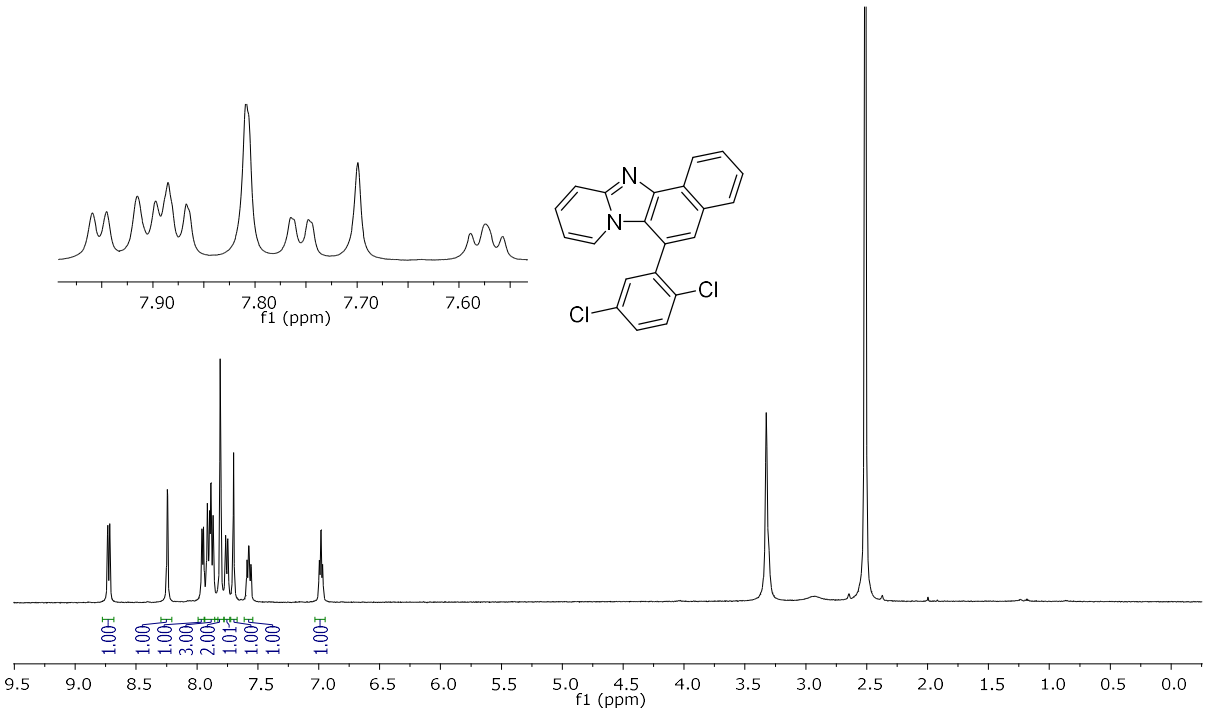
Compound **3f**: ^{1}H NMR (500 MHz, DMSO-d_6).



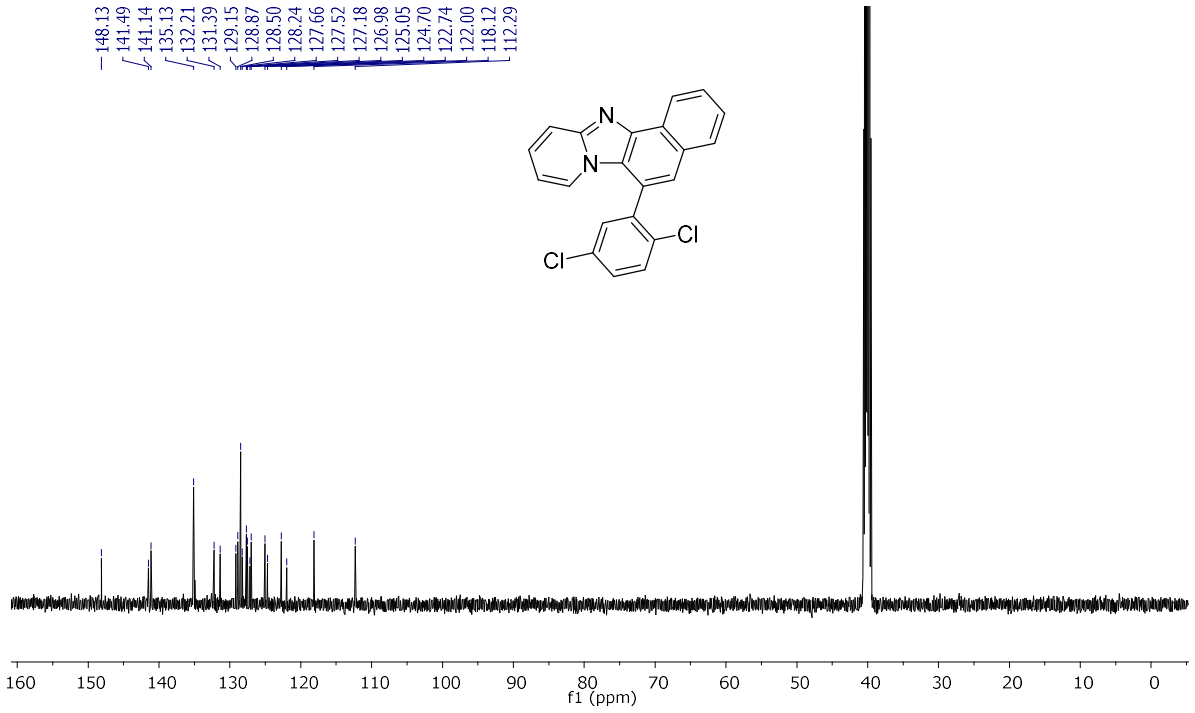
Compound **3f**: ^{13}C NMR (125 MHz, DMSO-d_6).



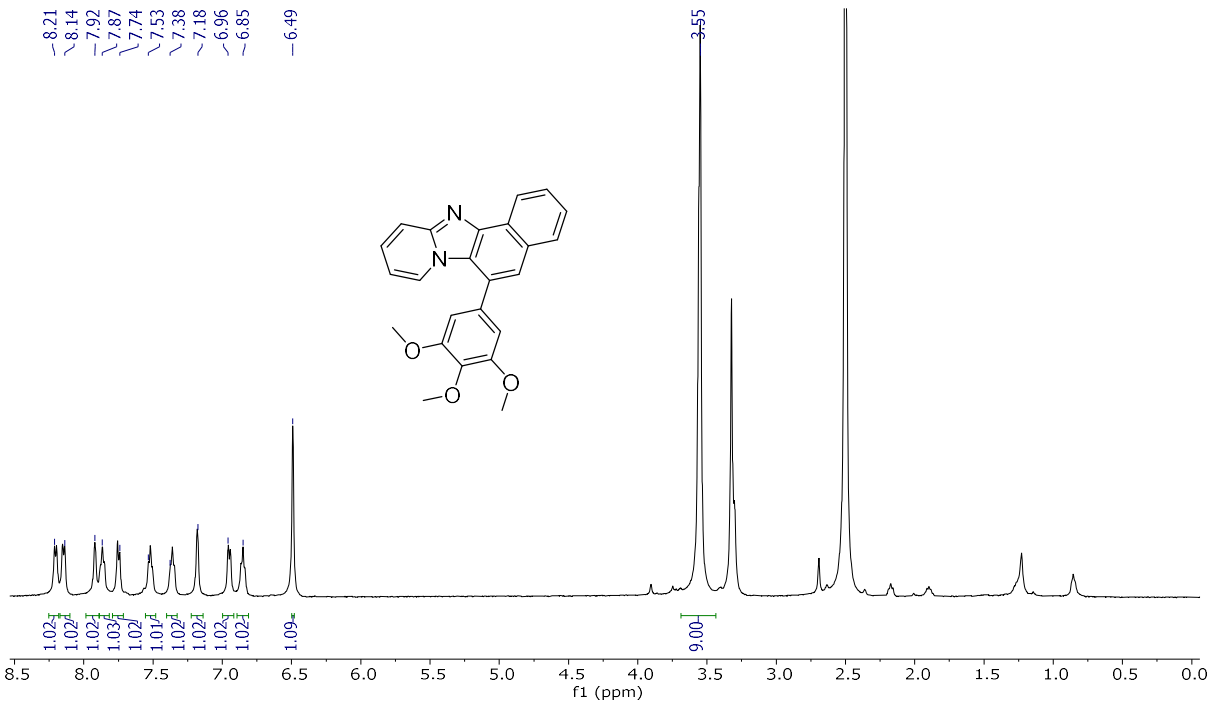
Compound **3f**: ^{19}F NMR (470 MHz, DMSO-d_6).



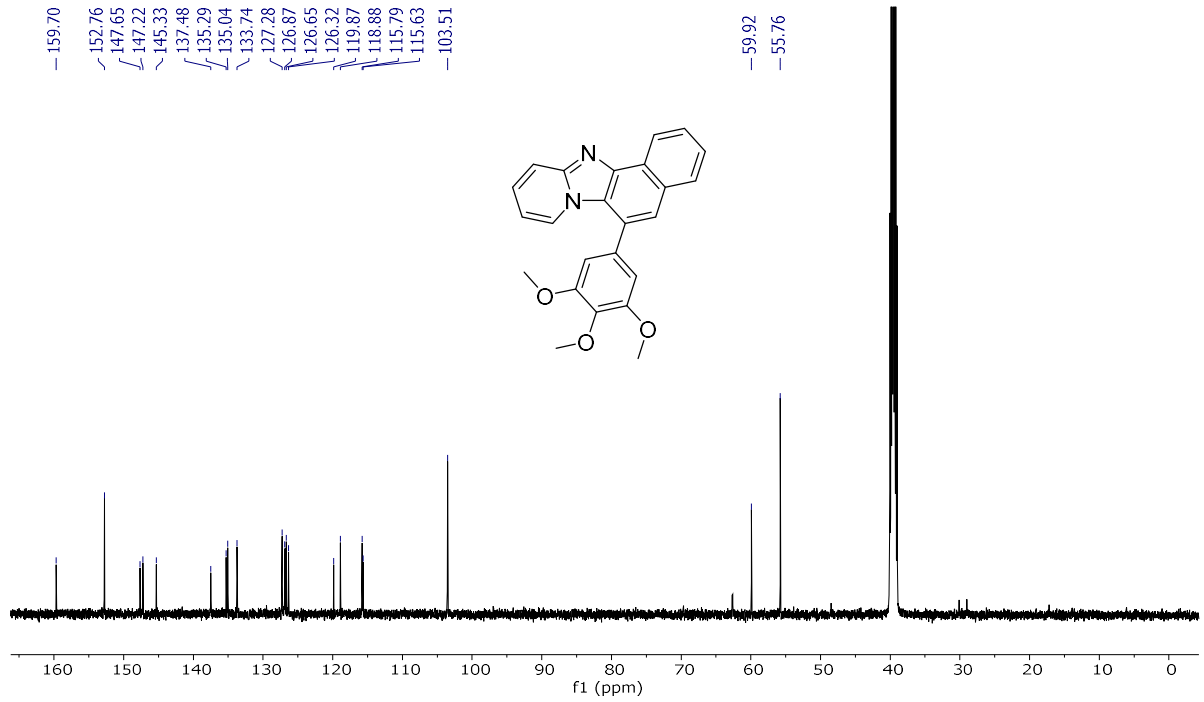
Compound **3g**: ^{1}H NMR (500 MHz, DMSO-d_6).



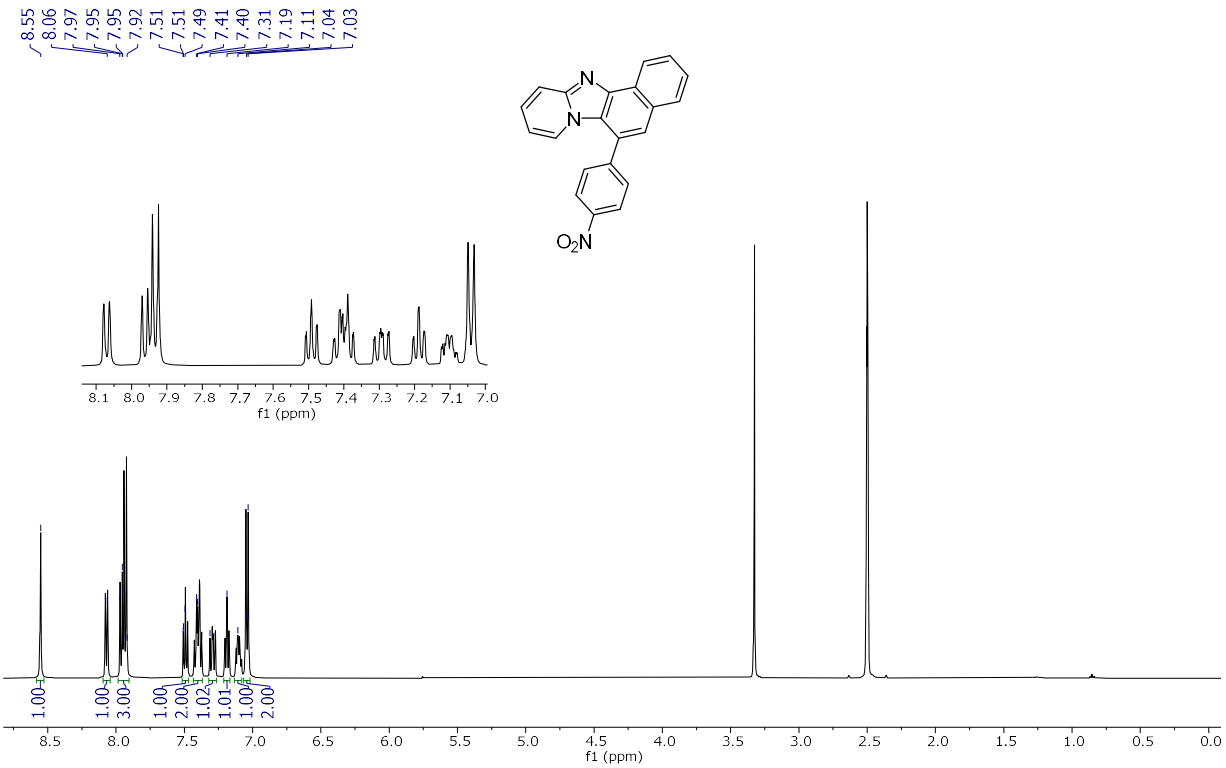
Compound **3g**: ^{13}C NMR (125 MHz, DMSO-d_6).



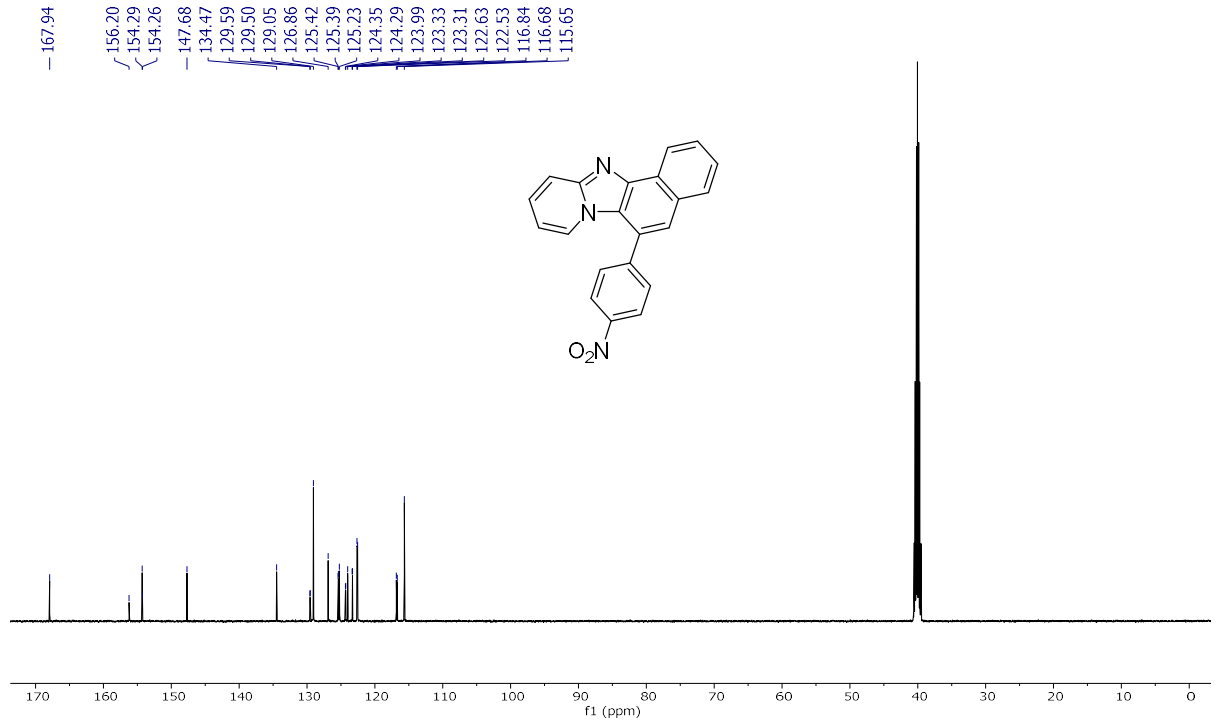
Compound **3h**: ^{1}H NMR (500 MHz, DMSO-d_6).



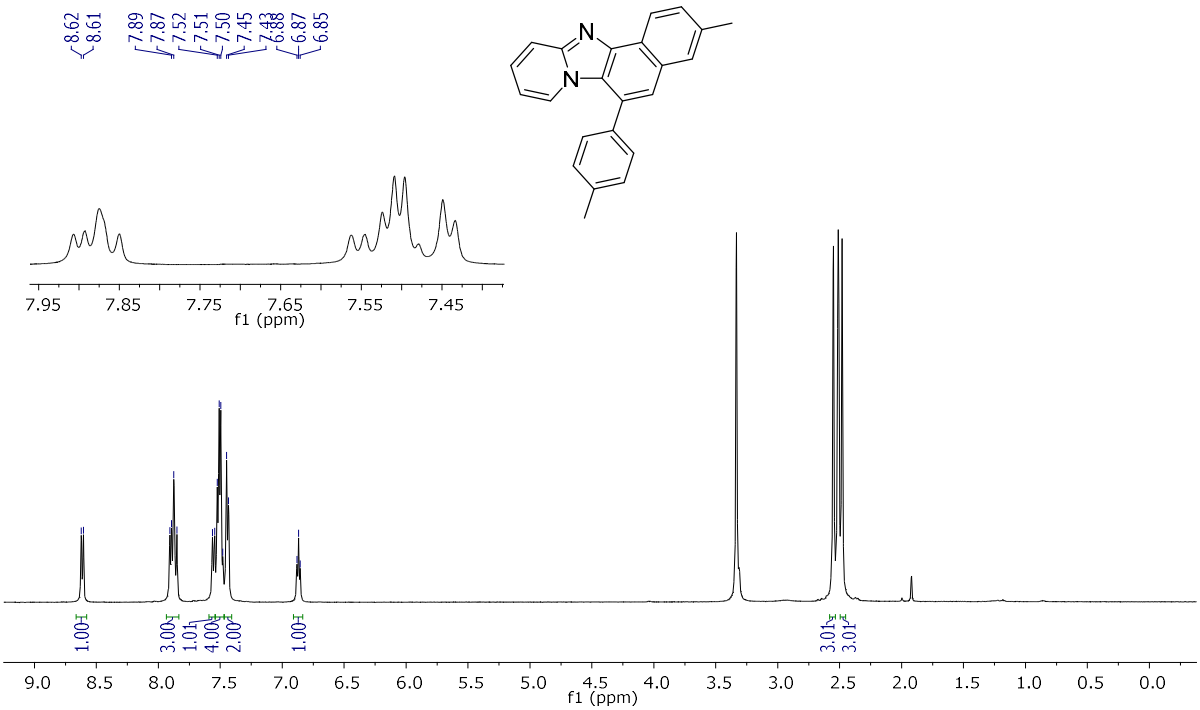
Compound **3h**: ^{13}C NMR (125 MHz, DMSO-d_6).



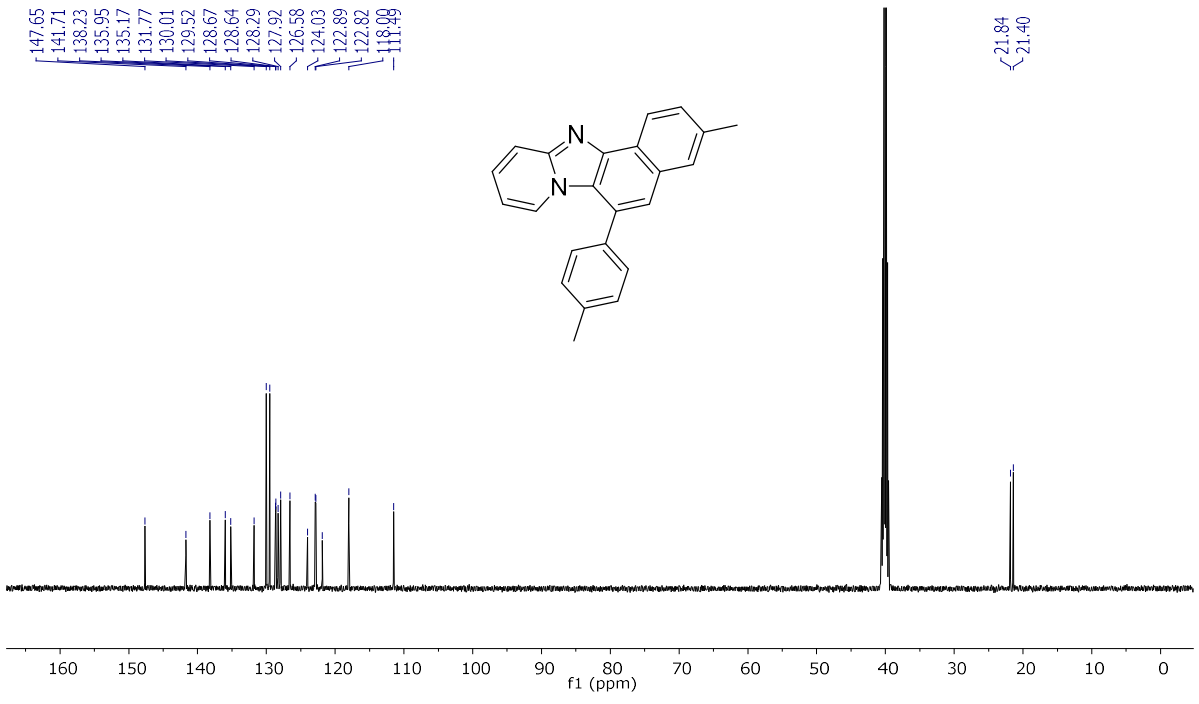
Compound **3i**: ^{1}H NMR (500 MHz, DMSO-d_6).



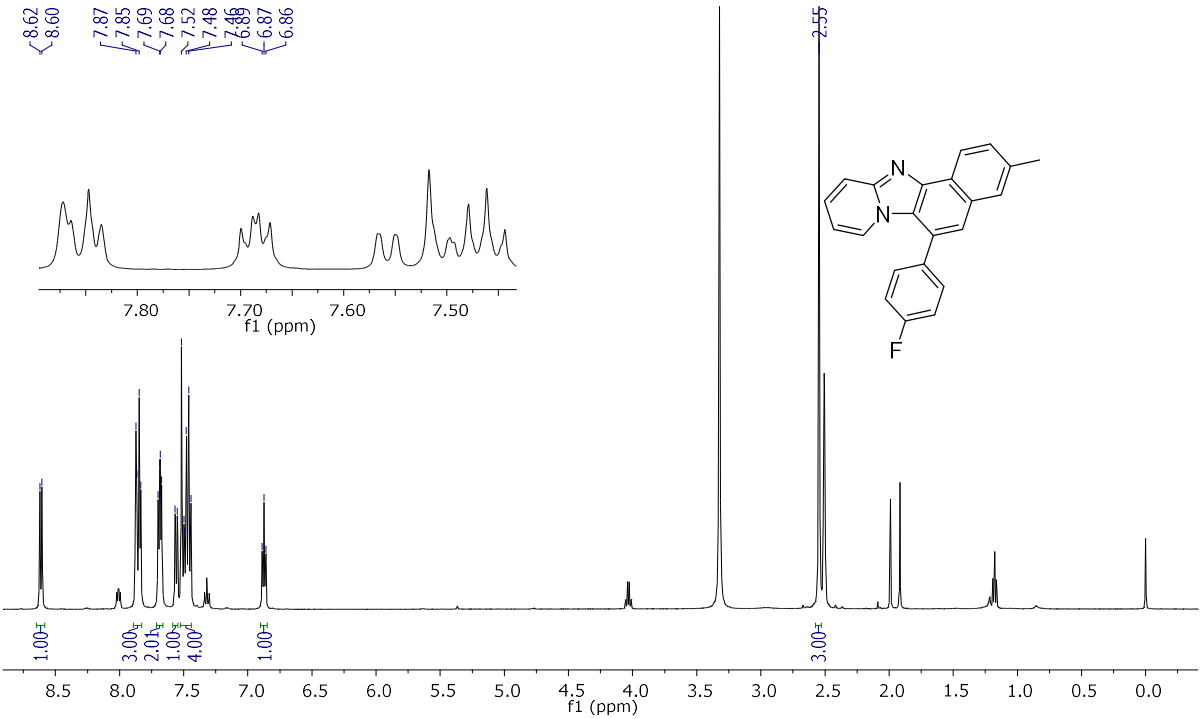
Compound **3i**: ^{13}C NMR (125 MHz, DMSO-d_6).



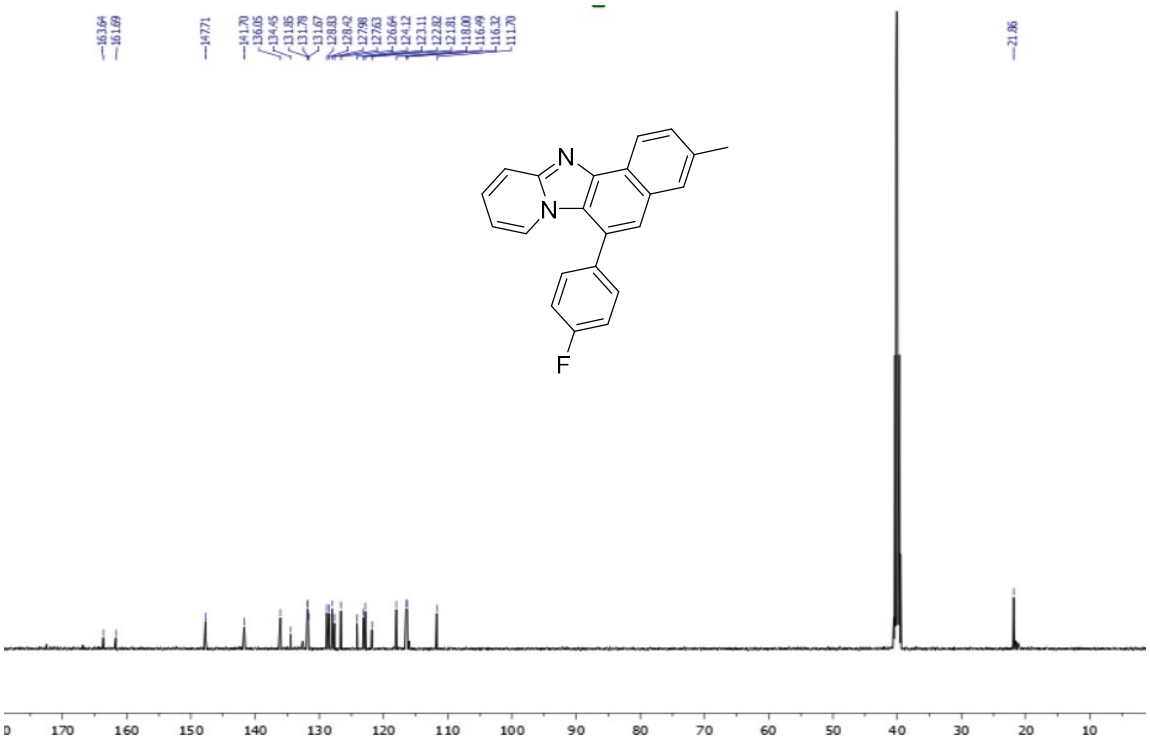
Compound **3j**: ^{1}H NMR (500 MHz, DMSO-d_6).



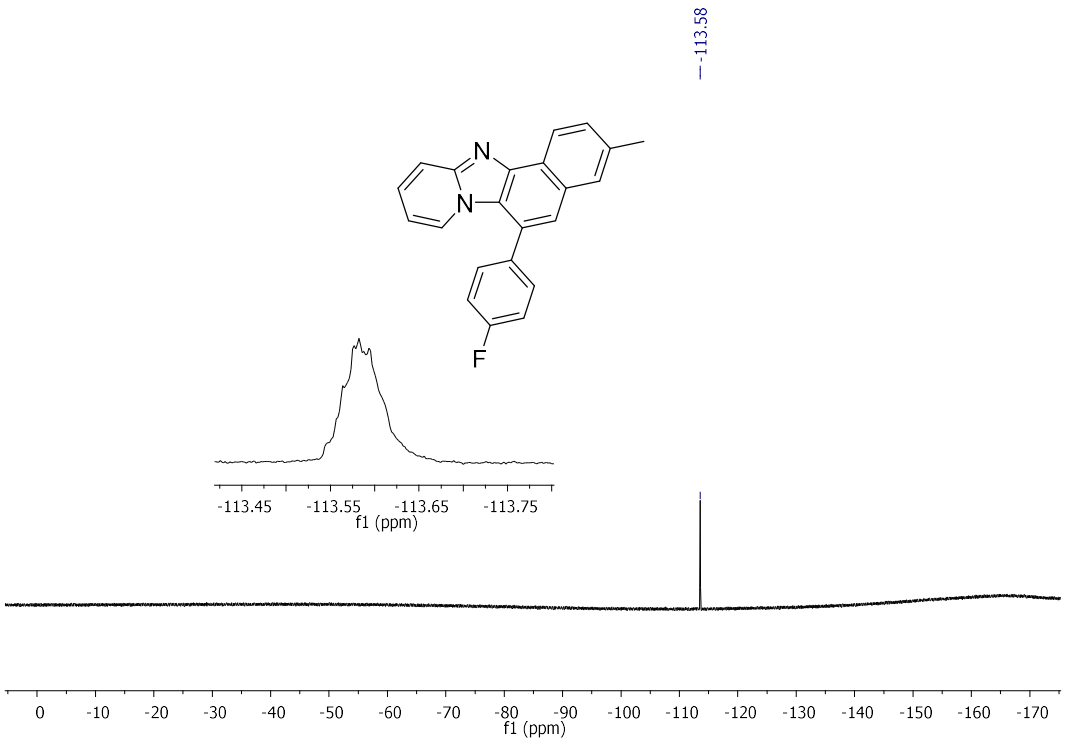
Compound **3j**: ^{13}C NMR (125 MHz, DMSO-d_6).



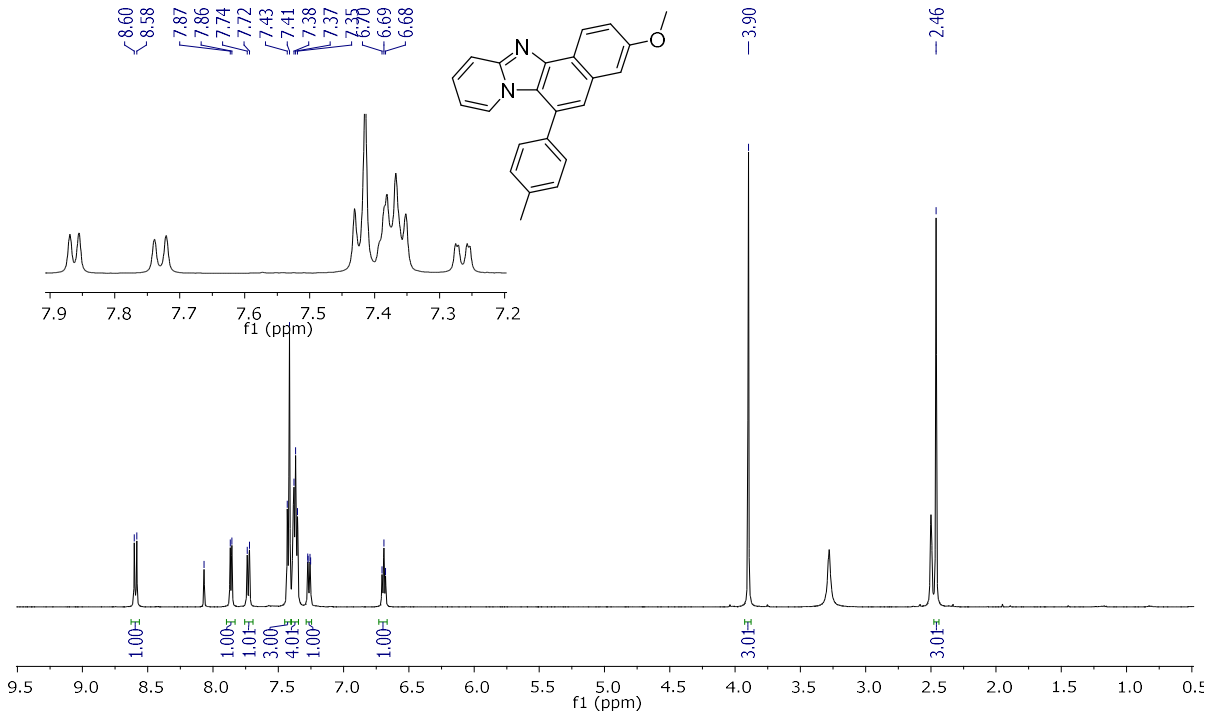
Compound **3k**: ^{1}H NMR (500 MHz, DMSO-d_6).



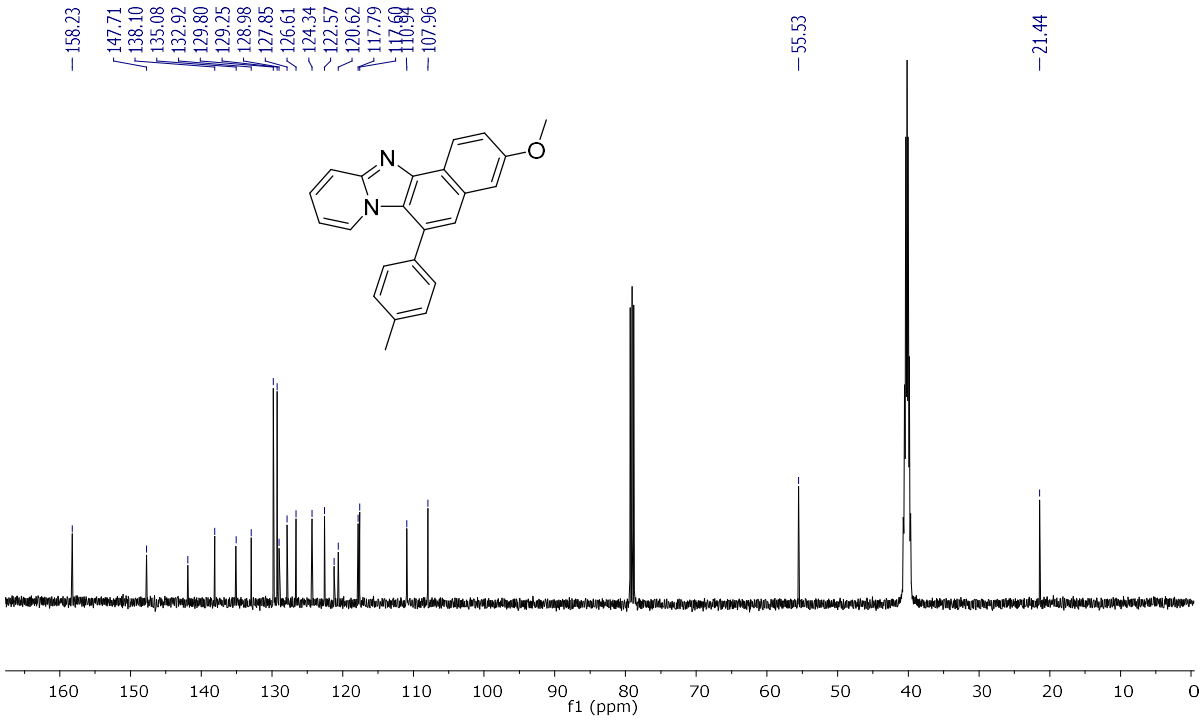
Compound **3k**: ^{13}C NMR (125 MHz, DMSO-d_6).



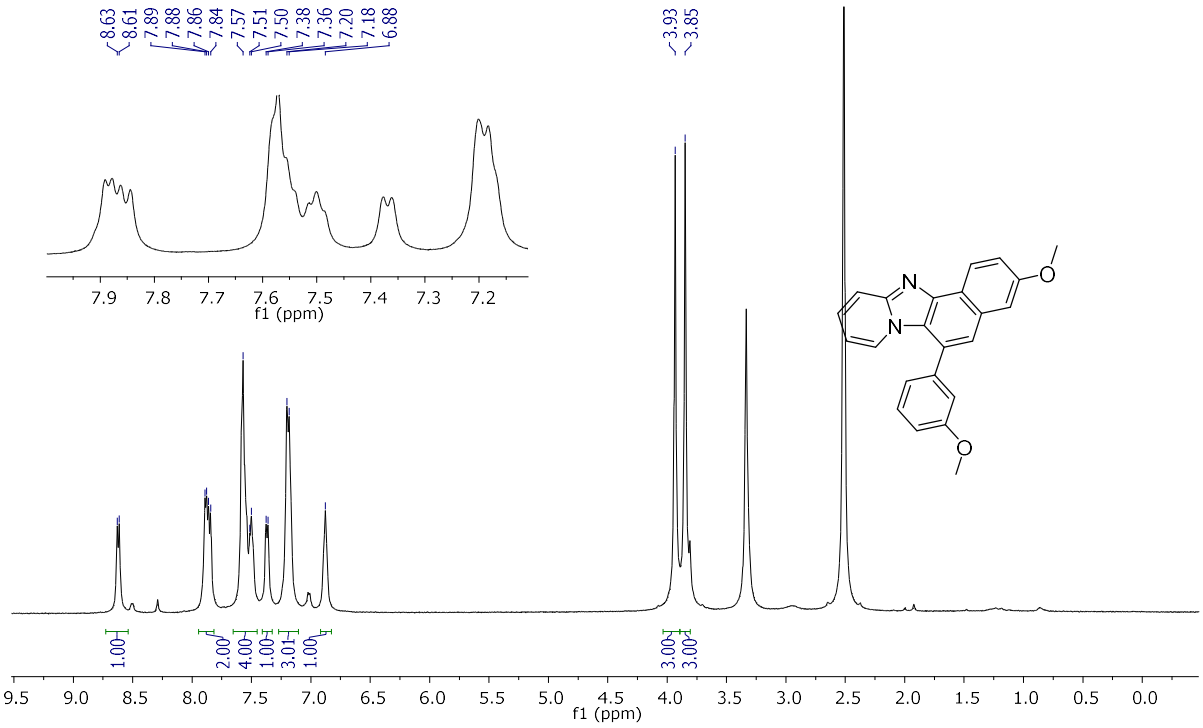
Compound **3k**: ^{19}F NMR (470 MHz, DMSO-d_6).



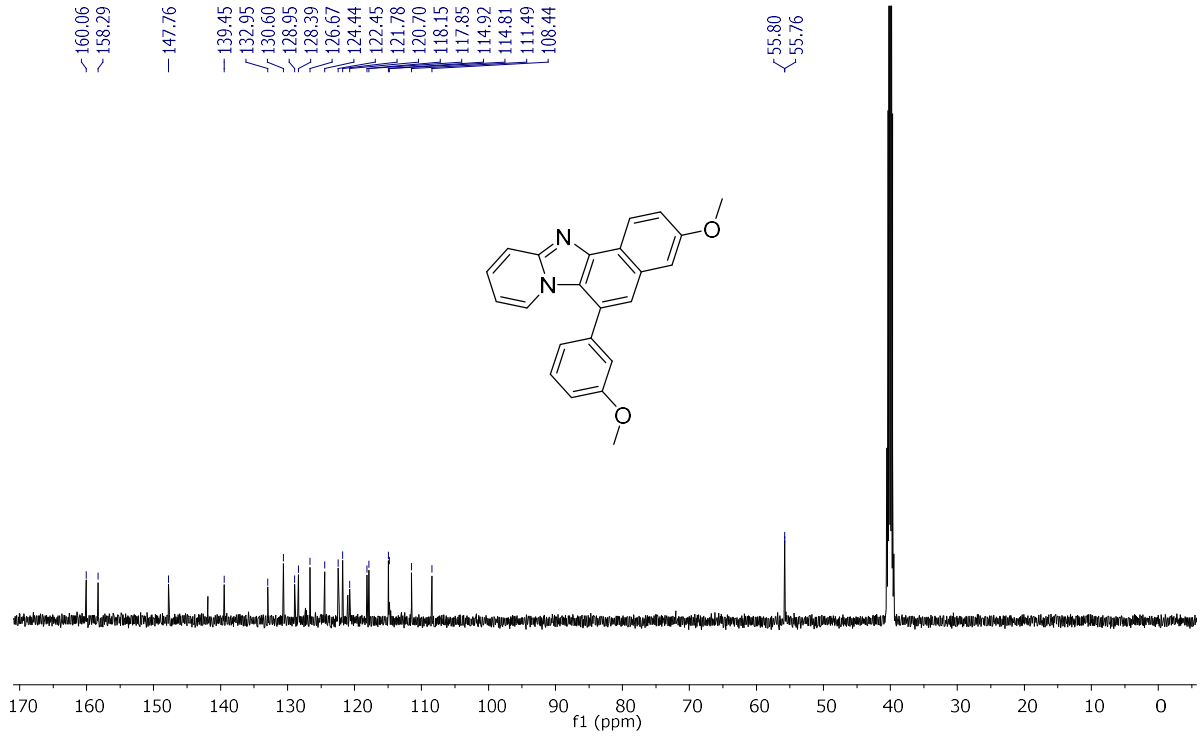
Compound **3l**: ^{1}H NMR (500 MHz, DMSO-d_6).



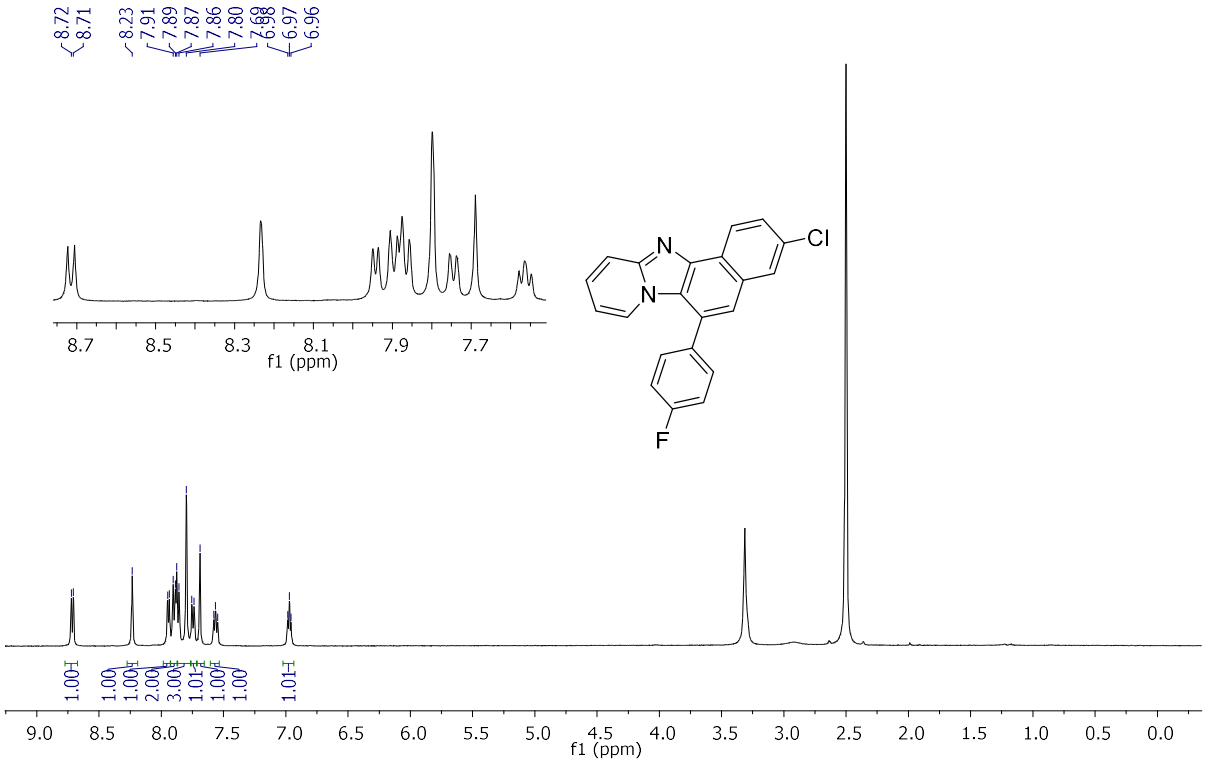
Compound **3l**: ^{13}C NMR (125 MHz, DMSO-d_6).



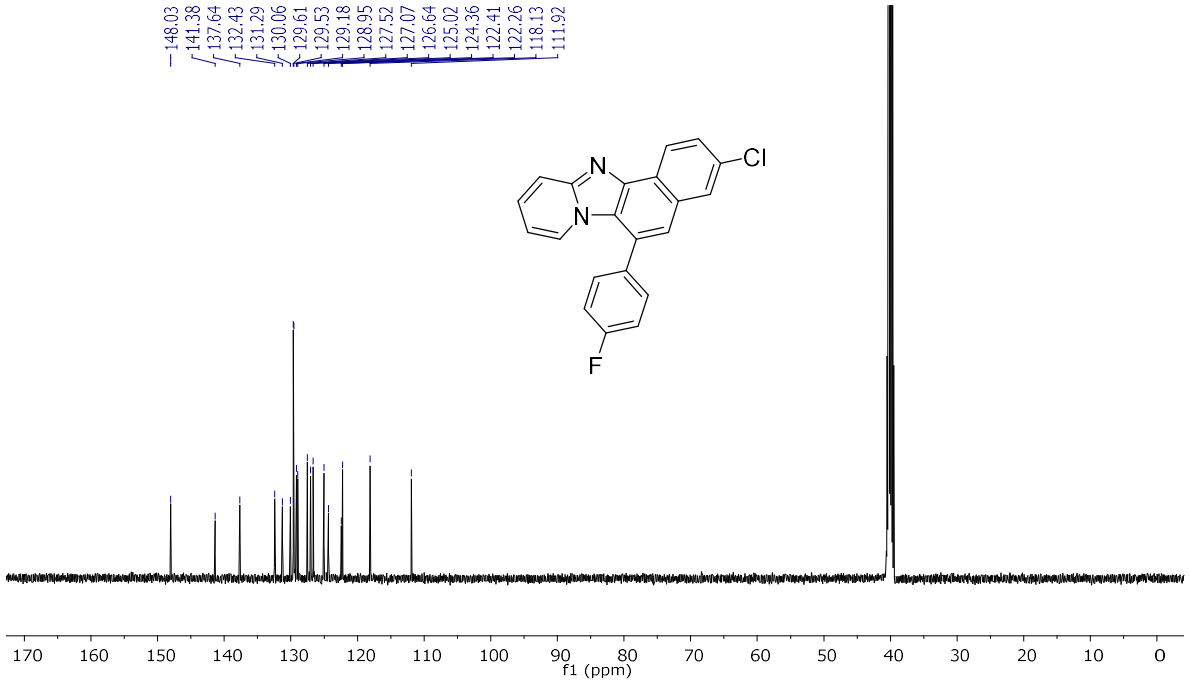
Compound **3m**: ^{1}H NMR (500 MHz, DMSO-d_6).



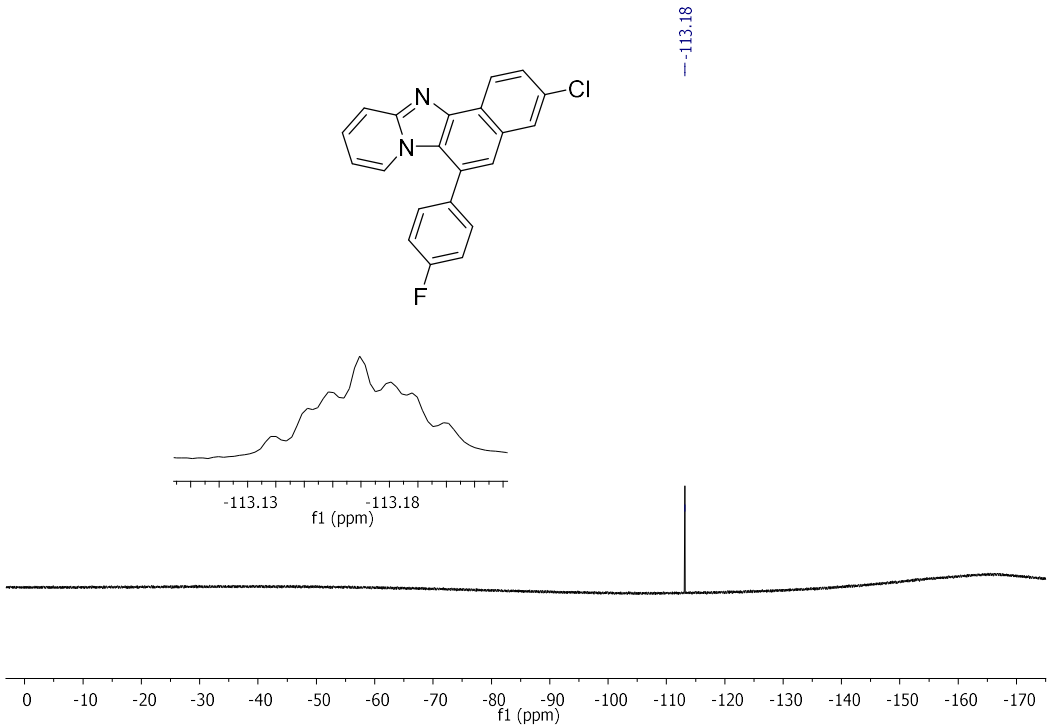
Compound **3m**: ^{13}C NMR (125 MHz, DMSO-d_6).



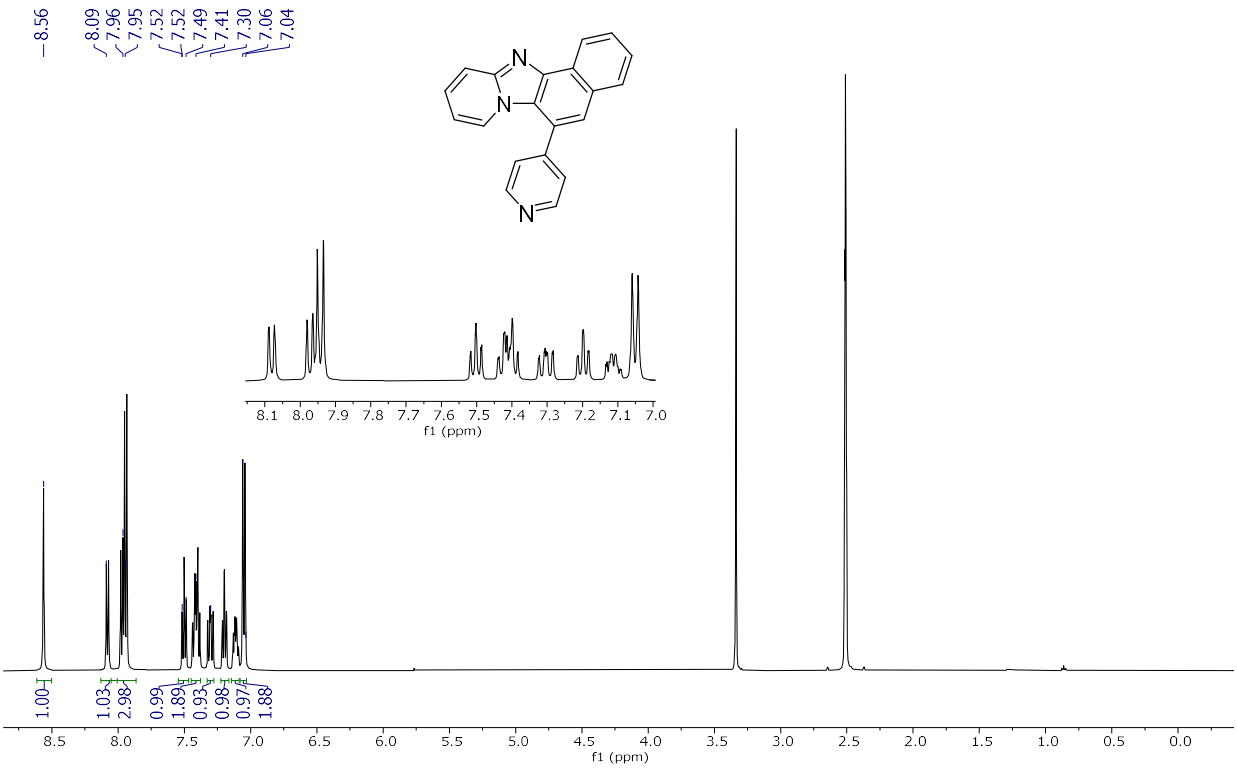
Compound **3n**: ^{1}H NMR (500 MHz, DMSO-d_6).



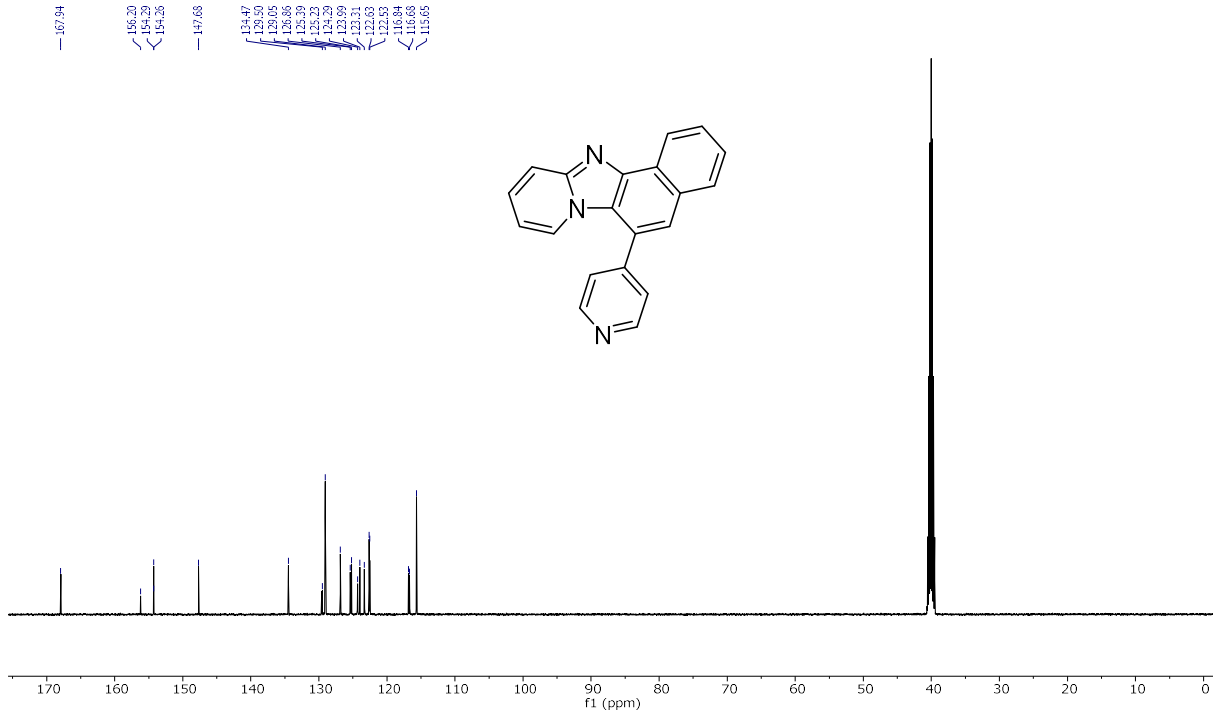
Compound **3n**: ^{13}C NMR (125 MHz, DMSO-d_6).



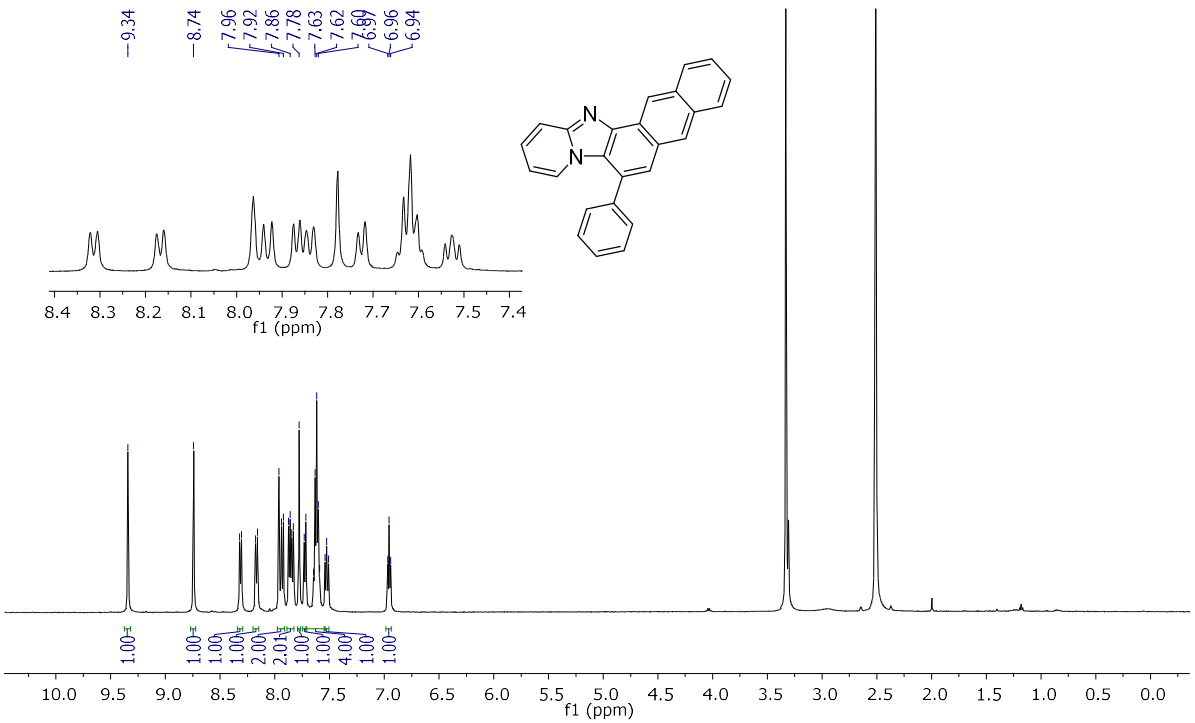
Compound **3n**: ^{19}F NMR (470MHz, DMSO-d_6).



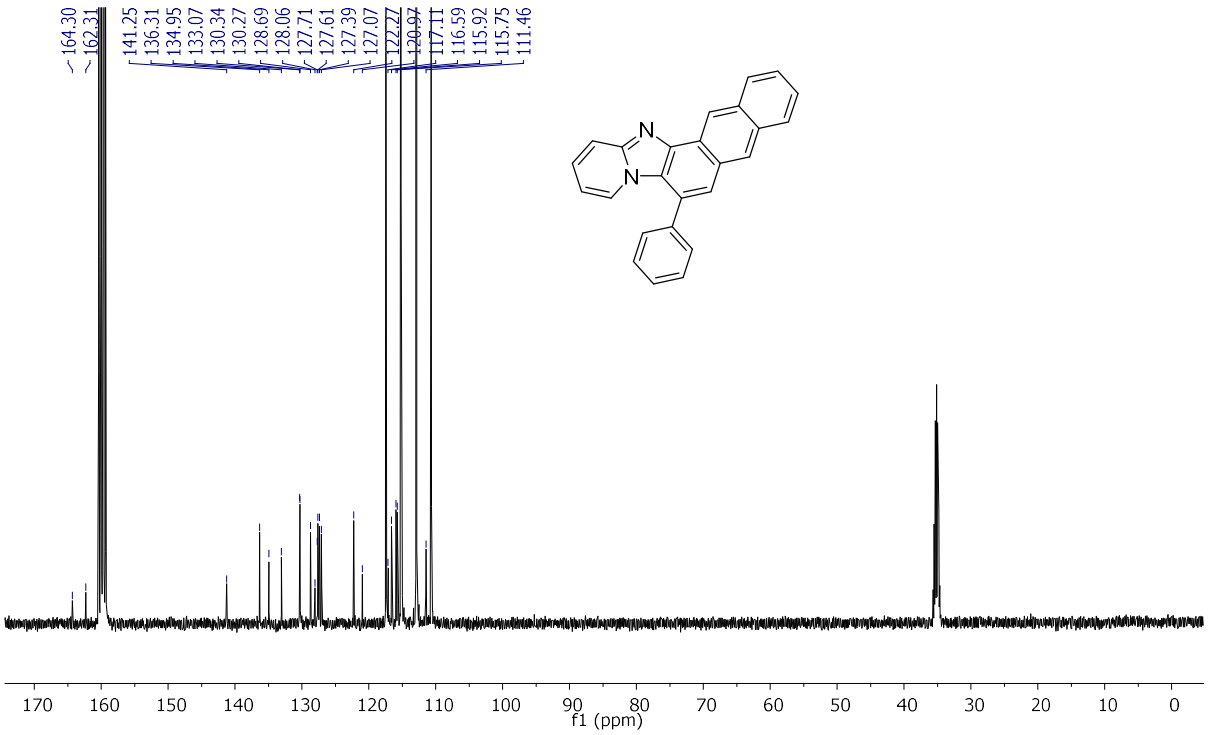
Compound **3o**: ^{1}H NMR (500 MHz, DMSO-d_6).



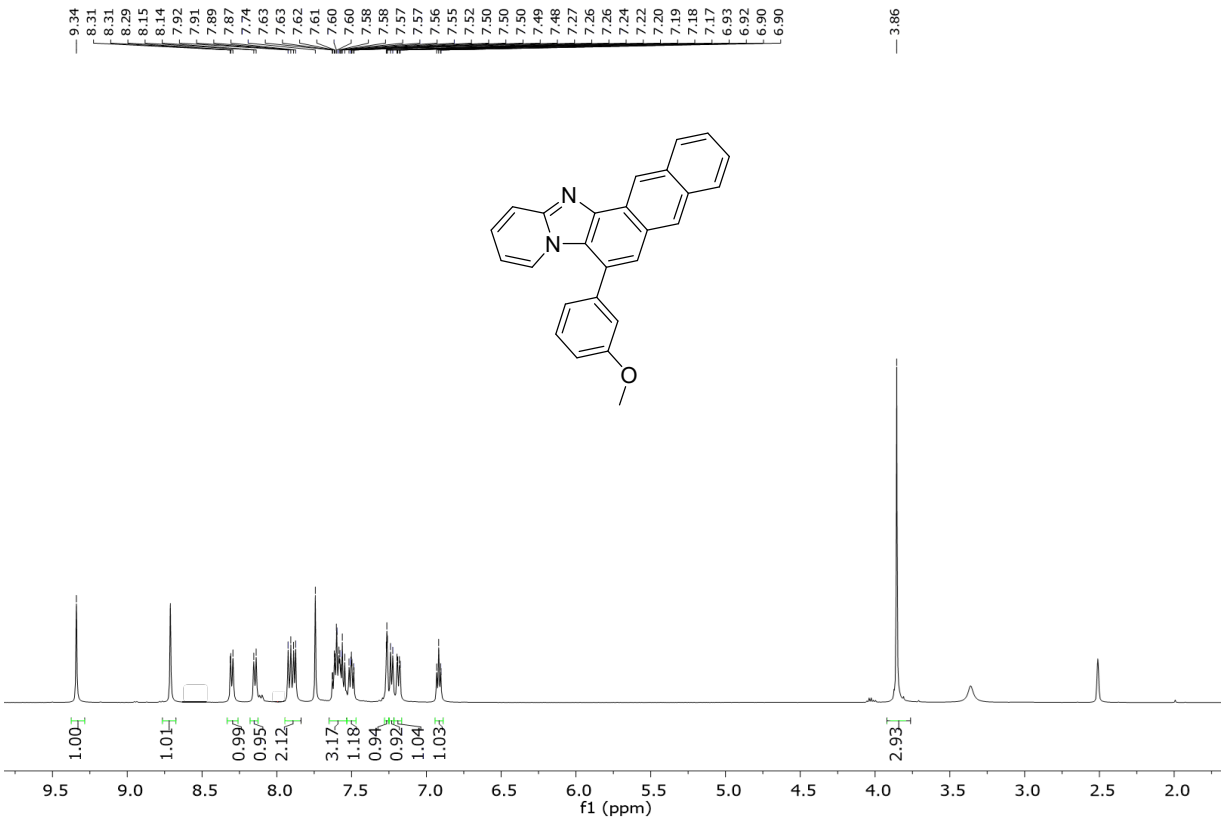
Compound **3o**: ^{13}C NMR (125 MHz, DMSO-d_6).



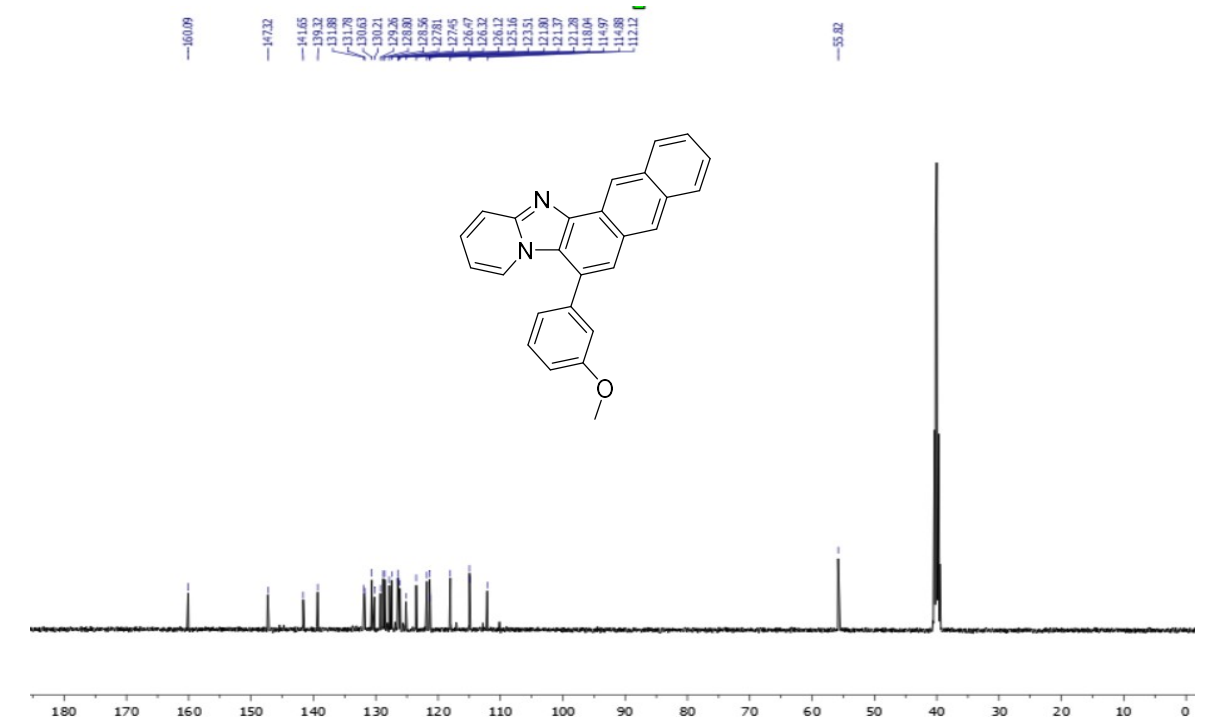
Compound **3p**: ^{1}H NMR (500 MHz, DMSO-d_6).



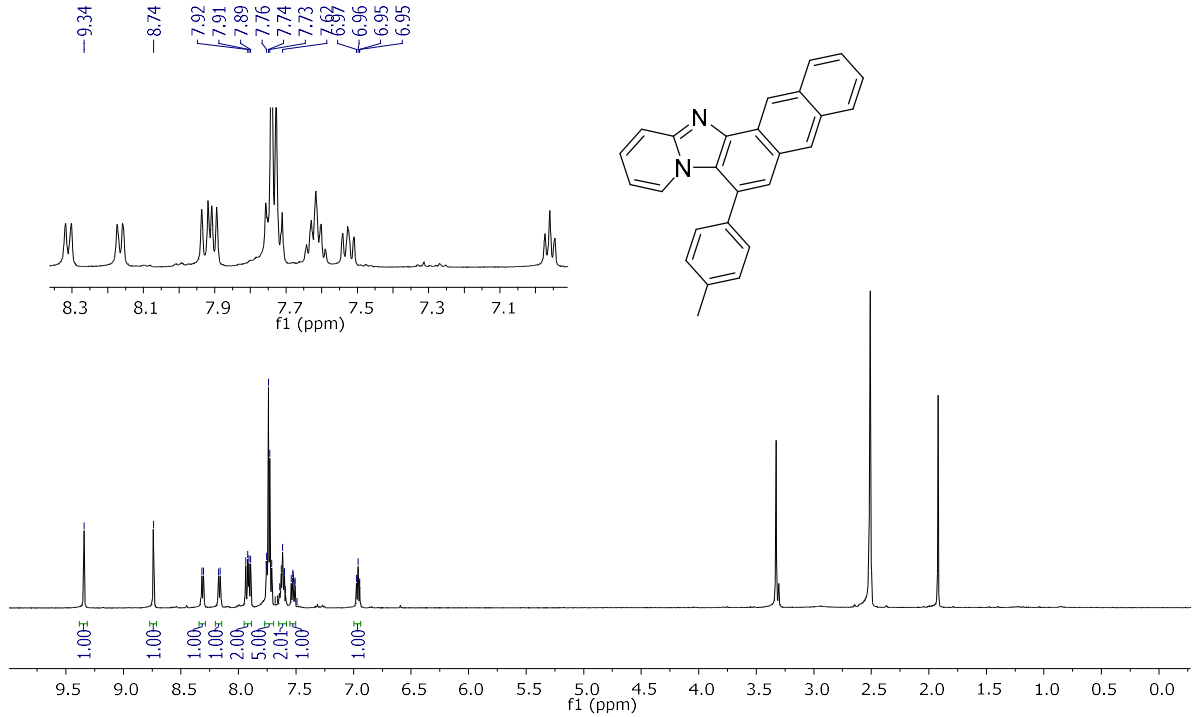
Compound **3p**: ^{13}C NMR (125 MHz, DMSO-d_6).



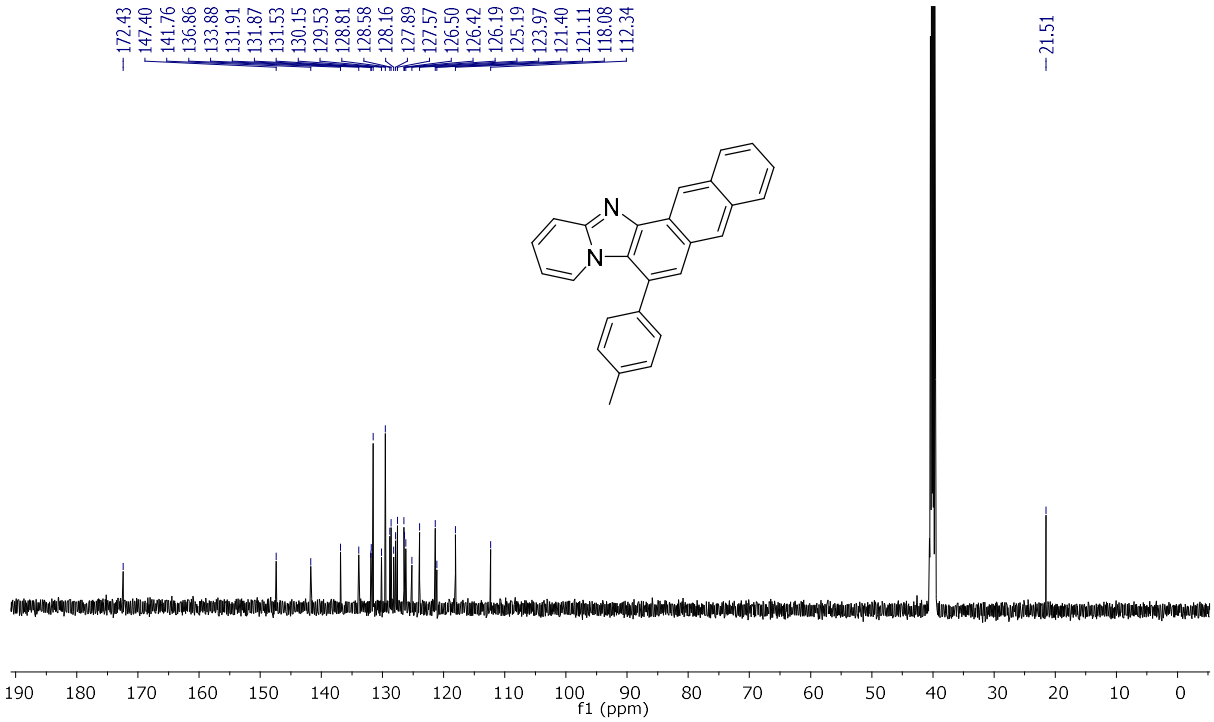
Compound **3q**: ^{1}H NMR (500 MHz, DMSO-d_6).



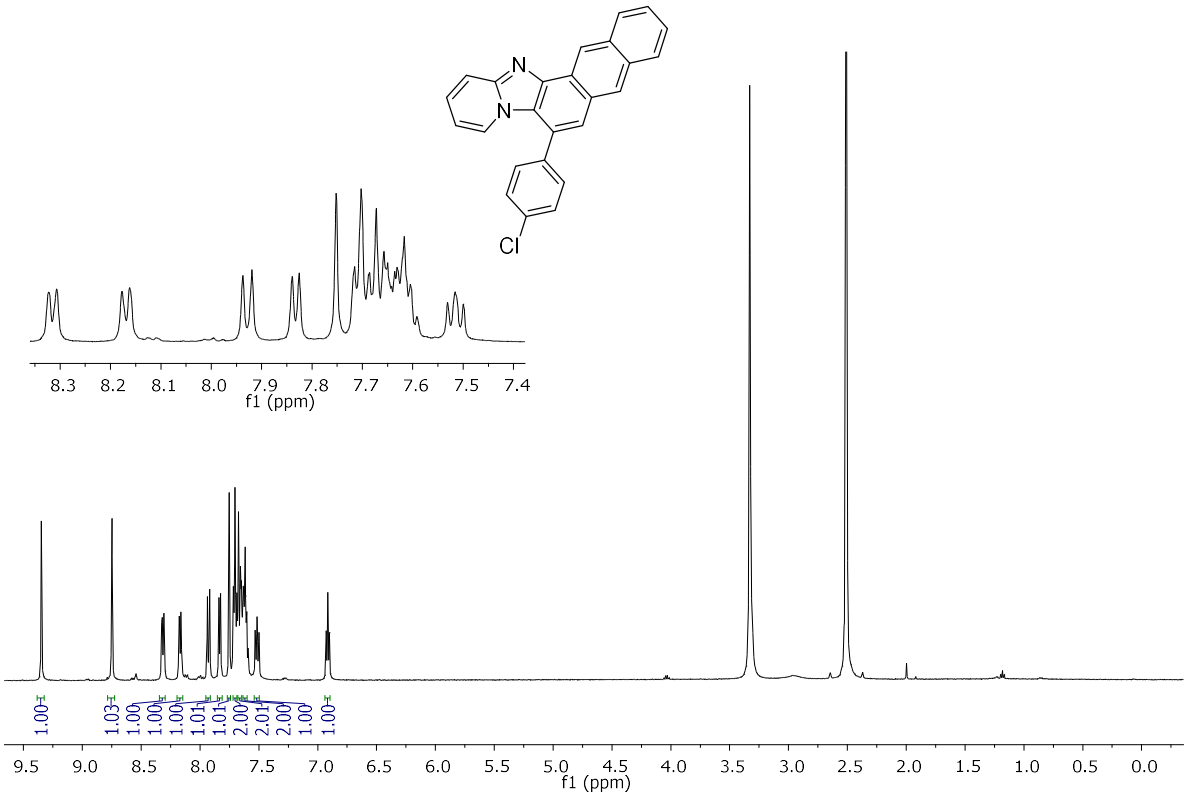
Compound **3q**: ^{13}C NMR (125 MHz, DMSO-d_6).



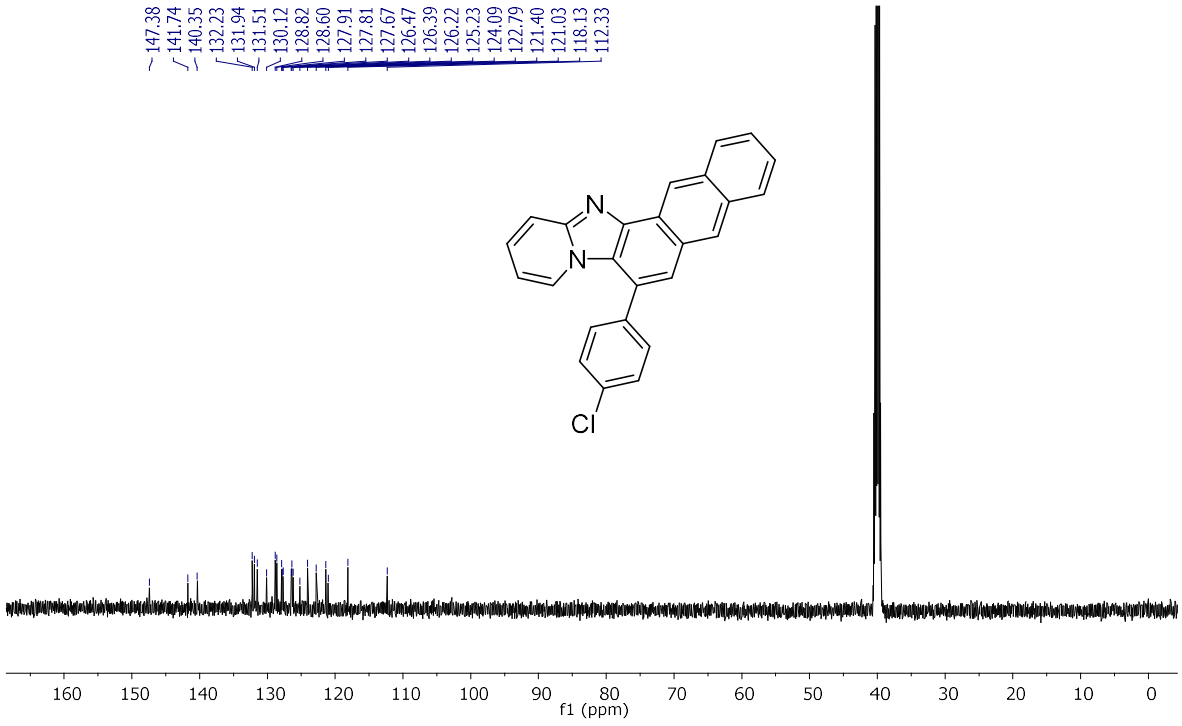
Compound **3r**: ^{1}H NMR (500 MHz, DMSO-d_6).



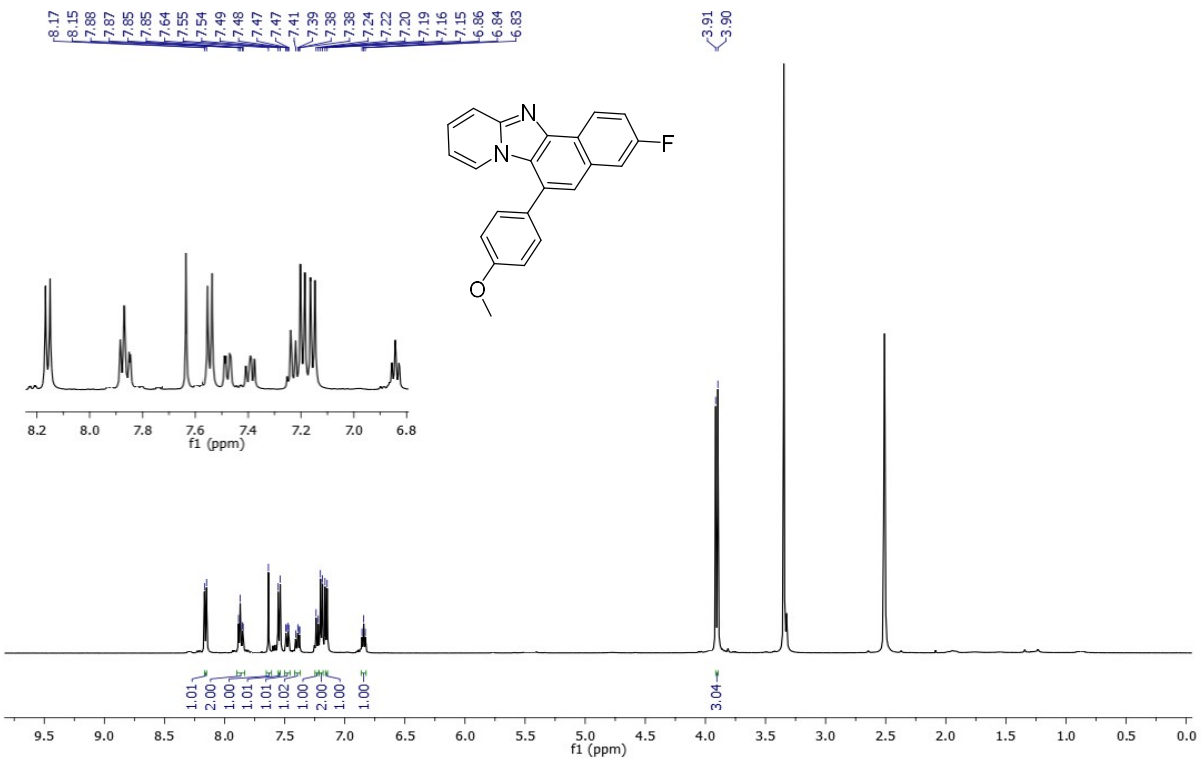
Compound **3r**: ^{13}C NMR (125 MHz, DMSO-d_6).



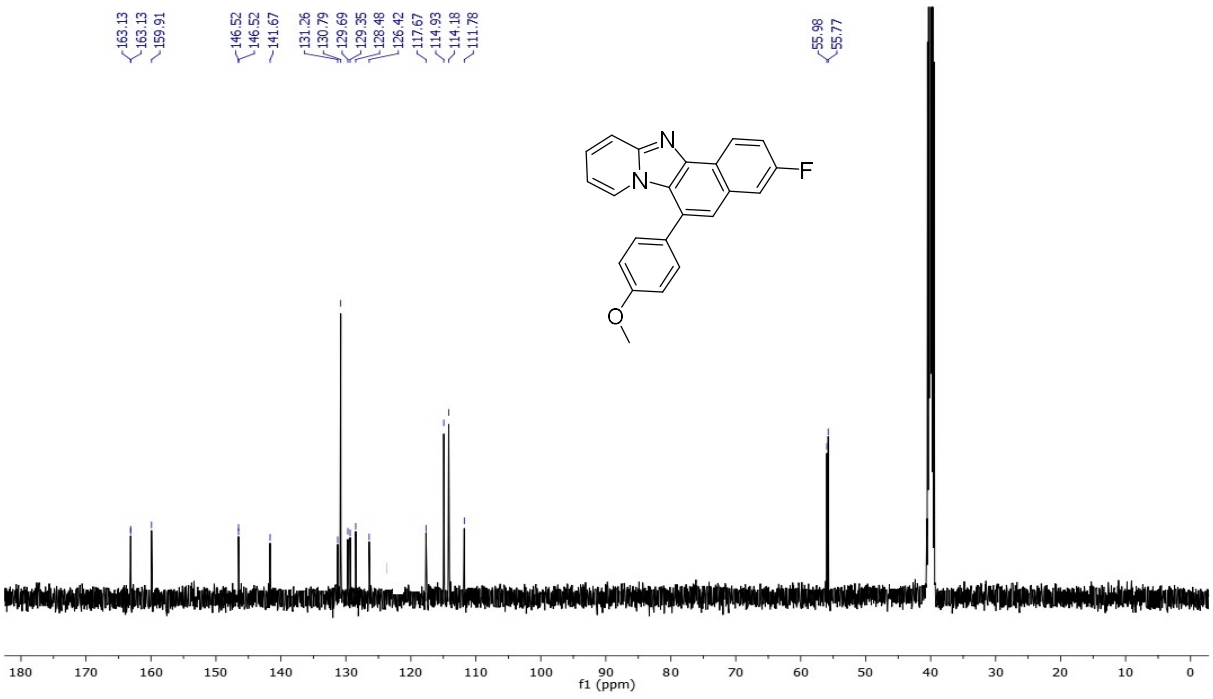
Compound **3s**: ^{1}H NMR (500 MHz, DMSO-d_6).



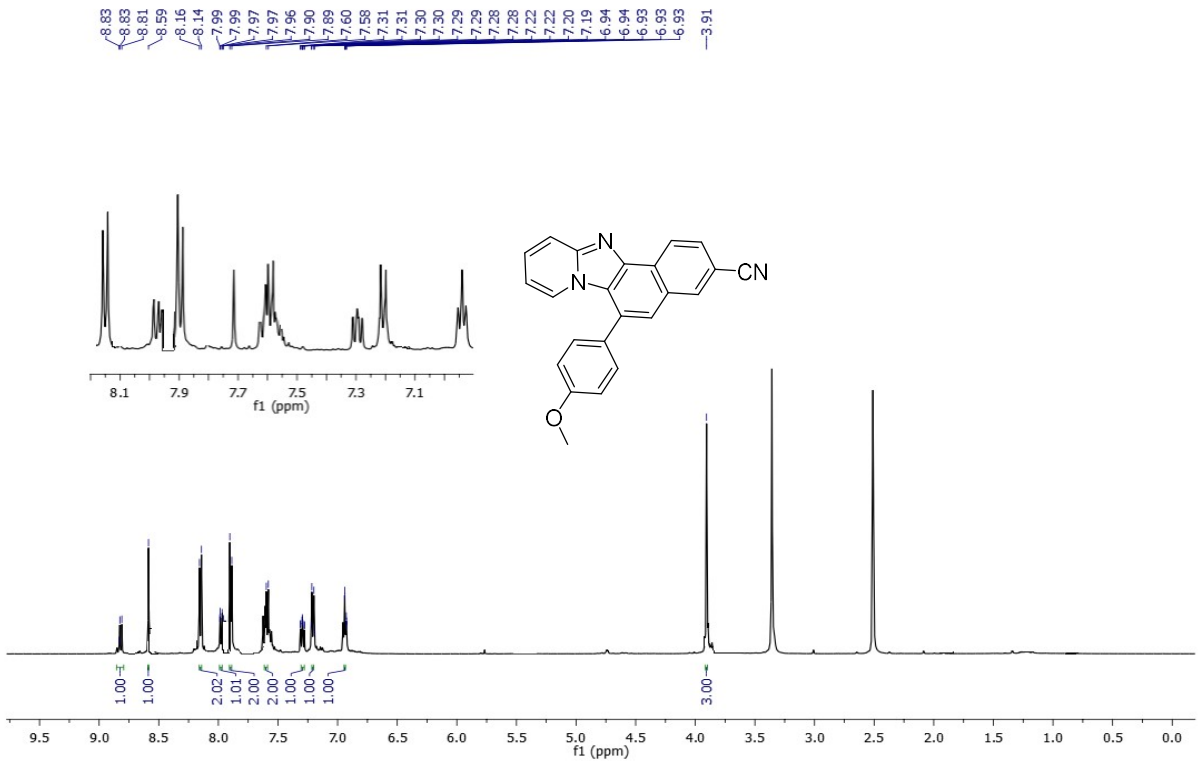
Compound **3s**: ^{13}C NMR (125 MHz, DMSO-d_6).



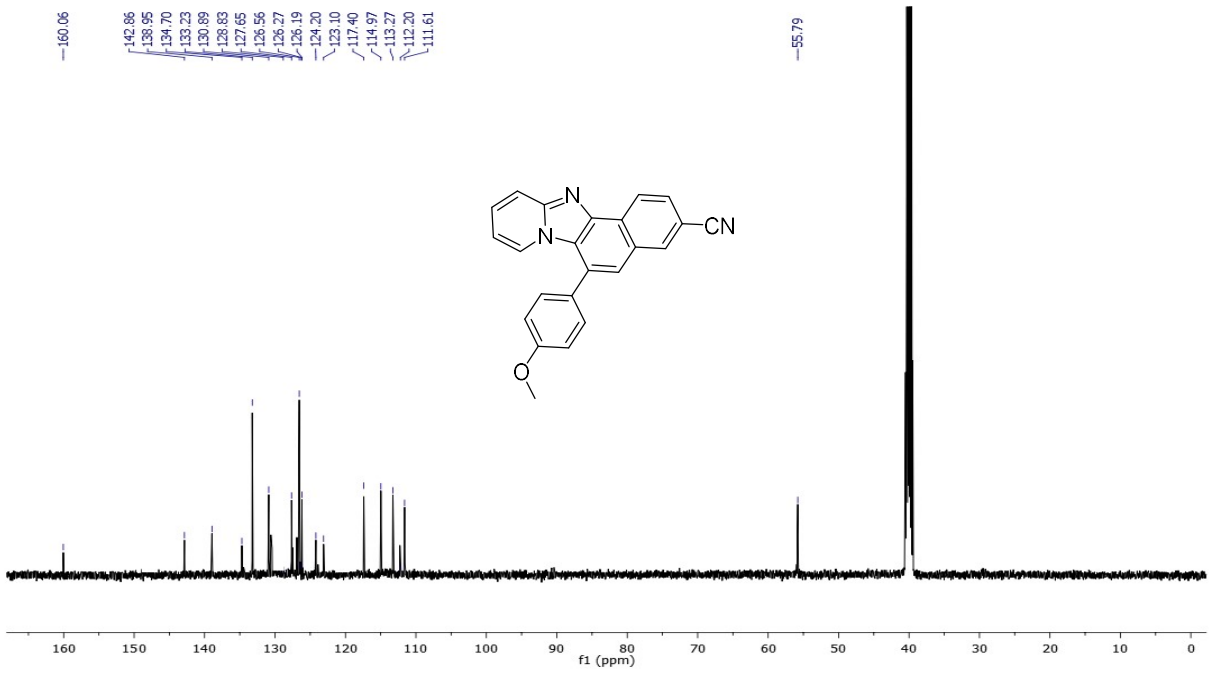
Compound **3t**: ^{1}H NMR (500 MHz, DMSO-d_6).



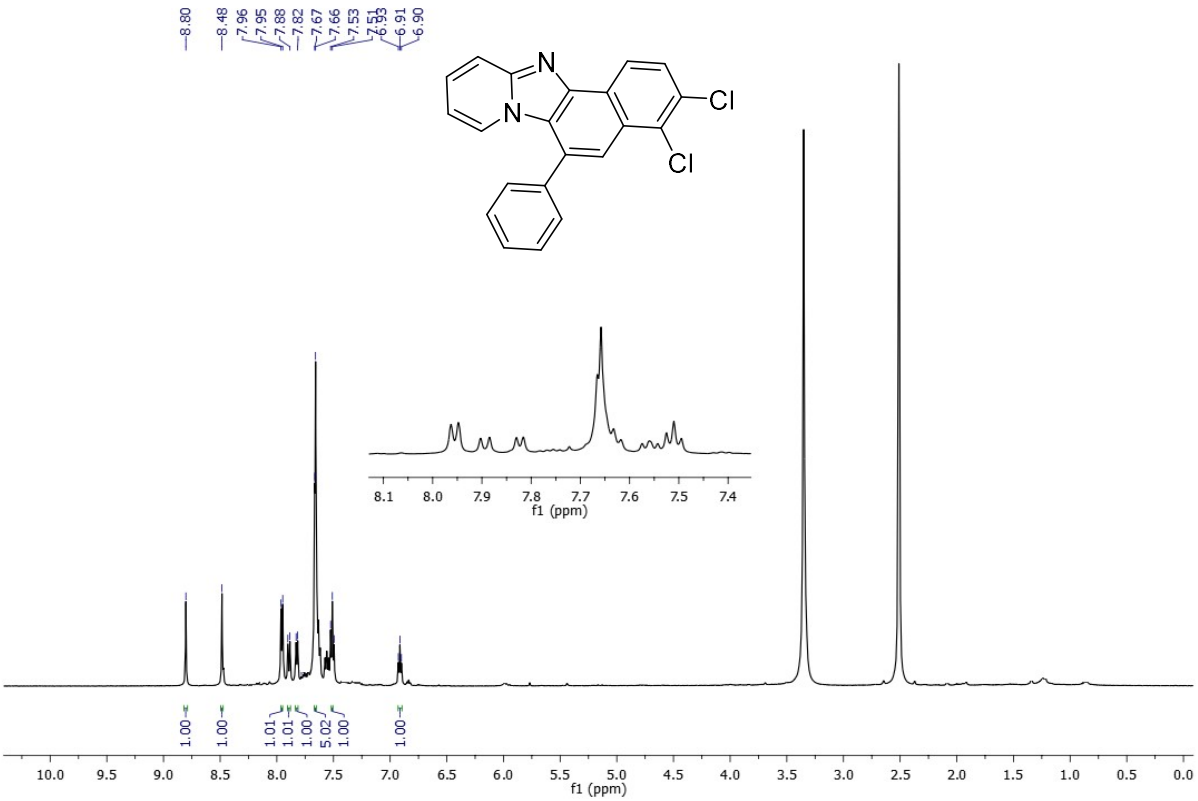
Compound **3t**: ^{13}C NMR (125 MHz, DMSO-d_6).



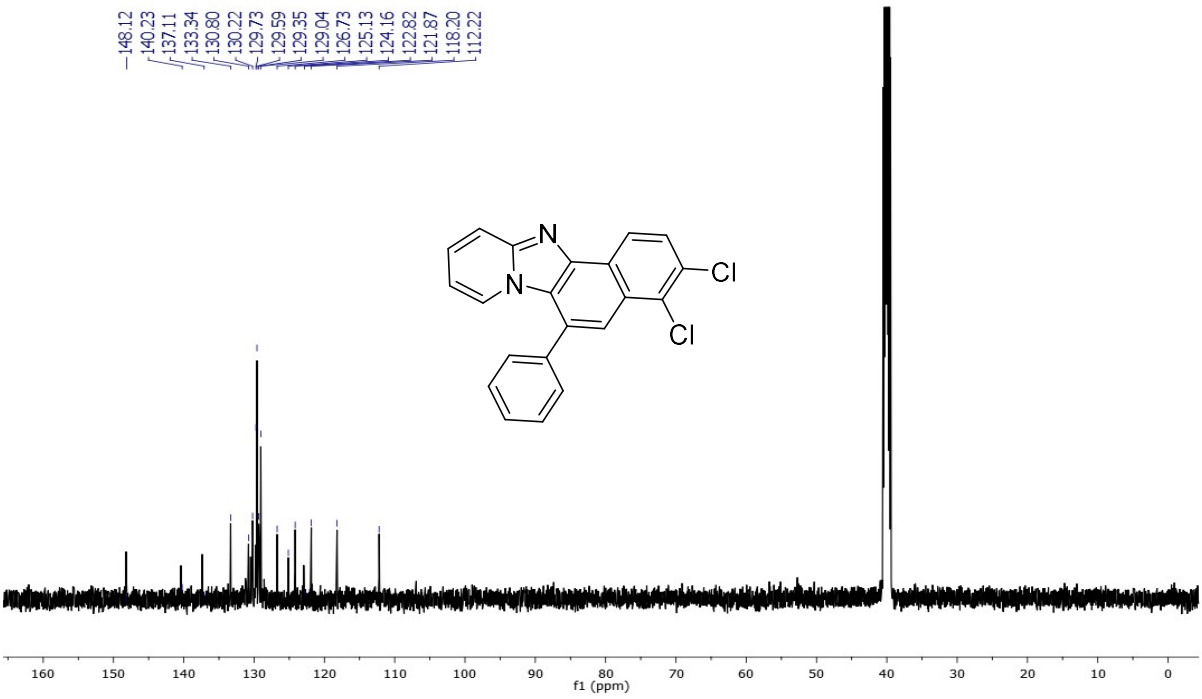
Compound **3u**: ^{1}H NMR (500 MHz, DMSO-d_6).



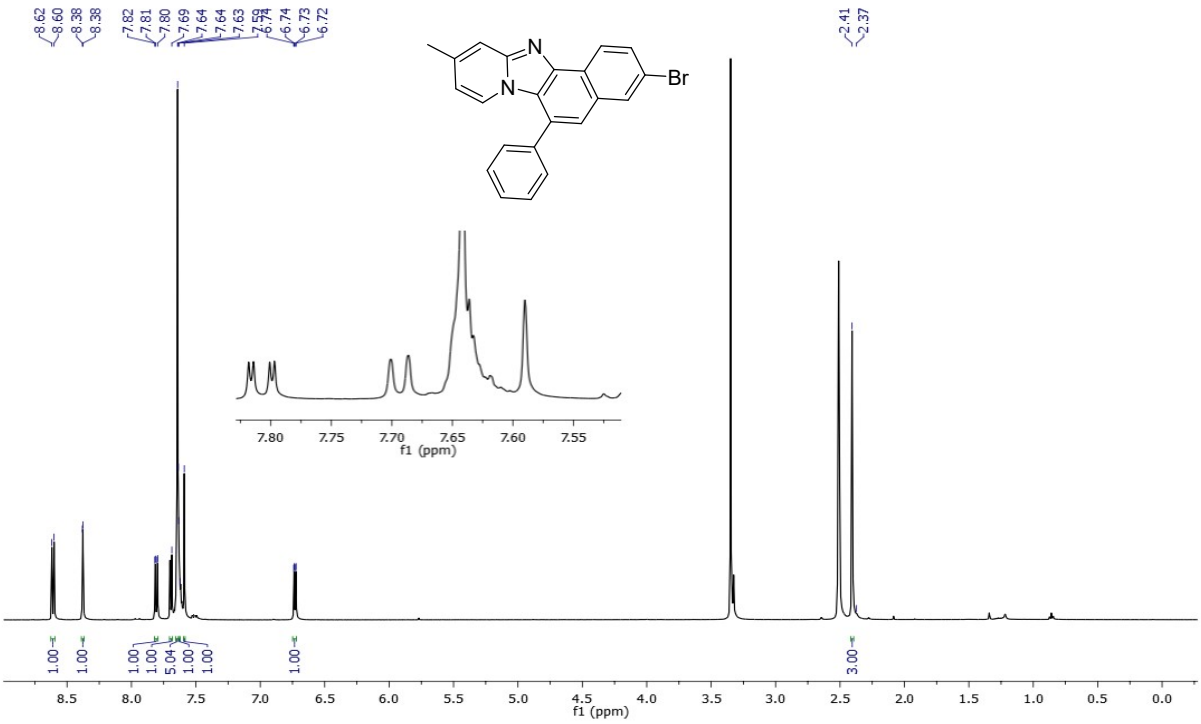
Compound **3u:** ^{13}C NMR (125 MHz, DMSO-d_6).



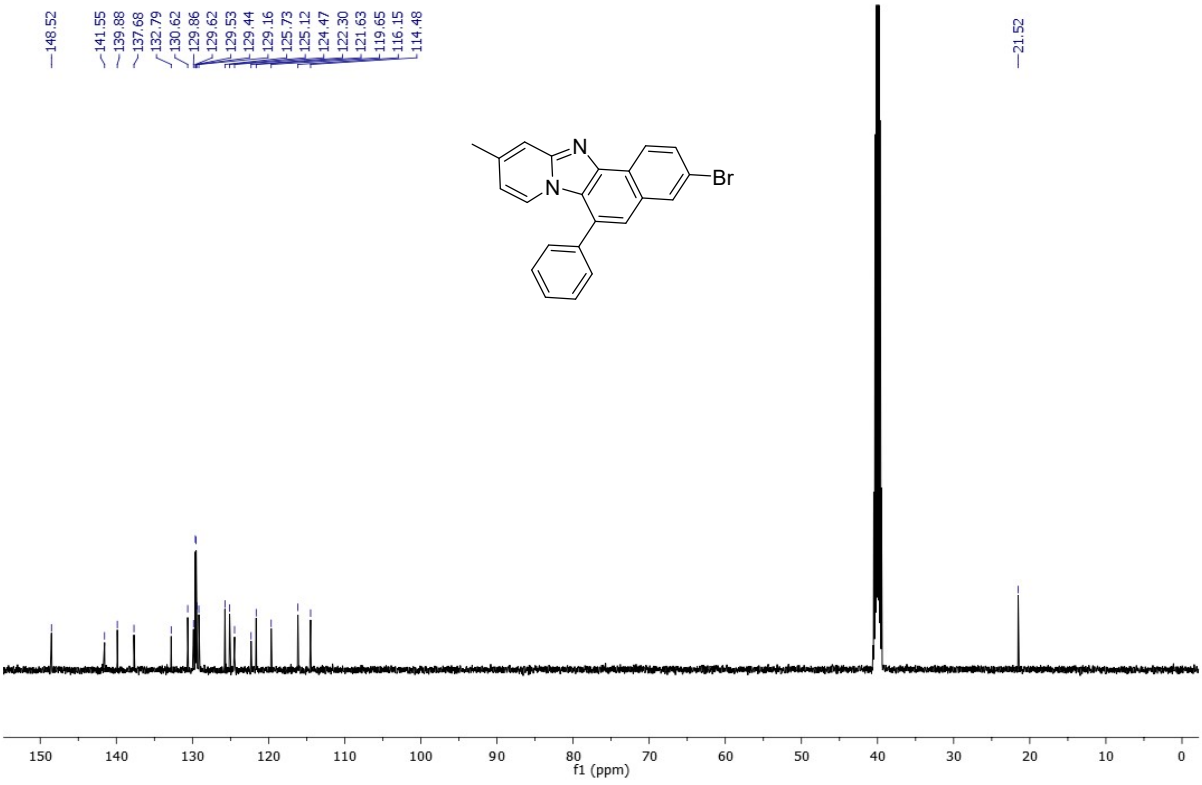
Compound **3v**: ^{1}H NMR (500 MHz, DMSO-d_6).



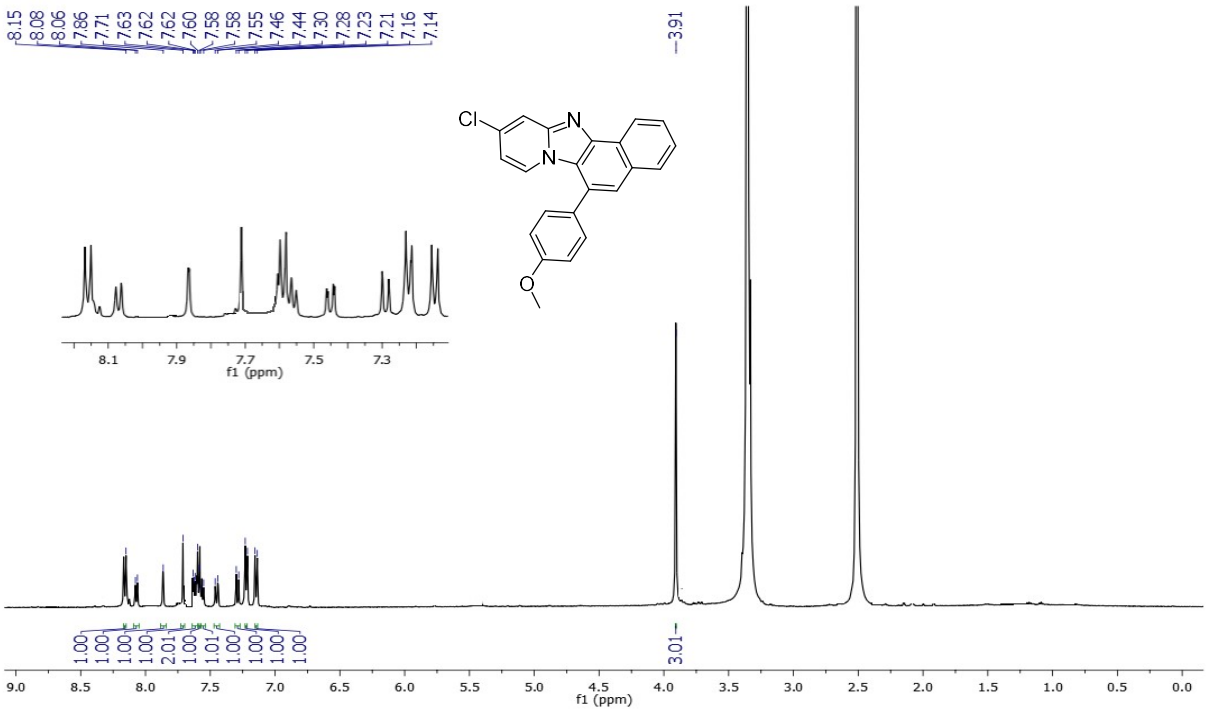
Compound **3v**: ^{13}C NMR (125 MHz, DMSO-d_6).



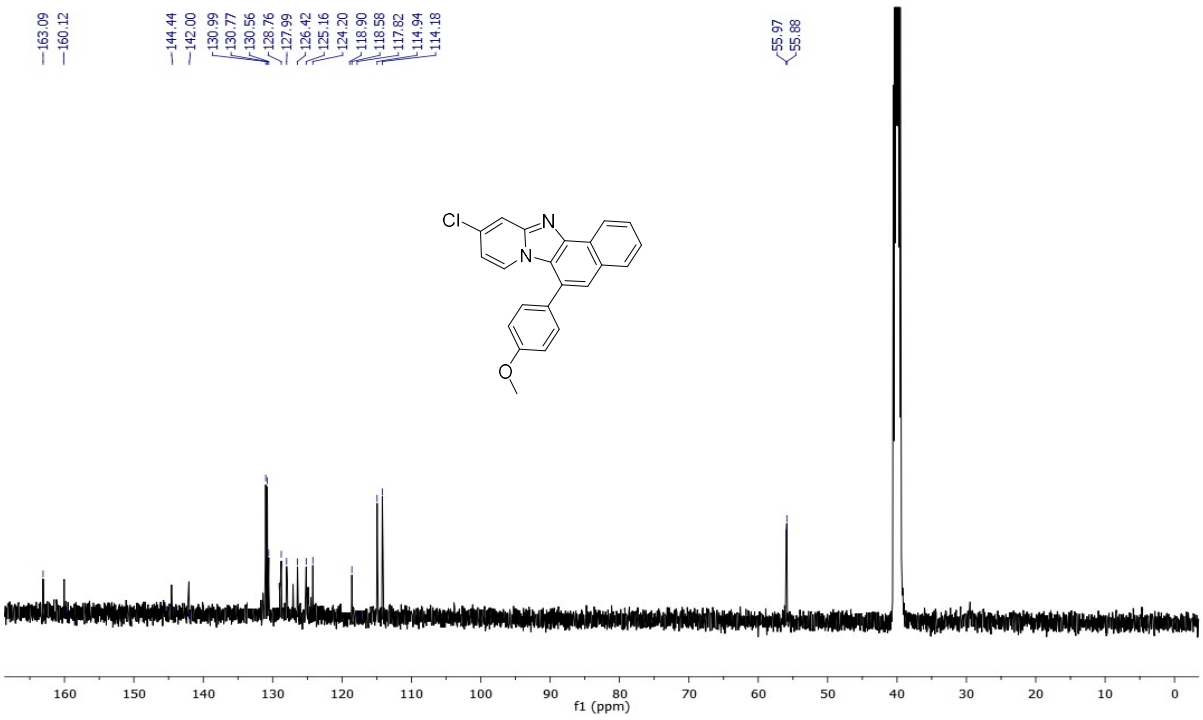
Compound **3w**: ^{1}H NMR (500 MHz, DMSO-d_6).



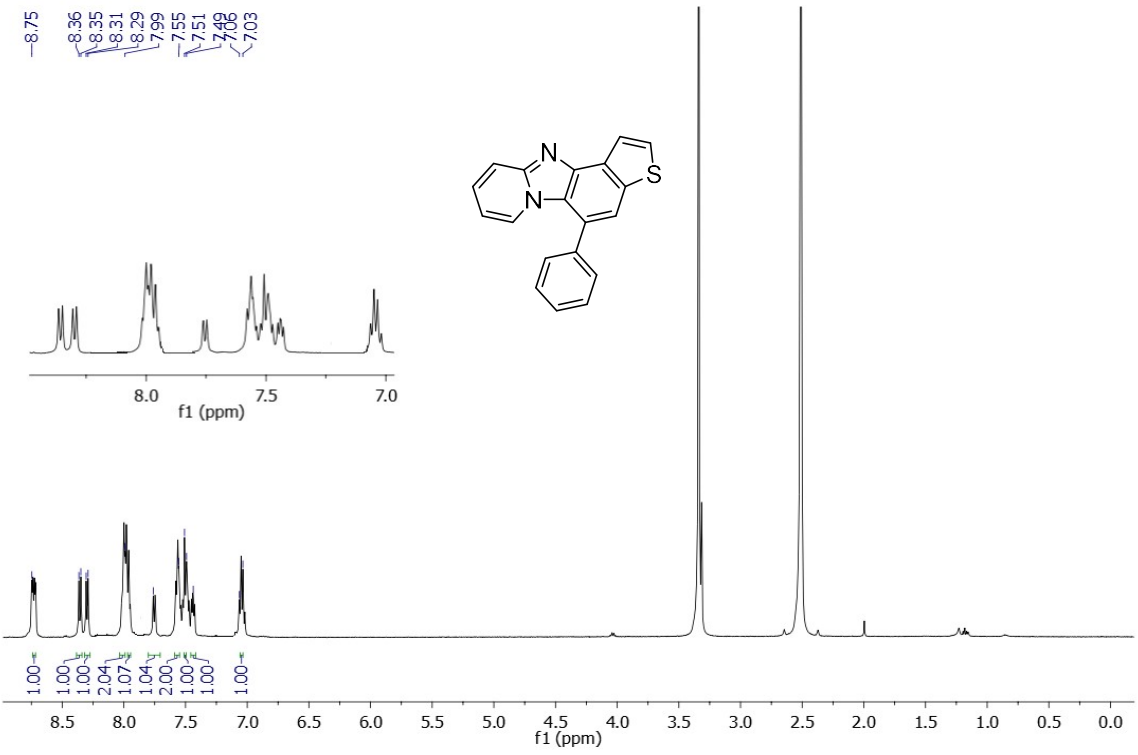
Compound **3w**: ^{13}C NMR (125 MHz, DMSO-d_6).



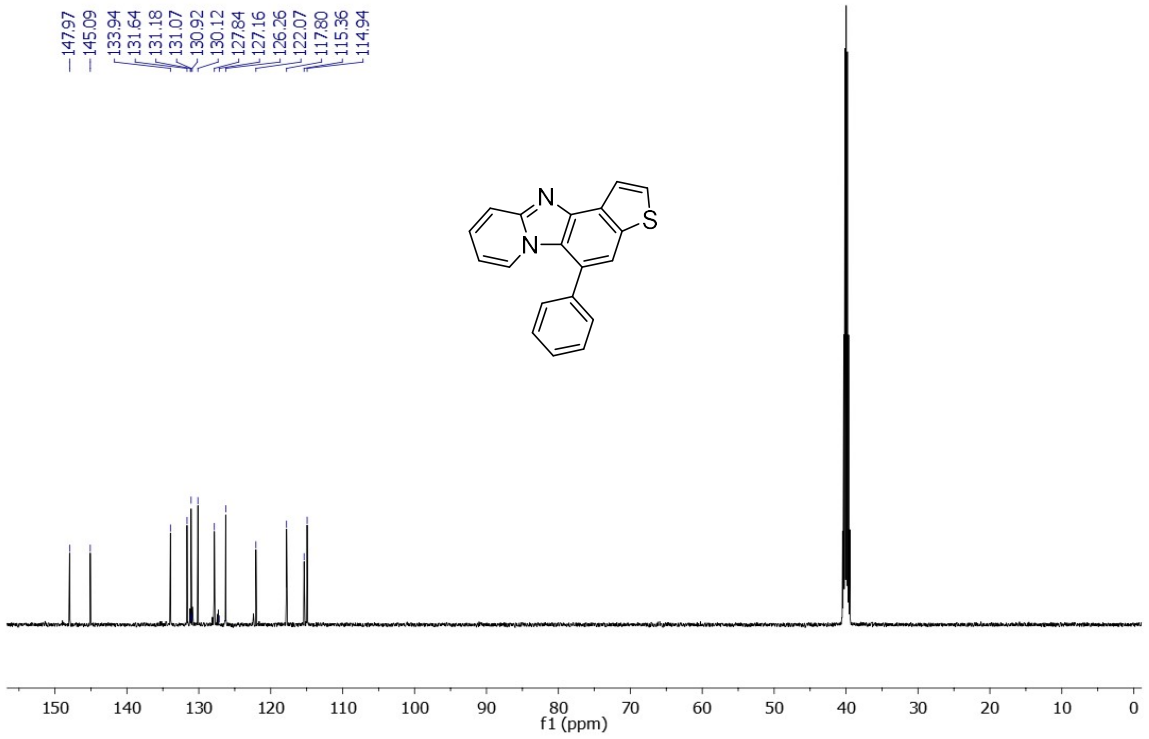
Compound **3x**: ^{1}H NMR (500 MHz, DMSO-d_6).



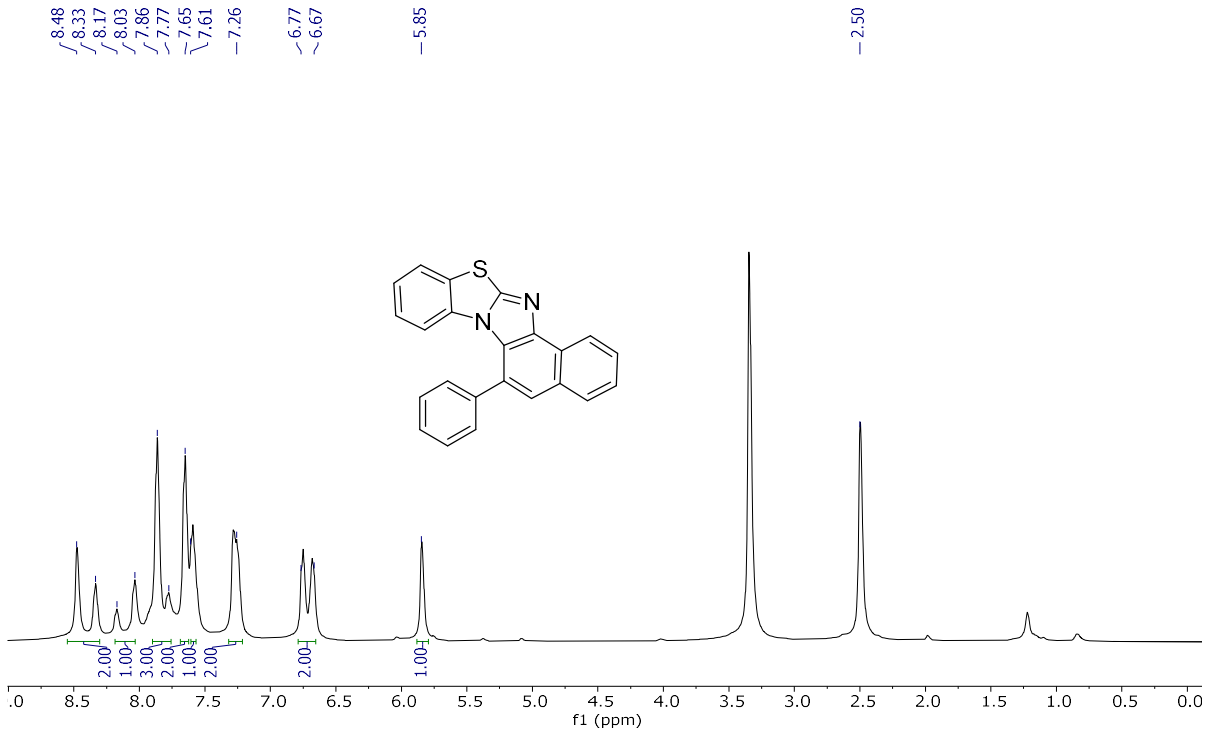
Compound **3x**: ^{13}C NMR (125 MHz, DMSO-d_6).



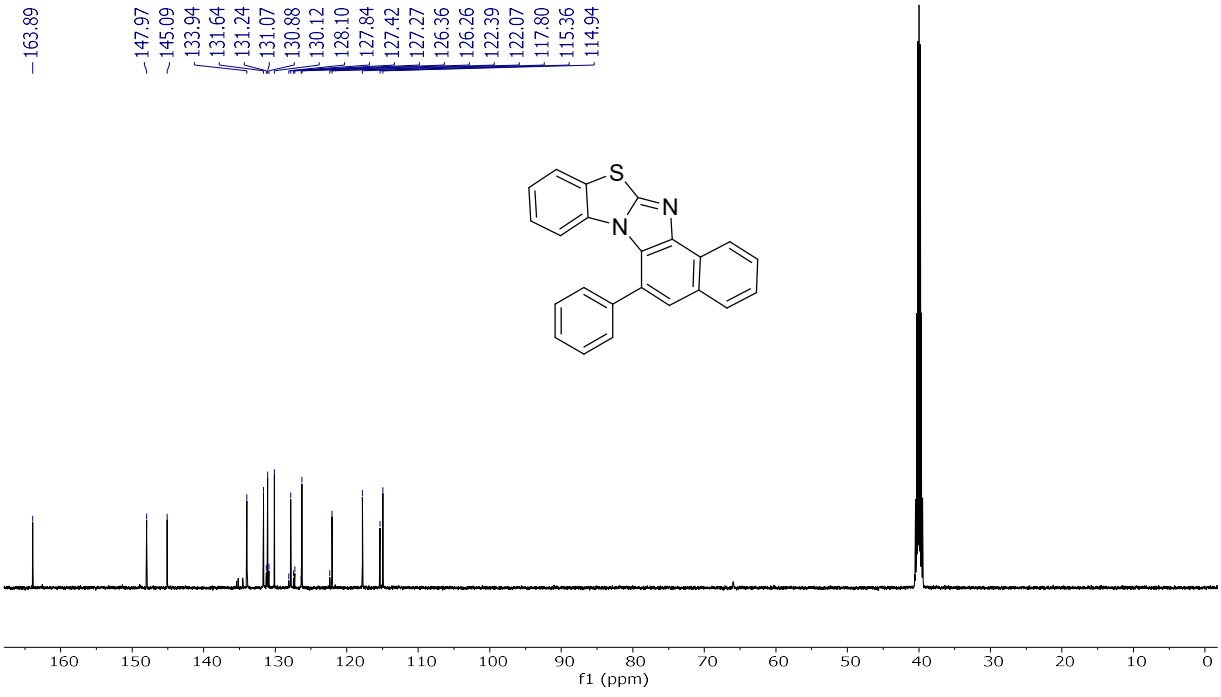
Compound **3y**: ^{1}H NMR (500 MHz, DMSO-d_6).



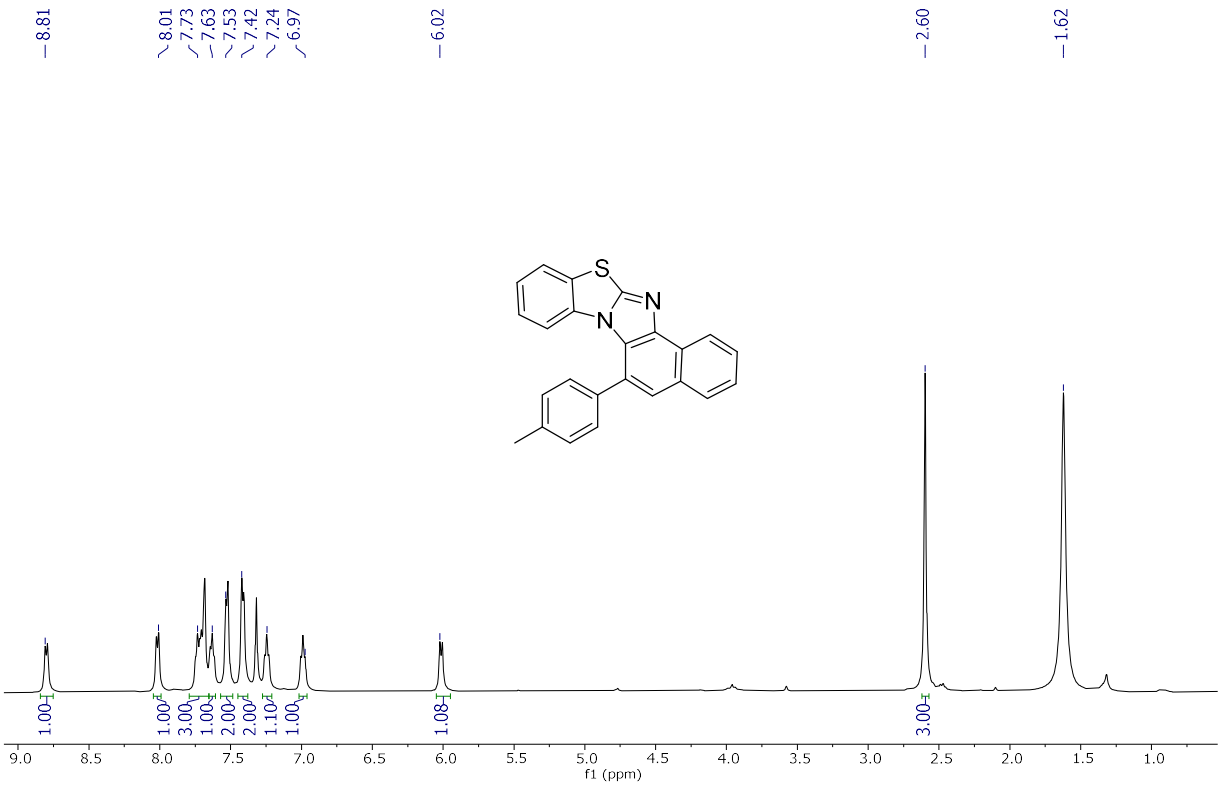
Compound **3y**: ^{13}C NMR (125 MHz, DMSO-d_6).



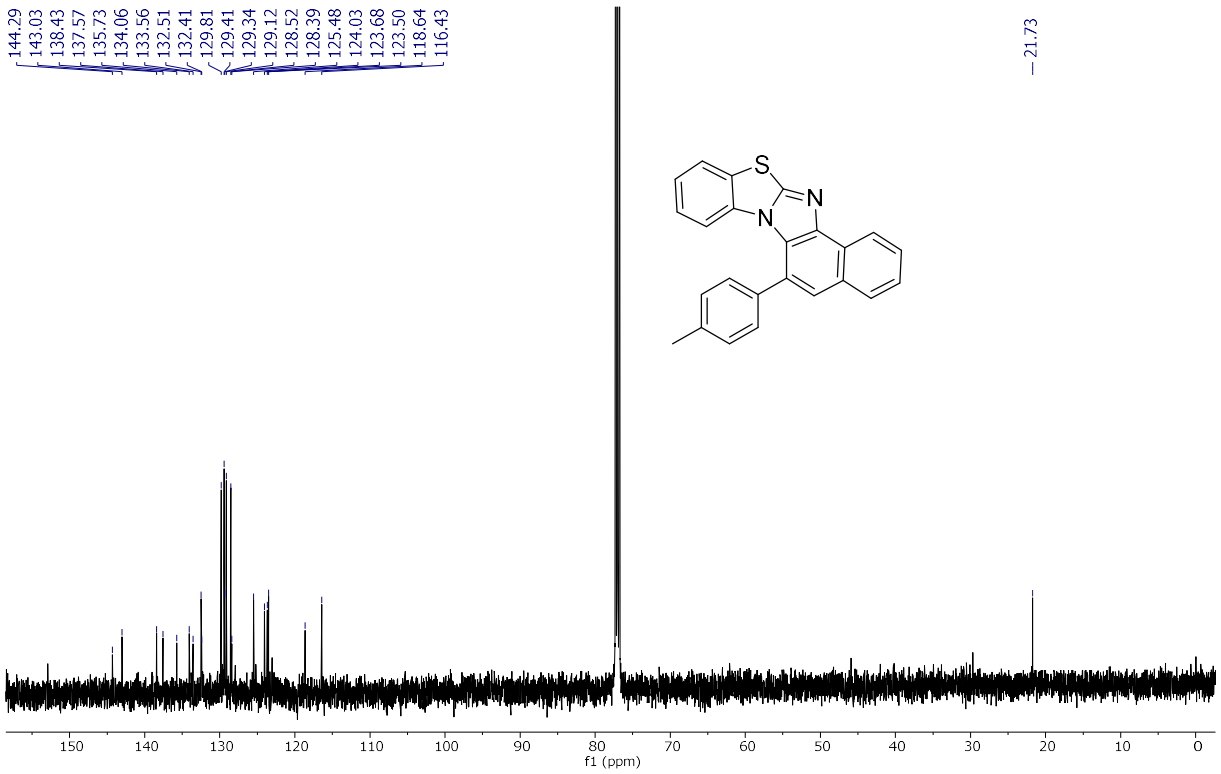
Compound **5a**: ^{1}H NMR (500 MHz, DMSO-d_6).



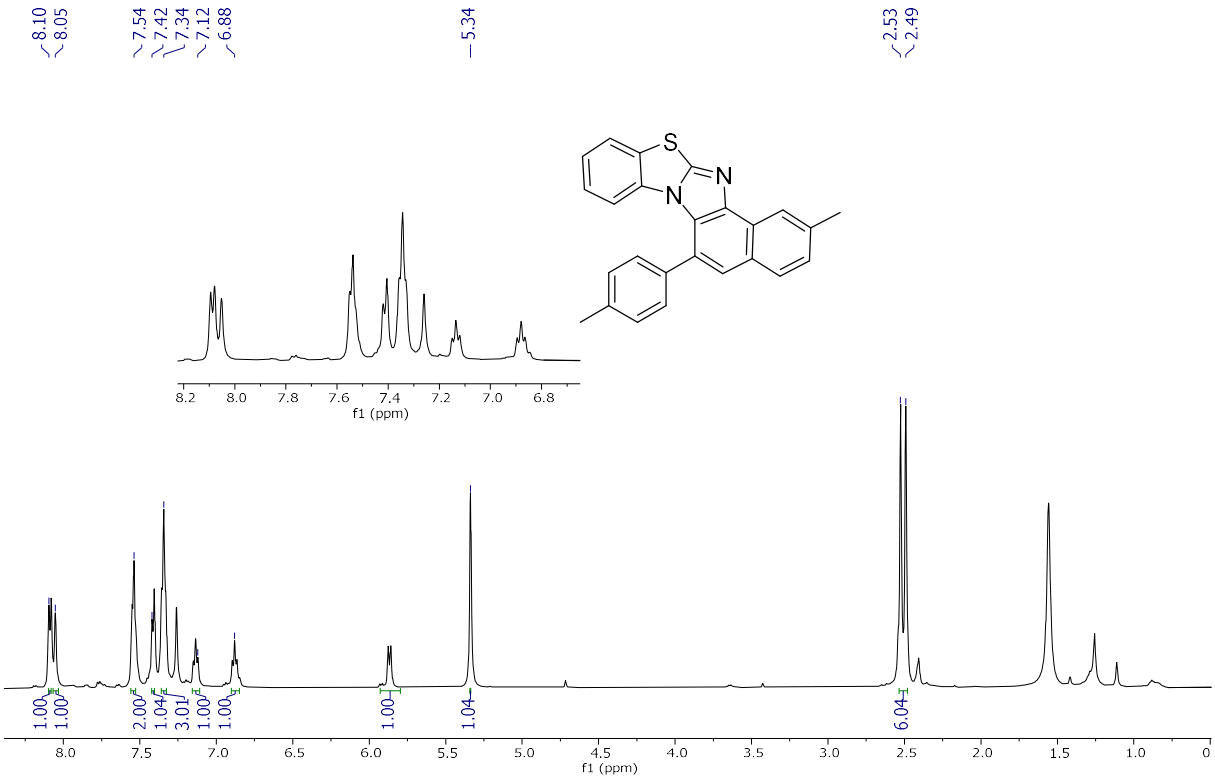
Compound **5a**: ^{13}C NMR (125 MHz, DMSO-d_6).



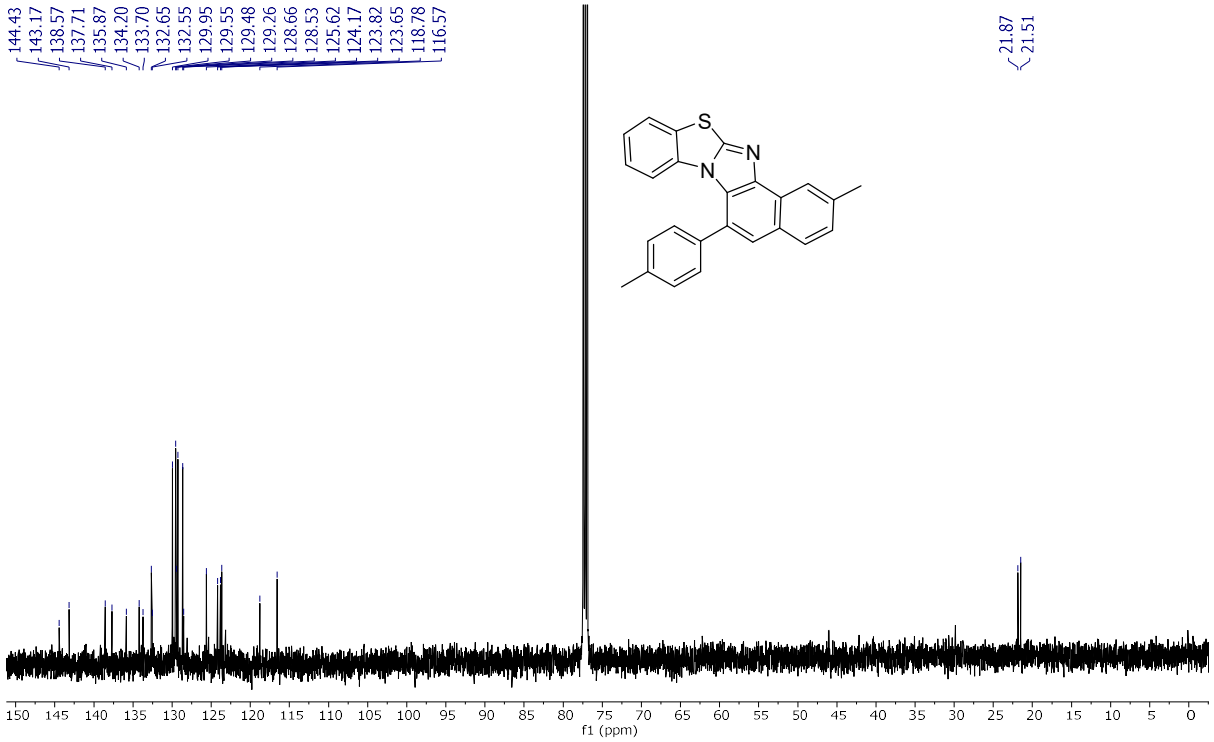
Compound **5b**: ^{1}H NMR (500 MHz, $CDCl_3$).



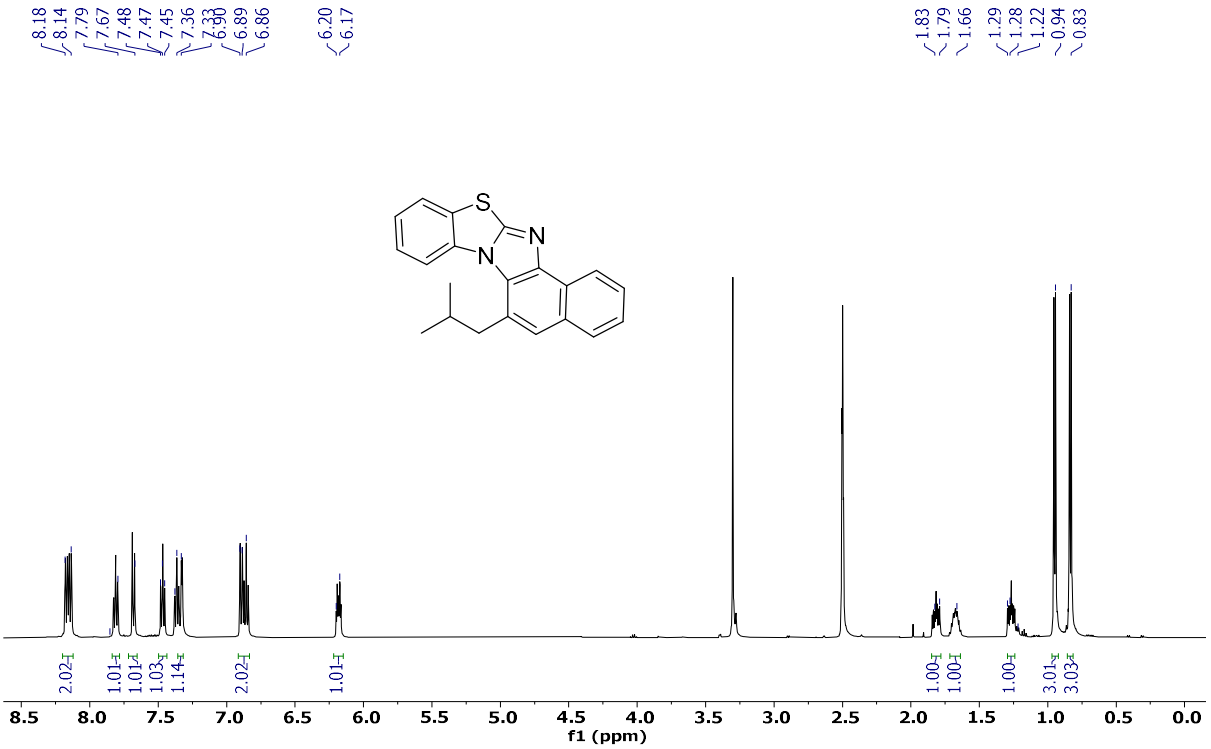
Compound **5b**: ^{13}C NMR (125 MHz, $CDCl_3$).



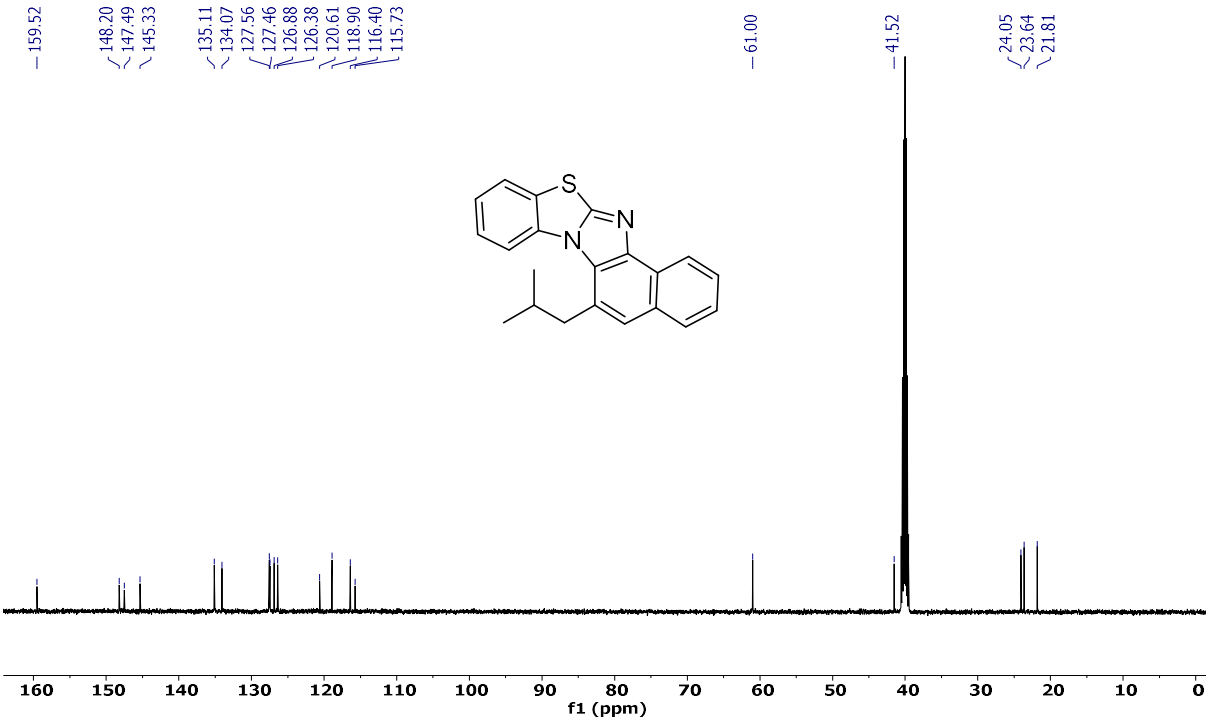
Compound **5c**: ^{1}H NMR (500 MHz, $CDCl_3$).



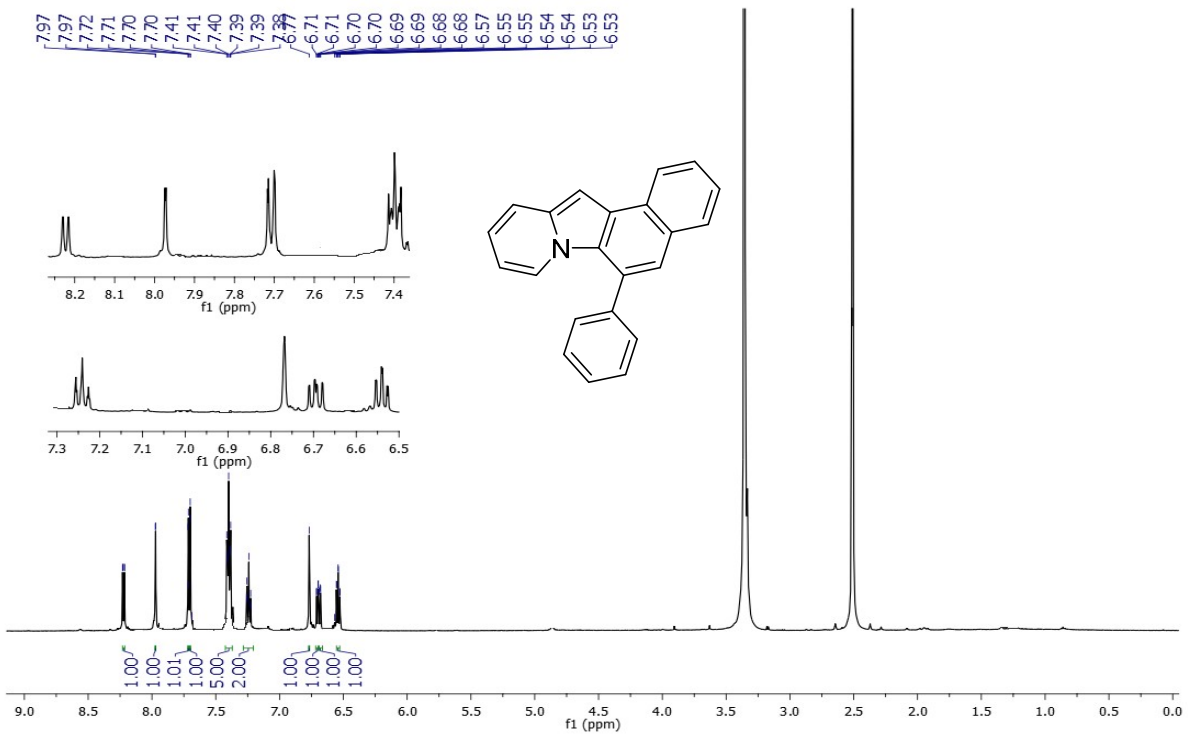
Compound **5c**: ^{13}C NMR (125 MHz, $CDCl_3$).



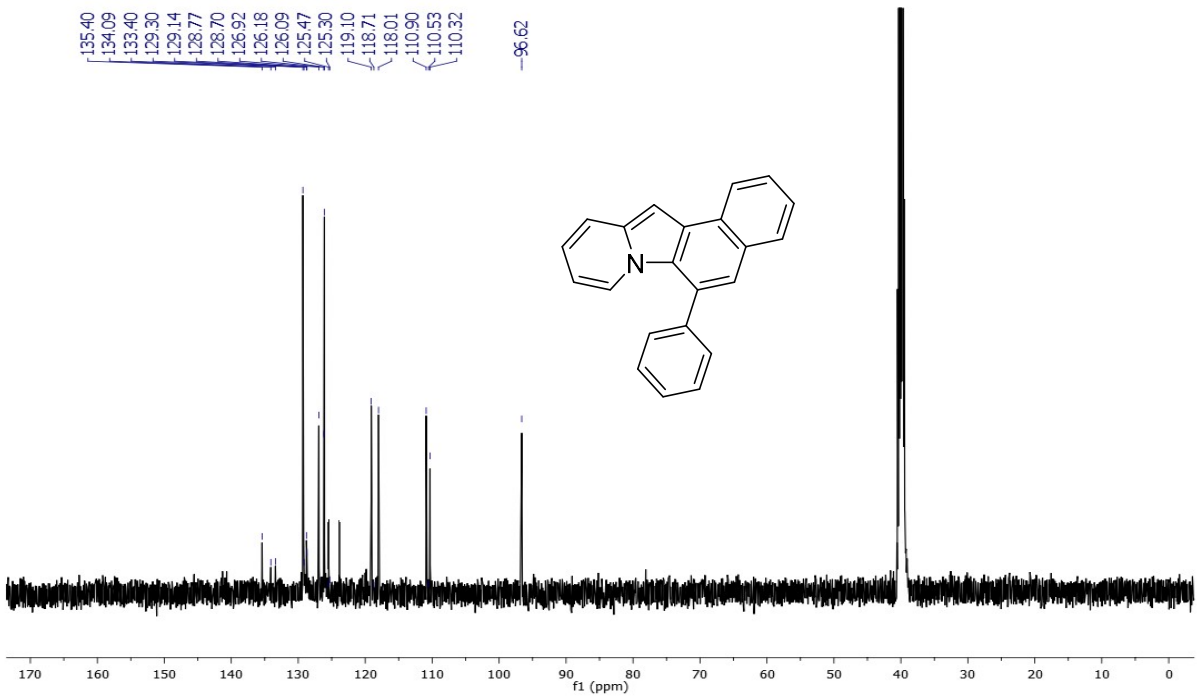
Compound **5d**: ^{1}H NMR (500 MHz, DMSO-d_6).



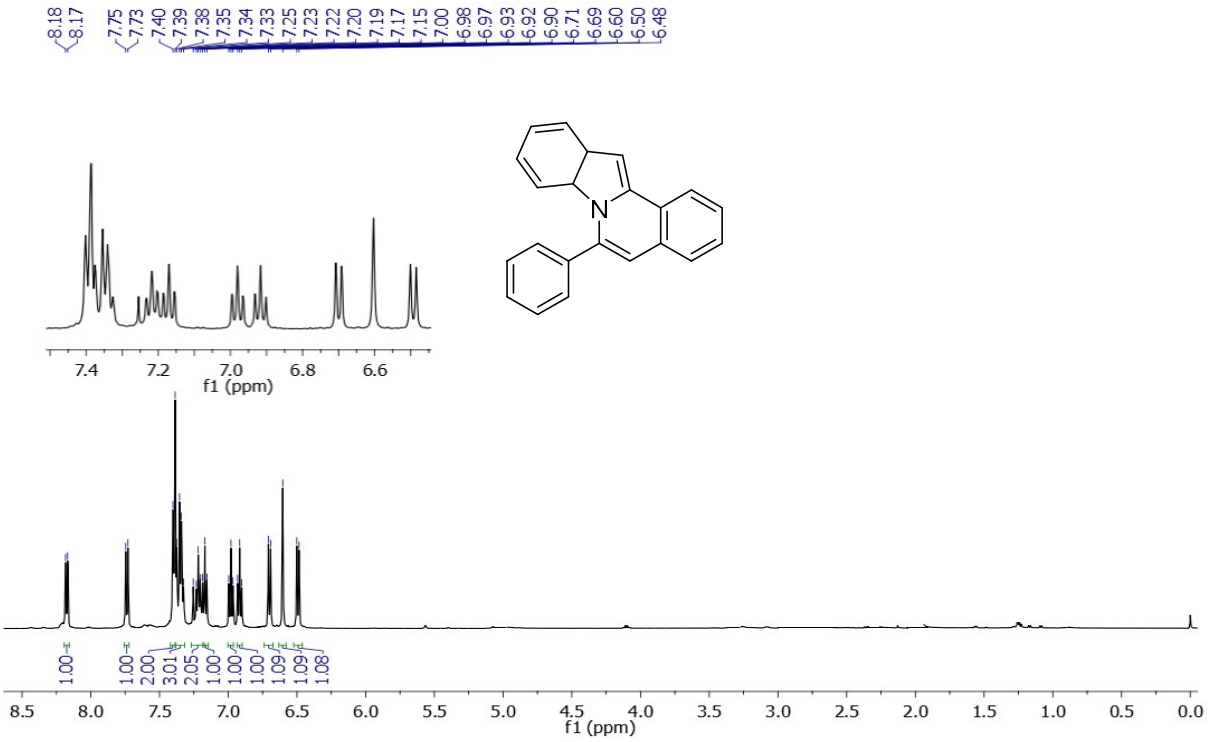
Compound **5d**: ^{13}C NMR (125 MHz, DMSO-d_6).



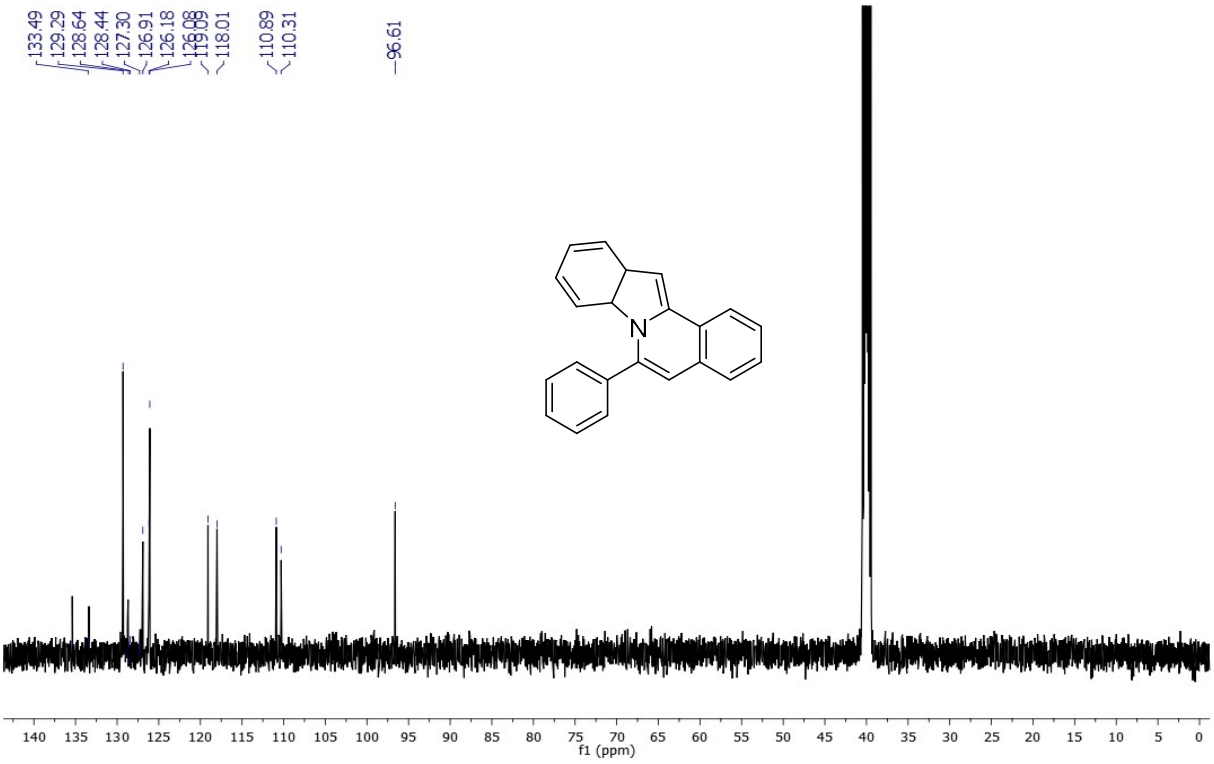
Compound **7a**: ^{1}H NMR (500 MHz, DMSO-d_6).



Compound **7a**: ^{13}C NMR (125 MHz, DMSO-d_6).



Compound **9a**: ^{1}H NMR (500 MHz, $CDCl_3$).



Compound **9a**: ^{13}C NMR (125 MHz, DMSO-d_6).