Electronic Supplementary Information

Simple inorganic base promoted C-N and C-C formation: Synthesis of benzo[4,5]imidazo[1,2-a]pyridines as functional AIEgen used for detecting picric acid

Kai Yang[a,b] Shi-He Luo*[a] Si-Hong Chen[a] Xi-Ying Cao[a] Yong-Jun Zhou[a] Yan-Lan Lin[a] Yan-Ping Huo*[c] and Zhao-Yang Wang*[a]

[a] School of Chemistry, South China Normal University, Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, Guangzhou 510006, P. R. China.
[b] College of pharmacy, Gannan Medical University, Ganzhou 341000, P. R. China.
[c] School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou, 510006, China.

E-mail: wangzy@scnu.edu.cn, pinky_r@163.com, yphuo@gdut.edu.cn; Fax: (+86) 20-39310187; Tel.: (+86) 20-39310258

Table of Contents

General Information.....[2]

Experimental Procedure for Compounds **1b-1u**.....[3]

Experimental Procedure for Compounds **3a-3n** and **4a-4k**.....[5]

Photophysical Properties of compounds **3a**, **3e**, **3f**, **3g**, **3n** and **4c** (**Figures S1-S21**).....[6-15]

Fluorescence Responses of **3b** to NAEs (**Figures S22-S23**, **Table S1**).....[16-18]

Data of Single-crystal X-ray Analysis (**Figures S24-S28**, **Table S2-S6**)…...…..…...…[19-23]

Characterization Data for All Products **3a-3o**, **4a-4l**, **3aa** and **3ab**.....[24-30]

^{1}H, ^{13}C and ^{19}F NMR Spectra for All Compounds **3a-3o**, **4a-4l**, **3aa** and **3ab**…...…...[31-60]

References……...….....……[61]

General Information

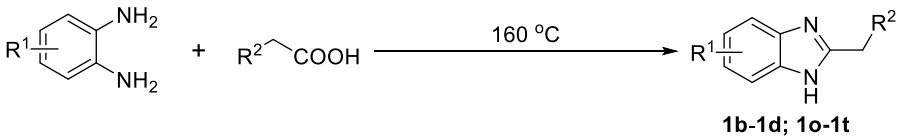
Melting point was performed on an X-5 digital melting point apparatus without correcting. ^{1}H, ^{13}C and ^{19}F NMR spectra were collected on a Varian AS600 spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard. The fluorescence spectra were recorded with a Hitachi F-4600 spectrophotometer at room temperature.

High-resolution mass spectra (HRMS) were obtained with a LCMS-IT-TOF mass spectrometer. Single-crystal X-ray analysis was obtained using Bruker APEX2 Smart CCD. Reactions were monitored using thin-layer chromatography (TLC) and visualized with UV light at 254 or 365 nm.

UV-*vis* absorption spectra were obtained with Shimadazu UV-2700 spectrophotometer at room temperature. Absolute PL quantum yields (Φ_F) were measured by Edinburgh FLS 980 fluorescence spectrometer with a calibrated integrating sphere. Dynamic light scattering (DLS) experiments were performed on Malvern Zetasizer Nano ZS90.

All reagents and solvents were purchased from commercial sources and used without further purification. 2-Substituted benzimidazoles **1** (except for **1a**) were synthesized from *o*-phenylenediamines and various acids according to the literature procedure[1, 2] (see the following for details).

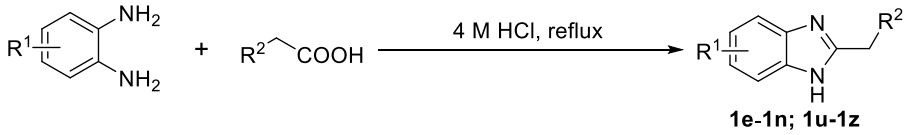
Experimental Procedure for Compounds 1b-1z



1b-1d; 1o-1t

R^1 = H, R^2 = Me (**1b**); R^1 = H, R^2 = Et (**1c**); R^1 = H, R^2 = *n*-Bu (**1d**);
R^1 = 4-Me, R^2 = H (**1o**); R^1 = 4-Cl, R^2 = H (**1p**); R^1 = 4,5-diMe, R^2 = H (**1q**);
R^1 = 4,5-diCl, R^2 = H (**1r**); R^1 = 4,5-diCl, R^2 = Me (**1s**); R^1 = 4,5-diF, R^2 = H (**1t**)

According to the reported procedure[1], compounds **1b-1d** and **1o-1t** were synthesized. The appropriate aromatic diamine (2.0 mmol, 1.0 equiv.) and carboxylic acid (10 equiv.) were heated in a sealed tube at 160 ℃ for 6 h. The reaction mixture was cooled to room temperature and ammonia solution was added. The mixture was cooled in ice until precipitate was formed. The resulting solid was recrystallised from aqueous ethanol to give the desired compound **1**.

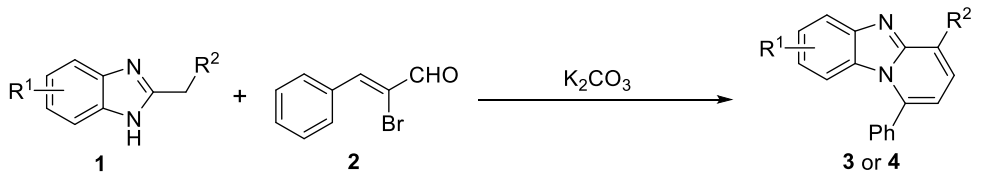


1e-1n; 1u-1z

R^1 = H, R^2 = Ph (**1e**); R^1 = H, R^2 = 4-Me-Ph (**1f**); R^1 = H, R^2 = 4-OMe-Ph (**1g**)
R^1 = H, R^2 = 4-Cl-Ph (**1h**); R^1 = H, R^2 = 4-Br-Ph (**1i**); R^1 = H, R^2 = 4-NO_2-Ph (**1j**)
R^1 = H, R^2 = 3-OMe-Ph (**1k**); R^1 = H, R^2 = 2-F-Ph (**1l**); R^1 = H, R^2 = 2-Br-Ph (**1m**)
R^1 = H, R^2 = 2-Naphthyl (**1n**); R^1 = 4-Me, R^2 = Ph (**1u**); R^1 = 4-Me, R^2 = 4-Cl-Ph (**1v**)
R^1 = 4-Me, R^2 = 4-Cl-Ph (**1w**); R^1 = 4,5-diMe, R^2 = 4-Cl-Ph (**1x**)
R^1 = 4,5-diCl, R^2 = 4-Cl-Ph (**1y**); R^1 = 4,5-diF, R^2 = 4-Cl-Ph (**1z**)

According to the reported procedure[2], compounds **1e-1n** and **1u-1z** were synthesized. A mixture of appropriate aromatic diamine (2.0 mmol, 1.0 equiv) and carboxylic acid (1.5 equiv) in 4 M HCl (20.0 mL) was refluxed for 6 h. After monitoring the end of the reaction on TLC, the mixture was cooled to room temperature and neutralized by ammonia solution. And the mixture was cooled in ice until precipitate was formed. The resulting solid was recrystallised from aqueous ethanol to give the desired compound **1**.

Experimental Procedure for Compounds 3a-3n and 4a-4k



The mixture of 2-substituted 1*H*-benzo[d]imidazole **1** (0.30 mmol), K_2CO_3 (0.75 mmol), and *α*-bromocinnamaldehyde **2** (0.45 mmol) in DMF (2 mL) was stirred at 140 °C (or 120 °C) for 12 h. After the completion of the reaction, the reaction mixture was quenched with H_2O (15 mL) and extracted with dichloromethane (3 × 15 mL). Then, the organic layer was dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel to afford the desired product **3** or **4**.

Photophysical Properties of Compounds 3a, 3e, 3f, 3g, 3n and 4c (Figures S1-S21)

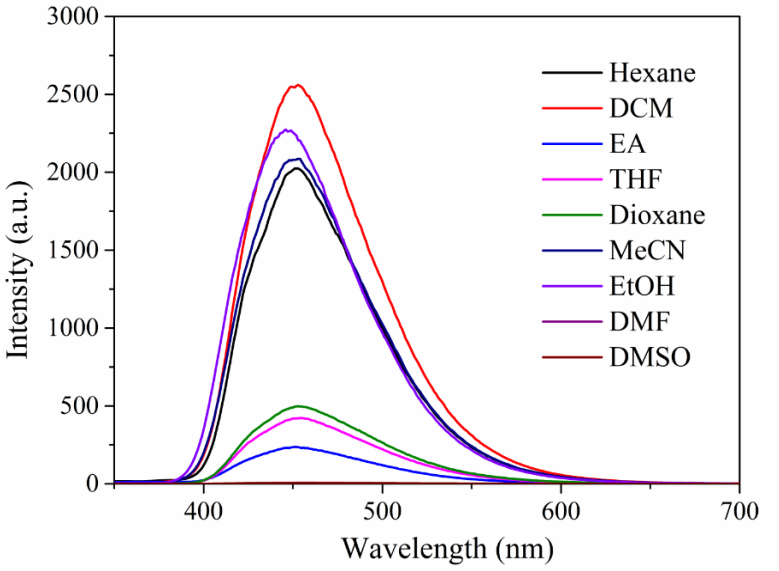


Figure S1 Emission spectra of compound **3b** in different solvents (c = 10 μM, λ_{ex} = 252 nm).

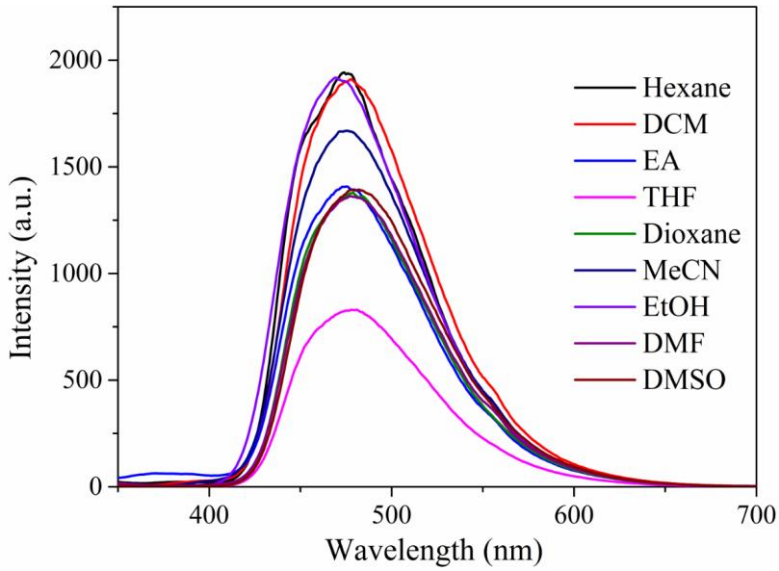


Figure S2 Emission spectra of compound **3e** in different solvents (c = 10 μM, λ_{ex} = 278 nm).

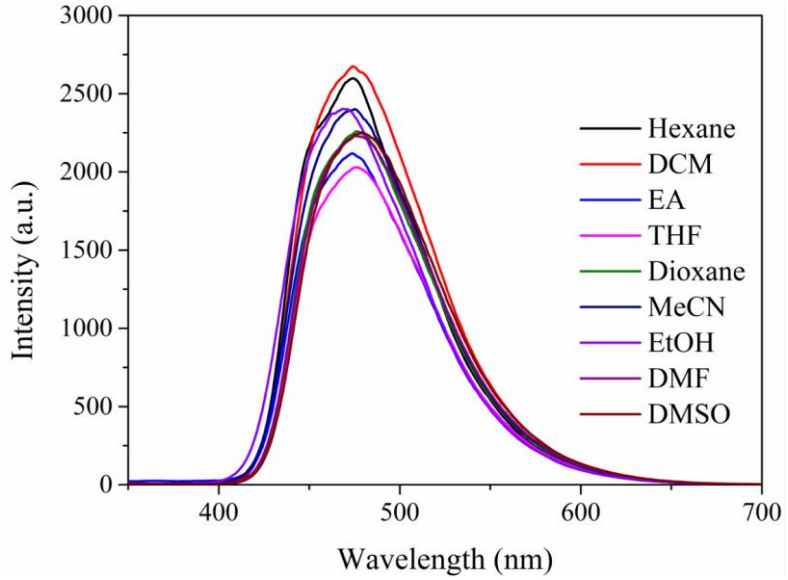


Figure S3 Emission spectra of compound **3f** in different solvents (c = 10 μM, λ_{ex} = 289 nm).

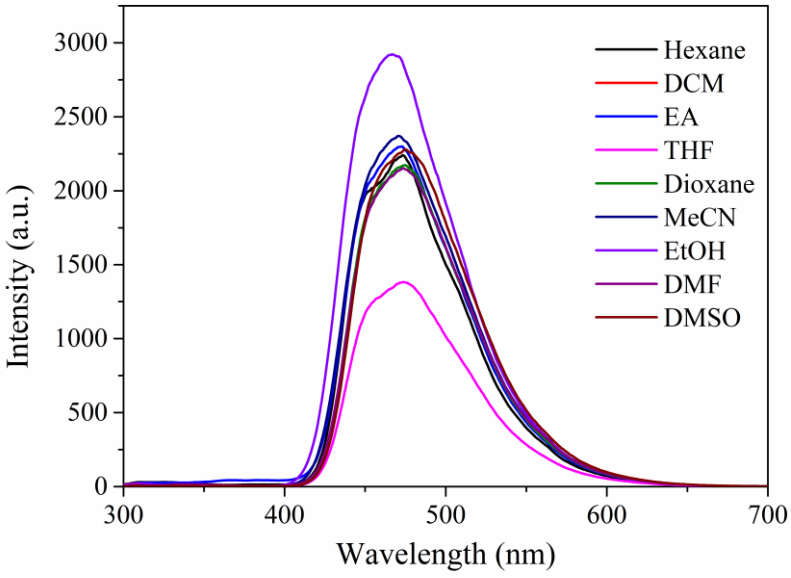


Figure S4 Emission spectra of compound **3g** in different solvents (c = 10 μM, λ_{ex} = 281 nm).

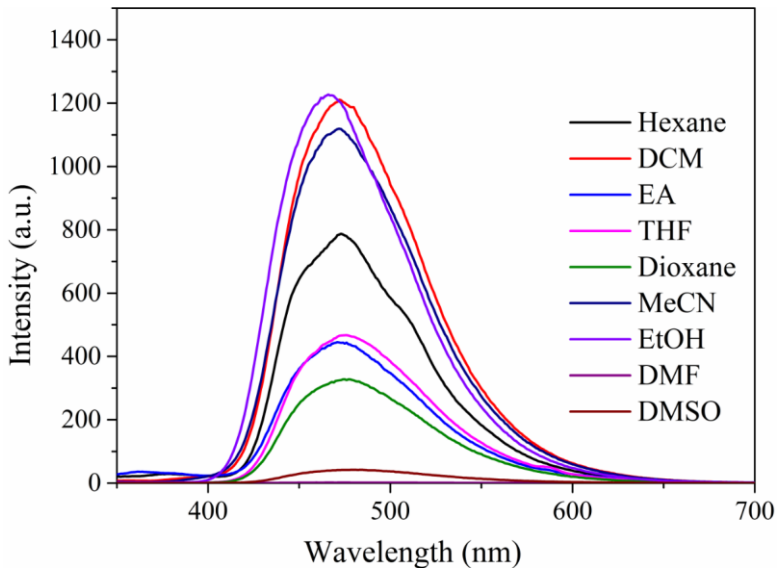


Figure S5 Emission spectra of compound **3n** in different solvents (c = 10 μM, λ_{ex} = 256 nm).

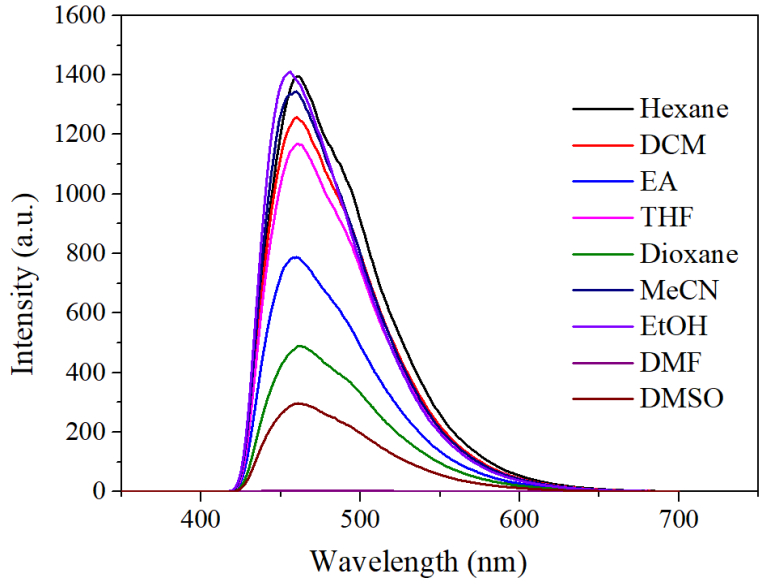


Figure S6 Emission spectra of compound **4c** in different solvents (c = 10 μM, λ_{ex} = 261 nm).

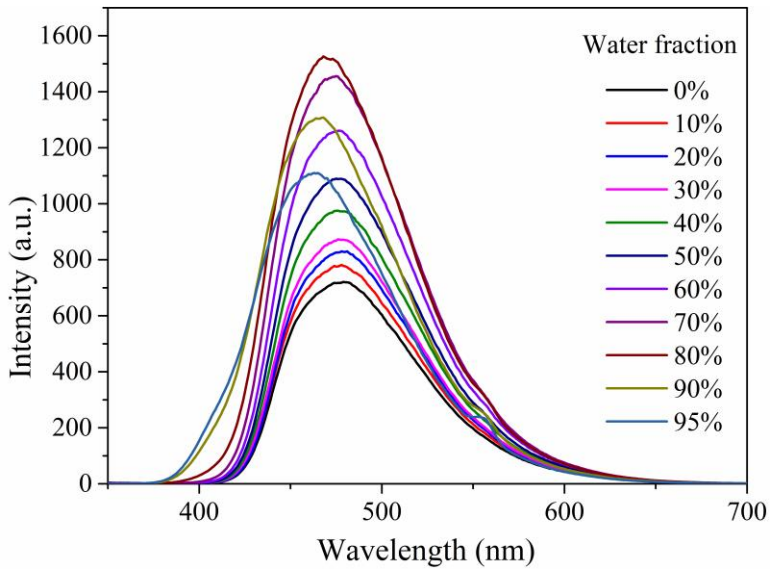


Figure S7 Emission spectra of compound **3e** upon increasing the fraction of water in THF (c = 10 μM, λ_{ex} = 278 nm).

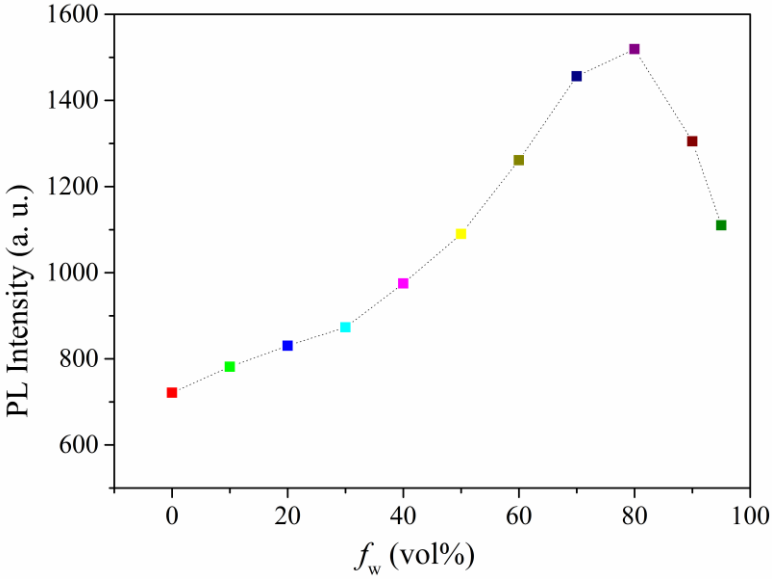


Figure S8 Emission profile of compound **3e** upon increasing the fraction of water in THF (c = 10 μM, λ_{ex} = 278 nm).

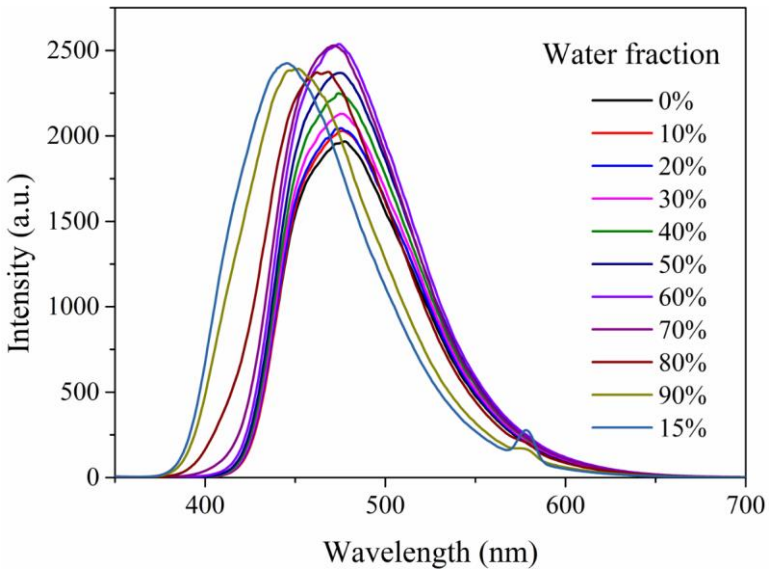


Figure S9 Emission spectra of compound **3f** upon increasing the fraction of water in THF (c = 10 μM, λ_{ex} = 289 nm).

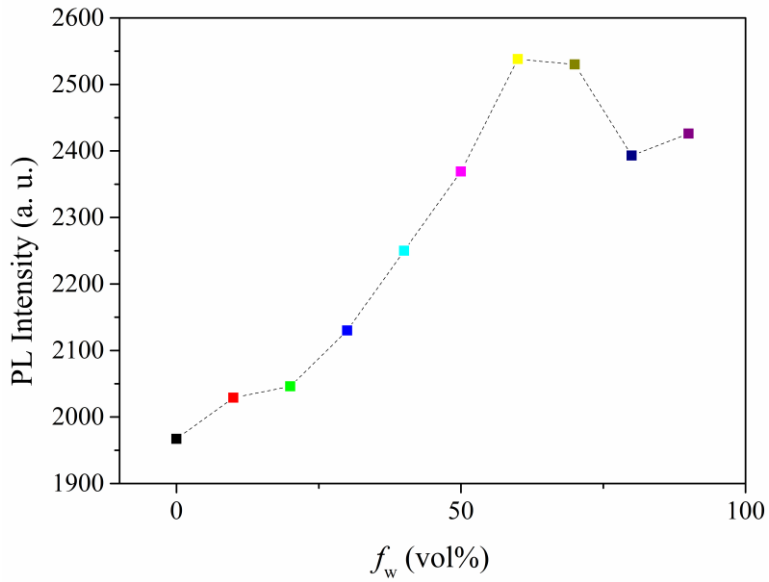


Figure S10 Emission profile of compound **3f** upon increasing the fraction of water in THF (c = 10 μM, λ_{ex} = 289 nm).

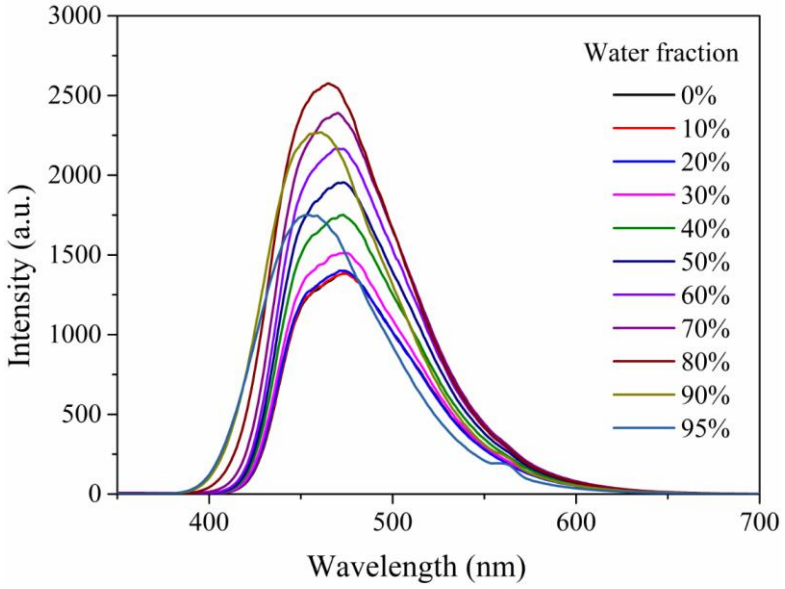


Figure S11 Emission spectra of compound **3g** upon increasing the fraction of water in THF (c = 10 μM, λ_{ex} = 281 nm).

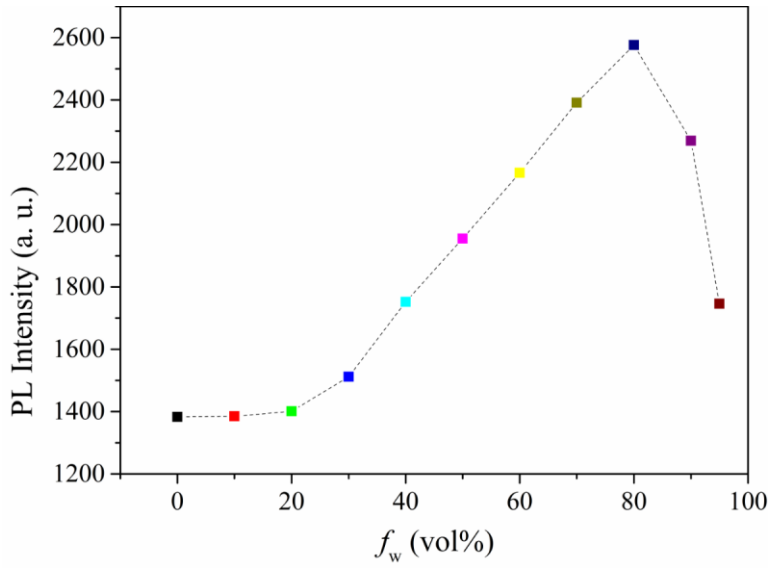


Figure S12 Emission profile of compound **3g** upon increasing the fraction of water in THF (c = 10 μM, λ_{ex} = 281 nm).

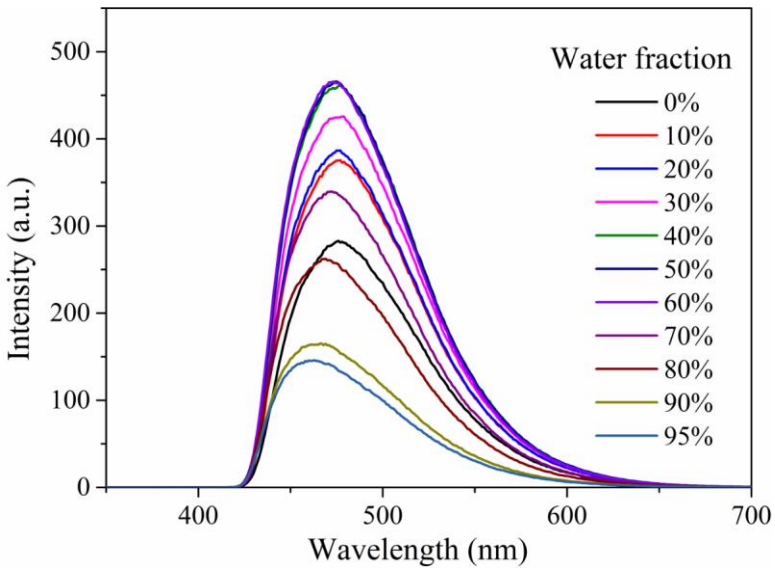


Figure S13 Emission spectra of compound **3n** upon increasing the fraction of water in THF (c = 10 μM, λ_{ex} = 256 nm).

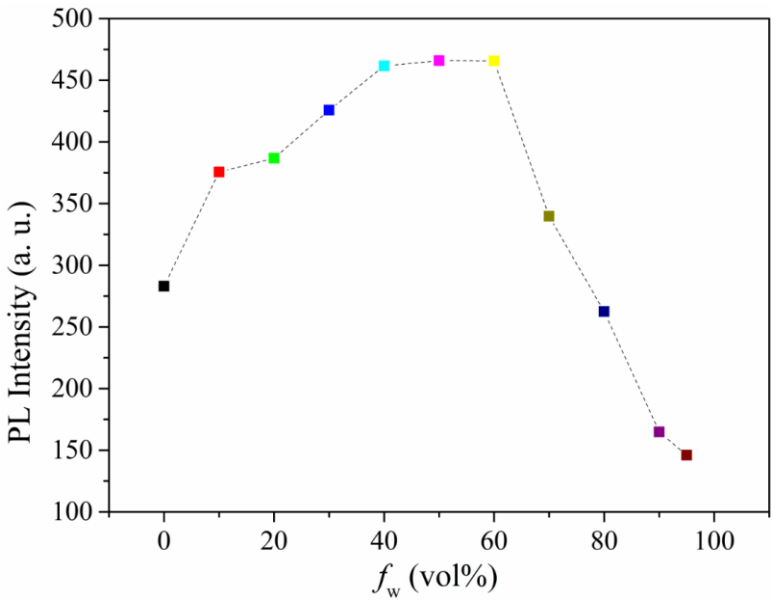


Figure S14 Emission profile of compound **3n** upon increasing the fraction of water in THF (c = 10 μM, λ_{ex} = 256 nm).

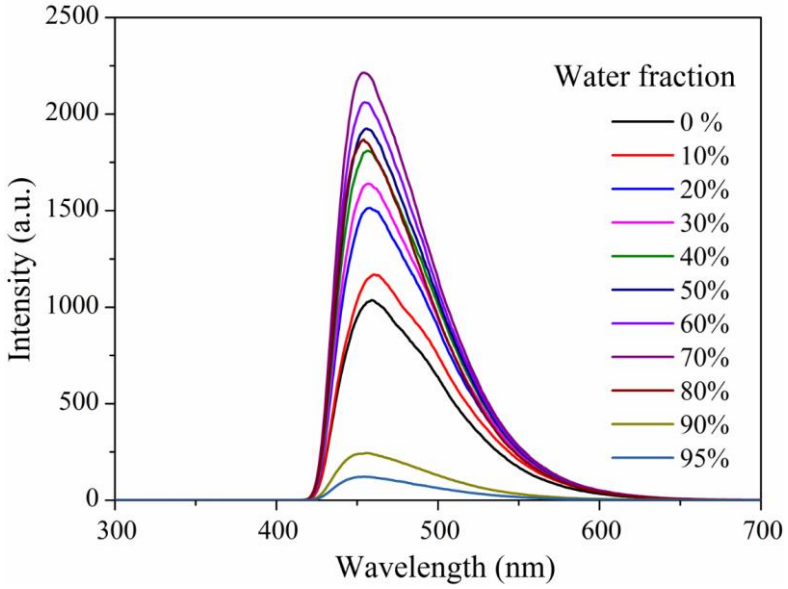


Figure S15 Emission spectra of compound **4c** upon increasing the fraction of water in THF (c = 10 μM, λ_{ex} = 261 nm).

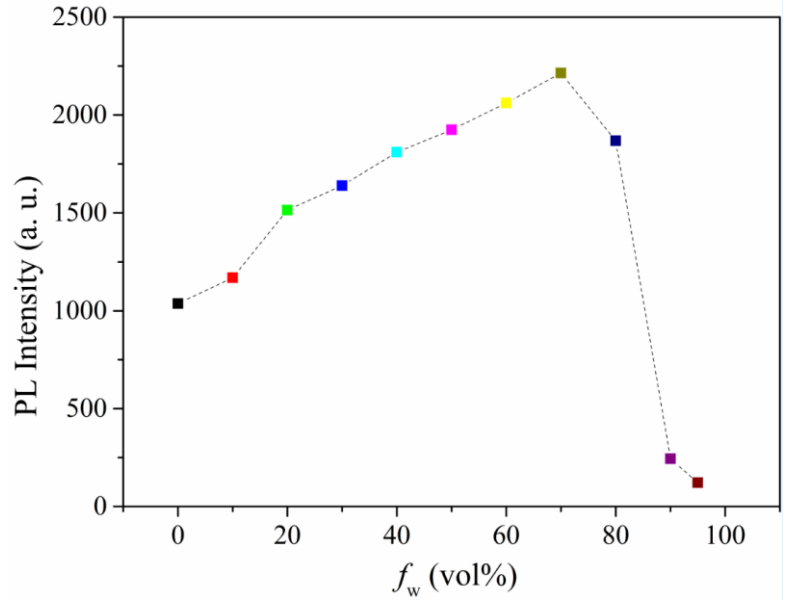


Figure S16 Emission profile of compound **4c** upon increasing the fraction of water in THF (c = 10 μM, λ_{ex} = 261 nm).

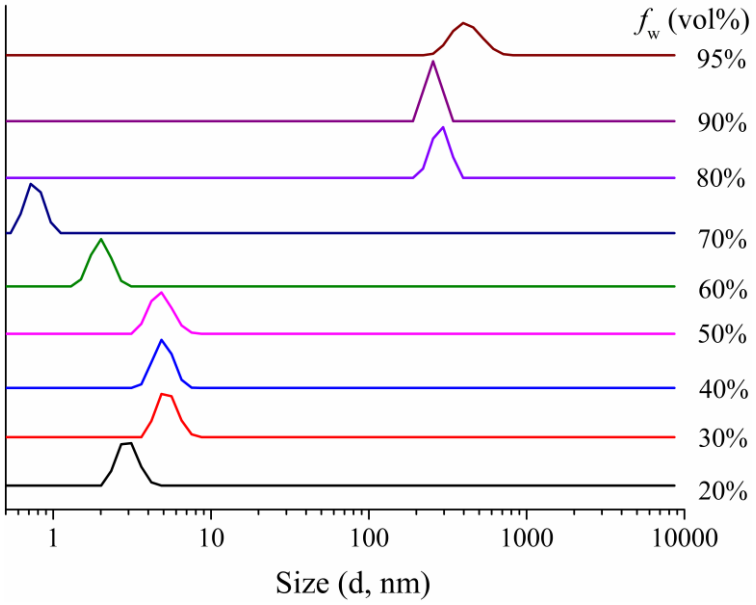


Figure S17 DLS curves of **3e** upon increasing the fraction of water in THF (c = 10 μM)

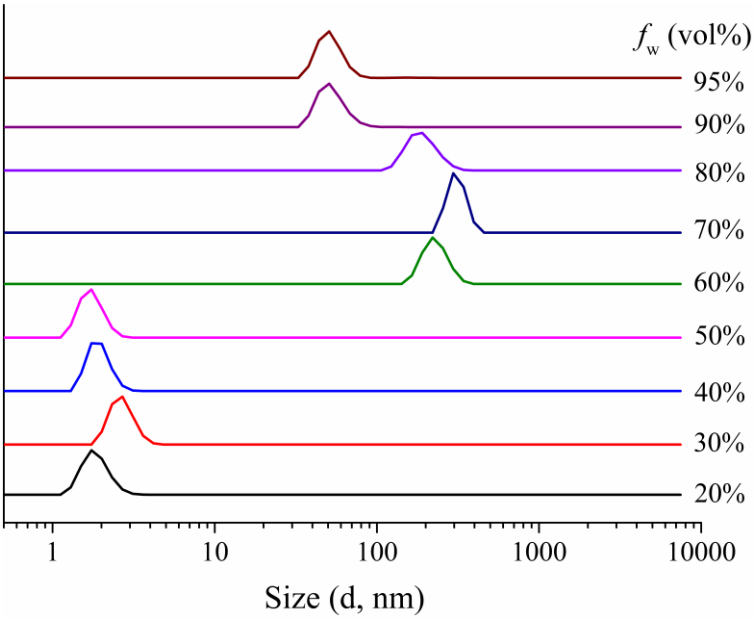


Figure S18 DLS curves of **3f** upon increasing the fraction of water in THF (c = 10 μM).

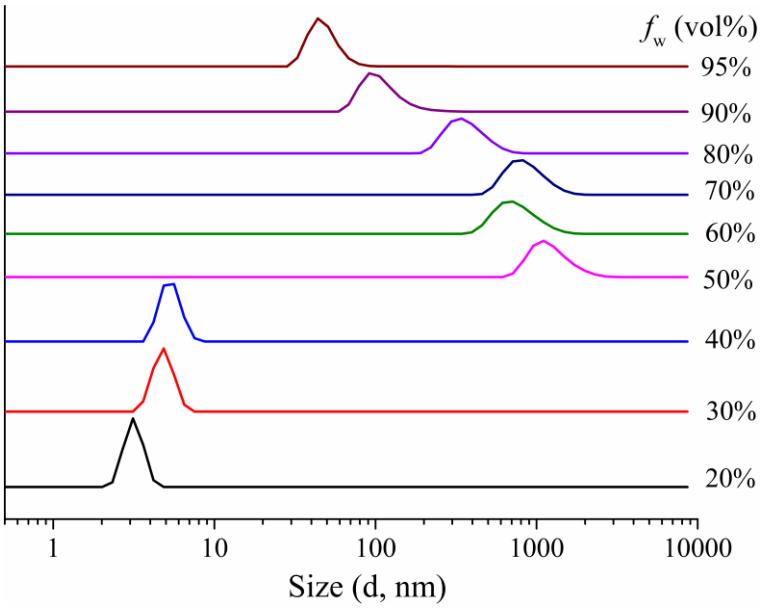


Figure S19 DLS curves of **3g** upon increasing the fraction of water in THF (c = 10 μM).

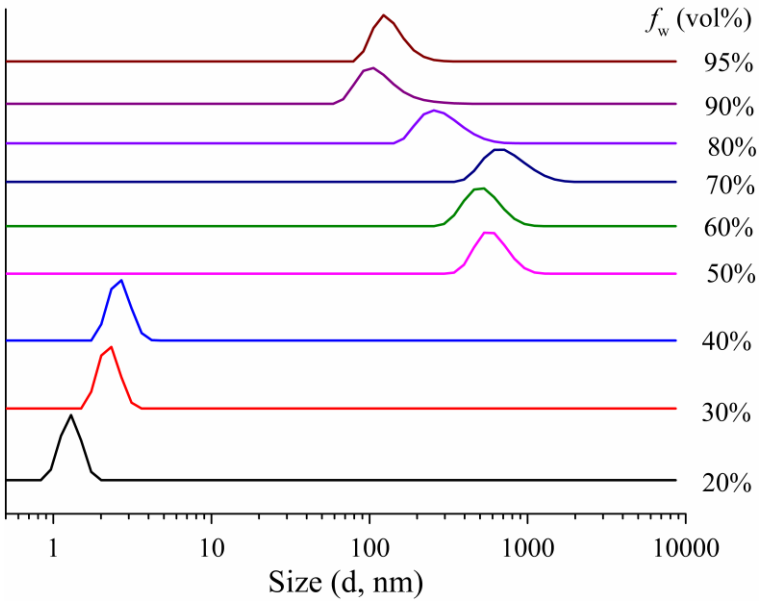


Figure S20 DLS curves of **3n** upon increasing the fraction of water in THF (c = 10 μM).

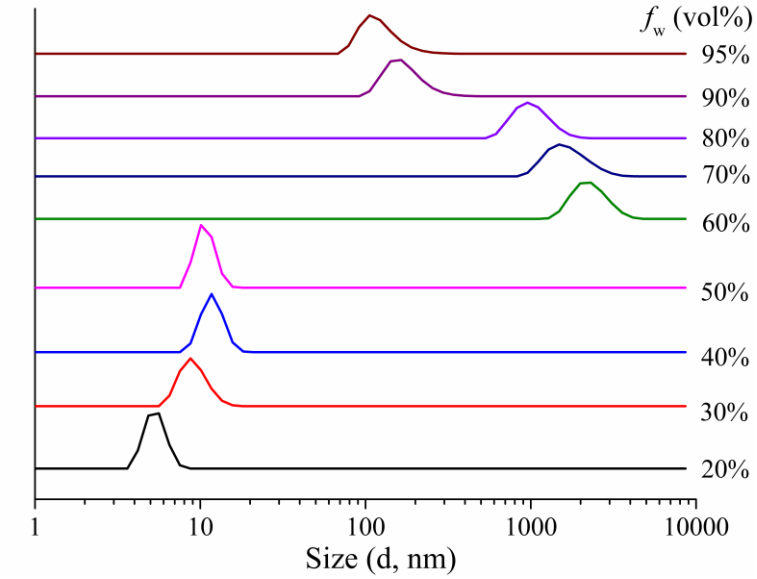


Figure S21 DLS curves of **4c** upon increasing the fraction of water in THF (c = 10 μM).

Fluorescence Responses of 3b to NAEs

Achieving the detection of nitroaromatic explosives (NAEs), e.g. picric acid (PA), is important for environmental protection and public security[3]. Compared with other NAEs, PA is of relatively high burst energy, toxicity and solubility in water. Therefore, the development of reliable sensing materials for rapid and sensitive detection of PA in aqueous solution has received special attention[4]. The charge-transfer emission quenching effect between PA, namely an electron-deficient compound, and electron-rich AIEgens is an approach for detecting PA[5, 6]. Thus, based on the research foundation of small-molecular fluorescent probes in our laboratory[6-10], we investigated the fluorescence detection application for NAEs, especially PA.

Caution! Aromatic explosives, e.g., picric acid (PA) and 2,4-dinitrophenol (DNP), used in the present study are highly explosive and should be used only in small quantities.

Compound **3b** has the best fluorescence intensity at 95% f_w of THF solvent, and it is conducive to the detection of water-soluble PA. In view of this fact, we used **3b** as an example to study the photoluminescence (PL) spectra of **3b** upon adding PA solution in THF/H_2O solvent (f_w = 95%). With the addition of PA solution (0-10 equiv.) into **3b** solution, the fluorescence intensity of compound **3b** at 440 nm is significantly decreased. Especially, when the PA concentration is 100 μM，the fluorescence quenching efficiency can reach to 95.7% (see **Figure 3** in the main text).

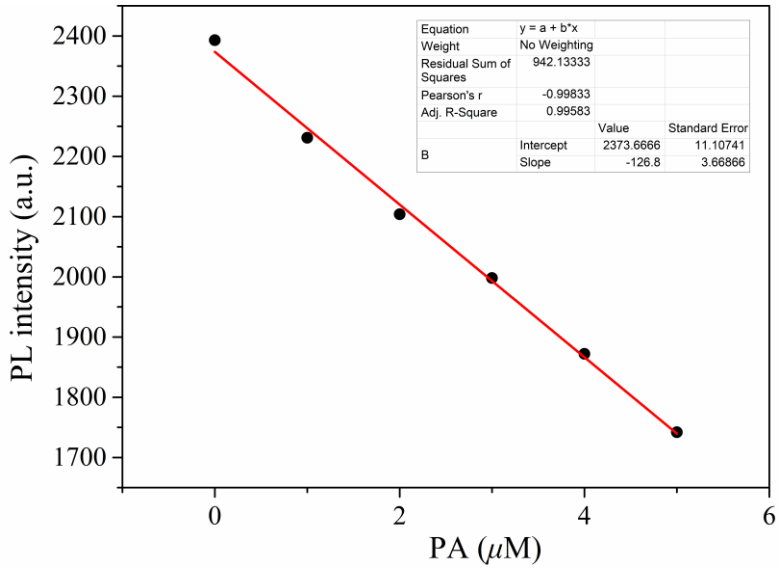


Figure S22 The fluorescence intensity of **3b** at 440 nm as a function of picric acid concentration.

Limit of detection (LOD) is usually used as the standard for judging probe sensitivity. First, the standard deviation (δ) of the blank measurements (n = 10) is calculated, and δ = 1.795. Then, a calibration curve is plotted between the luminescence intensity of **3b** and the concentration of PA, the slope of the calibration curve K = -126.8 (**Figure S22**).

According to the literature[8], LOD is determined by using the equation:

$$LOD = 3\delta/K$$

The corresponding LOD can be calculated to be 4.25 × 10^{-8} M (9.73 ppb). This value of LOD possesses certain advantages among the reported PA probes[6, 11-13].

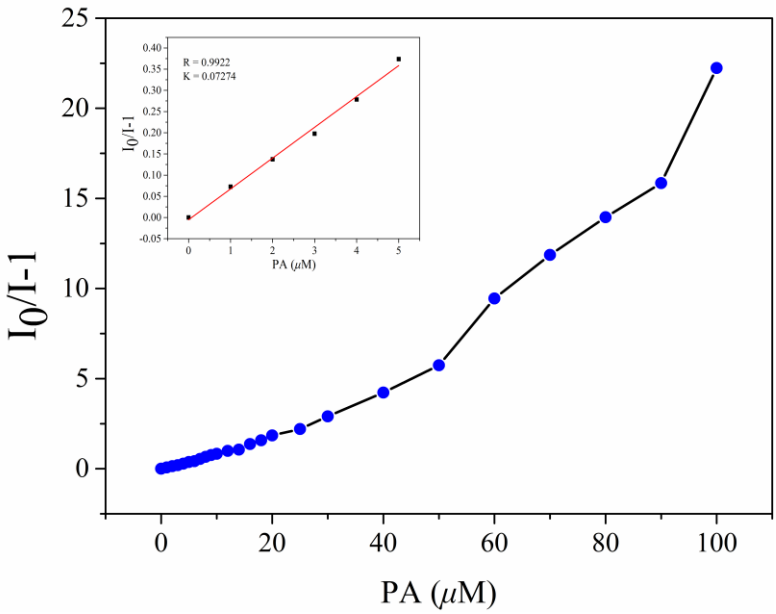


Figure S23 Stern-Volmer plot in response to PA.

To further evaluate the quenching efficiency, the fluorometric titration data of **3b** are transformed to the Stern-Volmer plot as shown in **Figure S23**. According to the literature[14], in this fluorescence quenching experiments, Stern-Volmer quenching constant (K*sv*) can be calculated according to the Stern-Volmer equation:

$$I_0 / I\text{-}1 = Ksv\,[Q]$$

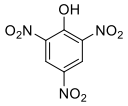
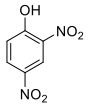
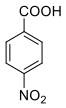
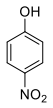
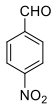
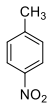
Where I_0 and I are the fluorescence intensities observed in the absence and presence of PA, respectively; [Q] is the quencher concentration.

Thus, the quenching constant K*sv* is calculated to be 7.27 × 10^4 M^{-1}, and this value is higher than those of some reported PA probes.[12, 13, 15-17]

We further explored the fluorometric detection experiments of other NAEs to study the

selectivity of **3b** for sensing PA (see **Table S1**). When 10 equivalents of other NAEs (or analogues) are added dropwise to the THF/H_2O (f_w = 95%) solution of **3b**, the fluorescence intensity is quenched to different degrees. Among them, **3b** has a moderate response to 2,4-dinitrophenol (2,4-DNP), 4-nitrobenzoic acid (4-NBAc), 4-nitrobenzaldehyde (4-NBA) and 1-methyl-2,4-dinitrobenzene (4-DNT), respectively. The quenching efficiency is between 41.0% and 75.0%. However, **3b** has no obvious response to phenol, nitrobenzene (NB), 4-nitrophenol (4-NP), 4-nitrotoluene (4-NT) and nitromethane (NM), respectively. The quenching efficiency is 20.4-29.2%.

Table S1 Sensing performance of **3b** towards NAEs (or analogues).

NAEs	Structure	Quenching efficiency[a]	NAEs	Structure	Quenching efficiency[a]
PA (picric acid)		95.7%	PhOH (phenol)		29.2%
2,4-DNP (2,4-dinitrophenol)		75.0%	**NB** (nitrobenzene)		26.0%
4-NBAc (4-nitrobenzoic acid)		68.7%	**4-NP** (4-nitrophenol)		22.4%
4-NBA (4-nitrobenzaldehyde)		61.6%	**4-NT** (4-nitrotoluene)		21.5%
4-DNT (1-methyl-2,4-dinitrobenzene)		41.0%	**NM** (Nitromethane)	CH_3NO_2	20.4%

[a] The quenching efficiency were calculated after adding 10 equiv. NACs into **3b** solution.

In a word, **3b** can be used as a fluorescent probe to detect PA by "turn-off" response in aqueous system and has the advantages of low detection limit and large quenching constant. At the same time, **3b** also has a moderate response to some other NAEs.

Data of Single-crystal X-ray Analysis

Table S2 Crystal data and structure refinement for **3b**.

Compound	**3b**
Empirical formula	$C_{18}H_{14}N_2$
Formula weight	258.31
Temperature (K)	297
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 1 21/n 1
Unit cell dimensions (Å, °)	a = 10.6034(8), b = 12.7690(11), c =10.6190(9) α = 90, β = 110.867(9), γ = 90
Volume ($Å^3$)	1343.5(2)
Z	4
Density (calculated) (Mg/m^3)	1.277
Absorption coefficient (mm^{-1})	0.076
F(000)	544.0
Theta range for data collection	6.768 to 49.996
Index ranges	-9<=h<=12, -12<=k<=15, -12<=l<=12
Reflections collected	6242
Independent reflections	2366 [R(int) = 0.0496, R(sigma) = 0.0672]
Completeness to theta = 24.998°	99.6%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.721
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2366 / 0 / 182
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R_1 = 0.0611, wR_2 = 0.1172
R indices (all data)	R_1 = 0.1017, wR_2 = 0.1372
Largest diff. peak and hole	0.14 and -0.22 e.$Å^{-3}$

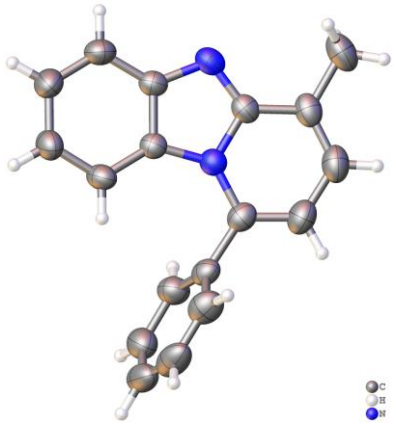


Fig. S24 The molecular structure of **3b**.

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

Compound	**3f**
Empirical formula	$C_{24}H_{18}N_2$
Formula weight	334.40
Temperature (K)	297
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 1 21/n 1
Unit cell dimensions (Å, °)	a = 9.9393(11), b = 10.0786(16), c = 10.2828(11) α = 106.688(12), β = 91.551(9), γ = 116.591(13)
Volume (Å^3)	867.6(2)
Z	2
Density (calculated) (Mg/m^3)	1.280
Absorption coefficient (mm^{-1})	0.075
F(000)	352.0
Theta range for data collection	7.364 to 58.794
Index ranges	-13<=h<=9, -11<=k<=13, -14<=l<=13
Reflections collected	6873
Independent reflections	3953 [R(int) = 0.0229, R(sigma) = 0.511]
Completeness to theta = 29.397°	82.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.778
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3953 / 0 / 237
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R_1 = 0.0544, wR_2 = 0.1159
R indices (all data)	R_1 = 0.1015, wR_2 = 0.1464
Largest diff. peak and hole	0.16 and -0.15 e.Å^{-3}

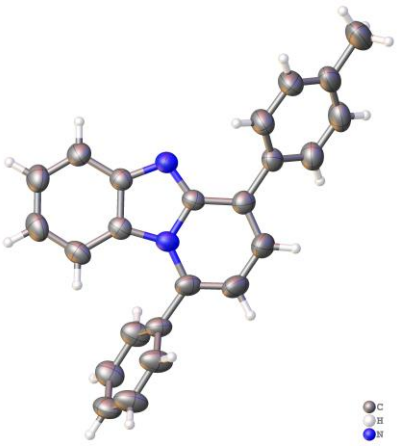


Fig. S25 The molecular structure of **3f**.

Table S4 Crystal data and structure refinement for **3i**.

Compound	**3i**
Empirical formula	C_{23} H_{15} Cl N_2
Formula weight	354.82
Temperature (K)	297
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 1 21/n 1
Unit cell dimensions (Å, °)	a = 9.8768(10), b = 9.9849(14), c =10.2735(14) α = 106.386 (12), β = 91.697(10), γ = 116.134(12)
Volume (Å^3)	858.6(2)
Z	2
Density (calculated) (Mg/m^3)	1.372
Absorption coefficient (mm^{-1})	0.231
F(000)	368.0
Theta range for data collection	7.358 to 58.816 deg
Index ranges	-13<=h<=13, -12<=k<=10, -12<=l<=14
Reflections collected	7162
Independent reflections	3948 [R(int) = 0.0245, R(sigma) = 0.0495]
Completeness to theta = 29.408°	83.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.937
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3948 / 0 / 236
Goodness-of-fit on F^2	1.021
Final R indices [I>2sigma(I)]	R_1 = 0.0528, wR_2 = 0.1064
R indices (all data)	R_1 = 0.0975, wR_2 = 0.1298
Largest diff. peak and hole	0.22 and -0.30 e.Å^{-3}

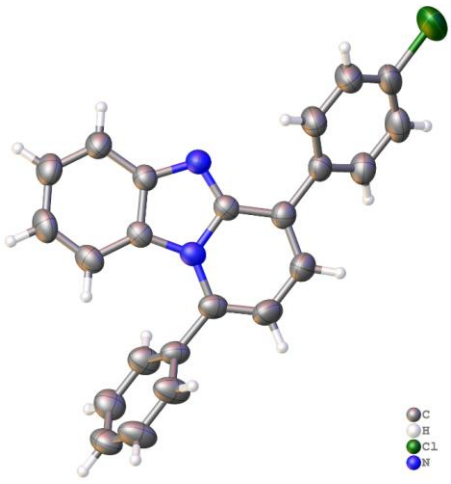


Fig. S26 The molecular structure of **3i**.

Table S5 Crystal data and structure refinement for **3j**.

Compound	**3j**
Empirical formula	$C_{23}H_{15}N_3O_2$
Formula weight	365.38
Temperature (K)	297
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 1 21/n 1
Unit cell dimensions (Å, °)	a = 9.9767(11), b = 10.2000(11), c =10.3359(12) α = 107.613(5), β = 91.055(9), γ = 117.427(11)
Volume (Å^3)	874.20(19)
Z	2
Density (calculated) (Mg/m^3)	1.388
Absorption coefficient (mm^{-1})	0.091
F(000)	380.0
Theta range for data collection	6.856 to 49.998 deg
Index ranges	-11<=h<=10, -8<=k<=12, -12<=l<=11
Reflections collected	6378
Independent reflections	3076 [R(int) = 0.0376, R(sigma) = 0.0719]
Completeness to theta = 24.999°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.937
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3076 / 0 / 253
Goodness-of-fit on F^2	1.017
Final R indices [I>2sigma(I)]	R_1 = 0.0626, wR_2 = 0.1243
R indices (all data)	R_1 = 0.1216, wR_2 = 0.1541
Largest diff. peak and hole	0.19 and -0.18 e.Å^{-3}

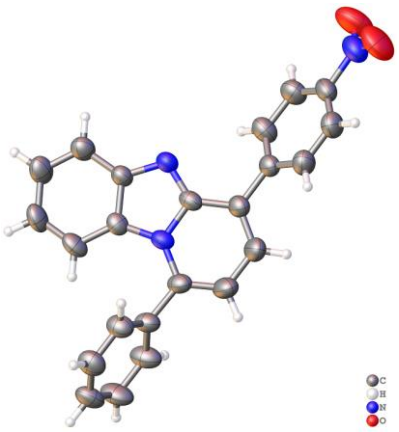


Fig. S27 The molecular structure of **3j**.

Table S6 Crystal data and structure refinement for **4i**.

Compound	**4i**
Empirical formula	$C_{25}H_{19}ClN_2$
Formula weight	382.87
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 1 21/n 1
Unit cell dimensions (Å, °)	a = 10.0520(9), b = 10.4783(11), c =18.7614(15) α = 90, β = 93.129 (8), γ = 90
Volume ($Å^3$)	1973.2(3)
Z	4
Density (calculated) (Mg/m^3)	1.289
Absorption coefficient (mm^{-1})	0.206
F(000)	800.0
Theta range for data collection	6.972 to 49.996
Index ranges	-11<=h<=11, -8<=k<=12, -22<=l<=22
Reflections collected	8419
Independent reflections	3462 [R(int) = 0.0309, R(sigma) = 0.0578]
Completeness to theta = 24.998°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.110
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3462 / 0 / 255
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R_1 = 0.0560, wR_2 = 0.1132
R indices (all data)	R_1 = 0.0934, wR_2 = 0.1327
Largest diff. peak and hole	0.20 and -0.31 e.$Å^{-3}$

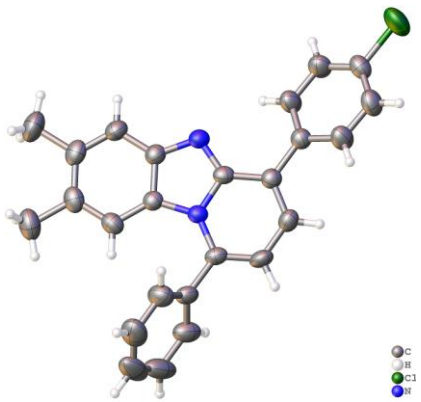


Fig. S28 The molecular structure of **4i**.

Characterization Data for All Products 3a-3n, 4a-4k, 3aa and 3ab

1-Phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**3a**), yellowish waxy (61 mg, 83%); ^{1}H NMR (600 MHz, $CDCl_3$), δ, ppm: 6.59 (*d*, *J* = 8.4 Hz, 1H), 6.67 (*d*, *J* = 6.6 Hz, 1H), 6.96-7.00 (*m*, 1H), 7.42 (*t*, *J* = 7.2 Hz, 1H), 7.45-7.49 (*m*, 1H), 7.55 (*d*, *J* = 7.2 Hz, 2H), 7.59-7.62 (*m*, 2H), 7.64-7.67 (*m*, 1H), 7.73 (*d*, *J* = 9.6 Hz, 1H), 7.93 (*d*, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 112.1, 114.7, 116.9, 119.7, 120.4, 125.2, 129.0, 129.1, 129.2, 129.3, 130.1, 134.5, 141.3, 145.0, 149.6; ESI-HRMS, *m/z*: Calcd for $C_{17}H_{13}N_2$ $[M+H]^+$, 245.1073, found: 245.1096.

4-Methyl-1-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**3b**), yellow solid (59 mg, 76%); m.p. 151-153 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), δ, ppm: 2.78 (*s*, 3H), 6.59-6.63 (*m*, 2H), 6.96-6.99 (*m*, 1H), 7.30 (*d*, *J* = 7.2 Hz, 1H), 7.42 (*t*, *J* = 7.2 Hz, 1H), 7.55 (*d*, *J* = 8.4 Hz, 2H), 7.59-7.66 (*m*, 3H), 7.98 (*d*, *J* = 9.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 17.7, 112.1, 114.7, 119.8, 120.3, 124.9, 126.4, 127.6, 129.0, 129.2, 129.7, 129.8, 134.7, 139.0, 144.7, 150.0; ESI-HRMS, *m/z*: Calcd for $C_{18}H_{15}N_2$ $[M+H]^+$, 259.1230, found: 259.1240.

4-Ethyl-1-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**3c**), yellow solid (60 mg, 74%); m.p. 99-101 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), δ, ppm: 1.51 (*t*, *J* = 7.2 Hz, 3H), 3.23 (*q*, *J* = 7.2 Hz, 2H), 6.60 (*d*, *J* = 8.4 Hz, 1H), 6.65 (*d*, *J* = 7.2 Hz, 1H), 6.95-6.99 (*m*, 1H), 7.31 (*d*, *J* = 7.2 Hz, 1H), 7.42 (*t*, *J* = 7.8 Hz, 1H), 7.56 (*d*, *J* = 7.8 Hz, 2H), 7.59-7.62 (*m*, 2H), 7.63-7.66 (*m*, 1H), 7.98 (*d*, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 13.1, 24.3, 112.1, 114.7, 119.7, 120.2, 124.9, 125.5, 129.0, 129.2, 129.7, 129.8, 132.1, 134.8, 138.8, 144.7, 149.6; ESI-HRMS, *m/z*: Calcd for $C_{19}H_{17}N_2$ $[M+H]^+$, 273.1386, found: 273.1388.

4-Butyl-1-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**3d**), yellowish waxy (69 mg, 77%); ^{1}H NMR (600 MHz, $CDCl_3$), δ, ppm: 1.03 (*t*, *J* = 7.2 Hz, 3H), 1.53-1.58 (*m*, 2H), 1.89-1.95 (*m*, 2H), 3.20 (*t*, *J* = 7.2 Hz, 2H), 6.60 (*d*, *J* = 8.4 Hz, 1H), 6.64 (*d*, *J* = 7.2 Hz, 1H), 6.95-6.98 (*m*, 1H), 7.29 (*d*, *J* = 7.2 Hz, 1H), 7.41 (*t*, *J* = 7.2 Hz, 1H), 7.55 (*d*, *J* = 7.2 Hz, 2H), 7.59-7.62 (*m*, 2H), 7.63-7.66 (*m*, 1H), 7.98 (*d*, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 14.1, 22.7, 30.7, 30.9, 112.1, 114.7, 119.7, 120.1, 124.9, 126.2, 129.0, 129.2, 129.7, 129.8, 130.8, 134.8, 138.8, 144.7, 149.7; ESI-HRMS, *m/z*: Calcd for $C_{21}H_{21}N_2$ $[M+H]^+$, 301.1699, found: 301.1696.

1,4-Diphenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**3e**), yellowish solid (87 mg, 90%); m.p. 146-148 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), δ, ppm: 6.65 (*d*, *J* = 8.4 Hz, 1H), 6.79 (*d*, *J* = 7.2 Hz, 1H), 6.99-7.03 (*m*, 1H), 7.44 (*t*, *J* = 7.2 Hz, 1H), 7.47 (*t*, *J* = 7.2 Hz, 1H), 7.56-7.90 (*m*, 8H), 8.02 (*d*, *J* = 8.4 Hz, 1H), 8.11 (*d*, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 112.4, 114.7, 120.2, 120.5, 125.0, 127.6, 128.4, 128.7, 129.1, 129.2, 129.5, 129.6, 130.0, 134.6, 136.9, 140.2, 145.1, 148.5; ESI-HRMS, *m/z*: Calcd for $C_{23}H_{17}N_2$ $[M+H]^+$, 321.1386,

found: 321.1393.

1-Phenyl-4-(*p*-tolyl)benzo[4,5]imidazo[1,2-*a*]pyridine (**3f**), yellowish solid (87 mg, 87%); m.p. 209-211 ºC; ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 2.49 (*s*, 3H), 6.65 (*d*, *J* = 8.4 Hz, 1H), 6.77 (*d*, *J* = 7.2 Hz, 1H), 6.99-7.02 (*m*, 1H), 7.40 (*d*, *J* = 7.8 Hz, 2H), 7.42-7.45 (*m*, 1H), 7.55 (*d*, *J* = 7.2 Hz, 1H), 7.60-7.67 (*m*, 5H), 8.00-8.03 (*m*, 3H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 21.4, 112.4, 114.7, 120.2, 120.4, 125.0, 127.2, 129.0, 129.1, 129.4, 129.5, 129.6, 130.0, 134.0, 134.7, 138.2, 139.9, 145.1, 148.7; ESI-HRMS, *m/z*: Calcd for $C_{24}H_{19}N_2$ $[M+H]^+$, 335.1543, found: 335.1557.

4-(4-Methoxyphenyl)-1-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**3g**), yellow solid (96 mg, 91%); m.p. 186-188 ºC; ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 3.92 (*s*, 3H), 6.64 (*d*, *J* = 8.4 Hz, 1H), 6.77 (*d*, *J* = 6.6 Hz, 1H), 6.97-7.01 (*m*, 1H), 7.12 (*d*, *J* = 8.4 Hz, 2H), 7.41-7.44 (*m*, 1H), 7.53 (*d*, *J* = 6.6 Hz, 1H), 7.60-7.67 (*m*, 5H), 8.00 (*d*, *J* = 7.8 Hz, 1H), 8.08 (*d*, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 55.4, 112.4, 114.1, 114.7, 120.2, 120.4, 124.9, 126.7, 129.1, 129.1, 129.2, 129.3, 129.6, 129.9, 130.3, 134.7, 137.7, 145.1, 148.7, 159.8; ESI-HRMS, *m/z*: Calcd for $C_{24}H_{19}N_2O$ $[M+H]^+$, 351.1492, found: 351.1535.

4-(4-Chlorophenyl)-1-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**3h**), yellow solid (99 mg, 93%); m.p. 212-214 ºC; ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 6.63 (*d*, *J* = 9.0 Hz, 1H), 6.79 (*d*, *J* = 6.6 Hz, 1H), 6.99-7.02 (*m*, 1H), 7.43 (*t*, *J* = 7.2 Hz, 1H), 7.53-7.57 (*m*, 3H), 7.60-7.69 (*m*, 5H), 7.98 (*d*, *J* = 7.8 Hz, 1H), 8.06 (*d*, *J* = 9.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 112.3, 114.7, 120.1, 120.6, 125.2, 127.5, 128.2, 128.8, 129.1, 129.2, 129.5, 130.1, 130.4, 134.3, 134.5, 135.2, 140.6, 145.0, 148.2; ESI-HRMS, *m/z*: Calcd for $C_{23}H_{16}ClN_2$ $[M+H]^+$, 355.0997, found: 355.0987.

4-(4-Bromophenyl)-1-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**3i**), yellow solid (106 mg, 89%); m.p. 236-238 ºC; ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 6.63 (*d*, *J* = 8.4 Hz, 1H), 6.79 (*d*, *J* = 6.6 Hz, 1H), 6.99-7.02 (*m*, 1H), 7.43 (*t*, *J* = 7.2 Hz, 1H), 7.56 (*d*, *J* = 6.6 Hz, 1H), 7.61 (*d*, *J* = 7.8 Hz, 2H), 7.63-7.65 (*m*, 2H), 7.67-7.71 (*m*, 3H), 7.98-8.01 (*m*, 3H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 112.3, 114.7, 120.1, 120.6, 122.6, 125.2, 127.5, 128.2, 129.0, 129.2, 129.5, 130.1, 130.7, 131.8, 134.5, 135.7, 140.6, 145.0, 148.2; ESI-HRMS, *m/z*: Calcd for $C_{23}H_{16}BrN_2$ $[M+H]^+$, 399.0491, found: 399.0502.

4-(4-Nitrophenyl)-1-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**3j**), yellow solid (50 mg, 45%); m.p. 268-270 ºC; ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 6.65 (*d*, *J* = 9.0 Hz, 1H), 6.85 (*d*, *J* = 7.2 Hz, 1H), 7.02-7.05 (*m*, 1H), 7.46 (*t*, *J* = 7.2 Hz, 1H), 7.62 (*d*, *J* = 6.6 Hz, 2H), 7.65-7.71 (*m*, 4H), 7.99 (*d*, *J* = 8.4 Hz, 1H), 8.34 (*d*, *J* = 9.0 Hz, 2H), 8.43 (*d*, *J* = 9.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 112.1, 114.8, 120.2, 121.0, 123.9, 125.5, 126.8, 128.5, 128.9, 129.3, 129.4, 129.9, 130.3, 134.2, 141.9, 143.3, 145.0, 147.5 (C-5), 147.7; ESI-HRMS, *m/z*: Calcd for $C_{23}H_{16}N_3O_2$ $[M+H]^+$, 366.1237, found: 366.1284.

4-(3-Methoxyphenyl)-1-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**3k**), yellowish solid (99 mg, 94%); m.p. 180-182 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), δ, ppm: 3.94 (*s*, 3H), 6.64 (*d*, *J* = 8.4 Hz, 1H), 6.78 (*d*, *J* = 6.6 Hz, 1H), 6.98-7.04 (*m*, 2H), 7.43 (*t*, *J* = 7.2 Hz, 1H), 7.47-7.50 (*m*, 1H), 7.58 (*d*, *J* = 6.6 Hz, 1H), 7.61-7.65 (*m*, 4H), 7.67 (*d*, *J* = 6.6 Hz, 2H), 7.71 (*s*, 1H), 8.00 (*d*, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 55.4, 112.3, 114.0, 114.7, 114.9, 120.4, 120.6, 121.6, 125.0, 127.7, 129.1, 129.2, 129.3, 129.5, 129.6, 130.0, 134.6, 138.2, 140.3, 145.1, 148.5, 159.7; ESI-HRMS, *m/z*: Calcd for $C_{24}H_{19}N_2O$ $[M+H]^+$, 351.1492, found: 351.1496.

4-(2-Fluorophenyl)-1-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**3l**), yellow solid (87 mg, 86%); m.p. 65-67 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), δ, ppm: 6.65 (*d*, *J* = 9.0 Hz, 1H), 6.79 (*d*, *J* = 7.2 Hz, 1H), 6.99-7.02 (*m*, 1H), 7.28-7.31 (*m*, 1H), 7.35-7.38 (*m*, 1H), 7.43 (*t*, *J* = 7.2 Hz, 1H), 7.45-7.48 (*m*, 1H), 7.59 (*d*, *J* = 7.2 Hz, 1H), 7.61-7.70 (*m*, 5H), 7.98-8.01 (*m*, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 112.0, 114.7, 116.2 (*d*, *J* = 22.5 Hz), 120.2, 120.5, 123.8, 124.3 (*d*, *J* = 3.0 Hz), 124.5 (*d*, *J* = 13.5 Hz), 125.1, 129.1, 129.2, 129.7 (*d*, *J* = 37.5 Hz), 130.0 (*d*, *J* = 25.5 Hz), 130.1, 132.1 (*d*, *J* = 3.0 Hz), 134.5, 140.9, 145.1, 148.4, 160.18 (*d*, *J* = 246.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$), δ, ppm: -115.1; ESI-HRMS, *m/z*: Calcd for $C_{23}H_{16}FN_2$ $[M+H]^+$, 339.1292, found: 339.1287.

4-(2-Bromophenyl)-1-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**3m**), yellow solid (99 mg, 83%); m.p. 79-81 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), δ, ppm: 6.66 (*d*, *J* = 9.0 Hz, 1H), 6.79 (*d*, *J* = 6.6 Hz, 1H), 6.98-7.02 (*m*, 1H), 7.33-7.36 (*m*, 1H), 7.42 (*t*, *J* = 7.8 Hz, 1H), 7.47-7.52 (*m*, 2H), 7.64-7.70 (*m*, 6H, ArH), 7.79 (*d*, *J* = 7.8 Hz, 1H), 7.97 (*d*, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 111.7, 114.7, 120.2, 120.5, 123.7, 125.1, 127.5, 129.0, 129.1, 129.2, 129.6, 129.8, 130.0, 130.1, 132.0, 133.4, 134.5, 137.7, 141.0 (C-6), 145.1, 148.4; ESI-HRMS, *m/z*: Calcd for $C_{23}H_{16}BrN_2$ $[M+H]^+$, 399.0491, found: 399.0502.

4-(Naphthalen-1-yl)-1-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**3n**), yellow solid (89 mg, 80%); m.p. 175-177 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), δ, ppm: 6.71 (*d*, *J* = 9.0 Hz, 1H), 6.85 (*d*, *J* = 7.2 Hz, 1H), 7.00-7.04 (*m*, 1H), 7.40-7.45 (*m*, 2H), 7.52-7.56 (*m*, 2H), 7.66-7.73 (*m*, 6H), 6.81 (*d*, *J* = 7.2 Hz, 1H), 7.85 (*d*, *J* = 8.4 Hz, 1H), 6.93 (*d*, *J* = 8.4 Hz, 1H), 7.98 (*d*, *J* = 8.4 Hz, 1H), 8.01 (*d*, *J* = 8.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 112.0, 114.7, 120.3, 120.5, 125.1, 125.6, 125.9, 126.0, 126.1, 128.0, 128.5, 128.9, 129.1, 129.2, 129.6, 130.1, 130.3, 132.1, 134.1, 134.6, 134.8, 140.8, 145.1, 149.4; ESI-HRMS, *m/z*: Calcd for $C_{27}H_{19}N_2$ $[M+H]^+$, 371.1543, found: 371.1554.

Mixture of 7-methyl-1-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**4a**) and 8-methyl-1-phenylbenzo[4,5]-imidazo[1,2-*a*]pyridine (**4a'**), inseparable white solid (**4a**/**4a'** = 3/4; 54 mg, 70%); ^{1}H NMR (600 MHz, $CDCl_3$), δ, ppm: 2.25 (*s*, 3H, **4a**), 2.47 (*s*, 3H, **4a'**), 6.32 (*s*, 1H, **4a**), 6.44 (*d*, *J* = 8.4 Hz, 1H, **4a'**), 6.62-6.64 (*m*, 1H, **4a**; 1H, **4a'**), 6.78 (*d*, *J* = 8.4 Hz, 1H, **4a'**),

7.23 (*d*, *J* = 7.8 Hz, 1H, **4a**), 7.39-7.44 (*m*, 1H, **4a**; 1H, **4a'**), 7.52-7.53 (*m*, 2H, **4a**; 2H, **4a'**), 7.56-7.64 (*m*, 3H, **4a**; 3H, **4a'**), 7.68-7.69 (*m*, 1H, **4a**; 2H, **4a'**), 7.78 (*d*, *J* = 8.4 Hz, 1H, **4a**); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 21.72 (**4a'**), 21.93 (**4a**), 111.85 (**4a'**), 114.18 (**4a'**), 114.54 (**4a**), 116.66 (**4a'**), 116.85 (**4a'**), 119.14 (**4a**), 122.12 (**4a'**), 126.88 (**4a**), 127.33 (**4a**), 128.61 (**4a'**), 128.88 (**4a'**), 129.00 (**4a**/**4a'**), 129.04 (**4a**), 129.08 (**4a'**), 129.33 (**4a**), 129.96 (**4a**), 129.99 (**4a'**), 130.09 (**4a**), 134.56 (**4a'**), 134.61 (**4a**), 135.18 (**4a**), 141.13 (**4a'**), 141.16 (**4a**), 143.10 (**4a**), 145.38 (**4a'**), 149.33 (**4a**), 149.65 (**4a'**); ESI-HRMS, *m/z*: Calcd for $C_{18}H_{15}N_2$ $[M+H]^+$, 259.1230, found: 259.1273.

7-Chloro-1-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**4b**), yellow solid (35 mg, 42%); m.p. 160-162 °C; ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 6.47 (*d*, *J* = 9.0 Hz, 1H), 6.71 (*d*, *J* = 6.6 Hz, 1H), 6.92-6.94 (*dd*, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 1H), 7.50-7.52 (*m*, 1H), 7.54 (*d*, *J* = 7.2 Hz, 2H), 7.60-7.63 (*m*, 2H), 7.65-7.68 (*m*, 1H), 7.72 (*d*, *J* = 9.0 Hz, 1H), 7.87 (*d*, *J* = 1.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 112.5, 115.4, 116.8, 119.0, 120.9, 127.8, 128.9, 129.3, 129.8, 130.3, 130.9, 134.1, 141.3, 145.8, 150.3; ESI-HRMS, *m/z*: Calcd for $C_{17}H_{12}ClN_2$ $[M+H]^+$, 279.0684, found: 279.0710.

8-Chloro-1-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**4b'**), yellow solid (36 mg, 43%); m.p. 184-186 °C; ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 6.52 (*d*, *J* = 1.8 Hz, 1H), 6.71 (*d*, *J* = 6.6 Hz, 1H), 7.38-7.40 (*dd*, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 1H), 7.48-7.51 (*m*, 1H), 7.55 (*d*, *J* = 7.2 Hz, 2H), 7.63-7.66 (*m*, 2H), 7.68-7.73 (*m*, 2H), 7.83 (*d*, *J* = 9.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 112.4, 114.7, 117.0, 120.4, 125.7, 125.9, 128.9, 129.3, 129.5, 129.6, 130.4, 133.9, 141.2, 143.5, 150.1; ESI-HRMS, *m/z*: Calcd for $C_{17}H_{12}ClN_2$ $[M+H]^+$, 279.0684, found: 279.0710.

7,8-Dichloro-1-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**4c**), yellowish solid (70 mg, 75%); m.p. 231-233 °C; ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 6.60 (*s*, 1H), 6.72 (*d*, *J* = 7.8 Hz, 1H), 7.51-7.53 (*m*, 3H), 7.63-7.66 (*m*, 2H), 7.69-7.70 (*m*, 2H), 7.95 (*s*, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 112.7, 115.9, 116.9, 120.3, 123.9, 128.1, 128.7, 129.4, 129.5, 130.3, 130.6, 133.5, 141.3, 144.2, 150.8; ESI-HRMS, *m/z*: Calcd for $C_{17}H_{11}Cl_2N_2$ $[M+H]^+$, 313.0294, found: 313.0289.

7,8-Dichloro-4-methyl-1-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**4d**), yellowish solid (70 mg, 72%); m.p. 253-255 °C; ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 2.74 (*s*, 3H), 6.63 (*s*, 1H), 6.67 (*d*, *J* = 7.2 Hz, 1H), 7.34 (*d*, *J* = 7.2 Hz, 1H), 7.52 (*d*, *J* = 7.2 Hz, 2H), 7.63-7.65 (*m*, 2H), 7.68-7.70 (*t*, *J* = 7.2 Hz, 1H), 8.03 (*s*, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 17.6, 112.7, 115.9, 120.5, 123.8, 128.6, 128.7, 129.0, 129.1, 129.4, 130.4, 130.4, 133.7, 138.9, 143.9, 151.3; ESI-HRMS, *m/z*: Calcd for $C_{18}H_{13}Cl_2N_2$ $[M+H]^+$, 327.0450, found: 327.0449.

7,8-Difluoro-1-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**4e**), yellowish solid (56 mg, 67%); m.p. 177-179 °C; ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 6.31-6.33 (*m*, 1H), 6.70 (*d*, *J* =

6.6 Hz, 1H), 7.47-7.49 (*m*, 1H), 7.53 (*d*, *J* = 7.2 Hz, 2H), 7.71-7.65 (*m*, 3H), 7.67-7.70 (*m*, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 102.7 (*d*, *J* = 24.0 Hz), 106.1 (*d*, *J* = 19.5 Hz), 112.4, 116.8, 124.0 (*d*, *J* = 10.5 Hz), 128.9, 129.3, 129.4, 130.5, 133.6, 140.7 (*d*, *J* = 9.0 Hz), 140.8, 145.8 (*dd*, J_1 = 241.5 Hz, J_2 = 15.0 Hz), 149.6 (*dd*, J_1 = 244.5 Hz, J_2 = 15.0 Hz), 150.7 (*d*, *J* = 3.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$), *δ*, ppm: -142.3, -138.2; ESI-HRMS, *m/z*: Calcd for $C_{17}H_{11}F_2N_2$ $[M+H]^+$, 281.0885, found: 281.0885.

7,8-Dimethyl-1-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**4f**), yellowish waxy (64 mg, 78%); ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 2.15 (*s*, 3H), 2.39 (*s*, 3H), 6.31 (*s*, 1H), 6.65 (*d*, *J* = 7.2 Hz, 1H), 7.41-7.44 (*m*, 1H), 7.56 (*d*, *J* = 7.2 Hz, 2H), 7.60-7.63 (*m*, 2H), 7.65-7.70 (*m*, 3H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 20.5, 20.7, 111.6, 114.7, 116.7, 119.4, 127.7, 128.4, 129.0, 129.1, 129.5, 129.9, 134.6, 134.7, 141.0, 143.7, 149.2; ESI-HRMS, *m/z*: Calcd for $C_{19}H_{17}N_2$ $[M+H]^+$, 273.1386, found: 273.1422.

Mixture of 4-(4-chlorophenyl)-7-methyl-1-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**4g**) and 4-(4-chlorophenyl)-8-methyl-1-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**4g'**), inseparable yellowish solid (**4g**:**4g'** = 1:1; 88 mg, 80%); ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 2.29 (*s*, 3H, **4g**), 2.50 (*s*, 3H, **4g'**), 6.39 (*s*, 1H, **4g**), 6.51 (*d*, *J* = 8.4 Hz, 1H, **4g**), 6.73-6.75 (*m*, 1H, **4g**; 1H, **4g'**), 6.84 (*d*, *J* = 8.4 Hz, 1H, **4g**), 7.27 (*d*, *J* = 8.4 Hz, 1H, **4g'**), 4.84-4.52 (*m*, 1H, **4g**; 1H, **4g'**), 7.52-7.54 (*m*, 2H, **4g**; 2H, **4g'**), 7.58-7.70 (*m*, 5H, **4g**; 5H, **4g'**), 7.77 (*s*, 1H, **4g'**), 7.87 (*d*, *J* = 8.4 Hz, 1H, **4g'**), 8.05-8.06 (*m*, 2H, **4g**; 2H, **4g'**); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 21.7 (**4g**), 22.0 (**4g'**), 112.0 (**4g'**), 114.2 (**4g**), 114.6 (**4g'**), 119.6 (**4g**), 119.6 (**4g'**), 122.3 (**4g**), 126.9 (**4g**), 126.9 (**4g'**), 127.2 (**4g'**), 127.6 (**4g**), 127.9 (**4g**), 128.1 (**4g'**), 128.8 (**4g**/**4g'**), 129.0 (**4g**), 129.0 (**4g'**), 129.1 (**4g**), 129.1 (**4g'**), 129.6 (**4g'**), 130.0 (**4g**), 130.0 (**4g'**), 130.4 (**4g**), 130.4 (**4g**), 130.4 (**4g'**), 134.2 (**4g**), 134.5 (**4g**), 134.6 (**4g'**), 135.2 (**4g**), 135.3 (**4g'**), 140.4 (**4g**), 140.4 (**4g'**), 143.2 (**4g**), 145.5 (**4g'**), 148.0 (**4g**), 148.3 (**4g'**); ESI-HRMS, *m/z*: Calcd for $C_{24}H_{18}ClN_2$ $[M+H]^+$, 369.1153, found:369.1192.

4-(4-Chlorophenyl)-7,8-difluoro-1-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**4h**), yellow solid (78 mg, 67%); m.p. 242-244 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 6.36-6.39 (*m*, 1H), 6.82 (*d*, *J* = 7.2 Hz, 1H), 7.54-7.59 (*m*, 5H), 7.66-7.73 (*m*, 4H), 8.02 (*d*, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 102.7 (*d*, *J* = 24.0 Hz), 106.1 (*d*, *J* = 19.5 Hz), 112.7, 124.3 (*d*, *J* = 10.5 Hz), 127.5, 128.3, 128.9, 129.0, 129.5, 130.3, 130.6, 133.6, 134.6, 134.8, 140.0, 140.8 (*d*, *J* = 10.5 Hz), 146.0 (*dd*, J_1 = 240.0 Hz, J_2 = 15.0 Hz), 149.5 (*d*, *J* = 3.0 Hz), 149.6 (*dd*, J_1 = 244.5 Hz, J_2 = 15.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$), *δ*, ppm: -141.9, -138.0; ESI- HRMS, *m/z*: Calcd for $C_{23}H_{14}ClF_2N_2$ $[M+H]^+$, 391.0808, found: 391.0808.

4-(4-Chlorophenyl)-7,8-dimethyl-1-phenylbenzo[4,5]imidazo[1,2-*a*]pyridine (**4i**), yellowish solid (94 mg, 82%); m.p. 238-240 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 2.17 (*s*, 3H), 2.39 (*s*, 3H), 6.36 (*s*, 1H), 6.72 (*d*, *J* = 6.6 Hz, 1H), 7.47 (*d*, *J* = 6.6 Hz, 1H), 7.52 (*d*, *J* = 8.4

Hz, 2H), 7.59 (*d*, *J* = 7.2 Hz, 2H), 7.62-7.64 (*m*, 2H), 7.68 (*d*, *t* = 7.2 Hz, 1H), 7.75 (*s*, 1H), 8.06 (*d*, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 20.5, 20.8, 111.8, 114.7, 119.9, 126.7, 127.9, 128.0, 128.8, 129.0, 129.1, 129.8, 129.9, 130.4, 134.1, 134.7, 135.4, 140.2, 143.9, 147.8; ESI-HRMS, *m/z*: Calcd for $C_{25}H_{20}ClN_2$ $[M+H]^+$, 383.1310, found: 383.1308.

Mixture of (*Z*)-3-(2-methyl-1*H*-imidazol-1-yl)-3-phenylacrylaldehyde and (*E*)-3-(2-methyl-1*H*-imidazol-1-yl)-3-phenylacrylaldehyde (**4j**), inseparable colorless waxy (4:1 (*E*/*Z*), 46 mg, 72%); ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 2.14 (*s*, 3H, *Z*), 2.20 (*s*, 3H, *E*), 6.23 (*d*, *J* = 7.8 Hz, 1H, *Z*), 6.63 (*d*, *J* = 7.8 Hz, 1H, *E*), 6.85 (*d*, *J* = 1.8 Hz, 1H, *Z*), 6.99 (*d*, *J* = 1.8 Hz, 1H, *Z*), 7.05 (*d*, *J* = 1.2 Hz, 1H, *E*), 7.13 (*d*, *J* = 1.2 Hz, 1H, *E*), 7.26 (*d*, *J* = 7.2 Hz, 2H, *E*), 7.35 (*d*, *J* = 8.4 Hz, 2H, *Z*), 7.42 (*m*, 2H, *E*), 7.49-7.53 (*m*, 1H, *E*; 2H, *Z*), 7.57-7.60 (*m*, 1H, *Z*), 9.41 (*d*, *J* = 7.8 Hz, 1H, *E*), 9.58 (*d*, *J* = 7.8 Hz, 1H, *Z*); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 13.5 (*E*), 15.2 (*Z*), 120.8 (*Z*), 122.6 (*E*), 123.0 (*Z*), 123.8 (*E*), 126.9 (*E*), 128.6 (*Z*), 128.9 (*E*), 129.1 (*Z*), 129.5 (*E*), 130.5 (*Z*), 131.9 (*Z*), 132.4 (*E*), 132.7 (*Z*), 134.1 (*E*), 146.0 (*Z*), 146.2 (*E*), 152.3 (*E*), 155.0 (*Z*), 190.2 (*E*), 191.7 (*Z*); ESI-HRMS, *m/z*: Calcd for $C_{13}H_{13}N_2O$ $[M+H]^+$, 213.1022, found: 213.1021.

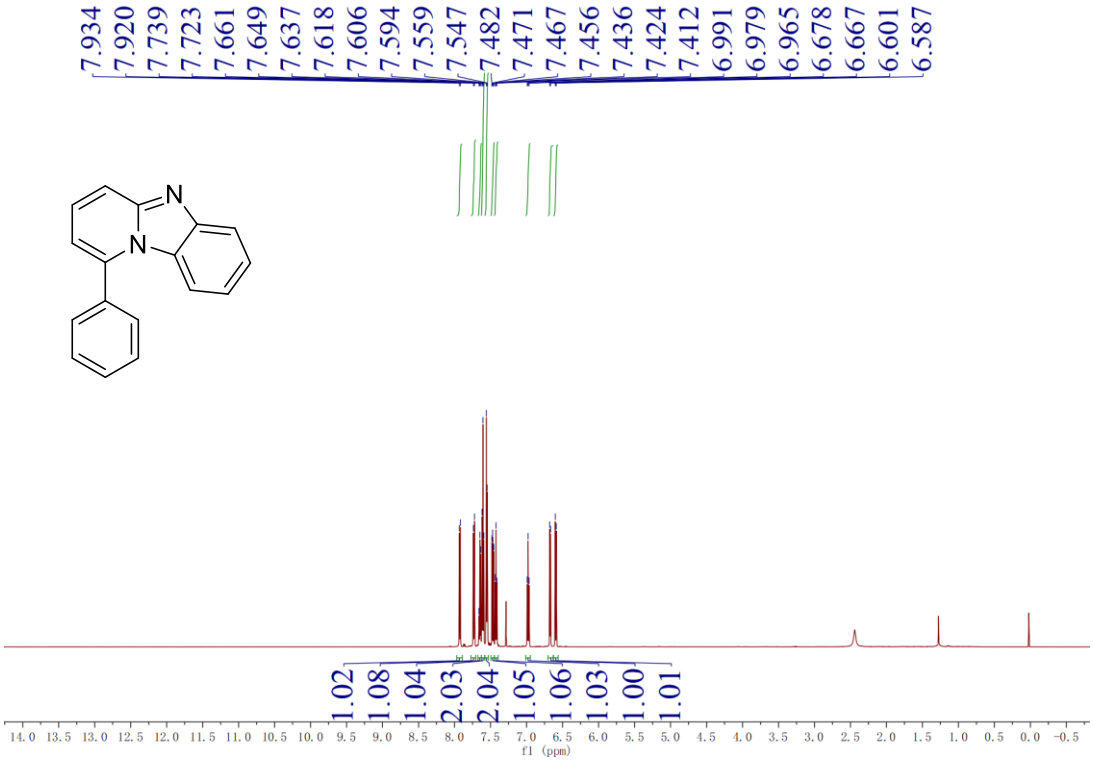
Mixture of (*Z*)-3-(2-ethyl-1*H*-imidazol-1-yl)-3-phenylacrylaldehyde and (*E*)-3-(2-ethyl-1*H*-imidazol-1-yl)-3-phenylacrylaldehyde (**4k**), inseparable colorless waxy (10:4 (*E*/*Z*), 48 mg, 70%); ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 1.16-1.20 (*m*, 3H, *Z*; 3H, *E*), 2.36-2.40 (*q*, *J* = 7.2 Hz, 2H, *E*), 2.43-2.47 (*q*, *J* = 7.2 Hz, 2H, *Z*), 6.22 (*d*, *J* = 7.2 Hz, 1H, *E*), 6.62 (*d*, *J* = 7.2 Hz, 1H, *E*), 6.84 (*d*, *J* = 1.2 Hz, 1H, *Z*), 7.00 (*d*, *J* = 1.2 Hz, 1H, *Z*), 7.03 (*d*, *J* = 1.2 Hz, 1H, *E*), 7.14 (*d*, *J* = 1.2 Hz, 1H, *E*), 7.24 (*d*, *J* = 7.2 Hz, 2H, *E*), 7.33 (*d*, *J* = 7.2 Hz, 2H, *Z*), 7.40-7.42 (*m*, 2H, *E*), 7.47-7.49 (*m*, 2H, *Z*; 1H, *E*), 7.55-7.58 (*m*, 1H, *Z*), 9.37 (*d*, *J* = 7.2 Hz, 1H, *E*), 9.58 (*d*, *J* = 7.2 Hz, 1H, *Z*); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 12.0 (*Z*), 12.1 (*E*), 20.6 (*E*), 21.7 (*Z*), 120.9 (*Z*), 122.4 (*E*), 123.5 (*Z*), 123.8 (*E*), 126.9 (*E*), 128.5 (*Z*), 128.8 (*E*), 129.1 (*Z*), 129.4 (*E*), 130.4 (*Z*), 132.0 (*Z*), 132.4 (*E*), 132.9 (*Z*), 134.2 (*E*), 150.8 (*Z*), 151.0 (*E*), 152.2 (*E*),154.9 (*Z*), 190.2 (*E*), 191.7 (*Z*); ESI-HRMS, *m/z*: Calcd for $C_{14}H_{15}N_2O$ $[M+H]^+$, 227.1179, found: 227.1177.

3-(2-Methyl-1*H*-benzo[d]imidazol-1-yl)-3-phenylacrylaldehyde (**3aa**), inseparable yellowish waxy (9:10 (*E*/*Z*), 62 mg, 71%); ^{1}H NMR (600 MHz, $CDCl_3$), *δ*, ppm: 2.30 (*s*, 3H, *Z*), 2.42 (*s*, 3H, *E*), 6.40 (*d*, *J* = 7.8 Hz, 1H, *Z*), 6.84 (*d*, *J* = 7.2 Hz, 1H, *E*), 7.07 (*d*, *J* = 8.4 Hz, 1H, *Z*), 7.09 (*d*, *J* = 8.4 Hz, 1H, *E*), 7.14-7.17 (*m*, 1H, *Z*), 7.18-7.21 (*m*, 1H, *E*), 7.22-7.30 (*m*, 4H, 3H, *E*; 1H, *Z*), 7.35-7.41 (*m*, 2H, *E*; 2H, *Z*), 7.48-7.51 (*m*, 1H, *E*; 2H, *Z*), 7.57-7.60 (*m*, 1H, *Z*), 7.71 (*d*, *J* = 7.8 Hz, 1H, *Z*), 7.78 (*d*, *J* = 7.8 Hz, 1H, *E*), 9.33 (*d*, *J* = 7.8 Hz, 1H, *E*), 9.81 (*d*, *J* = 7.8 Hz, 1H, *Z*); ^{13}C NMR (150 MHz, $CDCl_3$), *δ*, ppm: 14.4 (*E*), 15.7 (*Z*), 110.0 (*Z*), 111.0 (*E*), 119.5 (*Z*), 119.6 (*E*), 123.3 (*E*), 123.4 (*Z*), 123.5 (*Z*), 123.7 (*E*), 125.0 (*Z*), 125.7 (*E*), 126.8 (*Z*), 129.4 (*E*), 129.6 (*Z*), 130.3 (*E*), 132.1 (*Z*), 132.4 (*E*), 133.1 (*Z*), 133.7 (*E*), 135.3 (*E*),

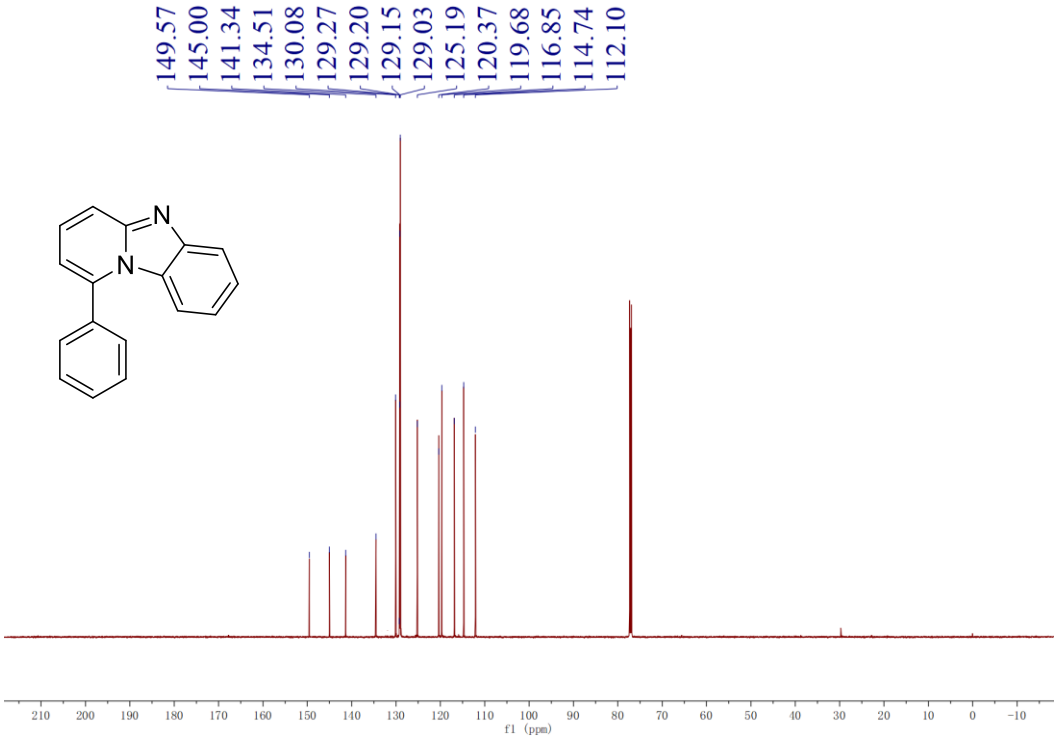
137.2 (*Z*), 142.7 (*E*), 143.0 (*Z*), 150.7 (*E*), 151.8 (*Z*), 151.9 (*Z*), 153.5 (*E*), 189.9 (*E*), 191.7 (*Z*); ESI-HRMS, *m/z*: Calcd for $C_{17}H_{15}N_2O$ $[M+H]^+$, 263.1179, found: 263.1200.

(*E*)-1-Methyl-2-(4-phenylbut-1-en-3-yn-1-yl)-1*H*-benzo[*d*]imidazole (**3ab**), yellowish solid (40 mg, 52%); m.p. 153-155 ^oC; ^1H NMR (600 MHz, $CDCl_3$), δ, ppm: 3.86 (*s*, 3H), 7.08 (*d*, *J* = 15.6 Hz, 1H), 7.24 (*d*, *J* = 15.6 Hz, 1H), 7.30-7.32 (*m*, 2H), 7.34-7.36 (*m*, 1H), 7.37-7.40 (*m*, 3H), 7.53-7.55 (*m*, 2H), 7.76-7.78 (*m*, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ, ppm: 29.8, 88.4, 95.3, 109.3, 116.7, 119.7, 122.8, 122.9, 123.1, 125.2, 128.5, 128.8, 131.8, 136.1, 143.1, 149.8; ESI-HRMS, *m/z*: Calcd for $C_{18}H_{15}N_2$ $[M+H]^+$, 259.1230, found: 259.1273.

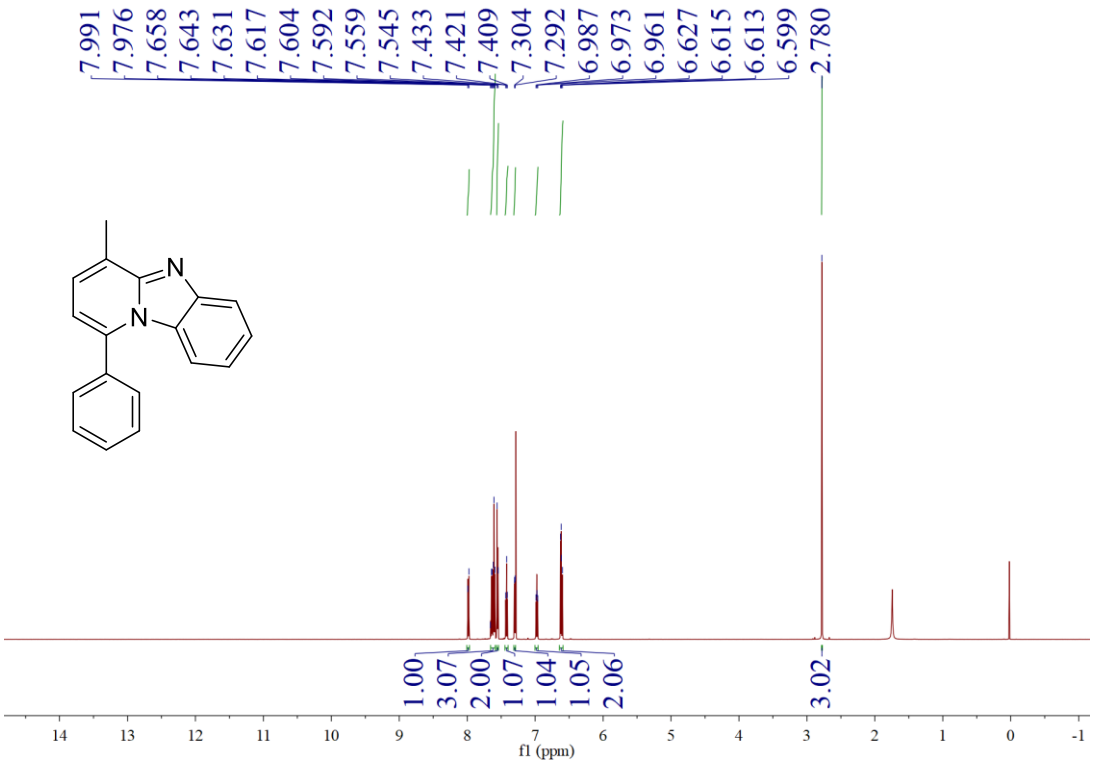
NMR Spectra for All Compounds 3a-3n, 4a-4k, 3aa and 3ab



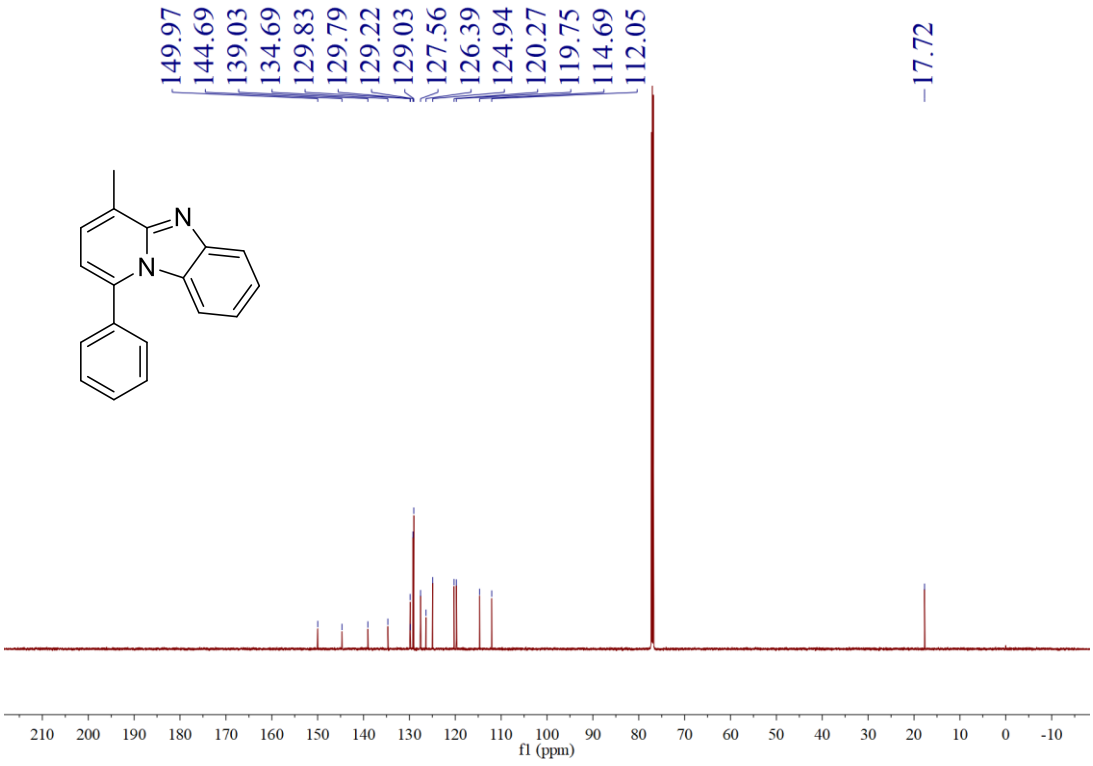
^{1}H NMR spectrum of compound **3a**



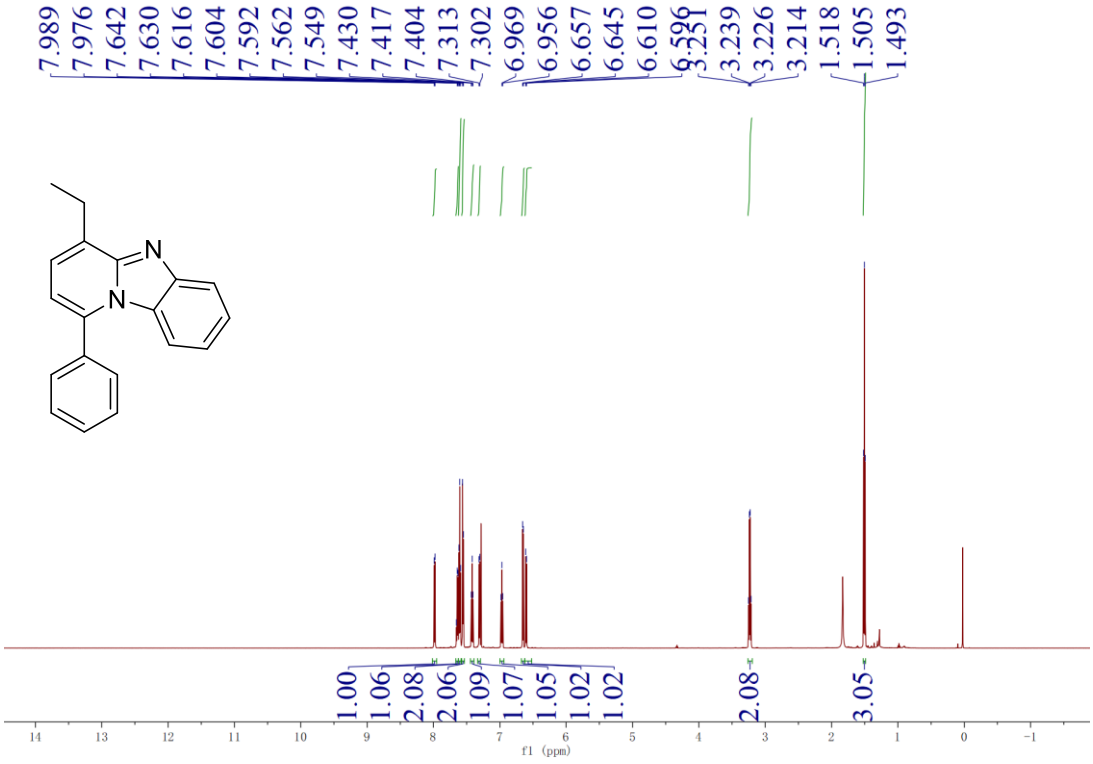
^{13}C NMR spectrum of compound **3a**



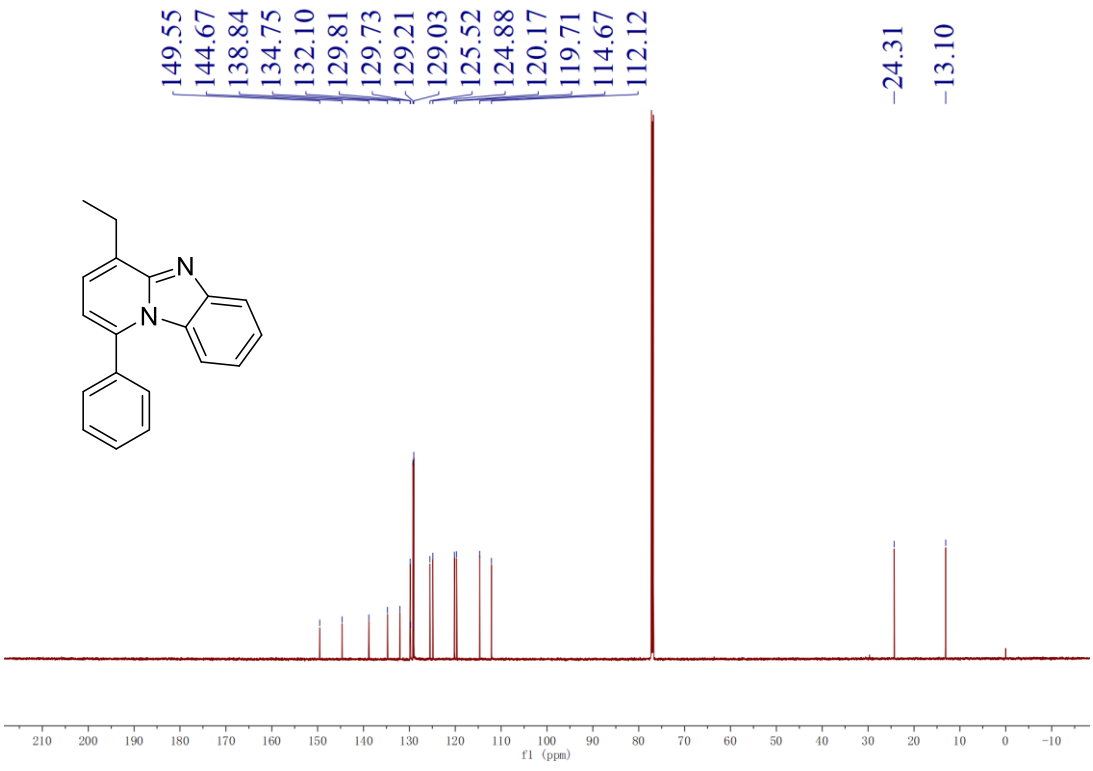
^{1}H NMR spectrum of compound **3b**



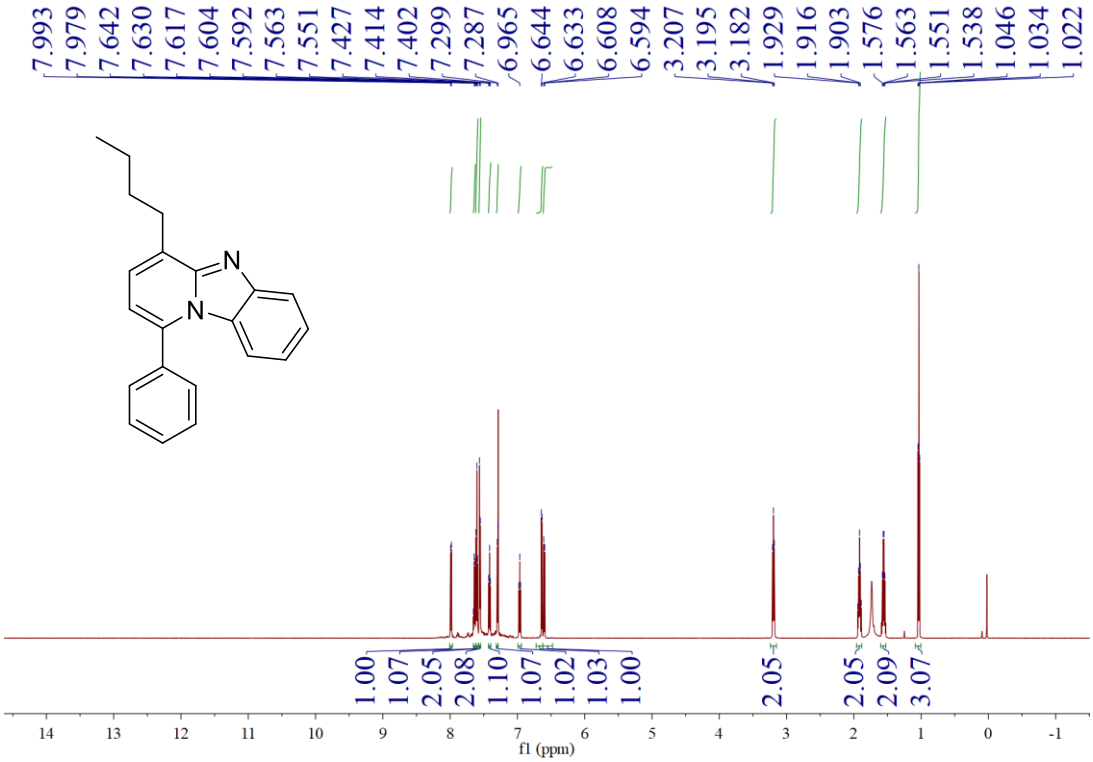
^{13}C NMR spectrum of compound **3b**



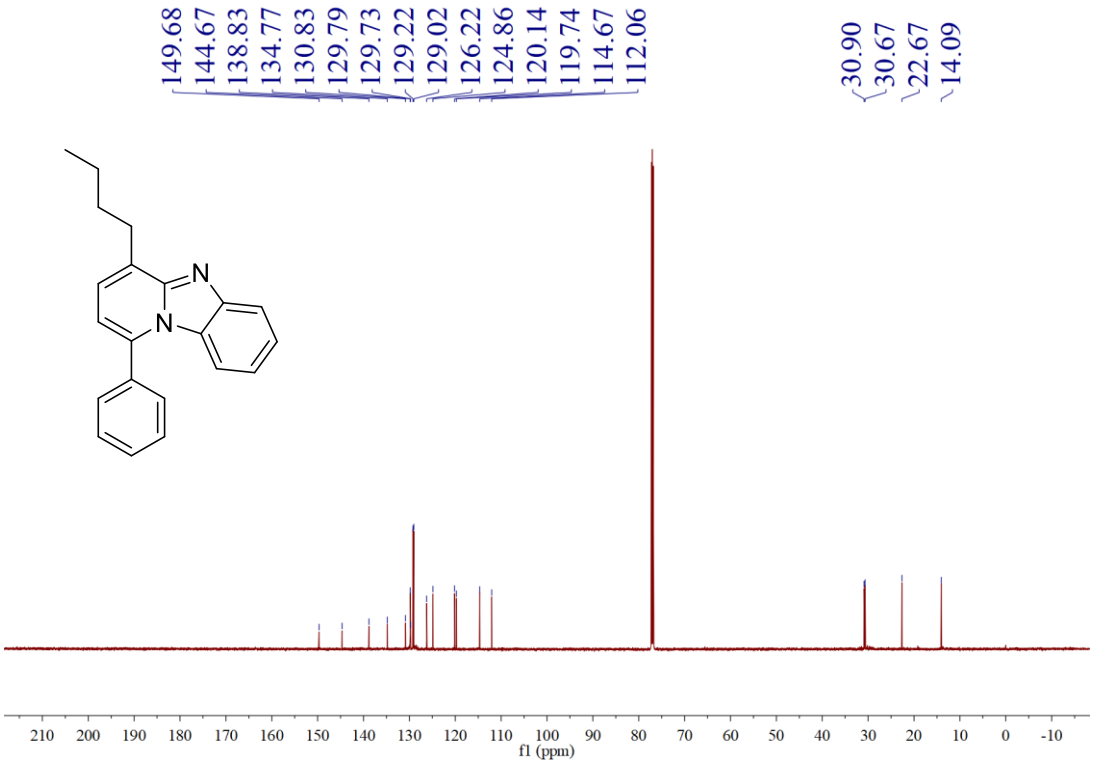
^{1}H NMR spectrum of compound **3c**



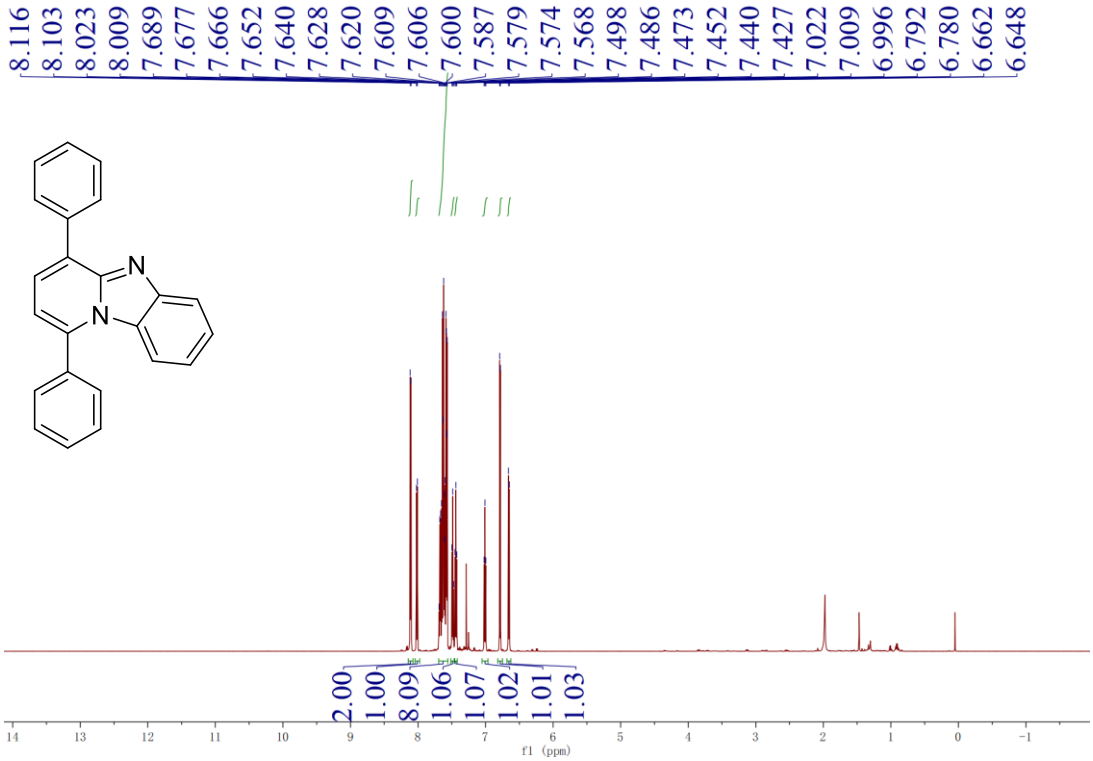
^{13}C NMR spectrum of compound **3c**



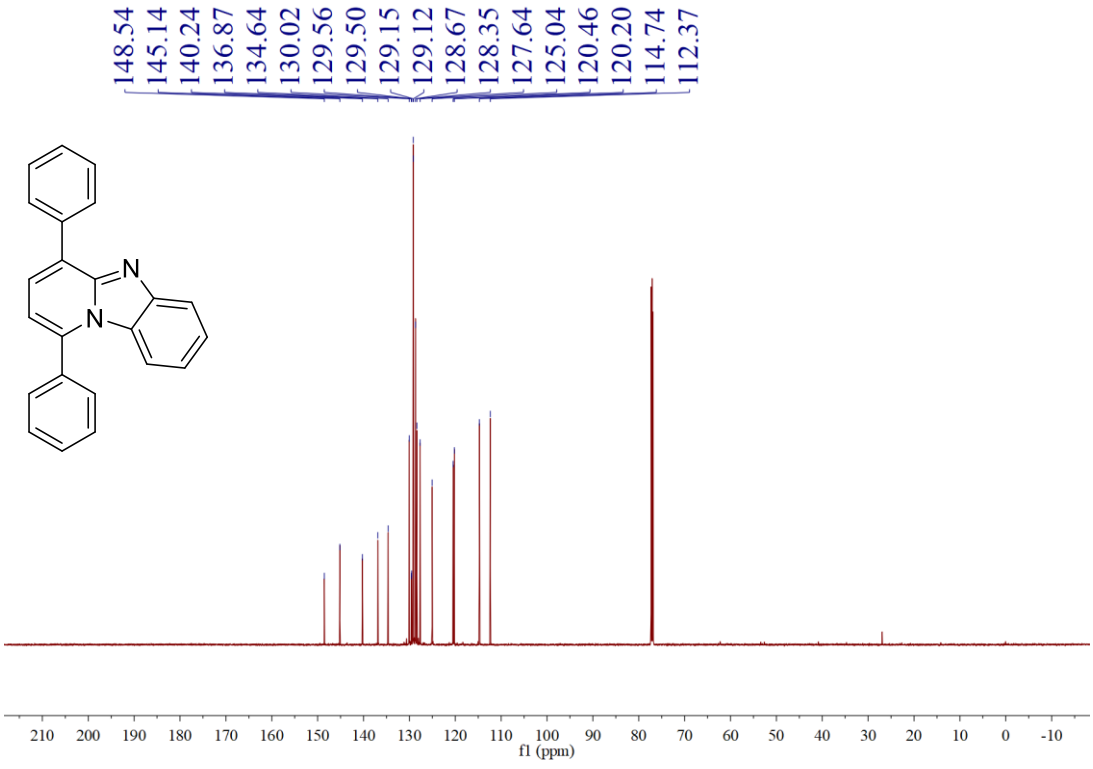
^{1}H NMR spectrum of compound **3d**



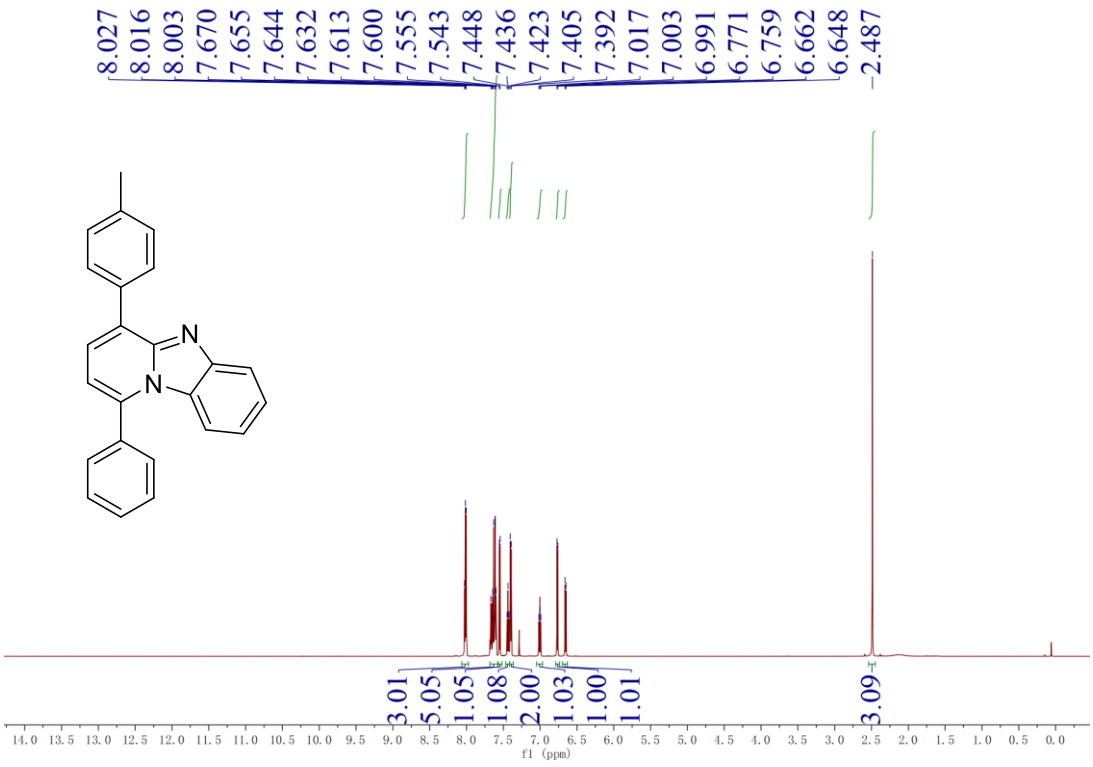
^{13}C NMR spectrum of compound **3d**



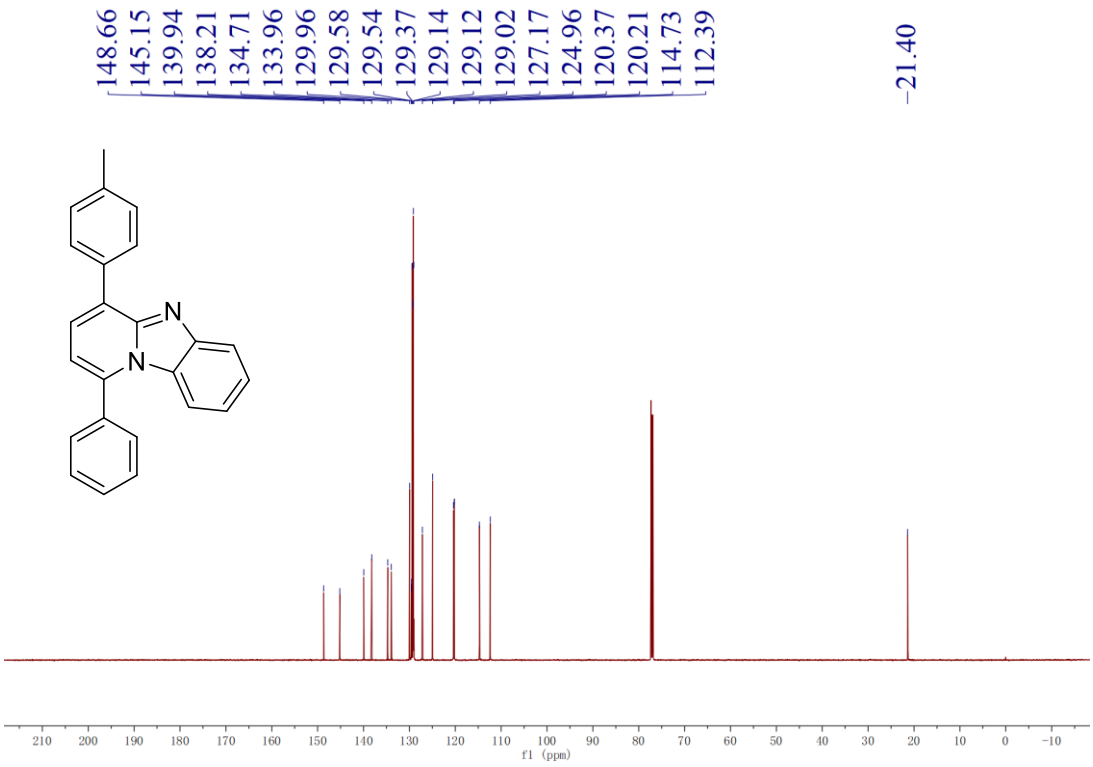
^{1}H NMR spectrum of compound **3e**



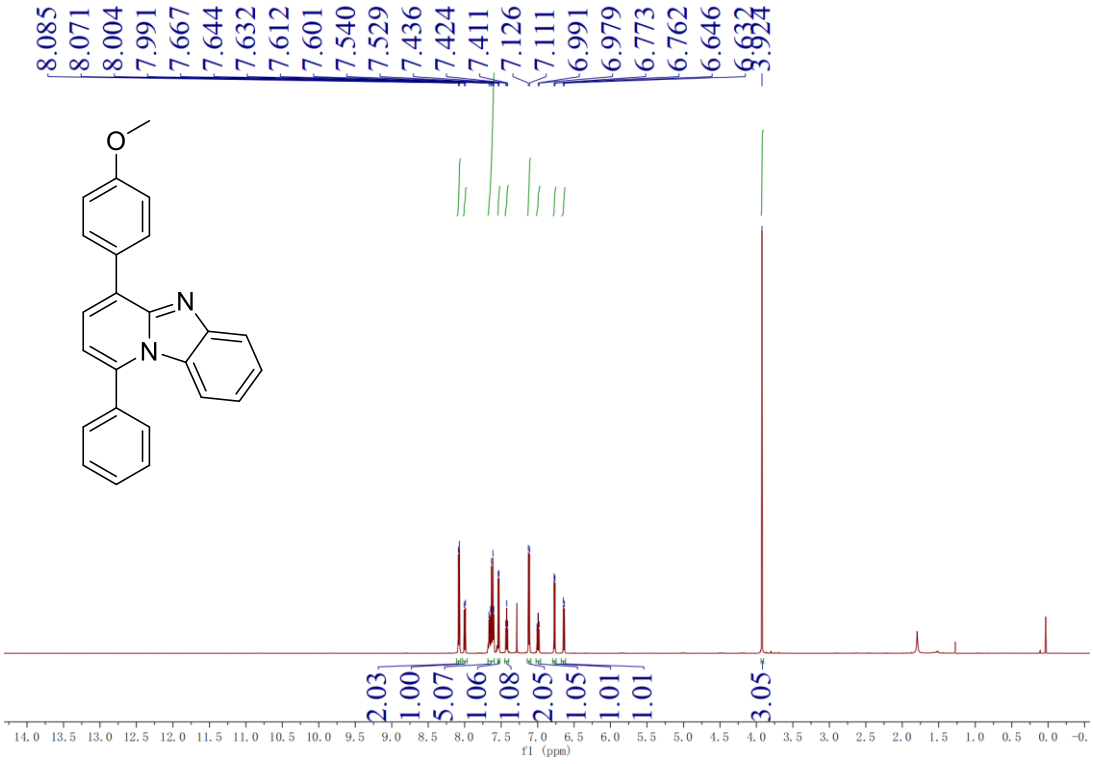
^{13}C NMR spectrum of compound **3e**



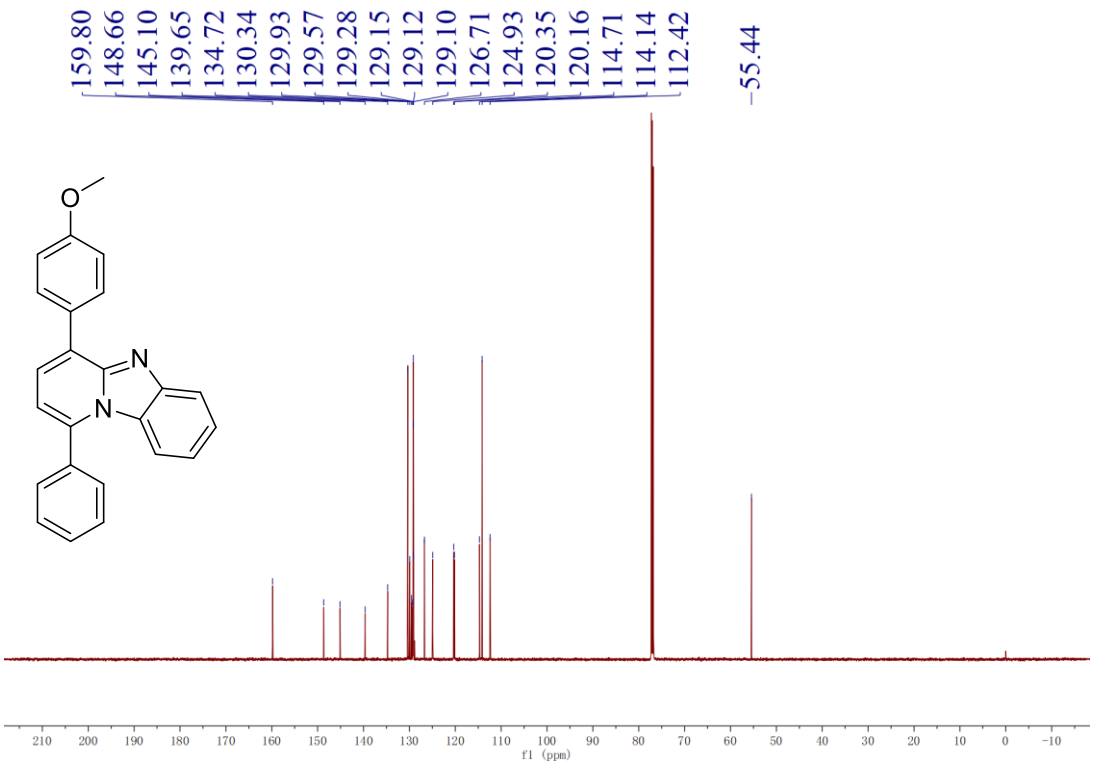
^{1}H NMR spectrum of compound **3f**



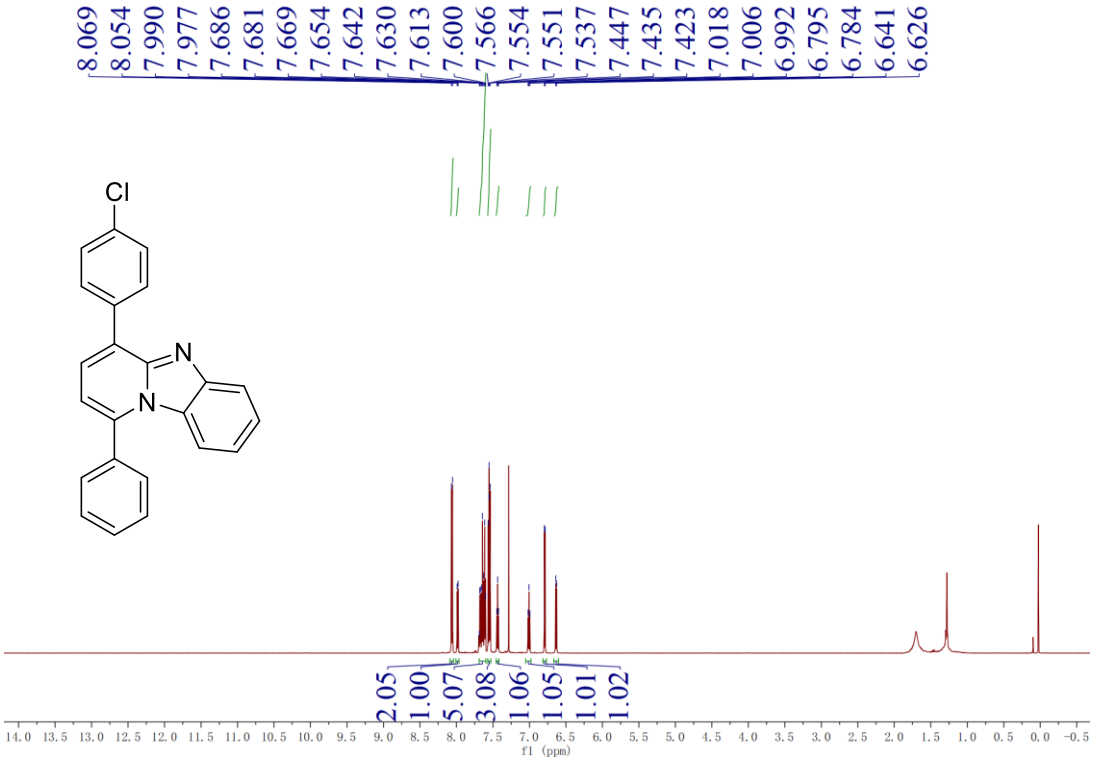
^{13}C NMR spectrum of compound **3f**



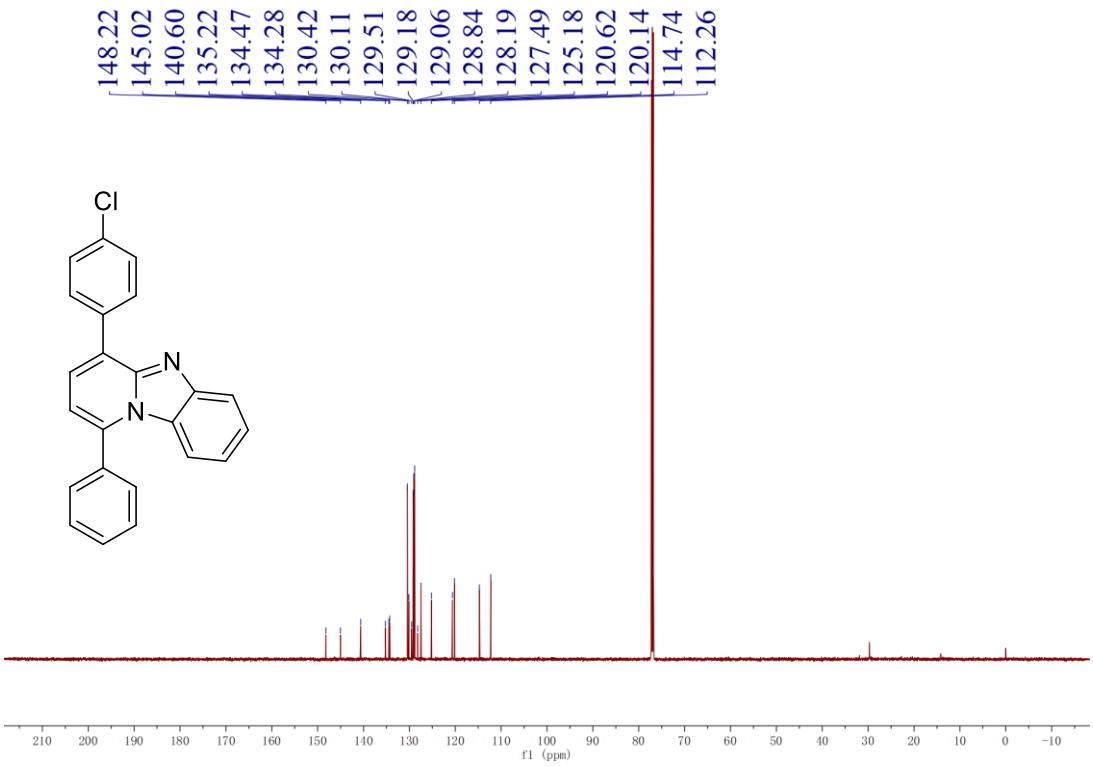
^{1}H NMR spectrum of compound **3g**



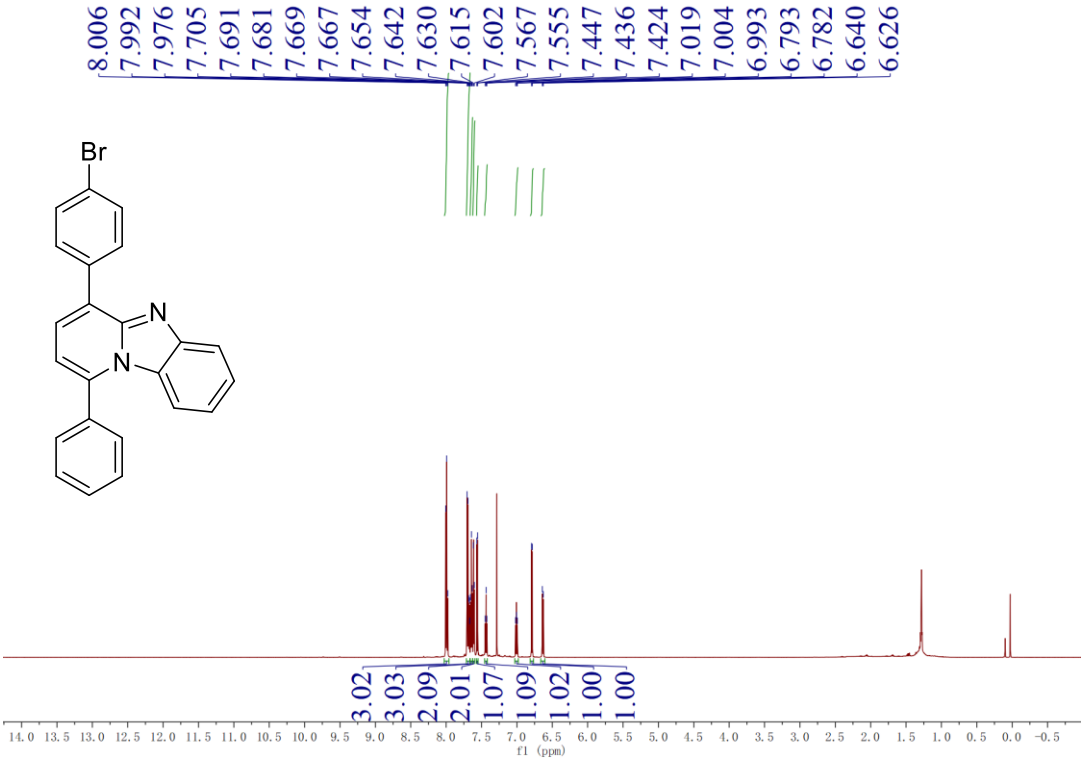
^{13}C NMR spectrum of compound **3g**



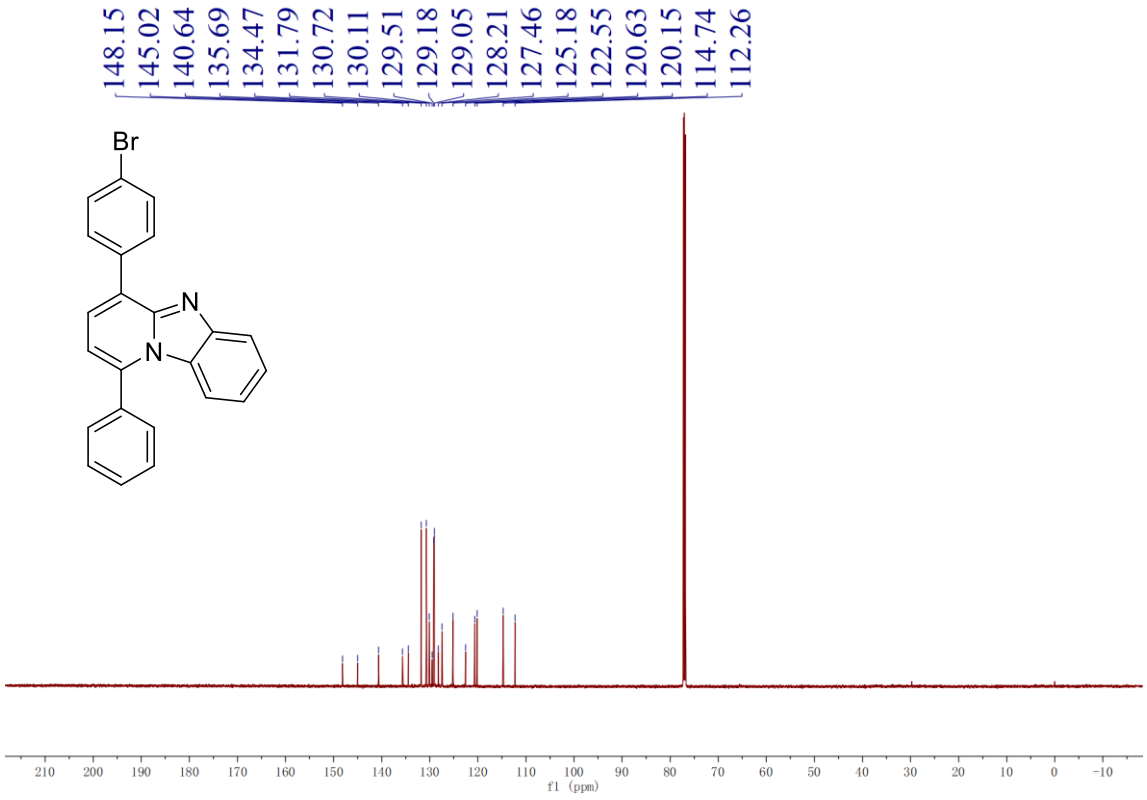
^{1}H NMR spectrum of compound **3h**



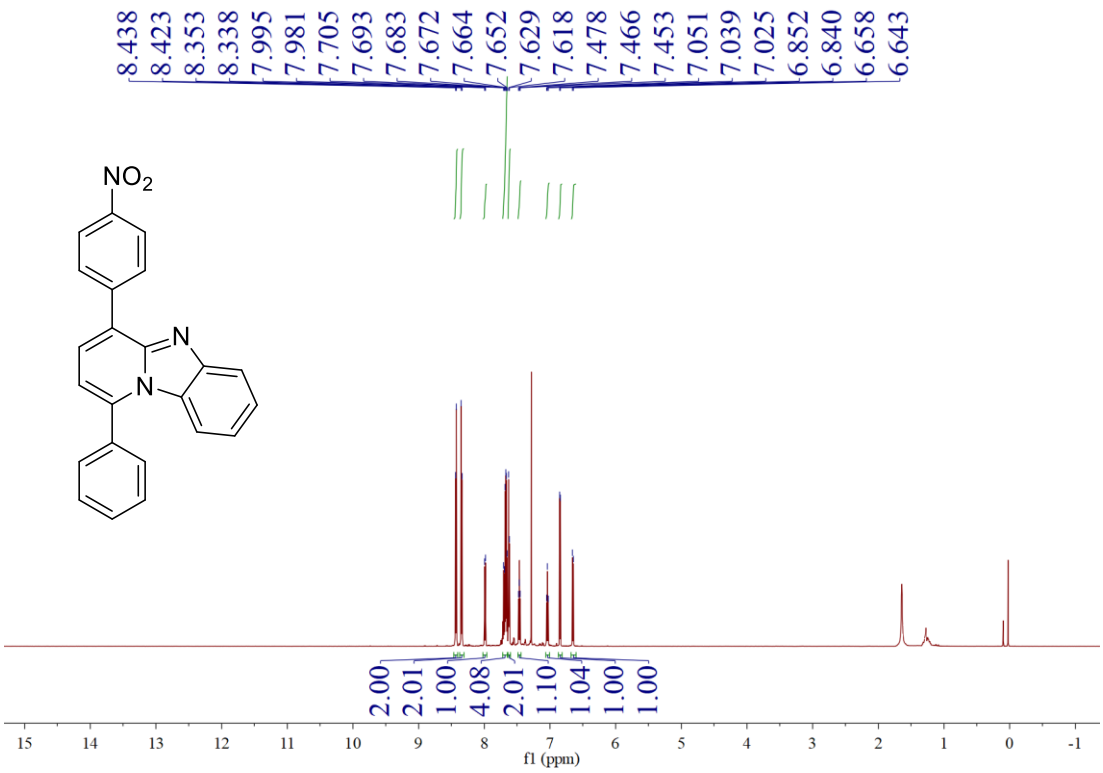
^{13}C NMR spectrum of compound **3h**



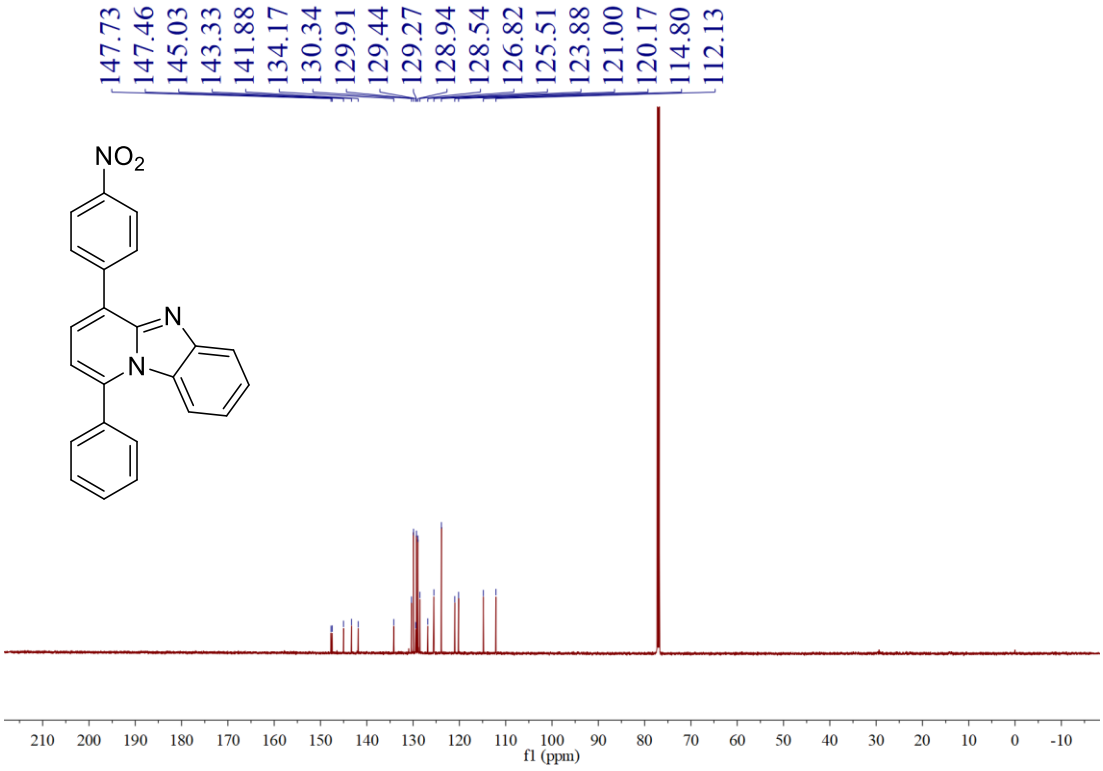
^{1}H NMR spectrum of compound **3i**



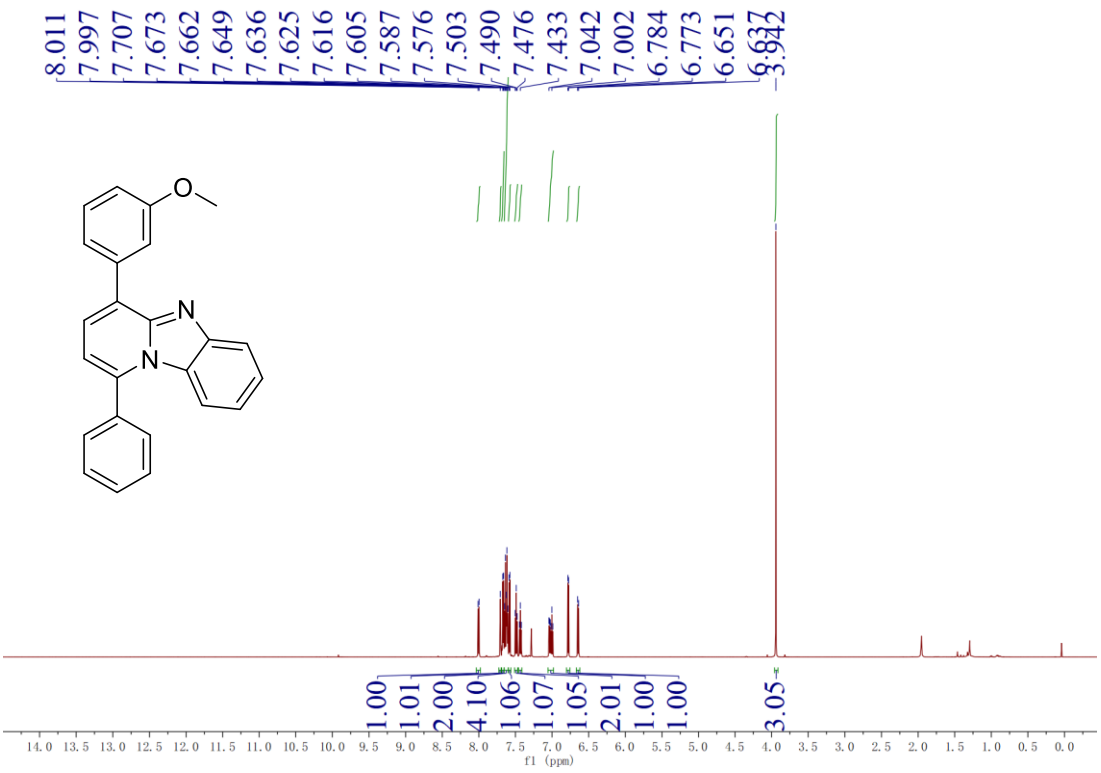
^{13}C NMR spectrum of compound **3i**



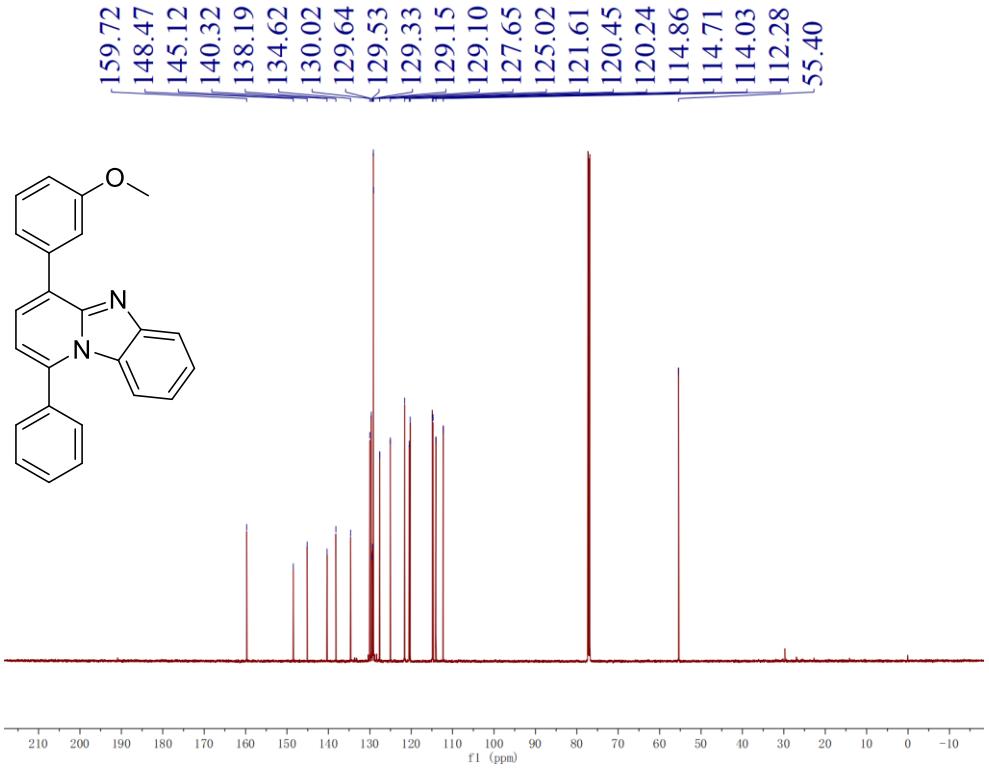
^{1}H NMR spectrum of compound **3j**



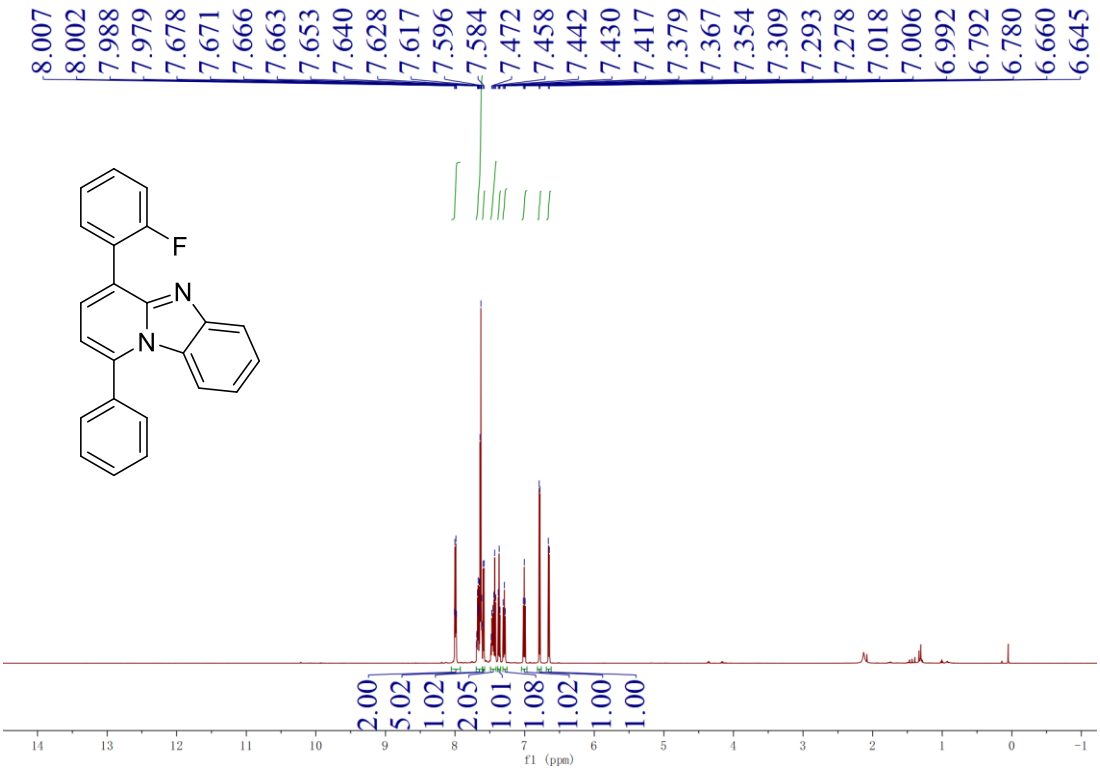
^{13}C NMR spectrum of compound **3j**



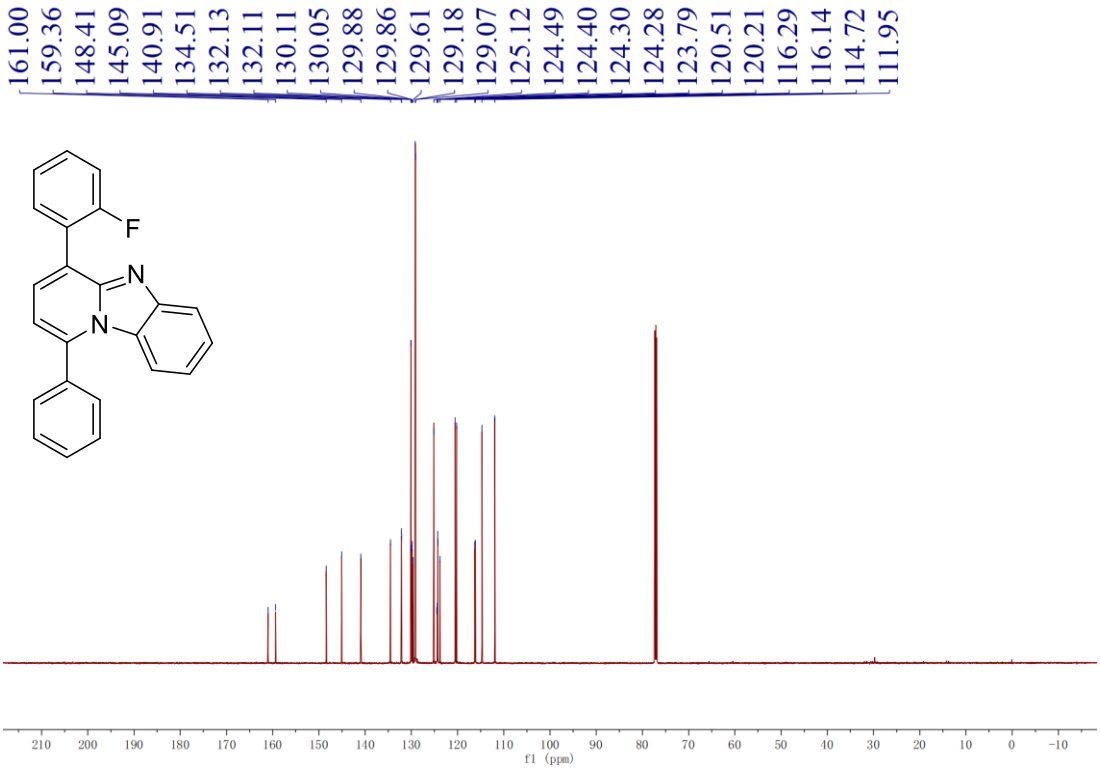
^{1}H NMR spectrum of compound **3k**



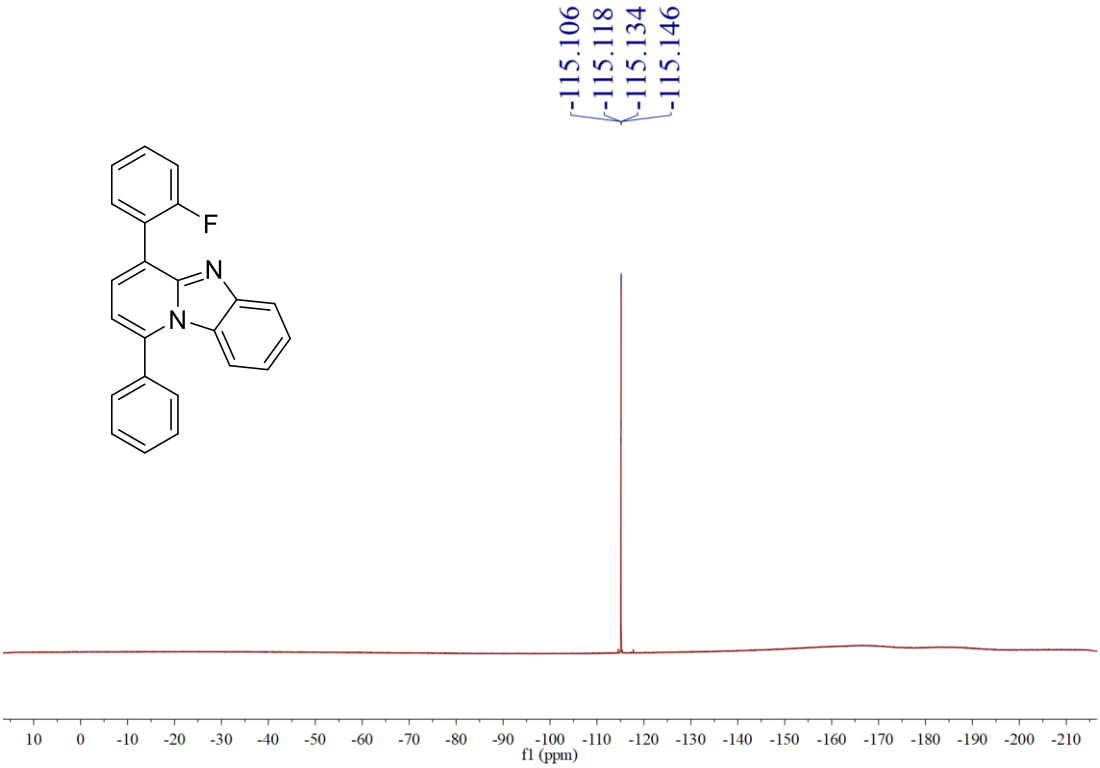
^{13}C NMR spectrum of compound **3k**



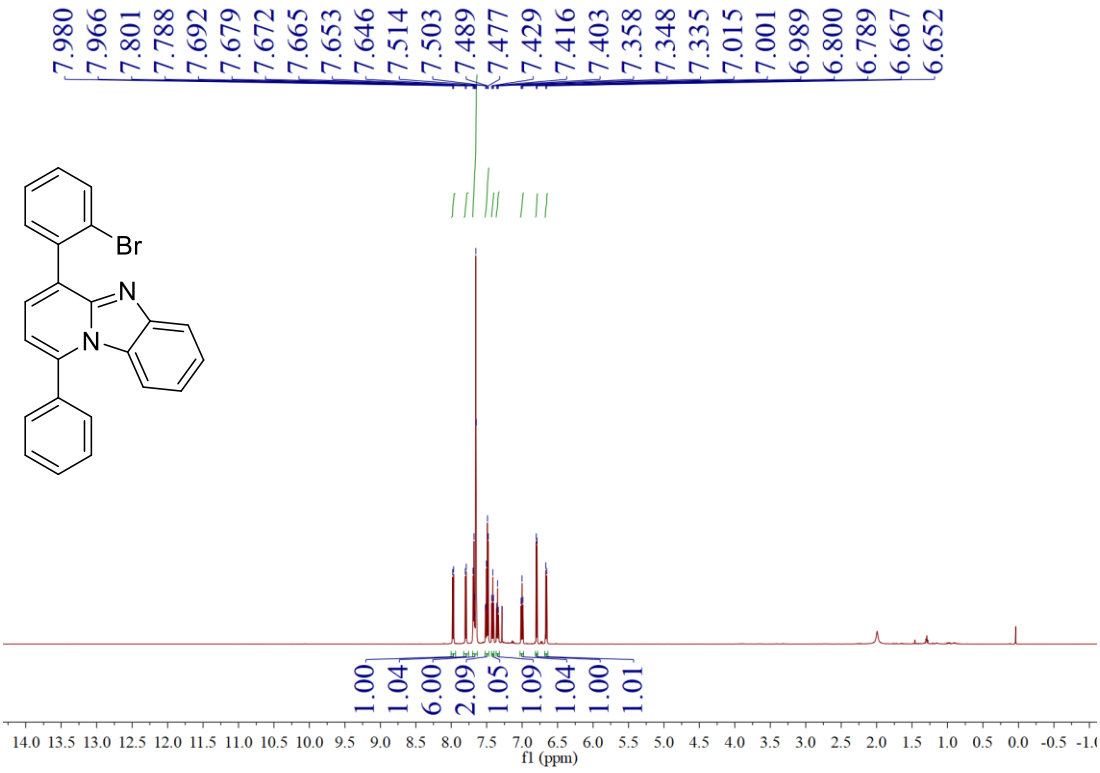
^{1}H NMR spectrum of compound **3l**



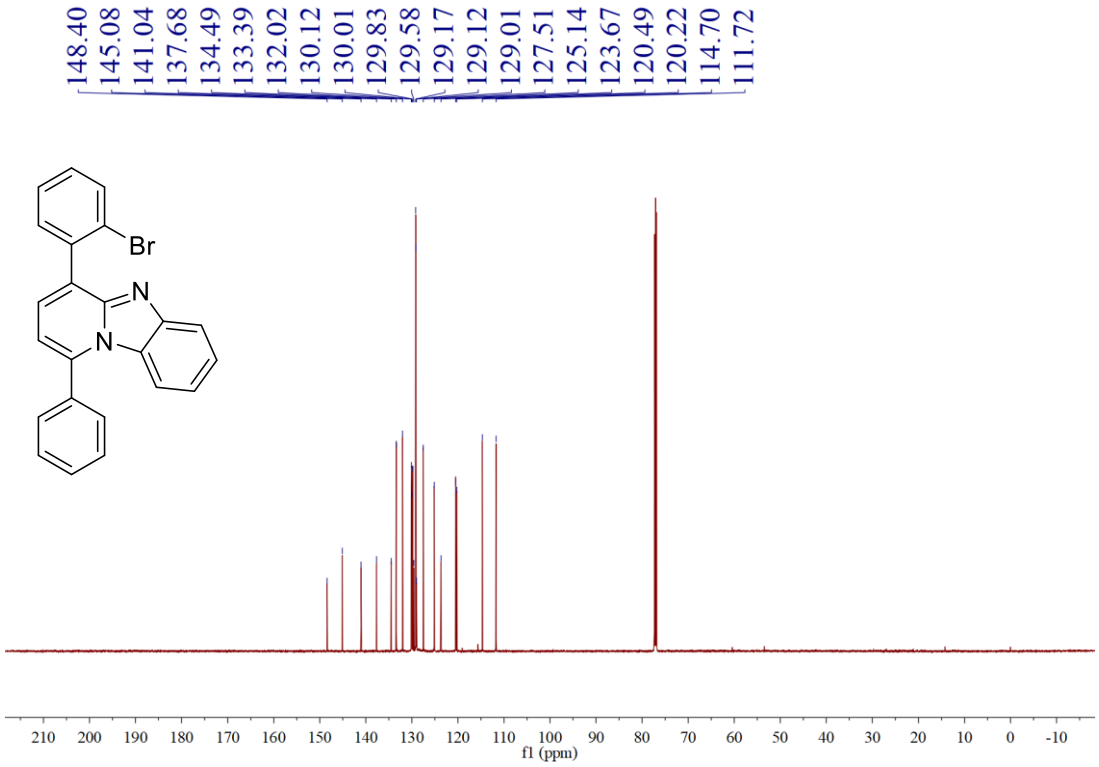
^{13}C NMR spectrum of compound **3l**



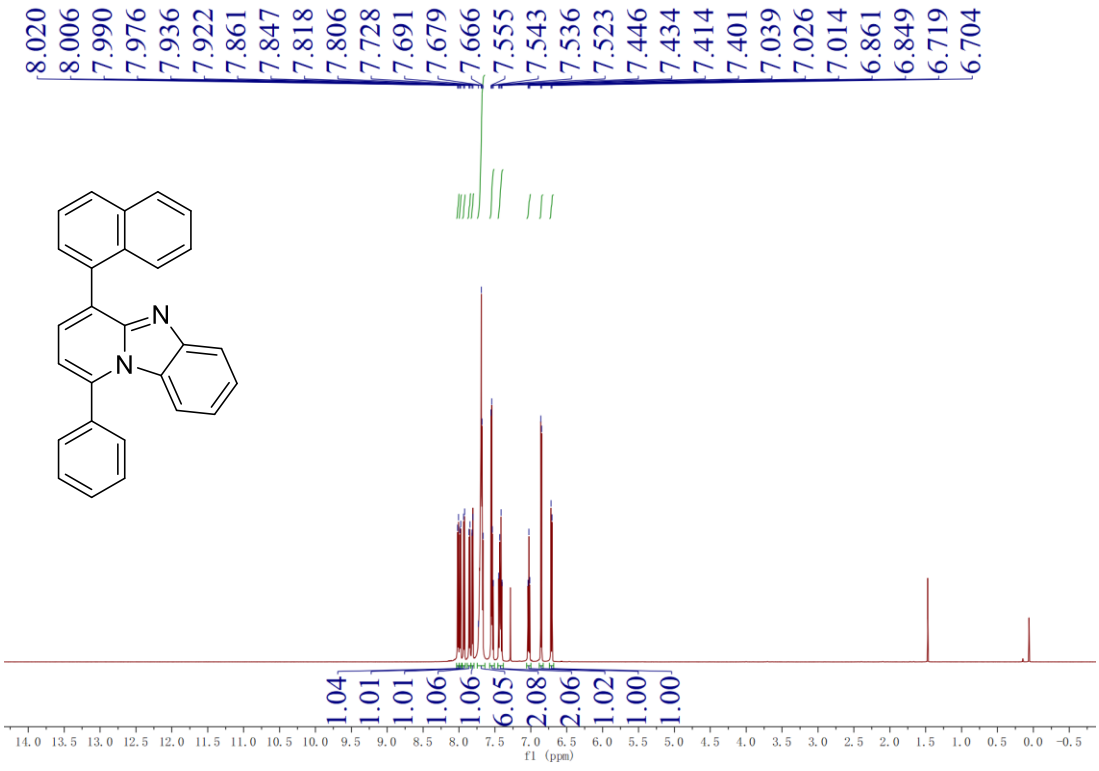
^{19}F NMR spectrum of compound **3l**



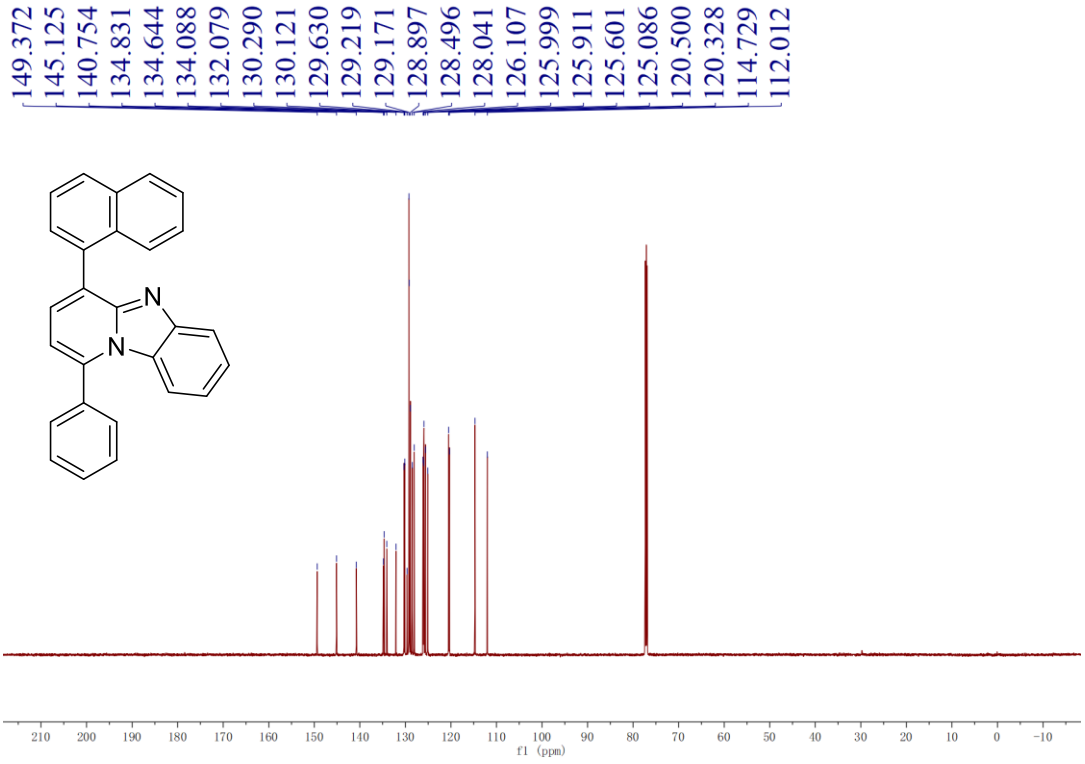
^{1}H NMR spectrum of compound **3m**



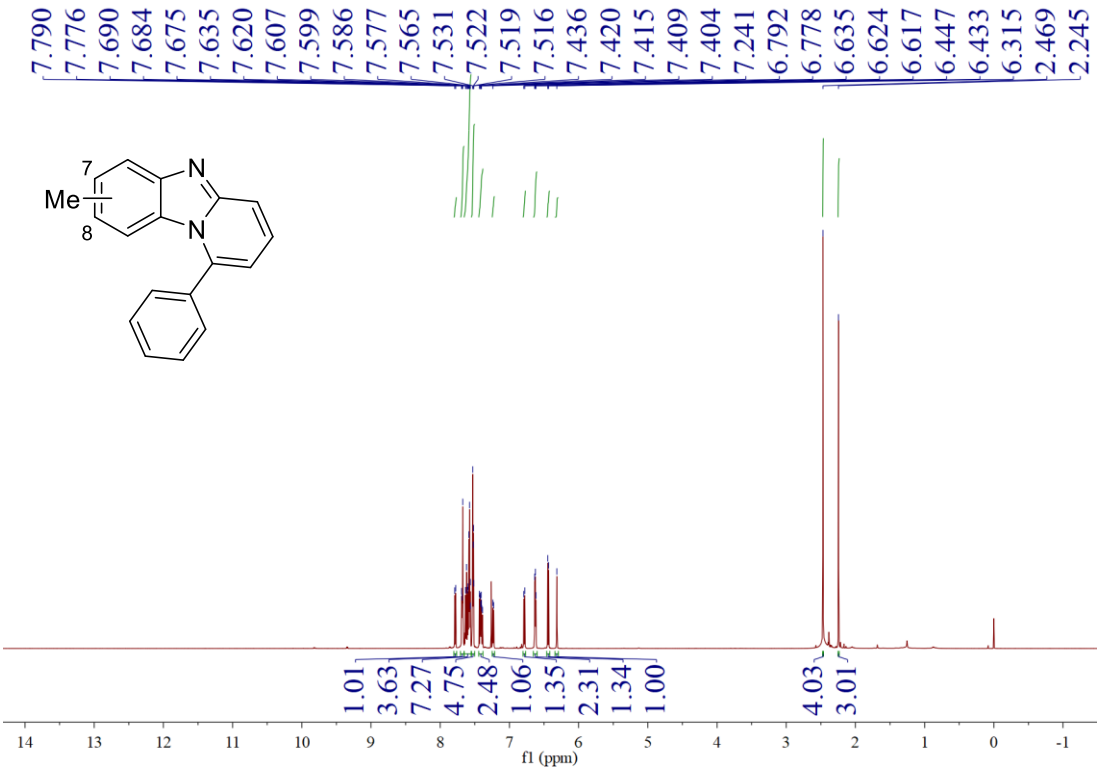
^{13}C NMR spectrum of compound **3m**



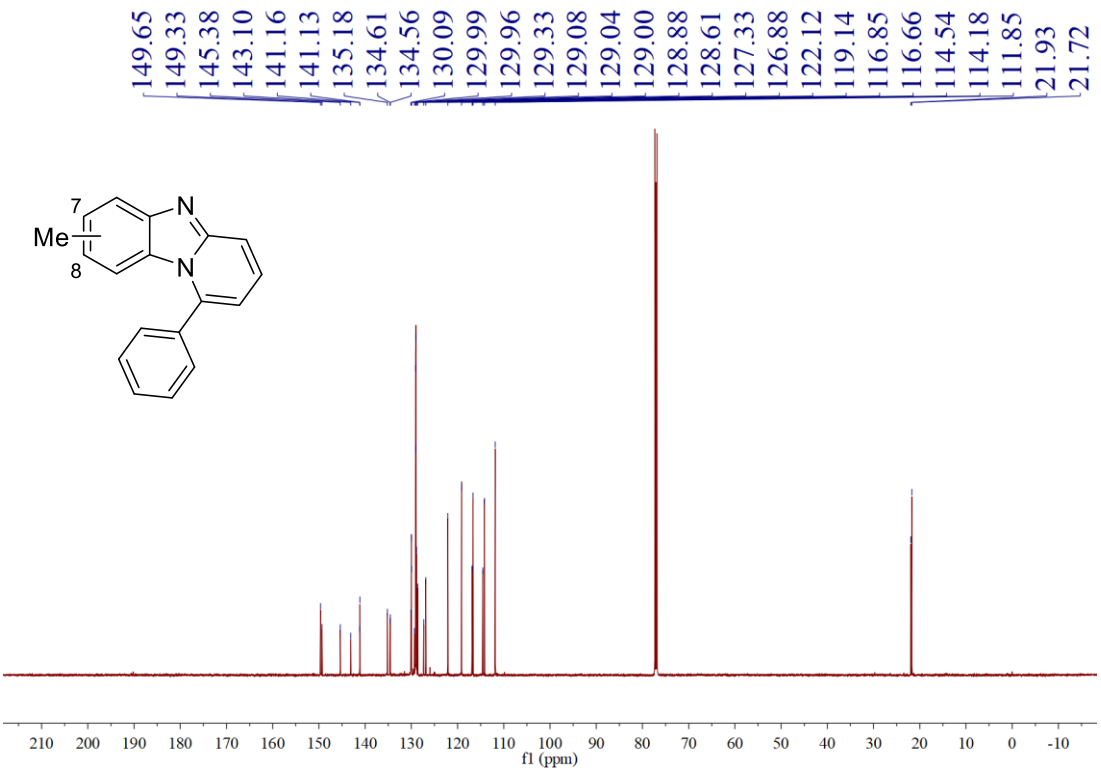
^{1}H NMR spectrum of compound **3n**



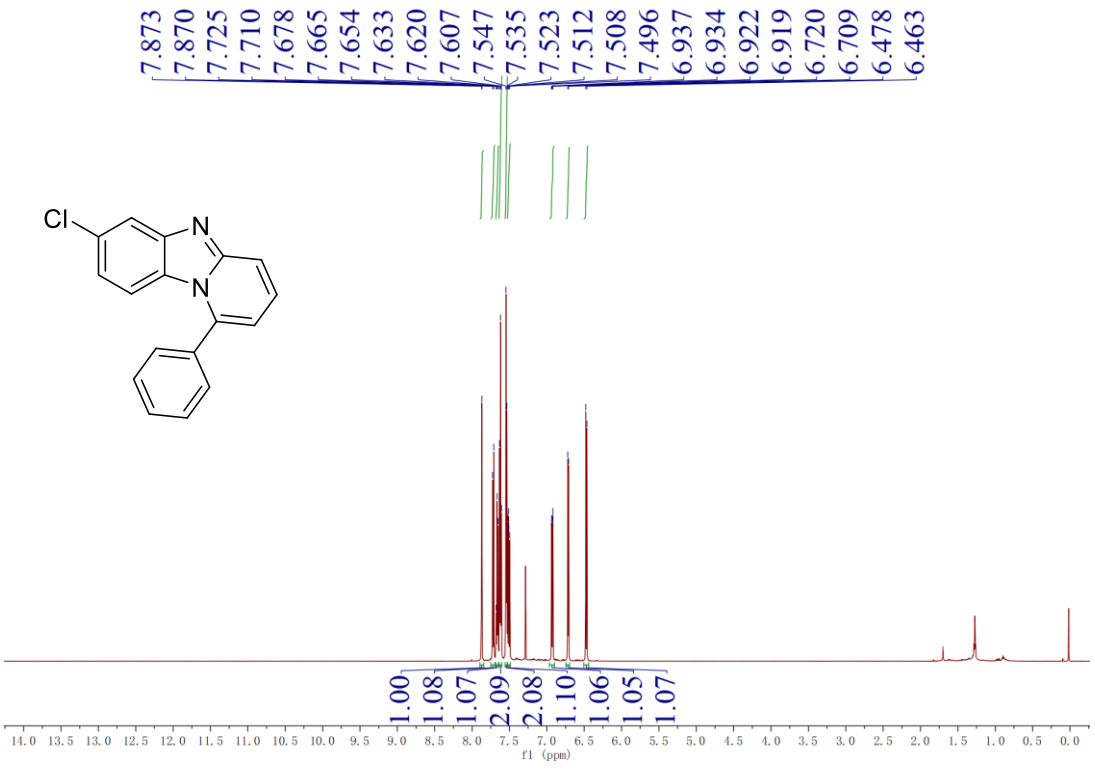
^{13}C NMR spectrum of compound **3n**



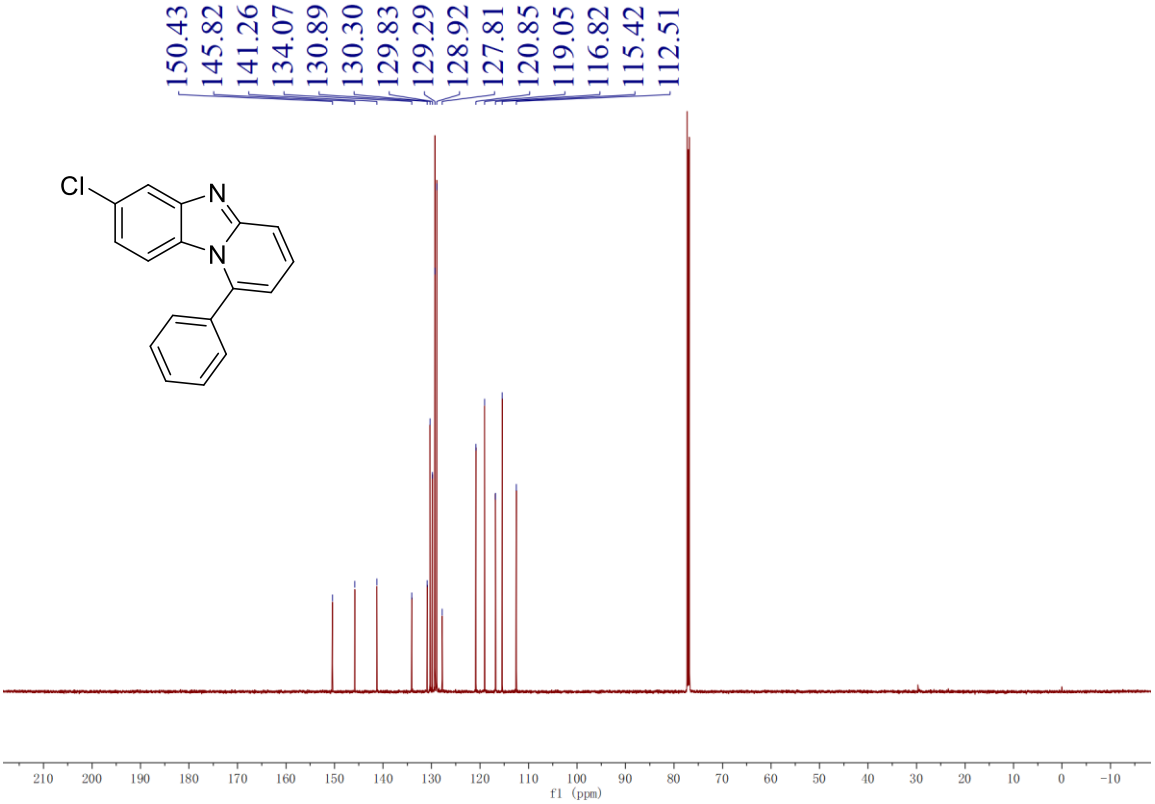
^{1}H NMR spectrum of compound **4a/4a'**



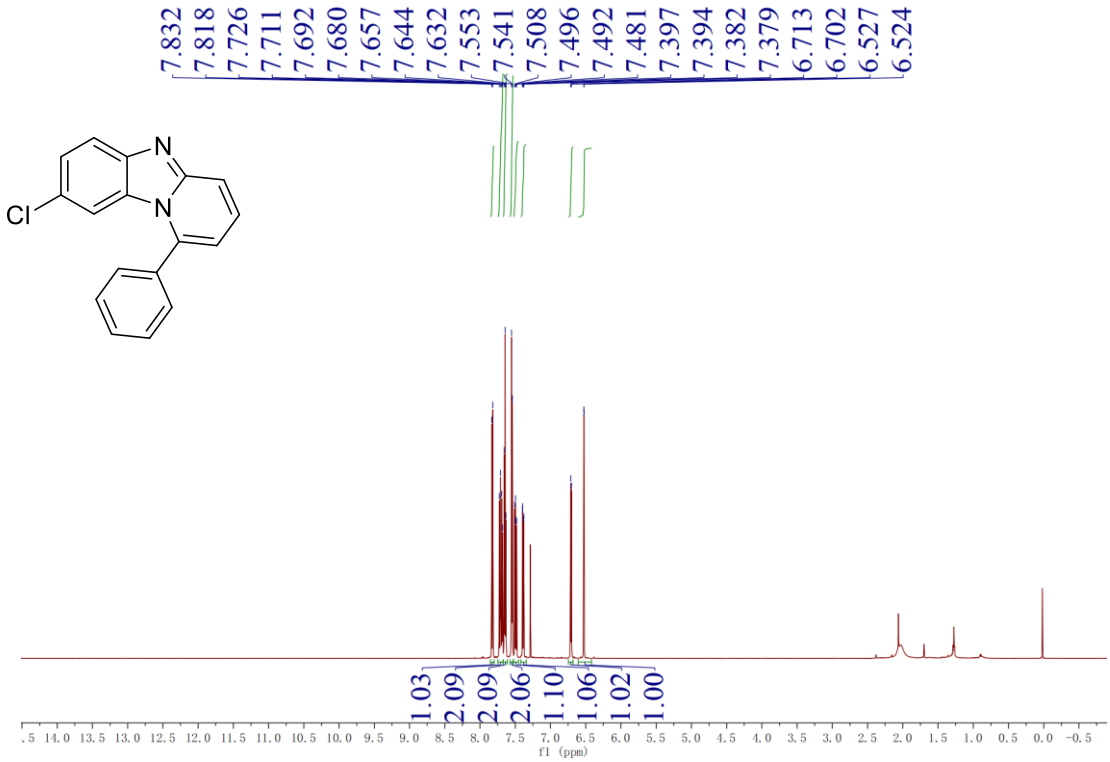
^{13}C NMR spectrum of compound **4a/4a'**



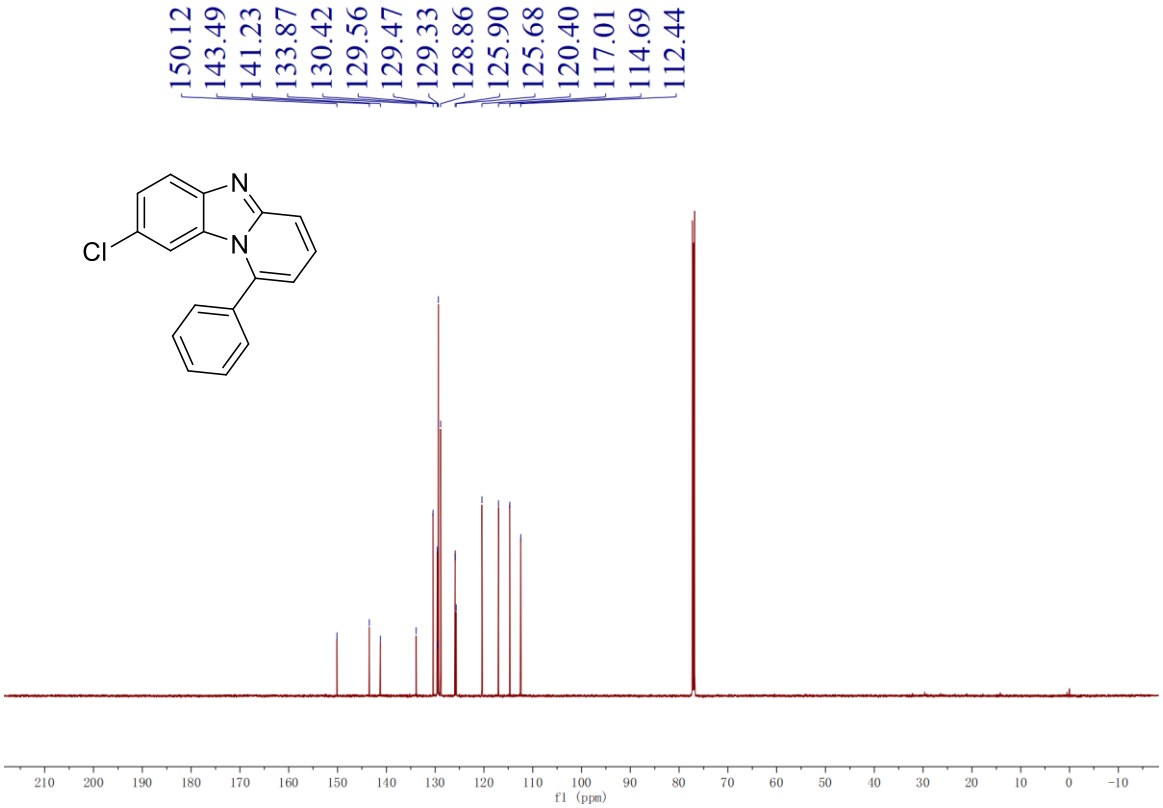
^{1}H NMR spectrum of compound **4b**



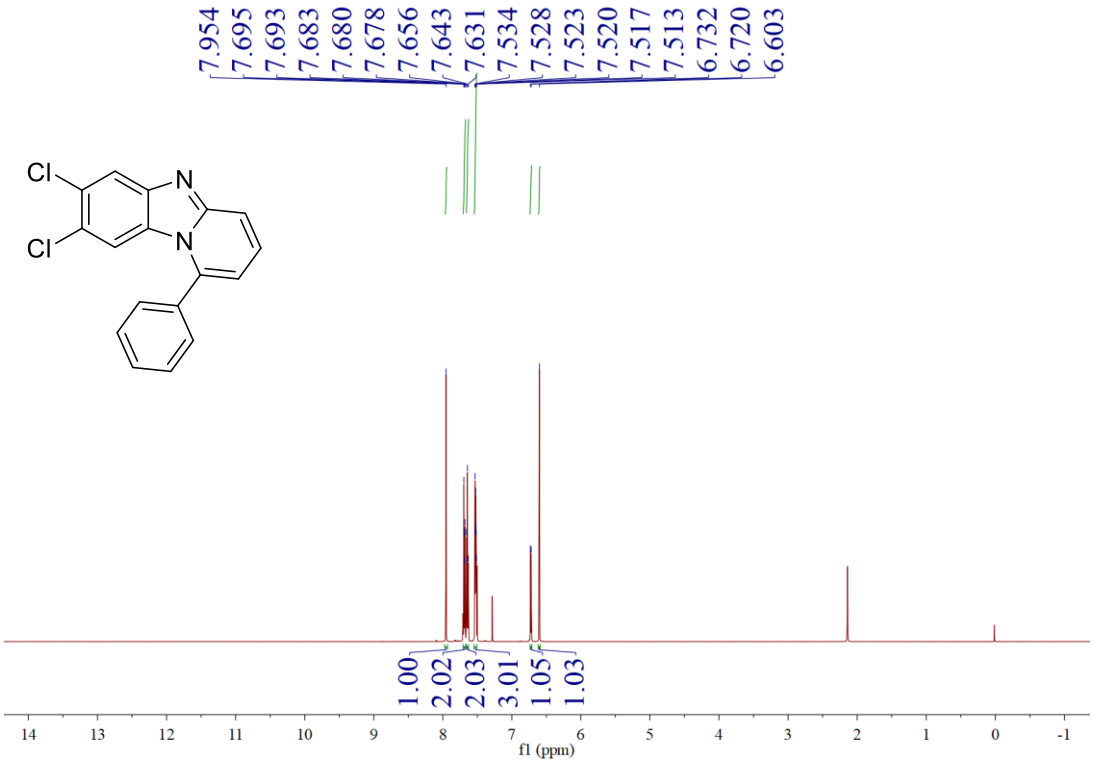
^{13}C NMR spectrum of compound **4b**



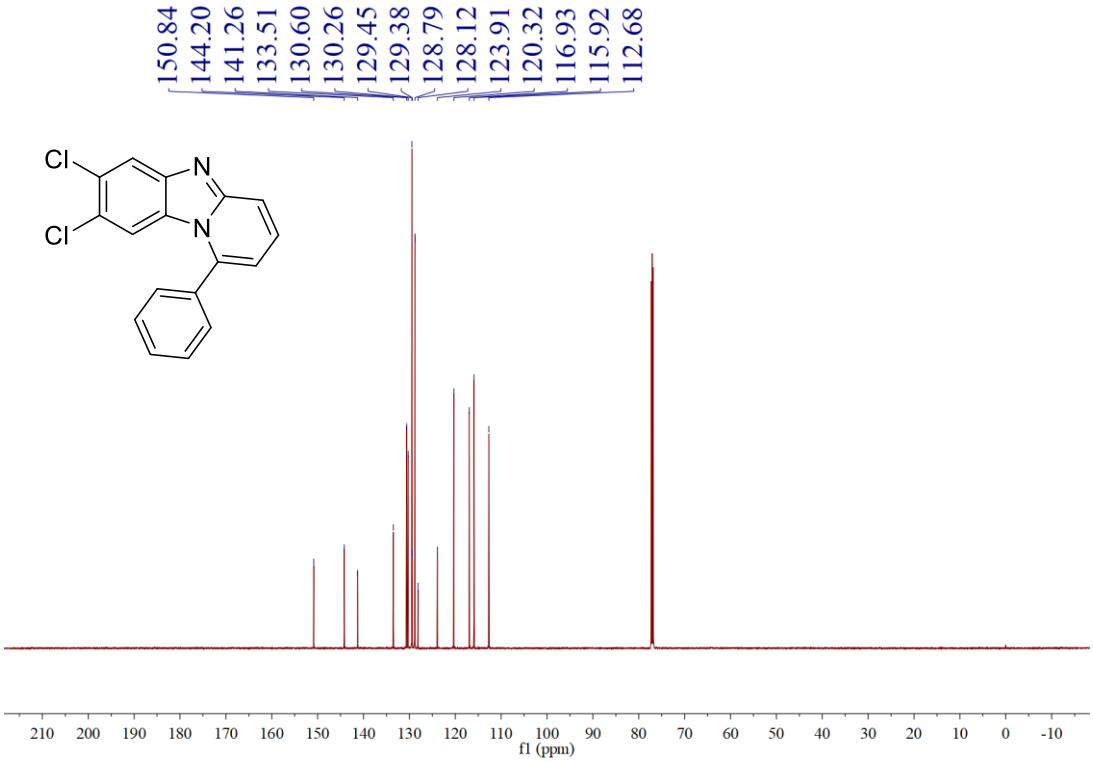
^{1}H NMR spectrum of compound **4b'**



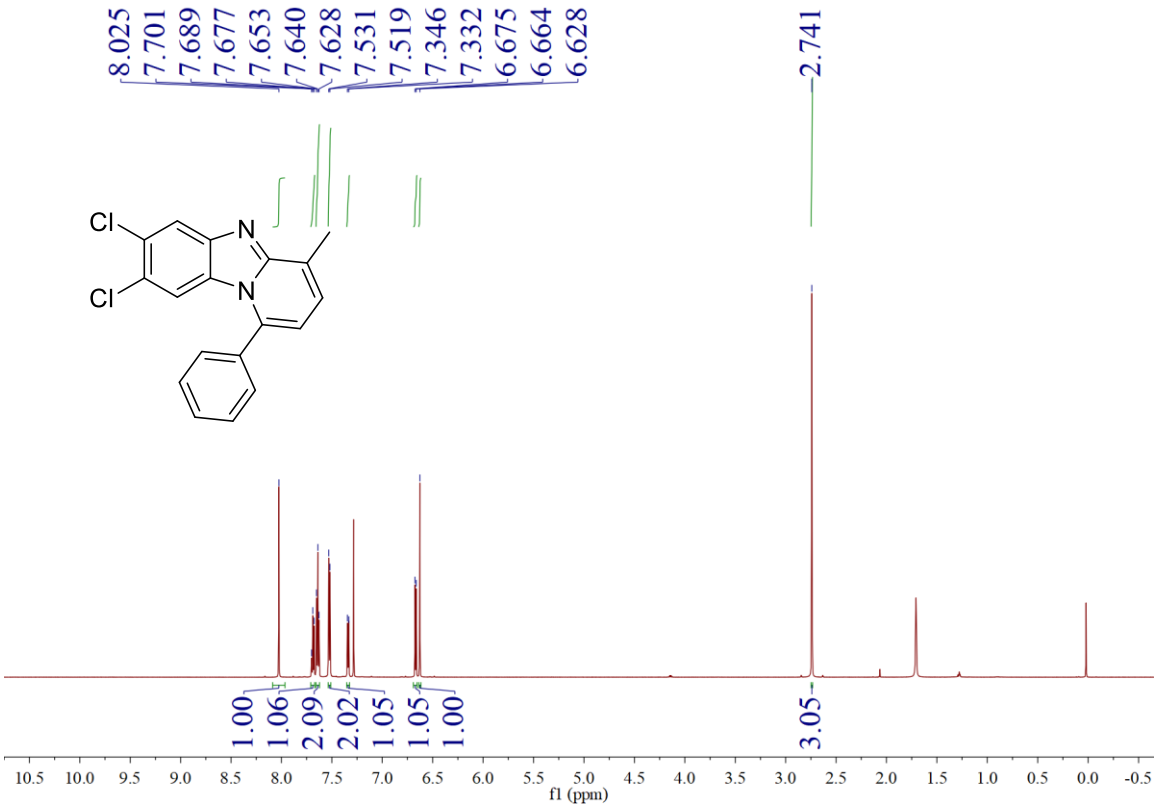
^{13}C NMR spectrum of compound **4b'**



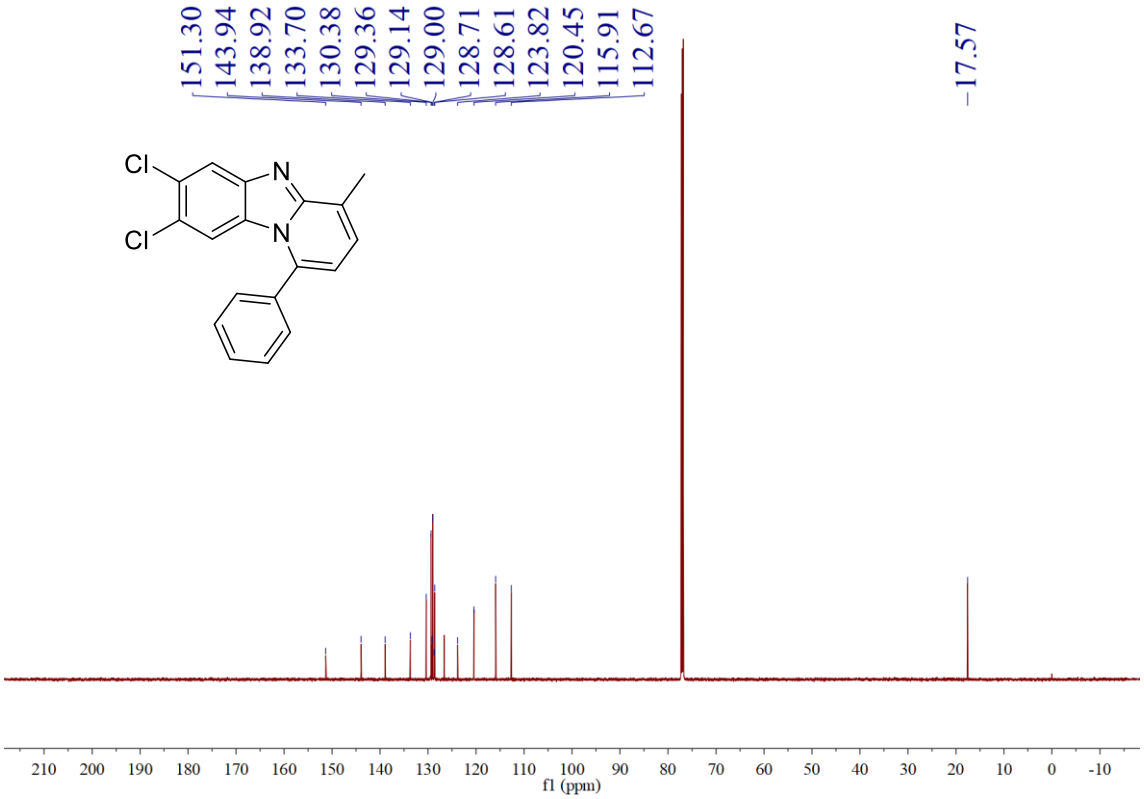
^{1}H NMR spectrum of compound **4c**



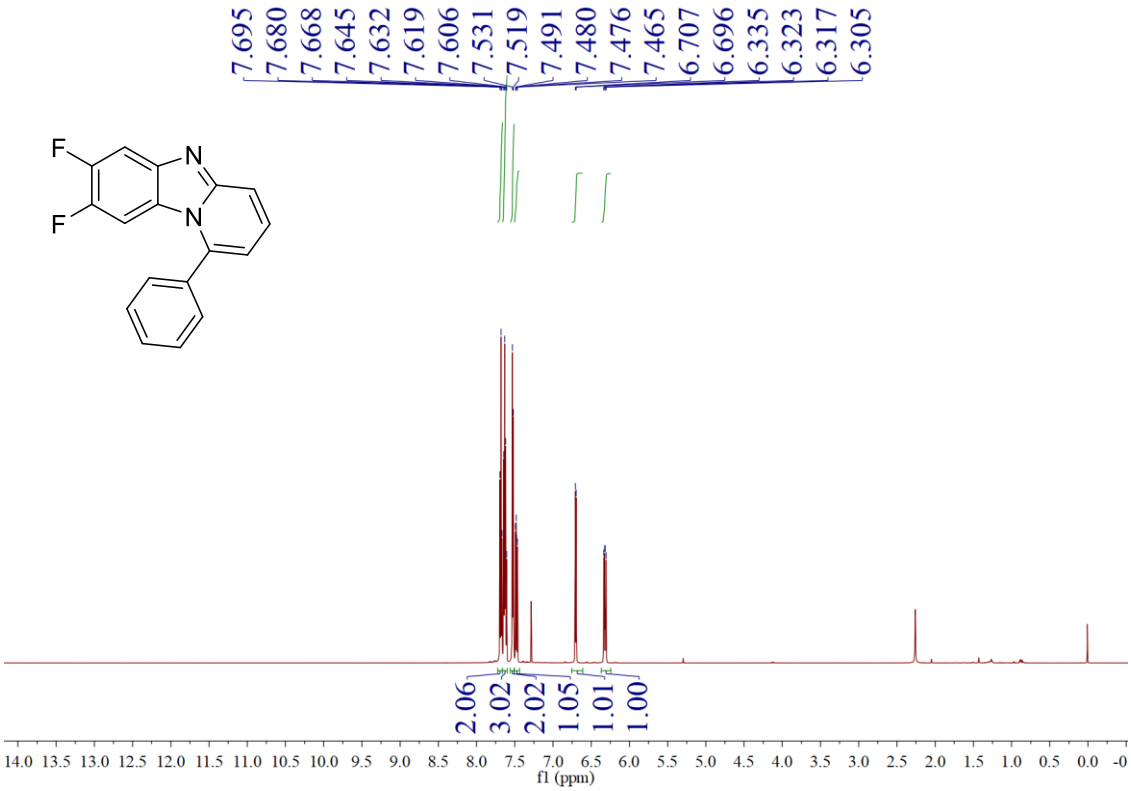
^{13}C NMR spectrum of compound **4c**



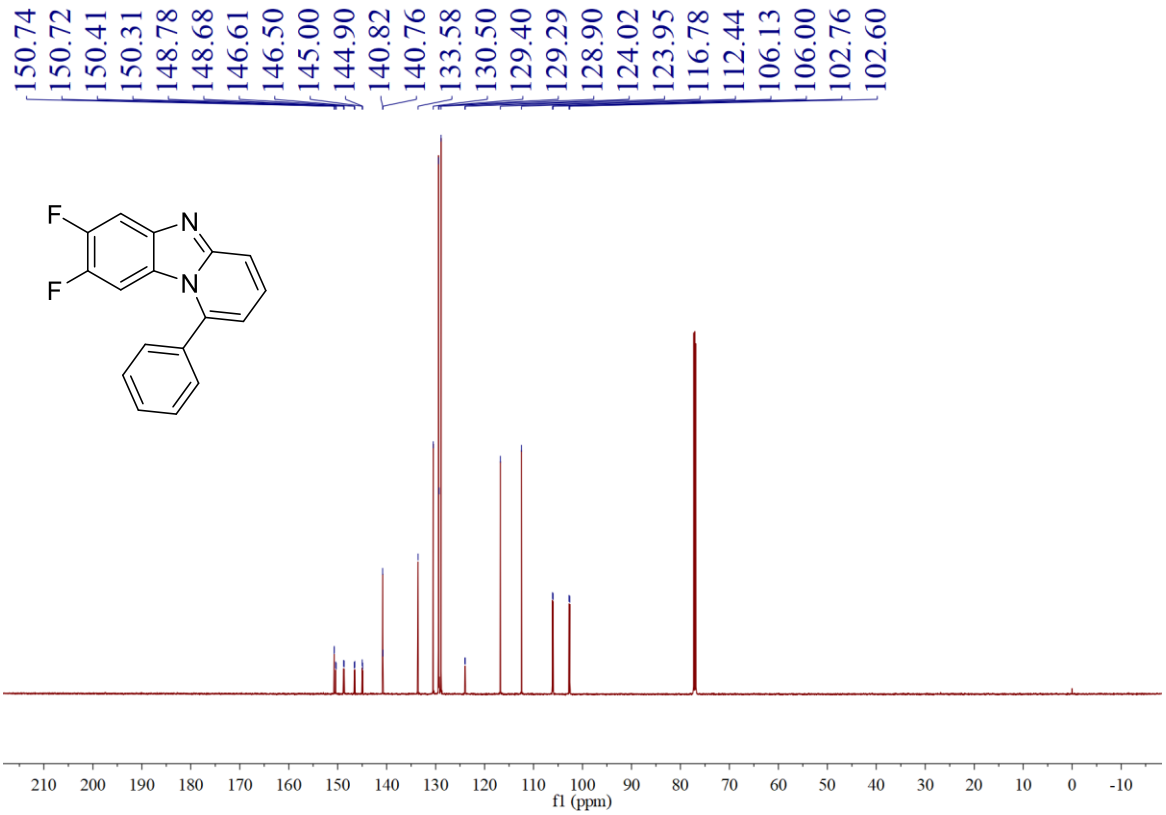
^{1}H NMR spectrum of compound **4d**



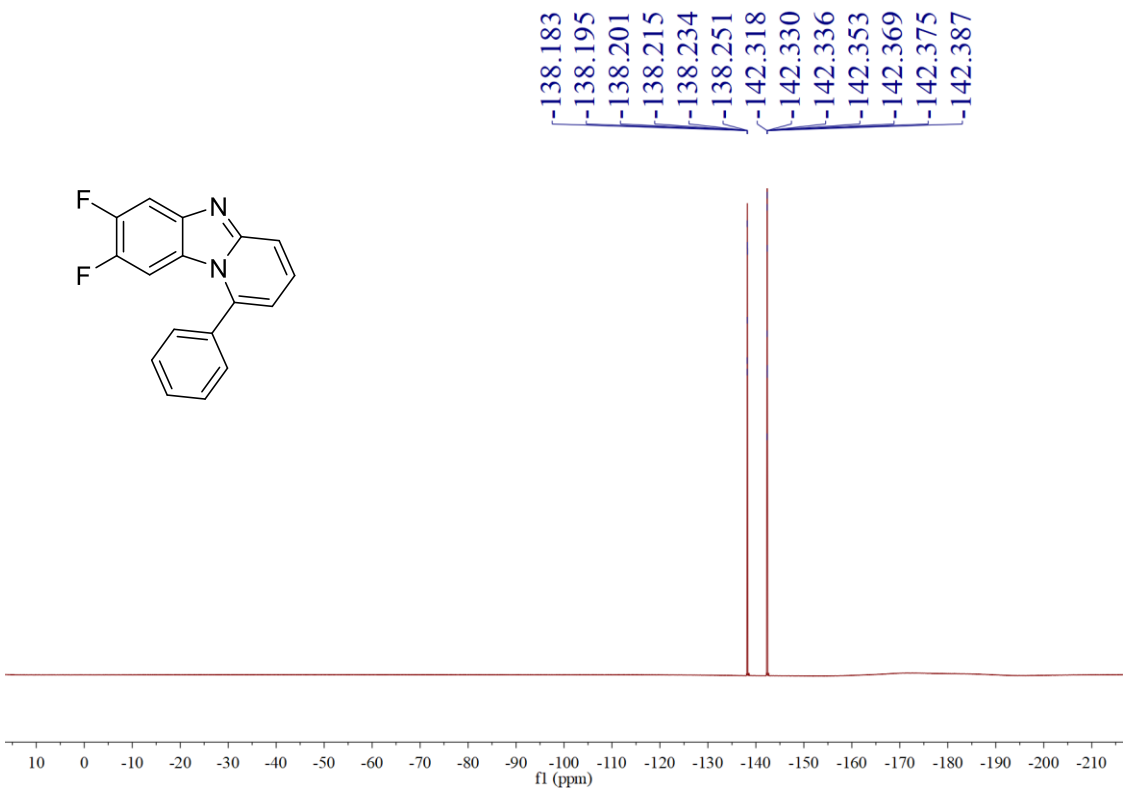
^{13}C NMR spectrum of compound **4d**



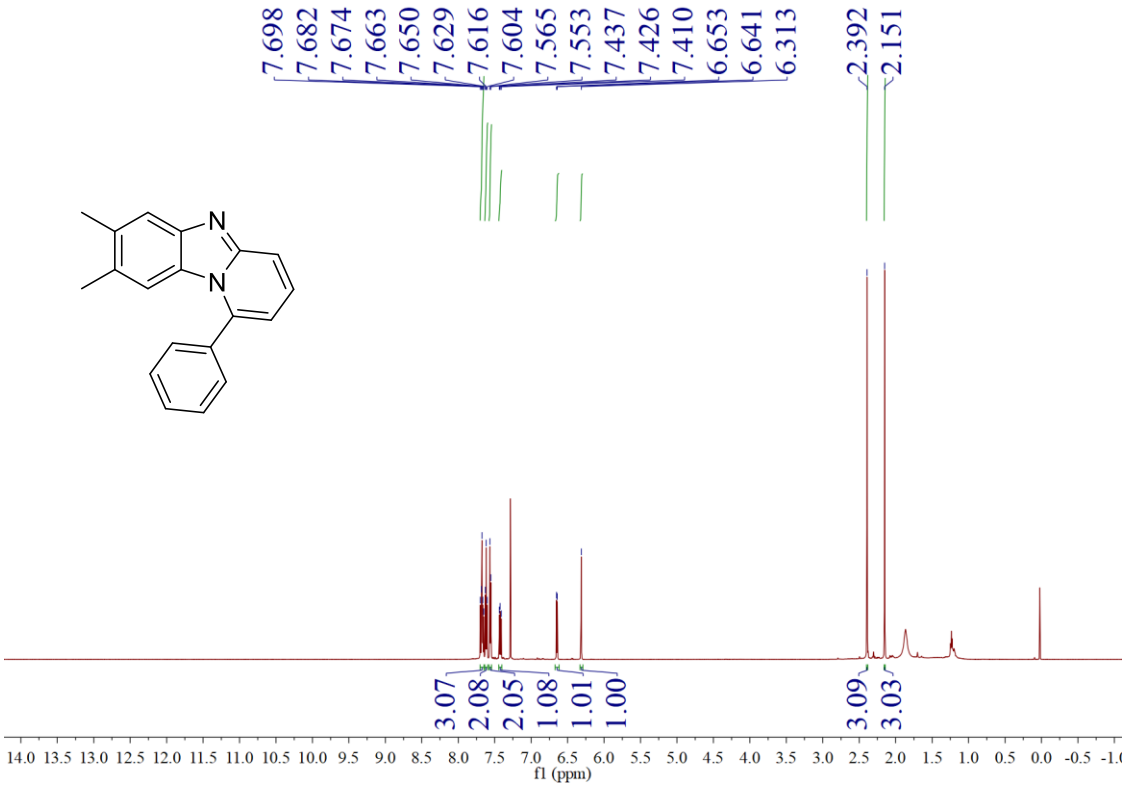
^{1}H NMR spectrum of compound **4e**



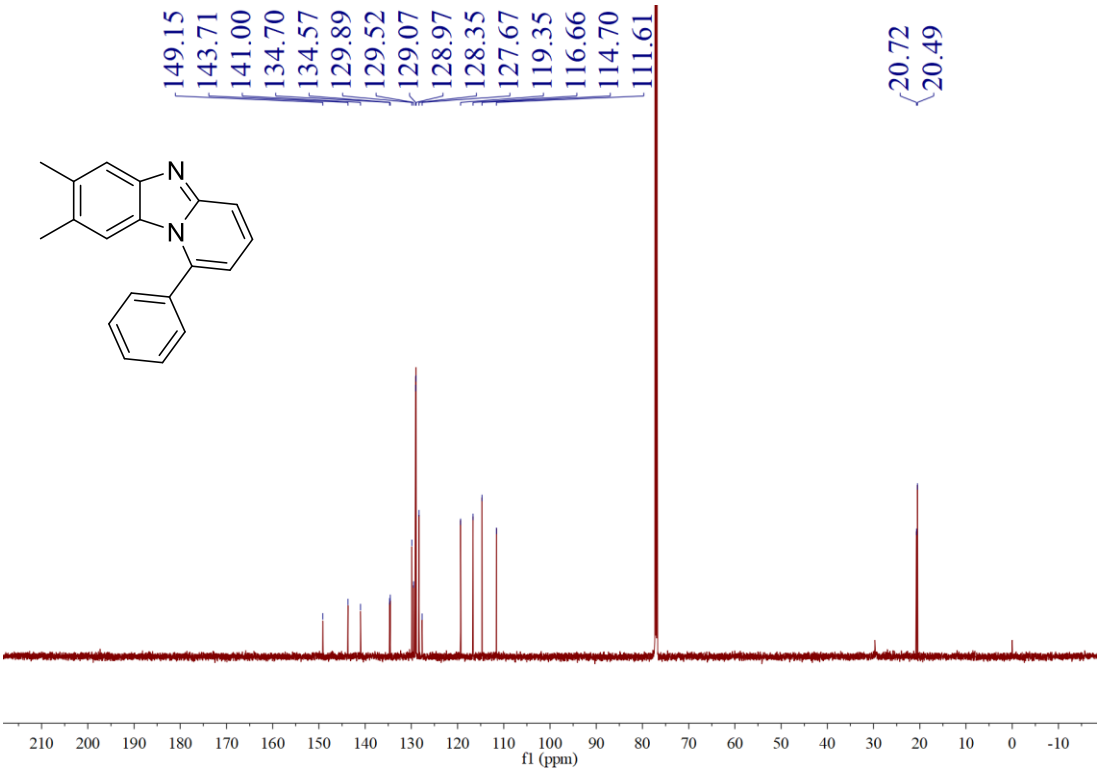
^{13}C NMR spectrum of compound **4e**



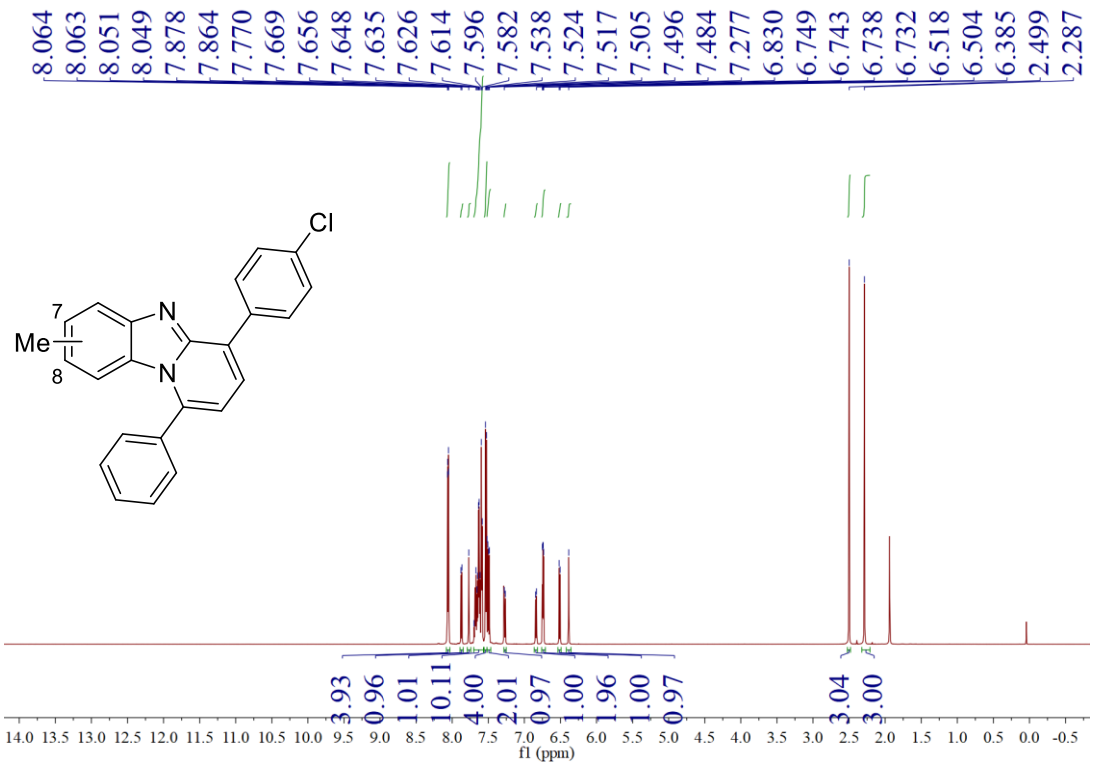
^{19}F NMR spectrum of compound **4e**



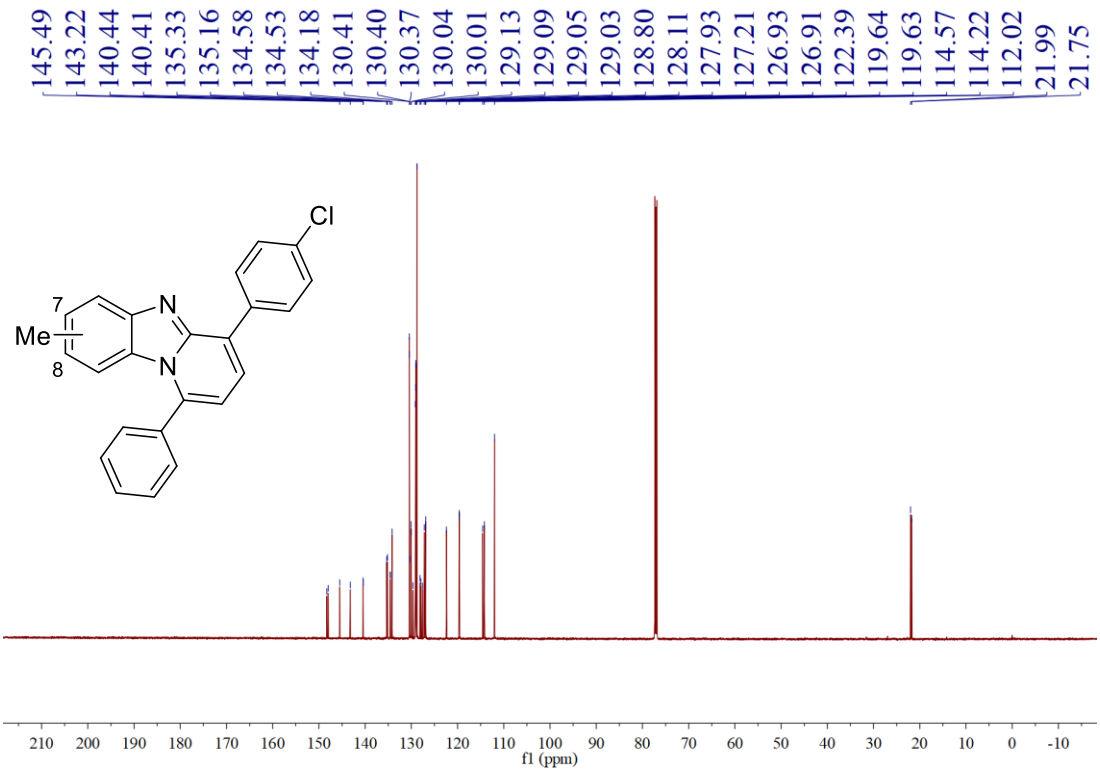
^{1}H NMR spectrum of compound **4f**



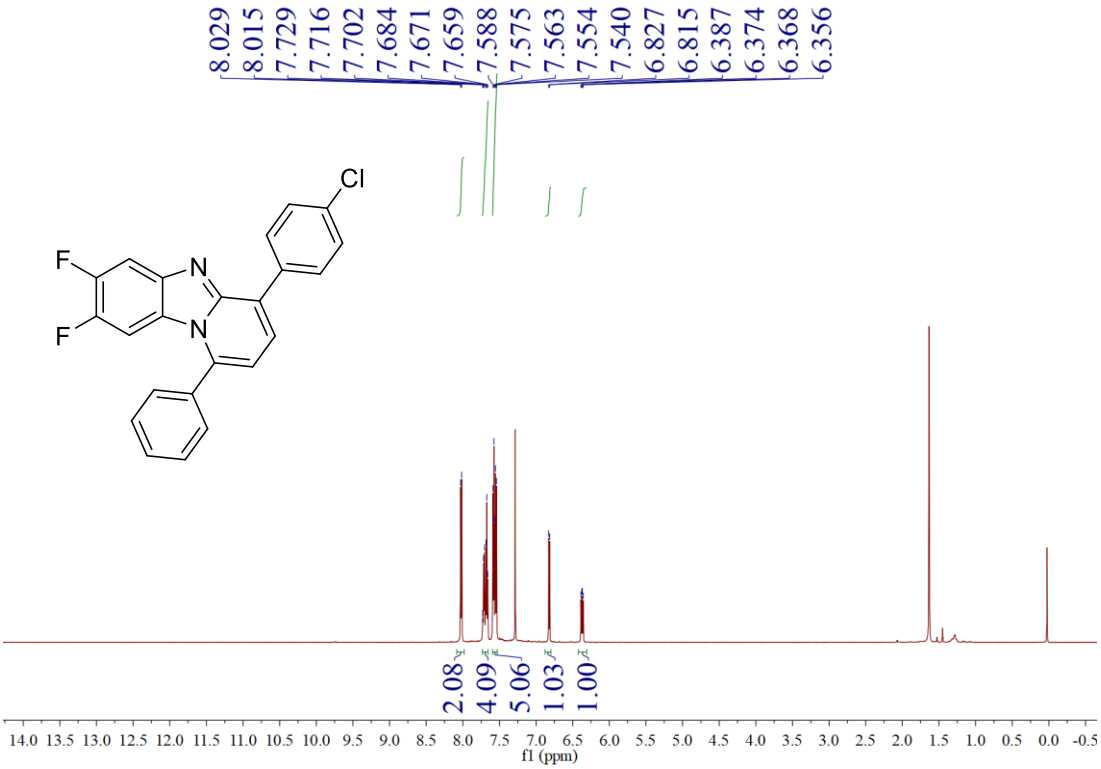
^{13}C NMR spectrum of compound **4f**



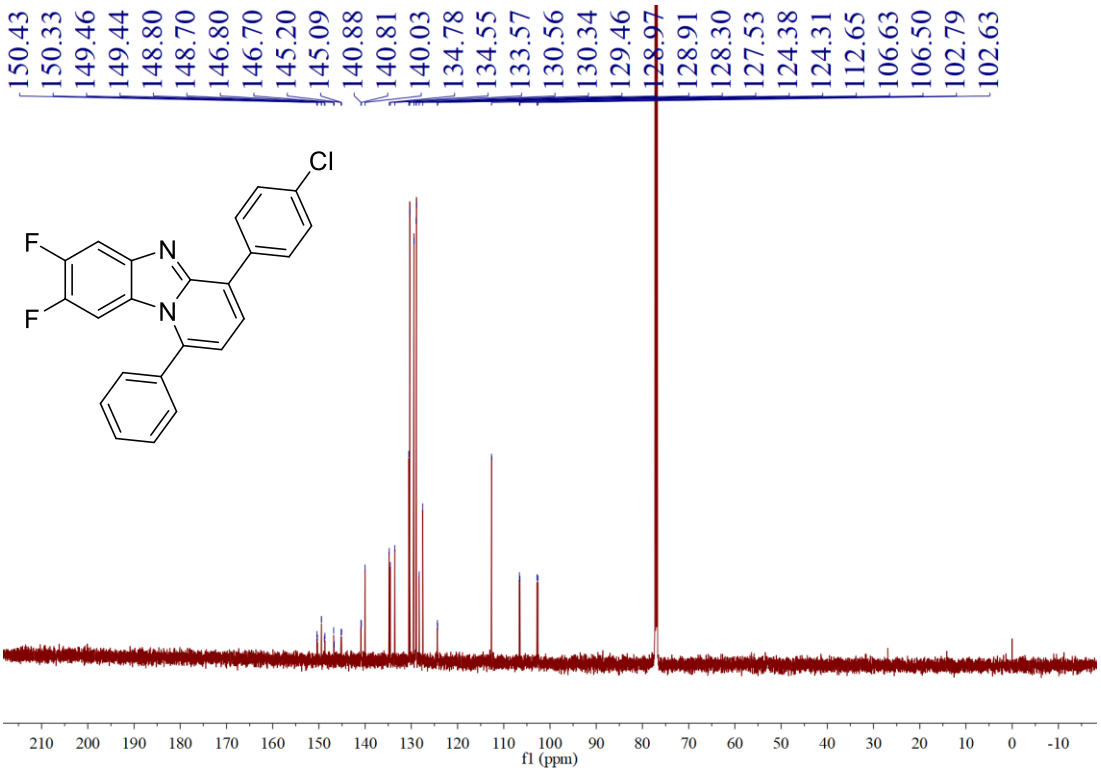
^{1}H NMR spectrum of compound **4g/4g'**



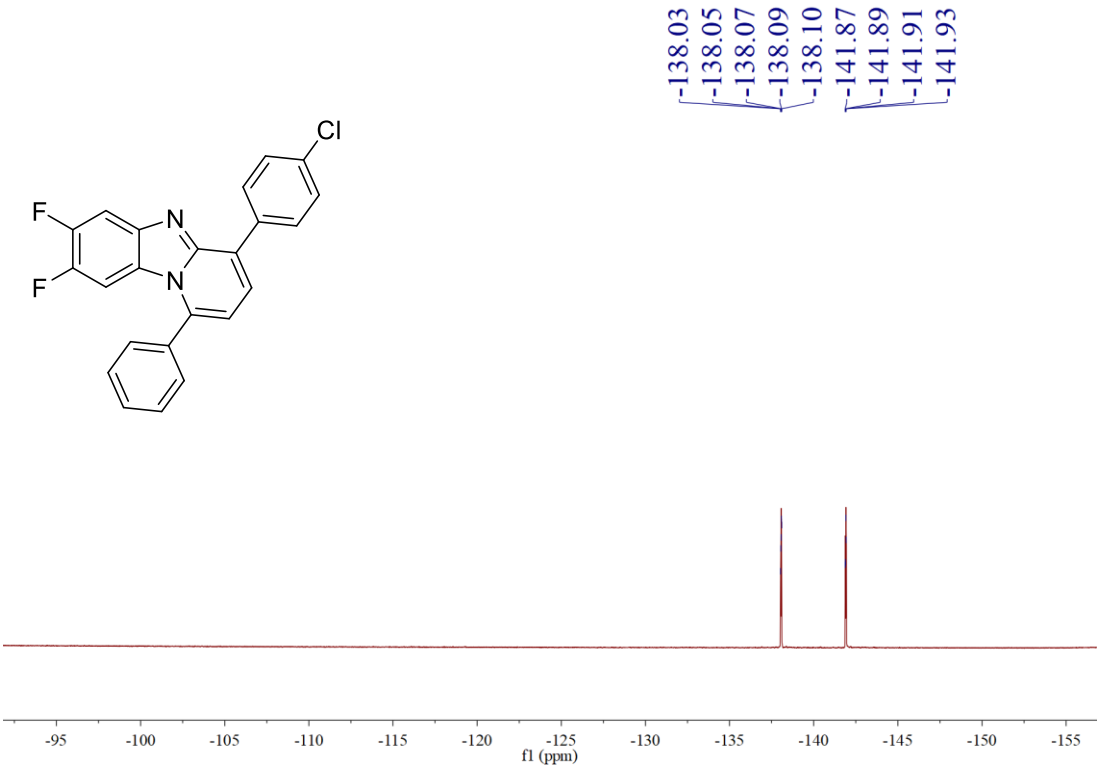
^{13}C NMR spectrum of compound **4g/4g'**



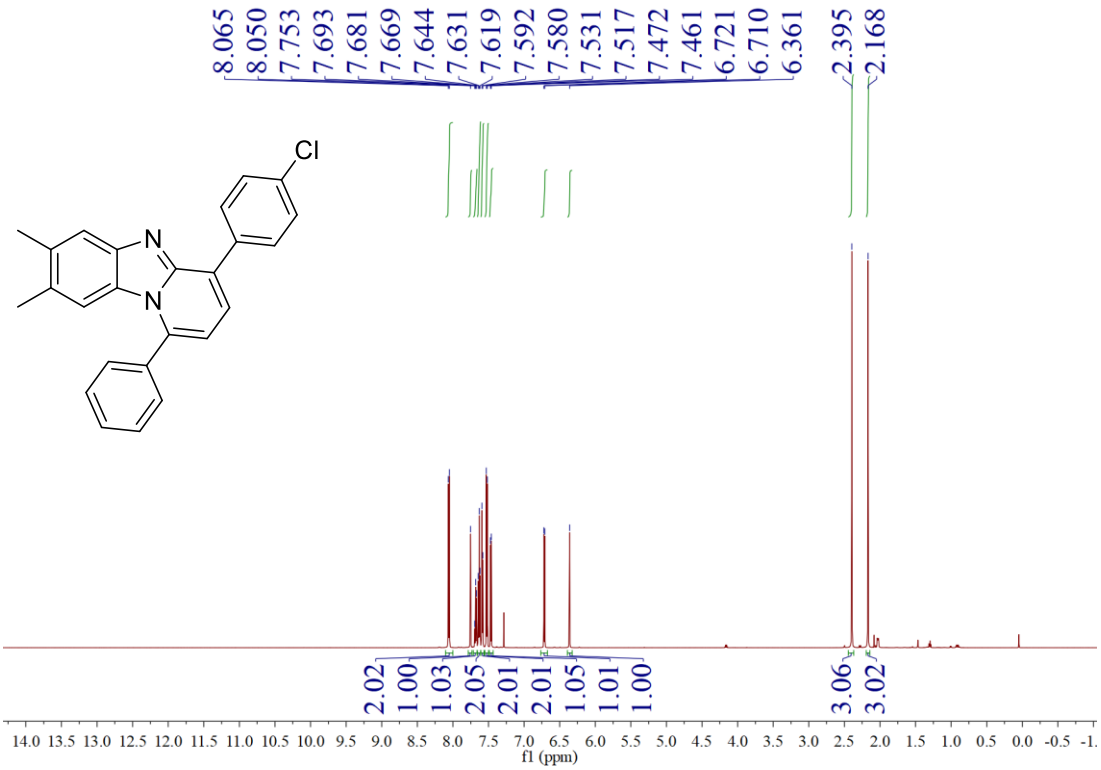
^{1}H NMR spectrum of compound **4h**



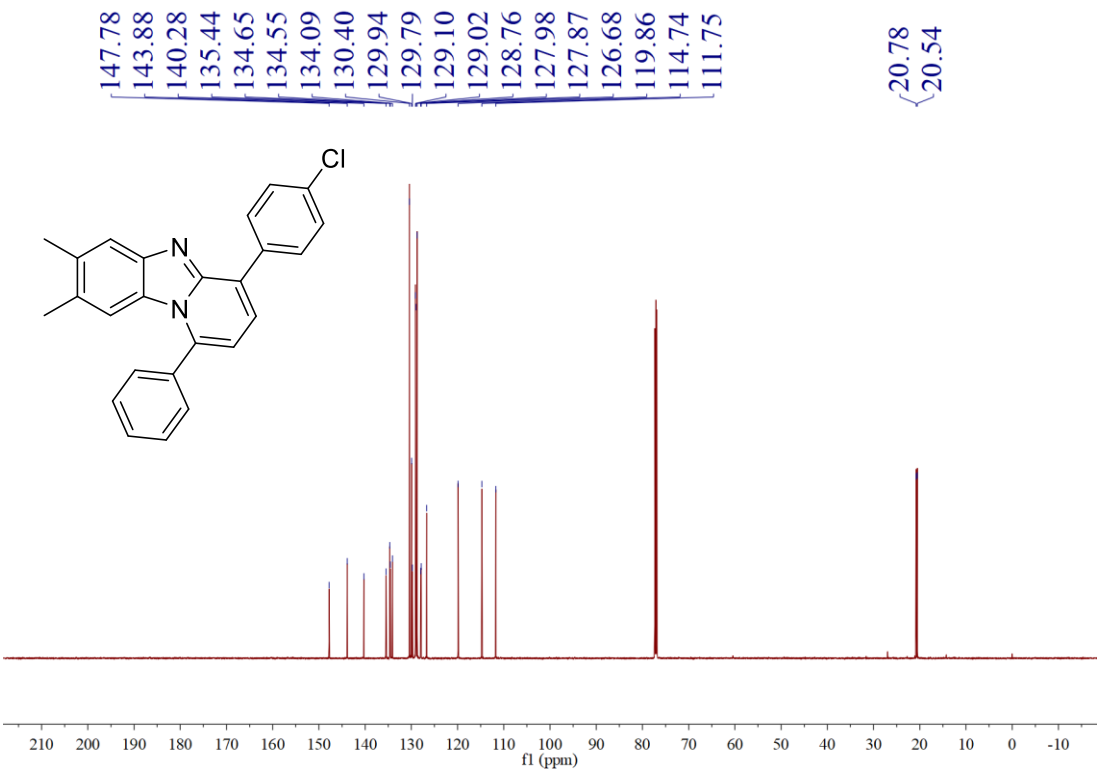
^{13}C NMR spectrum of compound **4h**



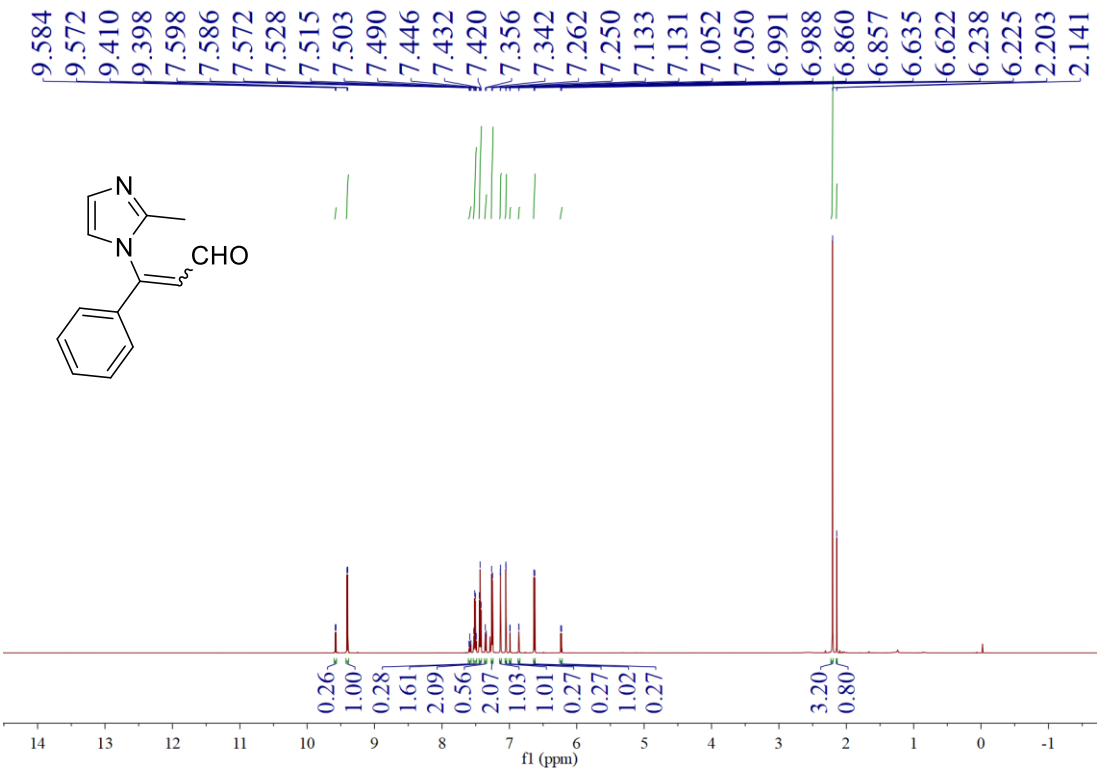
^{19}F NMR spectrum of compound **4h**



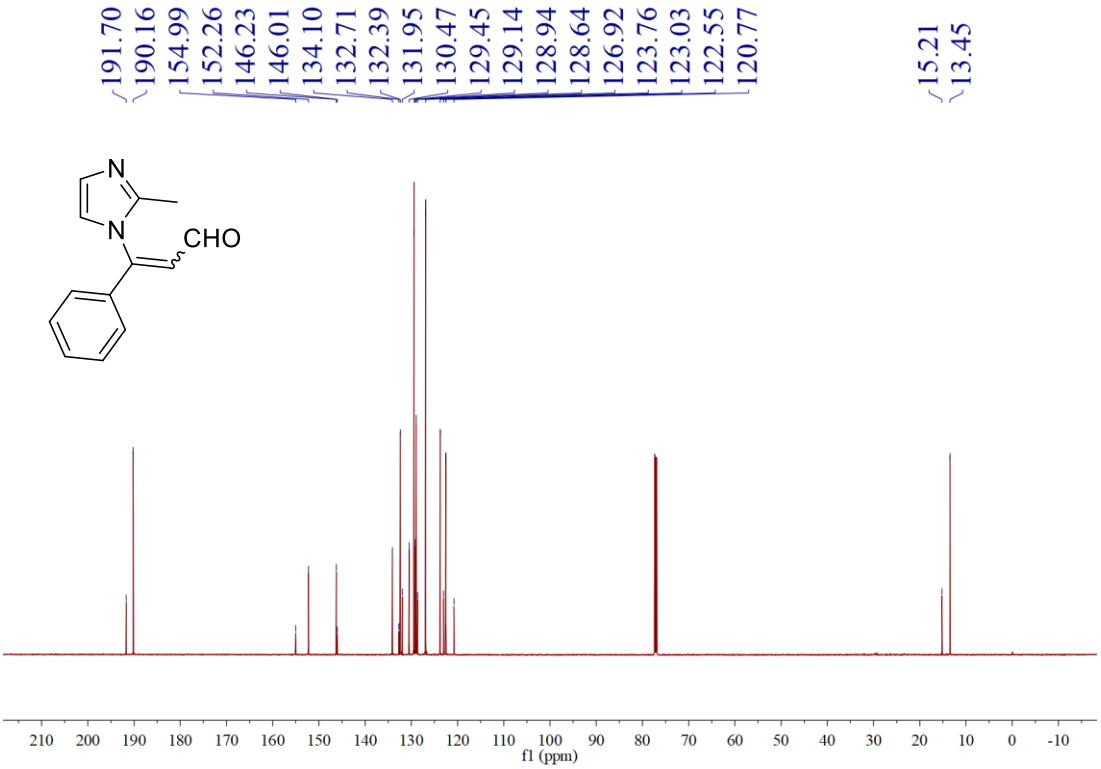
^{1}H NMR spectrum of compound **4i**



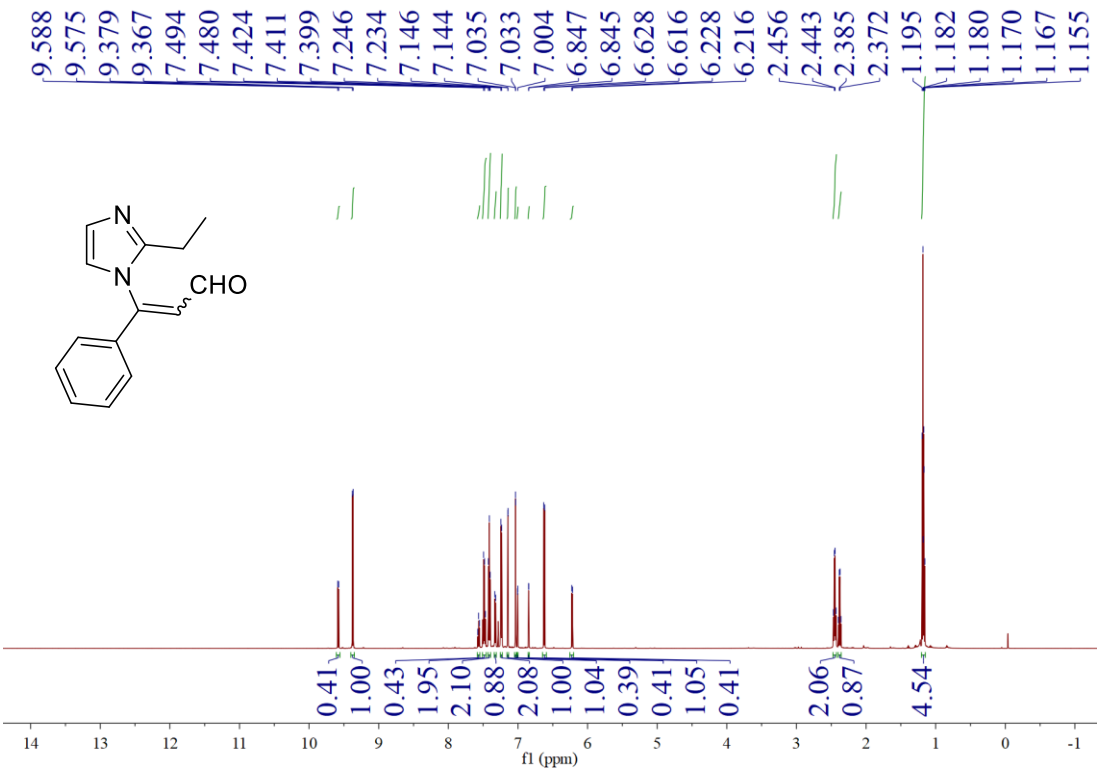
^{13}C NMR spectrum of compound **4i**



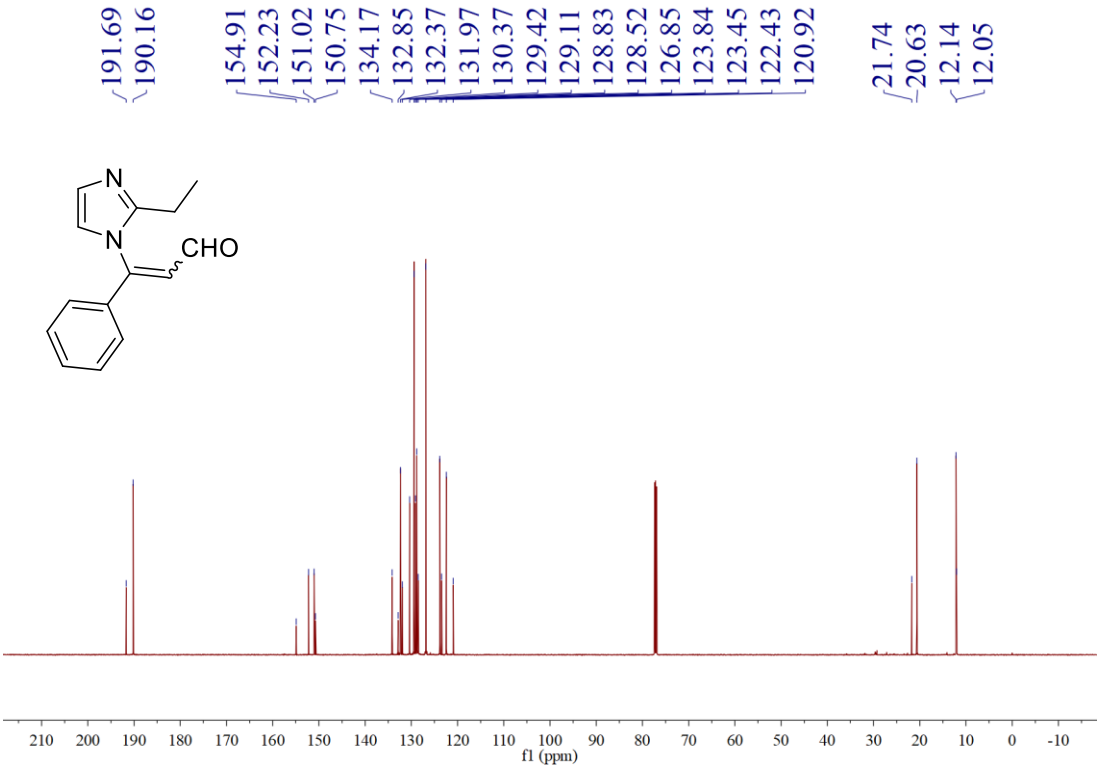
^{1}H NMR spectrum of compound **4j**



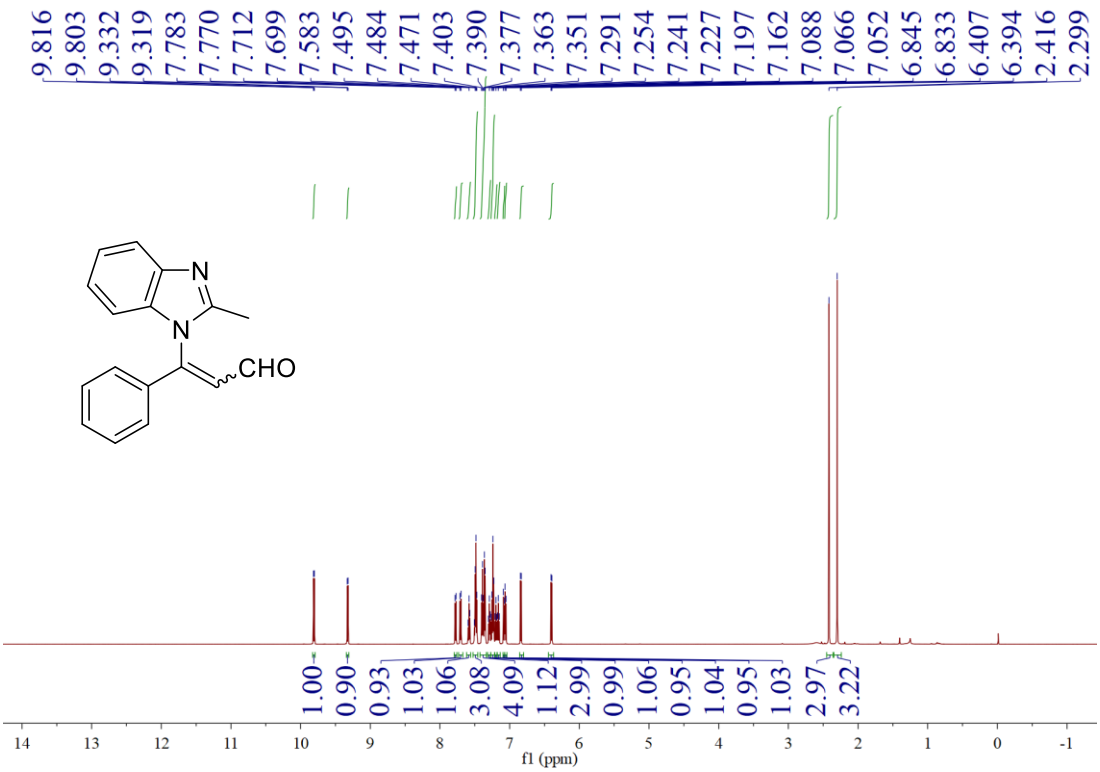
^{13}C NMR spectrum of compound **4j**



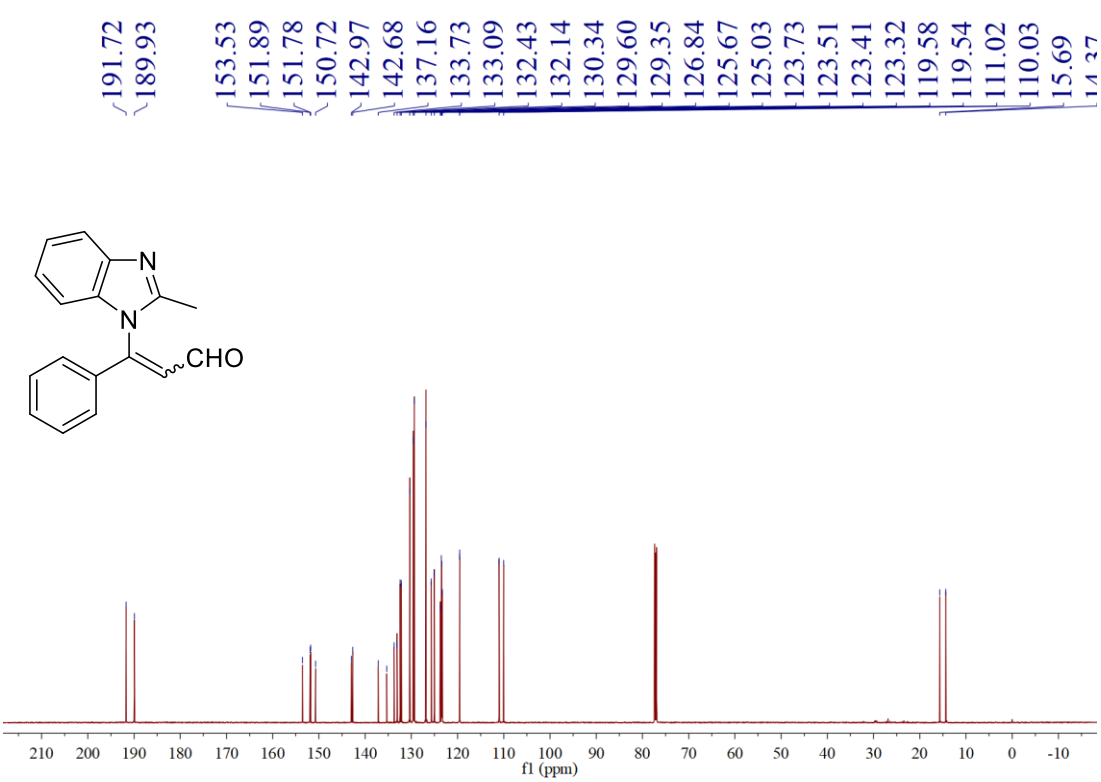
^{1}H NMR spectrum of compound **4k**



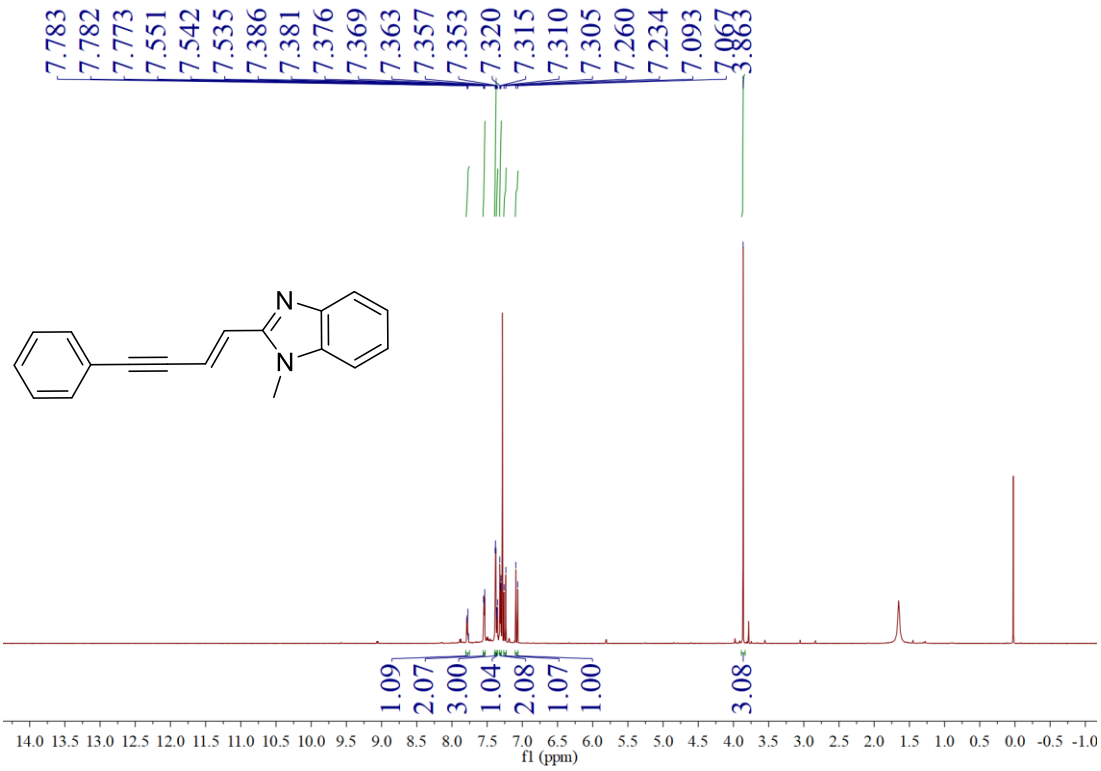
^{13}C NMR spectrum of compound **4k**



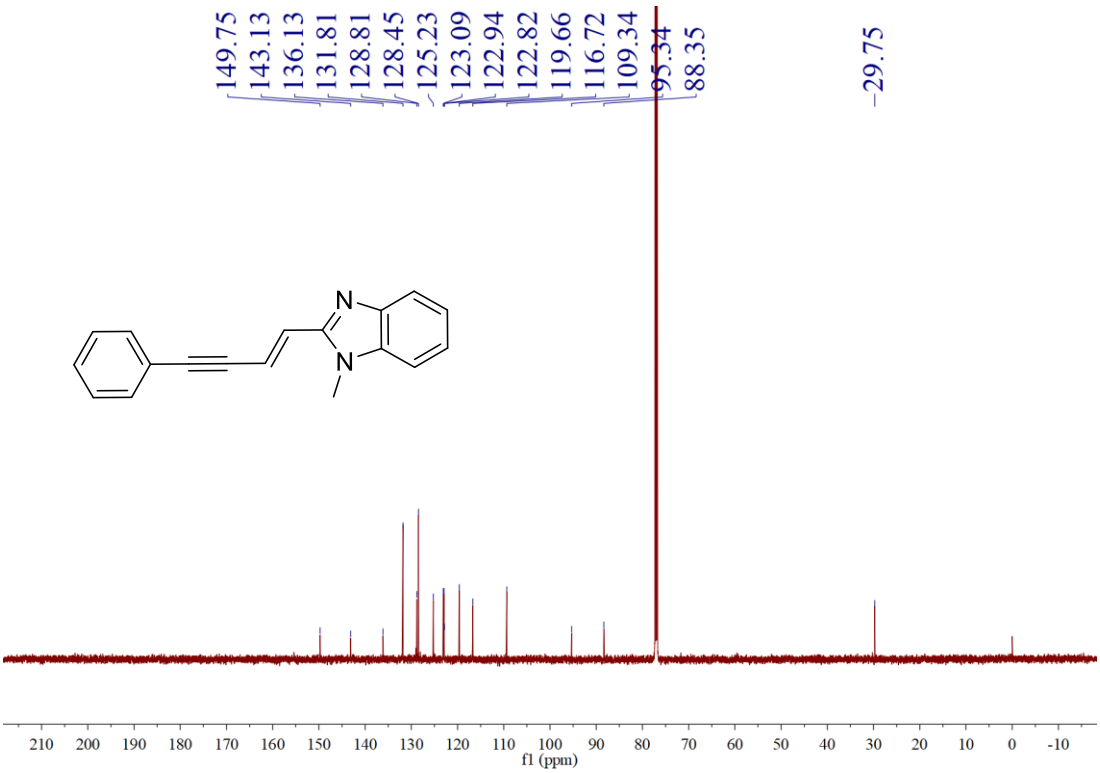
^{1}H NMR spectrum of compound **3aa**



^{13}C NMR spectrum of compound **3aa**



^{1}H NMR spectrum of compound **3ab**



^{13}C NMR spectrum of compound **3ab**

References

[1] D. Obermayer, D. Znidar, G. Glotz, A. Stadler, D. Dallinger, C. O. Kappe, *J. Org. Chem*., 2016, **81**, 11788.

[2] H. Qin, Y.-Y. Miao, J. Xu, Q.-R. Bi, W. Qu, W.-Y. Liu, F. Feng, H.-P. Sun, *Org. Chem. Front*., 2019, **6**, 205.

[3] Y.-F. Zhao, L.-B. Xu, F.-L. Kong, L. Yu, *Chem. Eng. J.*, 2021, **416**, 129090.

[4] C. Pherkkhuntod, V. Ervithayasuporn, S. Chanmungkalakul, C. Wang, X. G. Liu, D. J. Harding, S. Kiatkamjornwong, *Sens. Actuators, B*, 2021, **330**, 129287.

[5] W.-M. Wan, D. Tian, Y.-N. Jing, X.-Y. Zhang, W. Wu, H. Ren, H.-L. Bao, *Angew. Chem., Int. Ed.*, 2018, **57**, 15510.

[6] B.-W. Wang, K. Jiang, J.-X. Li, S.-H. Luo, Z.-Y. Wang, H.-F. Jiang, *Angew. Chem., Int. Ed*., 2020, **59**, 2338.

[7] Y.-C. Wu, J.-P. Huo, L. Cao, S. Ding, L.-Y. Wang, D.-R. Cao, Z.-Y. Wang, *Sens. Actuators, B*, 2016, **237**, 865.

[8] K. Jiang, S.-H. Luo, C.-M. Pang, B.-W. Wang, H.-Q. Wu, Z.-Y. Wang, *Dyes Pigm.*, 2019, **162**, 367.

[9] K. Jiang, S.-H. Chen, S.-H. Luo, C.-M. Pang, X.-Y. Wu, Z.-Y. Wang, *Dyes Pigm.*, 2019, **167**, 164.

[10] S.-H. Chen, K. Jiang, J.-Y. Lin, K. Yang, X.-Y. Cao, X.-Y. Luo, Z.-Y. Wang, *J. Mater. Chem. C*, 2020, **8**, 8257.

[11] M. Gupta, H. Lee, *ACS Appl. Mater. Interfaces*, 2018, **10**, 41717.

[12] S.-L. Yi, Z. Lu, Z.-H. Xie, L.-X. Hou, *Talanta*, 2020, **208**, 120372.

[13] Y.-P. Zhuang, J.-Y. Yao, Z.-Y. Zhuang, C.-J. Ni, H.-M. Yao, D.-L. Su, J.Zhou, Z.-J. Zhao, *Dyes Pigm*., 2020, **174**, 108041.

[14] K. Li, R.-H. Yu, C.-M. Shi, F.-R. Tao, T.-D. Li, Y.-Z. Cui, *Sens. Actuators, B*, 2018, **262**, 637.

[15] Z.-J. Luo, B. Liu, S.-F. Si, Y.-J. Lin, C.-S. Luo, C.-J. Pan, C. Zhao, L. Wang, *Dyes Pigm*., 2017, **143**, 463.

[16] X.-D. Yu, J.-B. Guo, P. Peng, F.-J. Shen, Y.-J. Li, L.-J. Geng, T. Wang, *Appl. Surf. Sci*., 2019, **487**, 473.

[17] W.-Y. Dong, Q.-H. Ma, Z.-H. Ma, Q. Duan, X.-L. Lu, N.-N. Qiu, T. Fei, Z.-M. Su, *Dyes Pigm*., 2020, **172**, 107799.