

# Supporting Information

## **I<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> mediated synthesis and photophysical properties of imidazole-fused heterocycles via [4+1] cyclization approach**

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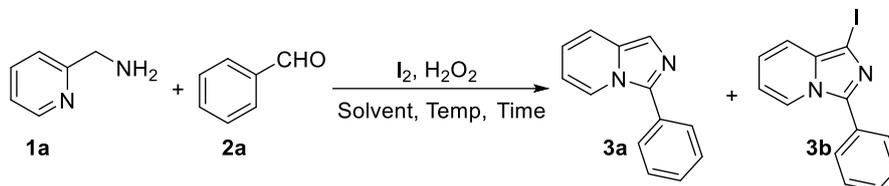
# 1. General Information

## Reagents, solvents, and analytical methods:

Unless otherwise noted, all reactions were carried out under an atmospheric atmosphere. All reagents were from commercial sources and used as received without further purification. All solvents were dried by standard techniques and distilled before use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (bp. 60~90 °C) and ethyl acetate as eluent. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance operating for <sup>1</sup>H NMR at 400 MHz, <sup>13</sup>C NMR at 101 MHz, and <sup>19</sup>F NMR at 376 MHz. NMR spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard and CDCl<sub>3</sub> (<sup>1</sup>H NMR δ 7.27, <sup>13</sup>C NMR δ 77.0), DMSO (<sup>1</sup>H NMR δ 5.20, <sup>13</sup>C NMR δ 39.52) as solvent. All coupling constants (J) are reported in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, dd = double doublet, ddd = double doublet of doublets, t = triplet, dt = double triplet, q = quatrimplet, m = multiplet, br = broad. High-resolution mass spectra (HRMS) are produced on Q-Exactive Orbitrap HR-MS (Thermo Fisher Scientific, Waltham, Massachusetts). All the amines and aldehydes used here were commercially available. The raw material used in the reaction were purchased from Aladdin, Macklin, and so on.

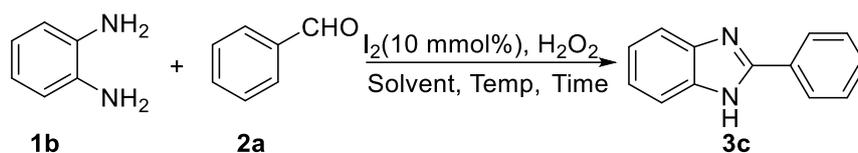
## 2. Optimization of Reaction Conditions and Control experiment

Table S1. Optimization for generating **3b**<sup>[a]</sup>



Entry	$I_2$ (x mmol)	$H_2O_2$ (mmol)	Solvent (5 mL)	Time (h)	Temp. (°C)	Yield (%) <sup>[b]</sup>	
						3a	3b
1	0	3	CH <sub>3</sub> CN	1.2	70	0	0
2	0.2	3	CH <sub>3</sub> CN	1.2	70	25	48
3	0.3	3	CH <sub>3</sub> CN	1.2	70	19	58
4	0.4	3	CH <sub>3</sub> CN	1.2	70	12	69
5	0.5	3	CH <sub>3</sub> CN	1.2	70	0	76
6	0.6	3	CH <sub>3</sub> CN	1.2	70	0	72
7	0.5	2	CH <sub>3</sub> CN	1.2	70	7	69
8	0.5	4	CH <sub>3</sub> CN	1.2	70	3	67
9	0.5	5	CH <sub>3</sub> CN	1.2	70	5	64
10	0.5	6	CH <sub>3</sub> CN	1.2	70	5	62
11	0.5	3	DMF	1.2	70	0	75
12	0.5	3	DMSO	1.2	70	0	74
13	0.5	3	THF	1.2	70	32	47
14	0.5	3	Dioxane	1.2	70	29	32
15	0.5	3	DCE	1.2	70	48	39
16	0.5	3	H <sub>2</sub> O	1.2	70	0	35
17	0.5	3	CH <sub>3</sub> CH <sub>2</sub> OH	1.2	70	10	73
18	0.5	3	CH <sub>3</sub> CN	0.5	70	11	69
19	0.5	3	CH <sub>3</sub> CN	1	70	7	77
20	0.5	3	CH <sub>3</sub> CN	2	70	0	84
21	0.5	3	CH <sub>3</sub> CN	3	70	0	61
22	0.5	3	CH <sub>3</sub> CN	4	70	0	54
23	0.5	3	CH <sub>3</sub> CN	5	70	0	39
24	0.5	3	CH <sub>3</sub> CN	2	20	0	67
25	0.5	3	CH <sub>3</sub> CN	2	40	0	87
26	0.5	3	CH <sub>3</sub> CN	2	60	0	86
27	0.5	3	CH <sub>3</sub> CN	2	80	0	81
28	0.5	3	CH <sub>3</sub> CN	2	90	5	79

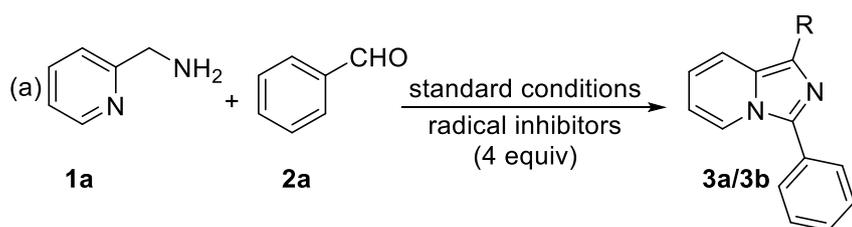
<sup>[a]</sup> Reaction conditions: **1a** (0.8 mmol), **2a** (1.6 mmol),  $I_2$  (0.5 mmol),  $H_2O_2$  (3 mmol), CH<sub>3</sub>CN (5 mL), 2 h, 40 °C, in an oil bath, opened tube, <sup>[b]</sup> isolated yield.

**Table S2.** Optimization for generating **3c**<sup>[a]</sup>

Entry	$H_2O_2$ (mmol)	<b>2a</b> (mmol)	Solvent (5 mL)	Time (h)	Temp. (°C)	Yield (%) <sup>[b]</sup> <b>3c</b>
1	2	1	CH <sub>3</sub> CN	2	50	59
2	3	1	CH <sub>3</sub> CN	2	50	67
3	4	1	CH <sub>3</sub> CN	2	50	69
4	5	1	CH <sub>3</sub> CN	2	50	71
5	6	1	CH <sub>3</sub> CN	2	50	73
6	7	1	CH <sub>3</sub> CN	2	50	76
7	8	1	CH <sub>3</sub> CN	2	50	70
8	7	0.4	CH <sub>3</sub> CN	2	50	66
9	7	0.6	CH <sub>3</sub> CN	2	50	74
10	7	0.75	CH <sub>3</sub> CN	2	50	77
11	7	1.25	CH <sub>3</sub> CN	2	50	80
12	7	1.75	CH <sub>3</sub> CN	2	50	81
13	7	2	CH <sub>3</sub> CN	2	50	78
14	7	1.75	DMF	2	50	66
15	7	1.75	DMSO	2	50	68
16	7	1.75	THF	2	50	53
17	7	1.75	Dioxane	2	50	39
18	7	1.75	DCE	2	50	63
19	7	1.75	H <sub>2</sub> O	2	50	41
20	7	1.75	CH <sub>3</sub> CH <sub>2</sub> OH	2	50	79
21	7	1.75	CH <sub>3</sub> CN	1	50	83
22	7	1.75	CH <sub>3</sub> CN	2.5	50	76
23	7	1.75	CH <sub>3</sub> CN	3	50	74
24	7	1.75	CH <sub>3</sub> CN	4	50	70
25	7	1.75	CH <sub>3</sub> CN	5	50	68
26	7	1.75	CH <sub>3</sub> CN	1	rt	69
27	7	1.75	CH <sub>3</sub> CN	1	45	78
28	7	1.75	CH <sub>3</sub> CN	1	60	85
29	7	1.75	CH <sub>3</sub> CN	1	80	90
30	7	1.75	CH <sub>3</sub> CN	1	90	86

<sup>[a]</sup> Reaction conditions: **1b** (1 mmol), **2a** (1.75 mmol),  $I_2$  (10 mmol%),  $H_2O_2$  (7 mmol), CH<sub>3</sub>CN (5 mL), 1 h, 80 °C, in an oil bath, opened tube, <sup>[b]</sup> isolated yield.

**Scheme S1. Control Experiment**



**For generating 3a: R = H, 1a:2a = 2:1, I<sub>2</sub> (10 mmol%), 3 h, 60 °C**

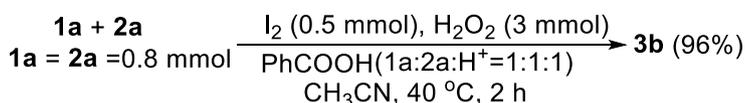
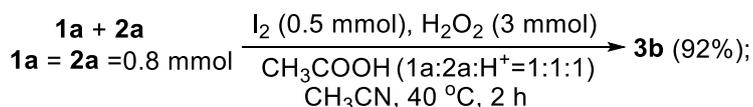
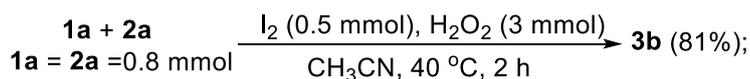
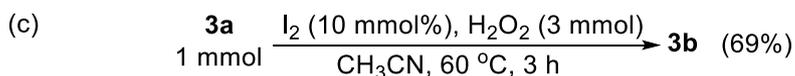
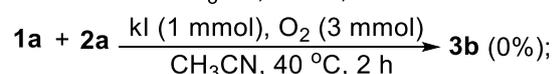
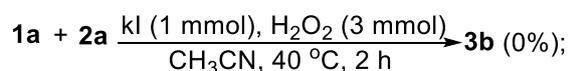
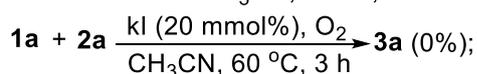
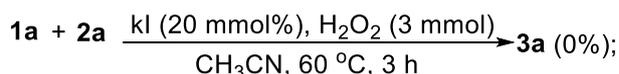
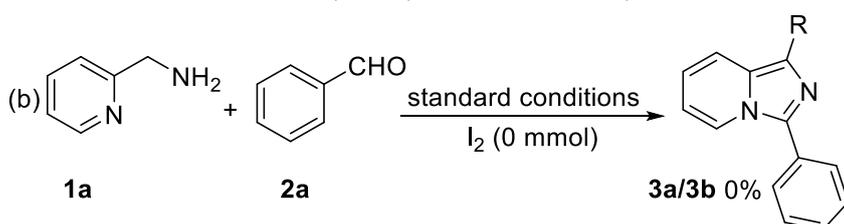
TEMPO (60 °C) 79% **3a** (without TEMPO, 84% **3a**)

BHT (60 °C) 71% **3a** (without BHT, 84% **3a**)

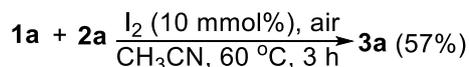
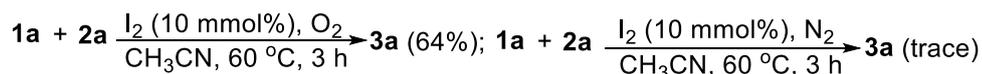
**For generating 3b: R = I, 1a:2a = 1:2, I<sub>2</sub> (0.5 mmol), 2 h, 40 °C**

TEMPO (40 °C) 84% **3b** (without TEMPO, 87% **3b**)

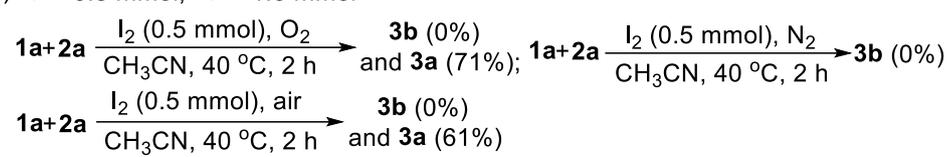
BHT (40 °C) 72% **3b** (without BHT, 87% **3b**)



(d) **1a = 0.8 mmol, 2a = 0.4 mmol**



(e) **1a** = 0.8 mmol, **2a** = 1.6 mmol



### 3. General Procedure

#### 1.1. General Procedure A

**General Procedures for the Synthesis of 3-phenyl-imidazo[1,5-a]pyridine by benzaldehyde and 2-pyridinemethanamine.1a** (0.8 mmol, 2 eq.), **2a** (0.4 mmol, 1 eq.), I<sub>2</sub> (25.4 mg, 10 mmol%), 30% hydrogen peroxide (3 mmol), CH<sub>3</sub>CN (5 mL) were transferred into a 25 mL round-bottom flask equipped with a spherical condensing tube. Then the reaction flask was placed in a heating block that was preheated to 60 °C. The reaction was monitored by checking the TLC. After some time of 3 h, the reaction flask was allowed to cool to room temperature. The mixture was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel eluting with petroleum ether/EtOAc (v/v = 20:1 to 5:1) to afford the products **3a**.

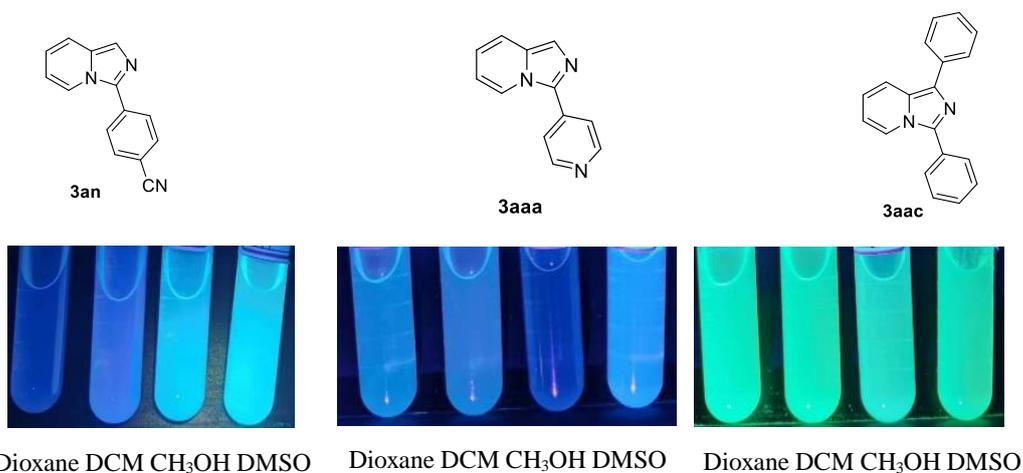
#### 1.2. General Procedure B

**General Procedures for the Synthesis of 1-iodo-3-phenyl-imidazo[1,5-a]pyridine, by benzaldehyde and 2-pyridinemethanamine.1a** (0.8 mmol, 1 eq.), **2a** (1.6 mmol, 2 eq.), I<sub>2</sub> (127 mg, 0.5 mmol), 30% hydrogen peroxide (3 mmol), CH<sub>3</sub>CN (5 mL) were transferred into a 25 mL round-bottom flask equipped with a spherical condensing tube. Then the reaction flask was placed in a heating block that was preheated to 40 °C. The reaction was monitored by checking the TLC. After some time of 2 h, the reaction flask was allowed to cool to room temperature. The mixture was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel eluting with petroleum ether/EtOAc (v/v = 15:1 to 3:1) to afford the products **3b**.

#### 1.3. General Procedure C

**General Procedures for the Synthesis of 2-phenyl-1H-benzimidazole by benzaldehyde and 1, 2-benzenediamine. 1b** (1 mmol, 1 eq.), **2a** (1.75 mmol, 1.75 eq.), I<sub>2</sub> (25.4 mg, 10 mmol%), 30% hydrogen peroxide (7 mmol), CH<sub>3</sub>CN (5 mL) were transferred into a 25 mL round-bottom flask equipped with a spherical condensing tube. Then the reaction flask was placed in a heating block that was preheated to 80 °C. The reaction was monitored by checking the TLC. After some time of 1 h, the reaction flask was allowed to cool to room temperature. The mixture was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel eluting with petroleum ether/EtOAc (v/v = 20:1 to 5:1) to afford the products **3c**.

## 4. Photophysical Properties of Selected Products



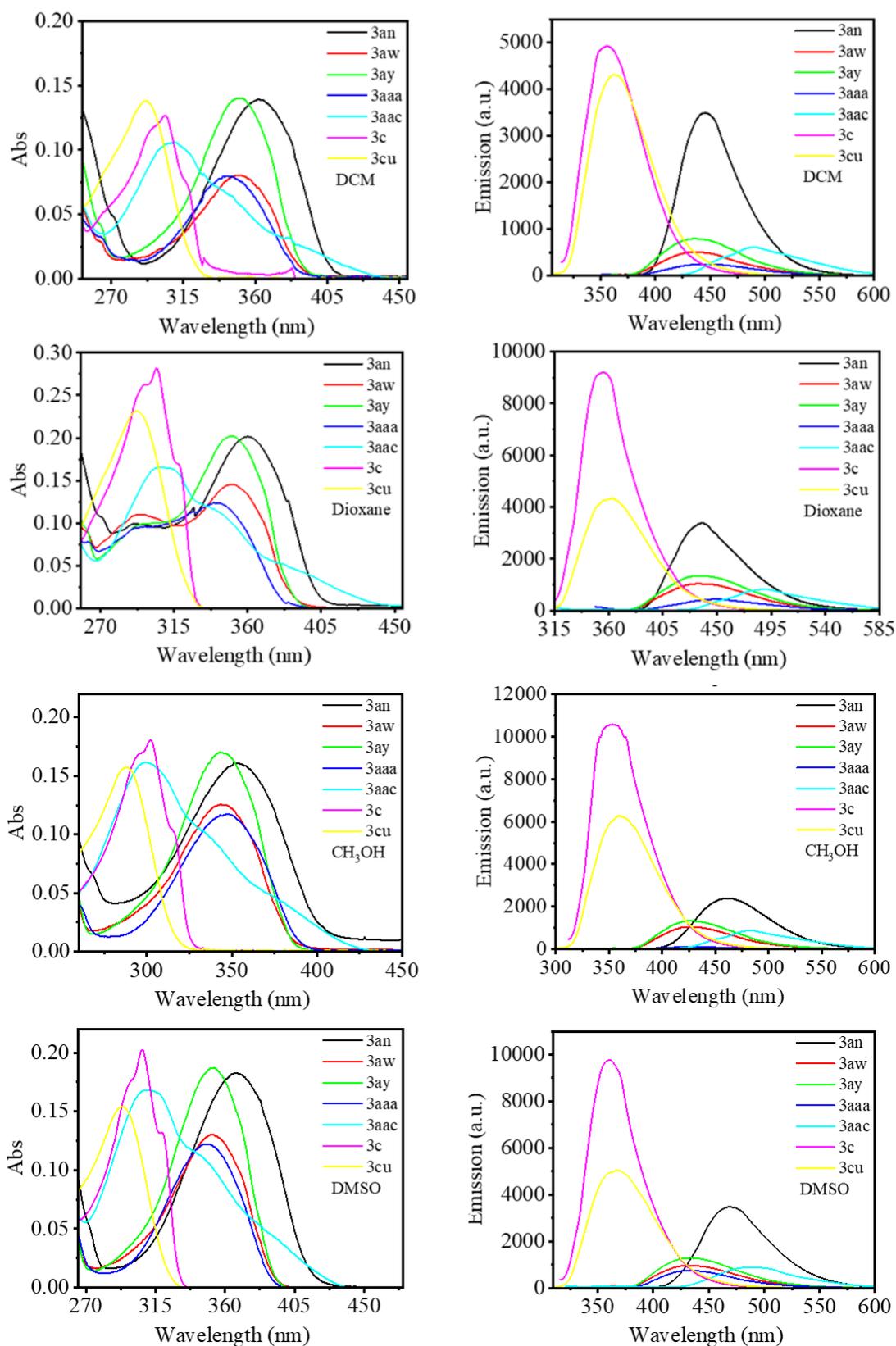
**Figure S1.** Partially selected emission of obtained **3an**, **3aaa**, and **3aac** in four solvents under 365nm irradiation.

**Table S3.** Wavelengths of maximum absorbance and maximum emission and Stokes shift and the fluorescence quantum yields of selected products in DCM, Dioxane, MeOH, and DMSO.

S.NO	$\lambda_{abs}(nm)$ (log $\epsilon$ )				$\lambda_{em}(nm)$ (Stokes shift $cm^{-1}$ )			
	DCM	Dioxane	MeOH	DMSO	DCM	Dioxane	MeOH	DMSO
<b>3a</b>	320 (3.84)	321 (4.15)	313 (4.00)	324 (4.16)	455 (9272)	457 (9271)	451 (9776)	460 (9125)
<b>3b</b>	329 (4.03)	328 (4.14)	320 (4.04)	331 (4.08)	468 (9028)	466 (9029)	459 (9464)	468 (8844)
<b>3ab</b>	315 (3.86)	310 (4.14)	309 (3.91)	316 (4.00)	451 (9573)	453 (10183)	443 (9789)	451 (9473)
<b>3ac</b>	326 (3.95)	322 (4.13)	320 (4.04)	329 (4.09)	457 (8793)	457 (9174)	451 (9077)	456 (8465)
<b>3ad</b>	315 (3.92)	307 (4.19)	309 (3.90)	318 (4.07)	461 (10054)	462 (10928)	454 (10336)	459 (9660)
<b>3an</b>	362 (4.14)	360 (4.30)	352 (4.18)	368 (4.26)	447(5253)	439 (4999)	463 (6811)	470 (5897)
<b>3ao</b>	338 (3.82)	340 (3.94)	333 (3.75)	346 (3.85)	453 (7511)	453 (7337)	448 (7709)	447 (6530)
<b>3ar</b>	315 (4.00)	313 (4.06)	309 (4.06)	320 (4.10)	462 (10101)	461 (10257)	456 (10433)	466 (9791)
<b>3at</b>	308 (4.07)	306 (4.18)	304 (4.04)	314 (4.19)	474 (11370)	468 (11312)	466 (11436)	473 (10705)
<b>3au</b>	329 (4.20)	332 (4.20)	324 (4.16)	336 (4.16)	468 (9028)	463 (8522)	462 (9219)	462 (8117)
<b>3av</b>	337 (4.04)	338 (4.15)	334 (4.07)	340 (4.16)	472 (8487)	472 (8399)	465 (8435)	476 (8403)
<b>3aw</b>	351 (3.90)	350 (4.16)	343 (4.09)	352 (4.11)	437 (5607)	438 (5740)	428 (5790)	434 (5368)
<b>3ax</b>	329 (4.23)	328 (4.21)	320 (4.06)	327 (4.16)	459 (8609)	458 (8654)	455 (9272)	461 (8889)
<b>3ay</b>	350 (4.14)	350 (4.31)	343 (4.23)	353 (4.27)	436 (5636)	438 (5740)	429 (5844)	435 (5340)
<b>3az</b>	330 (3.93)	328 (4.13)	327 (4.10)	334 (4.12)	455 (8325)	458 (8654)	449 (8309)	457 (8058)
<b>3aaa</b>	340 (3.89)	339 (4.09)	348 (4.07)	348 (4.09)	448 (7090)	450 (7276)	430 (5480)	434 (5694)
<b>3aab</b>	324 (3.96)	317 (4.17)	320 (3.84)	328 (4.10)	470 (9588)	467 (10132)	466 (9791)	470 (9211)
<b>3aac</b>	310 (4.02)	306 (4.17)	299 (4.21)	311 (4.23)	489 (11808)	491 (12313)	484 (12784)	489 (11704)
<b>3c</b>	303 (4.37)	305 (4.46)	302 (4.54)	306 (4.54)	357 (4992)	356 (4697)	355 (4944)	361 (4979)
<b>3cu</b>	292 (4.32)	293 (4.42)	288 (4.13)	292 (4.34)	365 (6849)	362 (6505)	357 (6711)	368 (7073)

**Table S4** Fluorescence quantum yields of 20 selected compounds in DCM, Dioxane, MeOH and DMSO

S.NO	Quantum Yield			
	DCM	Dioxane	MeOH	DMSO
<b>3a</b>	0.0720	0.0688	0.0757	0.0880
<b>3b</b>	< 0.05	< 0.05	< 0.05	< 0.05
<b>3ab</b>	0.0728	0.0588	0.0864	0.1064
<b>3ac</b>	0.0656	0.0656	0.0713	0.0920
<b>3ad</b>	0.0609	0.0435	0.0720	0.0856
<b>3an</b>	0.5125	0.3488	0.3411	0.4670
<b>3ao</b>	0.0782	0.0922	0.0909	0.1437
<b>3ar</b>	0.0520	0.0547	0.0598	0.0773
<b>3at</b>	< 0.05	< 0.05	0.0529	0.0642
<b>3au</b>	0.0539	0.0753	0.0729	0.1273
<b>3av</b>	< 0.05	< 0.05	< 0.05	0.0538
<b>3aw</b>	0.1658	0.2222	0.1822	0.2021
<b>3ax</b>	0.0540	0.0565	0.0635	0.0631
<b>3ay</b>	0.1490	0.1708	0.1691	0.1883
<b>3az</b>	0.0737	0.0846	< 0.05	0.0878
<b>3aaa</b>	0.0891	0.1090	< 0.05	0.1602
<b>3aab</b>	0.2694	0.2186	0.2817	0.2518
<b>3aac</b>	0.1587	0.1707	0.1218	0.1516
<b>3c</b>	0.6374	0.5777	0.5007	0.5601
<b>3cu</b>	0.4999	0.3822	0.5673	0.4688

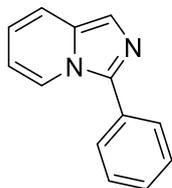


**Figure S2.** Partially electronic absorption and emission spectra of selected compounds recorded in DCM, Dioxane, MeOH, and DMSO ( $1 \times 10^{-5}$  M).

**Table S5.** Comparison of experimental absorption wavelengths for selected compounds with theoretical calculations: electron transition, HOMO and LUMO energies, oscillator intensity, and absorption wavelength.

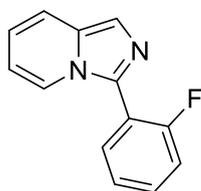
S.No.	Solvents	$\lambda_{\text{exp}}$ (nm)	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$\lambda_{\text{calc}}$ (nm)	$E$ (eV)	$f_{\text{osc}}$	Transitions
<b>3a</b>	DCM	320	-6.35	0.10	283	4.39	0.5419	H→L+1 0.65
	Dioxane	321	-6.32	0.07	283	4.38	0.5473	H→L+1 0.66
	MeOH	313	-6.38	0.11	280	4.43	0.5000	H→L+1 0.65
	DMSO	324	-6.37	0.11	283	4.38	0.5390	H→L+1 0.63
<b>3an</b>	DCM	362	-6.48	-0.73	325	3.81	0.6746	H→L 0.69
	Dioxane	360	-6.56	-0.75	322	3.85	0.6616	H→L 0.69
	MeOH	352	-6.48	-0.72	323	3.84	0.6233	H→L 0.69
	DMSO	368	-6.47	-0.73	326	3.80	0.6746	H→L 0.69
<b>3at</b>	DCM	308	-6.23	0.14	276	4.48	0.6238	H→L+1 0.68
	Dioxane	306	-6.18	0.13	277	4.48	0.6127	H→L+1 0.68
	MeOH	304	-6.27	0.14	275	4.51	0.5909	H→L+1 0.68
	DMSO	314	-6.25	0.14	276	4.48	0.6229	H→L+1 0.68
<b>3ay</b>	DCM	350	-6.36	-0.21	310	3.99	0.5956	H→L 0.66
	Dioxane	350	-6.30	-0.16	311	4.00	0.5623	H→L 0.63
	MeOH	343	-6.39	-0.24	309	4.01	0.5713	H→L 0.66
	DMSO	353	-6.39	-0.24	310	3.99	0.6009	H→L 0.66
<b>3aaa</b>	DCM	340	-6.52	-0.30	303	4.09	0.4361	H→L 0.66
	Dioxane	339	-6.56	-0.28	299	4.15	0.5299	H→L 0.65
	MeOH	348	-6.52	-0.30	302	4.11	0.4471	H→L 0.68
	DMSO	348	-6.52	-0.31	304	4.08	0.5160	H→L 0.69
<b>3aac</b>	DCM	310	-6.13	-0.11	292	4.25	0.4750	H→L+1 0.68
					267	4.64	0.4904	H→L+2 0.67
	Dioxane	306	-6.09	-0.11	293	4.24	0.4701	H→L+1 0.68
					266	4.66	0.5393	H→L+2 0.68
	MeOH	299	-6.17	-0.10	289	4.29	0.4496	H→L+1 0.68
					266	4.66	0.4561	H→L+2 0.67
	DMSO	311	-6.16	-0.11	291	4.25	0.4738	H→L+1 0.68
					267	4.64	0.4661	H→L+2 0.67
<b>3c</b>	DCM	303	-7.08	-0.30	269	4.60	0.9077	H→L 0.68
	Dioxane	305	-7.03	-0.25	268	4.62	0.9025	H→L 0.67
	MeOH	302	-7.13	-0.30	266	4.66	0.8551	H→L 0.67
	DMSO	306	-7.12	-0.31	268	4.63	0.8928	H→L 0.68
<b>3cu</b>	DCM	292	-7.15	-0.13	259	4.80	0.7549	H→L 0.65
	Dioxane	293	-7.06	-0.09	260	4.77	0.7732	H→L 0.65
	MeOH	288	-7.20	-0.13	256	4.84	0.6942	H→L 0.64
	DMSO	292	-7.19	-0.16	258	4.80	0.7479	H→L 0.65

## 5. Experimental Characterization Data for the Products



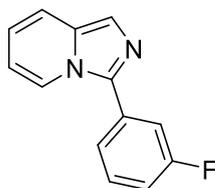
### 3-Phenyl-imidazo[1,5-a]pyridine (3a)<sup>[1]</sup>:

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and benzaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (65.2 mg, 84%) was obtained as a faint yellow solid.  $R_f = 0.3$  (petroleum ether / ethyl acetate = 20:1 - 5:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.10 (d,  $J = 6.8$  Hz, 1H), 7.66 (d,  $J = 6.76$  Hz, 2H), 7.49-7.16 (m, 5H), 6.55 (dd,  $J = 8.8, 6.0$  Hz, 1H), 6.38 (t,  $J = 6.8$  Hz, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 138.22, 131.61, 130.44, 128.96, 128.56, 127.89, 121.36, 120.63, 118.74, 113.03.



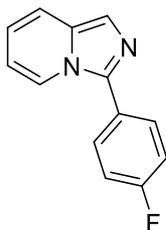
### 3-(2-fluorophenyl)-imidazo[1,5-a]pyridine (3ab)<sup>[2]</sup>:

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and 2-fluoro-benzaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (72.9 mg, 86%) was obtained as a faint yellow solid.  $R_f = 0.3$  (petroleum ether / ethyl acetate = 20:1 - 5:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.80-7.60 (m, 2H), 7.52 (s, 1H), 7.36 (s, 2H), 7.45-7.31 (m, 1H), 7.14 (t,  $J = 9.2$  Hz, 1H), 6.66 (dd,  $J = 8.4, 5.88$  Hz, 1H), 6.48 (t,  $J = 6.8$  Hz, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 159.92 (d,  $J = 247.7$  Hz), 133.54, 132.22, 132.19, 131.78, 130.84 (d,  $J = 8.2$  Hz), 124.85 (d,  $J = 3.6$  Hz), 122.35, 122.29, 120.93, 119.03, 118.39, 116.18 (d,  $J = 21.5$  Hz), 112.80;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -111.14.



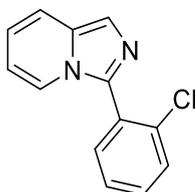
### 3-(3-fluorophenyl)-imidazo[1,5-a]pyridine (3ac)<sup>[2]</sup>:

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and 3-fluoro-benzaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (73.8 mg, 87%) was obtained as a faint yellow solid.  $R_f = 0.3$  (petroleum ether / ethyl acetate = 20:1 - 5:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.06 (d,  $J = 7.4$  Hz, 1H), 7.45-7.34 (m, 3H), 7.32-7.27 (m, 2H), 6.94 (td,  $J = 8.6, 2.2$  Hz, 1H), 6.54 (dd,  $J = 8.9, 5.6$  Hz, 1H), 6.39 (t,  $J = 6.9$  Hz, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 162.90 (d,  $J = 247.5$  Hz), 136.78, 132.44, 131.90, 130.50 (d,  $J = 9.3$  Hz), 123.13 (d,  $J = 2.9$  Hz), 121.16, 120.90, 119.03, 118.74, 115.31 (d,  $J = 21.1$  Hz), 114.83, 114.60, 113.42;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -111.82.



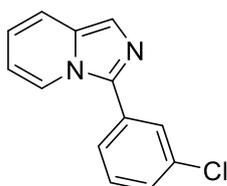
**3-(4-fluorophenyl)-imidazo[1,5-a]pyridine (3ad)<sup>[2]</sup>:**

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and 4-fluoro-benzaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (75.5 mg, 89%) was obtained as a faint yellow solid. *R*<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.09 (d, *J* = 7.2 Hz, 1H), 7.78-7.61 (m, 2H), 7.46 (s, 1H), 7.40 (d, *J* = 8.6 Hz, 1H), 7.13 (t, *J* = 8.6 Hz, 2H), 6.64 (dd, *J* = 8.8, 6.4 Hz, 1H), 6.48 (t, *J* = 6.9 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 162.91 (d, *J* = 249.8 Hz), 137.33, 131.59, 129.85 (d, *J* = 8.3 Hz), 126.66, 121.12, 120.59, 118.85, 118.76, 116.01 (d, *J* = 21.6 Hz), 113.22; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ: -112.10.



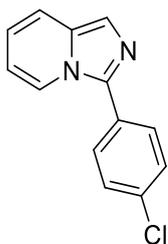
**3-(2-chlorophenyl)-imidazo[1,5-a]pyridine (3ae)<sup>[3]</sup>:**

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and 2-chlorobenzaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (76.6 mg, 84%) was obtained as a faint yellow solid. *R*<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.05 (d, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.43 (s, 1H), 7.35 (d, *J* = 8.5 Hz, 3H), 6.59 (dd, *J* = 9.0, 6.4 Hz, 1H), 6.43 (t, *J* = 6.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 137.01, 134.31, 131.82, 129.18, 129.00, 128.91, 121.14, 120.88, 118.92, 118.82, 113.37.



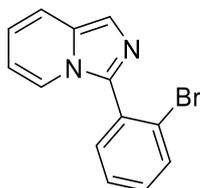
**3-(3-chlorophenyl)-imidazo[1,5-a]pyridine (3af)<sup>[3]</sup>:**

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and 3-chlorobenzaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (77.5 mg, 85%) was obtained as a faint yellow solid. *R*<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.04 (d, *J* = 7.0 Hz, 1H), 7.64 (s, 1H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.39 (s, 1H), 7.34-7.16 (m, 3H), 6.55 (t, *J* = 6.6 Hz, 1H), 6.39 (t, *J* = 6.5 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 135.45, 133.77, 131.02, 130.82, 129.06, 127.30, 126.65, 124.45, 120.02, 119.89, 117.99, 117.64, 112.38.



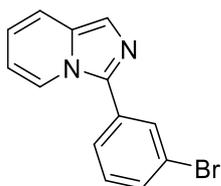
### 3-(4-chlorophenyl)-imidazo[1,5-a]pyridine (3ag)<sup>[1]</sup>:

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and 4-chlorobenzaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (76.6 mg, 84%) was obtained as a faint yellow solid. *R*<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.10 (d, *J* = 7.4 Hz, 1H), 7.85-7.65 (m, 2H), 7.46 (s, 1H), 7.41 (d, *J* = 9.1 Hz, 1H), 7.14 (t, *J* = 8.6 Hz, 2H), 6.66 (dd, *J* = 9.8, 6.3 Hz, 1H), 6.49 (t, *J* = 6.6 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 134.56, 133.06, 131.87, 129.98, 129.49, 128.82, 128.32, 125.98, 120.99, 119.05, 117.83, 117.23, 111.45.



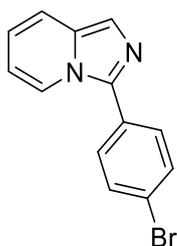
### 3-(2-bromophenyl)-imidazo[1,5-a]pyridine (3ah)<sup>[3]</sup>:

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and 2-bromobenzaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (91.4 mg, 84%) was obtained as a faint yellow solid. *R*<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.61 (d, *J* = 7.4 Hz, 1H), 7.51-7.42 (m, 3H), 7.39 (d, *J* = 8.6 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.29-7.20 (m, 1H), 6.64 (dd, *J* = 9.1, 6.8 Hz, 1H), 6.44 (t, *J* = 5.6 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 136.89, 133.26, 133.18, 131.58, 130.93, 127.69, 124.20, 122.12, 119.97, 119.02, 118.41, 112.62.



### 3-(3-bromophenyl)-imidazo[1,5-a]pyridine (3ai)<sup>[3]</sup>:

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and 3-bromobenzaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (92.4 mg, 85%) was obtained as a faint yellow solid. *R*<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.08 (d, *J* = 7.1 Hz, 1H), 7.83 (s, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.45-7.37 (m, 2H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 6.60 (dd, *J* = 8.9, 6.4 Hz, 1H), 6.44 (t, *J* = 7.6 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 136.49, 132.37, 131.94, 131.39, 130.69, 130.42, 126.09, 123.04, 121.15, 121.02, 119.13, 118.81, 113.54.



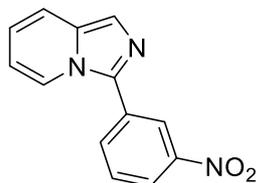
**3-(4-bromophenyl)-imidazo[1,5-a]pyridine (3aj)<sup>[1]</sup>:**

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and 4-bromobenzaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (92.4 mg, 85%) was obtained as a faint yellow solid. R<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.03 (d, *J* = 6.6 Hz, 1H), 7.58-7.40 (m, 4H), 7.41 (s, 1H), 7.32 (d, *J* = 9.5 Hz, 1H), 6.57 (dd, *J* = 8.8, 6.3 Hz, 1H), 6.41 (t, *J* = 6.7 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 136.99, 136.43, 132.11, 131.85, 129.33, 129.20, 122.48, 121.13, 120.93, 118.97, 118.82, 113.43.



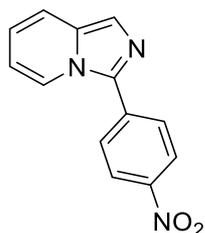
**3-(2-nitrophenyl)-imidazo[1,5-a]pyridine (3ak)<sup>[3]</sup>:**

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and 2-nitro-benzaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (85.1 mg, 89%) was obtained as a faint yellow solid. R<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.14 (d, *J* = 7.7 Hz, 1H), 7.80-7.70 (m, 2H), 7.67-7.57 (m, 3H), 7.52 (d, *J* = 7.7 Hz, 1H), 6.77 (dd, *J* = 9.2, 6.6 Hz, 1H), 6.56 (t, *J* = 6.6 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 148.67, 133.43, 133.29, 132.84, 131.65, 130.18, 125.07, 125.04, 120.96, 120.89, 119.40, 118.74, 113.53.



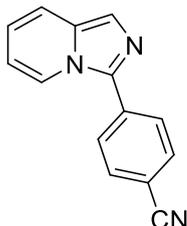
**3-(3-nitrophenyl)-imidazo[1,5-a]pyridine (3al)<sup>[3]</sup>:**

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and 3-nitro-benzaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (88.0 mg, 92%) was obtained as a faint yellow solid. R<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.70 (s, 1H), 8.36-8.25 (m, 2H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.63 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 6.84 (dd, *J* = 8.6, 6.1 Hz, 1H), 6.72 (t, *J* = 7.0 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 148.65, 135.63, 133.64, 132.44, 132.15, 130.14, 122.95, 121.97, 121.63, 120.92, 119.60, 119.08, 114.22.

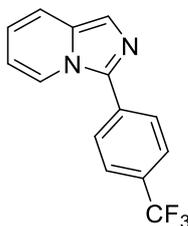


**3-(4-nitrophenyl)imidazo[1,5-a]pyridine (3am)<sup>[3]</sup>:**

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and 4-nitro-benzaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (89.9 mg, 94%) was obtained as a faint yellow solid. R<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.25 (d, *J* = 8.2 Hz, 3H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.54 (s, 1H), 7.46 (d, *J* = 8.9 Hz, 1H), 6.75 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.62 (t, *J* = 6.6 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 146.91, 136.50, 135.80, 132.93, 127.68, 124.36, 122.35, 121.29, 120.05, 119.13, 114.47.

**4-imidazo[1,5-a]pyridin-3-yl-benzonitrile (3an)<sup>[3]</sup>:**

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and 4-formylbenzonitrile (0.4 mmol, 1 eq.), following the general procedure A, the title compound (82.3 mg, 94%) was obtained as a faint yellow solid. R<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.22 (d, *J* = 7.2 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.54 (s, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 6.75 (dd, *J* = 9.0, 6.4 Hz, 1H), 6.60 (t, *J* = 6.8, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 136.11, 134.71, 132.77, 132.66, 127.75, 122.00, 121.19, 119.78, 119.10, 118.66, 114.21, 111.49.

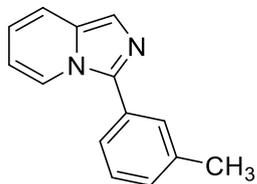
**3-(4-(trifluoromethyl)phenyl)imidazo[1,5-a]pyridine (3ao)<sup>[1]</sup>:**

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and 4-(trifluoromethyl)benzaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (102.7 mg, 98%) was obtained as a faint yellow solid. R<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.18 (d, *J* = 6.8 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.50 (s, 1H), 7.43 (d, *J* = 9.1 Hz, 1H), 6.69 (dd, *J* = 8.8, 6.4 Hz, 1H), 6.54 (t, *J* = 7.0, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 136.69, 133.90, 132.25, 130.22 (d, *J* = 32.8 Hz), 127.87, 126.00 (q, *J* = 3.7 Hz), 124.01 (d, *J* = 272.7 Hz), 121.41, 121.17, 119.35, 119.00, 113.78; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ: -62.65.

**3-(2-methylphenyl)imidazo[1,5-a]pyridine (3ap)<sup>[3]</sup>:**

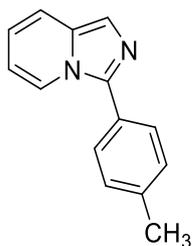
From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and 2-methylbenzaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (54.1 mg, 65%) was obtained as a faint

white solid. Rf = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.64 (d, *J* = 7.1 Hz, 1H), 7.58 (s, 1H), 7.48 (dd, *J* = 12.5, 9.4 Hz, 2H), 7.40-7.28 (m, 3H), 6.72 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.50 (t, *J* = 6.7 Hz, 1H), 2.24 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 138.41, 137.87, 130.83, 130.54, 130.38, 129.48, 129.36, 126.00, 121.49, 119.76, 118.56, 118.52, 112.59, 19.76.



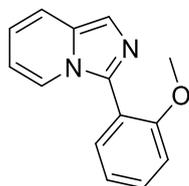
### 3-(3-methylphenyl)-imidazo[1,5-a]pyridine (3aq)<sup>[3]</sup>:

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and 3-methylbenzaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (54.9 mg, 66%) was obtained as a faint yellow solid. Rf = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.11 (d, *J* = 7.2 Hz, 1H), 7.51 (s, 1H), 7.48-7.38 (m, 2H), 7.34-7.20 (m, 2H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.55 (dd, *J* = 9.0, 6.4 Hz, 1H), 6.39 (t, *J* = 6.8 Hz, 1H), 2.31 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 138.78, 138.36, 131.54, 130.28, 129.38, 128.76, 124.68, 121.47, 120.48, 118.70, 118.68, 112.96, 21.47.



### 3-(4-methylphenyl)-imidazo[1,5-a]pyridine (3ar)<sup>[1]</sup>:

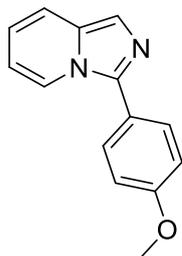
From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and 4-methylbenzaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (56.6 mg, 68%) was obtained as a faint yellow solid. Rf = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.13 (d, *J* = 7.2 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.44 (s, 1H), 7.37 (d, *J* = 9.1 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 2H), 6.60 (dd, *J* = 9.2, 6.3 Hz, 1H), 6.43 (t, *J* = 6.8 Hz, 1H), 2.33 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 138.56, 138.40, 131.46, 129.65, 129.61, 129.16, 127.83, 127.56, 127.50, 121.45, 120.41, 118.75, 118.57, 112.89, 21.40.



### 3-(2-methoxyphenyl)-imidazo[1,5-a]pyridine (3as)<sup>[3]</sup>:

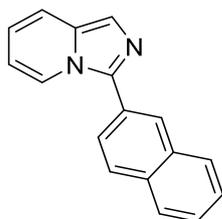
From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and 2-methoxy-benzaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (53.8 mg, 60%) was obtained as a faint yellow solid. Rf = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.59 (d, *J* = 13.2 Hz, 3H), 7.46 (d, *J* = 9.4 Hz, 2H), 7.17-6.95 (m, 2H), 6.77-6.64 (m, 1H), 6.49

(t,  $J = 6.7$  Hz, 1H), 3.78 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 157.30, 136.22, 132.46, 131.27, 130.63, 123.13, 121.10, 120.13, 119.42, 118.50, 118.17, 111.77, 111.22, 55.51.



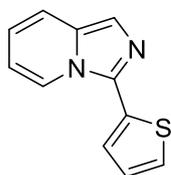
### 3-(2-methoxyphenyl)imidazo[1,5-a]pyridine (3at)<sup>[2]</sup>:

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and 4-methoxy-benzaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (63.6 mg, 71%) was obtained as a faint yellow solid.  $R_f = 0.3$  (petroleum ether / ethyl acetate = 20:1 - 5:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.06 (d,  $J = 7.3$  Hz, 1H), 7.61 (d,  $J = 7.5$  Hz, 2H), 7.42 (s, 1H), 7.34 (d,  $J = 9.2$  Hz, 1H), 6.94 (d,  $J = 6.7$  Hz, 2H), 6.57 (dd,  $J = 9.2, 6.3$  Hz, 1H), 6.40 (t,  $J = 6.8$  Hz, 1H), 3.76 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 159.84, 138.22, 131.28, 129.37, 122.92, 121.33, 120.20, 118.73, 118.43, 114.39, 112.82, 55.37.



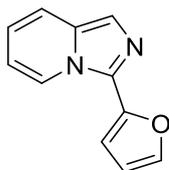
### 3-(naphthalen-2-yl)imidazo[1,5-a]pyridine (3au)<sup>[3]</sup>:

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and 2-naphthaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (71.2 mg, 73%) was obtained as a faint yellow solid.  $R_f = 0.3$  (petroleum ether / ethyl acetate = 20:1 - 5:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.41 (d,  $J = 7.3$  Hz, 1H), 8.29 (s, 1H), 8.04-7.91 (m, 4H), 7.64 (s, 1H), 7.58-7.52 (m, 3H), 6.82-6.73 (m, 1H), 6.62 (t,  $J = 6.8$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 138.28, 133.37, 133.15, 131.83, 128.81, 128.24, 127.85, 126.69, 126.66, 126.63, 125.72, 121.51, 120.96, 118.91, 113.25.



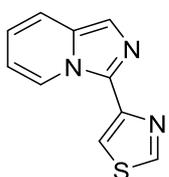
### 3-(thiophen-2-yl)imidazo[1,5-a]pyridine (3av)<sup>[1]</sup>:

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and thiophene-2-carbaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (56.8 mg, 71%) was obtained as a faint yellow solid.  $R_f = 0.3$  (petroleum ether / ethyl acetate = 20:1 - 5:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.21 (d,  $J = 7.2$  Hz, 1H), 7.47-7.36 (m, 3H), 7.31 (d,  $J = 5.2$  Hz, 1H), 7.08 (dd,  $J = 4.8, 3.6$  Hz, 1H), 6.64 (dd,  $J = 9.2, 6.4$  Hz, 1H), 6.54 (t,  $J = 7.2$ , 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 133.03, 132.73, 131.72, 127.62, 125.84, 124.30, 121.68, 120.93, 118.80, 118.79, 113.67.



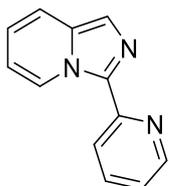
### 3-(furan-2-yl)imidazo[1,5-a]pyridine (3aw)<sup>[1]</sup>:

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and furan-2-carbaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (47.8 mg, 65%) was obtained as a faint yellow solid.  $R_f = 0.3$  (petroleum ether / ethyl acetate = 20:1 - 5:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.71 (s, 1H), 7.38 (s, 1H), 7.09 (s, 1H), 6.52 (s, 1H), 6.42-6.21 (m, 1H), 5.94 (s, 1H), 5.61 (s, 1H), 5.48 (s, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 151.11, 148.14, 136.53, 132.93, 126.04, 121.73, 121.58, 120.94, 120.16, 117.99, 113.55.



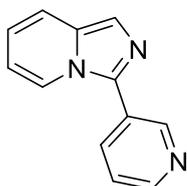
### 4-(imidazo[1,5-a]pyridin-3-yl)thiazole (3ax):

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and furan- thiazole-4-carbaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (55.5 mg, 69%) was obtained as a faint yellow solid.  $R_f = 0.3$  (petroleum ether / ethyl acetate = 20:1 - 5:1). m.p.: 95-97 °C; IR (KBr) 3116, 1629, 1541, 1502, 1458, 1344, 1308, 1253, 1134, 1097, 1002, 881, 810, 746, 694, 655  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 9.37 (d,  $J = 7.3$  Hz, 1H), 8.85 (s, 1H), 7.99 (s, 1H), 7.50-7.34 (m, 2H), 6.71 (dd,  $J = 9.1, 6.3$  Hz, 1H), 6.59 (t,  $J = 6.8$  Hz, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 152.62, 148.39, 132.93, 131.56, 124.72, 120.58, 119.36, 118.11, 115.39, 113.20; HRMS(ESI): calculated for  $\text{C}_{10}\text{H}_8\text{N}_3\text{S}^+$   $[\text{M}+\text{H}]^+$ : 202.0433, found: 202.0434.



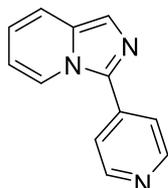
### 3-(pyridin-2-yl)imidazo[1,5-a]pyridine (3ay)<sup>[1]</sup>:

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and picolinaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (60.8 mg, 78%) was obtained as a faint yellow solid.  $R_f = 0.3$  (petroleum ether / ethyl acetate = 20:1 - 5:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 9.84 (d,  $J = 7.2$  Hz, 1H), 8.51 (d,  $J = 5.0$  Hz, 1H), 8.23 (d,  $J = 8.1$  Hz, 1H), 7.65 (t,  $J = 7.8$  Hz, 1H), 7.48 (s, 1H), 7.40 (d,  $J = 9.0$  Hz, 1H), 7.09-7.00 (m, 1H), 6.72 (dd,  $J = 9.1, 6.4$  Hz, 1H), 6.59 (t,  $J = 7.2$  Hz, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 151.15, 148.09, 136.45, 135.41, 132.91, 126.01, 121.64, 121.49, 121.02, 120.07, 117.92, 113.45.



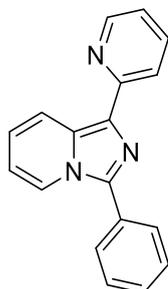
### 3-(pyridin-3-yl)imidazo[1,5-a]pyridine (3az)<sup>[3]</sup>:

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and nicotinaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (59.3 mg, 76%) was obtained as a faint yellow solid. R<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.99 (s, 1H), 8.56 (s, 1H), 8.14 (d, *J* = 7.2 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.50 (s, 1H), 7.41 (d, *J* = 9.1 Hz, 1H), 7.35 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.67 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.52 (t, *J* = 6.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 149.34, 148.47, 135.16, 132.12, 126.78, 123.77, 121.40, 120.95, 119.29, 118.91, 113.76.



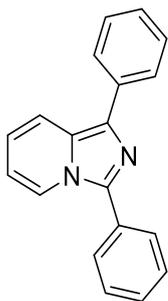
### 3-(pyridin-4-yl)imidazo[1,5-a]pyridine (3aaa)<sup>[3]</sup>:

From 2-pyridinemethanamine (0.8 mmol, 2 eq.) and isonicotinaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (64.0 mg, 82%) was obtained as a faint yellow solid. R<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.64 (d, *J* = 4.3 Hz, 2H), 8.28 (d, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 4.4 Hz, 2H), 7.53 (s, 1H), 7.45 (d, *J* = 9.1 Hz, 1H), 6.74 (dd, *J* = 9.1, 6.4 Hz, 1H), 6.61 (t, *J* = 6.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 150.41, 137.67, 135.18, 134.50, 132.84, 121.99, 121.41, 121.19, 119.87, 119.06, 114.26.



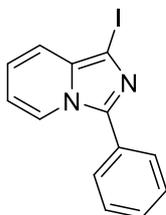
### 3-phenyl-1-(pyridin-2-yl)imidazo[1,5-a]pyridine (3aab)<sup>[1]</sup>:

From di(pyridin-2-yl)methanamine (0.8 mmol, 2 eq.) and benzaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (74.8 mg, 69%) was obtained as a faint yellow solid. R<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.61 (d, *J* = 9.2 Hz, 1H), 8.54 (d, *J* = 4.9 Hz, 1H), 8.15 (t, *J* = 7.9 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.04-6.95 (m, 1H), 6.81 (dd, *J* = 9.3, 6.3 Hz, 1H), 6.53 (t, *J* = 6.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 155.06, 148.99, 138.07, 136.26, 130.58, 130.23, 130.14, 129.07, 128.94, 128.40, 121.85, 121.61, 121.06, 120.47, 119.96, 113.93.



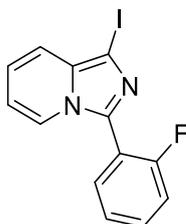
**1,3-diphenylimidazo[1,5-a]pyridine (3aac)<sup>[1]</sup>:**

From phenyl(pyridin-2-yl)methanamine (0.8 mmol, 2 eq.) and benzaldehyde (0.4 mmol, 1 eq.), following the general procedure A, the title compound (82.1 mg, 76%) was obtained as a faint yellow solid. *R*<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.16 (d, *J* = 7.2 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 3H), 7.50-7.43 (m, 2H), 7.42-7.34 (m, 3H), 7.26-7.19 (m, 1H), 6.71 (dd, *J* = 9.3, 6.3 Hz, 1H), 6.50 (t, *J* = 6.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 138.14, 134.99, 132.04, 130.21, 129.04, 128.83, 128.73, 128.35, 127.69, 126.83, 126.55, 121.79, 119.70, 119.19, 113.24.



**1-iodo-3-phenylimidazo[1,5-a]pyridine (3b)<sup>[4]</sup>:**

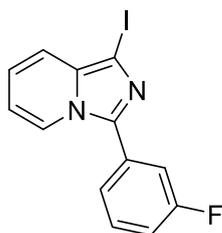
From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and benzaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (222.7 mg, 87%) was obtained as a faint yellow solid. *R*<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 15:1 – 3:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.95 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.36-7.18 (m, 3H), 7.10 (d, *J* = 9.2 Hz, 1H), 6.54 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.34 (t, *J* = 6.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 140.30, 133.32, 129.28, 129.01, 127.84, 121.73, 120.31, 118.76, 114.01, 74.27.



**3-(2-fluorophenyl)-1-iodoimidazo[1,5-a]pyridine (3bb):**

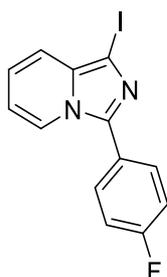
From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and 2-fluorobenzaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (235.2 mg, 87%) was obtained as a faint yellow solid. *R*<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 15:1 – 3:1). m.p.: 122-124 °C; IR (KBr) 3053, 1627, 1568, 1510, 1454, 1355, 1307, 1259, 1209, 1091, 1002, 943, 815, 765, 732, 684 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.77-7.67 (m, 2H), 7.45 (tdd, *J* = 7.5, 5.2, 1.8 Hz, 1H), 7.34 (d, *J* = 9.6 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.25-7.15 (m, 1H), 6.81 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.61 (t, *J* = 6.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 159.75 (d, *J* = 249.7 Hz), 135.68, 133.69, 132.40, 132.36, 131.34 (d, *J* = 8.3 Hz), 124.96 (d, *J* = 3.4 Hz), 122.86, 122.79, 120.54, 118.53,

117.36, 117.22, 116.12 (d,  $J = 21.4$  Hz), 113.74, 74.09;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -110.71; HRMS(ESI): calculated for  $\text{C}_{13}\text{H}_9\text{FIN}_2^+$   $[\text{M}+\text{H}]^+$ : 338.9789, found: 338.9797.



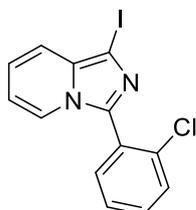
### 3-(3-fluorophenyl)-1-iodoimidazo[1,5-a]pyridine (3bc):

From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and 3-fluorobenzaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (238.0 mg, 88%) was obtained as a faint yellow solid.  $R_f = 0.3$  (petroleum ether / ethyl acetate = 15:1 – 3:1). m.p.: 66-68 °C; IR (KBr) 3076, 1612, 1583, 1504, 1463, 1368, 1419, 1442, 1116, 1018, 862, 788, 738, 692  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.24 (d,  $J = 7.2$  Hz, 1H), 7.57 (d,  $J = 7.8$  Hz, 1H), 7.54-7.45 (m, 2H), 7.38 (d,  $J = 9.2$  Hz, 1H), 7.19-7.09 (m, 1H), 6.84 (dd,  $J = 9.2, 6.4$  Hz, 1H), 6.67 (t,  $J = 6.8$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 163.00 (d,  $J = 247.3$  Hz), 139.10, 133.73, 131.39, 131.30, 130.70 (d,  $J = 8.5$  Hz), 123.32 (d,  $J = 3.0$  Hz), 121.70, 120.53, 119.13, 116.09, 115.88, 114.90 (d,  $J = 23.1$  Hz), 114.40, 74.55;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -111.49; HRMS(ESI): calculated for  $\text{C}_{13}\text{H}_9\text{FIN}_2^+$   $[\text{M}+\text{H}]^+$ : 338.9789, found: 338.9791.



### 3-(4-fluorophenyl)-1-iodoimidazo[1,5-a]pyridine (3bd)<sup>[4]</sup>:

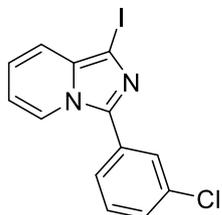
From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and 4-fluorobenzaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (240.7 mg, 89%) was obtained as a faint yellow solid.  $R_f = 0.3$  (petroleum ether / ethyl acetate = 15:1 – 3:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.01 (d,  $J = 7.2$  Hz, 1H), 7.67-7.56 (m, 2H), 7.22 (d,  $J = 9.2$  Hz, 1H), 7.08 (t,  $J = 8.7$  Hz, 2H), 6.67 (dd,  $J = 9.2, 6.4$  Hz, 1H), 6.49 (t,  $J = 6.8$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 162.96 (d,  $J = 249.7$  Hz), 139.44, 133.36, 129.90 (d,  $J = 8.4$  Hz), 125.53 (d,  $J = 3.4$  Hz), 121.54, 120.28, 118.97, 116.20 (d,  $J = 21.9$  Hz), 114.16, 74.06;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -111.06.



### 3-(2-chlorophenyl)-1-iodoimidazo[1,5-a]pyridine (3be):

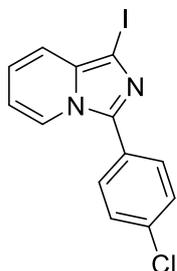
From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and 2-chlorobenzaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (252.0 mg, 89%) was obtained as a faint yellow solid.  $R_f = 0.3$  (petroleum ether / ethyl acetate = 15:1 – 3:1). m.p.: 145-146 °C; IR (KBr)

3070, 1629, 1560, 1500, 1425, 1355, 1303, 1255, 1124, 1058, 1001, 945, 742, 684  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.65-7.56 (m, 2H), 7.57-7.51 (m, 1H), 7.50-7.35 (m, 3H), 6.87 (dd,  $J = 9.2, 6.5$  Hz, 1H), 6.64 (t,  $J = 6.8$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 137.95, 134.05, 133.37, 133.19, 131.10, 129.98, 128.52, 127.26, 122.78, 120.48, 118.63, 113.54, 73.27; HRMS(ESI): calculated for  $\text{C}_{13}\text{H}_9\text{ClIN}_2^+$   $[\text{M}+\text{H}]^+$ : 354.9493, found: 354.9495.



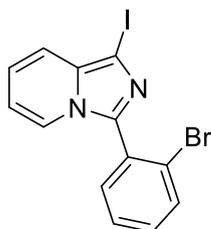
**3-(3-chlorophenyl)-1-iodoimidazo[1,5-a]pyridine (3bf):**

From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and 3-chlorobenzaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (254.9 mg, 90%) was obtained as a faint yellow solid.  $R_f = 0.3$  (petroleum ether / ethyl acetate = 15:1 – 3:1). m.p.: 103-105  $^\circ\text{C}$ ; IR (KBr) 3055, 1593, 1558, 1496, 1452, 1353, 1301, 1257, 1093, 1006, 947, 887, 786, 752, 690, 563  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.21 (d,  $J = 7.2$  Hz, 1H), 7.78 (s, 1H), 7.66 (dt,  $J = 7.4, 1.6$  Hz, 1H), 7.48-7.34 (m, 3H), 6.84 (dd,  $J = 9.2, 6.4$  Hz, 1H), 6.67 (t,  $J = 6.8$ , 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 138.88, 135.05, 133.73, 131.02, 130.27, 129.03, 127.89, 125.68, 121.65, 120.59, 119.09, 114.47, 74.64; HRMS(ESI): calculated for  $\text{C}_{13}\text{H}_9\text{ClIN}_2^+$   $[\text{M}+\text{H}]^+$ : 354.9493, found: 354.9493.



**3-(4-chlorophenyl)-1-iodoimidazo[1,5-a]pyridine (3bg)<sup>[4]</sup>:**

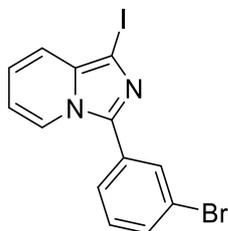
From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and 4-chlorobenzaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (257.7 mg, 91%) was obtained as a faint yellow solid.  $R_f = 0.3$  (petroleum ether / ethyl acetate = 15:1 – 3:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.14 (d,  $J = 7.1$  Hz, 1H), 7.68 (d,  $J = 7.9$  Hz, 2H), 7.45 (d,  $J = 8.3$  Hz, 2H), 7.34 (d,  $J = 9.1$  Hz, 1H), 6.88-6.73 (m, 1H), 6.68-6.53 (m, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 139.23, 134.87, 133.60, 129.28, 129.05, 127.80, 121.60, 120.43, 119.06, 114.34, 74.49.



**3-(2-bromophenyl)-1-iodoimidazo[1,5-a]pyridine (3bh):**

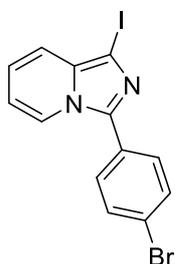
From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and 2-bromobenzaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (289.7 mg, 91%) was obtained as a faint

yellow solid. Rf = 0.3 (petroleum ether / ethyl acetate = 15:1 – 3:1). m.p.: 122-125 °C; IR (KBr) 3070, 1627, 1554, 1496, 1419, 1357, 1303, 1259, 1114, 1002, 945, 740, 686 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.73 (d, *J* = 8.0 Hz, 1H), 7.64-7.54 (m, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.44-7.35 (m, 2H), 6.88 (dd, *J* = 9.2, 6.5 Hz, 1H), 6.65 (t, *J* = 6.8, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 139.09, 133.62, 133.16, 132.98, 131.33, 130.61, 127.77, 123.94, 122.76, 120.48, 118.64, 113.51, 73.01; HRMS(ESI): calculated for C<sub>13</sub>H<sub>9</sub>BrIN<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 398.8988, found: 398.8993.



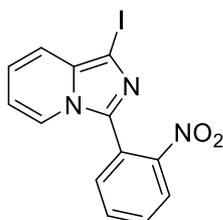
### 3-(3-bromophenyl)-1-iodoimidazo[1,5-a]pyridine (3bi):

From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and 3-bromobenzaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (302.5 mg, 95%) was obtained as a faint yellow solid. Rf = 0.3 (petroleum ether / ethyl acetate = 15:1 – 3:1). m.p.: 107-109 °C; IR (KBr) 3078, 1631, 1593, 1556, 1500, 1421, 1352, 1299, 1257, 1068, 1010, 950, 879, 740, 686 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.21 (d, *J* = 7.2 Hz, 1H), 7.95 (s, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.45-7.32 (m, 2H), 6.84 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.67 (t, *J* = 6.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 138.76, 133.75, 131.96, 131.27, 130.79, 130.49, 126.15, 123.14, 121.64, 120.60, 119.13, 114.48, 74.65; HRMS(ESI): calculated for C<sub>13</sub>H<sub>9</sub>BrIN<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 398.8988, found: 398.8987.



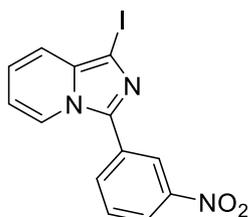
### 3-(4-bromophenyl)-1-iodoimidazo[1,5-a]pyridine (3bj)<sup>[4]</sup>:

From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and 4-bromobenzaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (305.7 mg, 96%) was obtained as a faint yellow solid. Rf = 0.3 (petroleum ether / ethyl acetate = 15:1 – 3:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.08 (d, *J* = 7.2 Hz, 1H), 7.55 (s, 4H), 7.28 (d, *J* = 9.2 Hz, 1H), 6.74 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.56 (t, *J* = 6.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 139.32, 133.67, 132.25, 129.32, 128.28, 123.13, 121.62, 120.43, 119.16, 114.36, 74.52.



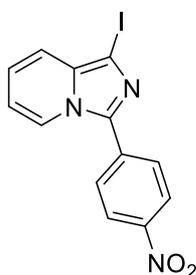
### 1-iodo-3-(2-nitrophenyl)imidazo[1,5-a]pyridine (3bk):

From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and 2-nitrobenzaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (262.8 mg, 90%) was obtained as a faint yellow solid. *R*<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 15:1 – 3:1). m.p.: 158-161 °C; IR (KBr) 3095, 1612, 1516, 1340, 1257, 1137, 1002, 945, 854, 786, 744, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.10 (t, *J* = 8.8 Hz, 1H), 7.72-7.55 (m, 3H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 9.1 Hz, 1H), 6.78 (t, *J* = 7.2 Hz, 1H), 6.54 (t, *J* = 6.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 148.25, 135.61, 133.80, 133.57, 133.52, 130.80, 125.18, 124.10, 121.51, 120.87, 118.90, 114.41, 73.66; HRMS(ESI): calculated for C<sub>13</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 365.9734, found: 365.9730.



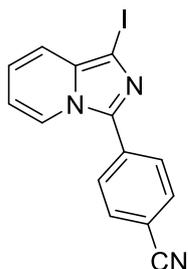
**1-iodo-3-(3-nitrophenyl)imidazo[1,5-a]pyridine (3bl):**

From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and 3-nitrobenzaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (277.4 mg, 95%) was obtained as a faint yellow solid. *R*<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 15:1 – 3:1). m.p.: 200-202 °C; IR (KBr) 3086, 1637, 1539, 1350, 1263, 1076, 1020, 896, 742, 682 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.58 (s, 1H), 8.20 (d, *J* = 8.6 Hz, 2H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 9.2 Hz, 1H), 6.84 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.69 (t, *J* = 6.9 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 148.60, 137.80, 134.23, 133.72, 131.06, 130.25, 123.42, 121.95, 121.36, 121.03, 119.38, 115.14, 75.30; HRMS(ESI): calculated for C<sub>13</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 365.9734, found: 365.9733.



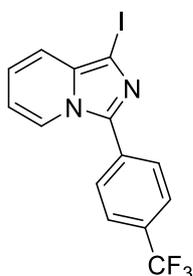
**1-iodo-3-(4-nitrophenyl)imidazo[1,5-a]pyridine (3bm):**

From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and 4-nitrobenzaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (286.2 mg, 98%) was obtained as a faint yellow solid. *R*<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 15:1 – 3:1). m.p.: 129-130 °C; IR (KBr) 3084, 1705, 1595, 1344, 1244, 1103, 1108, 1006, 854, 812, 738, 692 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.23 (s, 3H), 7.88 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.69 (t, *J* = 6.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 147.19, 137.97, 135.30, 134.67, 127.78, 124.38, 121.73, 121.47, 119.39, 115.38, 76.30; HRMS(ESI): calculated for C<sub>13</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 365.9734, found: 365.9737.



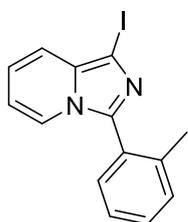
**4-(1-iodoimidazo[1,5-a]pyridin-3-yl)benzonitrile (3bn):**

From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and 4-formylbenzonitrile (1.6 mmol, 2 eq.), following the general procedure B, the title compound (262.2 mg, 95%) was obtained as a faint yellow solid.  $R_f = 0.3$  (petroleum ether / ethyl acetate = 15:1 – 3:1). m.p.: 167-169 °C; IR (KBr) 2221, 1606, 1494, 1359, 1263, 1120, 1010, 844, 740, 682  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.27 (d,  $J = 7.2$  Hz, 1H), 7.91 (d,  $J = 8.0$  Hz, 2H), 7.77 (d,  $J = 8.0$  Hz, 2H), 7.41 (d,  $J = 9.1$  Hz, 1H), 6.90 (dd,  $J = 9.2, 6.4$  Hz, 1H), 6.74 (t,  $J = 6.8$ , 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 138.25, 134.40, 133.51, 132.79, 127.76, 121.66, 121.24, 119.33, 118.49, 115.14, 111.93, 75.86; HRMS(ESI): calculated for  $\text{C}_{14}\text{H}_9\text{IN}_3^+$   $[\text{M}+\text{H}]^+$ : 345.9836, found: 345.9837.



**1-iodo-3-(4-(trifluoromethyl)phenyl)imidazo[1,5-a]pyridine (3bo)<sup>[4]</sup>:**

From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and 4-(trifluoromethyl)benzaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (304.2 mg, 98%) was obtained as a faint yellow solid.  $R_f = 0.3$  (petroleum ether / ethyl acetate = 15:1 – 3:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.09 (d,  $J = 7.3$  Hz, 1H), 7.75 (d,  $J = 8.2$  Hz, 2H), 7.61 (d,  $J = 8.2$  Hz, 2H), 7.23 (d,  $J = 9.2$  Hz, 1H), 6.71 (dd,  $J = 9.3, 6.4$  Hz, 1H), 6.54 (t,  $J = 6.8$  Hz, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 138.74, 133.98, 132.72, 130.48 (d,  $J = 32.6$  Hz), 127.80, 125.94 (q,  $J = 3.8$  Hz), 123.90 (d,  $J = 272.3$  Hz), 121.56, 120.83, 119.10, 114.71, 75.11;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -62.61.



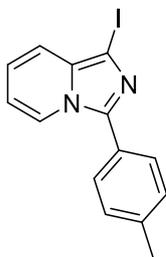
**1-iodo-3-(2-methylphenyl)imidazo[1,5-a]pyridine (3bp)<sup>[4]</sup>:**

From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and 2-methylbenzaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (197.7 mg, 74%) was obtained as a faint yellow solid.  $R_f = 0.3$  (petroleum ether / ethyl acetate = 15:1 – 3:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.59 (d,  $J = 7.2$  Hz, 1H), 7.48-7.21 (m, 5H), 6.78 (dd,  $J = 9.2, 6.4$  Hz, 1H), 6.54 (t,  $J = 6.7$  Hz, 1H), 2.20 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 140.05, 138.34, 132.53, 130.86, 130.48, 129.80, 128.46, 126.09, 121.94, 120.10, 118.67, 113.58, 72.89, 19.78.



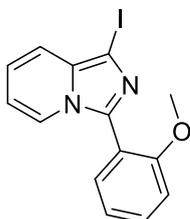
**1-iodo-3-(3-methylphenyl)imidazo[1,5-a]pyridine (3bq):**

From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and 3-methylbenzaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (211.1 mg, 79%) was obtained as a faint yellow solid. *R*<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 15:1 – 3:1). m.p.: 91-94 °C; IR (KBr) 2922, 1604, 1506, 1469, 1352, 1307, 1257, 1018, 948, 802, 751, 704 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.17 (d, *J* = 7.2 Hz, 1H), 7.57 (s, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 9.2 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 6.74 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.54 (t, *J* = 6.8 Hz, 1H), 2.41 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 140.59, 138.91, 133.30, 129.86, 129.21, 128.82, 128.79, 124.63, 121.90, 120.18, 118.86, 113.88, 74.08, 21.52; HRMS(ESI): calculated for C<sub>14</sub>H<sub>12</sub>I<sub>1</sub>N<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 335.0040, found: 335.0037.



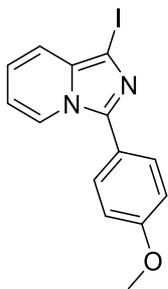
**1-iodo-3-(4-methylphenyl)imidazo[1,5-a]pyridine (3br)<sup>[4]</sup>:**

From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and 4-methylbenzaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (219.1 mg, 82%) was obtained as a faint yellow solid. *R*<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 15:1 – 3:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.20 (d, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 6.4 Hz, 2H), 7.46-7.30 (m, 3H), 6.79 (dd, *J* = 9.1, 6.3 Hz, 1H), 6.59 (t, *J* = 6.8 Hz, 1H), 2.44 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 140.66, 139.14, 133.24, 129.69, 127.91, 126.50, 121.90, 120.03, 118.98, 113.77, 73.89, 21.45.



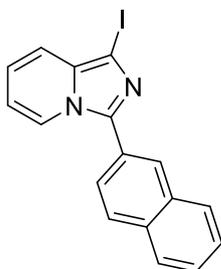
**1-iodo-3-(2-methoxyphenyl)imidazo[1,5-a]pyridine (3bs)<sup>[4]</sup>:**

From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and 2-methoxybenzaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (196.0 mg, 70%) was obtained as a faint yellow solid. *R*<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 15:1 – 3:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.58-7.45 (m, 2H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 9.1 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.73 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.48 (t, *J* = 6.8 Hz, 1H), 3.72 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 157.15, 138.47, 133.23, 132.74, 131.09, 123.71, 121.20, 119.97, 118.39, 112.66, 111.14, 73.09, 55.57.



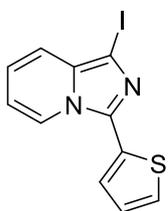
**1-iodo-3-(4-methoxyphenyl)imidazo[1,5-a]pyridine (3bt)<sup>[4]</sup>:**

From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and 4-methoxybenzaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (210.0 mg, 75%) was obtained as a faint yellow solid. *R*<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 15:1 – 3:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.03 (d, *J* = 7.2 Hz, 1H), 7.62-7.51 (m, 2H), 7.21 (d, *J* = 9.2 Hz, 1H), 6.95-6.90 (m, 2H), 6.66 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.47 (t, *J* = 6.8 Hz, 1H), 3.76 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 160.21, 140.49, 133.08, 130.05, 129.49, 121.81, 121.74, 119.98, 118.94, 114.47, 114.23, 113.78, 73.52, 55.44.



**1-iodo-3-(naphthalen-2-yl)imidazo[1,5-a]pyridine (3bu):**

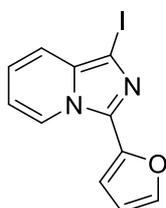
From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and 2-naphthaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (233.8 mg, 79%) was obtained as a faint yellow solid. *R*<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 15:1 – 3:1). m.p.: 120-121 °C; IR (KBr) 3055, 1628, 1598, 1498, 1438, 1363, 1265, 1199, 1112, 1008, 954, 860, 825, 744, 684 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.21 (d, *J* = 7.2 Hz, 1H), 8.10 (s, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.81-7.73 (m, 3H), 7.46-7.36 (m, 2H), 7.27 (d, *J* = 9.2 Hz, 1H), 6.70 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.51 (t, *J* = 6.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 140.48, 133.58, 133.29, 133.24, 128.87, 128.30, 127.86, 126.95, 126.88, 126.78, 126.70, 125.43, 121.90, 120.38, 119.08, 114.15, 74.50; HRMS(ESI): calculated for C<sub>17</sub>H<sub>12</sub>IN<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 371.0040, found: 371.0035.



**1-iodo-3-(thiophen-2-yl)imidazo[1,5-a]pyridine (3bv)<sup>[5]</sup>:**

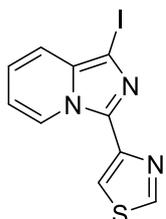
From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and thiophene-2-carbaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (200.8 mg, 77%) was obtained as a faint yellow solid. *R*<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 15:1 – 3:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.21 (d, *J* = 7.2 Hz, 1H), 7.44 (d, *J* = 3.7 Hz, 1H), 7.35 (d, *J* = 5.1 Hz, 1H), 7.29 (d, *J*

= 9.2 Hz, 1H), 7.10 (dd,  $J = 5.1, 3.6$  Hz, 1H), 6.75 (dd,  $J = 9.1, 6.4$  Hz, 1H), 6.62 (t,  $J = 6.8$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 135.20, 133.55, 131.18, 127.63, 126.45, 125.39, 122.14, 120.24, 119.08, 114.52, 74.41.



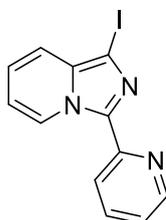
### 3-(furan-2-yl)-1-iodoimidazo[1,5-a]pyridine (3bw)<sup>[4]</sup>:

From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and furan-2-carbaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (186.0 mg, 75%) was obtained as a faint yellow solid.  $R_f = 0.3$  (petroleum ether / ethyl acetate = 15:1 – 3:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.33 (d,  $J = 7.2$  Hz, 1H), 7.55 (d,  $J = 3.7$  Hz, 1H), 7.46 (d,  $J = 5.1$  Hz, 1H), 7.40 (d,  $J = 9.2$  Hz, 1H), 7.20 (dd,  $J = 5.1, 3.7$  Hz, 1H), 6.86 (dd,  $J = 9.2, 6.4$  Hz, 1H), 6.73 (t,  $J = 6.8$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 147.19, 137.97, 135.30, 134.67, 127.78, 124.38, 121.73, 121.47, 119.39, 115.38, 76.30.



### 4-(1-iodoimidazo[1,5-a]pyridin-3-yl)thiazole (3bx):

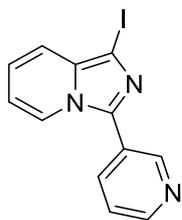
From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and thiazole-4-carbaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (211.9 mg, 81%) was obtained as a faint yellow solid.  $R_f = 0.3$  (petroleum ether / ethyl acetate = 15:1 – 3:1). m.p.: 117-119 °C; IR (KBr) 3074, 1625, 1500, 1452, 1342, 1303, 1257, 1103, 995, 956, 883, 813, 740, 686  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 9.44 (d,  $J = 7.3$  Hz, 1H), 8.93 (d,  $J = 2.2$  Hz, 1H), 8.12 (d,  $J = 2.2$  Hz, 1H), 7.37 (d,  $J = 9.2$  Hz, 1H), 6.87 (dd,  $J = 9.2, 6.5$  Hz, 1H), 6.71 (t,  $J = 6.9$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 152.73, 147.41, 135.28, 133.30, 125.27, 120.74, 118.33, 116.23, 113.99, 74.18; HRMS(ESI): calculated for  $\text{C}_{10}\text{H}_7\text{IN}_3\text{S}^+$   $[\text{M}+\text{H}]^+$ : 327.9400, found: 327.9398.



### 1-iodo-3-(pyridin-2-yl)imidazo[1,5-a]pyridine (3by)<sup>[4]</sup>:

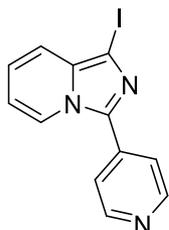
From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and picolinaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (215.7 mg, 84%) was obtained as a faint yellow solid.  $R_f = 0.3$  (petroleum ether / ethyl acetate = 15:1 – 3:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 9.77 (d,  $J = 7.3$  Hz, 1H), 8.46 (s, 1H), 8.19 (d,  $J = 8.1$  Hz, 1H), 7.62 (t,  $J = 7.6$  Hz, 1H), 7.25 (d,  $J = 9.1$  Hz, 1H), 7.05 (t,  $J = 6.2$  Hz, 1H), 6.77 (dd,  $J = 9.2, 6.4$  Hz, 1H), 6.60 (t,  $J = 6.9$  Hz, 1H);  $^{13}\text{C}$

NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ : 150.16, 148.08, 137.69, 136.50, 134.52, 126.49, 121.92, 121.85, 121.46, 118.15, 114.28, 75.02.



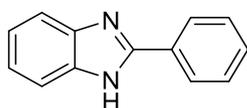
**1-iodo-3-(pyridin-3-yl)imidazo[1,5-a]pyridine (3bz):**

From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and nicotinaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (202.9 mg, 79%) was obtained as a faint yellow solid. *R*<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 15:1 – 3:1). m.p.: 102-104 °C; IR (KBr) 3037, 1629, 1585, 1494, 1406, 1363, 1263, 1172, 1099, 999, 941, 812, 744, 707, 678 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.94 (s, 1H), 8.56 (d, *J* = 4.9 Hz, 1H), 8.10 (d, *J* = 7.2 Hz, 1H), 7.99 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.35 (dd, *J* = 8.0, 4.9 Hz, 1H), 7.27 (d, *J* = 9.2 Hz, 1H), 6.75 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.58 (t, *J* = 6.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ : 149.78, 148.30, 137.29, 135.30, 133.91, 125.77, 123.84, 121.41, 120.78, 119.12, 114.71, 74.99; HRMS(ESI): calculated for C<sub>12</sub>H<sub>9</sub>IN<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup>: 321.9836, found: 321.9837.



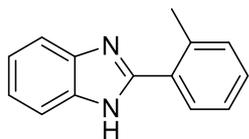
**1-iodo-3-(pyridin-4-yl)imidazo[1,5-a]pyridine (3bba):**

From 2-pyridinemethanamine (0.8 mmol, 1 eq.) and isonicotinaldehyde (1.6 mmol, 2 eq.), following the general procedure B, the title compound (210.6 mg, 82%) was obtained as a faint yellow solid. *R*<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 15:1 – 3:1). m.p.: 161-163 °C; IR (KBr) 3032, 1591, 1493, 1446, 1409, 1357, 1245, 1141, 985, 947, 833, 742, 676 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.66 (s, 2H), 8.26 (d, *J* = 7.2 Hz, 1H), 7.64 (d, *J* = 4.4 Hz, 2H), 7.35 (d, *J* = 9.2 Hz, 1H), 6.83 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.68 (t, *J* = 6.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ : 150.57, 137.49, 136.62, 134.60, 121.83, 121.23, 121.18, 119.39, 115.14, 75.95; HRMS(ESI): calculated for C<sub>12</sub>H<sub>9</sub>IN<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup>: 321.9836, found: 321.9834.



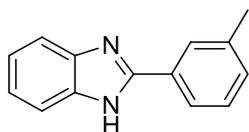
**2-phenyl-1H-benzo[d]imidazole (3c)<sup>[5]</sup>:**

From benzene-1,2-diamine (1 mmol, 1 eq.) and benzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (174.6 mg, 90%) was obtained as a faint yellow solid. *R*<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 8.28 (d, *J* = 7.6 Hz, 2H), 7.7-7.62 (m, 2H), 7.61-7.45 (m, 3H), 7.29-7.18 (m, 2H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 151.81, 139.96, 130.70, 130.30, 129.41, 129.22, 126.99, 122.63, 115.60.



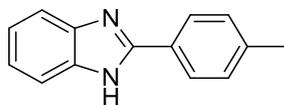
**2-(o-tolyl)-1H-benzo[d]imidazole (3cb)<sup>[5]</sup>:**

From benzene-1,2-diamine (1 mmol, 1 eq.) and 2-methylbenzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (174.7 mg, 84%) was obtained as a faint yellow solid. R<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 7.82-7.73 (m, 1H), 7.63 (s, 2H), 7.39 (s, 3H), 7.22 (s, 2H), 2.62 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 152.41, 137.49, 131.72, 130.53, 129.92, 129.78, 126.42, 122.35, 21.50.



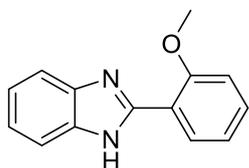
**2-(m-tolyl)-1H-benzo[d]imidazole (3cc)<sup>[5]</sup>:**

From benzene-1,2-diamine (1 mmol, 1 eq.) and 3-methylbenzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (178.9 mg, 86%) was obtained as a faint yellow solid. R<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 8.04 (s, 1H), 7.99 (d, J = 7.7 Hz, 1H), 7.71-7.54 (m, 2H), 7.45 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.28-7.16 (m, 2H), 2.42 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 151.63, 138.69, 131.18, 130.09, 129.36, 127.57, 124.17, 122.76, 115.46, 21.51.



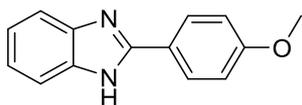
**2-(p-tolyl)-1H-benzo[d]imidazole (3cd)<sup>[5]</sup>:**

From benzene-1,2-diamine (1 mmol, 1 eq.) and 4-methylbenzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (185.1 mg, 89%) was obtained as a faint yellow solid. R<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 8.10 (d, J = 7.8 Hz, 2H), 7.61 (dd, J = 6.1, 3.1 Hz, 2H), 7.36 (d, J = 7.9 Hz, 2H), 7.27-7.15 (m, 2H), 2.37 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 151.81, 140.14, 139.64, 129.98, 129.81, 127.72, 126.92, 122.53, 115.39, 21.43.



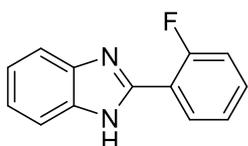
**2-(2-methoxyphenyl)-1H-benzo[d]imidazole (3ce)<sup>[5]</sup>:**

From benzene-1,2-diamine (1 mmol, 1 eq.) and 2-methoxybenzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (185.9 mg, 83%) was obtained as a faint yellow solid. R<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 8.34 (dd, J = 7.7, 1.8 Hz, 1H), 7.64 (dd, J = 6.0, 3.2 Hz, 2H), 7.54-7.44 (m, 1H), 7.29-7.17 (m, 3H), 7.13 (t, J = 7.5 Hz, 1H), 4.03 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 157.25, 149.36, 131.81, 130.21, 122.35, 121.35, 118.41, 112.57, 56.23.



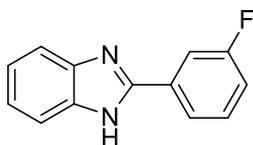
**2-(4-methoxyphenyl)-1H-benzo[d]imidazole (3cf) <sup>[5]</sup>:**

From benzene-1,2-diamine (1 mmol, 1 eq.) and 4-methoxybenzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (194.9 mg, 87%) was obtained as a faint yellow solid. R<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 8.17 (d, *J* = 8.9 Hz, 2H), 7.59 (dd, *J* = 6.0, 3.2 Hz, 2H), 7.19 (dd, *J* = 6.0, 3.2 Hz, 2H), 7.12 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 161.13, 151.82, 139.82, 128.54, 123.06, 122.30, 115.18, 114.83, 55.76.



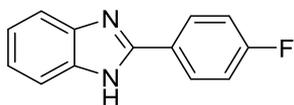
**2-(2-fluorophenyl)-1H-benzo[d]imidazole (3cg) <sup>[5]</sup>:**

From benzene-1,2-diamine (1 mmol, 1 eq.) and 2-fluorobenzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (186.6 mg, 88%) was obtained as a faint yellow solid. R<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 8.31 (t, *J* = 7.8 Hz, 1H), 7.78-7.63 (m, 2H), 7.58-7.49 (m, 1H), 7.47-7.35 (m, 2H), 7.26 (dd, *J* = 6.1, 3.2 Hz, 2H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 159.98 (d, *J* = 249.9 Hz), 146.95, 132.24 (d, *J* = 8.6 Hz), 130.74, 130.71, 125.50 (d, *J* = 3.3 Hz), 122.80, 118.68, 118.57, 116.94 (d, *J* = 21.7 Hz); <sup>19</sup>F NMR (376 MHz, DMSO-d<sub>6</sub>) δ: -114.57.



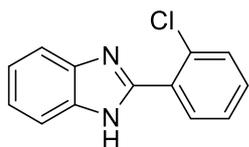
**2-(3-fluorophenyl)-1H-benzo[d]imidazole (3ch) <sup>[5]</sup>:**

From benzene-1,2-diamine (1 mmol, 1 eq.) and 3-fluorobenzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (192.9 mg, 91%) was obtained as a faint yellow solid. R<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 8.05 (d, *J* = 7.8 Hz, 1H), 8.02-7.93 (m, 1H), 7.77-7.55 (m, 3H), 7.38-7.30 (m, 1H), 7.24 (dd, *J* = 6.1, 3.1 Hz, 2H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 162.93 (d, *J* = 243.6 Hz), 150.45, 150.42, 133.01, 132.93, 131.60 (d, *J* = 8.4 Hz), 122.99 (d, *J* = 2.9 Hz), 117.06 (d, *J* = 21.2 Hz), 113.61, 113.37; <sup>19</sup>F NMR (376 MHz, DMSO-d<sub>6</sub>) δ: -112.39.



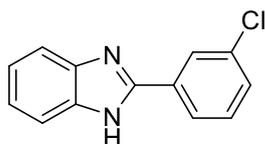
**2-(4-fluorophenyl)-1H-benzo[d]imidazole (3ci) <sup>[5]</sup>:**

From benzene-1,2-diamine (1 mmol, 1 eq.) and 4-fluorobenzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (197.2 mg, 93%) was obtained as a faint yellow solid. R<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 8.34-8.16 (m, 2H), 7.68-7.56 (m, 2H), 7.46-7.34 (m, 2H), 7.27-7.15 (m, 2H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 163.52 (d, *J* = 247.5 Hz), 150.90, 129.21 (d, *J* = 8.6 Hz), 127.29 (d, *J* = 3.0 Hz), 122.61, 116.40 (d, *J* = 21.9 Hz); <sup>19</sup>F NMR (376 MHz, DMSO-d<sub>6</sub>) δ: -111.17.



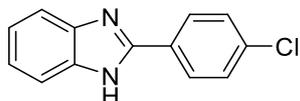
**2-(2-chlorophenyl)-1H-benzo[d]imidazole (3cj) [5]:**

From benzene-1,2-diamine (1 mmol, 1 eq.) and 2-chlorobenzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (205.2 mg, 90%) was obtained as a faint yellow solid. Rf = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 7.98-7.89 (m, 1H), 7.73-7.61 (m, 3H), 7.56-7.49 (m, 2H), 7.29-7.20 (m, 2H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 149.60, 132.56, 132.14, 131.64, 130.82, 130.46, 127.88, 122.70.



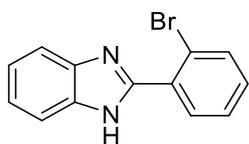
**2-(3-chlorophenyl)-1H-benzo[d]imidazole (3ck) [5]:**

From benzene-1,2-diamine (1 mmol, 1 eq.) and 3-chlorobenzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (212.0 mg, 93%) was obtained as a faint yellow solid. Rf = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 8.25 (s, 1H), 8.16 (d, J = 7.3 Hz, 1H), 7.69 (s, 1H), 7.63-7.52 (m, 3H), 7.23 (s, 2H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 150.20, 134.25, 132.67, 131.40, 130.00, 126.50, 125.48, 119.54, 111.94.



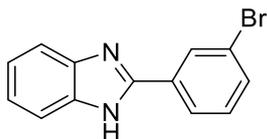
**2-(4-chlorophenyl)-1H-benzo[d]imidazole (3cl) [5]:**

From benzene-1,2-diamine (1 mmol, 1 eq.) and 4-chlorobenzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (216.6 mg, 95%) was obtained as a faint yellow solid. Rf = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 8.20 (d, J = 6.6 Hz, 2H), 7.69-7.56 (m, 4H), 7.27-7.16 (m, 2H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 150.63, 134.97, 133.01, 132.59, 132.48, 129.53, 129.51, 128.61, 122.78.



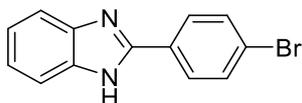
**2-(2-bromophenyl)-1H-benzo[d]imidazole (3cm) [5]:**

From benzene-1,2-diamine (1 mmol, 1 eq.) and 2-bromobenzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (247.5 mg, 91%) was obtained as a faint yellow solid. Rf = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 7.81 (t, J = 8.6 Hz, 2H), 7.73-7.59 (m, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.7 Hz, 1H), 7.36-7.11 (m, 2H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 150.93, 139.10, 133.88, 132.88, 132.75, 131.83, 128.25, 122.66, 122.07, 120.03, 115.83.



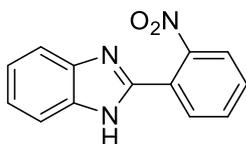
**2-(3-bromophenyl)-1H-benzo[d]imidazole (3cn) <sup>[5]</sup>:**

From benzene-1,2-diamine (1 mmol, 1 eq.) and 3-bromobenzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (250.2 mg, 92%) was obtained as a faint yellow solid. Rf = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 8.39 (t, *J* = 1.9 Hz, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.60-7.45 (m, 2H), 7.28-7.18 (m, 2H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 150.09, 144.11, 135.48, 132.88, 131.63, 129.36, 125.84, 123.42, 122.74, 122.41, 119.55, 111.99.



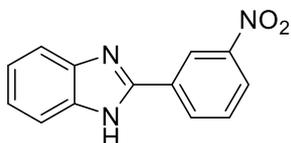
**2-(4-bromophenyl)-1H-benzo[d]imidazole (3co) <sup>[5]</sup>:**

From benzene-1,2-diamine (1 mmol, 1 eq.) and 4-bromobenzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (261.1 mg, 96%) was obtained as a faint yellow solid. Rf = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 8.13 (d, *J* = 7.5 Hz, 2H), 7.77 (d, *J* = 7.5 Hz, 2H), 7.61 (s, 2H), 7.27-7.16 (m, 2H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 150.68, 138.25, 132.98, 132.45, 129.86, 128.83, 123.72, 122.85, 122.76.



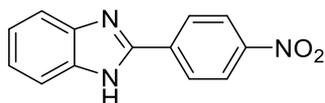
**2-(2-nitrophenyl)-1H-benzo[d]imidazole (3cp) <sup>[5]</sup>:**

From benzene-1,2-diamine (1 mmol, 1 eq.) and 2-nitrobenzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (207.9 mg, 87%) was obtained as a faint yellow solid. Rf = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 8.04 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.87 (t, *J* = 7.6 Hz, 1H), 7.76 (t, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 24.1 Hz, 2H), 7.26 (s, 2H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 149.44, 147.78, 144.09, 137.37, 135.07, 133.10, 131.38, 124.76, 124.71, 123.54, 122.36, 119.65, 112.14.



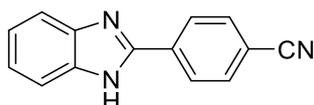
**2-(3-nitrophenyl)-1H-benzo[d]imidazole (3cq) <sup>[5]</sup>:**

From benzene-1,2-diamine (1 mmol, 1 eq.) and 3-nitrobenzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (212.7 mg, 89%) was obtained as a faint yellow solid. Rf = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 8.51-8.34 (m, 4H), 7.67 (s, 2H), 7.33-7.15 (m, 2H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 155.15, 149.46, 148.80, 148.28, 136.49, 131.29, 130.82, 129.73, 129.09, 127.86, 124.76, 123.46, 121.70.



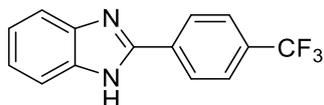
**2-(4-nitrophenyl)-1H-benzo[d]imidazole (3cr) <sup>[5]</sup>:**

From benzene-1,2-diamine (1 mmol, 1 eq.) and 4-nitrobenzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (217.5 mg, 91%) was obtained as a faint yellow solid. Rf = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 8.98 (s, 1H), 8.57 (d, *J* = 7.8 Hz, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 7.78 (t, *J* = 8.0 Hz, 1H), 7.63 (s, 2H), 7.25-7.20 (m, 2H).; <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 149.49, 148.71, 132.85, 132.15, 130.96, 124.51, 123.33, 121.24, 112.05.



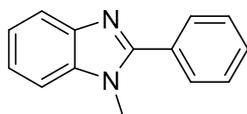
**4-(1H-benzo[d]imidazol-2-yl)benzonitrile (3cs) <sup>[5]</sup>:**

From benzene-1,2-diamine (1 mmol, 1 eq.) and 4-formylbenzonitrile (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (210.2 mg, 96%) was obtained as a faint yellow solid. Rf = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 8.34 (d, *J* = 7.6 Hz, 2H), 8.01 (d, *J* = 7.3 Hz, 2H), 7.65 (s, 2H), 7.32-7.20 (m, 2H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 149.83, 136.47, 134.71, 133.40, 133.24, 133.19, 130.27, 127.56, 127.43, 123.27, 119.08, 112.35.



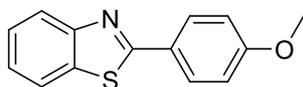
**2-(4-(trifluoromethyl)phenyl)-1H-benzo[d]imidazole (3ct) <sup>[5]</sup>:**

From benzene-1,2-diamine (1 mmol, 1 eq.) and 4-(trifluoromethyl)benzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (256.7 mg, 98%) was obtained as a faint yellow solid. Rf = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 8.41 (d, *J* = 8.1 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.65 (s, 2H), 7.29-7.20 (m, 2H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 150.12, 141.52, 134.45, 134.44, 130.24, 130.14, 129.92, 129.61, 127.54, 126.40 (q, *J* = 3.8 Hz), 125.95, 123.25; <sup>19</sup>F NMR (376 MHz, DMSO-d<sub>6</sub>) δ: -61.20.



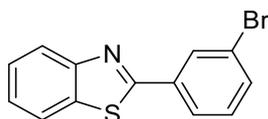
**1-methyl-2-phenyl-1H-benzo[d]imidazole (3cu) <sup>[5]</sup>:**

From benzene-1,2-diamine (1 mmol, 1 eq.) and 4-(trifluoromethyl)benzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (187.2 mg, 90%) was obtained as a faint yellow solid. Rf = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.98-7.79 (m, 1H), 7.79-7.64 (m, 2H), 7.54-7.41 (m, 3H), 7.37-7.24 (m, 3H), 3.75 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 153.71, 142.94, 136.58, 130.18, 129.71, 129.41, 128.67, 122.76, 122.41, 119.75, 109.71, 31.63.

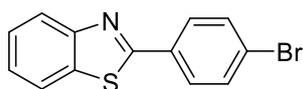


**2-(4-methoxyphenyl)-benzothiazole (3cv)** <sup>[5]</sup>:

From benzene-1,2-diamine (1 mmol, 1 eq.) and 4-methoxybenzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (163.9 mg, 68%) was obtained as a faint yellow solid. R<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.06-7.82 (m, 3H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 2H), 3.74 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 167.92, 161.93, 154.22, 134.86, 129.13, 126.41, 126.24, 124.82, 122.83, 121.54, 114.38, 55.46.

**2-(3-bromophenyl)-benzothiazole (3cw)** <sup>[5]</sup>:

From benzene-1,2-diamine (1 mmol, 1 eq.) and 3-bromobenzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (257.2 mg, 89%) was obtained as a faint yellow solid. R<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.19 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.47 (q, *J* = 7.9 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 165.85, 153.79, 135.34, 135.08, 134.35, 131.92, 129.61, 127.23, 126.79, 126.29, 123.56, 123.00, 122.84.

**2-(4-bromophenyl)-benzothiazole (3cx)** <sup>[5]</sup>:

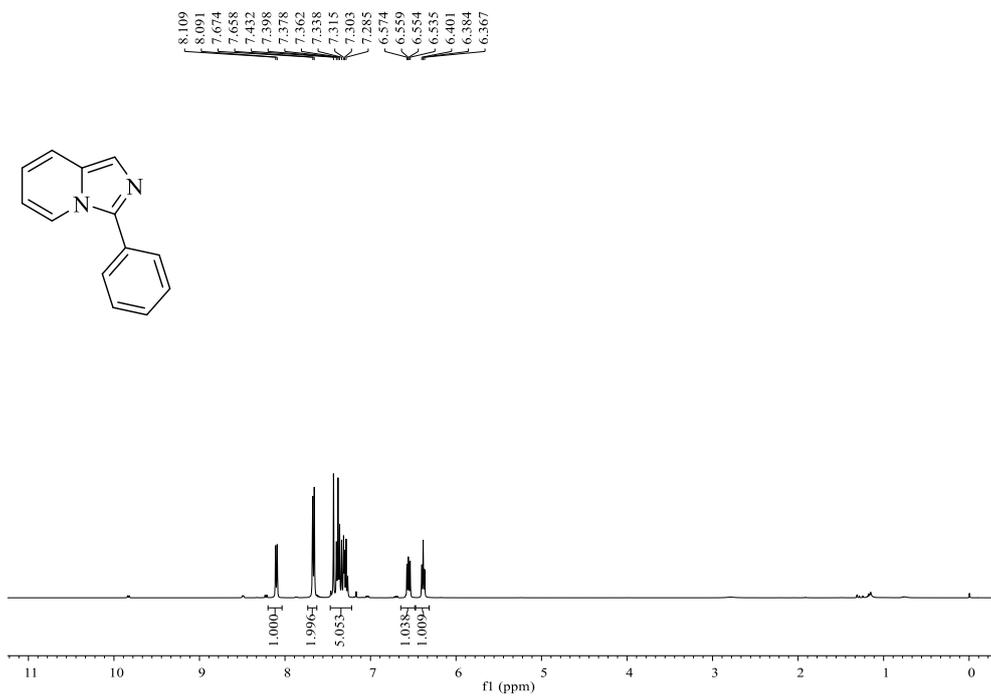
From benzene-1,2-diamine (1 mmol, 1 eq.) and 4-bromobenzaldehyde (1.75 mmol, 1.75 eq.), following the general procedure C, the title compound (262.9 mg, 91%) was obtained as a faint yellow solid. R<sub>f</sub> = 0.3 (petroleum ether / ethyl acetate = 20:1 - 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.09 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 2H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.56-7.47 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 166.70, 154.07, 135.04, 132.53, 132.24, 128.91, 126.53, 125.47, 125.44, 123.33, 121.69.

## 6. References

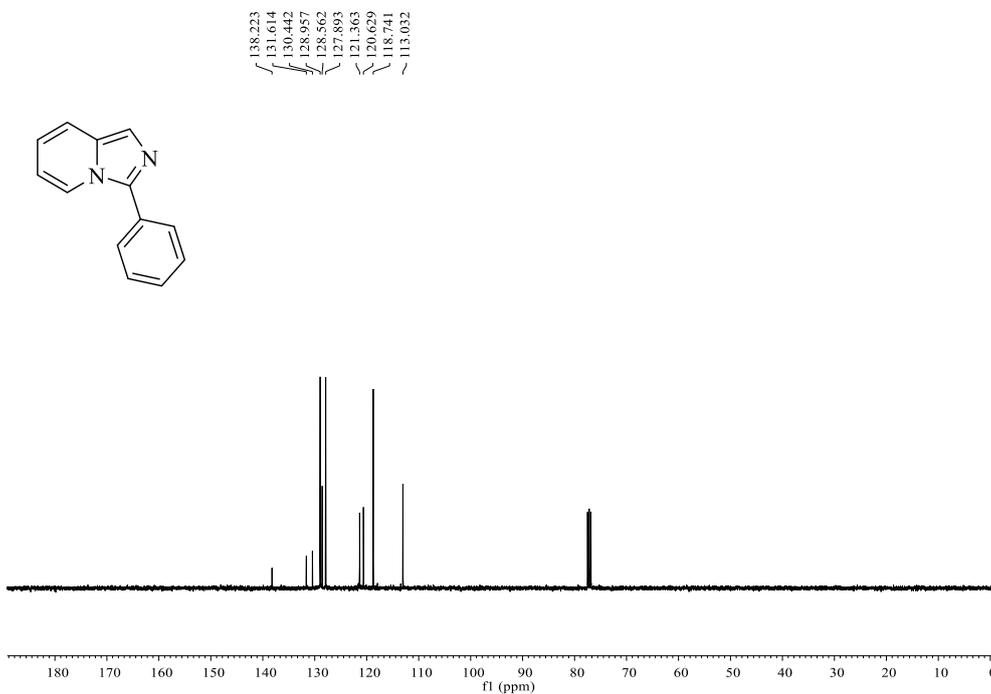
- (1) (a) Li, M.; Xie, Y.; Ye, Y.; Zou, Y.; Jiang, H.; Zeng, W. Cu(I)-catalyzed transannulation of N-heteroaryl aldehydes or ketones with alkylamines via C(sp<sup>3</sup>)-H amination. *Org. Lett.* **2014**, *16* (23), 6232-6235. (b) Li, Z.; Wu, S. S.; Luo, Z. G.; Liu, W. K.; Feng, C. T.; Ma, S. T. Copper-promoted double oxidative C-H amination cascade for the synthesis of imidazo[1,5-a]quinolines. *J. Org. Chem.* **2016**, *81* (10), 4386-4392. (c) Wang, H.; Xu, W.; Wang, Z.; Yu, L.; Xu, K. Copper-catalyzed oxidative amination of C(sp<sup>3</sup>)-H bonds under air: synthesis of 1,3-diarylated imidazo[1,5-a]pyridines. *J. Org. Chem.* **2015**, *80* (4), 2431-2435. (d) Wang, H.; Xu, W.; Xin, L.; Liu, W.; Wang, Z.; Xu, K. Synthesis of 1,3-disubstituted imidazo[1,5-a]pyridines from amino acids via catalytic decarboxylative intramolecular cyclization. *J. Org. Chem.* **2016**, *81* (9), 3681-3687.
- (2) (a) Yan, Y.; Zhang, Y.; Zha, Z.; Wang, Z. Mild metal-free sequential dual oxidative amination of C(sp<sup>3</sup>)-H bonds: efficient synthesis of imidazo[1,5-a]pyridines. *Org. Lett.* **2013**, *15* (9), 2274-2277. (b) Kamal, A.; Ramakrishna, G.; Raju, P.; Rao, A. V. S.; Viswanath, A.; Nayak, V. L.; Ramakrishna, S. Synthesis and anticancer activity of oxindole derived imidazo[1,5-a]pyrazines. *Eur. J. Med. Chem.* **2011**, *46* (6), 2427-2435. (c) Shibahara, F.; Kitagawa, A.; Yamaguchi, E.; Murai, T. Synthesis of 2-azaindolizines by using an iodine-mediated oxidative desulfurization promoted cyclization of N-2-pyridylmethyl thioamides and an investigation of their photophysical properties. *Org. Lett.* **2006**, *8* (24), 5621-5624.
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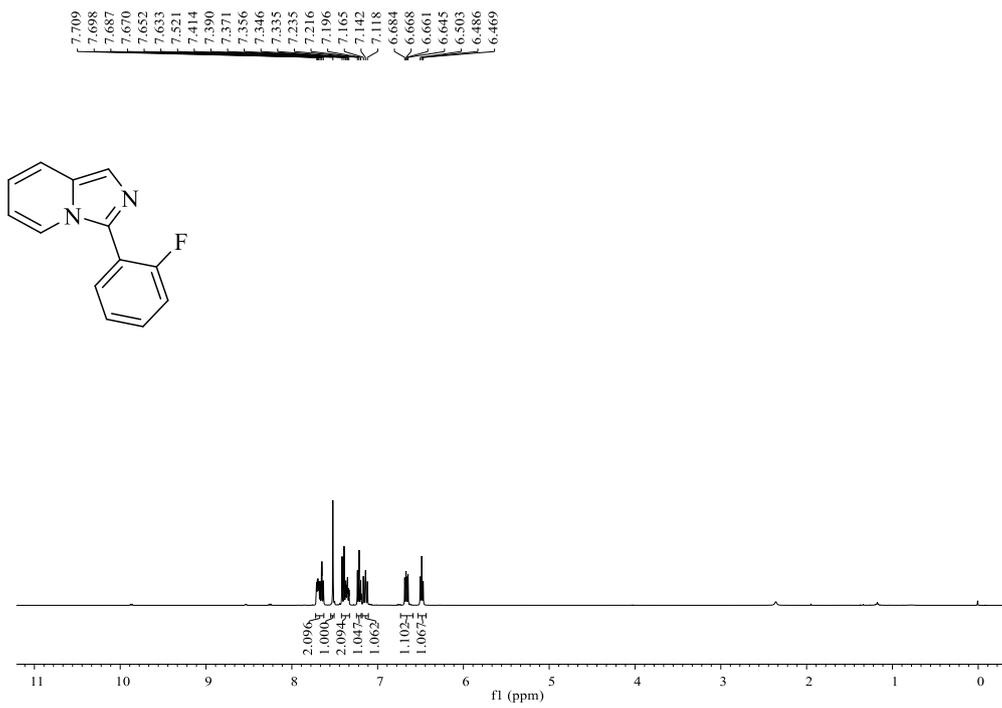
## 7. Copies of NMR Spectra for Compounds



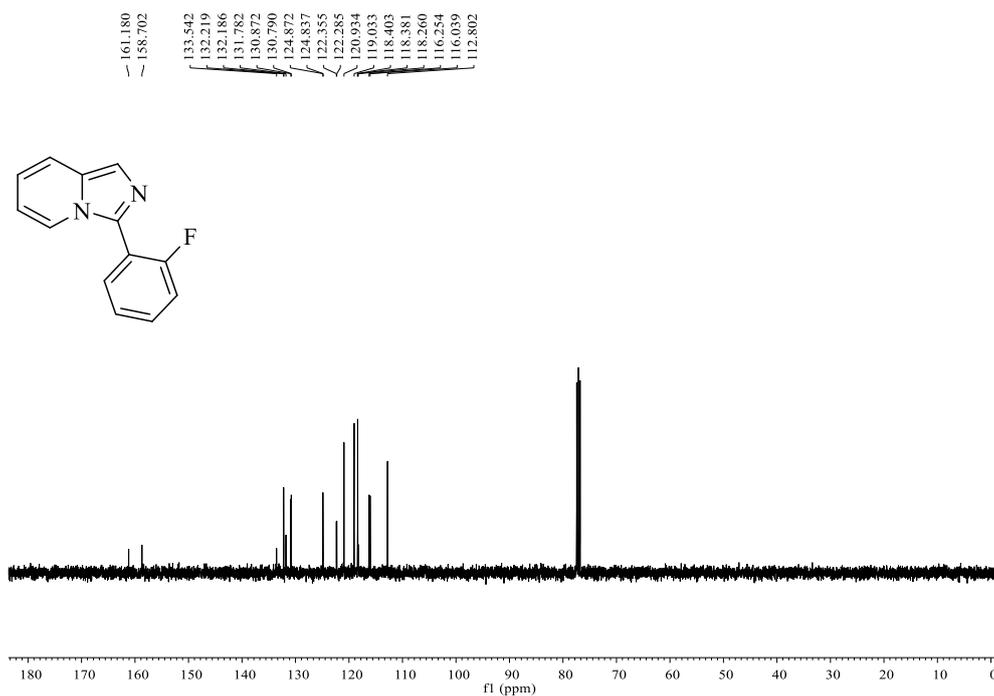
<sup>1</sup>H NMR Spectrum of **3a**



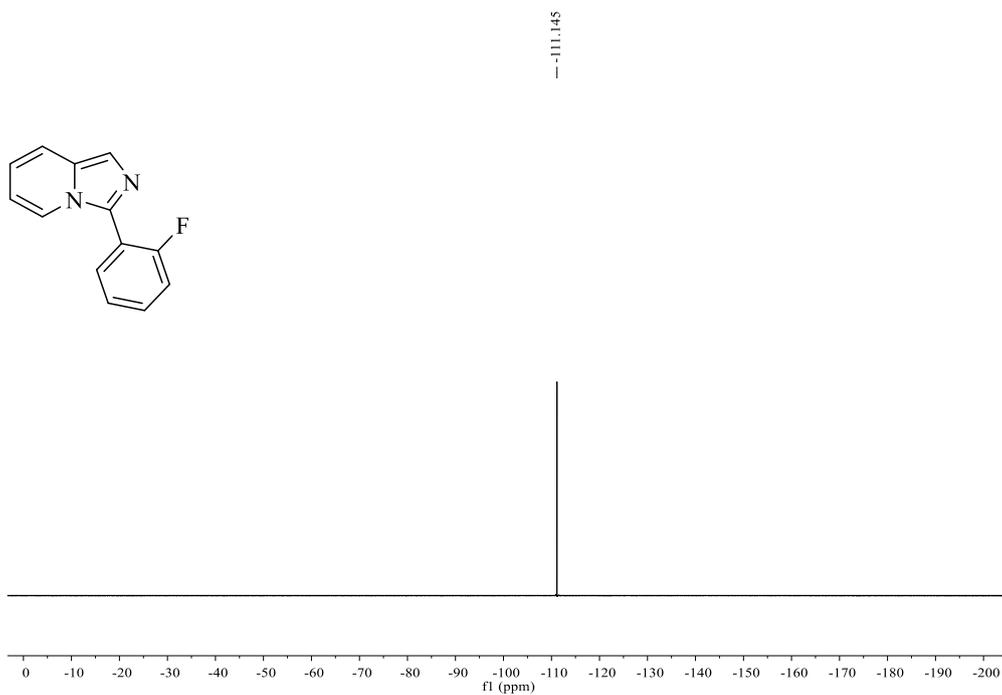
<sup>13</sup>C NMR Spectrum of **3a**



<sup>1</sup>H NMR Spectrum of **3ab**

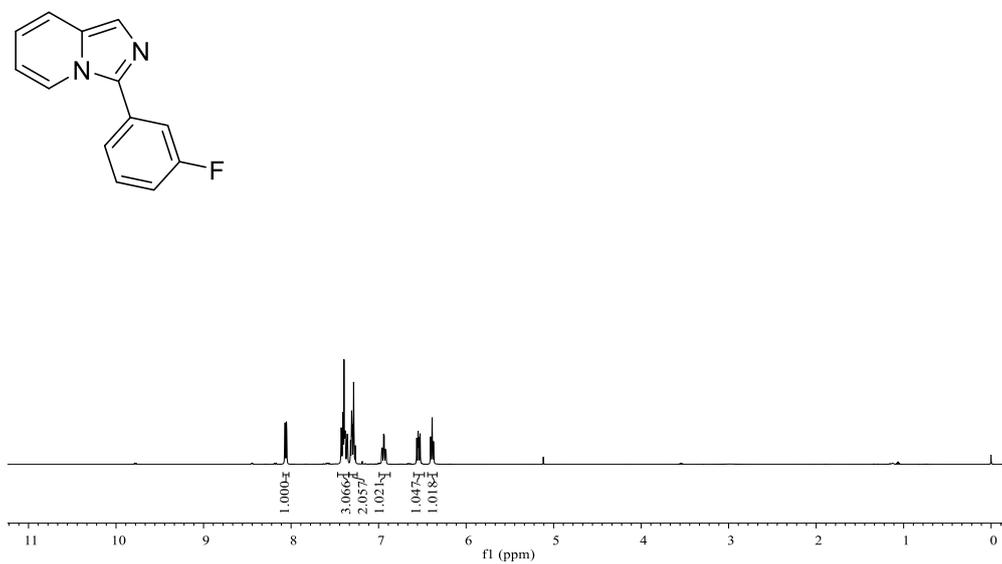


<sup>13</sup>C NMR Spectrum of **3ab**

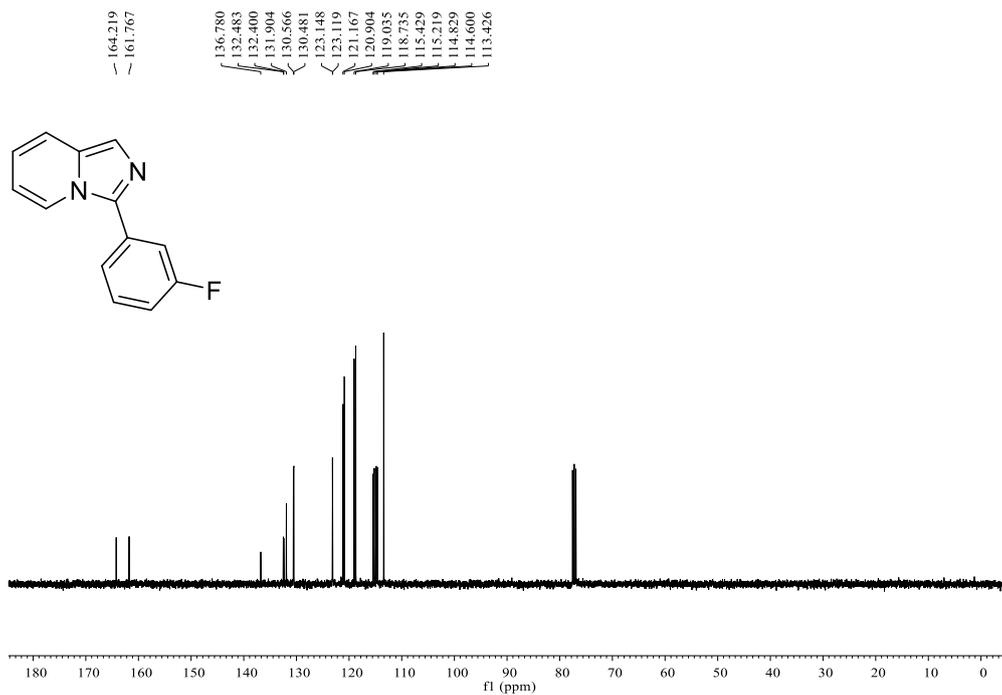


**<sup>19</sup>F NMR Spectrum of 3ab**

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6.525  
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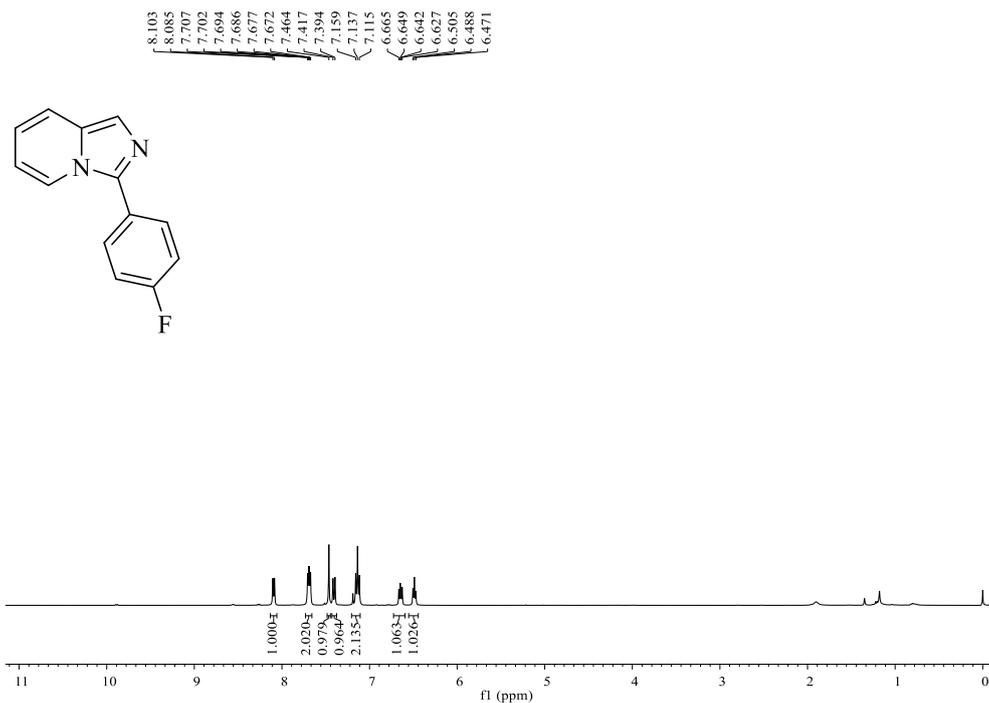
**<sup>1</sup>H NMR Spectrum of 3ac**



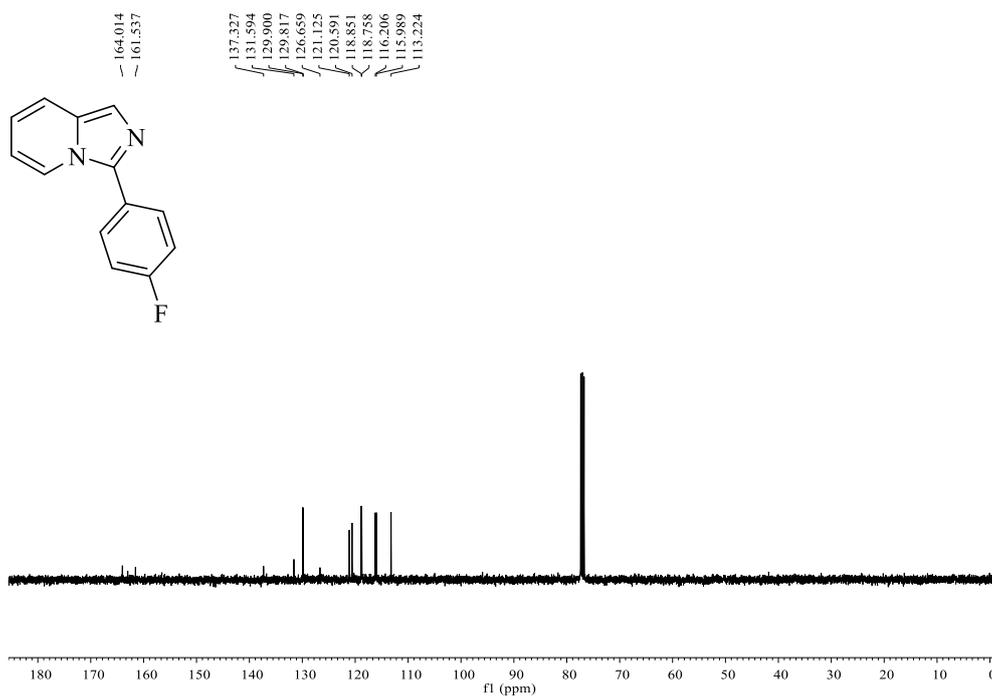
<sup>13</sup>C NMR Spectrum of 3ac



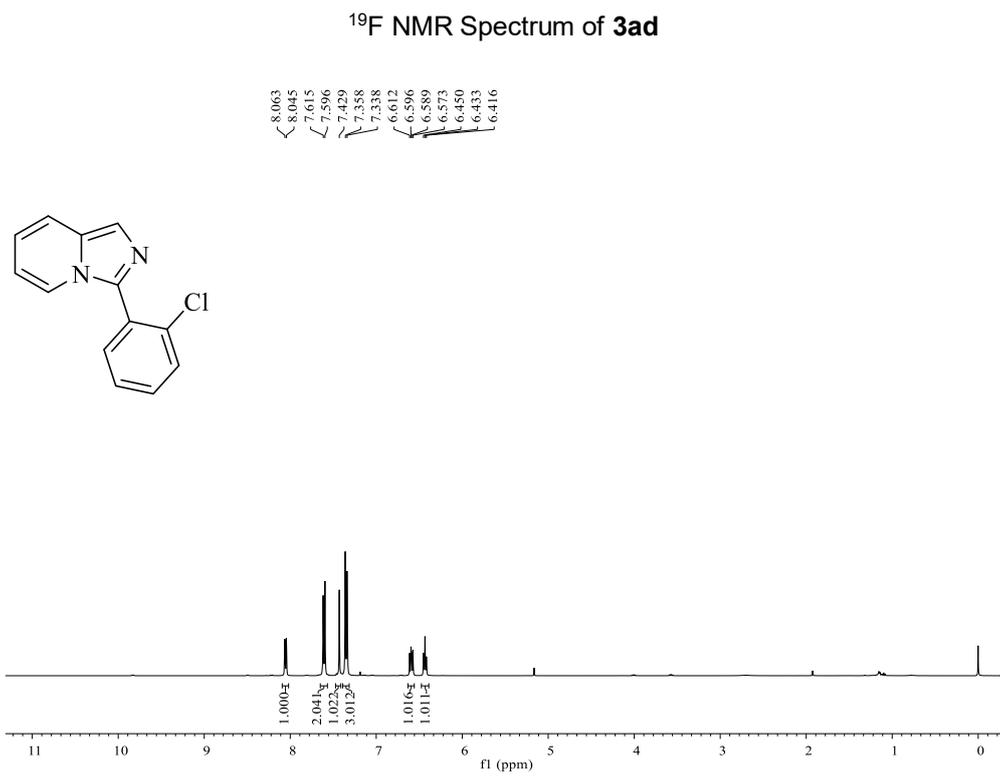
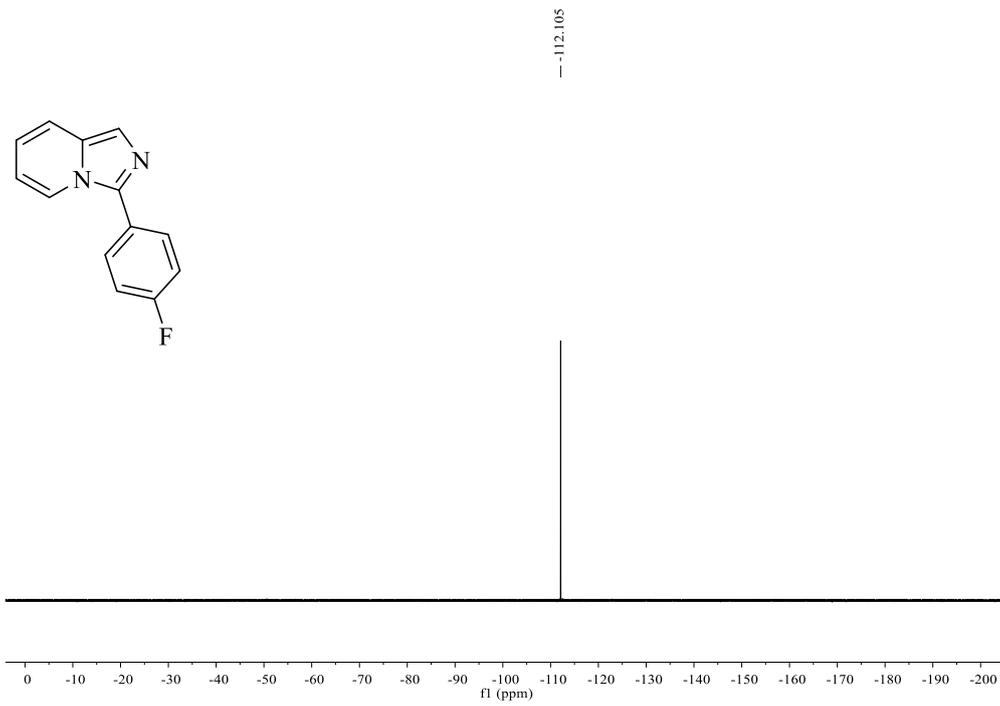
<sup>19</sup>F NMR Spectrum of 3ac

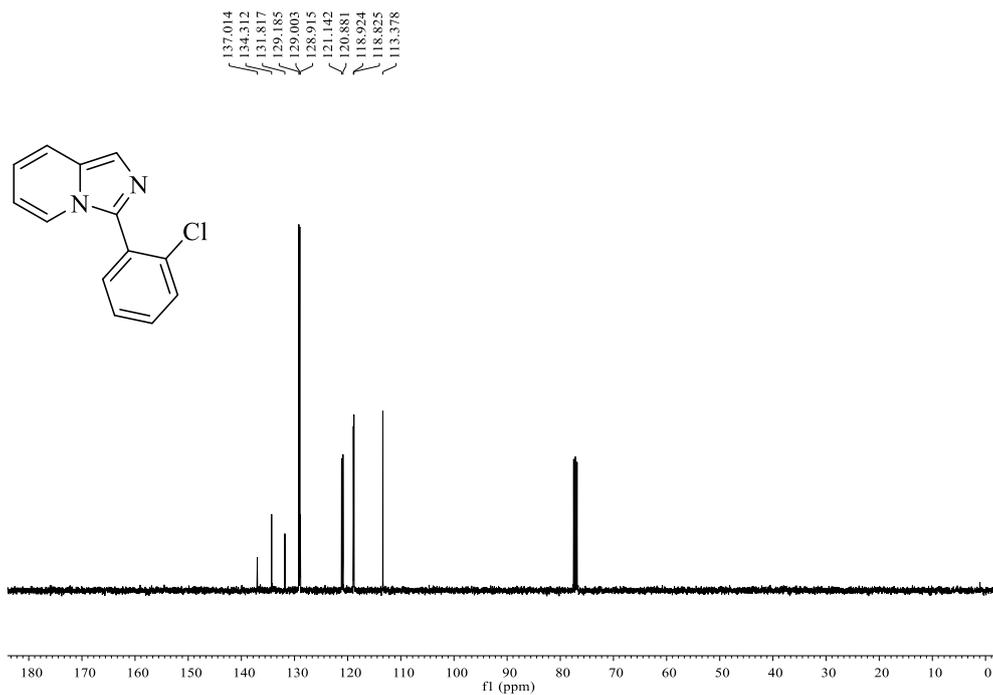


<sup>1</sup>H NMR Spectrum of 3ad

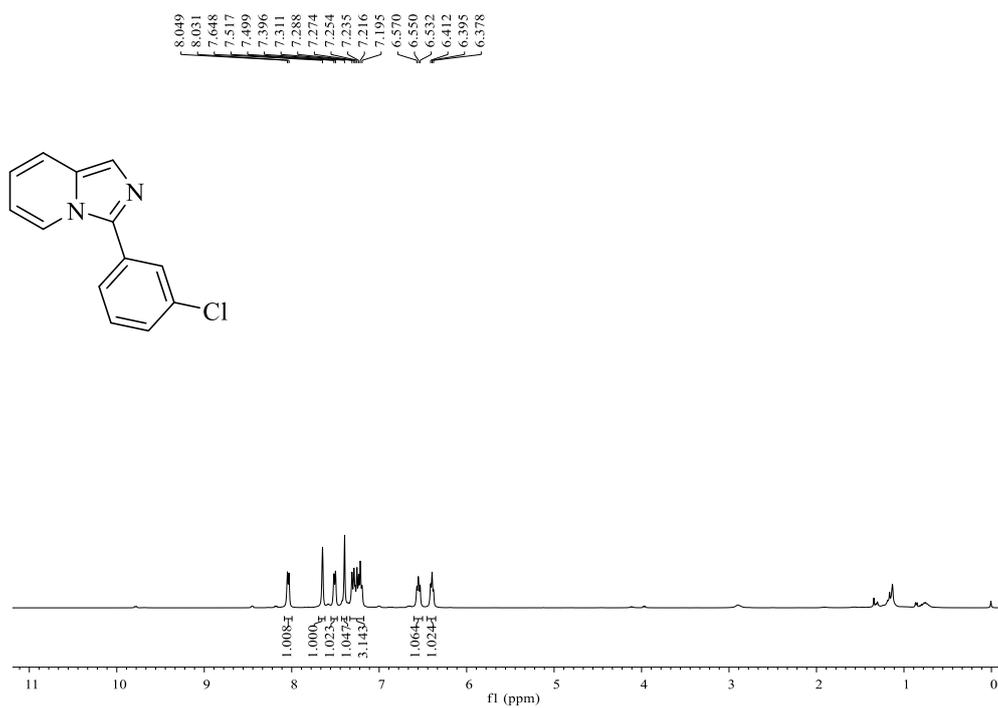


<sup>13</sup>C NMR Spectrum of 3ad

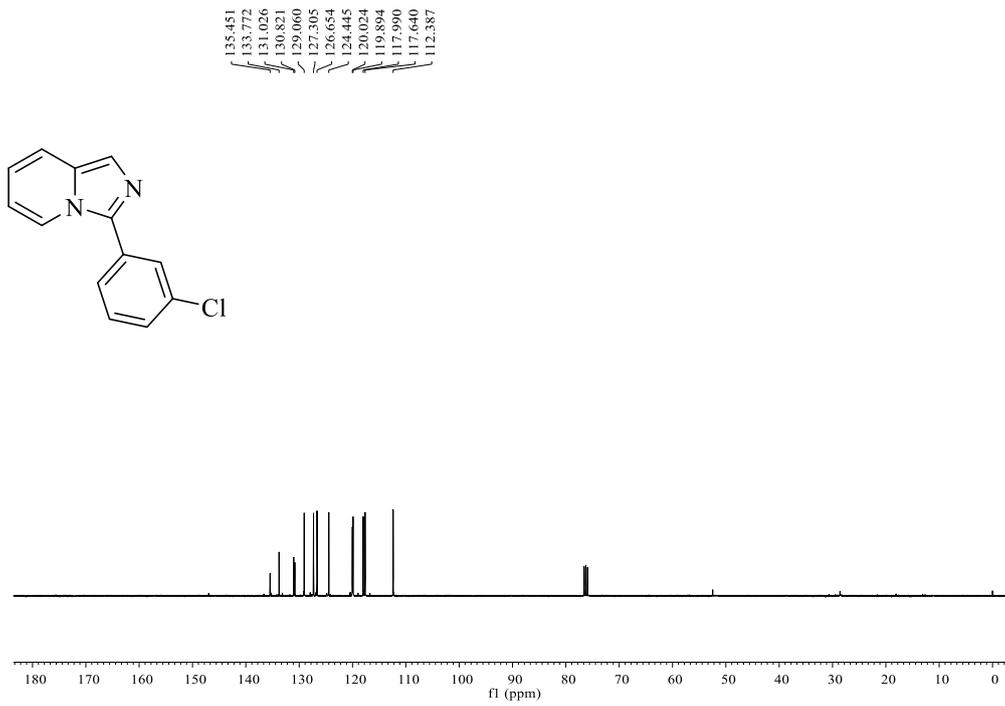




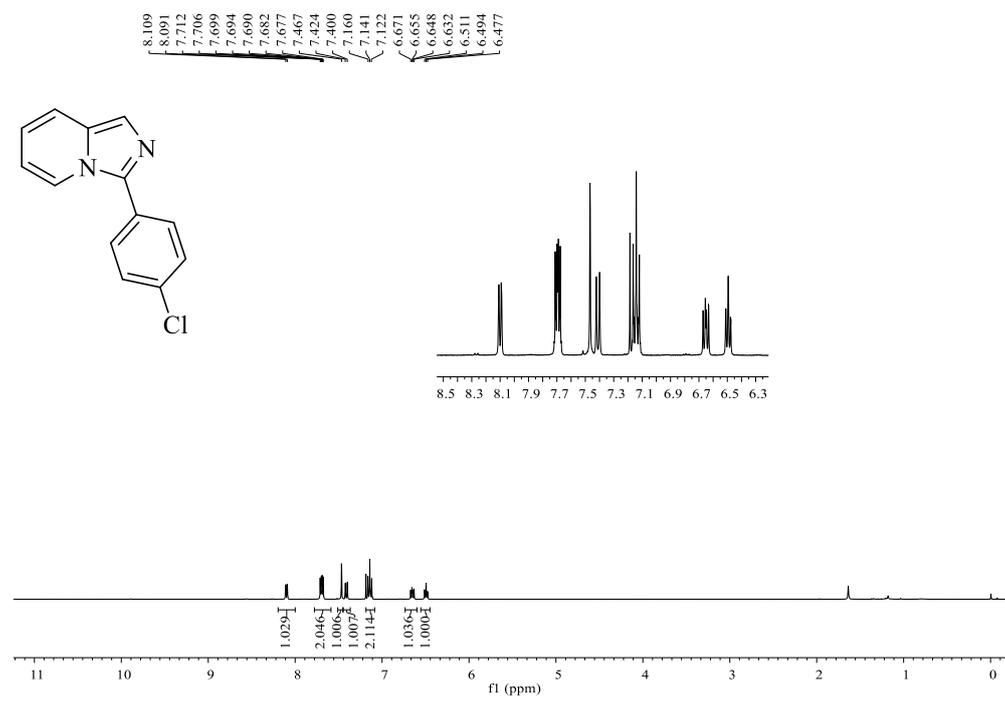
<sup>13</sup>C NMR Spectrum of 3ae



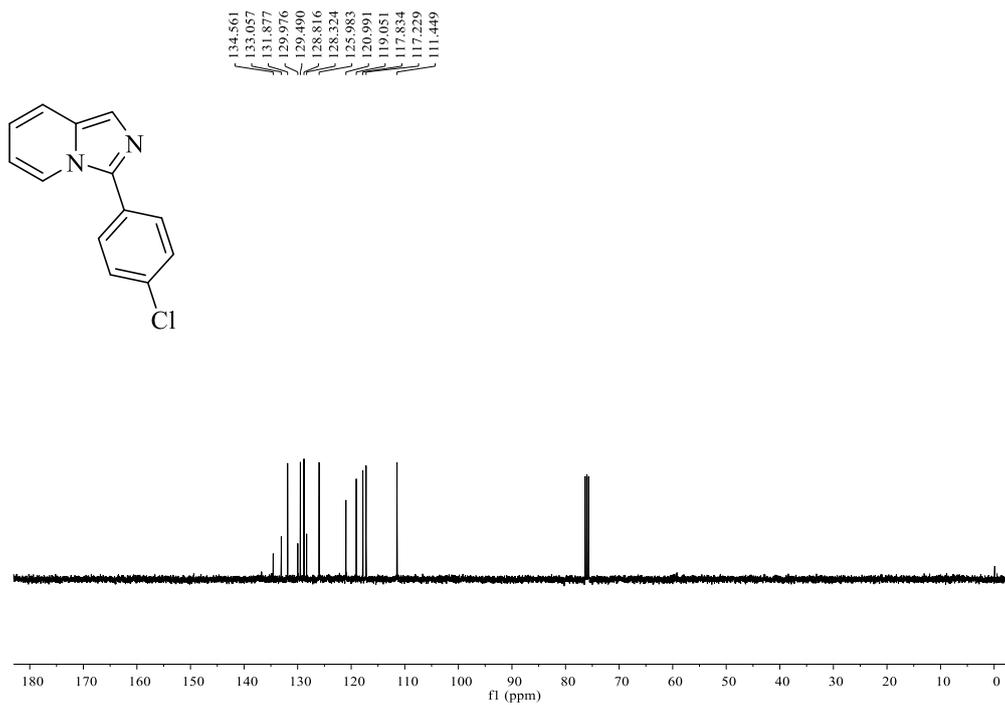
<sup>1</sup>H NMR Spectrum of 3af



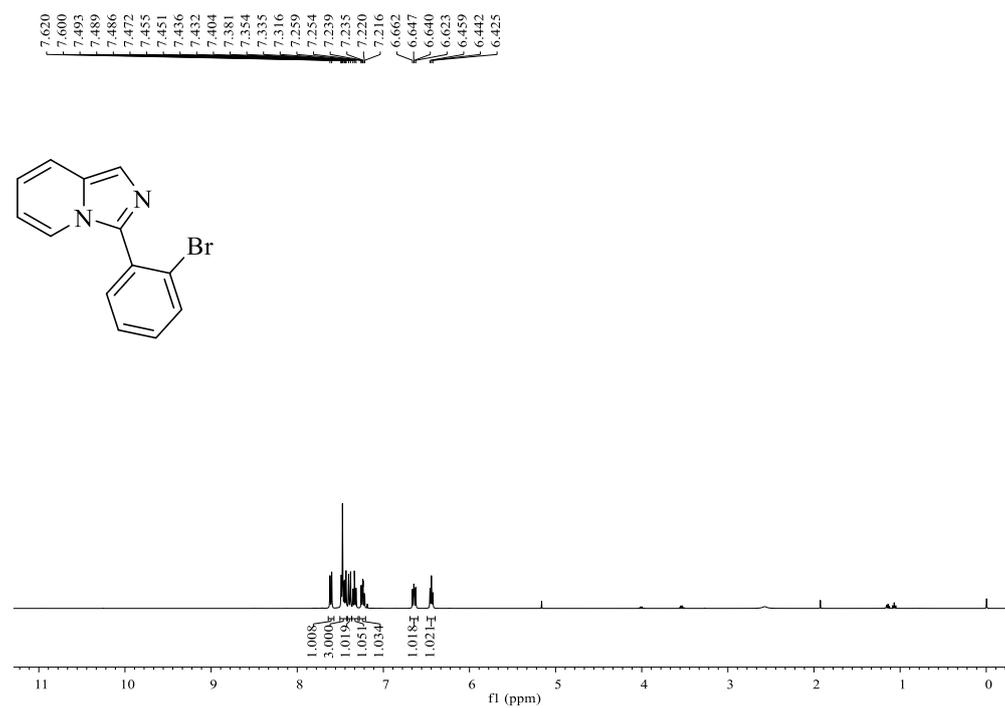
<sup>13</sup>C NMR Spectrum of **3af**



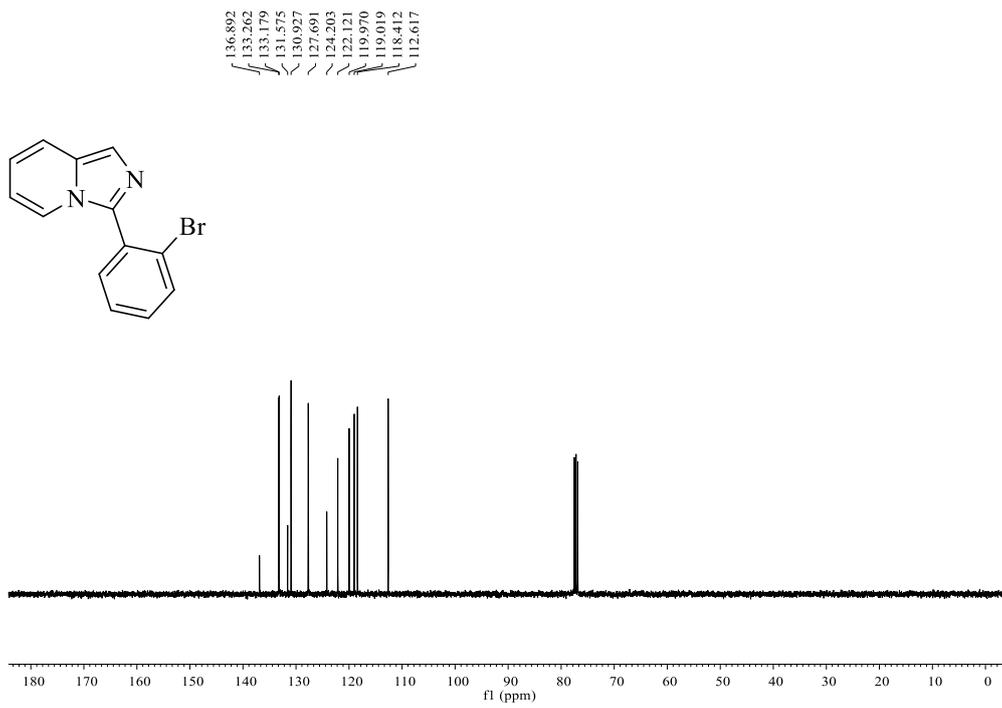
<sup>1</sup>H NMR Spectrum of **3ag**



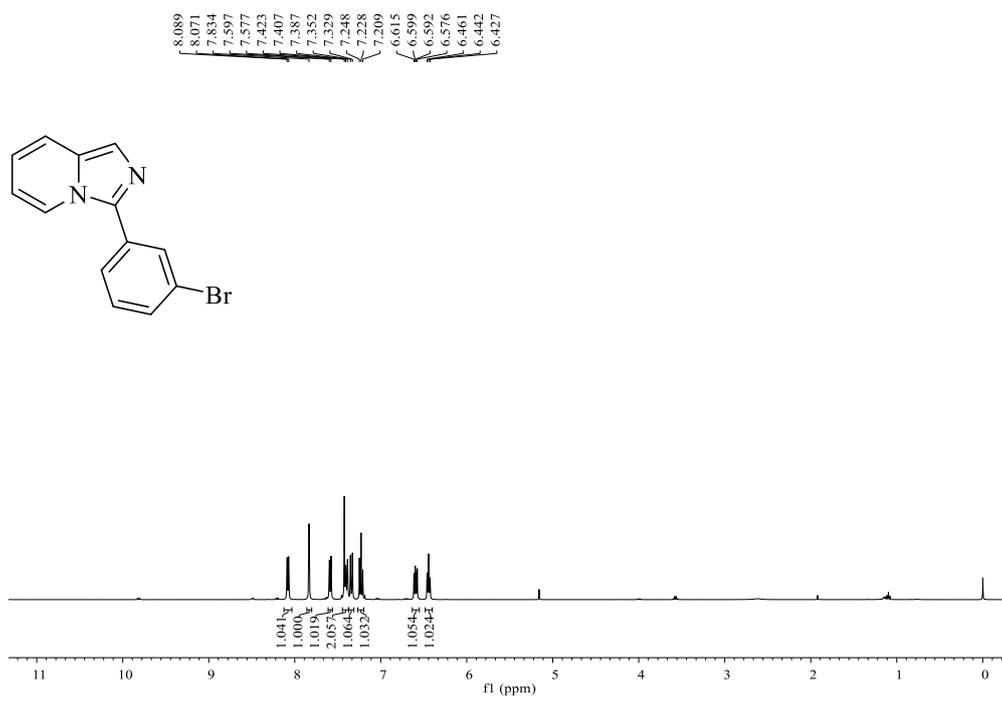
<sup>13</sup>C NMR Spectrum of 3ag



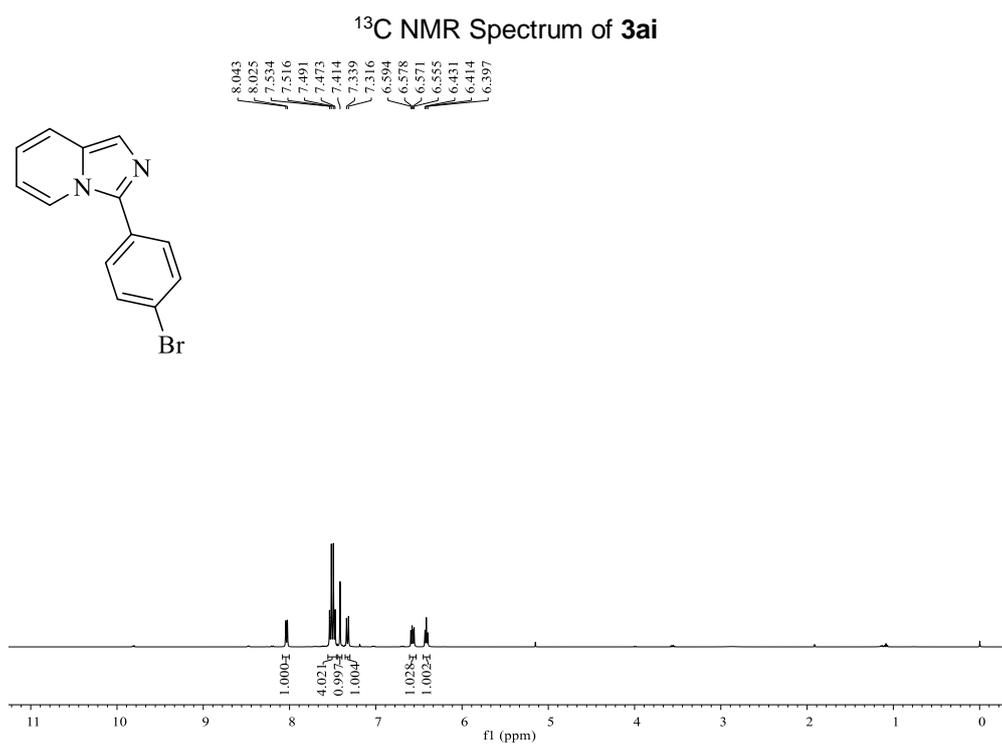
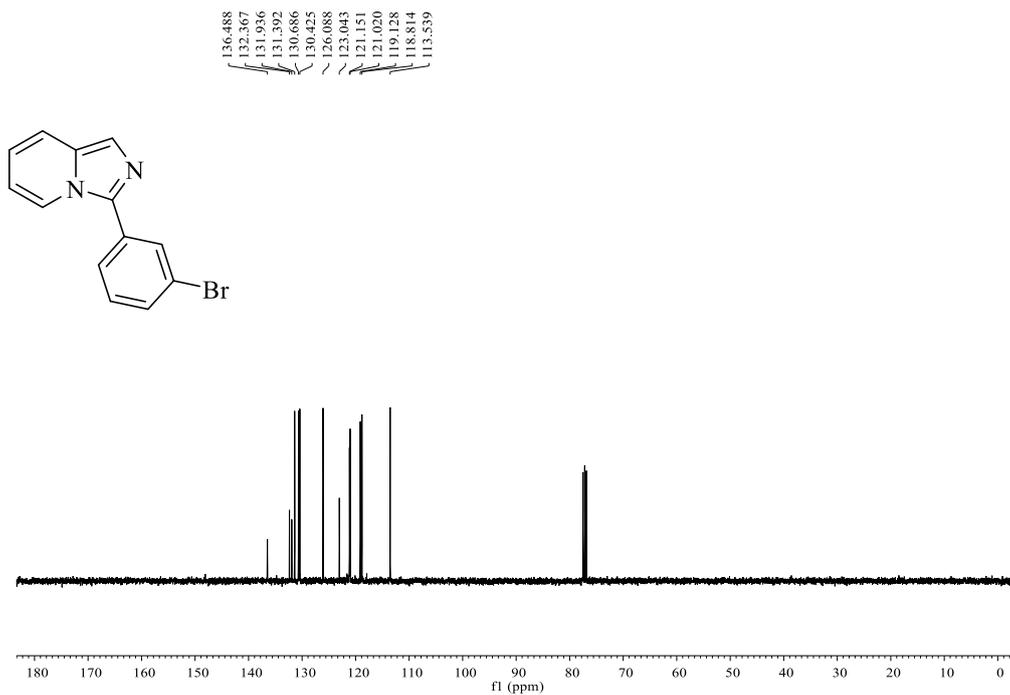
<sup>1</sup>H NMR Spectrum of 3ah



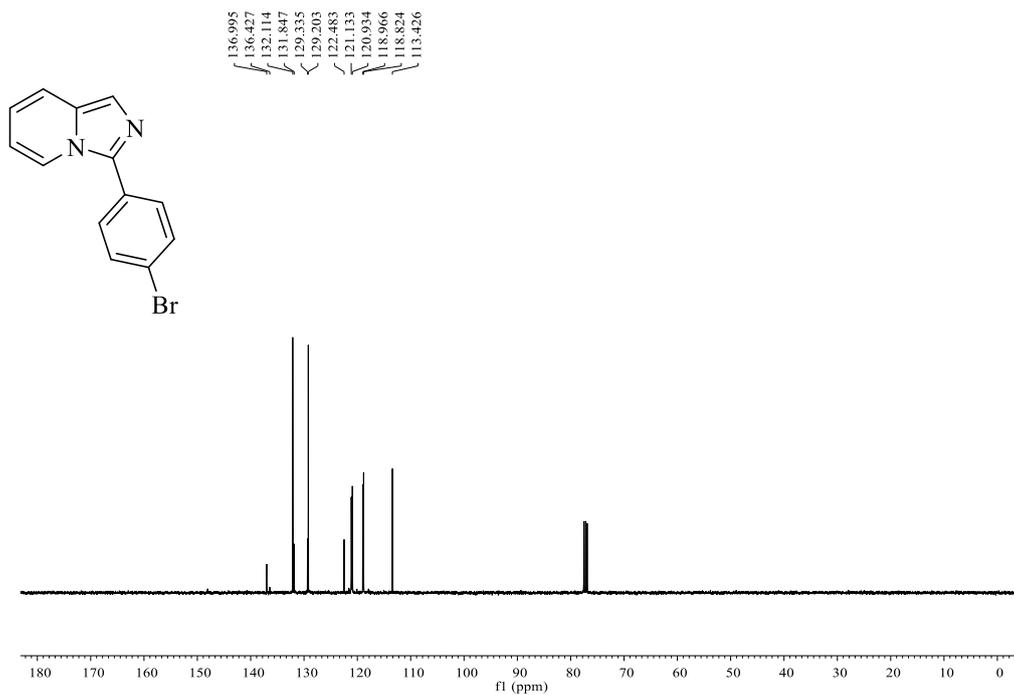
<sup>13</sup>C NMR Spectrum of 3ah



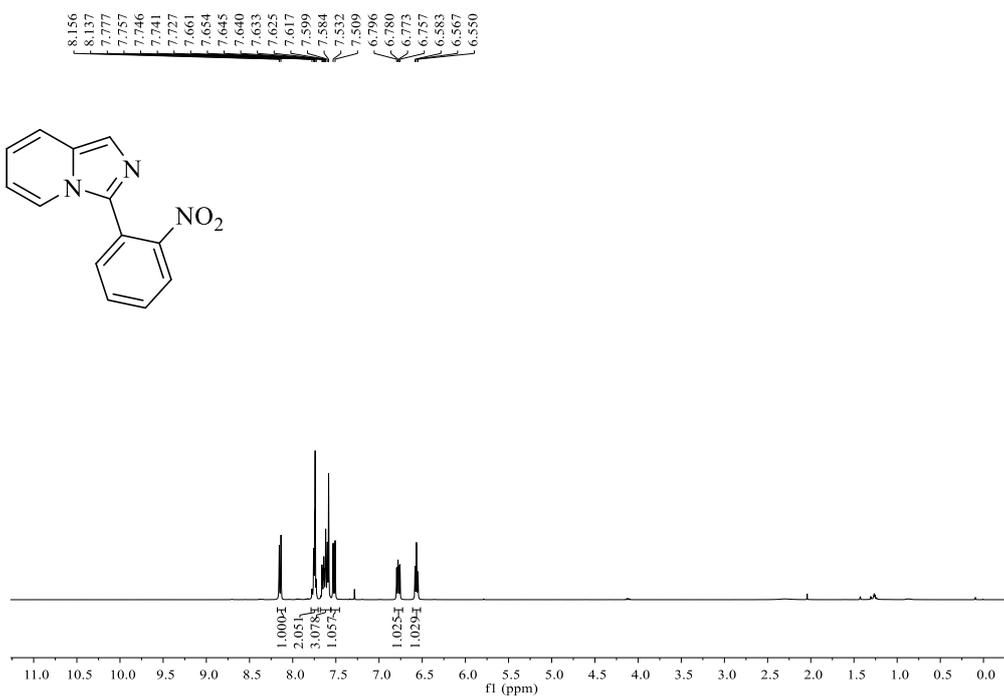
<sup>1</sup>H NMR Spectrum of 3ai



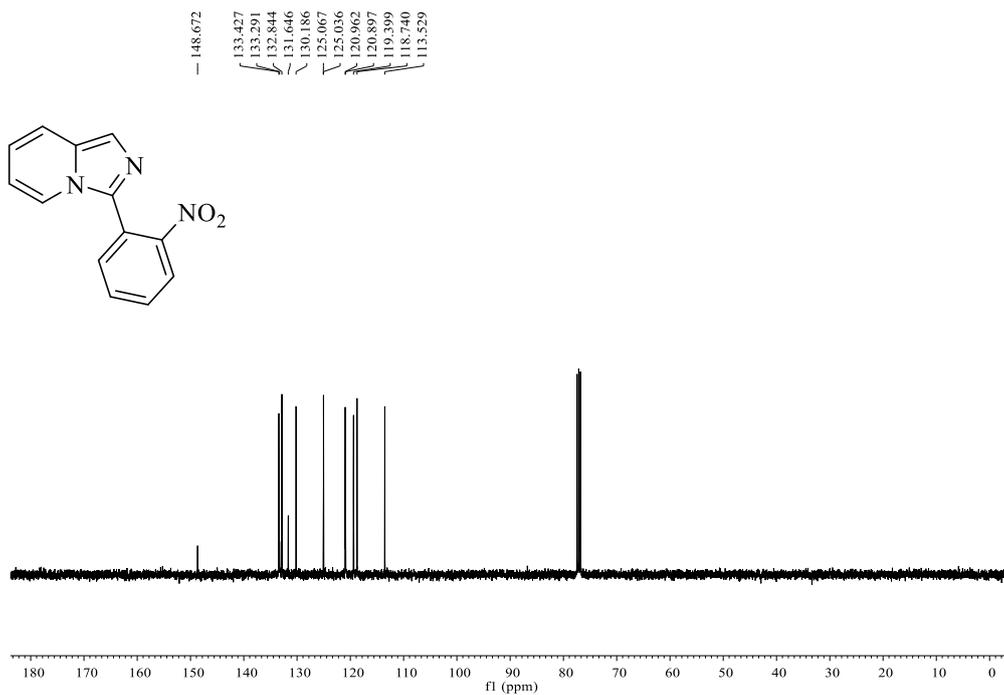
<sup>1</sup>H NMR Spectrum of **3aj**



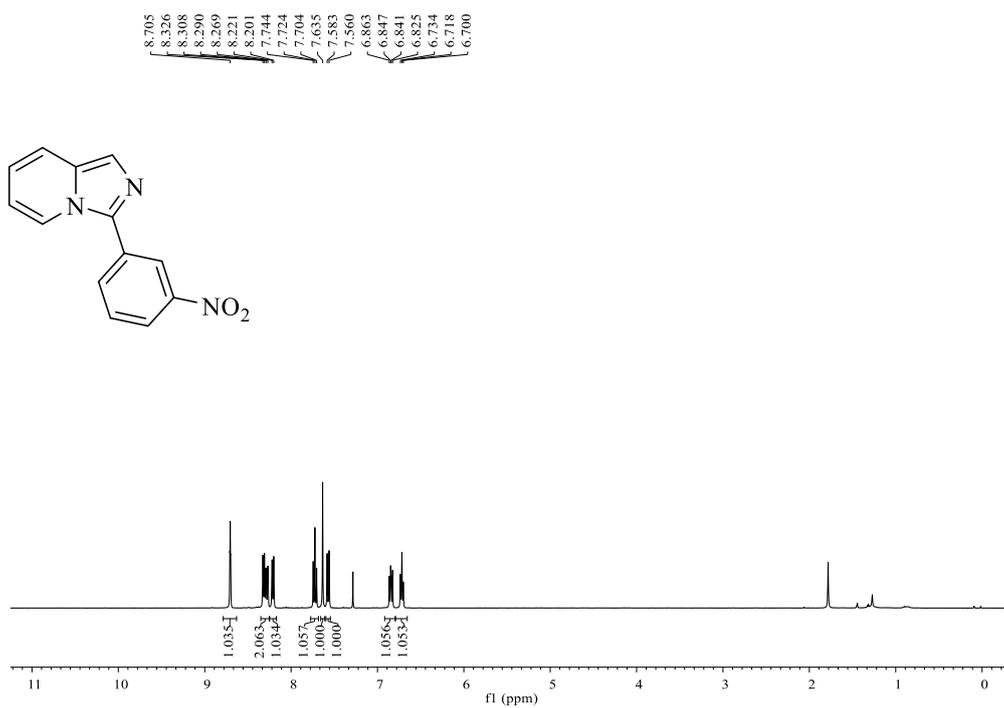
<sup>13</sup>C NMR Spectrum of 3aj



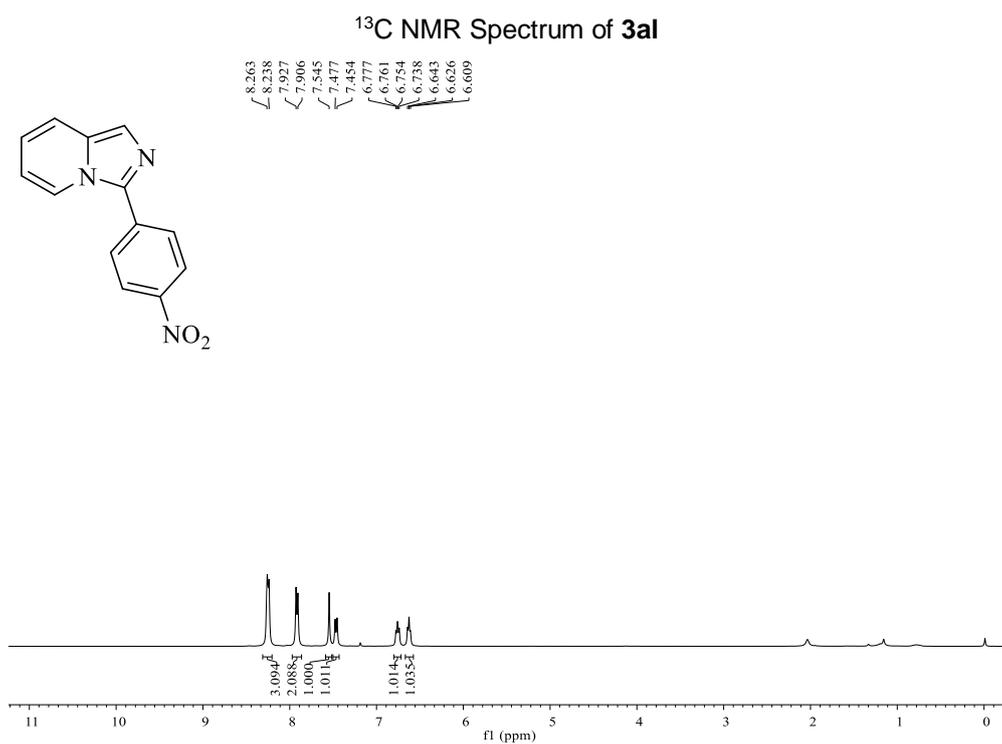
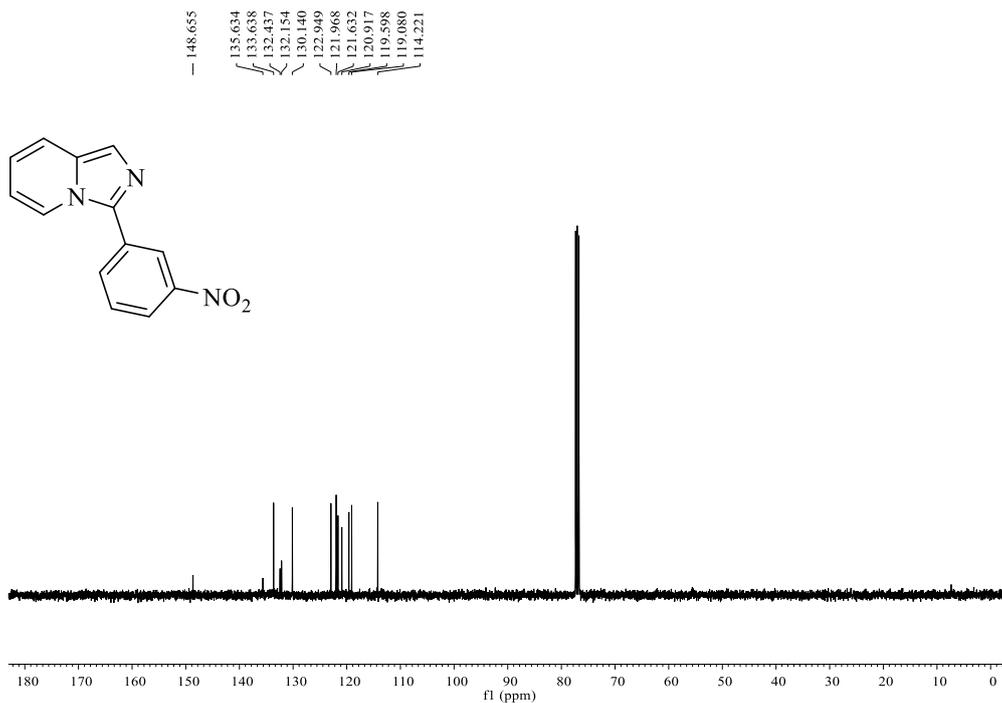
<sup>1</sup>H NMR Spectrum of 3ak



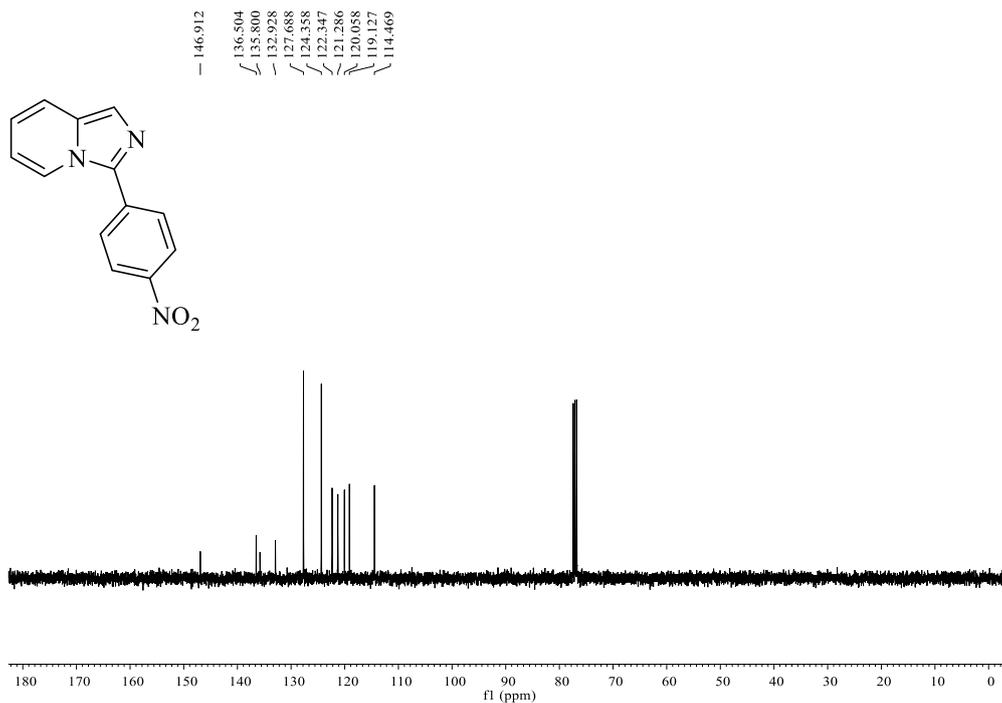
<sup>13</sup>C NMR Spectrum of 3a



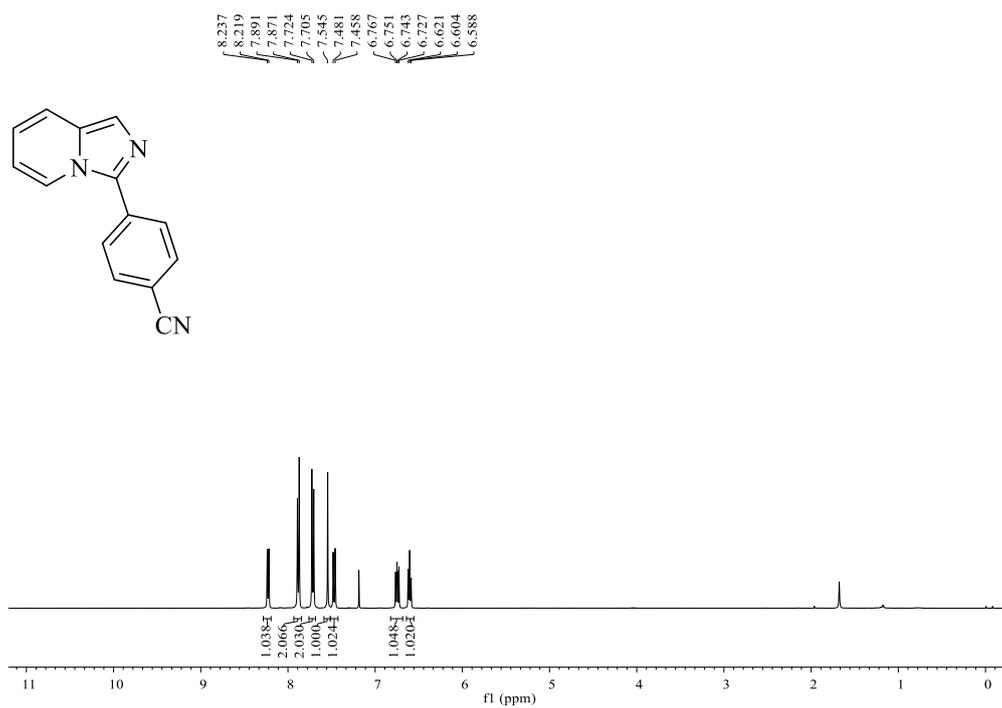
<sup>1</sup>H NMR Spectrum of 3al



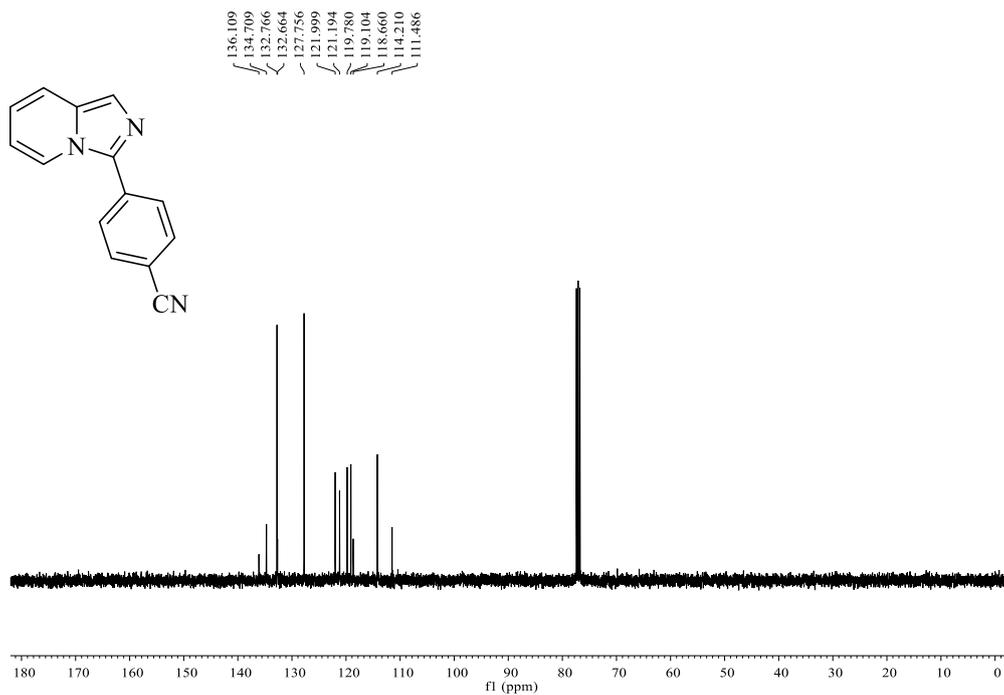
<sup>1</sup>H NMR Spectrum of **3am**



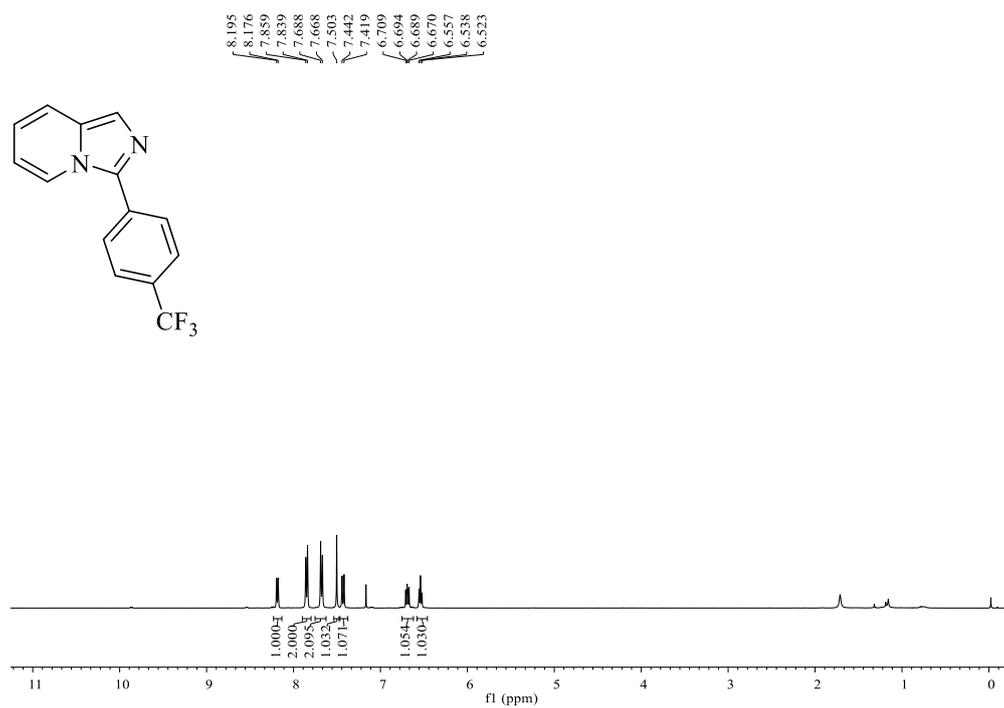
<sup>13</sup>C NMR Spectrum of 3a



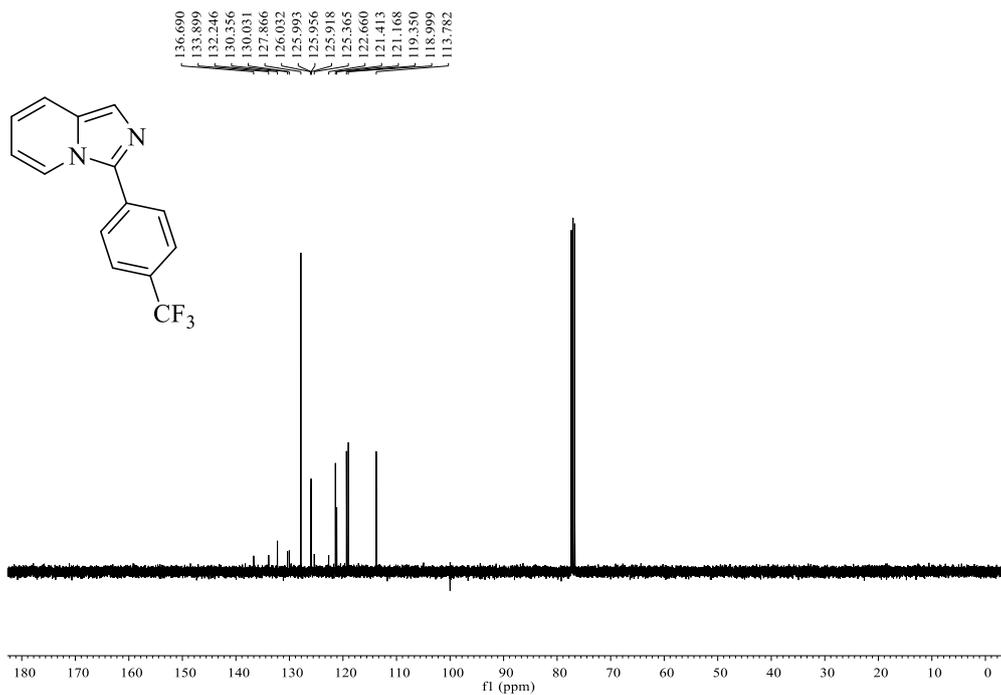
<sup>1</sup>H NMR Spectrum of 3b



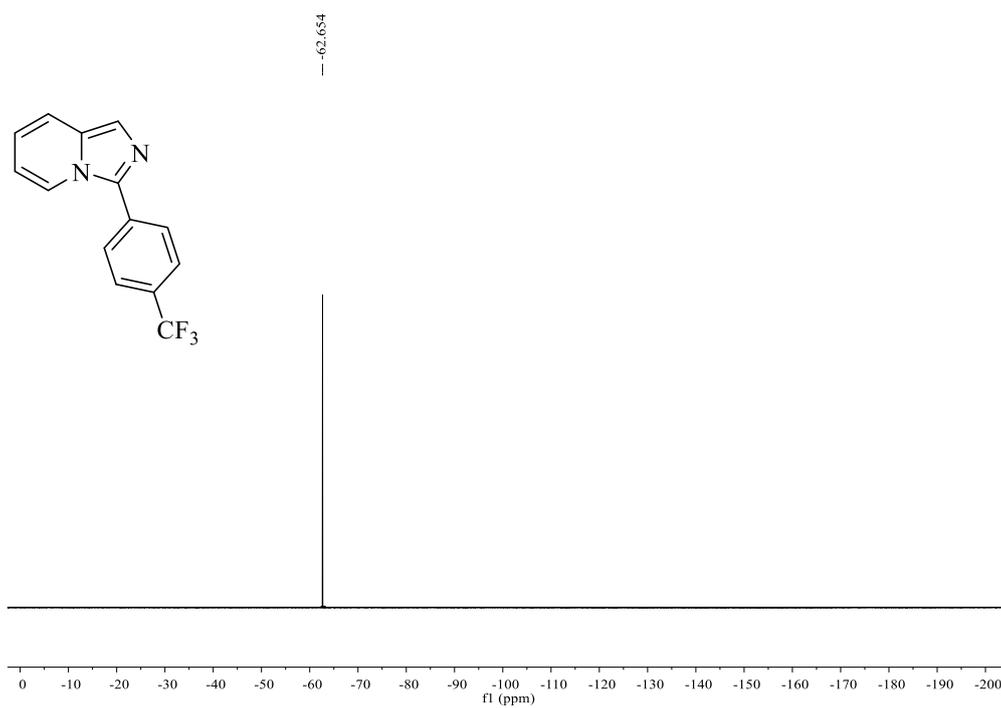
<sup>13</sup>C NMR Spectrum of 3an



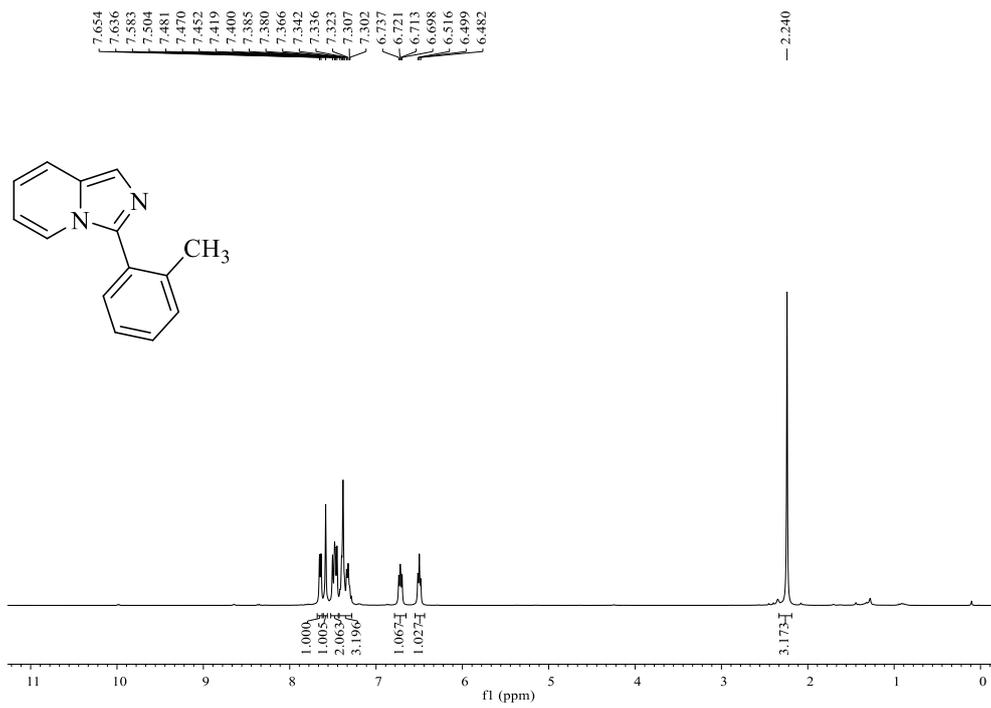
<sup>1</sup>H NMR Spectrum of 3ao



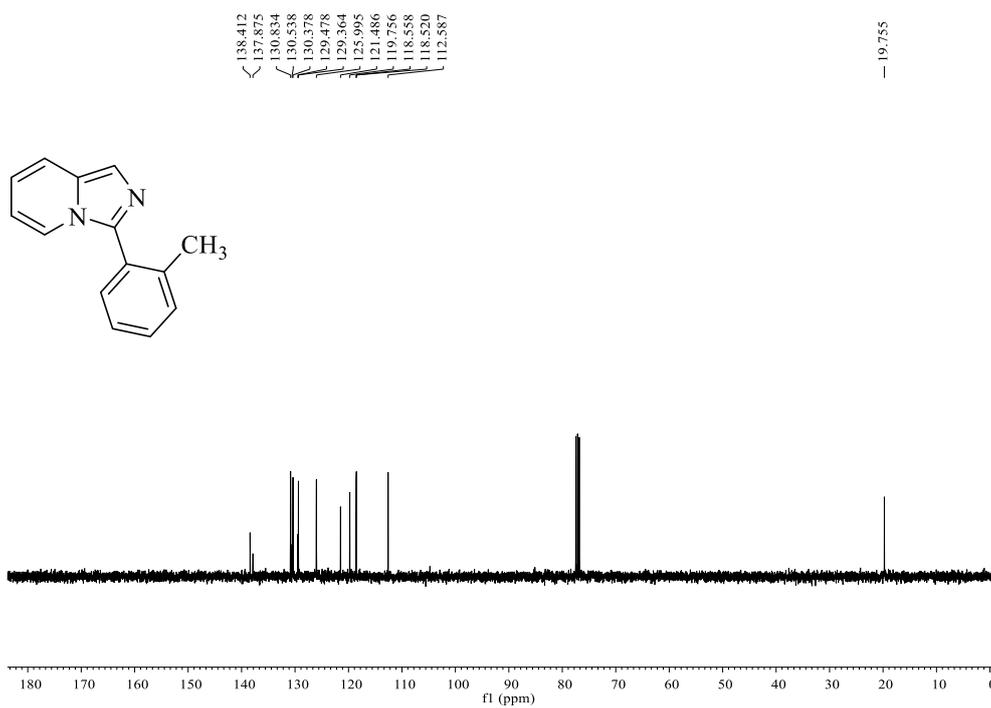
<sup>13</sup>C NMR Spectrum of 3ao



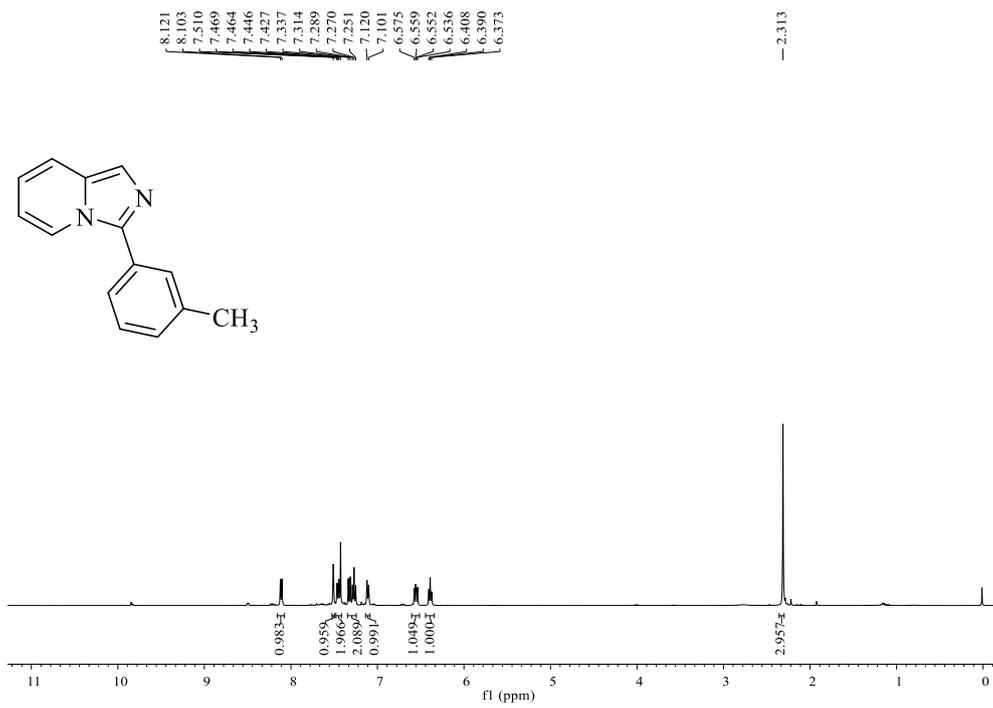
<sup>19</sup>F NMR Spectrum of 3ao



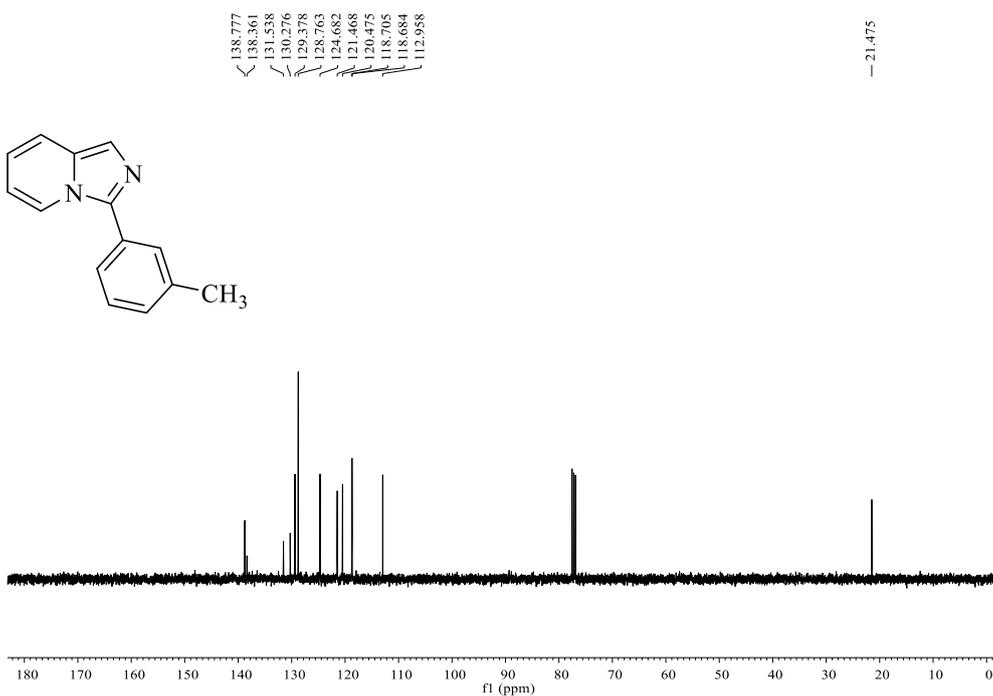
<sup>1</sup>H NMR Spectrum of 3ap



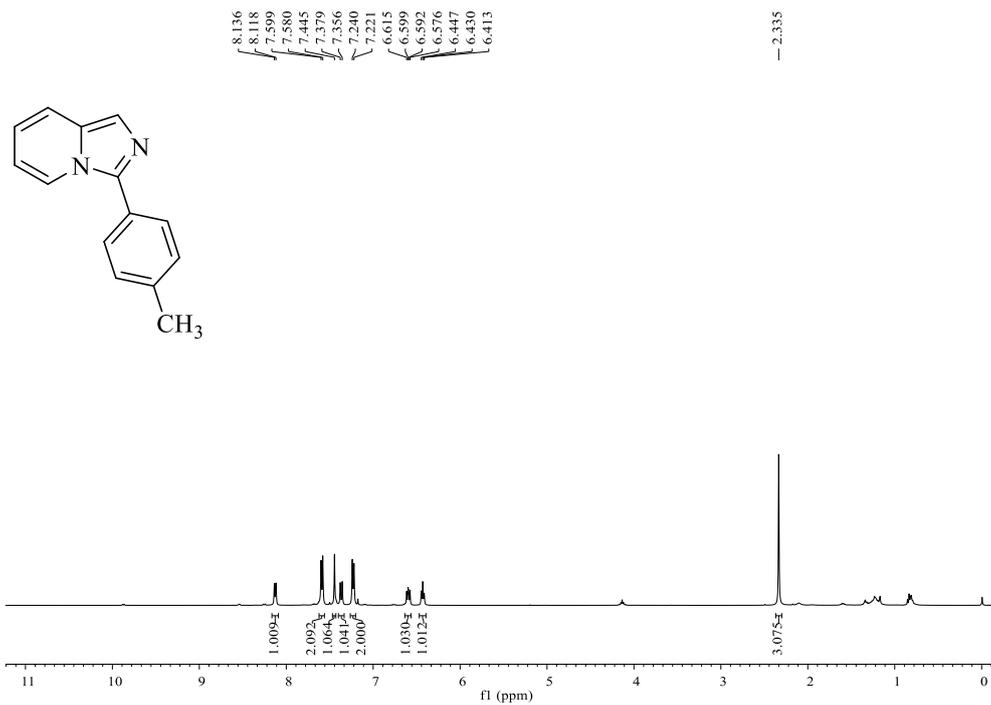
<sup>13</sup>C NMR Spectrum of 3ap



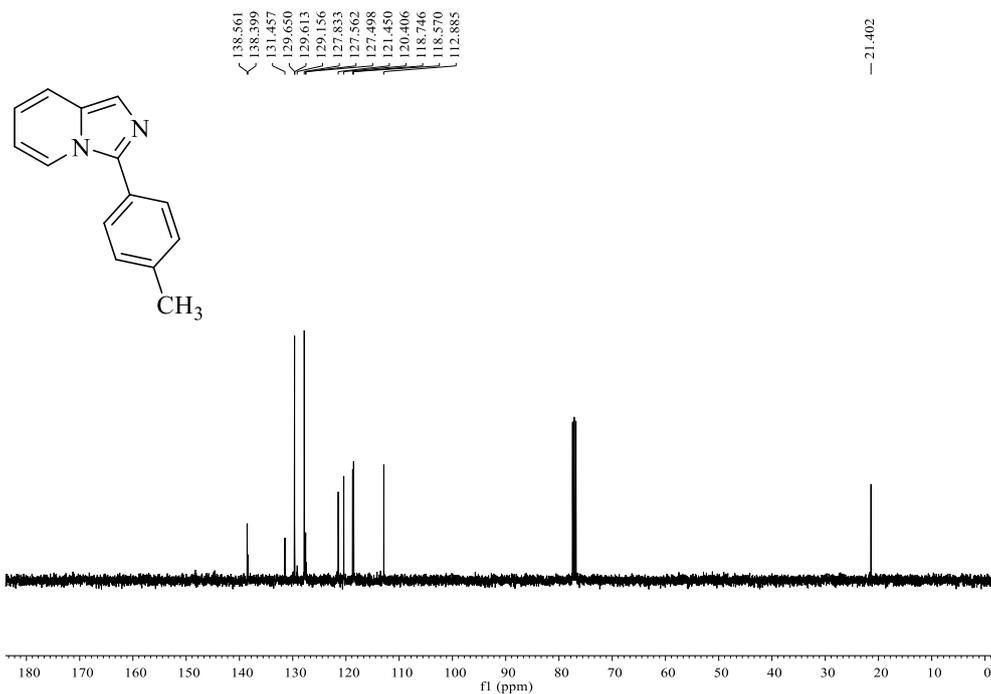
<sup>1</sup>H NMR Spectrum of 3aq



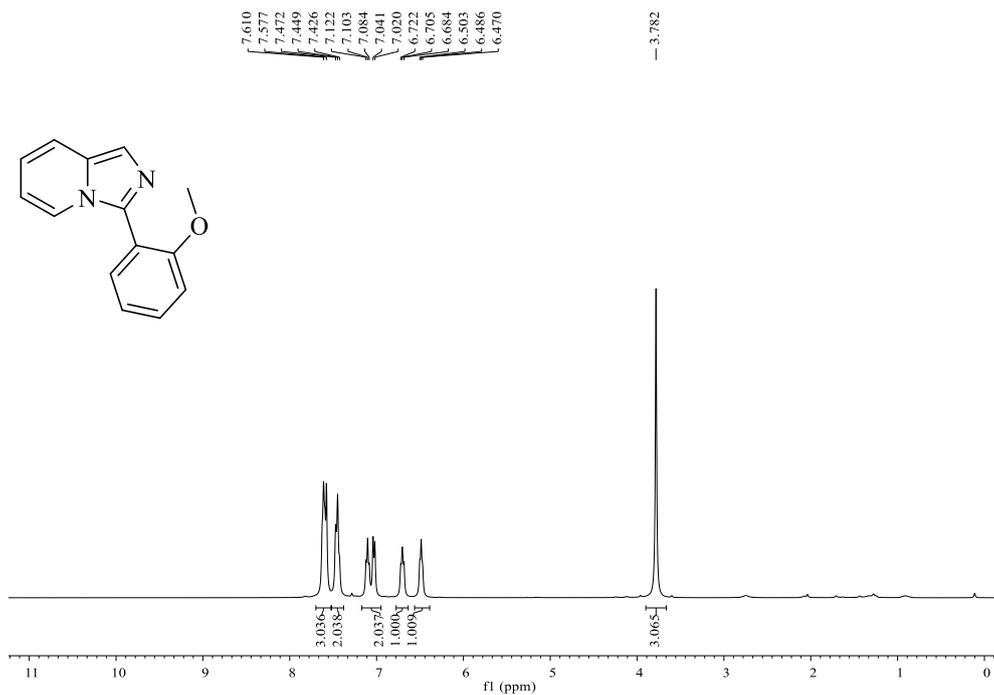
<sup>13</sup>C NMR Spectrum of 3aq



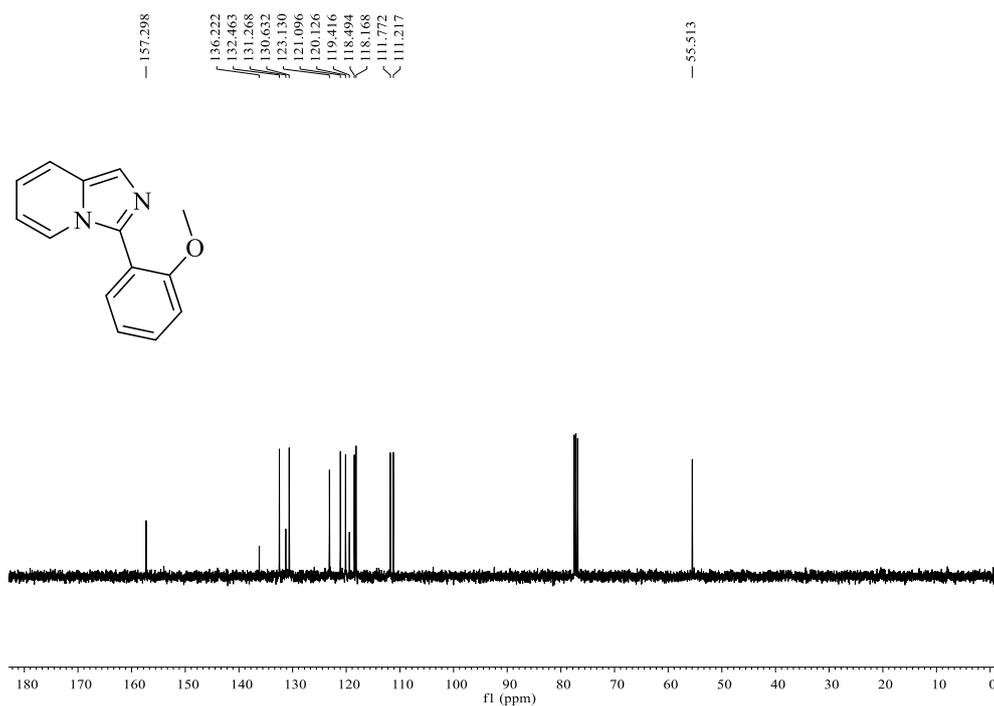
<sup>1</sup>H NMR Spectrum of 3ar



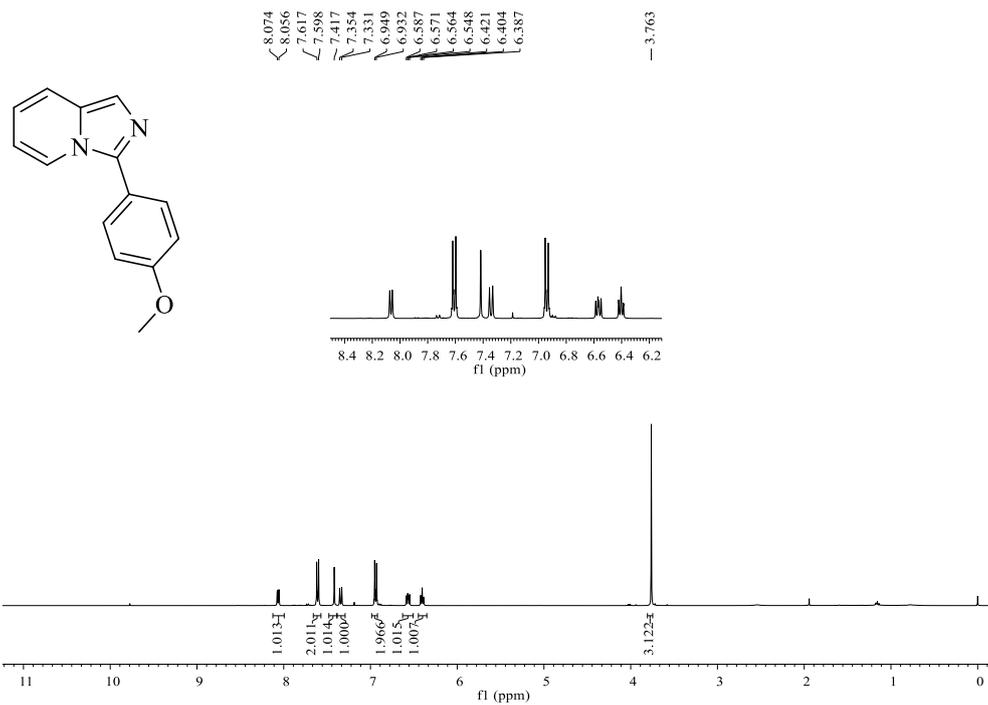
<sup>13</sup>C NMR Spectrum of 3ar



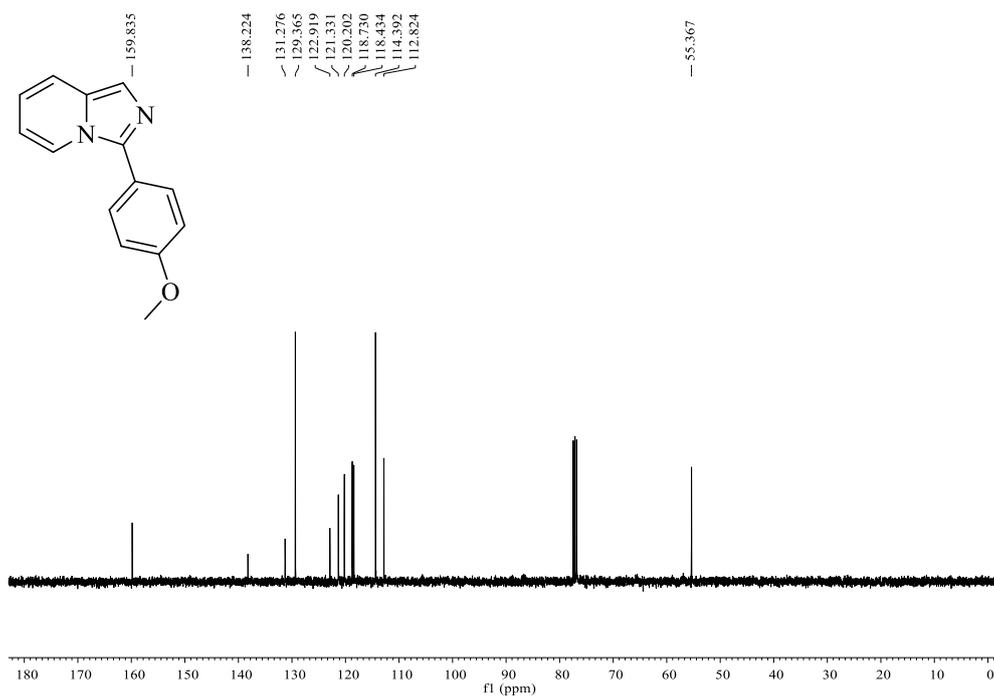
<sup>1</sup>H NMR Spectrum of 3as



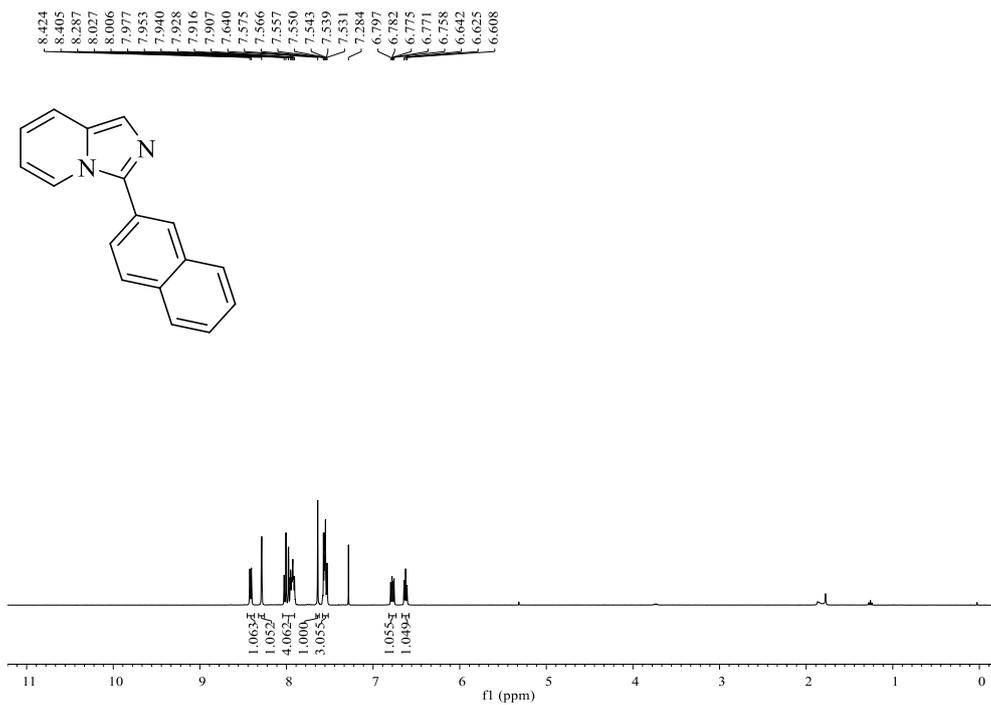
<sup>13</sup>C NMR Spectrum of 3as



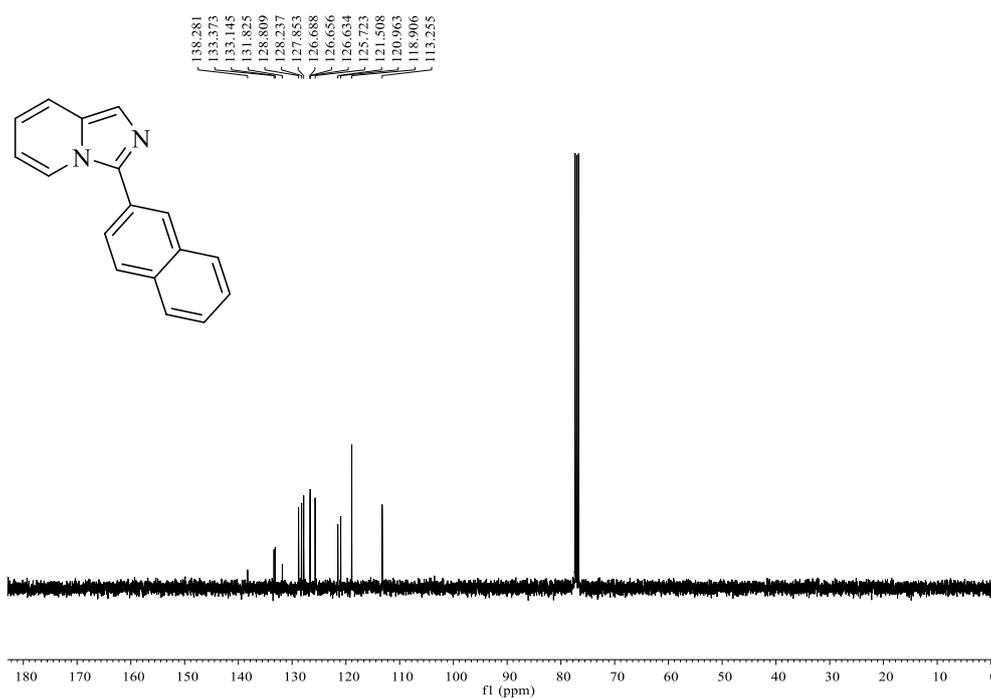
<sup>1</sup>H NMR Spectrum of 3at



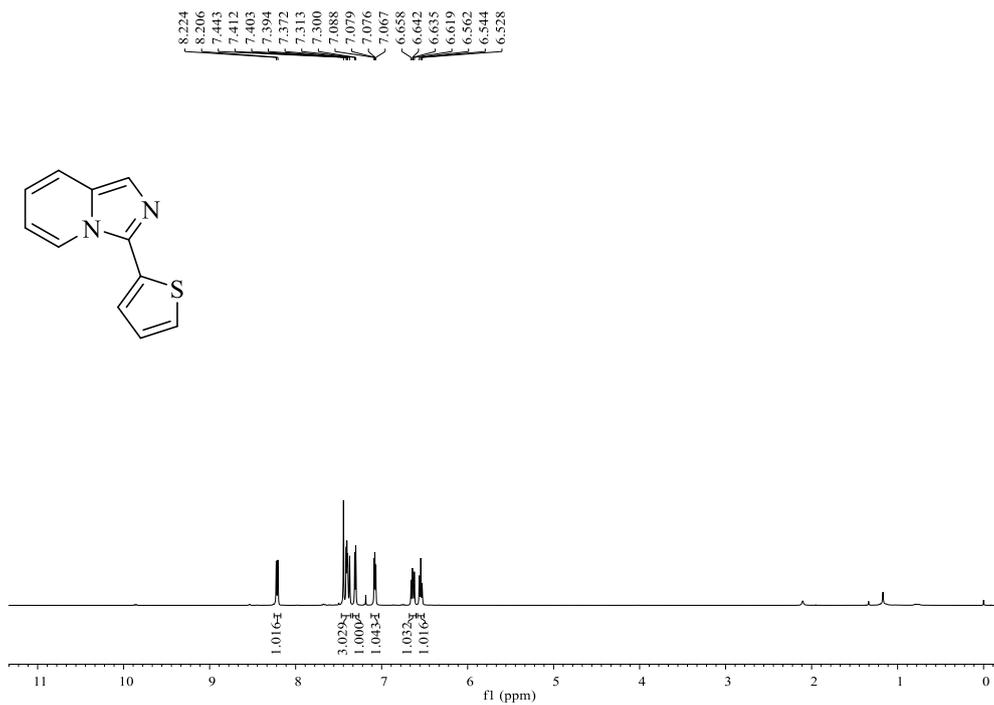
<sup>13</sup>C NMR Spectrum of 3at



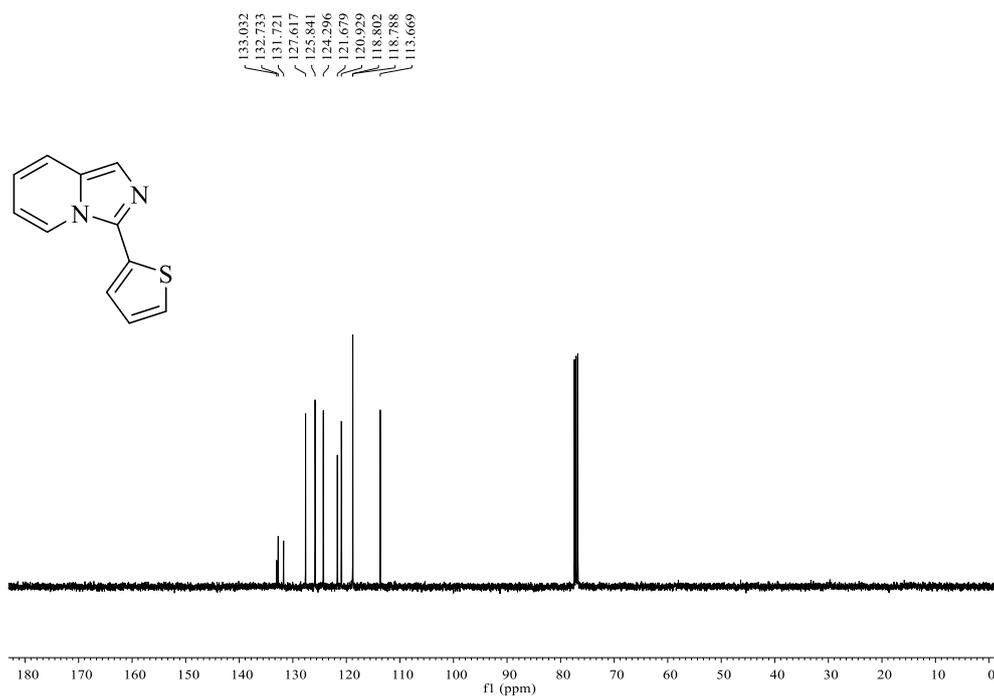
<sup>1</sup>H NMR Spectrum of **3au**



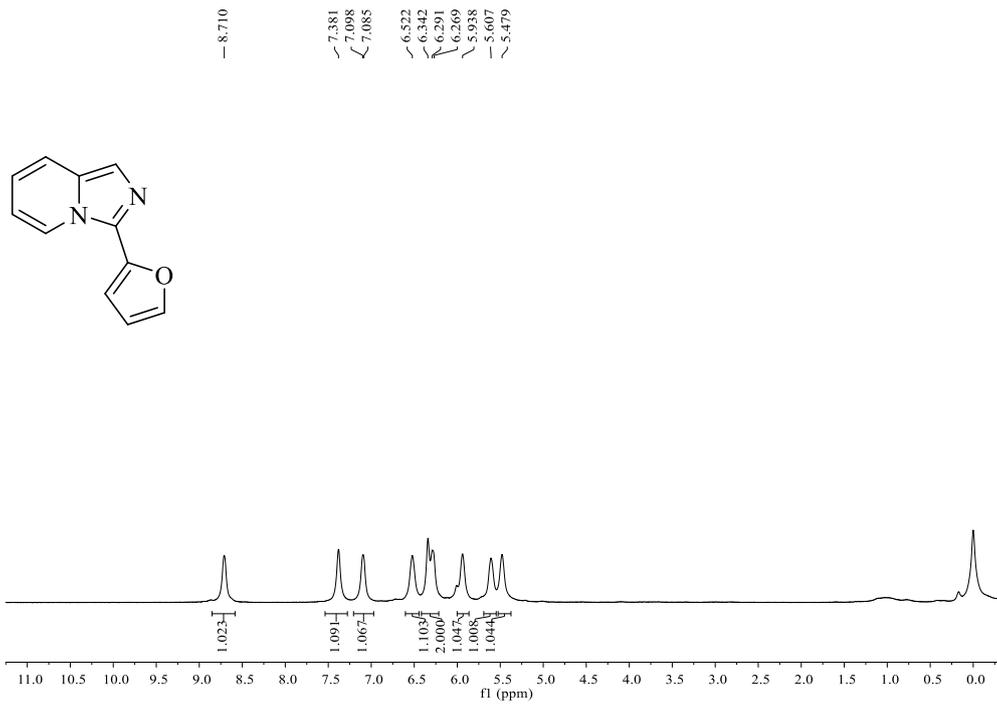
<sup>13</sup>C NMR Spectrum of **3au**



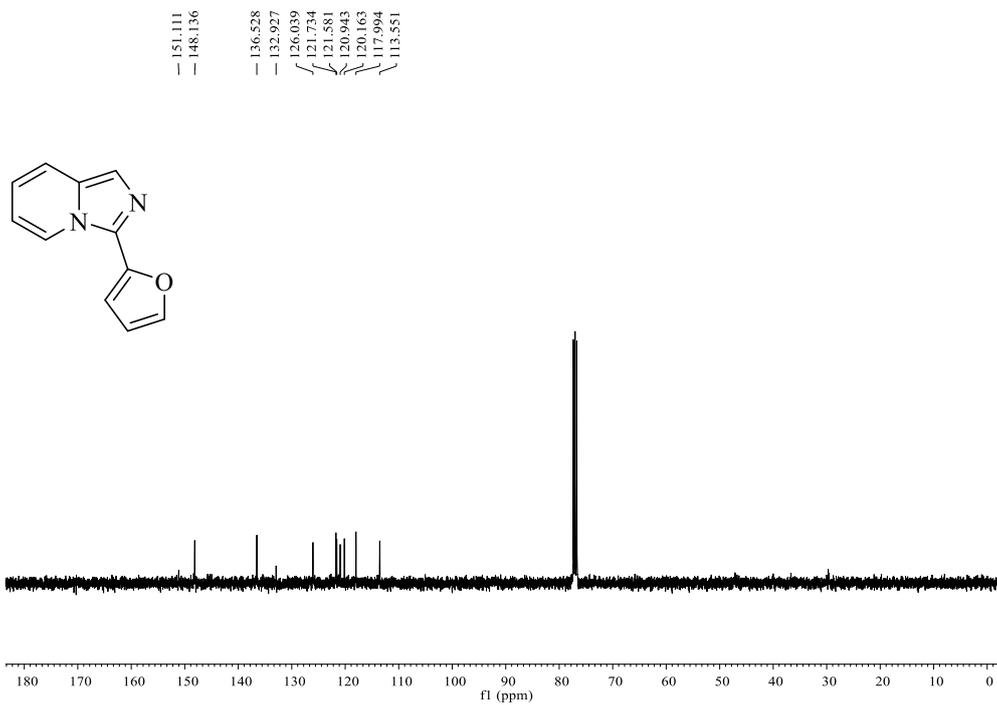
<sup>1</sup>H NMR Spectrum of **3av**



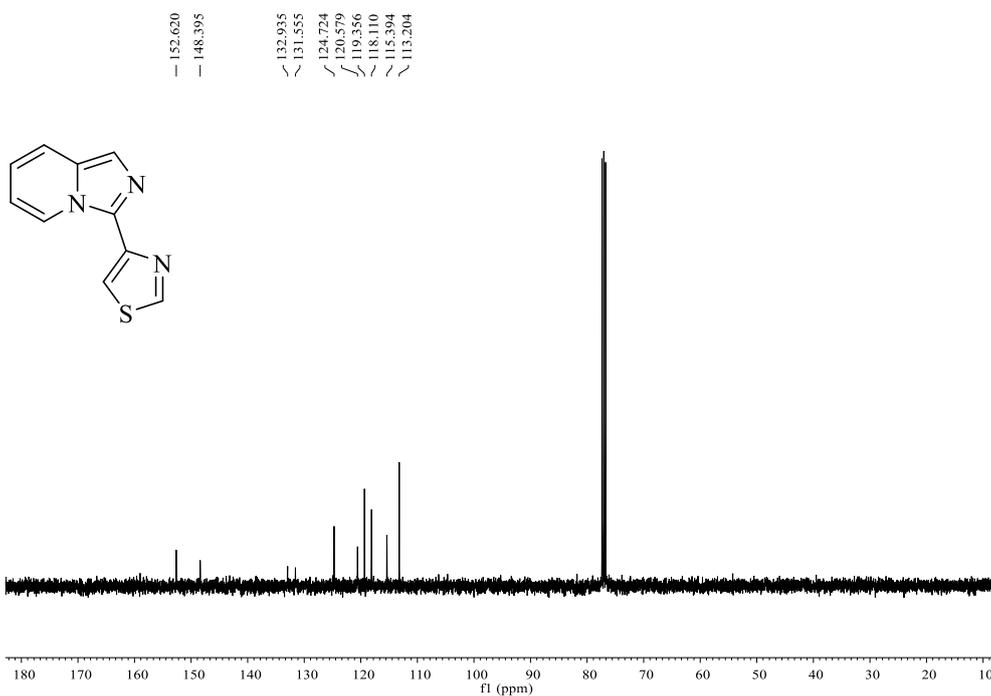
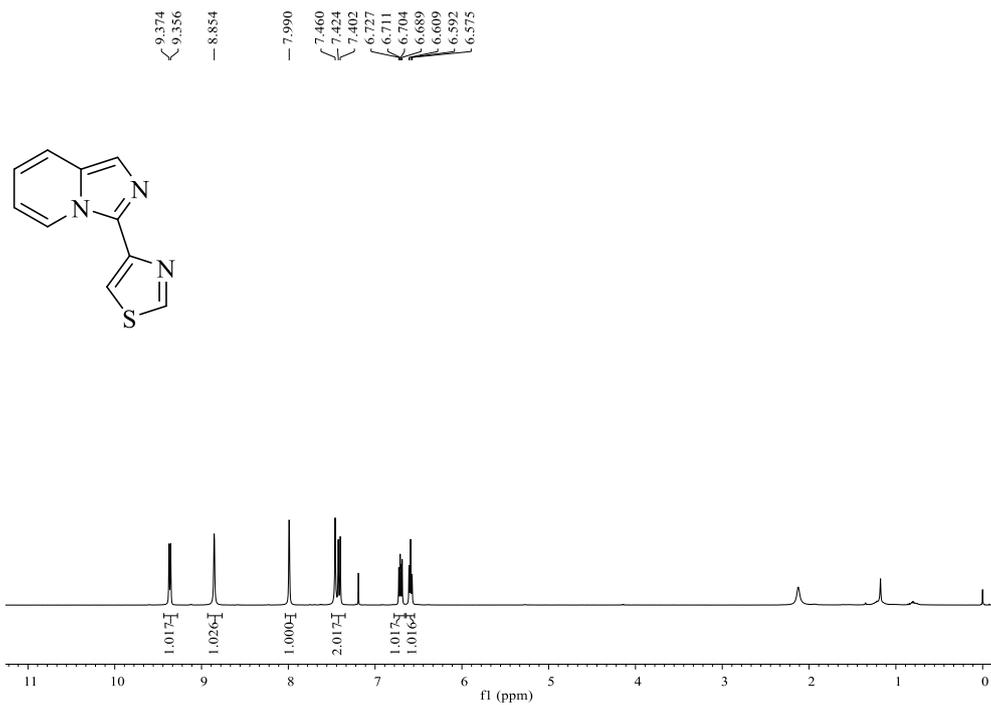
<sup>13</sup>C NMR Spectrum of **3av**

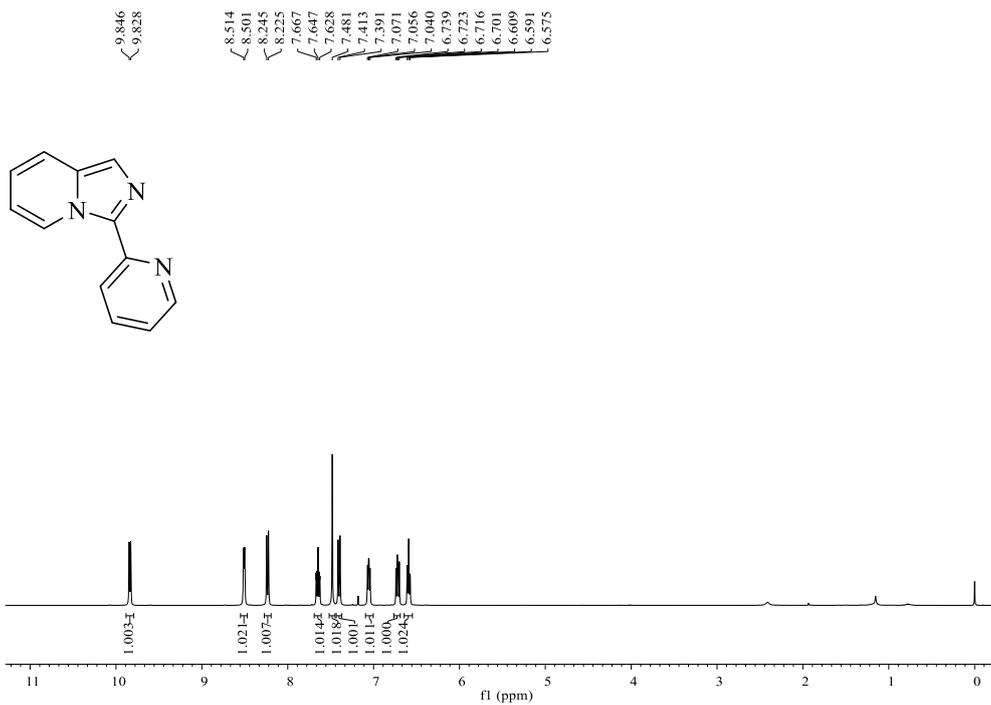


<sup>1</sup>H NMR Spectrum of 3aw

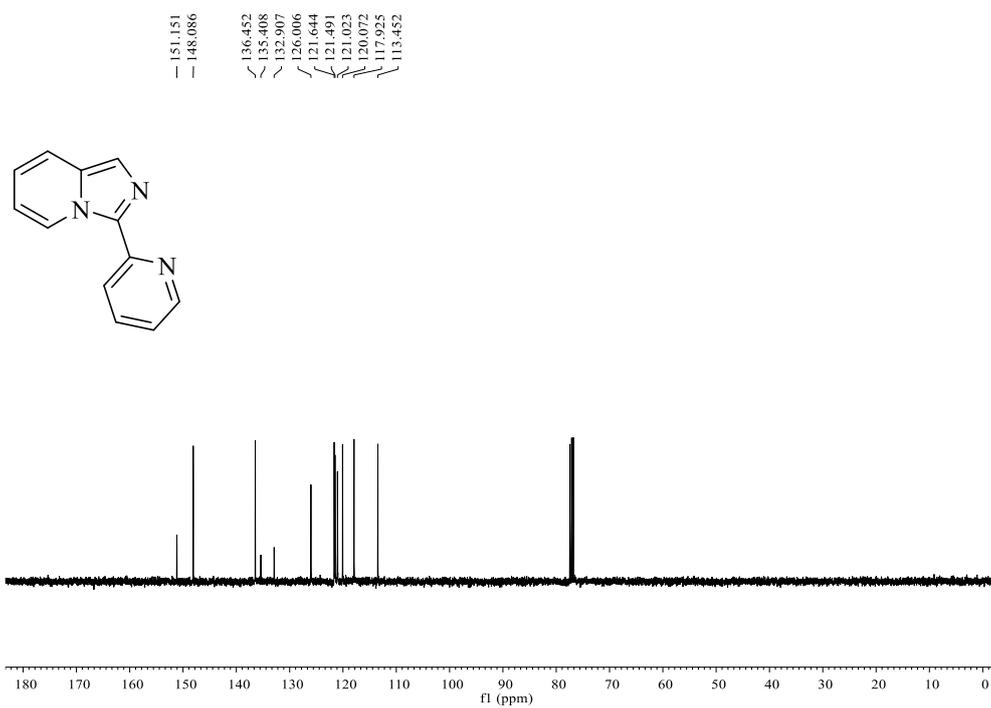


<sup>13</sup>C NMR Spectrum of 3aw

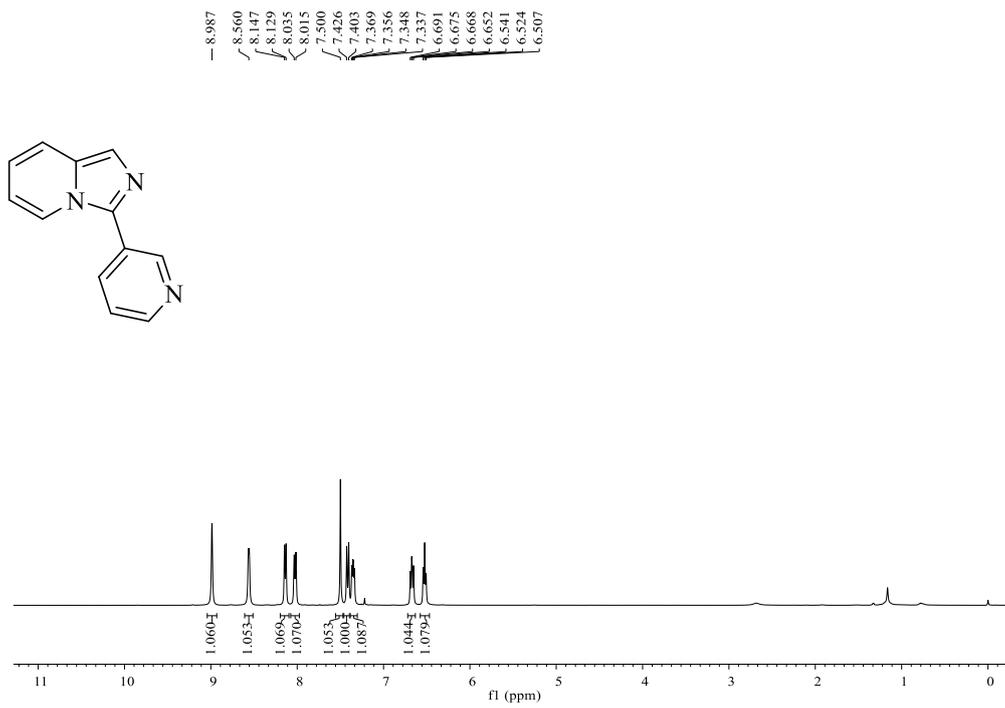




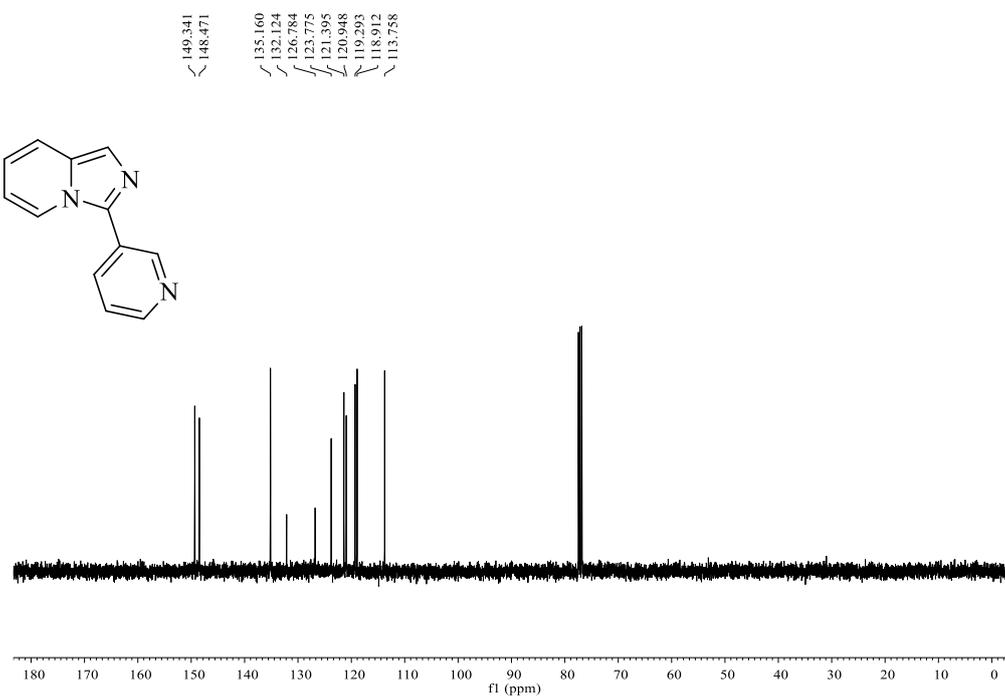
<sup>1</sup>H NMR Spectrum of 3ay



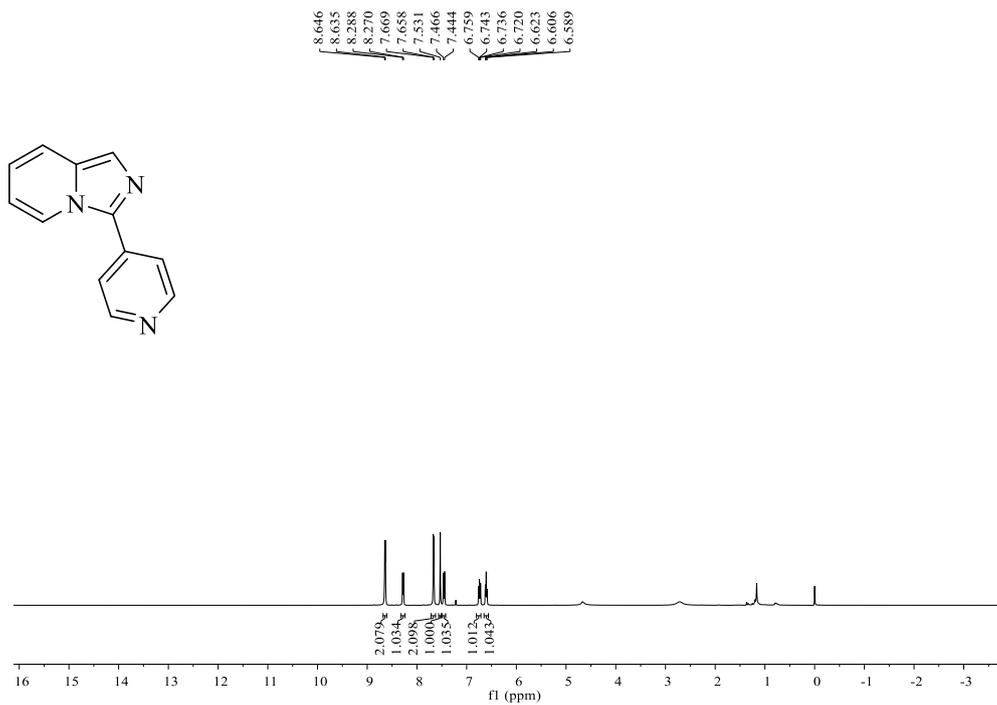
<sup>13</sup>C NMR Spectrum of 3ay



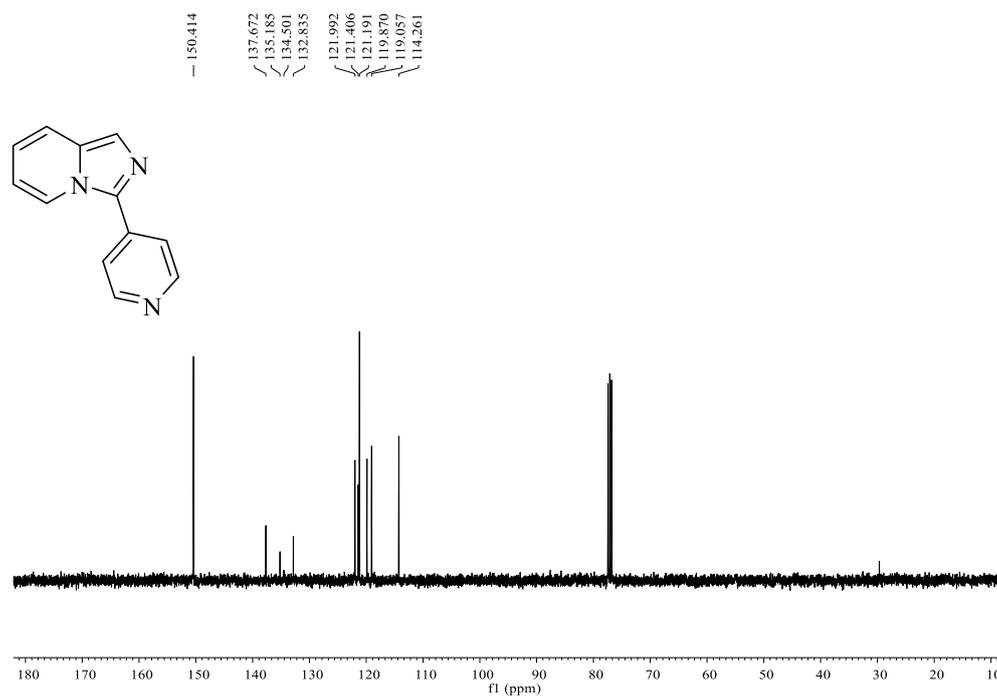
<sup>1</sup>H NMR Spectrum of 3az



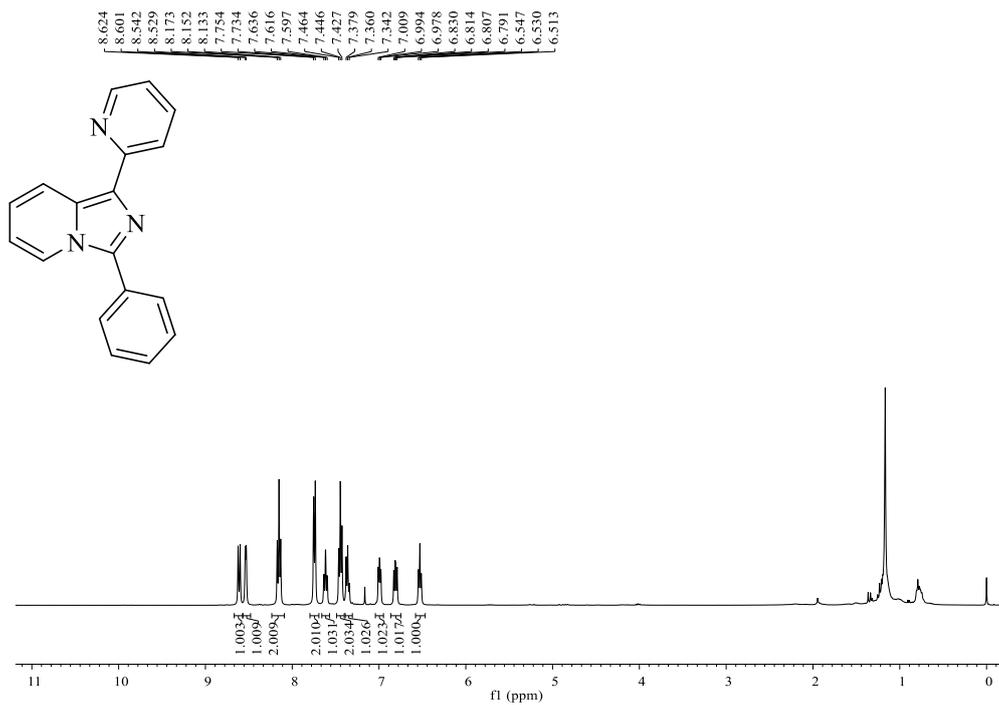
<sup>13</sup>C NMR Spectrum of 3az



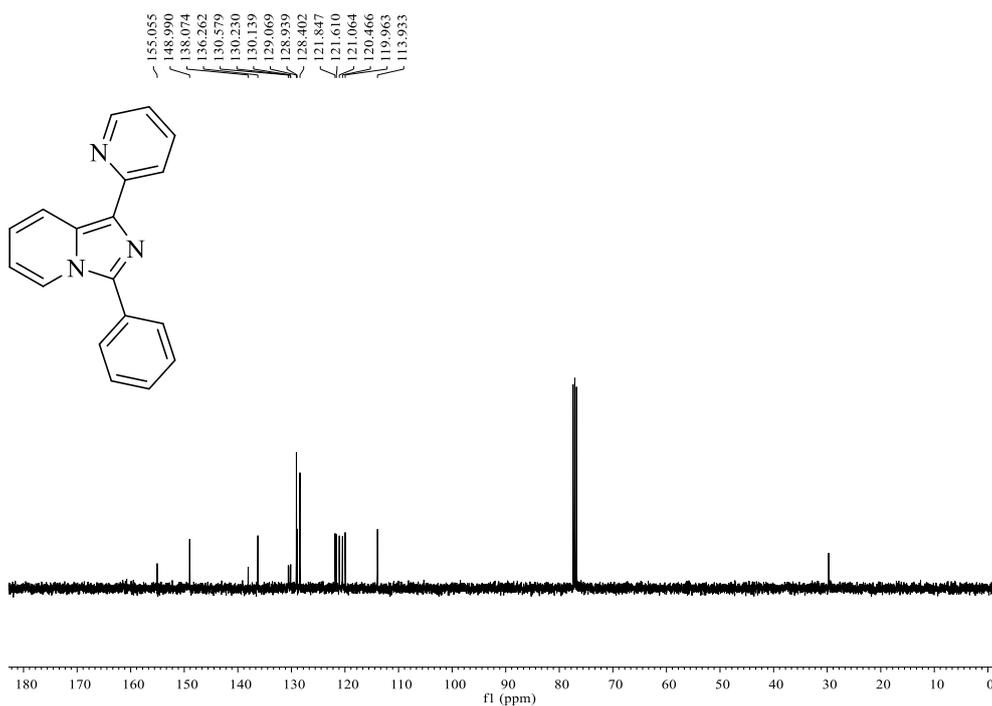
<sup>1</sup>H NMR Spectrum of 3aaa



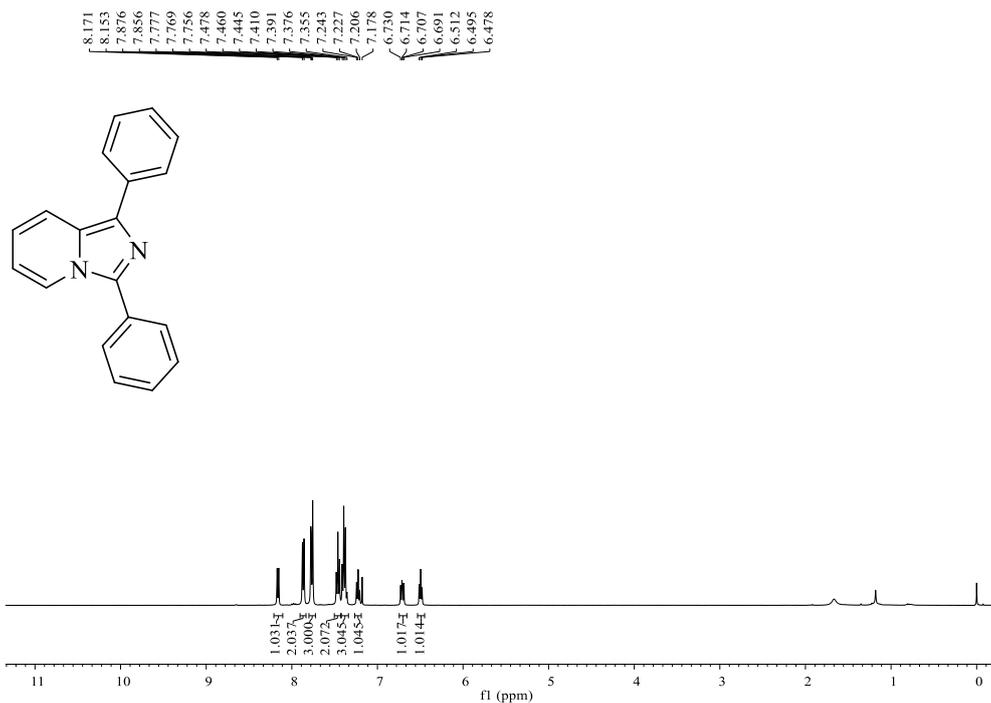
<sup>13</sup>C NMR Spectrum of 3aaa



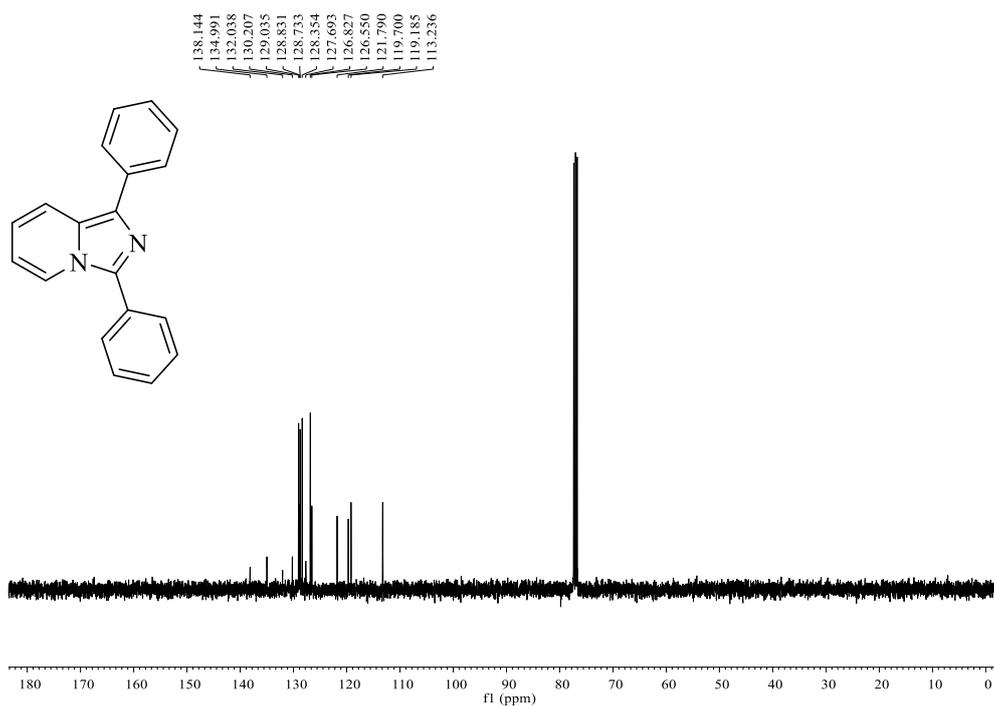
<sup>1</sup>H NMR Spectrum of 3aab



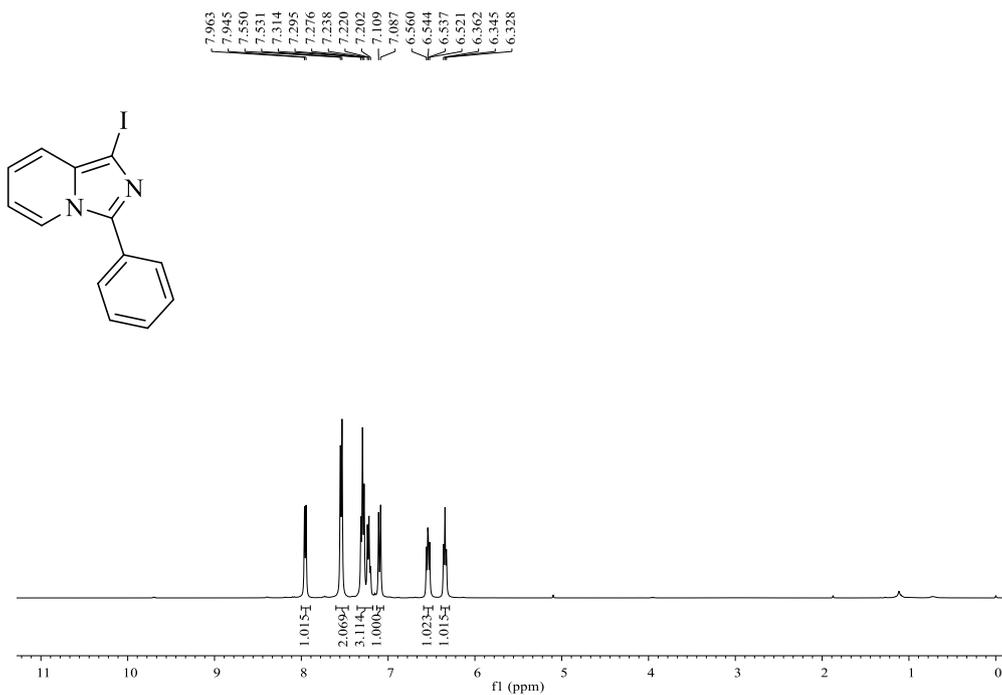
<sup>13</sup>C NMR Spectrum of 3aab



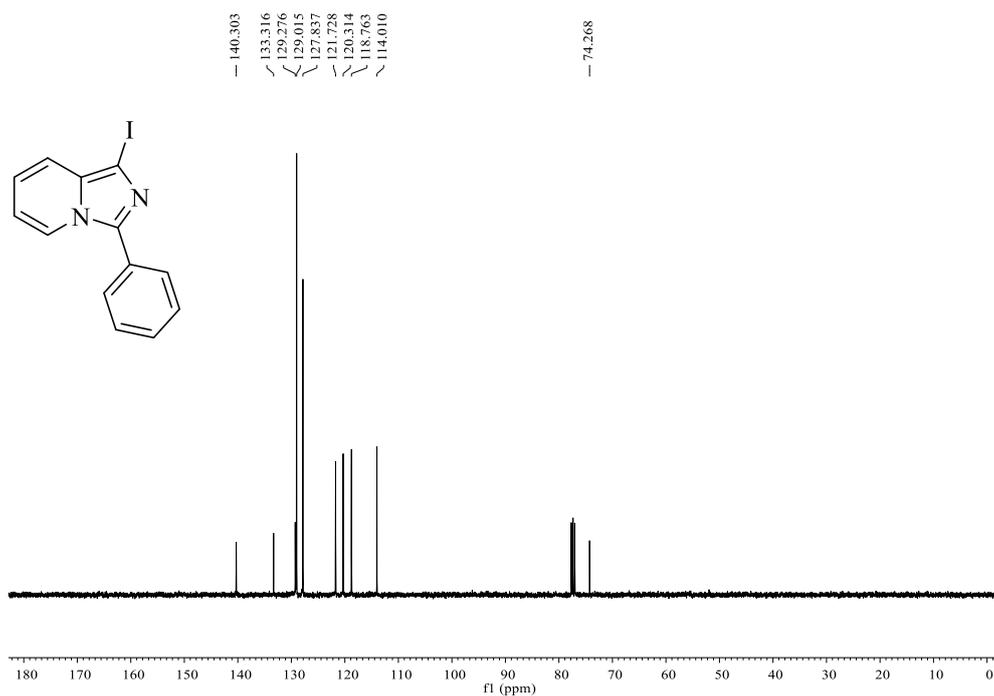
<sup>1</sup>H NMR Spectrum of 3aac



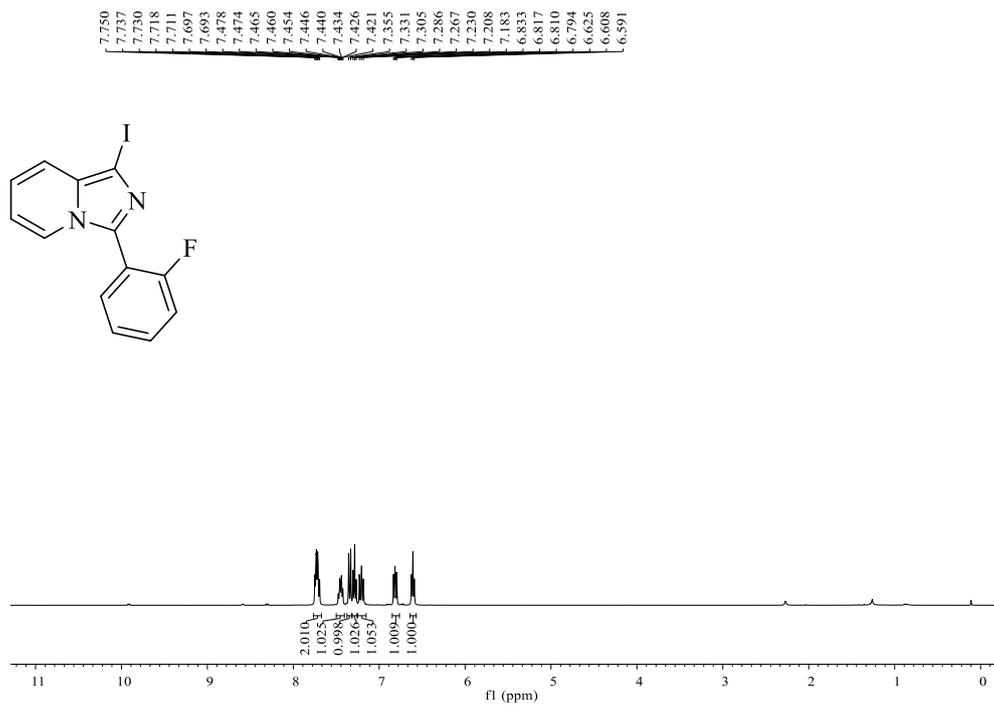
<sup>13</sup>C NMR Spectrum of 3aac



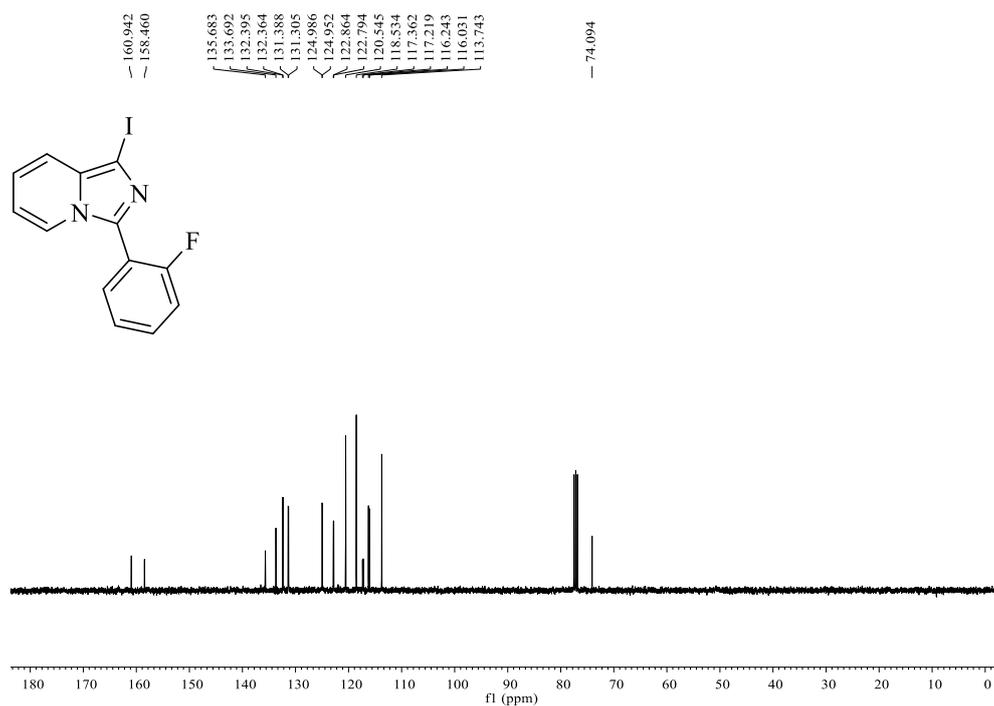
<sup>1</sup>H NMR Spectrum of **3b**



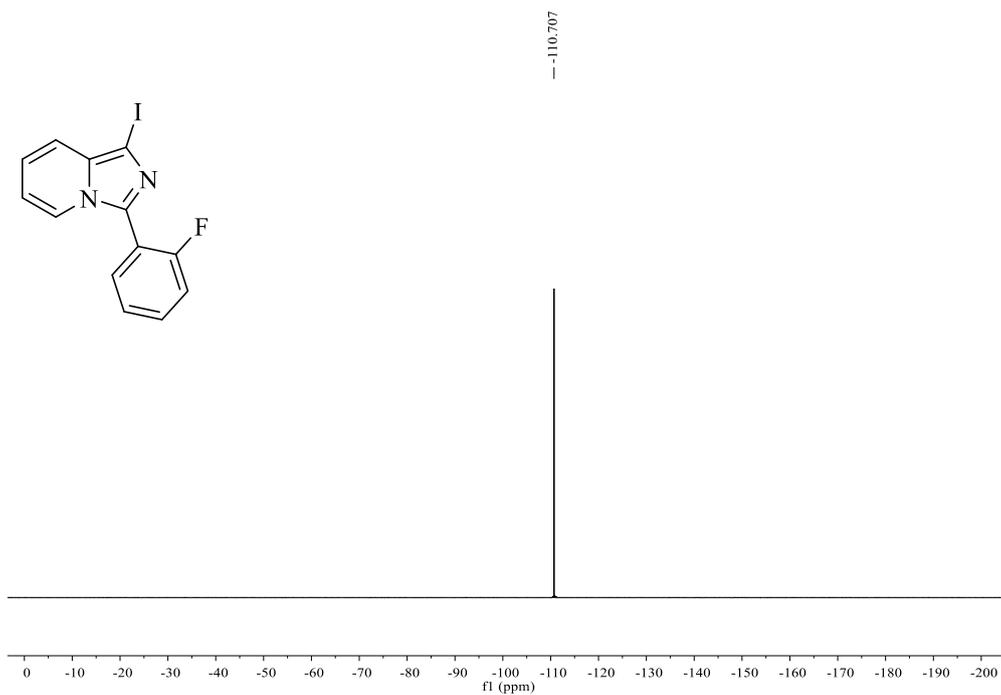
<sup>13</sup>C NMR Spectrum of **3b**



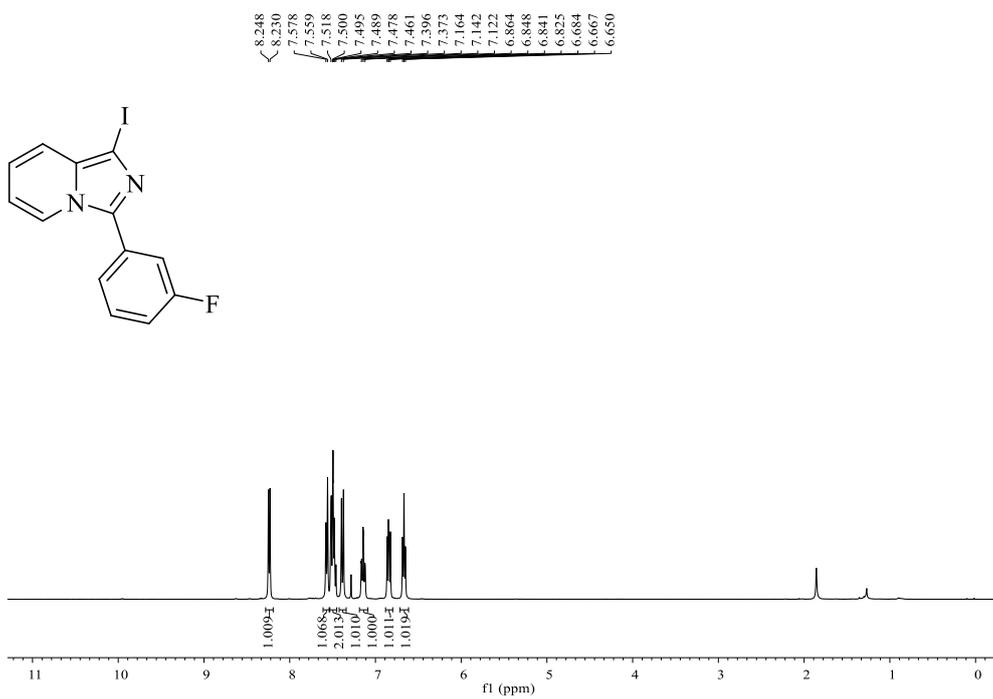
<sup>1</sup>H NMR Spectrum of 3bb



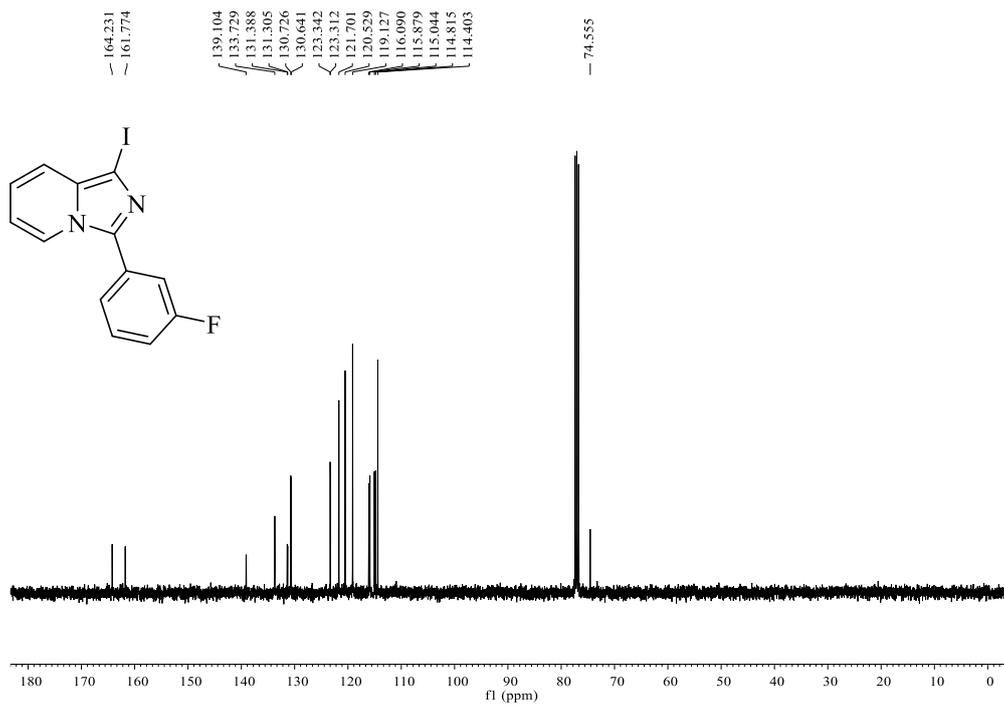
<sup>13</sup>C NMR Spectrum of 3bb



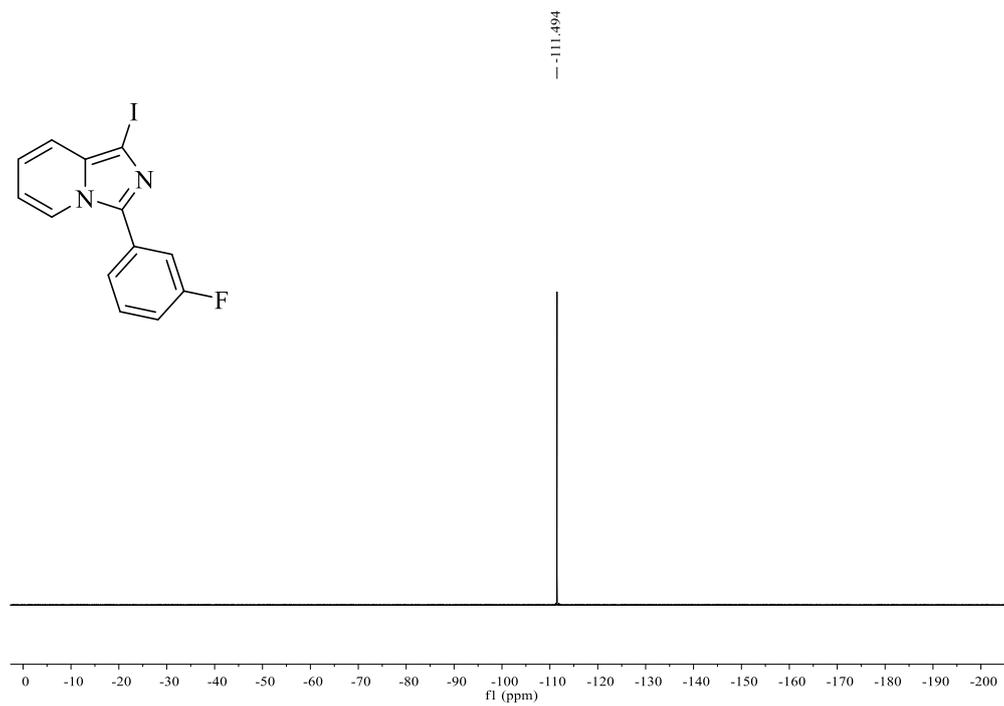
$^{19}\text{F}$  NMR Spectrum of **3b**



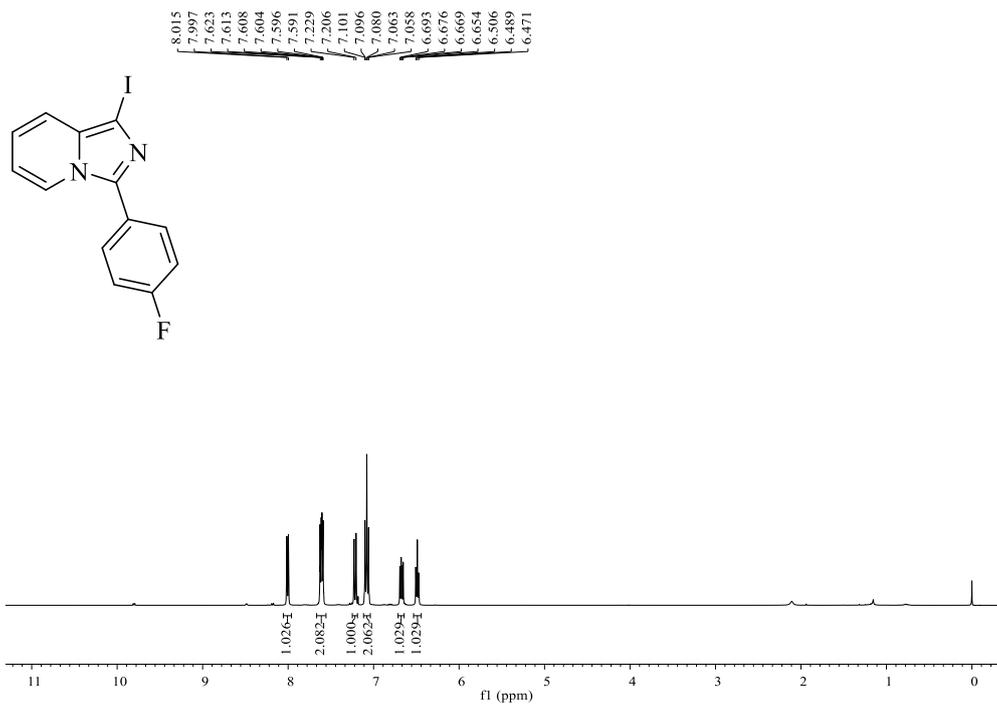
$^1\text{H}$  NMR Spectrum of **3bc**



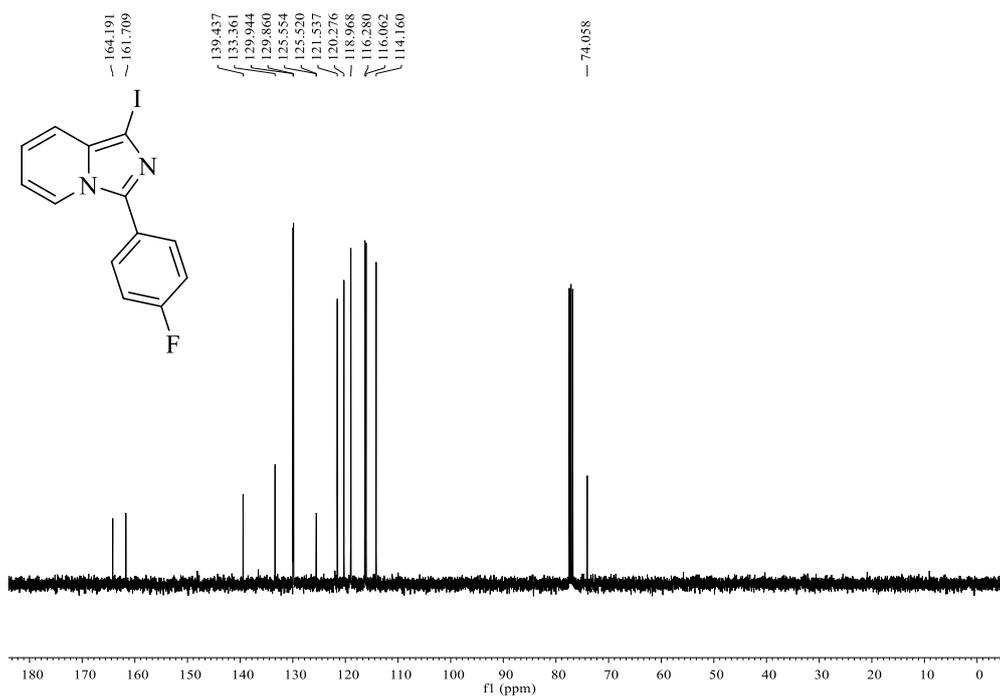
<sup>13</sup>C NMR Spectrum of **3bc**



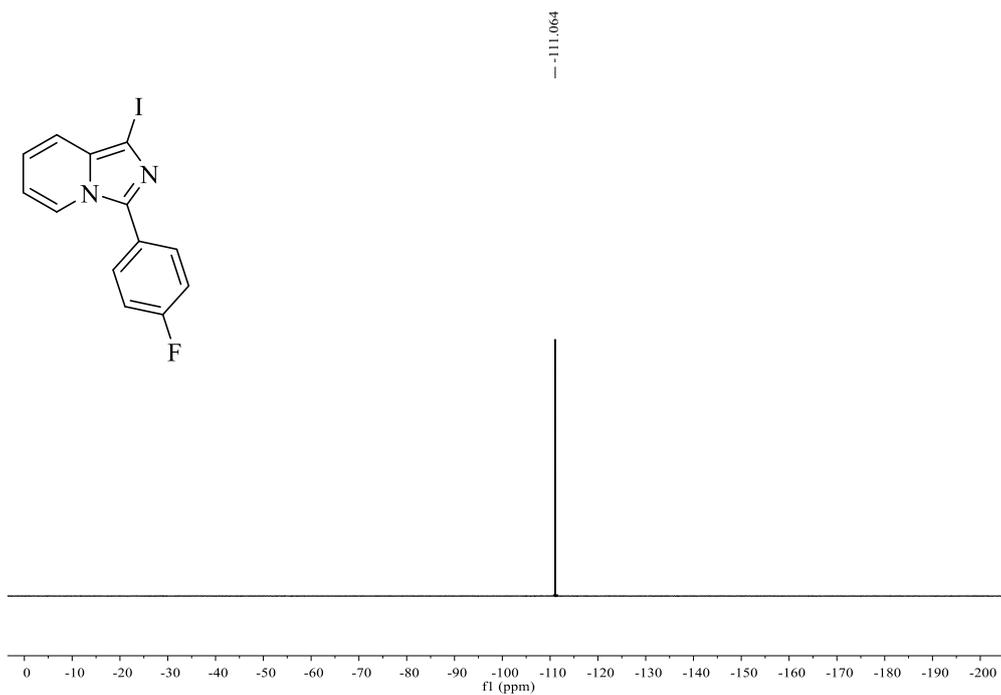
<sup>19</sup>F NMR Spectrum of **3bc**



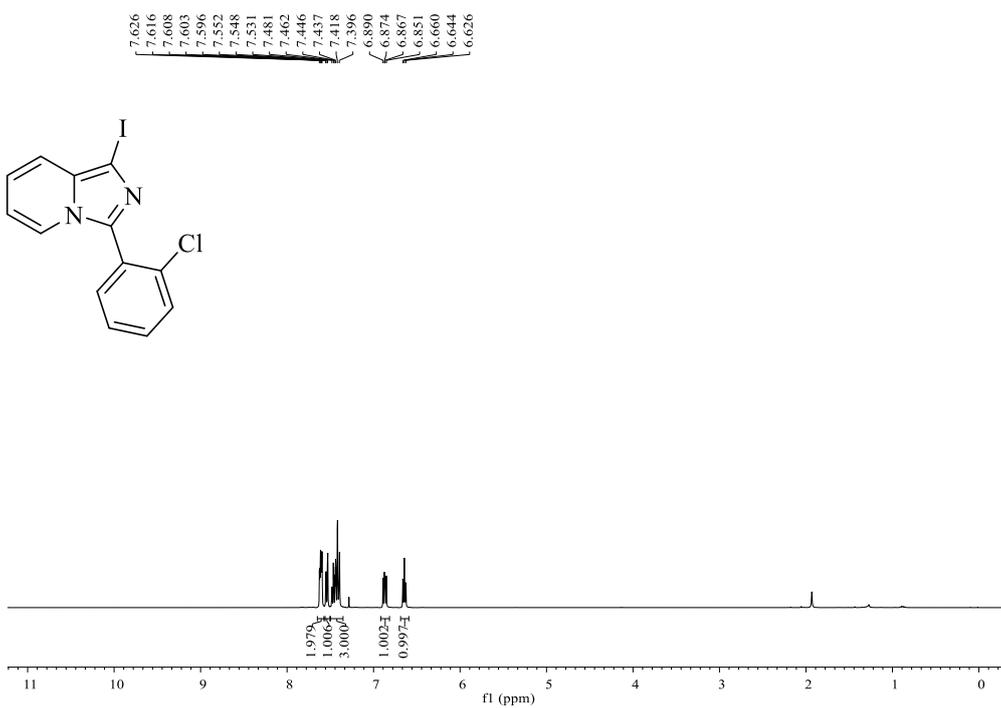
<sup>1</sup>H NMR Spectrum of **3bd**



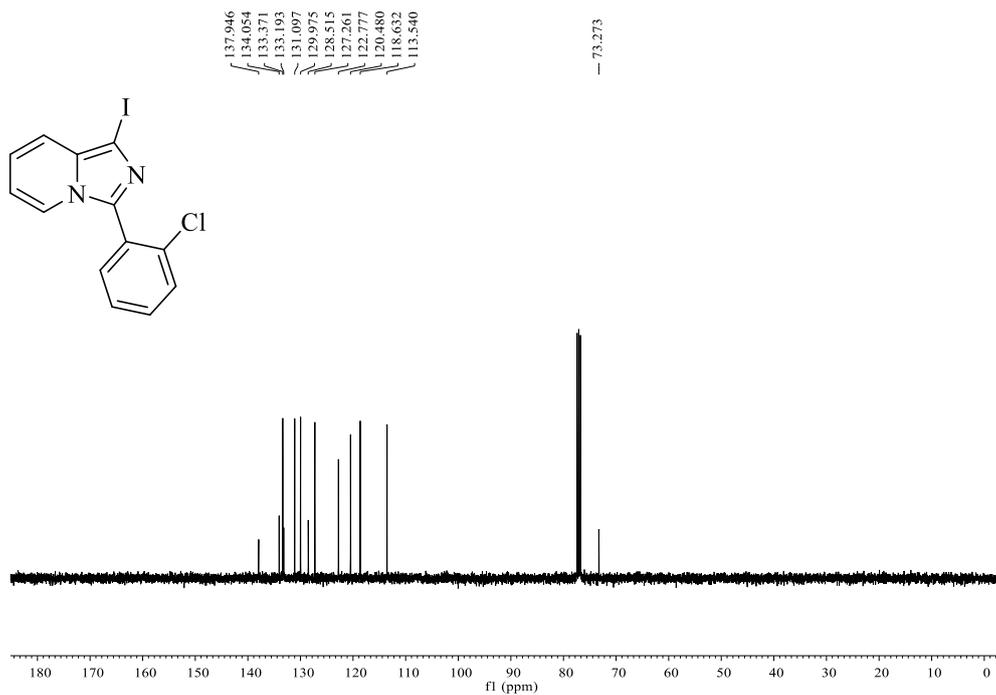
<sup>13</sup>C NMR Spectrum of **3bd**



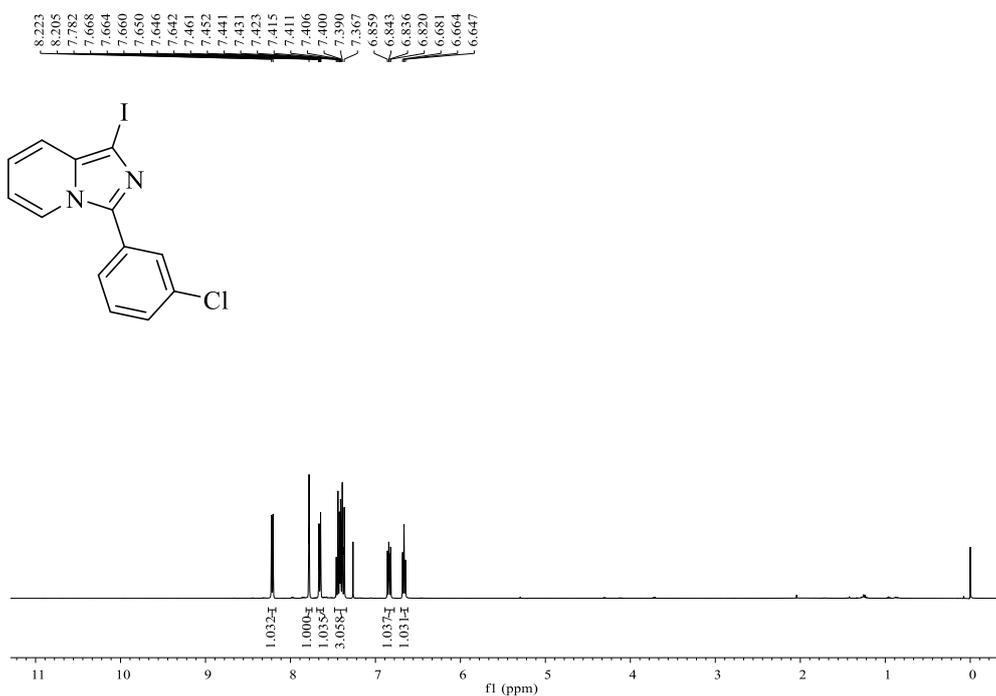
$^{19}\text{F}$  NMR Spectrum of 3bd



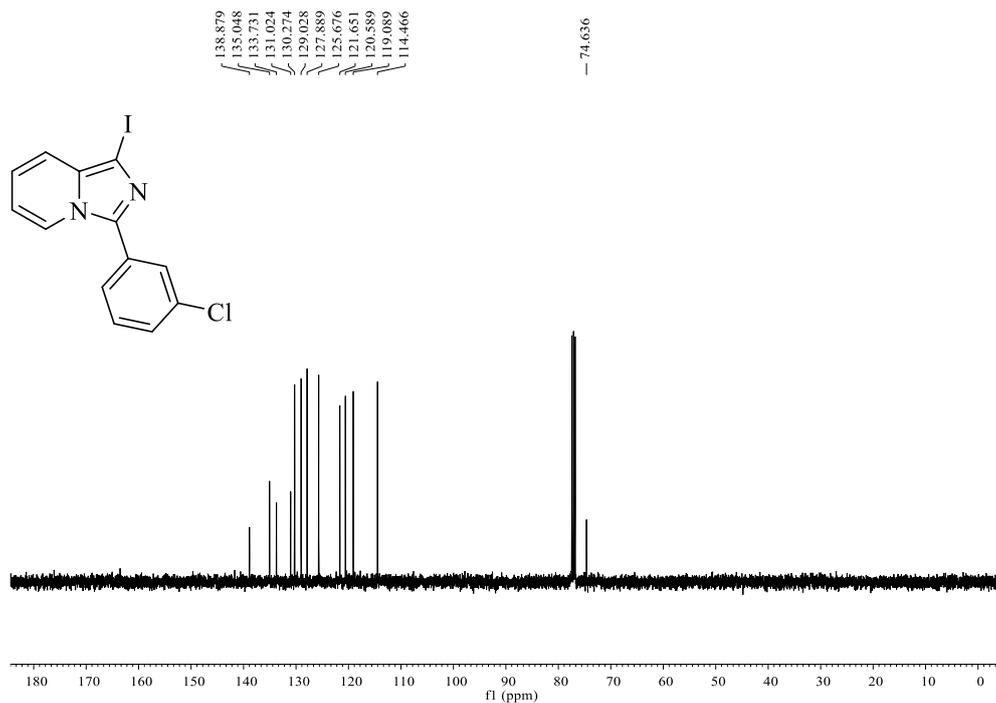
$^1\text{H}$  NMR Spectrum of 3be



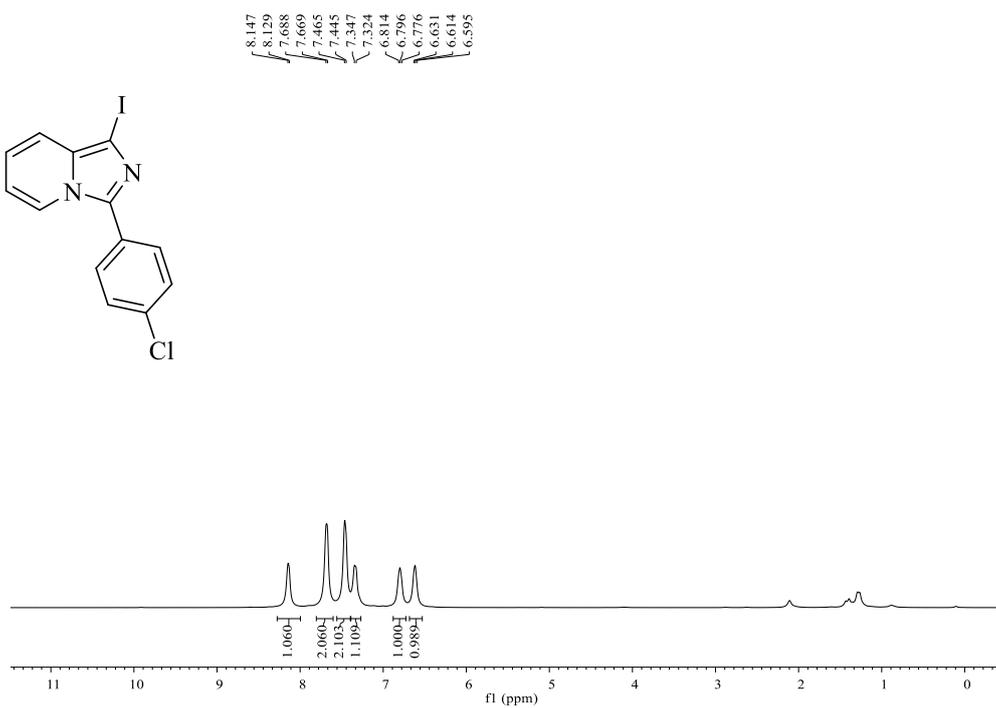
<sup>13</sup>C NMR Spectrum of 3be



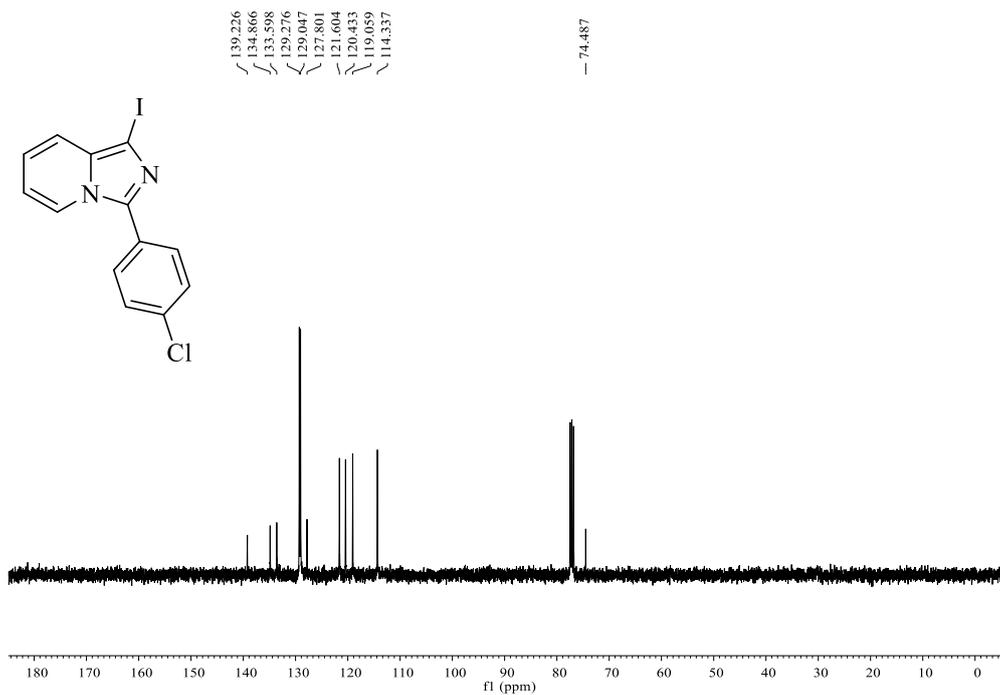
<sup>1</sup>H NMR Spectrum of 3bf



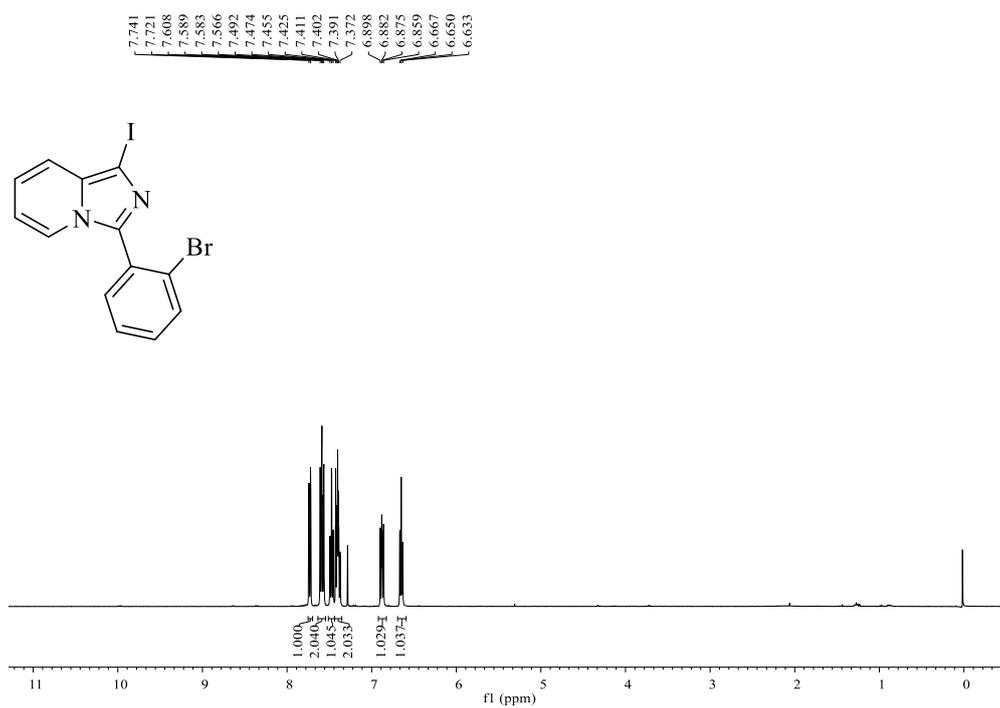
<sup>13</sup>C NMR Spectrum of **3bf**



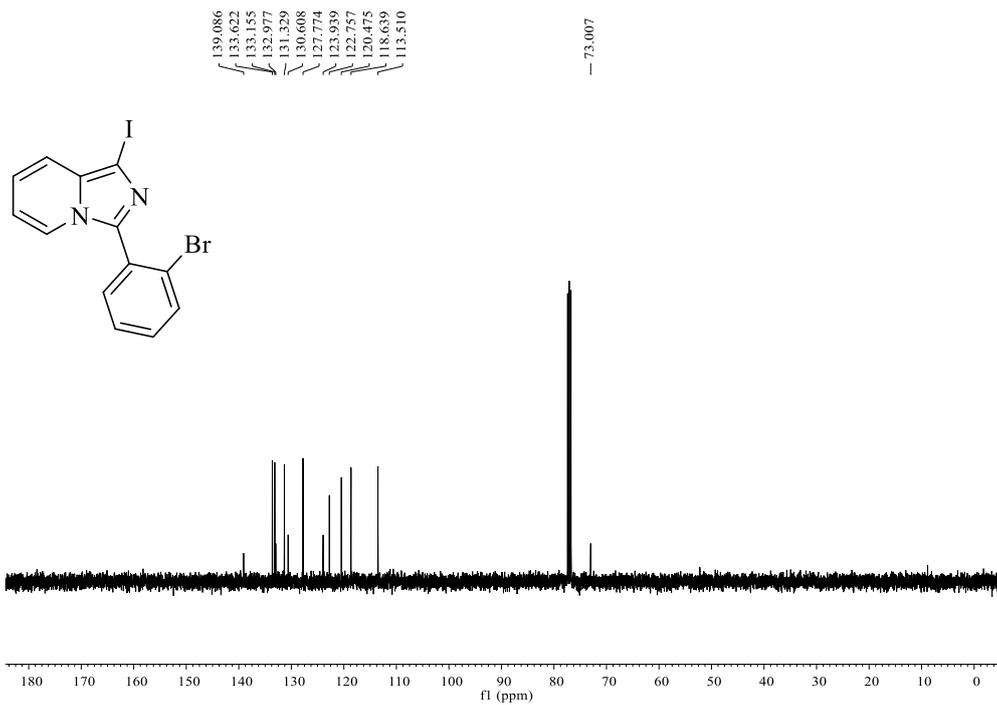
<sup>1</sup>H NMR Spectrum of **3bg**



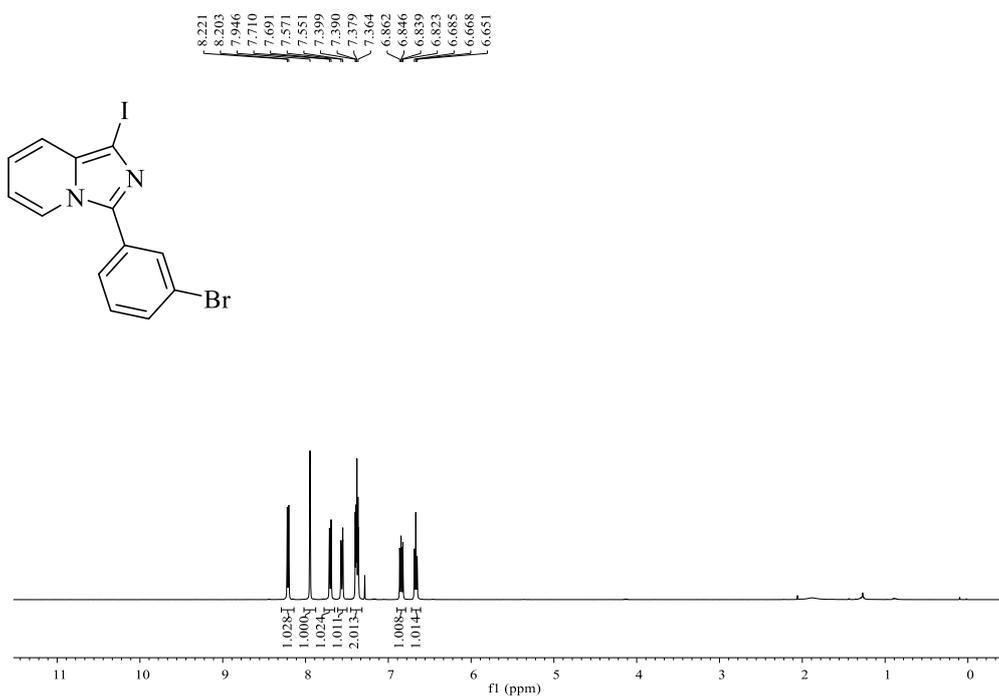
<sup>13</sup>C NMR Spectrum of **3bg**



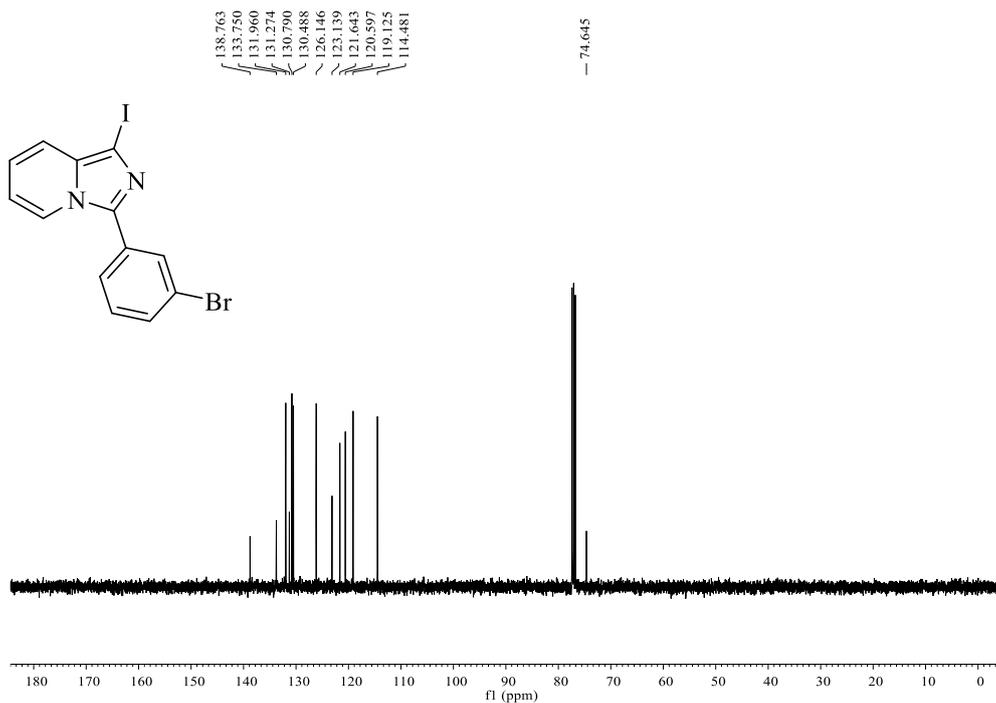
<sup>1</sup>H NMR Spectrum of **3bh**



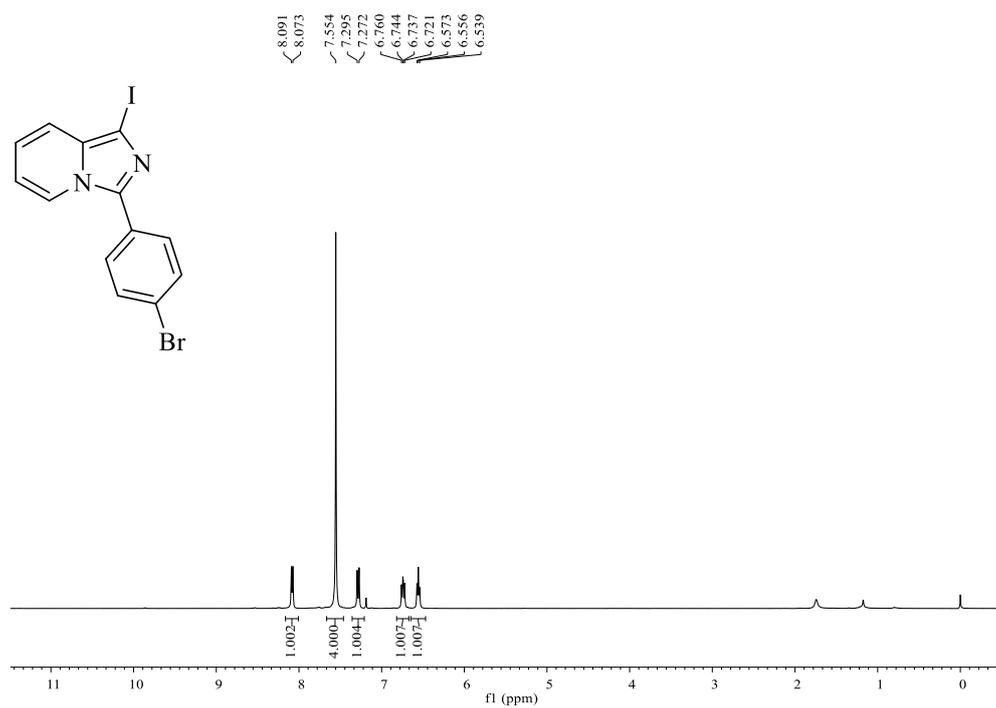
<sup>13</sup>C NMR Spectrum of 3bh



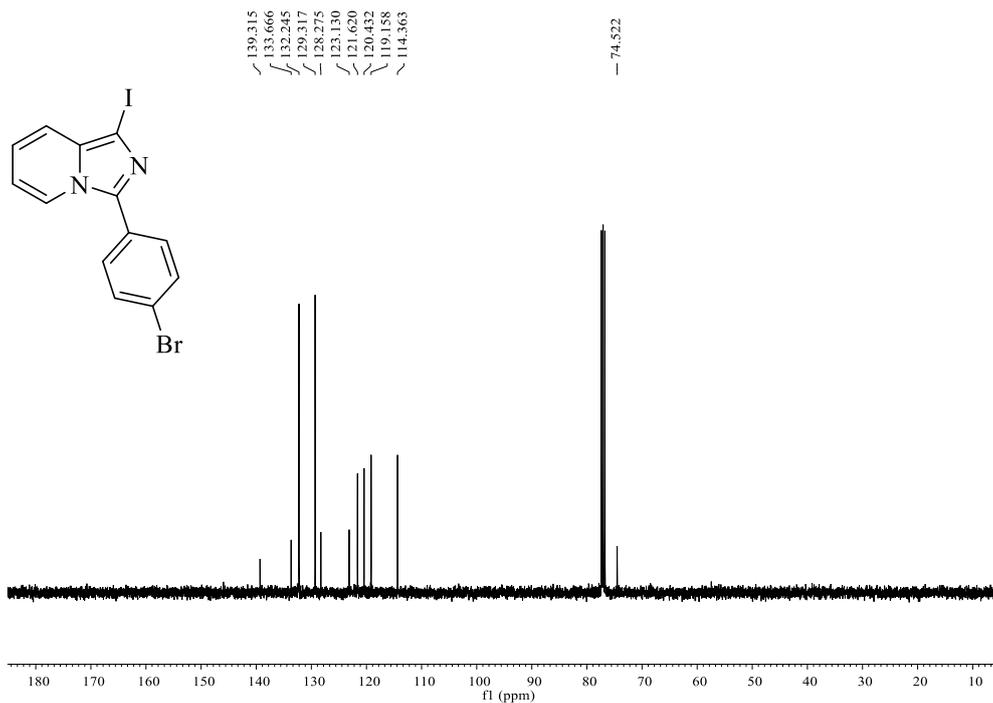
<sup>1</sup>H NMR Spectrum of 3bi



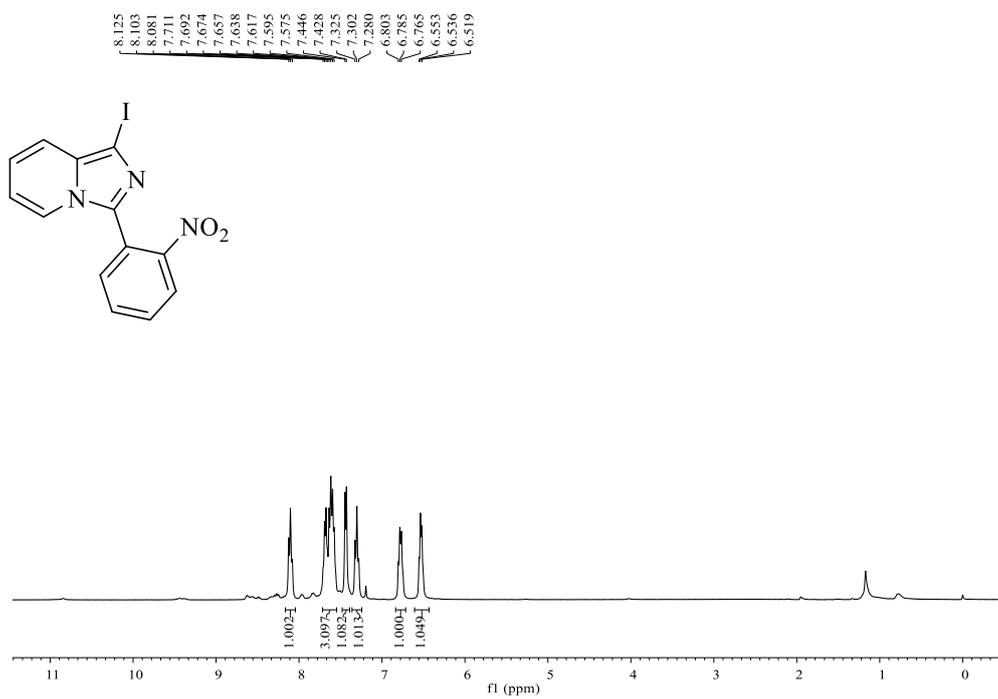
<sup>13</sup>C NMR Spectrum of **3bi**



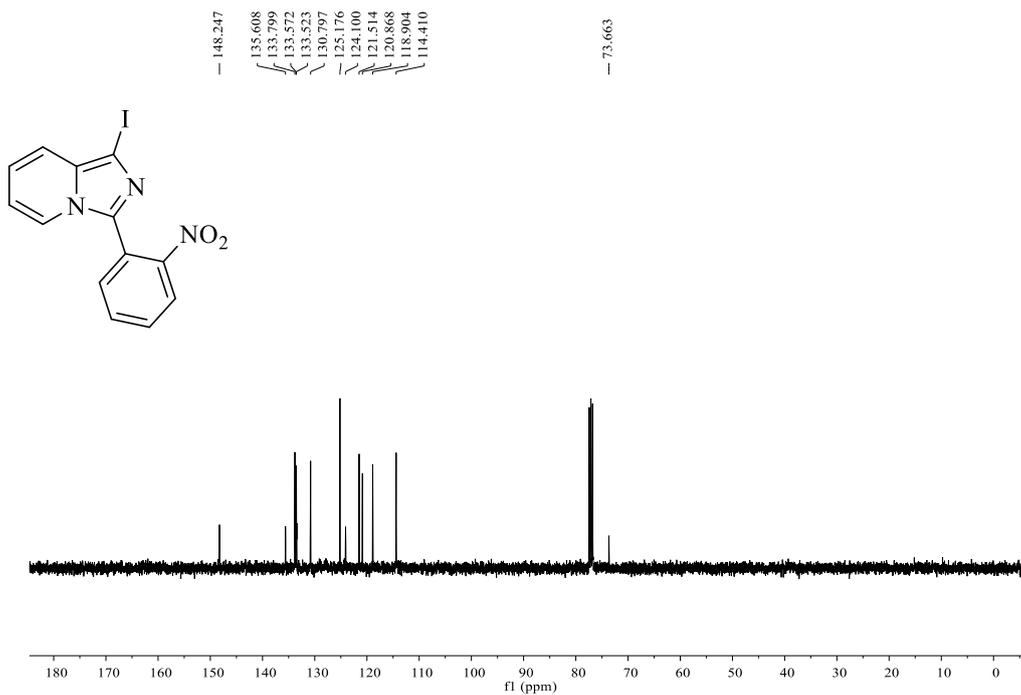
<sup>1</sup>H NMR Spectrum of **3bj**



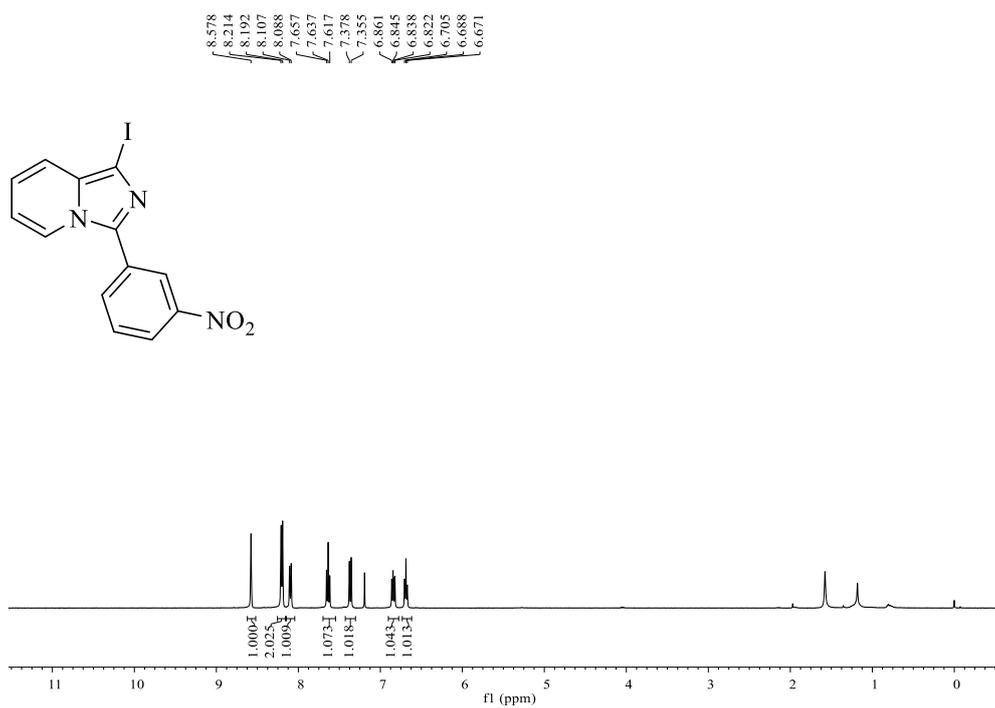
<sup>13</sup>C NMR Spectrum of **3bj**



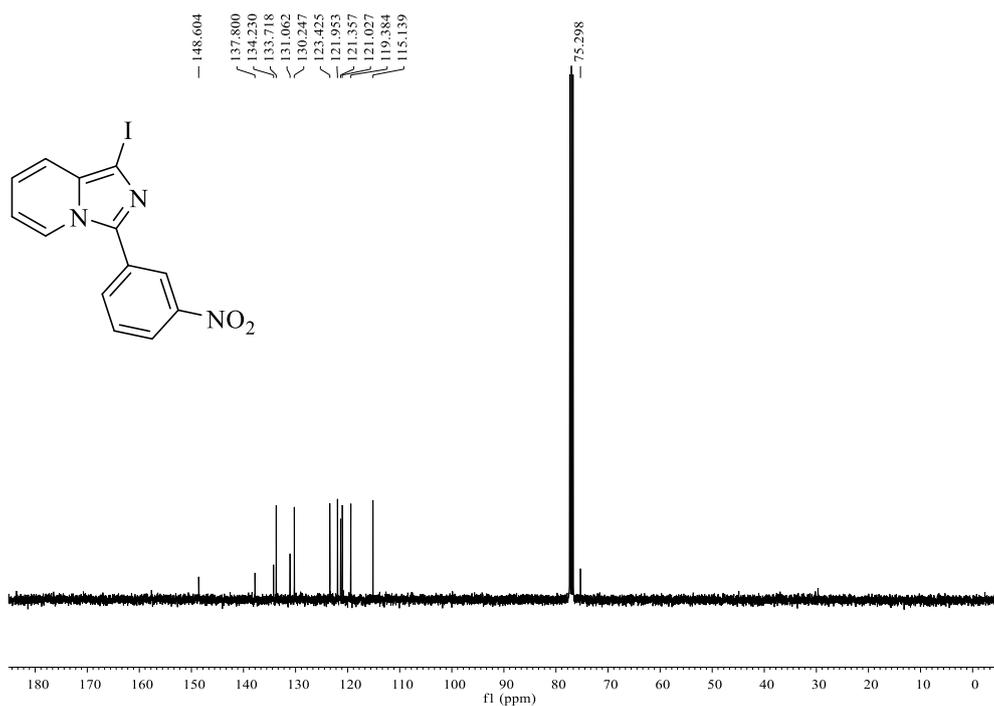
<sup>1</sup>H NMR Spectrum of **3bk**



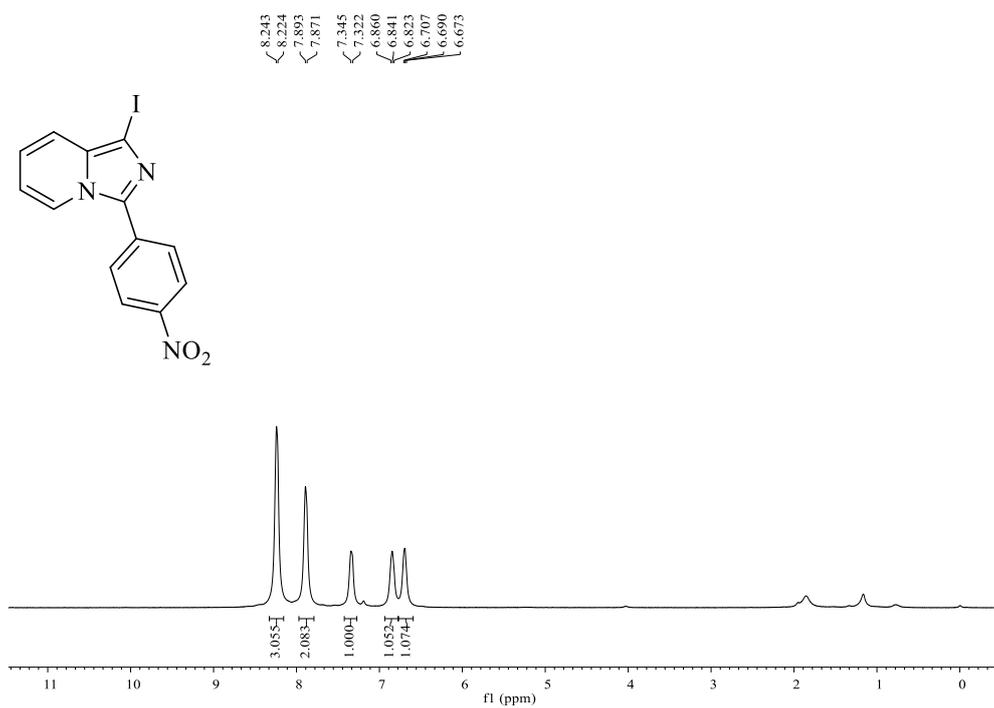
<sup>13</sup>C NMR Spectrum of **3bk**



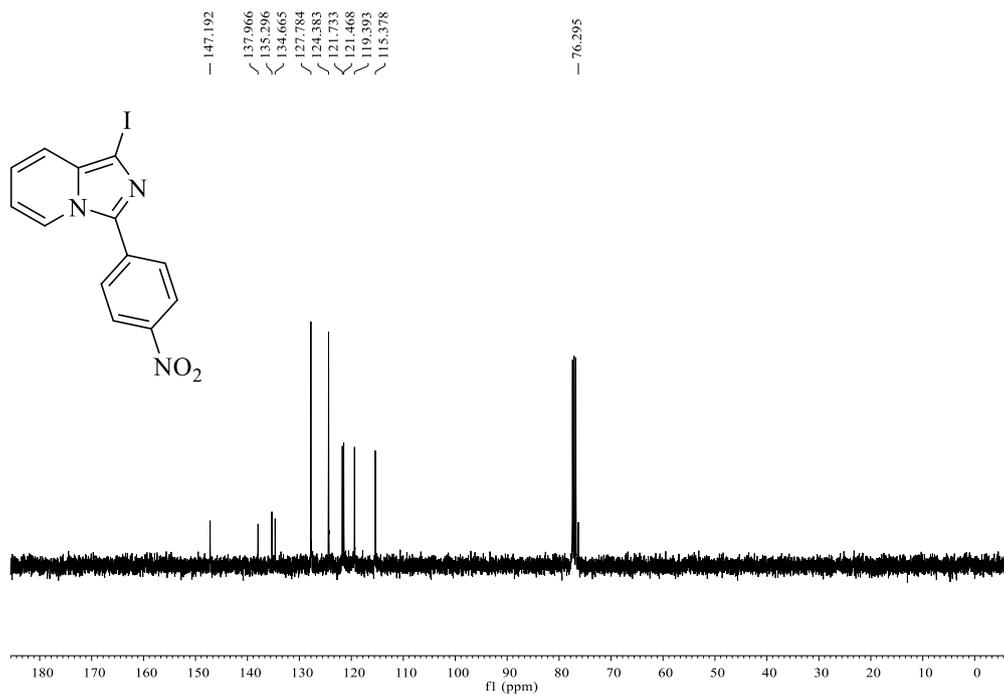
<sup>1</sup>H NMR Spectrum of **3bl**



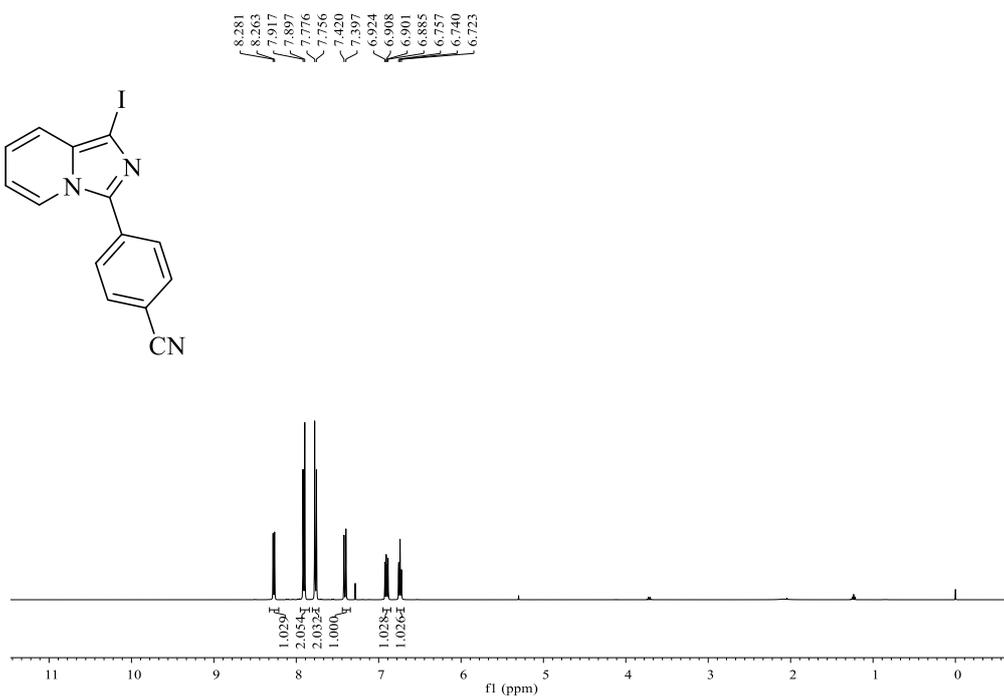
<sup>13</sup>C NMR Spectrum of **3bl**



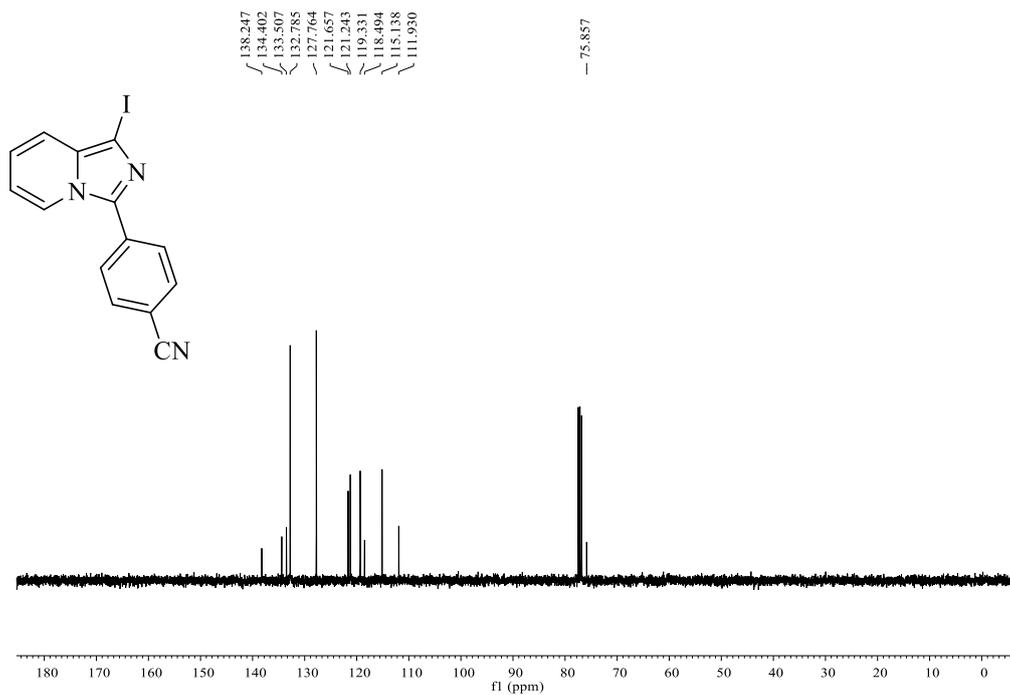
<sup>1</sup>H NMR Spectrum of **3bm**



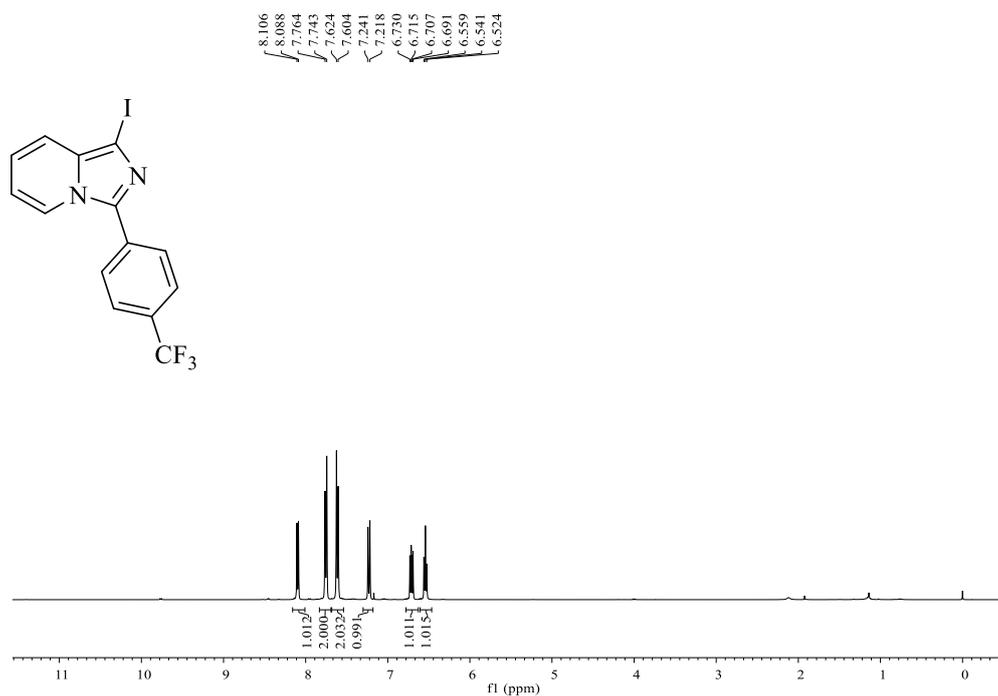
<sup>13</sup>C NMR Spectrum of **3bm**



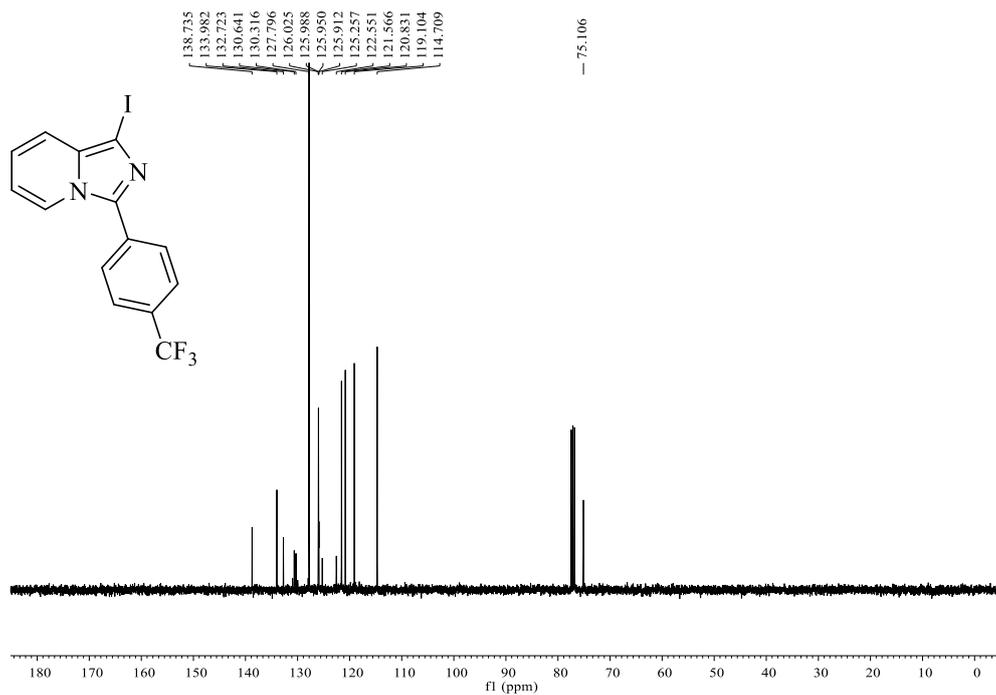
<sup>1</sup>H NMR Spectrum of **3bn**



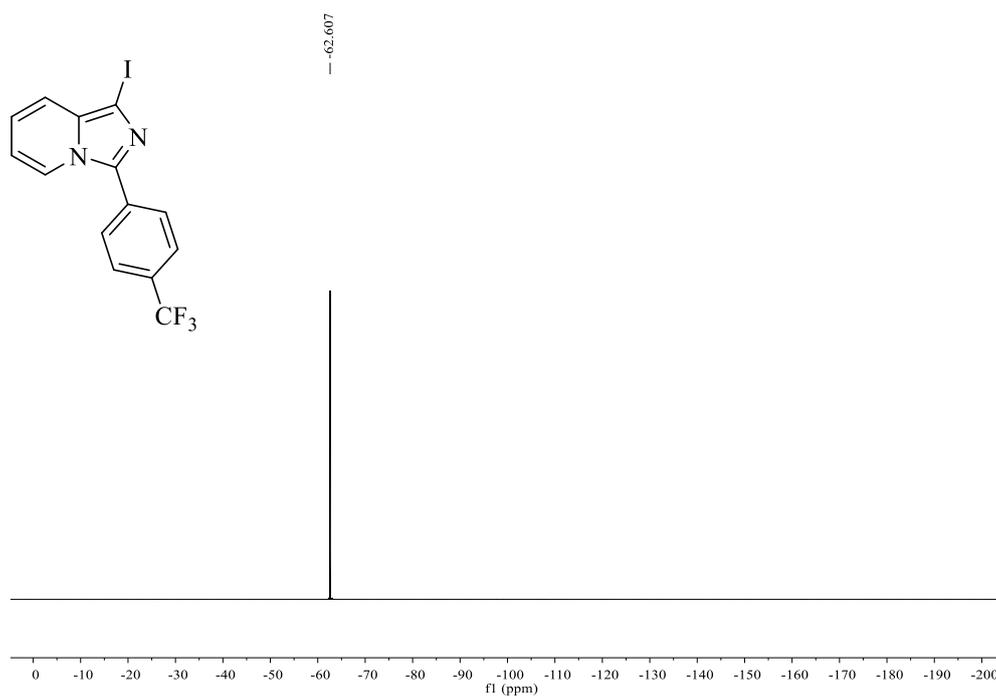
<sup>13</sup>C NMR Spectrum of **3bn**



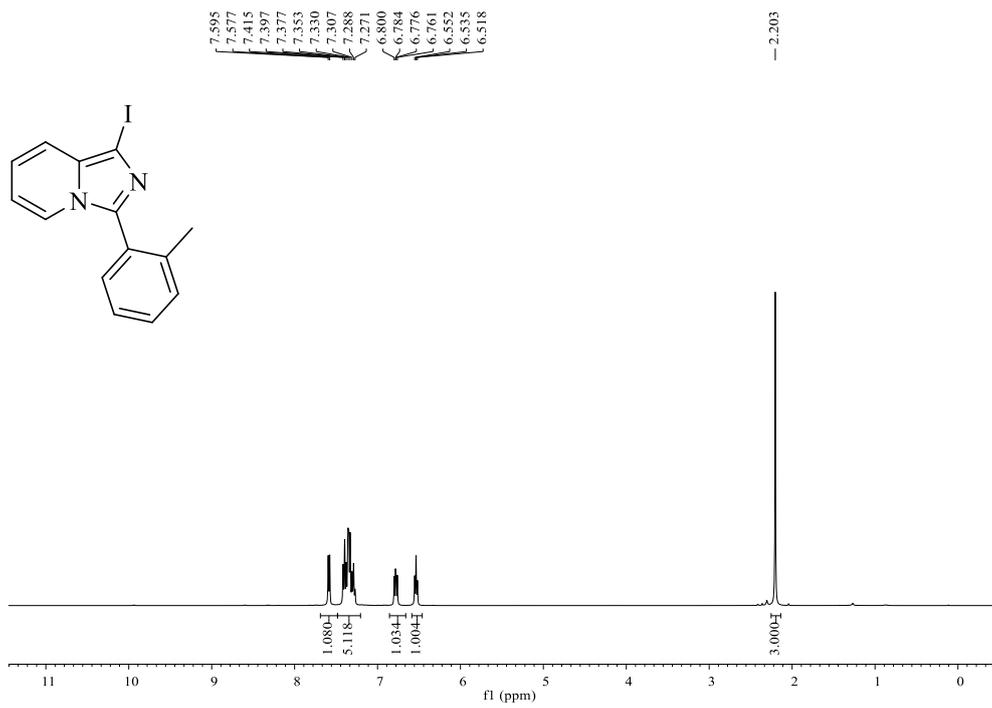
<sup>1</sup>H NMR Spectrum of **3bo**



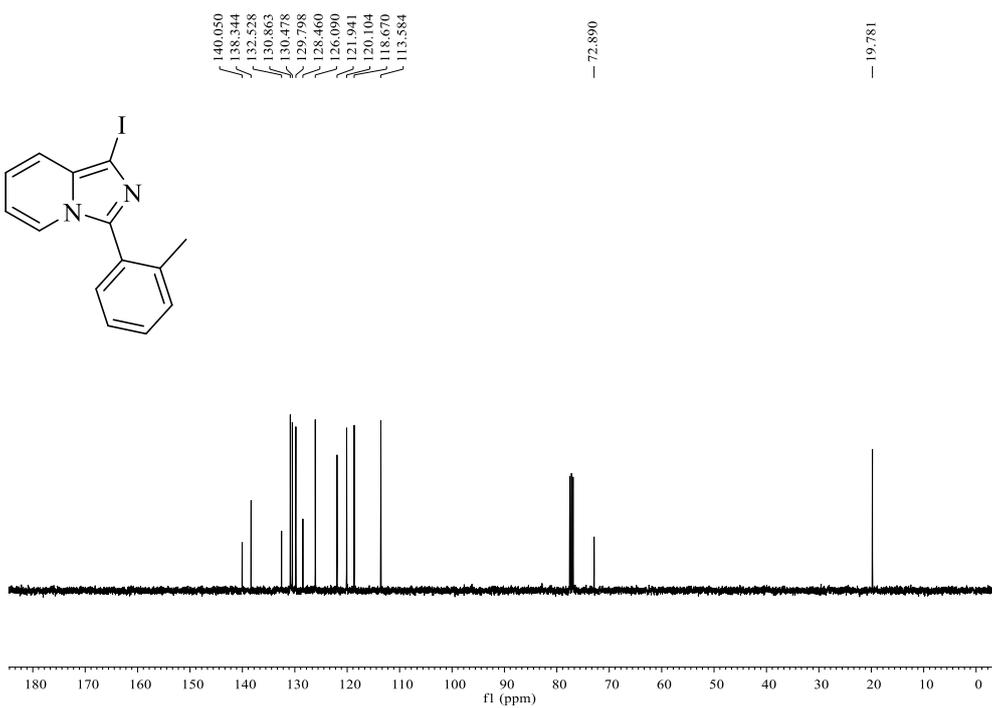
<sup>13</sup>C NMR Spectrum of **3bo**



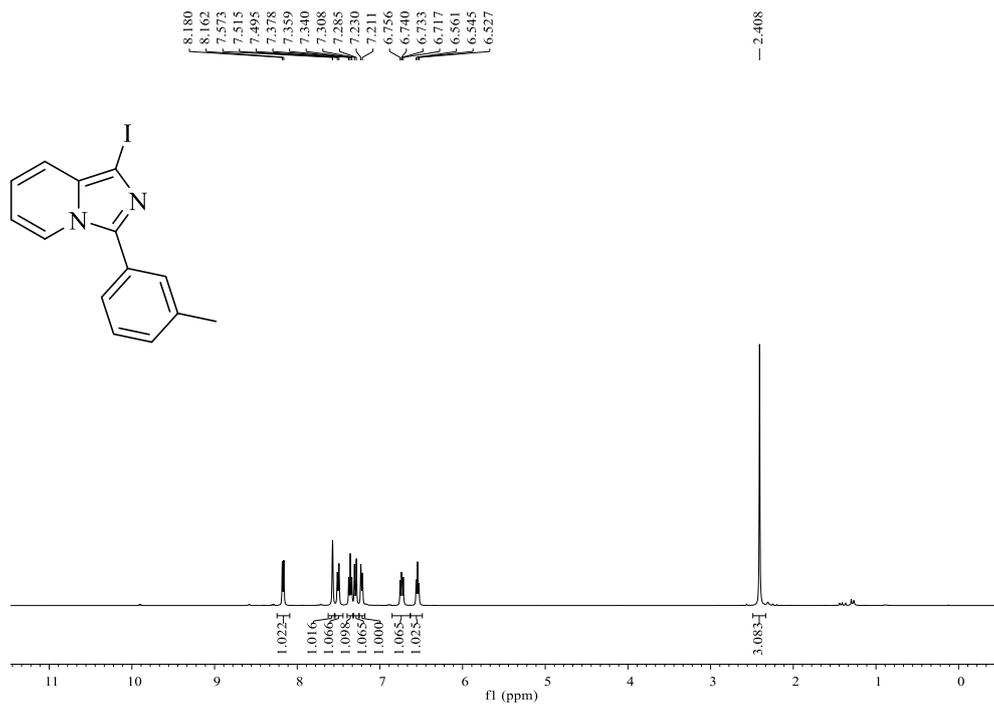
<sup>19</sup>F NMR Spectrum of **3bo**



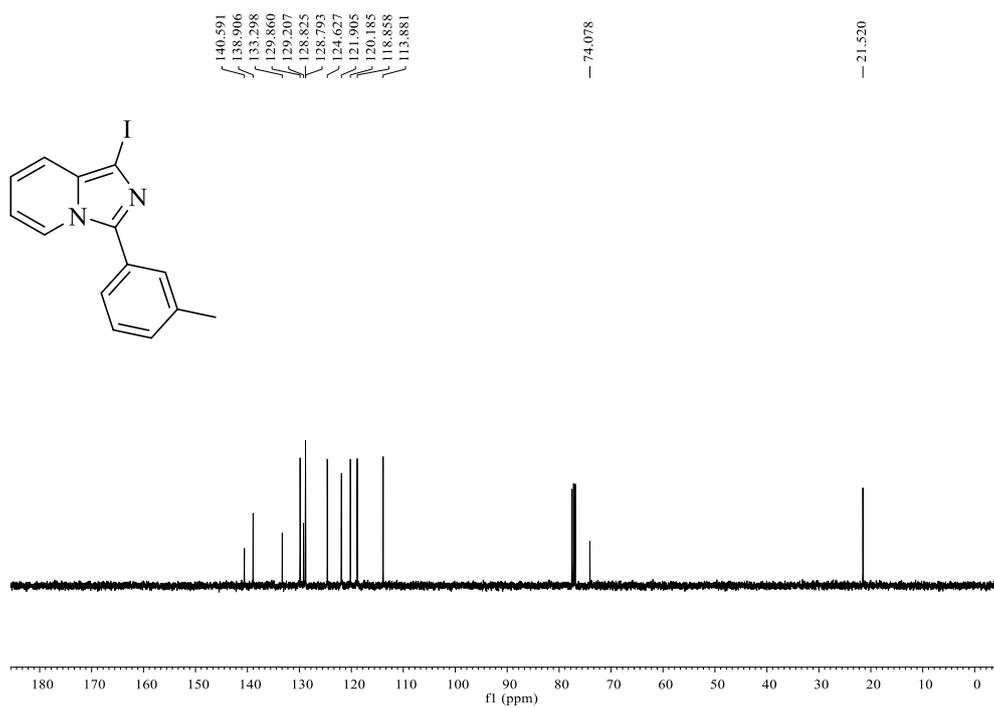
<sup>1</sup>H NMR Spectrum of 3bp



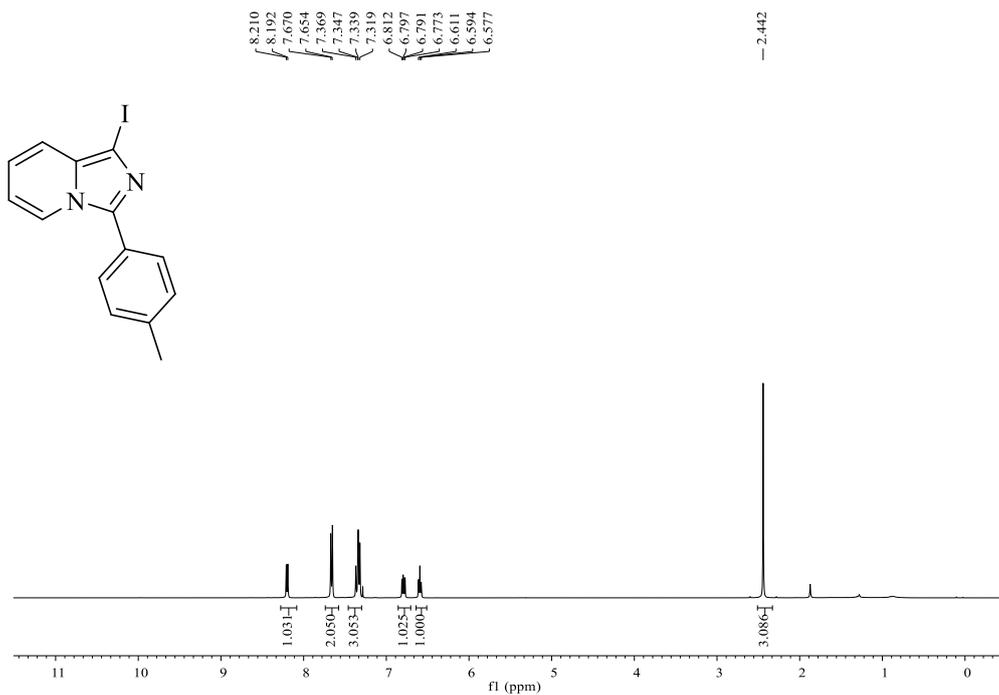
<sup>13</sup>C NMR Spectrum of 3bp



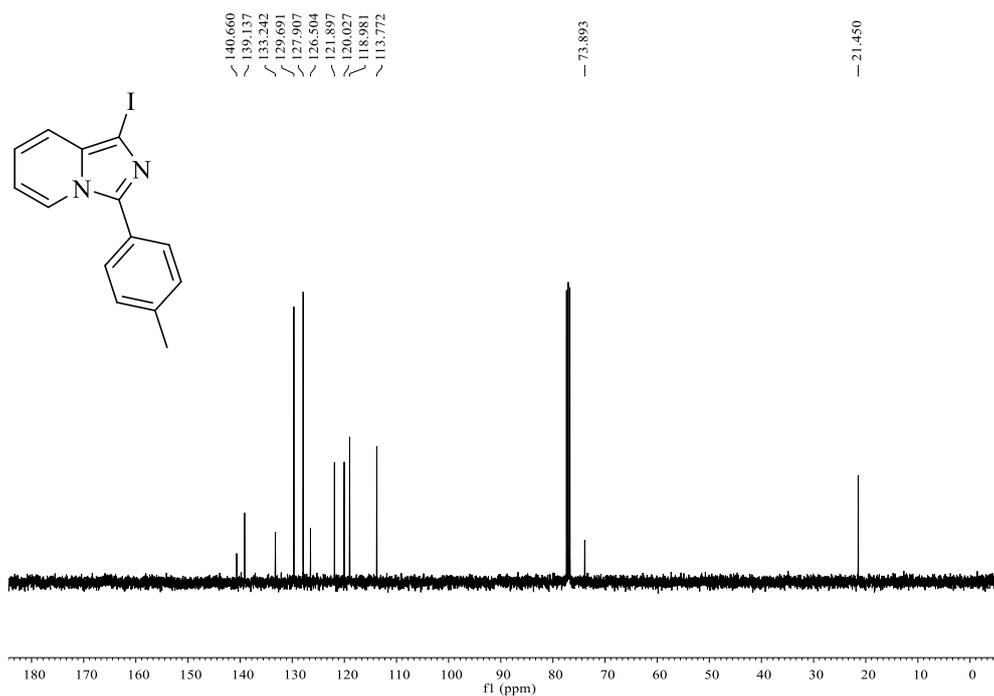
<sup>1</sup>H NMR Spectrum of 3bq



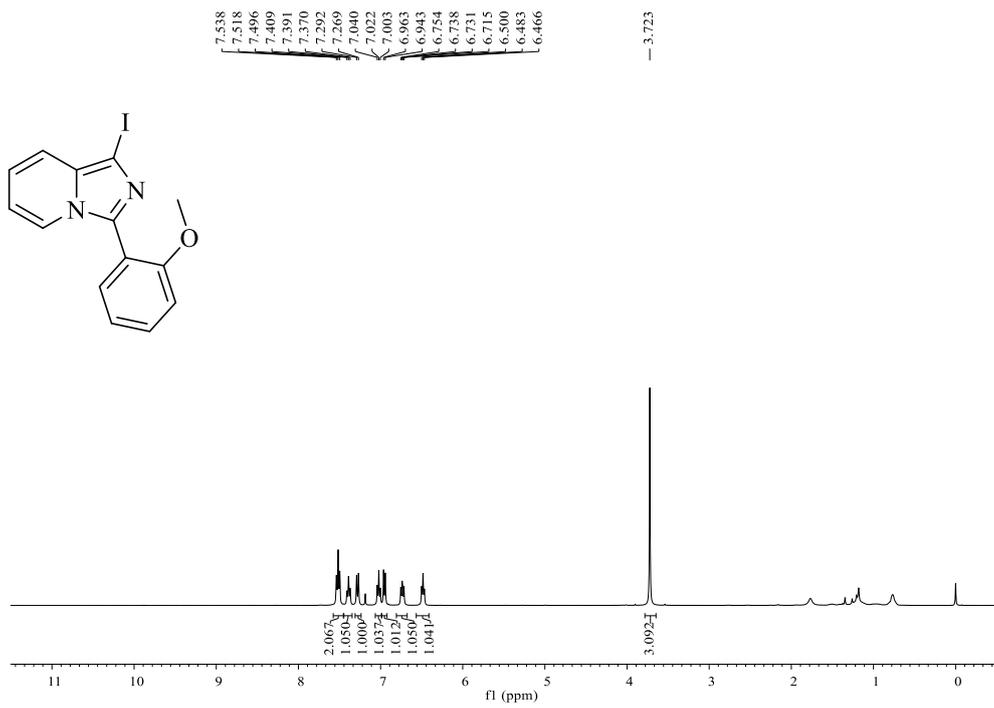
<sup>13</sup>C NMR Spectrum of 3bq



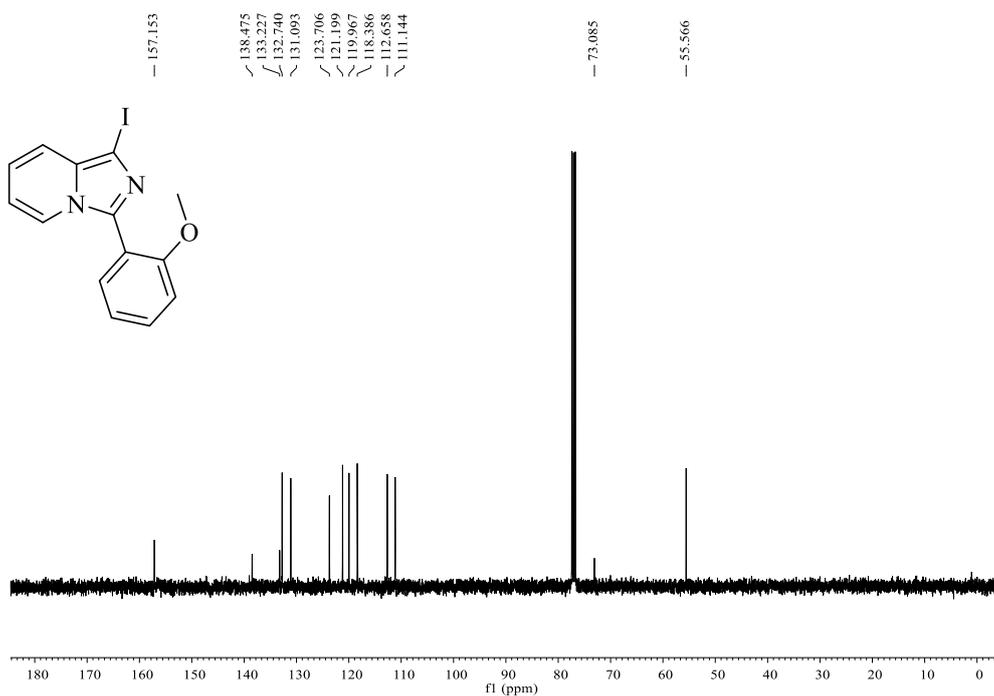
<sup>1</sup>H NMR Spectrum of 3br



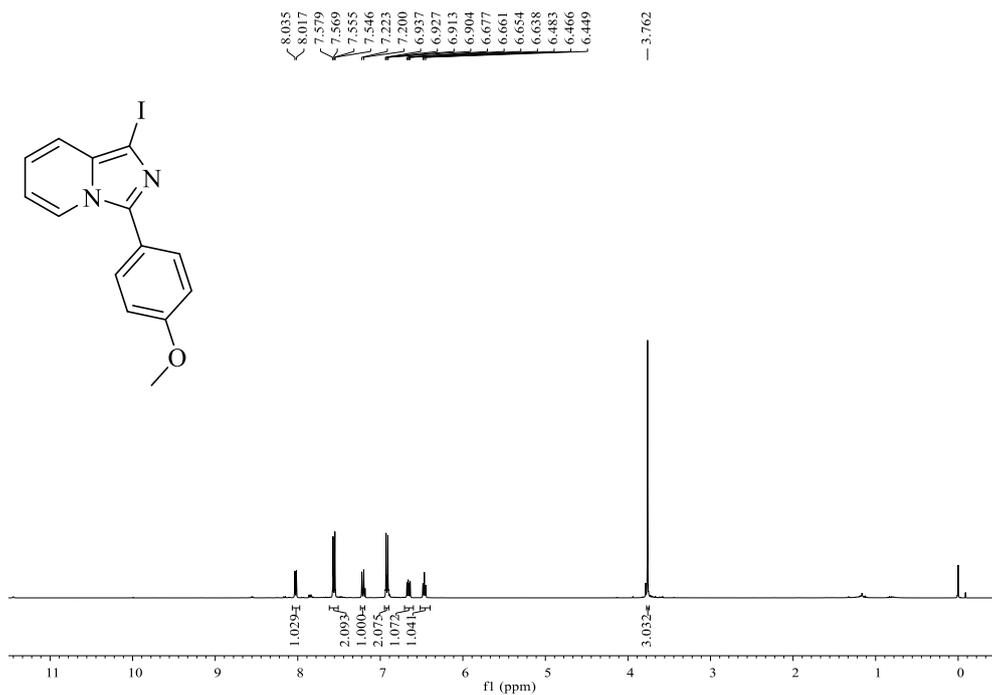
<sup>13</sup>C NMR Spectrum of 3br



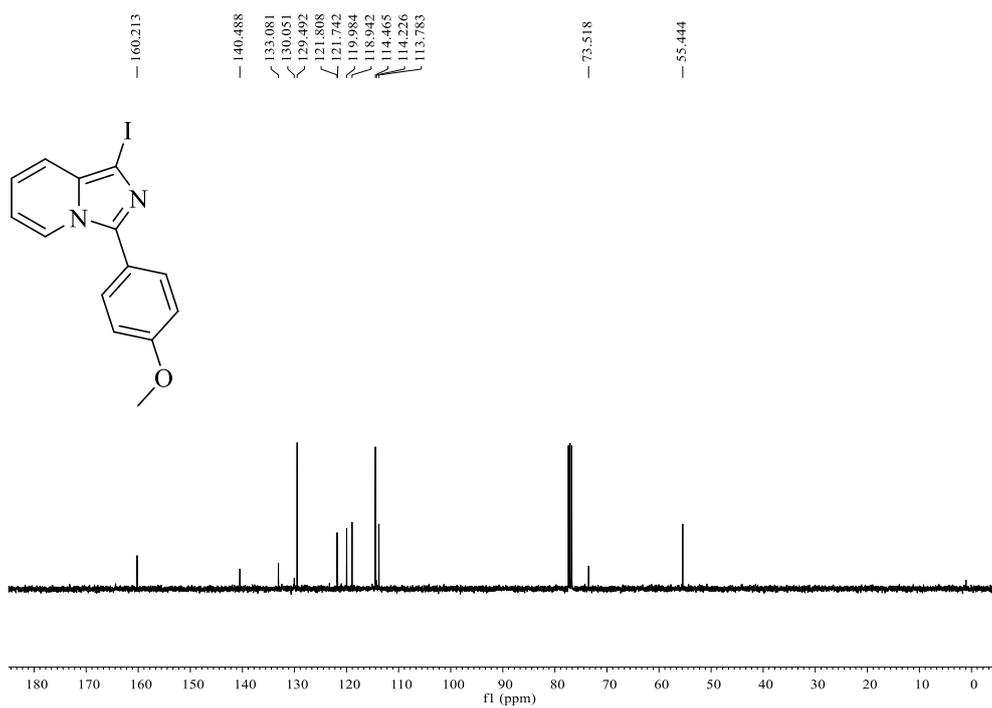
<sup>1</sup>H NMR Spectrum of 3bs



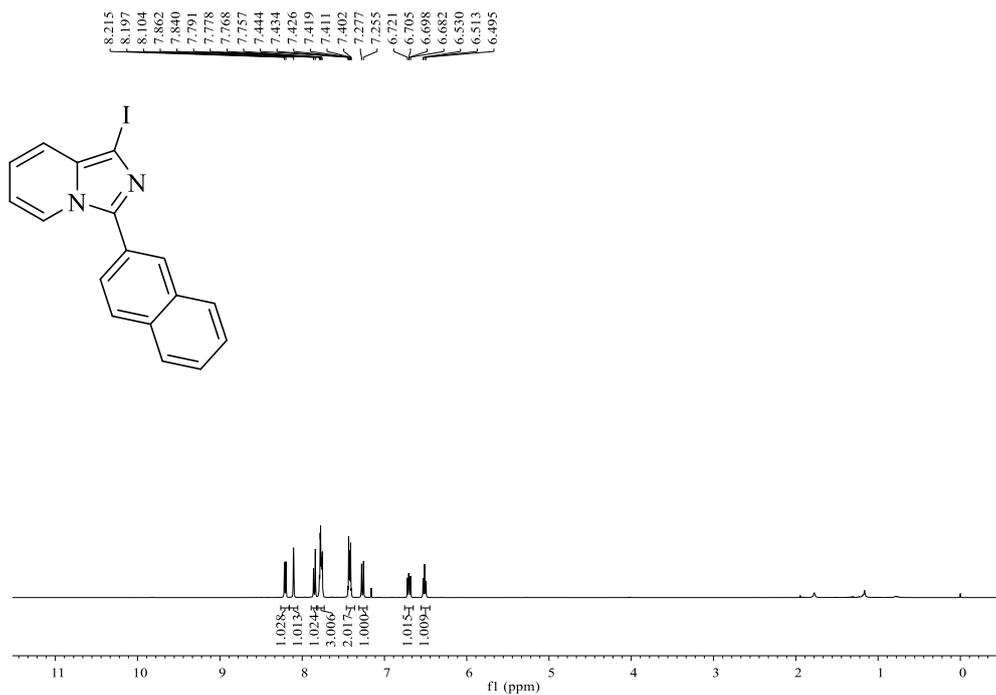
<sup>13</sup>C NMR Spectrum of 3bs



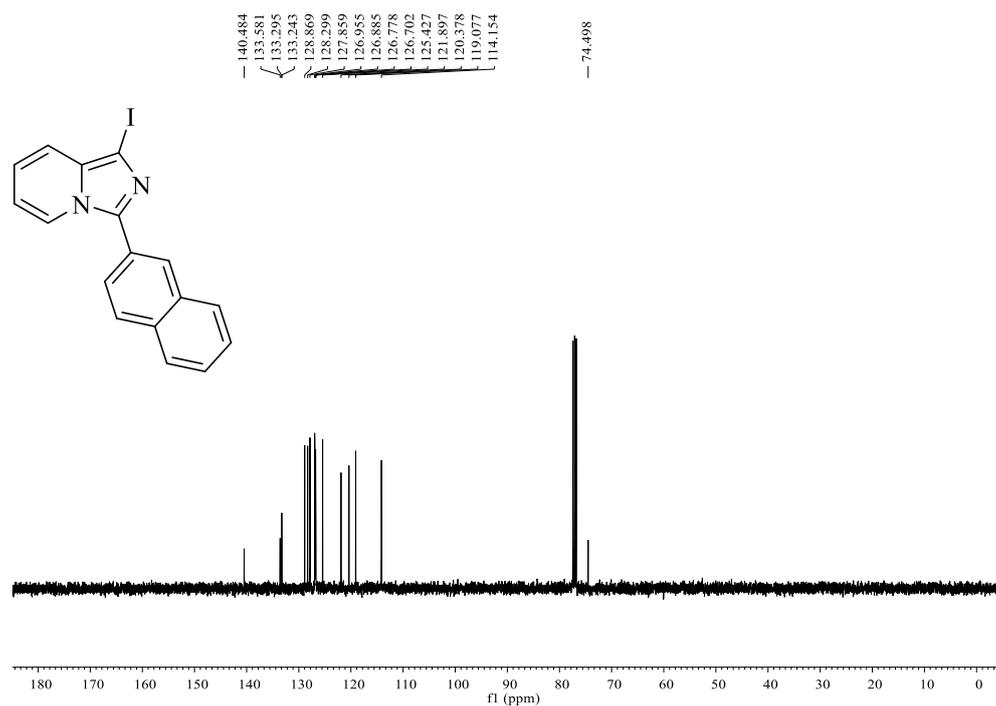
<sup>1</sup>H NMR Spectrum of 3bt



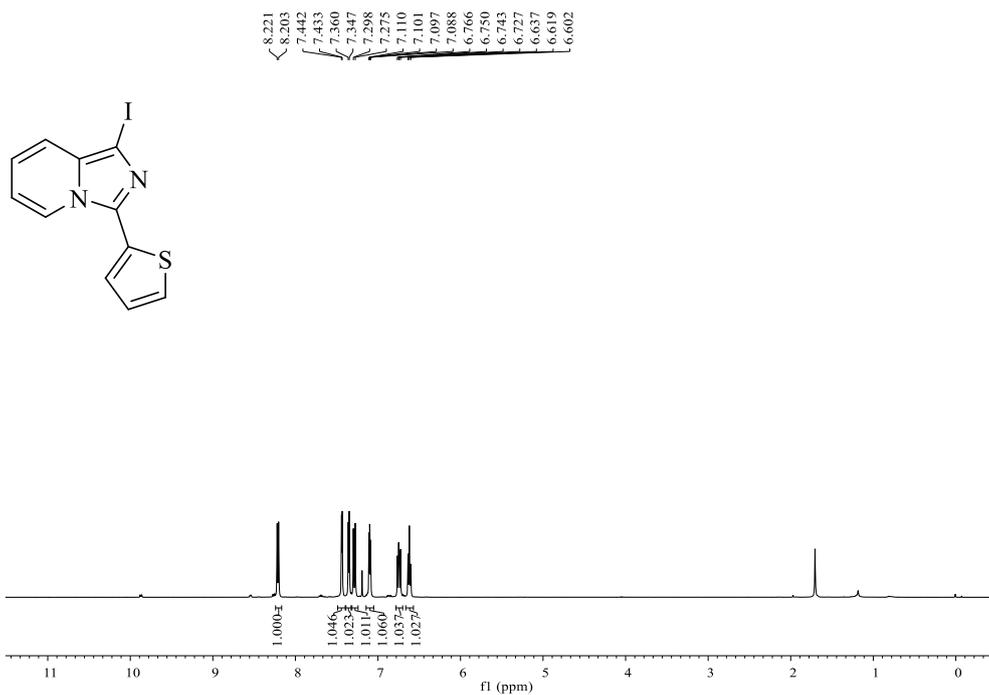
<sup>13</sup>C NMR Spectrum of 3bt



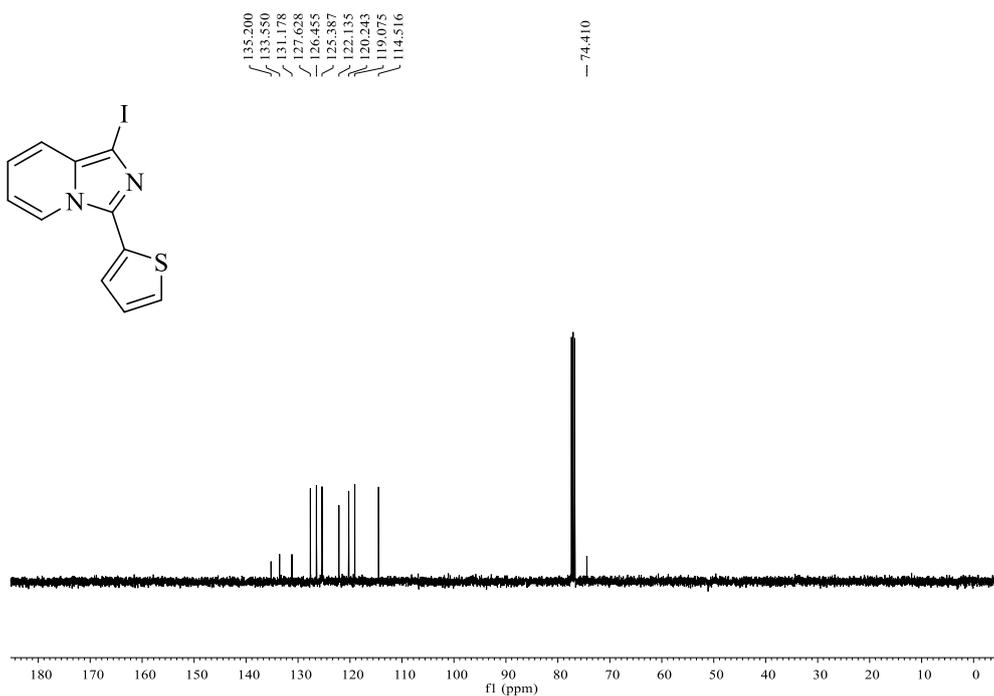
<sup>1</sup>H NMR Spectrum of 3bu



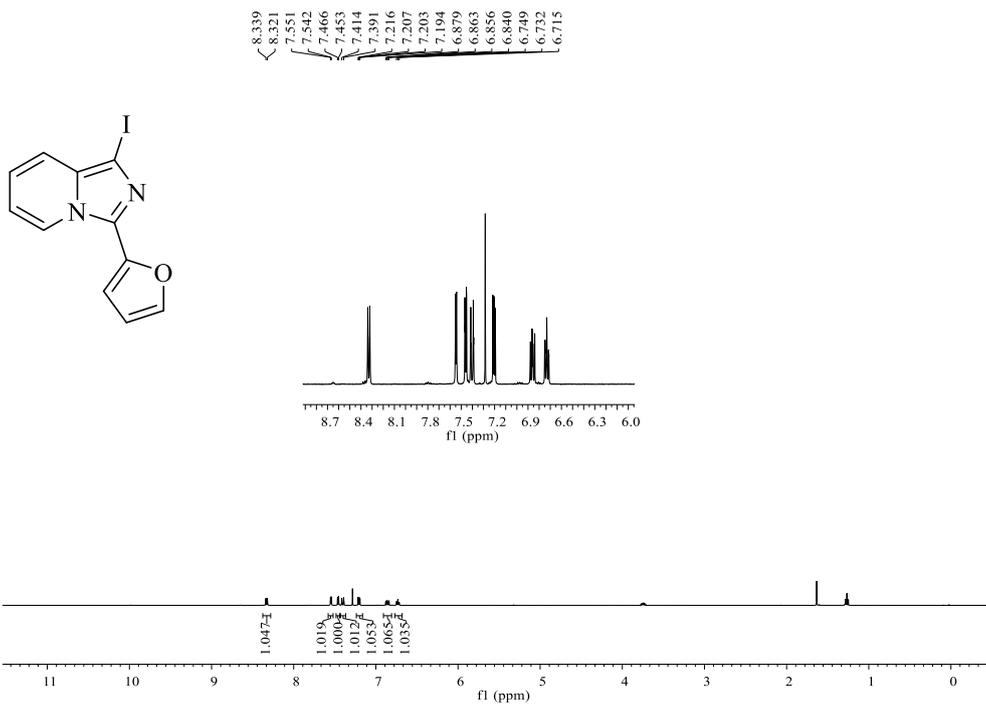
<sup>13</sup>C NMR Spectrum of 3bu



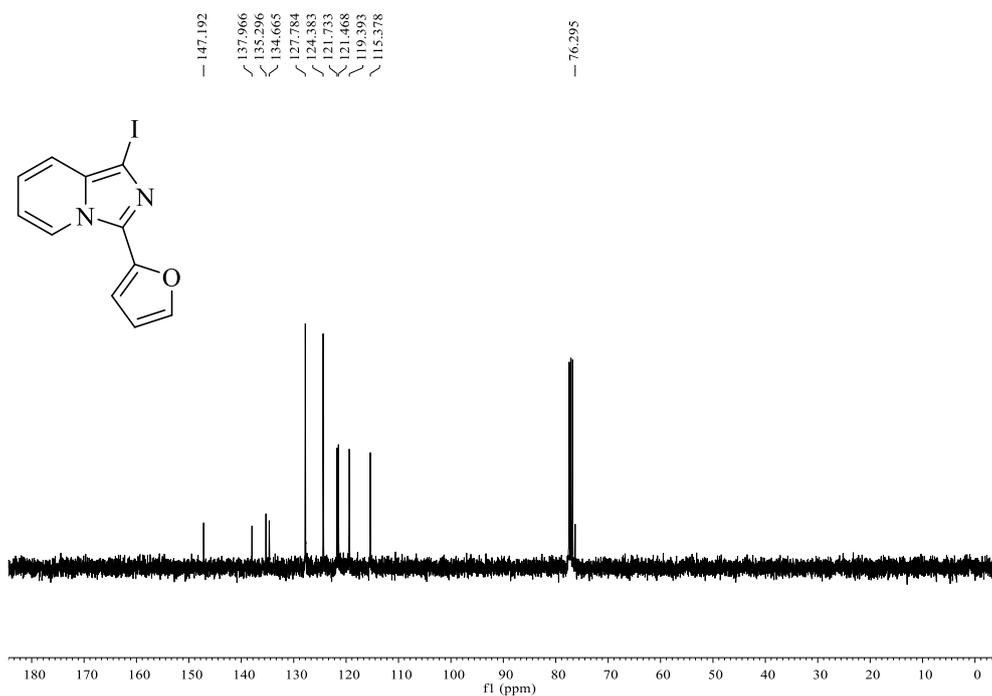
<sup>1</sup>H NMR Spectrum of 3bv



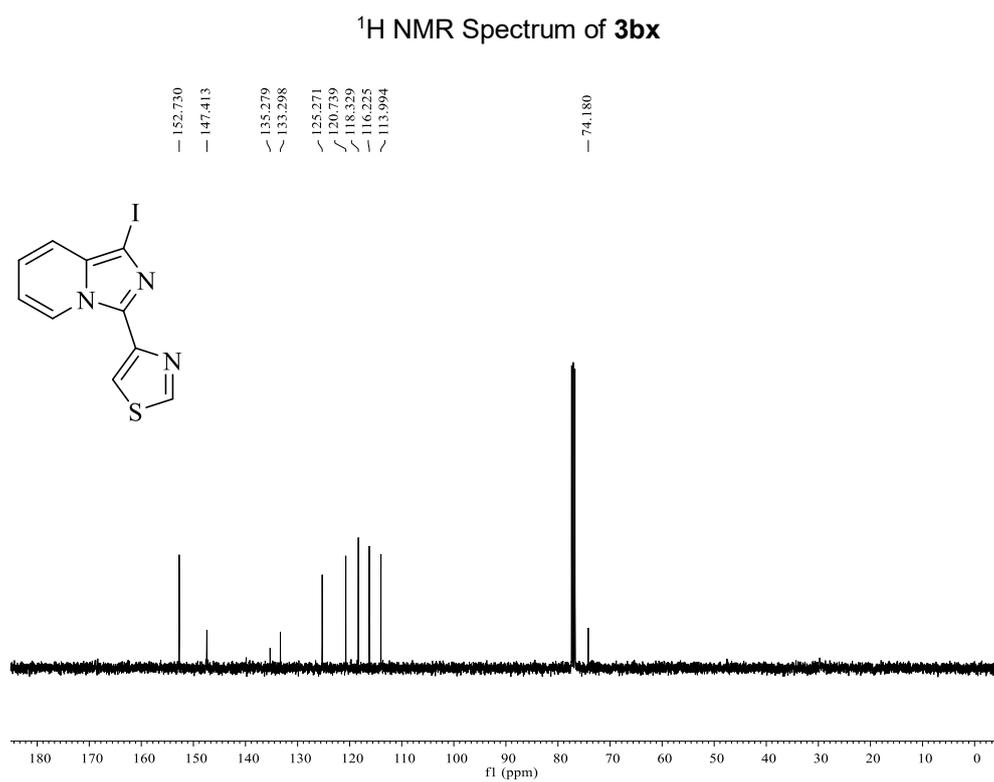
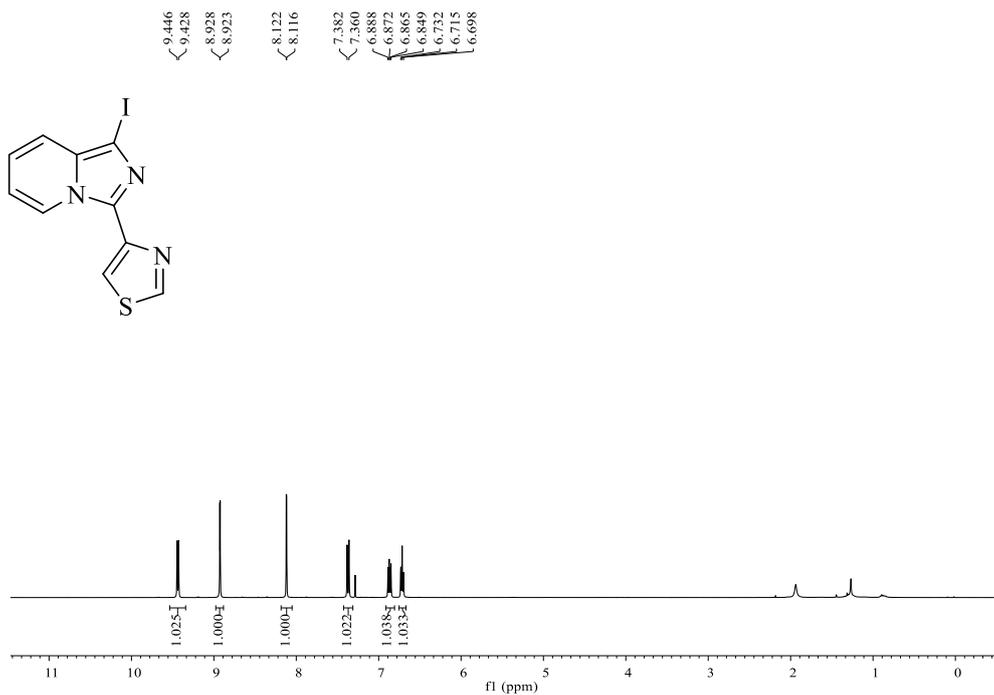
<sup>13</sup>C NMR Spectrum of 3bv

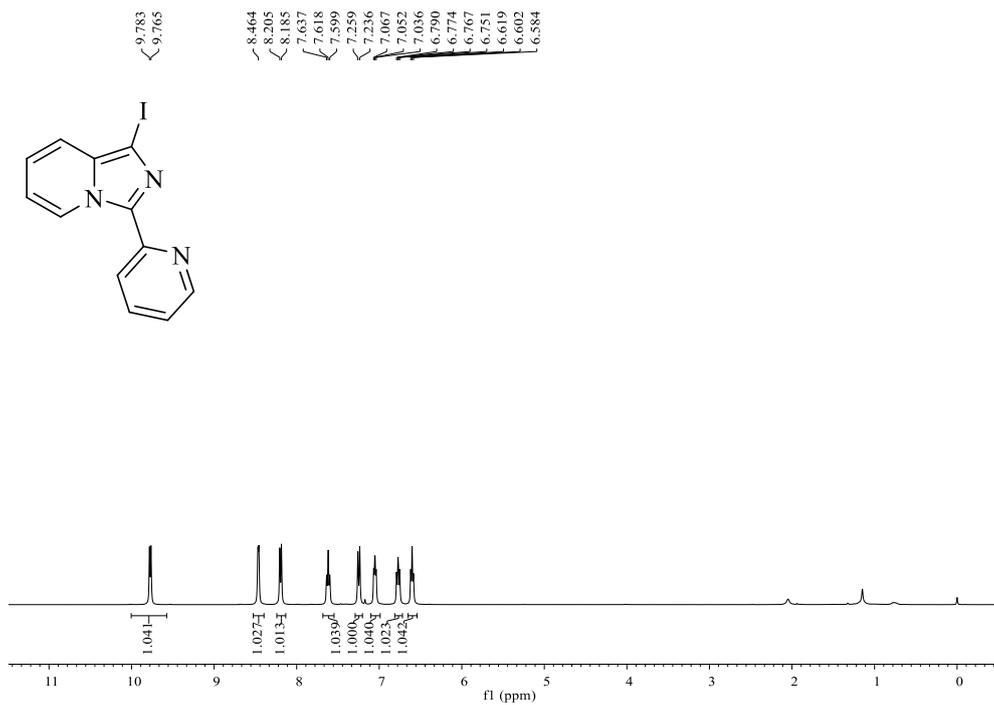


<sup>1</sup>H NMR Spectrum of **3bw**

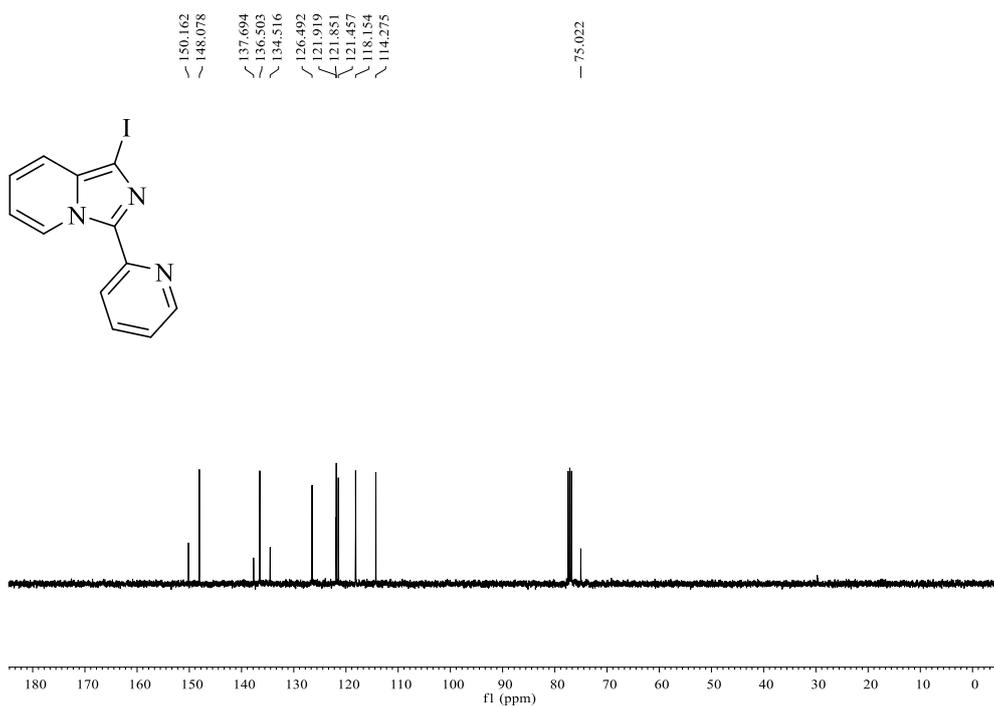


<sup>13</sup>C NMR Spectrum of **3bw**

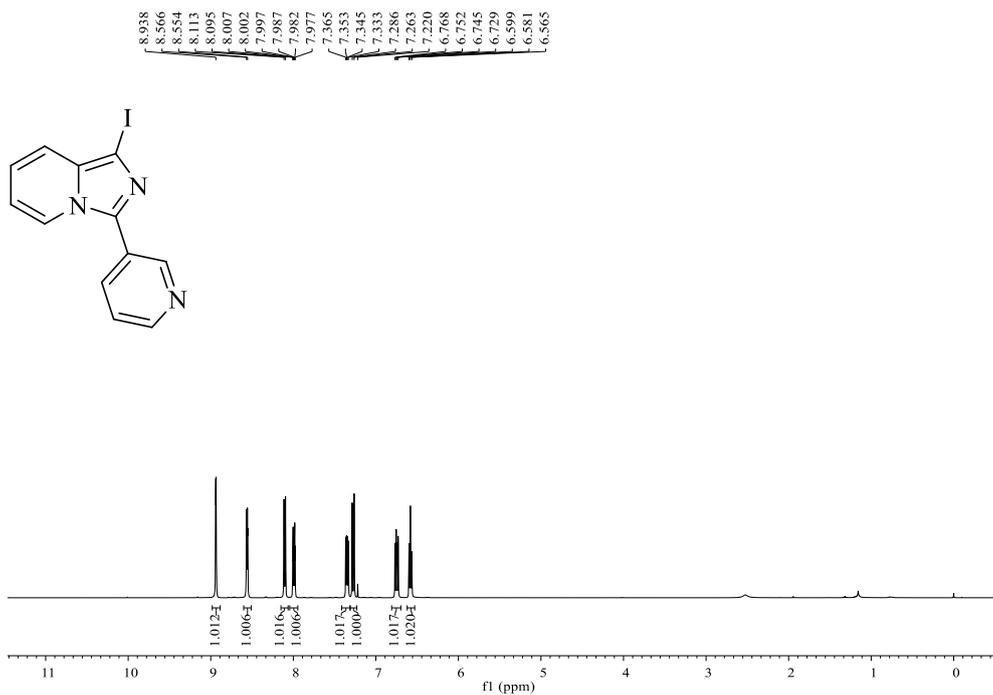




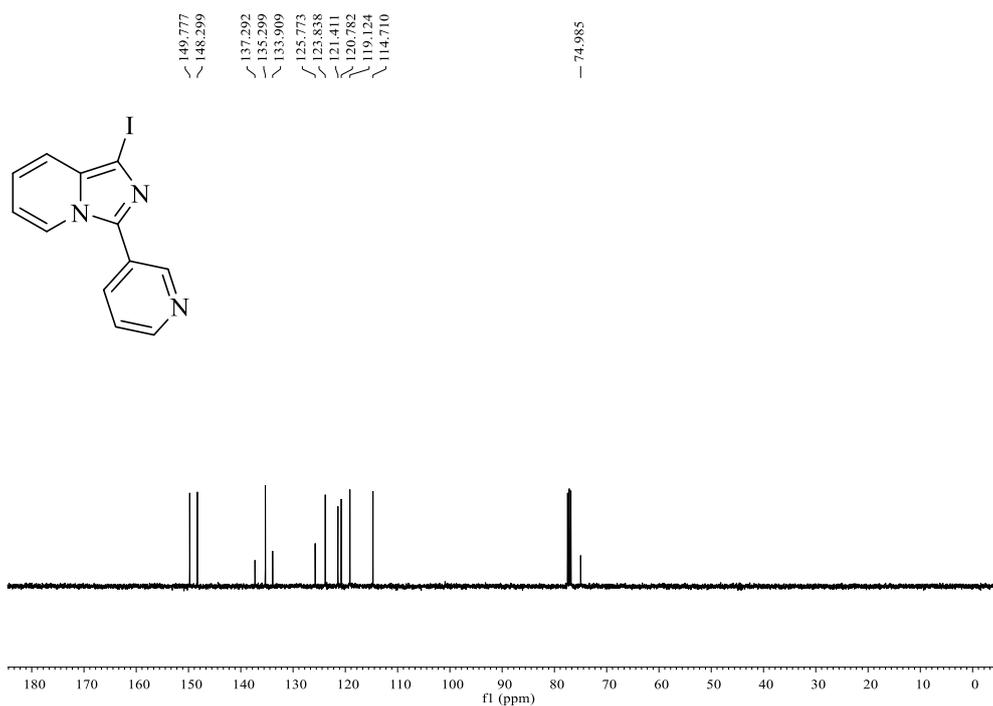
<sup>1</sup>H NMR Spectrum of 3by



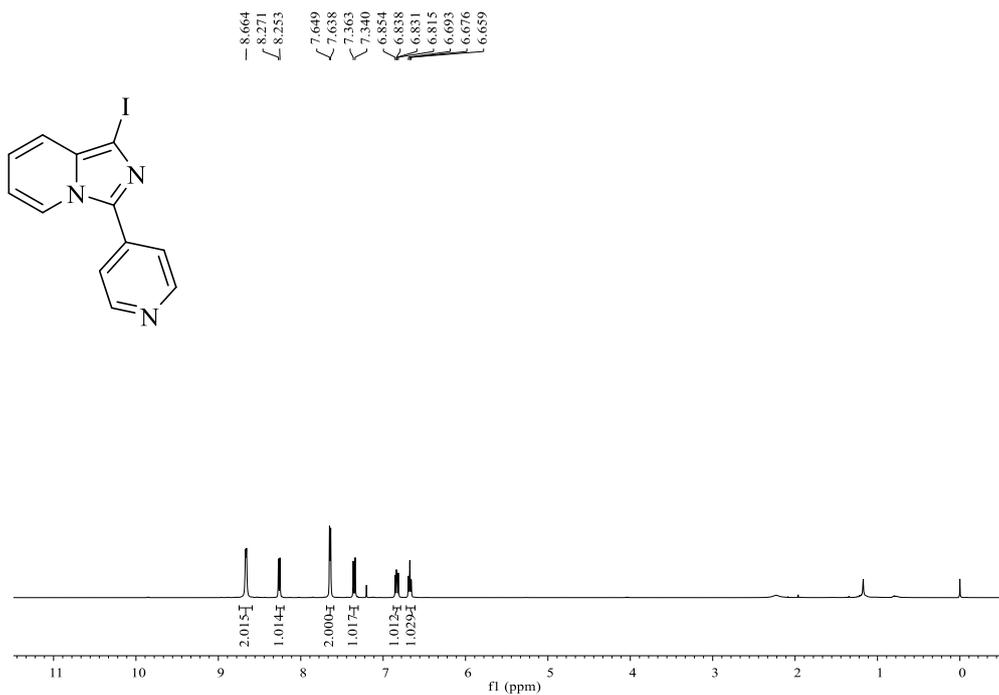
<sup>13</sup>C NMR Spectrum of 3by



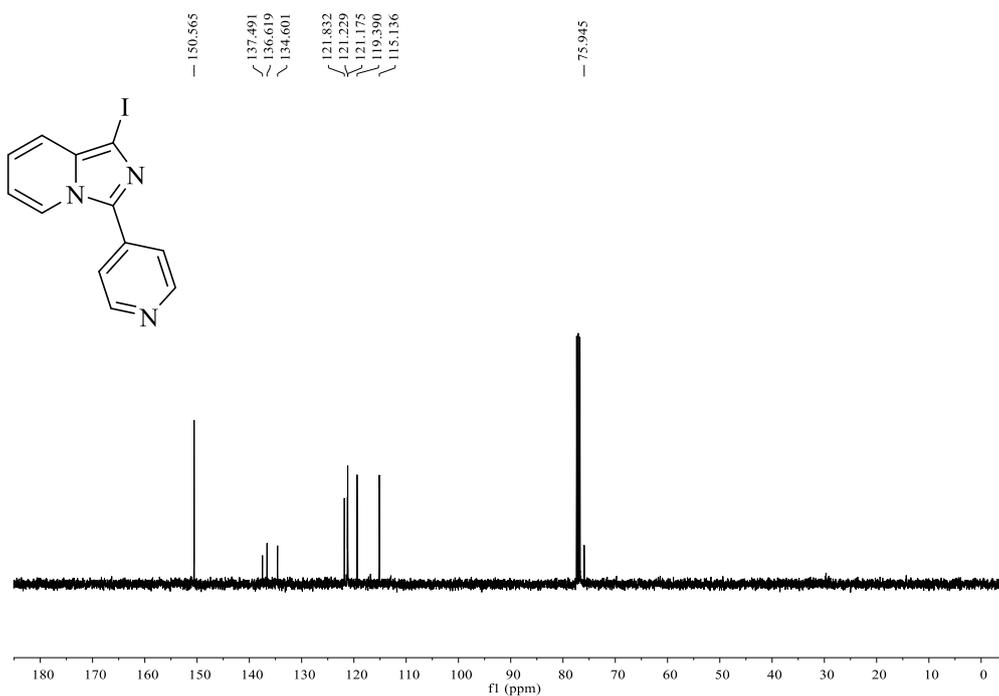
<sup>1</sup>H NMR Spectrum of **3bz**



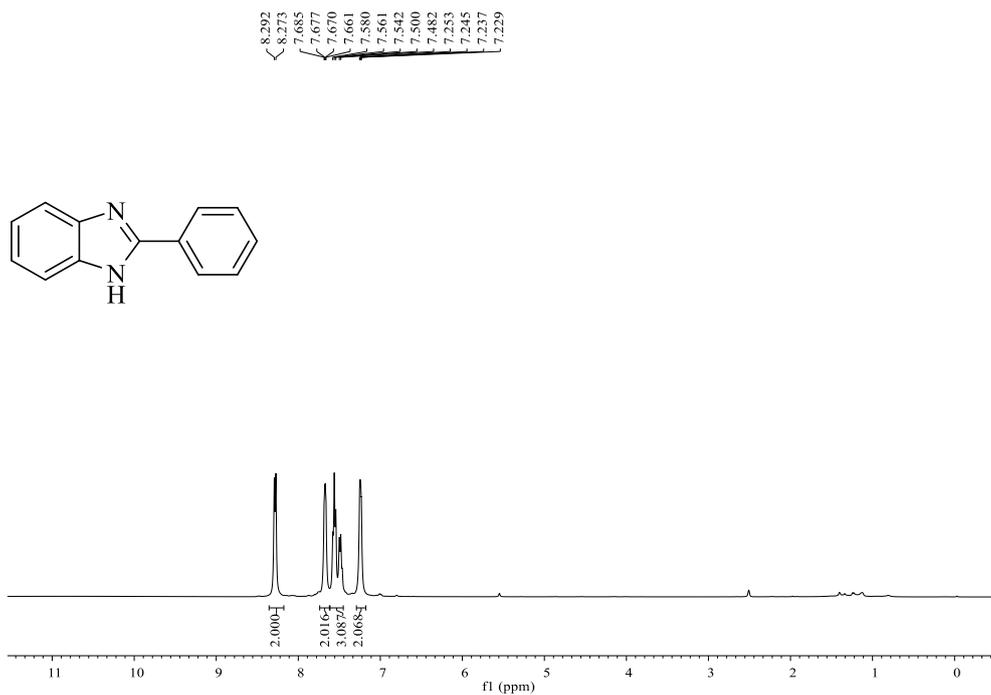
<sup>13</sup>C NMR Spectrum of **3bz**



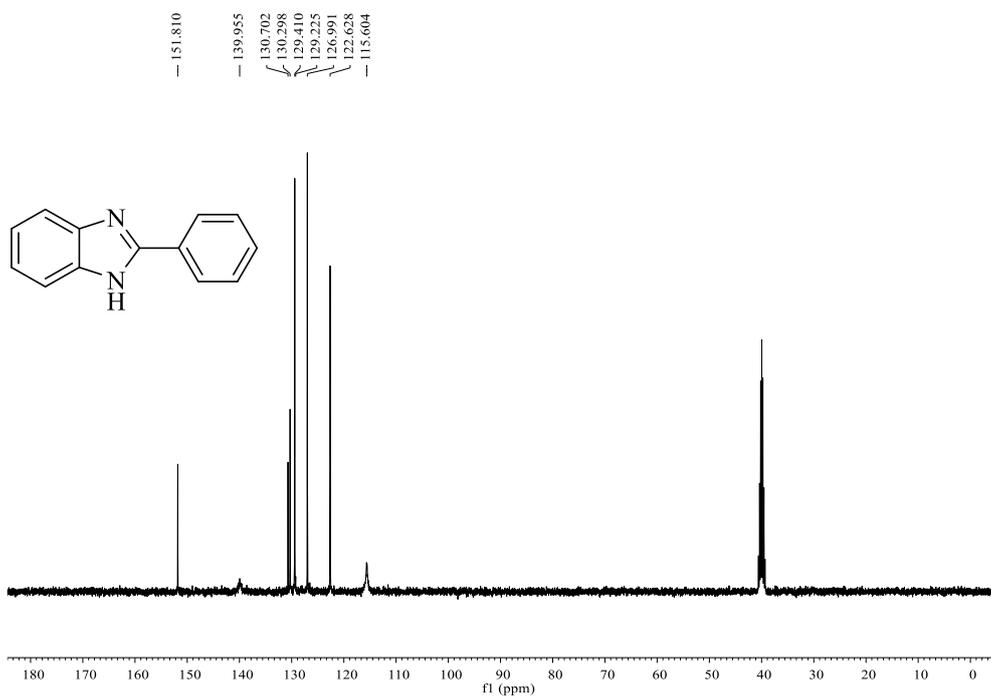
<sup>1</sup>H NMR Spectrum of 3bba



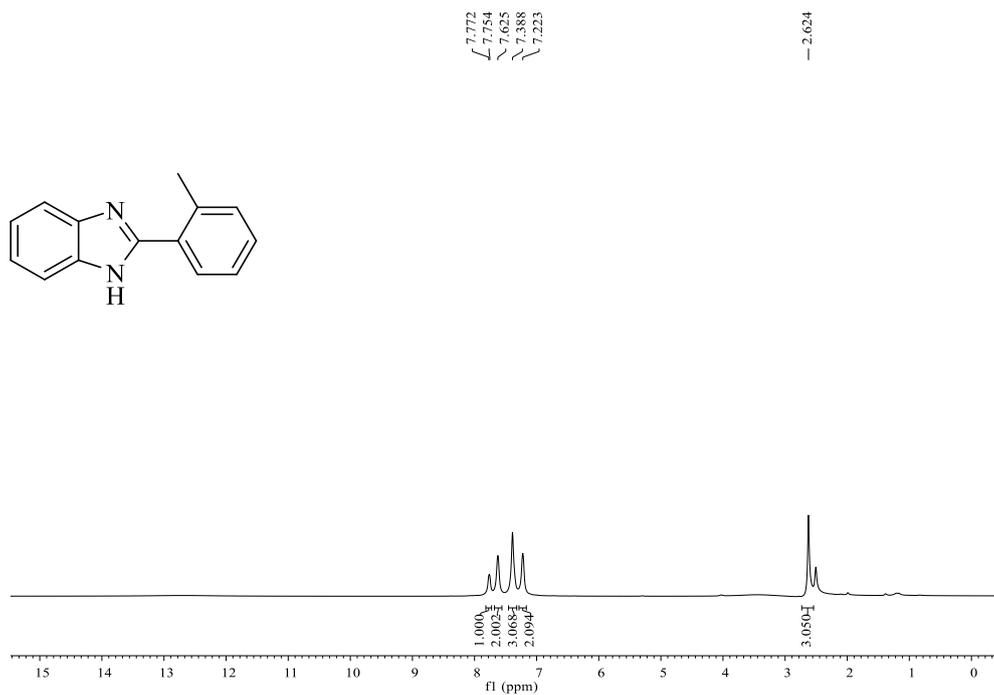
<sup>13</sup>C NMR Spectrum of 3bba



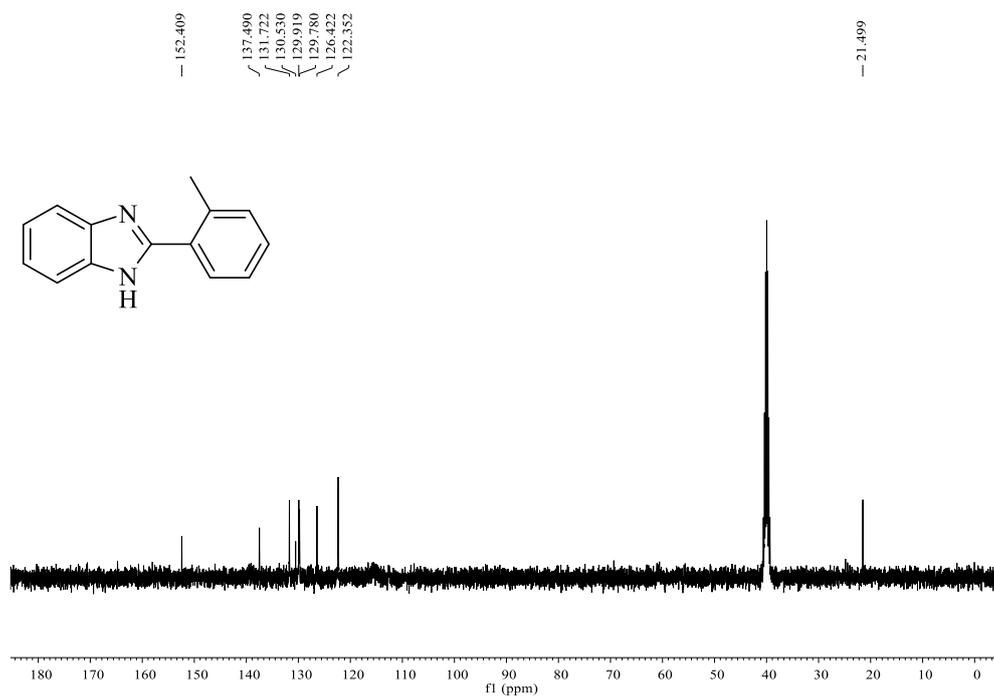
<sup>1</sup>H NMR Spectrum of **3c**



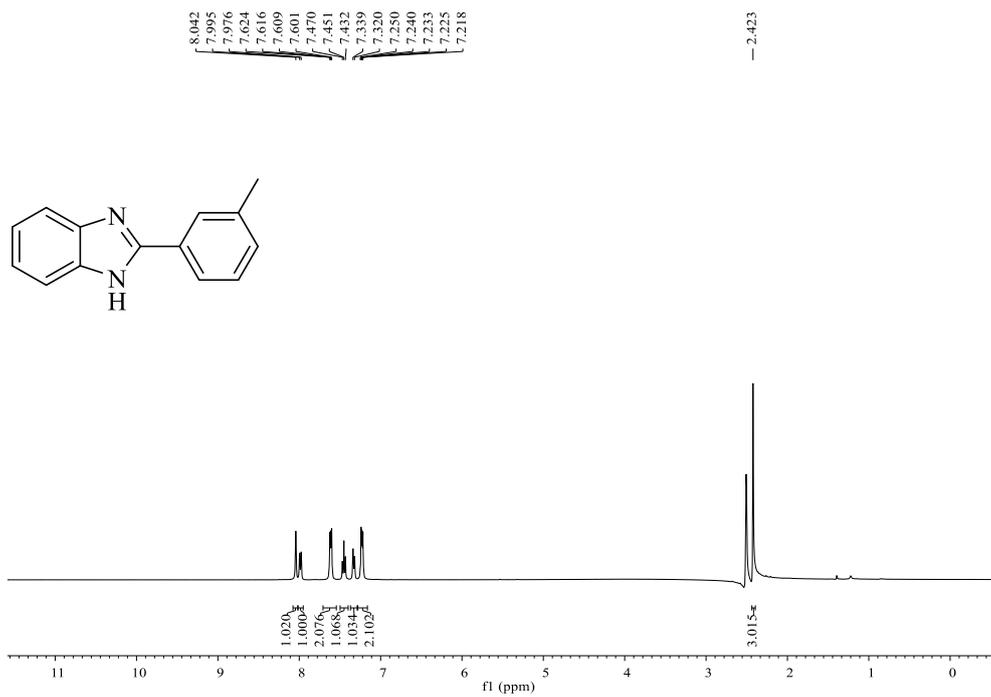
<sup>13</sup>C NMR Spectrum of **3c**



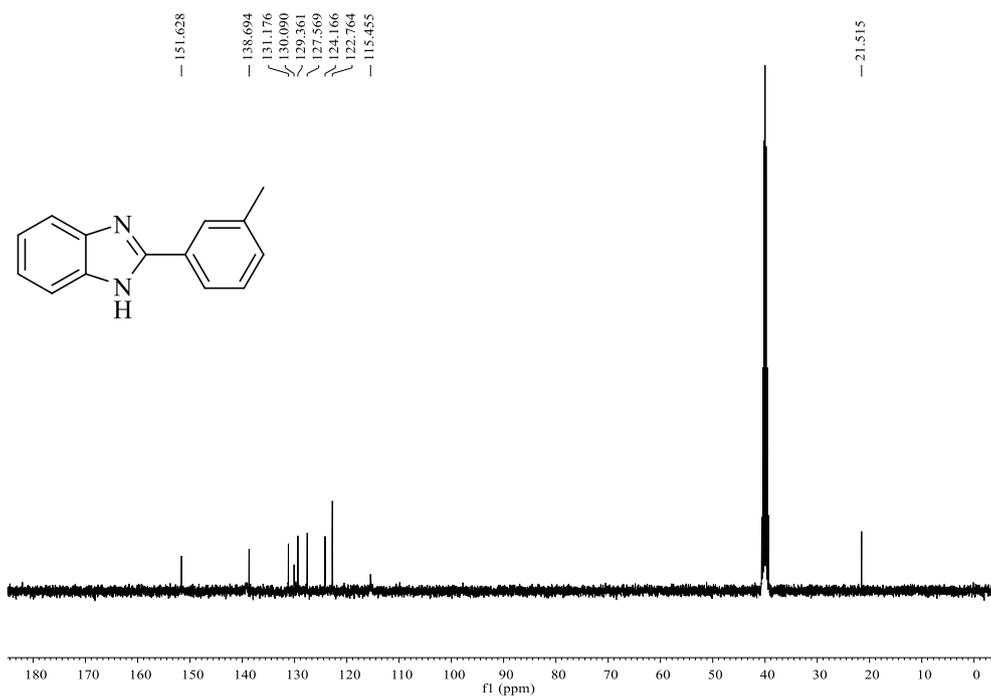
<sup>1</sup>H NMR Spectrum of 3cb



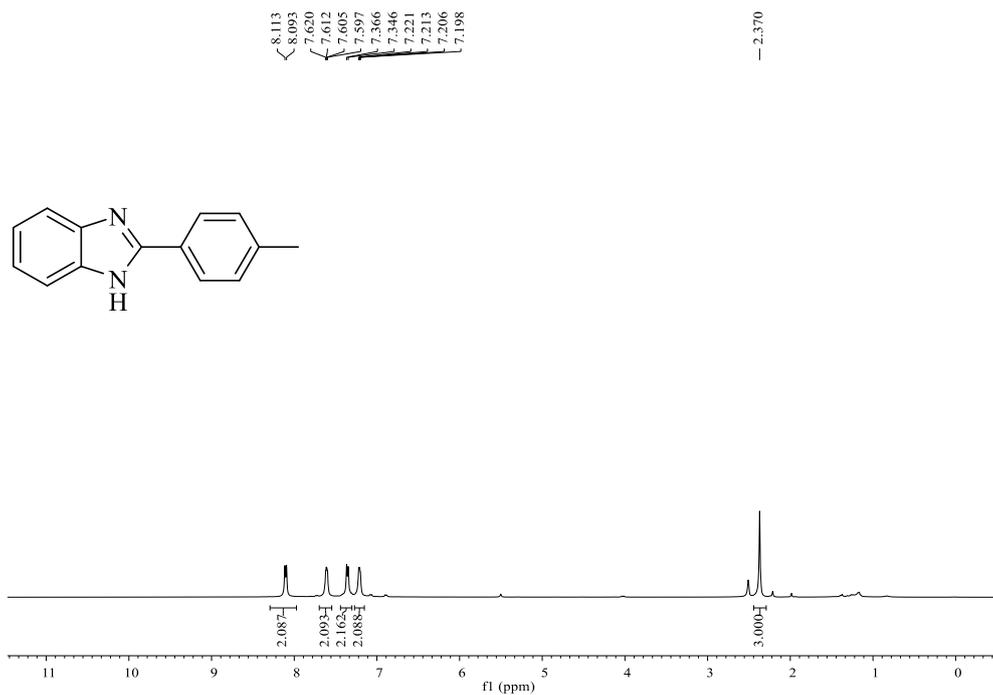
<sup>13</sup>C NMR Spectrum of 3cb



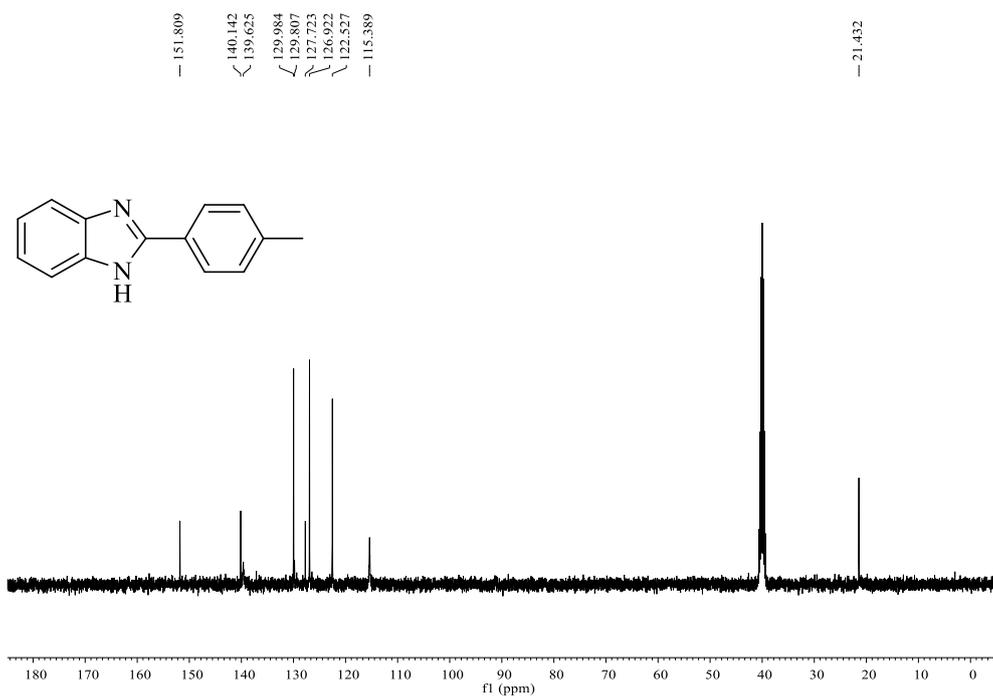
<sup>1</sup>H NMR Spectrum of **3cc**



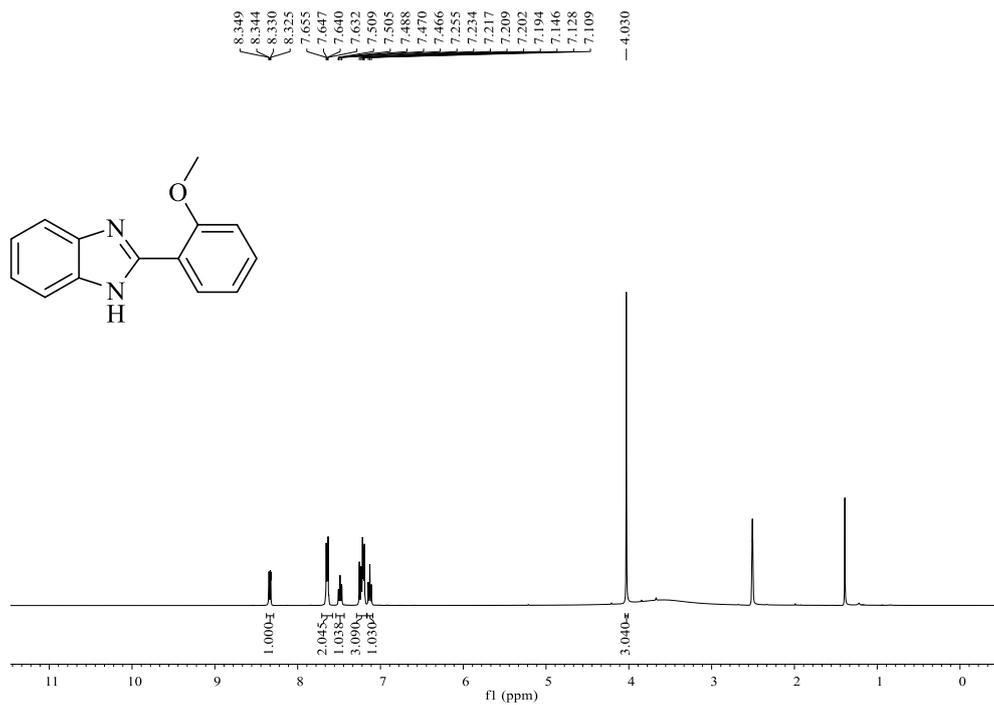
<sup>13</sup>C NMR Spectrum of **3cc**



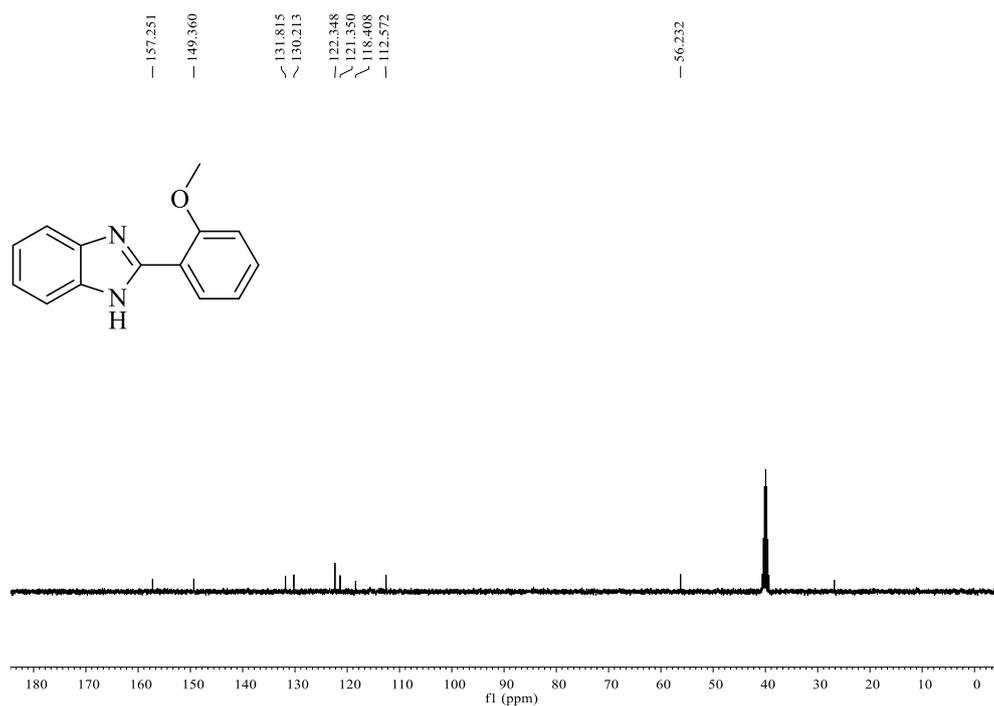
<sup>1</sup>H NMR Spectrum of 3cd



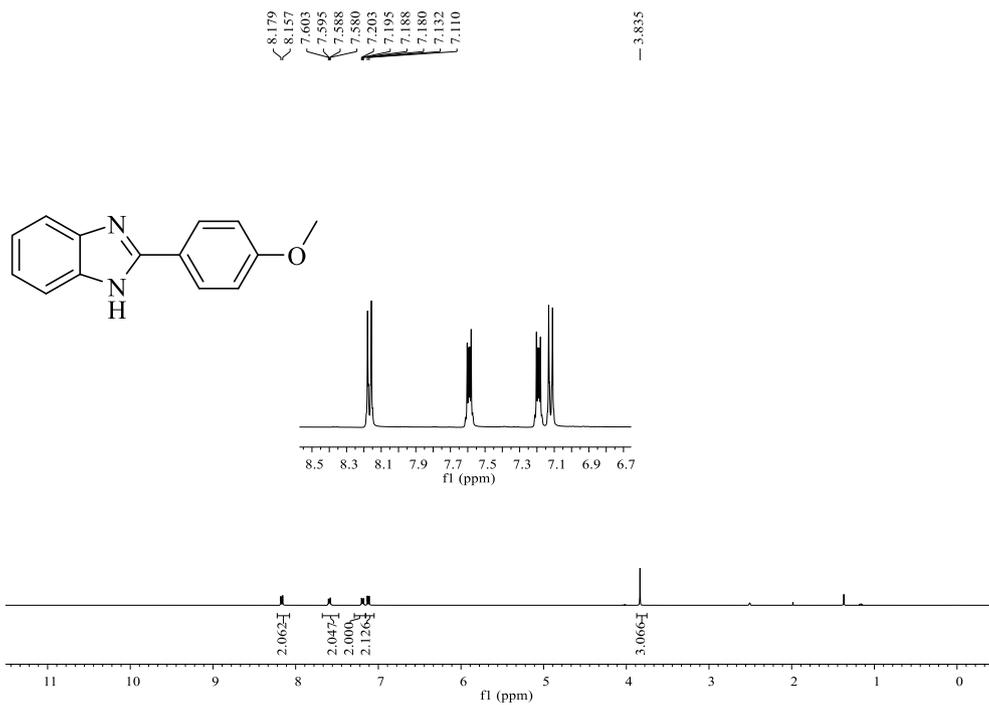
<sup>13</sup>C NMR Spectrum of 3cd



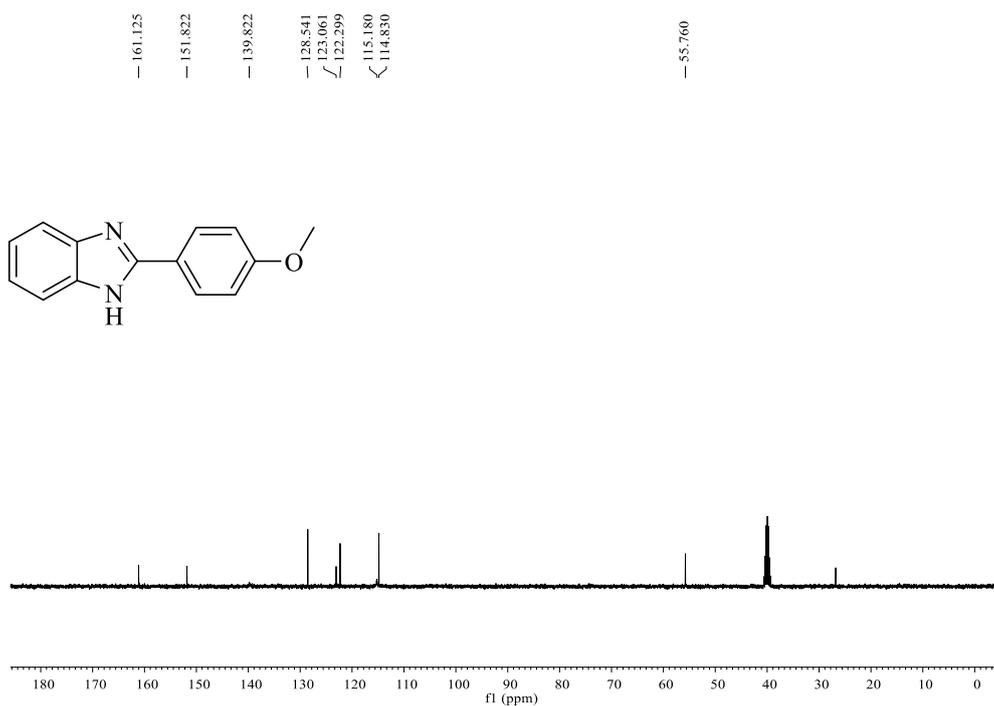
<sup>1</sup>H NMR Spectrum of 3ce



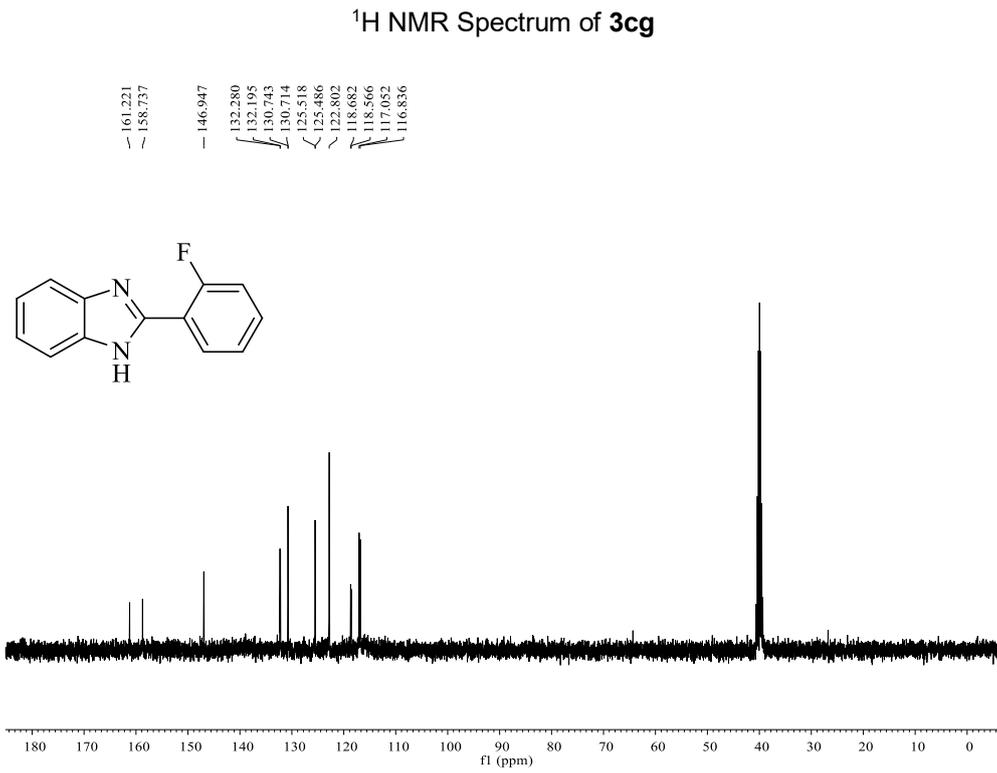
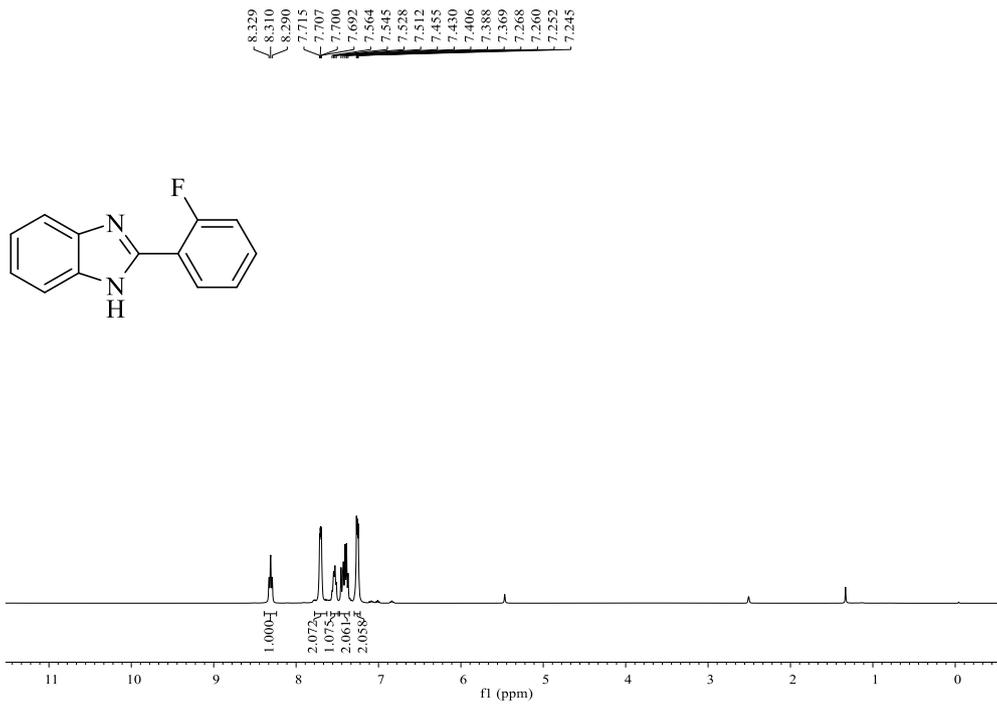
<sup>13</sup>C NMR Spectrum of 3ce

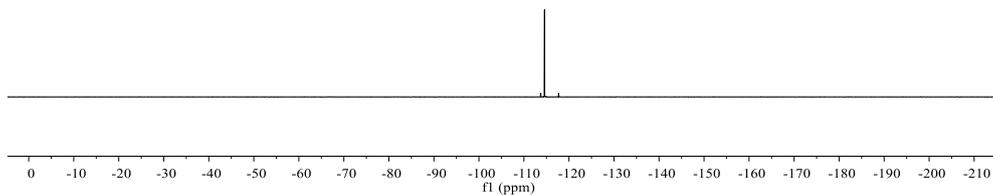
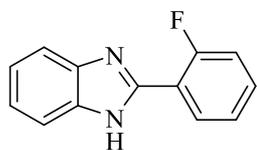


<sup>1</sup>H NMR Spectrum of 3cf



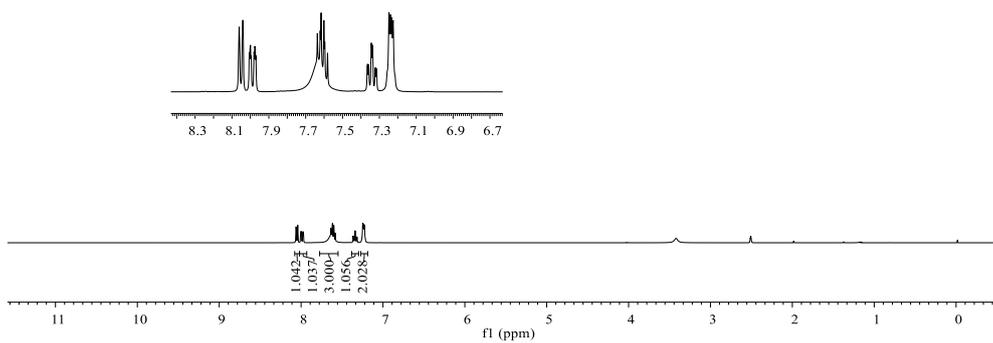
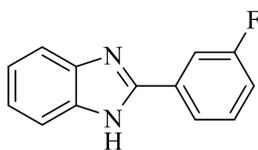
<sup>13</sup>C NMR Spectrum of 3cf



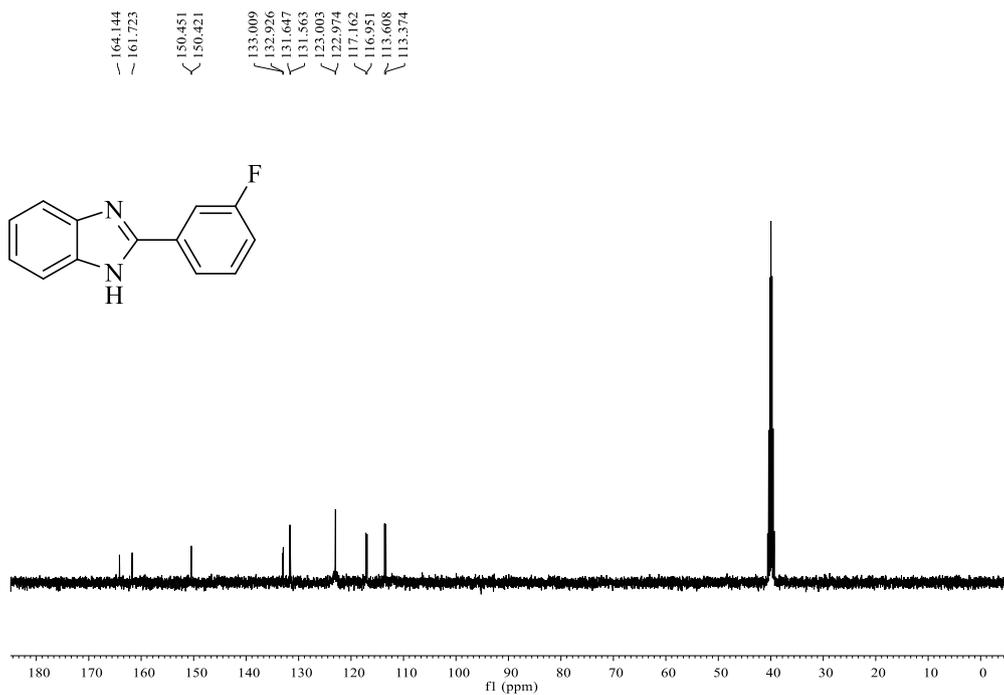


<sup>19</sup>F NMR Spectrum of 3cg

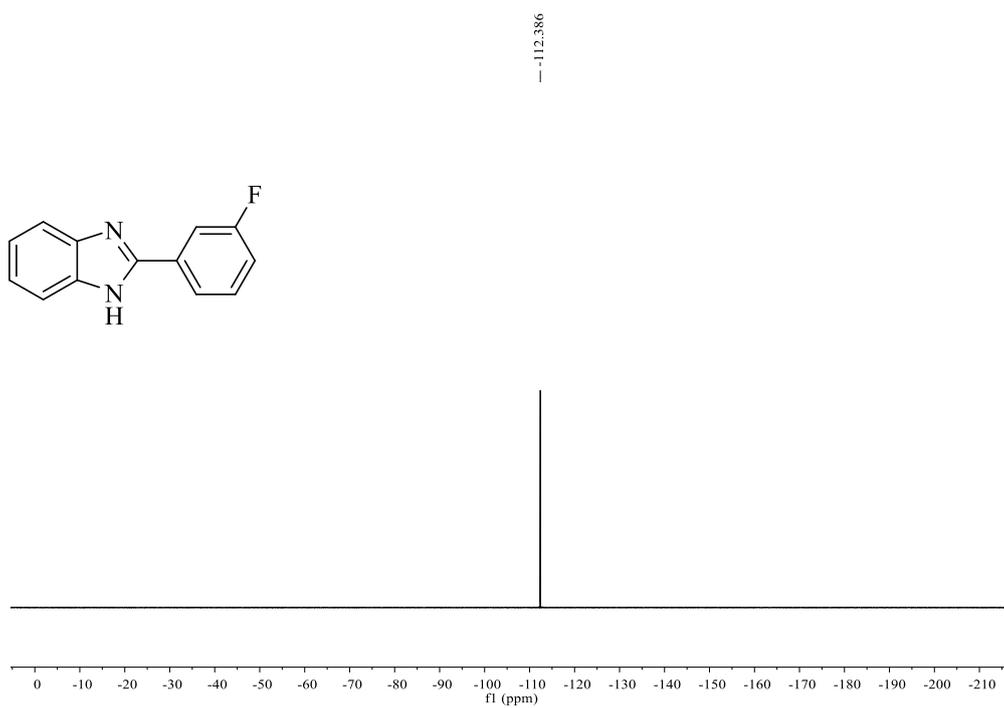
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8.006  
8.001  
7.996  
7.980  
7.975  
7.970  
7.636  
7.619  
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7.581  
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7.344  
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7.323  
7.316  
7.248  
7.240  
7.233  
7.225



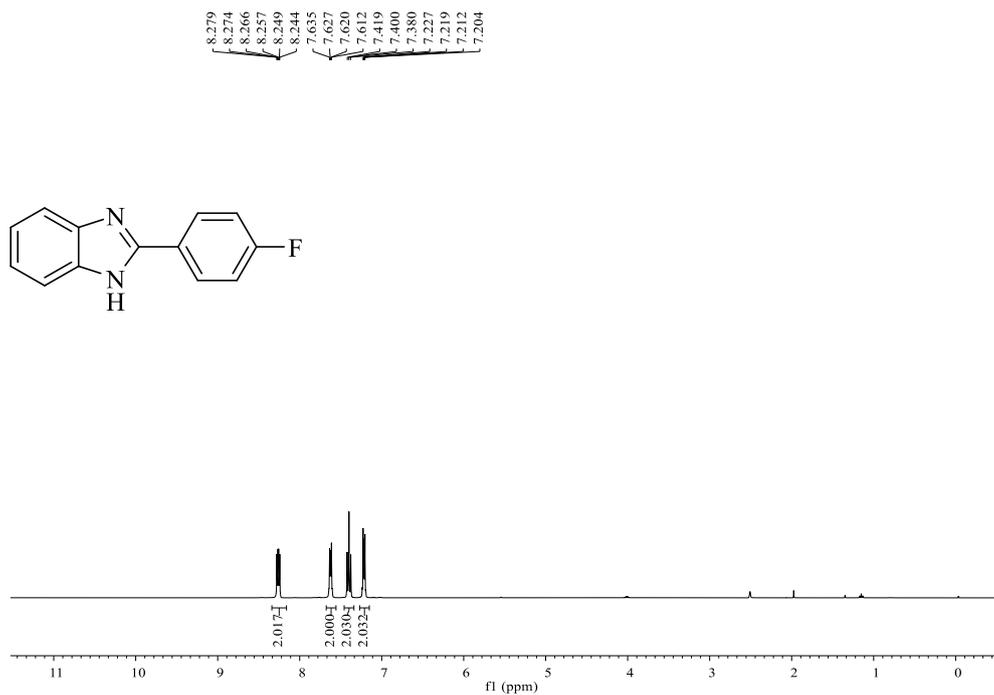
<sup>1</sup>H NMR Spectrum of 3ch



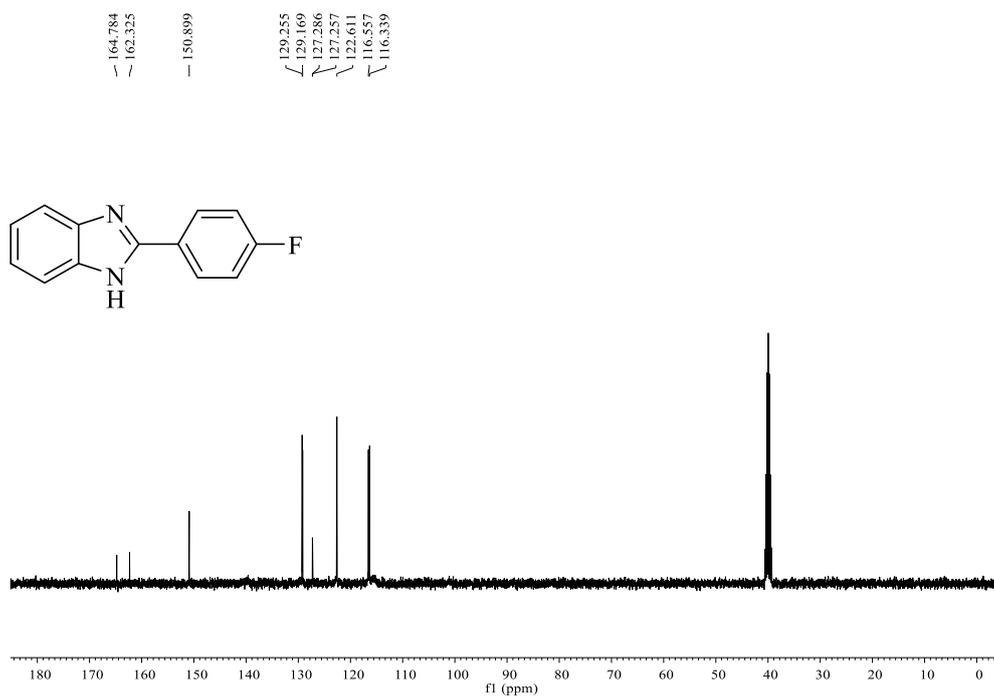
$^{13}\text{C}$  NMR Spectrum of **3ch**



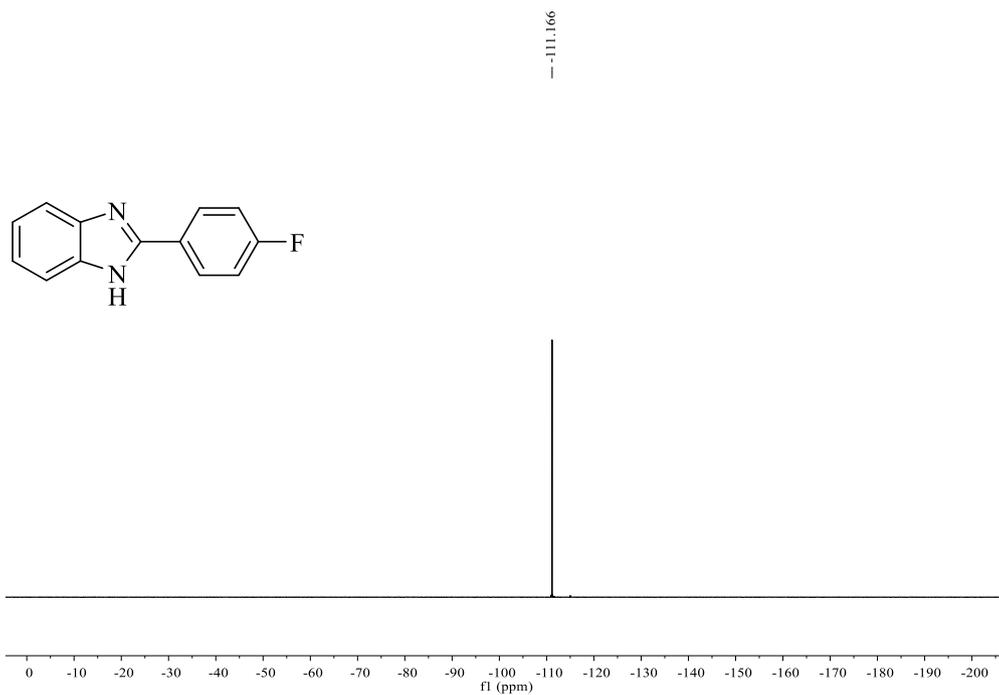
$^{19}\text{F}$  NMR Spectrum of **3ch**



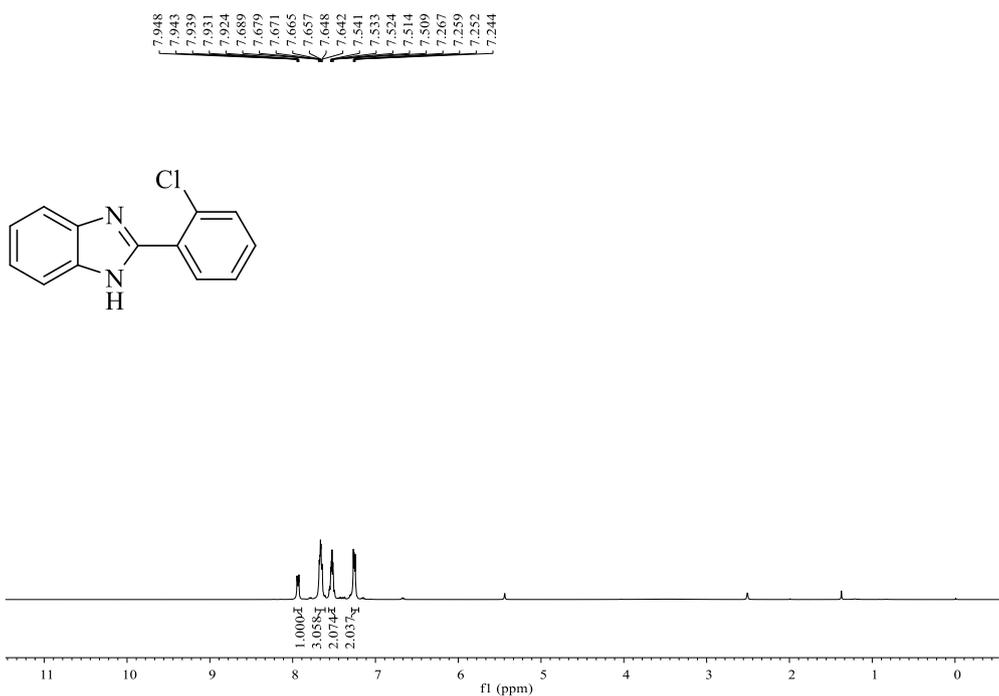
<sup>1</sup>H NMR Spectrum of **3ci**



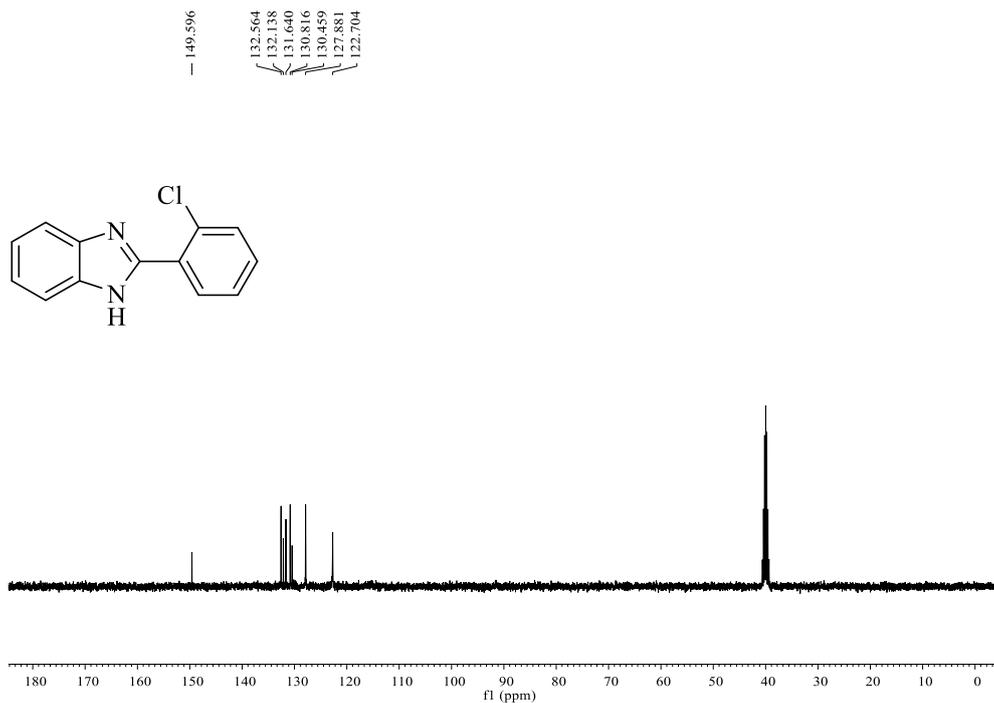
<sup>13</sup>C NMR Spectrum of **3ci**



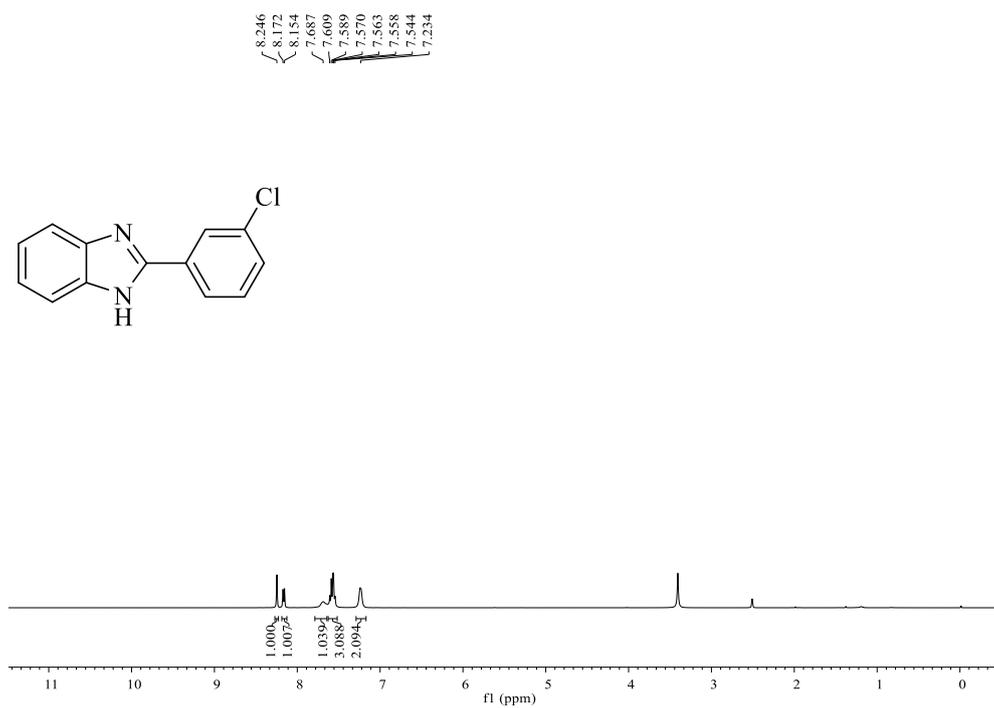
<sup>19</sup>F NMR Spectrum of **3ci**



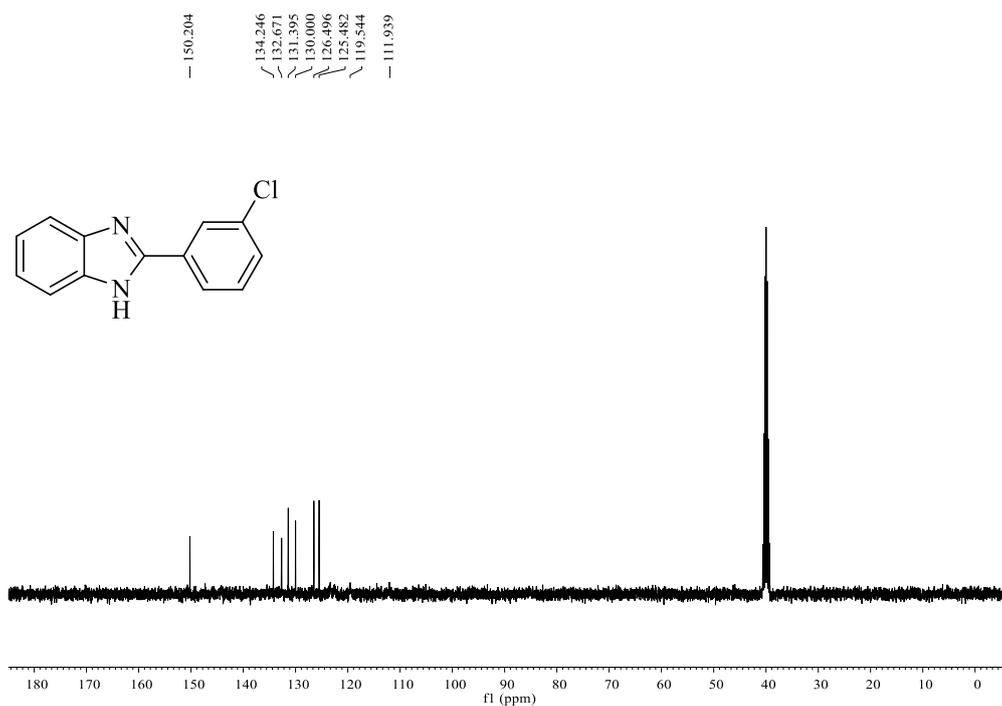
<sup>1</sup>H NMR Spectrum of **3cj**



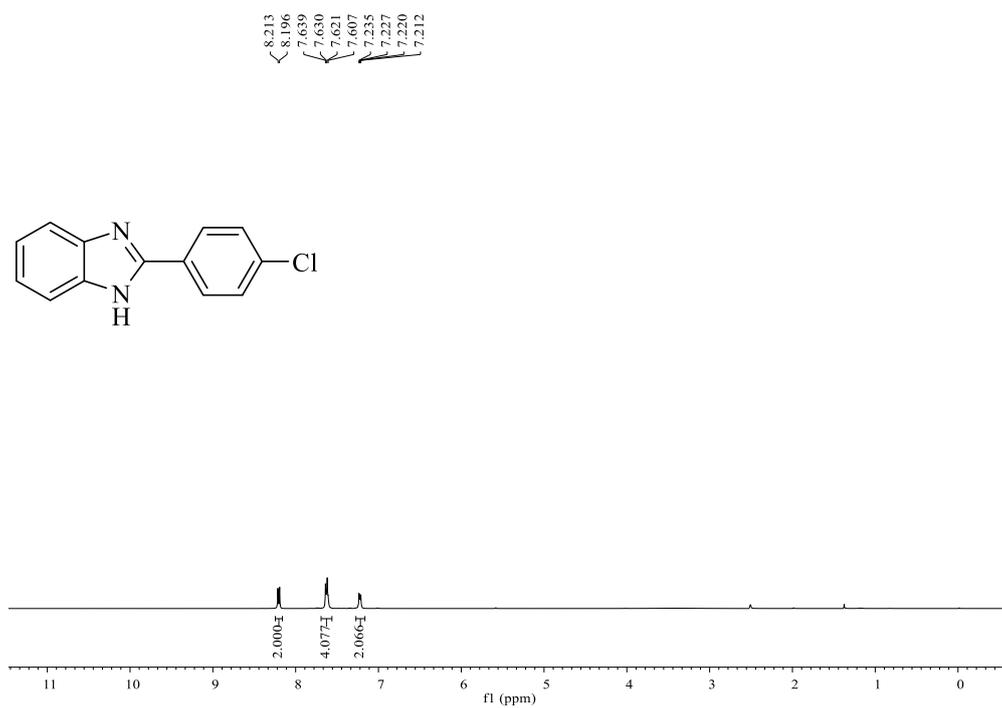
<sup>13</sup>C NMR Spectrum of 3c



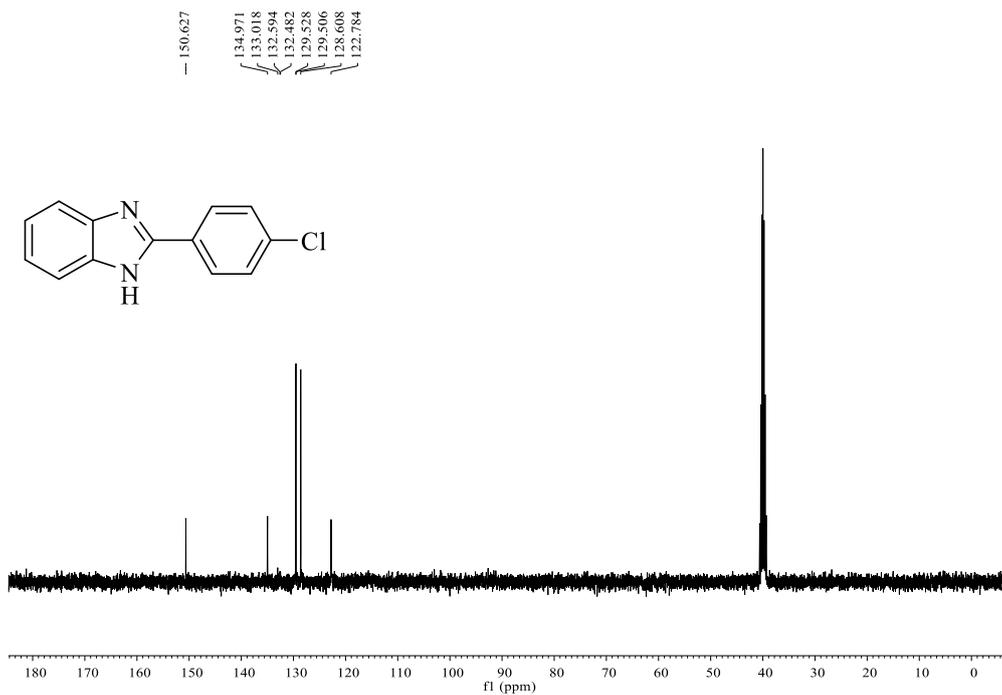
<sup>1</sup>H NMR Spectrum of 3k



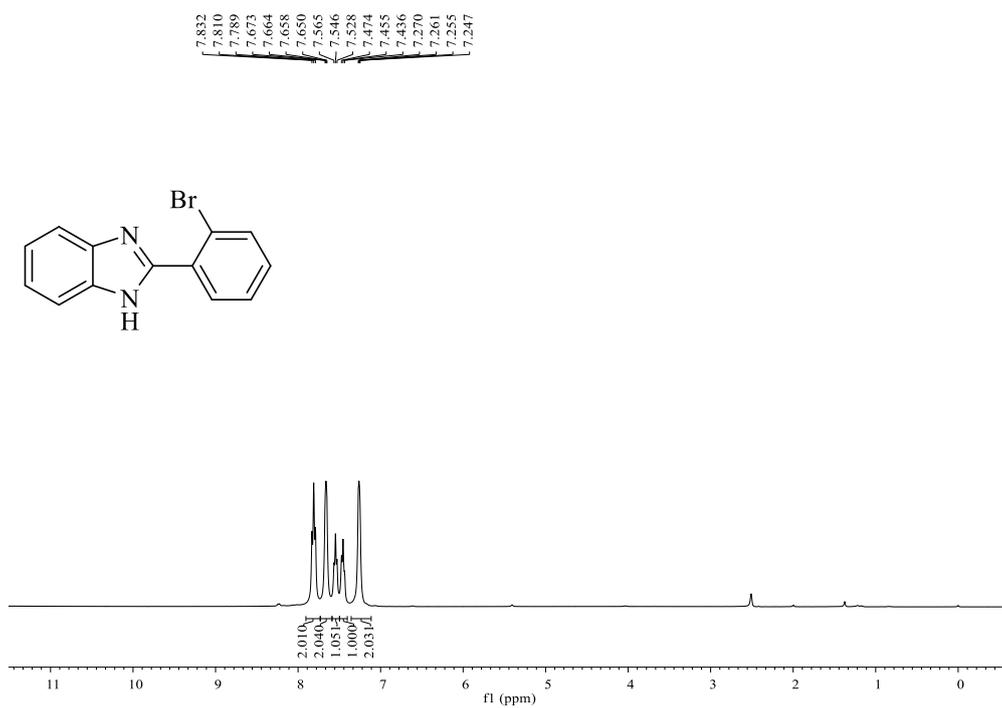
<sup>13</sup>C NMR Spectrum of 3ck



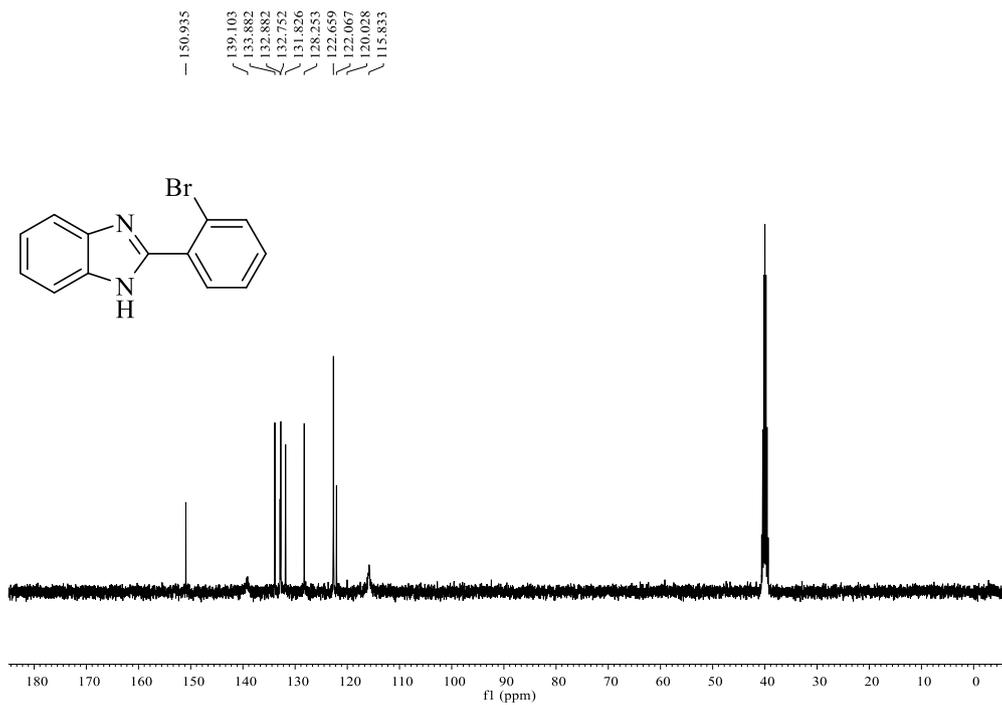
<sup>1</sup>H NMR Spectrum of 3ck



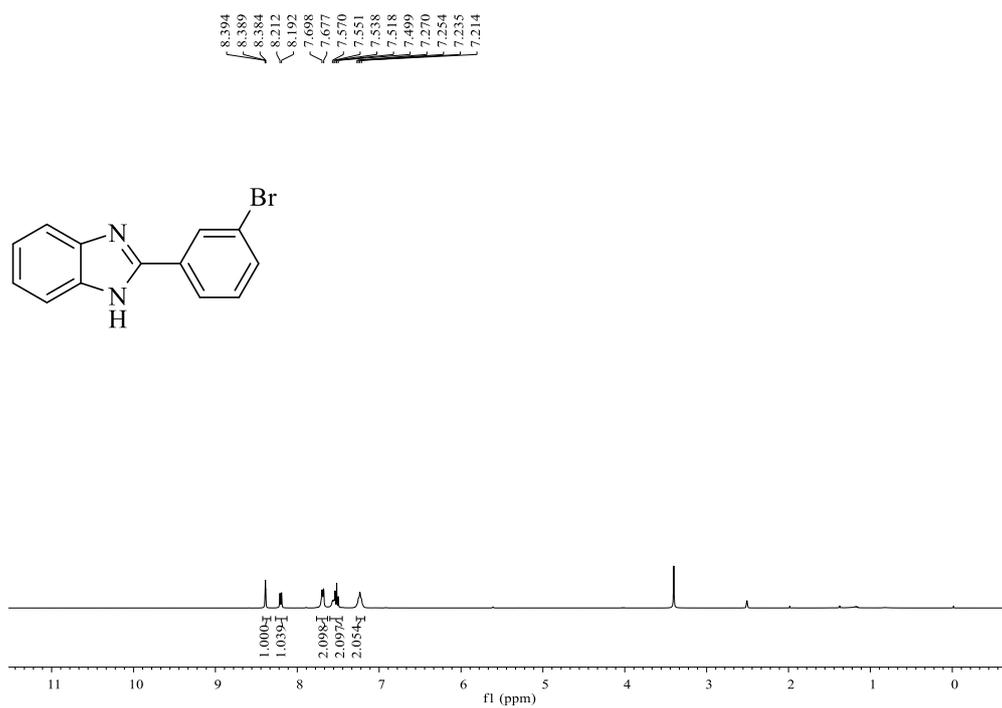
<sup>13</sup>C NMR Spectrum of 3c1



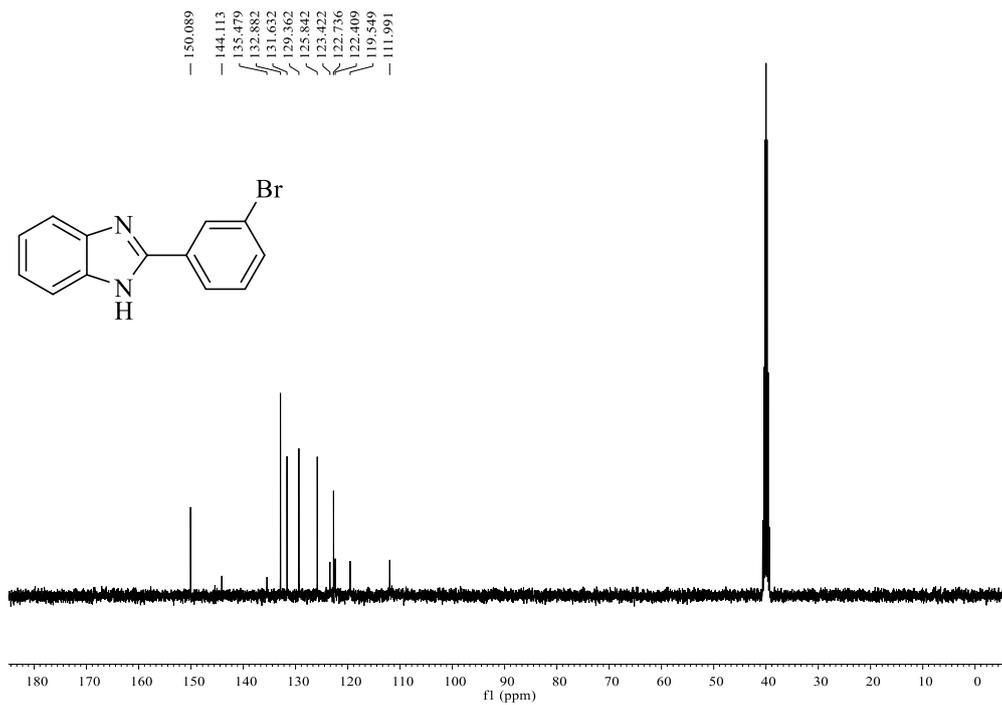
<sup>1</sup>H NMR Spectrum of 3cm



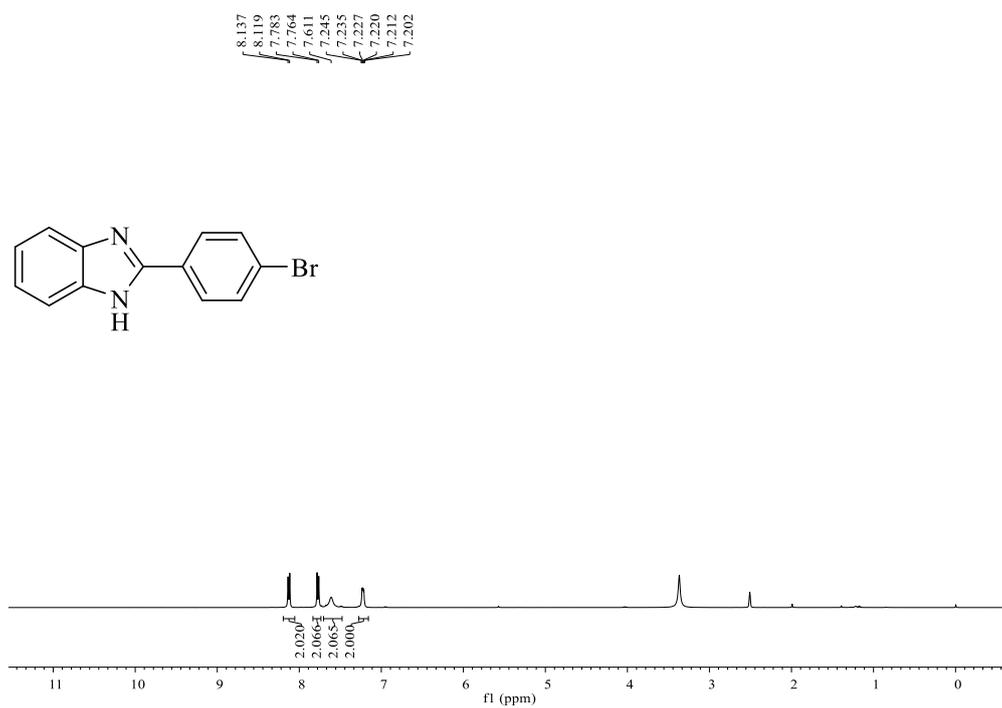
<sup>13</sup>C NMR Spectrum of **3cm**



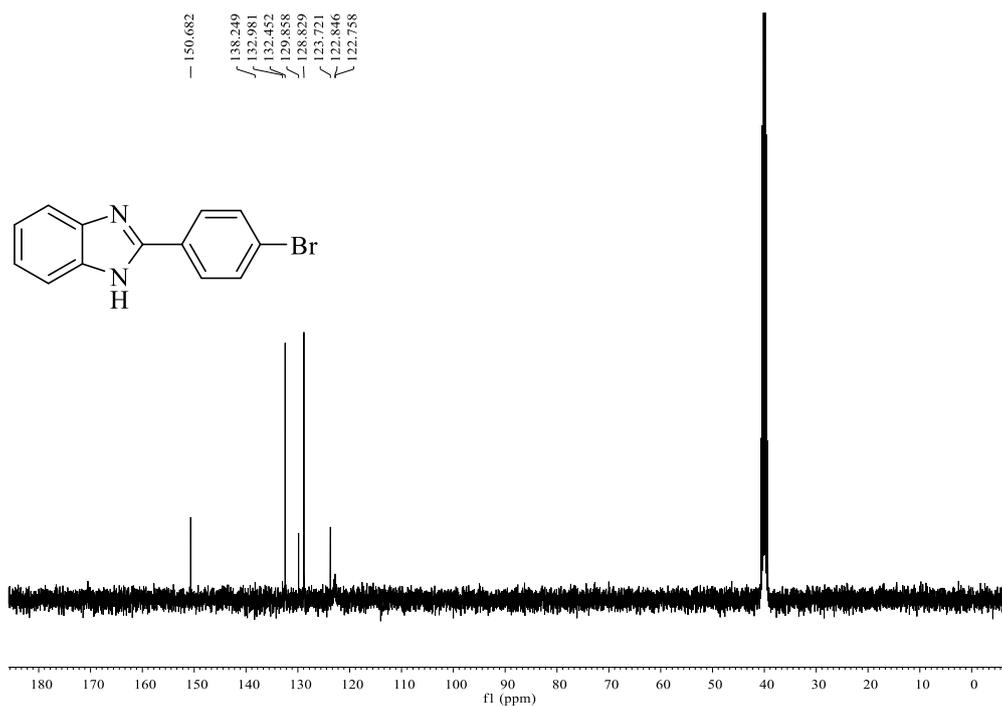
<sup>1</sup>H NMR Spectrum of **3cn**



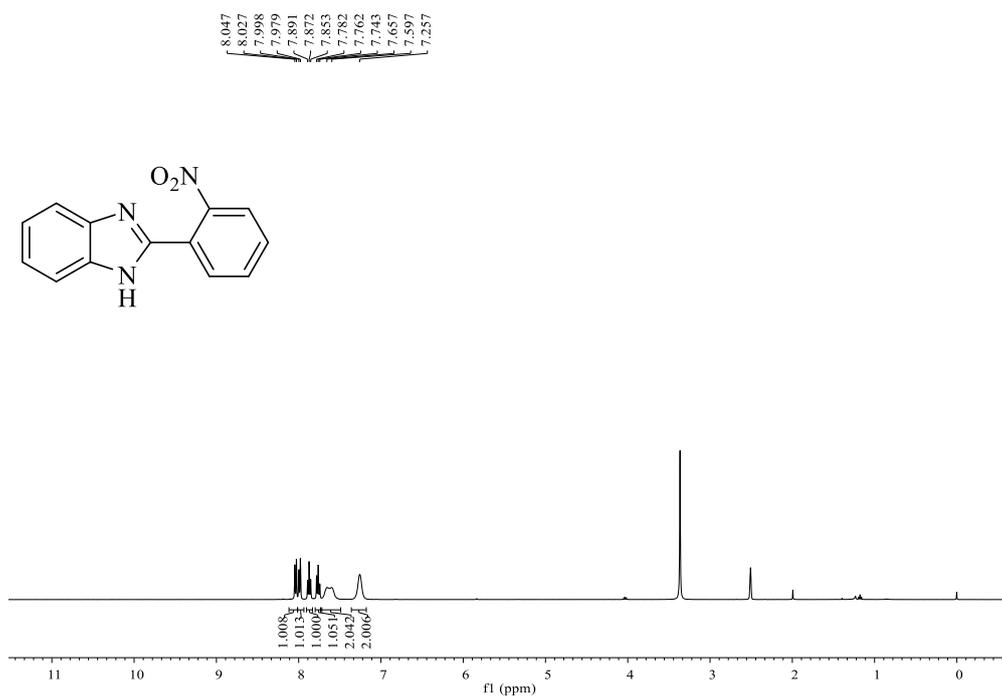
<sup>13</sup>C NMR Spectrum of 3cn



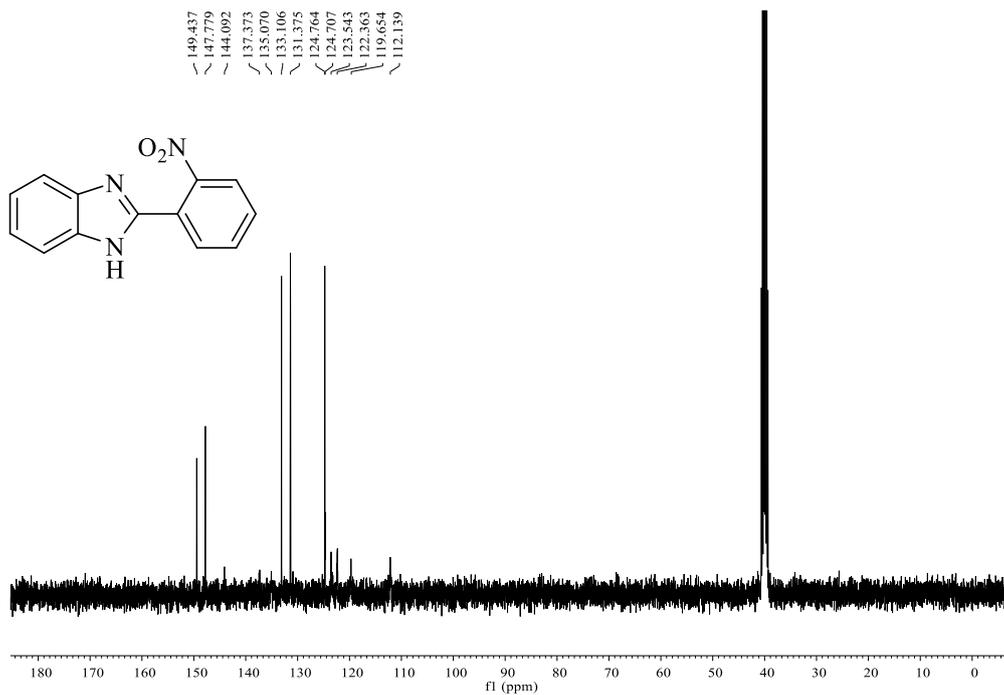
<sup>1</sup>H NMR Spectrum of 3co



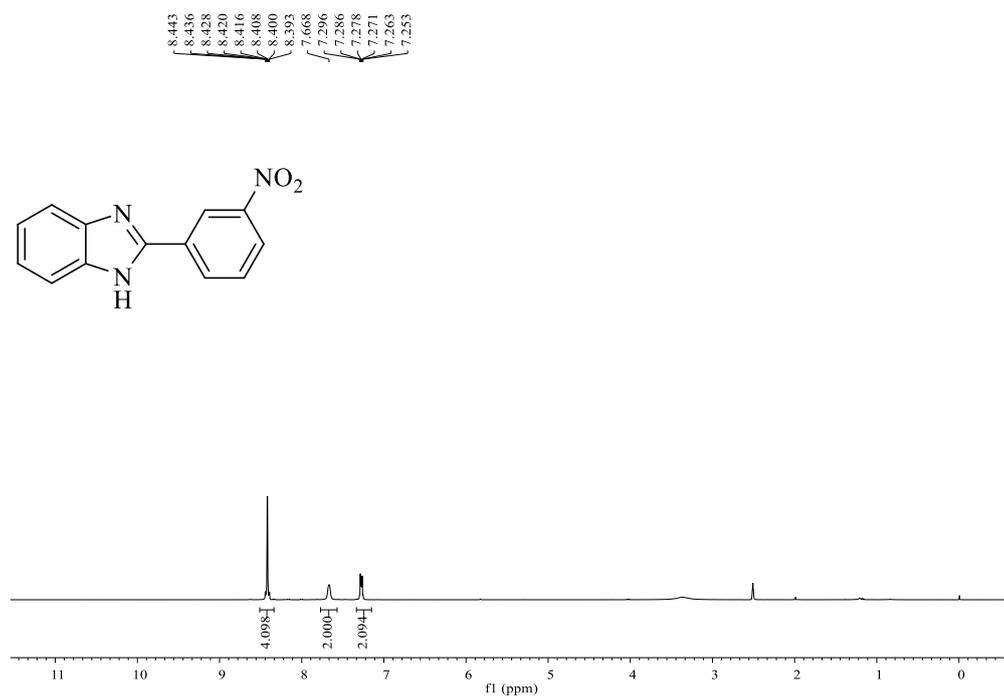
$^{13}\text{C}$  NMR Spectrum of 3co



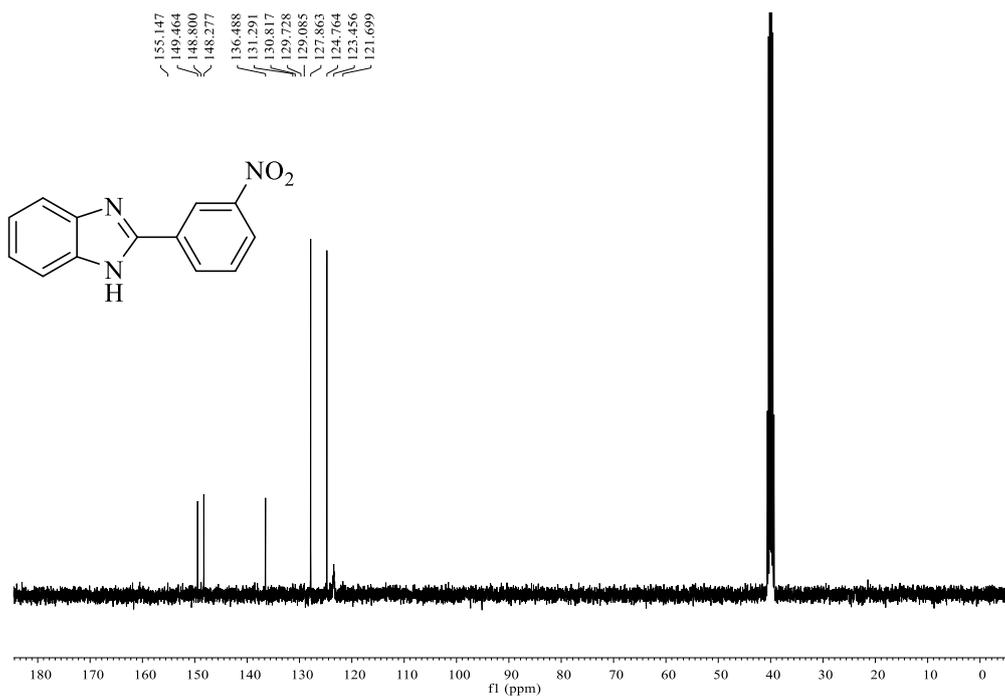
$^1\text{H}$  NMR Spectrum of 3cp



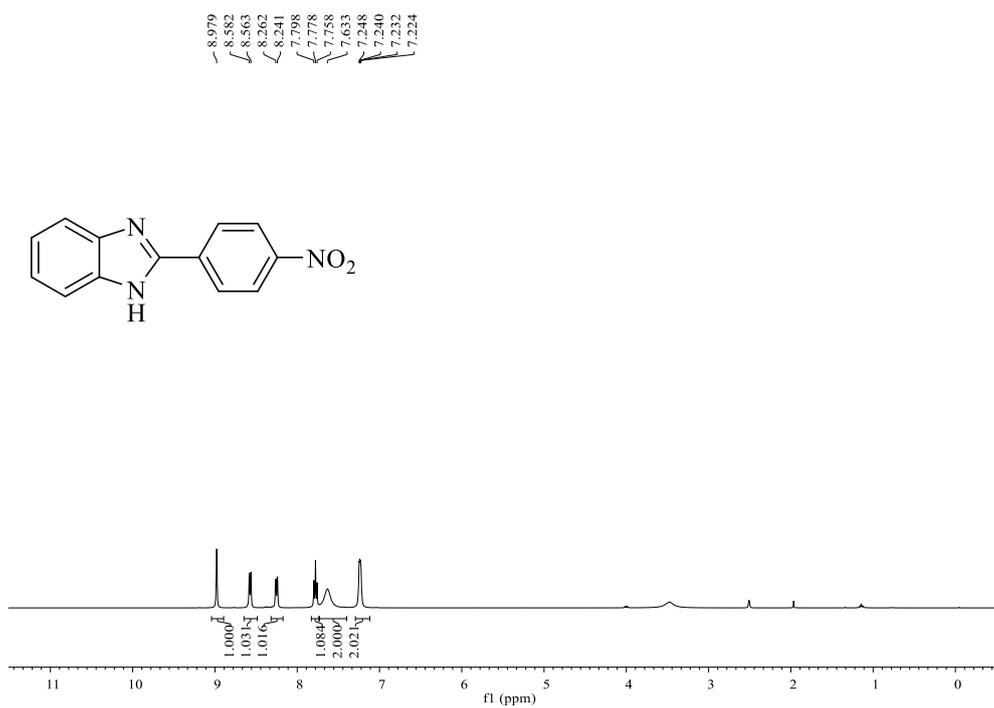
$^{13}\text{C}$  NMR Spectrum of **3cp**



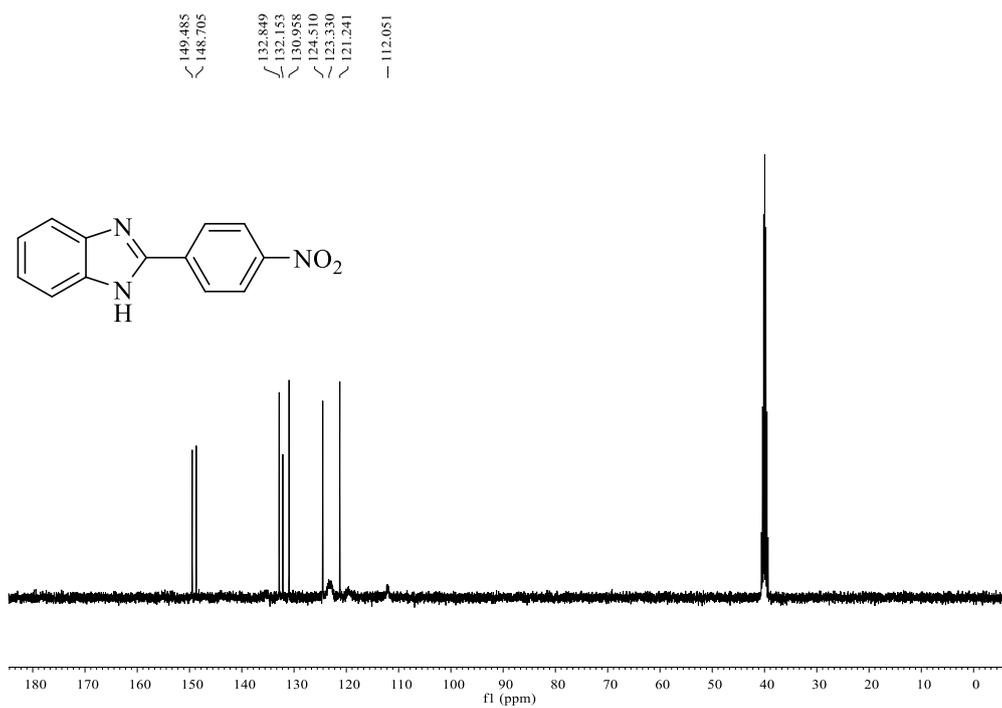
$^1\text{H}$  NMR Spectrum of **3cq**



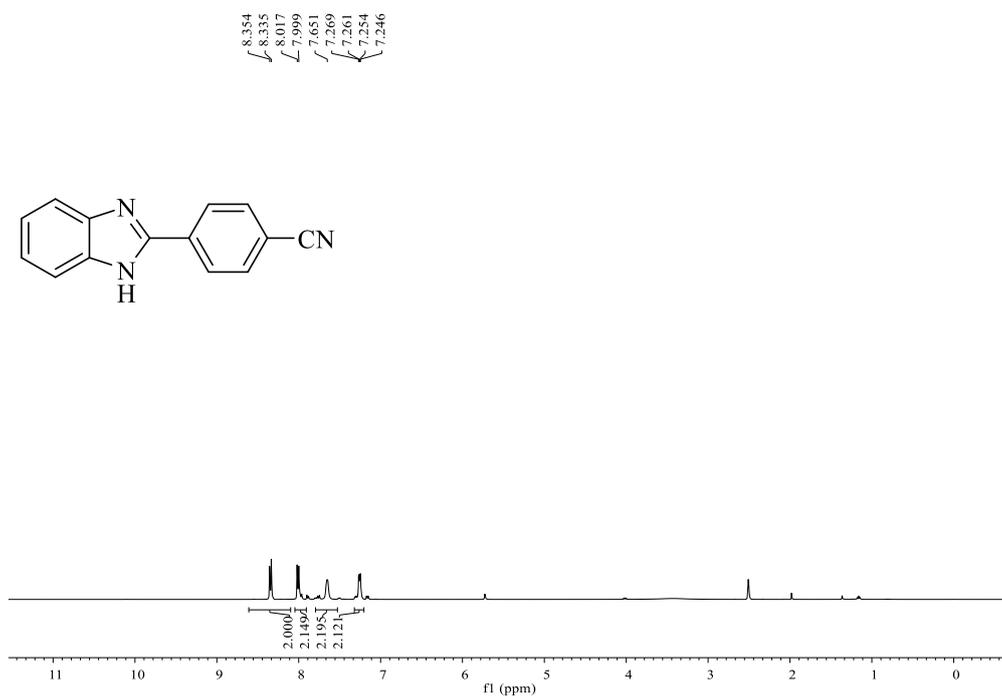
<sup>13</sup>C NMR Spectrum of **3cq**



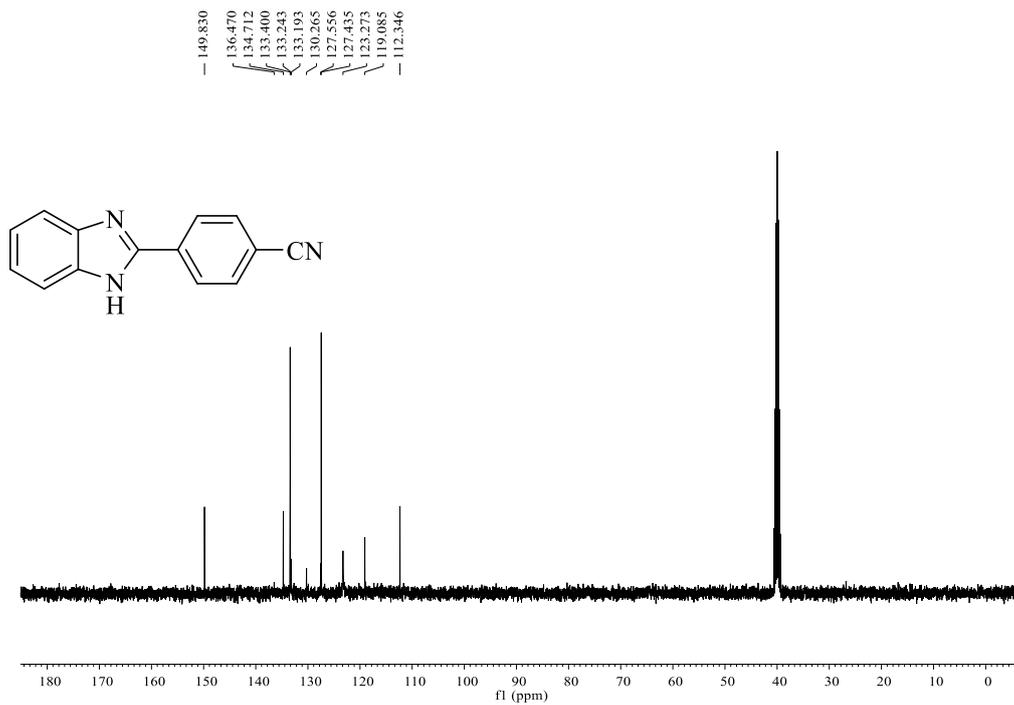
<sup>1</sup>H NMR Spectrum of **3cr**



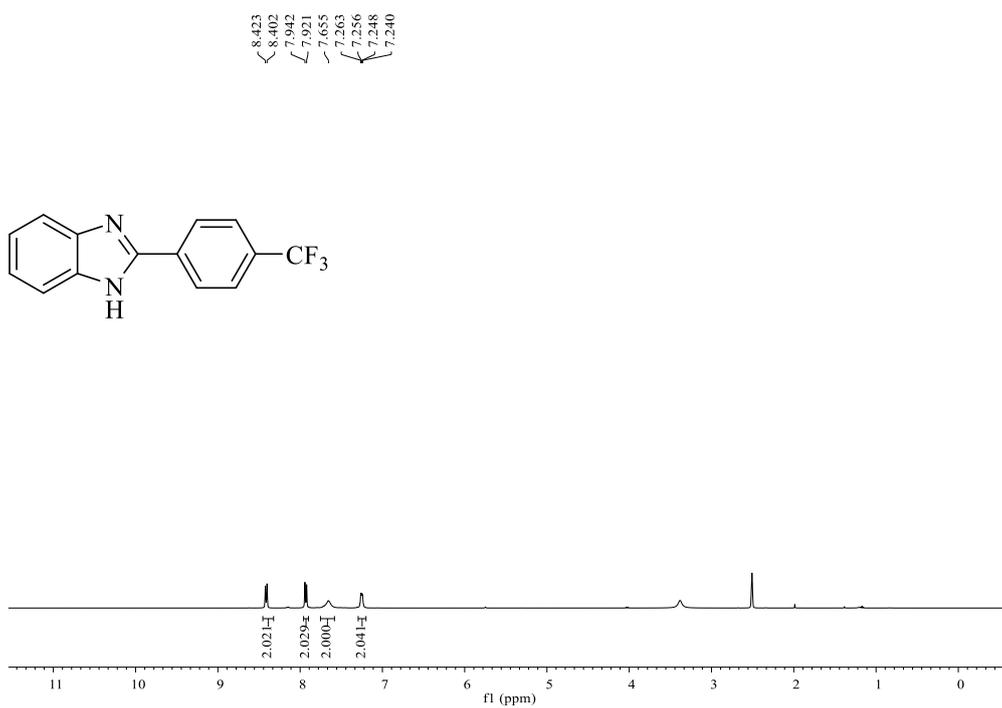
<sup>13</sup>C NMR Spectrum of **3c**



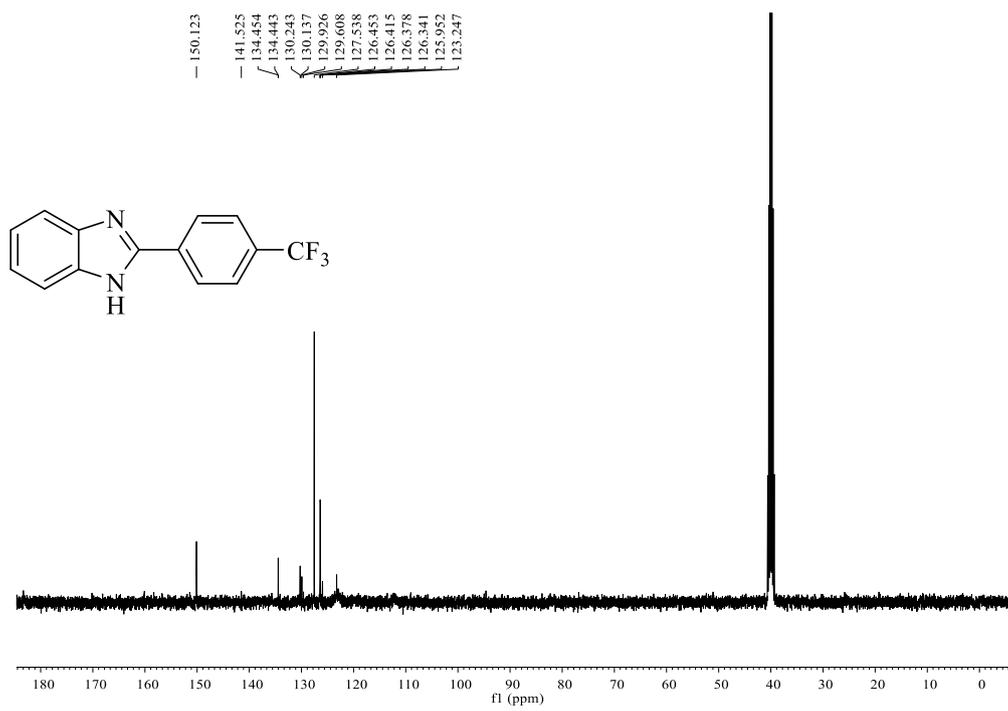
<sup>1</sup>H NMR Spectrum of **3cs**



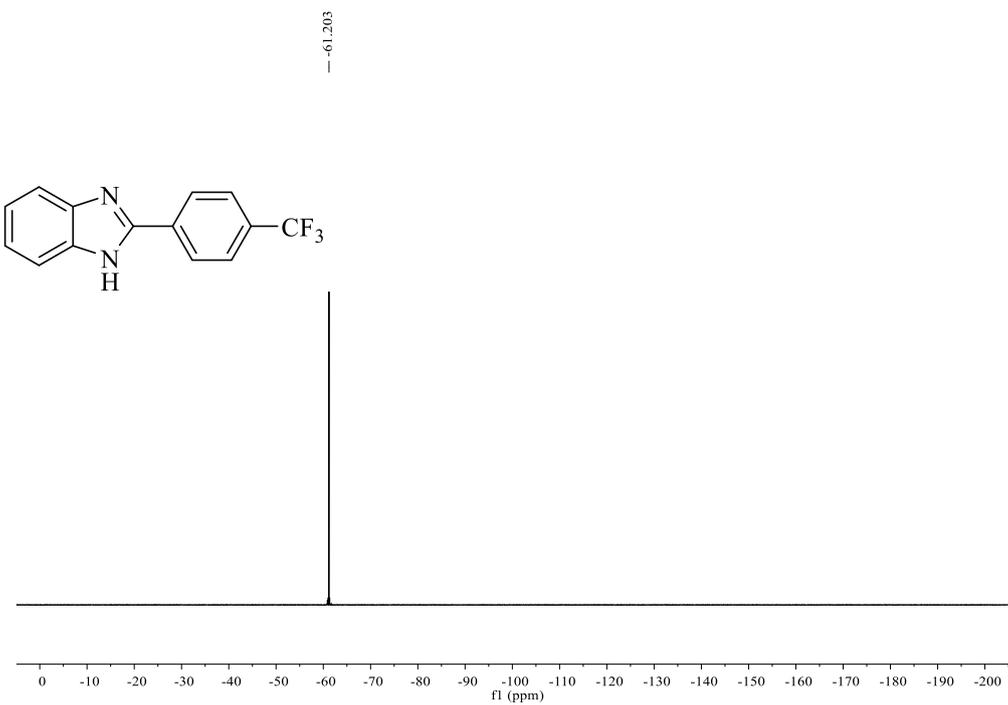
<sup>13</sup>C NMR Spectrum of 3c



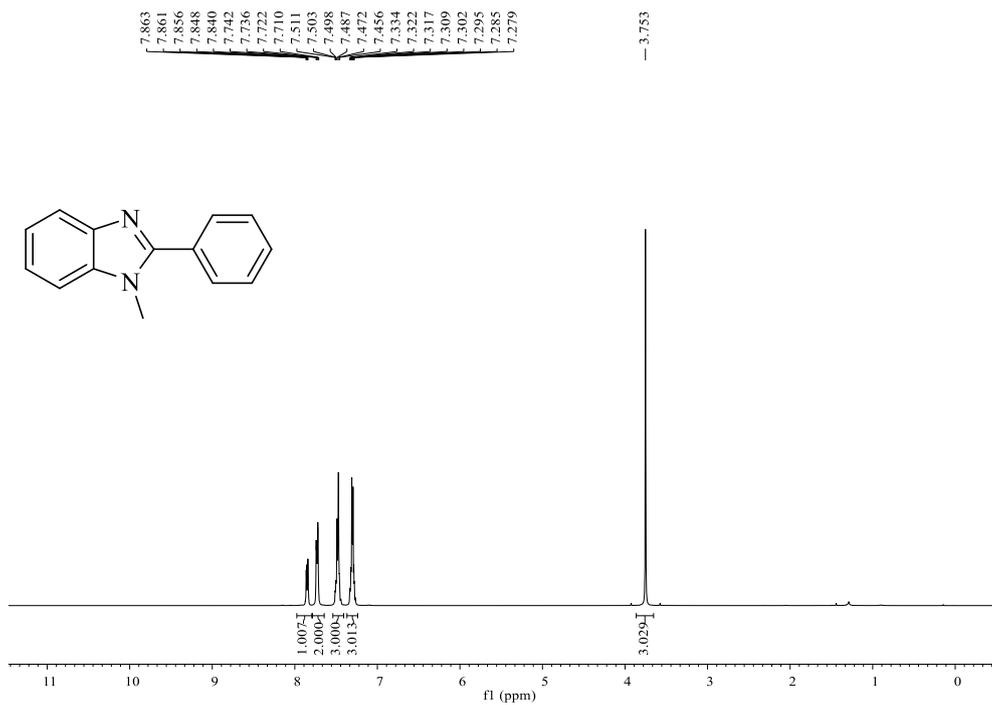
<sup>1</sup>H NMR Spectrum of 3ct



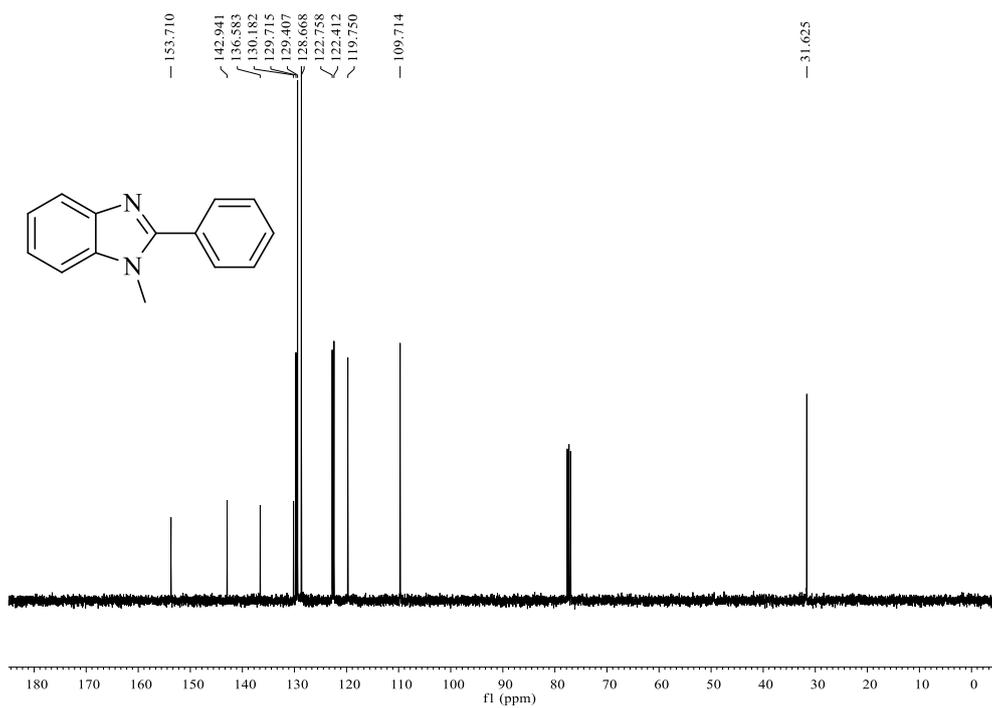
<sup>13</sup>C NMR Spectrum of **3ct**



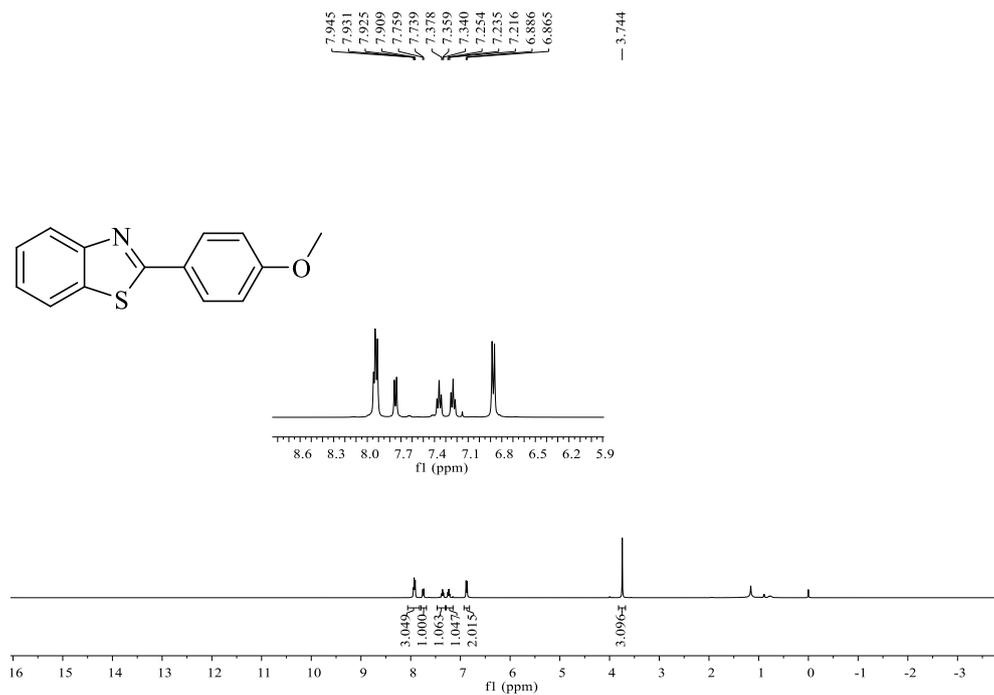
<sup>19</sup>F NMR Spectrum of **3ct**



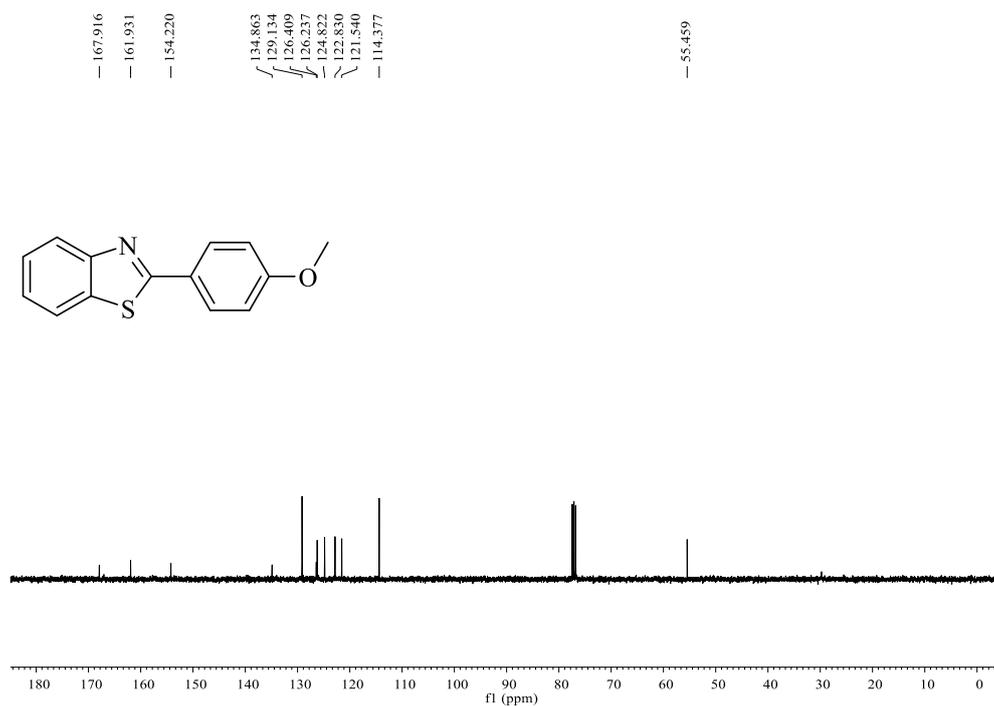
**<sup>1</sup>H NMR Spectrum of 3cu**



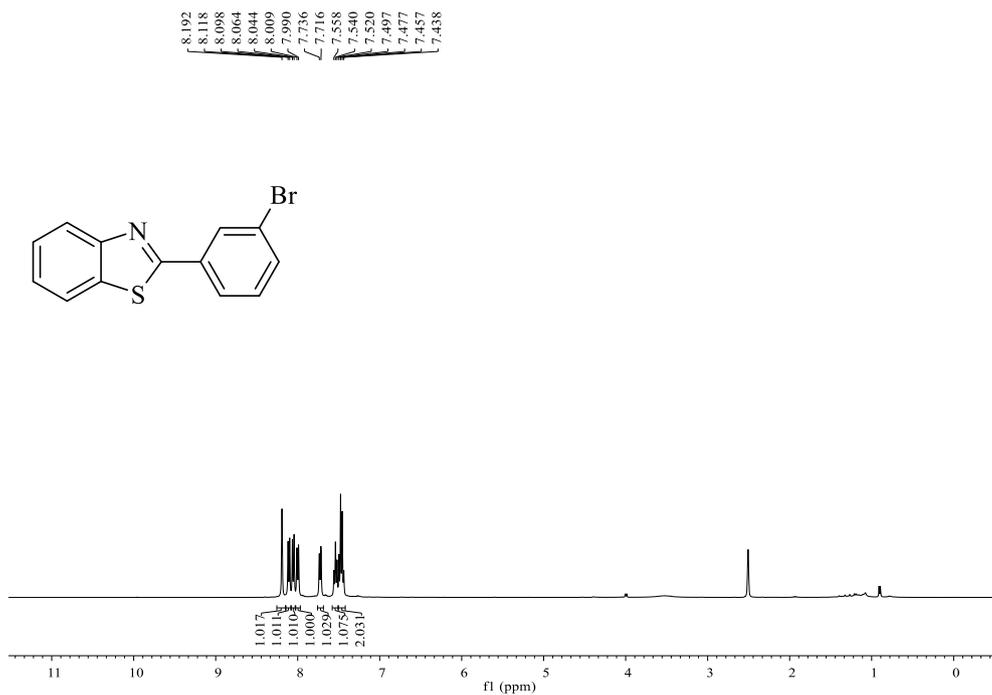
**<sup>13</sup>C NMR Spectrum of 3cu**



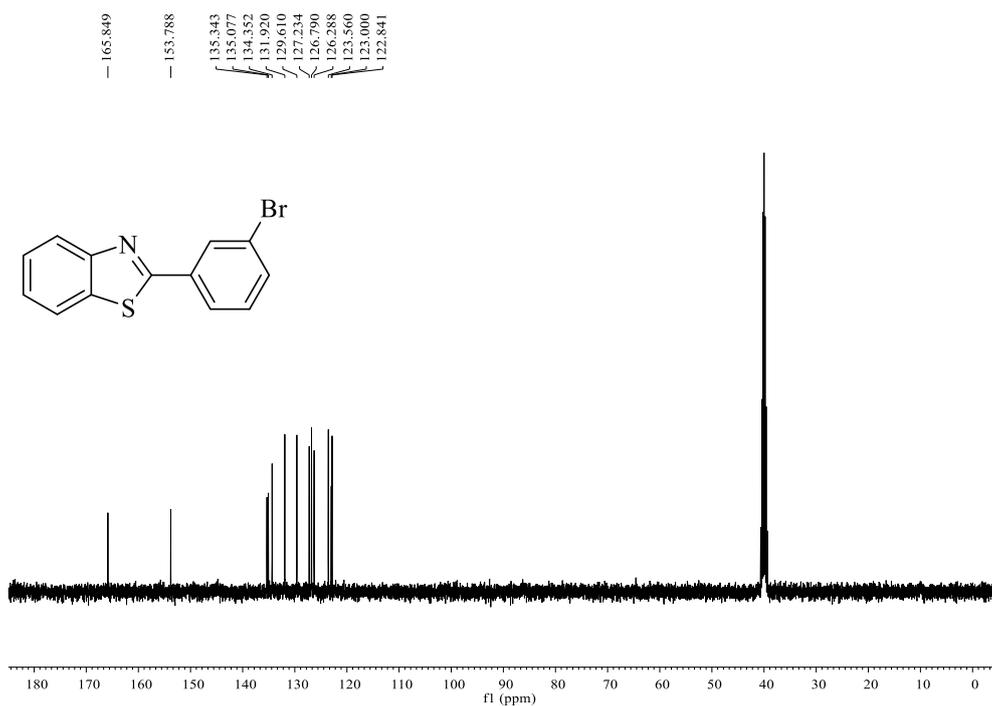
**<sup>1</sup>H NMR Spectrum of 3c**



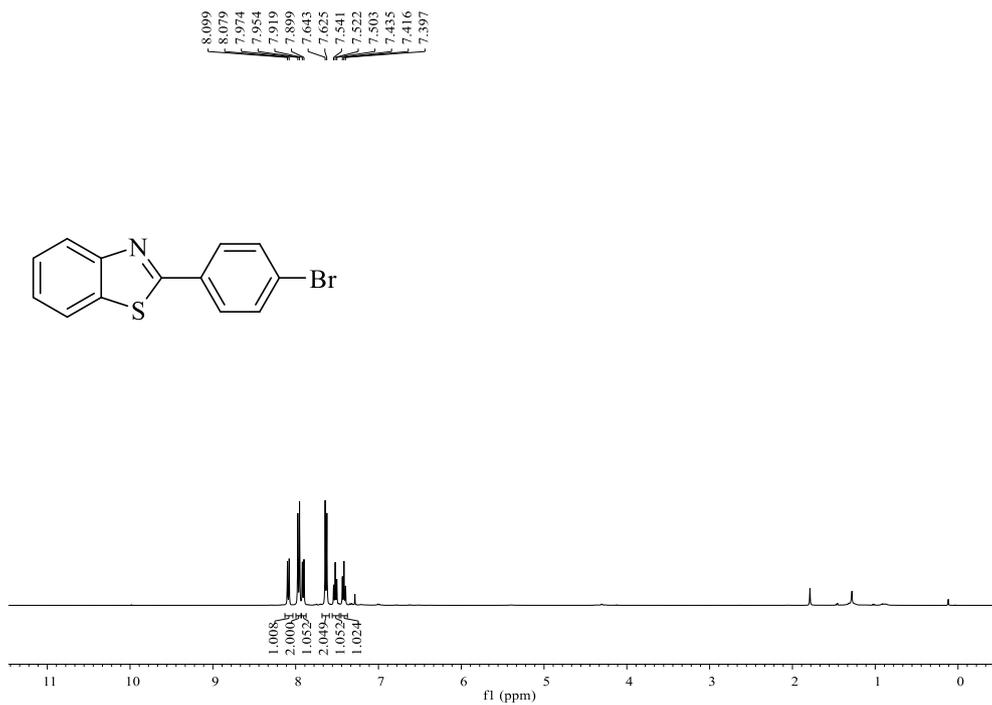
**<sup>13</sup>C NMR Spectrum of 3c**



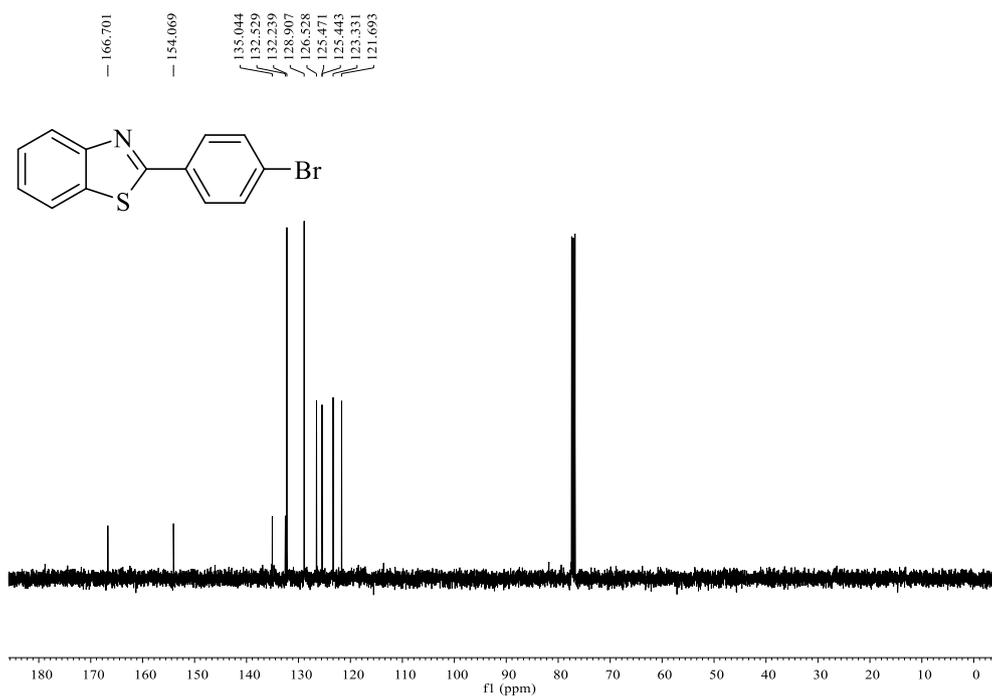
<sup>1</sup>H NMR Spectrum of **3cw**



<sup>13</sup>C NMR Spectrum of **3cw**



<sup>1</sup>H NMR Spectrum of **3cx**



<sup>13</sup>C NMR Spectrum of **3cx**