

## Supporting Information

### **Electrochemical oxidative C–H/N–H cross-coupling for C–N bond formation with hydrogen evolution**

Yi Yu,<sup>‡a</sup> Yong Yuan,<sup>‡b</sup> Huilin Liu,<sup>a</sup> Min He,<sup>a</sup> Mingzhu Yang,<sup>a</sup> Pan Liu,<sup>a</sup> Banying Yu,<sup>a</sup> Xuanchi  
Dong,<sup>a</sup> and Aiwen Lei,<sup>\*ab</sup>

<sup>‡</sup>Yi Yu and Yong Yuan contributed equally to this work

<sup>a</sup>National Research Center for Carbohydrate Synthesis, Jiangxi Normal University, Nanchang  
330022, P. R. China. E-mail: aiwenlei@whu.edu.cn

<sup>b</sup>College of Chemistry and Molecular Sciences, Institute for Advanced Studies (IAS), Wuhan  
University, Wuhan 430072, P. R. China.

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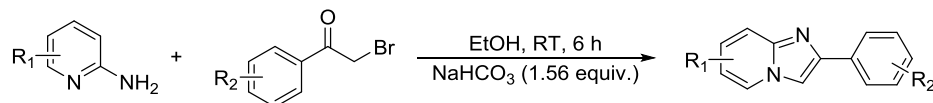
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## General information

Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (boiling point is between 60-90 °C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent, and they are listed as volume/volume ratios. NMR spectra were recorded on a Bruker spectrometer at 400 MHz ( $^1\text{H}$  NMR), 100 MHz ( $^{13}\text{C}$  NMR), 376 MHz ( $^{19}\text{F}$  NMR). Tetramethylsilane was used as an internal standard. All  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR data spectra were reported in delta ( $\delta$ ) units, parts per million (ppm) downfield from the internal standard. Coupling constants are reported in Hertz (Hz).

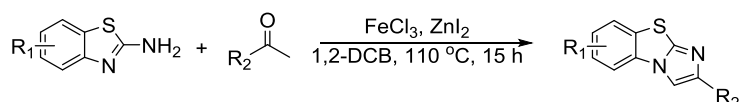
## Experimental procedure

### General procedure for the preparation of imidazopyridines:<sup>[1]</sup>



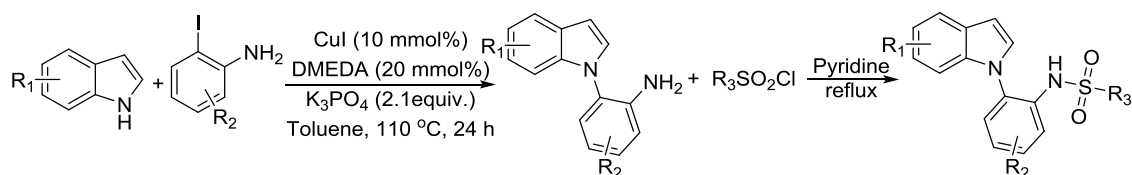
A mixture of 2-bromoacetophenones (10.0 mmol, 1.0 equiv.), 2-aminopyridines (12.5 mmol, 1.25 equiv.) and NaHCO<sub>3</sub> (15.6 mmol, 1.56 equiv.) was stirred in ethanol at room temperature for 6 hours. After completion of the reaction, the resulting mixture was diluted with water (30 mL) and extracted with ether (3 × 20 mL). The combined organic layer was washed with brine (25 mL), dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated under vacuum to give the crude product, which was purified by silica gel column with petroleum ether/ethyl acetate as the eluent to give the analytical pure imidazopyridines.

### General procedure for the preparation of benzo[d]-imidazo[2,1-*b*]thiazoles:<sup>[2]</sup>



A mixture of benzo[d]thiazol-2-amine (12.0 mmol, 1.2 equiv.), acetophenone (10.0 mmol, 1.0 equiv.), iron(III) chloride (2 mmol, 0.2 equiv.) and zinc(II) iodide (1 mmol, 0.1 equiv.) was stirred in 1,2-dichlorobenzene under 110 °C for 15 h. After completion (TLC), the reaction mixture was cooled to room temperature and extracted with dichloromethane (10 mL) followed by washing with brine (5 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of solvent the crude product was purified by column chromatography on silica gel using petroleum ether/ethylacetate (9:1) as eluent.

### General procedure for the preparation of substituted sulfonamide:<sup>[3,4]</sup>



**Step 1:** Substituted indole (6.0 mmol, 1.2 equiv.) was added to a mixture of CuI (95 mg, 0.5 mmol, 0.1 equiv.), K<sub>3</sub>PO<sub>4</sub> (2.3 g, 10.5 mmol, 2.1 equiv.), substituted 2-iodoaniline (5.0 mmol, 1.0 equiv.)

and N,N-dimethylethane-1,2-diamine(DMEDA) (88.1 mg, 1.0 mmol, 0.2 equiv.) in toluene (5 mL) at room temperature. The reaction tube was purged with argon and sealed with PTFE cap. After heated at 110 °C for 24 h, the mixture was cooled to room temperature, diluted with ethyl acetate (50 mL) and filtered through a plug of celite. The filtrate was concentrated in vacuo and the resulting residue was purified by silica gel column chromatography to give the 2-heteroaryl aniline, which was subsequently subjected to the next step.

**Step 2:** To a stirred solution of 2-heteroaryl aniline (1.0 mmol, 1.0 equiv.) in dry pyridine (2.0 mL), freshly recrystallized 4-substituted benzenesulfonyl chloride (1.1 mmol, 1.1 equiv.) was added. The reaction mixture was heated to reflux in dry nitrogen atmosphere until the reaction was completed by TLC analysis. Then, the reaction mixture was cooled, and diluted with water. After adjusting the pH to 1.5 by addition of 10% hydrochloric acid, the organic layer was extracted with ethyl acetate. The combined extracts were dried over anhydrous MgSO<sub>4</sub> and solvent was removed by reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired products.

**General procedure for electrochemical intermolecular oxidative C–H/N–H cross-coupling**

**reaction:** In an oven-dried undivided three-necked bottle equipped with a stir bar, **1** (0.3 mmol), **2** (0.6 mmol), NaNO<sub>3</sub> (0.3 mmol) were combined and added. The bottle was equipped with graphite rod (ϕ 6 mm, about 18 mm immersion depth in solution) as the anode and nickel plate (15 mm × 15 mm × 1 mm) as the cathode and was then charged with nitrogen. Under the protection of N<sub>2</sub>, ethanol (1.2 mL), purified water (1.0 mL) and CH<sub>3</sub>CN (4.8 mL) were injected respectively into the tubes via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA at 50 °C for 5 h. When the reaction was finished, the pure product was obtained by flash column chromatography on silica gel.

**General procedure for electrochemical intramolecular oxidative C–H/N–H cross-coupling**

**reaction:** In an oven-dried undivided three-necked bottle equipped with a stir bar, **4** (0.3 mmol), Cp<sub>2</sub>Fe (20 mol%), <sup>n</sup>Bu<sub>4</sub>NBF<sub>4</sub> (0.3 mmol) were combined and added. The bottle was equipped with graphite rod (ϕ 6 mm, about 18 mm immersion depth in solution) as the anode and nickel plate (15 mm × 15 mm × 1 mm) as the cathode and was then charged with nitrogen. Under the protection of

N<sub>2</sub>, ethanol (3.5 mL) and CH<sub>3</sub>CN (3.5 mL) were injected respectively into the tubes via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA at 70 °C for 4 h. When the reaction was finished, the pure product was obtained by flash column chromatography on silica gel.



Figure S1. The experimental setup for electrolysis.

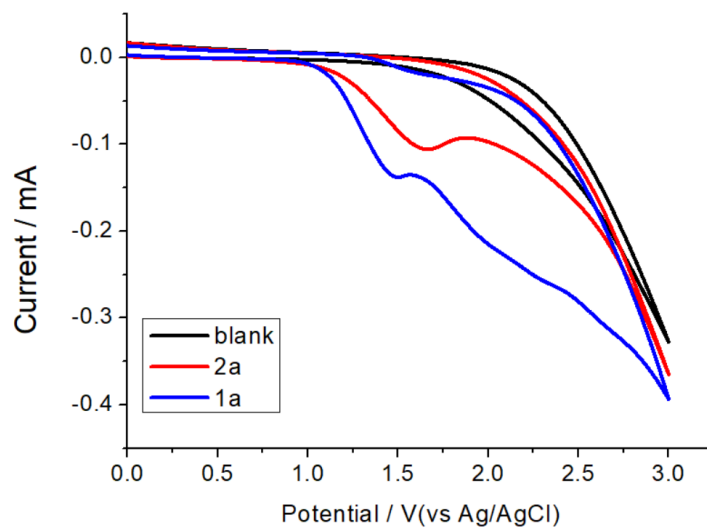
Table S1. Optimization of reaction conditions.<sup>a</sup>

Entry	Electrolysis conditions	Yield (%)
1	CH <sub>3</sub> CN (4.8 mL), EtOH (1.2 mL), H <sub>2</sub> O (1.0 mL), 50 °C, 5 h	n.d. <sup>b</sup>
2	<b>Cp<sub>2</sub>Fe (10 mmol%)</b> , CH <sub>3</sub> CN (4.8 mL), EtOH (1.2 mL), H <sub>2</sub> O (1.0 mL), 50 °C, 5 h	27
3	Cp <sub>2</sub> Fe (10 mmol%), CH <sub>3</sub> CN ( <b>3.5 mL</b> ), EtOH ( <b>3.5 mL</b> ), 50 °C, 5 h	31
4	Cp <sub>2</sub> Fe ( <b>20 mmol%</b> ), CH <sub>3</sub> CN (3.5 mL), EtOH (3.5 mL), 50 °C, 5 h	65
5	Cp <sub>2</sub> Fe (20 mmol%), CH <sub>3</sub> CN (3.5 mL), EtOH (3.5 mL), 50 °C, <b>4 h</b>	75
6	Cp <sub>2</sub> Fe (20 mmol%), CH <sub>3</sub> CN (3.5 mL), EtOH (3.5 mL), <b>70 °C</b> , 4 h	83

<sup>a</sup> Standard conditions: graphite rod anode, Nickel plate cathode, constant current = 8 mA, **4** (0.3 mmol), Cp<sub>2</sub>Fe (20 mol%), <sup>n</sup>Bu<sub>4</sub>NBF<sub>4</sub> (0.3 mmol), CH<sub>3</sub>CN (3.5 mL), EtOH (3.5 mL), 70 °C, 4 h, undivided cell. <sup>b</sup> n.d. = not detected.

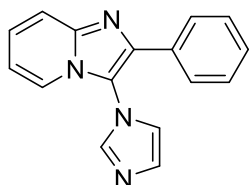
**Procedure for cyclic voltammetry (CV):** Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line under nitrogen at room temperature. The working electrode was a steady glassy carbon disk electrode, the counter electrode a platinum wire. The reference was an

Ag/AgCl electrode submerged in saturated aqueous KCl solution. 4.8 mL of acetonitrile, 1.2 mL ethanol and 1.0 mL of water containing  $n\text{Bu}_4\text{NBF}_4$  (0.1 mmol) were poured into the electrochemical cell in all experiments. The scan rate is 0.1 V/s, ranging from 0 V to 3.0 V.

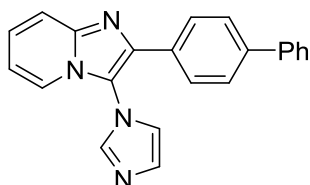


**Figure S2.** Cyclic voltammogram: **1a**, 0.1 mmol, **2a**, 0.2 mmol.

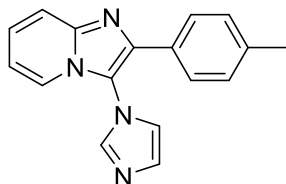
## Detailed descriptions for products



**3-(1H-imidazol-1-yl)-2-phenylimidazo[1,2-a]pyridine (3a).**<sup>[5]</sup> The desired pure product was obtained in 75% yield as a white solid, 58.7 mg. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.05 (s, 1H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.61 (s, 1H), 7.49 – 7.28 (m, 7H), 7.02 (t, *J* = 6.9 Hz, 1H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 142.3, 139.6, 138.2, 132.2, 130.9, 128.8, 128.4, 126.5, 126.1, 123.0, 121.7, 117.1, 114.3, 113.7.



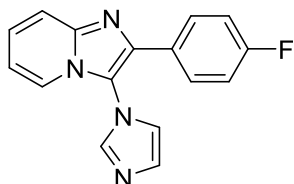
**2-([1,1'-Biphenyl]-4-yl)-3-(1H-imidazol-1-yl)imidazo[1,2-a]pyridine (3b).** The desired pure product was obtained in 58% yield as a white solid, 58.4 mg. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.09 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 4H), 7.65 (s, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 7.5 Hz, 3H), 7.42 (d, *J* = 13.5 Hz, 1H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.02 (t, *J* = 7.2 Hz, 1H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 142.4, 140.0, 139.6, 139.4, 137.9, 131.2, 131.0, 129.0, 127.7, 127.0, 126.7, 126.6, 126.6, 123.0, 121.8, 117.1, 114.4, 113.7. HRMS (ESI) calculated for C<sub>22</sub>H<sub>17</sub>N<sub>4</sub> [M+H]<sup>+</sup>: 337.1448; found: 337.1452.



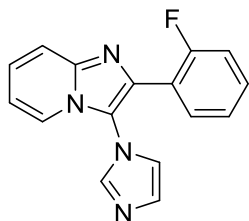
**3-(1H-Imidazol-1-yl)-2-(p-tolyl)imidazo[1,2-a]pyridine (3c).** The desired pure product was obtained in 85% yield as a white solid, 68.8 mg. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.03 (s, 1H), 7.76 – 7.68 (m, 2H), 7.59 (s, 1H), 7.40 (dd, *J* = 16.6, 7.3 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.16 (d,



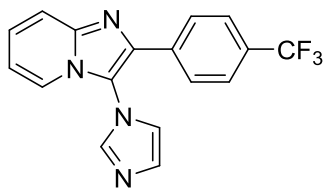
$J = 8.1$  Hz, 2H), 7.00 (t,  $J = 6.8$  Hz, 1H), 2.28 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  142.2, 139.6, 138.4, 137.9, 130.8, 129.4, 129.3, 126.4, 126.1, 122.9, 121.8, 117.0, 114.0, 113.6, 20.9. HRMS (ESI) calculated for  $\text{C}_{17}\text{H}_{15}\text{N}_4$   $[\text{M}+\text{H}]^+$ : 275.1291; found: 275.1295.



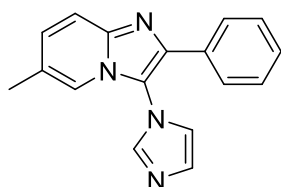
**2-(4-Fluorophenyl)-3-(1H-imidazol-1-yl)imidazo[1,2-a]pyridine (3d).** The desired pure product was obtained in 57% yield as a white solid, 47.7 mg.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.07 (s, 1H), 7.77 – 7.70 (m, 2H), 7.62 (s, 1H), 7.51 – 7.40 (m, 3H), 7.38 (s, 1H), 7.23 (t,  $J = 8.9$  Hz, 2H), 7.02 (t,  $J = 6.7$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  162.1 (d,  $J = 245.9$  Hz), 142.3, 139.6, 137.3, 131.0, 128.7, 128.2 (d,  $J = 8.3$  Hz), 126.6, 123.0, 121.7, 117.1, 115.9 (d,  $J = 22$  Hz), 114.1, 113.7.  $^{19}\text{F}$  NMR (376 MHz,  $\text{DMSO-}d_6$ )  $\delta$  -113.08. HRMS (ESI) calculated for  $\text{C}_{16}\text{H}_{12}\text{FN}_4$   $[\text{M}+\text{H}]^+$ : 279.1041; found: 279.1039.



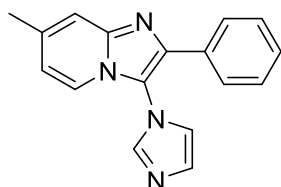
**2-(2-Fluorophenyl)-3-(1H-imidazol-1-yl)imidazo[1,2-a]pyridine (3e).** The desired pure product was obtained in 63% yield as a white solid, 52.5 mg.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  7.94 (s, 1H), 7.79 (d,  $J = 6.8$  Hz, 1H), 7.77 – 7.68 (m, 2H), 7.52 (s, 1H), 7.48 – 7.37 (m, 2H), 7.27 (t,  $J = 7.5$  Hz, 1H), 7.21 (d,  $J = 7.1$  Hz, 2H), 7.05 (t,  $J = 7.2$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  159.4 (d,  $J = 249.6$  Hz), 142.5, 139.5, 134.3, 131.4, 130.8 (d,  $J = 8.2$  Hz), 129.9, 126.6, 124.7, 123.0, 121.8, 120.0 (d,  $J = 14.3$  Hz), 117.3, 116.2, 116.0 (d,  $J = 21.7$  Hz), 113.8.  $^{19}\text{F}$  NMR (376 MHz,  $\text{DMSO-}d_6$ )  $\delta$  -109.49. HRMS (ESI) calculated for  $\text{C}_{16}\text{H}_{12}\text{FN}_4$   $[\text{M}+\text{H}]^+$ : 279.1041; found: 279.1045.



**3-(1H-Imidazol-1-yl)-2-(4-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (3f).** The desired pure product was obtained in 59% yield as a white solid, 58.1 mg.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.09 (s, 1H), 7.80 – 7.69 (m, 4H), 7.66 – 7.58 (m, 3H), 7.48 – 7.42 (m, 1H), 7.39 (s, 1H), 7.04 (t,  $J = 7.2$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  142.5, 139.5, 136.6, 136.2, 131.1, 128.5 (q,  $J = 32.3$  Hz), 127.1, 126.7, 125.9 (q,  $J = 3.6$  Hz), 124.2 (q,  $J = 270.5$  Hz), 123.2, 121.7, 117.3, 115.4, 114.1.  $^{19}\text{F}$  NMR (376 MHz,  $\text{DMSO-}d_6$ )  $\delta$  -61.21. HRMS (ESI) calculated for  $\text{C}_{17}\text{H}_{12}\text{F}_3\text{N}_4$   $[\text{M}+\text{H}]^+$ : 329.1009; found: 329.1013.

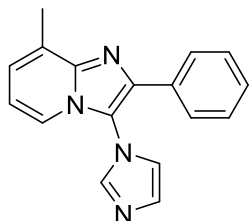


**3-(1H-Imidazol-1-yl)-6-methyl-2-phenylimidazo[1,2-a]pyridine (3g).** The desired pure product was obtained in 64% yield as a white solid, 52.4 mg.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.03 (s, 1H), 7.63 (d,  $J = 9.2$  Hz, 1H), 7.56 (d,  $J = 17.4$  Hz, 2H), 7.41 (dd,  $J = 8.2, 1.4$  Hz, 2H), 7.36 (d,  $J = 8.7$  Hz, 3H), 7.34 – 7.25 (m, 2H), 2.27 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  141.3, 139.5, 138.0, 132.3, 130.8, 129.4, 128.8, 128.2, 126.0, 123.2, 121.7, 120.2, 116.6, 114.0, 17.6. HRMS (ESI) calculated for  $\text{C}_{17}\text{H}_{15}\text{N}_4$   $[\text{M}+\text{H}]^+$ : 275.1291; found: 275.1297.

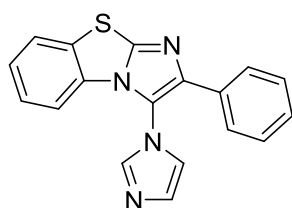


**3-(1H-Imidazol-1-yl)-7-methyl-2-phenylimidazo[1,2-a]pyridine (3h).** The desired pure product was obtained in 84% yield as a white solid, 68.7 mg.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.02 (s, 1H), 7.62 (d,  $J = 7.0$  Hz, 1H), 7.59 (s, 1H), 7.50 (s, 1H), 7.45 – 7.40 (m, 2H), 7.39 – 7.27 (m, 4H), 6.86 (dd,  $J = 7.0, 1.5$  Hz, 1H), 2.40 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  142.7, 139.6, 137.8,

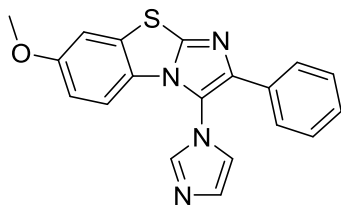
137.1, 132.3, 130.8, 128.8, 128.3, 126.0, 122.2, 121.8, 116.1, 115.3, 113.8, 20.9. HRMS (ESI) calculated for  $C_{17}H_{15}N_4$   $[M+H]^+$ : 275.1291; found: 275.1296.



**3-(1H-Imidazol-1-yl)-8-methyl-2-phenylimidazo[1,2-a]pyridine (3i).** The desired pure product was obtained in 51% yield as a white solid, 41.6 mg.  $^1H$  NMR (400 MHz,  $DMSO-d_6$ )  $\delta$  8.03 (s, 1H), 7.59 (s, 1H), 7.55 (d,  $J = 6.7$  Hz, 1H), 7.47 (d,  $J = 7.0$  Hz, 2H), 7.40 – 7.27 (m, 4H), 7.22 (d,  $J = 6.9$  Hz, 1H), 6.91 (t,  $J = 6.8$  Hz, 1H), 2.59 (s, 3H).  $^{13}C$  NMR (100 MHz,  $DMSO-d_6$ )  $\delta$  142.5, 139.5, 137.7, 132.3, 130.8, 128.8, 128.3, 126.7, 126.2, 124.8, 121.7, 120.6, 114.6, 113.7, 16.2. HRMS (ESI) calculated for  $C_{17}H_{15}N_4$   $[M+H]^+$ : 275.1291; found: 275.1296.

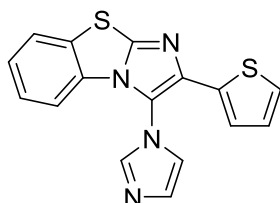


**3-(1H-Imidazol-1-yl)-2-phenylbenzo[d]imidazo[2,1-b]thiazole (3j).** The desired pure product was obtained in 82% yield as a white solid, 77.7 mg.  $^1H$  NMR (400 MHz,  $DMSO-d_6$ )  $\delta$  8.20 (s, 1H), 8.08 (s, 1H), 7.76 (s, 1H), 7.51 – 7.23 (m, 8H), 6.36 – 6.23 (m, 1H).  $^{13}C$  NMR (100 MHz,  $DMSO-d_6$ )  $\delta$  145.7, 139.8, 139.6, 132.1, 131.1, 129.5, 128.9, 128.1, 127.0, 125.6, 125.4, 122.2, 117.6, 111.9. HRMS (ESI) calculated for  $C_{18}H_{13}N_4S$   $[M+H]^+$ : 317.0855; found: 317.0868.

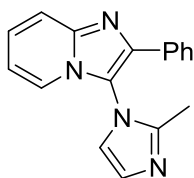


**3-(1H-Imidazol-1-yl)-7-methoxy-2-phenylbenzo[d]imidazo[2,1-b]thiazole (3k).** The desired pure product was obtained in 59% yield as a white solid, 60.8 mg.  $^1H$  NMR (400 MHz,  $DMSO-d_6$ )

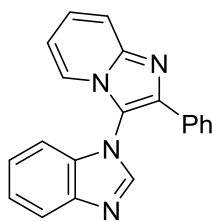
$\delta$  8.17 (s, 1H), 7.80 – 7.70 (m, 2H), 7.47 – 7.22 (m, 6H), 7.01 (dd,  $J$  = 9.0, 2.4 Hz, 1H), 6.19 (d,  $J$  = 9.0 Hz, 1H), 3.79 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  157.1, 145.0, 139.7, 139.1, 132.2, 131.0, 130.9, 128.9, 127.9, 125.3, 125.1, 122.1, 117.4, 114.3, 112.4, 109.7, 55.9. HRMS (ESI) calculated for  $\text{C}_{19}\text{H}_{15}\text{N}_4\text{OS}$   $[\text{M}+\text{H}]^+$ : 347.0961; found: 347.0963.



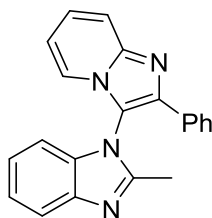
**3-(1H-Imidazol-1-yl)-2-(thiophen-2-yl)benzo[d]imidazo[2,1-b]thiazole (3l).** The desired pure product was obtained in 52% yield as a white solid, 50.0 mg.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.18 (s, 1H), 8.12 – 8.05 (m, 1H), 7.71 (s, 1H), 7.51 (dd,  $J$  = 5.0, 1.0 Hz, 1H), 7.42 (dd,  $J$  = 6.0, 3.3 Hz, 3H), 7.04 (dd,  $J$  = 5.0, 3.7 Hz, 1H), 6.78 (dd,  $J$  = 3.6, 1.0 Hz, 1H), 6.36 (dd,  $J$  = 4.7, 1.7 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  145.9, 139.7, 136.1, 134.6, 131.0, 129.4, 128.1, 127.1, 126.3, 125.6, 125.5, 123.4, 121.9, 116.2, 111.9. HRMS (ESI) calculated for  $\text{C}_{16}\text{H}_{11}\text{N}_4\text{S}_2$   $[\text{M}+\text{H}]^+$ : 323.0420; found: 323.0423.



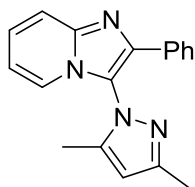
**3-(2-Methyl-1H-imidazol-1-yl)-2-phenylimidazo[1,2-a]pyridine (3m).** The desired pure product was obtained in 40% yield as a white solid, 32.7 mg.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.78 (d,  $J$  = 6.8 Hz, 1H), 7.74 (d,  $J$  = 9.1 Hz, 1H), 7.51 – 7.30 (m, 7H), 7.20 (s, 1H), 7.03 (t,  $J$  = 7.1 Hz, 1H), 1.97 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  146.1, 142.6, 138.2, 132.2, 129.6, 129.0, 128.5, 126.6, 126.0, 122.9, 121.6, 117.3, 114.1, 113.8, 12.3. HRMS (ESI) calculated for  $\text{C}_{17}\text{H}_{15}\text{N}_4$   $[\text{M}+\text{H}]^+$ : 275.1291; found: 275.1294.



**1-(2-Phenylimidazo[1,2-a]pyridin-3-yl)-1H-benzo[d]imidazole (3n).**<sup>[6]</sup> The desired pure product was obtained in 50% yield as a white solid, 46.5 mg. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.62 (s, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 9.1 Hz, 1H), 7.74 (d, *J* = 6.8 Hz, 1H), 7.49 – 7.44 (m, 1H), 7.42 – 7.35 (m, 3H), 7.33 – 7.25 (m, 4H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.97 (t, *J* = 7.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 145.3, 143.5, 143.0, 139.4, 134.0, 132.2, 128.9, 128.5, 126.8, 126.1, 124.4, 123.4, 123.3, 120.5, 117.4, 113.8, 112.1, 110.4.

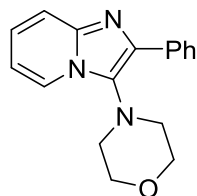


**2-Methyl-1-(2-phenylimidazo[1,2-a]pyridin-3-yl)-1H-benzo[d]imidazole (3o).** The desired pure product was obtained in 64% yield as a white solid, 62.0 mg. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.83 – 7.74 (m, 3H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.37 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.34 – 7.26 (m, 4H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 7.1 Hz, 2H), 2.21 (s, 3H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 152.8, 143.4, 143.1, 139.5, 135.1, 132.2, 129.1, 128.7, 127.1, 125.9, 123.6, 123.2, 123.1, 119.4, 117.6, 114.0, 111.7, 109.9, 13.3. HRMS (ESI) calculated for C<sub>21</sub>H<sub>17</sub>N<sub>4</sub> [M+H]<sup>+</sup>: 325.1448; found: 325.1454.

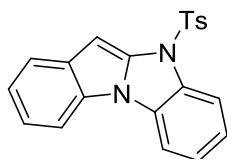


**3-(3,5-Dimethyl-1H-pyrazol-1-yl)-2-phenylimidazo[1,2-a]pyridine (3p).**<sup>[5]</sup> The desired pure product was obtained in 50% yield as a white solid, 43.2 mg. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.59 – 7.41 (m, 4H), 7.29 – 7.10 (m, 4H), 6.73 – 6.65 (m, 1H), 6.02 (s, 1H), 2.28 (s, 3H), 1.77 (s, 3H).

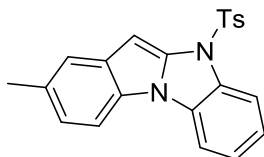
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.0, 143.0, 142.9, 139.8, 132.0, 128.5, 128.1, 126.5, 125.8, 122.5, 117.3, 115.9, 112.9, 106.9, 13.7, 10.50.



**4-(2-Phenylimidazo[1,2-a]pyridin-3-yl)morpholine (3q).**<sup>[7]</sup> The desired pure product was obtained in 53% yield as a white solid, 44.3 mg.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  8.37 (d,  $J$  = 6.8 Hz, 1H), 7.89 (d,  $J$  = 7.5 Hz, 2H), 7.57 – 7.43 (m, 3H), 7.36 (t,  $J$  = 7.4 Hz, 1H), 7.29 – 7.18 (m, 1H), 6.93 (t,  $J$  = 6.7 Hz, 1H), 3.85 – 3.75 (m, 4H), 3.15 – 3.07 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ )  $\delta$  140.9, 136.4, 134.6, 128.6, 128.4, 128.2, 127.6, 124.7, 124.1, 117.2, 112.0, 67.1, 49.6.

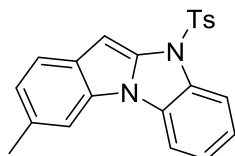


**10-Tosyl-10H-benzo[4,5]imidazo[1,2-a]indole (5a).**<sup>[8]</sup> The desired pure product was obtained in 83% yield as a white solid, 89.6 mg.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (d,  $J$  = 7.9 Hz, 1H), 7.78 (d,  $J$  = 8.4 Hz, 2H), 7.72 – 7.63 (m, 2H), 7.57 (d,  $J$  = 7.8 Hz, 1H), 7.31 (t,  $J$  = 7.2 Hz, 1H), 7.27 – 7.20 (m, 3H), 7.11 (d,  $J$  = 8.2 Hz, 2H), 6.56 (s, 1H), 2.25 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.5, 138.7, 133.3, 132.3, 129.8, 129.6, 126.9, 126.8, 124.9, 122.9, 121.5, 121.0, 120.5, 114.9, 110.5, 110.3, 81.9, 21.5.

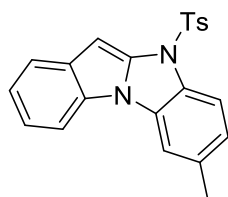


**2-Methyl-10-tosyl-10H-benzo[4,5]imidazo[1,2-a]indole (5b).**<sup>[8]</sup> The desired pure product was obtained in 67% yield as a white solid, 75.0 mg.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J$  = 8.0 Hz, 1H), 7.77 (d,  $J$  = 8.3 Hz, 2H), 7.53 (d,  $J$  = 6.4 Hz, 2H), 7.47 (s, 1H), 7.30 (t,  $J$  = 7.6 Hz, 1H), 7.21 (t,  $J$  = 7.5 Hz, 1H), 7.11 (d,  $J$  = 8.2 Hz, 2H), 7.05 (d,  $J$  = 8.2 Hz, 1H), 6.48 (s, 1H), 2.48 (s, 3H),

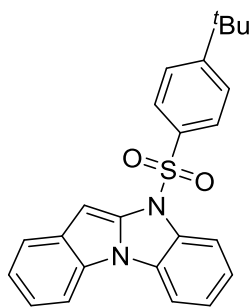
2.26 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.5, 138.8, 133.3, 133.2, 132.5, 131.0, 129.7, 129.6, 127.8, 126.9, 125.1, 124.9, 122.6, 121.9, 120.8, 114.8, 110.1, 81.5, 21.6, 21.5.



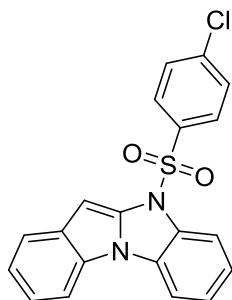
**3-Methyl-10-tosyl-10H-benzo[4,5]imidazo[1,2-a]indole (5c).** The desired pure product was obtained in 57% yield as a white solid, 63.8 mg.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J$  = 8.7 Hz, 1H), 7.76 (d,  $J$  = 8.4 Hz, 2H), 7.57 (d,  $J$  = 8.0 Hz, 2H), 7.47 (s, 1H), 7.30 (td,  $J$  = 7.7, 1.1 Hz, 1H), 7.21 (td,  $J$  = 8.0, 1.2 Hz, 1H), 7.09 (t,  $J$  = 8.7 Hz, 3H), 6.50 (s, 1H), 2.51 (s, 3H), 2.25 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.4, 138.3, 133.4, 133.3, 130.5, 130.0, 129.7, 129.6, 127.2, 126.9, 124.9, 123.1, 122.7, 120.6, 114.9, 110.7, 110.3, 81.8, 21.8, 21.6. HRMS (ESI) calculated for  $\text{C}_{22}\text{H}_{19}\text{N}_2\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 375.1162; found: 375.1157.



**7-Methyl-10-tosyl-10H-benzo[4,5]imidazo[1,2-a]indole (5d).** The desired pure product was obtained in 48% yield as a white solid, 53.5 mg.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J$  = 8.3 Hz, 1H), 7.75 (d,  $J$  = 8.3 Hz, 2H), 7.70 – 7.65 (m, 2H), 7.37 (s, 1H), 7.28 – 7.19 (m, 2H), 7.10 (d,  $J$  = 8.2 Hz, 2H), 7.02 (d,  $J$  = 8.3 Hz, 1H), 6.54 (s, 1H), 2.46 (s, 3H), 2.25 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.4, 139.0, 135.2, 133.3, 132.3, 131.2, 129.7, 127.0, 126.8, 123.5, 121.45, 120.9, 120.4, 114.6, 111.0, 110.6, 81.9, 21.6, 21.5. HRMS (ESI) calculated for  $\text{C}_{22}\text{H}_{19}\text{N}_2\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 375.1162; found: 375.1165.



**10-((4-(Tert-butyl)phenyl)sulfonyl)-10H-benzo[4,5]imidazo[1,2-a]indole (5e).** The desired pure product was obtained in 73% yield as a white solid, 87.9 mg.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J$  = 8.0 Hz, 1H), 7.76 (d,  $J$  = 8.4 Hz, 2H), 7.67 – 7.57 (m, 2H), 7.51 (d,  $J$  = 7.7 Hz, 1H), 7.31 – 7.10 (m, 6H), 6.48 (s, 1H), 1.11 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.3, 138.7, 133.4, 133.3, 132.3, 129.5, 126.8, 126.7, 126.3, 124.8, 122.9, 121.6, 121.0, 120.5, 114.7, 110.5, 110.3, 81.6, 35.2, 30.8. HRMS (ESI) calculated for  $\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 403.1475; found: 403.1476.



**10-((4-Chlorophenyl)sulfonyl)-10H-benzo[4,5]imidazo[1,2-a]indole (5f).** The desired pure product was obtained in 70% yield as a white solid, 79.3 mg.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J$  = 8.1 Hz, 1H), 7.81 (d,  $J$  = 8.7 Hz, 2H), 7.73 – 7.60 (m, 2H), 7.57 (d,  $J$  = 7.8 Hz, 1H), 7.37 – 7.13 (m, 6H), 6.55 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.1, 138.3, 134.4, 133.0, 132.1, 129.6, 129.5, 128.2, 126.9, 125.4, 123.0, 121.7, 121.1, 120.8, 114.9, 110.6, 110.5, 82.2. HRMS (ESI) calculated for  $\text{C}_{20}\text{H}_{14}\text{ClN}_2\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 381.0459; found: 381.0463.

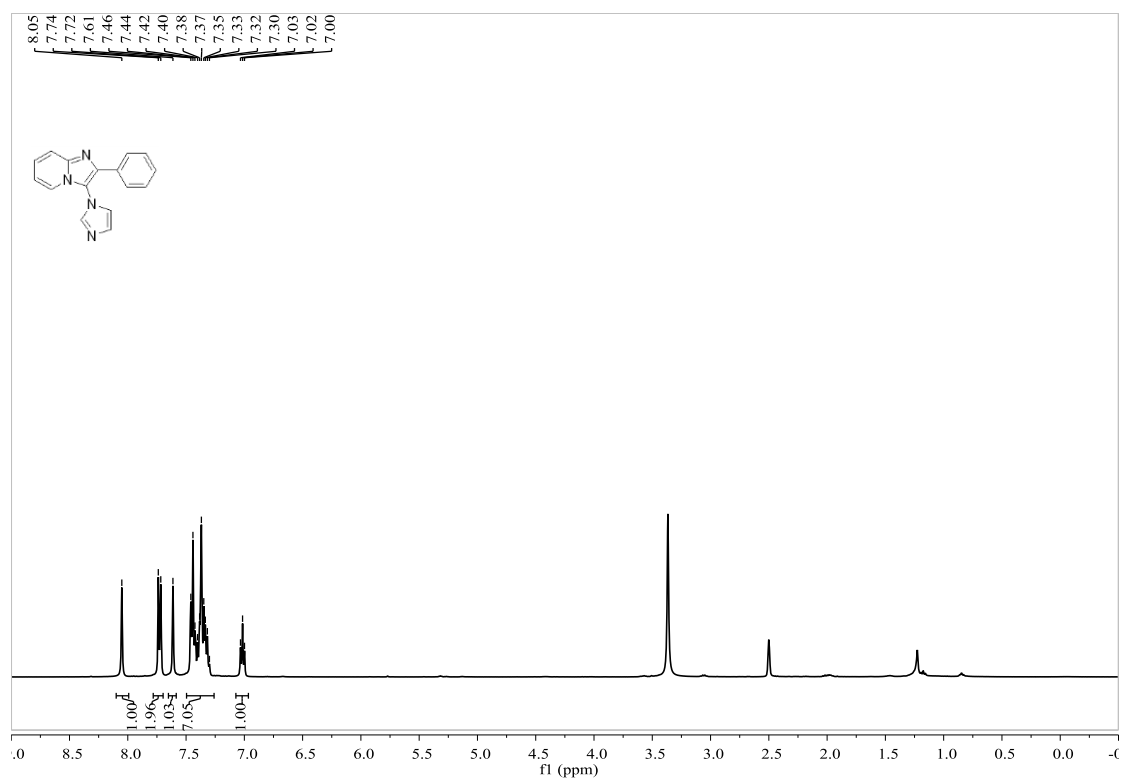


## References:

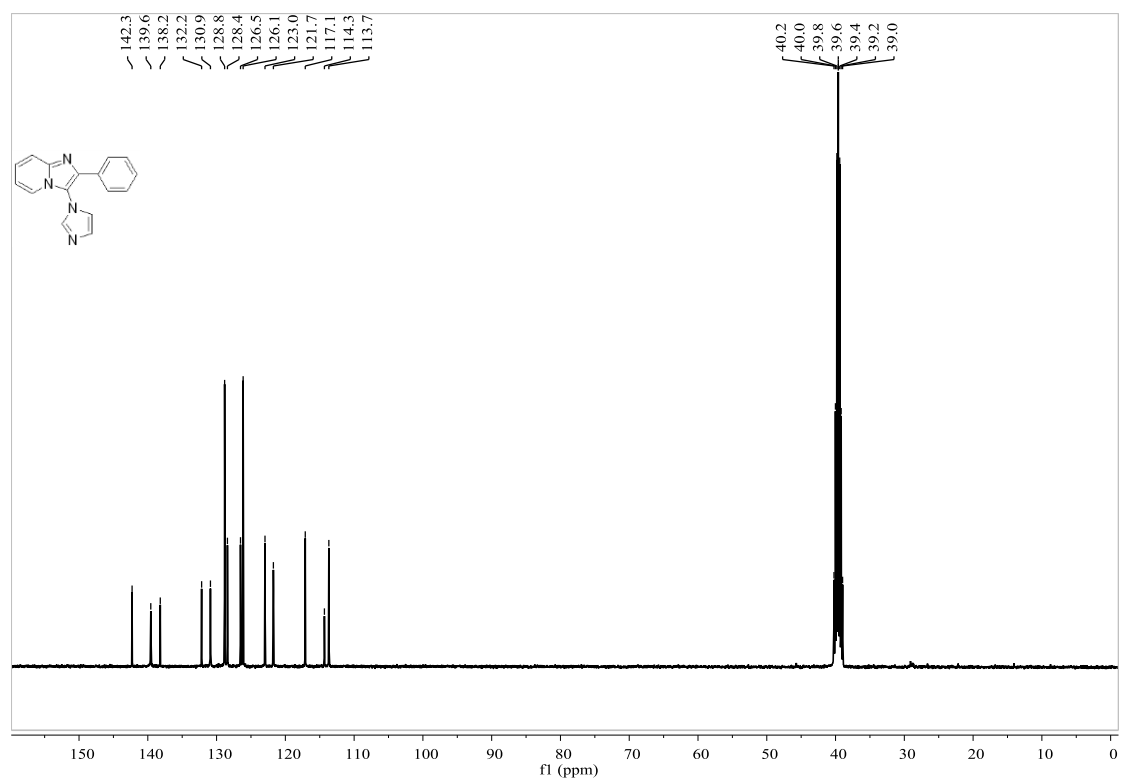
- [1] A. K. Bagdi, M. Rahman, S. Santra, A. Majee, A. Hajra, *Adv. Synth. Catal.* **2013**, 355, 1741-1747.
- [2] S. Mishra, K. Monir, S. Mitra, A. Hajra, *Org. Lett.* **2014**, 16, 6084-6087.
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## Copies of product NMR Spectra

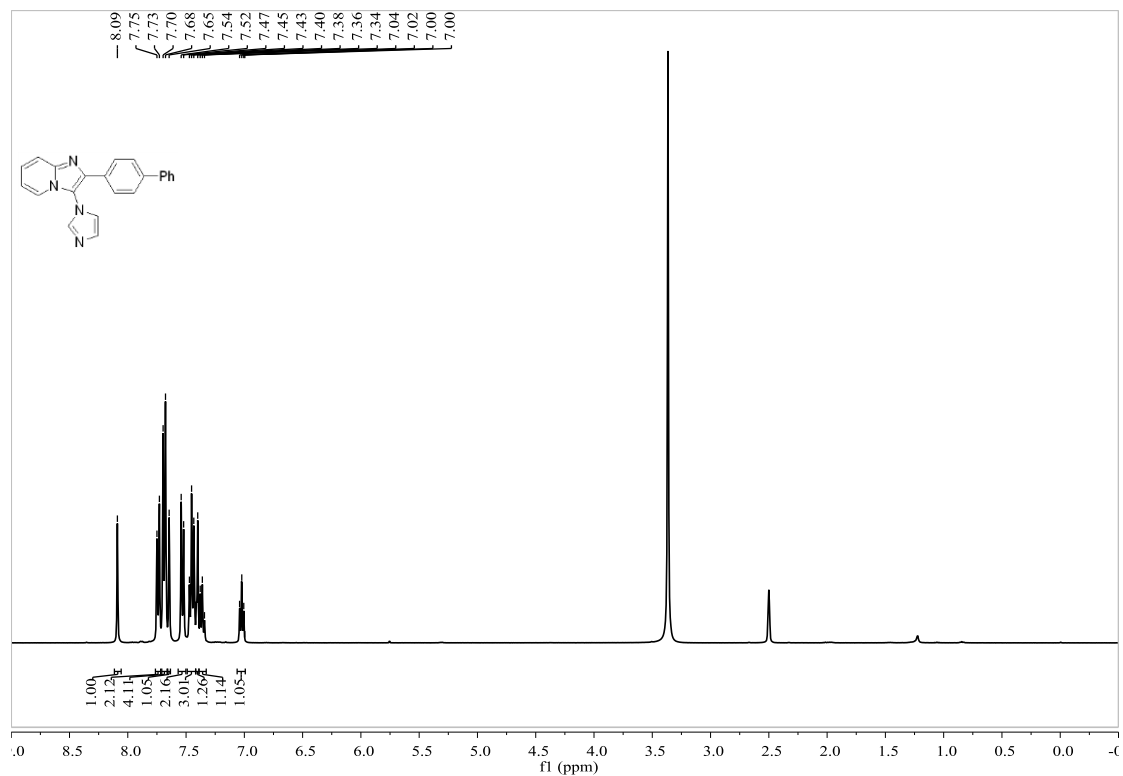
$^1\text{H}$  NMR of compound **3a**



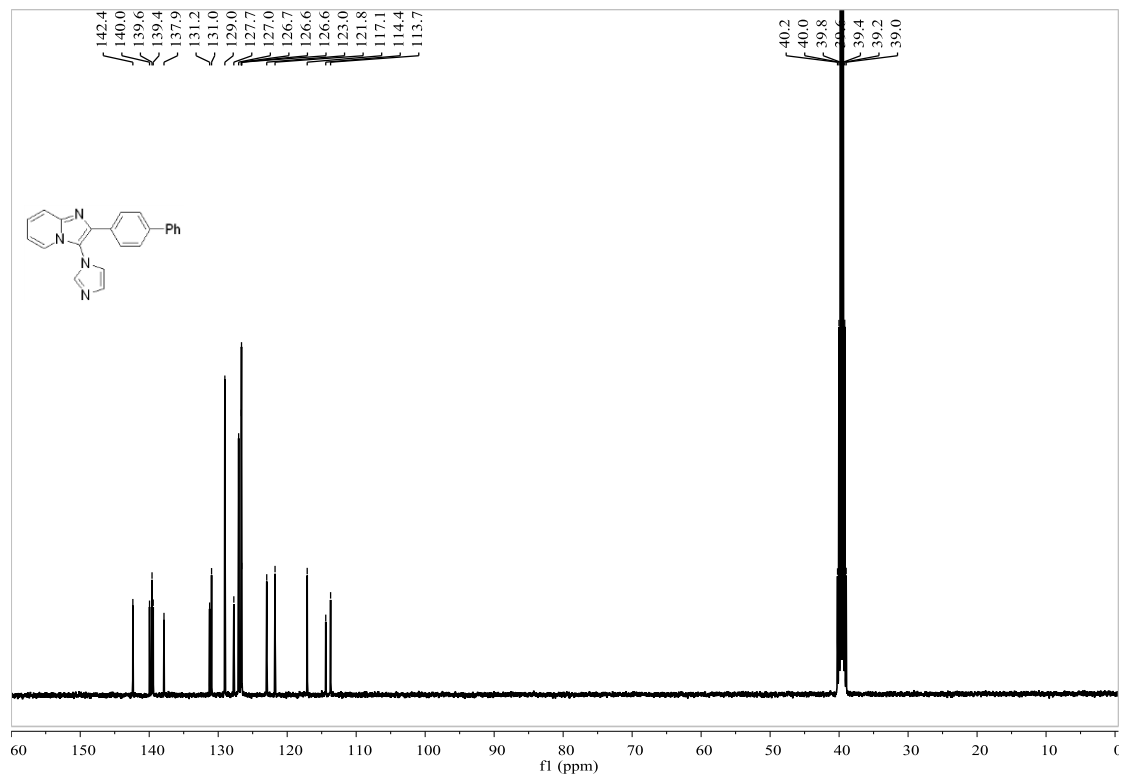
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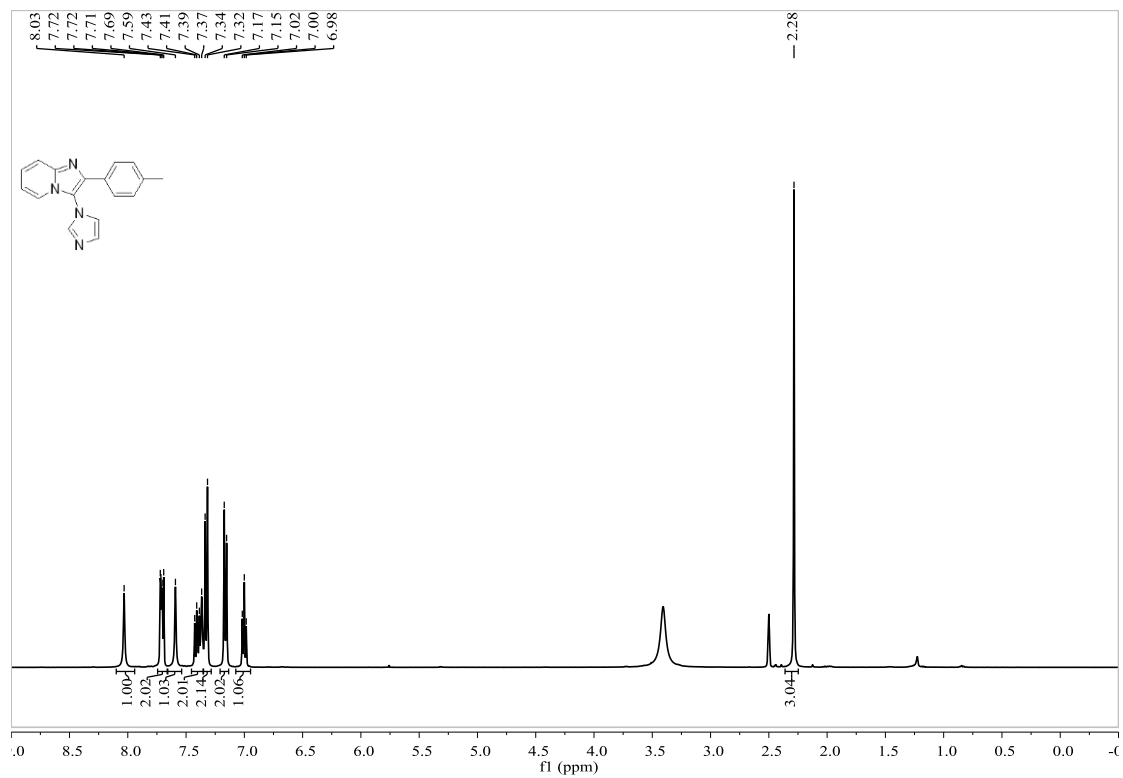
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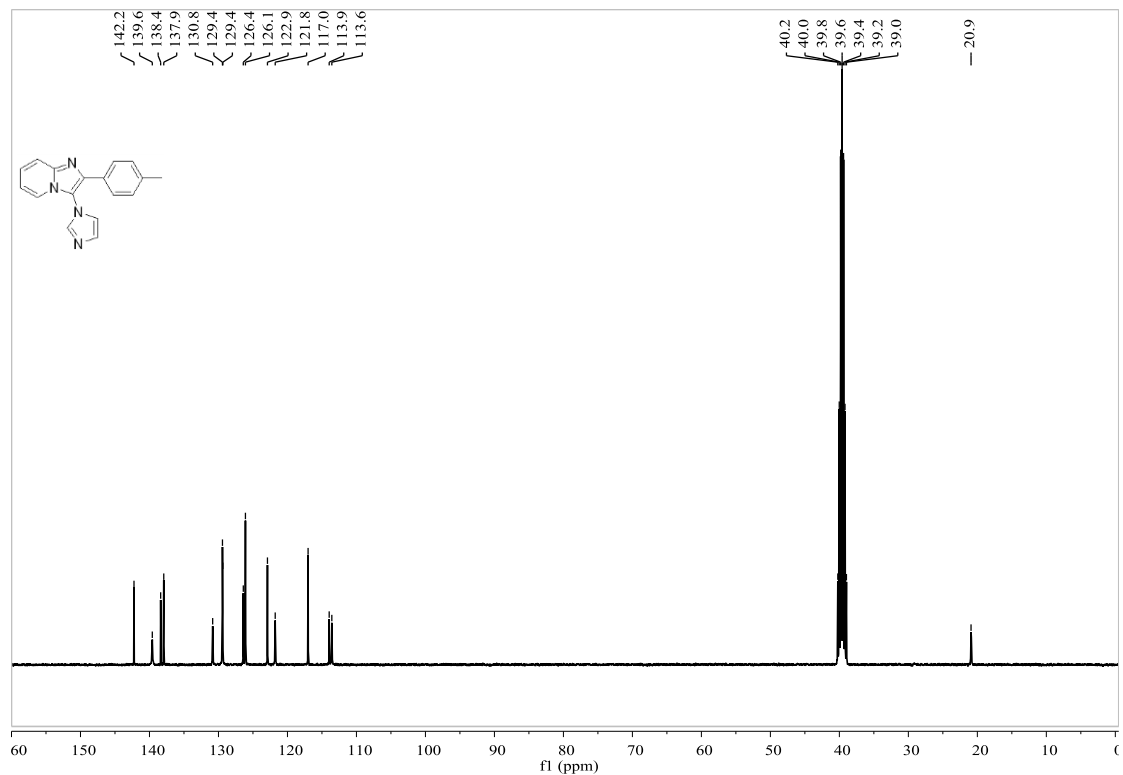
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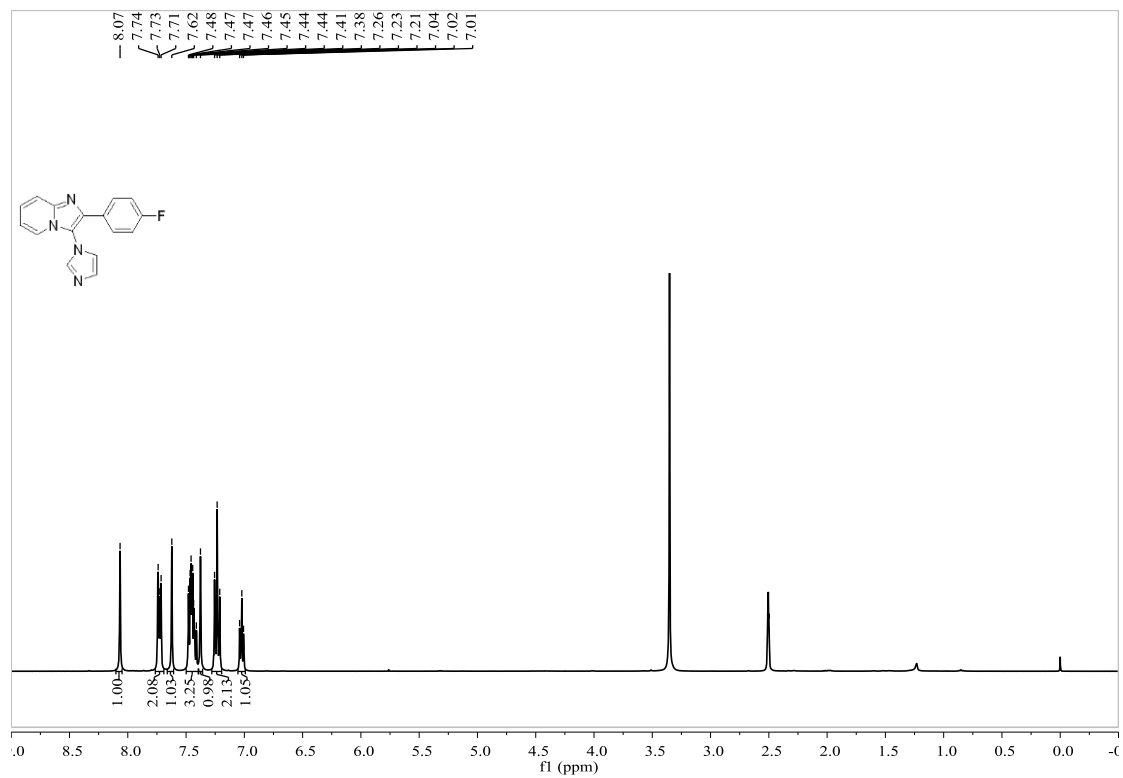
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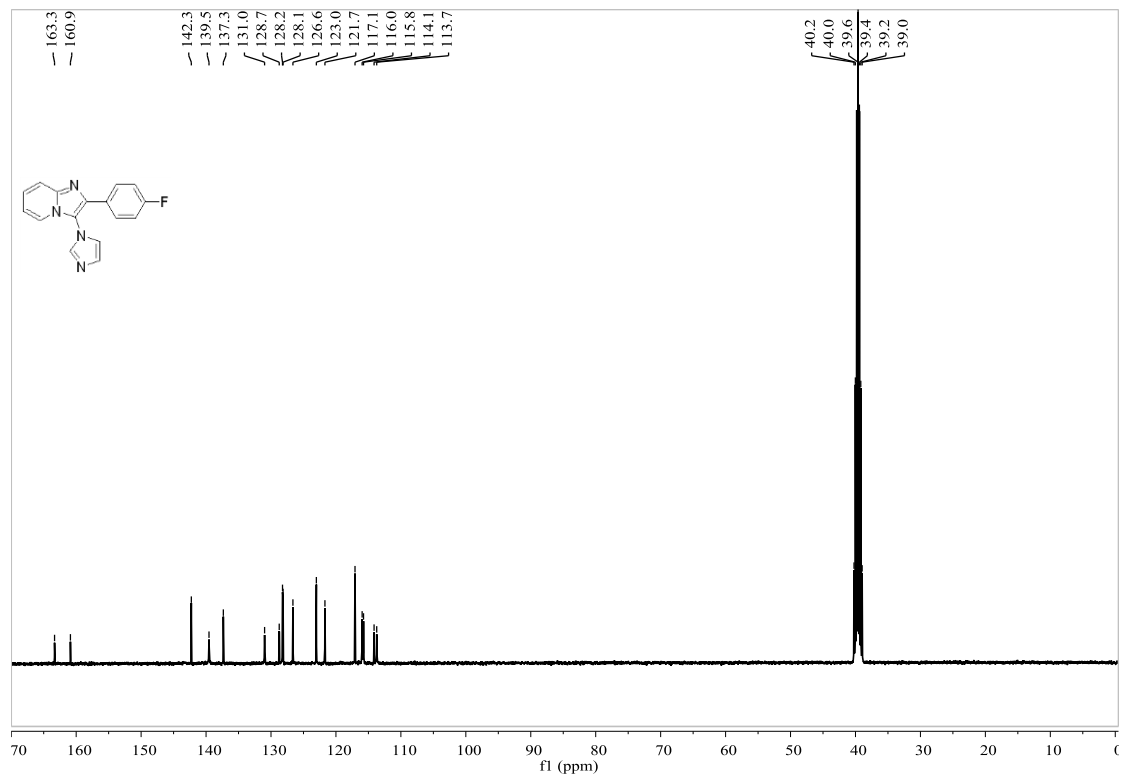
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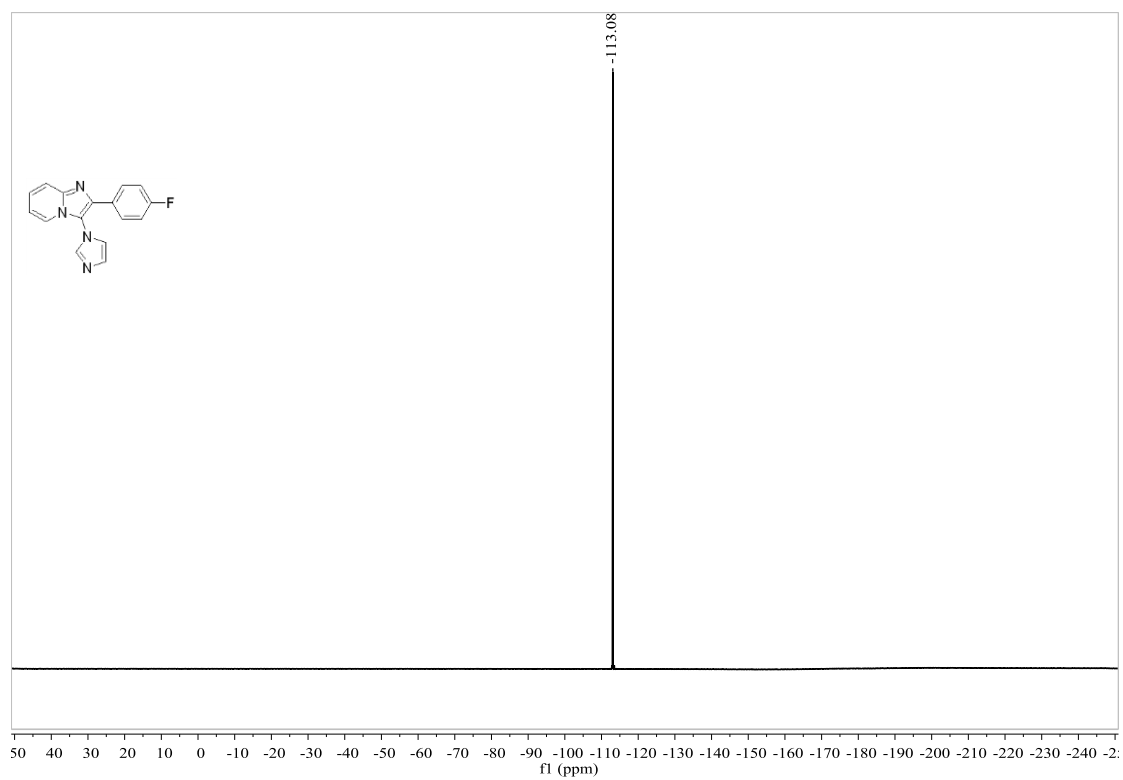
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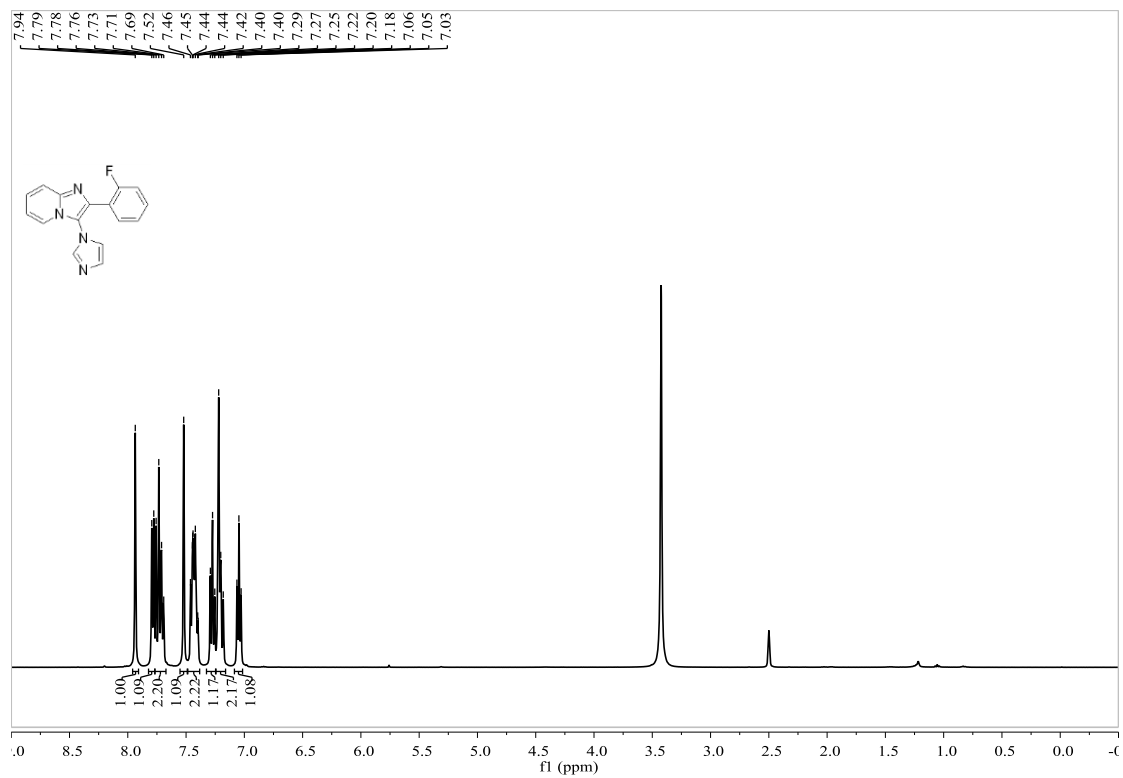
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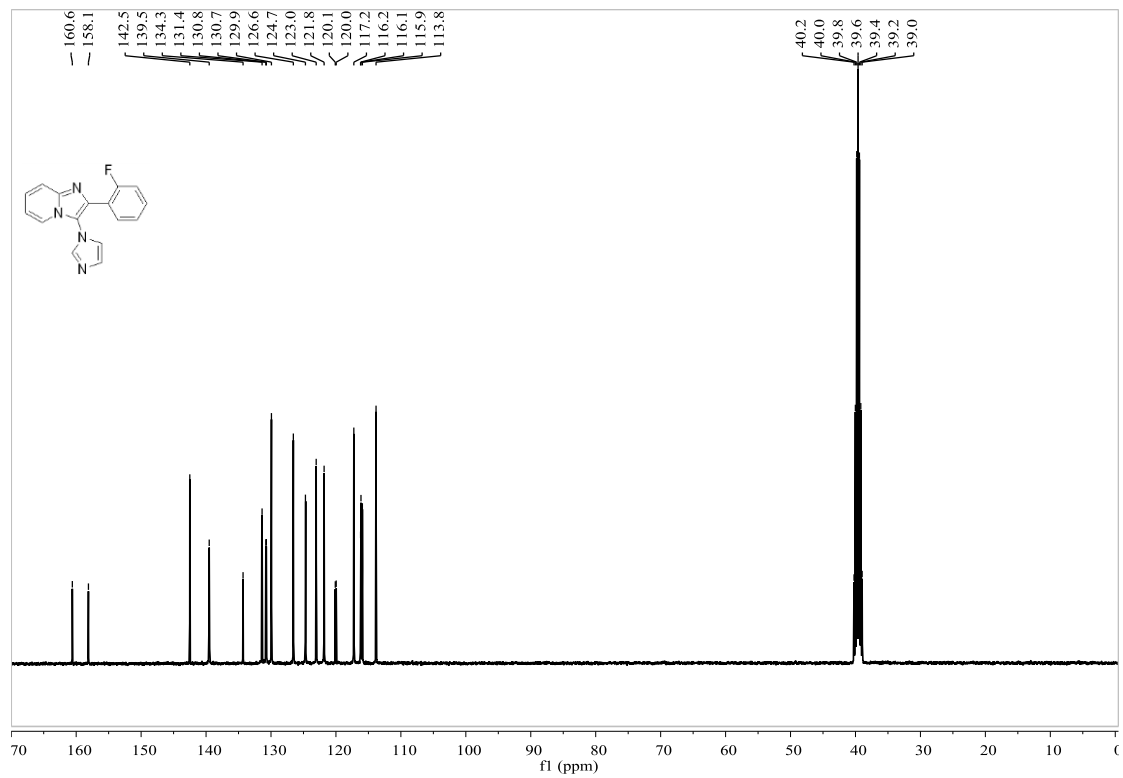
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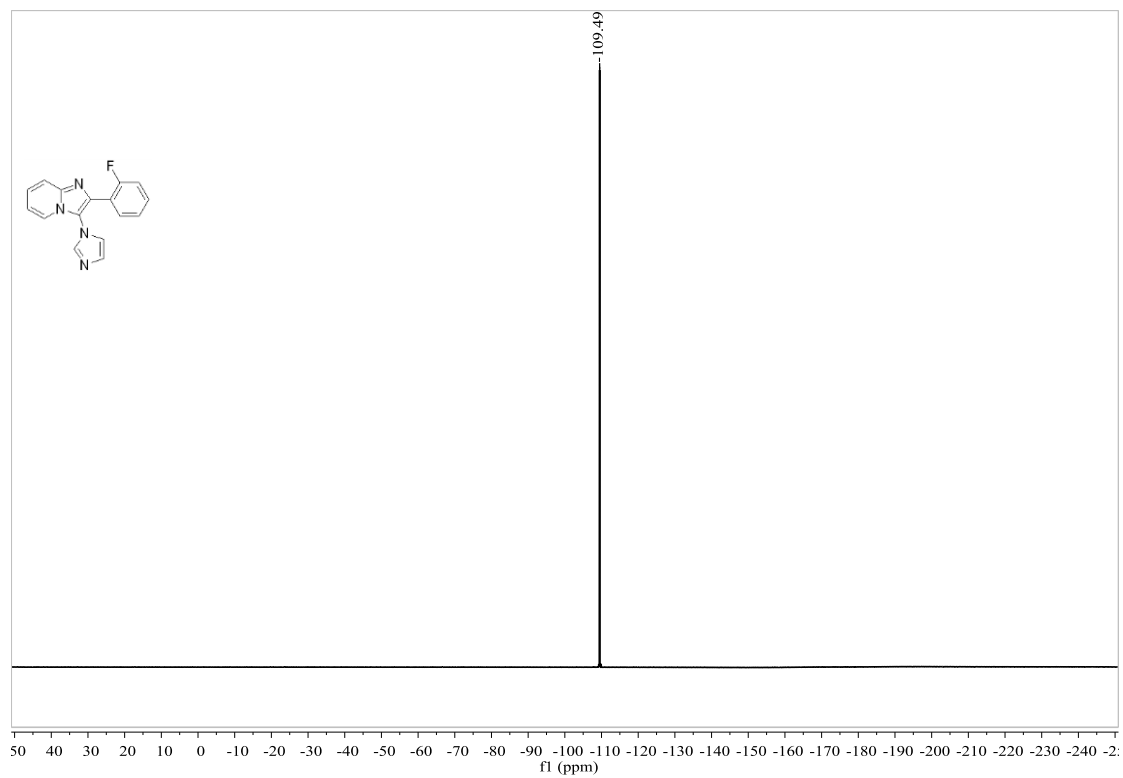
<sup>1</sup>H NMR of compound **3e**



<sup>13</sup>C NMR of compound **3e**

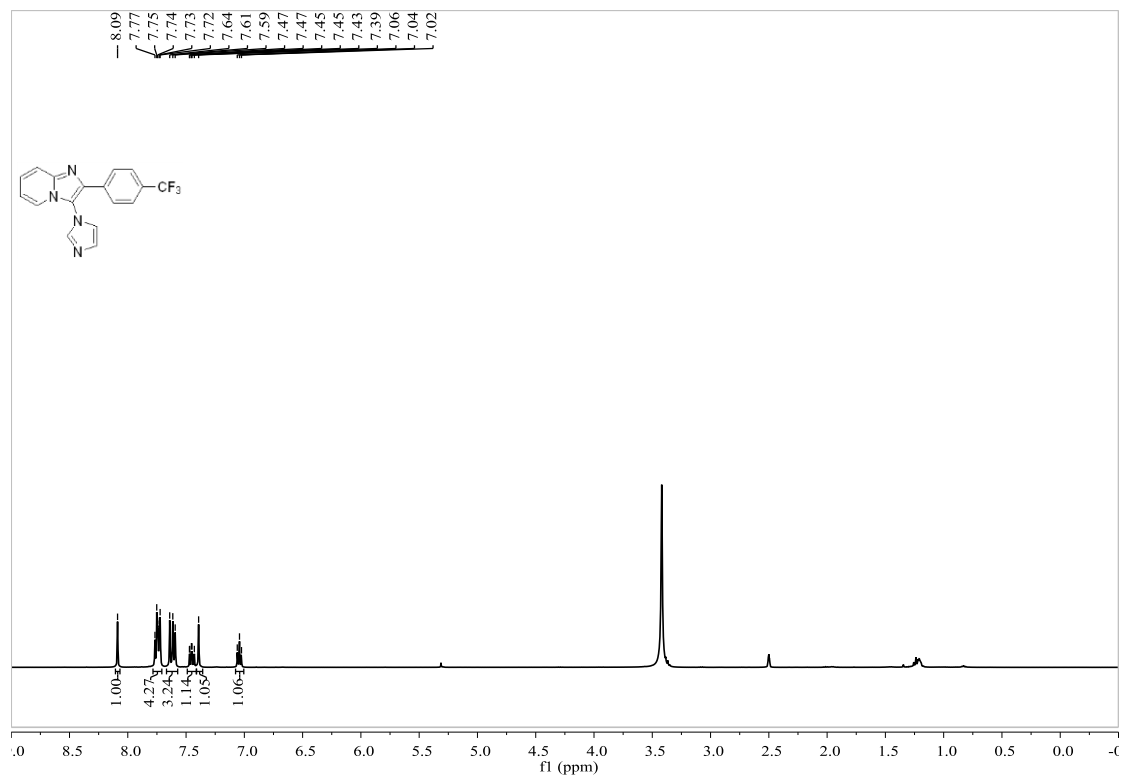


<sup>19</sup>F NMR of compound **3e**

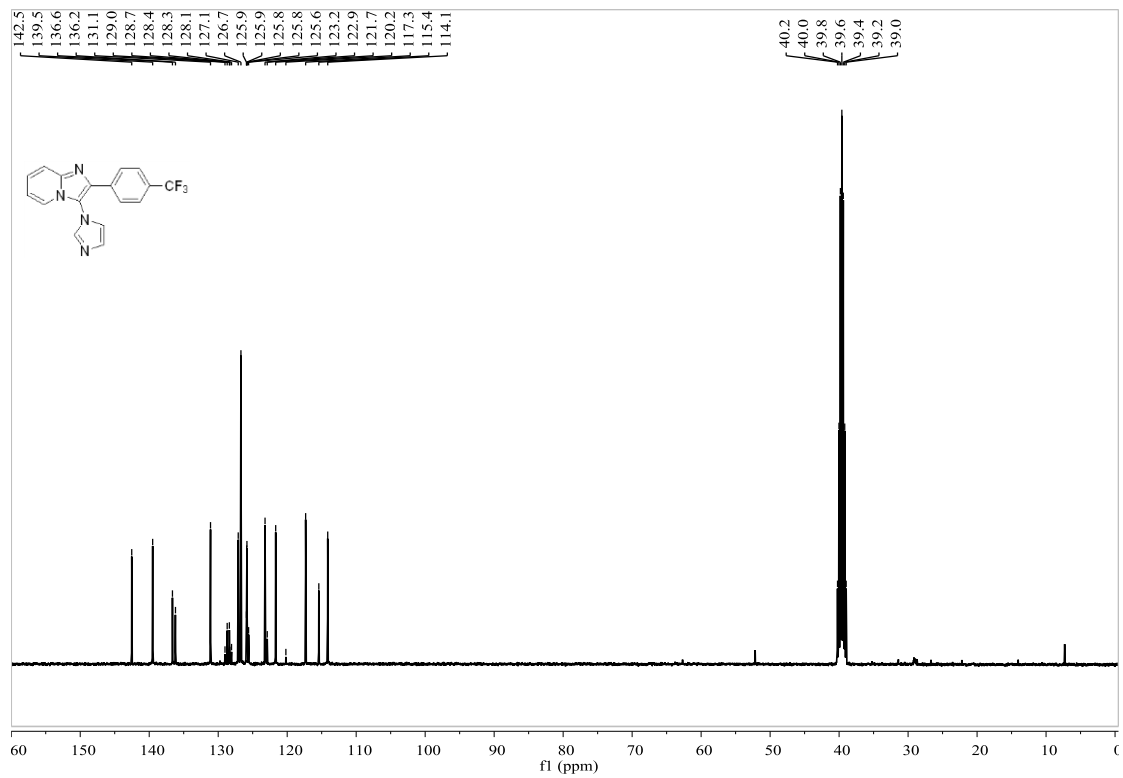




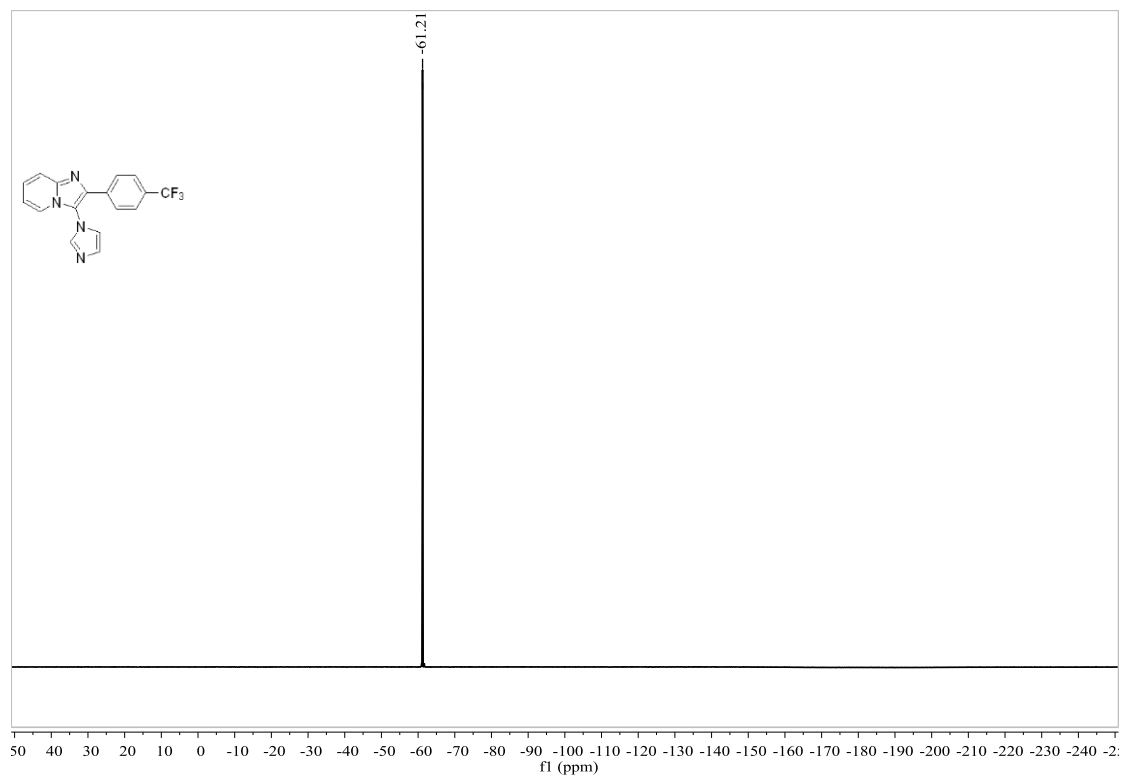
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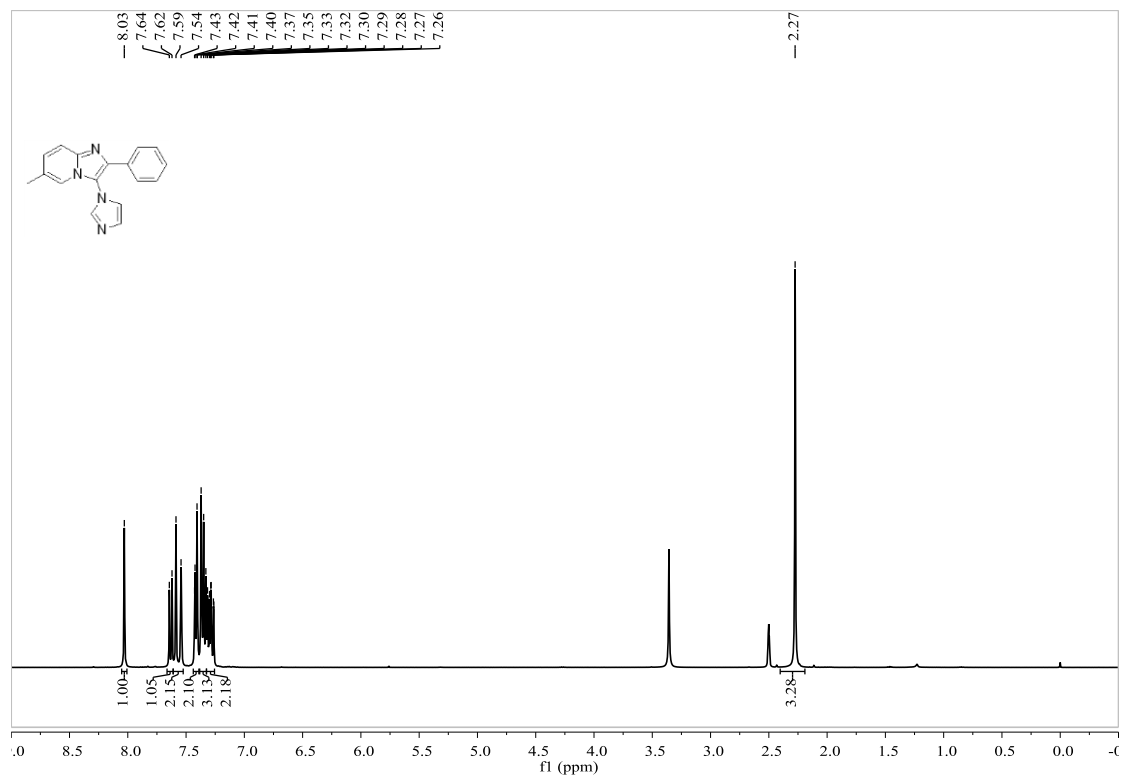
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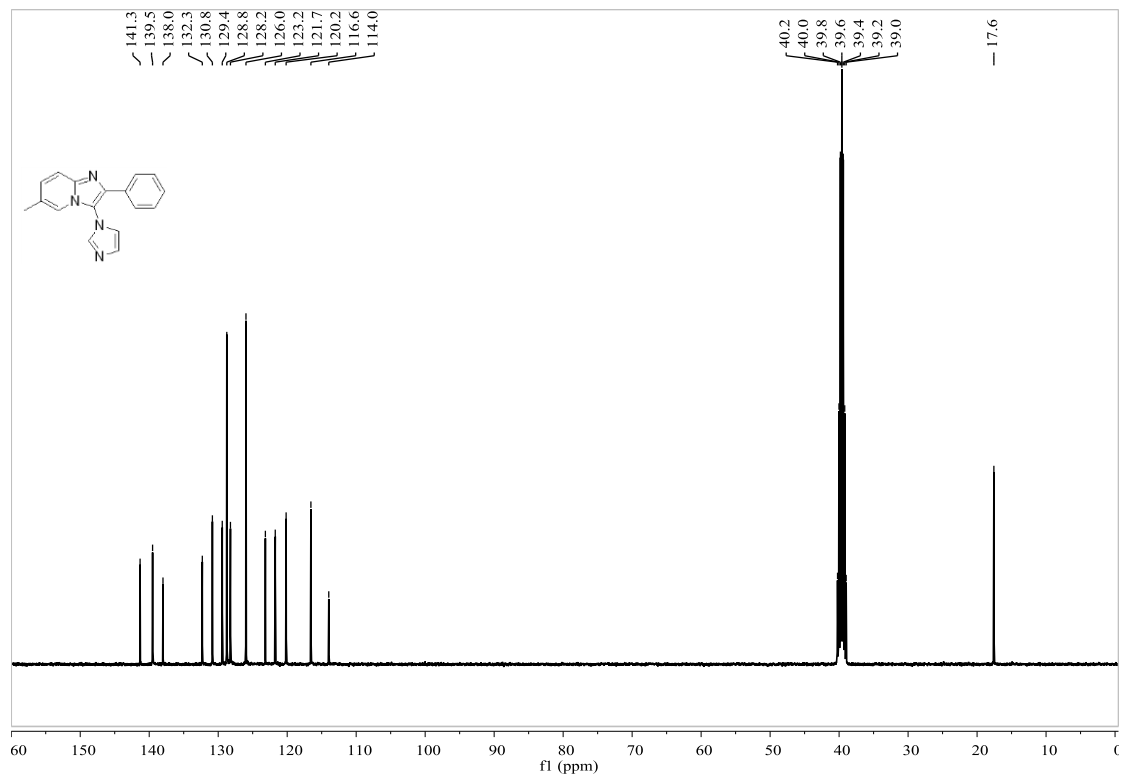
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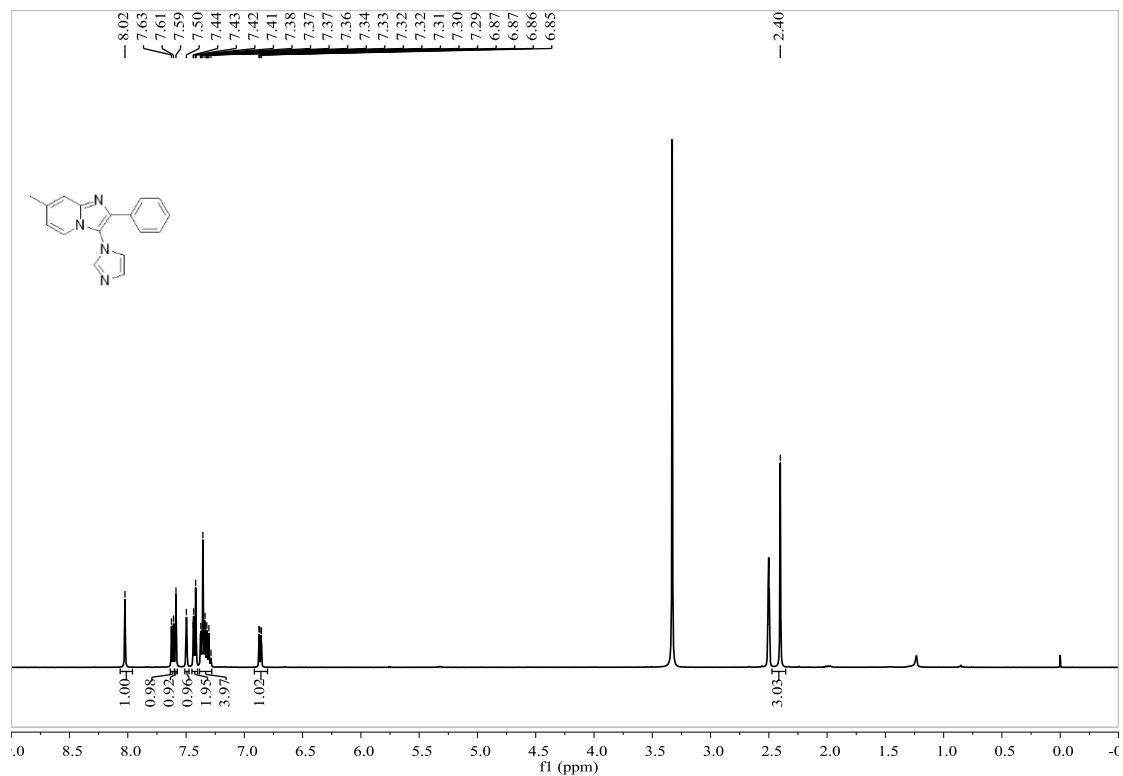
<sup>1</sup>H NMR of compound **3g**



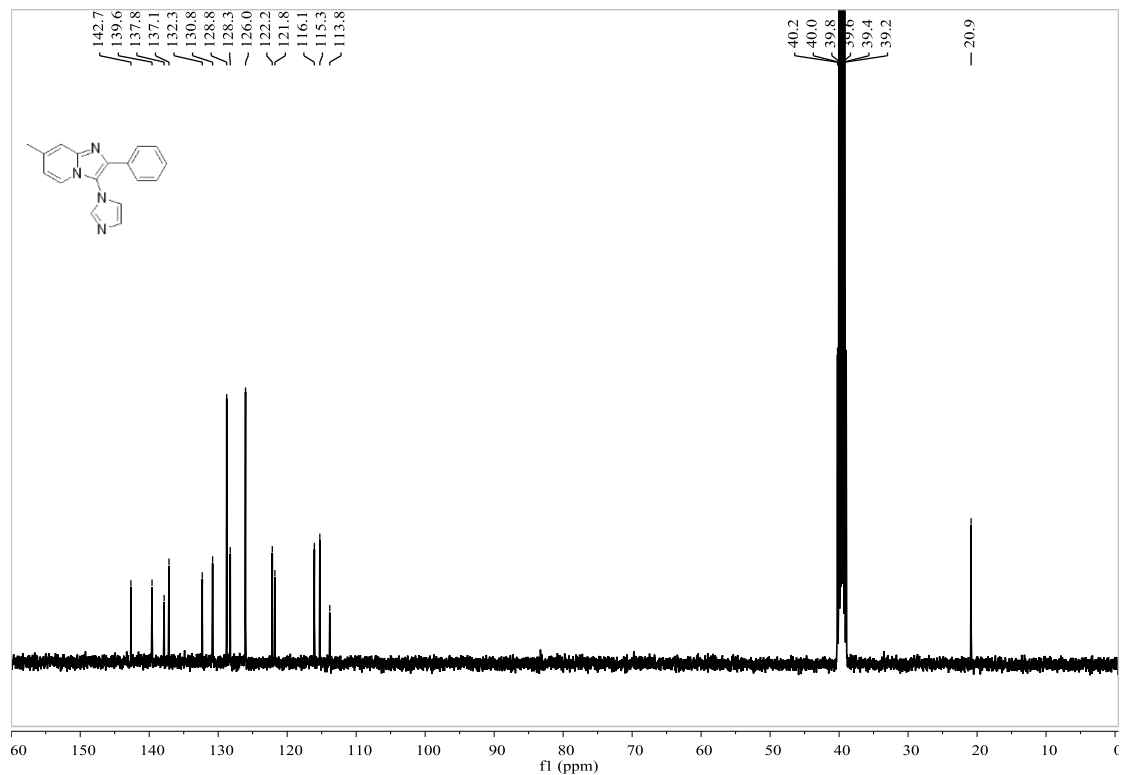
<sup>13</sup>C NMR of compound **3g**



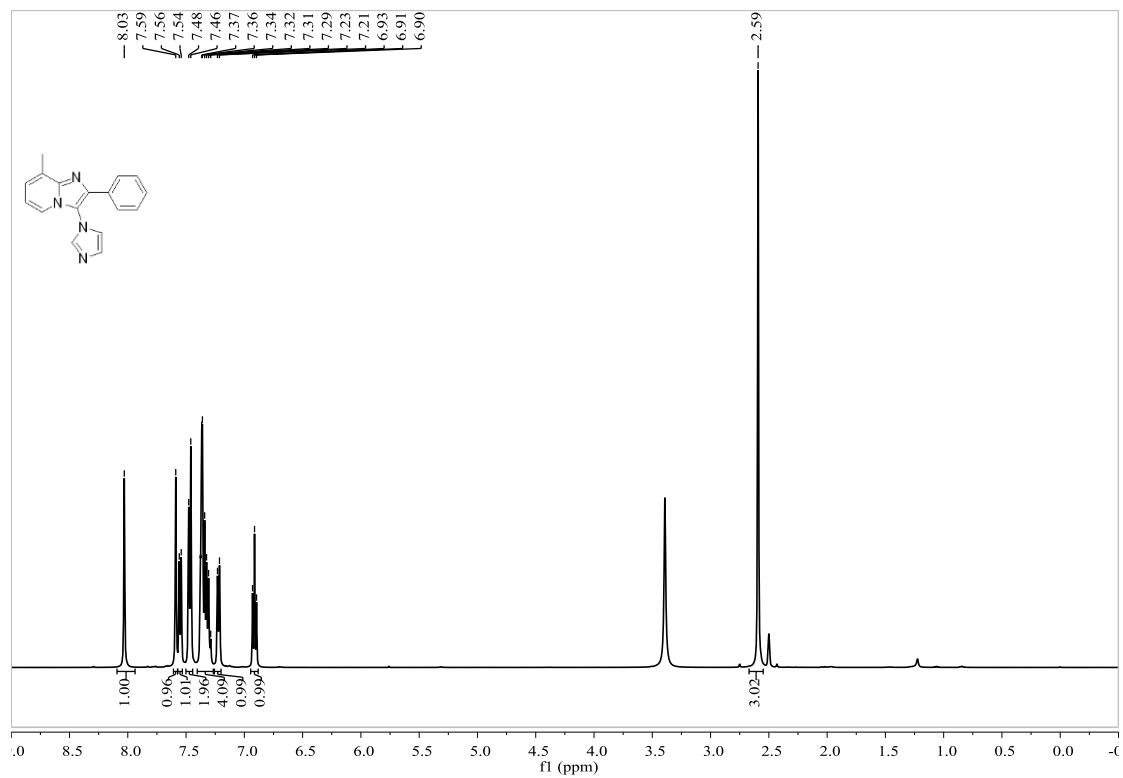
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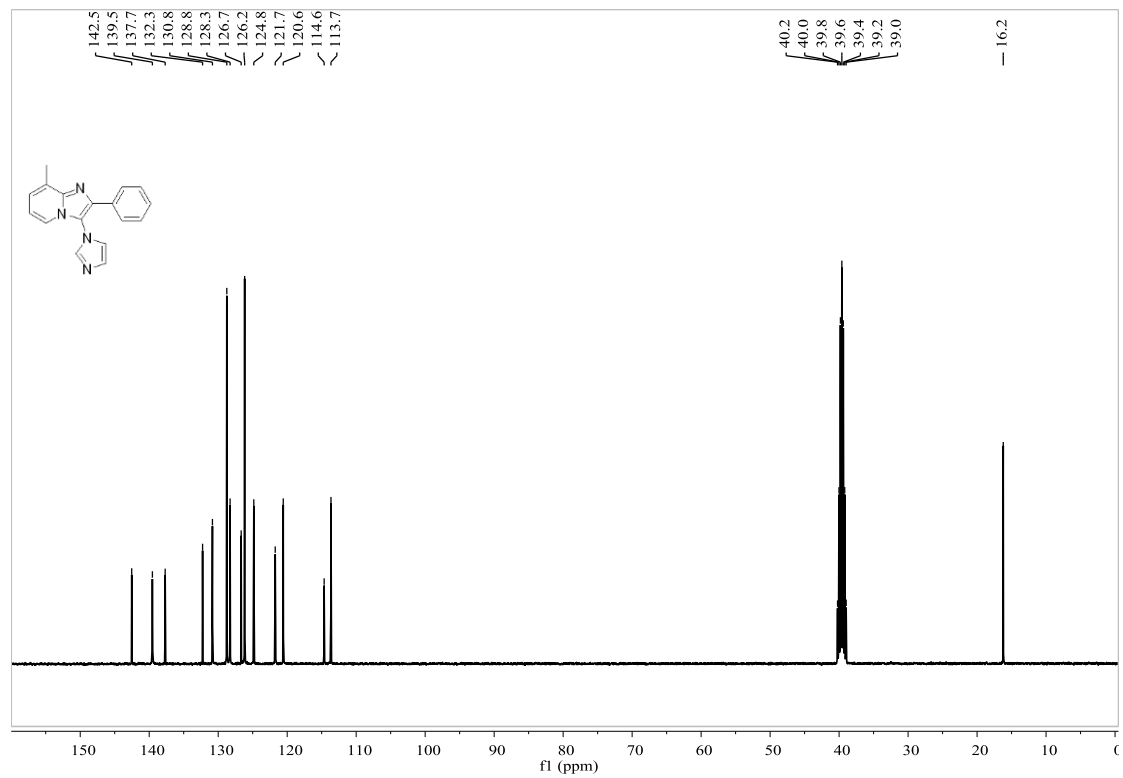
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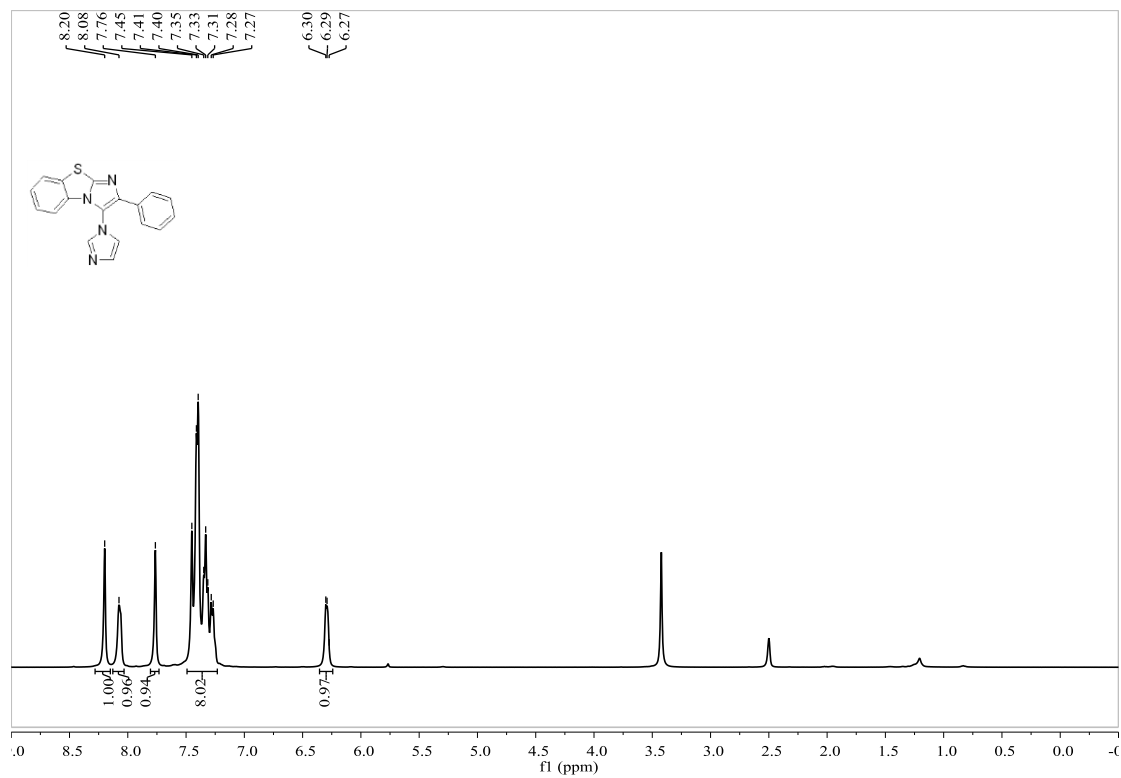
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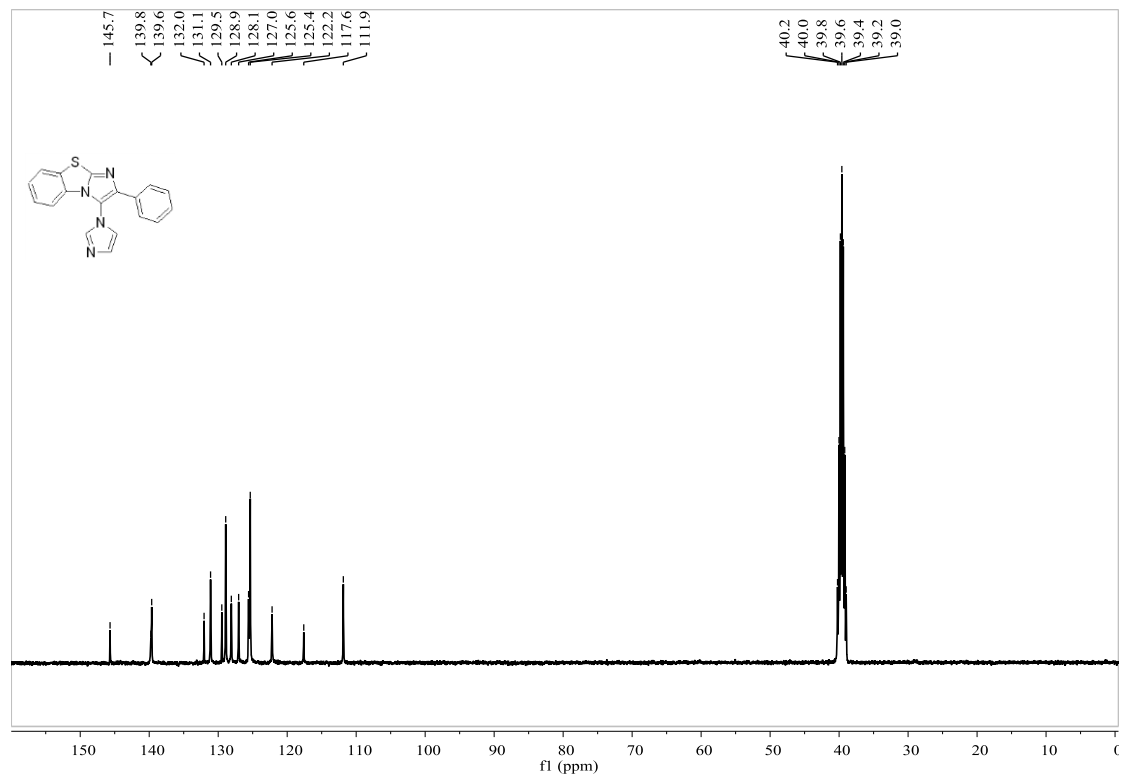
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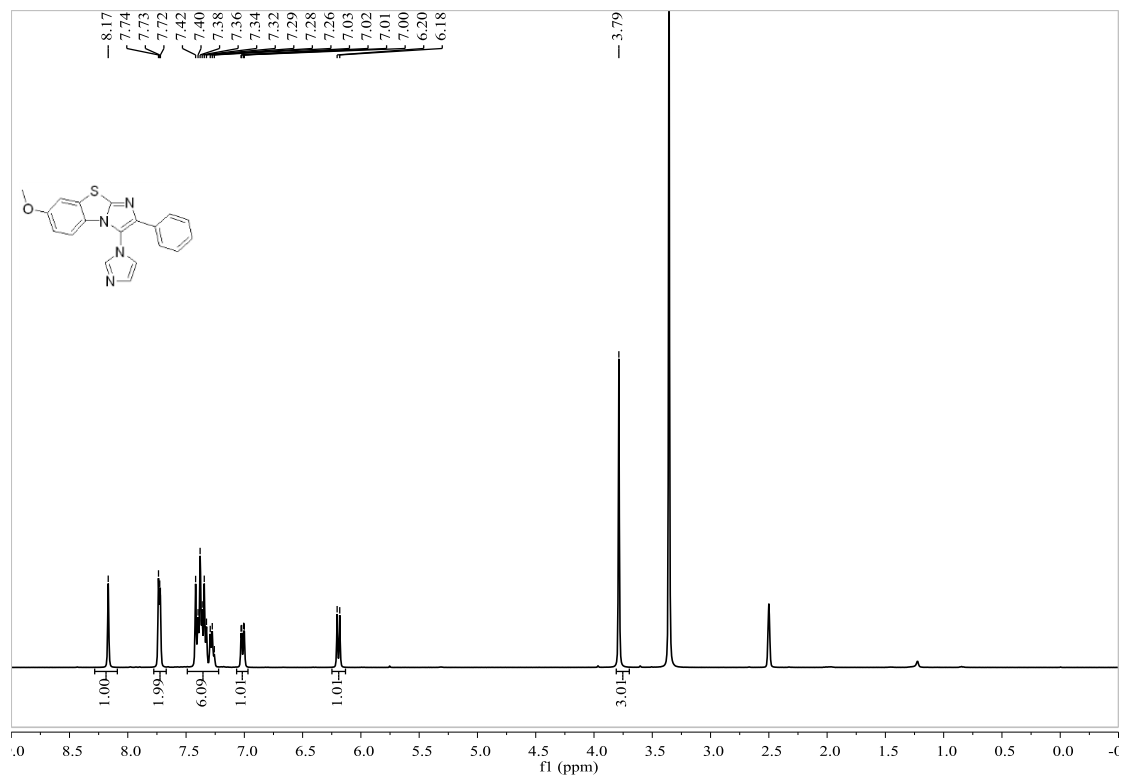
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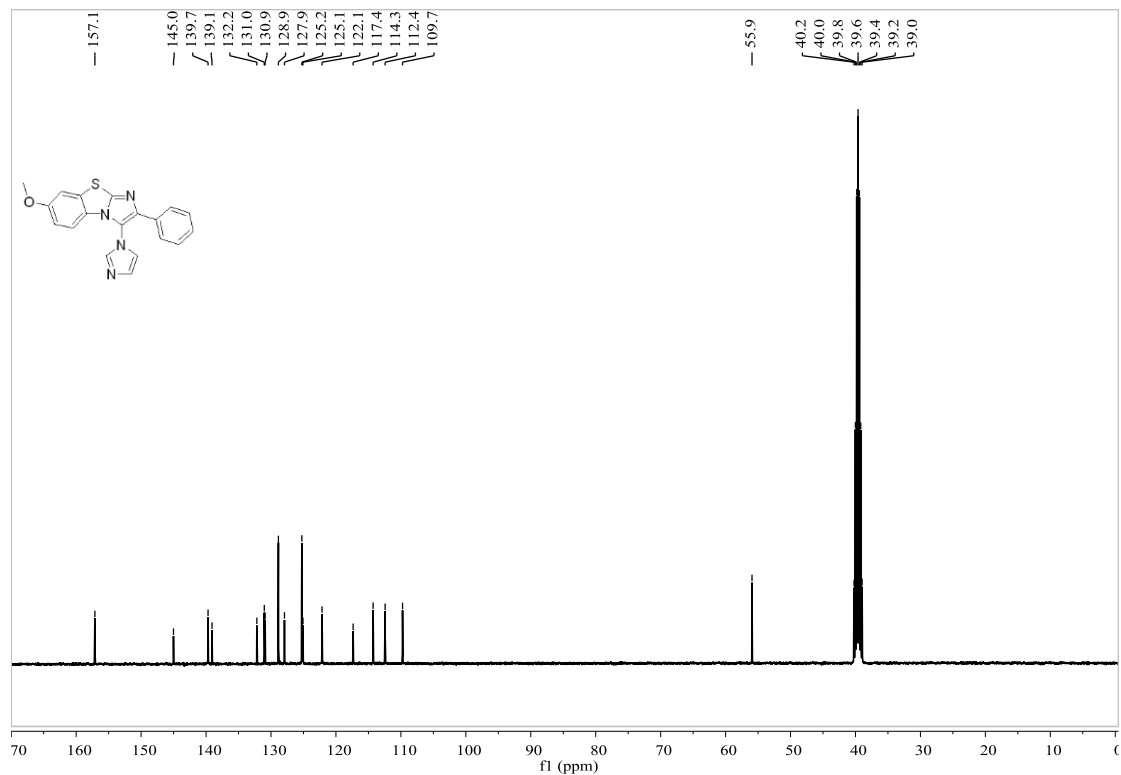
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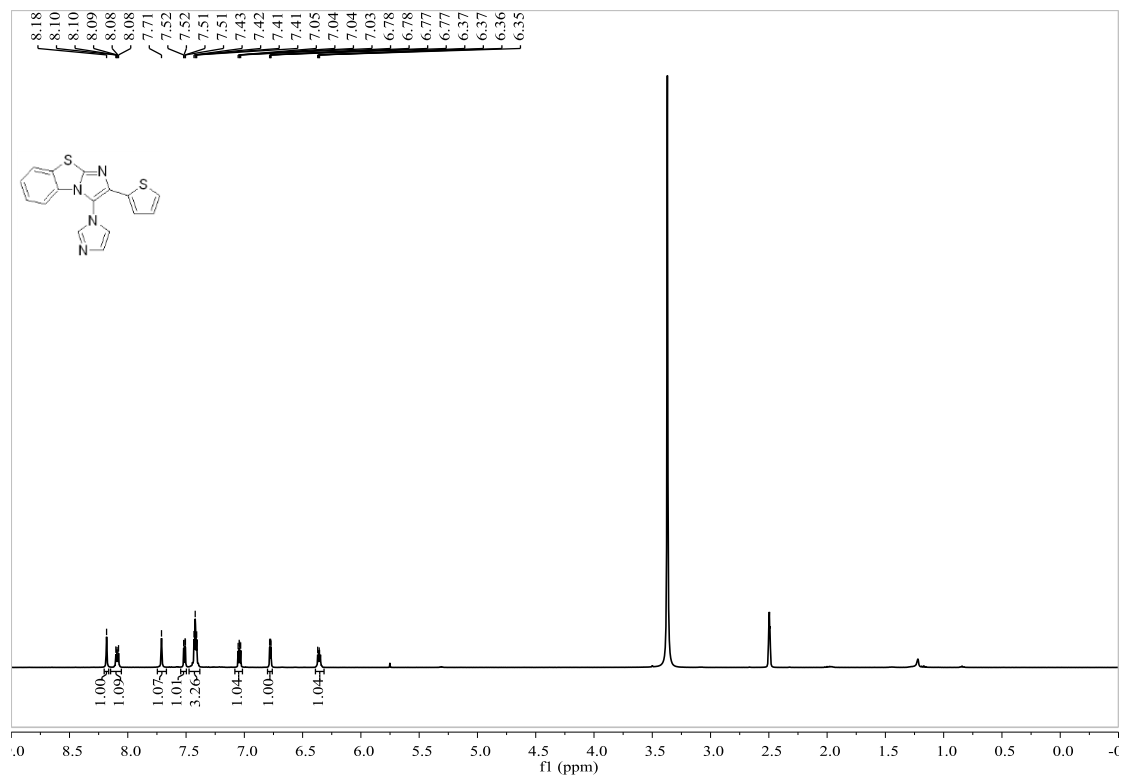
<sup>1</sup>H NMR of compound **3k**



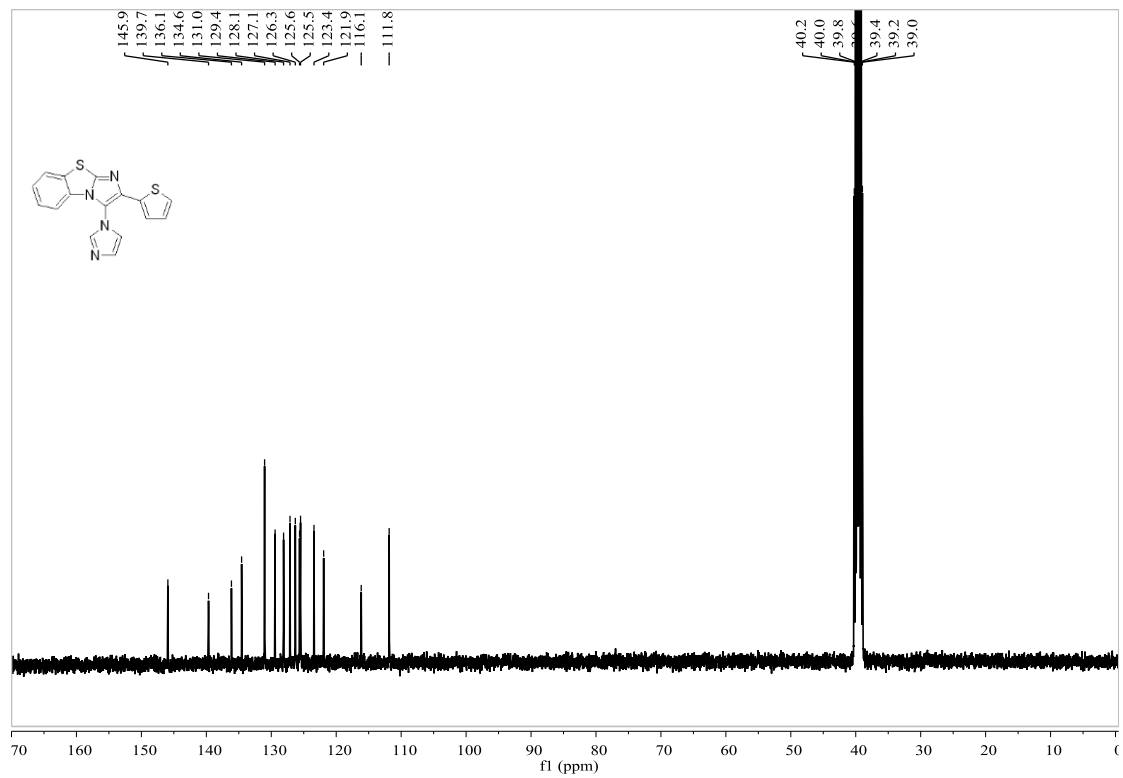
<sup>13</sup>C NMR of compound **3k**



<sup>1</sup>H NMR of compound **31**

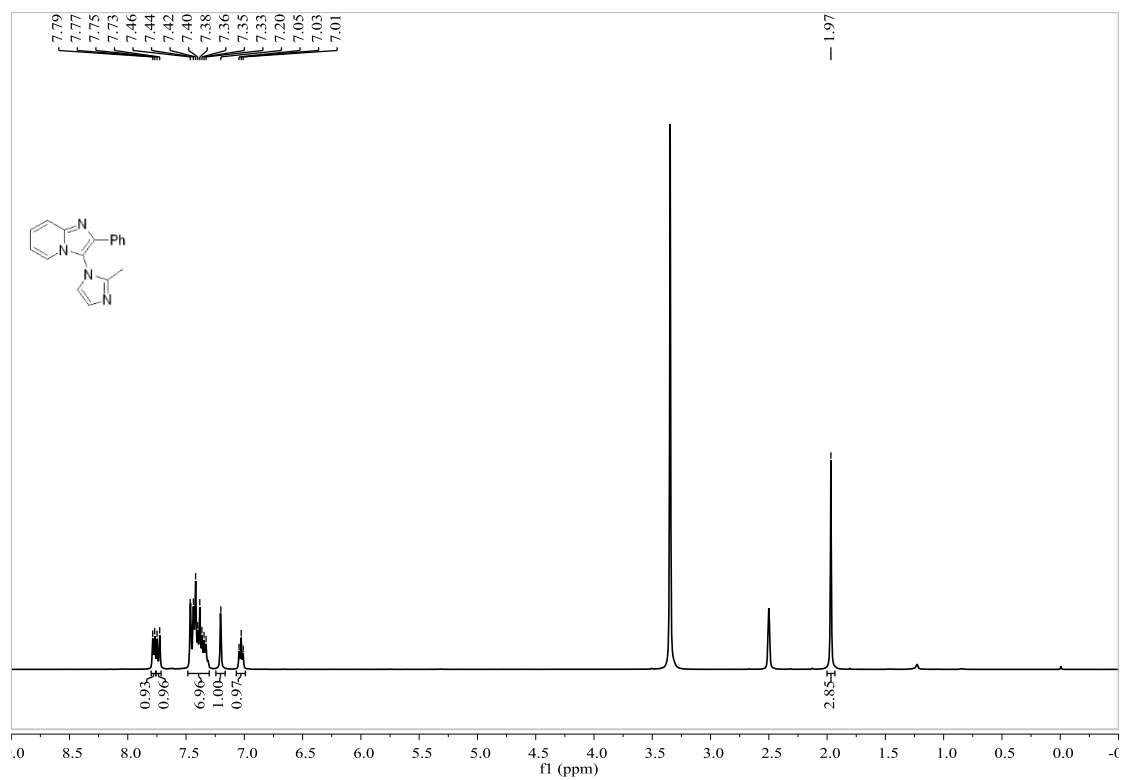


<sup>13</sup>C NMR of compound **31**

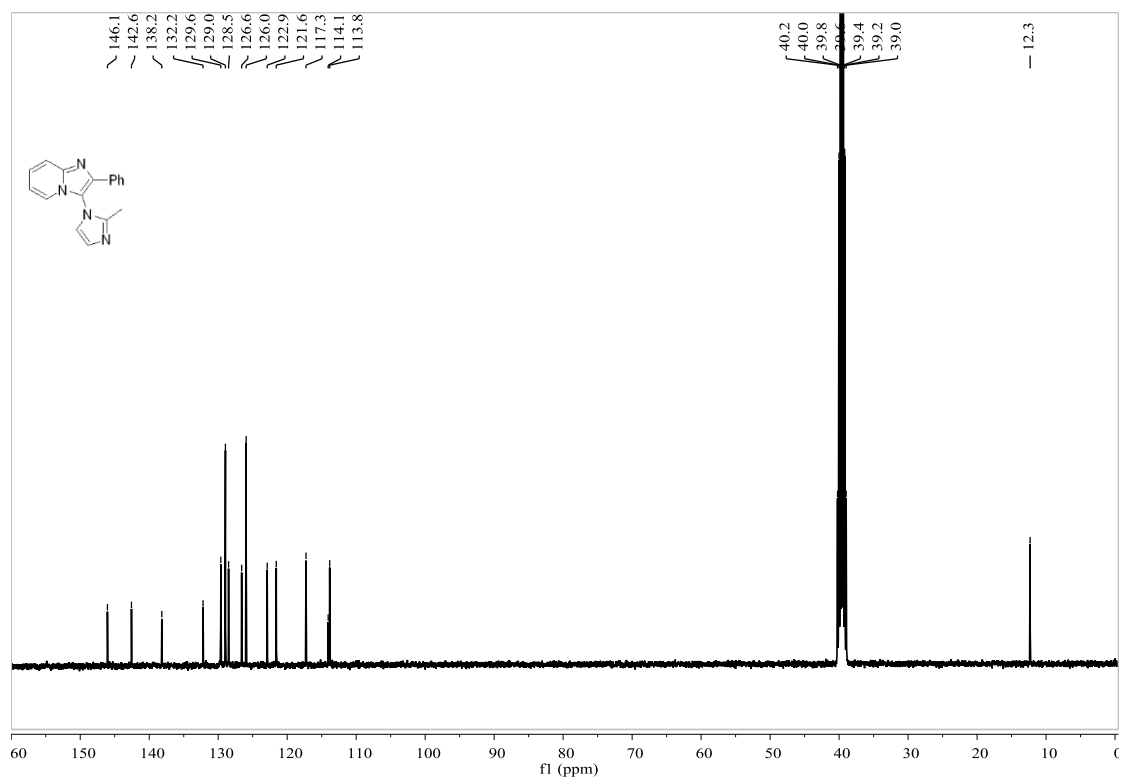




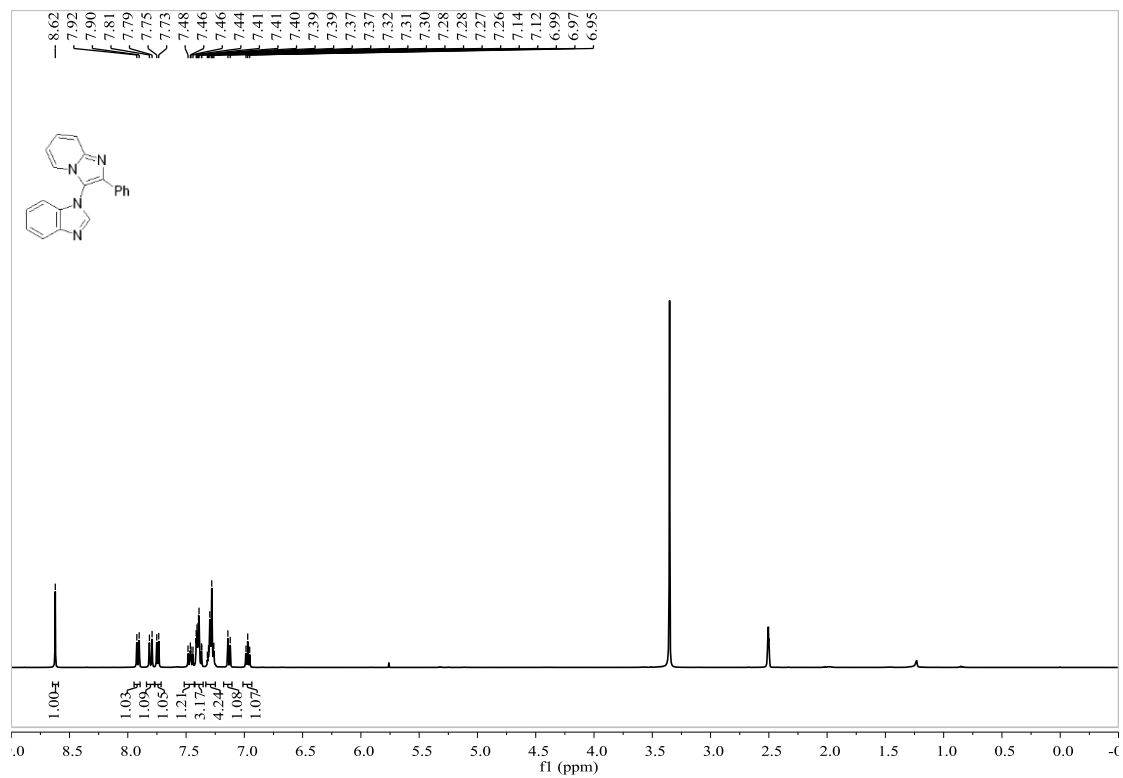
<sup>1</sup>H NMR of compound **3m**



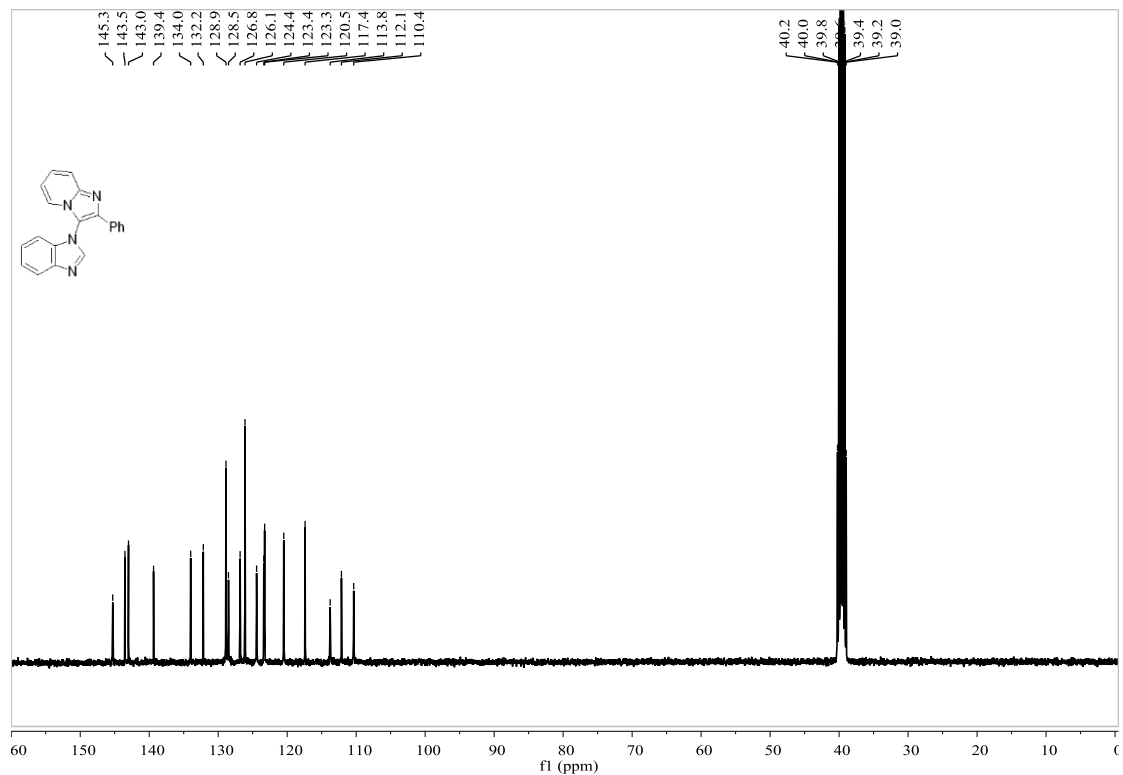
<sup>13</sup>C NMR of compound **3m**



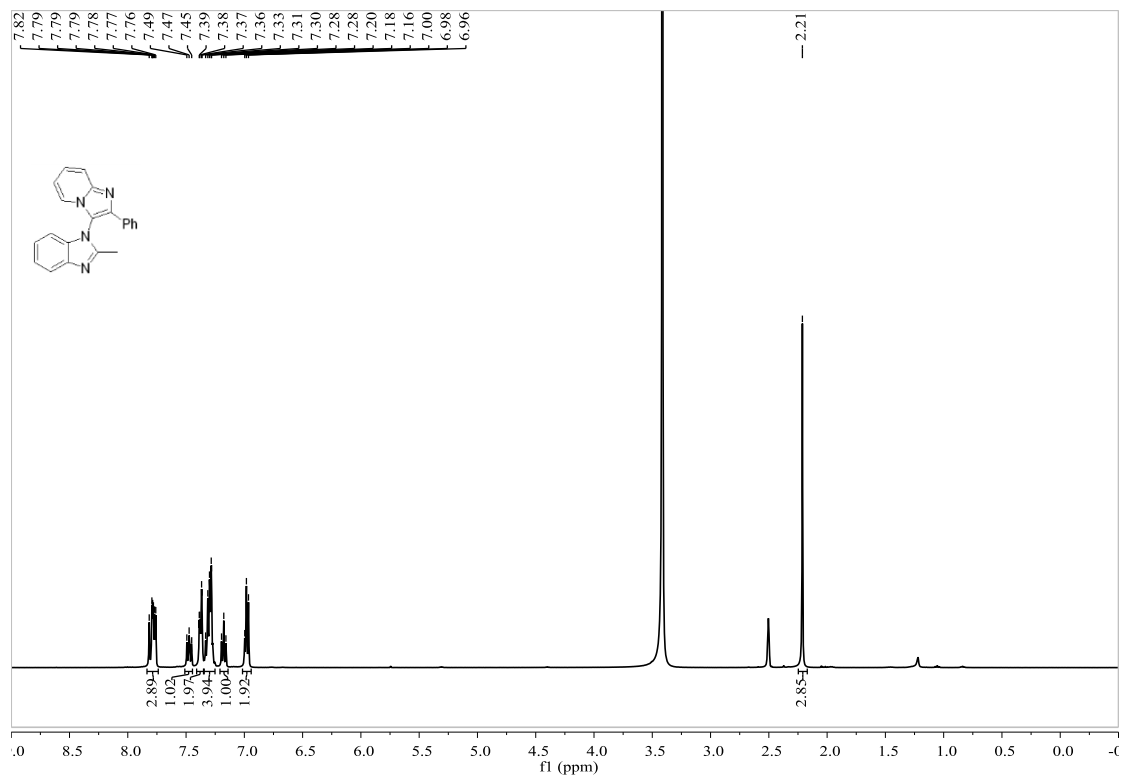
<sup>1</sup>H NMR of compound **3n**



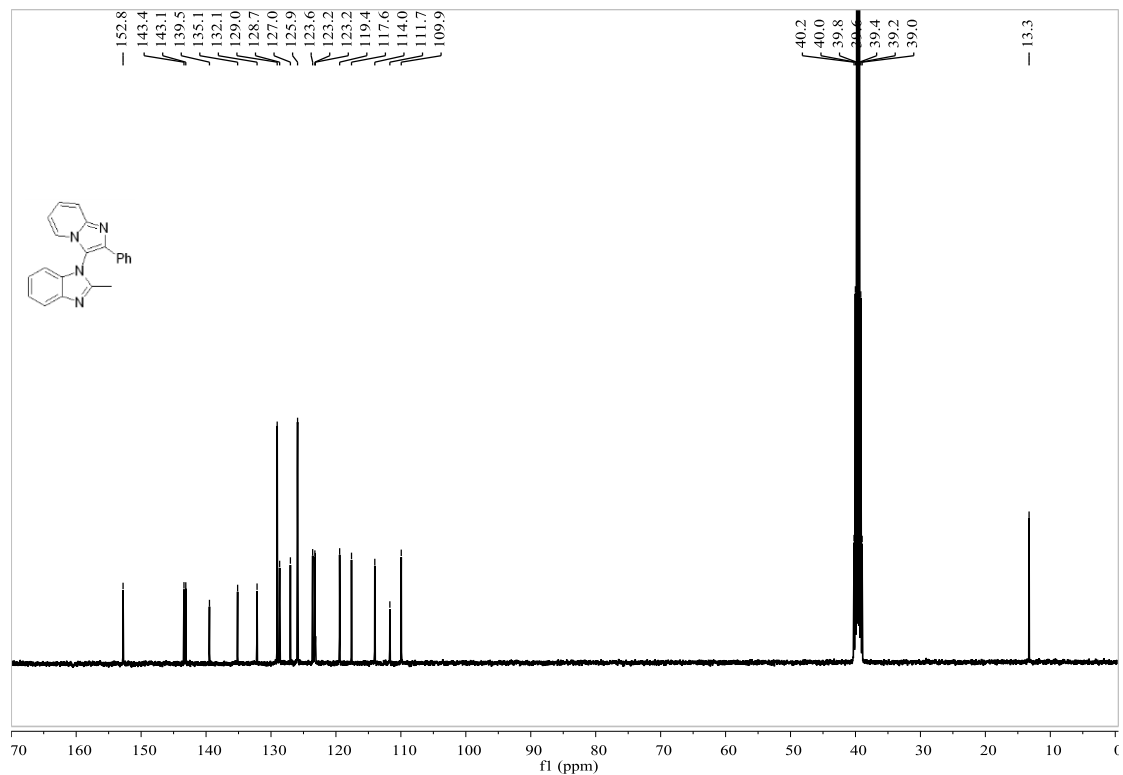
<sup>13</sup>C NMR of compound **3n**



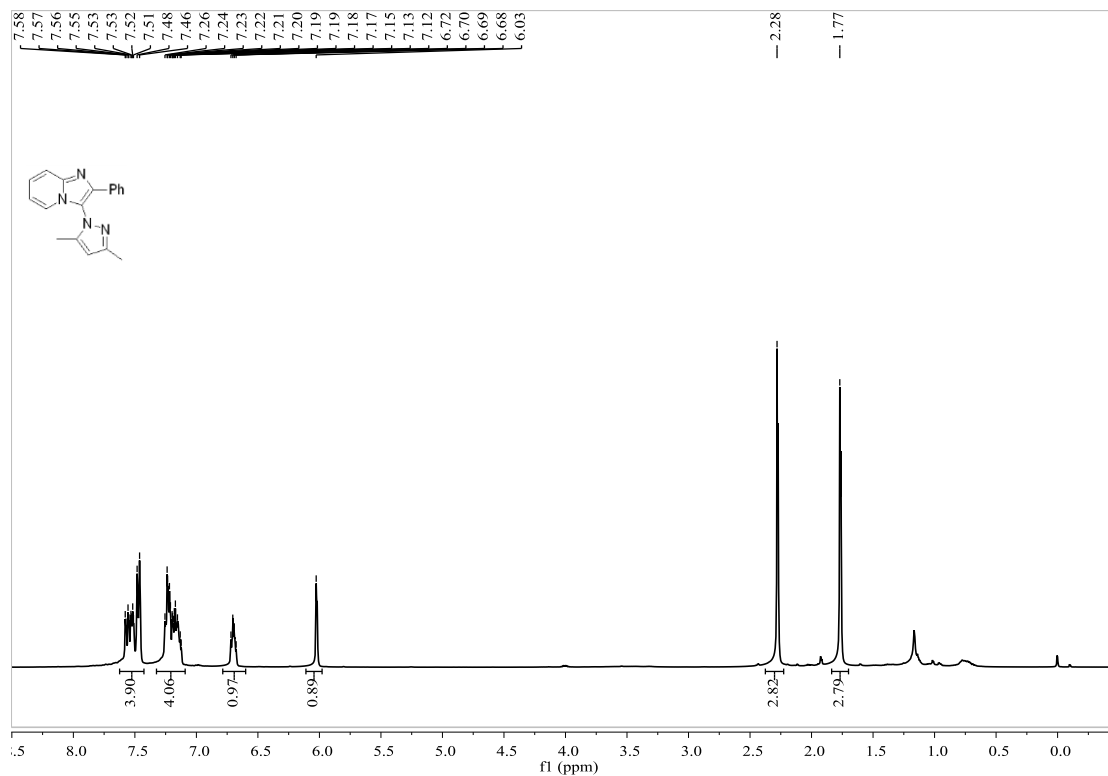
<sup>1</sup>H NMR of compound **3o**



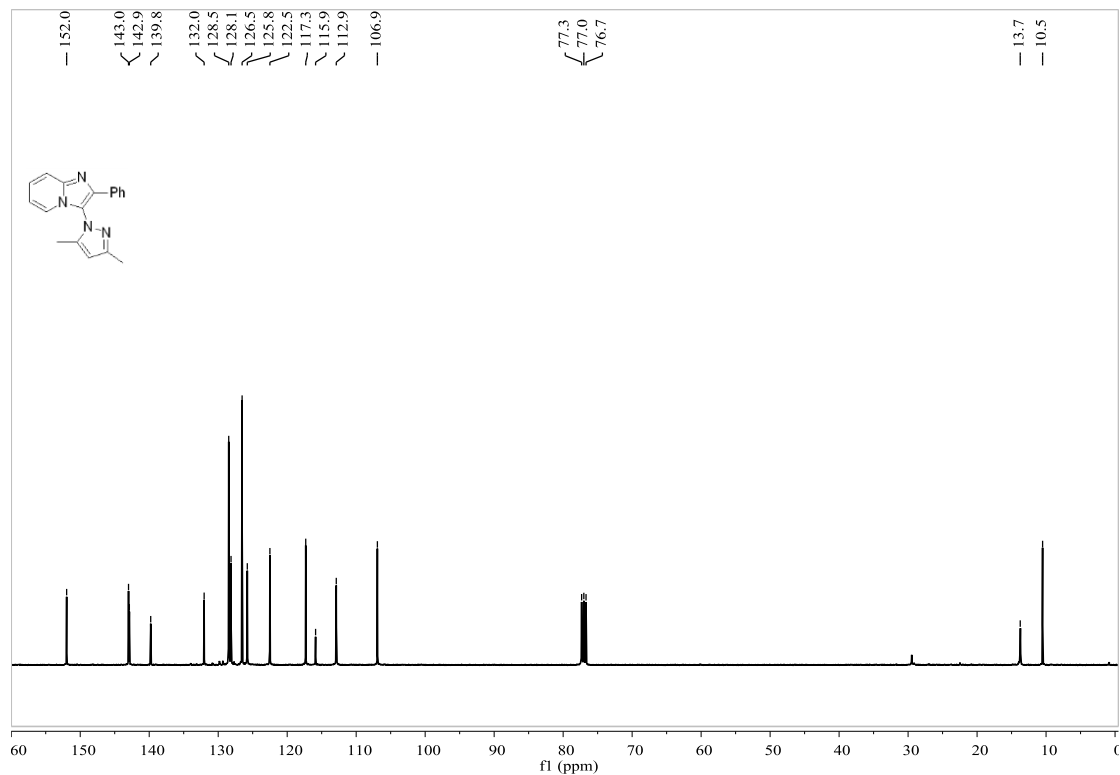
<sup>13</sup>C NMR of compound **3o**



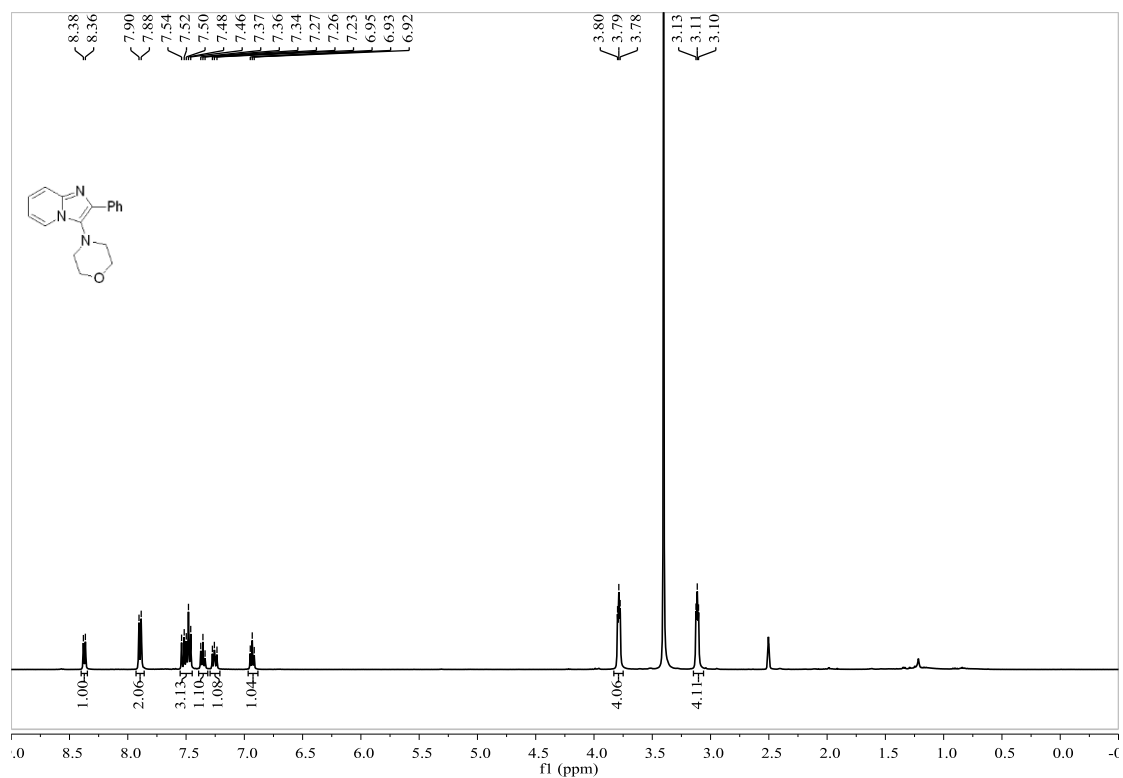
<sup>1</sup>H NMR of compound **3p**



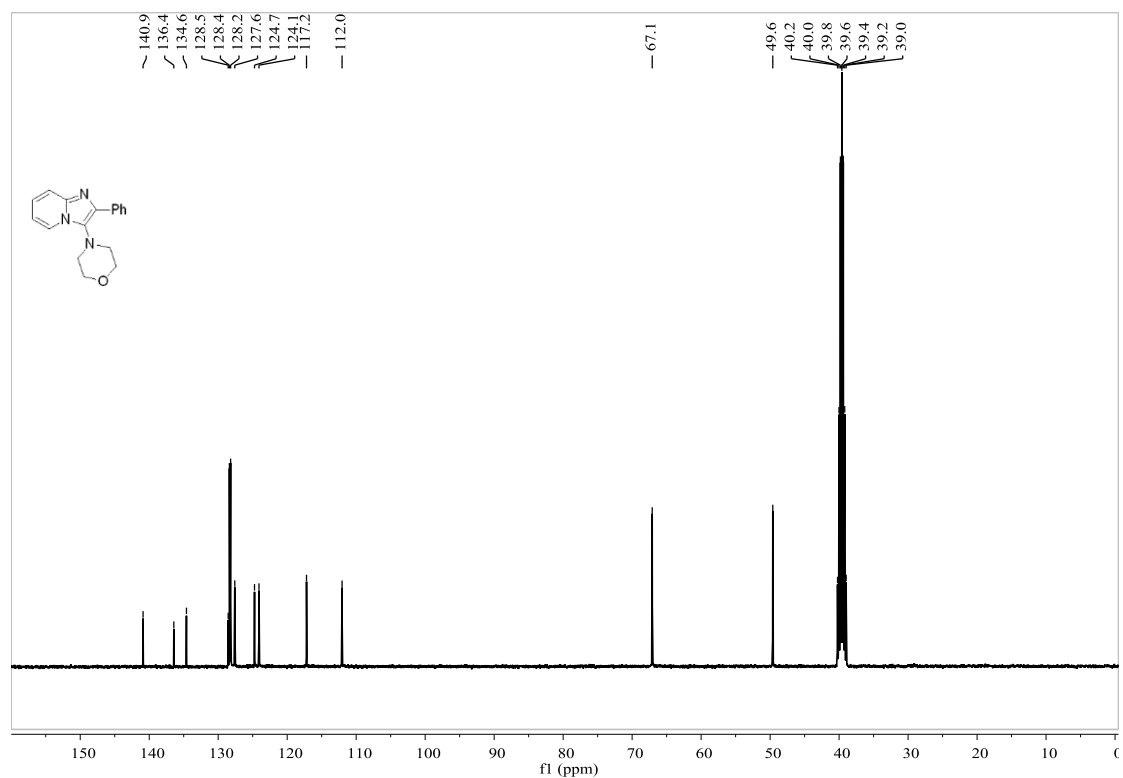
<sup>13</sup>C NMR of compound **3p**



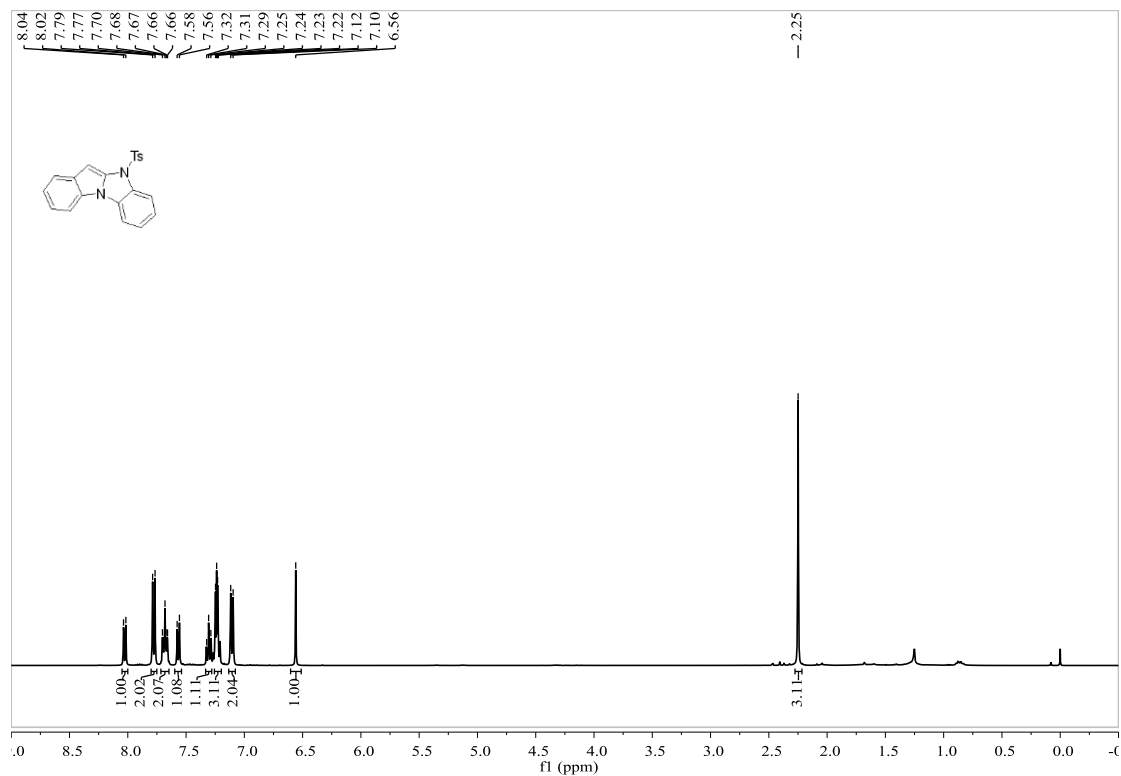
<sup>1</sup>H NMR of compound **3q**



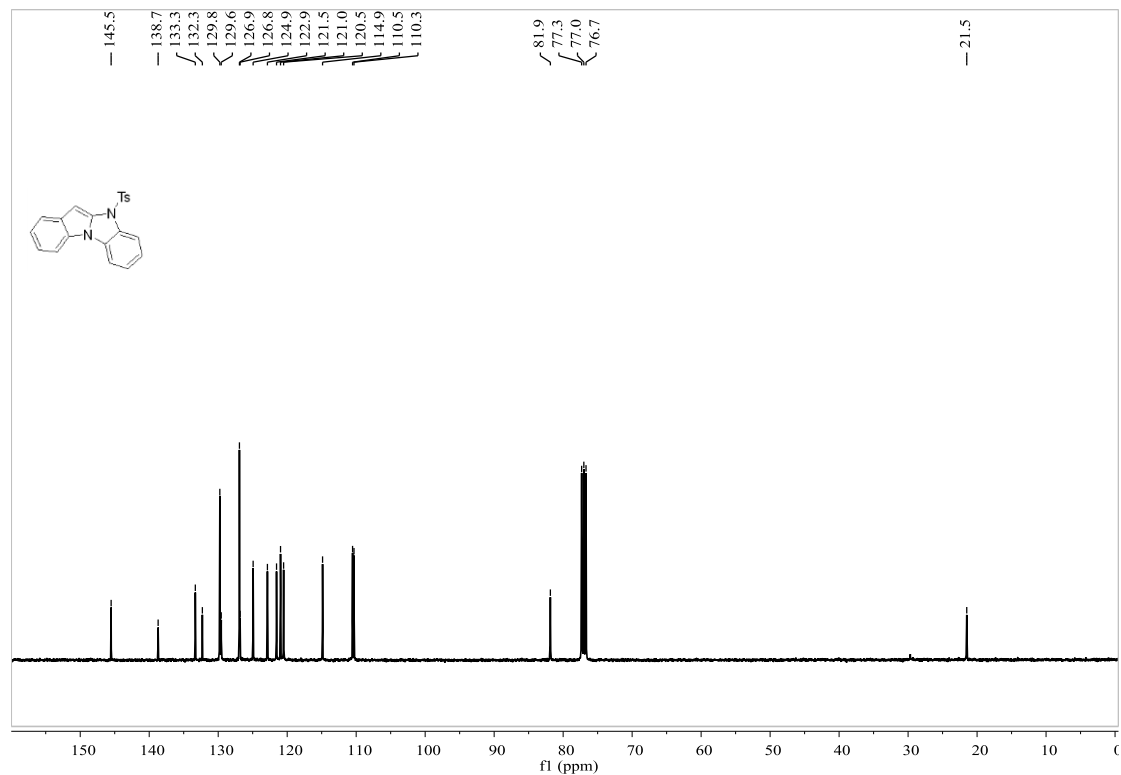
<sup>13</sup>C NMR of compound **3q**



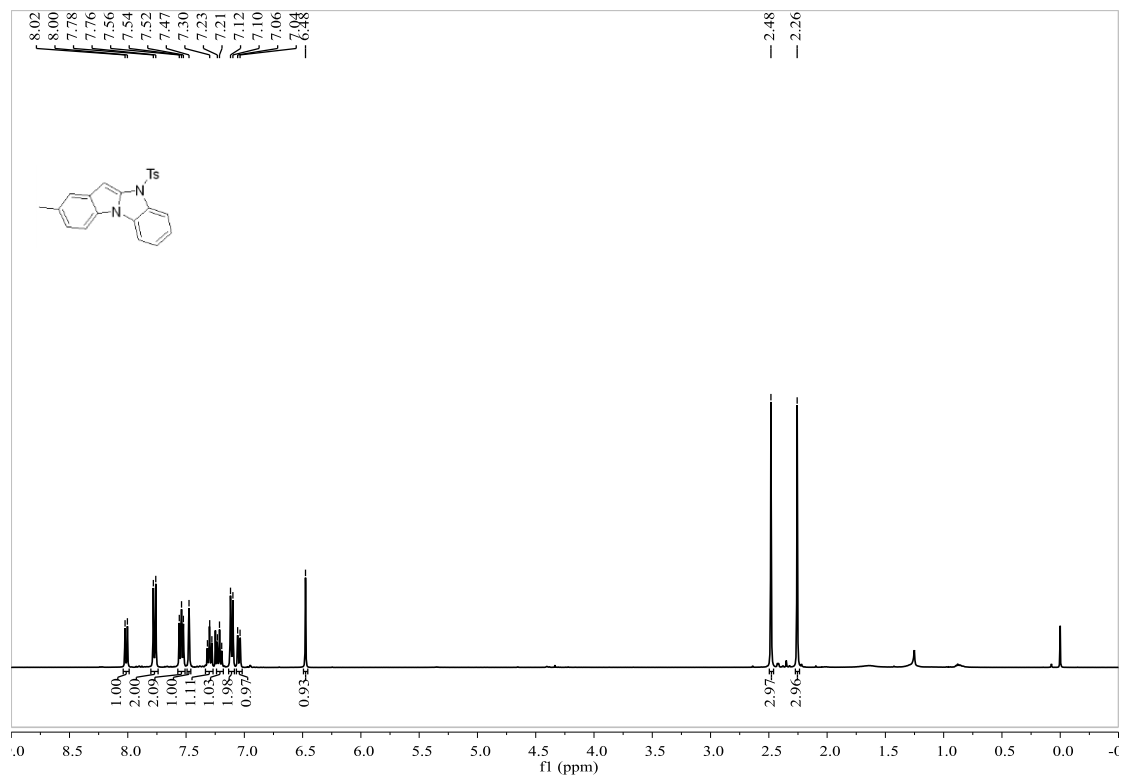
<sup>1</sup>H NMR of compound **5a**



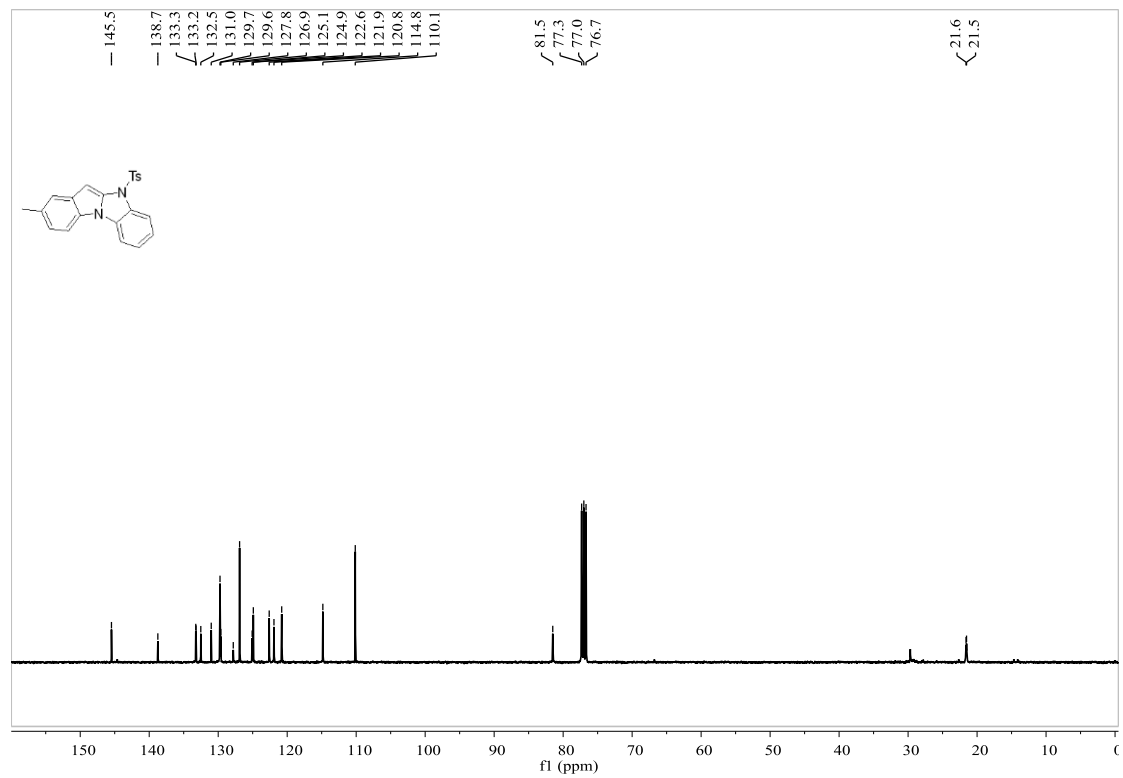
<sup>13</sup>C NMR of compound **5a**



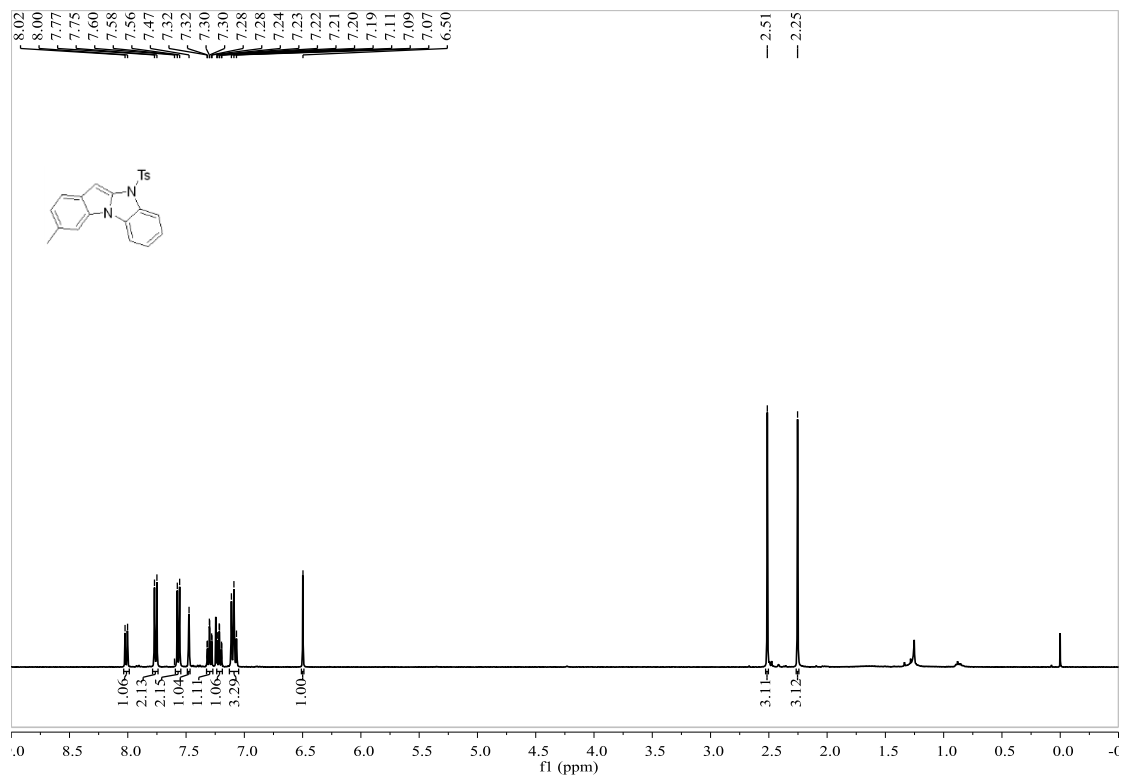
<sup>1</sup>H NMR of compound **5b**



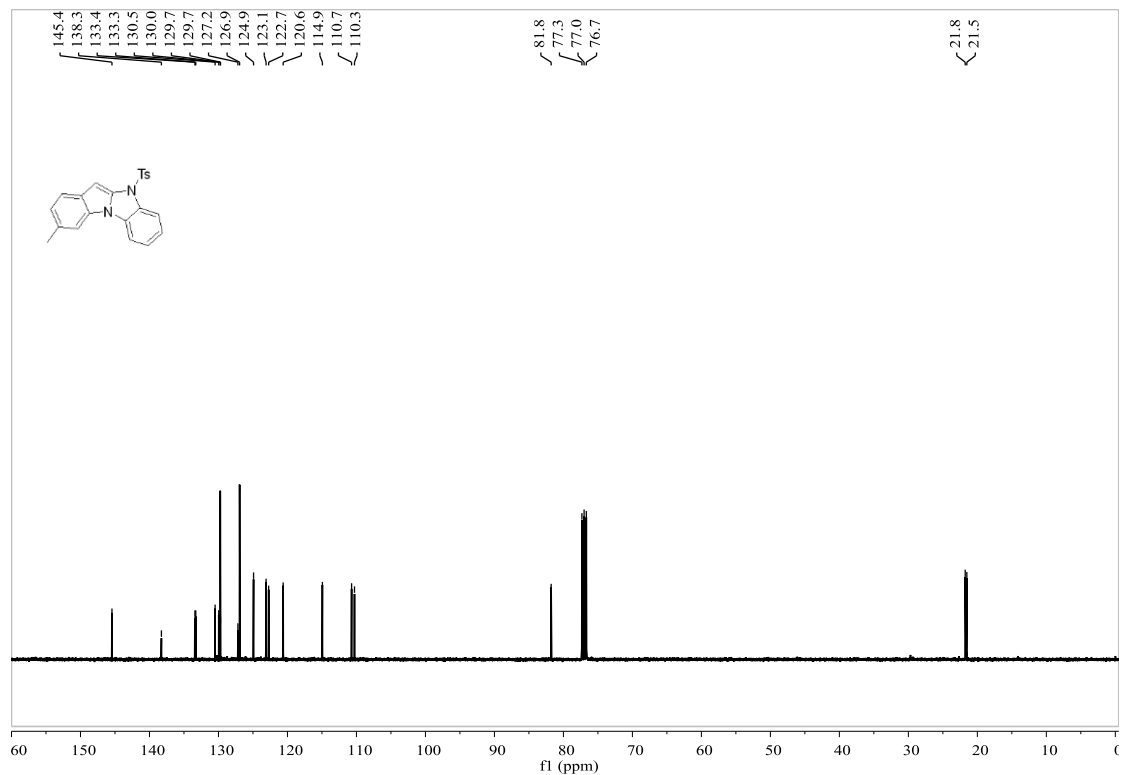
<sup>13</sup>C NMR of compound **5b**



<sup>1</sup>H NMR of compound **5c**

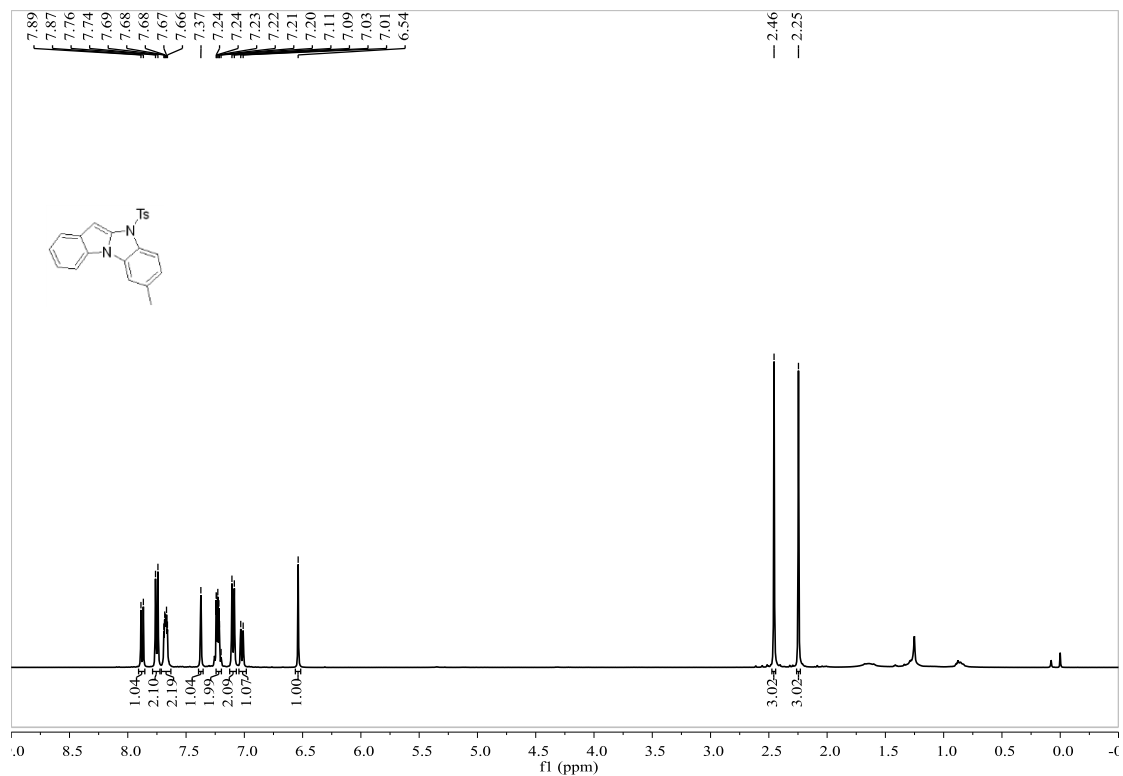


<sup>13</sup>C NMR of compound **5c**

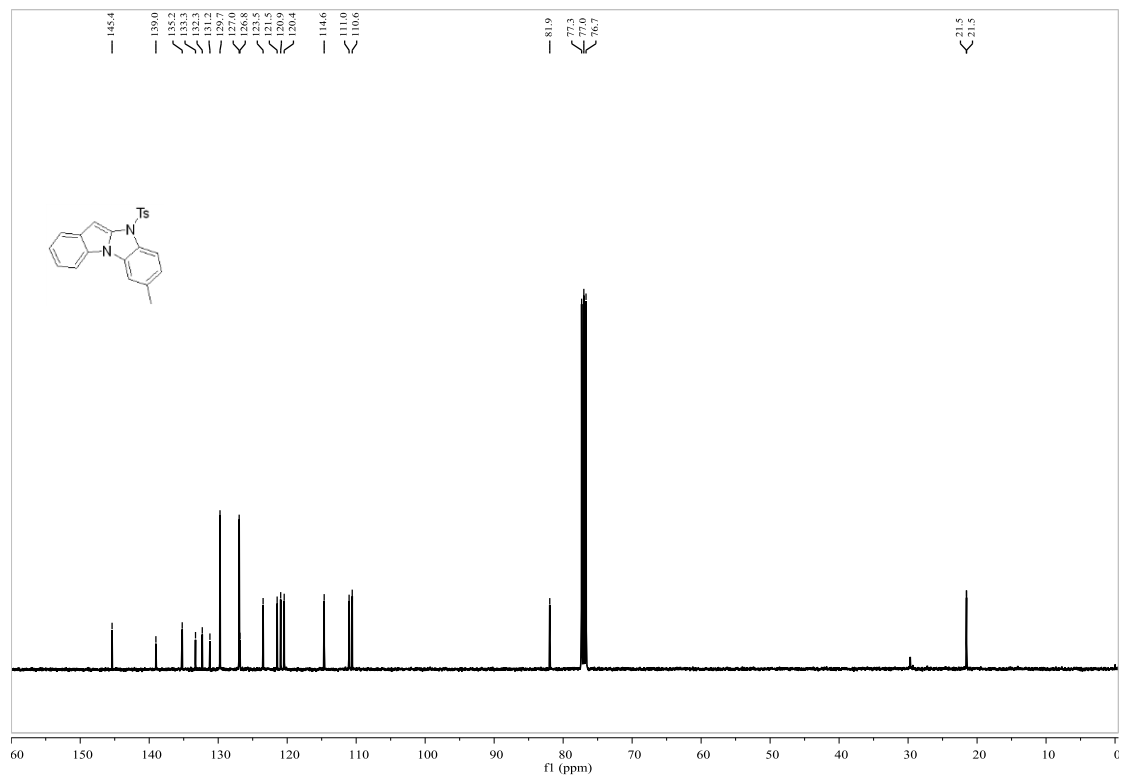




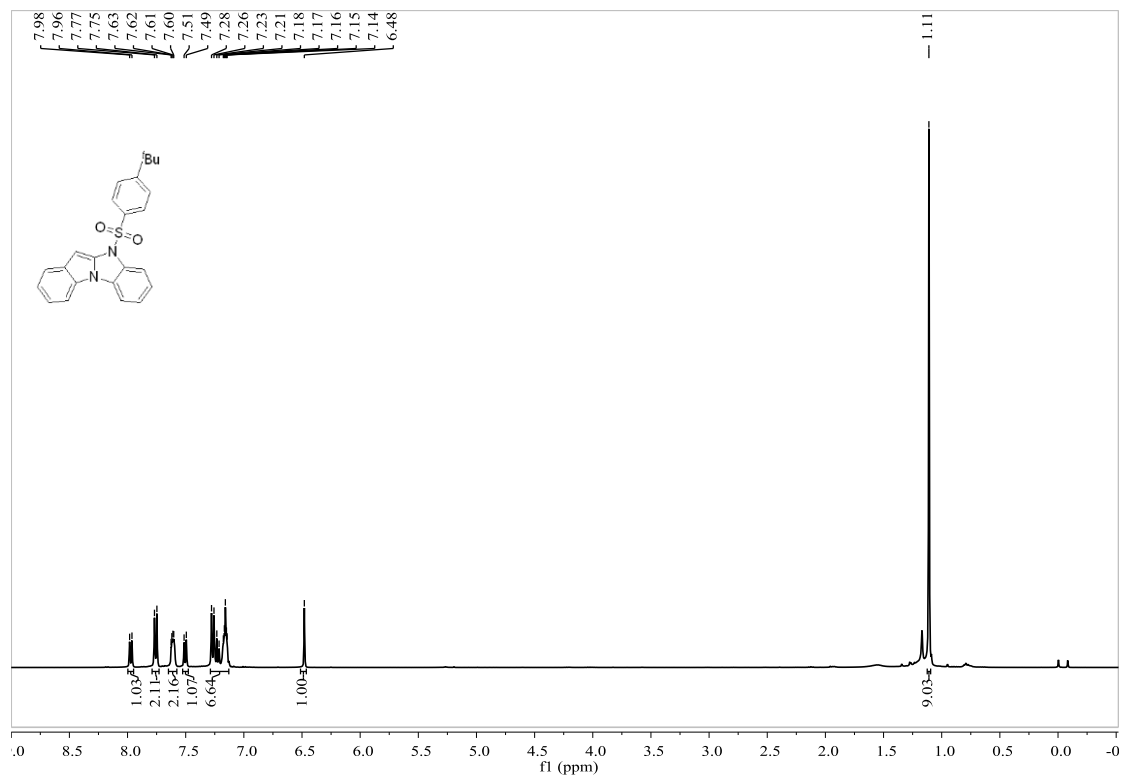
<sup>1</sup>H NMR of compound **5d**



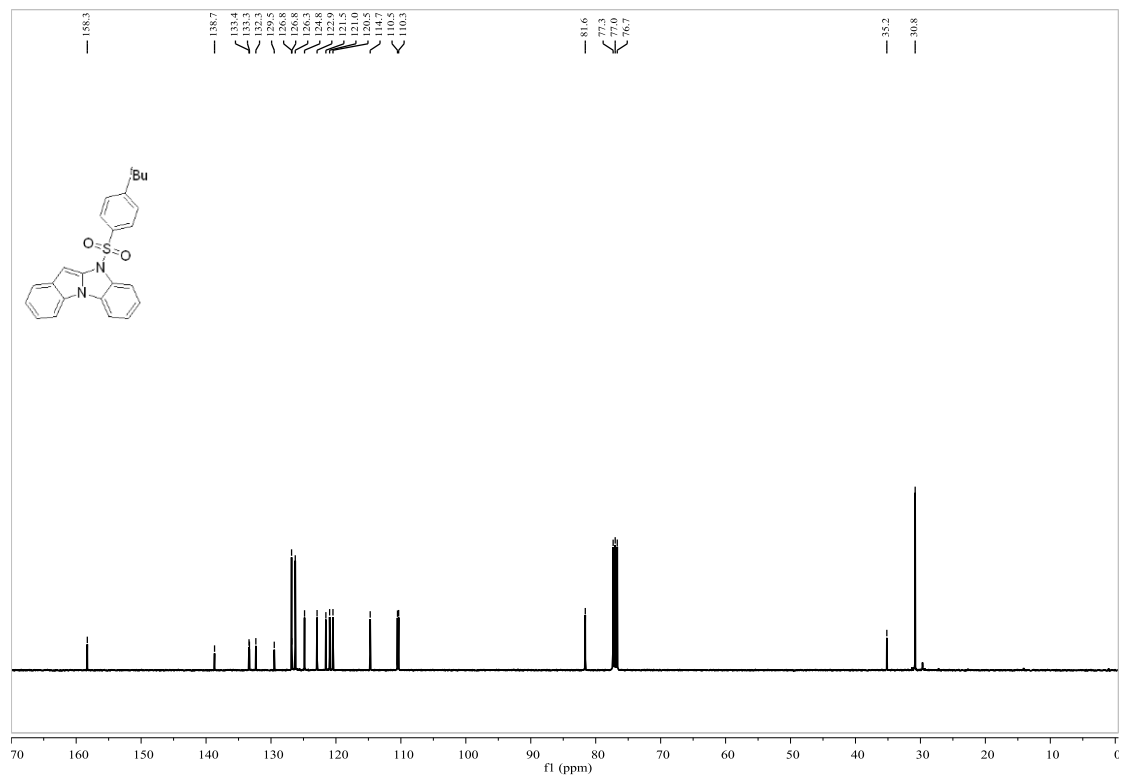
<sup>13</sup>C NMR of compound **5d**



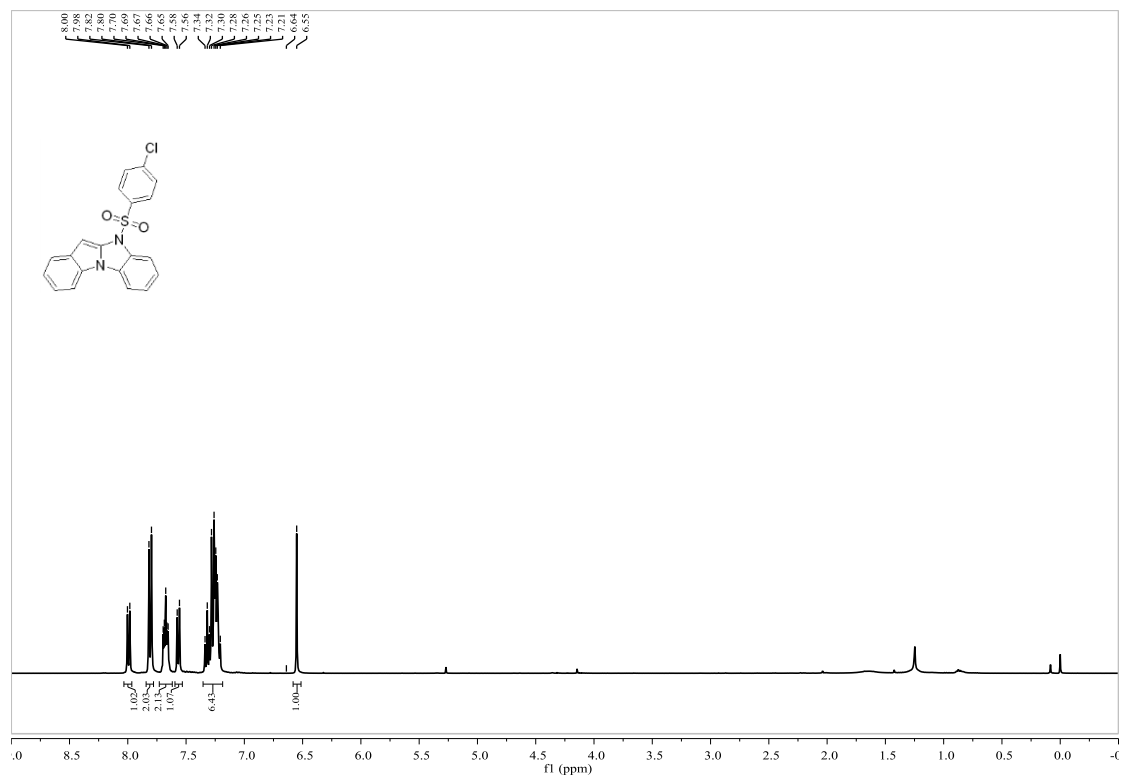
<sup>1</sup>H NMR of compound **5e**



<sup>13</sup>C NMR of compound **5e**



<sup>1</sup>H NMR of compound **5f**



<sup>13</sup>C NMR of compound **5f**

