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SUPPORTING INFORMATION

Brønsted acid-catalyzed regioselective ring opening of 2*H*-azirines by 2-mercaptopyridines and related heterocycles; One pot access to imidazo[1,2-*a*]pyridines and imidazo[2,1-*b*]thiazoles

Subrata Biswas,[a] Arnab Roy,[a] Surajit Duari,[a] Srabani Maity,[a] Asma M. Elsharif,[b] Srijit Biswas*[a]

[a] Department of Chemistry, University of Calcutta, 92, A. P. C. Road, Kolkata – 700 009, West Bengal, India; E-mail: sbchem@caluniv.ac.in; srijit_biswas@yahoo.co.in.

[b] Department of Chemistry, Imam Abdulrahman Bin Faisal University, P.O. Box 1982, Dammam, 31441, Saudi Arabia.

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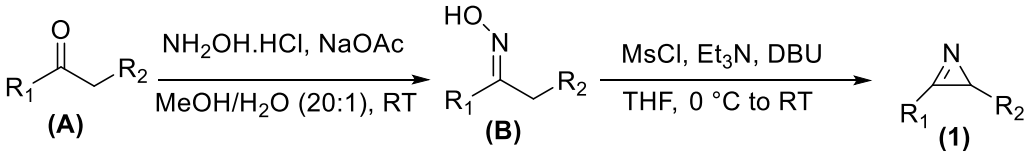
1. General considerations:

^{1}H and **^{13}C NMR** spectra were recorded with a 300 and 400 MHz spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to $CDCl_3$ (δ = 7.28) as an internal standard. All coupling constants are absolute values and are expressed in Hz. The description of the signals includes: s = singlet, d = doublet, t = triplet, q =quadrate, m = multiplet, dd = doublet of doublets, dq =doublet of quadrate, ddd = doublet of doublet of doublets, td = triplet of doublet, and brs. = broad singlet. **^{13}C NMR** spectra were recorded as solutions in $CDCl_3$ with complete proton decoupling. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to $CDCl_3$ (δ =77.16 ppm) as an internal standard. The molecular fragments in High Resolution Mass Spectra (HRMS) are quoted as the relation between mass and charge (m/z). The routine monitoring of reactions was performed with silica gel pre-coated Al plate, which was analysed with iodine and/or UV light and ^{1}H NMR analysis of the crude reaction mixture. All reactions were executed with oven-dried glassware under nitrogen atmosphere.

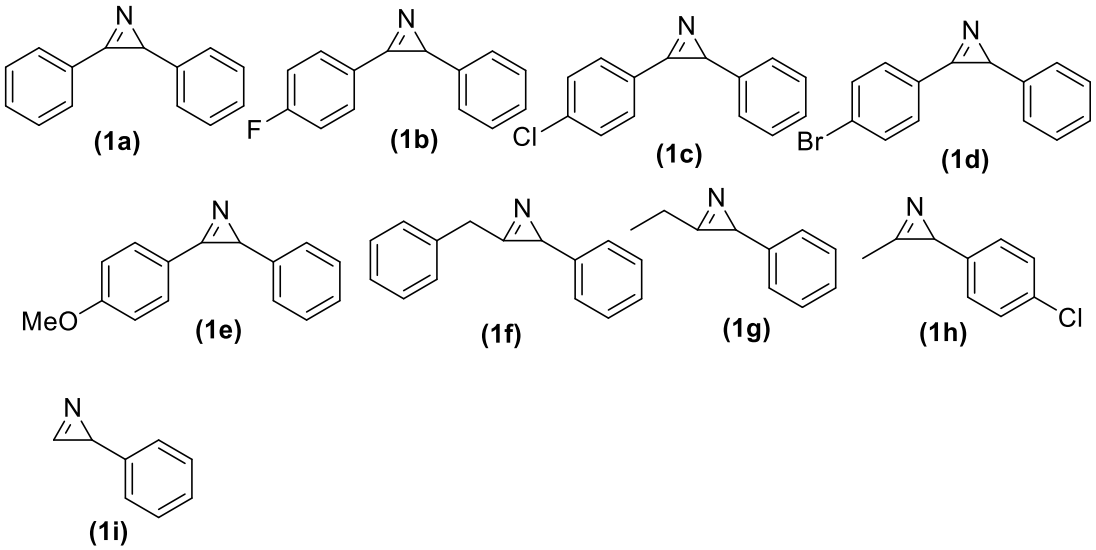
2. General procedure (A) for preparation of 2*H*-azirines:[1]



To a solution of ketone **A** (1.0 equiv.), $NH_2OH.HCl$ (1.5 equiv.) and NaOAc (1.5 equiv.) were added in a mixture of solvents MeOH:H_2O (20:1) and continued for stirring at room temperature. The completion of the reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was extracted by DCM and dried over anhydrous Na_2SO_4. After removal of the solvent in vacuo, the crude oxime (**B**) was used directly for the next step without further purification.

To a solution of crude oxime **B** (1.0 equiv.) in dry THF, triethylamine (1.5 equiv.) and methanesulfonylchloride (1.5 equiv.) were added sequentially at 0 °C to result a cloudy solution. The said solution was allowed to stir at 0 °C for 30 minutes. Then, DBU (1.5 equiv.) was added dropwise to the resulting mixture over 10-15 minutes. The mixture was allowed to stir for another 1 h and quenched with water. After that, it was worked up with DCM and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo, and the crude residue was purified by column chromatography on silica gel (Ethyl acetate: Hexane = 1:20) to afford the pure 2*H*-azirines (**1**).

3. 2*H*-azirines used in study:[1]



Representative **^{1}H** NMR description of **1a** and **1c**.

2,3-diphenyl-2*H*-azirine (1a) :[1a]

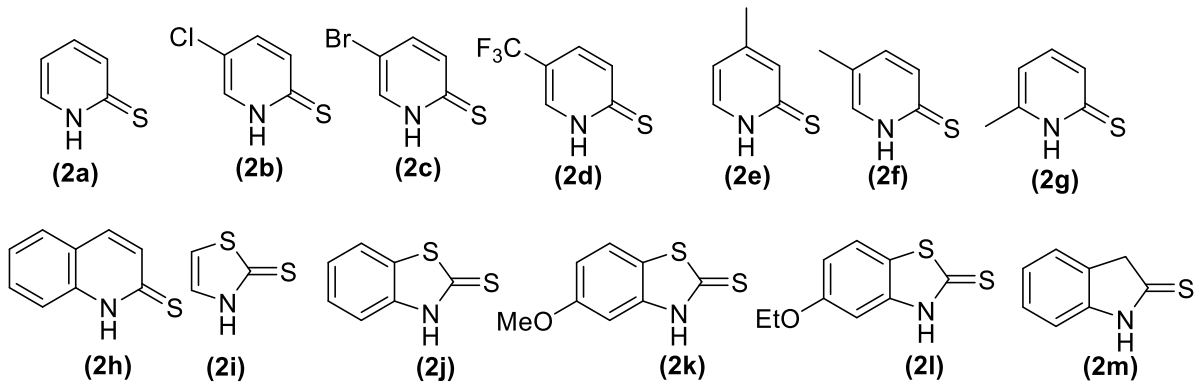
The title compound was prepared with 57% yield over 2 steps according to the general procedure (C) as described above. **^{1}H** NMR (300 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.66–7.54 (m, 3H), 7.33–7.26 (m, 3H), 7.18 (d, *J* = 7.4 Hz, 2H), 3.35 (s, 1H) ppm.

3-(4-chlorophenyl)-2-phenyl-2*H*-azirine (1c):[1a]

The title compound was prepared with 22% yield over 2 steps according to the general procedure (C) as described above. **^{1}H** NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.33–7.26 (m, 3H), 7.13 (d, *J* = 7.3 Hz, 2H), 3.34 (s, 1H) ppm.

The spectral data of all 2*H*-azirines, **1b**,[1d] **1d**,[1a] **1e**,[1a] **1f**,[1a] **1g**,[1b] **1h**,[1b] **1i,**[1d] used in this study exactly matched with reported data.[1]

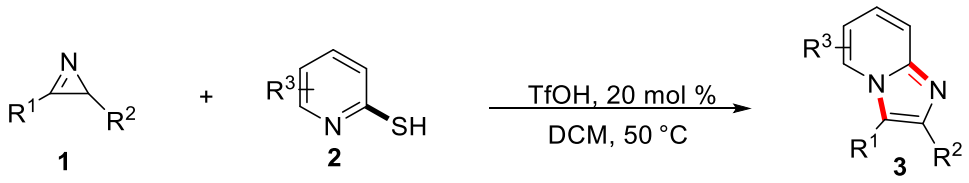
4. Nucleophiles used in study:



The compound **2b**,**2c**, **2e**,**2f**,**2g**, **2h** were prepared according to literature procedure.[2]

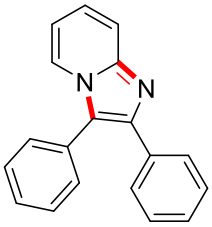
5. Experimental procedures and characterization data of all products

General Procedure B:



To solution of 2*H*-azirines (**1a–1i**, 1.0 equiv.) and 2-mercaptopyridine (**2a–2h**, 1.5 equiv.) in dry DCM (0.4 M) were taken in a 5 mL reaction vial containing a small magnet. Then TfOH (20 mol%) was added to the reaction mixture and the vial was capped and it was allowed to stir at 50 ºC in aluminium dry heating block for 12 hours. The completion of the reaction was monitored by TLC, and the crude was directly purified by silica gel flash column chromatography (230–400 mess) using hexane and hexane/ ethyl acetate to obtain the desired products.

2,3-Diphenylimidazo[1,2-*a*]pyridine (3a) :[3]

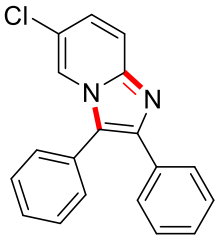


Following the general procedure B, reaction between 2,3-diphenyl-2*H*-azirine (**1a**, 38.6 mg, 0.2 mmol., 1 equiv.) and 2-marcaptopyridine (**2a**, 33.3 mg, 0.3 mmol., 1.5 equiv.) afforded the corresponding product **3a**, which was purified by silica gel flash column chromatography (using 20:80 ethyl acetate: hexane as eluent) to give the title compound as a white solid (44 mg, 0.16 mmol, 82%), m. p. 147–149 °C (lit. m. p. 145.3–148.1 °C).

Scaled-up synthesis of 3a: 2,3-diphenyl-2*H*-azirine (**1a,** 1g, 5.17 mmol, 1equiv.) and of 2-Mercaptopyridine (**2a,** 862.6 mg, 7.76 mmol, 1.5 equiv.) in 13 mL DCM were placed in a round bottom flask (RB) and refluxed at 50 °C under a nitrogen atmosphere. After the reaction was completed, 2,3-diphenylimidazo[1,2-*a*]pyridine, **3a**, was obtained as a white solid with an isolated yield of 84% (1.17g, 4.32 mmol.) after workup with ethyl acetate and purification via column chromatography.

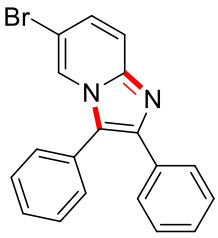
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 6.9 Hz, 1H), 7.72–7.68 (m, 3H), 7.58–7.41 (m, 5H), 7.38–7.24 (m, 3H), 7.22–7.18 (m, 1H), 6.73 (t, *J* = 6.8 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 144.82, 142.41, 134.19, 130.74, 129.88, 129.56, 128.91, 128.29, 128.12, 127.50, 124.71, 123.29, 121.10, 117.54, 112.30 ppm.

6-Chloro-2,3-diphenyl-2,3-dihydroimidazo[1,2-*a*]pyridine (3b) :[4]



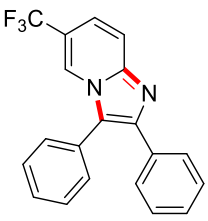
Following the general procedure B, reaction between 2,3-diphenyl-2*H*-azirine (**1a**, 38.6 mg, 0.2 mmol., 1 equiv.) and 5-chloro-2-marcaptopyridine (**2b**, 43.8 mg, 0.3 mmol., 1.5 equiv.) afforded the corresponding product **3b**, which was purified by silica gel flash column chromatography (using 20:80 ethyl acetate: hexane as eluent) to give the title compound as a yellow solid (49.1 mg, 0.16 mmol, 80%), m. p. 143–144 °C (lit. m. p. 142–144 °C). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 2.0 Hz, 1H), 7.69–7.63 (m, 3H), 7.60–7.53 (m, 3H), 7.48–7.45 (m, 2H), 7.33–7.26 (m, 3H), 7.18 (d, *J* = 9.5 Hz, 1H) ppm. **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 143.53, 143.17, 133.77, 130.64, 129.71, 129.34, 129.26, 128.30, 128.05, 127.74, 125.91, 121.62, 121.11, 120.61, 117.95 ppm.

6-Bromo-2,3-diphenylimidazo[1,2-*a*]pyridine (3c) :[4]



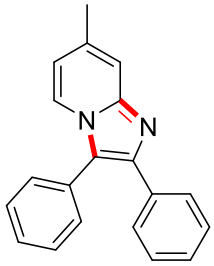
Following the general procedure B, reaction between 2,3-diphenyl-2*H*-azirine (**1a**, 38.6 mg, 0.2 mmol., 1 equiv.) and 5-bromo-2-marcaptopyridine (**2c**, 57mg, 0.3 mmol., 1.5 equiv.) afforded the corresponding product **3c**, which was purified by silica gel flash column chromatography (using 20:80 ethyl acetate: hexane as eluent) to give the title compound as a white solid (55.8 mg, 0.16 mmol, 80%), m. p. 201–202 °C (lit. m. p. 201–202 °C). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.08 (s, 1H), 7.71–7.63 (m, 2H), 7.62–7.50 (m, 4H), 7.48–7.42 (m, 2H), 7.35–7.22 (m, 4H) ppm. **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 143.24, 143.21, 133.67, 130.66, 129.77, 129.31, 129.23, 128.36, 128.06, 127.79, 123.34, 121.46, 118.22, 107.12 ppm.

2,3-Diphenyl-6-(trifluoromethyl)imidazo[1,2-*a*]pyridine (3d) :[3]



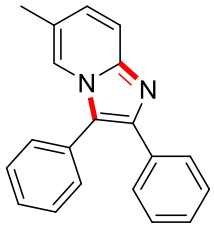
Following the general procedure B, reaction between 2,3-diphenyl-2*H*-azirine (**1a**, 38.6 mg, 0.2 mmol., 1 equiv.) and 5-(trifluoromethyl)-2-marcaptopyridine (**2d**, 53.7 mg, 0.3 mmol., 1.5 equiv.) afforded the corresponding product **3d**, which was purified by flash silica gel column chromatography (using 20:80 ethyl acetate: hexane as eluent) to give the title compound as a yellow solid (50.0 mg, 0.15 mmol, 74%), m. p. 143–144 °C (lit. m. p. 141.9–144.2 °C). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.30 (s, 1H), 7.86–7.72 (m, 1H), 7.70–7.68(m, 2H), 7.62–7.50 (m, 3H), 7.49–7.47 (m, 2H), 7.38–7.29 (m, 4H) ppm. **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 144.44, 144.25, 133.3, 130.6, 129.9, 129.5, 128.7, 128.4, 128.1, 128.0, 122.4 (q, $J_{C–F}$ = 5.8 Hz), 120.6 (q, $J_{C–F}$ = 2.6 Hz), 119.4, 118.2, 116.9 (q, $J_{C–F}$ = 34.3 Hz) ppm.

7-Methyl-2,3-diphenylimidazo[1,2-*a*]pyridine (3e) :[4]



Following the general procedure B, reaction between 2,3-diphenyl-2*H*-azirine (**1a**, 38.6 mg, 0.2 mmol., 1 equiv.) and 4-methyl-2-marcaptopyridine (**2e**, 37.5 mg, 0.3 mmol., 1.5 equiv.) afforded the corresponding product **3e**, which was purified by silica gel column chromatography (using 20:80 ethyl acetate: hexane as eluent) to give the title compound as a white solid (51.1 mg, 0.18 mmol, 90%), m. p. 130–132 °C (lit. m. p. 131–133 °C). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 7.0 Hz, 1H), 7.69–7.66 (m, 2H), 7.56–7.44 (m, 6H), 7.33–7.24 (m, 3H), 6.56 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H), 2.43 (s, 3H) ppm. **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 145.27, 142.02, 135.71, 134.31, 130.72, 130.06, 129.49, 128.73, 128.24, 128.06, 127.34, 122.53, 120.56, 115.86, 114.93, 21.33 ppm.

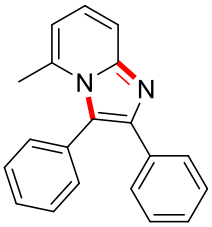
6-Methyl-2,3-diphenylimidazo[1,2-*a*]pyridine (3f) :[3]



Following the general procedure B, reaction between 2,3-diphenyl-2*H*-azirine (**1a**, 38.6 mg, 0.2 mmol., 1 equiv.) and 5-methyl-2-marcaptopyridine (**2f**, 37.5 mg, 0.3 mmol., 1.5 equiv.) afforded the corresponding product **3f**, which was purified by silica gel flash column chromatography (using 20:80 ethyl acetate: hexane as eluent) to give the title compound as a beige solid (50.0 mg, 0.17 mmol, 88%), m. p. 196–198 °C (lit. m. p. 196.5–197.7 °C). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.73–7.66 (m, 3H), 7.62–7.45 (m, 6H), 7.31–7.274 (m, 3H), 7.06 (d, *J* = 9.2 Hz, 1H), 2.27 (s, 3H) ppm. **^{13}C NMR** (75 MHz,

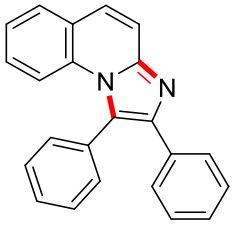
Chloroform-*d*) δ 143.93, 142.25, 134.36, 130.80, 130.16, 129.54, 128.80, 128.24, 128.01, 127.85, 127.33, 121.92, 120.89, 120.83, 116.88, 18.34 ppm.

5-Methyl-2,3-diphenylimidazo[1,2-*a*]pyridine (3g) :



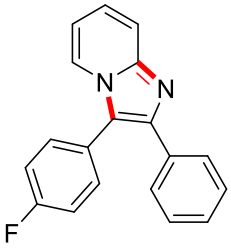
Following the general procedure B, reaction between 2,3-diphenyl-2*H*-azirine (**1a**, 38.6 mg, 0.2 mmol., 1 equiv.) and 6-methyl-2-marcaptopyridine (**2g**, 37.5 mg, 0.3 mmol., 1.5 equiv.) afforded the corresponding product **3g**, which was purified by silica gel flash column chromatography (using 20:80 ethyl acetate: hexane as eluent) to give the title compound as a yellow solid (52.2 mg, 0.18 mmol, 92%), m. p. 195–197 °C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.63–7.55 (m, 3H), 7.47–7.40 (m, 5H), 7.22 (d, *J* = 7.1 Hz, 3H), 7.10 (t, *J* = 7.9 Hz, 1H), 6.44 (d, *J* = 6.6 Hz, 1H), 2.07 (s, 3H) ppm. **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 145.98, 142.93, 136.57, 134.49, 132.98, 132.90, 129.05, 128.08, 128.02, 127.98, 127.17, 124.62, 122.20, 115.79, 113.51, 21.59 ppm. **HRMS** (ESI) calculated for $C_{20}H_{17}N_2$ $[M+H]^+$ m/z 285.1386 found m/z 285.1377.

1,2-Diphenylimidazo[1,2-*a*]quinoline (3h) :[5]



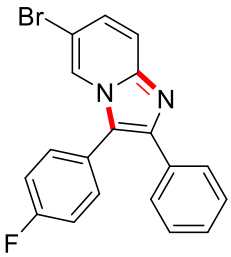
Following the general procedure A, reaction between 2,3-diphenyl-2*H*-azirine (**1a**, 38.6 mg, 0.2 mmol., 1 equiv.) and quinoline-2(1*H*)-thione (**2h**, 48.3 mg, 0.3 mmol., 1.5 equiv.) afforded the corresponding product **3h**, which was purified by silica gel flash column chromatography (using 25:75 ethyl acetate: hexane as eluent) to give the title compound as a white solid (61.5 mg, 0.19 mmol, 96%), m. p. 164–165 °C (lit. m. p. 166–167 °C). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 9.4 Hz, 1H), 7.62–7.17 (m, 14H) ppm. **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 143.89, 141.92, 134.32, 134.30, 133.01, 131.73, 129.63, 129.46, 129.22, 128.18, 127.86, 127.82, 127.12, 126.77, 124.69, 124.45, 124.30, 117.38, 116.68 ppm.

3-(4-Fluorophenyl)-2-phenylimidazo[1,2-*a*]pyridine (3i):[3]



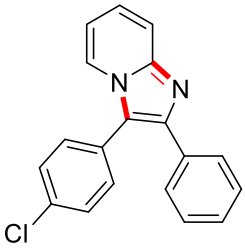
Following the general procedure B, reaction between 3-(4-fluorophenyl)-2-phenyl-2*H*-azirine (**1b**, 42.2 mg, 0.2 mmol., 1 equiv.) and 2-marcaptopyridine (**2a**, 33.3 mg, 0.3 mmol., 1.5 equiv.) afforded the corresponding product **3i**, which was purified by silica gel flash column chromatography (using 20:80 ethyl acetate: hexane as eluent) to give the title compound as a beige solid (47 mg, 0.16 mmol, 82%), m. p. 98–100 °C (lit. m. p. 93–95.5 °C). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 6.9 Hz, 1H), 7.71–7.65 (m, 3H), 7.45–7.41 (m, 2H), 7.33–7.19 (m, 6H), 6.75 (t, *J* = 6.8 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 162.96 (d, J_{C-F} = 248 Hz), 144.85, 142.62, 133.99, 132.72 (d, J_{C-F} = 8 Hz), 128.21 (d, J_{C-F} = 30 Hz), 127.61, 125.87, 124.81, 123.10, 121.12, 119.93, 117.60, 116.80 (d, J_{C-F} = 21 Hz), 112.46 ppm.

6-Bromo-3-(4-fluorophenyl)-2-phenylimidazo[1,2-*a*]pyridine (3j):



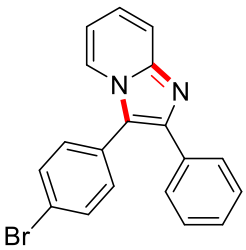
Following the general procedure B, reaction between 3-(4-fluorophenyl)-2-phenyl-2*H*-azirine (**1b**, 42.2 mg, 0.2 mmol., 1 equiv.) and 5-bromo-2-marcaptopyridine (**2c**, 57 mg, 0.3 mmol., 1.5 equiv.) afforded the corresponding product **3j**, which was purified by silica gel flash column chromatography (using 20:80 ethyl acetate: hexane as eluent) to give the title compound as a white solid (59.4 mg, 0.16 mmol, 81%), m. p. 162–163 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 1.8 Hz, 1H), 7.65 –7.59 (m, 3H), 7.47–7.43 (m, 2H), 7.34–7.26 (m, 6H) ppm. **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 163.19 (d, J_{C-F} = 248 Hz), 143.45, 143.25, 133.49, 132.69 (d, J_{C-F} = 10 Hz), 128.32 (d, J_{C-F} = 26 Hz), 127.99, 127.92, 125.21, 125.17, 123.18, 120.30, 118.30, 117.08 (d, J_{C-F} = 22 Hz), 107.27 ppm. **HRMS** (**ESI**) calculated for $C_{19}H_{13}BrFN_2$ $[M+H]^+$ m/z 367.0241 found m/z 367.0221.

3-(4-Chlorophenyl)-2-phenylimidazo[1,2-*a*]pyridine (3k):[4]



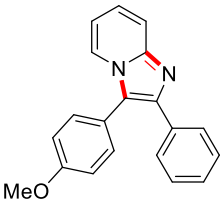
Following the general procedure B, reaction between 3-(4-chlorophenyl)-2-phenyl-2*H*-azirine (**1c**, 45.4 mg, 0.2 mmol., 1 equiv.) and 2-marcaptopyridine (**2a**, 33.3 mg, 0.3 mmol., 1.5 equiv.) afforded the corresponding product **3k**, which was purified by silica gel flash column chromatography (using 20:80 ethyl acetate: hexane as eluent) to give the title compound as a yellow semi solid (51.8 mg, 0.17 mmol, 85%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 6.9 Hz, 1H), 7.71–7.65 (m, 3H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.38–7.19 (m, 4H), 6.76 (t, *J* = 7.4 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 145.01, 142.84, 134.88, 133.91, 132.04, 129.91, 128.40, 128.35, 128.15, 127.70, 124.92, 123.05, 119.75, 117.68, 112.55 ppm.

3-(4-Bromophenyl)-2-phenylimidazo[1,2-*a*]pyridine (3l):[6]



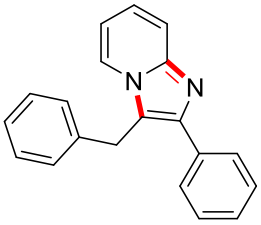
Following the general procedure A, reaction between 3-(4-bromophenyl)-2-phenyl-2*H*-azirine (**1d**, 54.4 mg, 0.2 mmol., 1 equiv.) and 2-marcaptopyridine (**2a**, 33.3 mg, 0.3 mmol., 1.5 equiv.) afforded the corresponding product **3l**, which was purified by silica gel flash column chromatography (using 20:80 ethyl acetate: hexane as eluent) to give the title compound as a yellow solid (58.6 mg, 0.16 mmol, 84%), m. p. 155–156 °C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 6.9 Hz, 1H), 7.72–7.64 (m, 5H), 7.36–7.21 (m, 6H), 6.78 (t, *J* = 6.8 Hz, 1H) ppm. **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 145.05, 142.84, 133.86, 132.87, 132.29, 128.83, 128.41, 128.17, 127.73, 124.95, 123.09, 123.05, 119.77, 117.70, 112.59 ppm.

3-(4-Methoxyphenyl)-2-phenylimidazo[1,2-*a*]pyridine (3m):[7]



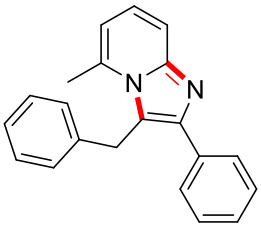
Following the general procedure B, reaction between 3-(4-methoxyphenyl)-2-phenyl-2*H*-azirine (**1e**, 44.6 mg, 0.2 mmol., 1 equiv.) and 2-marcaptopyridine (**2a**, 33.3 mg, 0.3 mmol., 1.5 equiv.) afforded the corresponding product **3m**, which was purified by silica gel flash column chromatography (using 20:80 ethyl acetate: hexane as eluent) to give the title compound as a white solid (54 mg, 0.18 mmol, 90%), m. p. 126–127 °C (lit. m. p. 125–126.1 °C). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 6.9 Hz, 1H), 7.73–7.67 (m, 3H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.32–7.17 (m, 4H), 7.10–7.03 (m, 2H), 6.72 (t, *J* = 6.8 Hz, 1H), 3.89 (s, 3H) ppm. **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 160.02, 144.65, 142.09, 134.29, 132.10, 128.28, 127.98, 127.40, 124.57, 123.33, 121.79, 120.91, 117.44, 115.06, 112.19, 55.37 ppm.

3-Benzyl-2-phenylimidazo[1,2-*a*]pyridine (3n):[8]



Following the general procedure B, reaction between 3-benzyl-2-phenyl-2*H*-azirine (**1f**, 41.4 mg, 0.2 mmol., 1 equiv.) and 2-marcaptopyridine (**2a**, 33.3 mg, 0.3 mmol., 1.5 equiv.) afforded the corresponding product **3n**, which was purified by silica gel flash column chromatography (using 20:80 ethyl acetate: hexane as eluent) to give the title compound as a yellow solid (47.2 mg, 0.16 mmol, 83%), m. p. 118–120 °C (lit. m. p. 118 °C). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 7.8 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.39-7.30 (m, 4H), 7.27–7.15 (m, 3H), 6.71 (t, *J* = 6.7 Hz, 1H), 4.51 (s, 2H) ppm. **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 144.91, 144.21, 136.83, 134.56, 129.06, 128.66, 128.24, 127.75, 127.73, 126.93, 124.18, 123.43, 117.70, 117.57, 112.20, 29.90 ppm.

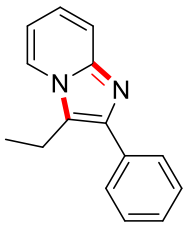
3-Benzyl-5-methyl-2-phenylimidazo[1,2-*a*]pyridine (3o):[8]



Following the general procedure B, reaction between 3-benzyl-2-phenyl-2*H*-azirine (**1f**, 41.4 mg, 0.2 mmol., 1 equiv.) and 6-methyl-2-marcaptopyridine (**2g**, 37.5 mg, 0.3 mmol., 1.5 equiv.) afforded the corresponding product **3o**, which was purified by silica gel flash column chromatography (using 20:80 ethyl acetate: hexane as eluent) to give the title compound as a grey solid (50.6 mg, 0.16 mmol, 85%), m. p. 134–135 °C (lit. m. p. 133–134 °C).**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 6.9 Hz,

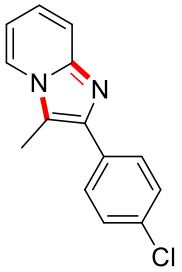
2H), 7.58 (d, *J* = 9.0 Hz, 1H), 7.42–7.32 (m, 5H), 7.29–7.25 (m, 1H), 7.10–7.05 (m, 3H), 6.44 (d, *J* = 6.8 Hz, 1H), 4.70 (s, 2H), 2.62 (s, 3H) ppm. **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 146.90, 145.93, 141.10, 136.27, 134.81, 129.09, 128.66, 128.47, 127.68, 127.58, 126.47, 124.53, 118.88, 115.95, 113.60, 31.77, 20.12 ppm.

3-Ethyl-2-phenylimidazo[1,2-*a*]pyridine (3p):[9]



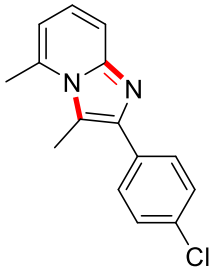
Following the general procedure B, reaction between 3-ethyl-2-phenyl-2*H*-azirine (**1g**, 29 mg, 0.2 mmol., 1 equiv.) and 2-marcaptopyridine (**2a**, 33.3 mg, 0.3 mmol., 1.5 equiv.) afforded the corresponding product **3p**, which was purified by silica gel flash column chromatography (using 20:80 ethyl acetate: hexane as eluent) to give the title compound as a yellow oil (34.6 mg, 0.15 mmol, 78%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 6.9 Hz, 1H), 7.81 (d, *J* = 9.3 Hz, 2H), 7.67 (d, *J* = 9.1 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.40–7.36 (m, 1H), 7.22–7.18 m, 1H), 6.86 (t, *J* = 6.8 Hz, 1H), 3.14 (q, *J* = 7.5 Hz, 2H), 1.39 (t, *J* = 7.5 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 144.42, 141.93, 134.91, 128.56, 128.22, 127.45, 123.59, 122.88, 121.81, 117.74, 112.06, 17.10, 12.27 ppm.

2-(4-Chlorophenyl)-3-methylimidazo[1,2-*a*]pyridine (3q):[10]



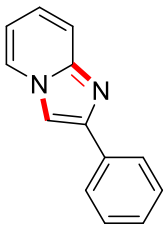
Following the general procedure B, reaction between 2-(4-chlorophenyl)-3-methyl-2*H*-azirine (**1h**, 33 mg, 0.2 mmol., 1 equiv.) and 2-marcaptopyridine (**2a**, 33.3 mg 0.3 mmol., 1.5 equiv.) afforded the corresponding product **3q**, which was purified by silica gel flash column chromatography (using 20:80 ethyl acetate: hexane as eluent) to give the title compound as a White solid (45.1 mg, 0.18 mmol, 93%), m. p. 117–120 °C (lit. m. p. 115–117 °C). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 6.8 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 2H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.86 (t, *J* = 6.7 Hz, 1H), 2.62 (s, 3H) ppm. **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 144.40, 141.26, 133.36, 133.28, 129.52, 128.71, 123.84, 122.89, 117.43, 116.06, 112.24, 9.64 ppm.

2-(4-Chlorophenyl)-3,5-dimethylimidazo[1,2-*a*]pyridine (3r):



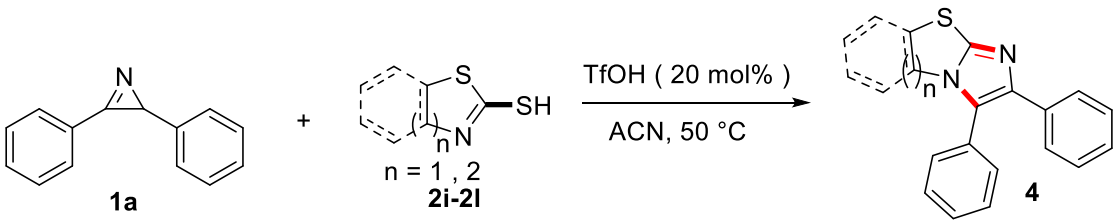
Following the general procedure B, reaction between 2-(4-chlorophenyl)-3-methyl-2*H*-azirine (**1h**, 33 mg, 0.2 mmol., 1 equiv.) and 6-methyl-2-marcaptopyridine (**2g**, 37.5 mg, 0.3 mmol., 1.5 equiv.) afforded the corresponding product **3r**, which was purified by silica gel flash column chromatography (using 20:80 ethyl acetate: hexane as eluent) to give the title compound as a white solid (46.7 mg, 0.18 mmol, 91%), m. p. 136–138 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.46 (t, *J* = 8.5 Hz, 3H), 7.05–7.01 (m, 1H), 6.48 (d, *J* = 6.8 Hz, 1H), 2.93 (s, 3H), 2.91 (s, 3H) ppm. **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 146.25, 142.93, 136.23, 133.55, 133.33, 130.34, 128.57, 124.30, 117.98, 115.97, 113.44, 20.83, 13.58 ppm. **HRMS (ESI)** calculated for $C_{15}H_{14}ClN_2$ $[M+H]^+$ m/z 257.08402 found m/z 257.0822.

2-Phenylimidazo[1,2-*a*]pyridine (3s):[11]



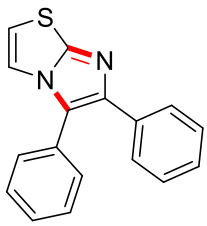
Following the general procedure B, reaction between 3-phenyl-2*H*-azirine (**1i**, 23.4 mg,0.2 mmol., 1 equiv.) and 2-marcaptopyridine (**2a**, 33.3 mg, 0.3 mmol., 1.5 equiv.) afforded the corresponding product **3s**, which was purified by silica gel flash column chromatography (using 10:90 ethyl acetate: hexane as eluent) to give the title compound as a white solid (32.2 mg, 0.16 mmol, 83%), m. p. 130–133 °C (lit. m. p. 131–133 °C). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 6.7 Hz, 1H), 7.95 (s, 2H), 7.81 (d, *J* = 6.3 Hz, 1H), 7.63 (d, *J* = 9.1 Hz, 1H), 7.44–7.42 (m, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.14 (t, *J* = 7.9 Hz, 1H), 6.72 (t, *J* = 5.8 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145.71, 145.66, 133.76, 128.75, 127.98, 126.05, 125.63, 124.69, 117.45, 112.41, 108.18 ppm.

General Procedure C:



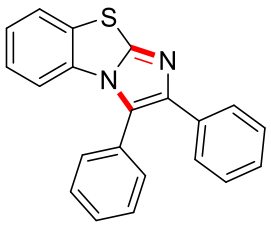
To a solution of 2*H*-azirine **1a** (1.0 equiv.) and thiazole-2-thiols (**2i–2l**, 1.5 equiv.) in dry acetonitrile (0.4 M) solvent taken in a 5 mL reaction vial containing a small magnet. Then TfOH (20 mol%) was added to the reaction mixture and the vial was capped and it was allowed to stir at 50 ºC in aluminium dry heating block for 12 hours. The completion of the reaction was monitored by TLC, and the crude was directly purified by silica gel flash column chromatography (230–400 mess) using hexane and hexane/ ethyl acetate to obtain the desired products.

5,6-Diphenylimidazo[2,1-*b*]thiazole (4a):[4]



Following the general procedure C, reaction between 2,3-diphenyl-2*H*-azirine (**1a**, 38.6 mg, 0.2 mmol., 1 equiv.) and thiazole-2(3H)-thione (**2i**, 35.1 mg, 0.3 mmol., 1.5 equiv.) afforded the corresponding product **4a**, which was purified by silica gel flash column chromatography (using 20:80 ethyl acetate: hexane as eluent) to give the title compound as a yellow liquid (61.5 mg, 0.19 mmol, 96%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.66–7.62 (m, 2H), 7.61–7.48 (m, 4H), 7.47–7.42 (m, 1H), 7.40 (d, *J* = 4.6 Hz, 1H), 7.33–7.30 (m, 2H), 7.27–7.25 (m, 1H), 6.83 (d, *J* = 4.5 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 149.00, 143.48, 134.47, 130.54, 129.25, 129.22, 128.37, 128.30, 127.60, 127.15, 122.84, 117.51, 112.48 ppm.

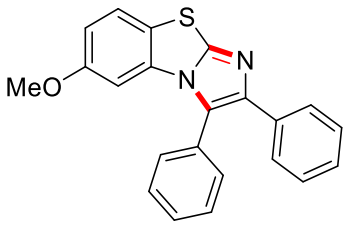
2,3-Diphenylbenzo[d]imidazo[2,1-*b*]thiazole (4b):[12]



Following the general procedure C, reaction between 2,3-diphenyl-2*H*-azirine (**1a**, 38.6 mg, 0.2 mmol., 1 equiv.) and benzo[*d*]thiazole-2(3*H*)-thione (**2j**, 50.1 mg, 0.3 mmol., 1.5 equiv.) afforded the

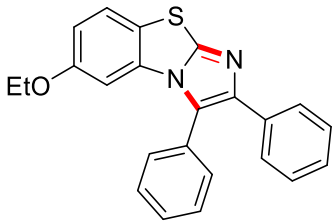
corresponding product **4b**, which was purified by silica gel flash column chromatography (using 10:90 ethyl acetate: hexane as eluent) to give the title compound as a yellow solid (41.1 mg, 0.12 mmol., 63 %), m. p. 142–145 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.61–7.59 (m, 7H), 7.29–7.25 (m, 3H), 7.24–7.19 (m, 1H), 7.18–7.14 (m, 1H), 6.86 (d, *J* = 8.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 147.13, 143.29, 134.17, 133.08, 131.33, 130.53, 130.36, 129.36, 128.27, 126.96, 125.75, 124.46, 113.40 ppm.

6-Methoxy-2,3-diphenylbenzo[d]imidazo[2,1-*b*]thiazole (4c):



Following the general procedure C, reaction between 2,3-diphenyl-2*H*-azirine (**1a**, 38.6 mg, 0.2 mmol., 1 equiv.) and 5-methoxybenzo[*d*]thiazole-2(3*H*)-thione (**2k**, 59.1 mg, 0.3 mmol., 1.5 equiv.) afforded the corresponding product **4c**, which was purified by silica gel flash column chromatography (using 10:90 ethyl acetate: hexane as eluent) to give the title compound as a yellow solid (44.9 mg, 0.12 mmol, 63 %), m. p. 155–157 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59–7.57 (m, 7H), 7.27–7.20 (m, 4H), 6.77–6.61 (m, 2H), 3.84 (s, 3H) ppm. **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 156.77, 146.51, 142.76, 134.28, 131.84, 131.29, 130.32, 129.42, 129.34, 128.25, 126.88, 126.85, 125.28, 124.19, 113.91, 112.80, 108.69, 55.85 ppm. **HRMS** (**ESI**) calculated for $C_{22}H_{17}N_2OS$ $[M+H]^+$ m/z 357.1056 found m/z 357.1052.

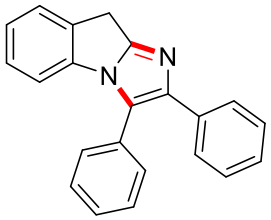
6-Ethoxy-2,3-diphenylbenzo[d]imidazo[2,1-*b*]thiazole (4d):



Following the general procedure C, reaction between 2,3-diphenyl-2*H*-azirine (**1a**, 38.6 mg, 0.2 mmol., 1 equiv.) and 5-ethoxybenzo[*d*]thiazole-2(3*H*)-thione (**2l**, 42.2 mg, 0.3 mmol., 1.5 equiv.) afforded the corresponding product **4d**, which was purified by silica gel flash column chromatography (using 10:90 ethyl acetate: hexane as eluent) to give the title compound as a yellow solid (44.3 mg, 0.13 mmol, 68 %), m. p. 182–183 °C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.60–7.57 (m, 7H), 7.27–7.17 (m, 4H), 6.77–6.69 (m, 2H), 4.05 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 156.21, 146.50, 142.98, 134.43, 131.86, 131.33, 130.56, 130.56, 129.27, 129.26,

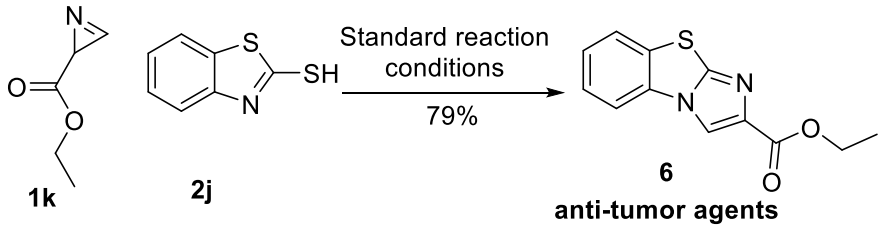
128.13, 127.31, 126.94, 124.16, 113.79, 113.38, 109.70, 64.33, 14.65 ppm. **HRMS (ESI)** calculated for $C_{23}H_{19}N_2OS$ $[M+H]^+$ m/z 371.1213found m/z 371.1211.

2,3-Diphenyl-9*H*-imidazo[1,2-*a*]indole (5):



Following the general procedure C, reaction between 2,3-diphenyl-2*H*-azirine (**1a**, 38.6 mg, 0.2 mmol., 1 equiv.) and 3*H*-indole-2-thiol (**2m**, 44.7 mg, 0.3 mmol., 1.5 equiv.) afforded the corresponding product **5,** which was purified by silica gel flash column chromatography (using 10:90 ethyl acetate: hexane as eluent) to give the title compound as a yellow liquid (57.3 mg, 0.18 mmol, 93 %). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.54 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.36 – 7.30 (m, 8H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.85 – 6.74 (m, 2H), 4.29 (s, 2H) ppm. **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.49, 149.16, 145.74, 134.81, 133.03, 132.04, 130.48, 129.61, 128.99, 128.71, 128.68, 128.32, 128.10, 127.79, 123.01, 118.79, 116.55, 36.63. **HRMS (ESI)** calculated for $C_{22}H_{17}N_2$ $[M+H]^+$ m/z 309.1386 found m/z 309.1377.

Ethyl benzo[*d*]imidazo[2,1-*b*]thiazole-2-carboxylate (6):[13]



Following the general procedure B, ethyl-2*H*-azirine-3-carboxylate (**1k,** 56.5 mg, 0.5 mmol, 1.0 equiv.) and benzo[*d*]thiazole-2-thiol (**2j**, 125.4 mg, 0.75 mmol, 1.5 equiv.) and dry DCM (3.75 mL) were taken in a 5 mL reaction vial containing a small magnet. Then TfOH (20 mol%) was added to the reaction mixture and the vial was capped and it was allowed to stir at 50 ºC in aluminium dry heating block for 14 hours. The completion of the reaction was confirmed by TLC, and the crude was directly purified by silica gel flash column chromatography (230–400 mess) using 30: 70 ethyl acetate: hexane to obtain the desired products **6** (white solid, 97.7 mg, 0.39 mmol, 79%), m. p. 98–100 °C (lit. m. p. 95–97 °C). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.37 (s, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 4.43 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 162.50, 148.62, 138.61, 131.45, 130.93, 126.55, 126.13, 124.58, 116.69, 113.36, 61.12, 14.40 ppm.

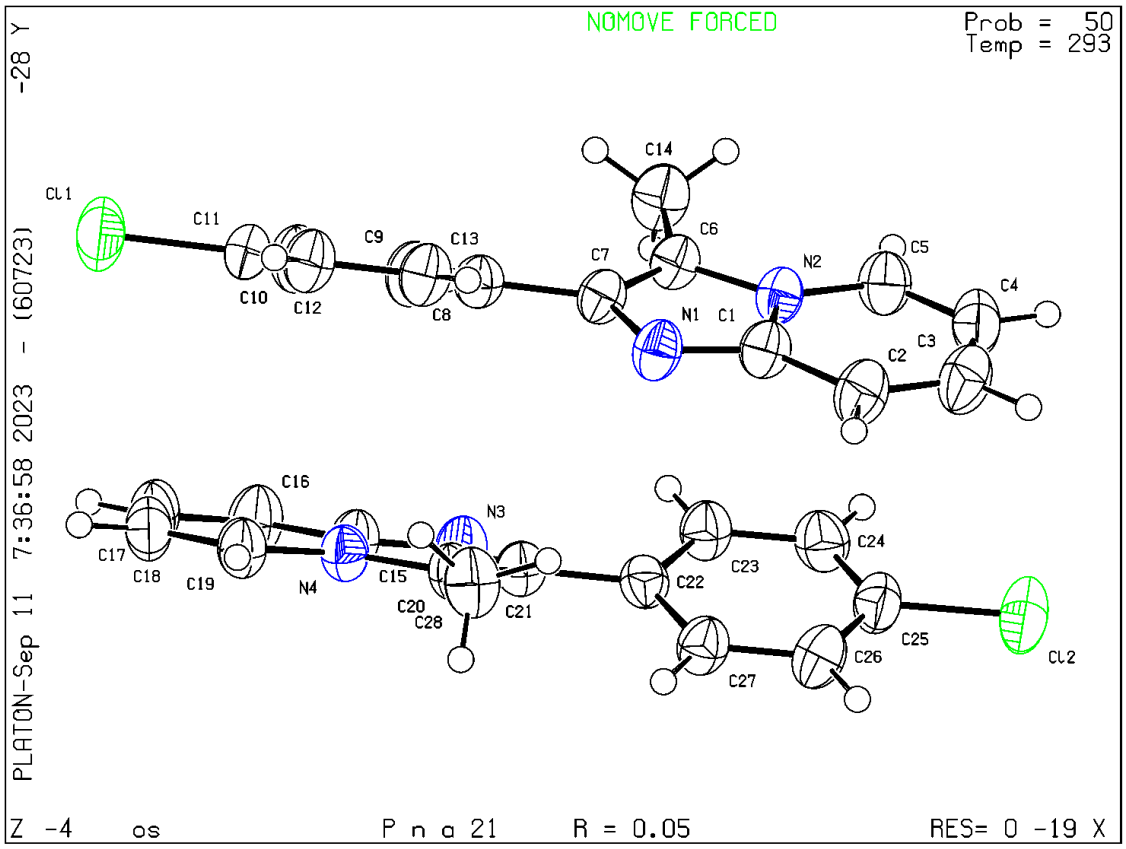
6. X-ray Crystallography:

Method for crystal growth:

120 mg of solid compound (**3q**), was dissolved in 2 mL of ethyl acetate, and diluted with equal amount of n-hexane in a 25 mL conical flask. Then the mixture was kept at 10 ºC for two weeks inside a fridge. After slow evaporation of the solvent the desired crystals were formed.

Single-crystal X-ray data of compound **3q** was collected on a Bruker SMART Apex-II CCD diffractometer in the presence of graphite-monochromated Mo Kα radiation (λ = 0.71073 A°) at room temperature. The Bruker Apex-II suite program was used to perform data processing, structure solution, and refinement. Reflections available in $2\Theta_{max}$ range were harvested and corrected for Lorentz and polarization factors with Bruker SAINT plus.[14] Reflections were then corrected for absorption, interframe scaling, and other systematic errors with SADABS.[15] The structures were solved using direct methods and refined by means of full-matrix least-squares techniques based on F^2 with with SHELX2017/1 software package.[16] Non-hydrogen atoms present in the structures were refined with anisotropic thermal parameters. C–H hydrogen atoms were introduced at geometrical positions with $U_{iso} = 1/2U_{eq}$ to those of the atoms to which they are attached.

6a. X-ray structure data for 3q:



6b. Crystal data and structure refinement for 3q.

Identification code	**3q**
Empirical formula	$C_{28}H_{22}Cl_2N_4$
Formula weight	485.39
Temperature/K	293.15
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	21.144(7)
b/Å	7.159(2)
c/Å	15.509(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2347.4(13)
Z	4
ρ_{calc}g/cm^3	1.373
μ/mm^{-1}	0.302
F(000)	1008.0
Crystal size/mm^3	0.6 × 0.2 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.664 to 54.308
Index ranges	$-27 \leq h \leq 27$, $-9 \leq k \leq 7$, $-19 \leq l \leq 19$
Reflections collected	24620
Independent reflections	5109 [R_{int} = 0.0921, R_{sigma} = 0.0707]
Data/restraints/parameters	5109/1/309
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0470, wR_2 = 0.1148
Final R indexes [all data]	R_1 = 0.0671, wR_2 = 0.1299
Largest diff. peak/hole / e Å^{-3}	0.22/-0.27
Flack parameter	0.27(4)
CCDC Deposit	2296438

7. References:

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(15) G. M. Sheldrick, *SHELXS-2013 and SHELXL-2013, Program for Refinement of Crystal Structures; University of Göttigen: Göttigen, Germany*, **2013.**

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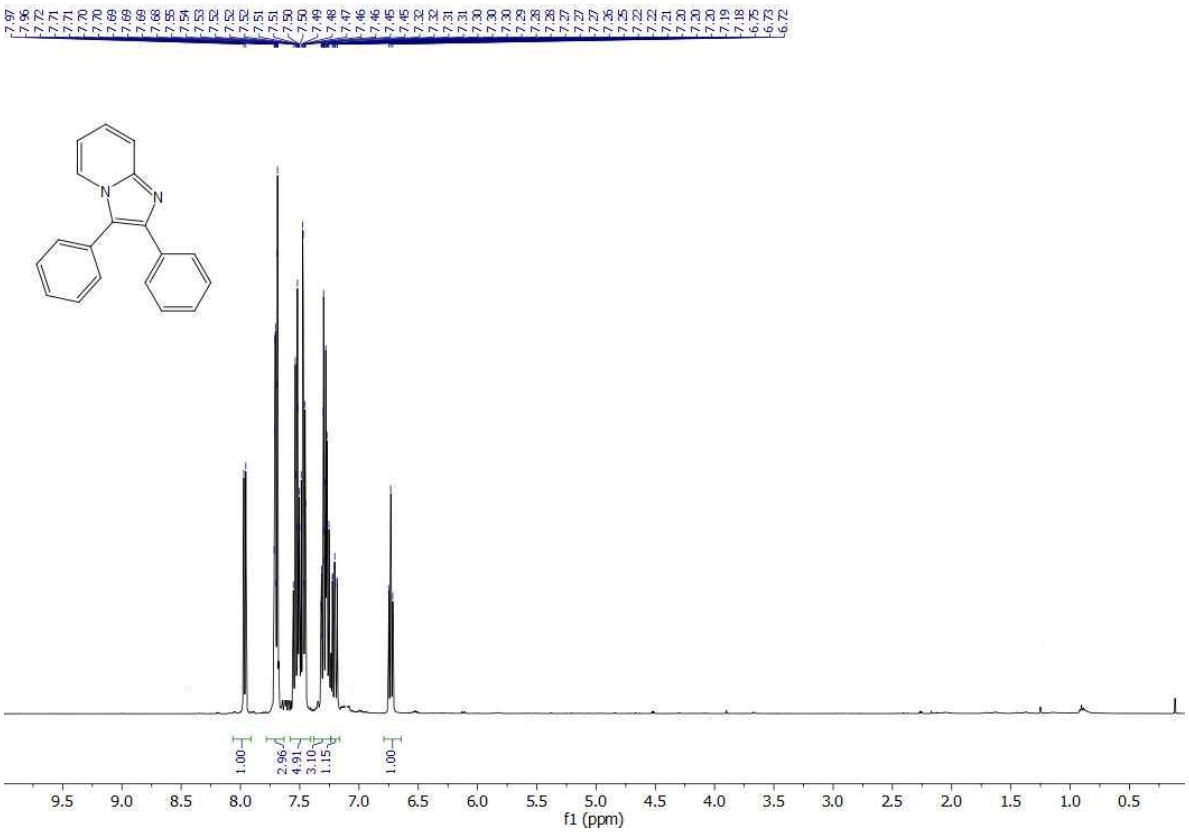
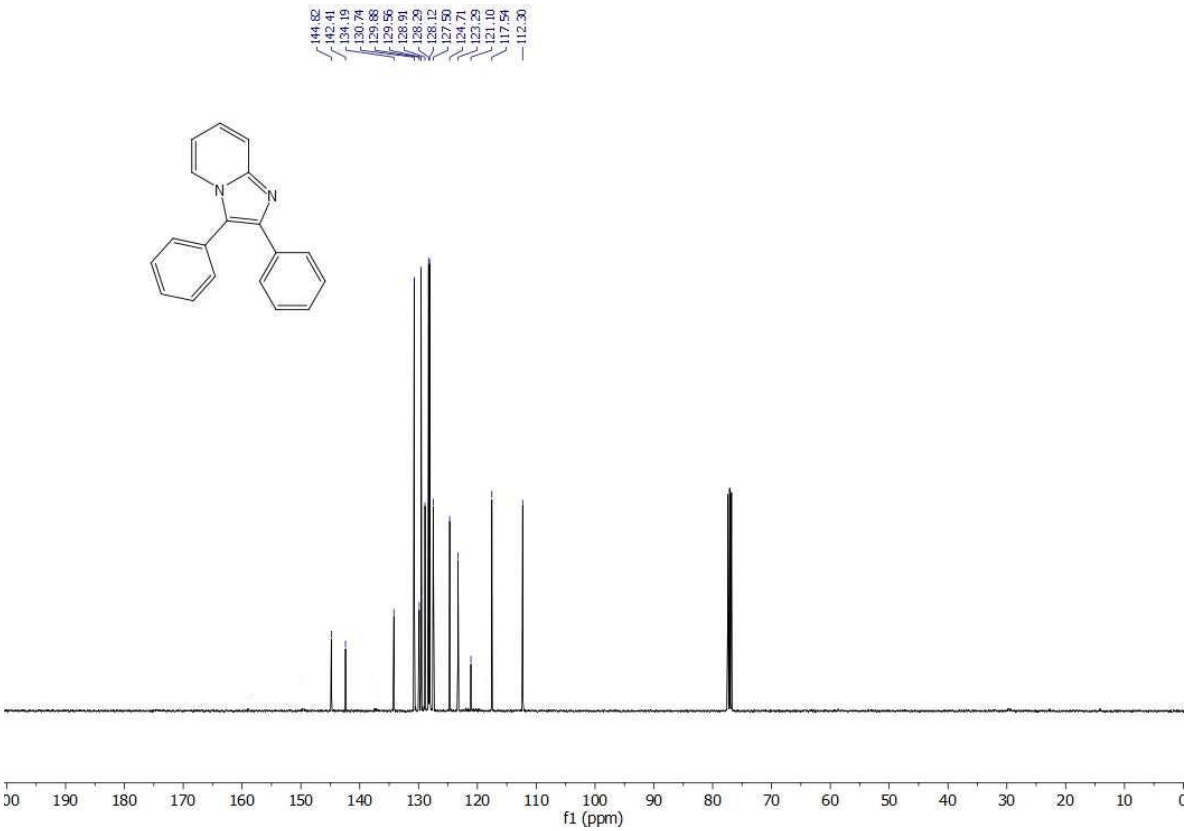
8. Copies of ^{1}H and ^{13}C NMR spectra of all products:

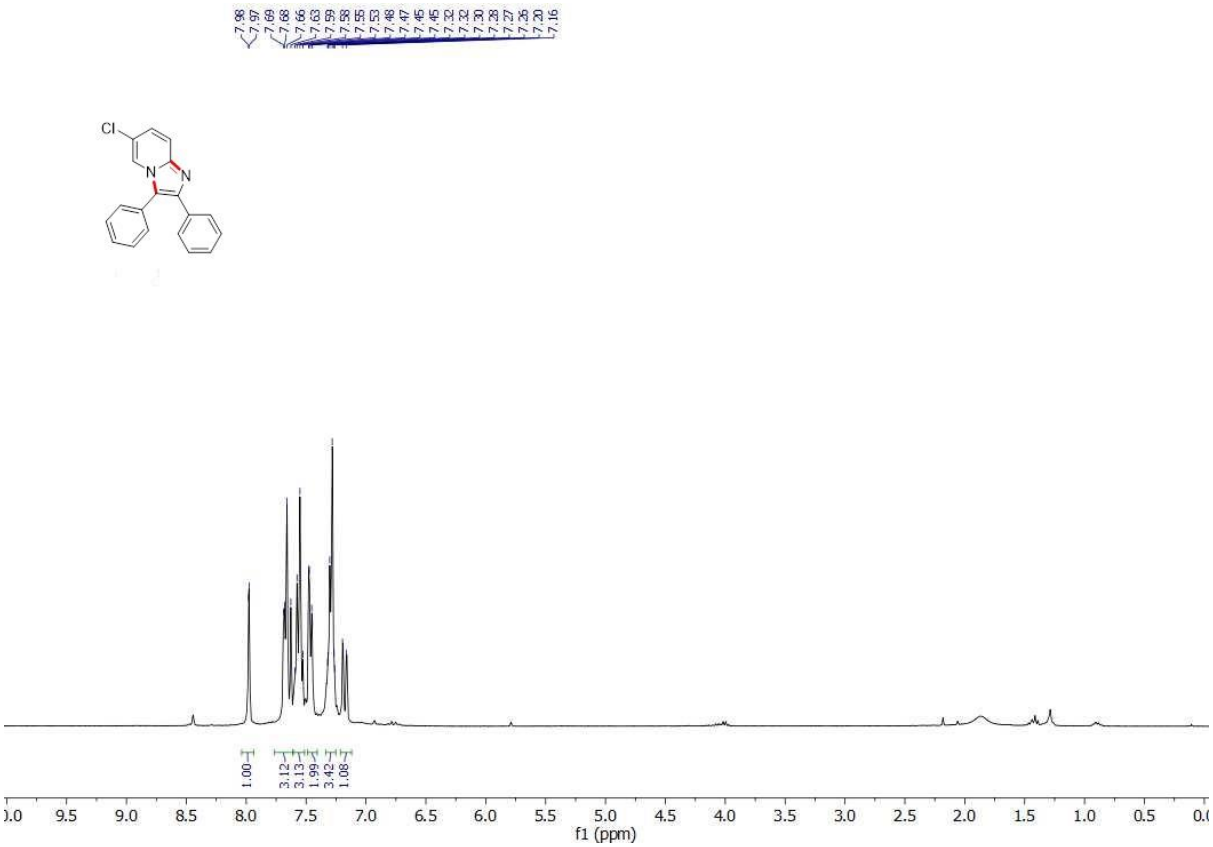
^{1}H NMR spectra of **3a** (400 MHz, $CDCl_3$);



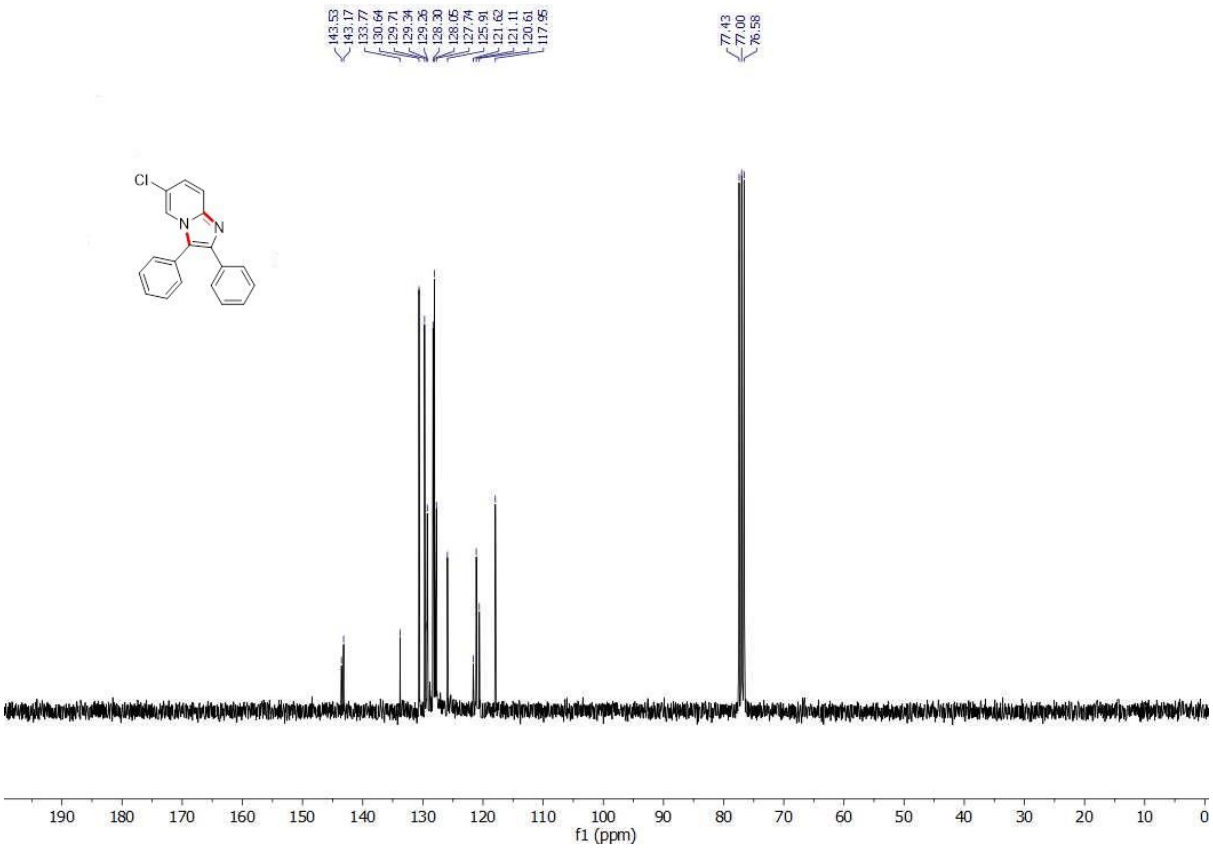
^{13}C NMR spectra of **3a** (100 MHz, $CDCl_3$);



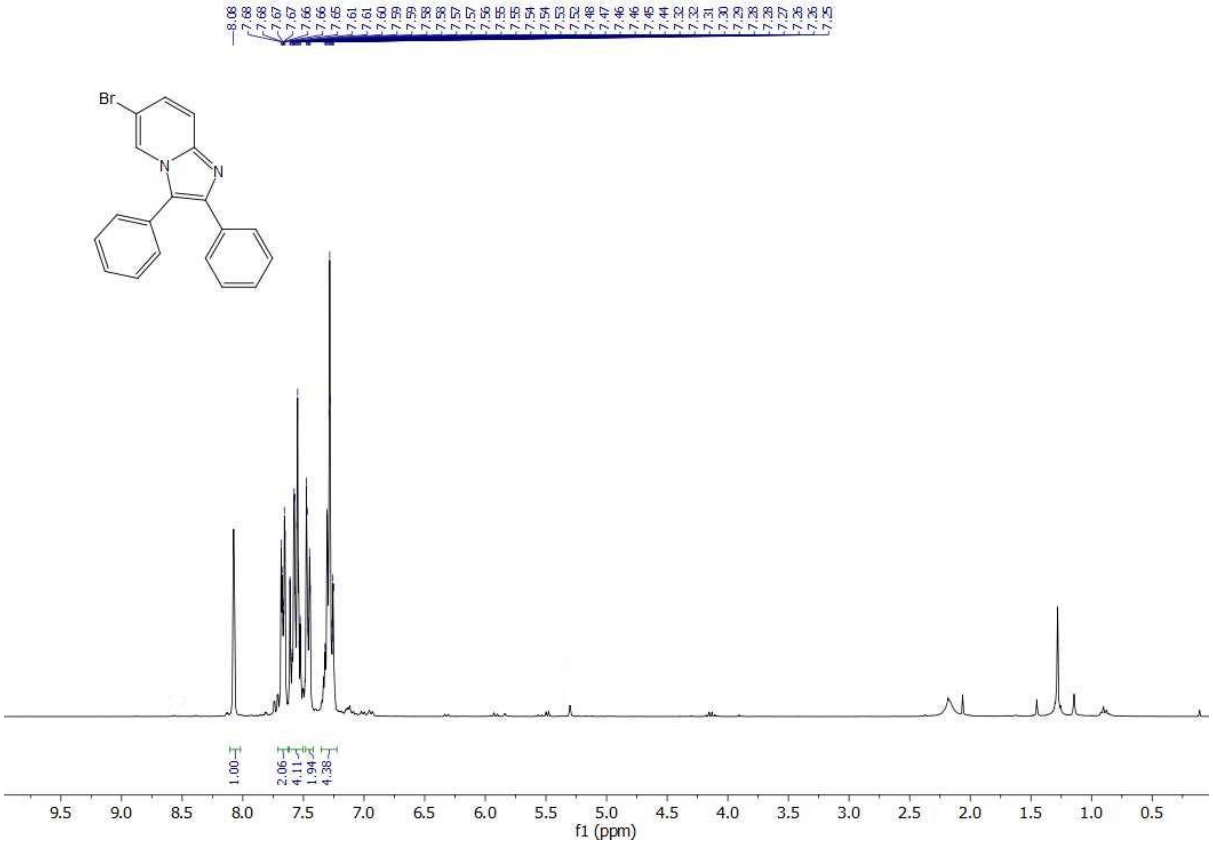
[1]H NMR spectra of **3b** (300 MHz, $CDCl_3$);



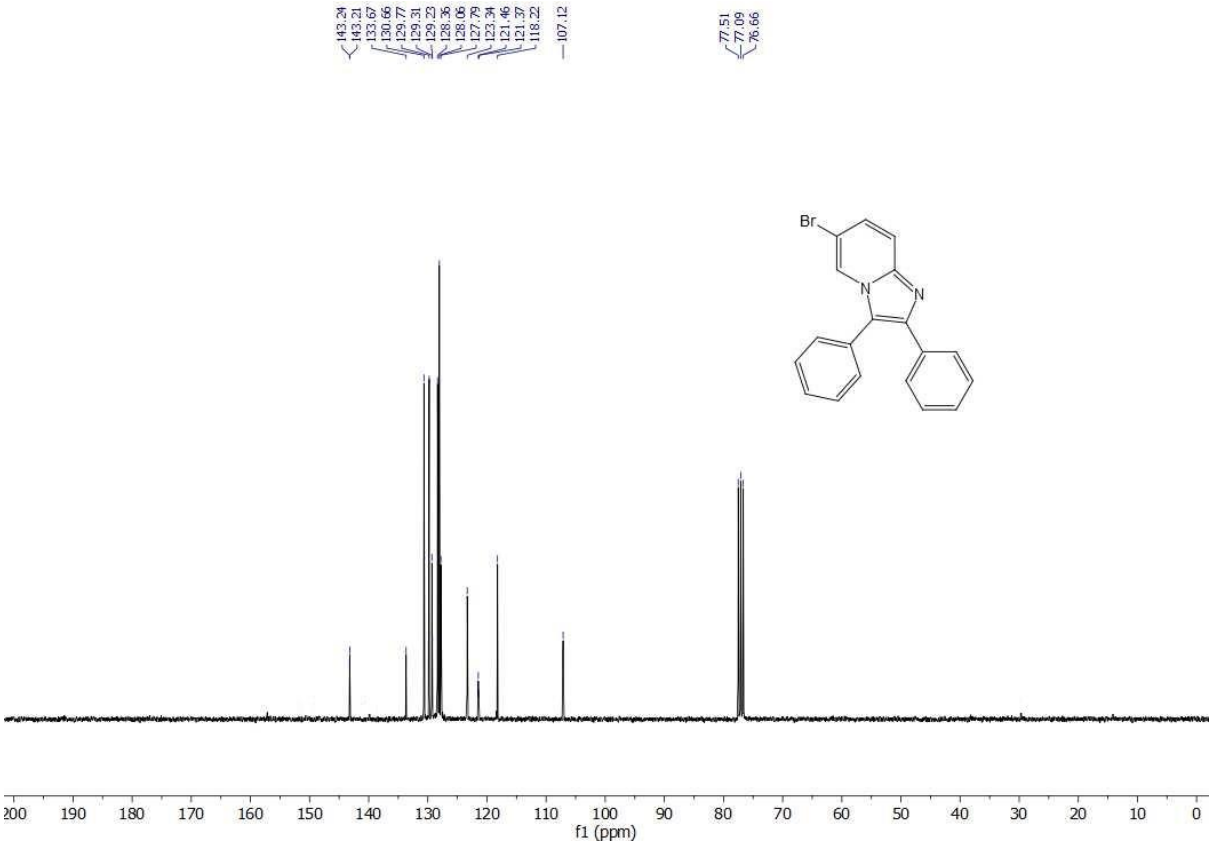
[13]C NMR spectra of **3b** (75 MHz, $CDCl_3$);



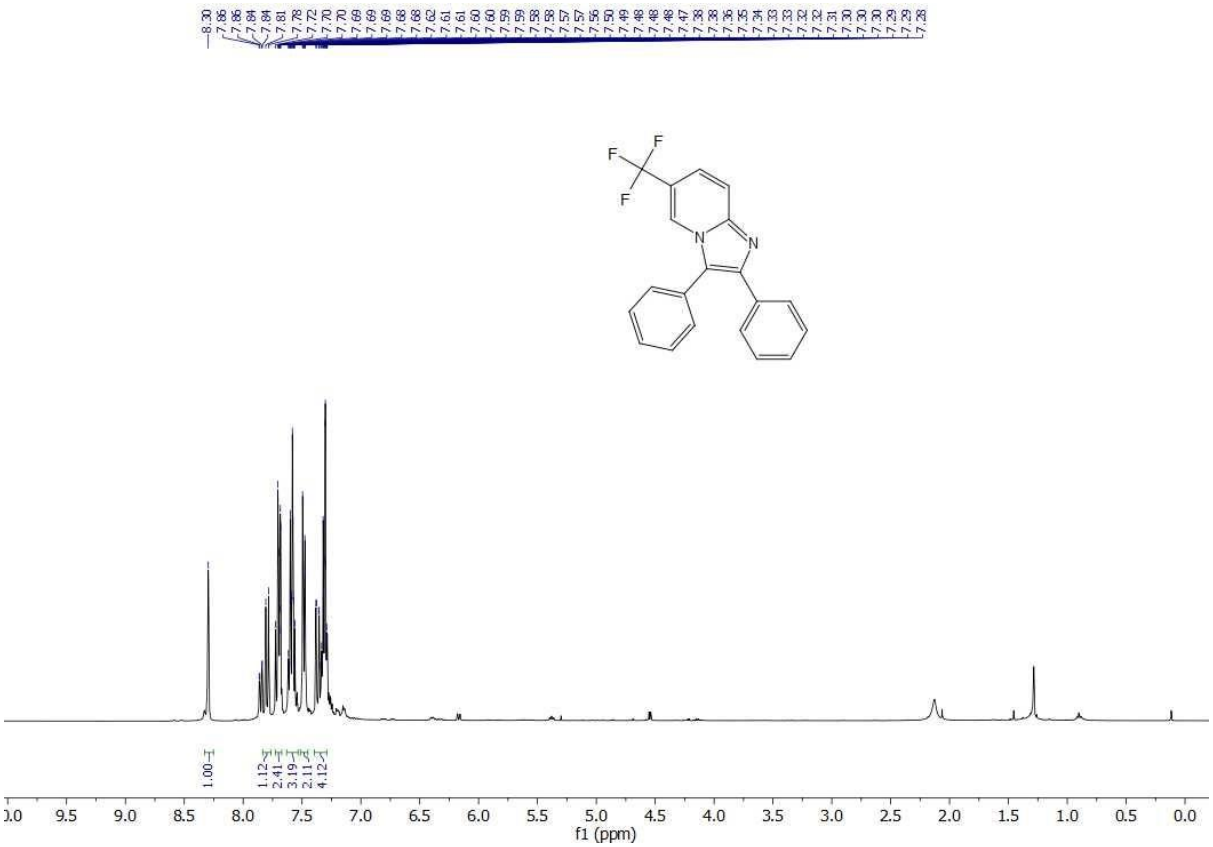
[1]H NMR spectra of **3c** (300 MHz, $CDCl_3$);



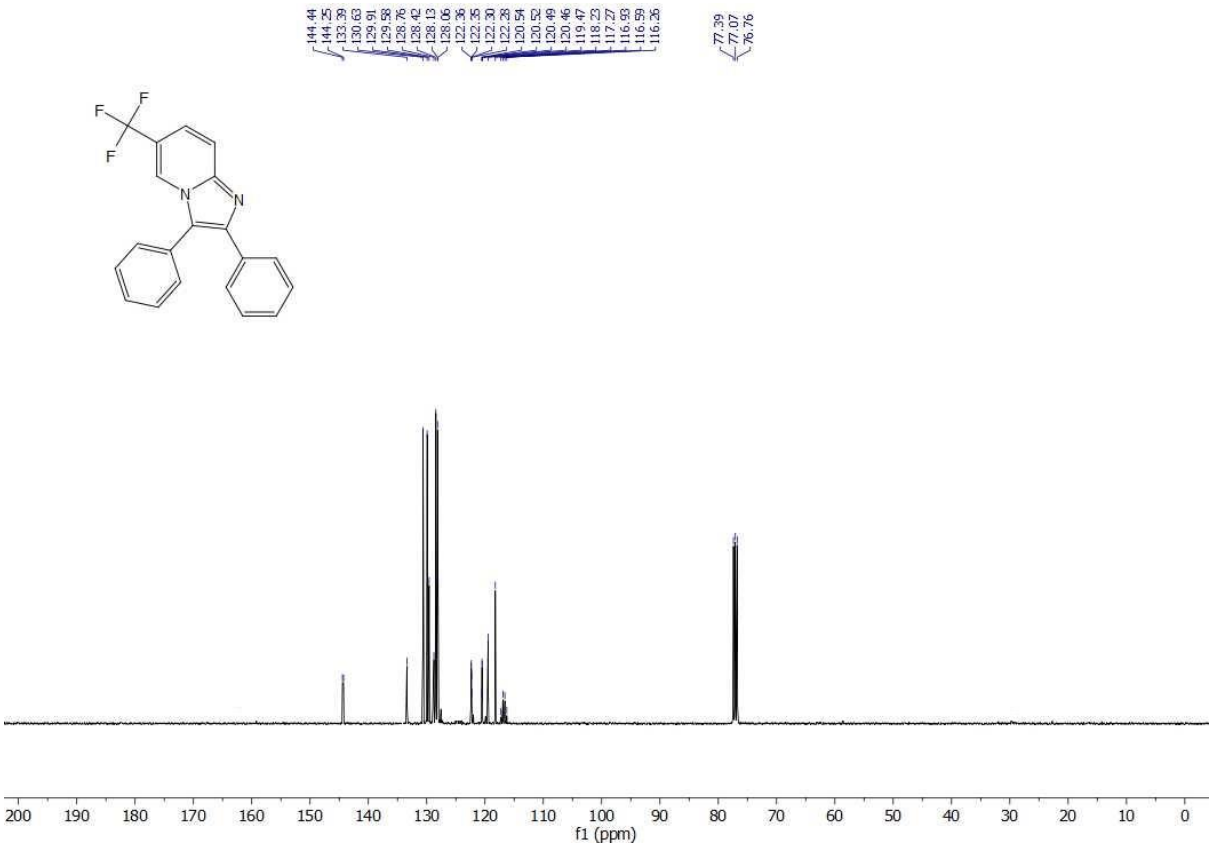
[13]C NMR spectra of **3c** (75 MHz, $CDCl_3$);



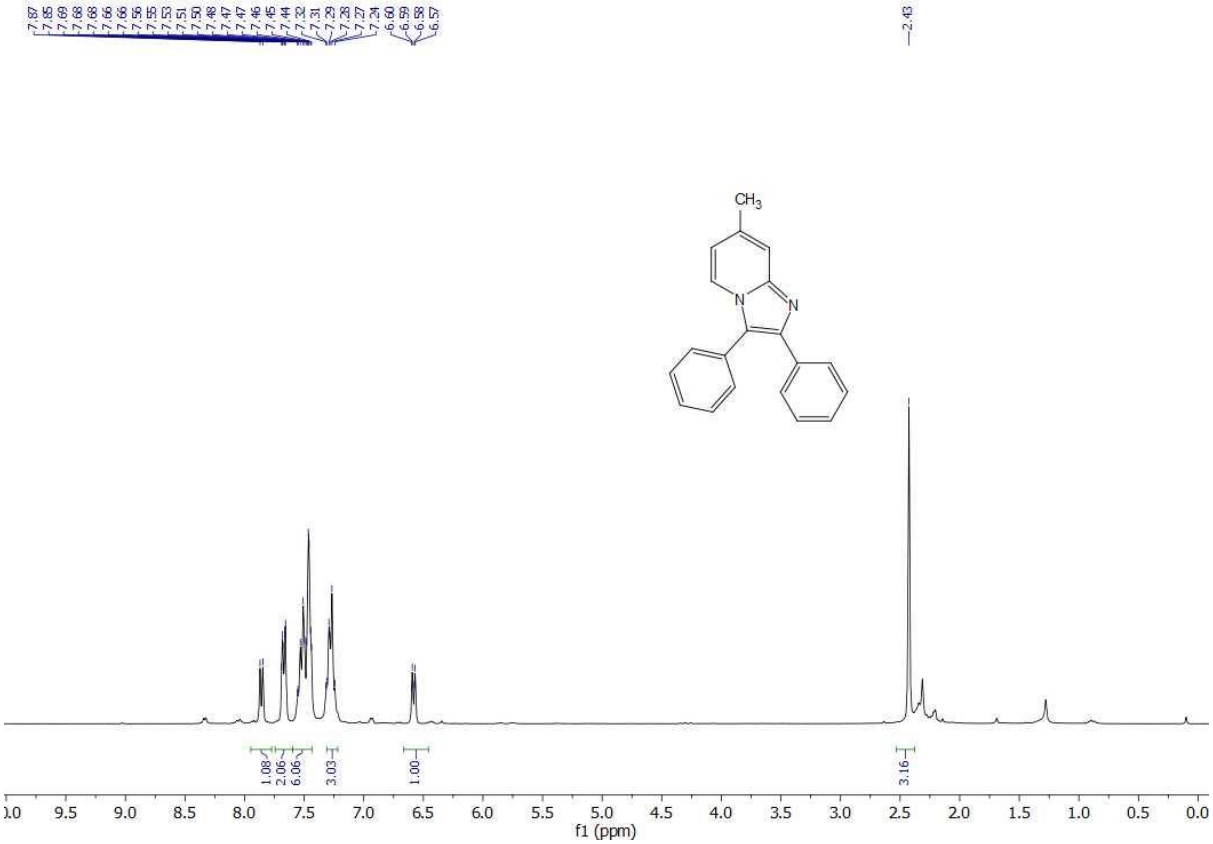
[1]H NMR spectra of **3d** (400 MHz, $CDCl_3$);



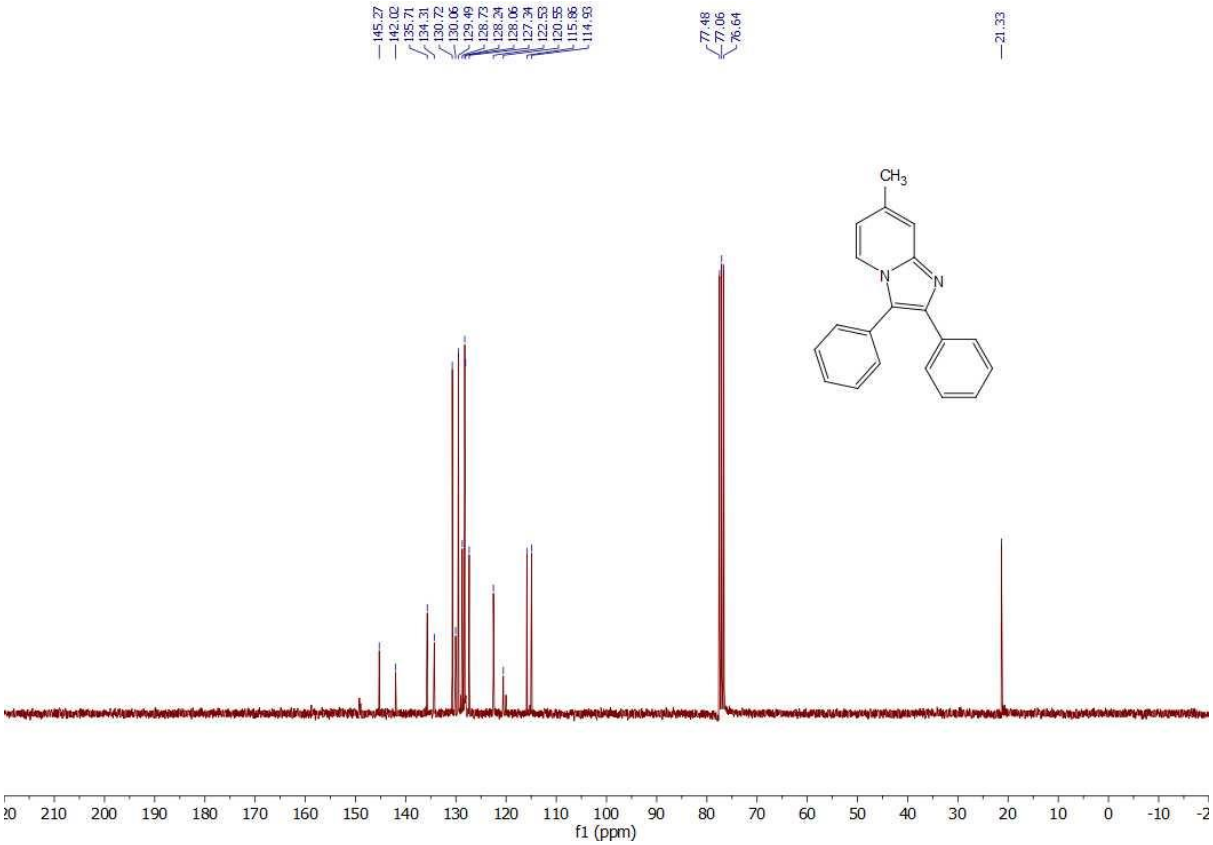
[13]C NMR spectra of **3d** (100 MHz, $CDCl_3$);



[1]H NMR spectra of **3e** (300 MHz, $CDCl_3$);



[13]C NMR spectra of **3e** (75 MHz, $CDCl_3$);



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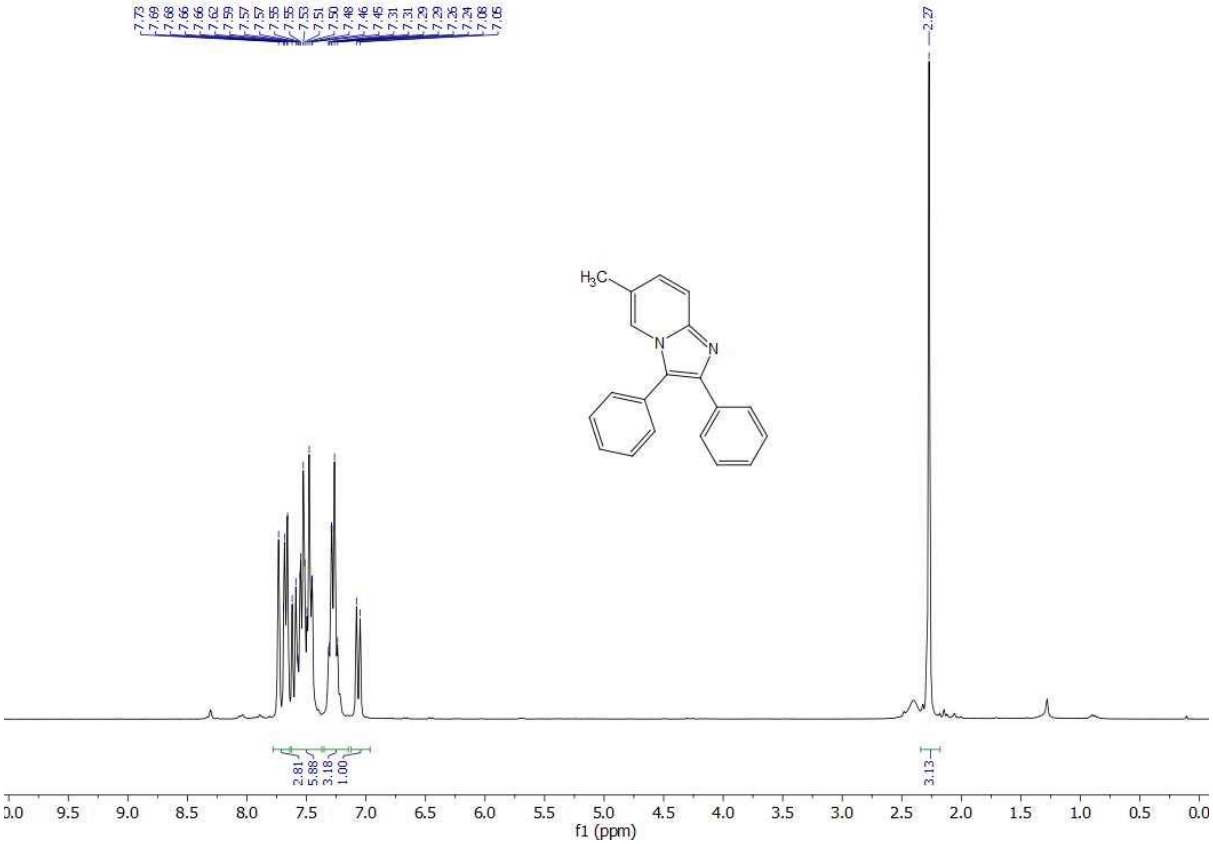

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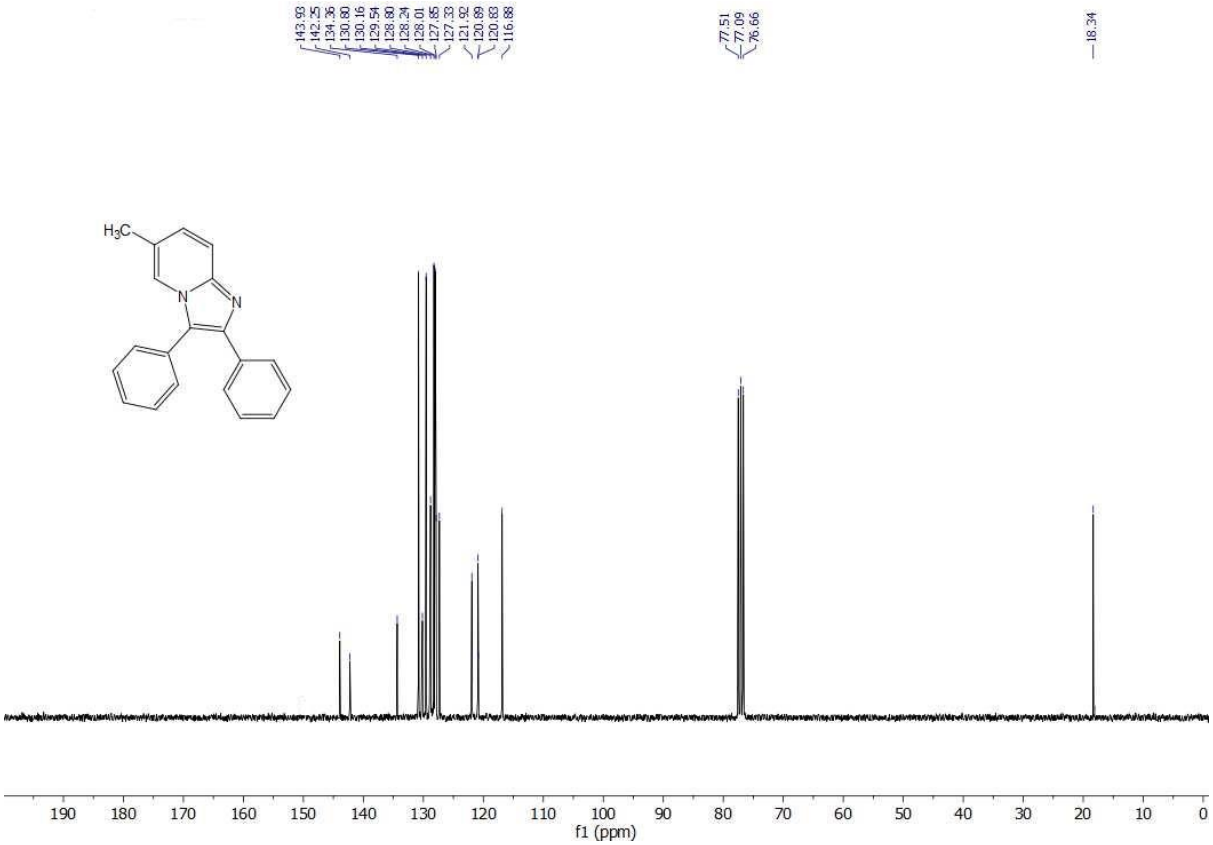

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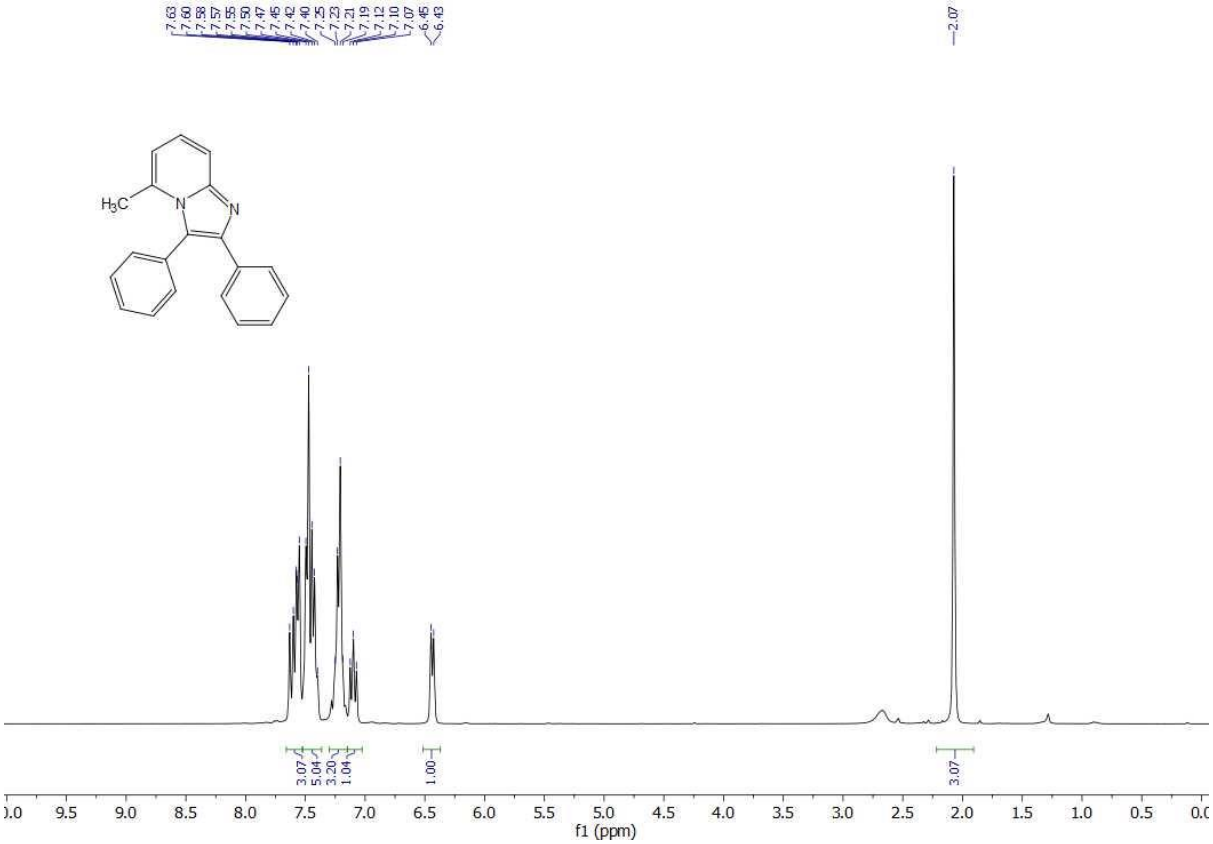

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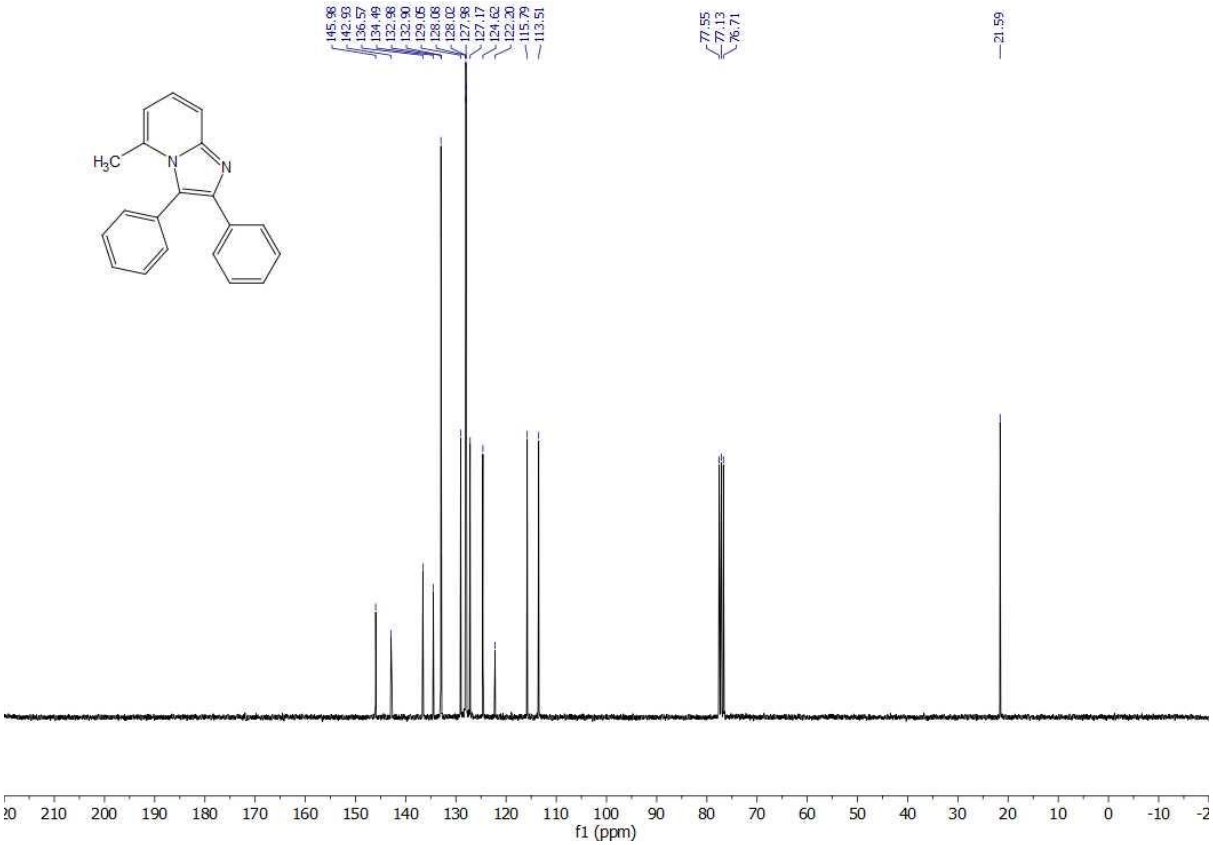
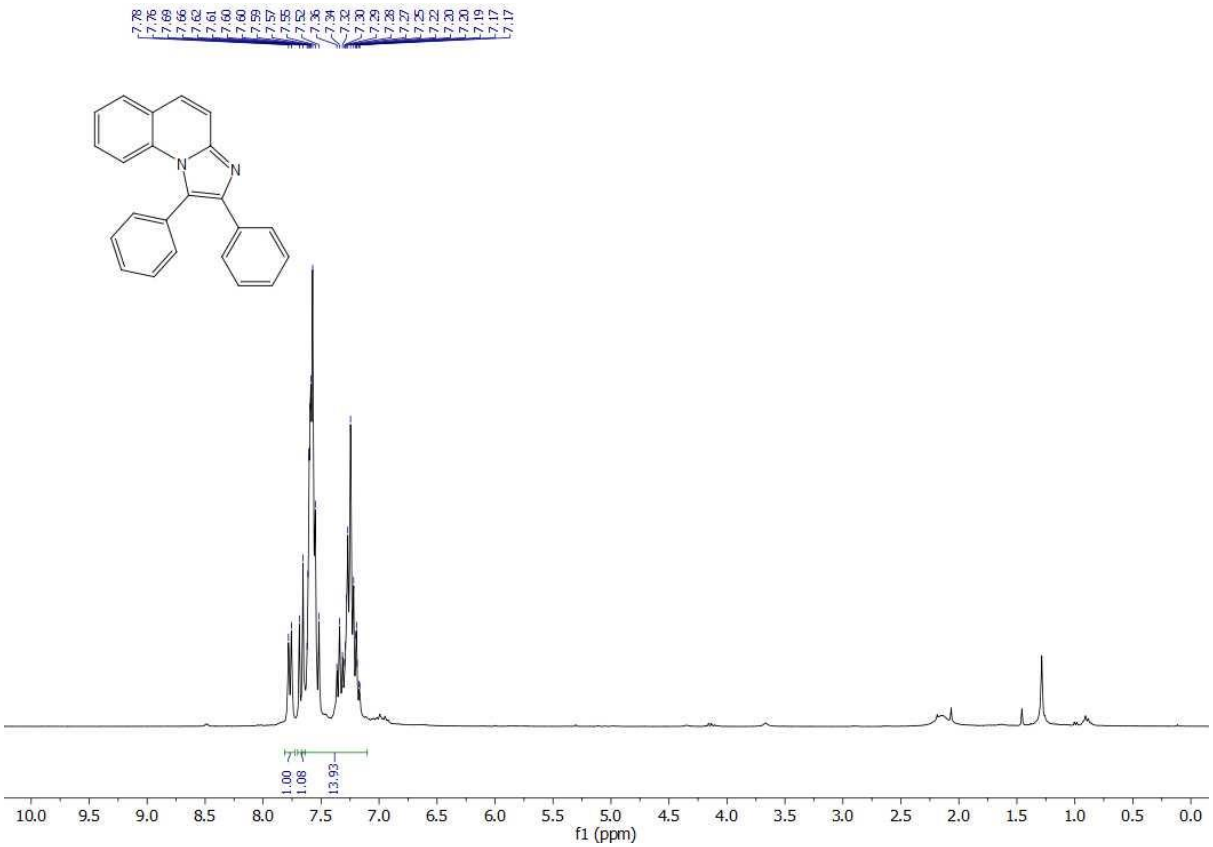
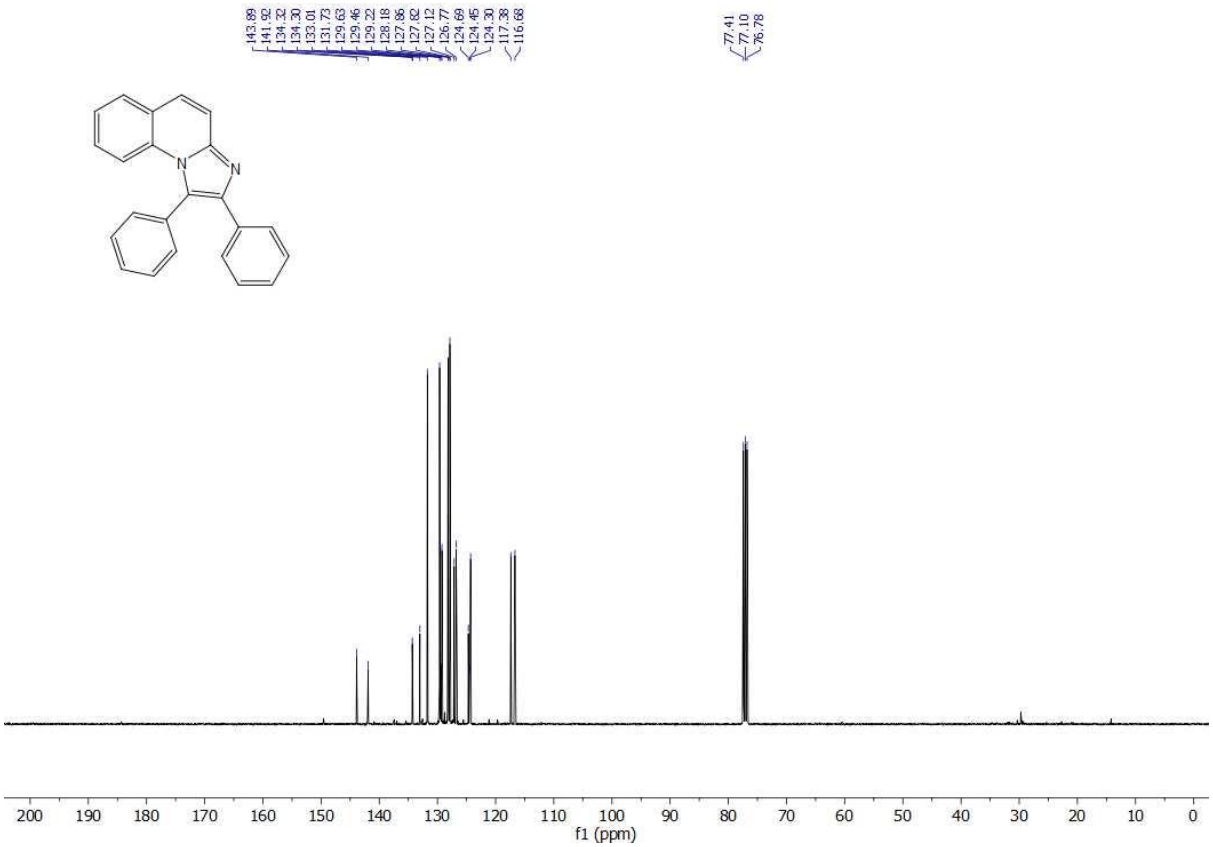


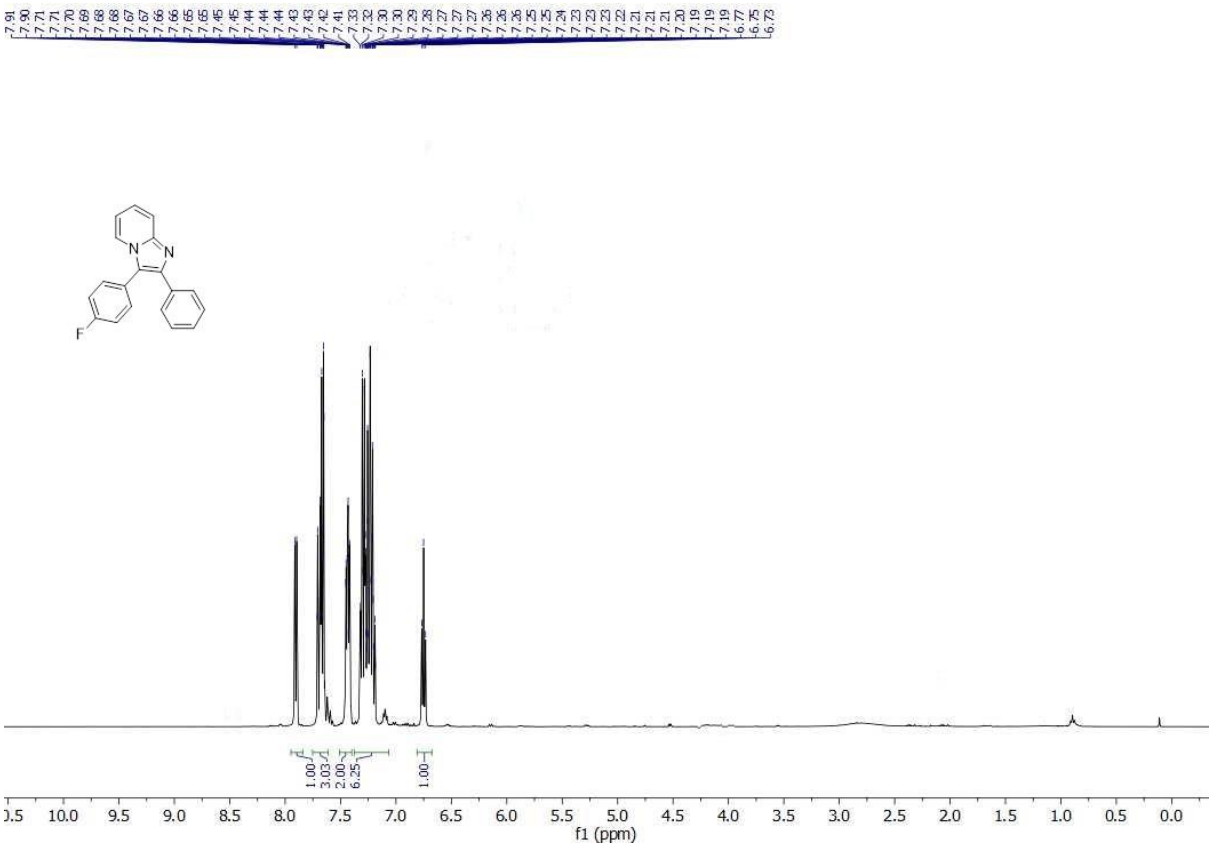
[1]H NMR spectra of **3h** (300 MHz, $CDCl_3$);



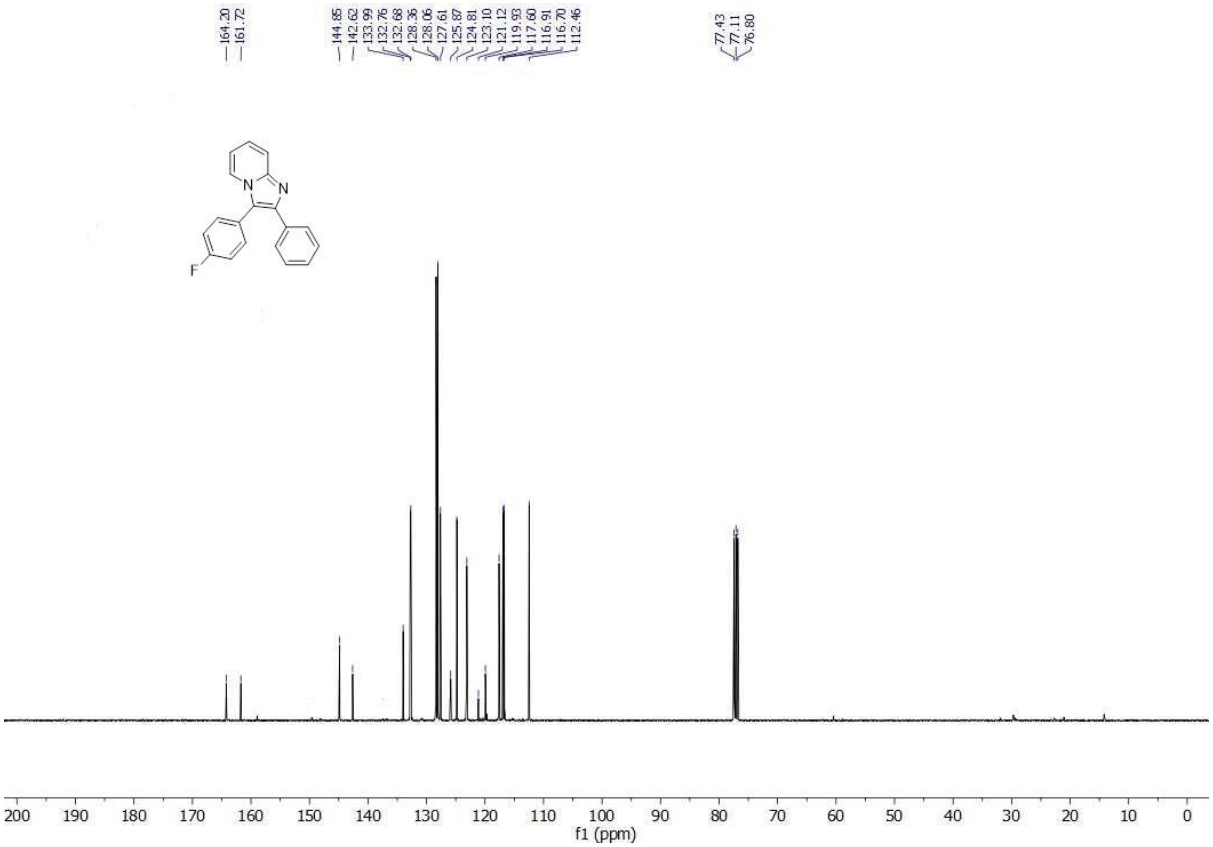
[13]C NMR spectra of **3h** (75 MHz, $CDCl_3$);



[1]H NMR spectra of **3i** (400 MHz, $CDCl_3$);



[13]C NMR spectra of **3i** (100 MHz, $CDCl_3$);



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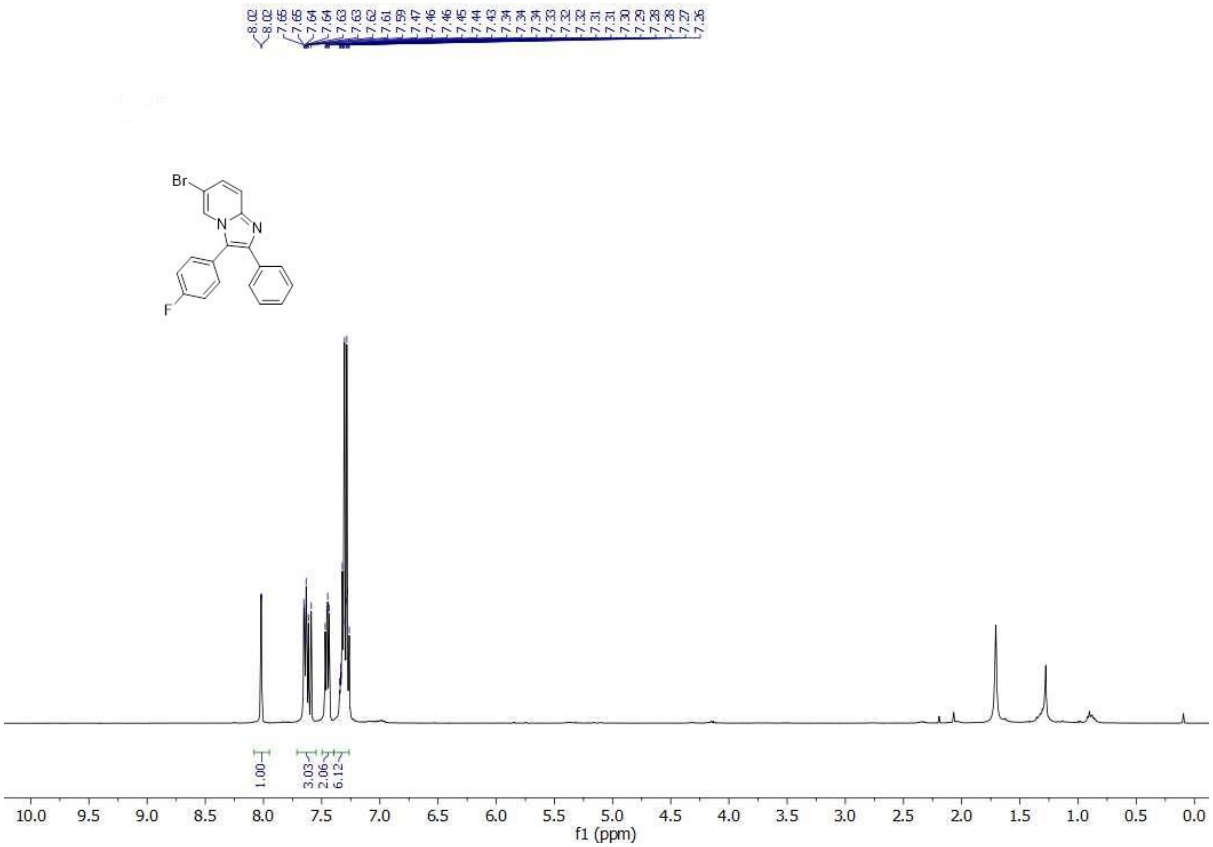

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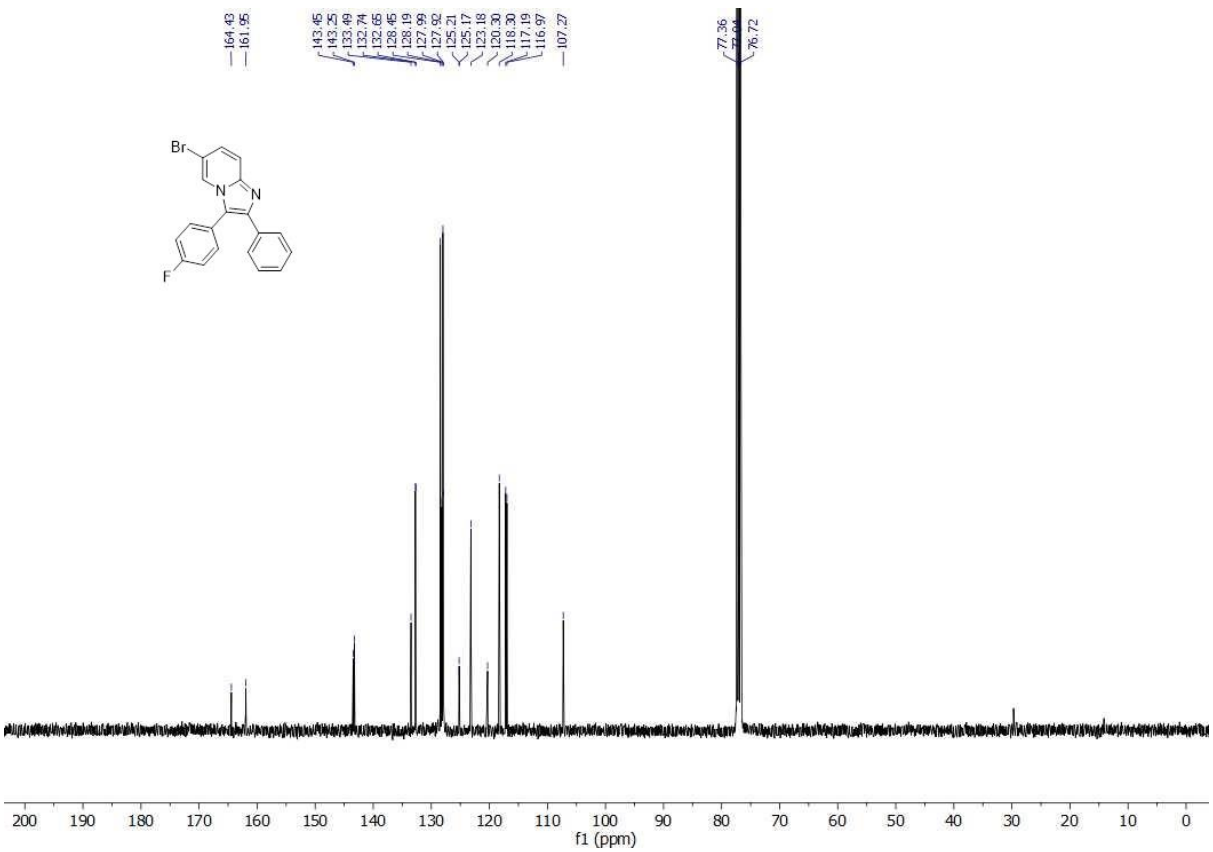

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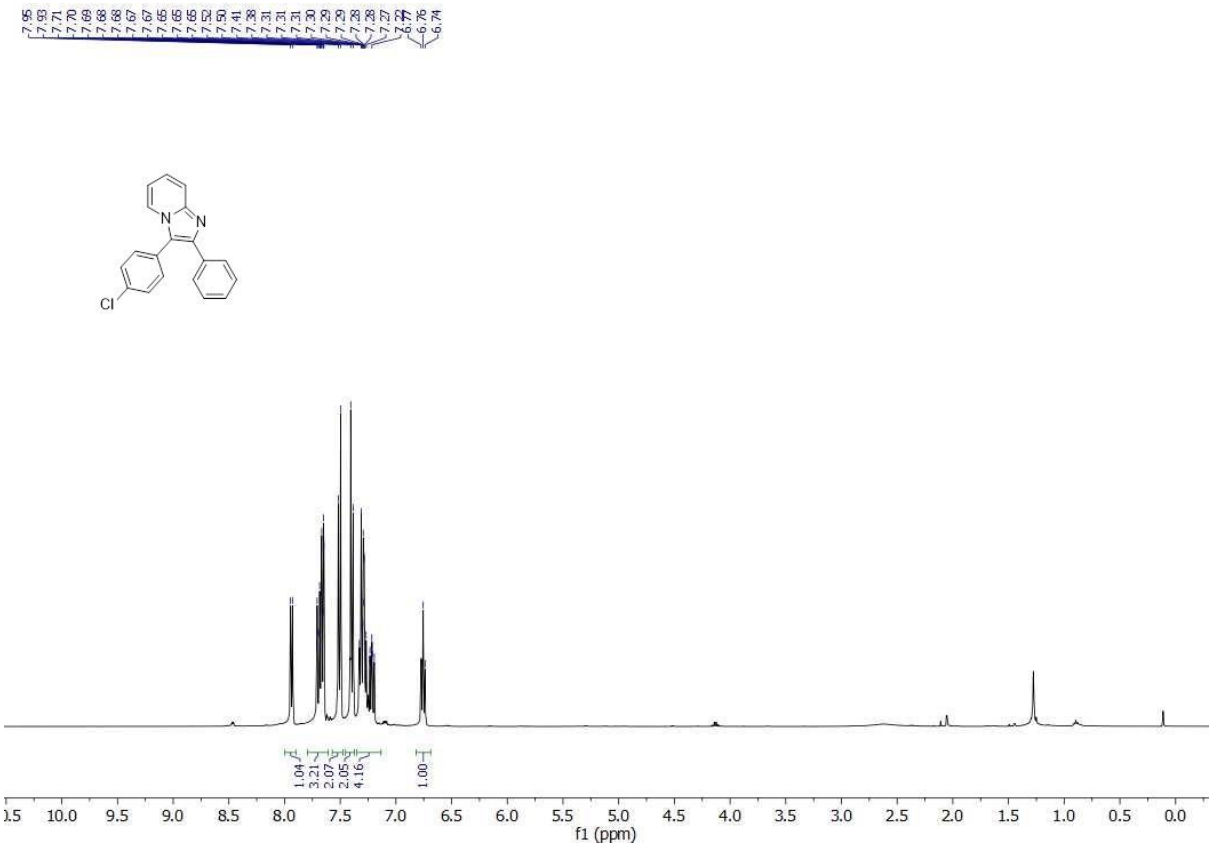
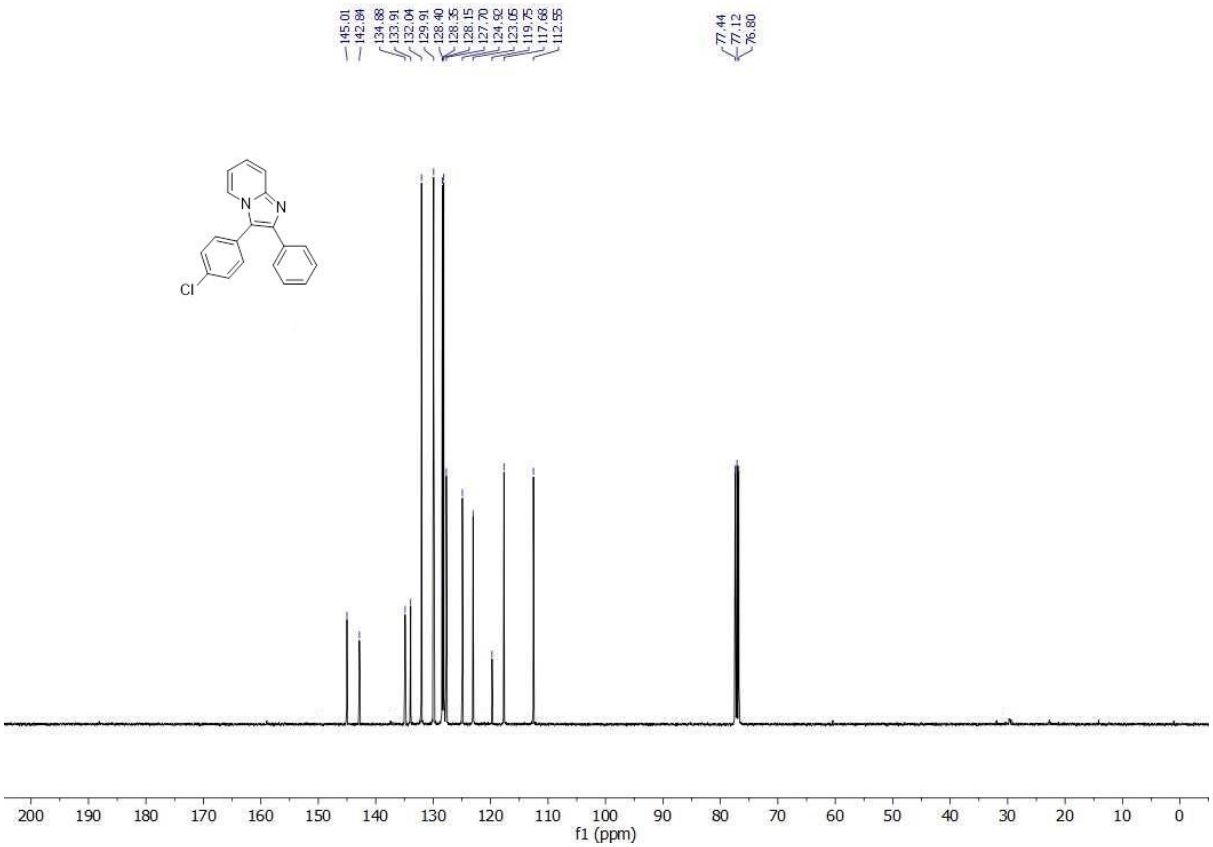
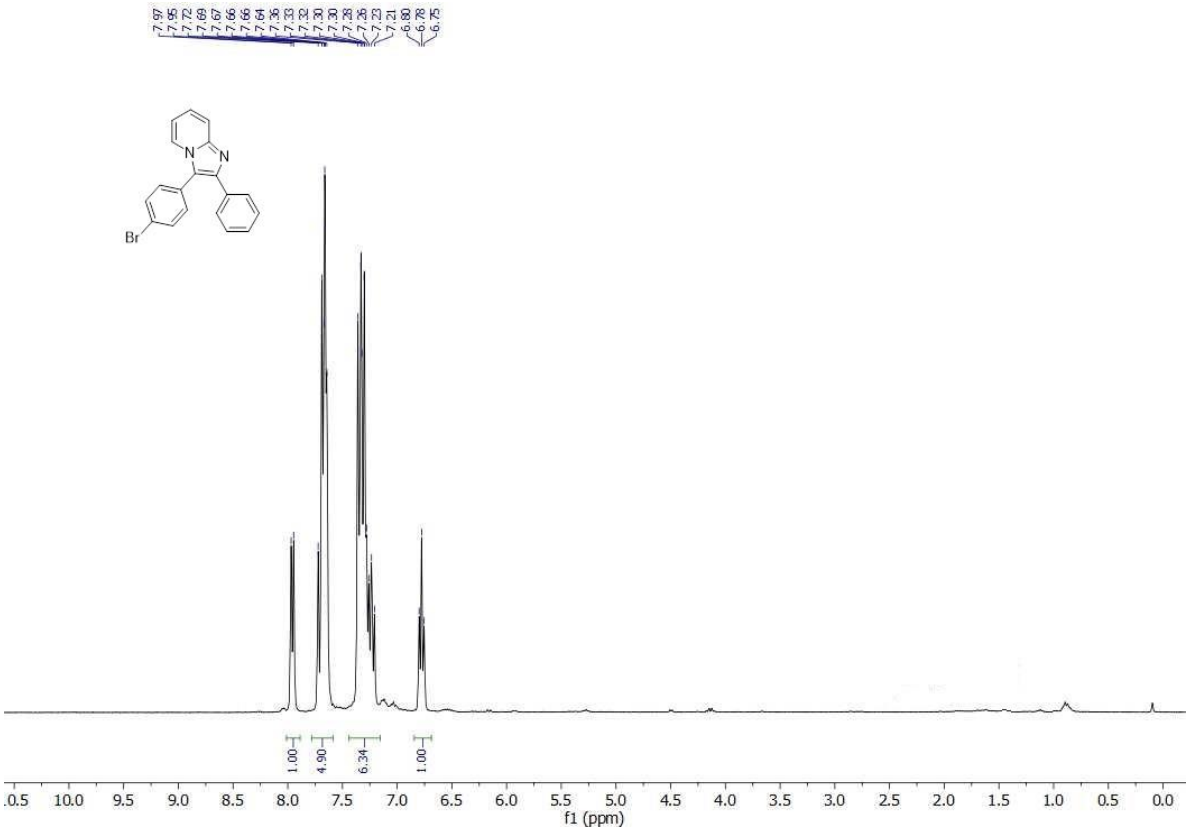


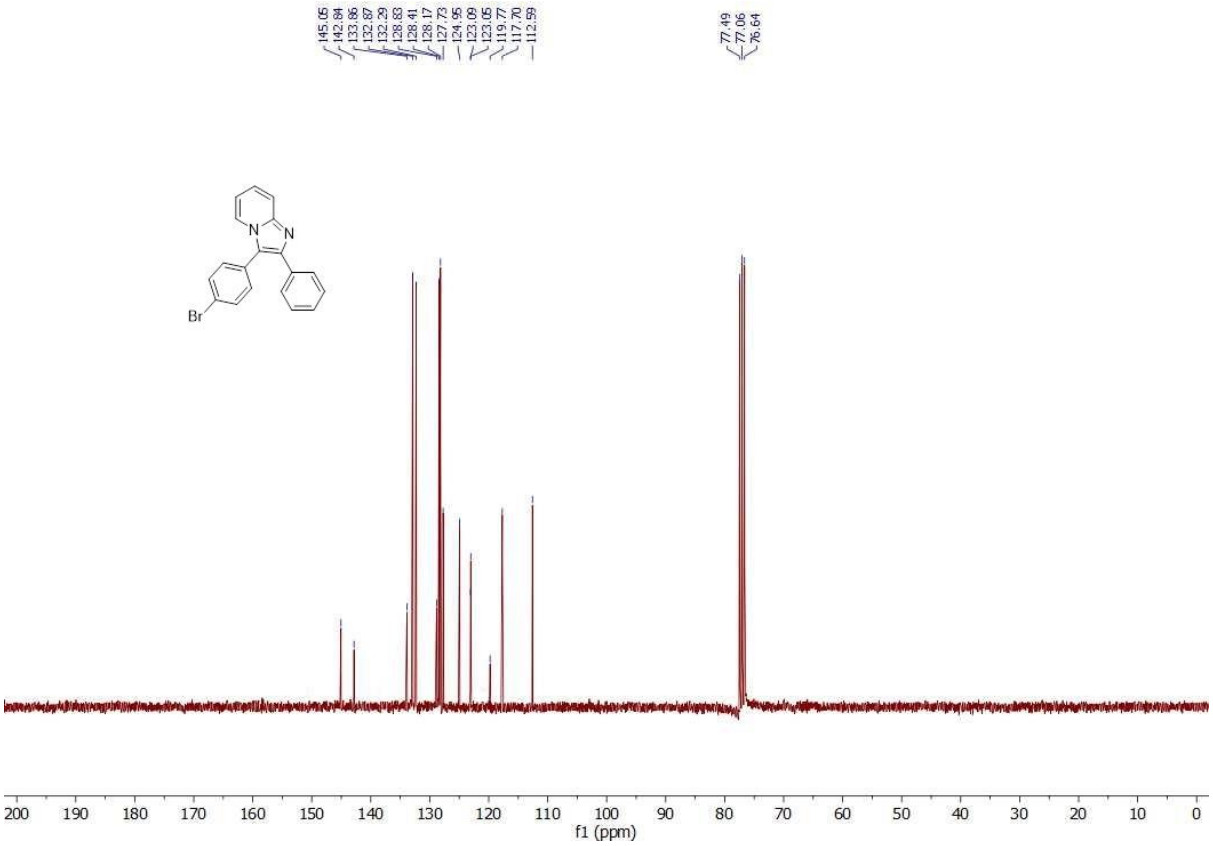
[13]C NMR spectra of **3k** (100 MHz, $CDCl_3$);



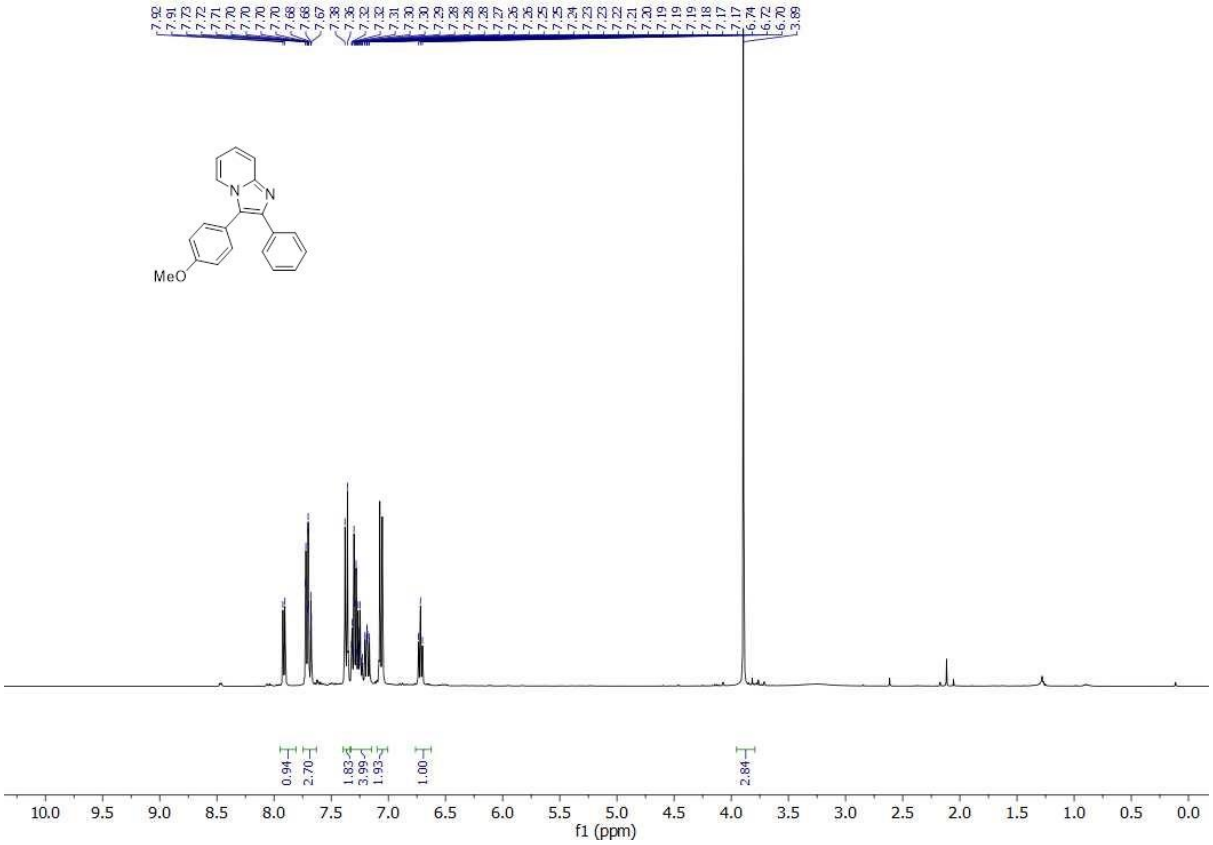
[1]H NMR spectra of **3l** (300 MHz, $CDCl_3$);



[13]C NMR spectra of **3l** (75 MHz, $CDCl_3$);



[1]H NMR spectra of **3m** (400 MHz, $CDCl_3$);



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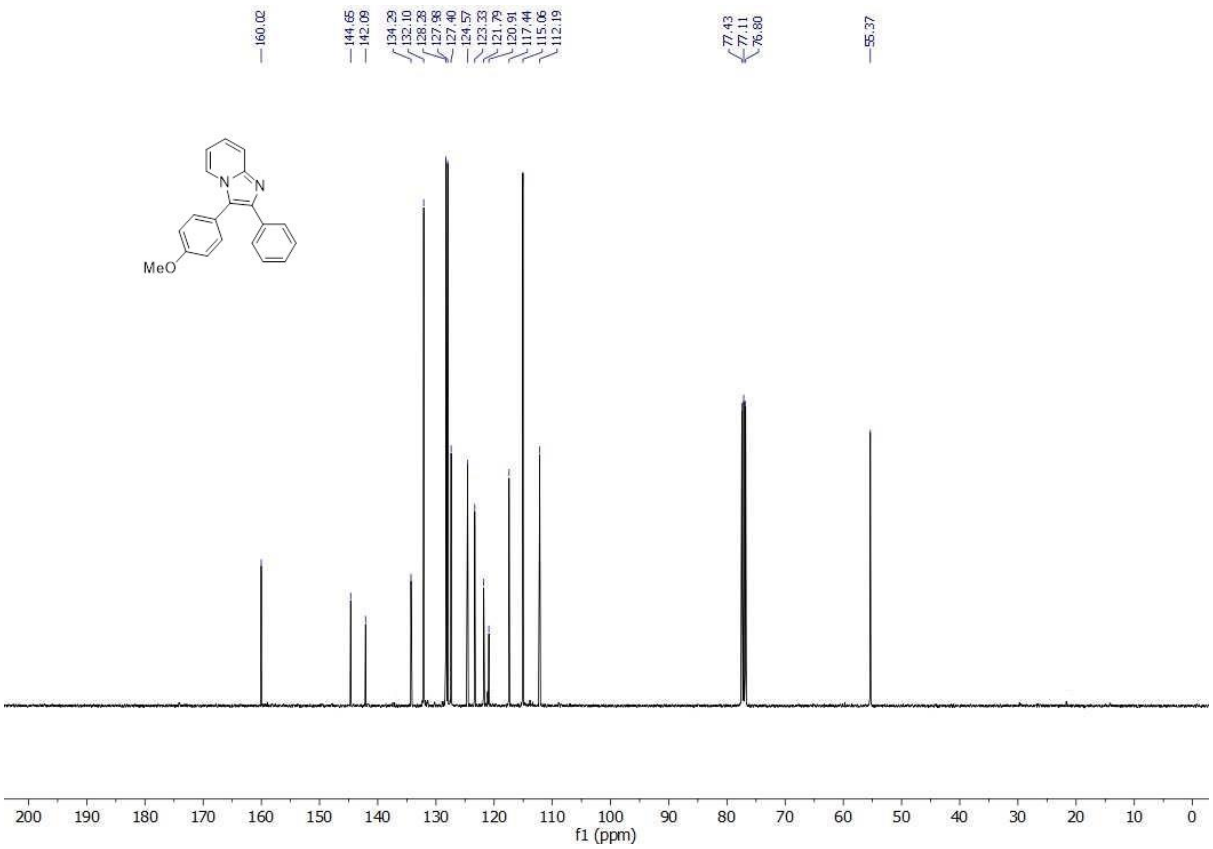
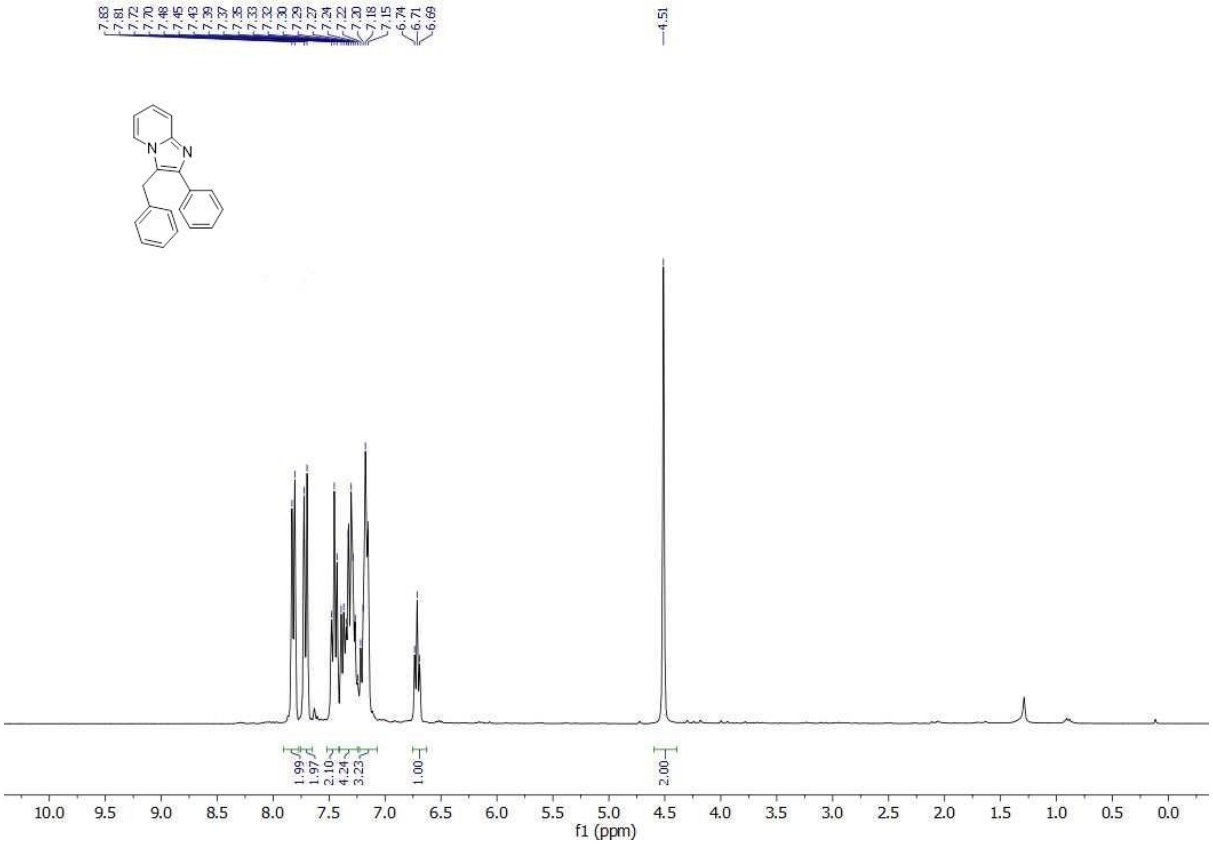


[1]H NMR spectra of **3n** (300 MHz, $CDCl_3$);



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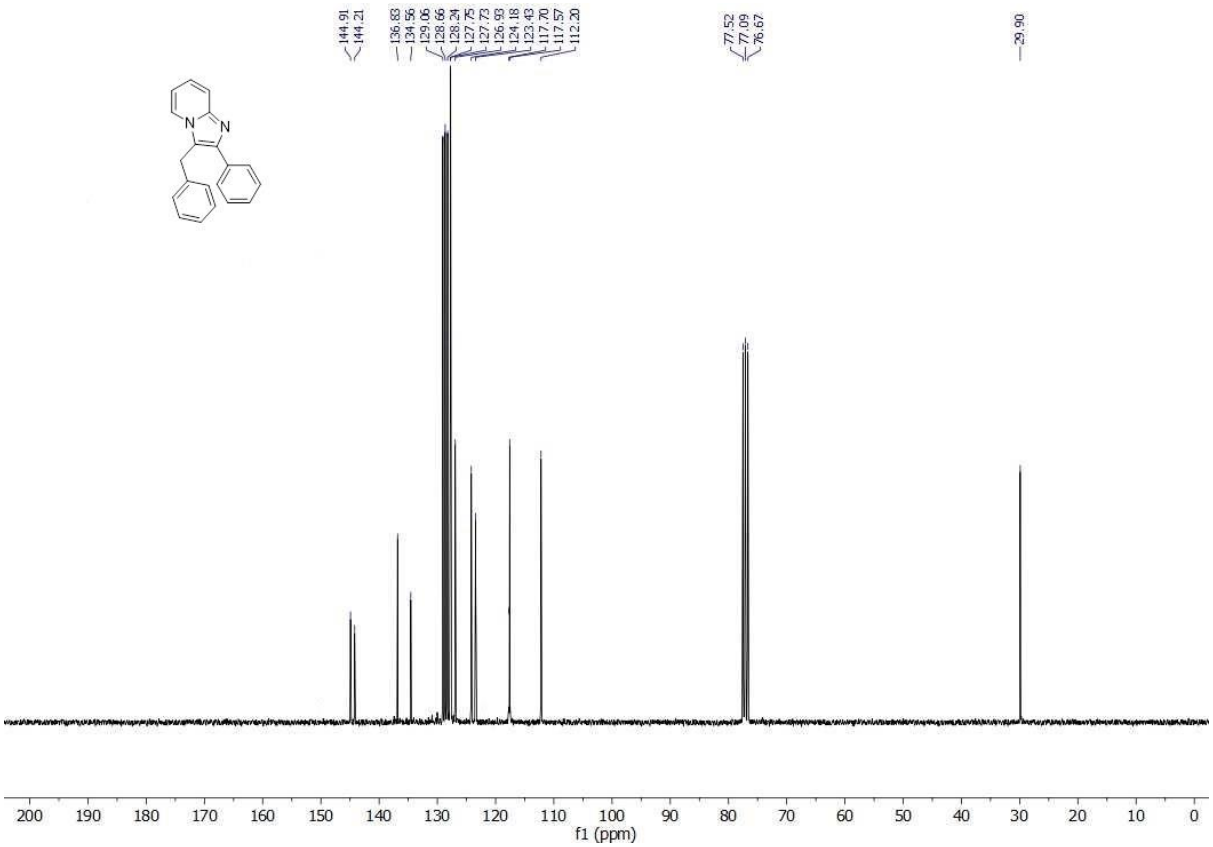

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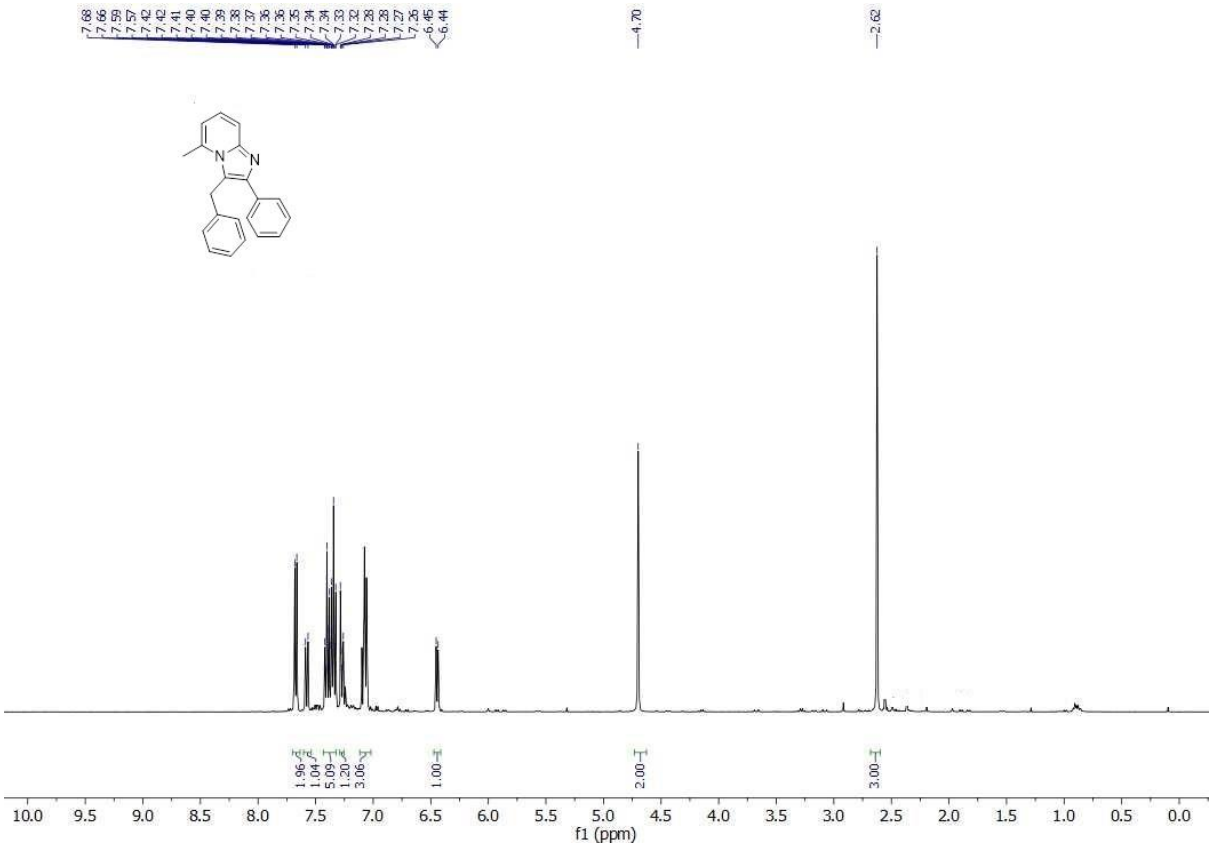

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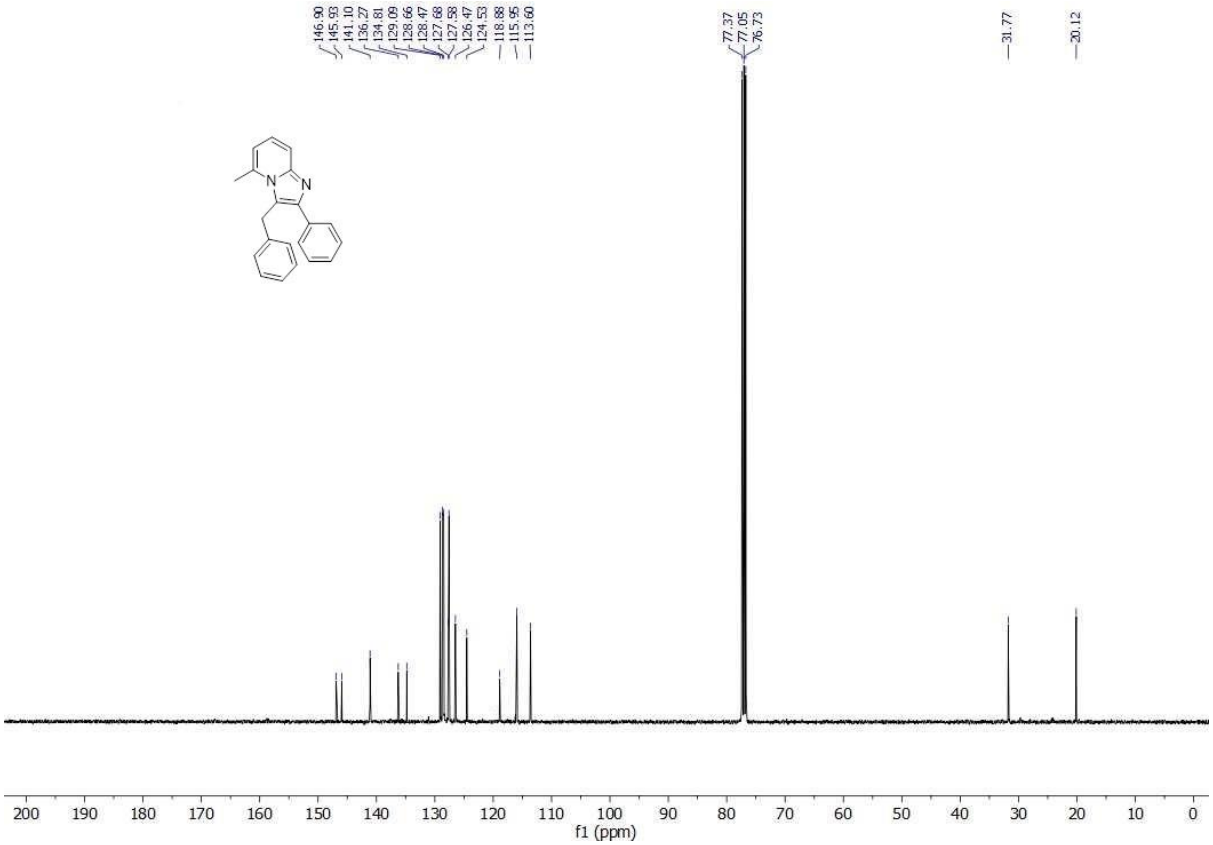
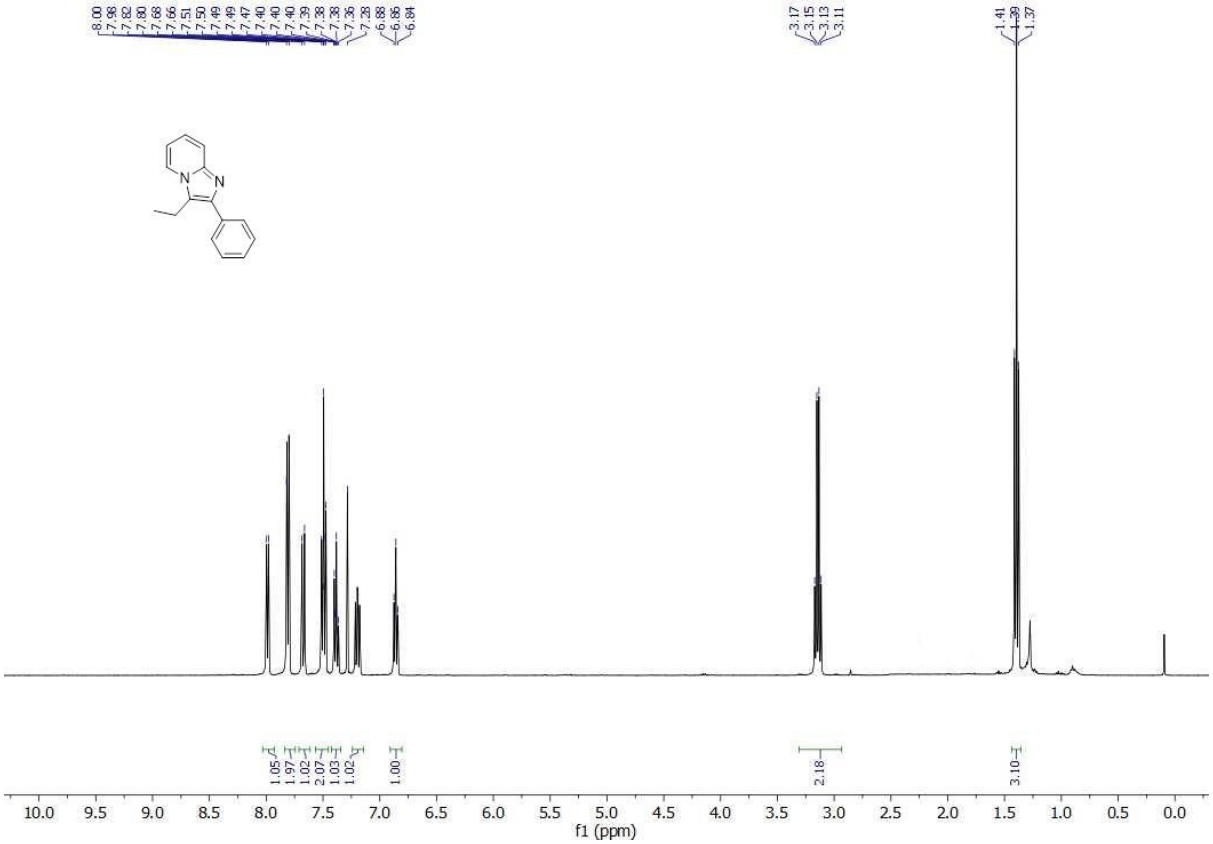
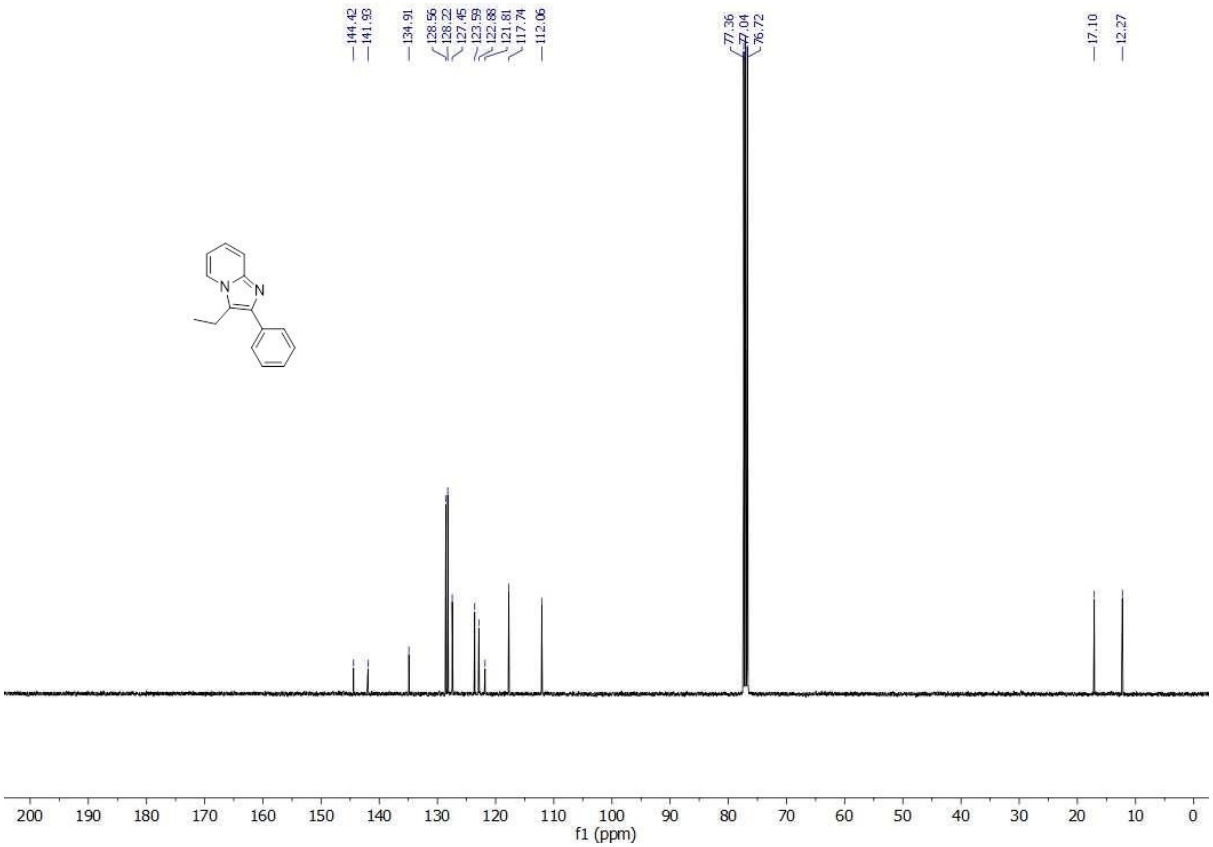


^{1}H NMR spectra of **3p** (400 MHz, $CDCl_3$);



^{13}C NMR spectra of **3p** (100 MHz, $CDCl_3$);



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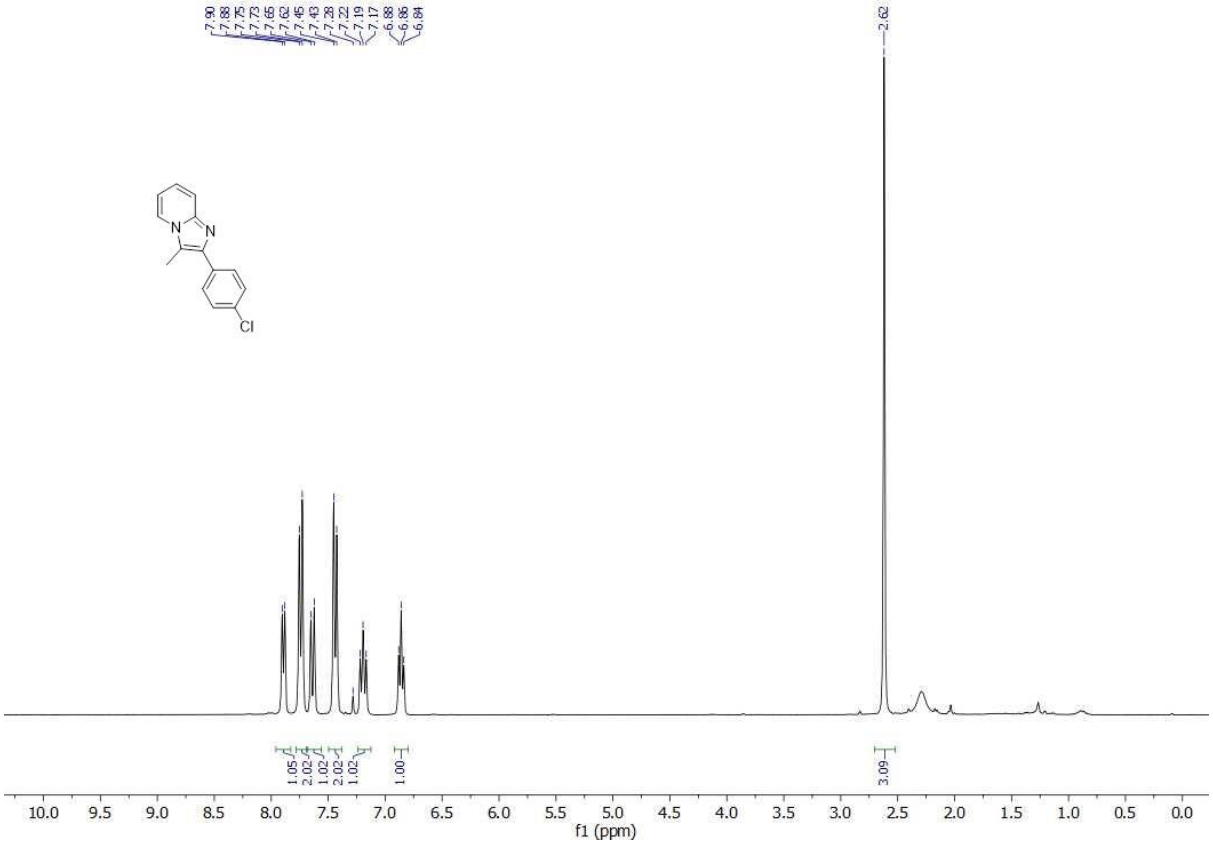
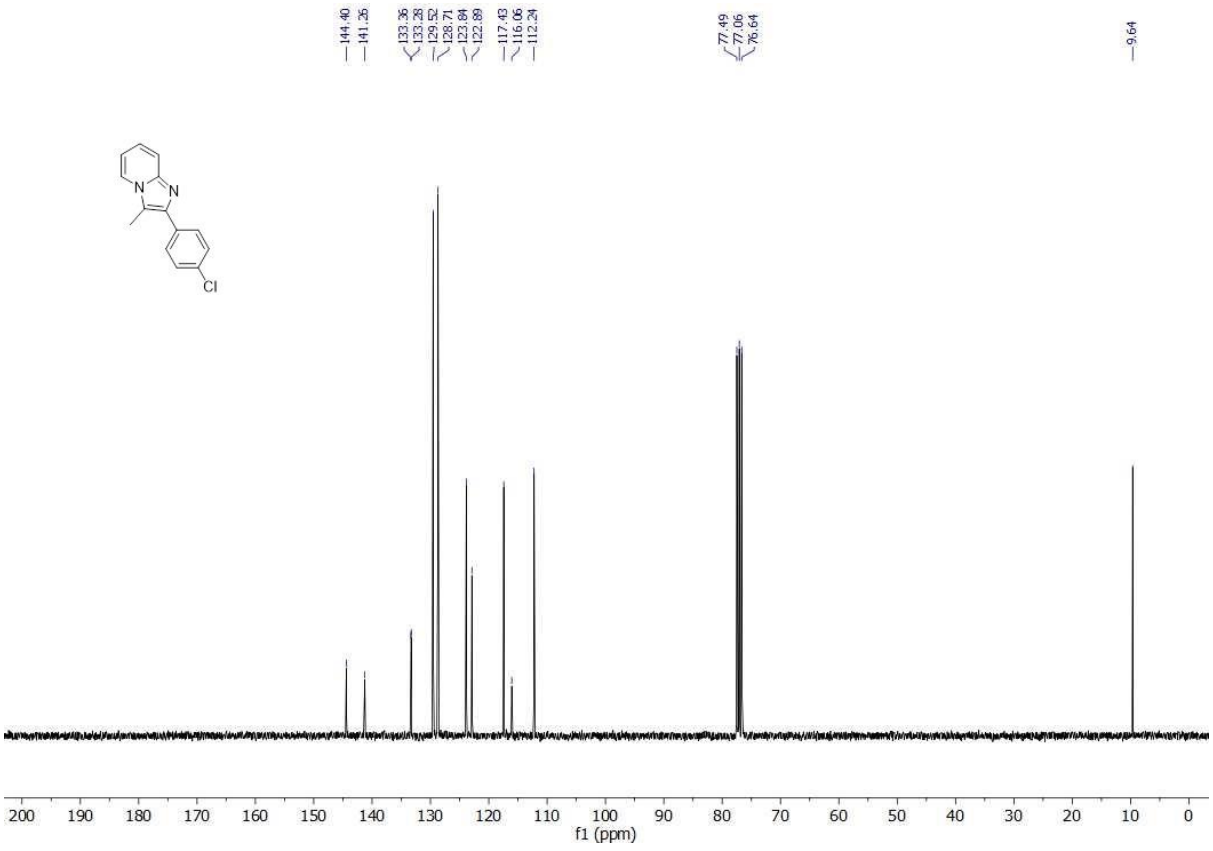


[13]C NMR spectra of **3q** (75 MHz, $CDCl_3$);



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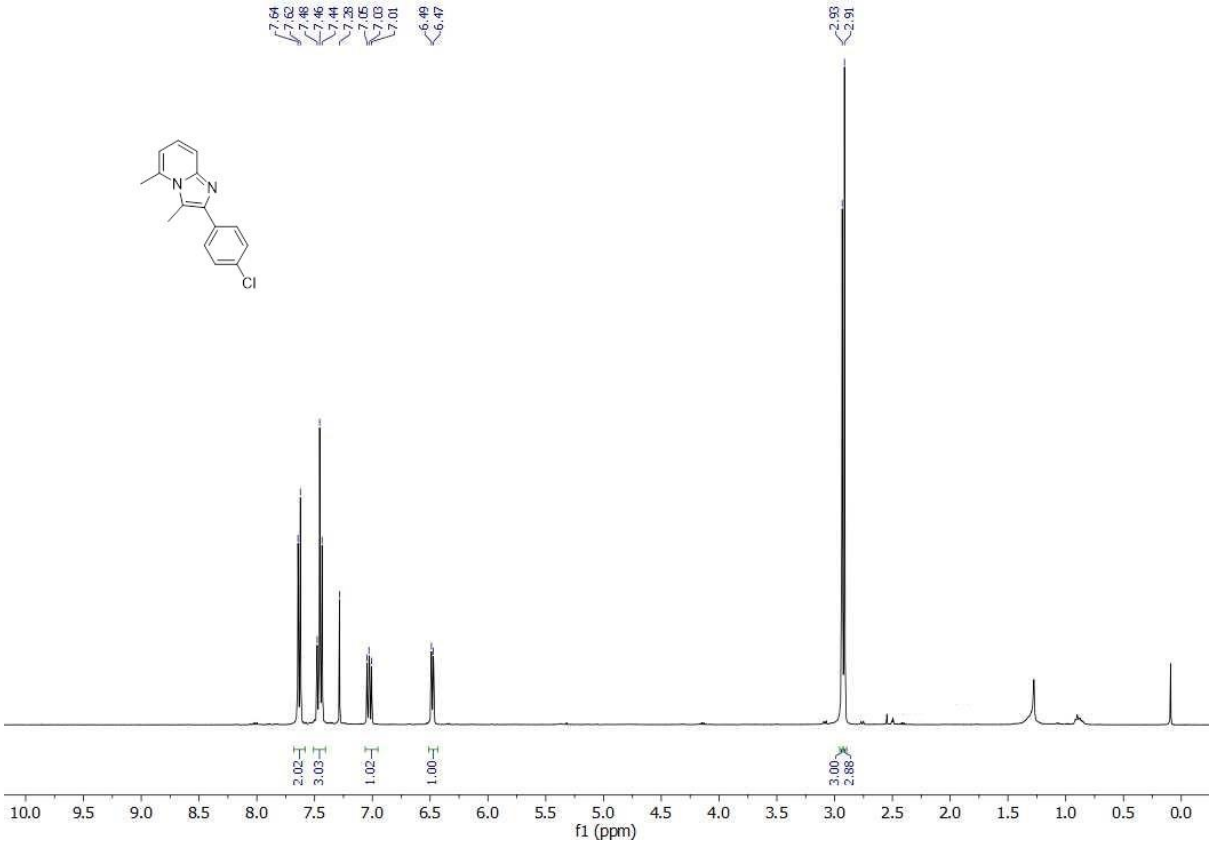

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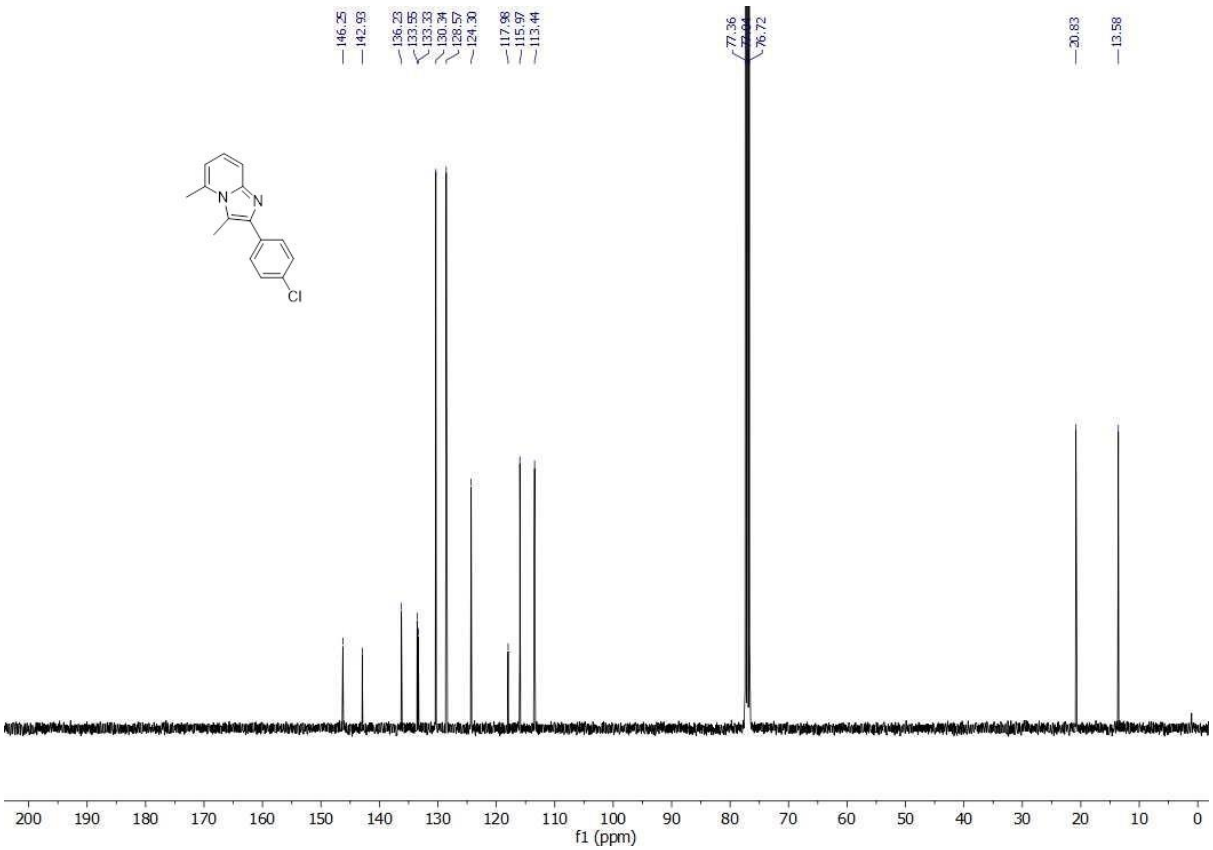
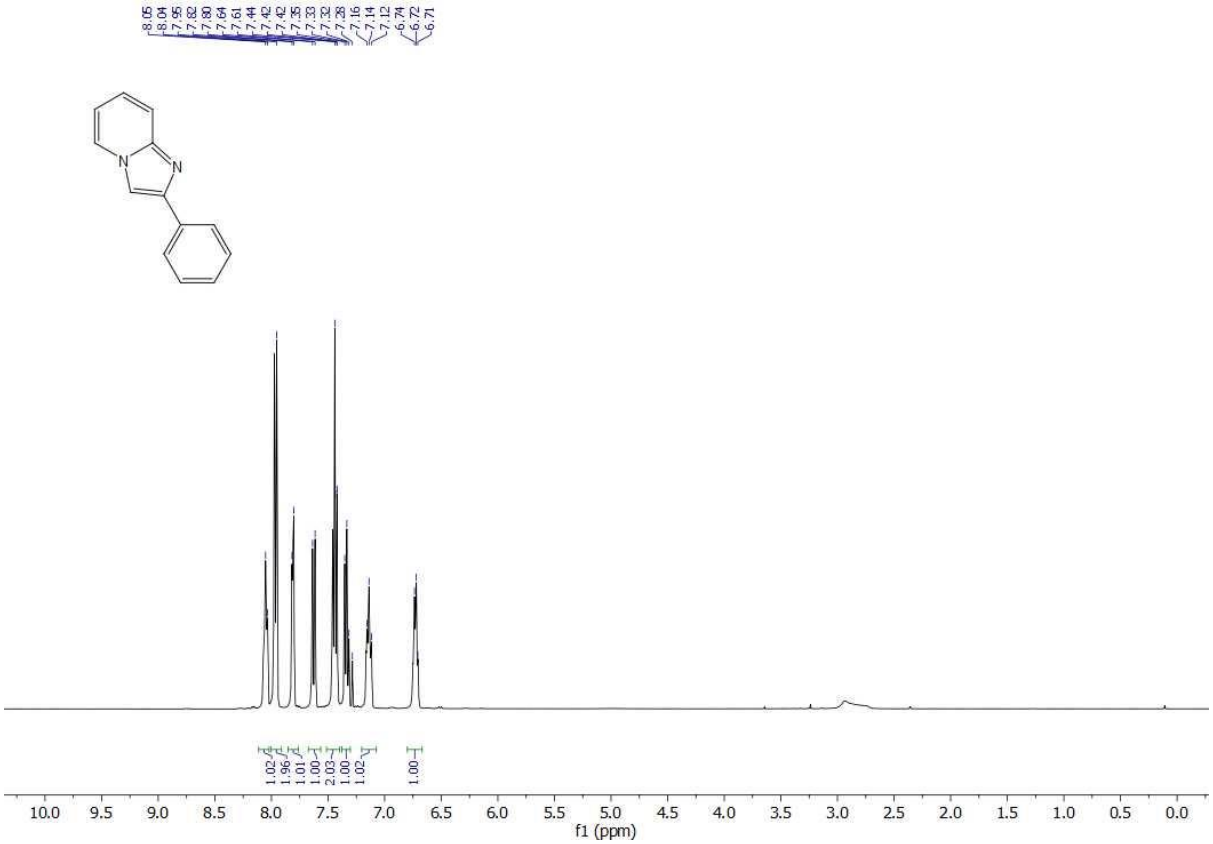


[1]H NMR spectra of **3s** (400 MHz, $CDCl_3$);



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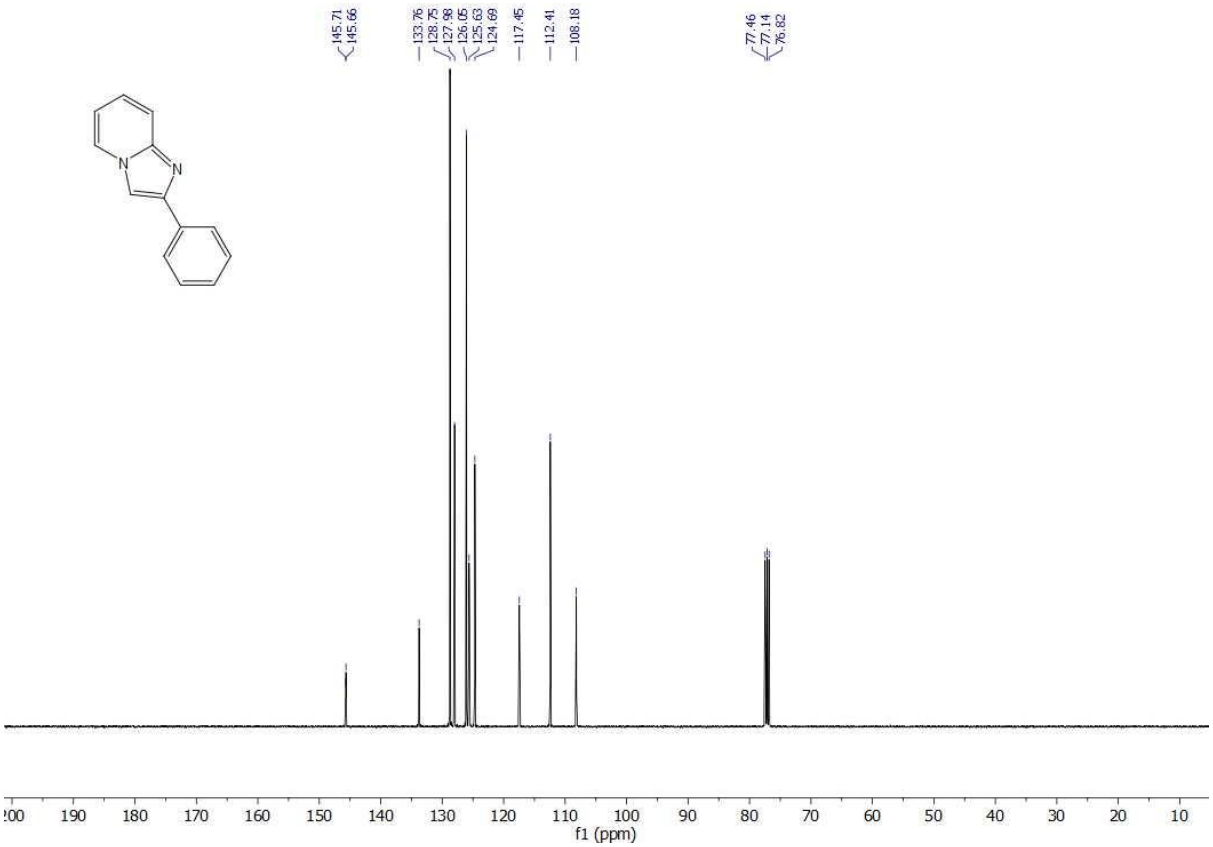

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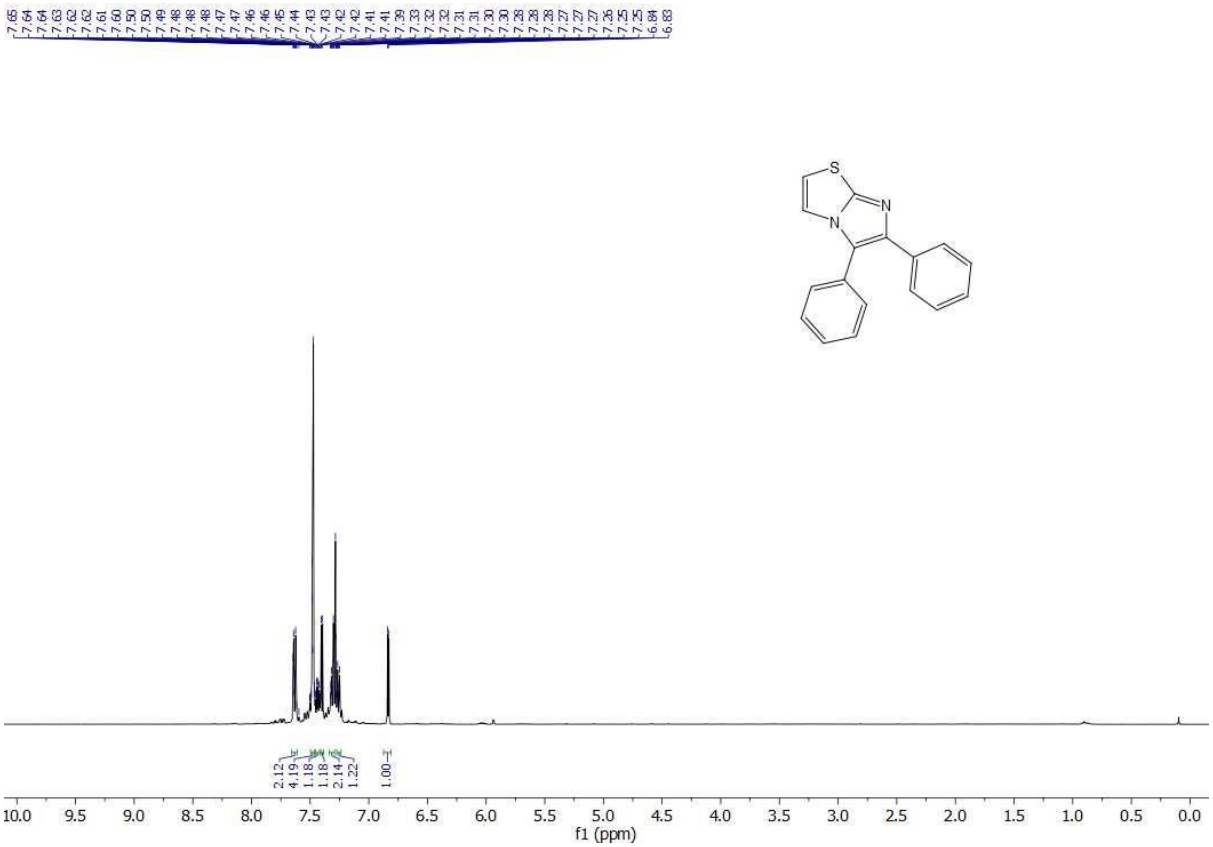

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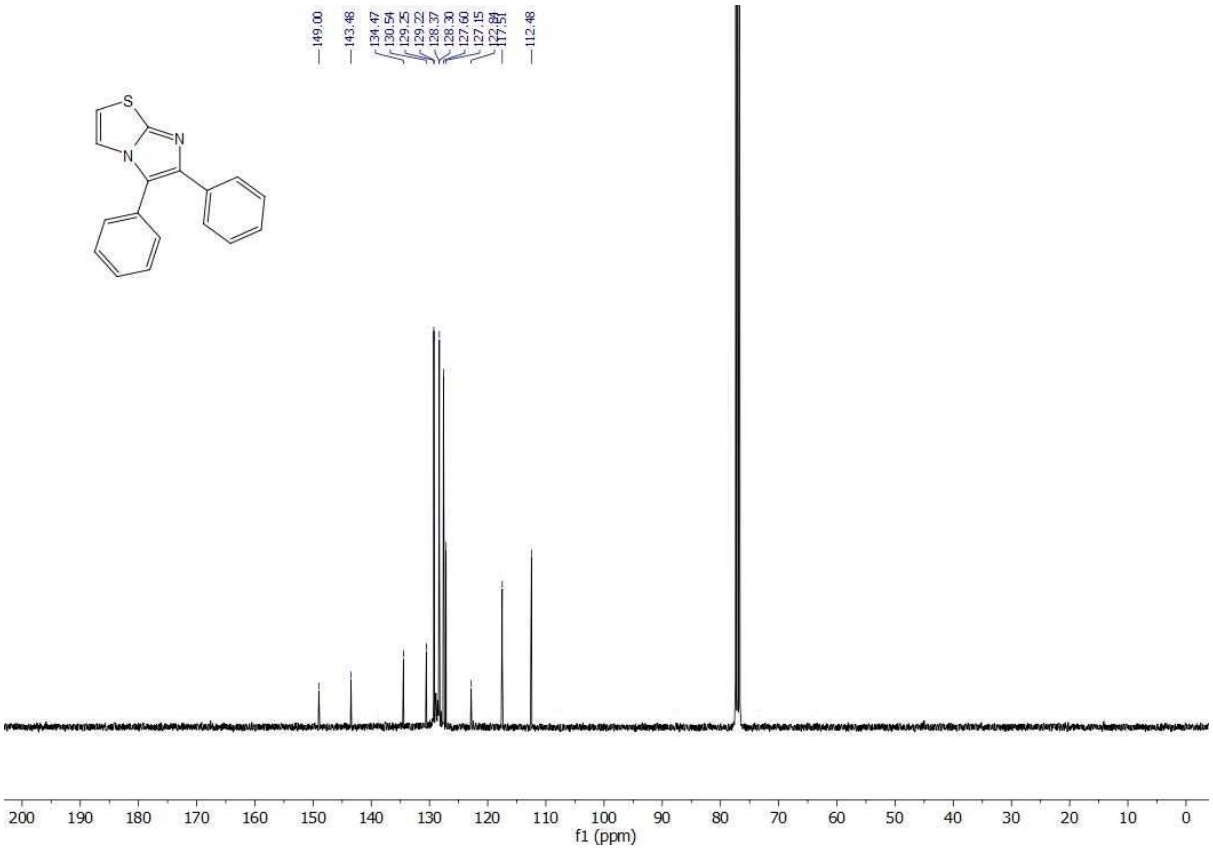

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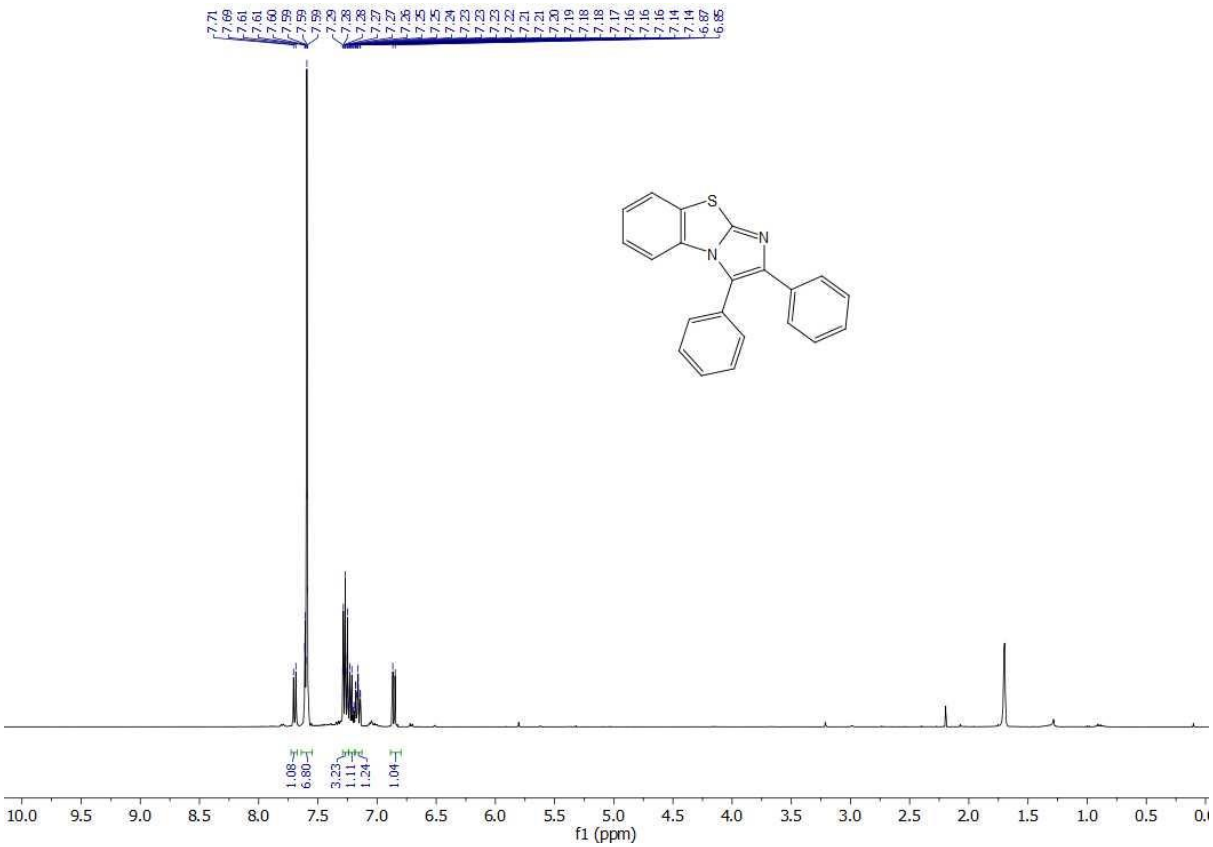

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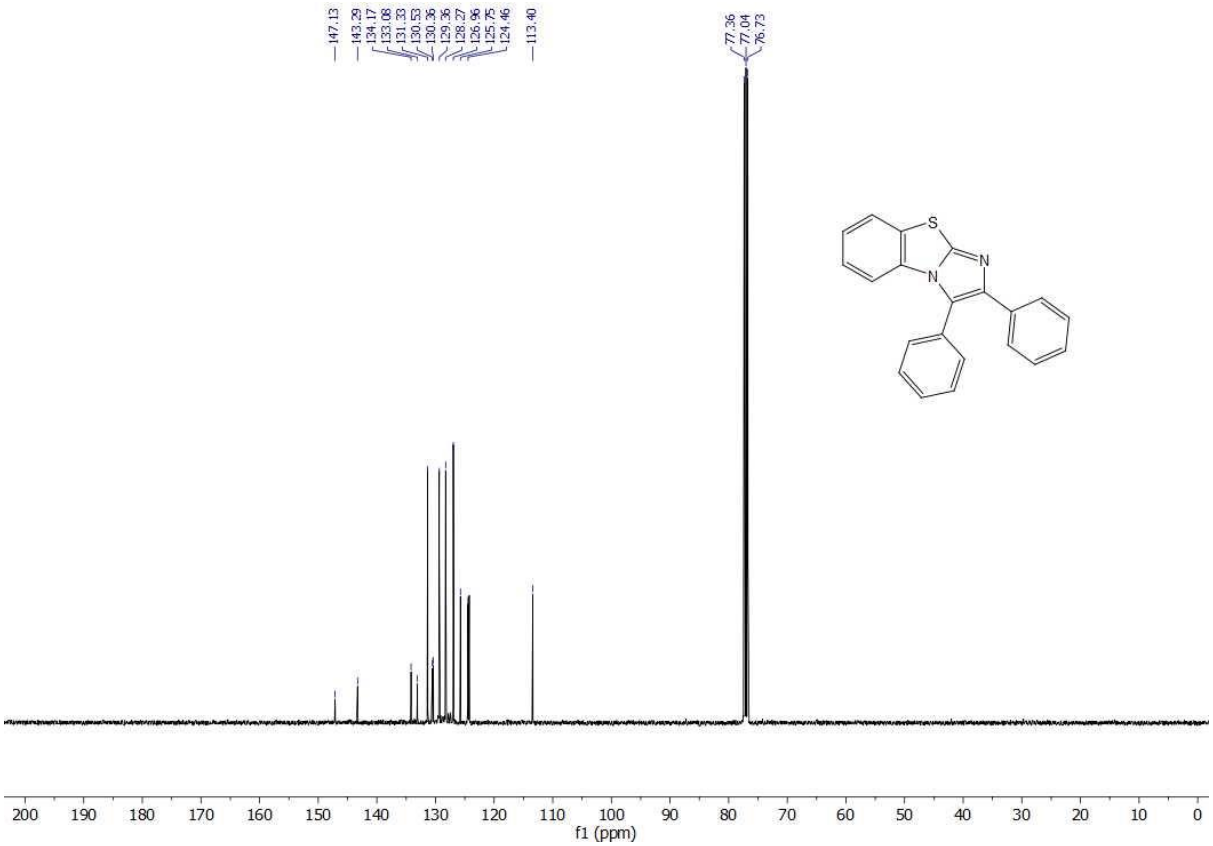

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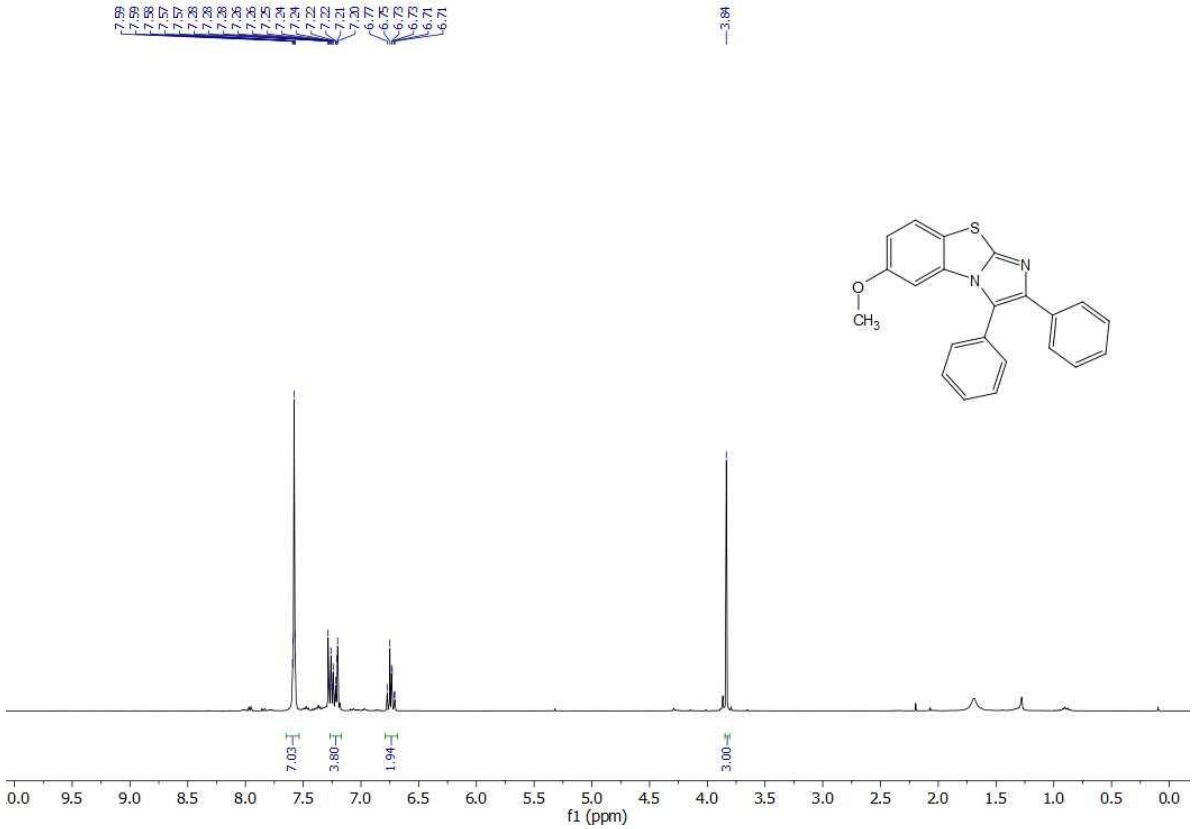

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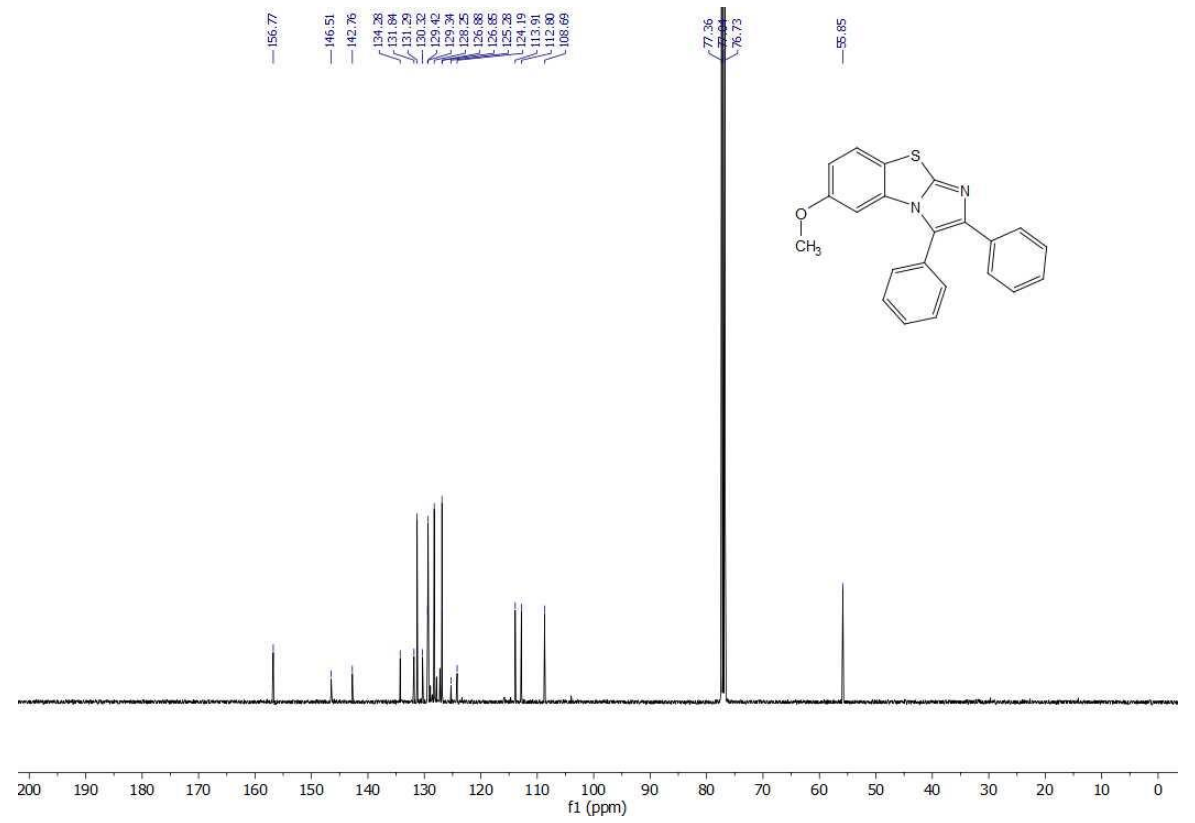
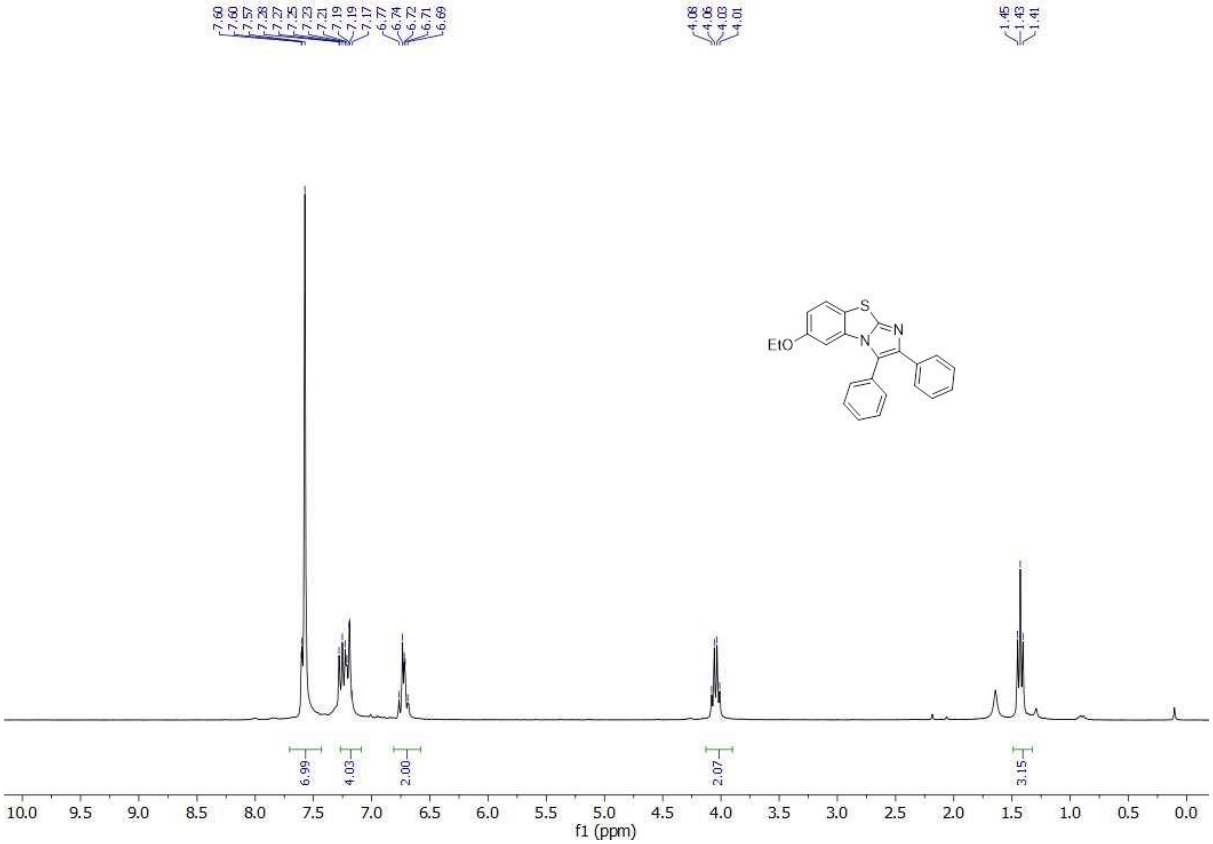
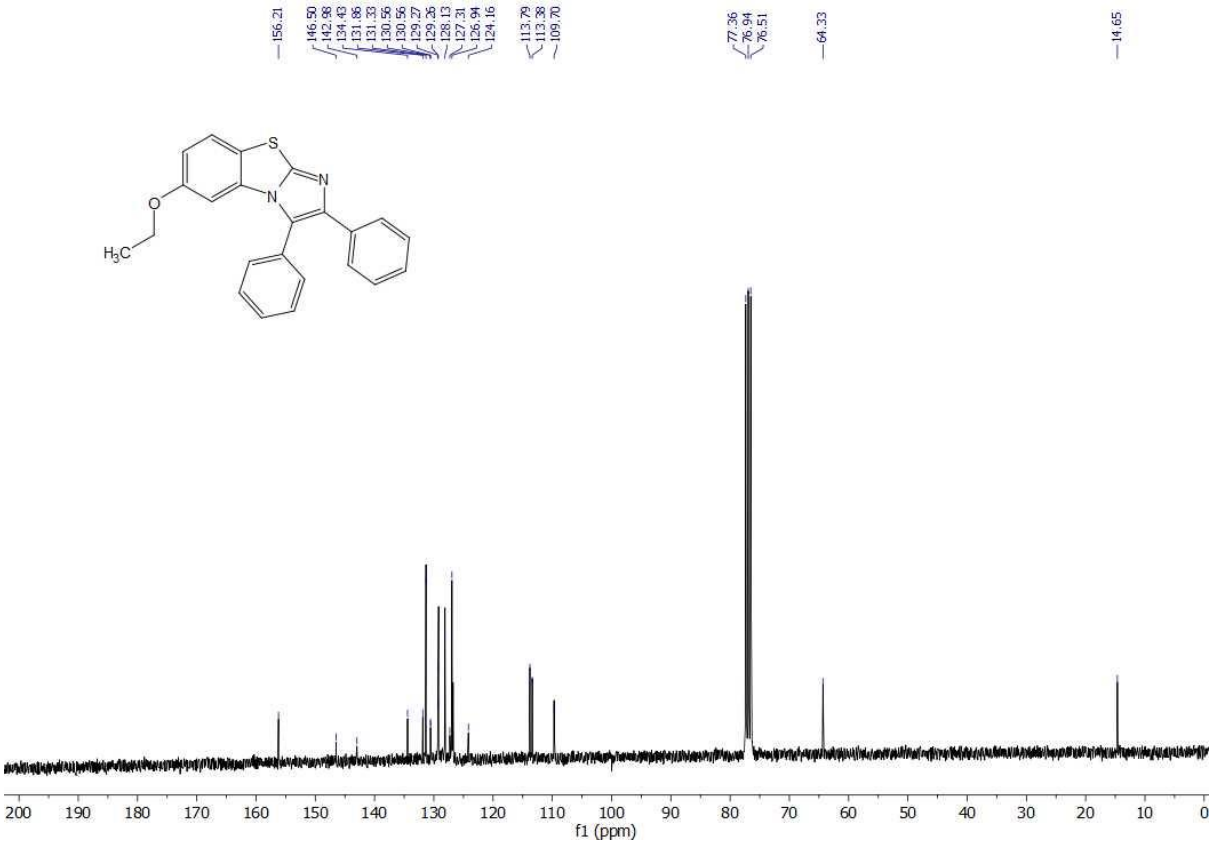


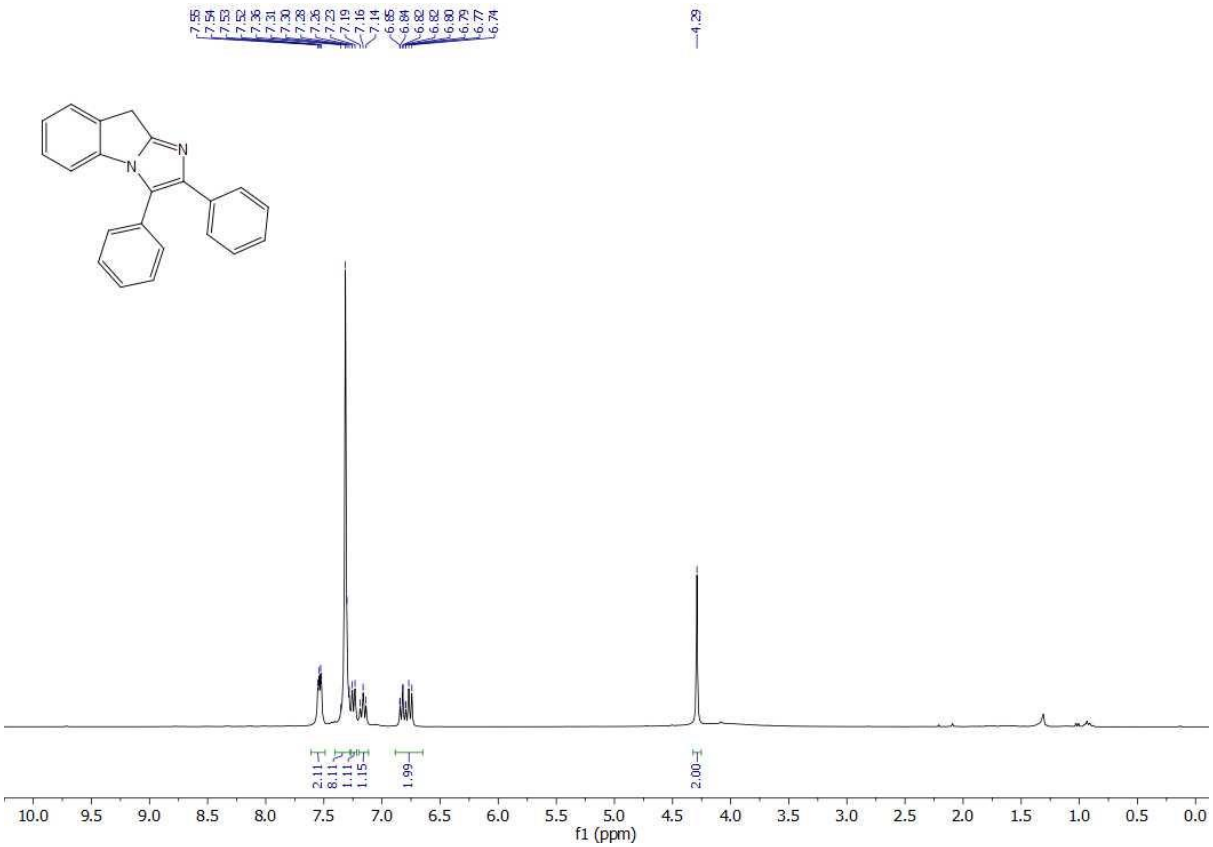
[1]H NMR spectra of **4d** (300 MHz, $CDCl_3$);



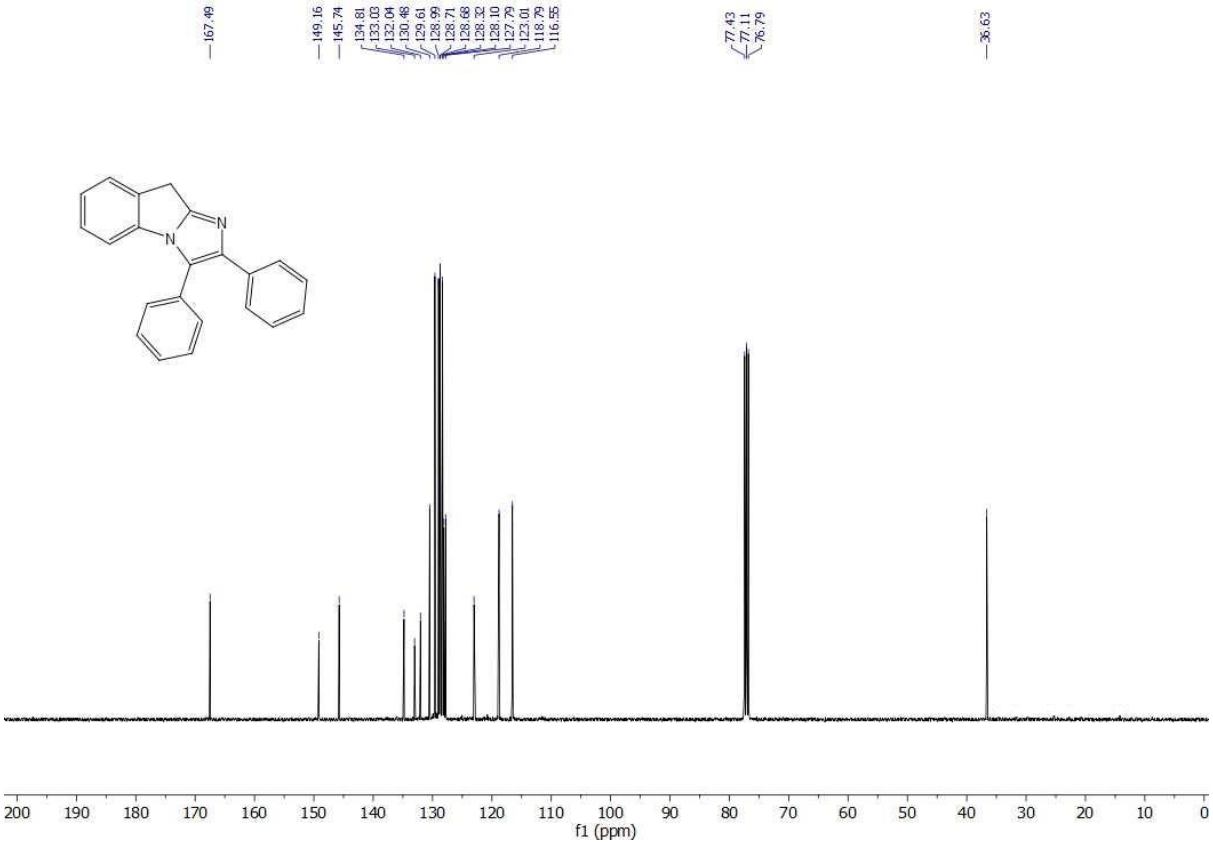
[13]C NMR spectra of **4d** (75 MHz, $CDCl_3$);



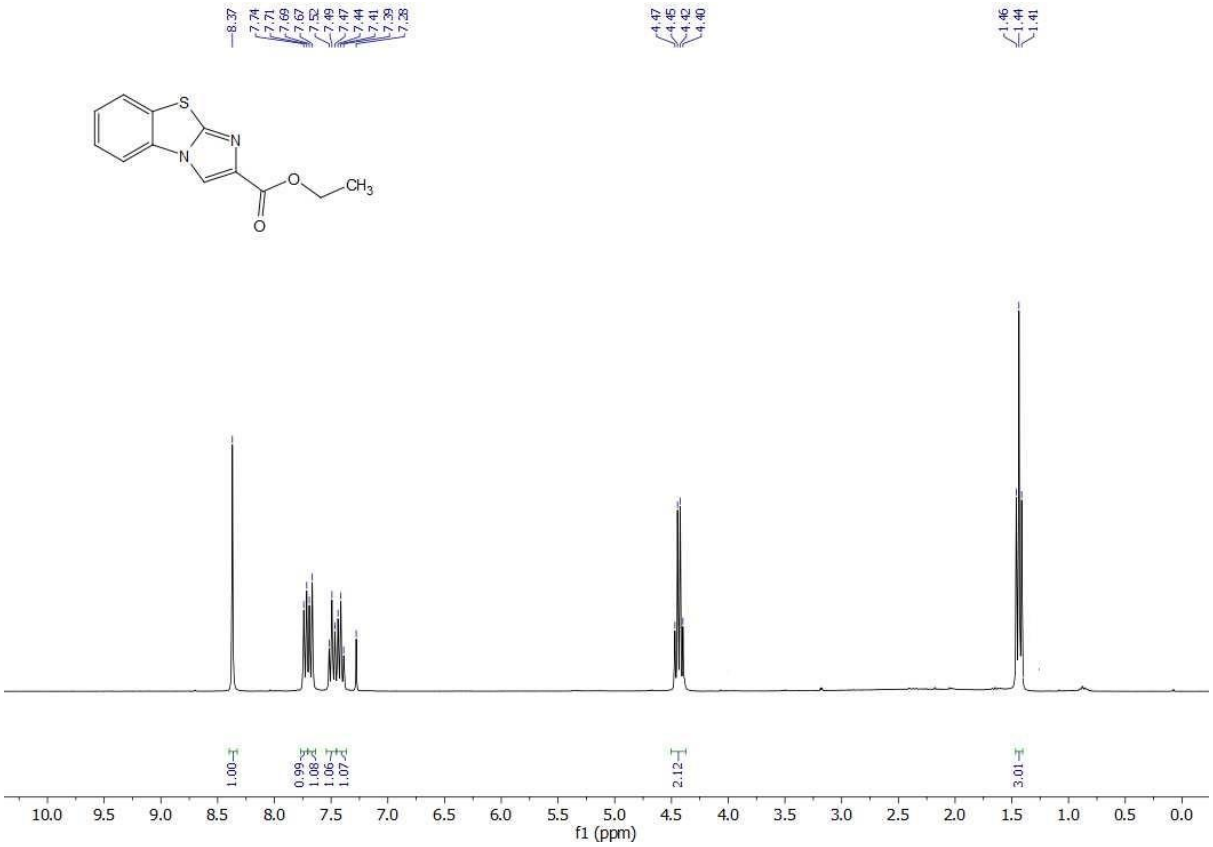
[1]H NMR spectra of **5** (300 MHz, $CDCl_3$);



[13]C NMR spectra of **5** (100 MHz, $CDCl_3$);



[1]H NMR spectra of **6** (300 MHz, $CDCl_3$);



[13]C NMR spectra of **6** (75 MHz, $CDCl_3$);