Supplementary Information

Copper(II)-mediated metalloradical activation: Denitrogenative/ decarboxylative annulation to 3-arylimidazo[1,2-a]pyridines using tetrazolo[1,5-a]pyridines and cinnamic acids

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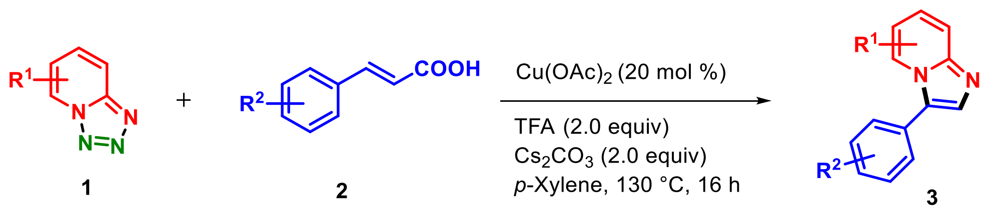
1. General information and materials

^{1}H, ^{13}C and ^{19}F Spectra were recorded on a JEOL ECZ 500R FT NMR spectrometer (^{1}H NMR at 500 MHz, ^{13}C NMR at 126 MHz, & ^{19}F NMR at 471 MHz), and Bruker Avance Neo 600 MHz NMR spectrometer (^{1}H NMR at 600 MHz, ^{13}C NMR at 151 MHz, & ^{19}F NMR at 564 MHz). Chemical shifts for protons and carbons are reported in parts per million downfield from tetramethylsilane, and are referenced to the residual deuterium in the solvent (^{1}H NMR: $CDCl_3$ at 7.26 ppm), and carbon of the solvent peak (^{13}C NMR: $CDCl_3$ at 77.16 ppm) respectively. NMR data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, and m = multiplet), coupling constant (*J*) (Hz), and integration. Mass spectra were recorded on a SCIEX X500R QTOF mass spectrometer. Single crystal X-ray data of the compound was collected on the XtaLAB Synergy, Dualflex, HyPix3000 HPAD detector, using Cu-Kα (λ = 1.54184 Å) radiation source. Analytical thin layer chromatography (TLC) was performed on Merck DC Kieselgel 60 F_{254} plates (thickness 0.25 mm). Visualization of TLC was performed with a 254 nm UV lamp. Organic solutions were concentrated under reduced pressure using a Büchi rotary evaporator. Purification of the crude products was done by column chromatography using silica gel 100–200 mesh. All the reactions were carried out in oven-dried open glass vessels. Yield refers to the isolated analytically pure material.

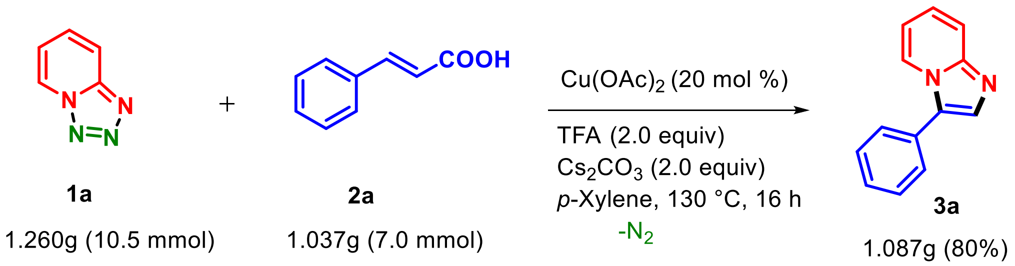
All the reagents including cinnamic acids and solvents were purchased from the Sigma-Aldrich, Merck, and TCI Chemicals. The reagents were used as such without further purification, whereas the solvents were purified by standard methods prior to its use. All the 1,2,3,4-tetrazoles were prepared adopting a known procedure.[1]

2. General procedure for the synthesis of the products 3a-3ad



A mixture of tetrazolo[1,5-a]pyridine (**1**, 0.75 mmol, 1.5 equiv.), cinnamic acid (**2**, 0.5 mmol, 1.0 equiv.), $Cu(OAc)_2$ (20 mmol %), trifluoroacetic acid (2.0 equiv.), Cs_2CO_3 (2.0 equiv.), and *p*-xylene (2.0 mL), placed in a 10 mL borosilicate vial, was stirred at 130 °C in an oil bath for 16 h. After completion of the reaction (monitored through TLC), a saturated $NaHCO_3$ aqueous solution (10 mL) was added to the reaction mixture, which was then extracted with ethyl acetate (3 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and then concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography using ethyl acetate/ n-hexane (25-50% v/v) as eluent to afford the product **3**.

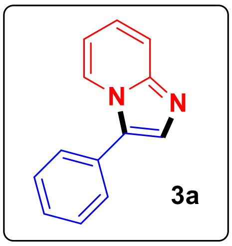
3. Gram-scale synthesis of the product 3a



A mixture of tetrazolo[1,5-a]pyridine (**1a**, 10.5 mmol, 1.5 equiv.), cinnamic acid (**2a**, 7.0 mmol, 1.0 equiv.), $Cu(OAc)_2$ (20 mmol %), trifluoroacetic acid (2.0 equiv.), Cs_2CO_3 (2.0 equiv.), and *p*-xylene (8.0 mL), placed in a 30 mL borosilicate vial, was stirred at 130 °C in an oil bath for 16 h. After completion of the reaction (monitored through TLC), a saturated $NaHCO_3$ aqueous solution (50 mL) was added to the reaction mixture, which was then extracted with ethyl acetate (3 × 50 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and then concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography using ethyl acetate/ n-hexane (25/75 v/v) as eluent to afford the product 3-phenylimidazo[1,2-a]pyridine (**3a**, 1.087 g, 80% yield).

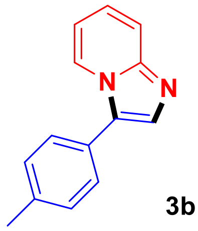
4. Physical and spectral data of the products 3a–3ad

3-Phenylimidazo[1,2-a]pyridine (3a)[1]



Viscous liquid (87 mg, 89%). Purification by column chromatography (ethyl acetate/hexane, v/v = 25/75). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.34 (d, *J* = 7.0 Hz, 1H), 7.69 (s, 1H), 7.67 (d, *J* = 9.0 Hz, 1H), 7.56 (d, *J* = 7.0 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 6.80 (t, *J* = 6.5 Hz, 1H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ 147.0, 132.2, 129.0, 128.9, 127.9, 127.8, 125.5, 123.9, 123.0, 117.9, 112.2.

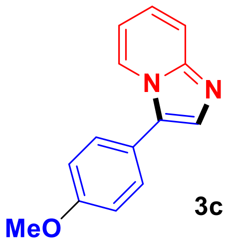
3-(*p*-Tolyl)imidazo[1,2-a]pyridine (3b)[1]



3b

Viscous liquid (97 mg, 93%). Purification by column chromatography (ethyl acetate/hexane, v/v = 25/75). **^{1}H NMR (500 MHz, CDCl$_3$):** δ 8.30 (d, J = 7.0 Hz, 1H), 7.66 – 7.64 (m, 2H), 7.44 (d, J = 7.5 Hz, 2H), 7.31 (d, J = 7.5 Hz, 2H), 7.17 (t, J = 7.5 Hz, 1H), 6.78 (t, J = 6.5 Hz, 1H), 2.42 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$):** δ 146.1, 138.3, 132.3, 129.9, 128.1, 126.4, 125.8, 124.1, 123.5, 118.3, 112.5, 21.4.

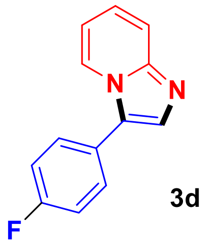
3-(4-Methoxyphenyl)imidazo[1,2-a]pyridine (3c)[1]



3c

Viscous liquid (108 mg, 96%). Purification by column chromatography (ethyl acetate/hexane, v/v = 40/60). **^{1}H NMR (500 MHz, CDCl$_3$):** δ 8.24 (d, J = 7.0 Hz, 1H), 7.64 (d, J = 9.0 Hz, 1H), 7.61 (s, 1H), 7.46 (d, J = 8.5 Hz, 2H), 7.16 (t, J = 7.5 Hz, 1H), 7.04 (d, J = 9.0 Hz, 2H), 6.77 (t, J = 7.0 Hz, 1H), 3.86 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$):** δ 159.7, 145.9, 132.1, 129.7, 125.6, 123.9, 123.3, 121.7, 118.3, 114.8, 112.4, 55.5.

3-(4-Fluorophenyl)imidazo[1,2-a]pyridine (3d)[1]

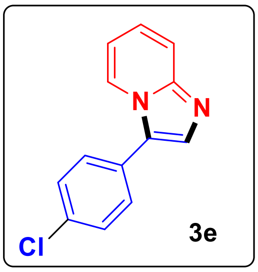


3d

Viscous liquid (86 mg, 81%). Purification by column chromatography (ethyl acetate/hexane, v/v = 25/75). **^{1}H NMR (500 MHz, CDCl$_3$):** δ 8.24 (d, J = 7.0 Hz, 1H), 7.69 – 7.67 (m, 2H), 7.54 – 7.52 (m, 2H), 7.24 – 7.19 (m, 3H), 6.82 (t, J = 6.5 Hz, 1H). **^{13}C{^{1}H} NMR (126 MHz,**

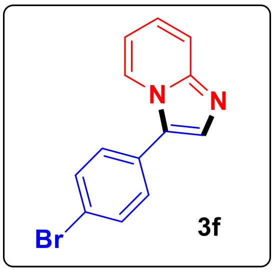
$CDCl_3$): δ 162.7 (d, J = 248.6 Hz), 146.1, 132.6, 130.1 (d, J = 8.4 Hz), 125.5, 124.8, 124.3, 123.2, 118.4, 116.4 (d, J = 21.8 Hz), 112.7. **^{19}F NMR (471 MHz, $CDCl_3$):** δ -112.6.

3-(4-Chlorophenyl)imidazo[1,2-a]pyridine (3e)[1]



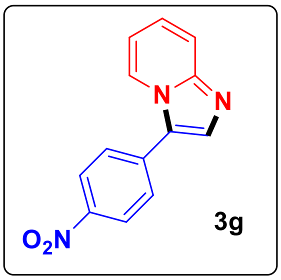
Viscous liquid (89 mg, 78%). Purification by column chromatography (ethyl acetate/hexane, v/v = 25/75). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.27 (d, *J* = 7.0 Hz, 1H), 7.67 (d, *J* = 9.5 Hz, 2H), 7.49 (s, 4H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.83 (t, *J* = 6.5 Hz, 1H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ 146.3, 134.0, 132.7, 131.1, 129.5, 129.2, 127.7, 124.4, 123.1, 118.4, 112.7.

3-(4-Bromophenyl)imidazo[1,2-a]pyridine (3f)[3]



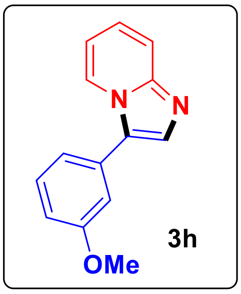
Viscous liquid (101 mg, 74%). Purification by column chromatography (ethyl acetate/hexane, v/v = 25/75). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.28 (d, *J* = 7.0 Hz, 1H), 7.72 (s, 2H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 7.0 Hz, 1H), 6.85 (t, *J* = 6.5 Hz, 1H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ 146.5, 132.7, 132.6, 131.4, 129.6, 128.2, 124.7, 123.3, 122.3, 118.5, 113.0.

3-(4-Nitrophenyl)imidazo[1,2-a]pyridine (3g)[1]



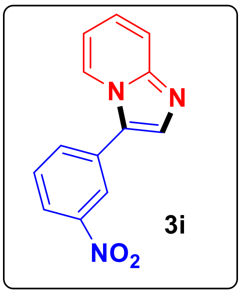
Yellow solid (104 mg, 87%). Purification by column chromatography (ethyl acetate/hexane, v/v = 40/60) **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.40 (d, *J* = 7.0 Hz, 1H), 8.37 (d, *J* = 8.5 Hz, 2H), 7.84 (s, 1H), 7.75 (d, *J* = 9.0 Hz, 2H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 6.92 (t, J = 6.5 Hz, 1H). **$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$):** δ 147.4, 146.9, 136.0, 134.8, 127.6, 125.5, 124.8, 123.8, 123.3, 118.9, 113.7.

3-(3-Methoxyphenyl)imidazo[1,2-a]pyridine (3h)[1]



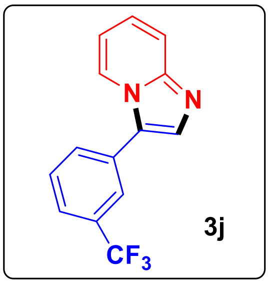
Viscous liquid (104 mg, 93%). Purification by column chromatography (ethyl acetate/hexane, v/v = 40/60). **^1H NMR (600 MHz, $CDCl_3$):** δ 8.30 (d, J = 7.2 Hz, 1H), 7.63 (s, 1H), 7.61 (d, J = 9.0 Hz, 1H), 7.37 (t, J = 8.4 Hz, 1H), 7.15 – 7.13 (m, 1H), 7.09 (d, J = 7.8 Hz, 1H), 7.02 (t, J = 2.4 Hz, 1H), 6.90 (dd, J = 8.4, 3.6 Hz, 1H), 6.75 (td, J = 6.6, 1.2 Hz, 1H), 3.80 (s, 3H). **$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$):** δ 159.2, 145.1, 131.4, 129.5, 129.3, 124.6, 123.4, 122.5, 119.3, 117.2, 112.8, 112.6, 111.6, 54.4.

3-(3-Nitrophenyl)imidazo[1,2-a]pyridine (3i)[2]



Viscous solid (99 mg, 83%). Purification by column chromatography (ethyl acetate/hexane, v/v = 40/60). **^1H NMR (500 MHz, $CDCl_3$):** δ 8.45 (s, 1H), 8.34 (d, J = 7.0 Hz, 1H), 8.26 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.81 (s, 1H), 7.73 – 7.69 (m, 2H), 7.28 (t, J = 7.5 Hz, 1H), 6.91 (t, J = 7.0 Hz, 1H). **$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$):** δ 148.9, 146.9, 133.9, 133.6, 131.2, 130.4, 125.1, 123.4, 122.9, 122.7, 122.2, 118.7, 113.5.

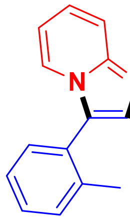
3-(3-(Trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (3j)[3]



Viscous liquid (106 mg, 81%). Purification by column chromatography (ethyl acetate/hexane, v/v = 25/75). **^{1}H NMR (500 MHz, CDCl$_3$):** δ 8.31 (d, *J* = 7.0 Hz, 1H), 7.83 (s, 1H), 7.77 (d, *J* = 4.2 Hz, 2H), 7.69 (dd, *J* = 22.1, 8.6 Hz, 3H), 7.25 (d, *J* = 8.5 Hz, 1H), 6.88 (t, *J* = 6.5 Hz, 1H). **^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$):** δ 146.6, 133.3, 131.8 (q, J = 32.5 Hz), 131.1, 130.3, 129.9, 124.8, 124.8, 124.6 (q, J = 3.6 Hz), 124.3, 123.0, 118.5, 113.1.

^{19}F NMR (471 MHz, CDCl$_3$): δ -62.6.

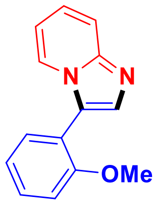
3-(*o*-Tolyl)imidazo[1,2-a]pyridine (3k)[2]



3k

Viscous liquid (92 mg, 88%). Purification by column chromatography (ethyl acetate/hexane, v/v = 25/75). **^{1}H NMR (500 MHz, CDCl$_3$):** δ 7.74 (d, *J* = 6.5 Hz, 1H), 7.67 (d, *J* = 9.0 Hz, 1H), 7.60 (s, 1H), 7.37 – 7.29 (m, 4H), 7.19 (t, *J* = 7.5 Hz, 1H), 6.75 (t, *J* = 7.0 Hz, 1H), 2.15 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$):** δ 145.6, 138.5, 132.9, 131.3, 130.8, 129.3, 128.4, 126.4, 124.8, 124.1, 123.8, 118.2, 112.4, 19.9.

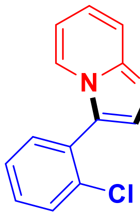
3-(2-Methoxyphenyl)imidazo[1,2-a]pyridine (3l)[1]



3l

Viscous liquid (102 mg, 91%). Purification by column chromatography (ethyl acetate/hexane, v/v = 40/60). **^{1}H NMR (500 MHz, CDCl$_3$):** δ 7.83 (d, *J* = 7.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.75 (t, *J* = 6.5 Hz, 1H), 3.79 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$):** δ 157.3, 145.9, 133.1, 131.9, 130.3, 125.4, 123.9, 123.2, 121.1, 118.1, 117.8, 111.6, 111.3, 55.5.

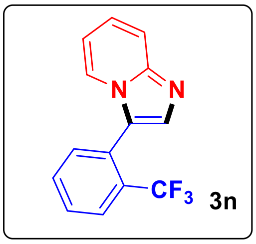
3-(2-Chlorophenyl)imidazo[1,2-a]pyridine (3m)[1]



3m

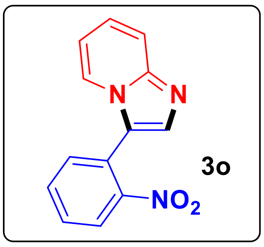
Viscous liquid (85 mg, 74%). Purification by column chromatography (ethyl acetate/hexane, v/v = 25/75). **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.84 (d, *J* = 6.9 Hz, 1H), 7.72 – 7.70 (m, 2H), 7.58 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.48 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.26 – 7.23 (m, 1H), 6.83 (td, *J* = 6.6, 0.6 Hz, 1H). **^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$):** δ 145.9, 134.7, 133.6, 132.8, 130.3, 130.3, 128.2, 127.2, 124.5, 124.4, 122.9, 118.0, 112.3.

3-(2-(Trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (3n)



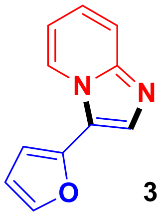
Viscous liquid (100 mg, 76%). Purification by column chromatography (ethyl acetate/hexane, v/v = 25/75). **^{1}H NMR (500 MHz, CDCl$_3$):** δ 7.87 (d, *J* = 7.5 Hz, 1H), 7.72 – 7.65 (m, 4H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 6.75 (t, *J* = 7.0 Hz, 1H). **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$):** δ 147.7, 138.5, 134.0, 133.3, 132.2, 131.4 (q, J = 30.2 Hz), 127.6, 127.0 (q, J = 5.0 Hz), 124.5, 123.7, 119.8, 117.9, 112.6. **^{19}F NMR (471 MHz, CDCl$_3$):** δ -59.6. **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{10}F_3N_2$, 263.0791; found, 263.0787.

3-(2-Nitrophenyl)imidazo[1,2-a]pyridine (3o)



Viscous liquid (97 mg, 81%). Purification by column chromatography (ethyl acetate/hexane, v/v = 40/60). **^{1}H NMR (600 MHz, CDCl$_3$)**: δ 8.20 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.77 (td, *J* = 7.2, 1.2 Hz, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.59 (dd, *J* = 7.8, 1.2 Hz, 3H), 7.28 – 7.25 (m, 1H), 6.82 (td, *J* = 6.6, 0.6 Hz, 1H). **^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$):** δ 148.9, 146.3, 133.9, 133.6, 133.6, 130.1, 125.2, 125.0, 123.8, 123.7, 120.8, 118.3, 112.9. **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{10}N_3O_2$, 240.0768; found, 240.0760.

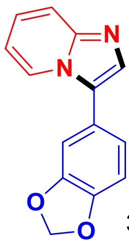
3-(Furan-2-yl)imidazo[1,2-a]pyridine (3p)



3p

Viscous liquid (89 mg, 88%). Purification by column chromatography (ethyl acetate/hexane, v/v = 25/75). **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.59 (d, *J* = 7.2 Hz, 1H), 7.86 (s, 1H), 7.70 (d, *J* = 9.6 Hz, 1H), 7.58 (d, *J* = 2.4 Hz, 1H), 7.27 – 7.24 (m, 1H), 6.92 (td, *J* = 6.6, 1.2 Hz, 1H), 6.64 (d, *J* = 3.6 Hz, 1H), 6.58 (dd, *J* = 3.0, 1.8 Hz, 1H). **$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$):** δ 145.8, 144.5, 142.2, 132.2, 125.1, 124.9, 119.7, 117.97, 113.2, 111.5, 106.9. **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{11}H_9N_2O$, 185.0709; found, 185.0702.

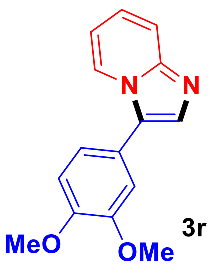
3-(Benzo[d][1,3]dioxol-5-yl)imidazo[1,2-a]pyridine (3q)



3q

Viscous liquid (113 mg, 95%). Purification by column chromatography (ethyl acetate/hexane, v/v = 50/50). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.25 (d, *J* = 7.0 Hz, 1H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.60 (s, 1H), 7.17 (t, *J* = 7.0 Hz, 1H), 7.01 – 6.98 (m, 2H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.78 (t, *J* = 7.0 Hz, 1H), 6.03 (s, 2H). **$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$):** δ 148.4, 147.8, 145.9, 132.2, 125.5, 124.2, 123.4, 122.9, 122.2, 118.3, 112.6, 109.2, 108.8, 101.5. **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{11}N_2O_2$, 239.0815; found, 239.0814.

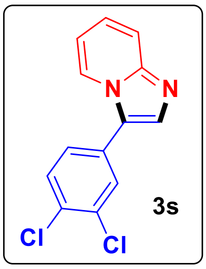
3-(3,4-Dimethoxyphenyl)imidazo[1,2-a]pyridine (3r)[1]



3r

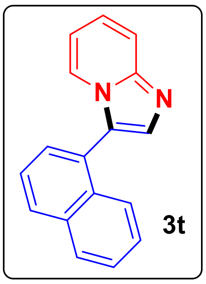
Viscous liquid (119 mg, 94%). Purification by column chromatography (ethyl acetate/hexane, v/v = 50/50). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.26 (d, *J* = 7.0 Hz, 1H), 7.65 (d, *J* = 9.5 Hz, 1H), 7.63 (s, 1H), 7.19 – 7.16 (m, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.79 (t, *J* = 7.0 Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H). **$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$):** δ 149.7, 149.4, 145.8, 131.9, 125.7, 124.1, 123.4, 121.9, 121.0, 118.2, 112.5, 111.9, 56.2, 56.1.

3-(3,4-Dichlorophenyl)imidazo[1,2-a]pyridine (3s)



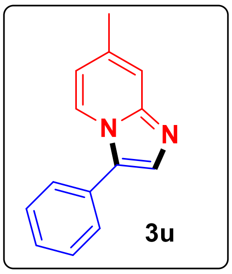
Viscous liquid (100 mg, 76%). Purification by column chromatography (ethyl acetate/hexane, v/v = 25/75). **^1H NMR (500 MHz, $CDCl_3$):** δ 8.29 (d, *J* = 7.0 Hz, 1H), 7.71 (d, *J* = 12.0 Hz, 2H), 7.67 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.40 (m, 1H), 7.27 – 7.24 (m, 1H), 6.88 (t, *J* = 6.5 Hz, 1H). **$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$):** δ 146.5, 133.6, 133.2, 132.2, 131.3, 129.5, 129.3, 127.0, 124.9, 123.4, 123.1, 118.5, 113.2. **HRMS** (ESI-TOF) m/z: [M+H]+ calcd for $C_{13}H_9Cl_2N_2$, 263.0137; found, 263.0130.

3-(Naphthalen-1-yl)imidazo[1,2-a]pyridine (3t)[1]



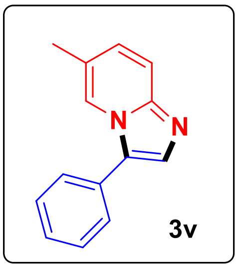
Viscous liquid (95 mg, 78%). Purification by column chromatography (ethyl acetate/hexane, v/v = 25/75). **^1H NMR (500 MHz, $CDCl_3$):** δ 7.99 – 7.95 (m, 2H), 7.79 (s, 1H), 7.73 (t, *J* = 10.0 Hz, 2H), 7.61 – 7.58 (m, 2H), 7.55 – 7.51 (m, 2H), 7.43 (t, *J* = 7.0 Hz, 1H), 7.22 (t, *J* = 7.0 Hz, 1H), 6.71 (t, *J* = 6.5 Hz, 1H). **$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$):** δ 145.9, 134.0, 133.9, 132.2, 129.7, 129.2, 128.8, 127.0, 126.5, 126.4, 125.7, 125.3, 124.4, 124.2, 123.8, 118.1, 112.4.

7-Methyl-3-phenylimidazo[1,2-a]pyridine (3u)[1]



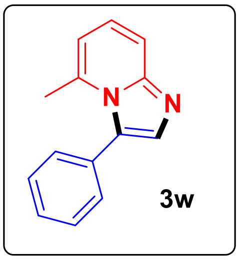
Viscous liquid (94 mg, 90%). Purification by column chromatography (ethyl acetate/hexane, v/v = 25/75). **^{1}H NMR (500 MHz, CDCl$_3$):** δ 8.21 (d, *J* = 7.0 Hz, 1H), 7.61 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.0 Hz, 2H), 7.42 – 7.37 (m, 2H), 6.63 (d, *J* = 7.5 Hz, 1H), 2.40 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$):** δ 146.7, 135.3, 132.2, 129.6, 129.3, 128.0, 127.9, 125.3, 122.7, 116.6, 115.3, 21.3.

6-Methyl-3-phenylimidazo[1,2-a]pyridine (3v)[1]



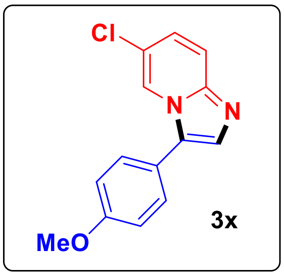
Viscous liquid (92 mg, 88%). Purification by column chromatography (ethyl acetate/hexane, v/v = 25/75). **^{1}H NMR (500 MHz, CDCl$_3$):** δ 8.11 (s, 1H), 7.65 (s, 1H), 7.56 – 7.49 (m, 5H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 9.0 Hz, 1H), 2.31 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$):** δ 148.1, 132.2, 129.5, 129.3, 128.9, 128.2, 128.1, 127.7, 122.4, 121.1, 117.6, 18.4.

5-Methyl-3-phenylimidazo[1,2-a]pyridine (3w)[1]



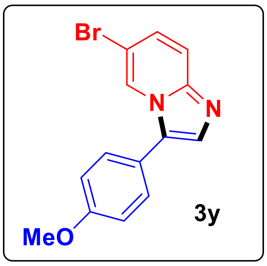
Viscous liquid (81 mg, 78%). Purification by column chromatography (ethyl acetate/hexane, v/v = 25/75). **^{1}H NMR (500 MHz, CDCl$_3$):** δ 7.58 (d, *J* = 7.5 Hz, 2H), 7.44 – 7.39 (m, 5H), 7.12 (t, *J* = 7.0 Hz, 1H), 6.50 (d, *J* = 6.5 Hz, 1H), 2.17 (s, 3H). **^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$):** δ 139.4, 138.7, 132.1, 131.7, 128.5, 127.4, 124.3, 119.2, 116.2, 113.3, 110.7, 21.9. **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{13}N_2$, 209.1073; found, 209.1064.

6-Chloro-3-(4-methoxyphenyl)imidazo[1,2-a]pyridine (3x)



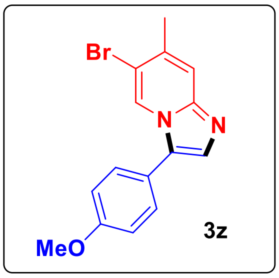
Viscous liquid (109 mg, 84%). Purification by column chromatography (ethyl acetate/hexane, v/v = 40/60). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.27 (s, 1H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 1H), 7.06 (d, *J* = 9.0 Hz, 2H), 3.88 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ 160.1, 132.8, 132.1, 131.6, 129.9, 125.6, 121.4, 121.1, 120.8, 118.6, 114.9, 55.5. **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{12}ClN_2O$, 259.0633; found, 259.0630.

6-Bromo-3-(4-methoxyphenyl)imidazo[1,2-a]pyridine (3y)



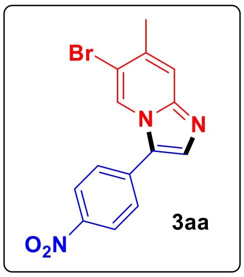
Viscous liquid (123 mg, 81%). Purification by column chromatography (ethyl acetate/hexane, v/v = 40/60). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.37 (s, 1H), 7.67 (s, 1H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 1H), 7.07 (d, *J* = 9.0 Hz, 2H), 3.89 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ 160.1, 148.8, 140.2, 132.8, 129.9, 127.4, 123.6, 120.9, 118.9, 114.9, 107.5, 55.5. **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{12}BrN_2O$, 303.0128; found, 303.0125.

6-Bromo-3-(4-methoxyphenyl)-7-methylimidazo[1,2-a]pyridine (3z)



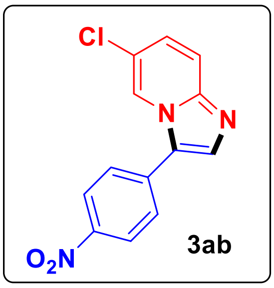
Viscous liquid (132 mg, 83%). Purification by column chromatography (ethyl acetate/hexane, v/v = 40/60). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.40 (s, 1H), 7.56 (s, 1H), 7.52 (s, 1H), 7.44 (d, *J* = 9.0 Hz, 2H), 7.06 (d, *J* = 9.0 Hz, 2H), 3.89 (s, 3H), 2.46 (s, 3H). **^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$):** δ 159.8, 145.1, 134.5, 132.3, 129.6, 125.1, 123.4, 121.1, 117.1, 114.8, 111.5, 55.4, 22.5. **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{14}BrN_2O$, 317.0284; found, 317.0276.

6-Bromo-7-methyl-3-(4-nitrophenyl)imidazo[1,2-a]pyridine (3aa)



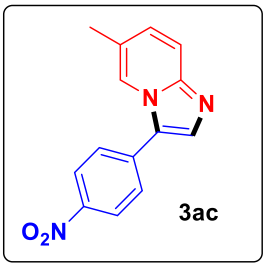
Viscous liquid (141 mg, 85%). Purification by column chromatography (ethyl acetate/hexane, v/v = 40/60). **^{1}H NMR (500 MHz, CDCl$_3$):** δ 8.56 (s, 1H), 8.40 (d, *J* = 8.0 Hz, 2H), 7.81 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.64 (s, 1H), 2.51 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$):** δ 147.1, 146.7, 136.7, 135.4, 134.8, 131.1, 127.6, 124.9, 123.3, 117.6, 112.9, 22.7. **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{11}BrN_3O_2$, 332.0029; found, 332.0026.

6-Chloro-3-(4-nitrophenyl)imidazo[1,2-a]pyridine (3ab)



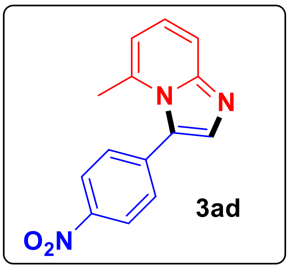
Viscous liquid (108 mg, 79%). Purification by column chromatography (ethyl acetate/hexane, v/v = 40/60). **^{1}H NMR (500 MHz, CDCl$_3$):** δ 8.40 (d, *J* = 9.0 Hz, 3H), 7.85 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 9.5 Hz, 1H), 7.26 (d, *J* = 9.0 Hz, 1H). **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$):** δ 147.3, 135.3, 131.1, 130.4, 127.9, 126.9, 124.9, 122.2, 121.2, 119.1, 118.2. **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{13}H_9ClN_3O_2$, 274.0378; found, 274.0370.

6-Methyl-3-(4-nitrophenyl)imidazo[1,2-a]pyridine (3ac):



Viscous liquid (103 mg, 81%). Purification by column chromatography (ethyl acetate/hexane, v/v = 50/50). **^{1}H NMR (500 MHz, CDCl$_3$):** δ 8.38 (d, *J* = 8.0 Hz, 2H), 8.19 (s, 1H), 7.81 (s, 1H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 9.0 Hz, 1H), 7.17 (d, *J* = 9.0 Hz, 1H), 2.38 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$):** δ 146.8, 146.4, 136.1, 134.4, 128.9, 127.6, 124.8, 123.6, 123.5, 120.9, 117.9, 18.5. **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{12}N_3O_2$, 254.0924; found, 254.0922.

5-Methyl-3-(4-nitrophenyl)imidazo[1,2-a]pyridine (3ad)



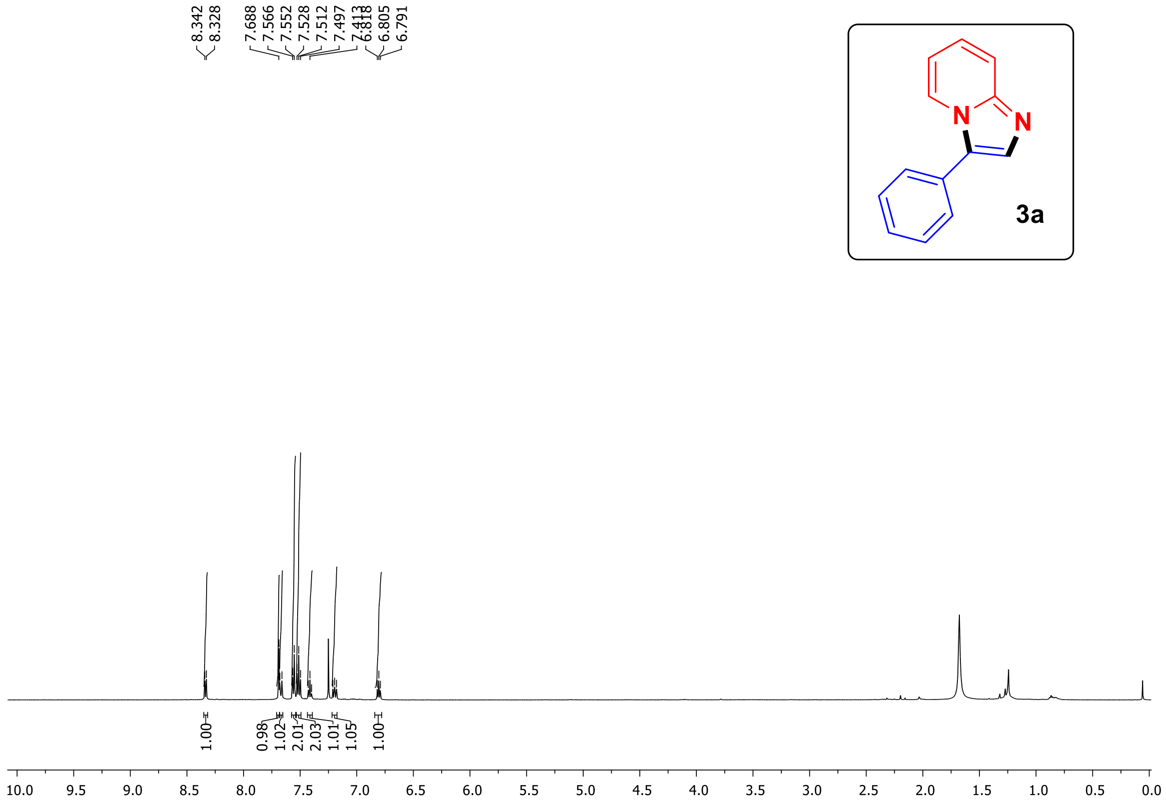
Viscous liquid (99 mg, 78%). Purification by column chromatography (ethyl acetate/hexane, v/v = 50/50). **^{1}H NMR (500 MHz, CDCl$_3$):** δ 8.28 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 7.0 Hz, 1H), 6.62 (d, *J* = 7.0 Hz, 1H), 2.22 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$):** δ 147.6, 138.6, 138.2, 136.1, 135.7, 131.5, 125.5, 124.1, 122.9, 116.4, 114.4, 22.5. **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{12}N_3O_2$, 254.0924; found, 254.0922.

5. References:

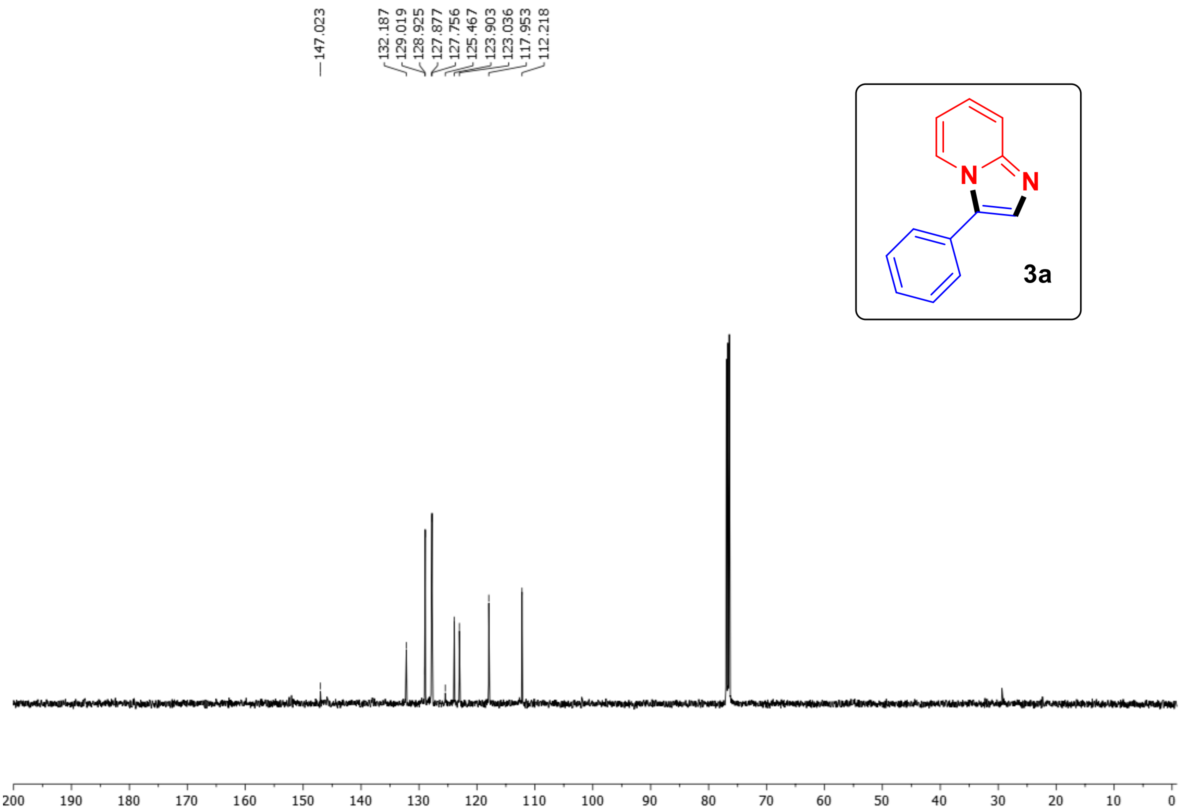
1. S. Roy, H. Khatua, S. K. Das, *Angew. Chem. Int. Ed.*, 2019, **58**, 11439-11443.
2. I. Beckers, A. Bugaev, D. De Vos, *Chem. Sci.*, 2023, **14**, 1176-1183.
3. F. Vuillermet, J. Bourret, G. Pelletier, *J. Org. Chem.*, 2020, **86**, 388-402.

6. **Copies of the ¹H, ¹³C, and ¹⁹F spectra of the products:**

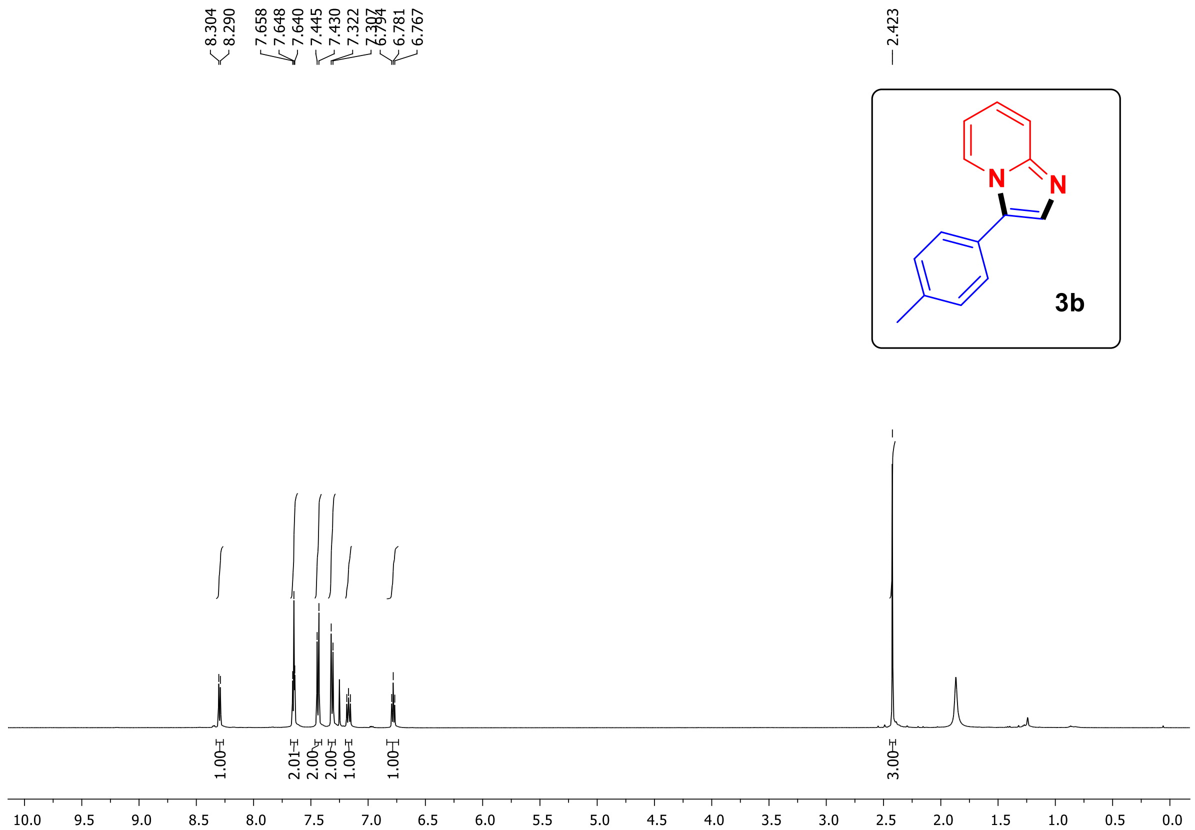
¹H NMR (500 MHz, $CDCl_3$):



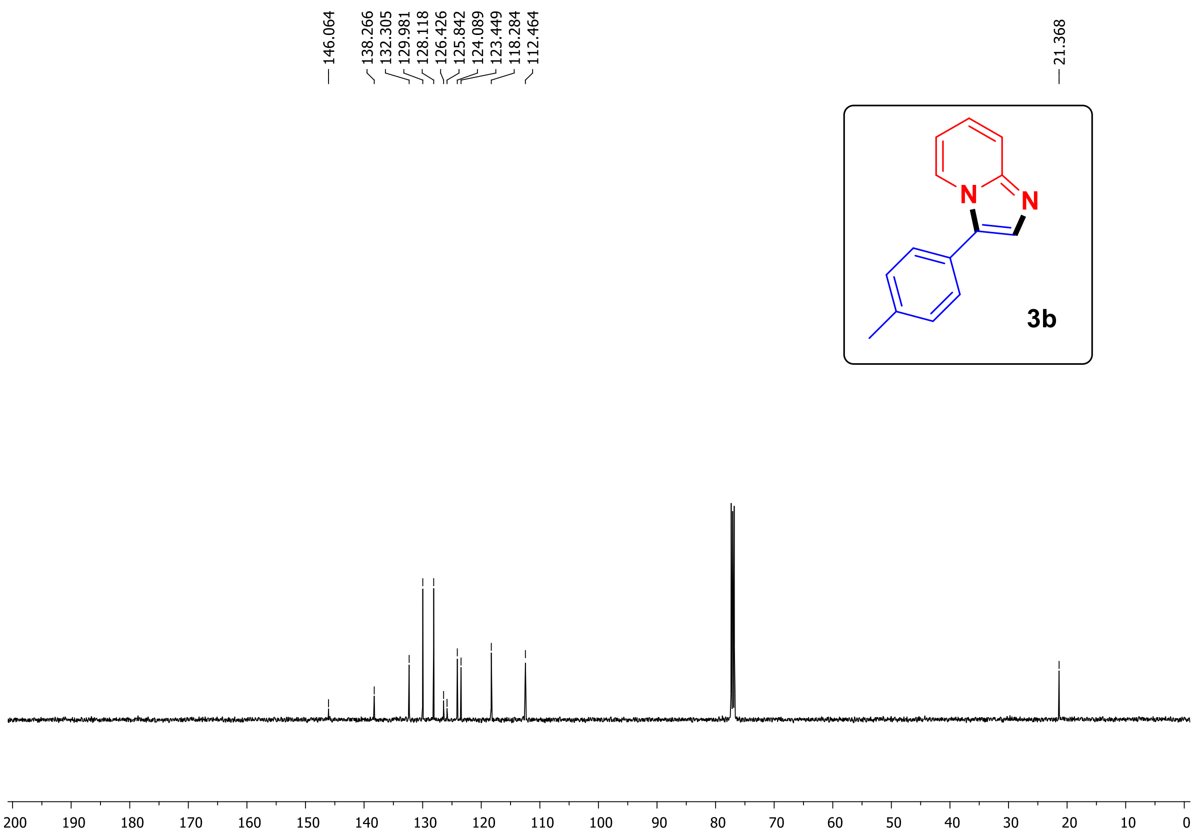
¹³C{¹H} NMR (126 MHz, $CDCl_3$):



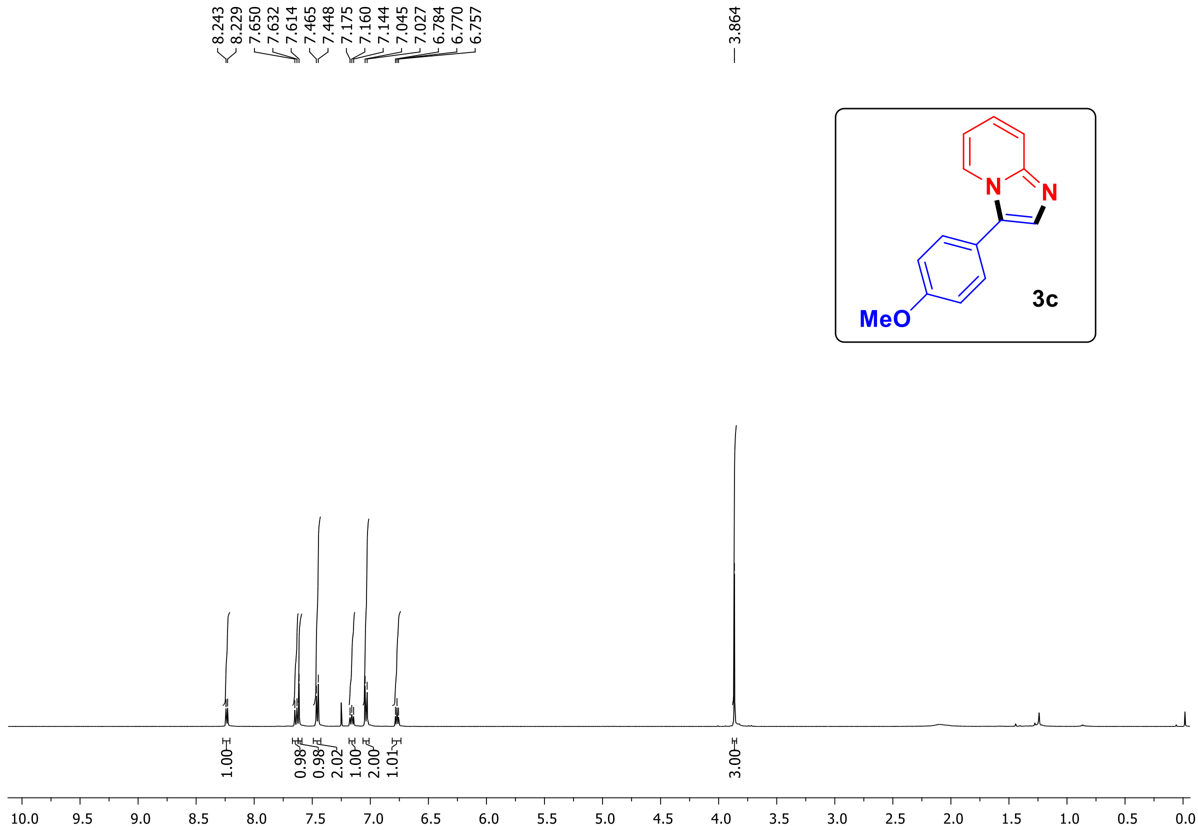
[1]H NMR (500 MHz, CDCl$_3$):



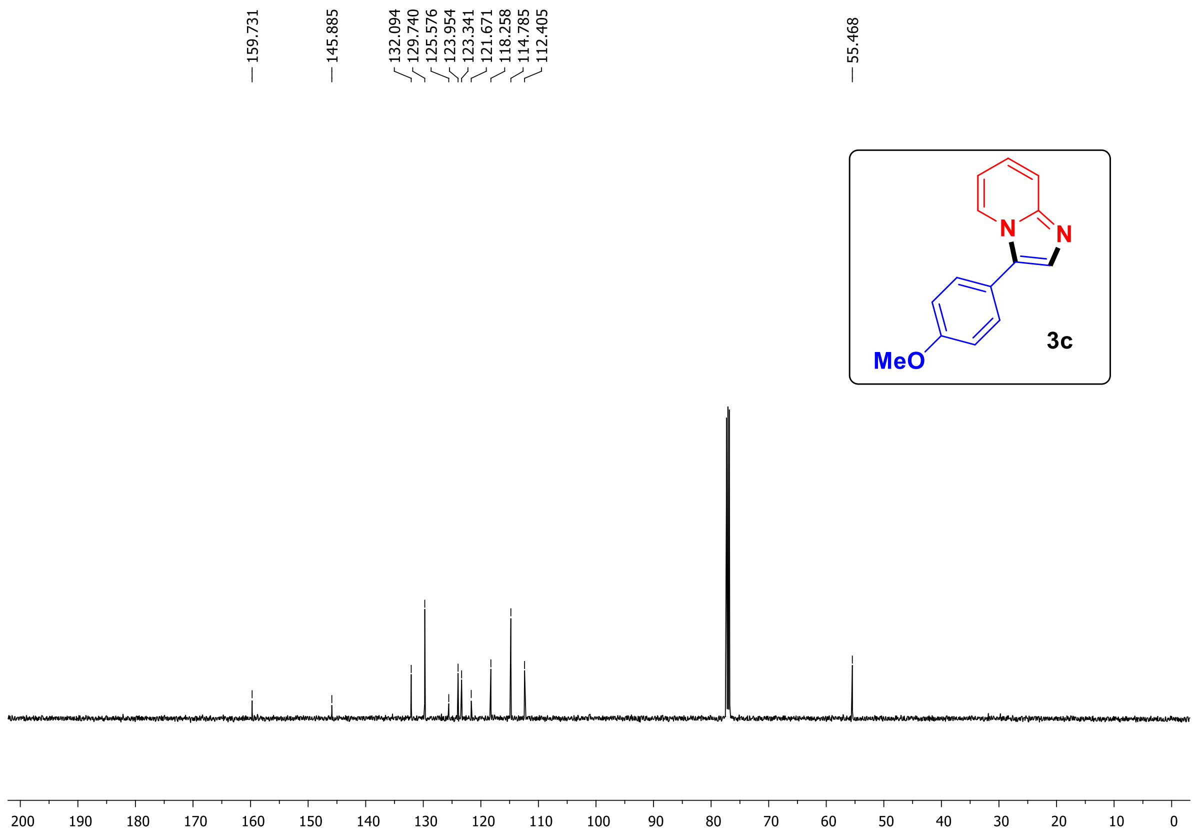
[13]C{[1]H} NMR (126 MHz, CDCl$_3$):



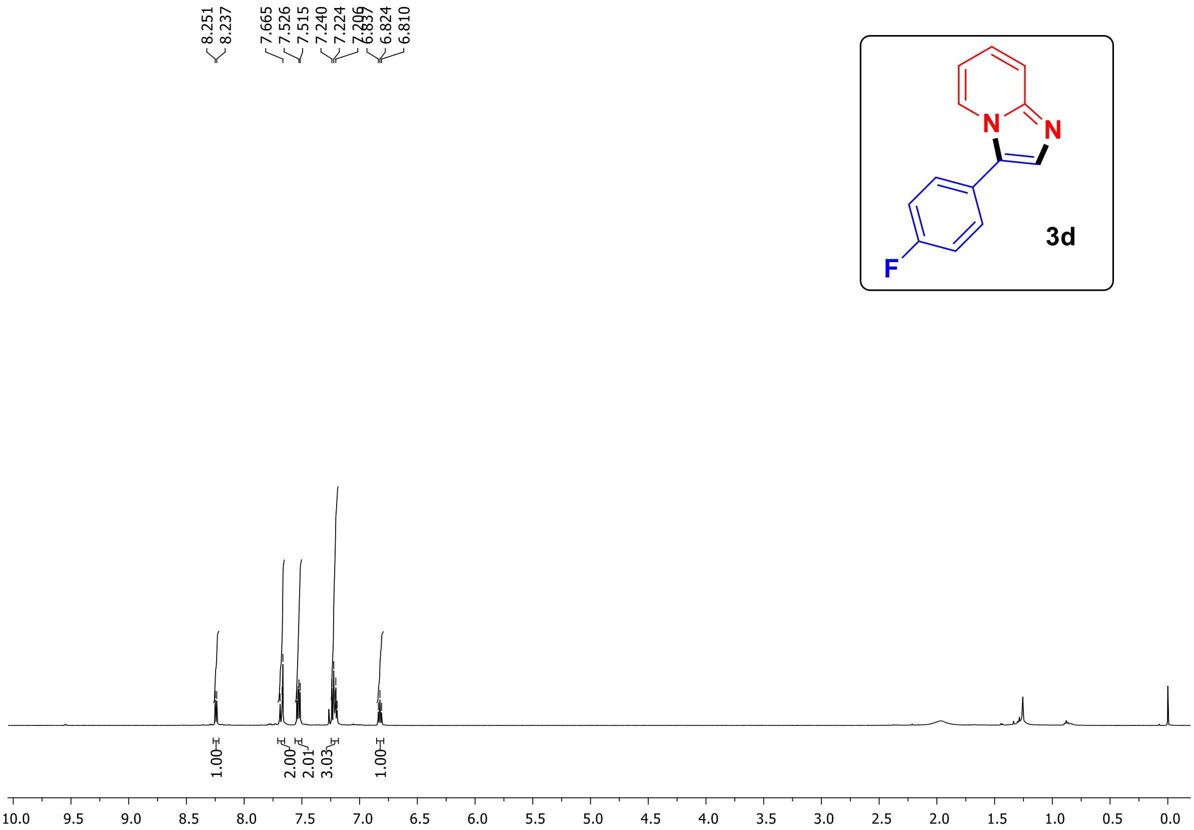
[1]H NMR (500 MHz, $CDCl_3$):



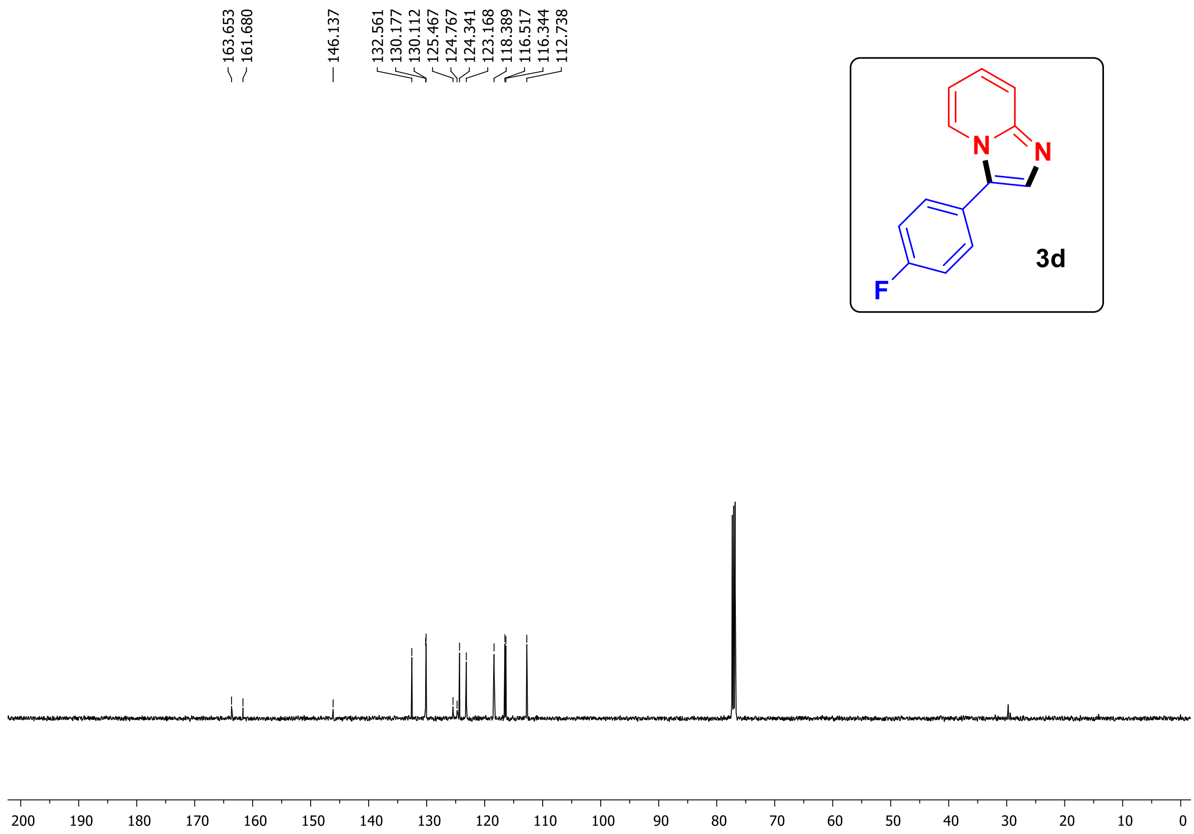
[13]C{[1]H} NMR (126 MHz, $CDCl_3$):



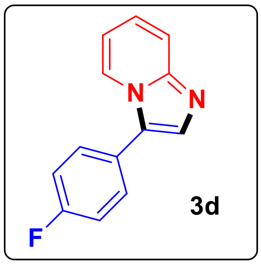
[1]H NMR (500 MHz, $CDCl_3$):

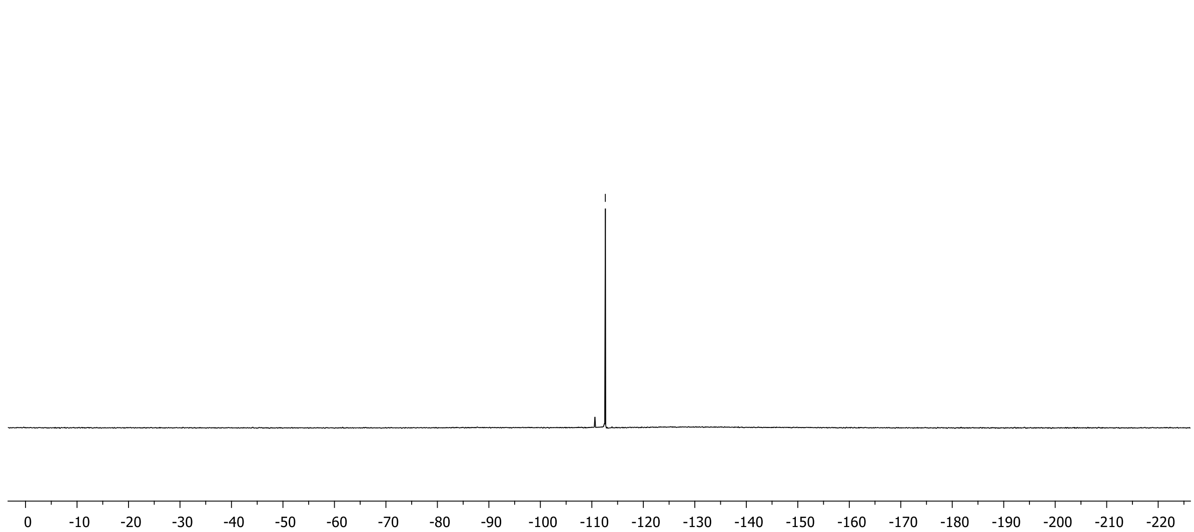


[13]C{[1]H} NMR (126 MHz, $CDCl_3$):

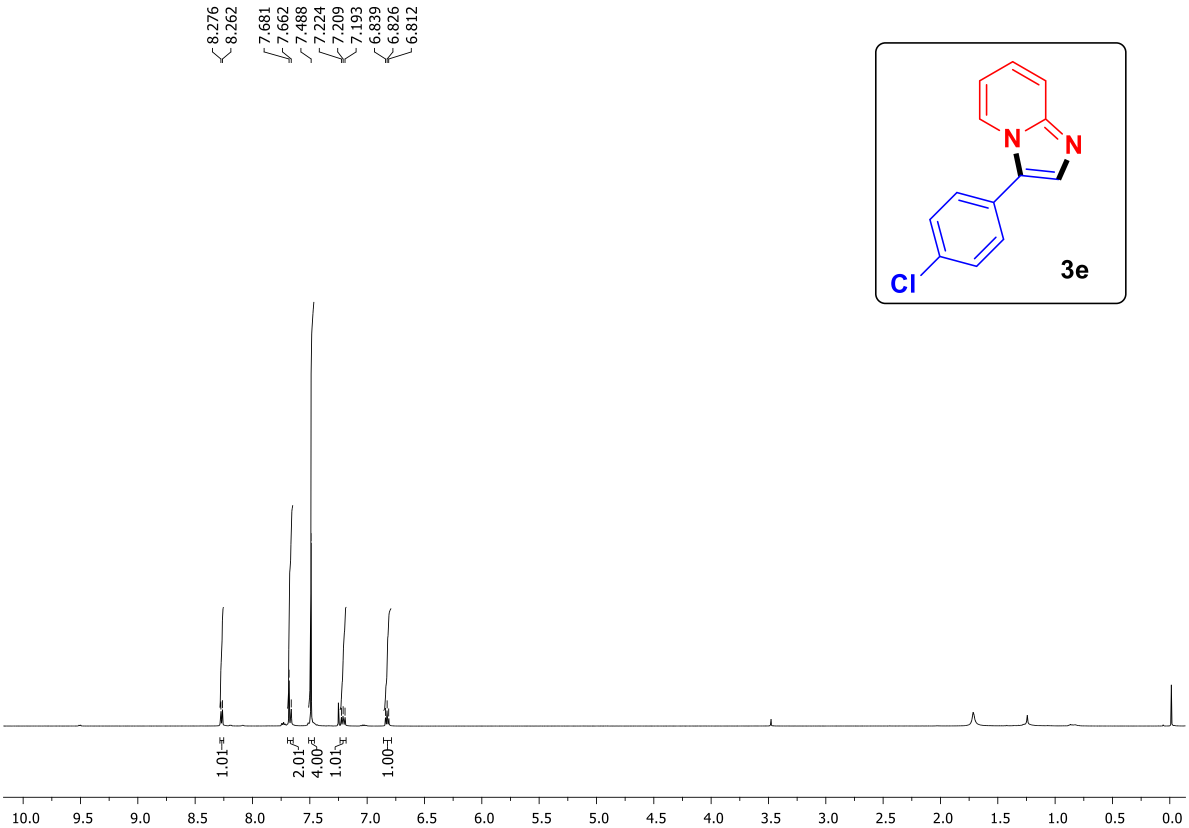


^{19}F NMR (471 MHz, CDCl$_3$):

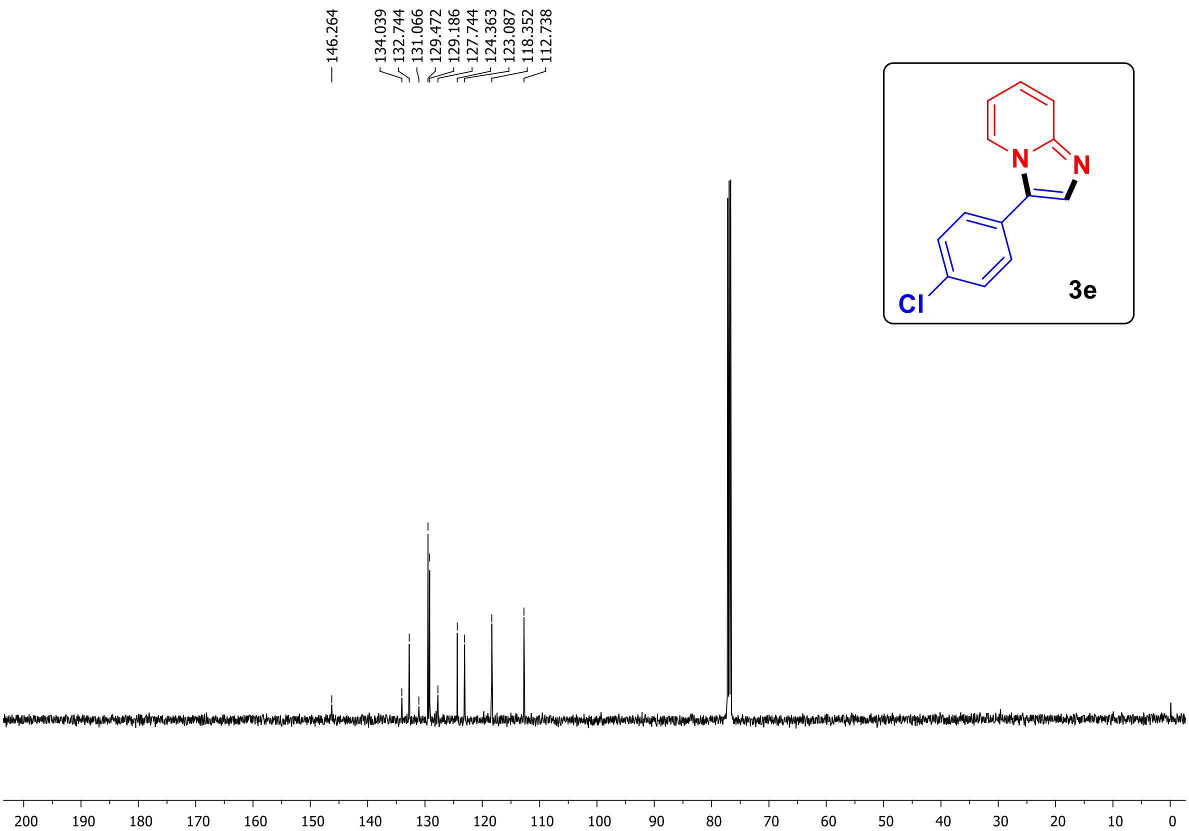




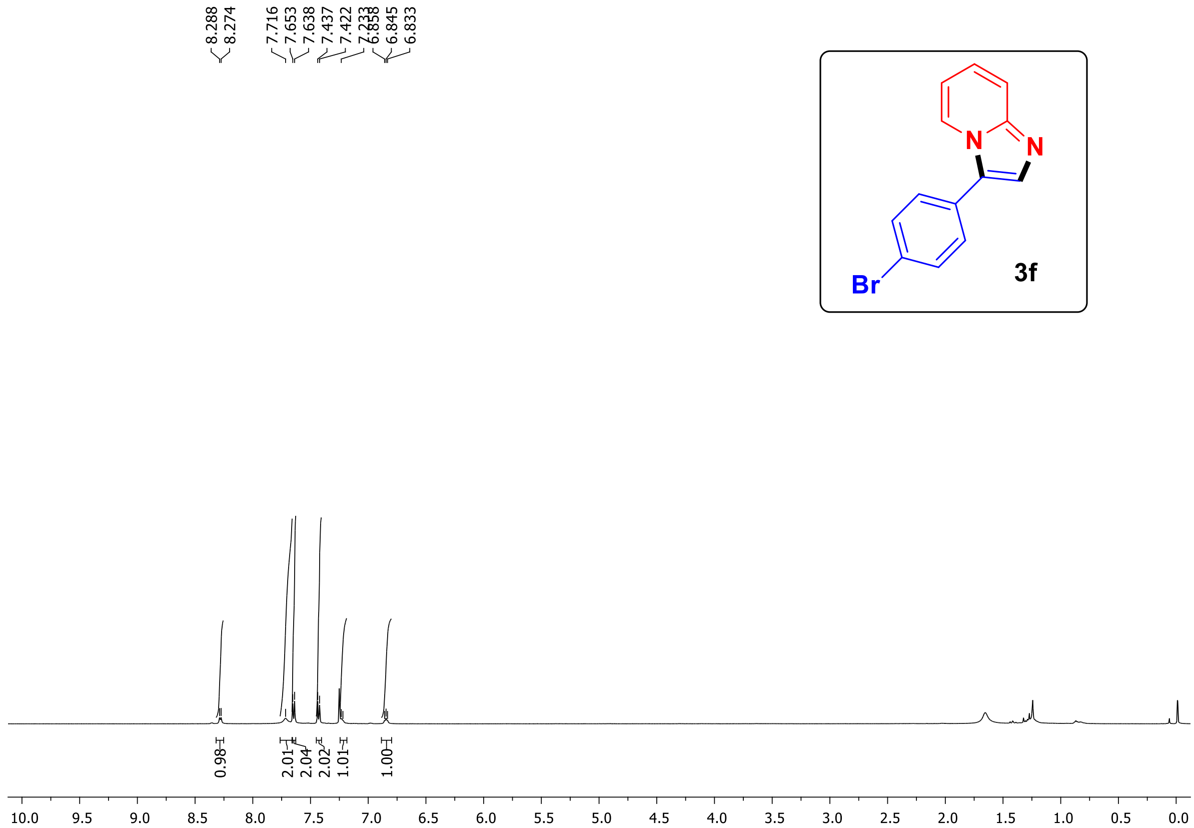
^{1}H NMR (500 MHz, $CDCl_3$):



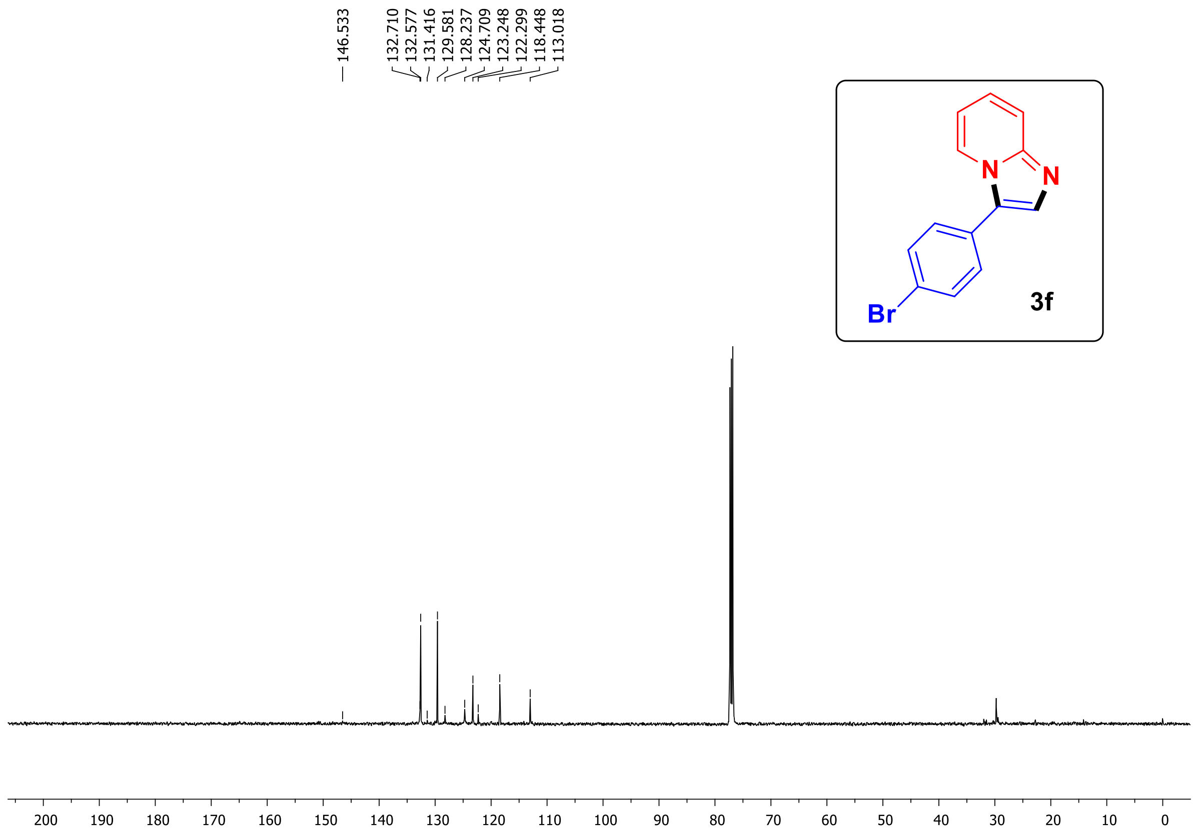
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$):



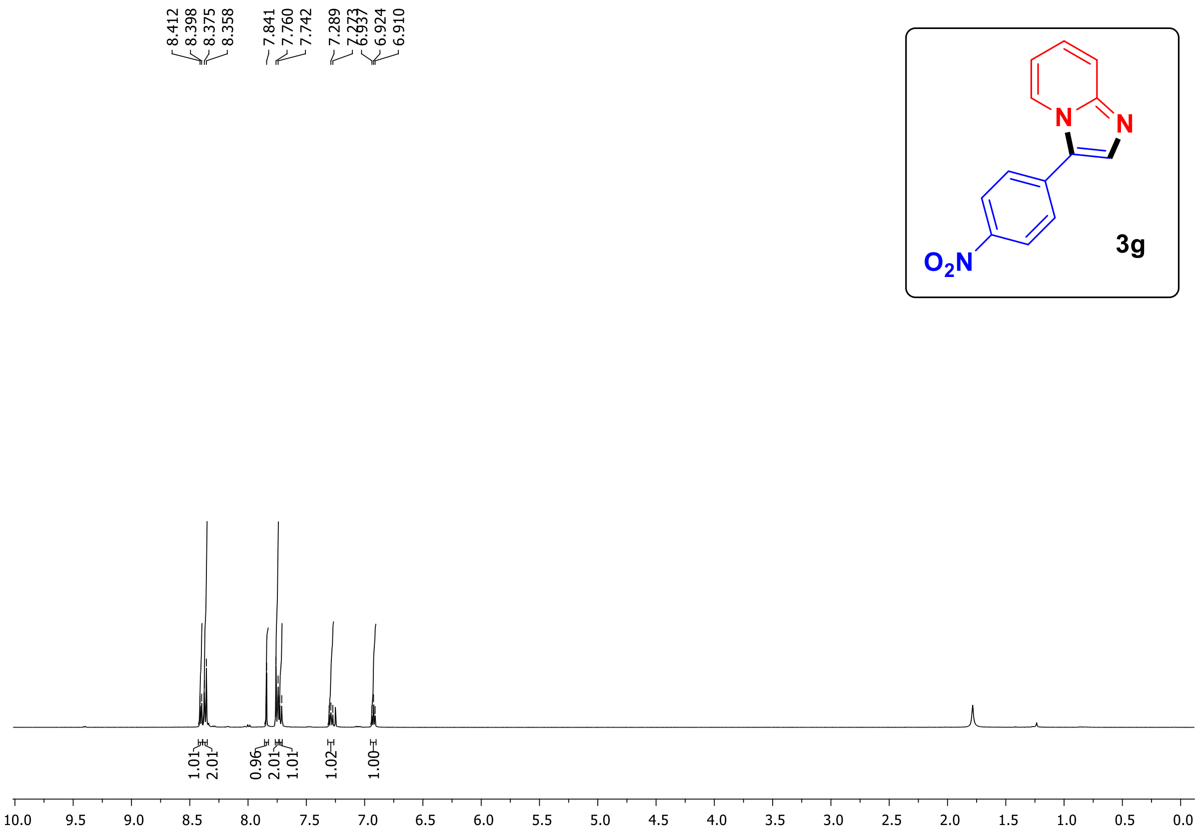
^{1}H NMR (500 MHz, $CDCl_3$):



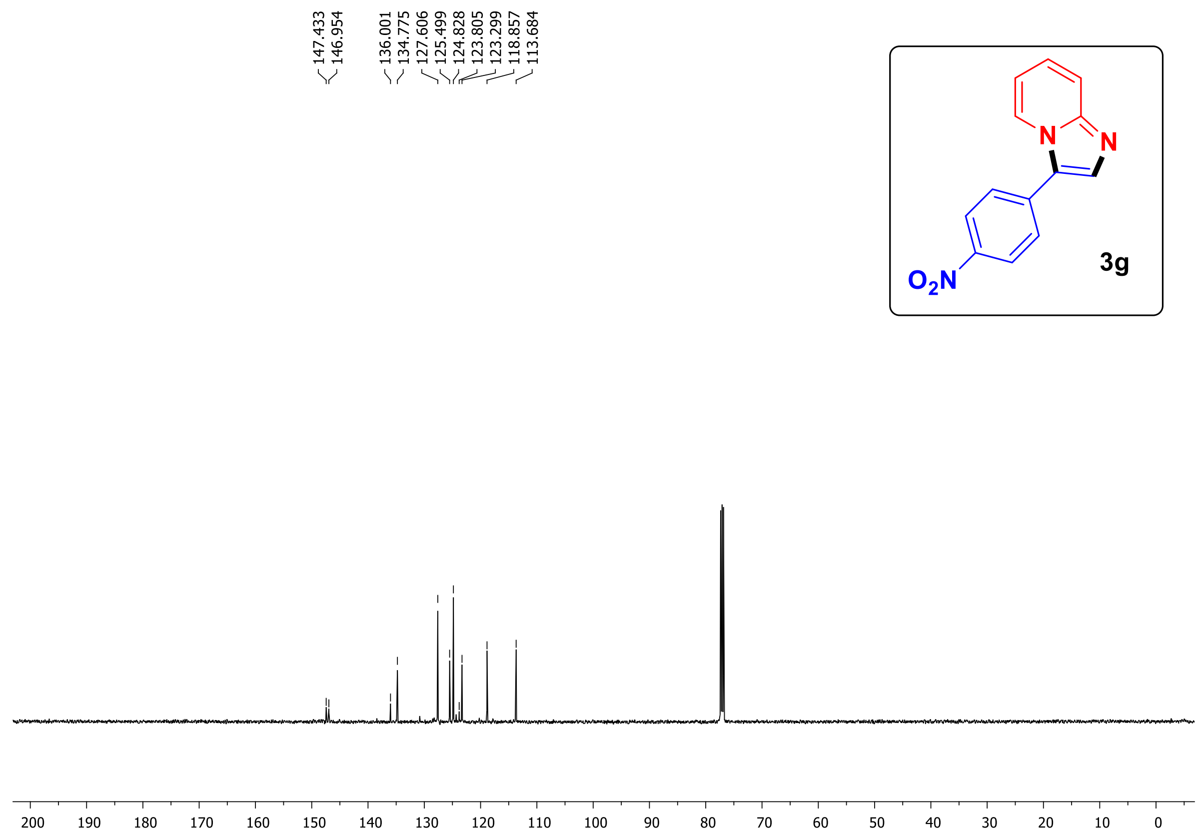
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$):



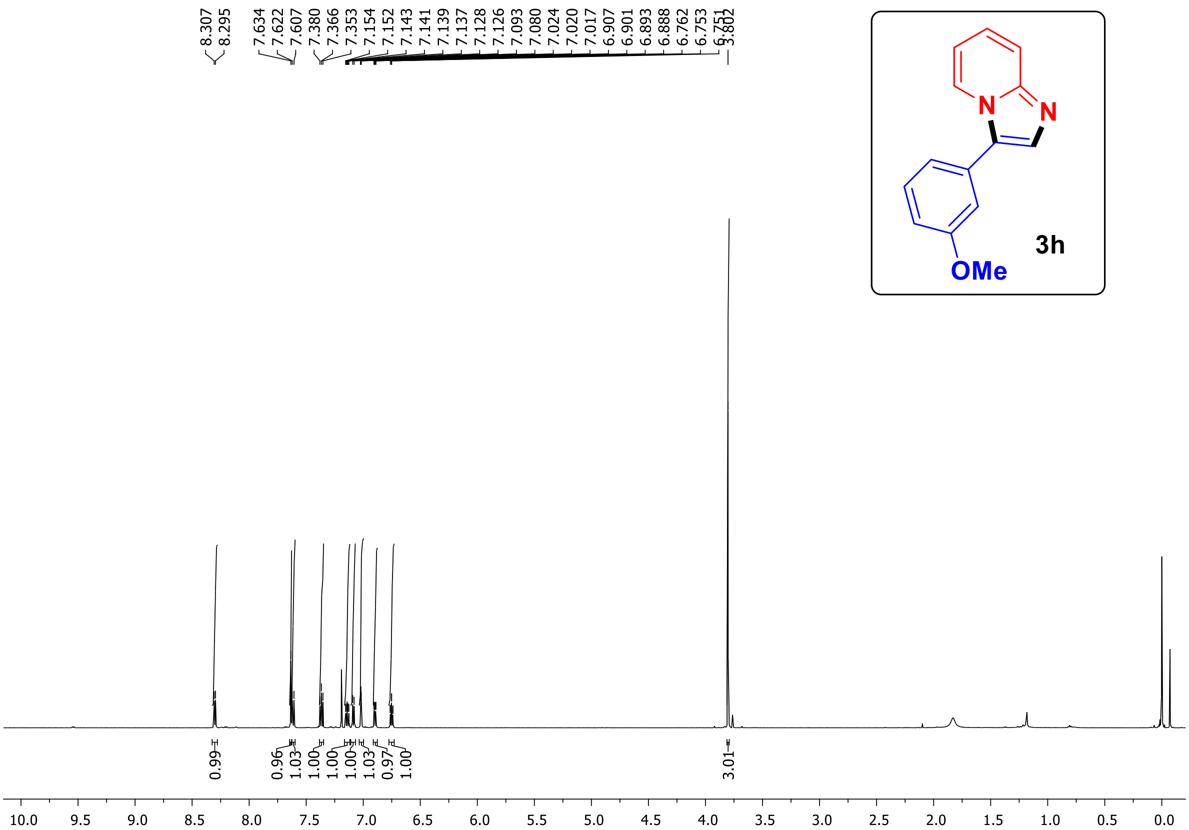
^{1}H NMR (500 MHz, CDCl$_3$):



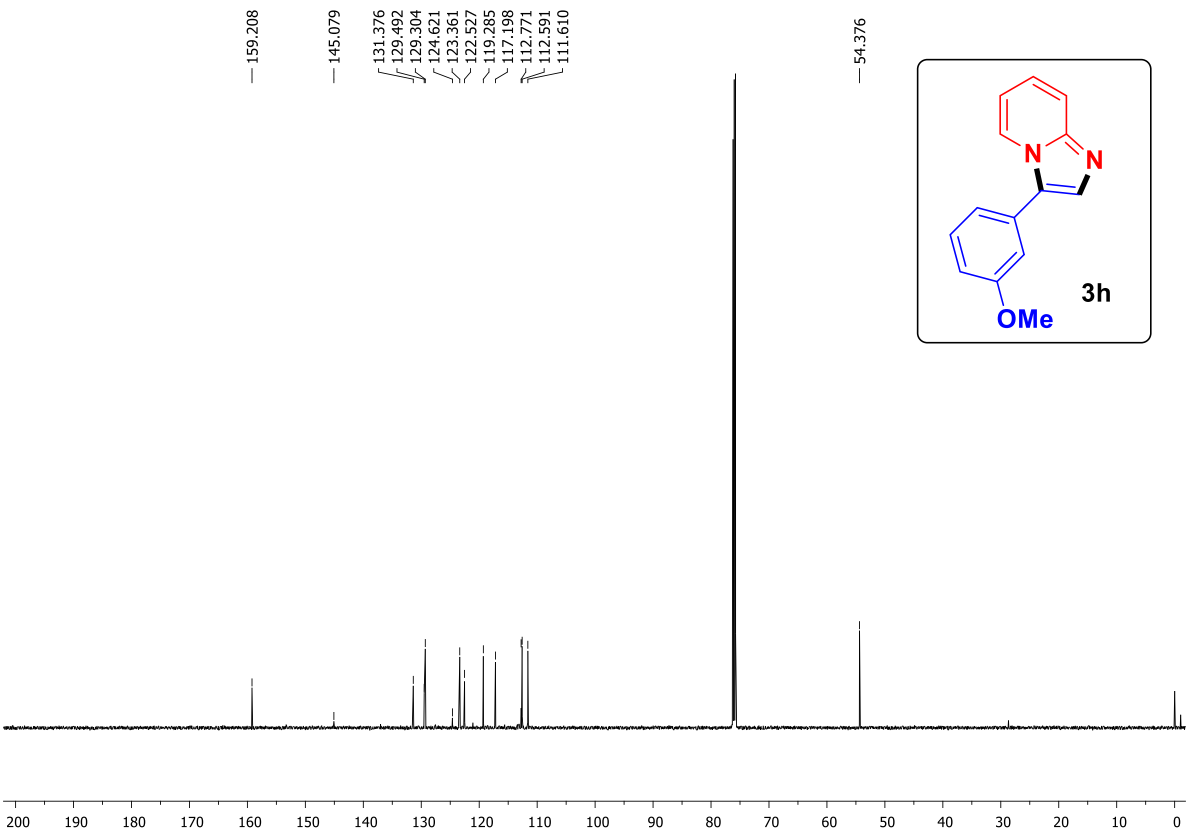
^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$):



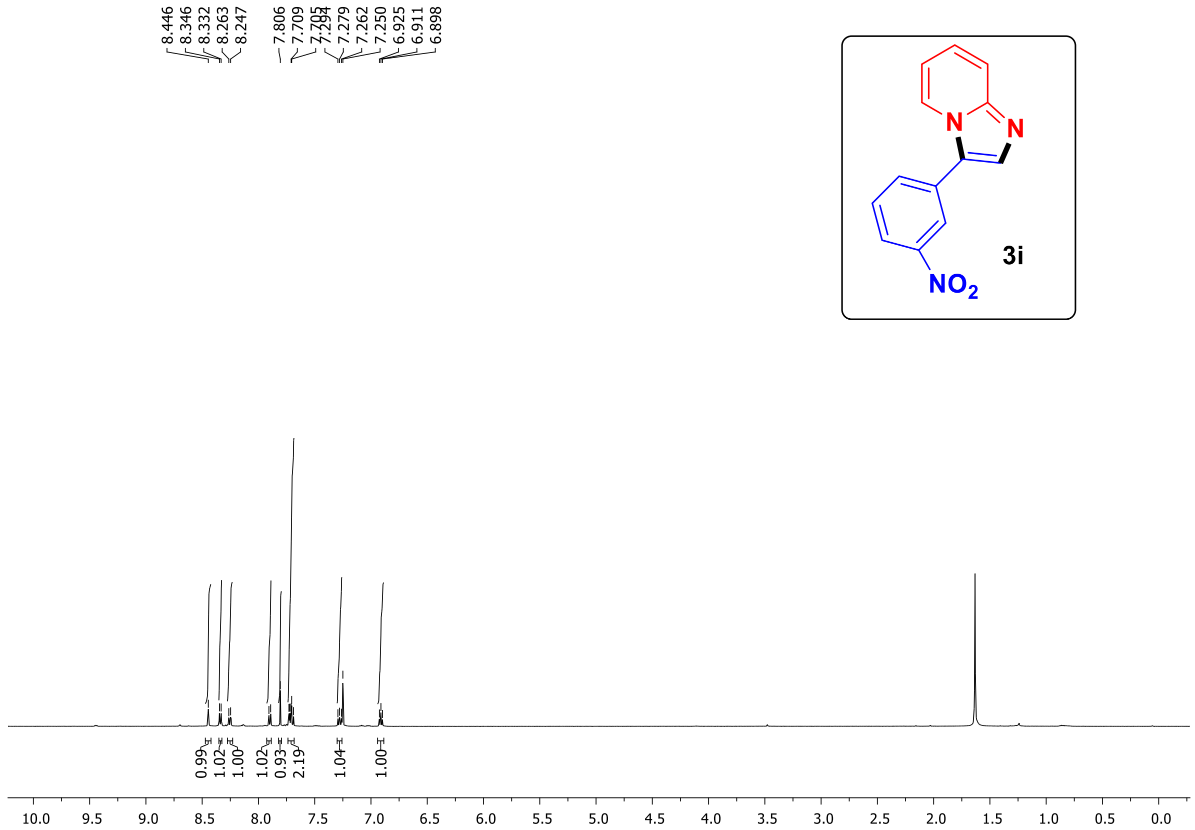
^{1}H NMR (600 MHz, CDCl$_3$):



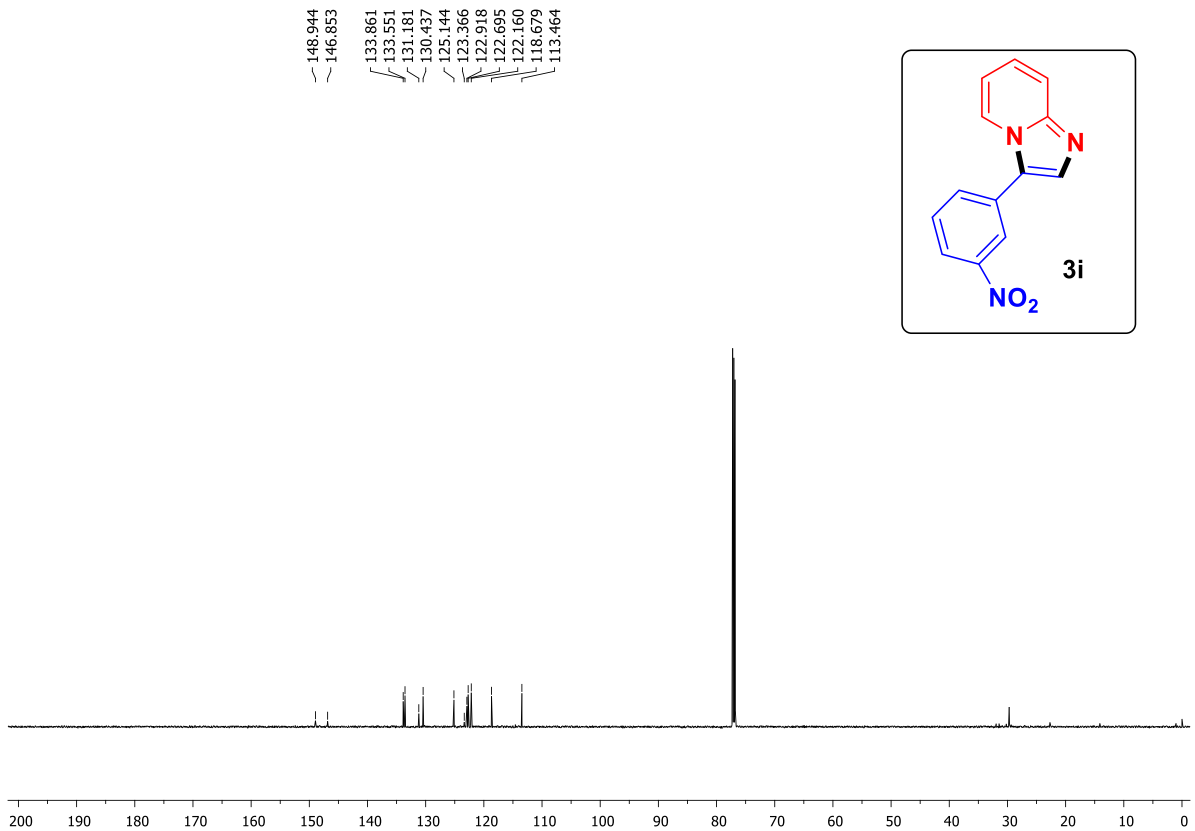
^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$):



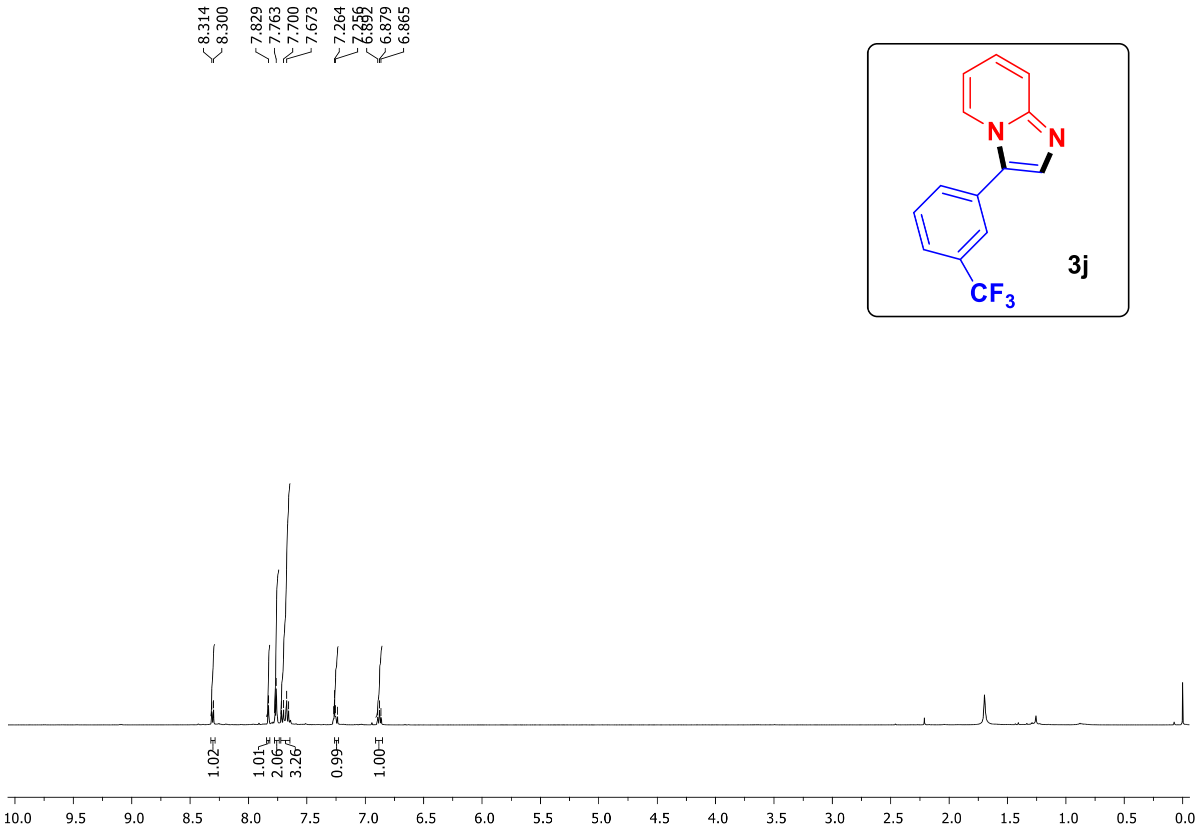
^{1}H NMR (500 MHz, $CDCl_3$):



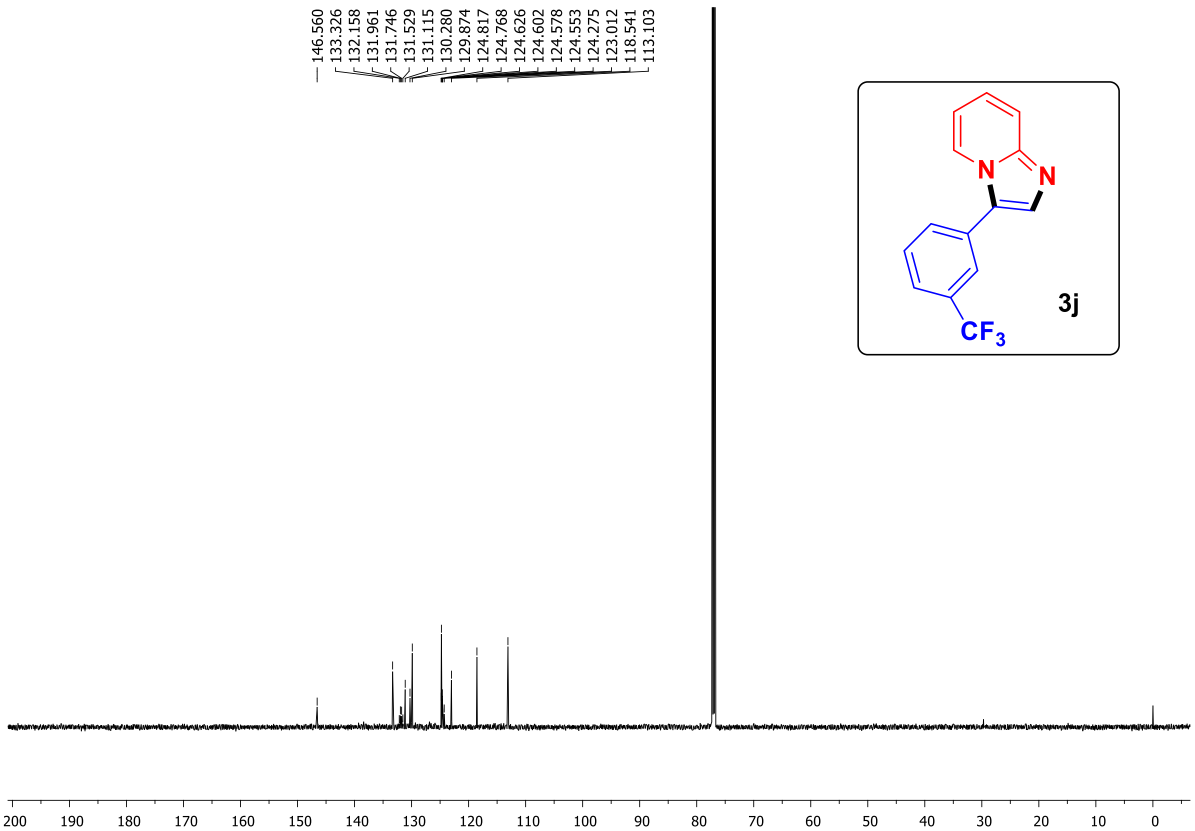
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$):



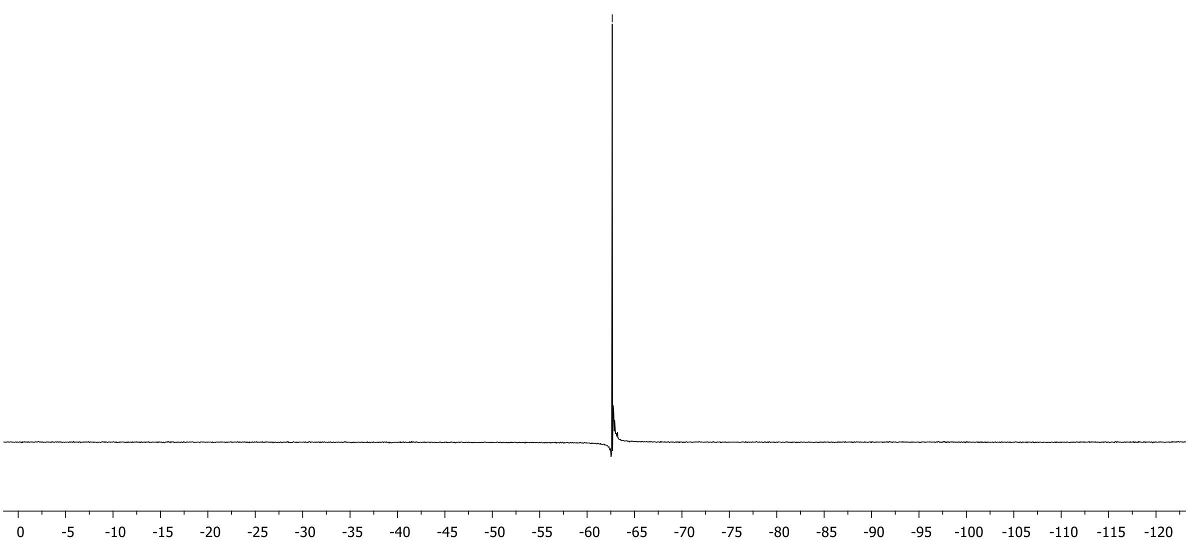
^{1}H NMR (500 MHz, CDCl$_3$):

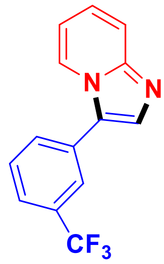


^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$):



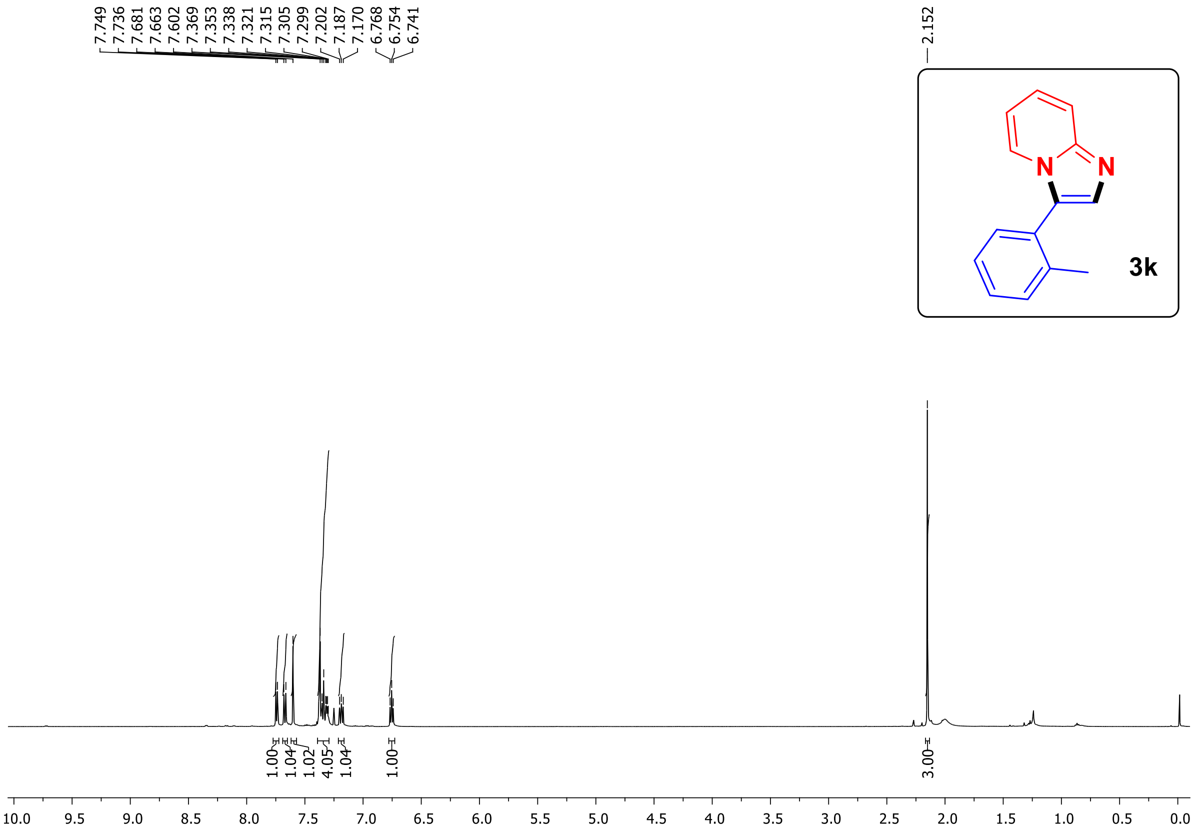
^{19}F NMR (471 MHz, $CDCl_3$):



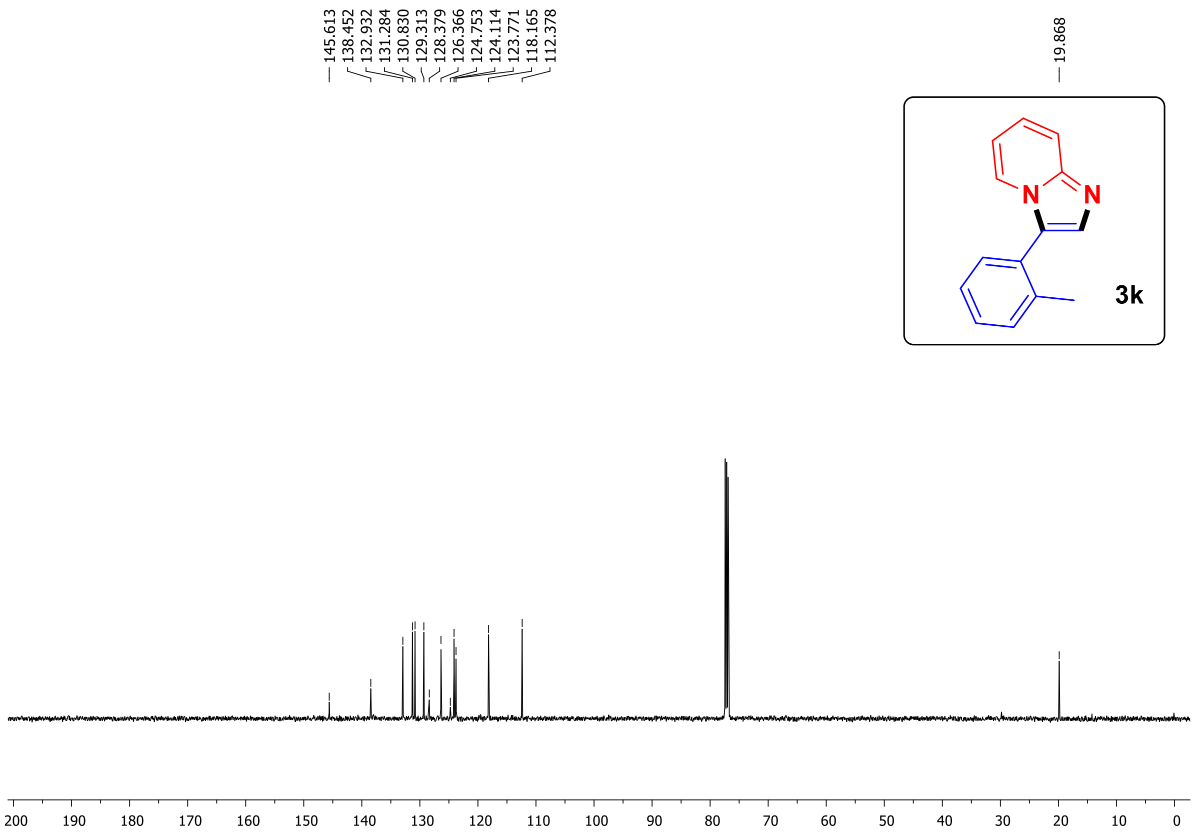


3j

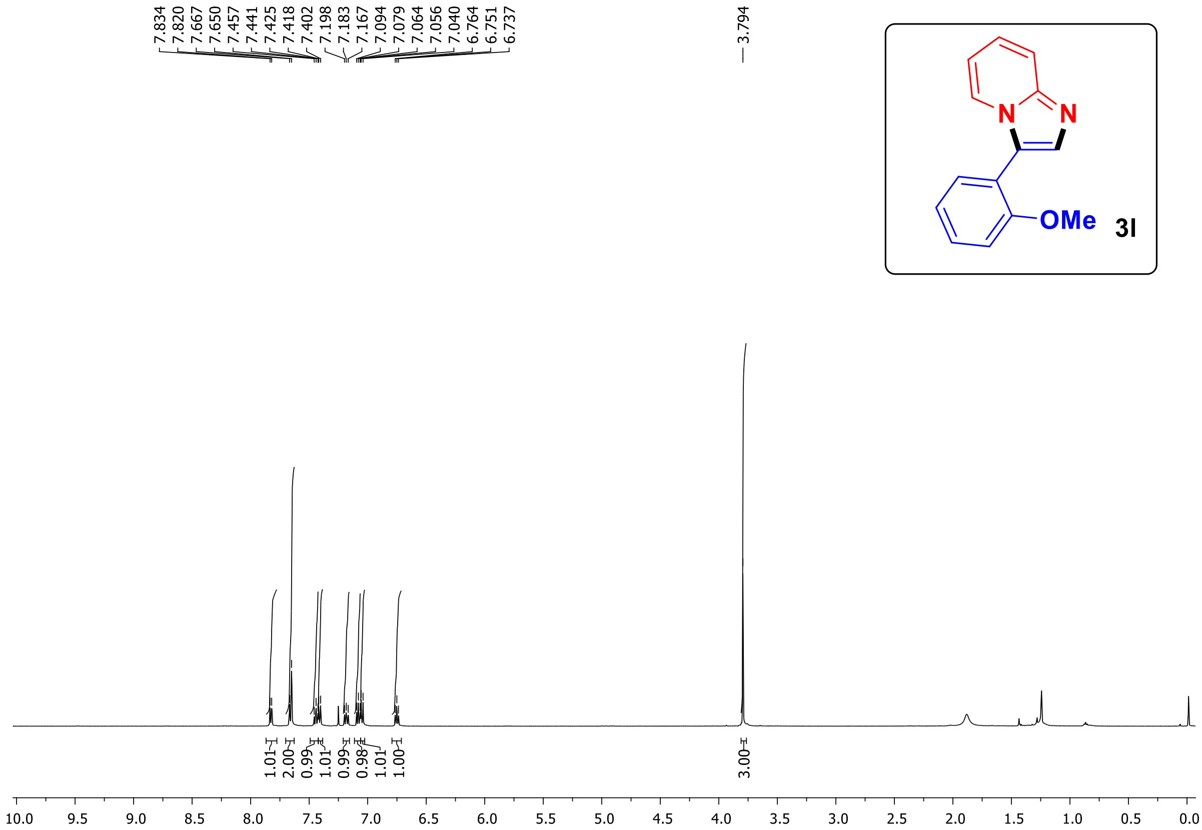
[1]H NMR (500 MHz, $CDCl_3$):



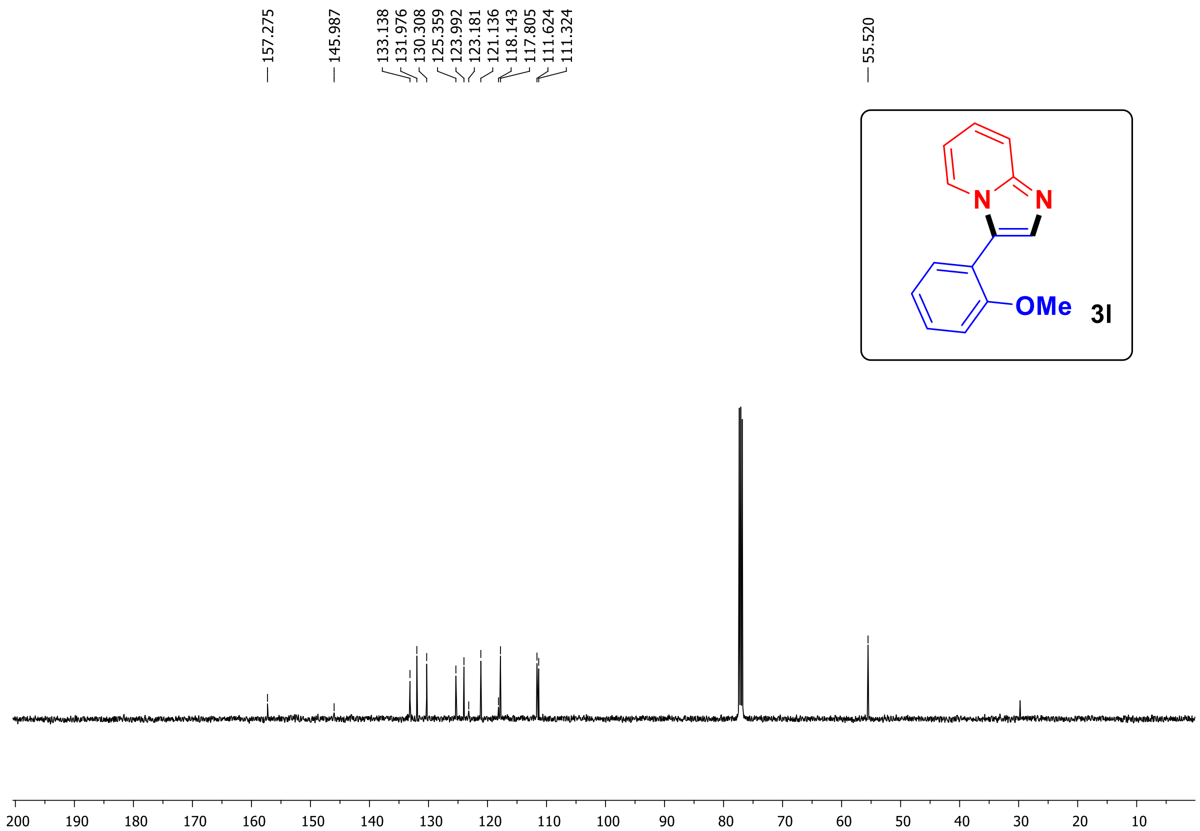
[13]C{[1]H} NMR (126 MHz, $CDCl_3$):



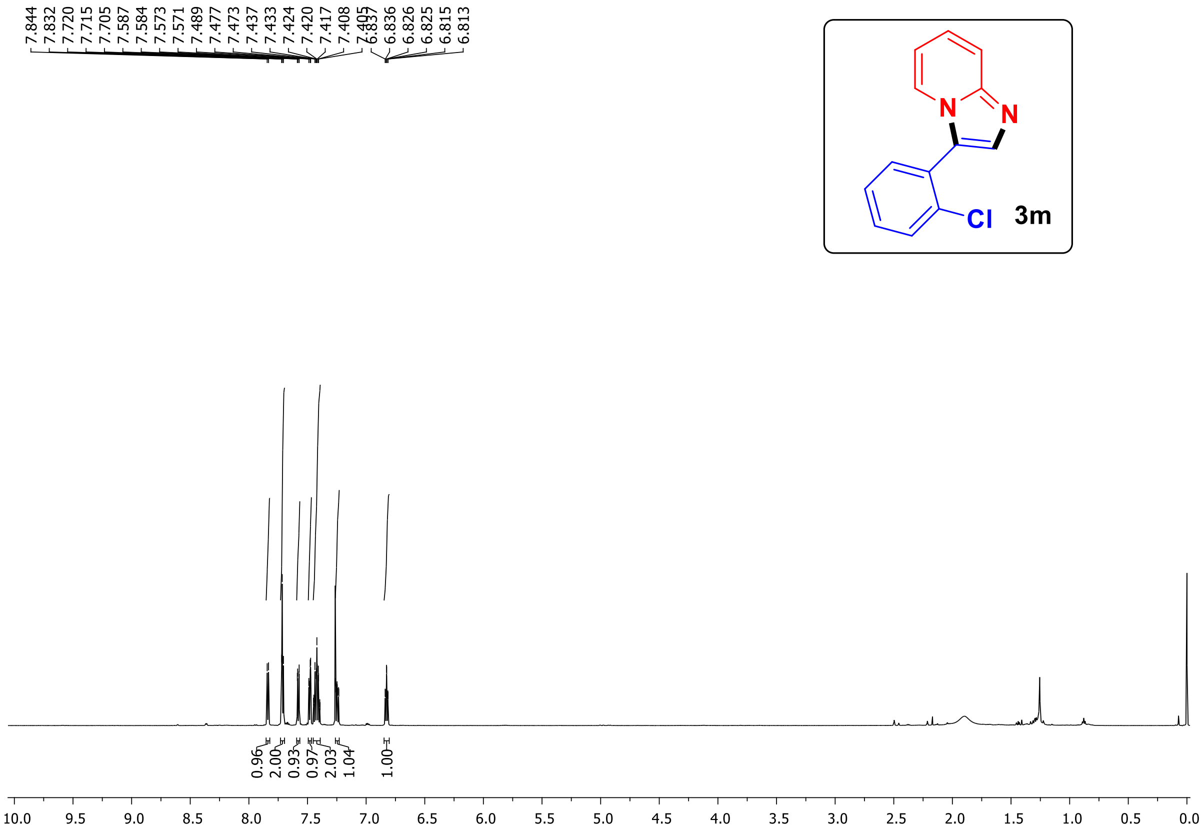
^{1}H NMR (500 MHz, $CDCl_3$):



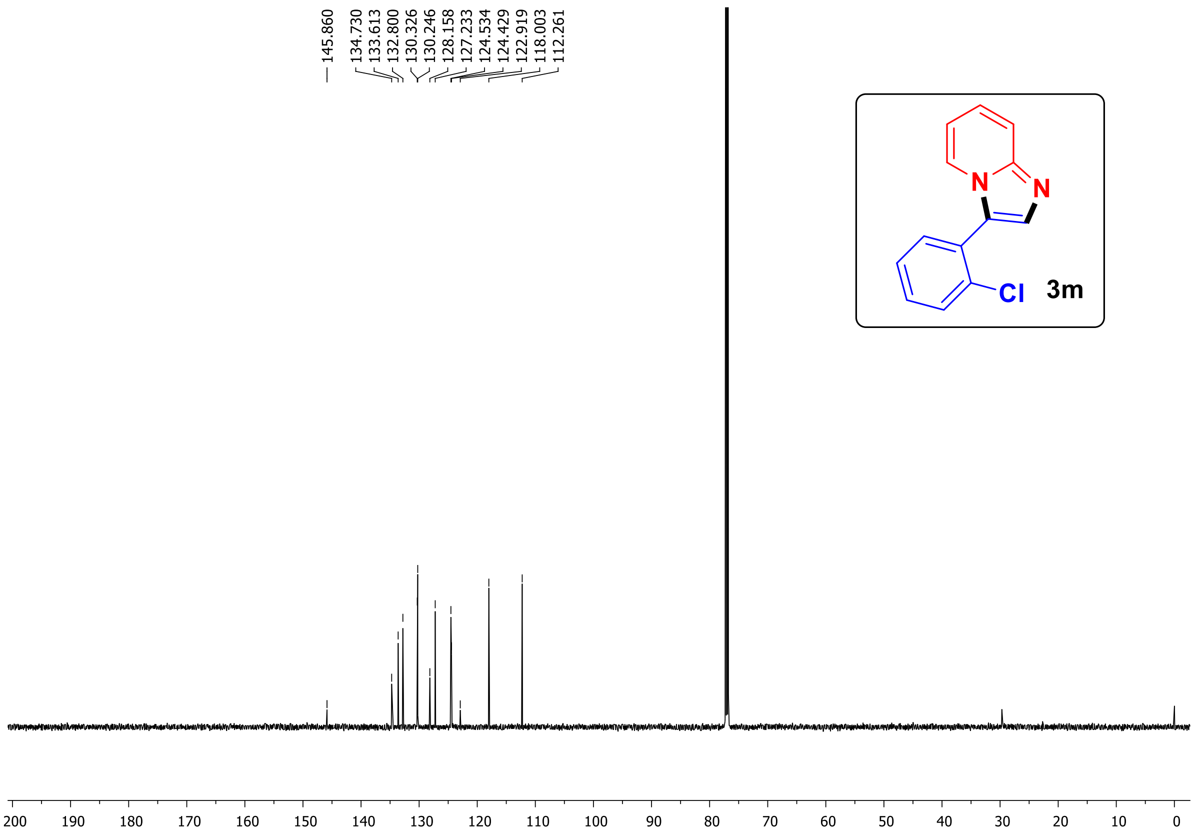
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$):



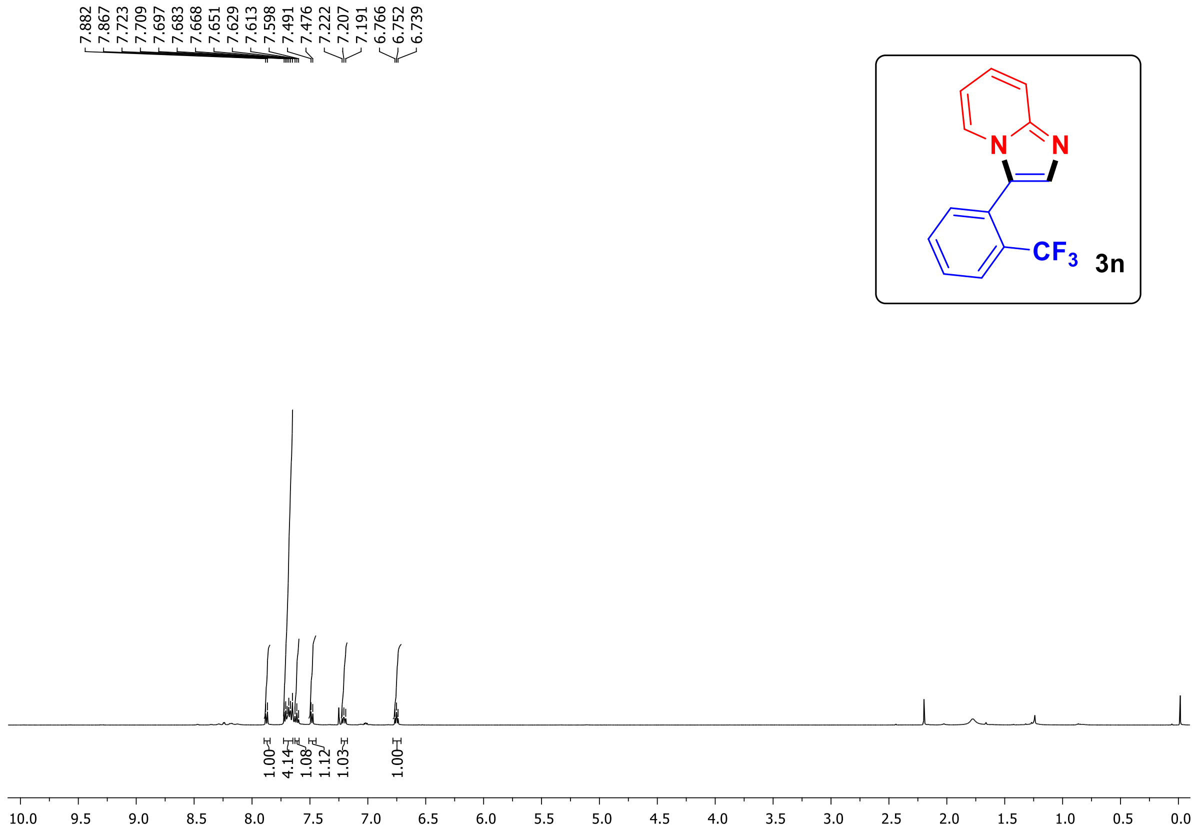
[1]H NMR (600 MHz, CDCl₃):



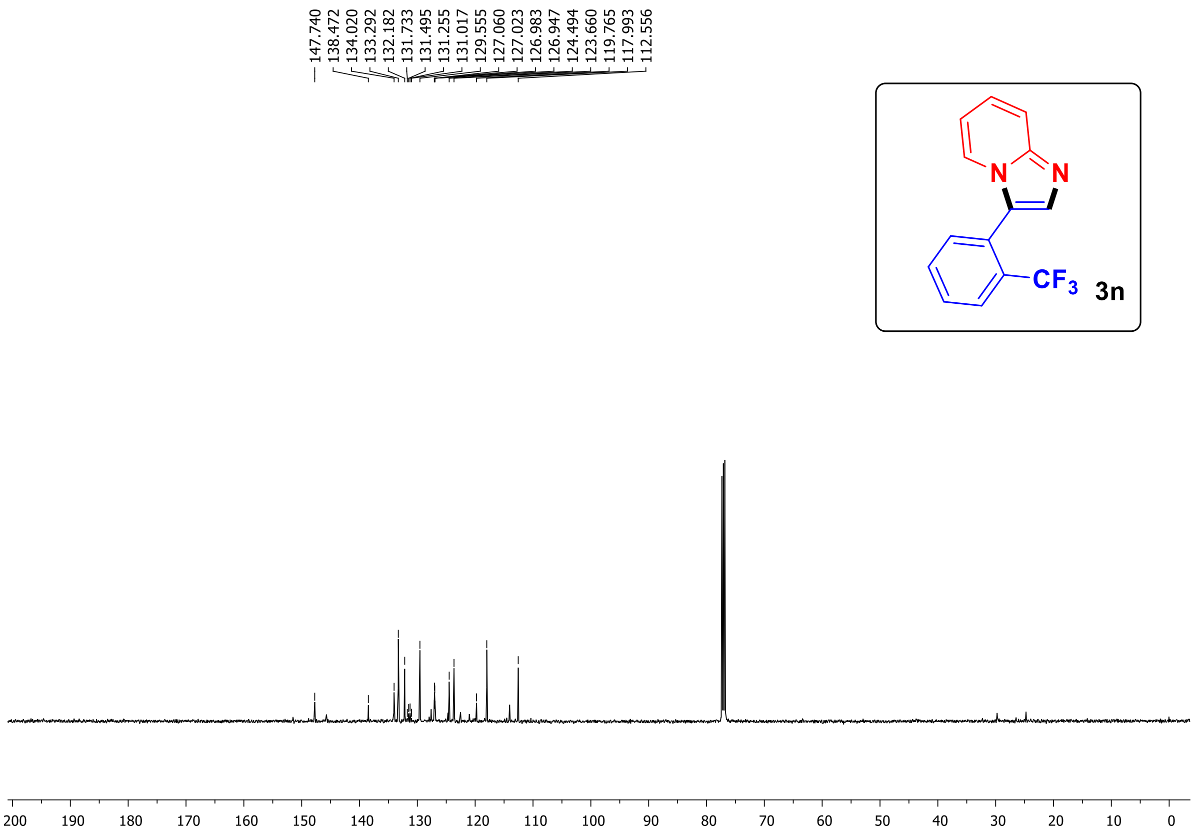
[13]C{[1]H} NMR (151 MHz, CDCl₃):



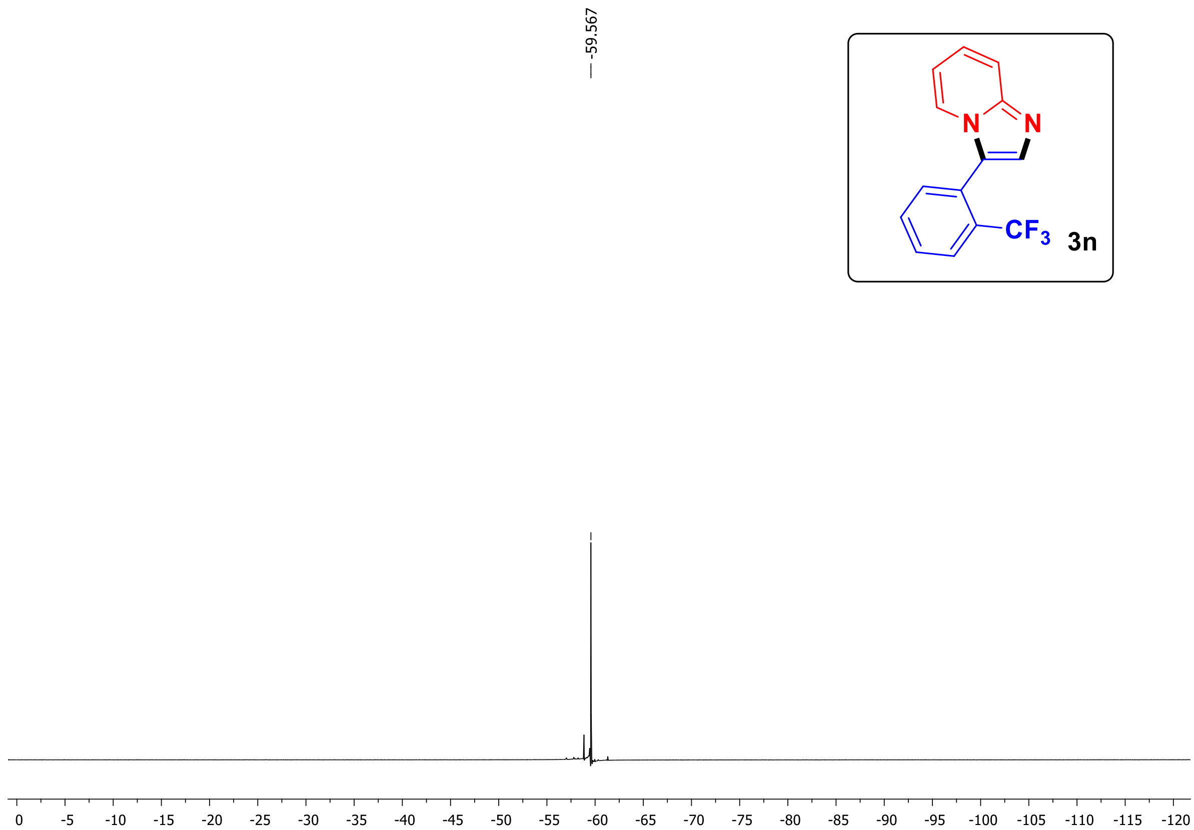
^{1}H NMR (500 MHz, $CDCl_3$):



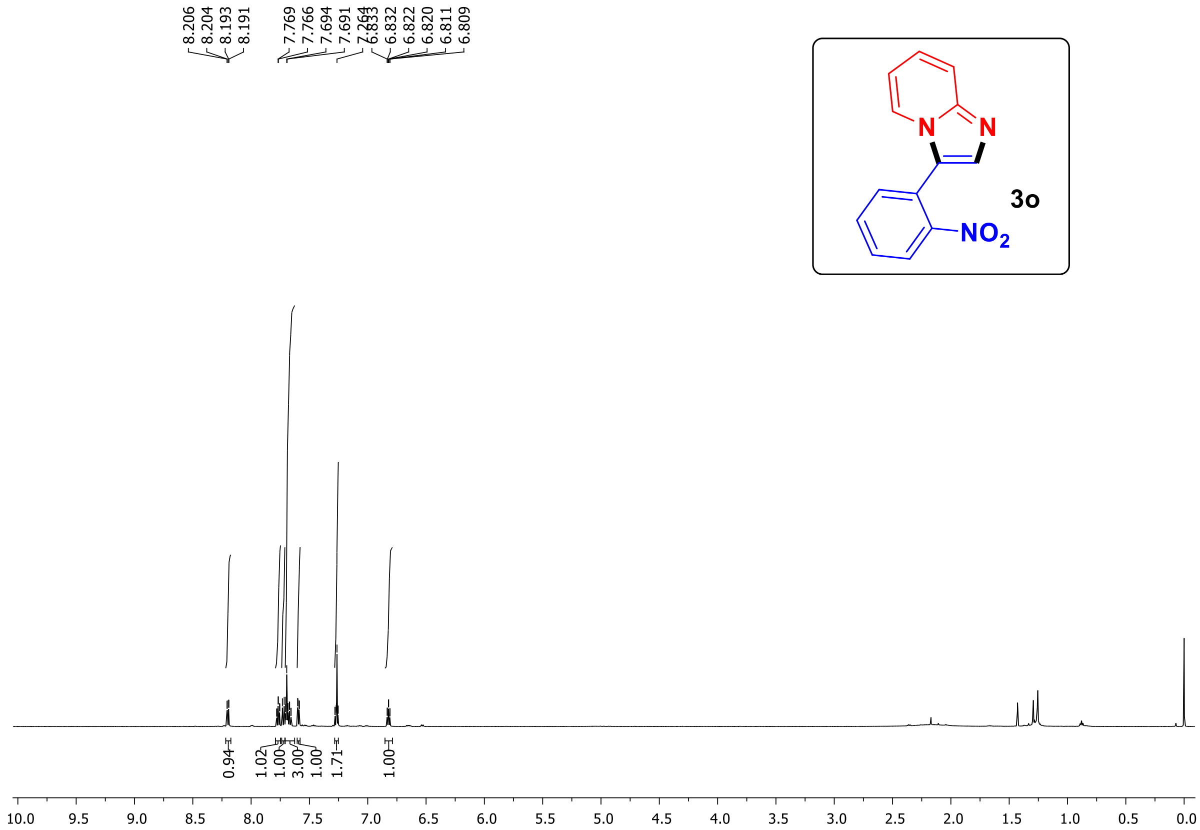
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$):



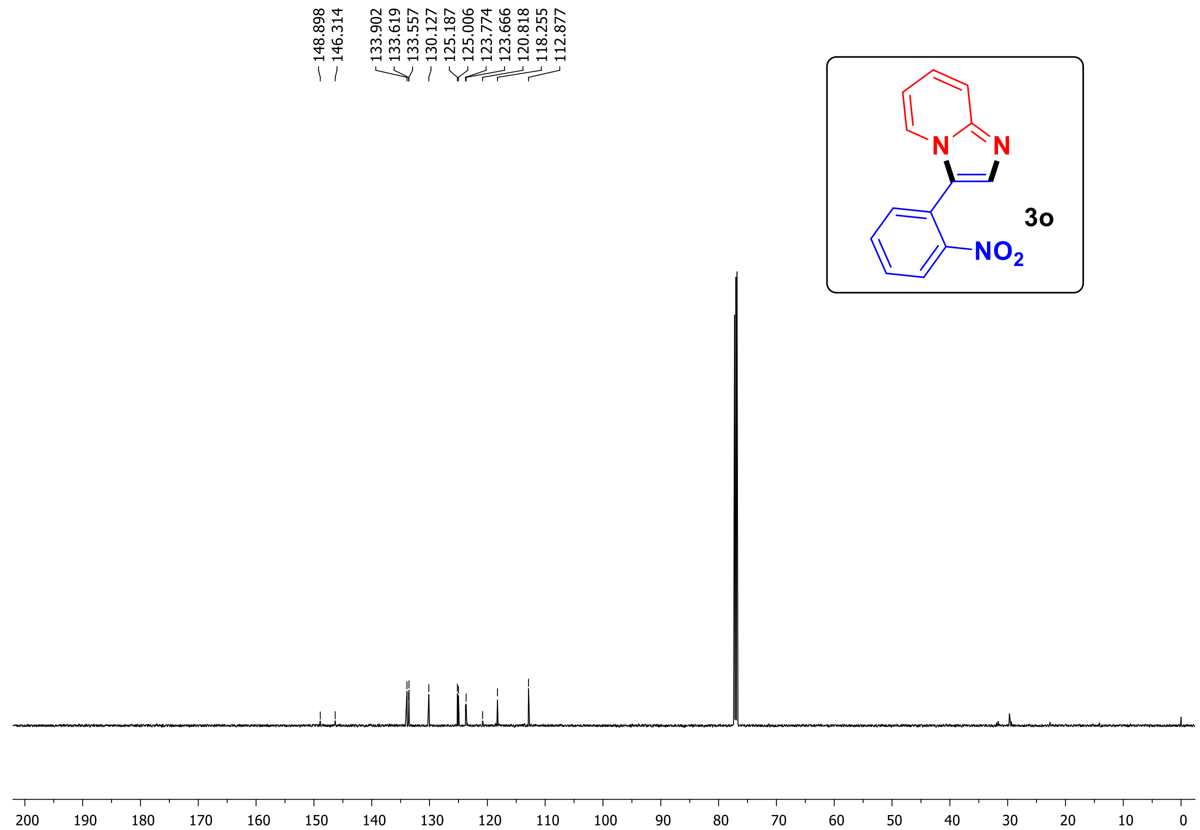
^{19}F NMR (471 MHz, $CDCl_3$):



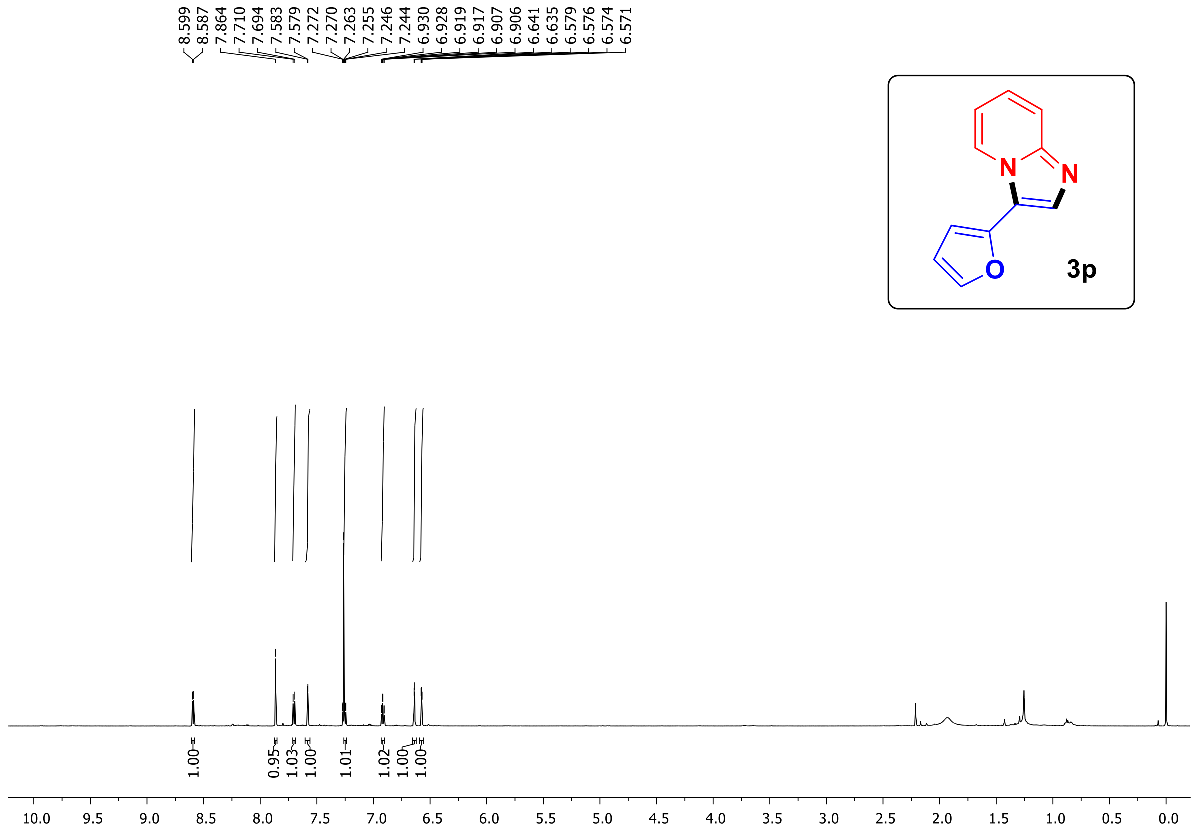
^{1}H NMR (600 MHz, $CDCl_3$):



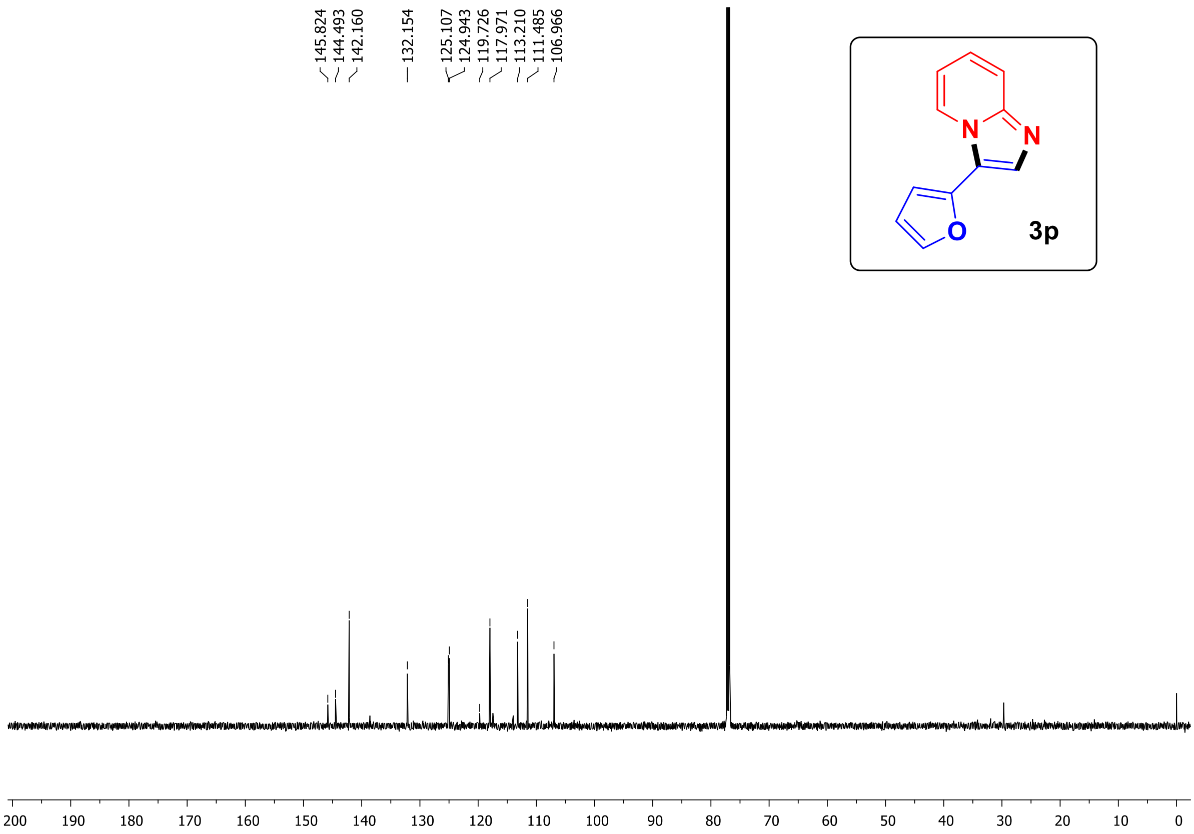
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$):



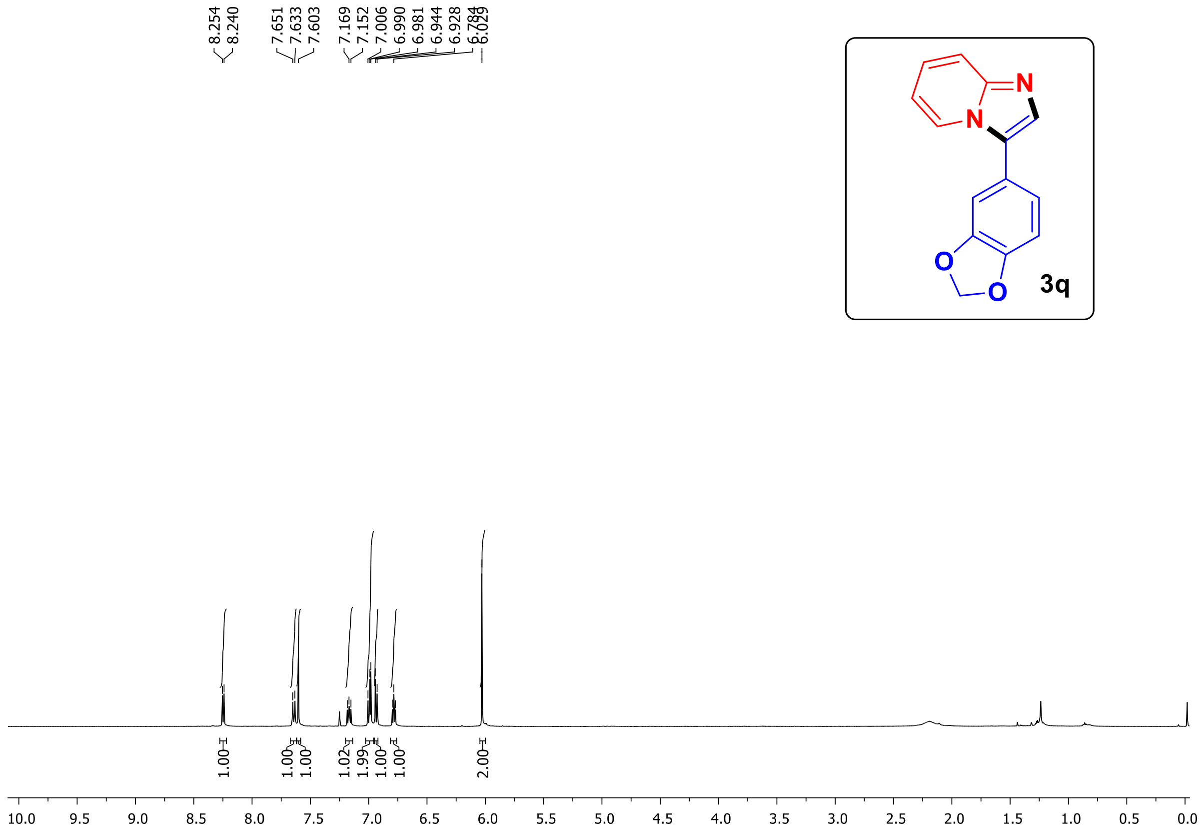
[1]H NMR (600 MHz, $CDCl_3$):



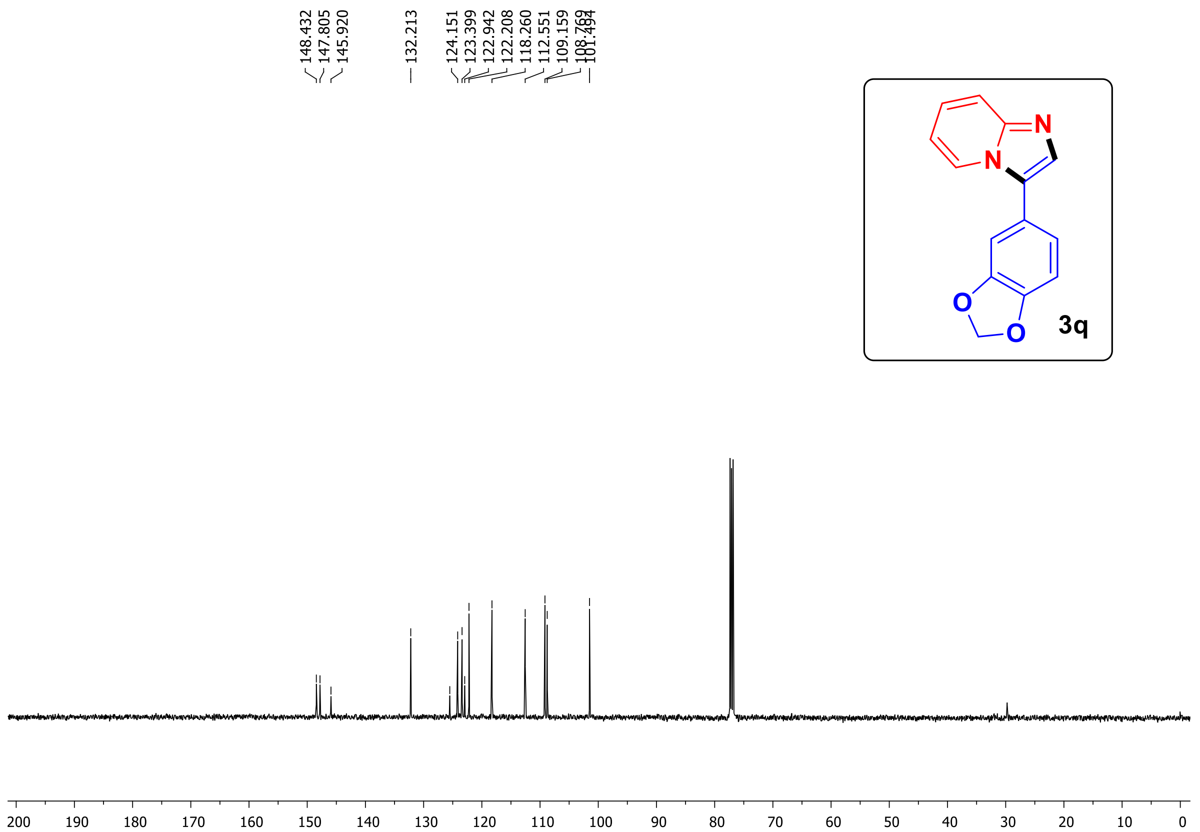
[13]C{[1]H} NMR (151 MHz, $CDCl_3$):



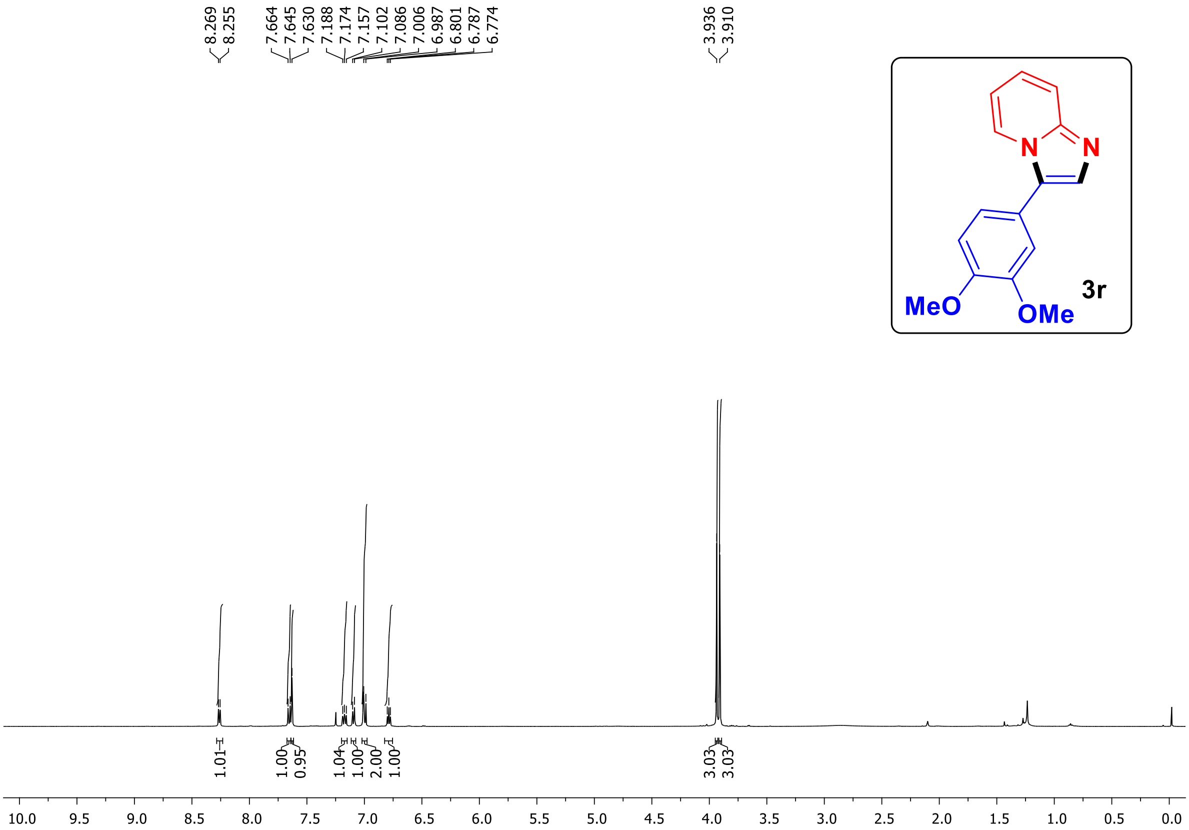
^{1}H NMR (500 MHz, $CDCl_3$):



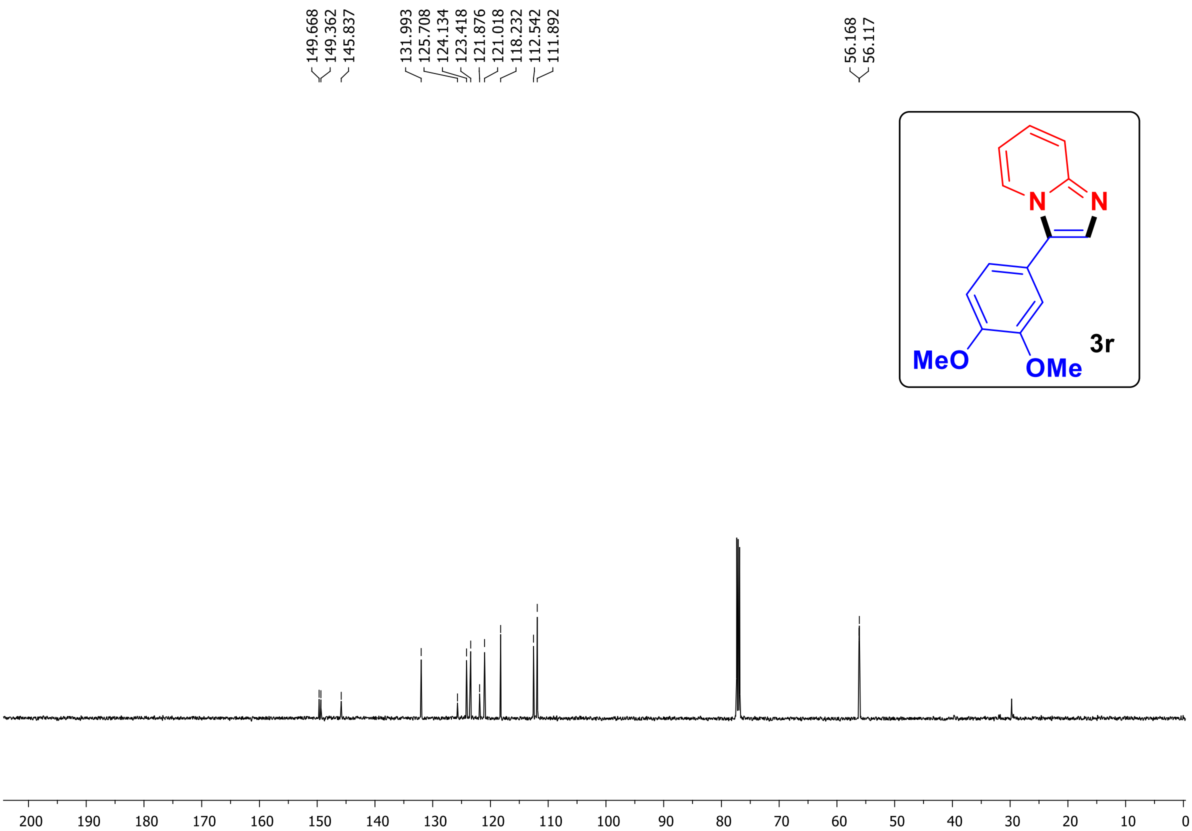
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):



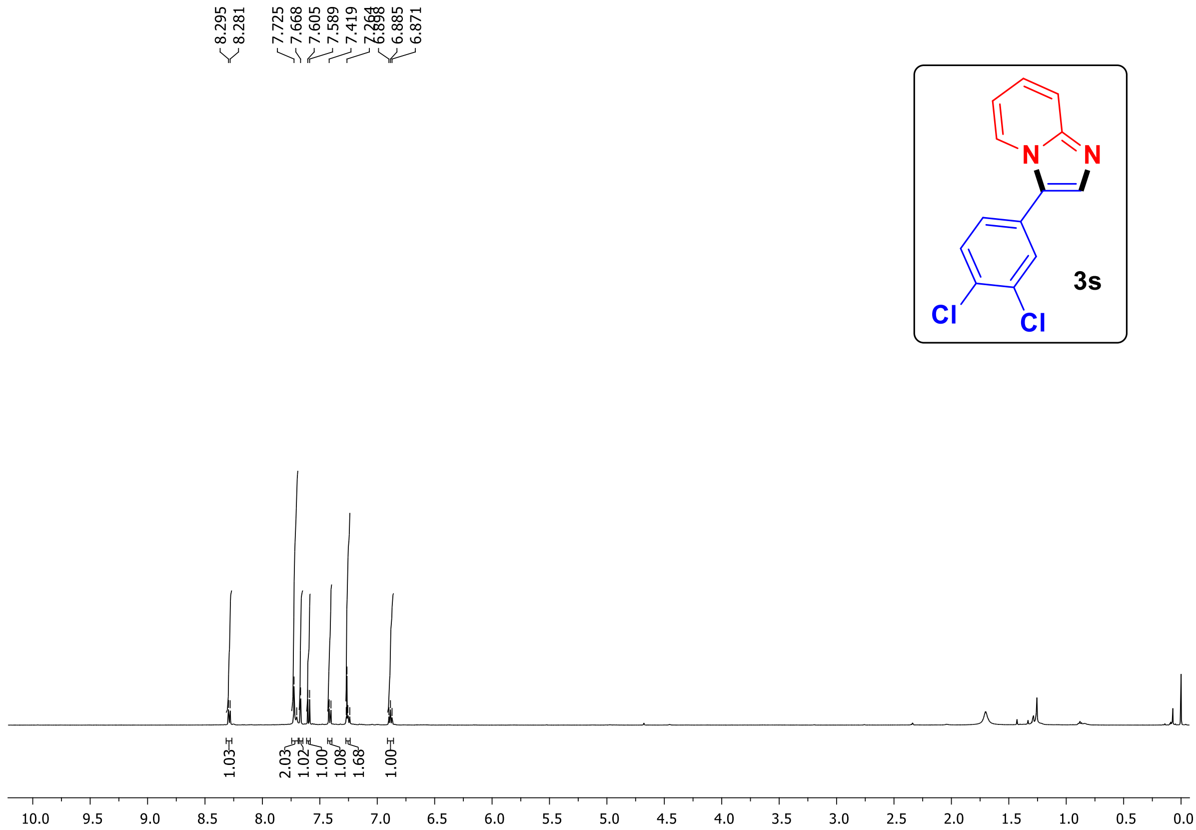
^{1}H NMR (500 MHz, $CDCl_3$):



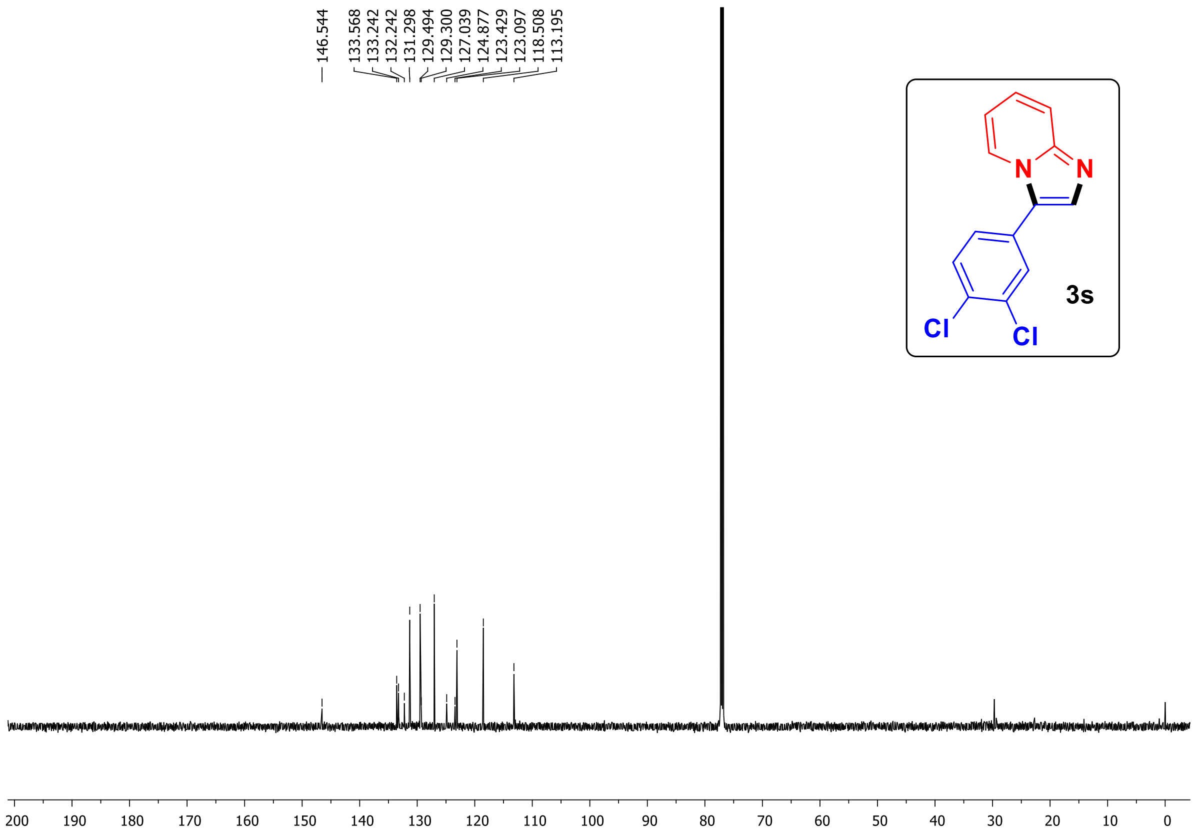
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):



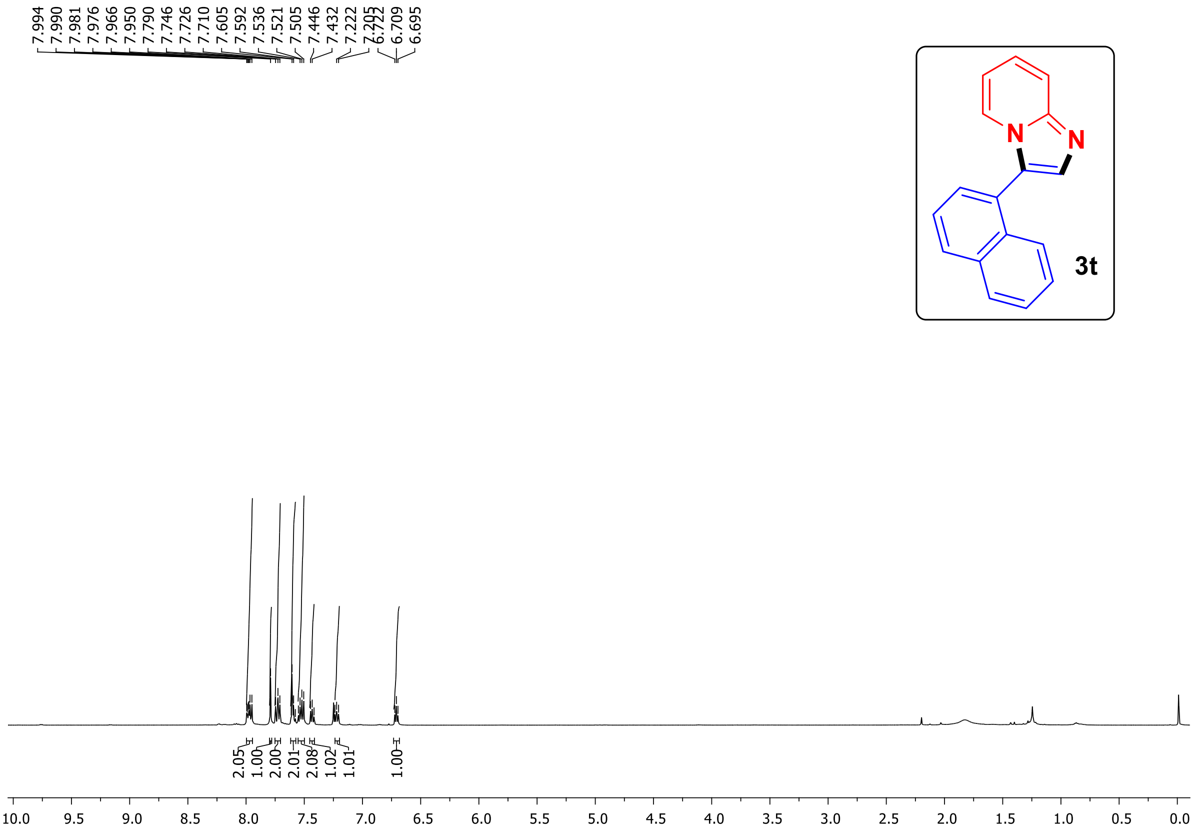
[1]H NMR (500 MHz, CDCl$_3$):



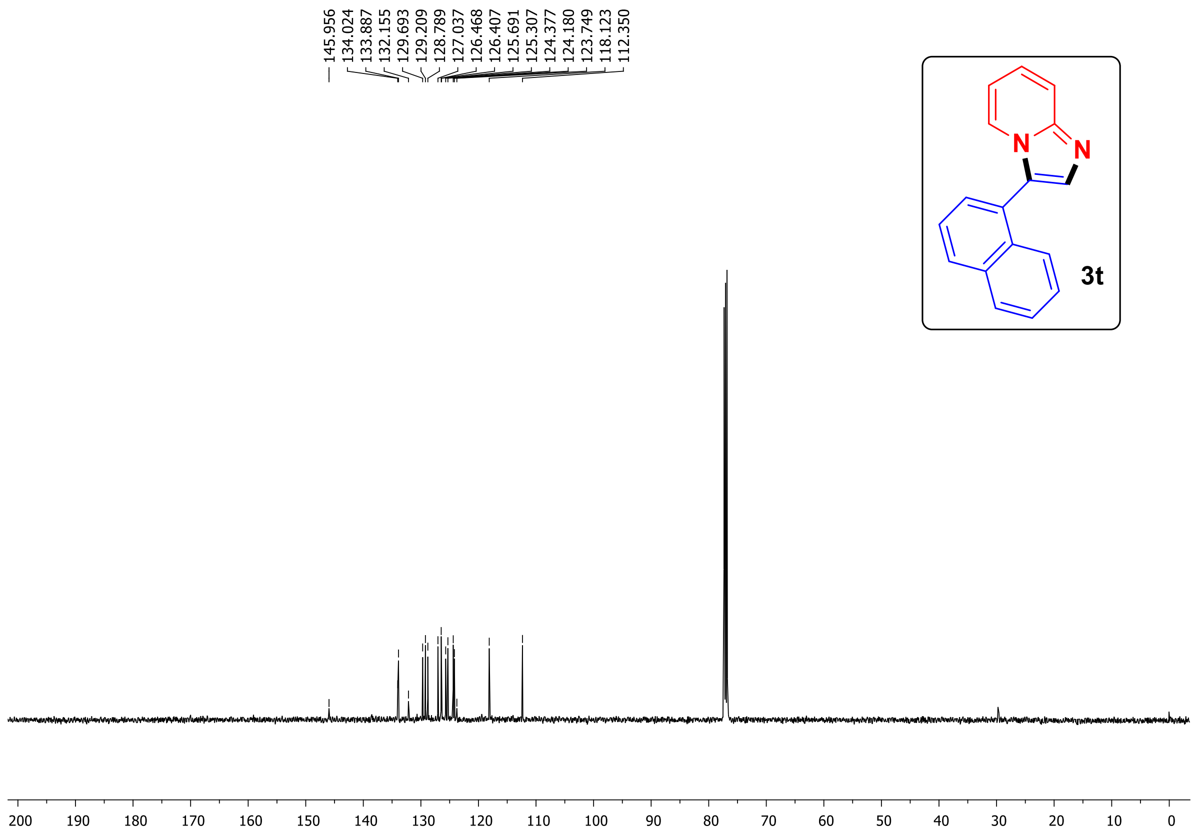
[13]C{[1]H} NMR (126 MHz, CDCl$_3$):



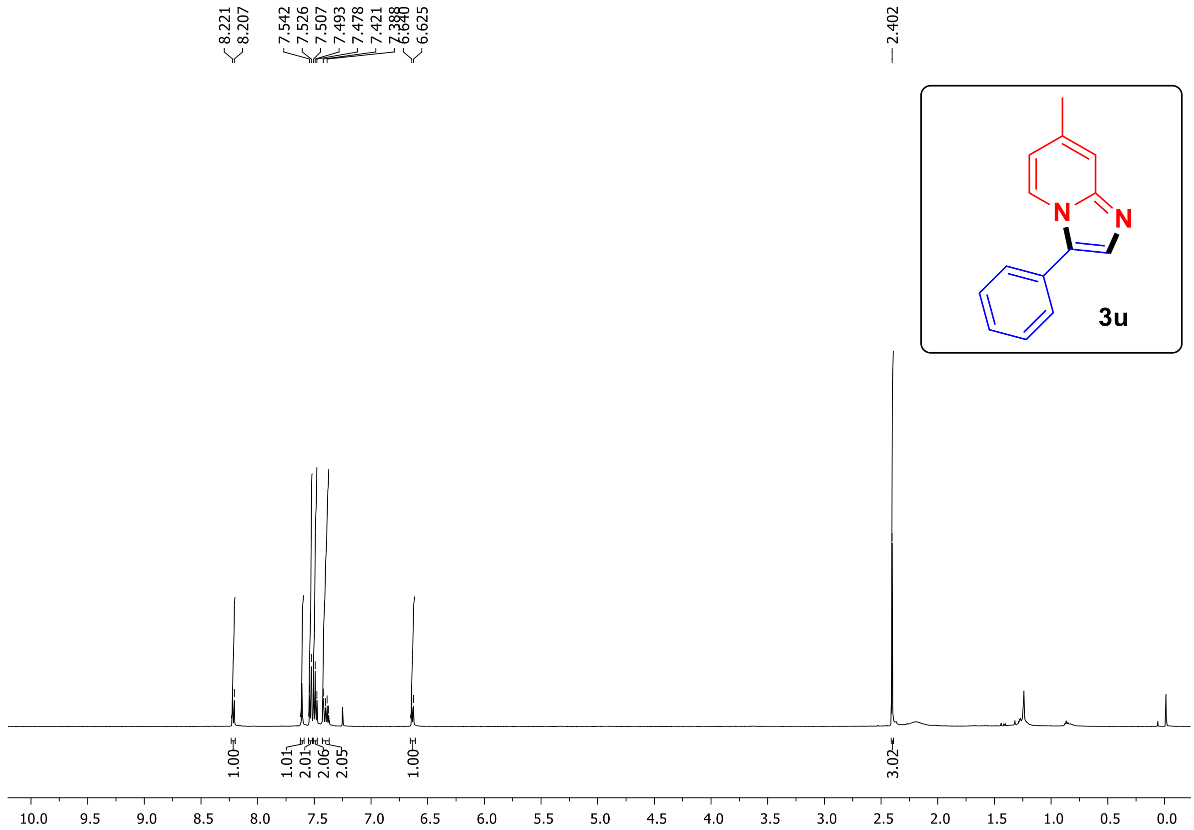
^{1}H NMR (500 MHz, $CDCl_3$):



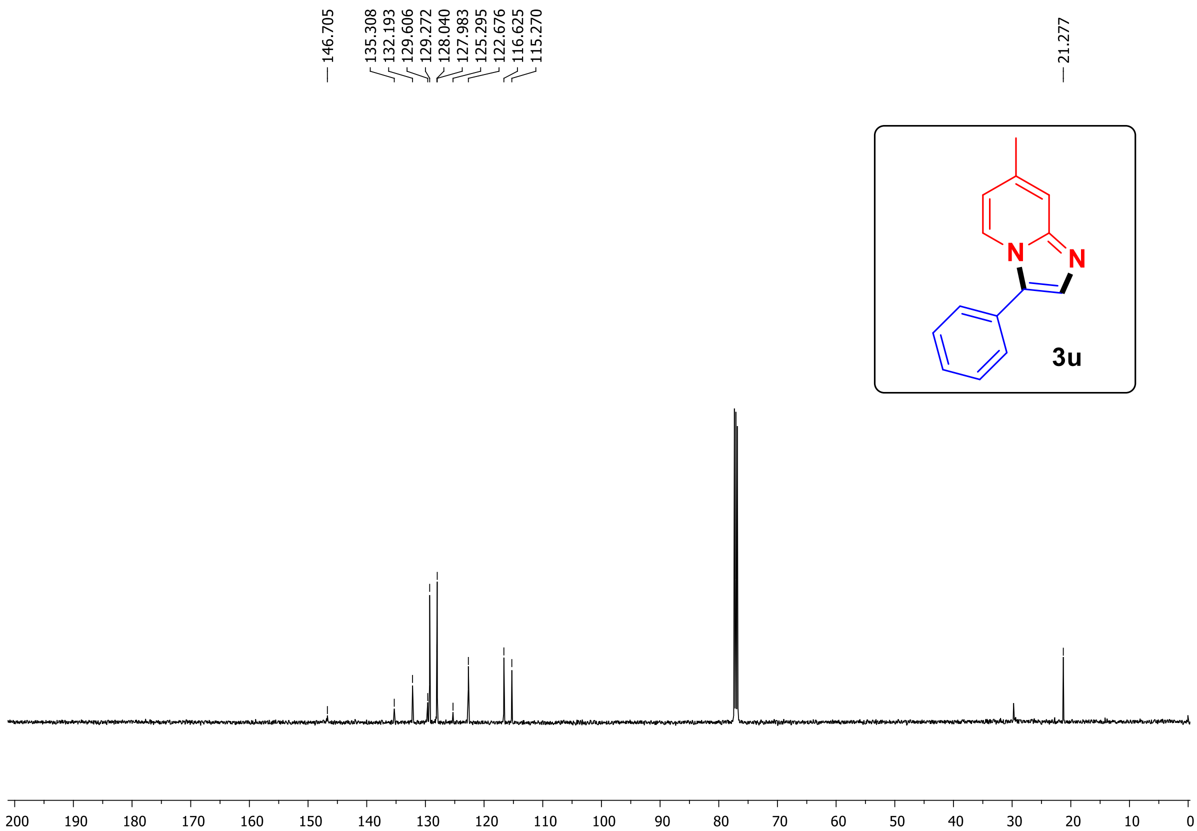
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$):



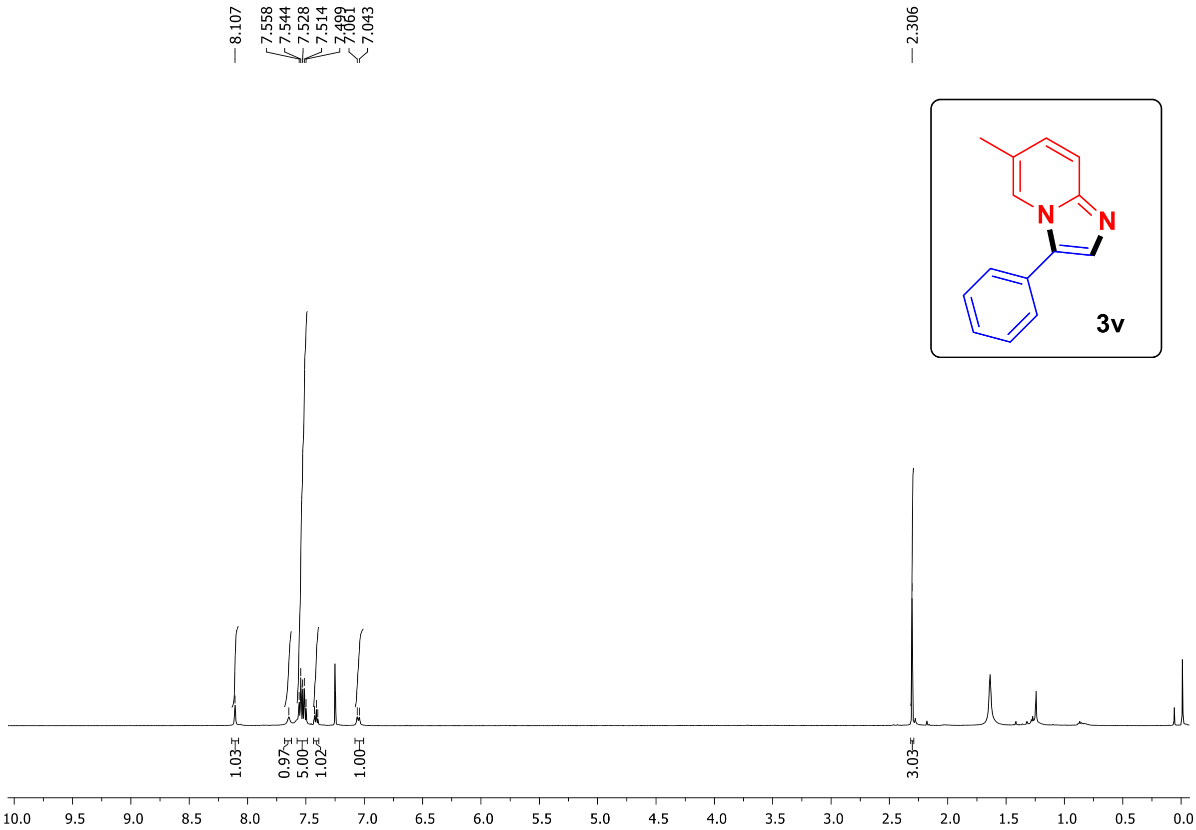
[1]H NMR (500 MHz, $CDCl_3$):



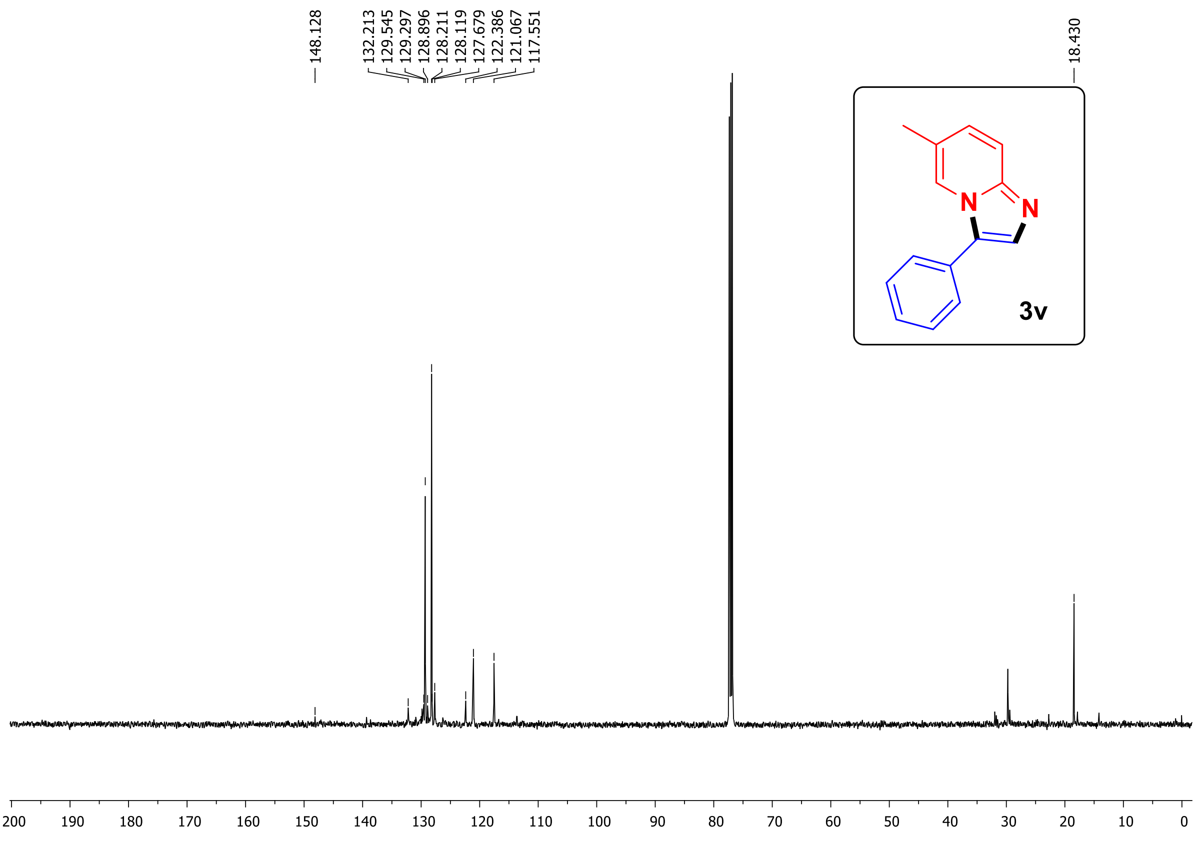
[13]C{[1]H} NMR (126 MHz, $CDCl_3$):



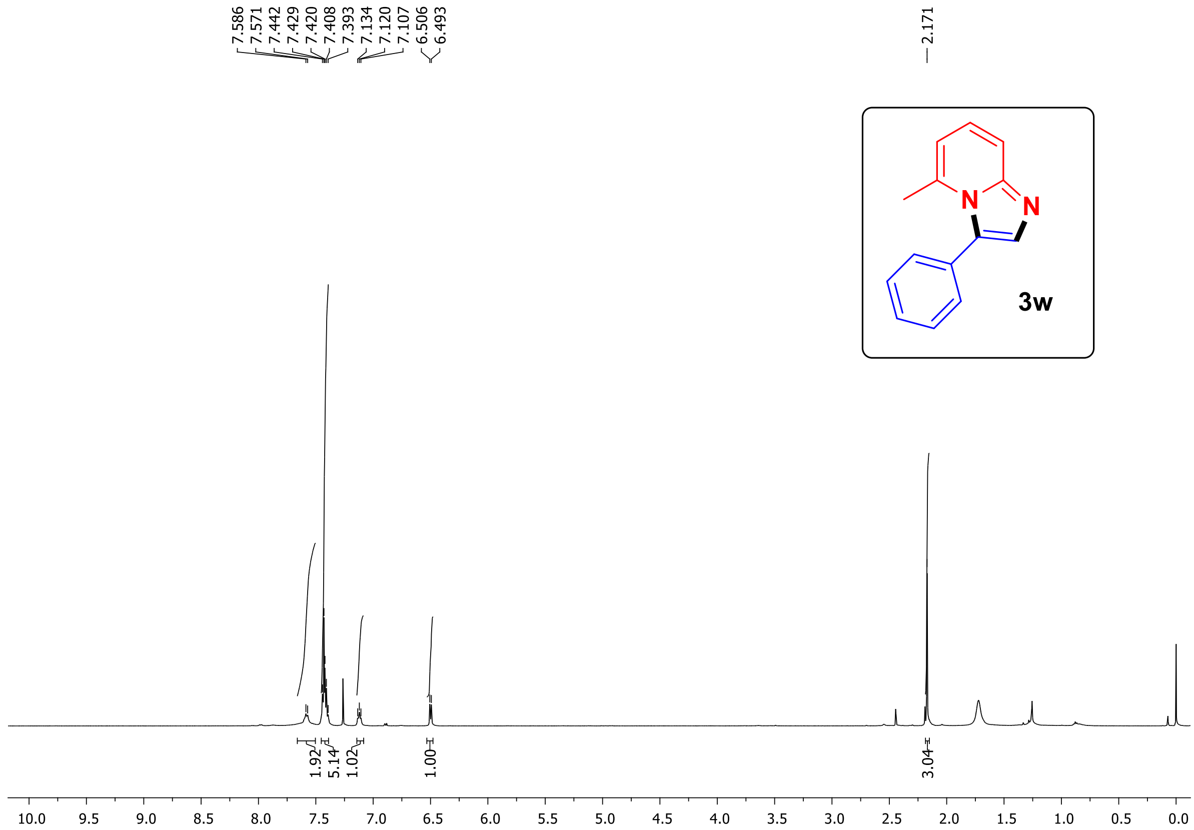
^{1}H NMR (500 MHz, $CDCl_3$):



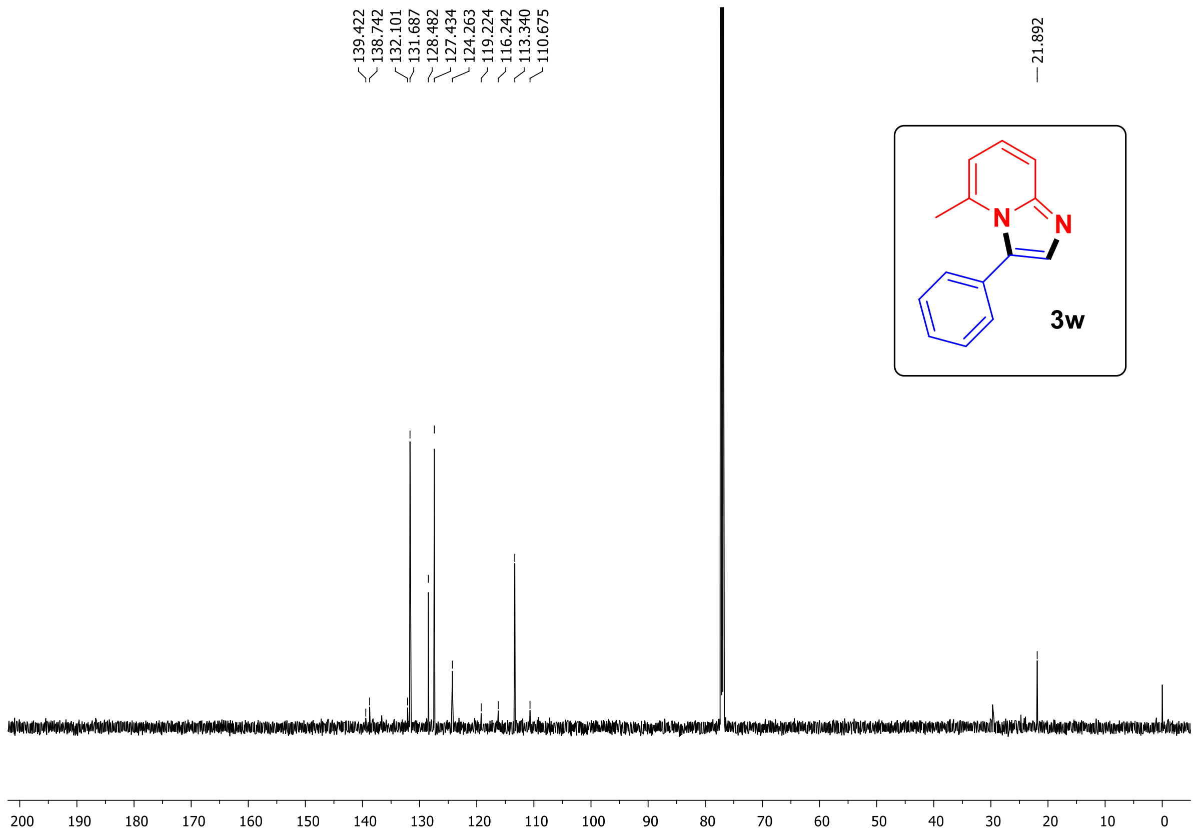
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$):



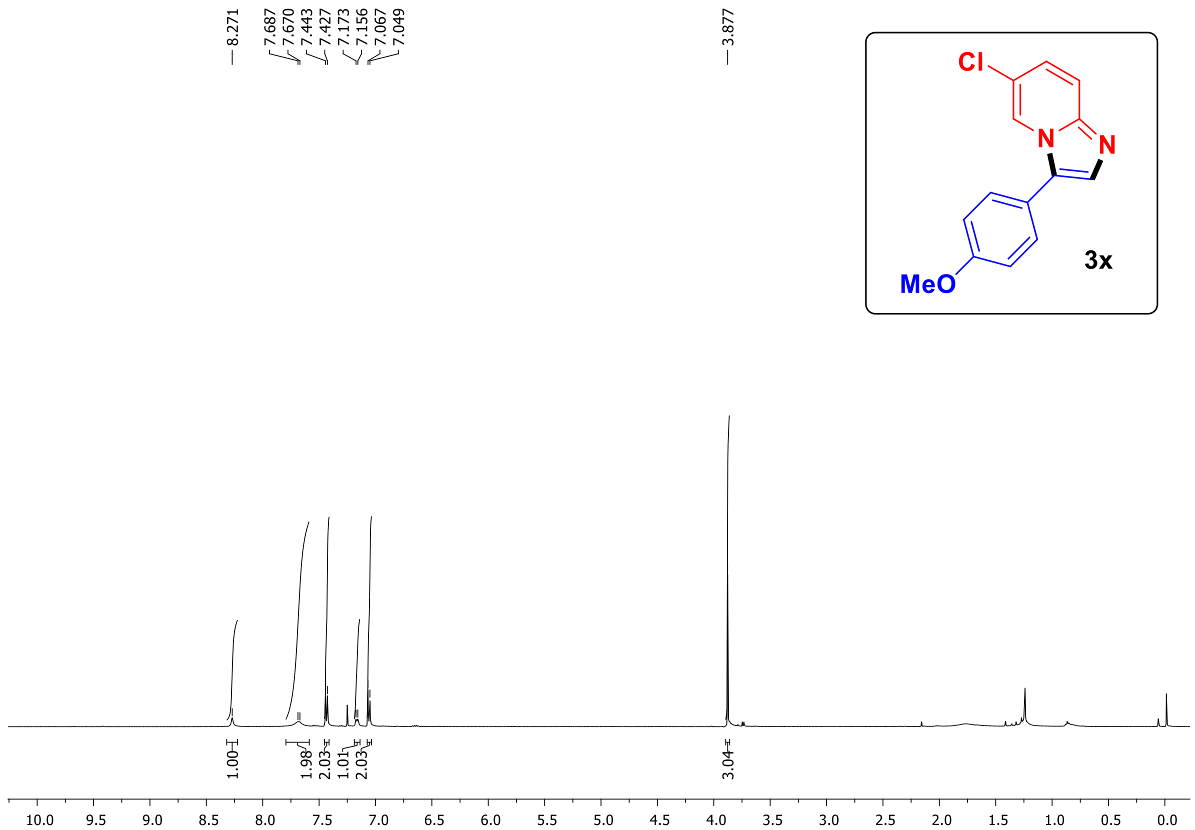
[1]H NMR (500 MHz, $CDCl_3$):



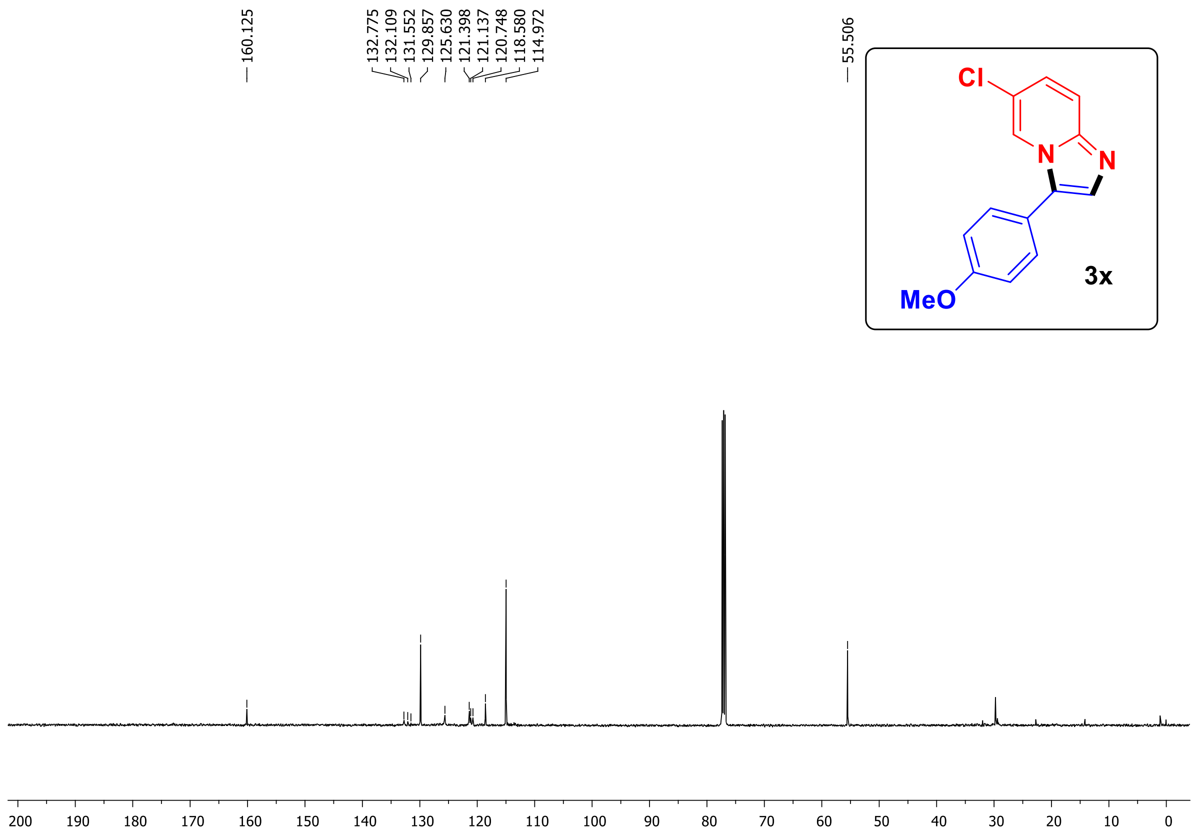
[13]C{[1]H} NMR (151 MHz, $CDCl_3$):



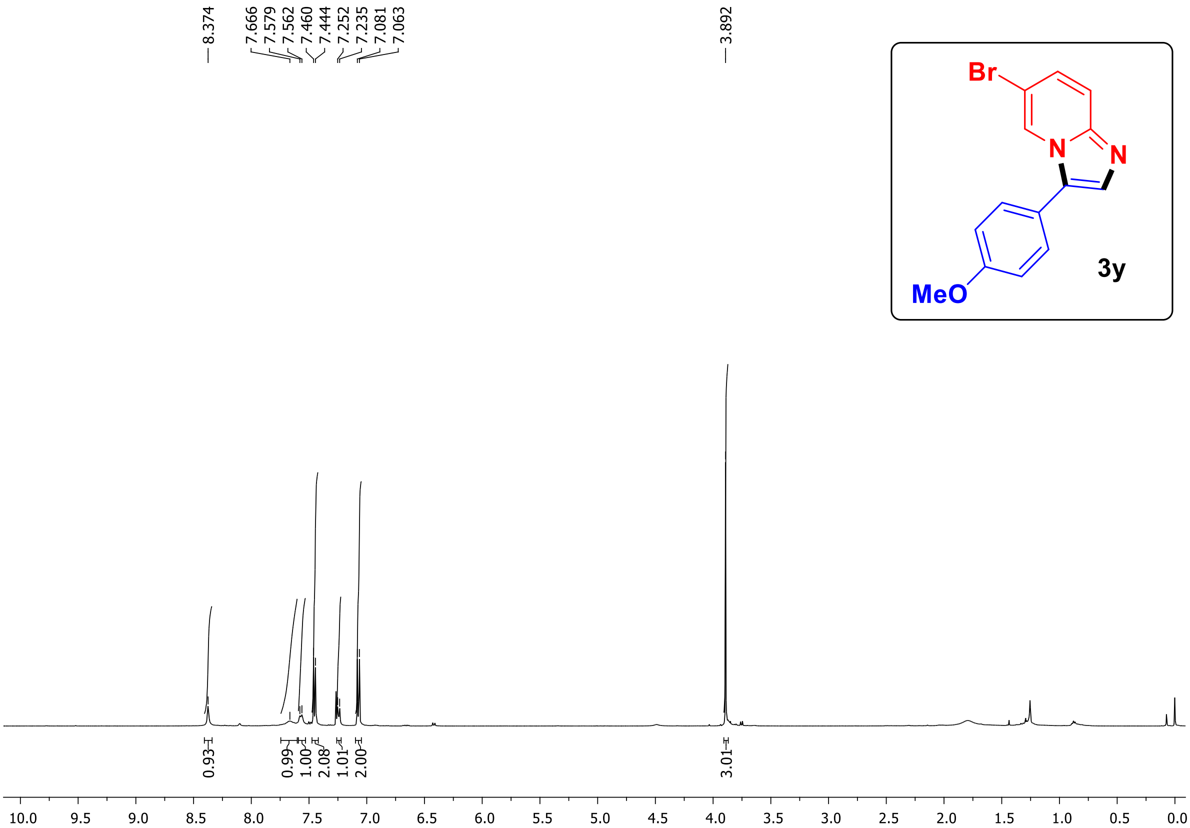
^{1}H NMR (500 MHz, $CDCl_3$):



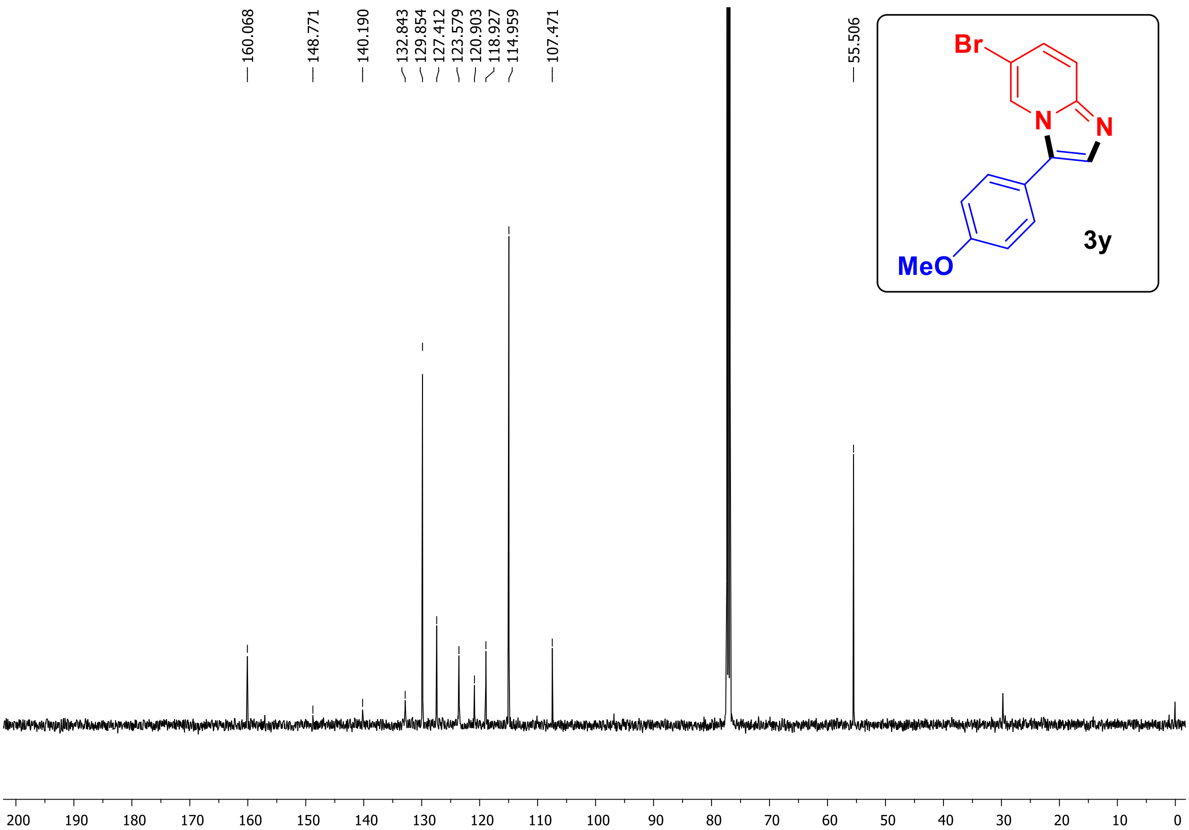
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$):



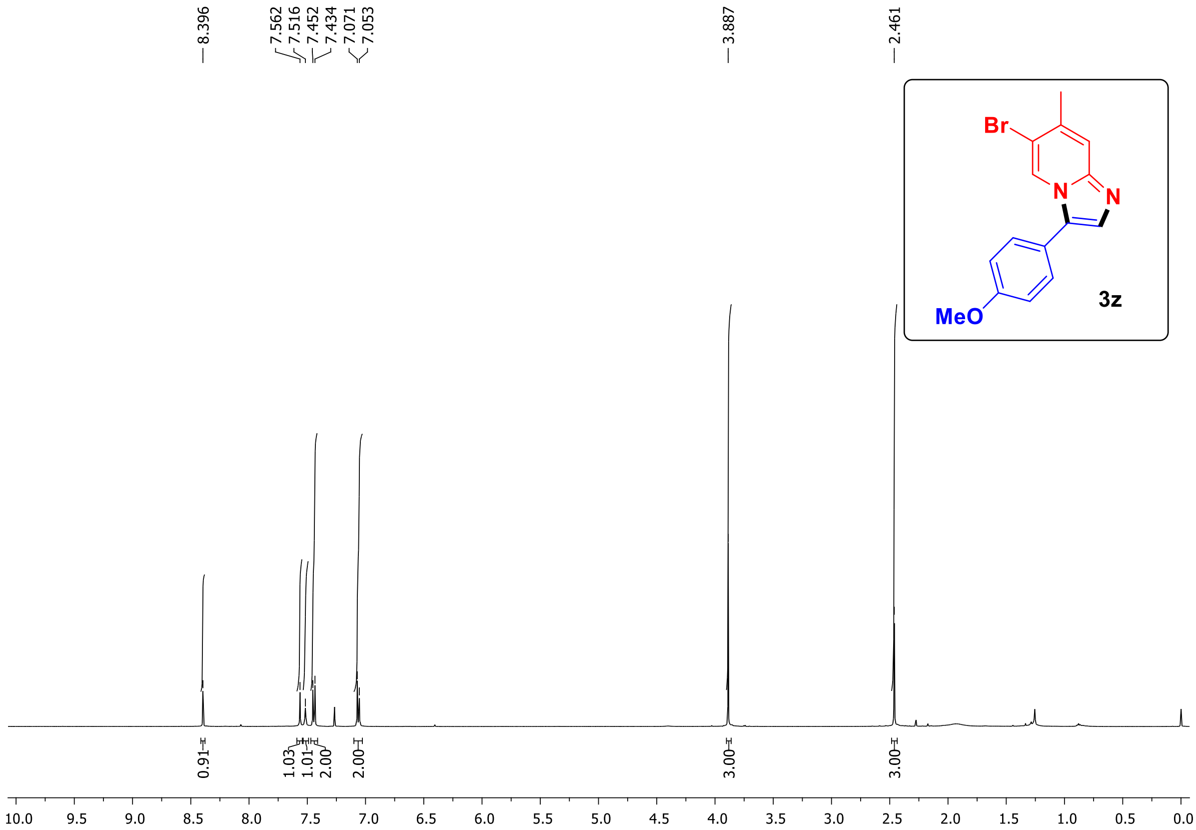
^{1}H NMR (500 MHz, $CDCl_3$):



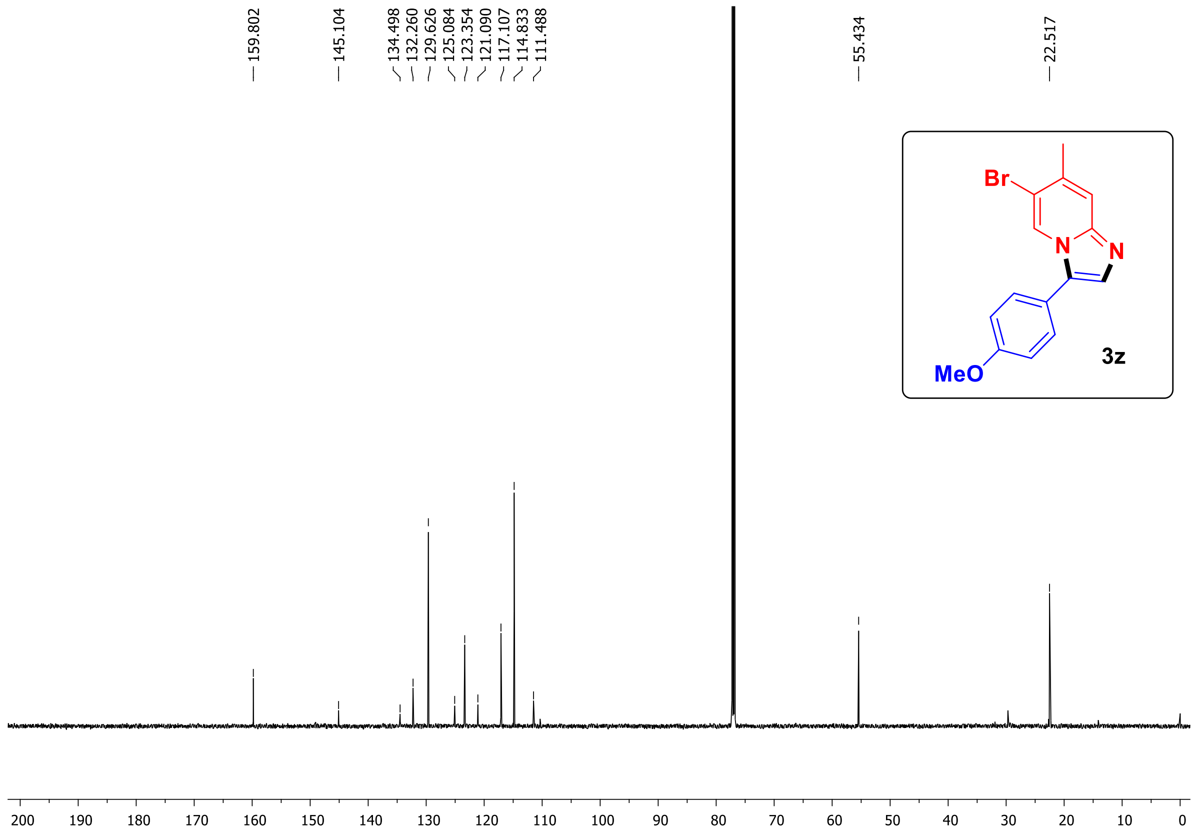
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$):



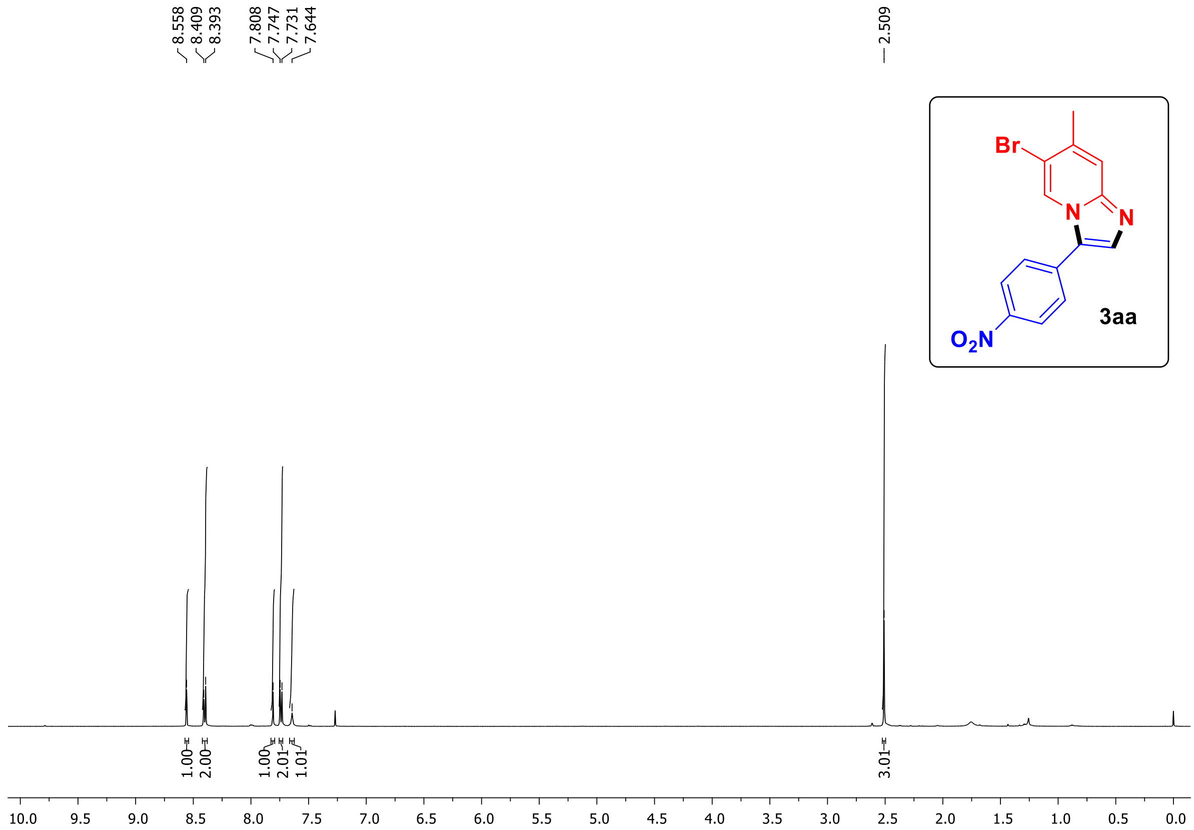
^{1}H NMR (500 MHz, $CDCl_3$):



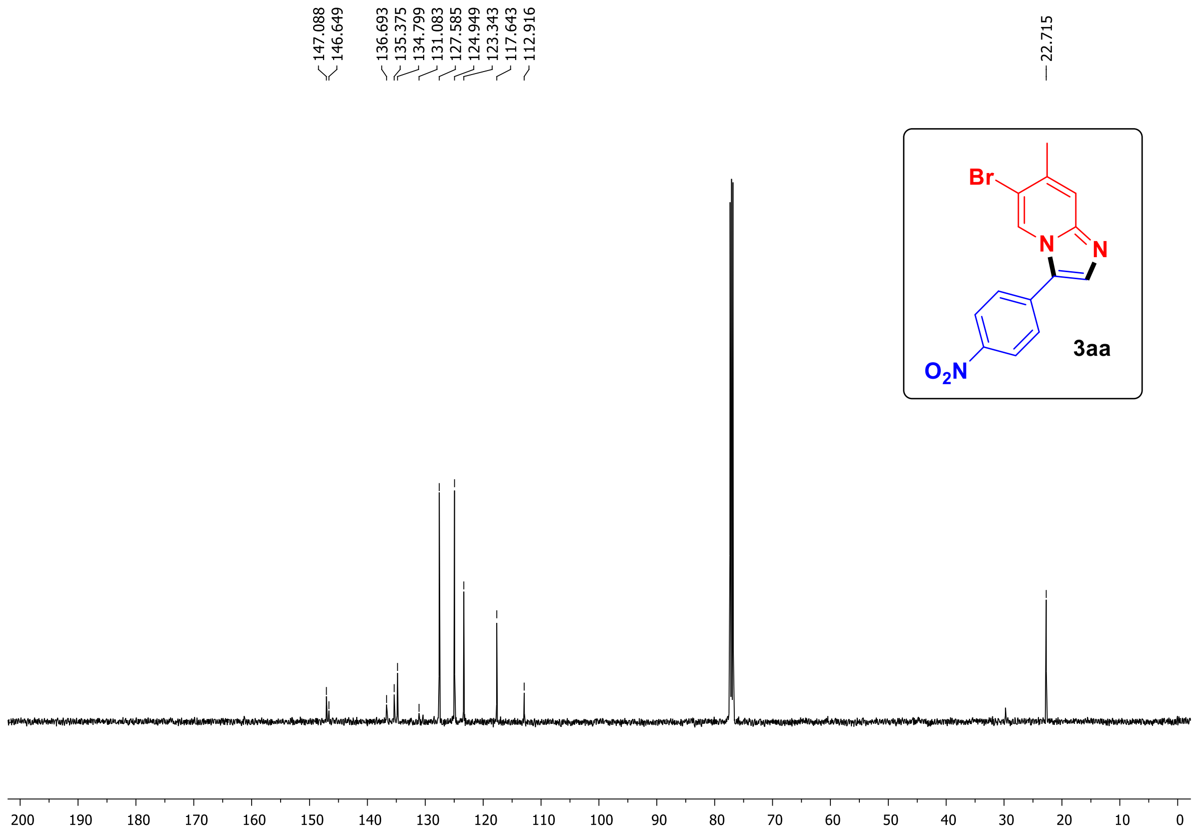
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$):



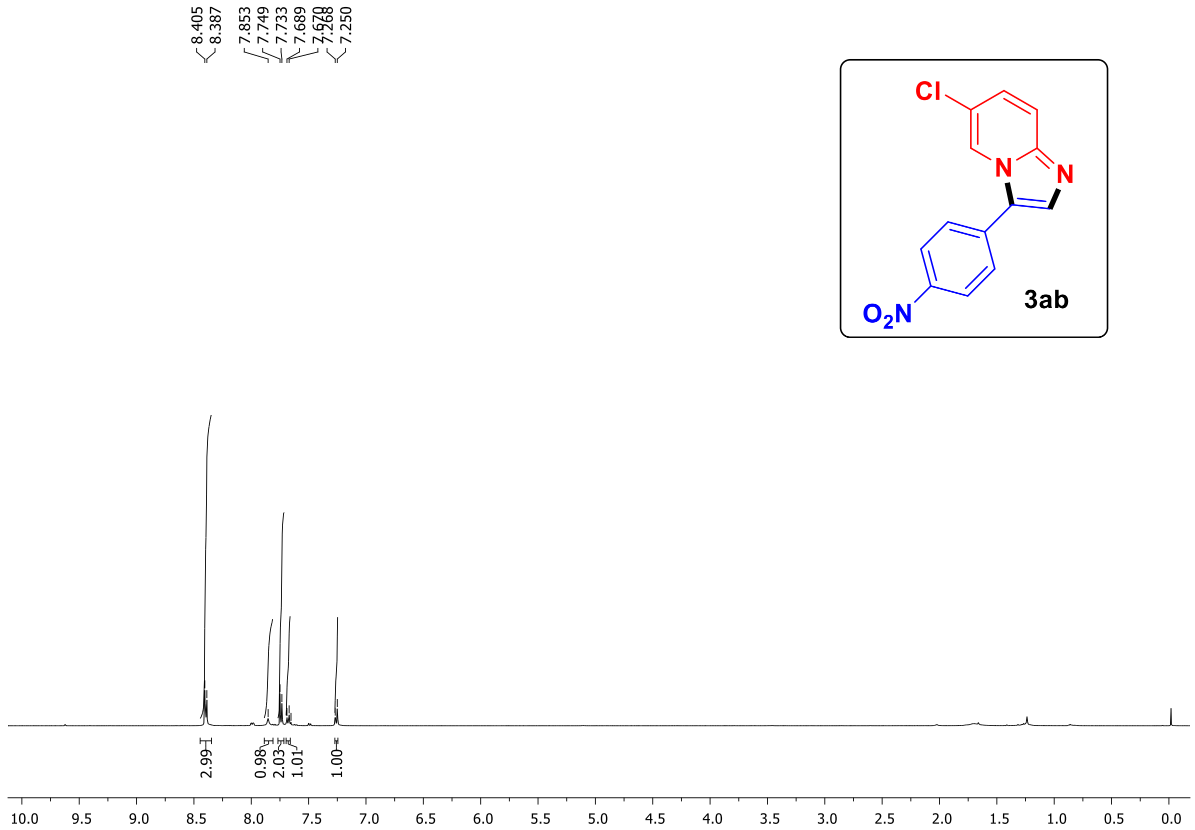
^{1}H NMR (500 MHz, CDCl$_3$):



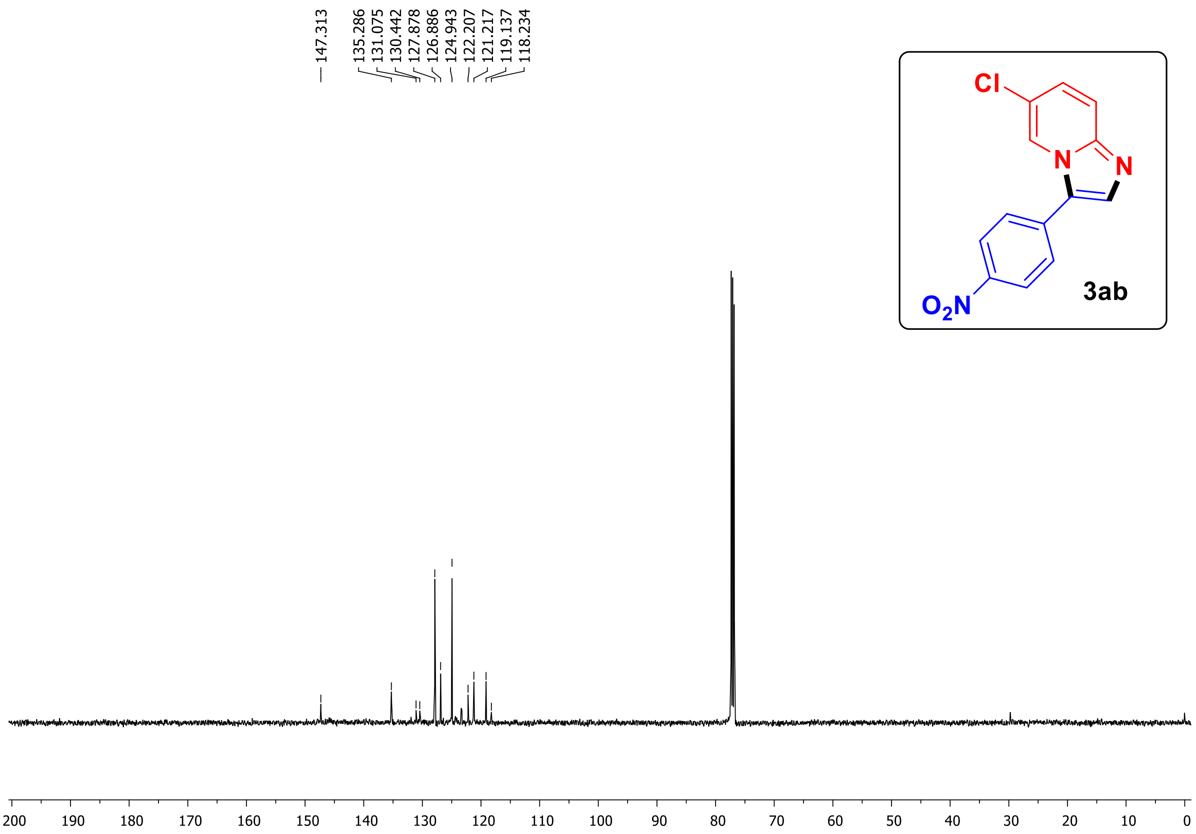
^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$):



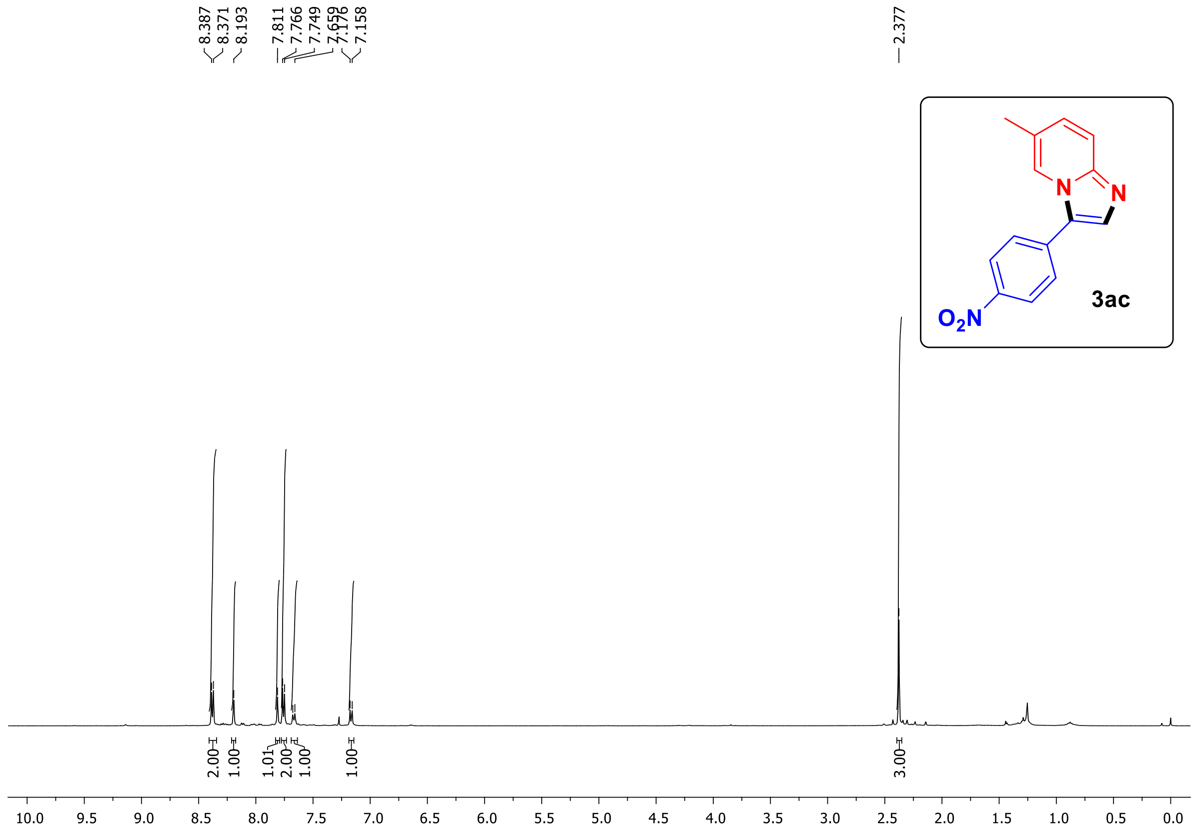
[1]H NMR (500 MHz, $CDCl_3$):



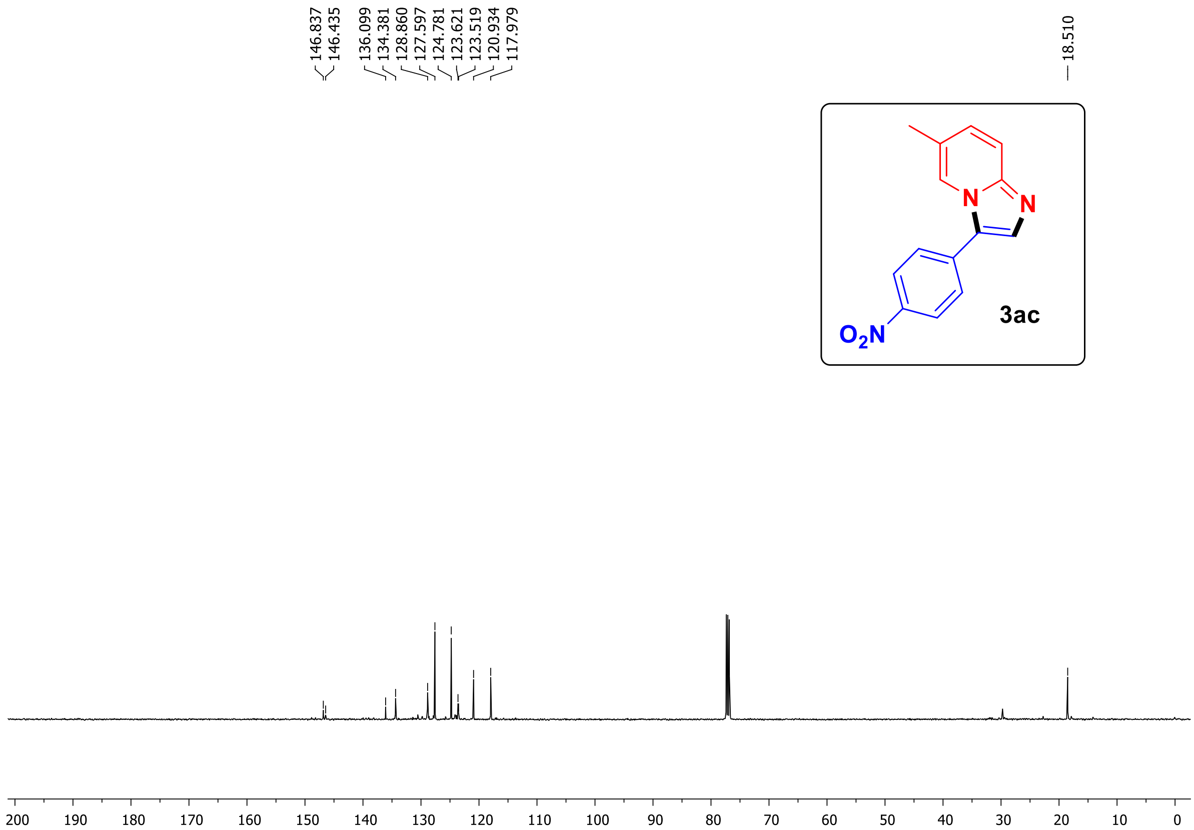
[13]C{[1]H} NMR (126 MHz, $CDCl_3$):



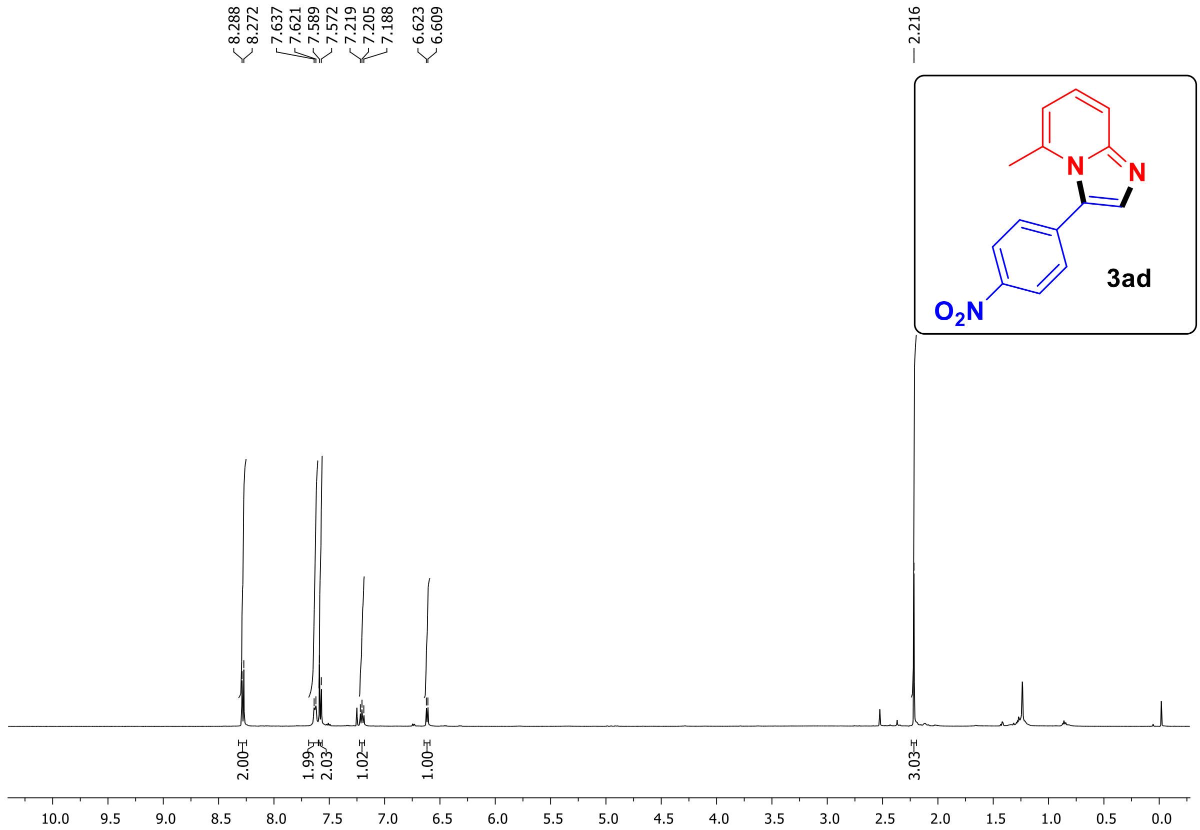
^{1}H NMR (500 MHz, CDCl$_3$):



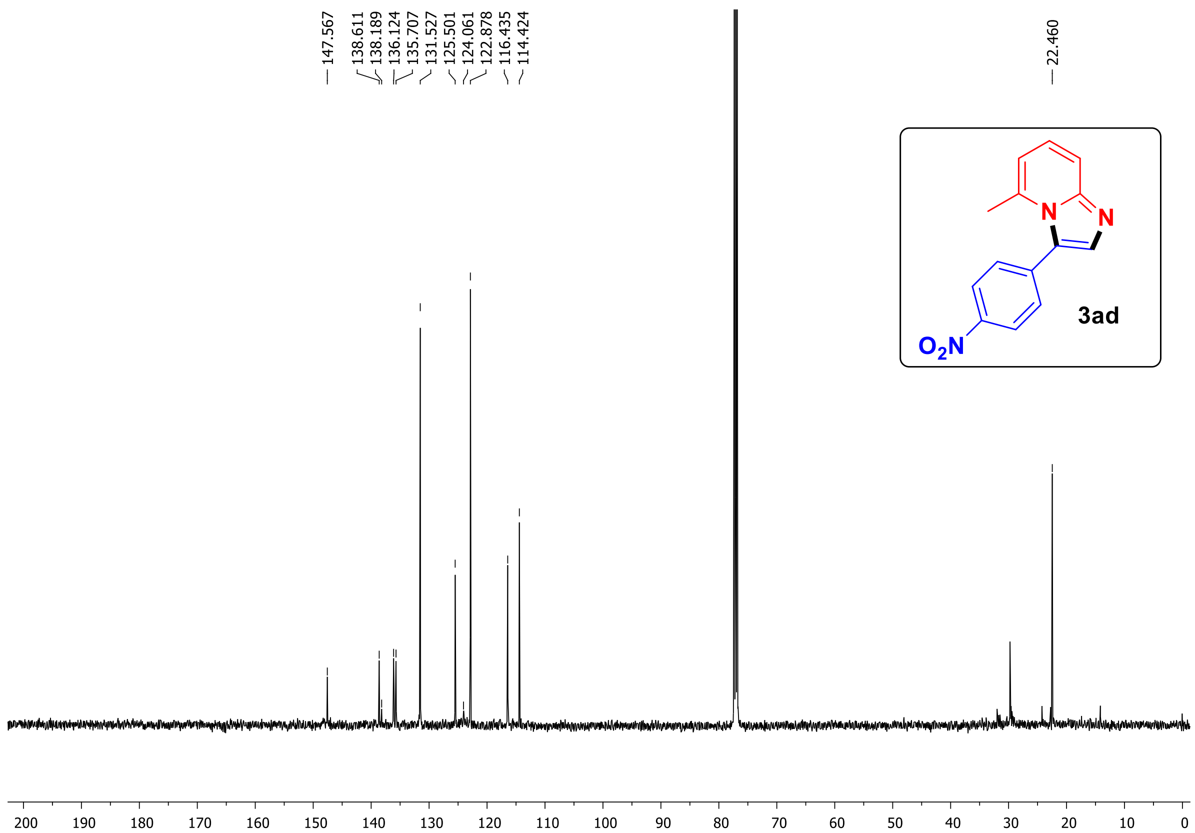
^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$):



^{1}H NMR (500 MHz, $CDCl_3$):

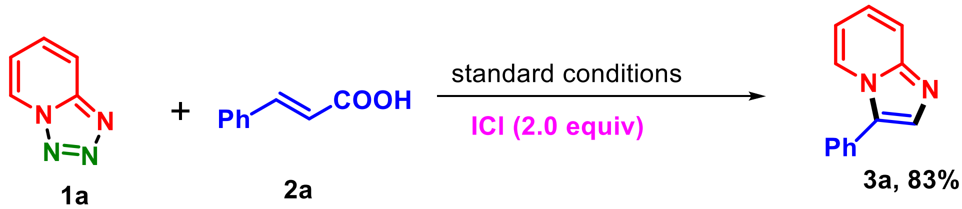


$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$):

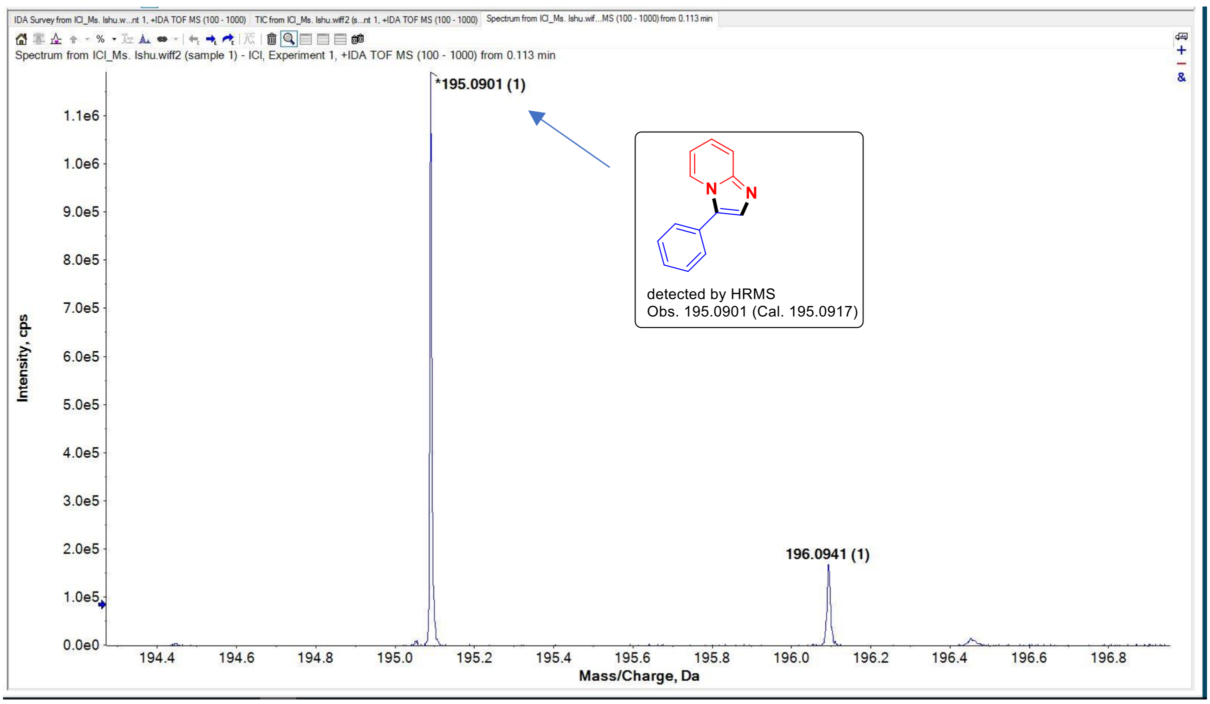


7. Control experiments:

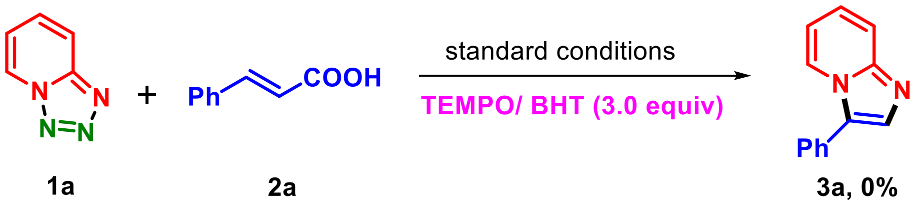
(i) Standard reaction using iodine monochloride (ICl):



A mixture of tetrazolo[1,5-a]pyridine (**1a**, 0.75 mmol, 1.5 equiv.), cinnamic acid (**2a**, 0.5 mmol, 1.0 equiv.), $Cu(OAc)_2$ (20 mmol %), trifluoroacetic acid (2.0 equiv.), Cs_2CO_3 (2.0 equiv.), ICl (2.0 equiv.) and *p*-xylene (2.0 mL), placed in a 10 mL borosilicate vial, was stirred at 130 °C in an oil bath for 16 h. After completion of the reaction (monitored through TLC), the reaction mixture was analysed by HRMS. Notably, no halo-adduct was formed, rather the product **3a** was exclusively obtained in 83% yield.

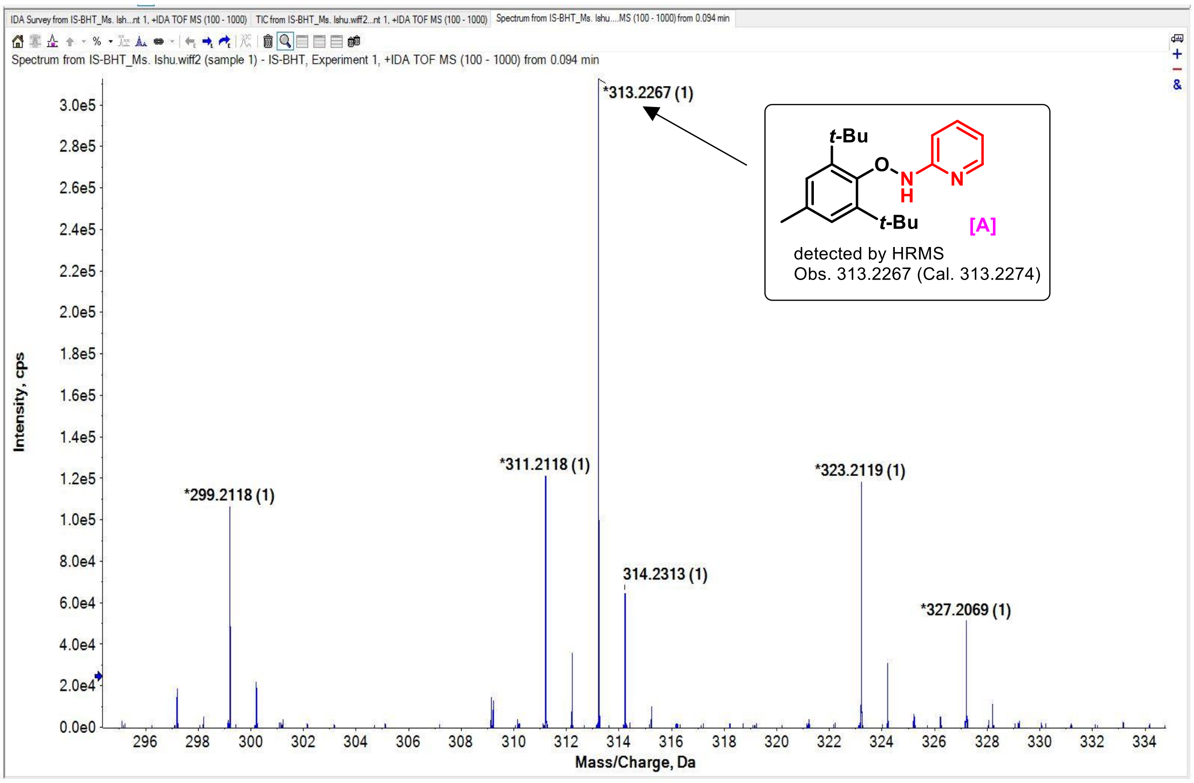


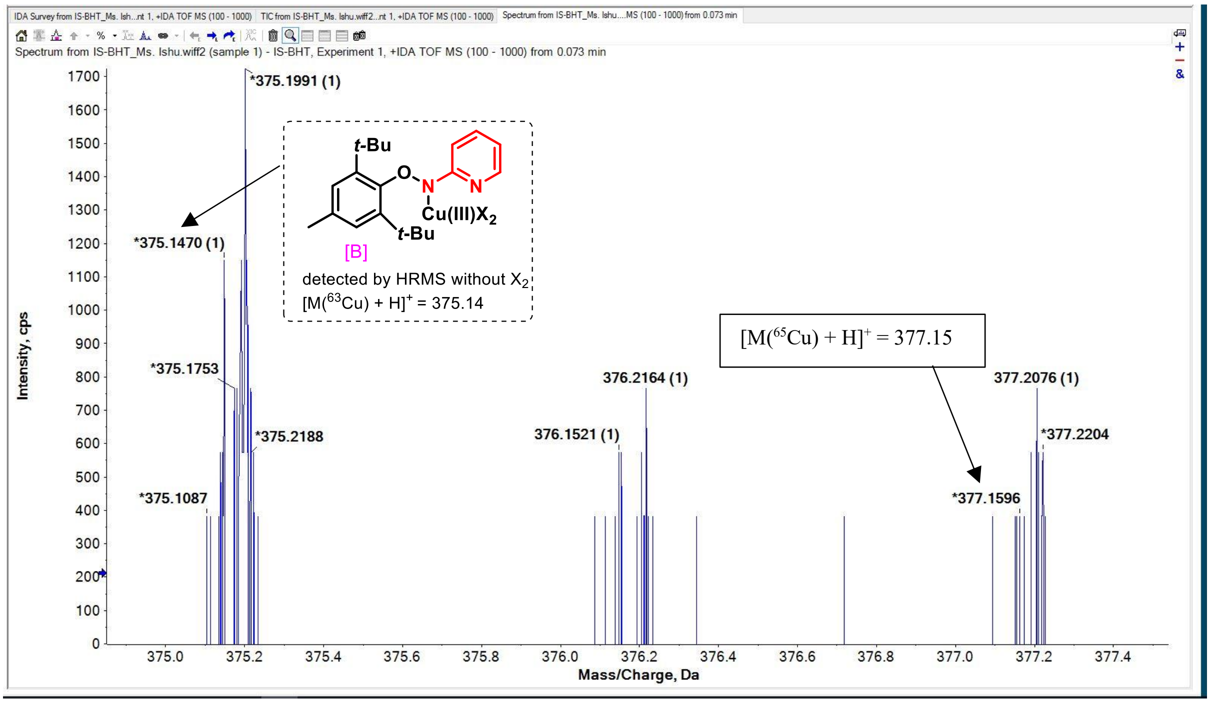
(ii) The standard reaction in the presence of TEMPO/BHT:



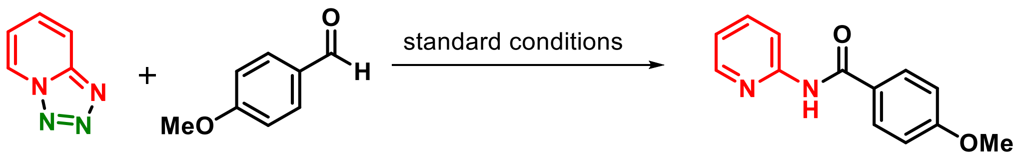
A mixture of tetrazolo[1,5-a]pyridine (**1a**, 0.75 mmol, 1.5 equiv.), cinnamic acid (**2a**, 0.5 mmol, 1.0 equiv.), $Cu(OAc)_2$ (20 mmol %), trifluoroacetic acid (2.0 equiv.), Cs_2CO_3 (2.0 equiv.), TEMPO/ BHT (3.0 equiv) and *p*-xylene (2.0 mL), placed in a 10 mL borosilicate vial, was stirred at 130 °C in an oil bath for 16 h. After completion of the reaction (monitored through TLC), the reaction mixture was subjected to HRMS analysis, which completely excluded the formation of the desired product **3a**, due to radical trapping by the TEMPO/ BHT.

The resulting BHT-adducts [**A**] and [**B**] are well detected by the HRMS.





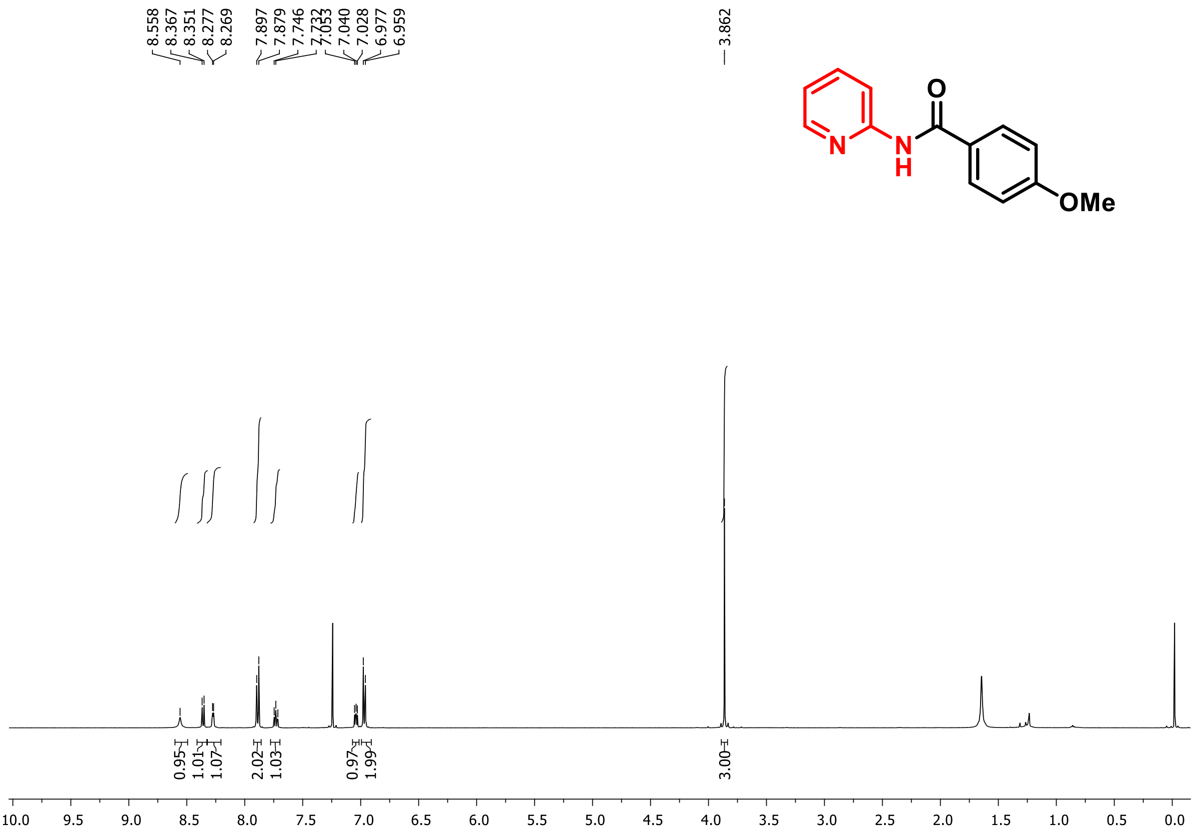
(iii) Reaction of tetrazolo[1,5-a]pyridine with p-anisaldehyde:



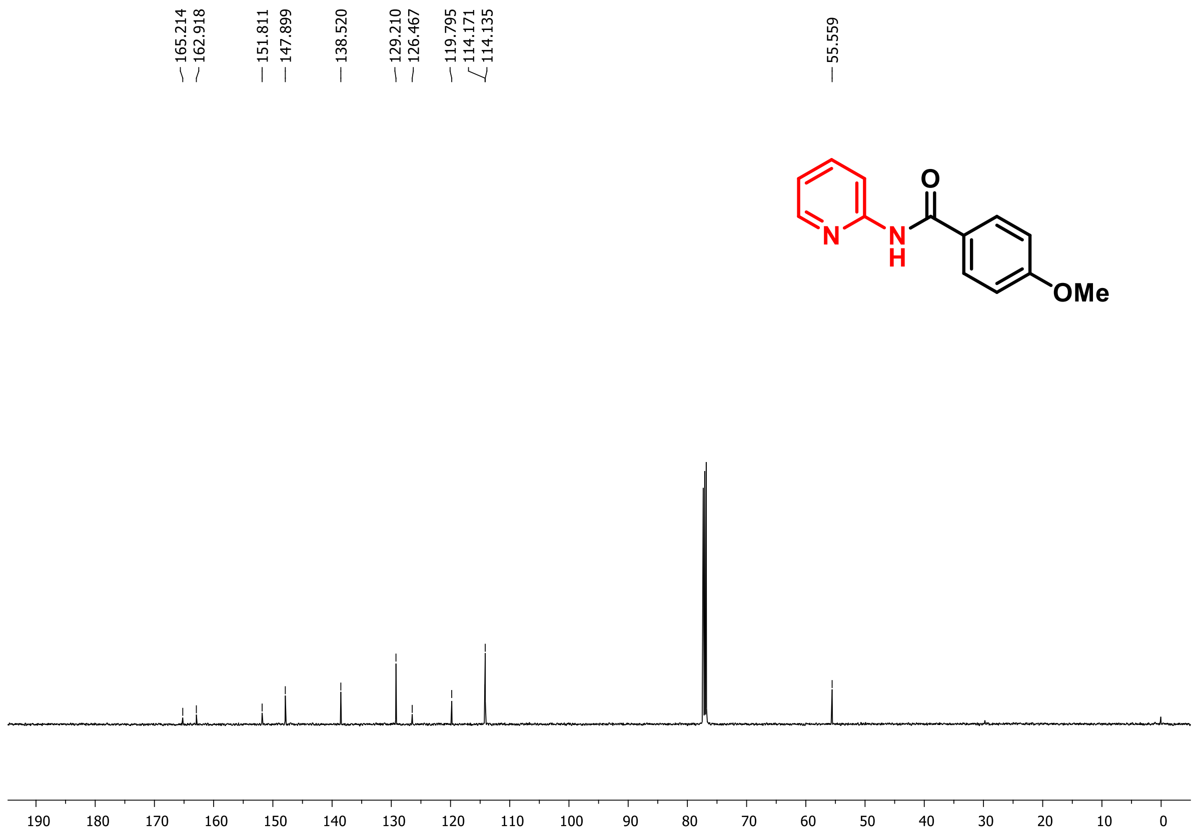
A mixture of tetrazolo[1,5-a]pyridine (**1a**, 0.75 mmol, 1.5 equiv.), *p*-anisaldehyde (**4**, 0.5 mmol, 1.0 equiv.), $Cu(OAc)_2$ (20 mmol %), trifluoroacetic acid (2.0 equiv.), Cs_2CO_3 (2.0 equiv.), and *p*-xylene (2.0 mL), placed in a 10 mL borosilicate vial, was stirred at 130 °C in an oil bath for 16 h. After completion of the reaction (monitored through TLC), a saturated $NaHCO_3$ aqueous solution (10 mL) was added to the reaction mixture, which was then extracted with ethyl acetate (3 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and then concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography using ethyl acetate/ n-hexane (20/80 v/v) as eluent to afford the product 4-methoxy-N-(pyridin-2-yl) benzamide (**5**) in 39% yield**.**

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.56 (s, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 4.0 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 2H), 7.73 (t, *J* = 8.0 Hz, 1H), 7.05 – 7.03 (m, 1H), 6.97 (d, *J* = 9.0 Hz, 2H), 3.86 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ 165.2, 162.9, 151.8, 147.9, 138.5, 129.2, 126.5, 119.8, 114.1, 55.6. **HRMS** (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{13}N_2O_2$, 229.0972; found, 229.0970.

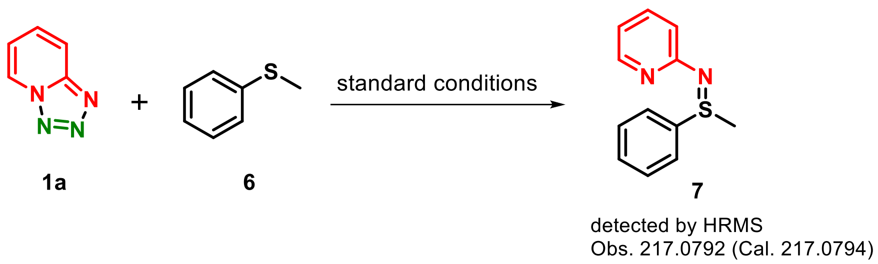
^{1}H NMR (500 MHz, $CDCl_3$):



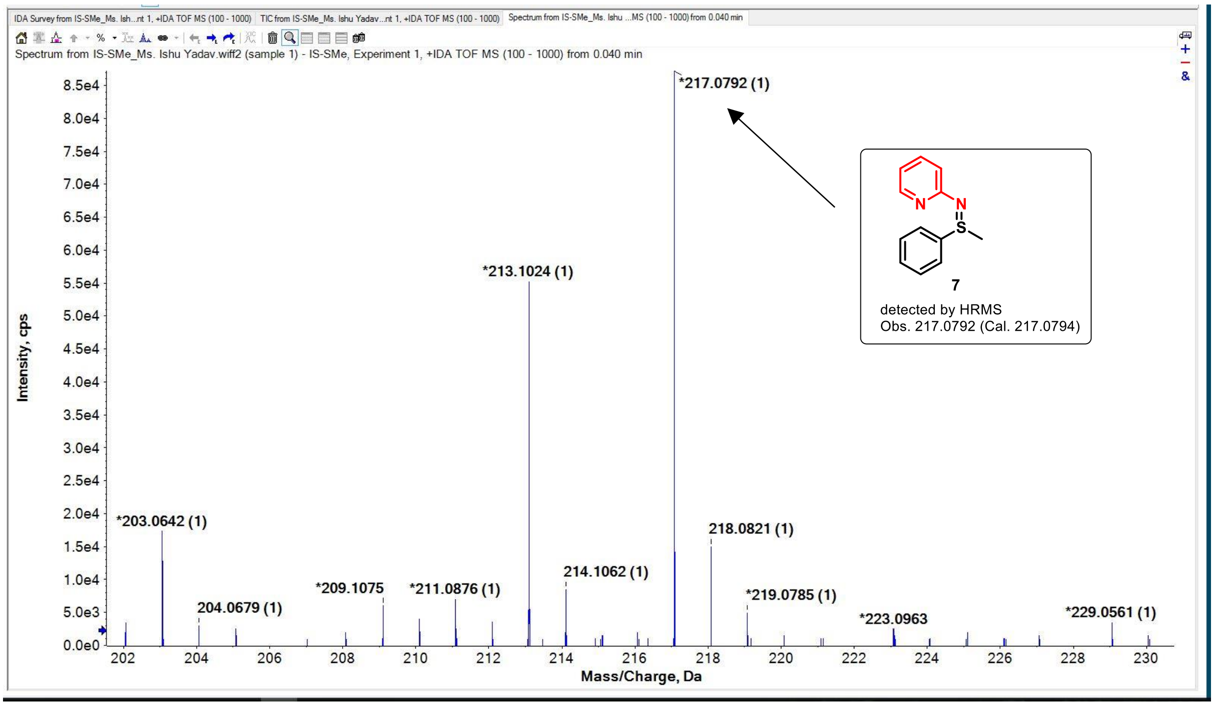
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$):



(iv) Reaction of tetrazolo[1,5-a]pyridine with methyl(phenyl)sulfane (6):



A mixture of tetrazolo[1,5-a]pyridine (**1a**, 0.75 mmol, 1.5 equiv.), methyl(phenyl)sulfane (**6**, 0.5 mmol, 1.0 equiv.), $Cu(OAc)_2$ (20 mmol %), trifluoroacetic acid (2.0 equiv.), Cs_2CO_3 (2.0 equiv.), and *p*-xylene (2.0 mL), placed in a 10 mL borosilicate vial, was stirred at 130 °C in an oil bath for 16 h. After completion of the reaction (monitored through TLC), the reaction mixture was analysed by HRMS, which confirmed the formation of the expected product (*Z*)-1-methyl-1-phenyl-N-(pyridin-2-yl)-λ^4-sulfanimine (**7**).



8. Crystallographic data:

Crystal of the product **3g** was grown by slow evaporation of a solution of the compound in $CDCl_3$.

Specification: Crystallographic data measurements were obtained on Rigaku XtaLAB Synergy-i dualflex X-ray diffractometer using graphite monochromated Cu-Kα radiation (λ = 1.54184 Å) based diffraction at 293 K. The extracted data was evaluated using CrysAlisPro CCD software. The crystal structure was solved by direct methods using SHELXT 2018/2 and refined by the full-matrix least-squares methods through Olex2.

X-ray crystallographic data 3g

Empirical formula	$C_{13}H_9N_3O_2$
Formula weight	239.23
Temperature/K	293
Crystal system	Triclinic,
Space group	P-1
a/Å	7.2977 (2)
b/Å	13.0084 (4)
c/Å	13.3204 (4)
α/°	63.202 (3)
β/°	85.744 (2)
γ/°	78.104 (2)
Volume/Å^3	1104.22 (6)
Z	4
ρ_{calc}g/cm^3	1.439
μ/mm^{-1}	0.834
F(000)	680.0
Crystal size/mm^3	0.5 × 0.02 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.436 to 136.29
Index ranges	$-6 \leq h \leq 8$, $-15 \leq k \leq 15$, $-15 \leq l \leq 15$
Reflections collected	21315
Independent reflections	4006 [Rint = 0.0640, Rsigma= 0.0320]
Data/restraints/parameters	4006/0/325
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1= 0.0698, wR_2 = 0.2001
Final R indexes [all data]	R1= 0.0790, wR2 = 0.2107
Largest diff. peak/hole / e Å^{-3}	0.38/-0.26

ORTEP diagram of the product 3g

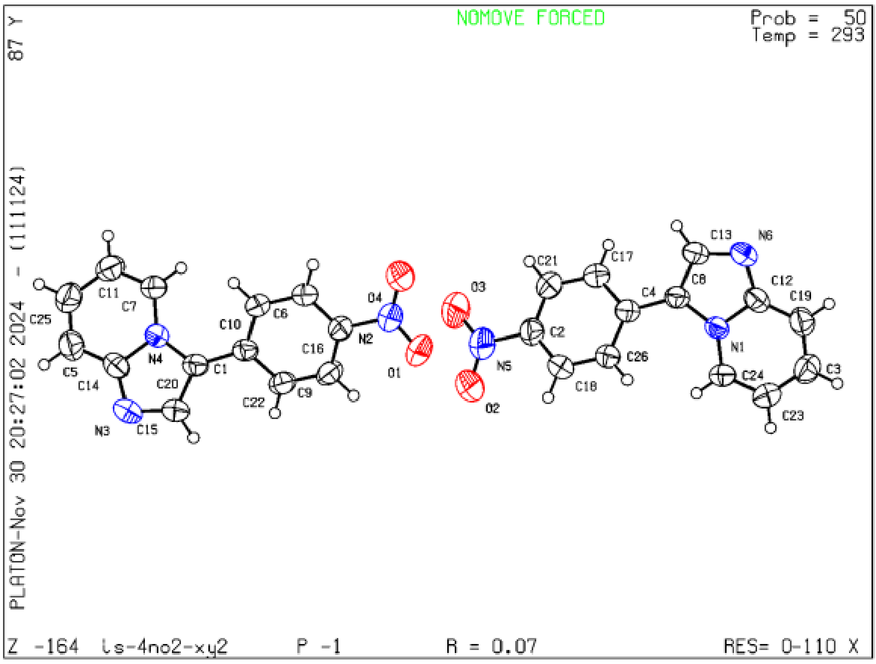


Fig S1. View of the molecular structure of the product **3g**. Displacement ellipsoids are drawn at the 50% probability level.