Supporting Information

Iodine-mediated regioselective C-3 sulfenylation using elemental sulfur and arylhydrazine hydrochloride to access 3-sulfenylated imidazo[1,2-*a*]pyridines

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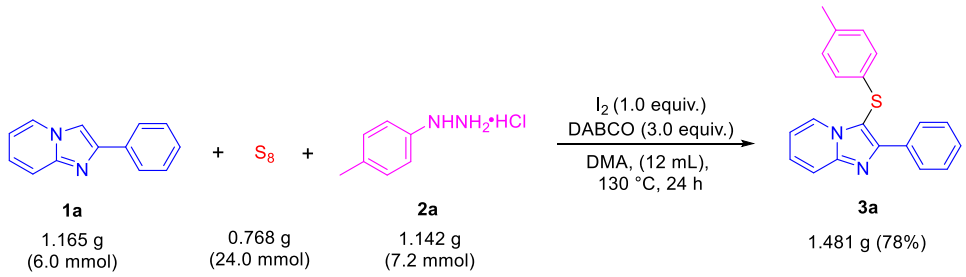
1. General Information and Materials

^{1}H, $^{13}C\{^{1}H\}$, and ^{19}F NMR spectra were recorded on a JEOL ECZ 500R FT-NMR spectrometer (^{1}H NMR at 500 MHz, $^{13}C\{^{1}H\}$ NMR at 126 MHz, and ^{19}F at 471 MHz). Chemical shifts are reported in ppm 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 77.160 ppm) respectively. NMR data are represented as follows: chemical shift, multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, and m = multiplet), coupling constant (*J*) (Hz), and integration. Mass spectra were recorded on a SCIEX X500R QTOF mass spectrometer. Crystallographic data measurements were obtained on a Rigaku XtaLAB Synergy-i dual flex X-ray diffractometer using graphite monochromated Cu-Kα radiation (λ=1.54184 Å) based diffraction at 273 K. Thin layer chromatography (TLC) was performed on Merck Kieselgel 60GF254 plates (thickness 0.25 mm). Visualization of TLC was made using a 254 nm UV lamp and by staining in an I_2 chamber. Organic solutions were concentrated under reduced pressure using a Buchi rotary evaporator. Purification of the crude product was done by column chromatography using silica gel 100−200 mesh. All the reactions were carried out using oven-dried glassware. Yield refers to the isolated analytically pure material.

All the chemicals/reagents and solvents were purchased from Sigma-Aldrich, Merck, and TCI Chemicals Ltd. The reagents were used as such without any further purification, whereas the solvents were purified by standard methods prior to its use. 2-Arylimidazo[1,2-*a*]pyridines were prepared adopting the known procedure.[1]

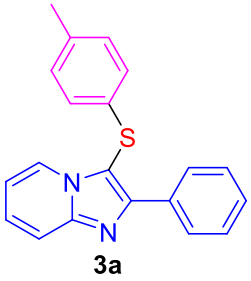
2. Procedure for Gram Scale Preparation of the Product 3a



A mixture of 2-phenylimidazo[1,2-*a*]pyridine (**1a**, 1.165 g, 6.0 mmol), S_8 (0.768 g, 24.0 mmol), *p*-tolylhydrazine hydrochloride (**2a**, 1.142 g, 7.2 mmol), I_2 (1.522 g, 6.0 mmol), DABCO (2.019 g, 18 mmol), and DMA (12 mL), placed in a 50 mL round-bottom flask, was stirred at 130 °C in an oil bath for 24 h under open air atmosphere. After completion of the reaction (monitored through TLC), an aqueous solution of the sodium thiosulfate pentahydrate was added to the reaction mixture, which was then extracted with ethyl acetate (3×30 mL). The combined organic phase was washed with brine solution, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude product was finally purified by silica gel column chromatography using *n*-hexane and ethyl acetate as eluent to afford the product **3a** (1.481g, 78%).

3. Physical and Spectral Data of the Products 3a-3x

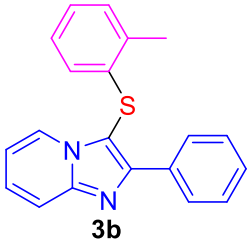
2-Phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3a)[2]



3a

Yellow solid (147.1 mg, 93% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 15:85); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, J = 7.0 Hz, 1H), 8.22 (d, J = 8.5 Hz, 2H), 7.73 (d, J = 9.0 Hz, 1H), 7.44 (t, J = 8.0 Hz, 2H), 7.37 (t, J = 7.5 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.03 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H), 6.87 (t, J = 7.0 Hz, 1H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.4, 147.2, 136.2, 133.6, 131.7, 130.4, 128.7, 128.5, 128.5, 126.7, 126.0, 124.7, 117.8, 113.1, 107.0, 21.0.

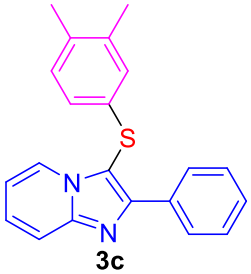
2-Phenyl-3-(*o*-tolylthio)imidazo[1,2-*a*]pyridine (3b)[2]



3b

Reddish brown solid (139.2 mg, 88% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 15:85); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (t, J = 8.0 Hz, 3H), 7.76 (d, J = 9.0 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.38 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.21 (d, J = 7.5 Hz, 1H), 7.05 (t, J = 7.5 Hz, 1H), 6.91 (t, J = 7.5 Hz, 1H), 6.86 (t, J = 7.0 Hz, 1H), 6.44 (d, J = 8.0 Hz, 1H), 2.53 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 152.0, 147.5, 135.2, 134.3, 133.6, 130.8, 128.7, 128.5, 127.1, 126.7, 125.9, 124.7, 124.4, 117.9, 113.2, 105.8, 19.9.

3-((3,4-Dimethylphenyl)thio)-2-phenylimidazo[1,2-*a*]pyridine (3c)

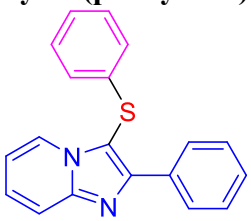


3c

Yellow solid (147.0 mg, 89% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 15:85); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, J = 6.5 Hz, 1H), 8.23 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 9.5 Hz, 1H), 7.44 (t, J = 8.0 Hz, 2H), 7.38 – 7.31 (m, 3H), 6.97 (d, J = 8.0 Hz, 1H), 6.86 (t, J = 7.0 Hz, 2H), 6.72 (d, J = 8.0 Hz, 1H), 2.17 (s, 3H), 2.14 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.3, 147.2, 138.2, 134.9, 133.6, 131.8, 130.8, 129.0,

128.6, 128.5, 127.1, 126.6, 124.8, 123.4, 117.8, 113.1, 107.2, 19.9, 19.4; HRMS (ESI-TOF) m/z: $(M+H)^+$ calcd for $C_{21}H_{19}N_2S^+$, 331.1263; found, 331.1235.

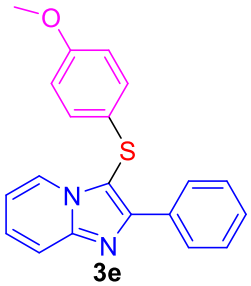
2-Phenyl-3-(phenylthio)imidazo[1,2-*a*]pyridine (3d)[2]



3d

Yellow solid (136.1 mg, 90% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 15:85); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, J = 6.5 Hz, 1H), 8.21 (d, J = 7.0 Hz, 2H), 7.75 (d, J = 9.0 Hz, 1H), 7.44 (t, J = 7.0 Hz, 2H), 7.38 (t, J = 7.0 Hz, 1H), 7.34 (t, J = 7.0 Hz, 1H), 7.21 (t, J = 7.0 Hz, 2H), 7.14 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 8.0 Hz, 2H), 6.87 (t, J = 6.5 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.6, 147.3, 135.4, 133.5, 129.6, 128.7, 128.6, 128.5, 126.8, 126.2, 125.7, 124.6, 117.8, 113.2, 106.5.

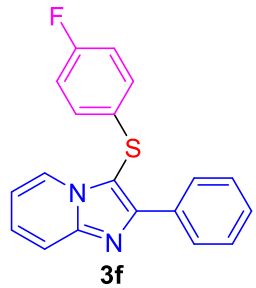
3-((4-Methoxyphenyl)thio)-2-phenylimidazo[1,2-*a*]pyridine (3e)[2]



3e

Yellow solid (142.9 mg, 86% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 20:80); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, J = 6.5 Hz, 1H), 8.27 (d, J = 7.5 Hz, 2H), 7.71 (d, J = 9.0 Hz, 1H), 7.45 (t, J = 8.0 Hz, 2H), 7.38 (t, J = 7.5 Hz, 1H), 7.30 (t, J = 7.0 Hz, 1H), 7.00 (d, J = 8.0 Hz, 2H), 6.84 (d, t = 7.0 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 3.70 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.7, 151.0, 147.0, 133.6, 128.6, 128.5, 128.1, 126.6, 125.6, 124.6, 117.8, 115.3, 113.0, 107.9, 55.4.

3-((4-Fluorophenyl)thio)-2-phenylimidazo[1,2-*a*]pyridine (3f)[2]

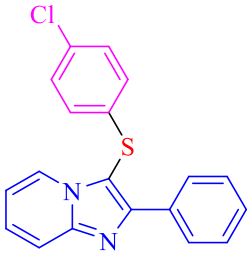


3f

Yellow solid (136.2 mg, 85% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, J = 6.5 Hz, 1H), 8.21 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 9.5 Hz, 1H), 7.45 (t, J = 7.0 Hz, 2H), 7.39 (t, J = 7.0 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H), 7.00 – 6.97 (m, 2H), 6.94 – 6.88 (m, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.7 (d, $J_{C\text{-}F}$ = 248.1 Hz), 151.5, 147.3, 133.4, 130.3, 128.8, 128.6 (d, $J_{C\text{-}F}$ = 11.8 Hz), 127.8

(d, $J_{C\text{-}F}$ = 7.6 Hz), 126.9, 124.5, 117.9, 116.8 (d, $J_{C\text{-}F}$ = 22.7 Hz), 113.3, 106.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ −115.9.

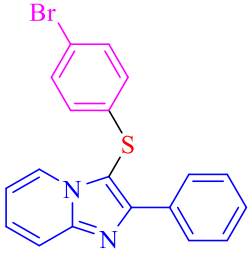
3-((4-Chlorophenyl)thio)-2-phenylimidazo[1,2-*a*]pyridine (3g)[2]



3g

Light yellow solid (139.8 mg, 83% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, J = 6.5 Hz, 1H), 8.19 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 9.0 Hz, 1H), 7.44 (t, J = 7.0 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.18 – 7.16 (m, 2H), 6.93 – 6.87 (m, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.8, 147.4, 133.9, 133.3, 132.2, 129.7, 128.9, 128.6, 128.4, 127.0, 124.4, 117.9, 113.4, 105.9.

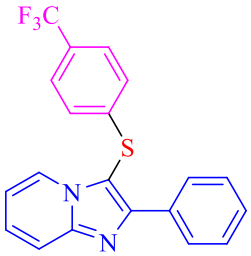
3-((4-Bromophenyl)thio)-2-phenylimidazo[1,2-*a*]pyridine (3h)[2]



3h

Yellow solid (156.3 mg, 82% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, J = 7.0 Hz, 1H), 8.18 (d, J = 7.5 Hz, 2H), 7.75 (d, J = 9.0 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 7.40 (d, J = 7.0 Hz, 1H), 7.36 (d, J = 7.5 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 6.90 – 6.85 (m, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.8, 147.4, 134.6, 133.3, 132.6, 128.9, 128.6, 128.4, 127.2, 127.0, 124.4, 120.0, 117.9, 113.4, 105.7.

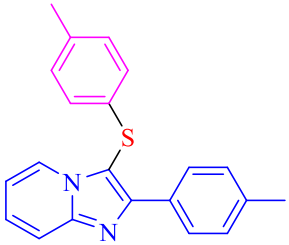
2-Phenyl-3-((4-(trifluoromethyl)phenyl)thio)imidazo[1,2-*a*]pyridine (3i)[2]



3i

Yellow solid (157.4 mg, 85% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 20:80); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, J = 6.5 Hz, 1H), 8.17 (d, J = 7.0 Hz, 2H), 7.77 (d, J = 9.0 Hz, 1H), 7.46 – 7.43 (m, 4H), 7.40 – 7.36 (m, 2H), 7.07 (d, J = 8.5 Hz, 2H), 6.91 (t, J = 7.0 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 152.3, 147.6, 140.7, 133.2, 129.0, 128.8 ($J_{C\text{-}F}$ = 33.3 Hz), 128.6, 128.4, 127.1, 126.5 (q, $J_{C\text{-}F}$ = 3.2 Hz), 125.4, 124.4, 123.0, 118.1, 113.5, 104.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ −62.4.

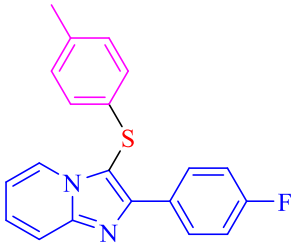
2-(*p*-Tolyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3j)[2]



3j

Yellow solid (148.7 mg, 90% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 15:85); ^{1}HNMR (500 MHz, $CDCl_3$) δ 8.28 (d, J = 7.0 Hz, 1H), 8.12 (d, J = 7.5 Hz, 2H), 7.72 (d, J = 9.0 Hz, 2H), 7.31 (t, J = 8.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H), 6.85 (t, J = 6.5 Hz, 1H), 2.38 (s, 3H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.5, 147.2, 138.6, 136.1, 131.8, 130.8, 130.3, 129.3, 128.4, 126.6, 126.0, 124.6, 117.7, 113.0, 106.6, 21.5, 21.0.

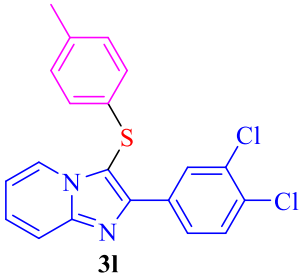
2-(4-Fluorophenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3k)[2]



3k

Yellow solid (143.8 mg, 86% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 – 8.21 (m, 3H), 7.71 (d, J = 9.0 Hz, 1H), 7.30 (t, J = 7.0 Hz, 1H), 7.11 (t, J = 9.0 Hz, 1H), 7.02 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 9.0 Hz, 2H), 6.83 (t, J = 7.0 Hz, 1H), 2.24 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.1(d, $J_{C\text{-}F}$ = 248.3 Hz), 150.3, 147.0, 136.2, 131.4, 130.3 (d, $J_{C\text{-}F}$ = 4.9 Hz), 130.2, 129.7, 126.8, 125.8, 124.6, 117.6, 115.5 (d, $J_{C\text{-}F}$ = 21.5 Hz), 113.1, 106.7, 20.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ −112.9.

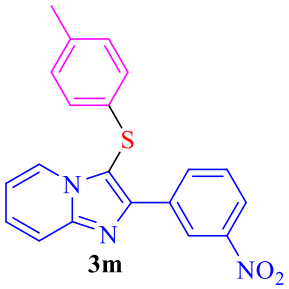
2-(3,4-Dichlorophenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3l)



3l

Yellow solid (150.3 mg, 78% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.30 (d, J = 6.5 Hz, 1H), 8.13 – 8.12 (m, 1H), 7.72 (d, J = 9.0 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.03 (d, J = 8.0 Hz, 2H), 6.90 – 6.88 (m, 3H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 148.6, 147.1, 136.6, 133.6, 132.8, 132.6, 130.9, 130.5, 130.2, 127.5, 127.1, 126.2, 124.7, 117.9, 113.5, 107.9, 21.0; HRMS (ESI-TOF) m/z: $(M+H)^+$ calcd for $C_{20}H_{15}Cl_2N_2S^+$, 385.0328; found, 385.0306.

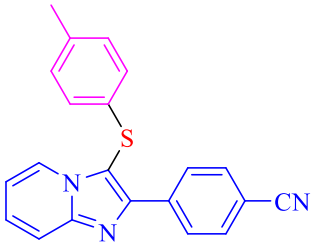
2-(3-Nitrophenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3m)[3]



3m

Yellow solid (130.1 mg, 72% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 30:70); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.60 (d, J = 7.5 Hz, 1H), 8.35 (d, J = 7.0 Hz, 1H), 8.21 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 9.5 Hz, 1H), 7.59 (t, J = 8.0 Hz, 1H), 7.38 (t, J = 8.0 Hz, 1H), 7.04 (d, J = 8.0 Hz, 2H), 6.92 (t, J = 9.0 Hz, 3H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 148.7, 148.4, 147.2, 136.8, 135.4, 134.1, 130.8, 130.5, 129.4, 127.3, 126.3, 124.8, 123.4, 123.2, 118.0, 113.7, 108.6, 21.0.

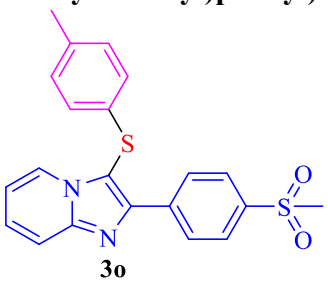
4-(3-(*p*-Tolylthio)imidazo[1,2-*a*]pyridin-2-yl)benzonitrile (3n)[3]



3n

Yellow solid (131.4 mg, 77% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 30:70); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, J = 8.5 Hz, 2H), 8.31 (d, J = 6.5 Hz, 1H), 7.71 (t, J = 9.0 Hz, 3H), 7.37 (t, J = 7.5 Hz, 1H), 7.04 (d, J = 8.0 Hz, 2H), 6.92 – 6.88 (m, 3H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 148.8, 147.2, 138.1, 136.6, 132.3, 130.8, 130.5, 128.8, 127.3, 126.0, 124.8, 119.1, 118.0, 113.7, 111.9, 108.6, 21.0.

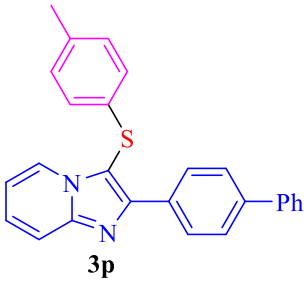
2-(4-(Methylsulfonyl)phenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3o)[4]



3o

Light yellow solid (171.6 mg, 87% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 50:50); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, J = 9.0 Hz, 2H), 8.33 (d, J = 7.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 9.0 Hz, 1H), 7.38 (t, J = 7.0 Hz, 1H), 7.04 (d, J = 8.0 Hz, 2H), 6.93 – 6.88 (m, 3H), 3.07 (s, 3H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 148.8, 147.3, 140.0, 139.0, 136.7, 130.8, 130.5, 129.2, 127.6, 127.3, 126.1, 124.8, 118.1, 113.7, 108.8, 44.7, 21.0.

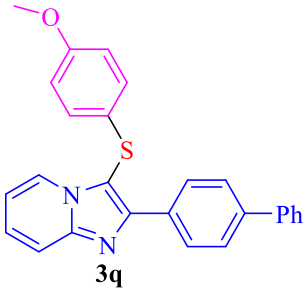
2-([1,1'-Biphenyl]-4-yl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3p)[5]



3p

Yellow solid (164.8 mg, 84% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 15:85); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, J = 8.0 Hz, 2H), 8.25 (d, J = 7.0 Hz, 1H), 7.70 (d, J = 9.0 Hz, 1H), 7.64 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 7.5 Hz, 2H), 7.39 (t, J = 7.0 Hz, 2H), 7.29 (t, J = 7.5 Hz, 1H), 6.99 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 8 Hz, 2H), 6.81 (t, J = 6.5 Hz, 1H), 2.21 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.9, 147.2, 141.3, 140.8, 136.2, 132.5, 131.6, 130.4, 128.9, 128.8, 127.5, 127.2, 127.2, 126.8, 126.0, 124.6, 117.7, 113.1, 107.1, 21.0.

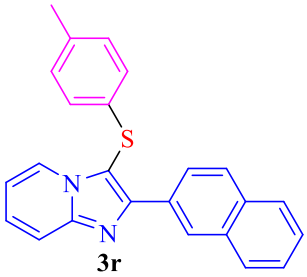
2-([1,1'-Biphenyl]-4-yl)-3-((4-methoxyphenyl)thio)imidazo[1,2-*a*]pyridine (3q)



3q

Yellow solid (163.4 mg, 80% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 25:75); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (t, J = 8.5 Hz, 3H), 7.73 – 7.65 (m, 5H), 7.45 (t, J = 7.0 Hz, 2H), 7.36 – 7.32 (m, 2H), 7.03 (d, J = 8.0 Hz, 2H), 6.88 (t, J = 7.0 Hz, 1H), 6.78 (d, J = 8.5 Hz, 2H), 3.73 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.8, 150.6, 147.1, 141.3, 140.9, 132.6, 128.9, 128.9, 128.2, 127.5, 127.2, 127.2, 126.7, 125.6, 124.6, 117.8, 115.4, 113.1, 108.0, 55.5; HRMS (ESI-TOF) m/z: $(M+H)^+$ calcd for $C_{26}H_{21}N_2OS^+$, 409.1369; found, 409.1364.

2-(Naphthalen-2-yl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3r)[6]

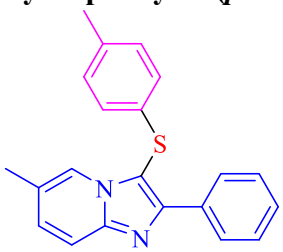


3r

Yellow solid (142.9 mg, 78% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 20:80); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.41 (d, J = 10 Hz, 1H), 8.34 (d, J = 6.5 Hz, 1H), 7.91 – 7.89 (m, 2H), 7.85 – 7.83 (m, 1H), 7.77 (d, J = 8.5 Hz, 1H), 7.48 – 7.47 (m, 2H), 7.35 (t, J = 7.5 Hz, 1H), 7.04 (d, J = 8.5 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 6.89 (t, J = 6.5 Hz, 1H) 2.26 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.2, 147.3,

136.3, 134.0, 133.5, 131.6, 131.0, 130.4, 128.9, 128.1, 128.0, 127.8, 126.8, 126.5, 126.3, 126.2, 126.1, 124.6, 117.8, 113.2, 107.6, 21.0.

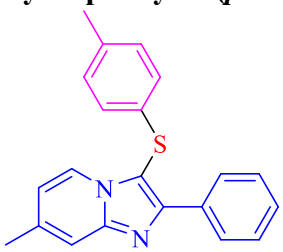
6-Methyl-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3s)[7]



3s

Yellow solid (135.5 mg, 82% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 15:85); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, J = 7.0 Hz, 2H), 8.08 (s, 1H), 7.63 (d, J = 9.0 Hz, 1H), 7.42 (t, J = 7.0 Hz, 2H), 7.36 (t, J = 7.0 Hz, 1H), 7.18 (d, J = 9.5 Hz, 1H), 7.04 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 7 Hz, 2H), 2.31 (s, 3H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.2, 146.2, 136.0, 133.7, 132.0, 130.3, 129.8, 128.5, 128.5, 128.4, 125.8, 123.0, 122.4, 117.1, 106.4, 21.0, 18.5.

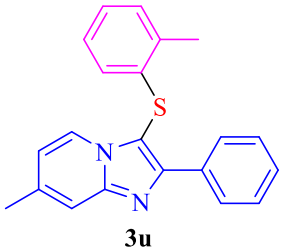
7-Methyl-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3t)[7]



3t

Yellow solid (138.8 mg, 84% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 15:85); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, J = 8.0 Hz, 2H), 8.14 (d, J = 7.0 Hz, 1H), 7.48 (s, 1H), 7.43 (t, J = 7.0 Hz, 2H), 7.36 (t, J = 8.0 Hz, 1H), 7.02 (d, J = 8.5 Hz, 2H), 6.91 (d, J = 7.5 Hz, 2H), 6.68 (d, J = 8.0 Hz, 1H), 2.42 (s, 3H), 2.25 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.2, 147.5, 137.9, 136.0, 133.7, 132.0, 130.3, 128.5, 128.5, 128.4, 125.9, 123.8, 116.3, 115.7, 106.1, 21.5, 21.0.

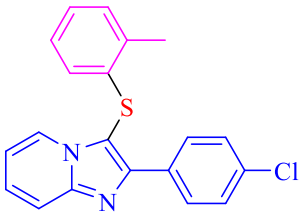
7-Methyl-2-phenyl-3-(*o*-tolylthio)imidazo[1,2-*a*]pyridine (3u)[8]



3u

Yellow solid (128.9 mg, 78% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 15:85); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 8.0 Hz, 2H), 8.06 (d, J = 6.5 Hz, 1H), 7.50 (s, 1H), 7.42 (t, J = 7.0 Hz, 2H), 7.35 (t, J = 7.0 Hz, 1H), 7.20 (d, J = 7.0 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.91 (t, J = 7.5 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 6.43 (d, J = 8.0 Hz, 1H), 2.51 (s, 3H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ ^{13}C NMR (126 MHz,) δ 151.8, 147.8, 138.0, 135.0, 134.6, 133.7, 130.8, 128.6, 128.5, 128.5, 127.0, 125.7, 124.3, 123.8, 116.4, 115.8, 104.9, 21.5, 19.9.

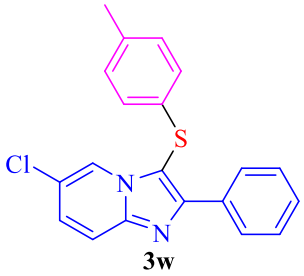
2-(4-Chlorophenyl)-3-(*o*-tolylthio)imidazo[1,2-*a*]pyridine (3v)



3v

Yellow solid (136.6 mg, 79% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 15:85); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, J = 6.5 Hz, 1H), 8.12 (d, J = 9.0 Hz, 2H), 7.74 (d, J = 9.0 Hz, 1H), 7.40 – 7.34 (m, 3H), 7.21 (d, J = 7.5 Hz, 1H), 7.06 (t, J = 7.0 Hz, 3H), 6.93 – 6.87 (m, 2H), 6.39 (d, J = 7.5 Hz, 1H), 2.52 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.7, 147.4, 135.2, 134.7, 134.0, 132.0, 130.9, 129.7, 128.8, 127.2, 127.0, 126.0, 124.7, 124.2, 117.8, 113.4, 106.0, 19.9; HRMS (ESI-TOF) m/z: $(M+H)^+$ calcd for $C_{20}H_{16}ClN_2S^+$, 351.0717; found, 351.0716.

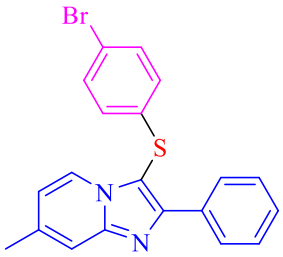
6-Chloro-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3w)[3]



3w

Yellow solid (135.1 mg, 77% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (brs, 1H), 8.22 (d, J = 7.5 Hz, 2H), 7.66 (d, J = 9.5 Hz, 1H), 7.44 (t, J = 8.0 Hz, 2H), 7.38 (t, J = 7.5 Hz, 1H), 7.29 – 7.27 (m, 1H), 7.05 (d, J = 7.5 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 2.27 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 152.1, 145.4, 136.5, 133.1, 131.0, 130.4, 128.9, 128.6, 128.4, 128.0, 126.1, 122.6, 121.6, 118.1, 108.0, 21.0.

3-((4-Bromophenyl)thio)-7-methyl-2-phenylimidazo[1,2-*a*]pyridine (3x)



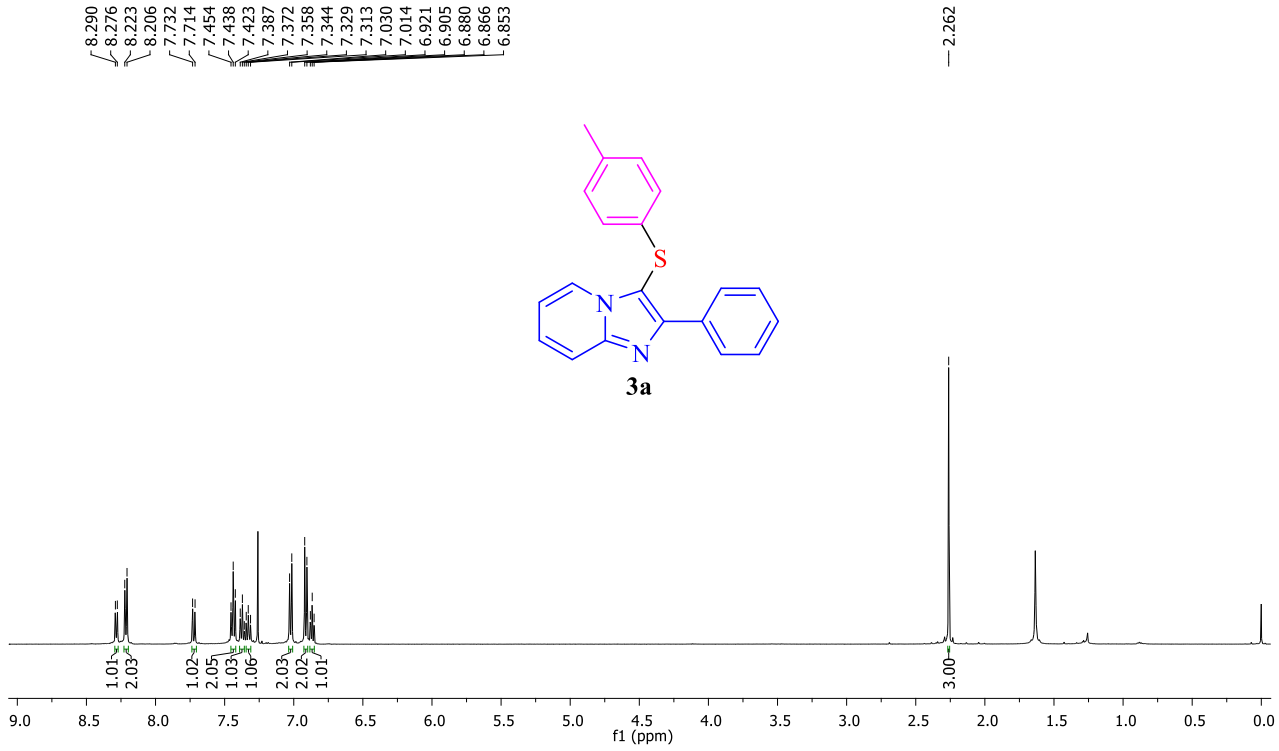
3x

Yellow solid (164.1 mg, 83% yield); Purification by column chromatography (ethyl acetate/hexane, v/v = 10:90); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 8.0 Hz, 2H), 8.09 (d, J = 7.0 Hz, 1H), 7.49 (s, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 8.0 Hz, 2H), 6.71 (d, J = 7.5 Hz, 1H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.7, 147.8, 138.2, 135.0, 133.4, 132.5, 128.7, 128.5, 128.4, 127.2, 123.6, 119.8, 116.4, 116.0, 104.8, 21.5; HRMS (ESI-TOF) m/z: $(M+H)^+$ calcd for $C_{20}H_{16}BrN_2S^+$, 395.0212; found, 395.0194.

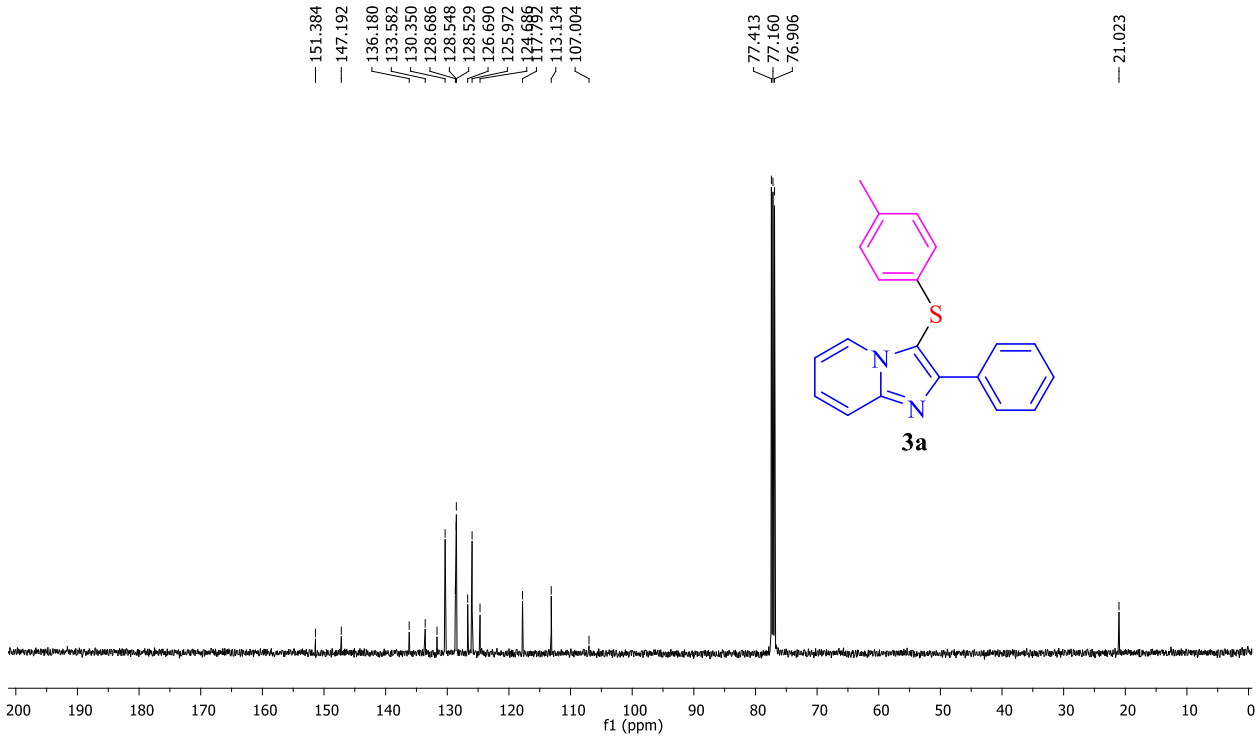
4. Copies of the ^{1}H, $^{13}C\{^{1}H\}$, and ^{19}F NMR Spectra of the Products 3a-3x

2-Phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3a)

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

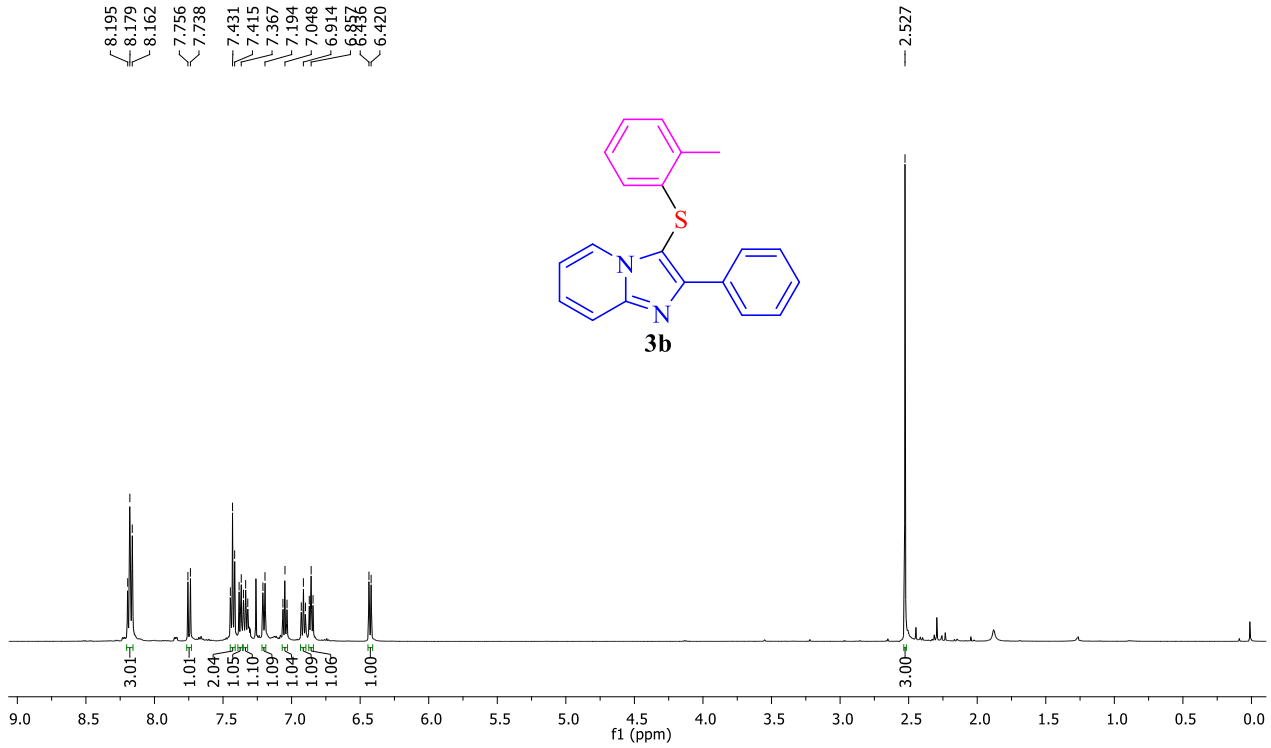


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

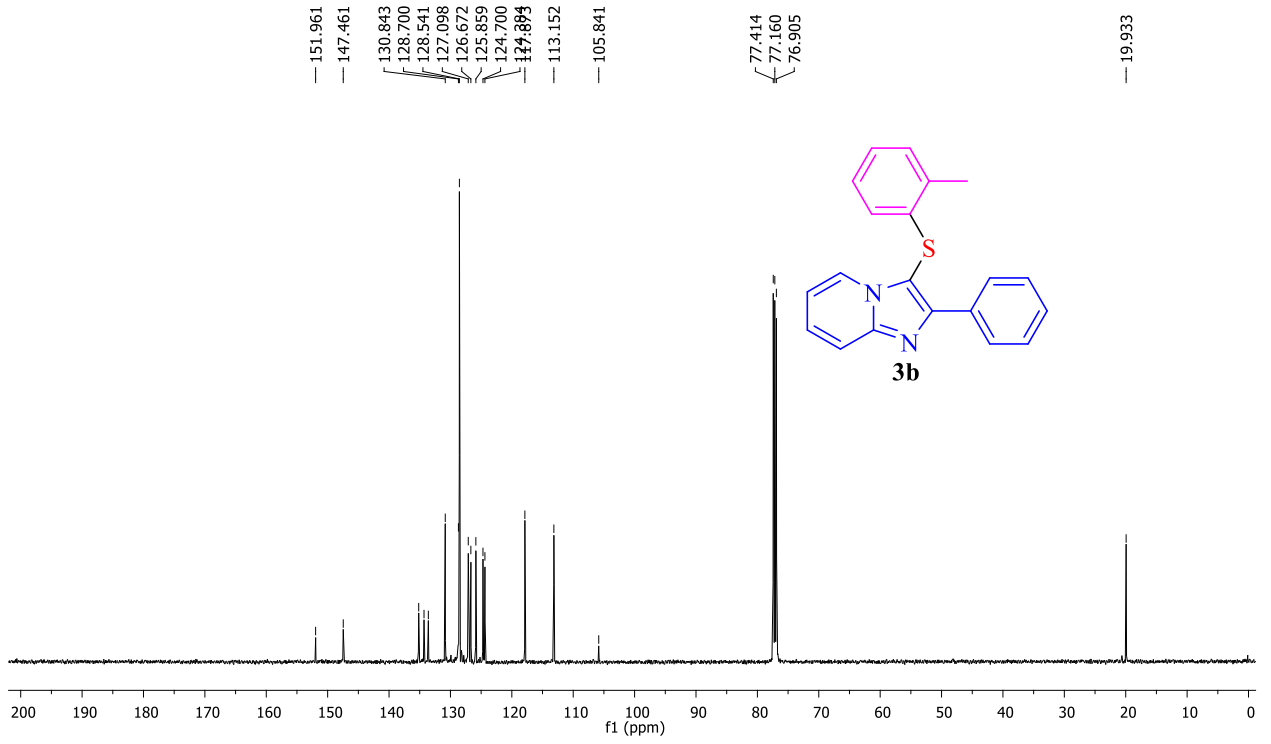


2-Phenyl-3-(*o*-tolylthio)imidazo[1,2-*a*]pyridine (3b)

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

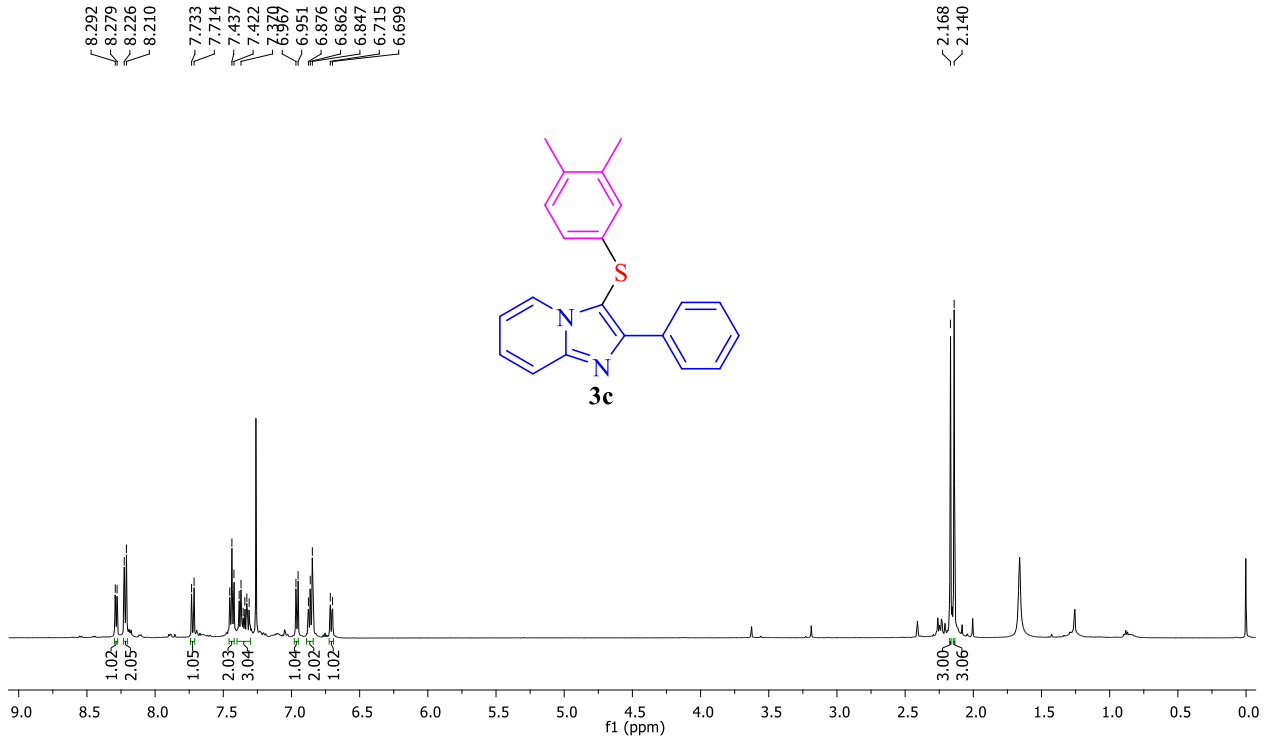


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

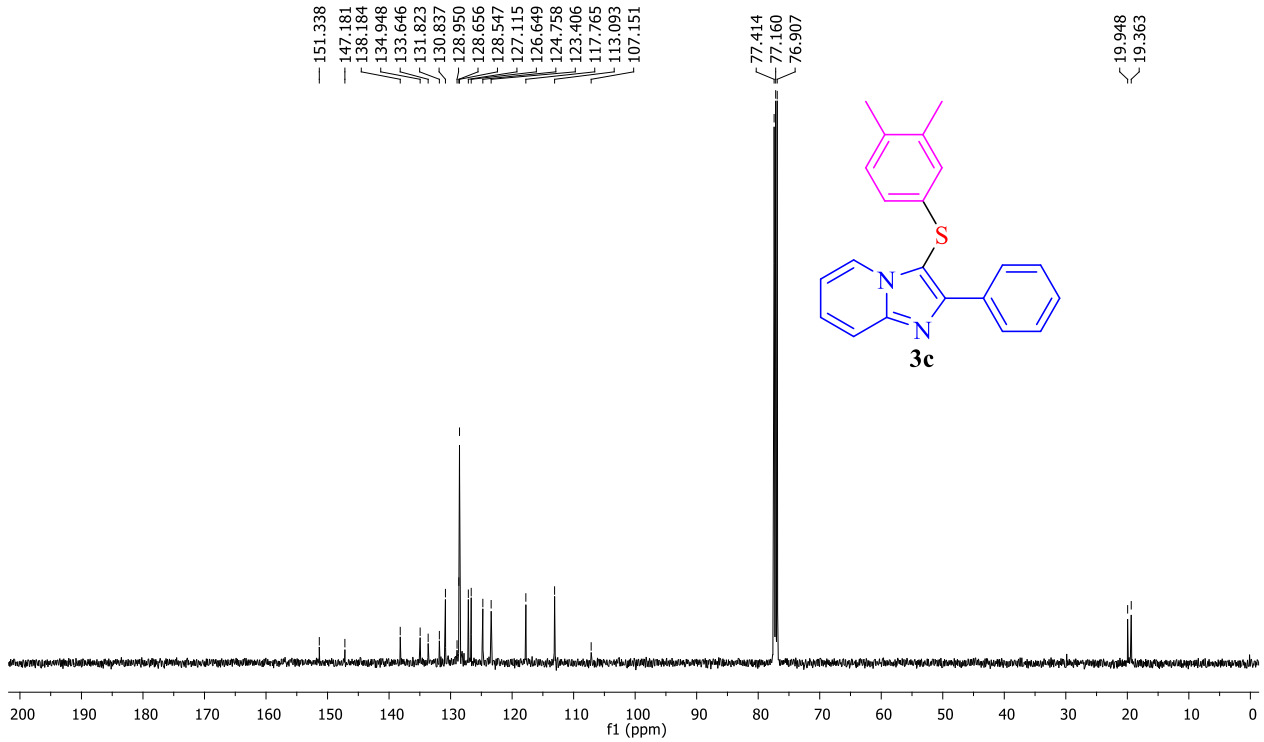


3-((3,4-Dimethylphenyl)thio)-2-phenylimidazo[1,2-*a*]pyridine (3c)

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

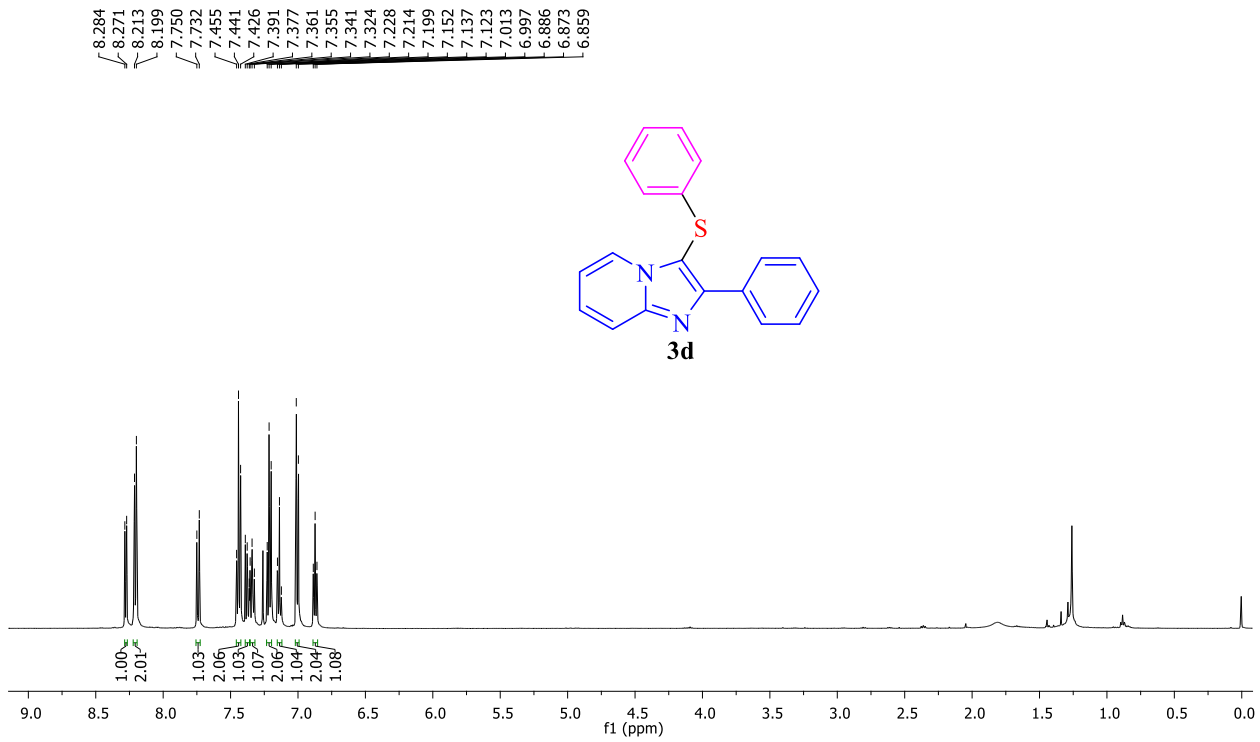


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

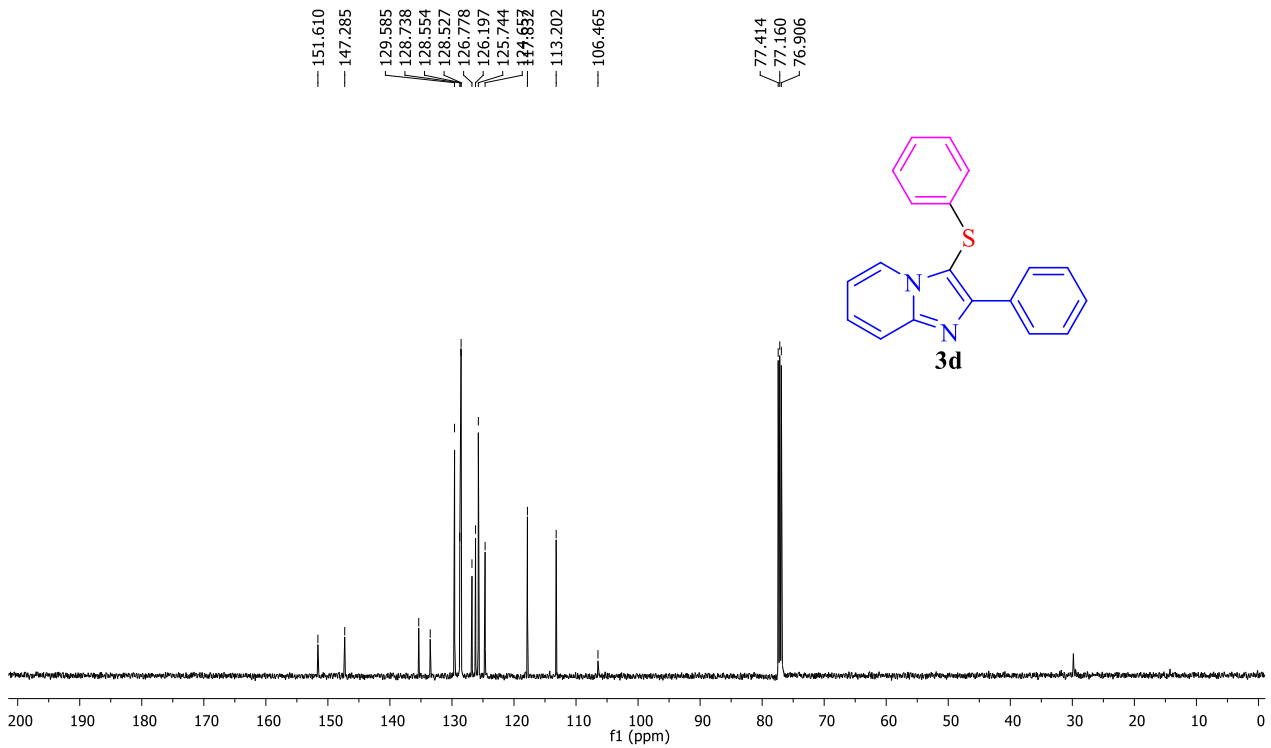


2-Phenyl-3-(phenylthio)imidazo[1,2-*a*]pyridine (3d)

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

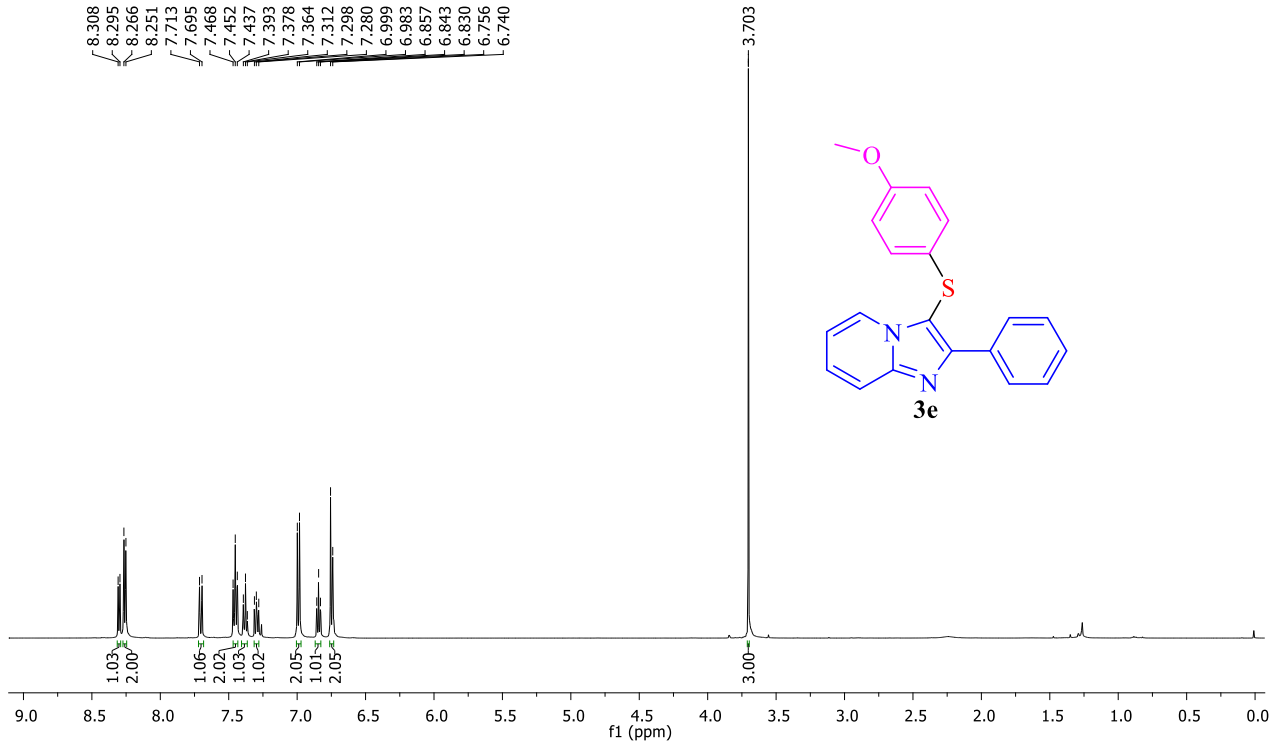


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

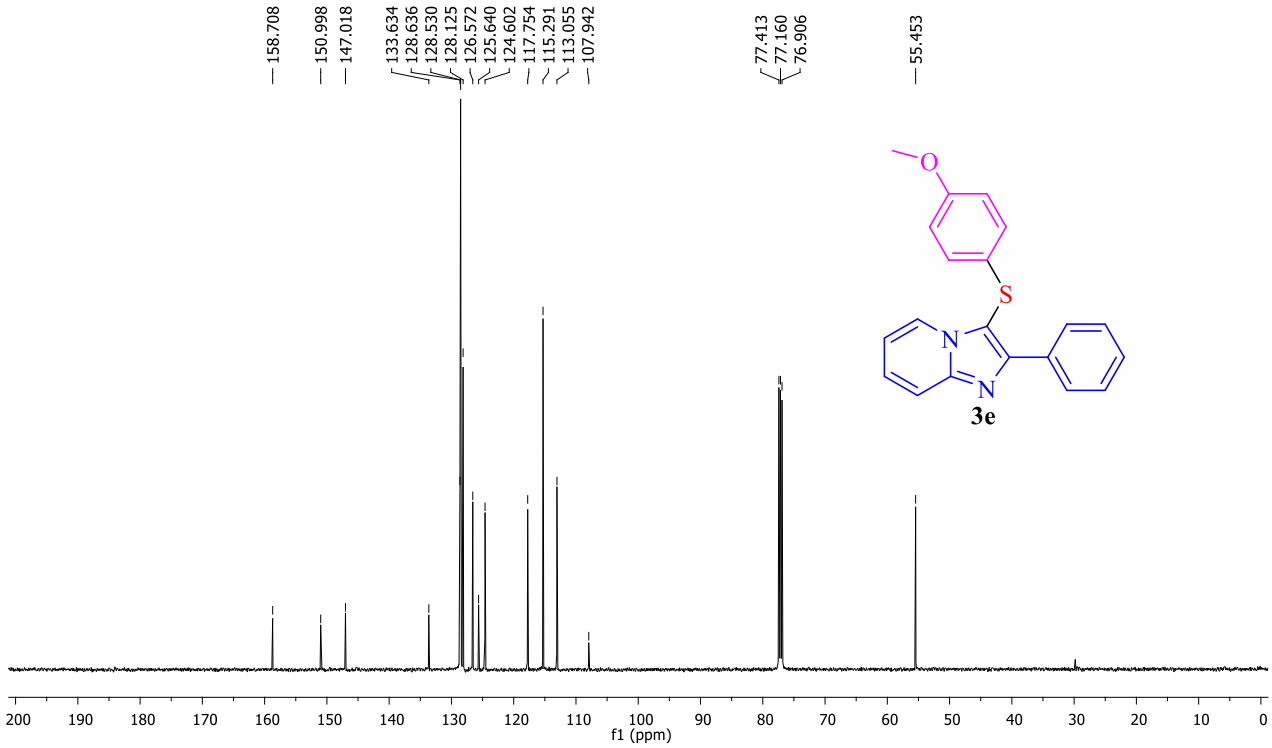


3-((4-Methoxyphenyl)thio)-2-phenylimidazo[1,2-*a*]pyridine (3e)

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

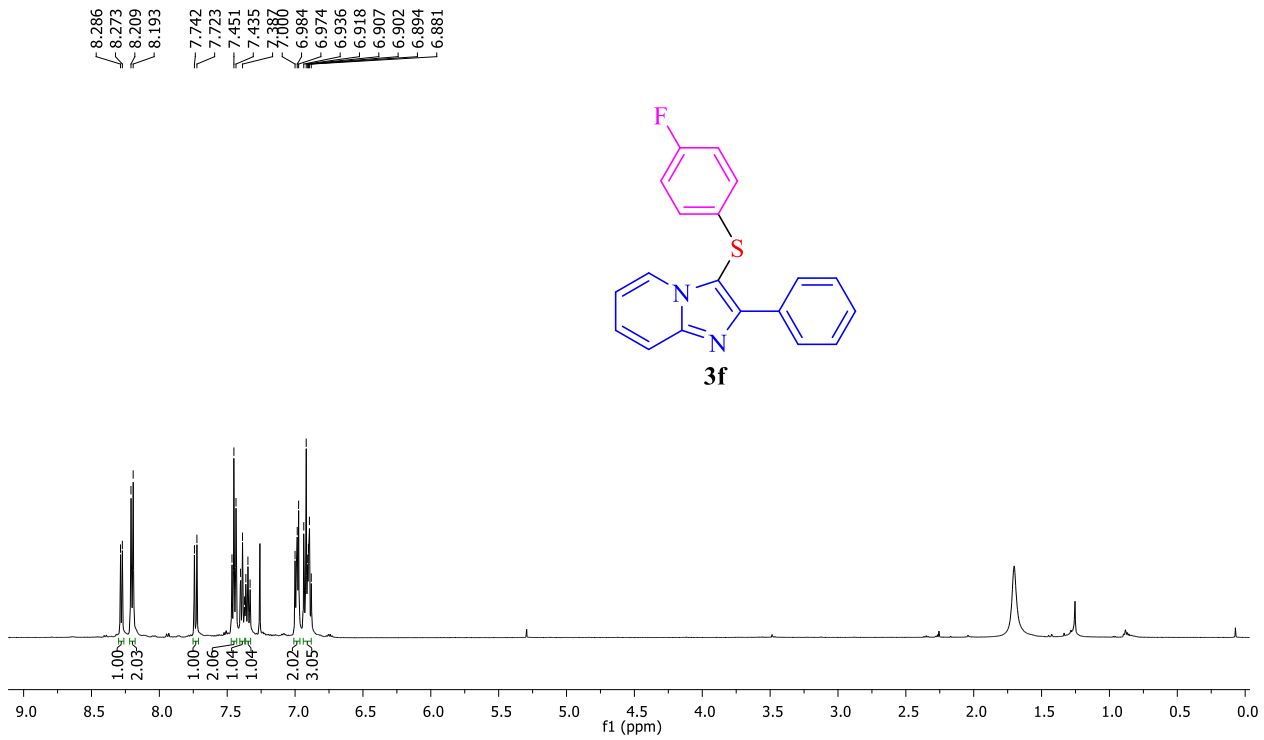


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

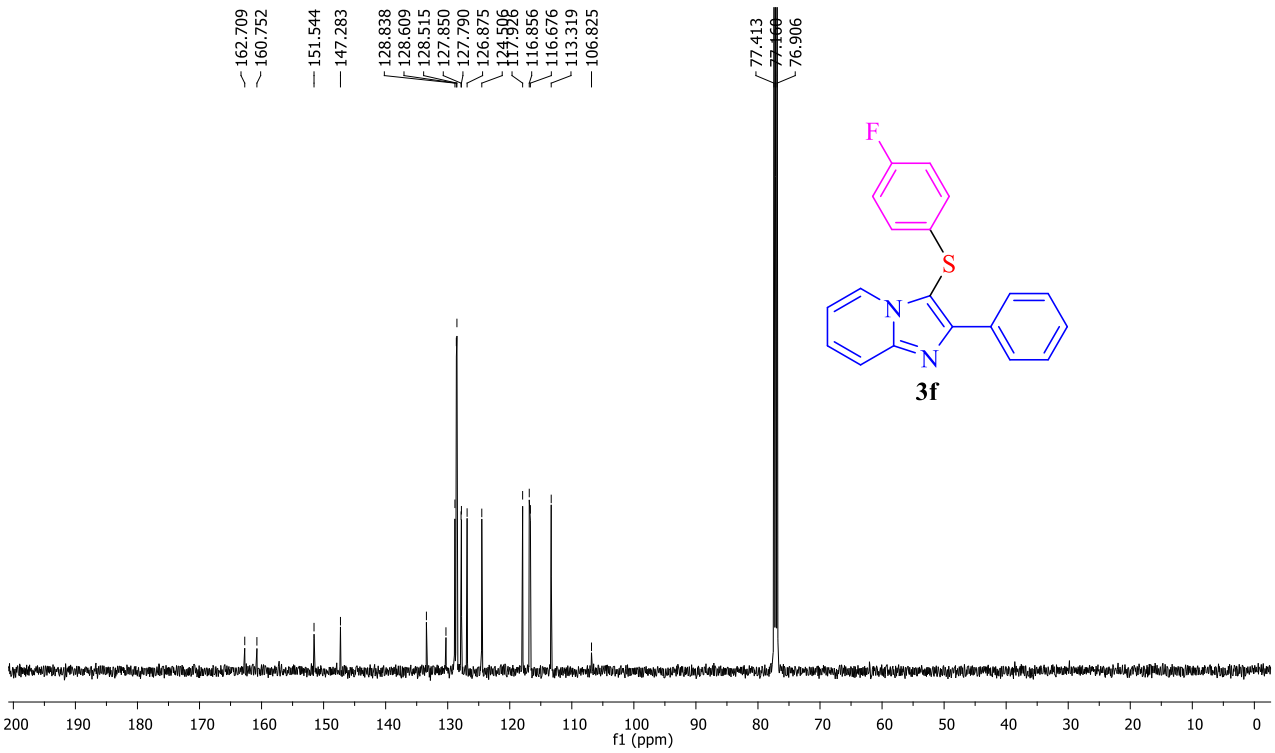


3-((4-Fluorophenyl)thio)-2-phenylimidazo[1,2-*a*]pyridine (3f)

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

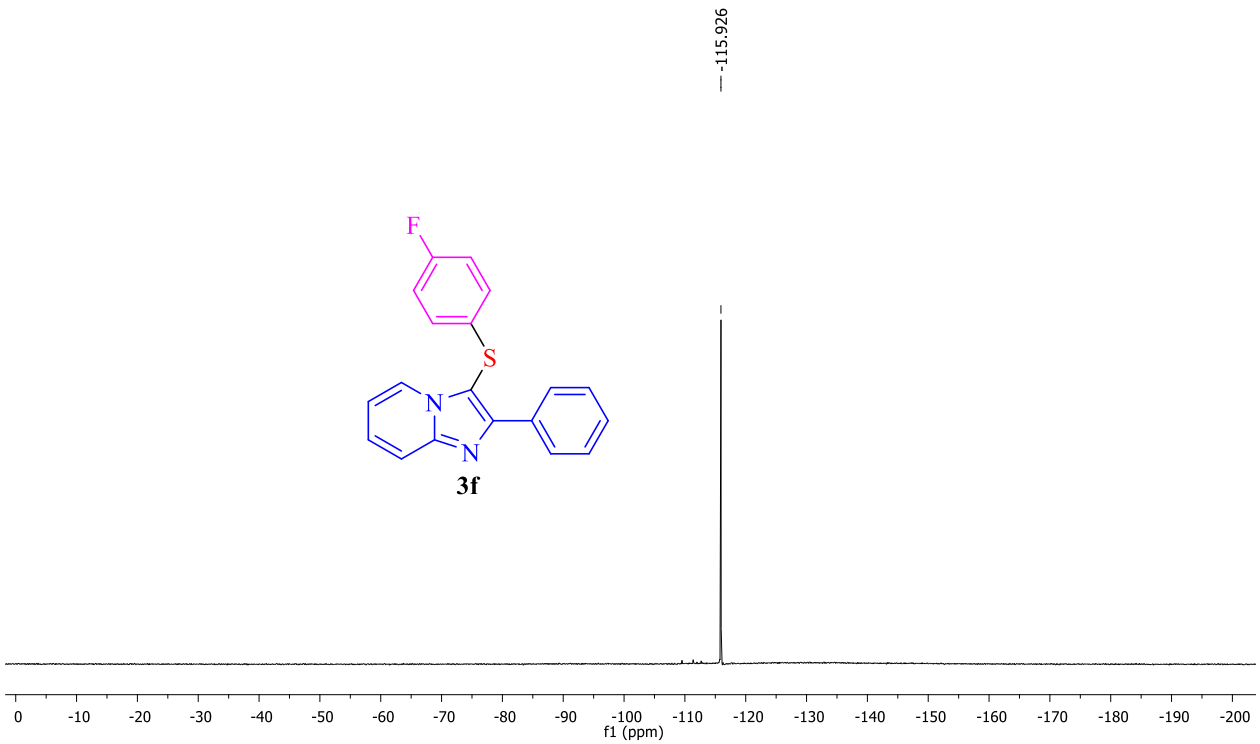


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



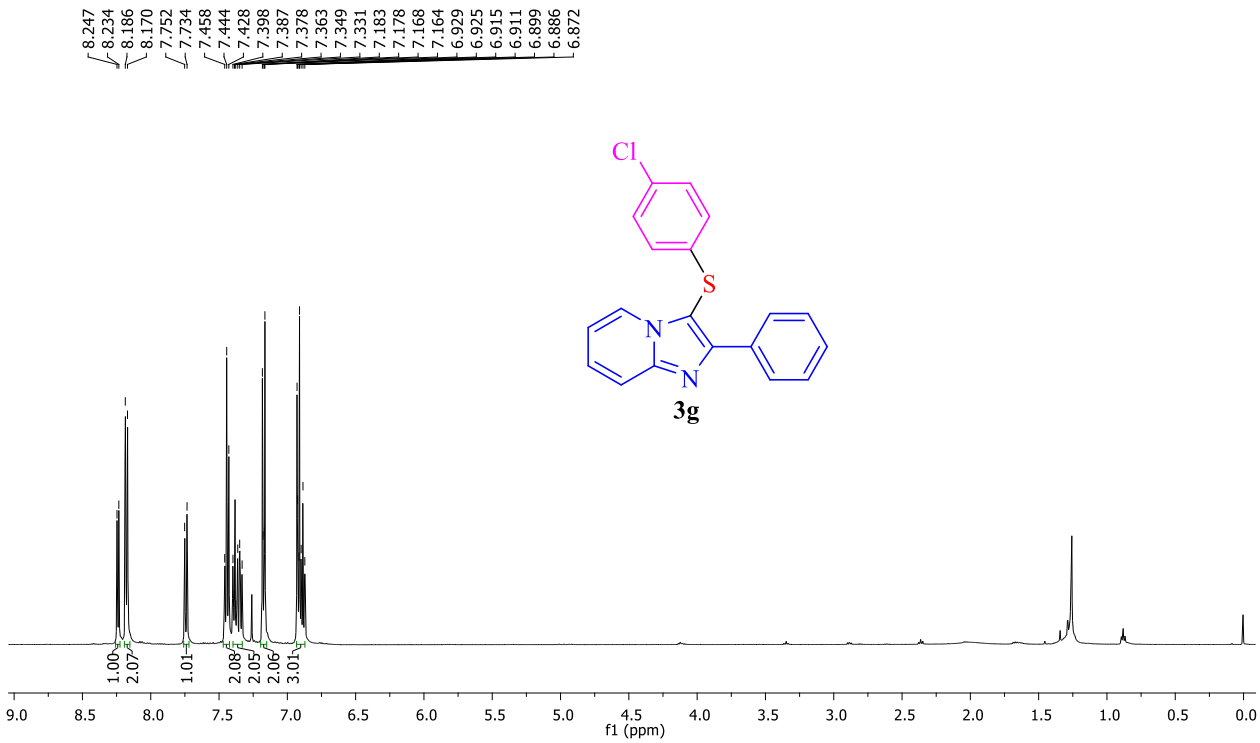
3-((4-Fluorophenyl)thio)-2-phenylimidazo[1,2-*a*]pyridine (3f)

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

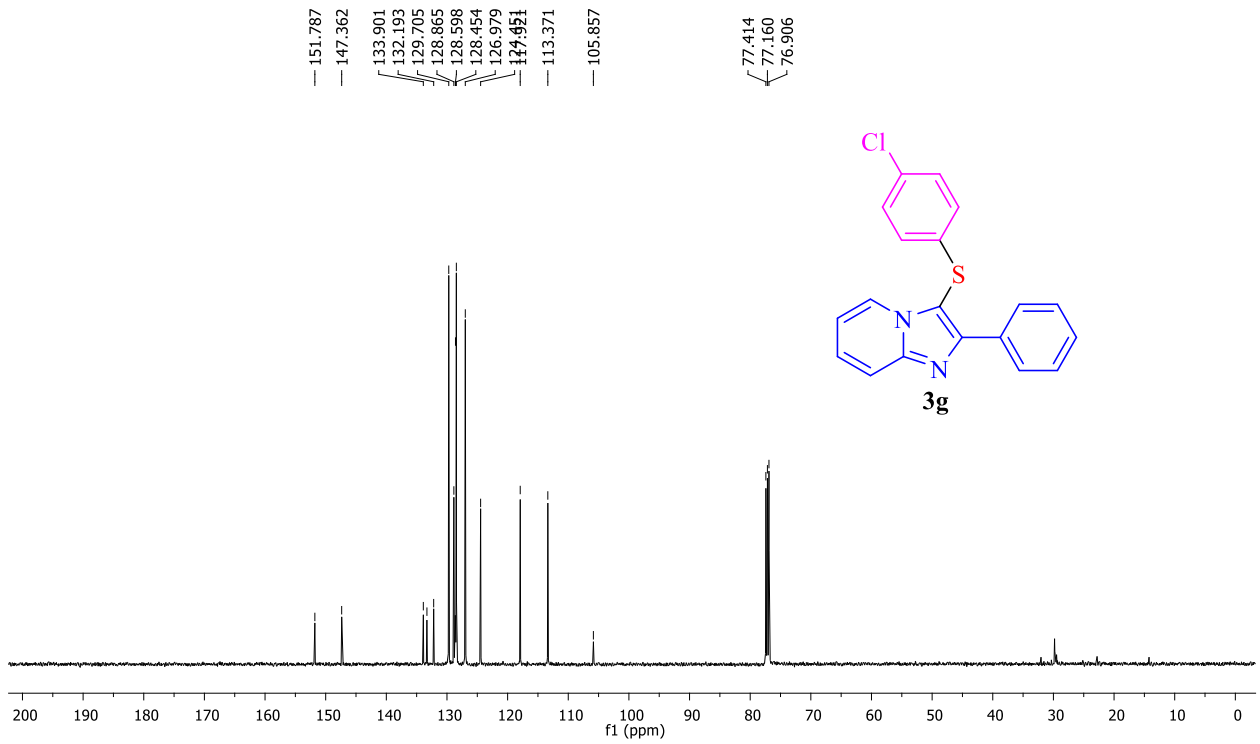


3-((4-Chlorophenyl)thio)-2-phenylimidazo[1,2-*a*]pyridine (3g)

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

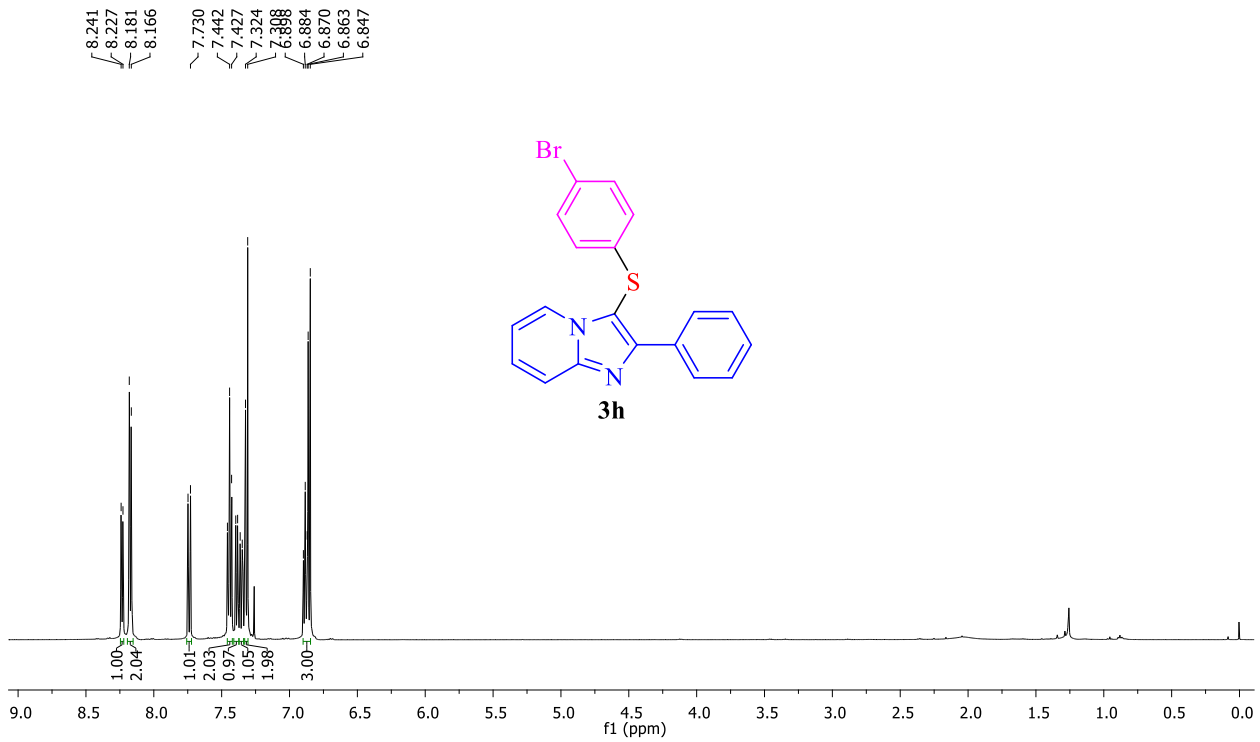


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

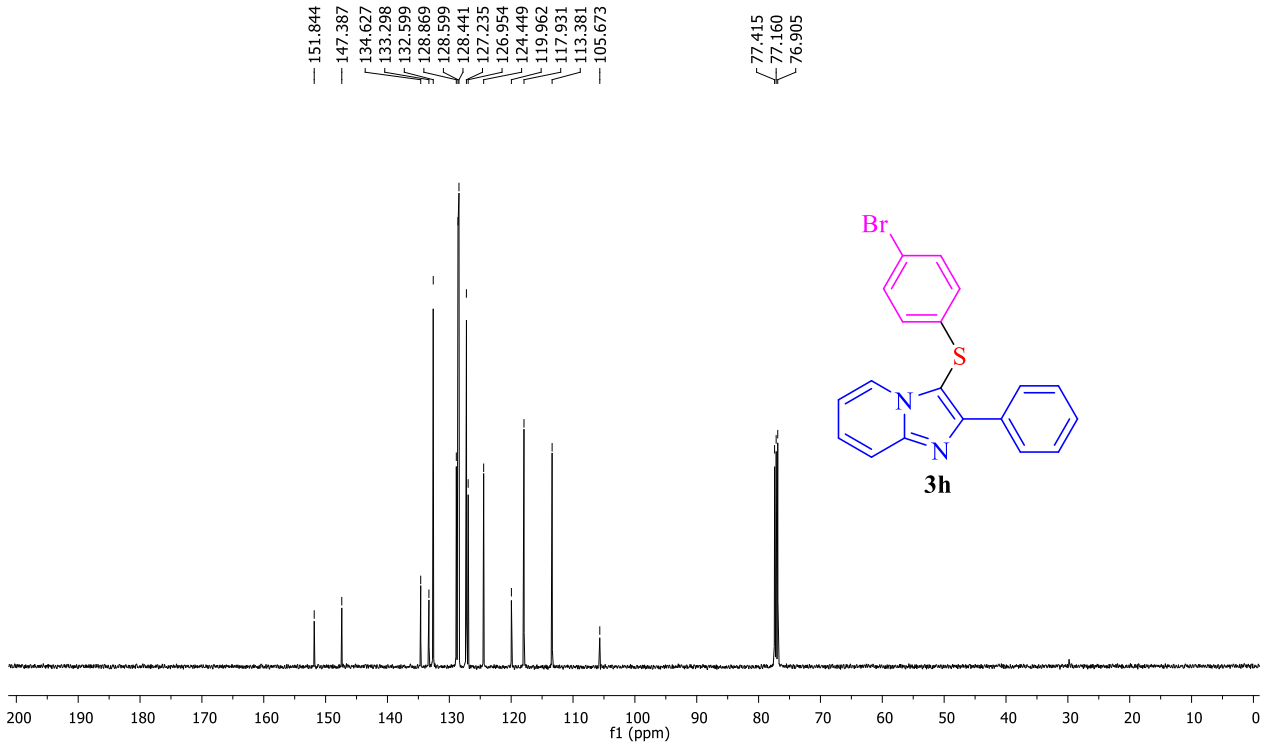


3-((4-Bromophenyl)thio)-2-phenylimidazo[1,2-*a*]pyridine (3h)

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

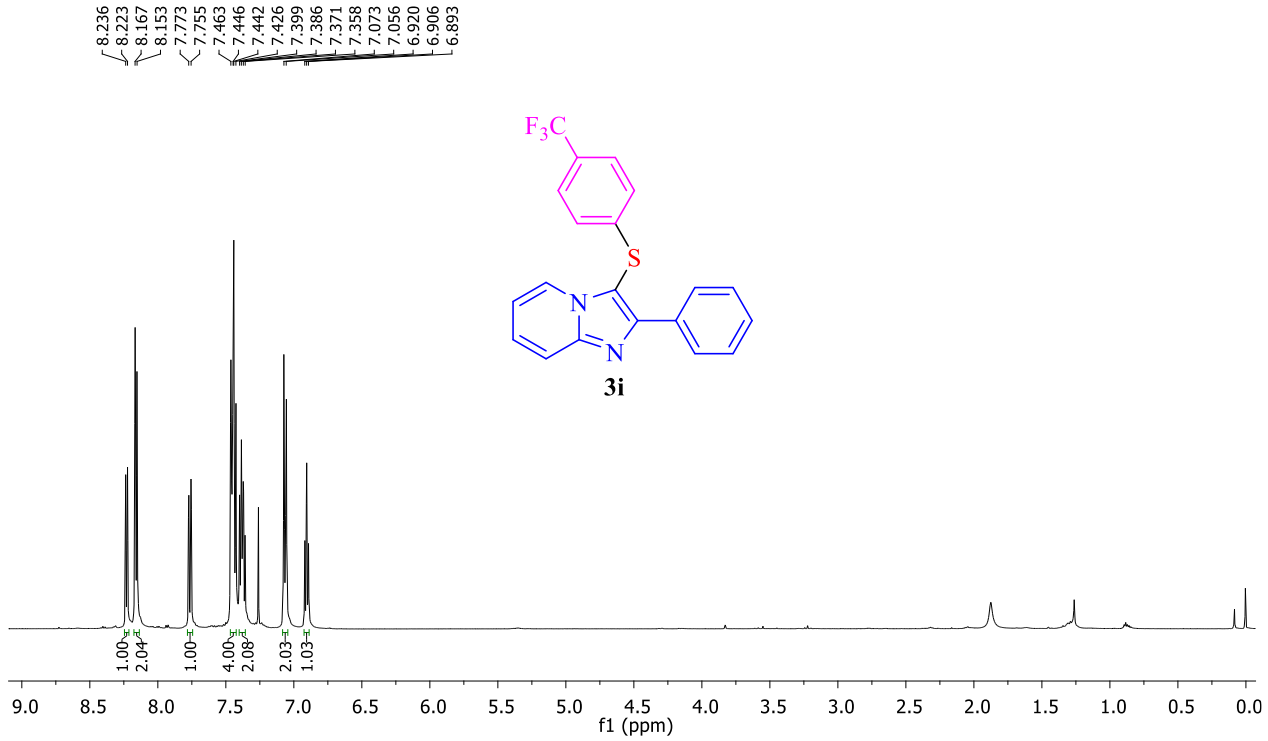


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

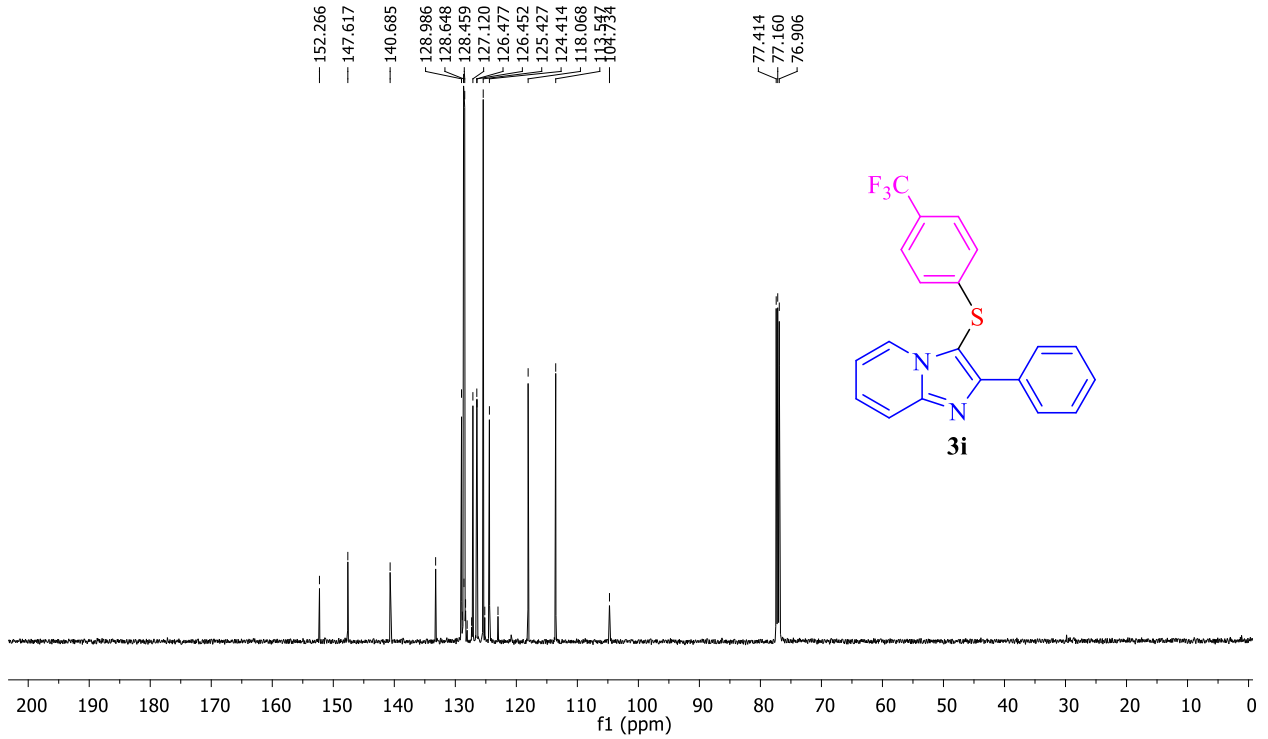


2-Phenyl-3-((4-(trifluoromethyl)phenyl)thio)imidazo[1,2-*a*]pyridine (3i)

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

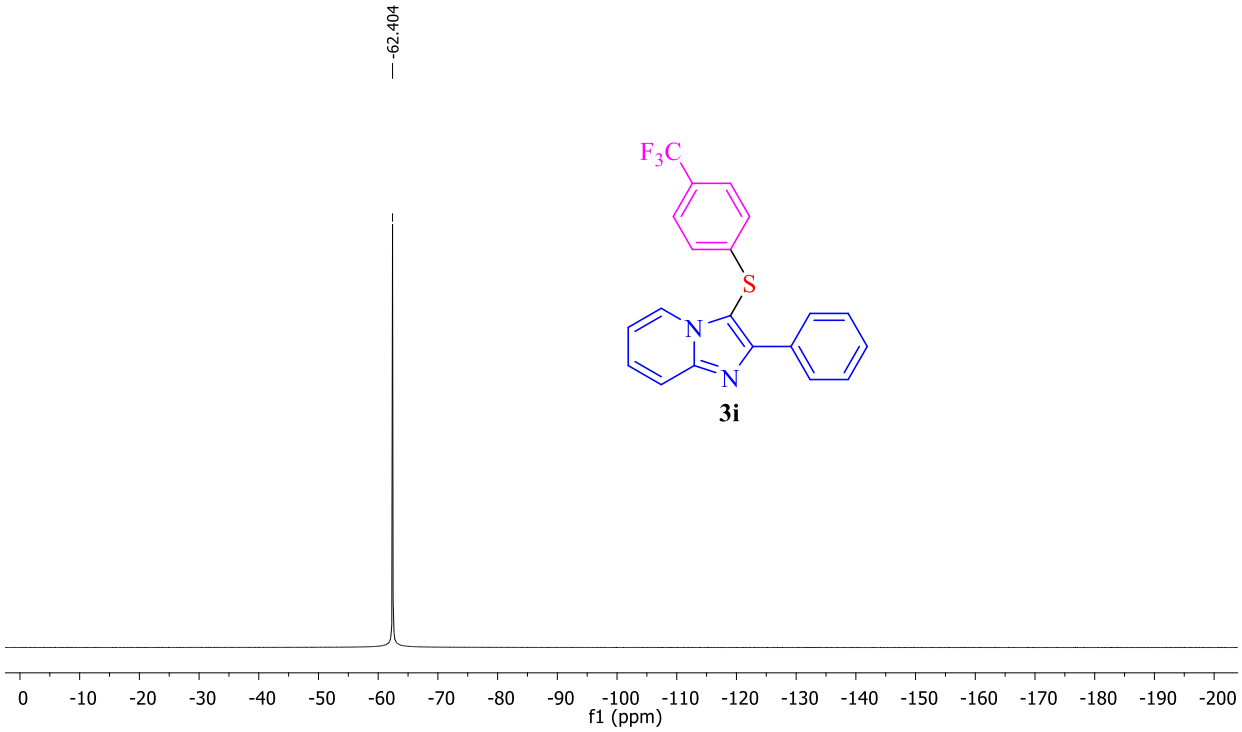


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



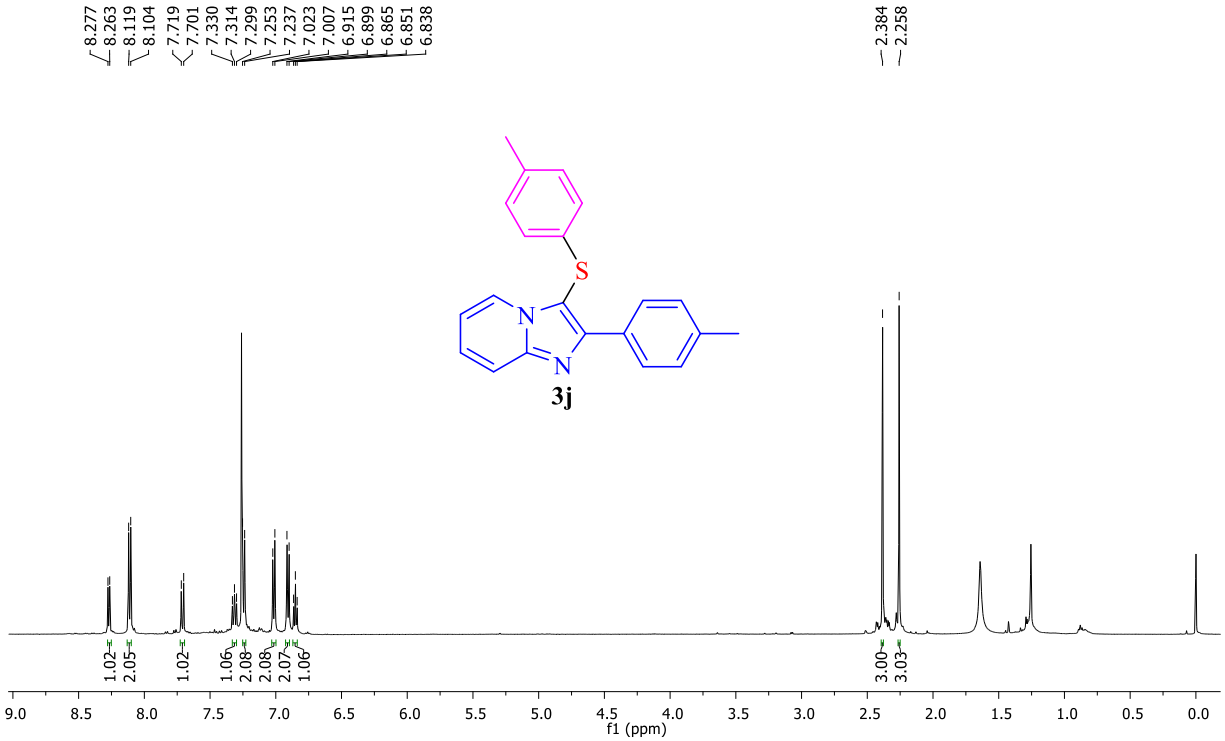
2-Phenyl-3-((4-(trifluoromethyl)phenyl)thio)imidazo[1,2-*a*]pyridine (3i)

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

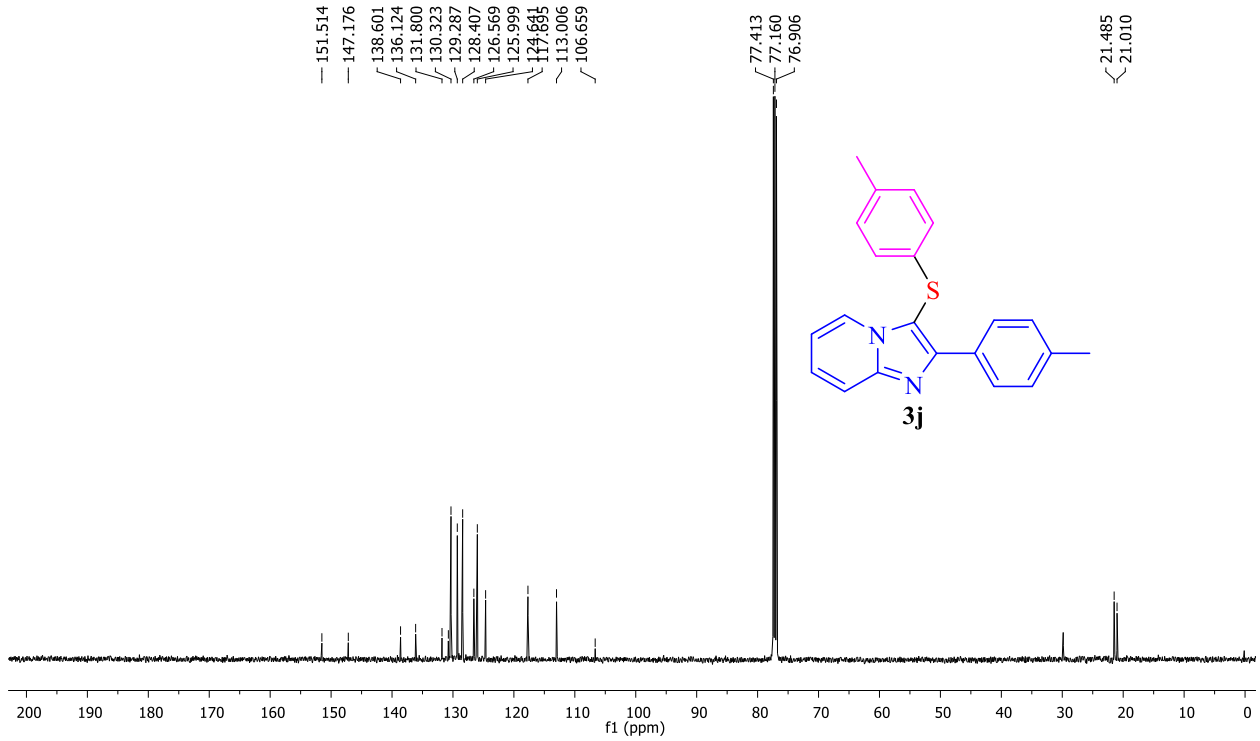


2-(*p*-Tolyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3j)

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

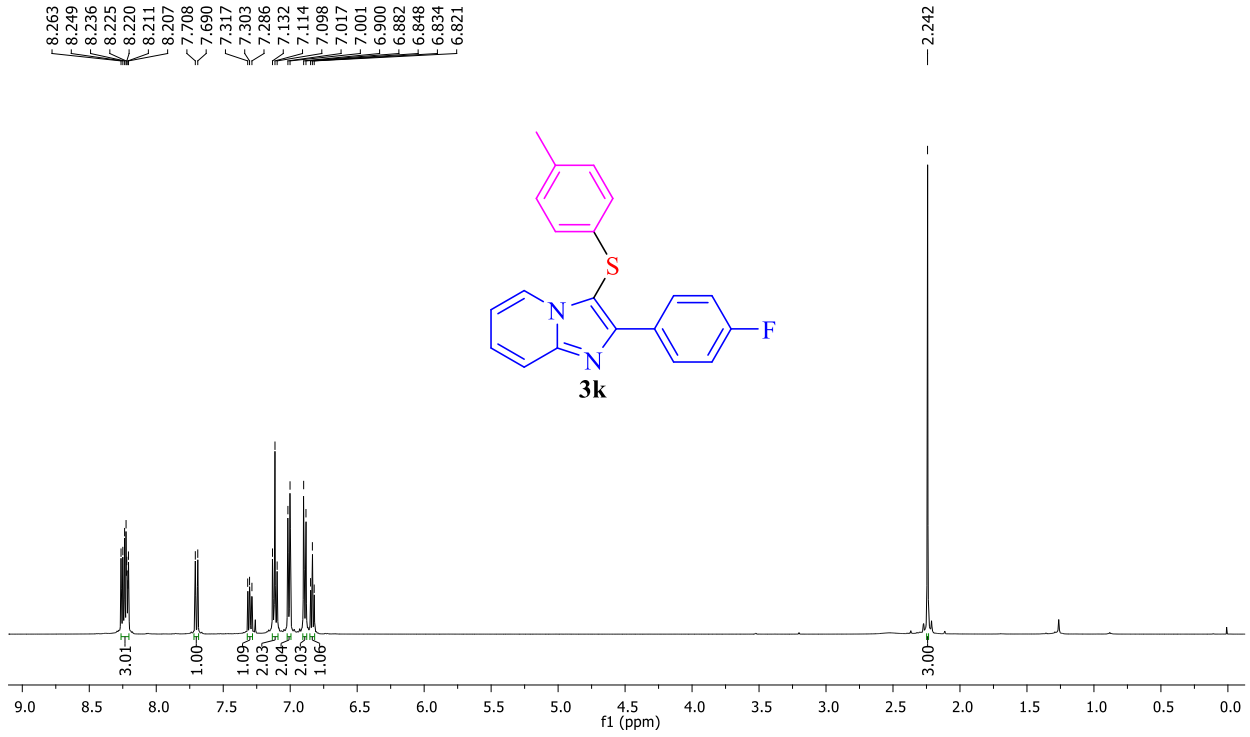


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

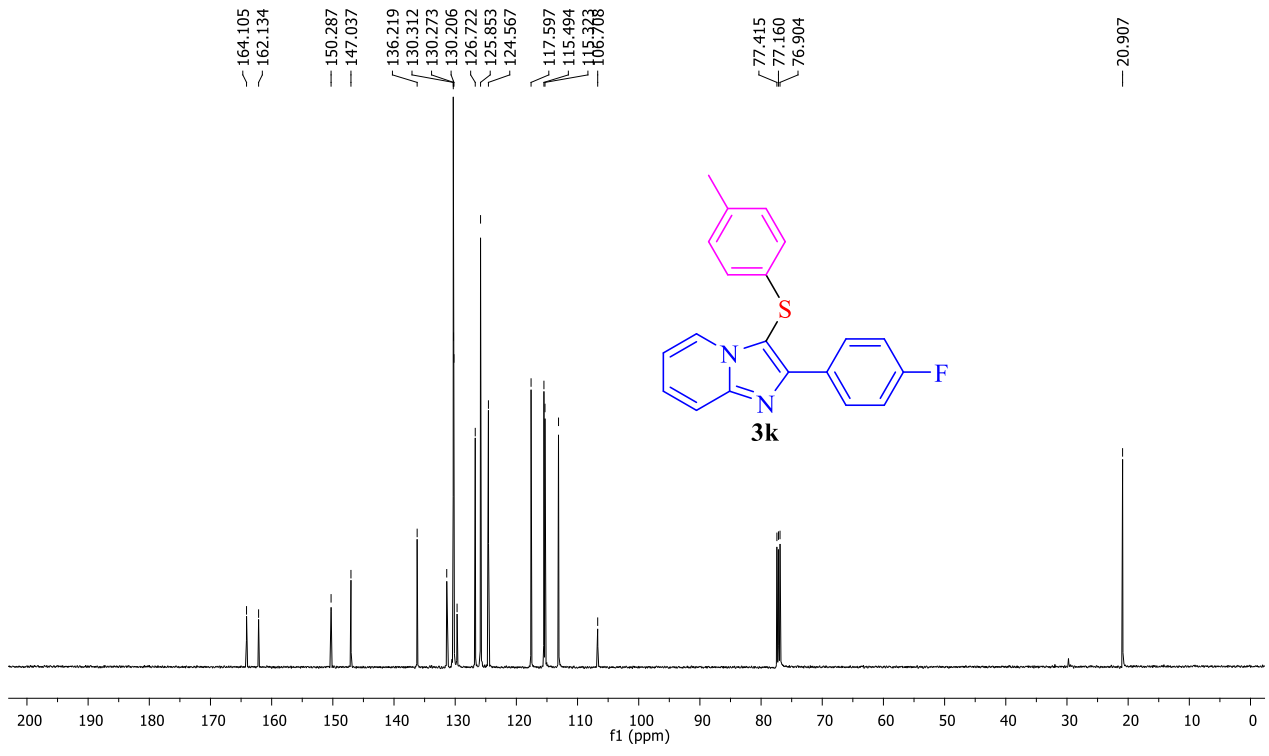


2-(4-Fluorophenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3k)

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

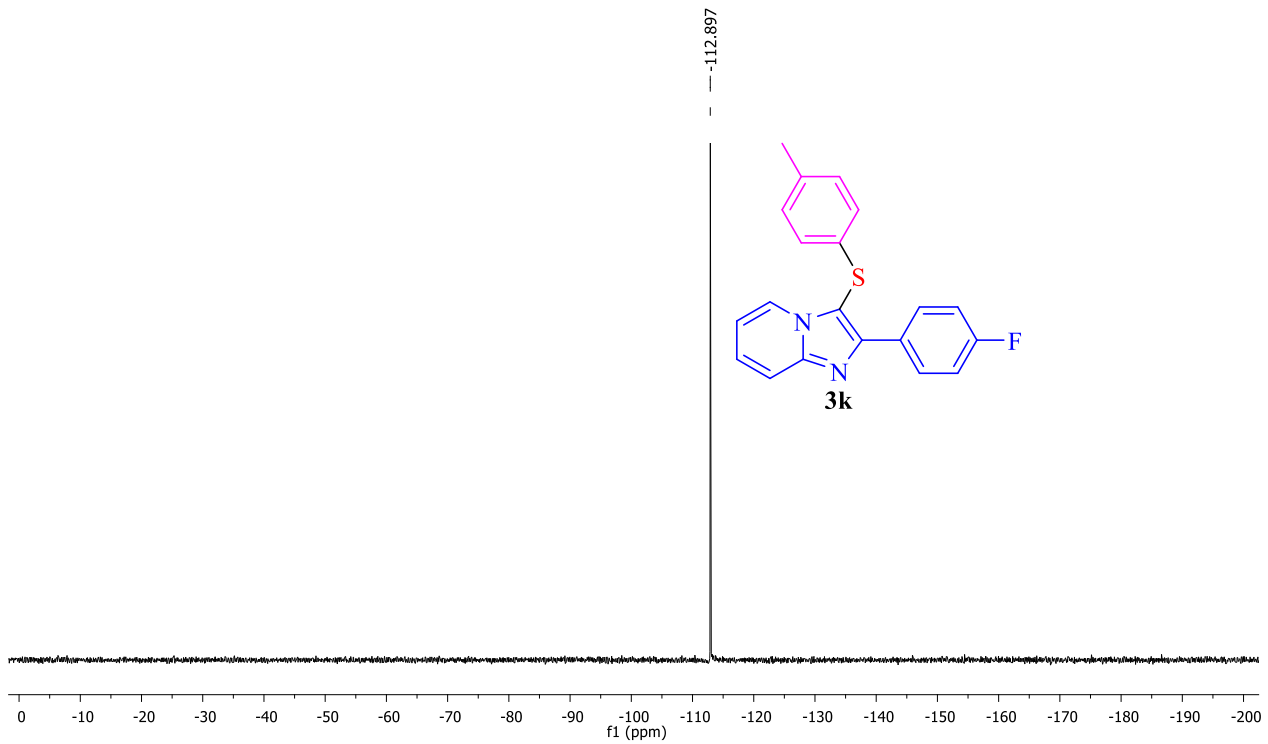


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



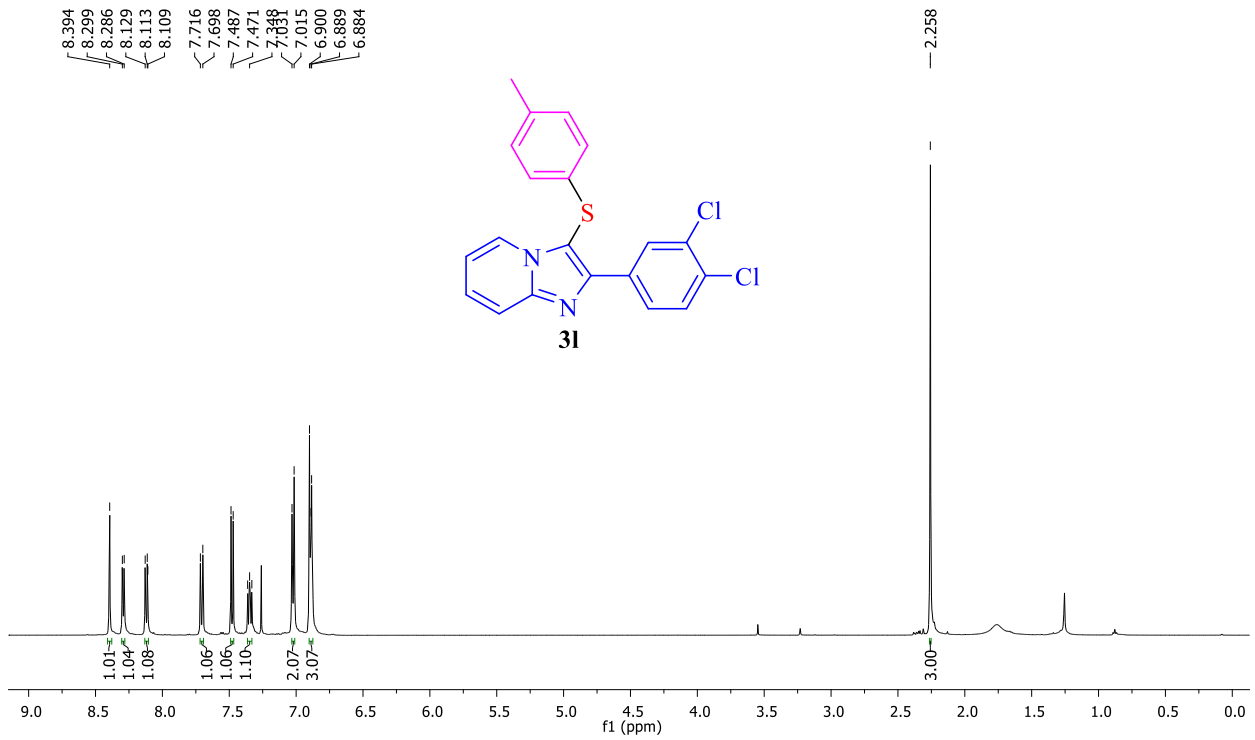
2-(4-Fluorophenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3k)

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

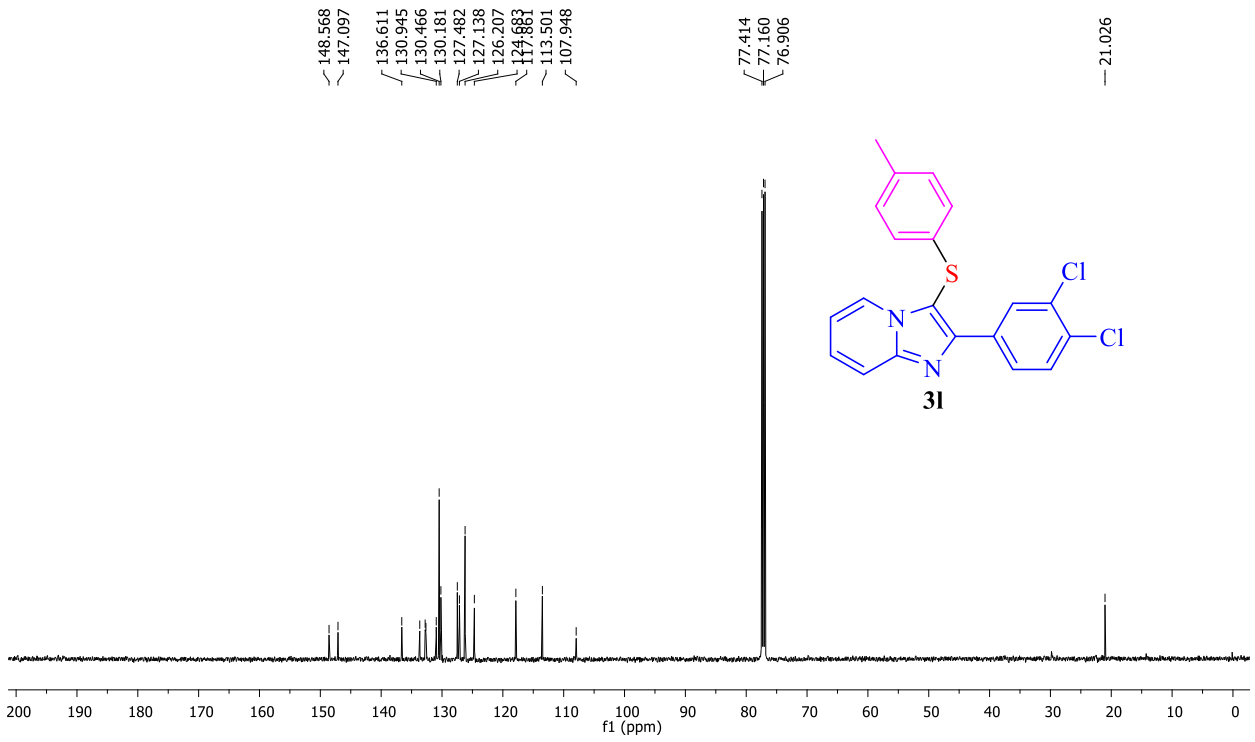


2-(3,4-Dichlorophenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3l)

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

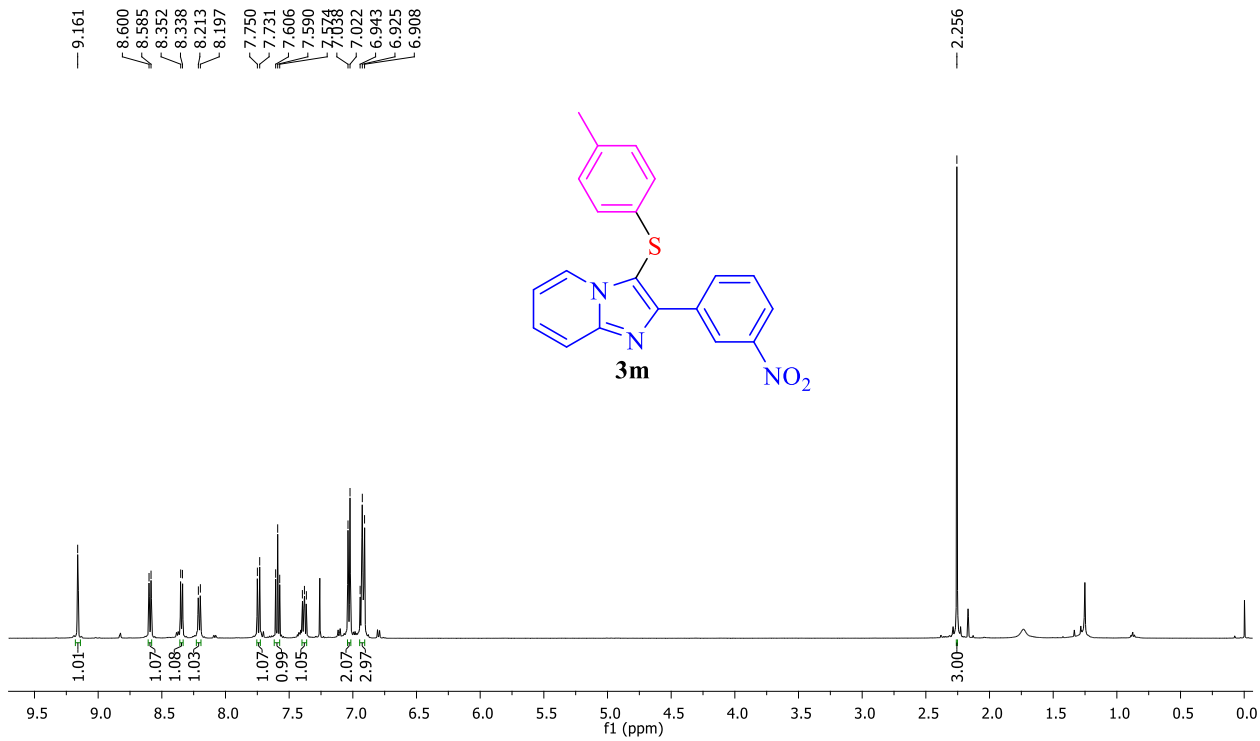


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

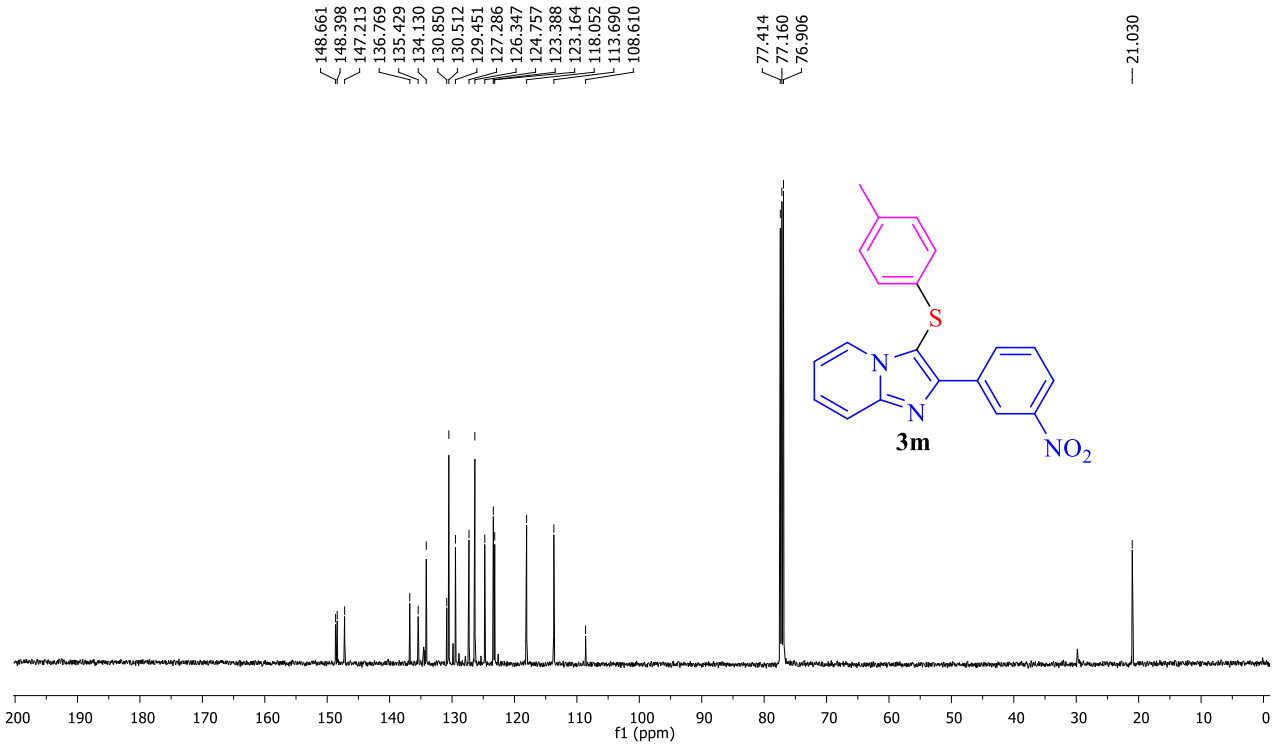


2-(3-Nitrophenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3m)

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

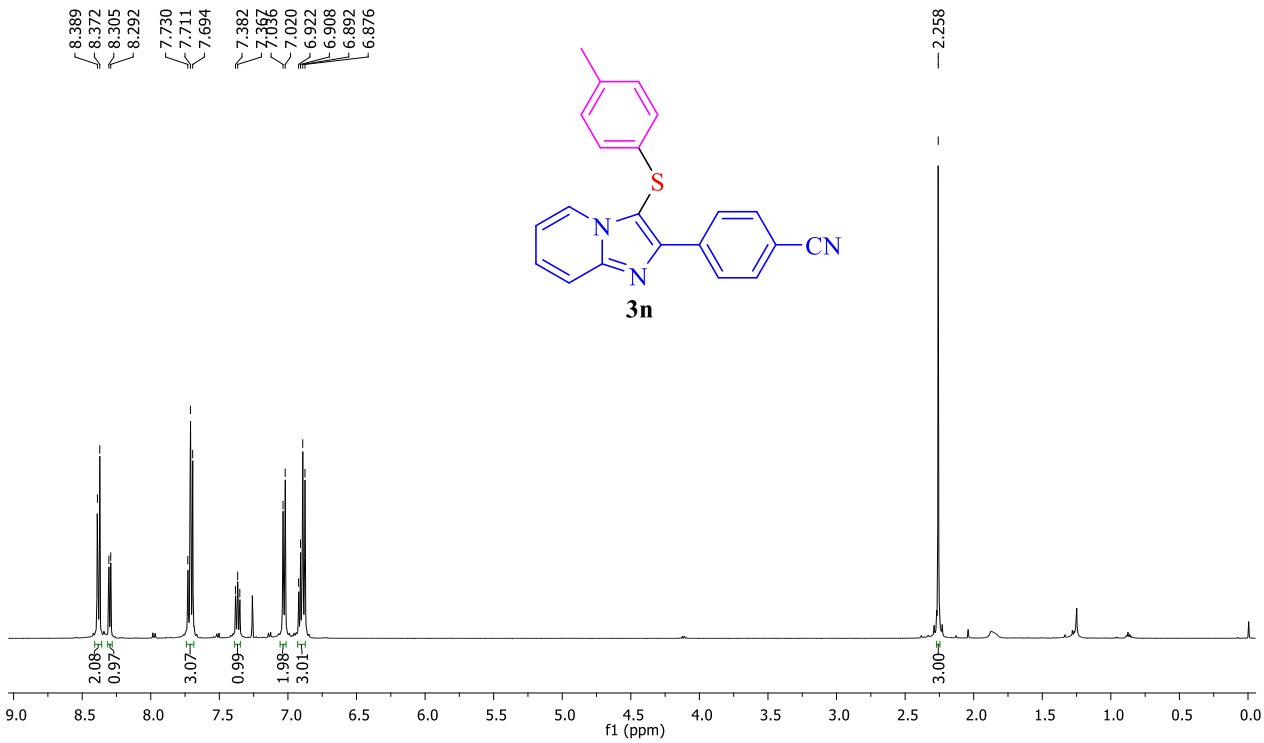


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

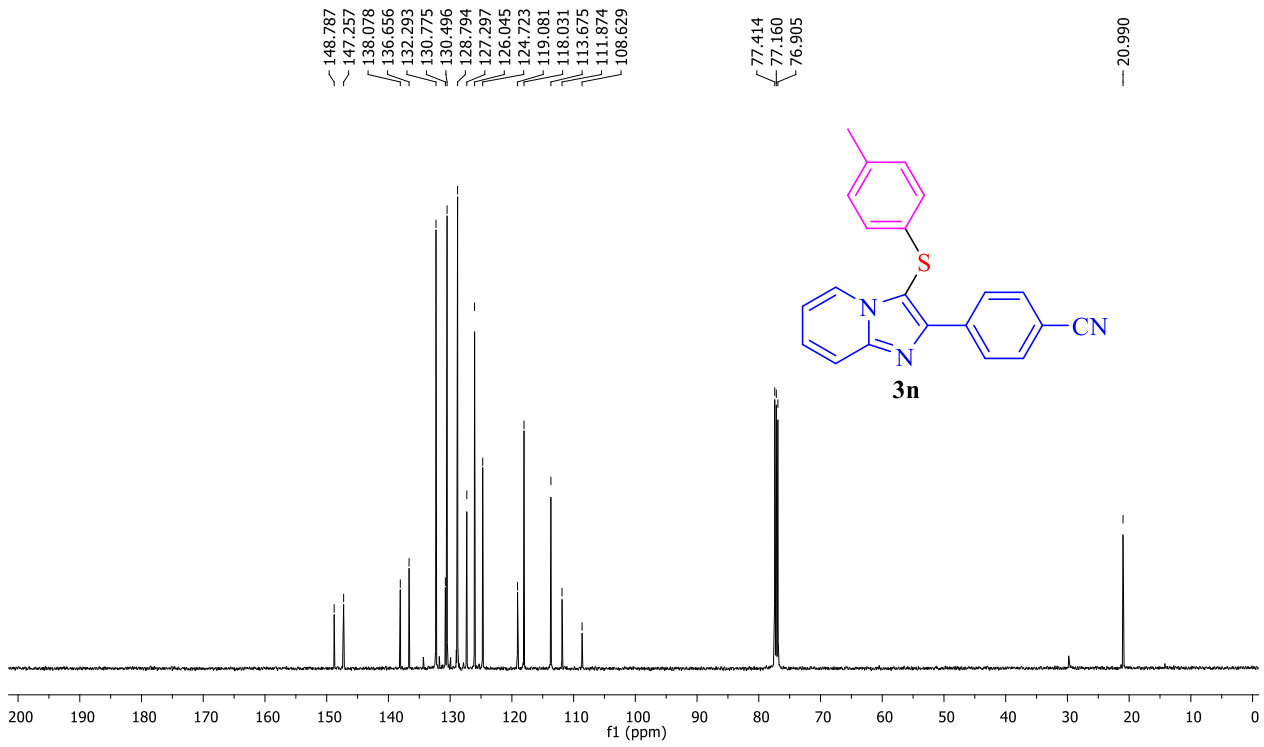


4-(3-(*p*-Tolylthio)imidazo[1,2-*a*]pyridin-2-yl)benzonitrile (3n)

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

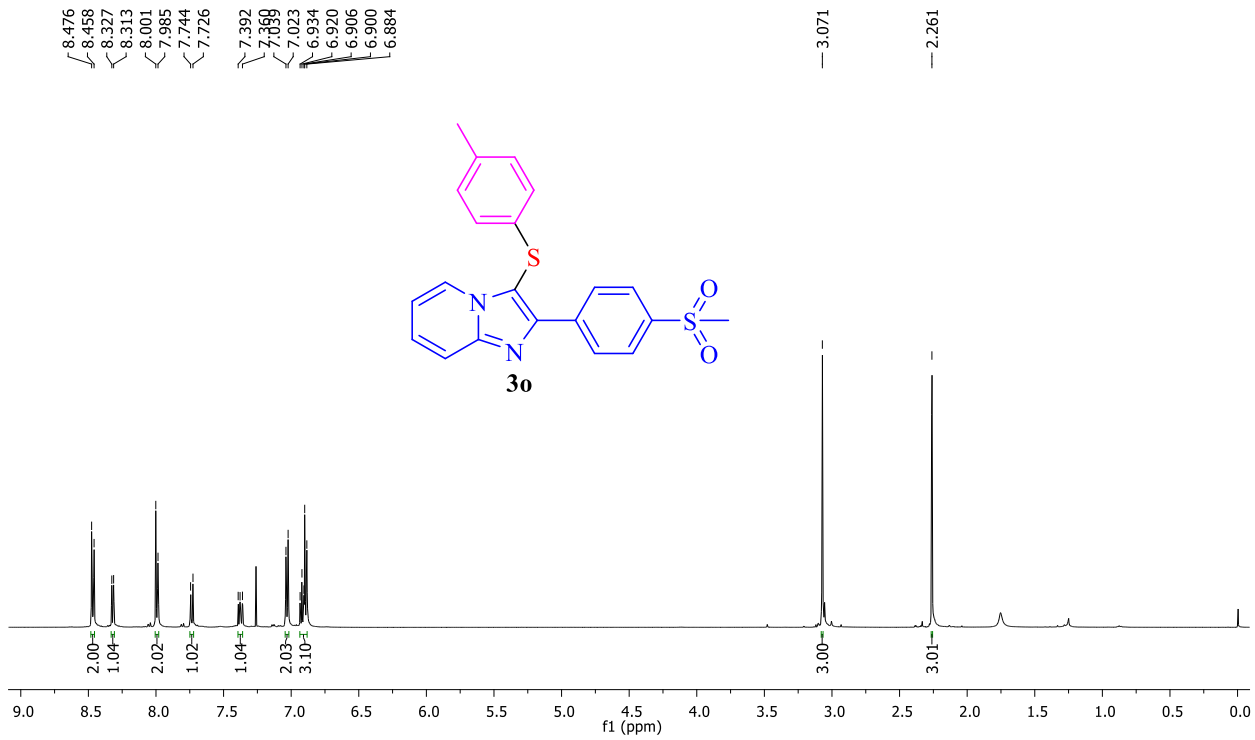


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

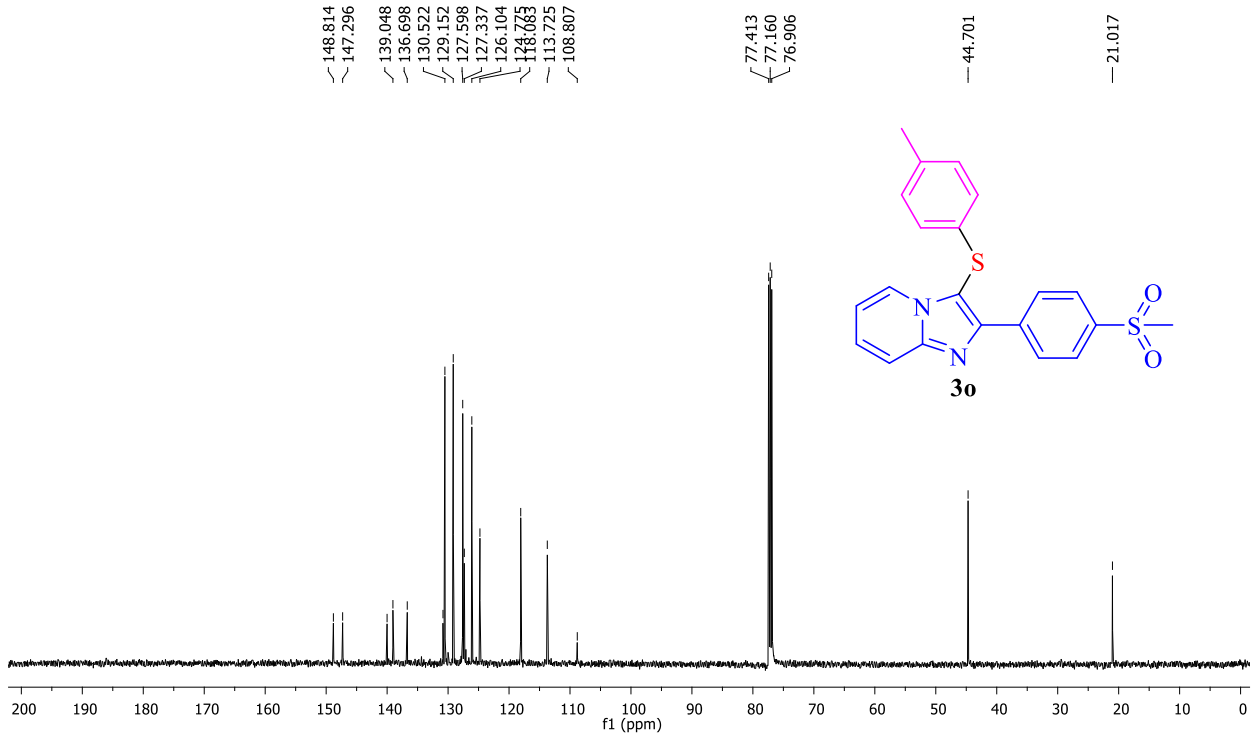


2-(4-(Methylsulfonyl)phenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3o)

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

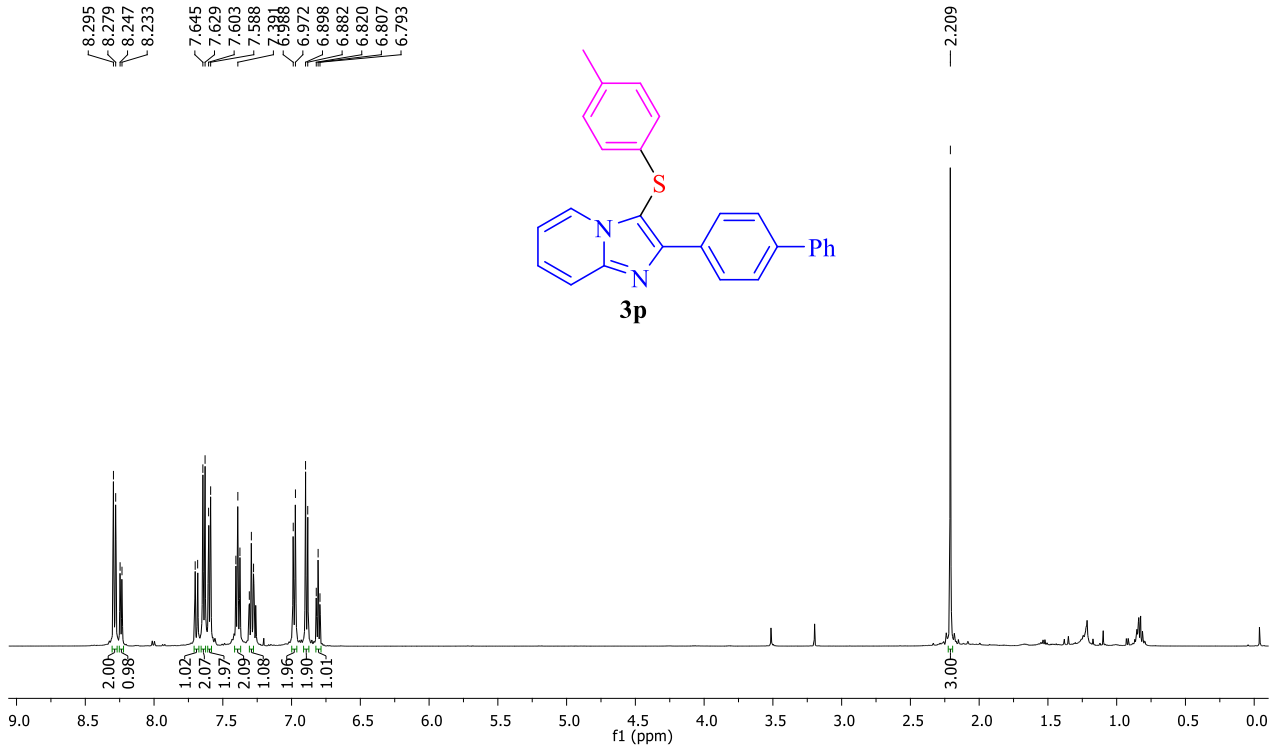


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

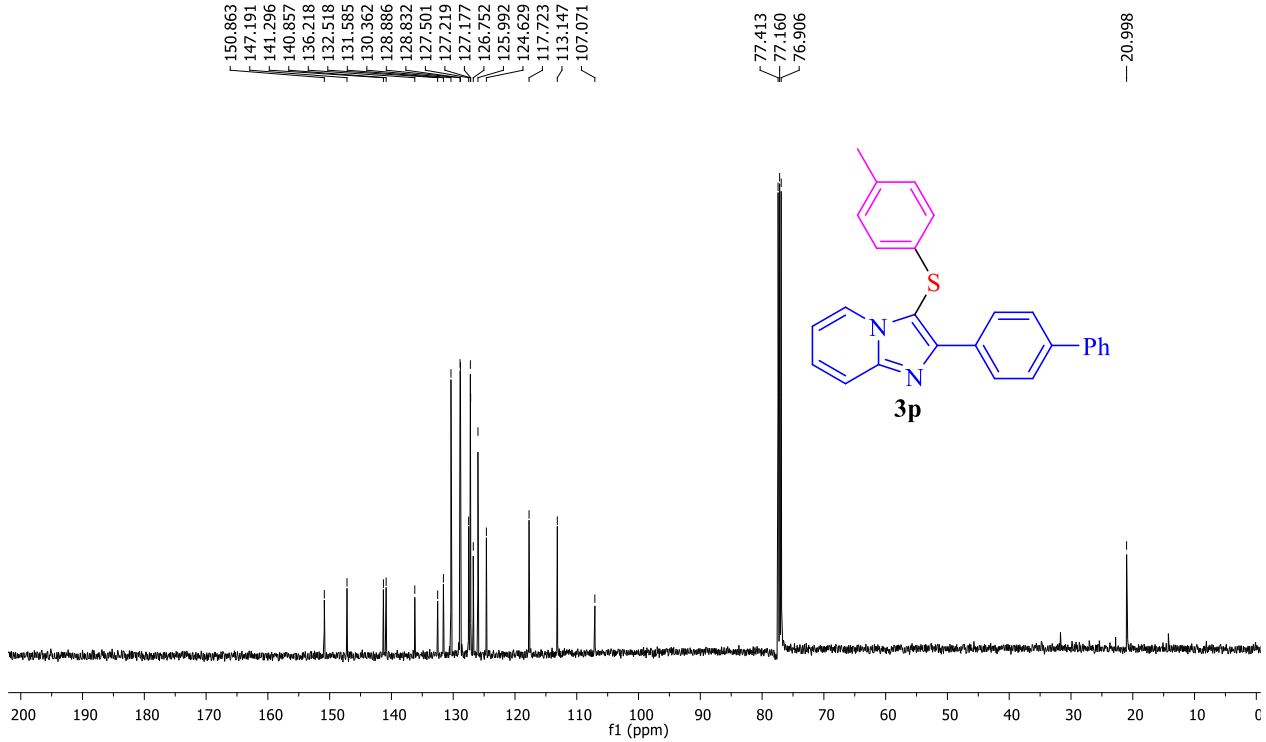


2-([1,1'-Biphenyl]-4-yl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3p)

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

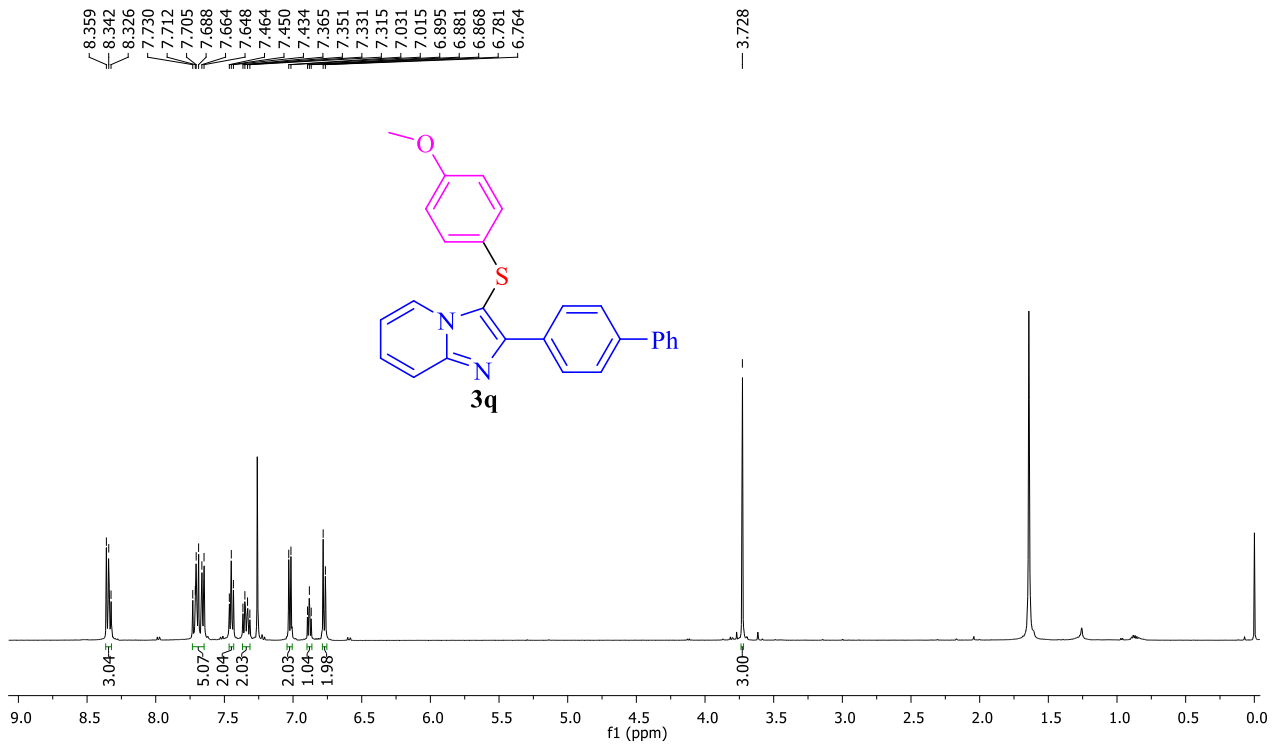


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

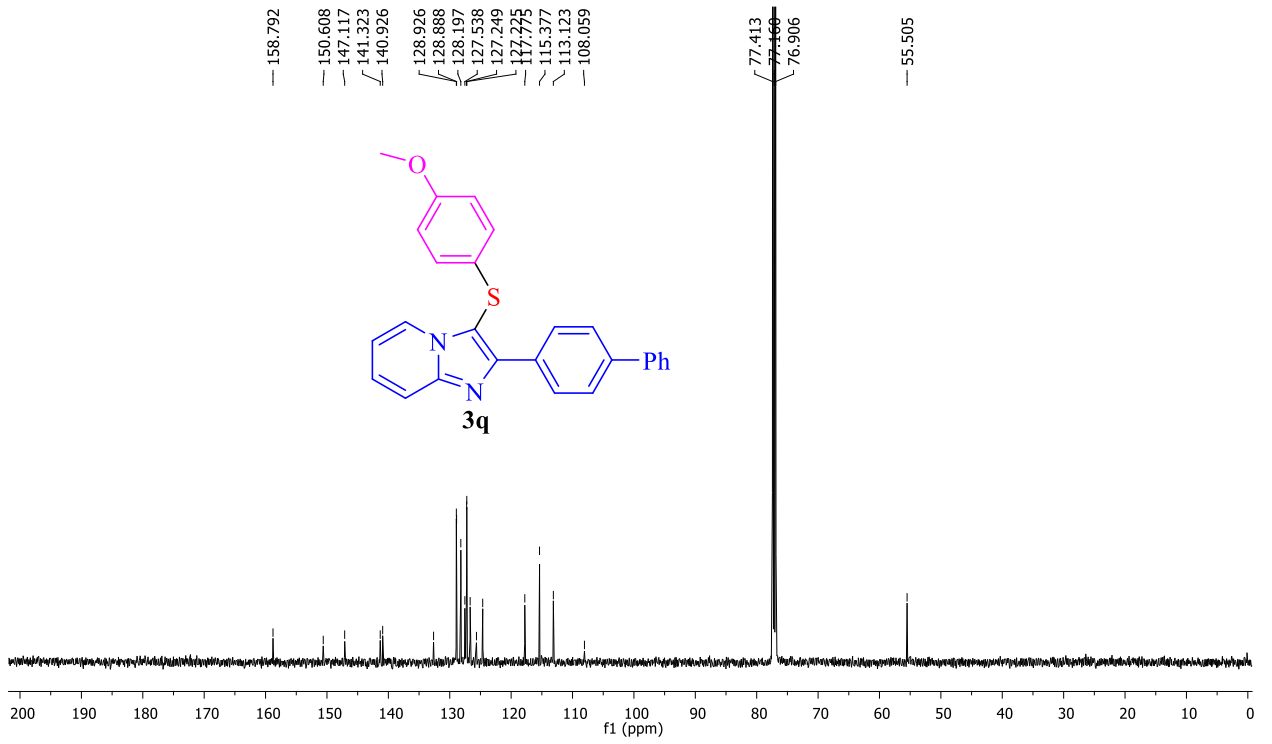


2-([1,1'-Biphenyl]-4-yl)-3-((4-methoxyphenyl)thio)imidazo[1,2-*a*]pyridine (3q)

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

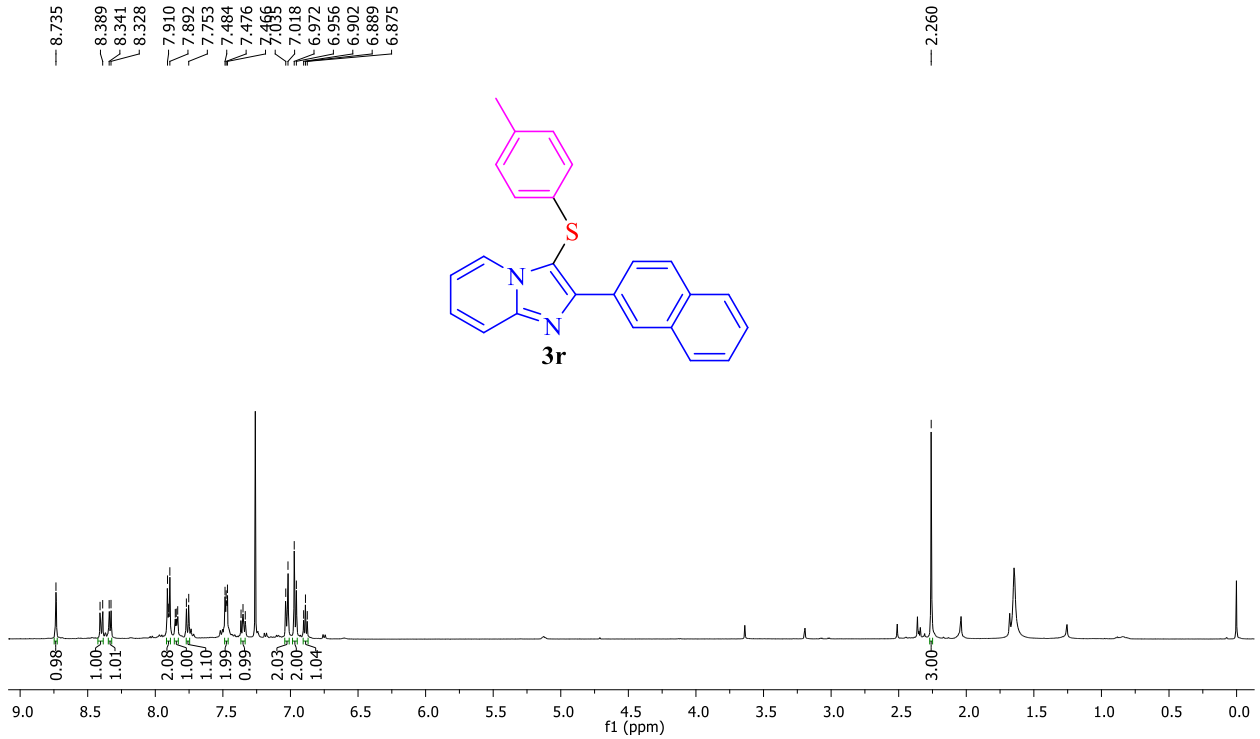


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

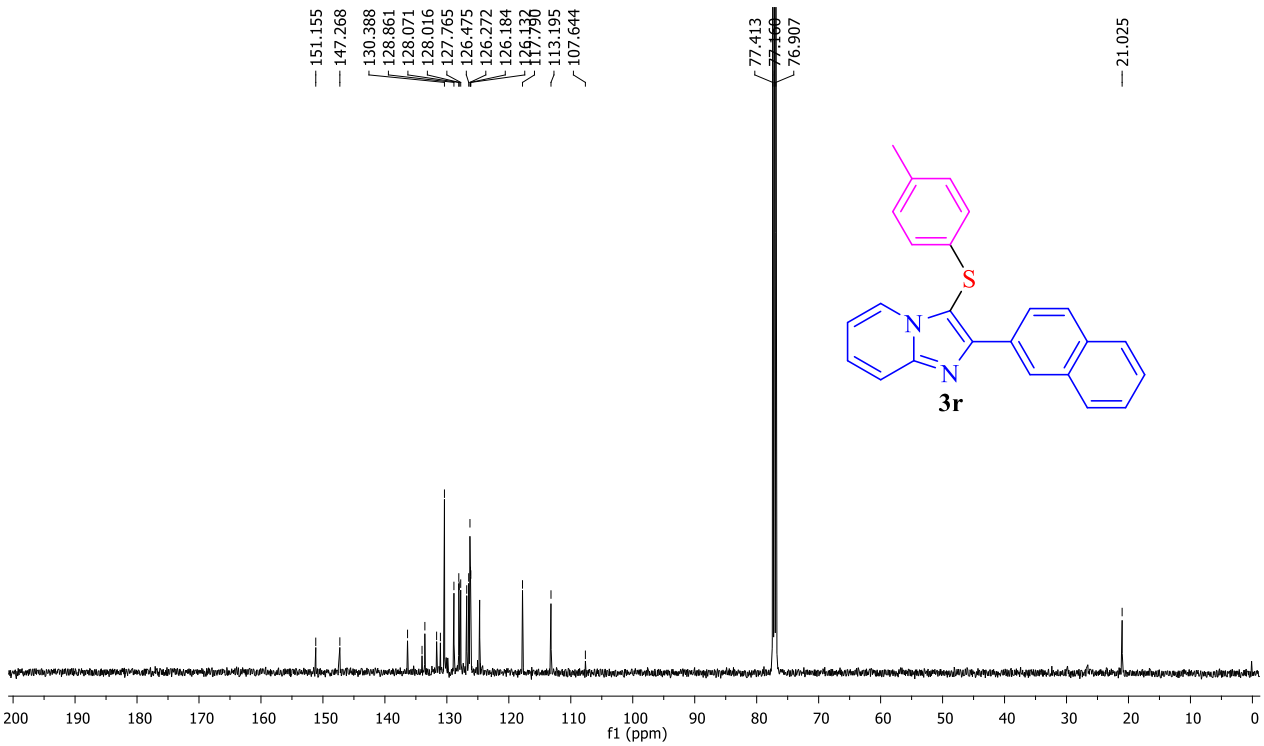


2-(Naphthalen-2-yl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3r)

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

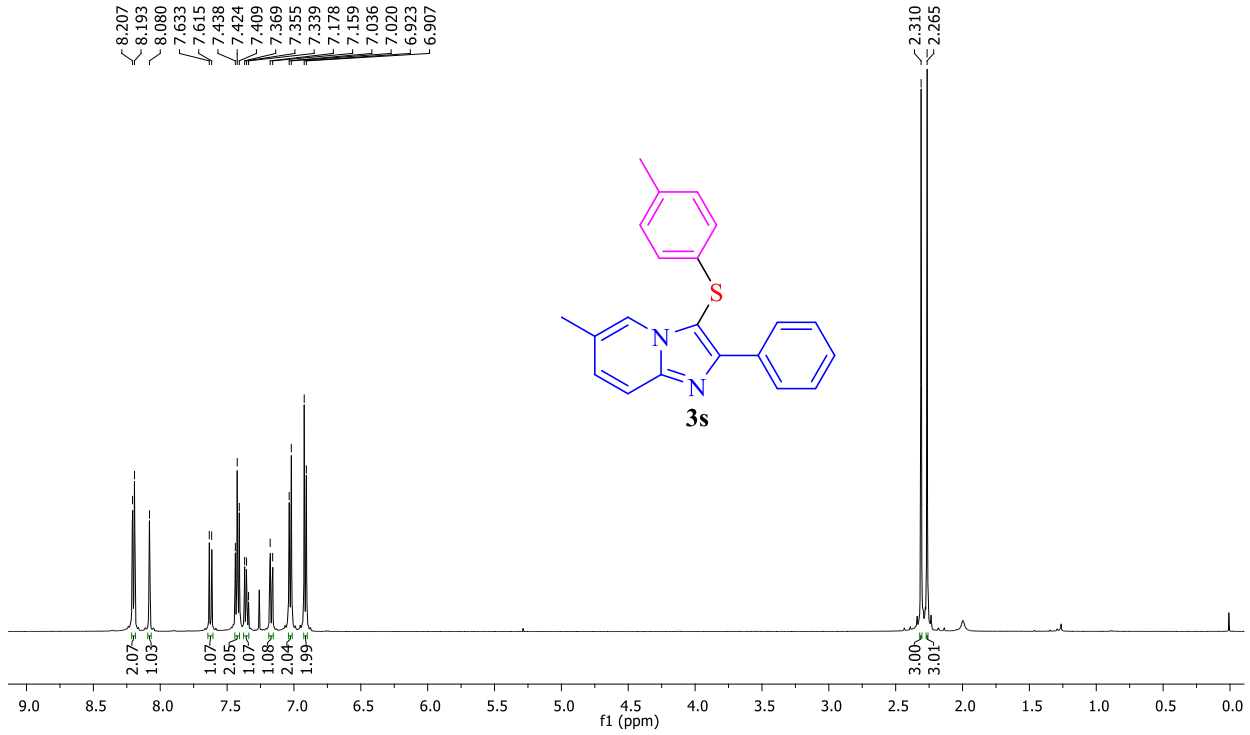


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

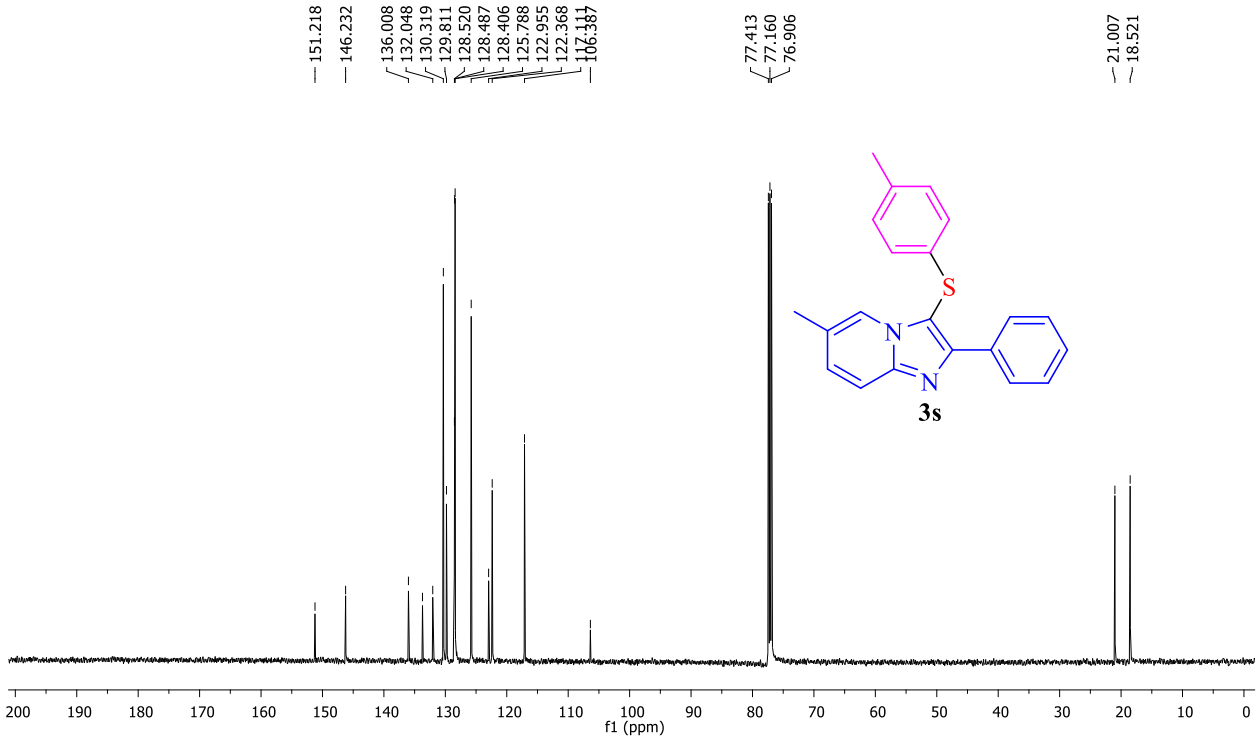


6-Methyl-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3s)

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

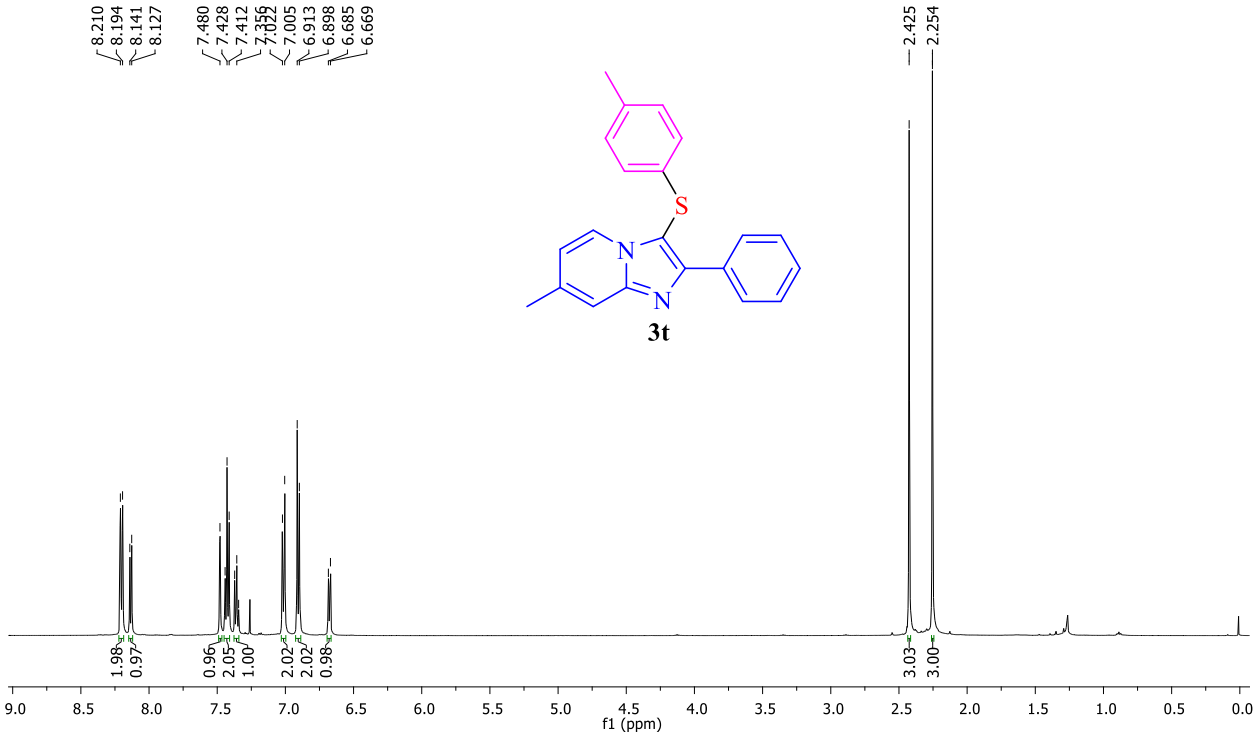


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

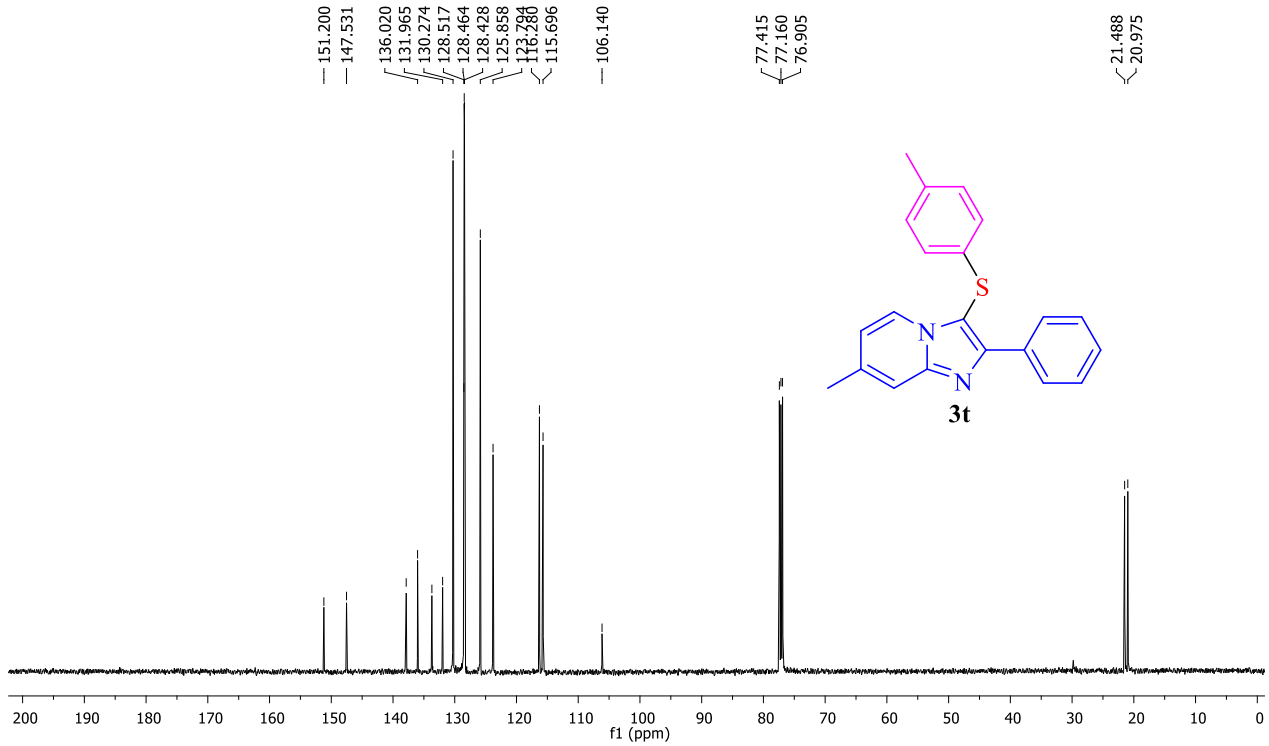


7-Methyl-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3t)

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

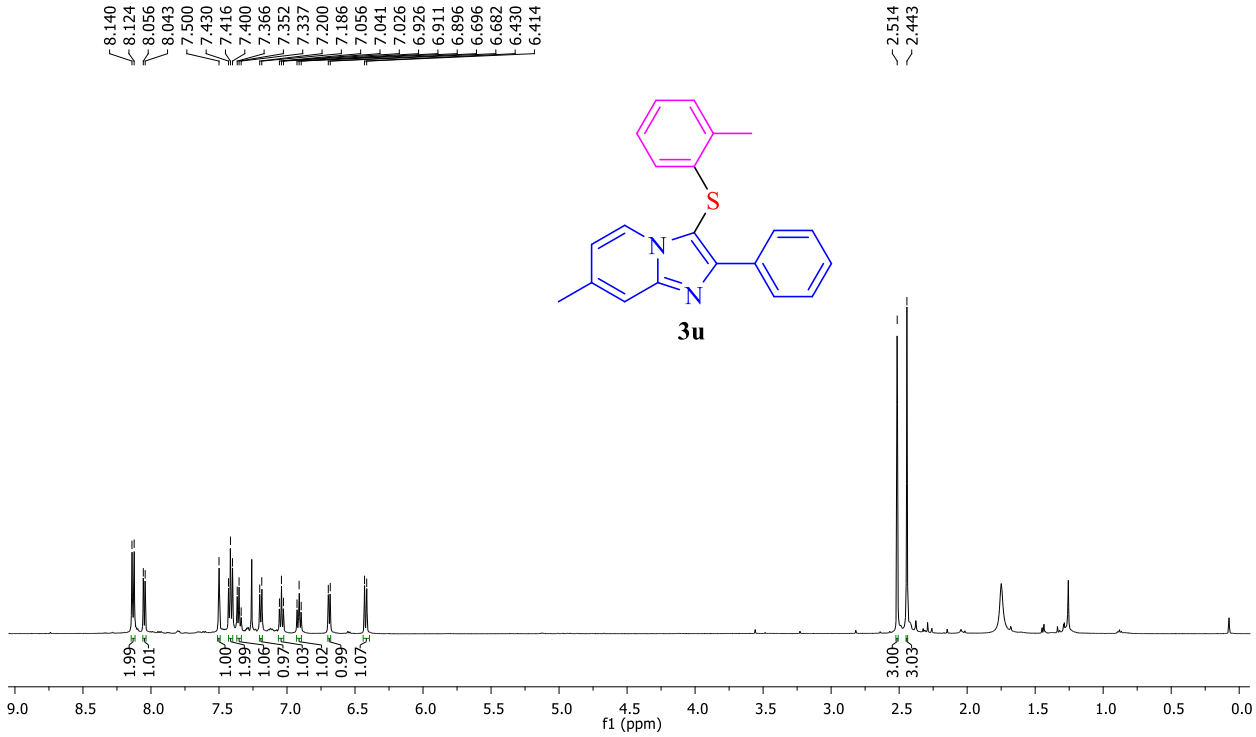


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

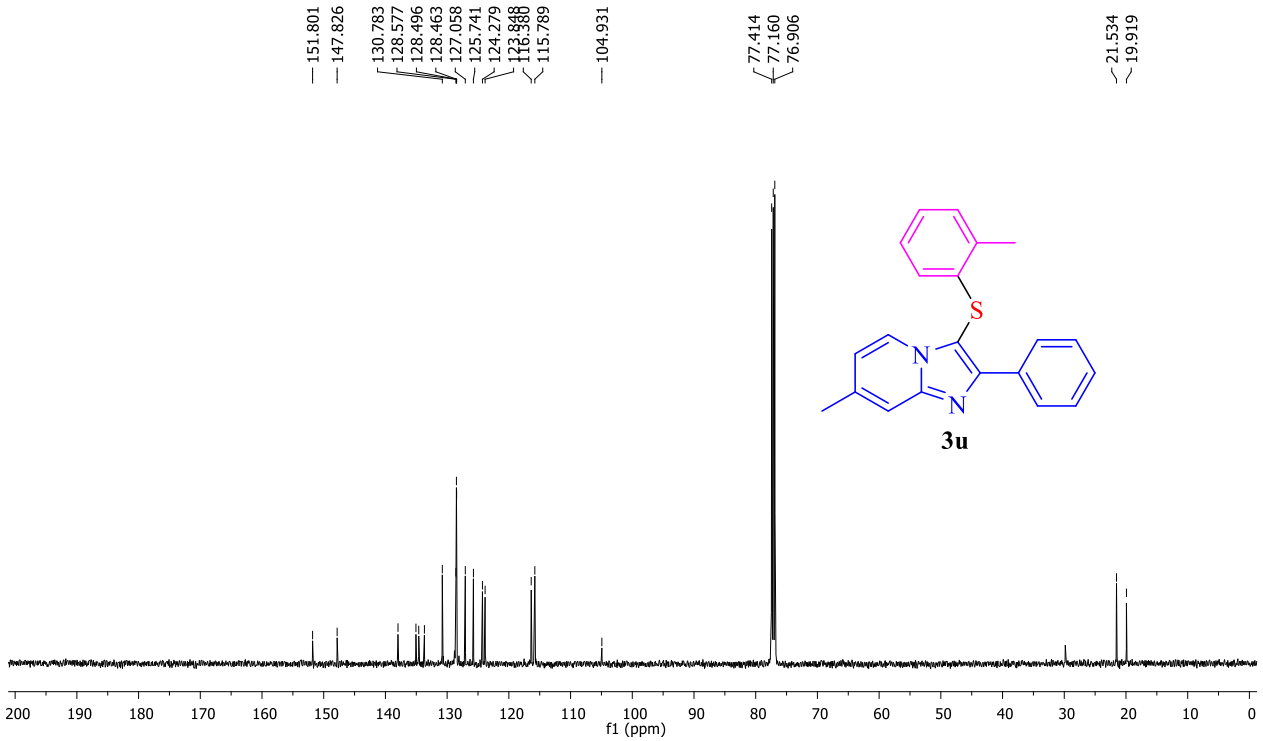


7-Methyl-2-phenyl-3-(*o*-tolylthio)imidazo[1,2-*a*]pyridine (3u)

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

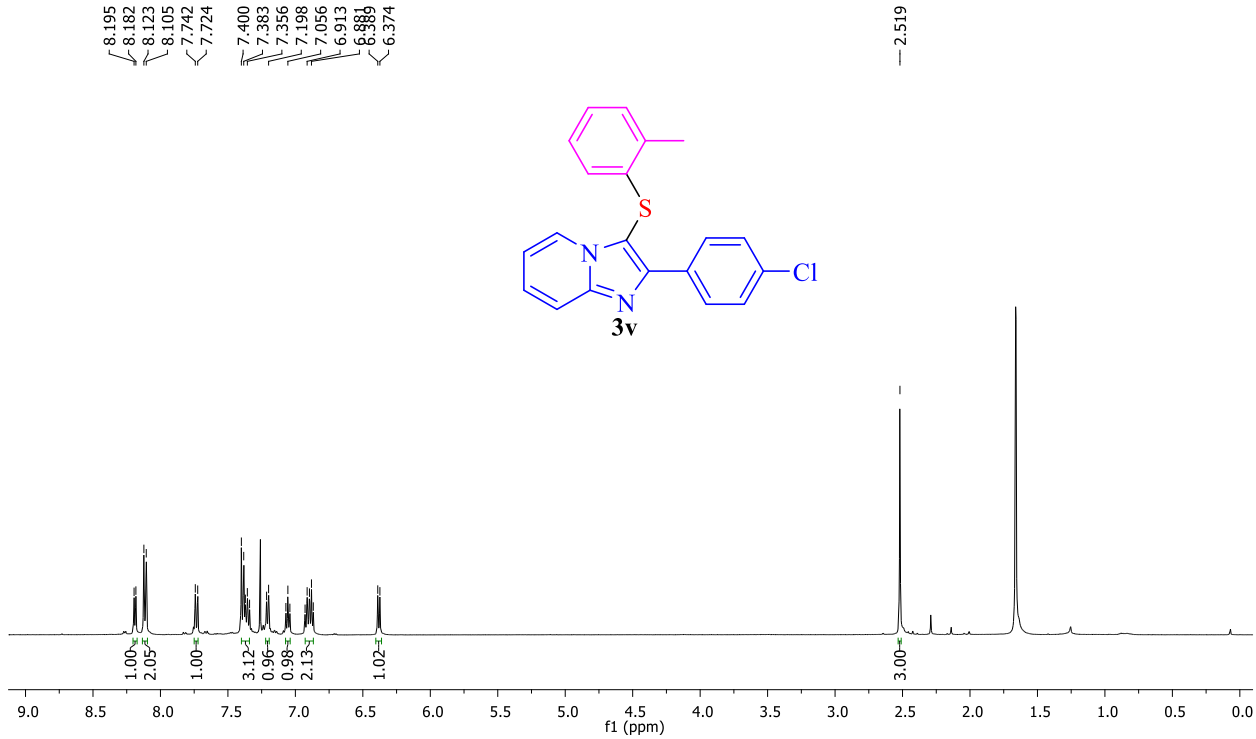


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

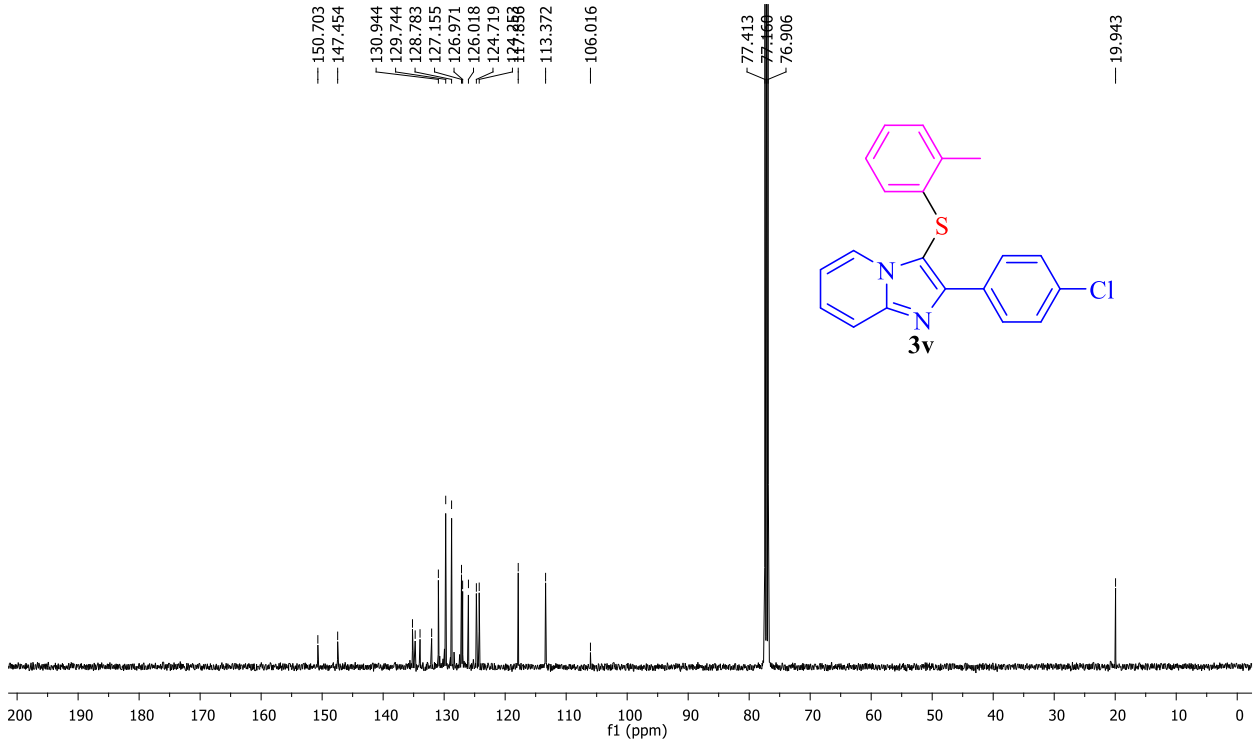


2-(4-Chlorophenyl)-3-(*o*-tolylthio)imidazo[1,2-*a*]pyridine (3v)

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

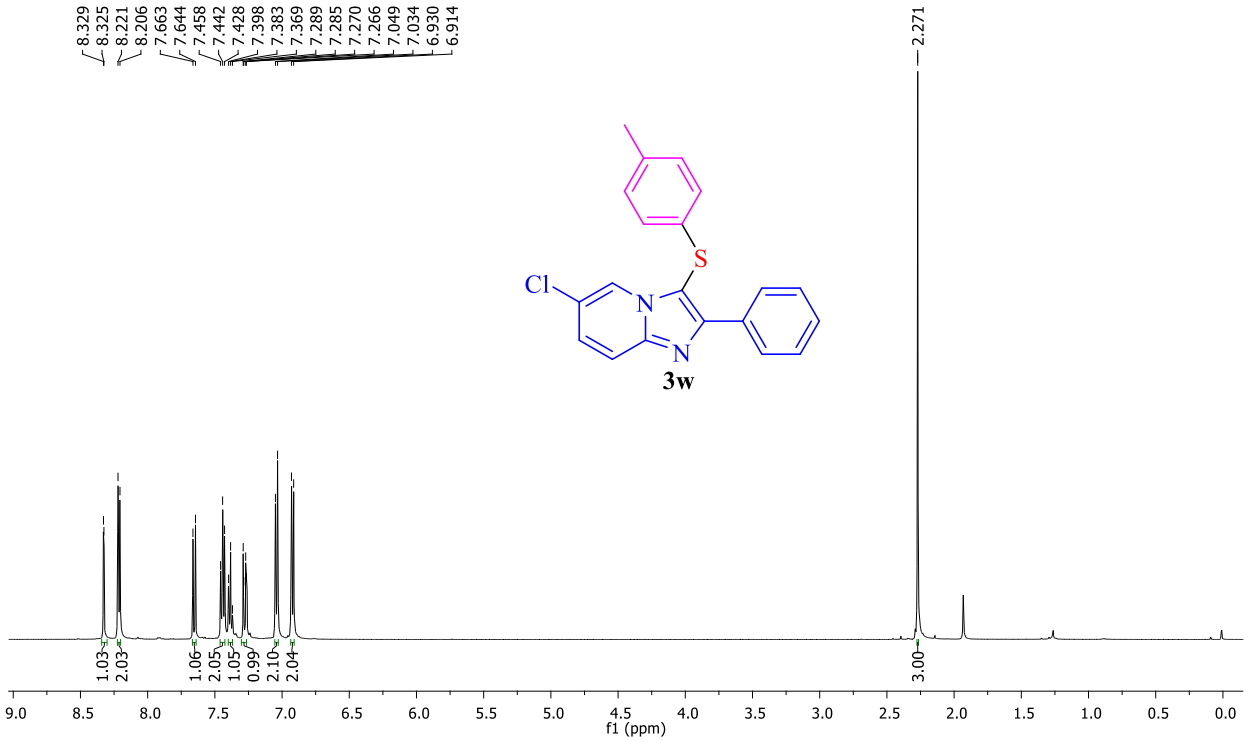


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

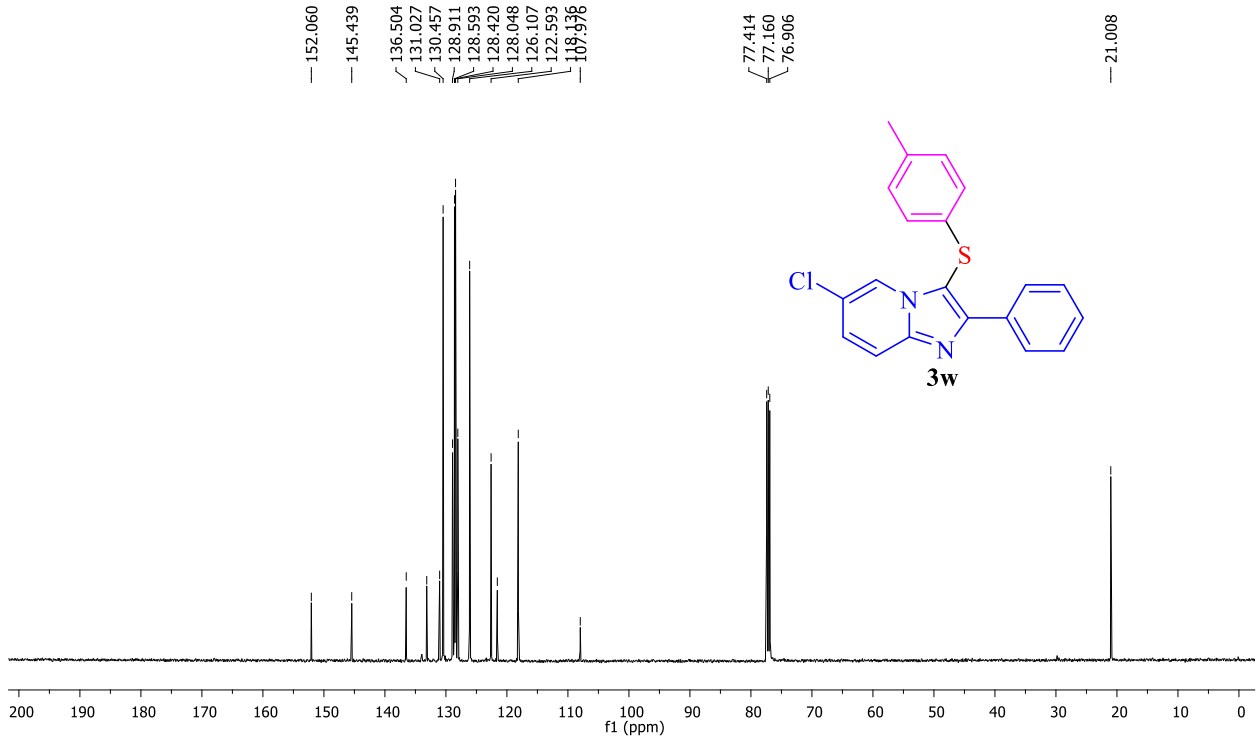


6-Chloro-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3w)

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

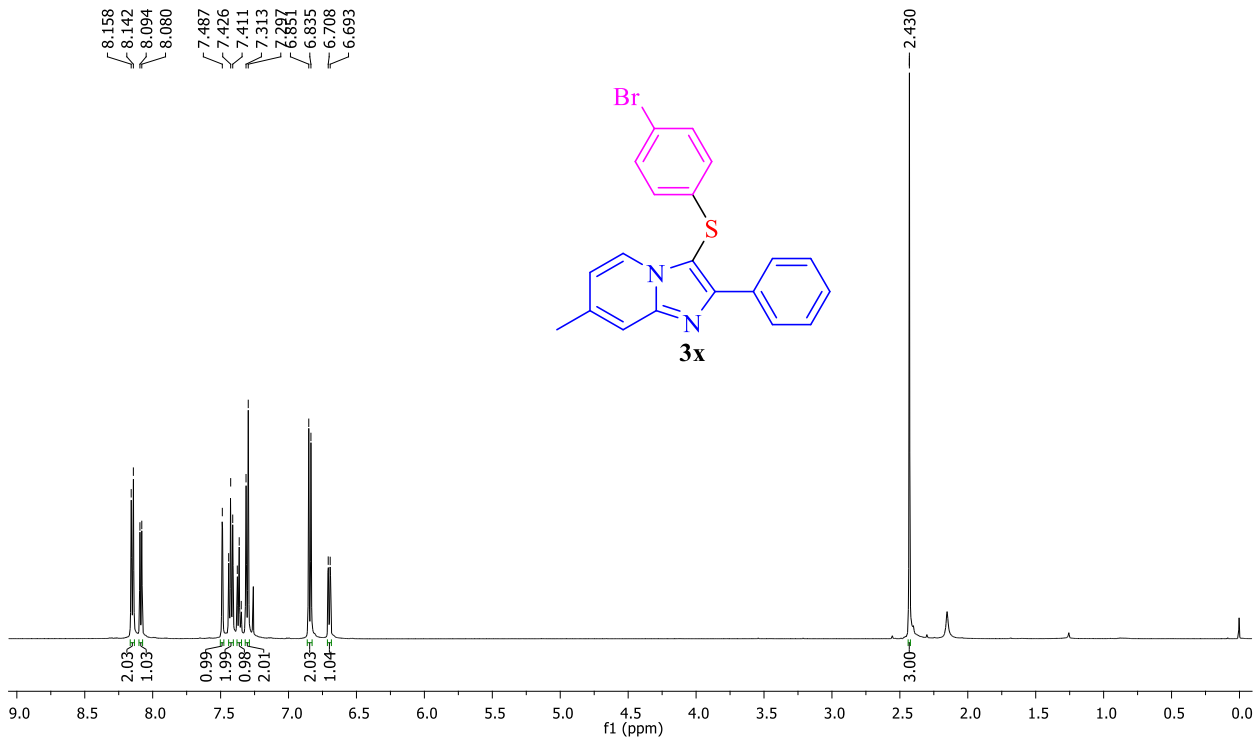


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

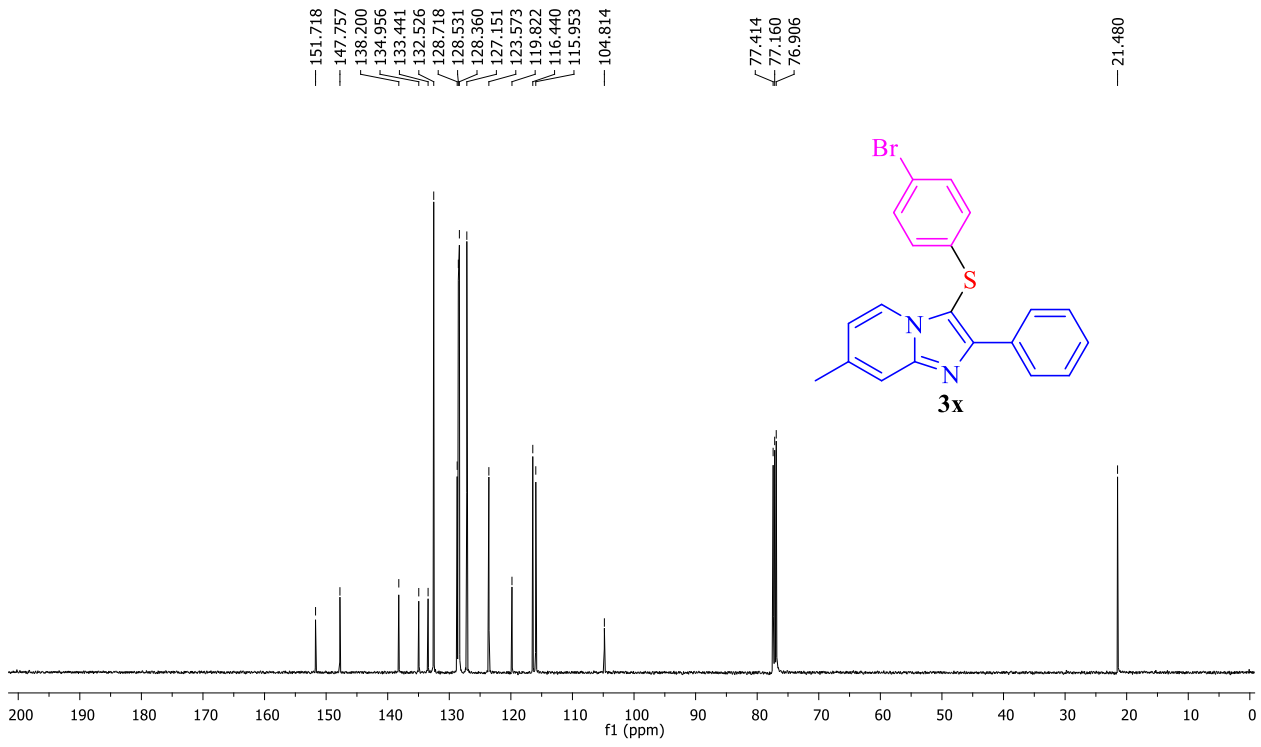


3-((4-Bromophenyl)thio)-7-methyl-2-phenylimidazo[1,2-*a*]pyridine (3x)

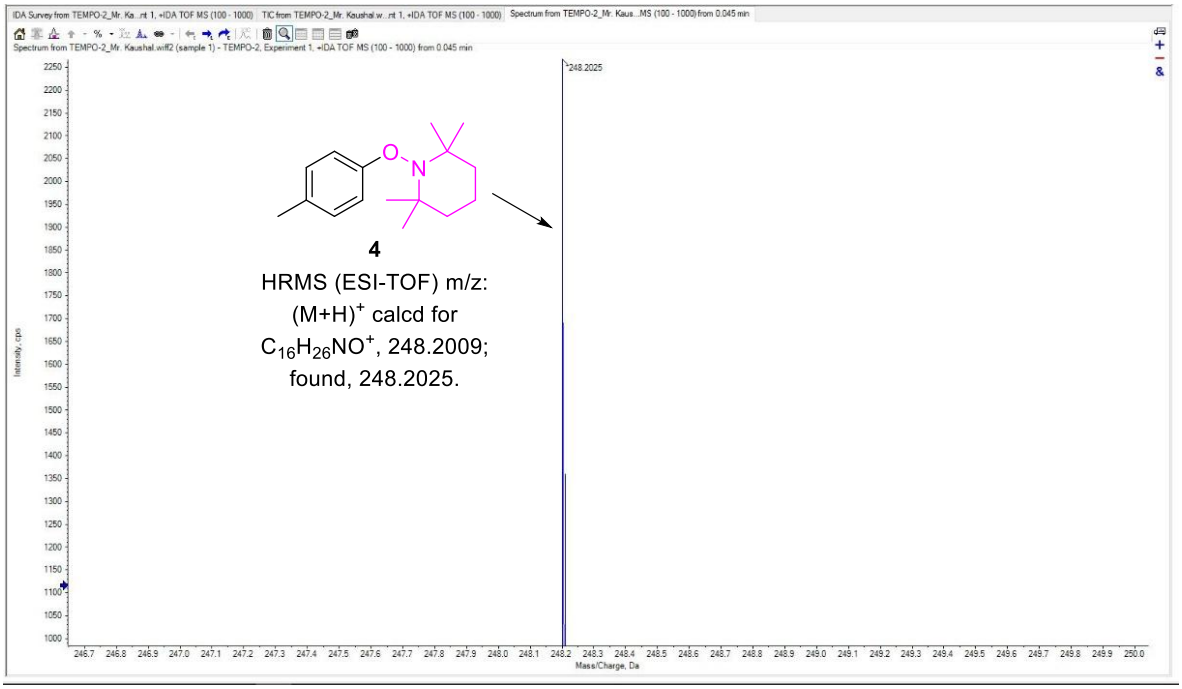
^{1}H NMR (500 MHz, $CDCl_3$)



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



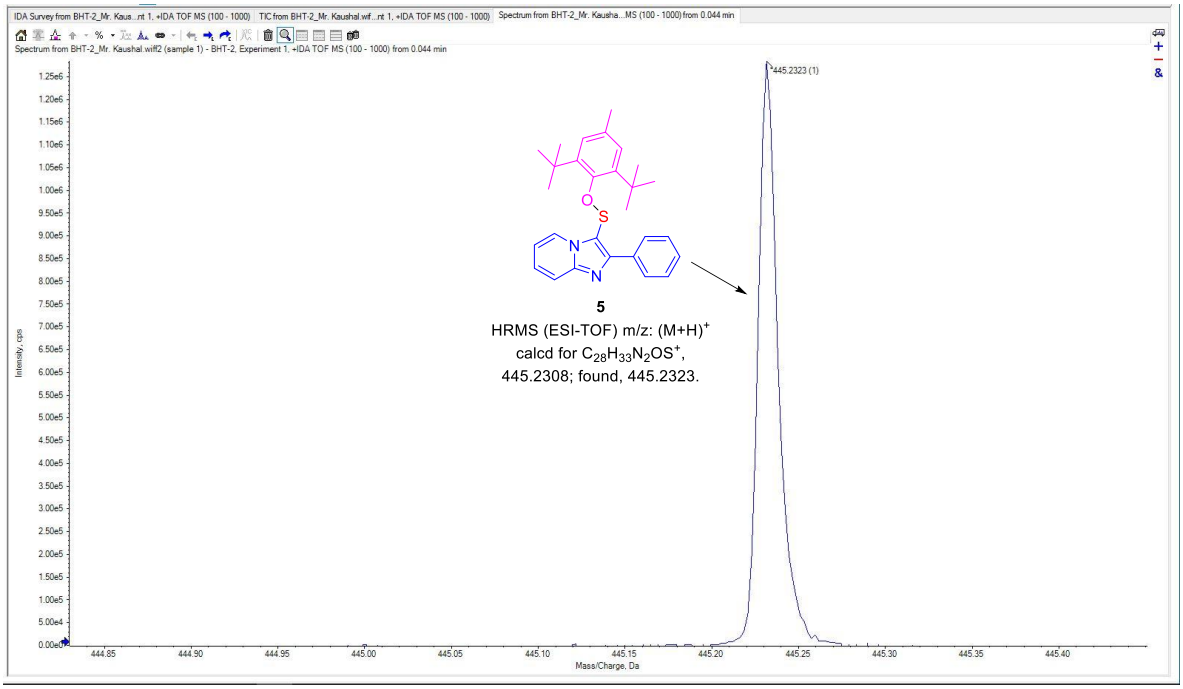
5. HRMS of the TEMPO Adduct 4



4

HRMS (ESI-TOF) m/z: $(M+H)^+$ calcd for $C_{16}H_{26}NO^+$, 248.2009; found, 248.2025.

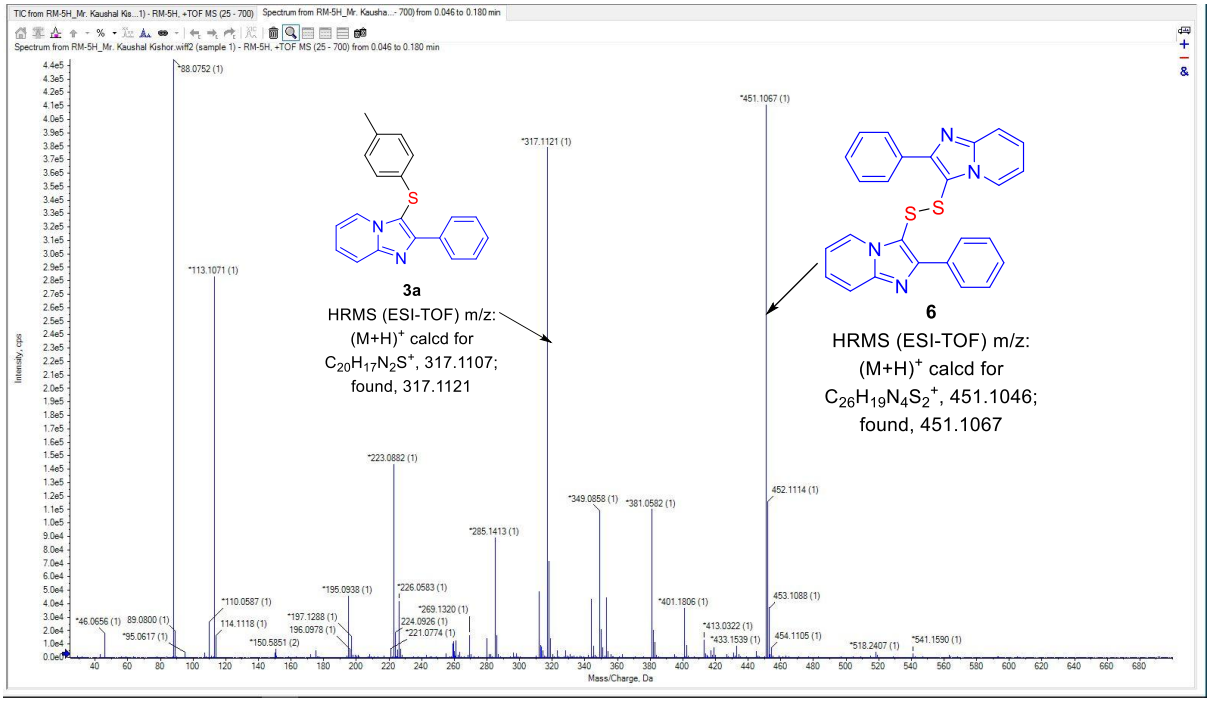
6. HRMS of the BHT Adduct 5



5

HRMS (ESI-TOF) m/z: $(M+H)^+$ calcd for $C_{28}H_{33}N_2OS^+$, 445.2308; found, 445.2323.

7. HRMS of the Intermediate 6, and the Product 3a



8. Crystallographic Data of the Product 3i

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

Specification: 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. The structure was solved using SHELXT-2018/2 and was refined by full-matrix least-squares procedures using the SHELXL-2019/3 software package through the OLEX2 suite.

Crystallized from	Chloroform
Empirical formula	$C_{20}H_{13}F_3N_2S$
Formula weight [g mol^{-1}]	370.38
Temperature [K]	293(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	8.7193(10)
b/Å	10.18290(10)
c/Å	18.9834(2)
α/°	90
β/°	90.138(10)
γ/°	90
V[$Å^3$]	1685.49(3)
Z	4
ρ[g/cm^3]	1.460
μ [mm^{-1}]	2.045
F(000)	760.0
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.318 to 136.118
Reflections collected	21745
Independent reflections	3052 [R_{int} = 0.0485, R_{sigma} = 0.0228]
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0355, wR_2 = 0.0941
Final R indexes [all data]	R_1 = 0.0391, wR_2 = 0.0970
Largest diff. peak/hole / e $Å^{-3}$	0.16/-0.23

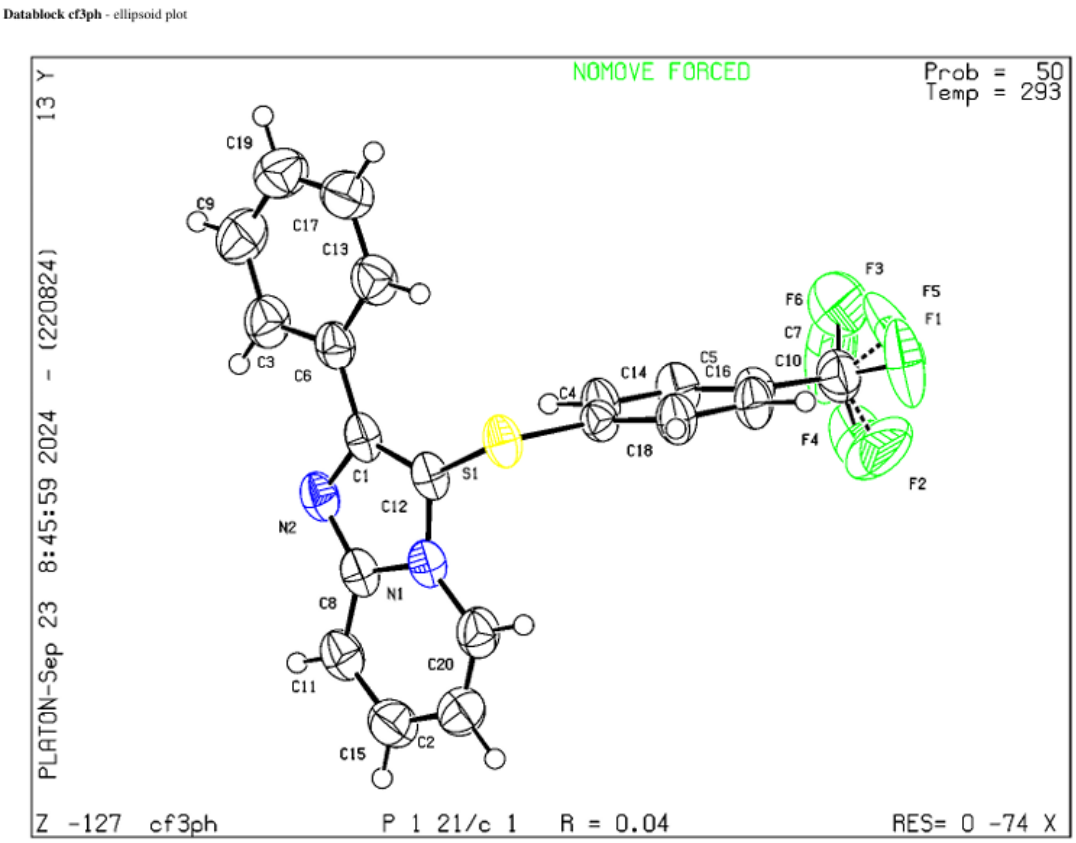


Figure S1: View of the molecular structure of the product **3i**. Displacement ellipsoids are drawn at the 50% probability level.

9. References

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