Electronic Supplementary Material (ESI) for Green Chemistry.

Iodine-catalyzed regioselective sulfenylation of imidazoheterocycles in PEG_{400}

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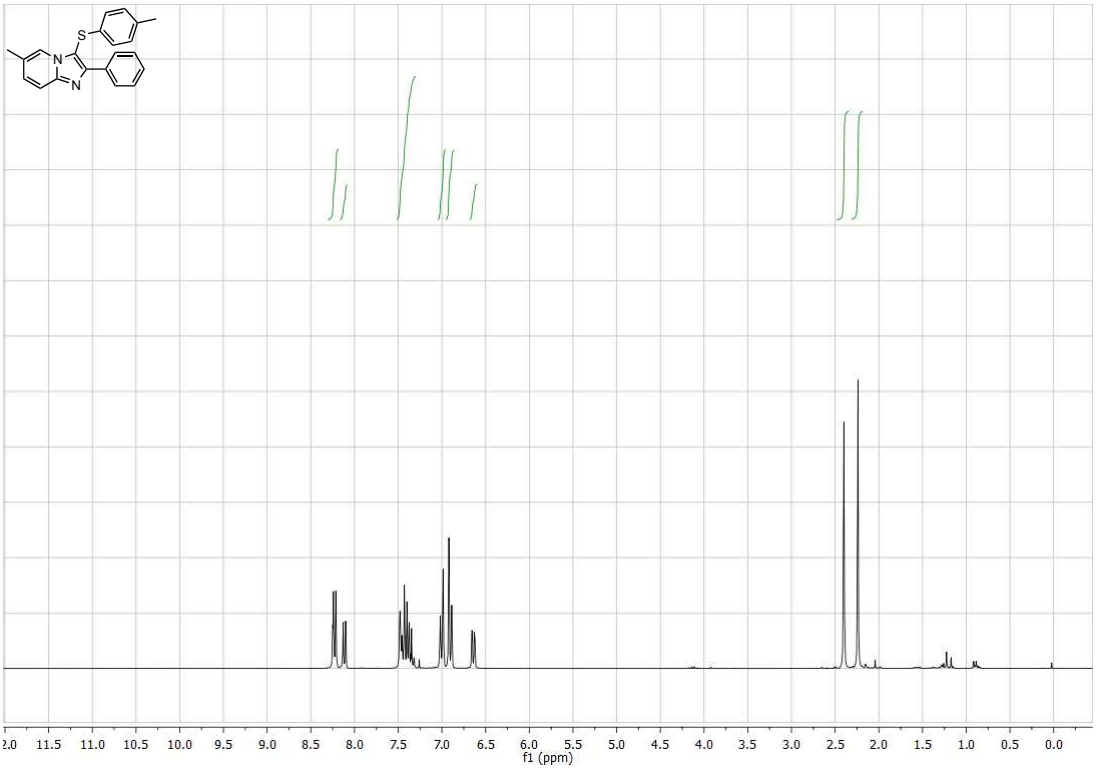
General information

All reagents were purchased from commercial suppliers and were used without further purification and imidazoheterocycles were synthetized following the procedure reported in the literature.[i] The reactions were monitored by thin-layer chromatography (TLC) analysis using silica gel (60 F254) plates. Compounds were visualized by UV irradiation. Flash column chromatography was performed on silica gel 60 (230-400 mesh, 0.040-0.063 mm). Melting points (mp [°C]) were taken on samples in open capillary tubes and are uncorrected. The infrared spectra of compounds were recorded on a Thermo Scientific Nicolet iS10. ^{1}H and ^{13}C NMR spectra were recorded on a Brüker spectrometer at 250 MHz (^{13}C, 62.9 MHz). Chemical shifts are given in parts per million from tetramethylsilane (TMS) as internal standard. The following abbreviations are used for the proton spectra multiplicities: b : broad, s: singlet, d: doublet, t: triplet, q: quartet, p: pentuplet, m: multiplet. Coupling constants (*J*) are reported in Hertz (Hz). High-resolution mass spectra (HRMS (ESI)) were performed on a Maxis Bruker 4G by the "Federation de Recherche" ICOA/CBM (FR2708) platform.

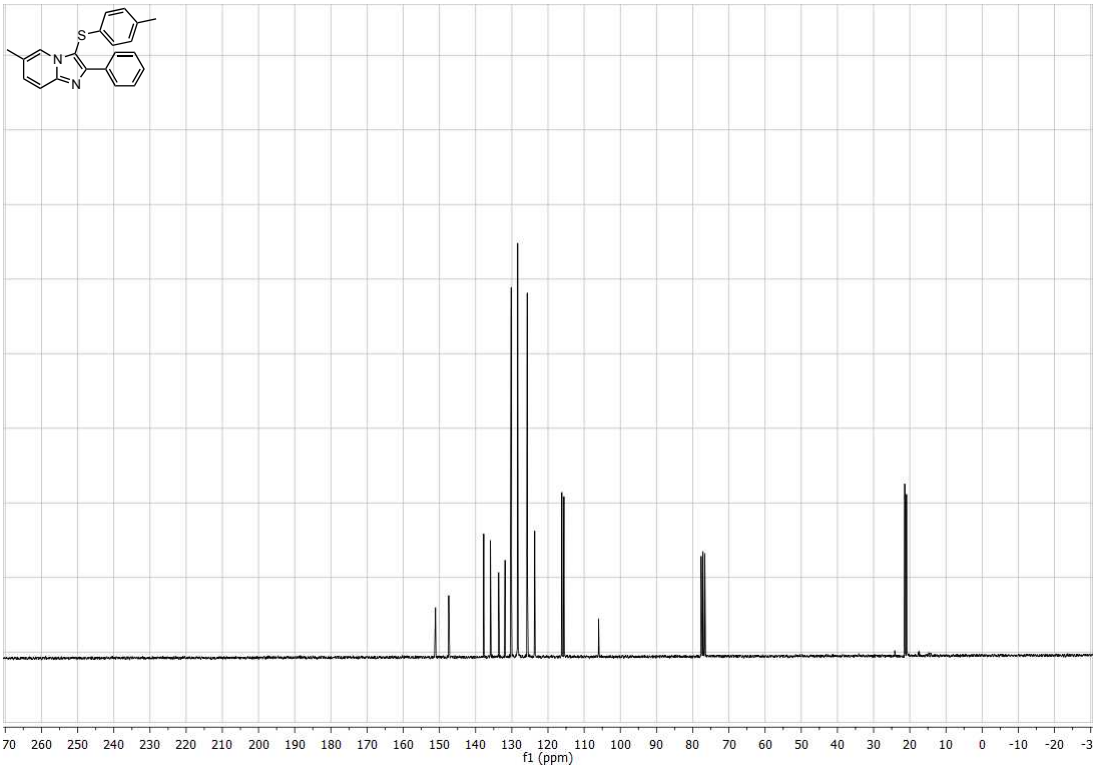
General procedure for the sulfenylation of imidazoheterocycles

Imidazoheterocycles (0.5 mmol), thiophenol (0.55 mmol) were dissolved in PEG_{400} (1 mL). Hydrogen peroxide (0.55 mmol) with iodine (13 mg, 0.05 mmol) were next added before heating up to 50 °C for the required time. After completion the reaction mixture was diluted in EtOAc (20 mL). The organic phase was washed with a saturated solution of sodium carbonate (3 x 10 mL) and sodium thiosulfate (10 mL), dried with $MgSO_4$ and concentrated under reduced pressure. The crude material was purified by flash chromatography on silica gel to provide the expected product.

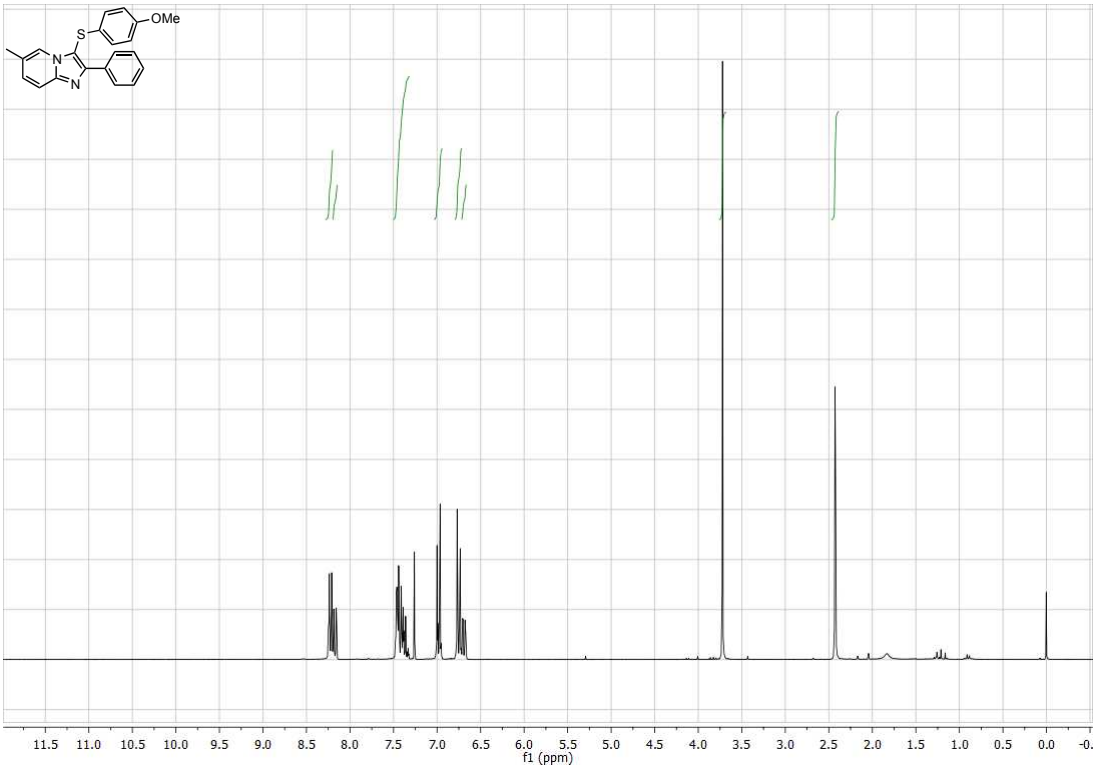
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 6-methyl-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3a**)



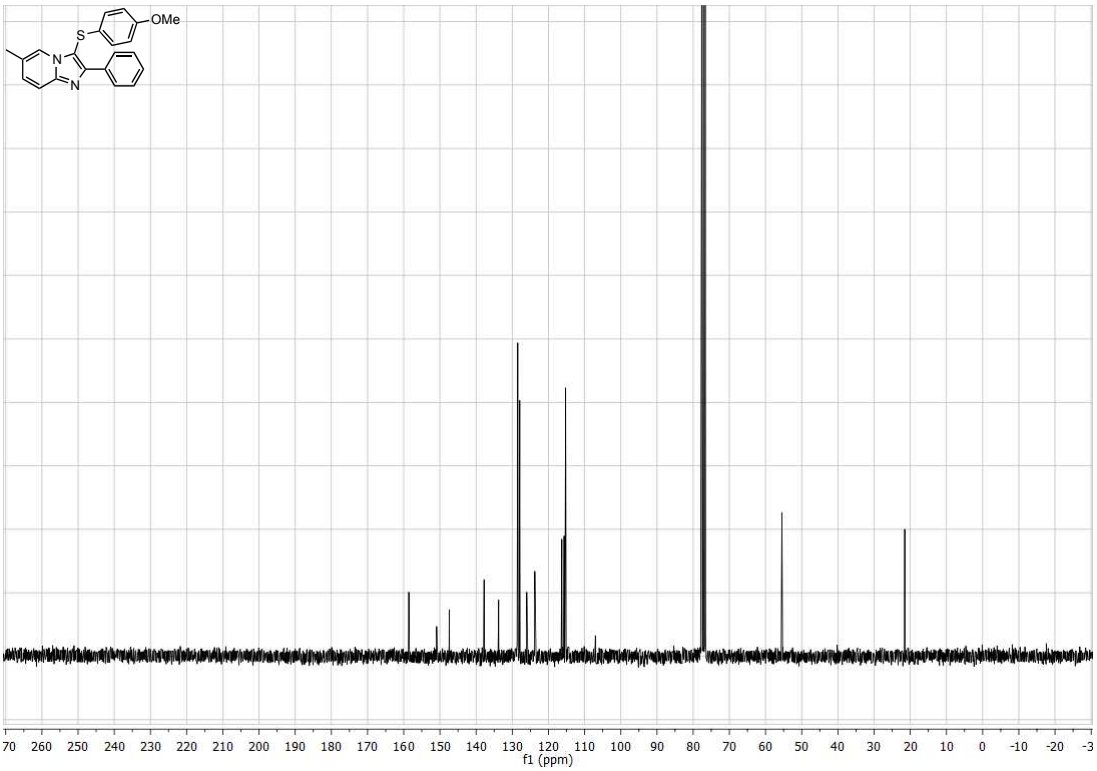
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 6-methyl-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3a**)



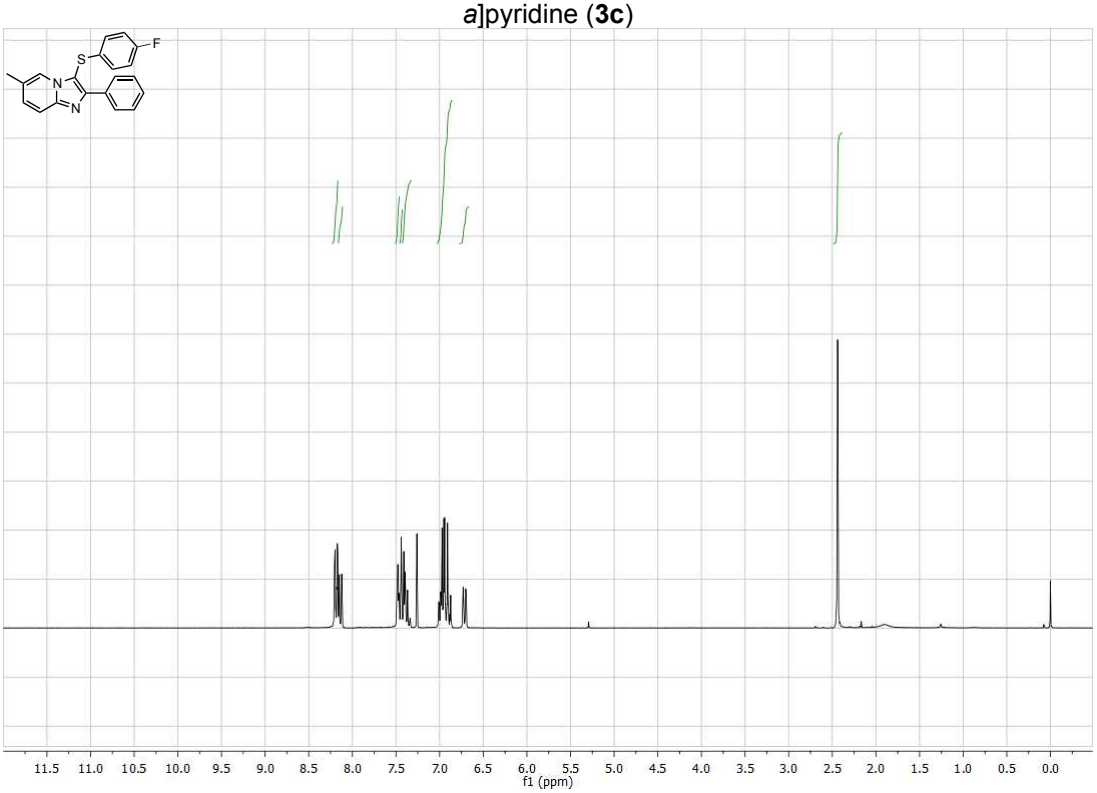
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 3-((4-methoxyphenyl)thio)-6-methyl-2-phenylimidazo[1,2-*a*]pyridine (**3b**)



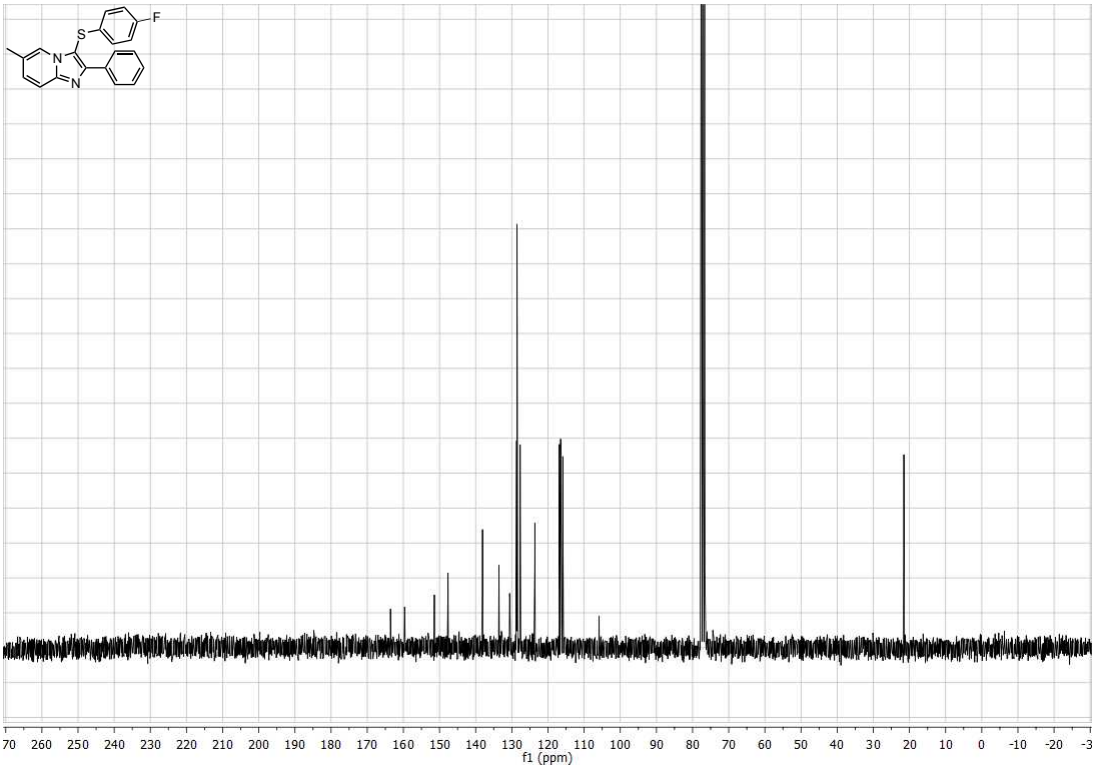
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 3-((4-methoxyphenyl)thio)-6-methyl-2-phenylimidazo[1,2-*a*]pyridine (**3b**)



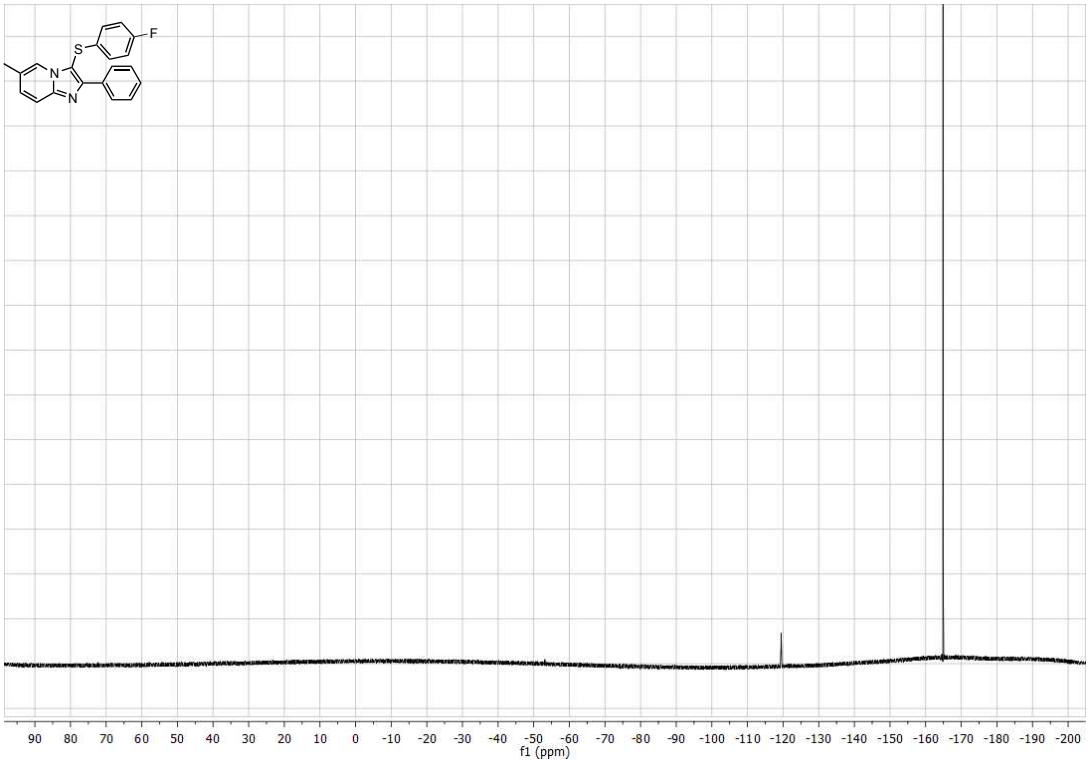
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 3-((4-fluorophenyl)thio)-6-methyl-2-phenylimidazo[1,2-*a*]pyridine (**3c**)



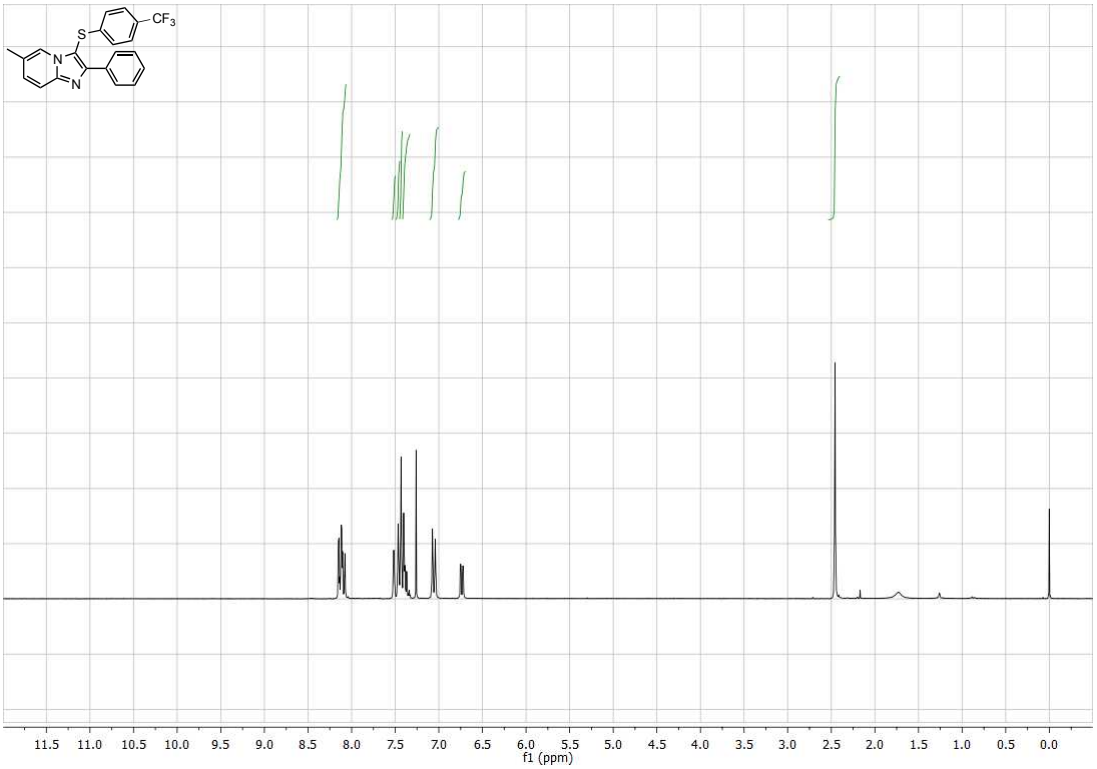
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 3-((4-fluorophenyl)thio)-6-methyl-2-phenylimidazo[1,2-*a*]pyridine (**3c**)



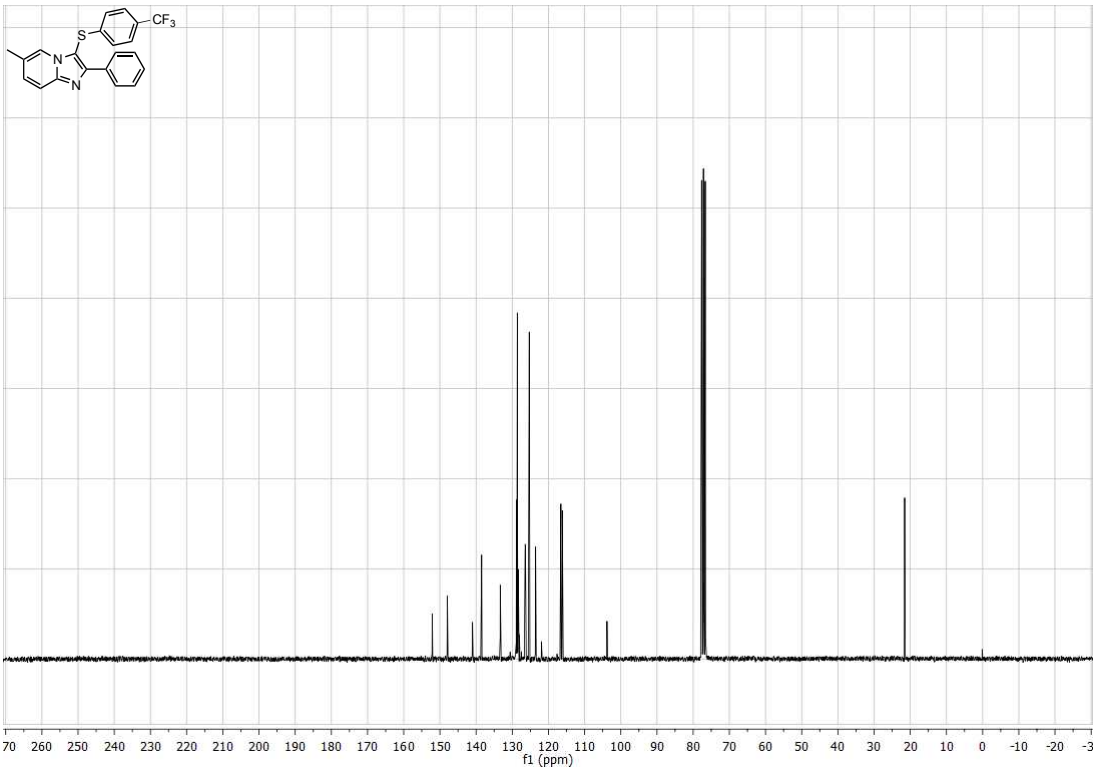
^{19}F NMR ($CDCl_3$, 235 MHz) spectrum of 3-((4-fluorophenyl)thio)-6-methyl-2-phenylimidazo[1,2-*a*]pyridine (**3c**)



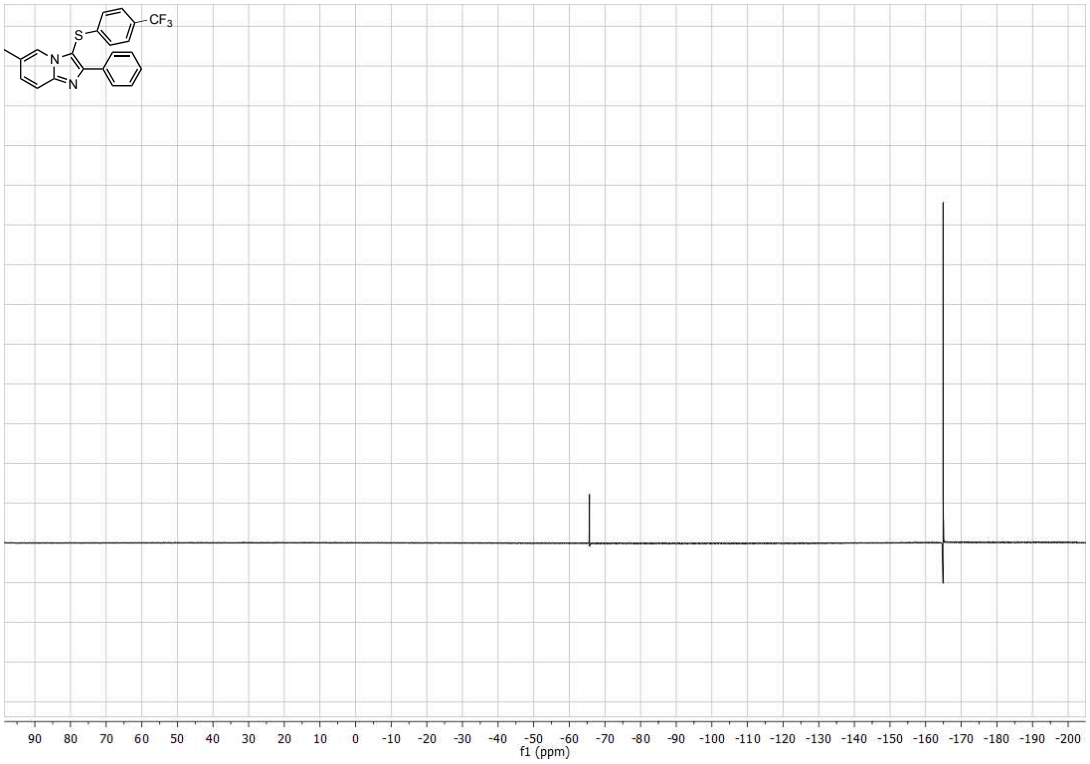
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 6-methyl-2-phenyl-3-((4-(trifluoromethyl)phenyl)thio)imidazo[1,2-*a*]pyridine (**3d**)



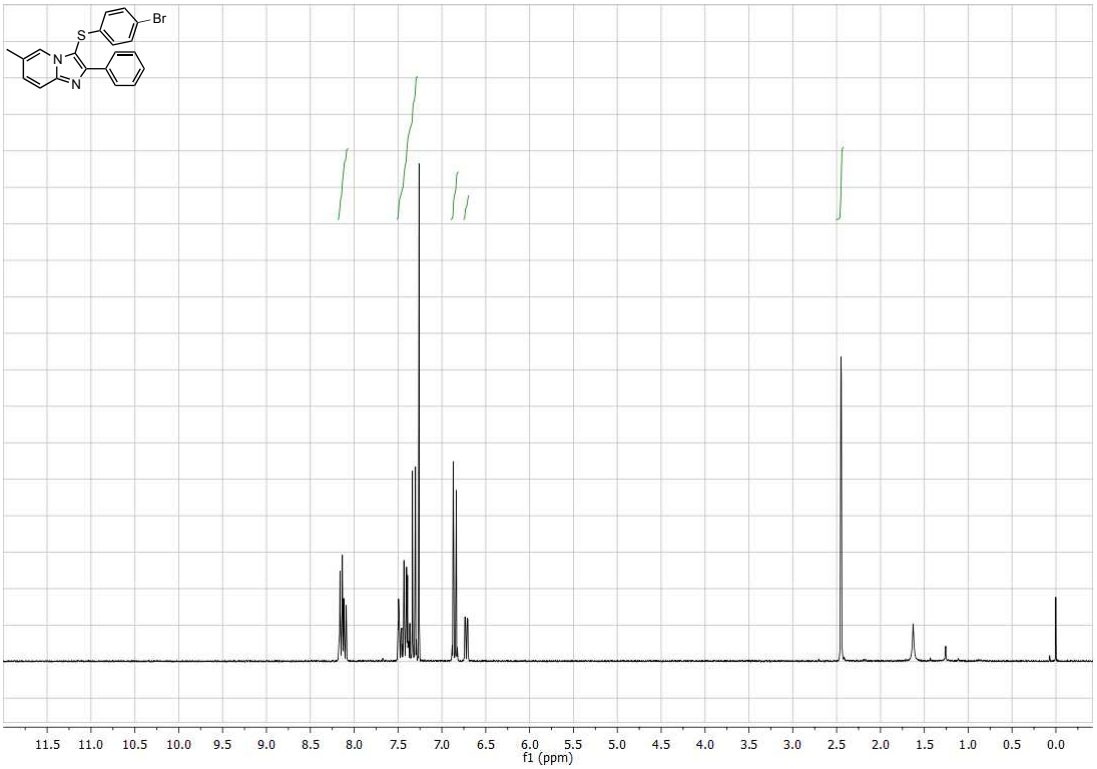
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 6-methyl-2-phenyl-3-((4-(trifluoromethyl)phenyl)thio)imidazo[1,2-*a*]pyridine (**3d**)



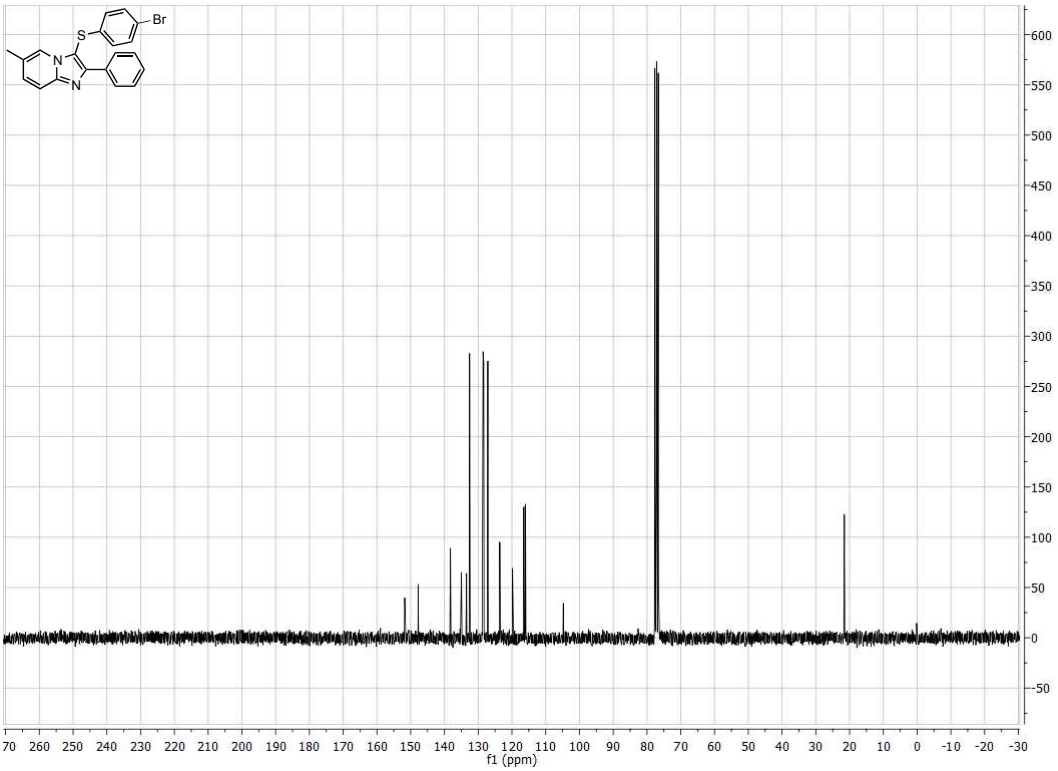
^{19}F (235 MHz, $CDCl_3$) spectrum of 6-methyl-2-phenyl-3-((4-(trifluoromethyl)phenyl)thio)imidazo[1,2-*a*]pyridine (**3d**)



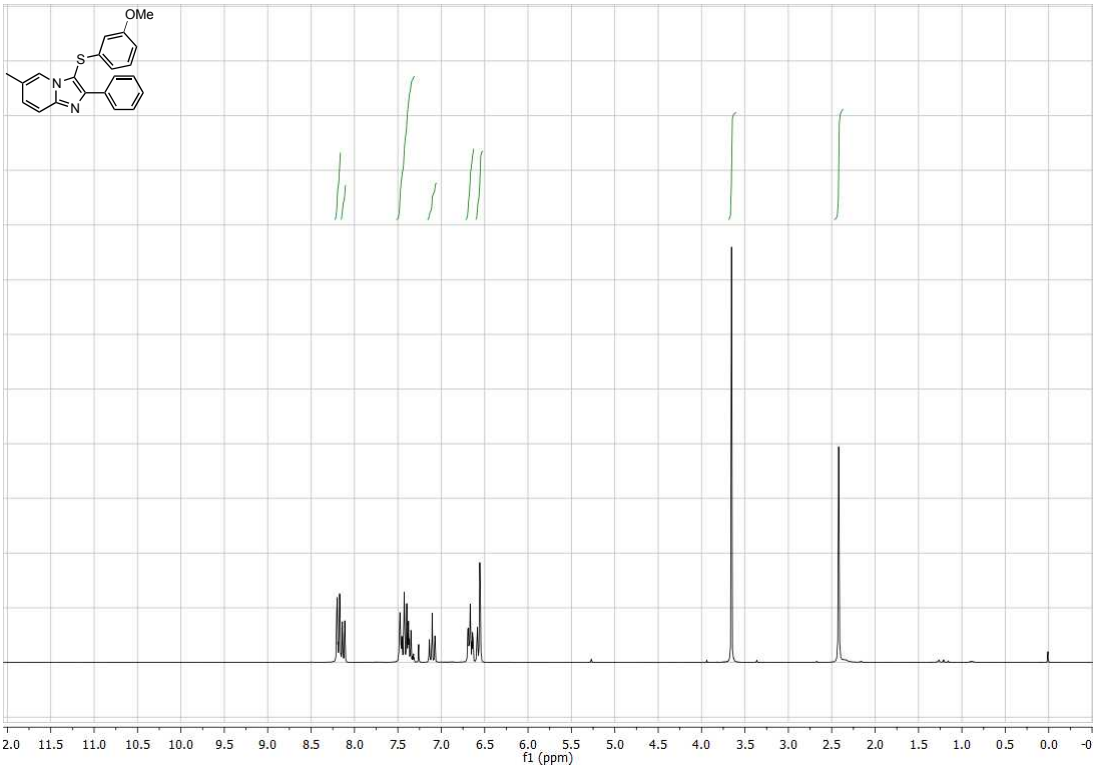
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 3-((4-bromophenyl)thio)-6-methyl-2-phenylimidazo[1,2-*a*]pyridine (**3e**)



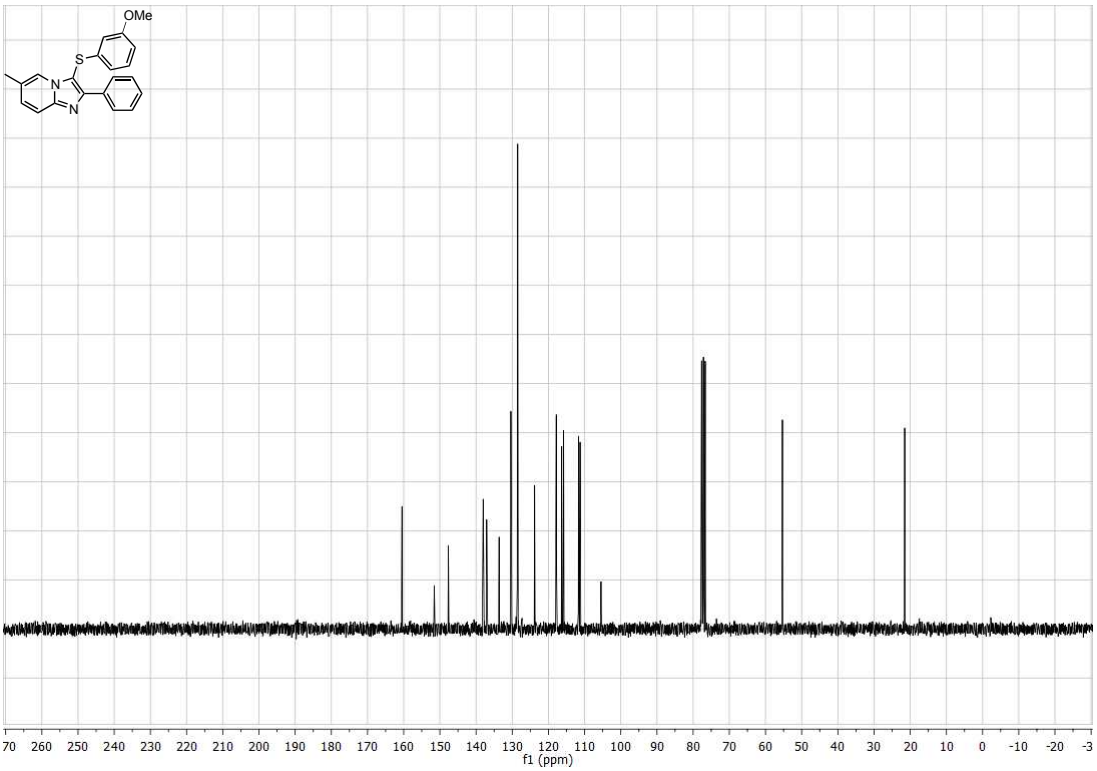
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 3-((4-bromophenyl)thio)-6-methyl-2-phenylimidazo[1,2-*a*]pyridine (**3e**)



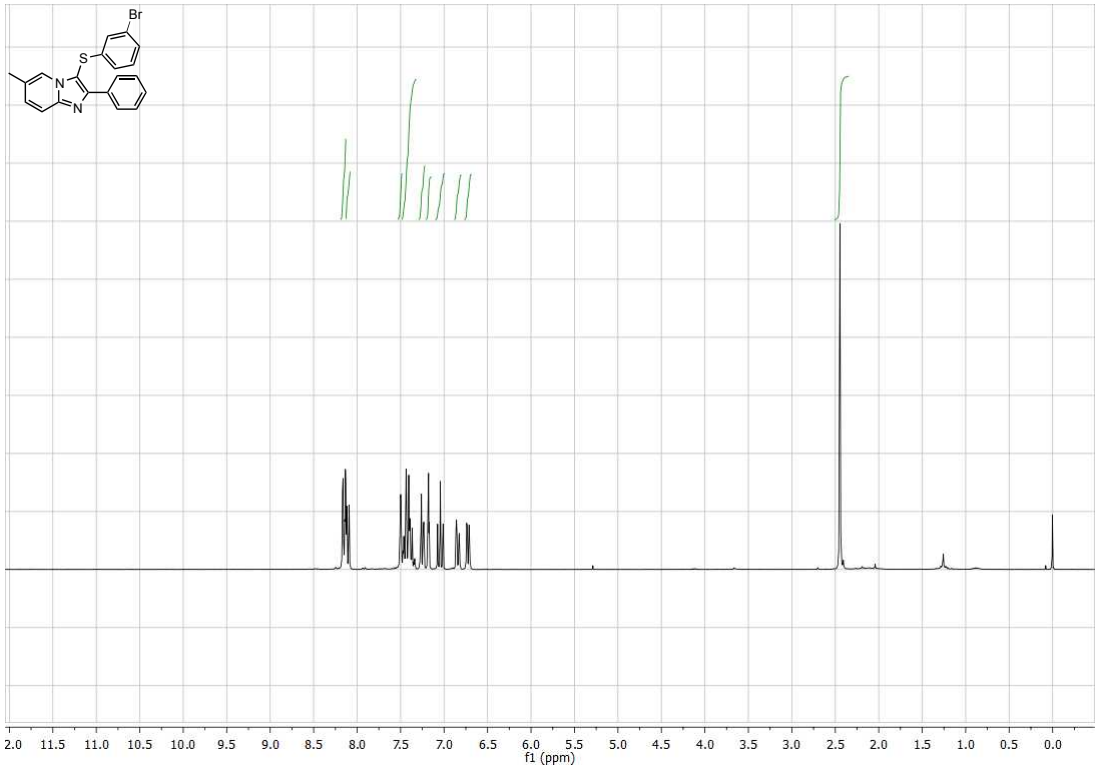
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 3-((3-methoxyphenyl)thio)-6-methyl-2-phenylimidazo[1,2-*a*]pyridine (**3f**)



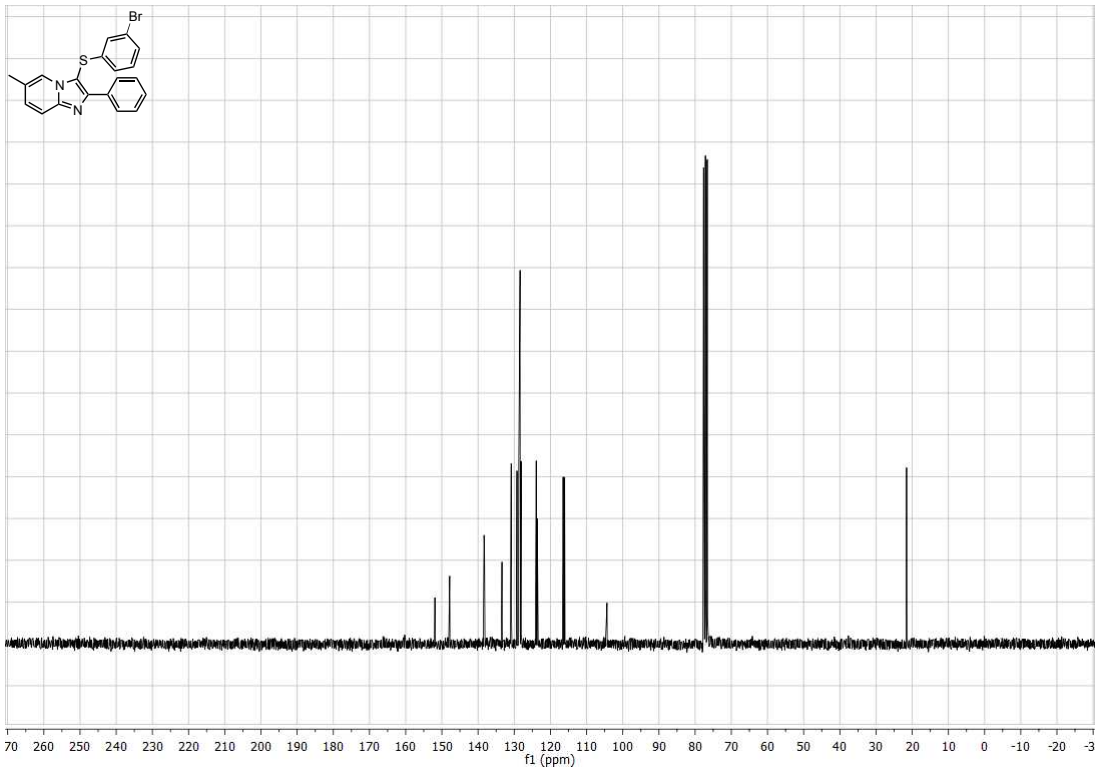
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 3-((3-methoxyphenyl)thio)-6-methyl-2-phenylimidazo[1,2-*a*]pyridine (**3f**)



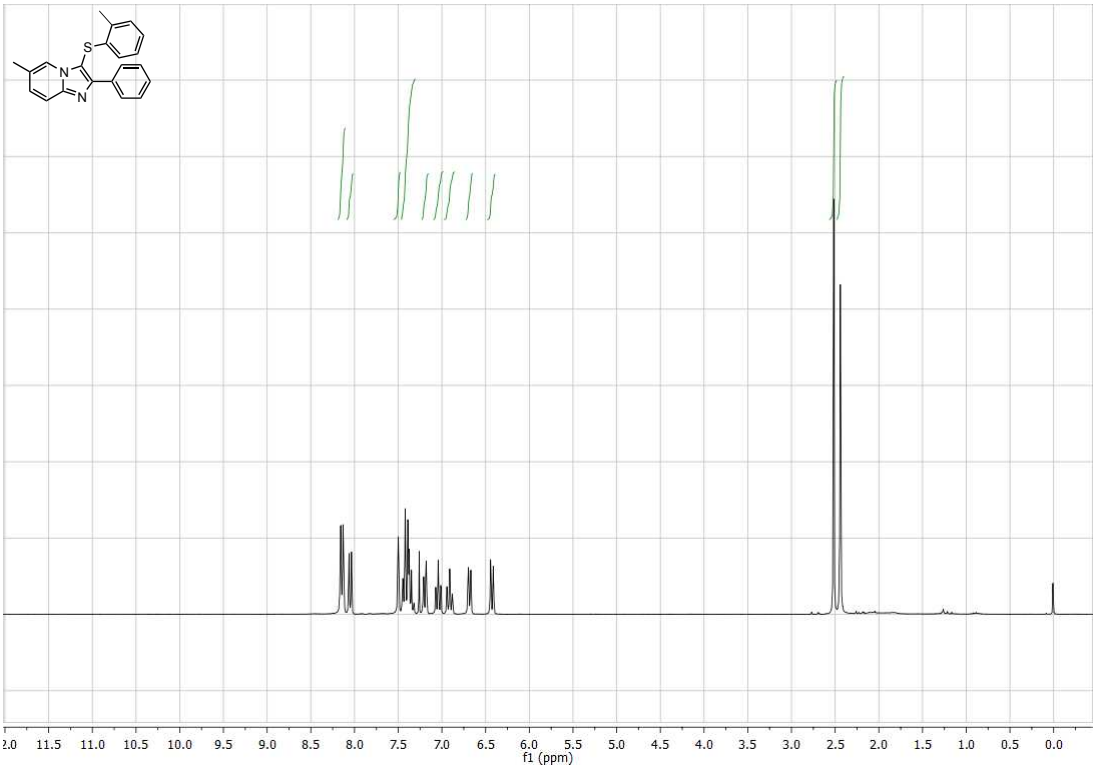
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 3-((3-bromophenyl)thio)-6-methyl-2-phenylimidazo[1,2-*a*]pyridine (**3g**)



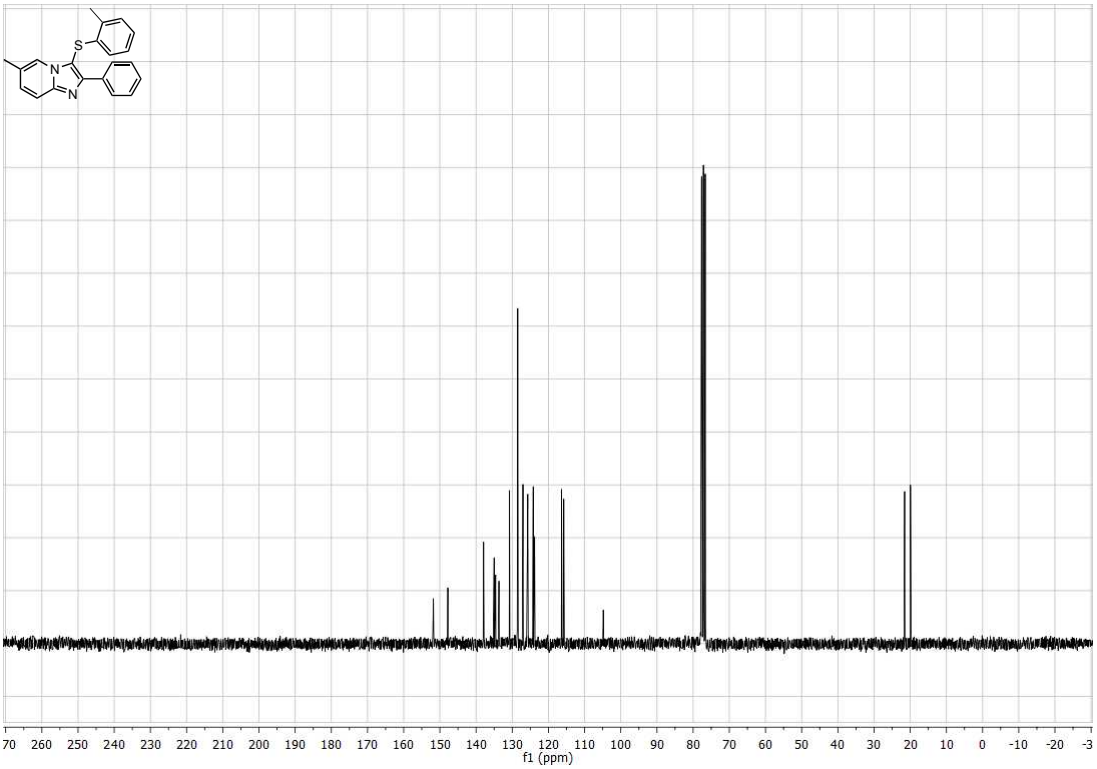
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 3-((3-bromophenyl)thio)-6-methyl-2-phenylimidazo[1,2-*a*]pyridine (**3g**)



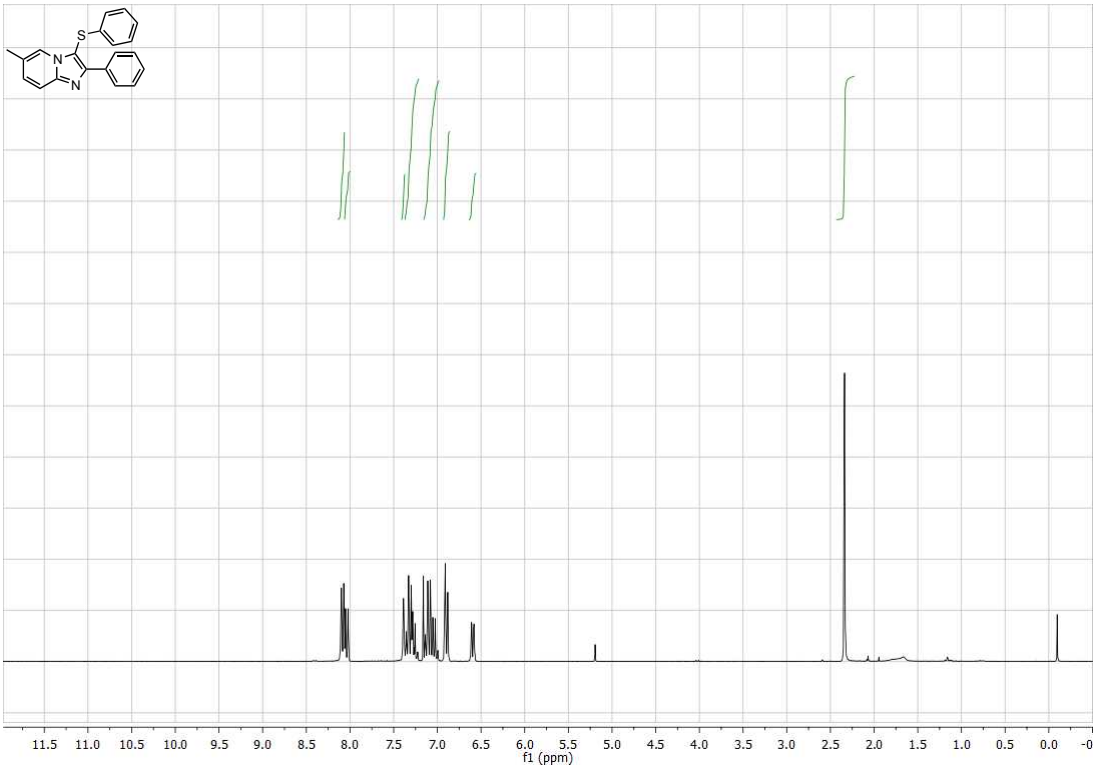
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 6-methyl-2-phenyl-3-(*o*-tolylthio)imidazo[1,2-*a*]pyridine (**3h**)



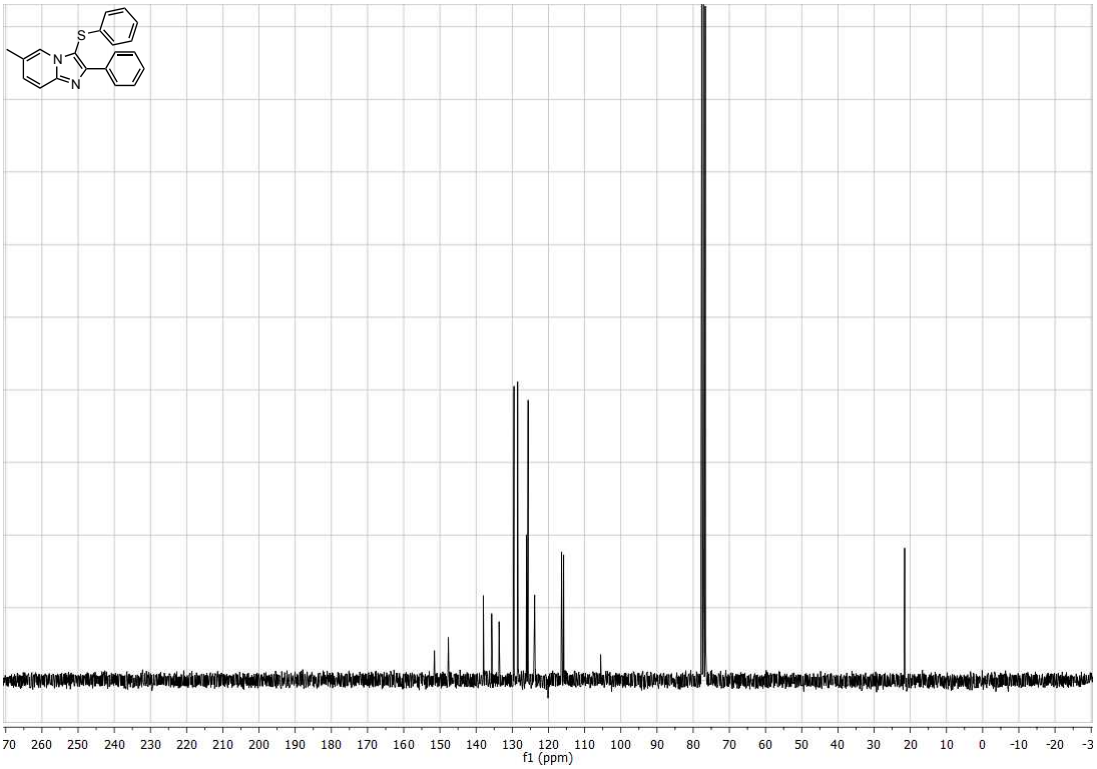
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 6-methyl-2-phenyl-3-(*o*-tolylthio)imidazo[1,2-*a*]pyridine (**3h**)



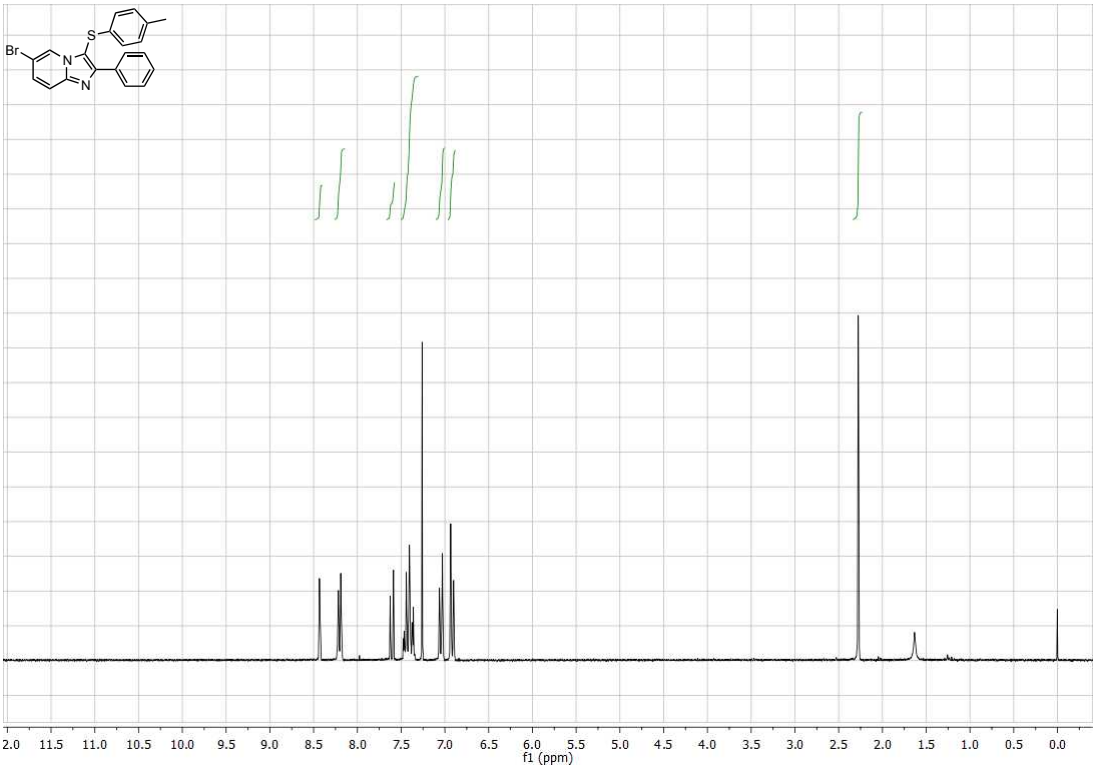
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 6-methyl-2-phenyl-3-(phenylthio)imidazo[1,2-*a*]pyridine (**3i**)



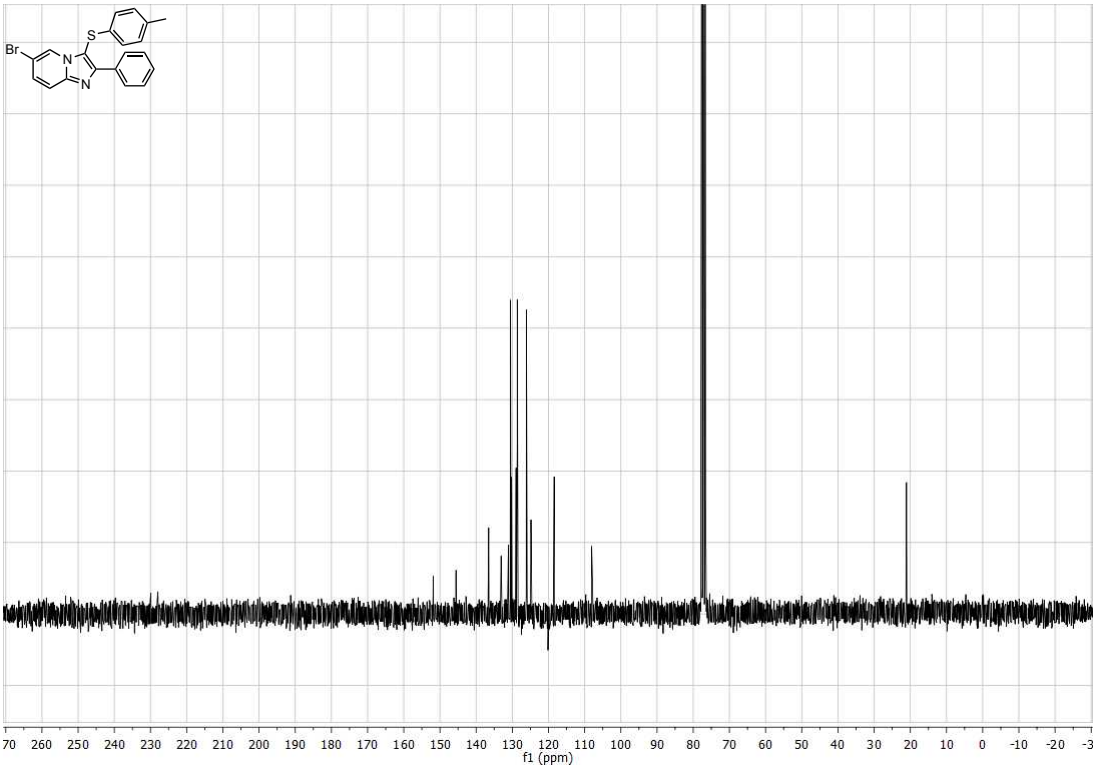
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 6-methyl-2-phenyl-3-(phenylthio)imidazo[1,2-*a*]pyridine (**3i**)



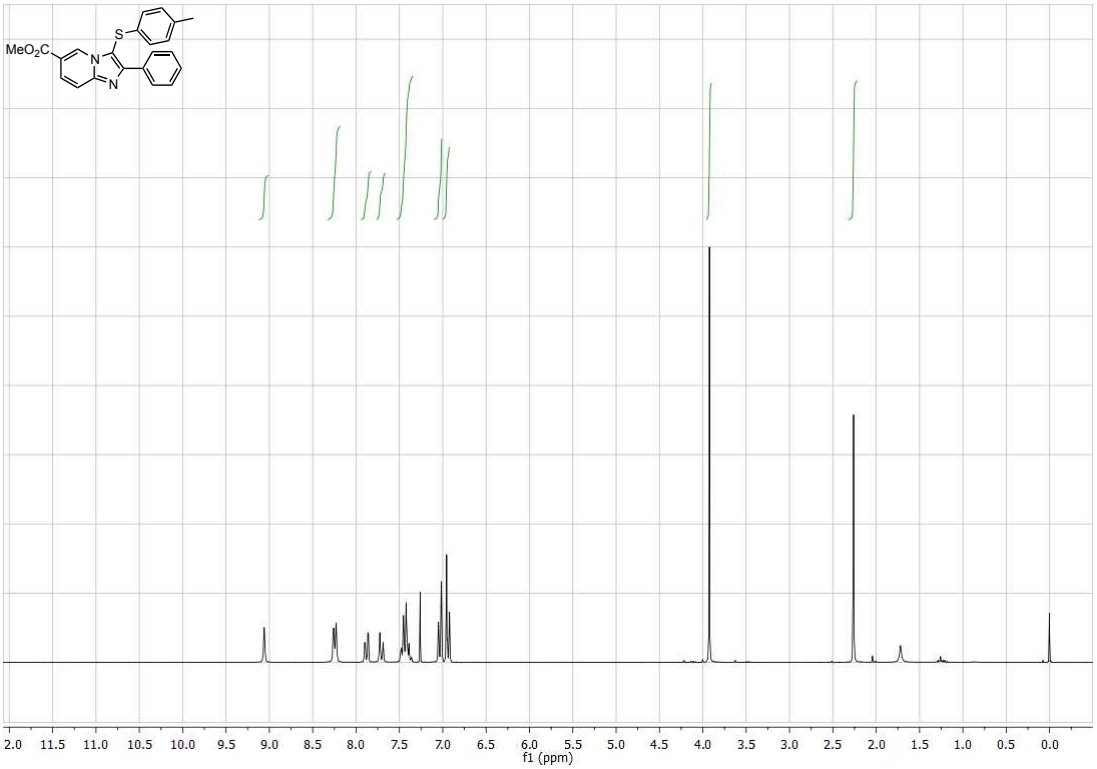
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 6-bromo-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3j**)



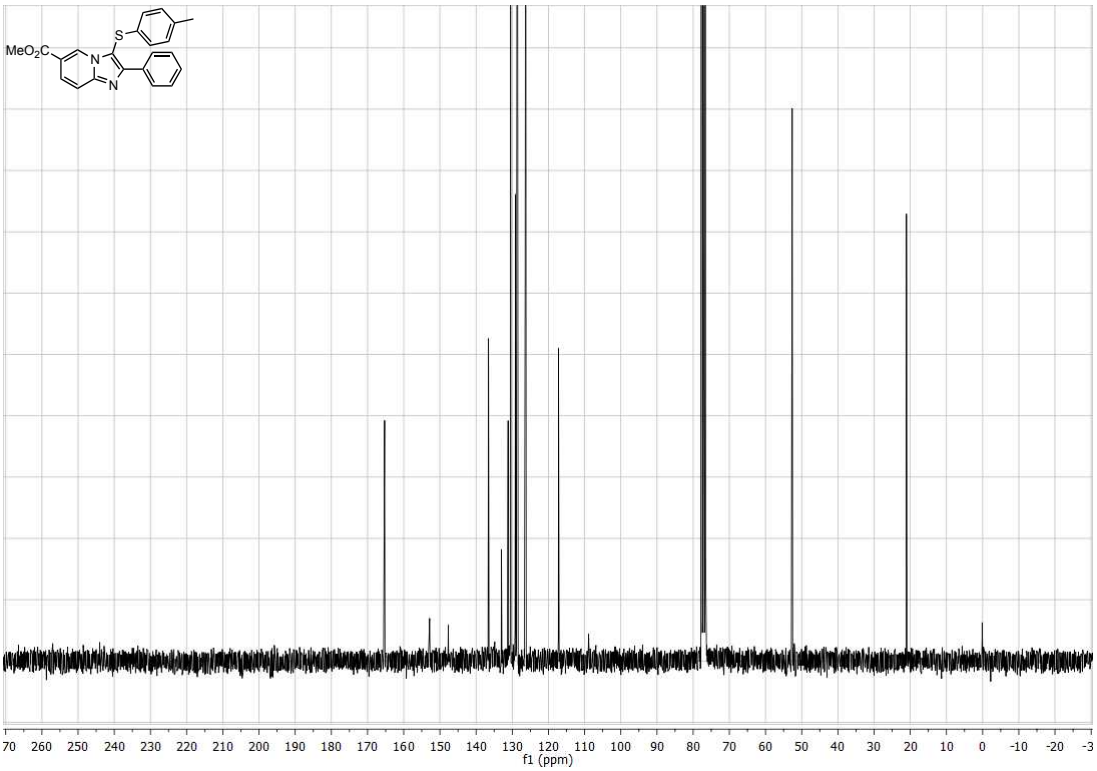
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 6-bromo-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3j**)



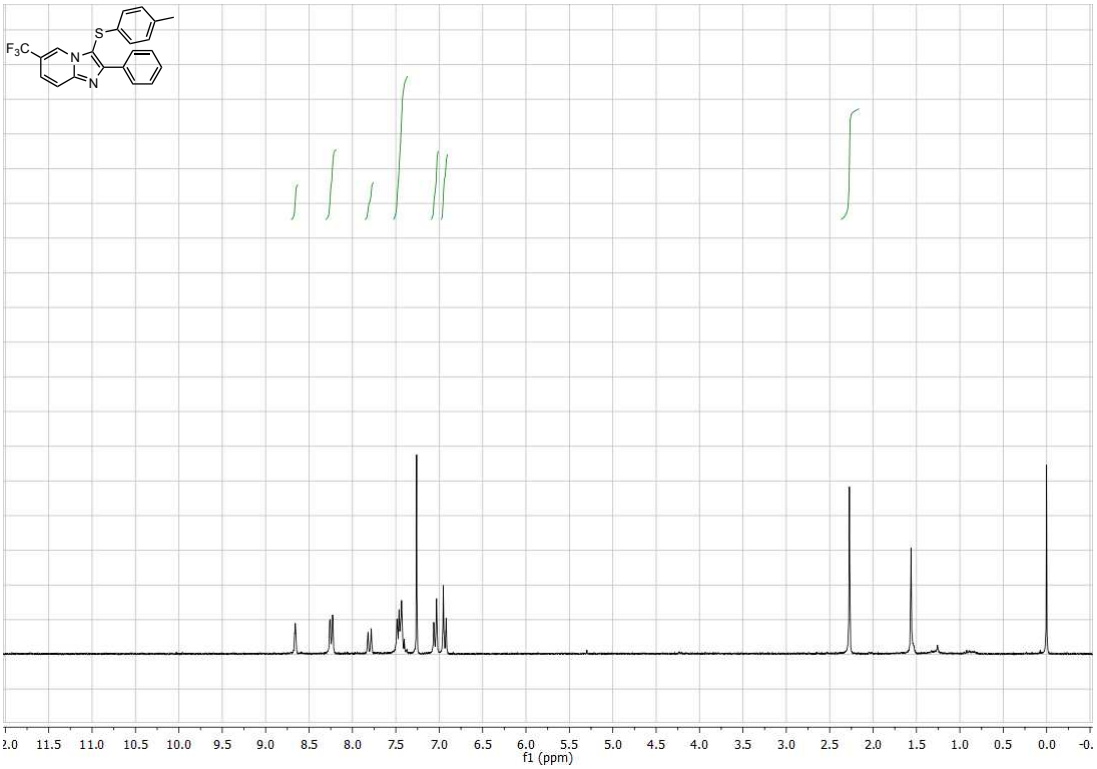
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of methyl 2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine-6-carboxylate (**3k**)



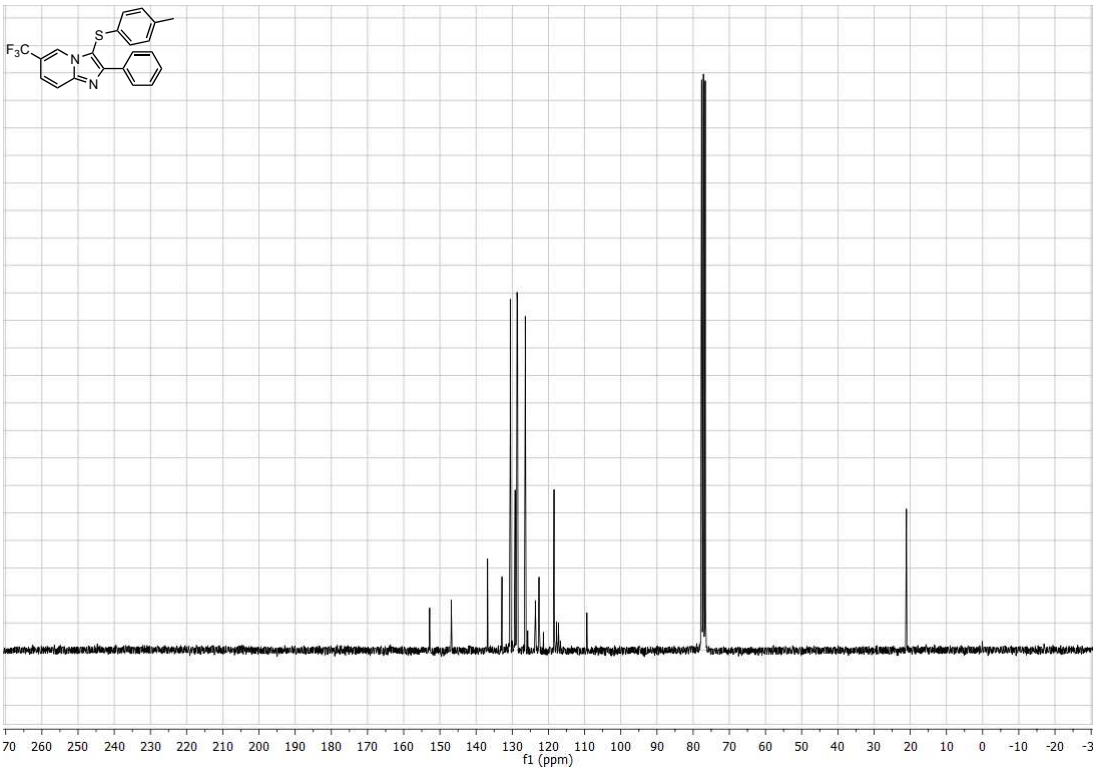
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of methyl 2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine-6-carboxylate (**3k**)



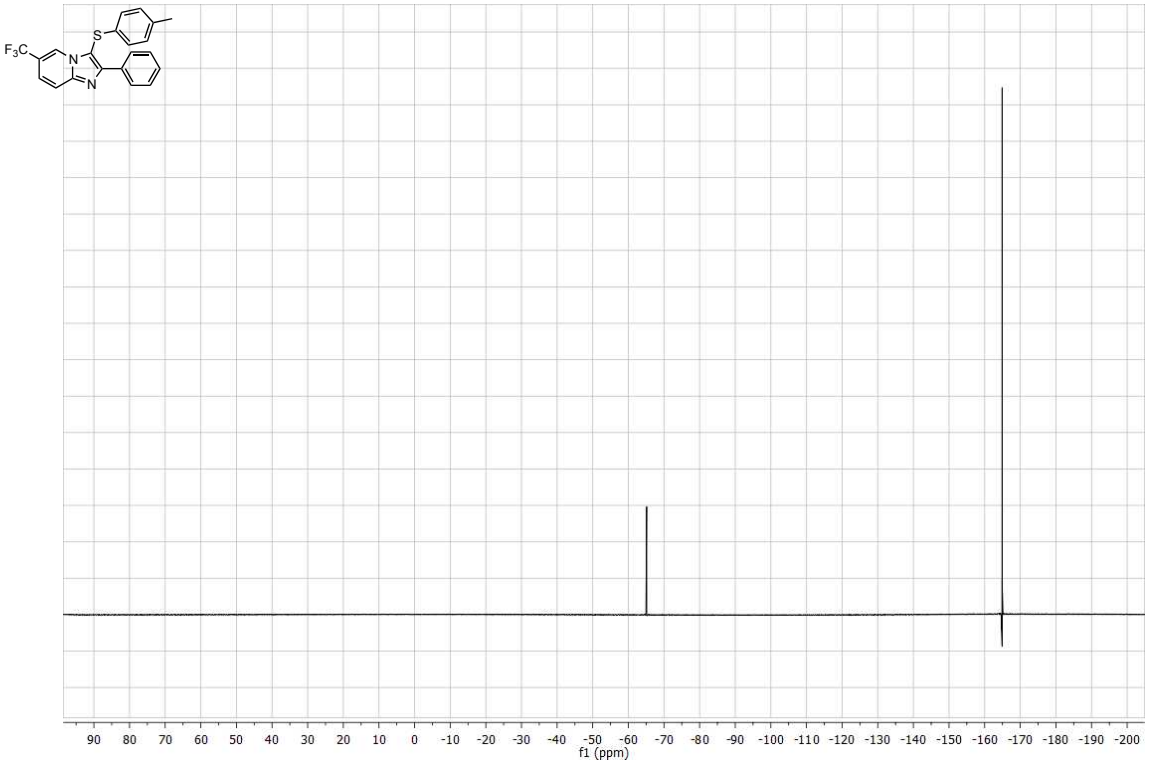
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 2-phenyl-3-(*p*-tolylthio)-6-(trifluoromethyl)imidazo[1,2-*a*]pyridine (**3l**)



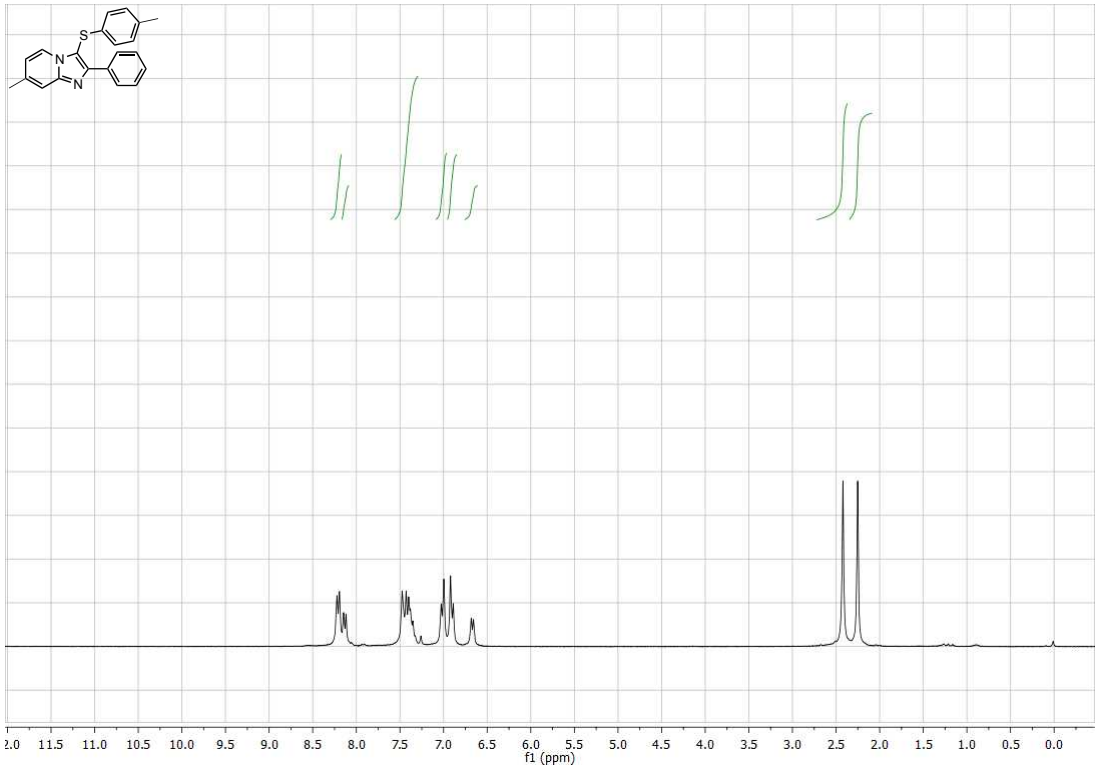
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 2-phenyl-3-(*p*-tolylthio)-6-(trifluoromethyl)imidazo[1,2-*a*]pyridine (**3l**)



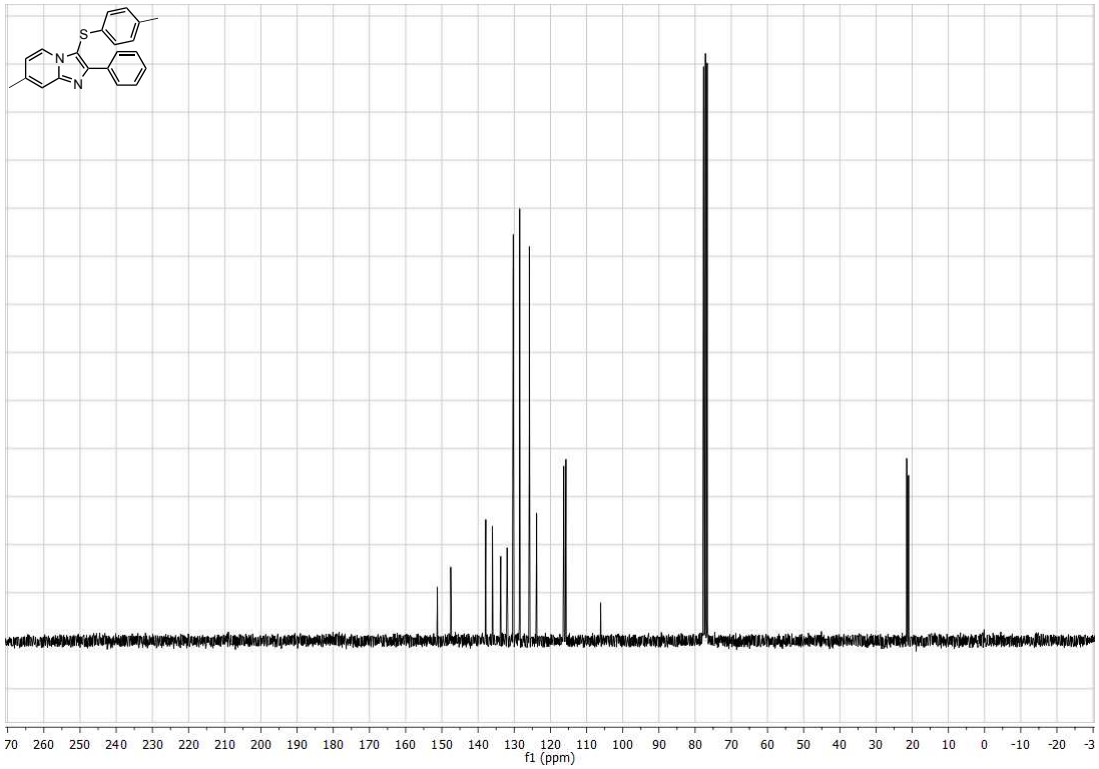
^{19}F (235 MHz, $CDCl_3$) spectrum of 2-phenyl-3-(*p*-tolylthio)-6-(trifluoromethyl)imidazo[1,2-*a*]pyridine (**3l**)



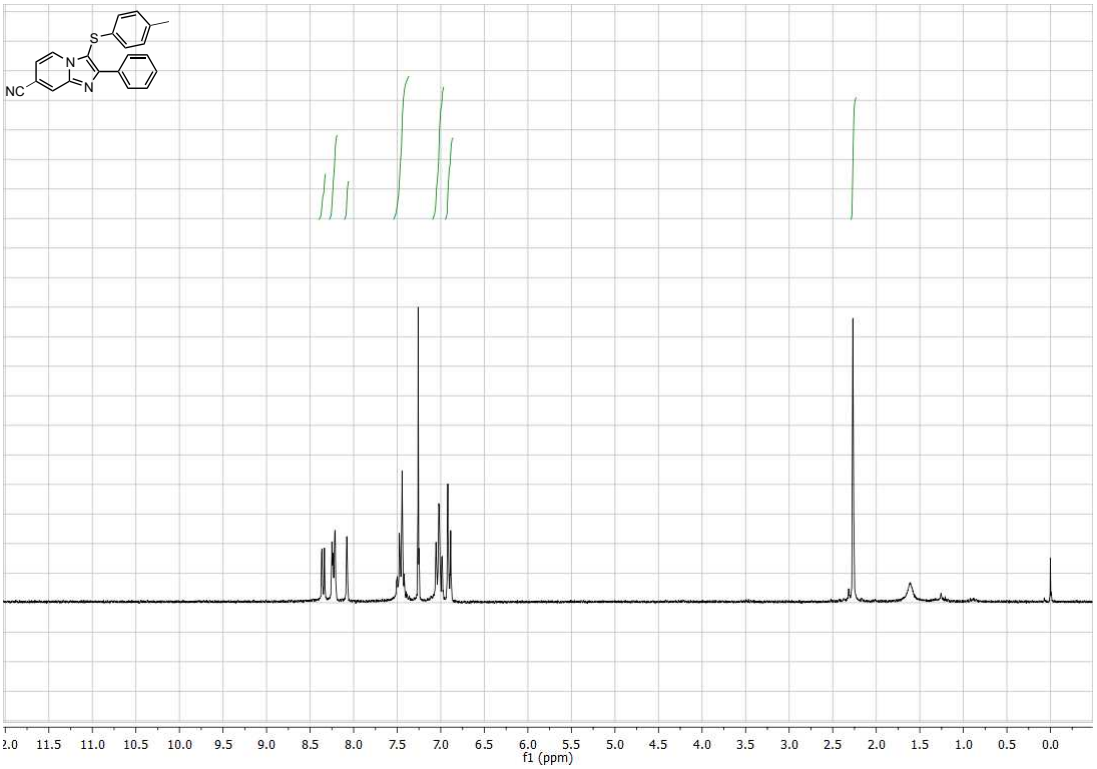
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 7-methyl-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3m**)



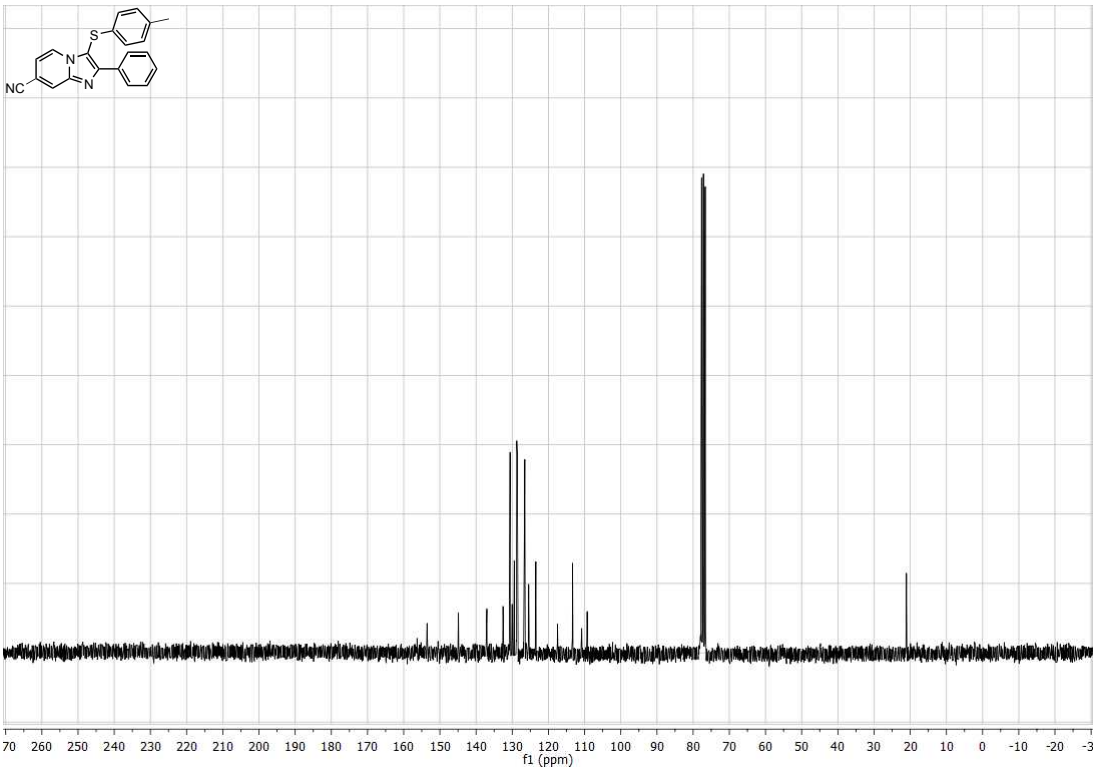
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 7-methyl-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3m**)



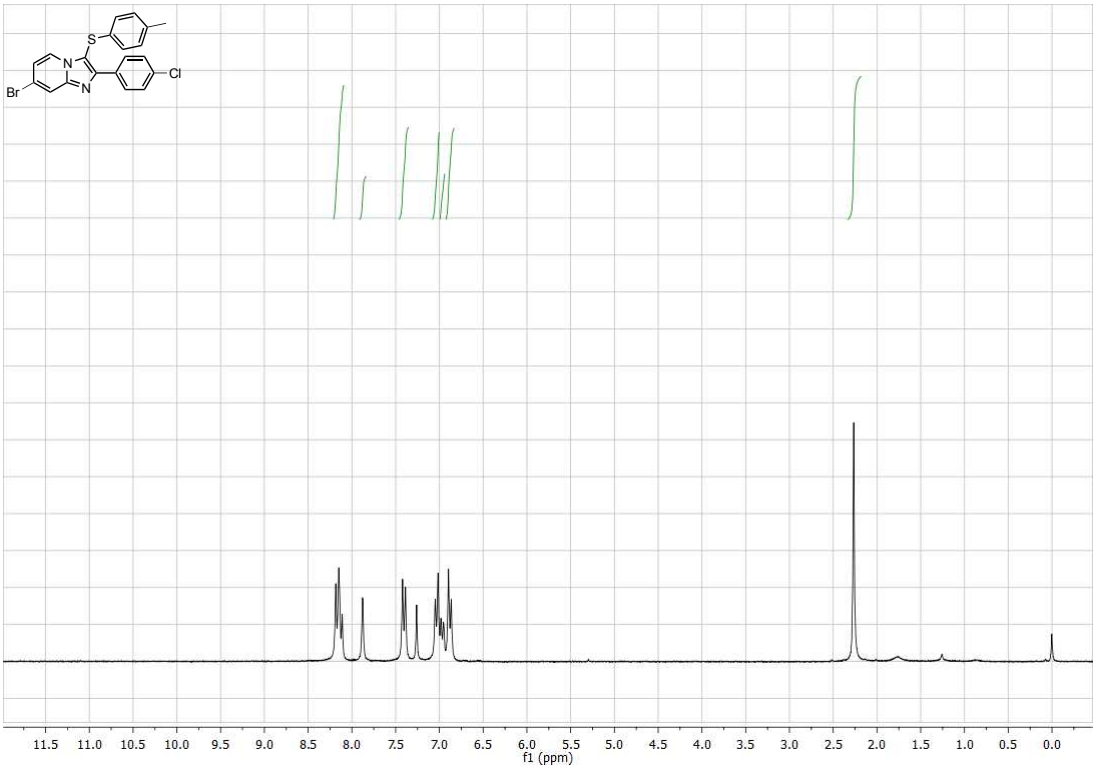
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine-7-carbonitrile (**3n**)



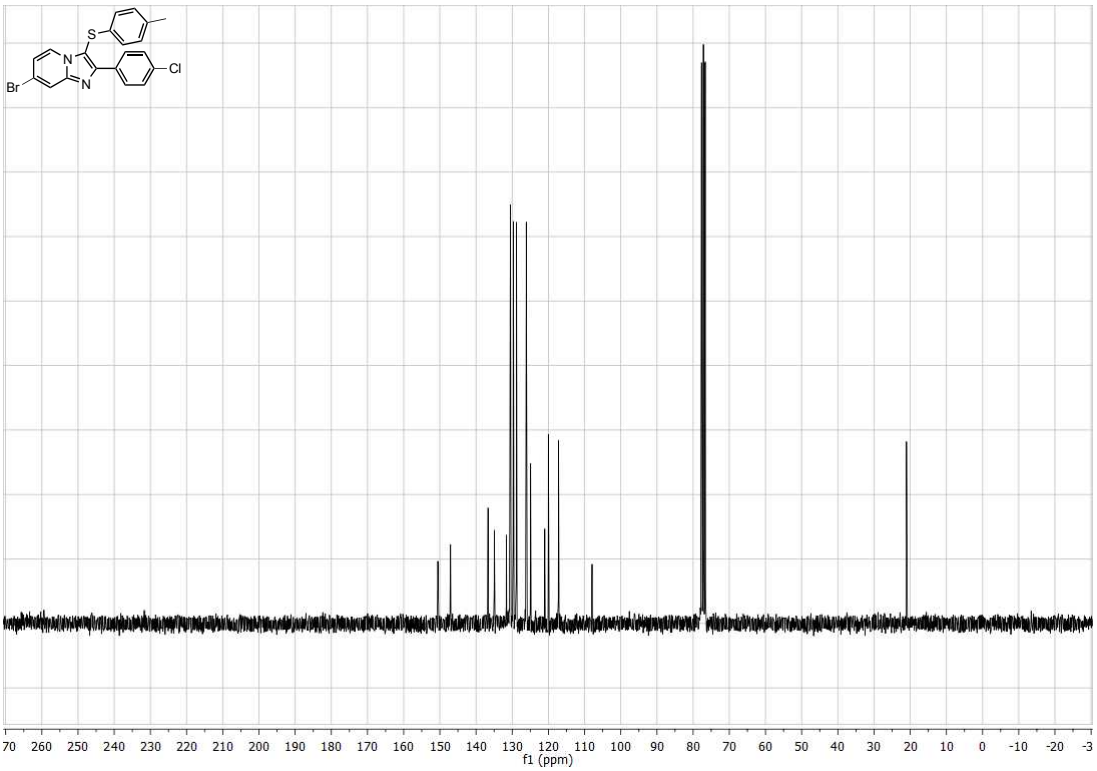
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine-7-carbonitrile (**3n**)



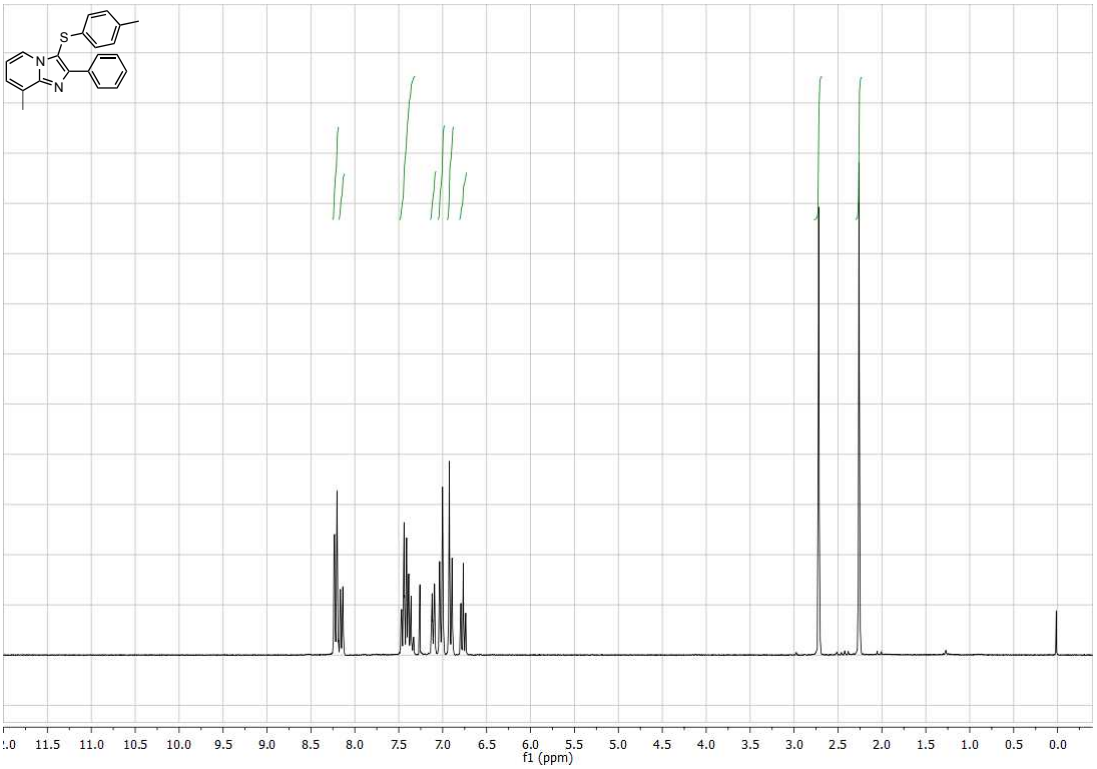
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 7-bromo-2-(4-chlorophenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3o**)



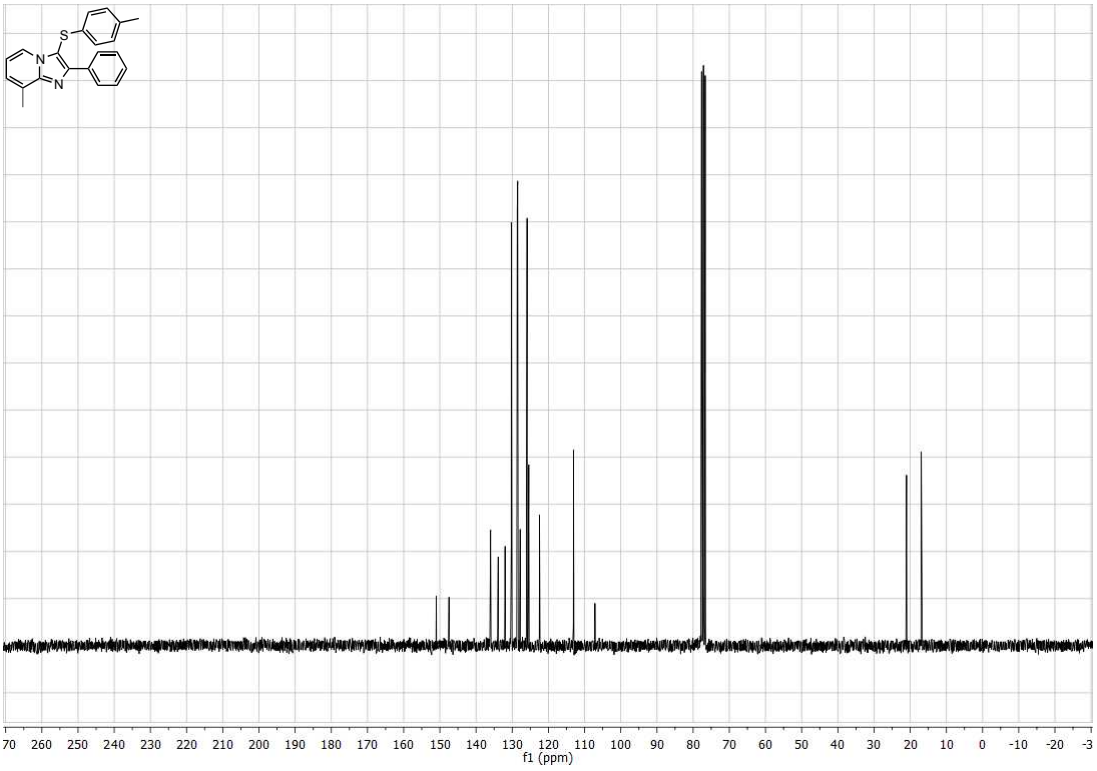
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 7-bromo-2-(4-chlorophenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3o**)



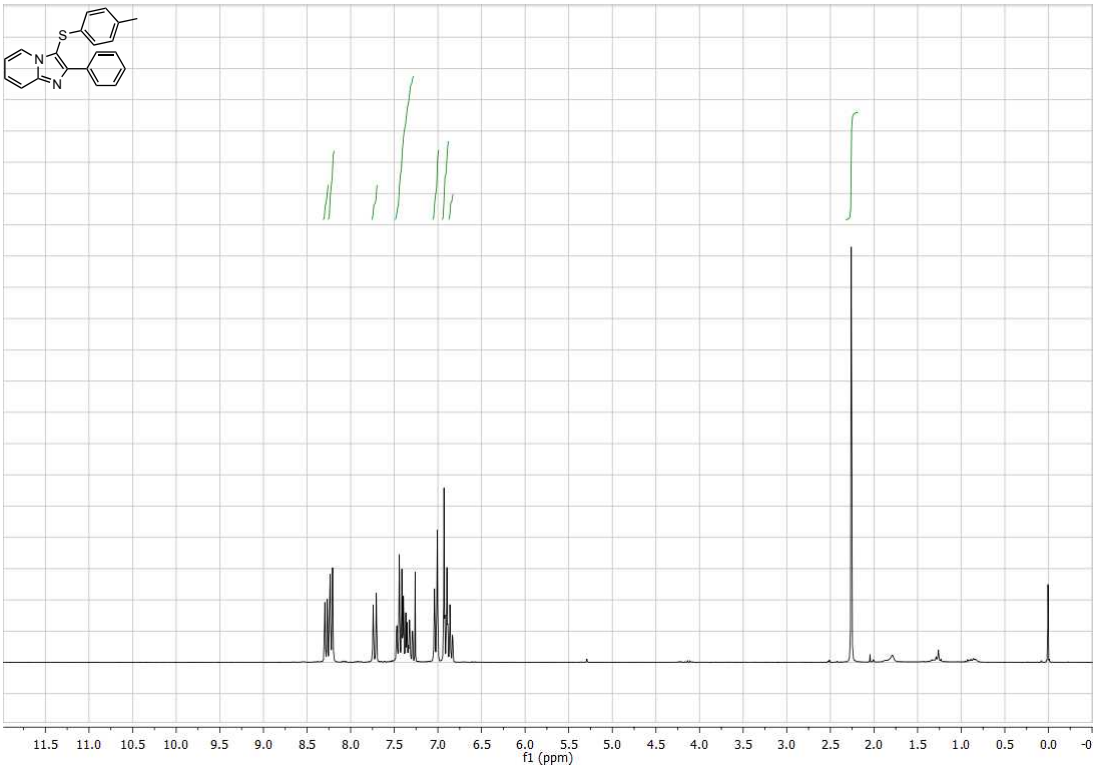
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 8-methyl-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3p**)



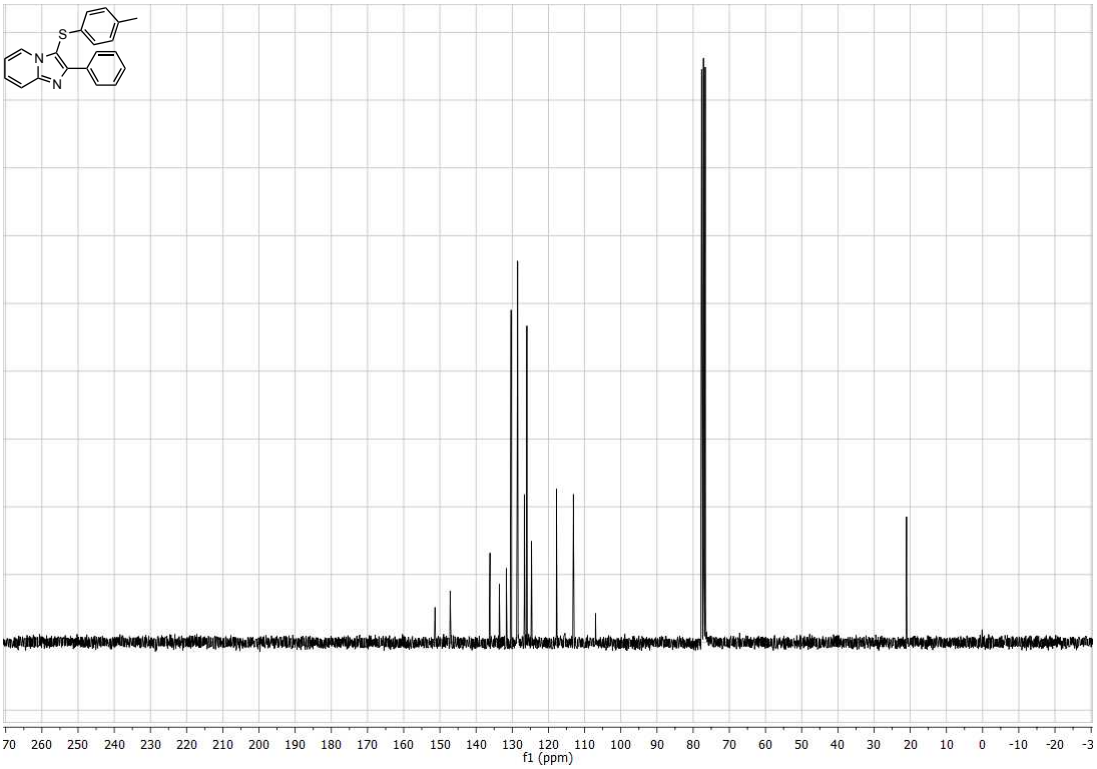
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 8-methyl-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3p**)



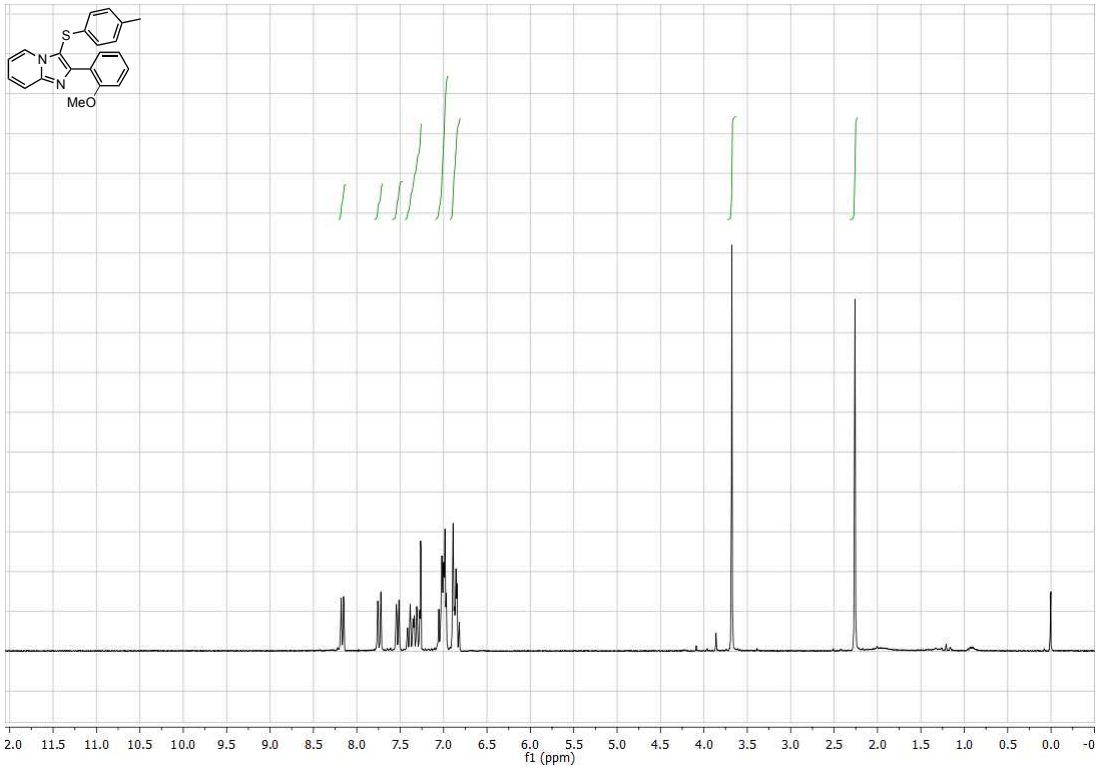
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3q**)



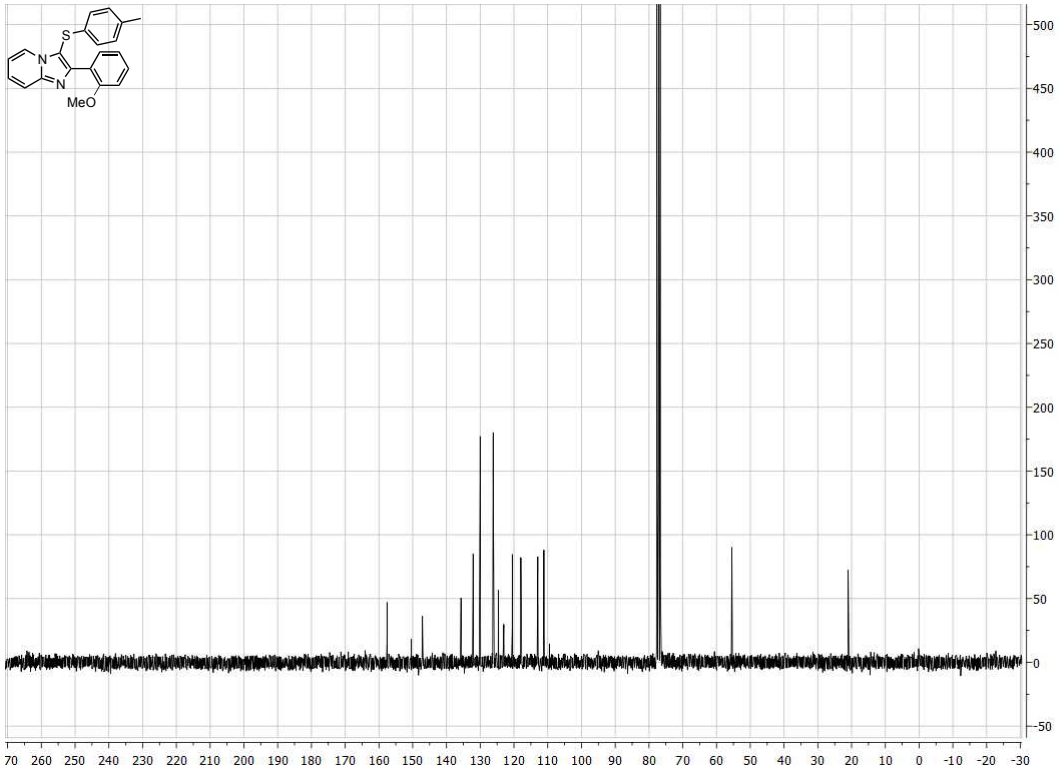
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3q**)



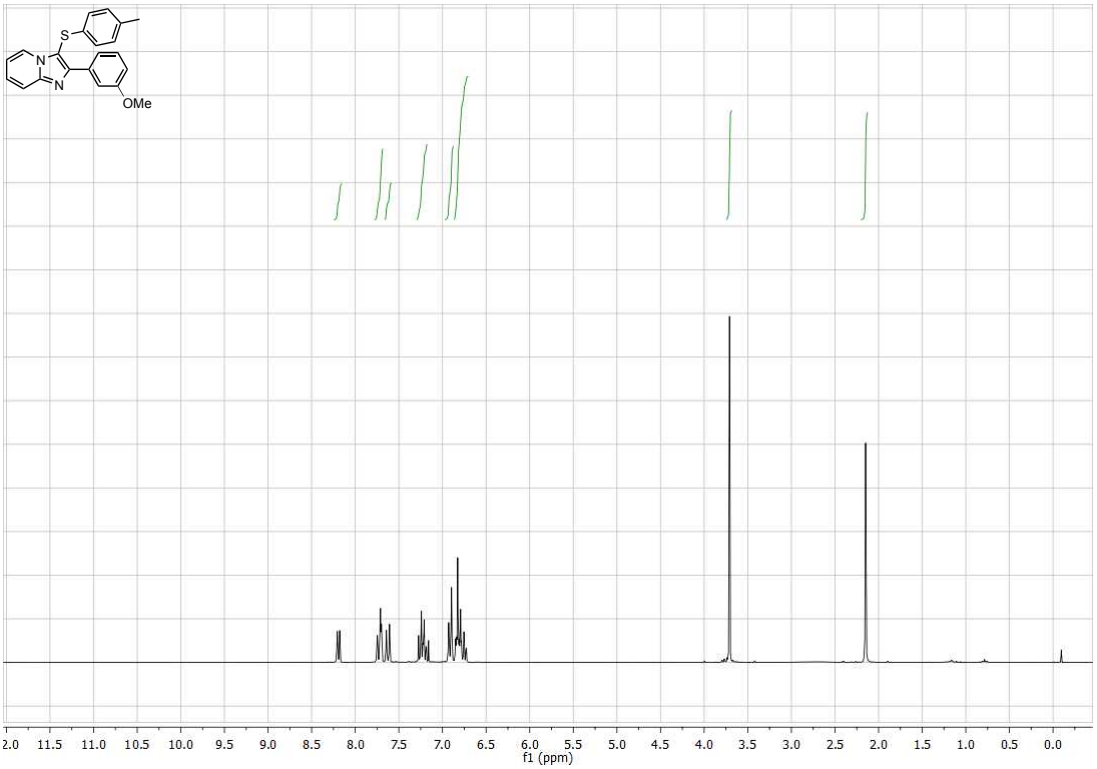
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 2-(2-methoxyphenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3r**)



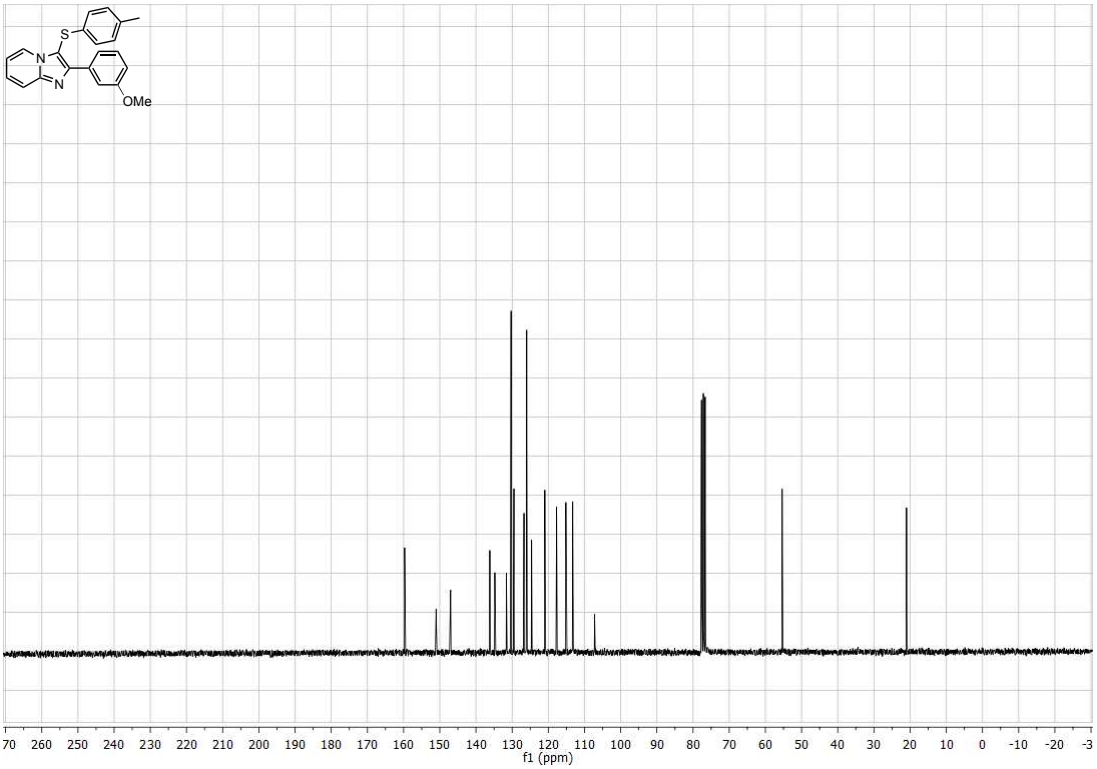
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 2-(2-methoxyphenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3r**)



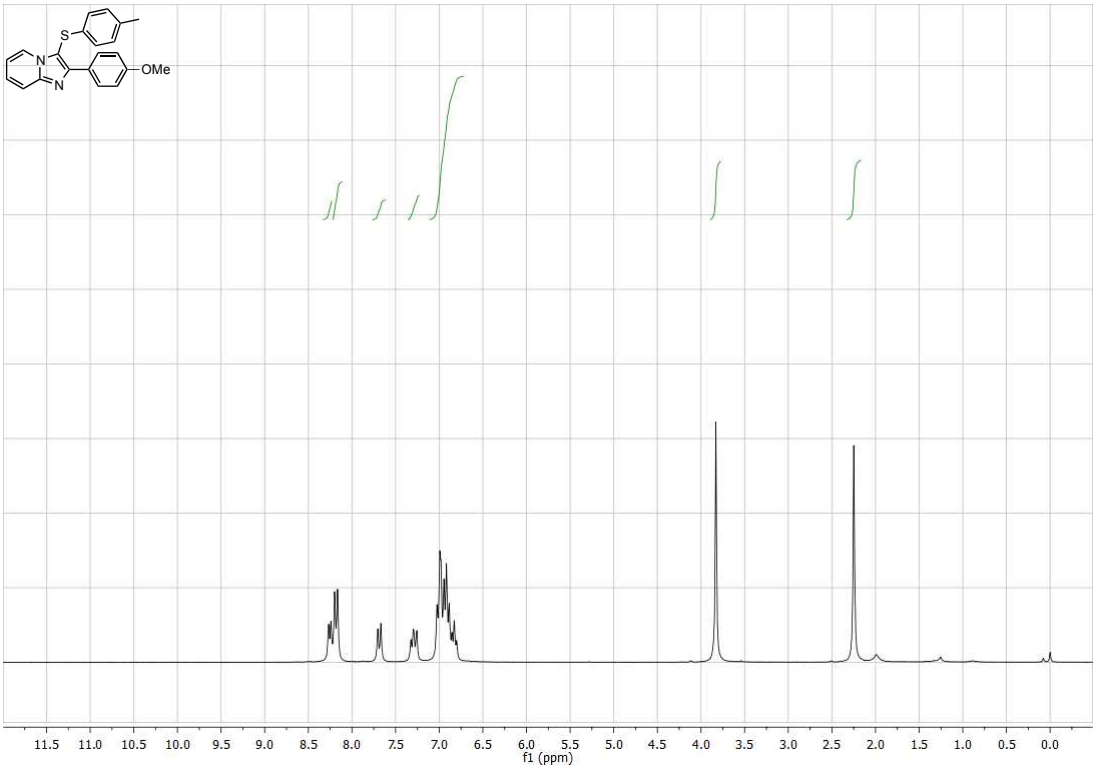
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 2-(3-methoxyphenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3s**)



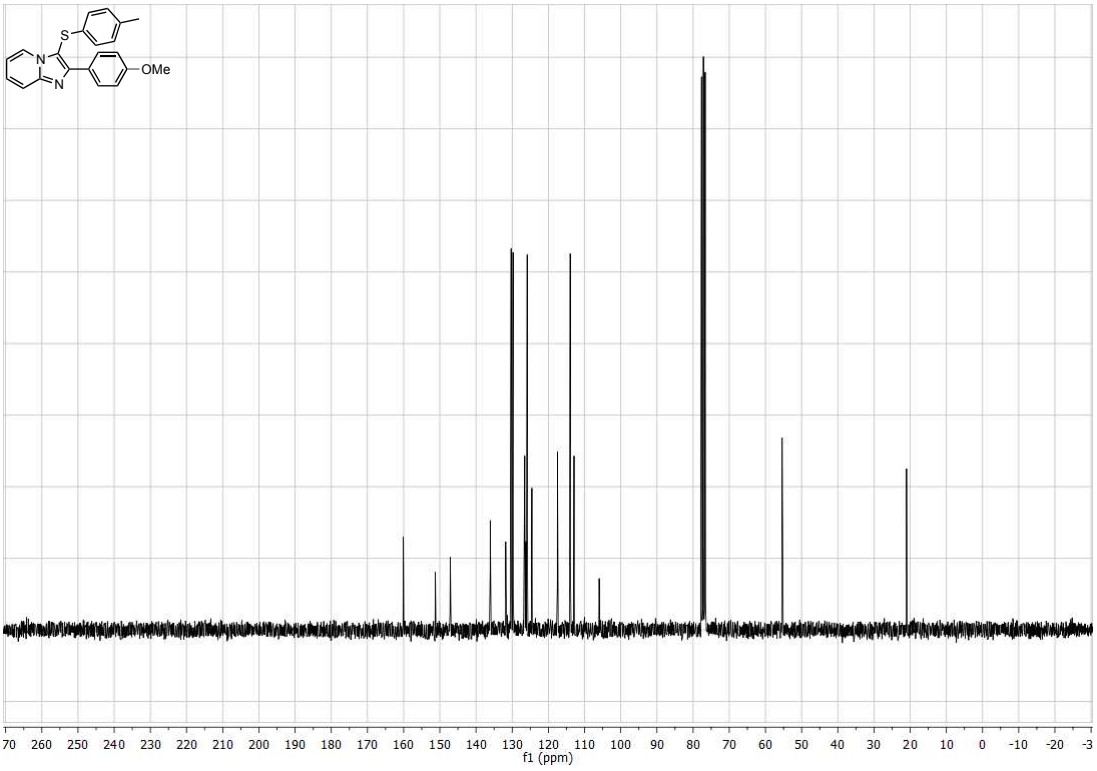
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 2-(3-methoxyphenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3s**)



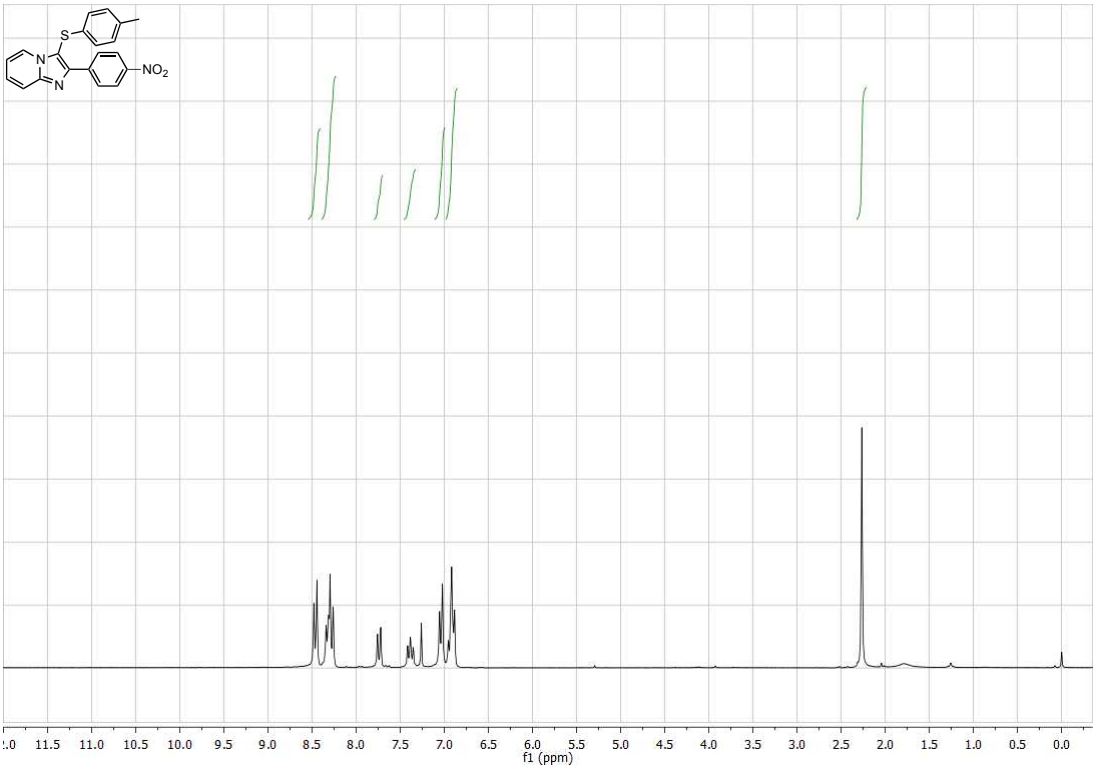
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 2-(4-methoxyphenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3t**)



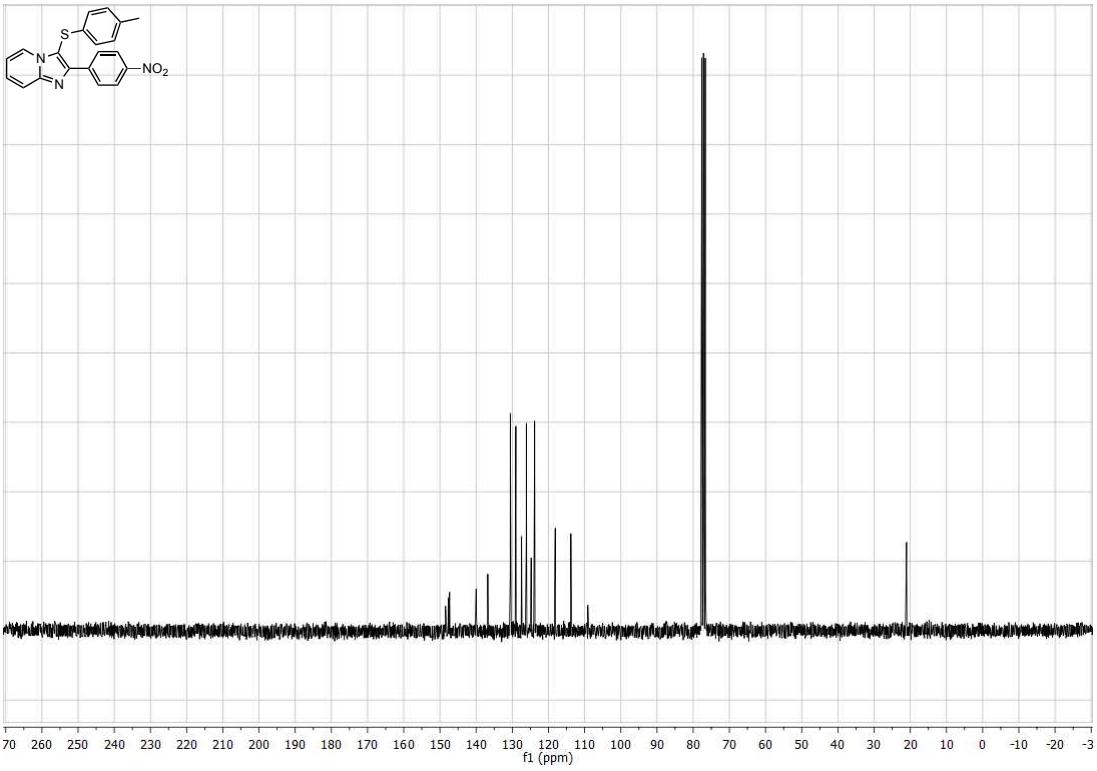
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 2-(4-methoxyphenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3t**)



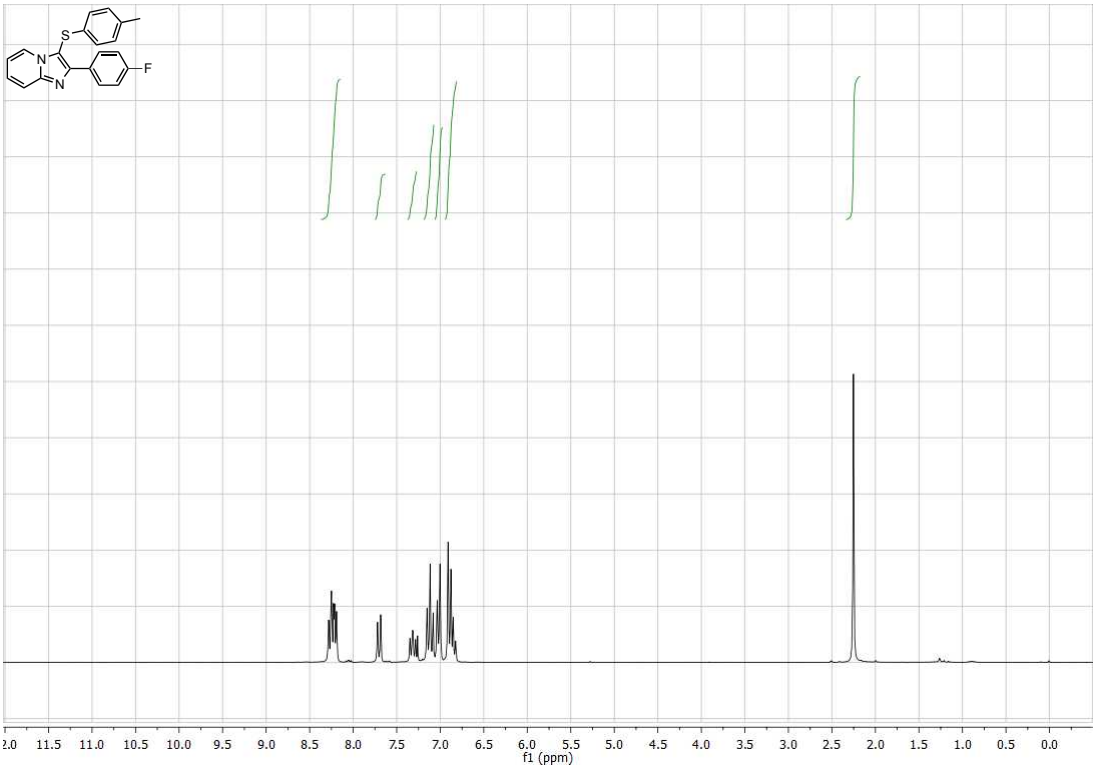
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 2-(4-nitrophenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3u**)



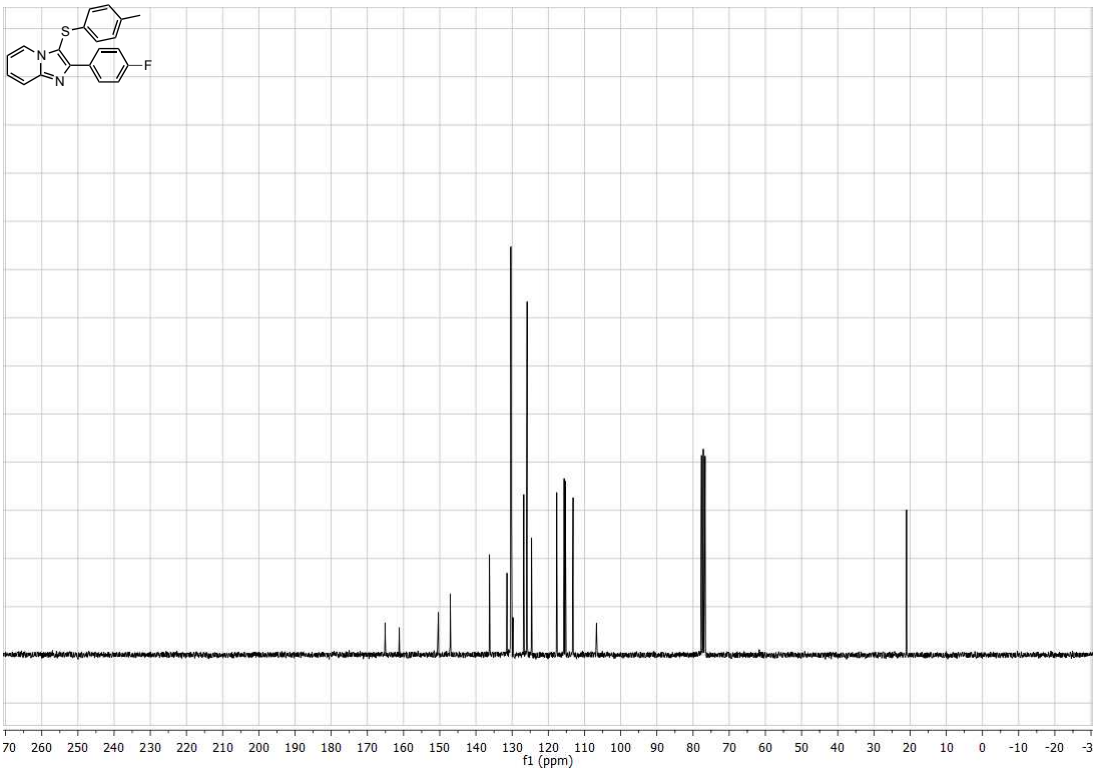
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 2-(4-nitrophenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3u**)



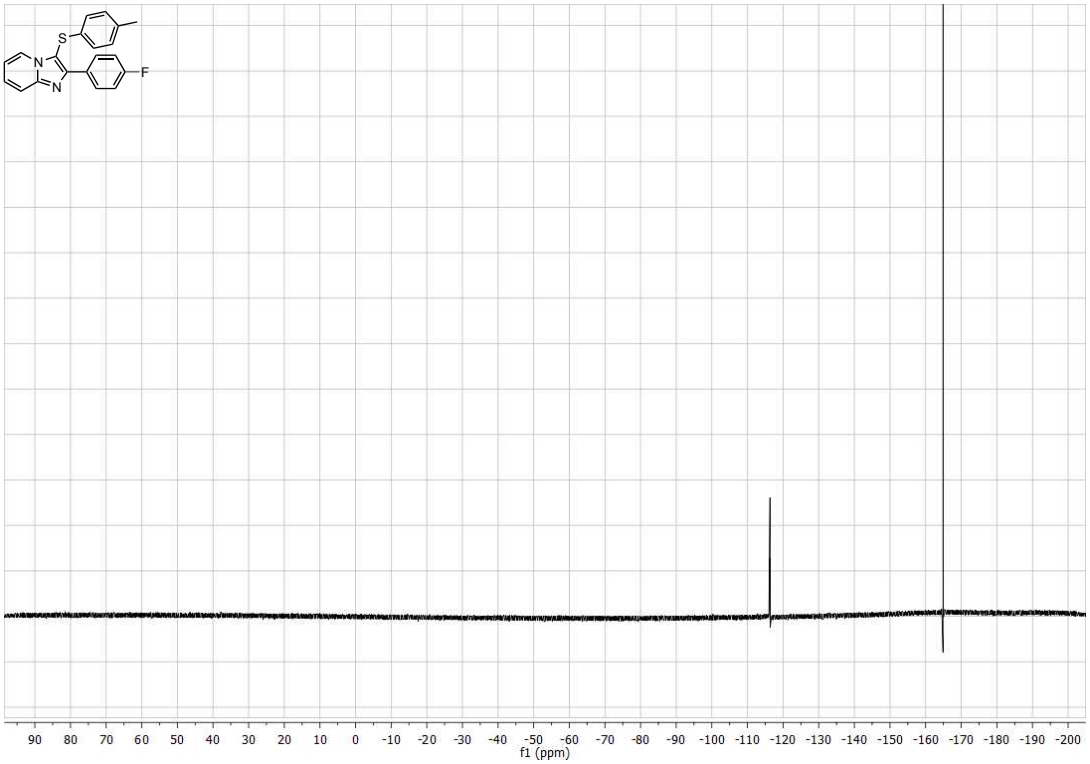
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 2-(4-fluorophenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3v**)



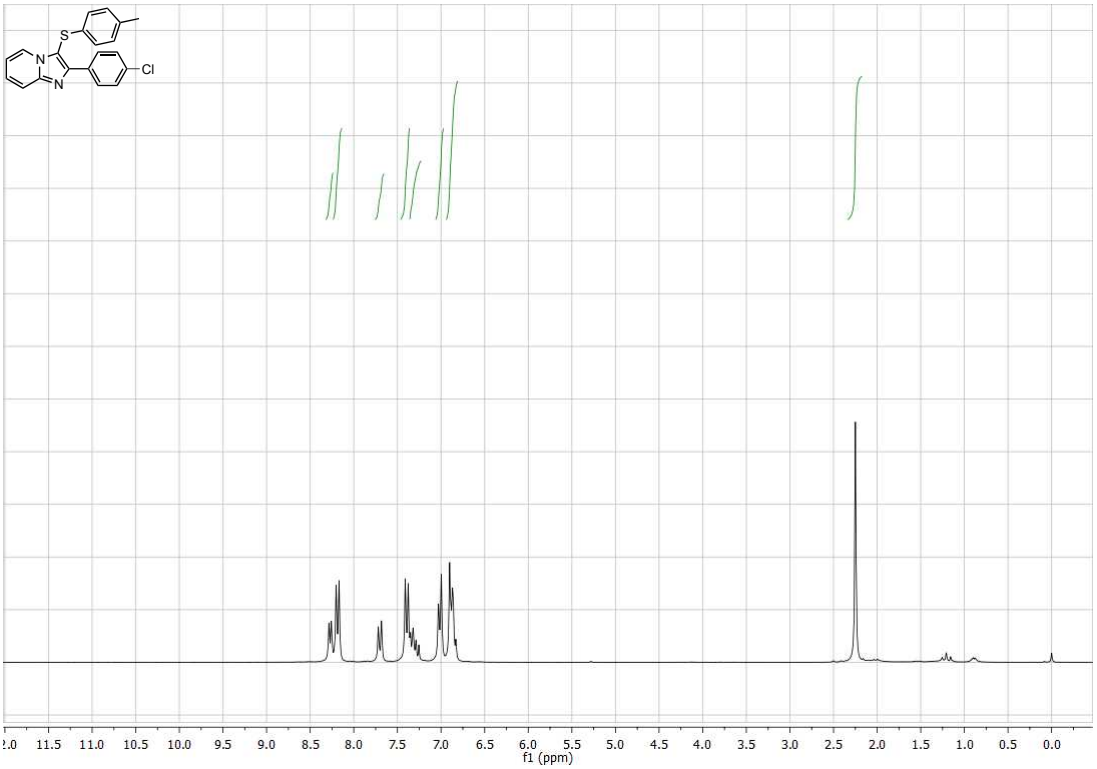
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 2-(4-fluorophenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3v**)



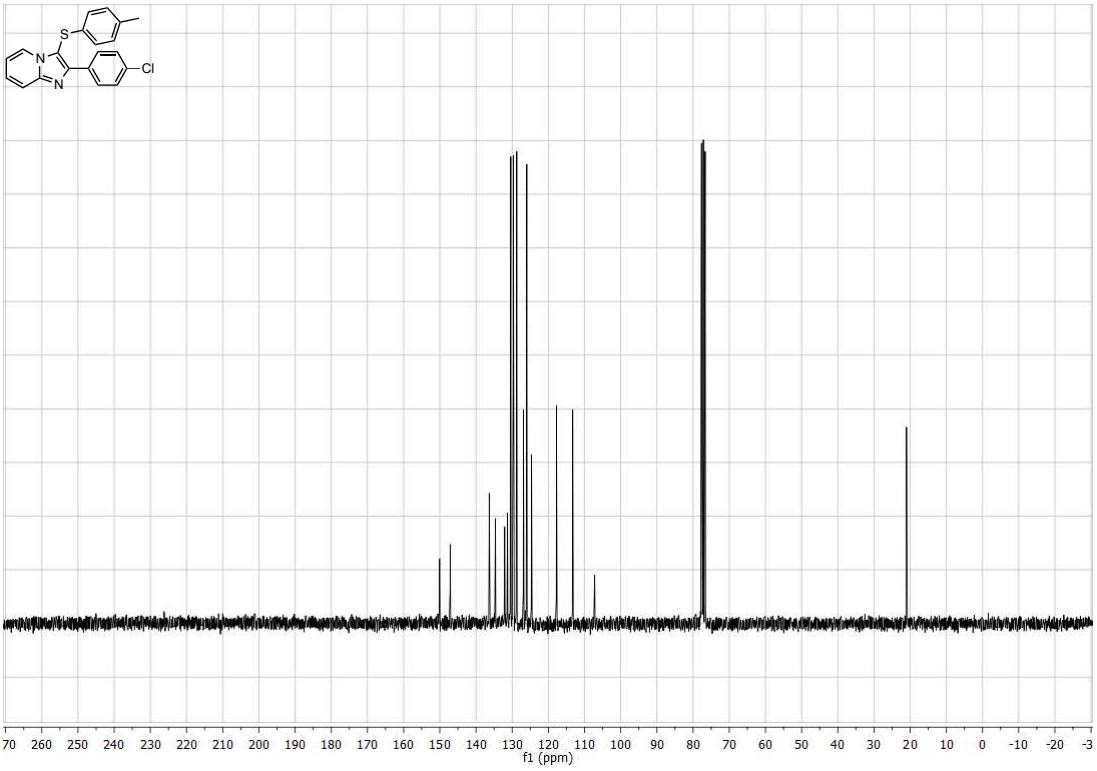
^{19}F (235 MHz, $CDCl_3$) spectrum of 2-(4-fluorophenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3v**)



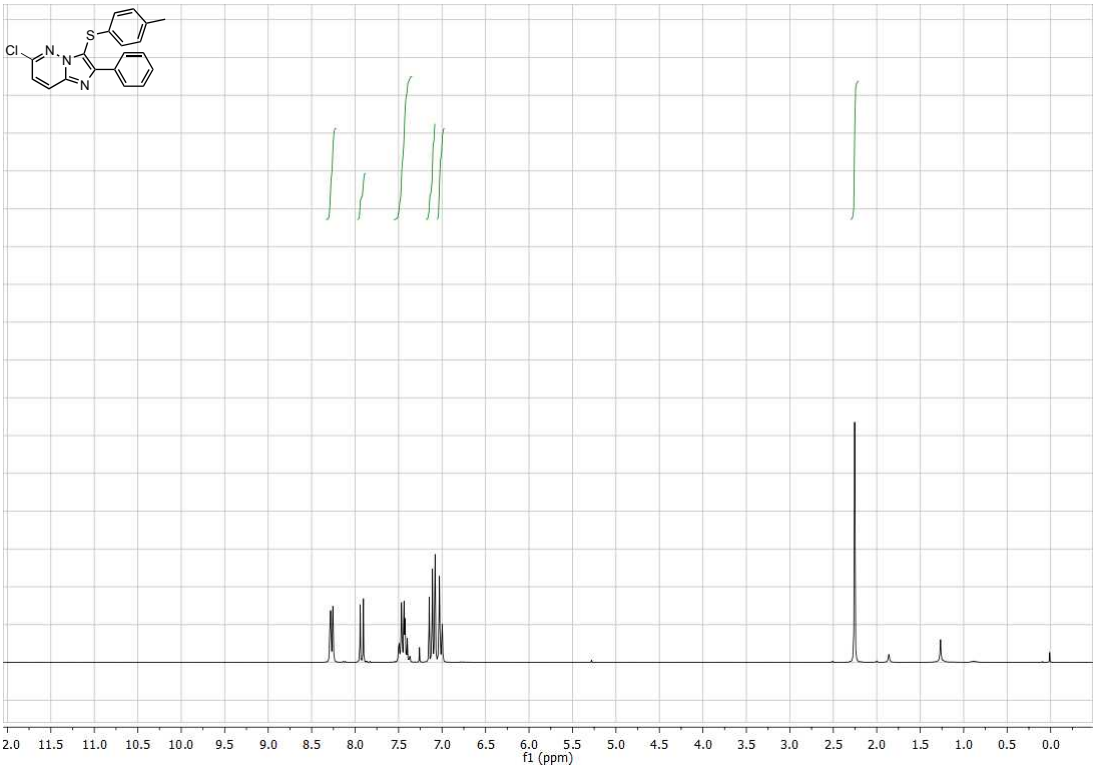
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 2-(4-chlorophenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3w**)



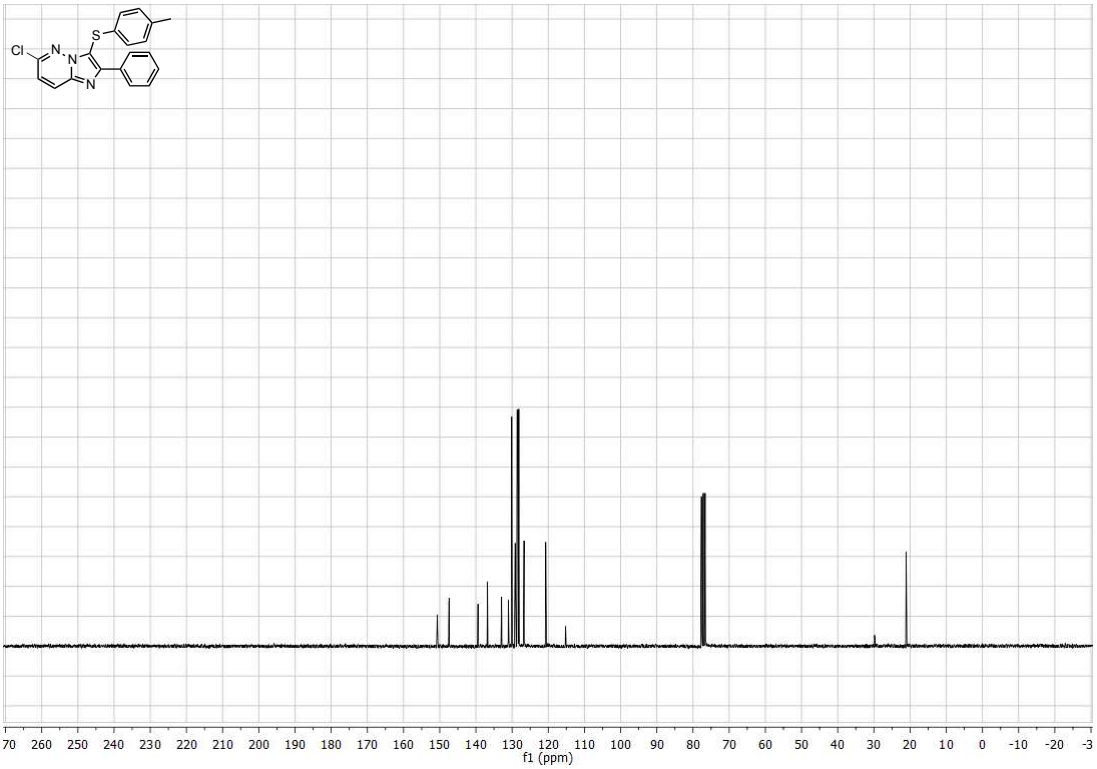
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 2-(4-chlorophenyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (**3w**)



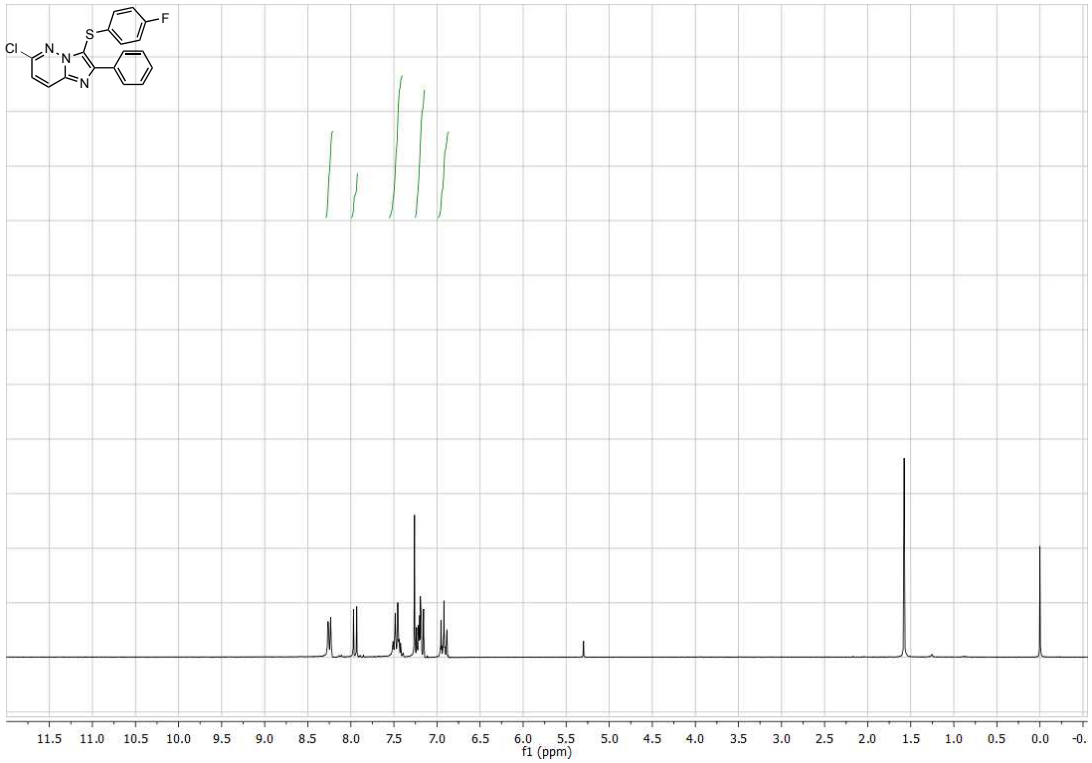
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 6-chloro-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*b*]pyridazine (**4a**)



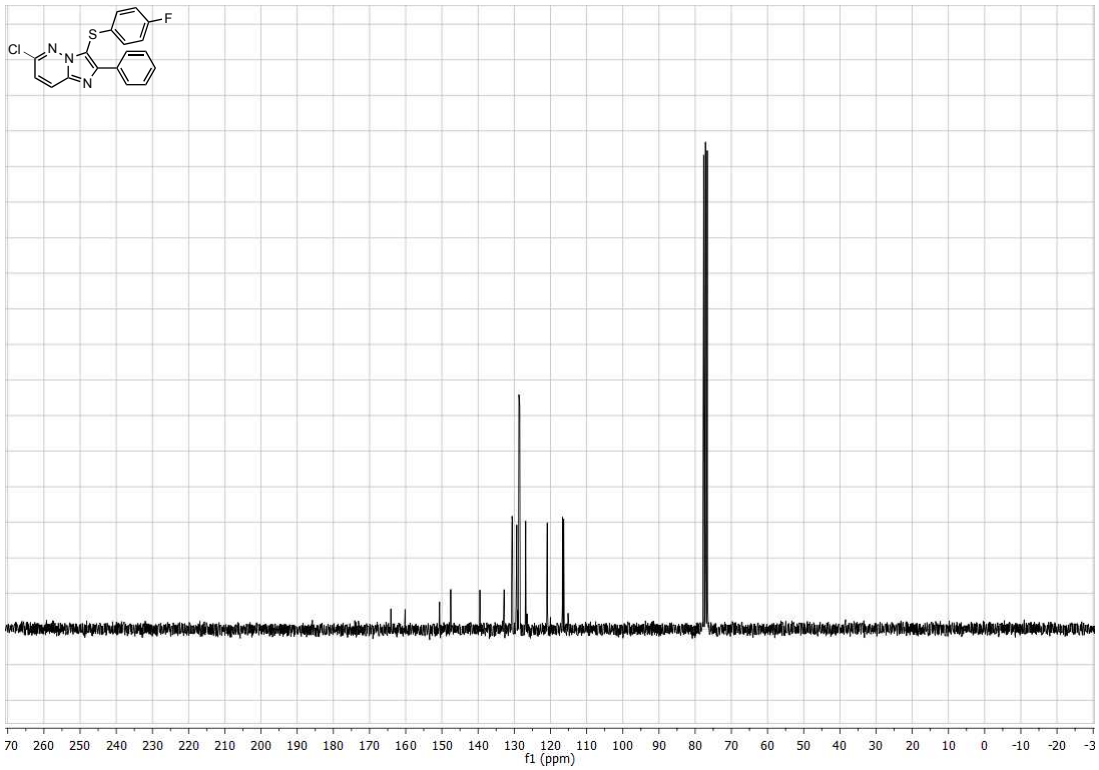
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 6-chloro-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*b*]pyridazine (**4a**)



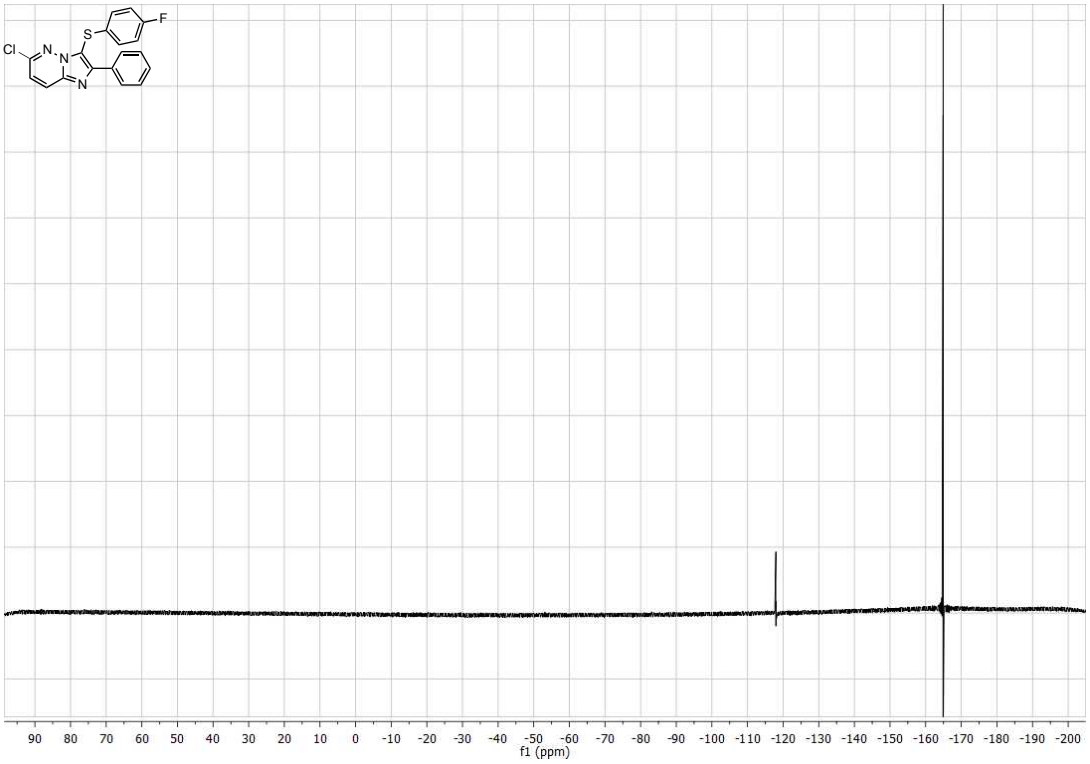
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 6-chloro-3-((4-fluorophenyl)thio)-2-phenylimidazo[1,2-*b*]pyridazine (**4b**)



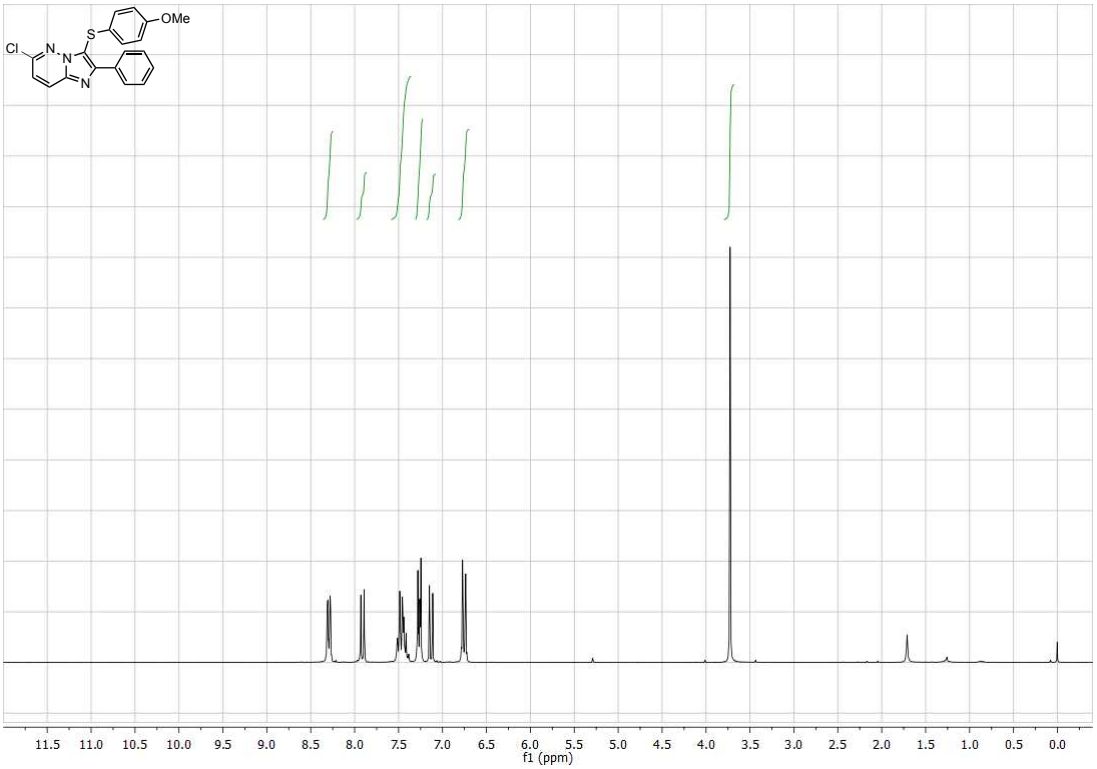
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 6-chloro-3-((4-fluorophenyl)thio)-2-phenylimidazo[1,2-*b*]pyridazine (**4b**)



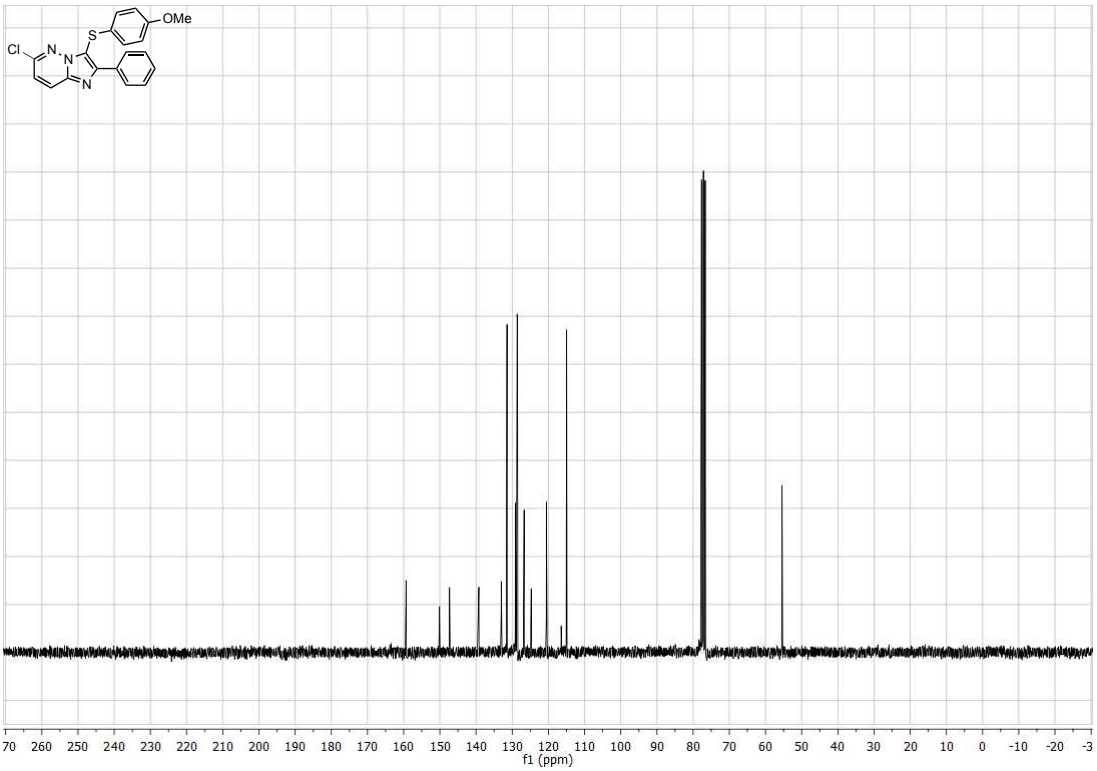
^{19}F (235 MHz, $CDCl_3$) spectrum of 6-chloro-3-((4-fluorophenyl)thio)-2-phenylimidazo[1,2-*b*]pyridazine (**4b**)



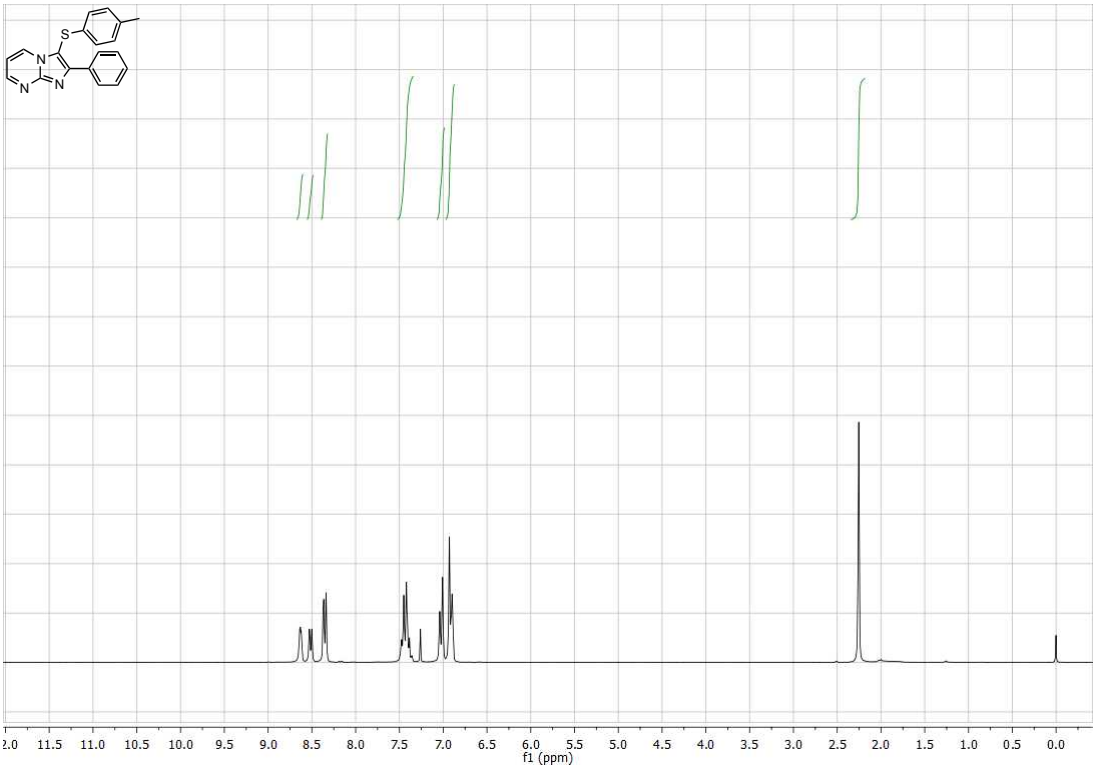
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 6-chloro-3-((4-methoxyphenyl)thio)-2-phenylimidazo[1,2-*b*]pyridazine (**4c**)



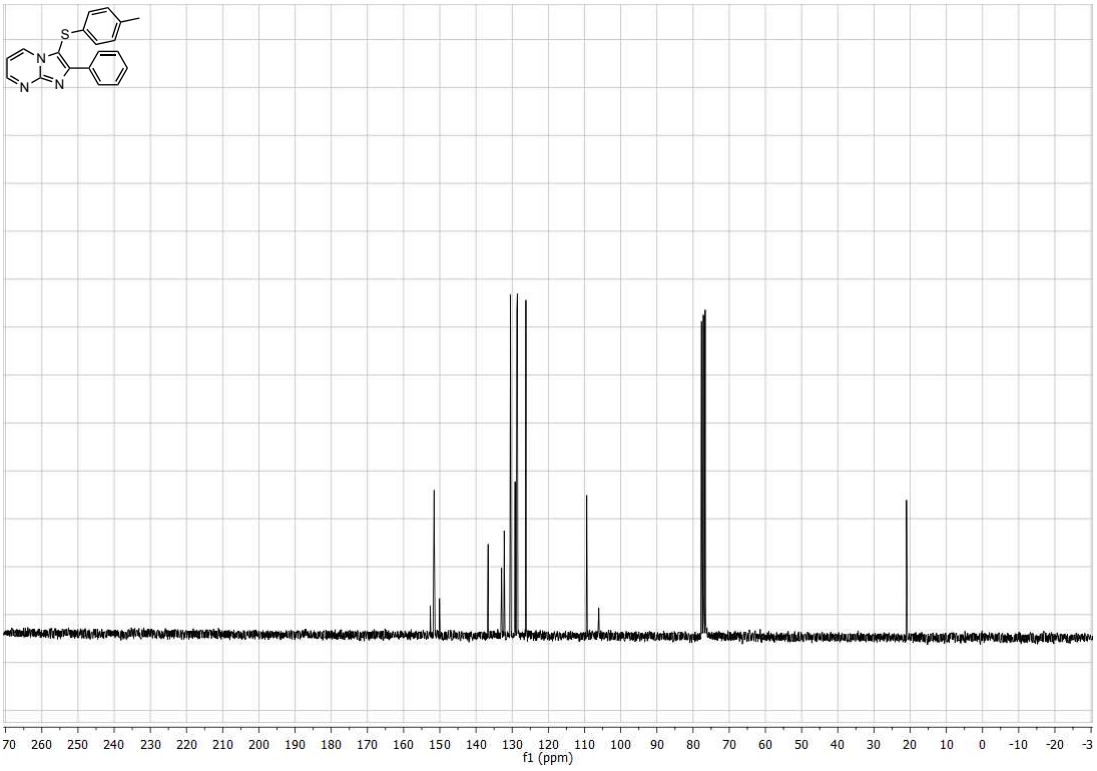
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 6-chloro-3-((4-methoxyphenyl)thio)-2-phenylimidazo[1,2-*b*]pyridazine (**4c**)



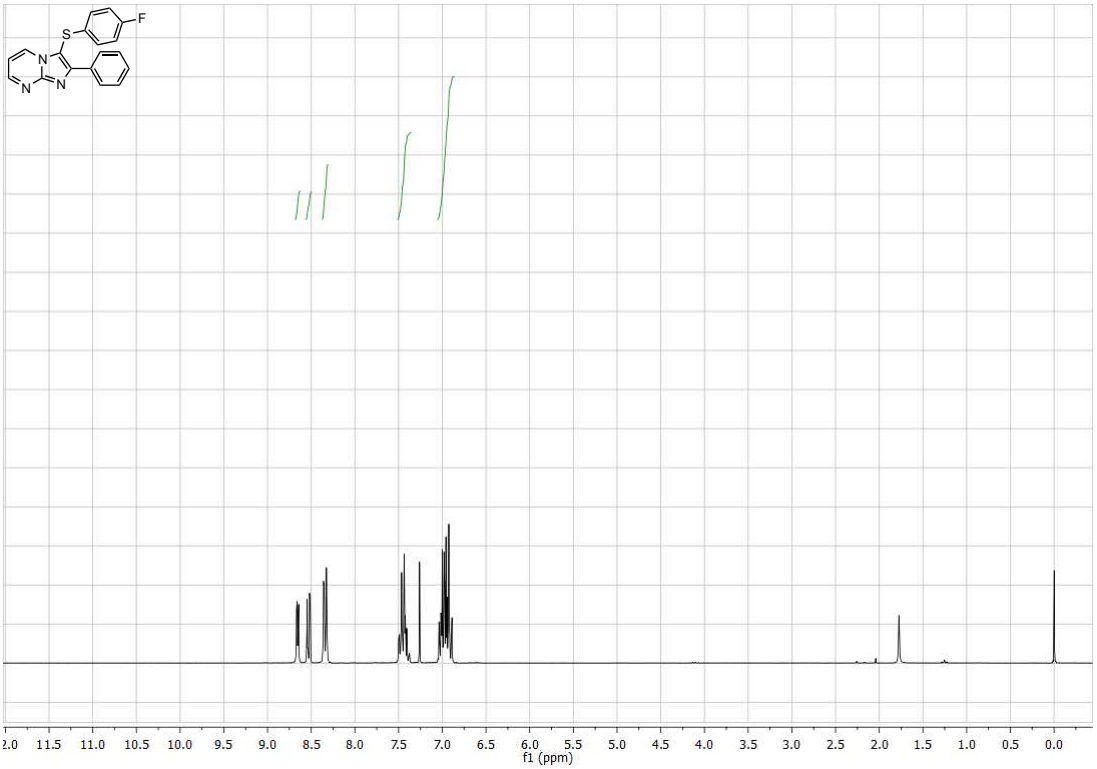
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyrimidine (**4d**)



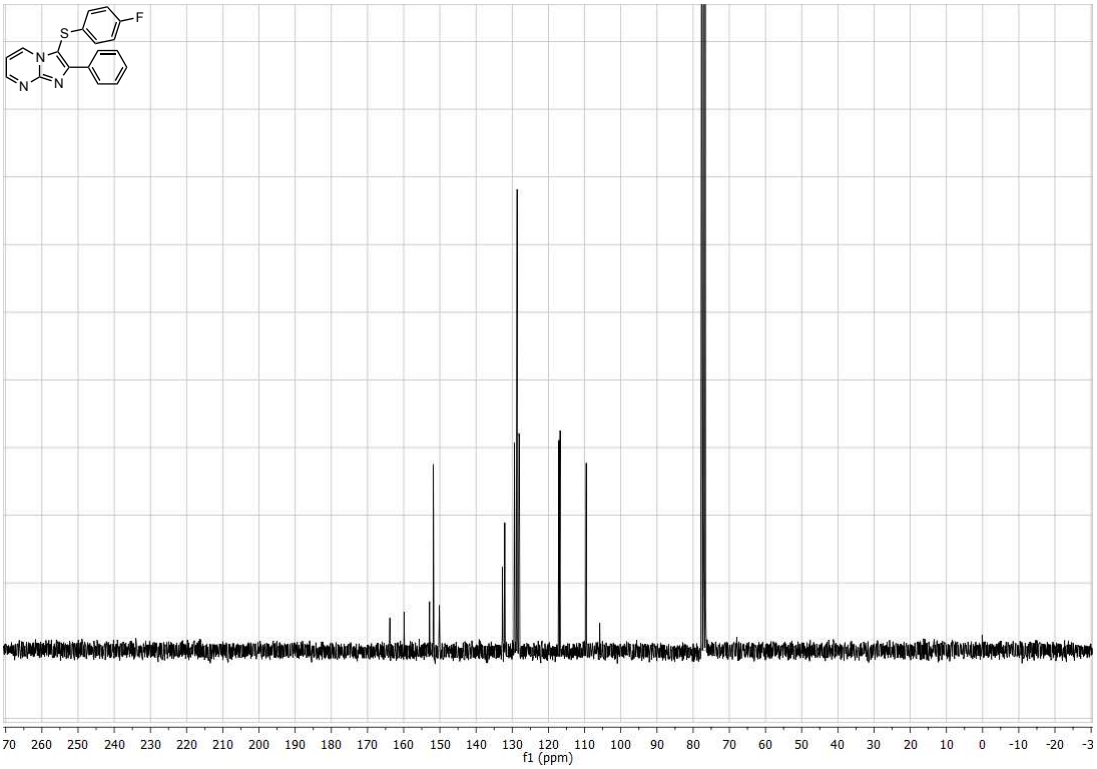
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyrimidine (**4d**)



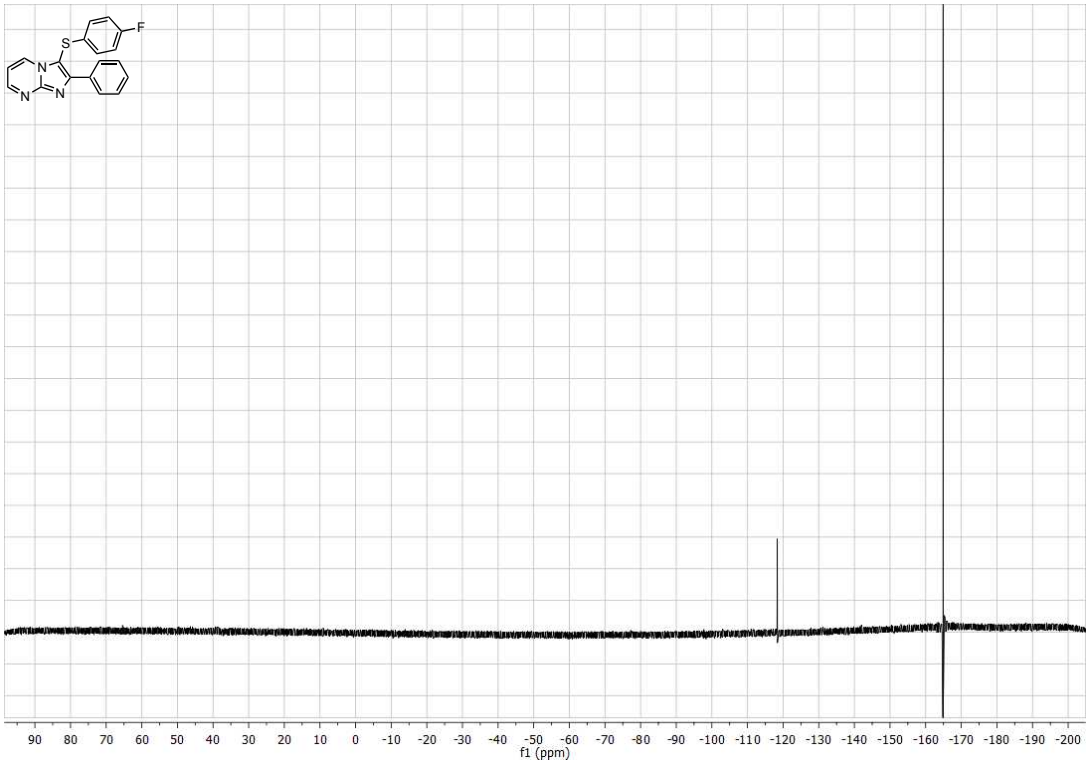
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 3-((4-fluorophenyl)thio)-2-phenylimidazo[1,2-*a*]pyrimidine (**4e**)



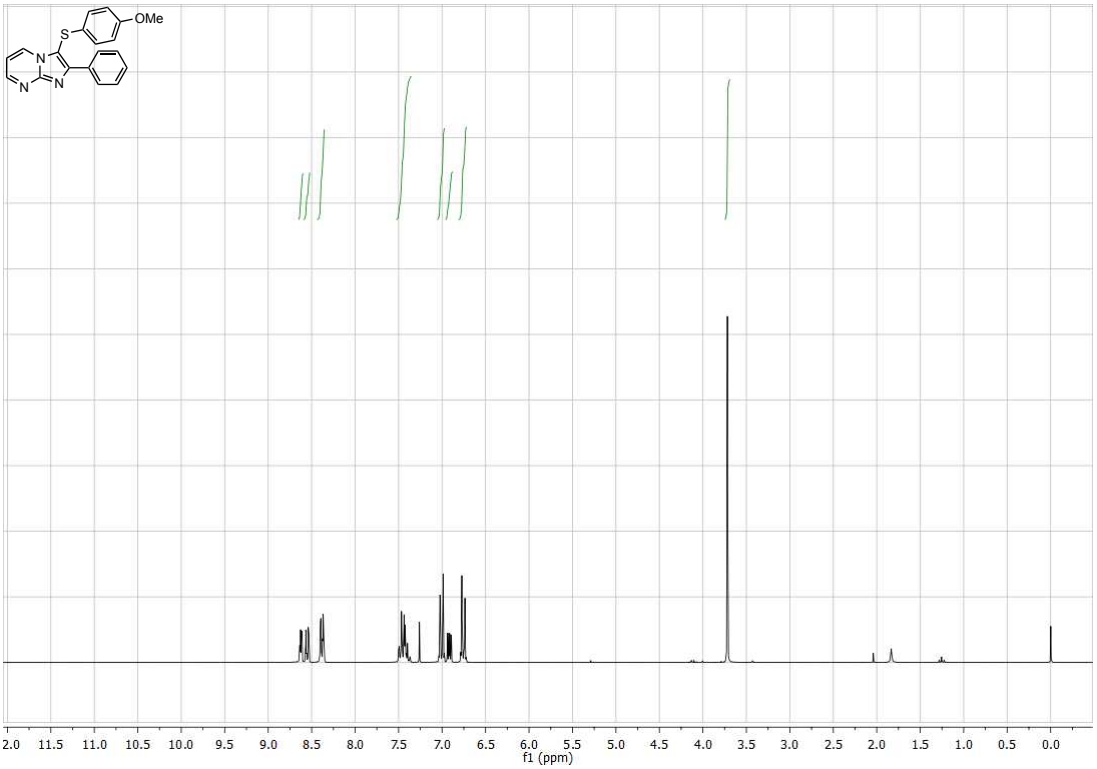
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 3-((4-fluorophenyl)thio)-2-phenylimidazo[1,2-*a*]pyrimidine (**4e**)



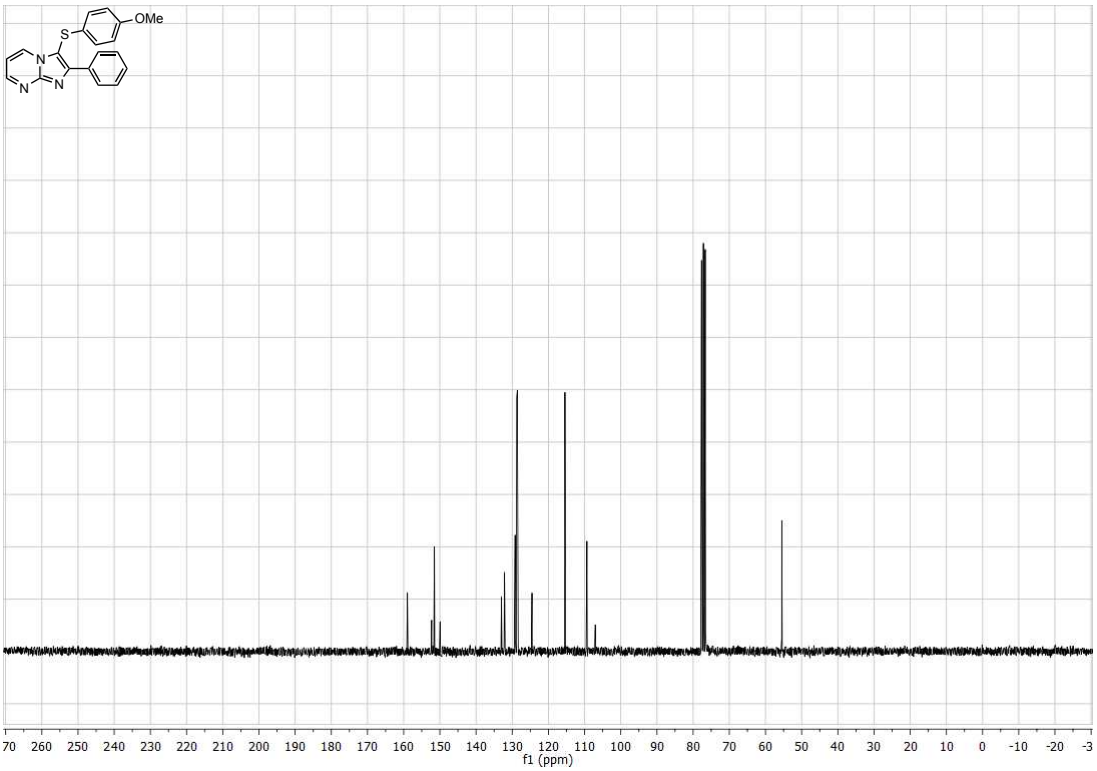
^{19}F (235 MHz, $CDCl_3$) spectrum of 3-((4-fluorophenyl)thio)-2-phenylimidazo[1,2-*a*]pyrimidine (**4e**)



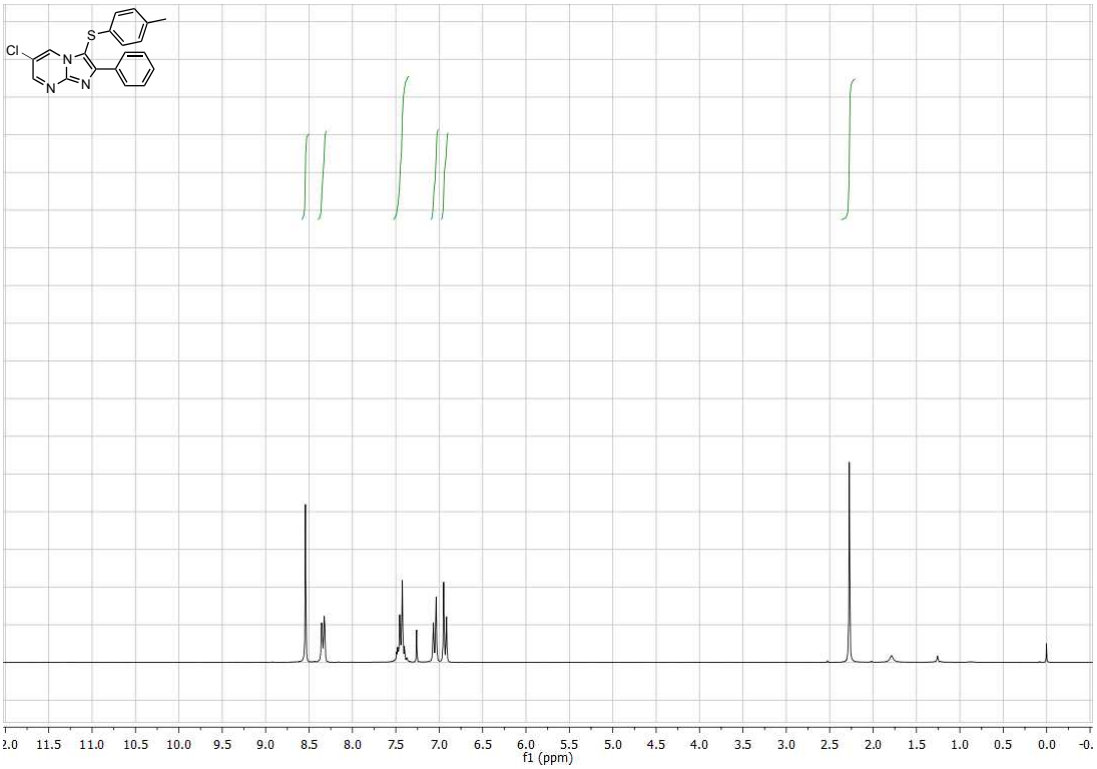
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 3-((4-methoxyphenyl)thio)-2-phenylimidazo[1,2-*a*]pyrimidine (**4f**)



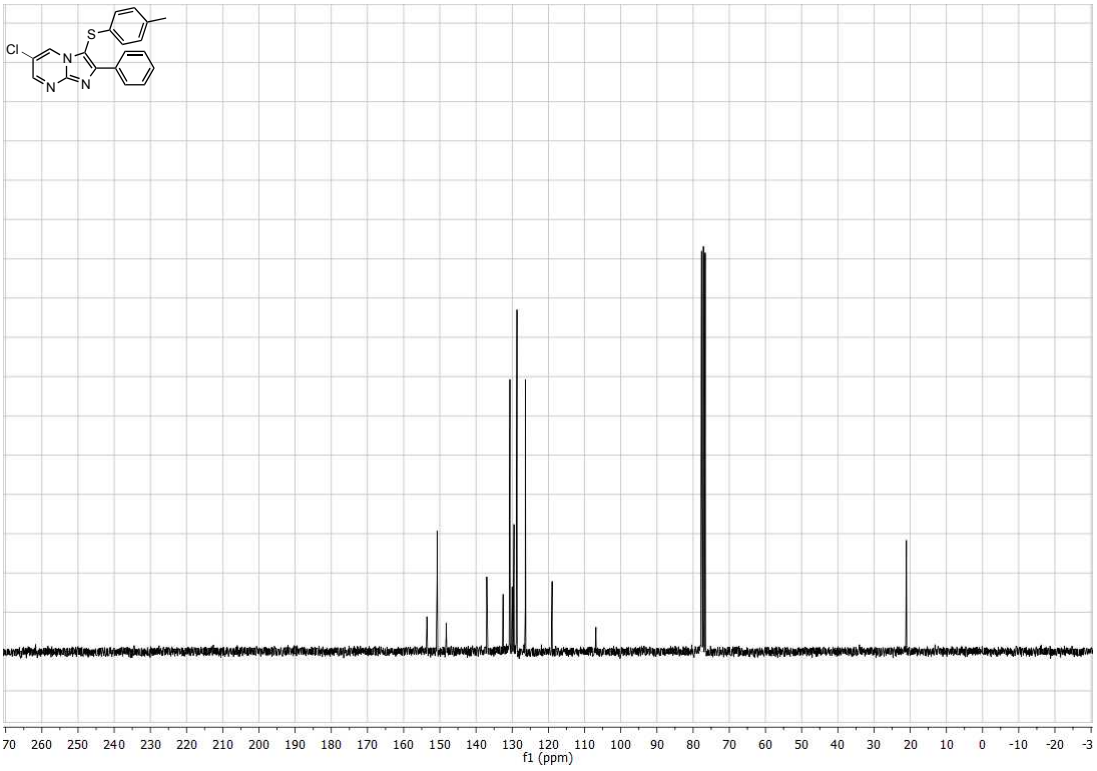
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 3-((4-methoxyphenyl)thio)-2-phenylimidazo[1,2-*a*]pyrimidine (**4f**)



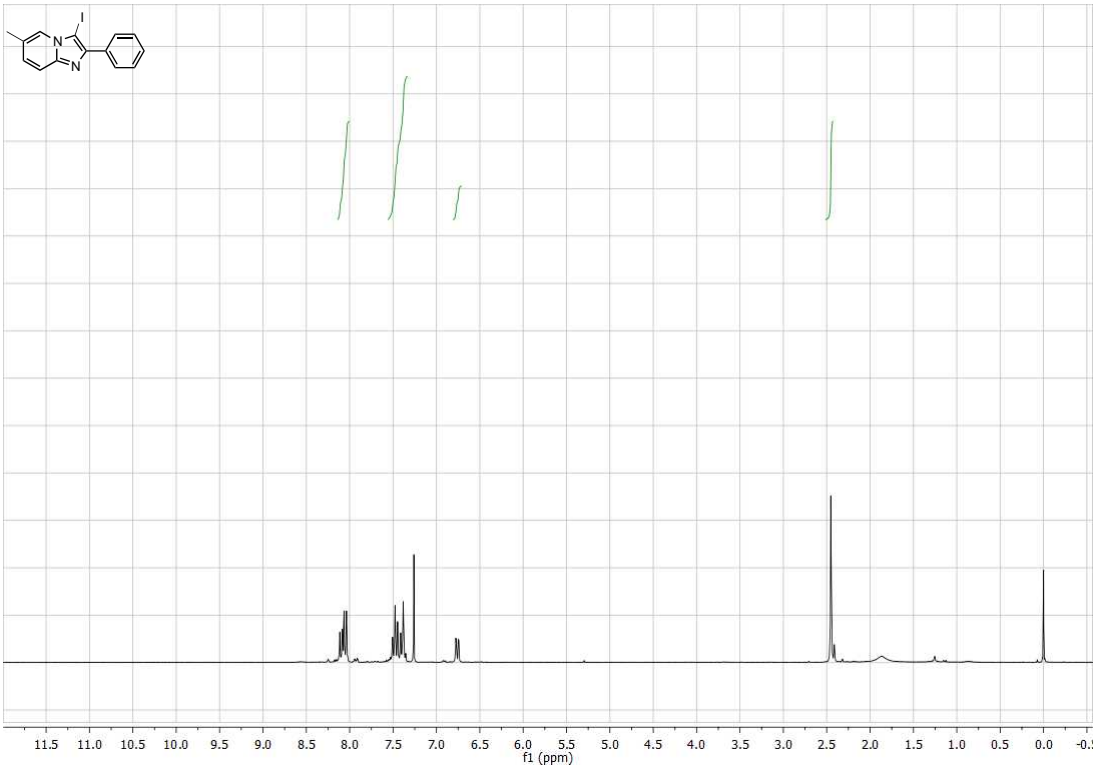
^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 6-chloro-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyrimidine (**4g**)



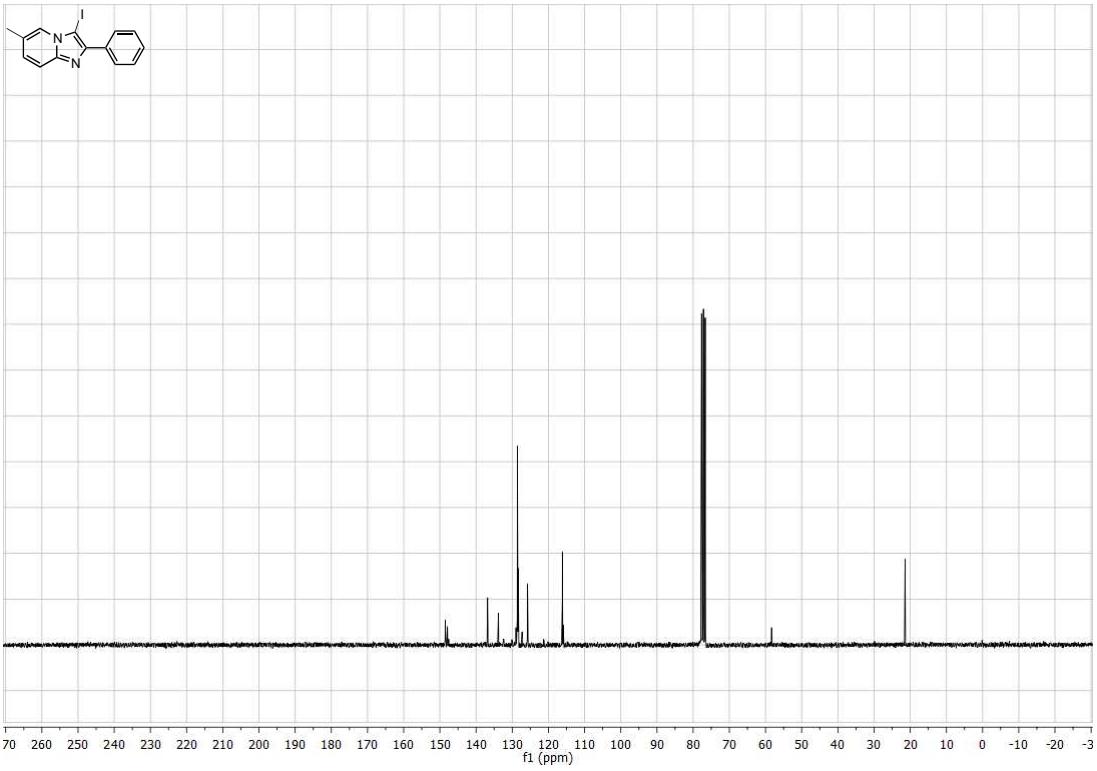
^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 6-chloro-2-phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyrimidine (**4g**)



^{1}H NMR ($CDCl_3$, 250 MHz) spectrum of 3-iodo-6-methyl-2-phenylimidazo[1,2-*a*]pyridine (**5**)



^{13}C NMR ($CDCl_3$, 62.5 MHz) spectrum of 3-iodo-6-methyl-2-phenylimidazo[1,2-*a*]pyridine (**5**)



[i] Hiebel, M.-A.; Fall, Y.; Scherrmann, M.-C.; Berteina- Raboin, S. *Eur. J. Org. Chem.* **2014**, 4643.