

Supporting Information
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Supporting information

Oxidative Cross-Dehydrogenative C–H Bond Amination of Imidazo[1,2-*a*]pyridines in Aqueous Media Under Metal-free Conditions

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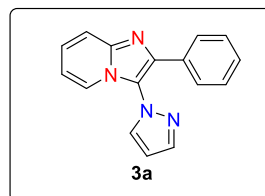
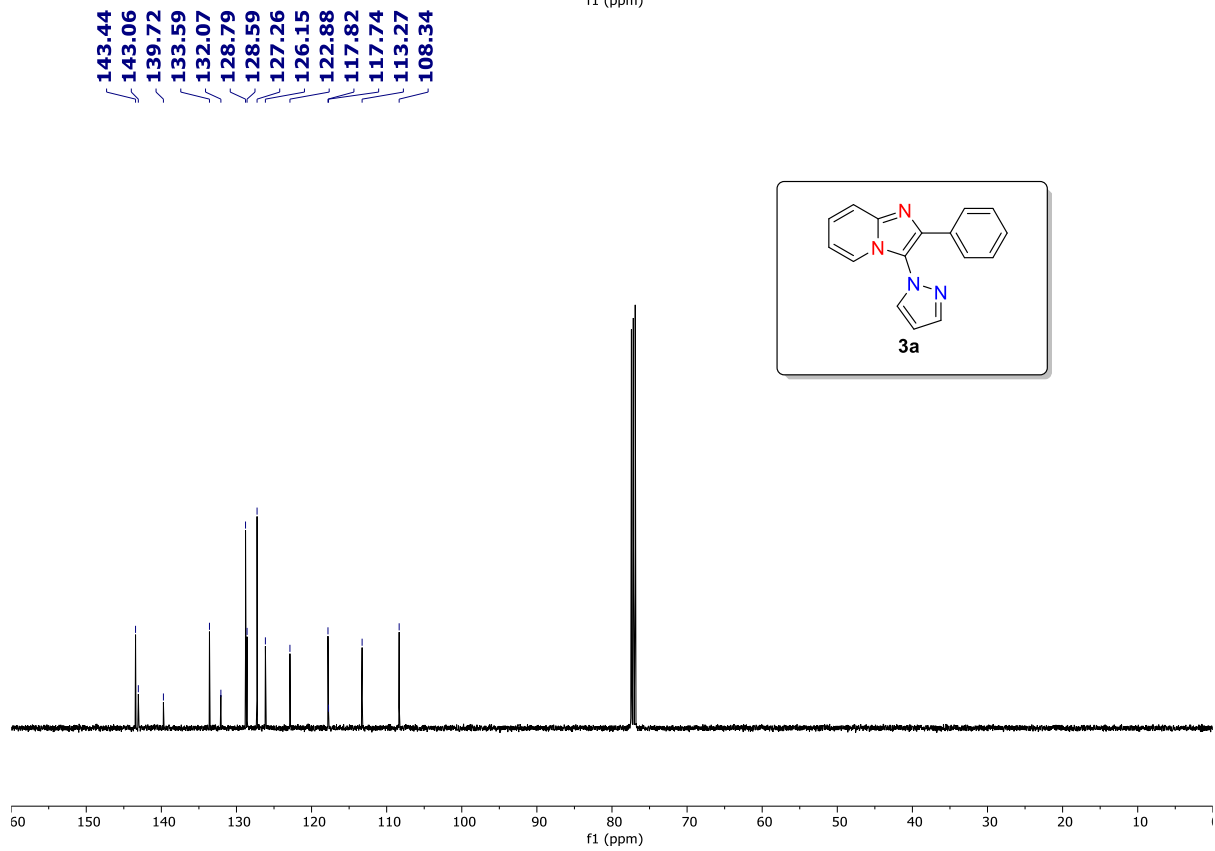
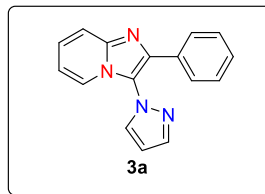
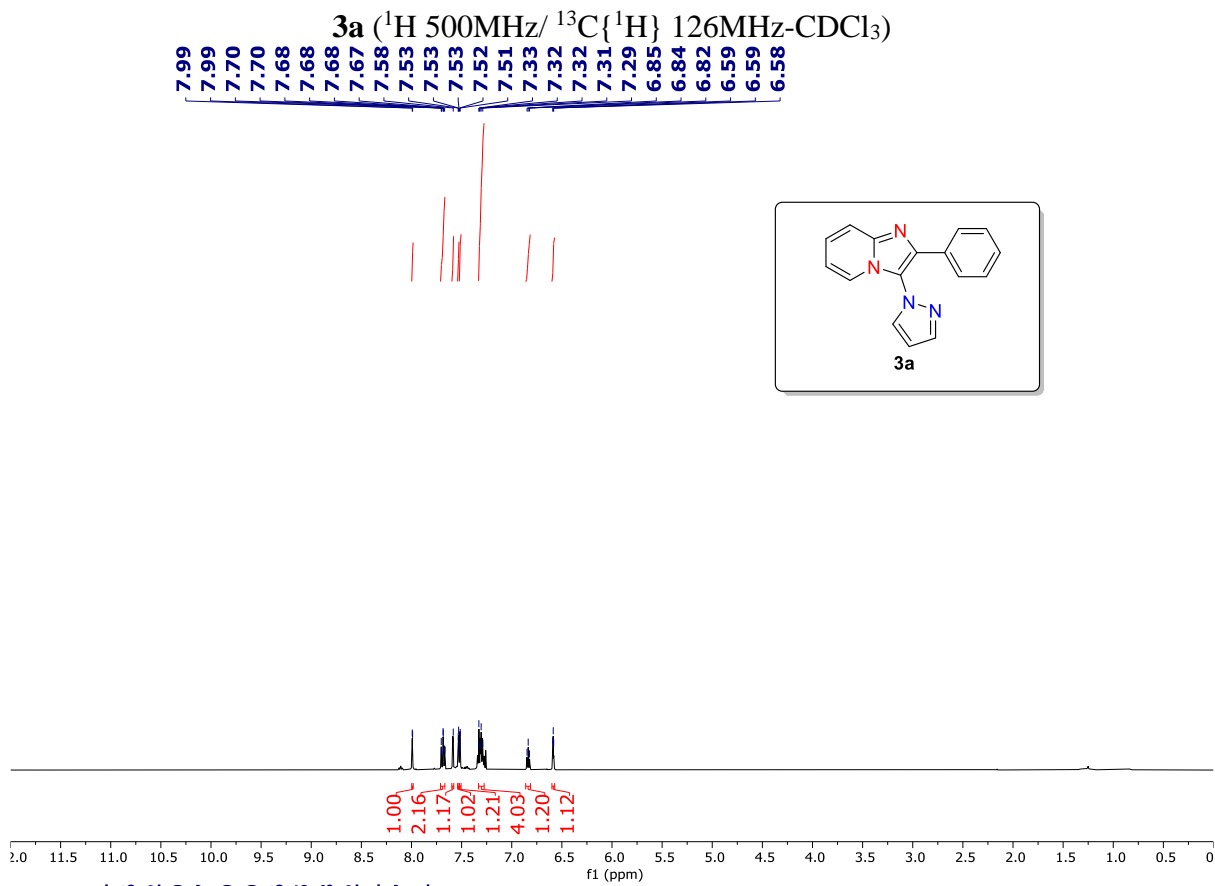
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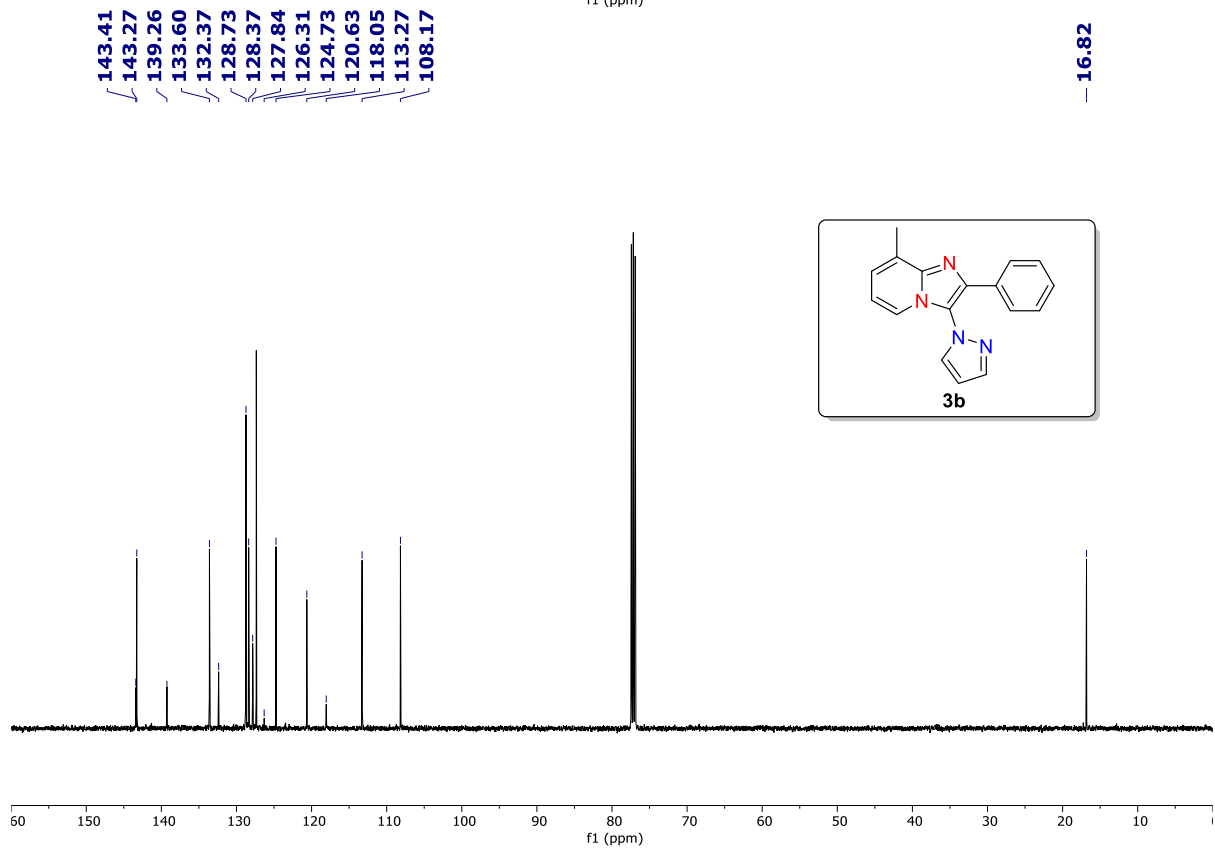
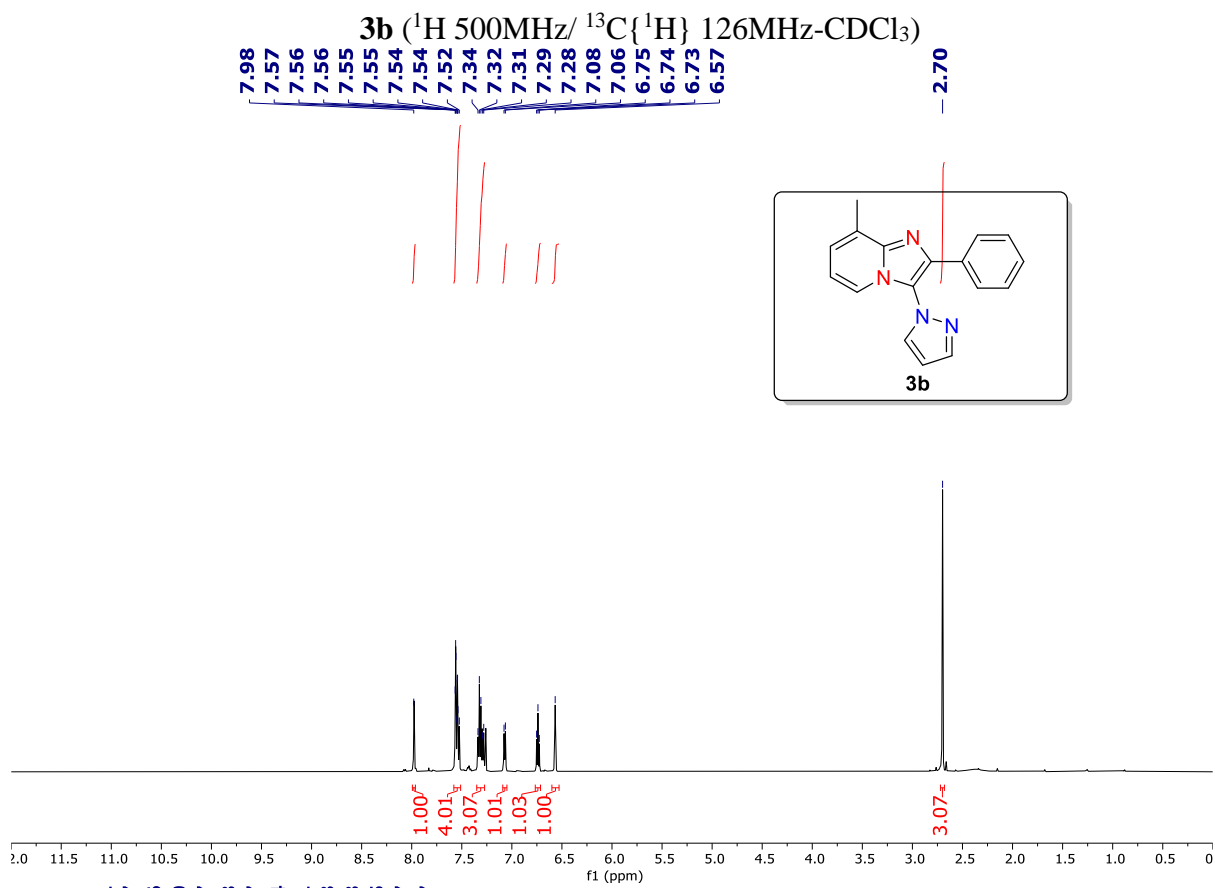
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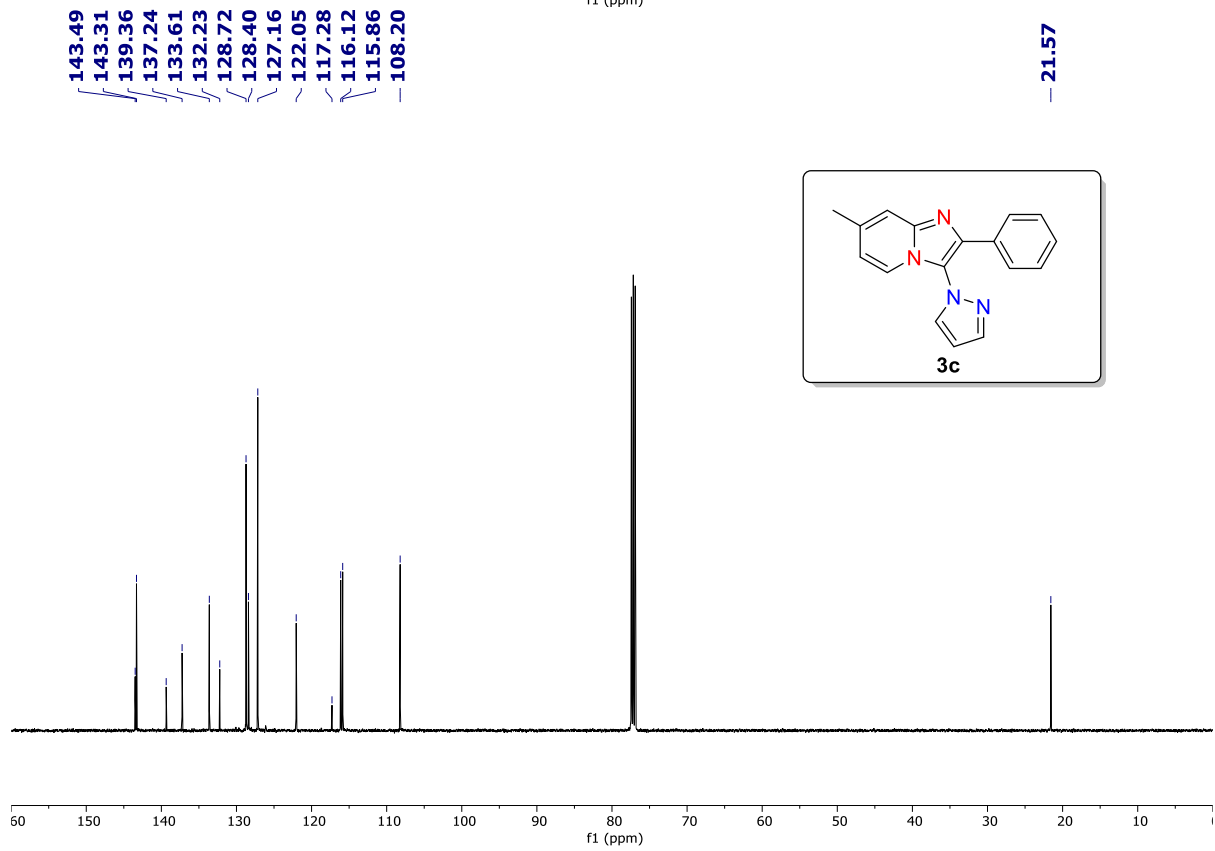
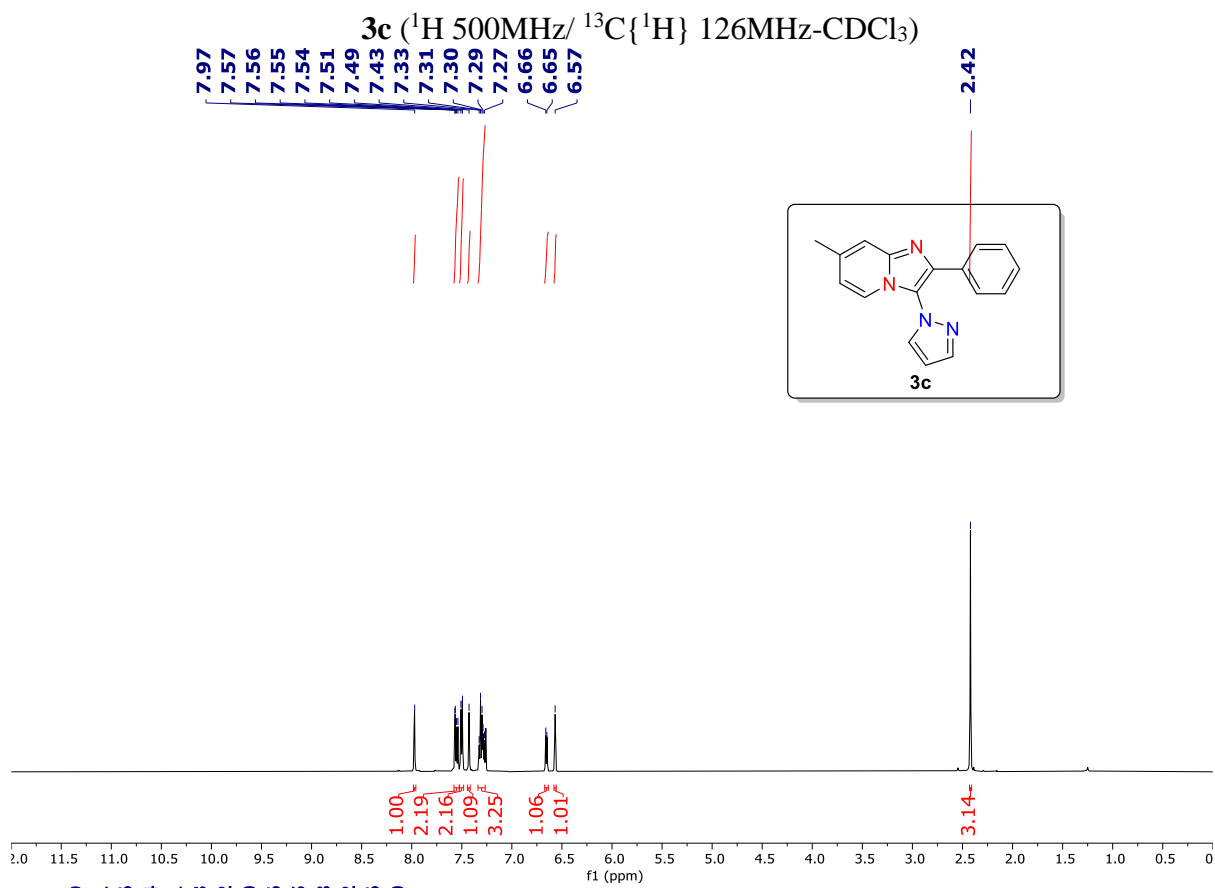
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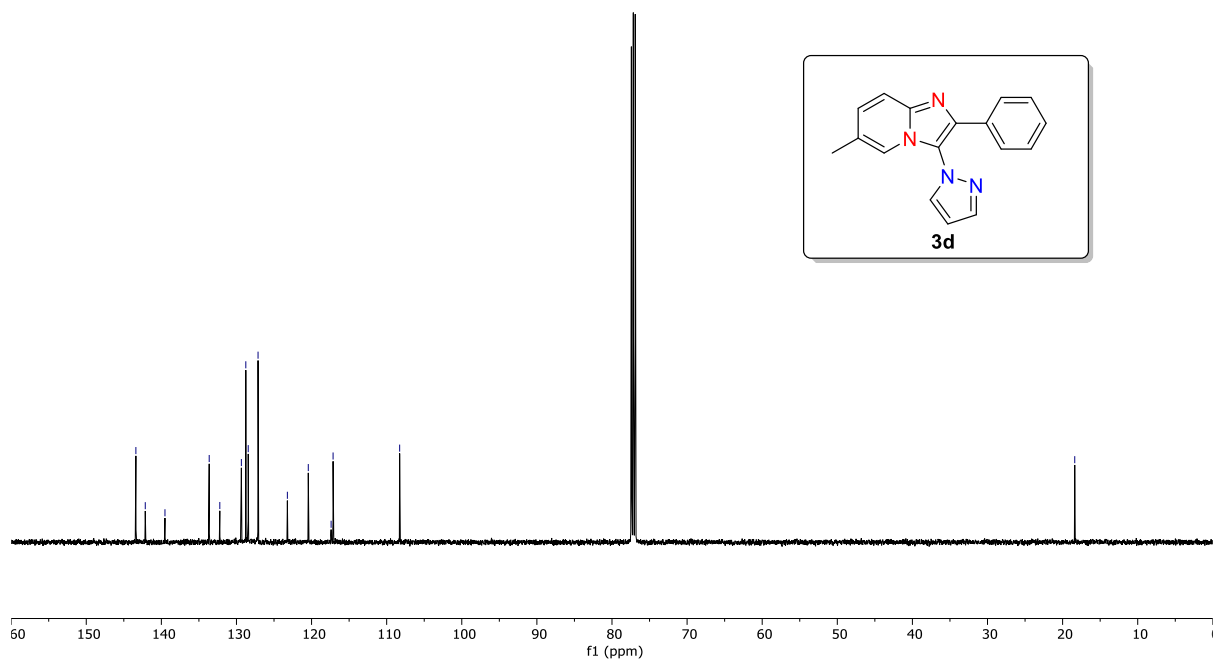
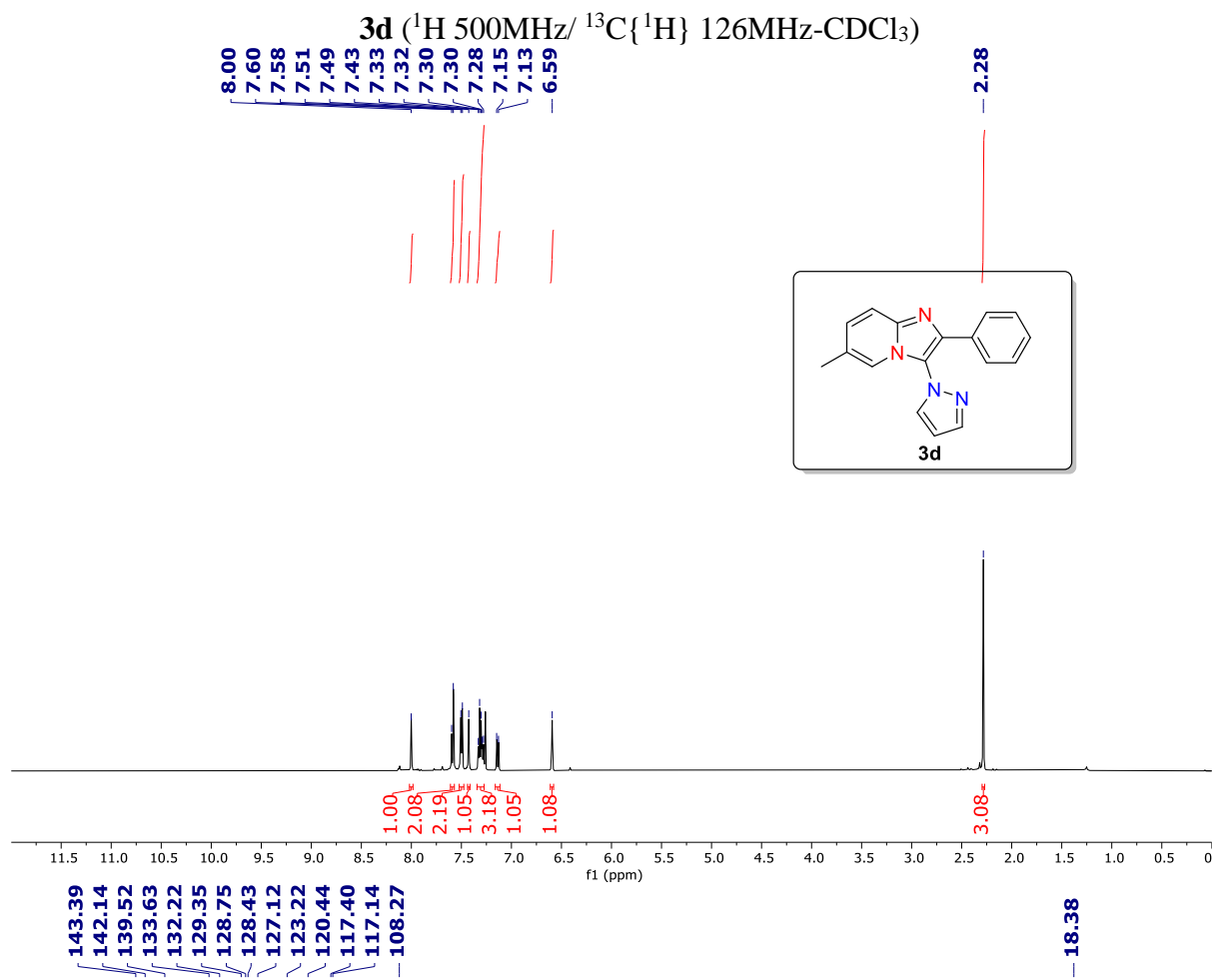
General Information: All the commercial reagents were purchased from Spectrochem, TCI, Sigma-Aldrich and BLD-Pharma and used without further purification. Organic solutions were concentrated under reduced pressure on the Heidolph rotary evaporator. All the reactions were performed within borosilicate glass screw cap test tubes. Organic extracts were dried over anhydrous sodium sulfate. Thin layer chromatography (TLC) was carried out on Merck silica gel 60F₂₅₄ pre-coated aluminium sheets and was visualized using UV light (254nm). Silica gel column chromatographic purification of products was performed using 60-120 mesh silica gel using hexane/ethyl acetate as eluent. ¹H and ¹³C NMR spectra were recorded on a Fourier transform nuclear magnetic resonance spectrometer (model Avance NEO Ascend 500 Bruker BioSpin International AG). The spectra were recorded in CDCl₃ as a solvent. Chemical shift values are reported in δ values (ppm), (δ 7.26 ppm for ¹H NMR, δ 77.0 ppm for ¹³C NMR) downfield from tetramethylsilane (δ 0 ppm). Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets), etc. and coupling constants (*J*) were given in Hz. High-resolution mass spectrometric analyses (HRMS) were executed employing an electrospray ionization time-of-flight mass spectrometer (ESITOF-MS) consisting of Dionex Ultimate 3000 and YL9100 components. Melting points provided were ascertained using an electrothermal melting point apparatus without rectification.

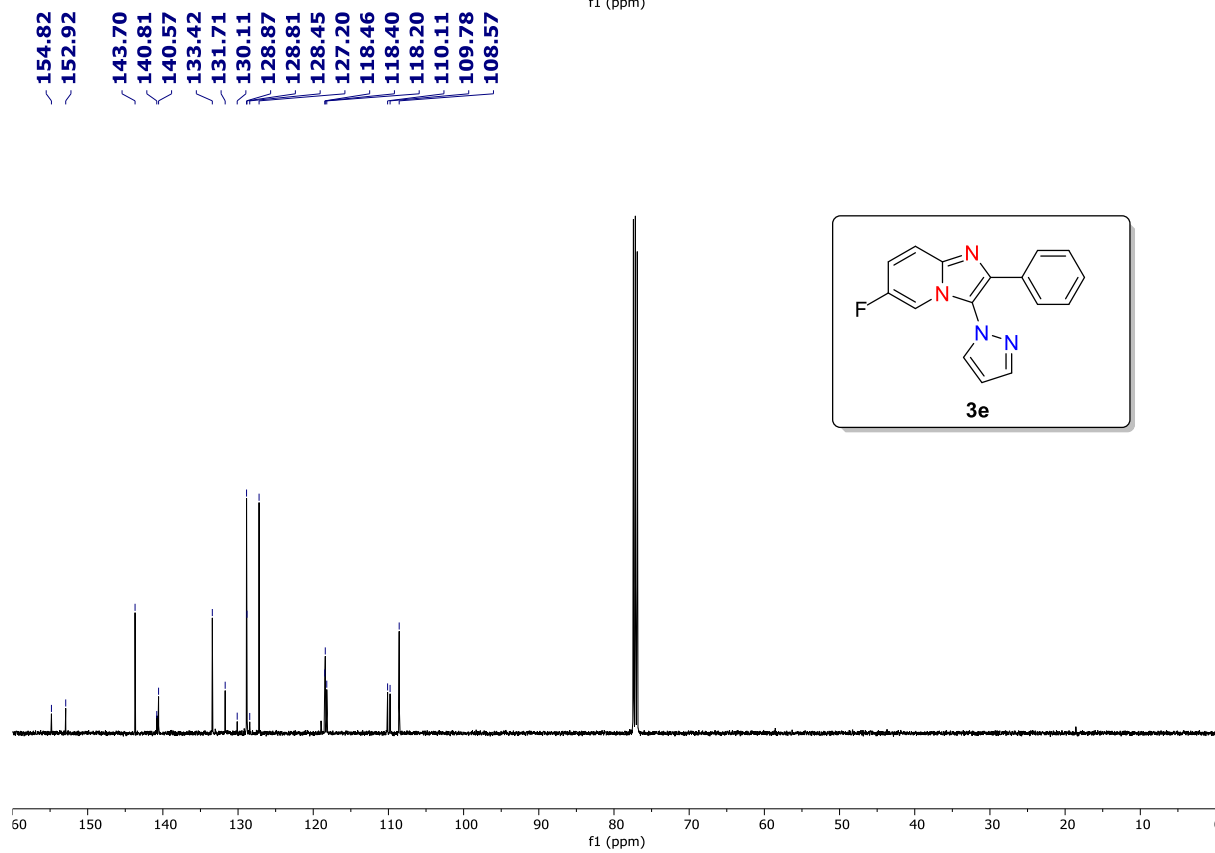
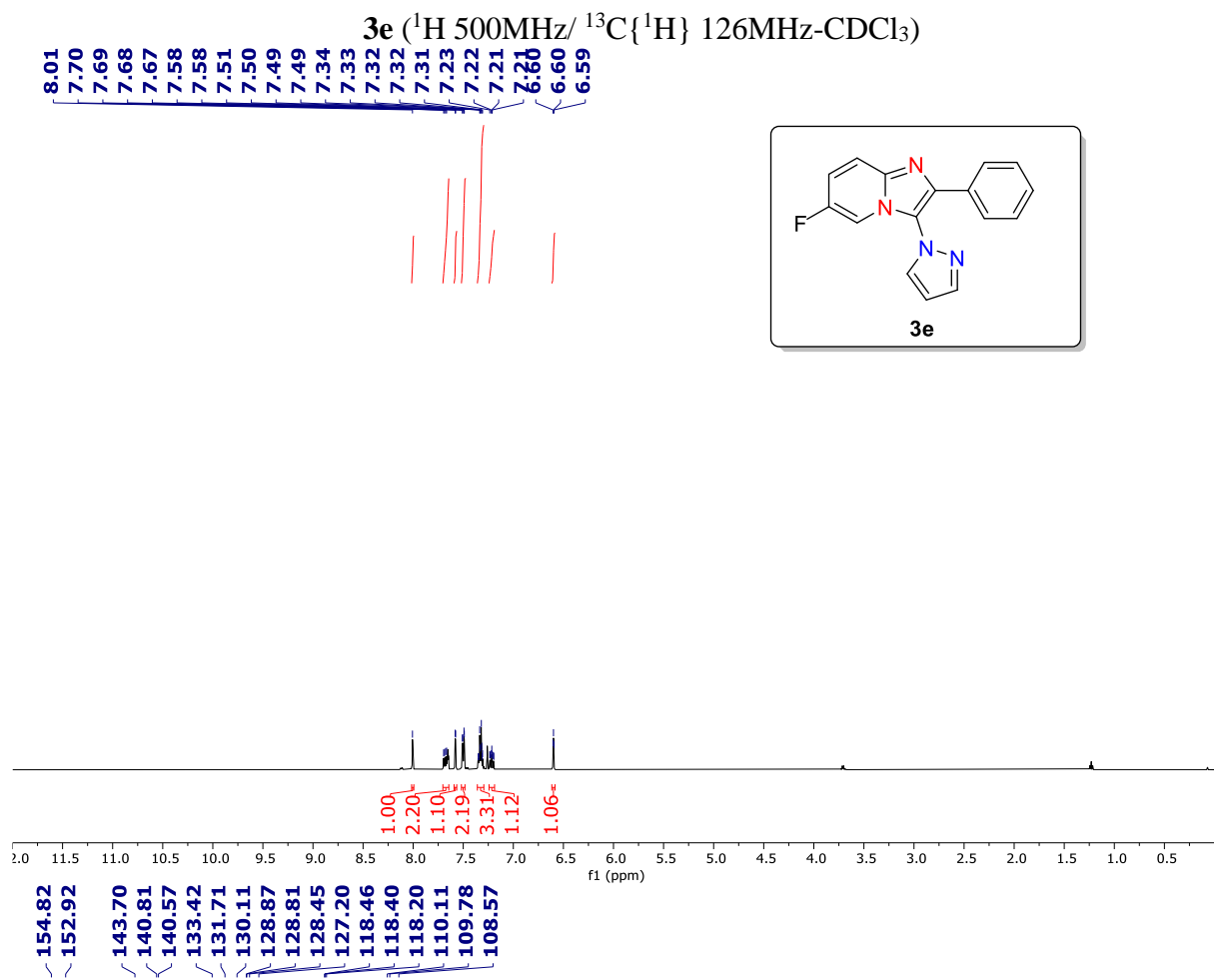
Gram-scale Synthesis of 2-phenyl-3-(1H-pyrazol-1-yl)imidazo[1,2-*a*]pyridine(3). In a 50 mL of borosilicate RB flask, a mixture of 2-arylimidazo[1,2-*a*]-pyridines **1** (1.0g, 1.0 equiv. 5.15 mmol), Pyrazole **2** (0.52g, 1.5 equiv., 7.73 mmol), and K₂S₂O₈ (2.78g, 2.0 equiv., 10.30 mmol), in H₂O was stirred at 80 °C in preheated silicon oil, for 6 h. After completion of the reaction (monitored via TLC), the reaction mixture was diluted with brine solution (10 mL) and extracted with EtOAc (20 mL \times 3). The combined organic phase was dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by silica gel (60–120 mesh) column chromatography using hexane/ethyl acetate (8:2) as eluent to afford the desired product **3**.





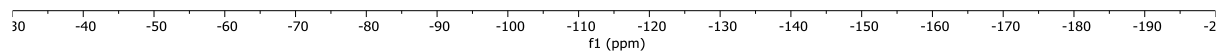
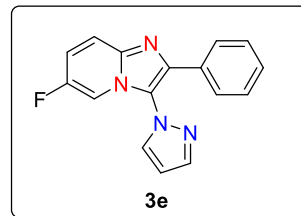


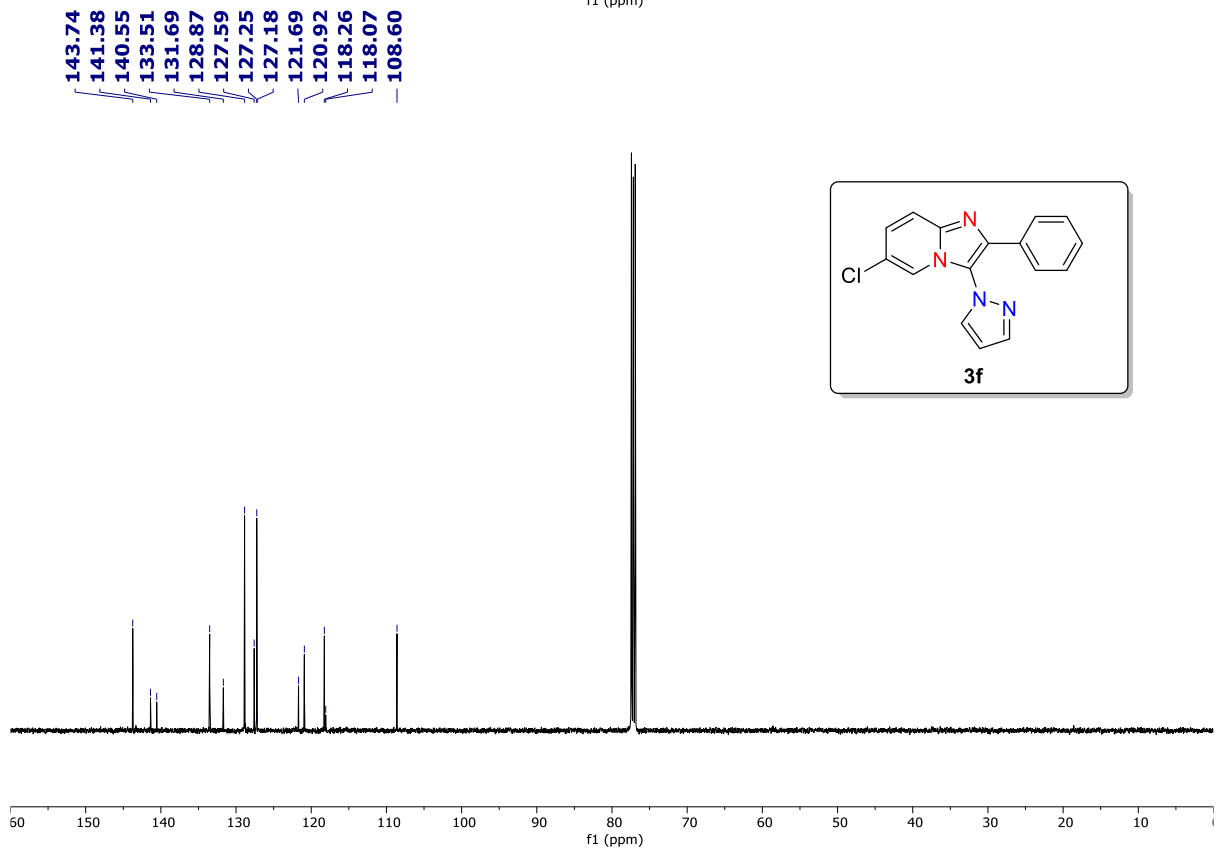
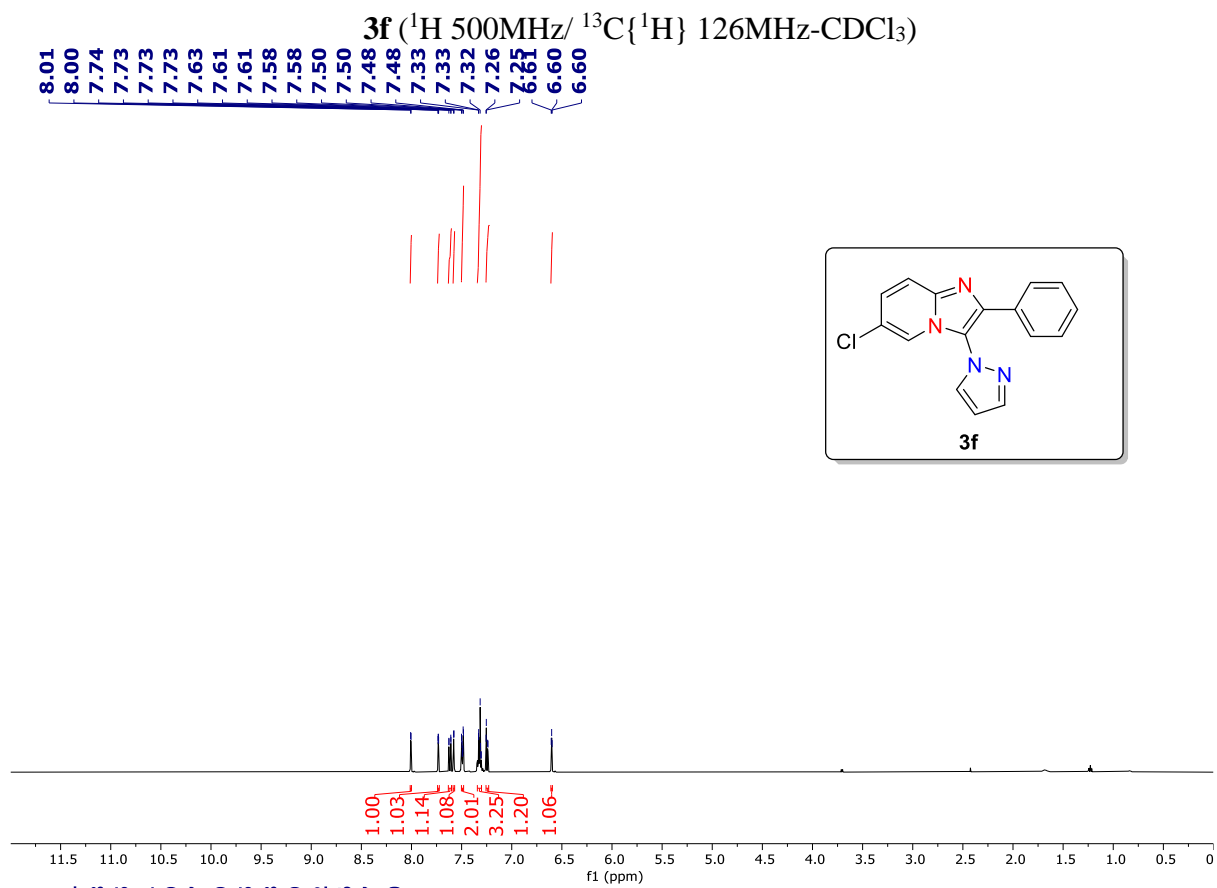


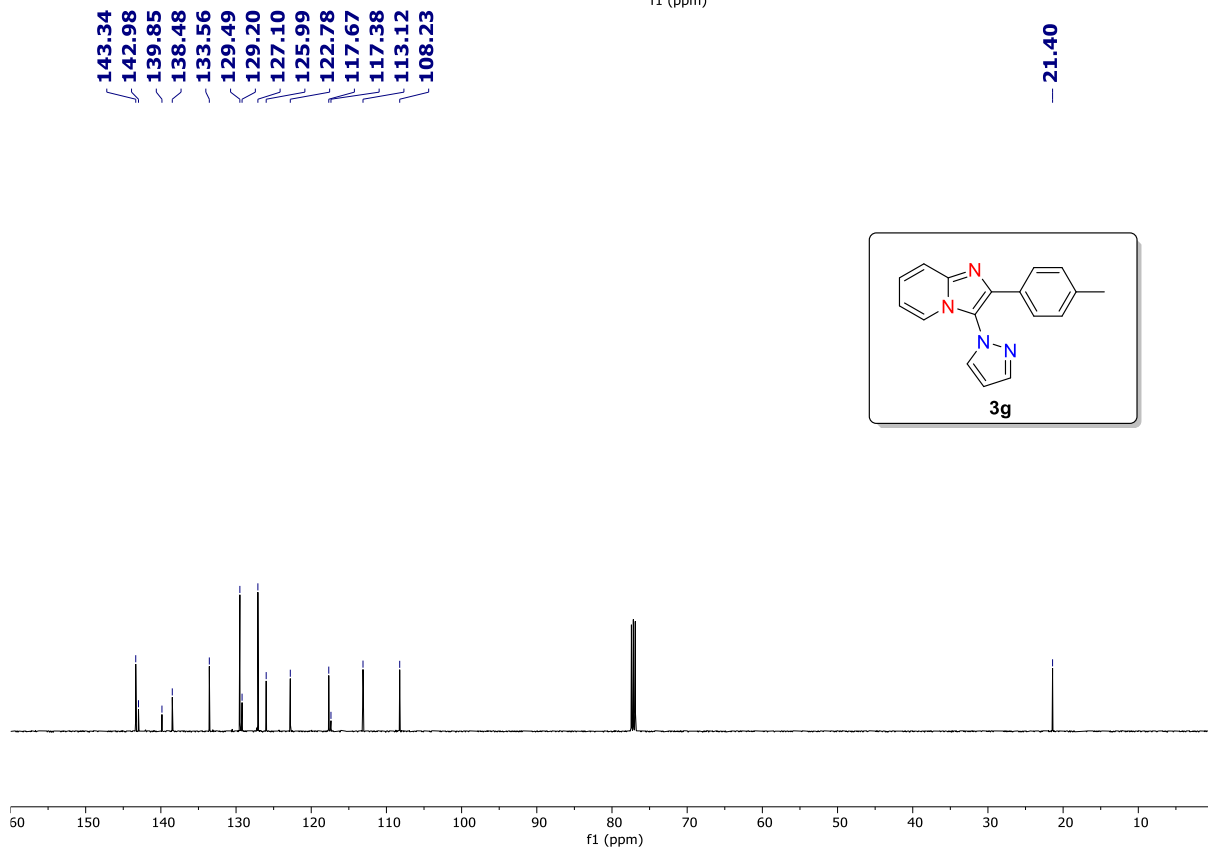
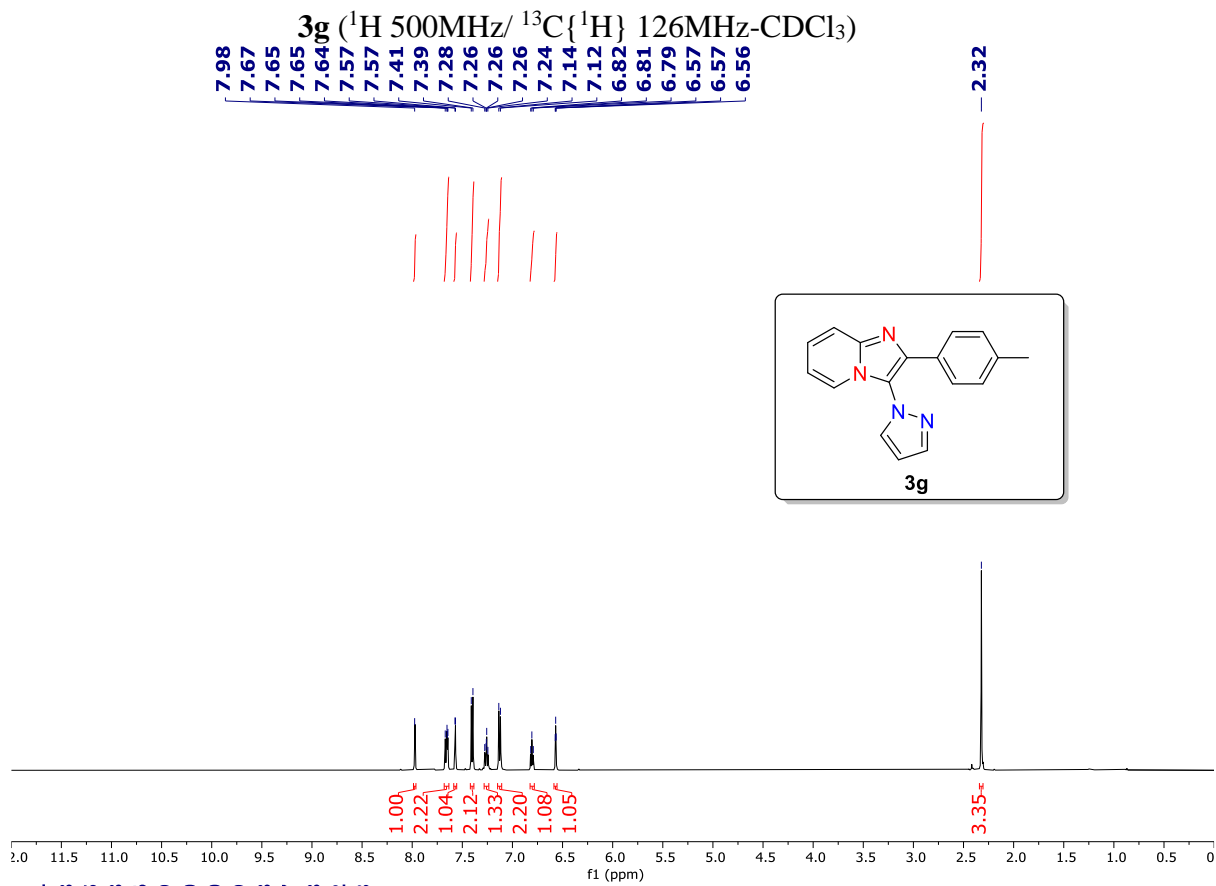


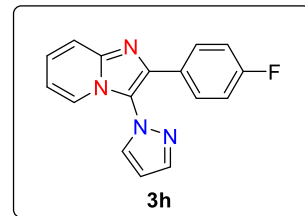
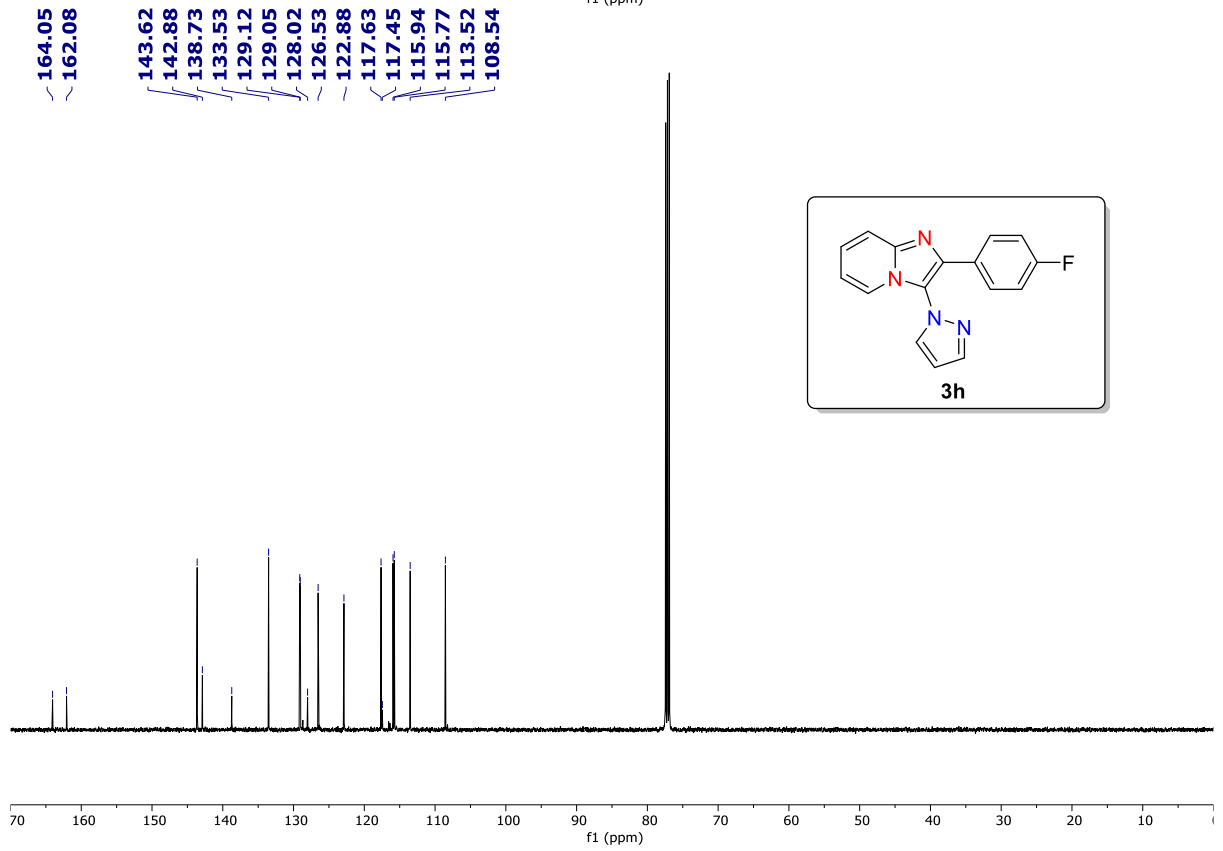
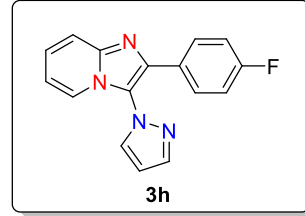
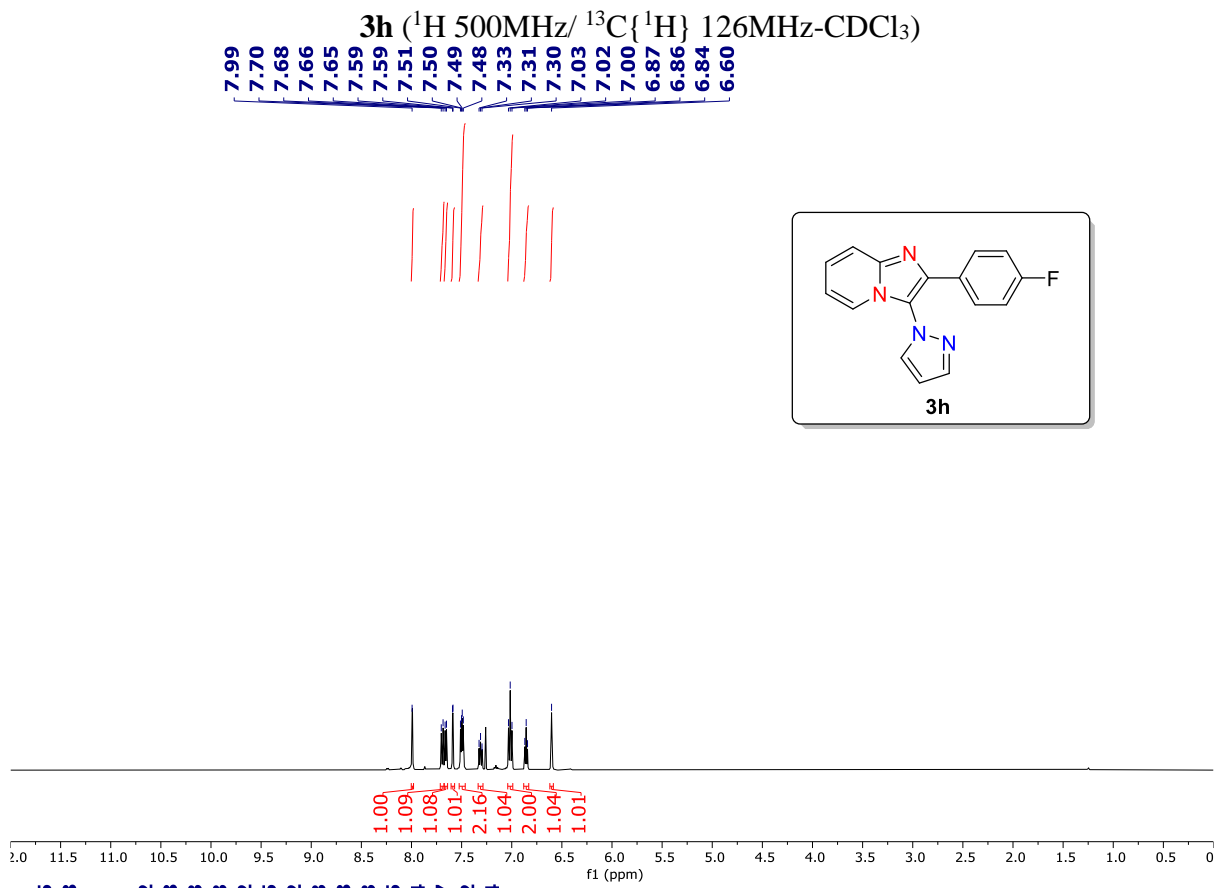
3e (^{19}F 471MHz- CDCl_3)

-138.04



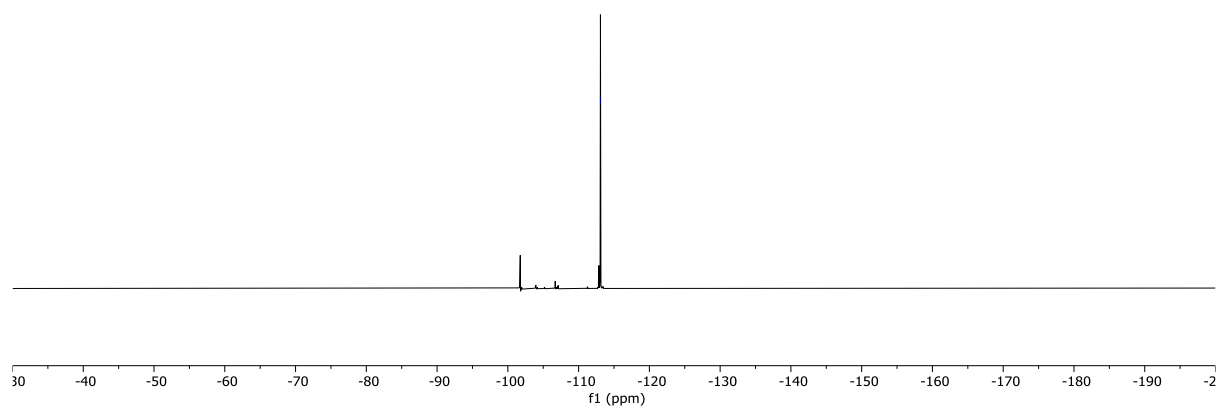
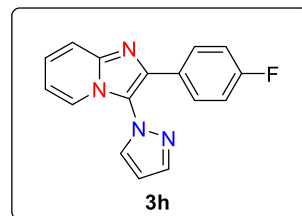


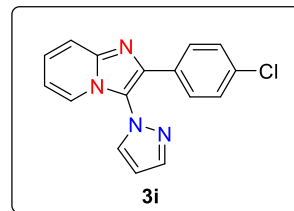
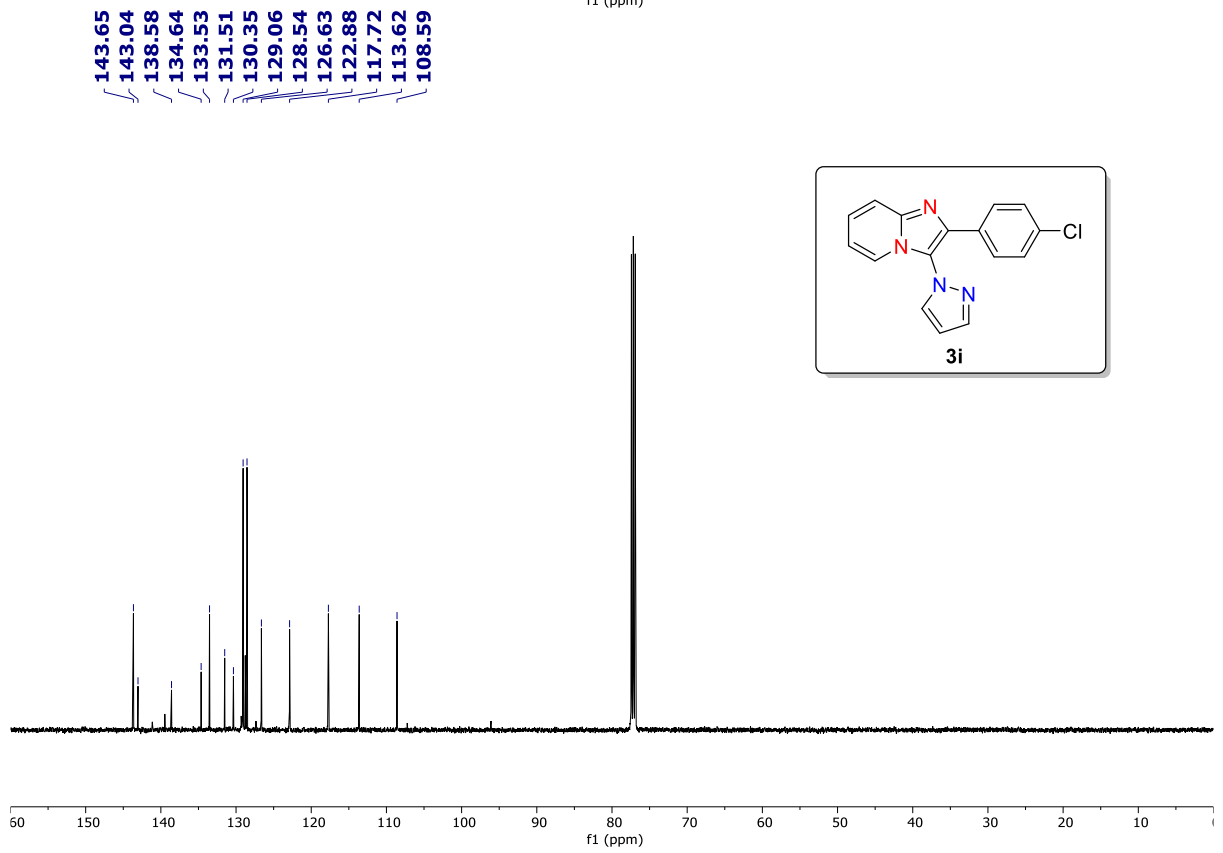
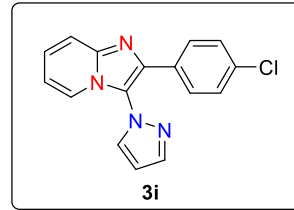
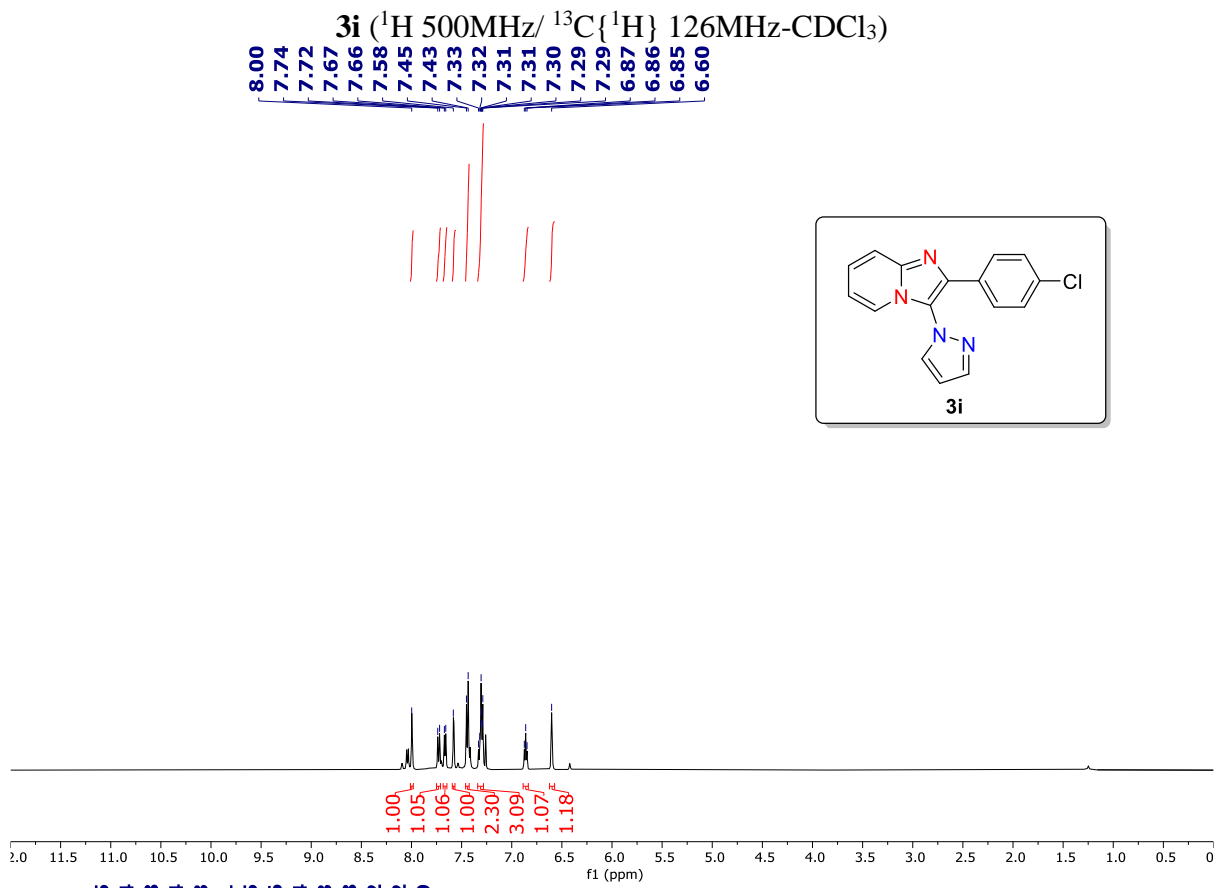




3h (^{19}F 471MHz- CDCl_3)

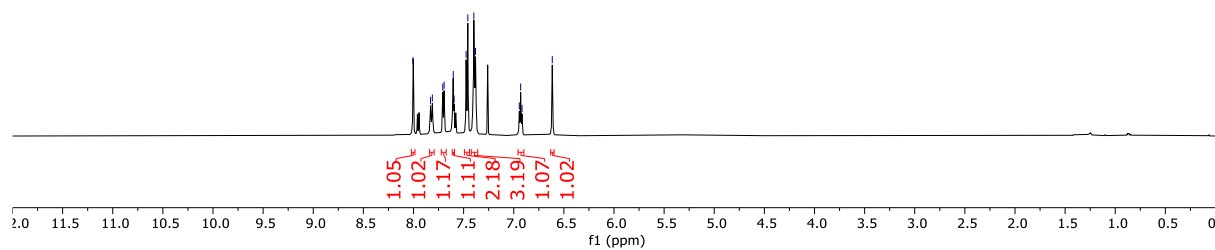
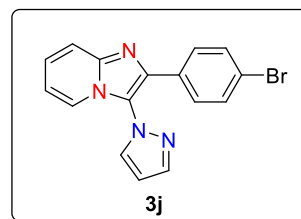
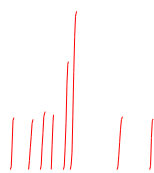
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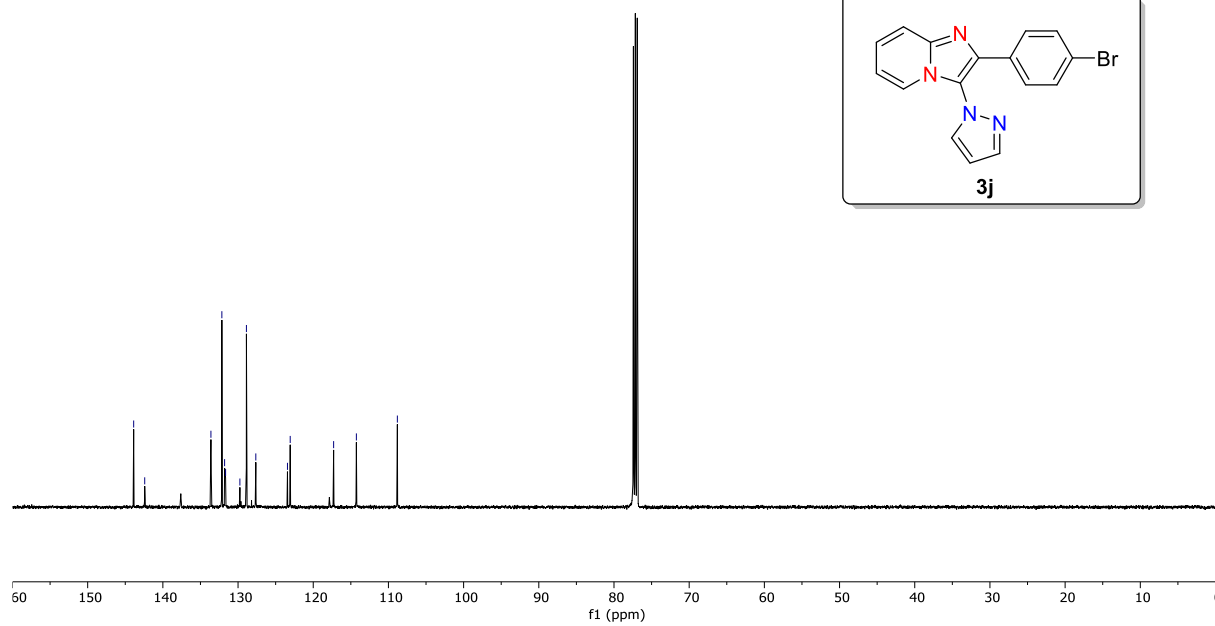


3j (^1H 500MHz/ ^{13}C { ^1H } 126MHz- CDCl_3)

8.01
7.83
7.81
7.71
7.69
7.60
7.59
7.47
7.46
7.40
7.38
6.94
6.93
6.92
6.62

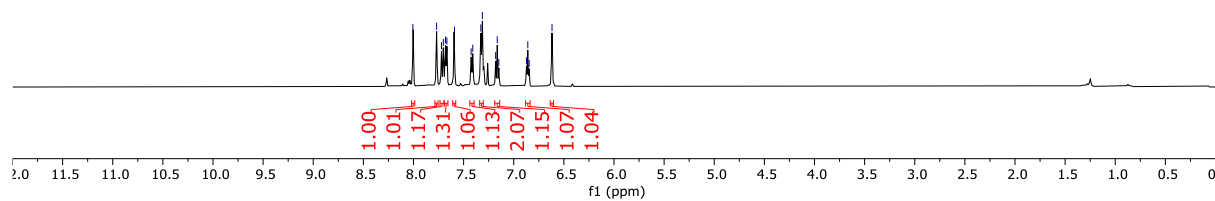
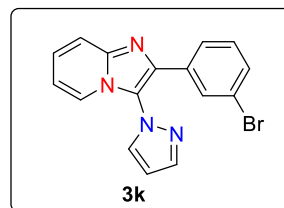
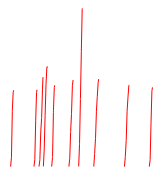


143.88
142.41
133.61
132.15
131.79
131.66
129.76
128.89
127.64
123.43
123.06
117.29
114.26
108.81

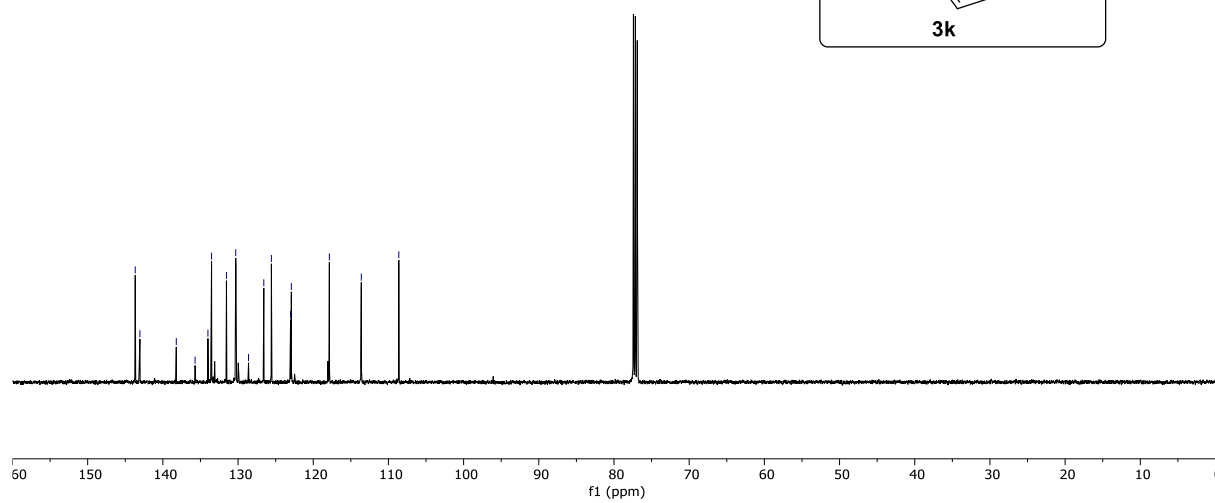
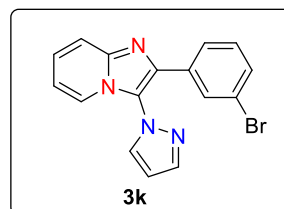


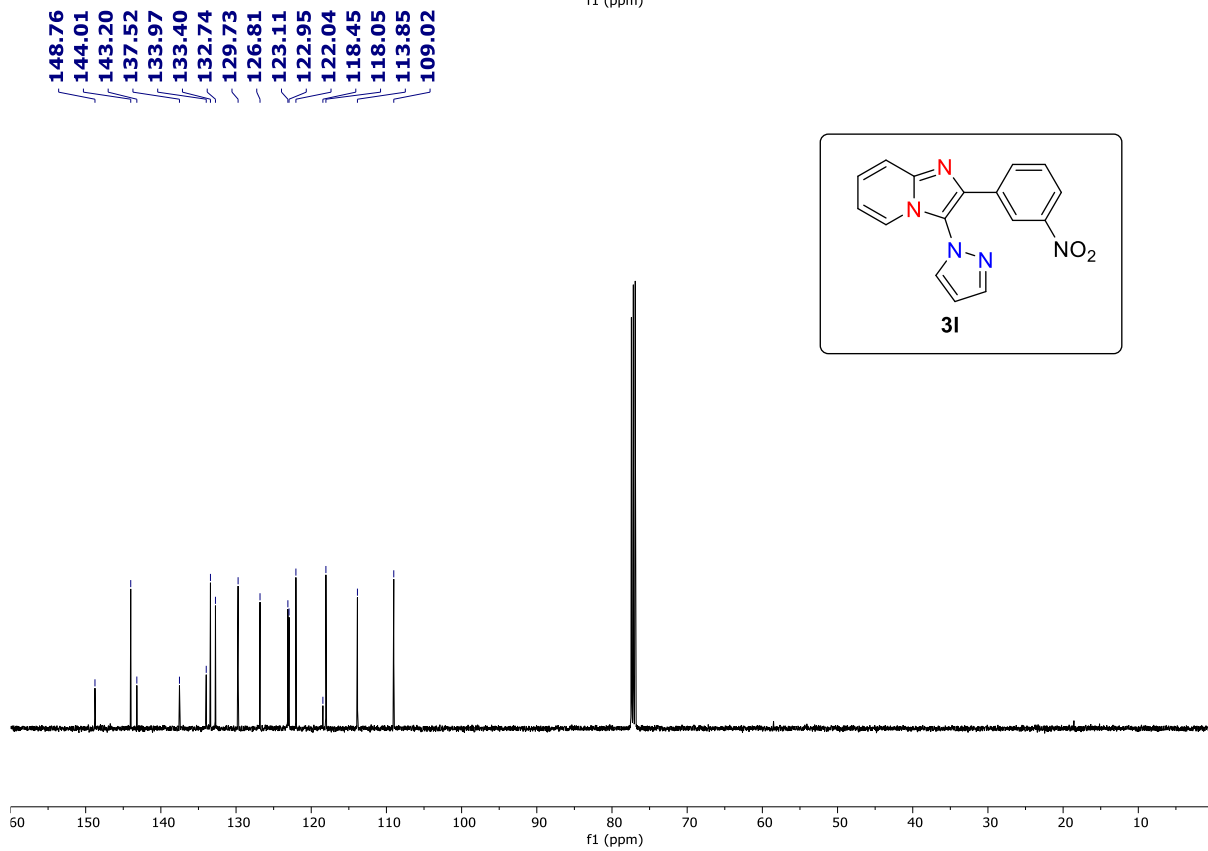
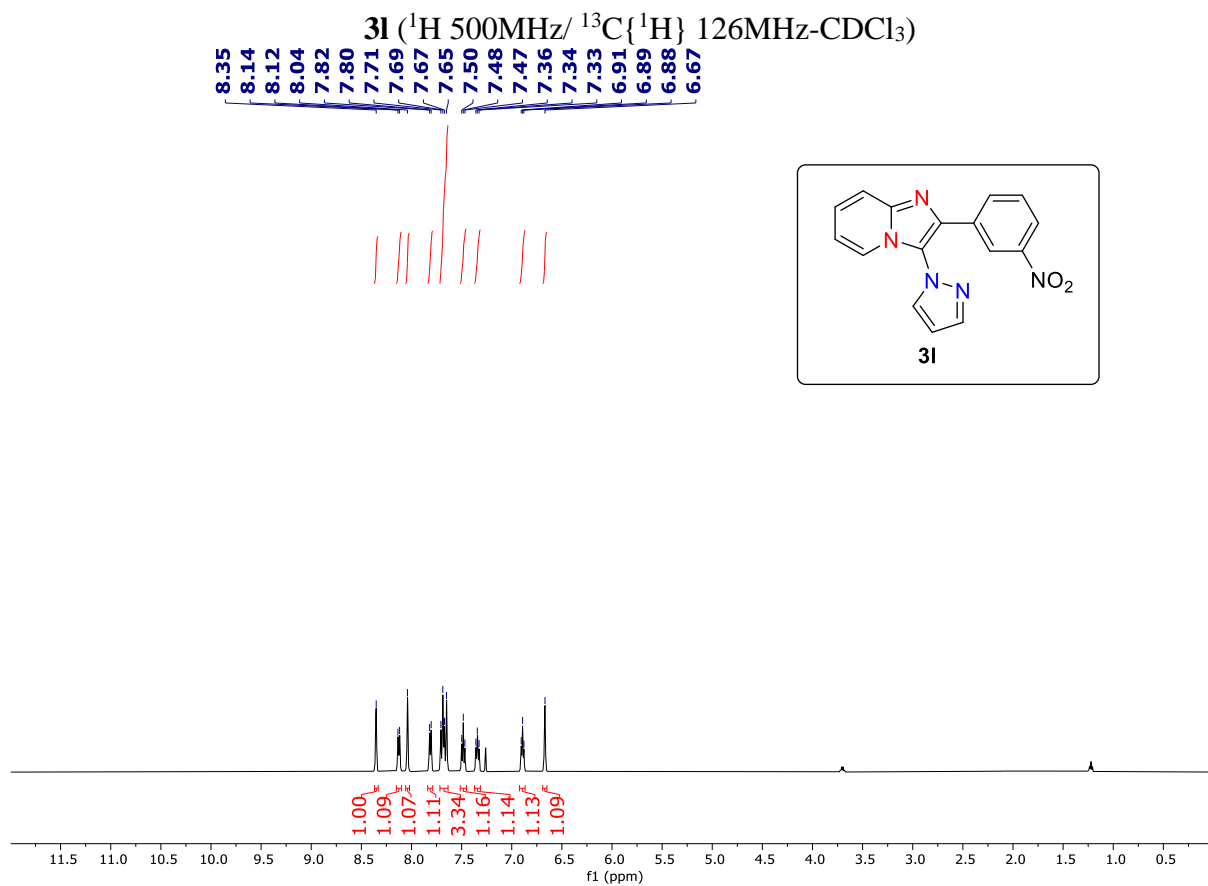
3k (^1H 500MHz/ $^{13}\text{C}\{^1\text{H}\}$ 126MHz- CDCl_3)

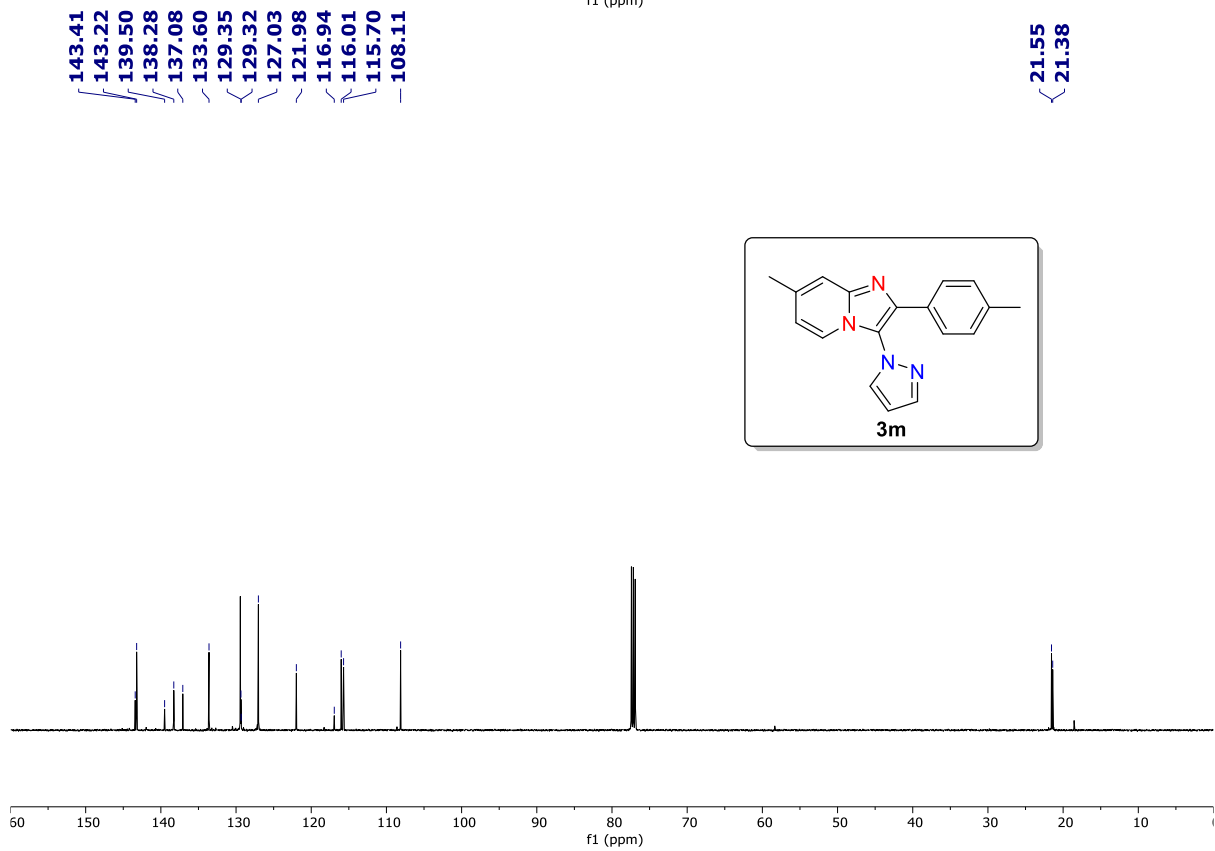
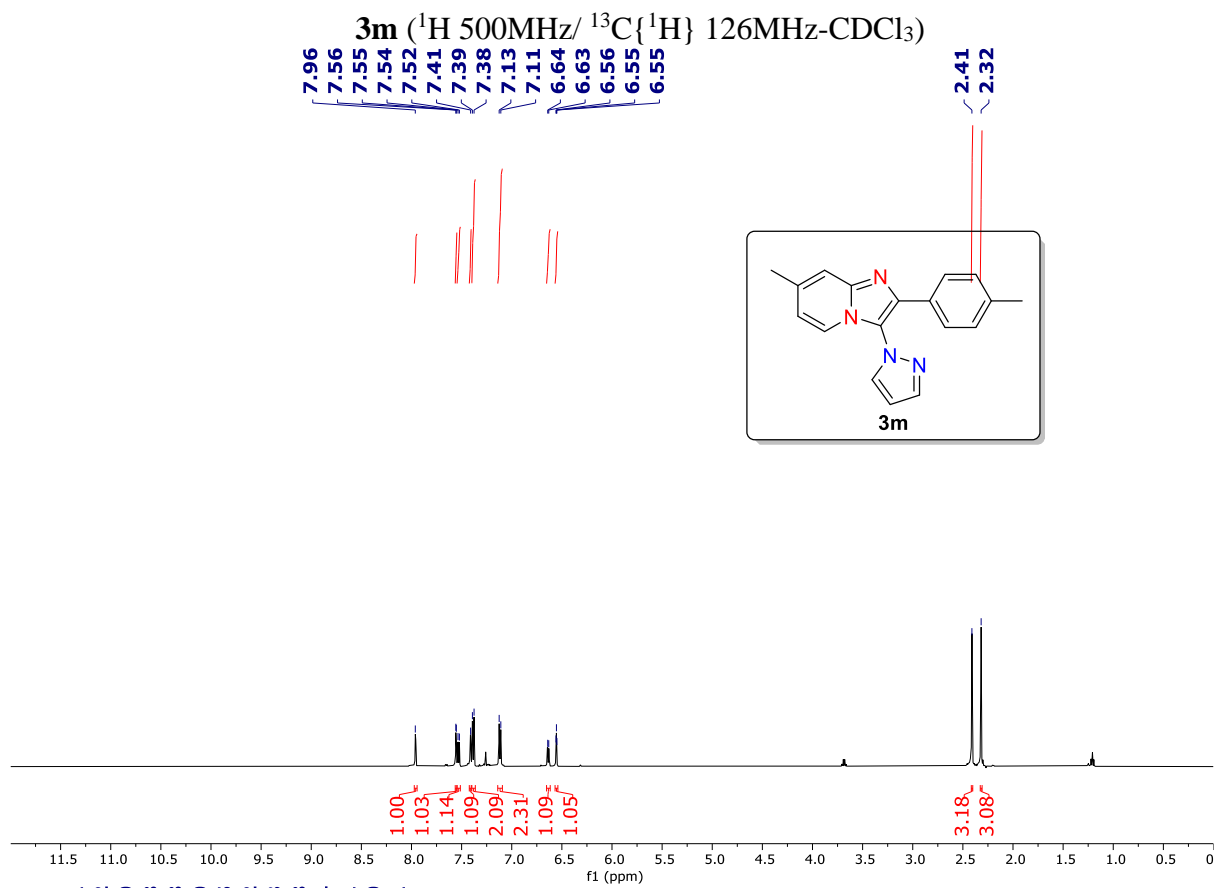
8.01
7.77
7.72
7.70
7.68
7.67
7.59
7.42
7.41
7.33
7.31
7.18
7.16
7.15
6.87
6.86
6.85
6.62

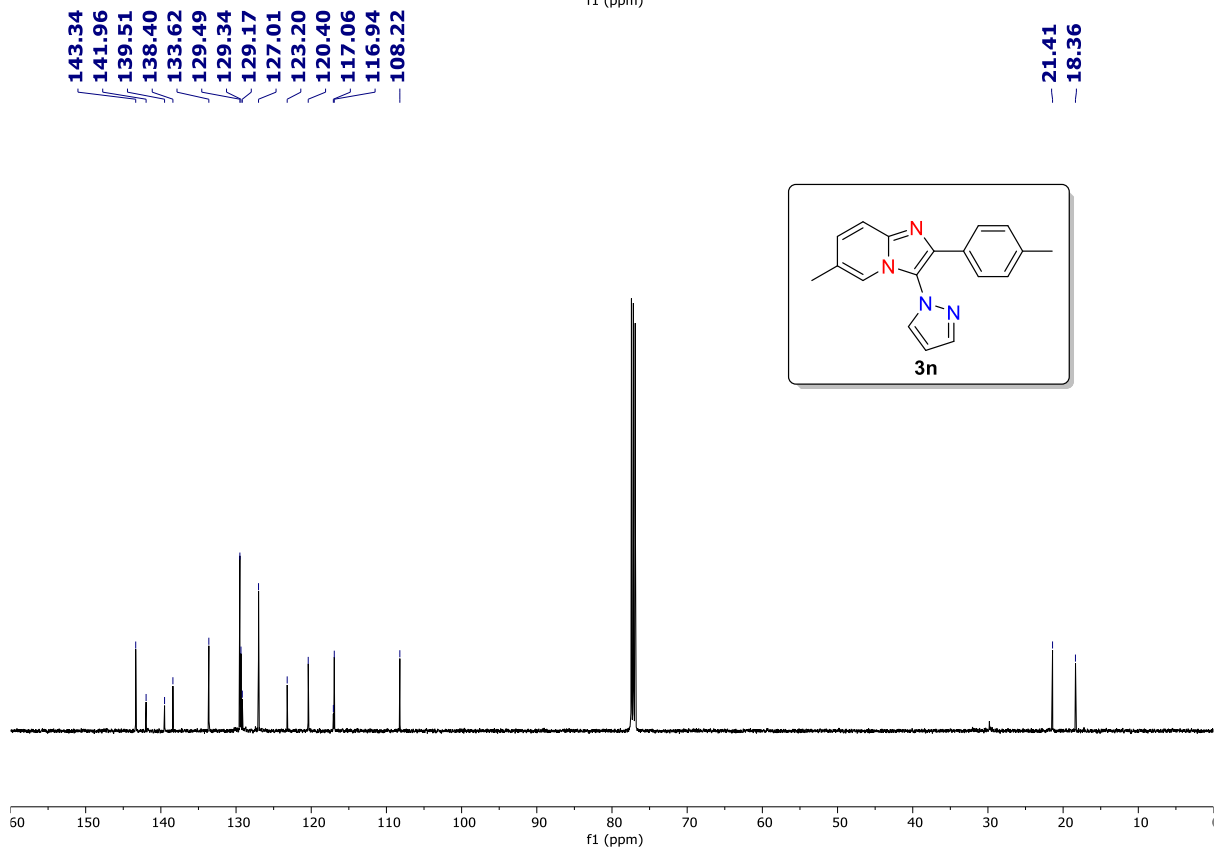
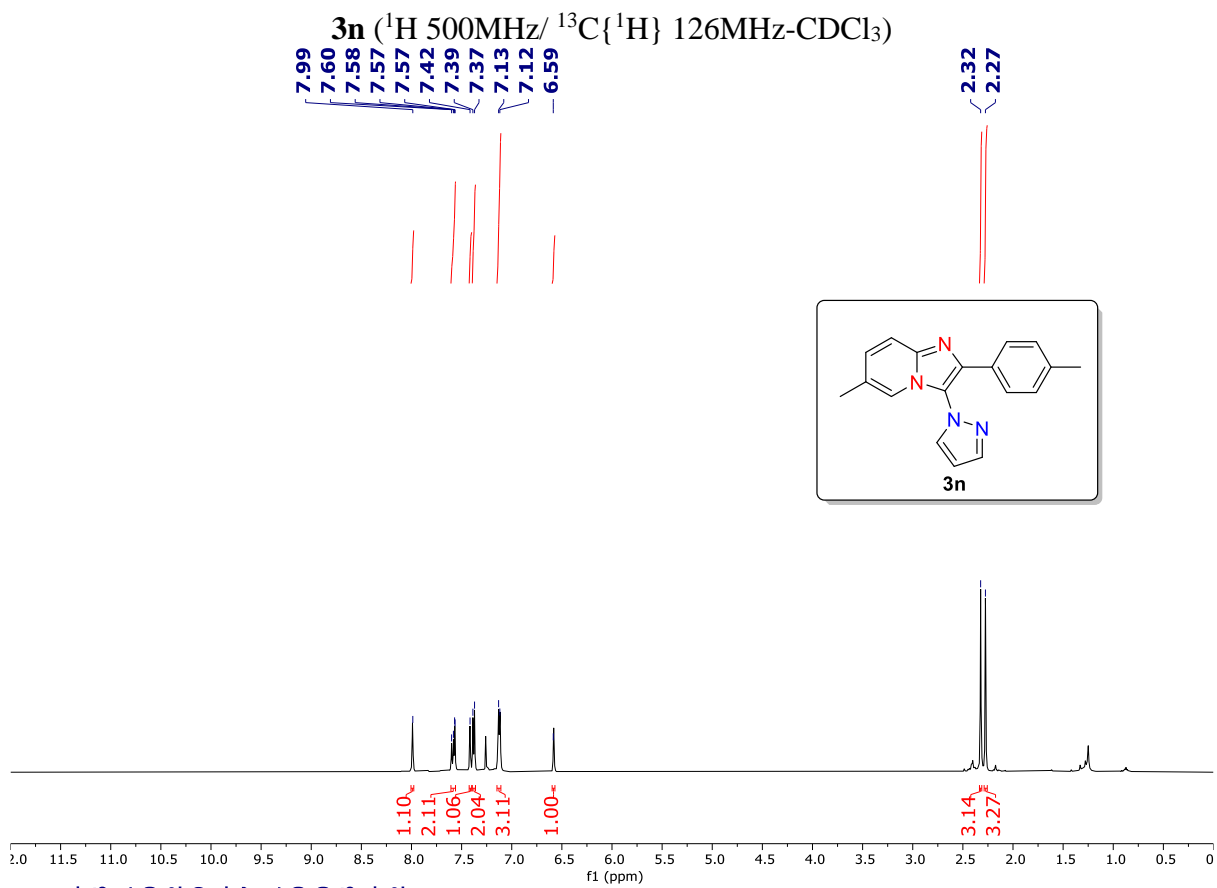


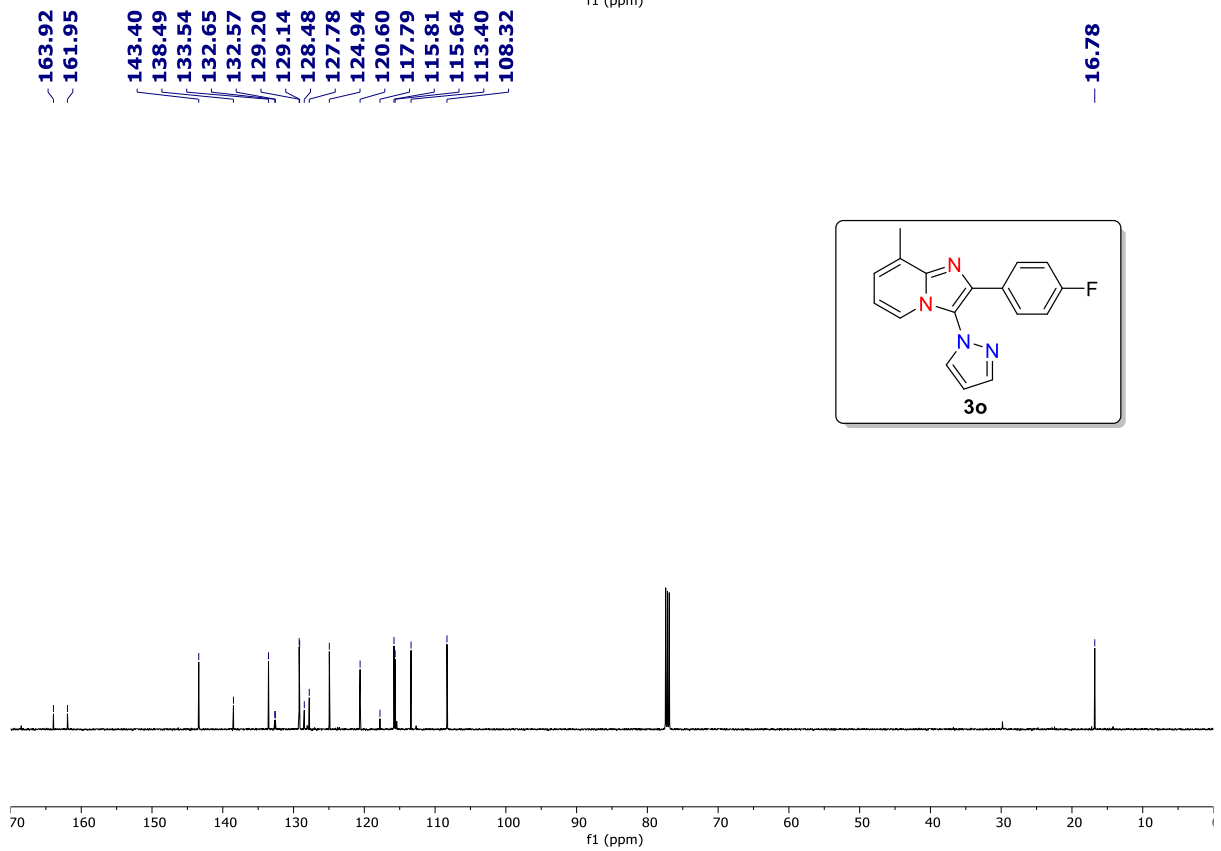
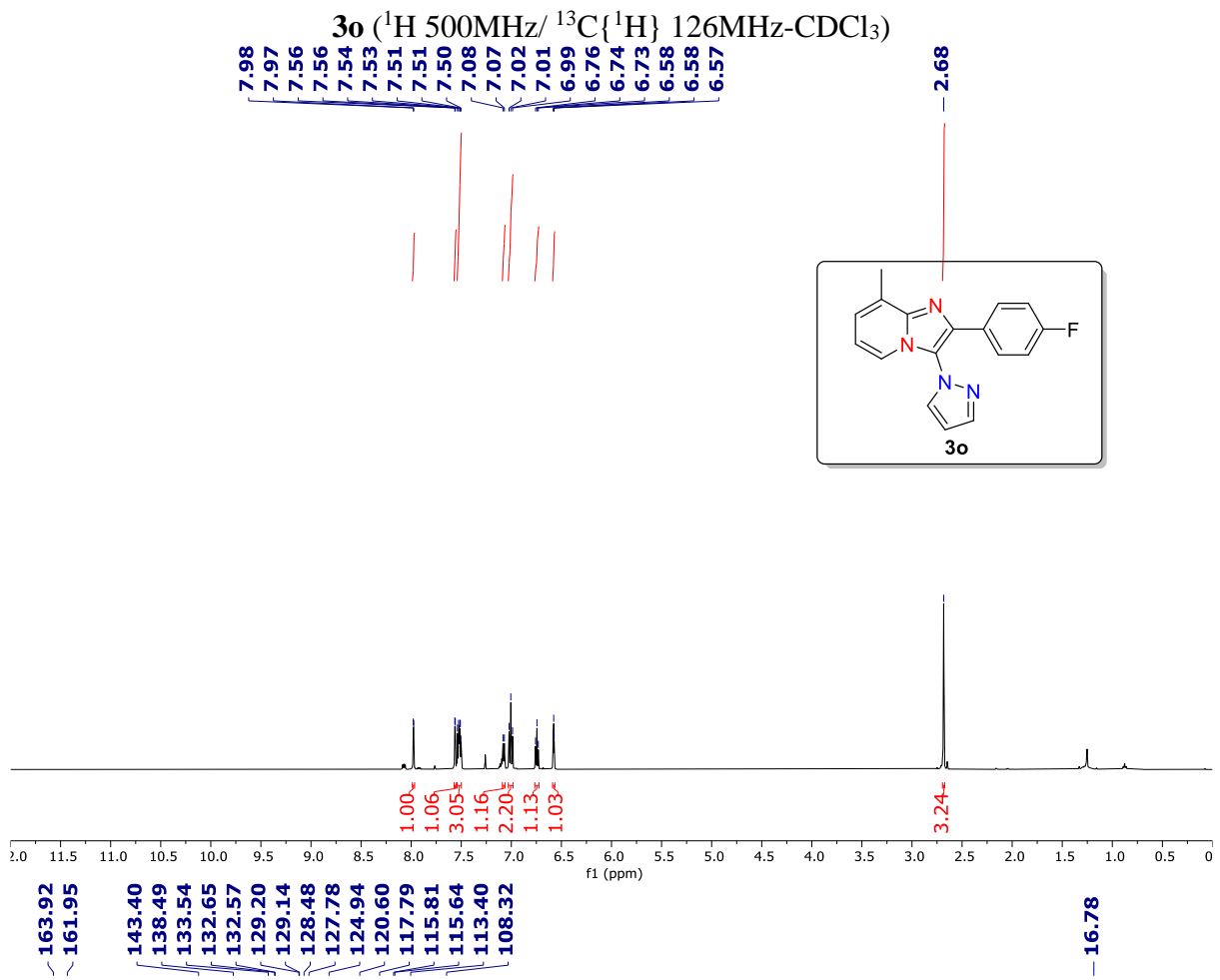
143.67
143.05
138.22
135.72
134.01
133.52
131.54
130.31
128.61
126.57
125.57
123.02
122.91
117.86
113.61
108.62





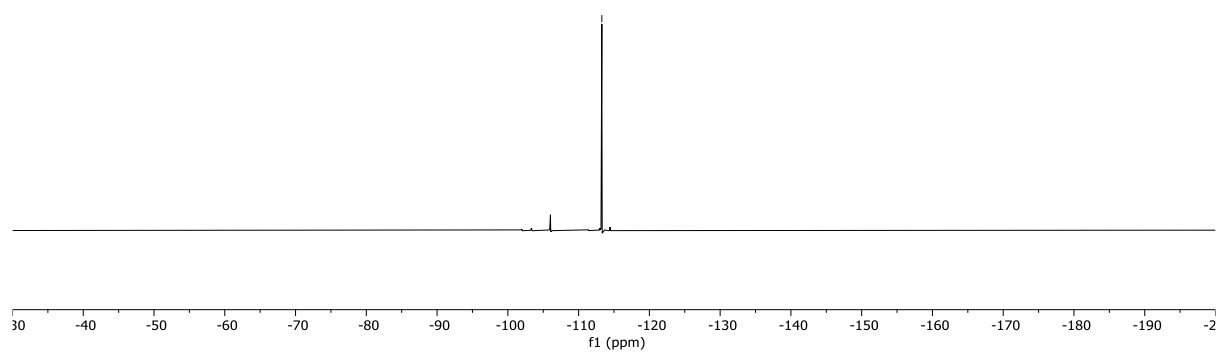
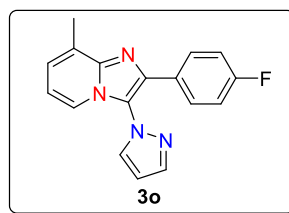


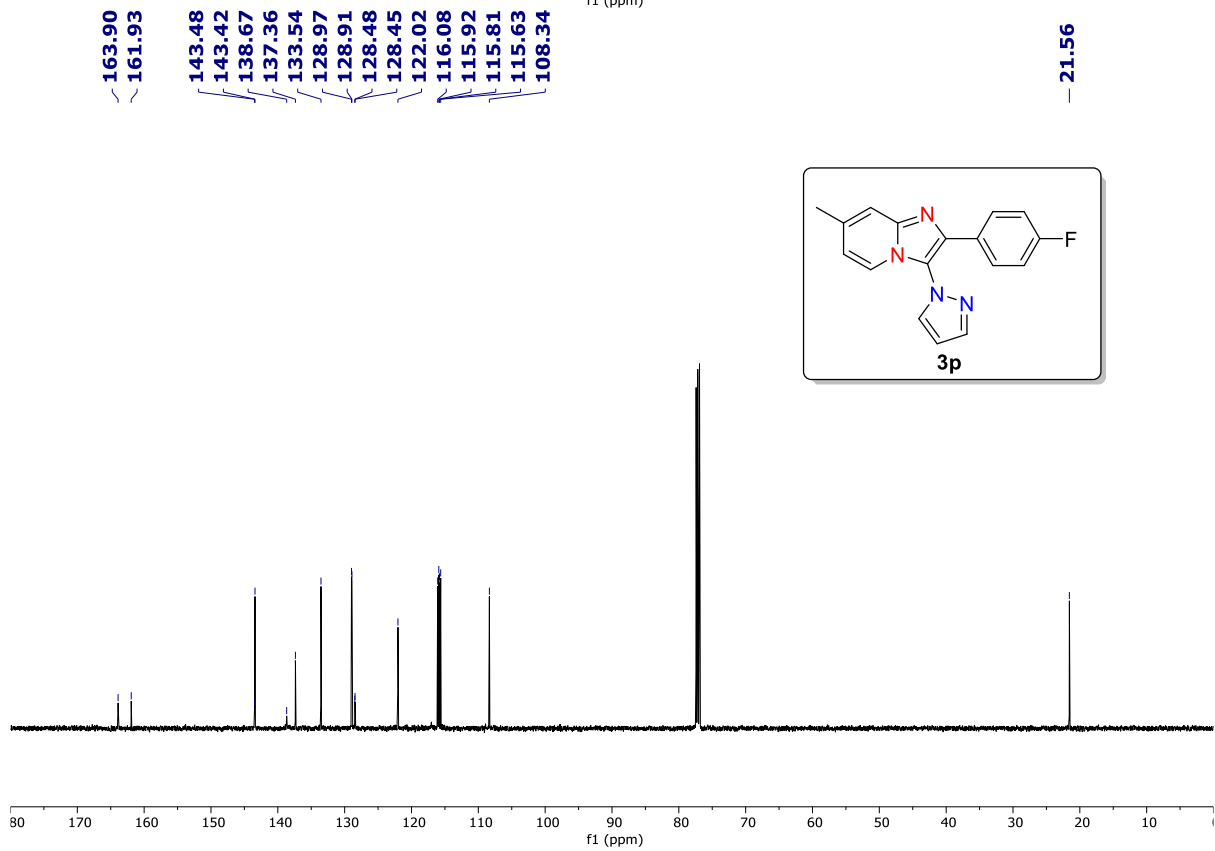
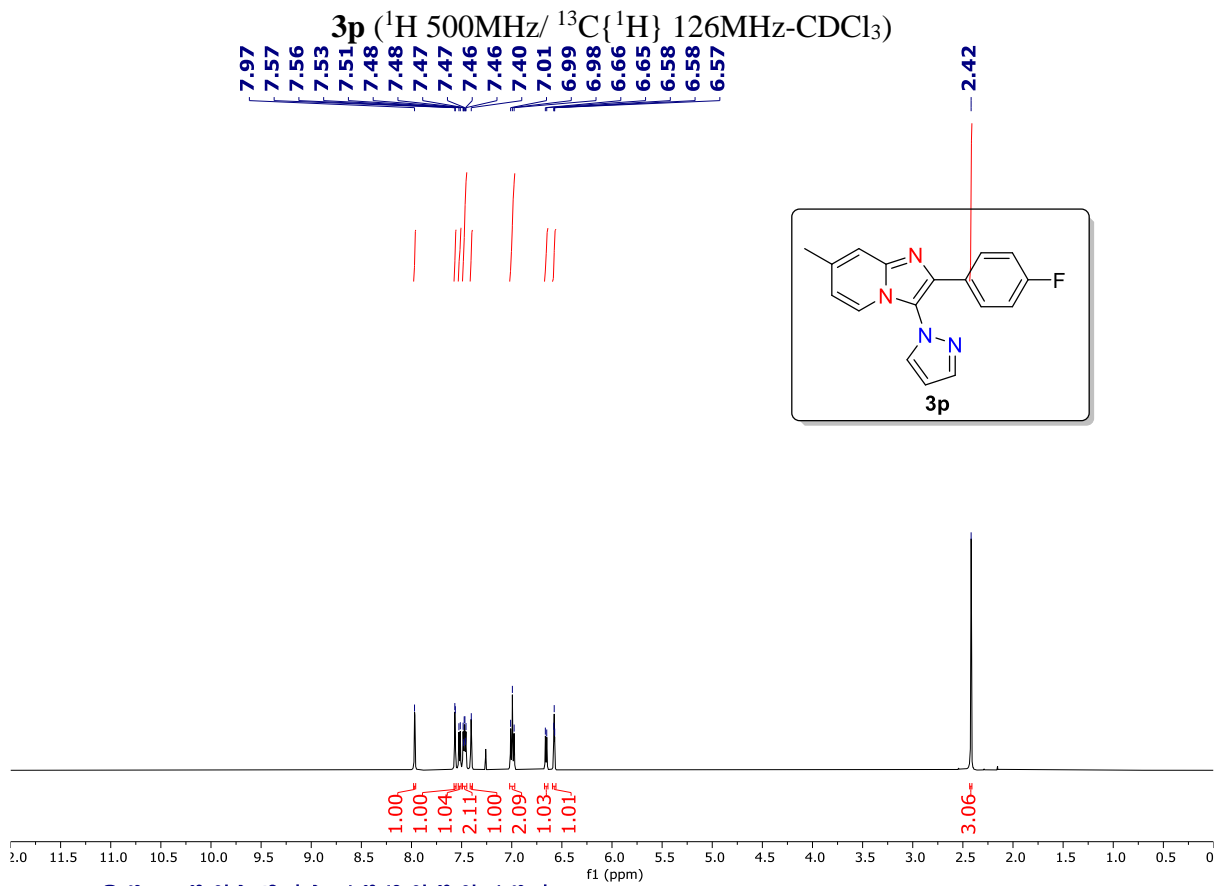




3o (^{19}F 471MHz- CDCl_3)

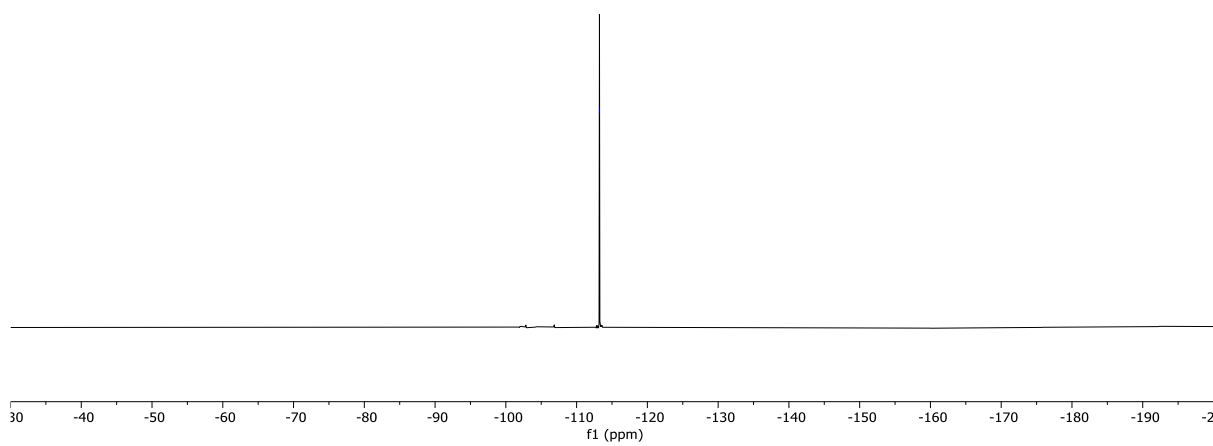
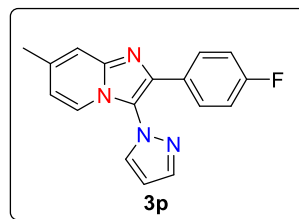
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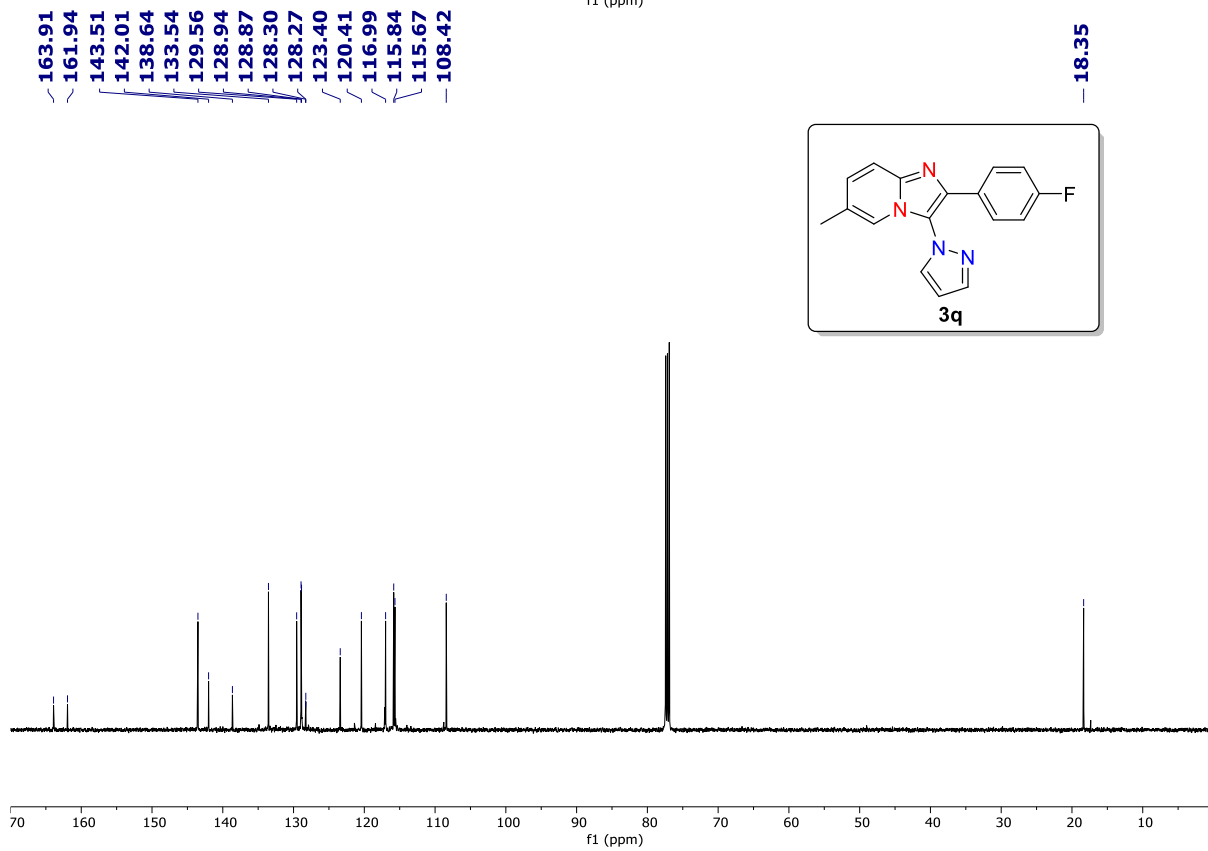
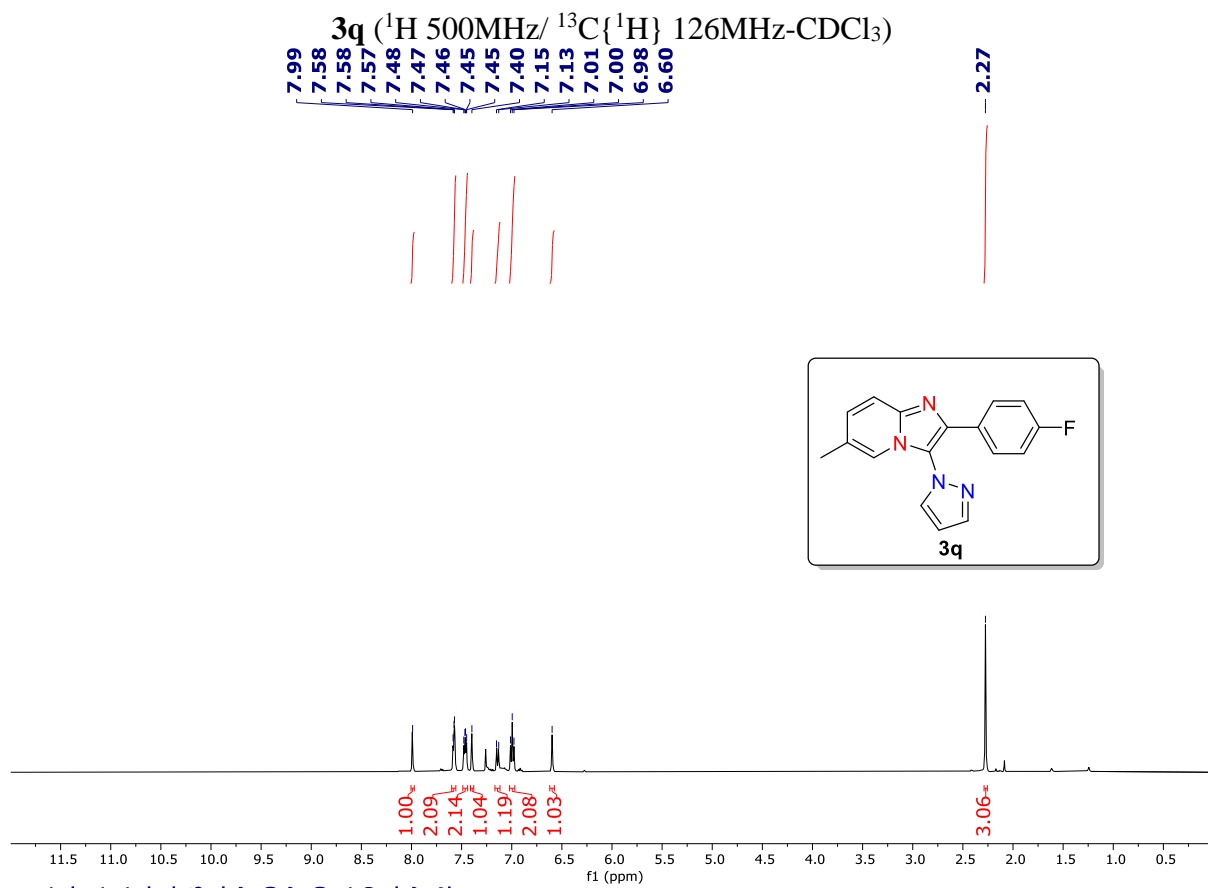




3p (^{19}F 471MHz- CDCl_3)

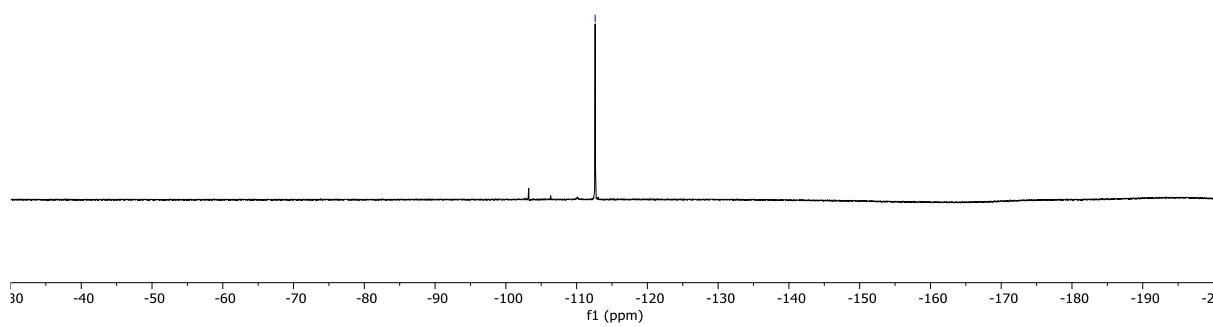
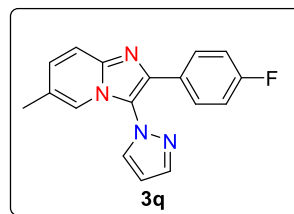
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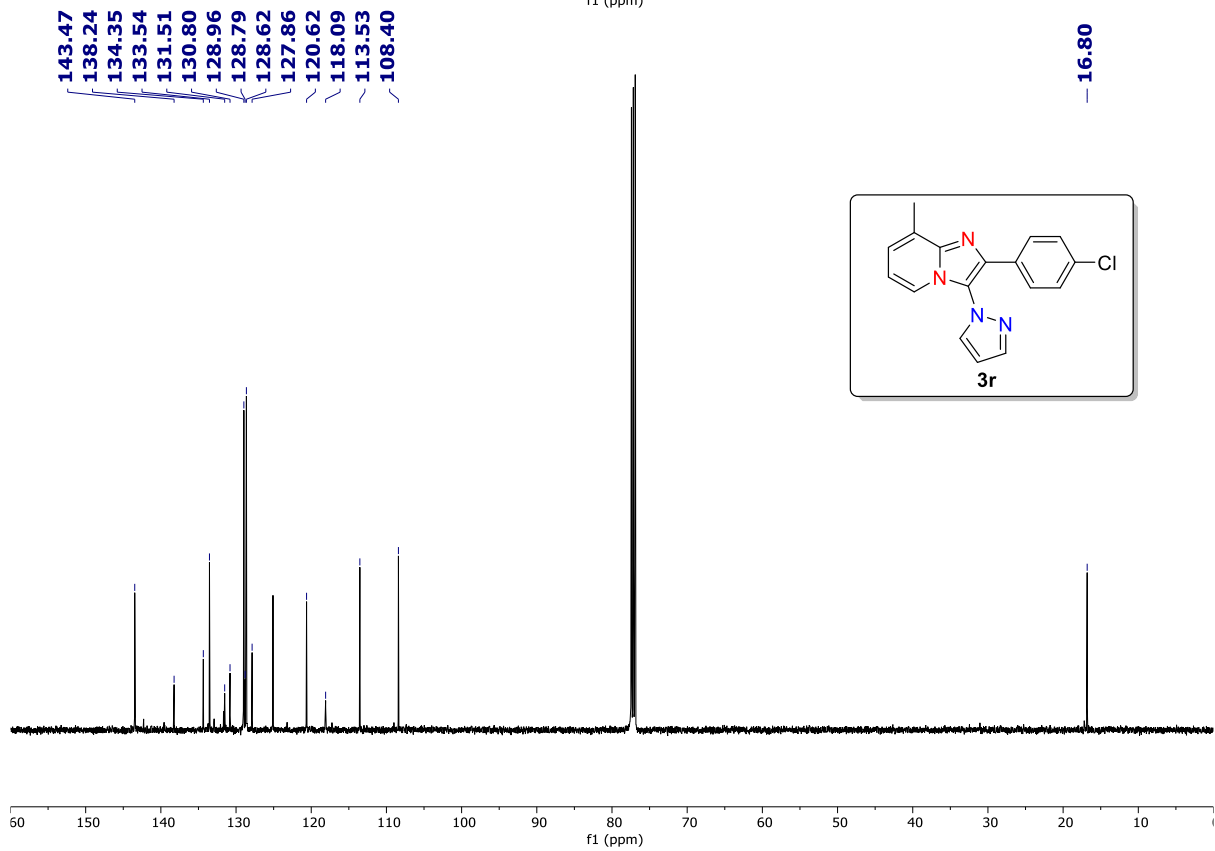
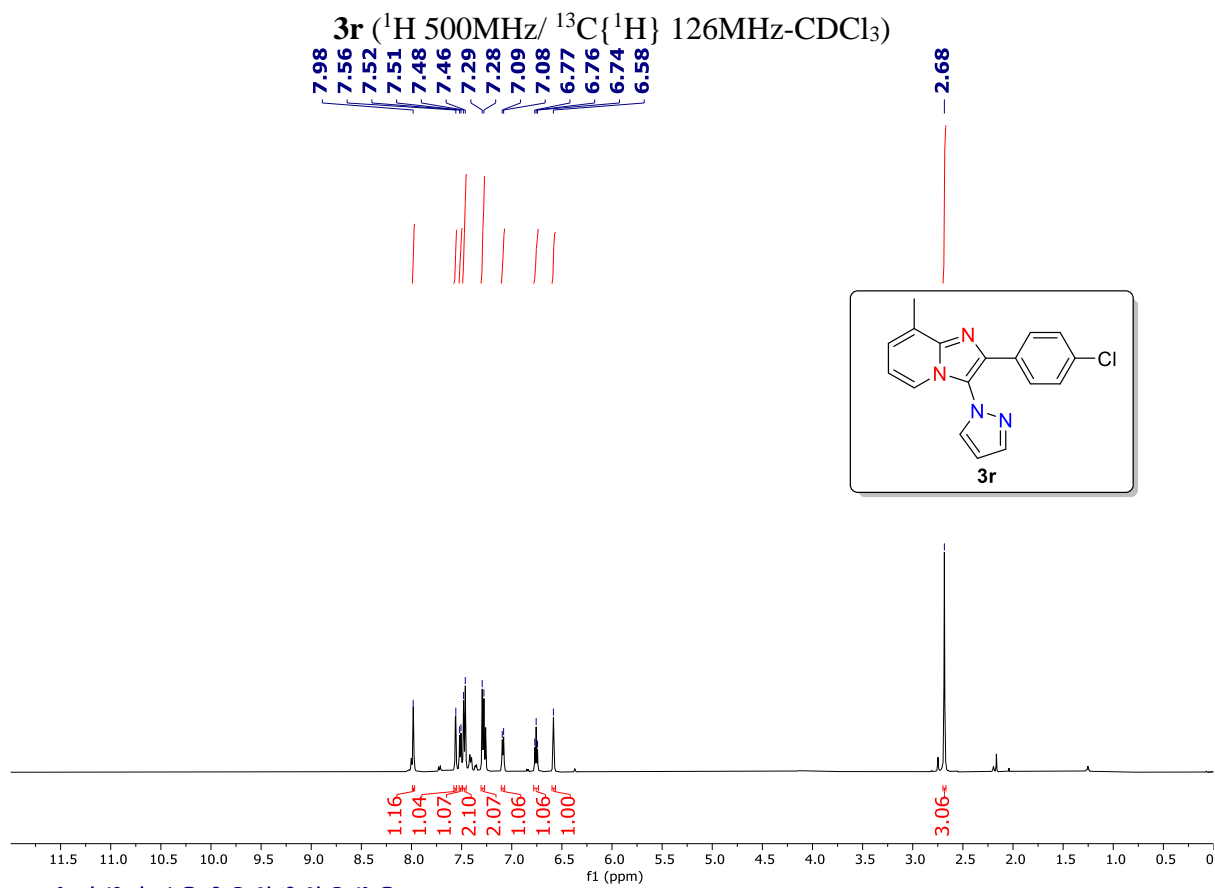


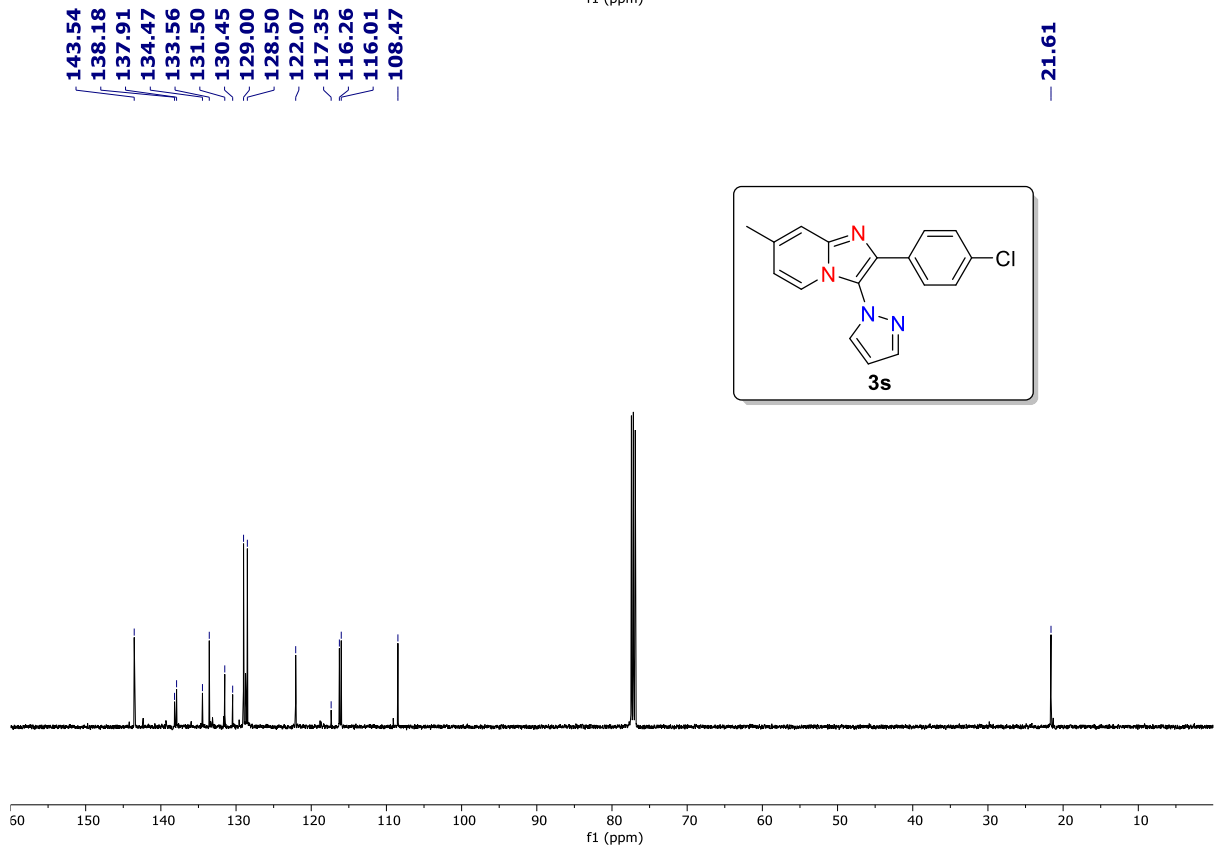
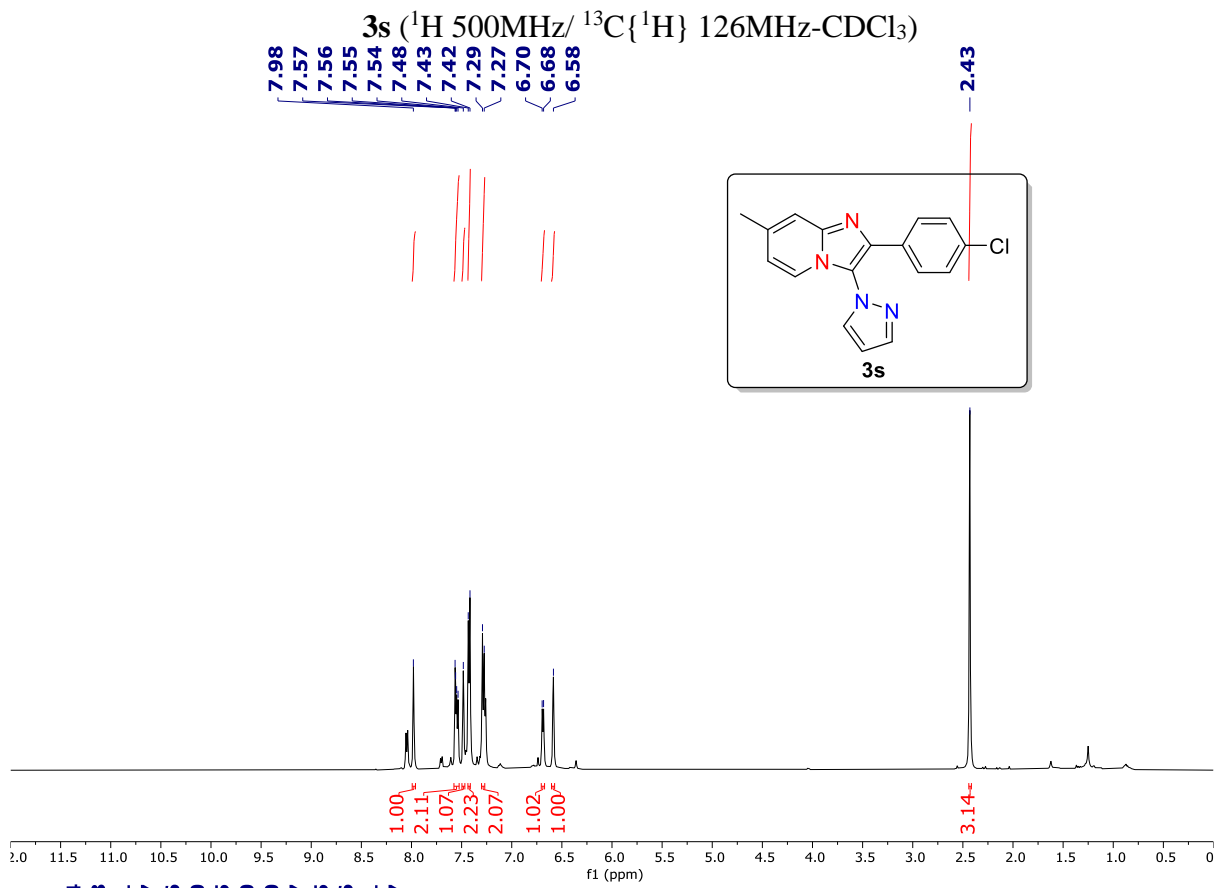


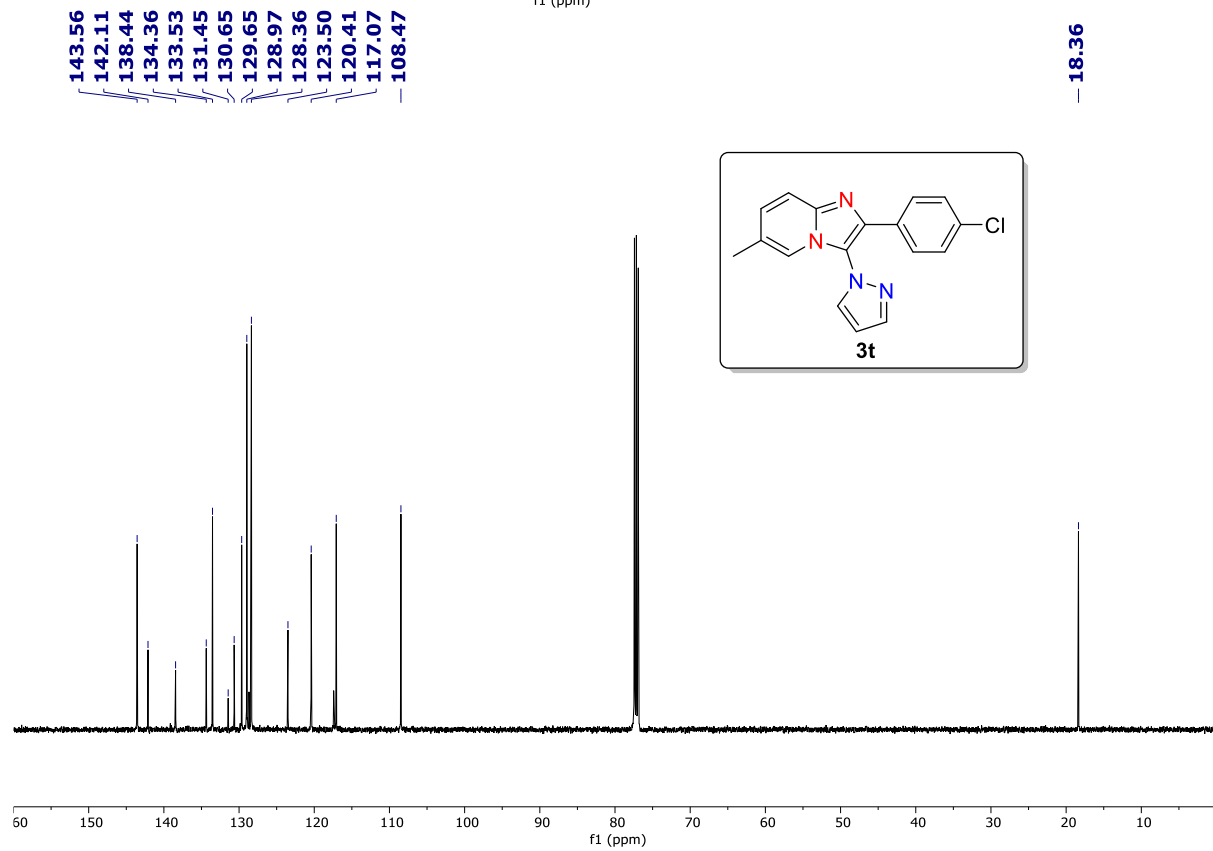
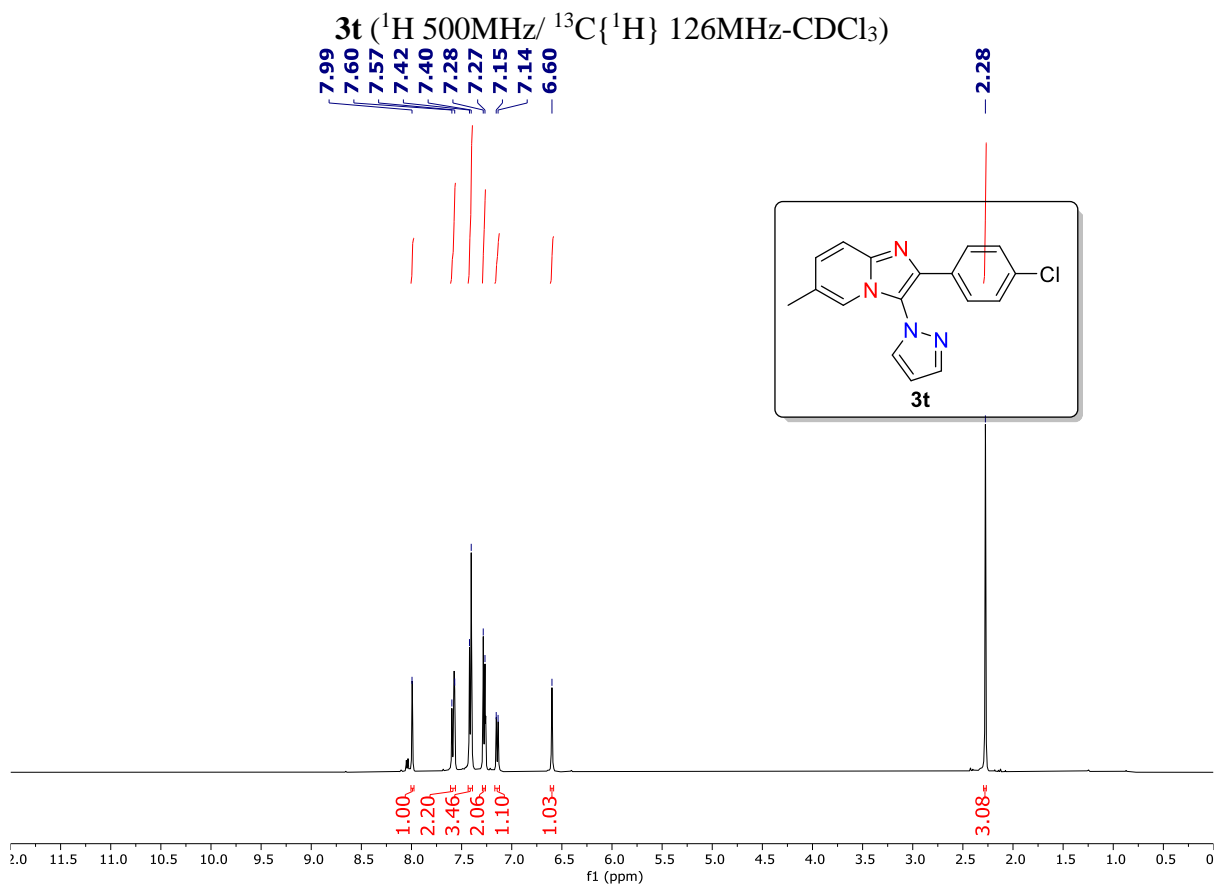
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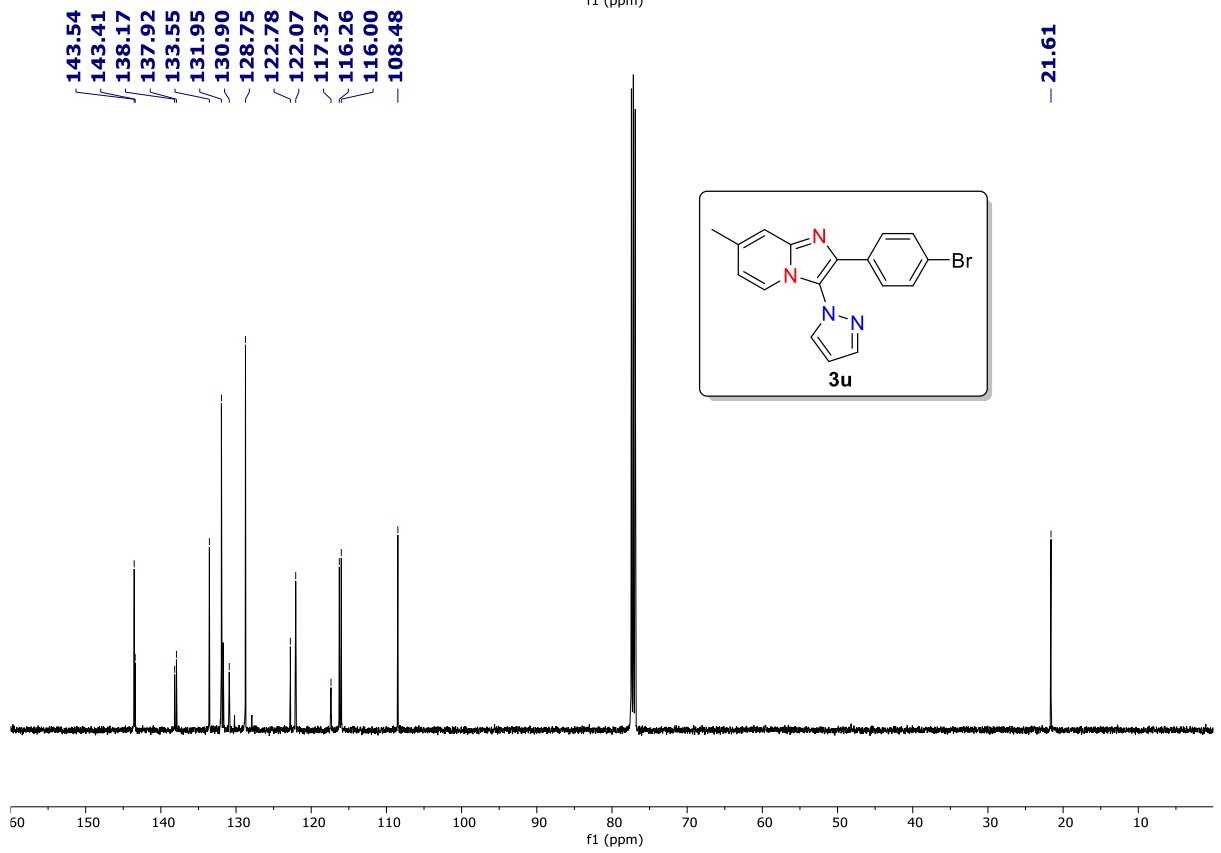
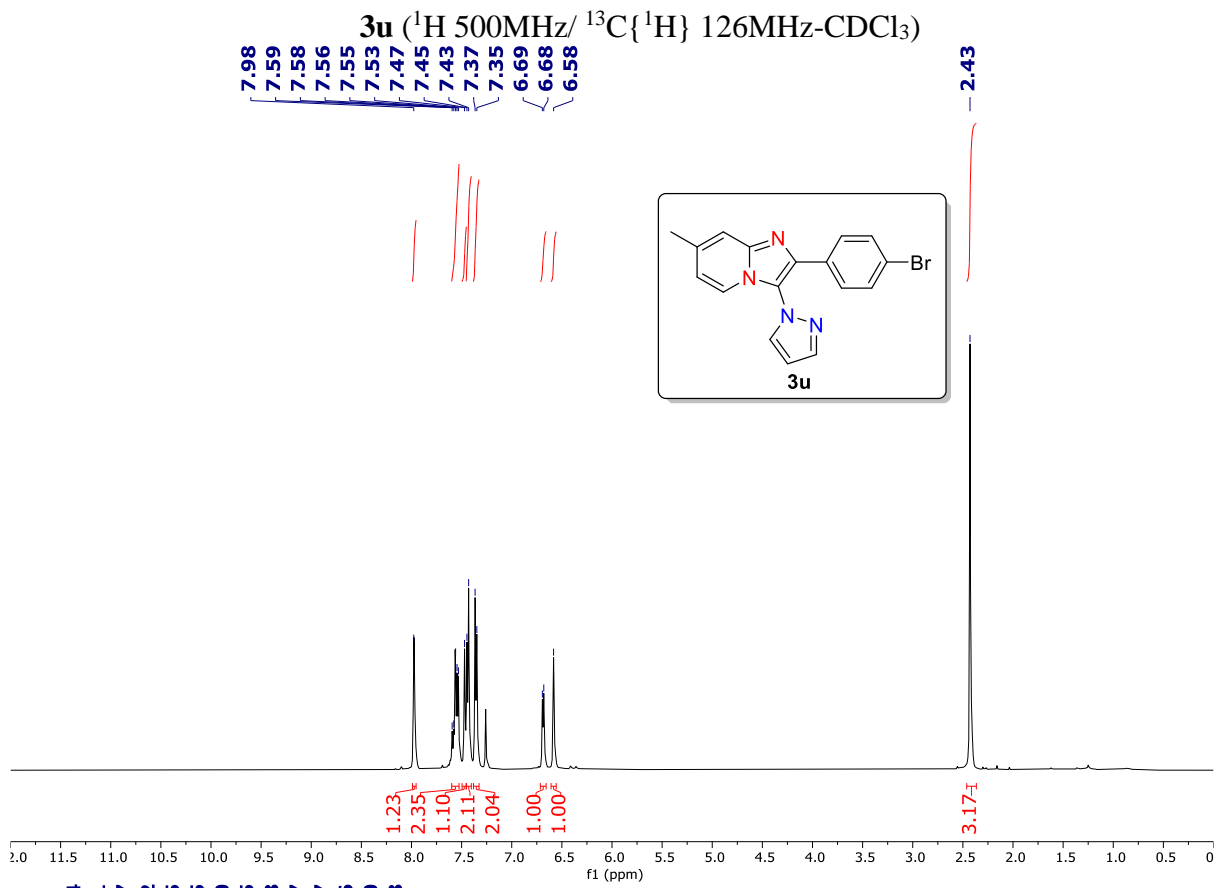
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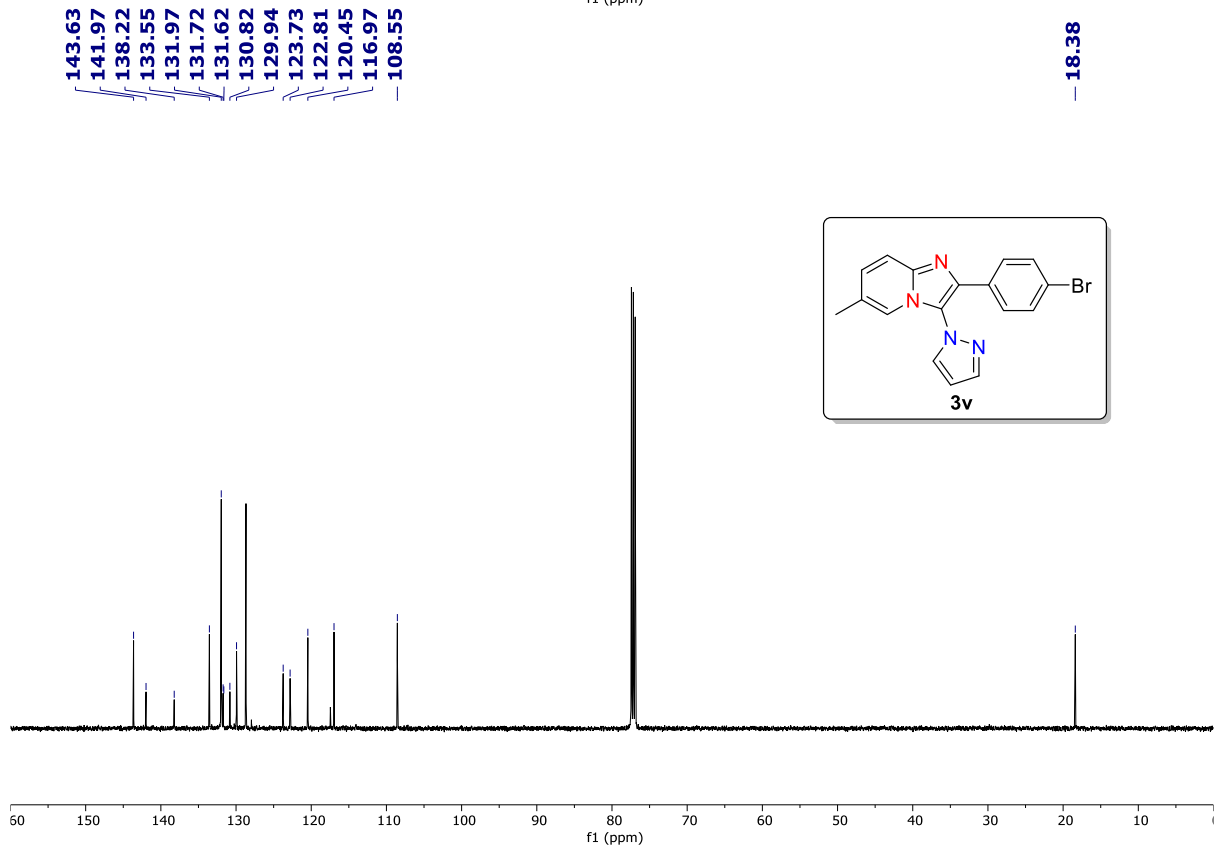
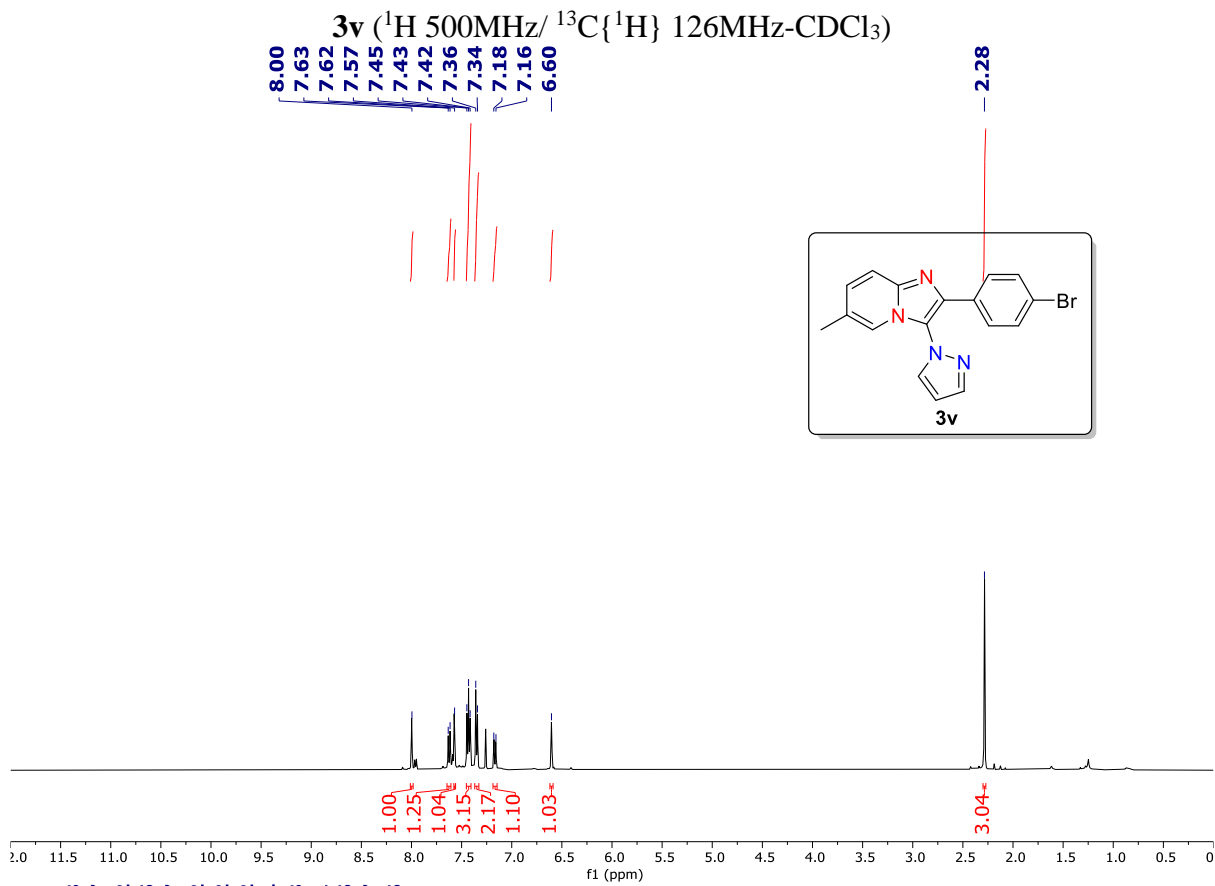


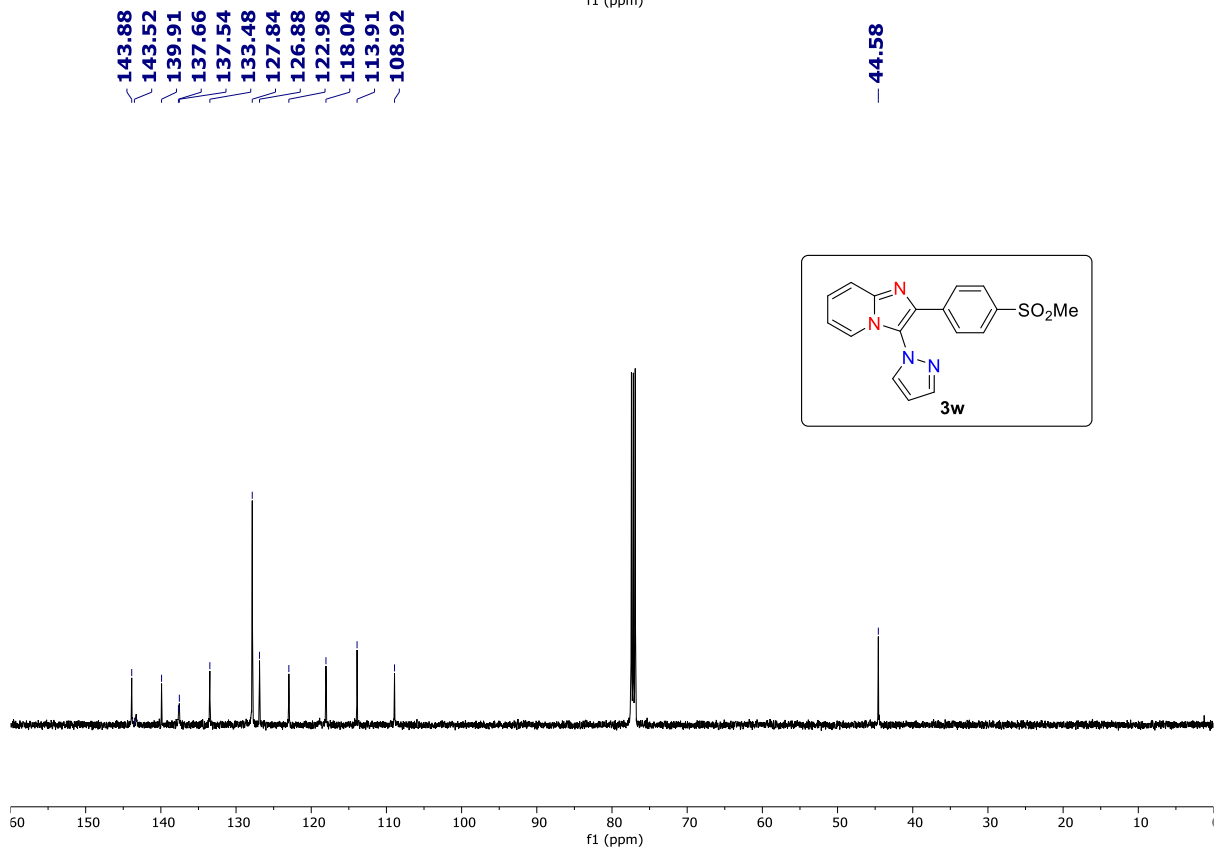
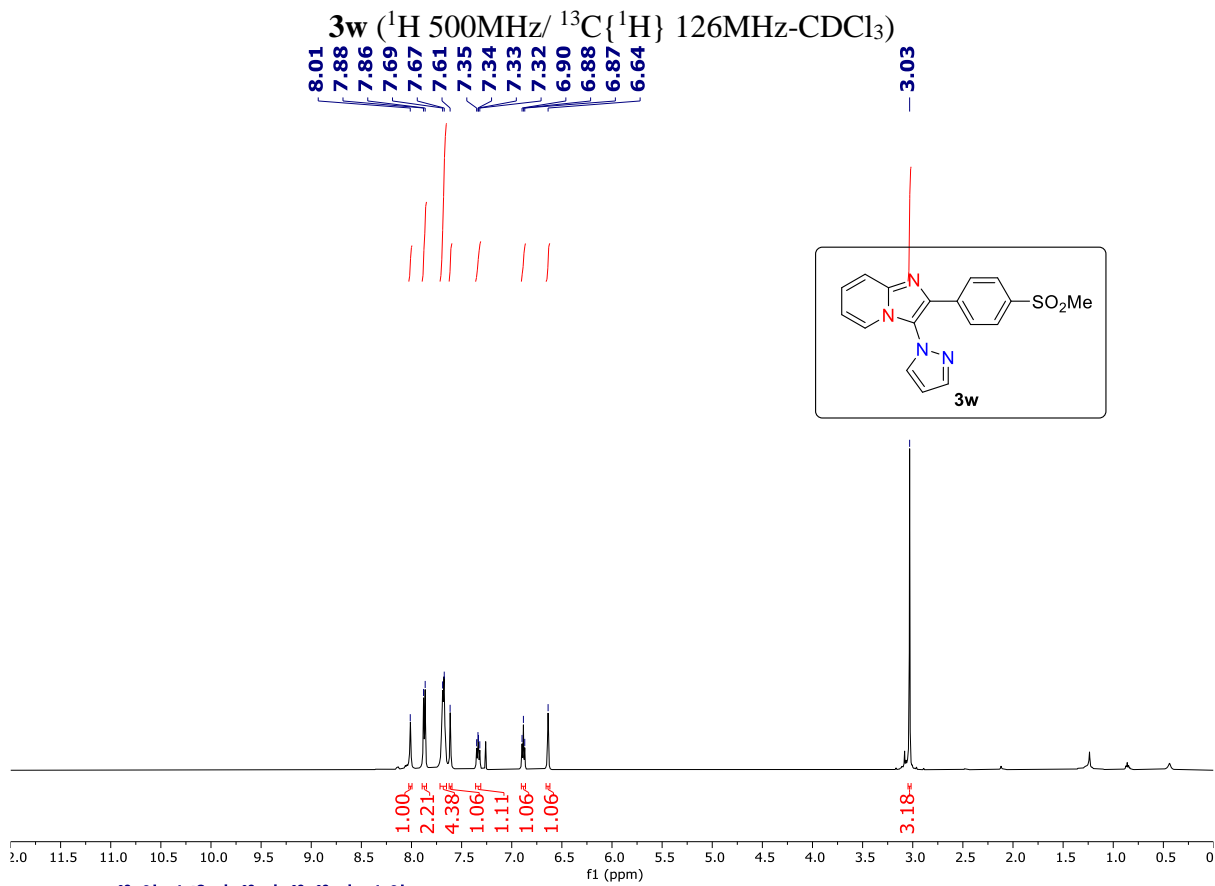


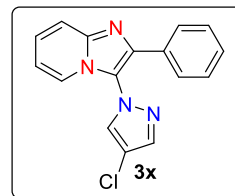
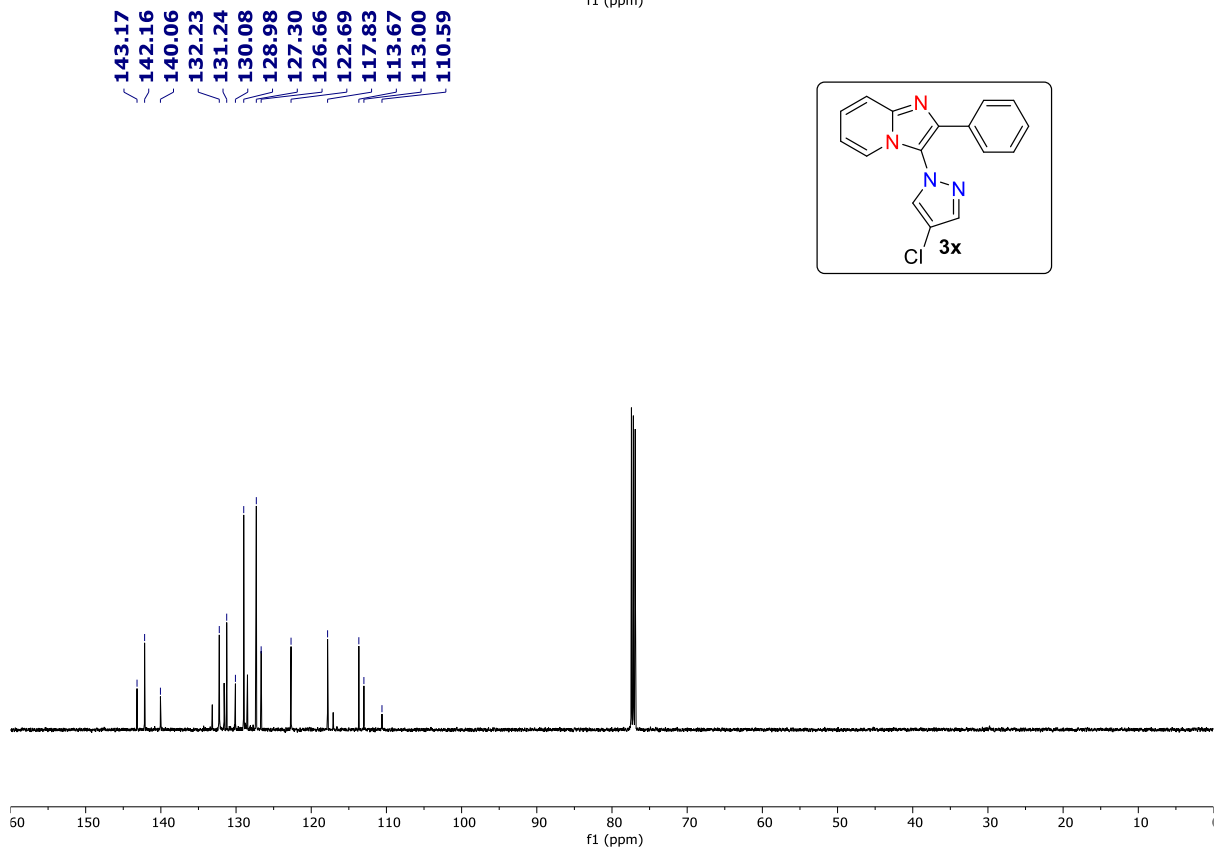
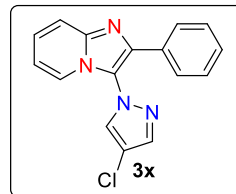
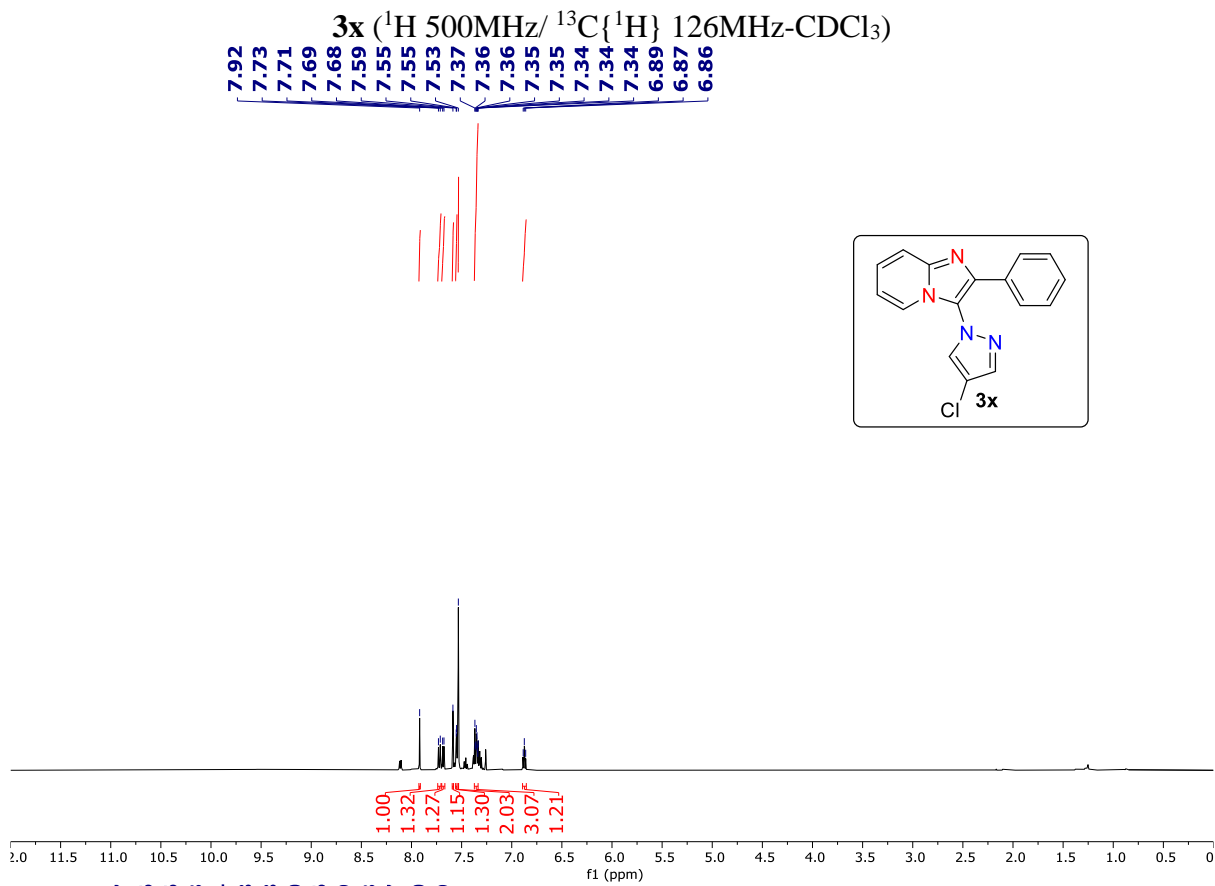




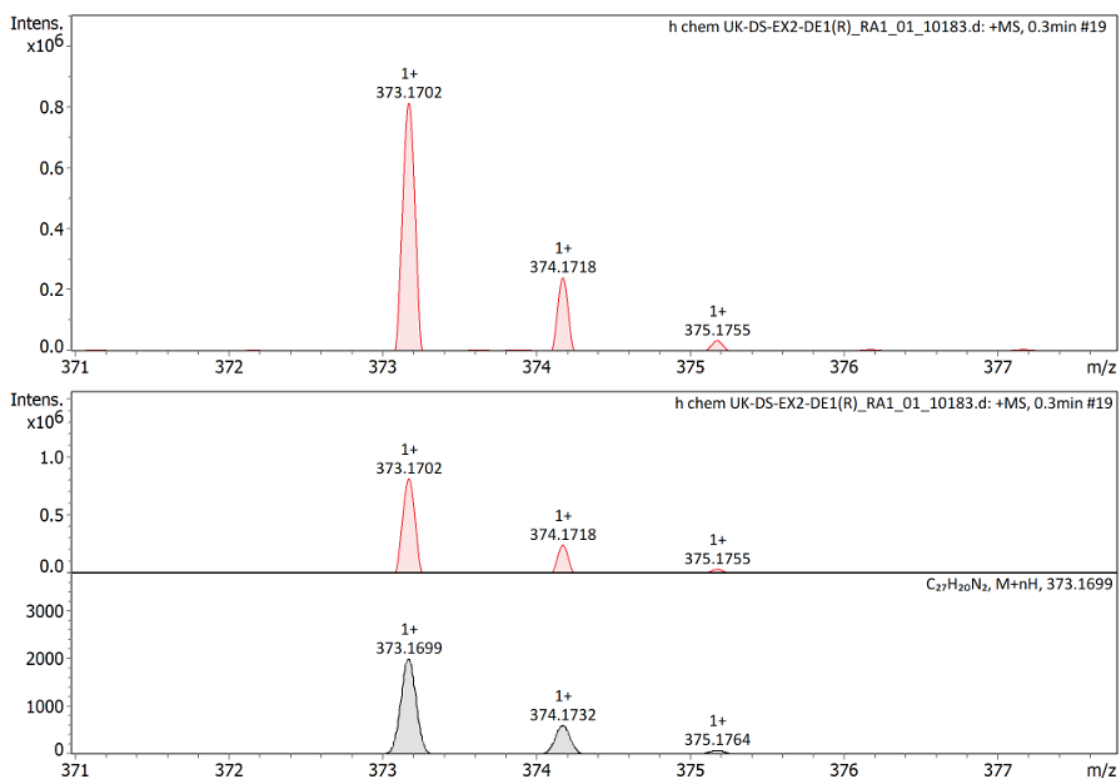




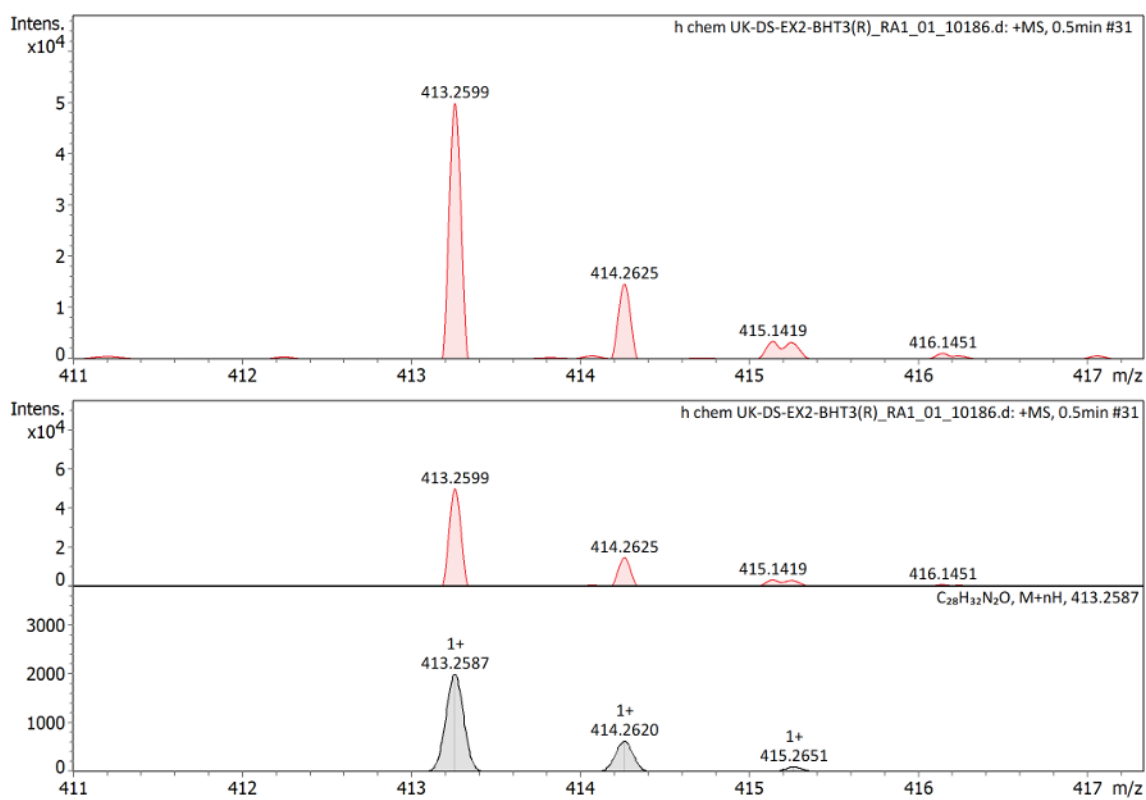




Radical Trapping Experiments Data (HRMS)-



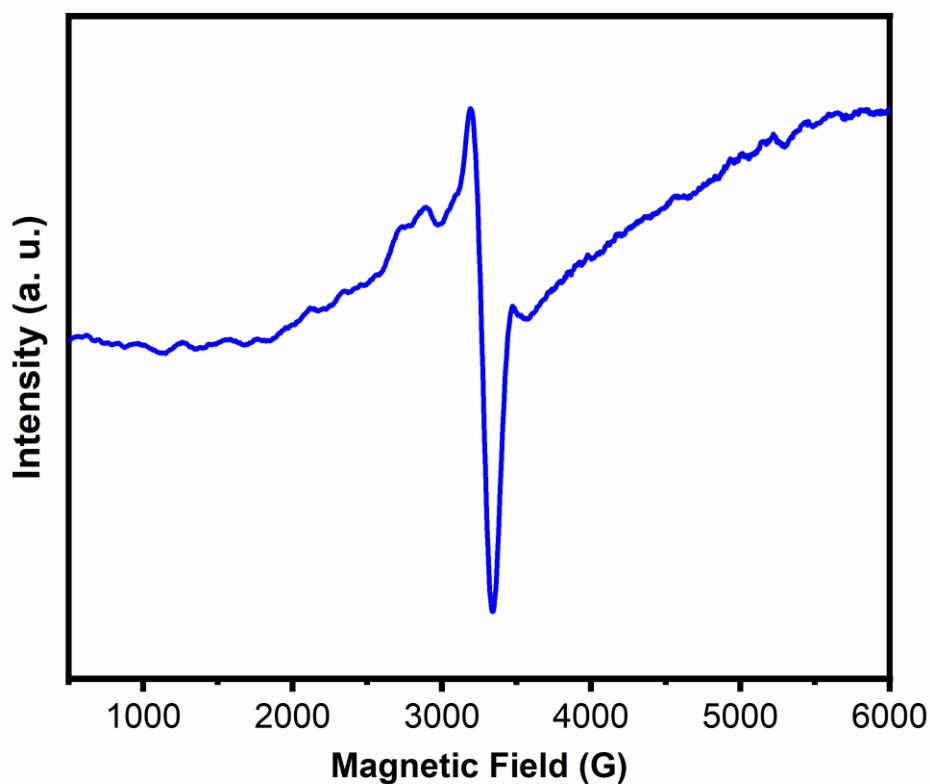
Spectra-1 ESI-MS spectrum of 1,1-Diphenylethylene-trapped adduct **4**



Spectra-2 ESI-MS spectrum of 2,6-di-tert butyl-4-methylphenol-trapped adducts **5a** or **5b** or **5c**

Electron Paramagnetic Resonance Spectroscopy Study-

To identify the radical, Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker Biospin GmbH spectrometer at 120K temperature, and the spectra were measured at a Microwave frequency of 9.4 GHz at the X-band. The sample required for EPR analysis was prepared in MeCN solvent. A signal was found of an incomplete reaction mixture with a g value of 2.0663, which corroborates the presence of organic free radicals in the reaction medium.



Graph-3 Electron paramagnetic resonance (EPR) spectra of the reaction mixture (X band, 120K temperature).