

Electronic Supplementary Information for New Journal of Chemistry

Novel Approach for the Synthesis of Imidazo and Triazolopyridines from Dithioesters

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Mahanthawamy Hiremath,^a Kempegowda Mantelingu^{a*} and Kanchugarakoppal. S. Rangappa,^{a*}

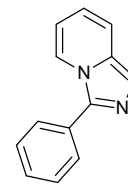
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General Information: 2-methylaminopyridine, 2-hydrazinylpyridine and T3P were purchased from commercial sources and used as received. Reagent grade THF was purchased from Sigma-Aldrich and distilled over sodium. Purification of reaction products was carried out by flash column chromatography using Sorbent Technologies Standard Grade silica gel (60 Å, 230–400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60 F254 plates. Visualization was accomplished with UV light, potassium permanganate and DragendorffMunier stains followed by heating. Melting points were recorded on a Thomas Hoover capillary melting point apparatus and are uncorrected. Proton nuclear magnetic resonance spectra (¹H-NMR) were recorded on Agilent-400 MHz and are reported in ppm using CDCl₃ and DMSO-d₆ as the internal standard. Data are reported as app = apparent, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = complex, br = broad; and coupling constant(s) in Hz. Proton-decoupled carbon nuclear magnetic resonance spectra (¹³C-NMR) were recorded on a Agilent-400 MHz and are reported in ppm using chloroform as the internal standard (77.0 ppm). Mass spectra were recorded on Agilent mass spectrum

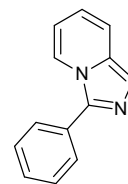
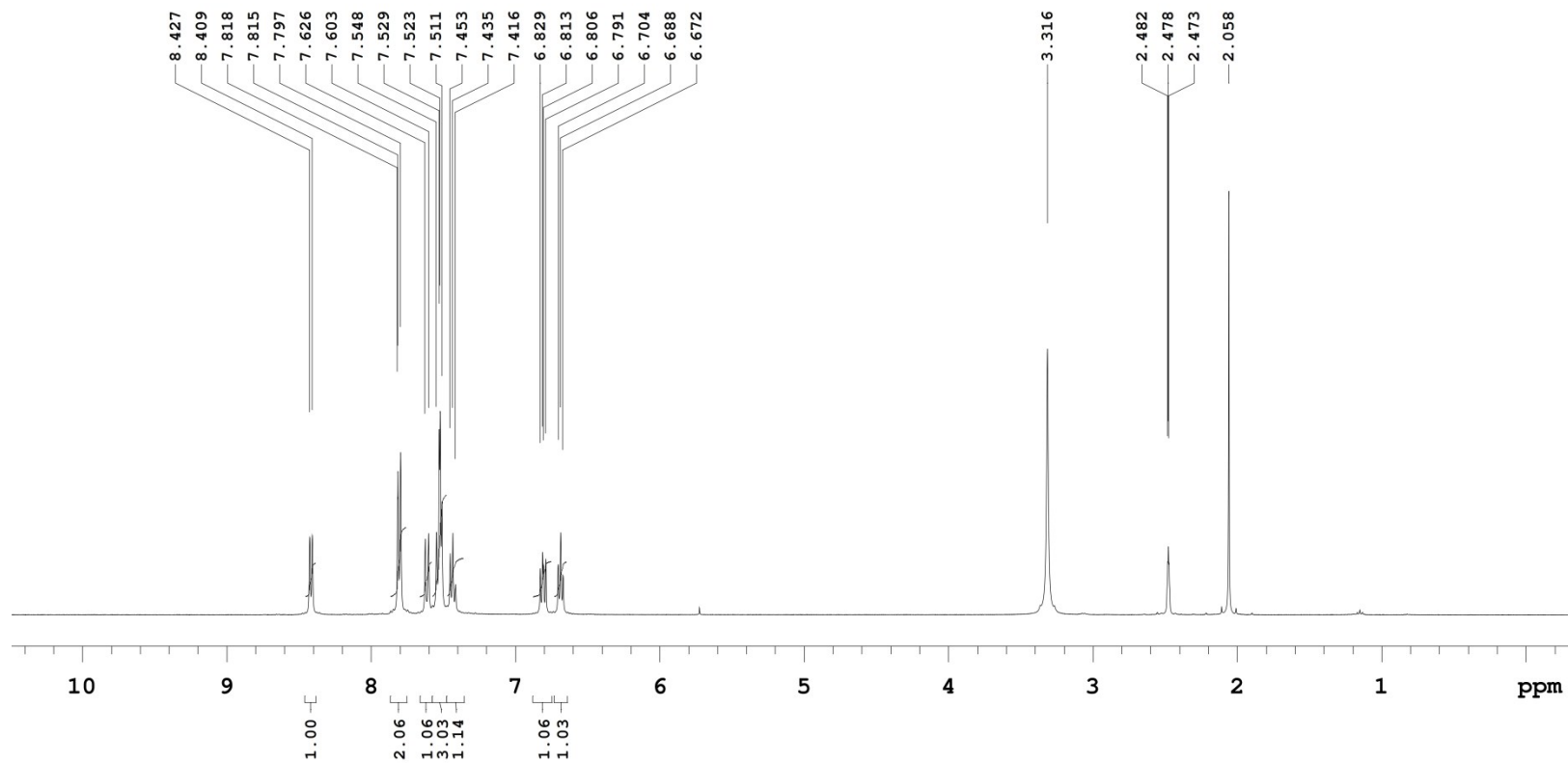
General Procedure for the oxidative desulfurative cyclization of dithioesters : To a solution of dithioester (1.0 eq, 1.0 mmol) in THF (2 mL) was added amine or hydrazine (1.1 eq, 1.1 mmol) at room temperature, the resulting mixture was stirred for 45 min. monitored the dithioester could no longer be detected. To the above mixture was added T3P (1.0 equiv, 50% solution in EtOAc) and DMSO (2.0 eq). The mixture was stirred at room temperature for 1.5 h and progress was monitored by TLC. The reaction mixture was diluted with EtOAc neutralized with saturated sodium bicarbonate solution, separated organic layer; the aqueous layer was extracted with EtOAc (25 mL X 3). The combined organic layers were washed with water, dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure; the residue was purified by silica gel chromatography.

General Procedure for the synthesis of dithioesters (phenyl dithioester) : Magnesium (1.2 eq, 1.2 mmol) was added to THF (2ml) and the solution was warmed till the brisk effervescence observed. After the activation of magnesium, the solution was ice cooled and solution of bromo benzene (1.0 eq, 1.0 mmol) was added drop wise. Then the solution was stirred for 20 min at room temperature and then carbon disulphide (1.0 eq, 1.0 mmol) was added drop wise (the solution turns to orange color) under ice cooled condition. The reaction mixture was stirred for 2 h at room temperature. Methyl iodide (1.0 eq, 1.0 mmol) was added drop wise under ice cooled condition and the mixture was stirred at room temperature for 3 h and progress was monitored by TLC. Ice cold water was added slowly and then reaction mixture was diluted with hexane; the aqueous layer

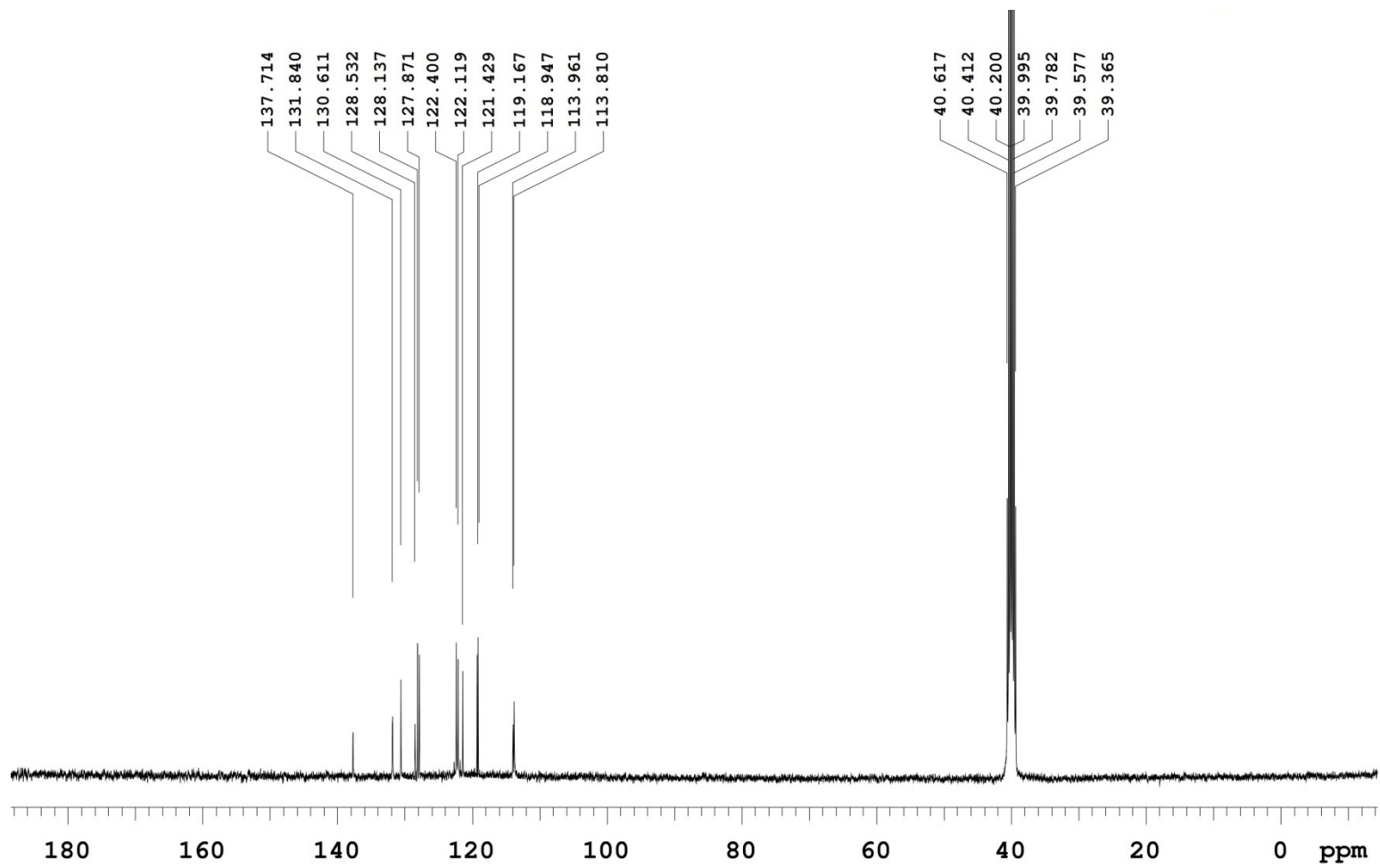
was extracted with hexane (25 mL X 3). The combined organic layers were washed with water, dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure; the residue was purified by silica gel chromatography.



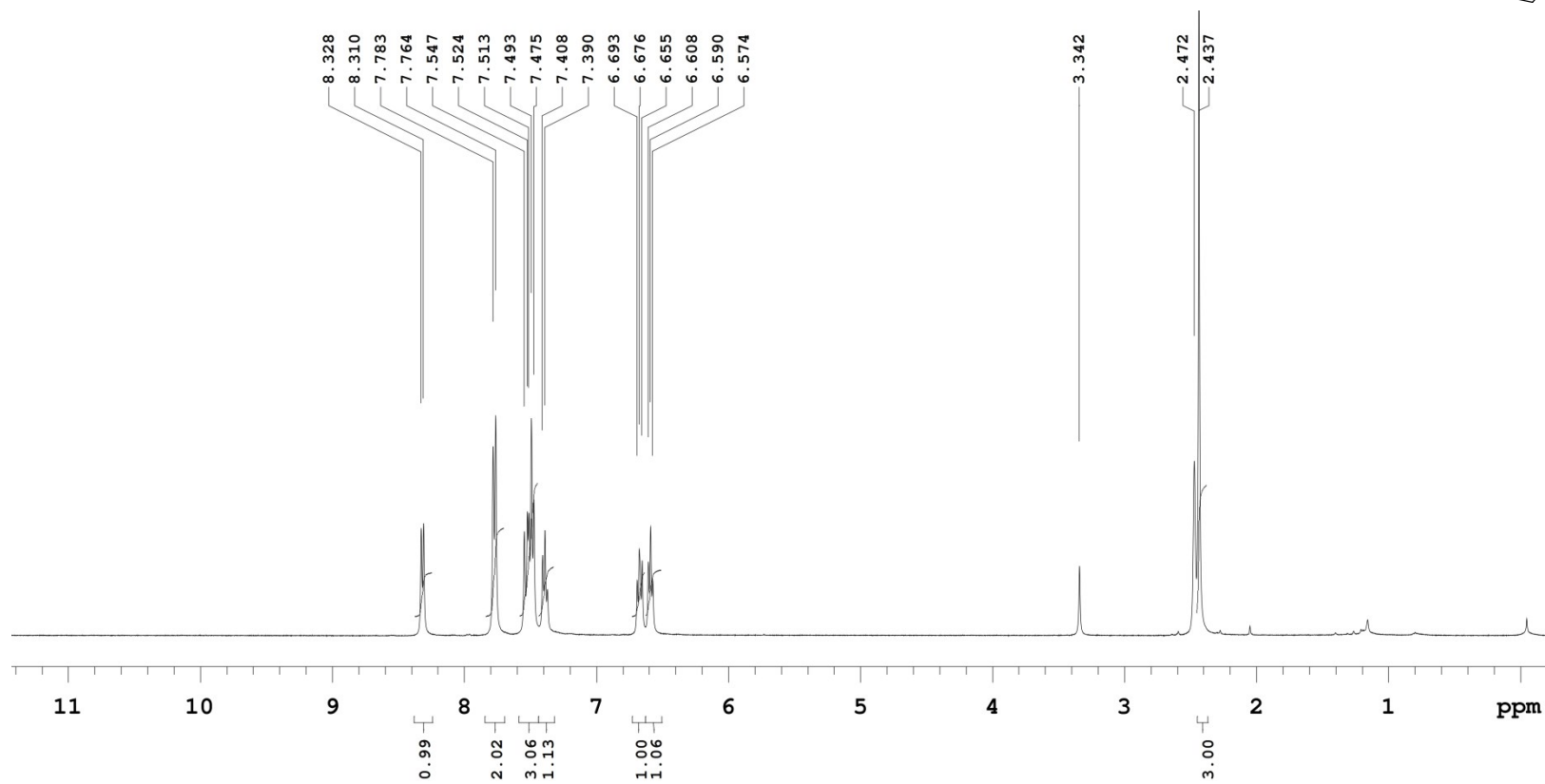
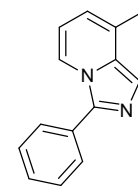
¹H NMR of 3a



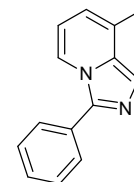
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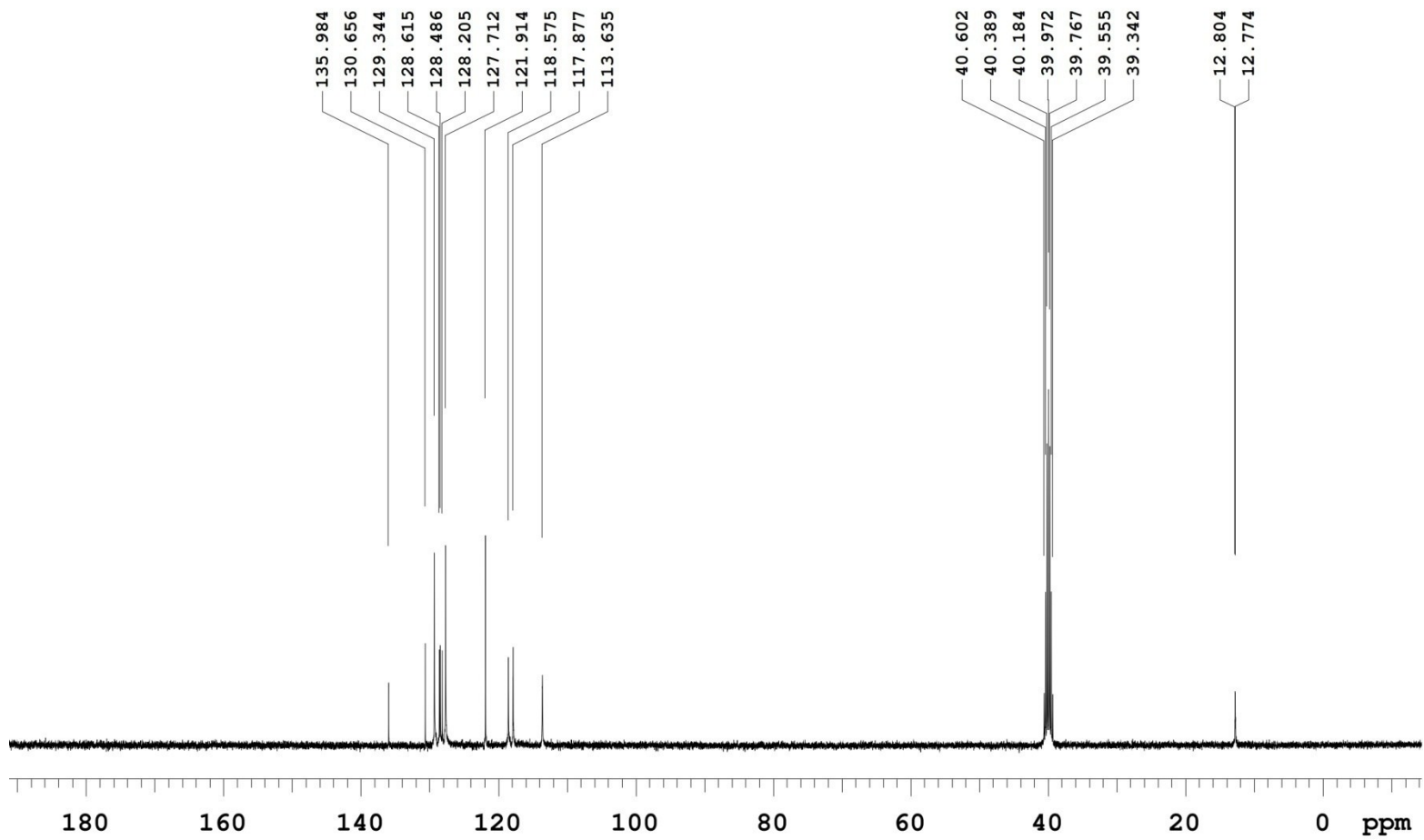


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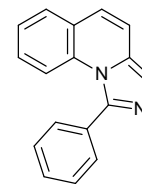


¹³C NMR of 3b

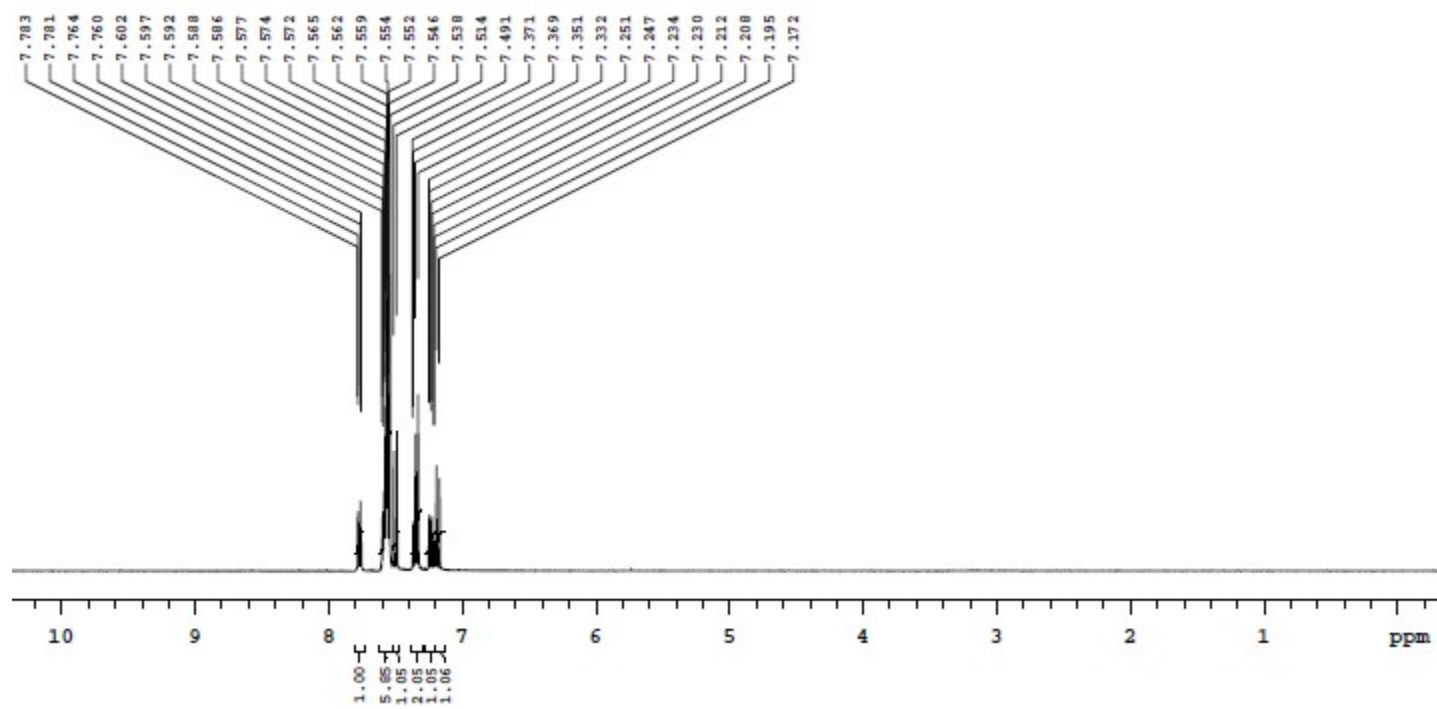




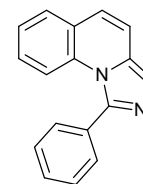
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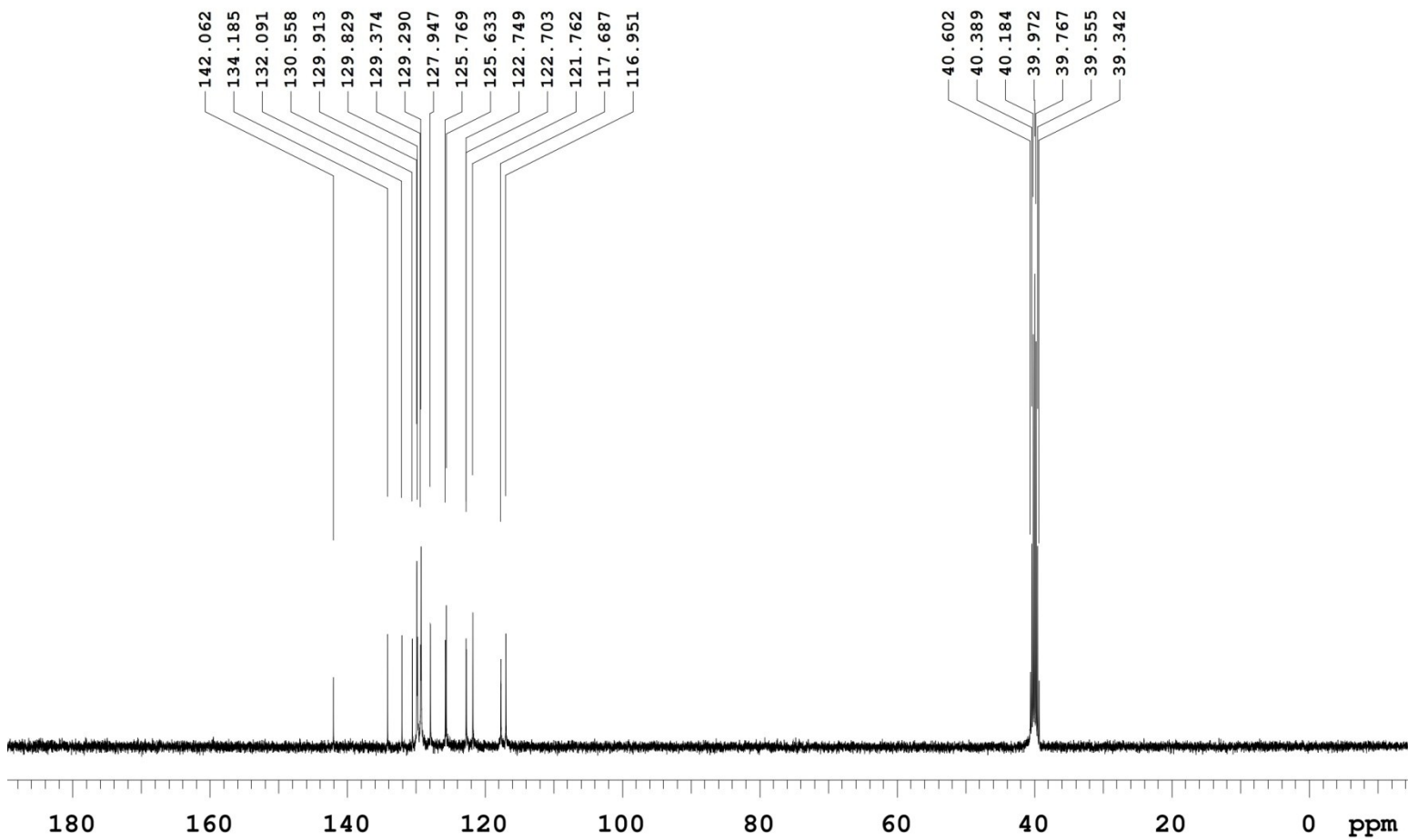


¹H NMR of 3c

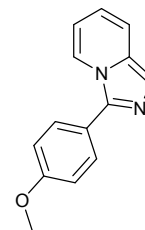


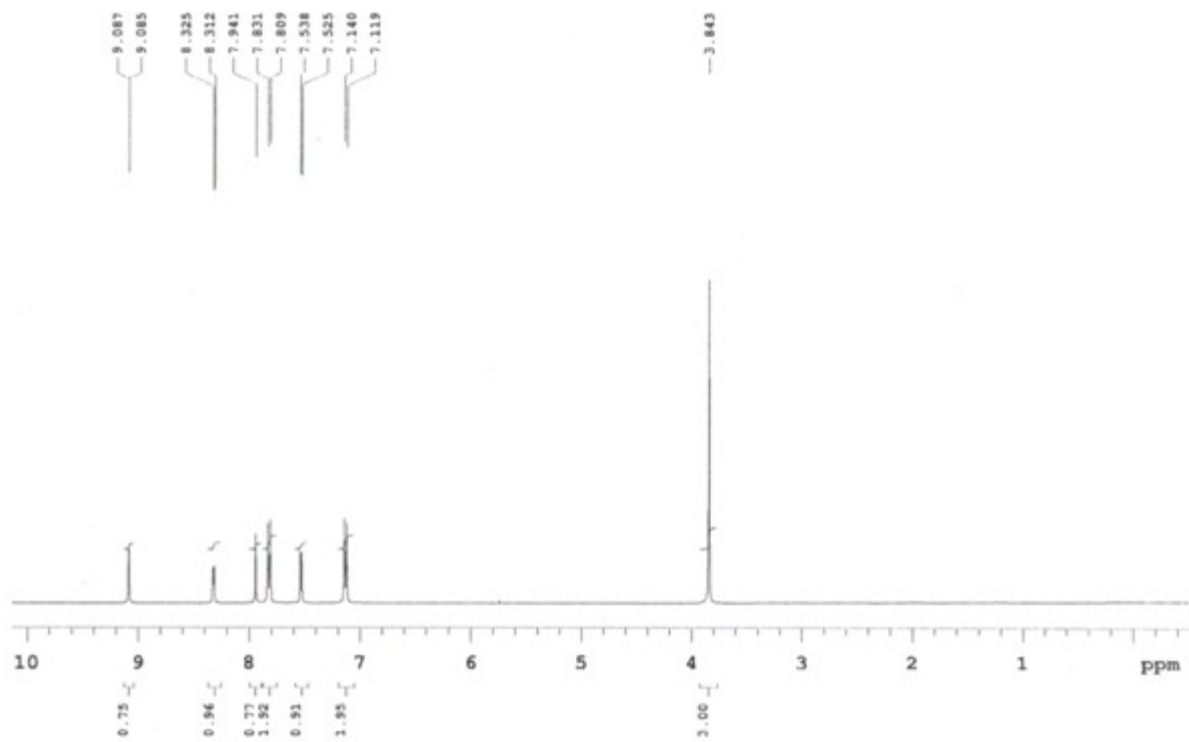
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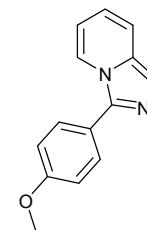


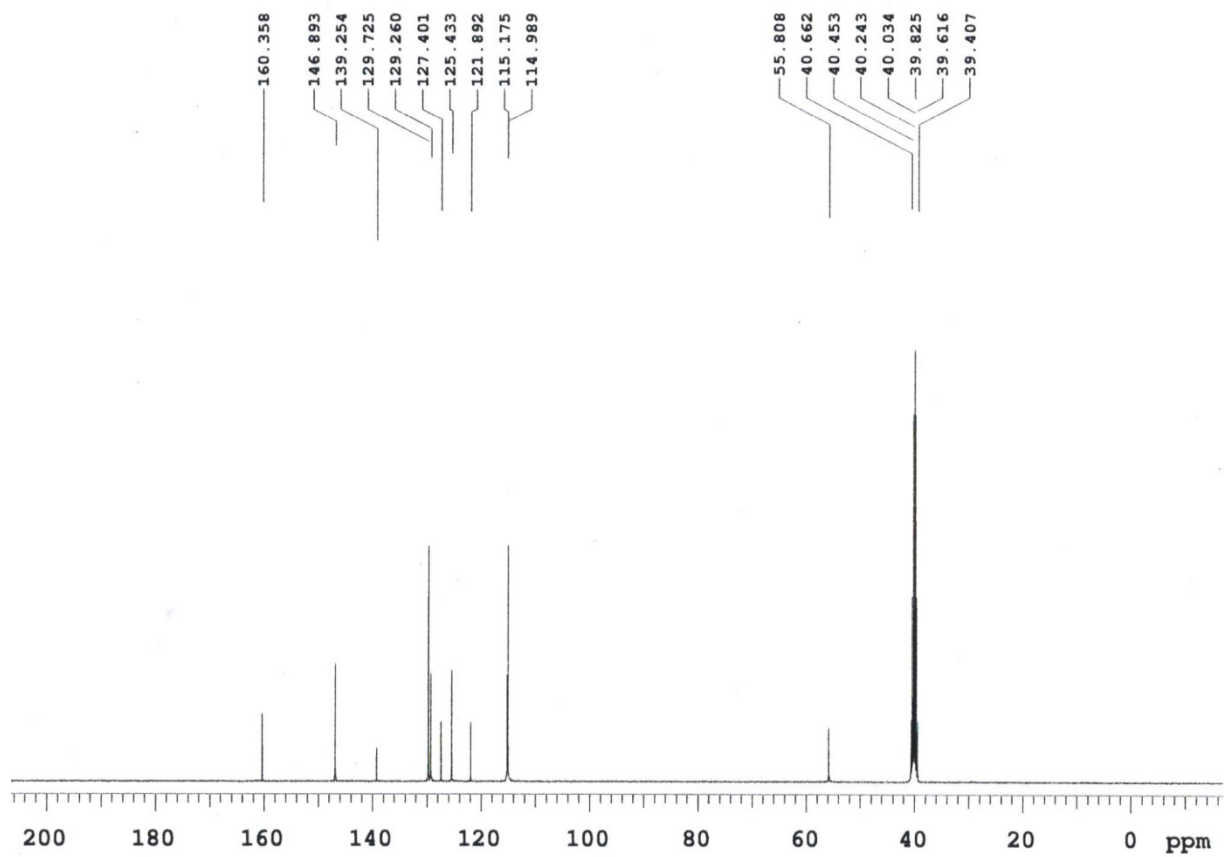
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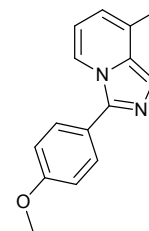


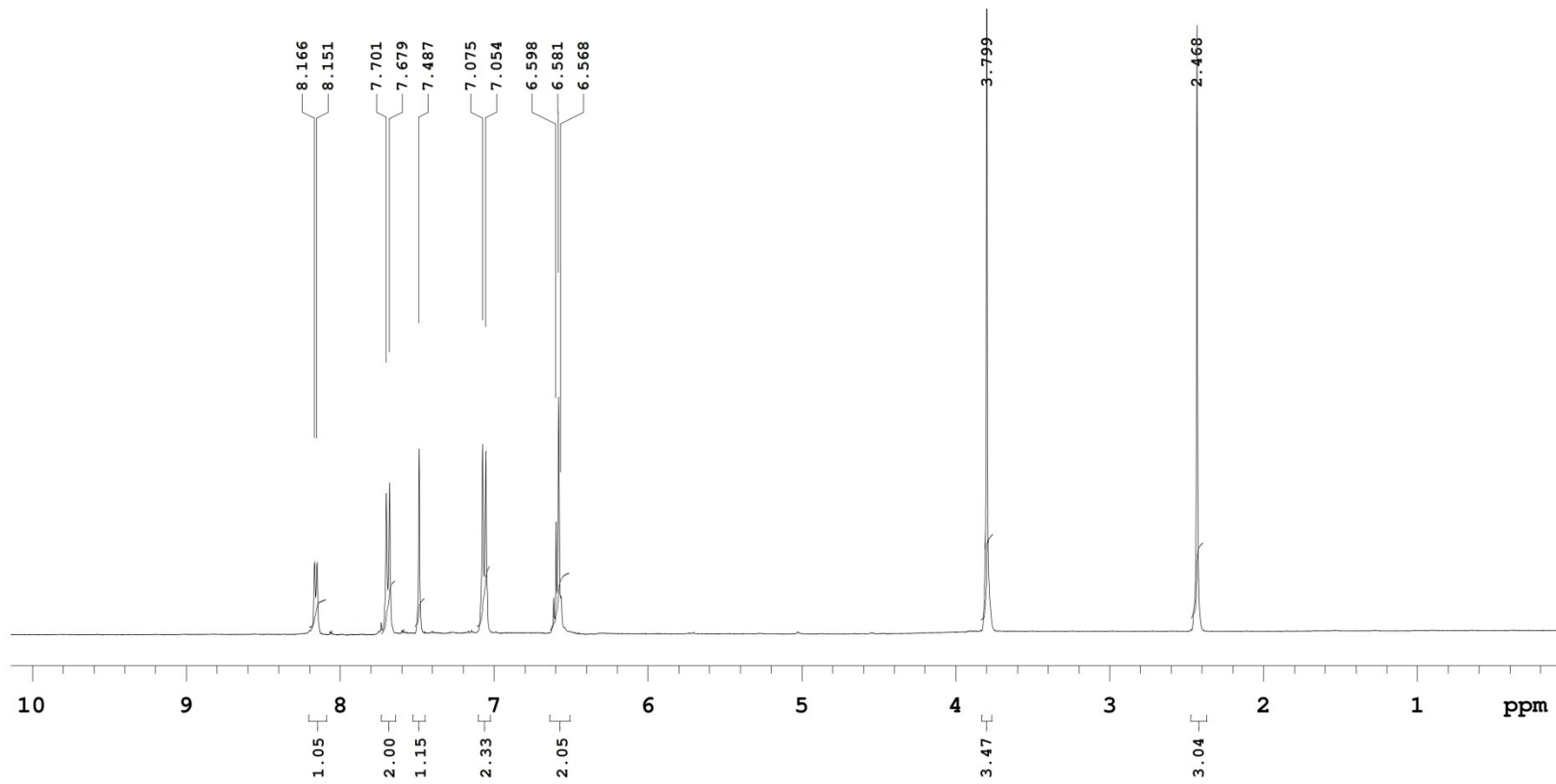
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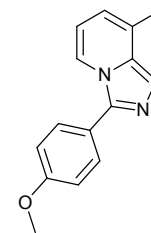


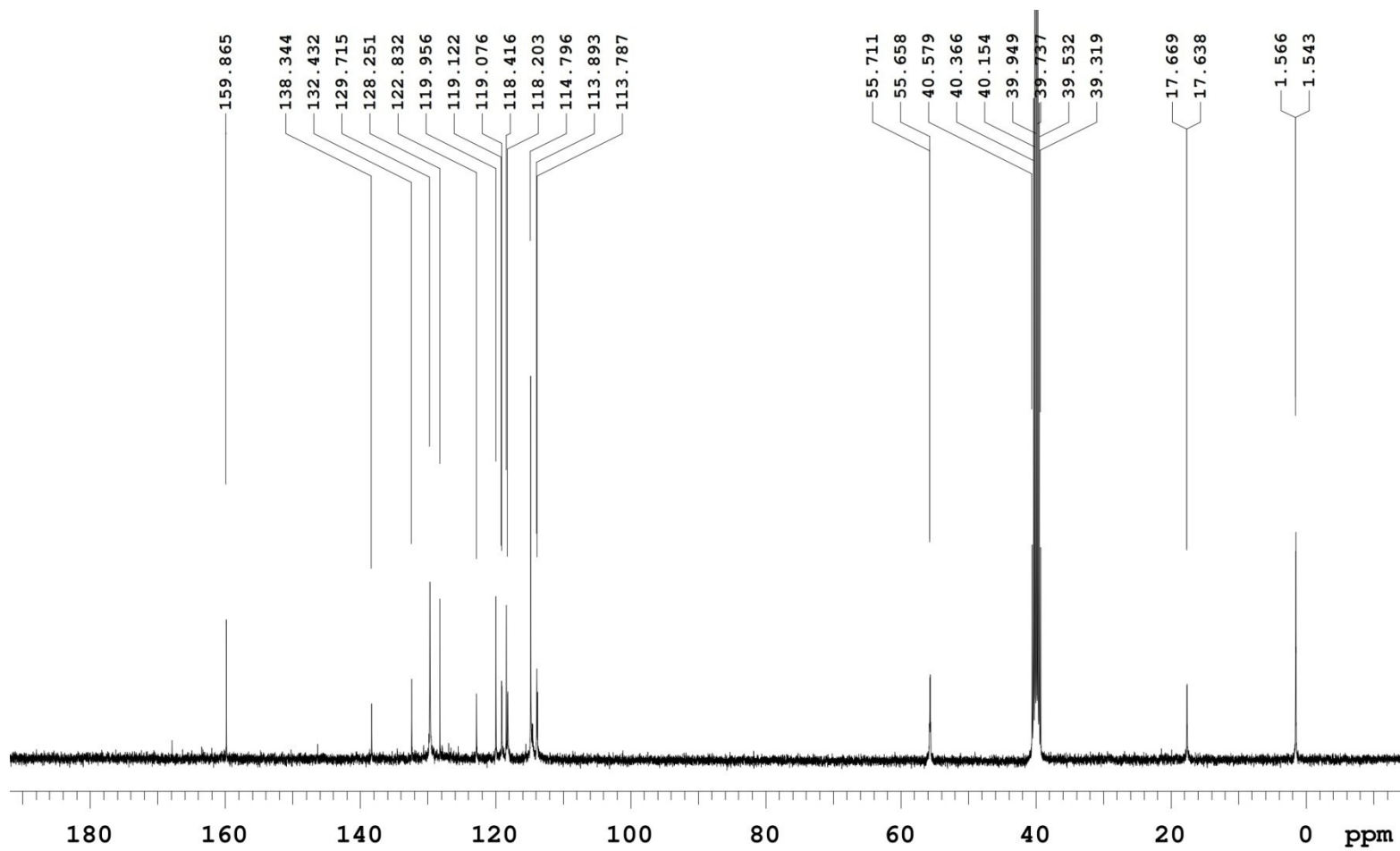
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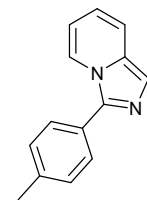


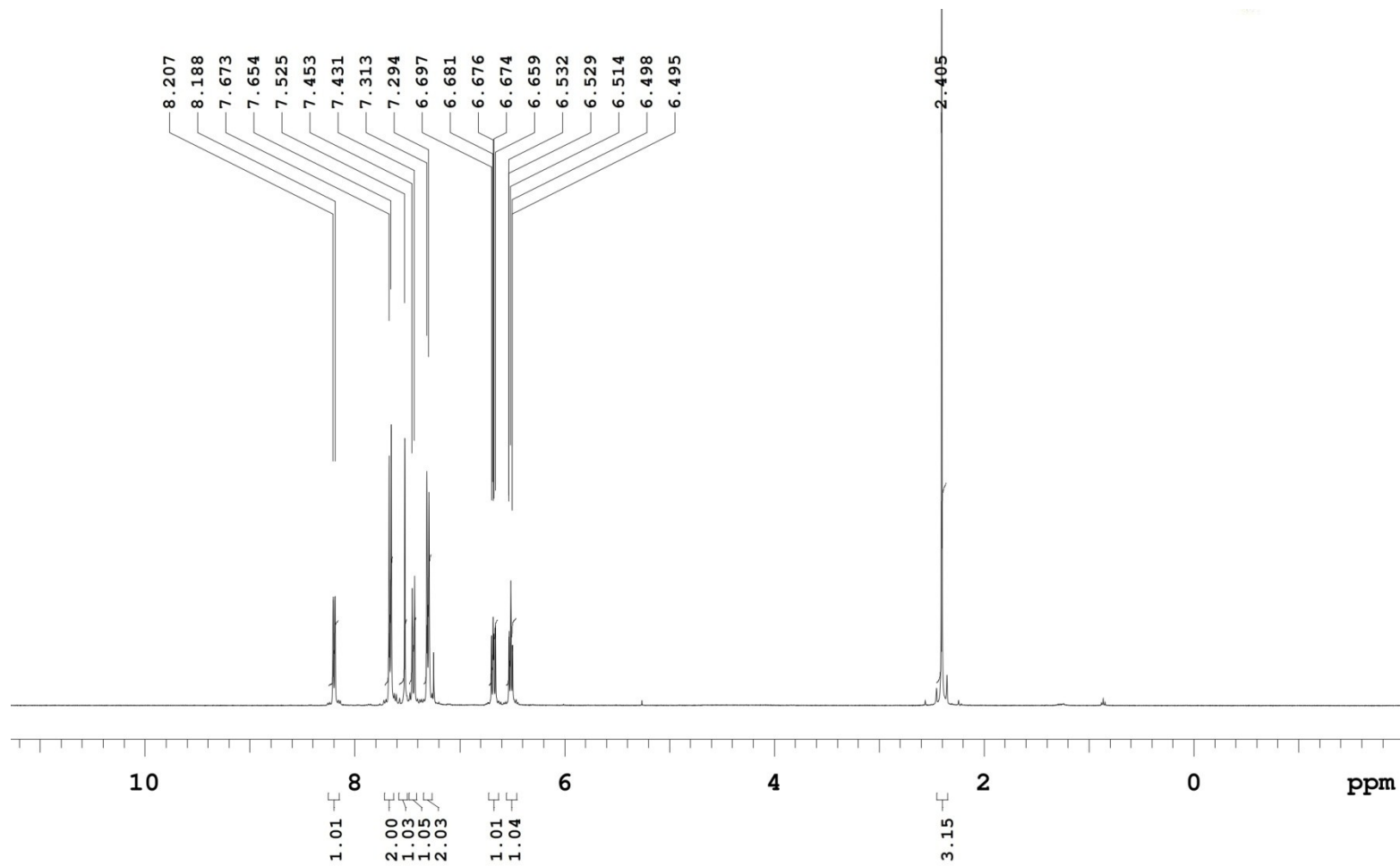
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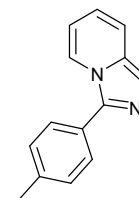


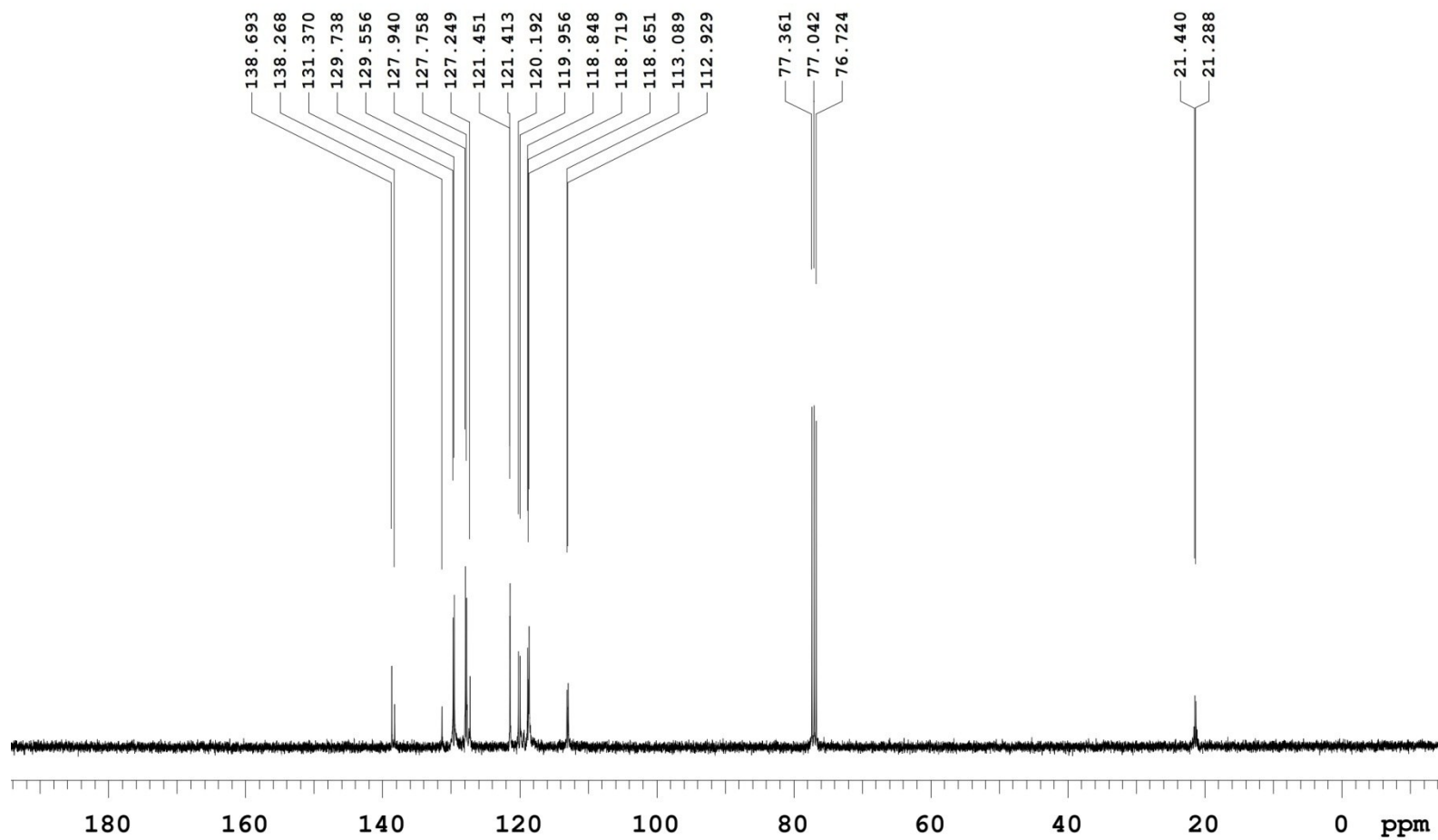
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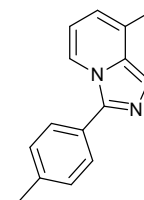


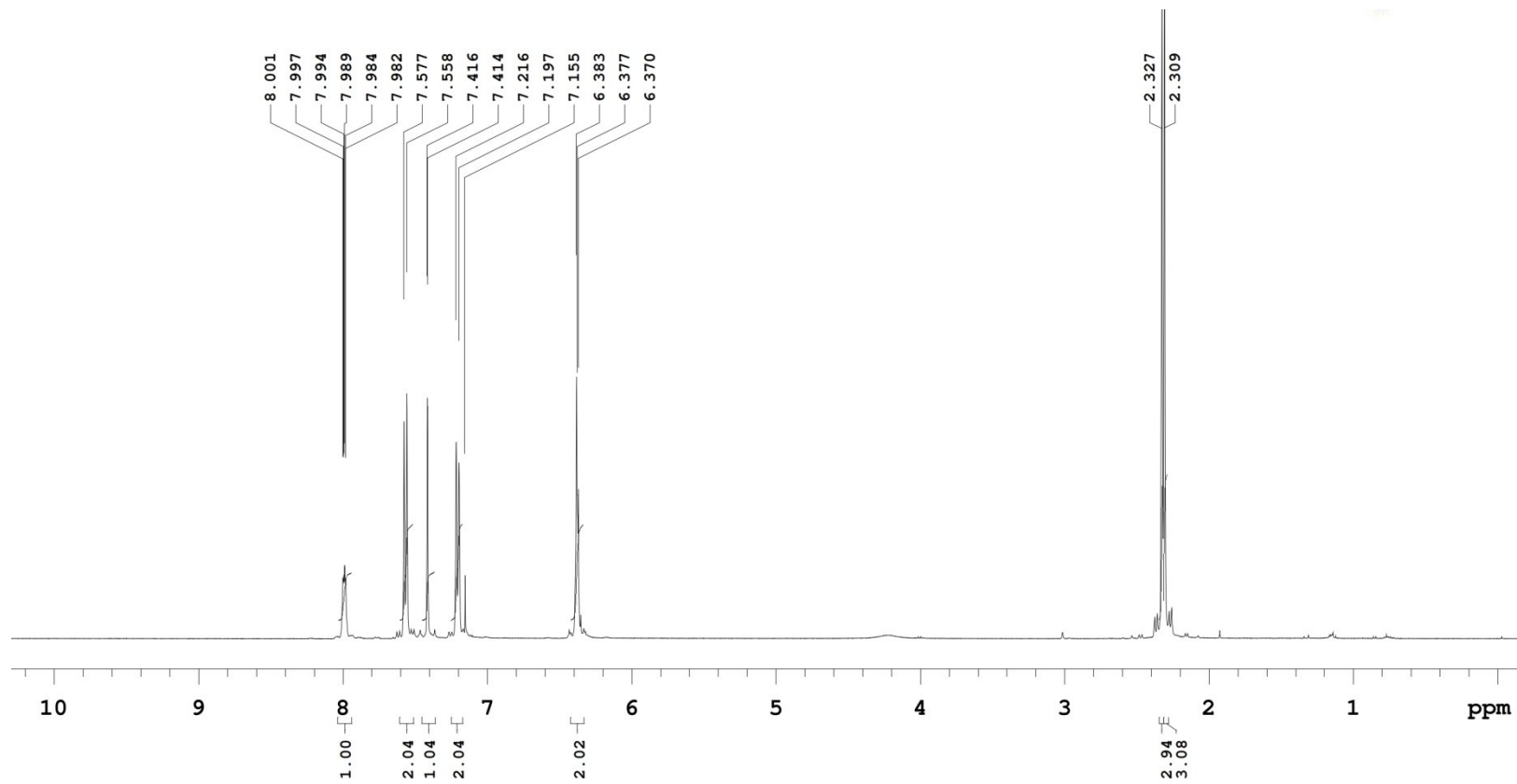
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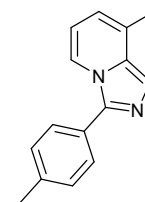


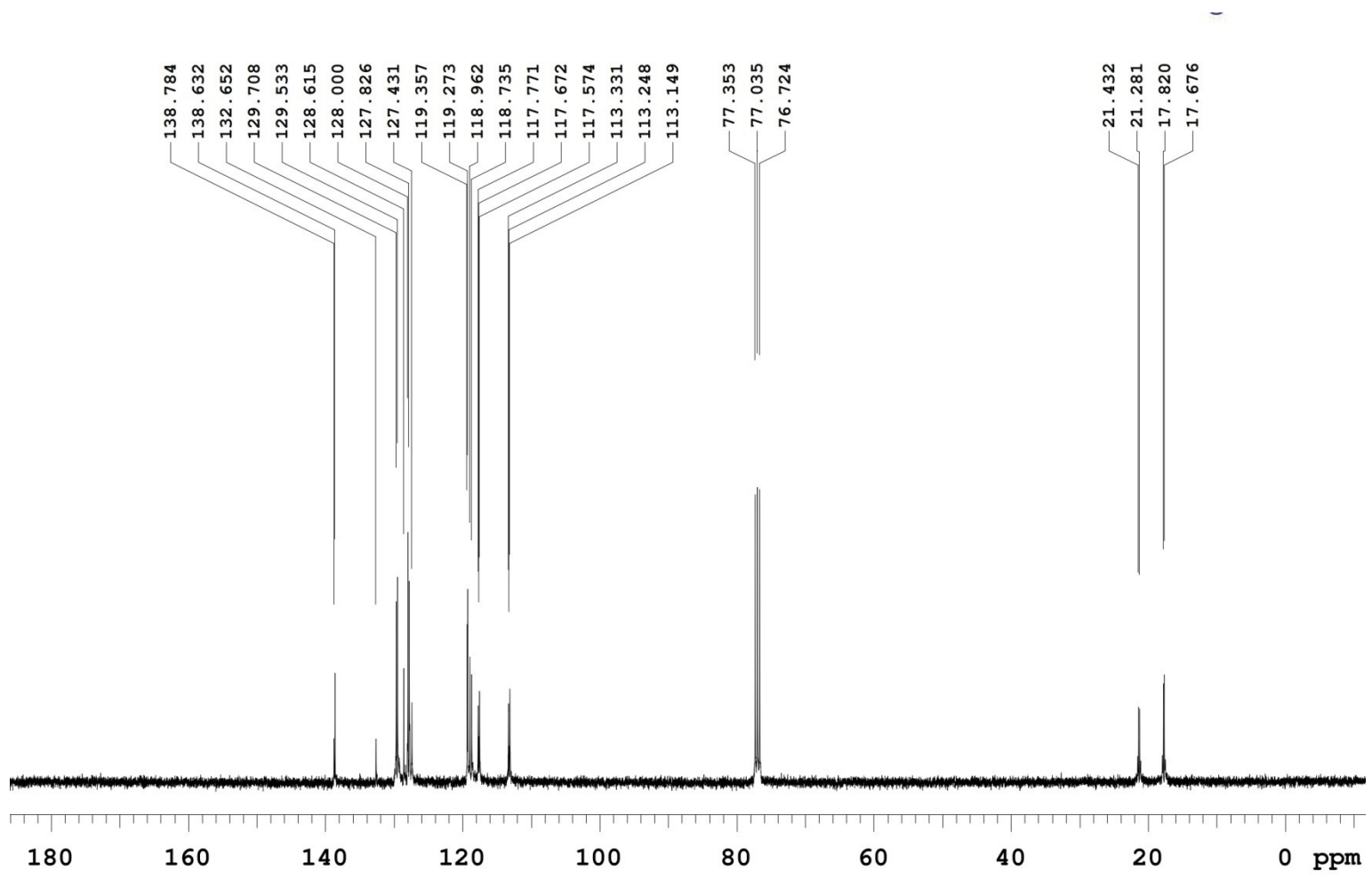
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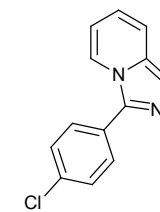


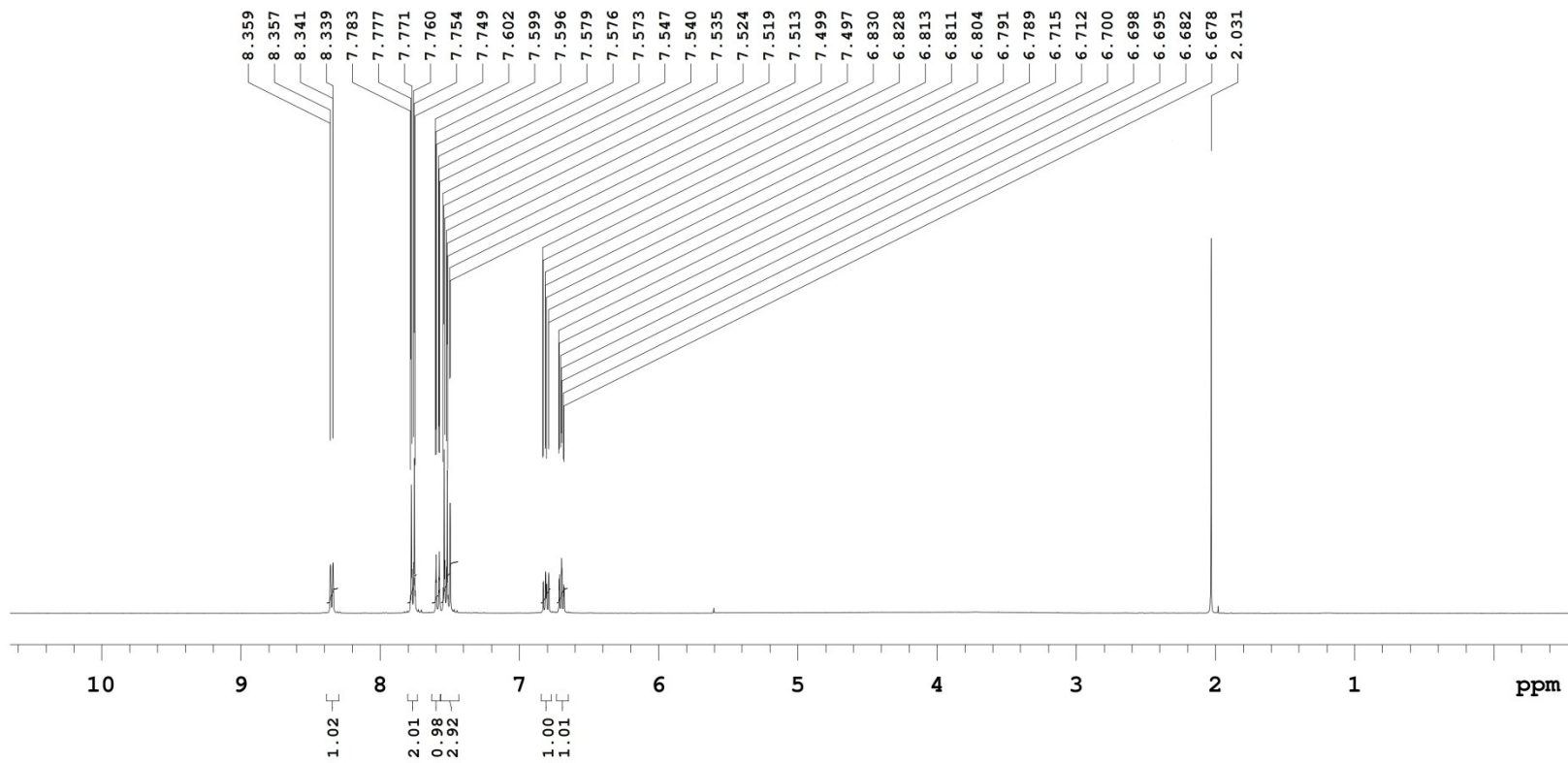
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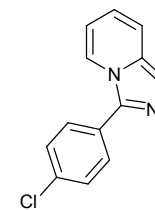


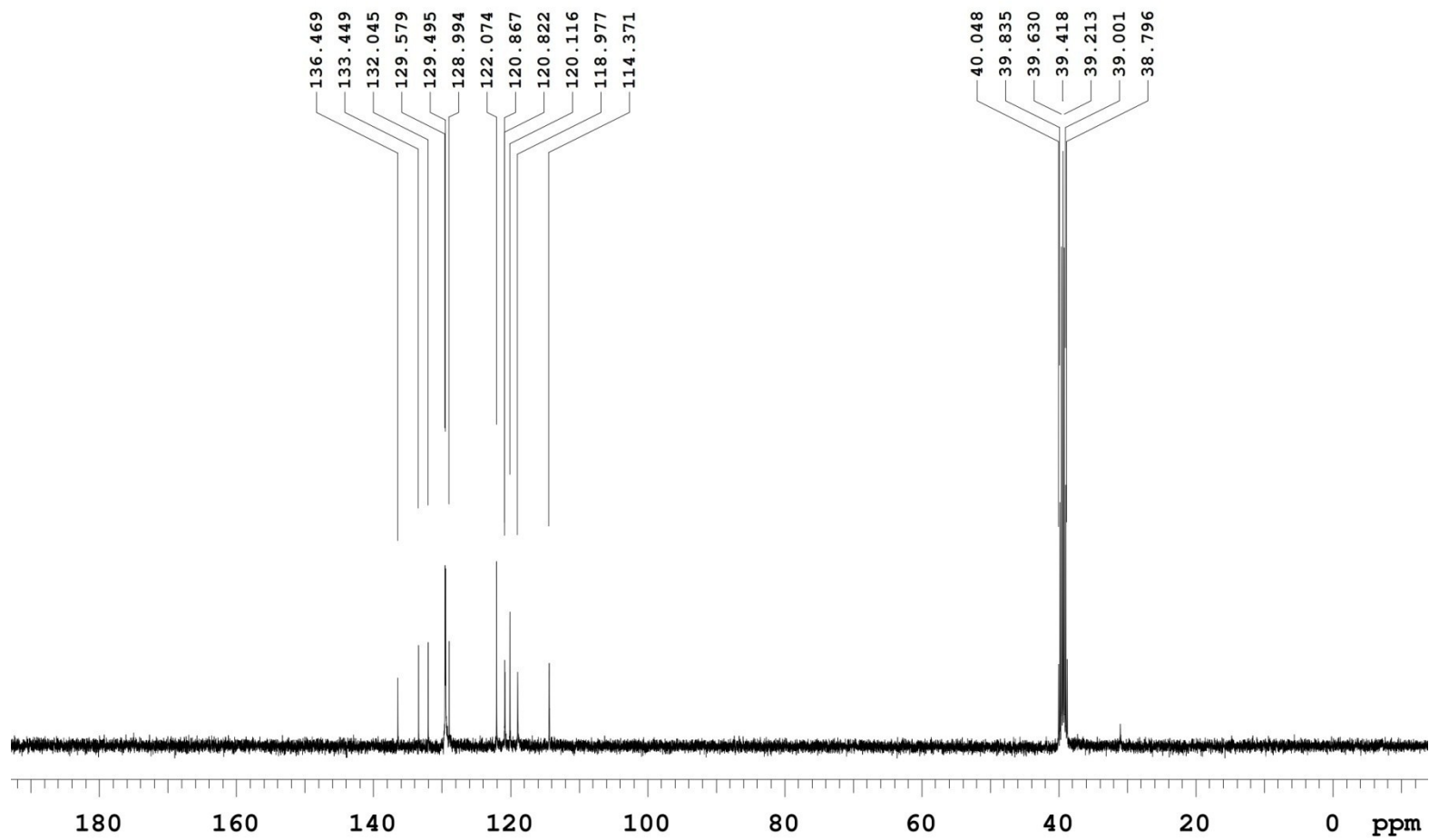
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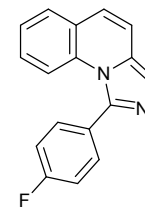
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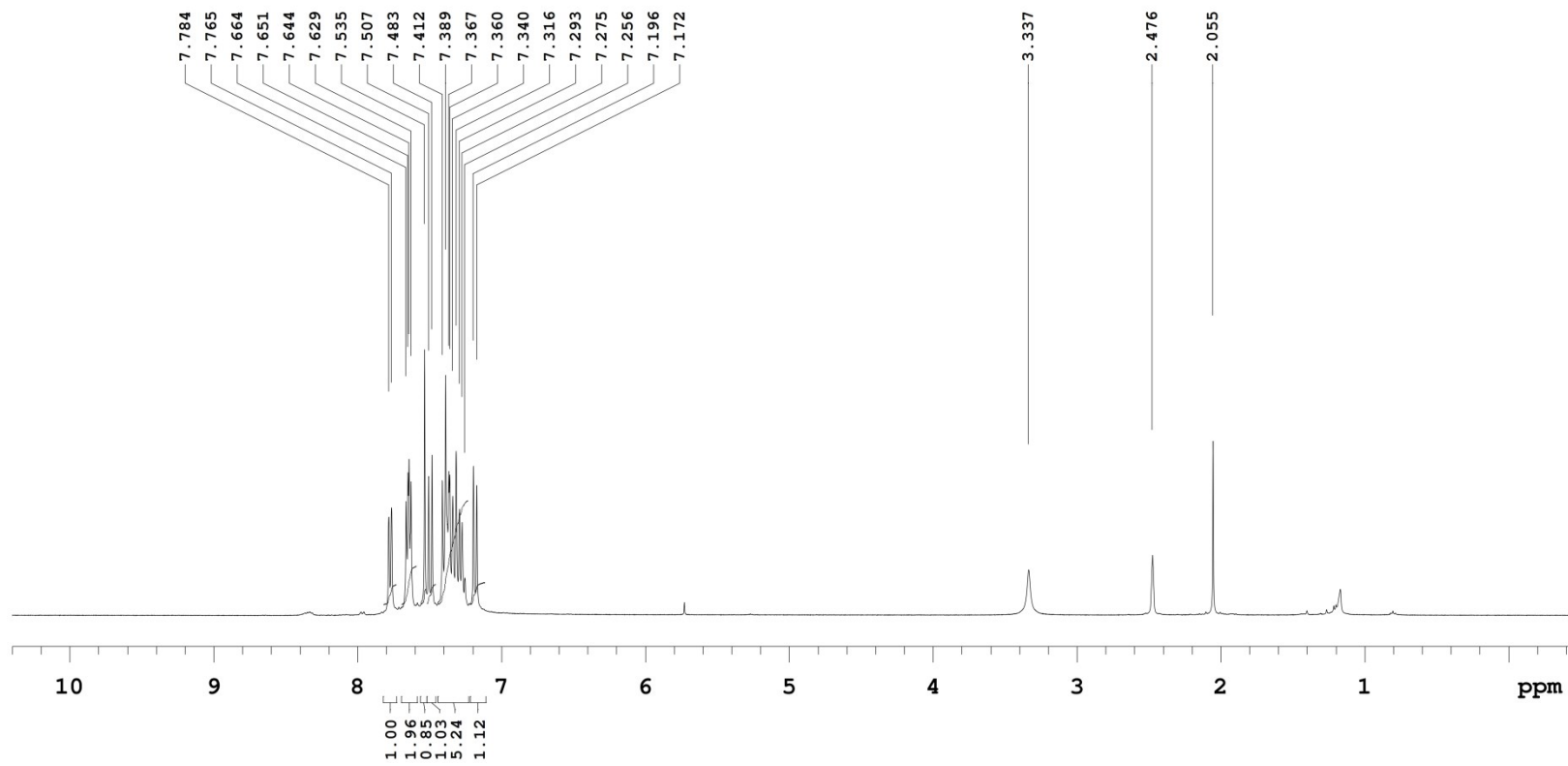




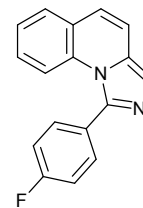
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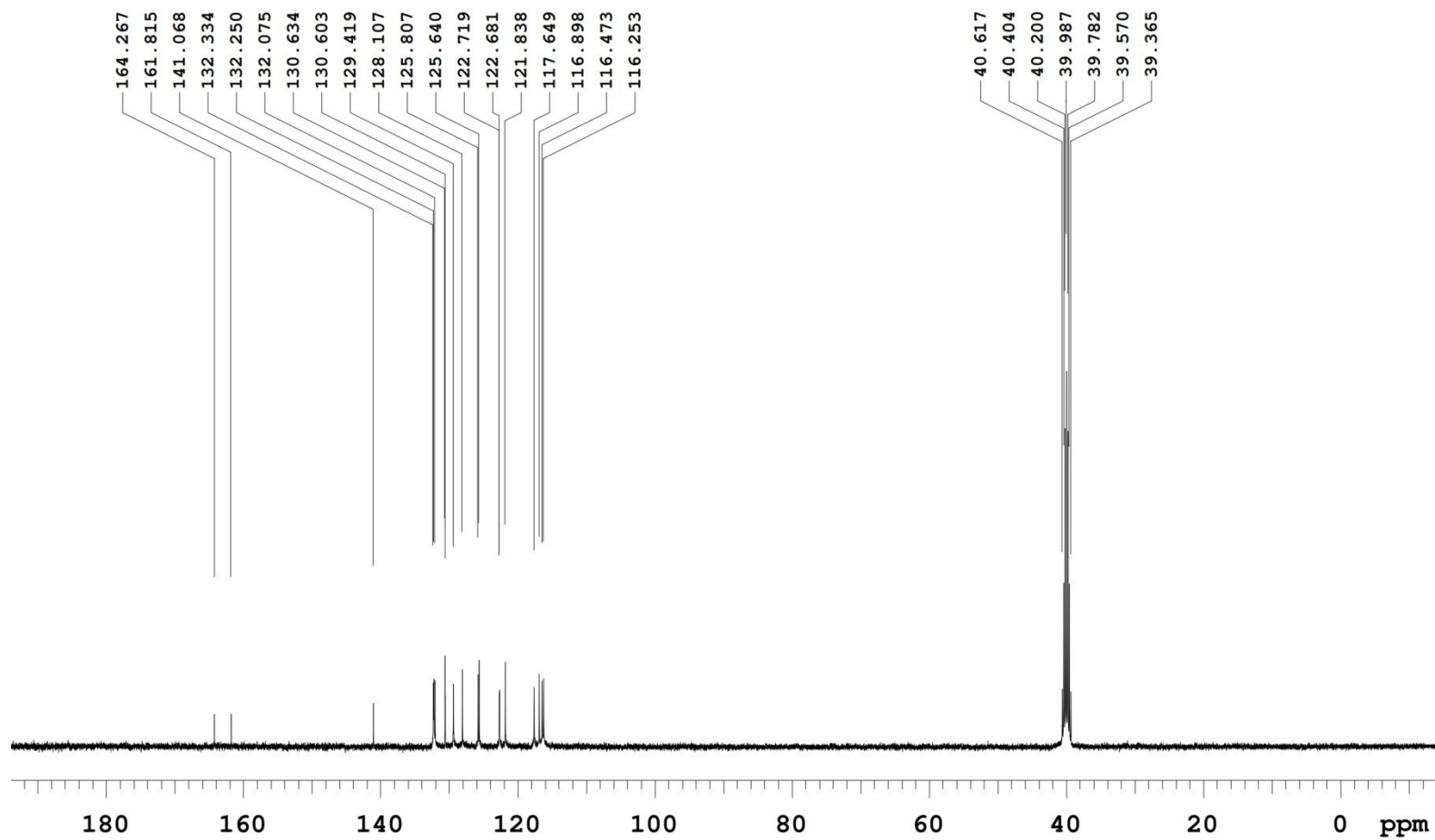
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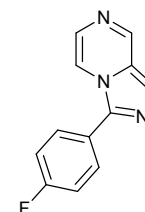
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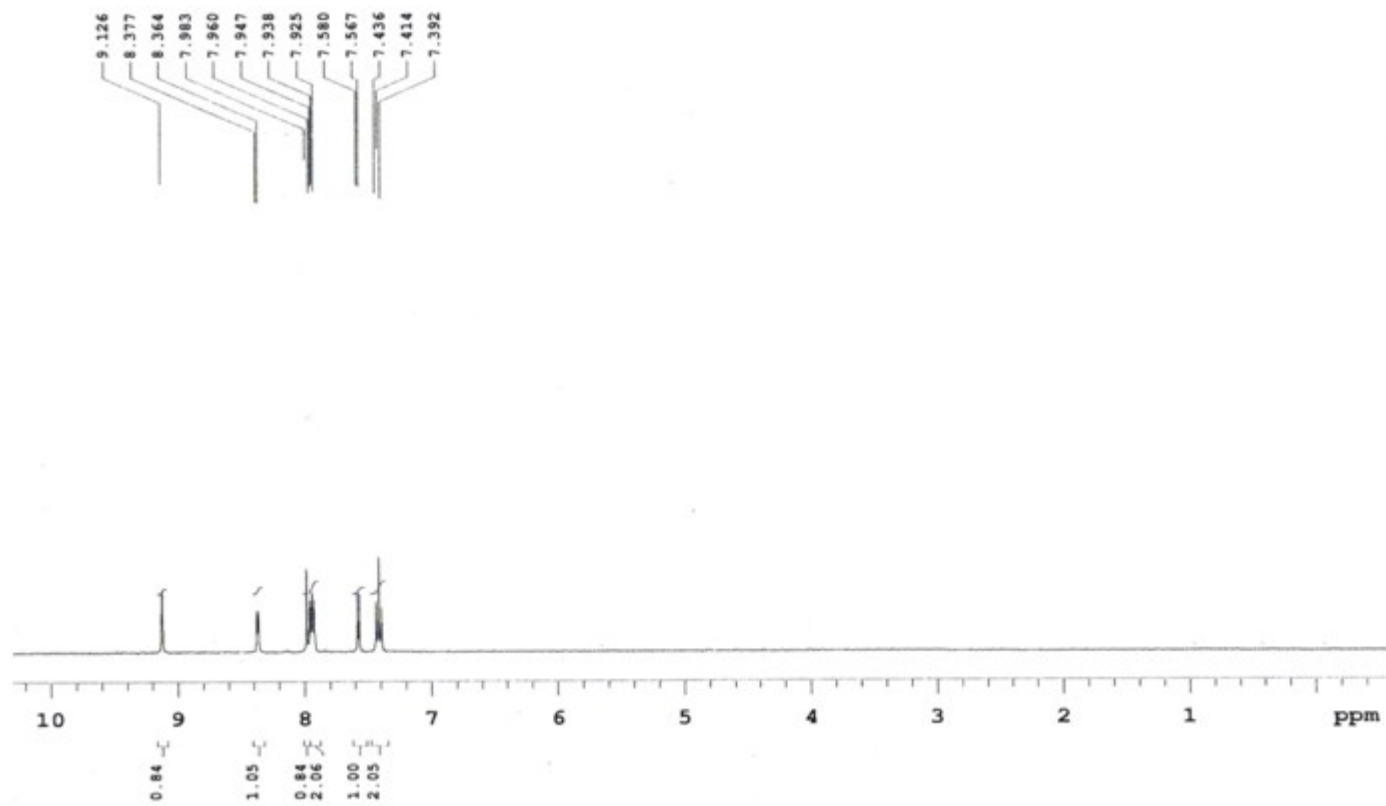




¹H NMR of 3k

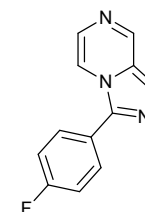
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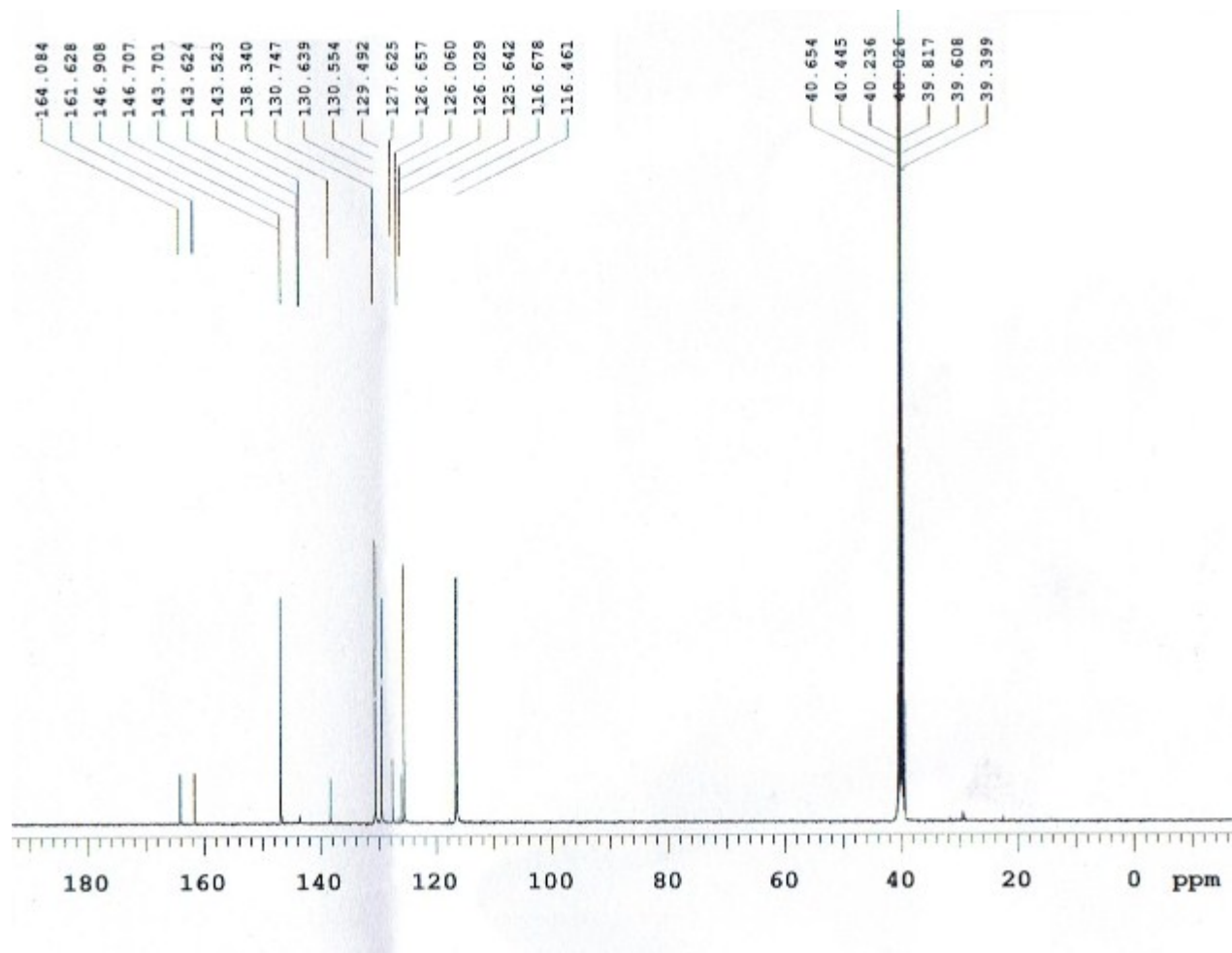




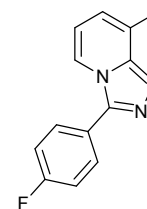
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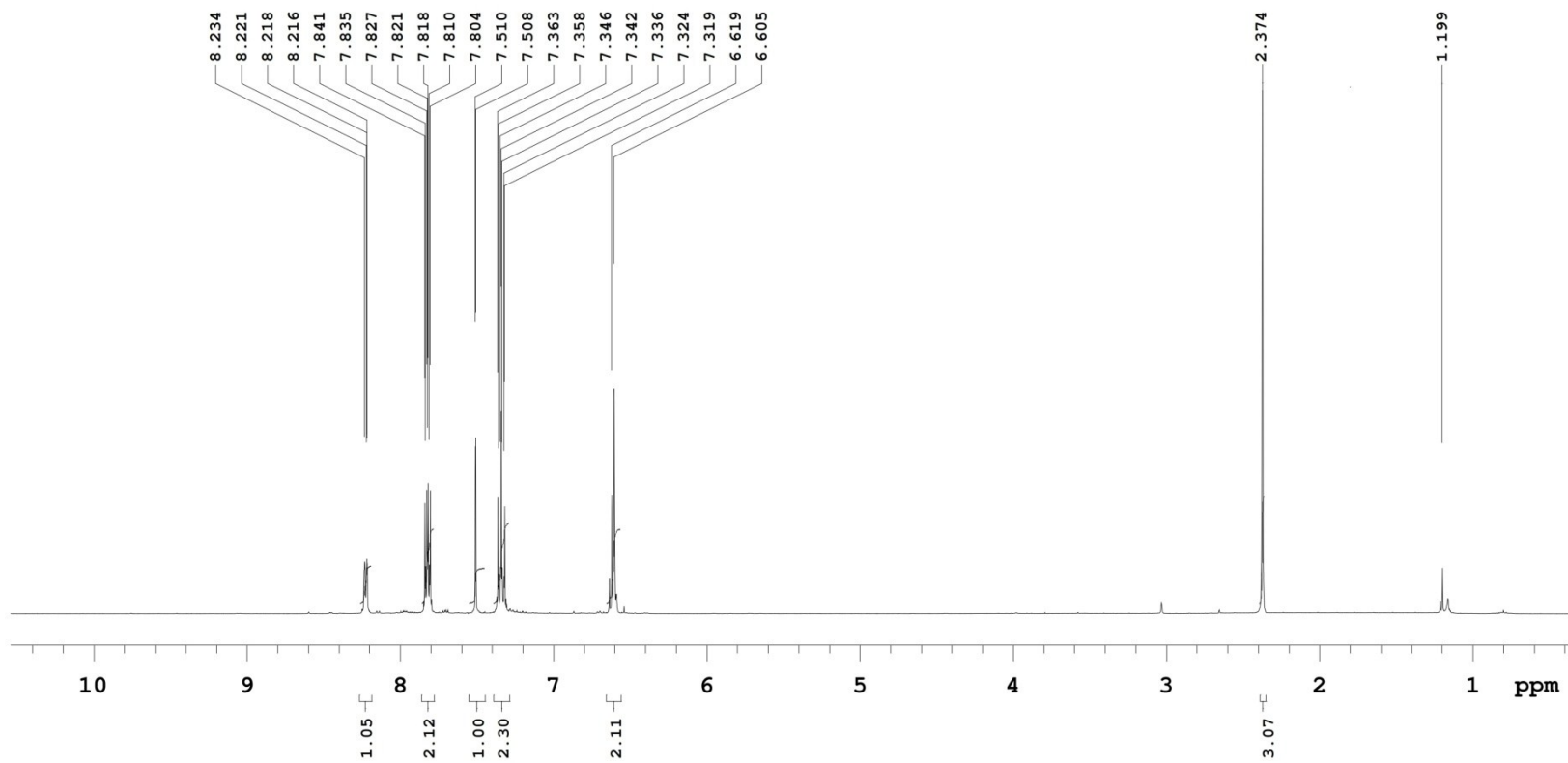
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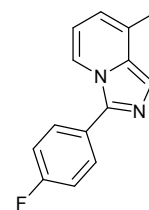


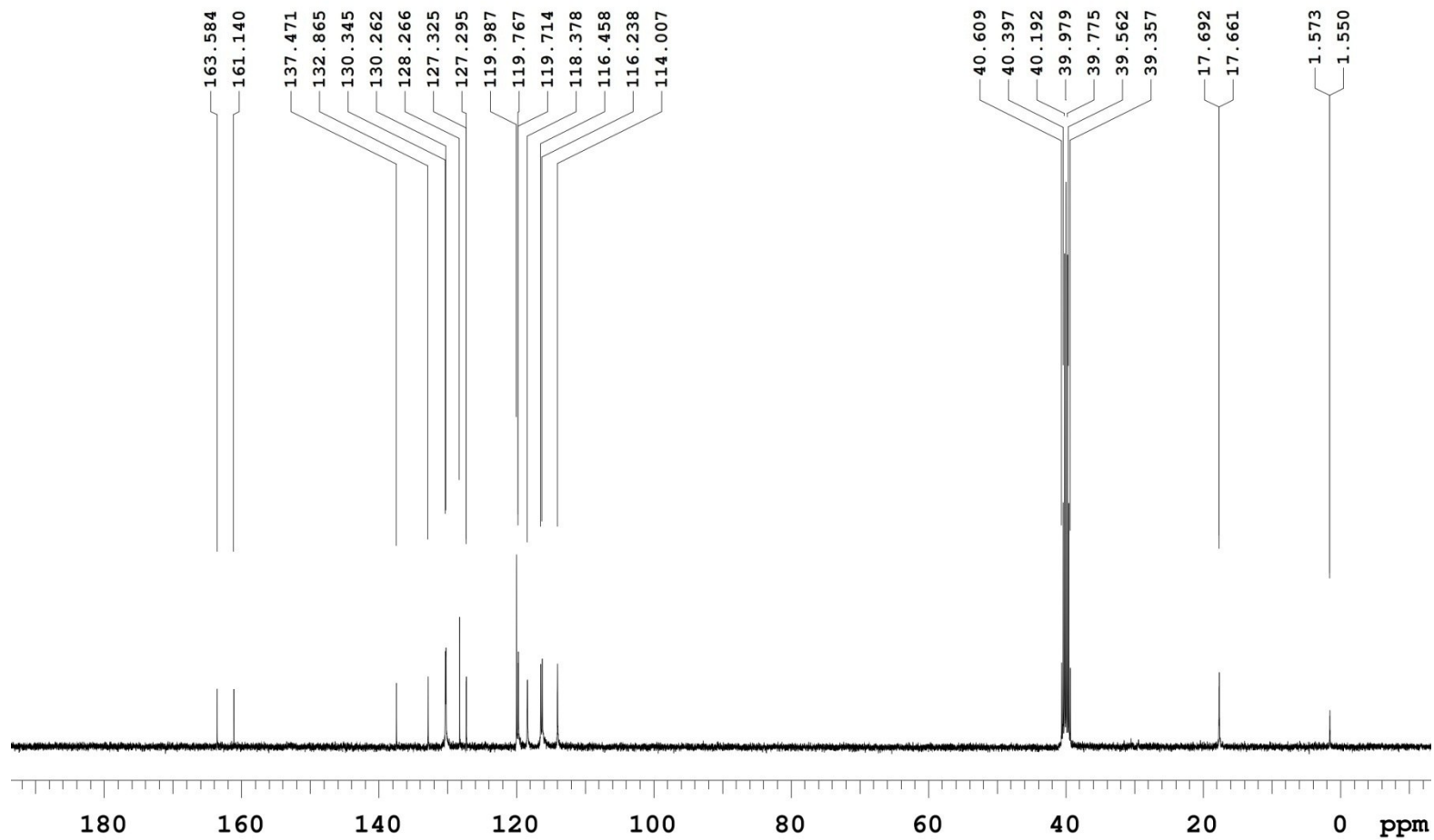
¹H NMR of 3i



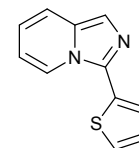


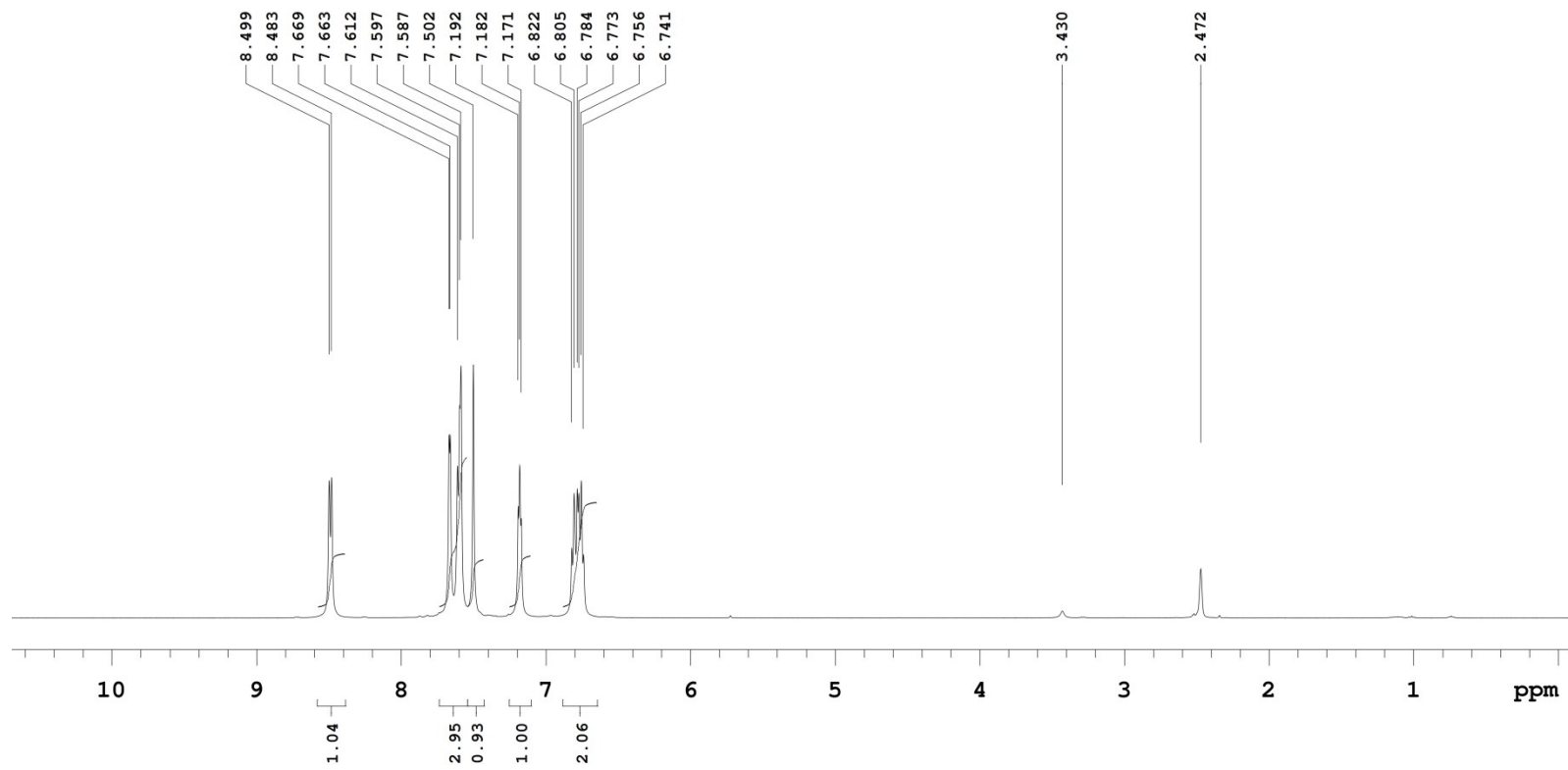
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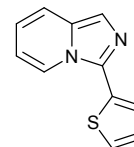


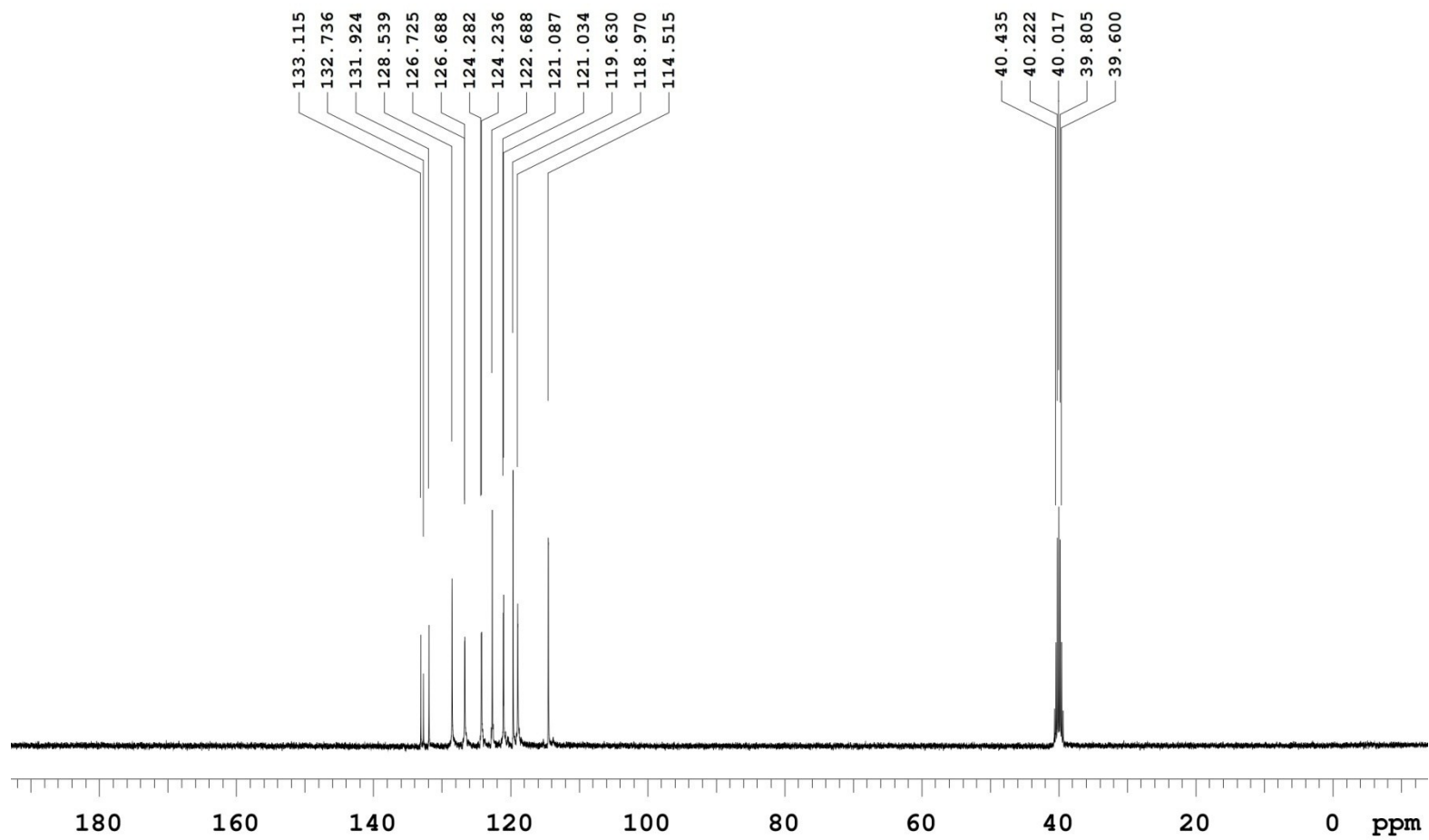
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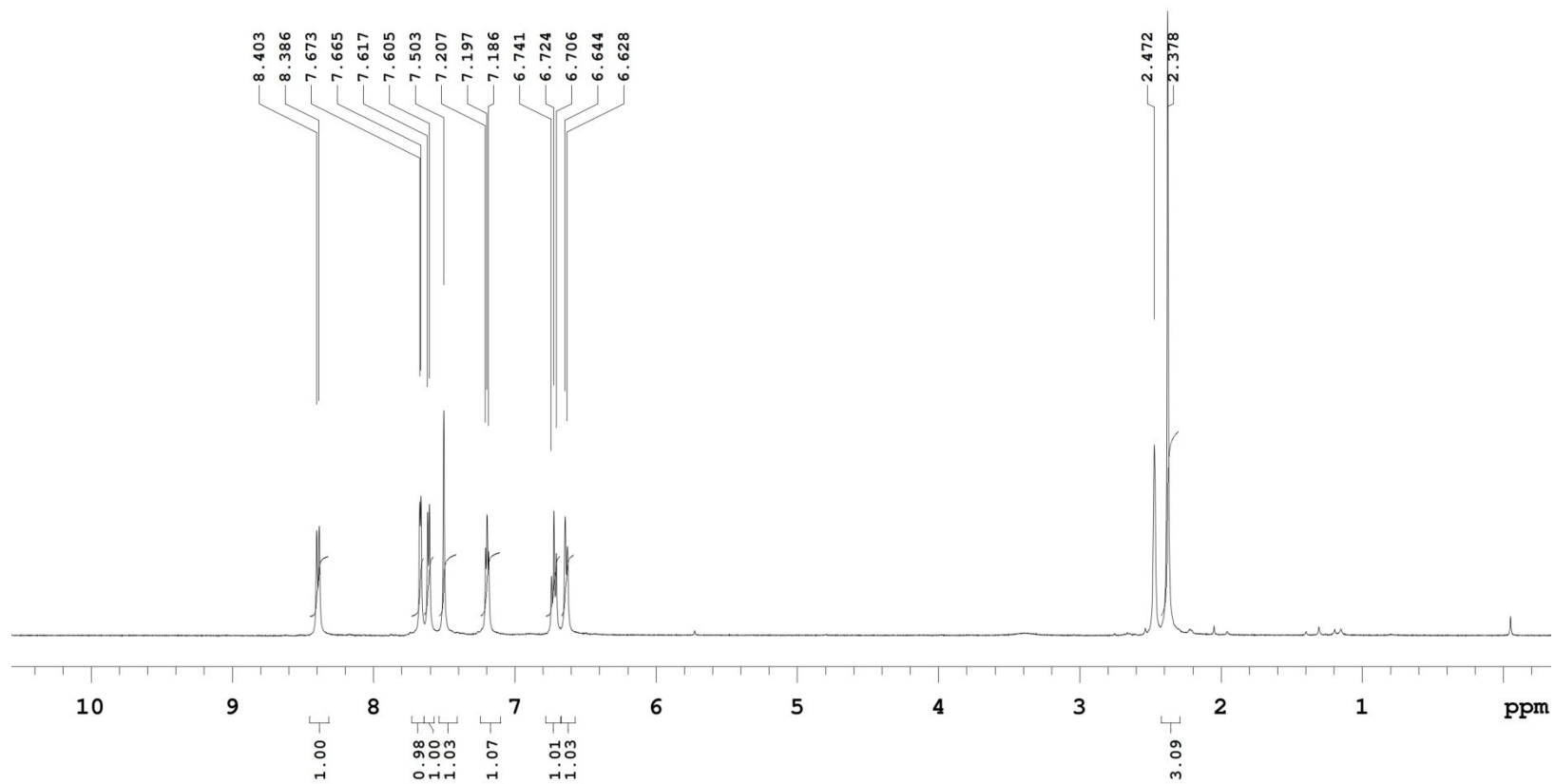
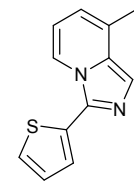


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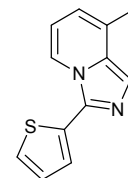


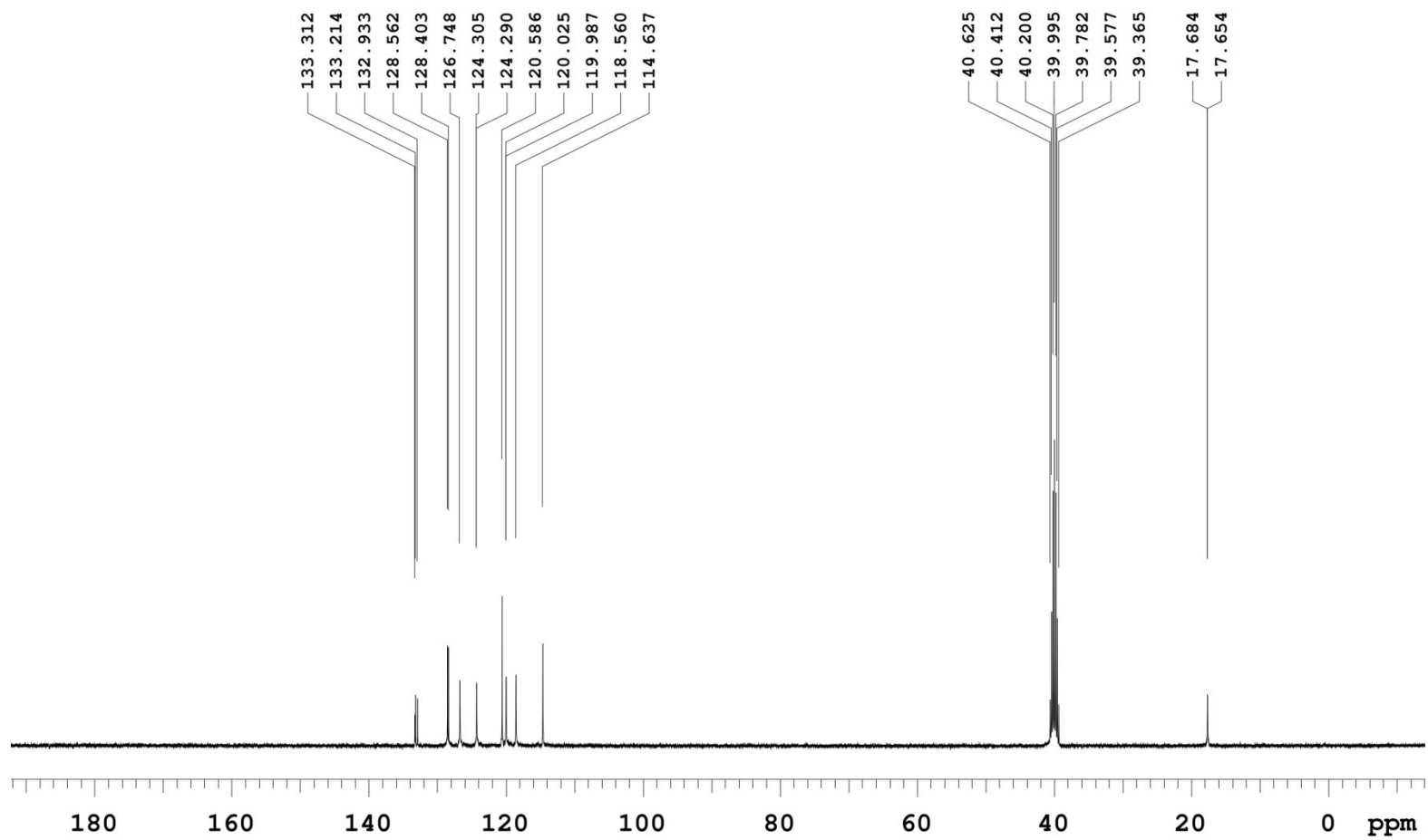


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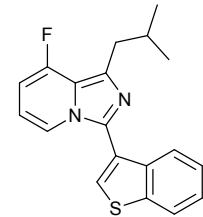
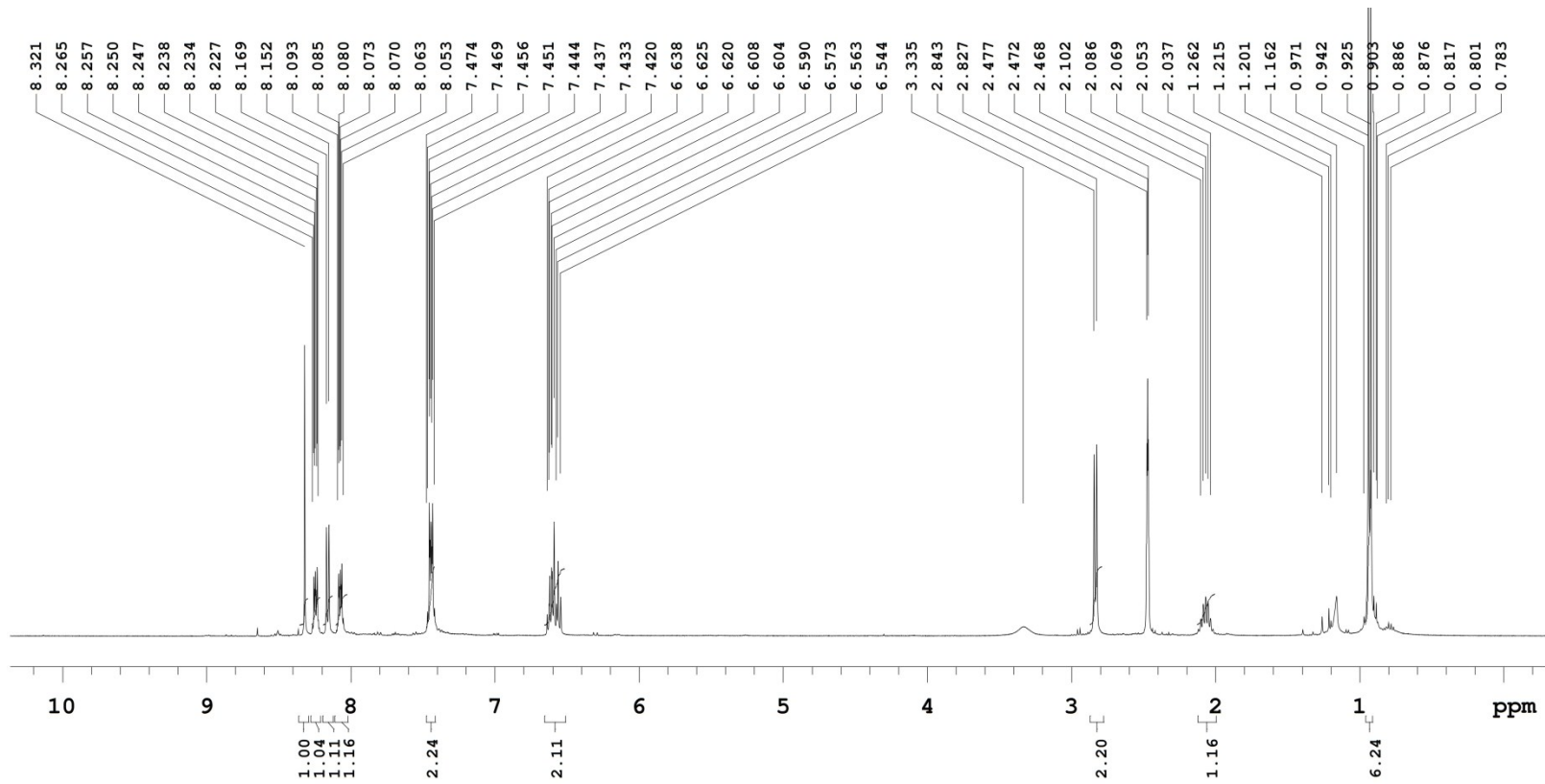


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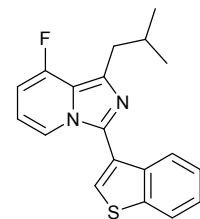


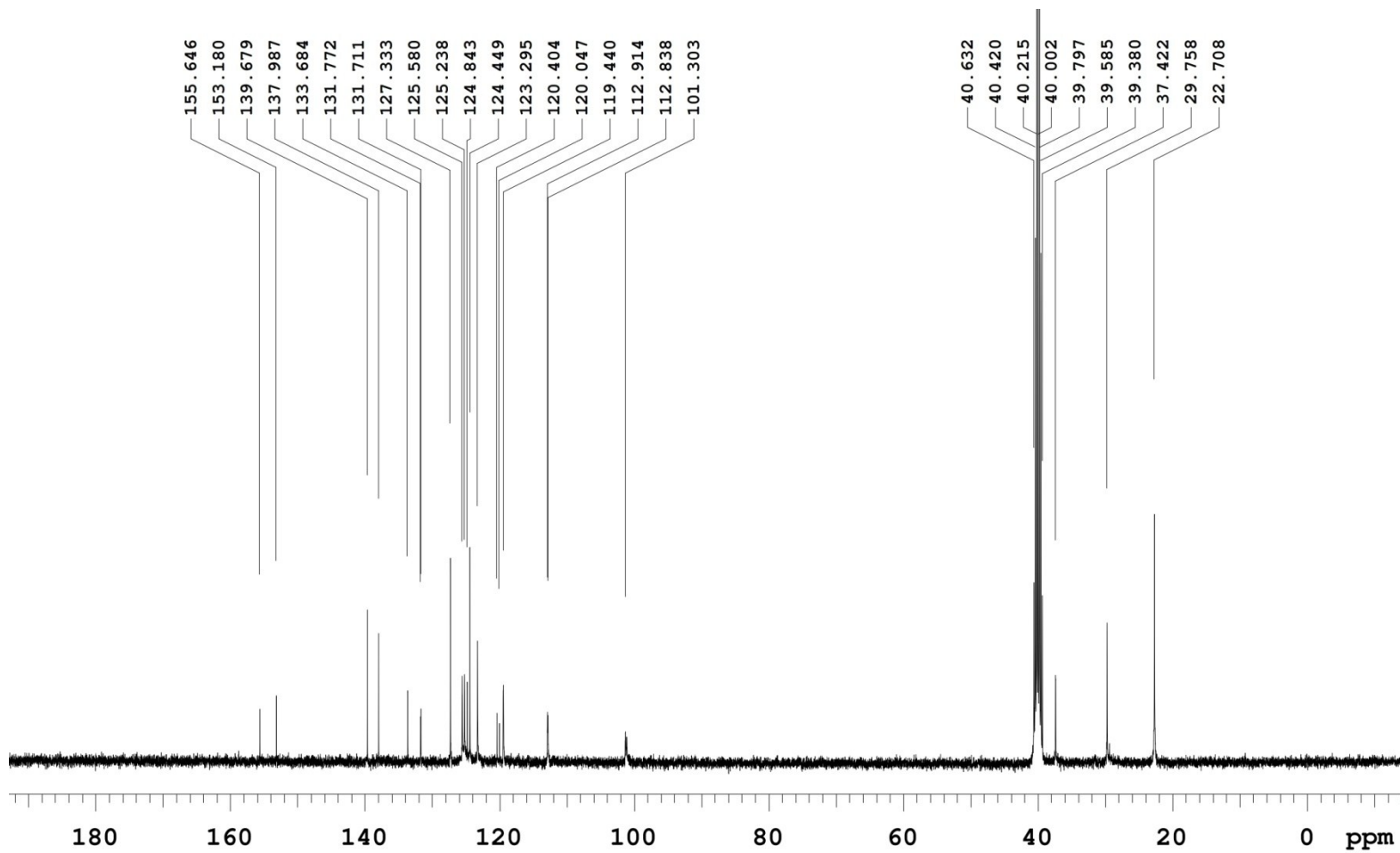


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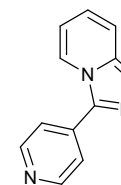


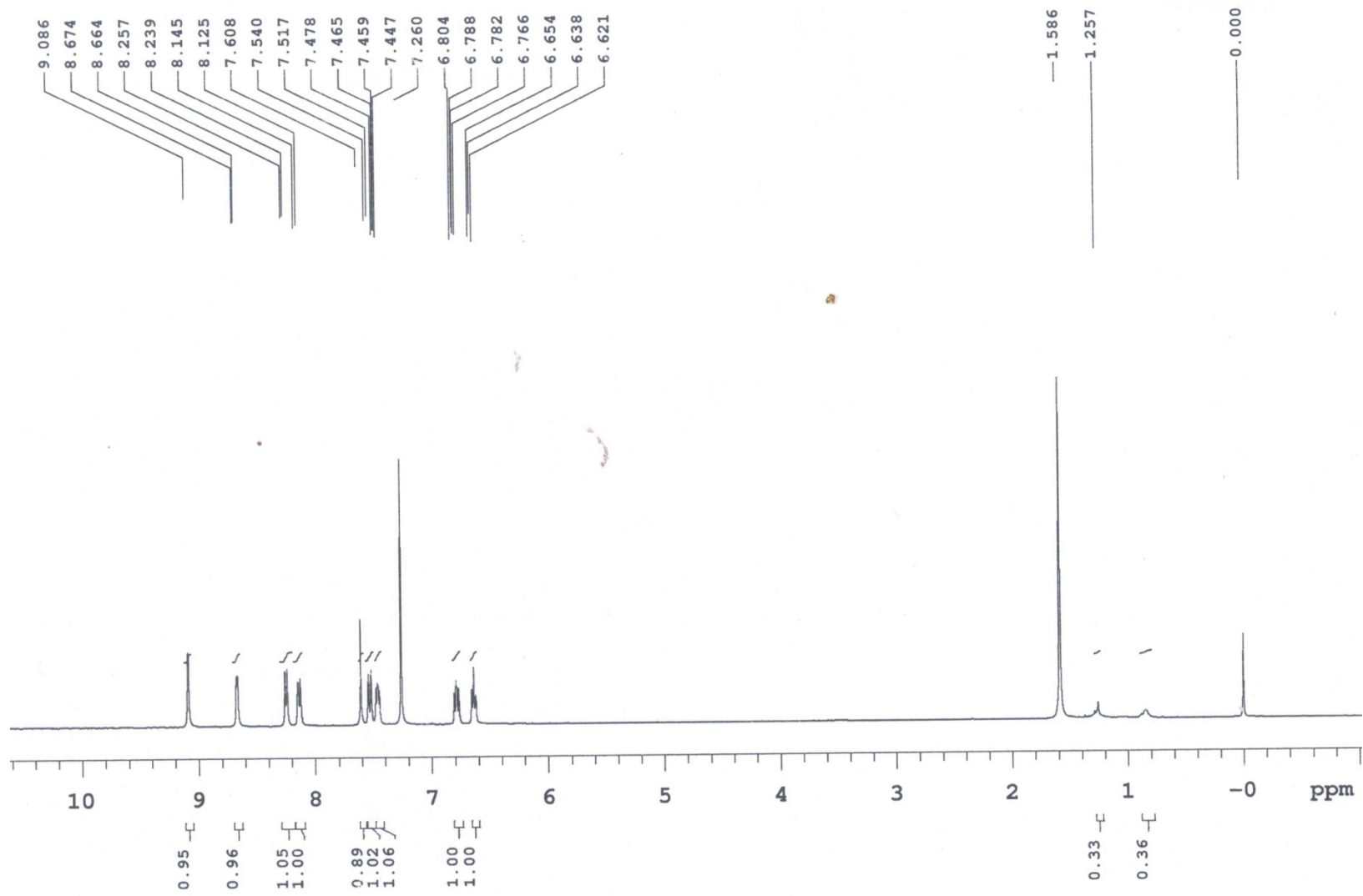
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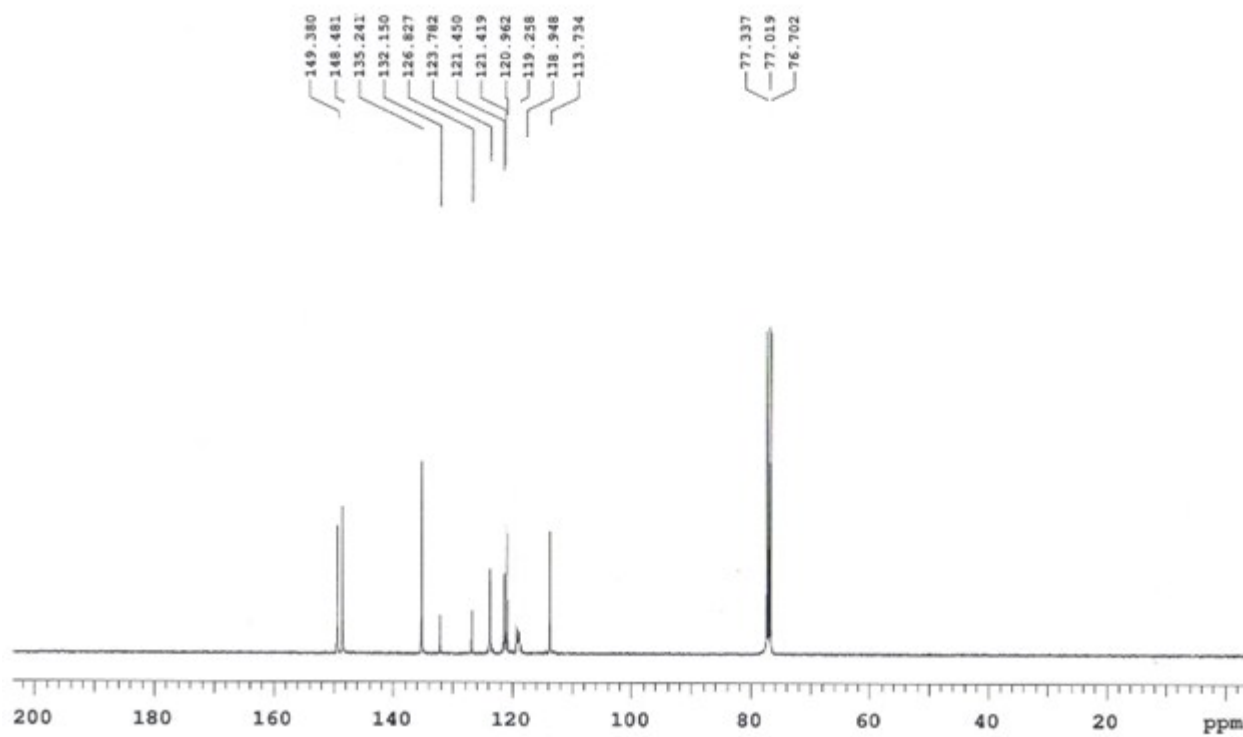
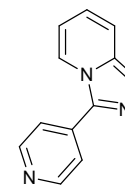


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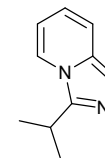
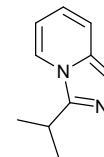
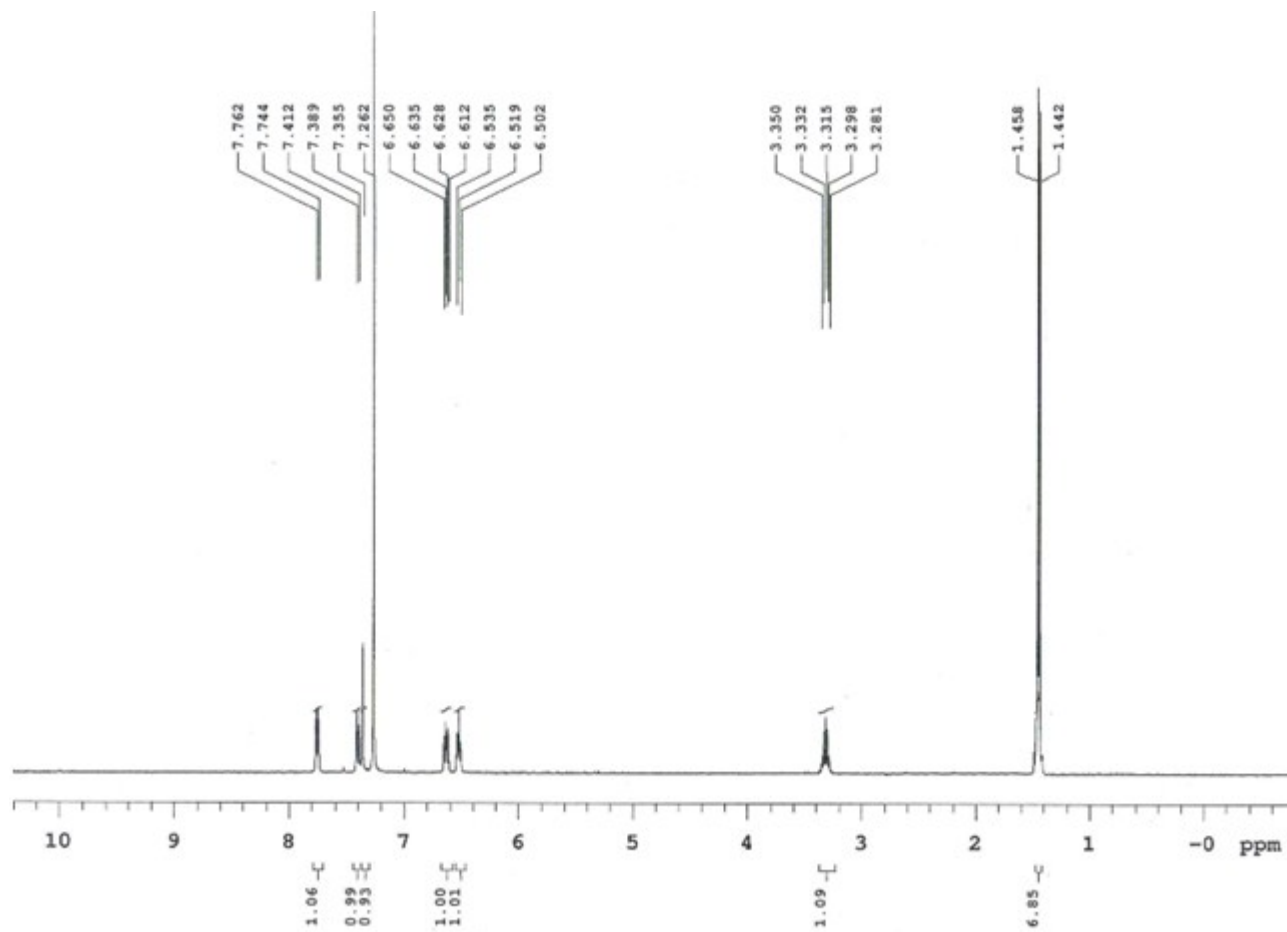




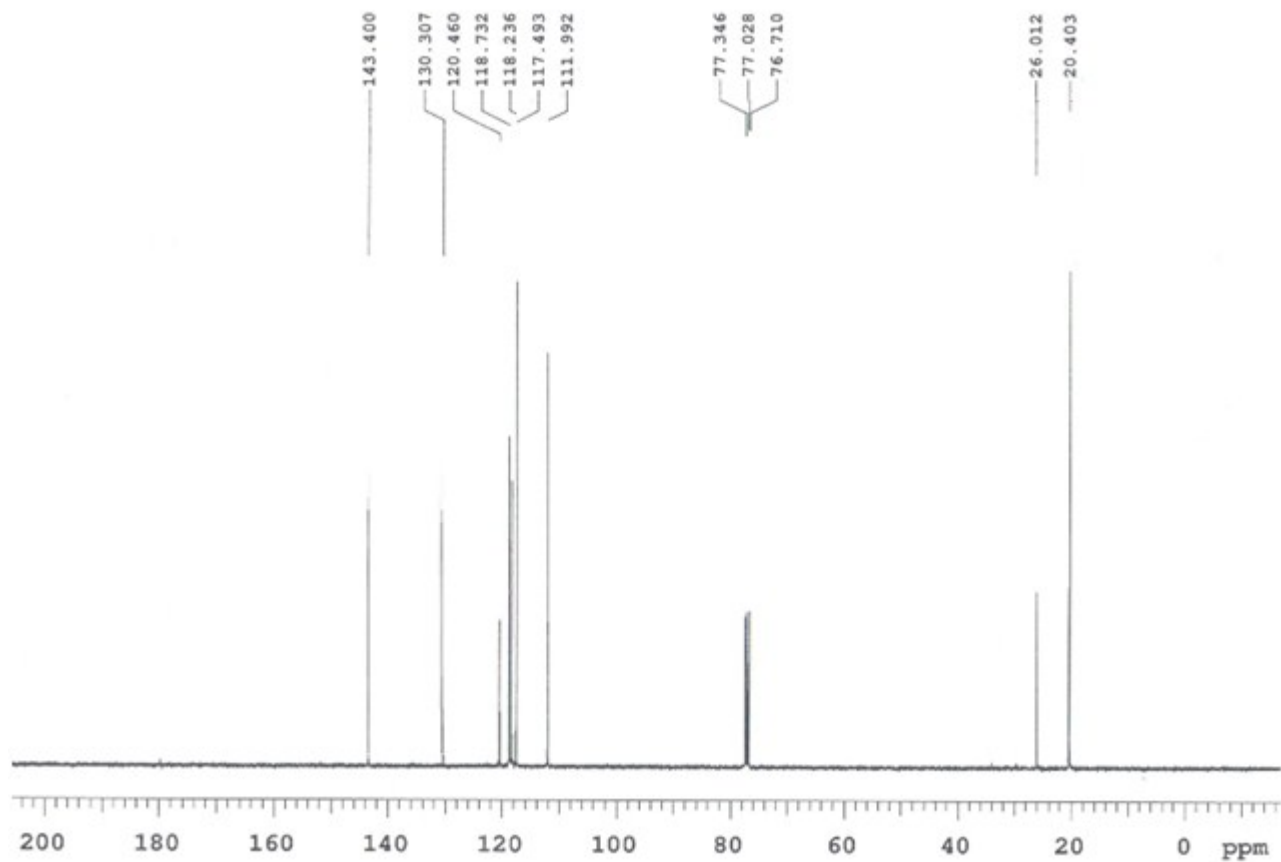
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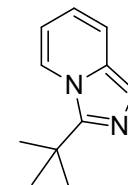
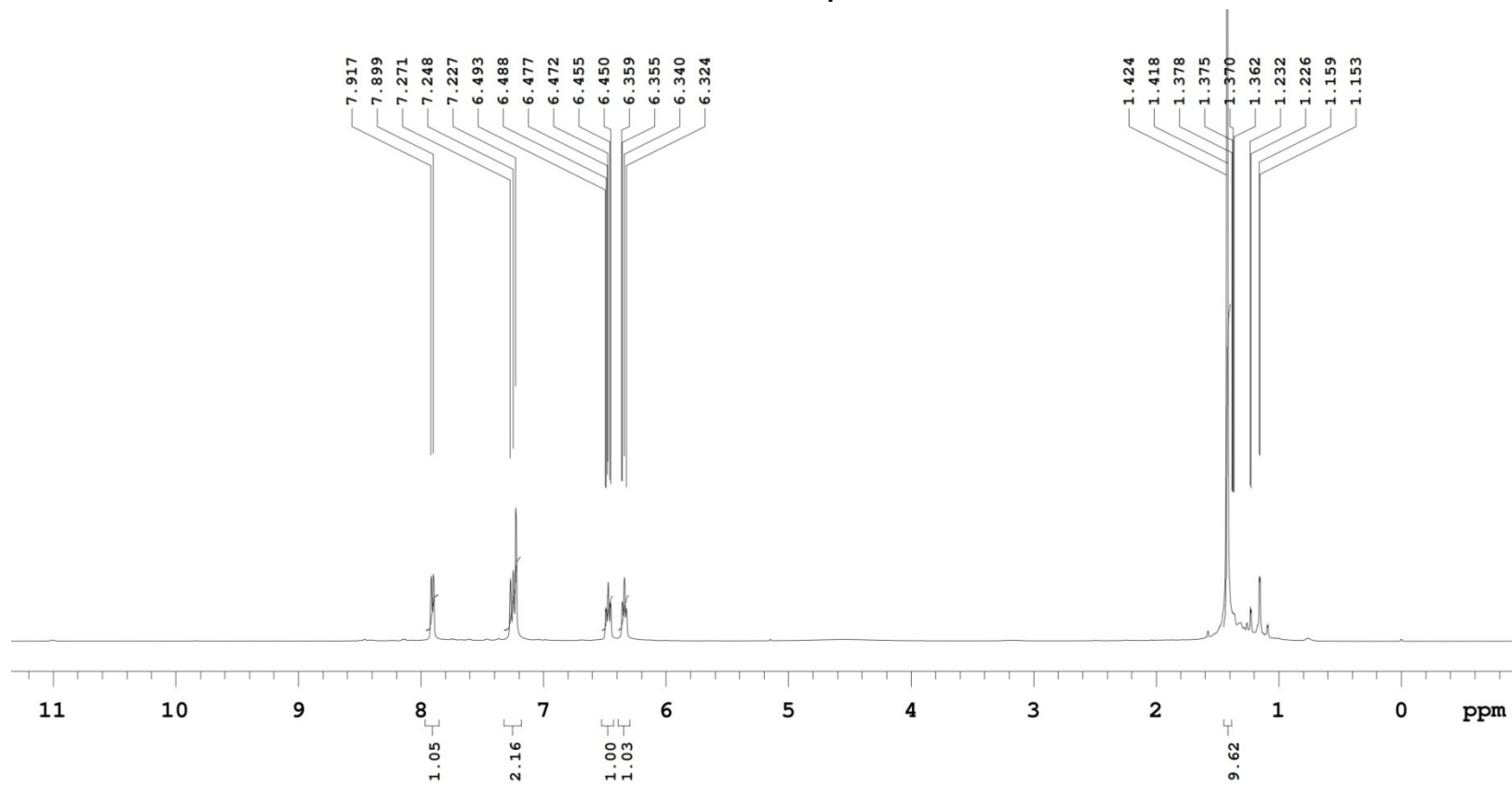
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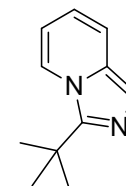
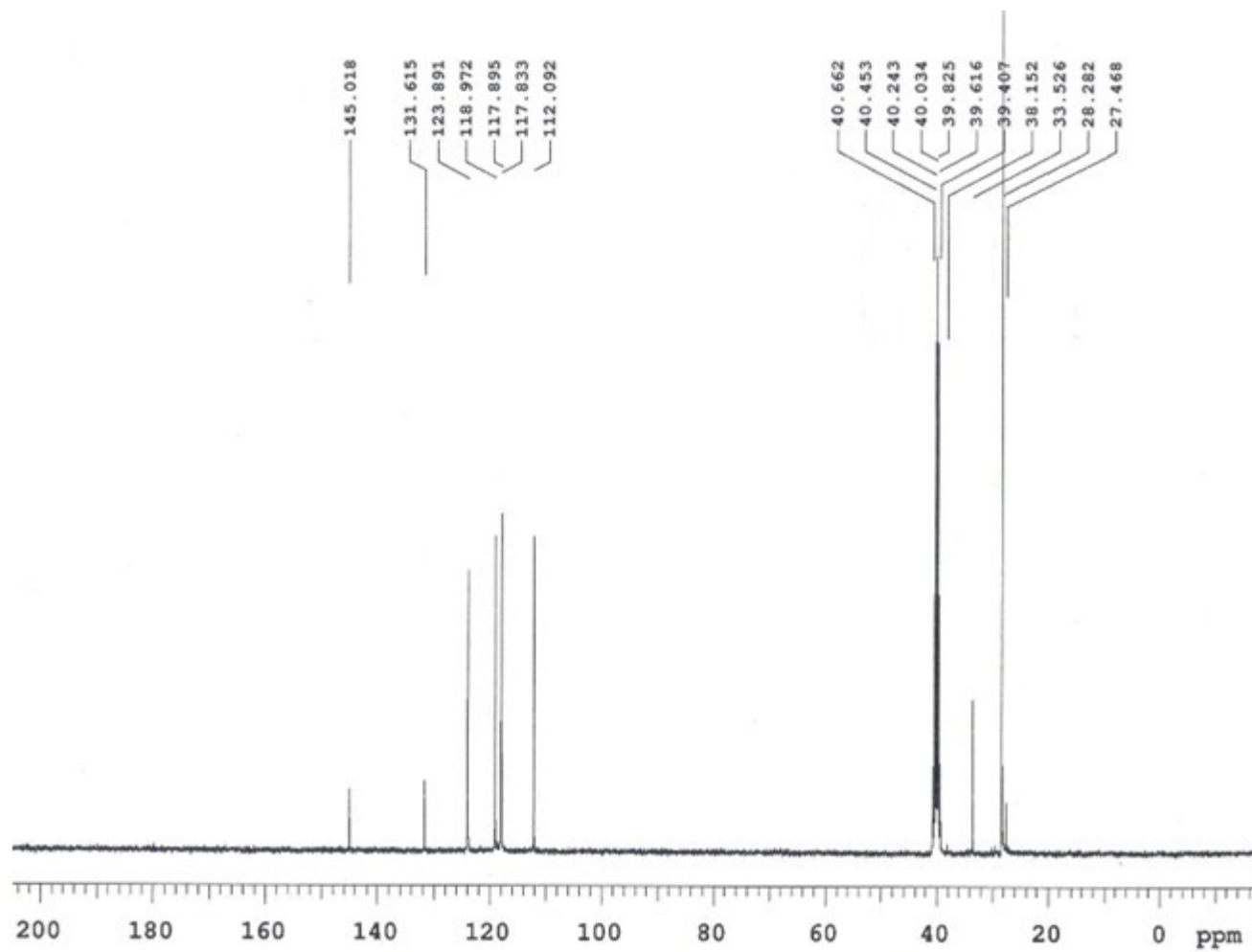
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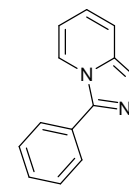


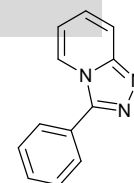
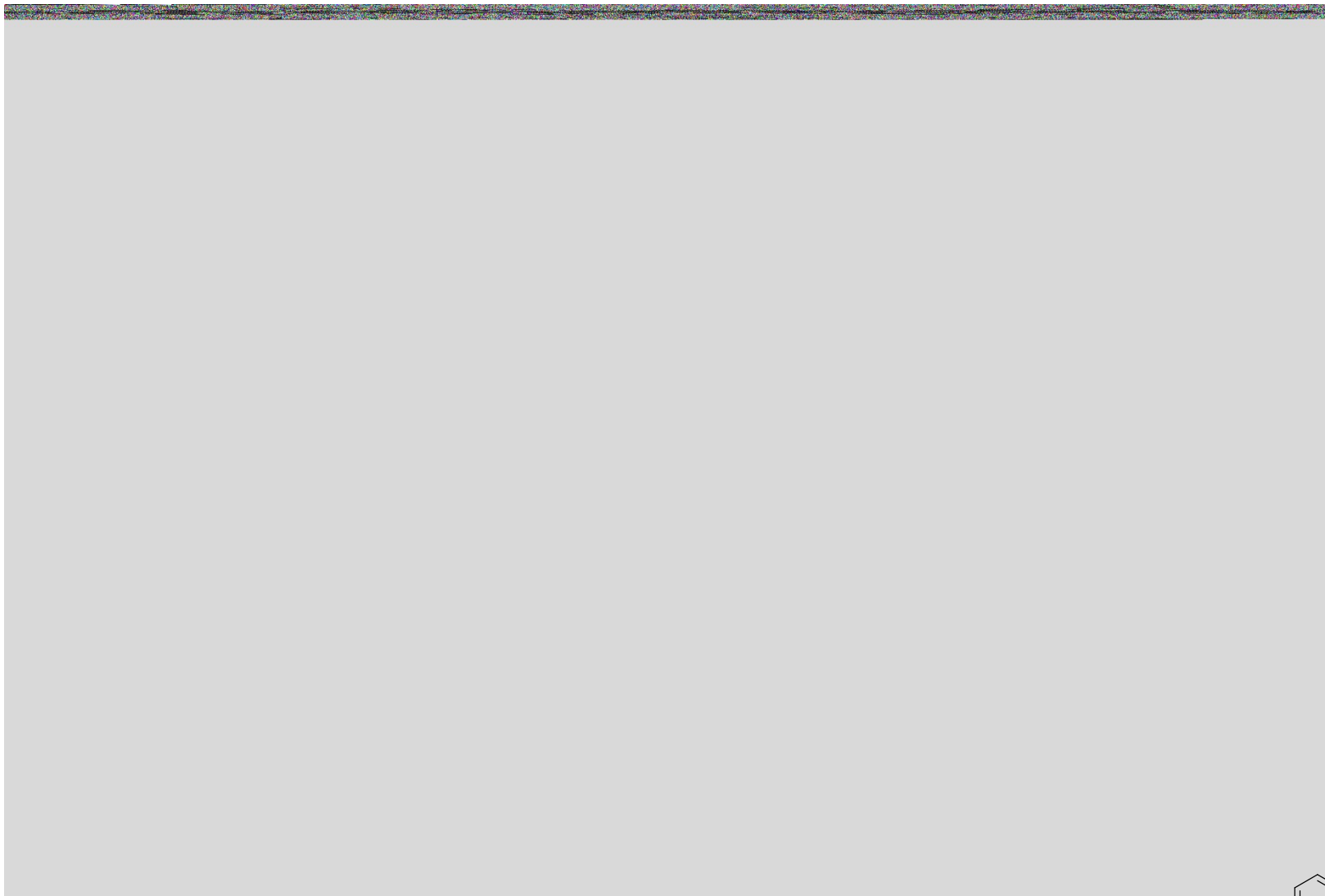
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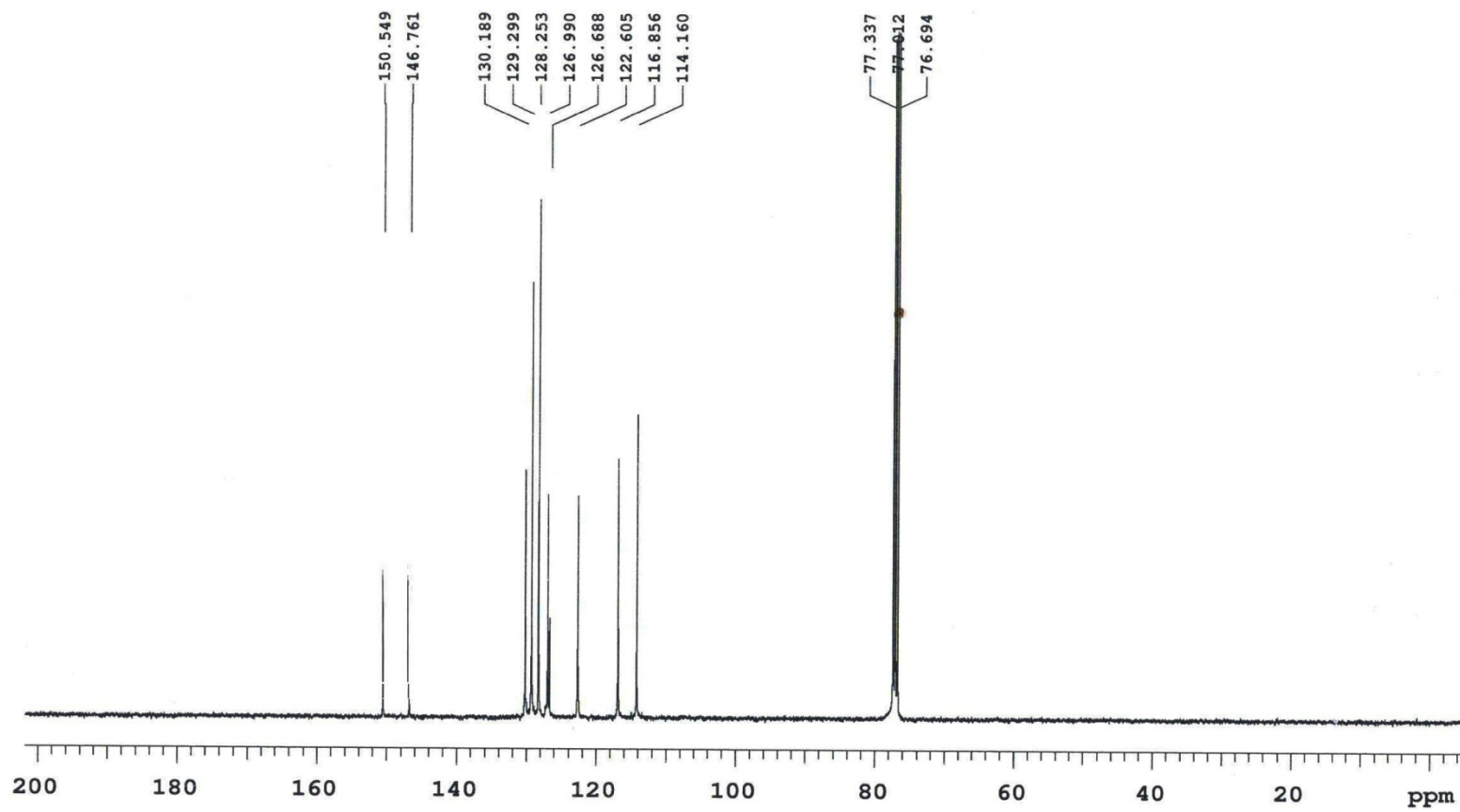
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S37



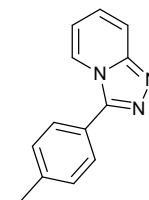


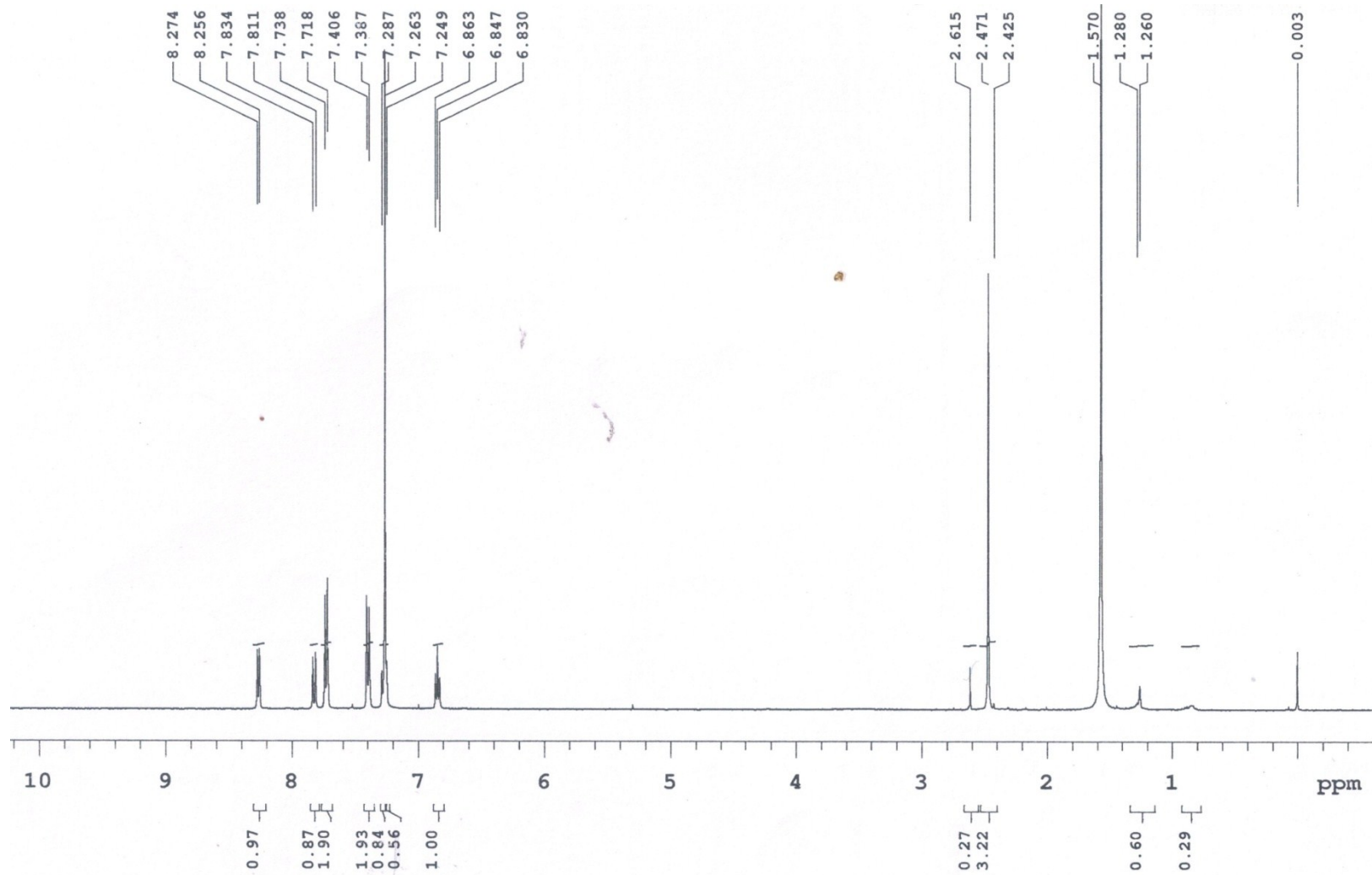
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¹H NMR of 5b

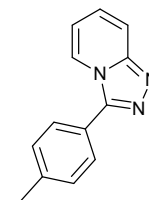
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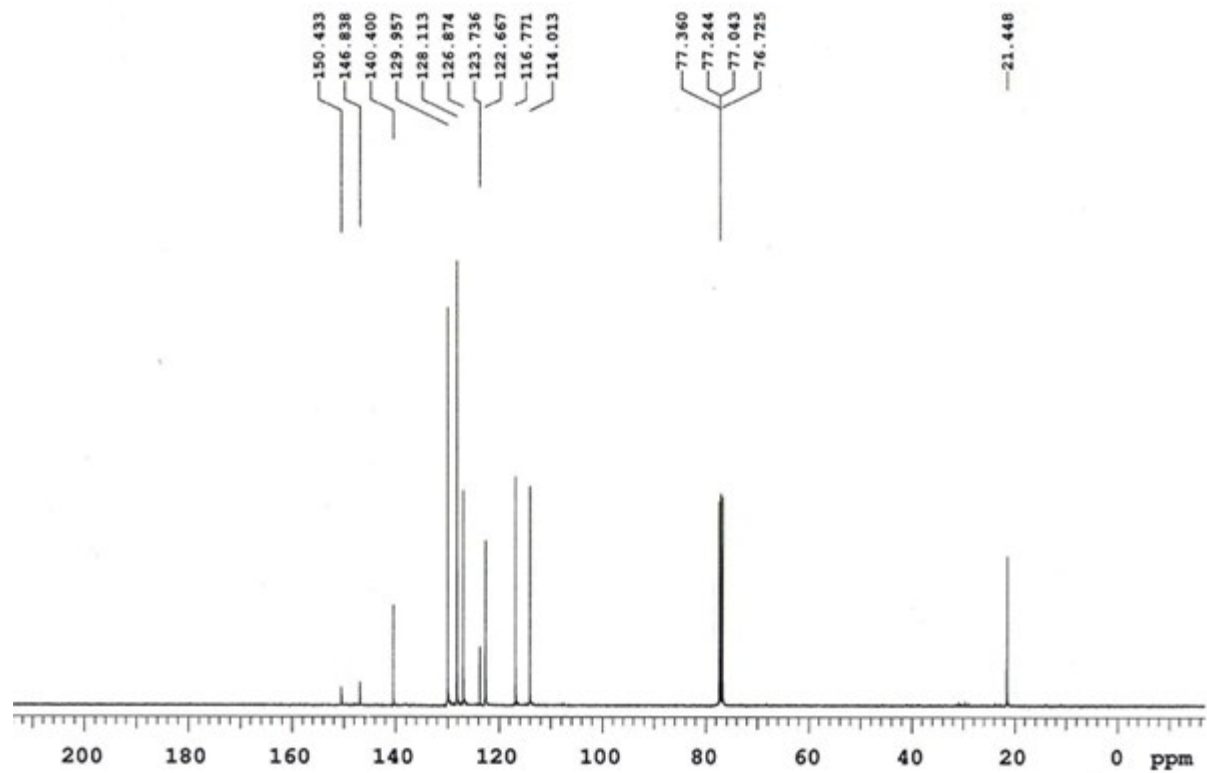




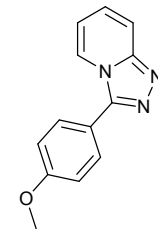
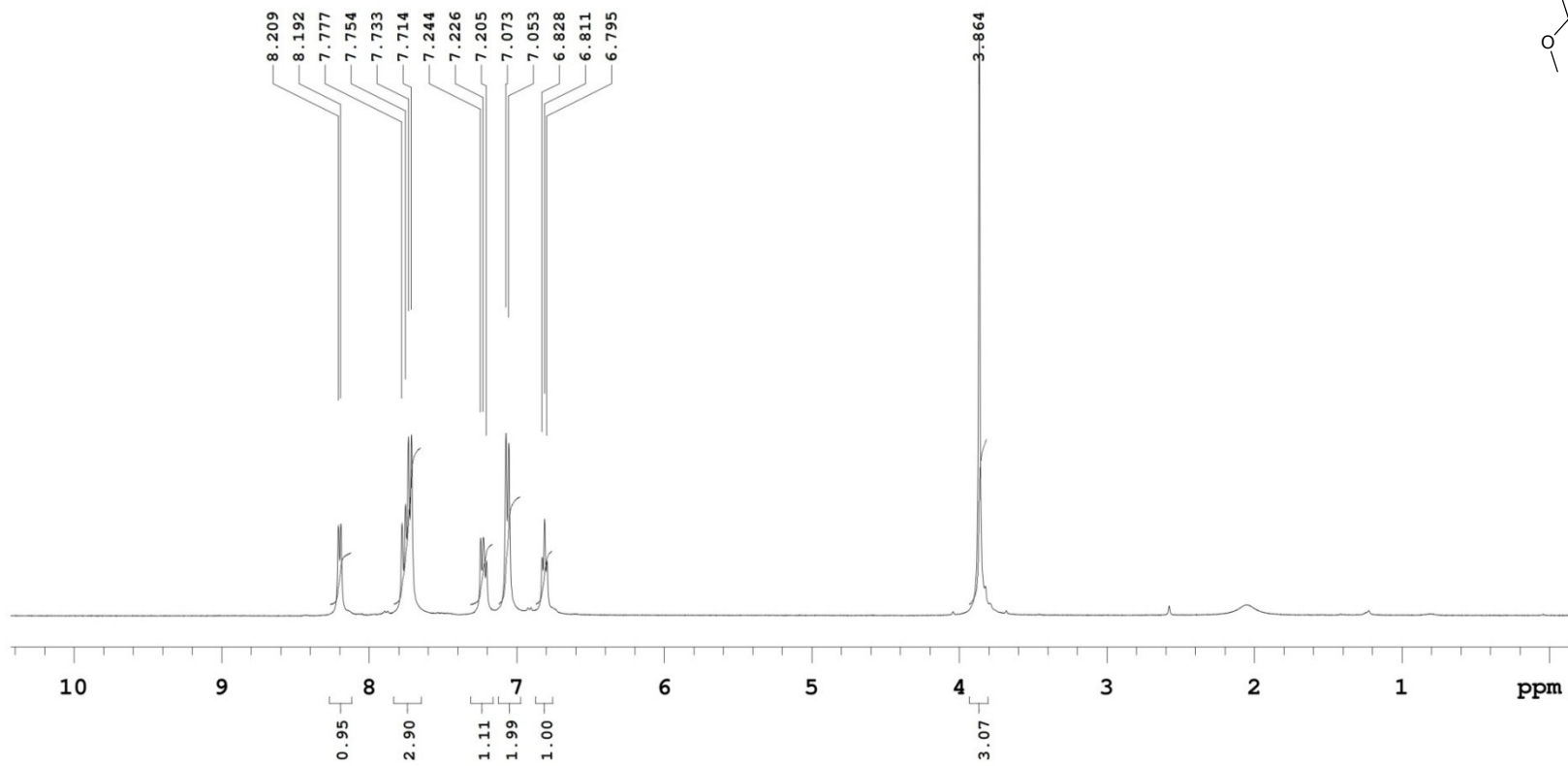
¹³C NMR of 5b

S40



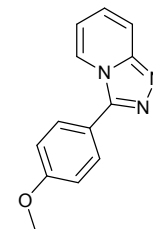


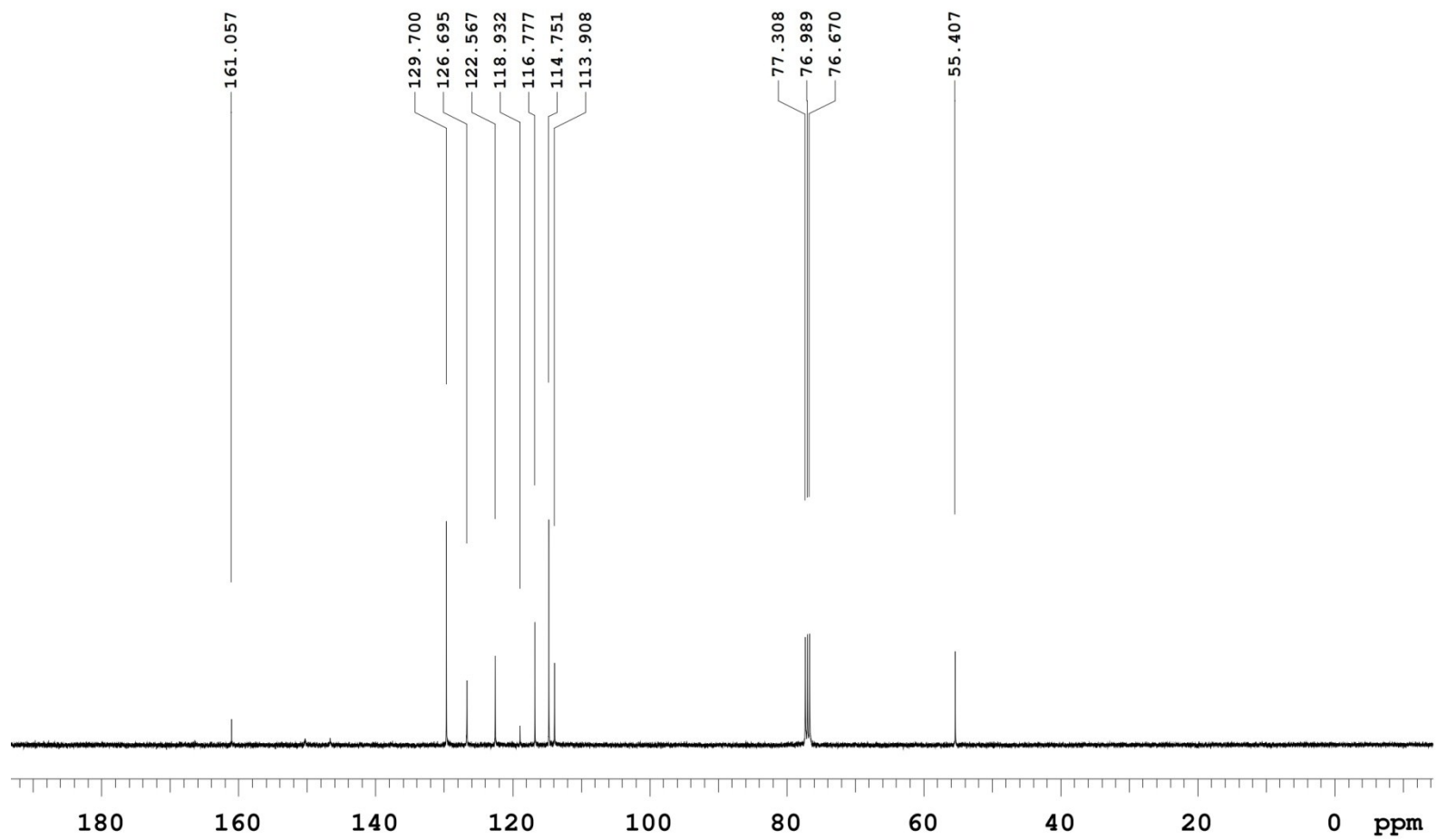
^{13}C NMR of 5c



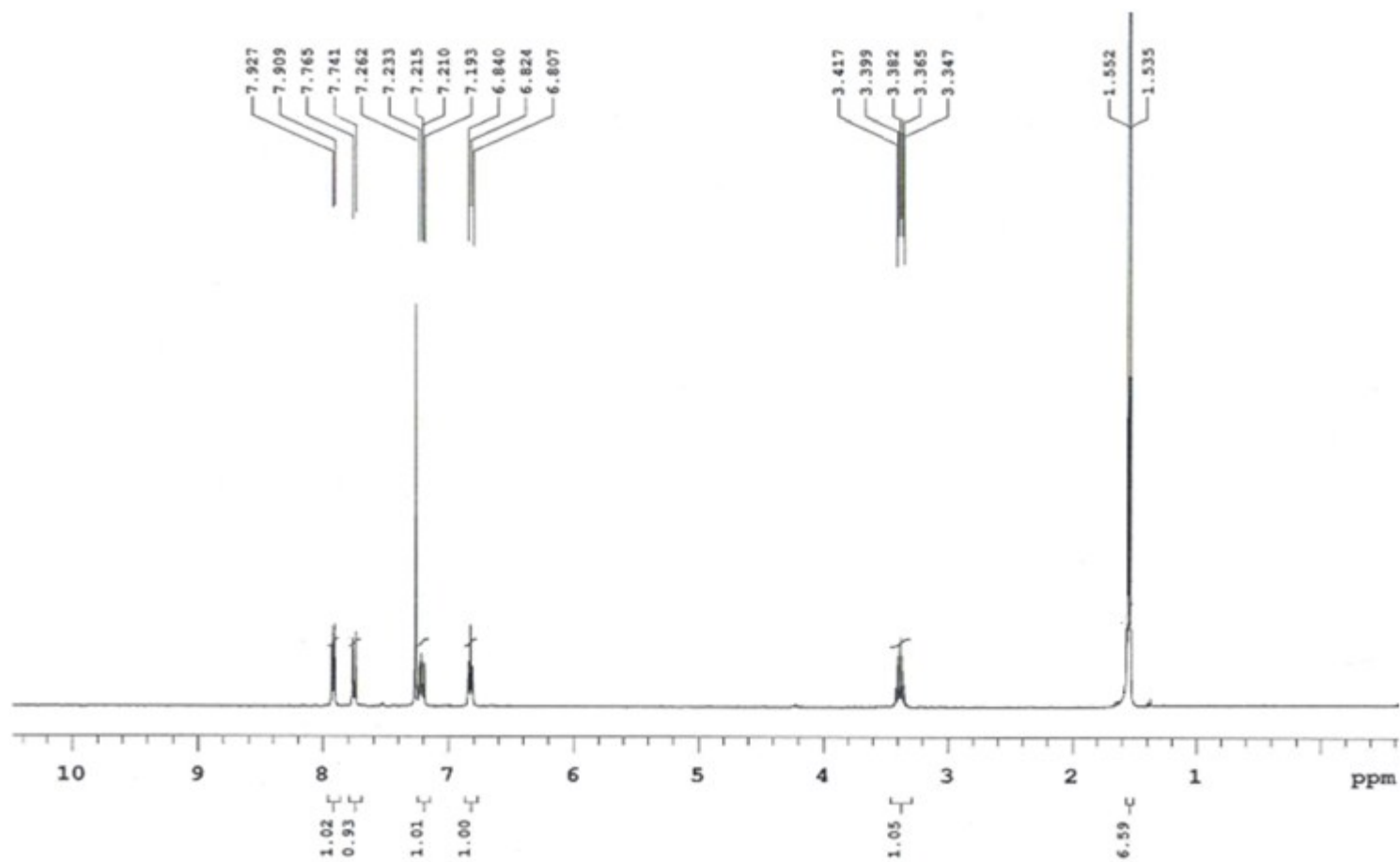
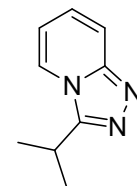
¹³C NMR of 5c

S42

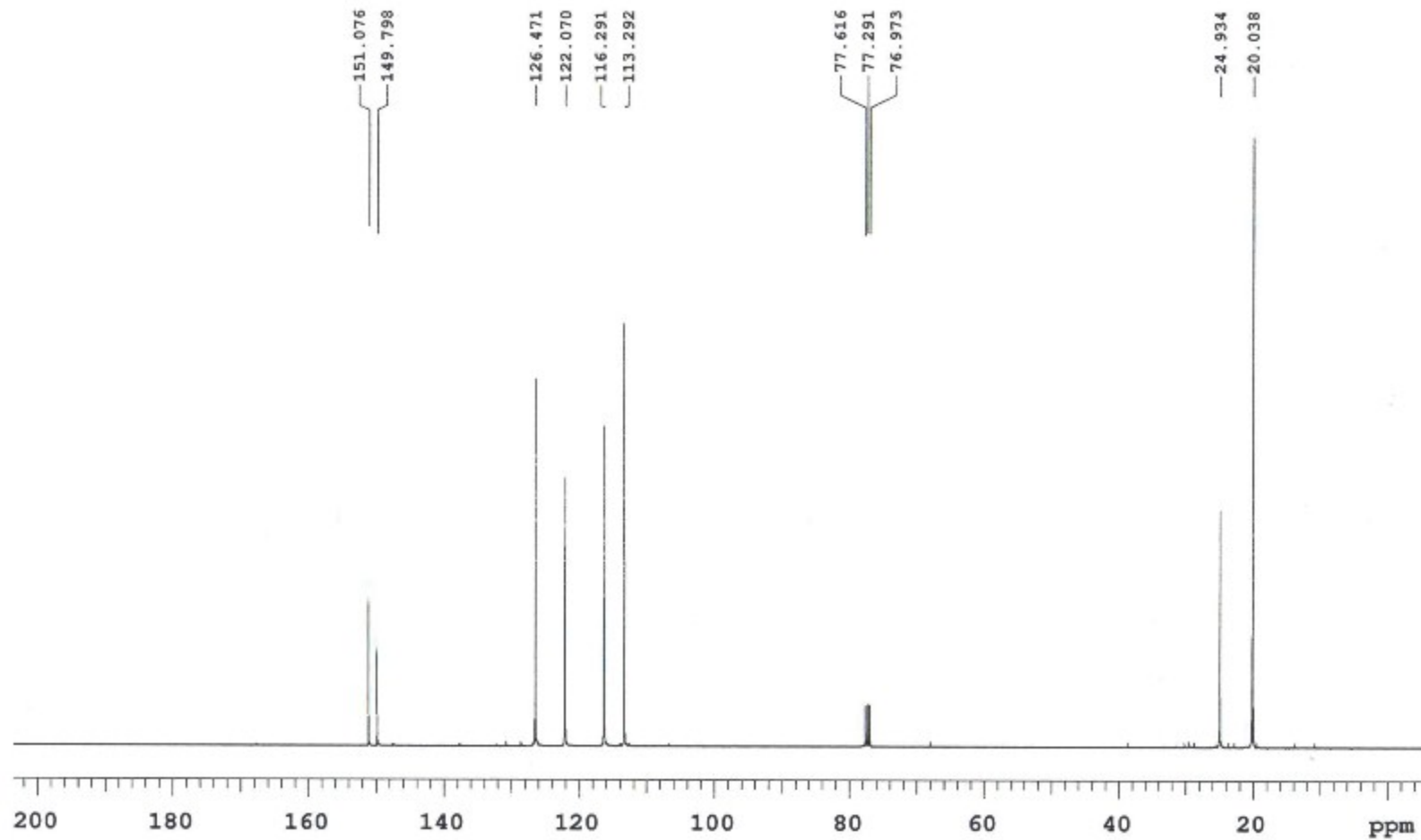
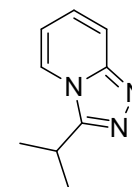


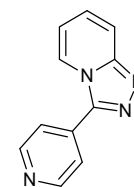


¹H NMR of 5d

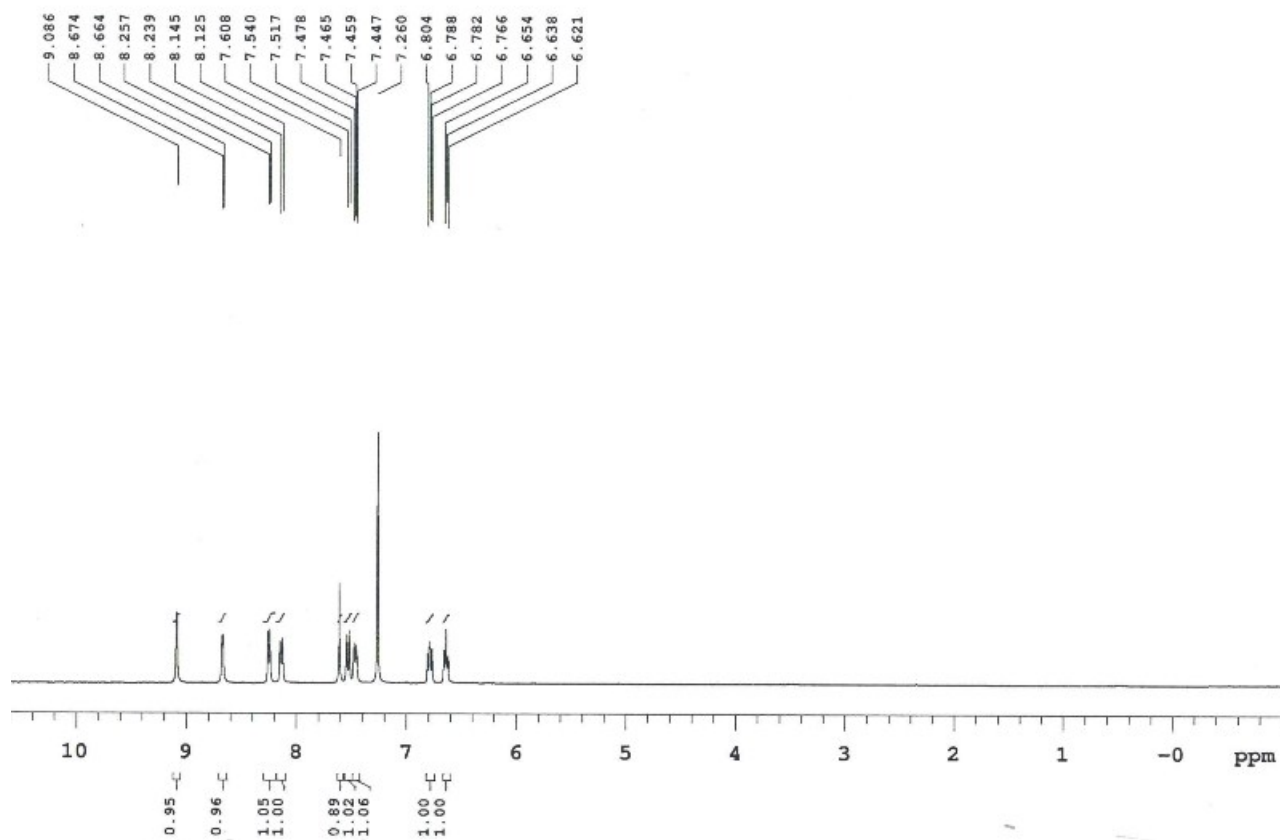


¹³C NMR of 5d





¹H NMR of 5e



¹³C NMR of 5e

