Supporting Information

Iodine-catalyzed regioselective thiolation of imidazo[1,2-a]pyridines using sulfonyl hydrazides as a thiol surrogate

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General: ¹H NMR spectra were determined on a Bruker 400 (400 MHz) spectrometer as solutions in CDCl₃. Chemical shifts are expressed in parts per million (δ) and are referenced to tetramethylsilane (TMS) as internal standard and the signals were reported as s (singlet), d (doublet), t (triplet), m (multiplet) and coupling constants *J* were given in Hz. ¹³C NMR spectra were recorded at 100 MHz in CDCl₃ solution. All reactions were carried out in open air conditions. TLC was done on silica gel coated glass slide (Merck, Silica gel G for TLC). Silica gel (60-120 mesh, SRL, India) was used for column chromatography. Petroleum ether refers to the fraction boiling in the range of 60-80 °C unless otherwise mentioned. All solvents were dried and distilled before use. Solvents, reagents and chemicals were purchased from Aldrich. All the imidazopyridines were synthesized by following reported methodology.¹

1. Typical procedure for the synthesis of 2-phenyl-3-p-tolylsulfanyl-imidazo[1,2-a]pyridine (3aa):

To a solution of 2-phenyl-imidazo[1,2-*a*]pyridine **1a** (97 mg, 0.5 mmol) in ethanol (0.1 mL), *p*-toluene sulfonylhydrazide **2a** (110 mg, 0.6 mmol) and I₂ (20 mol-%) was added. The mixture was stirred at 70 °C for 10 h (TLC). After completion, the reaction mixture was cooled to room temperature and ethanol was evaporated. Subsequently, the mixture was extracted with dichloromethane (5 mL) followed by washing with brine (3 mL). The combined organic phases were dried over anhydrous Na₂SO₄. The crude product was concentrated in vacuo and was purified by column chromatography on silica gel using petroleum ether/ethylacetate (15:1 to 10:1) as eluent.

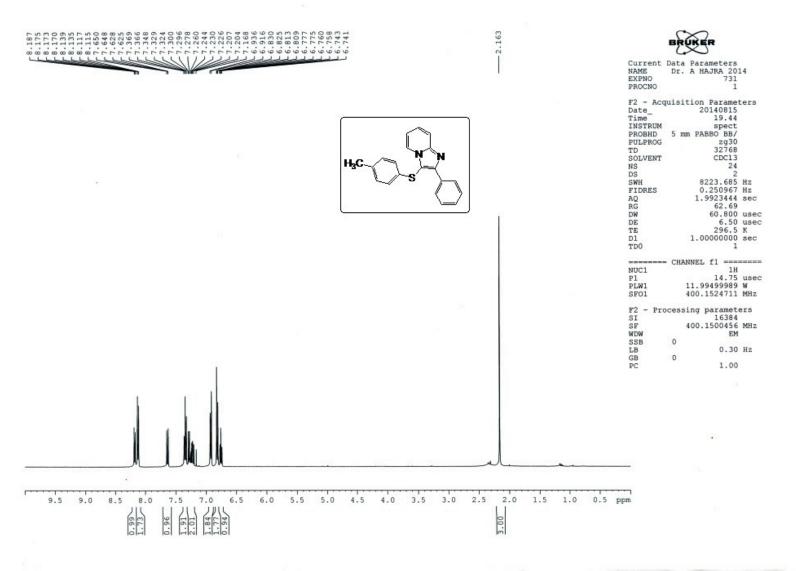
2. Typical procedure for the synthesis of 6-phenyl-5-(p-tolylthio)imidazo[2,1-b]thiazole (5aa):

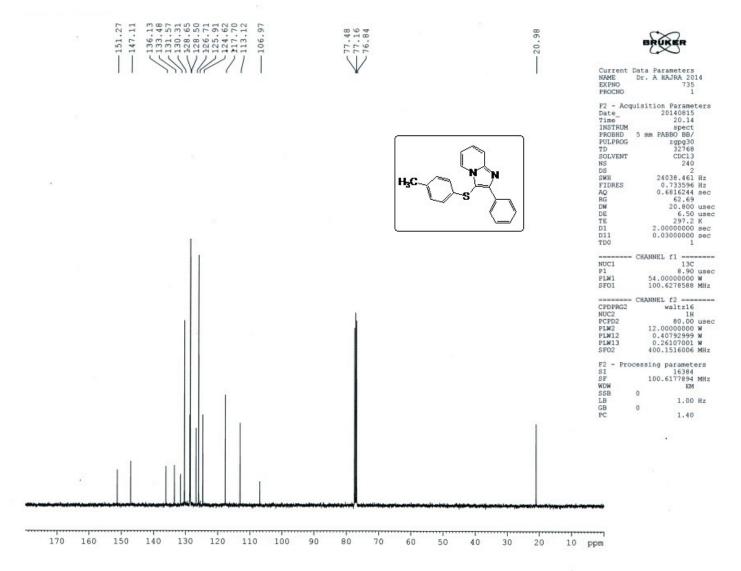
A mixture of 2-phenyl-imidazo[1,2-a]thiazole **4a** (100 mg, 0.5 mmol) and p-toluene sulfonylhydrazide **2a** (110 mg, 0.6 mmol) was stirred in presence of I₂ (20 mol%) in ethanol (0.1 mL) at 70 0 C for 10h (TLC). After completion, the reaction mixture was cooled to room temperature and extracted with dichloromethane (5 mL) followed by washing with brine (3 mL) and dried over Na₂SO₄. After evaporation of solvent the crude product was purified by column chromatography on silica gel using petroleum ether/ethylacetate as eluent.

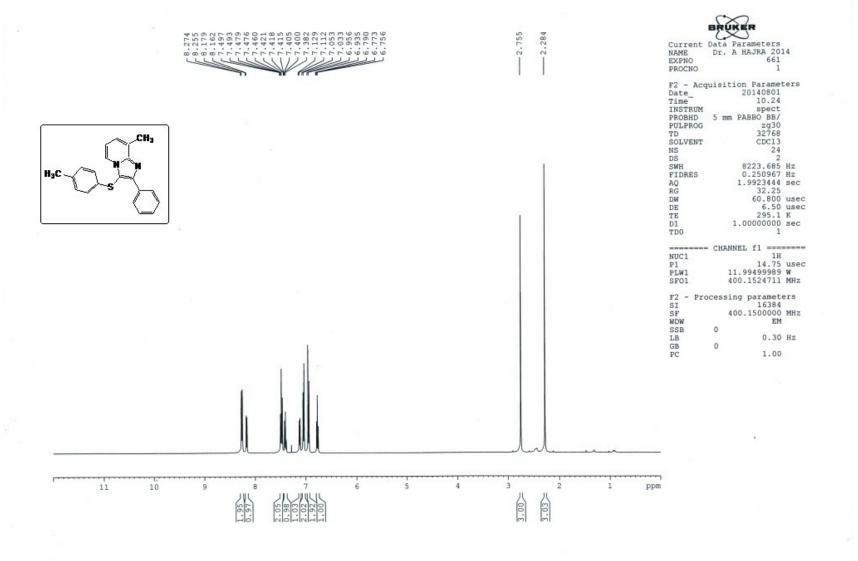
3. Typical procedure for the synthesis of 2-Phenyl-3-p-tolylsulfanylbenzo[d]imidazo[2,1-b]thiazole (7aa):

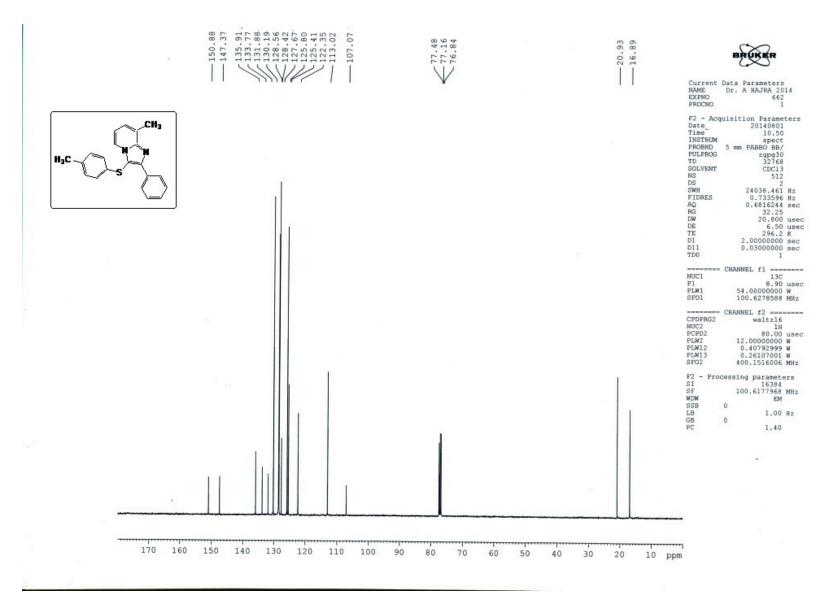
A mixture of 2-phenyl-benzo[d]imidazo[2,1-b]thiazole **6a** (125 mg, 0.5 mmol) and p-toluene sulfonylhydrazide **2a** (110 mg, 0.6 mmol) was stirred in presence of I₂ (20 mol%) in ethanol (0.1 mL) at 70 0 C for 10h (TLC). After completion, the reaction mixture was cooled to room temperature and extracted with dichloromethane (5 mL) followed by washing with brine (3 mL) and dried over Na₂SO₄. After evaporation of solvent the crude product was purified by column chromatography on silica gel using petroleum ether/ethylacetate as eluent.

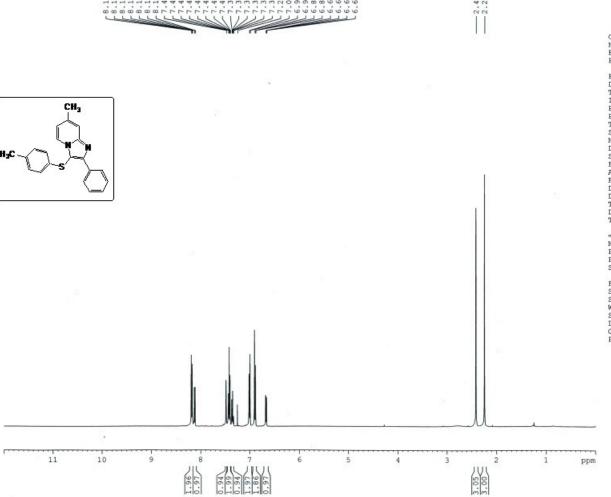
¹H and ¹³C NMR spectra







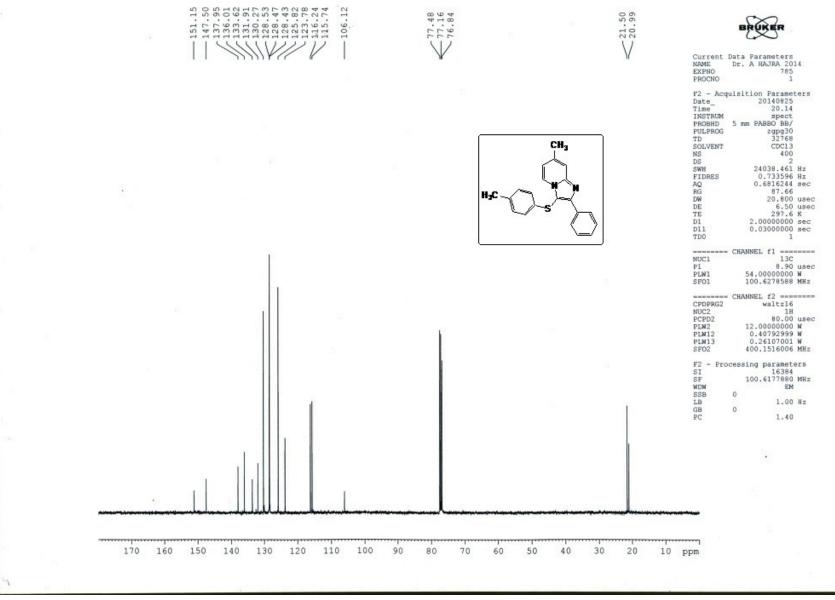


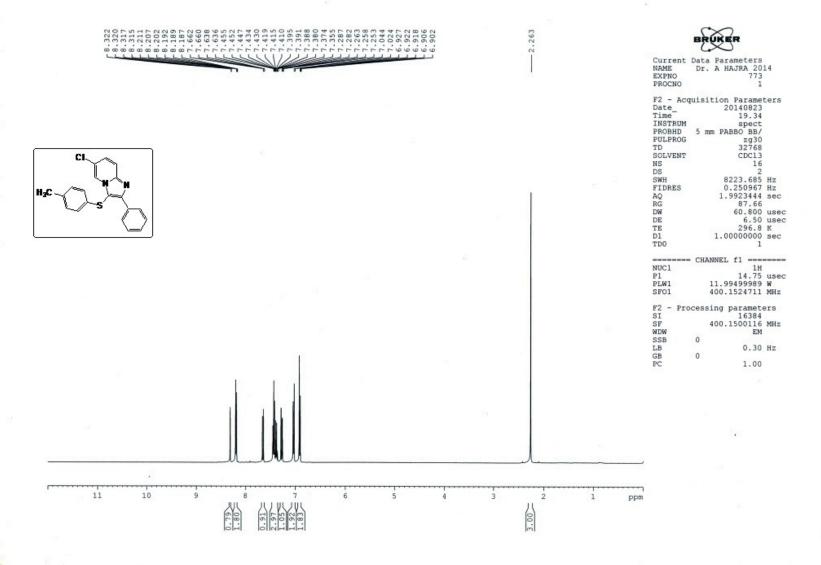


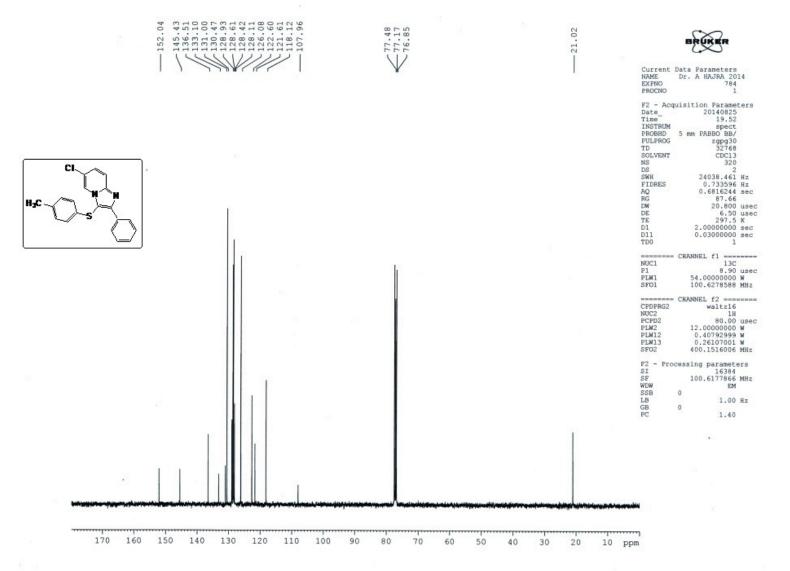


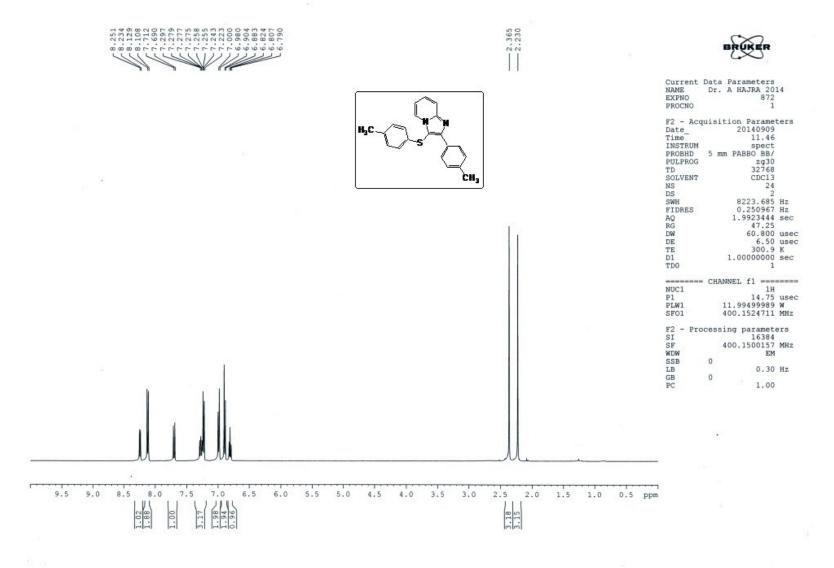
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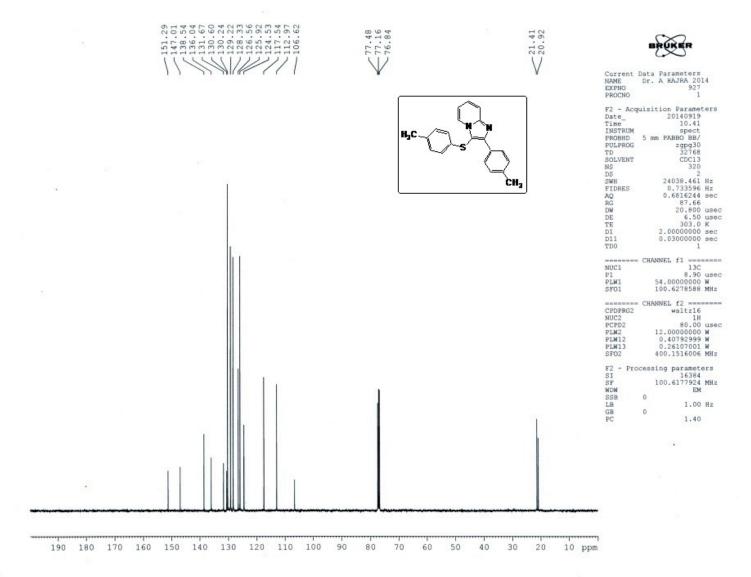
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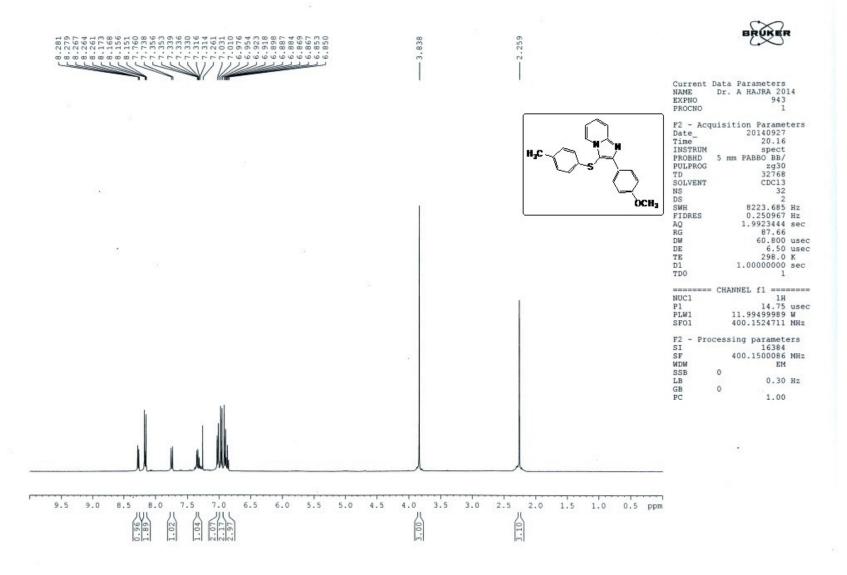


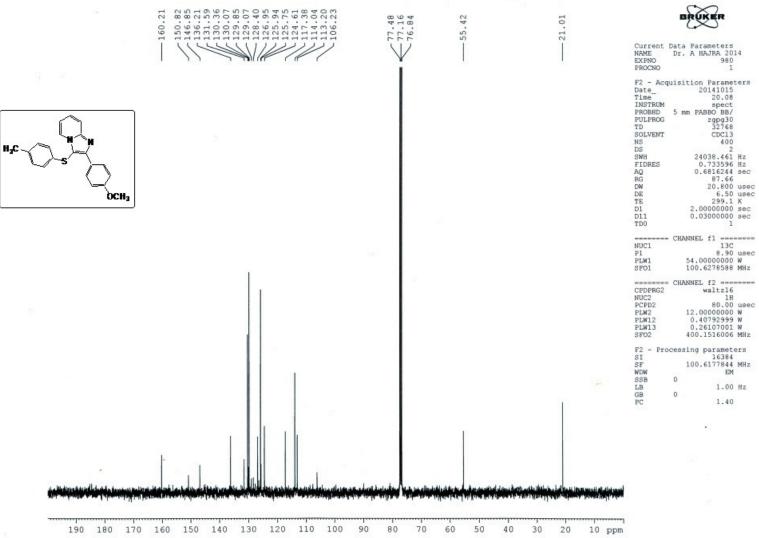


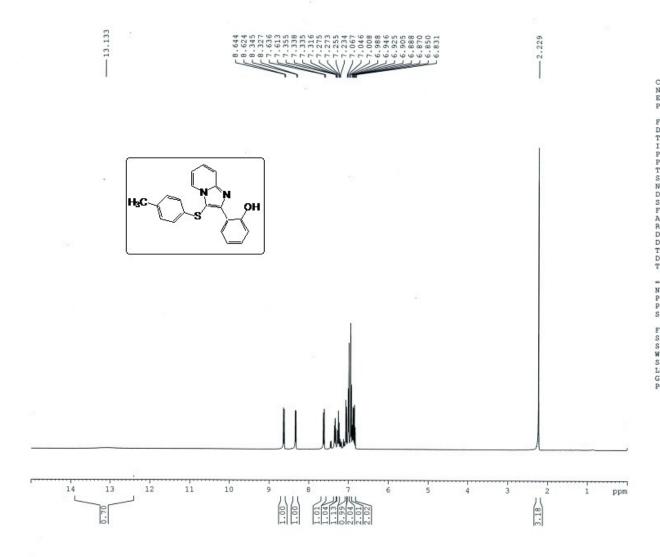






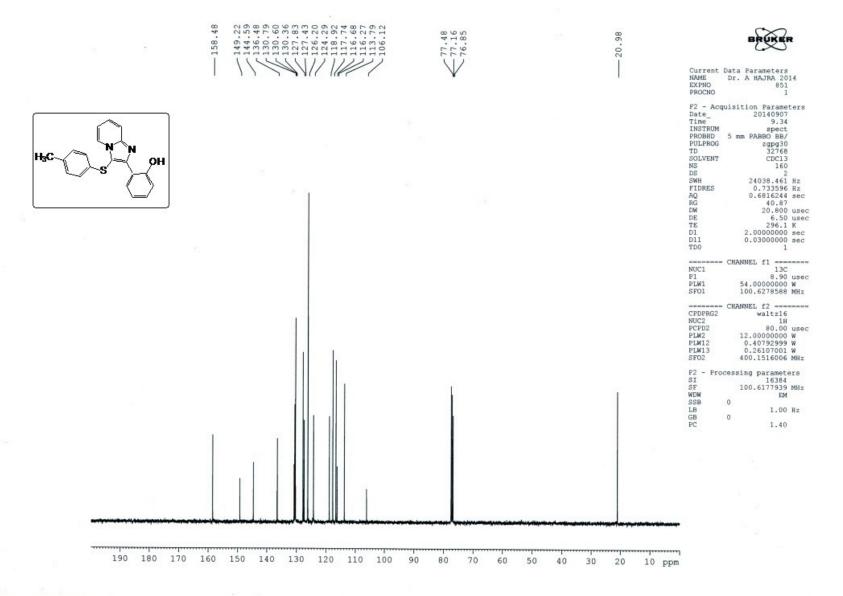


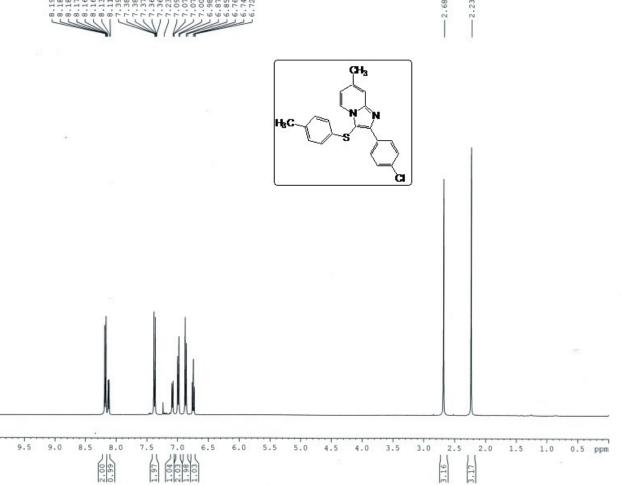






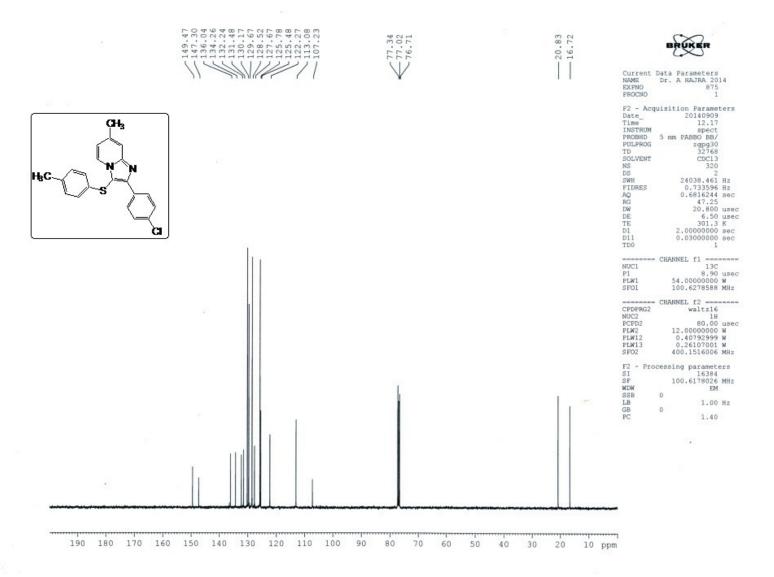
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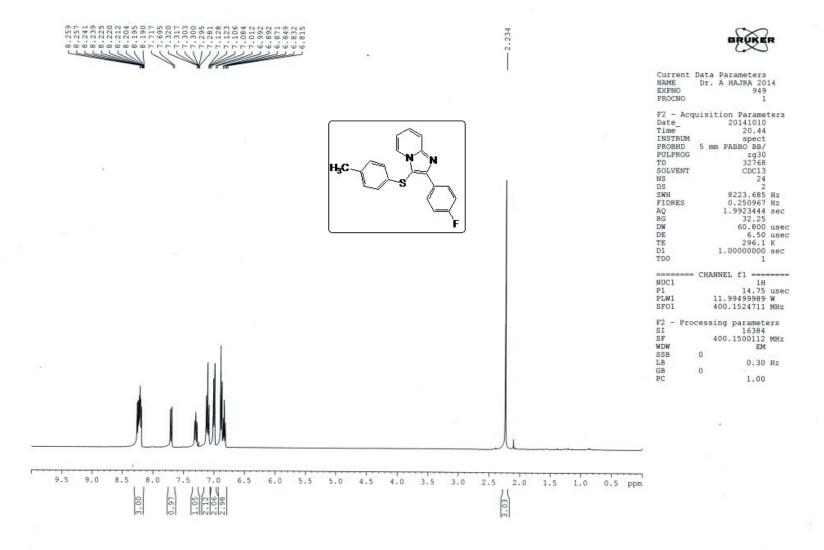


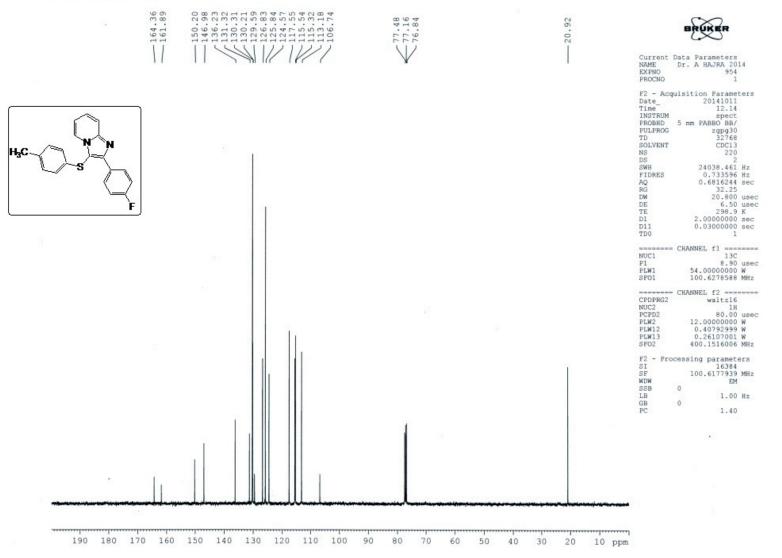


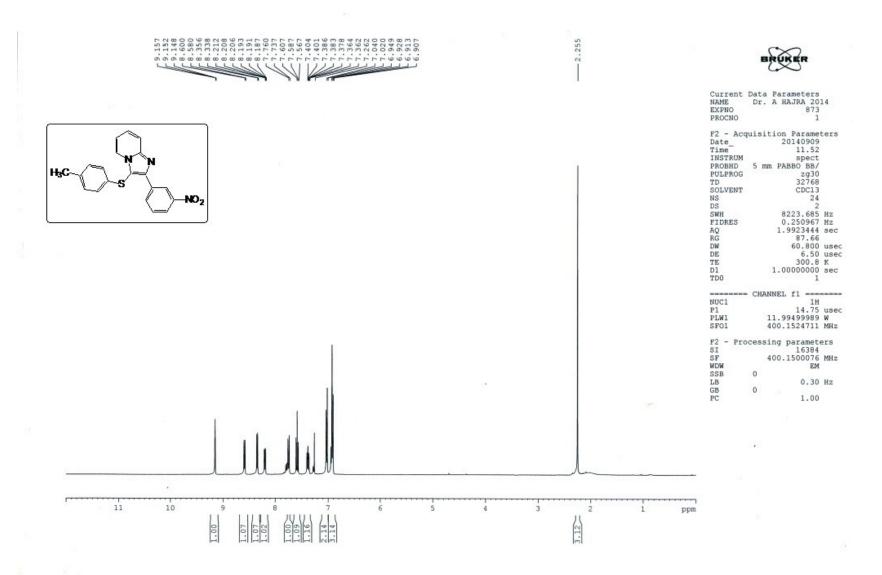


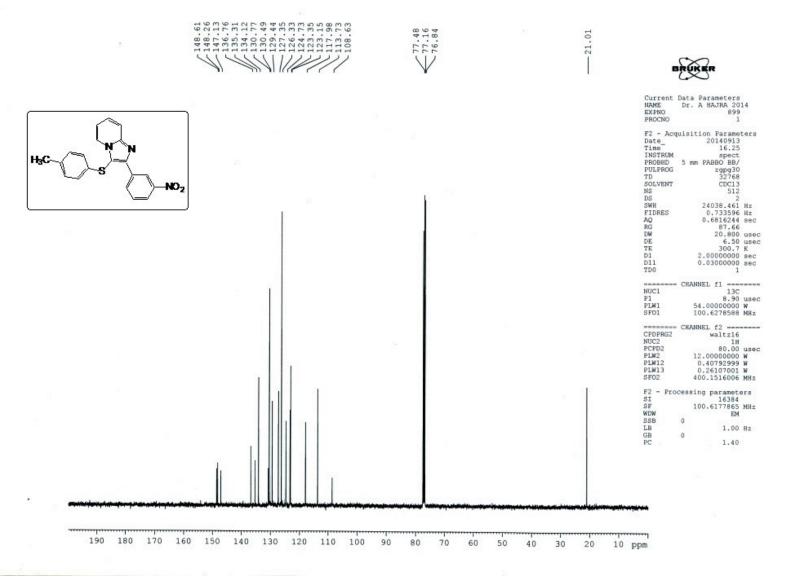
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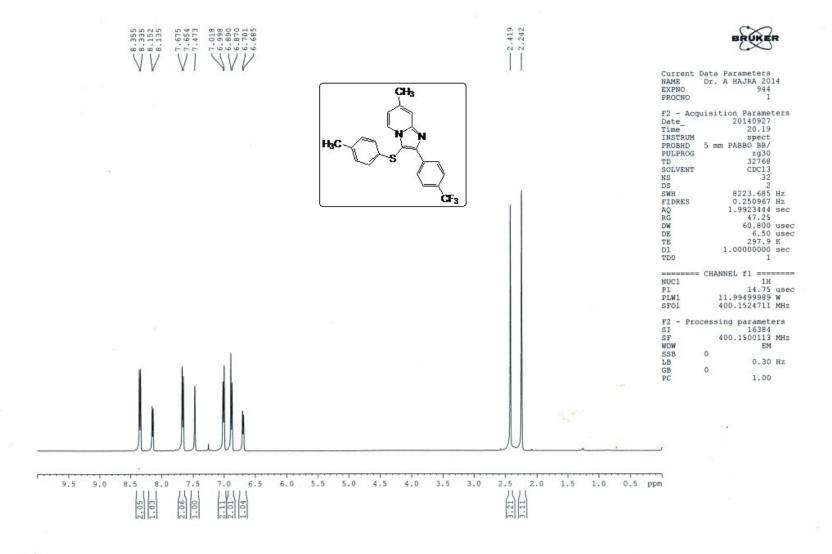


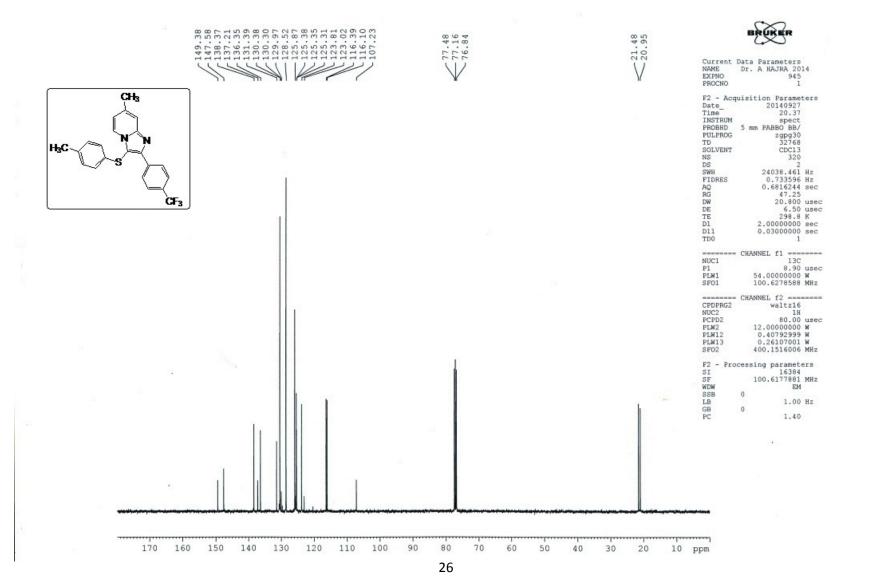


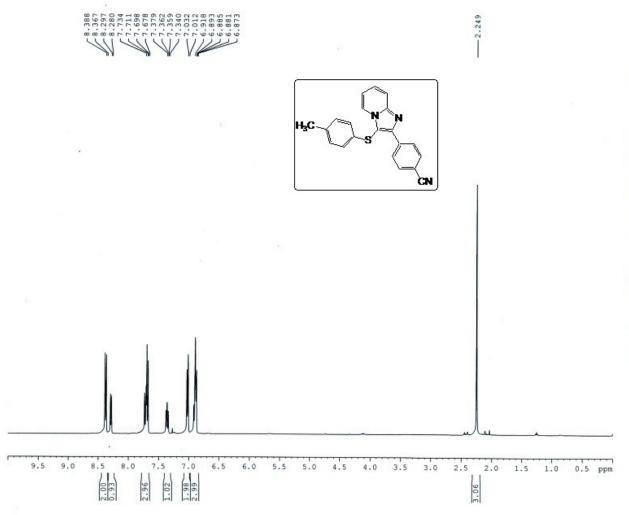






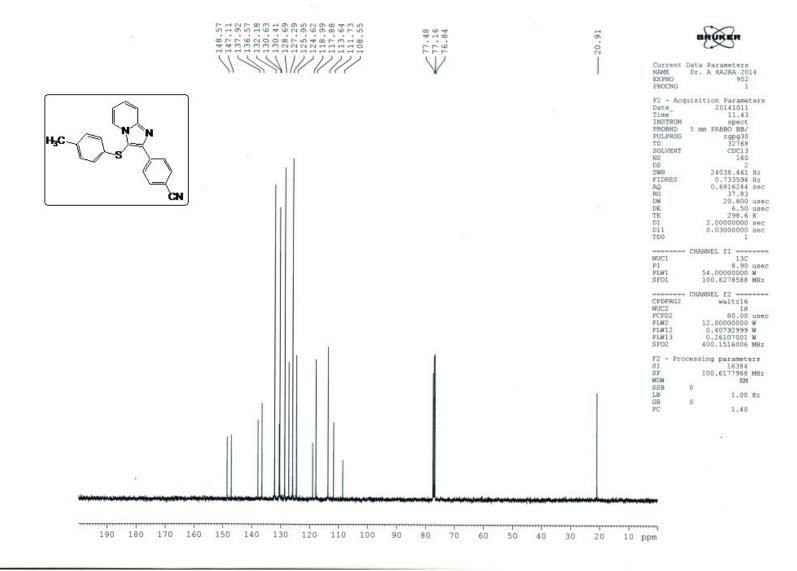


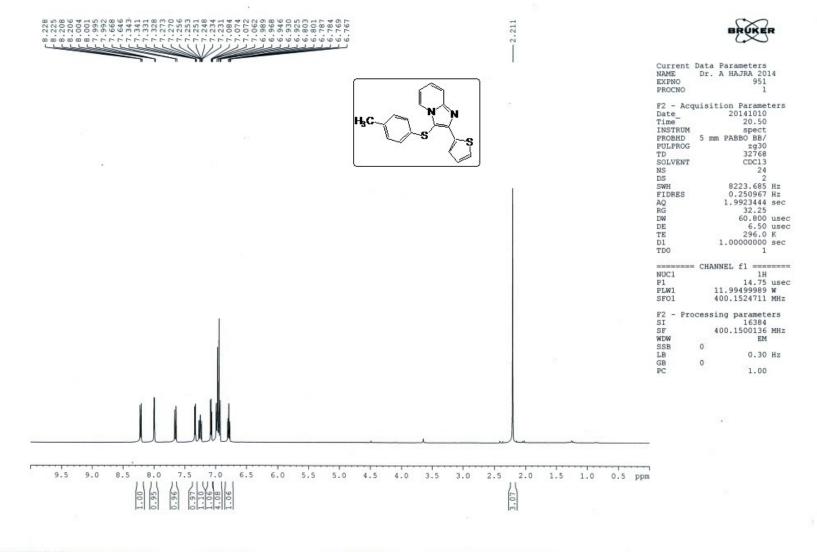


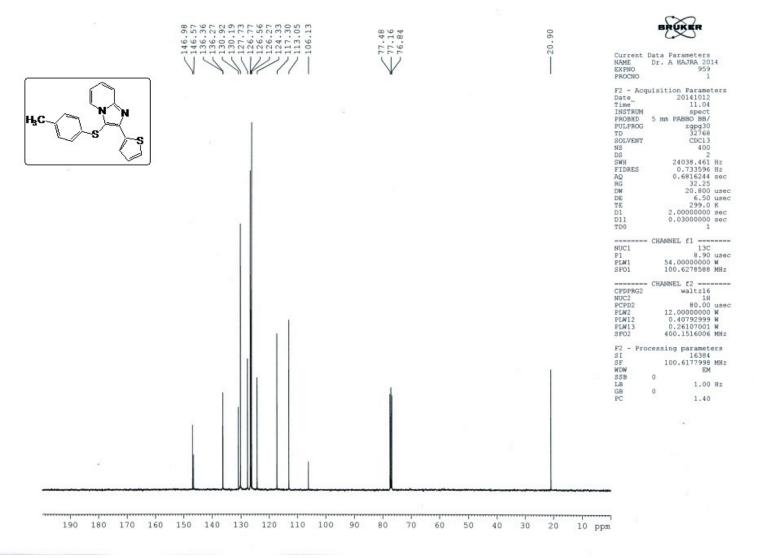


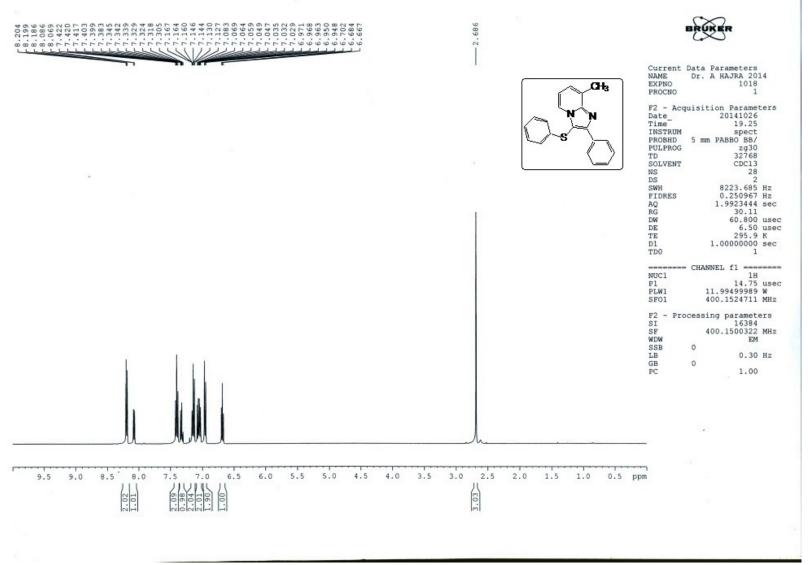


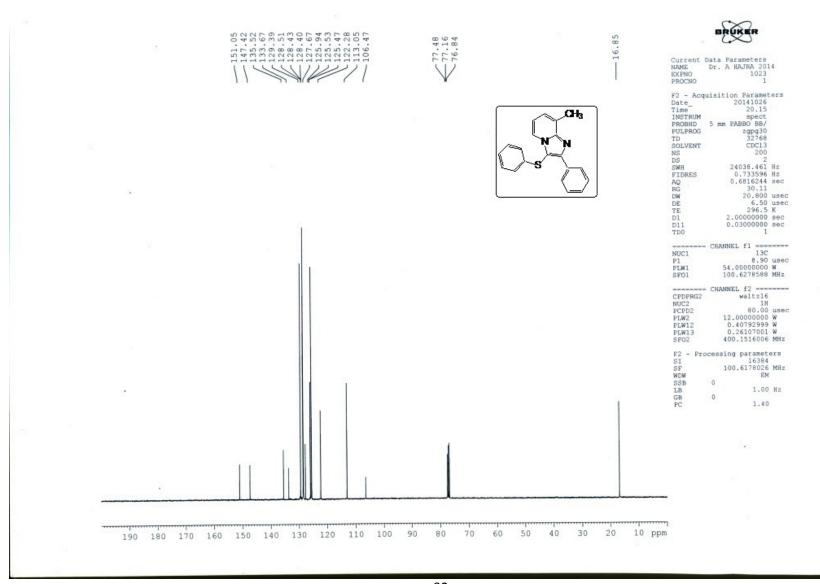
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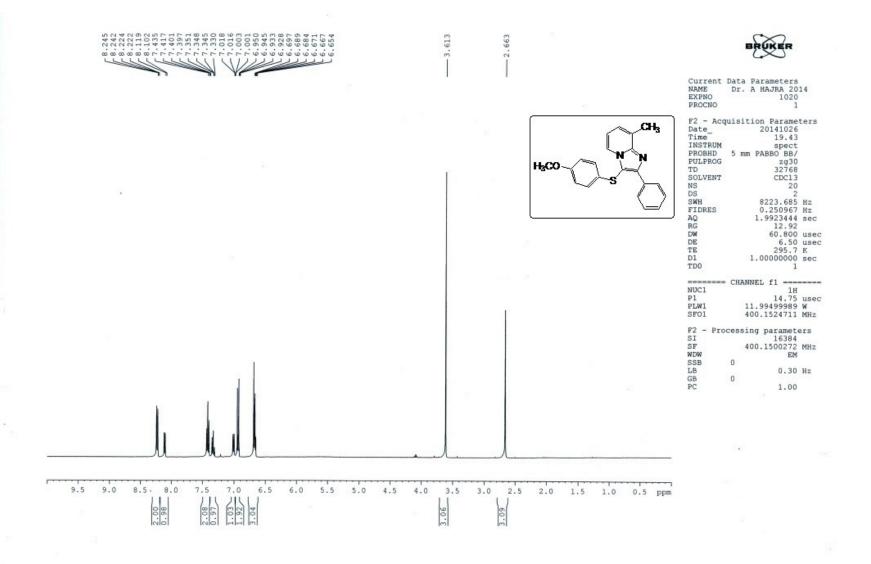


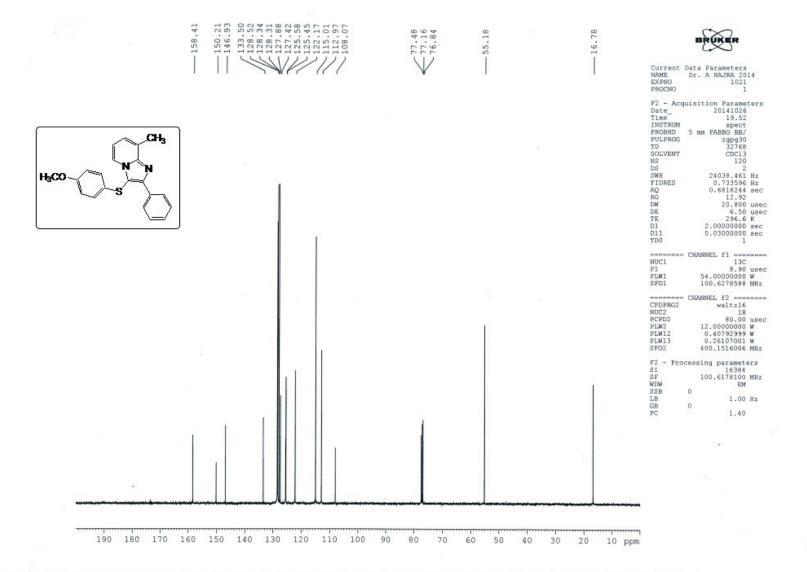


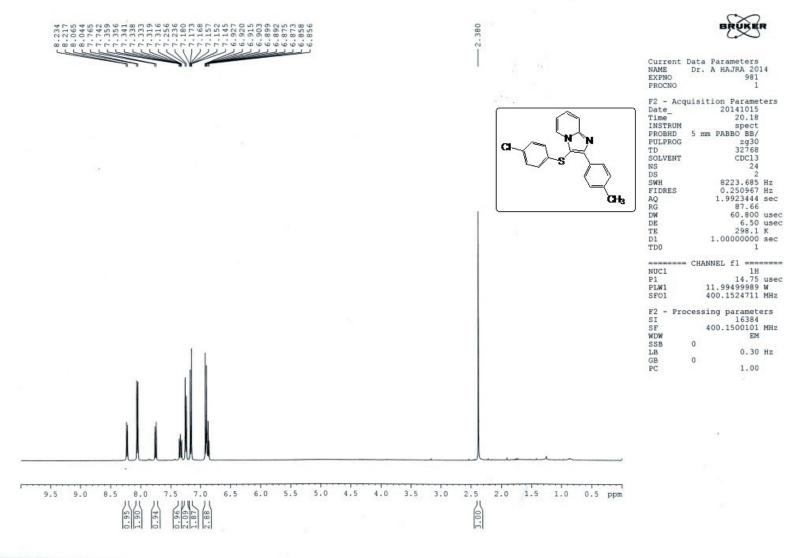


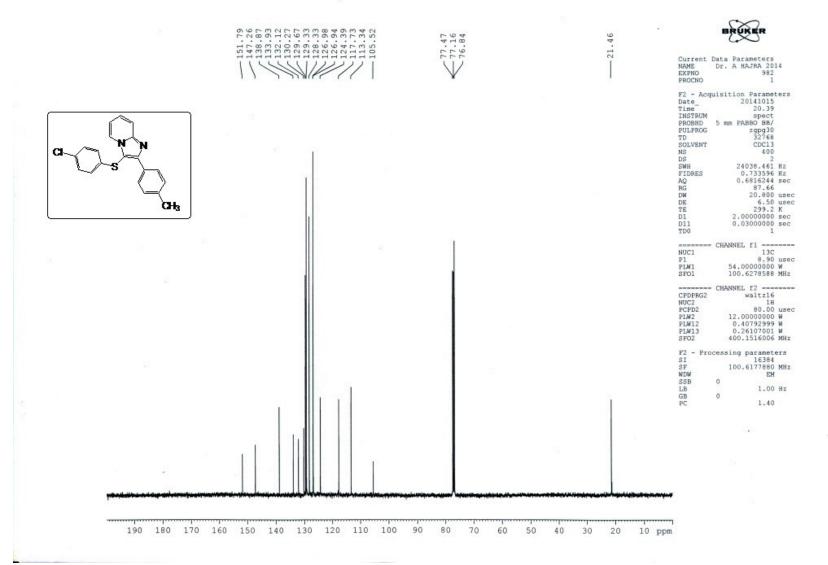


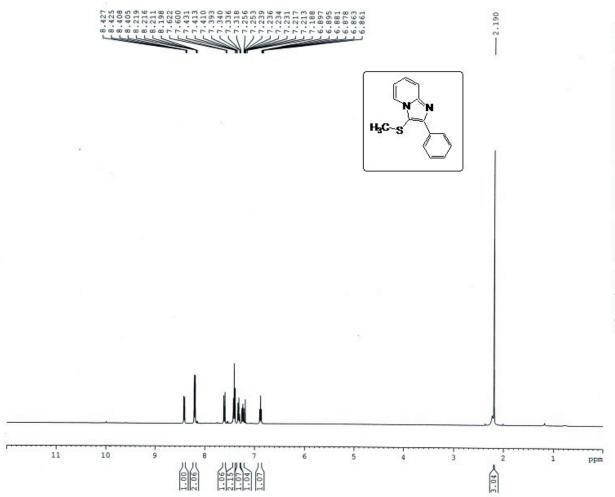






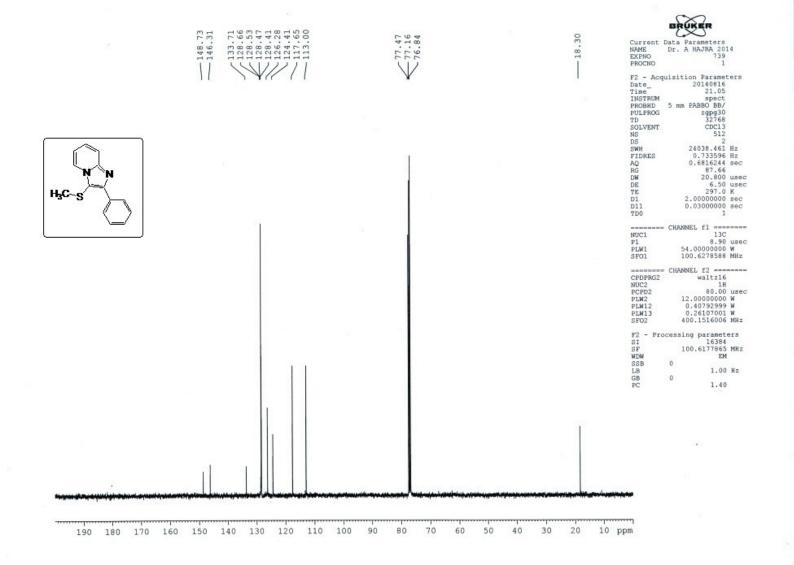


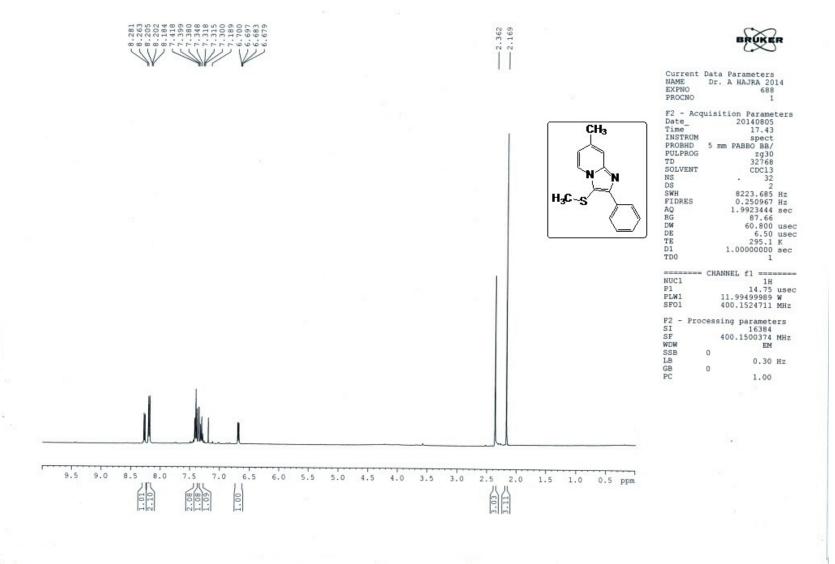


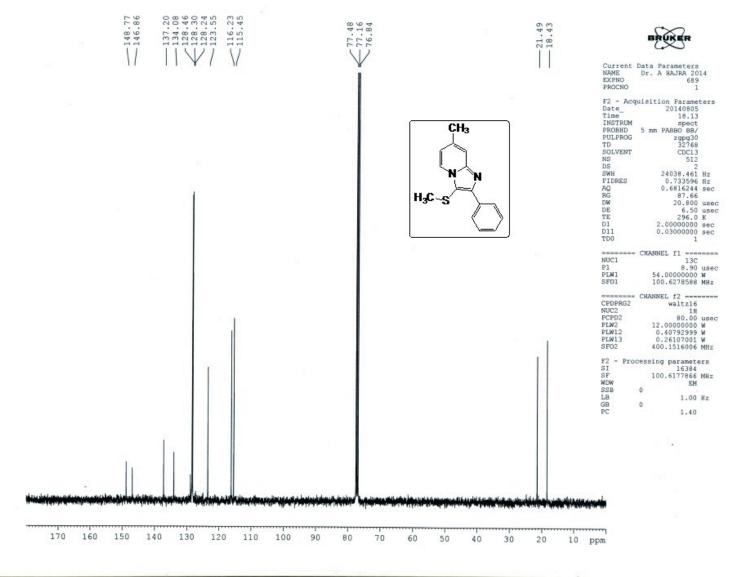


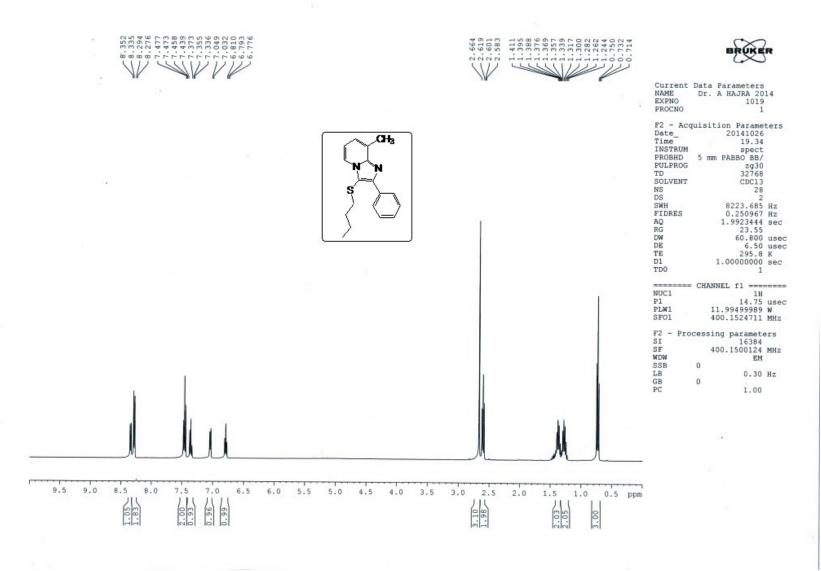


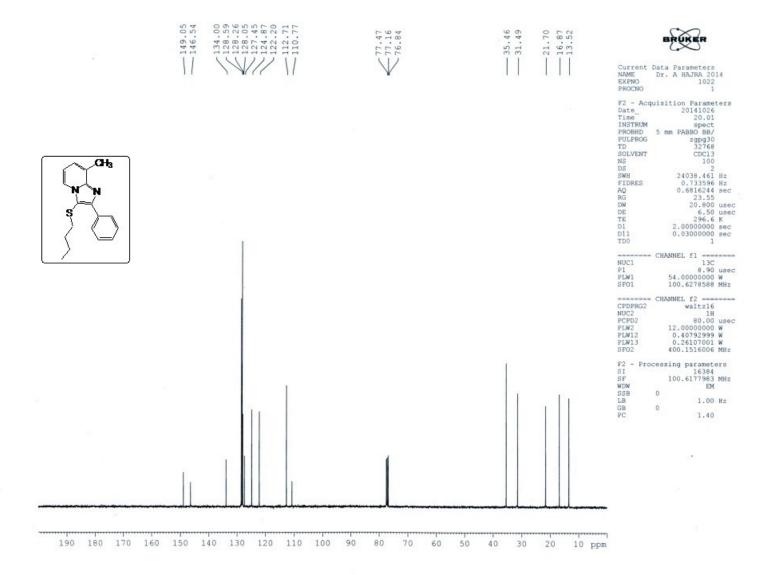
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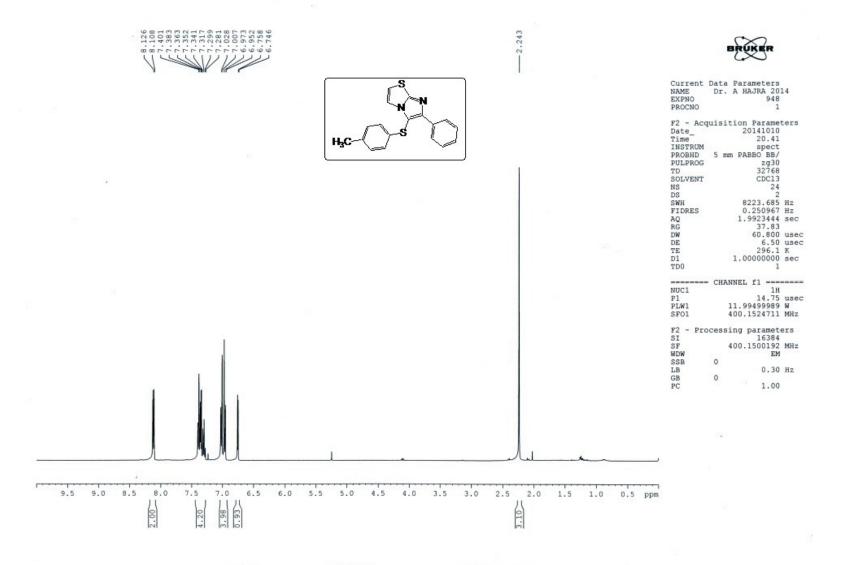


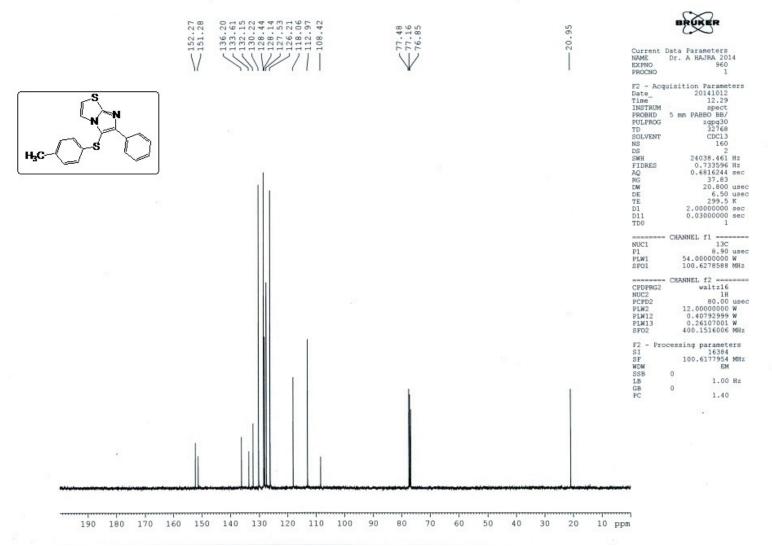


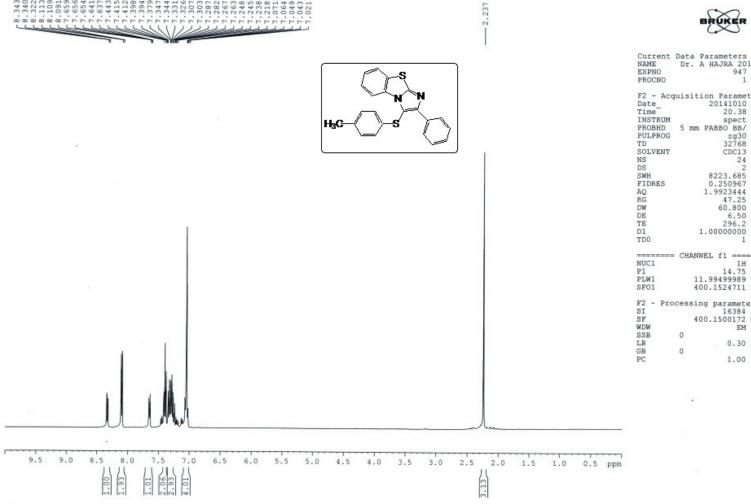














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