

Synthesis of Substituted Benzo[*ij*]imidazo[2,1,5-*de*]quinolizine by Rhodium(III)-Catalyzed Multiple C–H Activation and Annulation

Qingmei Ge,[†] Bin Li,[†] Baiquan Wang^{*,†,‡,§}

[†]State Key Laboratory of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, People's Republic of China

[‡]Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300071, China

[§]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China

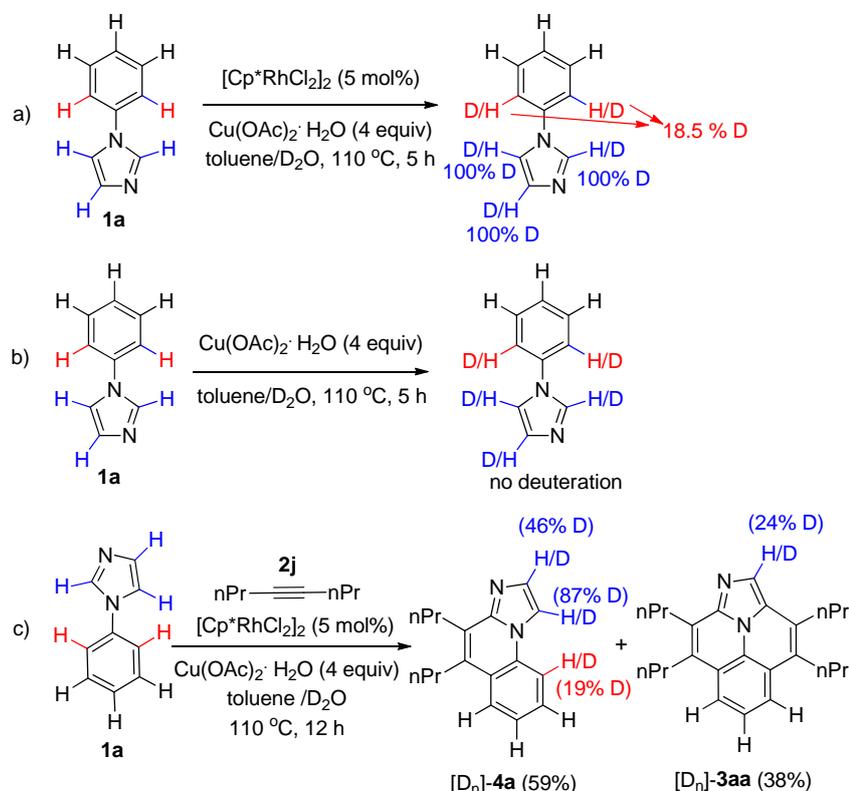
bqwang@nankai.edu.cn

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1. Mechanistic Studies

(1) Deuterium Exchange Experiment



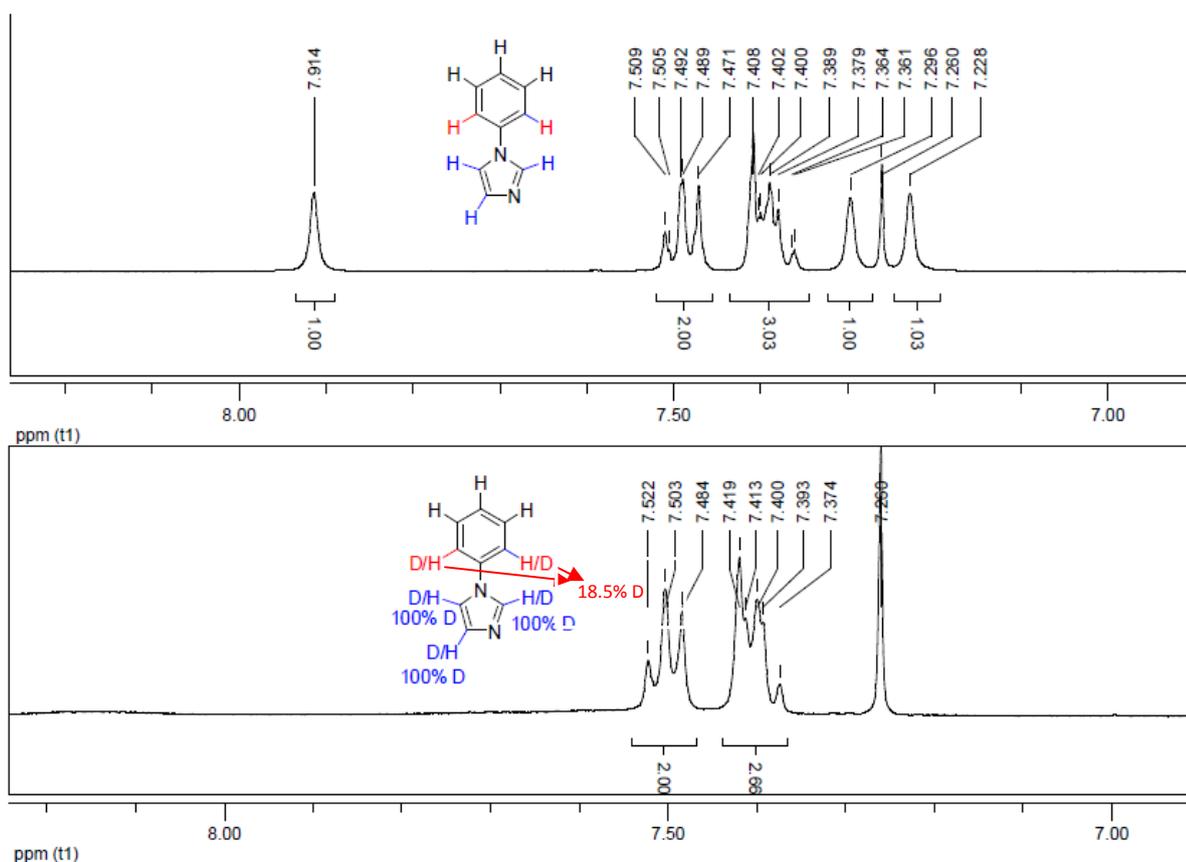
a) A mixture of phenylimidazole **1a** (28.8 mg, 0.2 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (6.2 mg, 0.01 mmol), and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (160.0 mg, 0.8 mmol) were weighted in a Schlenk tube equipped with a stir bar. Dry toluene (1.8 mL) and D_2O (0.2 mL) were added and the mixture was stirred at 110 °C for 5 h under Ar atmosphere. After the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was absorbed onto small amounts of alumina. The mixed products were purified by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/2-1/1).

b) A mixture of phenylimidazole **1a** (28.8 mg, 0.2 mmol) and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (160.0 mg, 0.8 mmol) were weighted in a Schlenk tube equipped with a stir bar. Dry toluene (1.8 mL) and D_2O (0.2 mL) were added and the mixture was stirred at 110 °C for 5 h under Ar atmosphere. After the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was absorbed onto small amounts of alumina. The mixed products were purified by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/2-1/1).

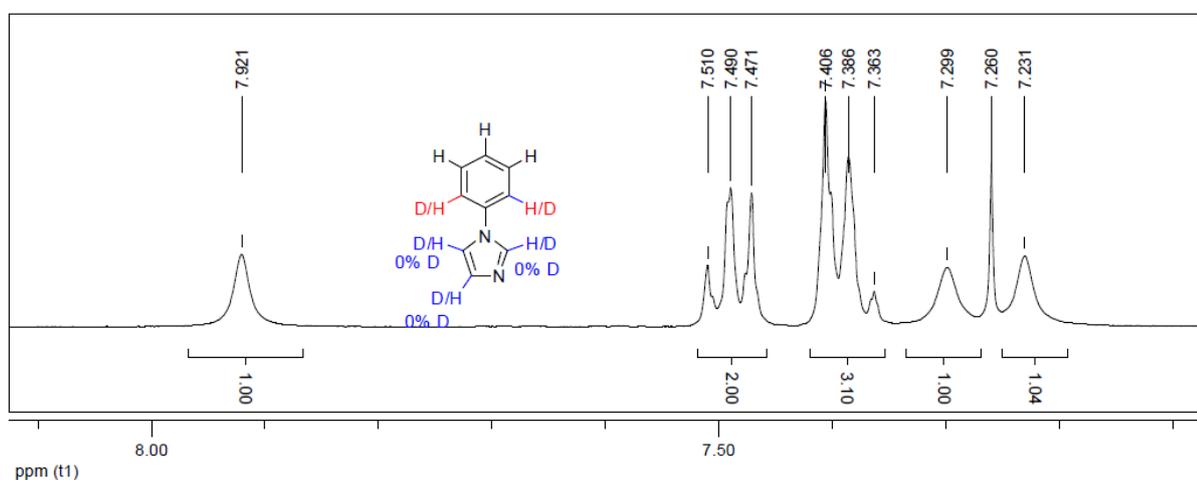
c) A mixture of phenylimidazole **1a** (28.8 mg, 0.2 mmol), 4-Octyne **2j** (48.5 mg, 0.44 mmol),

[Cp*RhCl₂]₂ (6.2 mg, 0.01 mmol), and Cu(OAc)₂·H₂O (160.0 mg, 0.8 mmol) were weighted in a Schlenk tube equipped with a stir bar. Dry toluene (1.8 mL) and H₂O (0.2 mL) were added and the mixture was stirred at 110 °C for 12 h under Ar atmosphere. After the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was absorbed onto small amounts of alumina. The mixed products were purified by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/8).

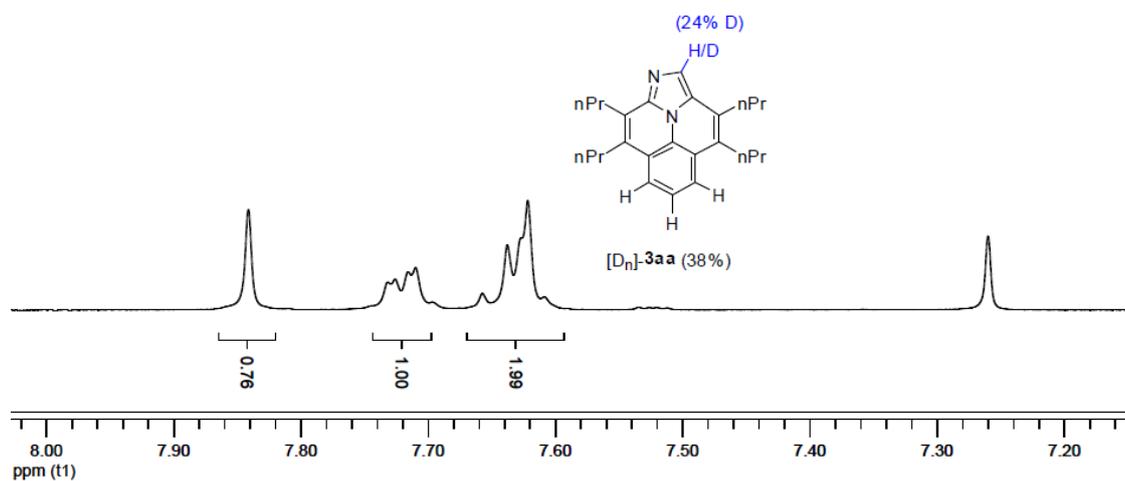
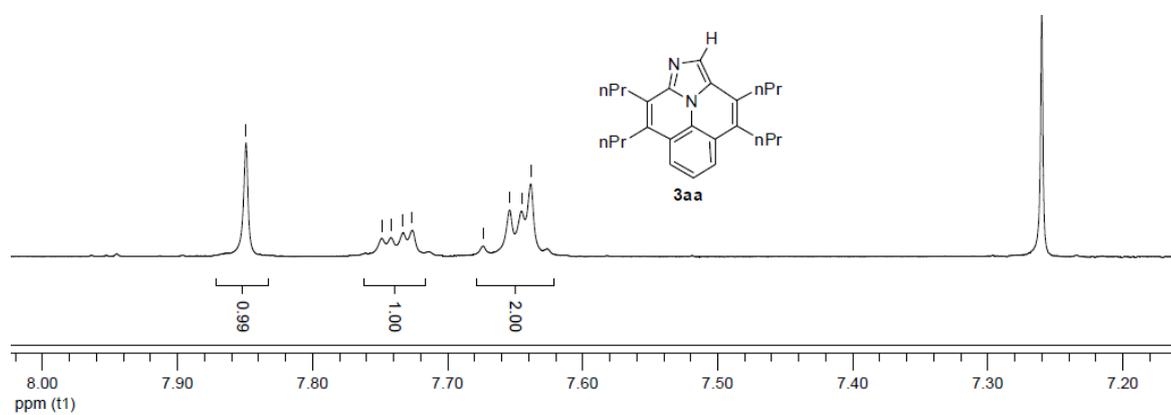
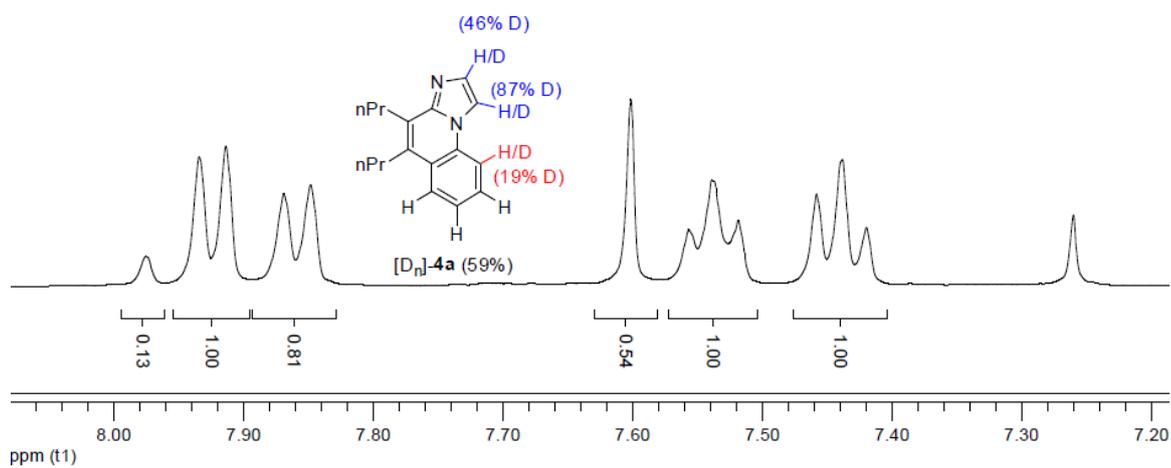
a) ¹H NMR of the substrate recovered in the reaction without 4-Octyne.



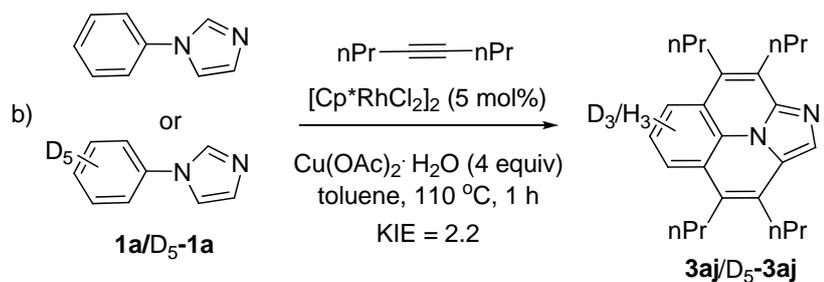
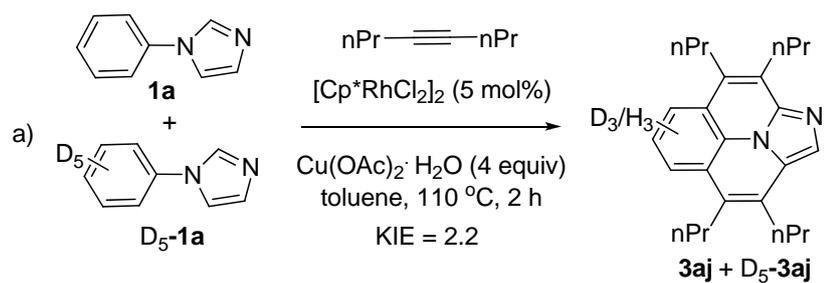
b) ¹H NMR of the substrate recovered in the reaction without 4-Octyne and [Cp*RhCl₂]₂.



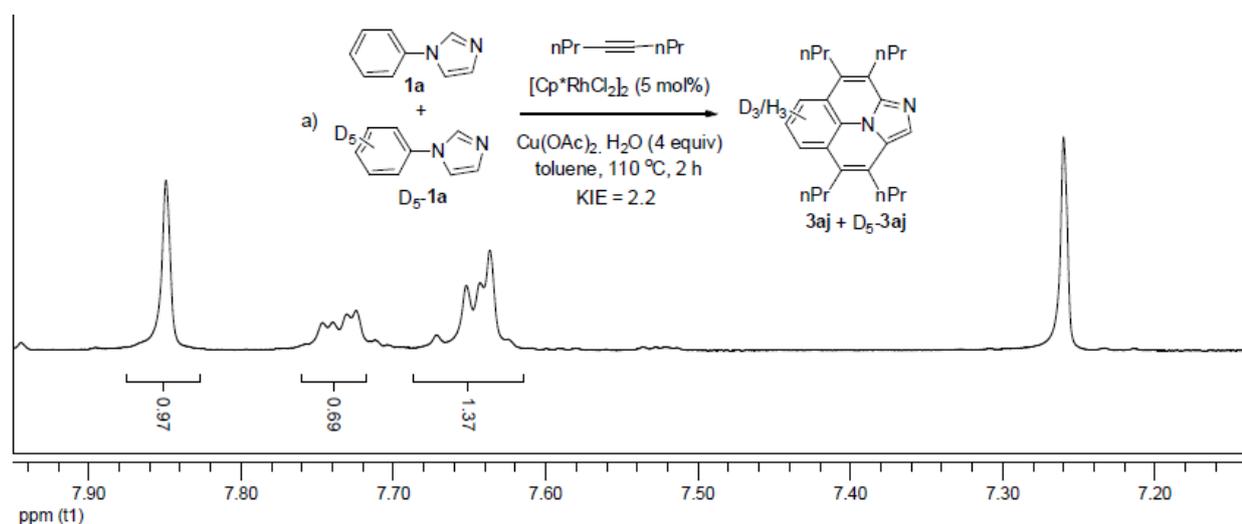
c) ^1H NMR of the the product obtained in the reaction in the presence of 4-Octyne.



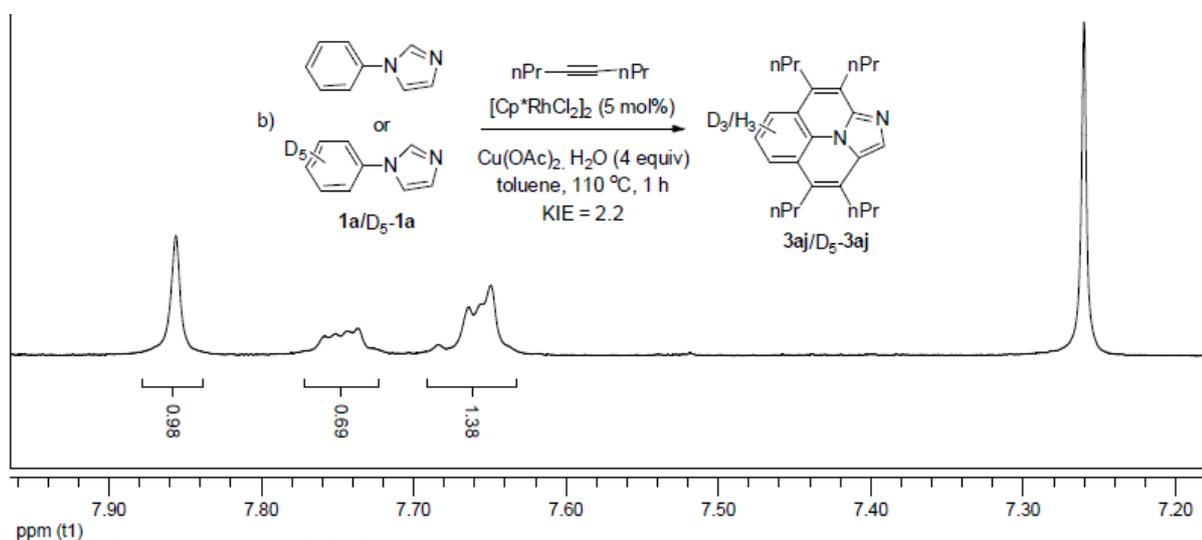
(2) KIE Experiments



a) Competition Experiment between **1a** and **[D₅]-1a**

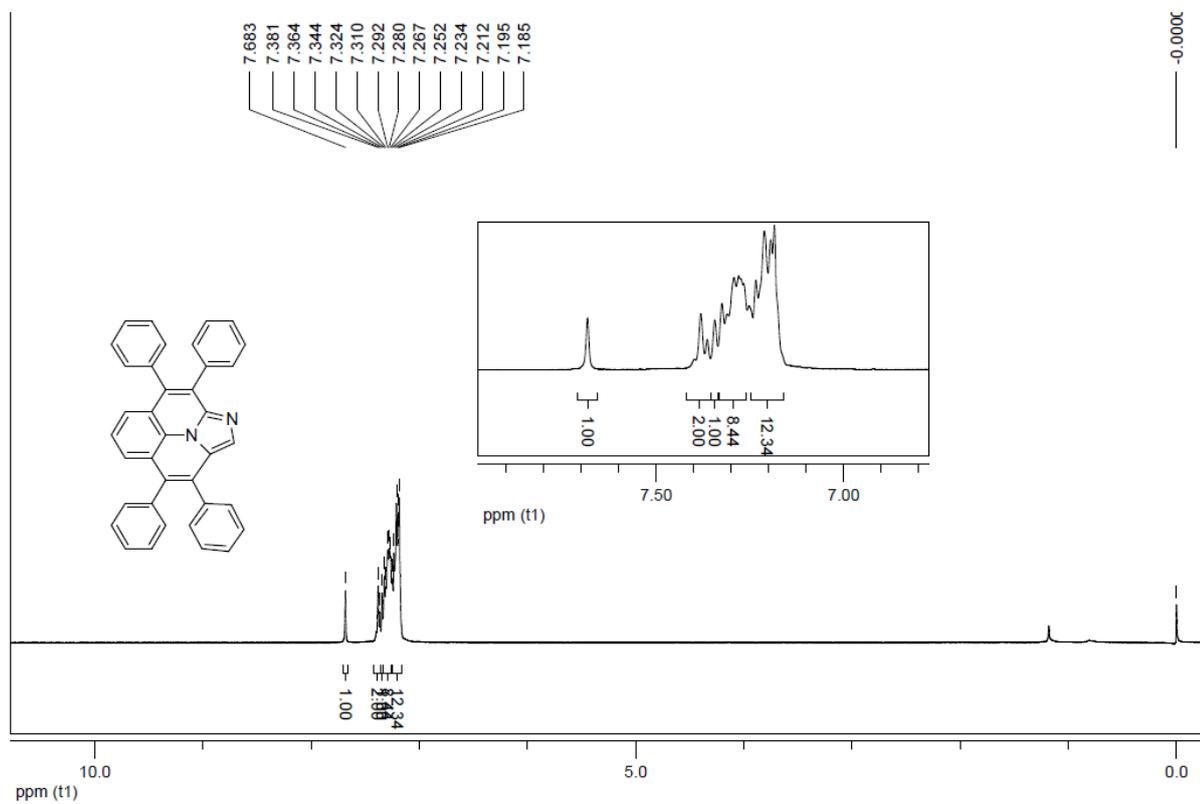


b) Independent Experiment Using the Deuterated and the Protonated Substrates

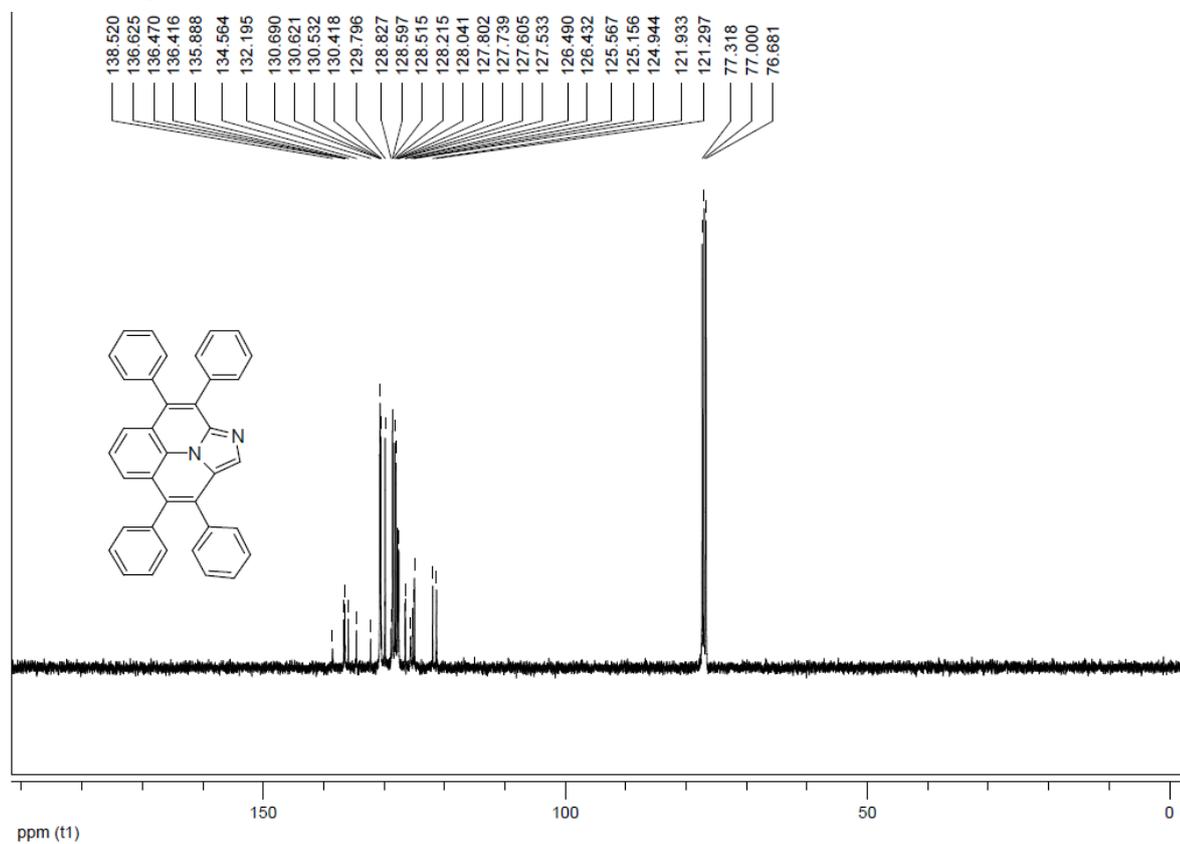


2. Copies of ^1H , ^{13}C and ^{19}F NMR Spectra for Compounds

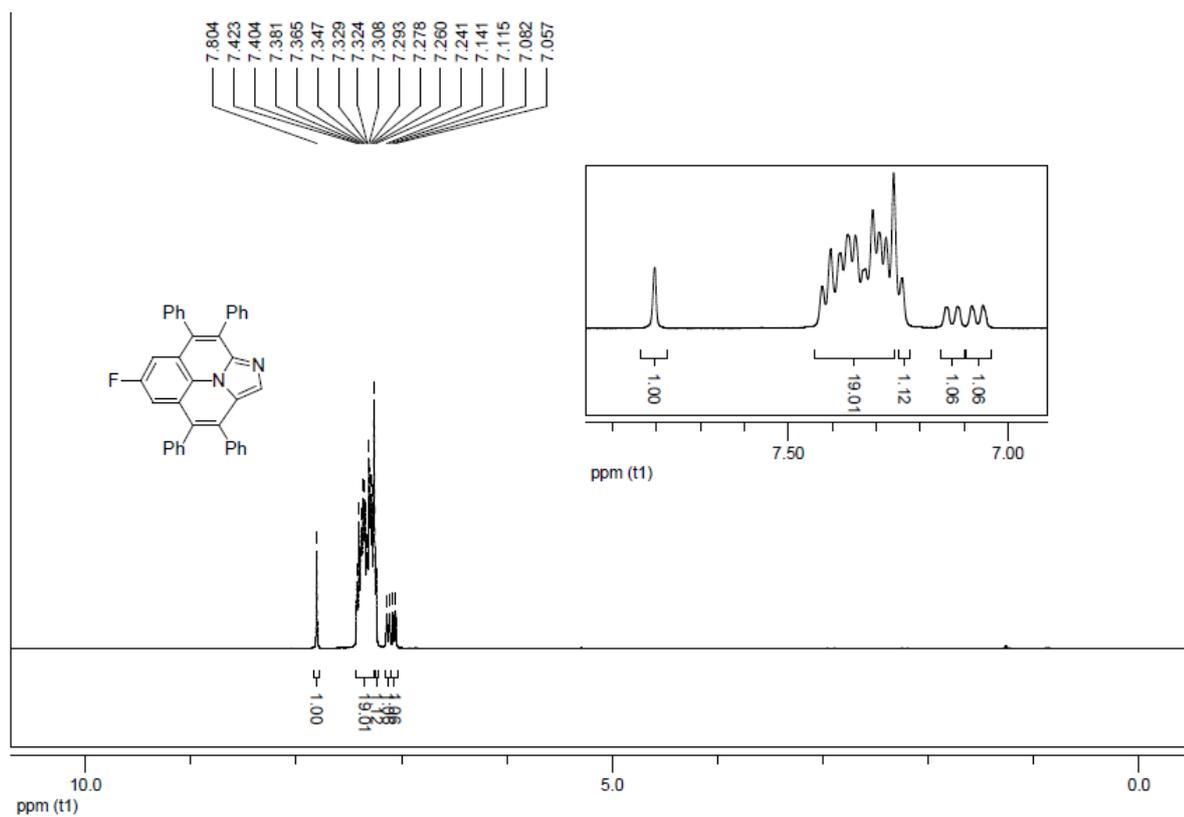
^1H NMR spectrum of **3aa**



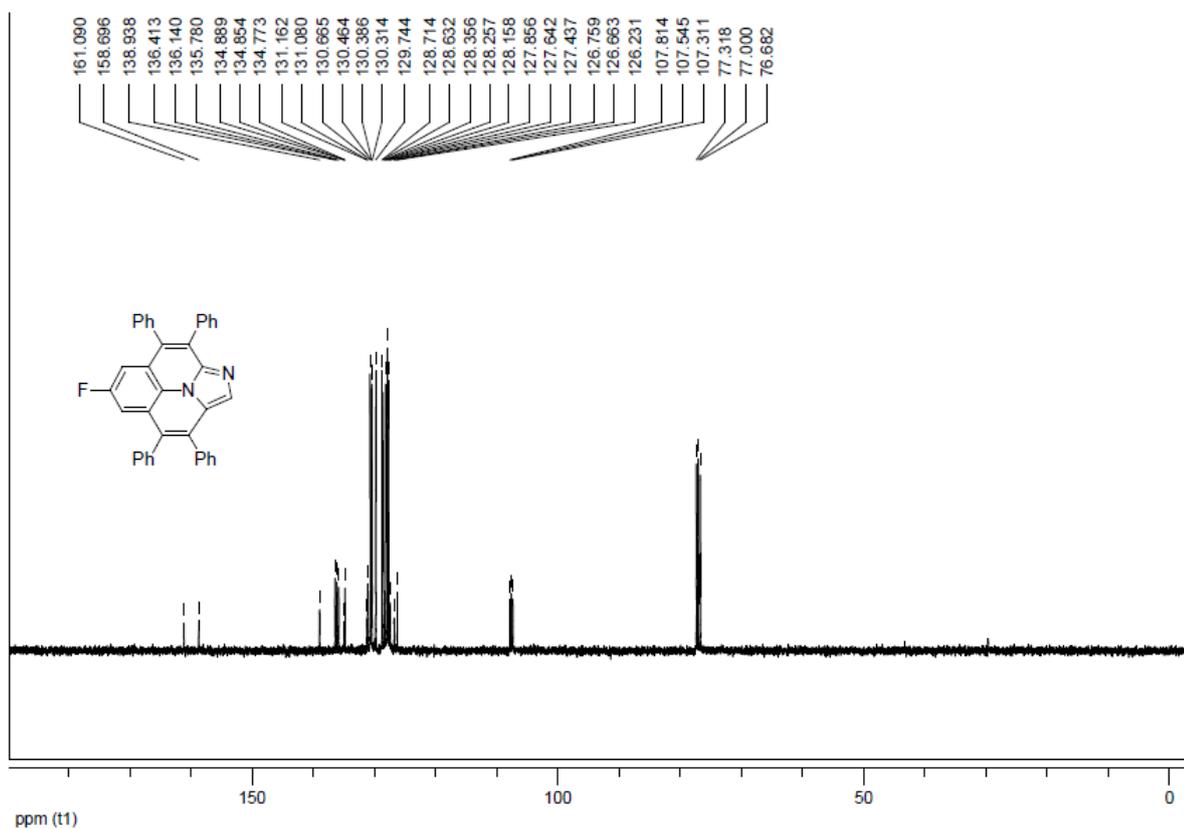
^{13}C NMR spectrum of **3aa**



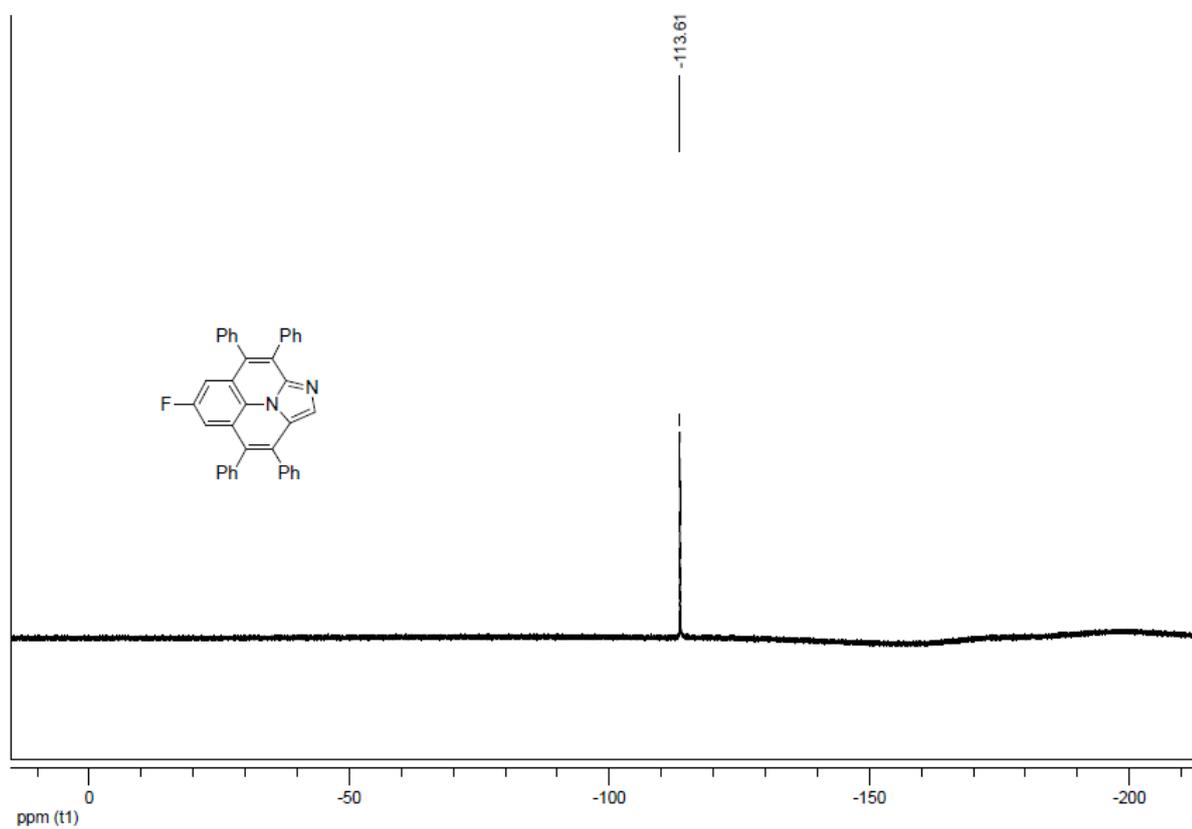
¹H NMR spectrum of **3ba**



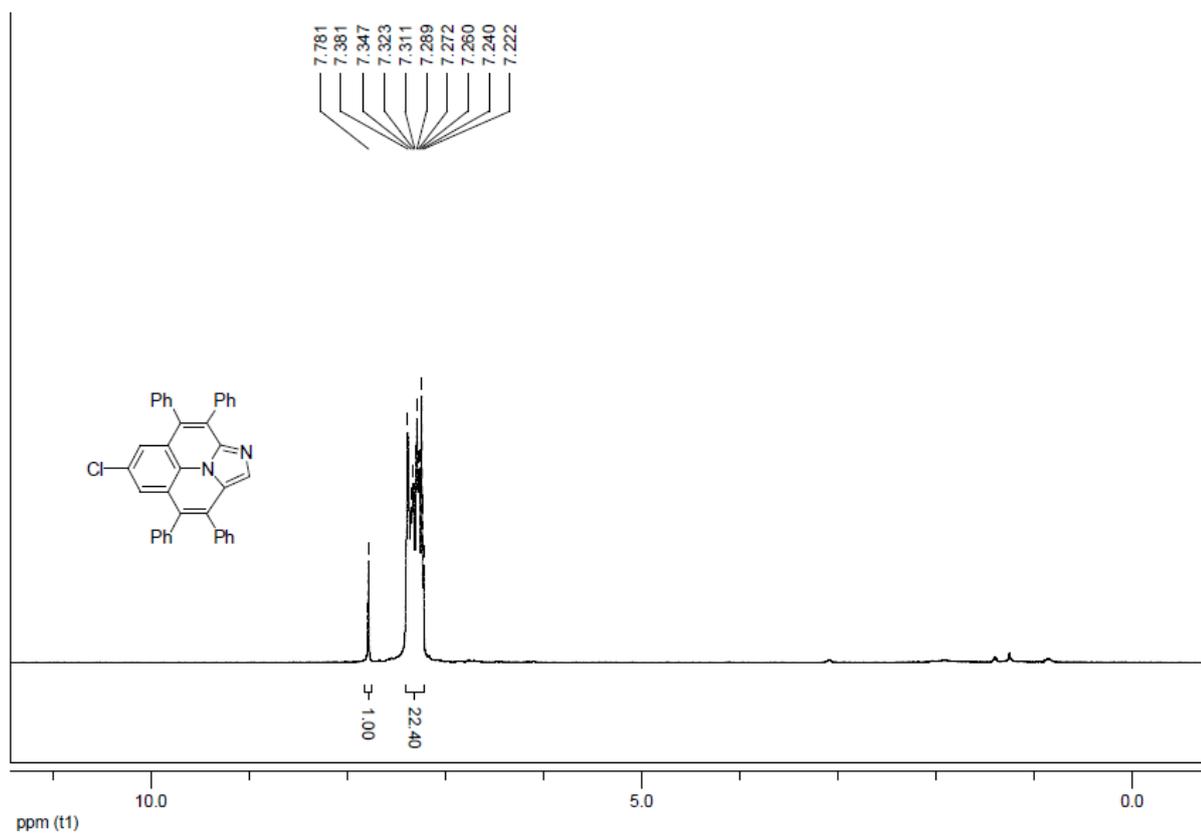
¹³C NMR spectrum of **3ba**



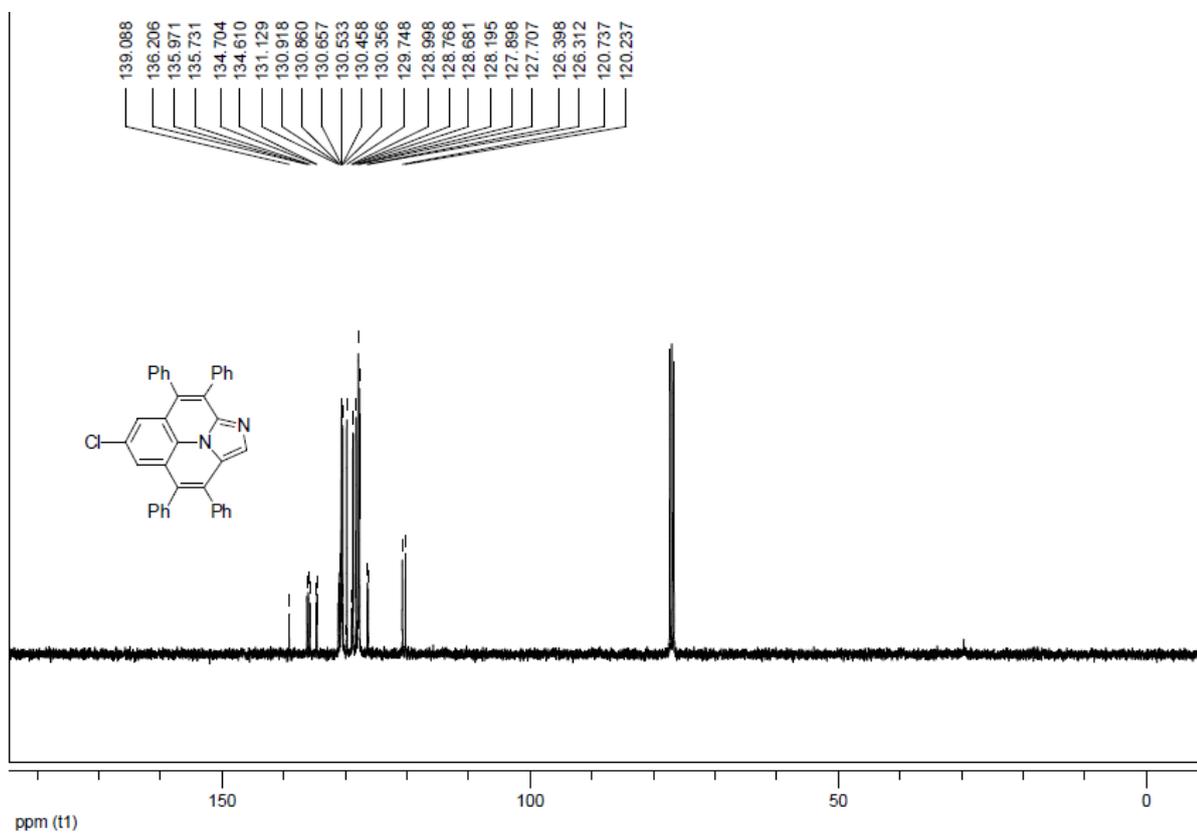
¹⁹F NMR spectrum of **3ba**



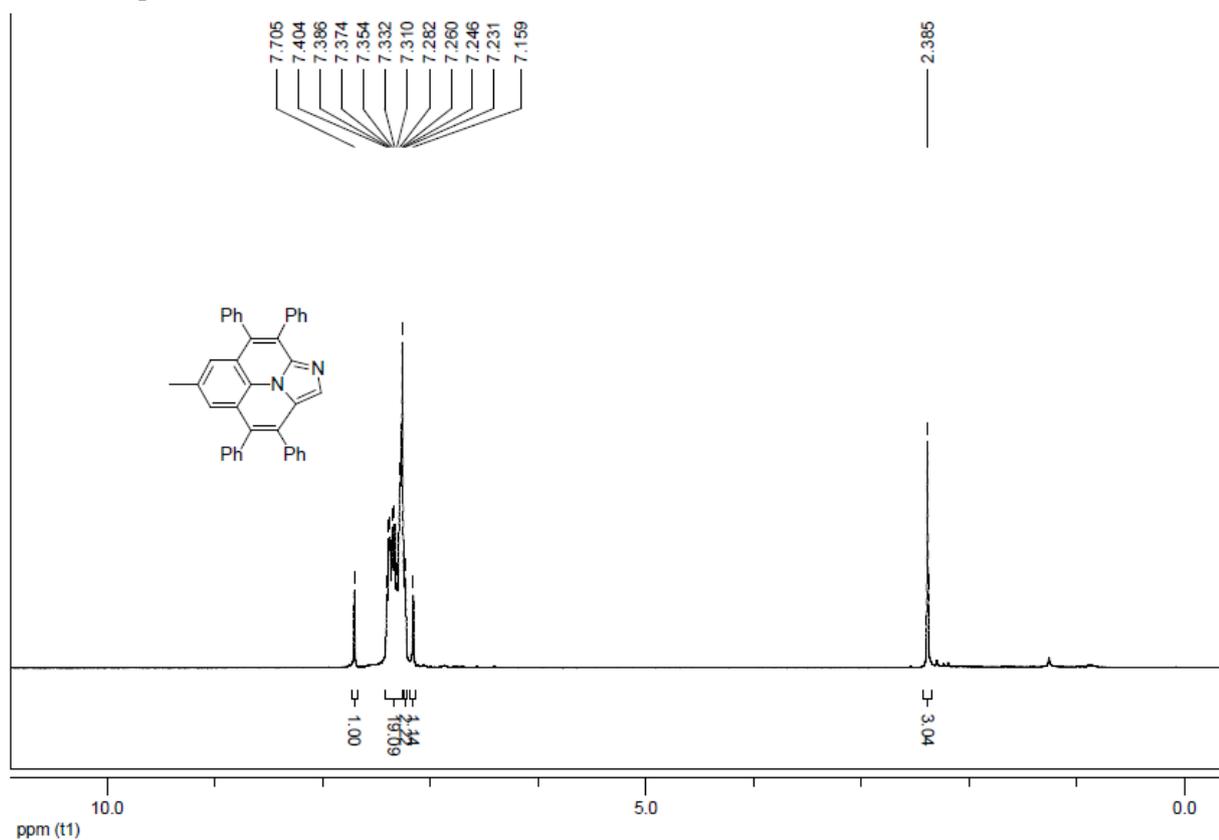
¹H NMR spectrum of **3ca**



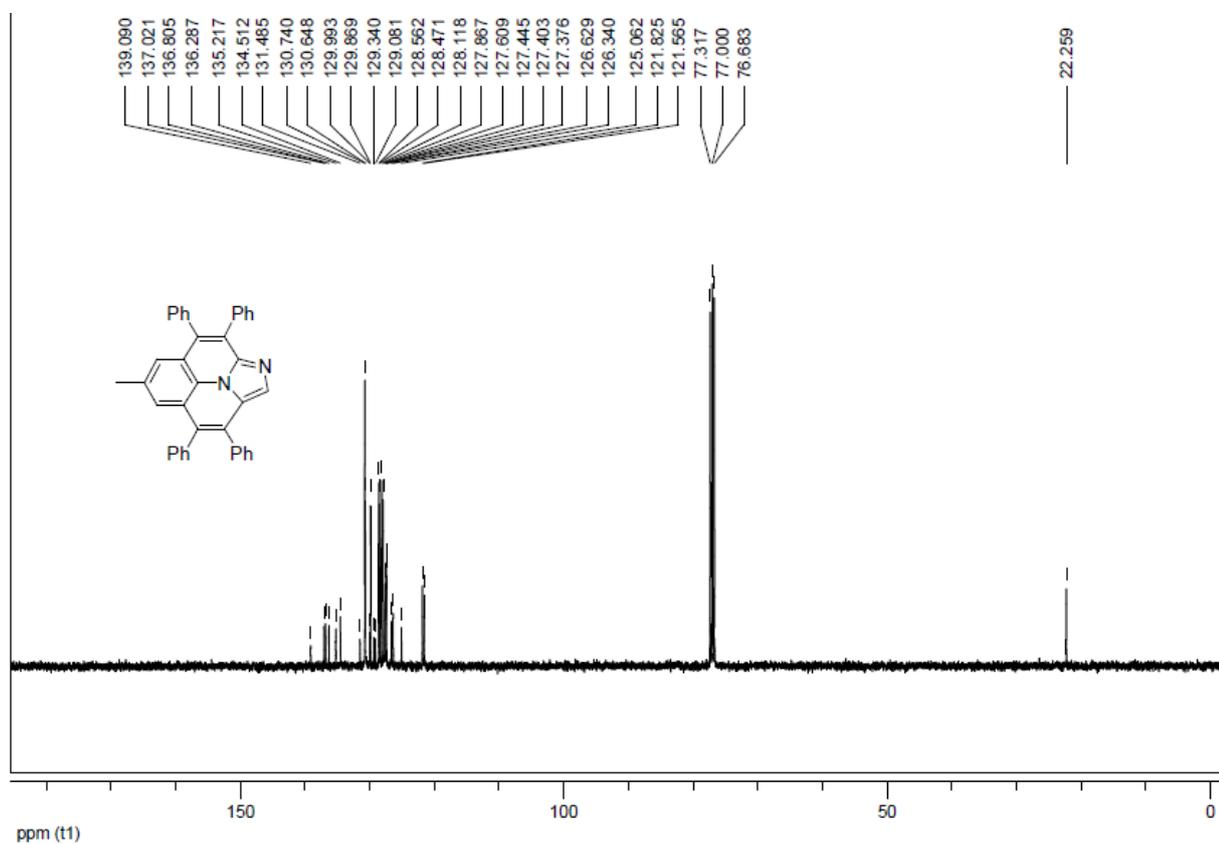
¹³C NMR spectrum of **3ca**



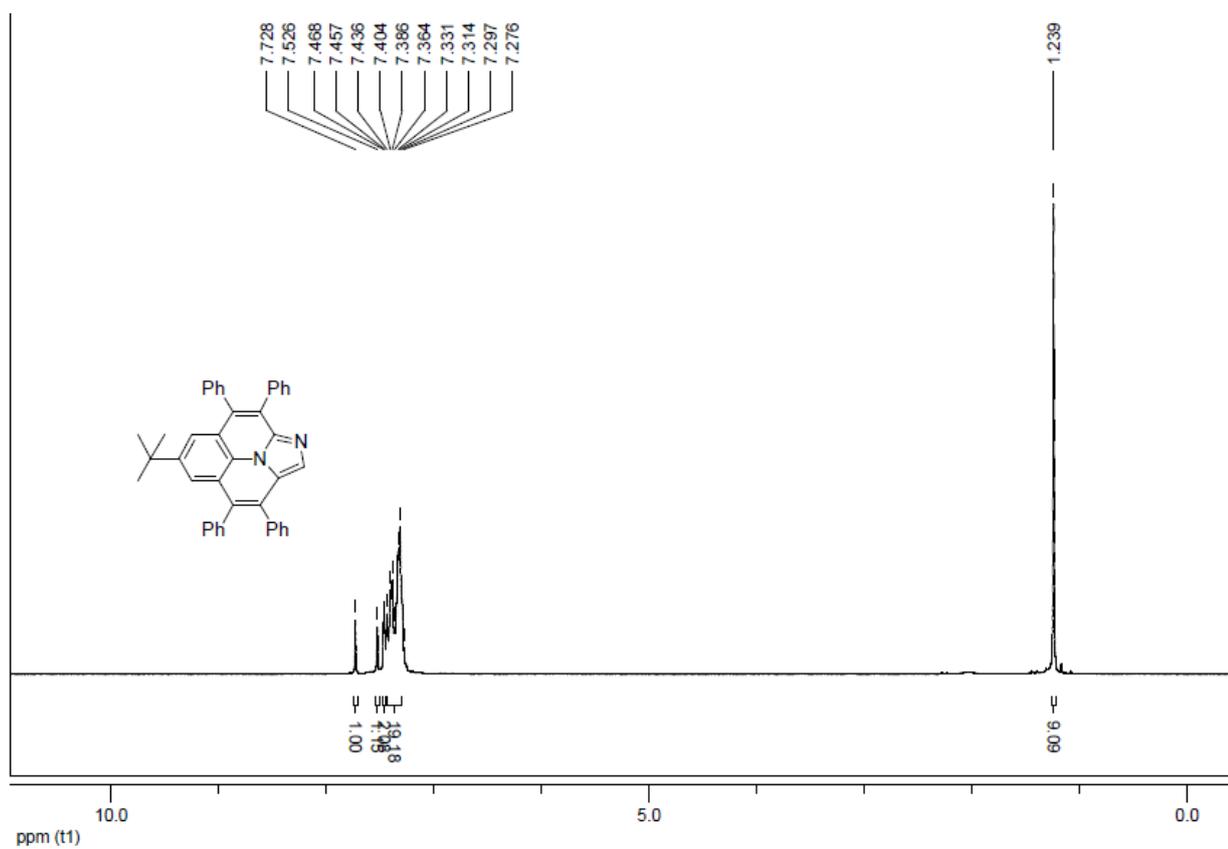
¹H NMR spectrum of **3ea**



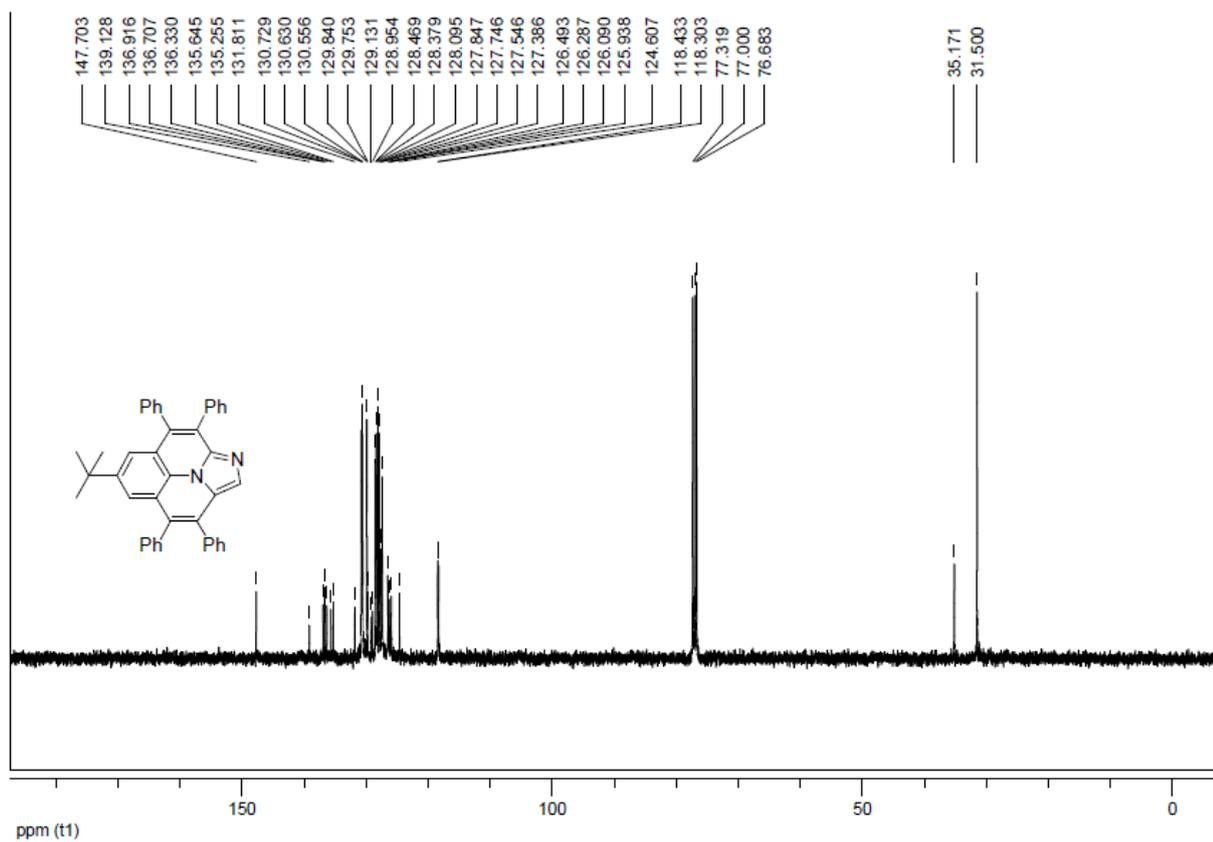
¹³C NMR spectrum of **3ea**



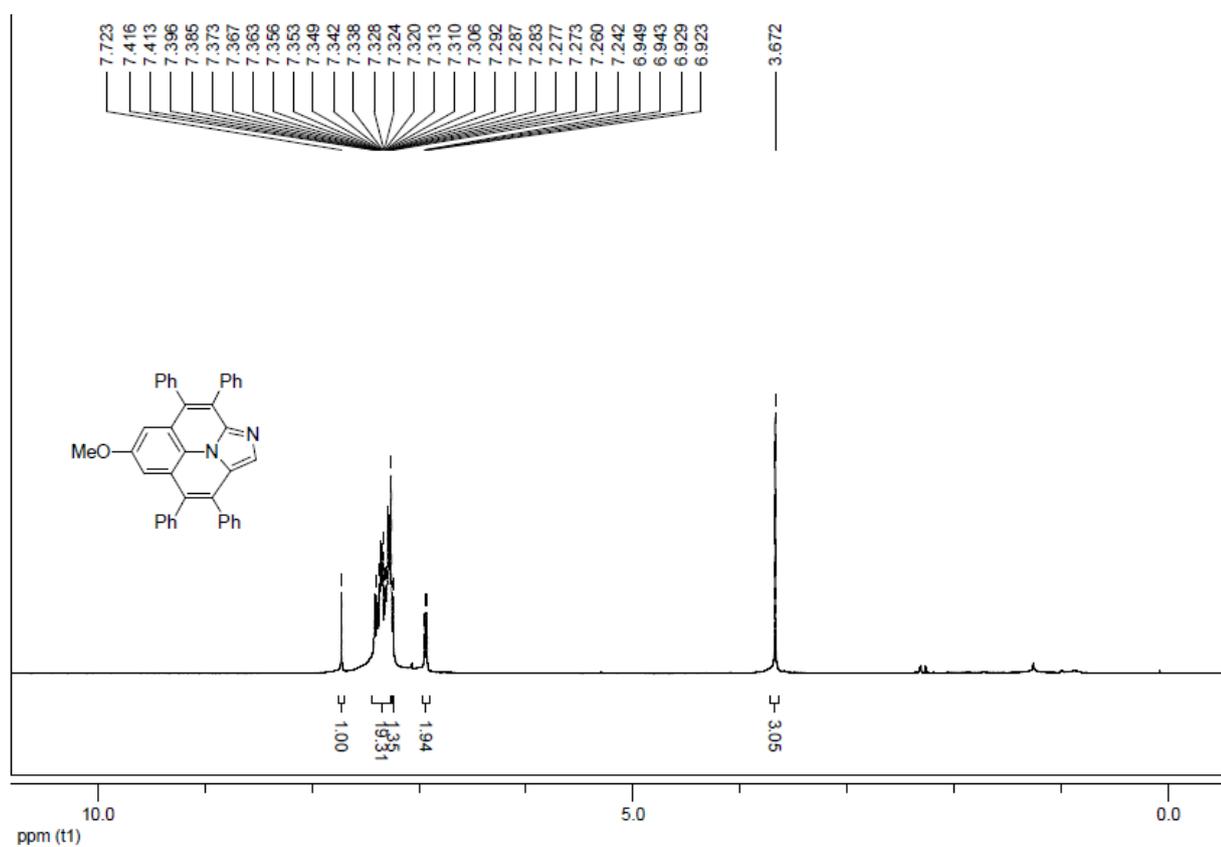
¹H NMR spectrum of **3fa**



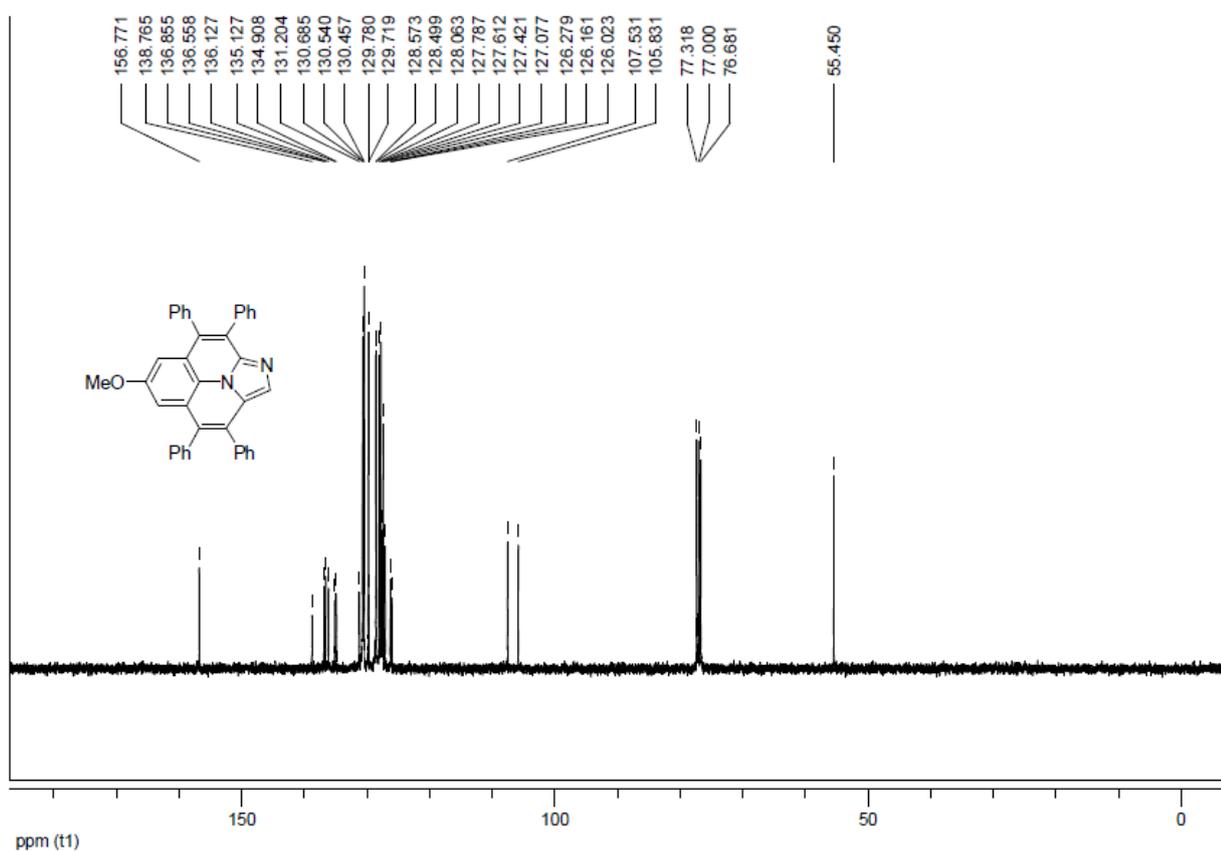
¹³C NMR spectrum of **3fa**



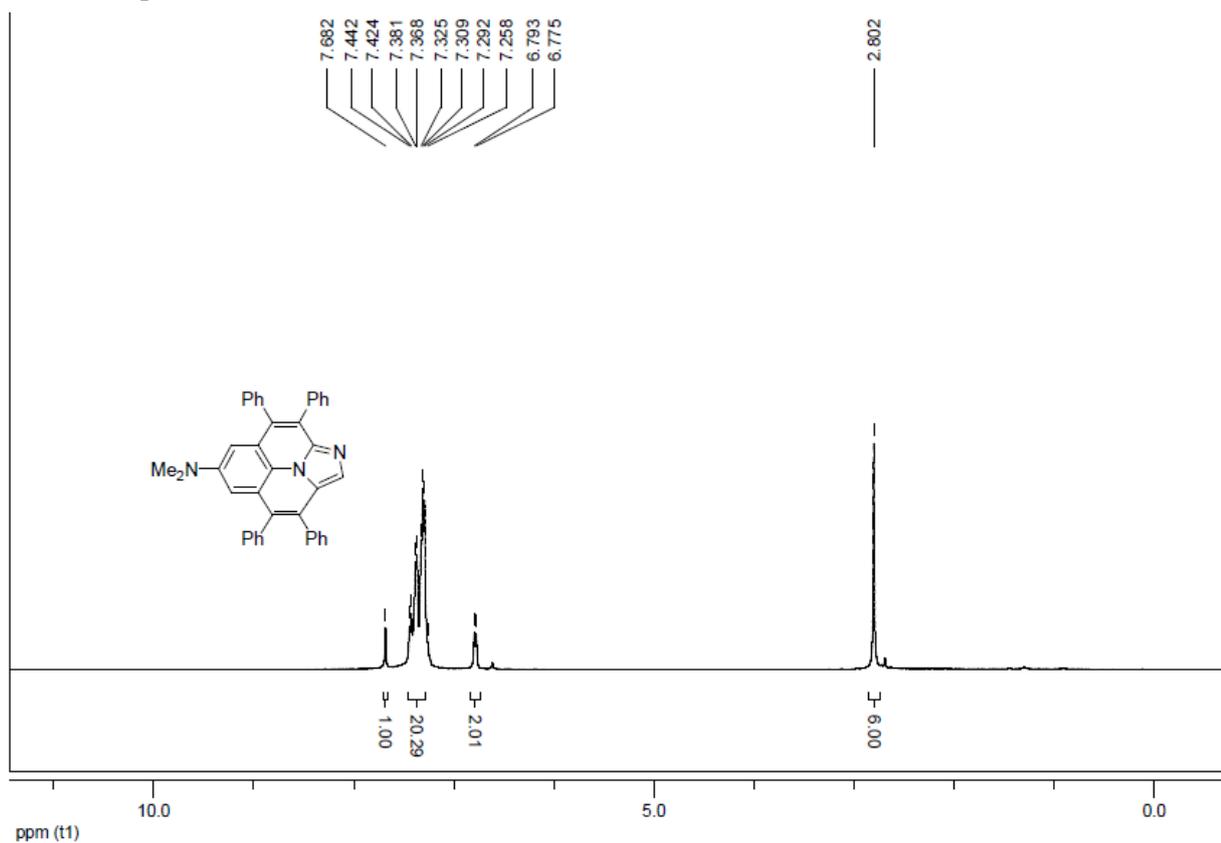
¹H NMR spectrum of **3ga**



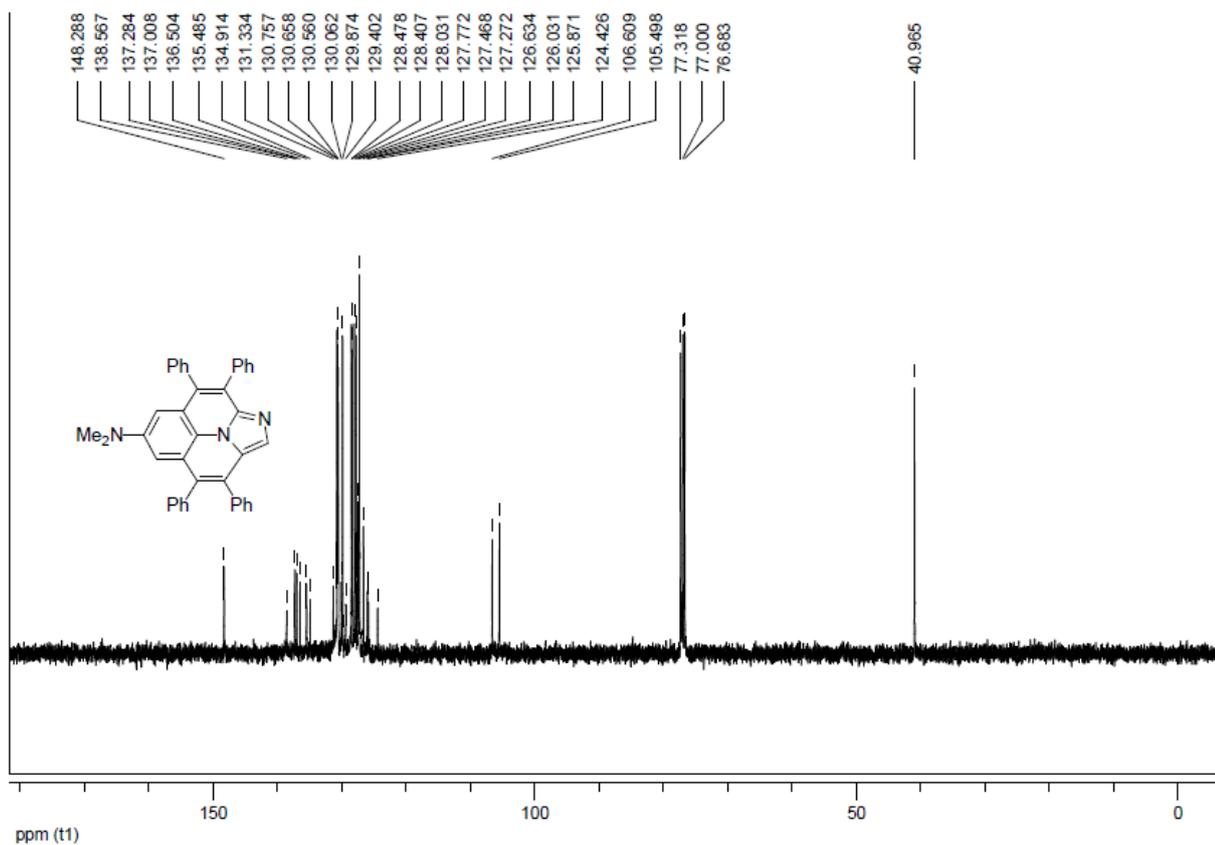
¹³C NMR spectrum of **3ga**



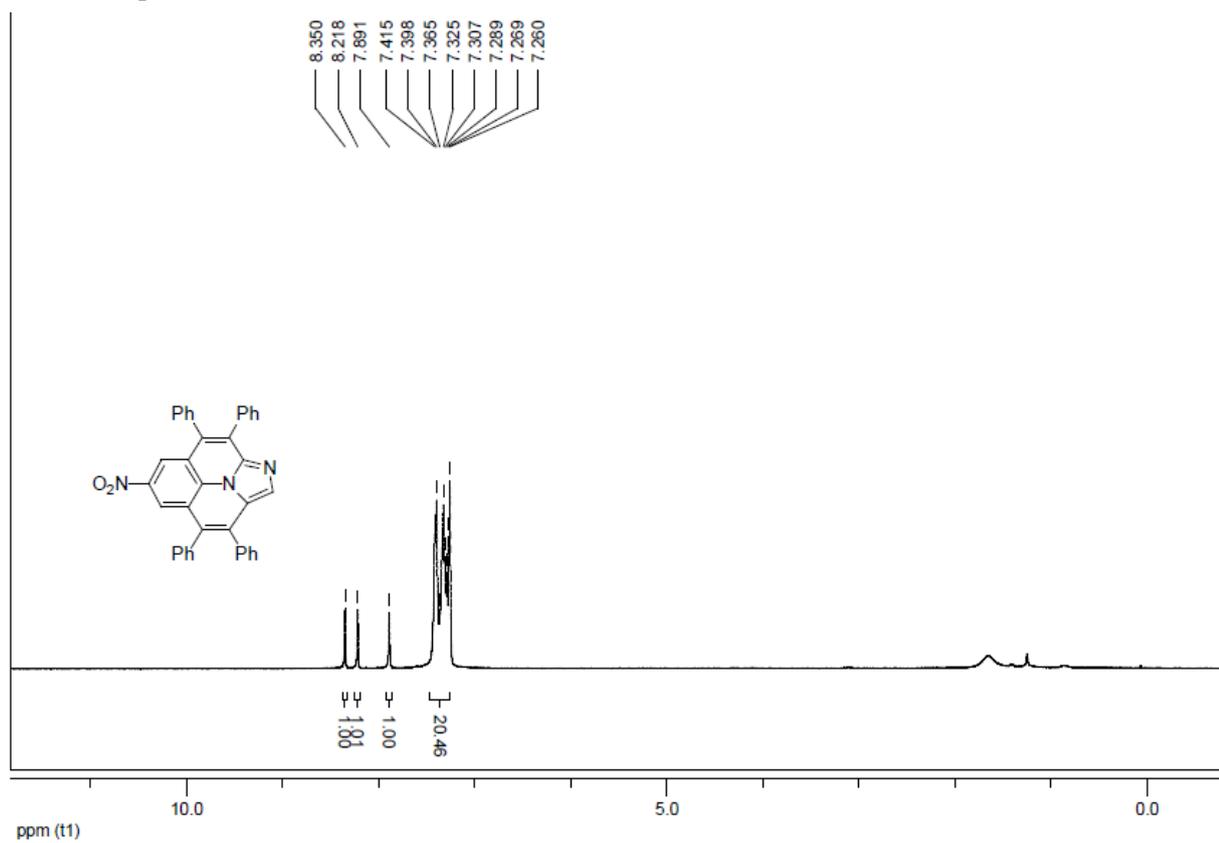
¹H NMR spectrum of **3ha**



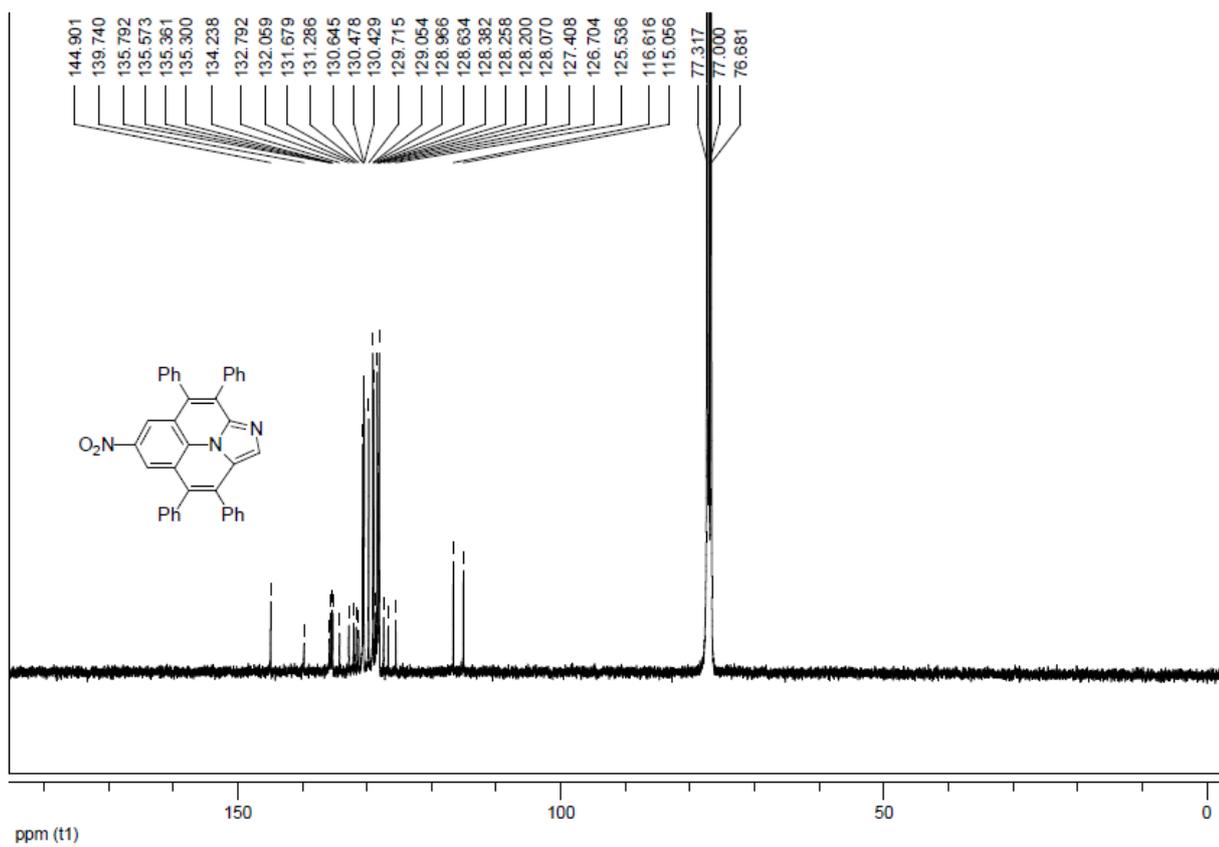
¹³C NMR spectrum of **3ha**



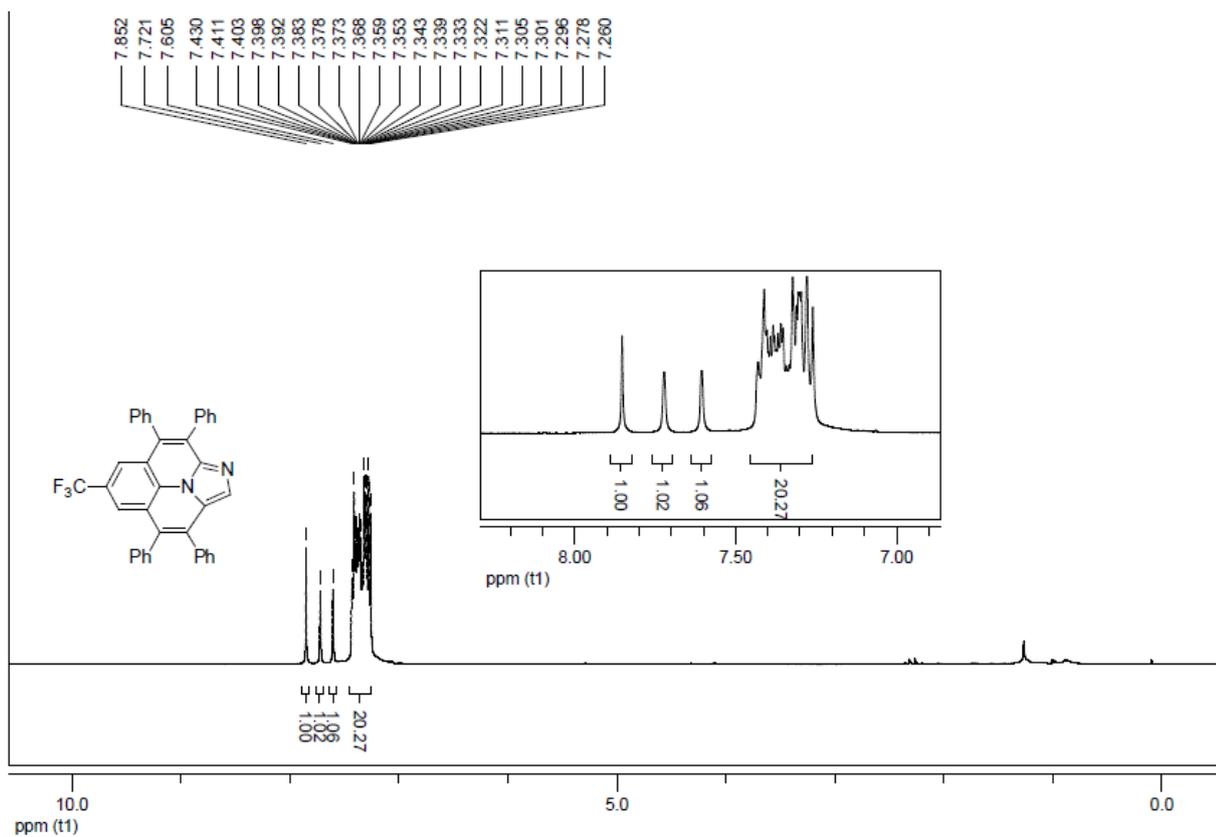
¹H NMR spectrum of **3ia**



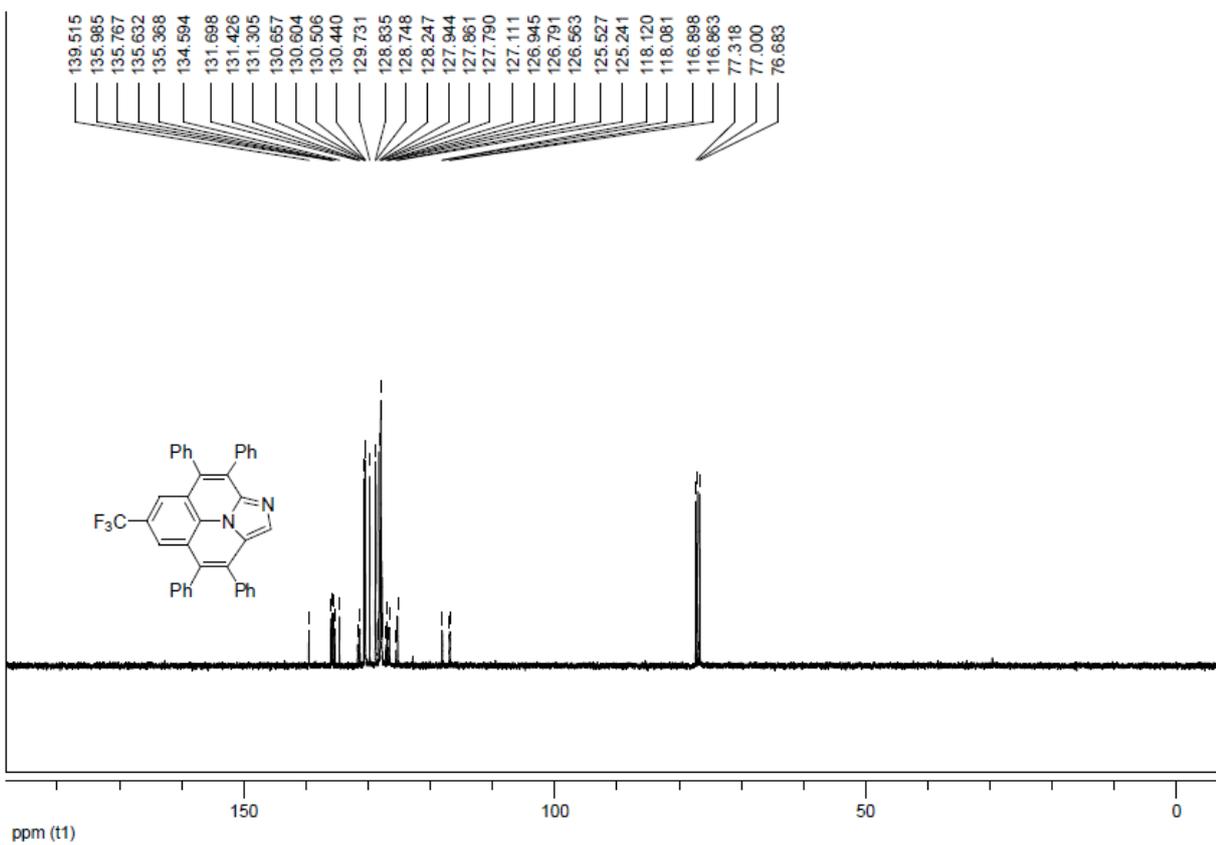
¹³C NMR spectrum of **3ia**



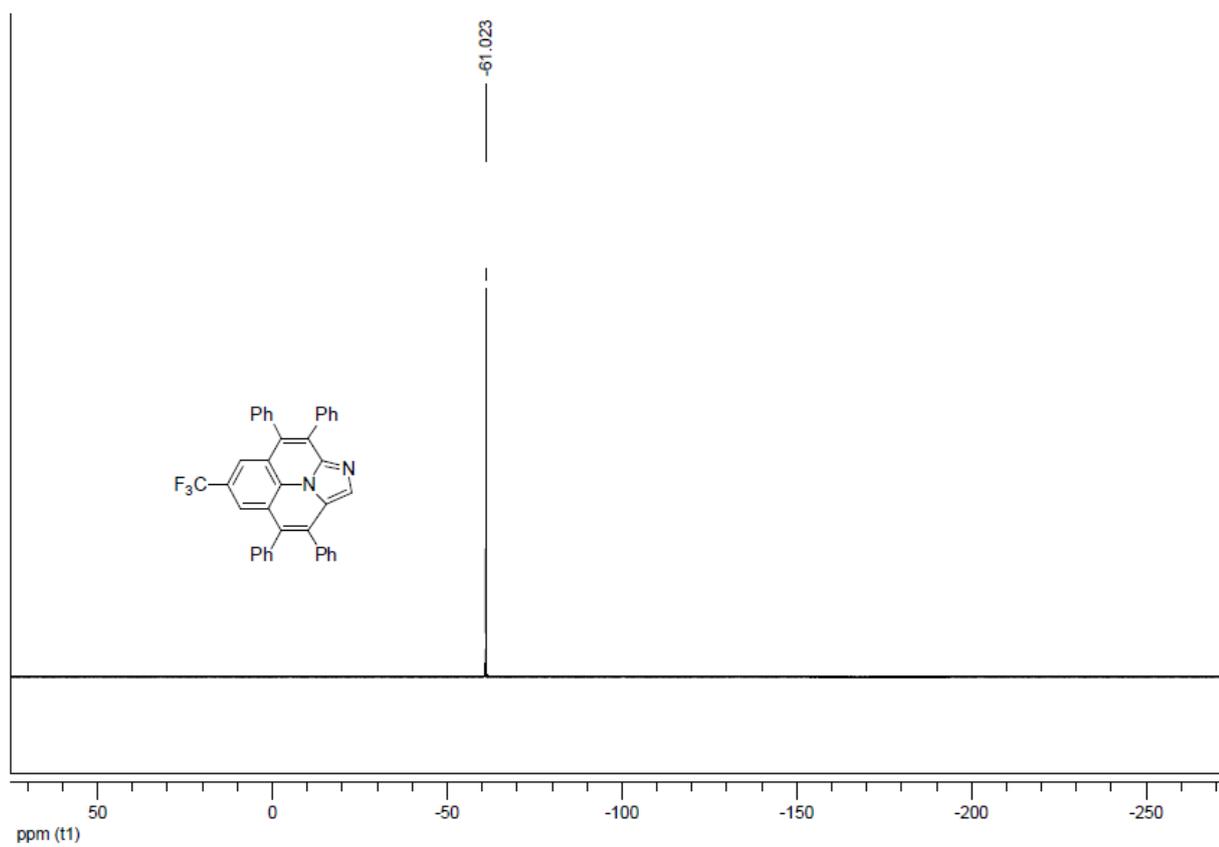
¹H NMR spectrum of **3ja**



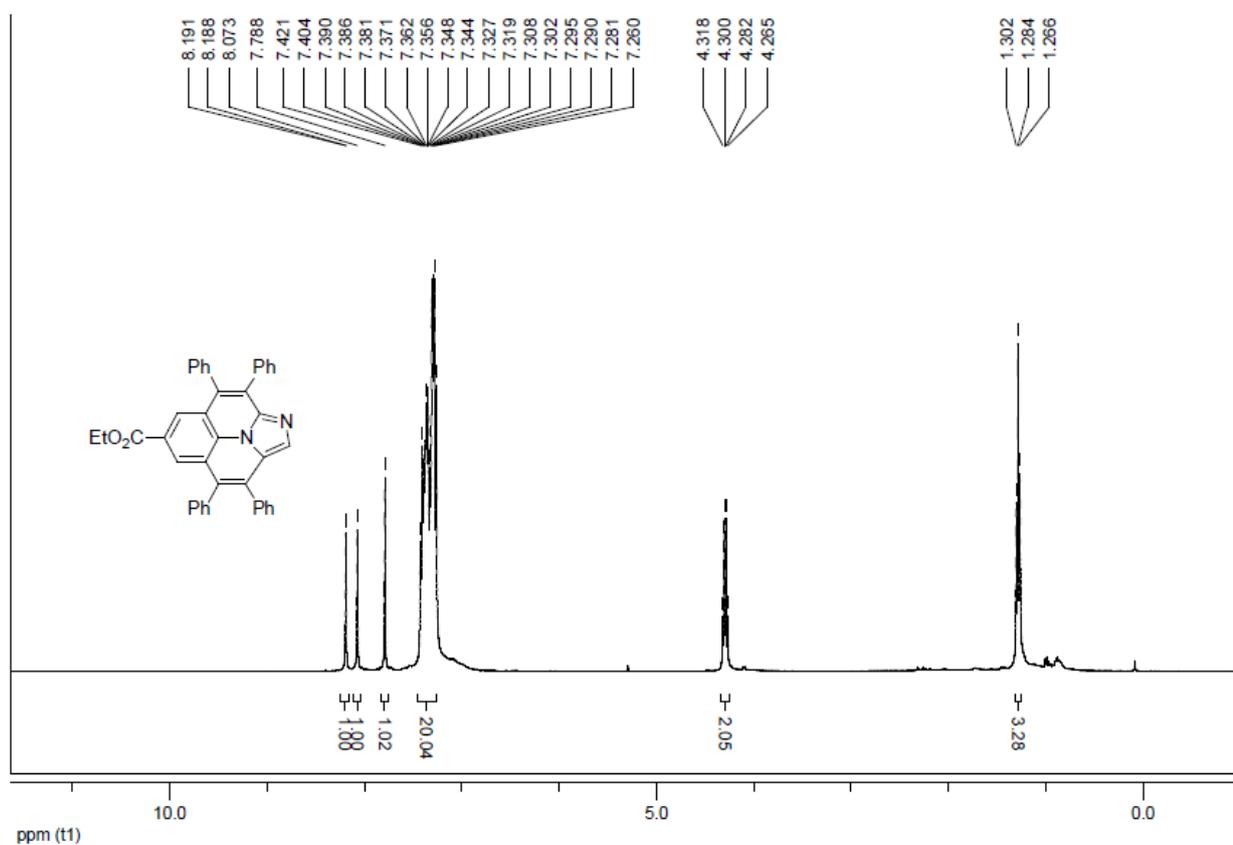
¹³C NMR spectrum of **3ja**



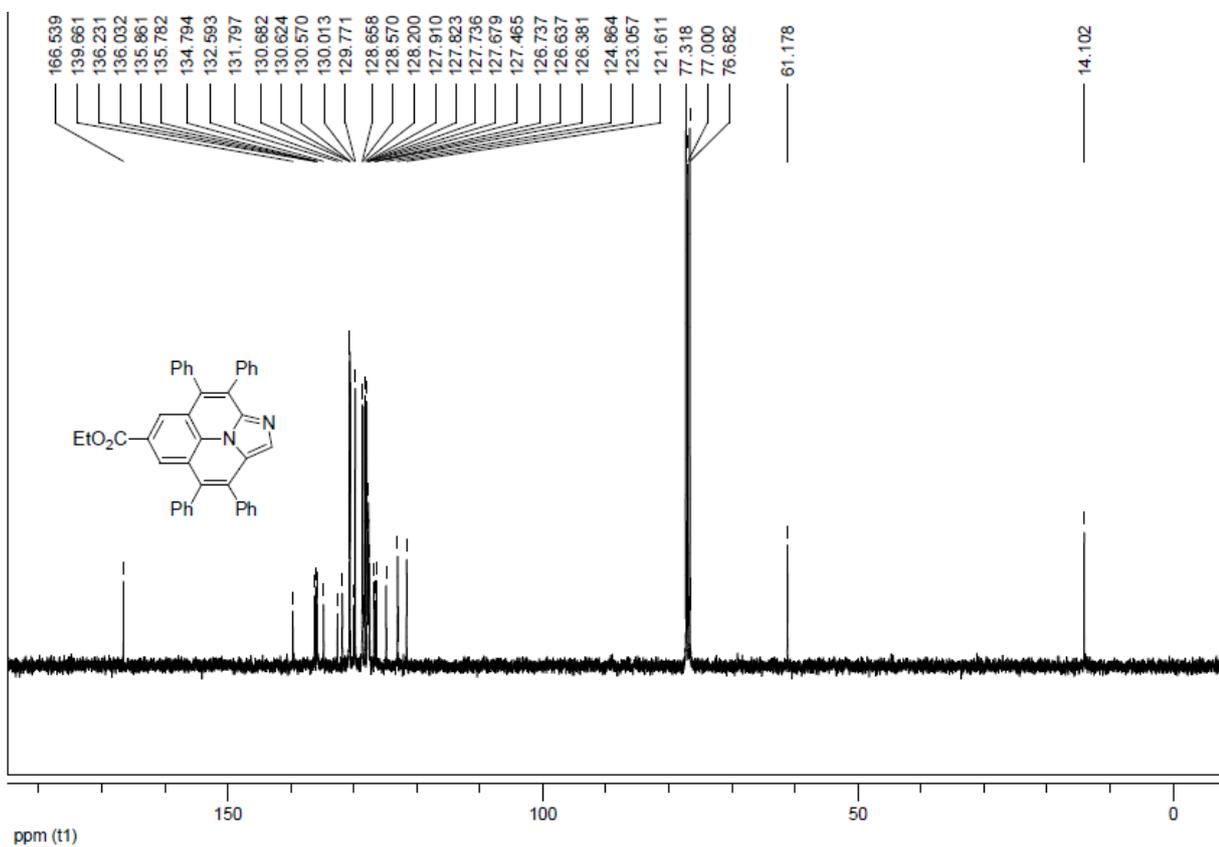
¹⁹F NMR spectrum of **3ja**



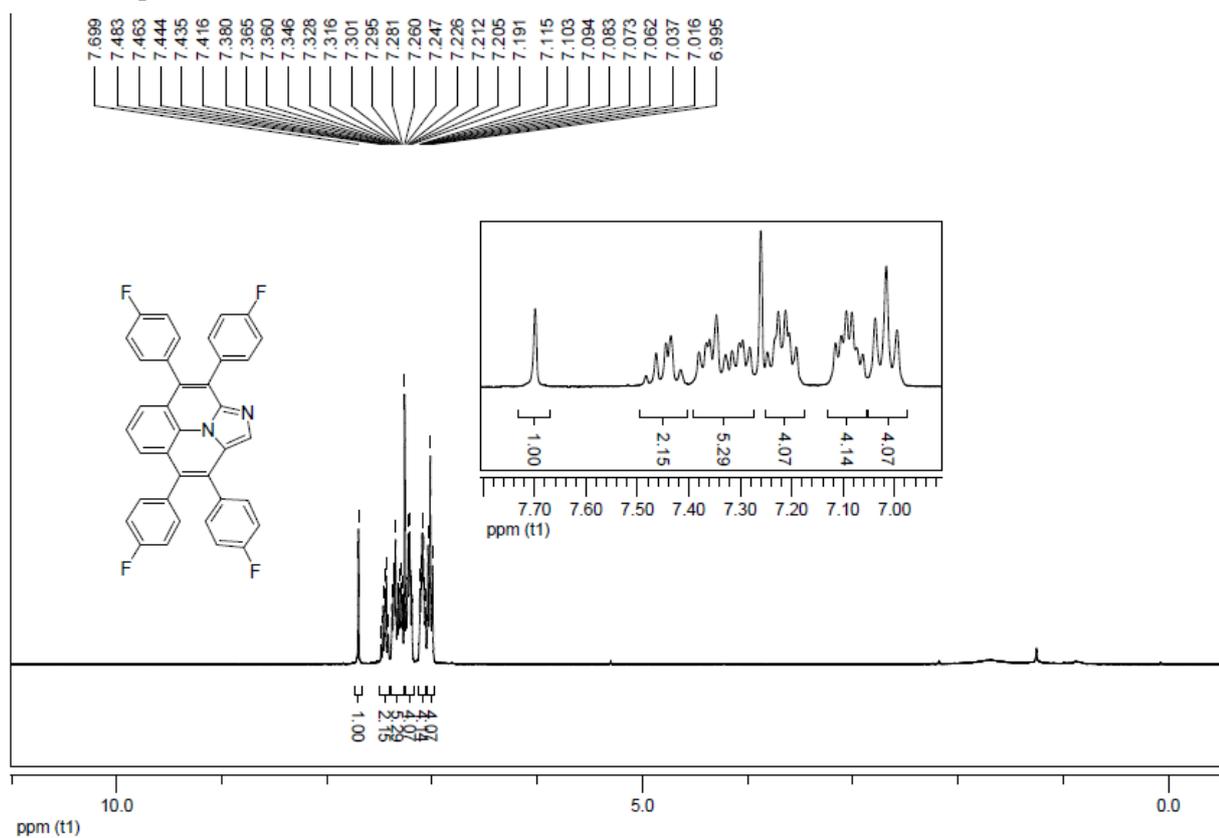
¹H NMR spectrum of **3ka**



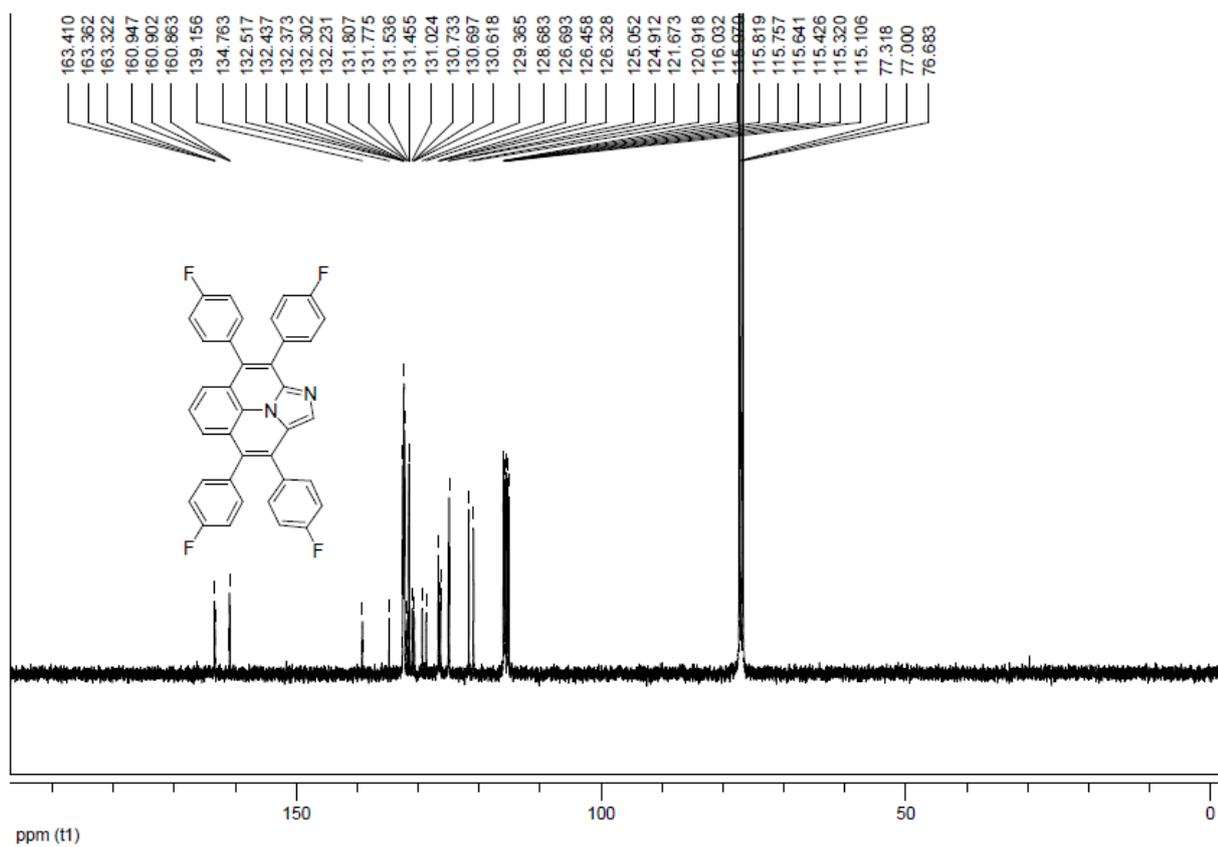
¹³C NMR spectrum of **3ka**



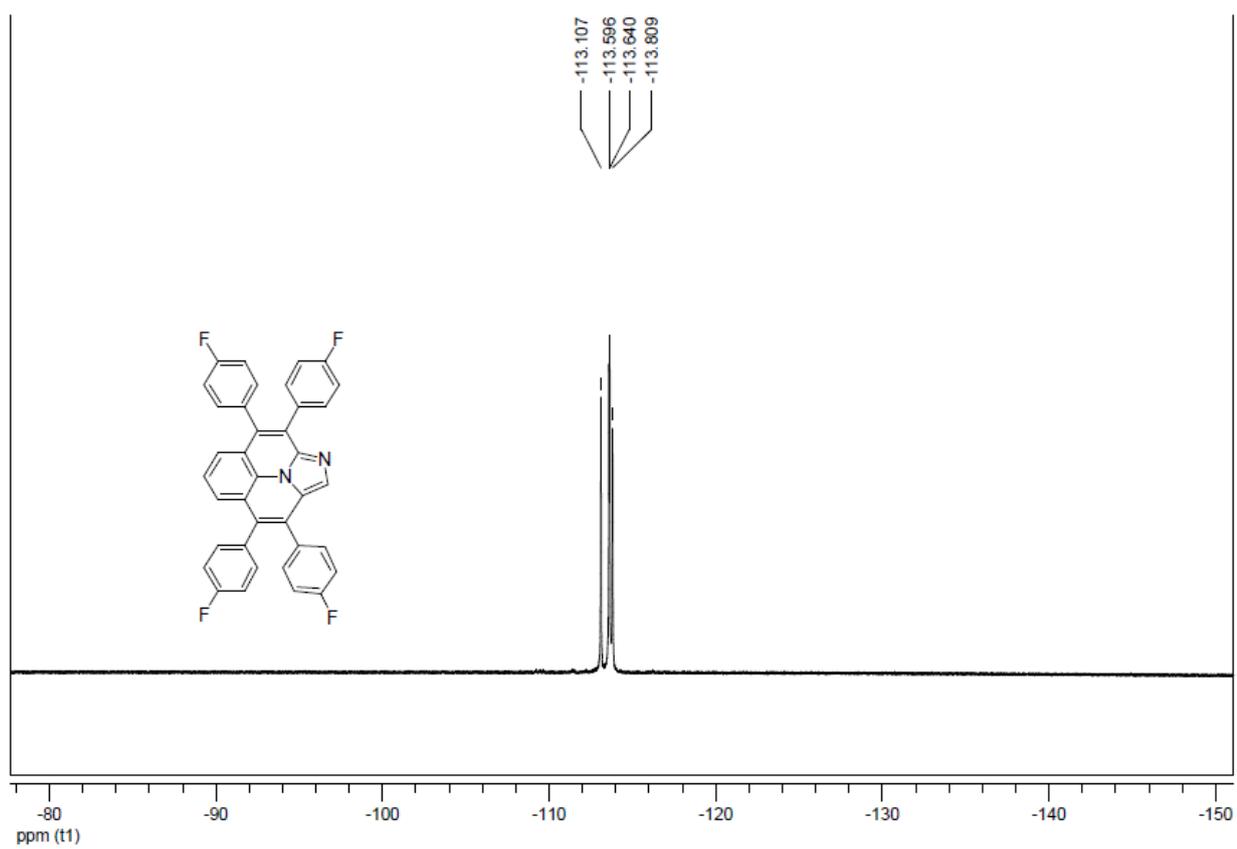
¹H NMR spectrum of **3ab**



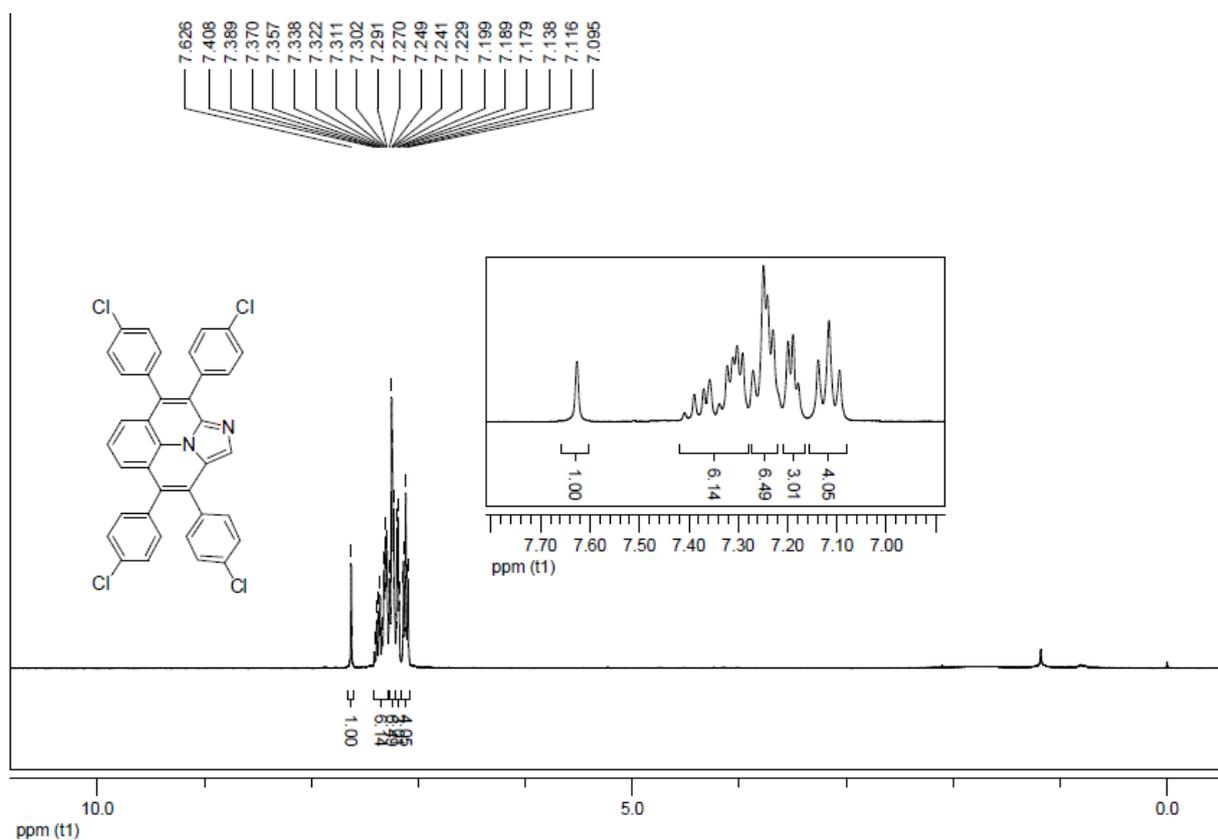
¹³C NMR spectrum of **3ab**



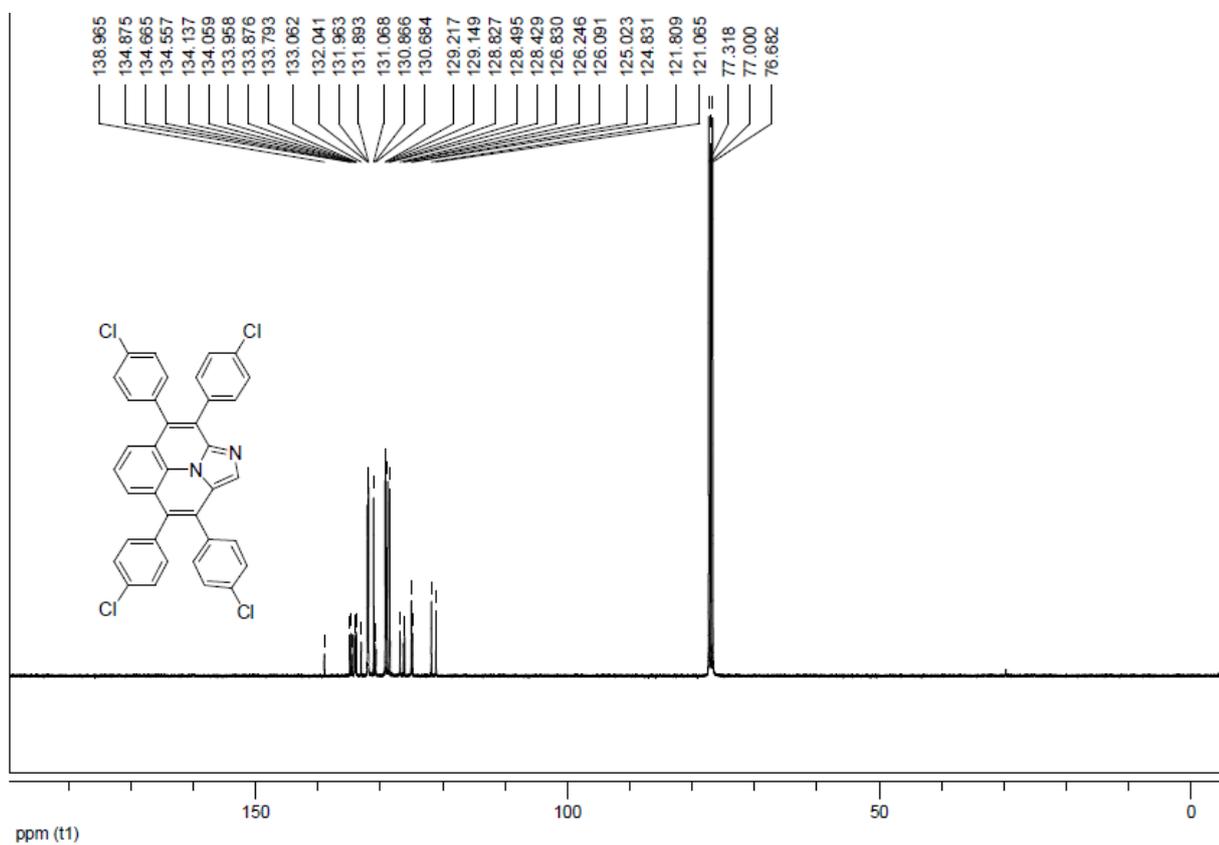
^{19}F NMR spectrum of **3ab**



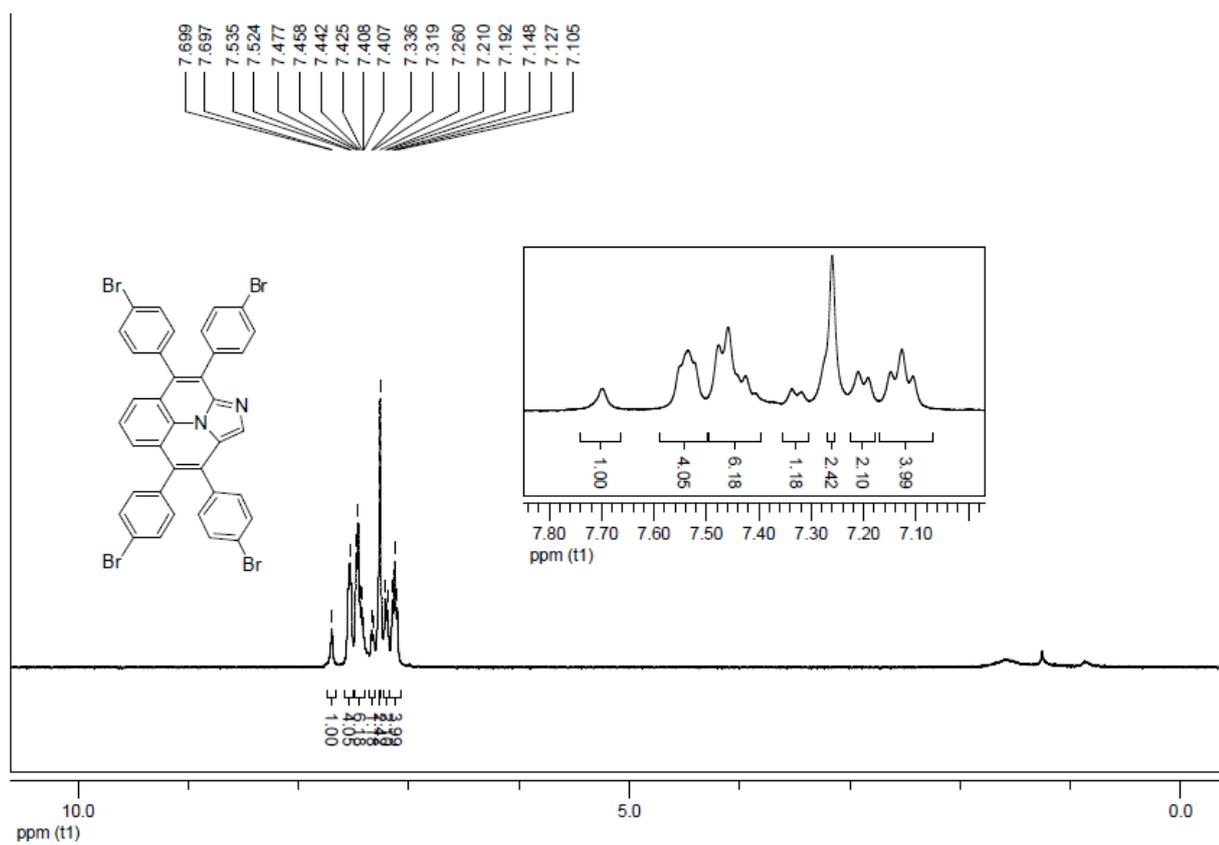
¹H NMR spectrum of **3ac**



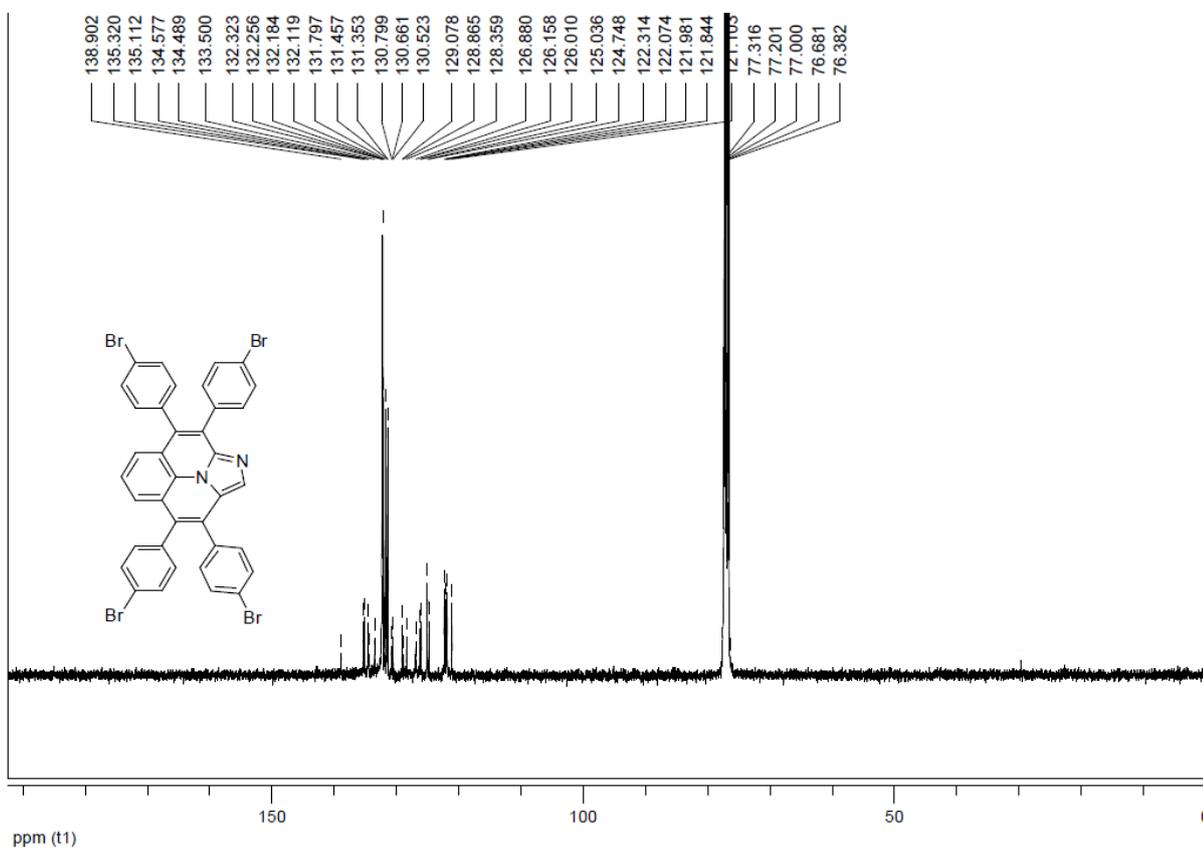
¹³C NMR spectrum of **3ac**



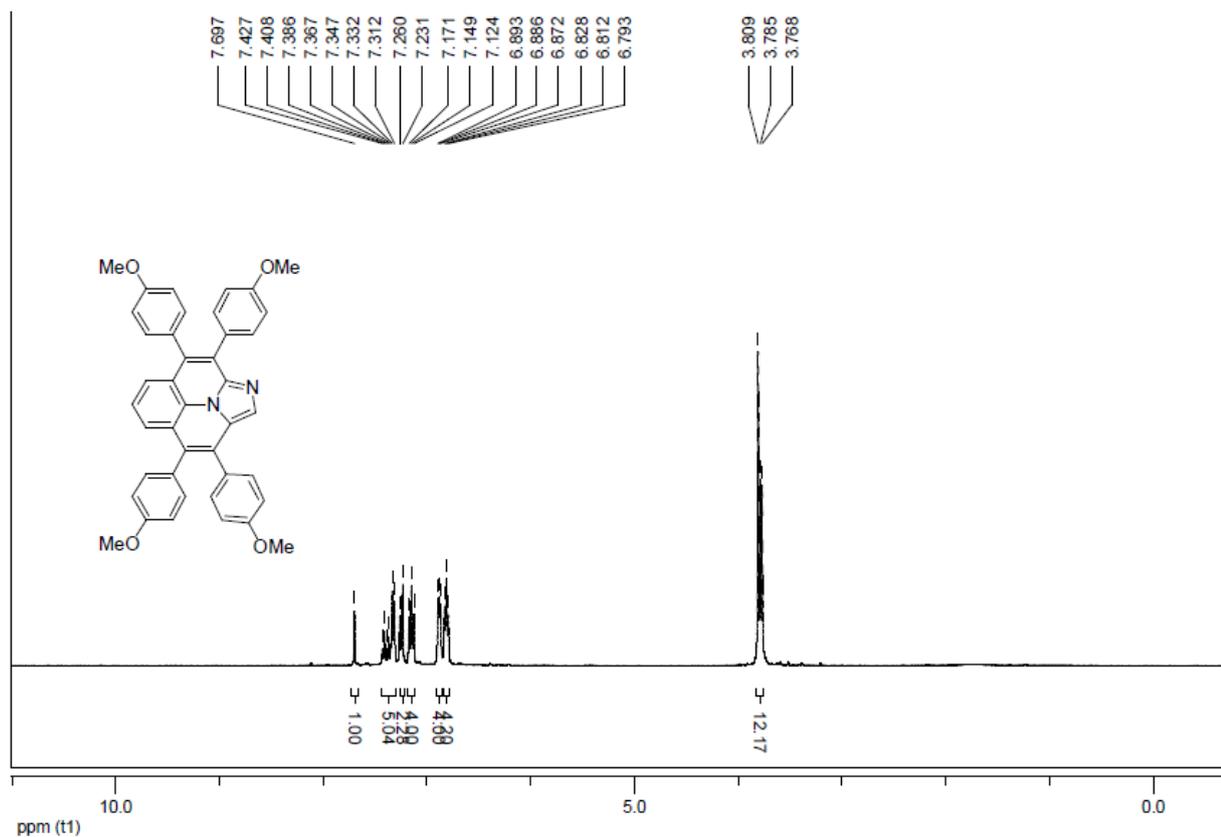
¹H NMR spectrum of **3ad**



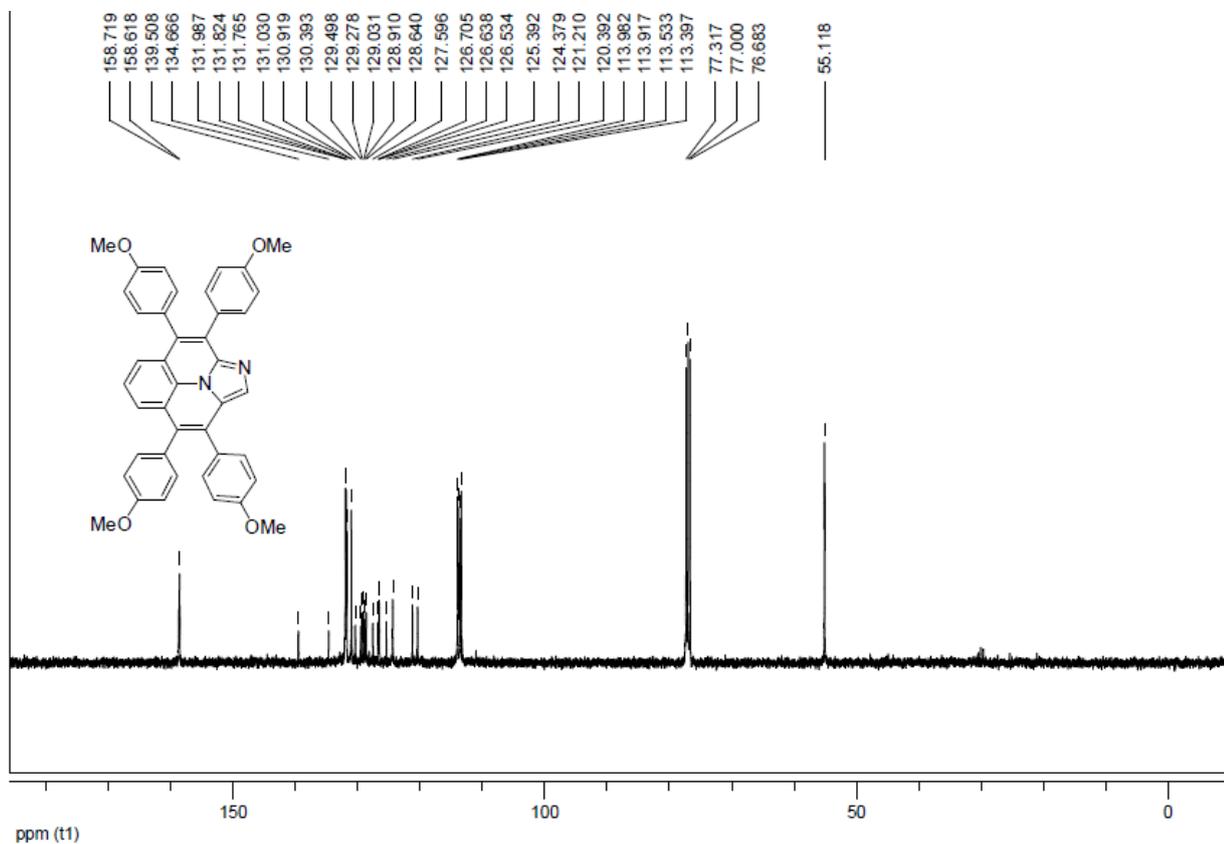
¹³C NMR spectrum of **3ad**



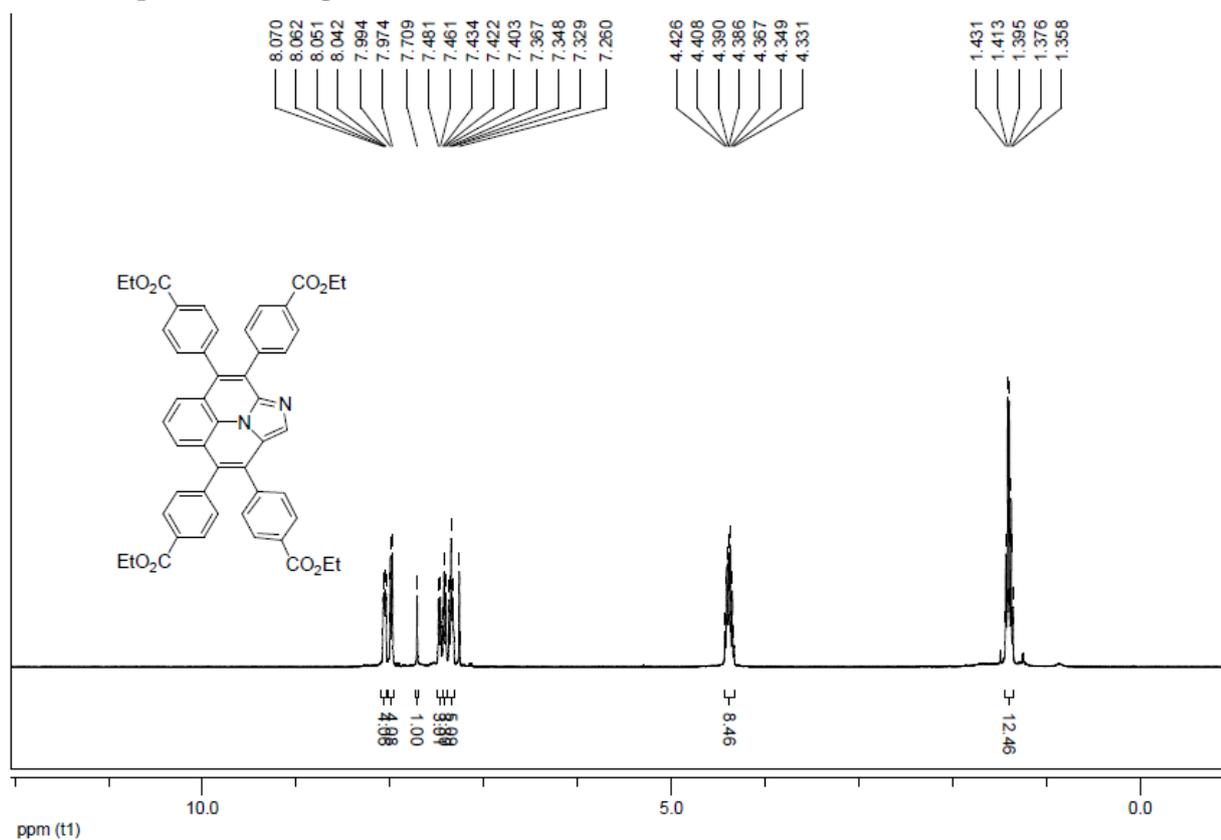
¹H NMR spectrum of **3af**



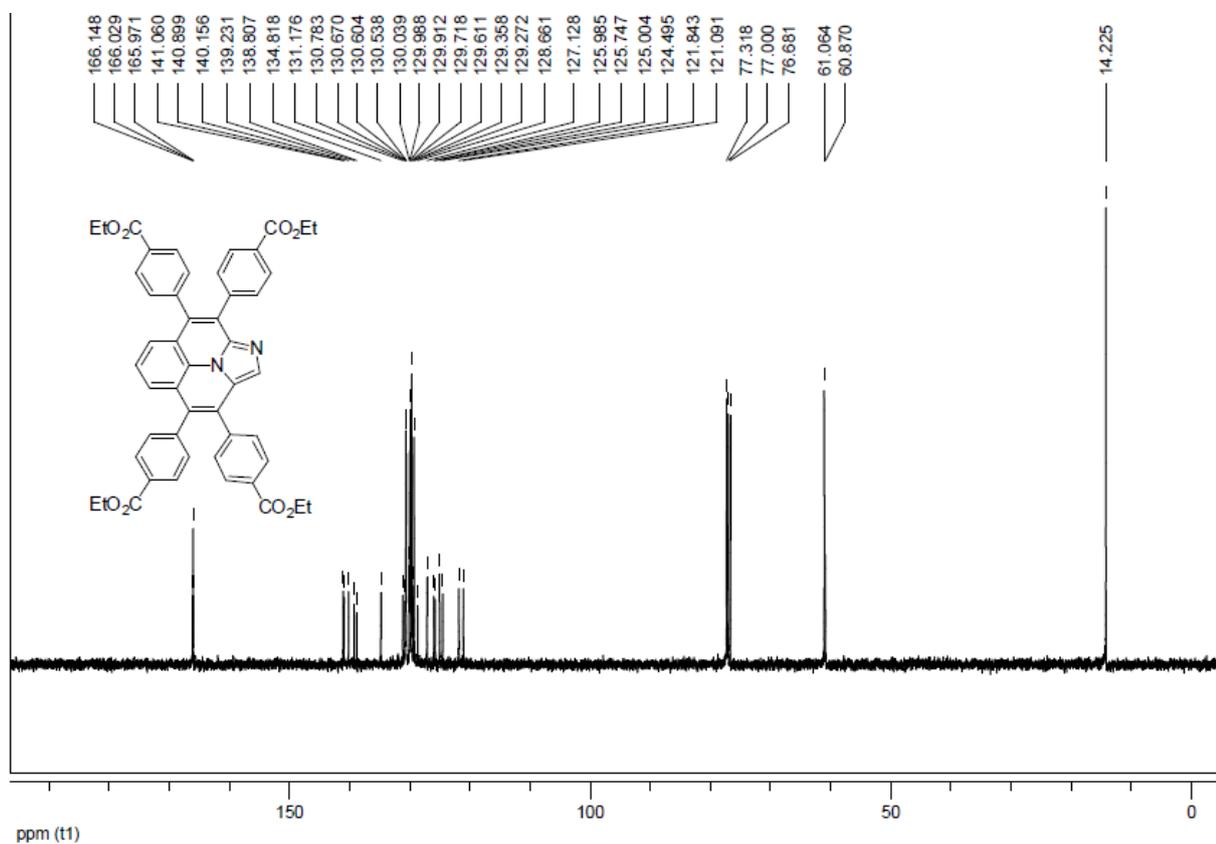
¹³C NMR spectrum of **3af**



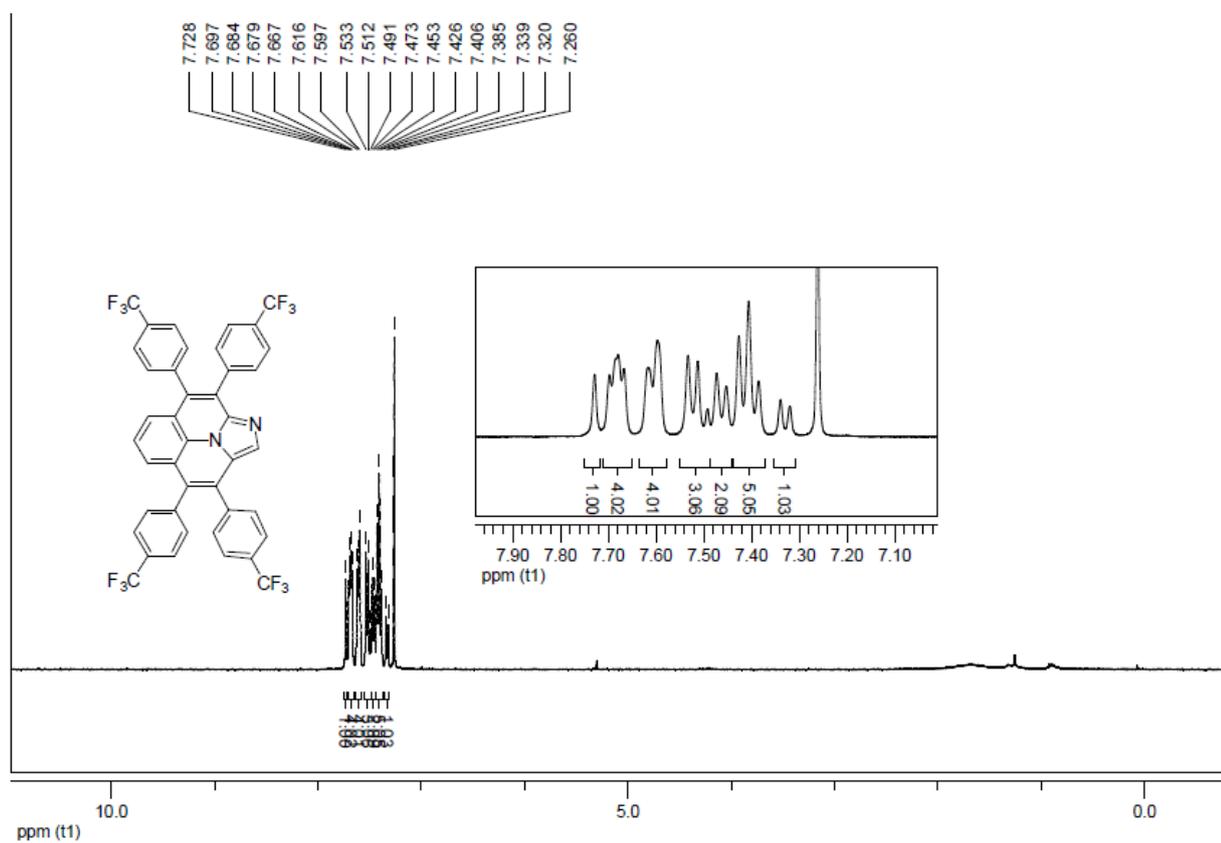
¹H NMR spectrum of **3ag**



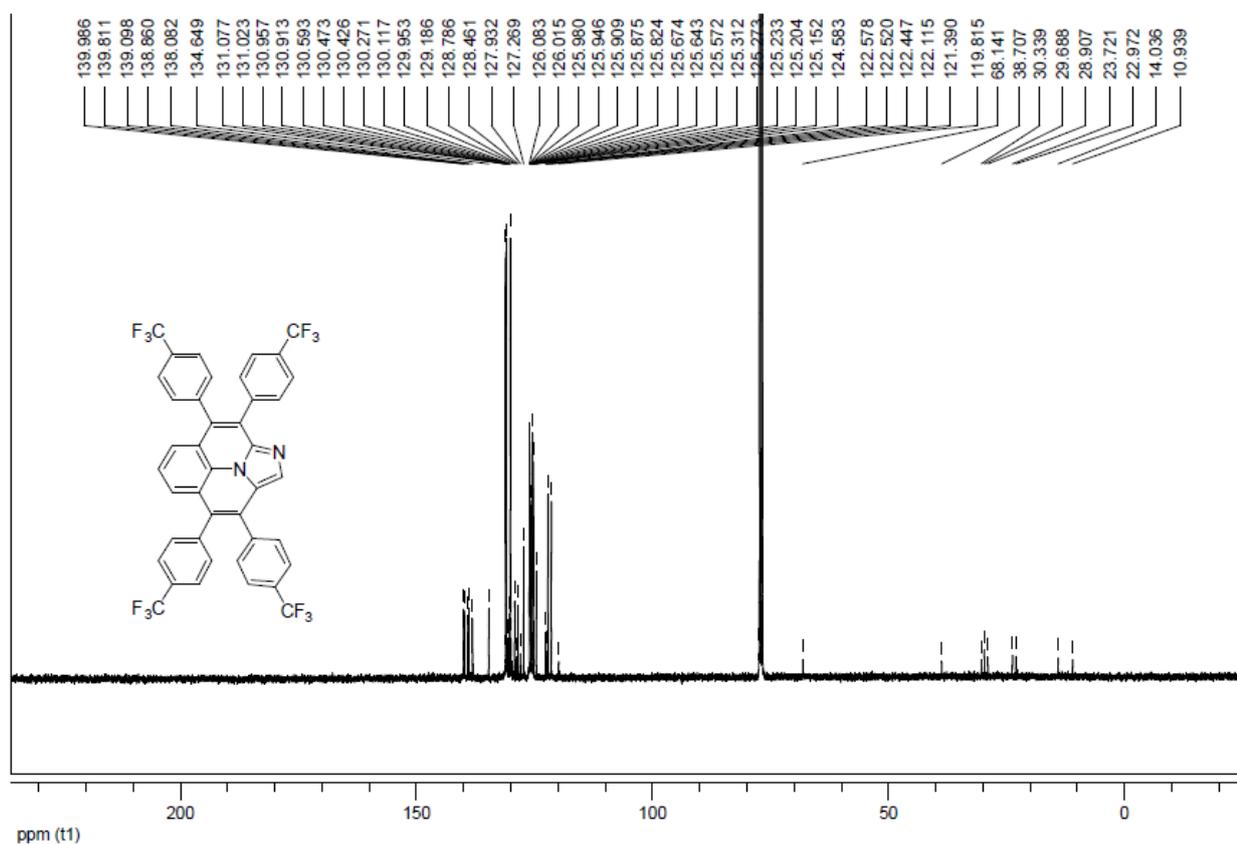
¹³C NMR spectrum of **3ag**



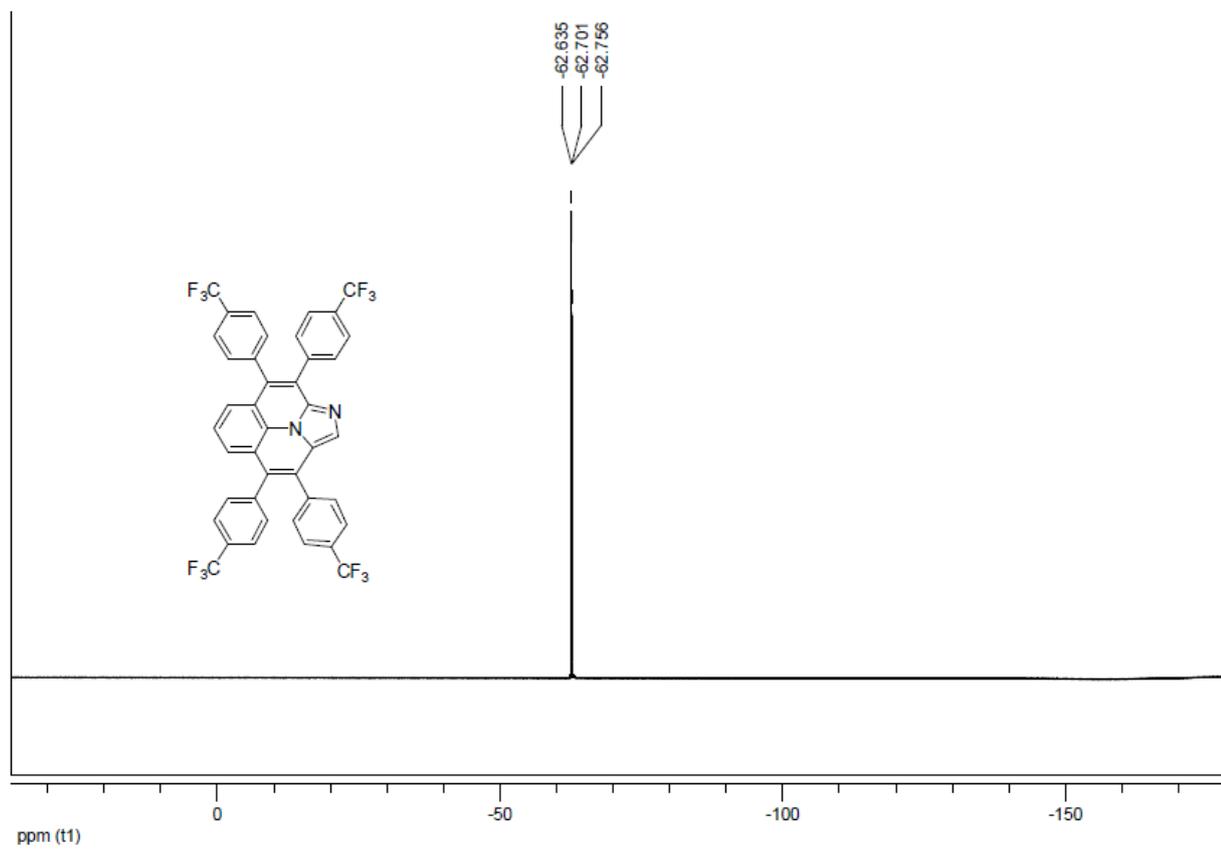
¹H NMR spectrum of **3ah**



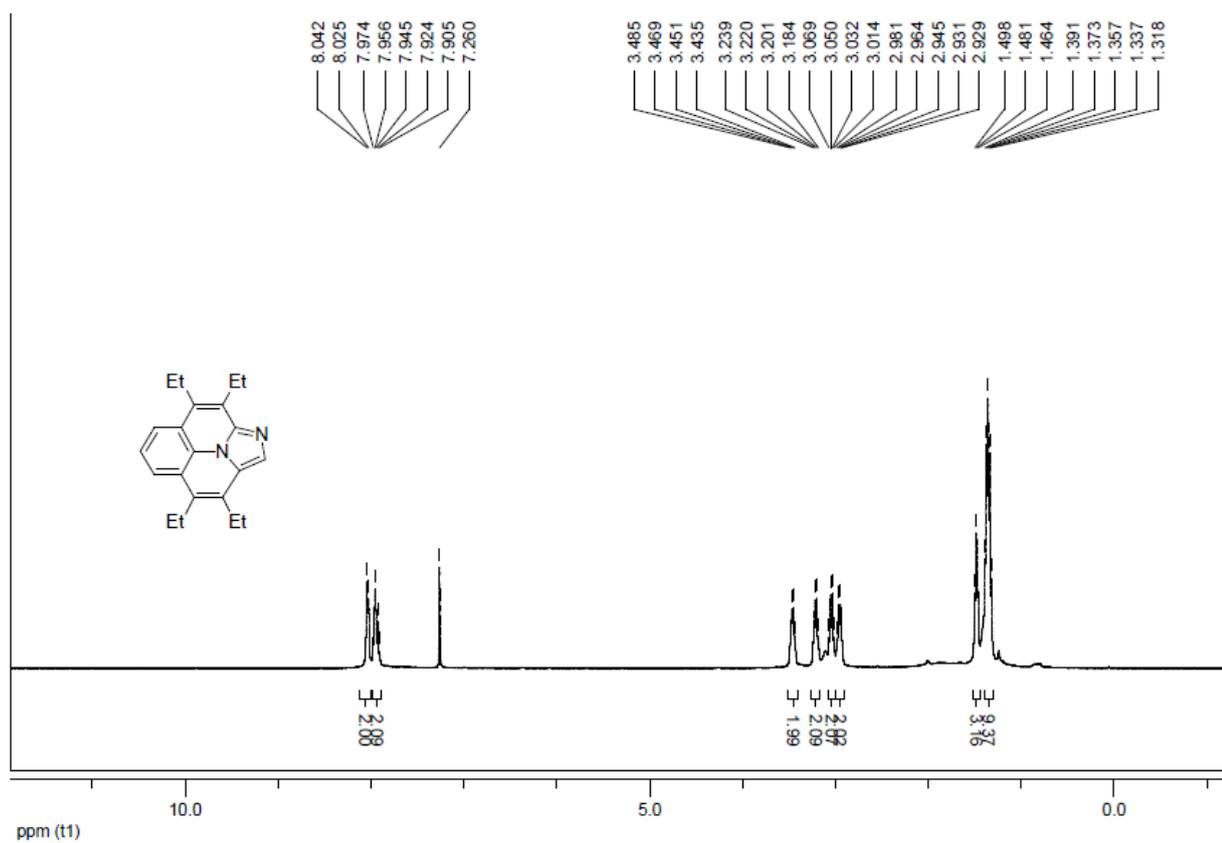
¹³C NMR spectrum of **3ah**



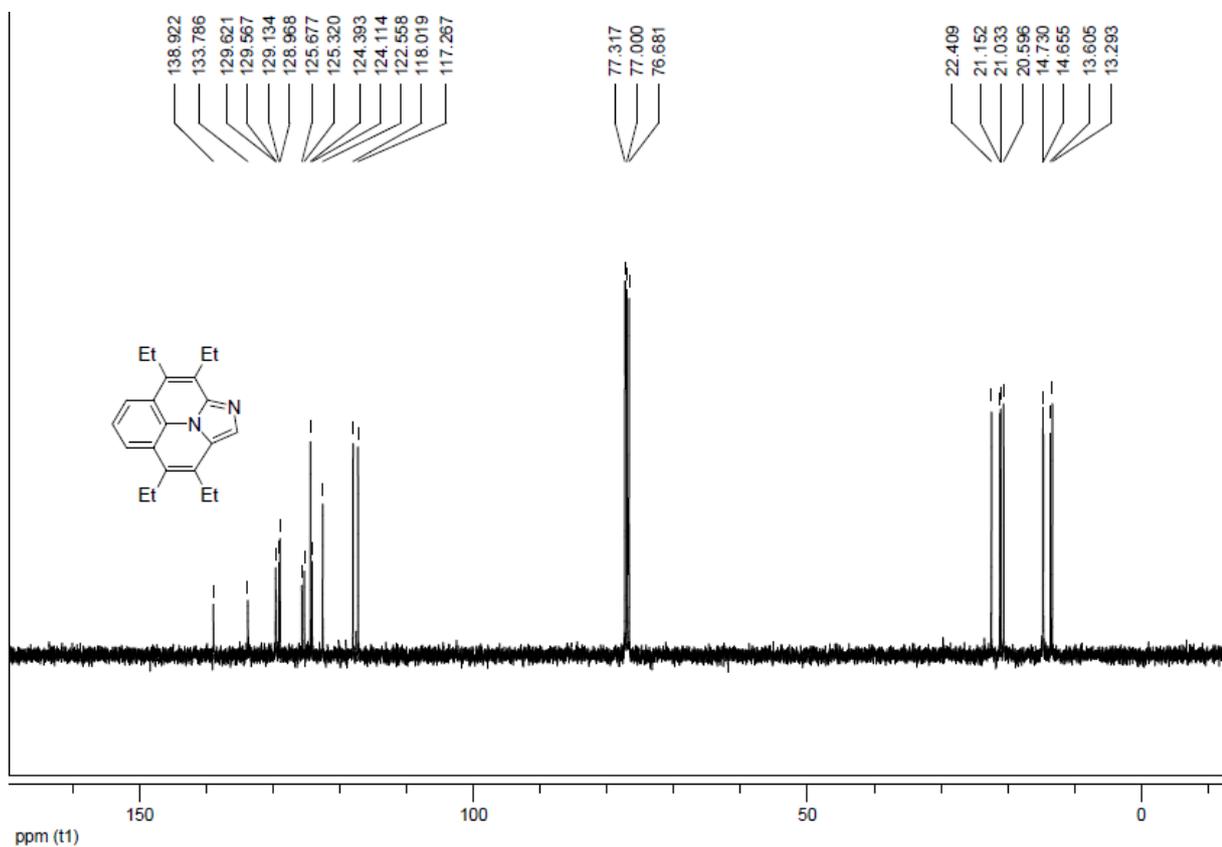
¹⁹F NMR spectrum of **3ah**



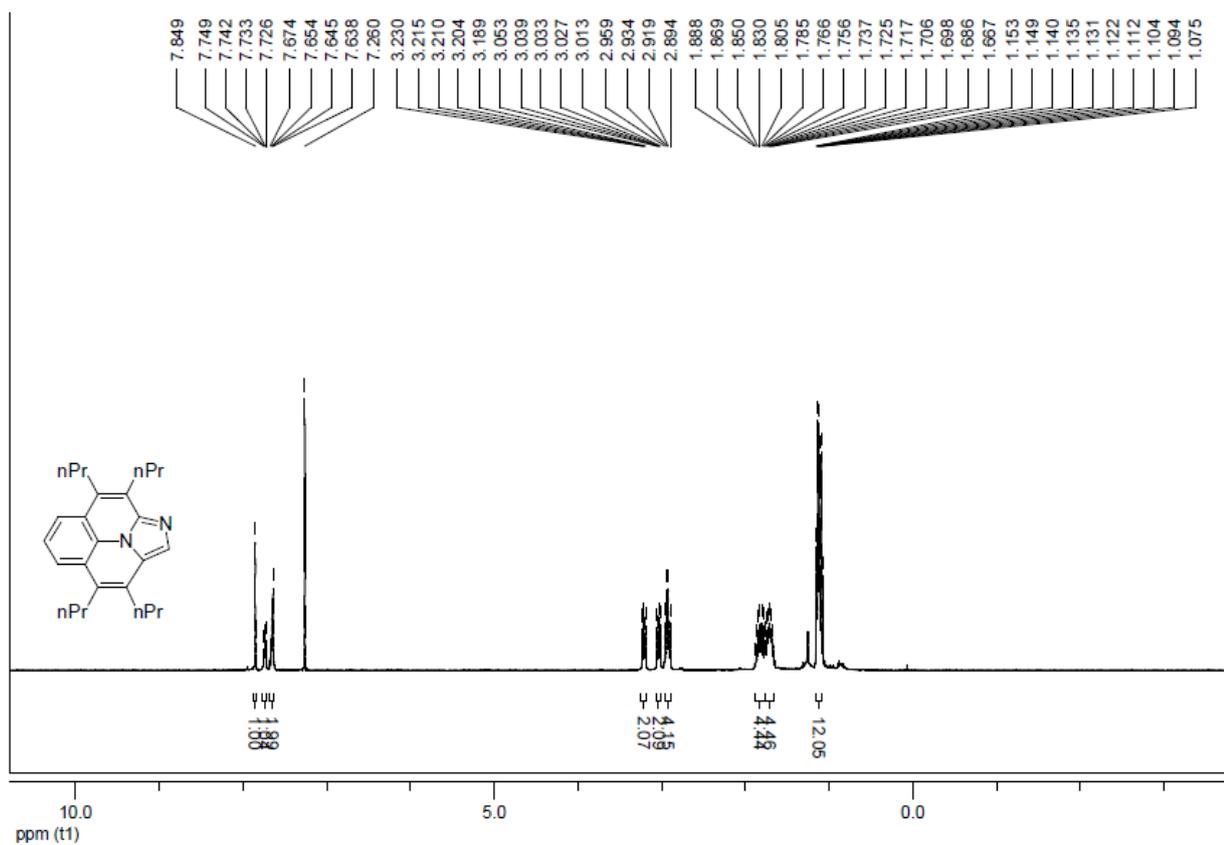
¹H NMR spectrum of **3ai**



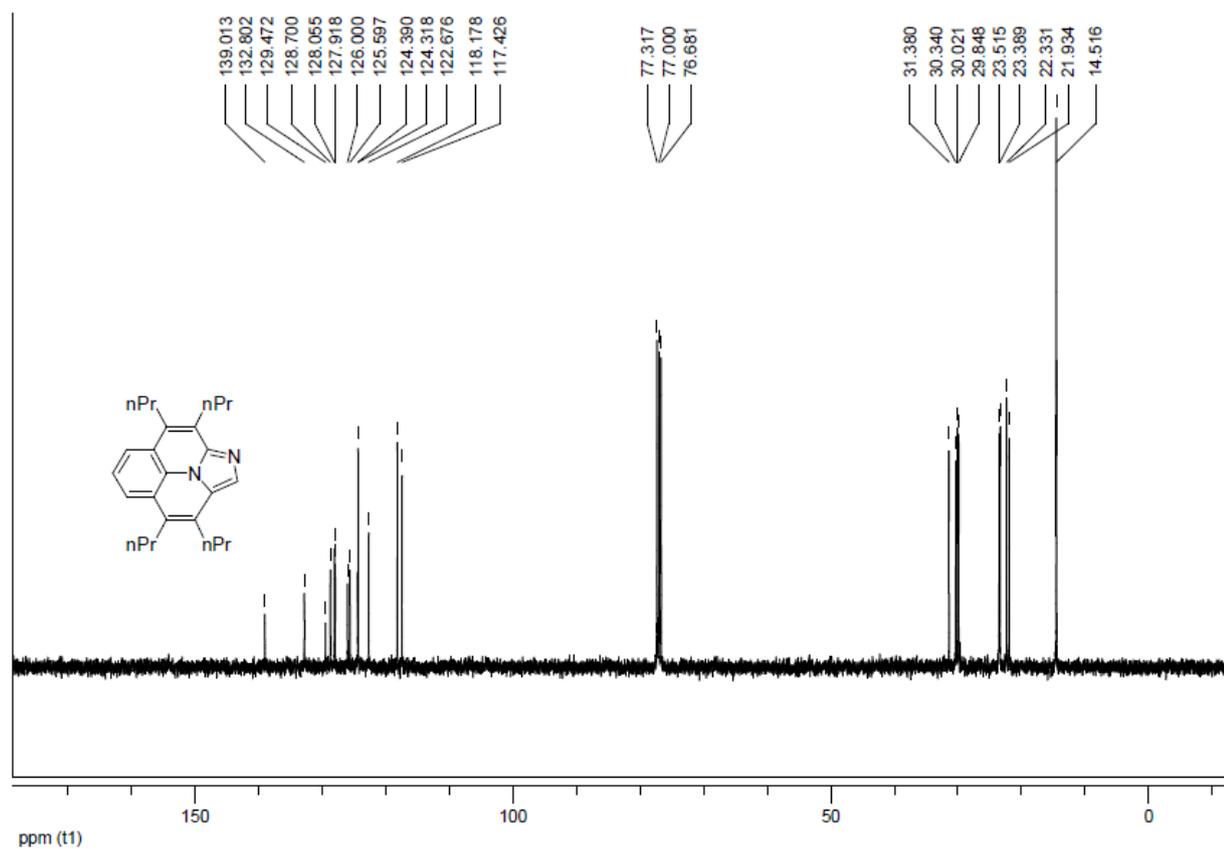
¹³C NMR spectrum of **3ai**



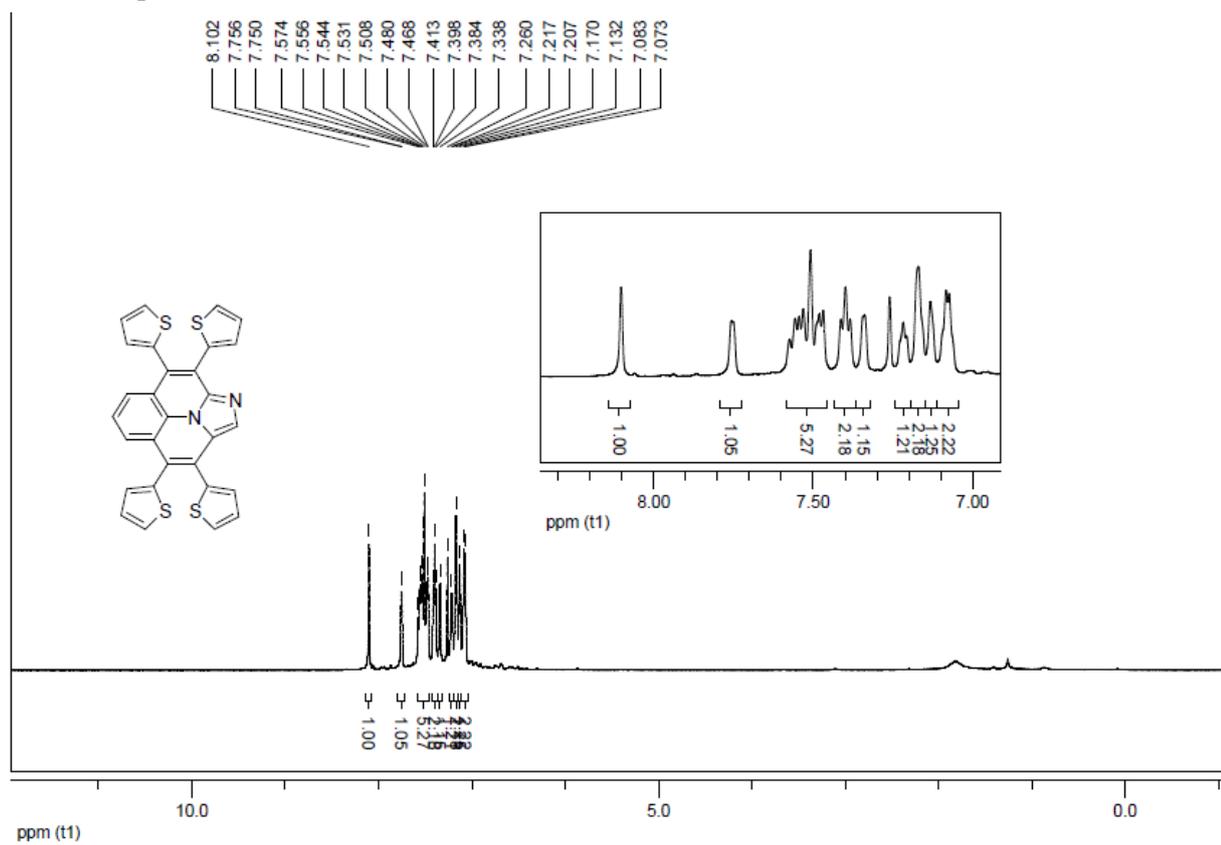
¹H NMR spectrum of **3aj**



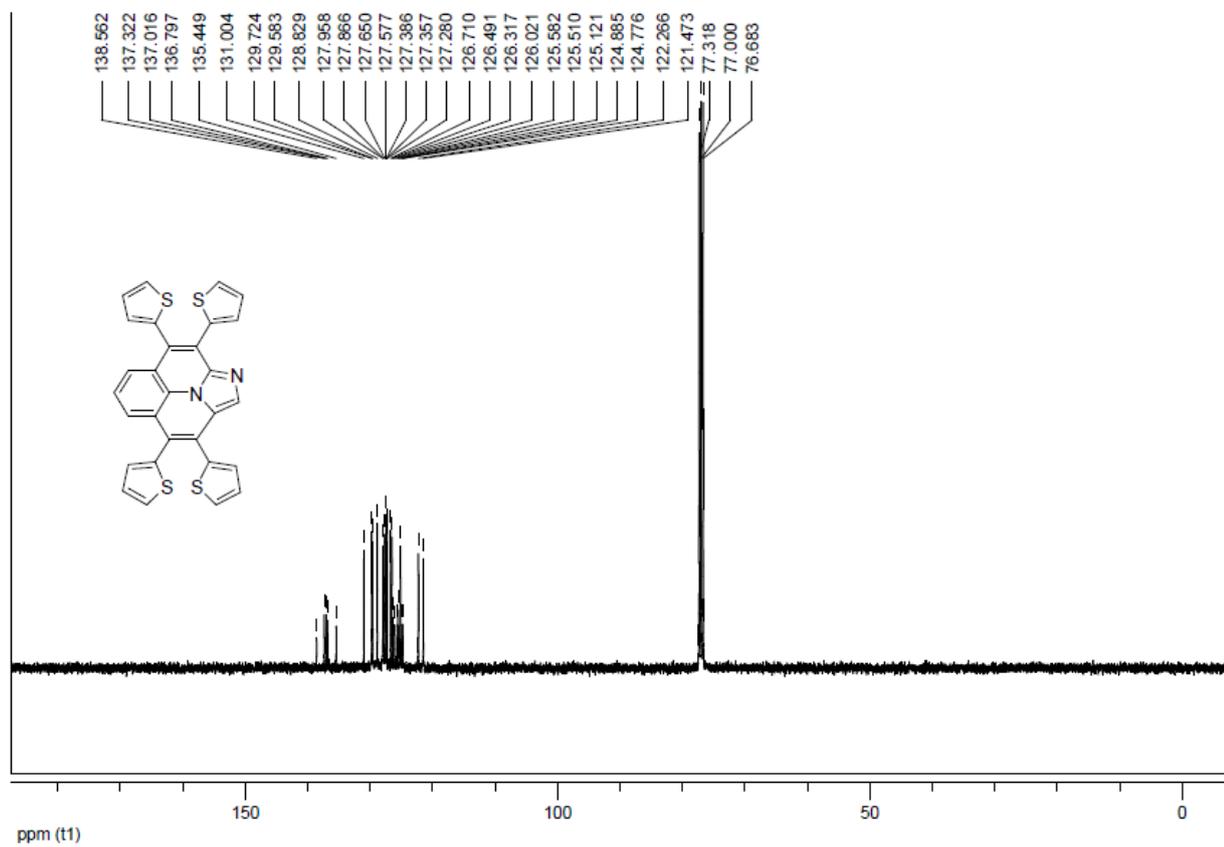
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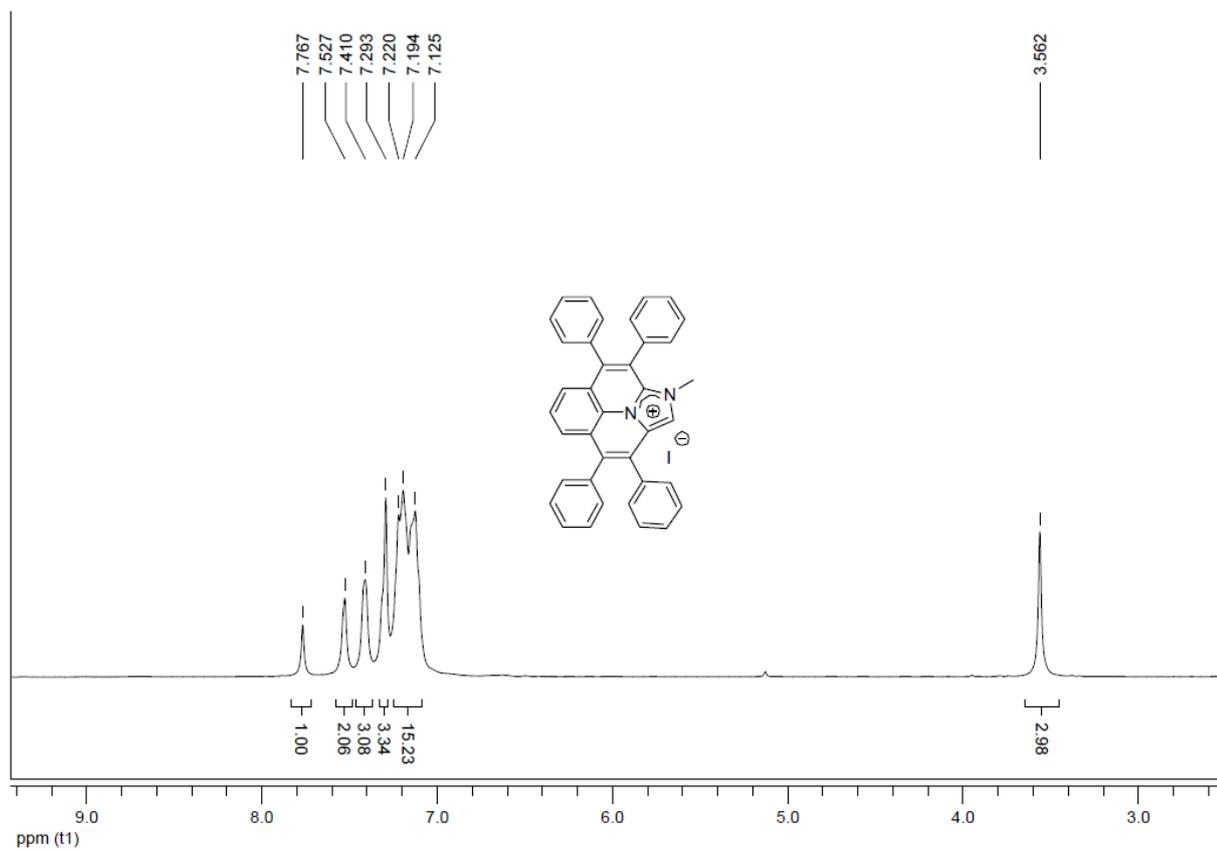
¹H NMR spectrum of **3ak**



¹³C NMR spectrum of **3ak**



¹H NMR spectrum of **5aa**



¹³C NMR spectrum of **5aa**

