Supplementary Information

Cp*Co(III)-catalyzed annulation of azines by C-H/N-N bond activation for the synthesis of isoquinolines

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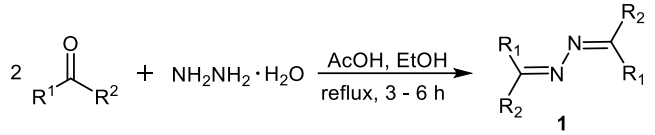
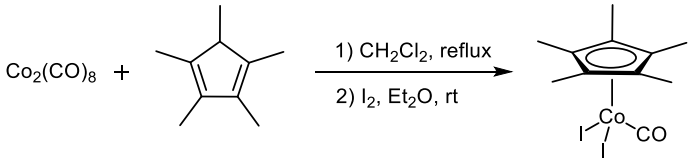
1. General experimental procedure for synthesis of ketazines[1]:



Ketazines were prepared by using of carbonyl compounds (10 mmol) and hydrazine hydrate 99% (5 mmol) in EtOH (15 mL) and glacial HOAc (0.3 mL). The reaction mixture was heated with a reflux condenser and magnetic stirrer at 75 ^{o}C for 3-6 h to obtain the corresponding ketazine. The progress of reaction was monitored by TLC. After completion of reaction, the solvent was evaporated under reduced pressure. The crystalline product was washed thoroughly with 30 mL of hexane (4-5 times) and dried to afford pure product.

2. Experimental procedure for synthesis of [Cp*Co(CO)I_2] catalyst[2]:



To a well-dried 2-necked 500-mL flask were successively added $Co_2(CO)_8$ (14.6 mmol), degassed CH_2Cl_2 (100 mL) and pentamethylcyclopentadiene (35.4 mmol). The mixture was refluxed under argon stream for 6 h and then cooled to room temperature. The solvent was removed in vacuo. The residue was dissolved in degassed Et_2O (50 mL) and then iodine (35.5 mmol) in degassed Et_2O (50 mL) was added dropwise at room temperature with stirring. After the mixture was stirred at room temperature for 1 h, the solvent was evaporated. Resulting residue was purified by silica gel column chromatography (hexane then CH_2Cl_2/hexane=4/1) to afford deep purple crystalline solid.

3. Mechanistic studies: (ESI-MS analysis of intermediates)[3]

ESI-MS analysis of the reaction mixture was carried out to predict the mechanism of the transformation. Annulation reaction of **1aa** with **2aa** was performed under standard reaction condition for the period of 3 hour in order to isolate the possible intermediates and metal complexes. After performing the reaction for 3 hour, the reaction mixture was cooled, filtered through a celite pad and diluted with methanol. ESI-MS analysis of the diluted reaction mixture was performed. The spectra obtained clearly indicates the formation of intermediate **III** and **VI** along with starting azine **1a** and final product **3aa** as shown in proposed reaction mechanism (Scheme 3).

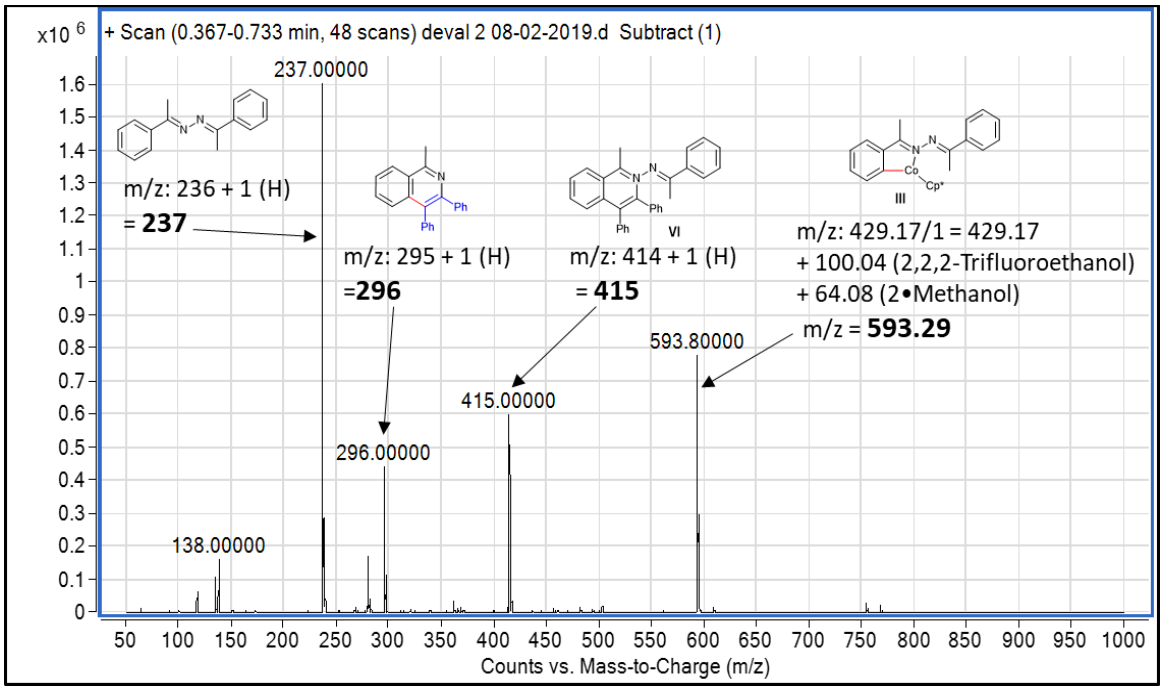


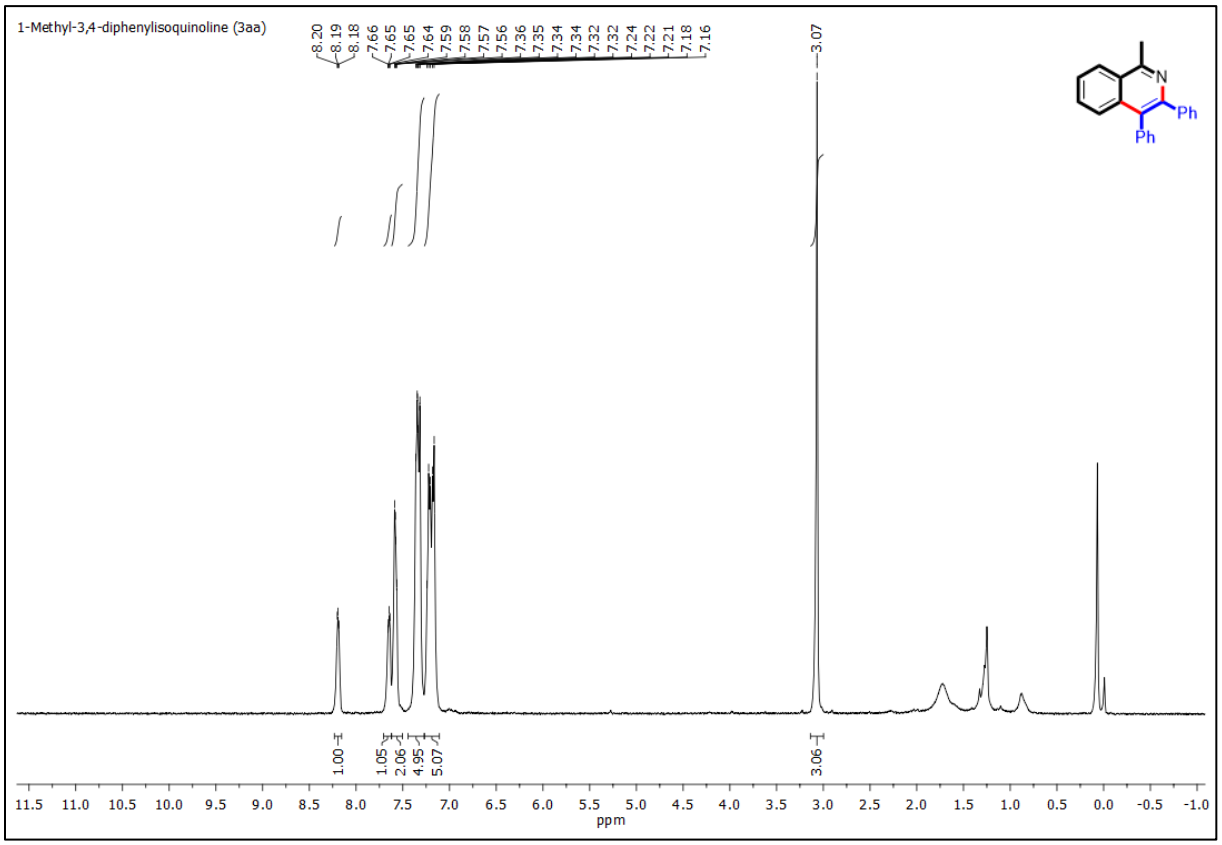
Fig. ESI-MS analysis of the reaction mixture

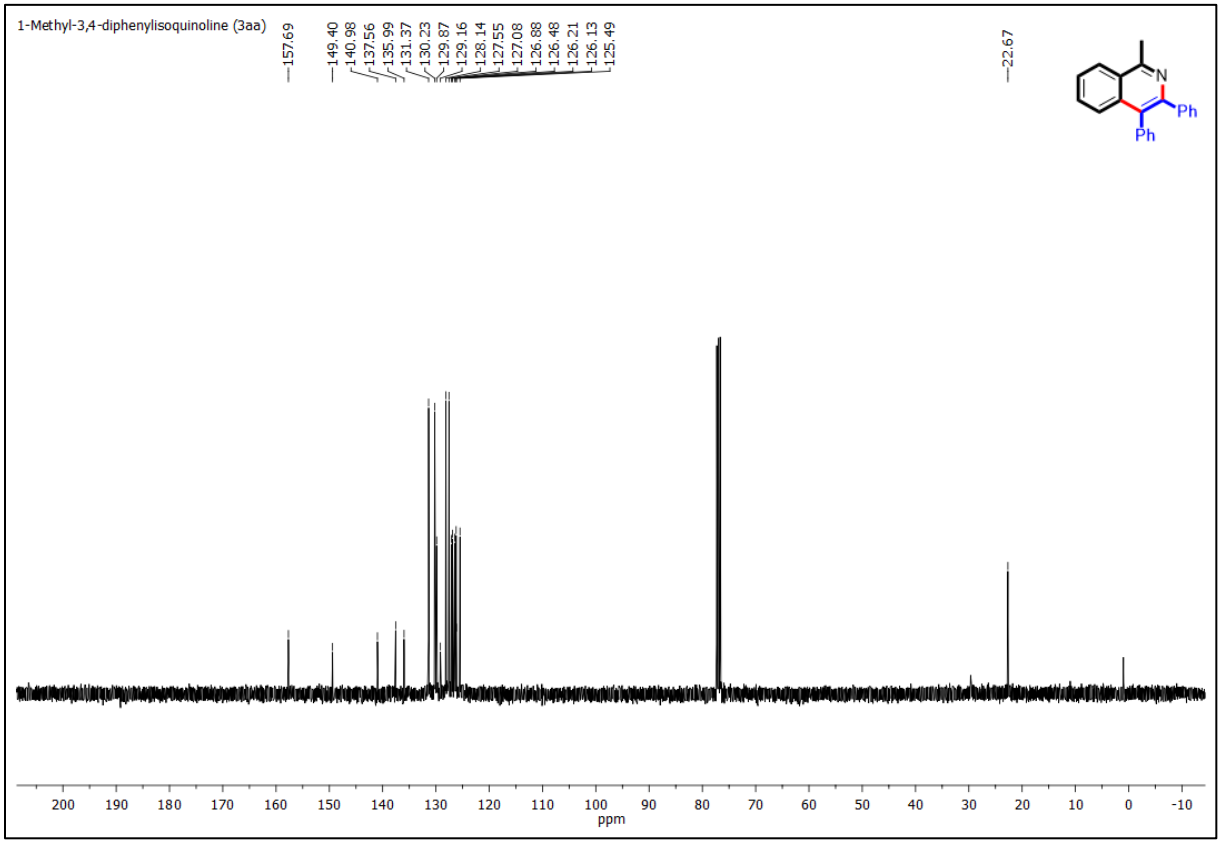
References:

1. G. H. Daub and L. F. Cannizzo, *J. Org. Chem.*, 1982, **47**, 5035.
2. B. Sun, T. Yoshino, S. Matsunaga and M. Kanai, *Adv. Synth. Catal.*, 2014, **356**, 1491.
3. (a) D. Phapale, A. Kushwaha and D. Das, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2019, **214**, 111; (b) G. J. Park, G. R. You, Y. W. Choi and C. Kim, *Sensors and Actuators B*, 2016, **229**, 257 (c) S. K. Patil and Dipanwita Das, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2019, **210**, 44 (d) D. Phapale, A. Gaikwad and D. Das, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2017, **178**, 160.

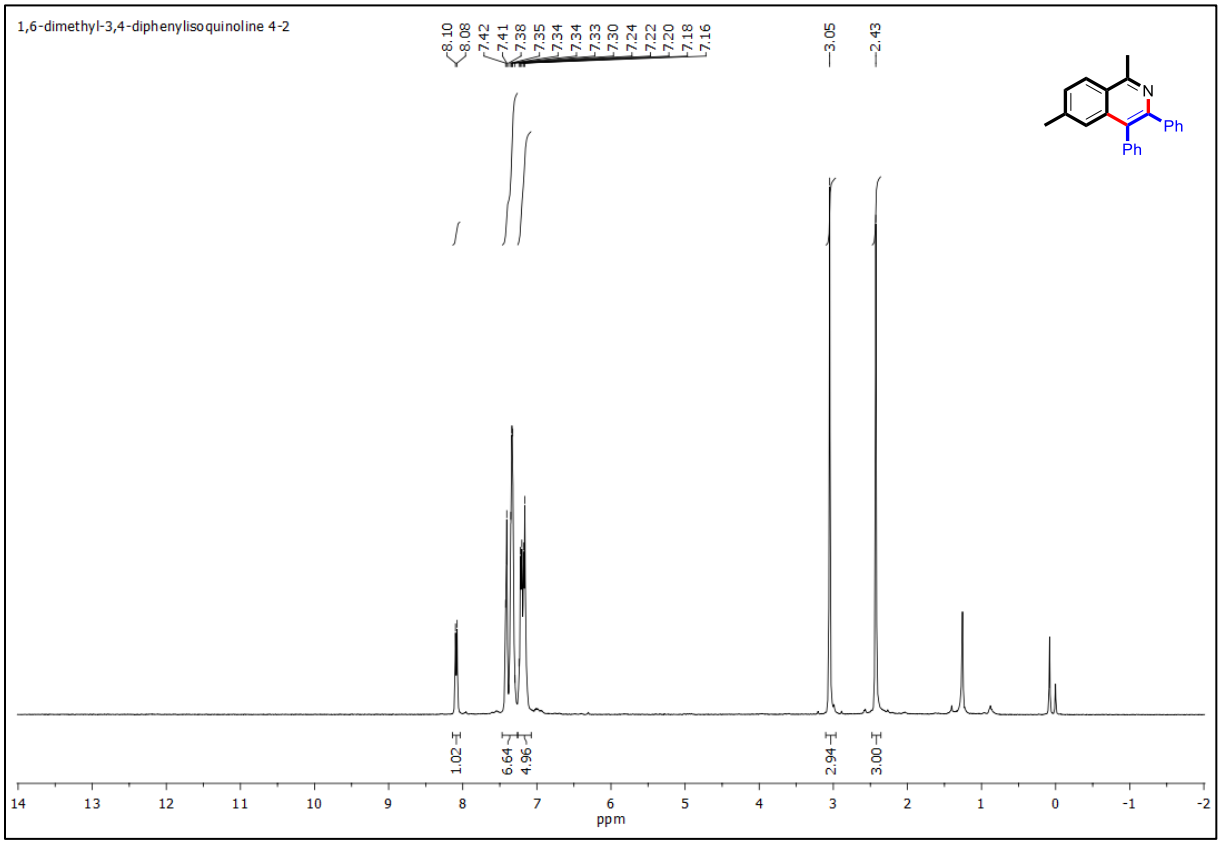
4. Copies for ^{1}H NMR and ^{3}C NMR spectra of the isoquinoline products (3)

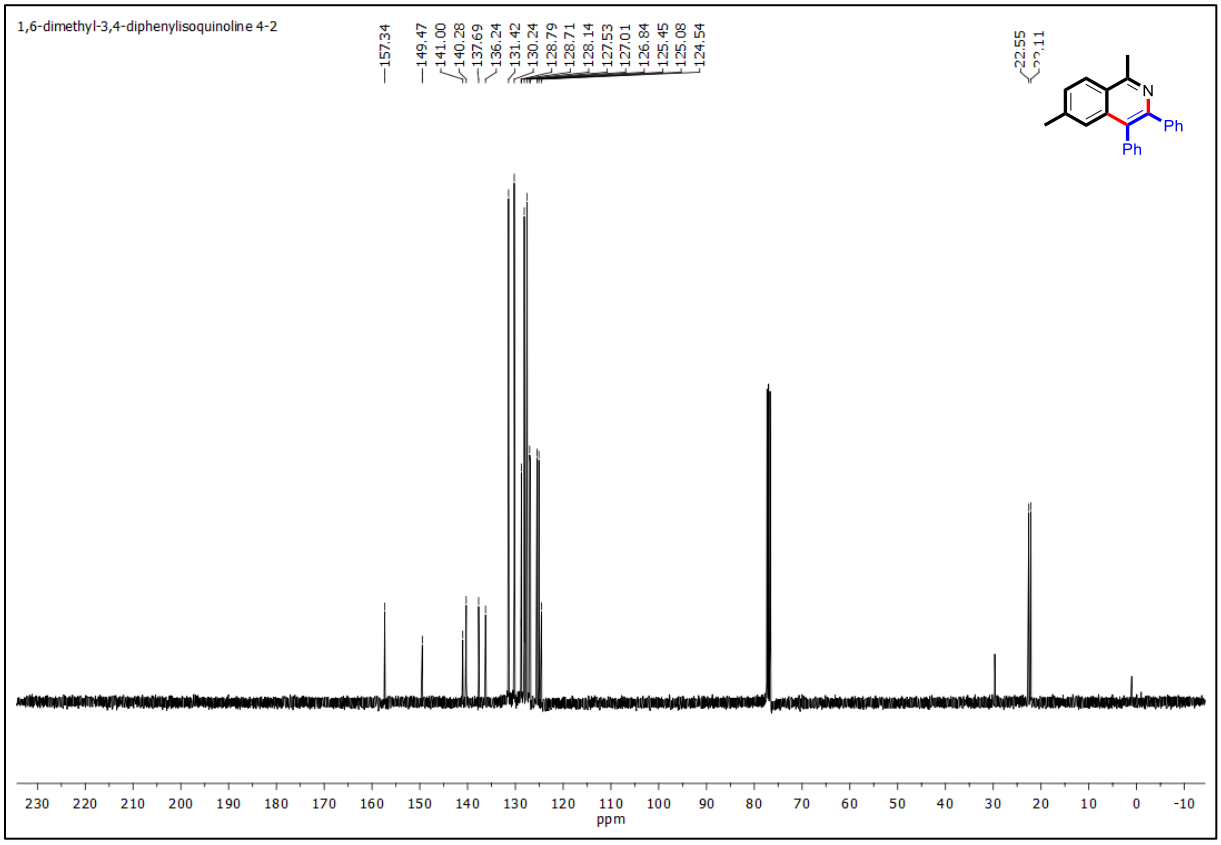
^{1}H & ^{13}C NMR of 1-Methyl-3,4-diphenylisoquinoline (3aa)



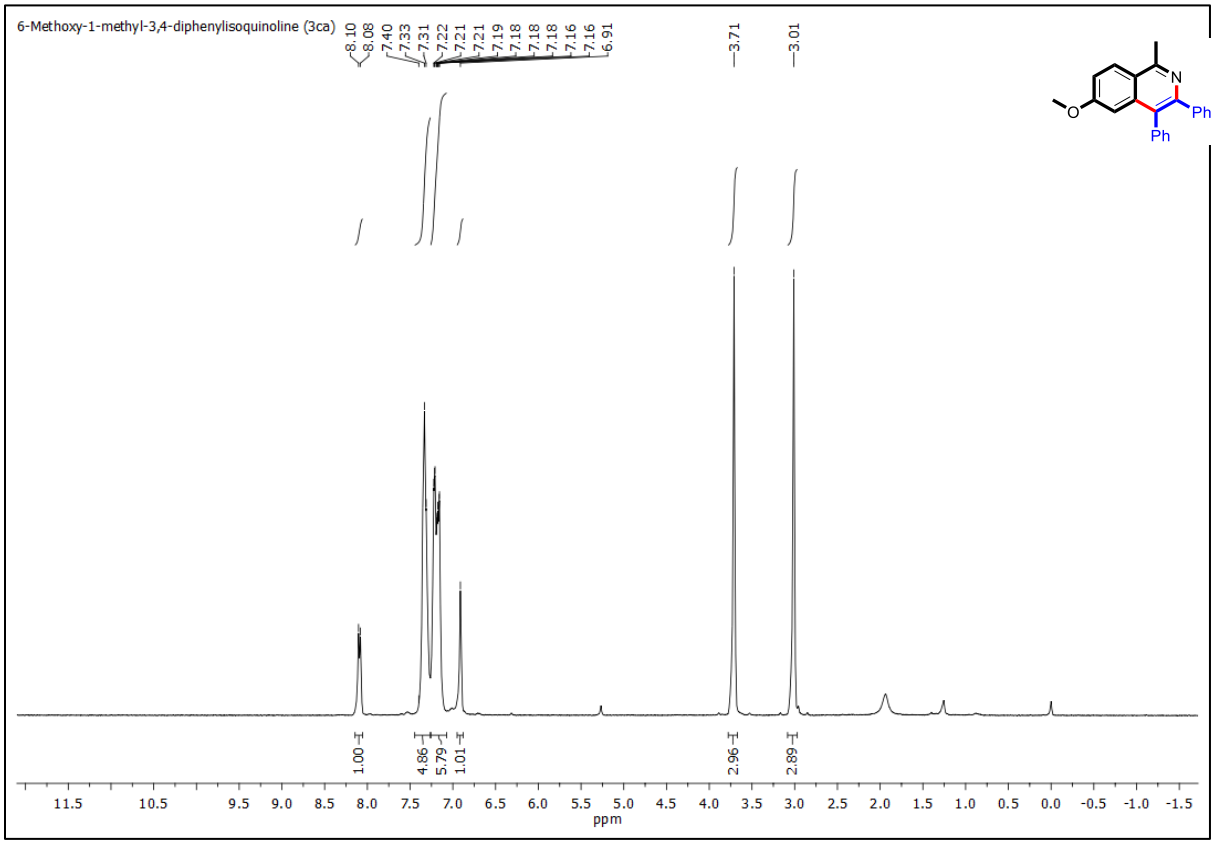


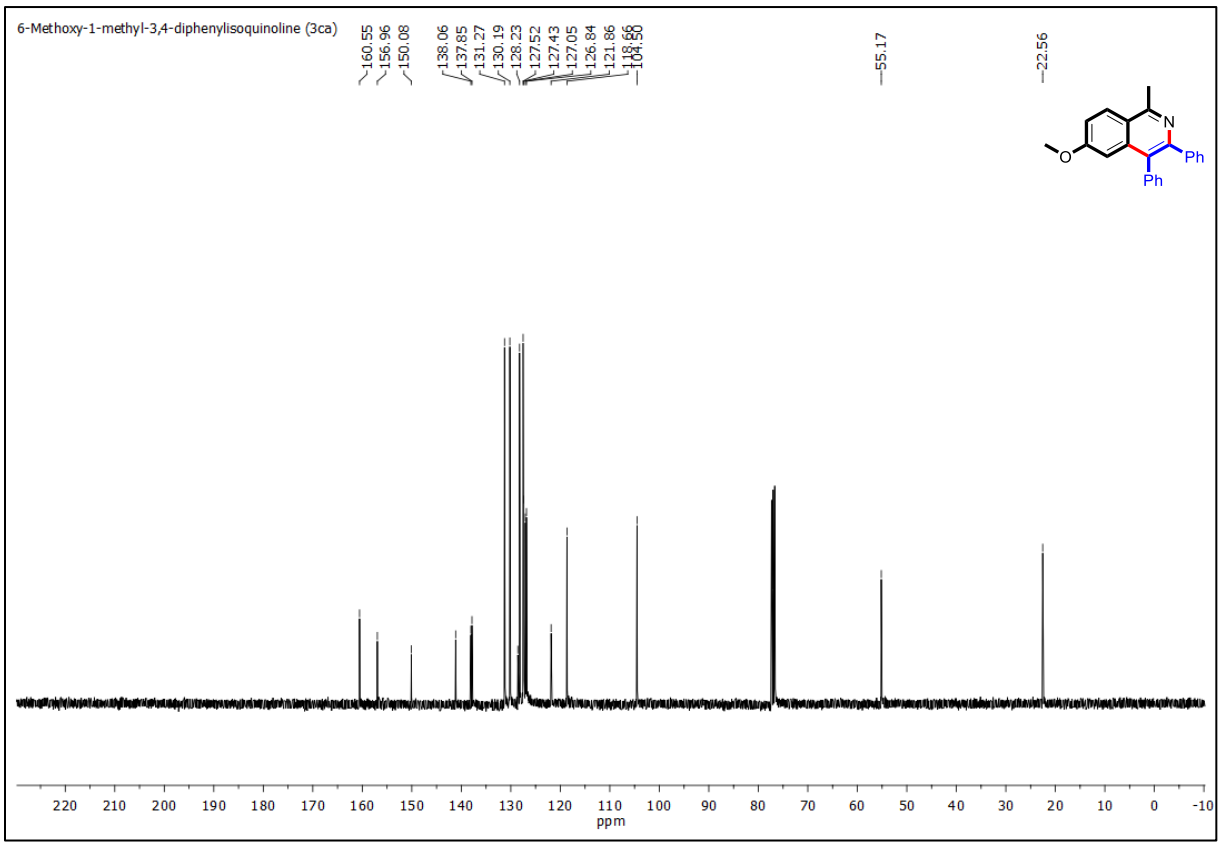
^{1}H & ^{13}C NMR of 1,6-Dimethyl-3,4-diphenylisoquinoline (3ba)



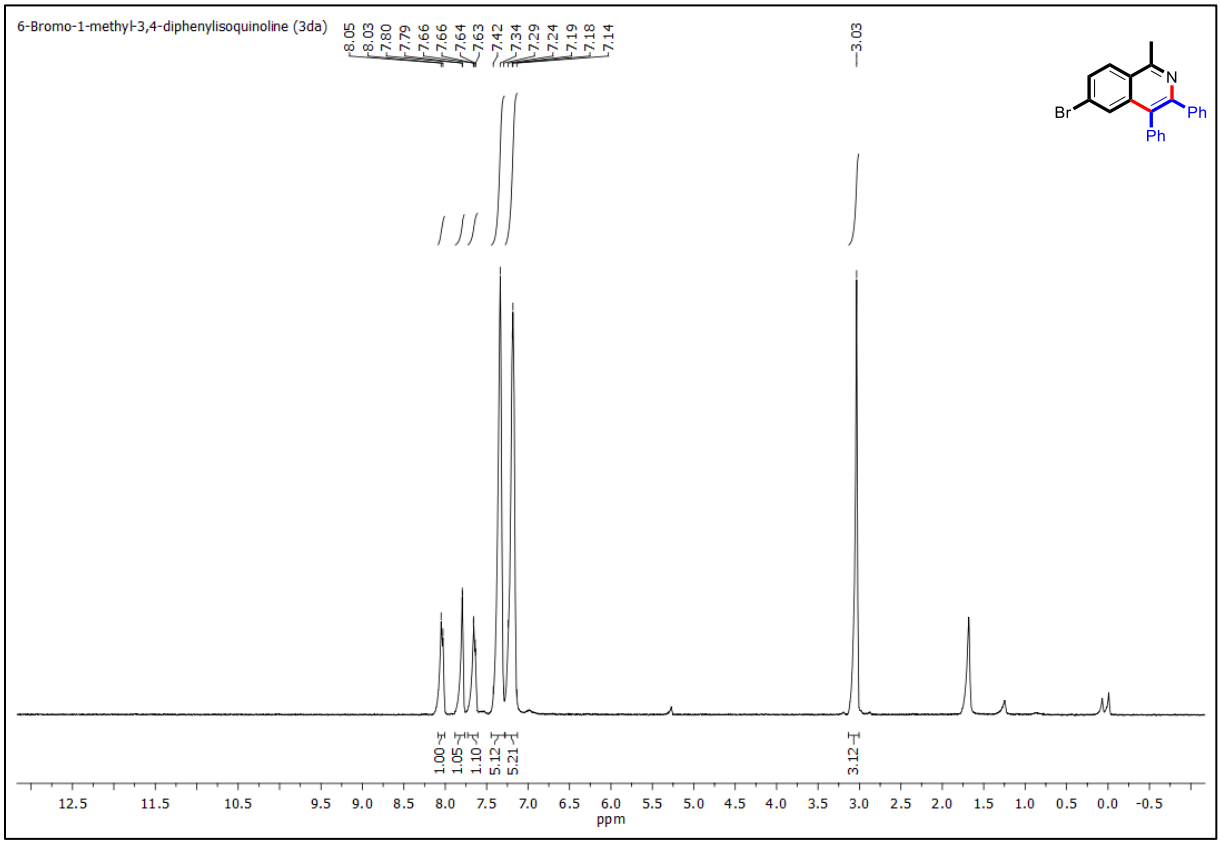


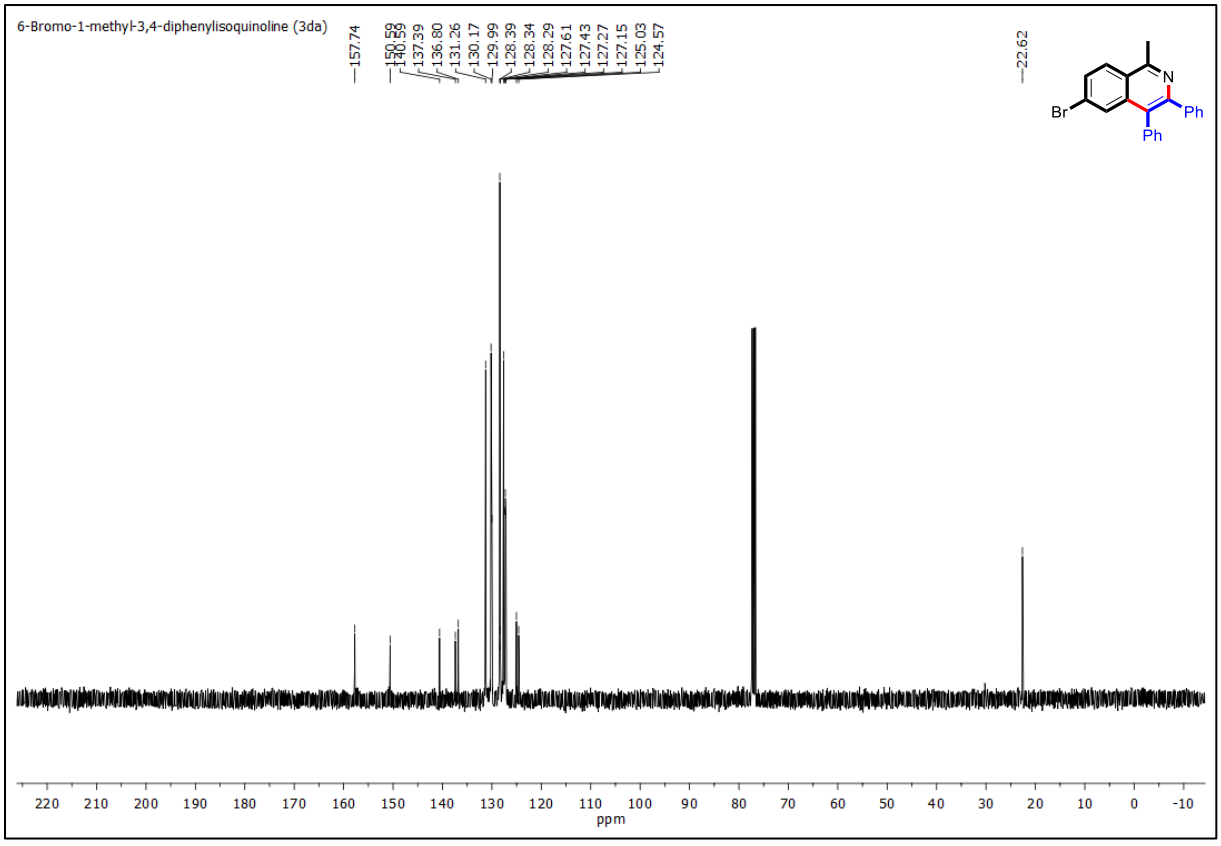
^{1}H & ^{13}C NMR of 6-Methoxy-1-methyl-3,4-diphenylisoquinoline (3ca)



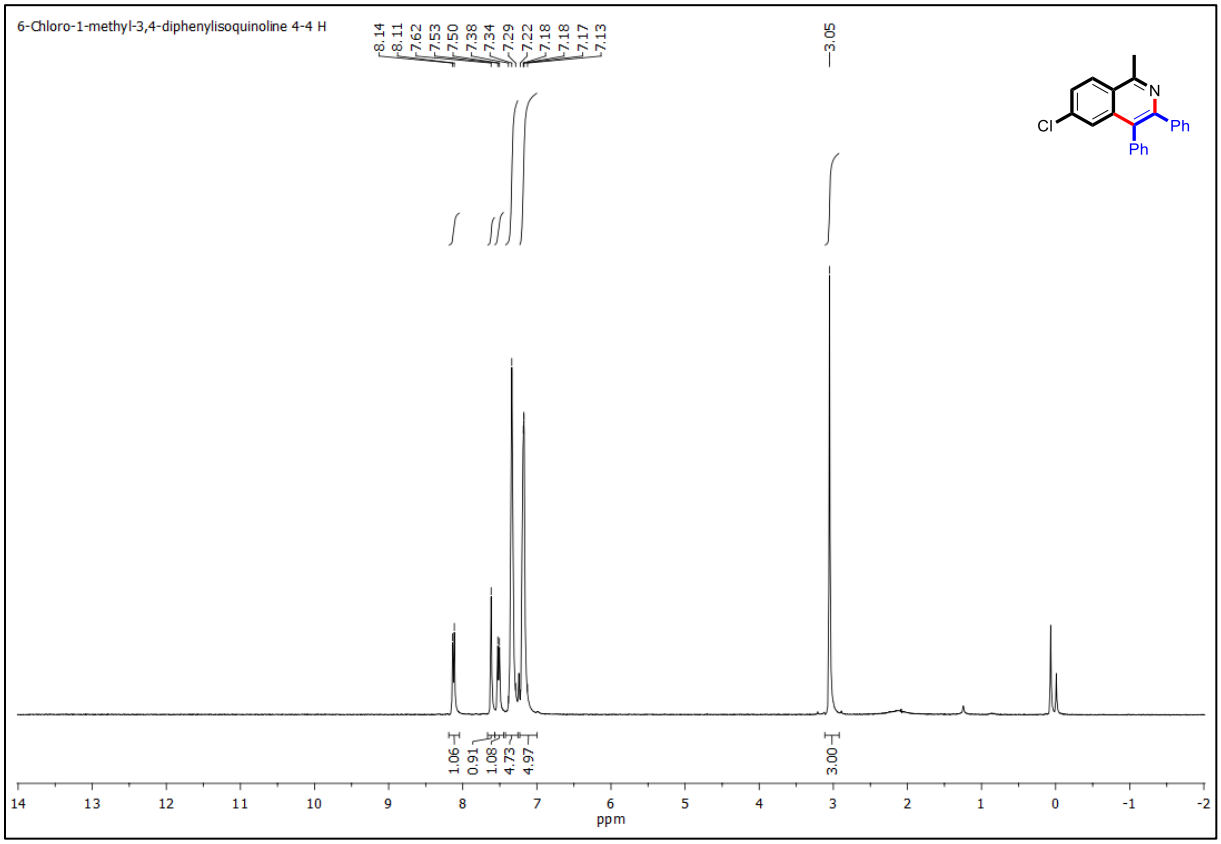


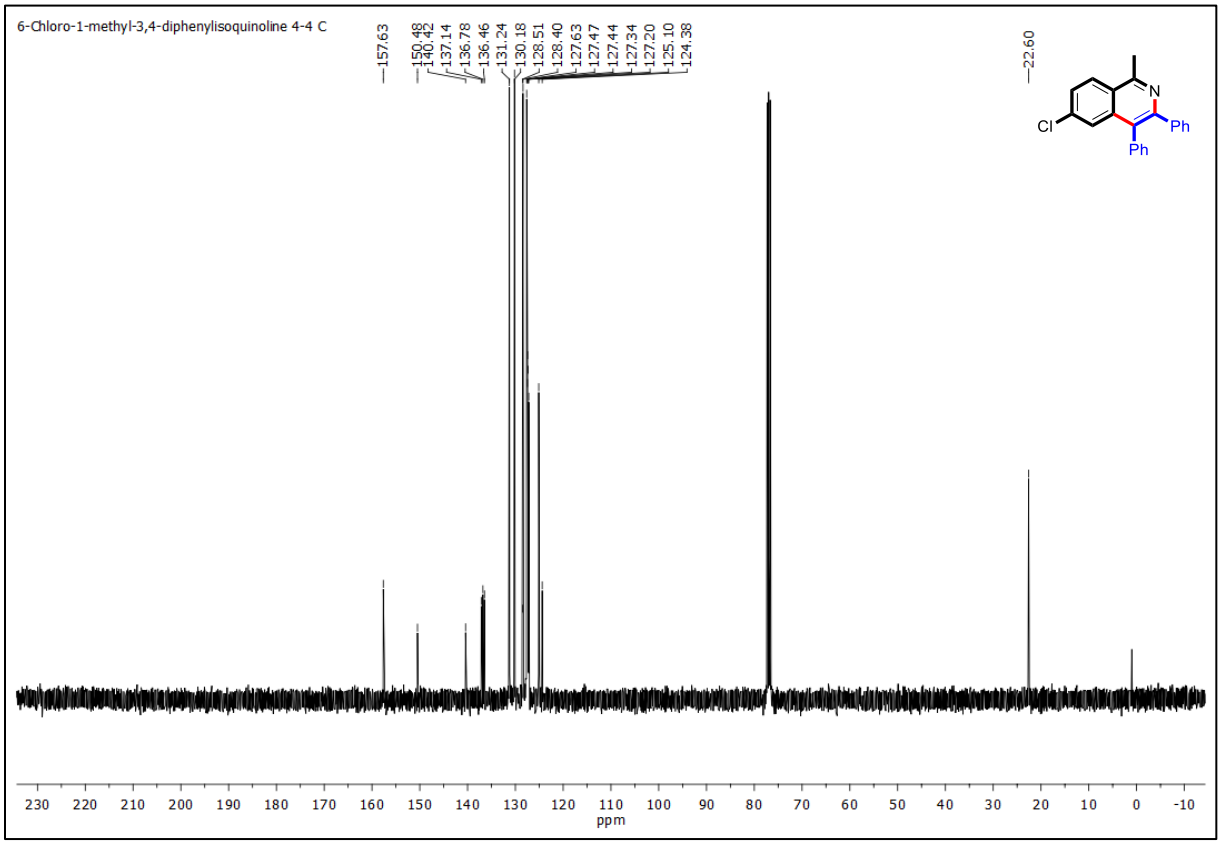
^{1}H & ^{13}C NMR of 6-Bromo-1-methyl-3,4-diphenylisoquinoline (3da)





^{1}H & ^{13}C NMR of 6-Chloro-1-methyl-3,4-diphenylisoquinoline (3ea)





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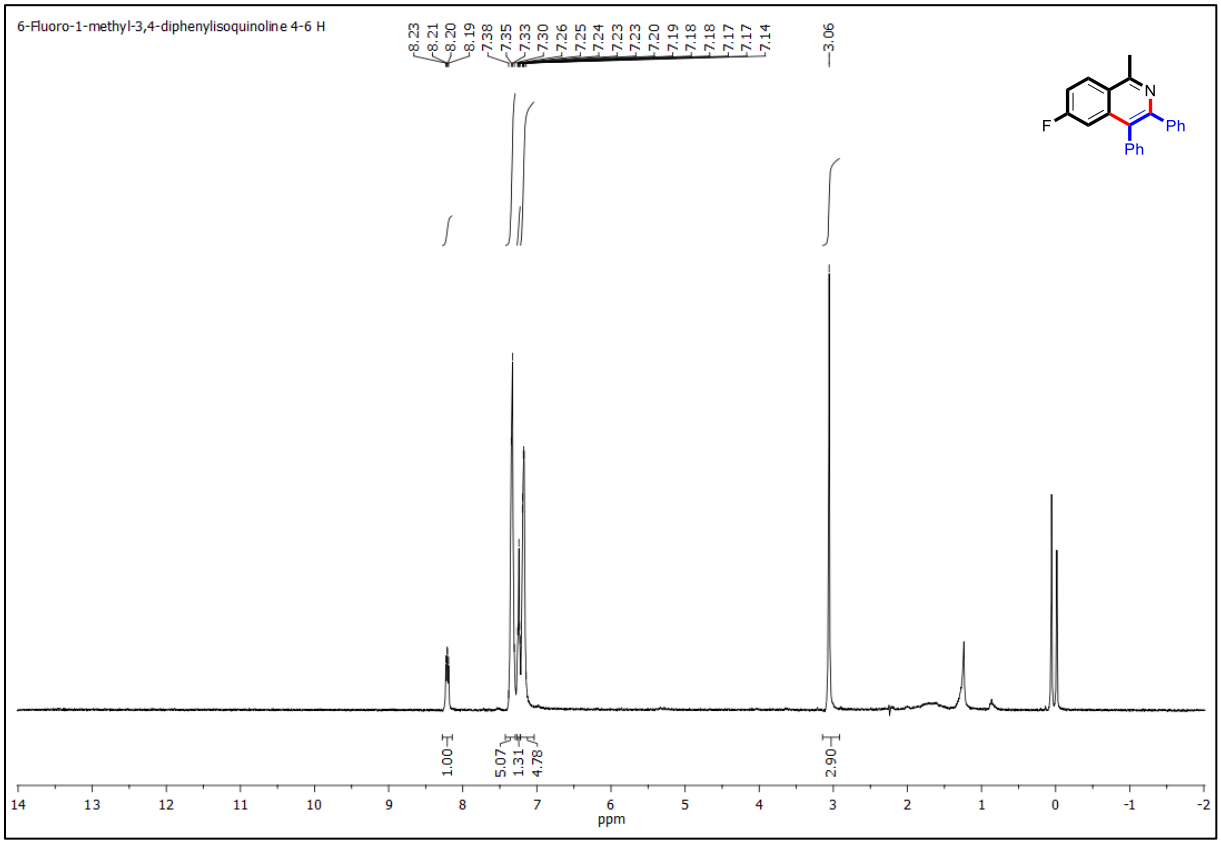
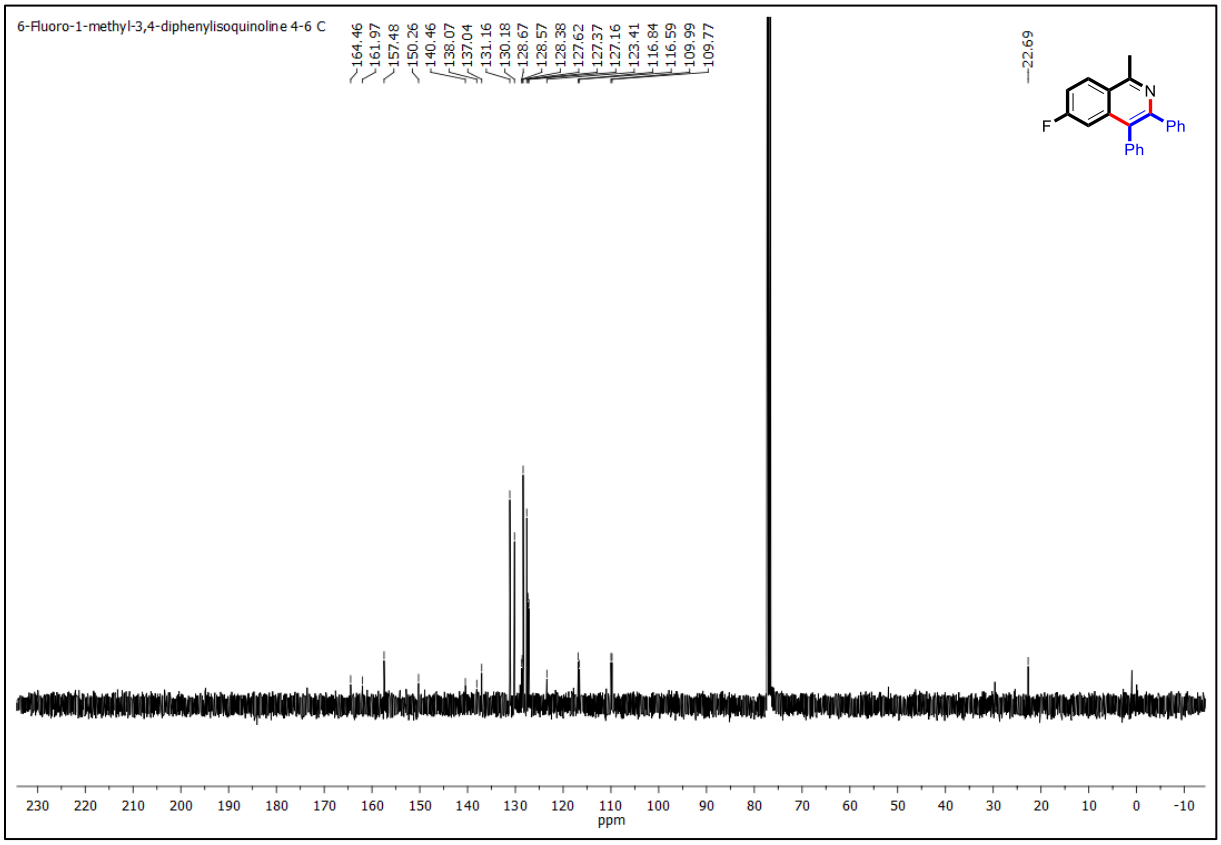
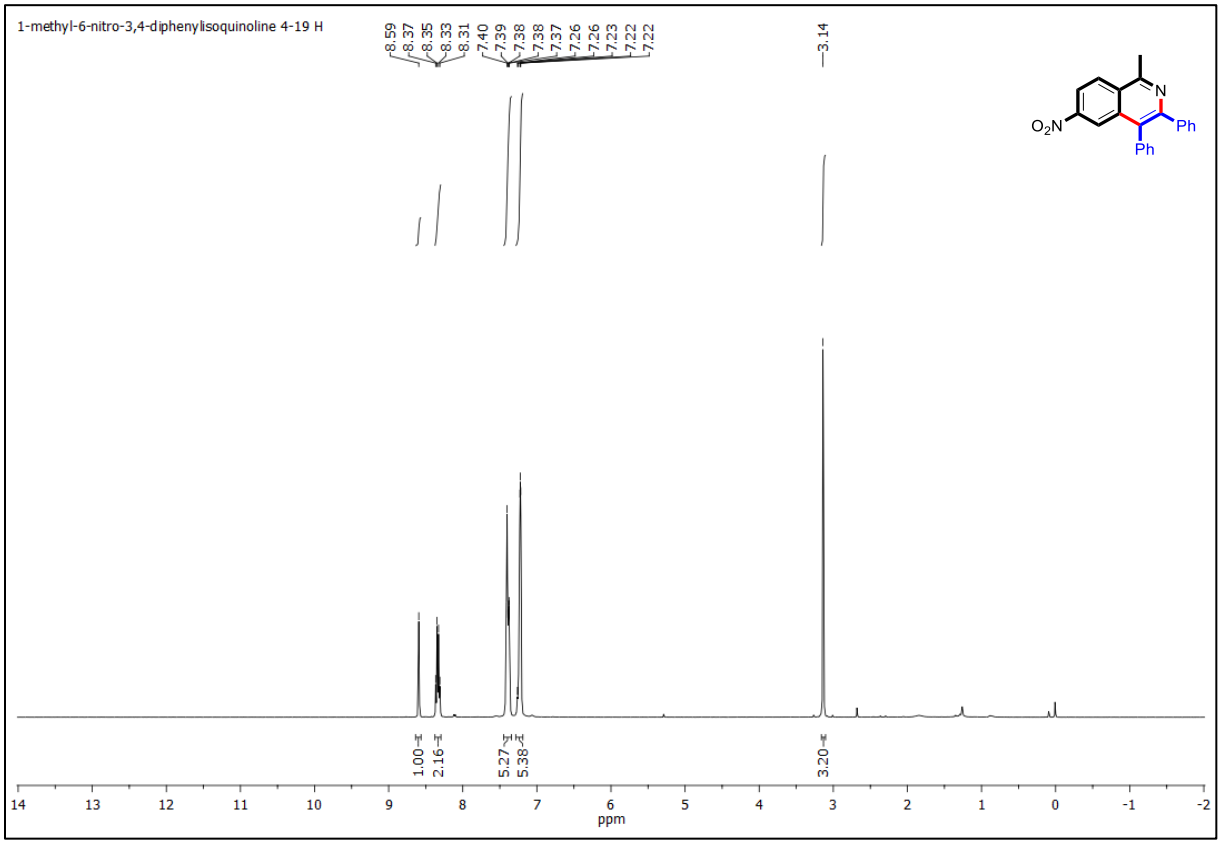
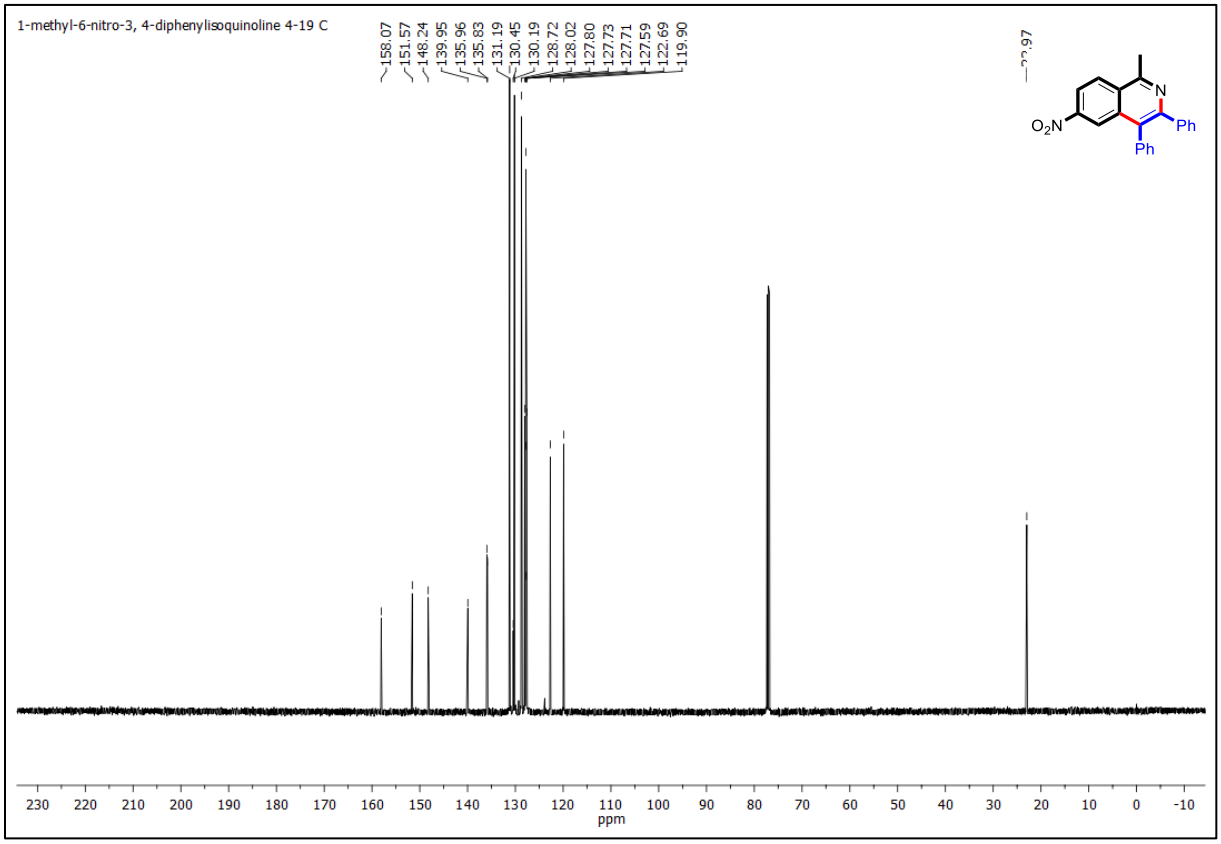


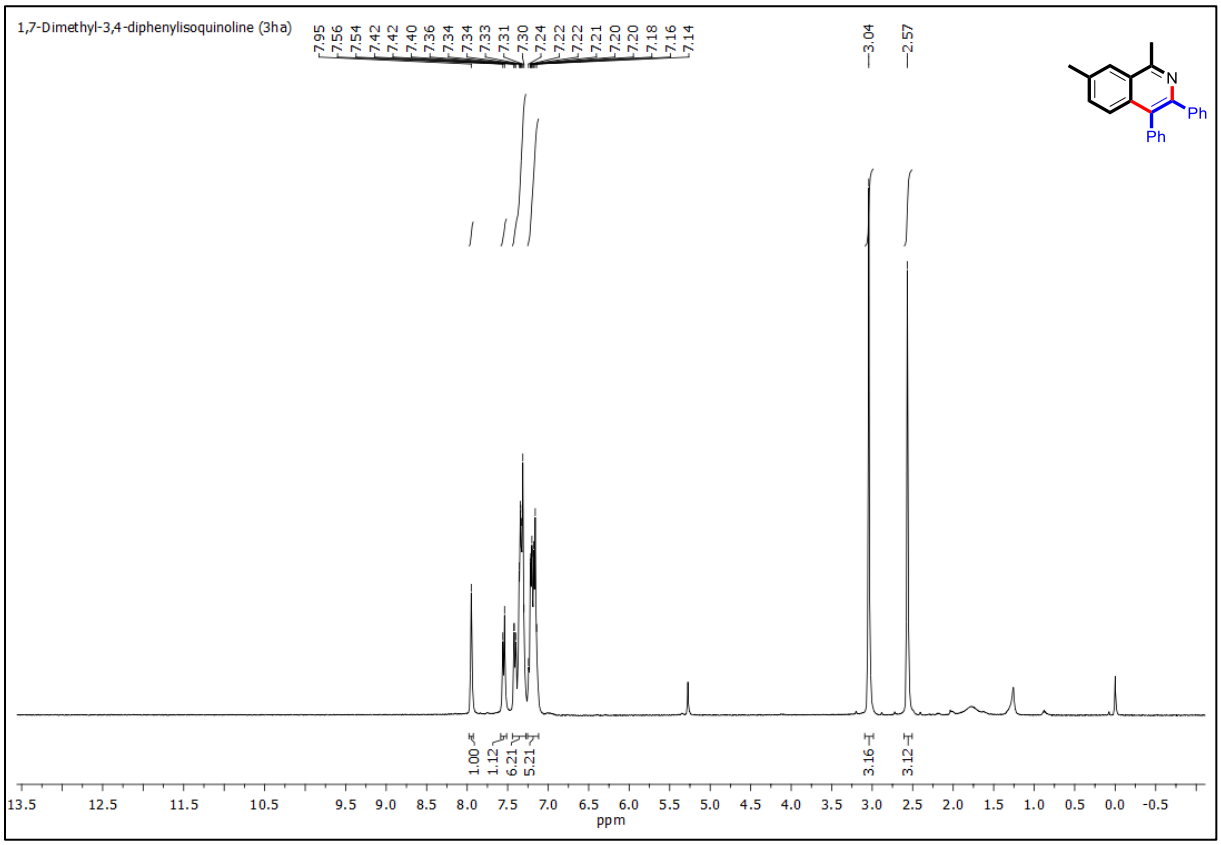


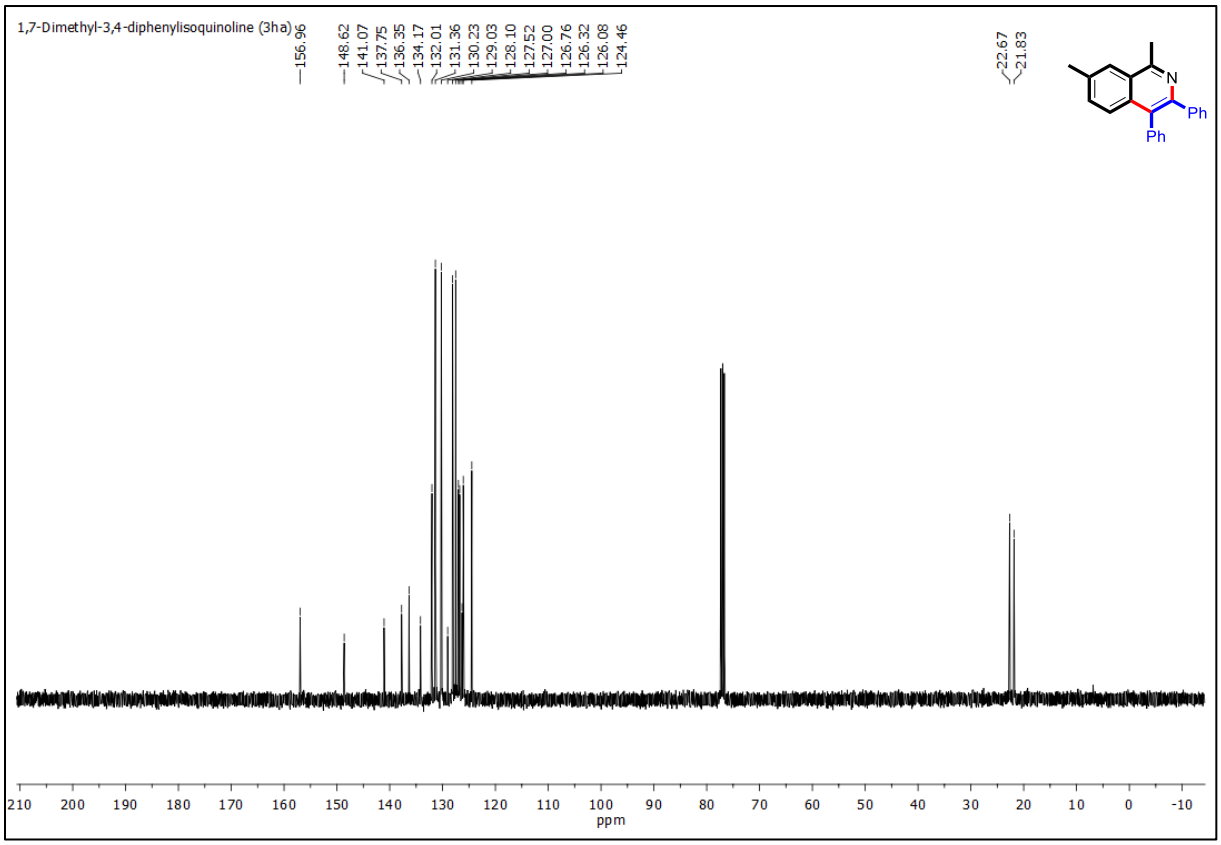
^{1}H & ^{13}C NMR of 1-Methyl-6-nitro-3,4-diphenylisoquinoline (3ga)



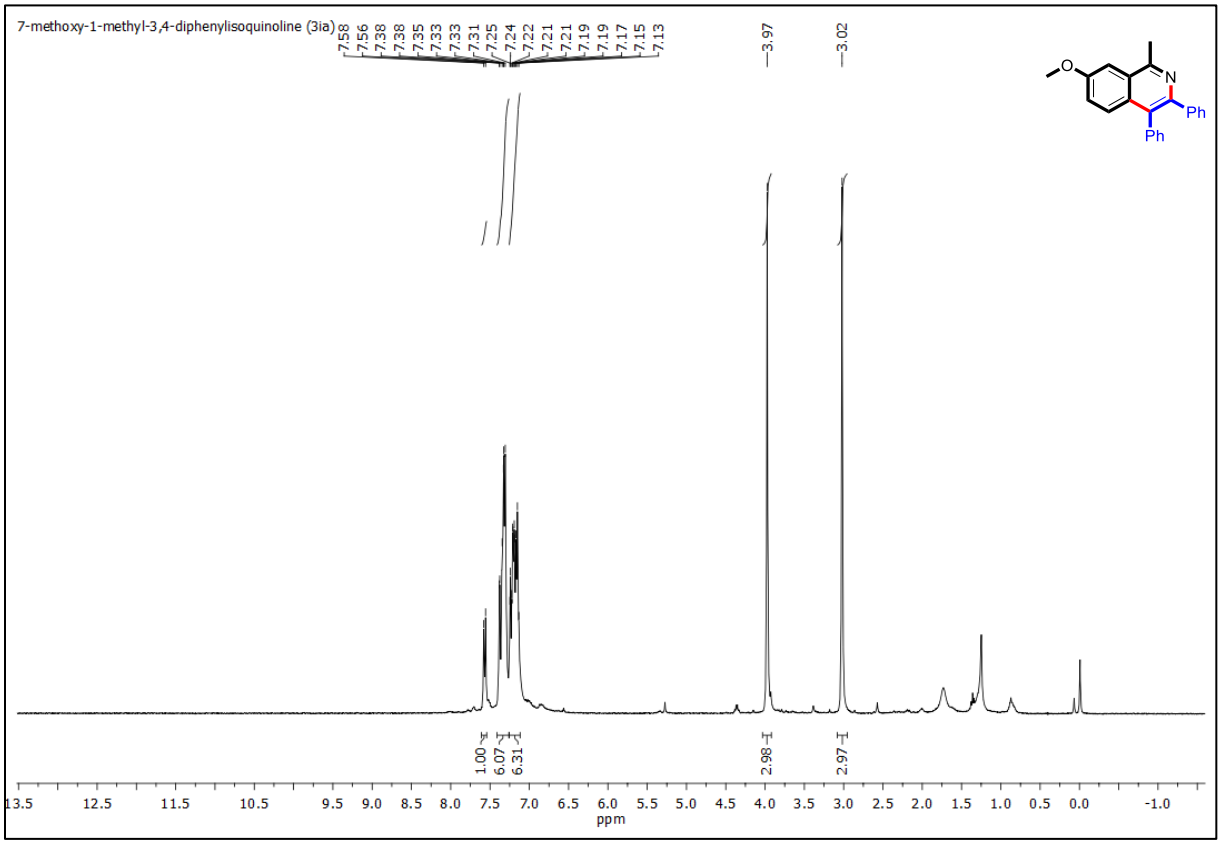


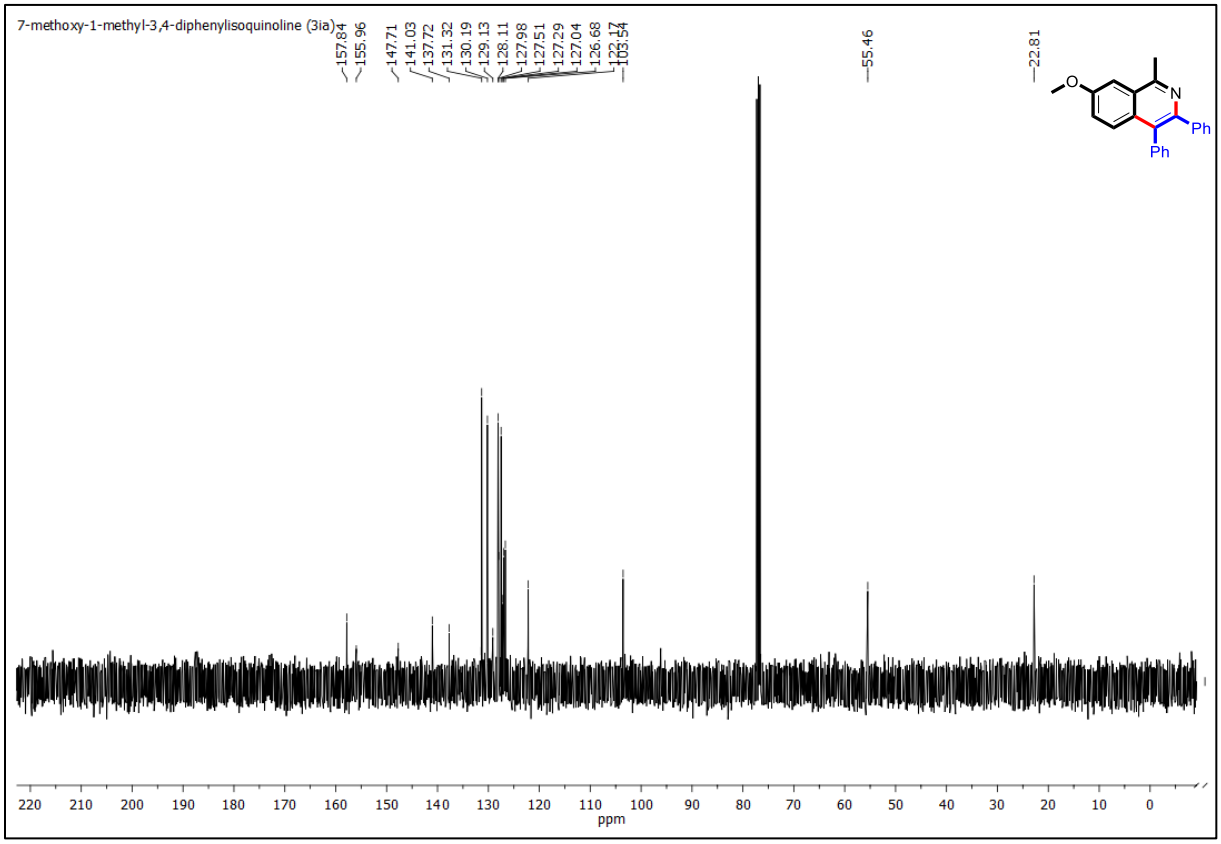
^{1}H & ^{13}C NMR of 1,7-Dimethyl-3,4-diphenylisoquinoline (3ha)



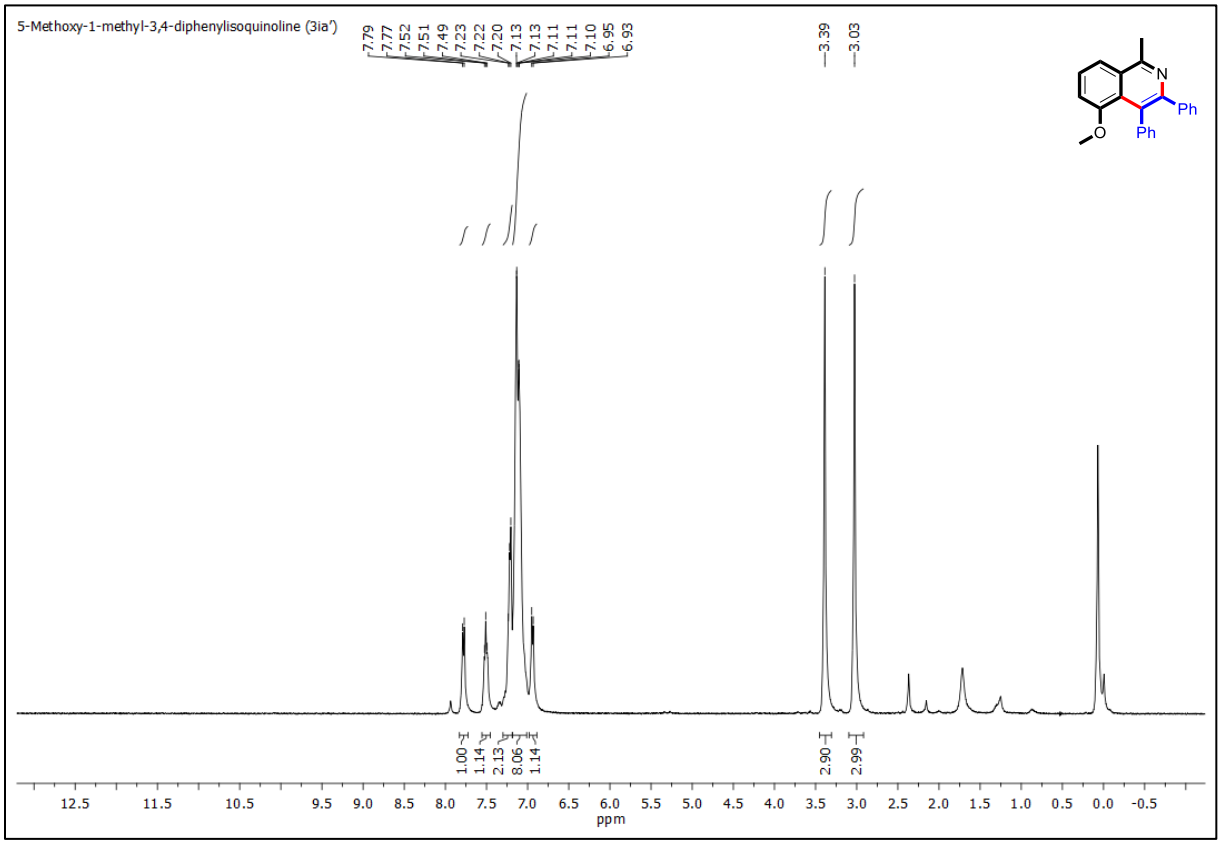


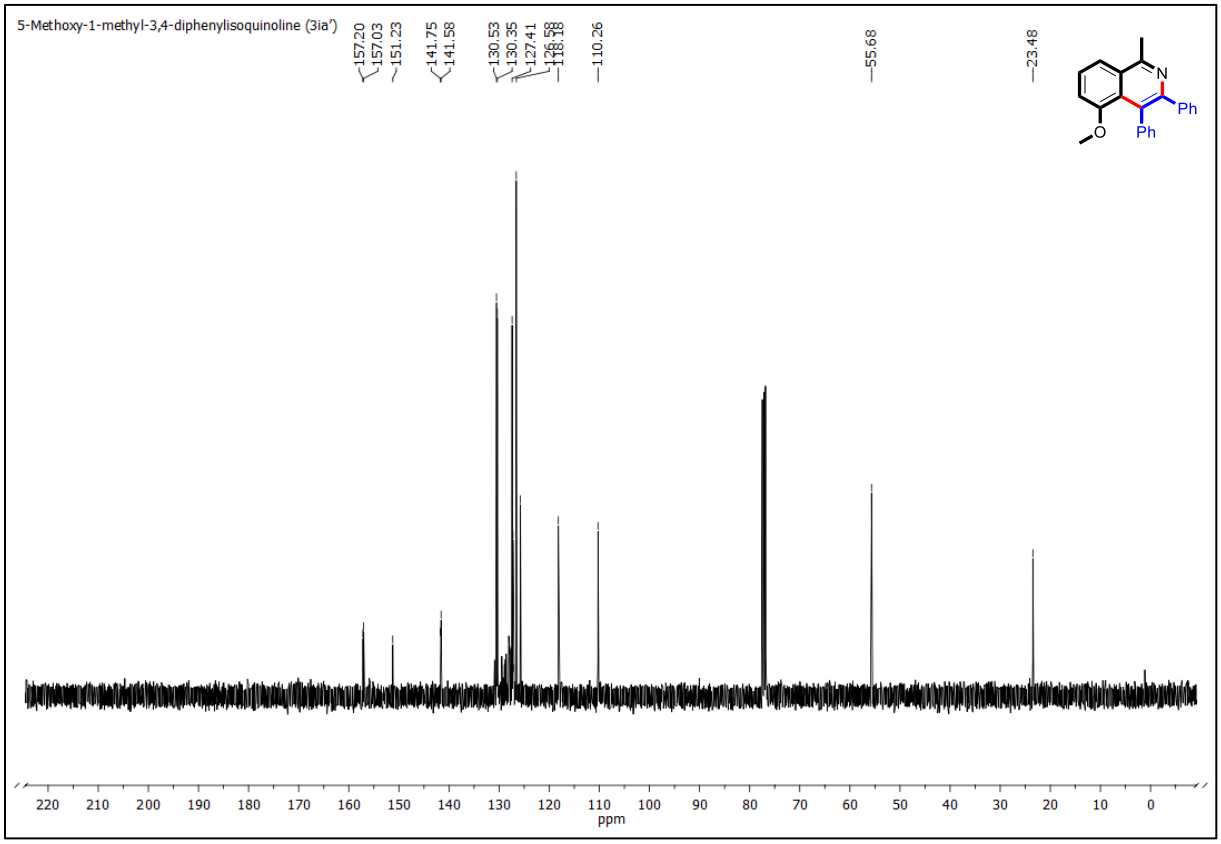
^{1}H & ^{13}C NMR of 7-Methoxy-1-methyl-3,4-diphenylisoquinoline (3ia)



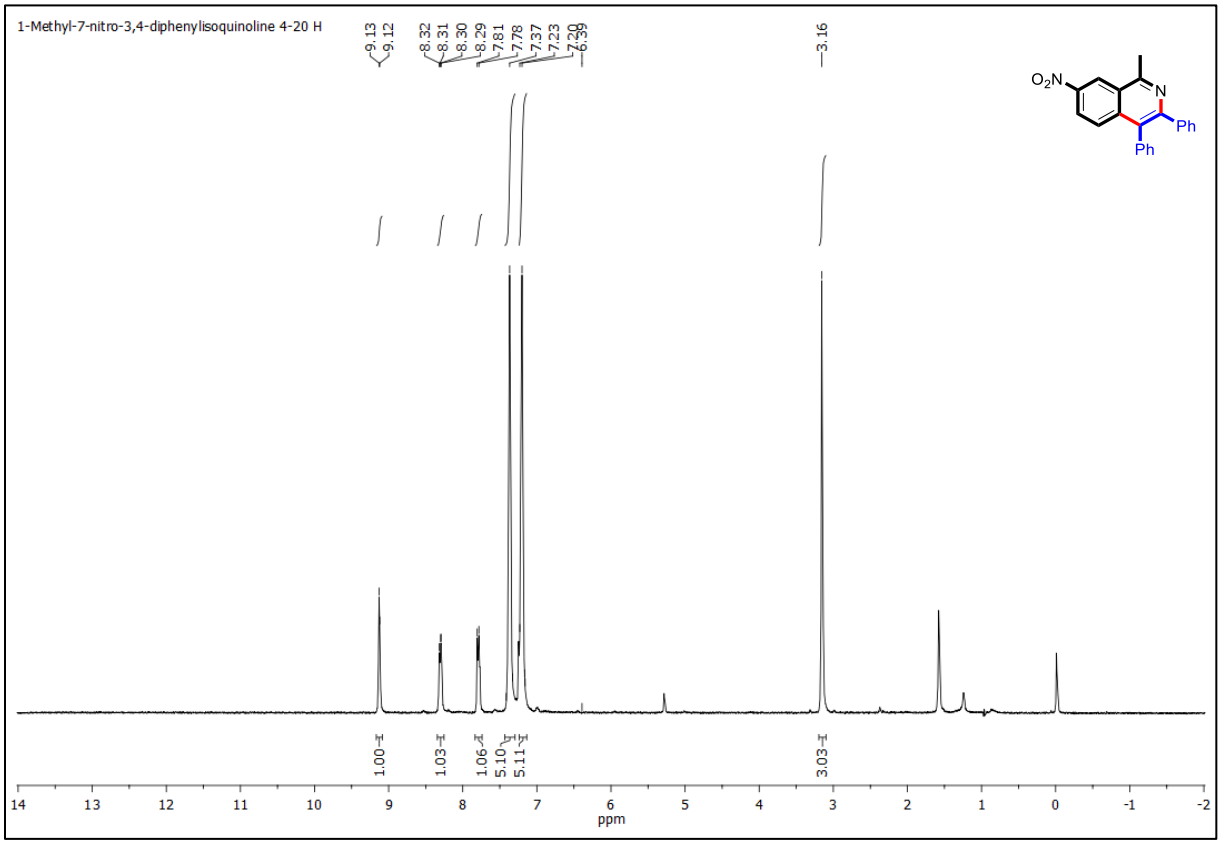


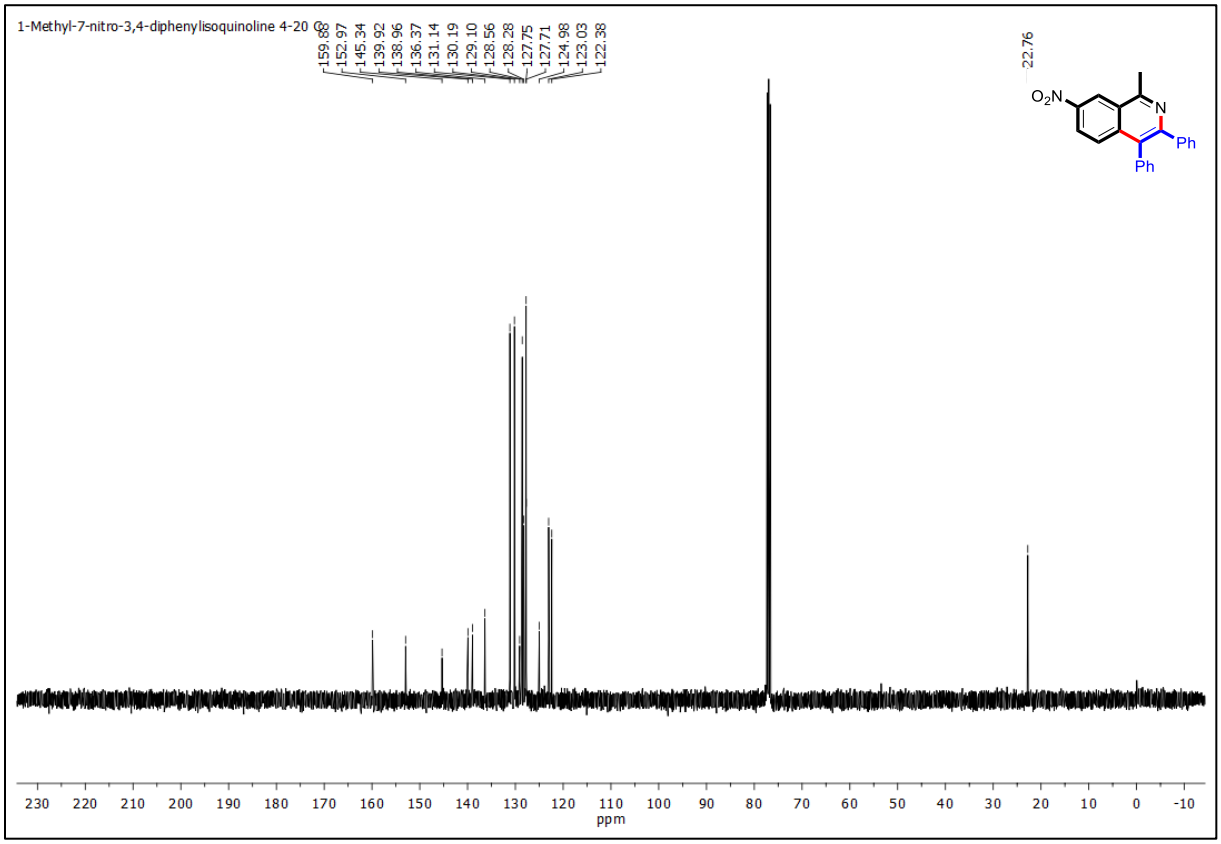
^{1}H & ^{13}C NMR of 5-Methoxy-1-methyl-3,4-diphenylisoquinoline (3ia')



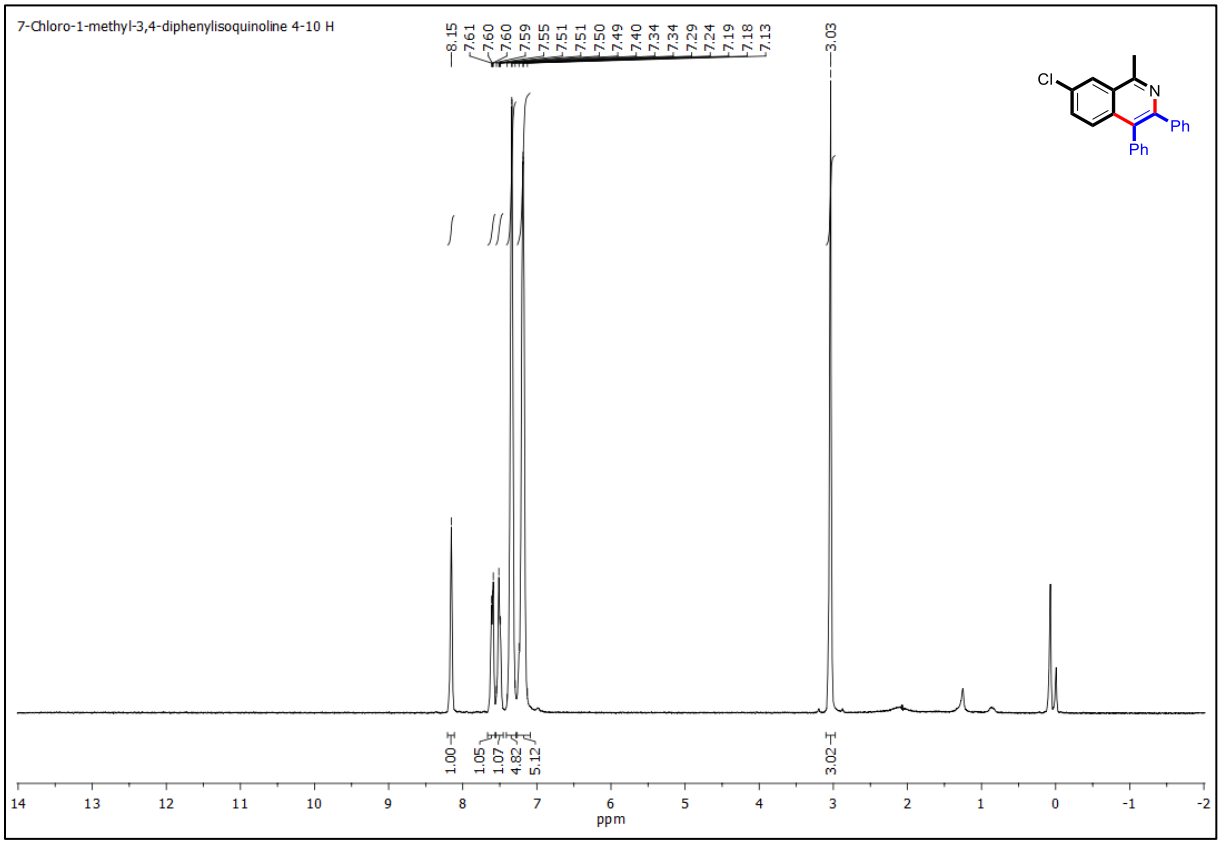


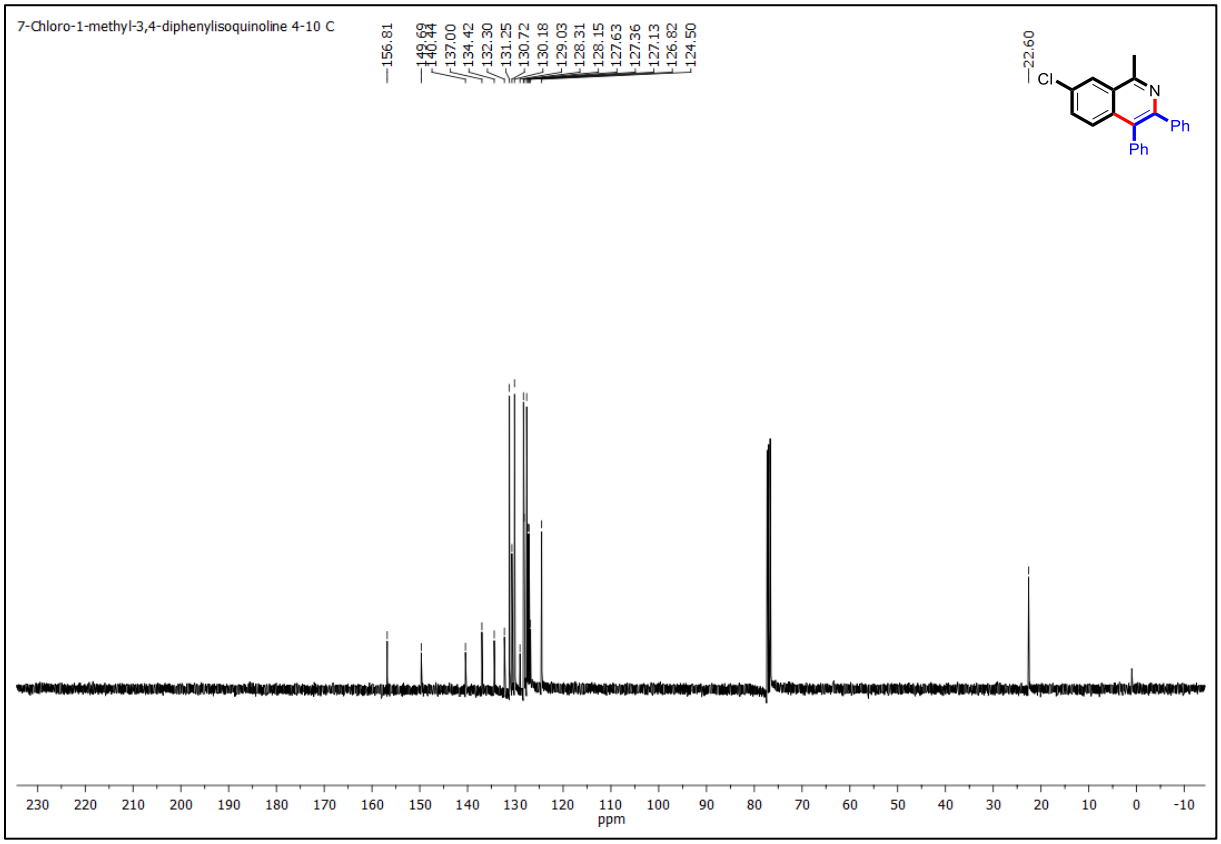
^{1}H & ^{13}C NMR of 1-Methyl-7-nitro-3,4-diphenylisoquinoline (3ja)



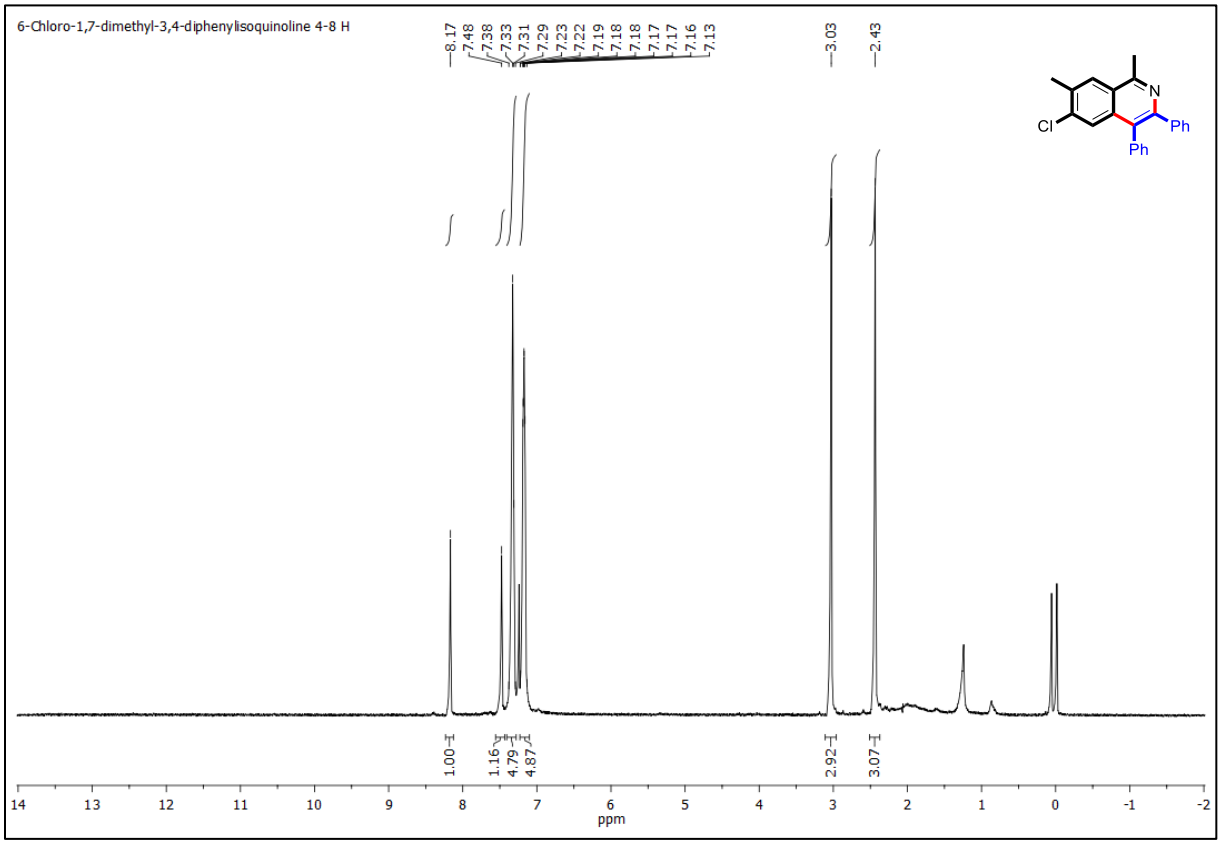


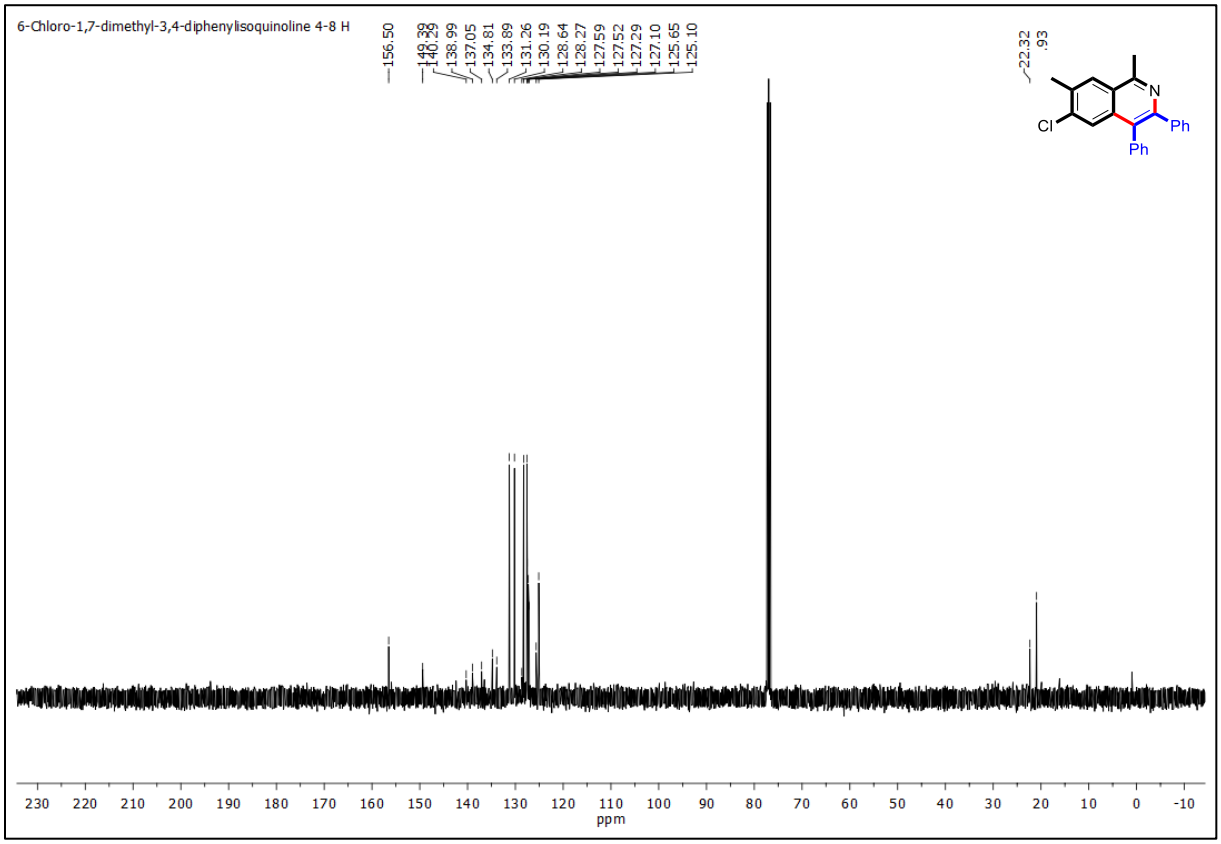
^{1}H & ^{13}C NMR of 7-Chloro-1-methyl-3,4-diphenylisoquinoline (3ka)



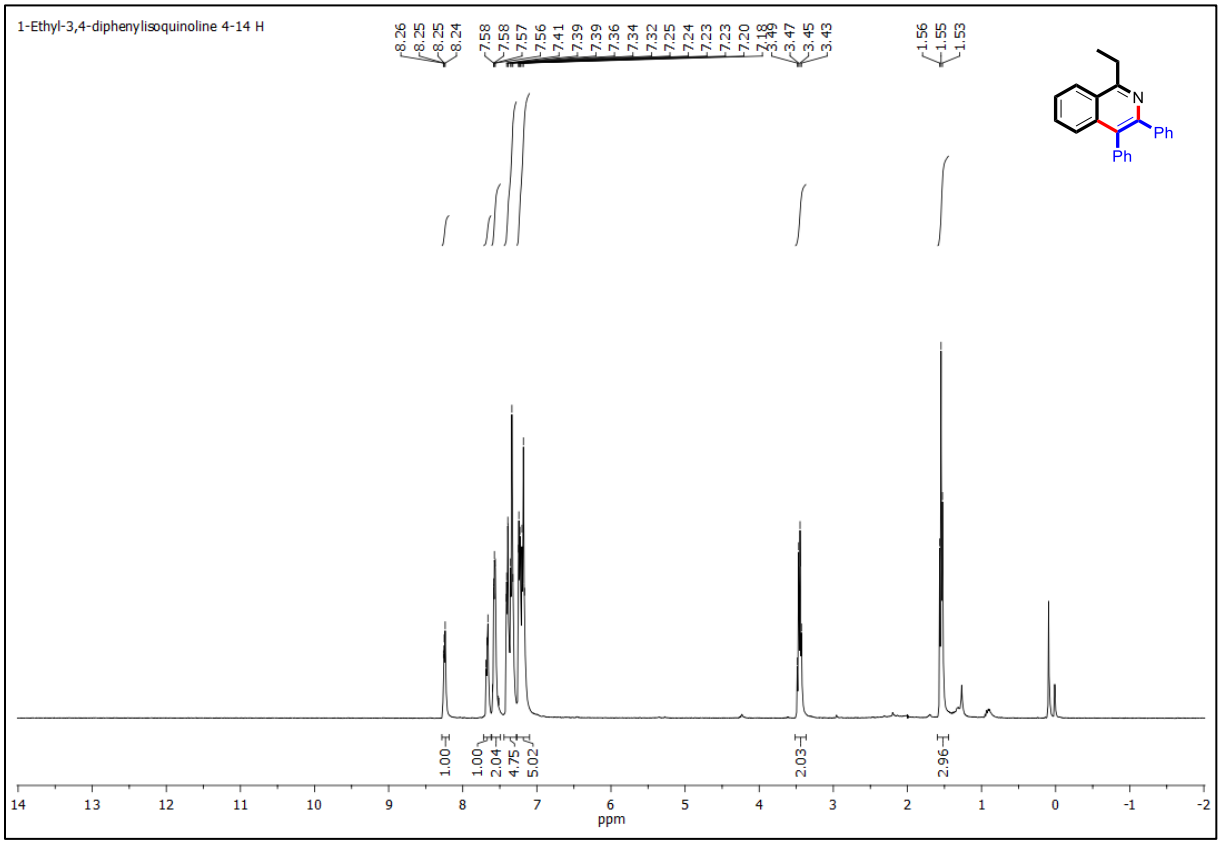


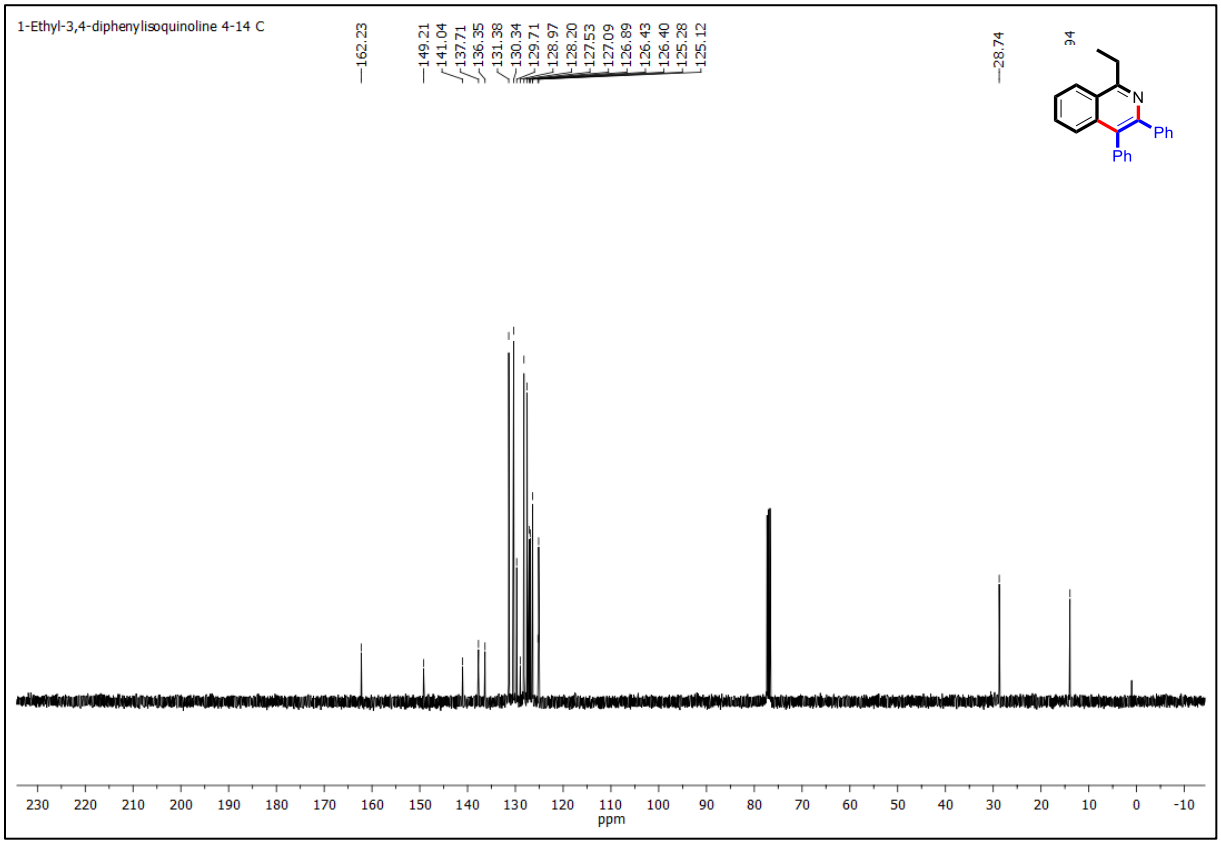
^{1}H & ^{13}C NMR of 6-Chloro-1,7-dimethyl-3,4-diphenylisoquinoline (3la)





^{1}H & ^{13}C NMR of 1-Ethyl-3,4-diphenylisoquinoline (3ma)





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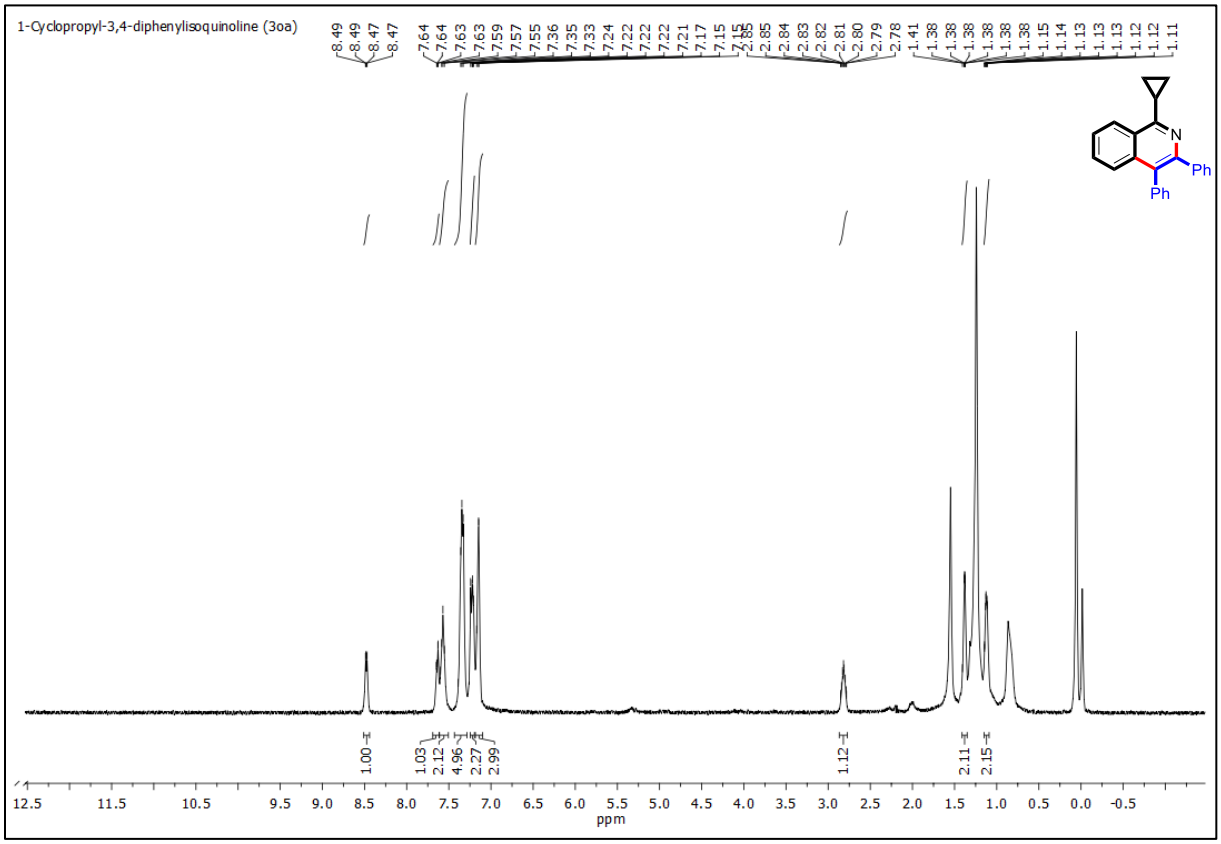
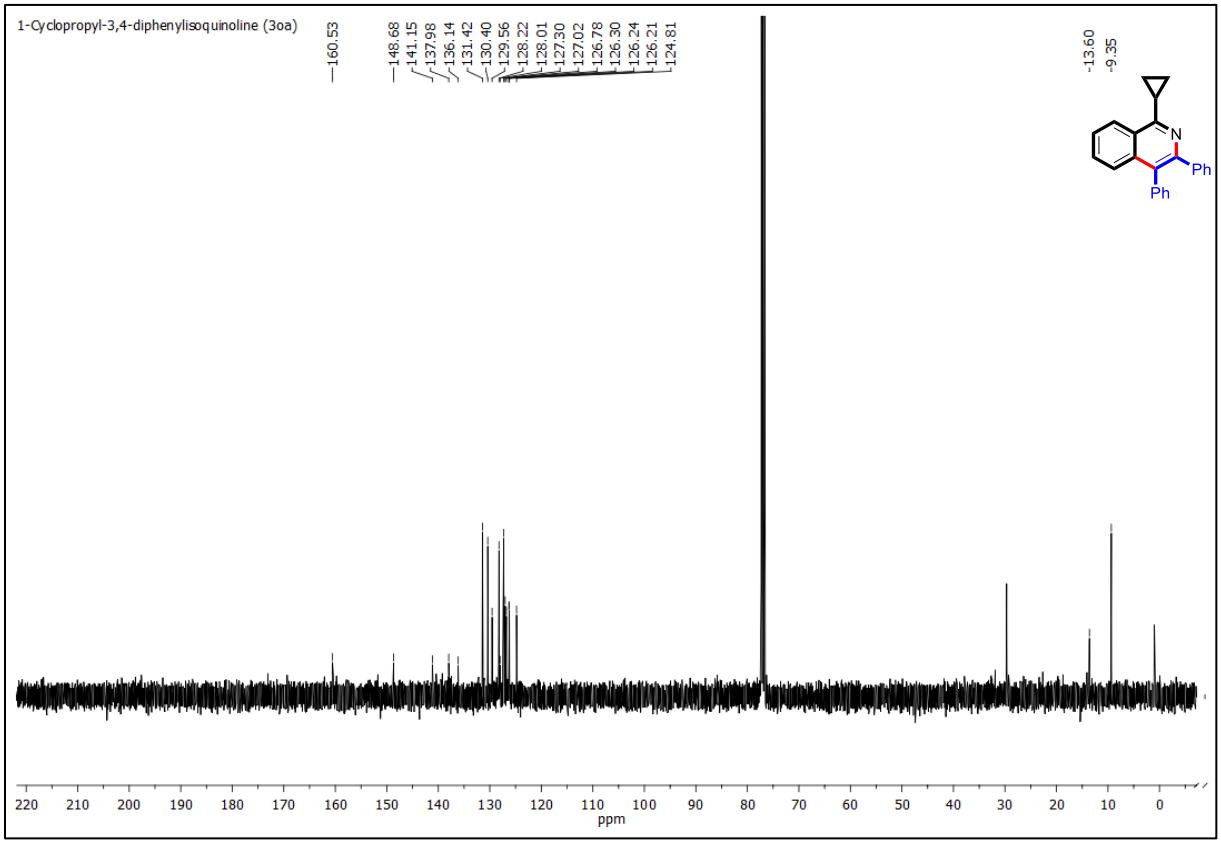
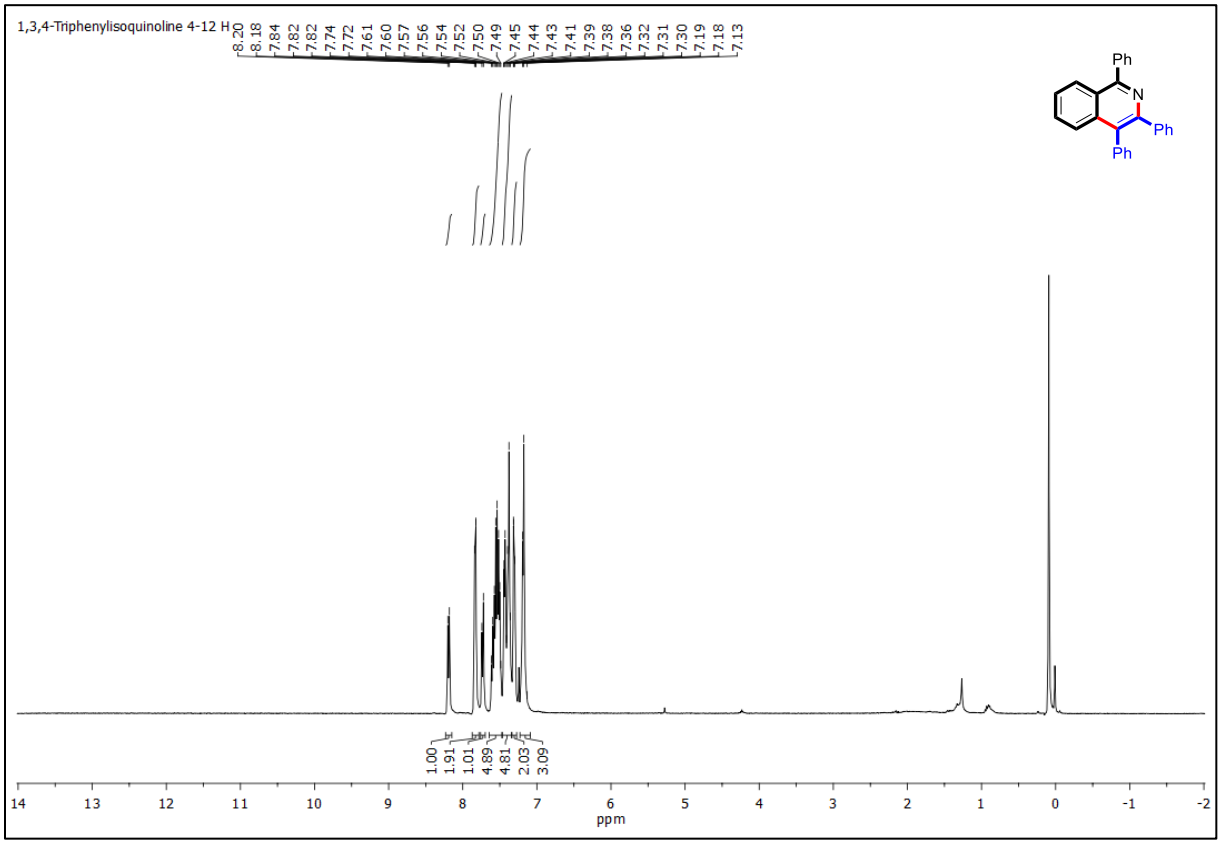
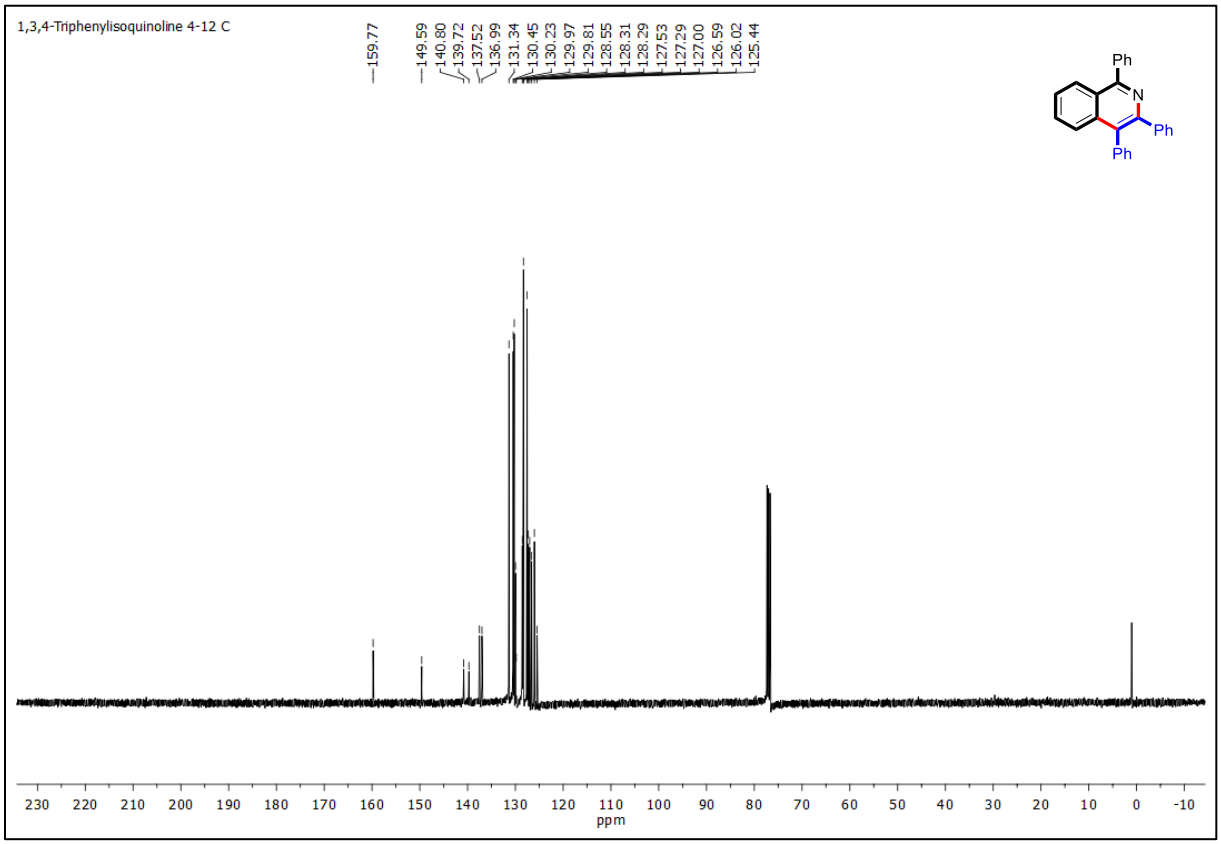


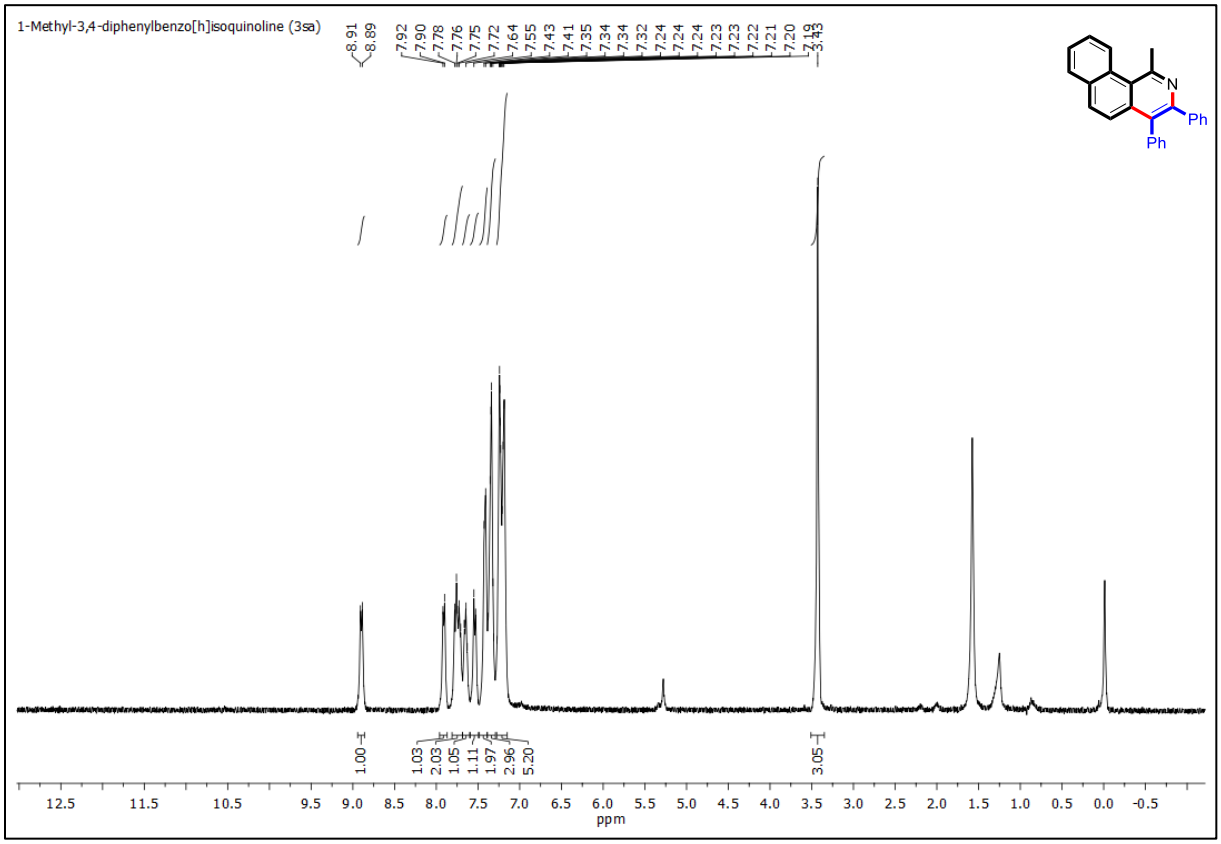


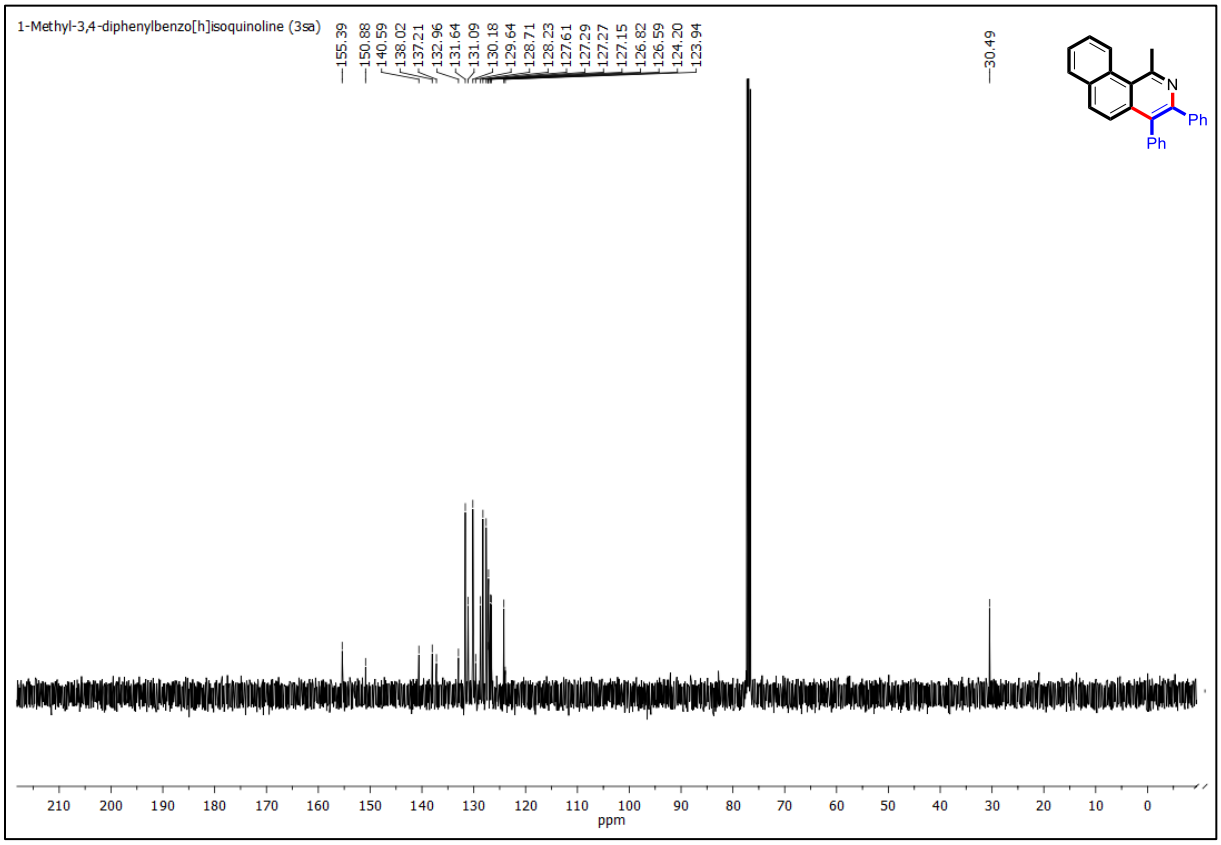
^{1}H & ^{13}C NMR of 1,3,4-Triphenylisoquinoline (3oa)





^{1}H & ^{13}C NMR of 1-Methyl-3,4-diphenylbenzo[h]isoquinoline (3pa)





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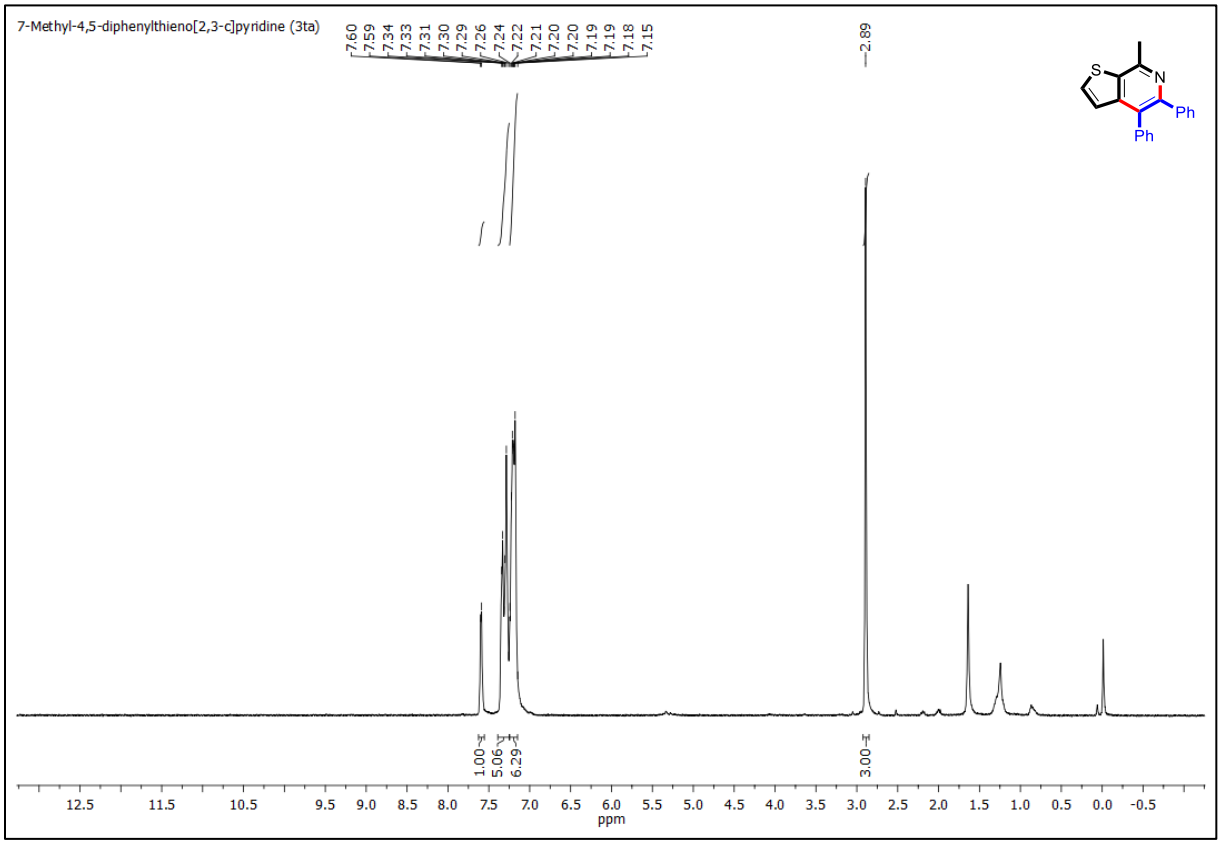

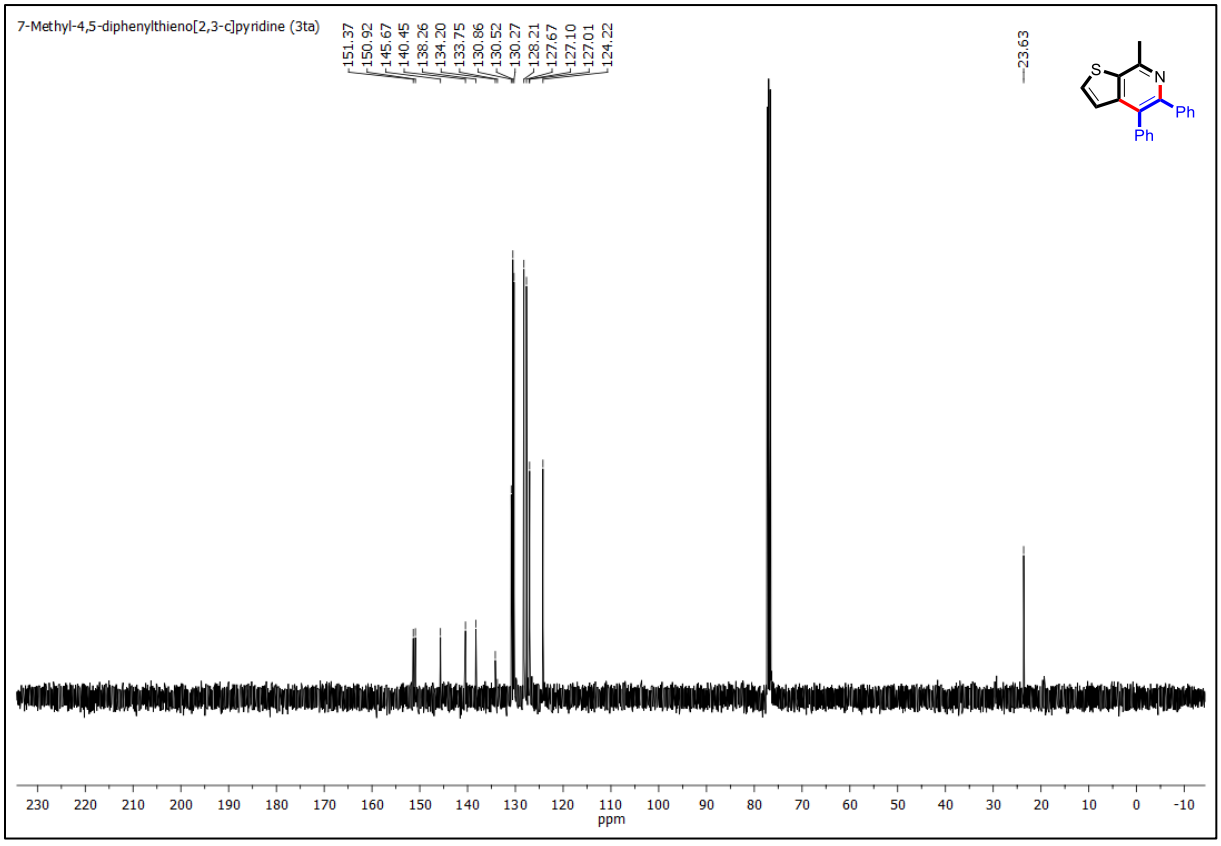

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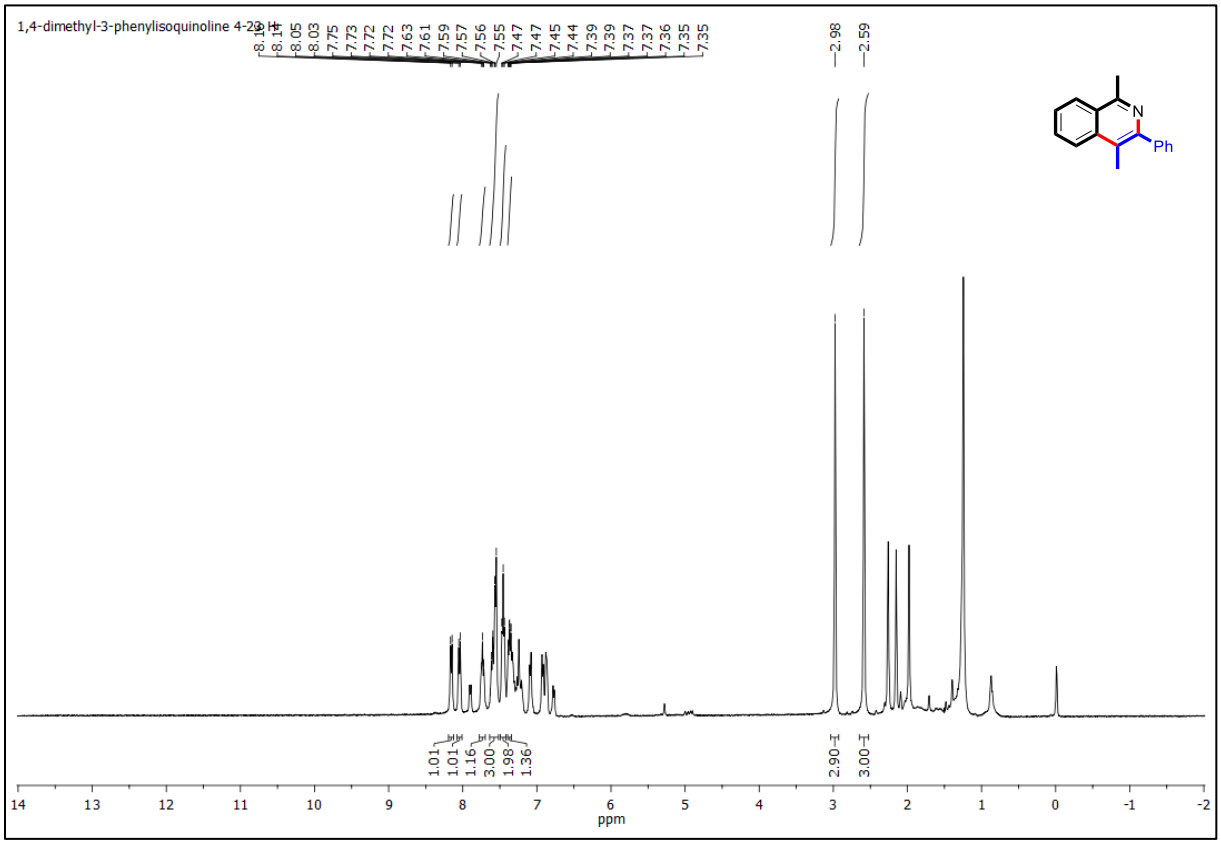

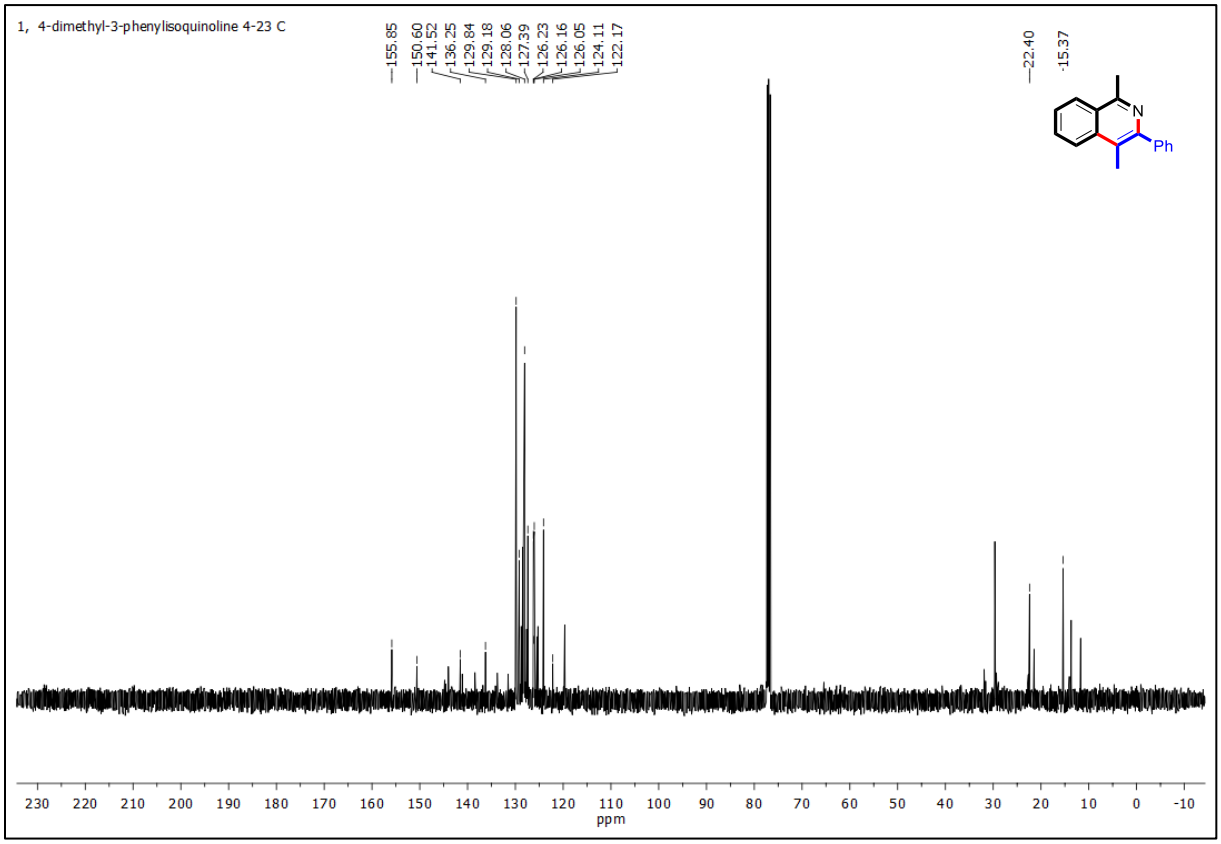

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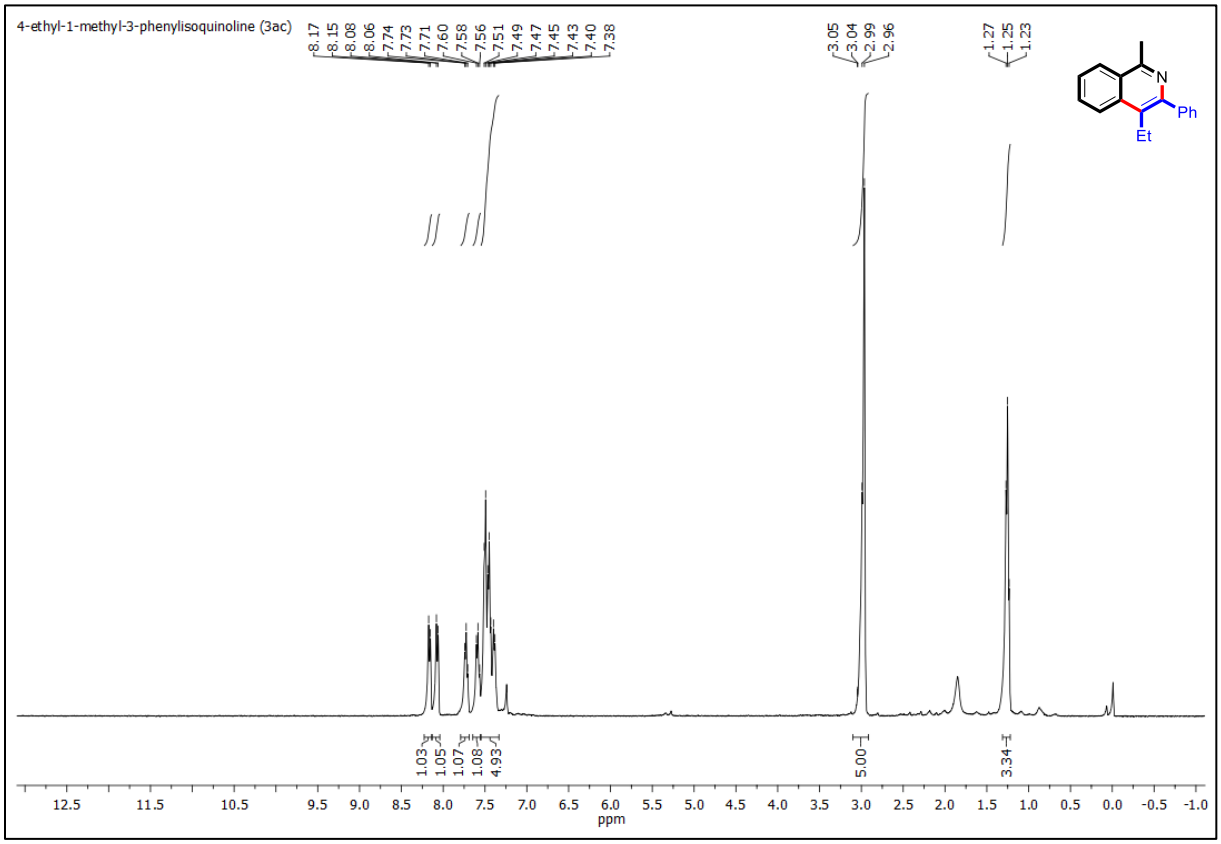
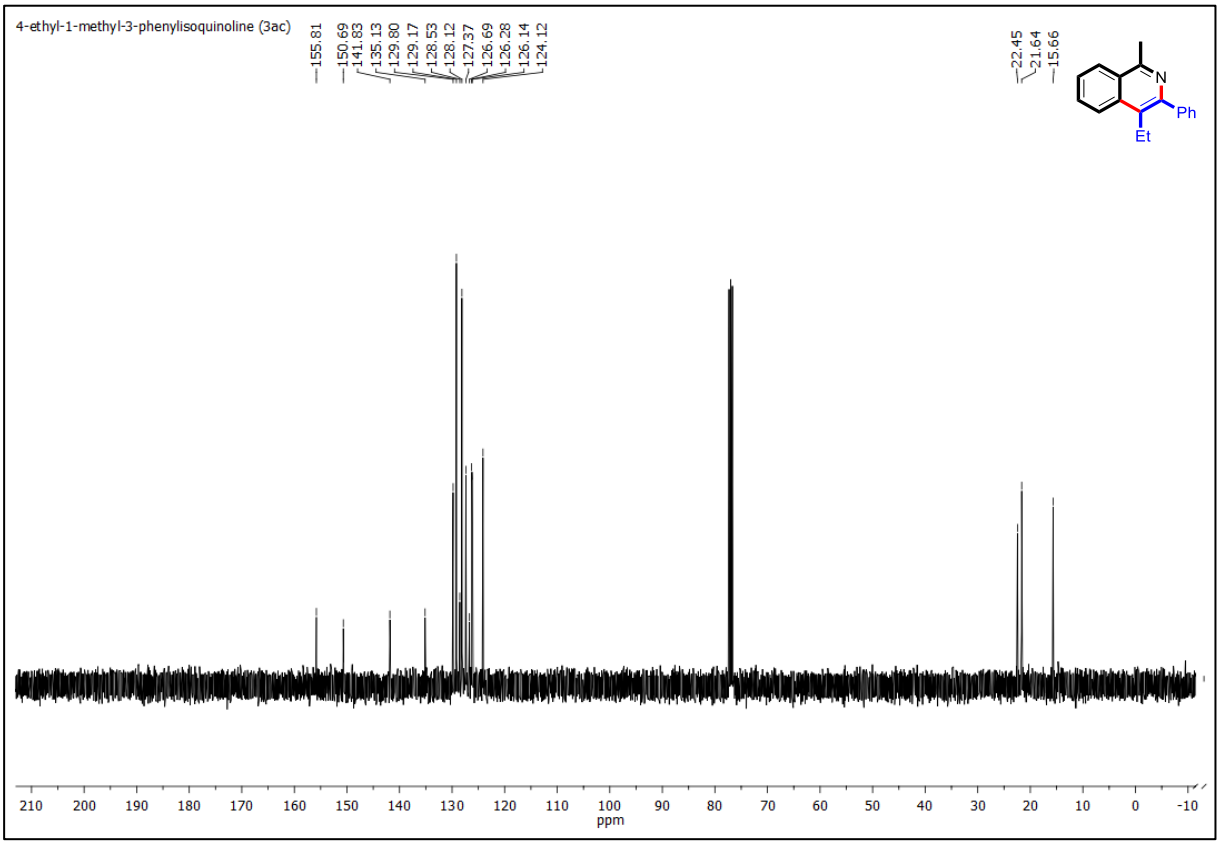
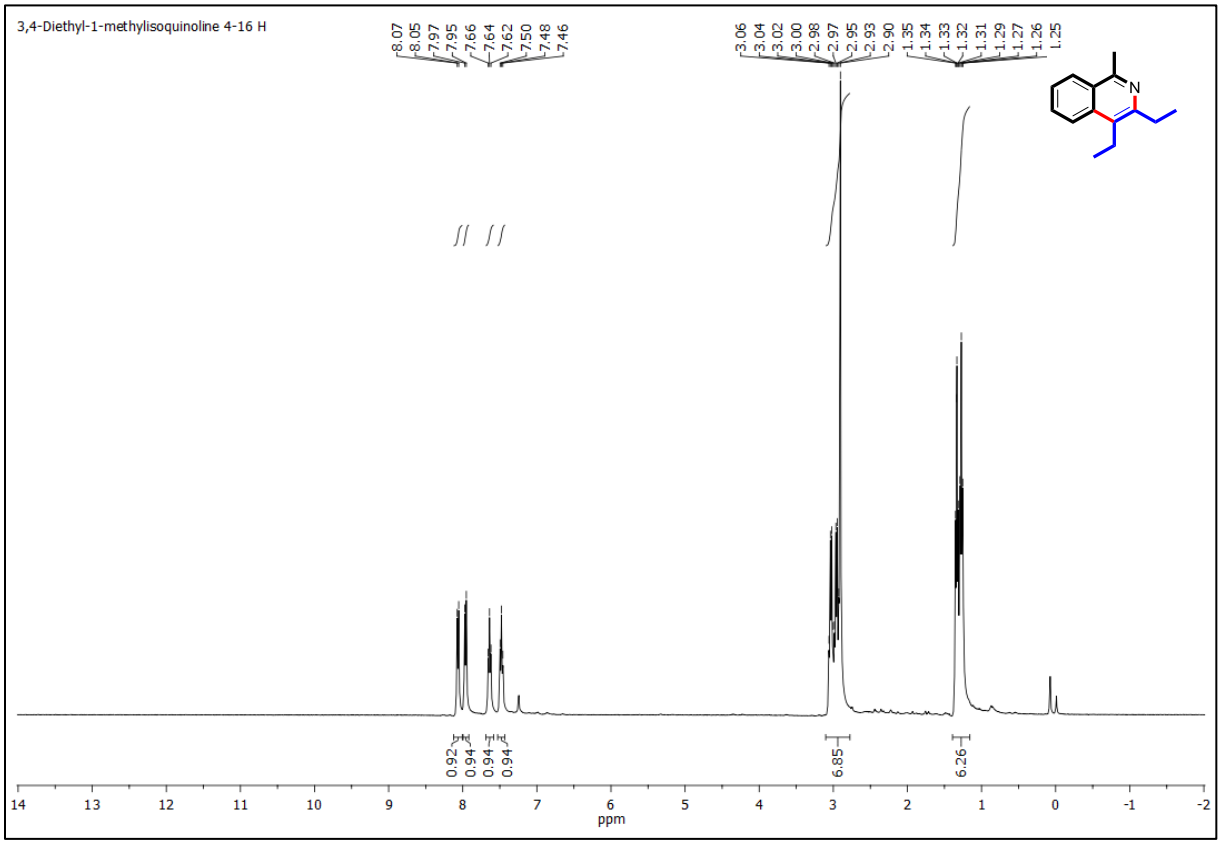
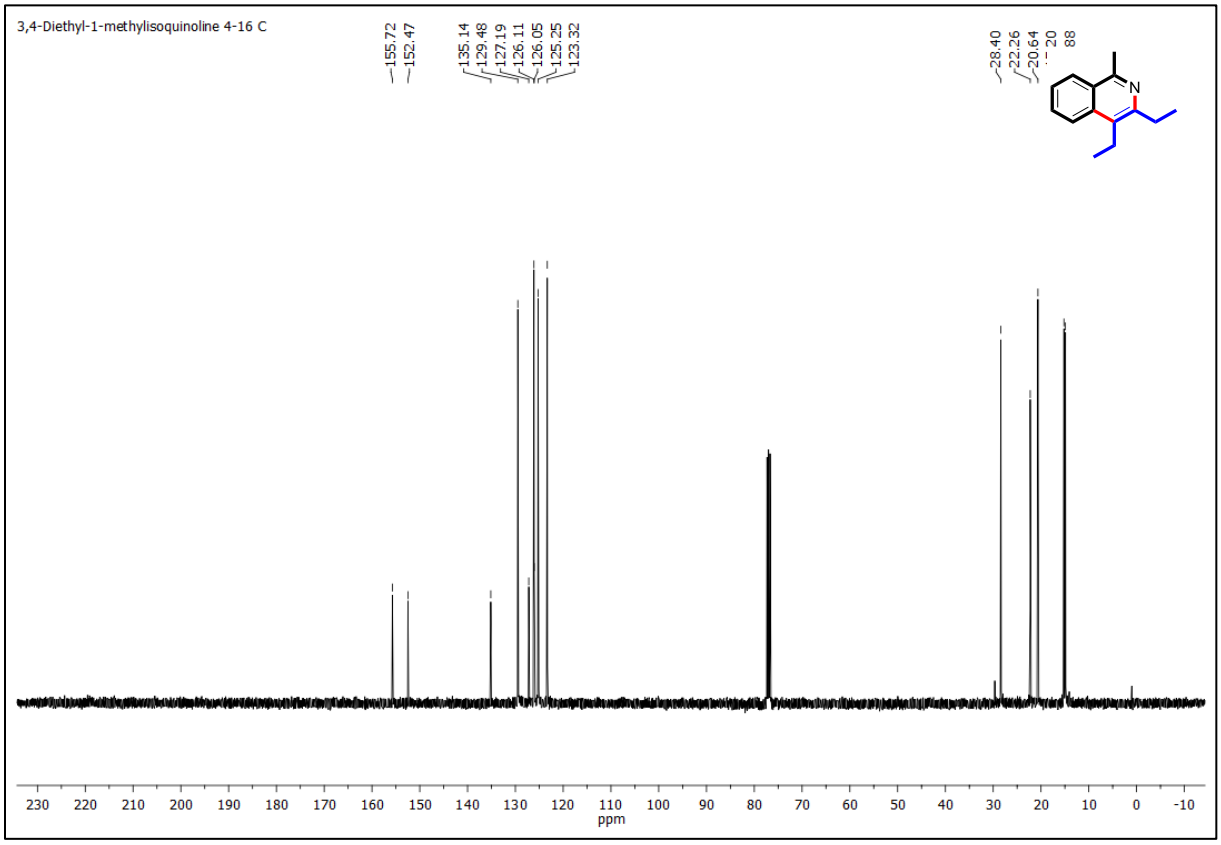




^{1}H & ^{13}C NMR of 3,4-Diethyl-1-methylisoquinoline (3ad)





^{1}H & ^{13}C NMR of 1-Methyl-3,4-di*p*-tolylisoquinoline (3ae)