

Acid-catalyzed allenylation of pyrazolones with propargyl alcohols

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General information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All reactions were carried out in Schlenk tube under an argon atmosphere. All solvents were purified and dried according to standard methods prior to use. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash chromatography was carried out utilizing silica gel 200-300 mesh. ^1H NMR, ^{19}F NMR spectra were recorded on a Bruker Avance II 400 MHz and Bruker Avance III 377 MHz respectively, ^{13}C NMR spectra were recorded on a Bruker Avance II 101 MHz. The solvent used for NMR spectroscopy was CDCl_3 , using tetramethylsilane as the internal reference. Data for ^1H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, dd = double doublet, dt = double triplet, td = triple doublet, coupling constants in Hz, integration). Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (δ , ppm). HRMS (ESI) was determined by an HRMS/MS instrument (LTQ Orbitrap XLTM). The relative configuration of **3aa** was assigned by the X-ray analysis.

pyrazolones were prepared according to the literature.¹ propargyl alcohols were synthesized according to literature procedures.²

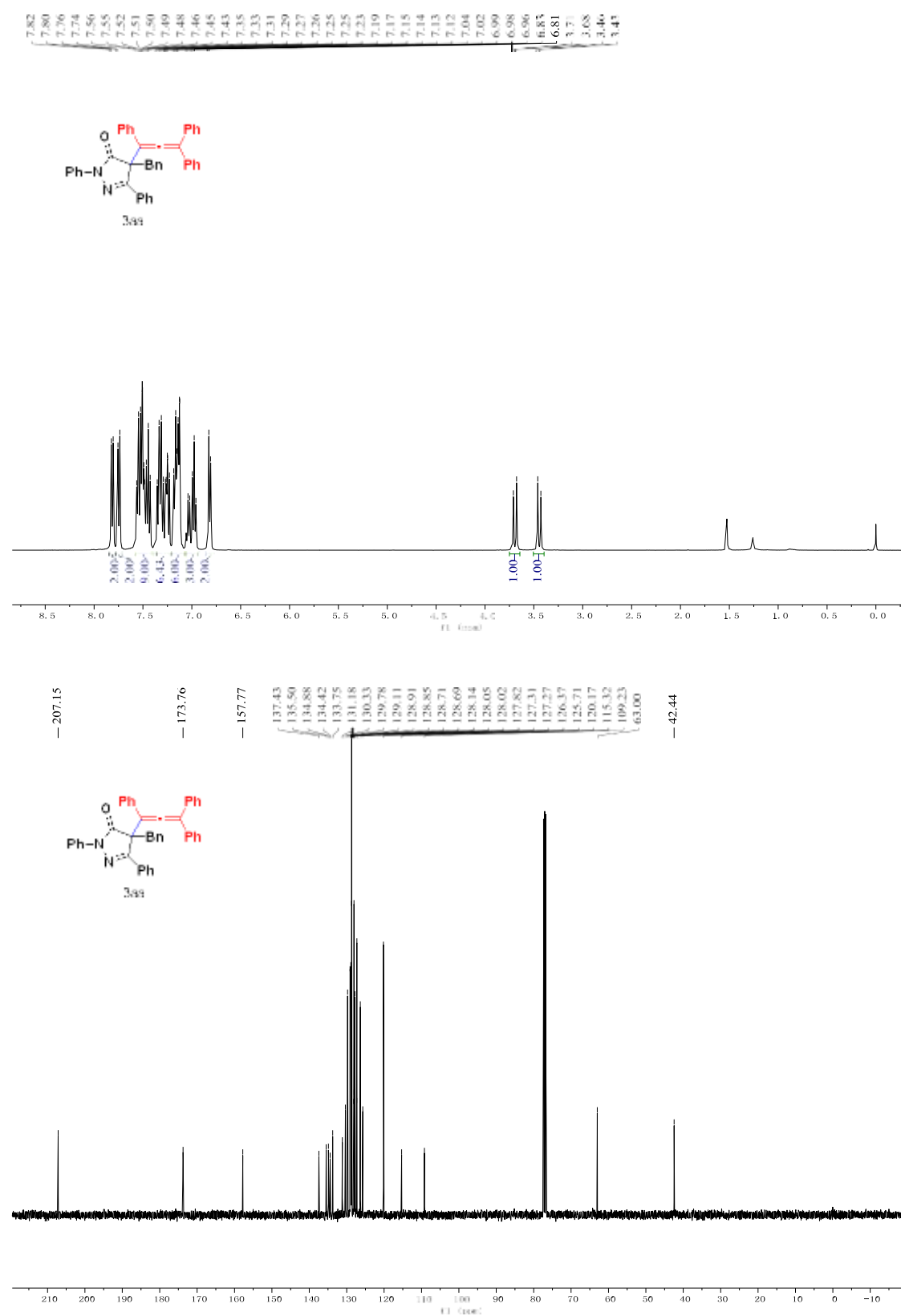
Experimental procedures of products **3aa-3al**

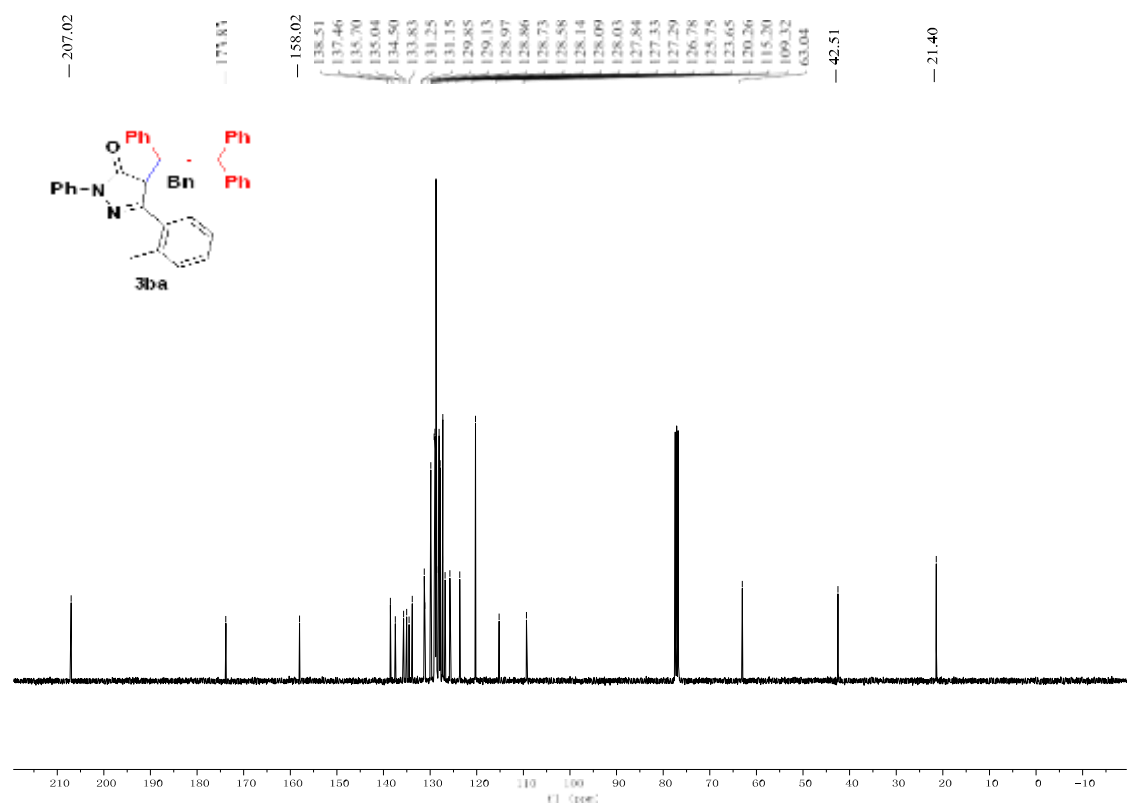
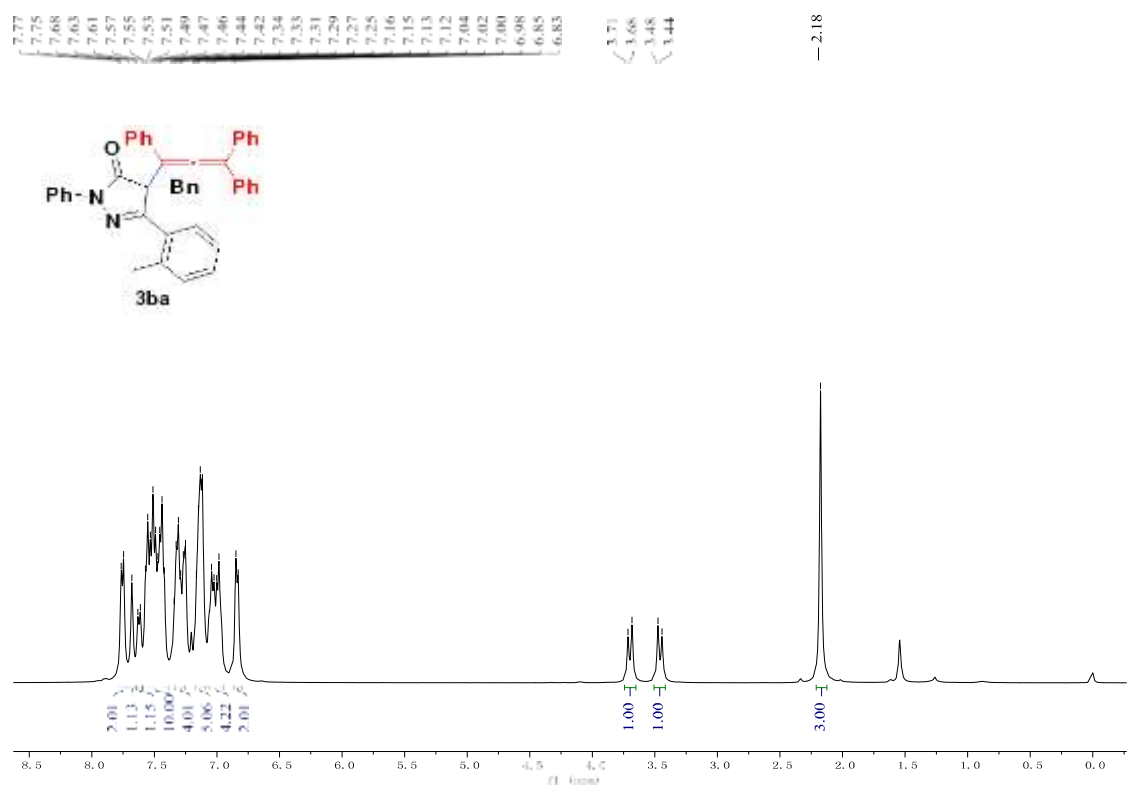
In a Schlenk tube, pyrazolone **1a-v** (0.20 mmol, 1.0 eq), TsOH (0.02 mmol, 0.1 eq) were added into Toluene (2.0 mL) under argon atmosphere. Then acetylene alcohol **2a-l** (0.24 mmol, 1.2 eq) was added and the reaction solution was stirred at 80 °C. After the reaction was complete (monitored by TLC), the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/80 to 1/40) on silica gel to give the product **3aa-3al** as a light yellow solid.

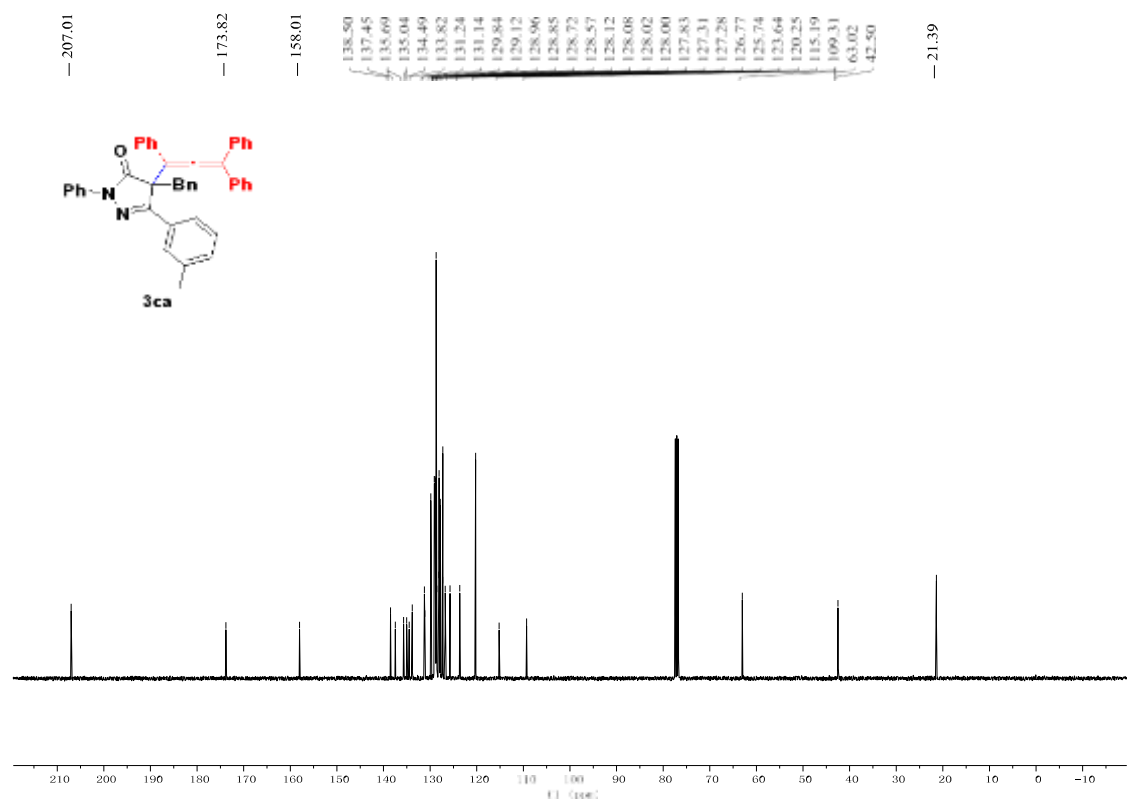
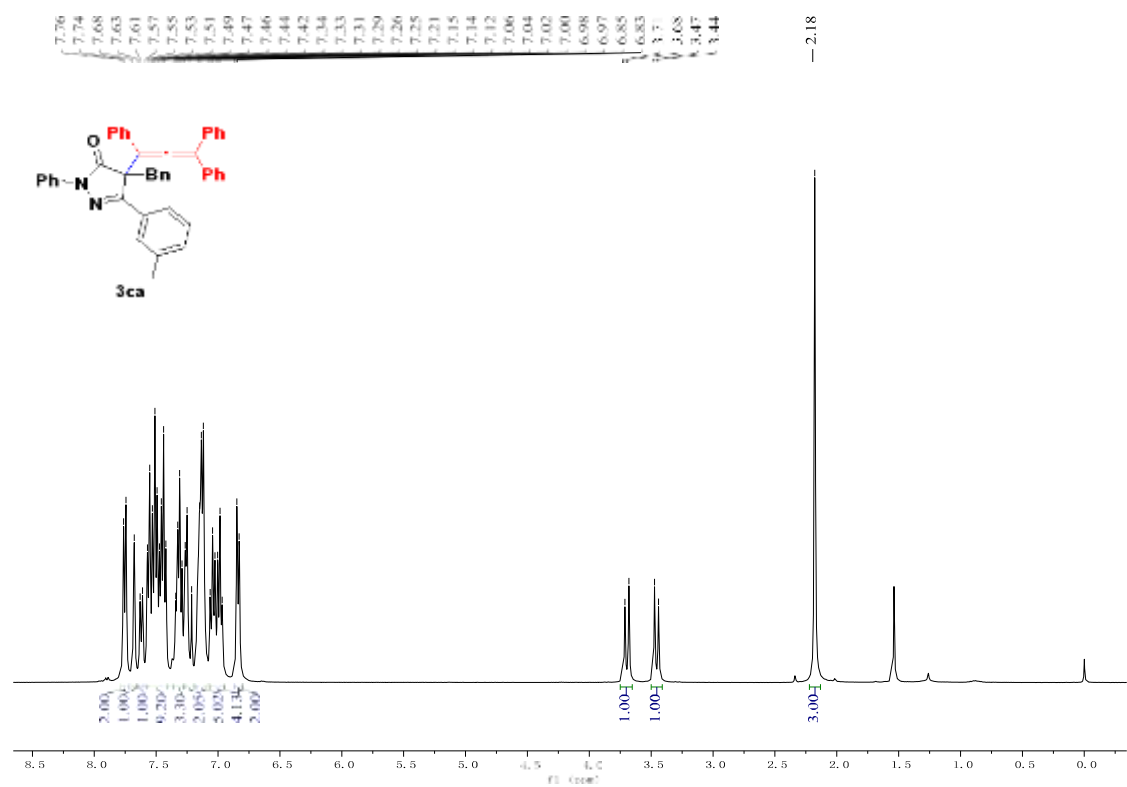
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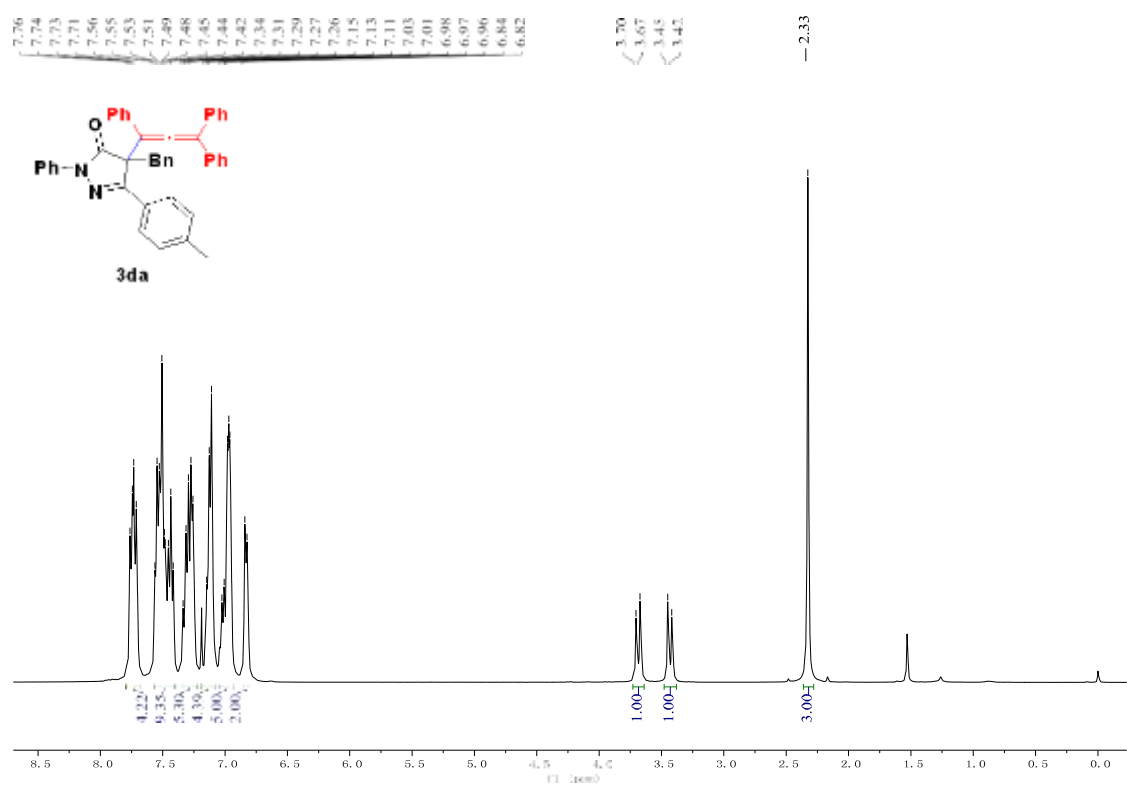
- 1 (a) M. Kamlar, I. Císařová and J. Veselý, Alkynylation of heterocyclic compounds using hypervalent iodine reagent, *Org. biomol. Chem.*, 2015, **13**, 2884-2889; (b) X. Sheng, J. Zhang, H. Yang and G. Jiang, Tunable Aerobic Oxidative Hydroxylation/Dehydrogenative Homocoupling of Pyrazol-5-ones under Transition-Metal-Free Conditions, *Org. lett.*, 2017, **19**, 2618-2621.
- 2 H. Zhang, H. Tanimoto, T. Morimoto, Y. Nishiyama and K. Kakiuchi, Regioselective rapid synthesis of fully substituted 1, 2, 3-triazoles mediated by propargyl cations, *Org. lett.*, 2013, **15**, 5222-5225.

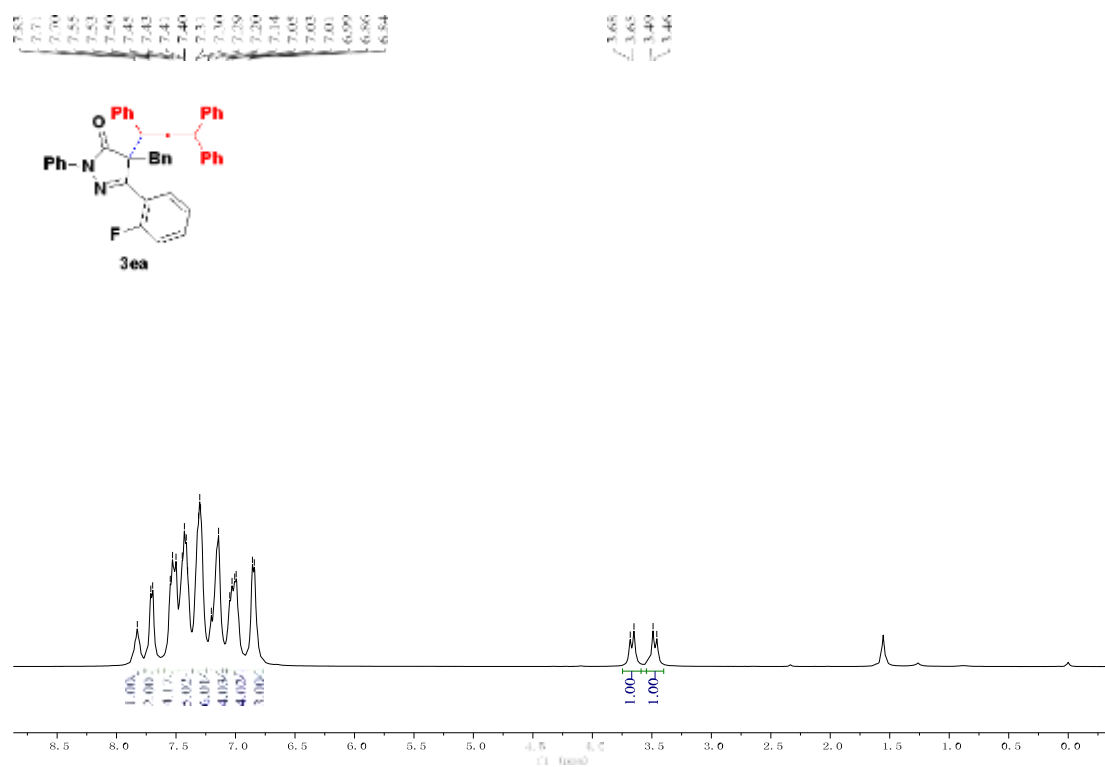
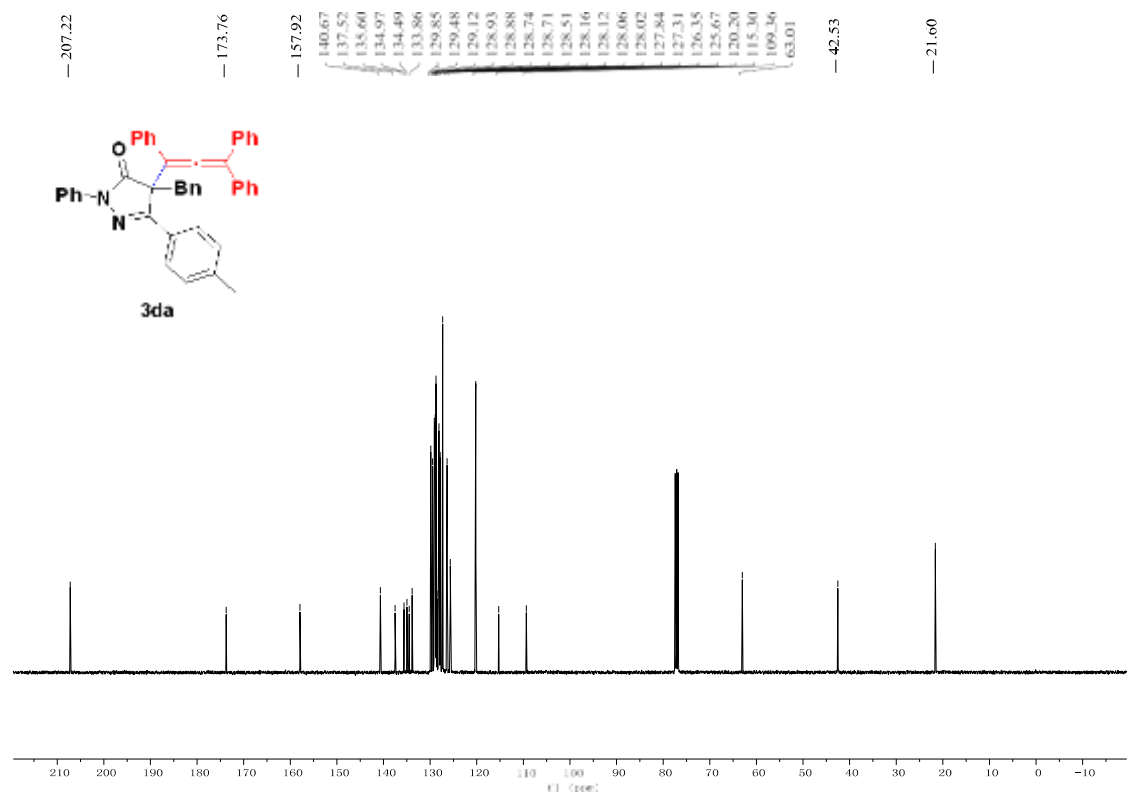
NMR spectra for compounds

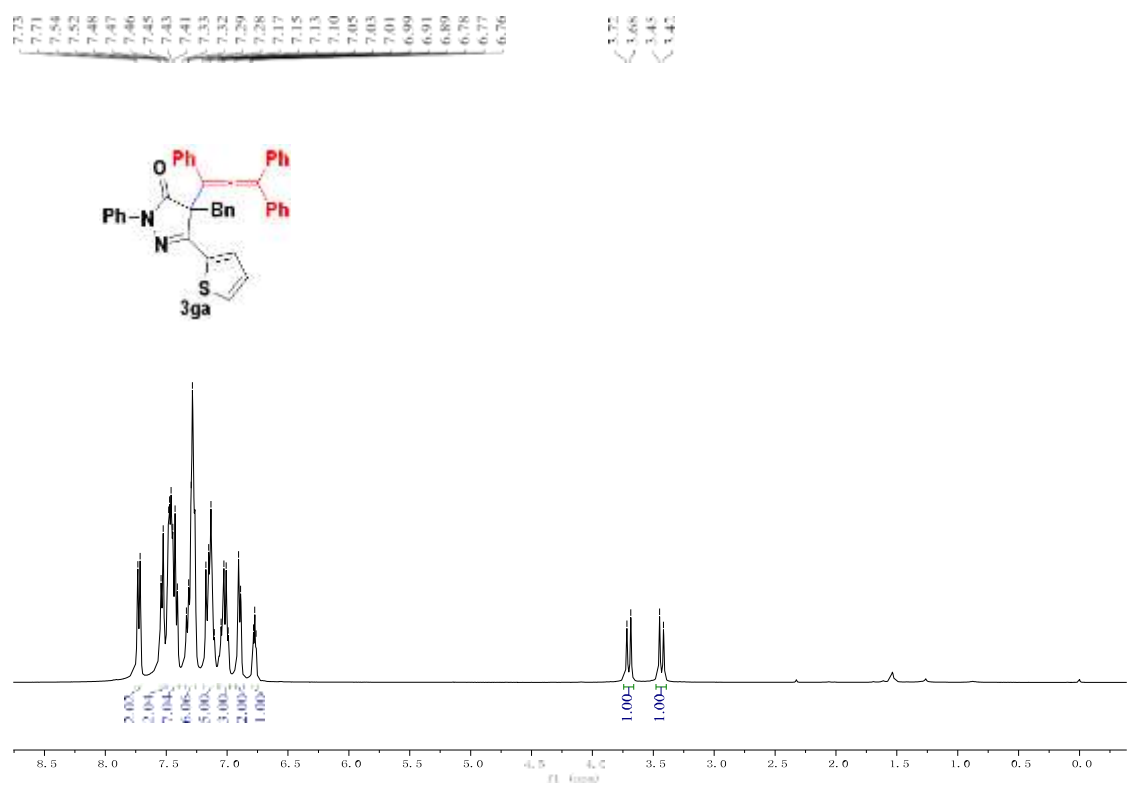
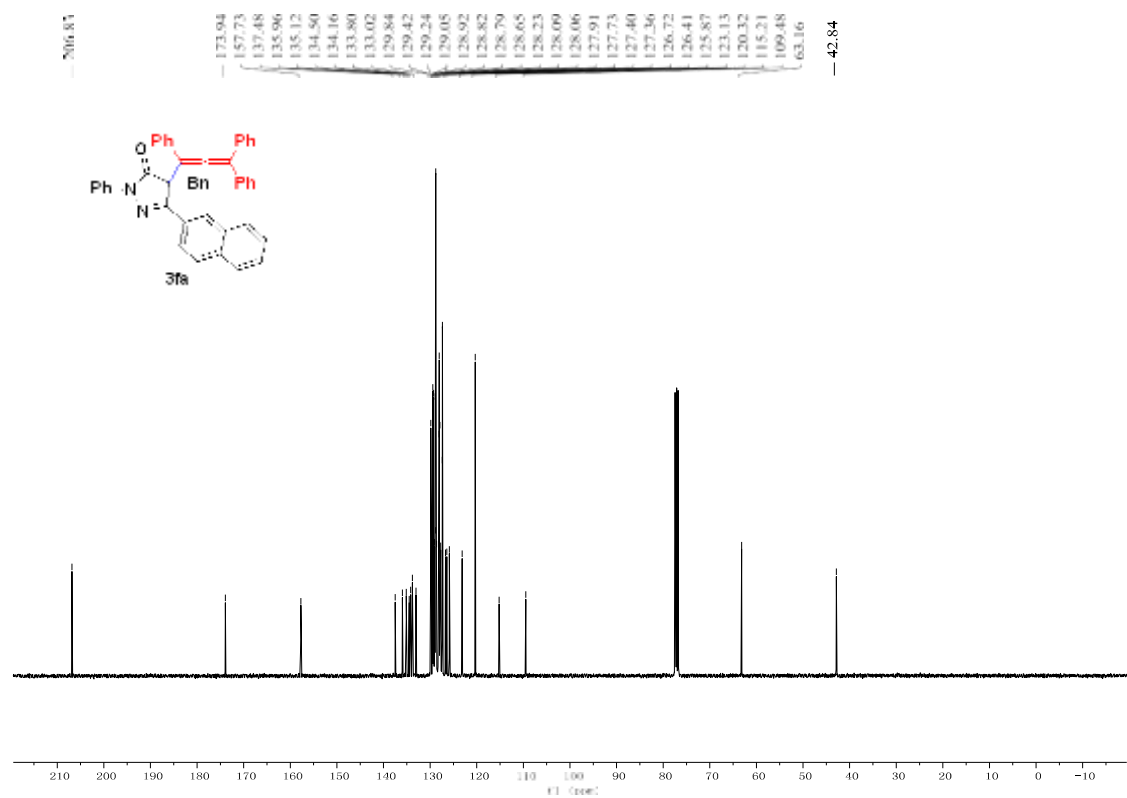


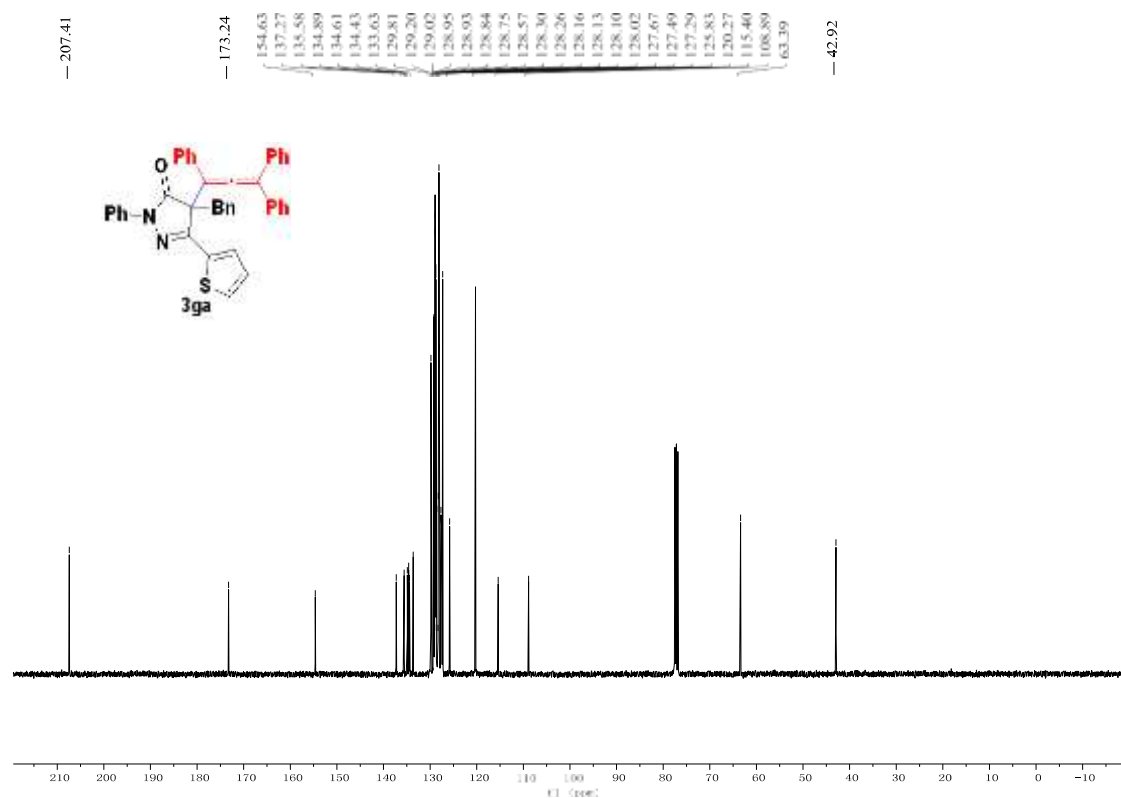


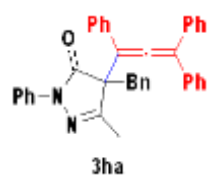
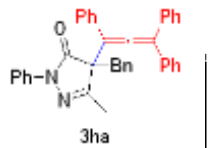


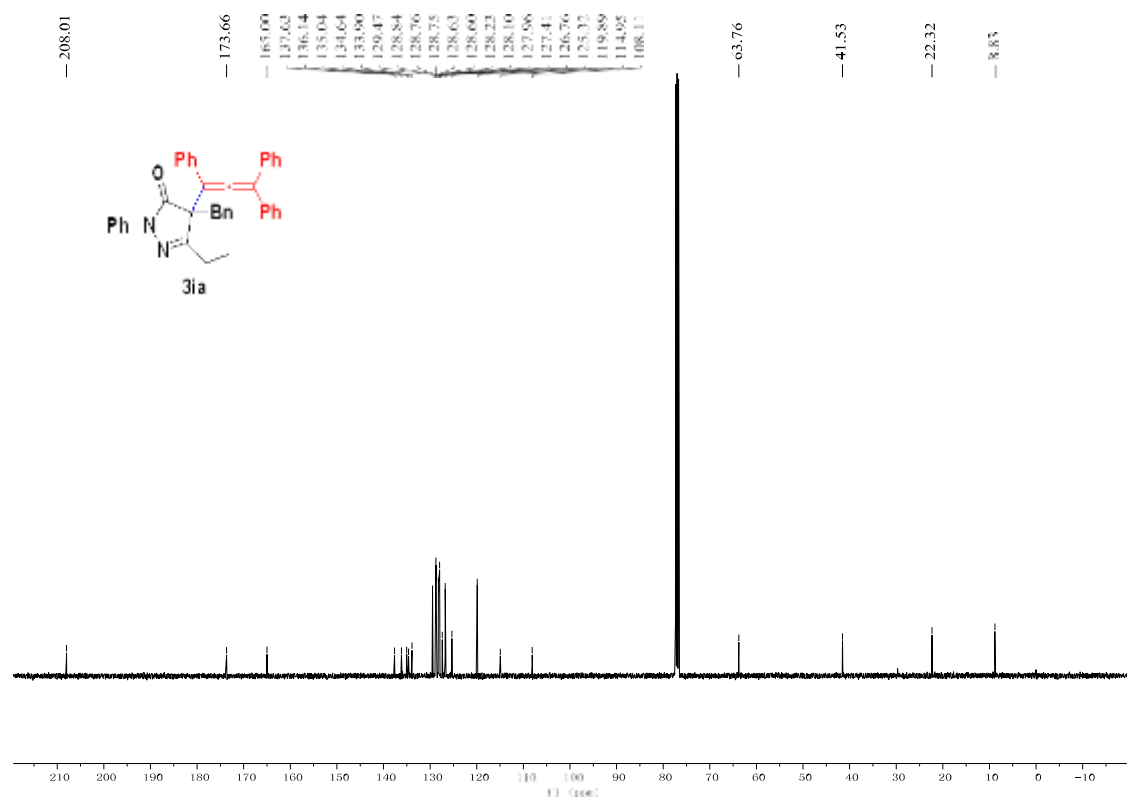
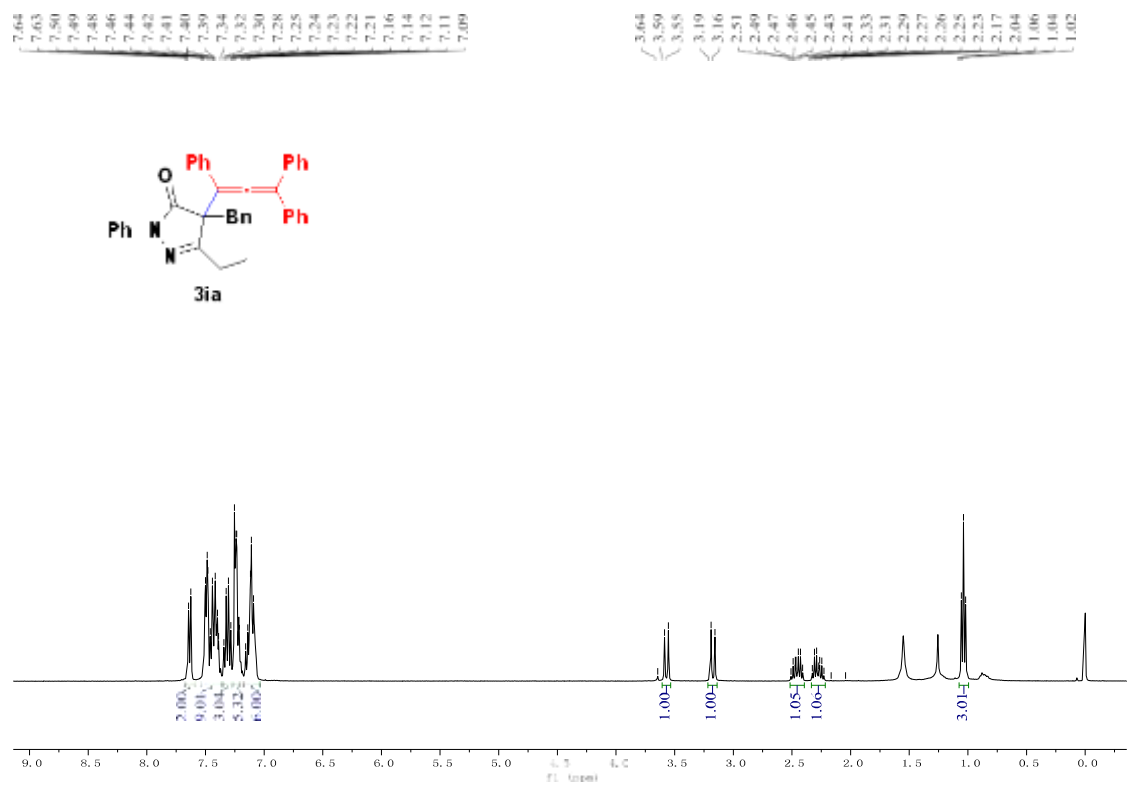


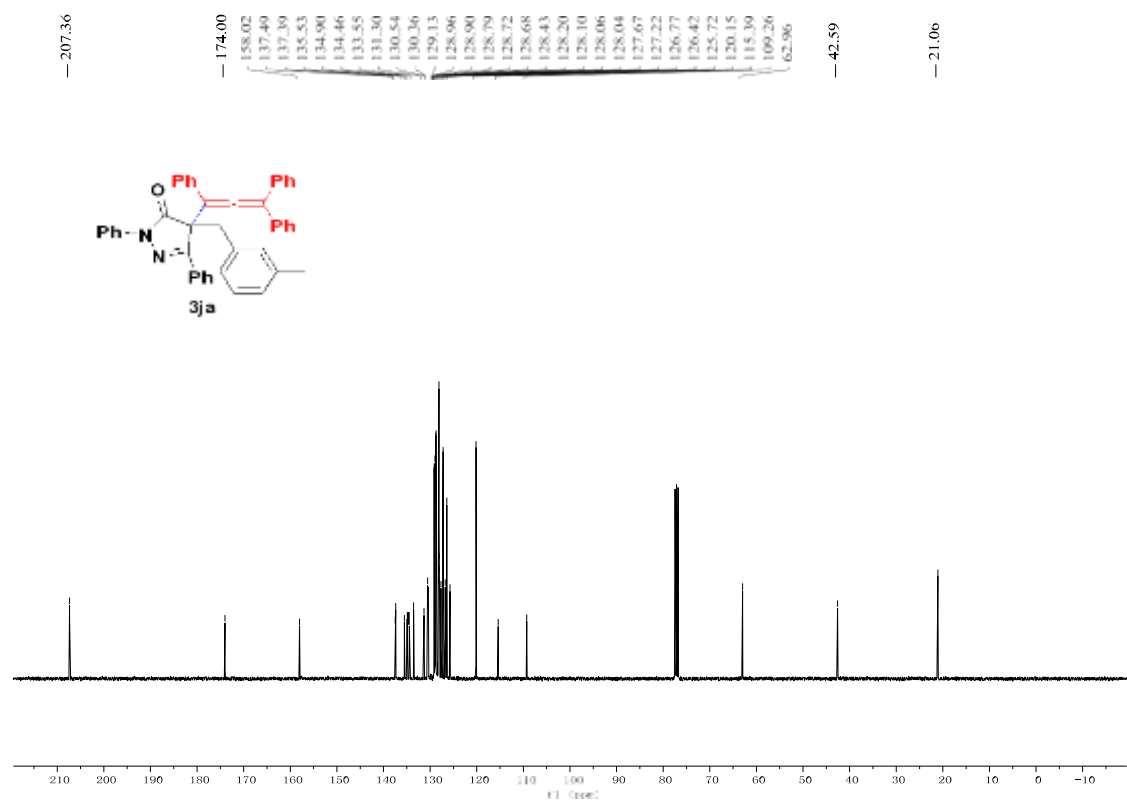
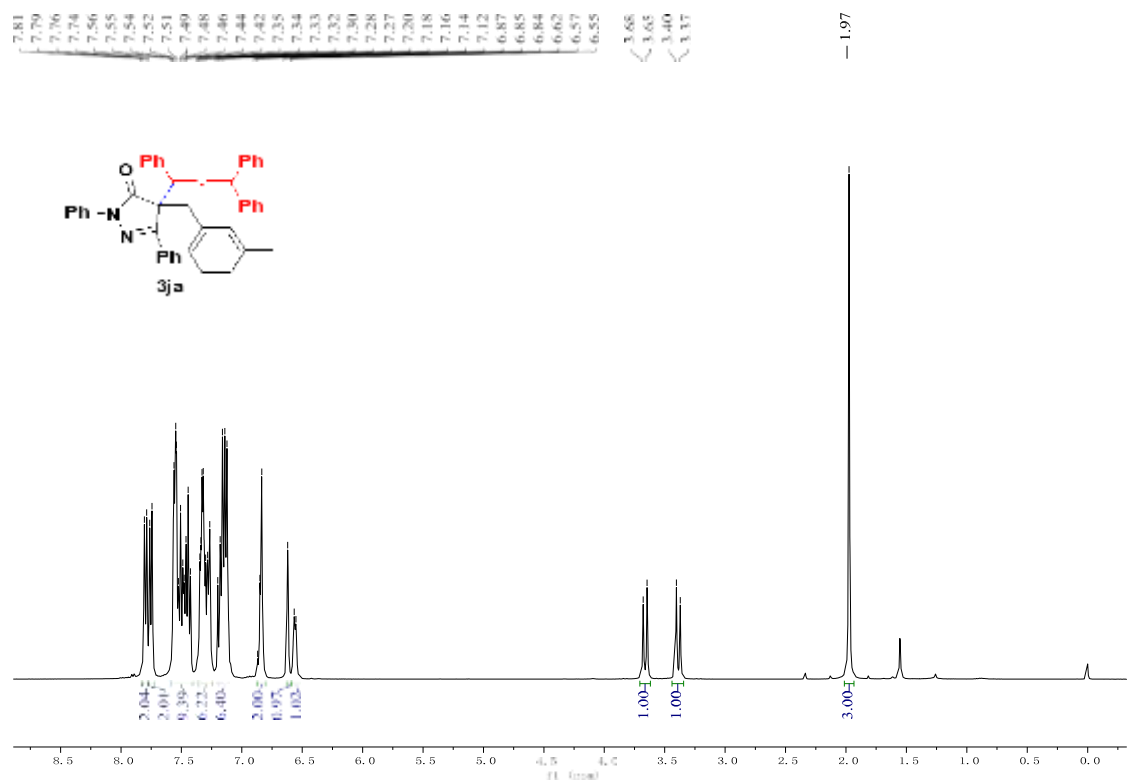


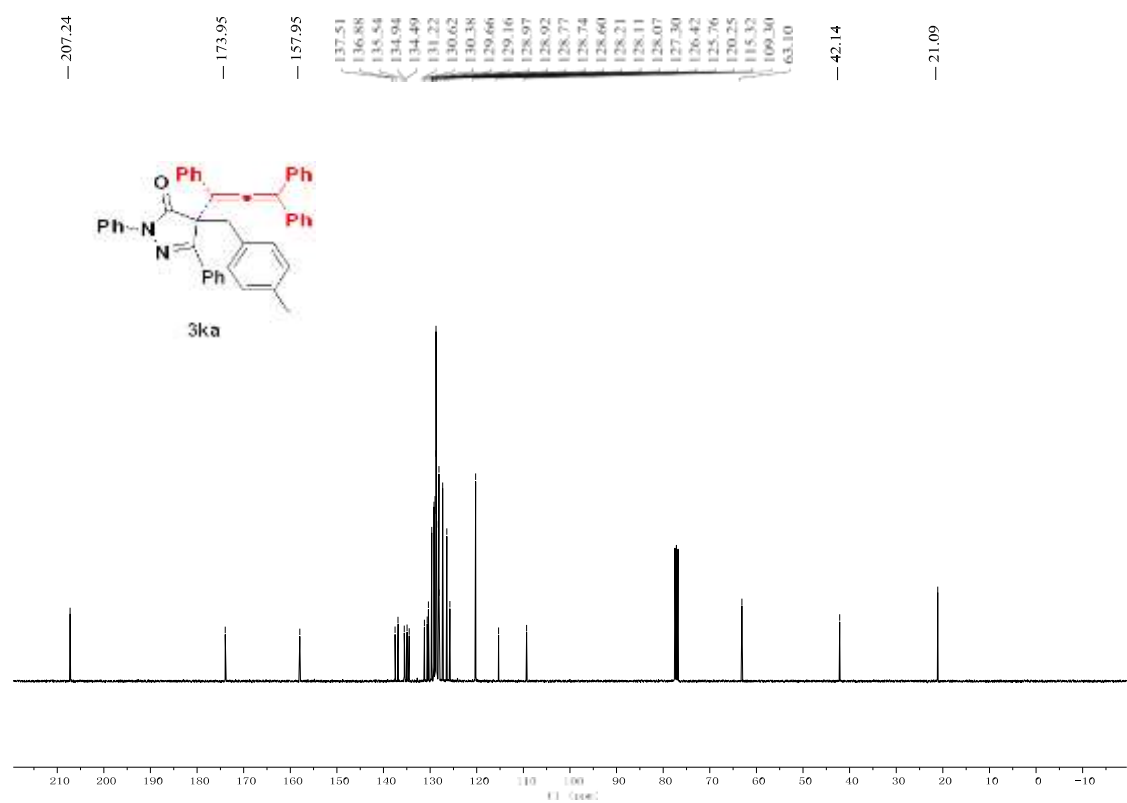
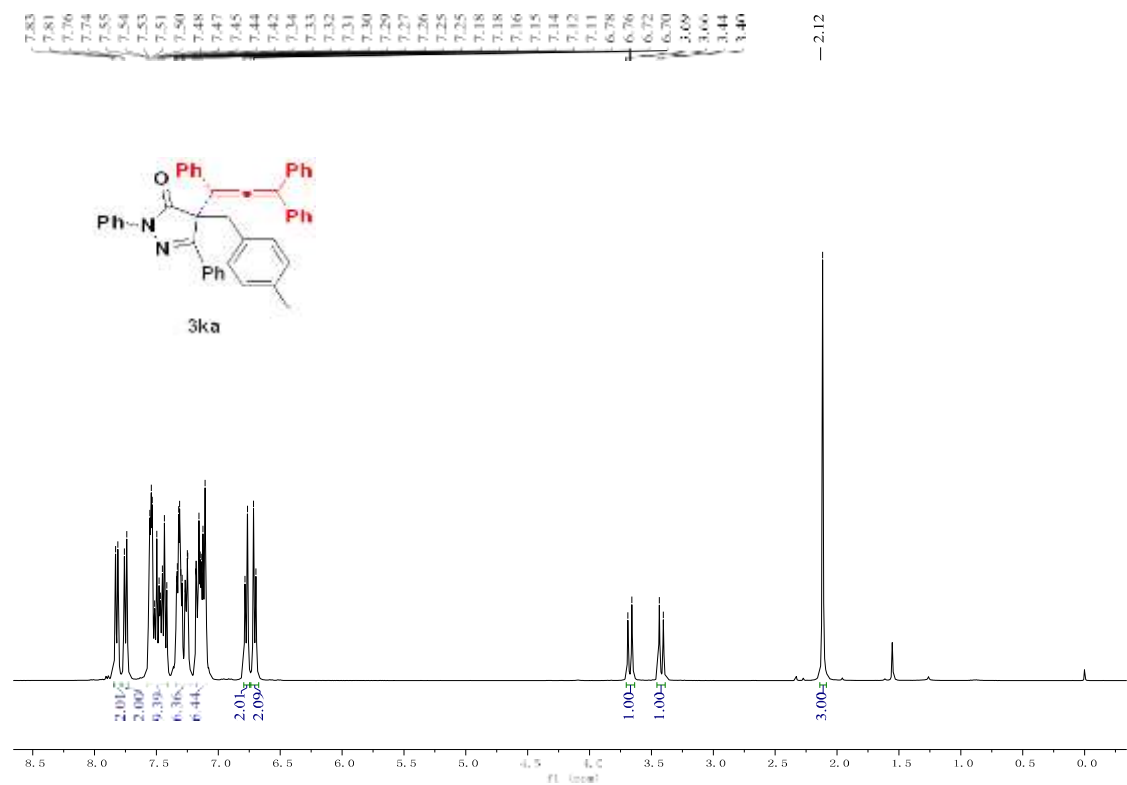


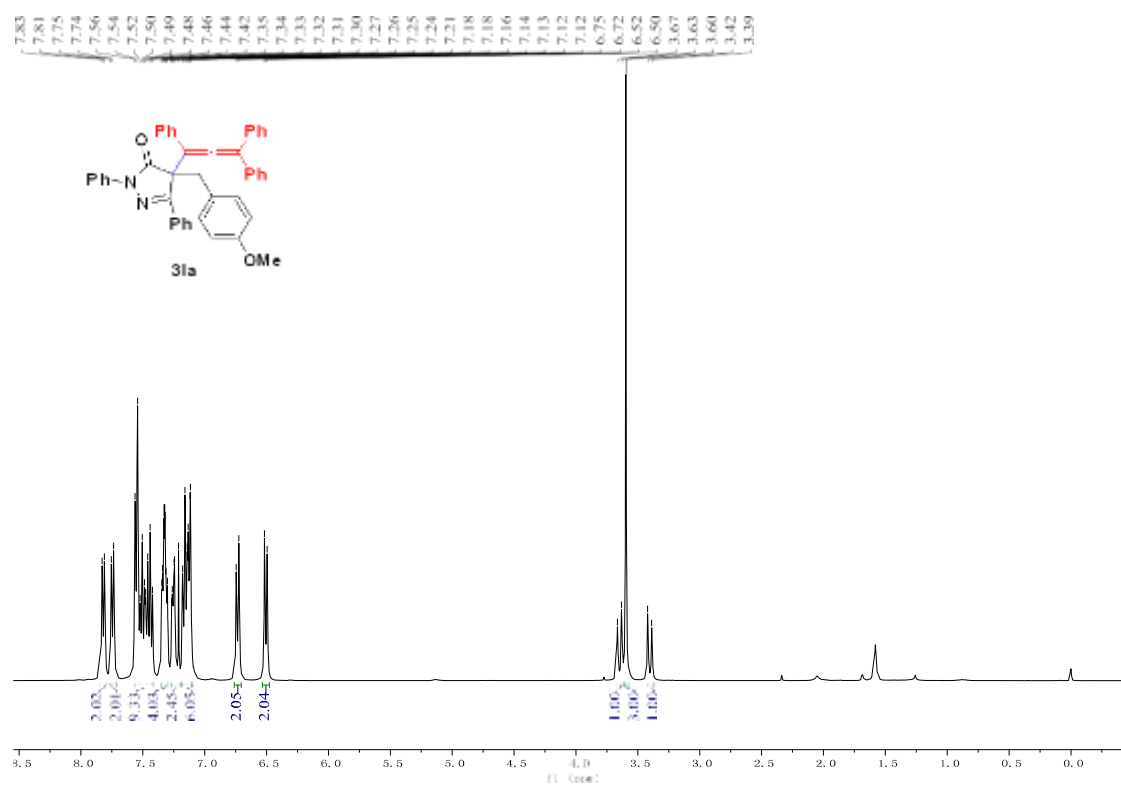


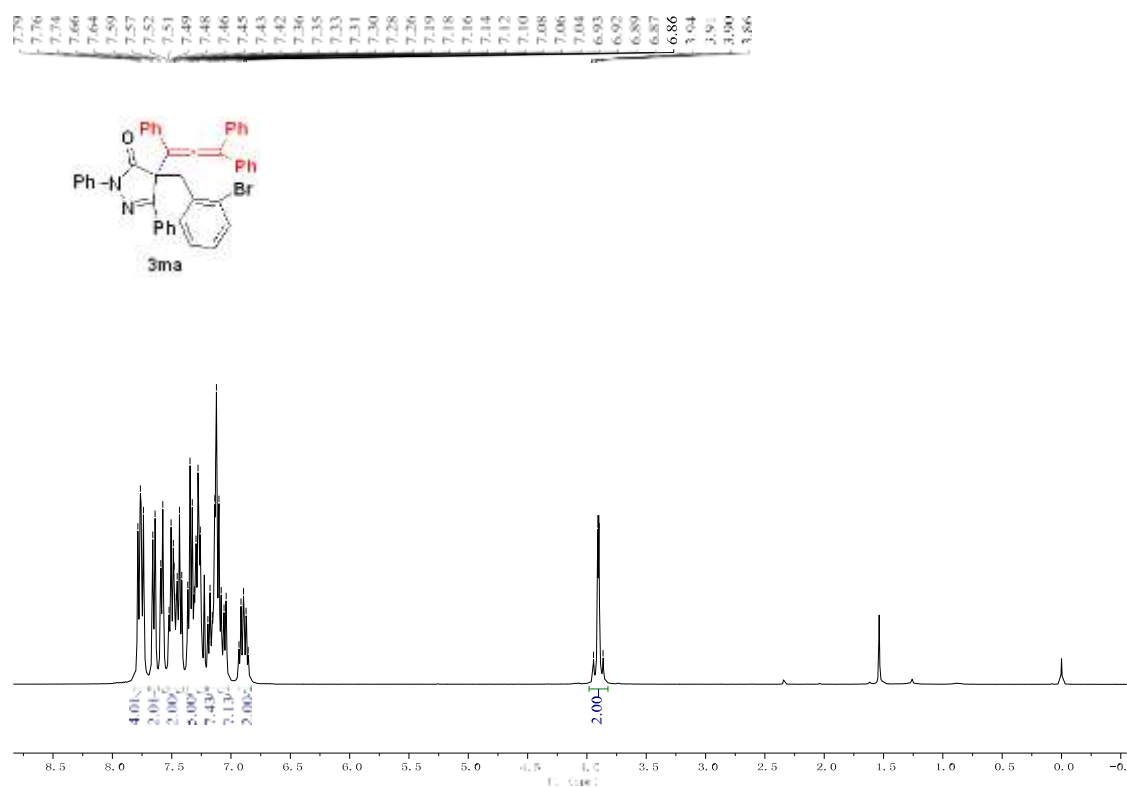
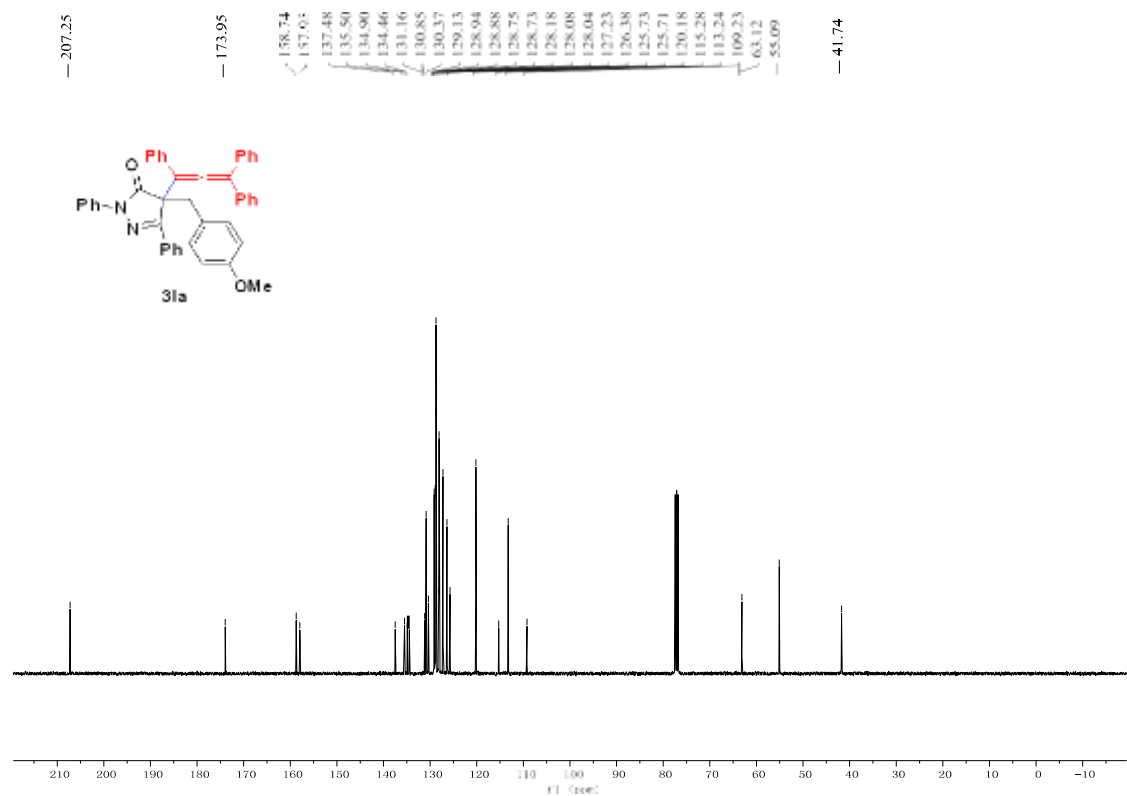


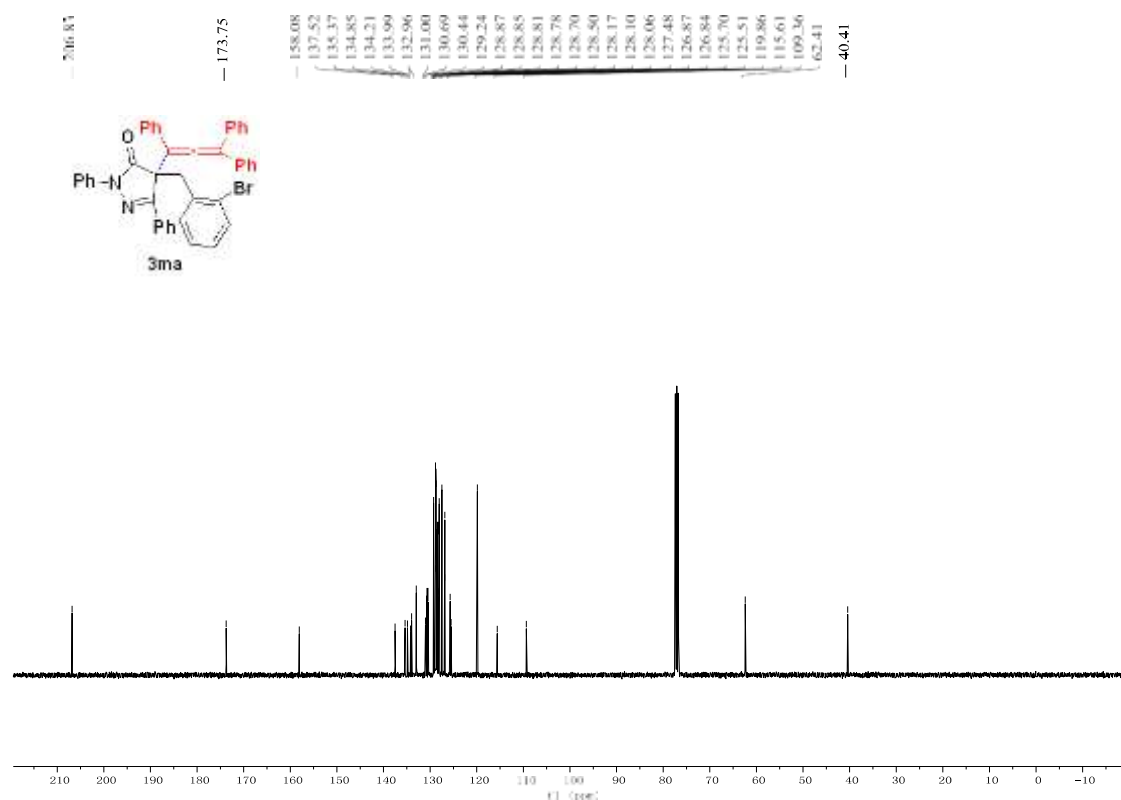


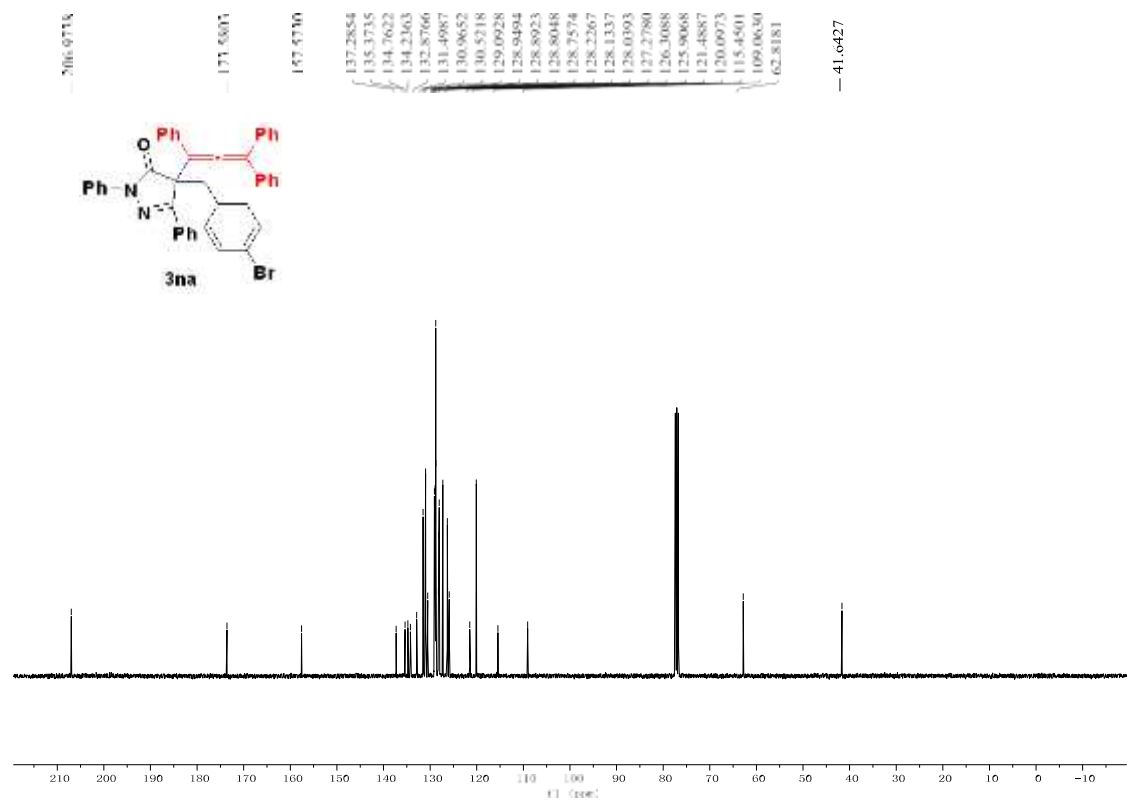
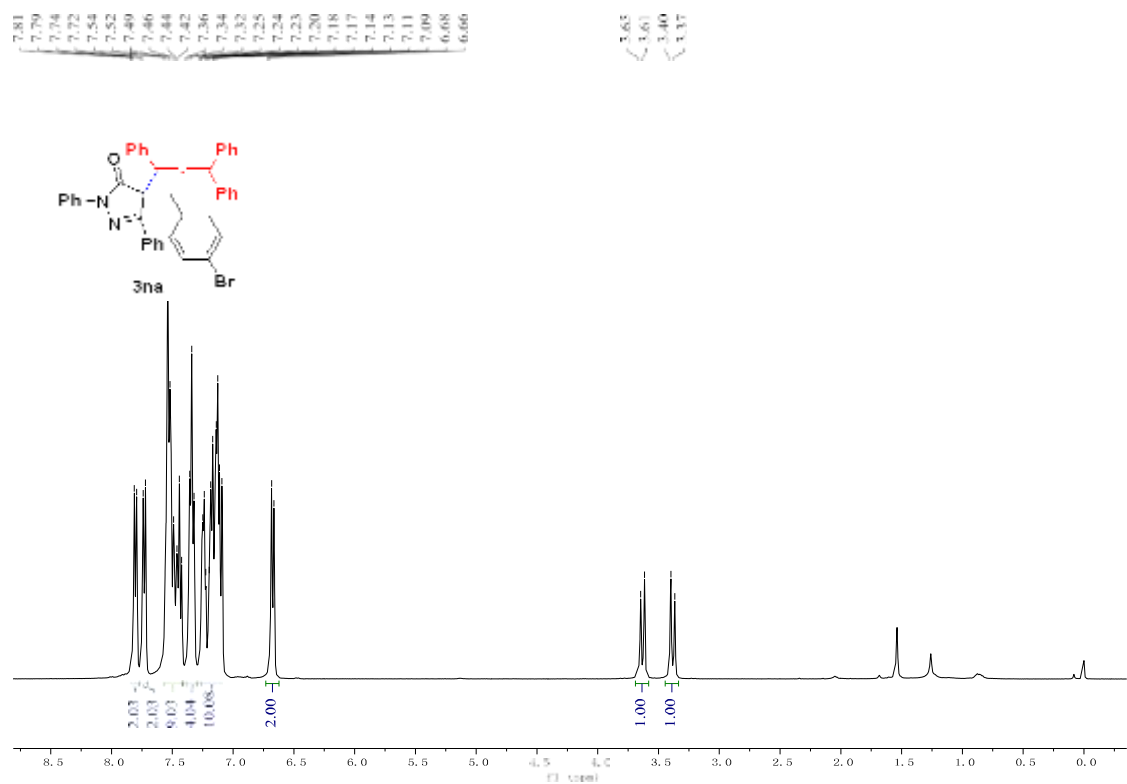


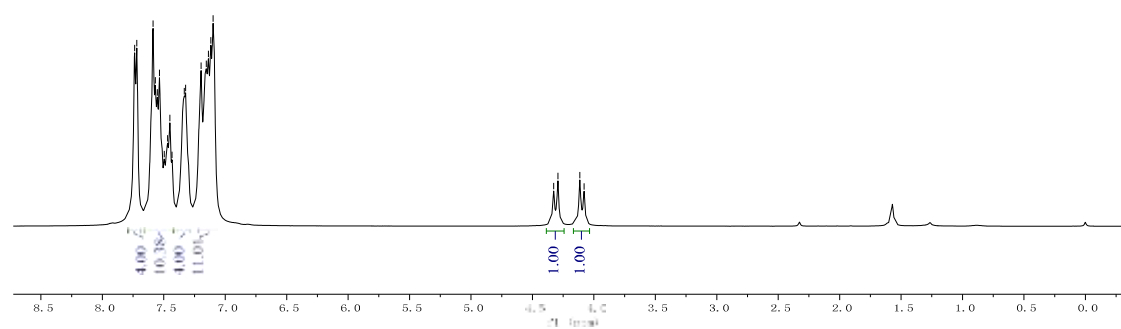
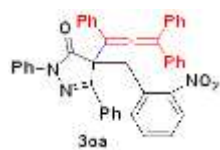












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