

Supplementary Information

Copper catalyzed acylation of pyrazolones with aldehydes toward 4-acylpyrazolones

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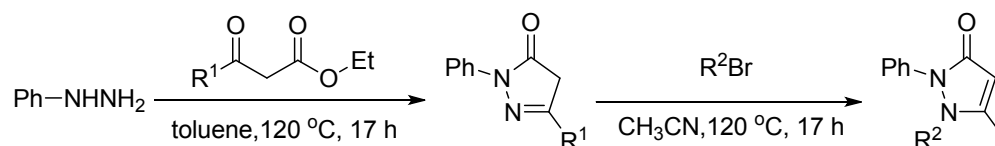
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1. General Information

Unless otherwise noted, all the reactions were carried out under nitrogen atmosphere using standard Schlenk technique, and all chemicals were purchased from commercial suppliers and used without further purification. The ^1H NMR spectra were recorded on a 300 MHz or 400 MHz NMR spectrometer. The ^{13}C NMR spectra were recorded at 75 MHz or 100 MHz. NMR experiments are reported in δ units, parts per million (ppm), and were referenced to CDCl_3 (δ 7.26 or 77.0 ppm) as the internal standard. The coupling constants J are given in Hz. High-resolution mass spectra (HRMS) were obtained using a Bruker micro-TOF II focus spectrometer (ESI). Column chromatography was performed using EM Silica gel 60 (300-400 mesh), and the eluent was a mixture of petroleum ether (PE) and ethyl acetate (EA). All melting points were tested after recrystallization with CH_2Cl_2 .

2. Synthesis and Reaction

2.1 Preparation of N-Substituted pyrazolone Substrates **1**¹

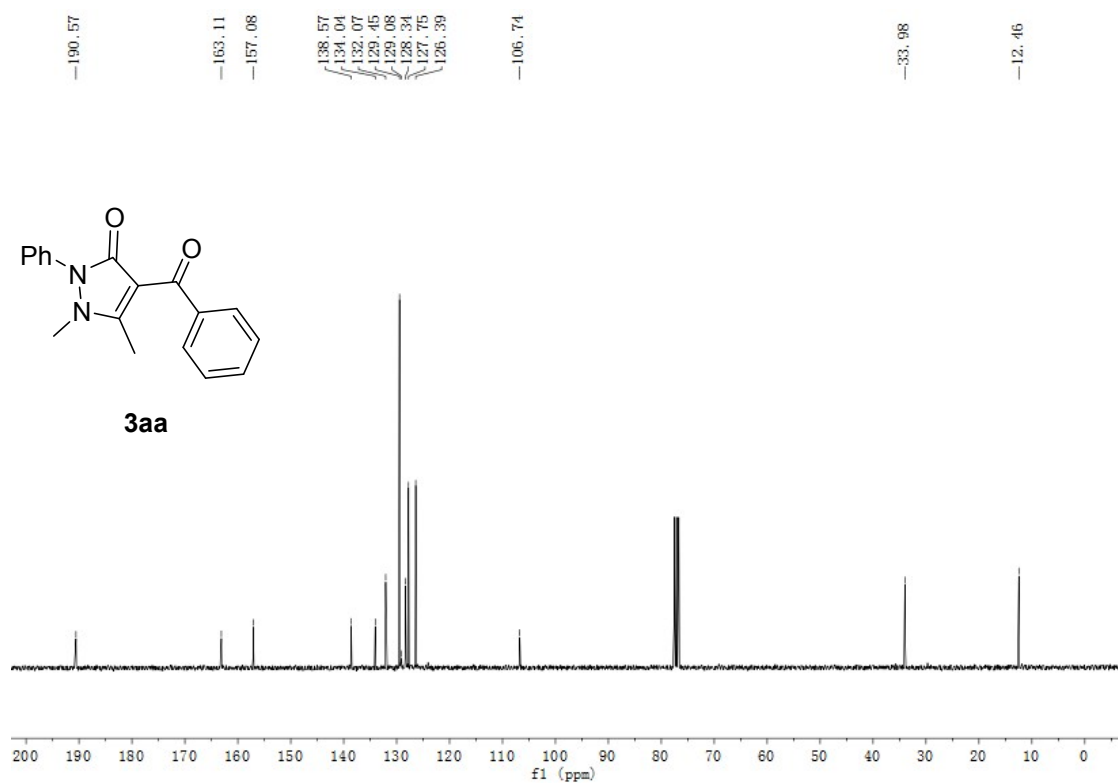
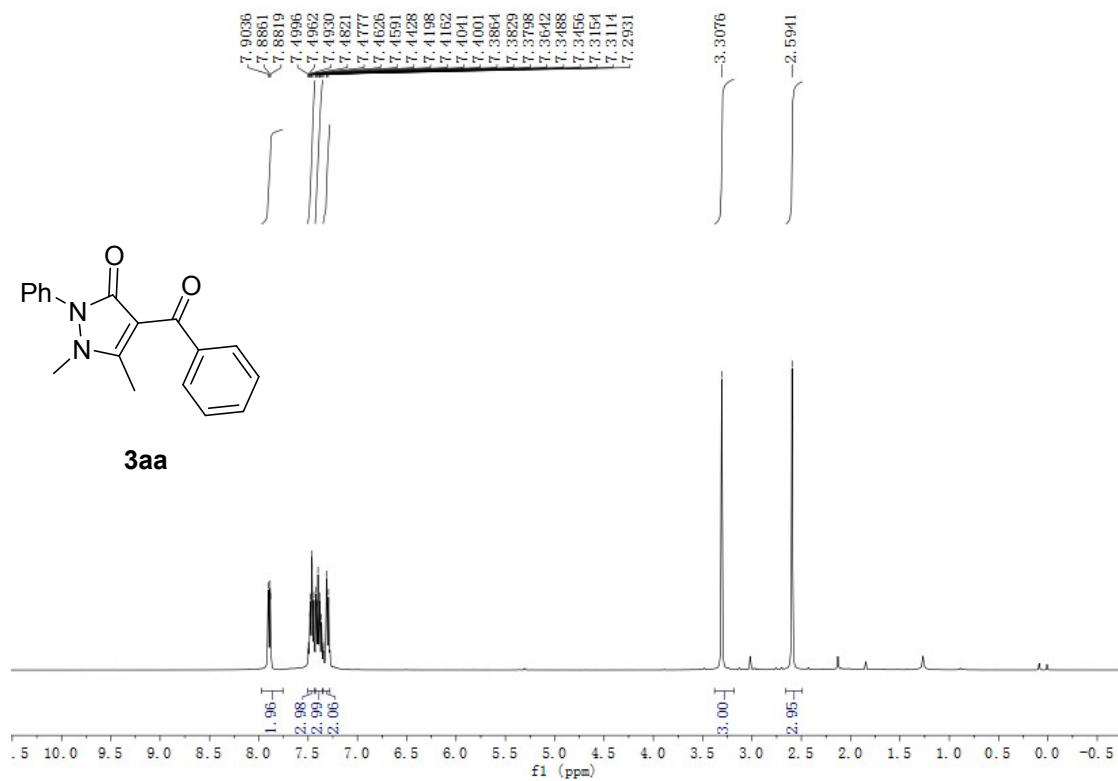


A reaction mixture containing aryl hydrazine (5 mmol), ethyl acetoacetate or ethyl 3-oxo-3-phenylpropanoate (5 mmol) and toluene (10 mL) was stirred at $120\text{ }^\circ\text{C}$ in an oil bath. After 17 h, the reaction mixture was cooled to room temperature. To this mixture, acetonitrile (10 mL) and alkyl bromide (10 mmol) were added, successively. The residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc (V_1/V_2 , 1:1) as the eluent to give the desired products.

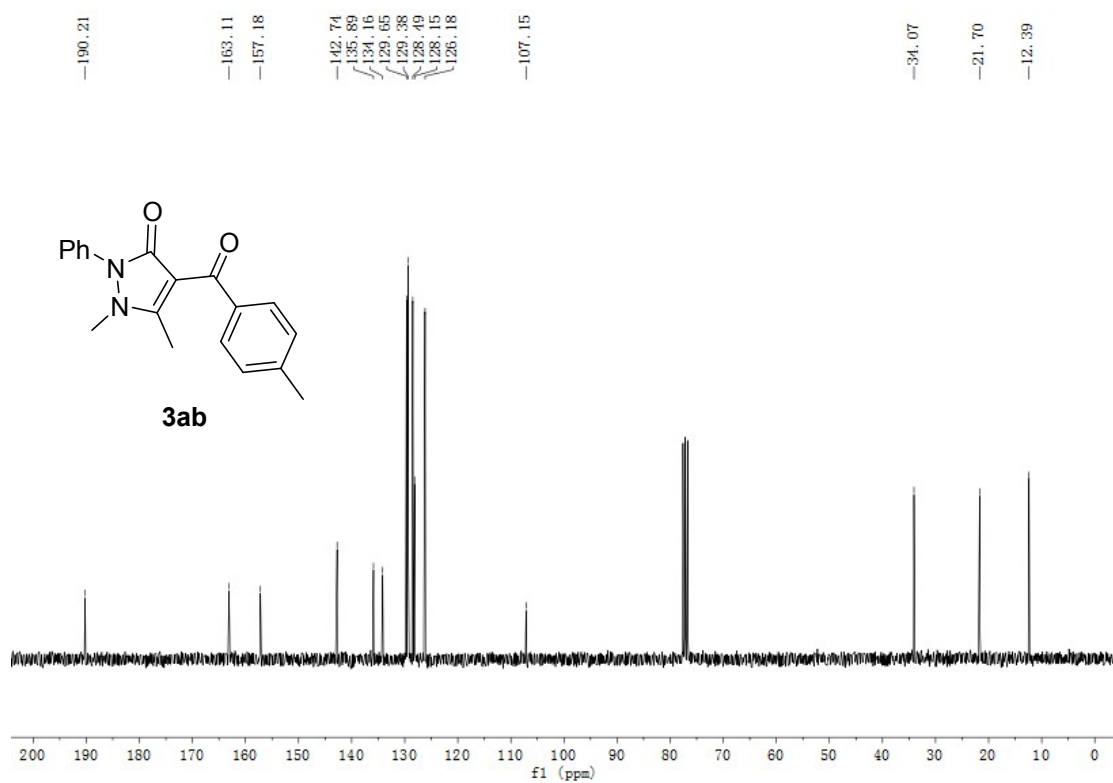
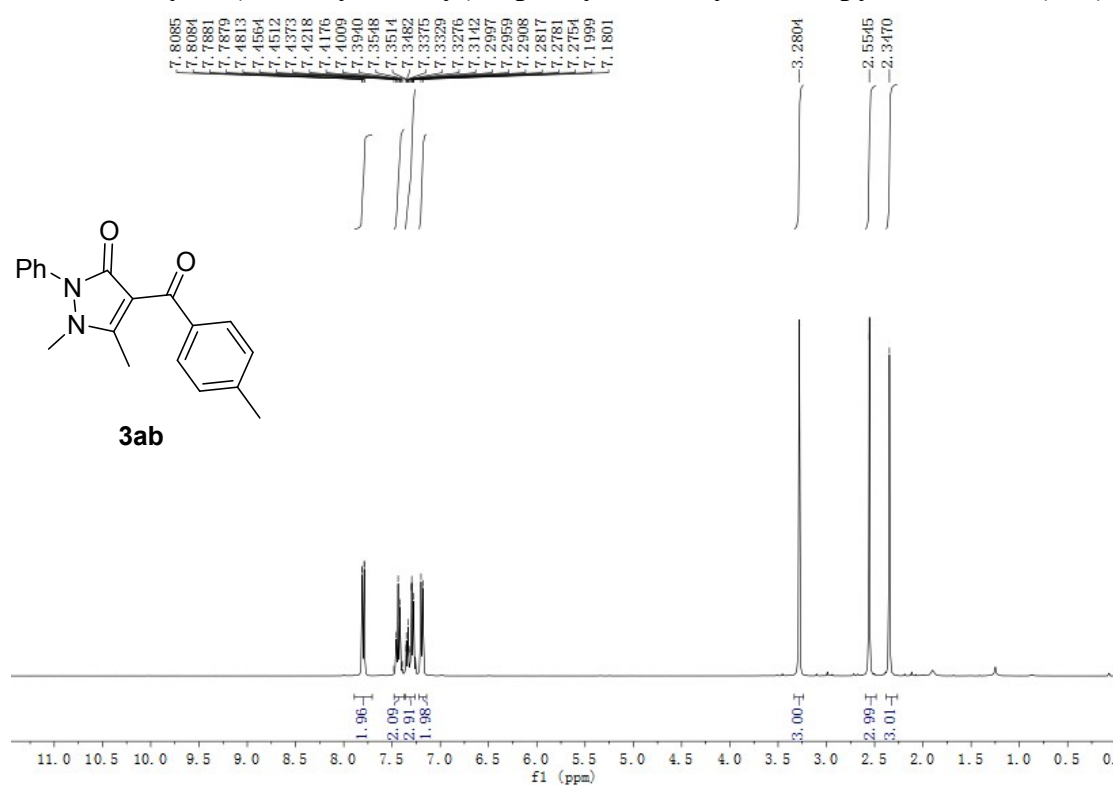
3. Reference.

1. Y. Yang, H. Gong, C. Kuang. *Eur. J. Org. Chem.*, 2013, **24**, 5276.

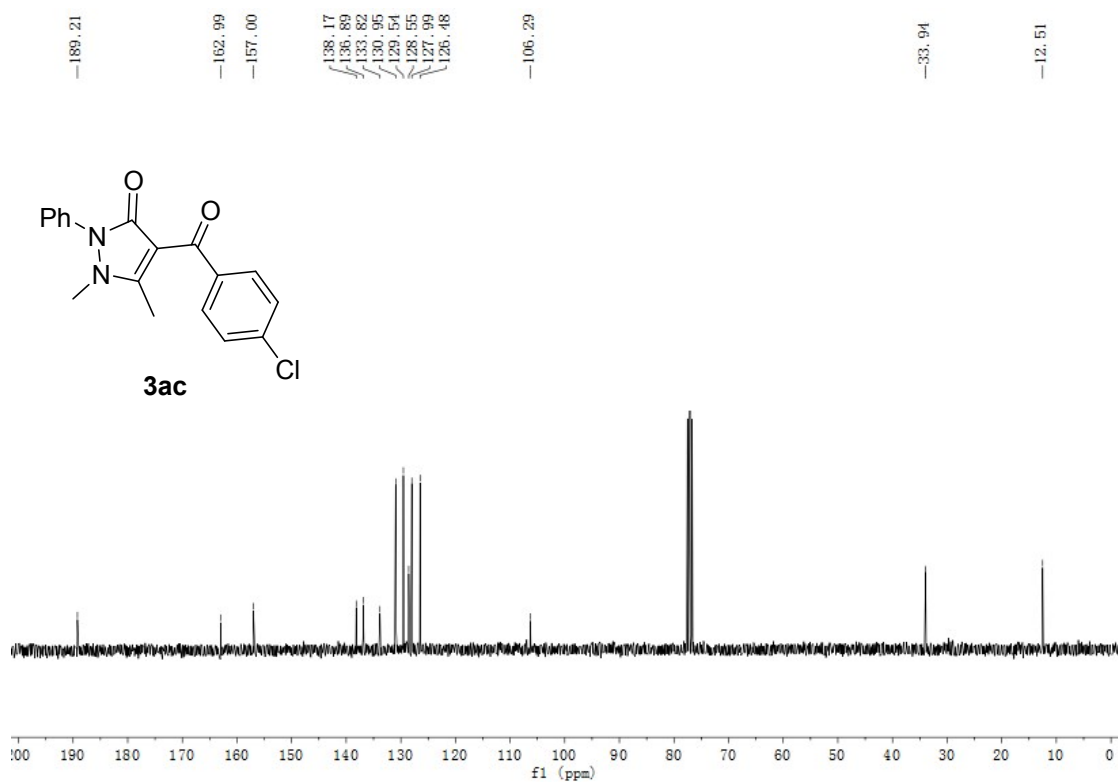
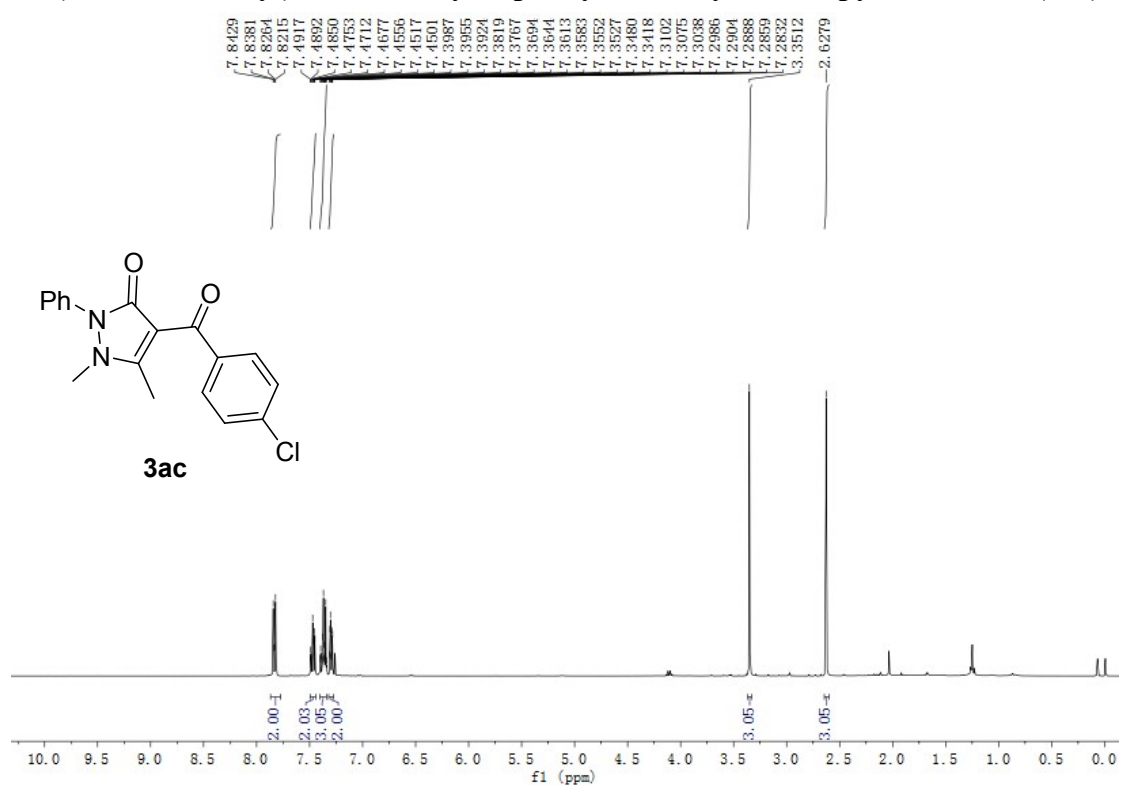
4. Copies of ^1H NMR and ^{13}C NMR spectra of 3aa-3ia
 4-benzoyl-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (3aa):



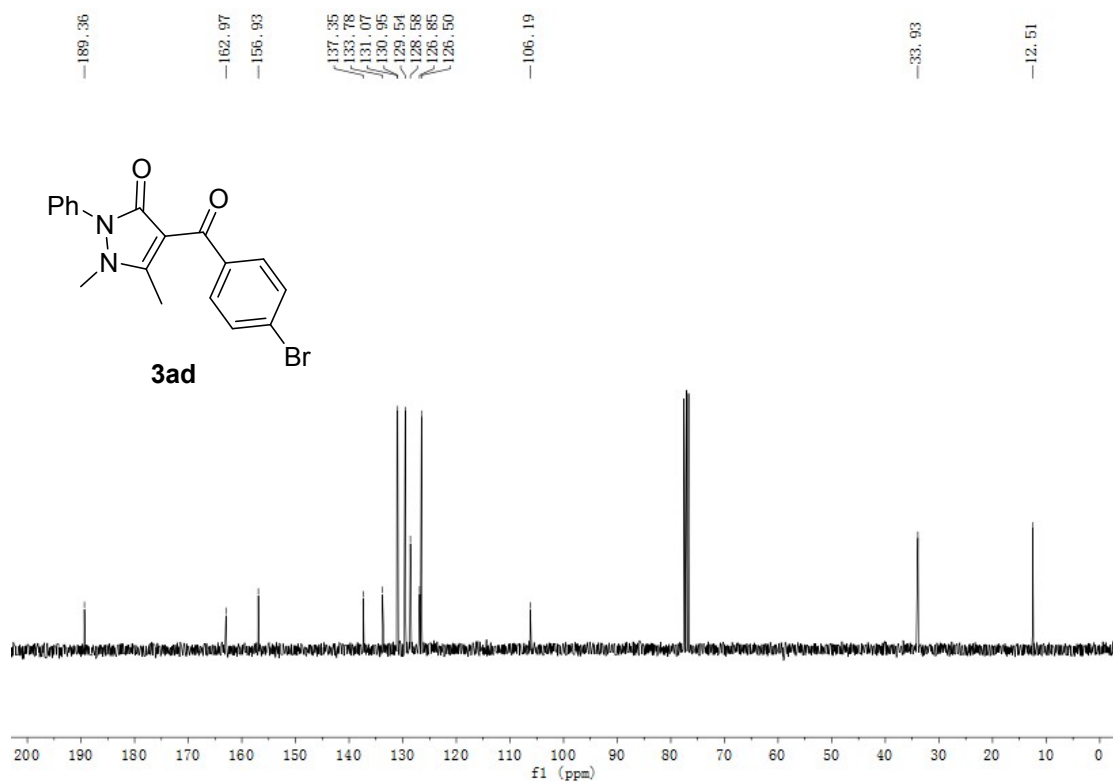
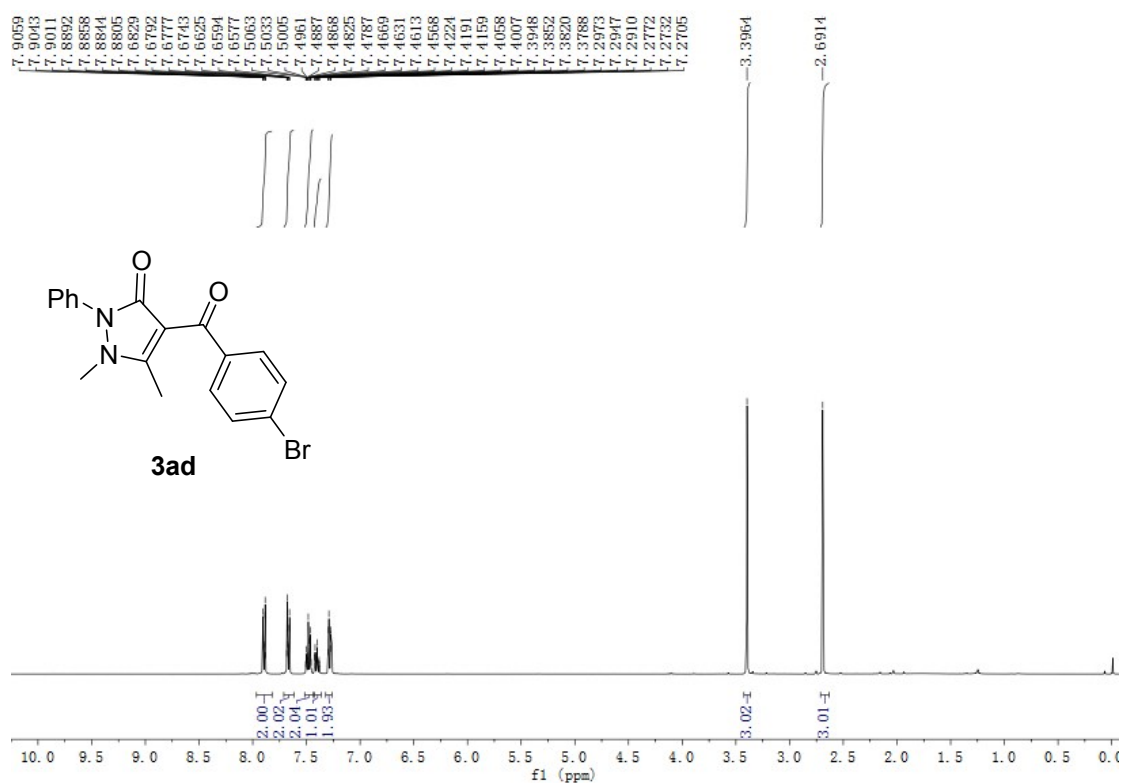
1,5-dimethyl-4-(4-methylbenzoyl)-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (3ab)



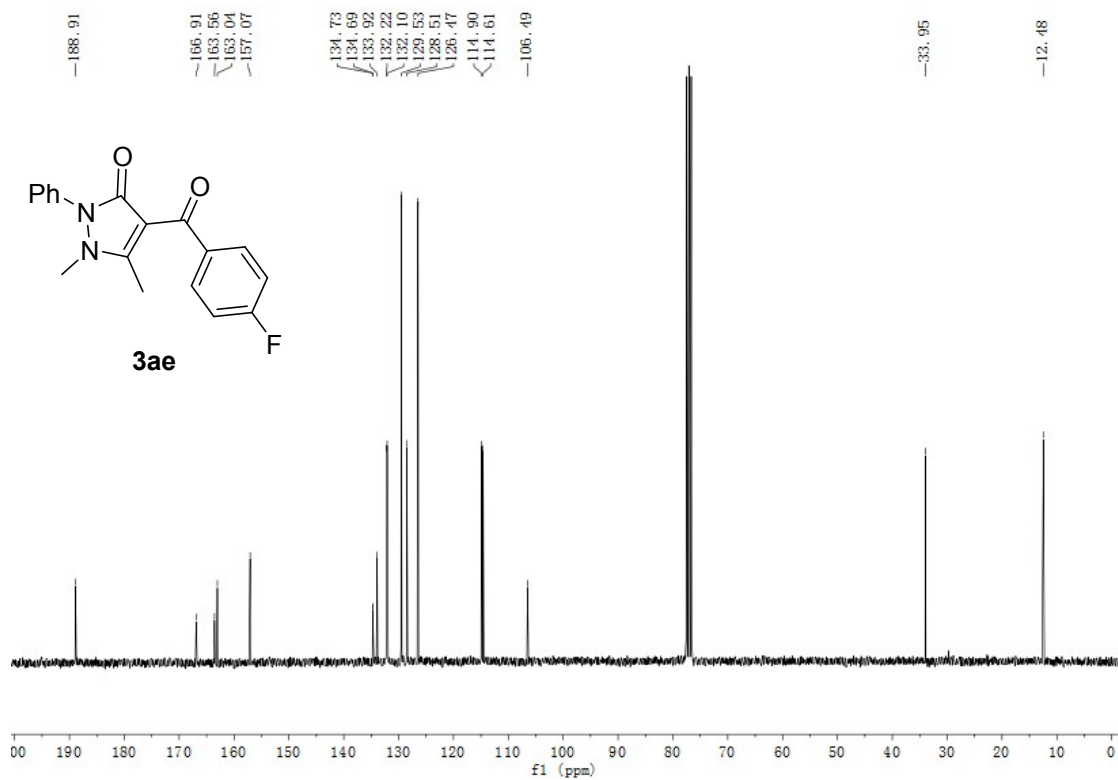
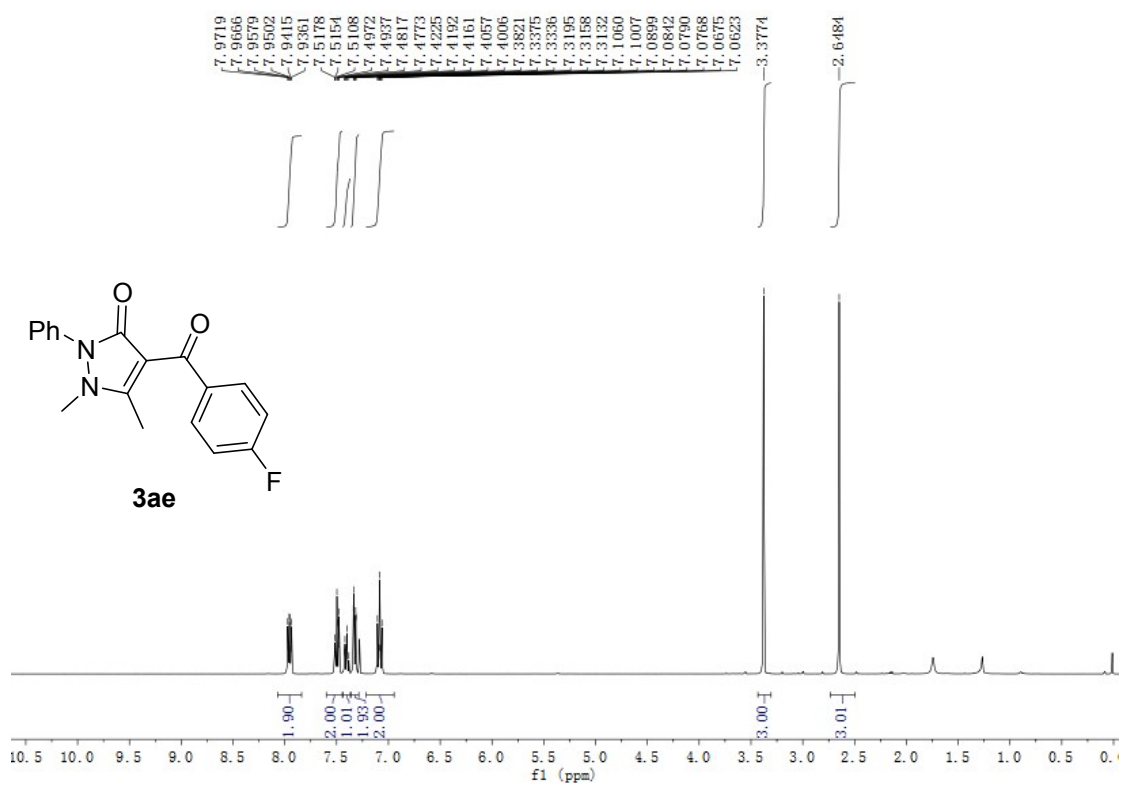
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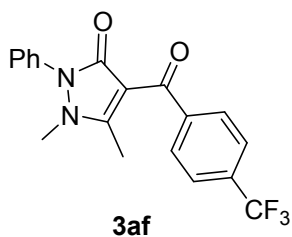
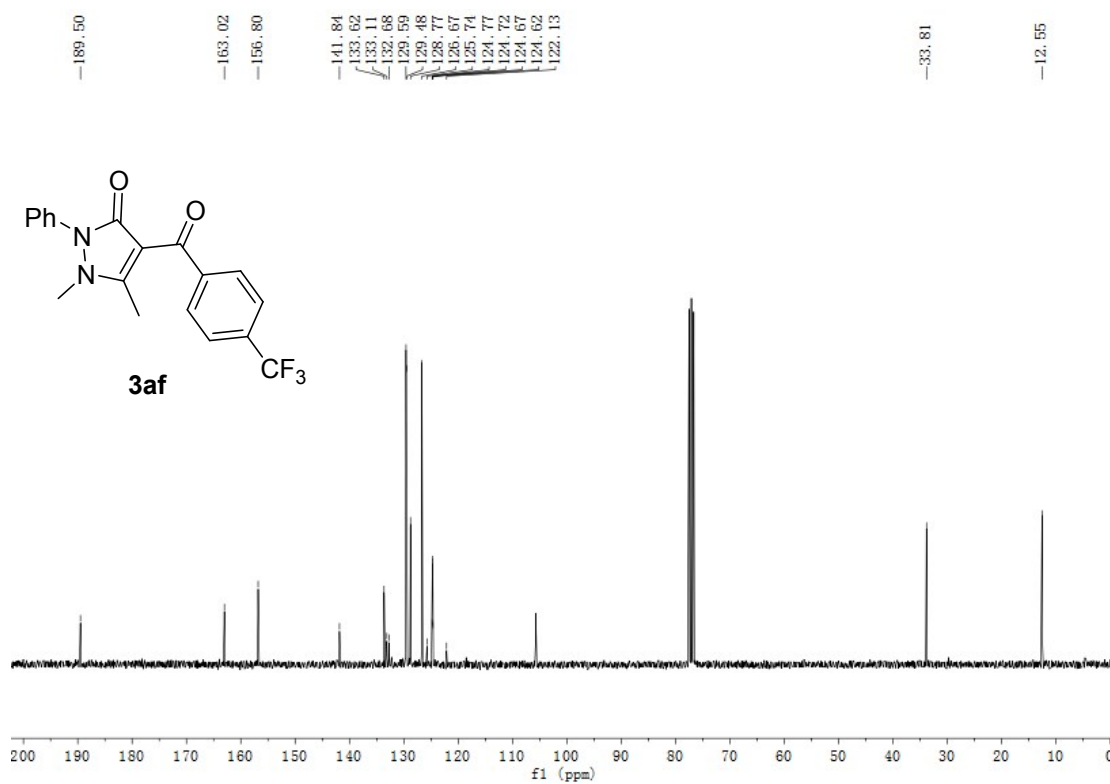
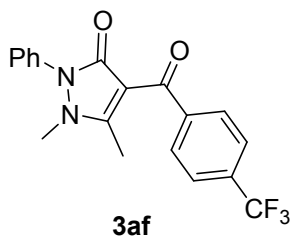
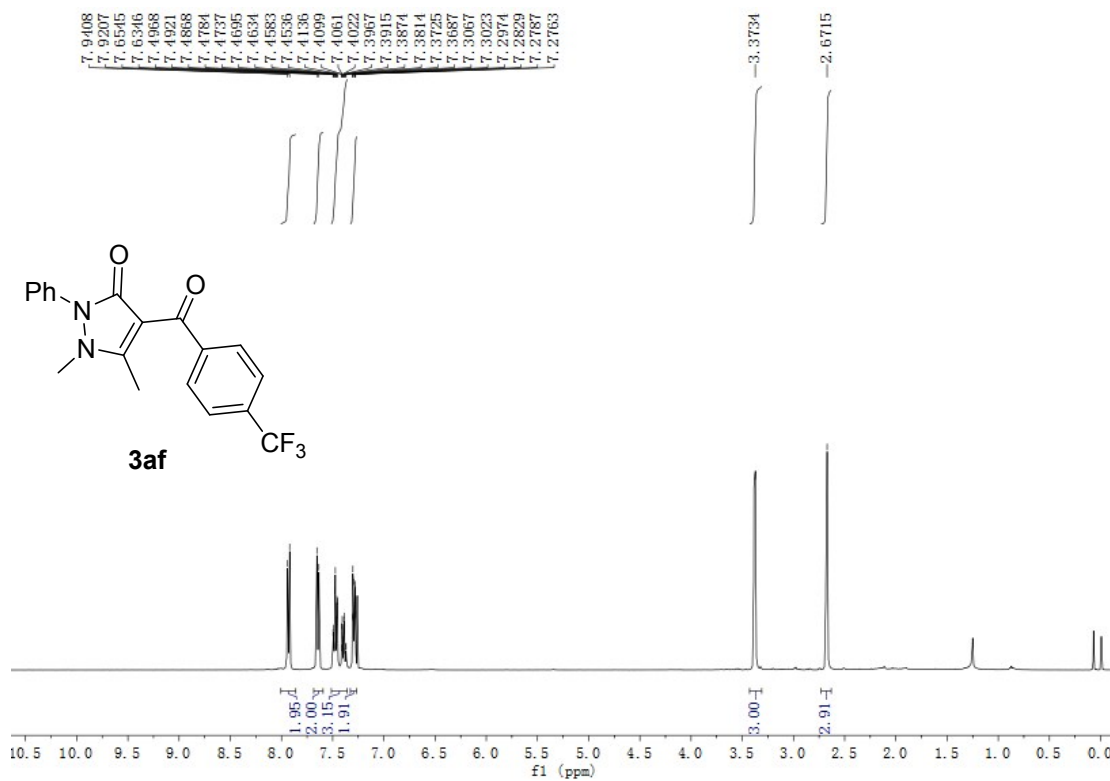
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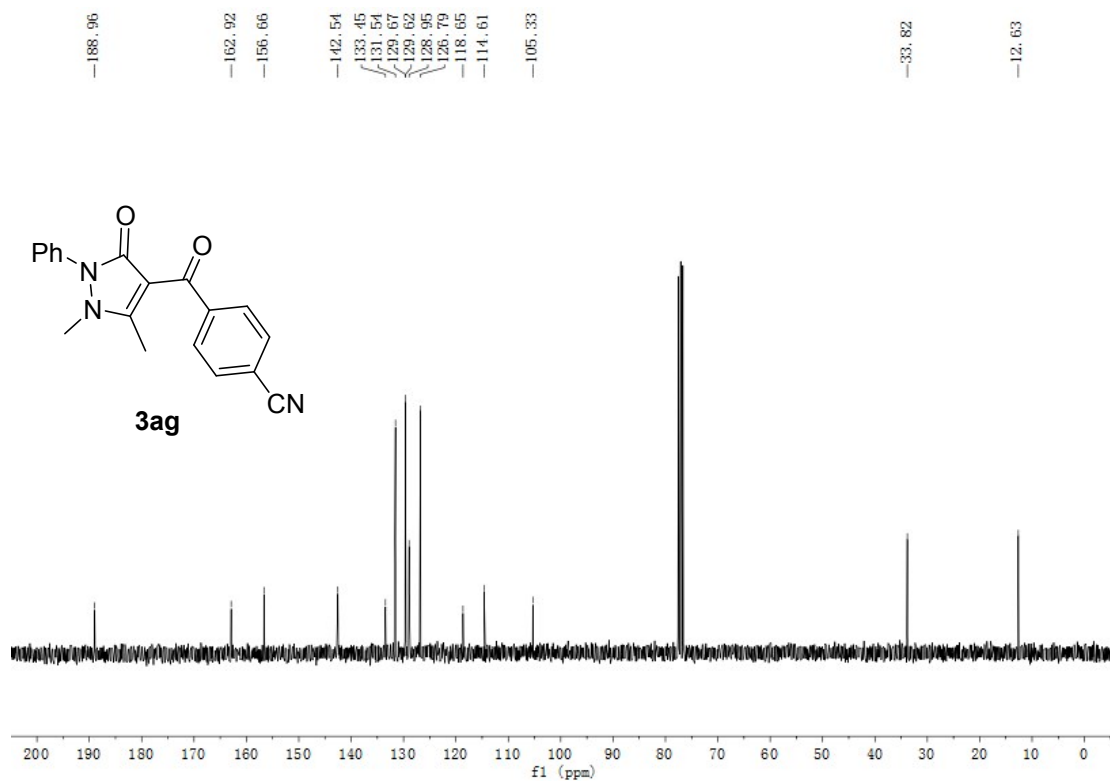
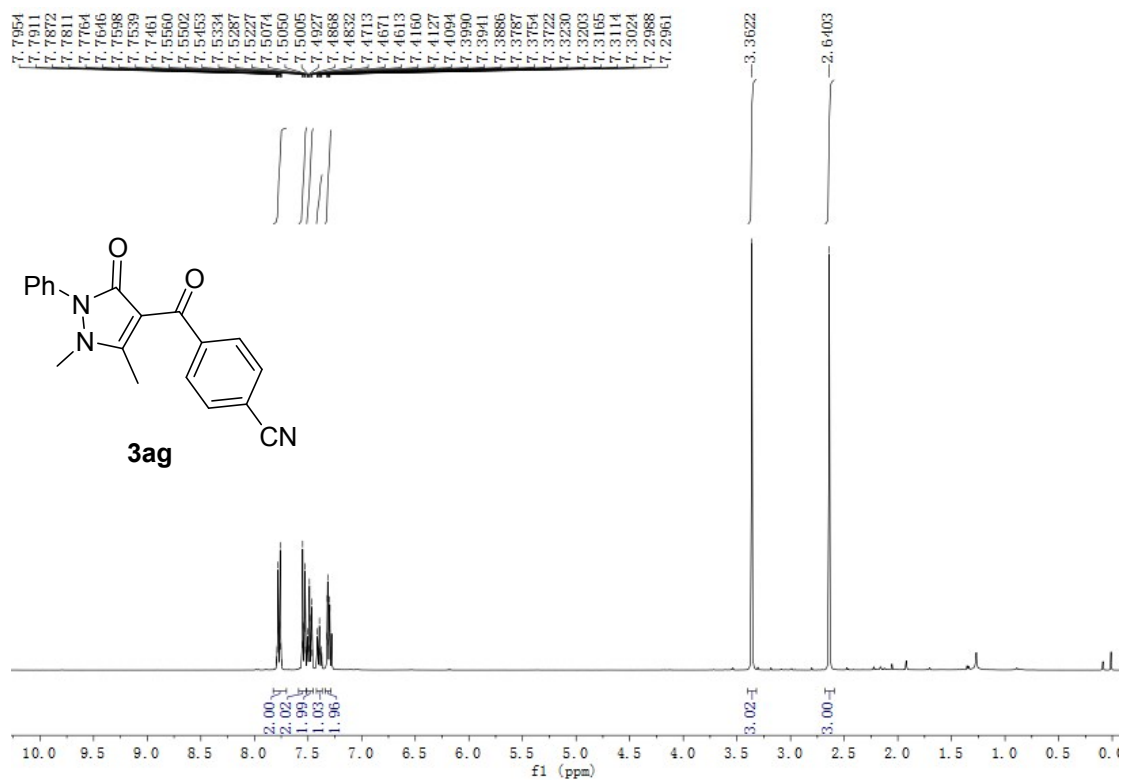
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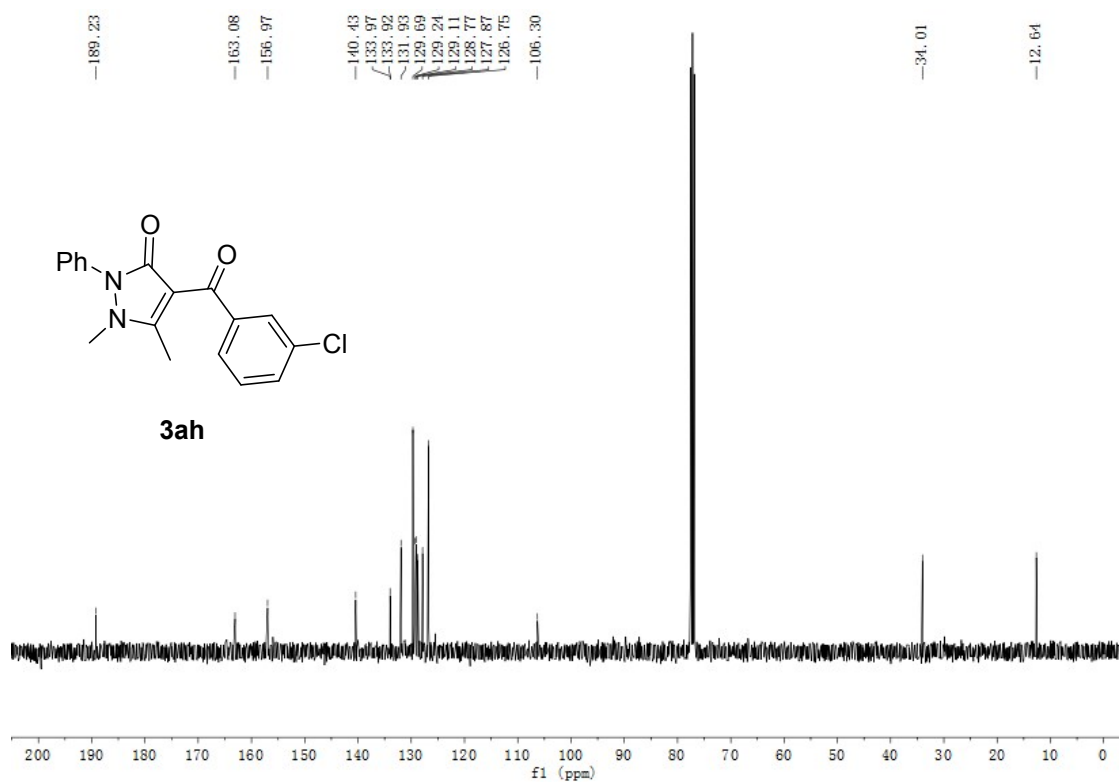
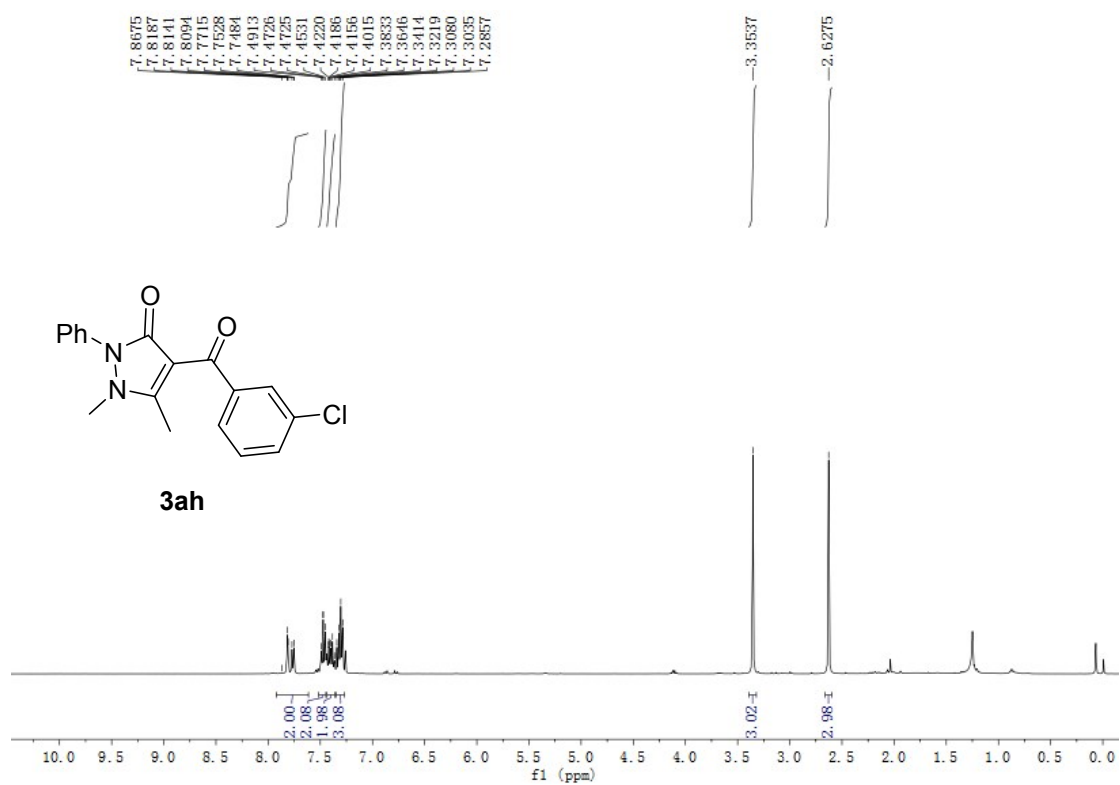
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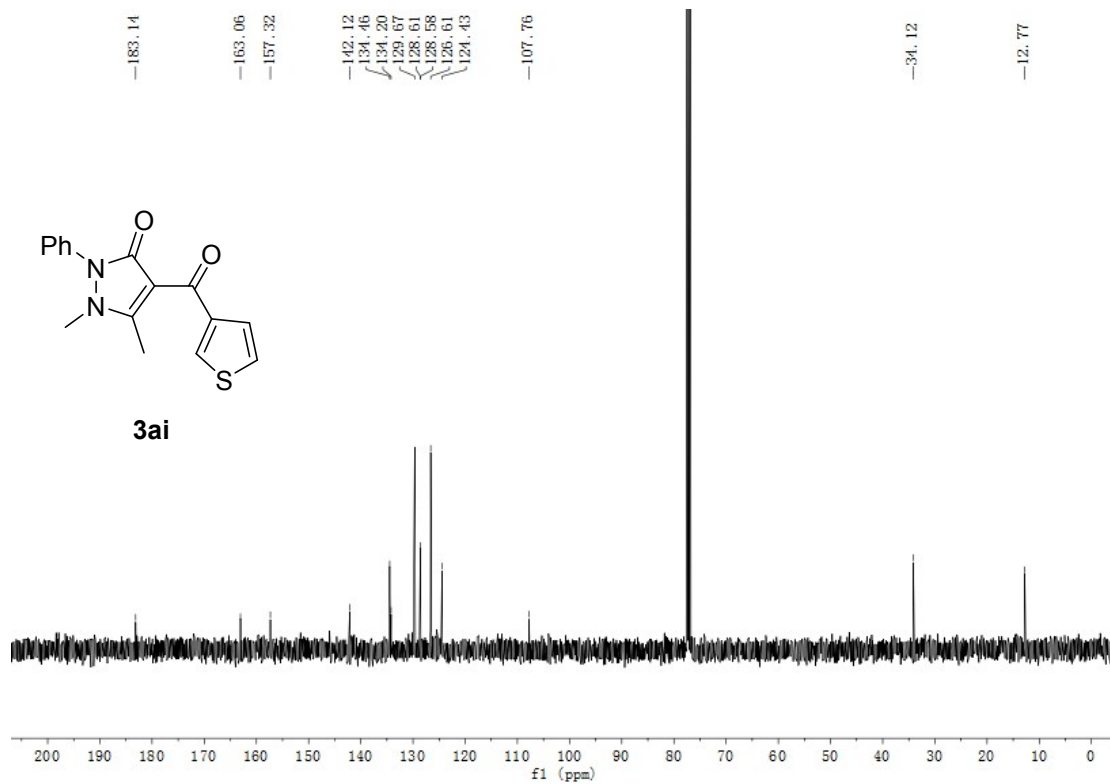
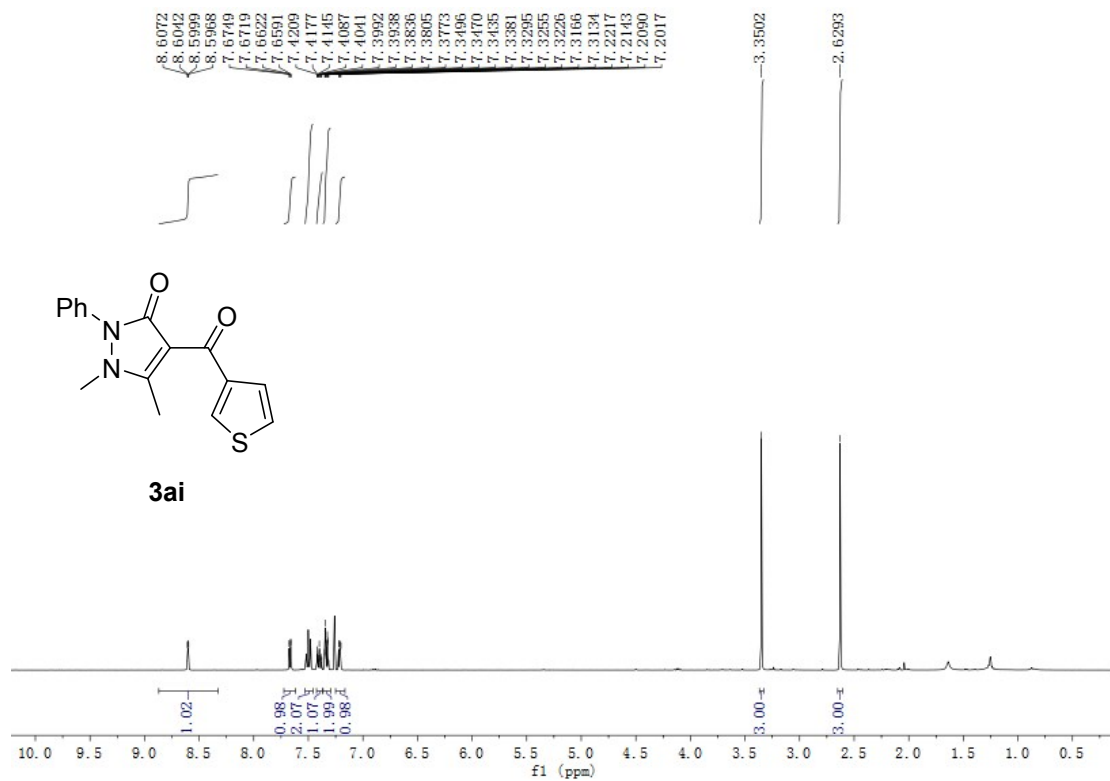
4-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazole-4-carbonyl)benzonitrile (3ag):



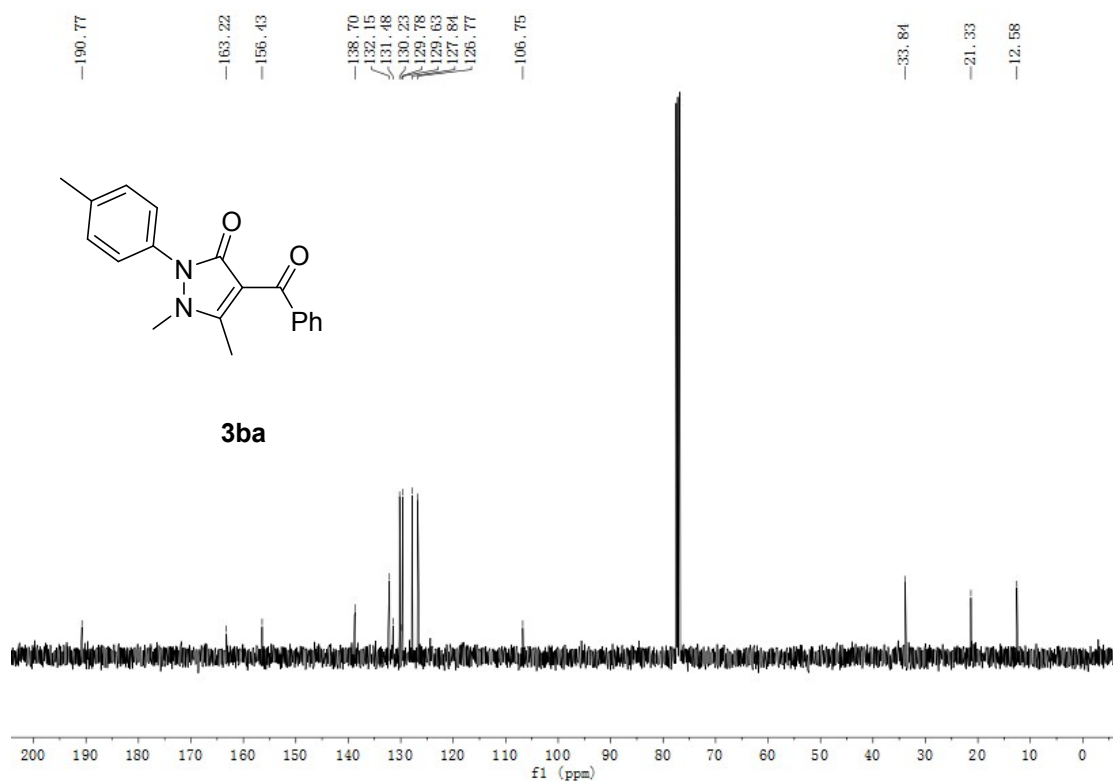
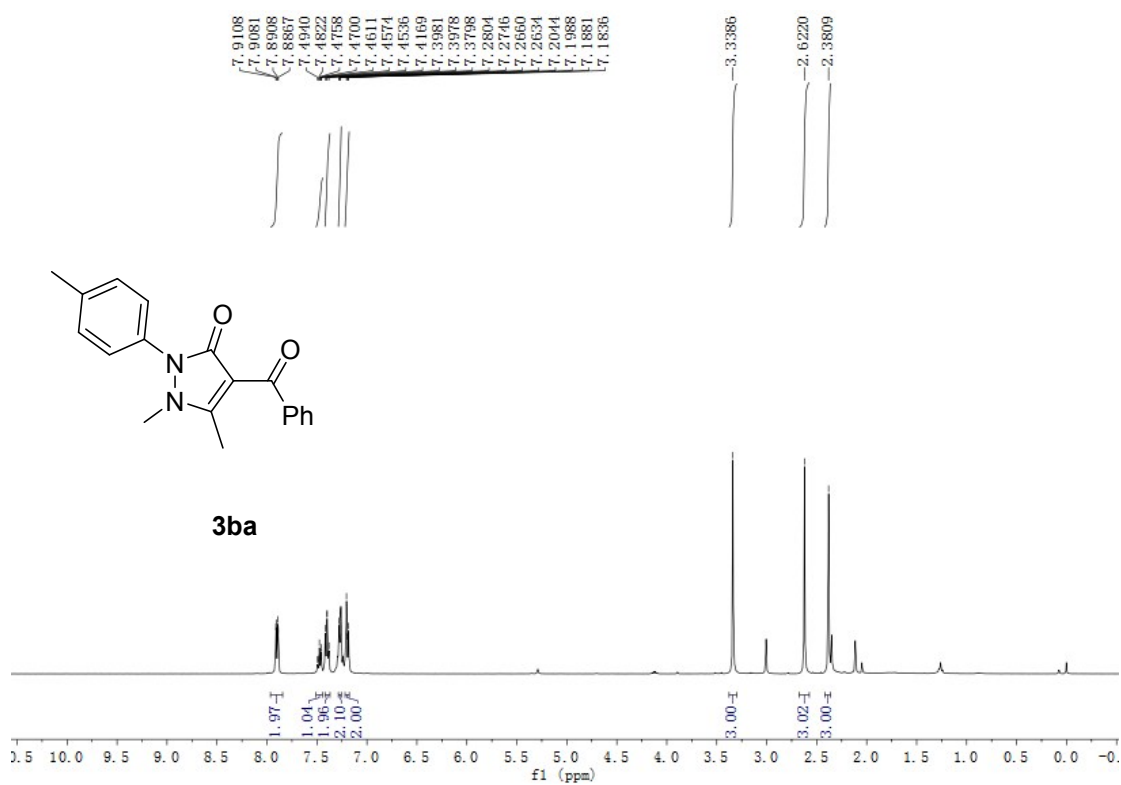
4-(3-chlorobenzoyl)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (3ah):



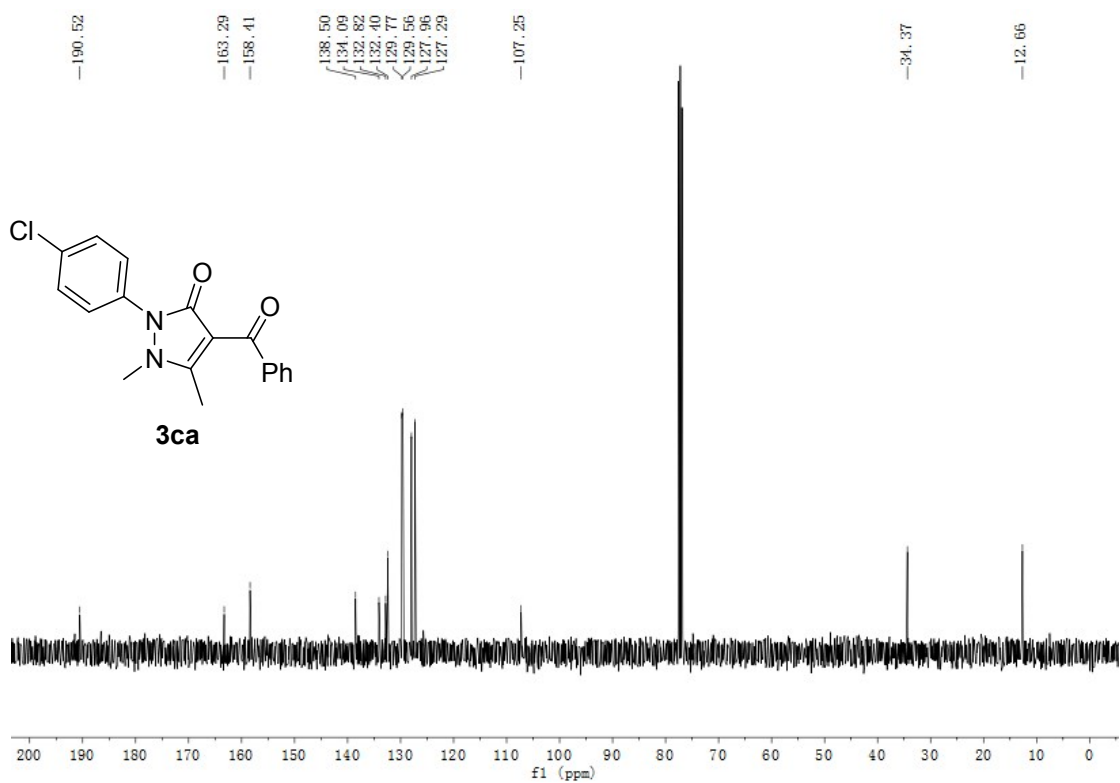
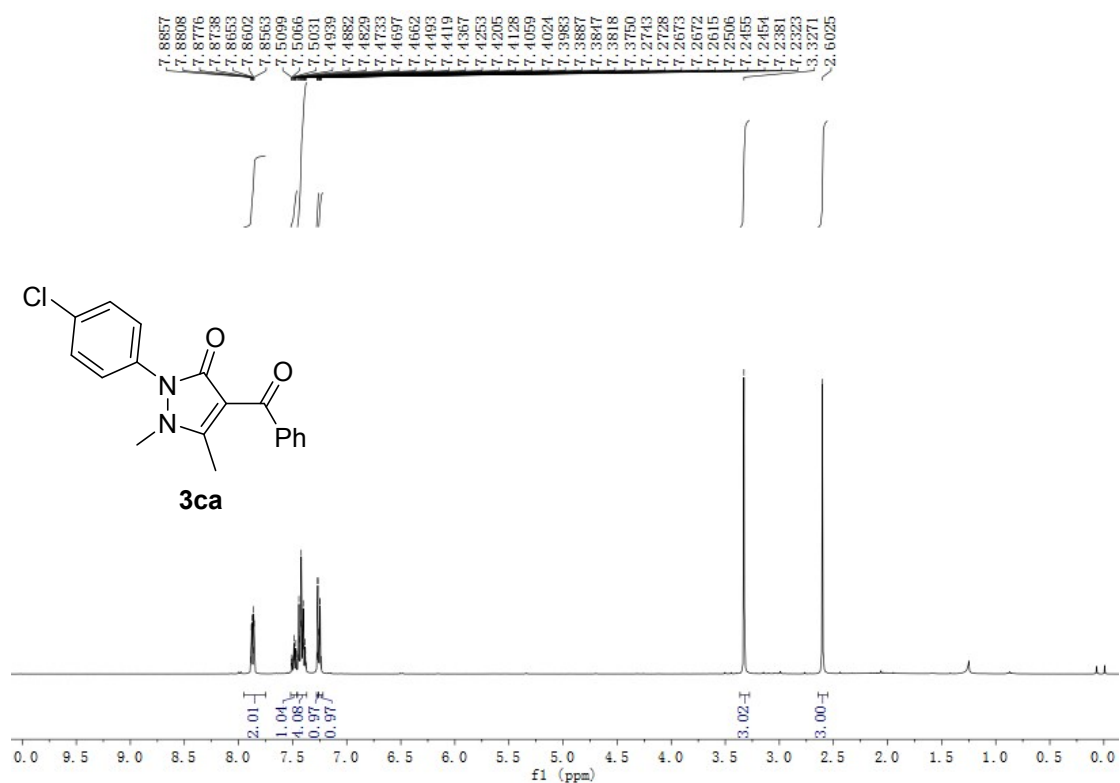
**1,5-dimethyl-2-phenyl-4-(thiophene-3-carbonyl)-1,2-dihydro-3H-pyrazol-3-one
(3ai):**



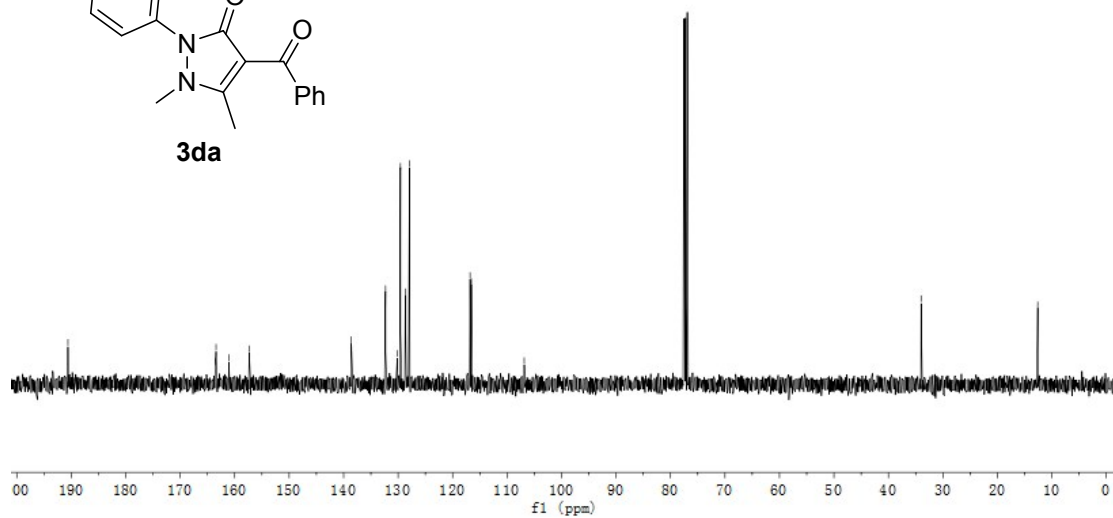
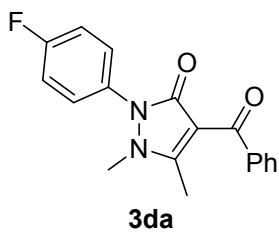
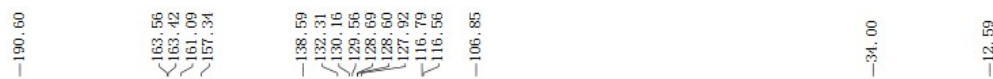
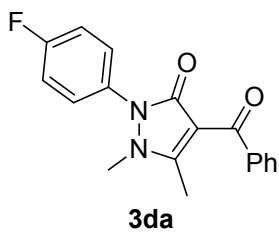
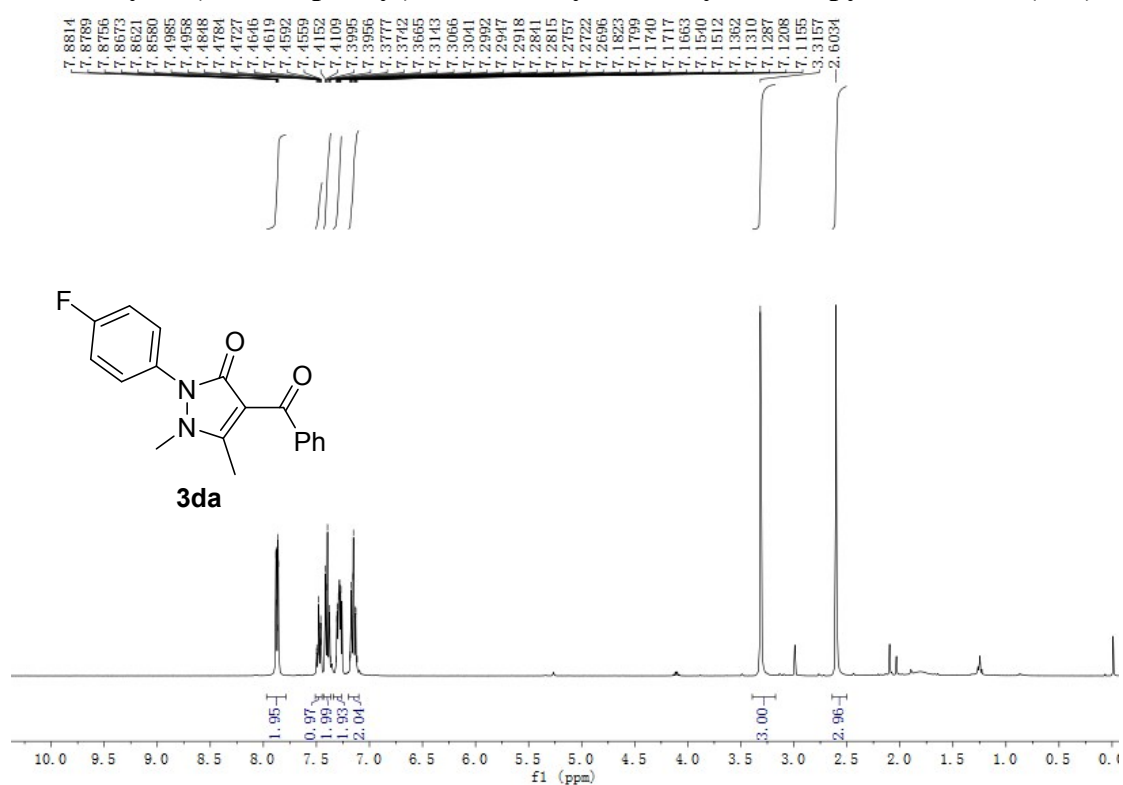
4-benzoyl-1,5-dimethyl-2-(p-tolyl)-1,2-dihydro-3H-pyrazol-3-one (3ba):



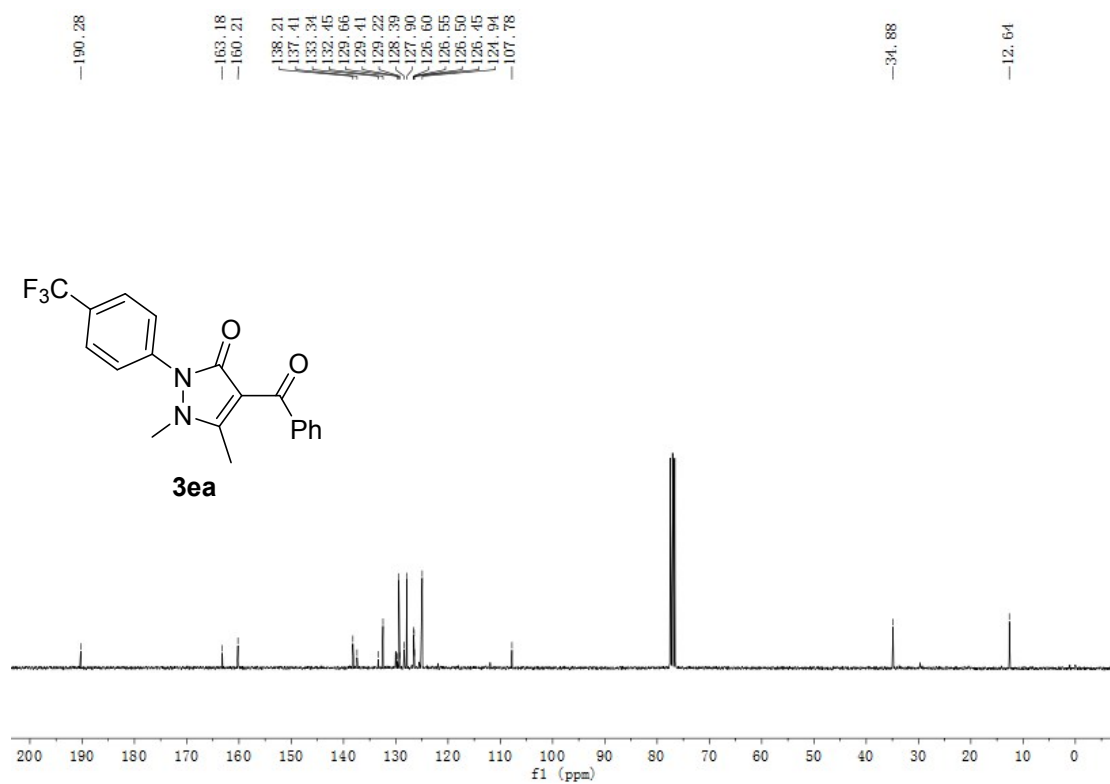
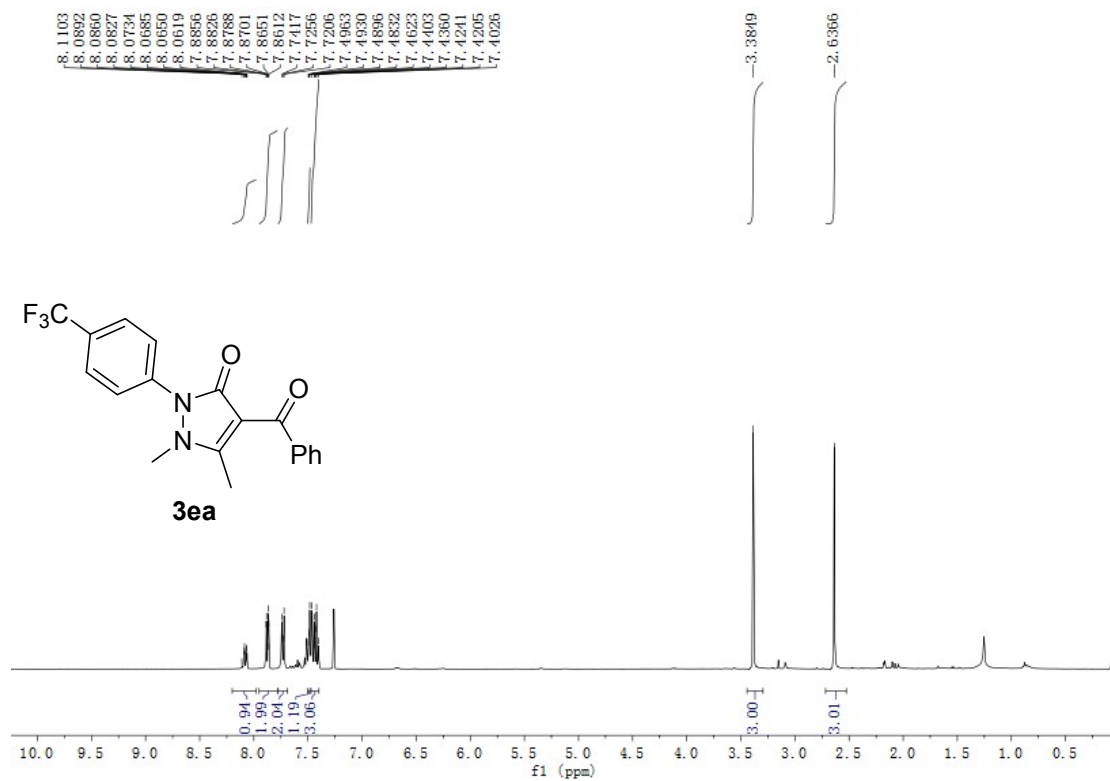
4-benzoyl-2-(4-chlorophenyl)-1,5-dimethyl-1,2-dihydro-3H-pyrazol-3-one (3ca):



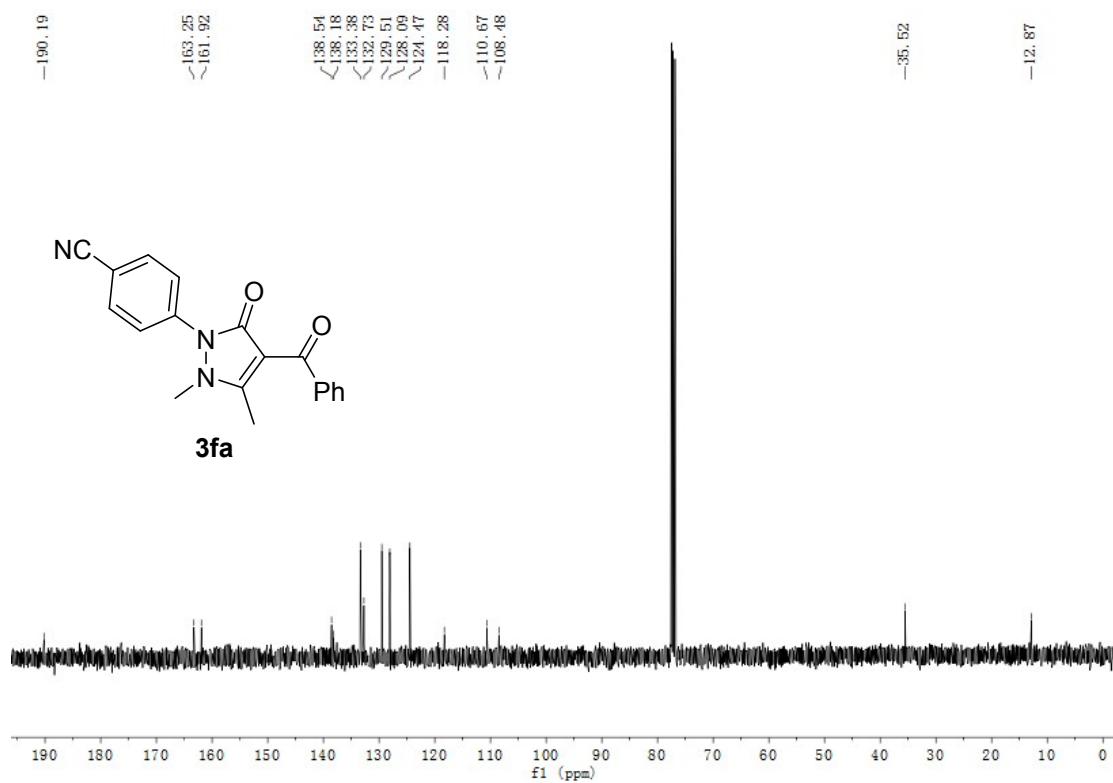
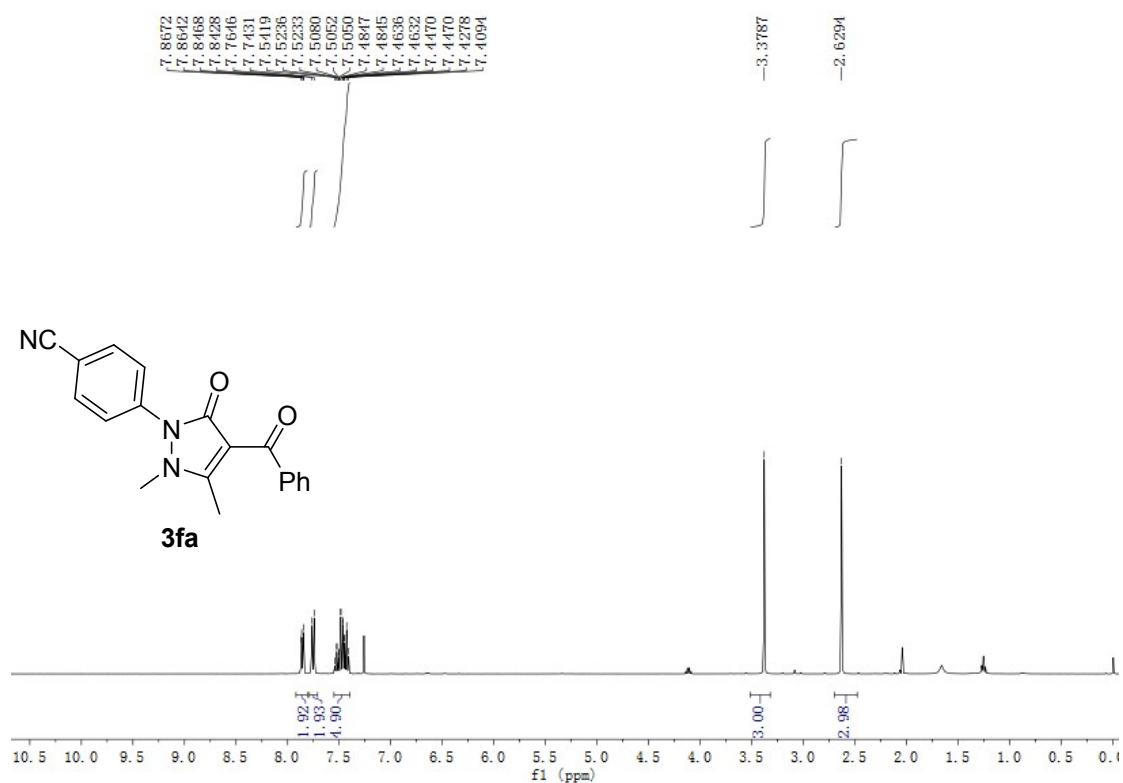
4-benzoyl-2-(4-fluorophenyl)-1,5-dimethyl-1,2-dihydro-3H-pyrazol-3-one (3da):



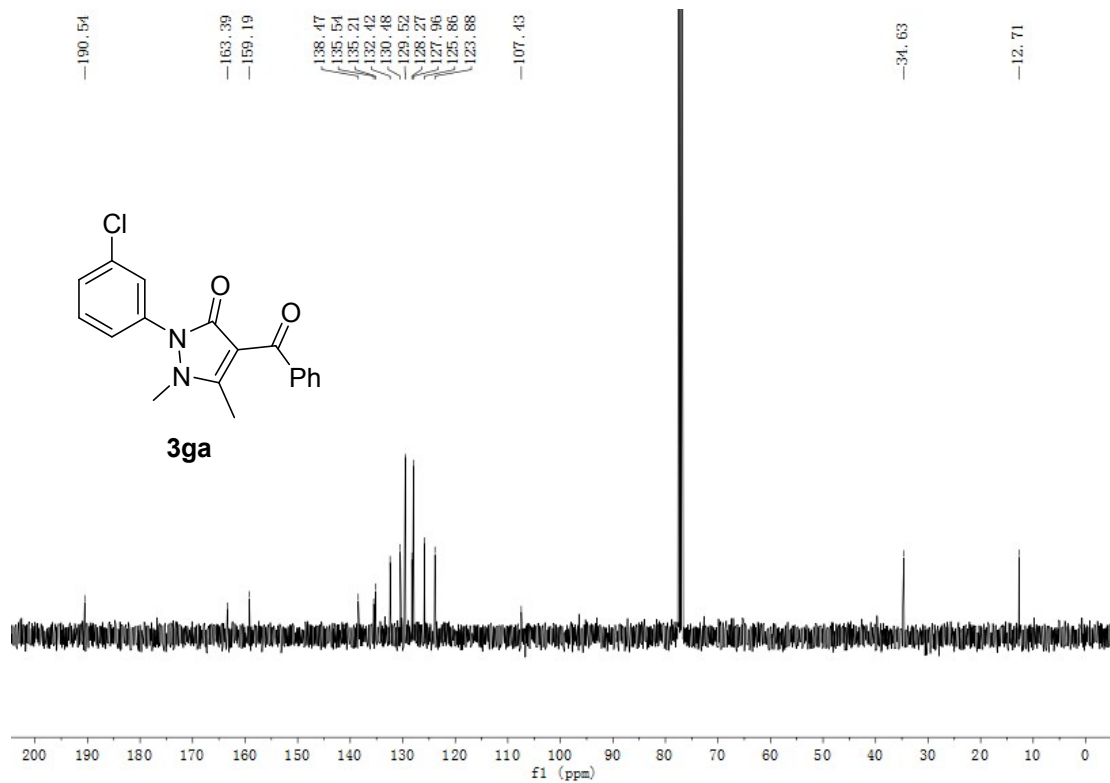
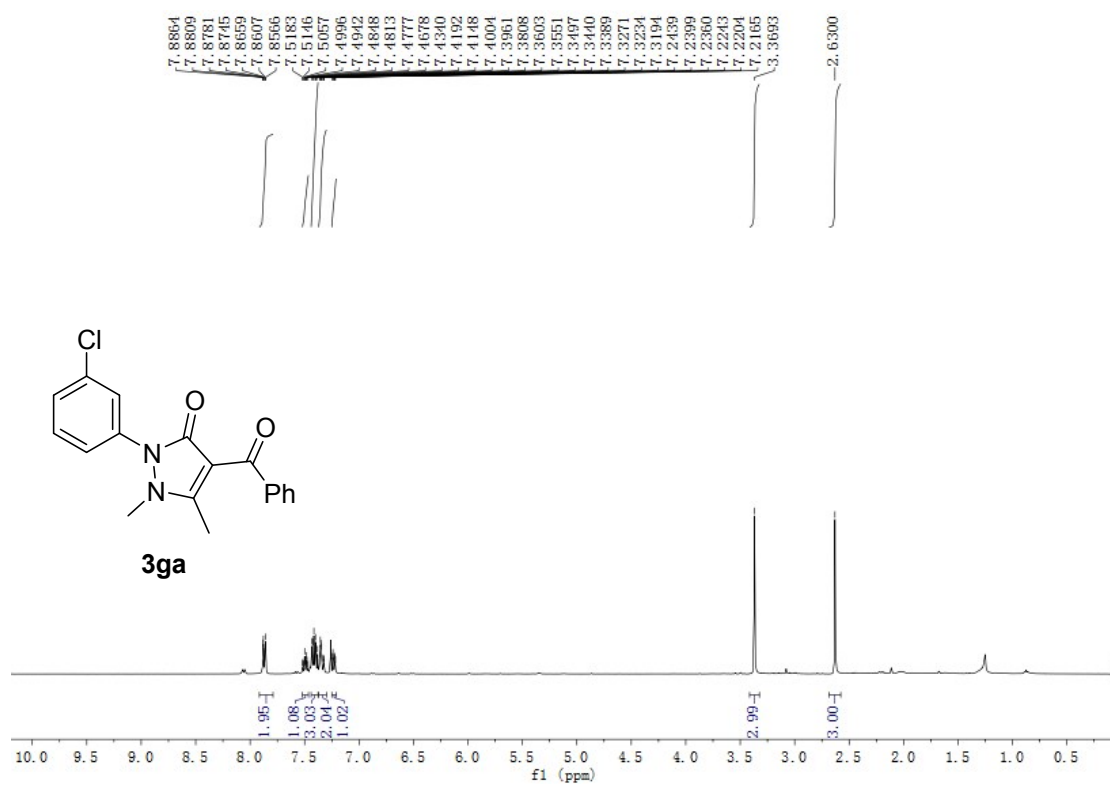
4-benzoyl-1,5-dimethyl-2-(4-(trifluoromethyl)phenyl)-1,2-dihydro-3H-pyrazol-3-one (3ea):



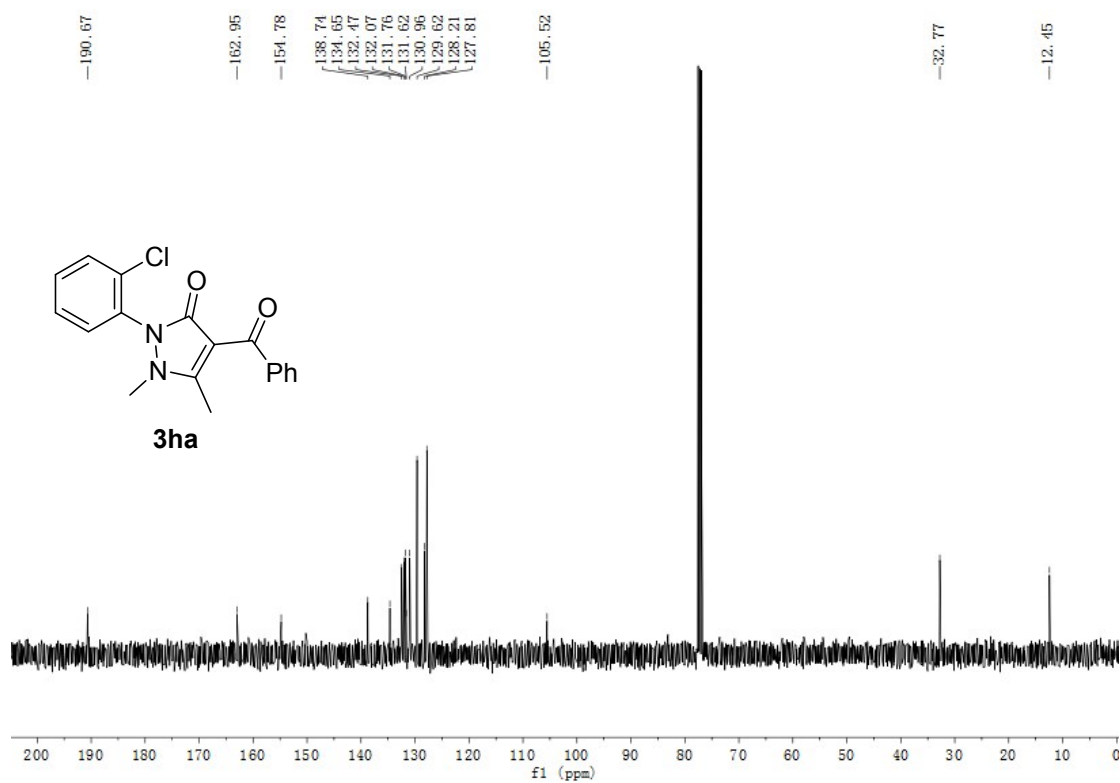
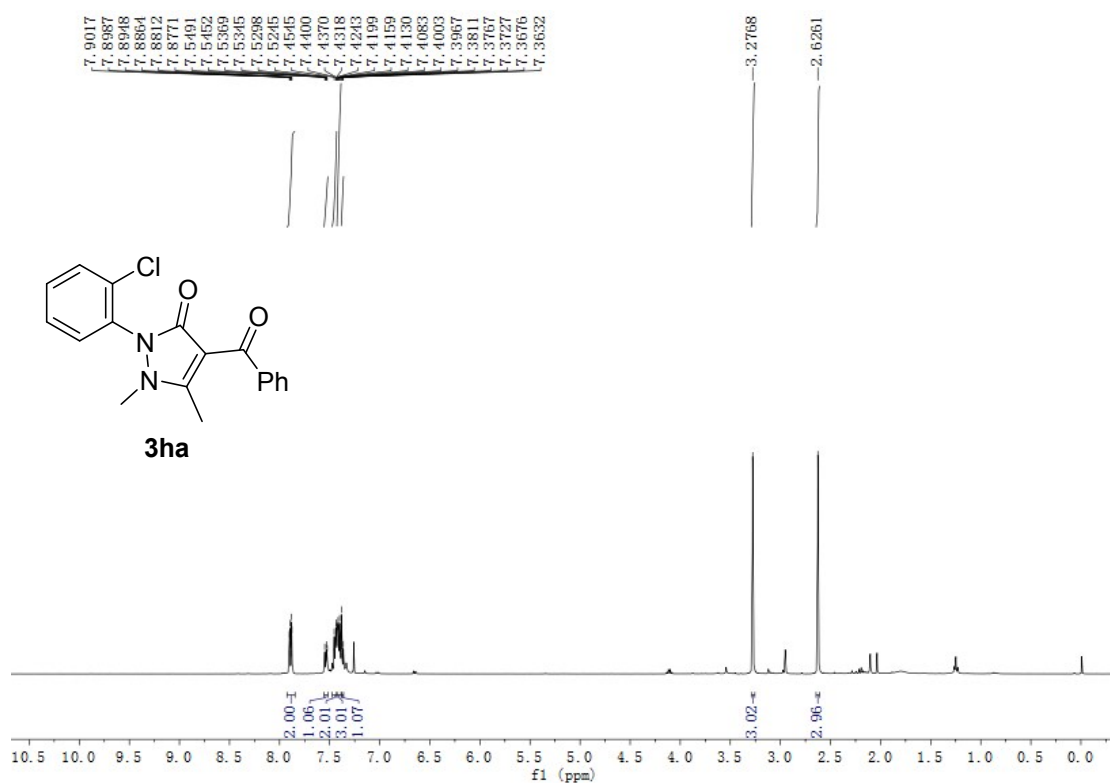
4-(4-benzoyl-2,3-dimethyl-5-oxo-2,5-dihydro-1H-pyrazol-1-yl)benzonitrile (3fa):



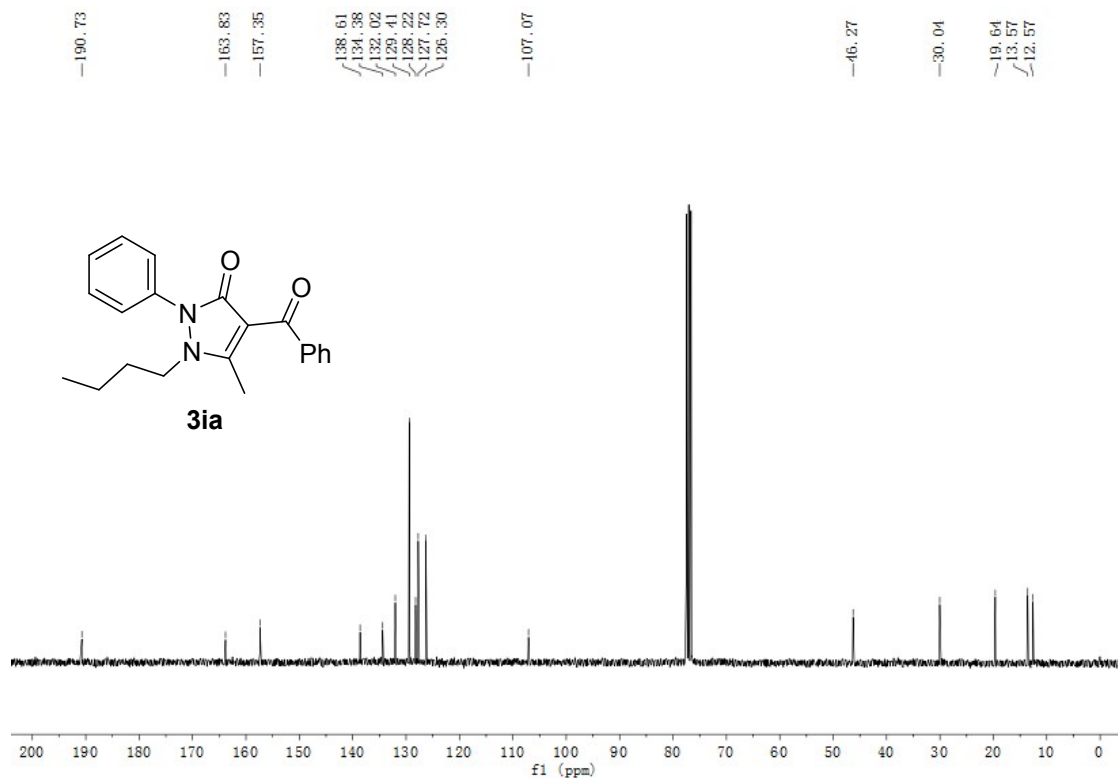
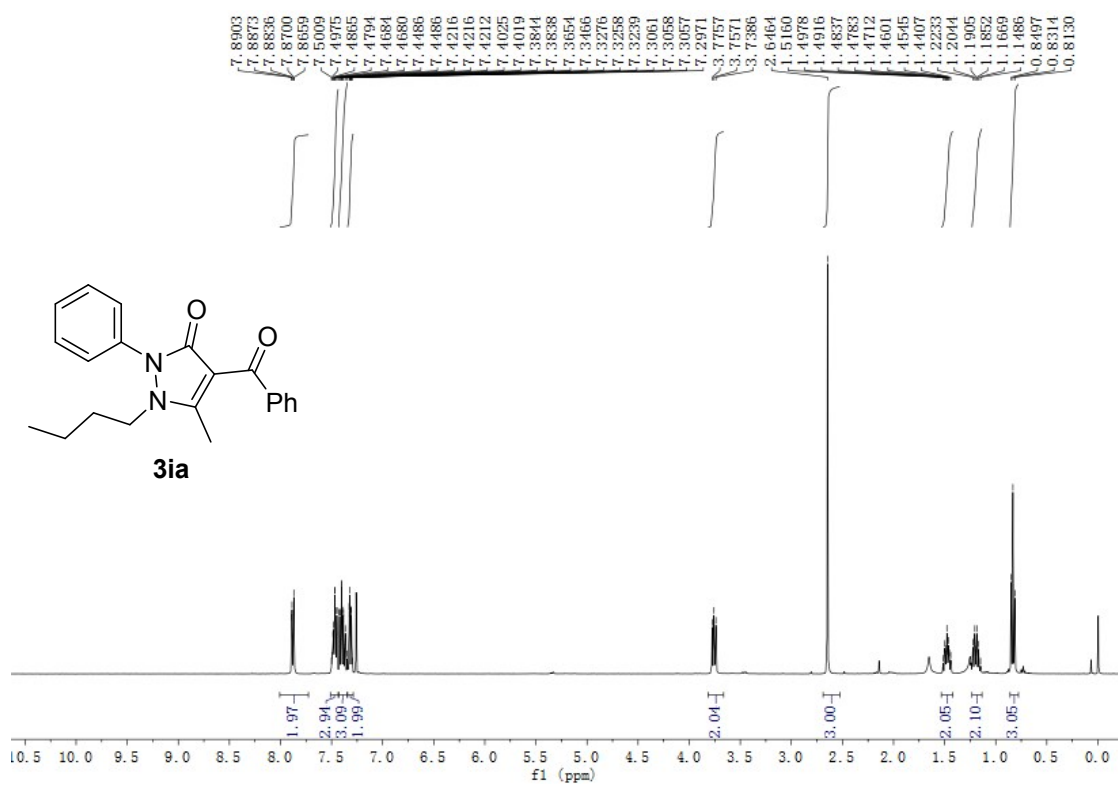
4-benzoyl-2-(3-chlorophenyl)-1,5-dimethyl-1,2-dihydro-3H-pyrazol-3-one (3ga):



4-benzoyl-2-(2-chlorophenyl)-1,5-dimethyl-1,2-dihydro-3H-pyrazol-3-one (3ha):



4-benzoyl-1-butyl-5-methyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (3ia):



4-benzoyl-1-methyl-2-phenyl-5-propyl-1,2-dihydro-3H-pyrazol-3-one (3ja)

