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# Synthesis of 4-Arylidenepyrazolones by a Gold-Catalyzed Cyclization/Arylidene Group Transfer Cascade of *N*-Propioloyl Hydrazones

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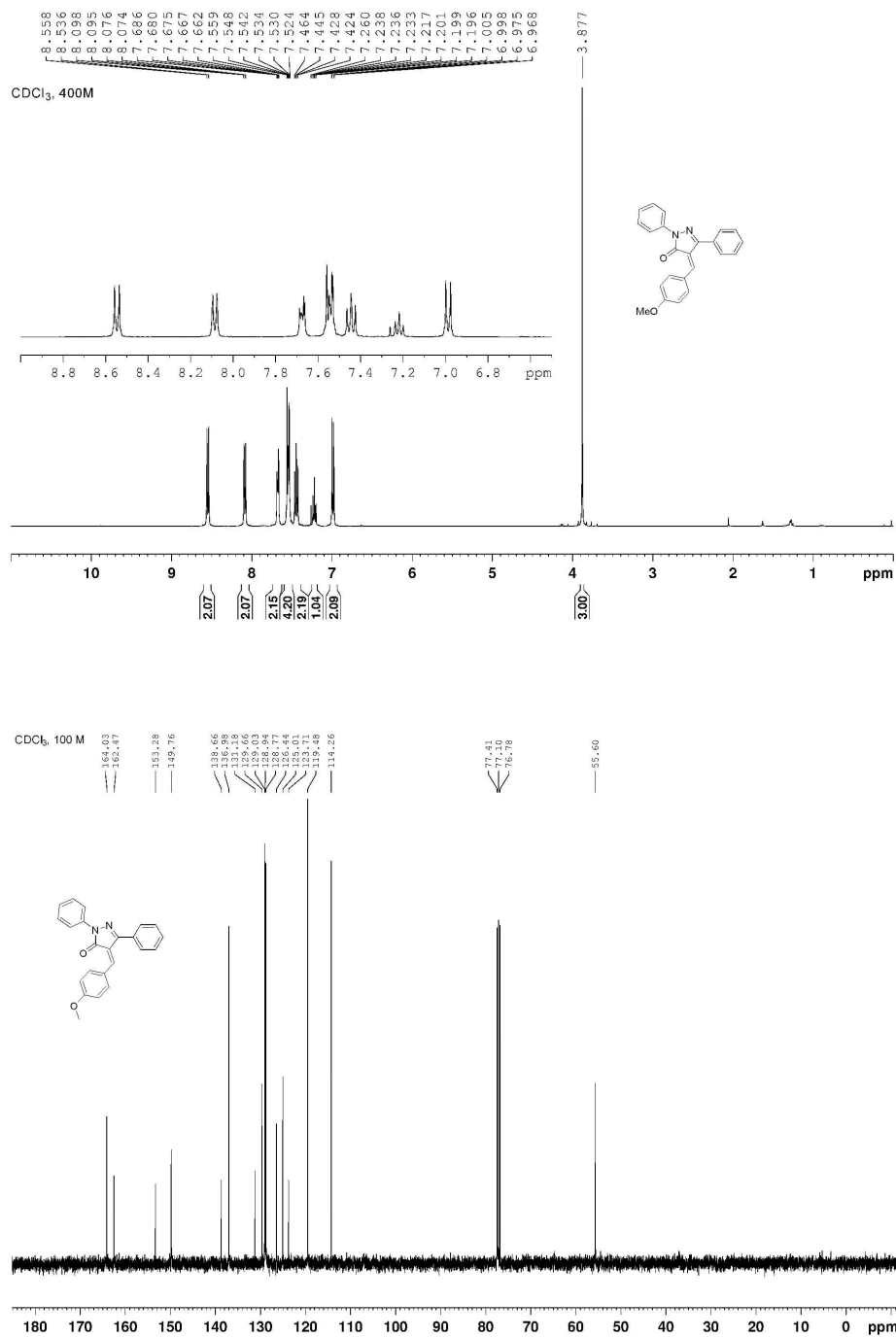
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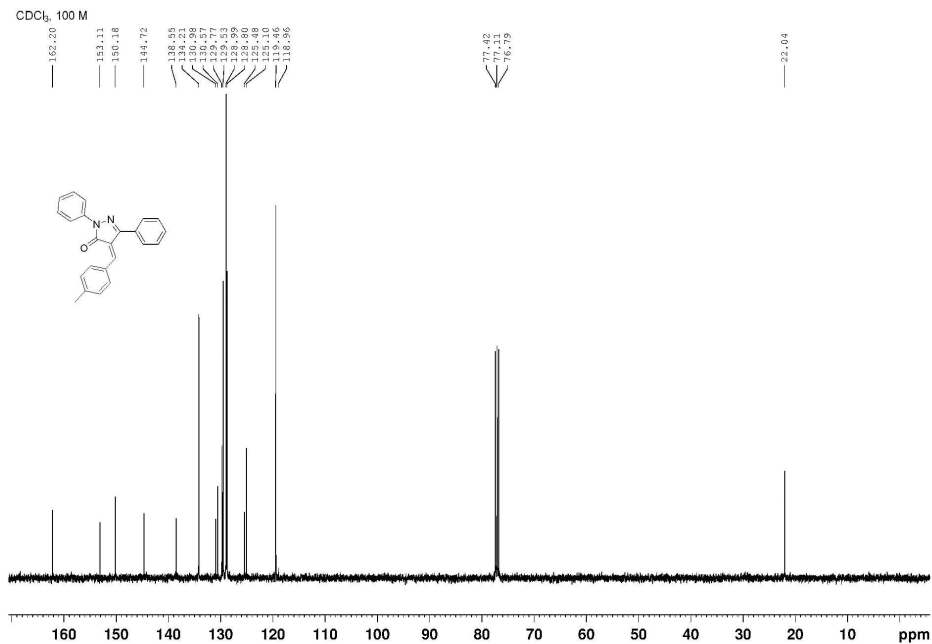
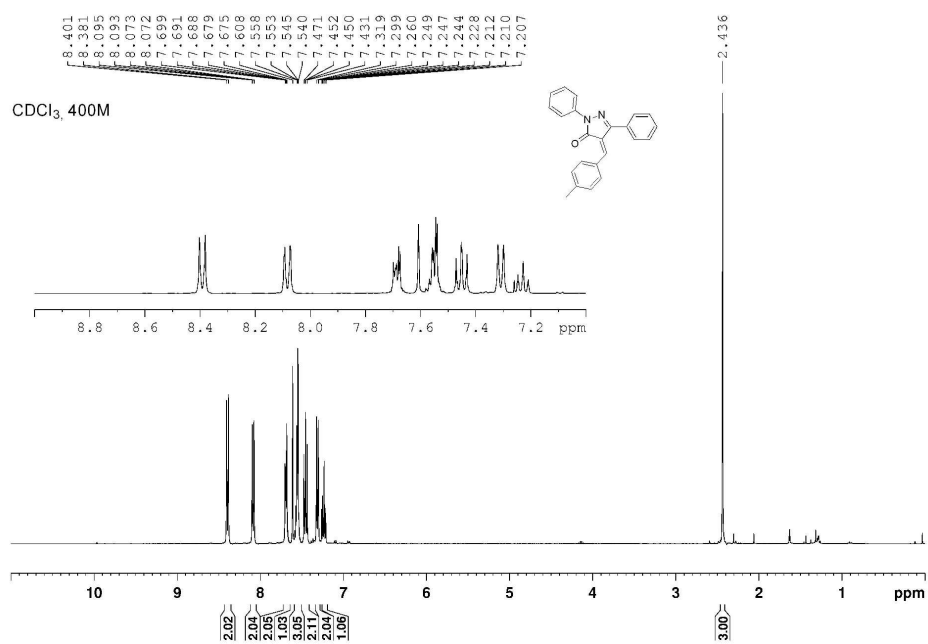
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Copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for all products

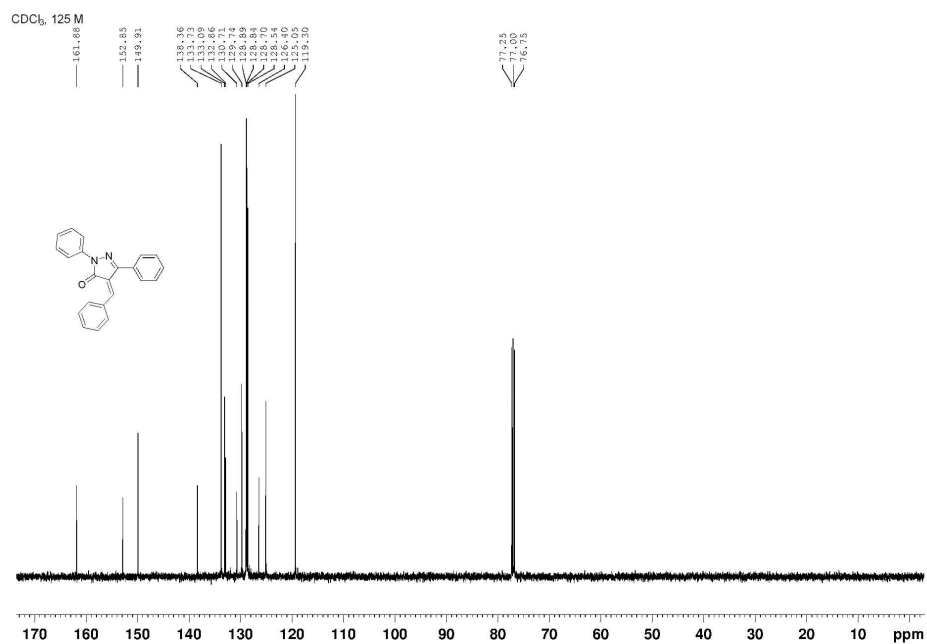
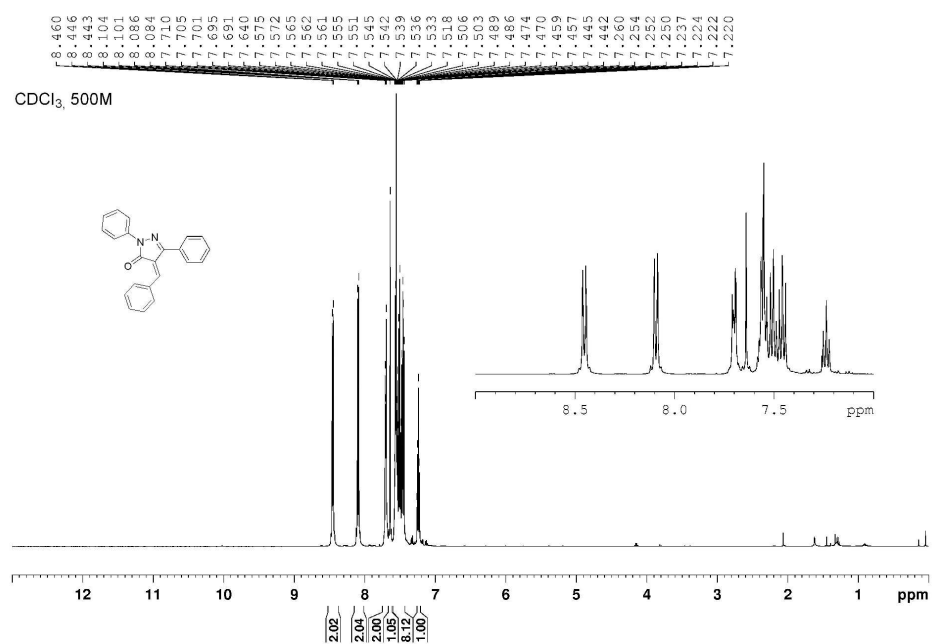
*(Z)*-4-(4-methoxybenzylidene)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (**2a**)



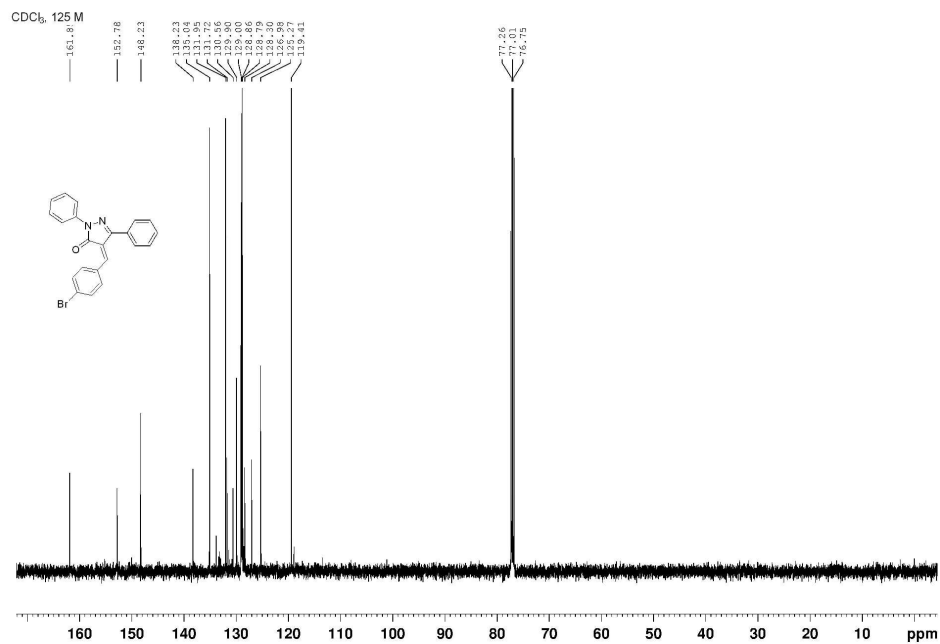
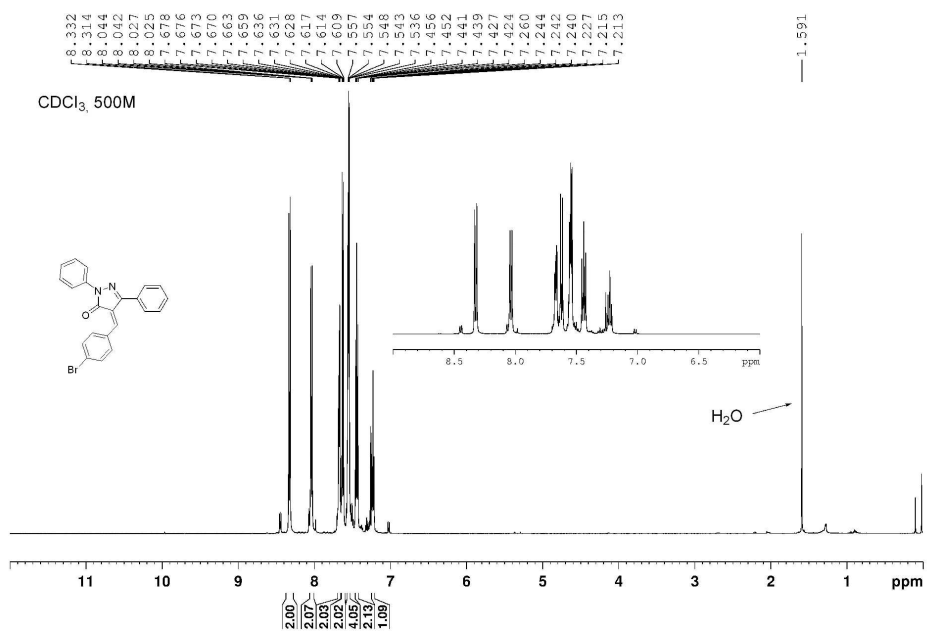
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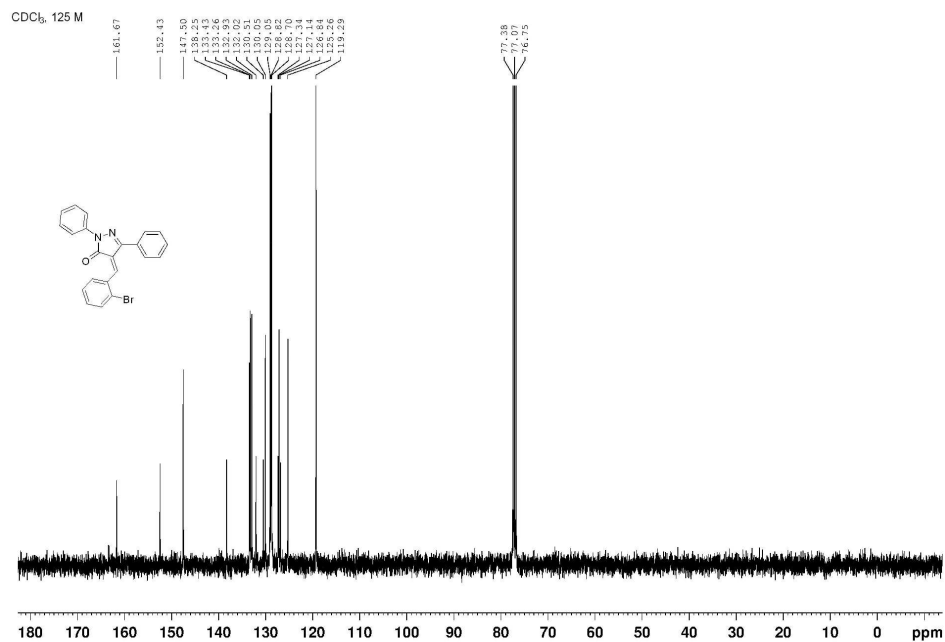
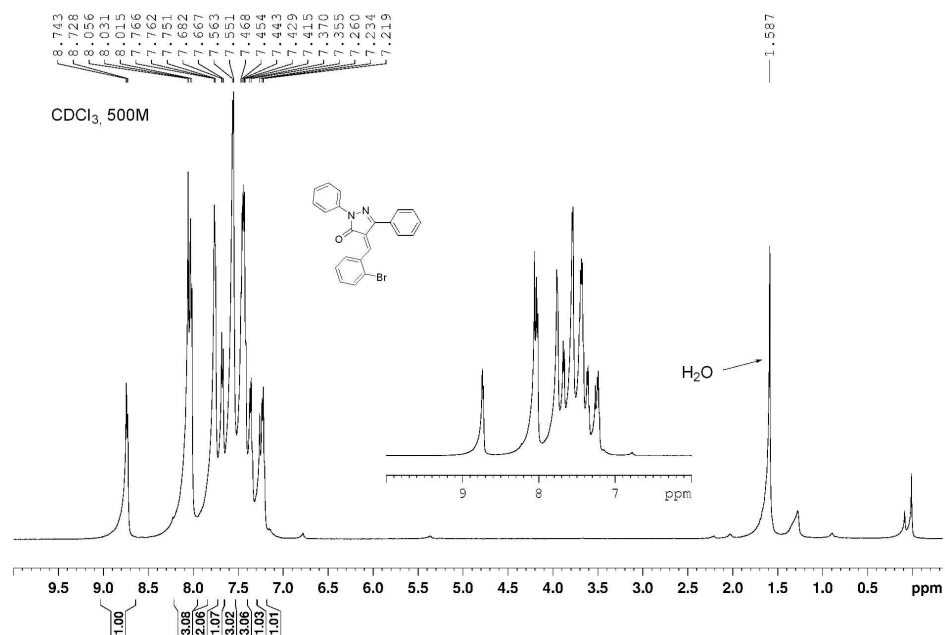
*(Z)*-4-benzylidene-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (**2c**)



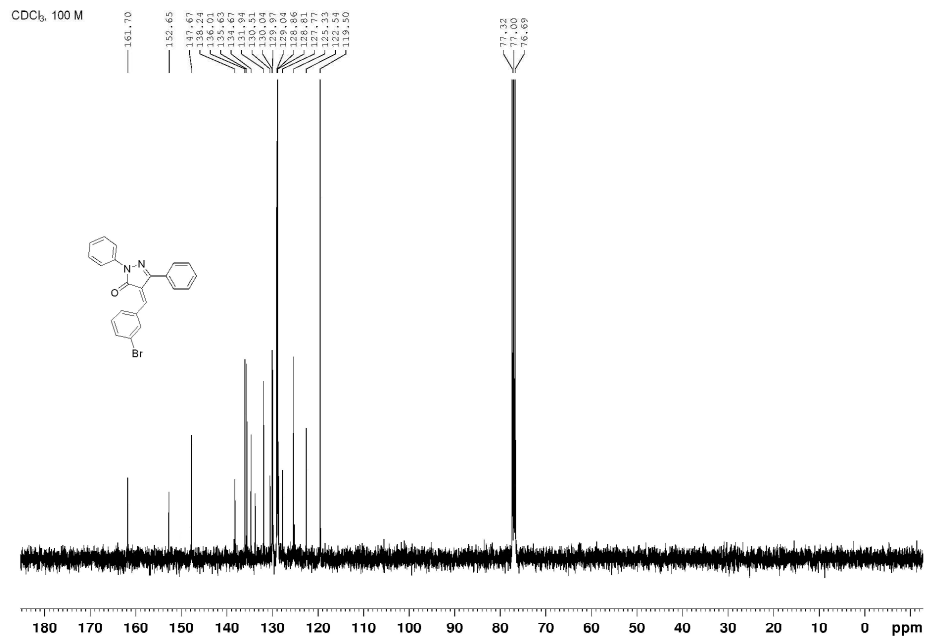
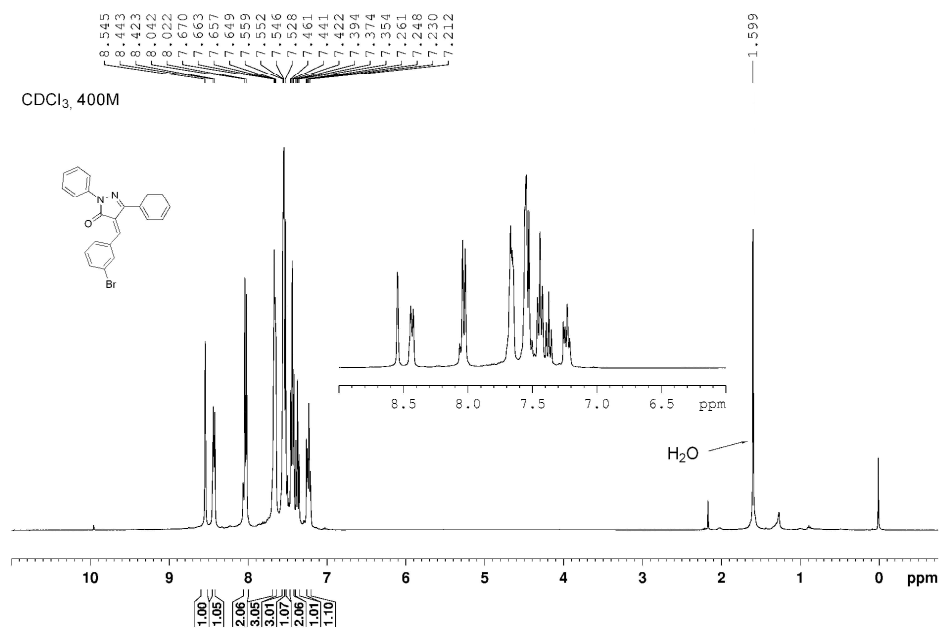
(Z)-4-(4-bromobenzylidene)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (**2d**)



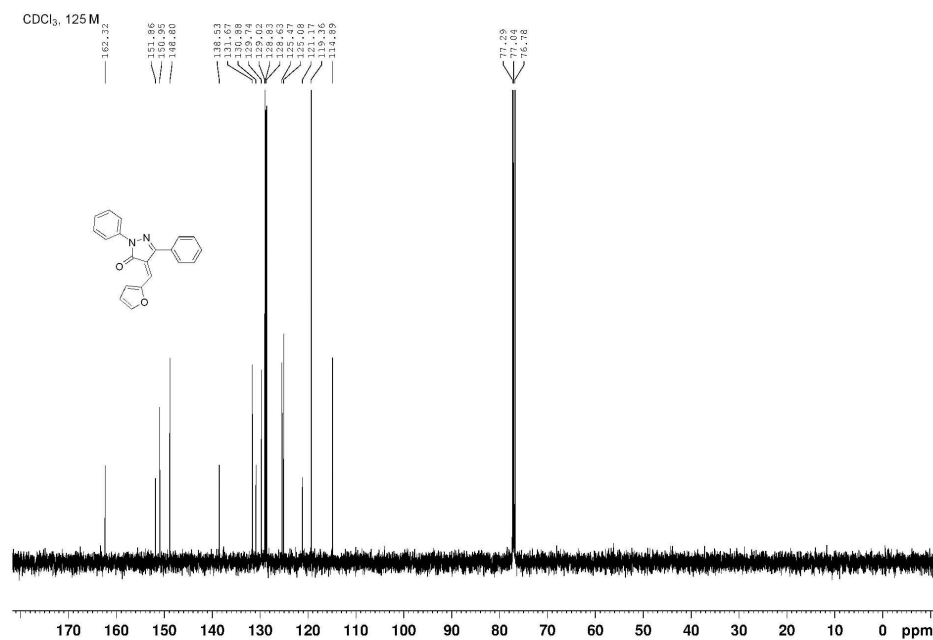
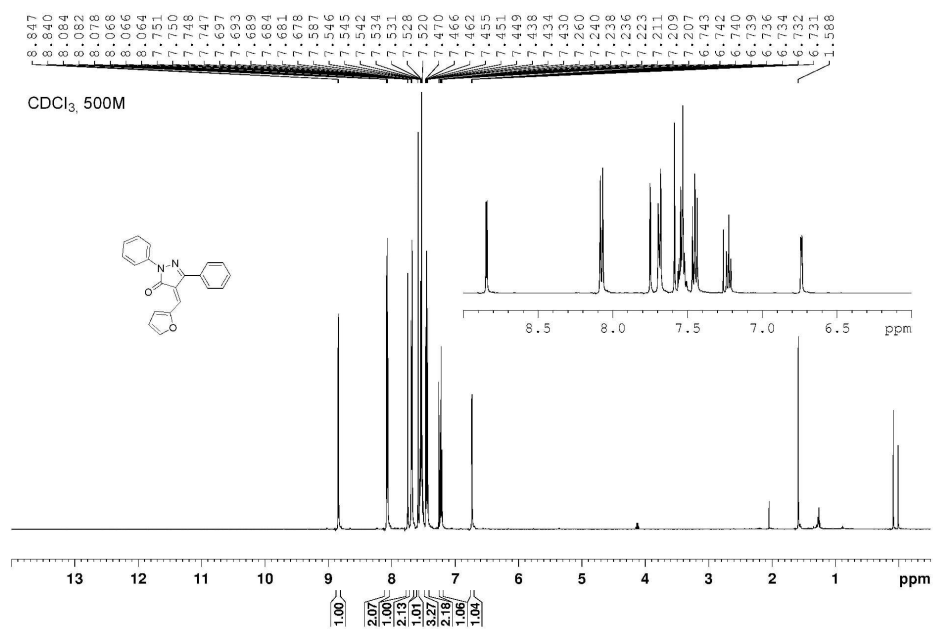
(Z)-4-(2-bromobenzylidene)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (**2e**)



(Z)-4-(3-bromobenzylidene)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (2f)

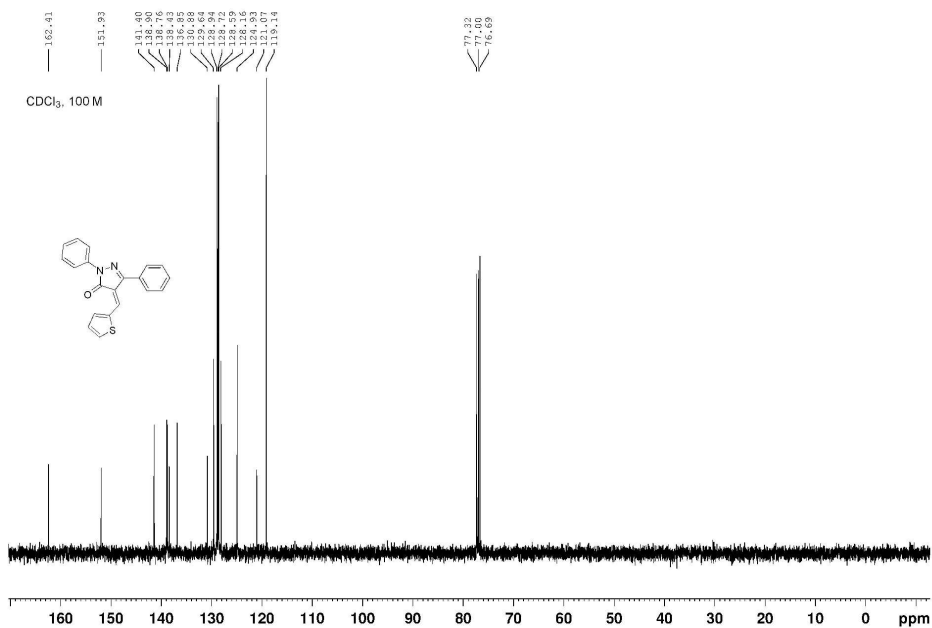
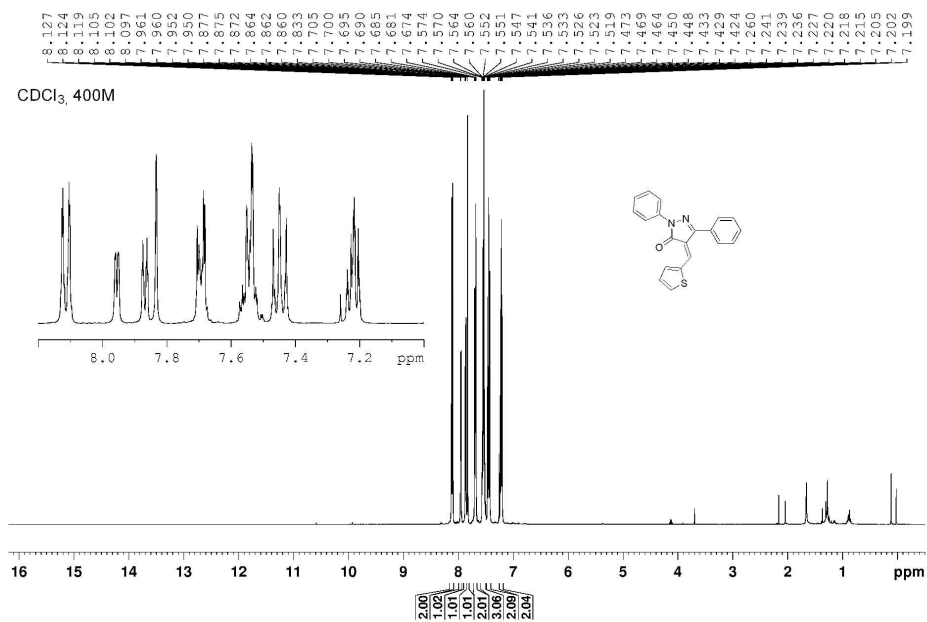


(Z)-4-(furan-2-ylmethylene)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (2g)

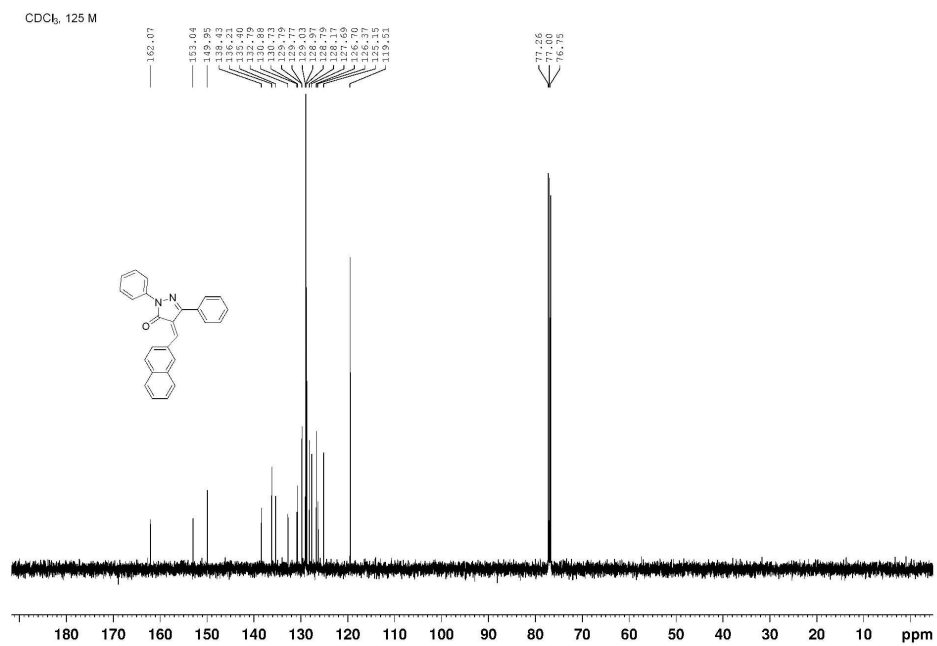
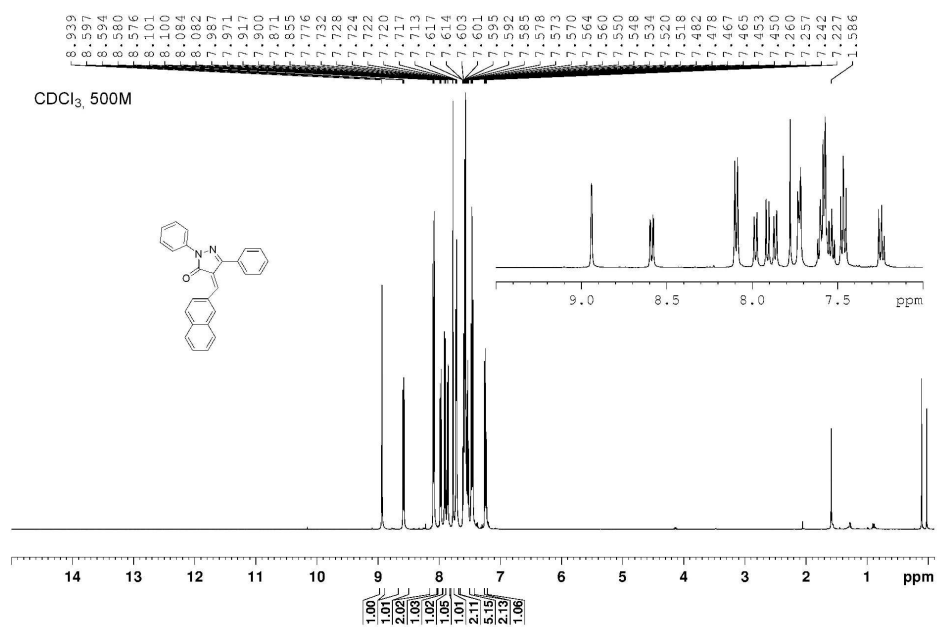




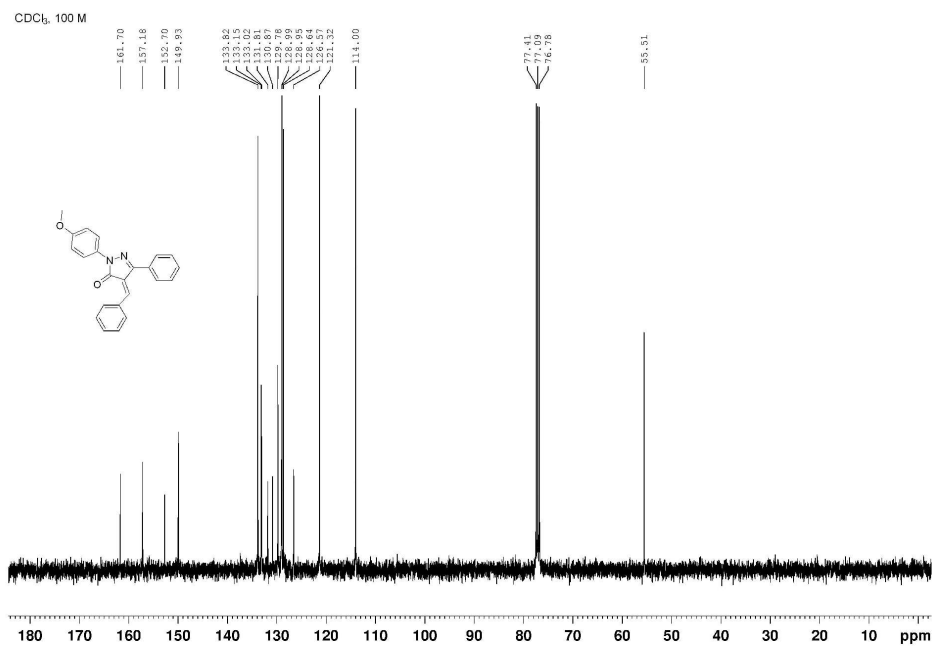
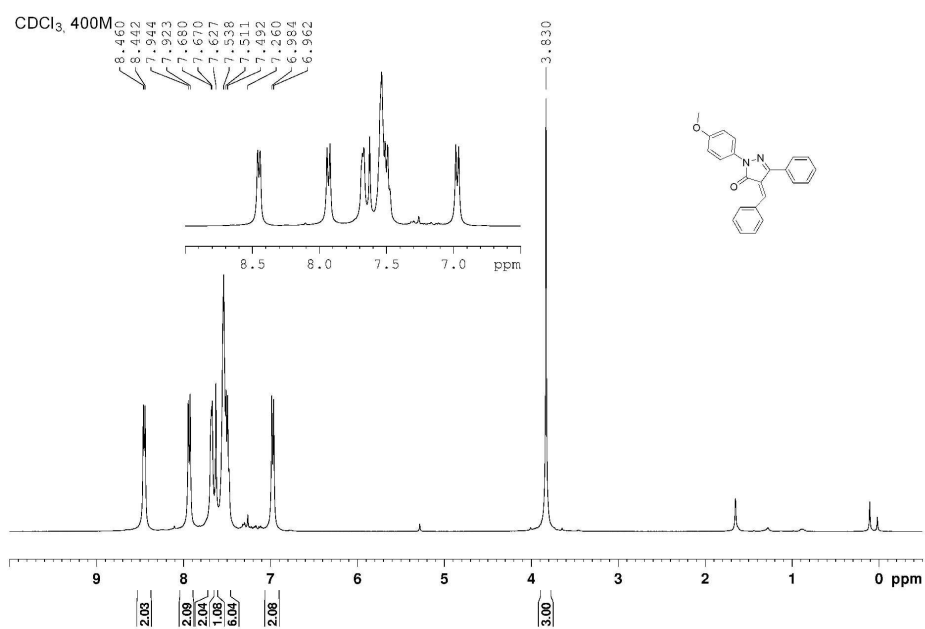
(Z)-2,5-diphenyl-4-(thiophen-2-ylmethylene)-2,4-dihydro-3H-pyrazol-3-one (**2h**)



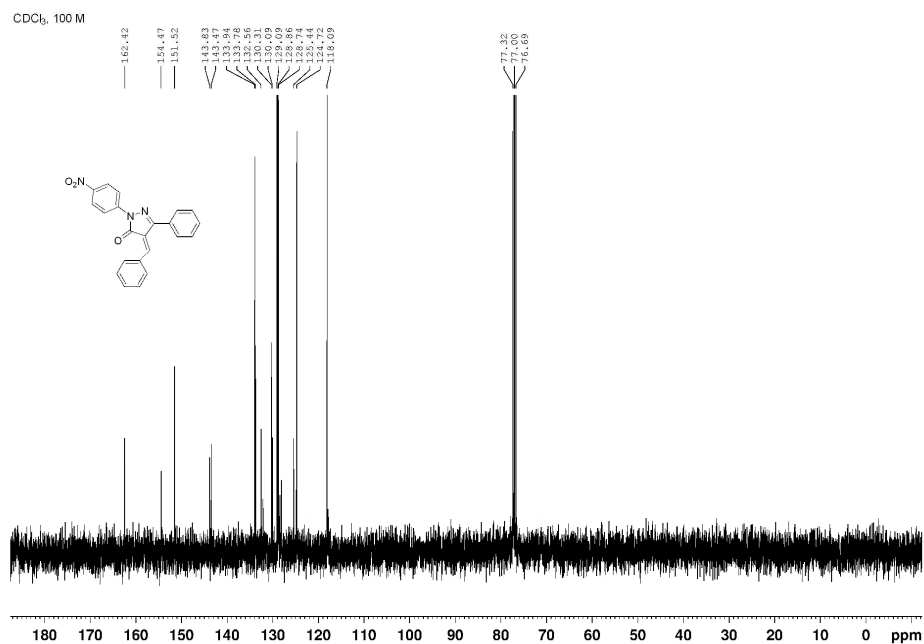
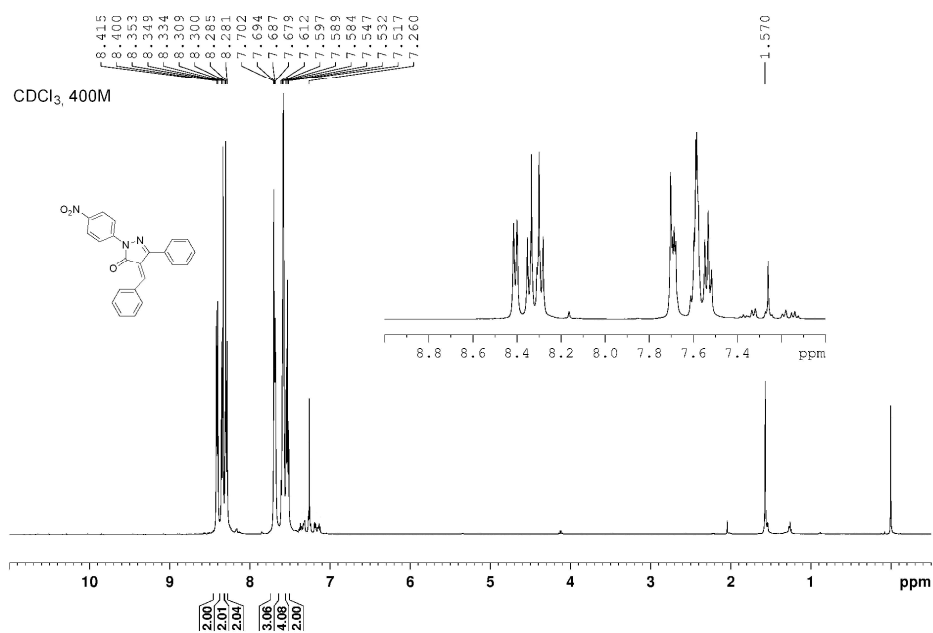
(Z)-4-(naphthalen-2-ylmethylene)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (2i)



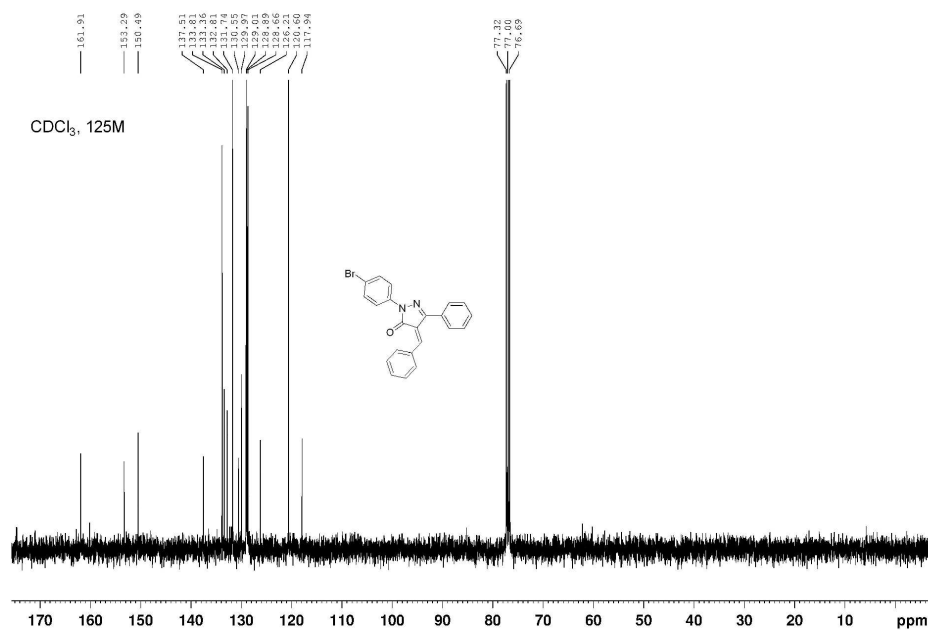
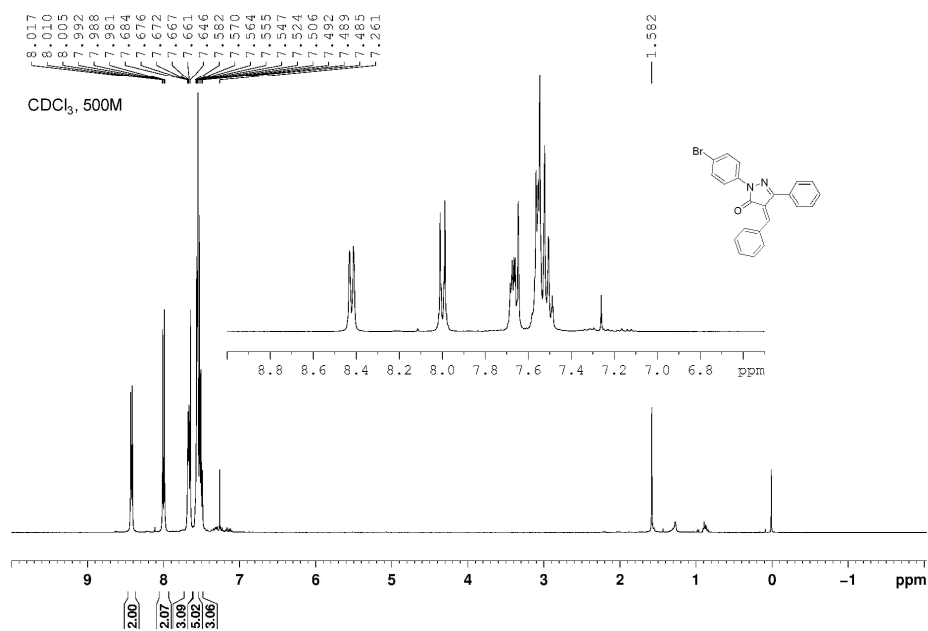
(Z)-4-benzylidene-2-(4-methoxyphenyl)-5-phenyl-2,4-dihydro-3H-pyrazol-3-one (2j)



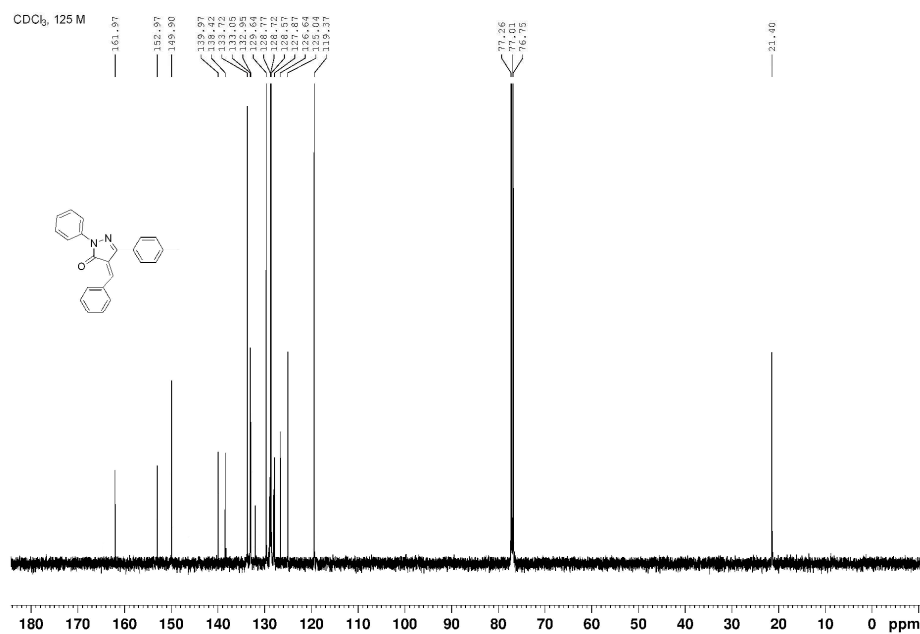
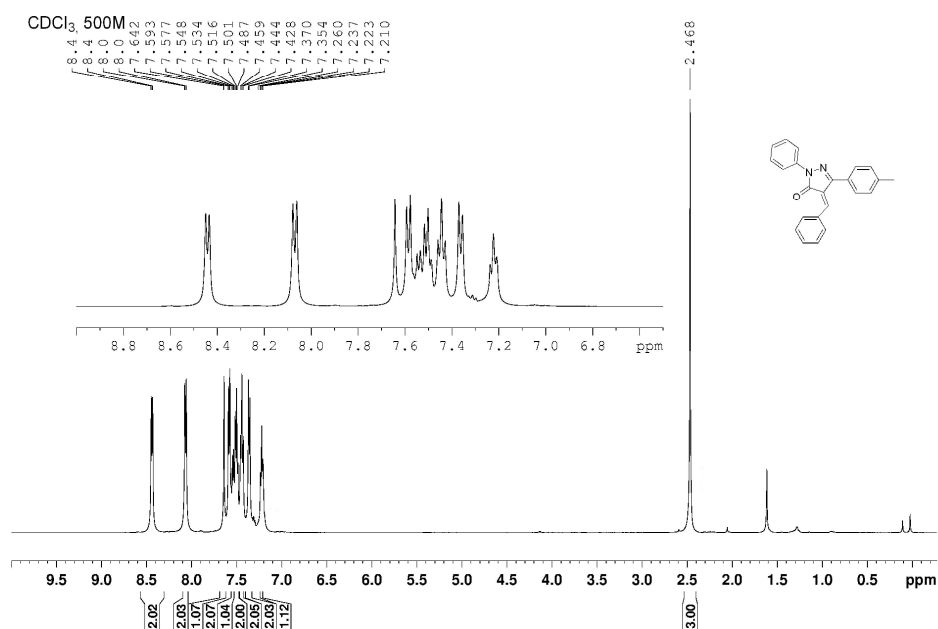
(Z)-4-benzylidene-2-(4-nitrophenyl)-5-phenyl-2,4-dihydro-3H-pyrazol-3-one (**2k**)



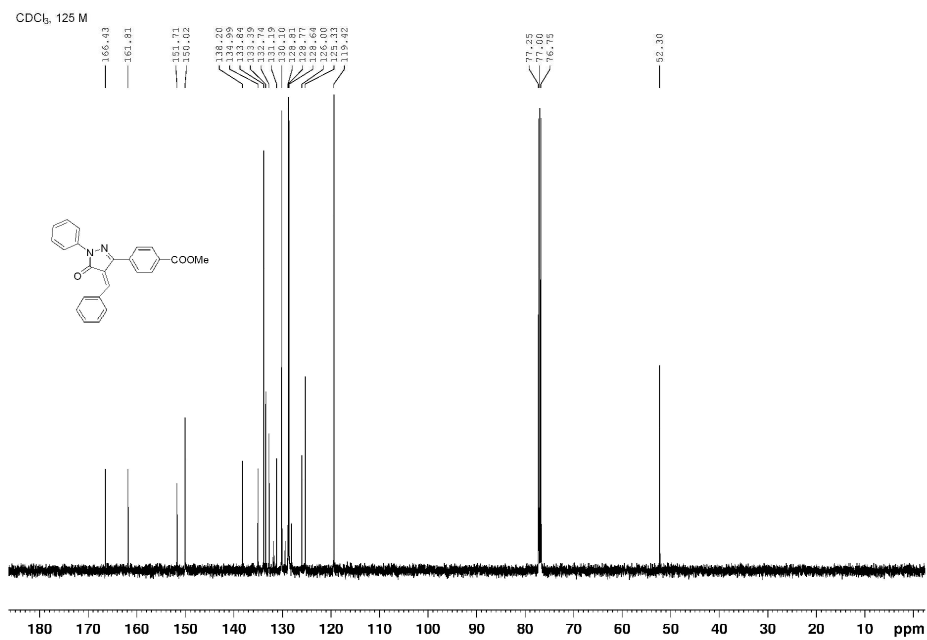
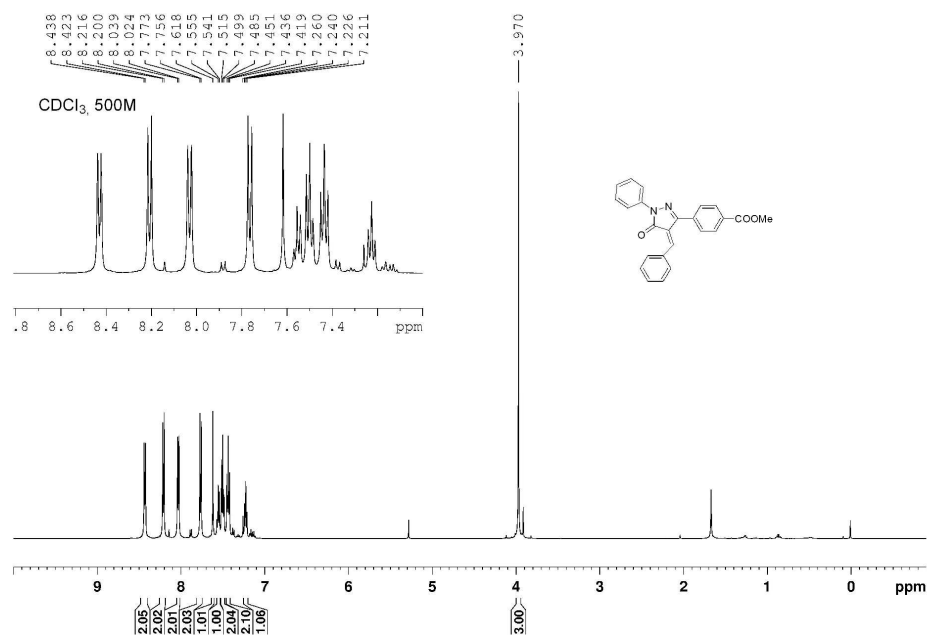
(Z)-4-benzylidene-2-(4-bromophenyl)-5-phenyl-2,4-dihydro-3H-pyrazol-3-one (2I)



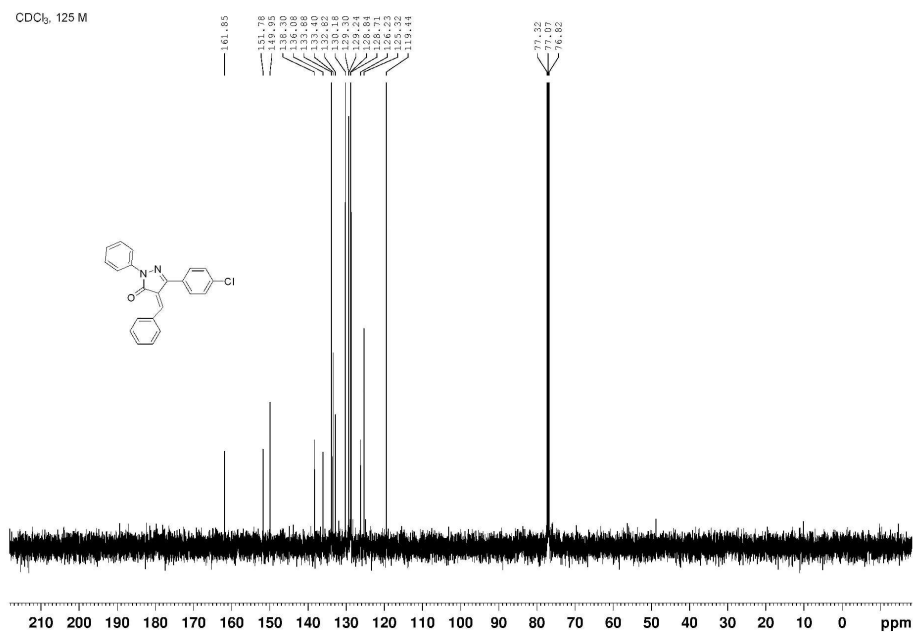
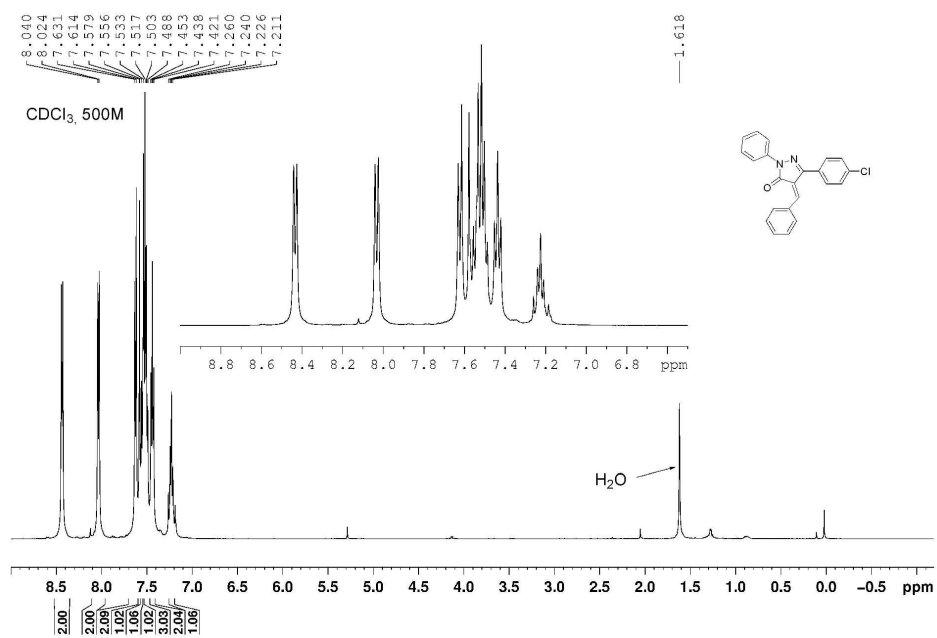
(Z)-4-benzylidene-2-phenyl-5-(p-tolyl)-2,4-dihydro-3H-pyrazol-3-one (**2o**)



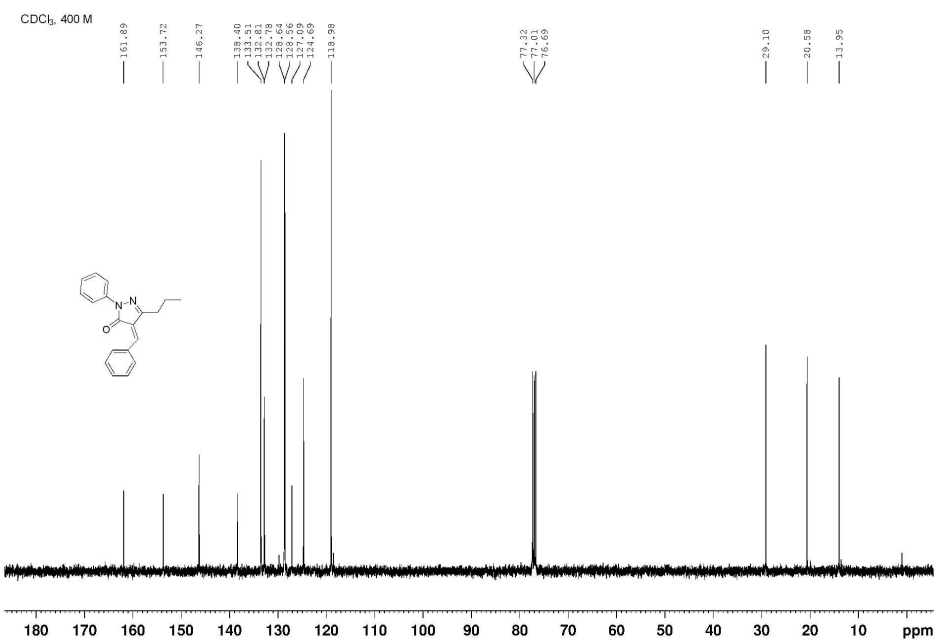
*methyl (Z)-4-(4-benzylidene-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)benzoate (2p)*

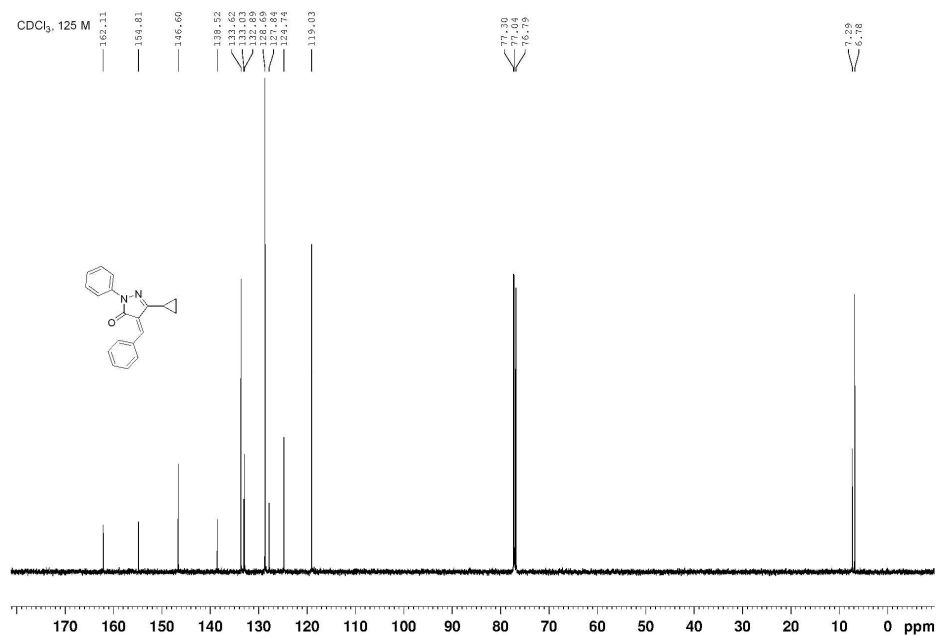


(Z)-4-benzylidene-5-(4-chlorophenyl)-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (2q)

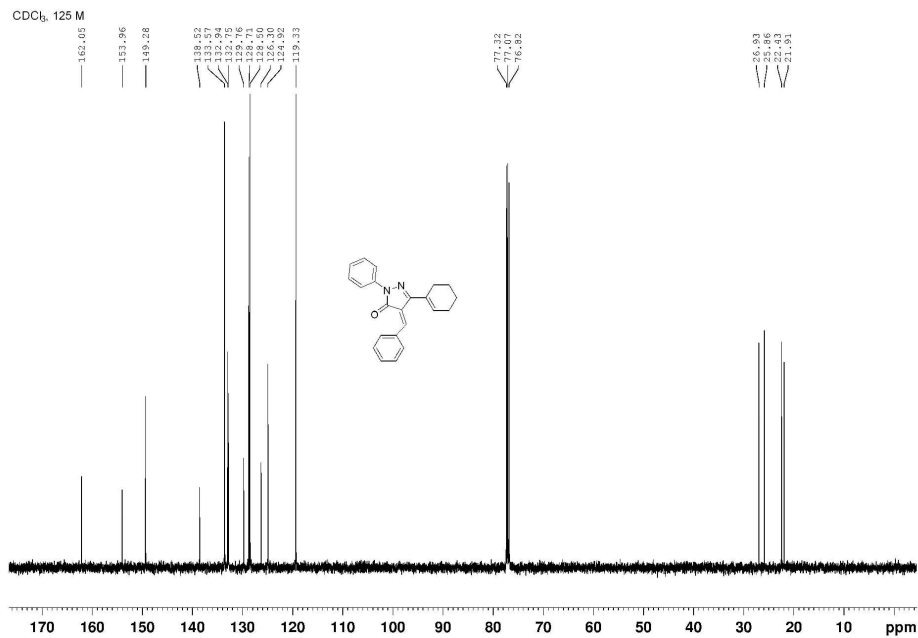
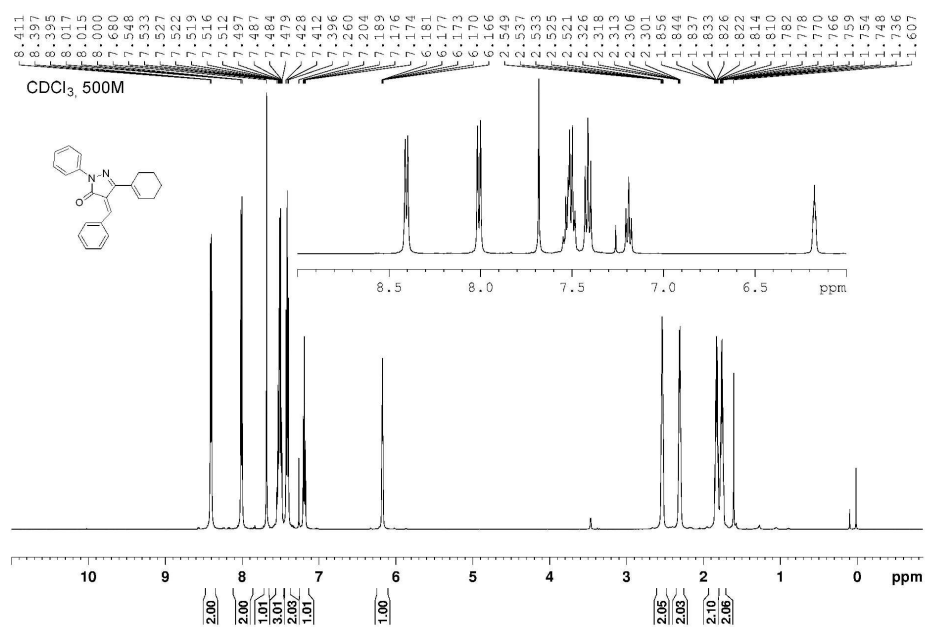




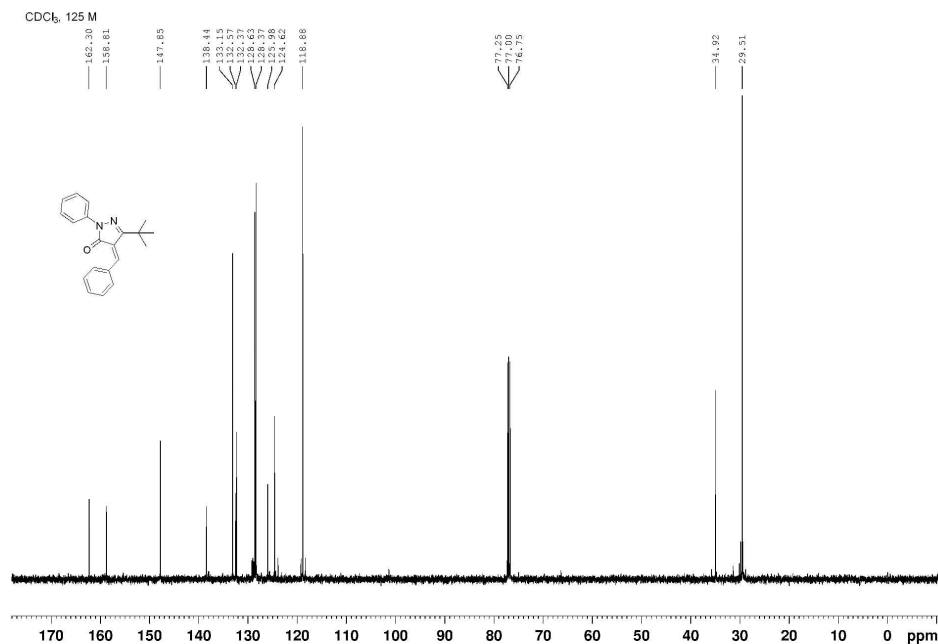
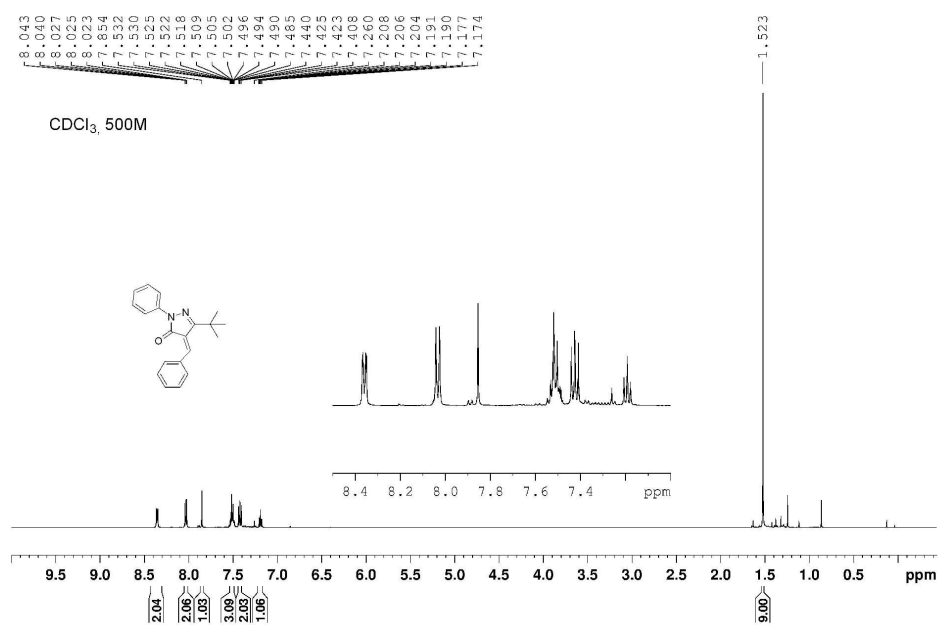




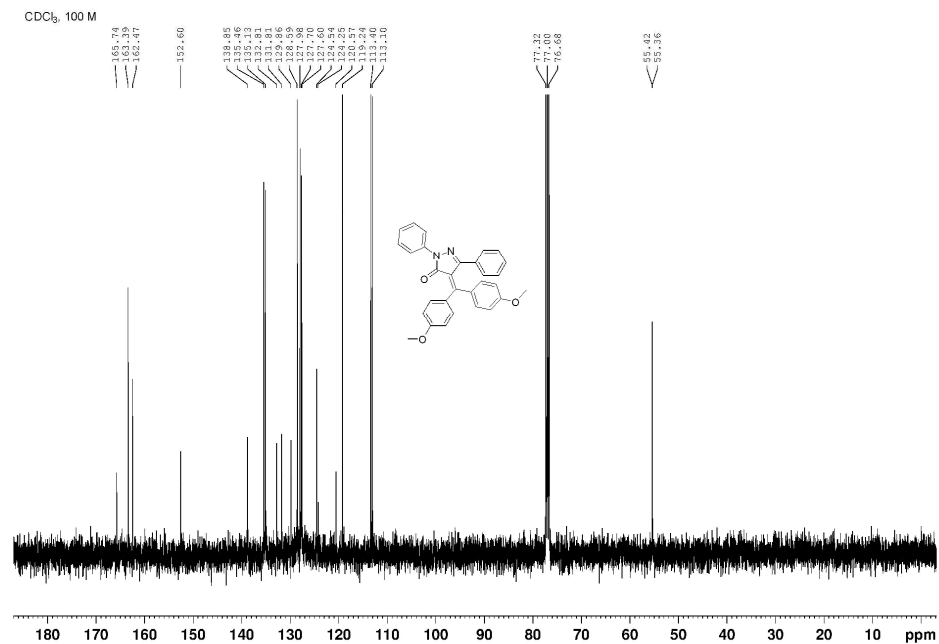
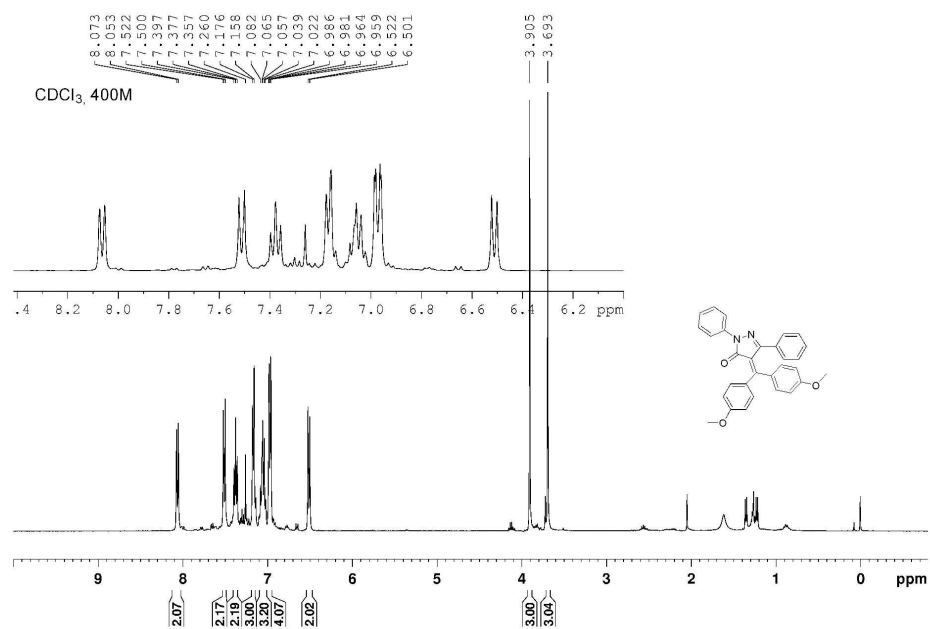
(Z)-4-benzylidene-5-(cyclohex-1-en-1-yl)-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (2t)

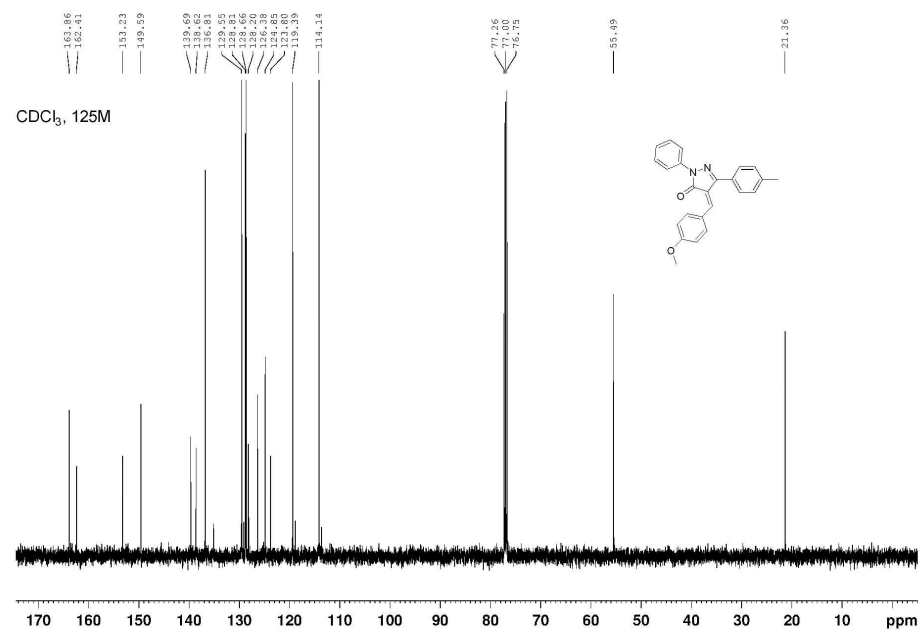


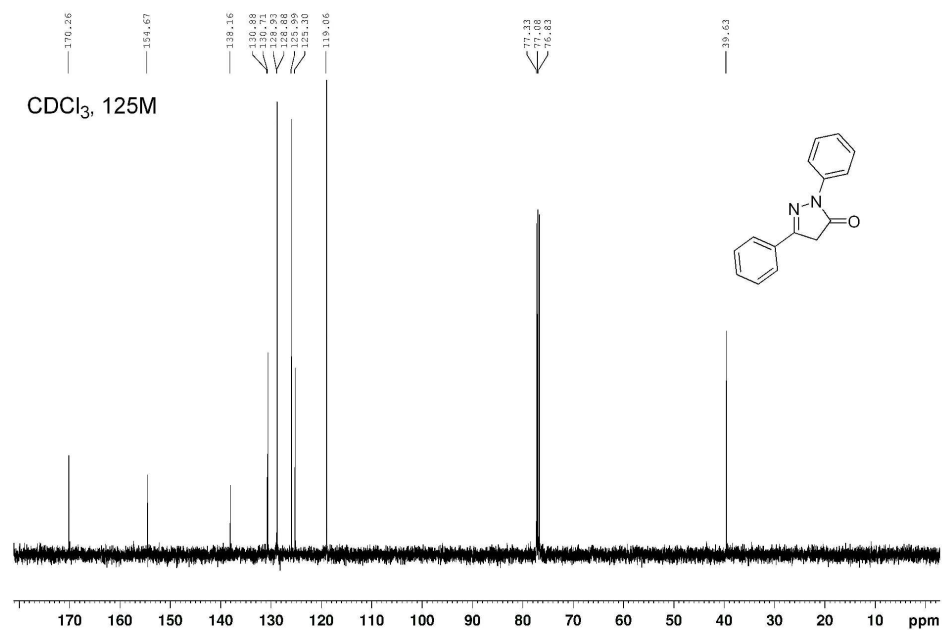
(Z)-4-benzylidene-5-(tert-butyl)-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (**2u**)



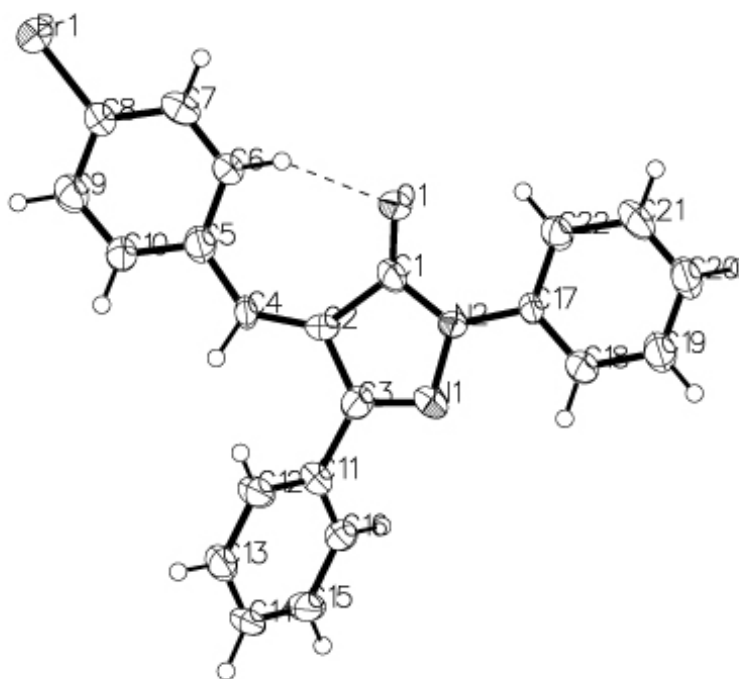
*4-(bis(4-methoxyphenyl)methylene)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (2w)*







### Single crystal X-ray structure for **2d**



**Figure 2.** Single crystal X-ray structure for **2d** (drawn with 30% probability).

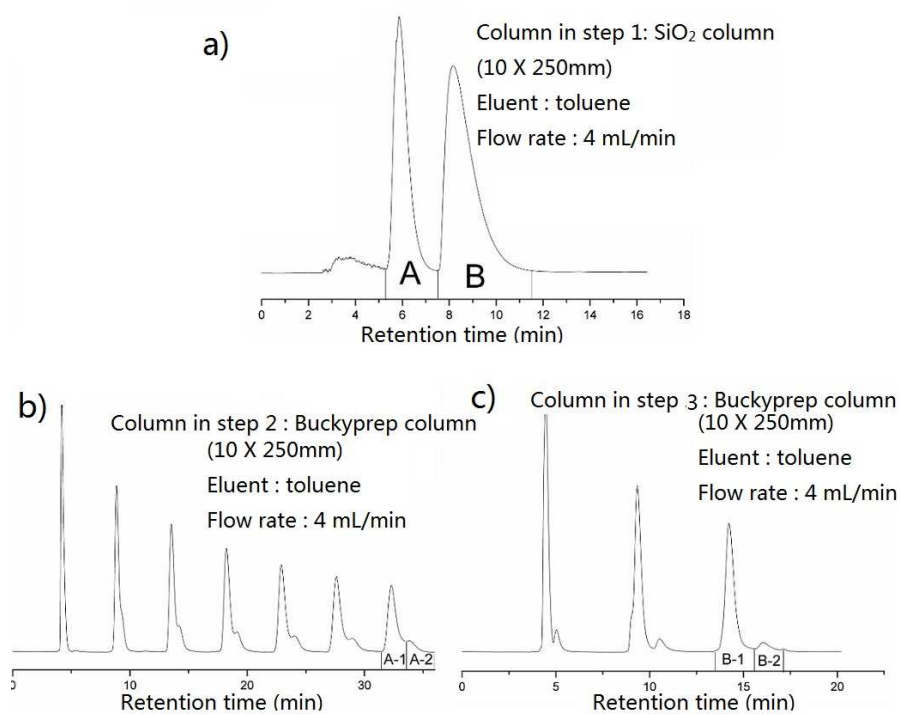
Data collections were performed on a Rigaku R-Axis RAPID imaging Plate single-crystal diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Multi-scan absorption corrections (SADABS) were applied. All of the data were corrected for absorption effects using the multi-scan technique. The structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least-squares on  $F^2$  using the SHELXTL-97 and olex2 GUI crystallographic software package. Non-H atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms. Crystal of **2d** suitable for X-ray diffraction was grown from a CDCl<sub>3</sub> solution of **2d** layered with *n*-hexane. CCDC-1419950 (**2d**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



### HPLC Separation of the crossover experimental products

Separation of the mixture was carried out by multistep HPLC alternately on two HPLC columns: SiO<sub>2</sub> and Buckyprep. Products **2c** and **2m** show the retention time of 5.2 to 7.5 min and products **2x** and **2a** show the retention time of 7.5 to 11.6 min in a SiO<sub>2</sub> column, which was eluted using toluene at a flow rate of 4 mL/min. (Figure 3, a).

The HPLC procedure includes three stages of HPLC run for the crossover experimental products separation (Figure 3), among which the first stage was carried out using a SiO<sub>2</sub> column (i.d. = 10 mm × 250 mm) at a flow rate of 4 mL/min, and the component with the retention time ranging from 5.2 to 7.5 min was collected for the following separation to A and from 7.5 to 11.6 min to B (Figure 3, a). In the secondary HPLC stage, the collected component A was separated by a Buckyprep column (i.d. = 20 mm × 250 mm, Cosmosil) with a recycling HPLC mode at a flow rate of 4 mL/min, and we obtained the separated components A-1 and A-2 (Figure 3, b). The similar method was used to get components B-1 and B-2 (Figure 3, c). (A-1=**2c**; A-2=**2m**; B-1=**2x**; B-2=**2a**)



**Figure 3 : HPLC Separation of Crossover Experimental Products**