

Supplementary Information

DABCO-Catalyzed Silver-Promoted Direct Thiolation of Pyrazolones with Diaryl Disulfides

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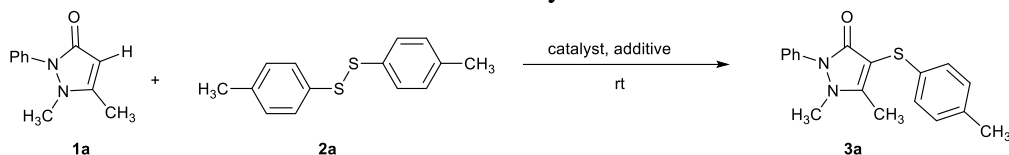
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I. Reaction Optimization

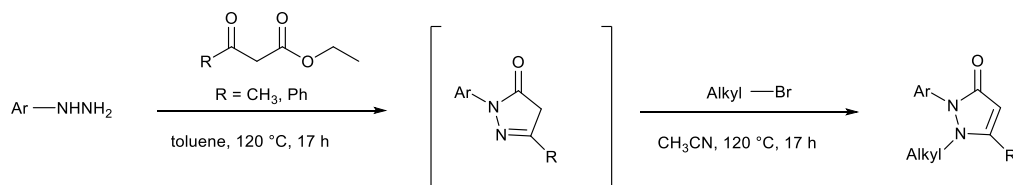
Table S1 Effect of catalyst and additives.^a



Entry	Catalyst (mol %)	Additive (equiv.)	Yield (%) ^b
1	DABCO (2)	FeCl ₃ (1.5)	no reaction
2	DABCO (2)	CuI (1.5)	no reaction
3	DABCO (2)	CuBr (1.5)	trace
4	DABCO (2)	CuBr ₂ (1.5)	11
5	DABCO (2)	Cu(OAc) ₂ (1.5)	14
6	DABCO (2)	CuCl (1.5)	10
7	DABCO (2)	NaOAc (1.5)	11
8	DABCO (2)	AgOAc (1.5)	99
9	DABCO (2)	AgOAc (2)	99
10	DABCO (2)	AgOAc (1)	84
11	NEt ₃ (2)	AgOAc (1.5)	76
12	PPh ₃ (2)	AgOAc (1.5)	76

^a Conditions: **1a** (0.25 mmol, 1 equiv.), **2a** (0.375 mmol, 1.5 equiv.), solvent (1 ml), rt. ^b GC yield.

II. Preparation of *N*-Substituted Pyrazolone Substrates

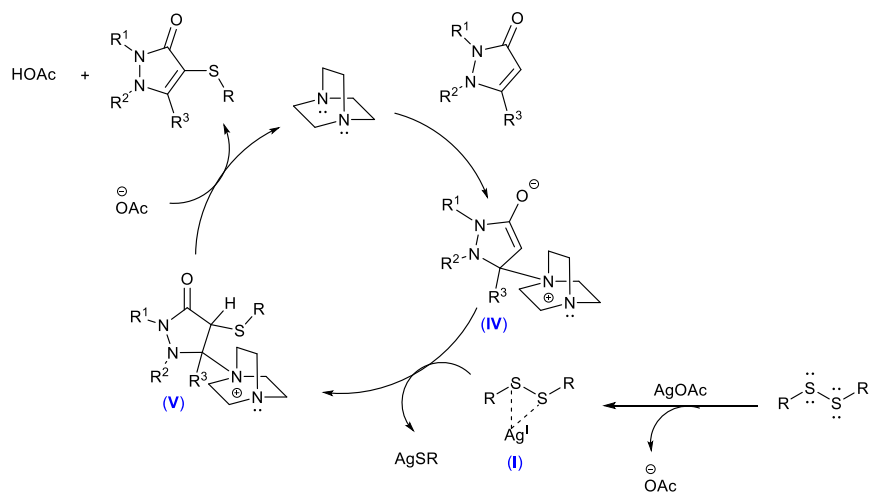


A reaction mixture containing hydrazine (5 mmol), ethyl acetoacetate or ethyl 3-oxo-3-phenylpropanoate (5 mmol) and toluene (10 ml) was stirred at 120 °C in an oil bath. After 17 h, the reaction mixture was cooled to room temperature. To this mixture, acetonitrile (10 ml) and alkyl bromide (10 mmol) were added, successively. The reaction mixture was stirred and heated at 120 °C for additional 17 h. After that, the resulting mixture was cooled to room temperature and the solvent was evaporated *in vacuo*. The organic residue was purified by flash column chromatography (ethyl acetate) to yield *N*-substituted pyrazolone.

Reference: C. Yang, H. Gong and C. Kuang, *Eur. J. Org. Chem.*, 2013, **24**, 5276–5279.

III. Alternative mechanism

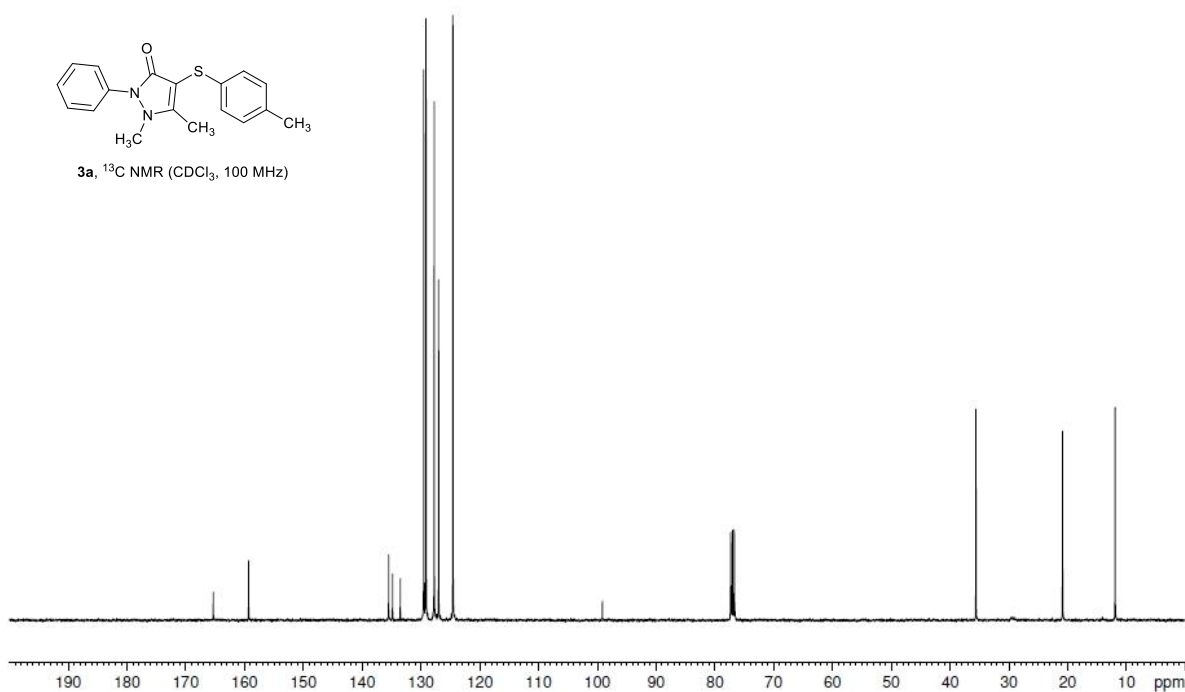
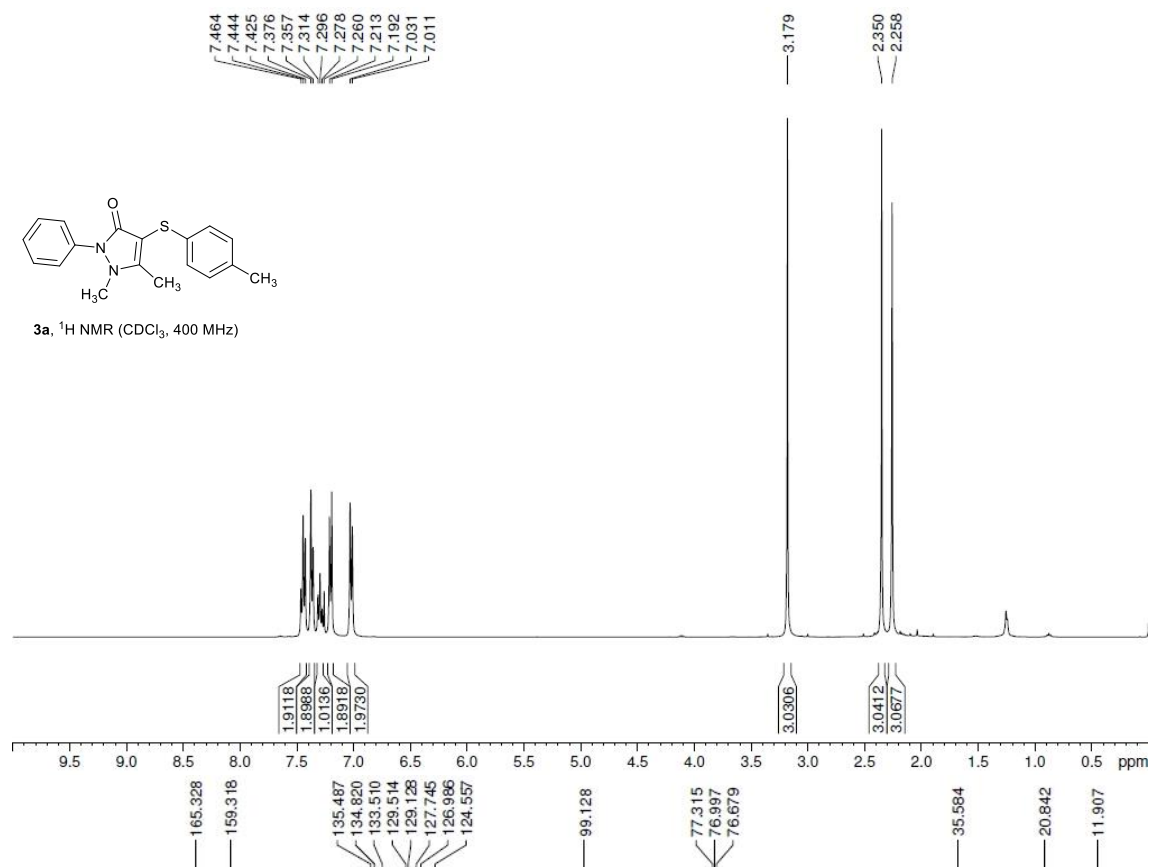
This transformation could also proceed *via* a Baylis-Hillman type reaction, in which the pyrazolone substrate might be activated by a direct attack of DABCO catalyst *via* 1,4-addition, generating intermediate **IV**. This *in situ*-generated intermediate **IV** would act as a nucleophile to react further with the disulfide-silver intermediate **I**, leading to a formation of intermediate **V**. Finally, elimination of the catalyst could provide the product and reproduce DABCO to start another catalytic cycle.



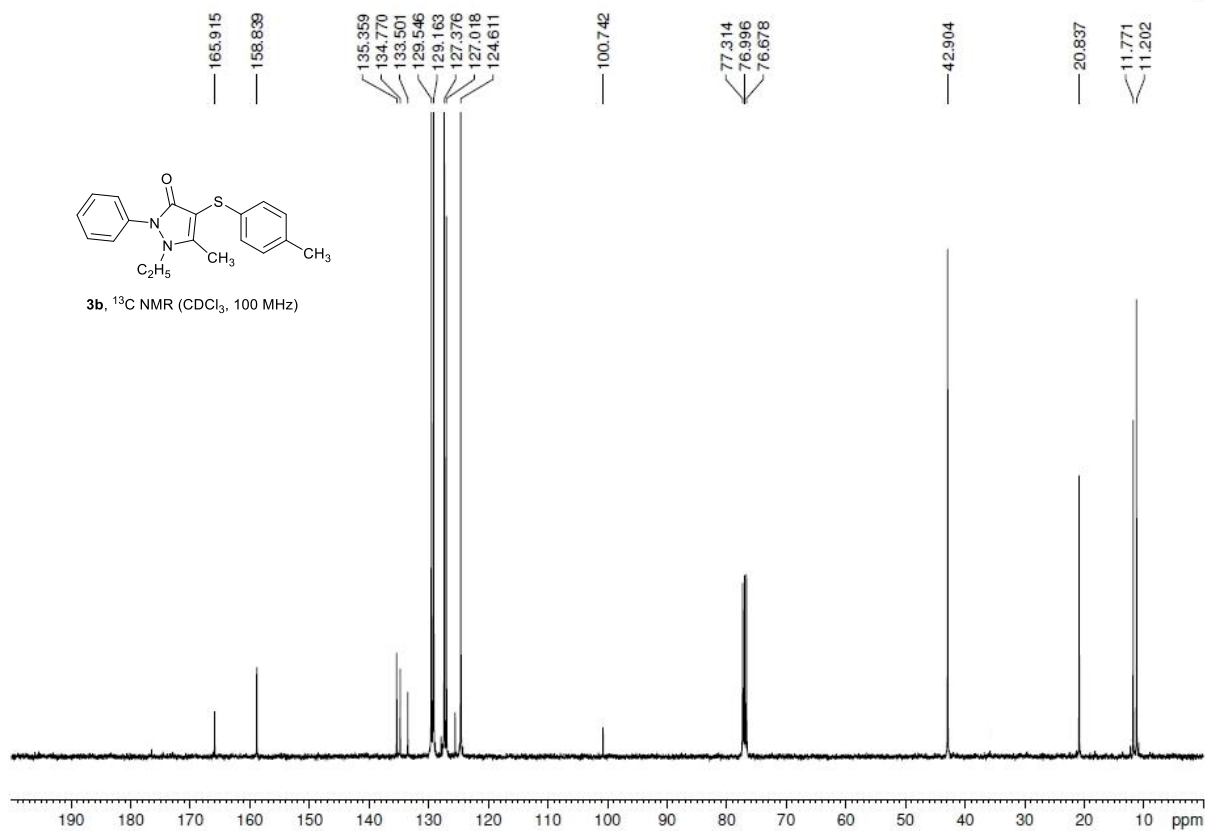
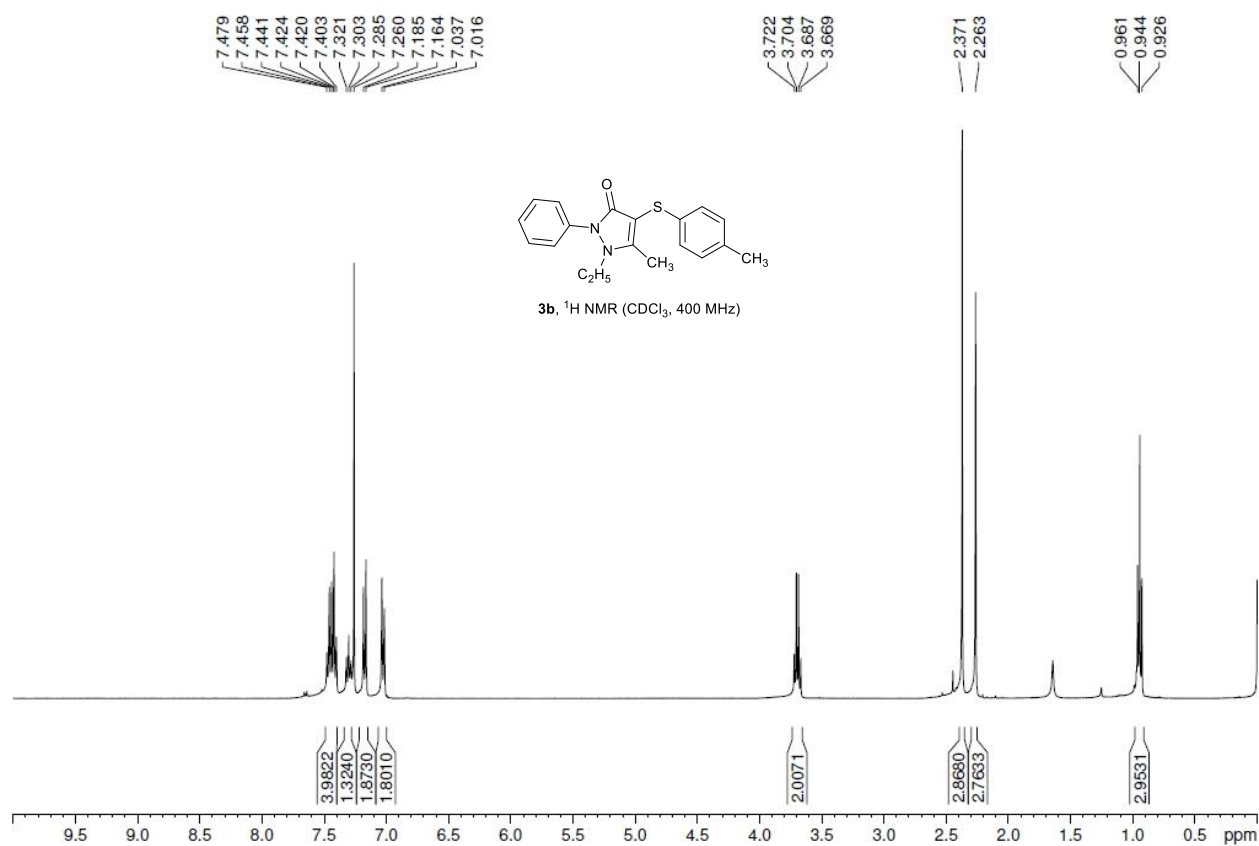
Although we believed that this Baylis-Hillman pathway is less likely to occur because 40% of the product was obtained in the absence of DABCO catalyst, additional studies such as isotope labeling and kinetic experiments will be conducted to gain further insight into the reaction mechanism.

IV. ^1H and ^{13}C NMR Spectra of Compounds 3a–3m and 4a–4n

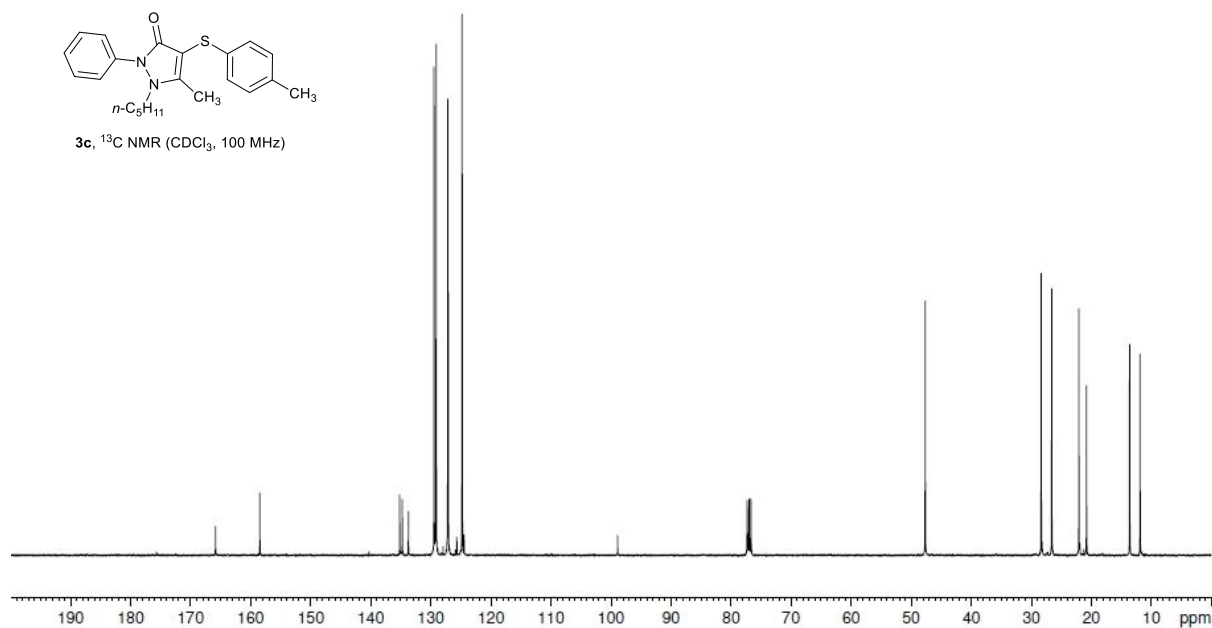
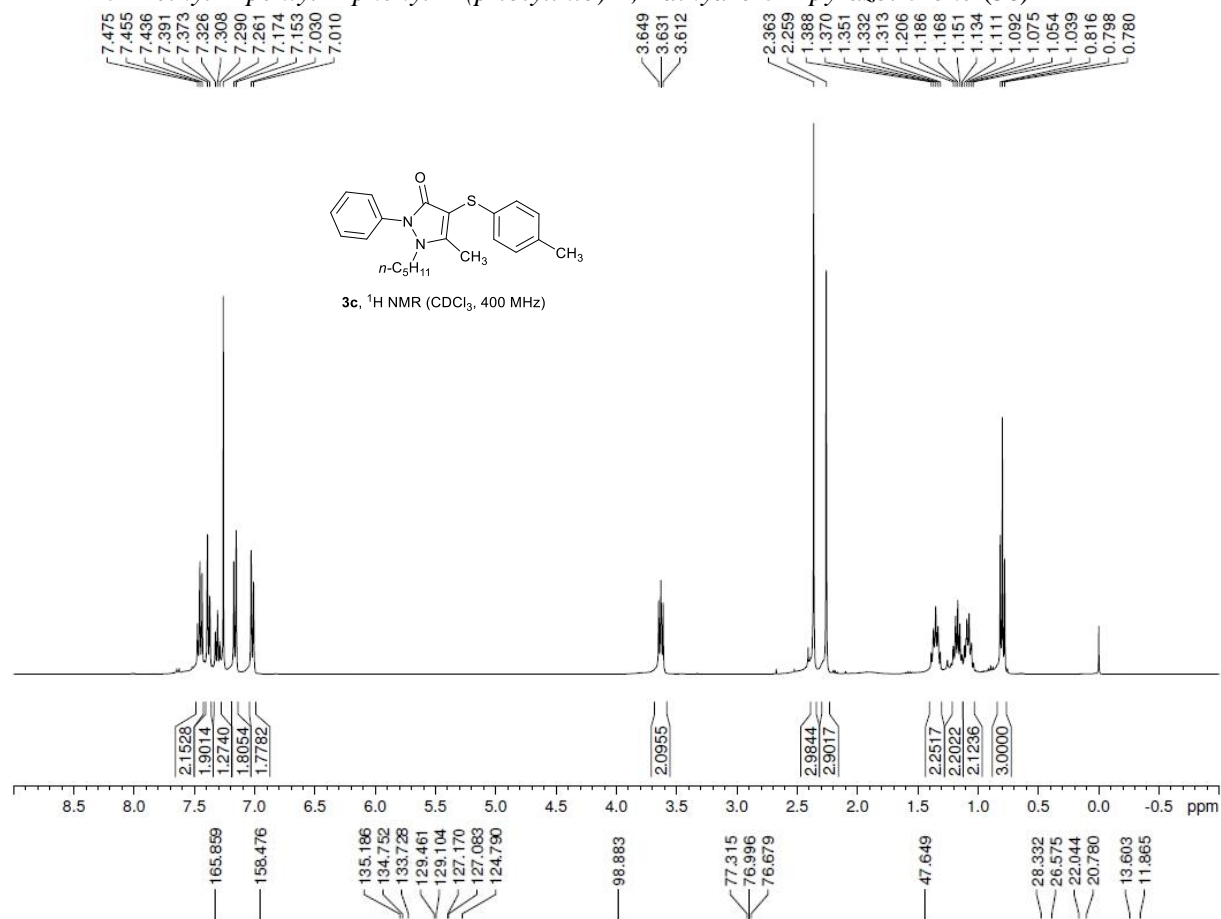
1,5-Dimethyl-2-phenyl-4-(p-tolylthio)-1,2-dihydro-3H-pyrazol-3-one (3a)



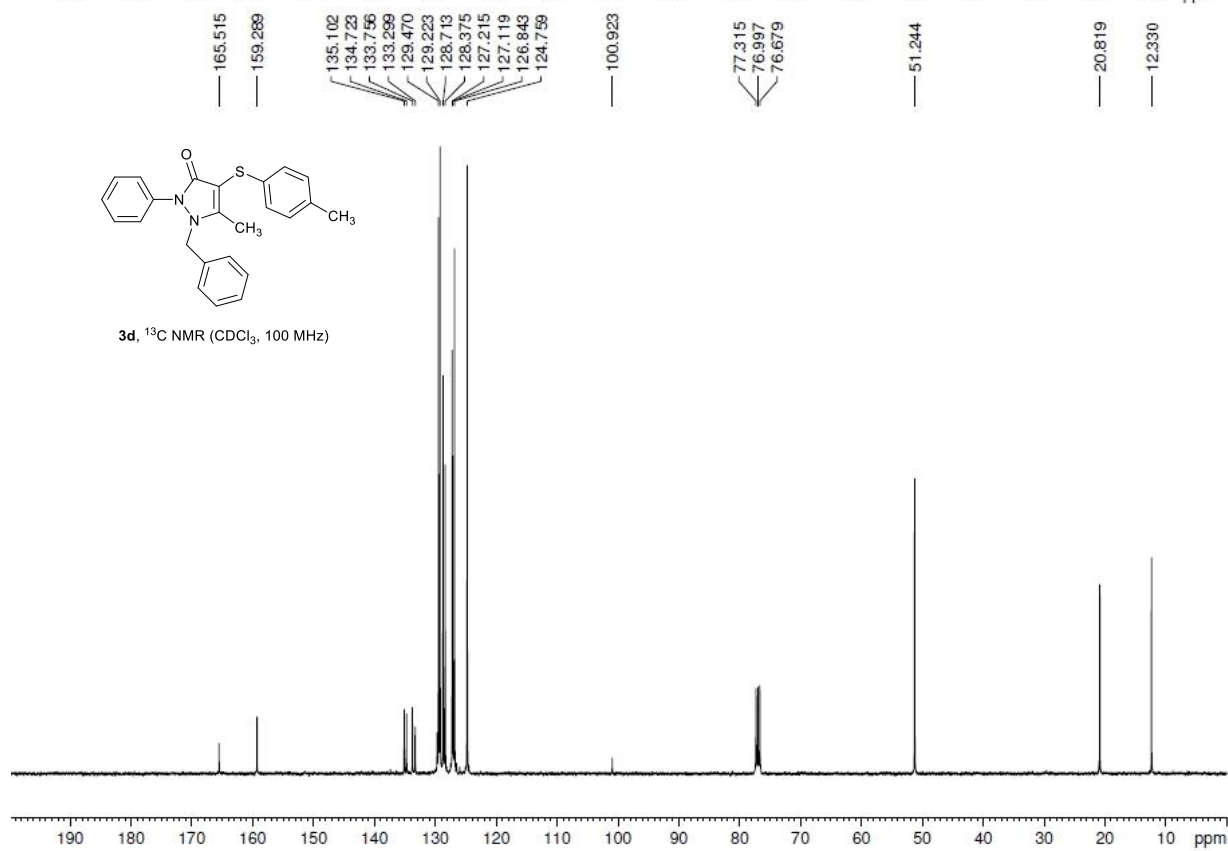
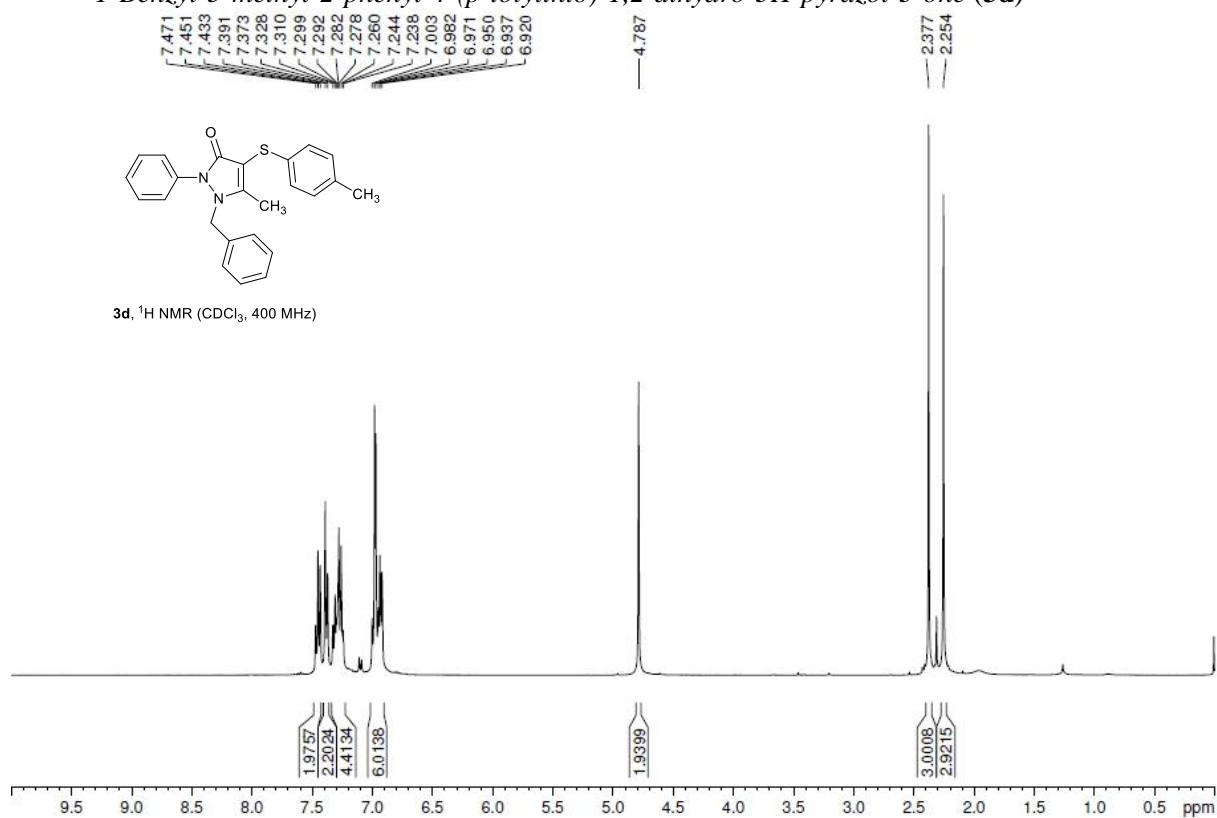
1-Ethyl-5-methyl-2-phenyl-4-(p-tolylthio)-1,2-dihydro-3H-pyrazol-3-one (3b)



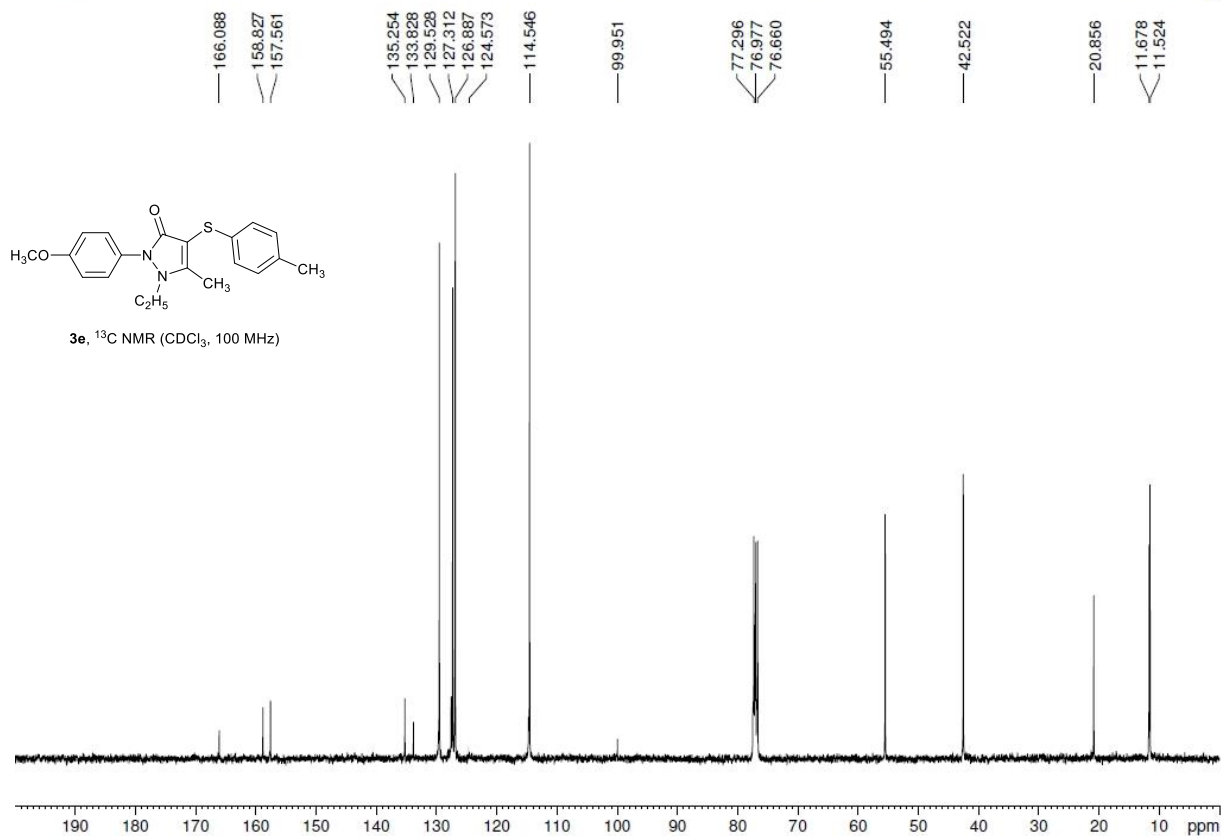
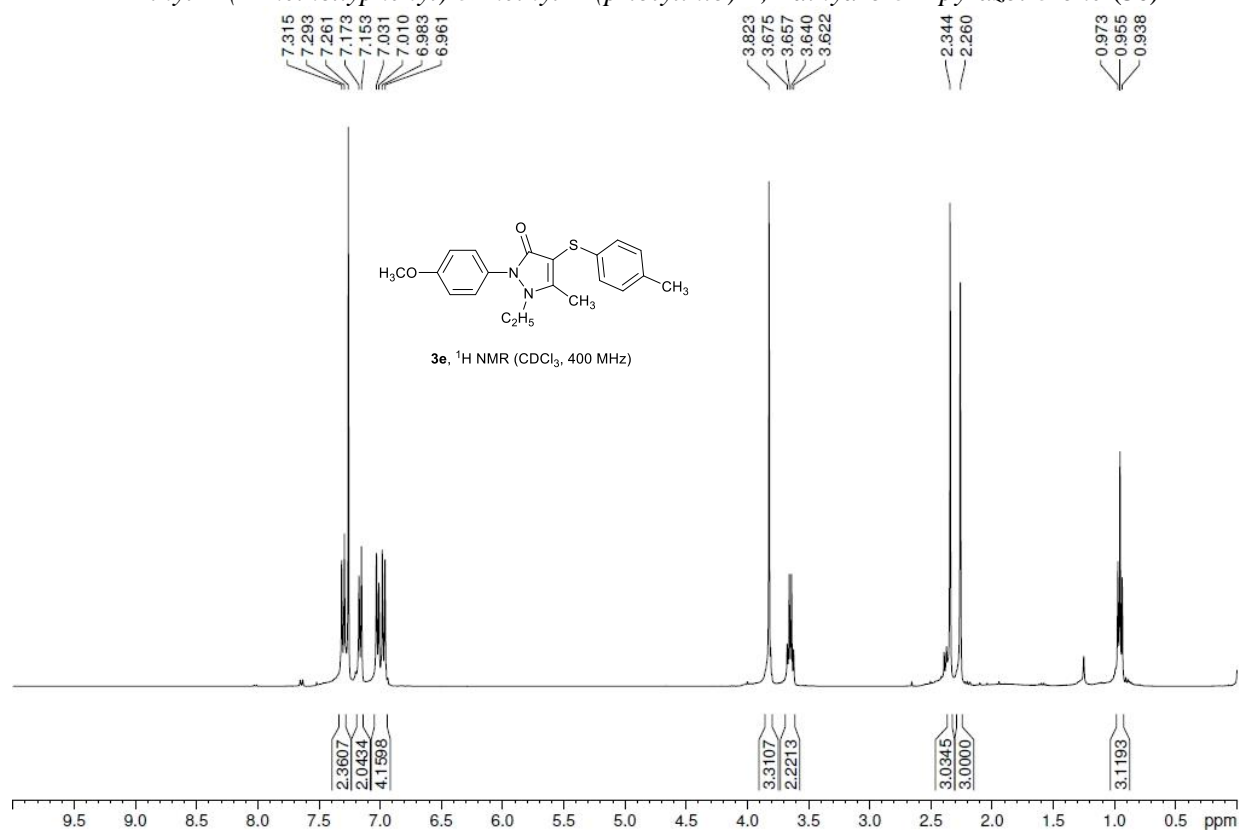
5-Methyl-1-pentyl-2-phenyl-4-(p-tolylthio)-1,2-dihydro-3H-pyrazol-3-one (3c)



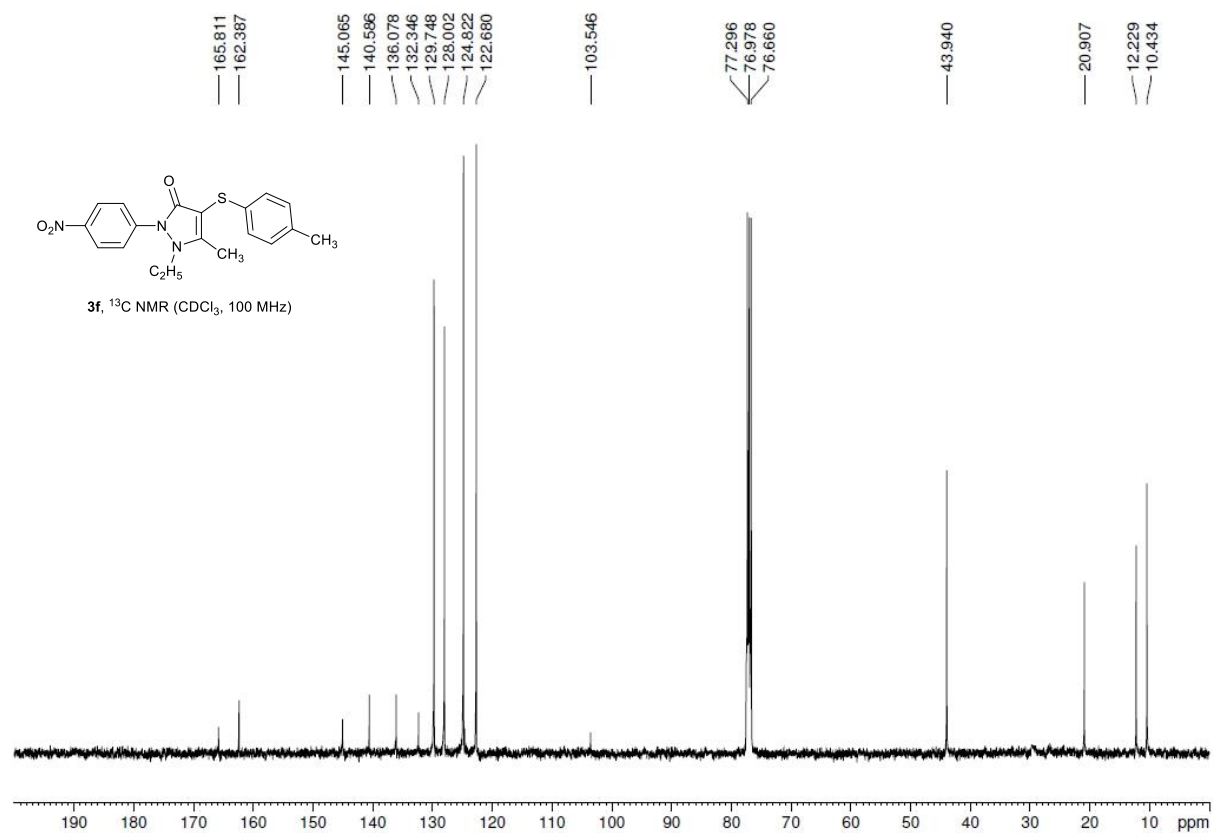
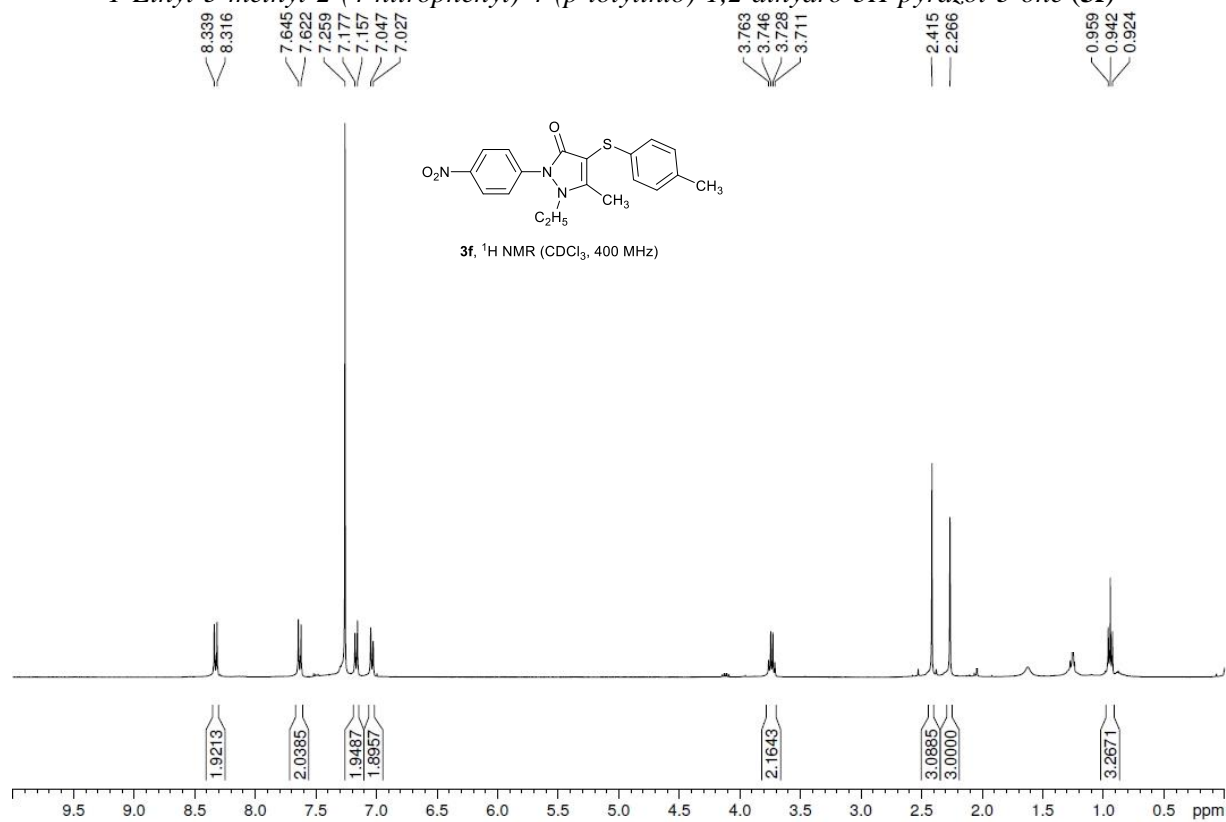
1-Benzyl-5-methyl-2-phenyl-4-(p-tolylthio)-1,2-dihydro-3H-pyrazol-3-one (3d)



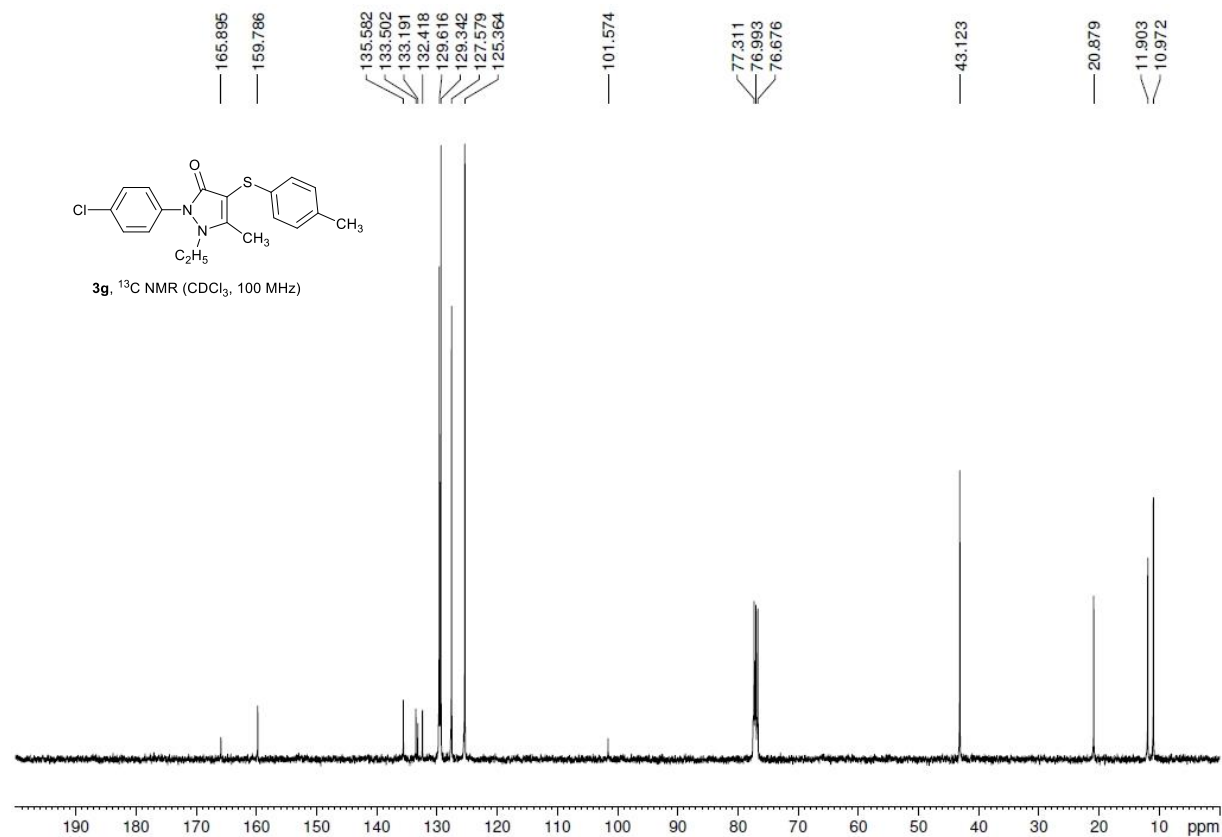
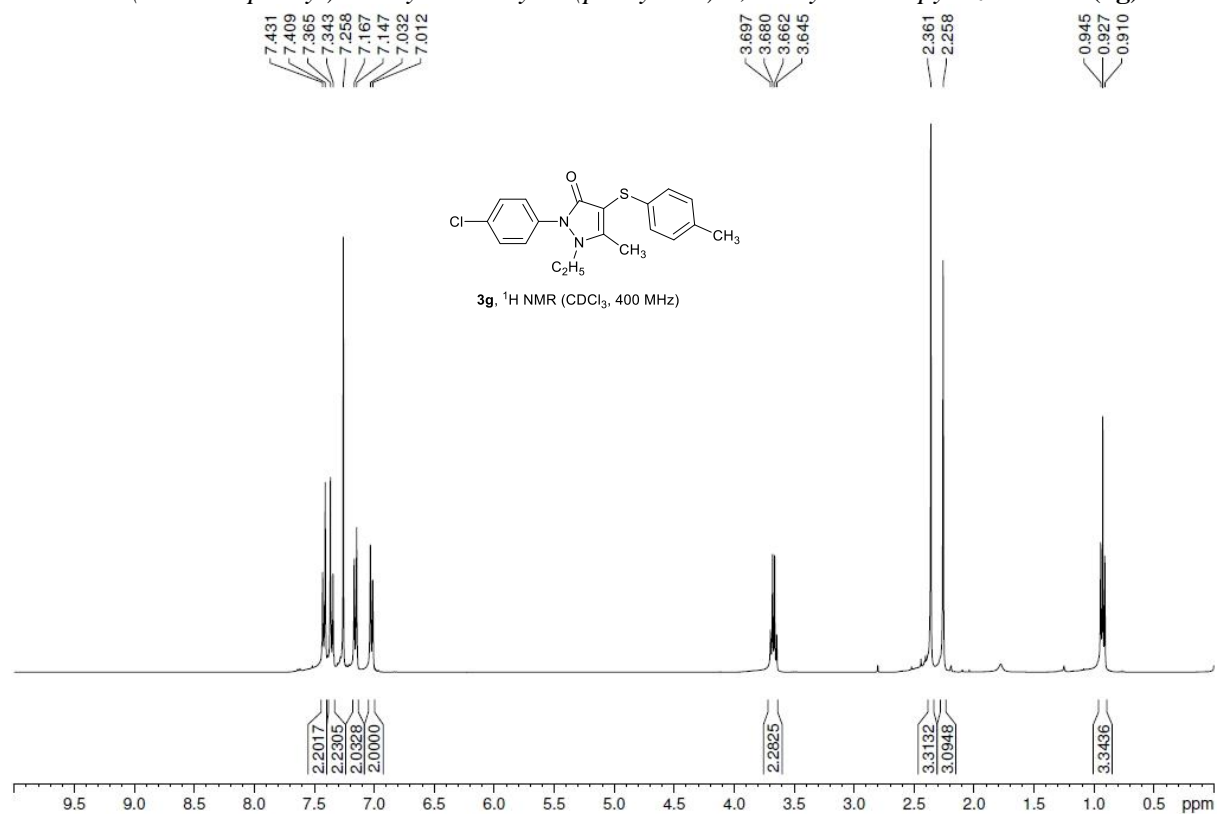
1-Ethyl-2-(4-methoxyphenyl)-5-methyl-4-(p-tolylthio)-1,2-dihydro-3H-pyrazol-3-one (3e)



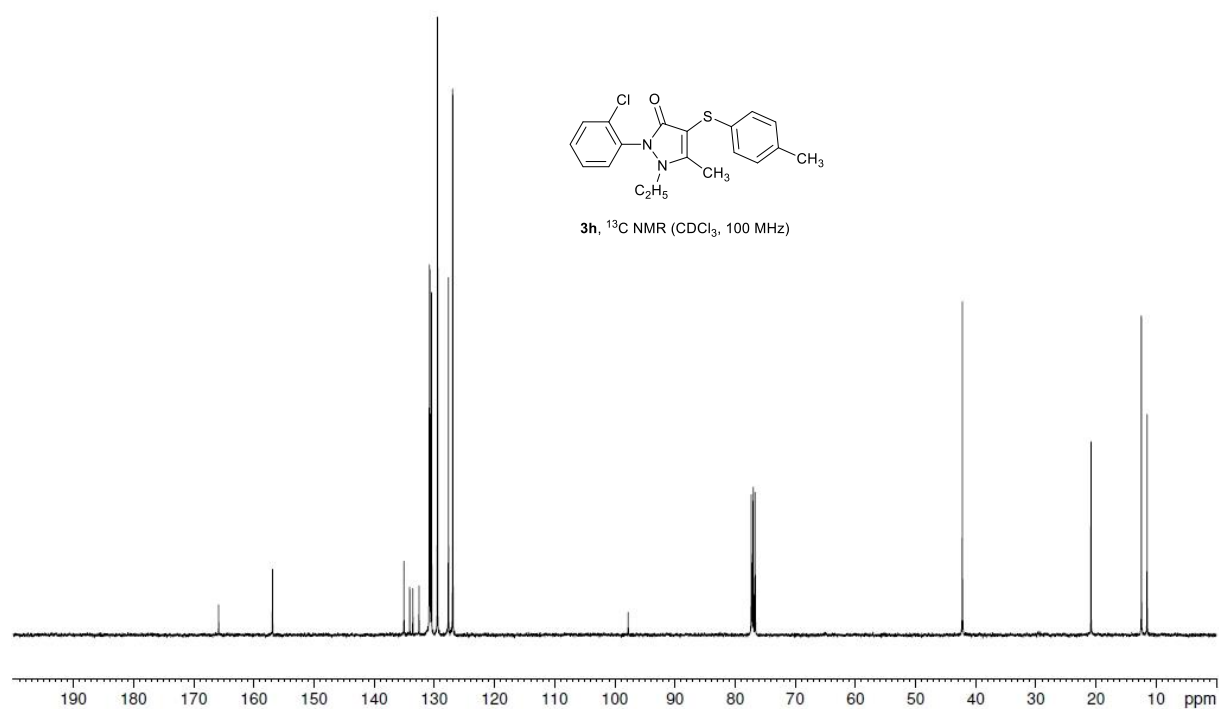
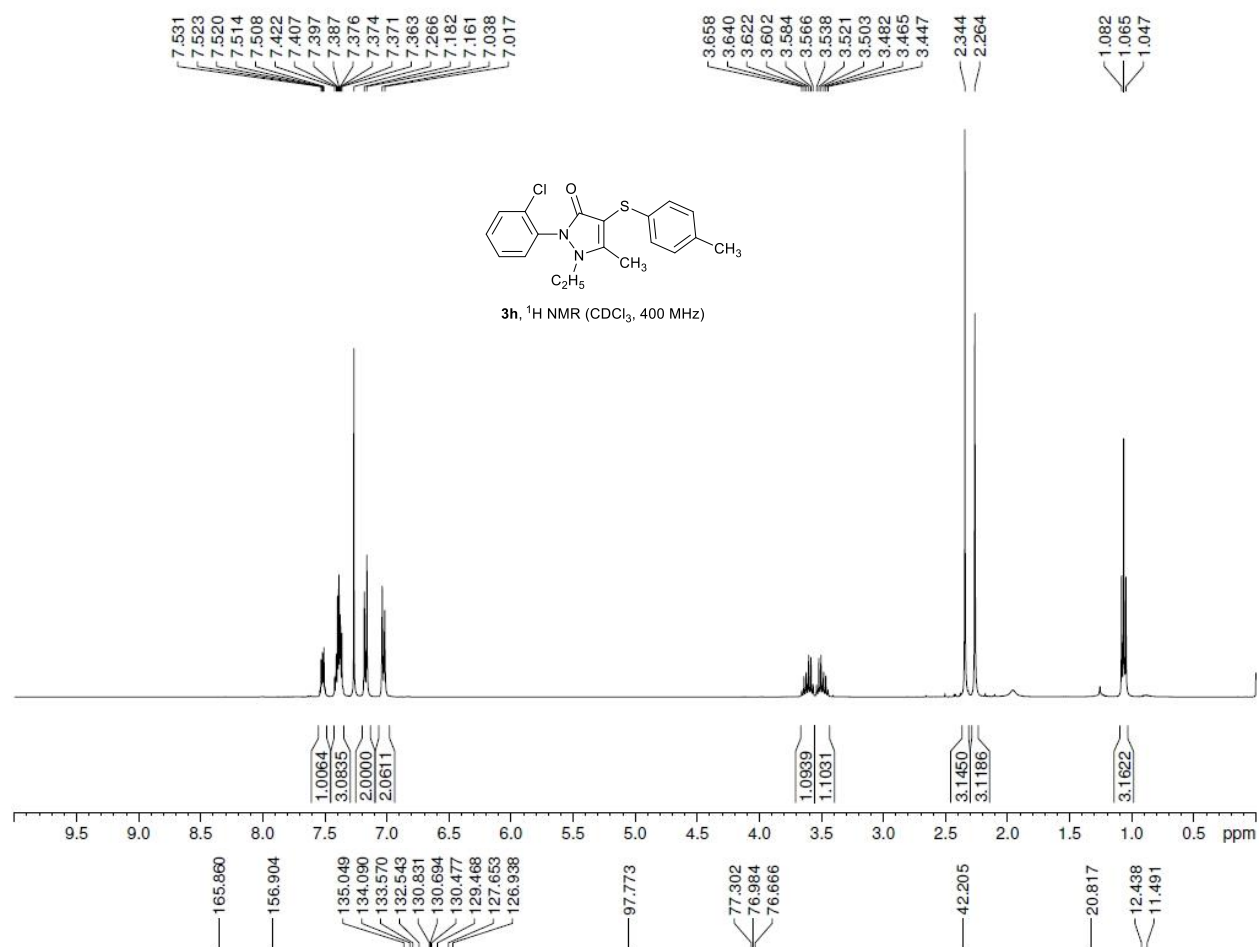
1-Ethyl-5-methyl-2-(4-nitrophenyl)-4-(p-tolylthio)-1,2-dihydro-3H-pyrazol-3-one (3f)



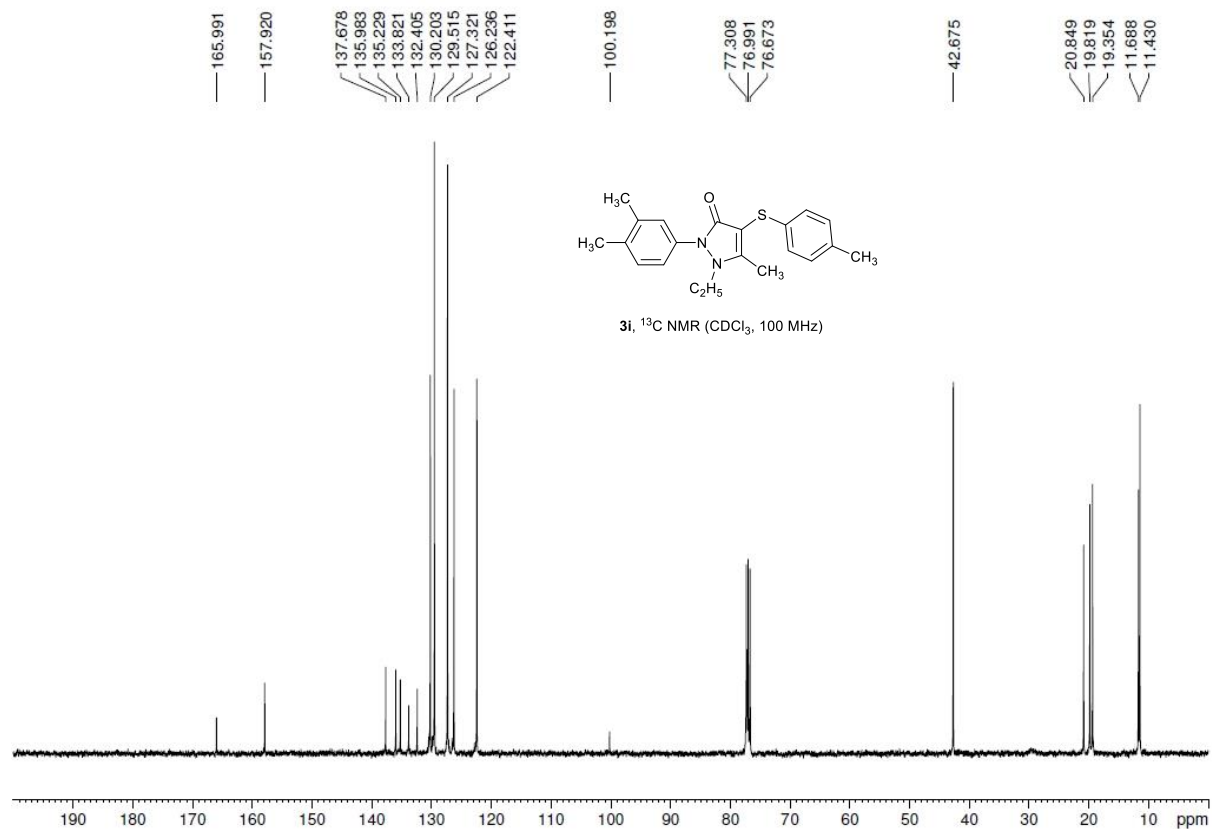
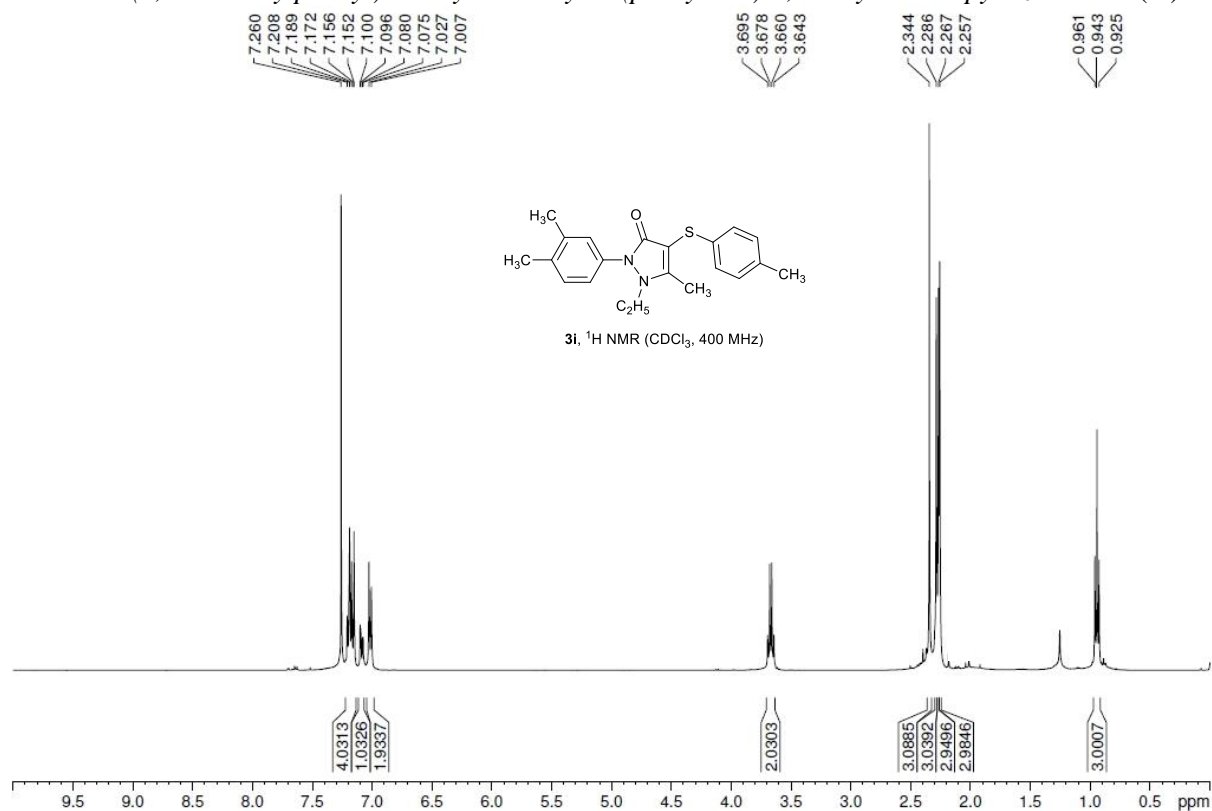
2-(4-Chlorophenyl)-1-ethyl-5-methyl-4-(p-tolylthio)-1,2-dihydro-3H-pyrazol-3-one (**3g**)



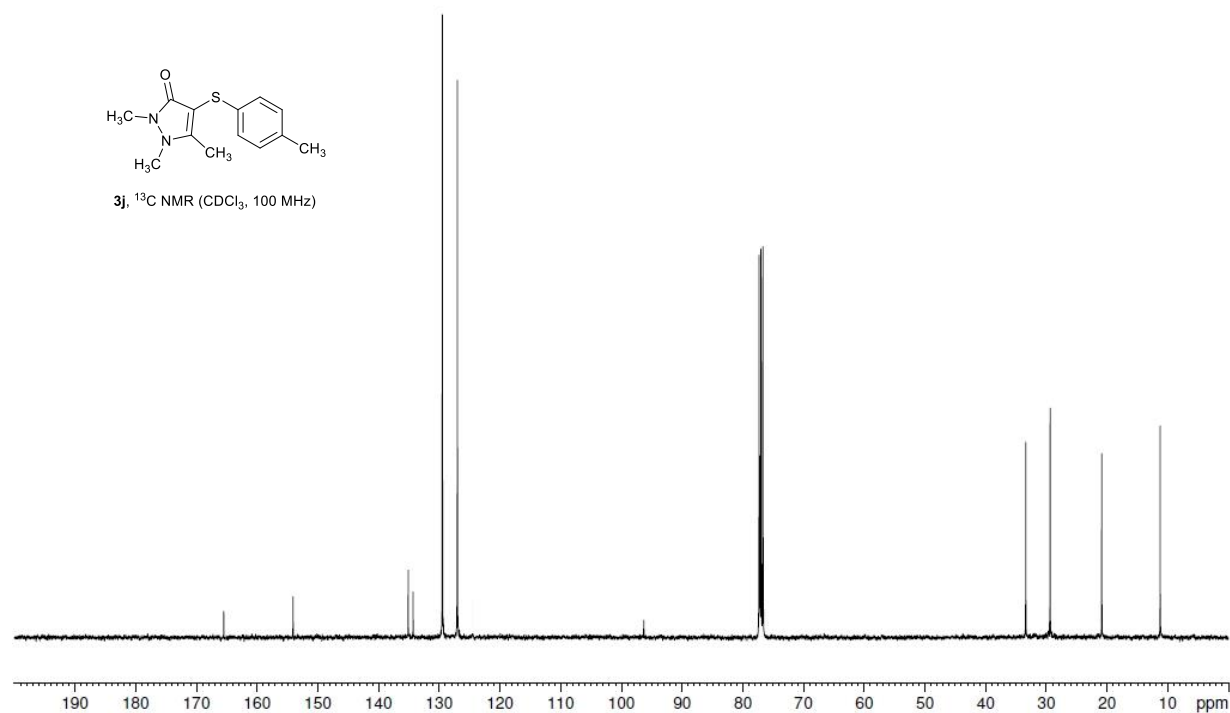
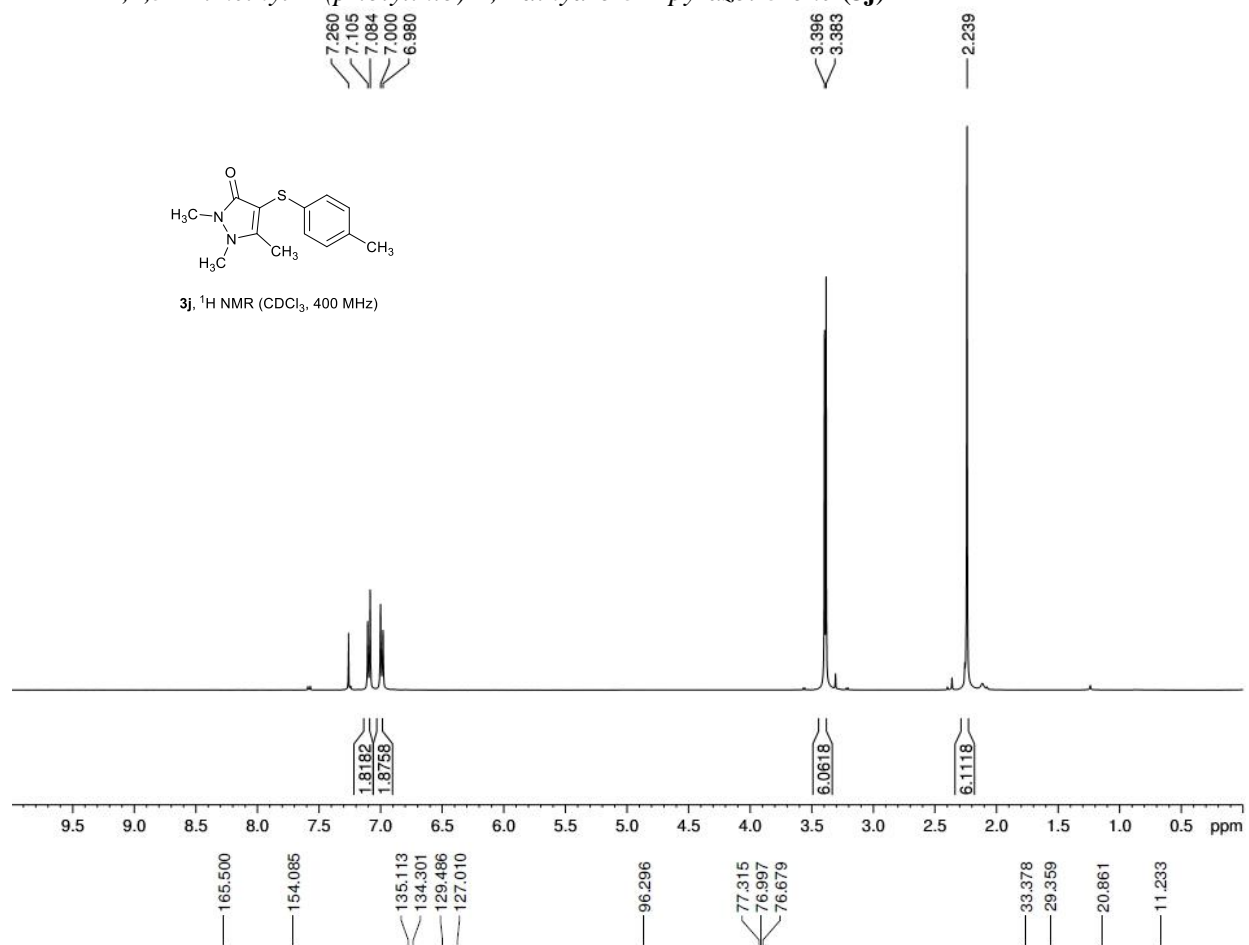
2-(2-Chlorophenyl)-1-ethyl-5-methyl-4-(p-tolylthio)-1,2-dihydro-3H-pyrazol-3-one (**3h**)



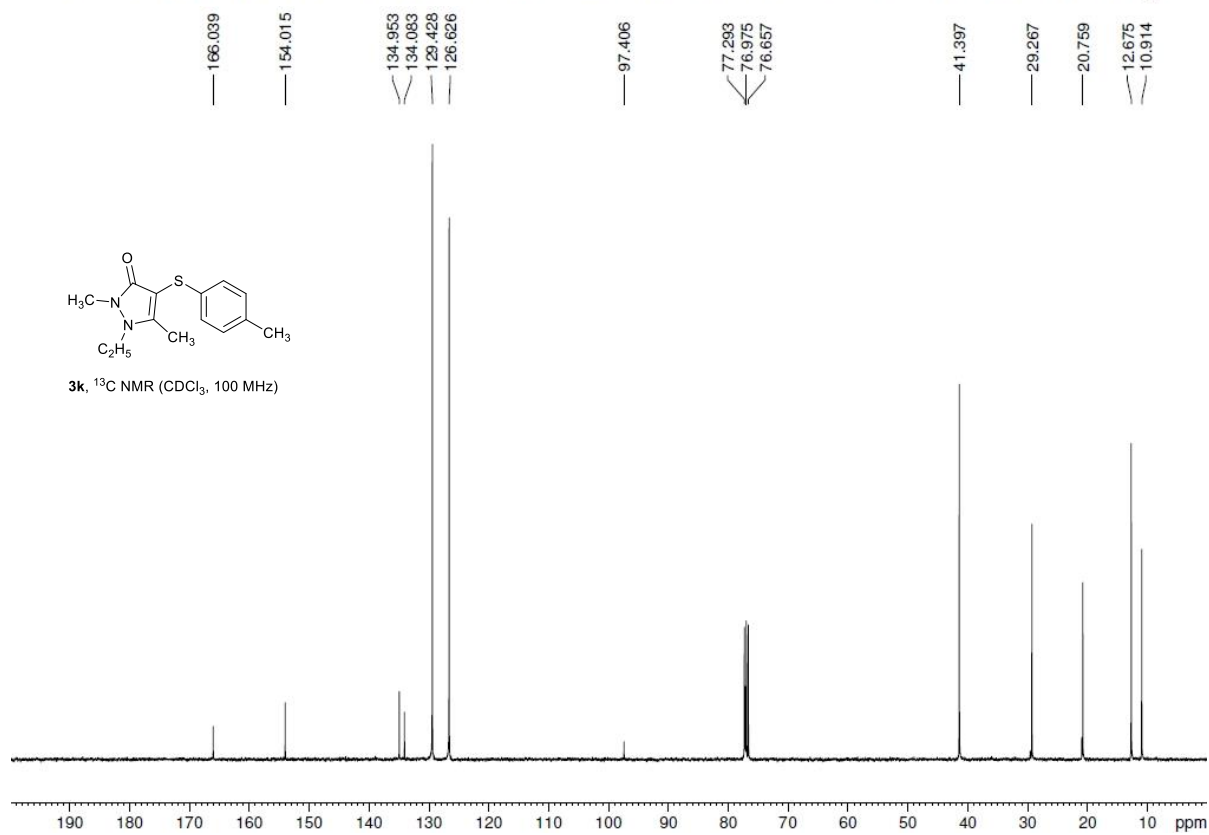
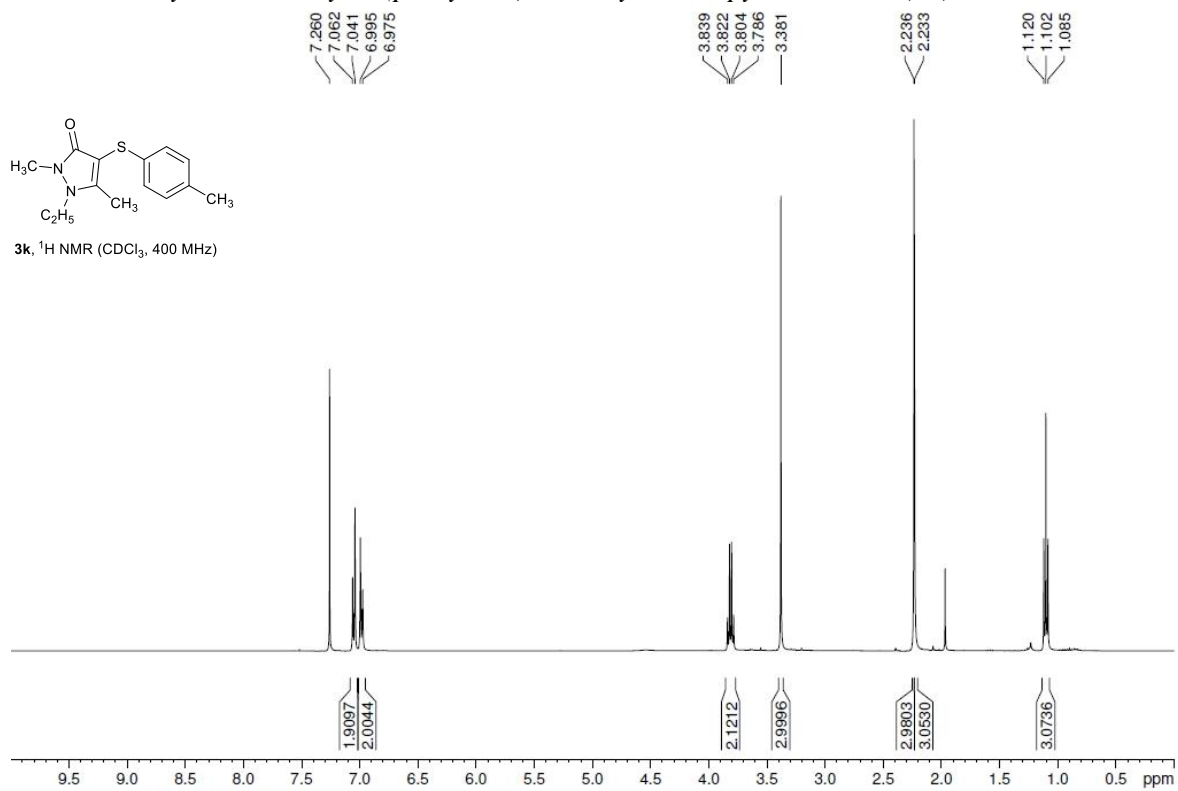
2-(3,4-Dimethylphenyl)-1-ethyl-5-methyl-4-(p-tolylthio)-1,2-dihydro-3H-pyrazol-3-one (**3i**)



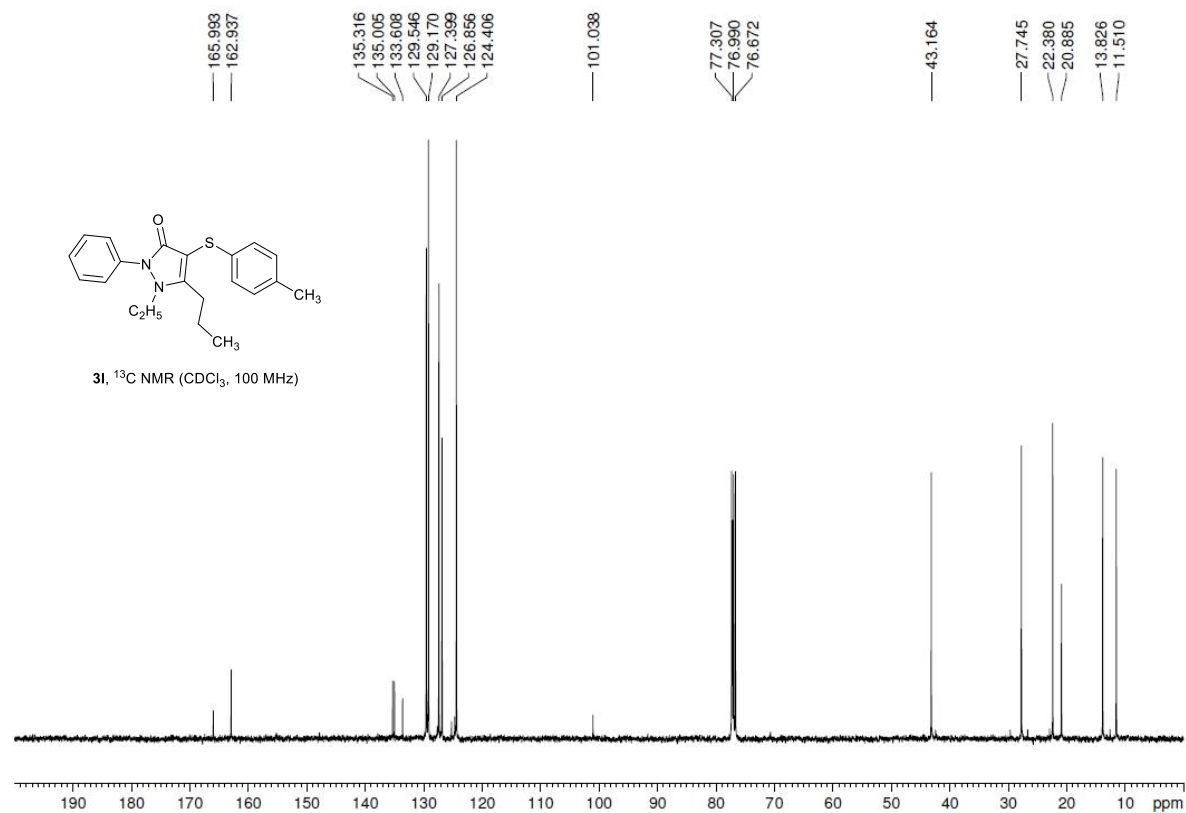
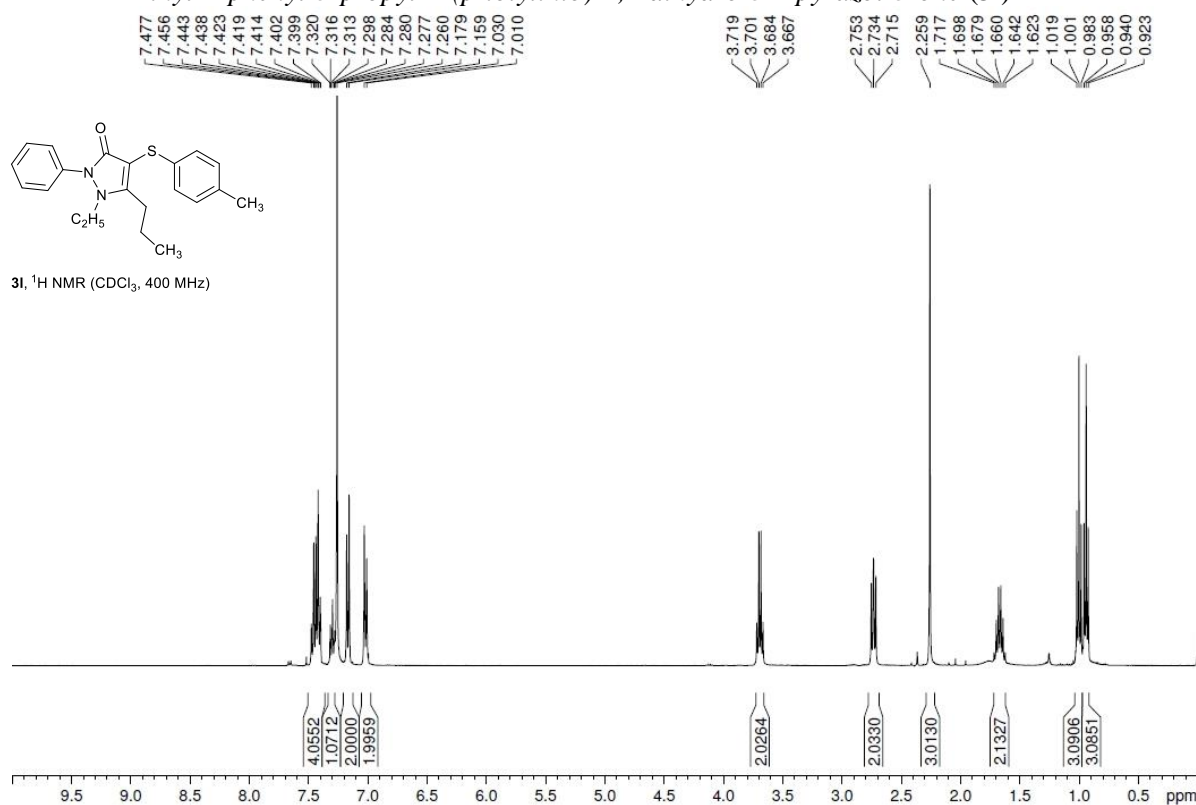
1,2,5-Trimethyl-4-(p-tolylthio)-1,2-dihydro-3H-pyrazol-3-one (3j)



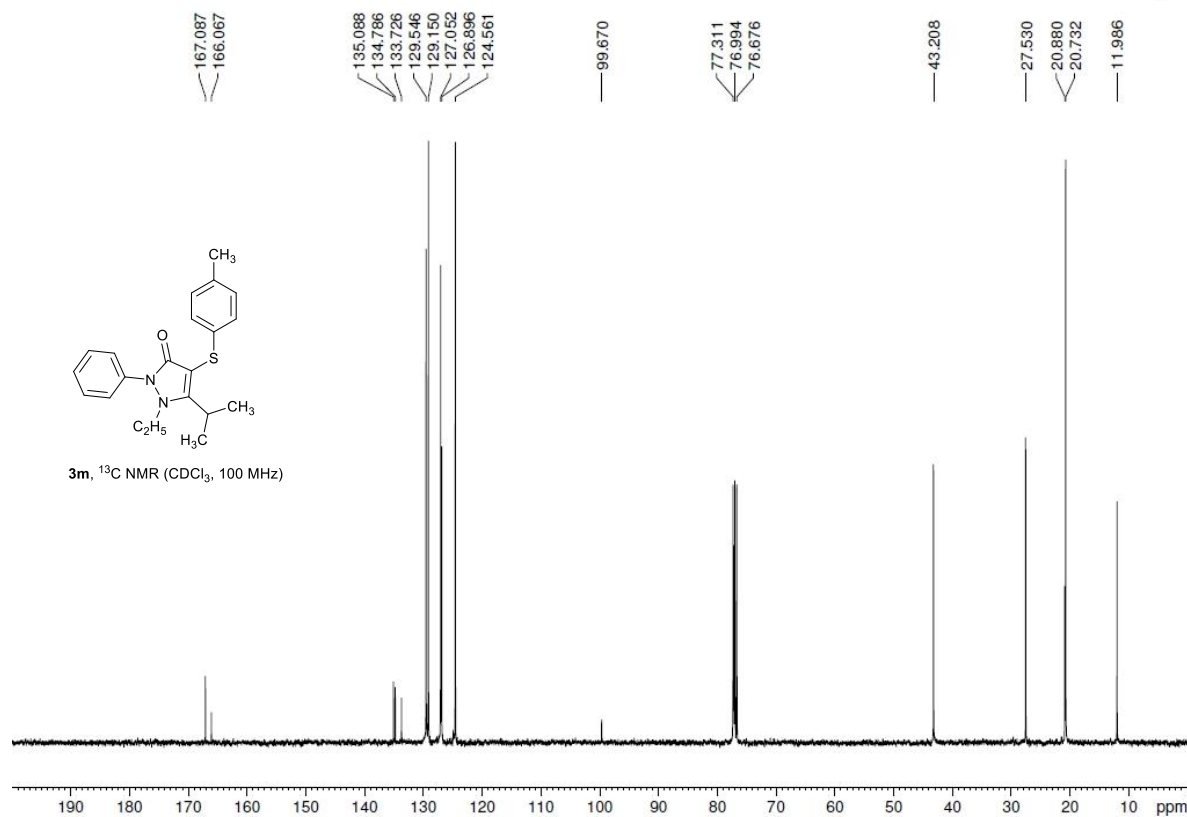
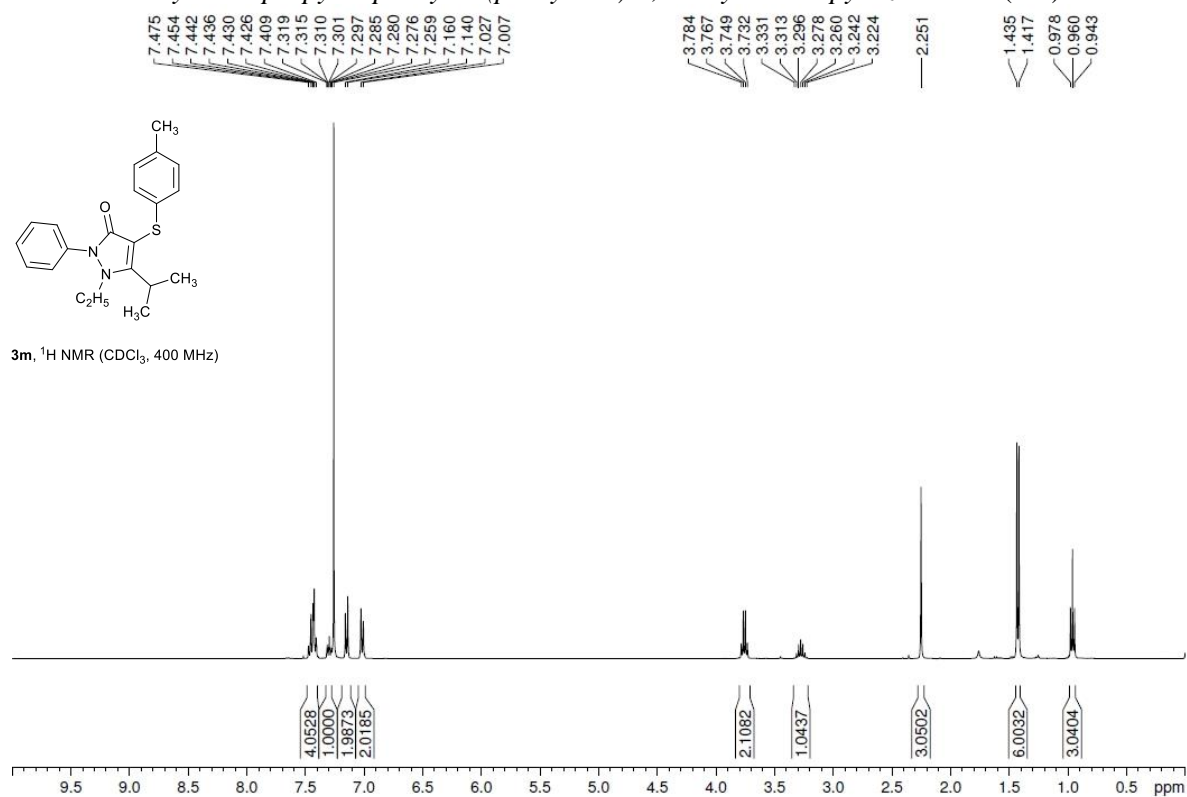
1-Ethyl-2,5-dimethyl-4-(p-tolylthio)-1,2-dihydro-3H-pyrazol-3-one (3k)



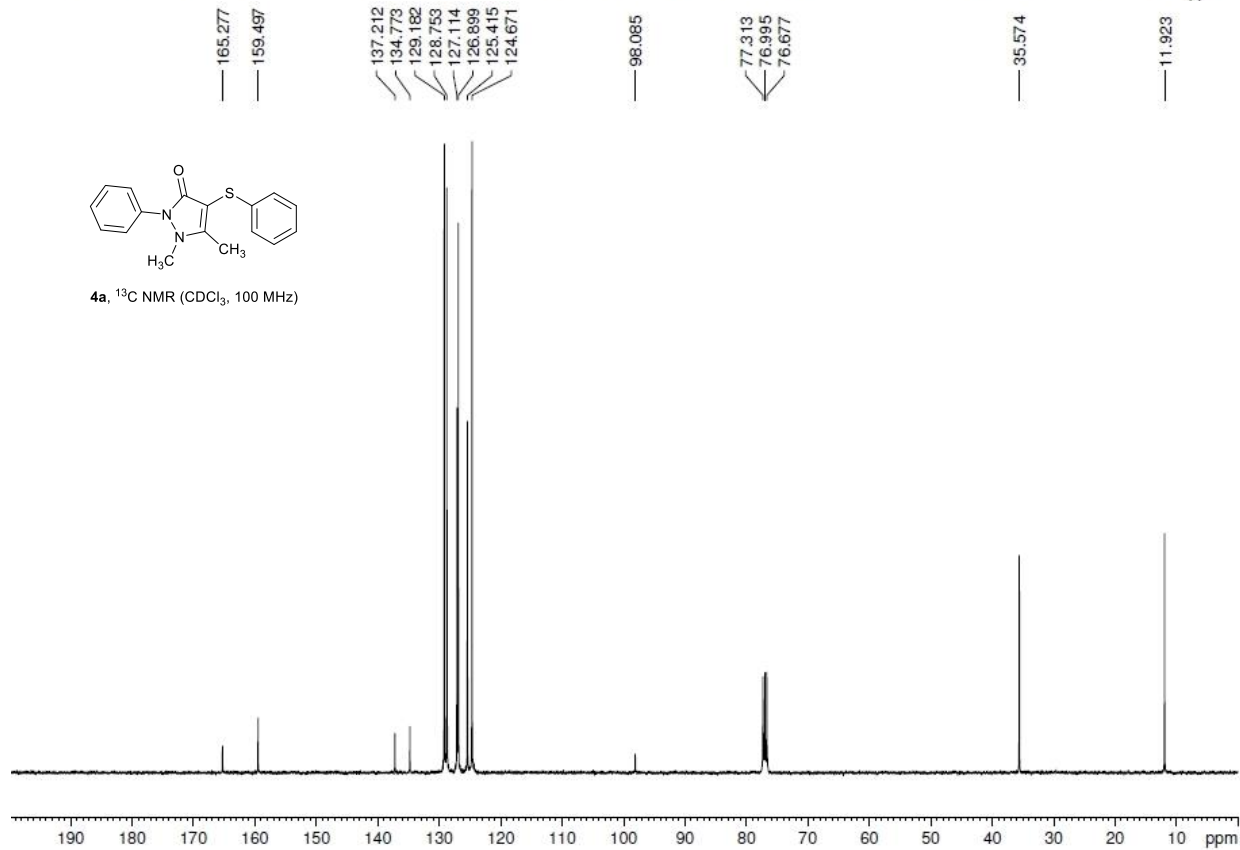
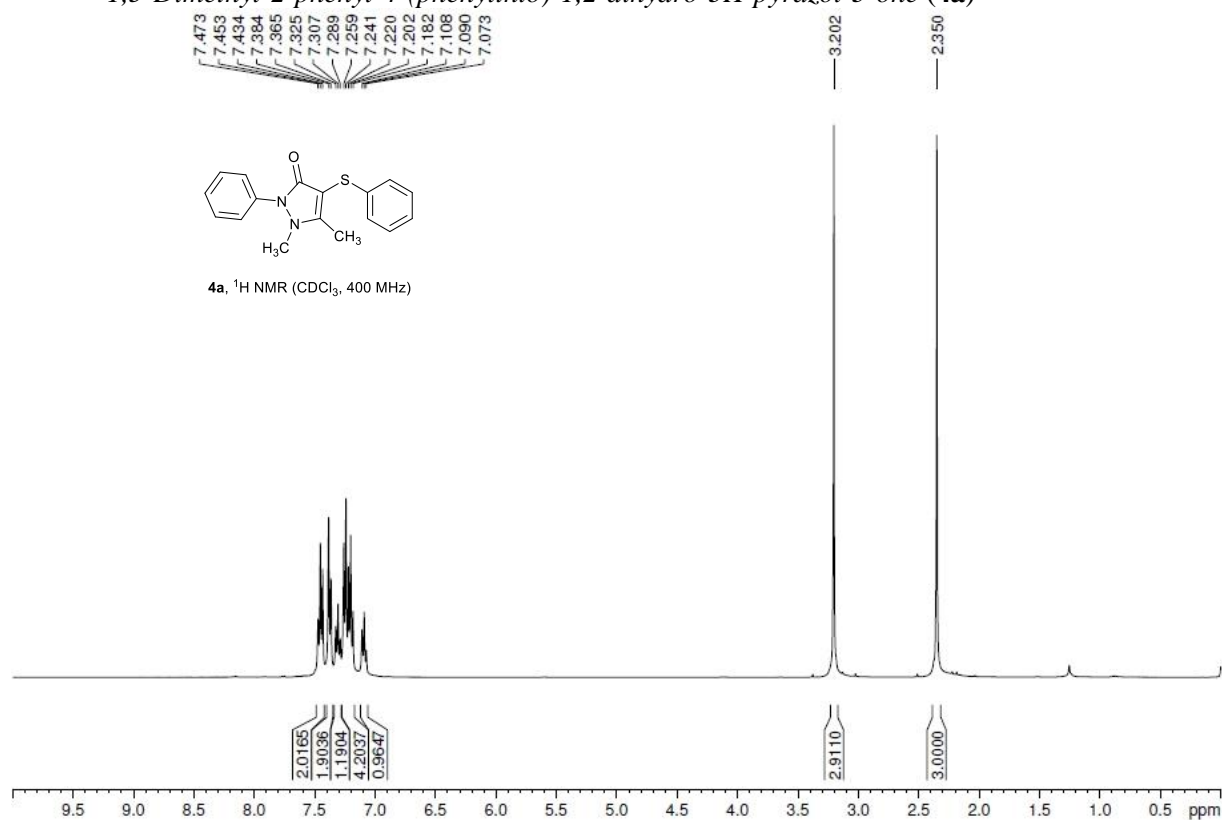
1-Ethyl-2-phenyl-5-propyl-4-(p-tolylthio)-1,2-dihydro-3H-pyrazol-3-one (3I)



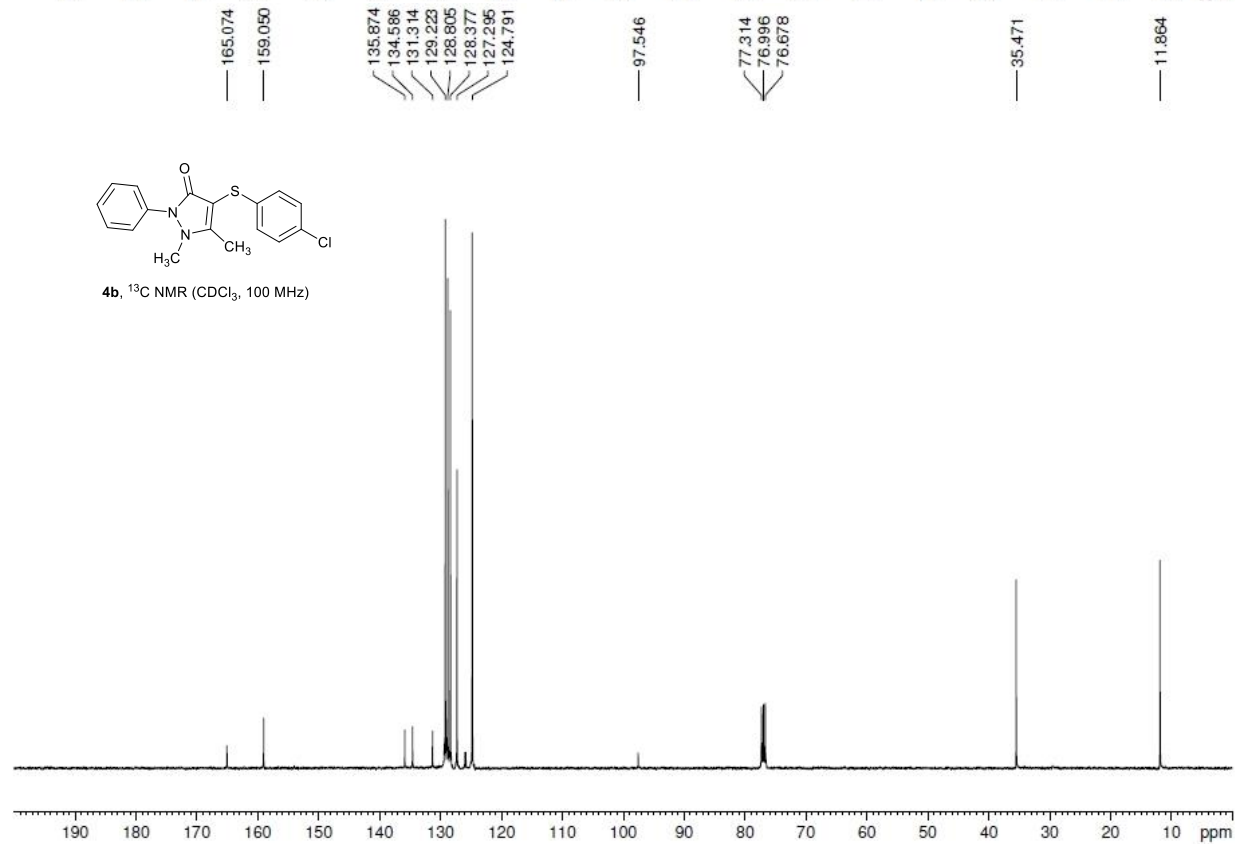
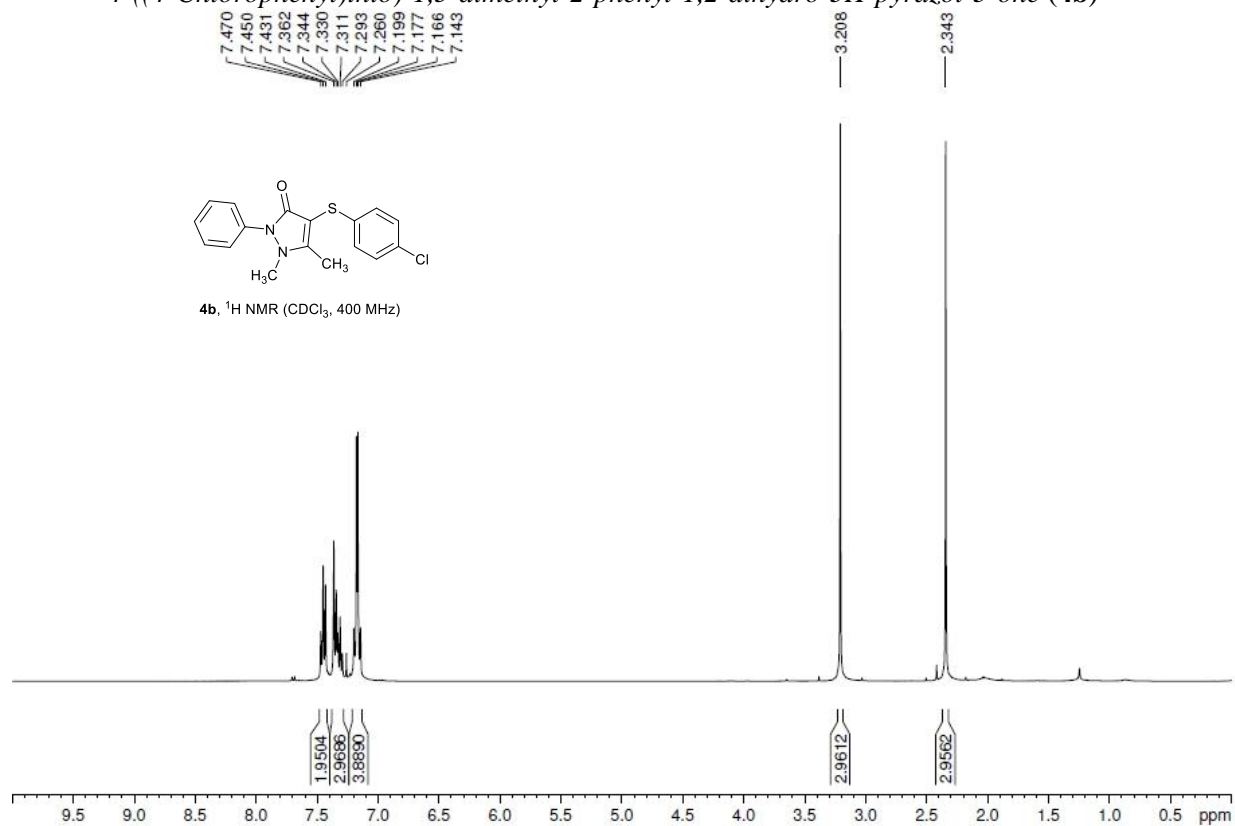
1-Ethyl-5-isopropyl-2-phenyl-4-(p-tolylthio)-1,2-dihydro-3H-pyrazol-3-one (3m)



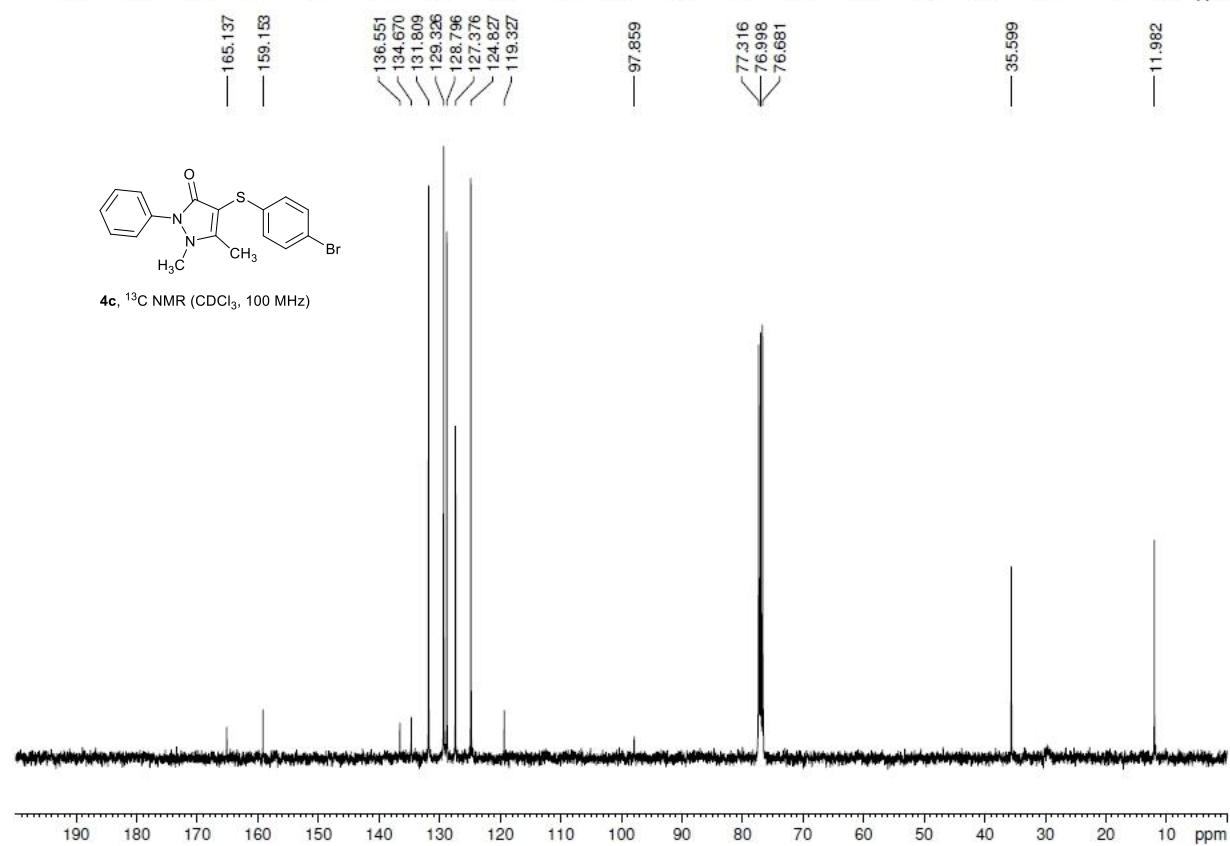
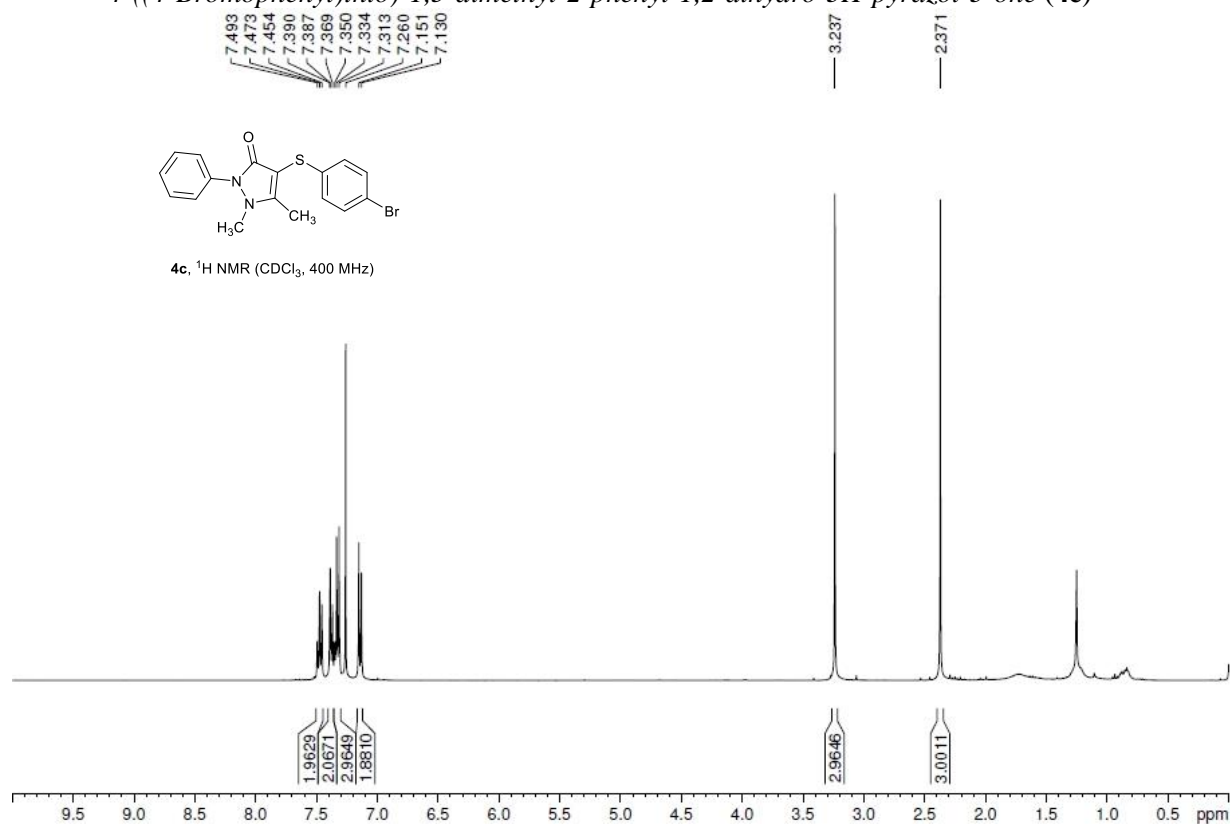
1,5-Dimethyl-2-phenyl-4-(phenylthio)-1,2-dihydro-3H-pyrazol-3-one (4a)



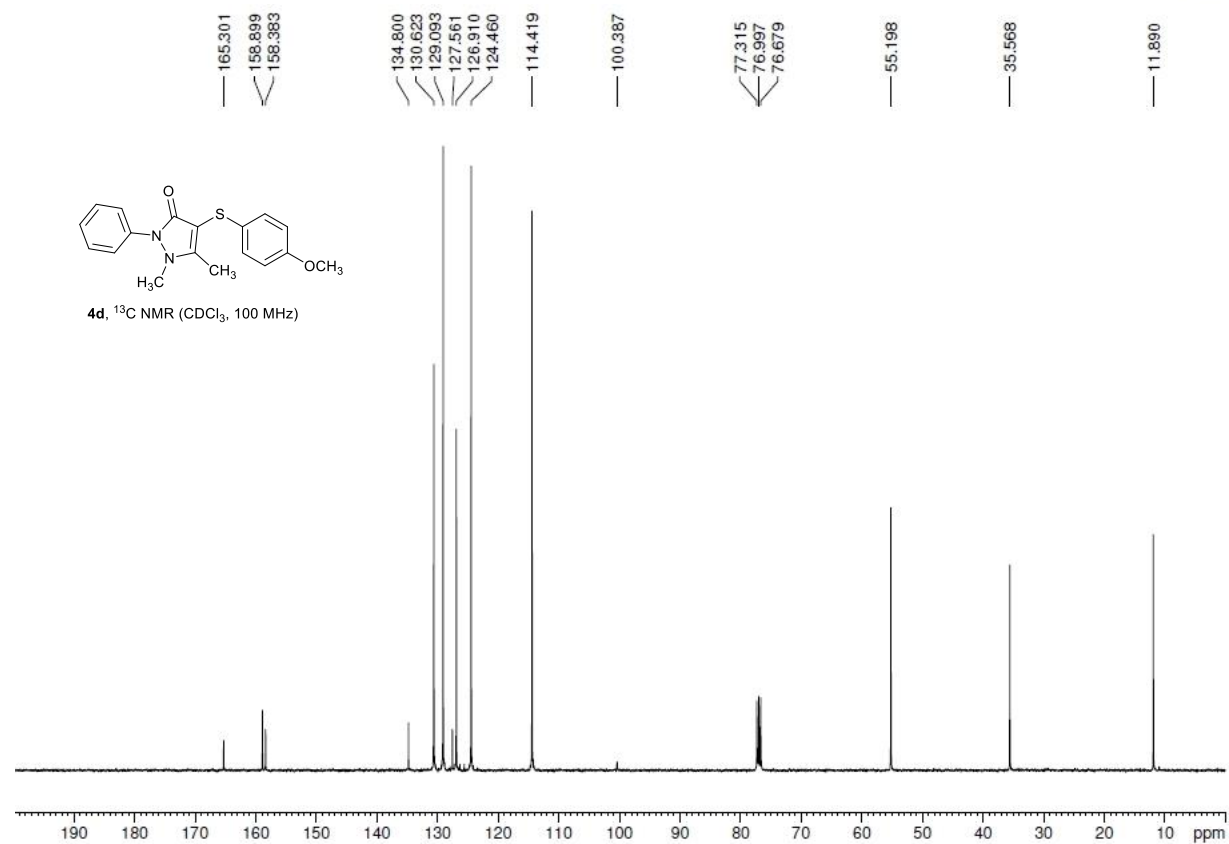
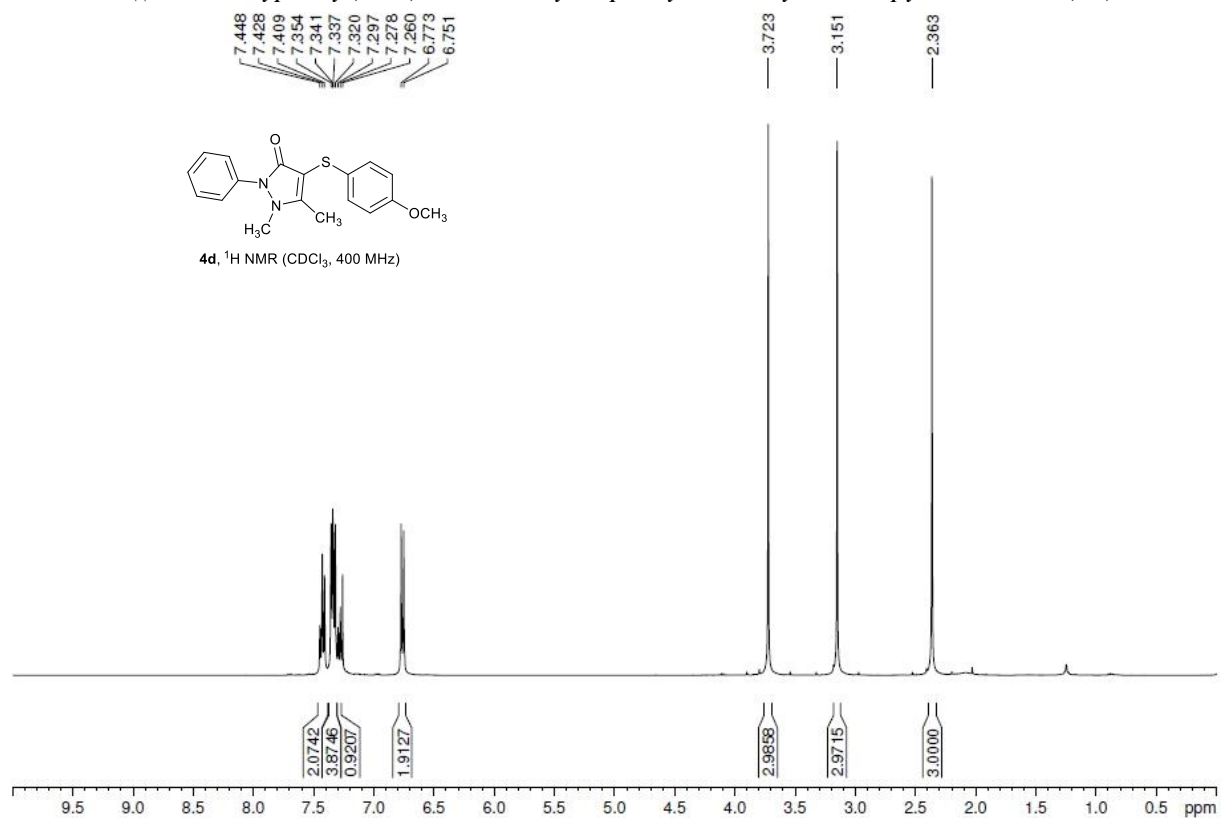
4-((4-Chlorophenyl)thio)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (4b)



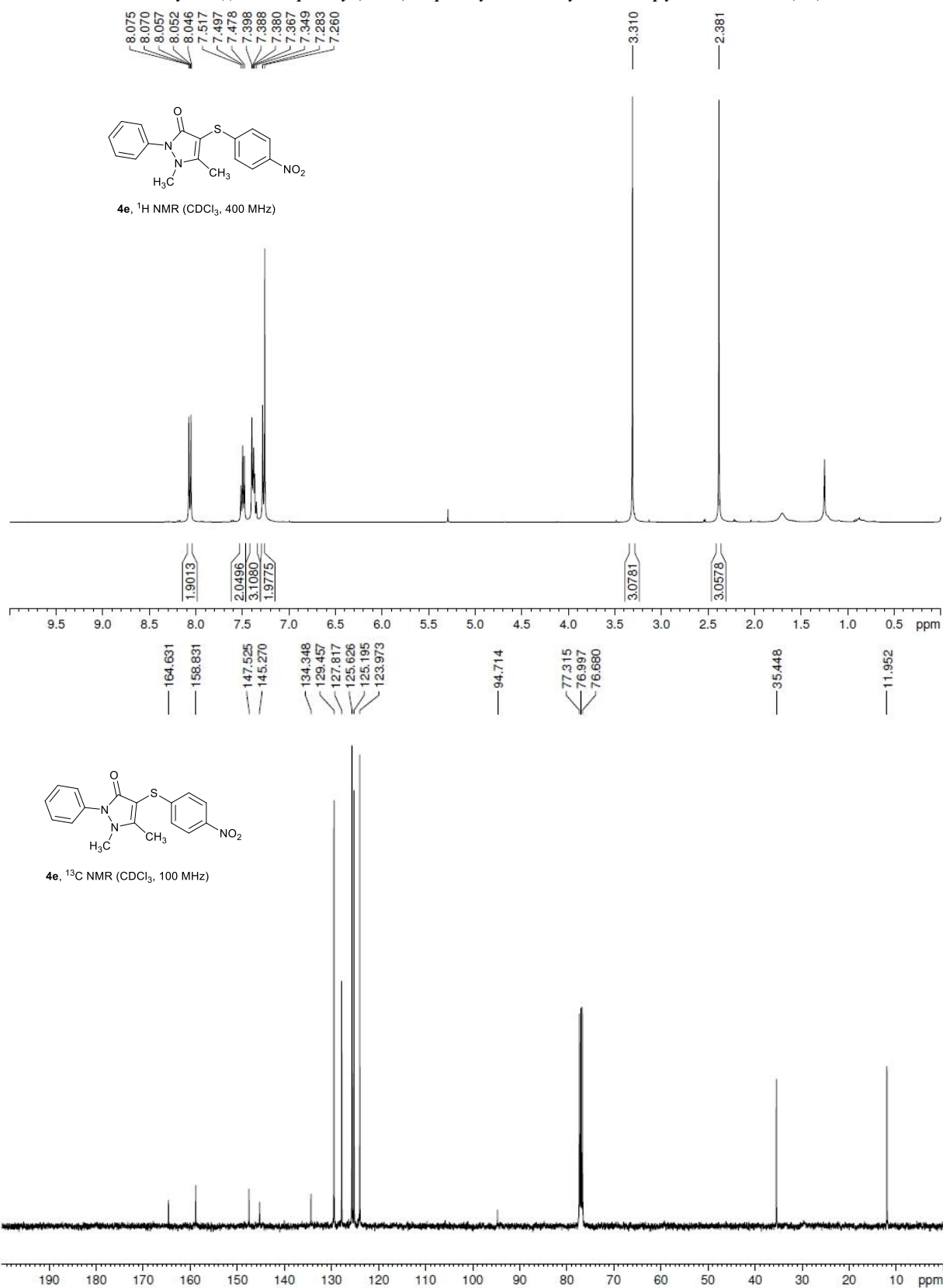
4-((4-Bromophenyl)thio)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (4c)



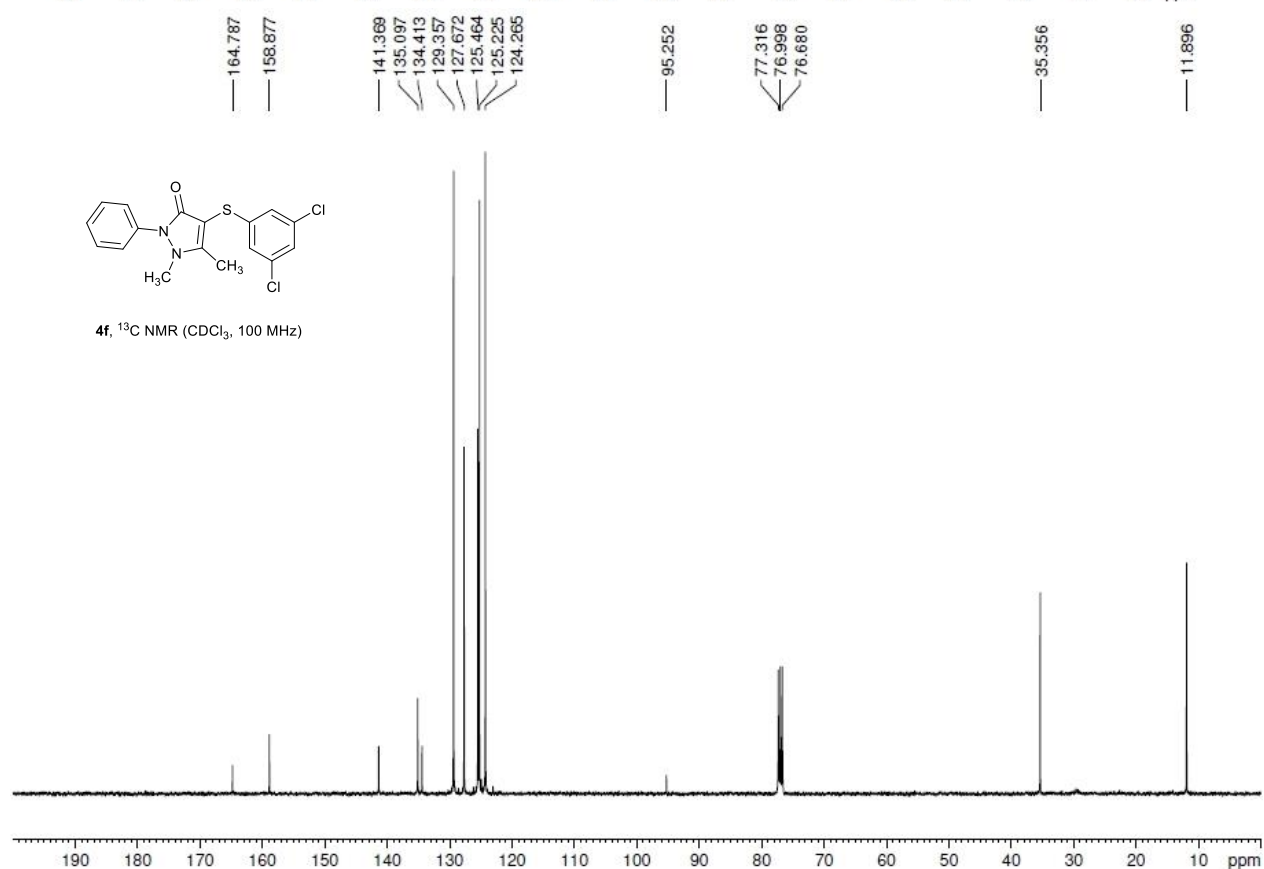
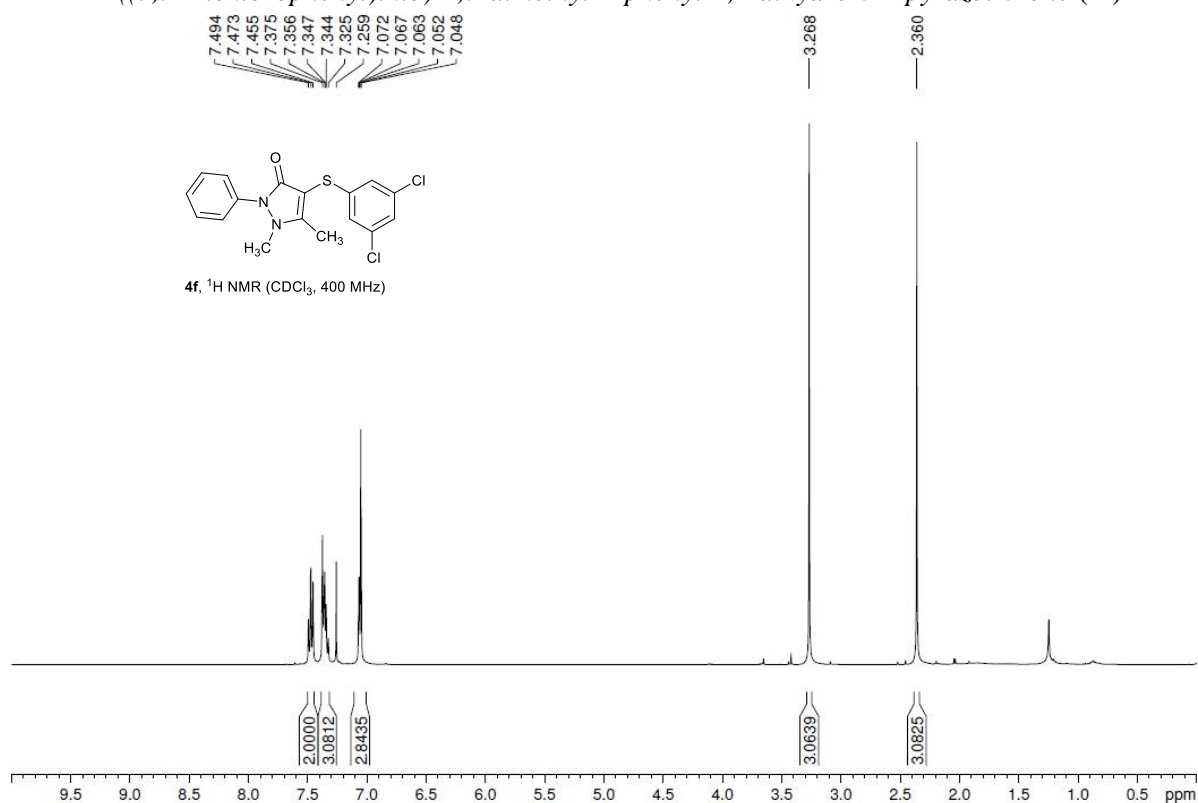
4-((4-Methoxyphenyl)thio)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (4d)



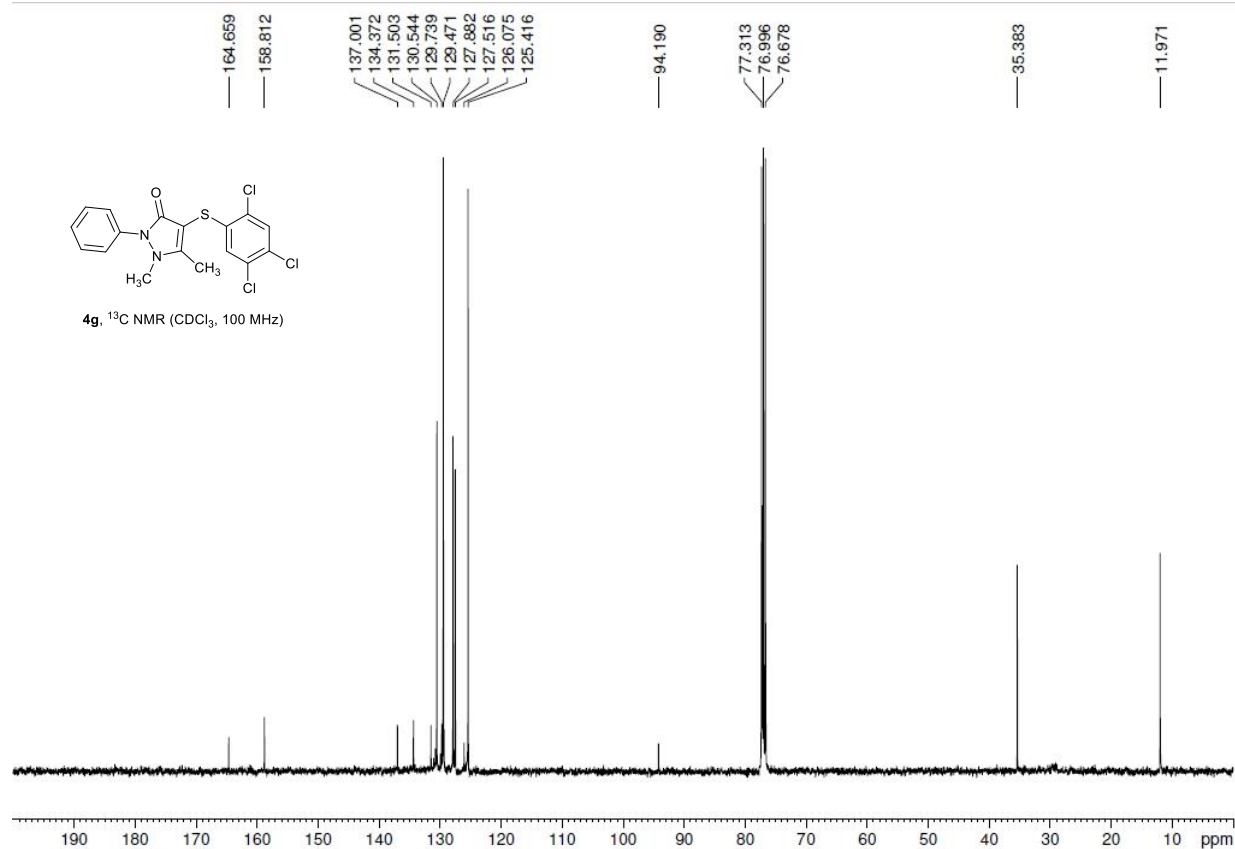
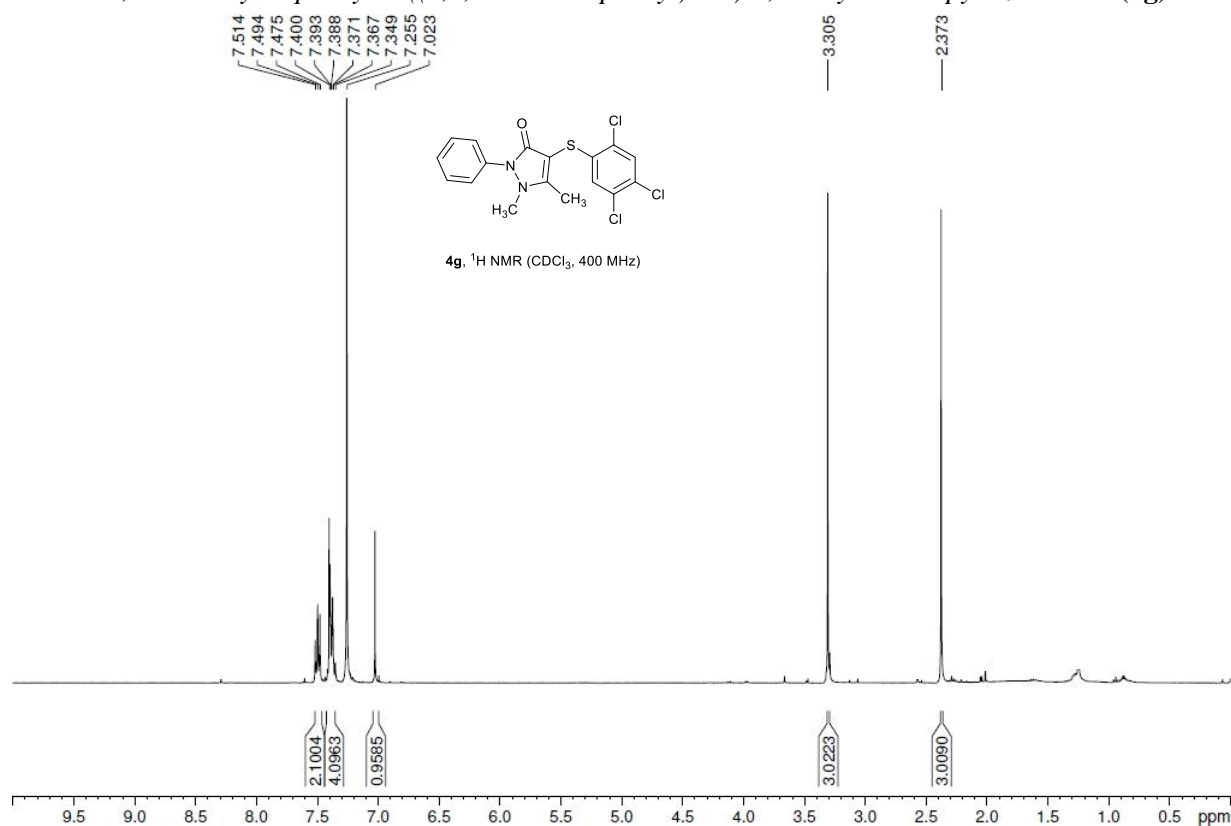
1,5-Dimethyl-4-((4-nitrophenyl)thio)-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (4e)



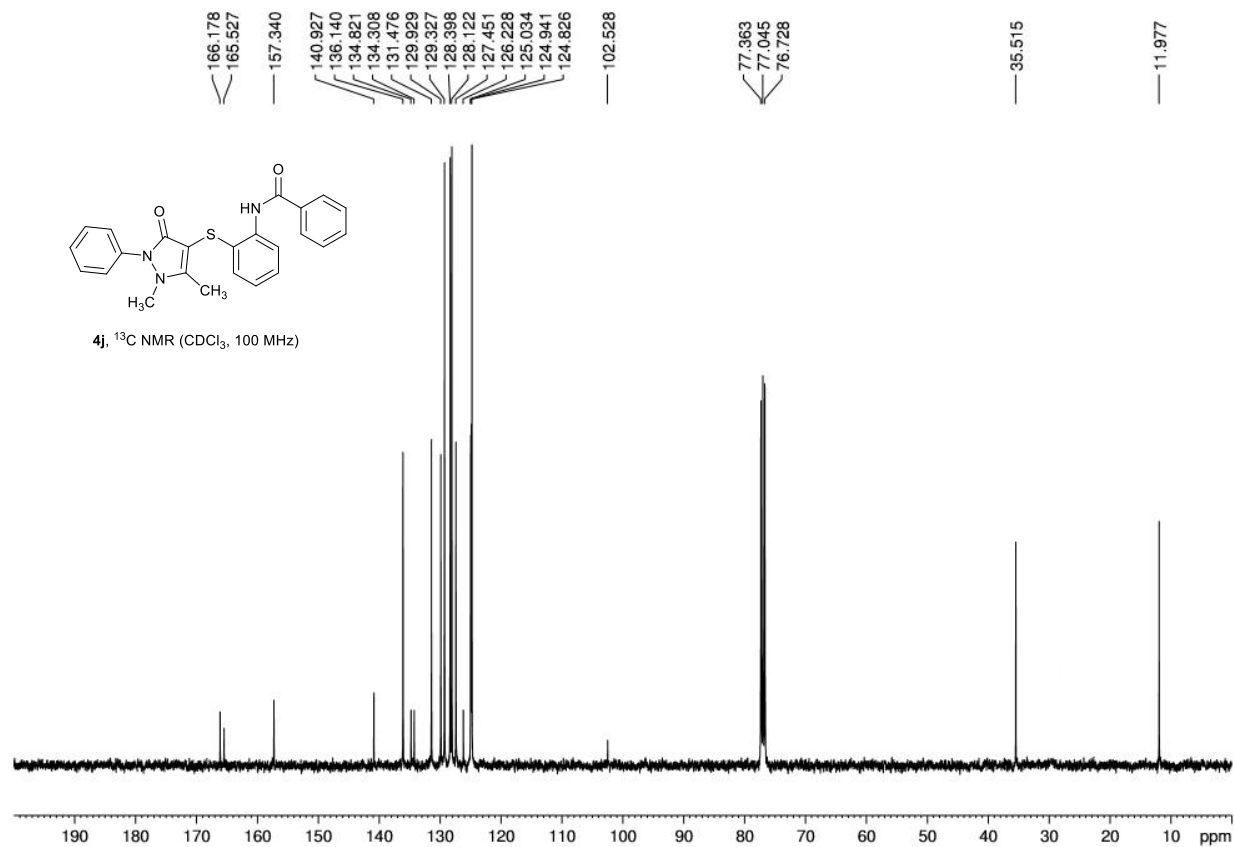
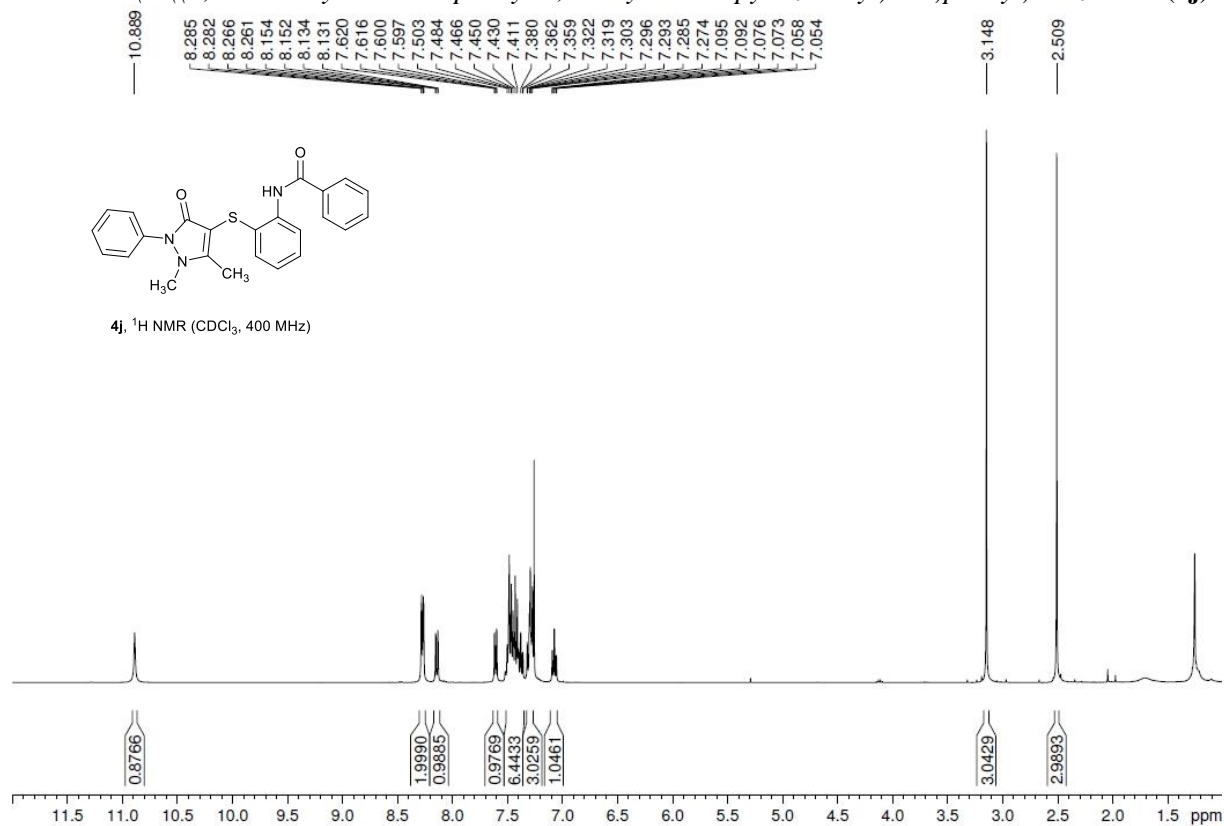
4-((3,5-Dichlorophenyl)thio)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (**4f**)



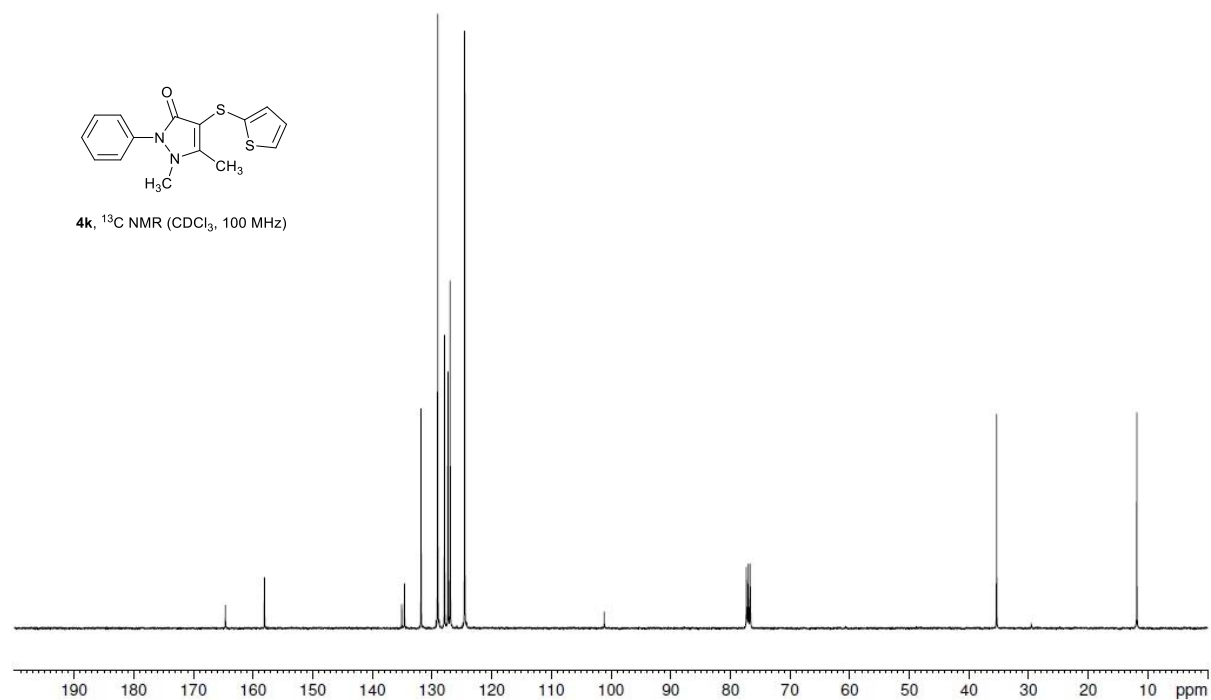
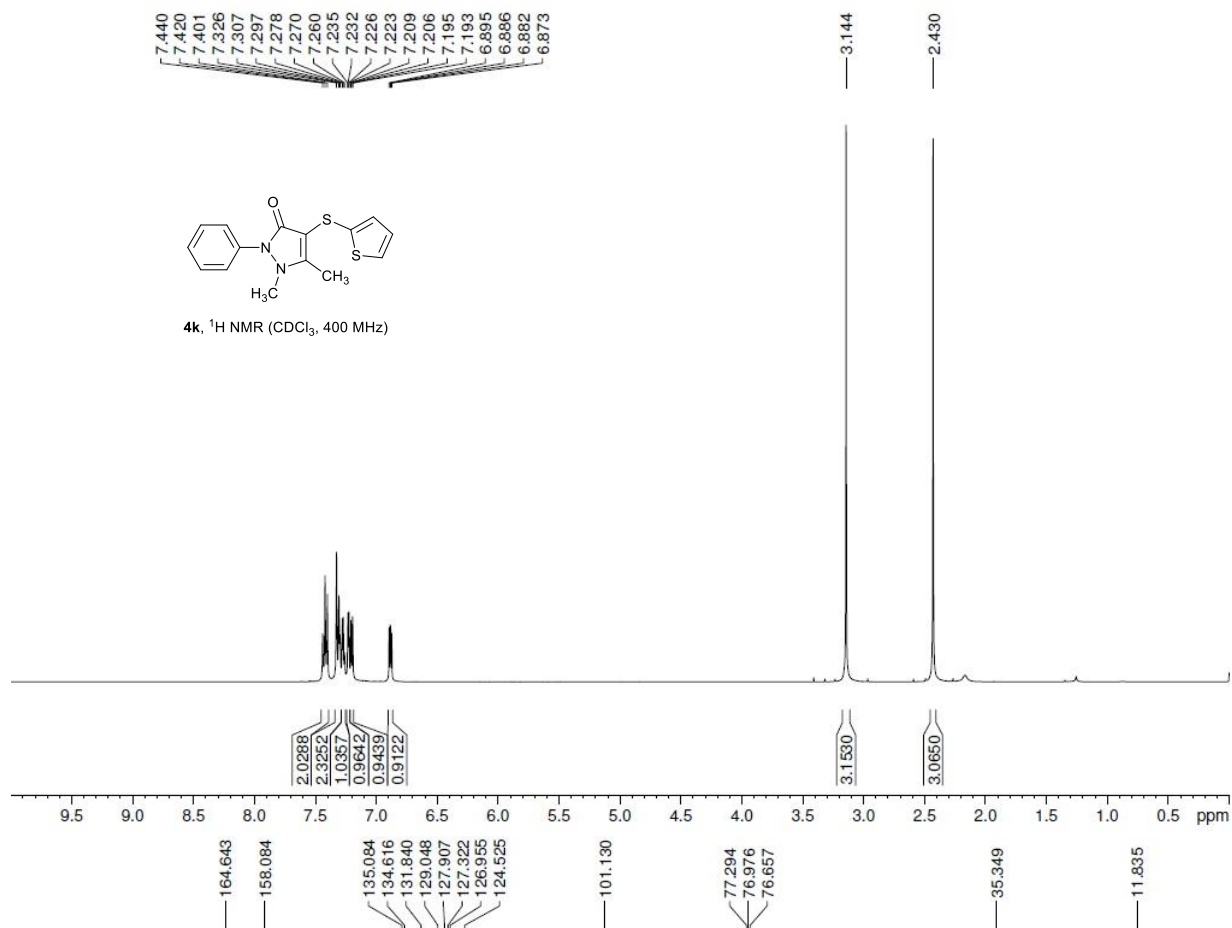
1,5-Dimethyl-2-phenyl-4-((2,4,5-trichlorophenyl)thio)-1,2-dihydro-3H-pyrazol-3-one (4g)



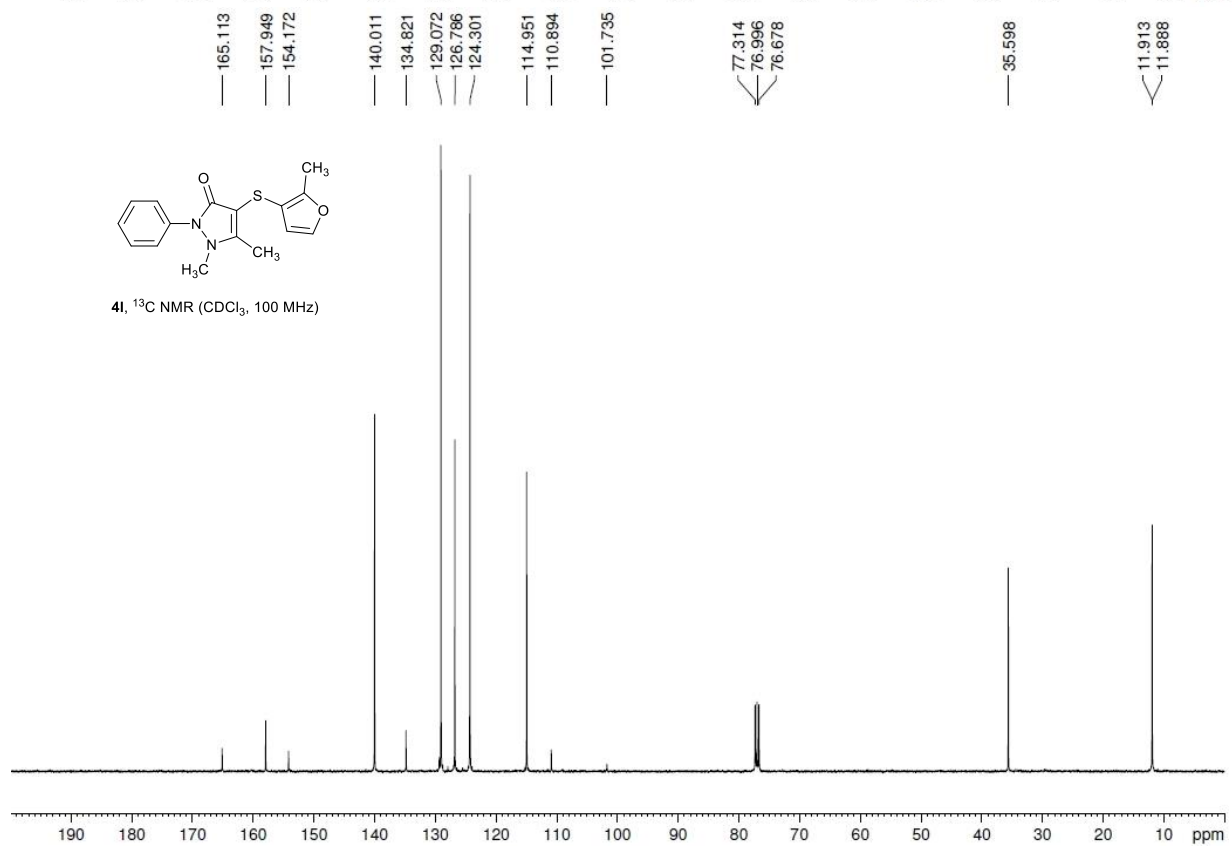
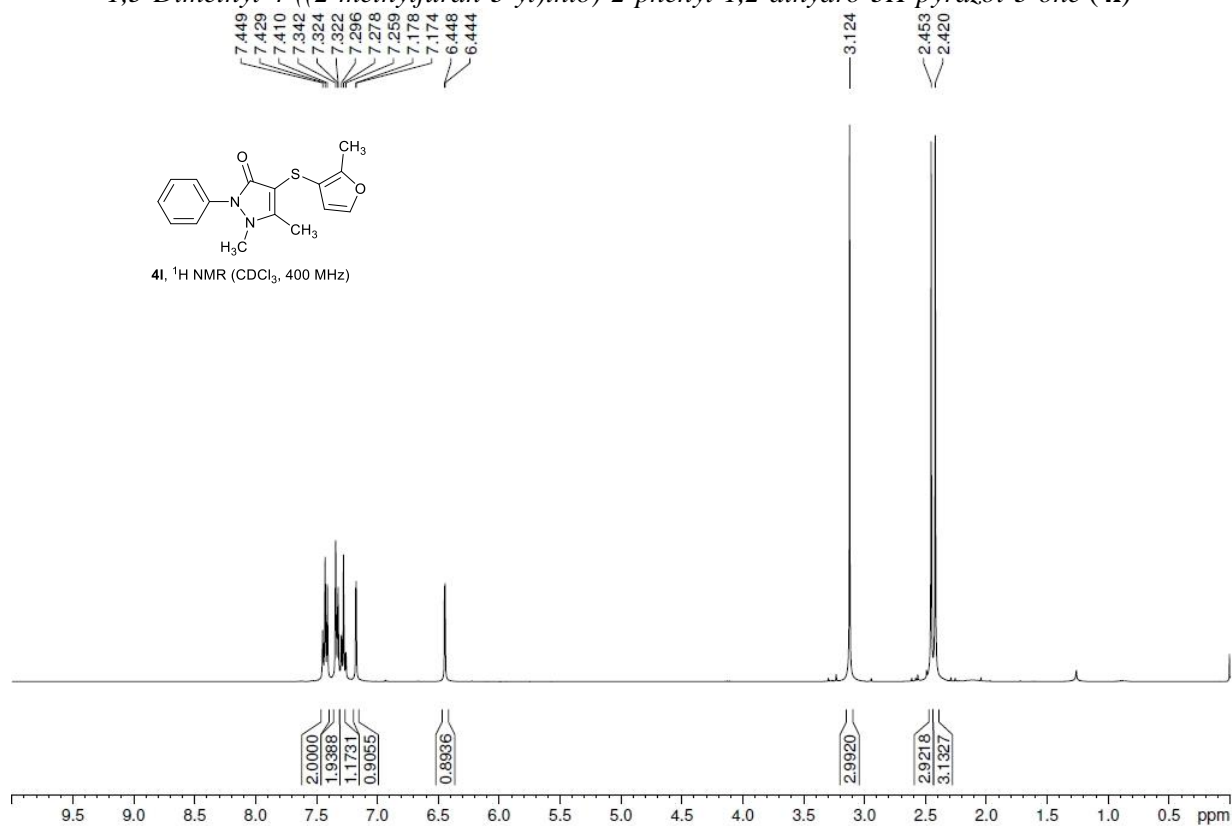
N-(2-((1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)thio)phenyl)benzamide (**4j**)



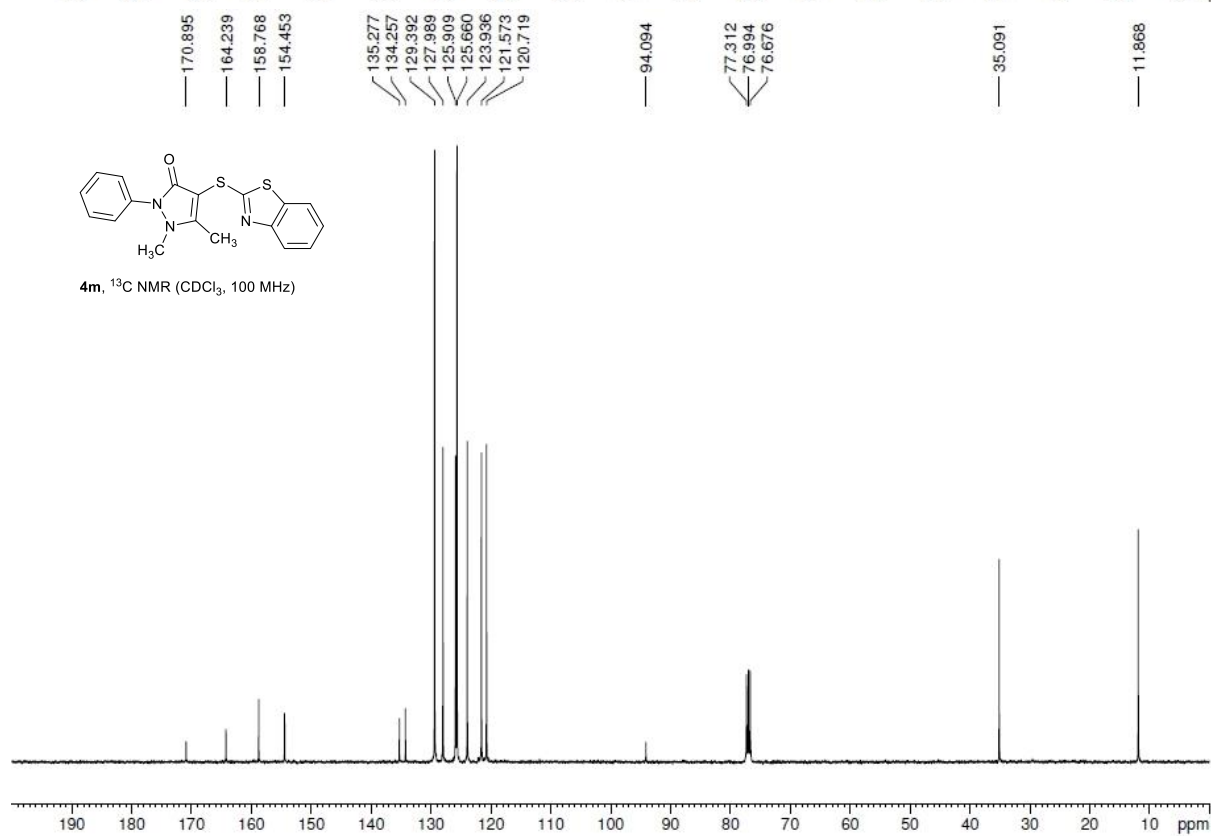
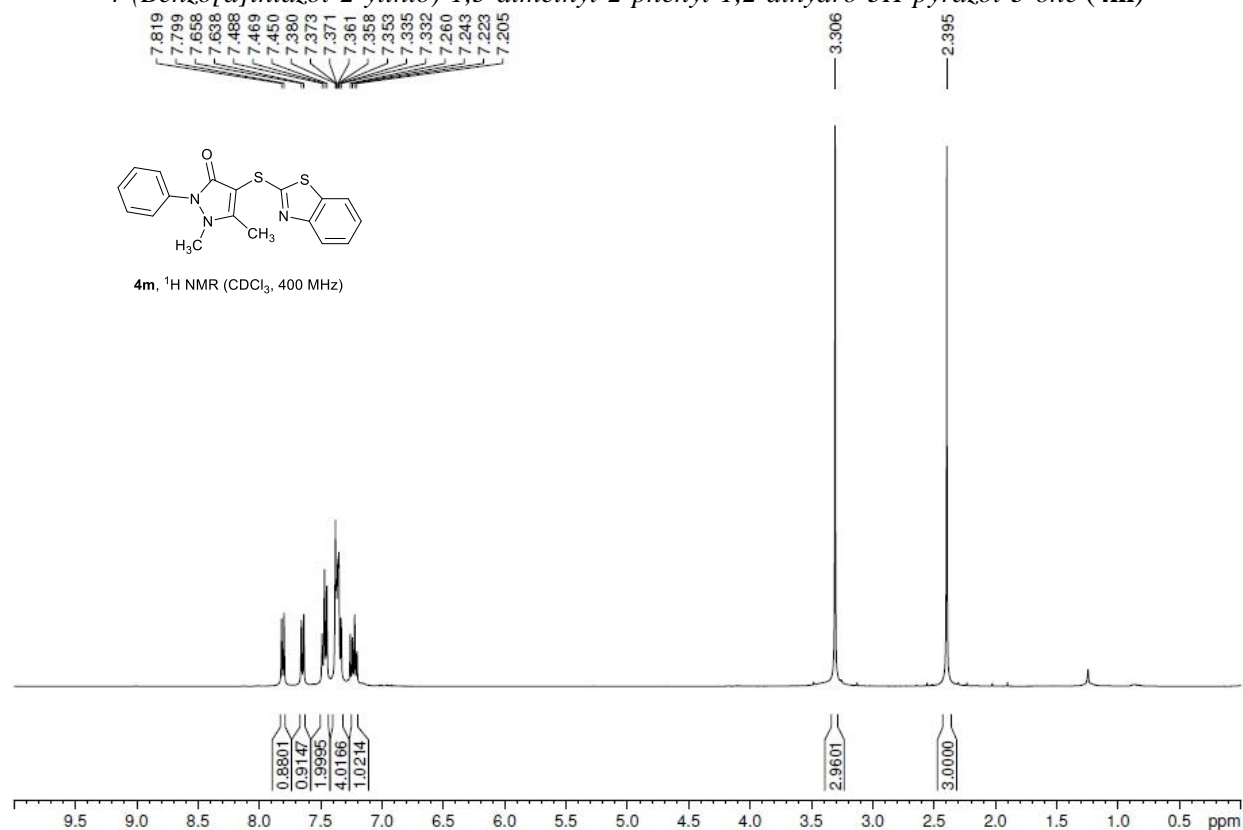
1,5-Dimethyl-2-phenyl-4-(thiophen-2-ylthio)-1,2-dihydro-3H-pyrazol-3-one (4k)



1,5-Dimethyl-4-((2-methylfuran-3-yl)thio)-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (41)



4-(Benzo[d]thiazol-2-ylthio)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (4m)



1,5-Dimethyl-2-phenyl-4-(phenylselanyl)-1,2-dihydro-3H-pyrazol-3-one (4n)

