Supporting Information

NHC-catalyzed regiodivergent syntheses of difunctionalized 3-pyrazolidinone from *α*-bromoenal and monosubstituted hydrazine

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†Electronic Supplementary Information (ESI) available: ^{1}H and ^{13}C NMR spectra.

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‡These authors contributed equally to the work.

1. General methods

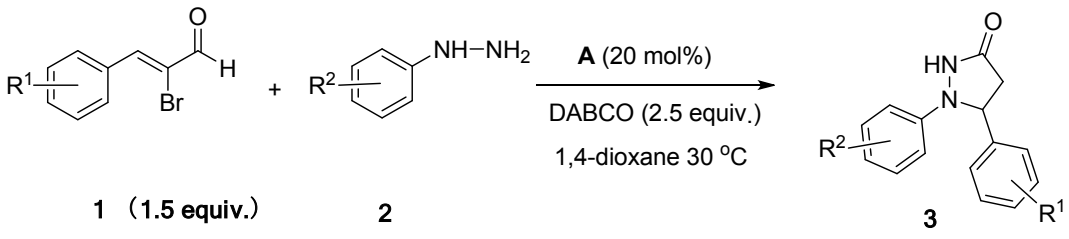
Common reagents and materials were purchased from commercial sources and purified by recrystallization or distillation. Melting points were determined in open capillaries and were uncorrected. IR spectra were taken on a FT-IR-Tensor 27 spectrometer in KBr pellets and reported in cm^{-1}**.** ^{1}H NMR spectra were measured on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ (100 MHz, ^{13}C NMR) with chemical shift (δ) given in ppm relative to TMS as internal standard. High-resolution mass spectra (HRMS) were obtained on a micrOTOF-Q Ⅱ HRMS/MS instrument (Bruker) with the technique of electrospray ionization.

2. Abstract

A formal [3+2] annulation of α-bromoenal with monosubstituted hydrazine could give 1,5 or 2,5-difunctionalized 3-pyrazolidinone regiodivergently by tuning the structure of N-Heterocyclic Carbene (NHC) catalyst. The moderate to high yield, mild reaction condition, good regioselectivity and potential biological significance of the final product made this protocol attractive for the assembly of 3-pyrazolidinone.

3. Experimental section

3.1. General procedure for the preparation of compounds 3a-3k

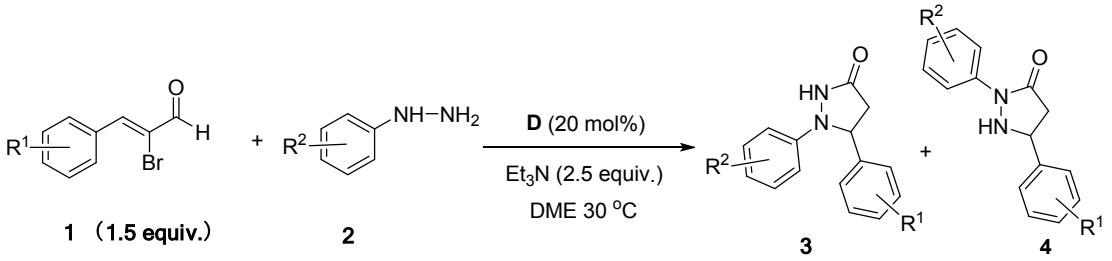


1 （1.5 equiv.） 2 3

An oven-dried 10-mL Schlenk tube equipped with a magnetic stir bar was charged with imidazolium salt **A** (13.6 mg, 0.04 mmol), DABCO (56.4 mg, 0.5

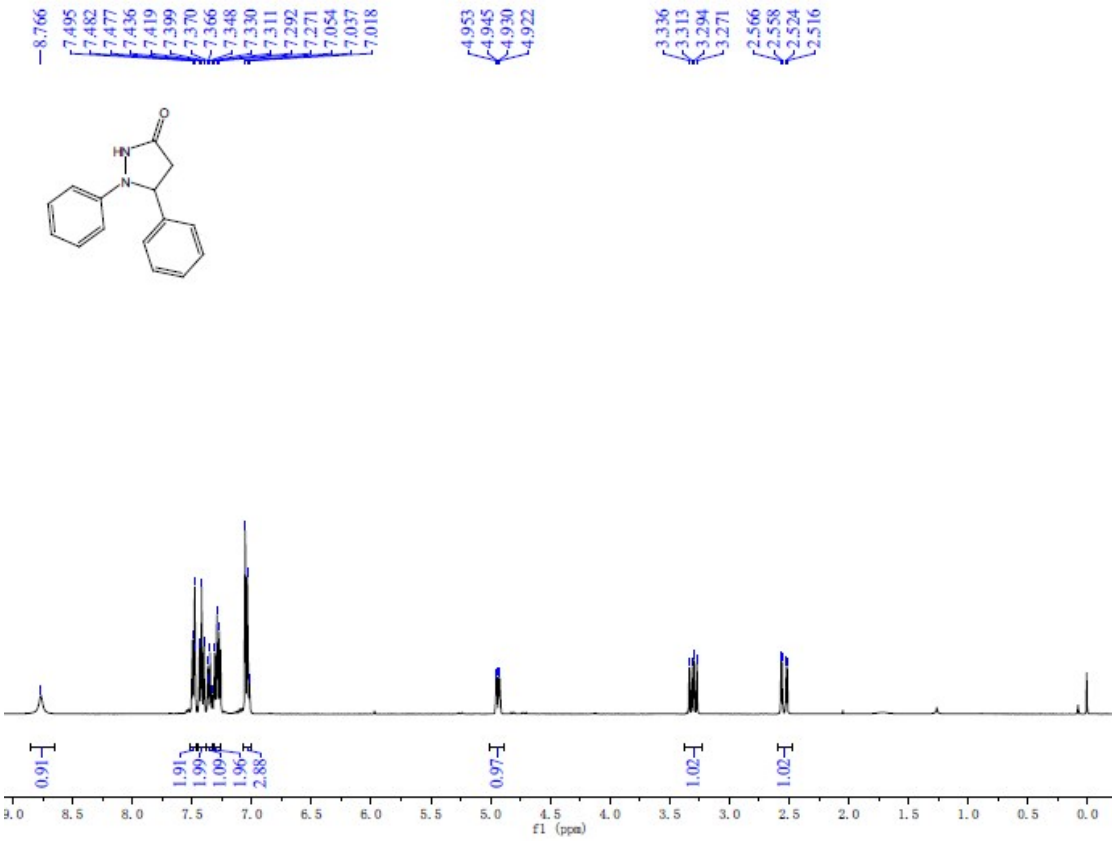
mmol), phenylhydrazine (0.2 mmol) and α-bromoenal (0.3 mmol). To this mixture was added freshly distilled 1,4-dioxane (3 mL). This tube was closed with a septum, removed from the atmosphere and put under positive N_2 pressure. The mixture was stirred at 30 ^oC until completion (monitored by TLC). After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel, mixtures of ethyl acetate/petroleum ether, 1:3, v/v).

3.2. General procedure for the preparation of compounds 4a-4l.

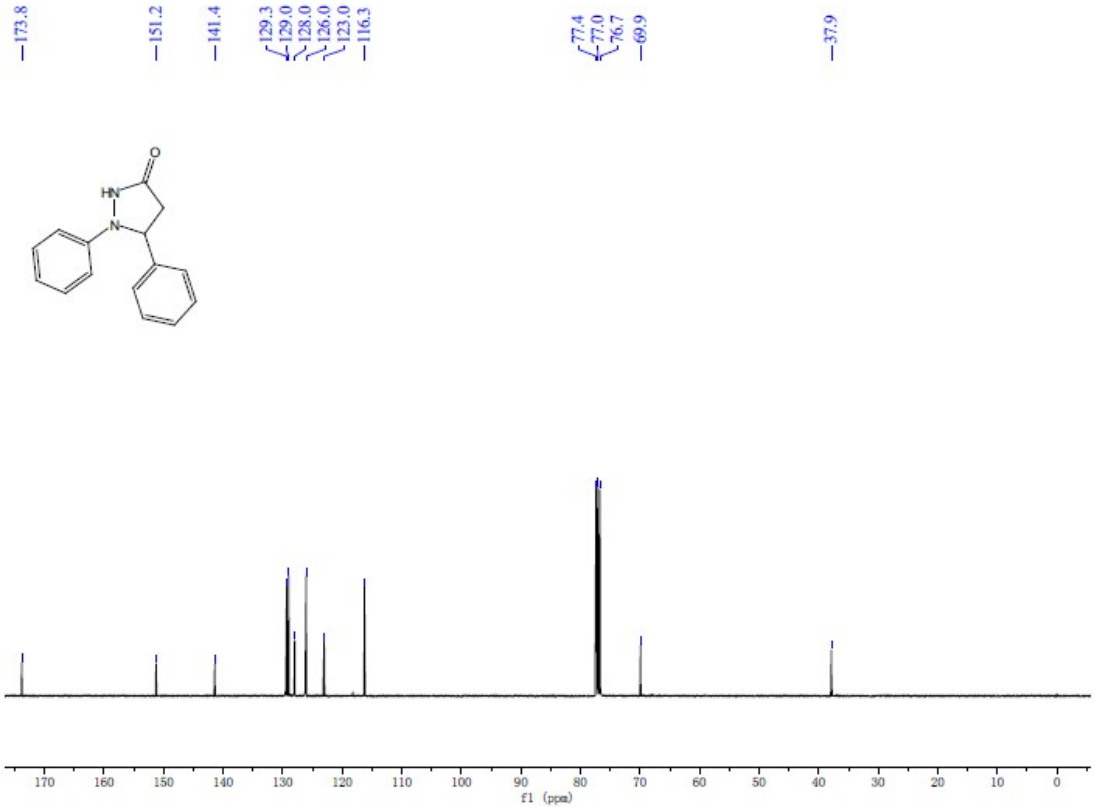


Into an oven-dried 10-mL Schlenk tube were weighed triazolium salt **D** (12.6 mg, 0.04 mmol), Et_3N (50.5 mg, 0.5 mmol), phenylhydrazine (0.2 mmol) and α-bromoenal (0.3 mmol), which equipped with a magnetic stir bar. Freshly distilled DME (3 mL) to this mixture. This tube was closed with a septum, removed from the atmosphere and put under positive N_2 pressure. The mixture was stirred at 30 ^oC until completion (monitored by TLC). After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel, mixtures of ethyl acetate/petroleum ether, 1:4, v/v).

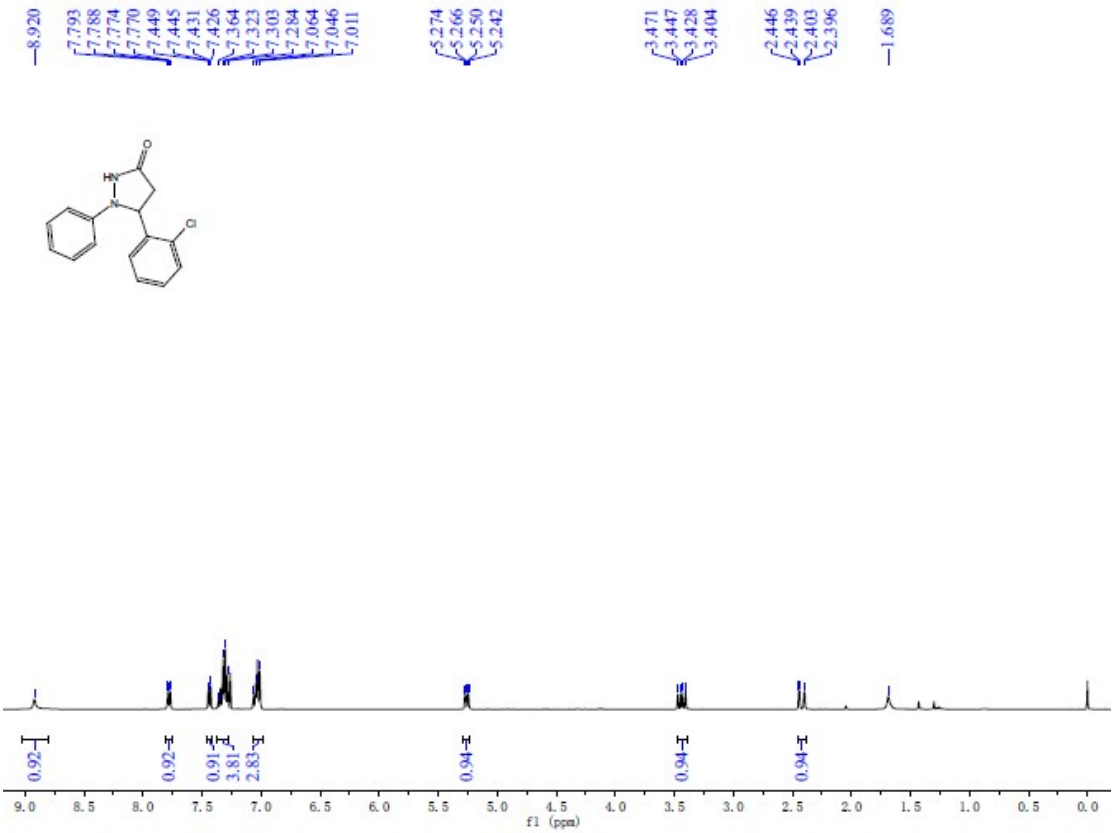
4. NMR Spectra



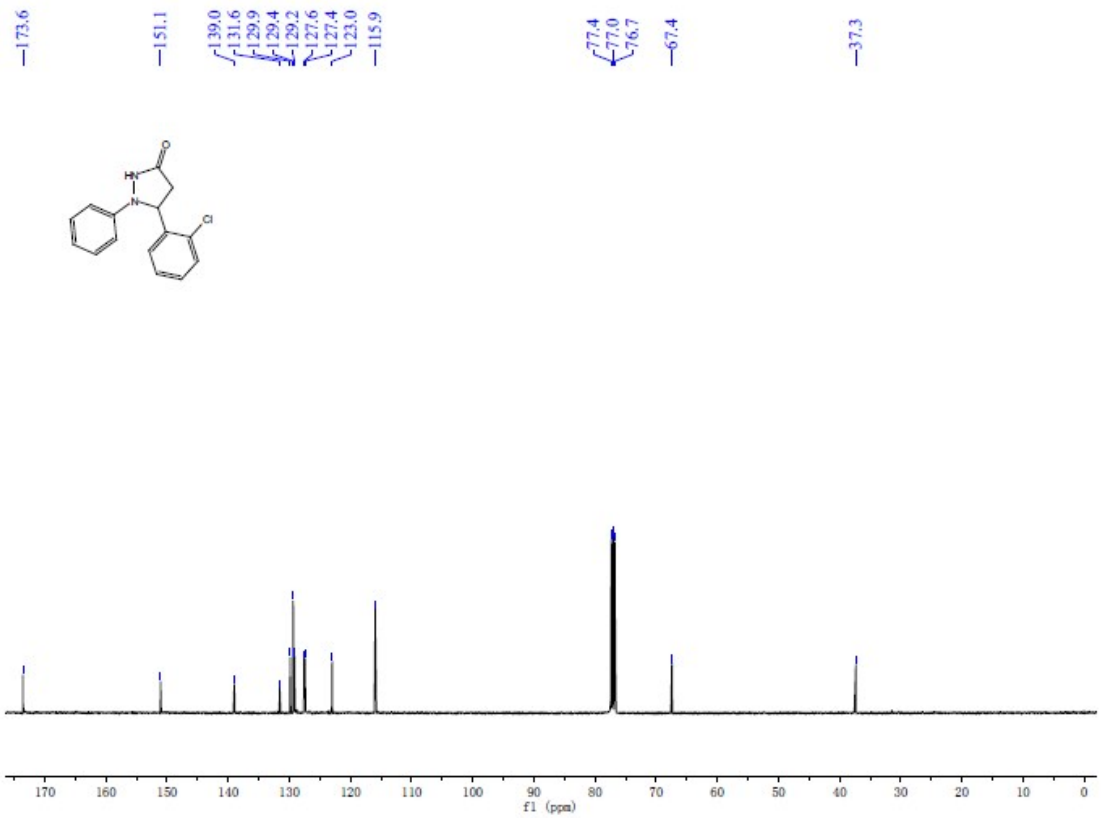
^{1}H NMR Spectrum of Compound (3a)



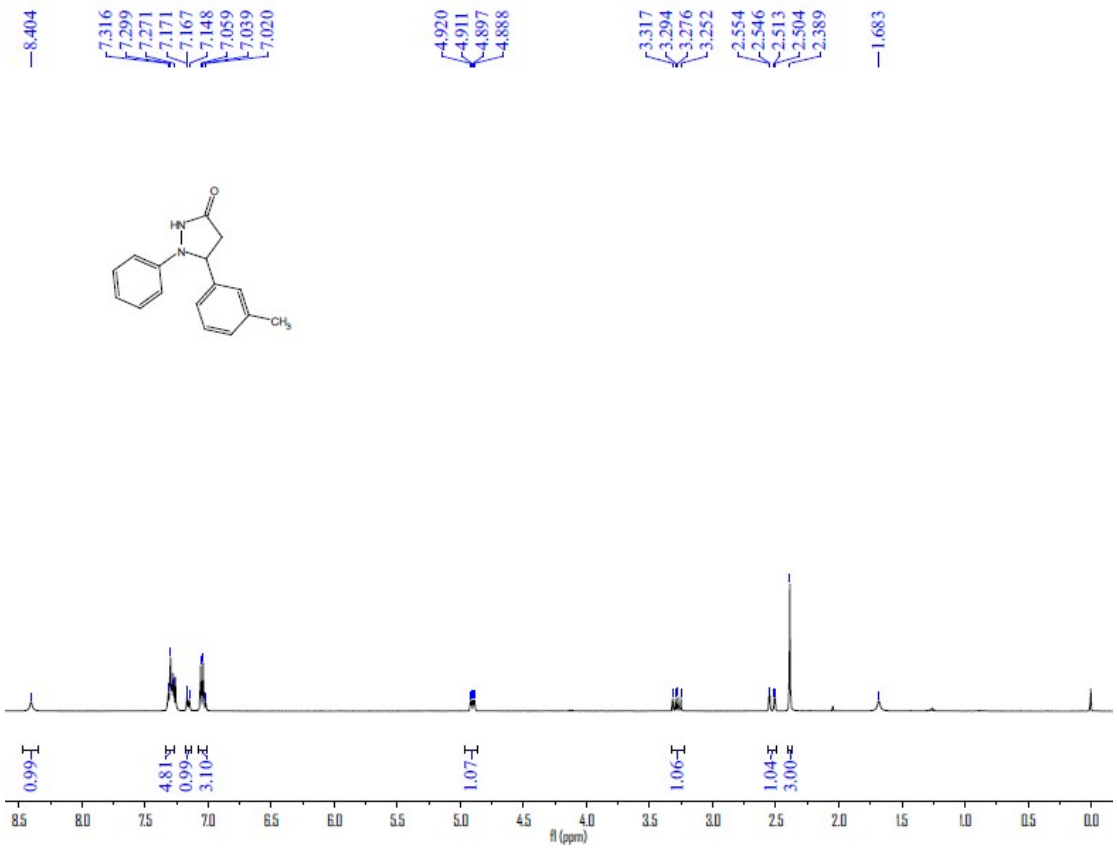
^{13}C NMR Spectrum of Compound (3a)



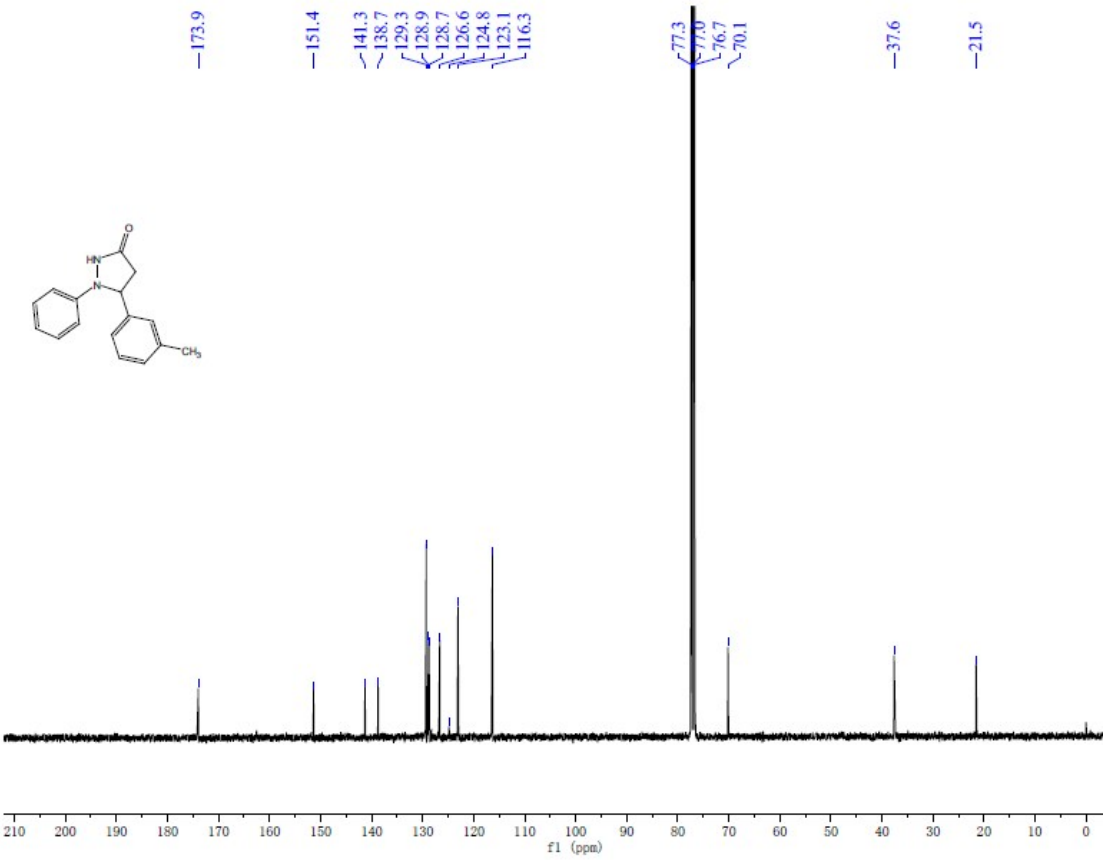
^{1}H NMR Spectrum of Compound (3b)



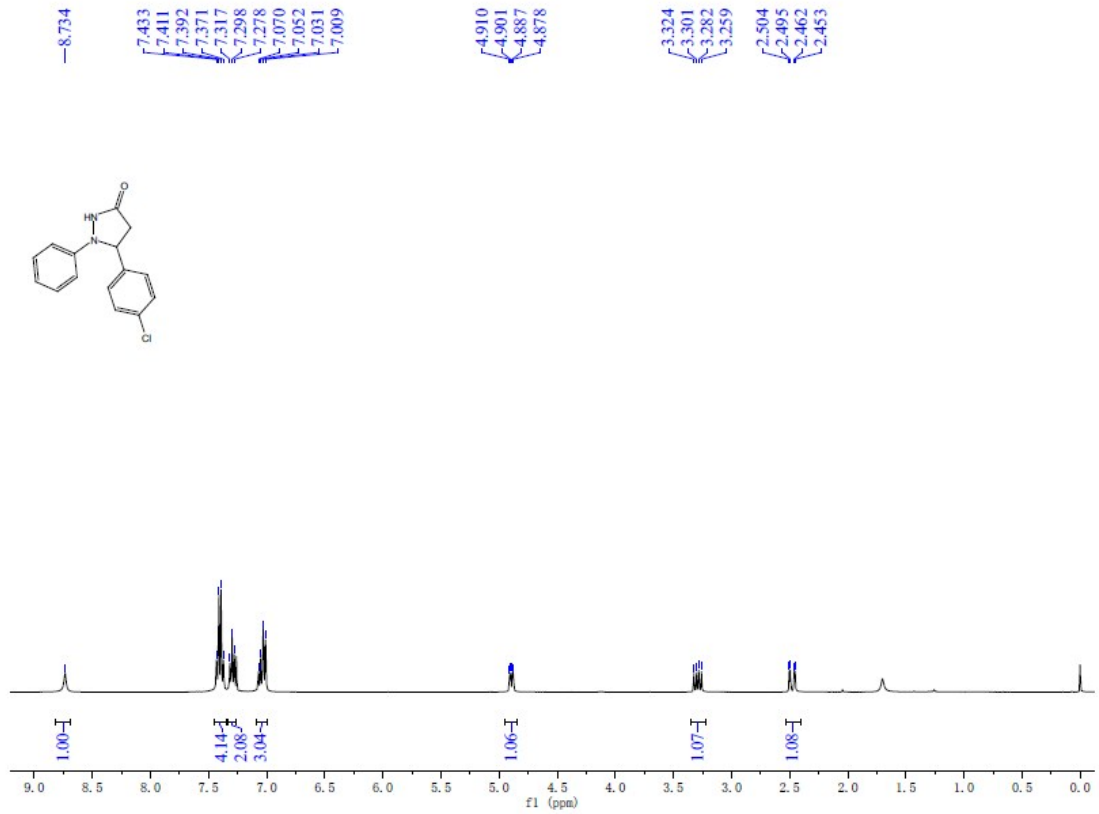
^{13}C NMR Spectrum of Compound (3b)



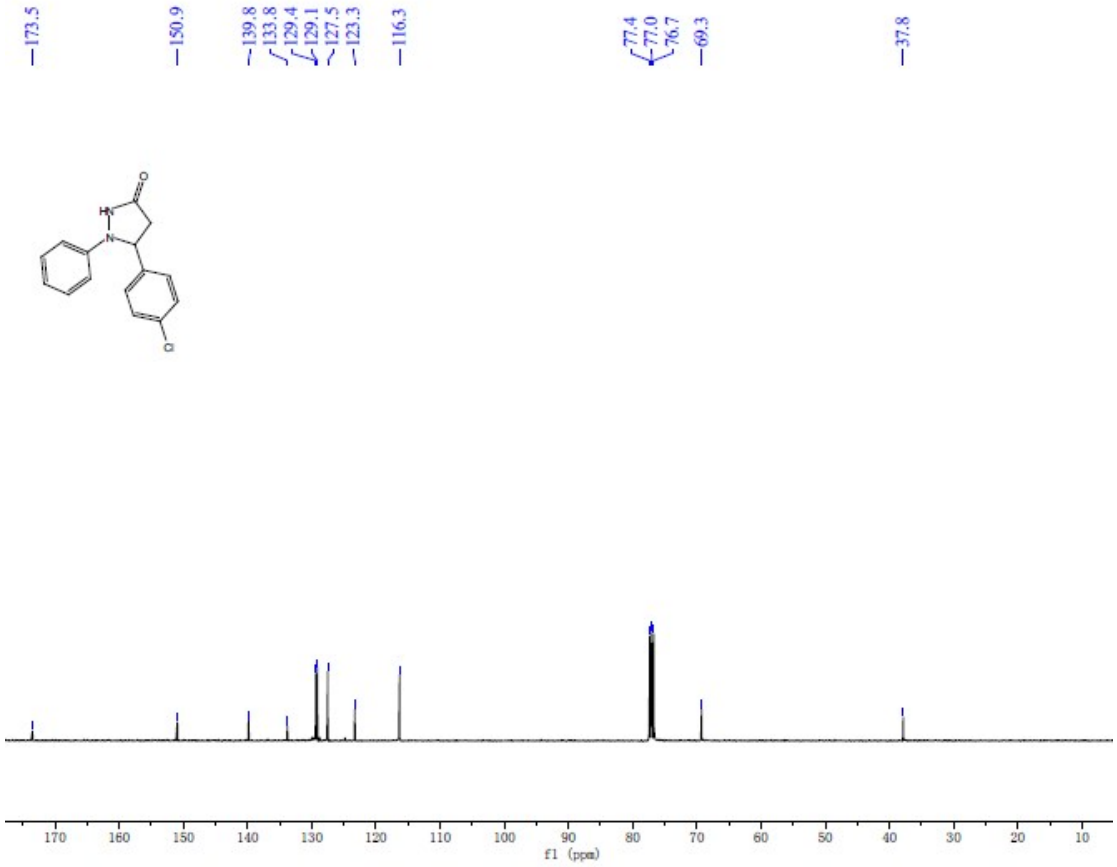
^{1}H NMR Spectrum of Compound (3c)



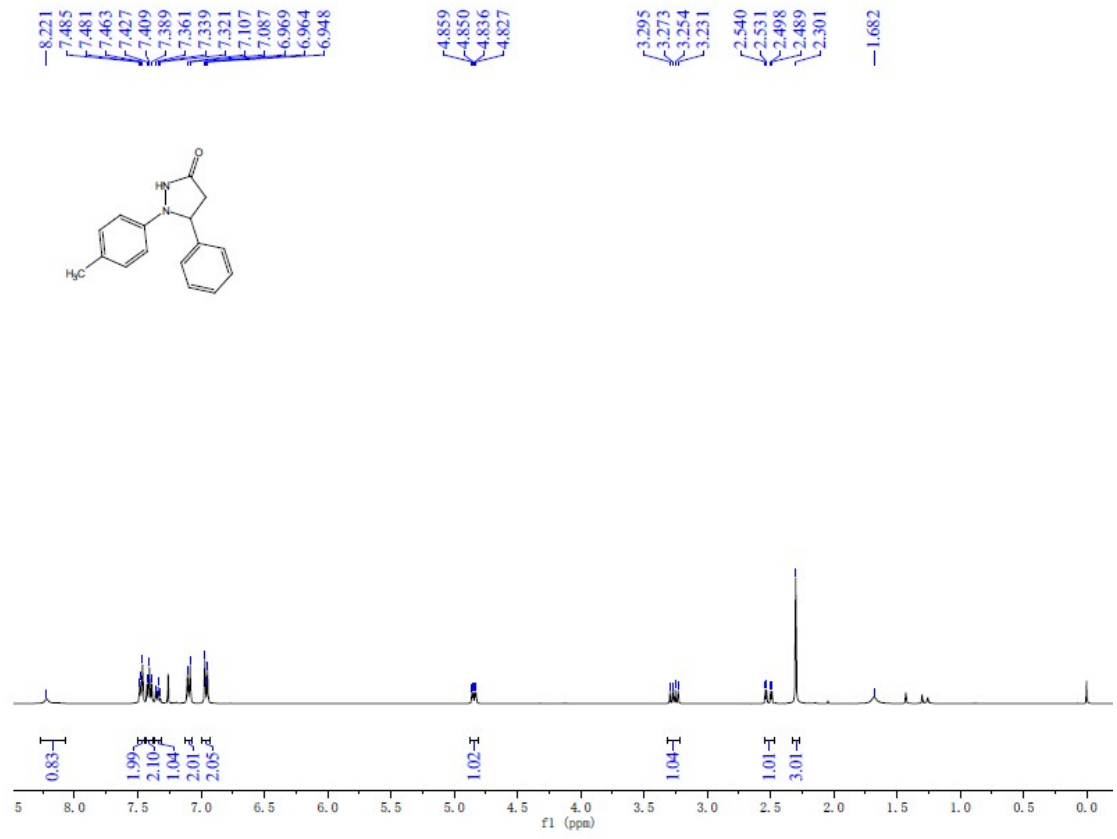
^{13}C NMR Spectrum of Compound (3c)



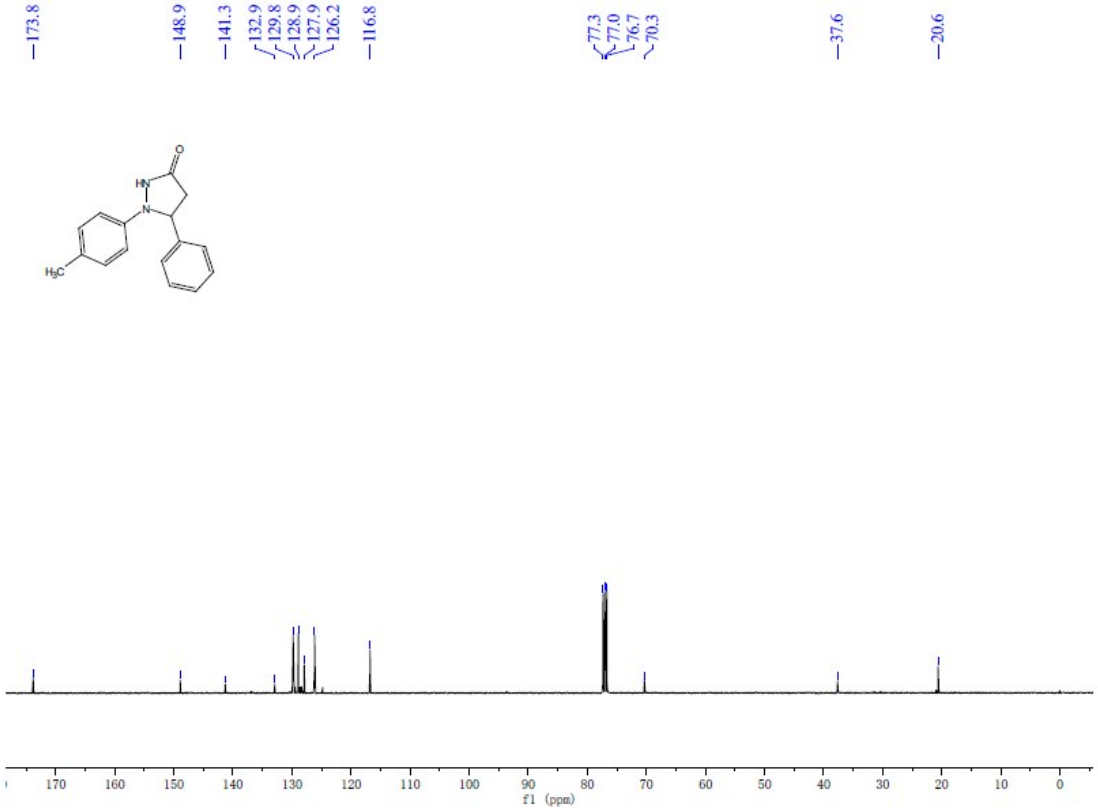
^{1}H NMR Spectrum of Compound (3d)



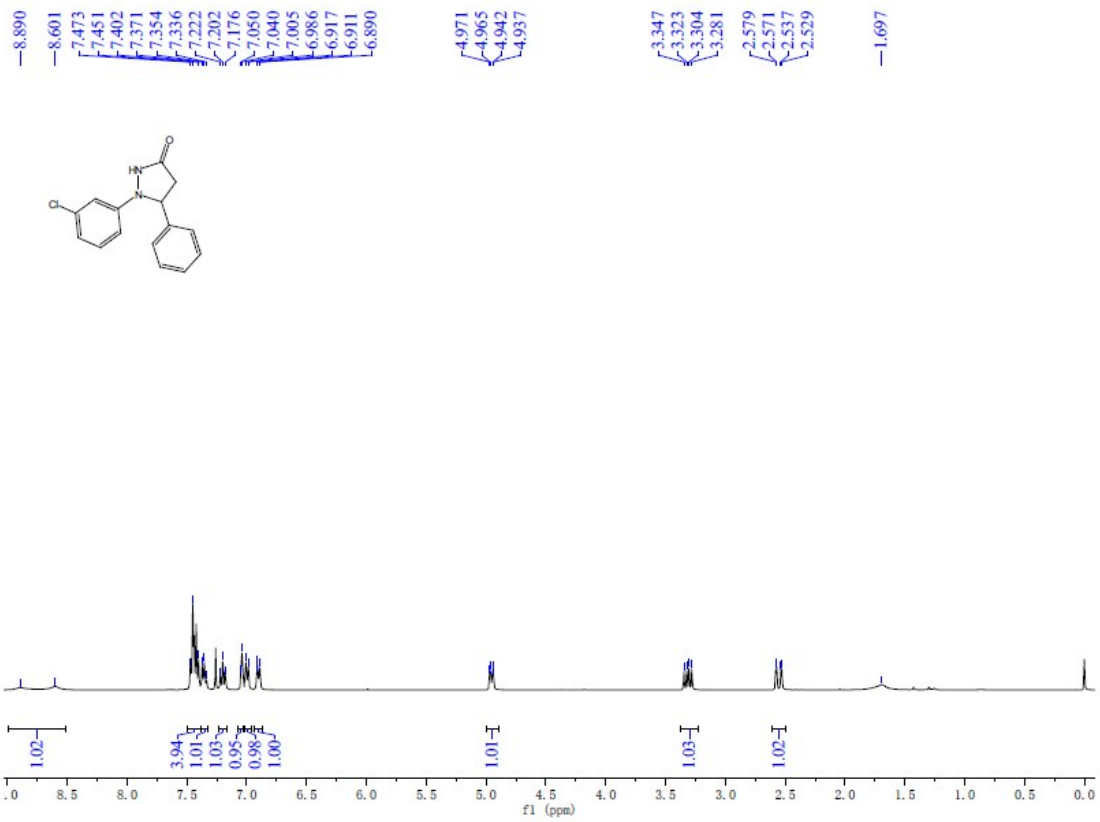
^{13}C NMR Spectrum of Compound (3d)



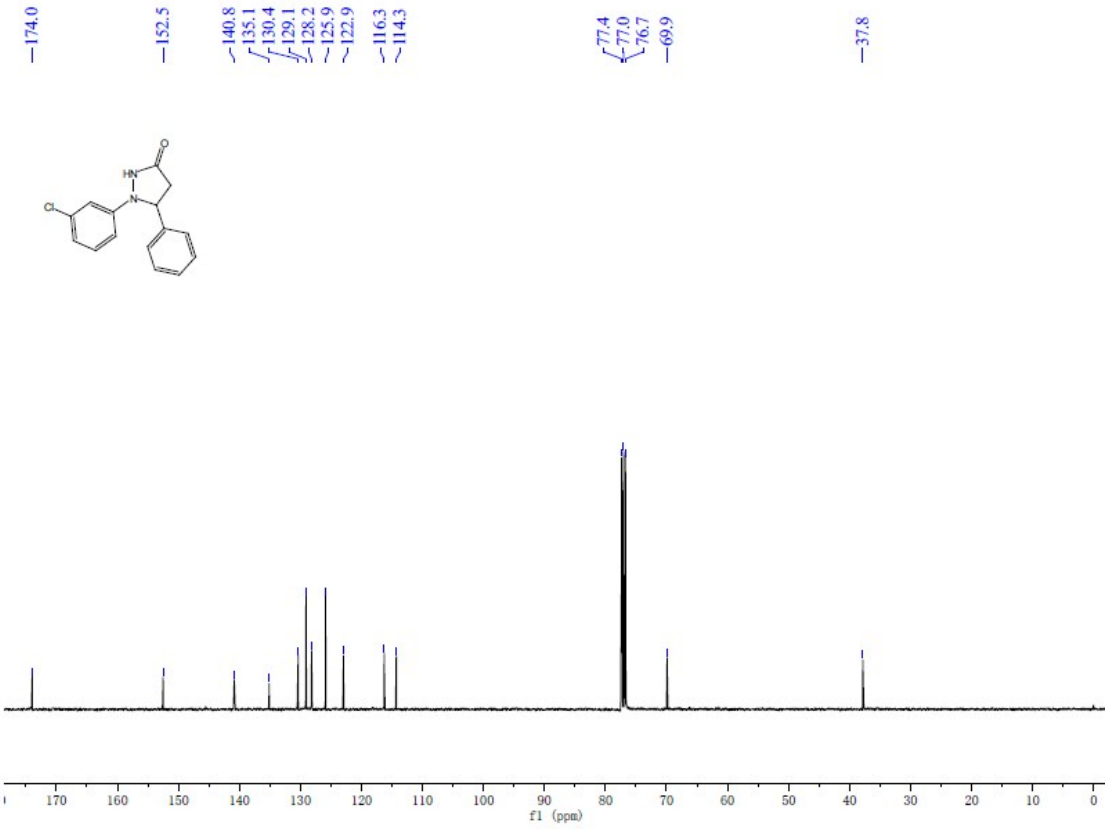
^{1}H NMR Spectrum of Compound (3e)



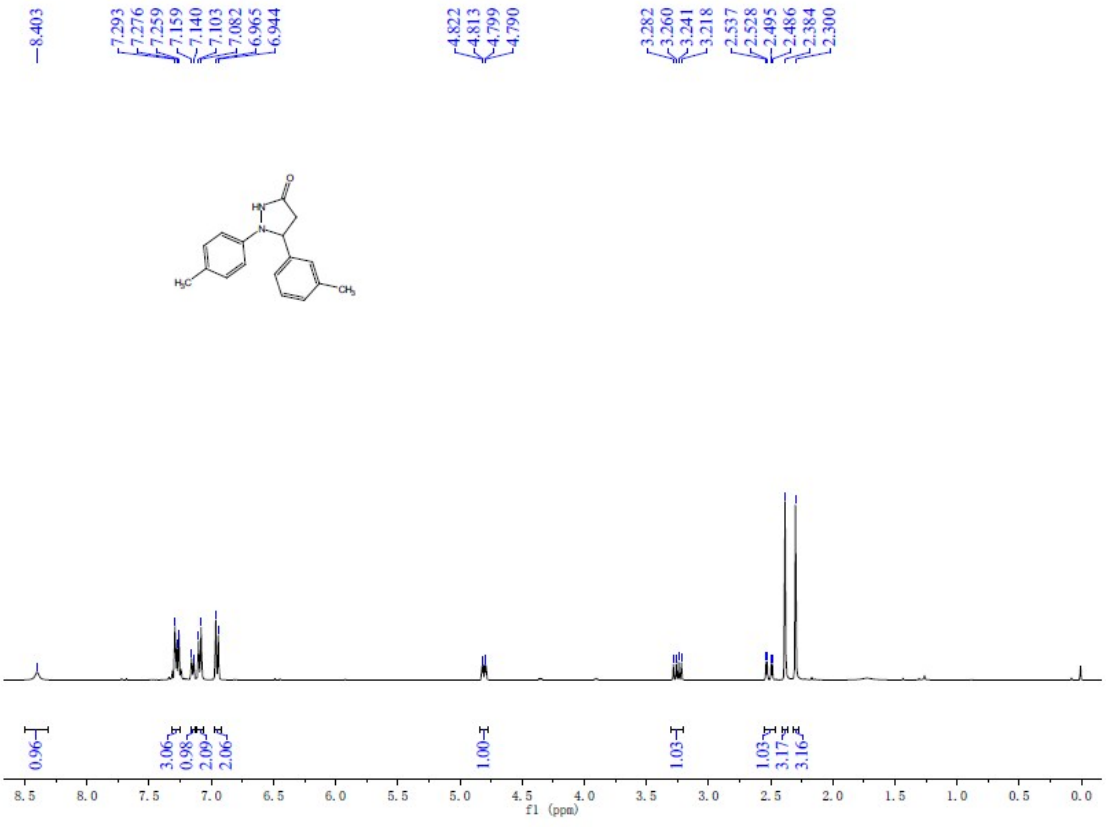
^{13}C NMR Spectrum of Compound (3e)



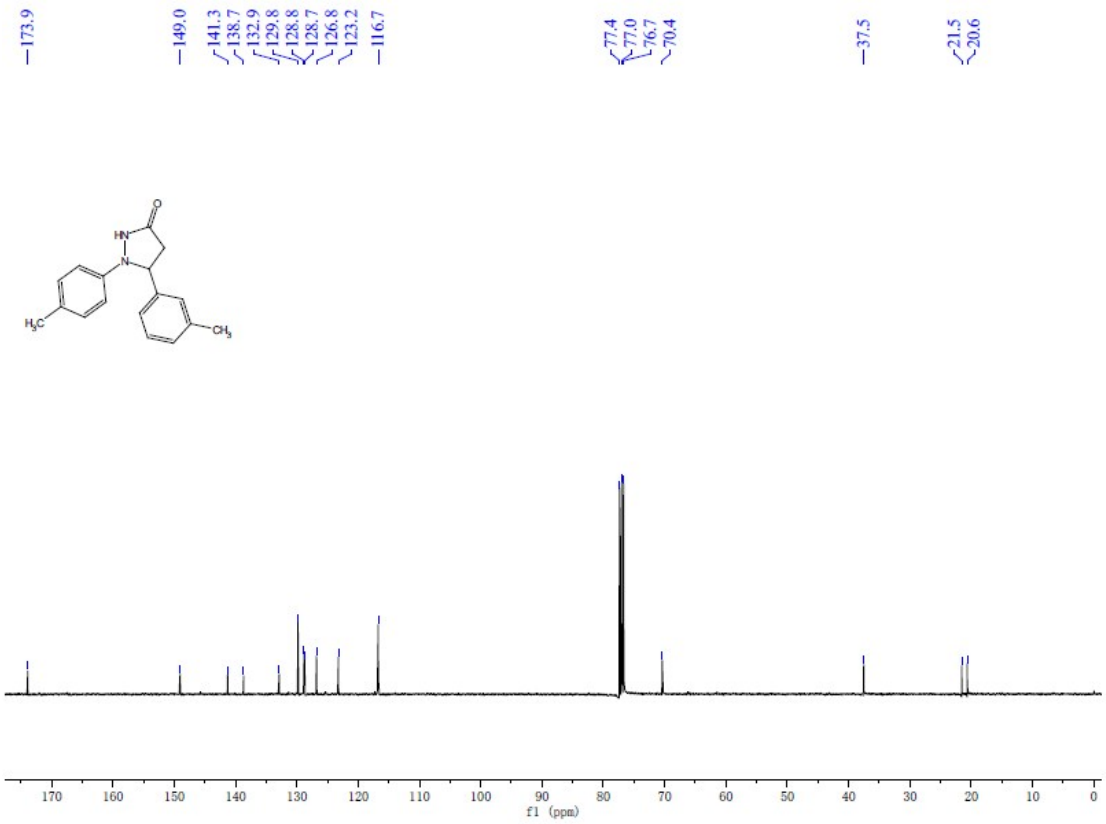
^{1}H NMR Spectrum of Compound (3f)



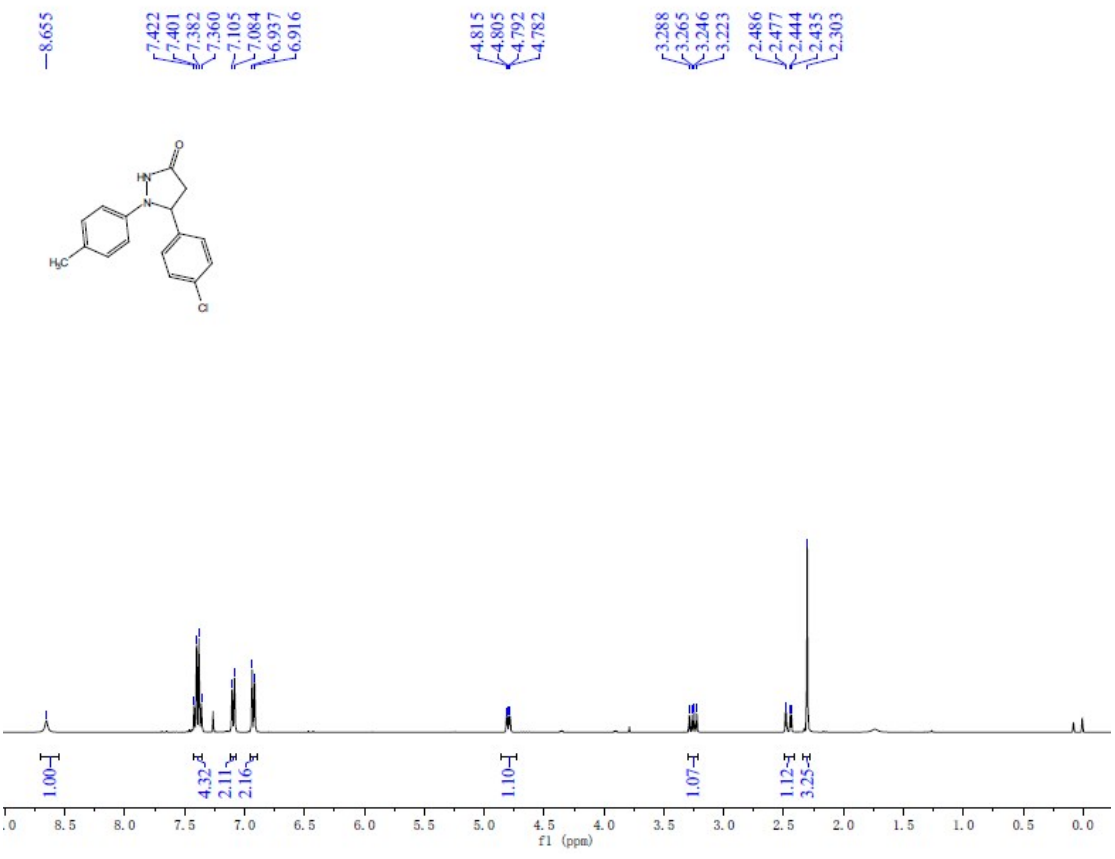
^{13}C NMR Spectrum of Compound (3f)



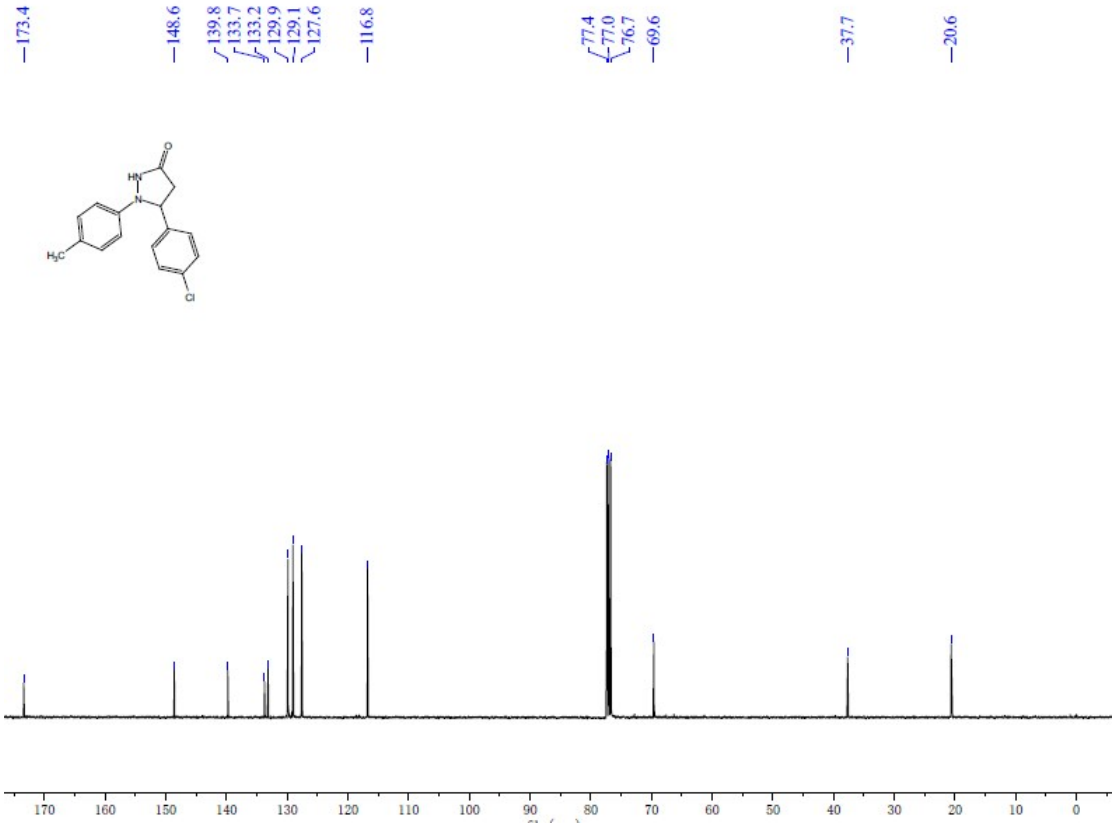
^{1}H NMR Spectrum of Compound (3g)



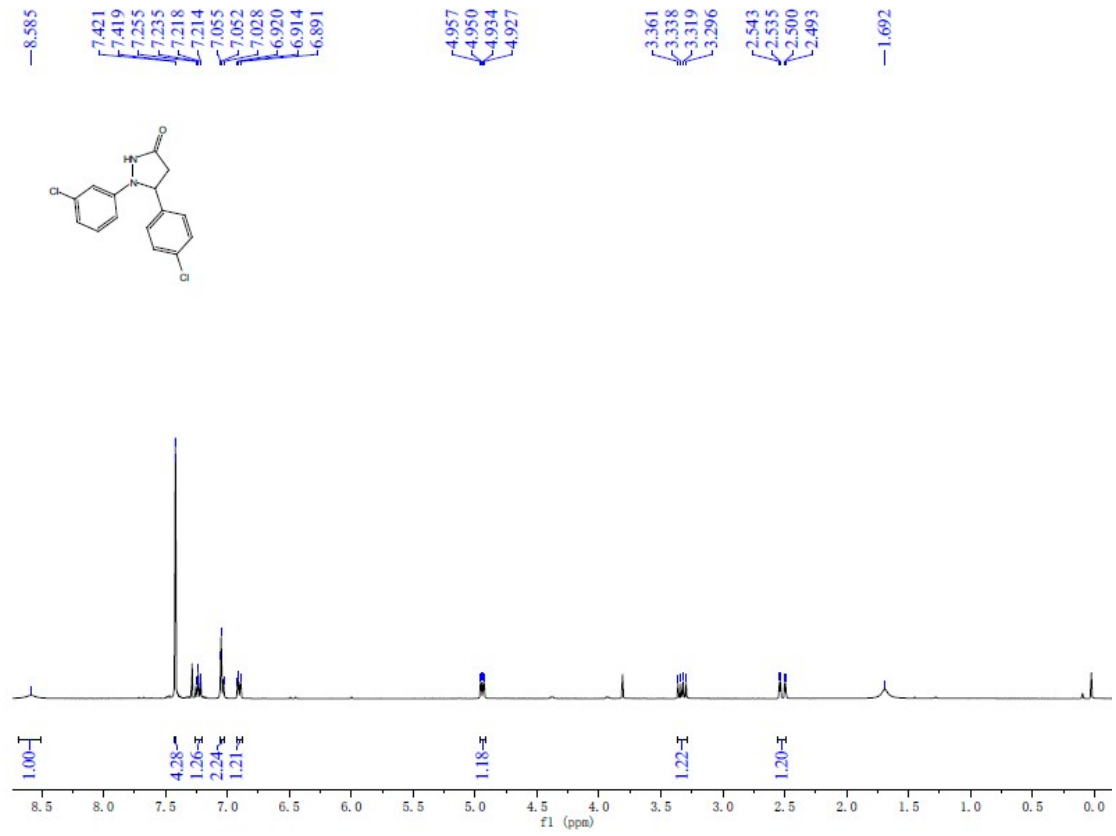
^{13}C NMR Spectrum of Compound (3g)



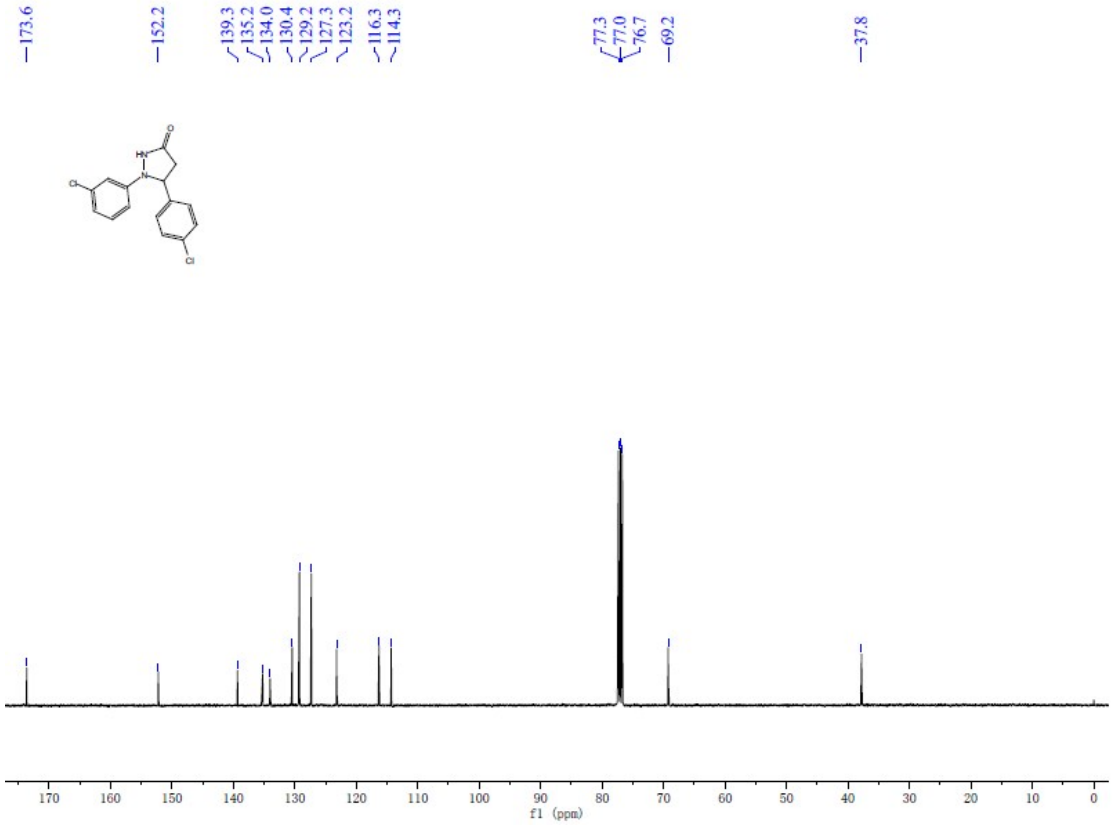
^{1}H NMR Spectrum of Compound (3h)



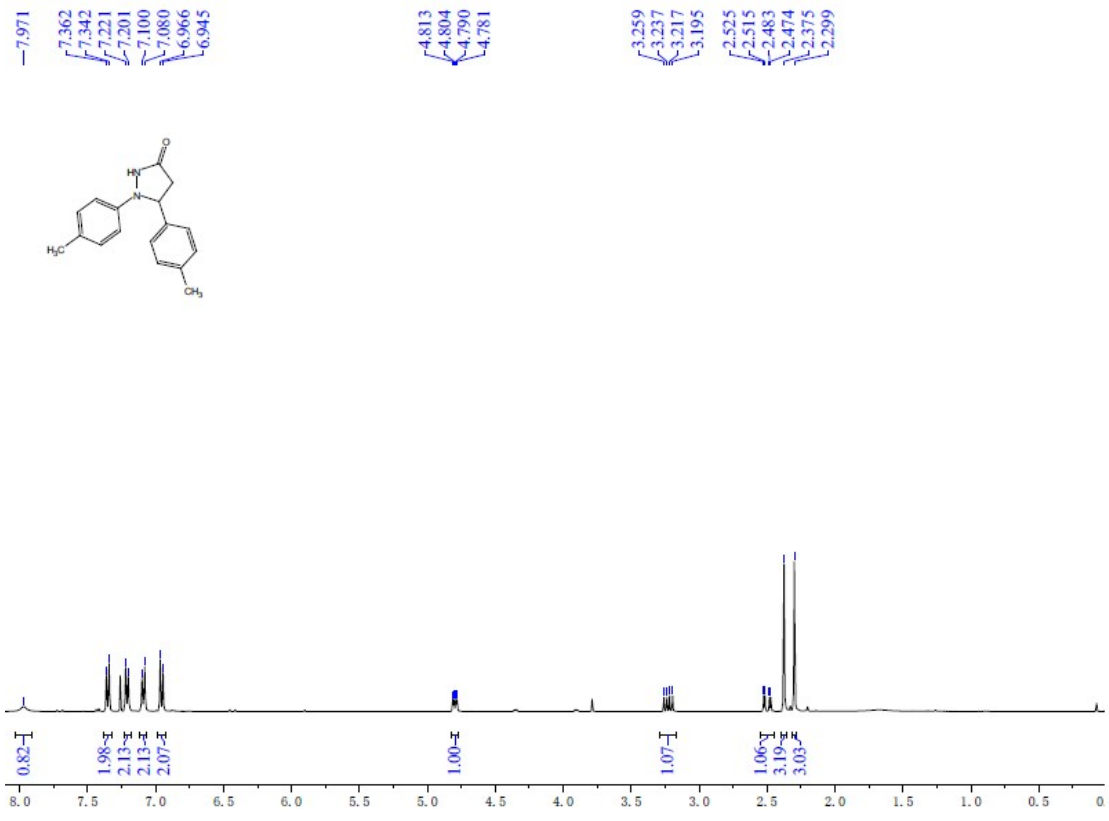
^{13}C NMR Spectrum of Compound (3h)



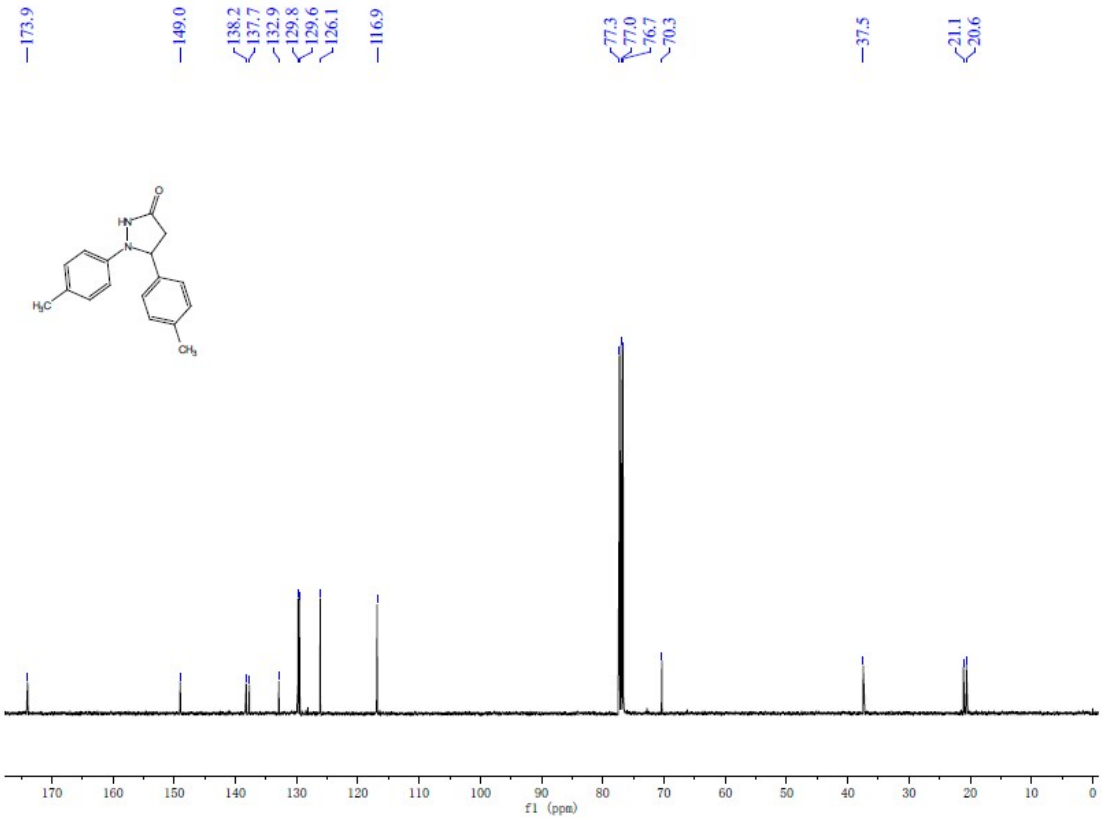
^{1}H NMR Spectrum of Compound (3i)



^{13}C NMR Spectrum of Compound (3i)



^{1}H NMR Spectrum of Compound (3j)



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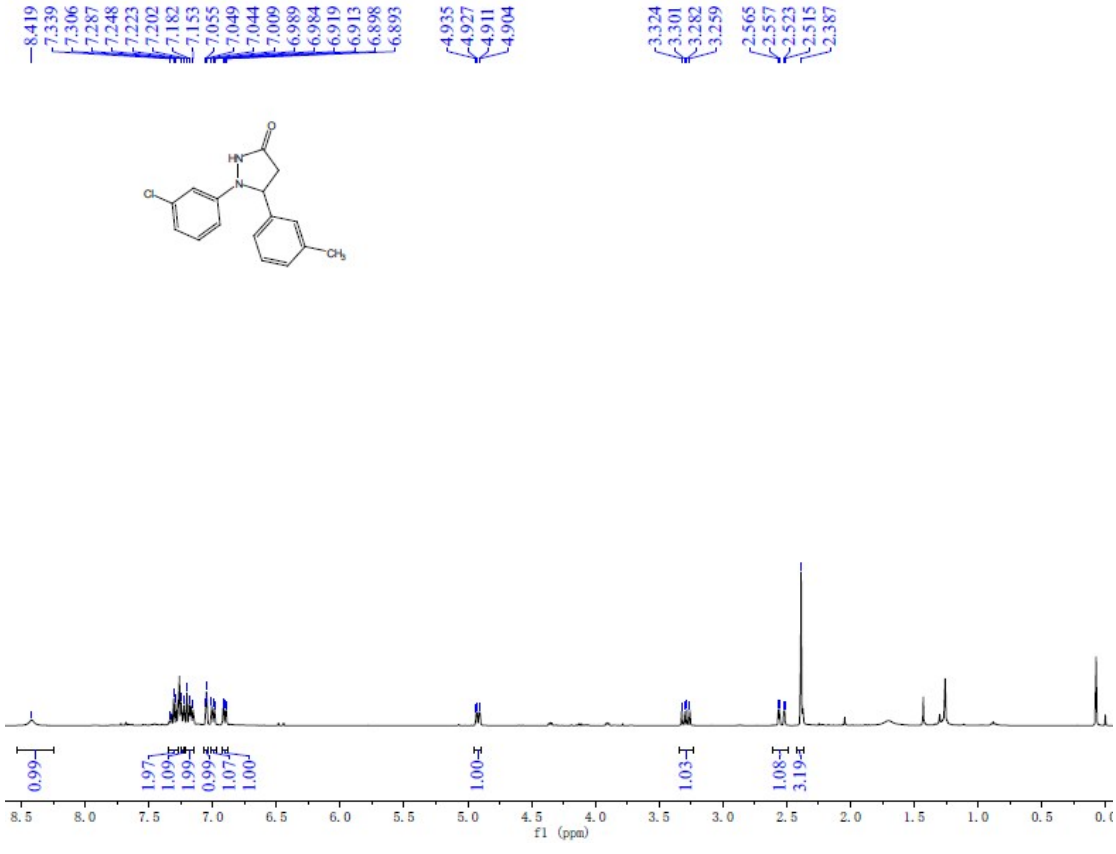
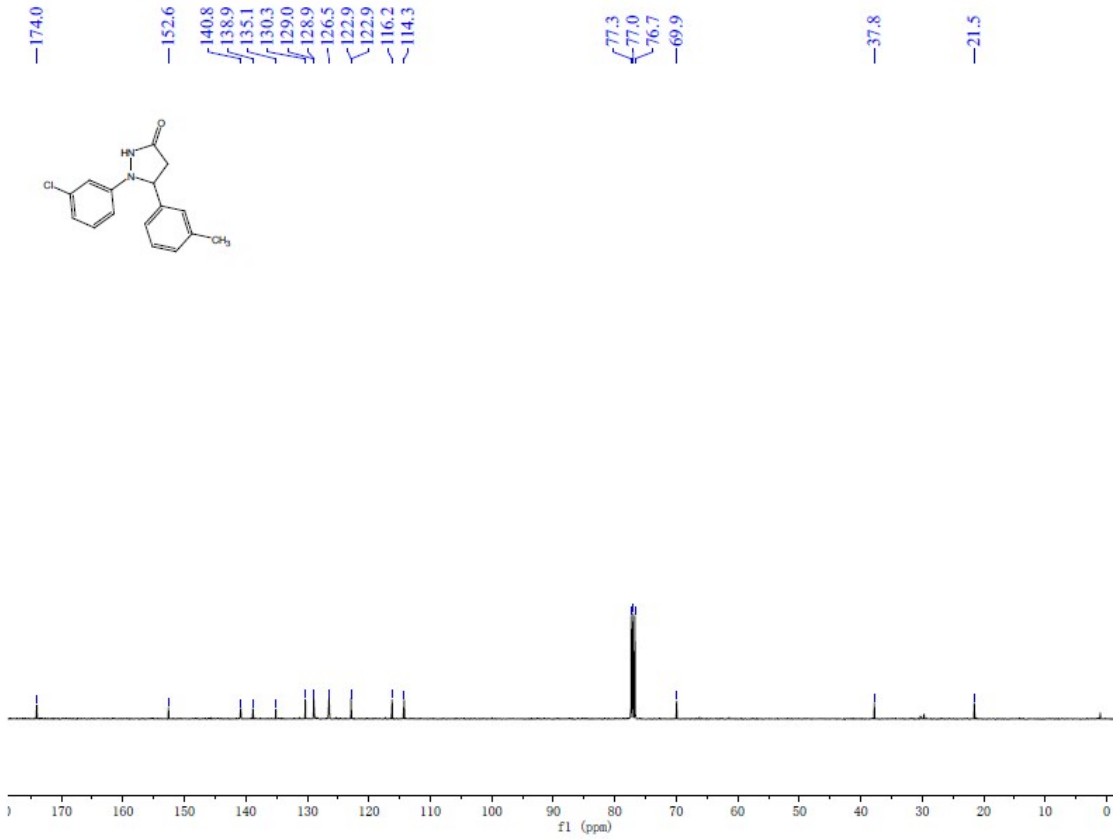
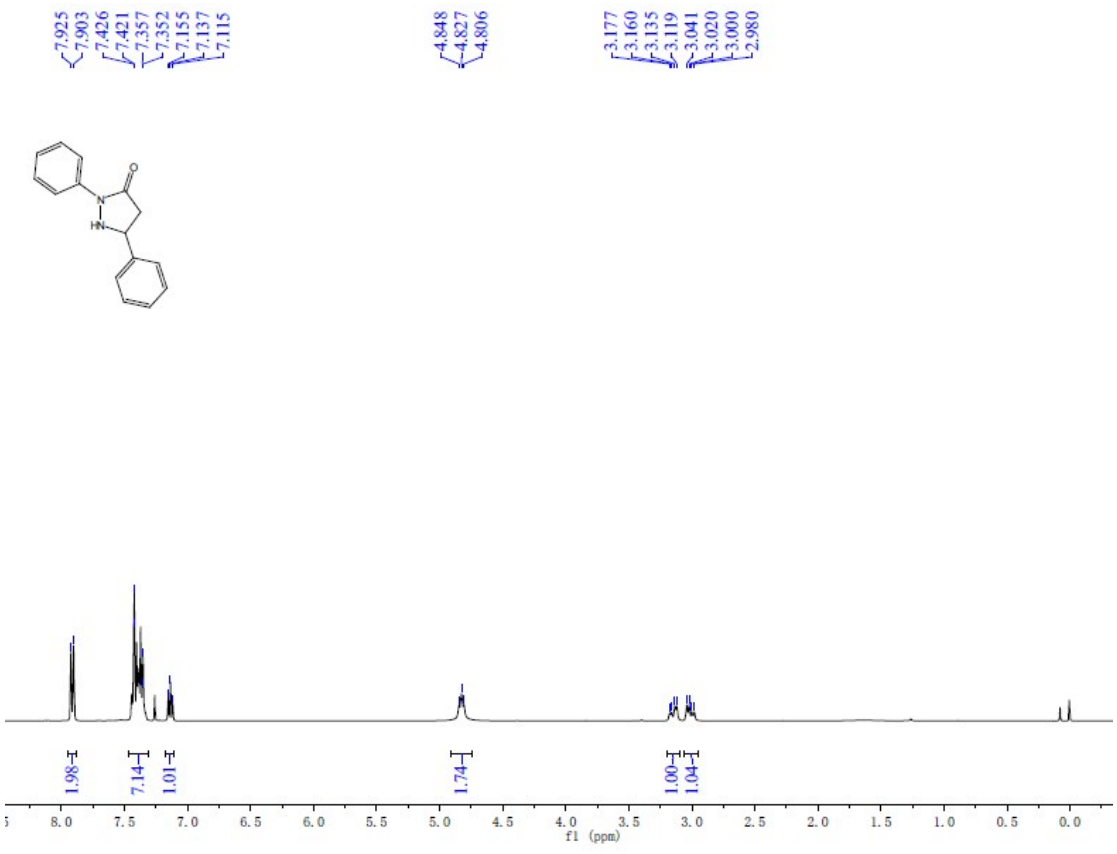


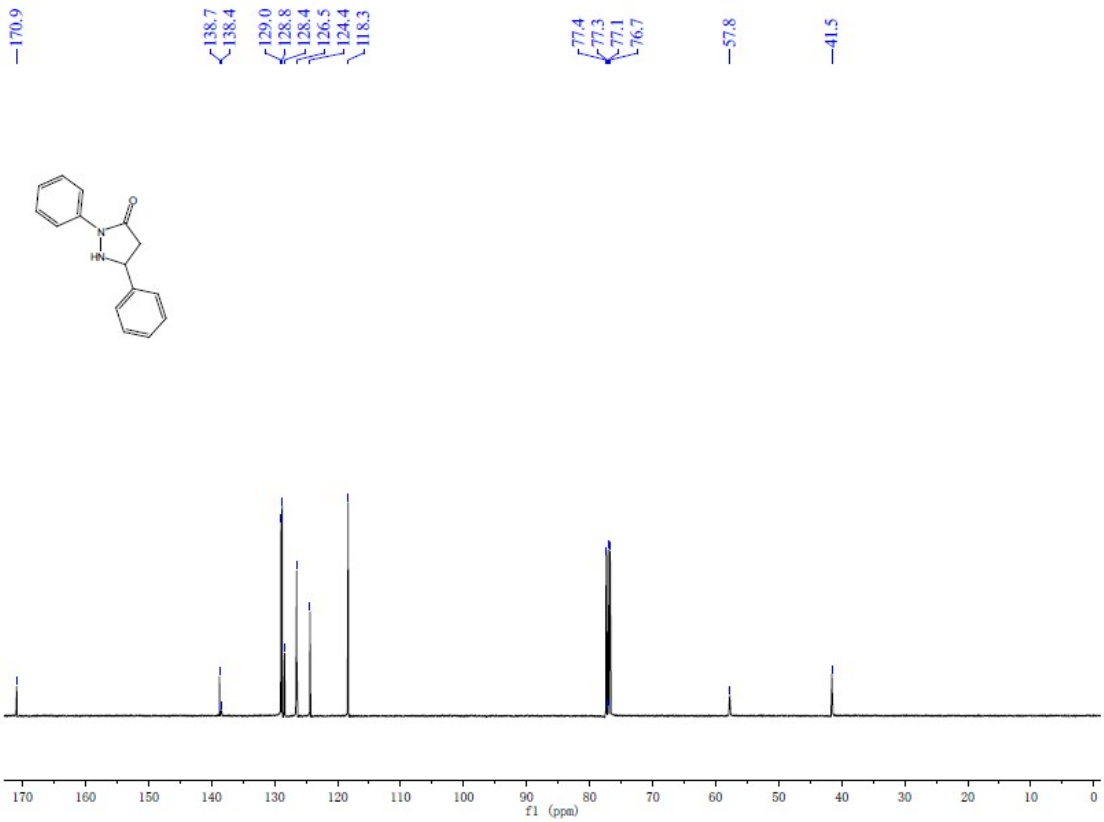
^{1}H NMR Spectrum of Compound (3k)



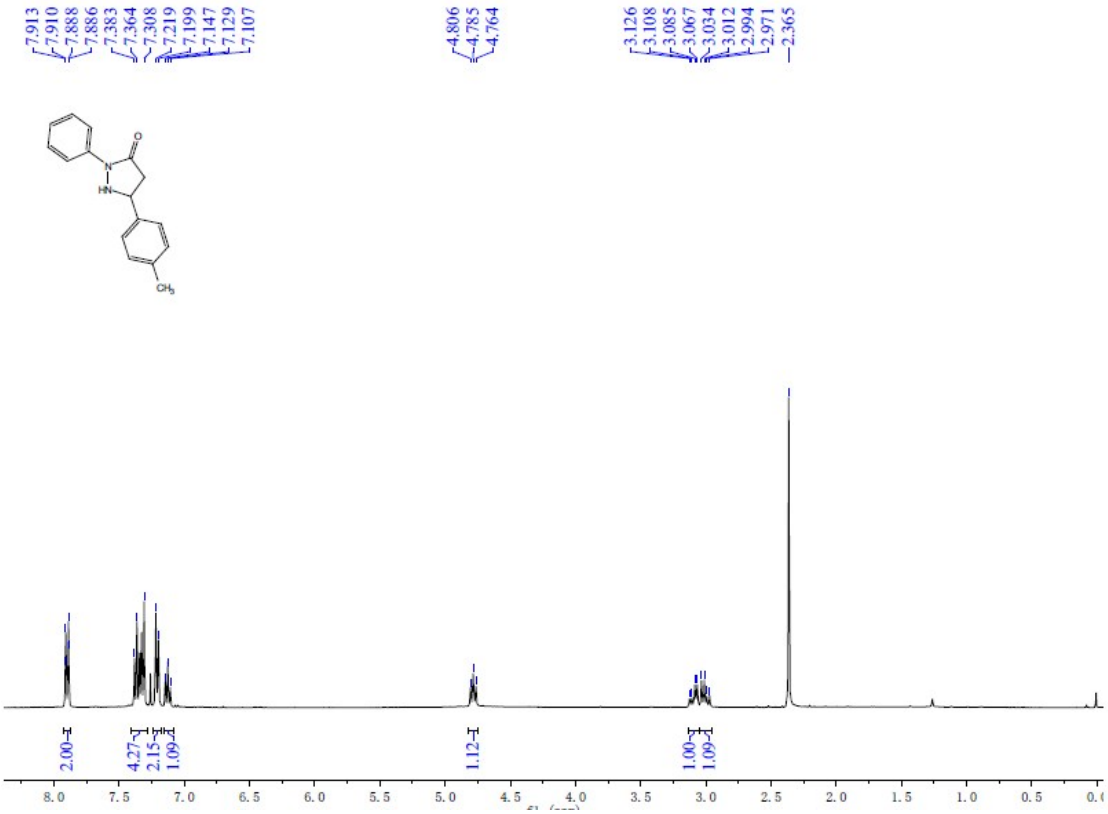
^{13}C NMR Spectrum of Compound (3k)



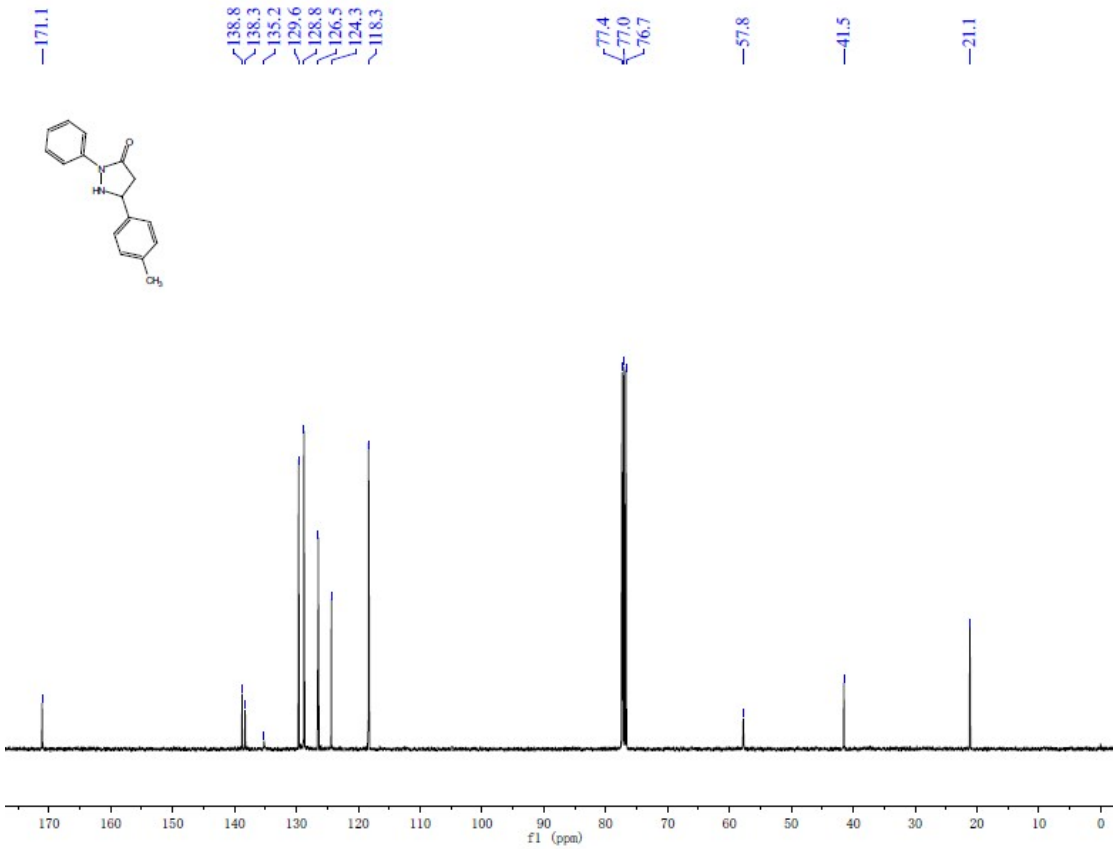
^{1}H NMR Spectrum of Compound (4a)



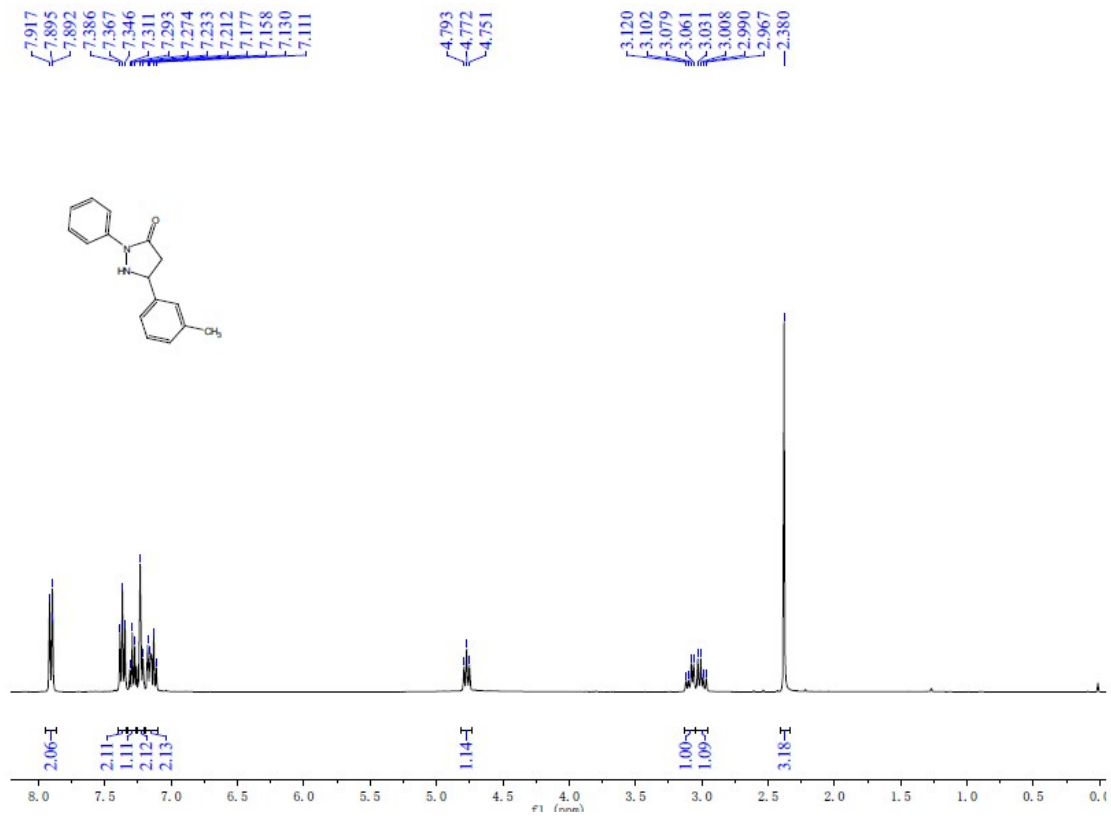
^{13}C NMR Spectrum of Compound (4a)



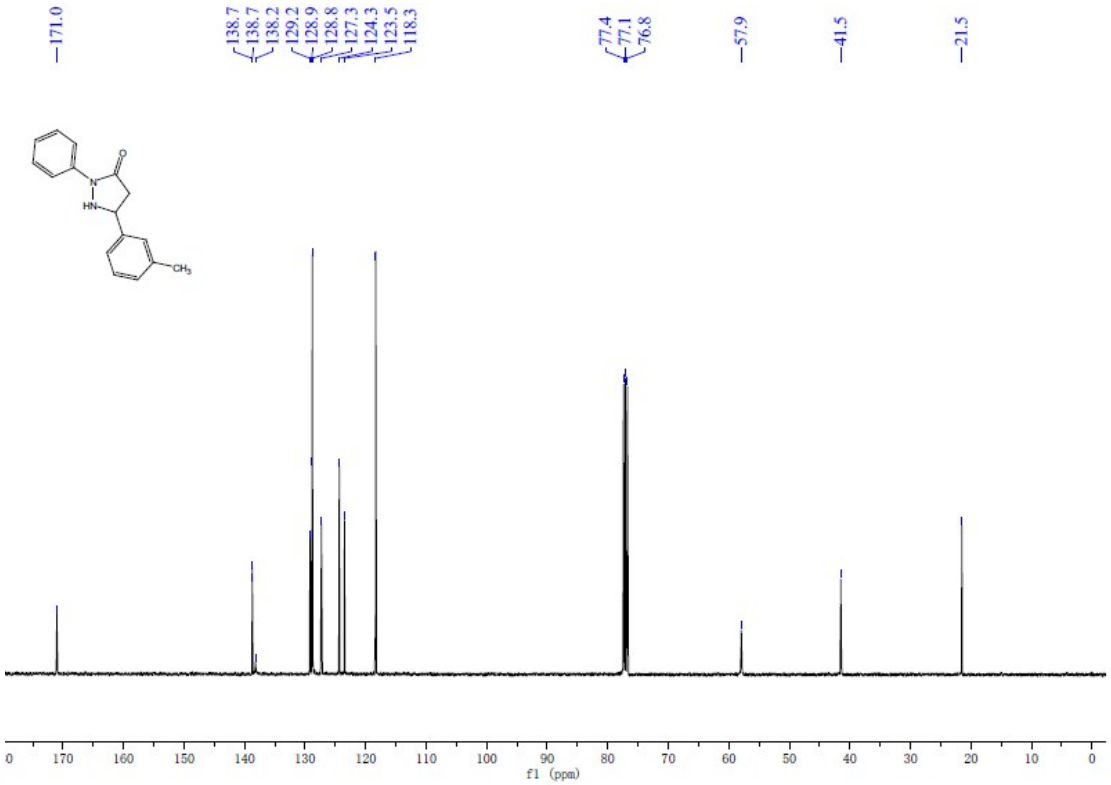
^{1}H NMR Spectrum of Compound (4b)



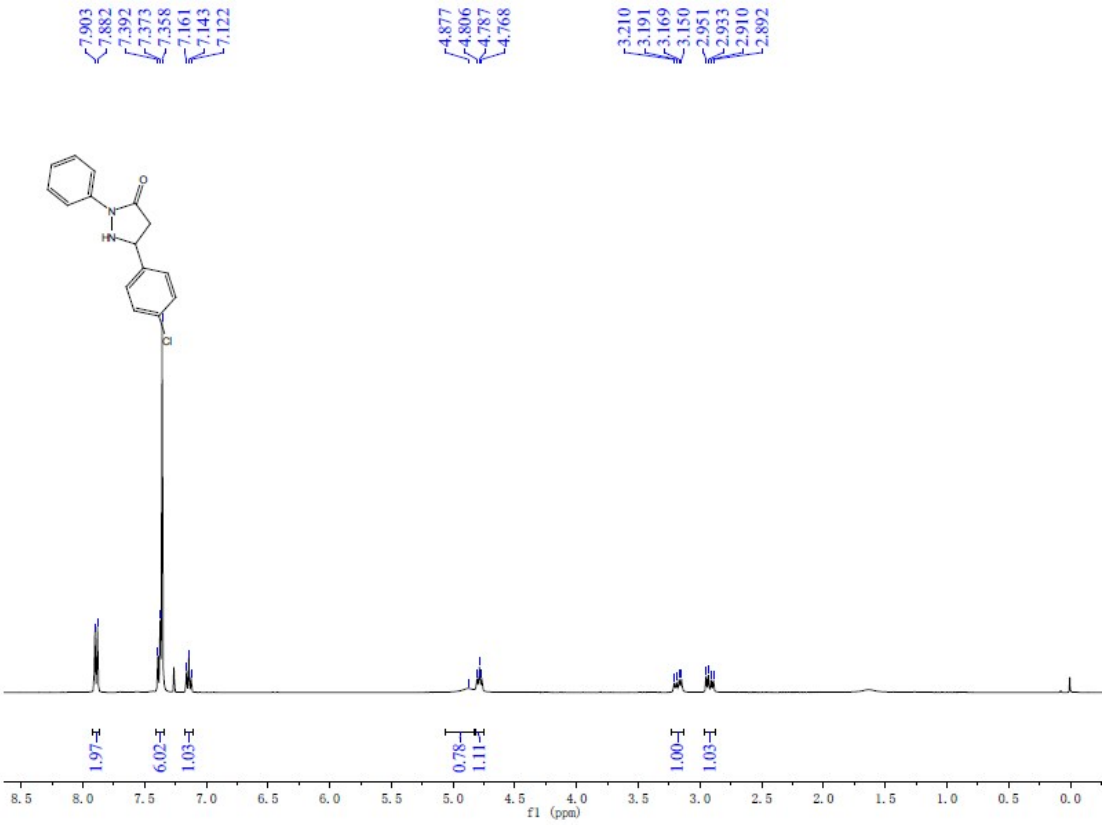
^{13}C NMR Spectrum of Compound (4b)



^{1}H NMR Spectrum of Compound (4c)



^{13}C NMR Spectrum of Compound (4c)



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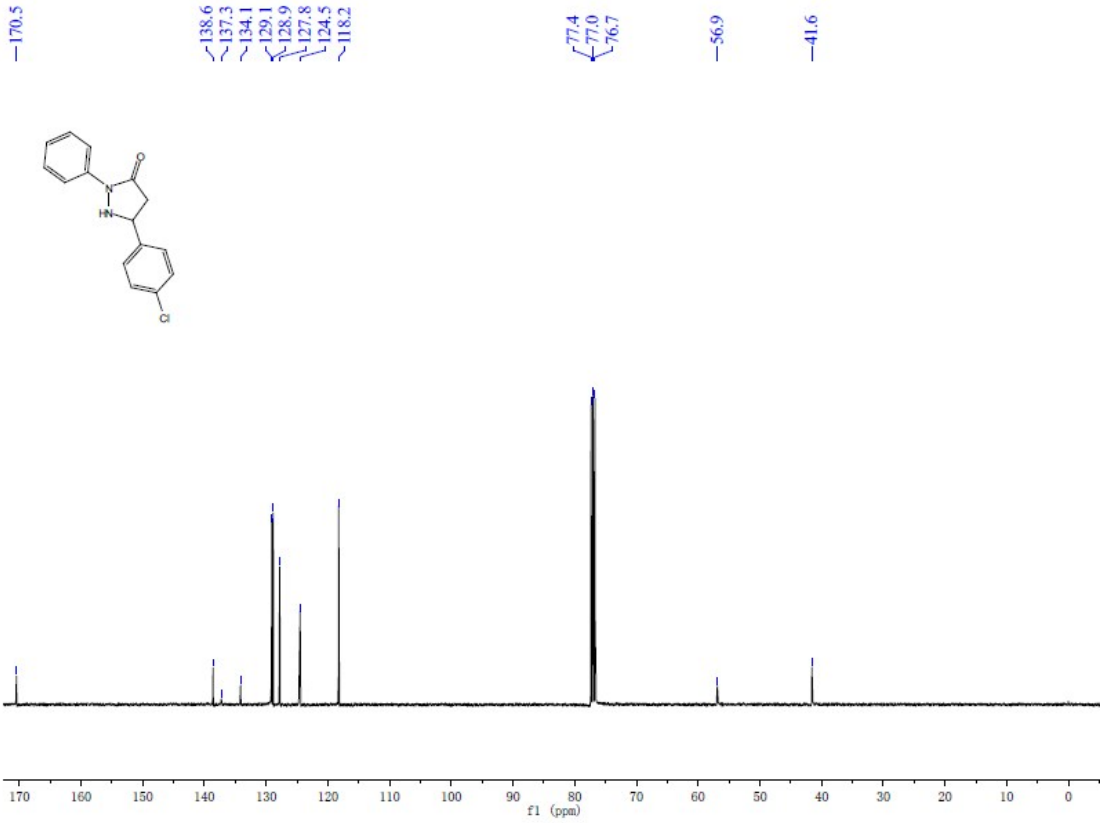
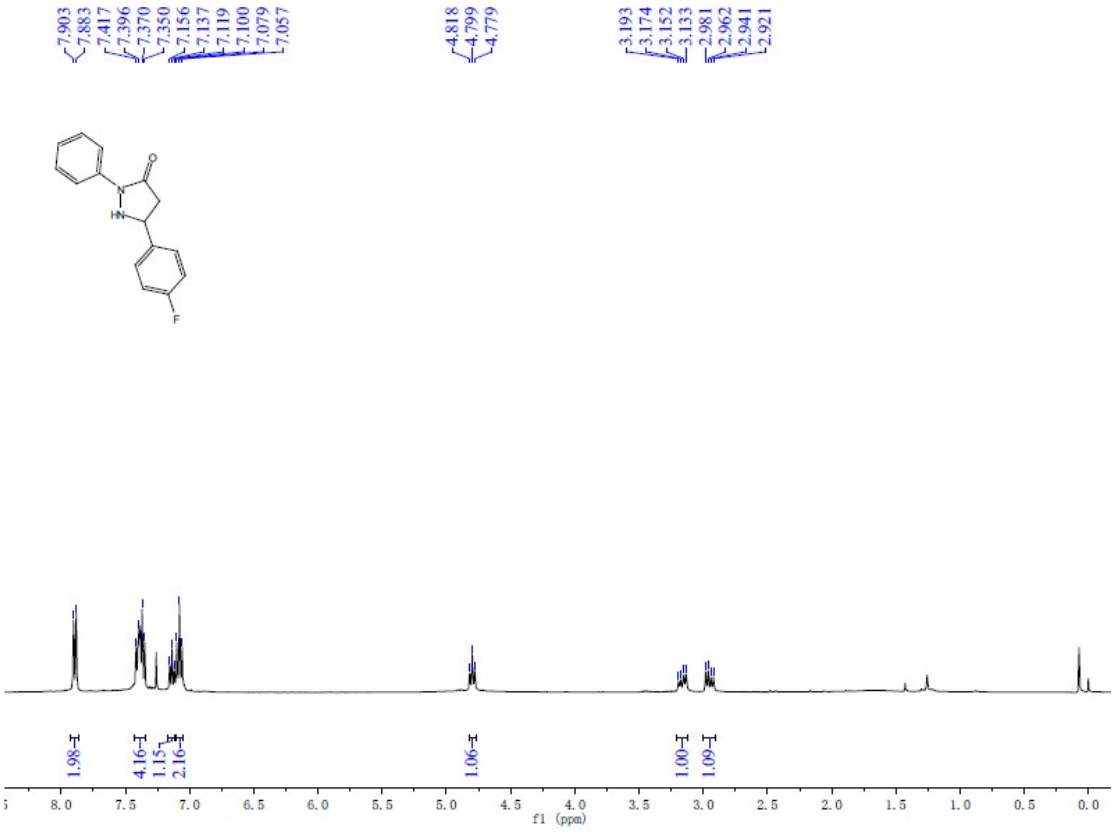
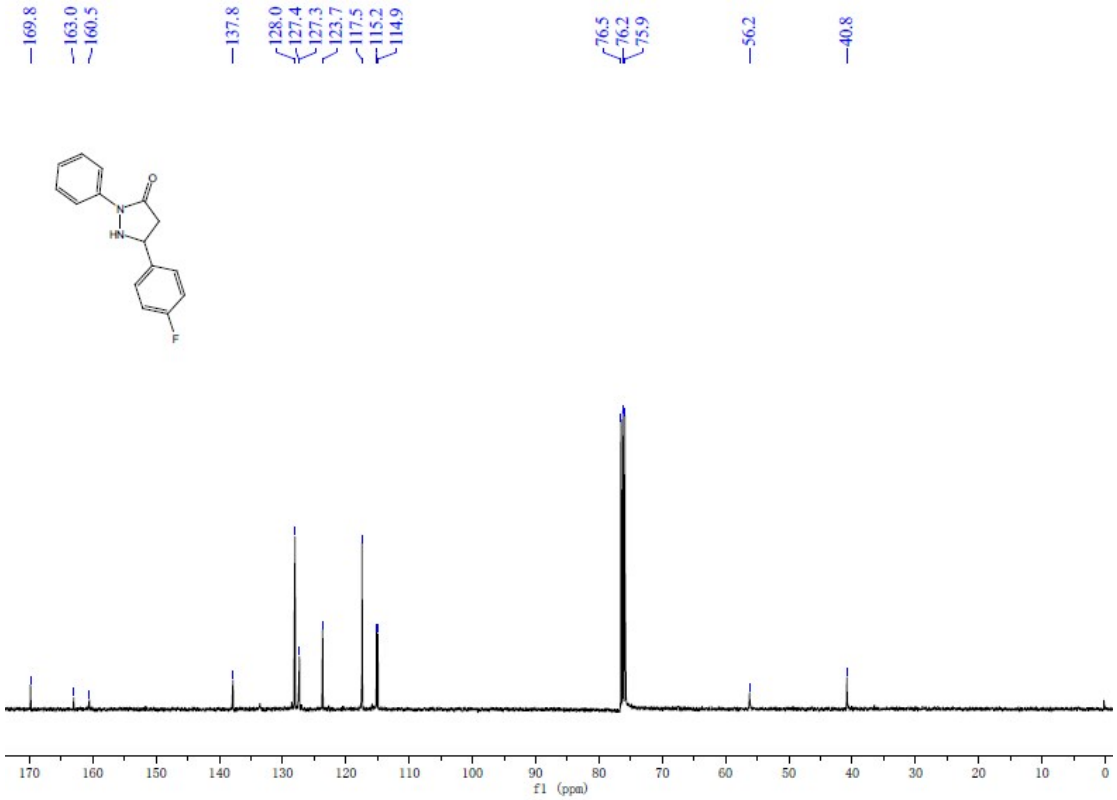


^{13}C NMR Spectrum of Compound (4d)



^{1}H NMR Spectrum of Compound (4e)



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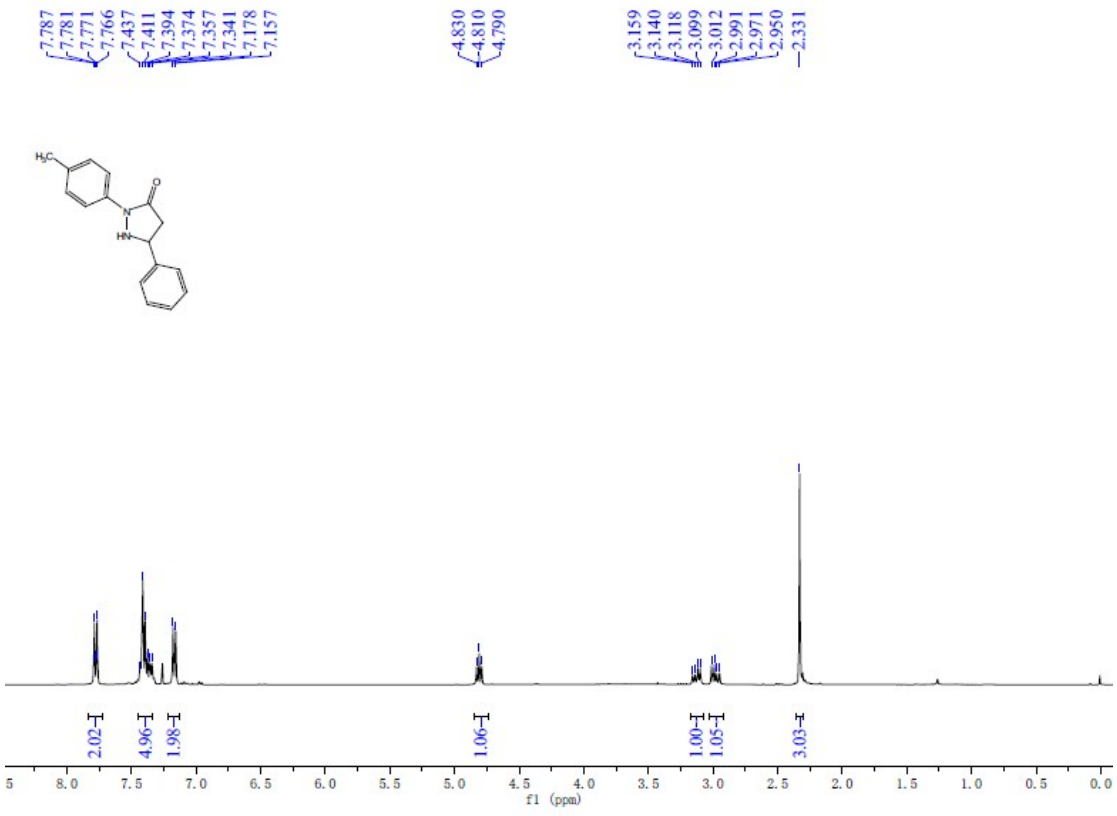
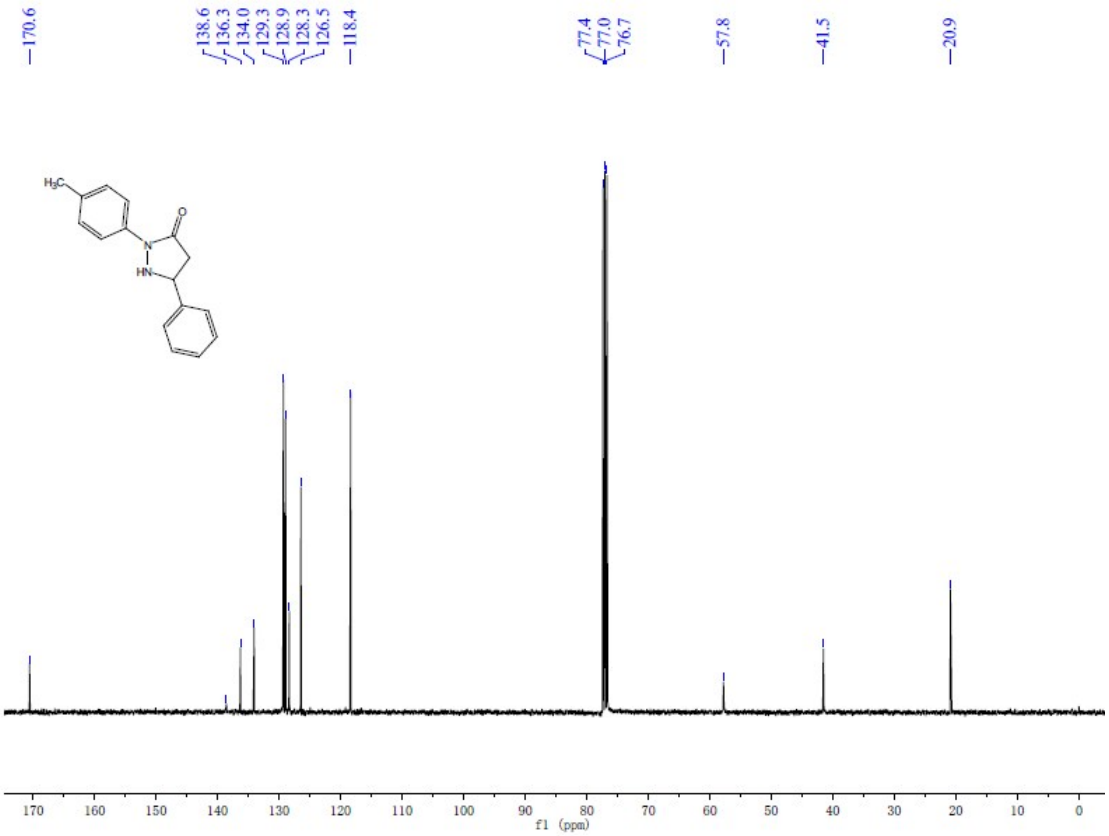
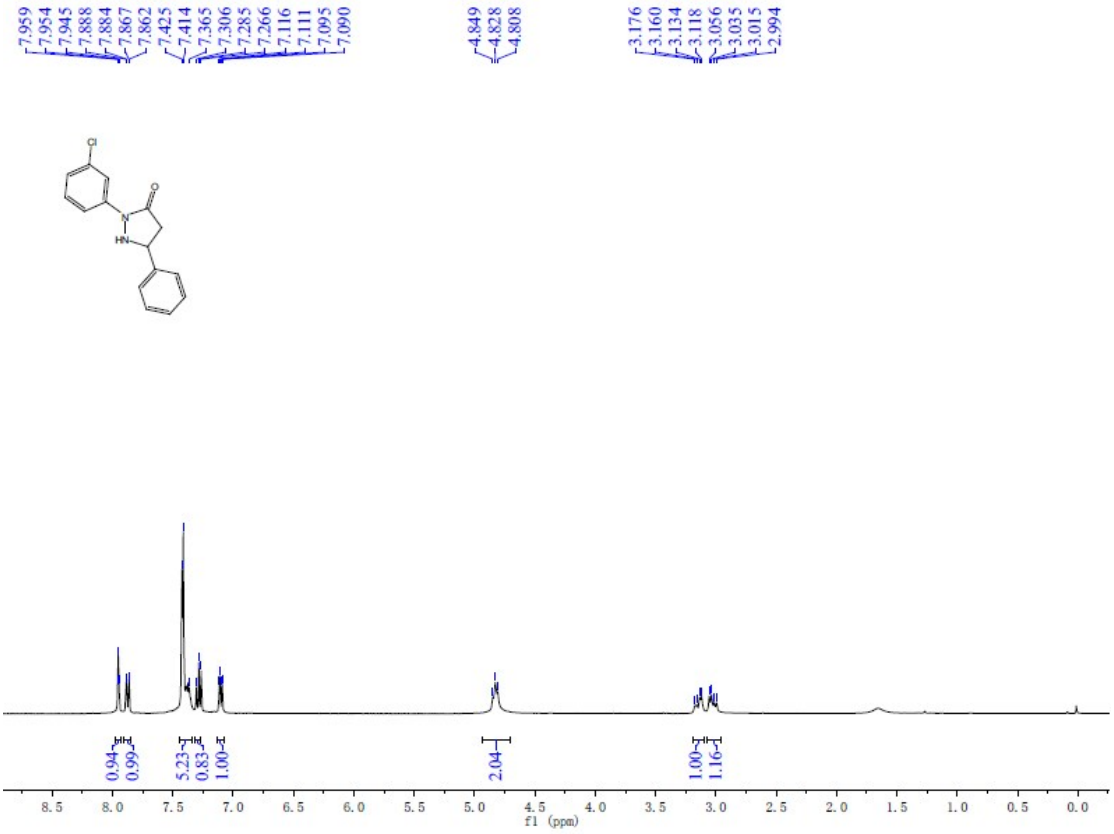


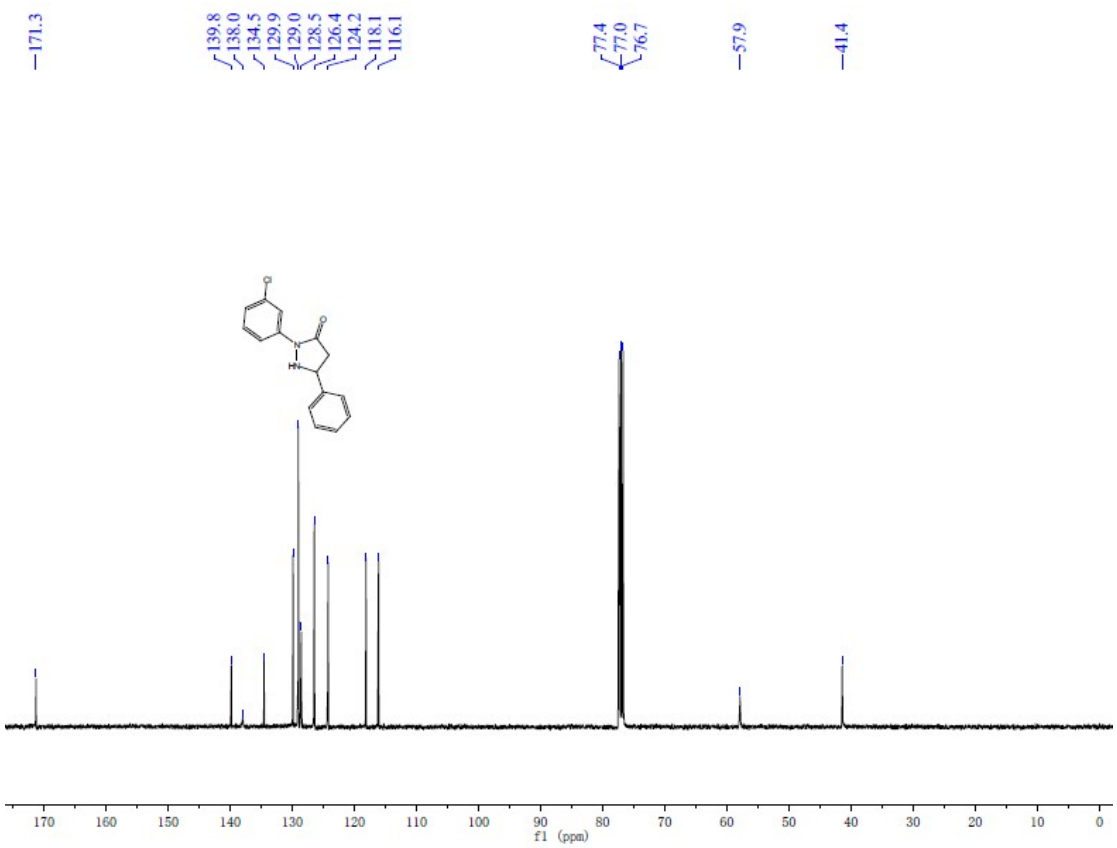
^{1}H NMR Spectrum of Compound (4f)



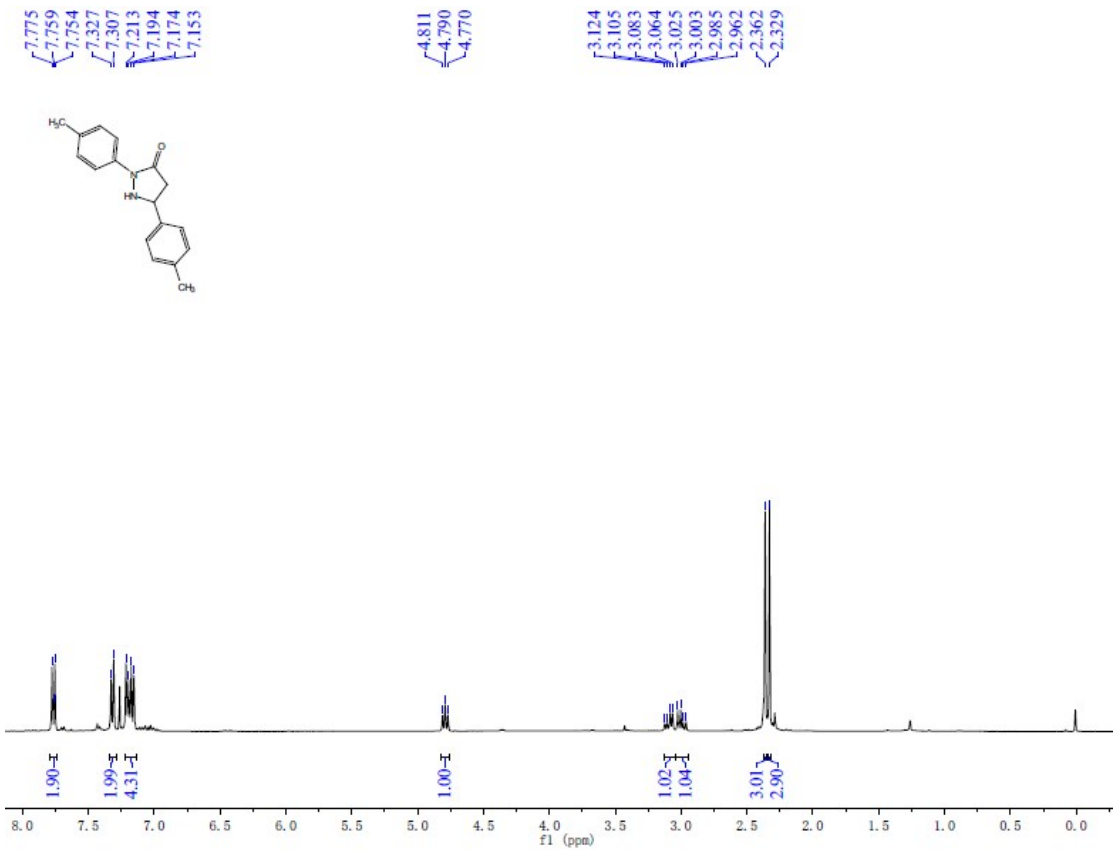
^{13}C NMR Spectrum of Compound (4f)



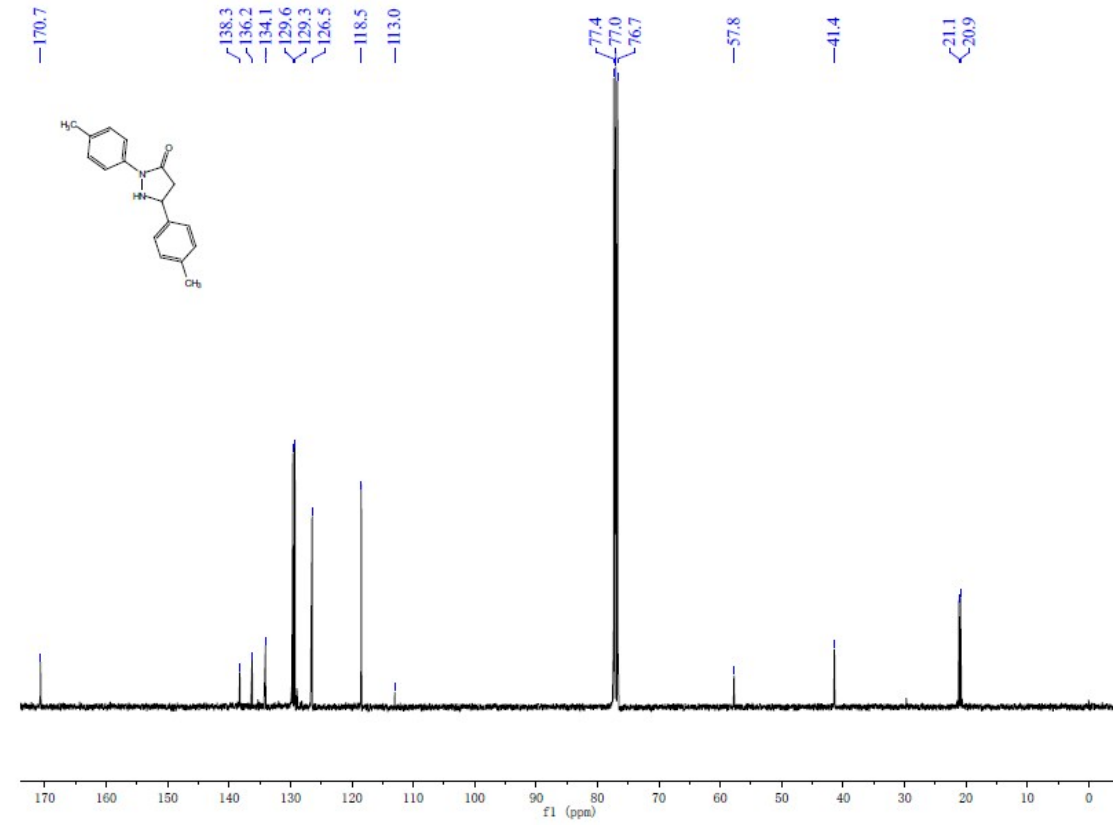
^{1}H NMR Spectrum of Compound (4g)



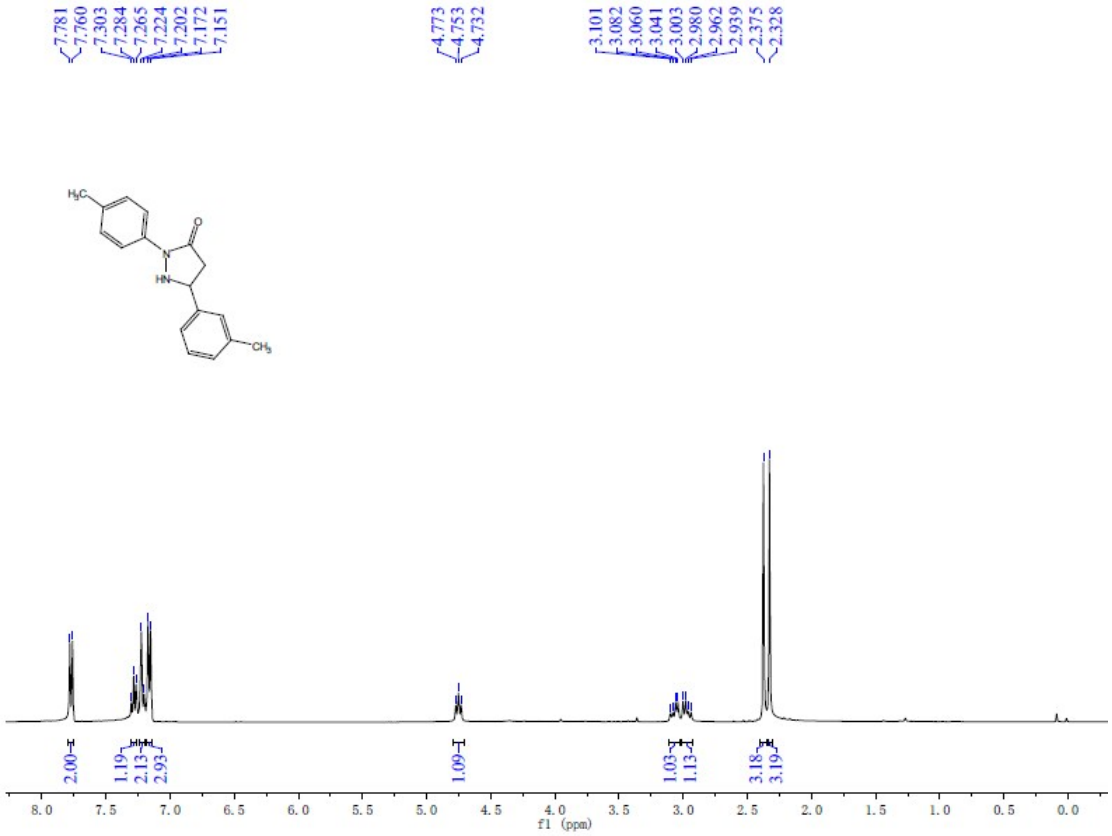
^{13}C NMR Spectrum of Compound (4g)



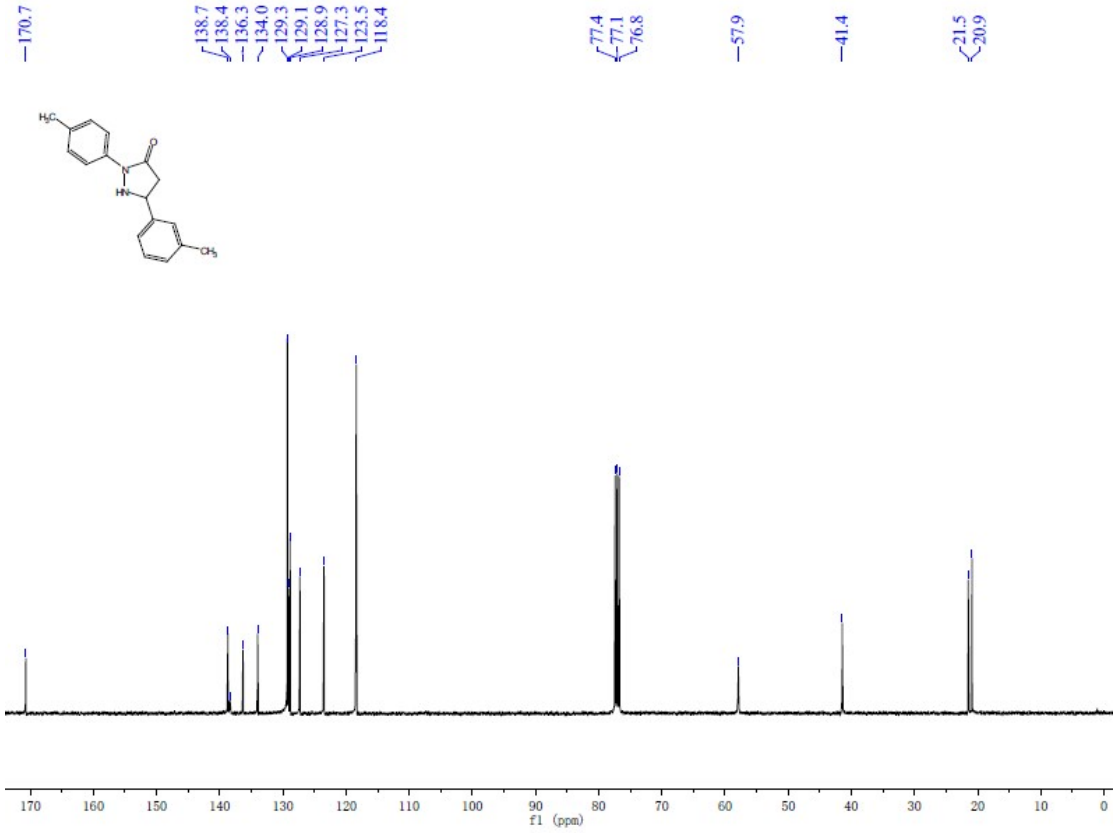
^{1}H NMR Spectrum of Compound (4h)



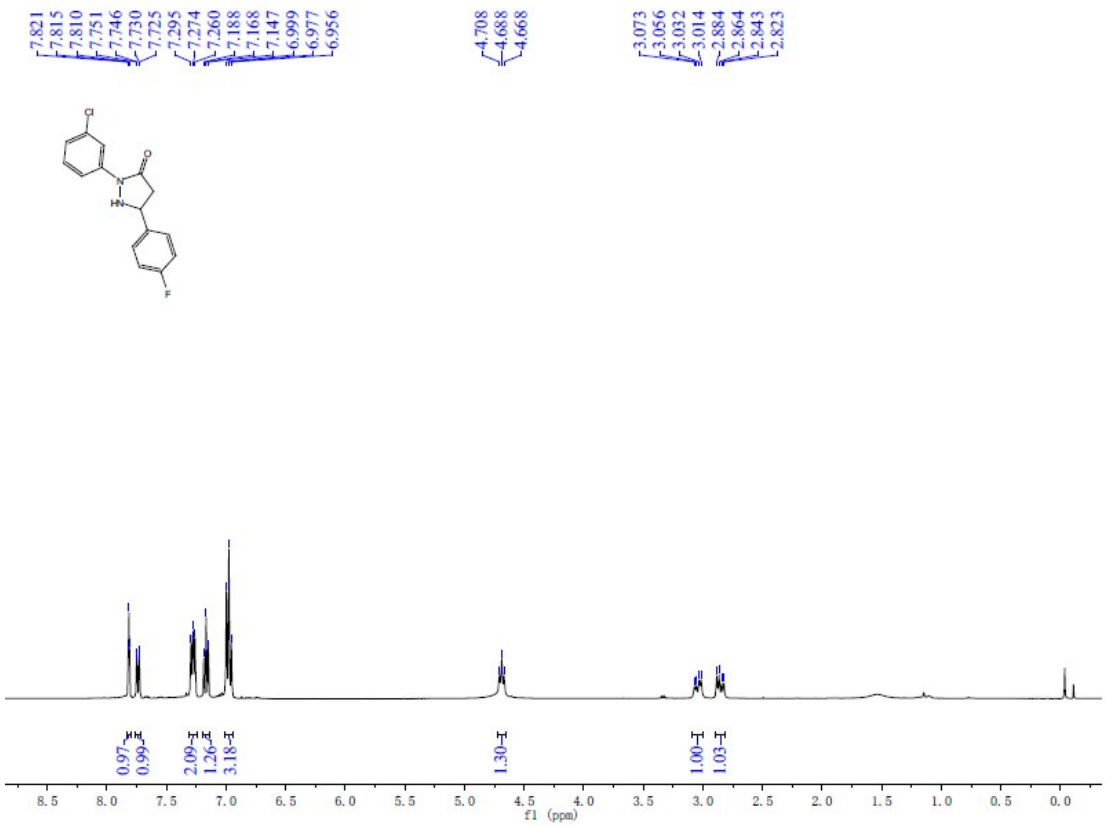
^{13}C NMR Spectrum of Compound (4h)



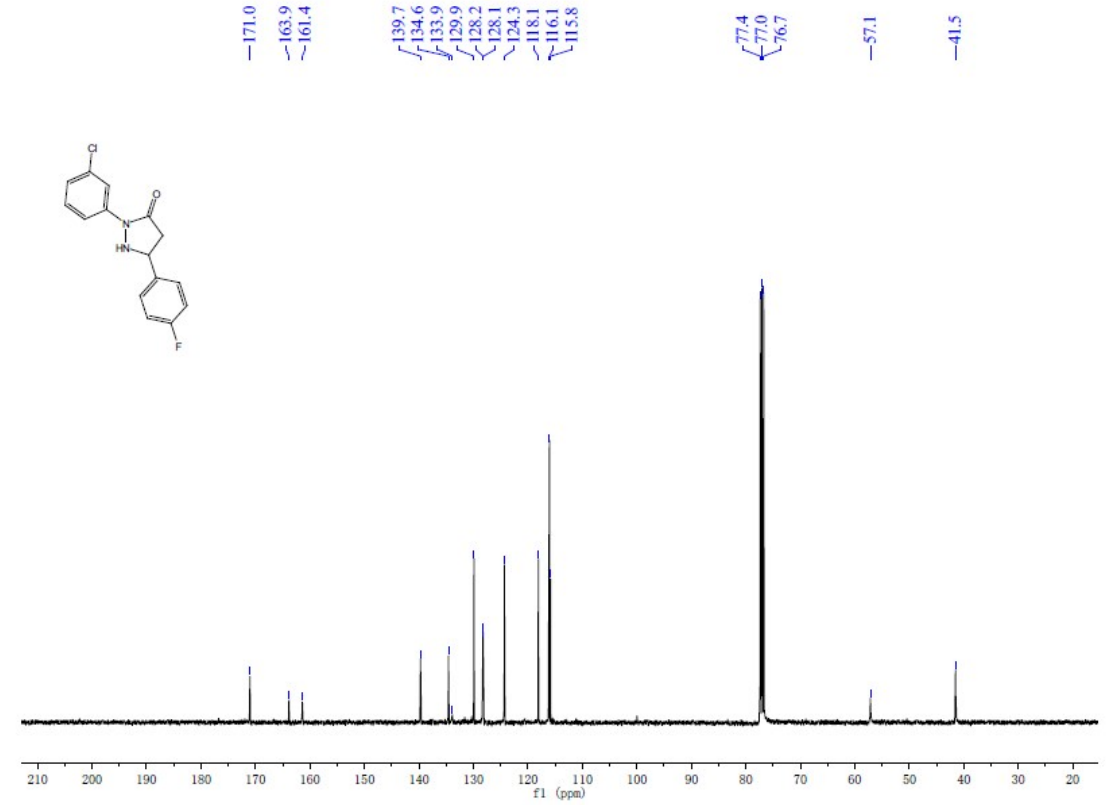
^{1}H NMR Spectrum of Compound (4i)



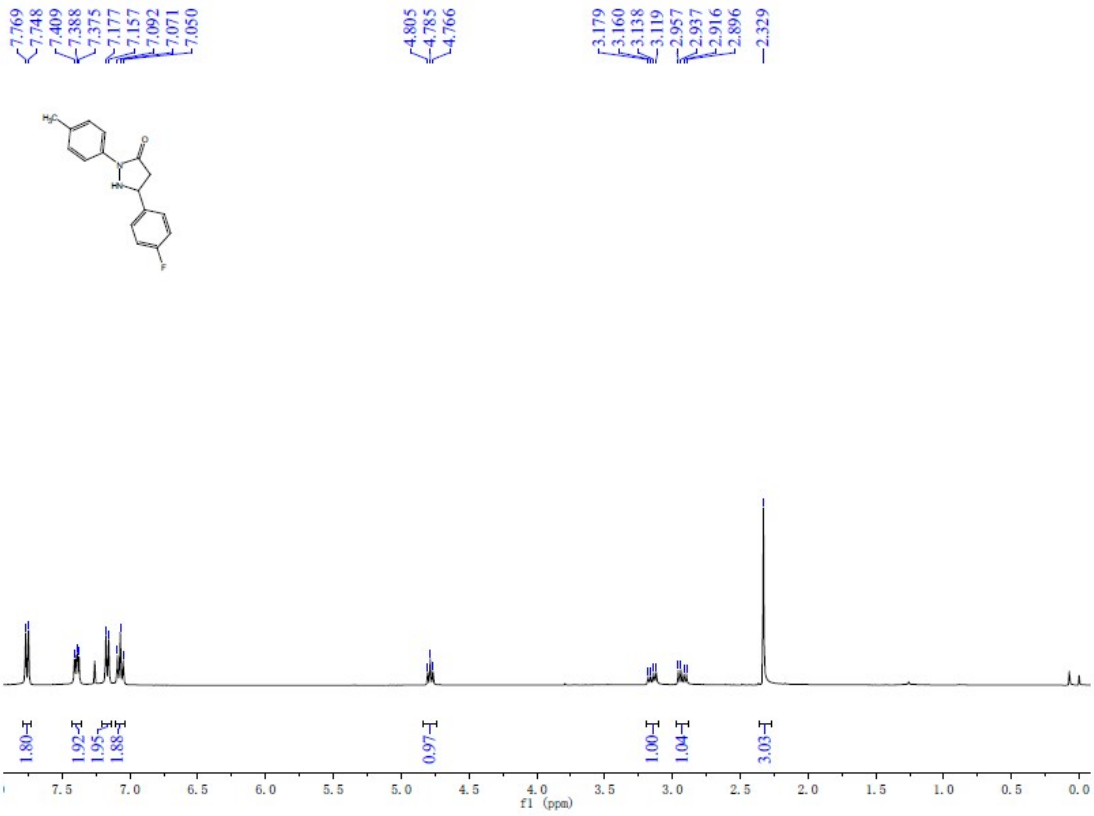
^{13}C NMR Spectrum of Compound (4i)



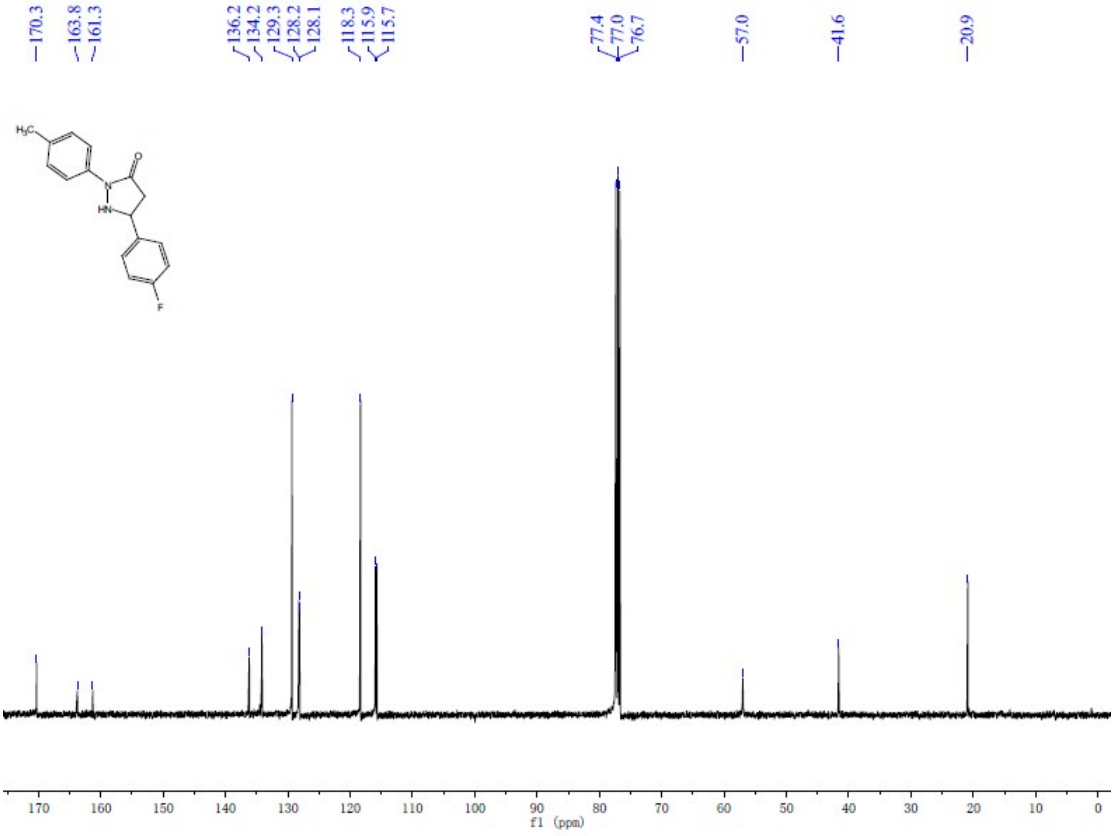
^{1}H NMR Spectrum of Compound (4j)



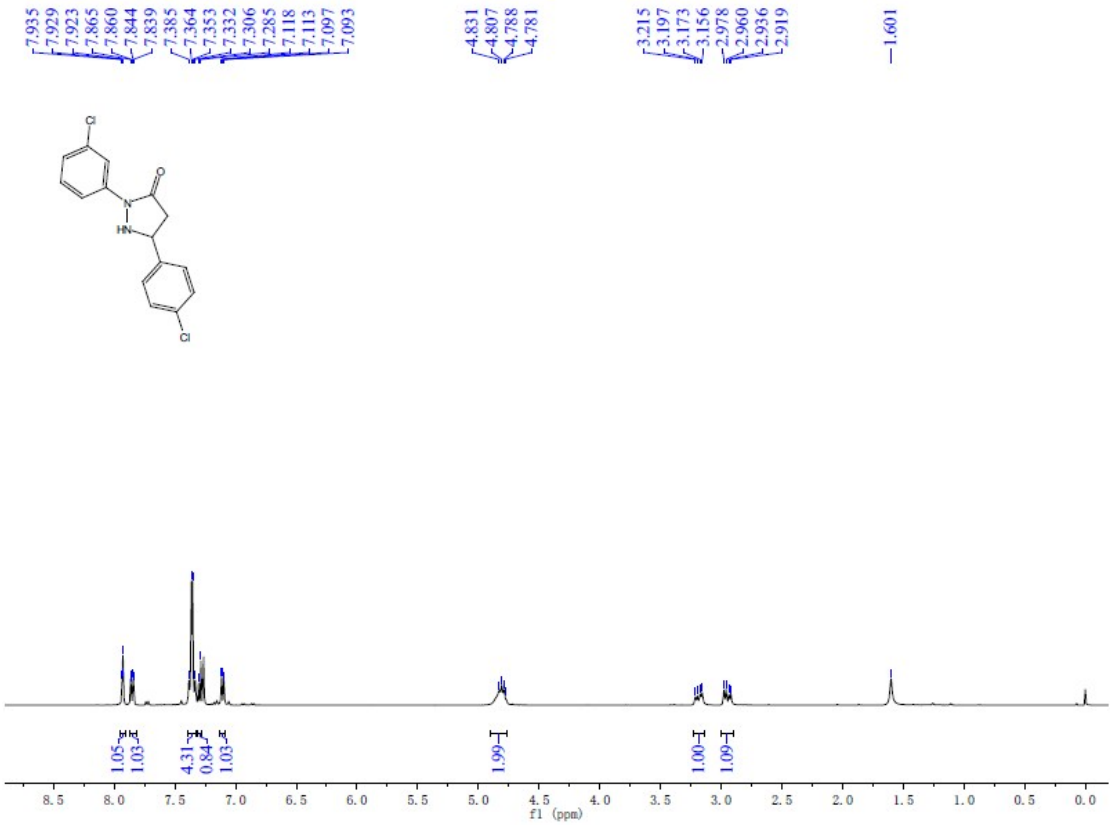
^{13}C NMR Spectrum of Compound (4j)



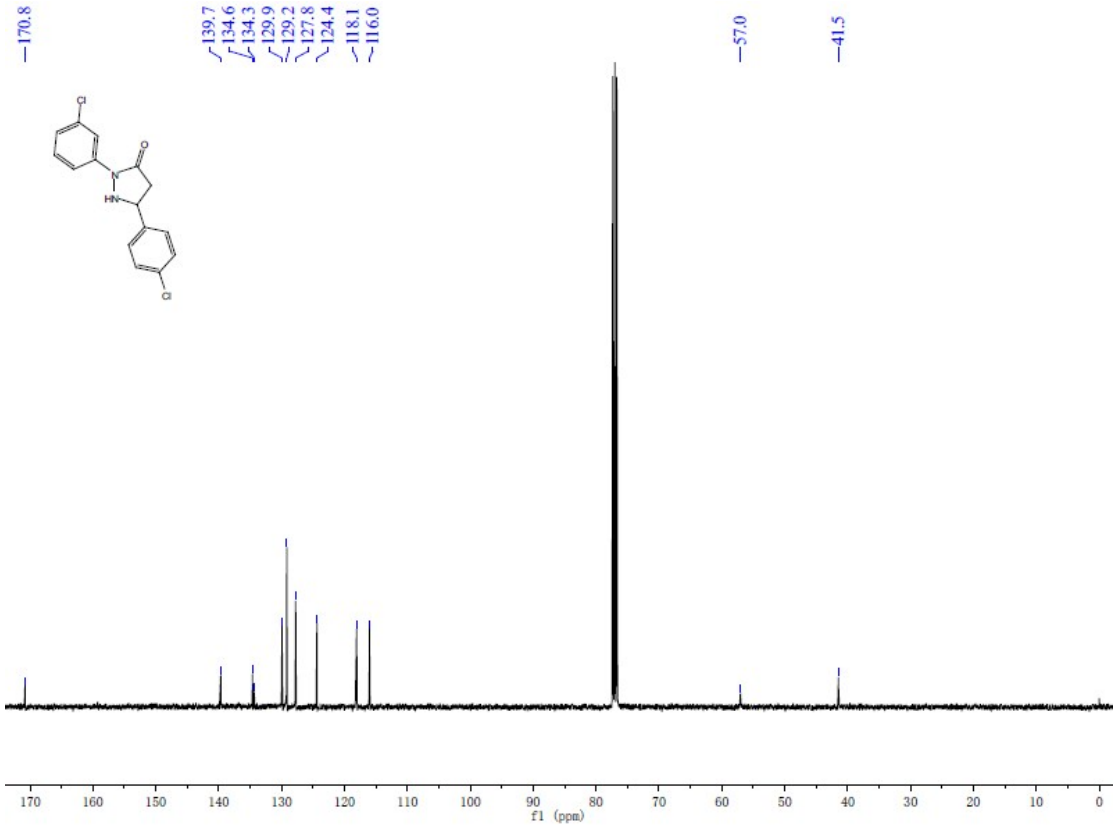
^{1}H NMR Spectrum of Compound (4k)



^{13}C NMR Spectrum of Compound (4k)

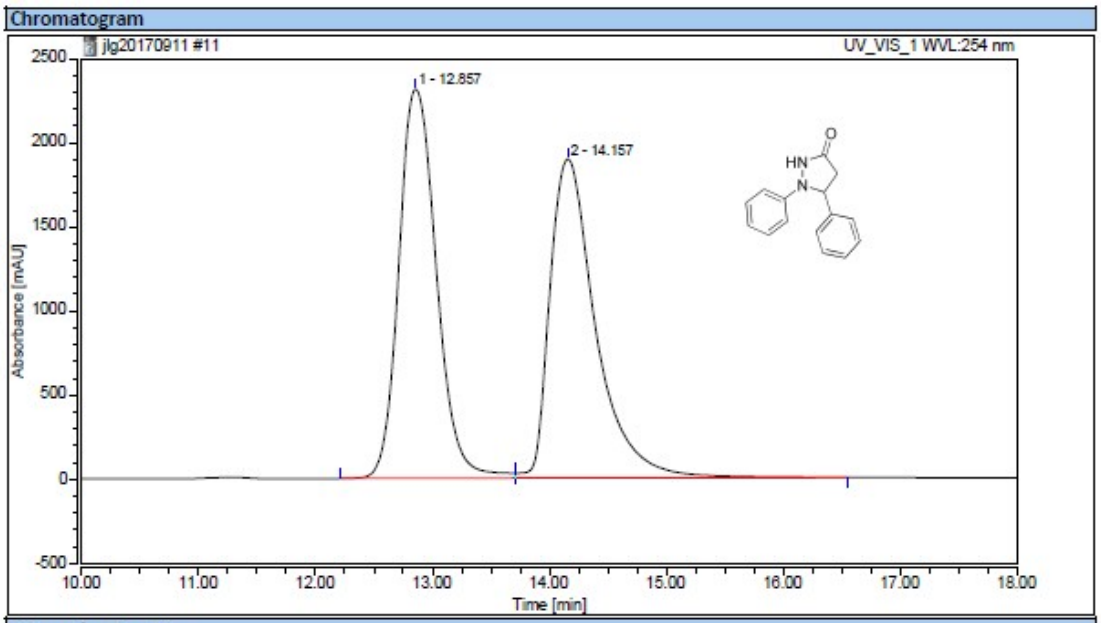


^{1}H NMR Spectrum of Compound (4l)



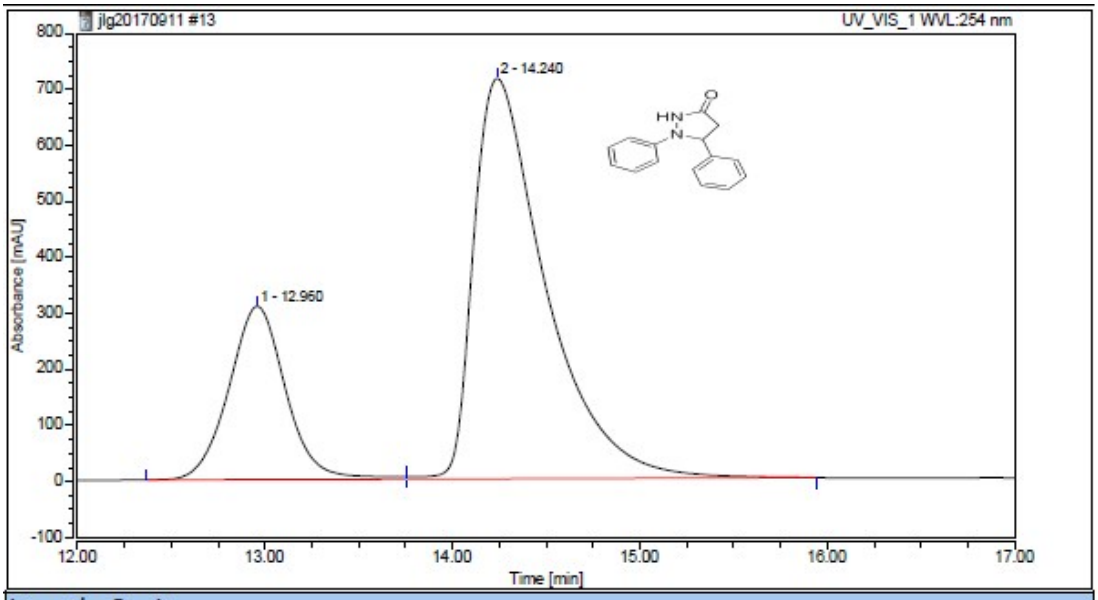
^{13}C NMR Spectrum of Compound (4l)

5. HPLC Spectra



Integration Results

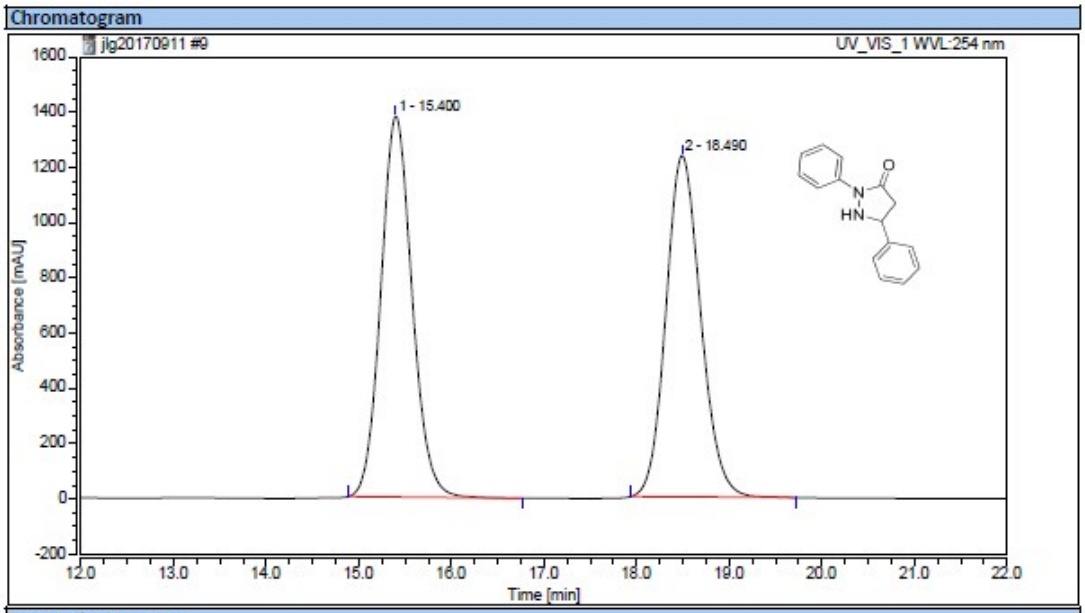
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.857	861.842	2313.686	50.05	54.96	n.a.
2		14.157	860.037	1896.236	49.95	45.04	n.a.
Total:			**1721.879**	**4209.921**	**100.00**	**100.00**	



Integration Results

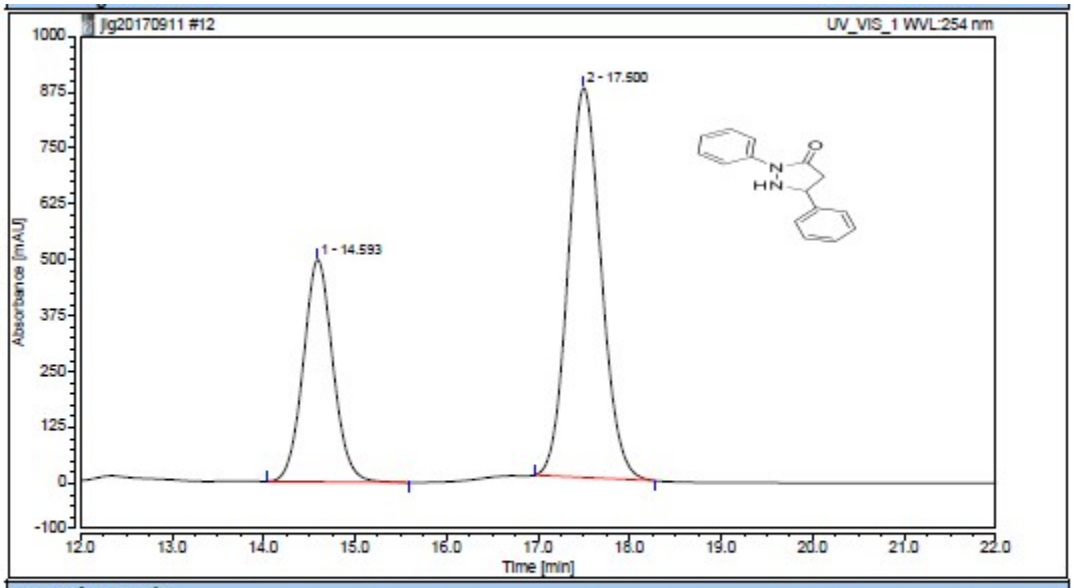
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.960	108.426	309.323	25.43	30.21	n.a.
2		14.240	317.907	714.578	74.57	69.79	n.a.
Total:			**426.333**	**1023.902**	**100.00**	**100.00**	

HPLC analysis: 49% ee, [Daicel Chiralpak IA-H, n-hexane/2-propanol = 85/15, v = 0.8 mL.min^{-1}, λ = 254 nm, t (major) = 12.9 min, t (minor) = 14.2 min].



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.400	538.584	1379.194	50.04	52.73	n.a.
2		18.490	537.700	1236.418	49.96	47.27	n.a.
Total:			**1076.285**	**2615.612**	**100.00**	**100.00**	

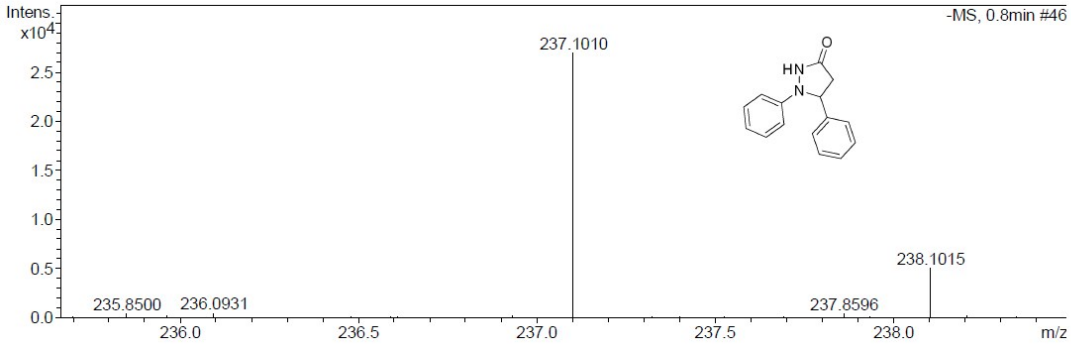


Integration Results

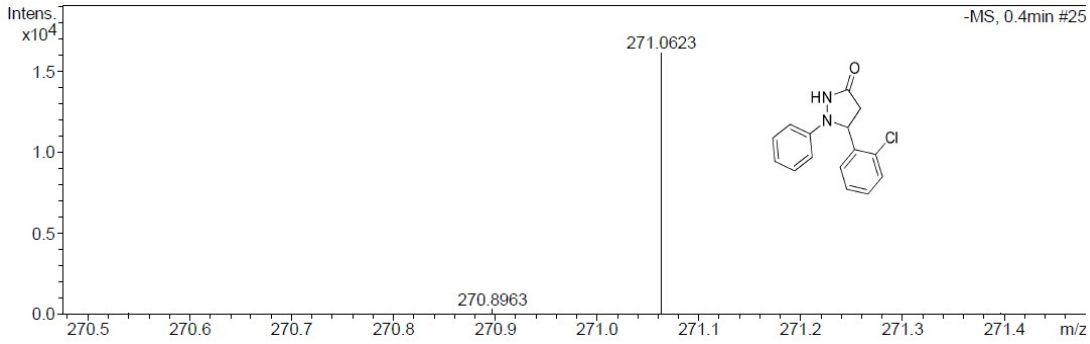
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.593	186.470	497.374	33.88	36.31	n.a.
2		17.500	363.926	872.271	66.12	63.69	n.a.
Total:			**550.396**	**1369.645**	**100.00**	**100.00**	

HPLC analysis: 32% ee, [Daicel Chiralpak IA-H, n-hexane/2-propanol = 85/15, v = 0.8 mL.min^{-1}, λ = 254 nm, t (major) = 14.5 min, t (minor) = 17.5 min].

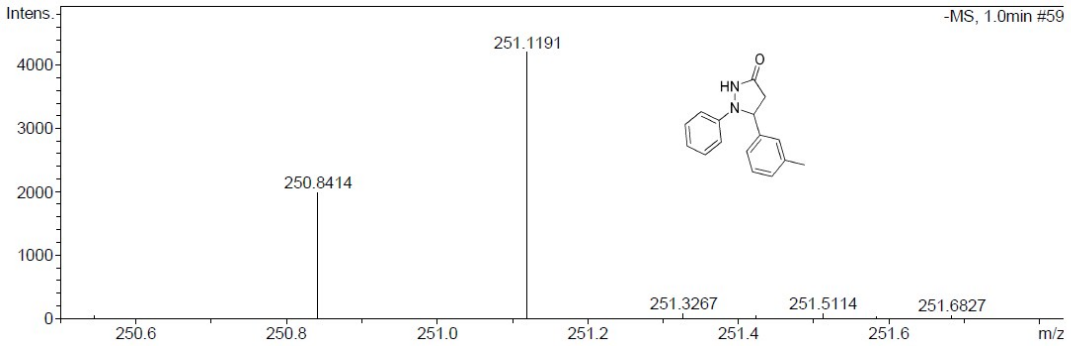
6. HRMS Spectra



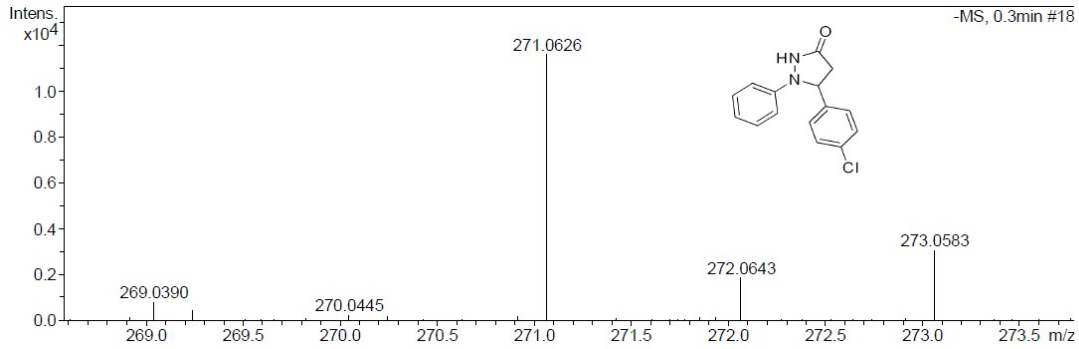
HRMS Spectrum of Compound (3a)



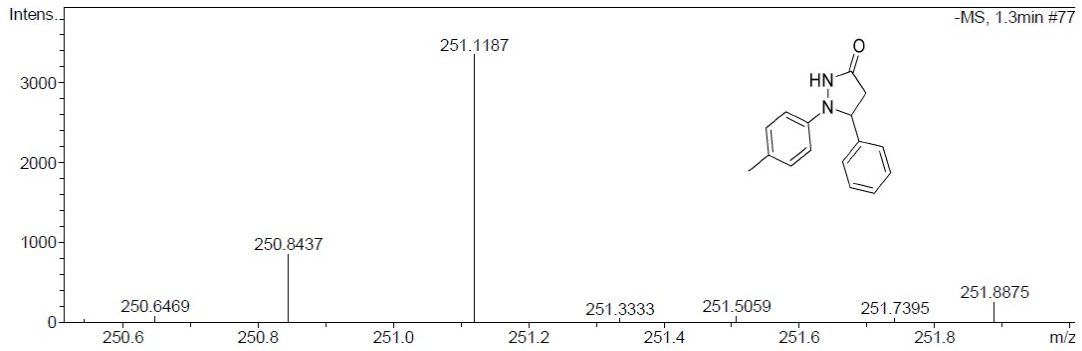
HRMS Spectrum of Compound (3b)



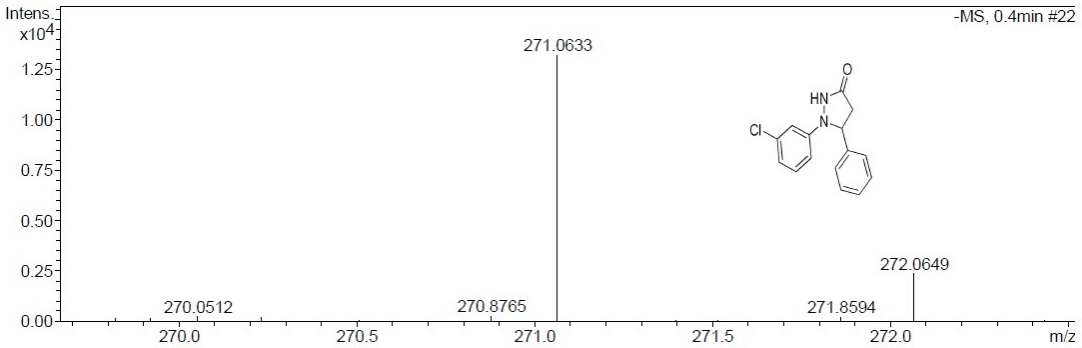
HRMS Spectrum of Compound (3c)



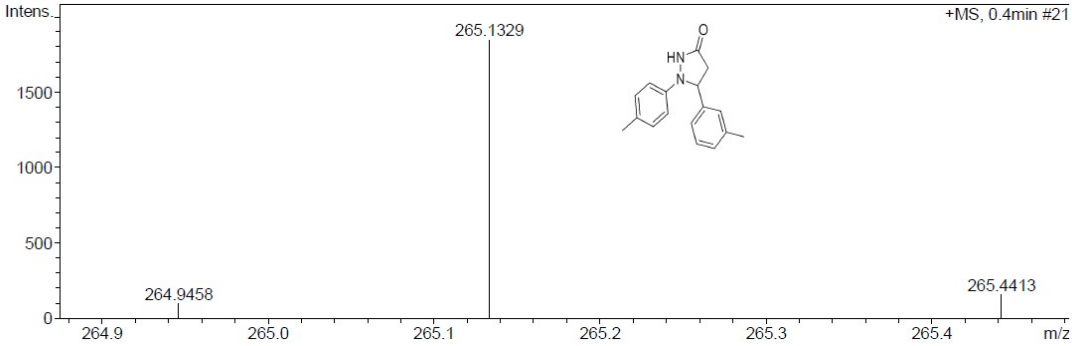
HRMS Spectrum of Compound (3d)



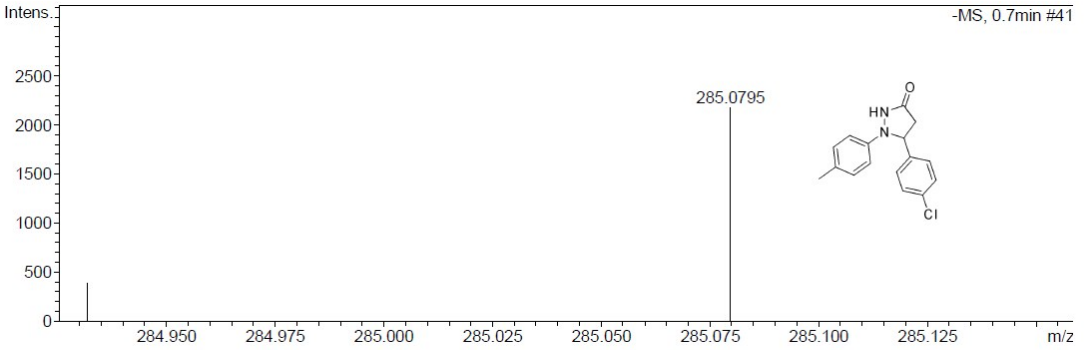
HRMS Spectrum of Compound (3e)



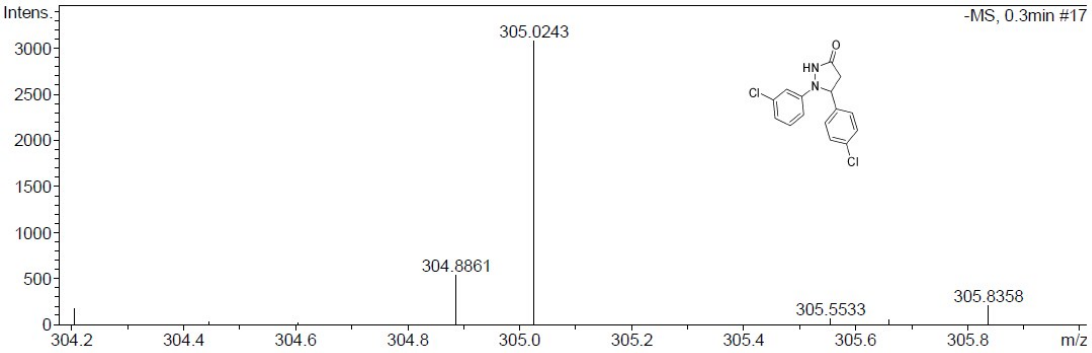
HRMS Spectrum of Compound (3f)



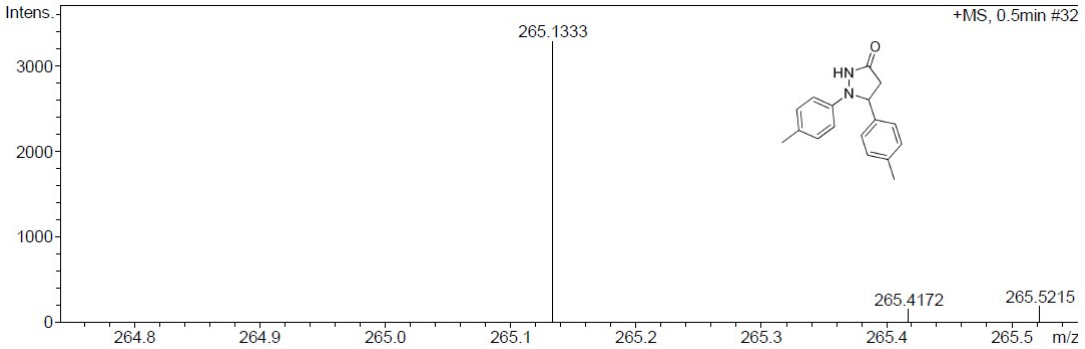
HRMS Spectrum of Compound (3g)



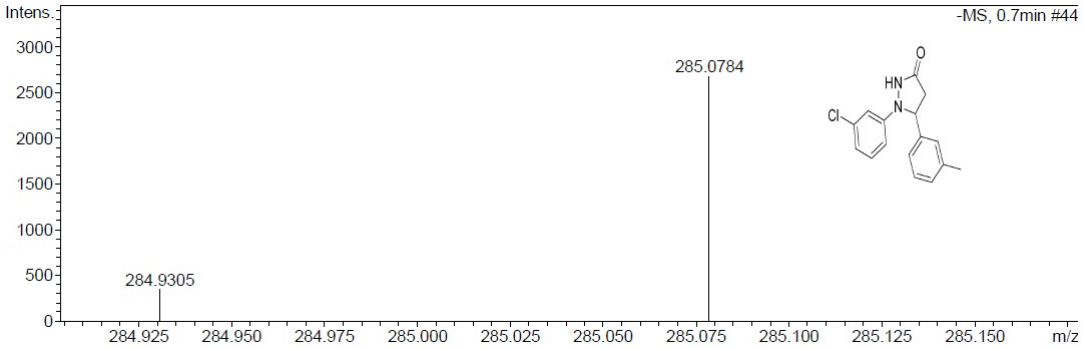
HRMS Spectrum of Compound (3h)



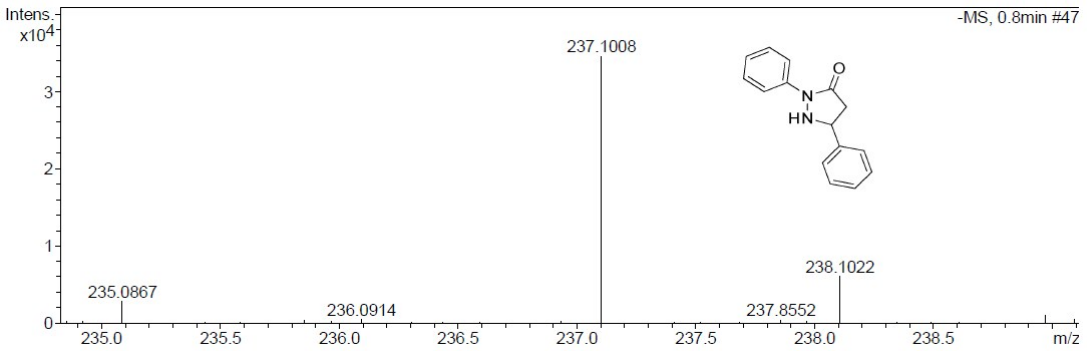
HRMS Spectrum of Compound (3i)



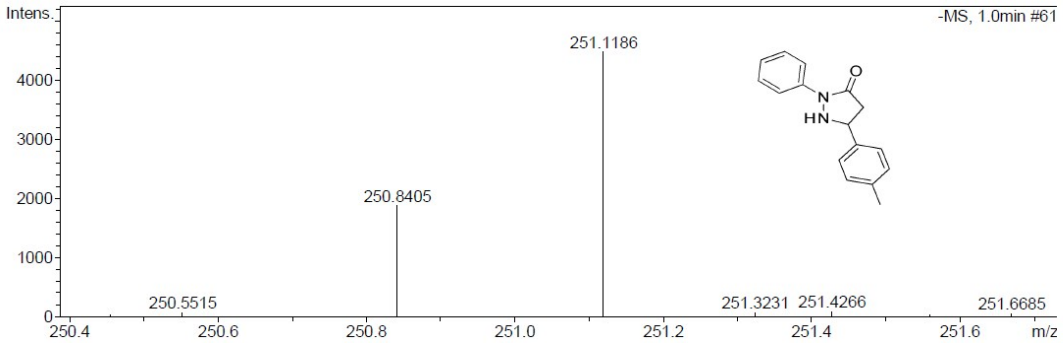
HRMS Spectrum of Compound (3j)



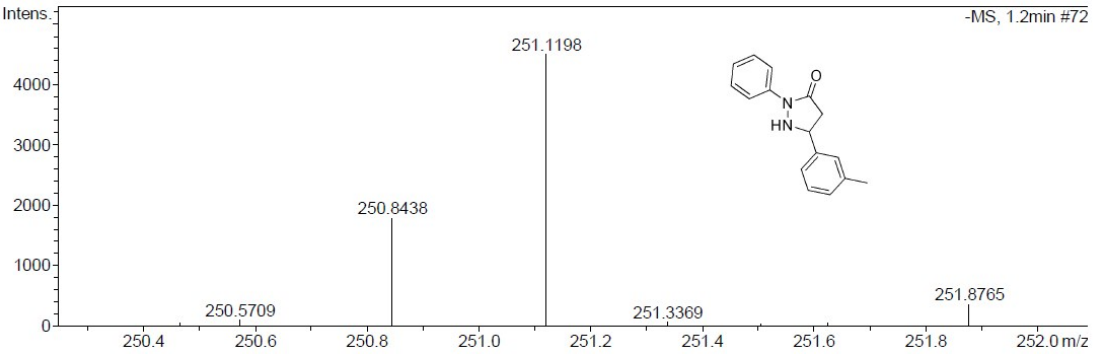
HRMS Spectrum of Compound (3k)



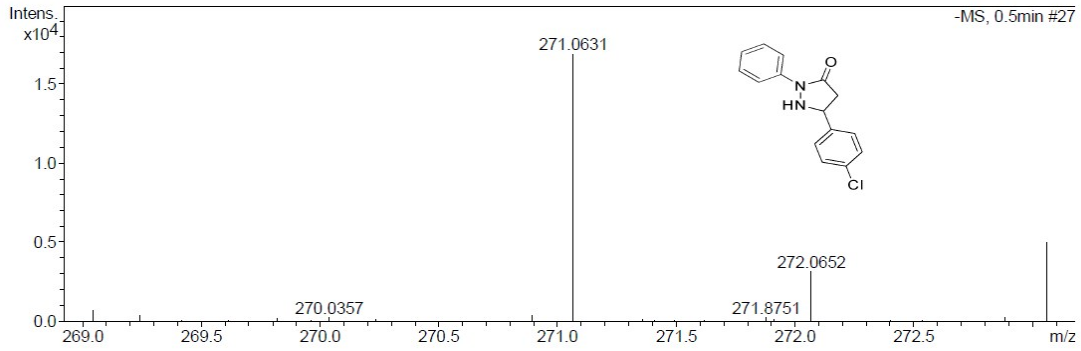
HRMS Spectrum of Compound (4a)



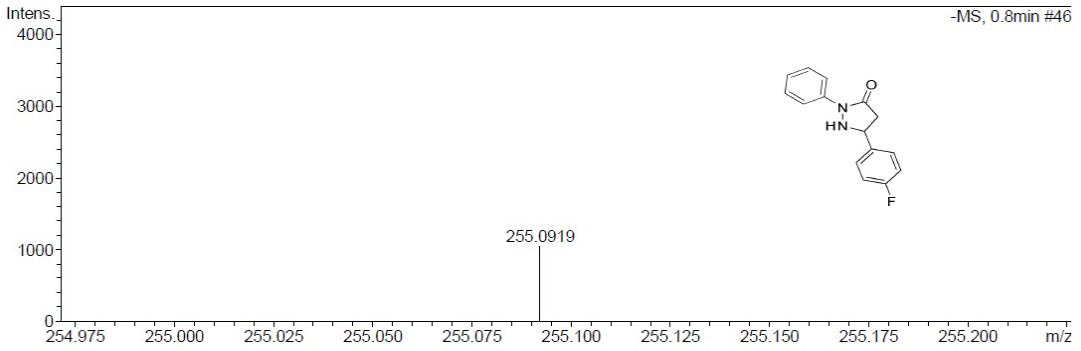
HRMS Spectrum of Compound (4b)



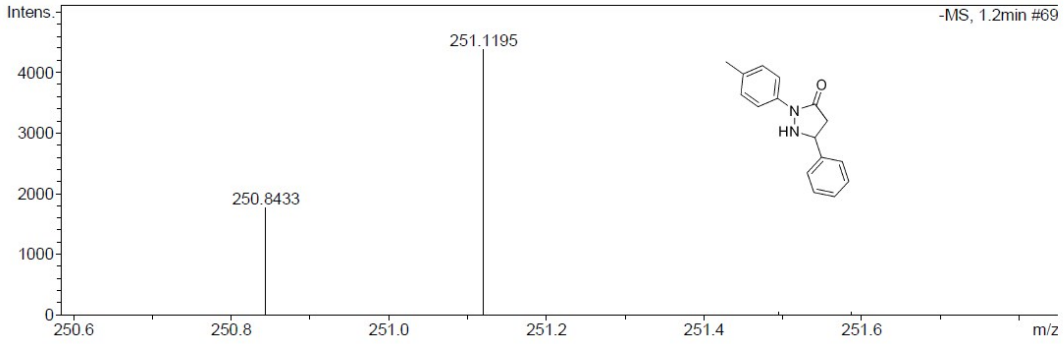
HRMS Spectrum of Compound (4c)



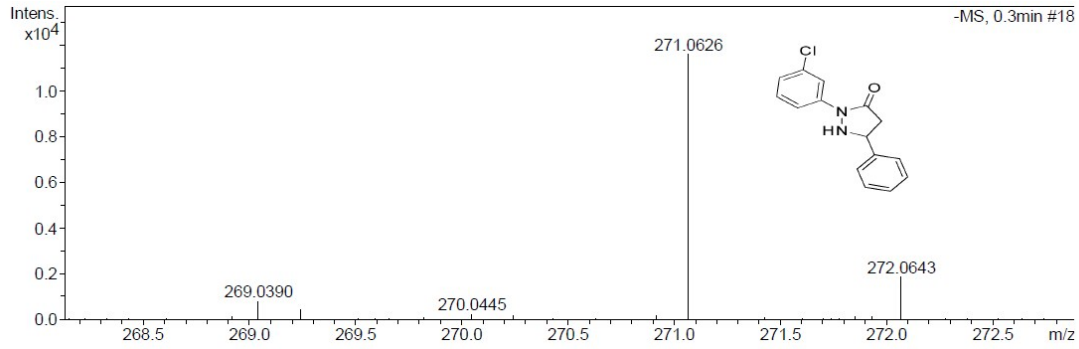
HRMS Spectrum of Compound (4d)



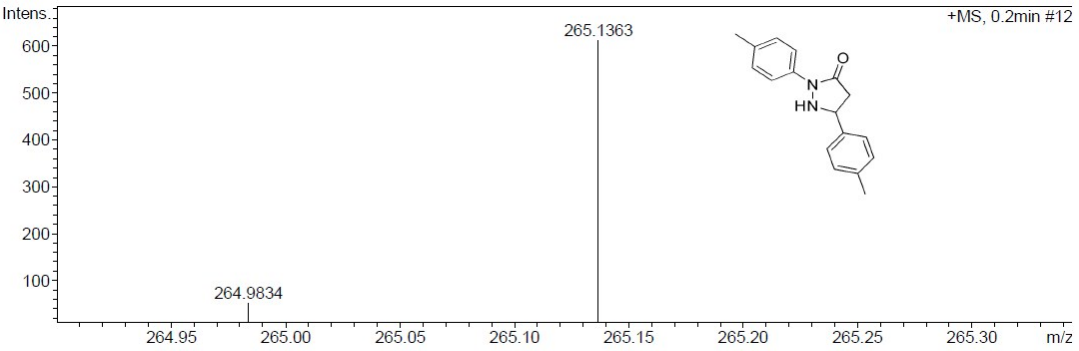
HRMS Spectrum of Compound (4e)



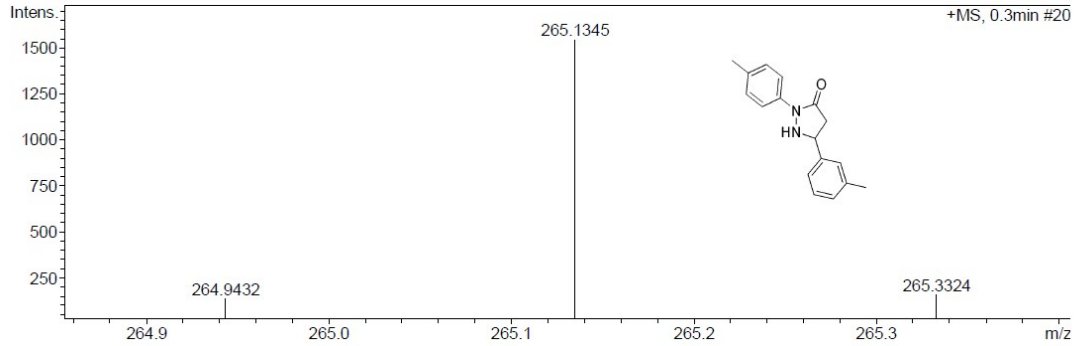
HRMS Spectrum of Compound (4f)



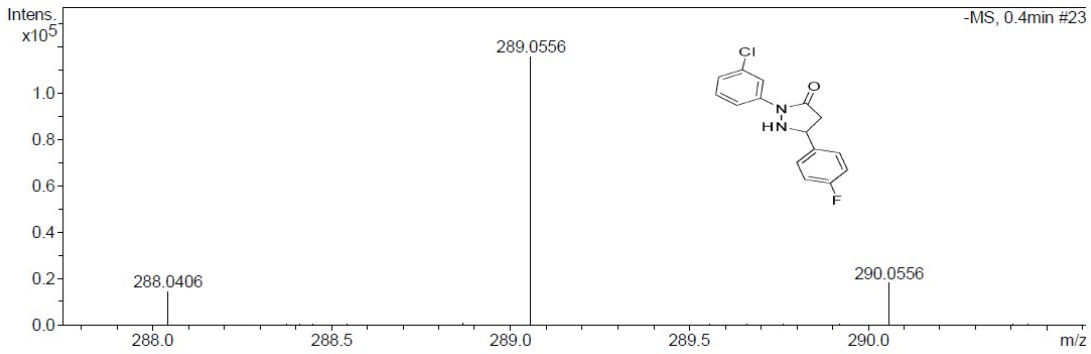
HRMS Spectrum of Compound (4g)



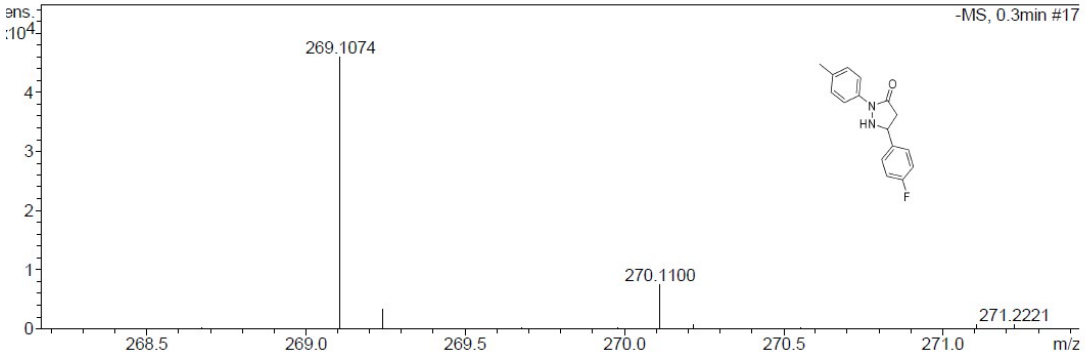
HRMS Spectrum of Compound (4h)



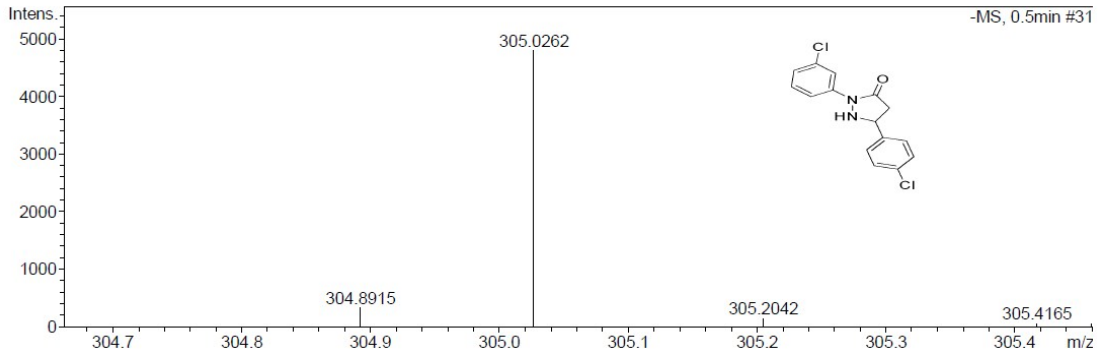
HRMS Spectrum of Compound (4i)



HRMS Spectrum of Compound (4j)



HRMS Spectrum of Compound (4k)



HRMS Spectrum of Compound (4l)