International Journal of Chemical Studies

P-ISSN: 2349-8528
E-ISSN: 2321-4902
www.chemijournal.com
IJCS 2025; 13(1): 13-23

Received: 13-10-2024
Accepted: 18-11-2024

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Metal free protocol for the synthesis of pyrazole derivative using *Dillenia indica* fruit core extract

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DOI: https://doi.org/10.22271/chemi.2025.v13.i1a.12487

Abstract
Dillenia indica, is a medicinal plant that is grown in humid and evergreen forest of Northeastern India in particular. Its, leaves, bark and fruits are rich in various phytochemicals. In this study, we intend to extract the juice from fruit core i.e. usually a discarded waste in Indian traditional medicine and traditional cuisine. An ethanolic extract was prepared using *Dillenia indica* fruit core and the presence of various phytochemicals were also confirmed by performing various tests and also the pH was measured to be 4.87. Based on the acidic nature of the extract it has the potential to be used as an acid catalyst for the synthesis of Pyrazole and its derivatives under mild reaction conditions.

Keywords: Pyrazole, 1,3-Diketones, hydrazine, *Dillenia indica*, Metal-free

Introduction
Elephant apple (*Dillenia indica*) (Family: Dilleniaceae) is an evergreen tree that grows upto 30-80 feet high and produces fruit that is 3-5 inches in diameter [1]. Elephant apple tree, is indigenous to Southeast Asia, which includes Bangladesh, China, India, Nepal, and Sri Lanka. In particular, it is widely grown in humid and evergreen forest of Northeastern India's [2]. The fruit pulp, which has a bitter-sour taste, is mostly utilized in Indian traditional medicine and traditional cuisine [3]. The leaves, bark and fruits of elephant apples are rich in various phytochemicals (such as flavonoids, phenolic compounds, alkaloids etc.) that contribute to the potential therapeutic application of the elephant apple [2]. Its therapeutic use includes treating illnesses like fever, diarrhea, constipation, diabetes, constipation, abdominal and joint pain and anti-oxidant properties [3, 4].
Literature search reveals Singh *et al*., reported the synthesis of silver nanoparticles by a novel green method in which the extract of *Dillenia indica* fruit was used as reducer in place of sodium borohydride [5]. Thereafter, Sett *et al*. reported a novel method of gold nanoparticle (AuNP) synthesis using aqueous fruit extract of *Dillenia indica*. The phytochemicals present the fruit extract's acts as a potent reducing and capping agent during the synthesis of AuNPs [3]. Another research group reported the synthesis of stable silver nanoparticles using the bark extract from *Dillenia indica* [6]. In another work, Das *et al*. reported the synthesis of cerium oxide nanoparticles (CeO_2 NPs) through a green route using *Dillenia indica* aqueous extract [7]. Mohanta *et al*. utilized ethanolic bark extract of *Dillenia indica* for green synthesis of copper nanoparticles (CuNPs) [8]. Recently, Gupta *et al*. utilized the flower extract for the synthesis of silver nanoparticles (AgNPs) [9].

Pyrazole and pyazole derivatives:
Pyrazole is an organic compound which bears an azole group having the formula $C_3H_3N_2H$. Pyrazoles and pyrazolines are heterocyclic rings with five members that have two nitrogen heteroatoms arranged in adjacent places. An essential structural framework in the field of agrochemical and medicinal sciences is represented by pyrazoles and their derivatives. They are specifically referred to be antiviral, antibacterial, antifugal, anticancer, antidepressant, anti-inflammatory, and anti-tuberculosis drugs [10, 11]. They are also said to be inhibitors of protein glycation. These days, pyrazole complexes have gained more attention as biomolecules because of their remarkable pharmacological properties. Some pyrazole-containing compounds, for instance, have been effectively developed into commercial drugs, such as the insecticide Fipronil and drugs such as Celebrex, Acomplia and Viagra [12, 13].
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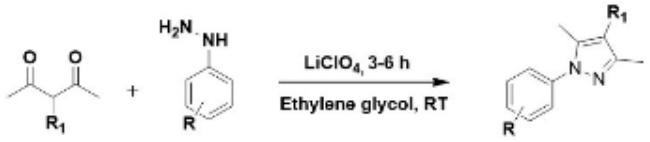
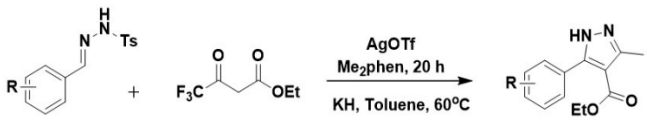
Literature review of synthesis of pyrazole and pyrazole derivatives: Our review of the literature revealed no references to the synthesis of pyrazole derivatives using a natural catalyst As a result, only references that used metal catalysts, long reaction time, temperature, and highly acidic conditions were located. A handful of the references that were covered here have been highlighted:

Pyrazoles from 1,3-Diketones: A fast and easy technique to yield polysubstituted pyrazoles is the cycloaddition of hydrazine derivatives with 1,3-dicarbonyl compounds. Knorr and his collabortors accomplished the initial synthesis of substituted pyrazoles in 1883 [14]. Konwar *et al*. established an eco-friendly procedure for synthesizing pyrazole derivatives, employing lithium perchlorate as Lewis acid catalyst (Scheme 1)[15].



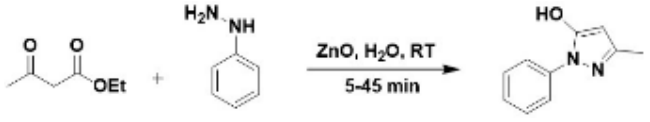
Scheme 1: Synthesis of 1,3,5-substitued pyrazoles from substituted acetylacetone.

Xu *et al*. reported the synthesis of 5-aryl-3-trifluoromethyl pyrazoles, which involved a silver-catalysed reaction using N^1 -benzylidene tolylsulfonohydrazides and ethyl 4,4,4-trifluoro-3-oxobutanoate as precursors Scheme 2 [16].



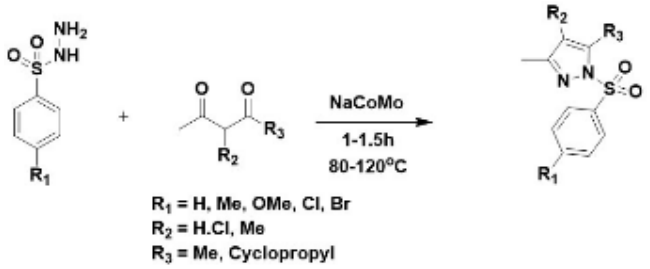
Scheme 2: Synthesis of 5-aryl-3-trifluoromethyl pyrazoles in the presence of a silver catalyst.

Girish *et al*. conducted a remarkable study where they introduced a highly efficient and environmentally friendly approach using nano-ZnO catalyst for synthesizing 1,3,5-substitued pyrazole derivatives [17] The process involved the condensation of phenyl hydrazine with ethyl acetoacetate under controlled conditions (Scheme 3).



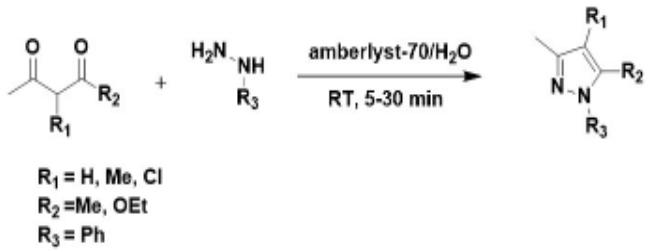
Scheme 3. Synthesis of 3-methyl-1-phenyl-*1H*-pyrazol-5-ol using Nano-ZnO as catalyst.

Yang *et al*. made a remarkable discovery by uncovering a new metal-oxo-clusters based inorganic framework called "3D platelike ternary-oxo-cluster" (NaCoMo), which serves as an efficient catalyst for the synthesis of novel pyrazole derivatives Scheme 4 [18].



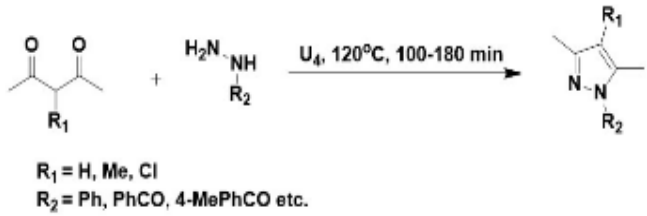
Scheme 4: Synthesis of substituted pyrazoles using NaCoMo as catalyst.

Chandak and his collaborators documented an environmentally friendly and efficient aqueous synthesis of pyrazole via the condensation of hydrazines or hydrazines with 1,3-diketones at room temperature, utilizing Amberlyst -70 as the catalyst (Scheme 5) [19].



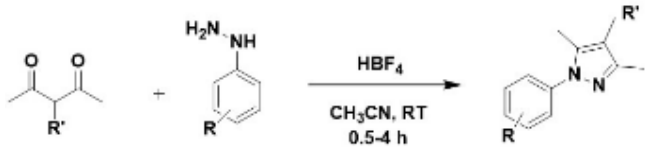
Scheme 5: Amberlyst-70 catalyzed the synthesis of pyrazole derivatives.

Liu *et al*. made an exciting discovery of a novel Keggin-based U-POW (U(VI)- containing polytungstates) tetramer,referred to as U_4 [20]. This tetramer showcased remarkable bifunctional Lewis's acid-base catalytic properties and exhibited excellent performance in the synthesis of pyrazoles via the condensation of diverse hydrazines with 1,3-diketones under mild reaction conditions (Scheme 6).



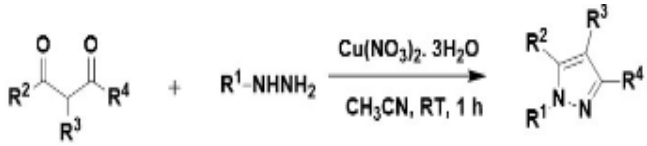
Scheme 6: Synthesis of pyrazole derivatives catalyzed by U_4.

Hazarika *et al*. reported a new and effective approach for the synthesis of pyrazoles using fluoroboric acid as the acid catalyst [13]. Here, the substrates used were easily accessible 1,3-diketone and hydrazine derivatives Scheme 7.



Scheme 7: Synthesis of pyrazoles using fluoroboric acid as the acid catalyst

Wang *et al*. reported an efficient method for the synthesis of pyrazoles via. copper-catalyzed condensation reaction (Scheme 8) [21].

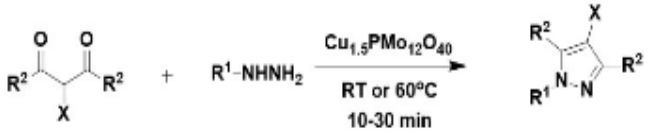


Scheme 8

Synthesis of pyrazoles using Copper nitrate.

Another significant contribution in this field has been made by Yang *et al*. In this work they have synthesized an polyoxometalate i.e. $Cu_{1.5}PMo_{12}O_{40}$ and utilized it as catalyst

for the synthesis of pyrazole derivatives using hydrazines/hydrazide and 1,3-diketones under mild reaction conditions [22].



Scheme 9: Synthesis of pyrazoles using polyoxometalate i.e. $Cu_{1.5}PMo_{12}O_{40}$

In spite of significant progress over the past few decades, the practical uses of this technology are limited. Therefore, there is an urgent need to develop a method that is much more convenient, considerably greener, and appropriate for industrial production processes. In this work, we would like to describe a novel method using *Dillenia indica* fruit core extract as a natural acid catalyst to synthesize pyrazole and its derivatives under mild reaction conditions

Materials and Methods

Dillenia indica fruit were purchased from the local market of Guwahati. Chemicals used in this work were of analytical grade and procured from commercial sources. Silica gel (230-400 mesh) was used in Column chromatography for the purification of crude reaction mixture. ^{1}H and ^{13}C NMR spectra were obtained from Bruker 300 MHz spectrometer with $CDCl_3$ as the solvent using TMS internal standard.

Preparation of Extract from Elephant Apple:

The fruit core of the elephant apple was cut into many tiny pieces by using a knife. These tiny pieces were chopped into solid paste using mixer. 120 mL of ethanol was added to the paste, sonicated at 50 ℃ for one hour. Then the mixture was filtered to yield the desired core extract. The pH of the extract was measured at 25 ℃ as 4.87 (**Figure 1**). Due to the acidic pH of the extract, it can be a probable candidate for its use as acid catalyst for further experimental processes.

A B C

D E

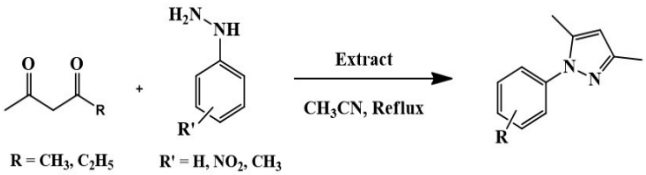
Fig 1: (A) Elephant apple fruit (B) Elephant apple fruit core (C) Grinded elephant apple fruit in a conical flask (D) Filtration of elephant apple core and ethanol mixture (E) Measurements of the pH of the extract of the prepared *Dillenia indica* fruit core using pH meter

Results and Discussions

Catalytic activity of the *Dillenia indica* fruit core extract for the Synthesis of pyrazole derivatives:

Experimental Procedure

During the synthesis of pyrazole derivative, the reaction was carried out by taking 1 mmol of phenyl hydrazine (substrate 1) and 1.2 mmol of acetyl acetone (substrate 2) in a round bottom flask. 5 mL of acetonitrile and 1 mL of extract was added to the above mixture. The reaction mixture was then subjected to reflux condition for 12 h. The progress of the reaction was monitored by using thin layer chromatography. Upon completion of 12 h, usual work up was performed with the reaction mixture using ethyl acetate as solvent. Thereafter the reaction mixture was concentrated under reduced pressure. Purification of the crude residue was done with column chromatography by using silica gel (230-400) and a combination of petroleum ether and ethyl acetate as an eluent. Thereafter, similar experimental method is followed with other substrates.



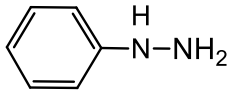
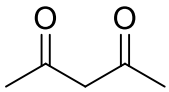
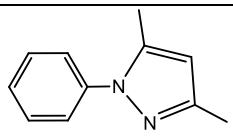
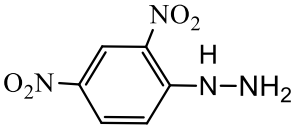
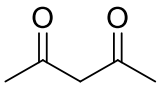
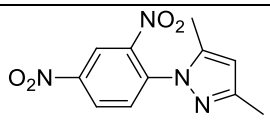
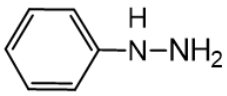
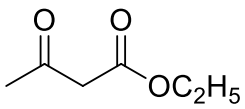
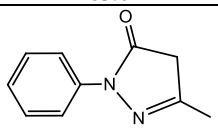
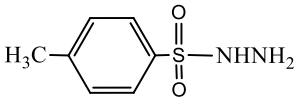
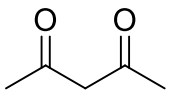
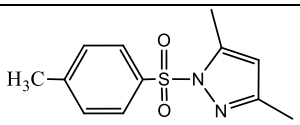
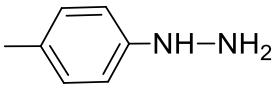
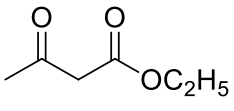
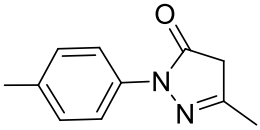
Scheme 10: General Scheme for the synthesis of pyrazoles using *Dillenia indica* fruit core extract. Phenyl Hydrazine and Acetyl-acetone were used as model substrates for the reaction's optimization, and the effects of the solvent, time, and fruit extract quantity were examined. The table 1 below provides a summary of the reaction's optimization outcomes.

Table 1: Optimization Table

Sl. No.	Substrate 1 Phenyl Hydrazine (mmol)	Substrate 2 Acetyl- Acetone (mmol)	Extract (mL)	Solvent (mL)	Time (h)	Yield (%)
1.	1	1.2	1	Acetonitrile (5)	3	Trace
2.	1	1.2	1	Acetonitrile (5)	6	46%
3.	1	1.2	1	Acetonitrile (5)	9	73%
4.	1	1.2	1	Acetonitrile (5)	12	77%
5.	1	1.2	1	Methanol (5)	12	68%
6.	1	1.2	1	Ethanol (5)	12	69%
7.	1	1.2	2	Acetonitrile (5)	12	79%
8.	1	1.2	--	Acetonitrile (5)	24	Trace
9.	1	1.2	1	Water (5)	24	N.R

To investigate the reaction's compatibility with other substrates, the reaction was conducted using a variety of substrates after the optimized conditions were established. The substrates were substituted for various derivatives of diketones and hydrazines, with varied substituents, and the reaction was conducted under ideal circumstances i.e. summarized in table 2:

Table 2: Substrate Scope

Sl. No.	Substrate 1 Structure	Substrate 2 Structure	Product (Yield)
1.			 77%
2.			 65%
3.			 68%
4.			 72%
5.			 75%

Reaction Condition: Substrate 1 (1 mmol), Substrate 2 (1.2 mmol), Catalyst = Fruit Extract (1mL); Reflux, time = 12 h

Spectral Analysis

3,5-Dimethyl-1-phenyl-1H-pyrazole

^{1}H(300 MHz, $CDCl_3$) δ ppm: 7.39-7.38 (m, 4H), 7.30-7.28 (m, 1H), 5.947 (s, 1H), 2.264 (s, 3H), 2.237 (s, 3H); **^{13}C**(75 MHz, $CDCl_3$) δ ppm: 148.6, 139.6, 139.1, 128.9, 128.7, 128.5, 127.1, 126.9, 124.7, 124.5, 106.7, 13.2, 12.0.

1-(2,4-Dinitrophenyl)-3,5-dimethyl-1H-pyrazole

^{1}H(300 MHz, $CDCl_3$) δ ppm: 8.77 (s, 1H), 8.52-8.51 (J = 1.8 Hz, d, 1H), 7.69-7.67 (J = 4.8 Hz, d, 1H), 6.08 (s, 1H), 2.25 (s, 3H). 2.24 (s, 3H); **^{13}C**(75 MHz, $CDCl_3$) δ ppm: 152.4, 146.3, 145.7, 140.9, 137.9, 129.4, 127.3, 121.0, 108.9, 13.4, 11.6.

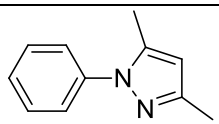
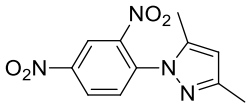
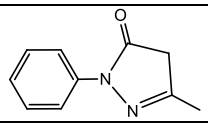
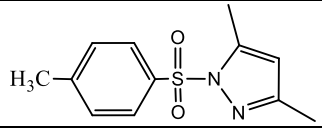
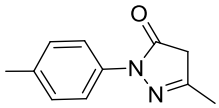
3-Methyl-1-phenyl-1H-pyrazol-5(4H)-one: ^{1}H(300 MHz, $CDCl_3$) δ ppm: 7.85-7.83 (J = 4.8 Hz, d, 2H), 7.38-7.35 (J = 4.8 Hz, t, 2H), 7.17-7.14 (J = 4.2 Hz, t, 1H), 3.39 (s, 2H), 2.16 (s, 3H); **^{13}C**(75 MHz, $CDCl_3$) δ ppm: 170.5, 156.2, 138.0, 128.8, 124.9, 118.8, 43.0, 16.9.

3,5-Dimethyl-1-tosyl-1H-pyrazole

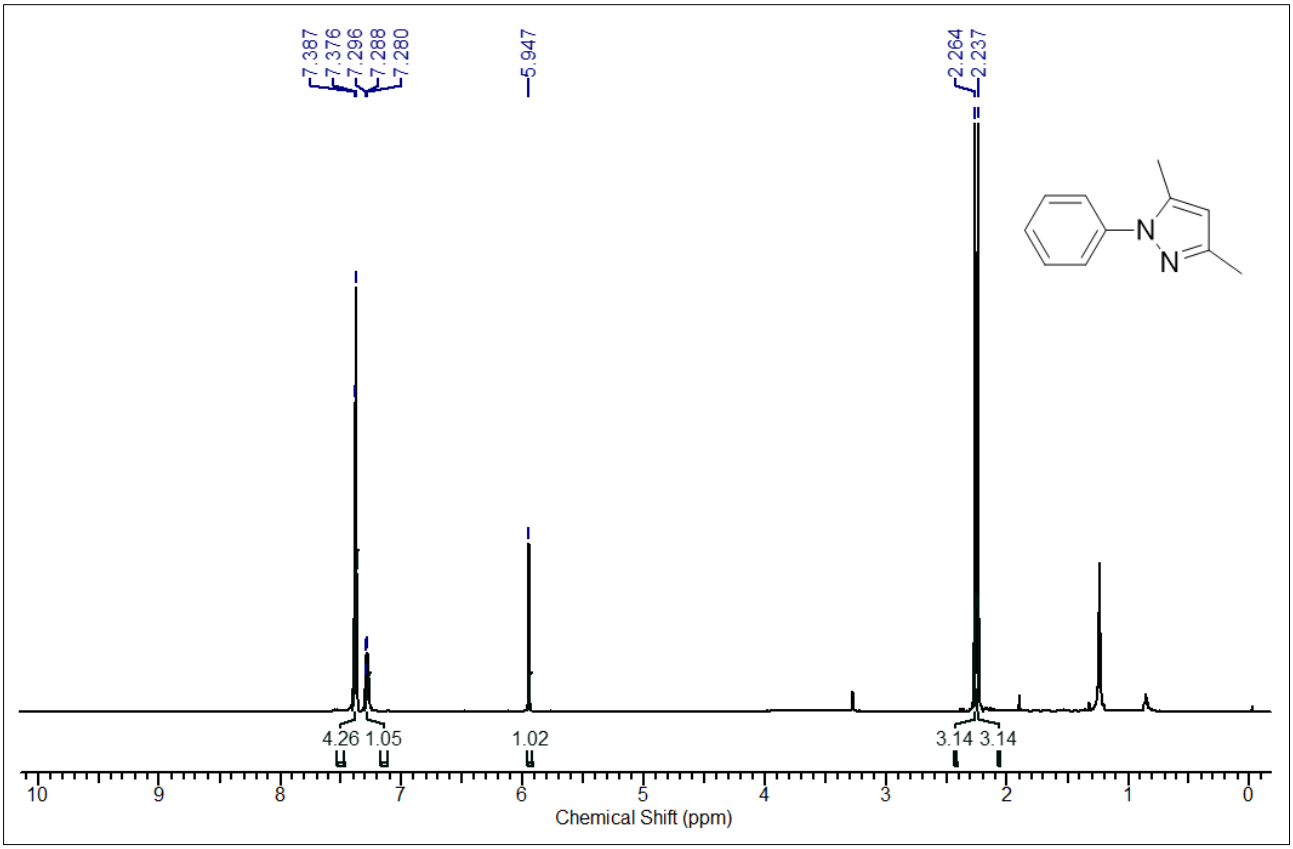
^{1}H(300 MHz, $CDCl_3$) δ ppm: 7.80-7.79 (J = 4.8 Hz, d, 2H), 7.28-7.26 (J = 3.9 Hz, d, 2H), 5.86 (s, 1H), 2.46 (s, 3H), 2.38 (s, 3H), 2.16 (s, 3H); **^{13}C**(75 MHz, $CDCl_3$) δ ppm: 153.3, 145.1, 144.0, 135.3, 129.8, 127.5, 110.7, 21.6, 13.7, 13.0.

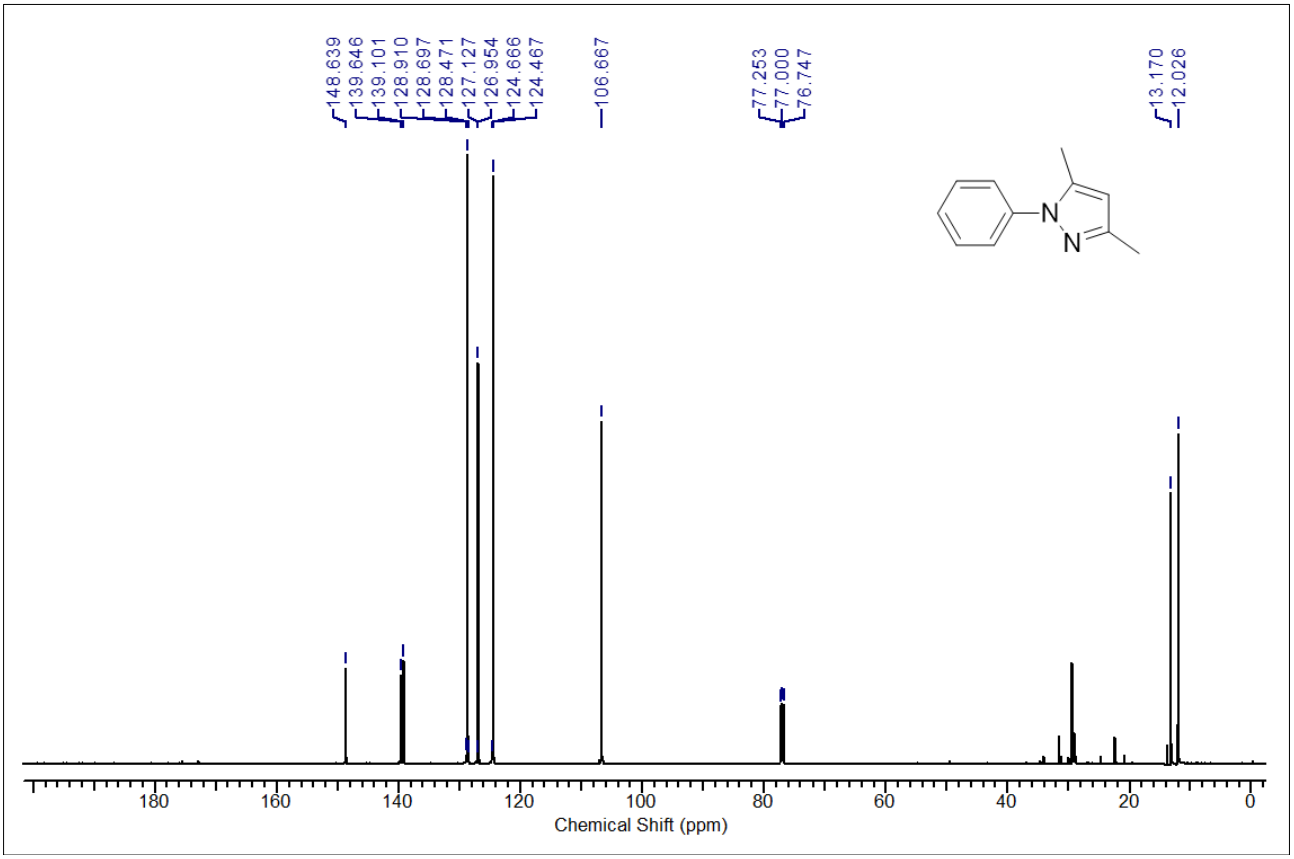
3-Methyl-1-(p-tolyl)-1H-pyrazol-5(4H)-one: ^{1}H(300 MHz, $CDCl_3$) δ ppm: 7.71-7.69 (J = 4.8 Hz, d, 2H), 7.17-7.15 (J = 4.8 Hz, d, 2H), 3.36 (s, 2H), 2.31 (s, 3H), 2.14 (s, 3H); ^{13}C(75

MHz, $CDCl_3$) δ ppm: 170.34, 156.04, 135.58, 134.59, 129.22, 118.85, 42.92, 20.82, 16.84.

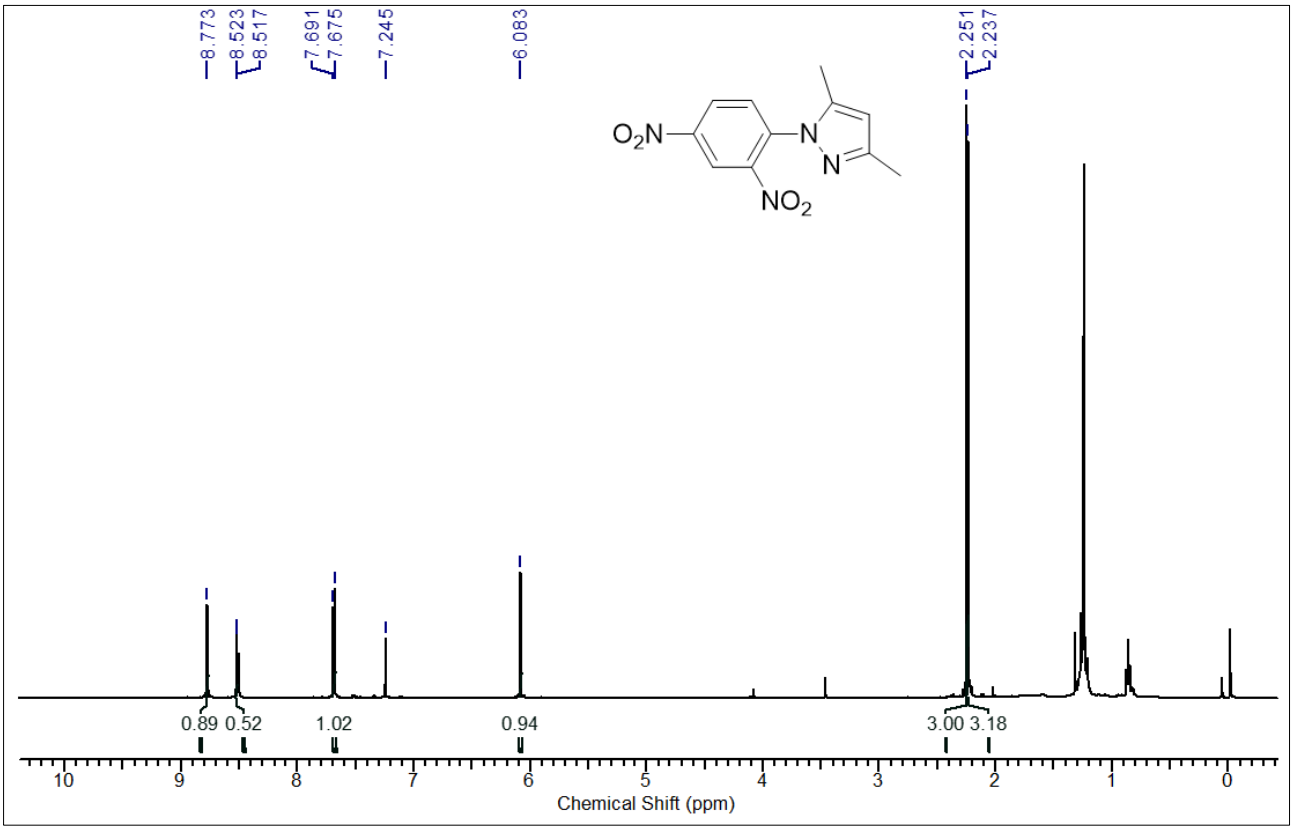
3,5-Dimethyl-1-phenyl-1H-pyrazole [1]	
^{1}H(300 MHz, $CDCl_3$) δ ppm: 7.39-7.38 (m, 4H), 7.30-7.28 (m, 1H), 5.947 (s, 1H), 2.264 (s, 3H), 2.237 (s, 3H) ^{13}C(75 MHz, $CDCl_3$) δ ppm: 148.6, 139.6, 139.1, 128.9, 128.7, 128.5, 127.1, 126.9, 124.7, 124.5, 106.7, 13.2, 12.0	
1-(2,4-Dinitrophenyl)-3,5-dimethyl-1H-pyrazole [1]	
^{1}H(300 MHz, $CDCl_3$) δ ppm: 8.77 (s, 1H), 8.52-8.51 (J = 1.8 Hz, d, 1H), 7.69-7.67 (J = 4.8 Hz, d, 1H), 6.08 (s, 1H), 2.25 (s, 3H). 2.24 (s, 3H) ^{13}C(75 MHz, $CDCl_3$) δ ppm: 152.4, 146.3, 145.7, 140.9, 137.9, 129.4, 127.3, 121.0, 108.9, 13.4, 11.6	
3-Methyl-1-phenyl-1H-pyrazol-5(4H)-one [2]	
^{1}H(300 MHz, $CDCl_3$) δ ppm: 7.85-7.83 (J = 4.8 Hz, d, 2H), 7.38-7.35 (J = 4.8 Hz, t, 2H), 7.17-7.14 (J = 4.2 Hz, t, 1H), 3.39 (s, 2H), 2.16 (s, 3H). ^{13}C(75 MHz, $CDCl_3$) δ ppm: 170.5, 156.2, 138.0, 128.8, 124.9, 118.8, 43.0, 16.9.	
3,5-Dimethyl-1-tosyl-1H-pyrazole [1]	
^{1}H(300 MHz, $CDCl_3$) δ ppm: 7.80-7.79 (J = 4.8 Hz, d, 2H), 7.28-7.26 (J = 3.9 Hz, d, 2H), 5.86 (s, 1H), 2.46 (s, 3H), 2.38 (s, 3H), 2.16 (s, 3H) ^{13}C(75 MHz, $CDCl_3$) δ ppm: 153.3, 145.1, 144.0, 135.3, 129.8, 127.5, 110.7, 21.6, 13.7, 13.0.	
3-Methyl-1-(p-tolyl)-1H-pyrazol-5(4H)-one [2]	
^{1}H(300 MHz, $CDCl_3$) δ ppm: 7.71-7.69 (J = 4.8 Hz, d, 2H), 7.17-7.15 (J = 4.8 Hz, d, 2H), 3.36 (s, 2H), 2.31 (s, 3H), 2.14 (s, 3H). ^{13}C(75 MHz, $CDCl_3$) δ ppm: 170.34, 156.04, 135.58, 134.59, 129.22, 118.85, 42.92, 20.82, 16.84.	 3-methyl-1-(*p*-tolyl)-1*H*-pyrazol-5(4*H*)-one

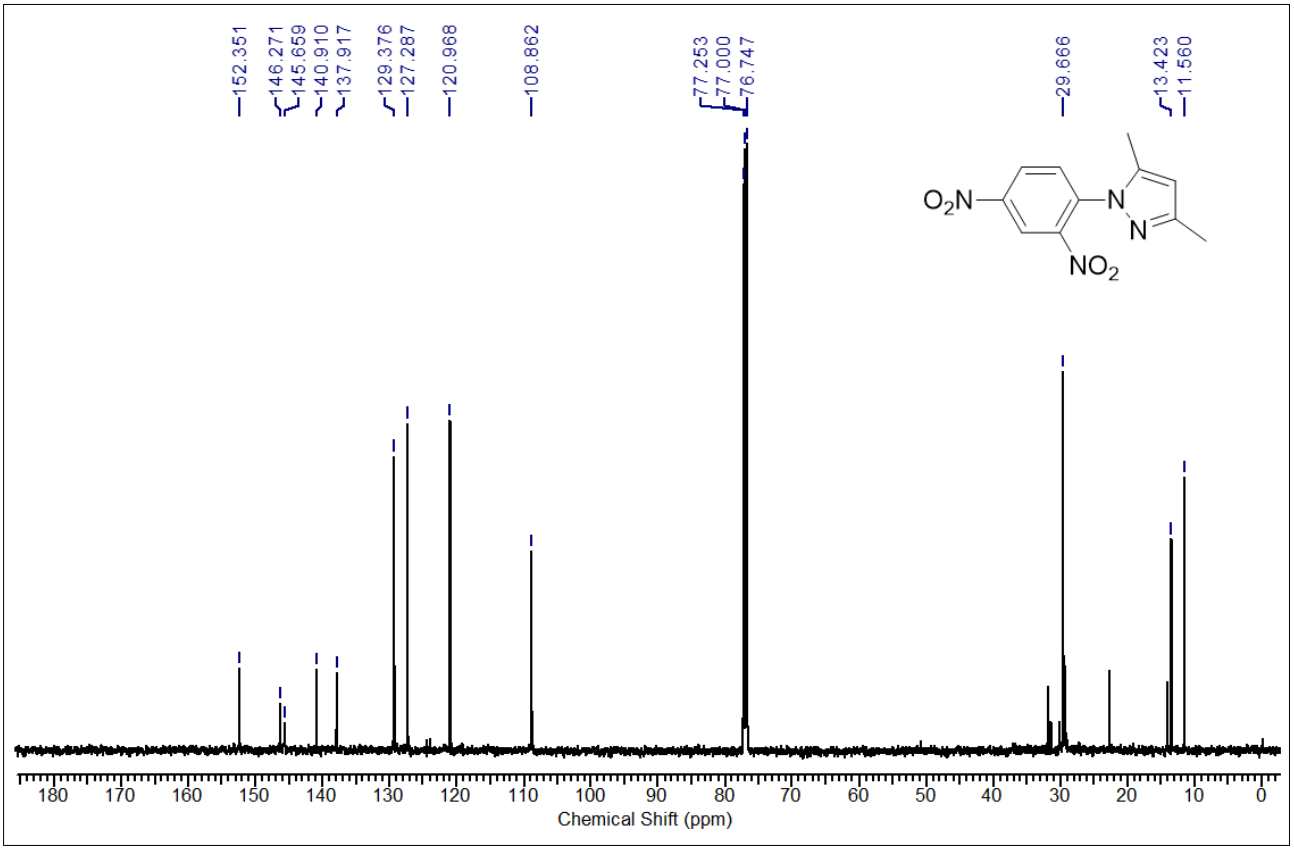
3,5-dimethyl-1-phenyl-1H-pyrazole (^{1}H NMR)



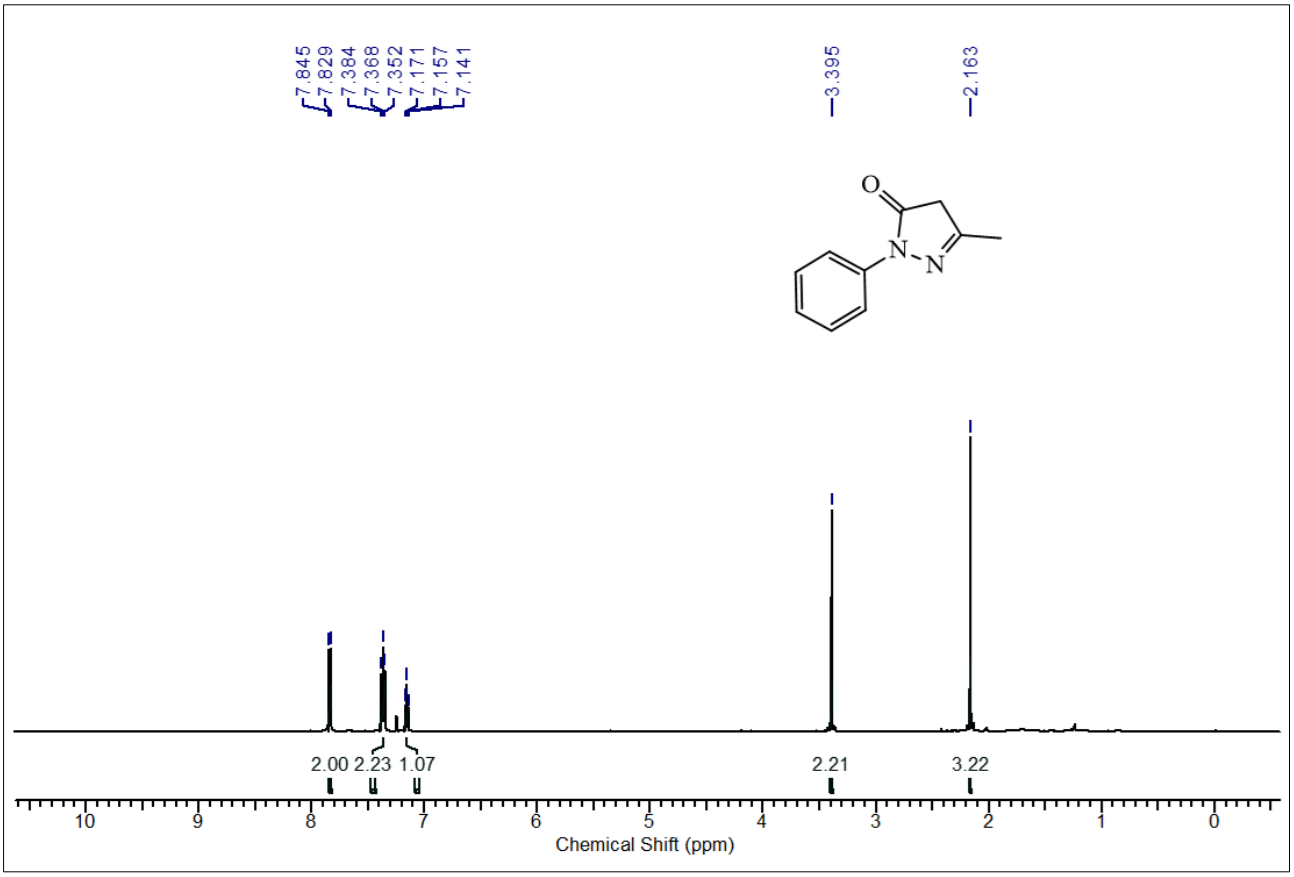


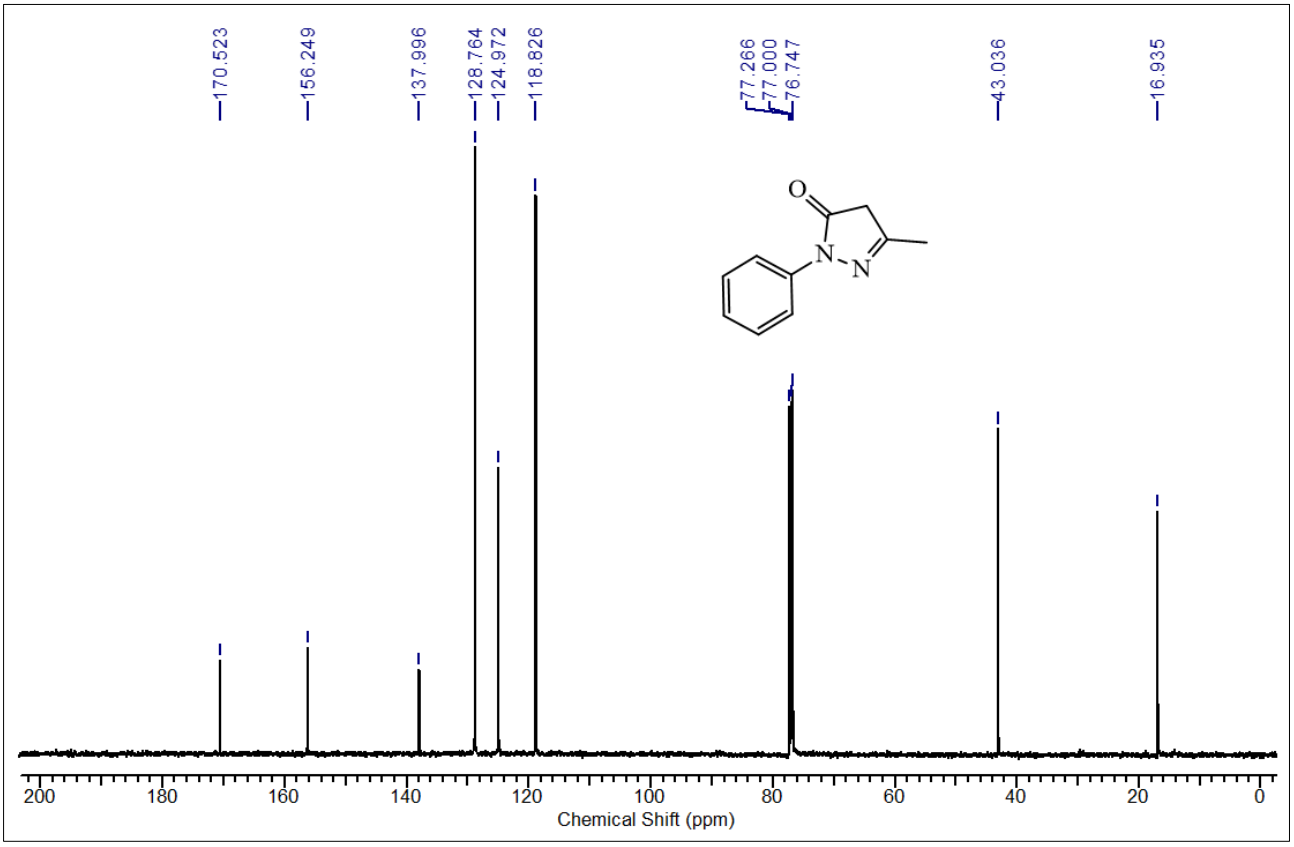
1-(2,4-dinitrophenyl)-3,5-dimethyl-1H-pyrazole



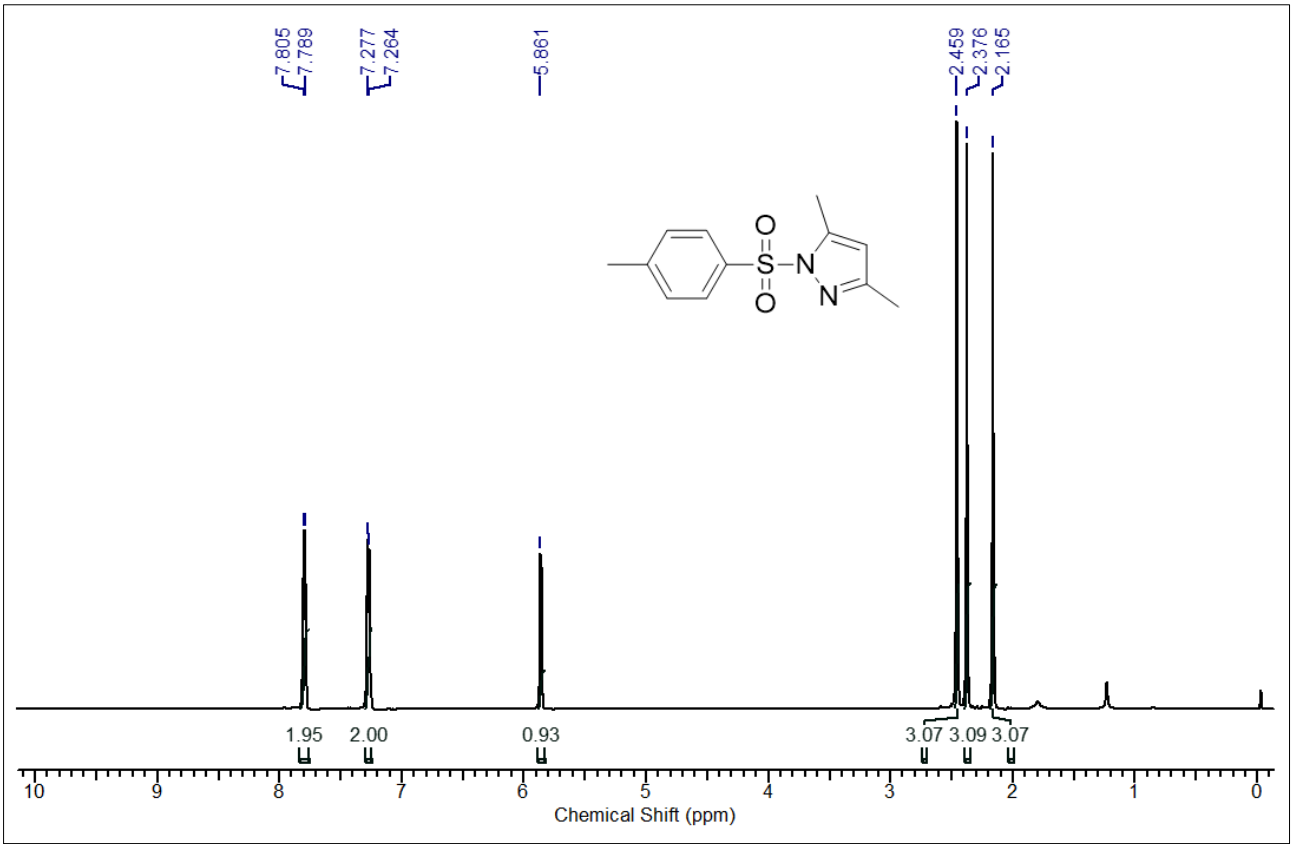


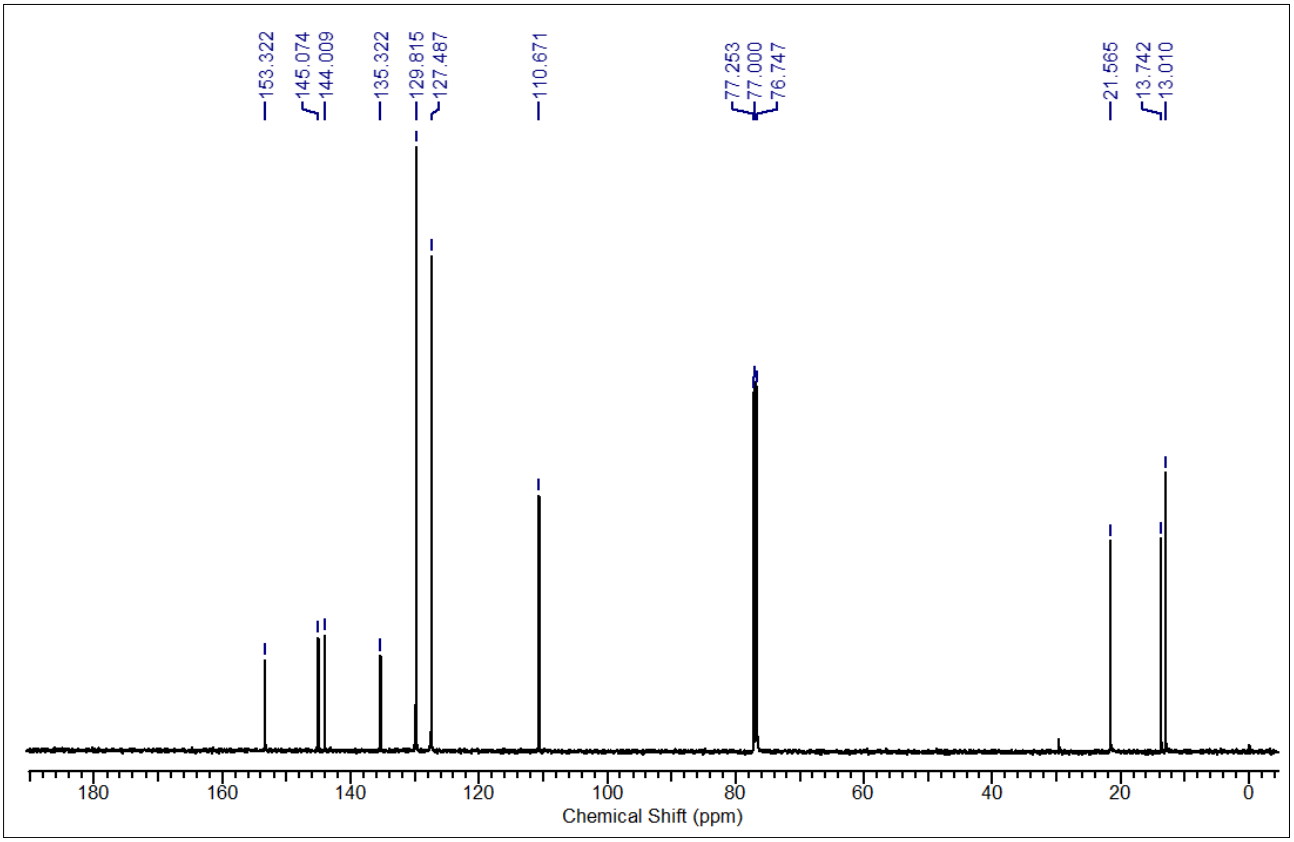
3-methyl-1-phenyl-1H-pyrazol-5(4H)-one



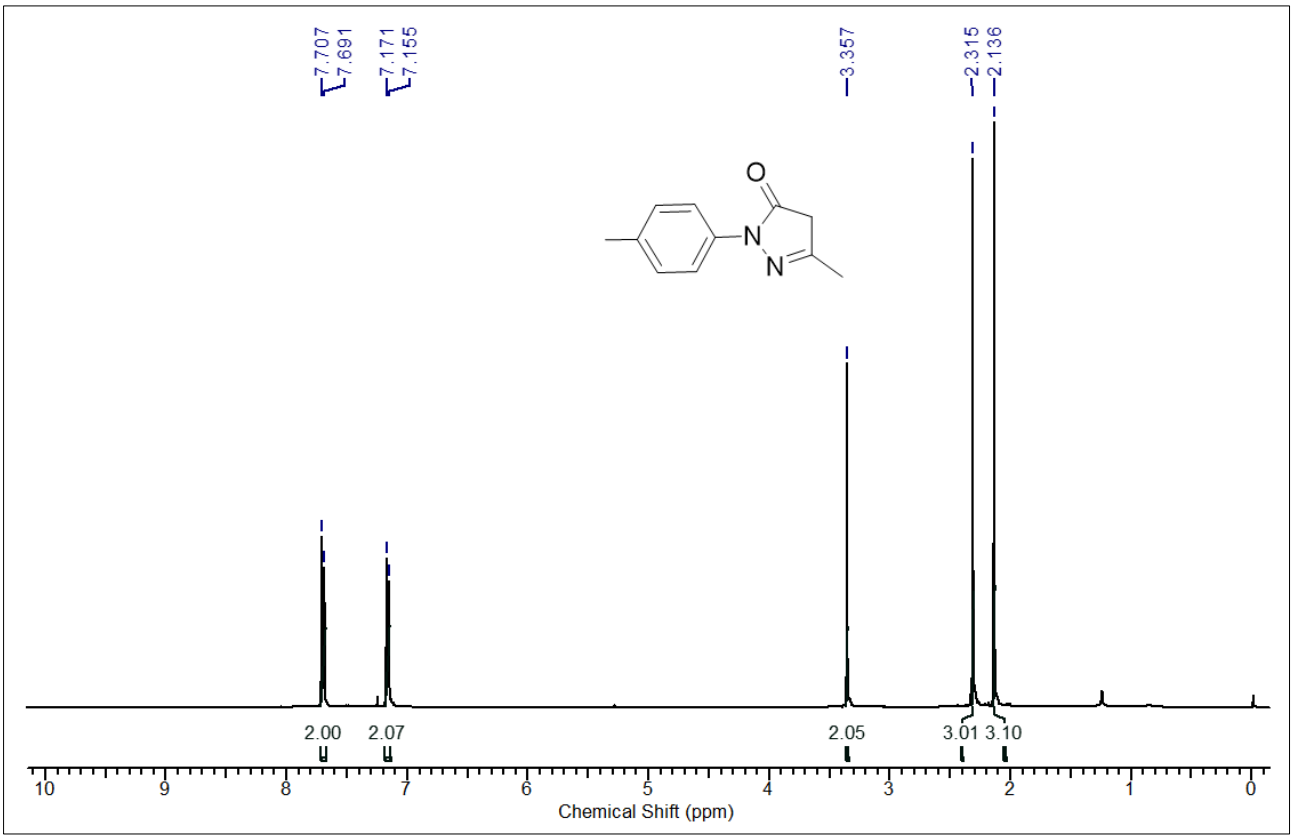


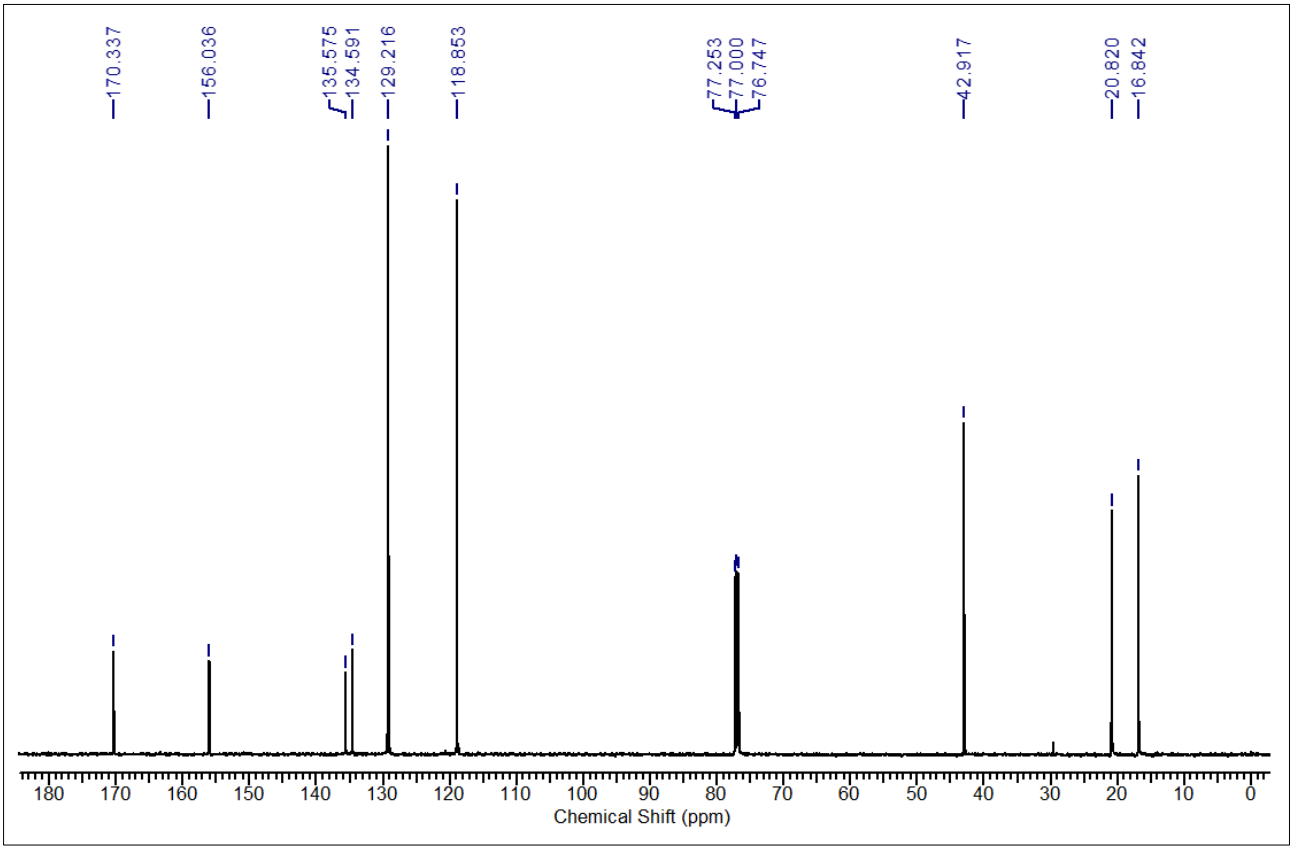
3,5-dimethyl-1-tosyl-1H-pyrazole





3-methyl-1-(p-tolyl)-1H-pyrazol-5(4H)-one





Conclusion

An efficient metal free protocol has been developed for the synthesis of pyrazole derivatives using *Dillenia indica* fruit extract. Strong acids and metal catalysts, which are often corrosive and harmful to both humans and the environment, can be replaced by the extract's acidic nature. Various reactions were performed using phenyl hydrazine and substituted-phenyl hydrazine such as *p*-tolunesulphonylhydrazide, 2,4-Dinitro phenyl hydrazine, 4-Methyl phenyl hydrazine and diketone derivatives as substrates to yield the desired products in moderate to good yields.

Conflict of interests

There are no conflicts to declare.

Acknowledgement:

Financial support from Arya Vidyapeeth College -IRG [grant no. AVC/RC/2023/931-38] is gratefully acknowledged. We also acknowledge support from the Department of Chemistry, Gauhati University, SAIF-GU for all the analytical facilities used during the course of this investigation.

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