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$SiO_2/ZnBr_2$ mediated expeditious approach to 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one derivatives in water under microwave irradiation

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Abstract

A new one-pot three-component green approach has been developed for the synthesis of a series of pyrazolone derivatives **2** (**a-s**) from differently substituted aldehydes, ethylacetoacetate and phenylhydrazine/2,4-Dinitrophenylhydrazine in excellent yields (94-98%), employing $SiO_2/ZnBr_2$ as a recyclable Lewis acid catalyst in water under microwave heating. The molecular structure of compounds **2a** and **2d** were well supported by single crystal X-ray crystallographic analysis. The present protocol bears wide substrate tolerance and is believed to be more practical, efficient, eco-friendly and compatible as compare to existing methods.

Keywords: $SiO_2/ZnBr_2$, Pyrazolone, Microwave, X-ray analysis, Eco-friendly.

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Introduction

In the last few decades application of clean technologies in chemical synthesis has turn out to be the major area of research in green chemistry.[1] The eco-friendly and reusable heterogeneous catalysts have been the major constituent for providing such clean technologies. Due to rapid advances in medicinal chemistry, great attention has been paid towards the development of novel clean processes employing nontoxic reagents, catalysts and solvents.[2]

Pyrazolone derivatives are an important class of heterocyclic compounds as they play a vital role both in medicinal chemistry and in organic synthesis.[3] These compounds exhibit remarkable pharmaceutical properties such as analgesic, antitubercular, antimicrobial, anti-inflammatory and antioxidant.[4-8] Moreover compounds possessing pyrazolones moiety are gaining much importance especially in drug discovery programs[9] and have been used as cardiotonics,[10,11] anticancer (TELIN)[12] and as potent inhibitors of the enzyme GSK3b.[13] Pyrazolones are traditionally synthesized by treatment of δ-keto esters with hydrazine substrates under acidic conditions.[14] A number of alternative methods have been documented in the literature for the synthesis of pyrazolone derivatives such as solid-state condensation,[15] electrocatalytic procedure[16] and ultrasonic irradiation technique[17] for this synthesis. Moreover, Rajeev and co-workers reported its synthesis under microwave irradiation[18] (**Scheme 1**). Various catalysts have also been used for the preparation of these compounds *via* the condensation reaction. These catalysts include acetic acid or piperidine,[19] silica-bonded S-sulfonic acid,[20] sodium dodecyl sulfate,[21] CAN,[22] and ETBA.[23] Now a day's a great deal of interest has been placed towards the reactions in presence of water.[24] Breslow and Lindstrom reported that hydrophobic effect of water is responsible for the organic reaction.[25,26]

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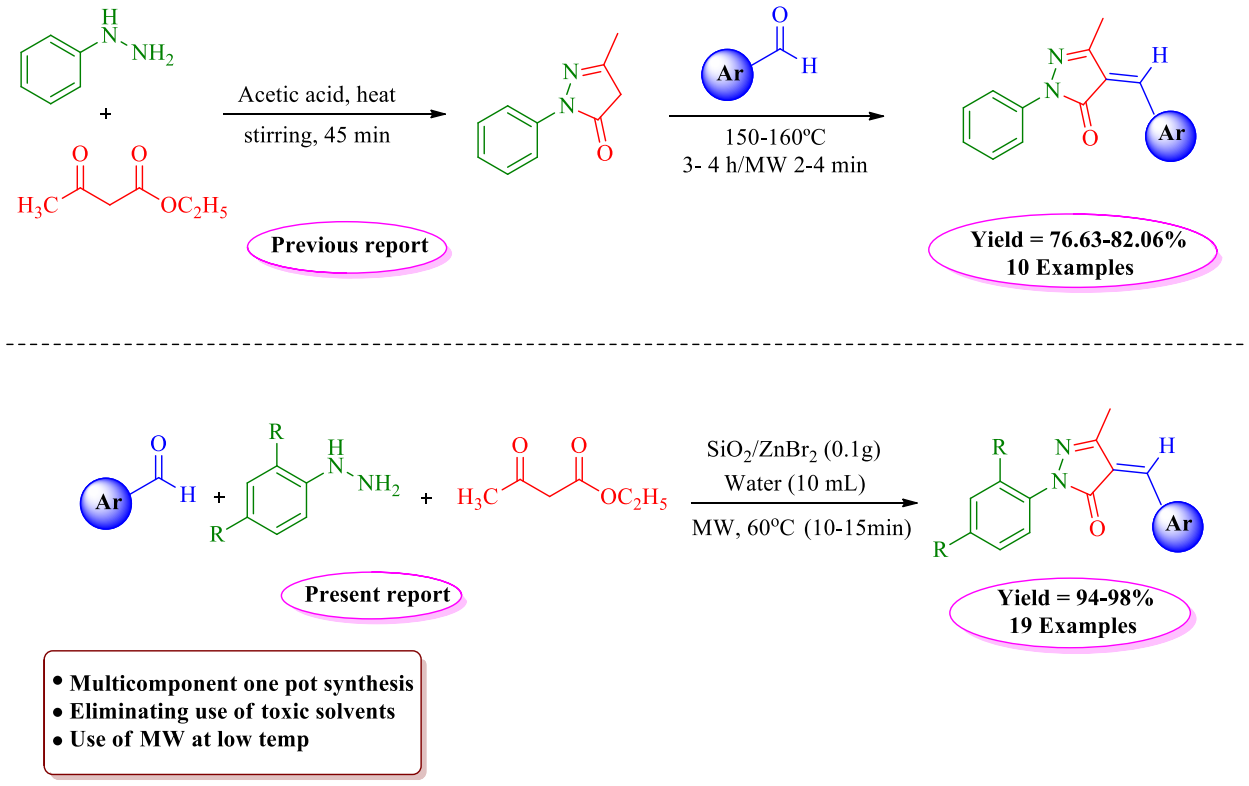

Scheme 1 Synthetic route for pyrazolone using microwave

Although the reported protocol has lots of significance in advance chemistry due to cheap, nontoxic and nonflammable nature of water, serves as environmentally benign solvent and good yields of the products, but long reaction time and solubility of the substrate makes it less applicable. Moreover the combination of water with microwaves has lead to the development of rapid, effective and environmentally benign synthetic methodologies.[27] To the best of our knowledge silica supported zinc bromide ($SiO_2/ZnBr_2$) has not been used as a catalyst for the synthesis of 3-methyl-1-phenyl-1*H*-pyrazol-5(*4H*)-one derivatives. As a part of our research

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program on the development of new synthetic methods[28-30] under the aspects of green chemistry, herein, we report for the first time the development of an efficient, economical and recyclable silica supported $ZnBr_2$ promoted synthesis of pyrazolone derivatives in excellent yields *via* three component reaction of aromatic aldehydes, ethylacetoacetate and phenylhydrazine/2,4-Dinitrophenylhydrazine (2,4-DNP) in water under microwave heating.

The $SiO_2/ZnBr_2$ catalyst has emerged as a promising heterogeneous solid catalyst for various organic transformations. Keivanloo *et.al* exploited $SiO_2/ZnBr_2$ for the synthesis of ynones[31] by cross-coupling of acid chloride with terminal alkynes and synthesis of 4,5-disubstituted 1,2,3-(*NH*)- triazoles.[32] Moreover, Kodomari and co-workers[33] also reported the synthesis of triarylmethanes and 9,10-diarylanthracenes and Clark *et al*[34] reported bromination of aromatic substrate using $SiO_2/ZnBr_2$ catalyst. The catalyst possesses inherent environmentally benevolent properties such as non-toxicity, biocompatibility, physiological inertness, recyclability, inexpensiveness and thermal stability. The catalyst was prepared by employing standard procedures depicted in the literature[31] and recycled up to six runs. The formation of $SiO_2/ZnBr_2$ system was evaluated by FT-IR, powder XRD and SEM-EDX analysis. The stability of the catalyst was shown by TGA/DTA analysis.

Results and discussion

Characterization of catalyst ($SiO_2/ZnBr_2$)

The FT-IR spectrum of the catalyst ($SiO_2/ZnBr_2$) is depicted in Fig. 1. The FT-IR spectrum of the catalytic system displayed a symmetrical stretching band at 3483.37 cm^{-1} for hydroxyl group and the band resonating at 1632 cm^{-1} was attributed to the bending vibration of adsorbed water.[35] Moreover, asymmetric and symmetric stretching vibration band for Si-O-Si appeared at 1093.14

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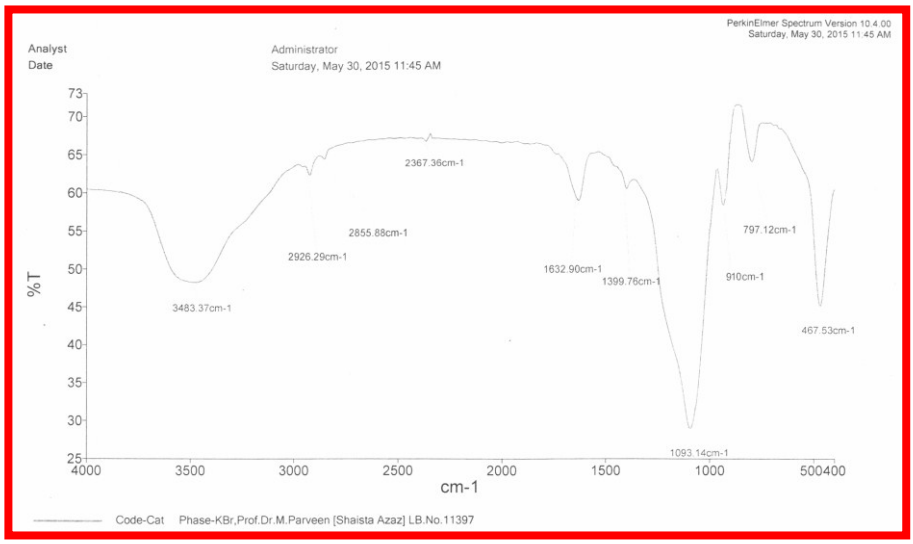

Fig. 1 FT-IR Spectrum of catalyst ($SiO_2/ZnBr_2$)

cm^{-1} and 797.12 cm^{-1}, respectively. In addition the peak resonating at 910 and 467.53 cm^{-1} has been assigned for the stretching vibration of Si-OH[35] and Zn-Br, respectively. Thus, FT-IR spectrum of the catalytic system authenticates the coating of $ZnBr_2$ on the SiO_2 surface as all the characteristic peaks related to silica and $ZnBr_2$ has been present in the spectrum of $SiO_2/ZnBr_2$.

Formation of the catalytic system ($SiO_2/ZnBr_2$) was further confirmed by powder XRD analysis (Fig. 2). X-ray diffractograms (XRD) of the catalyst were recorded in the 2θ range of 20-80°. A single broad peak in the range of 2θ = 20-30° ascribed to the amorphous nature of silica. The characteristic diffraction peaks of pure $ZnBr_2$ were reported to appear at 13.7°, 21.1°, 27.5°, 46.1° and 53.4°.[36] The XRD analysis of $SiO_2/ZnBr_2$ exhibited diffraction peak for $ZnBr_2$ only at 46.2° and 53.4°. However, the other characteristic peaks (21.1° and 27.5°) were merged with the broad peak of SiO_2 (2θ = 20-30°). The appearance of these characteristics peaks indicating the dispersion of $ZnBr_2$ on the silica material and thus confirming the formation of $SiO_2/ZnBr_2$ matrix.

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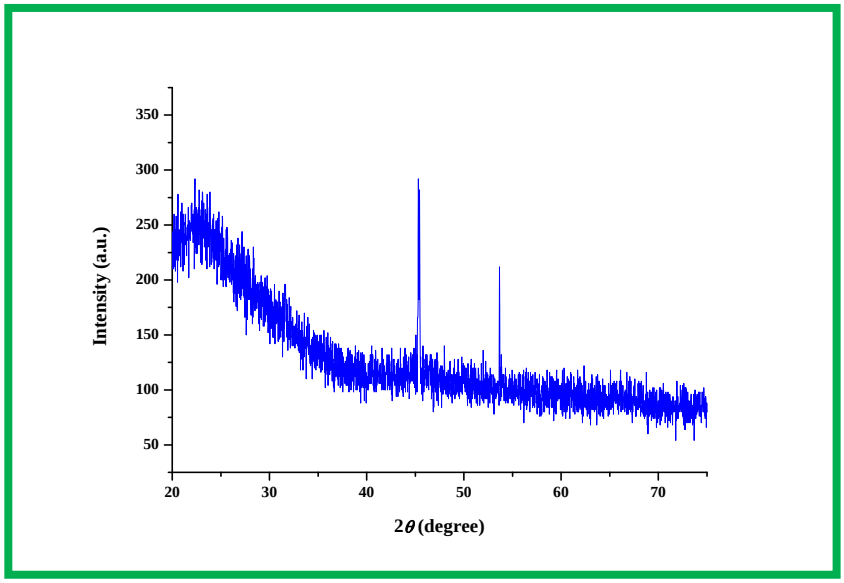

Fig. 2 Powder XRD pattern of catalyst ($SiO_2/ZnBr_2$)

SEM analysis was employed to study the surface morphology of the catalytic system (Fig. 3). SEM micrographs of the catalyst showed that the particles of $ZnBr_2$ were well dispersed on silica surface. The 3D surface plot (Fig. S1) (ESI†) of pure silica and $SiO_2/ZnBr_2$ were provided to further verify the adsorption of $ZnBr_2$ on silica surface. The white area of plot in figure S1(b) confirmed the successful adsorption of $ZnBr_2$ on the silica surface. The successful incorporation of zinc bromide was also confirmed by EDX analysis (Fig. 4). EDX spectrum showed the presence of Zn and Br in addition to O and Si elements.

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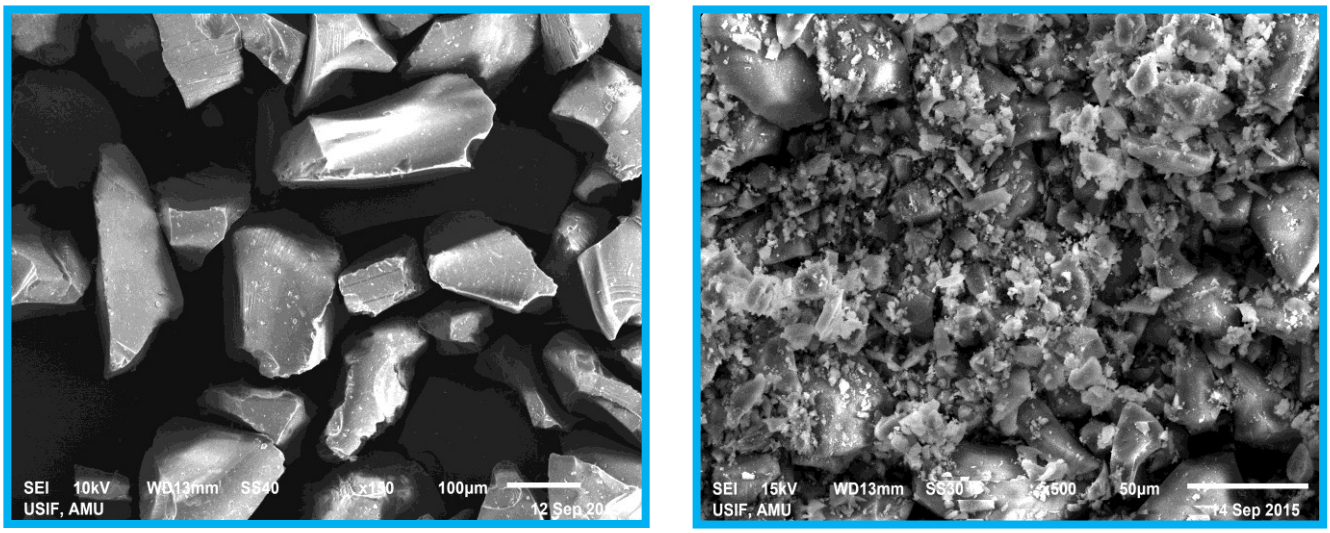

(a) **(b)**

Fig. 3 SEM micrograph of (a) pure SiO_2 (b) $SiO_2/ZnBr_2$ catalyst

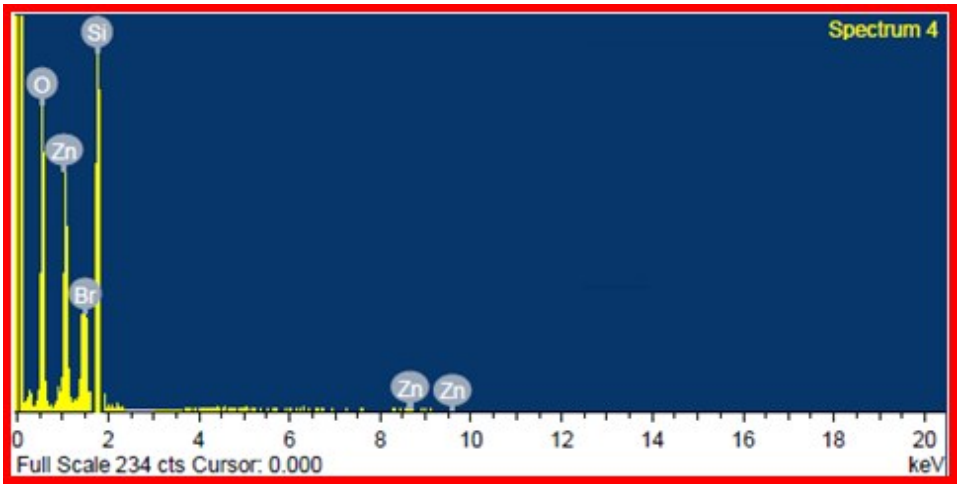

Fig. 4 EDX analysis of the catalyst ($SiO_2/ZnBr_2$)

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The thermal stability of the catalyst was determined by TGA analysis (Fig. 5). The only weight loss of 16.94% in the range of 40-120 °C was attributed to loss of physically adsorbed water molecules in the silica gel framework. TGA is further supported by DTA analysis in which a prominent peak at 93.04 °C showed endothermic reaction which help in the removal of water molecule (Fig. 5). Further there is no weight loss upto 800 °C. Therefore it can be concluded that physiosorbed and chemisorbed $ZnBr_2$ on silica surfaces is stable upto 800 °C.[37]

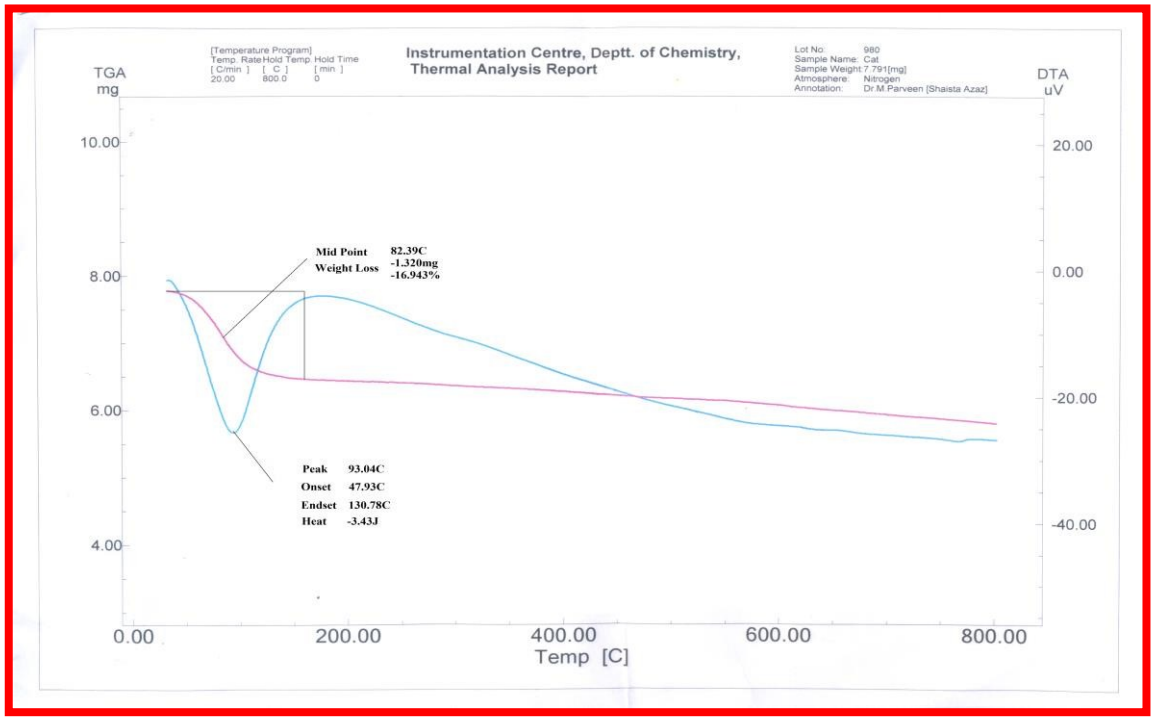

Fig. 5 TGA/DTA of catalyst ($SiO_2/ZnBr_2$)

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Optimization of reaction condition

In the present study a series of 3-methyl-1-phenyl-1*H*-pyrazol-5(*4H*)-one derivatives **2** (**a**-**s**) have been synthesized (**Scheme 2**), *via* a facile environmentally benign cyclization reaction, involving various aromatic aldehydes with ethylacetoacetate and phenylhydrazine to yield target 3-methyl-1-phenyl-1*H*-pyrazol-5(*4H*)-one derivatives in excellent yields (94-98%) with high purity.

To optimize the best reaction condition for these transformations, we investigate the solvent effect, catalyst loading, effect of temperature and recyclability of the catalyst on the model reaction. Initially, indole-3-carbaldehyde (**1a**, 2 mmol), phenylhydrazine (2 mmol) and ethylacetoacetate (2 mmol) were refluxed in water (10 mL) at 60 ^{o}C without any catalyst. The reaction took a longer time period of 24 h to complete and afforded desired product **2a** in less yield (Table 1, entry 1), signifying the need of a catalyst. The reaction was then studied in the presence of different catalysts such as $AlCl_3$, $ZnBr_2$, $FeCl_3$, SiO_2-Cl, $SiO_2/ZnBr_2$. Our analysis revealed that the catalytic activity of various catalysts in water at 60 ^{o}C was found to be in the order of $SiO_2/ZnBr_2$ > $AlCl_3$> $FeCl_3$ > $ZnBr_2$ > SiO_2-Cl (Table 1, entries 2-6). To compare the efficiency as well as competence of the reactions under aqueous condition, the model reaction was also examined in the presence of $SiO_2/ZnBr_2$ in different solvents like MeOH, EtOH, CH_3COOH, CH_2Cl_2, DMF and THF. The use of relatively less polar aprotic solvents CH_2Cl_2, DMF and THF yielded the product **2a** in moderate yield (58-62 %), after extended reaction time (Table 1, entries 10-12). However, in polar protic solvents MeOH, EtOH, and AcOH relatively high yield (65-70%) of the product **2a** was obtained with dip in reaction time (Table 1, entries 7-9), whereas when reaction was performed in water in the presence of $SiO_2/ZnBr_2$, there was remarkable increase in the yield (86%) of the product **2a** with prominent fall in reaction time (Table 1, entry 6).

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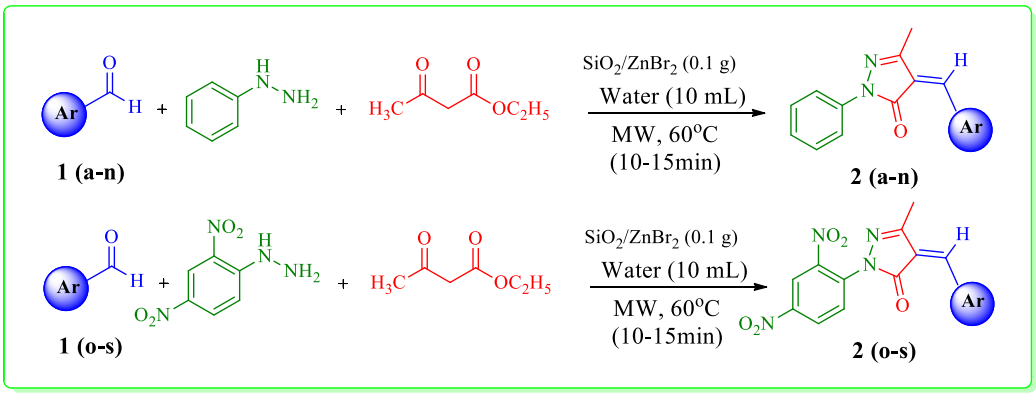

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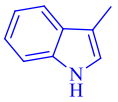
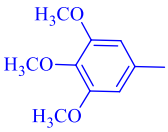
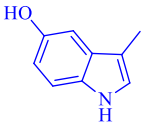
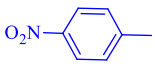
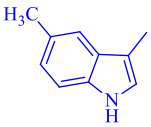
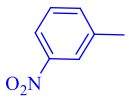
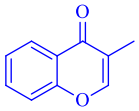
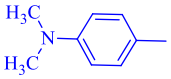
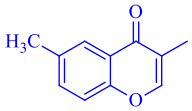
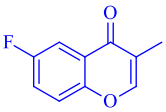
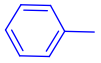
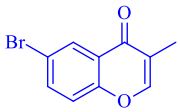
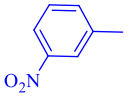
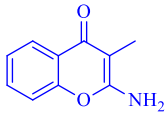
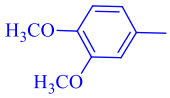
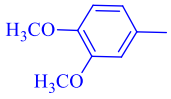
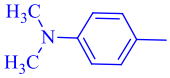
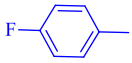
2a		2j	
2b		2k	
2c		2l	
2d		2m	
2e		2n	
2f		2o	
2g		2p	
2h		2q	
2i		2r	
		2s	

Scheme 2 Synthetic scheme for the synthesis of pyrazolone derivatives **2 (a-s)**

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Table 1 Effect of different reaction media on model reaction (**2a**)[a]

S.No.	Solvent	Condition	Time (h)[b]	Yield (%)[c]
1	Water	60 °C, without catalyst	24h	46
2	Water	60 °C, $AlCl_3$	8h	56
3	Water	60 °C, $ZnBr_2$	10h	52
4	Water	60 °C, $FeCl_3$	12h	53
5	Water	60 °C, SiO_2-Cl	16h	51
6	Water	60 °C, $SiO_2/ZnBr_2$	4h	86
7	MeOH	60 °C, $SiO_2/ZnBr_2$	6h	65
8	EtOH	60 °C, $SiO_2/ZnBr_2$	8h	70
9	CH_3COOH	60 °C, $SiO_2/ZnBr_2$	6h	68
10	CH_2Cl_2	60 °C, $SiO_2/ZnBr_2$	10h	62
11	DMF	60 °C, $SiO_2/ZnBr_2$	14h	60
12	THF	60 °C, $SiO_2/ZnBr_2$	18h	58
13	Water	60 °C, $SiO_2/ZnBr_2$, MW	10 min	98

[a]*Reaction condition*: indole-3-carbaldehyde (**1a**, 2 mmol), phenylhydrazine (2 mmol), and ethylacetoacetate (2 mmol), different solvent (10 mL), different catalyst (0.10 g)
[b]Reaction progress monitored by TLC
[c]Isolated yield of products

In order to further improve the protocol to make it more energy efficient we introduced microwaves. The use of microwaves (Anton Paar, Monowave 300) enhanced the protocol remarkably with high yield of the product **2a** (98%) and short reaction period (10 min) (Table 1, entry 13).

To achieve the optimum concentration of the catalyst, the model reaction (**2a**) was investigated at different concentrations 0.02-0.12 g (Table 2, entries 1-6) of the catalyst $SiO_2/ZnBr_2$ at 60 ^oC in water under MW. The best results were obtained with the use of 0.10 g of catalyst. Using less than 0.10 g of catalyst, moderate yields of the product **2a** (66-83%) were obtained with extended reaction times, while increasing catalyst amount 0.10-0.12 g, there was

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no further increase in the yield of the product **2a**, possibly due to the saturation of the catalyst. The above results signify that 0.10 g of $SiO_2/ZnBr_2$ is optimum dose in terms of efficient yield and reduced reaction time.

Table 2 Effect of catalyst loading on the yield and reaction time of model reaction (**2a**)[a]

Entry	Catalyst (g)	Time (min)[b]	Yield (%)[c]
1	0.02	35	60
2	0.04	30	68
3	0.06	28	75
4	0.08	25	83
5	0.10	10	98
6	0.12	10	98

[a]*Reaction condition*: indole-3-carbaldehyde (**1a**, 2 mmol), phenylhydrazine (2 mmol), and ethylacetoacetate (2 mmol), water (10 mL), $SiO_2/ZnBr_2$ (0.02-0.12 g), MW-60 °C
[b]Reaction progress monitored by TLC
[c]Isolated yield of products

To optimize the reaction temperature, the model reaction was carried out at different temperatures in water under microwave heating (Table 3, entries 1-7). It was observed that increase in temperature from 25 ^oC to 60 ^oC, has a noteworthy effect on the model reaction in terms of yield and reaction time (Table 3, entries 1-6). However, no further enhancement in the yield of product **2a** was observed when the reaction temperature was raised from 60 ^oC to 65 ^oC (Table 3, entry 7).

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Table 3 Effect of reaction temperature on the model reaction (**2a**)[a]

Entry	Temperature (^oC)	Time (min)[b]	Yield (%)[c]
1	25	75	72
2	40	50	74
3	45	35	78
4	50	30	84
5	55	25	88
6	60	10	98
7	65	10	98

[a]*Reaction condition*: indole-3-carbaldehyde (**1a**, 2 mmol), phenylhydrazine (2 mmol), and ethylacetoacetate (2 mmol), water (10 mL), $SiO_2/ZnBr_2$ (0.10 g), MW, different temperature (25-65 °C)
[b]Reaction progress monitored by TLC
[c]Isolated yield of products

After optimization of the reaction conditions, the catalyst $SiO_2/ZnBr_2$ was examined under the optimized reaction conditions using both conventional and microwave heating. A wide range of aromatic aldehydes reacted with ethylacetoacetate and phenylhydrazine to afford the target pyrazolone in excellent yields. We Further explored this devised protocol using 2,4-Dinitrophenylhydrazine (2,4-DNP) to expand its product diversity and scope (Table 4). The catalyst showed good efficiency under conventional heating giving the products in 4-6 h. However, microwave induction produced excellent yields (94-98%) of products in 10-15 min. The above results demonstrate that $SiO_2/ZnBr_2$ is an efficient catalyst for the synthesis of wide range of pyrazolones in high yields under mild aqueous conditions.

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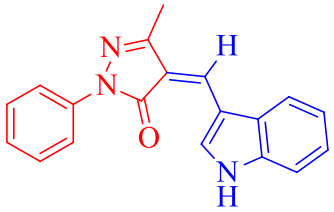
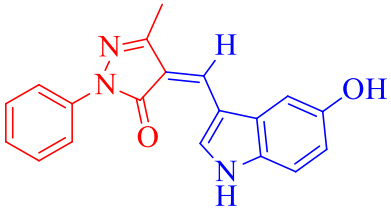
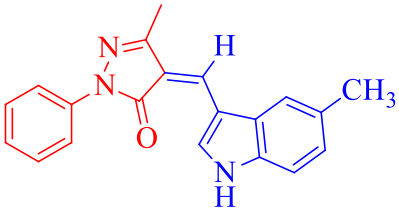
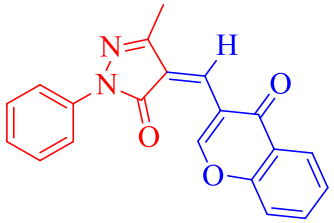
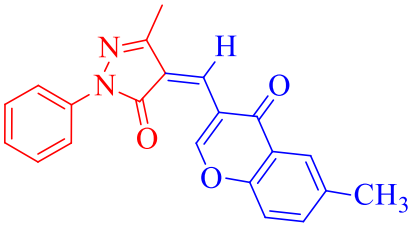
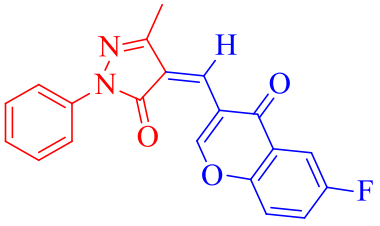
Table 4 Synthesis of pyrazolones derivatives **2 (a-s)**

S. No.	Products	Conventional Method[a]		Microwave irradiation[b]	
		Time (h)[c]	Yield (%)[d]	Time (min)[c]	Yield (%)[d]
2a		4	81	10	98
2b		4.5	77	10	95
2c		4.5	80	15	98
2d		4	84	10	98
2e		5	78	15	95
2f		4.5	82	15	96

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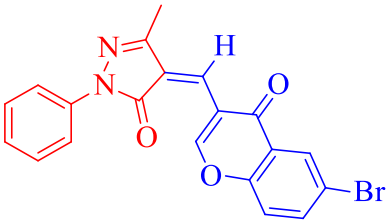
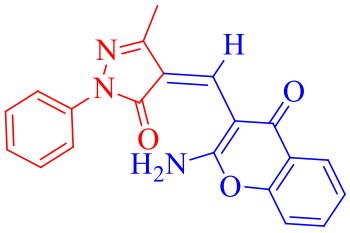
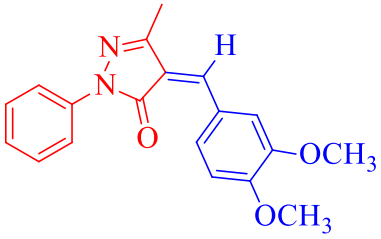
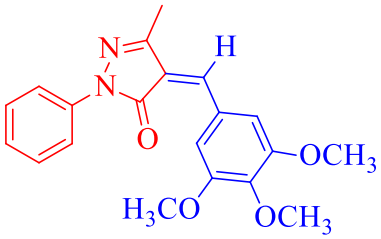
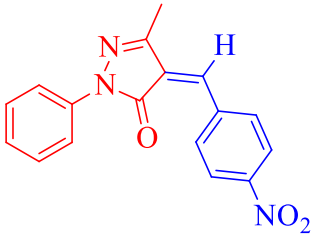
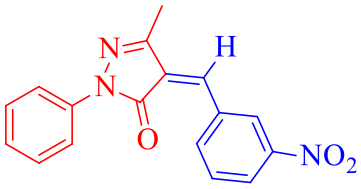
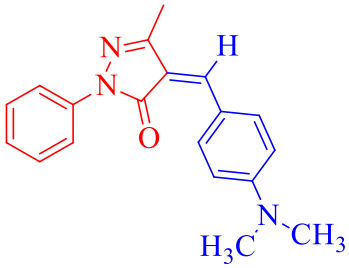
2g		6	79	15	94
2h		5.0	76	15	95
2i		5.5	81	10	97
2j		6.0	74	15	94
2k		4	83	10	97
2l		4.5	75	10	94
2m[39]		5.5	84	10	98

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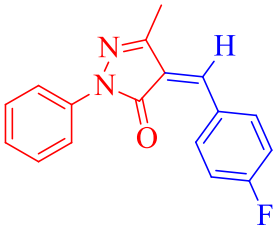
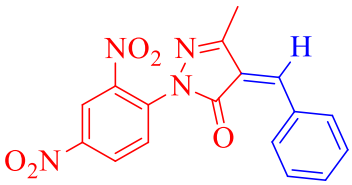
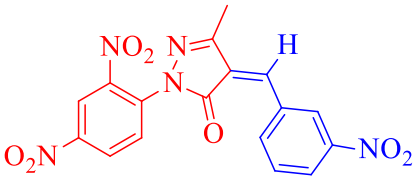
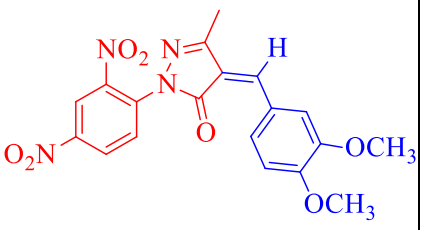
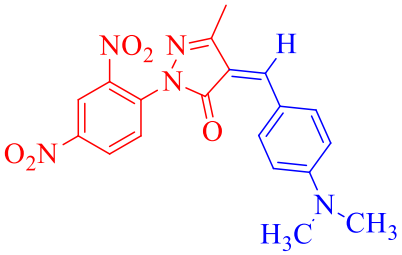
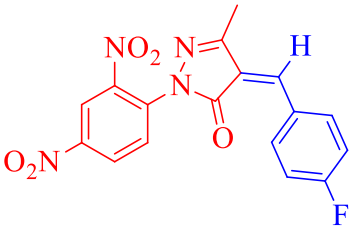
2n[39]		5	76	15	96
2o[40]		6	74	15	94
2p[41]		4.5	78	10	97
2q[40]		5	76	15	95
2r[40]		4	82	10	98
2s[41]		5.5	75	15	94

[a]*Reaction condition*: indole-3-carbaldehyde (**1a**, 2 mmol), phenylhydrazine (2 mmol), and ethylacetoacetate (2 mmol), water (10 mL), $SiO_2/ZnBr_2$ (0.10 g), 60 °C
[b]*Reaction condition*: indole-3-carbaldehyde (**1a**, 2 mmol), phenylhydrazine (2 mmol), and ethylacetoacetate (2 mmol), water (10 mL), $SiO_2/ZnBr_2$ (0.10 g), MW-60 °C
[c]Reaction progress monitored by TLC.
[d]Isolated yield of the products

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Chemistry

The structural elucidation of the synthesized compounds **2** (**a-s**) was established on the basis of elemental analysis (IR, ^{1}H NMR, ^{13}C NMR) and mass spectral studies. The analytical results for C, H and N were within ±0.3% of the theoretical values. The absence of peak for aldehydic carbonyl in IR spectrum, confirmed the reaction at the carbonyl moiety. Moreover, all the compounds displayed a characteristic peak for C=N and C=O groups, resonating at around 1578-1603 cm^{-1} and 1680-1700 cm^{-1}, respectively, which signifies the formation of a pyrazolone ring. Characteristic peaks for the different functional groups such as methoxy, nitro and hydroxyl etc. have been discussed in experimental section. In ^{1}H NMR spectrum, each compound displayed a sharp singlet at around δ 7.32-7.99 ascribed to the olefinic proton, a broad singlet at around 12.02-12.46 (D_2O exchangeable) has been ascribed to –NH proton of indole ring. Similarly, a sharp singlet at around 9.32-9.82 corresponds to the H-2 proton of indole ring (**2a-2c**). Furthermore, sharp singlets resonating at around δ 10.64, 10.04, 10.12, 10.10 each integrating for one proton, has been attributed to H-2 protons of *γ*-pyrone ring of chromones **2d**, **2e**, **2f** and **2g** respectively. ^{13}C NMR spectra, showed a series of signals resonating at around δ 105.13-162.18 which have been assigned to aromatic carbons, peaks resonating at around δ 137.31-153.80 and δ 163.05-170.16 corresponds to -C=N and -C=O moiety of pyrazolone ring, respectively. Similarly signals at δ 174.19-174.69 have been attributed to carbonyl group ($C=O_{\gamma\text{-pyrone}}$) of compounds (**2d-2h**). The mass spectral analysis of the synthesized compounds was also in good conformity with the proposed structures. The selective *Z*-geometry across C=C was authenticated by single crystal X-ray crystallographic analysis of compound **2a** and **2d** (Fig. 6), which was found to be stabilized by an intricate array of H-bonding (Fig. 7) and π…π interactions (Fig. 8). The crystallographic data of compound **2a** and **2d** have been presented in Table 5. Moreover, the

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selected bond distances (Å), bond angles (°) and packing diagram of compound **2a** and **2d** are shown in Table S1-S2 and Fig. S2-S4 (ESI†).

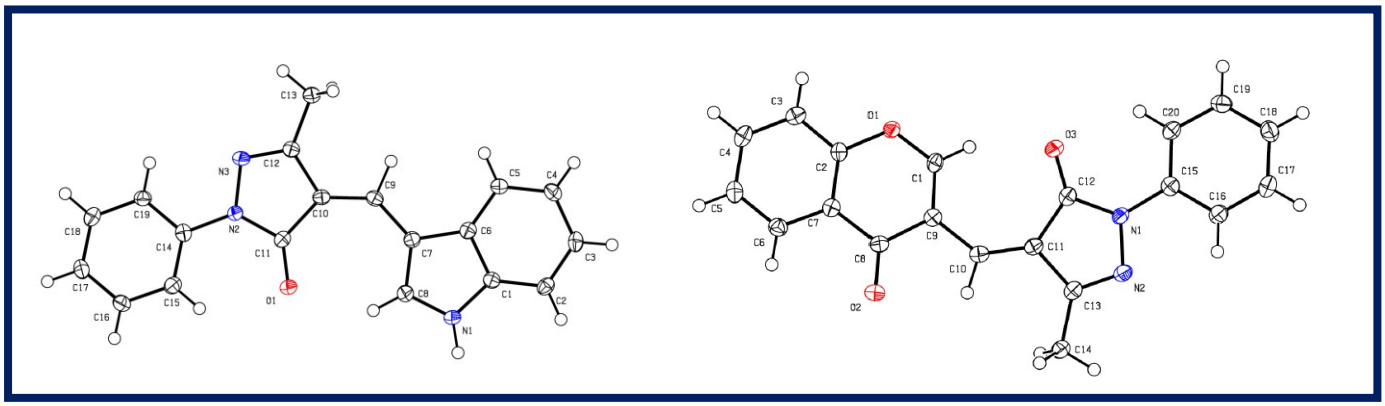
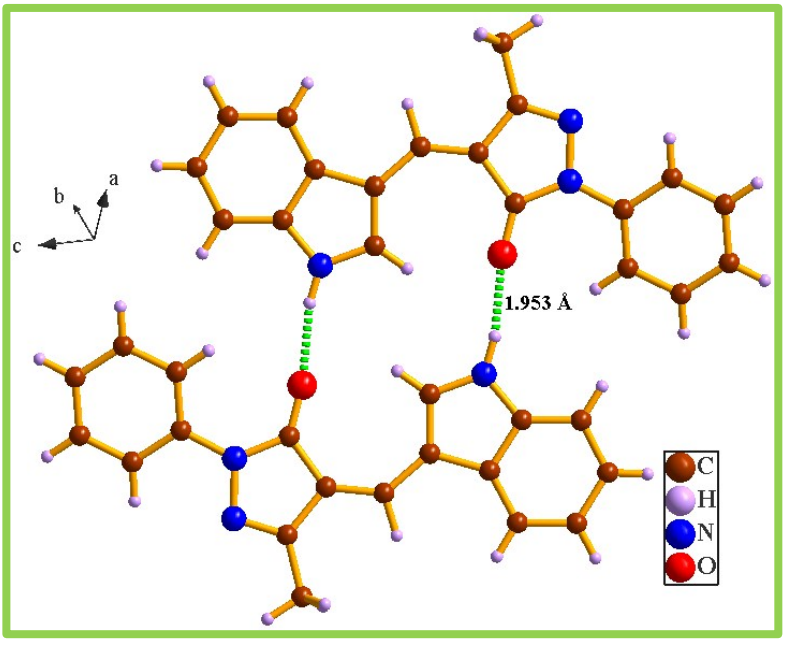


Fig. 6 Asymmetric unit showing thermal ellipsoids (50% probability level) of **(a)** compound **2a** **(b)** compound **2d**



(a)

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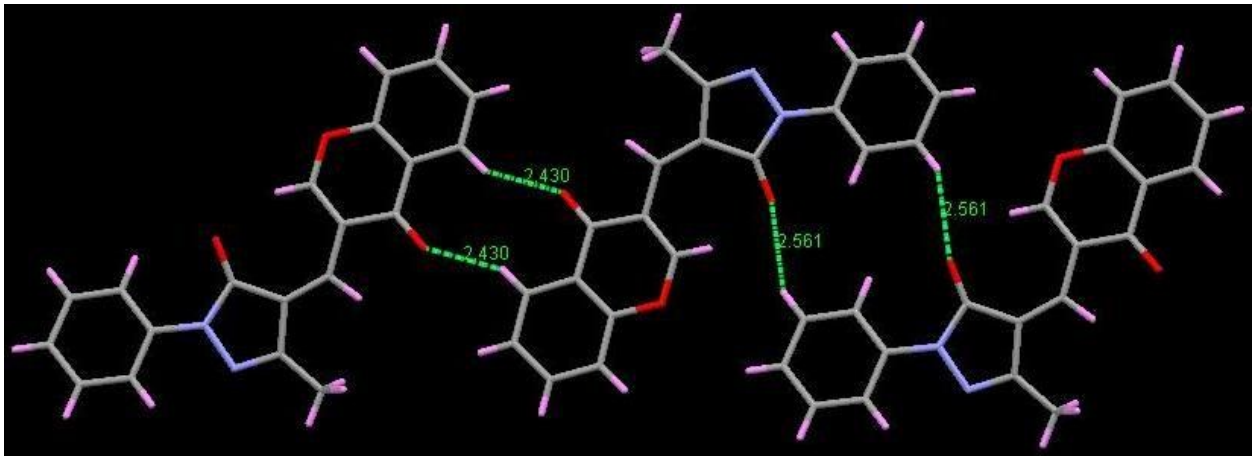
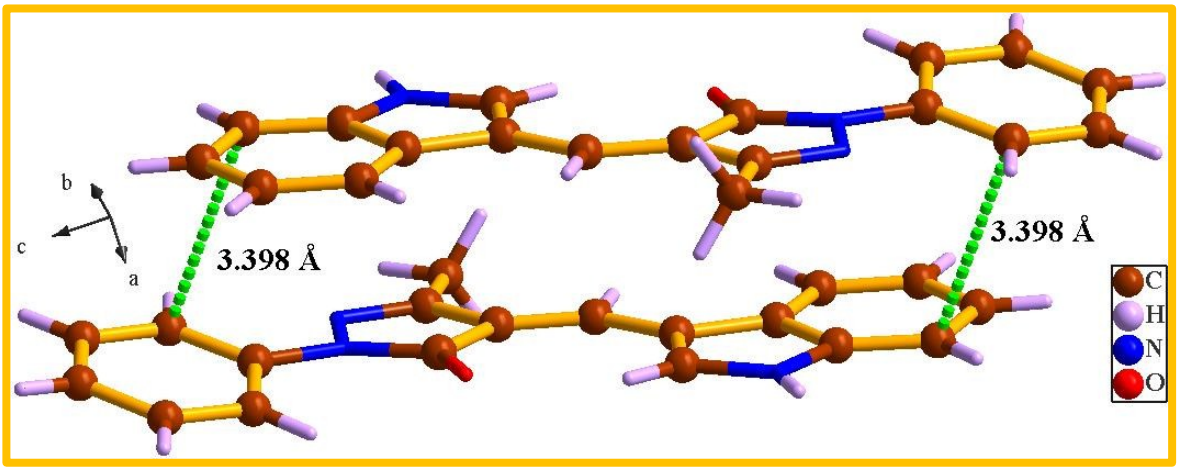


(b)

Fig. 7 2D view showing intricate H-bonding interactions in **(a)** compound **2a (b)** compound **2d**



(a)

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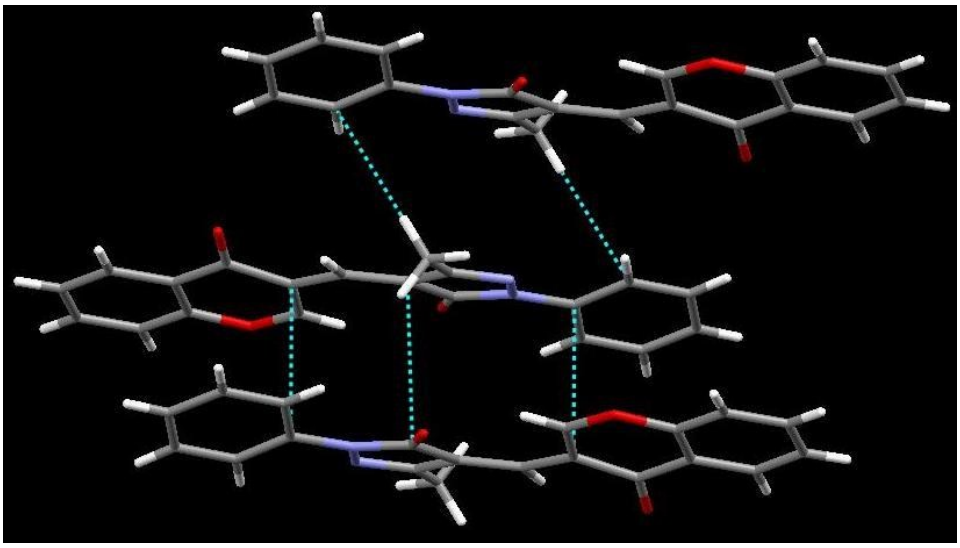

(b)

Fig. 8 Diagrammatic representation of π…π interactions in **(a)** compound **2a,** π…π and –CH …π interactions in **(b)** compound **2d**

Reusability of the catalyst

The reusability of the catalyst ($SiO_2/ZnBr_2$) was also explored for the selected model reaction in order to reduce the cost of the process (Fig. 9). After the first fresh run with 98% yield, the catalyst was removed by simple filtration, washed with ethylacetate and dried at 160 ^oC for 10 hrs. The recovered catalyst was further tested up to five more reaction cycles. The results revealed that there is little drop in the yield of the product after every successive run of the catalyst. This little drop in the catalytic activity is believed to be due to the leaching of $ZnBr_2$. SEM and EDX analysis of the recovered catalyst was also performed to ascertain its morphology and composition (Fig. S4). It was observed that the composition of the catalytic system was almost consistent with the fresh catalyst (Fig. 3) and there have been no significant changes in the morphology of the catalyst.

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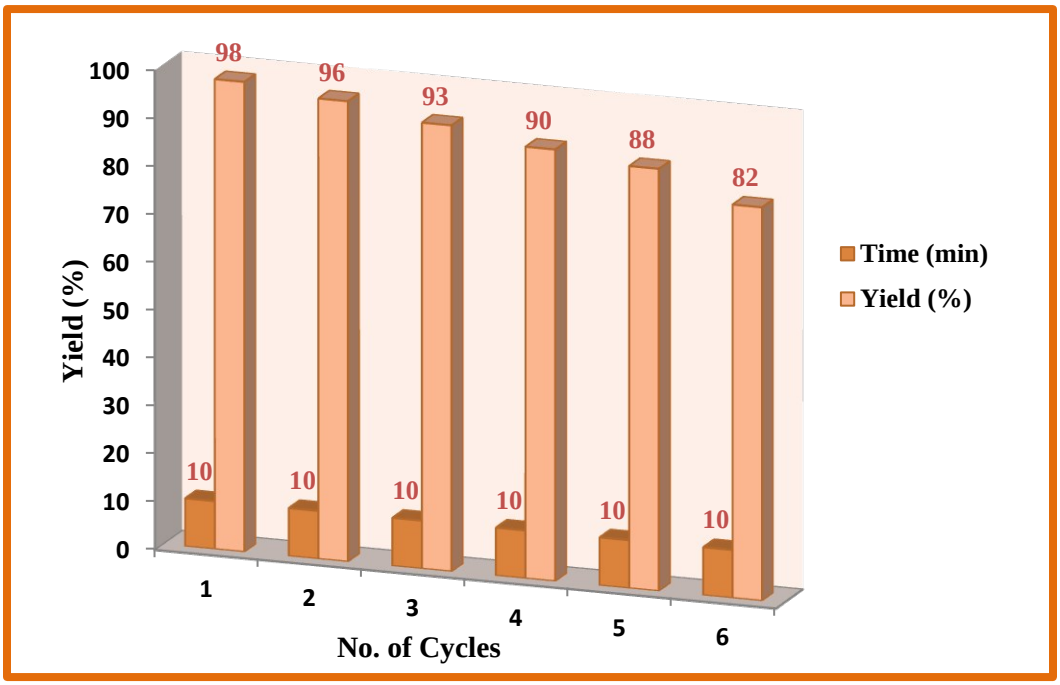

Fig. 9 Recycling data of the catalyst ($SiO_2/ZnBr_2$) for the model reaction

Experimental

Materials and general methods

All the chemicals and reagents were purchased from Merck and Sigma-Aldrich (India) as 'synthesis grade' and used without further purification. The microwave synthesis was performed in Anton Paar, Monowave 300 microwave synthesizer. Melting points were determined on a Kofler apparatus and are uncorrected. Elemental analysis (C, H, N) was conducted using Carlo Erba analyzer model 1108. The IR spectra were recorded with a Shimadzu IR-408 Perkin-Elmer1800 instrument (FTIR) and the values are given in cm^{-1}. ^1H NMR and ^{13}C NMR spectra were run in DMSO-d_6 /$CDCl_3$ on a Bruker Avance-II 400 MHz instrument with TMS as an internal standard and J values were measured in Hertz (Hz). Chemical shifts are reported in ppm (δ) relative to TMS. Mass spectra were recorded on a JEOL D-300 mass spectrometer. X-ray

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diffractograms (XRD) of the catalyst were recorded in the 2θ range of 20-80^{o} with a scan rate of 41 min^{-1} on a Shimadzu-6100 X-ray diffractometer with Ni-filtered Cu Kα radiation at a wavelength of 1.54060 Å. The scanning electron microscope (SEM-EDX) analysis was obtained using a JEOL (JSM-6510) equipped with an energy dispersive X-ray spectrometer at different magnification. TGA has been carried out with DTG-60H (Simultaneous DTA-TG Apparatus), Shimadzu instrument. Thin layer chromatography (TLC) glass plates (20×5 cm) were coated with silica gel G (Merck) using benzene-acetone (8:2) mixture as mobile phase and exposed to iodine vapors to check the homogeneity as well as the progress of the reaction.

Preparation of the silica-supported zinc bromide ($SiO_2/ZnBr_2$) catalyst

Silica gel (70-230 mesh) (10g) was added to a solution of $ZnBr_2$ (12 mmol, 2.7 g) in EtOH (50 ml), and the mixture was heated at reflux for 1 h. The solvent was removed using rotary evaporator, and the product was dried under vacuum at 160 ^{o}C for 10 h.[31] The other catalyst i.e. SiO_2-Cl used for the comparative study has been synthesized according to the previously published standard procedures.[38]

General procedure for the synthesis of pyrazolones under microwave irradiation

A mixture of substituted aromatic aldehyde (2 mmol), ethylacetoacetate (2 mmol), phenylhydrazine/2,4-Dinitrophenylhydrazine (2 mmol) and catalyst (0.10 g) in 10 mL water was taken in a G30 vial and irradiated using microwaves with continuous stirring at 60 °C for 10-15 min. After completion of reaction (monitored by TLC), the reaction mixture was allowed to cool at room temperature and diluted with cold water (5 mL). The catalyst was separated by filtration and the resulting solution was extracted with ethyl acetate (3×10 mL). The combined organic

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layers were washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was crystallized with chloroform-methanol to afford the pure product. The recovered catalyst was reused for subsequent cycles without a significant loss in yield.

Spectral characterization

***(Z)-4-((1H-indol-3-yl)methylene)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one* (2a)**

Orange crystalline solid, yield 98%, m.p. 245-250 ^{o}C. IR (KBr, cm^{-1}): 1157, 1456 ($C=C_{aromatic}$), 1594 (C=N), 1680 (C=O). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.19-7.96 (m, 5H, phenyl ring), 7.9 (s, 1H, -C=H), 12.46 (brs, 1H, -NH, D_2O exchangeable), 7.14-7.67 (m, 4H, indole ring), 2.39 (s, 3H, $-CH_3$), 9.82 (s, 1H, indole ring). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 165.65 (C=O), 133.44 (C=C), 147.89 (-C=N), 143.23 (-C=H), 118.24-140.54 (phenyl ring), 111.64-137.65 (indole ring), 12.93 (CH_3). Analytical cal. $C_{19}H_{15}N_3O$: C, 75.73; H, 5.02; N, 13.94; found: C, 75.70; H, 5.03; N, 13.96. MS (EI): (m/z) [$M^{+\bullet}$] 301.12

***(Z)-4-((5-hydroxy-1H-indol-3-yl)methylene)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one* (2b)**

Yellow crystalline solid, yield 95%, m.p. 256 $^{\circ}$C. IR (KBr, cm^{-1}): 1150, 1450 ($C=C_{aromatic}$), 1578 (C=N), 1685 (C=O). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.23-7.98 (m, 5H, phenyl ring), 7.83 (s, 1H, -C=H), 11.22 (brs, 1H, -NH, D_2O exchangeable), 6.86-7.17 (m, 3H, indole ring), 2.31 (s, 3H, $-CH_3$), 9.70 (s, 1H, indole ring), 10.20 (s, 1H, -OH, D_2O exchangeable). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 165.63 (C=O), 133.44 (C=C), 147.89 (-C=N), 143.23 (-C=H), 118.20-140.51 (phenyl ring), 111.64-137.65 (indole ring), 13.15 (CH_3). Analytical cal.

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$C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N, 13.24; found: C, 71.90; H, 4.79; N, 13.22.MS (EI): (m/z) [$M^{+\bullet}$] 317.12

(Z)-3-methyl-4-((5-methyl-1H-indol-3-yl)methylene)-1-phenyl-1H-pyrazol-5(4H)-one **(2c)**

Yellow solid, yield 98%, m.p. 248 °C. IR (KBr, cm^{-1}): 1152, 1452 (C=$C_{aromatic}$), 1603 (C=N), 1688 (C=O). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.26-7.91 (m, 5H, phenyl ring), 7.71 (s, 1H, -C=H), 12.02 (brs, 1H, -NH, D_2O exchangeable), 6.89-7.27 (m, 3H, indole ring), 2.31 (s, 1H, -CH_3), 9.32 (s, 1H, indole ring). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 164.55 (C=O), 133.04 (C=C), 146.87 (-C=N), 142.13 (-C=H), 116.24-142.54 (phenyl ring), 112.64-135.65 (indole ring), 14.23 (CH_3). Analytical cal. $C_{20}H_{17}N_3O$: C, 76.17; H, 5.43; N, 13.32; found: C, 76.18; H, 5.40; N, 13.34. MS (EI): (m/z) [$M^{+\bullet}$] 317.12

(Z)-3-methyl-4-((4-oxo-4H-chromen-3-yl)methylene)-1-phenyl-1H-pyrazol-5(4H)-one **(2d)**

Red crystalline solid, yield 98%, m.p. 222 °C. IR (KBr, cm^{-1}): 1153, 1452 (C=$C_{aromatic}$), 1600 (C=N), 1692 (C=O). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.12-7.34 (m, 5H, phenyl ring), 7.99 (s, 1H, -C=H), 10.64 (s, 1H, γ-pyrone ring), 8.19-7.27 (m, 4H, chromone ring), 2.33 (s, 1H, -CH_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 163.35 (C=O), 134.67 (C=C, C-1′), 137.81 (-C=N), 155.47 (-C=H, C-2′), 118.38-142.54 (phenyl ring), 150.67 (C-2,γ-pyrone ring), 118.54 (C-3), 174.29 (C-4, C=O, γ- pyrone ring) 14.23 (CH_3), 123.10 (C-4a), 125.75 (C-5), 124.56 (C-6), 135.92 (C-7), 117.59 (C-8), 161.83 (C-8b). Analytical cal. $C_{20}H_{14}N_2O_3$: C, 72.72; H, 4.27; N, 8.48; found: C, 72.70; H, 4.30; N, 8.47. MS (EI): (m/z) [$M^{+\bullet}$] 330.10

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***(Z)-3-methyl-4-((6-methyl-4-oxo-4H-chromen-3-yl)methylene)-1-phenyl-1H-pyrazol-5(4H)-one* (2e)**

Orange solid, yield 95%, m.p. 230 °C. IR (KBr, cm^{-1}): 1156, 1456 ($C=C_{aromatic}$), 1598 (C=N), 1699 (C=O). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.10-7.31 (m, 5H, phenyl ring), 7.69 (s, 1H, -C=H), 10.04 (s, 1H, γ-pyrone ring), 8.09-7.20 (m, 3H, chromone ring), 2.30 (s, 1H, $-CH_3$). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 163.05 (C=O), 134.17 (C=C, C-1′), 137.61 (-C=N), 155.27 (-C=H, C-2′), 118.21-142.24 (phenyl ring), 150.22 (C-2,γ-pyrone ring), 118.74 (C-3), 174.19 (C-4, C=O, γ- pyrone ring), 14.13 (CH_3), 123.18 (C-4a), 125.32 (C-5), 124.56 (C-6), 135.52 (C-7), 117.49 (C-8), 161.53 (C-8b). Analytical cal. $C_{21}H_{16}N_2O_3$: C, 73.24; H, 4.68; N, 8.13; found: C, 73.26; H, 4.69; N, 8.10. MS (EI): (m/z) [$M^{+\bullet}$] 344.12

***(Z)-4-((6-fluoro-4-oxo-4H-chromen-3-yl)methylene)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one* (2f)**

Red solid, yield 96%, m.p. 214 °C. IR (KBr, cm^{-1}): 1157, 1455 ($C=C_{aromatic}$), 1599 (C=N), 1696 (C=O). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.02-7.11 (m, 5H, phenyl ring), 7.72 (s, 1H, -C=H), 10.12 (s, 1H, γ-pyrone ring), 8.07-7.23 (m, 3H, chromone ring), 2.31 (s, 1H, $-CH_3$). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 163.25 (C=O), 134.19 (C=C, C-1′), 137.41 (-C=N), 155.23 (-C=H, C-2′), 118.27-142.21 (phenyl ring), 150.29 (C-2,γ-pyrone ring), 118.64 (C-3), 174.69 (C-4, C=O, γ- pyrone ring), 14.18 (CH_3), 123.38 (C-4a), 125.30 (C-5), 124.52 (C-6), 135.56 (C-7), 117.41 (C-8), 161.50 (C-8b). Analytical cal. $C_{20}H_{13}FN_2O_3$: C, 68.96; H, 3.76; N, 8.04; found: C, 68.97; H, 3.78; N, 8.01. MS (EI): (m/z) [$M^{+\bullet}$] 348.09

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***(Z)-4-((6-bromo-4-oxo-4H-chromen-3-yl)methylene)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one* (2g)**

Brown solid, yield 94%, m.p. 248 °C. IR (KBr, cm^{-1}): 1158, 1451 ($C=C_{aromatic}$), 1580 (C=N), 1699 (C=O). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.42-7.18 (m, 5H, phenyl ring), 7.76 (s, 1H, -C=H), 10.10 (s, 1H, γ-pyrone ring), 8.03-7.21 (m, 3H, chromone ring), 2.35 (s, 1H, $-CH_3$). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 163.23 (C=O), 133.19 (C=C, C-1′), 137.31 (-C=N), 155.54 (-C=H, C-2′), 118.19-142.29 (phenyl ring), 150.24 (C-2,γ-pyrone ring), 118.64 (C-3), 174.47 (C-4, C=O, γ- pyrone ring), 14.22 (CH_3), 123.34 (C-4a), 125.39 (C-5), 120.41(C-6), 135.36 (C-7), 117.46 (C-8), 161.76 (C-8b). Analytical cal. $C_{20}H_{13}BrN_2O_3$: C, 58.70; H, 3.20; N, 6.85; found: C, 58.71; H, 3.22; N, 6.82. MS (EI): (m/z) [$M^{+\bullet}$] 408.01

***(Z)-4-((2-amino-4-oxo-4H-chromen-3-yl)methylene)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one* (2h)**

Brown solid, yield 95%, m.p. 240 °C. IR (KBr, cm^{-1}): 1157, 1450 ($C=C_{aromatic}$), 1580 (C=N), 1681 (C=O). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.32-7.17 (m, 5H, phenyl ring), 7.72 (s, 1H, -C=H), 8.57 (s, 2H, -NH, D_2O exchangeable), 8.08-7.27 (m, 4H, chromone ring), 2.33 (s, 1H, $-CH_3$). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 163.28 (C=O), 133.29 (C=C, C-1′), 137.38 (-C=N), 155.34 (-C=H, C-2′), 118.25-142.37 (phenyl ring), 170.24 (C-2,γ-pyrone ring), 118.61 (C-3), 174.41 (C-4, C=O, γ- pyrone ring), 14.22 (CH_3), 123.28 (C-4a), 125.33 (C-5), 123.41(C-6), 135.16 (C-7), 117.26 (C-8), 161.66 (C-8b). Analytical cal. $C_{20}H_{15}N_3O_3$: C, 69.56; H, 4.38; N, 12.17; found: C, 69.53; H, 4.39; N, 12.19. MS (EI): (m/z) [$M^{+\bullet}$] 345.11.

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***(Z)-4-(3,4-dimethoxybenzylidene)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one* (2i)**

Yellow solid, yield 97%, m.p. 208 °C. IR (KBr, cm^{-1}): 1157, 1450 ($C=C_{aromatic}$), 1578 (C=N), 1700 (C=O). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.19-7.97 (m, 5H, phenyl ring), 7.32 (s, 1H, -C=H), 7.28-7.32 (m, 3H, phenyl ring), 2.31 (s, 1H, $-CH_3$), 3.38 (s, 6H, 2×$-OCH_3$). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 163.26 (C=O), 133.22 (C=C, C-1′), 155.14 (-C=H, C-2′), 137.32 (-C=N), 118.21-142.39 (phenyl ring), 128.24 (C-1), 115.23 (C-2), 148.61 (C-3), 149.41 (C-4), 111.74 (C-5), 122.25 (C-6), 14.62 (CH_3), 56.06 ($O-CH_3$). Analytical cal. $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69; found: C, 70.71; H, 5.60; N, 8.71. MS (EI): (m/z) [$M^{+\bullet}$] 322.13.

***(Z)-3-methyl-1-phenyl-4-(3,4,5-trimethoxybenzylidene)-1H-pyrazol-5(4H)-one* (2j)**

Yellow crystalline solid, yield 94%, m.p. 214 °C. IR (KBr, cm^{-1}): 1150, 1456 ($C=C_{aromatic}$), 1600 (C=N), 1691 (C=O). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.19-7.97 (m, 5H, phenyl ring), 7.35 (s, 1H, -C=H), 7.12 (s, 2H, phenyl ring), 2.32 (s, 1H, $-CH_3$), 3.34 (s, 9H, 3×$-OCH_3$). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 163.28 (C=O), 133.29 (C=C, C-1′), 155.39 (-C=H, C-2′), 137.38 (-C=N), 118.52-142.29 (phenyl ring), 129.24 (C-1), 105.13 (C-2 and C-6), 154.11 (C-3 and C-4), 134.34 (C-5), 14.89 (CH_3), 56.36 ($O-CH_3$). Analytical cal. $C_{20}H_{20}N_2O_4$: C, 68.17; H, 5.72; N, 7.95; found: C, 68.20; H, 5.70; N, 7.94. MS (EI): (m/z) [$M^{+\bullet}$] 352.14.

***(Z)-3-methyl-4-(4-nitrobenzylidene)-1-phenyl-1H-pyrazol-5(4H)-one* (2k)**

Orange crystalline solid, yield 97%, m.p. 210 °C. IR (KBr, cm^{-1}): 1157, 1456 ($C=C_{aromatic}$), 1578 (C=N), 1687 (C=O), 1522, 1365 (NO_2). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.20-7.99 (m, 5H, phenyl ring), 7.49 (s, 1H, -C=H), 8.12 (d, 2H, C-2 and C-6), 8.18 (d, 2H, C-3 and C-5), 2.36 (s, 1H, $-CH_3$). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 163.25 (C=O), 128.21 (C=C, C-1′),

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145.69 (-C=H, C-2′), 145.88 (-C=N), 118.12-142.22 (phenyl ring), 139.24 (C-1), 132.17 (C-2 and C-6), 124.18 (C-3 and C-4), 148.14 (C-5), 15.09 (CH_3). Analytical cal. $C_{17}H_{13}N_3O_3$: C, 66.44; H, 4.26; N, 13.67; found: C, 66.41; H, 4.28; N, 13.68. MS (EI): (m/z) [$M^{+\bullet}$] 307.10.

***(Z)-3-methyl-4-(3-nitrobenzylidene)-1-phenyl-1H-pyrazol-5(4H)-one* (2l)**

Yellow solid, yield 94%, m.p. 202 °C. IR (KBr, cm^{-1}): 1152, 1454 (C=$C_{aromatic}$), 1579 (C=N), 1693 (C=O), 1520, 1360 (NO_2). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.22-7.95 (m, 5H, phenyl ring), 7.47 (s, 1H, -C=H), 7.67-8.42 (m, 4H, phenyl ring), 2.32 (s, 1H, -CH_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 163.29 (C=O), 127.23 (C=C, C-1′), 144.63 (-C=H, C-2′), 146.98 (-C=N), 118.15-142.32 (phenyl ring), 133.34 (C-1), 125.17 (C-2), 147.08 (C-3), 123.08 (C-4), 128.18 (C-5), 123.36 (C-6), 15.19 (CH_3). Analytical cal. $C_{17}H_{13}N_3O_3$: C, 66.44; H, 4.26; N, 13.67; found: C, C, 66.41; H, 4.27; N, 13.69. MS (EI): (m/z) [$M^{+\bullet}$] 307.10.

***(Z)-4-(4-(dimethylamino)benzylidene)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one* (2m)**

Orange crystalline solid, yield 98%, m.p. 194 °C, reported 188-192 °C.[39] IR (KBr, cm^{-1}): 1154, 1452 (C=$C_{aromatic}$), 1591 (C=N), 1689 (C=O). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.13-7.97 (m, 5H, phenyl ring), 7.58 (s, 1H, -C=H), 2.30 (s, 1H, -CH_3), 6.84-8.66 (m, 4H, phenyl ring), 3.13 (s, 1H, 2×CH_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 170.16 (C=O), 128.69 (C=C, C-1′), 151.56 (-C=H, C-2′), 153.80. (-C=N), 118.09-138.84 (phenyl ring), 123.92 (C-1), 137.43 (C-2 and C-6), 111.32 (C-3 and C-5), 148.18 (C-4), 15.19 (CH_3), 41.28 (N-CH_3). Analytical cal. $C_{19}H_{19}N_3O$: C, 74.73; H, 6.27; N, 13.76; found: C, 74.70; H, 6.28; N, 13.78. MS (EI): (m/z) [$M^{+\bullet}$] 305.15.

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***(Z)-4-(4-fluorobenzylidene)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one* (2n)**

Yellow solid, yield 96%, m.p. 104 °C, reported 98-102 °C.[39] IR (KBr, cm^{-1}): 1156, 1455 ($C=C_{aromatic}$), 1593 (C=N), 1697 (C=O). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.19-7.97 (m, 5H, phenyl ring), 7.42 (s, 1H, -C=H), 2.34 (s, 1H, $-CH_3$), 7.14-7.86 (m, 4H, phenyl ring). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 168.12 (C=O), 127.60 (C=C, C-1′), 145.50 (-C=H, C-2′), 148.85. (-C=N), 118.02-139.81 (phenyl ring), 128.91 (C-1), 132.03 (C-2 and C-6), 115.36 (C-3 and C-5), 162.18 (C-4), 15.02 (CH_3). Analytical cal. $C_{17}H_{13}FN_2O$: C, 72.85; H, 4.67; N, 9.99; found: C, 72.82; H, 4.69; N, 10.00. MS (EI): (m/z) [$M^{+\bullet}$] 280.10.

***(Z)-4-benzylidene-1-(2,4-dinitrophenyl)-3-methyl-1H-pyrazol-5(4H)-one* (2o)**

Yellow solid, yield 94%, m.p. 194 °C.[40] IR (KBr, cm^{-1}): 1152, 1450 ($C=C_{aromatic}$), 1597 (C=N), 1686 (C=O), 1528, 1368 (NO_2). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.20-9.08 (m, 3H, phenyl ring), 7.42 (s, 1H, -C=H), 2.36 (s, 1H, $-CH_3$), 7.40-7.66 (m, 5H, phenyl ring). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 170.12 (C=O), 126.69 (C=C, C-1′), 150.56 (-C=H, C-2′), 150.80. (-C=N), 120.14-144.09 (phenyl ring), 123.02 (C-1), 136.43 (C-2 and C-6), 111.48 (C-3 and C-5), 148.88 (C-4), 15.20 (CH_3). Analytical cal. $C_{17}H_{12}N_4O_5$: C, 57.96; H, 3.43; N, 15.90; found: C, 57.93; H, 3.45; N, 15.91. MS (EI): (m/z) [$M^{+\bullet}$] 352.08.

***(Z)-1-(2,4-dinitrophenyl)-3-methyl-4-(3-nitrobenzylidene)-1H-pyrazol-5(4H)-one* (2p)**

Yellow crystalline solid, yield 95%, m.p. 274 °C, reported 272-274 °C.[41] IR (KBr, cm^{-1}): 1152, 1454 ($C=C_{aromatic}$), 1593 (C=N), 1700 (C=O), 1520, 1360 (NO_2). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.22-9.02 (m, 3H, phenyl ring), 7.54 (s, 1H, -C=H), 7.68-8.30 (m, 4H, phenyl ring), 2.34 (s, 1H, $-CH_3$). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 164.20 (C=O), 127.10 (C=C, C-1′),

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144.03 (-C=H, C-2′), 146.99 (-C=N), 120.15-145.32 (phenyl ring), 133.04 (C-1), 124.17 (C-2), 147.88 (C-3), 123.28 (C-4), 128.28 (C-5), 122.06 (C-6), 15.20 (CH_3). Analytical cal. $C_{17}H_{11}N_5O_7$: C, 51.39; H, 2.79; N, 17.63; found: C, 51.36; H, 2.80; N, 17.65. MS (EI): (m/z) [$M^{+\bullet}$] 397.30.

(Z)-4-(3,4-dimethoxybenzylidene)-1-(2,4-dinitrophenyl)-3-methyl-1H-pyrazol-5(4H)-one **(2q)**

Yellow solid, yield 97%, m.p. 224 °C.[40] IR (KBr, cm^{-1}): 1157, 1456 ($C=C_{aromatic}$), 1594 (C=N), 1688 (C=O), 1522, 1362 (NO_2). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.20-9.04 (m, 3H, phenyl ring), 7.46 (s, 1H, -C=H), 7.20-7.31 (m, 3H, phenyl ring), 2.32 (s, 1H, -CH_3), 3.36 (s, 6H, 2×-OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 164.26 (C=O), 130.22 (C=C, C-1′), 150.14 (-C=H, C-2′), 139.32 (-C=N), 120.21-144.39 (phenyl ring), 128.14 (C-1), 115.53 (C-2), 148.68 (C-3), 149.45 (C-4), 111.72 (C-5), 122.25 (C-6), 14.88 (CH_3), 56.02 (O-CH_3). Analytical cal. $C_{19}H_{16}N_4O_7$: C, 55.34; H, 3.91; N, 13.59; found: C, 55.31; H, 3.93; N, 13.60. MS (EI): (m/z) [$M^{+\bullet}$] 412.10.

(Z)-4-(4-(dimethylamino)benzylidene)-1-(2,4-dinitrophenyl)-3-methyl-1H-pyrazol-5(4H)-one **(2r)**

Orange crystalline solid, yield 98%, m.p. 240 °C.[40] IR (KBr, cm^{-1}): 1156, 1452 ($C=C_{aromatic}$), 1593 (C=N), 1691 (C=O), 1526, 1361 (NO_2). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.28-9.01 (m, 3H, phenyl ring), 7.49 (s, 1H, -C=H), 2.32 (s, 1H, -CH_3), 6.80-8.46 (m, 4H, phenyl ring), 3.10 (s, 1H, 2×CH_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 170.12 (C=O), 126.69 (C=C, C-1′), 150.56 (-C=H, C-2′), 150.80. (-C=N), 120.14-144.09 (phenyl ring), 123.02 (C-1), 136.43 (C-2 and C-6), 111.48 (C-3 and C-5), 148.88 (C-4), 15.20 (CH_3), 41.31 (N-CH_3). Analytical cal.

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$C_{19}H_{17}N_5O_5$: C, 57.72; H, 4.33; N, 17.71; found: C, 57.73; H, 4.30; N, 17.73. MS (EI): (m/z) [$M^{+\bullet}$] 395.12.

(Z)-1-(2,4-dinitrophenyl)-4-(4-fluorobenzylidene)-3-methyl-1H-pyrazol-5(4H)-one **(2s)**

Yellow solid, yield 94%, m.p. 162 °C, reported 160-163 °C.[41] IR (KBr, cm^{-1}): 1159, 1453 (C=$C_{aromatic}$), 1598 (C=N), 1698 (C=O), 1526, 1360 (NO_2). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.96-7.98 (m, 3H, phenyl ring), 7.42 (s, 1H, -C=H), 2.36 (s, 1H, -CH_3), 7.18-7.80 (m, 4H, phenyl ring). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 169.10 (C=O), 127.60 (C=C, C-1′), 145.50 (-C=H, C-2′), 148.85. (-C=N), 120.23-145.84 (phenyl ring), 128.91 (C-1), 132.00 (C-2 and C-6), 115.31 (C-3 and C-5), 162.18 (C-4), 15.01 (CH_3). Analytical cal. $C_{17}H_{11}FN_4O_5$: C, 55.14; H, 2.99; N, 15.13; found: C, 55.15; H, 2.96; N, 15.15. MS (EI): (m/z) [$M^{+\bullet}$] 370.07.

Single crystal X-ray crystallographic studies of compound 2a and 2d

Single crystal X-ray data of compounds **2a** and **2d** were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite monochromated MoKa radiation (λ = 0.71073 Å). The linear absorption coefficients, scattering factors for the atoms and the anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography.[42] The data integration and reduction were carried out with SAINT software.[43] An empirical absorption correction was applied to the collected reflections with SADABS, and the space group was determined using XPREP.[44] The structure was solved by direct methods using SHELXTL-97 and refined on F2 by full-matrix least-squares using the SHELXL-97[45] program package. All non-hydrogen atoms were refined anisotropically. Pertinent crystallographic data for compounds **2a** and **2d** are summarized in Table 5. The crystal data have been deposited at the Cambridge

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Crystallographic Data Centre (CCDC) with reference number, compound **2a** with CCDC 1409997 and compound **2d** with CCDC 1432605.

Table 5 Crystallographic data and structure refinement of compounds **2a** and **2d**

Parameters	**Compound 2a**	**Compound 2d**
Empirical formula	$C_{19}H_{15}N_3O$	$C_{20}H_{14}N_2O_3$
Formula wt.	301.34	330.33
Crystal system	Monoclinic	Triclinic
Space group	*P*21/*n*	*P*-1
a, Å	5.810(5)	7.870(5)
b, Å	9.256(5)	8.298(3)
c, Å	26.893(5)	11.843(5)
α (°)	90	85.806(4)
β (°)	94.997(5)	80.900(5)
γ (°)	90	89.987(5)
U, Å^3	1440.7(15)	761.6(7)
Z	4	2
ρ_{calc} Mg/m^3	1.389	1.441
μ, mm^{-1}	0.089	0.099
Temperature (K)	100	100
θ max	25.50	25.50
F(000)	632	344
Refl. collected	11010	9548
Independent refl.	2087	2314
GOF[a]	1.038	1.037
Final *R*[b] indices [$I>2\sigma(I)$]	*R*1 = 0.0501 w*R*2 = 0.1268	*R*1 = 0.0402 w*R*2 = 0.0970
R indices (all data)	*R*1 = 0.0675 w*R*2 = 0.1380	*R*1 = 0.0524 w*R*2 = 0.1038

[a]GOF is defined as $\{\sum[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$ where *n* is the number of data and *p* is the number of parameters. [b]$R = \{\sum||F_o| - |F_c||/\sum|F_o|\}$, $wR_2 = \{\sum w(F_o^2 - F_c^2)^2/ \sum w(F_o^2)^2 \}^{1/2}$.

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Conclusion

In summary, we have developed a simple, efficient, cost effective and green procedure for one-pot synthesis of a series of pyrazolone derivatives **2** (**a-s**) in excellent yields (94-98%) by employing recyclable and reusable $SiO_2/ZnBr_2$ Lewis acid catalyst in water under microwave heating. The scheme not only offers use of microwave at low temperature and substantial yield of products but also affords mild reaction conditions, water as a green solvent, shorter reaction times, high purity, operational simplicity and easy workup. We believe that this synthetic approach provides a better scope for the synthesis of pyrazolone analogues and will be a more practical alternative to the other existing methods.

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Graphical Abstract (Pictogram)

$SiO_2/ZnBr_2$ mediated expeditious approach to 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one derivatives in water under microwave irradiation

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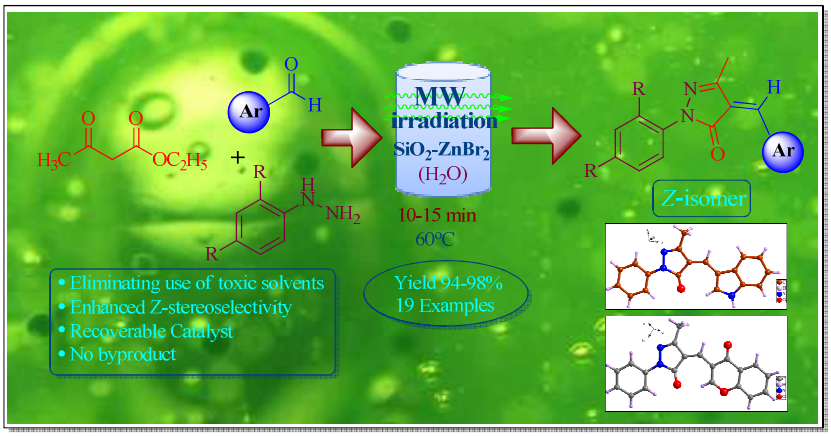

An efficient and eco-friendly synthesis of pyrazolone derivatives