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$ZnFe_2O_4$ Nanoparticles: An efficient and reusable catalyst for 2*H*-indazolo [2, 1-*b*] phthalazine-triones synthesis under solvent free condition

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Abstract

A new, efficient and environmentally benign protocol for the one-pot, four-component synthesis of 2,2-dimethyl-13-phenyl-2,3-dihydro-1*H*-indazolo[2,1-b]phthalazine-1,6,11(13*H*)-trione by condensation of phthalic anhydride, hydrazinium hydroxide, aromatic aldehydes and dimedone catalyzed by $ZnFe_2O_4$ as an ecofriendly nanocatalysts with high catalytic activity under solvent-free conditions at room temperature is reported. The reaction proceeds to completion within 20-30 min in 75–90% yield.

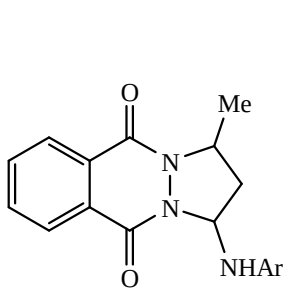
Introduction

Multicomponent reactions (MCRs) are defined as one-pot processes in which three or more substrates combine either simultaneously (so-called tandem or domino reactions), or through a sequential addition procedure that does not require any change of solvent. MCRs are gaining more and more importance especially in the total synthesis of natural products and medicinal heterocyclic compounds because of their simplicity, high yield of the products and short reaction times.[1,2] Solvent-free organic reactions have attracted much interest particularly from the viewpoint of green chemistry. Solid-state reactions (or solvent-free reactions) have many advantages, such as reduced pollution, low costs and simplicity in the process and handling.[3] The possibility of performing multicomponent reactions under solvent-free conditions with a heterogeneous catalyst could enhance their efficiency from economic and ecological points of

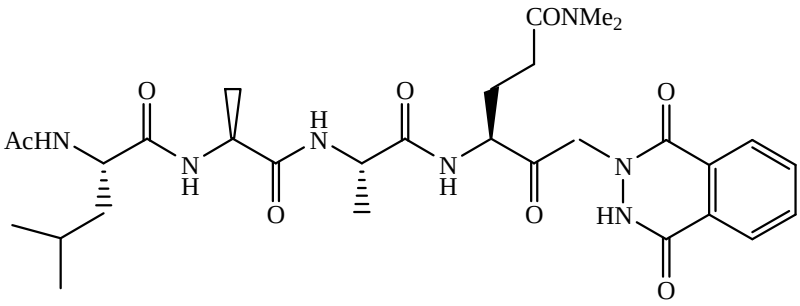
view.[4] The rapid assembly of molecular diversity utilizing multicomponent reaction (MCRs) has received a great deal of attention, most notably for the construction of heterocyclic 'drug-like' libraries.[4b-d] These methodologies have great utility, particularly, when they lead to the formation of privileged medicinal heterocyclic compounds.

In the past few decades, the synthesis of new heterocyclic compounds has been a subject of great interest due to their wide applicability. Heterocyclic compounds occur very widely in nature and are essential to life. Among a large variety of heterocyclic compounds, heterocycles containing phthalazine moiety are of interest because they show some pharmacological and biological activities (Fig. 5.1).[5-7]

Phthalazine derivatives, which have two bridgehead nitrogen atoms in a fused ring system, possess cytotoxic,[8] antimicrobial,[9] anticonvulsant,[10] antifungal,[11] anticancer[12] and anti-inflammatory[13] activities. Moreover, these compounds exhibited good promise as new luminescent materials or fluorescence probes.[14] Despite the available methods, the development of new synthetic methods for the efficient preparation of heterocycles containing Phthalazine ring fragment is therefore an interesting challenge.



antihypoxic and antipyretic agent[5]



HAV 3C inhibitor[6]

(**Figure 5.1**)

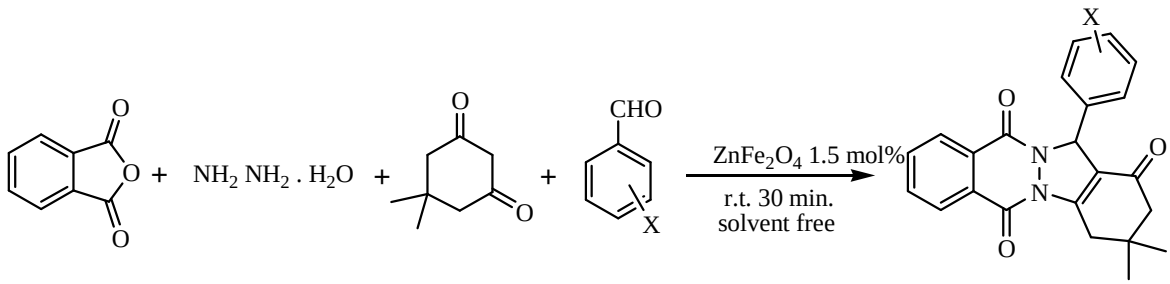
The first synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-triones was reported by Bazgir *et al*. using *p*-toluenesulfonic acid (*p*-TSA) as a catalyst[15]. In recent years, silica sulfuric acid,[16] H_2SO_4 in water–ethanol or an ionic liquid,[17] silica-supported polyphosphoric acid,[18] Mg(HSO4)2,[19] heteropoly acids,[20] *N*-halosulfonamides,[21] sulfonated poly(ethylene glycol),[22] wet cyanuric chloride,[23] molecular iodine[24] and nanosilica sulfuric acid,[25] have been utilized for the three-component condensation of 1,3-dicarbonyls, aromatic or aliphatic aldehydes and phthalhydrazide/urazole. Moreover, there are a few reports about the four-component

condensation of phthalic anhydride, hydrazinium hydroxide, aromatic aldehydes and dimedone using $Ce(SO_4)_2 \cdot 4H_2O$[26] or 1-butyl-3- methylimidazolium bromide ([Bmim]Br).[27a] Unfortunately, many of these methods are plagued with a number of limitations, such as harsh reaction conditions, unsatisfactory yields, tedious work-up procedures, relatively long reaction times, poor solvent scope and the use of stoichiometry and relatively expensive reagents. Therefore, improved methods, in terms of operational simplicity, reusability and economic viability are highly desirable.

In the continuation of our goal of ferroferic oxide nanoparticle has been utilized for organic transformations.[27b] The doping of Zn feature on Fe_3O_4 nanoparticles act as strong oxiding agents as heterogeneous catalyst which is easy separate out from the reaction mixtures. Additionally, advantages such as easy preparation by co-precipitation methods, eco-friendly nature, ease of handling, non-toxic nature make $ZnFe_2O_4$ nanoparticles an attractive catalyst for a variety of synthetic transformations. Regulatory pressures are increasingly focusing on the use, manufacture and disposal of organic solvents, and thus, the development of non-hazardous alternatives (one of the several goals for green chemistry and engineering) is vitally important for the continued and sustainable development of the chemical processes. Keeping within our theme of green chemistry for the developments of cheap and environmentally benign methodologies for the synthesis of 1-*H*-indazolo[1,2-*b*]phthalazine-1,6,11-triones .

Result and Discussion

The presented protocol is to highlight the synergistic effects of the combined use of MCRs and reactions under solvent-free conditions with heterogeneous acid nanocatalyst for the development of a new eco-compatible strategy for the synthesis of heterocyclices. Therefore, a straightforward convergent one-pot synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-trione derivatives using $ZnFe_2O_4$ nanoparticle an efficient catalyst under solvent-free conditions through the domino Knoevenagel condensation/Michael addition/intermolecular cyclodehydration sequence was examined (**Scheme 5.4**).



Yeild (70% to 87%)

Scheme 5.4

To evaluate the catalytic activity of $ZnFe_2O_4$ nanoparticles in the preparation of 2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione derivatives, a model four-component coupling reaction of phthalic anhydride (1 mmol), hydrazinium hydroxide(1.2 mmol), aromatic aldehydes (1mmol) and dimedone (1 mmol) under solvent-free conditions at room temperature in the absence and presence of $ZnFe_2O_4$nanoparticles were examined. It was found that in the absence of solid acid catalyst; only trace amount of the desired product was observed on TLC plate even after 1 h of heating**. (Table I)**. When the reaction was performed in the presence of $ZnFe_2O_4$ nanoparticle, it proceeded rapidly to give the desired product.

In order to evaluate the appropriate catalyst loading, a model reaction was performed using 0.5 mol% to 2.5 mol % catalyst without solvent **(Table I)**. It was found that 1.5 mol % of the catalyst resulted in the maximum yield in the minimum time. A higher percentage of loading of the catalyst (2.5 mol %) neither increased the yield nor shortened the conversion time. It was observed that the reaction was proceeding at room temperature. Elevating the reaction room temperature proved helpful and the yield of excellent product increased considerably. It was gratifying to find that the reaction proceeded smoothly and almost complete conversion to the product was observed at r.t, affording 3,4-dihydro-3,3-dimethyl-13-phenyl-2*H*-indazolo[2,1-*b*]phthalazine- 1,6,11(13*H*)-trione in 87 % yield within a short time

Table I Catalytic activity evaluation for the Synthesis 2H-Indazolo[2, 1-b] Phthalazine- Trione by $ZnFe_2O_4$

Entry	Fe_3O_4	Time in Minute/Hr	Yields[b]
1	—	20 Hr	35 %
2	0.5	3 Hr	60 %
3	**1.0**	**1 Hr**	**70 %**
4	**1.5**	**30 min**	**87 %**
5	2.0	25 min	80 %
6	2.5	10 min	70 %

[b]Isolated Yields

Table II Study of Various Lewis acid loading on the reaction at r.t.

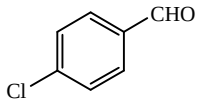
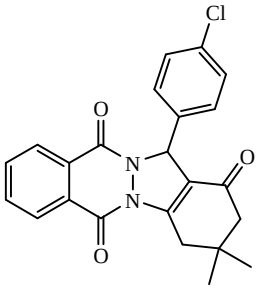
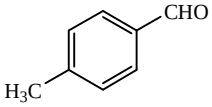
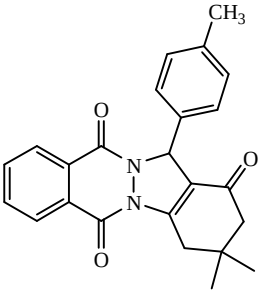
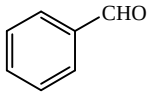
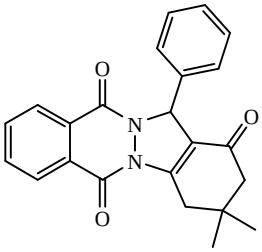
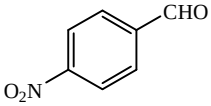
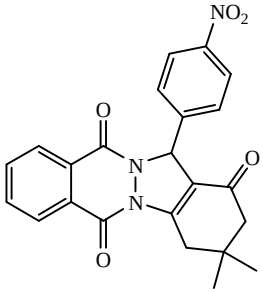
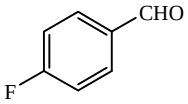
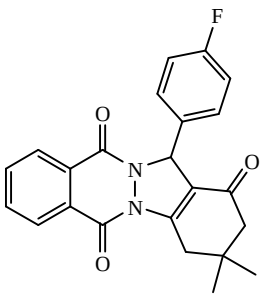
Entry	Catalyst	Time in Minute/Hr	Yields[b]
1	$InCl_2$	12Hr	42 %
2	$FeCl_2$	8 Hr	46 %
3	I_2	5.5 Hr	60 %
4	$CuSO_4$	7 Hr	56 %
5	CAN	2 Hr	45 %
6	$ZnCl_2$	10 Hr	53 %
7	$AlCl_3$	8 Hr	**57 %**
8	**$ZnFe_2O_4$**	**30 min.**	**87 %**

[b]Isolated Yields

To compare the advantages of the employment of $ZnFe_2O_4$ over other reported Lewis acid catalysts, the model reaction of dimedone, phthalic anhydride, hydrazinium hydroxide and benzaldehyde was considered as a representative example **(Table II).** While in most of these cases, comparative yields of the product were obtained as when the $ZnFe_2O_4$nanoparticles catalyzed procedure was followed, the reported procedures required high catalyst loading **(entry 1-7 in Table II)** .These results clearly demonstrate that $ZnFe_2O_4$ is an more efficient catalyst for this four-component reaction.

Subsequently, with optimal conditions at hand, *i.e*., 1:1:1.2:1 molar ratios of aromatic aldehydes (1 mmol), a phthalic anhydride (1 mmol), hydrazinium hydroxide(1.2 mmol), and dimedone (1 mmol) under solvent-free conditions and 1.5 mol % nanoparticles of $ZnFe_2O_4$ at room temperture under solvent-free conditions, the generality and synthetic scope of this coupling protocol were demonstrated by synthesizing a series of 2*H*-indazolo[2,1-*b*]phthalazine-1,6,11-triones **(Table III)**.

Table III Synthesis of 2H-Indazolo [2, 1-b] Phthalazine-1, 6, 11(13H)-Trione[a] by $ZnFe_2O_4$nanoparticle

Entry	Substrate	Product	Time(Min/Hr)	Yield[b] %	M.P.[o] C (Ref.25,27)
1			40 min	87 %	261-263
2			30 min	85 %	227-229
3			30 min	86 %	203-205
4			45 min	80 %	223-225
5			50 min	76%	218-220

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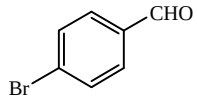
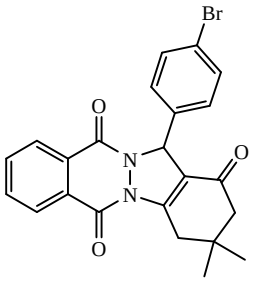
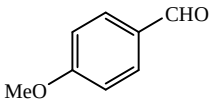
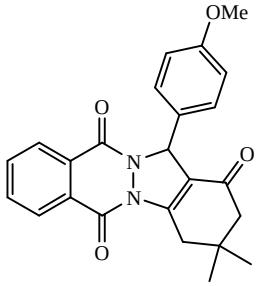
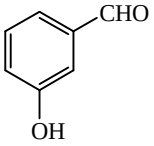
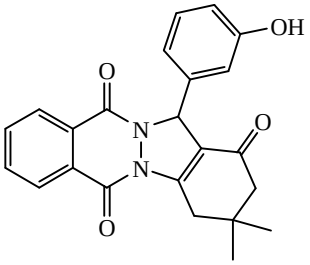
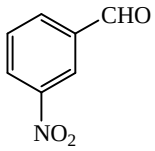
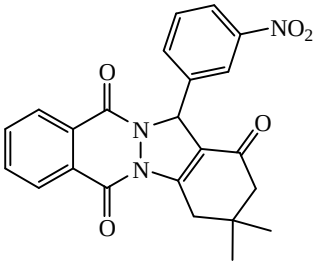
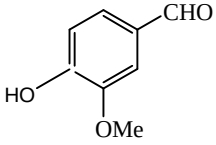
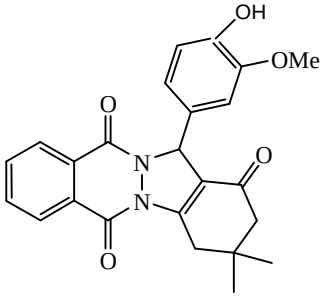
Entry	Substrate	Product	Time(Min/Hr)	Yield[b] %	M.P.^{o}C
6			40 min	80%	265-267
7			45 min	89 %	202-206
8			1.5 Hr	85 %	266-268
9			1.5 Hr	82 %	228-232
10			1 Hr	78 %	202-206

[b] Yield refer to Isolated Pure Product.

[a] Reaction Condition: Dimidone(1mmole) and aromatic aldehyde (1mmole) was added into the mixture of the appropriate phthalic anhydride (1mmole), hydrazine hydrate (1.2 mmole) in the molar ratio of 1:1:1:1:2 , $ZnFe_2O_4$ (1.5mol %) , stirred at R.T for 30 minute.

Gratifyingly, a wide range of aromatic aldehydes was well tolerated under the optimized reaction conditions. The time taken for complete conversion (monitored by TLC) and the isolated yields are presented in **Table III**. All new compounds were characterized by their satisfactory spectral (IR, ^{1}H-NMR and ^{13}C-NMR) studies, and the known compounds by comparison of their physical and spectral data with those reported.As shown in **Table III**, aromatic aldehydes having electron-releasing, as well as electron-withdrawing, groups were uniformly transformed into the corresponding 1*H*-indazolo[1,2-*b*]phthalazine-triones in high to excellent yields within 1hr. Substituent's on the aromatic ring had no obvious effect on yield or reaction time under the above optimal conditions.

Conclusion

$ZnFe_2O_4$ nanoparticles as acid catalyst is useful for the efficient catalytic method has been developed for the preparation of 1*H*-indazolo [1, 2-*b*] phthalazine-1, 6, 11- trione derivatives. The notable features of this clean one-pot procedure are the mild reaction conditions, improved yields, enhanced reaction rates, solvent free condition, recyclability of catalyst and operational simplicity. This protocol represents a useful and attractive process for the synthesis of 1*H*-indazolo [1, 2-*b*] phthalazine-1, 6, 11-trione derivatives

Experimental Section

(a) Materials

$ZnFe_2O_4$ nanoparticles were synthesized from co-precipitation methods[27b]. The other chemicals such as aromatic aldehydes, hydrazine hydrate, phthalic anhydride, Dimedone and solvents such as dichloromethane, diethyl ether, ethanol etc. were purchased from S. D. fine chemicals, India and qualigens. All the solvents were distilled and whenever necessary, double distilled before use. The progress of the reaction was monitored by thin layer chromatography using silica gel (60-120 mesh) coated plates. The petroleum ether used refers to the fraction 60-80. The products were purified by column chromatography or by recrystalization with appropriate solvent wherever possible.

(b) General procedures for the synthesis of 2*H*-indazolo [2, 1-*b*]phthalazine- triones

Dimidone(1mmole) and aromatic aldehyde (1mmole) was added into the mixture of the appropriate phthalic anhydride (1mmole), hydrazine hydrate (1.2 mmole) in the molar ratio

of 1:1.2 , $ZnFe_2O_4$ nanoparticles (1.5mol %) and resulting mixture was stirred at room temperature for 30 minute and corresponding the resulting product. It was dissolve in ethanol and filter the reaction mixture by filtration methods to afford precipitated product and corresponding separate out the nanoparticle of $ZnFe_2O_4$. The further purification was done by recrystalization with absolute ethanol or Ethyl acetate and n-hexane. The pure 2*H*-indazolo [2, 1-*b*]phthalazine- triones were obtained in 75-90 % isolated yields.

Spectral analysis

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on Spectrum BX FT-IR, Perkin Elmer (υmax in cm^{-1}) on KBr disks. ^1H NMR and ^{13}C NMR (400, 300 MHz and 100, 75 MHz respectively) spectra were recorded on Bruker Avance II-400 spectrometer in $CDCl_3$ (chemical shifts in δ with TMS as internal standard).

13-(4-chlorophenyl)-3,4-dihydro-3,3-dimethyl-2*H*-indazo[1,2-*b*]phthalazine-1,6,11(13*H*)-trione :**Entry (1):** Yellow solid. IR (KBr): 2939, 2229, 1666 cm^{-1}.^1H NMR ($CDCl_3$) δ = 8.29-8.18 (m, 2H), 7.80-7.78 (m, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.34 (s, 1H), 3.35-3.13 (AB system, *J* = 18.2 Hz, 2H), 2.26 (s, 2H), 1.13 (s, 6H). ^{13}C NMR ($CDCl_3$,) δ = 192.1, 156.0, 154.3, 151.1, 134.9, 134.6, 134.5, 133.6, 128.97, 128.93, 128.91, 128.5, 128.0, 127.7, 118.0, 64.3, 50.8, 38.0, 34.6, 28.6, 28.4. ESI- MS: *m/z* 407, 409 [M + H]+. Anal. Calcd for $C_{23}H_{19}ClN_2O_3$: C, 67.90; H, 4.71; N, 6.89. Found: C, 68.17; H, 4.87; N, 6.98.

3,4-dihydro-3,3-dimethyl-13-*p*-tolyl-2*H*-indazolo[1,2-*b*]phthalazine-1,6,11(13*H*)-trione : Entry (2)Yellow solid. IR (KBr): cm^{-1} .^1H NMR ($CDCl_3$) δ =8.28-8.18 (m, 2H), 7.78- 7.76 (m, 2H), 7.23 7.07 (d, *J* = 7.6 Hz, 2H), (d, *J* = 7.6 Hz, 2H), 6.34 (s, 1H), 3.36-3.13 (AB system, *J* = 18.2 Hz, 2H), 2.26 (s, 2H), 2.22 (s, 3H), 1.13 (s, 6H). ESI- MS: *m/z* 387 [M + H]+. Anal. Calcd for $C_{24}H_{22}N_2O_3$: C, 74.59; H, 5.74; N, 7.25. Found: C, 74.51; H, 5.80; N, 7.08.

3,4-dihydro-3,3-dimethyl-13-phenyl-2*H*-indazolo[1,2-*b*]phthalazine-1,6,11(13*H*)-trione :Entry (3)Yellow solid. IR (KBr): 2965, 2375, 1666 cm^{-1} .^1H NMR ($CDCl_3$) δ = 8.28- 8.17 (m, 2H), 7.79-7.75 (m, 2H), 7.34-7.19 (m, 5H), 6.37 (s, 1H), 3.36-3.13 (AB system, *J* = 18.4 Hz, 2H), 2.26 (s, 2H), 1.13 (s, 6H). . ESI- MS: *m/z* 373 [M + H]+. Anal. Calcd for $C_{23}H_{20}N_2O_3$: C, 74.18; H, 5.41; N, 7.52. Found: C, 74.07; H, 5.35; N, 7.35.

13-(4-bromophenyl)-3,4-dihydro-3,3-dimethyl-2*H*-indazo[1,2-*b*]phthalazine-1,6,11(13*H*)-trione :**Entry(6)**

Yellow solid. IR (KBr): cm^{-1} .^{1}H NMR ($CDCl_3$) δ = 8.29-8.18 (m, 2H), 7.80- 7.78 (m, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.32 (s, 1H), 3.35-3.13 (AB system, *J* = 18.2 Hz, 2H), 2.26 (s, 2H), 1.13 (s, 3H), 1.30 (s, 3H). ^{13}C NMR ($CDCl_3$) δ = 192.1, 156.0, 154.3, 151.1, 135.4, 134.6, 133.7, 131.9, 128.9, 128.89, 128.82, 128.0, 127.7, 122.7, 118.0, 64.4, 50.8, 38.0, 34.6, 28.6, 28.4. ESI- MS: *m/z* 451, 453 [M + H]+. Anal. Calcd for $C_{23}H_{19}$ BrN_2O_3: C, 61.21; H, 4.24; N, 6.21. Found: C, 61.40; H, 4.12; N, 6.48.

13-(4-methoxyphenyl)-3,4-dihydro-3,3-dimethyl-2*H*-indazo[1,2-*b*]phthalazine-1,6,11(13*H*)-trione :**Entry (7):**

Yellow solid. IR (KBr): 2963, 2376, 1660 cm^{-1} .^{1}H NMR ($CDCl_3$) δ = 8.28- 8.18 (m, 2H), 7.78-7.75 (m, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 6.34 (s, 1H), 3.69 (s, 3H), 3.37-3.13 (AB system, *J* = 19.2 Hz, 2H), 2.27 (s, 2H), 1.15 (s, 3H), 1.13 (s, 3H). ESI- MS: *m/z* 403 [M + H]+. Anal. Calcd for $C_{24}H_{22}N_2O_4$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.83; H, 5.65; N, 6.87.

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