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ARTICLE

Synthesis of 4-((2-hydroxynaphthalen-1-yl)(aryl)methyl)-5-methyl-2-phenyl-1H-pyrazol-3(2H)-ones using nano-Zn-[2-boromophenyl-salicylaldimine-methylpyranopyrazole]Cl_2 nanoparticles

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Nano-Zn-[2-boromophenyl-salicylaldimine-methylpyranopyrazole]Cl_2 (nano-[Zn-2BSMP]Cl_2) as a nanoparticle Schiff base complex and a catalyst was introduced for the solvent-free synthesis of 4-((2-hydroxynaphthalen-1-yl)(aryl)methyl)-5-methyl-2-phenyl-1H-pyrazol-3(2H)-ones by the multicomponent condensation reaction of various aromatic aldehydes, β-naphthol, ethyl acetoacetate, and phenyl hydrazine at room temperature.

KEYWORDS

4-((2-hydroxynaphthalen-1-yl)(aryl)methyl)-5-methyl-2-phenyl-1H-pyrazol-3(2H)-one, multicomponent reaction, nano-[Zn-2BSMP]Cl_2, schiff base complex, solvent-free

1 | INTRODUCTION

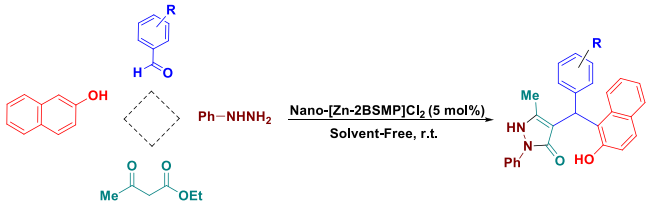
Newly, to study heterocyclic compounds in many natural products and their applications in pharmacological chemistry, researchers have made many attempts for the synthesis of similar compounds and their derivatives using multicomponent reactions (MCRs) as an effective protocol in organic synthesis. MCRs show a remarkable pattern in combinatorial chemistry by their ability to provide the desired products with greater efficiency and atom economy by producing structural complexity in a single step from three or more reactants.[1–8]

Pyrazolone derivatives are an important group of heterocyclic compounds because of their important antipyretic,[9] antibactericidal,[10] inflammatory,[11] and herbicidal properties.[12] Moreover, they have been reported for their antifilarial activities,[13] gastric secretion stimulatory properties,[14] and also, they are used to treat depression.[15] Various catalysts were used for the synthesis of 4-((2-hydroxynaphthalen-1-yl)(aryl)methyl)-5-methyl-2-phenyl-1H-pyrazol-3(2H)-ones including PTSA,[16] CuI nanoparticles,[17] $ZrOCl_2.8H_2O$, ZrO_2, ZrP_2O_7 NPs,[18] and [2,2′-BPyH][$C(CN)_3$]$_2$.[19]

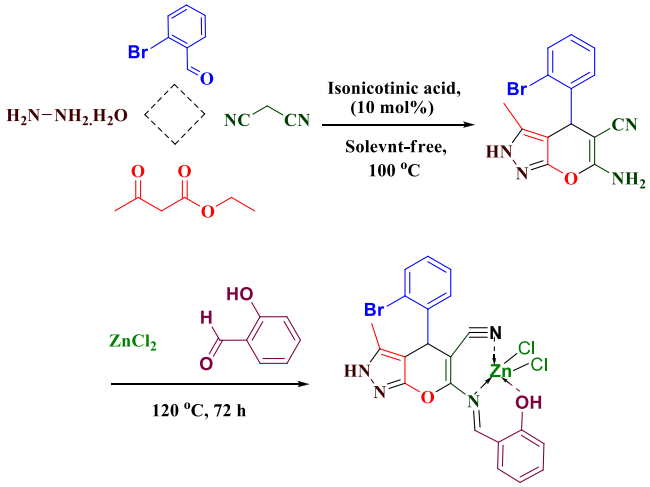
Schiff base compounds are widely introduced as one of the important groups of ligands because of their easy and convenient protocols for the synthesis and their interesting coordination chemistry.[20] Lately, we have prepared and identified a new category of Schiff base complexes by the reaction of pyranopyrazole derivatives with salicylaldehyde and different metal salts.[21–25] Herein, in continuing our previous investigations, we have prepared and characterized nano-Zn-[2-boromophenyl-salicylaldimine-methylpyranopyrazole]Cl_2 (nano-[Zn-2BSMP]Cl_2) and applied it, as an active complex and effective catalyst, for the synthesis of 4-((2-hydroxynaphthalen-1-yl)(aryl)methyl)-5-methyl-2-phenyl-1H-pyrazol-3(2H)-ones (Scheme 1).

2 | RESULTS AND DISCUSSION

Nano-Zn-[2-boromophenyl-salicylaldimine-methylpyranopyrazole]Cl_2 (nano-[Zn-2BSMP]Cl_2) was prepared by the condensation of 2-bromobenzaldehyde with ethyl acetoacetate,



SCHEME 1 The preparation of 4-((2-hydroxynaphthalen-1-yl)(aryl) methyl)-5-methyl-2-phenyl-1H-pyrazol-3(2H)-ones using nano-[Zn-2BSMP]Cl_2



SCHEME 2 The proposed structures of nano-[Zn-2BSMP]Cl_2

malononitrile, and hydrazine hydrate to obtain the corresponding pyranopyrazole according to previous literature.[26] The prepared pyranopyrazole reacted with salicylaldehyde and $ZnCl_2$ to give Nano-Zn-[2-boromophenyl-salicylaldimine-methylpyranopyrazole]Cl_2 (nano-[Zn-2BSMP]Cl_2) as a nano-Schiff base complex (Scheme 2).[25]

Energy-dispersive X-ray spectroscopy (EDX) of nano-[Zn-2BSMP]Cl_2 was conducted and the presence of the desired elements in the structure of the catalyst, namely carbon, oxygen, nitrogen, bromine, zinc, and chlorine, was confirmed. Therefore, the existence of related elements in nano-[Zn-2BSMP]Cl_2 was completely approved by EDX analysis (Figure 1).[25]

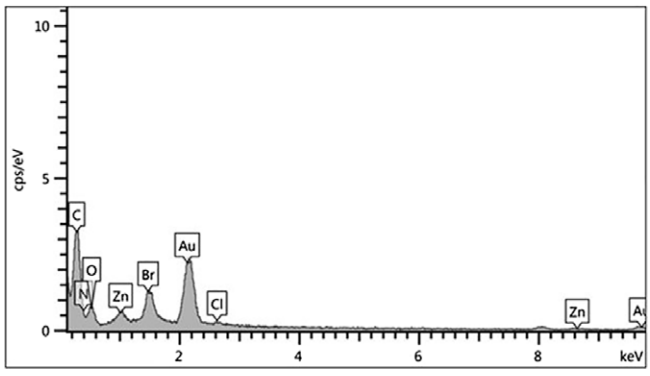


FIGURE 1 Energy-dispersive X-ray spectroscopy (EDX) of Nano-[Zn-2BSMP]Cl_2

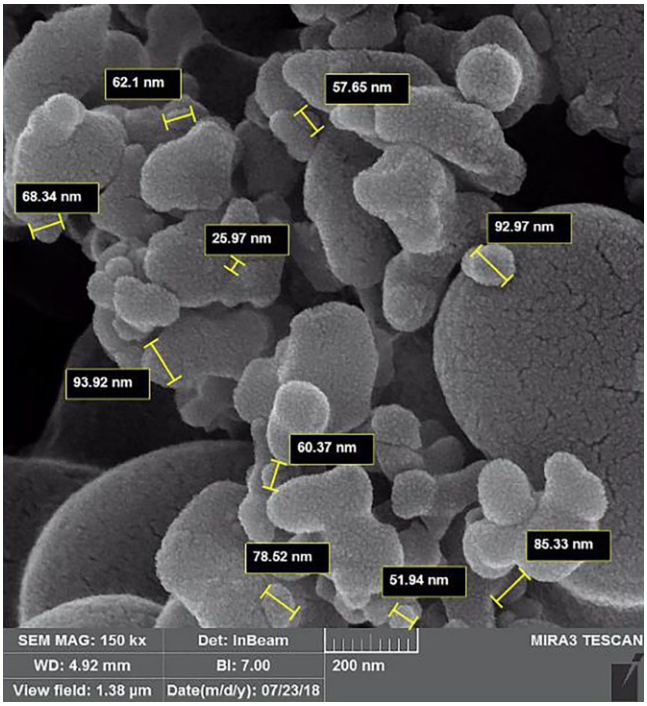


FIGURE 2 SEM micrograph of Nano-[Zn-2BSMP]Cl_2

The scanning electron micrographs (SEM) of nano-[Zn-2BSMP]Cl_2 were also obtained, which displayed that particles were made of size less than 100 nm (Figure 2).

To optimize the reaction conditions, the condensation of 2-naphthol, 4-chlorobenzaldehyde, phenylhydrazine, and ethyl acetoacetate was selected as a model reaction. In the next step, the model reaction was tested in the presence of various amounts of nano-[Zn-2BSMP]Cl_2 in the range of 25–80°C under solvent-free conditions. The best result was obtained using 5 mol% of nano-[Zn-2BSMP]Cl_2 at room temperature under solvent-free conditions. Increasing the

TABLE 1 The effect of the different amounts of the catalyst, types of solvents, and various temperatures on the reaction of 2-naphthol, 4-chlorobenzaldehyde, phenylhydrazine, and ethyl acetoacetate

Entry	Catalyst (mol%)	Solvent	Temperature (°C)	Time (min)	Yield[a] (%)
1	—	—	r.t.	120	10
2	—	—	80	120	15
3	2	—	r.t.	30	75
4	5	—	r.t.	10	90
5	7	—	r.t.	10	90
6	5	—	60	10	72
7	5	—	80	10	65
8	5	Hexane	r.t.	65	67
9	5	H_2O	r.t.	15	85
10	5	CH_3CN	r.t.	20	75
11	5	Ethyl acetate	r.t.	45	70
12	5	Acetone	r.t.	30	20
13	5	Dichloromethane	r.t.	17	69
14	5	Ethanol	r.t.	15	80

[a] Isolated yield.

TABLE 2 The synthesis of 4-((2-hydroxynaphthalen-1-yl)(aryl)methyl)-5-methyl-2-phenyl-1H-pyrazol-3(2H)-ones using nano-[Zn-2BSMP]Cl_2

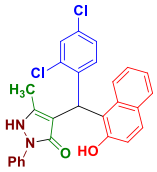
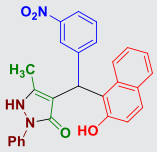
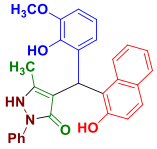
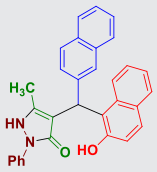
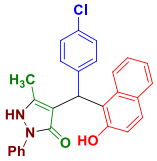
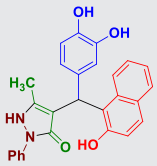
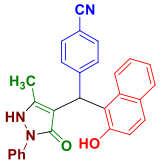
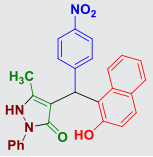
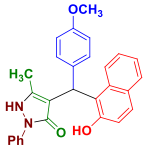
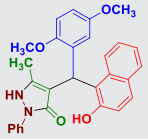
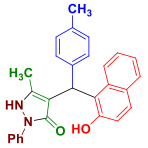
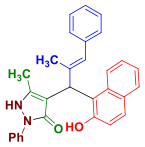
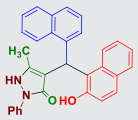
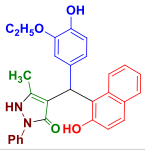
Entry	Product	Time (min)	Yield[a] (%)	M.p. °C (L)
1		12	85	209 (207–209) [19]
2		13	85	183 (183–185) [19]
3		23	78	175–178 (173–175) [19]
4		13	85	200–204 (197–199) [19]
5		10	90	224–228 (225–227) [19]
6		25	73	244–247 (245–247) [19]
7		10	90	220–224 (224–226) [19]
8		6	92	200–202 (199–201) [19]
9		20	80	185–188 (187–189) [19]
10		18	80	147–152 (149–152) [19]
11		20	80	202–203 (203–204) [19]

TABLE 2 (Continued)

Entry	Product	Time (min)	Yield[a] (%)	M.p. °C (L)
12		17	83	160–162 (157–159) [19]
13		15	93	240–242 (241–243) [19]
14		22	85	192 (197–199) [19]

[a] Isolated yield.

reaction time did not improve the yield of product (Table 1). The model reaction was also tested in various kinds of solvents in comparison with solvent-free conditions, which did not make much remarkable priority. The catalyst-free conditions were also tested, which did not have much to be desired in comparison with using of catalyst (Table 1, entries 1 and 2).

To study the generality and scope of nano-[Zn-2BSMP]Cl_2, we have continued our investigation using the catalyst (5 mol%) with various aromatic aldehydes to afford a series of 4-((2-hydroxynaphthalen-1-yl)(aryl)methyl)-5-methyl-2-phenyl-1H-pyrazol-3(2H)-ones at room temperature under solvent-free conditions. Various aromatic aldehydes containing electron-withdrawing substituents, electron-releasing substituents, and halogens on their aromatic rings were tested successfully in this reaction, and gave the desired products in high yields and in short reaction times (Table 2).

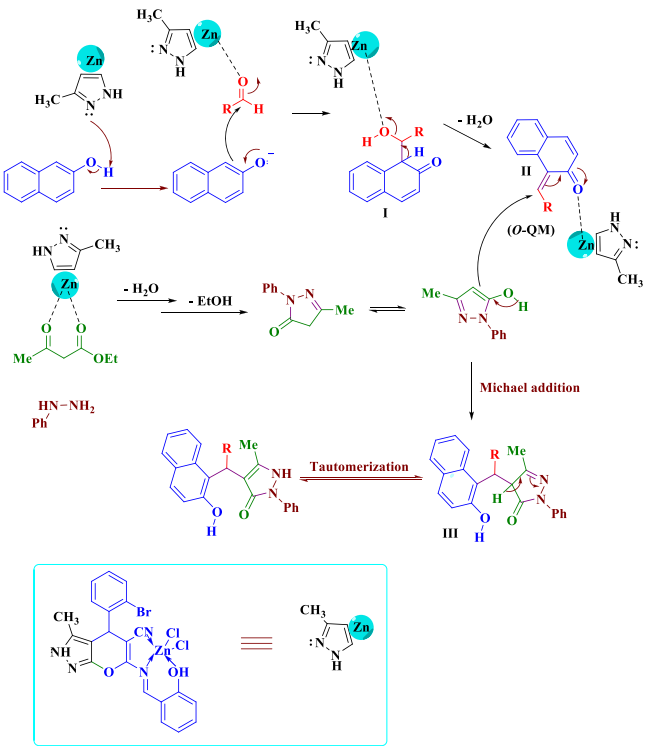
In a plausible mechanism, at first, aromatic aldehyde is activated by nano-[Zn-2BSMP]Cl_2, and then 2-naphthol attacks on the carbonyl group of the activated aldehyde and affords intermediate **I**. Then, orthoquinone methide (***o*-QM**, **II**) is prepared after removing one molecule of H_2O from intermediate **I**. In another part of the mechanism, ethyl acetoacetate is activated by nano-[Zn-2BSMP]Cl_2 and phenyl hydrazine attacks on the carbonyl group of the activated ethyl acetoacetate. Nucleophilic attack by another NH_2 group of phenyl hydrazine on the next carbonyl group of ethyl acetoacetate affords 5-methyl-2,4-dihydropyrazol-3-one after removing of one molecule of H_2O and EtOH, respectively. Finally, by the Michael addition reaction of 5-methyl-2,4-dihydropyrazol-3-one with orthoquinone methide (***o*-QM**, **II**), the desired product is prepared after tautomerization of intermediate **III** (Scheme 3).

Reusability of the catalyst was also tested on the reaction of 2-naphthol (1 mmol), 4-chlorobenzaldehyde (1 mmol), phenylhydrazine (1 mmol), and ethyl acetoacetate (1 mmol). After completion of the reaction, as monitored by TLC, the reaction mixture was extracted by warm dry ethyl acetate and separated from the catalyst after filtration. The catalyst was dried to reuse for another reaction. We observed that the catalytic activity of the catalyst was restored within the limits of the experimental errors for four successive runs (Figure 3).

3 | EXPERIMENTAL

3.1 | General

All chemicals were purchased from Merck or Fluka Chemical Companies. The known products were identified by comparison



SCHEME 3 The proposed mechanism for the synthesis of 4-((2-hydroxynaphthalen-1-yl)(aryl)methyl)-5-methyl-2-phenyl-1H-pyrazol-3(2H)-ones

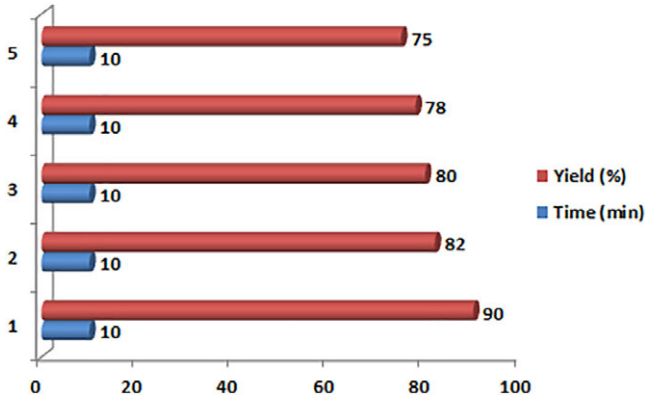


FIGURE 3 The reaction of 2-naphthol, 4-chlorobenzaldehyde, phenylhydrazine, and ethyl acetoacetate in the presence of nano-[Zn-2BSMP]Cl_2

of their melting points and spectral data with those reported in the literature. Progress of the reactions was monitored by TLC using silica gel SIL G/UV 254 plates.

3.2 | Procedure for the synthesis of nano-Zn-[2-boromophenyl-salicylaldimine-methylpyranopyrazole] Cl2 (nano-[Zn-2BSMP]Cl_2)

A mixture of 2-bromobenzaldehyde (1 mmol), malononitrile (0.066 g, 1 mmol), ethyl acetoacetate (0.13 g, 1 mmol) hydrazine hydrate (1.25 mmol), and isonicotinic acid (0.1 mmol) (0.0123 g, 10 mol%) was added in a 25 mL round-bottomed flask connected to a reflux condenser, and stirred at 100°C. After the completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature. Water was added to the reaction mixture to dissolve isonicotinic acid and the aqueous layer was separated from the reaction mixture. Then, the solid residue (crude product) was triturated by a mixture of ethanol and water (19/1) to furnish 6-amino-3-methyl-4-(4-nitrophenyl)-2,-4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile as an amine and product.[26] The prepared amine (1 mmol) and $ZnCl_2$ (1 mmol) were pulverized in a mortar for 10 min, and then transferred to a 25 mL round-bottomed flask containing salicylaldehyde (1.5 mmol), connected to a reflux condenser and stirred at 120°C for 72 hr. After this time, the reaction mixture was washed by ethylacetate and hexane (9/1) three times to purify nano-[Zn-2BSMP]Cl_2 from excess salicylaldehyde (Scheme 2).[25]

3.3 | General procedure for the synthesis of 4-((2-hydroxynaphthalen-1-yl)(aryl)methyl)-5-methyl-2-phenyl-1H-pyrazol-3(2H)-ones using nano-[Zn-2BSMP]Cl_2

To a mixture of 2-naphthol (1 mmol), 4-chlorobenzaldehyde (1 mmol), phenylhydrazine (1 mmol), and ethyl acetoacetate (1 mmol) in a 25 mL round-bottomed flask connected to a reflux condenser, nano-[Zn-2BSMP]Cl_2 (5 mol%) was added, and the resulting mixture was stirred at room temperature. After completion of the reaction, as monitored by TLC, warm ethyl acetate was added to the reaction mixture. The reaction mixture was soluble in warm ethyl acetate and the catalyst was insoluble in this solvent. The catalyst was separated from the reaction mixture by filtration and reused for another reaction. Finally, the crude product was purified by recrystallization from hexane/ethyl acetate (4:1). The spectra of compounds have been reported in supporting information.

4 | CONCLUSIONS

In summary, we have prepared and characterized nano-[Zn-2BSMP]Cl_2 as an efficient and heterogeneous catalyst for the one-pot multicomponent synthesis of 4-((2-hydroxynaphthalen-1-yl)(aryl)methyl)-5-methyl-2-phenyl-1H-pyrazol-3(2H)-ones by the MCR of various aromatic aldehydes, β-naphthol, ethyl acetoacetate, and phenyl hydrazine at room temperature under solvent-free conditions.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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