A Novel Hybrid Catalytic System Based on Immobilization of Phosphomolybdic Acid on Ionic Liquid Decorated Cyclodextrin-Nanosponges: Efficient Catalyst for the Green Synthesis of Benzochromeno-pyrazole Through Cascade Reaction: Triply green

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Abstract

An efficient hybrid catalyst was developed by immobilization of Keggin type heteropolyacid, phosphomolybdic acid, in the nanocavities of ionic liquid-modified cyclodextrin nanosponges. This immobilized species was characterized by SEM/EDX, FTIR, TGA, ICP-AES and XRD. The catalytic activity of the hybrid catalyst was confirmed in the synthesis of benzochromeno-pyrazole derivatives via cascade reaction of hydrazine hydrate, ethyl acetoacetate, α or β -naphthol and benzaldehyde. To establish the synergetic effects of conjugation of heteropolyacid and ionic liquid, the catalytic activity of the hybrid catalyst was compared with that of bare ionic liquid-modified cyclodextrin nanosponges. The obtained results indicated the superior activity of the former, from different points of view such as product yield and reaction time. **Noteworthy,**

the catalyst was reusable and could be recovered and reused for several reaction runs. The comparison of obtained results with previous reports was performed. Moreover, the potential utility of the catalyst under ultrasonic and microwave irradiation has been proved.

Keywords: Heteropolyacids, Cyclodextrin nanosponge, Catalyst, Benzochromeno-pyrazole, Cascade reaction.

1. Introduction

Green chemistry is a new field of chemistry with the goal of developing new eco-friendly and efficient procedures for the synthesis of chemicals by minimizing the waste and byproducts, using renewable resources, applying green solvents or solvent-less procedures etc. [1]

Cascade reactions, also referred as “Tandem”, “Sequential” or “Domino” reactions, are a class of one-pot reactions that consist of at least two sequential reactions such that each subsequent reaction takes place spontaneously only as a consequence of the chemical functionality formed in the previous step. These reactions benefit from some advantages such as reduced waste production, atom economy, and formation of several bonds [2] in one sequential process which make them as promising ways for synthesis of various chemicals [3-4] via greener routes. The classification of cascade reactions is still under debate. In one classification, introduced by K. C. Nicolaou [5], the cascade reactions were categorized according to the mechanism involved in the steps such as nucleophilic/electrophilic, radical, pericyclic or transition-metal-catalyzed reactions. If two or more types of this classification are involved in a one-pot reaction, it can be called cascade according to the major theme.

Organic chemistry plays an important role in our daily life and in our societies. However, the importance of environmental issues has distressed its public image due to possible negative effects on the ecologies. Therefore, the demand for environmental friendly strategies has increased from the green chemistry points of view. The design of a route, control of waste, finding acceptable procedures, transformation of resources and reducing of production cost are the other matters which should be well-thought-out as a part of this state of art [6]. Although, the ‘ideal synthesis’ is implausible and organic chemistry is still often hindered by different restrains, it is proved and well-recognized that conducting the organic reactions in a one-vessel manner circumvents some of the problems involved. In a one-pot reaction, the amounts of reagents, solvents, energy, time and man-power would be considerably reduced, thus besides the economical chemical production, the conduction of process in green conditions is also anticipated [7-8].

Chromone derivatives and their fused corresponding heterocycles can be found in many natural products, showing broad range of biological and pharmaceutical activities [9] such as antifungals, antibacterials [10], mutagenicity [11], antimicrobial [12] as well as DNA stand-breaking activity [13]. Chromone scaffold containing pyrazole moiety has attracted growing interest due to their biological activities. A great deal of research has been devoted to development of new derivatives of chromenopyrazoles [14-15].

Cyclodextrin nanosponges, CDNS, are porous hyper-crosslinked polymers obtained from reaction of biocompatible and commercially available cyclodextrin (CD) monomers with a suitable cross-linking agent; usually carbonyl diimidazole, diisocyanates and diarylcarbonates [16-17]. The outstanding feature of CDNS which distinguishes it from CD is its capability of hosting a broad range of hydrophobic and hydrophilic guest molecules [18-19], high stability and

resistance against high temperature and wide range of pH as well as insolubility in most of conventional organic solvents [16, 20-22]. These features make CDNS a good candidate for encapsulation of various drugs and chemicals. Up to now, the utility of CDNS and modified CDNS have been proved in many research fields such as catalysis [23-26], gas trapping, cosmetics and drug delivery [27-28], agrochemistry, pharmaceuticals [24], water treatment [29] and rubbers [16].

Heteropolyacids, HPA, are bifunctional green catalysts [30] with both redox potentiality and strong Bronsted acidity [31-32]. This class of catalysts possesses excellent properties such as sensitivity to electricity and light, non-corrosive entity and tune-ability. To date various types of HPAs have been widely used for promoting various organic [33-34], petrochemical [35], electrochemical [36-37] and photochemical reactions [38-39]. One strategy to improve the performance of HPAs is formation of HPA-based hybrid catalytic systems and taking advantages of the synergetic effects between HPA and the second component in the hybrid composition [40-43]. In this regard, combining HPAs with ionic liquids, ILs, which are considered as green compounds, has attracted much attention and several catalysts based on IL-HPAs have been synthesized and applied for catalysis [44-49].

In the last decade, we have manipulated HPAs as potential catalyst for promoting a wide range of organic transformations [22,23] especially in construction of various heterocyclic systems such as 4-hydroxycoumarin [50] and pyrazolo[3,4-d] pyrimidine derivatives [51] etc. Very recently we established the utility of the nanocavities of bare CDNS and amine-functionalized CDNS for embedding catalytic species, phosphomolybdic acid, and developing new hybrid catalysts for promoting organic reactions [52]. In continuation of our research on potential utility

of CDNS in catalysis and in attempt to develop a green catalyst, in this paper, we wish to introduce a novel catalytic hybrid system, HPA-IL/CDNS, based on immobilization of Keggin type heteropolyacid, phosphomolybdic acid, on ionic liquid functionalized CDNS, IL/CDNS. The catalytic activity of this hybrid system for the synthesis of benzochromeno-pyrazole derivatives via cascade reaction of hydrazine hydrate, ethyl acetoacetate, α or β -naphthol and benzaldehyde (Scheme 1) was studied and compared with those of bare IL/CDNS as well as sulfamic acid.

Scheme 1.

2. Experimental

2.1. Synthesis of CDNS

CDNS was prepared according to previously reported procedure [18-19, 27]. In short, 1 mmol of pre-heated β -cyclodextrin was slowly added to the molten mixture of 2 mmol diphenyl carbonate. Then the reaction between the components was promoted by vigorous stirring at 120 °C for 12h. The obtained white product was manually crushed in the course of reaction. After completion of reaction, the white solid was cooled and milled. Un-reacted β -cyclodextrin was removed by washing with distilled water, while the byproducts were washed out with acetone. More purification was performed by soxhlet extraction with ethanol, resulting a white solid after evaporation of EtOH. This white solid was dried overnight in an oven at 60 °C.

2.2. Synthesis of 1-methyl-3-(trimethoxysilylpropyl)-imidazolium chloride ([pmim]Cl)

[pmim]Cl was synthesized according to previously reported procedure [48]. Briefly, 1 mol *N* methyl-imidazole was mixed with 1mol of (3-chloropropyl)trimethoxysilan. The mixture was subsequently refluxed at 95 °C for 24 h. After cooling to room temperature, the mixture was washed with diethyl ether and dried under vacuum at 40 °C.

2.3. Grafting of [pmim]Cl on CDNS: Synthesis of IL/CDNS

CDNS (1 g) was reacted with [pmim]Cl (0.5 g) in 50 mL dried toluene and the mixture was refluxed for 24h. After cooling to room temperature, the obtained white solid was filtered and dried under vacuum at 70 °C. The removal of unreacted [pmim]Cl was carried out by 48 h extraction with boiling dichloromethane. The obtained white solid, denoted as of IL/CDNS was dried for 10 h at 50 °C.

2.4. Preparation of immobilized HPA-based ionic liquid (HPA-IL/CDNS)

To immobilize HPA, $H_4[Mo_{12}PO_{40}]$ (20 w%) was added to the suspension of IL/CDNS in 50 ml of deionized water and the mixture was stirred for 24 h at room temperature. The obtained solid was isolated by filtration and washed several times with deionized water, dried at 60 °C to give the designed novel catalyst.

2.5. Synthesis of Benzochromeno-pyrazole : General procedure

Initially hydrazine hydrate (1.1 mmol) was added drop wise to ethyl acetoacetate (1mmol) and then other components containing β -naphthol or α -naphthol (1mmol), benzaldehyde (1mmol) and HPA-IL/CDNS (0.04 g) were added at once and the mixture was heated at 80 °C. The progress of reaction was monitored by TLC using 2:1 mixture of n-hexane: ethyl acetate as eluent. After completion of the reaction, in the time as indicated in Table 2 the heterogeneous catalyst was separated by simple filtration and the mixture was cooled to room temperature. Subsequently, 5 ml of water was added. The precipitated product was separated

by filtration, washed three times with water, and deride at 60–70 °C. The corresponding products were recrystallized from ethanol to afford the pure products Tables 2 and 3.

2.6. Catalyst Characterization

The synthesized catalysts were characterized by using SEM/EDX, XRD, FTIR and TGA techniques. SEM/EDX images of the catalysts were taken by a Tescan instrument, using Au-coated samples and acceleration voltage of 20 kV. Room temperature powder X-ray diffraction patterns were collected using a Philips X-ray Diffractometer. Cu $\text{CuK}\alpha$ radiation was used from a sealed tube. Data were collected in the 2θ range 10–88° with a step of 0.02 and an exposure per step of 2s. FTIR analyses were carried out by employing PERKIN-ELMER- Spectrum 65 instrument.

3. Result and discussion

3.1. Characterization of catalysts

3.1.1. Characterization IL/CDNS

The FTIR spectrum of IL/CDNS is depicted in Figure 1. The appearance of a new peak at 1770 cm^{-1} is the characteristic peak of carbonyl group indicating formation of CD. The characteristic peaks at 1027 cm^{-1} (Si–O stretching) and 1623 cm^{-1} (C=N stretching) established the formation of IL. The peak at 2827 cm^{-1} was assigned to $-\text{CH}_2$ stretching.

Figure 1.

The SEM/EDX images of IL/CDNS are illustrated in Figure 2 and 3. The presence of C and O atoms in EDX image are assigned to CDNS while N and Si proved the presence of IL. The

worm-like morphology observed in SEM images of IL/CDNS is clearly different from the bare CDNS (Figure 4), indicating the role of IL functionalization on the morphology of CDNS.

Figure 2.

Figure 3.

Figure 4. [52].

The XRD pattern of IL/CDNS (Figure 5) shows relative crystalline structure and is similar to that of bare CDNS. According to previous reports this observation can be attributed to high dispersion of IL on the CDNS [53].

Figure 5.

To calculate the amount of IL grafted on the CDNS, thermal gravimetric analysis (TGA) of IL/CDNS was carried out (Figure 6). As shown, three degradation stages can be observed over the range of 50–500 °C. The first degradation (weight loss at about 100 °C) can be due to the loss of adsorbed molecules of water. The second weight loss (weight loss at about 250 °C) can be attributed to the thermal decomposition of IL. It has been previously found out that the CDNS degradation occurs at about 340 °C (the last stage) [16]. In conclusion, the content of IL was determined being 43.05%.

Figure 6.

1.1.1. Characterization HPA-IL/CDNS

The SEM-EDX images of HPA-IL/CDNS are depicted in Figure 7 and 8. The obtained worm-like morphology was similar to that of IL/CDNS to some extent. However, it was less aggregated. The presence of P in EDX proved the conjugation of the used HPA. It is worth noting that the peak related to Mo overlapped with P atom. Therefore, it was not recognized in EDX.

Figure 7.

Figure 8.

The FTIR spectrum of HPA-IL/CDNS is shown in Figure 9. Apart from the characteristic peaks for IL and CDNS, the observed peaks at 1085, 875, 798, 962 cm^{-1} can be assigned to symmetric stretching of P–O, Mo–Oc–Mo, Mo–Oe–Mo and Mo–Ot respectively. It is worth noting that the XRD analysis of the HPA-IL/CDNS was also performed. However, the XRD pattern was similar to that of IL/CDNS (Figure 5) indicating high dispersion of IL on the CDNS [53].

Figure 9.

Immobilization of HPA on IL/CDNS can be achieved not only through physical entrapment, but also it can be the result of electrostatic interactions between positively charged IL and negatively charged HPA. This dual immobilization manner has been observed previously [48].

For evaluation of the content of HPA in hybrid system, the HPA was digested in concentrated hydrochloric and nitric acids solution. The resulting extract was analyzed using ICP-AES analysis. The content of HPA was determined to be 6.4 % w/w.

Catalytic activity

It was demonstrated that carbamate CDNS has low surface area ($1\text{--}2\text{ m}^2\text{g}^{-1}$) [16]. However, it has high loading capacity and can embed various guests such as drugs. It is assumed that embedding

the guest does not proceed via a conventional surface adsorption but transportation into the bulk of CD-nanosponges. The inclusion is a downhill process which occurs spontaneously with ΔG° 10-13 kcalmol⁻¹ (at 298K) [16]. Taking advantages of this feature as well as its insolubility in conventional solvents, we established the utility of CDNS and amine-functionalized CDNS for hosting heteropolyacids [52] and developing a heterogeneous catalysts which could promote synthesis of xanthenes. To expand the use of CDNS which can be easily prepared from biocompatible cyclodextrin monomers and developing hybrid catalysts which can benefit from synergistic effects of two or more components, we introduced here a novel catalyst based on embedding IL within the nanocavities of CDNS and then conjugating HPA to obtain HPA-IL/CDNS. Noteworthy, both components used for synthesis of this hybrid catalyst, IL and HPA, are of green entities. Moreover, the support, CDNS, is obtained from porous carbohydrate monomers, cyclodextrin, which is a green monomer.

In our previous study [14] we disclose synthesis of benzochromeno-pyrazoles via three component reaction of 3-methyl-1*H*-pyrazol-5(4*H*)-one, β -naphthol and benzaldehyde under refluxing in acetonitrile in the presence of sulfamic acid.

Motivated by the green nature of the novel catalyst and in attempt to develop a greener and more atom economical procedure for synthesis of benzochromeno-pyrazoles, we studied whether the novel catalyst could promote synthesis of these conjugated heterocycles by a cascade reaction of hydrazine hydrate, ethyl acetoacetate, α or β -naphthol and benzaldehyde.

It was thought it is worthy to investigate whether the four component reaction for the synthesis of the benzochromeno-pyrazoles proceeds in the absence of any catalyst. To come to conclusion we conducted our model reaction involving hydrazine hydrate, ethyl acetoacetate, α -naphthol and

benzaldehyde in the absence of any catalyst. The progress of the reaction was monitored by TLC. The reaction seemed to proceed smoothly to give a product. We observed in the absence of catalyst only the reaction of hydrazine hydrate and ethyl acetoacetate takes place resulting in the facile formation of 3-methyl-1*H*-pyrazol-5(4*H*)-one. Besides, a trace of another by-product derived from the Knoevenagel condensation of benzaldehyde and ethyl acetoacetate was detected. Thus, we realized to achieve our target compound via a four component reaction the reaction must be promoted via catalysis. Secondly, it was studied whether the individual IL/CDNS can exhibit catalytic activity. For this purpose, the model reaction under IL/CDNS catalysis was performed using IL/CDNS in CH₃CN. The promising result, motivated more experiments for optimizing reaction condition. In this regard, the model reaction was performed in various solvents (Table 1). As obvious in this table, the best yield was obtained under solvent-free condition. Moreover, the best catalysts amount was recognized as 0.04 g per 1 mmol of reagents.

Table 1

Securing this optimum reaction conditions, different benzochromeno-pyrazole derivatives were synthesized by using differently substituted benzaldehydes bearing electron donating and electron withdrawing groups and α or β -naphthol to establish the generality of the process. Gratifyingly, all substrates led to high - excellent yields in relatively short reaction times. However, using β -naphthol as reagent resulted in slightly higher yields compared to α -naphthol. This can be attributed to less steric effects in the case of α -naphthol. These results indicated the catalytic activity of IL/CDNS system for synthesis of organic compounds. It is worth noting that in comparison to our previous three-component procedure [14] for synthesis of benzochromeno-pyrazoles which was performed under sulfamic acid catalysis, this IL/CDNS catalyzed cascade

process led to desired products in higher yields under green conditions and shorter reaction times.

Table 2

The observed catalytic activity of IL/CDNS can be attributed to the presence of the IL, 1-methyl-3-(trimethoxysilylpropyl)-imidazolium chloride ([pmim]Cl). Literature survey revealed that [54-55], the naked ILs itself can exhibit catalytic activity and has been used successfully as efficient catalysts for promoting various organic transformations. The immobilization of the IL on the CDNS support can render the catalyst heterogeneous and improve its catalytic reusability. It is worth to mention that although CDNS does not possess acidic property, it can exhibit the catalytic activity to some extent [52]. This can emerge from the formation of inclusion complex of reagents and CDNS through formation of hydrogen bonds and their concentration guests.

Motivated by high catalytic activity of IL/CDNS, the catalytic activity of heteropolyacid conjugated counterpart, HPA-IL/CDNS was also studied for the abovementioned reaction (Table 3). The results established the excellent catalytic activity of HPA-IL/CDNS for the synthesis of a broad range of benzochromeno-pyrazoles. According to our previous work on catalytic utility of cyclodextrin nanosponges [52] the catalytic activity of this catalyst not only can be attributed to the presence of two catalytic active species, HPA and IL, but also to the possibility of formation of inclusion complex of reagents and CDNS and concentrating reagents as well as formation of hydrogen bonds with substrate.

The comparison of catalytic activities of IL/CDNS and HPA-IL/CDNS proved the superior catalytic activity of the latter. All products were obtained in higher yields and shorter reaction

time. According to previous [56] reports this observation was ascribed to the synergistic effects of HPA and IL.

Table 3

The proposed mechanism of the cascade reaction is depicted in Scheme 2. It is suggested that initially, thermodynamically-favored reaction of hydrazine hydrate with ethyl acetoacetate affords 3-methyl-1*H*-pyrazol-5(4*H*)-one which subsequently tolerates Knoevenagel condensation with benzaldehyde to furnish an intermediate. The latter undergoes reaction with α or β -naphthol to form a new intermediate. The final product is achieved through ring closure and dehydration.

Scheme 2.

It is worth noting that in some previous reports in which the three component reactions of 3-methyl-1*H*-pyrazol-5(4*H*)-one, β -naphthol and benzaldehyde were performed in the presence of various catalysts such as K_2CO_3 , Et_3N , NH_4OAc and pyridine, the ring closure step was not occurred and 4-[(2-hydroxynaphthalen-1-yl)(phenyl)methyl]-3-methyl-1*H*-pyrazol-5-ol derivatives were obtained as the major products [57]. The novel bifunctional catalyst which possesses both Bronsted acidity and oxidation potential, however, was capable of promoting Knoevenagel condensation as well as ring closure and dehydration to afford the corresponding benzochromeno-pyrazole.

It is worthwhile to mention that the four component reaction of hydrazine, ethyl acetoacetate, aldehyde and β -naphthol was reported before in the presence of some catalysts such as CuI nanoparticles [58] and Ce/SiO₂ composite [59]. However, they led to the formation of 2-aryl-5-methyl-2,3-dihydro-1*H*-3-pyrazolones as major products.

To establish the versatility of the procedure and the activity of the catalyst under nonconventional green conditions, the model reaction was carryout out under ultrasonic and microwave irradiation. The results established that under microwave irradiation, the reaction was completed in a very short reaction time, 5 min. However, the yield of the desired product was lower (70%) due to formation of several byproducts. Gratifyingly, ultrasonic irradiation at 60 °C could promote the model reaction in short reaction time, 15 min, and high yield, 94%. These results proved that using the novel catalyst, even more green and efficient procedures can be developed.

Reusability of the catalyst

To investigate the reusability of the catalyst, HPA-IL/CDNS, the catalyst was recovered after the completion of the model reaction and then washed with EtOH and dried overnight at 100 °C. The recovered catalyst was used for promoting the consecutive reaction runs (Figure 10). As obvious, the reused catalyst exhibited almost the similar catalytic activity compared to the fresh one and only a slight loss of the catalytic activity was observed. These results established that this catalyst could be reused successfully. To study the HPA leaching, hot filtration test was performed using ICP-AES. The results demonstrated only negligible HPA leaching. This observation ruled out the possibility of homogeneous catalysis. As the used HPA was highly soluble in water, the very low leaching established that the IL/CDNS system could effectively immobilized and heterogeonized the HPA.

Figure 10

Conclusion

In summary, HPA-IL immobilized in the cavities of CDNS has been synthesized and used for promoting cascade reaction of hydrazine hydrate, ethyl acetoacetate, α or β -naphthol and benzaldehyde to afford the corresponding benzochromeno-pyrazole derivatives. The results showed a superior catalytic activity of HPA-IL/CDNS compared to IL/CDNS indicating the synergetic effects of HPA and IL. Notably, using the presented protocol the benzochromeno-pyrazoles could be synthesized for the first time via cascade procedure under green and mild reaction conditions. In comparison to previously reported three-component method catalyzed by sulfamic acid, this protocol led to higher yields and shorter reaction times. The catalyst can be applied under other green procedures such as microwave and ultrasonic irradiation.

More research for developing a true heterogeneous catalyst based on catalysts immobilized in CDNS is under process.

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Figure 1. FTIR spectrum of IL/CDNS.

Figure 2. SEM image of IL/CDNS

Figure 3. EDX analysis of IL/CDNS

Figure 4. SEM image of CDNS [52].

Figure 5. XRD pattern of CDNS and IL/CDNS.

Figure 6. The TGA analysis of IL/CDNS

Figure 7. SEM image of HPA-IL/CDNS.

Figure 8. EDX analysis of HPA-IL/CDNS.

Figure 9. FTIR spectrum of HPA-IL/CDNS.

Figure 10. The reusability of the catalyst.

Table 1 Effect of varying the solvent on the yield of **6a** under IL/CDNS

Entry	Solvent	Time (h)	Yield (%) ^a
1	EtOH	5	77
2	H ₂ O	6	55
3	CH ₃ CN	6	85
4	-	4	92

^a Yields refer to isolated products

Table 2 Synthesis of benzochromeno-pyrazole via cascade reaction using IL/CDNS

Entry	α/β -Naphthol	Ar	Product	Time (h)	Yield (%) ^a	M. P. Obs. °C	M. P. Rep. °C
1	β -Naphthol	4-NO ₂ -C ₆ H ₄	5a	3	82	241-243	242-244
2	β -Naphthol	4-OH-C ₆ H ₄	5b	3.5	75	200-202	201-202
3	β -Naphthol	4-MeO-C ₆ H ₄	5c	3	85	213-214	211-213
4	β -Naphthol	4-Me-C ₆ H ₄	5d	3	88	213-215	215-217
5	β -Naphthol	1-naphthyl	5e	5	82	269-272	270-271
6	α -Naphthol	4-F-C ₆ H ₄	6a	2.5	90	231-233	232-234
7	α -Naphthol	4-Cl-C ₆ H ₄	6b	2.5	90	230-232	231-232
8	α -Naphthol	4-NO ₂ -C ₆ H ₄	6c	2	92	258-261	260-261
9	α -Naphthol	3-NO ₂ -C ₆ H ₄	6d	3	89	230-233	232-234
10	α -Naphthol	1-naphthyl	6e	4.5	85	268-271	269-270

^a Yields refer to isolated products

Table 3 Synthesis of benzochromeno-pyrazole via cascade reaction in the presence of HPA-IL/CDNS

Entry	α/β -Naphthol	Ar	Product	Time (h)	Yield (%) ^a	M. P. Obs. °C	M. P. Rep. °C
1	β -Naphthol	4-NO ₂ -C ₆ H ₄	5a	2.5	88	242-243	242-244
2	β -Naphthol	4-OH-C ₆ H ₄	5b	3	84	200-201	201-202
3	β -Naphthol	4-MeO-C ₆ H ₄	5c	2.5	90	212-214	211-213
4	β -Naphthol	4-Me-C ₆ H ₄	5d	2.5	92	214-216	215-217
5	β -Naphthol	1-naphthyl	5e	3.5	90	270-271	270-271
6	α -Naphthol	4-F-C ₆ H ₄	6a	2.5	95	232-233	232-234
7	α -Naphthol	4-Cl-C ₆ H ₄	6b	2.5	94	229-231	231-232
8	α -Naphthol	4-NO ₂ -C ₆ H ₄	6c	2	95	260-261	260-261
9	α -Naphthol	3-NO ₂ -C ₆ H ₄	6d	2.5	91	231-232	232-234
10	α -Naphthol	1-naphthyl	6e	3.5	89	269-271	269-270

**A Novel Hybrid Catalytic System Based on Immobilization of Phosphomolybdic Acid on
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Synthesis of Benzochromeno-pyrazole Through Cascade Reaction: Triply green**