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Highly Reduced Graphene Oxide-Phosphomolybdic Acid Catalyzed Synthesis of Quinazoline Derivatives in Deep Eutectic Solvent: An Expeditious Approach

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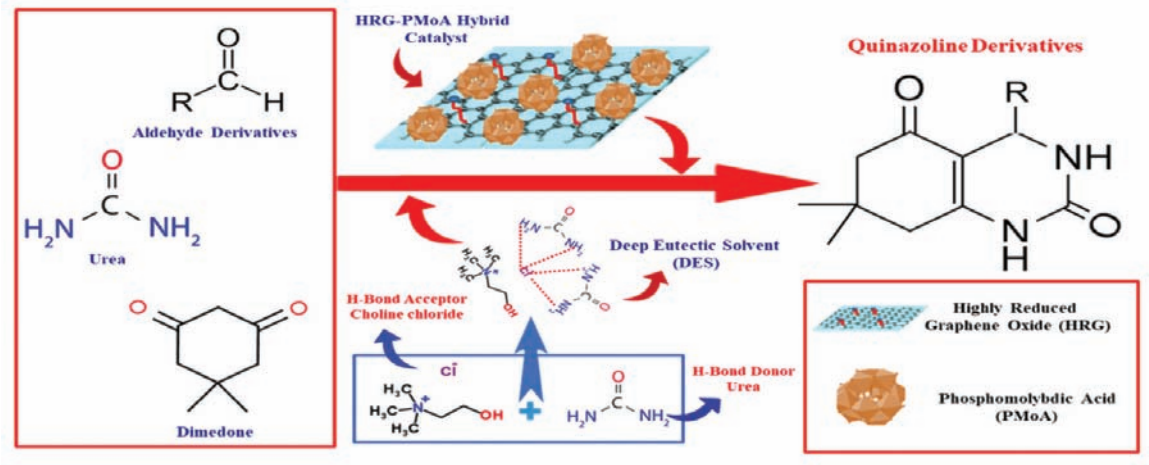
ABSTRACT Nanocomposite of highly reduced graphene oxide (HRG) with phosphomolybdic acid (PMoA) exhibits excellent catalytic activities toward the synthesis of quinazoline derivatives. The hybrid catalyst is cost effective, easy to apply and has shown encouraging results due to the combined effect of unique structural characteristics of HRG and efficient catalytic activity of PMoA. The prepared nanocatalyst was characterized by FTIR spectroscopy, X-ray diffraction study, Brunauer–Emmett–Teller, and scanning electron microscope analyses. In the present study, we have reported the synthesis of quinazoline derivatives through a three-component reaction system using a new strategy of recyclable nanocatalyst in another recyclable green solvent, namely, HRG-PMoA and deep eutectic solvent (DES), respectively. Hence, this concept adopted the doubly green approach and the process becomes expeditious. In conclusion, catalyst and DES were reused up to four times devoid of any significant change in its activity.



KEYWORDS Highly reduced-graphene oxide, Phosphomolybdic acid, Quinazoline, Deep eutectic solvent.

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INTRODUCTION

Synthesis of quinazoline through multicomponent reactions (MCRs) has potential benefits of facile execution, simple procedures, high selectivity, and atom economy.[1] Quinazoline is one of the most medicinally important fused scaffolds, which exhibits diverse biological activities such as antibacterial,[2] anticancer,[3,4] antiviral,[5] and antimalarial.[6] Several methods have been available in the literature for the synthesis of quinazoline derivatives, Biginelli being one of the oldest.[3] One of the recent researches toward the synthesis of quinazoline was reported in absolute ethanol with low yield (up to 69%).[7] Previously, Biginelli reactions have been employed for the synthesis of dihydropyrimidinone with the condensation of carbonyl compounds and urea, in the presence of many Lewis acid catalysts such as $LiBr_3$, $Mn(OAc)_3$, $ZrCl_4$, VCl_3, and $La(OTf)_3$.[8,9] As far as the importance of the quinazoline motif is concerned, various derivatives with restricted multistep procedures with the low-atom economy have been reported.[10,11] Furthermore, in some instances, metal-catalysts were used to enhance the reaction rate; but contamination of metal with the product is still a serious issue.[12,13] In spite of these hurdles, many easy, cost effective, and eco-friendly procedures have been reported to prepare quinazolines.[14,15]

One of the most important issues for the synthetic organic chemist is minimizing waste and maximizing sustainability to achieve green chemistry goals. However, over the last decade, more efforts have been taken to design environmentally benign recyclable heterogeneous catalyst which can work for the target reaction, economically feasible, and produce minimum waste. In this regard, the application of graphene-based materials as metal-free carbocatalyst has gained significant attention in the recent past in many organic transformations.[16,17] The presence of structural defects and various oxygen functionalities such as epoxy, hydroxyl, and carboxyl groups on the surface of graphene have immensely contributed to the mild acidic as well as oxidative properties of these materials.[18] Such types of graphene-like materials are typically referred to as highly reduced graphene oxide (HRG), which are often functionalized with various substances including solid acids such as phosphomolybdic acid (PMoA) through strong electrostatic interaction to enhance their physicochemical properties and catalytic potential.[19]

Recently, the demand for the exploration of eco-friendly solvents which are biodegradable and reusable has enhanced exponentially due to the increased threat of global warming. Among various solvents, water,[20] glycols,[21] supercritical liquids,[22] and ionic liquids have emerged as potential green solvents that have excellent ability to replace many organic solvents.[23,24] However, the utility of these solvents is limited due to their poor solubility and stability in many organic reagents. Alternatively, deep eutectic solvents (DESs) have gained decent popularity as compared to conventional solvents due to their low toxicity, biodegradability, wide range of liquid temperatures, recyclability, less volatility, and relatively high solvation ability for varieties of organic substances.[25,26] DESs are simply prepared from mixing an organic hydrogen bond donor (HBD) (e.g., urea) and hydrogen bond acceptor (e.g., choline chloride, and benzalkonium chloride). In these types of mixtures, the melting point of the resultant mixture is less than the individual HBD and hydrogen bond acceptor (HBA).[27,28] Due to this, plenty of organic conversions was successfully performed by the utilization of DESs.[29,30]

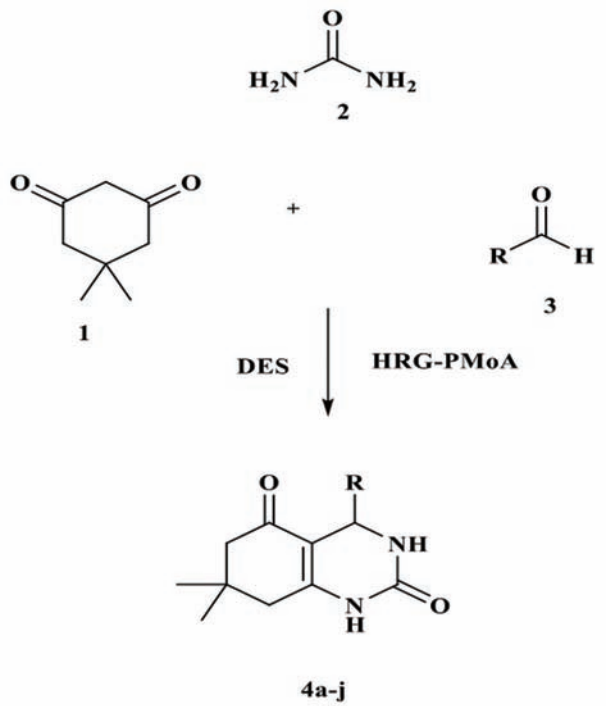
In the continuation of our ongoing research toward the development of greener methodologies for various organic conversions,[31,32] herein we present the concept of applying HRG incorporated PMoA (HRG-PMoA) as catalyst for the direct synthesis of some quinazolines from one-pot three-component reaction system using DES [**Scheme 1**].

RESULTS AND DISCUSSION

Catalyst characterization

Fourier-transform infrared spectroscopy (FTIR) spectra of HRG-PMoA

FTIR spectra of (a) HRG, (b) PMoA, (c) HRG-PMoA, and (d) HRG-PMoAT are shown in **Figure 1**. HRG exhibits various characteristics bands at ~2332, ~2158, ~2027, ~1976, ~1577, ~611, and ~585 cm^{-1}. These bands represent various oxygen-containing functional groups such as carbonyl, carboxylic acid, epoxy, and hydroxyl groups on the surface of HRG. Most of these bands are also present in the FTIR spectrum of reduced graphene oxide (RGO);[33] however, the intensities of these bands are significantly reduced in the IR spectrum of HRG. The decreased intensities of these bands designate the reduction of the RGO, i.e., oxygen-containing functional groups reduced after the reduction. The presence of characteristic IR bands of both HRG and PMoA in the IR spectrum of HRG-PMoA points toward the successful functionalization of HRG with



Scheme 1: Synthesis of quinazoline derivatives

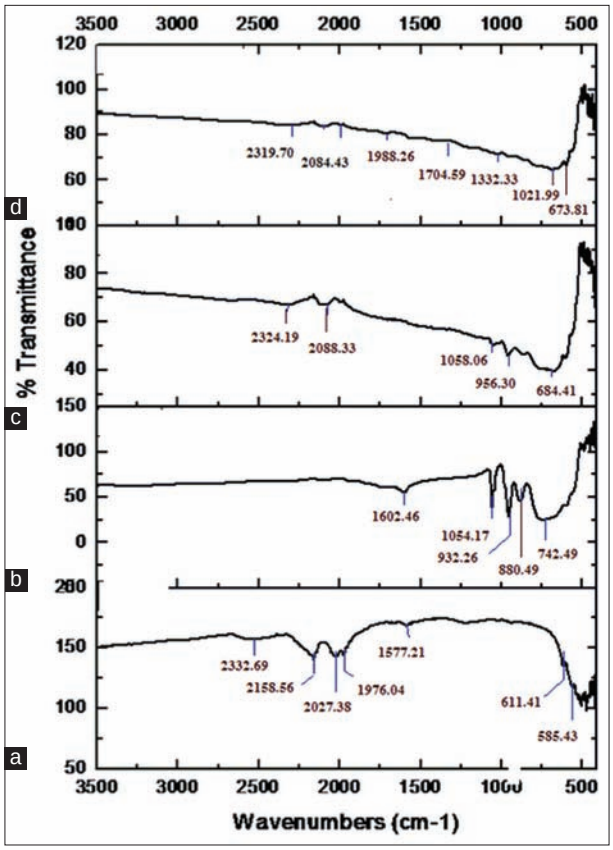


Figure 1: FTIR spectra of (a) HRG, (b) PMoA, (c) HRG-PMoA, and (d) HRG-PMoAT

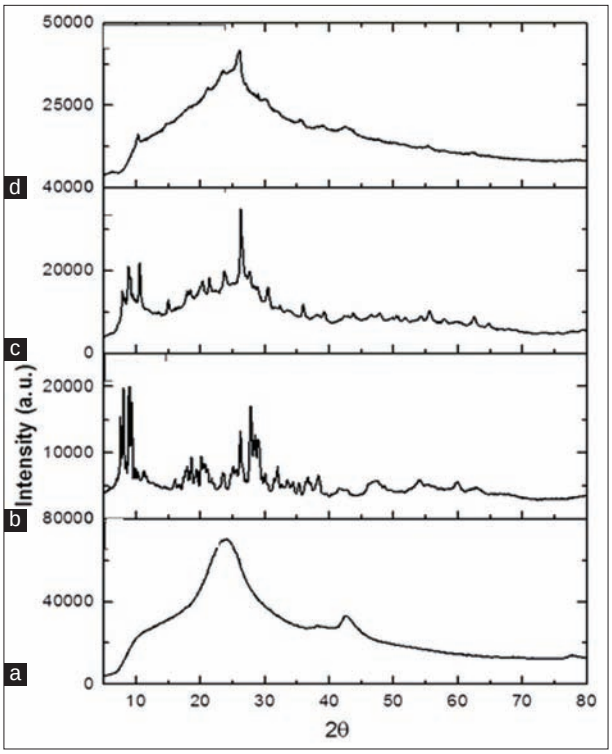


Figure 2: XRD diffraction pattern of (a) HRG, (b) PMoA, (c) HRG-PMoA, and (d) HRG-PMoAT

PMoA. For instance, the presence of various bands in the range of 1700–2400 cm^{-1} in HRG-PMoA and HRG-PMoAT, which is assigned to the carbon skeleton of HRG such as C=C of aromatic and CH-CH of aliphatic functional groups.[33,34] Notably, these bands are not present in the IR spectrum of PMoA, whereas some strong bands of PMoA around 1054.17, 932.26, 880.49, and 742.49 cm^{-1} corresponds to the stretching vibrations of P-O, Mo-O terminal, Mo-O vertex, and Mo-O-Mo corner bond, respectively, were later disappeared or became less prominent after effective interaction with RGO during the formation of HRG-PMoA catalyst.[19] The behavior of catalysts was examined up to four consecutive applications in the organic reactions. As far as bands intensity is concerned after repetitive use, not much change is observed in fresh HRG-PMoA and treated HRG-PMoAT.

X-ray diffraction (XRD) analysis of HRG-PMoA

The XRD pattern of (a) HRG, (b) PMoA, (c) HRG-PMoA, and (d) HRG-PMoAT was studied to access the crystallinity of catalyst, as shown in **Figure 2**. A broadband at around $2\theta \approx 25°$ and absence of a peak at $2\theta \approx 10°$ of RGO were observed in XRD of HRG after reduction due to the removal of oxygen functionalities. This confirms the successful reduction of RGO to HRG, whereas the XRD spectrum of PMoA exhibited several intense peaks which represent the characteristics of keggin-type polyoxometalate.[35] In this case, the XRD spectrum points toward the triclinic phase of PMoA consisting of a characteristic strong peak at ~9°. These characteristics diffraction peaks of kegging geometry of PMoA were still preserved in HRG-PMoA hybrid, signifying the quite dispersed nature of PMoA in the HRG-PMoA catalyst.[35] The crystallinity of HRG-PMoA catalyst after successive use in organic reactions was shifted toward the more amorphous side as in HRG-PMoAT.

Brunauer–Emmett–Teller (BET) surface area measurements of HRG-PMoA

HRG-PMoA catalyst texture properties at multi-point and adsorption/desorption isotherm at 77.35 K under nitrogen gas flow at low relative pressure are shown in **Table 1**. Low pore volume (0.041 cm^3g^{-1}) of the HRG-PMoA was calculated based on the BJH absorption/distribution method which is characteristic of mesoporous-like material.[36] The effect of the addition of PMoA to HRG can be quantified by BET surface area measurements as well as pore size distribution. It was reported that the BET surface area of RGO and HRG is about 25 and 400 m^2g^{-1}, respectively, depending on the method of reduction.[37] As a result of the RGO reduction, it might increase the porosity of the HRG because of the loss of oxygen functional groups.

Further, on the impregnation of PMoA on HRG, the BET surface area decreases by many folds. This may be attributed to the attachment of complex keggin-type polyoxometalate framework of PMoA on the surface of HRG that can block the pores and thus reduce surface area (1.870 m^2g^{-1}) and pore size (17.057, and 19.098 Å) of HRG-PMoA.

Scanning electron microscope (SEM) morphology of HRG-PMoA

The presence of morphological features of the HRG before and after interaction with PMoA is presented in

Table 1: Texture properties of highly reduced graphene oxide-phosphomolybdic acid catalyst

Method	BET (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)
Multi-point BET	1.870	-	-
BJH pore size distribution-absorption	5.114	0.041	19.098
BJH pore size distribution-desorption	6.290	0.041	17.057

BET: Brunauer–Emmett–Teller, BJH: Barrett-Joyner-Halenda pore size and volume analysis

Figure 3. HRG and HRG-PMoA images are distinguishable as formerly revealed as folded sheets and in latter PMoA seems as embedded granules on to the surface of reduced graphene. Compared with HRG, HRG-PMoA shows identical crumbling with the clear layered structure in both SEM images. This unique feature of two-dimensional graphene sheets made accessible for acid-catalyzed reactions and reactants get easily finds the active site over the surface of the catalyst.[38] SEM image of the catalyst was further evaluated after use in organic reactions many times. A slight change in catalyst (HRG-PMoAT) basic structure with clear voids was found more visible than before. Furthermore, the dispersed PMoA was not identified on the surface of HRG as compared to the fresh catalyst (HRG-PMoA). This might be due to the repeated use in organic synthesis, PMoA particles converted into a tiny size and unevenly distributed on the whole surface of HRG.

Catalyst activity

The catalytic potential of HRG-PMoA hybrid was examined for the synthesis of quinazoline derivatives (**4a-j**) from dimedone (1.4 mmol), urea (1.2 mmol), and aldehydes (1 mmol) in a typical MCR [**Scheme 1**].

Considering a general experimental procedure, we assessed the effect of catalysts on the synthesis of quinazoline derivatives under different conditions. Initially, a pilot reaction was attempted to set up by randomly chosen some conventional aldehydes. Under optimized conditions, quinazoline-containing 4-Cl-benzaldehyde showed the best results and regarded as a model compound (**4b**). The obtained results are presented in **Table 2**.

In the beginning, to run the model reaction, amount of catalyst loading was selected as 10, 20,30, 40, 50, and 60 mg with the corresponding change of DESs 2, 4, 6, 8, and 10 mL at a temperature from RT to 100°C [**Table 2** entries, 1-7]. A maximum yield (97%) of the model compound was achieved using a catalyst load of 50 mg, DES 8 mL with an optimum temperature of 80°C in 40 min only [**Table 2** entry 5]. A good correlation was found among the catalyst (HRG-PMoA) amount, solvent (DES), and temperature [**Table 2** entries 1-7] to achieve a target model compound. The yield of the model compound was increased with the simultaneous increase in catalyst load, solvent, and temperature along with the gradual decline in reaction time [**Table 2** entries 1-5]. The product yield was further reduced when catalyst load, amount of solvent, and temperature were raised to the next higher level [**Table 2** entries 6-7]. Under standard operating conditions (entry 5), the reaction was assessed without catalyst load (entry 8). As a result, only 35% yield was obtained. This confirmed that the DES has

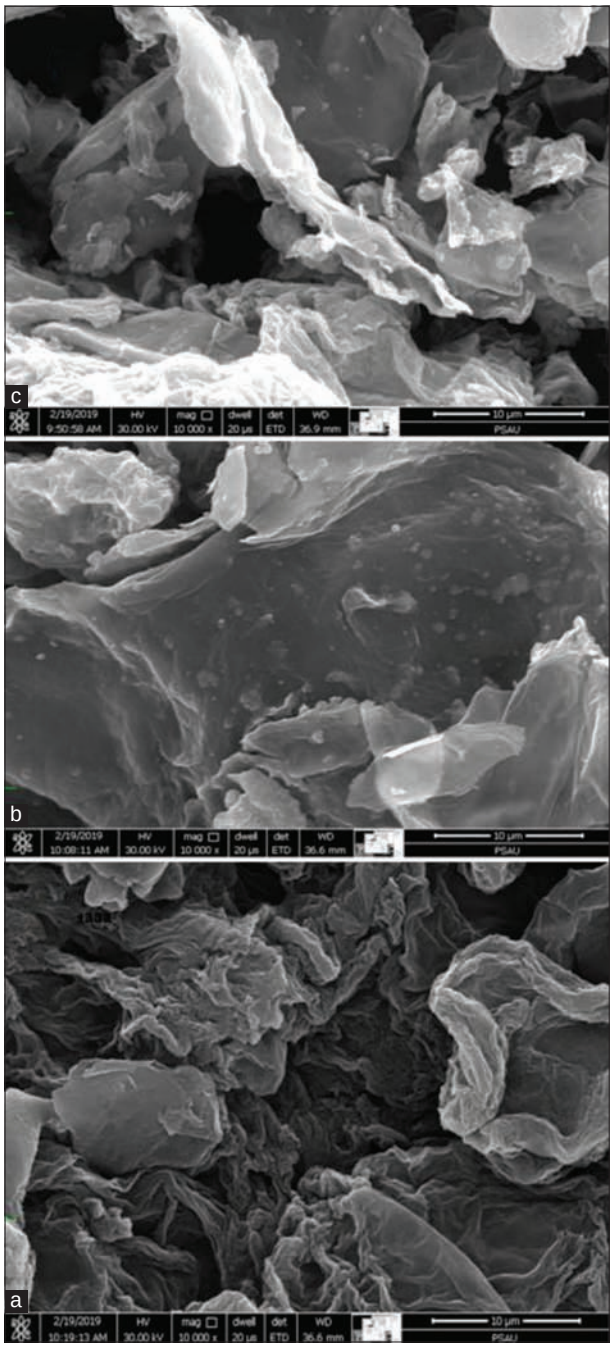
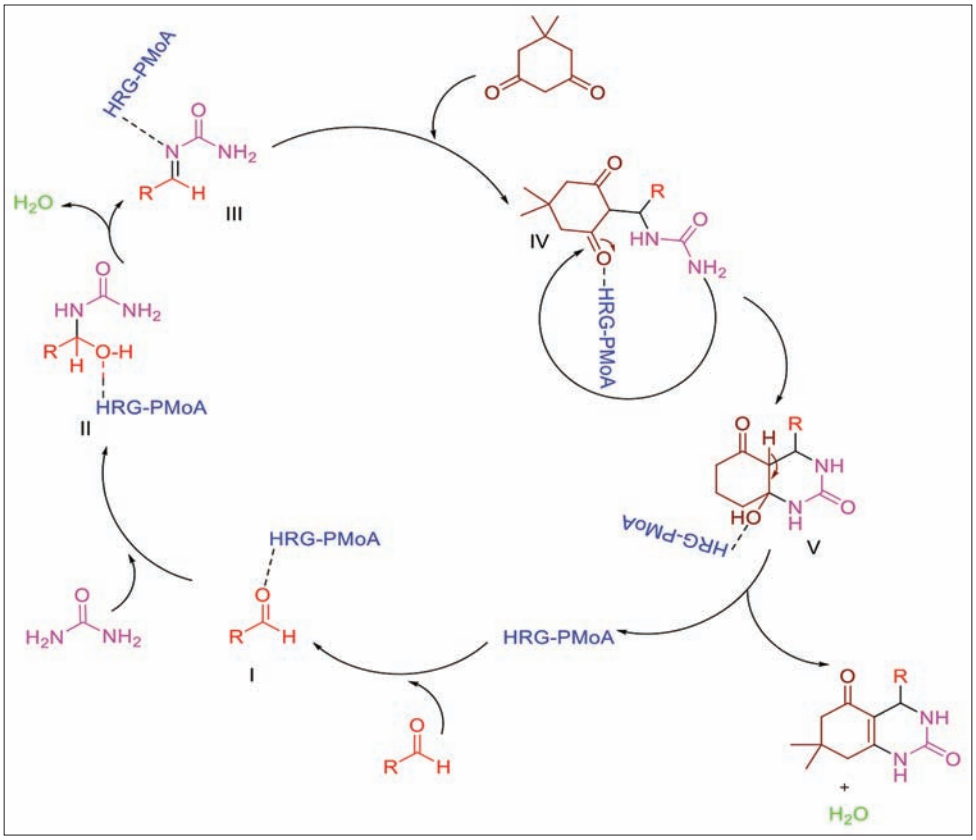


Figure 3: SEM morphology of (a) HRG, (b) HRG-PMoA, and (c) HRG-PMoAT

also played a worthy role to made such a reaction possible without a catalyst.

Maintaining the catalyst load (50 mg), DES (8 mL), and temperature (80°C), the model reaction was further optimized by taking separately PMoA, HRG, and compared



Scheme 2: A proposed mechanism for the synthesis of quinazoline derivatives using HRG-PMoA catalyst

Table 2: Effect of catalyst loading (highly reduced graphene oxide-phosphomolybdic acid), amount of deep eutectic solvent and temperature for the synthesis of model compound 4b

Entry	Catalyst load (mg)	DES (mL)	Temperature (°C)	Time	Yield[a] (%)
1	10	2	RT	5 h	45
2	20	4	40	4 h	52
3	30	6	50	3.5 h	62
4	40	8	60	1 h	81
5	50	8	80	40 min	97
6	50	10	80	50 min	91
7	60	8	100	1 h	88
8	-	8	80	40 min	35

[a]Isolated yields obtained under optimized conditions. DES: Deep eutectic solvent, RT: Room temperature

with the results of hybrid catalyst (HRG-PMoA) [**Table 3** entries 1-3].

Under above-mentioned optimized condition, PMoA delivered only 58% yield in 3 h, while HRG gave 65% in 2.5 h [**Table 3** entries 1-2] as compared to the maximum yield of 97% obtained in the case of HRG-PMoA [**Table 3** entry 3]. Better performance of hybrid catalyst (HRG-PMoA) was due to the presence of polyoxometalate/PMoA on the surface of HRG and responsible for a synergistic effect in the enhancement of product yield with regard to the individual HRG and PMoA. The overall surface Lewis acid properties may interplay to the performance of catalyst after the attachment of PMoA on the HRG.[19]

Considering the economic and environmental points of view, water and ethanol were selected for a model reaction.

Table 3: Catalyst optimization for the synthesis of model compound 4b[a]

Entry	Catalyst	Time	Yield[b] (%)
1	PMoA	3 h	58
2	HRG	2.5 h	65
3	HRG-PMoA	40 min	97

[a]Reaction conditions: Dimedone (1.4 mmol), urea (1.2 mmol), 4-Cl-benzaldehyde (1 mmol), DES (8 mL), catalyst (50 mg), [b]Isolated yields obtained under optimized conditions. HRG-PMoA: Highly reduced graphene oxide-phosphomolybdic acid, DES: Deep eutectic solvent

Under the influence of conc. H_2SO_4 as an acid catalyst in distilled water at RT conversion was 79% at 4 h [**Table 4** entry 1]. A shifting of ethanol as a solvent with the same catalyst at refluxing temperature, a trace amount of model compound was obtained even after 10 h [**Table 4** entry 2].

Table 4: Effect of different reaction conditions on the synthesis of model compound 4b

Entry	Catalyst	Solvent	Temperature (°C)	Time	Yield (%)	References[a]
1	Concentrated H_2SO_4	H_2O	RT	4 h	73	[8]
2	Concentrated H_2SO_4	Ethanol	80	10 h	Trace	[9]
3	Concentrated HCl	Ethanol	Reflux	7 h	Trace	[9]
4	*p*-TsOH	Toluene	100	8 h	Trace	[39]
5	Al_2O_3	Solvent-Free	-	1.5 h	Trace	[40]
6	Graphene oxide	DMSO/H_2O(5:1)	130	22 h	52%	[40]
7	HRG-PMoA	DES	80	40 min	97	This work

[a]Reactions performed according to the given literature. HRG-PMoA: Highly reduced graphene oxide-phosphomolybdic acid, DES: Deep eutectic solvent, RT: Room temperature, DMSO: Dimethyl sulfoxide

Table 5: Highly reduced graphene oxide-phosphomolybdic acid-catalyzed various quinazolines in deep eutectic solvent

Entry	R	Product	Time (min)	Yield[a,b] (%)	Melting Point (°C)		References
					Found	Reported	
1	C_6H_5	**4a**	45	94	292–293	290–91	[7]
2	4-Cl-C_6H_4	**4b**	40	97	298	>300	[7]
3	4-Me-C_6H_4	**4c**	60	93	302	>300	[9,41]
4	4-OCH_3-C_6H_4	**4d**	55	95	249–250	246–247	[42]
5	3-OCH_3,4-OH-C_6H_3	**4e**	50	96	191–192	192–194	[43]
6	3,4,5-$(OCH_3)_3$ C_6H_2	**4f**	60	91	141–142	139–140	[44]
7	4-OH-C_6H_4	**4g**	50	92	303–304	300–302	[44]
8	1-C_8H_6N	**4h**	80	88	254–256	-	-
9	1-C_2H_6	**4i**	100	75	210–212	-	-
10	1-C_3H_8	**4j**	120	74	228–30	231–233	[3]

[a]All reactions were performed in a stoichiometric ratio of each reacting species with 50 mg of HRG-PMoA as a catalyst and 8 mL DES at a refluxing temperature of 80°C, [b]Isolated yields. HRG-PMoA: Highly reduced graphene oxide-phosphomolybdic acid, DES: Deep eutectic solvent

When the reaction was again tried in absolute ethanol in another mineral acid (conc. HCl), result was the same after 7 h [**Table 4** entry 3].

With the influence of some pieces of literature, catalysts: Solvents duo were examined for the model reaction [**Table 4**]. When the reaction was carried out in p-toluenesulfonic acid (TsOH) in toluene and Al_2O_3 under the solvent-free condition in a different time frame, it exhibits a very negligible yield [**Table 4** entries 4-5]. The reaction was further tested with solid acid catalyst, i.e., graphene oxide (GO) in DMSO/H_2O (5:1) yielded just 52 % in 22 h. Briefly, our new studied catalyst exhibits better performance in a recyclable, eco-friendly DES [**Table 4**, entry 7].

Next, we expanded the overview of this process by considering a wide range of aromatic, aliphatic, and heterocyclic aldehydes under the determined reaction conditions to afford target quinazoline derivatives (**4a-j**) [**Table 5**]. The obtained results are presented in **Table 5** (entries 1-10).

All the substrates were effectively consumed and cyclized to produce high yields in minimum time. The reaction of dimedone (1) and urea (2) with unsubstituted aromatic aldehydes or bearing electron-withdrawing groups (Compound **4a**, **4b**) displayed excellent yield within 50 min [**Table 5** entries 1-2]. Again, the reaction was replaced by electron-donating aromatic aldehydes (OCH_3, OH, and CH_3), the yields of the products dropped by 2-7 digits with the expense of extra time [**Table 5** entries 3-7]. We have also tried one reaction with heteroaromatic aldehydes and got excellent results in just 50 min [**Table 5** entry 8]. Encouraged by these results, we have also examined some known aliphatic aldehydes (propionaldehyde and butyraldehyde). Unfortunately, we could not get any satisfactory results. Aliphatic side chains bearing aldehyde displayed only 75 and 74% yield, expending almost three-fold reaction time [**Table 5** entries 9 and10].

Role of DES

Further, we have examined the effect of solvent (DES) to the synthesis of model compound by selecting different molar ratio of DES1, DES2, DES3 and DES4 respectively **[Table 6]**. Keeping all the optimized conditions identical to achieve the best performance, we have tried a different molar ratio of DES against model reaction and found the best outcome against DES 2 [**Table 6** entry 2].

Therefore, the most stable mixture of DES (1:2) was chosen for all reactions in the present study. This was further confirmed by some available pieces of literature[45,46] that the DES ratio (1:2) is more suitable for such types of organic reactions due to their high solubility, low toxicity, and cost effectiveness. Although we have taken DES in all the reactions as a green solvent, we cannot ignore the

role in potentiating the reaction along with the catalyst to the enhancement of product yields in each run. Thus, DES acts as a perfect, stable, recyclable green solvent devoid of any change up to four consecutive uses along with the catalyst.

Plausible mechanism

HRG-PMoA catalyzed quinazoline synthesis was further claimed by a probable mechanism that is presented as **Scheme 2**. As shown, the carbonyl group of aldehyde is activated by HRG-PMoA catalyst to form an intermediate I, then condensation with urea and subsequent dehydration afforded iminium intermediate III, followed by reaction with dimedone to provide intermediate intravenous, which cyclizes by the removal of water to get target quinazoline.

Recyclability of the HRG-PMoA

We studied the recycling attributes of the HRG-PMoA catalyst for the synthesis of a representative compound **4b**. Once the reaction was completed, the catalyst was recovered. A total of four runs was performed with the same catalyst against the same substrates and did not found any significant change in results, as presented in **Figure 4**.

After repetitive use, catalyst behavior was slightly changed, which was confirmed by-product yield reduction from just 97 to 92% as shown in **Figure 4**. Possibly, the reduction in the hybrid catalyst activity after repeated use can be attributed to (i) the electrostatic interaction between HRG and PMoA in the hybrid of HRG-PMoA may be weakened after successive heating during organic reactions as its thermal stability is poor,[20] and (ii) decreased surface acid properties of the catalysts due to repetitive washing, which was also confirmed by treated catalyst (HRG-PMoAT) behavior from FTIR, XRD, and SEM spectra.

Table 6: Effect of deep eutectic solvent in the synthesis of model compound 4b

Entry	DES	Molar ratio	Yield[a,b] (%)
1	DES 1	1:1	86
2	DES 2	1:2	97
3	DES 3	1:3	89
4	DES 4	1:4	88

[a]Reactions were performed in a stoichiometric ratio of each reacting species with 50 mg of HRG-PMoA as a catalyst and 8 mL of respective DES at a refluxing temperature of 80°C, [b]Isolated yields. HRG-PMoA: Highly reduced graphene oxide-phosphomolybdic acid, DES: Deep eutectic solvent

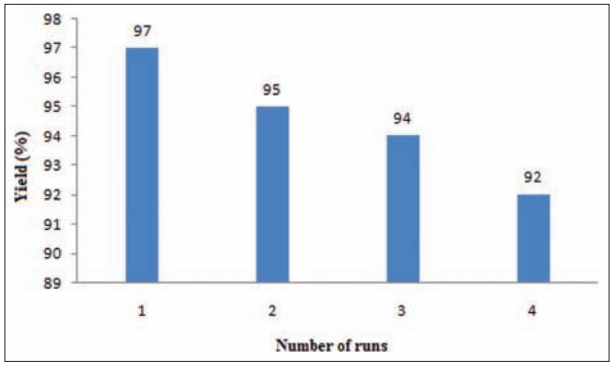


Figure 4: Recyclability ability of HRG-PMoA

MATERIALS AND METHODS

Materials

Materials and chemicals utilized in this research were purchased from Sigma-Aldrich. FTIR spectra of the catalyst (HRG-PMoA) and synthesized compounds were recorded using Thermo Scientific iD5 ATR Diamond Nicolet IS5 FTIR spectrometer with data spacing of 0.482 cm^{-1}, single beam OMINIC software. XRD diffractogram of the catalyst was identified with the help of D2 Phaser X-ray diffractometer (Bruker Optik GmbH, Ettlingen, Germany), Cu Kα radiation (λ=1.5418 Å). BET for the surface area of the catalyst was carried out by Quantachrome ASiQwin, version 5.0., USA. Morphological features of the catalyst were characterized by Quanta FEG 250 SEM (FEI, Holland). Synthesized quinazoline derivatives were elucidated by ^{1}H-NMR spectra and ^{13}C by Bruker-Plus (500MHz) NMR instrument using tetramethylsilane as an internal standard.

Synthesis of HRG-PMoA

For the preparation of HRG-PMoA, initially, GO was prepared which is further exfoliated and then reduced with hydrazine hydrate to obtain HRG. GO was prepared and further reduced to HRG according to our previously reported methods.[33] Briefly, 500 mg of graphite powder and 500 mg of $NaNO_3$ were poured in a 250 ml beaker containing conc. H_2SO_4 (23 ml). The mixture was stirred for ~10 min under an ice bath. Thereafter, 3 g of $KMnO_4$ was poured slowly which turned the mixture to dark green color. The mixture was vigorously stirred, and after some time, the ice bath is replaced with a water bath, and the system was maintained at a temperature of 35–40°C for 1 h. This has resulted in the formation of a thick paste. Then, some amount of water (40 ml) was added, and the mixture was allowed to stir for another 30 min at ~90°C. Hundred milliliter of water was added to this mixture and then 3 ml of H_2O_2 was slowly added which resulted in the change in the color of the mixture from dark brown to yellow. The mixture was cooled, filtered and washed with water (100 ml). Finally, a thick brown paste was obtained which was dispersed in water (100 ml) and centrifuged at a low speed (1000 rpm) for a couple of minutes. This step was repeated several times (4–5 times), to remove all the unsettled particles. The resulting mixture was centrifuged again at a high speed of 8000 rpm for further purification of GO. After this, the resultant paste of GO was dispersed in water through mild sonication for the exfoliation of GO to obtain RGO.[33]

The prepared RGO is reduced with hydrazine hydrate to obtain HRG. For this purpose, RGO (100 mg) is dispersed in 30 ml of water through sonication. The obtained suspension was heated to 100°C, and after some time, 3 ml of hydrazine hydrate was added. The suspension was stirred for 24 h under a slightly reduced temperature of 98°C, which resulted in the formation of black powder. The powder was filtered and washed several times with water to remove excessive hydrazine.

The composite of HRG-PMoA was prepared using the following method.[33] Initially, 25 mg of HRG was dispersed in 10 ml of distilled water through sonication for 30 min. This dispersion is added to the solution of PMoA in distilled water (10 ml) and the mixture was stirred for 48 h at RT and then sonicated for 6 h at 20ºC. Then, the mixture was centrifuged 3 h to remove the excess of PMoA. The un-adsorbed PMoA was removed by further purification. To achieve this, the black mixture is re-dispersed in 5 mL of freshwater and sonicated for 30 min at 20°C. Subsequently, the black suspension is centrifuged for 1 h, and the product is isolated by decanting the resulting mixture. This process was repeated in triplicate until the solution in the centrifuge tube turned colorless. The product was dried under vacuum overnight.

Synthesis of DESs

The DESs were synthesized by mixing choline chloride (hydrogen bond acceptor) and urea in a different molar ratio, as mentioned in **Table 6,** as per the reported method.[31] Both the reacting components of the mixture were heated around 85°C under the influence of the sonicator until a clear liquid was obtained.

General procedure for the synthesis of quinazoline derivatives (4a-j)

In a 100 mL round bottom flask, a mixture of dimedone (1.4 mmol), urea (1.2 mmol), and various aldehydes (1 mmol) were stirred in the presence of HRG-PMoA catalyst in 8 mL of DES at 80°C. Progress of the reaction mixture was observed by thin-layer chromatography (solvent system:ethyl acetate and acetone (3:7). On completion of the reaction, the reaction mixture was filtered, while the filtrate contained crude products along with DES; the residual HRG based catalysts remained on the filter paper in the form of black powder. The catalyst was later washed with distilled water and ethanol, dried, and reused for the next reaction. On the other hand, the desired product present in DES was obtained by filtration and re-crystallization using dioxane containing few drops of DMF, using a separating funnel. The separated DES was also dried under vacuum and recovered for the next experiment.

Spectroscopic data of synthesized quinazolines (4a-j)

7,7-Dimethyl-4-phenylhexahydroquinazoline-2,5(1H,3H)-dione (4a)

White solid; FTIR (cm^{-1}, ATR); 3033 and 2953 (NH), 1671 (C=O, ring), 1624 (C=O, urea), 1466 (C=C); ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.46 (s, 1H, NH), 9.07 (s, 1H, NH), 7.30-8.49 (m, 5H, Ar-H), 5.55 (1H, s, CH), 2.57-2.41 (q, 2H, *J* = 26.6 Hz, CH_2), 2.10 (s, 2H, CH_2), 1.02 (s, 6H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 198-196.8 (C=O), 167.3 (NC=O), 159.3 (NC=C), 144.1, 140.4, 138.9, 137.0,130.0, 125.8, 124.3, 122.9, 121.5, 118.2, 113.5, 112.3 (ArC), 99.3 (OC-C=C), 53.4 (C-NH), 51.9 (CH_2), 32.7 (1C, CH_2), 30.2 (1C, CH_2), 28.5, 28.3 ($2CH_3$); MS (ESI) m/z 271(M^++1).

4-(4-Chlorophenyl)-7,7-dimethyl-4, 6,7,8-tetrahydroquinazoline-2,5(1H,3H)-dione (4b)

Creamy white solid; FTIR (cm^{-1}, ATR); 3433 and 3338 (NH), 1676 (C=O, ring), 1622 (C=O, urea), 1462 (C=C); ^{1}H NMR (DMSO-d_6, 400 MHz): 10.01 (s, 1H, NH), 8.63(s, 1H, NH), 7.96-7.94 (d, 2H, *J* = 8.3 Hz, Ar-H), 7.27-7.19 (d, 2H, *J* = 40.1 Hz), 4.50 (1H, s, CH), 2.56-2.53 (q, 2H, *J* = 13.4 Hz, CH_2), 2.25-2.10 (dd, 2H, *J* = 73.1 Hz, CH_2), 1.03-0.89 (d, 6H, *J* = 68.2 Hz, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 196.6 (C=O), 167.5 (NC=O), 143.7 (NC=C), 131.1, 130.4, 129.7, 129.0, 128.3 (ArC), 114.4 (OC-C=C), 50.3 (C-NH and CH_2), 32.7 (1C, CH_2), 32.3-31.4 (1C, CH_2), 29.0, 26.9 ($2CH_3$); MS (ESI) m/z 305 (M^++1).

7,7-dimethyl-4-(p-tolyl)-4, 6,7,8-tetrahydroquinazoline-2,5(1H,3H)-dione (4c)

Creamy white solid; FTIR (cm^{-1}, ATR); 3316 and 3248 (NH), 1706 (C=O, ring), 1672 (C=O, urea), 1485 (C=C); ^{1}H NMR (DMSO-d_6, 400 MHz): 9.41 (s, 1H, NH), 7.70 (s, 1H, NH), 7.14-7.09 (m, 4H, Ar-H), 5.12 (1H, s, CH), 2.43-2.25 (q, 2H, *J* = 27.5 Hz, CH_2), 2.21-2.00 (d, 2H, *J* = 34.5 Hz, CH_2), 1.02-0.89 (d, 6H, *J* = 61.6 Hz, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 193.2 (C=O), 152.6-152.4 (NC=O), 142.2 (NC=C), 136.0, 129.2, 126.6 (ArC), 108.0 (OC-C=C), 52.1 (C-NH), 50.3 (CH_2), 32.7 (1C, CH_2), 29.2 (1C, CH_2), 27.7, 21.3 ($2CH_3$), 19.0 (CH_3); MS (ESI) m/z 285(M^++1).

4-(4-Methoxyphenyl)7,7-dimethyl-4,6,7,8-tetrahydroquinazoline-2,5(1H,3H)-dione (4d)

Yellowish white solid; FTIR (cm^{-1}, ATR); 3003 and 2957 (NH), 1677 (C=O, ring), 1661 (C=O, urea), 1510 (C=C); ^{1}H NMR (DMSO-d_6, 400 MHz): 8.41-8.12 (d, 1H, *J* = 9.7 Hz, NH), 7.79 (s, 1H, NH), 7.08-7.06 (d, 2H, *J* = 9.9 Hz, Ar-H), 6.78-6.76 (d, 2H, *J* = 9.8 Hz, Ar-H), 4.47 (1H, s, CH), 3.68 (s, 3H, OCH_3), 2.58-2.47 (q, 2H, *J* = 18.4 Hz, CH_2), 2.28-2.06 (dd, 2H, *J* = 20.2 Hz, CH_2), 1.03-0.91 (d, 6H, *J* = 63.1 Hz, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 196.5 (C=O), 163.1 (NC=O), 158.02 (C-OCH_3), 136.8 (NC=C), 136.8, 129.4, 127.9, 115.0 (ArC), 113.6 (OC-C=C), 55.3 (1C, OCH_3), 50.5 (C-NH & (CH_2), 32.3 (1C, CH_2), 31.7 (1C, CH_2), 30.7, 29.1, 28.4, 26.9 ($2CH_3$); MS (ESI) m/z 285(M^++1).

4-(4-Hydroxy-3-methoxyphenyl)-7,7-dimethyl-4,6,7,8-tetrahydroquinazoline-2,5(1H,3H)-dione (4e)

White solid; FTIR (cm^{-1}, ATR); 3468 and 3307 (NH), 1652 (C=O, ring), 1582 (C=O, urea), 1512 (C=C); ^{1}H NMR (DMSO-d_6, 400 MHz): 10.26 (s, 1H, OH), 9.77 (s, 1H, NH), 8.75 (s, 1H, NH), 7.43-7.39 (t, 1H, *J* = 10.8 Hz, Ar-H), 6.97-6.95 (d, 1H, *J* = 9.9 Hz, Ar-H), 6.63-6.52 (m, 1H, Ar-H), 5.41 (1H, s, CH), 3.94 (s, 3H, OCH_3), 2.58-2.47 (q, 2H, *J* = 19.3 Hz, CH_2), 2.39-2.20 (q, 2H, *J* = 32.0 Hz, CH_2), 1.29-0.85 (m, 6H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 191.4 (C=O), 153.4 (NC=O), 148.6 (ArC-OCH_3), 147.3 (ArC-OH), 145.3 (NC=C), 135.8, 129.1, 126.5, 120.7, 115.8, 111.1 (ArC), 101.4 (OC-C=C), 64.5 (1C, OCH_3), 56.0 (C-NH), 50.7(CH_2), 32.5-32.3 (1C, CH_2), 28.1 (1C, CH_2), 27.8, 26.8 ($2CH_3$); MS (ESI) m/z 317(M^++1).

7,7-dimethyl-4-(3,4,5-trimethoxyphenyl)-4,6,7,8-tetrahydroquinazoline-2,5(1H,3H)-dione (4f)

White solid; FTIR (cm^{-1}, ATR); 2952 and 2930 (NH), 1665 (C=O, ring), 1624 (C=O, urea), 1459 (C=C); ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.89-9.87 (d, 1H, *J* = 10.6 Hz, NH), 8.14 (s, 1H, NH), 7.76-6.42 (m, 2H, Ar-H), 4.50 (1H, s, CH), 3.69-3.34 (s, 9H, OCH_3), 2.56-2.50 (q, 2H, *J* = 8.7 Hz, CH_2), 2.30-2.11 (dd, 2H, *J* = 20.2 Hz, CH_2), 1.04-0.95 (d, 6H, *J* = 48.5 Hz, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 196.6 (C=O), 163.5 (ArC-OCH_3), 152.8 (NC=O), 140.3 (NC=C), 136.4, 114.7 (ArC), 105.9 (OC-C=C), 60.3 (3C, OCH_3), 56.2 (C-NH), 50.5 (CH_2), 32.3 (1C, CH_2), 31.6 (1C, CH_2), 29.1, 26.8 ($2CH_3$); MS (ESI) m/z 361(M^++1).

4-(4-hydroxyphenyl)-7,7-dimethyl-4,6,7,8-tetrahydroquinazoline-2,5(1H,3H)-dione (4g)

White solid; FTIR (cm^{-1}, ATR); 3383 and 2955 (NH), 1646 (C=O, ring), 1612 (C=O, urea), 1461 (C=C); ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.64 (s, 1H, OH), 9.15 (s, 1H, NH), 7.27-7.24 (d, 1H, *J* = 34.1 Hz, NH), 6.96-6.94 (d, 1H, *J* = 10.3 Hz, Ar-H), 6.60-6.58 (d, 1H, *J* = 10.2 Hz, Ar-H), 4.43 (s, 1H, CH), 2.53-2.50 (d, 2H, *J* = 11.8 Hz, CH_2), 2.30-2.27 (d, 2H, CH_2), 1.03-0.90 (d, 6H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 196 (C=O), 163.0 (ArC-OH), 156.0 (NC=O), 135.2 (NC=C),129.3, 115.2-115.0 (ArC), 50.7 (C-NH & (CH_2), 32.3 (1C, CH_2), 30.6 (1C, CH_2), 29.1, 26.9 ($2CH_3$); MS (ESI) m/z 287(M^++1).

4-(1H-indol-3-yl)-7,7-dimethyl-4,6,7,8-tetrahydroquinazoline-2,5(1H,3H)-dione (4h)

Reddish brown; FTIR (cm^{-1}, ATR); 3193 and 3060 (NH), 1671 (C=O, ring), 1613 (C=O, urea), 1491 (C=C); ^{1}H NMR (DMSO-d_6, 400 MHz): δ 12.65 (s, 1H, NH, Indole), 9.49 (s, 1H, NH), 8.50 (s, 1H, NH), 7.86-6.93 (m, 5H, Ar-H), 4.81 (s, 1H, CH), 2.57 (s, 2H, CH_2), 2.27-1.99 (dd, 2H, *J* = 46.6 Hz, CH_2), 1.02-0.80 (s, 6H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 197 (C=O), 162.6 (NC=O), 140.3 (NC=C), 138.9, 137.0, 130.0, 124.9, 124.0, 122.9, 118.2, 114.8, 113.5, 112.3 (ArC), 111.8 (OC-C=C), 53.4 (C-NH), 51.9 (CH_2), 32.1 (1C, CH_2), 30.2 (1C, CH_2), 29.1, 28.5 ($2CH_3$); MS (ESI) m/z 310(M^++1).

4-Ethyl-7,7-dimethyl-4,67,8-tetrahydroquinazoline-2,5(1H,3H)-dione (4i)

White solid; FTIR (cm^{-1}, ATR); 3431 and 3335 (NH), 1649 (C=O, ring), 1610 (C=O, urea), 1461 (C=C); ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.40 (s, 1H, NH), 7.14 (s, 1H, NH), 4.36 (s, 1H, CH), 2.50 (s, 2H, CH_2), 2.27-2.23 (d, 2H, *J* = 23.7 Hz, CH_2), 1.44-1.41 (d, 2H, *J* = 6.9 Hz, CH_2), 1.18-1.04 (d, 6H, *J* = 68.8 Hz, CH_3), 0.62 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 400 MHz): δ 197.1 (C=O), 164.9 (NC=O), 113.3 (OC-C=C), 50.6 (C-NH & CH_2), 32.1 (1C, CH_2), 29.2 (1C, CH_2), 27.0, 26.0, 25.6 ($2CH_3$), 9.2 (1C, CH_3); MS (ESI) m/z 223(M^++1).

7,7-dimethyl-4-propyl-4,6,7,8-tetrahydroquinazoline-2,5 (1H,3H)-dione (4j)

White solid; FTIR (cm^{-1}, ATR); 3431 and 3340 (NH), 1674 (C=O, ring), 1590 (C=O, urea), 1460 (C=C); ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.23 (s, 1H, NH), 6.96 (s, 1H, NH), 4.16 (s, 1H, CH), 2.45-2.43 (d, 2H, *J* = 6.3 Hz, CH_2), 2.25 (s, 2H,CH_2), 1.82-1.80 (d, 2H, *J* = 9 Hz, CH_2), 1.35-1.04 (s, 6H, CH_3), 0.77 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 196.5 (C=O), 163.5 (NC=O), 143.7 (NC=C), 114.4 (OC-C=C), 50.4 (C-NH & CH_2), 32.3 (1C, CH_2), 31.4 (1C, CH_2), 29.0, 26.9, ($2CH_3$); MS (ESI) m/z 237(M^++1).

CONCLUSION

A simple operational procedure was used to develop an HRG-PMoA catalyst and later used in the synthesis of some quinazoline derivatives through MCR in DES as a green solvent. The results obtained in mild conditions to accomplish excellent yield. Moreover, catalyst and solvent recovery were very simple and convenient with the use of a simple filtration method. The present catalyst in DES was the first time utilized to establish synthetic transformation. Further, many other reactions trials are under investigation to access the activity of the catalyst.

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CONFLICTS OF INTEREST

The authors confirm that the content of this article has no conflicts of interest.

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