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A magnetically retrievable copper ionic liquid nanocatalyst for cyclooxidative synthesis of 2-phenylquinazolin-4(3*H*)-ones†

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In the present work, we report the design and fabrication of a copper-containing ionic liquid supported magnetic nanocatalyst *via* a convenient and straightforward synthetic approach for the formation of 2-phenylquinazolin-4(*3H*)-ones using *o*-aminobenzamide and benzaldehydes as the reaction partners. The successful formation and properties of the as-prepared catalyst have been thoroughly investigated using diverse physico-chemical techniques including FT-IR, XRD, FE-SEM, TEM, ICP, VSM, BET and TGA. Using this nanocatalytic system, a variety of 2-phenylquinazolin-4(*3H*)-ones are synthesized in excellent yields with operational ease and short reaction times in an environmentally preferable solvent under open air and without using any external oxidizing agent. Besides, the catalyst possessed facile magnetic recoverability and remarkable reusability for six consecutive runs without any appreciable decrease in the catalytic efficiency.

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Introduction

Since the 1980s, ionic liquids (ILs) have increasingly fascinated a wide domain of researchers due to their remarkable physical and chemical properties, particularly low volatility, wide tunability, high thermal stability, good conductivity and reusability.¹⁻⁴ They are being used as green and sustainable alternatives to traditional volatile solvents and as potential catalytic entities in organic synthesis. Over the past few years, transition metal-containing ionic liquids (MetILs) have garnered substantial interest in the field of basic and applied sciences owing to their advantages over conventional ILs, such as enhanced solubility and chemical availability of metal salts, strong magnetic response and an appealing color rendering characteristic, which originate from the incorporation of metal species into the intrinsic structure of the ILs.^{5–7} Several groups have explored the catalytic competency of homogeneous MetILs in a variety of organic transformations, C-C bond formation,⁸ hydroformylation,⁹ debromination,¹⁰ allylic oxidation,¹¹ cycloaddition¹² and depolymerization,¹³ to mention a few. In spite of the outstanding performances of these catalytic MetILs, certain constraints have limited their practical

utility in large-scale industrial applications, such as large IL requirements, high costs, limited metal reservoirs, product contamination and tedious recycling protocols that often lead to the decomposition of the ILs.¹⁴ Besides, their high viscosity also impedes the substrate diffusion which slows down the overall reaction rate.

To overcome these limitations, the concept of heterogenization of ILs came into picture, which aims to transfer the desired properties of ILs onto a solid support material.¹⁵⁻¹⁹ Numerous promising immobilized MetILs have been prepared in the past few years for catalyzing the synthesis of significant organic molecules with easier operation and better performance. Previously, Iwasawa and co-workers immobilized a series of first row transition metal-containing alkylimidazolium salts onto hydrophilic silica and evaluated their catalytic efficacy in the Kharasch addition reaction.²⁰ Later, Bhanage et al. designed immobilized palladium- and iron-containing IL catalysts for conducting various carbonylation reactions²¹ and chemoselective hydrogenation,²² respectively. Another polymer-supported metal-containing imidazolium salt catalyst (PS-(Im)₂MX₂) was also prepared for the synthesis of glycerol carbonate.²³ These successive works encourage the design and development of other heterogeneous MetILs with improved recycling ability and practical relevance. In recent years, silicacoated magnetic nanoparticles (SMNPs) have emerged as an excellent support material due to some of their exceptional features including large surface area to volume ratios, ease of functionalization, high thermal and chemical stability and



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effortless magnetic recoverability.^{24,25} Taking these advantages into account and in continuation of our efforts for the development of sustainable magnetic nanocatalysts,^{26–35} we herein report the fabrication of a copper-containing IL supported magnetic nanocatalyst using a convenient and straightforward approach. The catalytic application of the as-synthesized material is investigated in the formation of 2-phenylquinazolin-4(3*H*)-ones.

Quinazolin-4(3H)-ones represent a ubiquitous class of azaheterocyclic moieties. They are found in a wide array of natural products and biologically active compounds (Fig. 1). They are also used as a pharmacophore in drug designing due to their remarkable performance in anticancer, antibacterial, antituanti-inflammatory and berculosis, antihypertensive activities.36-40 In recent years, 2-aryl substituted quinazolin-4 (3H)-ones' activities are being evaluated in treating numerous disorders; Apabetalone or RVX-208 is under clinical trials for the treatment of atherosclerosis and other cardiovascular diseases,41,42 Bouchardatine has been found to act as an inhibitor of adipogenesis/lipogenesis,43 and 2-(4-nitrophenyl) quinazolin-4(3H)-one is being investigated as a potential NLRP3 inflammasome inhibitor,⁴⁴ to name a few. Considering their wide utility, a variety of approaches have been reported in the past towards the construction of quinazolinone skeletons. One such conventional method involves an Ullmann-type N-arylation for the preparation of heterocyclic compounds using copper salts or complexes.^{45–48} Another most frequently used protocol includes the cascade reaction of alcohols/aldehydes with o-aminobenzamides using complexes of various precious and base metals such as Ir,^{49,50} Ru,⁵¹ Pd,⁵² Ni,⁵³ Cu,⁵⁴ Fe,⁵⁵ Co,⁵⁶ Zn⁵⁷ and V.⁵⁸

Although each of the above-mentioned catalytic routes and reaction protocols holds its own merits, nearly all of them are associated with the use of metals under homogeneous conditions. However, due to their limited reserves, difficulty in recovery and probability towards product contamination, their use is considered neither safe nor sustainable from the viewpoint of environmental safety and human health. Hence, in order to combat these issues, numerous heterogeneous systems have been reported to date such as α -MnO₂,⁵⁹ ZnO



2-(4-Nitrophenyl)quinazolin-4(3H)-one

Fig. 1 Structures of some of the biologically active 2-arylquinazolin-4 (3*H*)-ones.

modified rare earth oxide,⁶⁰ iron porphyrin-based porous organic polymers,⁶¹ zeolite-supported platinum metal nanoclusters,⁶² Cu₃(BTC)₂ MOF⁶³ and so forth. Although many of these demonstrated superior product yields, wide substrate scope and reusability for multiple runs, their recovery still remains challenging due to tedious and time-consuming centrifugation and filtration procedures. In this regard, a few magnetically supported catalysts have been prepared and successfully utilized including magnetic nanoparticle immobilized Cu (1)⁶⁴ and 1,4-diazabicyclo[2.2.2]octane tribromide,⁶⁵ graphene oxide/Fe₃O₄-CuI⁶⁶ and Fe₃O₄-carbon dot nanocomposites.⁶⁷ However, apart from the benefits they offer, most of the previously reported methods suffer from one or more drawbacks such as use of non-green reaction media, need for ligands or additives or bases, large excess of oxidizing agents, high reaction temperatures and long reaction time. Hence, the development of other sustainable and green catalysts with high activity and easy and efficient recyclability is extremely important. The present work describes the use of a magnetically recoverable copper-containing IL for the one-pot cyclooxidative synthesis of 2-phenylquinazolin-4(3H)-ones under mild reaction conditions with excellent product yields and multiple recyclable runs. To the best of our knowledge, this is the first report wherein a magnetically immobilized metal-containing IL nanocatalyst has been utilized for the synthesis of 2-phenylquinazolin-4(3H)-ones.

Results and discussion

Design and synthesis of the nanocatalyst (CuIL@SMNP)

The design and synthesis of the catalyst is shown in Scheme 1. It involves the discrete synthesis of a magnetic support (SMNPs) and functionalized IL (FIL) followed by its immobilization on the prepared support (IL@SMNPs) and further com-



Scheme 1 Schematic illustration of the fabrication of CuIL@SMNPs.

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plexation with the metal salt to obtain the final immobilized MetIL (CuIL@SMNPs).

Characterization of CuIL@SMNP

Functional group analysis. In order to ascertain the successful formation of nanomaterials and attachment of various groups on the support, FT-IR analysis was conducted. Fig. 2a shows a split intense peak at wavenumbers 632 and 585 cm⁻¹ which emerged due to the Fe-O vibration present in the Fe₃O₄ nanoparticles.⁶⁸ Besides, a broad band at 3436 cm⁻¹ represents the large number of surface hydroxyl groups. Furthermore, silica coating on these magnetite spheres was confirmed by the appearance of new and strong peaks at 1090, 957, 808 and 462 cm⁻¹ that are ascribed to Si-O-Si stretching, Si-OH stretching, Si-O bending and Si-O-Si bending, respectively (Fig. 2b).⁶⁹ Fig. 2c shows the FT-IR spectrum of the final CuIL@SMNP whose formation is confirmed by the peaks at 2928 and 2852 cm⁻¹, which corresponds to the C-H antisymmetric and symmetric stretching bands of the methylene group.⁷⁰ Additional bands appear at 1632 and 1570 cm⁻¹ which arise due to the -C=C- and -CN stretching vibrations, respectively, present in the imidazolium ring.71,72

Phase and structural characterization. For the determination of the crystallinity, structural integrity and size of the synthesized nanomaterials, XRD studies were carried out. Fig. 3a reveals the presence of six diffraction peaks at 2θ = 30.19°, 35.63°, 43.29°, 53.60°, 57.37° and 62.92°. It was observed that the position of all the peaks in the concerned XRD spectrum are in good agreement with the standard XRD pattern of the cubic inverse spinel structure of Fe₃O₄ (Joint Committee on Powder Diffraction Standards (JCPDS) card no. 19-0629) and correspond to the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) crystalline planes of the magnetite phase, respectively.⁶⁷ Fig. 3b and c also show the presence of the above-mentioned peaks, with no extra peaks, which proves that the structural integrity of the magnetic core is retained even after silica coating or functionalization with the copper-containing IL. Nevertheless, the signals pertaining to copper metal and silica coating were not observed in the XRD spectra of the SMNPs



Fig. 2 FT-IR spectra of (a) MNPs, (b) SMNPs and (c) CulL@SMNPs



Fig. 3 XRD spectra of (a) MNPs, (b) SMNPs and (c) CulL@SMNPs.

and CuIL@SMNPs, which implies their high dispersity over the nanoparticles.⁷³ Apart from evaluating the crystallinity, the XRD spectrum was also used for the determination of the size of the magnetite nanoparticles. For this, the Scherrer equation was used according to which $D_{hkl} = k\lambda/\beta \cos \theta$, where D_{hkl} is the mean size of the crystalline domains in a direction perpendicular to the lattice plane, hkl are the Miller indices of the plane under consideration, k is a dimensionless shape factor (0.89 for spherical particles), λ is the wavelength of the X-ray used (0.15418 nm for Cu K-alpha), β is the full line width at half maximum intensity (FWHM; in radians) and θ is the Bragg angle (in degrees). After taking into account the diffraction peak with maximum intensity, the size of the MNPs was found to be 11 nm in diameter.

Shape, size, morphology and surface area determination. The shape and morphological studies were conducted using electron microscopic techniques. Fig. 4 shows the FE-SEM images of the MNPs, SMNPs and CuIL@SMNPs. The micrograph of the MNPs clearly depicts their uniform spherical nature whose surface becomes spongy and rough after coating a silica layer over it. A similar surface nature was observed in the case of the CuIL@SMNPs as well which suggests that no substantial morphological changes occurred even after the immobilization of the MetIL over the SMNPs.

Furthermore, to gain valuable information about the inner structure of the nanoparticles, TEM images were recorded. Fig. 5a shows uniform spherical MNPs with a diameter of around 10.5 nm, which is in good agreement with the XRD



Fig. 4 FE-SEM images of (a) MNPs, (b) SMNPs and (c) CulL@SMNPs.



Fig. 5 TEM images of (a) MNPs, (b) SMNPs and (c) CulL@SMNPs.

results. Fig. 5b illustrates the internal core-shell structure of the SMNPs with a dense magnetic core at the centre and a uniform silica shell at the outer surface which is approximately 4-5 nm in thickness. Besides, a similar internal structure was observed for the CuIL@SMNP nanocatalyst justifying that modification with the MetIL does not disrupt the internal structure of the SMNPs (Fig. 5c). For the determination of the size of the nanoparticles, discrete particles were analyzed and size distribution histograms were plotted according to which the MNPs, SMNPs and CuIL@SMNPs were of sizes between 9-10, 18-20 and 20-22 nm (Fig. S1[†]). Besides, the specific surface area of the as-synthesized MNPs and CuIL@SMNPs was also evaluated using BET analysis and was found to be 69.27 and 16.15 m² g⁻¹, respectively. There was an expected decrease in the specific surface area of the catalyst which implies the effective immobilization of CuIL over the magnetic support.

Thermal stability analysis. TGA analysis was performed in order to assess the thermal stability of the prepared nanocatalyst (Fig. 6). For this, the sample was heated from 37 °C to 950 °C and its corresponding weight was recorded. The curve represents that a weight loss of approximately 4.5% takes place upon initial heating to 237 °C, which is attributed to the removal of the adsorbed water and other organic solvents that were utilized during the preparation of the catalyst. With the subsequent increase in the temperature, further weight loss is observed from 237 to 410 °C and from 410 to738 °C, which could be due to the decomposition of the organic species used for the formation of the CuIL. Afterwards, no significant loss was observed which indicates the high thermal stability of the



Fig. 6 TGA curve of CulL@SMNPs

magnetic support utilized throughout the study. To reinforce the above statement, TGA analysis of the MNPs and SMNPs was also carried out (Fig. S3†) and the results authenticate that no substantial weight loss occurs even at high temperatures.

Elemental analysis. To illustrate the elemental composition of the synthesized nanocatalyst, SEM-coupled EDAX analysis was performed. Fig. 7 clearly depicts the presence of Fe, Si, C, N, O, Cl and Cu in the final IL immobilized nanoparticles. Furthermore, the copper metal loading in the catalyst was estimated using ICP-MS and was found to be 0.83 mmol g^{-1} . The existence and semi-quantitative estimation of copper in the catalyst were also confirmed using a standalone benchtop EDXRF elemental analyzer (Fig. S2†).

Magnetic property analysis. The evaluation of the magnetic properties of the material becomes highly significant when it comes to the fabrication of a magnetic nanocatalyst. Due to this, the nanocomposites were subjected to VSM analysis at room temperature at a magnetic field varying from $-10\,000$ Oe to $+10\,000$ Oe. Fig. 8a depicts that the synthesized MNPs have a saturation magnetization value (M_s) of 73.2 emu g⁻¹. However, upon the coating of these MNPs with diamagnetic silica, the M_s value decreases to 40.7 emu g⁻¹ (Fig. 8b). This value further goes down to 28.6 emu g⁻¹ upon the immobiliz-



Fig. 7 SEM-coupled EDAX spectrum of CuIL@SMNPs.



Fig. 8 Magnetization curves of (a) MNPs, (b) SMNPs and (c) CulL@SMNPs.

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ation of the CuIL over the SMNPs (Fig. 8c); nevertheless, it was sufficiently magnetic to be recovered from the reaction mixture with the application of a simple external magnet. In addition, all of the synthesized nanomaterials possess superparamagnetic nature as no hysteresis loop, remanence or coercivity was observed in any of the cases.

Catalytic activity test

With an aim to develop an environmentally friendly catalyst which gives excellent yields of the desired compounds with efficient recovery and recyclability, the catalytic activity of the prepared SMNP immobilized CuIL nanocatalyst was investigated in the synthesis of 2-phenylquinazolin-4(3H)-ones using *o*-aminobenzamide and benzaldehydes as the reaction partners.

Optimization of reaction conditions. In order to maximize the yield of 2-phenylquinazolin-4(3H)-ones with the use of a safe and benign solvent under improved reaction conditions, various reaction parameters were optimized. For this, o-aminobenzamide and benzaldehyde were chosen as the model substrates. After careful study of the previously reported methods and reaction conditions, initially, the two of these precursors were allowed to react in the absence of any catalyst in ethanolic solution under reflux conditions for 12 h under an air atmosphere (Table 1, entry 1). However, poor conversion was observed with dihydroquinazolinone (1) as the dominant product over the desired quinazolinone (2). This prompted the application of the CuIL@SMNPs as catalytic species. To our delight, high conversion and >99% of quinazolinone were perceived under identical conditions and in the absence of any external oxidizing agent (Table 1, entry 2). With these encouraging results in hand, experiments were performed to know if the reaction conditions could be further refined. Hence, various solvents and solvent systems were also screened, such as water, acetonitrile and ethanol-water mixture, but the best results were obtained in ethanol as a solvent (Table 1, entries 3-5). Furthermore, the temperature was brought down to 60 °C (Table 1, entry 6), but unfortunately, the yield decreased by >44%. Afterwards, the effect of time was studied and it was found that 4 h is the optimum time for obtaining the maximum yield of the desired product (Table 1, entries 7-10). Now, with the optimized parameter obtained so far, the catalytic amount was varied from 75 mg to 40 mg and >99% of quinazolinone was obtained with just 50 mg of the catalyst, i.e. CuIL@SMNPs (Table 1, entries 11-12). The catalytic aptitude of various precursors formed during catalyst fabrication was also evaluated; however, no significant product yield was observed in any of the cases, justifying the exclusive utility of the CuIL@SMNPs for the efficient synthesis of quinazolinones (Table 1, entries 13-15).

Substrate scope. Having these optimized conditions in hand, a variety of benzaldehydes were reacted with *o*-aminobenzamide in ethanol as the solvent system and 50 mg of CuIL@SMNPs as the catalyst under reflux conditions for the required time. The results are summarized in Fig. 9. A wide range of benzaldehydes were obtained in good to excellent yields in short reaction times, *i.e.* from just 30 min to 4 h. The unsubstituted benzaldehyde however took longer time than the substituted ones. Many electron donating groups bearing benzaldehydes, such as -OH, -Me, -OMe, and halo groups containing benzaldehydes, such as -Cl and -Br, were obtained in excellent yields; nevertheless, those with electron withdraw-

 Table 1
 Optimization of the reaction parameters for the synthesis of 2-phenylquinazolin-4(3H)-one^a

	+ CNH
(1)	(2)

S. no.	Catalyst (amount)	Solvent	Temp. (°C)	Time (h)	% Yield ^b	
					% 1	% 2
1	_	Ethanol	Reflux	12	35	5
2	CuIL@SMNP (75 mg)	Ethanol	Reflux	12	_	>99
3	CuIL@SMNP (75 mg)	H_2O	Reflux	12	60	5
4	CuIL@SMNP (75 mg)	CH ₃ CN	Reflux	12	42	7
5	CuIL@SMNP (75 mg)	$EtOH: H_2O(1:1)$	Reflux	12	55	8
6	CuIL@SMNP (75 mg)	Ethanol	60 °C	12	15	55
7	CuIL@SMNP (75 mg)	Ethanol	Reflux	8	_	>99
8	CuIL@SMNP (75 mg)	Ethanol	Reflux	6	_	>99
9	CuIL@SMNP (75 mg)	Ethanol	Reflux	4	_	>99
10	CuIL@SMNP (75 mg)	Ethanol	Reflux	3	12	85
11	CuIL@SMNP (50 mg)	Ethanol	Reflux	4	_	>99
12	CuIL@SMNP (40 mg)	Ethanol	Reflux	4	5	81
13	FIL@SMNP (75 mg)	Ethanol	Reflux	12	55	15
14	SMNP (75 mg)	Ethanol	Reflux	12	40	8
15	MNP (75 mg)	Ethanol	Reflux	12	40	8

^a Reaction conditions: o-aminobenzamide (0.5 mmol), benzaldehyde (0.5 mmol), solvent 3.0 mL. ^b GC-MS yield.



Fig. 9 Catalytic efficacy of CulL@SMNPs in the synthesis of various 2-phenylquinazolin-4(*3H*)-ones with the data representing the isolated product yield, time taken and product code. Reaction conditions: *o*-aminobenzamide (0.5 mmol), benzaldehyde (0.5 mmol), ethanol 3.0 mL, CulL@SMNPs (50 mg), reflux, under air.

ing groups such as -NO₂ and -NHCOCH₃ gave comparatively lesser yields, irrespective of their substitution position.

Catalytic stability test

In order to check the stability of the catalyst and to assess any possible leaching of the catalytic species from the magnetic support, a split test was conducted. For this, o-aminobenzamide and benzaldehyde were allowed to react under the optimized conditions. After 2 h, the catalyst was removed from the reaction mixture using an external magnet and the leftover mixture was divided into two equal halves. One of the parts was kept aside and the other was heated at the same temperature for 3 h, but now, in the absence of catalyst. Afterwards, both of the parts were subjected to GC-MS analysis and it was observed that both of them yielded nearly the same amount of quinazolinone. This illustrates that no substantial leaching occurred during the reaction. To validate this point, after the removal of the catalyst from the reaction mixture, the recovered catalyst was analyzed via ICP-MS to estimate the amount of copper present in it. To our delight, only a negligible decrease in the copper loading was observed, *i.e.* 0.008 mmol g^{-1} , which again proved the truly heterogeneous nature of the catalyst.

Catalytic reusability test

With the fabrication of the heterogeneous catalyst, the responsibility of assessing its reusability becomes highly imperative. To evaluate this, the model reaction was chosen. After the catalyst was removed from the reaction mixture using a simple external magnet, it was washed thoroughly with acetone and water and subsequently dried in a vacuum oven for an hour at 60 °C. Later on, the same reaction was conducted again using this recycled catalyst and the results were recorded. Fig. 10 shows that the immobilized CuIL can be effectively utilized for six consecutive



Fig. 10 Recyclability test for the synthesis of 2-phenylquinazolin-4 (*3H*)-one using CulL@SMNPs. Reaction conditions: *o*-aminobenzamide (0.5 mmol), benzaldehyde (0.5 mmol), recovered catalyst, ethanol (3.0 mL), reflux, 4 h, under air.

runs without any appreciable loss in the catalytic activity. Any morphological or structural changes in the recycled catalyst were analyzed by various characterization techniques. Fig. S4 and S5† illustrate the FT-IR, VSM, FE-SEM, TEM and XRD results of the fresh and recovered catalyst after the sixth run which authenticate that the functionalities, magnetism, morphology and structural integrity of the catalyst remain intact even after six runs. Table S1† shows the comparison of our prepared catalyst with many other previously reported ones and it depicts that the present CuIL immobilized SMNPs remain superior amongst many others in terms of product yields, mild reaction conditions and better recyclability.

Plausible reaction mechanism

A plausible reaction mechanism has been proposed based on the optimization studies and relevant literature investigation, according to which initially benzaldehyde in the presence of *o*-aminobenzamide and the catalyst, *i.e.* CuIL@SMNPs, forms an aminal intermediate called 2,3-dihydroquinazolin-4(1*H*)one (a) *via* intermolecular cyclization, which is also detected by GC-MS when the reaction mixture is analyzed at shorter reaction times (Scheme 2, step 1). This intermediate is then dehydrogenated in the presence of CuIL and aerial oxygen to form the desired product 2-phenylquinazolin-4(3*H*)-one (Scheme 2, step 2).^{59,67,74} This step is also validated when no desired product was obtained under a nitrogen atmosphere.



Scheme 2 Reaction mechanism for the formation of 2-phenylquinazolin-4(3*H*)-one.

Conclusions

In summary, a copper metal-containing IL immobilized silicacoated magnetic nanocatalyst was designed, prepared and characterized, and was further utilized for the tandem cyclization and oxidative synthesis of 2-phenylquinazolin-4(3H)-ones using o-aminobenzamide and benzaldehydes in an environmentally benign solvent under mild reaction conditions and in short reaction times. The catalyst transforms a wide variety of substrates in good to excellent yields without any additional purification that conventionally requires column chromatography. The quasi-homogeneous nature of the IL on the SMNPs and better chemical availability of the metallic species in the form of the MetIL account for the exceptional catalytic activity of the system. Besides, the magnetic feature of the catalyst imparted facile catalytic recovery and outstanding reusability for six successive runs with negligible loss of catalytic activity. All of the above-mentioned features imply the effective use of MetIL@SMNPs in various significant heterogeneous organic transformations.

Experimental section

Chemicals and instruments

All of the reagents were procured from commercial sources and used without further purification. Ferric sulfate hydrate and ferrous sulfate heptahydrate were purchased from Fischer Scientific. Tetraethyl orthosilicate (TEOS) and (3-chloropropyl) trimethoxysilane (CPTMS) were obtained from Sigma Aldrich. *N*-Methylimidazole and copper chloride were purchased from Spectrochem. All other chemical reagents, organic compounds and solvents used were of high purity and were procured from Alfa Aesar and Merck. Besides, double distilled water was used throughout the study and was prepared in our laboratory.

The developed catalyst was characterized using various analytical techniques. Fourier-transform infrared spectra were obtained on a PerkinElmer Spectrum 2000 using the KBr pellet method in the range of 4000 to 400 cm⁻¹. X-ray diffractograms were obtained using a Rigaku MiniFlex diffractometer in the 2θ range of 20–70° with a scan rate of 2° min⁻¹. Fieldemission scanning electron micrographs were acquired using a Hitachi SU8010 FE-SEM. Prior to imaging, finely crushed and dried powdered nanoparticles were mounted on carbontaped clean metal stubs followed by coating with gold using a sputter coater. Transmission electron microscopic images were obtained on a FEI TECNAI G² T20 TEM instrument. The samples were prepared by first dispersing the nanoparticles in ethanol and then casting a drop of it on carbon-coated copper grids. The size of the nanoparticles was determined using ImageJ software. An SEM-coupled EDAX system was used to analyze the elemental composition of the supported MetIL. A MicroSense ADE-EV9 vibrating sample magnetometer was used to measure the magnetization values of the nanomaterials. The analyses were carried out at room temperature in the magnetic field range of -10 000 Oe to +10 000 Oe. The

thermogravimetric curve was obtained using a Linseis TGA under a nitrogen atmosphere with a gas flow of 2 L h^{-1} and in the temperature range from 37 °C to 950 °C with a heating rate of 10 °C min⁻¹. The copper content present in the nanocatalyst was determined using a PerkinElmer Optima 2100 DV inductively coupled plasma-mass spectrometer. Furthermore, the Brunauer-Emmett-Teller (BET) surface areas were measured using an ASI-CT-11 Quantachrome instrument at a degassing temperature of 150 °C. The optimization of the reaction conditions was carried out using an Agilent gas chromatograph (6850 GC) having a HP-5MS capillary column (stationary phase: 5% phenyl methyl siloxane; column length: 30 m; internal diameter: 0.25 mm; film thickness: 0.25 µm) and a quadrupole mass filter equipped 5975C mass selective detector (MSD) using helium as a carrier gas. Operation conditions: injection temperature: 250 °C, detector temperature: 250 °C, helium gas flow: 1.0 mL min⁻¹. Temperature programming: initial column temperature = 60 °C, hold time = 5 min; next temperature = 150 °C, rate of temperature ramp 1 = 10 °C min^{-1} , hold time = 0 min; final temperature = 250 °C, rate of temperature ramp 2 = $15 \circ C \min^{-1}$, hold time = 2 min. Finally, the organic compounds were characterized using ¹H (400 MHz) and ¹³C (100 MHz) JEOL JNM-EXCP-400 nuclear magnetic resonance spectrophotometers. The spectra were recorded in either CDCl₃ or DMSO- d_6 . Chemical shifts (δ) for proton and carbon are reported in parts per million (ppm) units downfield from tetramethylsilane (internal standard).

Synthesis of the magnetic support

The first step included the synthesis of SMNPs which were chosen as a support for immobilizing the MetIL. Initially, magnetite nanoparticles (MNPs) were prepared according to a coprecipitation method. In a typical procedure, 6.0 g of ferric sulfate hydrate and 4.2 g of ferrous sulfate heptahydrate were dissolved in 250 mL of double distilled water followed by stirring at 60 °C till the solution became yellowish-orange in color. Later, 15 mL of 25% ammonium hydroxide was added to set the pH around 10. After 30 minutes of continuous stirring at the same temperature, the black colored nanoparticles were separated magnetically, washed with water and further with ethanol till the solution became neutral and finally dried in a vacuum oven. The MNPs were coated with a layer of silica using a sol-gel approach. For this, 0.5 g of MNPs was activated by adding 2.2 mL of 0.1 M HCl. Furthermore, the solution was kept under sonication for 30 minutes after the addition of 200 mL of ethanol and 50 mL of water. Afterwards, 5 mL of ammonium hydroxide and 1 mL of TEOS were added in a dropwise fashion. The solution was then stirred for 6 h at 60 °C. Finally, the as-obtained brown colored SMNPs were separated magnetically, washed with ethanol until neutral pH and dried in a vacuum oven.

Synthesis of the functionalized IL

Initially, a silyl-functionalized methylimidazolium chloride homogeneous IL was synthesized. For this, equal moles of *N*-methylimidazole and CPTMS were heated at 80 °C for 48 h under solvent-free conditions. Later, the as-synthesized colorless and viscous IL was washed with diethyl ether to remove any unreacted materials. It was further dried in a vacuum oven to obtain a pure functionalized IL.

Immobilization of the FIL on the SMNPs

To support the FIL on the SMNPs, 1.0 g of SMNPs was thoroughly dispersed under sonication in 100 mL of $CHCl_3$ for 30 minutes. Next, 10 mmol of FIL was added into the dispersed solution of the SMNPs. The solution was then refluxed for 48 h. The IL immobilized SMNPs were later separated magnetically, washed with $CHCl_3$ and further with ethanol to remove any unreacted FIL and finally dried in a vacuum oven.

Formation of the SMNP supported copper-containing IL

Finally, to obtain the SMNP supported copper-containing IL, 1.0 g of IL@SMNPs was dispersed in 100 mL of ethanol. Later, 5 mmol of CuCl₂ was added and the resulting solution was refluxed for 3 h. The immobilized MetIL was finally washed with ethanol and dried in a vacuum oven.

General reaction procedure for the synthesis of 2-phenylquinazolin-4(3*H*)-ones

For the synthesis of quinazolinones, *o*-aminobenzamide and benzaldehydes were chosen as the substrates. To begin the reaction, 0.5 mmol of *o*-aminobenzamide and 0.5 mmol of benzaldehyde were added into an oven-dried round bottom flask containing 3 mL of ethanol. Furthermore, 50 mg of CuIL@SMNPs was added and the solution was refluxed under constant stirring. The progress of the reaction was monitored by TLC. After the completion of the reaction, the catalyst was separated from the reaction mixture using an external magnet. Furthermore, water was added to the reaction mixture. The precipitate so obtained was filtered and washed thoroughly with water. It was then dried in a vacuum oven. In order to derive the purified product, it was washed once with a small amount of ethyl acetate to remove any unreacted precursors (except when R = H and Me).

Conflicts of interest

There are no conflicts to declare.

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