Indian Journal of Chemistry
Vol. 62, January 2023, pp. 16-23
DOI: 10.56042/ijc.v62i1.70348

Fe_3O_4 supported acidic ionic liquid: An efficient and recyclable magnetic nanoparticles catalyst for one-pot synthesis of Bis(indolyl)methanes

Jims World Star Rani[a,b], Geetmani Sing Nongthombam[c], Chingrishon Kathing[d], Ridaphun Nongrum[e], George Kupar Kharmawlong[a] & Rishanlang Nongkhlaw [a,*]

[a]Centre for Advanced Studies in Chemistry, Department of Chemistry, North-Eastern Hill University, Shillong, Meghalaya-793 022, India
[b]Department of Chemistry, Union Christian College, Umiam Khwan, Ri-Bhoi District, Meghalaya-793 122, India
[c]Applied Organic Synthesis Group, Chemical Science & Technology Division, CSIR-NEIST, Jorhat, Assam-785 006, India
[d]Department of Chemistry, Gargi College, University of Delhi, Siri Ford Road, New Delhi-110 049, India
[e]Department of Chemistry, Sankardev College, Bishnupur, Shillong, Meghalaya-793 004, India
*E-mail: rlnongkhlaw@nehu.ac.in, rlnongkhlaw@gmail.com

Received 27 August 2021; accepted (revised) 14 December 2022

Bis(indolyl)methane derivatives are efficiently synthesized from indole/2-methyl indole and aldehydes using acidic ionic liquid immobilized on magnetic Fe_3O_4 nanoparticles. Catalyst used in this methodology is synthesized and characterized using various techniques like FT-IR, TGA, TEM, EDX, Powdered XRD and VSM. The catalyst can be easily retrieved by an external magnet and has been reused up to five runs without any appreciable loss of its catalytic activity.

Keywords: Bis(indolyl)methanes, Magnetic ferrite nanoparticles, Acidic ionic liquid, Green solvent (ethanol-water mixture), Environment benign synthesis

Indole derivatives have been classified as one of the important nitrogen containing heterocycles as they possess broad spectrum of biological and pharmacological activities[1,2]. Bis(indolyl)alkanes moiety is found in various bioactive natural products isolated from marine sponge alkaloids[3,4]. Bis(indolyl) methanes (BIMs) have also been recognized as one of the important scaffolds because of their wide range of biological applications such as anti-fungal[5], anti-bacterial[6], anti-inflammatory[7], anticancer[8,9] and analgesic activities.

Literature reports revealed that a number of catalysts have been used for the synthesis of bis(indolyl)methanes (BIMs), including protic acids like CH_3COOH[10], $V(HSO_4)_3$[11], polyvinylsulfonic acid (PVSA)[12], camphor sulfonic acid (CSA)[13], oxalic acid[14], squaric acid[15], dodecylbenzenesulfonic acid (ABS)[16], *p*-TsOH[17] *etc.*; Lewis acids like $InCl_3$[18], $FeCl_3$[19], $In(OTf)_3$[20], $Fe(HSO_4)_3$[21], $ZrCl_4$[22], $LiClO_4$[23], $Al(OTf)_3$[24]; and silica-supported acids like H_2SO_4-SiO_2[25], HBF_4-SiO_2[26], H_3PO_4-SiO_2[27] etc. Some of the reported methods have disadvantages such as long reaction time, low yield, the use of volatile solvent and corrosive catalysts, catalyst recyclability problem and tedious work-up procedures. So, the development of more efficient and environmental friendly methodologies for synthesis of BIMs still remains a challenging and an active field of research.

Ionic liquids (ILs) have attracted considerable attention because of their unique properties like high thermal stability, negligible vapour pressure, wide liquid range and can solvate many organic and inorganic compounds[28-30]. Acidic ionic liquids like [Hmim][Tfa]/[Hmim][HSO_4][31], [bnmim][HSO_4][32], [Msim][X] (where X= [$FeCl_4$], [$ZnCl_3$], [$CuCl_2$])[33], [Msim]Cl[34], etc. have been reported to catalyse the synthesis of BIMs. However these methods too, suffer from certain drawbacks such as high viscosity which results in less catalytic activity, homogeneity resulting in difficulty of isolation and in catalyst separation and recyclability. These problems were addressed by immobilisation of an ILs on magnetic solid support like Fe_3O_4 nanoparticles making the catalyst heterogeneous for easy recovery.

The heterogeneous magnetic nanocatalyst offers advantages over homogeneous ILs in term of stability, efficacy because of large surface area, simple recovery step with the help of an external magnetic field and reusability[35-40]. In view of these aspects and also with the advancement in nanotechnology, we herein, report a green approach towards the synthesis of BIMs utilizing acidic imidazole-based ionic liquid immobilized on magnetic Fe_3O_4 nanoparticles (NPs) (Scheme 1).

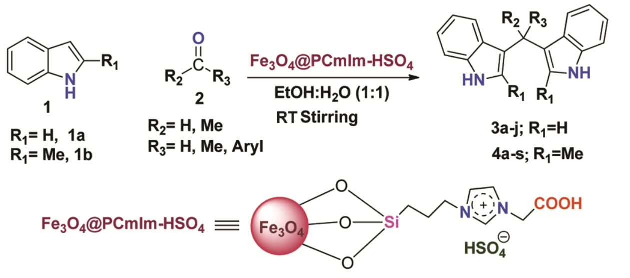
Experimental Details

Materials and method

All the chemicals used in the synthesis were purchased from Alfa Aesar, Sigma-Aldrich & Merck and were used without further purification. The purity of the synthesized products was confirmed by various analytical techniques *viz.,* melting point, infrared (FT-IR), ^{1}H NMR, ^{13}C NMR, and mass spectroscopy. The melting points are recorded in open capillaries in an Optics Technology melting point apparatus and found uncorrected. FT-IR spectra were recorded in KBr pellets on a Perkin Elmer Spectrum 400 FT-IR instrument, and the frequencies are expressed in cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance II-400 and Bruker DRX-300 spectrometers in DMSO-d_6. Mass spectral data were obtained with a Waters ZQ-4000 and Water UPLC-TQD (ESI) mass spectrometer. Single crystal XRD data were obtained with a Xcalibur-Eos-Gemini instrument and powder XRD analysis was conducted with a D8 Advance (Bruker) instrument. Ultra-sound irradiation was carried out in a Bandelin Sonorex ultrasonic bath: Model RK 52H Incarp Germany (50/60 Hz, 60/240 W). VSM analysis was carried out in Lakeshore, model: 7410 series instrument. The TEM images were captured using a transmission electron microscope of JEM-2100 make, 200 kV (JEOL). EDS analysis was recorded with ZEISS, Sigma microscope. All reactions were monitored by thin-layer chromatography (TLC) using pre-coated aluminum sheets (silica gel 60 F 254 0.2 mm thickness) and developed in iodine chamber or UVGL-15 mineral light 254 nm lamp.

Procedure for preparation of Fe_3O_4 nanoparticles

A solution of Fe(II)/ Fe(III) salts (1:2 equivalent ratio) in 100 mL deionized water was reduced by dropwise addition of 1.5 M NaOH solution under vigorous stirring for 1-2 h. The pH of the solution was maintained between 11 to 12. The black precipitate formed was collected using an external magnet and washed repeatedly with deionized water till the pH became neutral. The resultant product was then washed with diethyl ether and dried at room temperature.



Scheme 1 — Synthesis of bis(indolyl)methane derivatives catalysed by Fe_3O_4@PCmIm-HSO_4

Encapsulation of Fe_3O_4 nanoparticles with ionic liquid

A suspension of Fe_3O_4 nanoparticles (1 g) in ethanol (80 mL) was ultrasonicated for 10 min at ambient temperature. Then, 1.5 mL of 1((3-triethoxysilyl)-propyl)-1*H*-imidazole was added dropwise into the solution of Fe_3O_4 NPs for 1 h with vigorous stirring under inert atmosphere at room temperature. The reaction was stirred continuously at 60°C for 12 h. The functionalized NPs was recovered from the reaction mixture through magnetic decantation, washed with water followed by ethanol and dried.

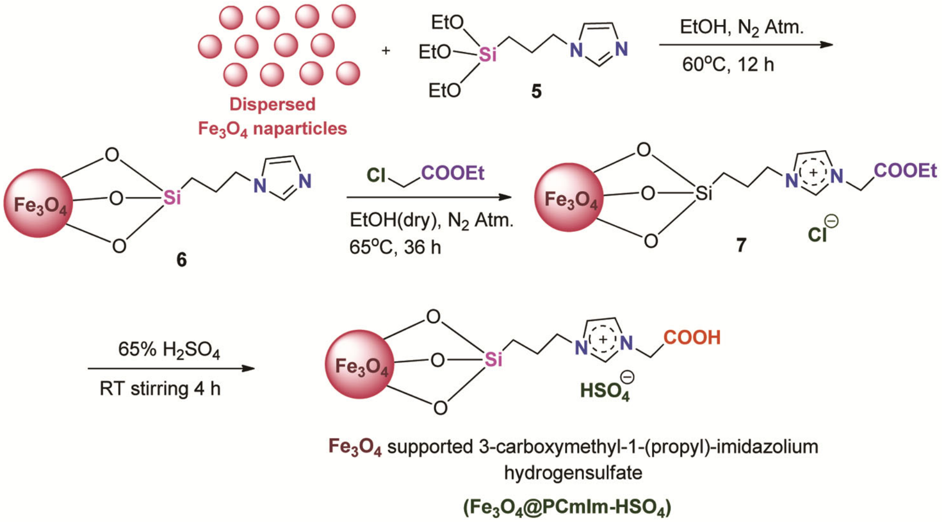
The solution of the obtained NPs (1 g) in dry ethanol (80 mL) was ultrasonicated for 2 min, then ethylchloroacetate (6 mmol) was added to this solution and stirred under inert atmosphere at 65°C for 36 h. The reaction mixture was then cooled to room temperature, 65% H_2SO_4 (1 mL) was then added and stirred under room temperature for 4 h. Fe_3O_4@PCmIm-HSO_4 NPs thus formed was recovered with an external magnet, washed with water (3 x 20 mL), then with di-ethyl ether (2 x 10 mL) and dried at room temperature.

General procedure for the synthesis of 3a-j, 4a-s

A solution of indole/2-methyl indole (2 mmol), aliphatic/aromatic carbonyl compounds (1 mmol) and nanocatalyst (15 mg) in ethanol:water (1:1, 10 mL) was stirred in a 50 mL round bottom flask at room temperature. On completion of the reaction (monitored with TLC), the catalyst was recovered from the reaction mixture by an external magnet. The precipitated solid products were filtered and washed repeatedly with water and dried. The obtained product was further purified by recrystallization from hot ethanol (15 mL). The complete characterization data for the synthesized compounds are given in the Supplementary Information.

Results and Discussion

In continuation with our on-going research for developing eco-friendly catalyst for efficient and green protocols towards the syntheses of different heterocycles[41,42], we designed a modified imidazole-based acidic ionic liquid as a nanocatalyst for the



Scheme 2 — Schematic representation for the synthesis of Fe_3O_4@PCmIm-HSO_4

synthesis of BIM derivatives. The acidic character of ionic liquid is achieved by functionalization of the imidazole moiety with -COOH and -HSO_4 (counter anion) functional groups. In addition, to make the catalyst recovery more easy and simple, it was immobilized on the magnetic ferrite NPs.

Preparation and characterisation of catalyst (Fe_3O_4@PCmIm-HSO_4)

Initially, Fe_3O_4 NPs were prepared by the chemical reduction of Fe(II) and Fe(III) salts. The prepared NPs were characterized with FT-IR, TEM and powder XRD techniques. Encapsulation of acidic ionic liquid on the surface of the prepared Fe_3O_4 NPs is presented in Scheme 2. 1-((3-triethoxysilyl)-propyl)-1*H*-imidazole (**5**) is treated with the dispersed Fe_3O_4 NPs, whereby functionalized Fe_3O_4 NPs (**6**) is obtained. The obtained NPs were further functionalized with ethylchloroacetate in ethanol under nitrogen atmosphere to achieve the precursor magnetic ionic liquid NPs (**7**). Finally, the Fe_3O_4 supported 3-carboxymethyl-1-propyl-1*H*-imidazolium hydrogen sulfate NP (Fe_3O_4@PCmIm-HSO_4) was afforded by the hydrolysis of **7** with 65% H_2SO_4. This acid hydrolysis of **7**, converted –COOEt to –COOH functional group and the counter anion Cl^- was replaced by $[HSO_4]^-$. The acidic nature of the prepared NPs was enhanced due to the presence of two acidic functional groups (-COOH and $[HSO_4]^-$). The size and characteristics of the synthesized NPs were confirmed with the help of different analytical techniques such as FT-IR, TGA, TEM, EDS, powder XRD and VSM.

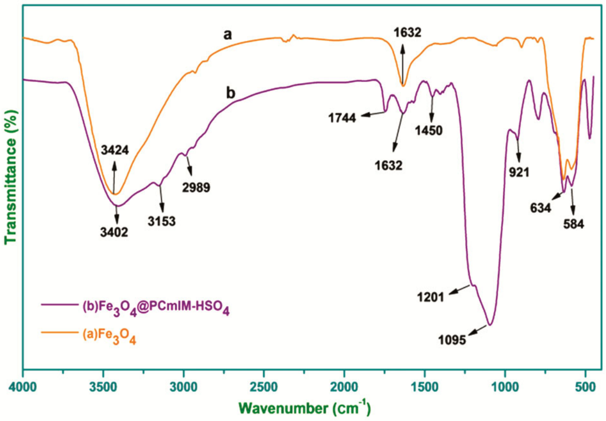


Fig. 1 — FT-IR spectra

The FT-IR spectrum of the prepared Fe_3O_4 NPs (Fig. 1) showed O-H stretching and deformation vibration at around 3424 cm^{-1} and 1632 cm^{-1}, respectively. The absorption bands at 634 cm^{-1} and 584 cm^{-1} corresponds to Fe-O stretching vibration. The FT-IR spectrum of the synthesized Fe_3O_4@PCmIm-HSO_4 nanoparticles (Fig. 1b) showed C-H stretching vibration at 3153 cm^{-1} and 2989 cm^{-1}. The absorption band at 1744 cm^{-1} is assigned to the C=O stretching vibration of –COOH, whereas absorption bands at 1632 cm^{-1} and 1450 cm^{-1} are assigned to C=N and C=C stretching vibrations of imidazole ring, respectively. The appearance of strong absorption bands around 3402 cm^{-1} and 1201 cm^{-1} is attributed to the O-H and S=O stretching vibrations respectively, which also confirmed the exchange of Cl^- ion by $[HSO_4]^-$ ion. Bands at 1095 cm^{-1} and 921 cm^{-1} correspond to the asymmetric and symmetric stretching vibration of Si-O bond; which further suggest the successful immobilization of acidic ionic liquid on the surface of Fe_3O_4 nanoparticles.

The TEM images of the synthesized Fe_3O_4@PCmIm-HSO_4 NPs (Fig. 2) clearly indicated a layer of ionic liquid encapsulated on the surface of the Fe_3O_4 NPs. The size of the NPs ranges from 15 nm to 35 nm and bulk coated particles showed sizes >50 nm. The EDS spectrum of the synthesised Fe_3O_4@PCmIm-HSO_4NPs (Fig. 3), indicated a fair amount of Si, S and N (components of ionic liquid) besides Fe and O (components of core Fe_3O_4 NPs).

The TGA plot (Fig. 4a) of the synthesized nanoparticles demonstrated the weight losses of about 2.3% and 10.38% within the temperature range of 40-122ºC and 233-485ºC, respectively. This could be attributed to the elimination of the adsorbed water molecules (2.3%) and the decomposition of the ionic liquid layer (10.38%) from the surface of Fe_3O_4 nanoparticles, respectively. This TGA data suggests that the amount of ionic liquid present in 10 mg of Fe_3O_4@PCmIm-HSO_4 is roughly about 1 mg approximately.

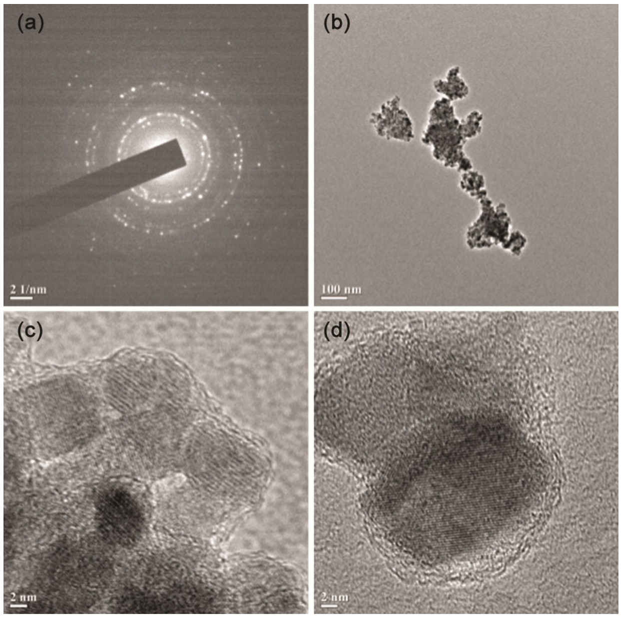


Fig. 2 — (a) SAED pattern, (b), (c) & (d) TEM images of Fe_3O_4@PCmIm-HSO_4

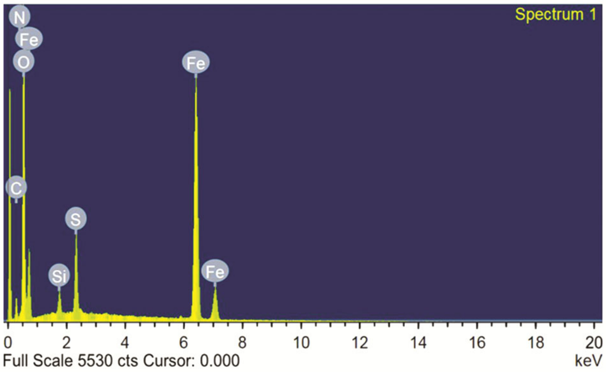


Fig. 3 — EDS spectrum of Fe_3O_4@PCmIm-HSO_4

The nature of the prepared NPs was further characterized with powder XRD and VSM analysis. The powder XRD plot (Fig. 5) shows diffraction peaks at 30.44°, 35.84°, 43.33°, 54.01°, 57.34° and 63.02° which correspond to the (220), (311), (400), (422), (511) and (440) planes of Fe_3O_4 NPs respectively[43]. The VSM analysis (Fig. 6) reveals the superparamagnetic nature of the synthesized NPs (catalyst) with saturation magnetization value of 42.26 emu/g, which is lower as compared to uncoated ferrite NPs (59.76 emu/g)[40].

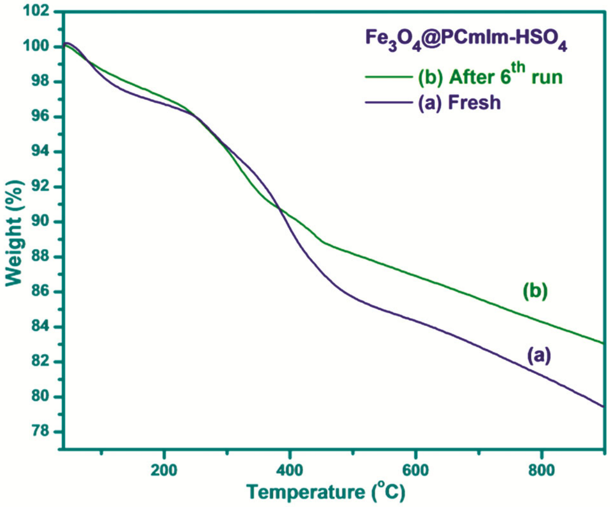


Fig. 4 — TGA plot of Fe_3O_4@PCmIm-HSO_4; (a) Fresh and (b) after 6 cycles

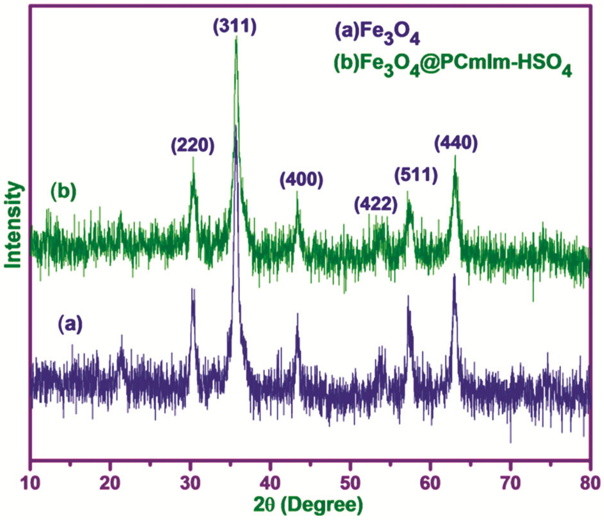


Fig. 5 — Powder XRD plot

Synthesis of BIMs derivatives using Fe_3O_4@PCmIm-HSO_4 as catalyst

The catalytic efficacy of the synthesized NPs (Fe_3O_4@PCmIm-HSO_4) was investigated in the model reaction between indole (**1a**), (2 mmol) and benzaldehyde (**2**), (1 mmol) (Scheme 1) which afforded 88% of BIM (**3a**).

For optimization of the reaction conditions, we examined the catalytic activity of Fe_3O_4@PCmIm-HSO_4 NPs for the model reaction under different conditions (Table 1). Initially, the model reaction was carried out in aqueous medium which afforded low yield (65%) of product (**3a**). The product yield improved (76%) in ethanol as the medium and a 88% yield is achieved in ethanol-water (1:1) medium. Further change in the proportion of ethanol in the ethanol-water mixture lead to the decrease in product yields. Other solvents like methanol, ethyl acetate and dichloromethane were also examined for the model reaction, but products are obtained at lower yields. Hence, ethanol-water mixture (1:1) was considered as the most suitable medium for this reaction under room temperature stirring condition.

Catalyst loading was also investigated for the synthesis of **3a** and the results revealed that 15 mg was the optimum amount of catalyst required to effectively catalyse the reaction giving maximum yield (88%) within 18 min, (Table 1, Fig. 7). Further increase in the catalyst amount did not show

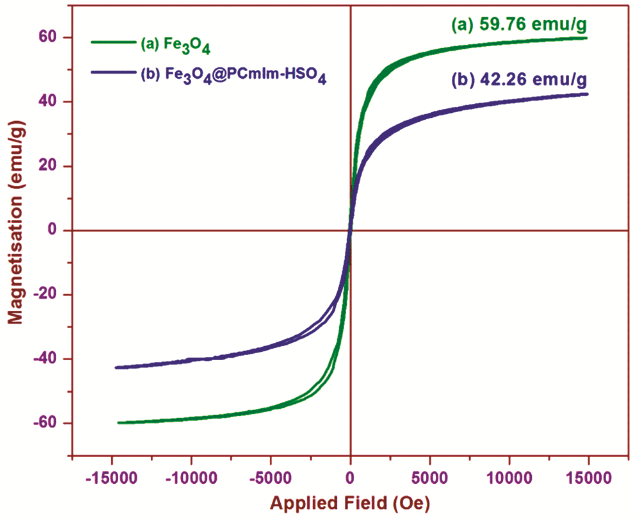


Fig. 6 — VSM plot

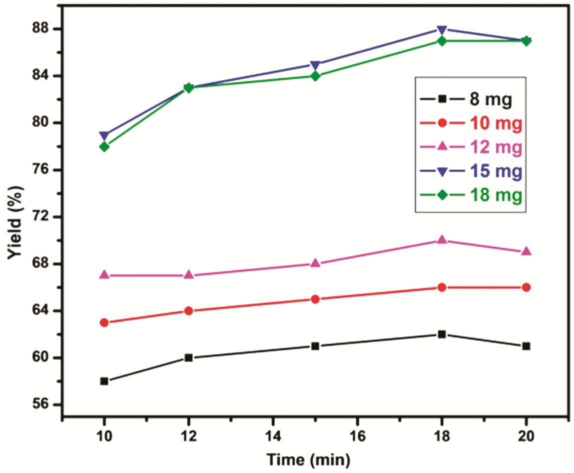


Fig. 7 — Effect of catalyst loading on reaction yields

Table 1 — Optimization for the synthesis of 3a

Catalyst	Amount (mg)	Condition	Time (min)	Isolated yield (%)
Fe_3O_4	10	H_2O, Room temp.	20	35
Fe_3O_4	15	EtOH, Room temp.	30	60
Fe_3O_4	20	EtOH, Room temp.	30	63
Fe_3O_4	25	EtOH-H_2O(1:1), Room temp.	30	65
Fe_3O_4@PCmIm-HSO_4	5	H_2O, Room temp.	10	60
Fe_3O_4@PCmIm-HSO_4	10	H_2O, Room temp.	10	65
Fe_3O_4@PCmIm-HSO_4	15	EtOH, Room temp.	30	76
Fe_3O_4@PCmIm-HSO_4	15	EtOH-H_2O(1:2), Room temp.	22	72
Fe_3O_4@PCmIm-HSO_4	15	EtOH-H_2O(1:1), Room temp.	18	88
Fe_3O_4@PCmIm-HSO_4	20	EtOH-H_2O(1:1), Room temp.	18	86
Fe_3O_4@PCmIm-HSO_4	20	EtOH-H_2O(1:1), Room temp.	30	83
Fe_3O_4@PCmIm-HSO_4	15	EtOH-H_2O(1:1), reflux	30	77
Fe_3O_4@PCmIm-HSO_4	15	EtOH-H_2O(2:1), Room temp.	30	79
Fe_3O_4@PCmIm-HSO_4	20	EtOH-H_2O(2:1), Room temp.	35	75
Fe_3O_4@PCmIm-HSO_4	25	EtOH-H_2O(2:1), reflux	30	70
Fe_3O_4@PCmIm-HSO_4	15	MeOH, Room temp.	30	73
Fe_3O_4@PCmIm-HSO_4	15	Ethylacetate, Room temp.	30	71
Fe_3O_4@PCmIm-HSO_4	15	CH_2Cl_2	30	65

Table 2 — Synthesis of BIMs catalyzed by Fe_3O_4@PCmIm-HSO_4 NPs at room temperature

Indole	Carbonyl compound	Product	Time (min)	Isolated yield (%)	Melting point (ºC)
1a	C_6H_5-CHO	3a	18	88	145-147
1a	*p*-CH_3O-C_6H_4-CHO	3b	25	85	186-188
1a	*m*-CH_3O-C_6H_4-CHO	3c	23	83	184-186
1a	*p*-HO-C_6H_4-CHO	3d	27	88	125-127
1a	*p*-CH_3-C_6H_4-CHO	3e	20	90	91-93
1a	*p*-HO,m-CH_3O-C_6H_3-CHO	3f	26	87	103-105
1a	*p*-NO_2-C_6H_4-CHO	3g	17	87	226-228
1a	*p*-Cl-C_6H_4-CHO	3h	15	84	82-84
1a	*p*-Br-C_6H_4-CHO	3i	18	85	130-132
1a	Indole-3-CHO	3j	17	90	240-242
1b	C_6H_5-CHO	4a	10	89	244-246
1b	*p*-Cl-C_6H_4-CHO	4b	7	89	234-236
1b	*p*-NO_2-C_6H_4-CHO	4c	5	93	241-243
1b	*p*-F-C_6H_4-CHO	4d	4	91	258-260
1b	*o*-Cl-C_6H_4-CHO	4e	5	93	218-220
1b	*o*-NO_2-C_6H_4-CHO	4f	6	90	234-236
1b	*p*-Br-C_6H_4-CHO	4g	5	92	242-244
1b	*m*-Br-C_6H_4-CHO	4h	8	87	278-280
1b	H-CHO	4i	12	89	110-112
1b	CH_3-CHO	4j	18	87	179-181
1b	CH_3-CO-CH_3	4k	26	84	188-190
1b	*p*-CH_3O-C_6H_4-CHO	4l	15	86	196-198
1b	*m*-CH_3O-C_6H_4-CHO	4m	18	89	150-152
1b	*o*-HO-C_6H_4-CHO	4n	12	88	228-230
1b	*p*-HO,m-CH_3O-C_6H_3-CHO	4o	16	91	228-230
1b	*p*-C_2H_5O-C_6H_3-CHO	4p	14	90	184-186
1b	*p*-CH_3-C_6H_4-CHO	4q	13	93	179-181
1b	2-Naphthaldehyde	4r	5	89	204-206
1b	1-HO-2-Naphthaldehyde	4s	8	90	249-251

significant improvement in the product yield. The catalytic activity of the uncoated Fe_3O_4 NPs was also studied for the model reaction which yielded only 65% of the product even at a longer reaction time. Hence, it can be concluded that the core Fe_3O_4 nanoparticles acts merely as an anchor for the prepared catalyst, thereby aiding easy catalyst recovery with an external magnet.

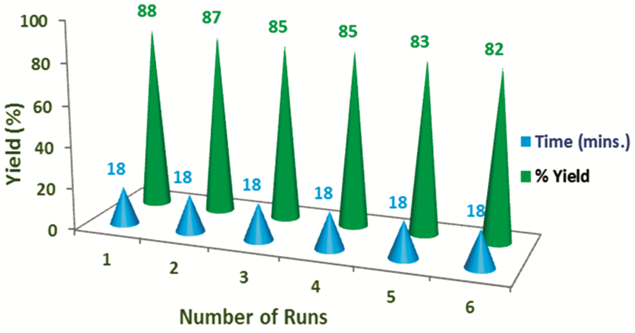
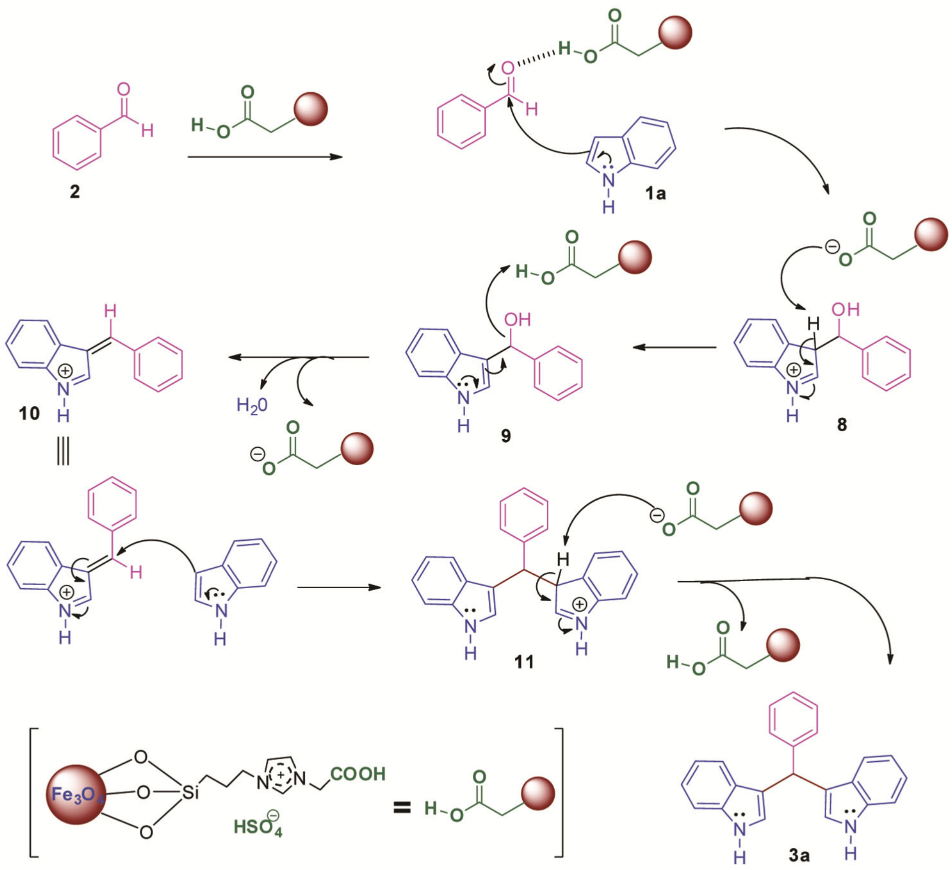


Fig. 8 — Catalyst reusability plot for the synthesis of **3a**

Study on catalyst recyclability and reusability was performed on the model reaction for the synthesis of **3a** (Scheme 1, Table 2). On completion of the reaction the catalyst was recovered from the reaction mixture with the help of an external magnet, washed with water, diethylether and after drying it at room temperature, the catalyst was reused for the next set of reaction (synthesis of **3a**). The catalyst could be recycled and reused upto a minimum of six cycles without any significant loss of its catalytic activity (Fig. 8). A slight decrease in the product yield may be attributed to the leaching and aggregation of the nanocatalyst. TGA analysis of the nanocatalyst after 6th run suggested that a good amount of IL remain intact on the core Fe_3O_4 NPs (Fig. 4b).

The plausible mechanism for the formation of **3a** is suggested in Scheme 3[44]. The reaction is initiated by the activation of the carbonyl group of benzaldehyde (**2**) by the acidic (-COOH) group of the catalyst and



Scheme 3 — Plausible mechanism for the synthesis of **3a**

proceeds *via* the formation of azafulvenium salt (**10**), which further reacts with another molecule of indole (**1a**) to form intermediate **11**. Consequently, abstraction of a proton by the conjugate base of the catalyst, leads to the formation of 3-alkylated bis(indolyl) derivative (**3a**).

The versatility of this method was established by extending the reaction of indole/2-methylindole (1a/1b) with various carbonyl compounds (**2**) to furnish corresponding bis(indolyl)methane derivatives (**3/4,** Scheme 1). Under the optimized condition a series of derivatives (**3a-j, 4a-s**) were successfully synthesized in a good to excellent yields (83-93%) in a short reaction time (4-27 min**,** Table 2). This method tolerated well to aromatic aldehydes with a wide range of substituents like $–NO_2$, -Cl, -OH, $-CH_3$, etc.

The results from Table 2 indicated that the substituents on the aromatic aldehydes did not have profound effect on the yield of the products. However, aromatic aldehydes with electron withdrawing substituents were found to react faster as compared to those with electron donating substituents. Also, 2-methylindole (**1b**) afforded the desired products faster as compared to indole (**1a**), which could be attributed to the increase nucleophilicity of the indole ring due to the positive inductive effect of the methyl group. All the synthesized compounds were characterized using various analytical techniques *viz.* melting point, FT-IR, NMR and Mass spectrometry. The analytical data of all synthesized compounds were found to be in accordance with the literature reports.

The single crystal X-ray diffraction (XRD) data for **4g** was collected at 295 K with Mo Kα radiation (λ = 0.71073 Å) using Agilent Xcalibur (Eos, Gemini) diffractometer equipped with a graphite monochromator. The software used for data collection CrysAlis PRO (Agilent, 2011), data reduction CrysAlis PRO and cell refinement CrysAlis PRO. The structures were solved by direct methods and refined by Olex2.refine. The detailed information and ORTEP images of synthesized compounds are given in the Supplementary Information.

Conclusion

In conclusion, we have developed a new acidic ionic liquid supported on ferrite nanoparticles

(Fe_3O_4@PCmIm-HSO_4), which effectively catalyzed the synthesis of bis(indolyl)alkanes. Easy recyclability and reusability of the catalyst helps in promoting green methodology to the next level. The method demonstrated the versatility of the catalyst whereby a good number of carbonyl compounds effectively reacted with indole/2-methylindole to give good yields of the desired products in a short reaction time.

Acknowledgement

Authors acknowledged SAIF NEHU, CDRI, Lucknow and CSIR-NEIST Jorhat, CIF IIT Guwahati, Department of Chemistry, NEHU and IIT-Madras for their analytical assistance. J. Rani acknowledged UGC for providing financial support in the form of fellowship (RGNF-2013-14-ST-MEG-44454). Financial support from DST is gratefully acknowledged (SERB EEQ 2016000646).

Supplementary Information

Supplementary information is available in the website http://nopr.niscpr.res.in/handle/123456789/58776.

References

1 Sundberg R J, *Indoles,* (Academic Press: USA) 1996, p. 1-2.
2 Netz N & Opatz T, *Marine Drugs*, 13 (2015) 4814.
3 Morris S A & Andersen R J, *Tetrahedron*, 46 (1990) 715.
4 Miyake F Y, Yakushijin K & Horne D A, *Org Lett*, 4 (2002) 941.
5 Sivaprasad G, Perumal P T, Prabavathy V R & Mathivanan N, *Bioorg Med Chem Lett*, 16 (2006) 6302.
6 Bell R, Carmeli S & Sar N, *J Nat Prod*, 57 (1994) 1587.
7 Kuppusamy S, Perumal P T, Doraisamy M & Melani R, *Indian J Chem*, 48B (2009) 267.
8 Rahman K M W, Li Y, Wang Z, Sarkar S H & Sarkar F H, *Cancer Res*, 66 (2006) 4952.
9 Hong C, Firestone G L & Bjeldanes L F, *Biochem Pharmacol*, 63 (2002) 1085.
10 Zahran M, Abdin Y & Salama H, *Arkivoc*, (xi) (2008) 256.
11 Shirini F, Yahyazadeh A, Abedini M & Imani Langroodi D, *Bull Korean Chem Soc*, 31 (2010) 1715.
12 Ekbote S S, Deshmukh K M, Qureshi Z S & Bhanage B M, *Green Chem Lett Rev*, 4 (2011) 177.
13 Mishra S & Ghosh R, *Indian J Chem*, 50B (2011) 1630.
14 Ghorbani-Vaghei R, Veisi H, Keypour H & Dehghani-Firouzabadi A A, *Mol Diversity*, 14 (2010) 87.
15 Azizi N, Gholibeghlo E & Manocheri Z, *Sci Iran*, 19 (2012) 574.
16 Li J T, Sun M X, He G Y & Xu X Y,*Ultrason Sonochem*, 18 (2011) 412.
17 Raju B C & Rao J M, *Indian J Chem*, 47B (2008) 623.
18 Babu G, Sridhar N & Perumal P T, *Synth Commun*, 30 (2000) 1609.
19 Xia M, Wang S H & Yuan W B, *Synth Commun*, *34* (2004) 3175.
20 Ji S J, Zhou M F, Gu D G, Wang S Y & Loh T P, *Synlett*, 24 (2003) 2077.
21 Rahimizadeh M, Eshghi H, Bakhtiarpoor Z & Pordel M, *J Chem Res*, 2009 (2009) 269.
22 Nagawade R R & Shinde D B, *Bull Korean Chem Soc*, 26 (2005) 1962.
23 Yadav J S, Reddy B V S, Murthy C V S R, Kumar G M & Madan C, *Synthesis*, 5 (2001) 783.
24 Kamal A, Khan M N A, Reddy K S, Srikanth Y V V, Ahmed S K, Kumar K P, Murthy U S N, *J Enzyme Inhib Med Chem*, 24 (2009) 559.
25 Zhang Y, Chen X, Liang J & Shang Z C, *Synth Commun*, 41 (2011) 2446.
26 Bandgar B P, Patil A V & Kamble V T, *Arkivoc*, (xvi) (2007) 252.
27 Chakrabarty M, Mukherjee R, Mukherji A, Arima S & Harigaya Y, *Heterocycles*, 68 (2006) 1659.
28 Wasserscheid P & Keim W, *Angew Chemie Int Ed*, 39 (2000) 3772.
29 Giernoth R, *Angew Chemie Int Ed*, 49 (2010) 2834.
30 Pârvulescu V I & Hardacre C, *Chem Rev*, 107 (2007) 2615.
31 Dabiri M, Salehi P, Baghbanzadeh M, Shakouri M, Otokesh S, Ekrami T & Doosti R. *J Iran Chem Soc*, 4 (2007) 393.
32 Sadaphal S, Shelke K , Sonar S & Shingare M, *Open Chemistry*, 6 (2008) 622.
33 Gogoi P, Dutta A K, Sarma P & Borah R, *Appl Catal A Gen*, 492 (2015) 133.
34 Zolfigol M A, Khazaei A, Moosavi-Zare A R & Zare A, *Org Prep Proced Int*, 42 (2010) 95.
35 Zarnegar Z & Safari J, *J Nanoparticle Res*,16 (2014) 2509.
36 Khalafi-Nezhad A & MohammadiS, *ACS Combinatorial Science*, 15 (2013) 512.
37 Alinezhad H, Tajbakhsh M & Ghobadi N, *Synth Commun*, 45 (2015) 1964.
38 Zhang Q, Su H, Luo J & Wei Y, *Green Chem*, 14 (2012) 201.
39 Rastegari F, Mohammadpoor-Baltork I, Khosropour A R, Tangestaninejad S, Mirkhani V & Moghadam M, *RSC Adv*, 5 (2015) 15274.
40 Safari J & Zarnegar Z, *New J Chem*, 38 (2014) 358.
41 Nongrum R, Nongthombam G S, Kharkongor M, Rani J W S, Rahman N, Kathing C, Myrboh B & Nongkhlaw R, *RSC Adv*, 6 (2016) 108384.
42 Rahman N, Nongthombam G S, Rani J W S, Nongrum R, Kharmawlong G K & Nongkhlaw R, *Curr Organocatalysis*, 5 (2018) 150.
43 Ying A, Qiu F, Wu C, Hu H & Yang J, *RSC Adv*, 4 (2014) 33175.
44 Zolfigol M A, Ayazi-Nasrabadi R & Baghery S, *Appl Organomet Chem*, 30 (2016) 273.