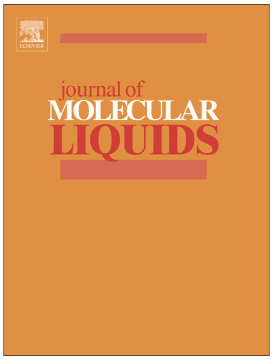

Design, synthesis, characterization, and catalytic properties of g-C3N4-SO3H as an efficient nanosheet ionic liquid for one-pot synthesis of pyrazolo[3,4-b]pyridines and bis(indolyl)methanes

Hojat Veisi, Pourya Mohammadi, Turan Ozturk

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Design, Synthesis, Characterization, and Catalytic Properties of g-C_3N_4-SO_3H as an Efficient Nanosheet Ionic Liquid for One-pot Synthesis of Pyrazolo[3,4-b]pyridines and Bis(indolyl)methanes

Hojat Veisi,[a,]* Pourya Mohammadi,[a,]* Turan Ozturk[b,c]

[a]*Department of Chemistry, Payame Noor University, Tehran, Iran.*
[b]*Department of Chemistry, Istanbul Technical University, Maslak, Istanbul 34469, Turkey*
[c]*TUBITAK-UME, Chemistry Group Laboratories, PO Box 54, 41471, Gebze, Kocaeli, Turkey*
Emails: hojatveisi@yahoo.com (H. Veisi); pourya.mohammadi93@yahoo.com (P. Mohammadi)

Abstract. A novel sulfonic-functionalized ionic liquid, C_3N_4 (C_3N_4-SO_3H (IL)), was prepared and its structure was characterized using FTIR, TEM, XRD, CHNS elemental analysis and FESEM-EDX mapping. Catalytic activity of the liquid was studied for the syntheses of pyrazolo[3,4-*b*]pyridine and bis(indolyl)methane derivatives under moderate conditions. The catalyst was demonstrated to be reused at least 5 runs without considerable decrease in its activity. Some of the important advantages of the methodology were proved to be good yields, easy work-up, short reaction time and broad scope of substrates.

Key words: g-C_3N_4, acidic ionic liquid, pyrazolo[3,4-b]pyridine, bis(indolyl)methane

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Introduction

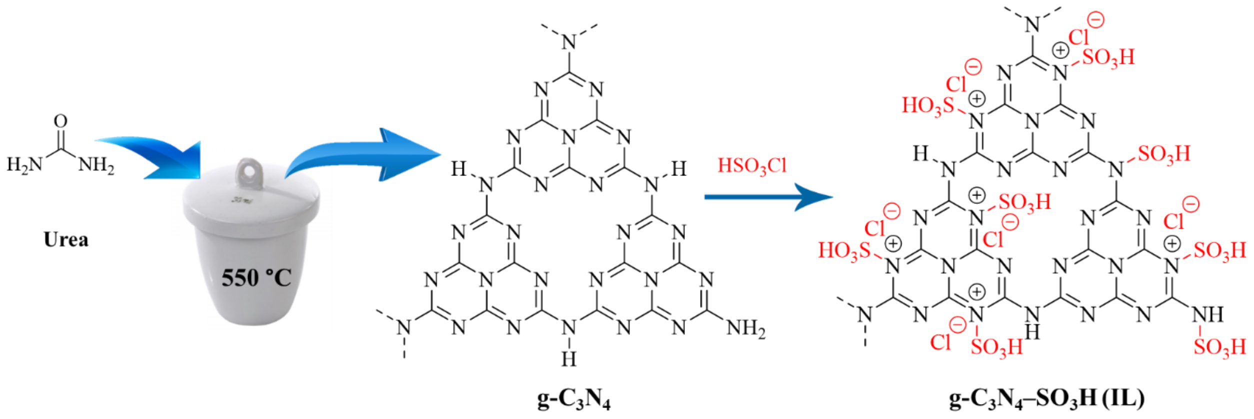
Utilization of ionic liquids (ILs) as efficient catalysts has been one of the most important development in the field of green chemistry. In spite of their goodness advantages, they could not find enough attention, mainly due to some disadvantages, such as hard to separate from the reaction mixture, high viscosity, high cost and uneconomic reuse procedures [1,2]. In order to overcome these problems, the supported ionic liquid catalyzres (SILC) with their high catalytic activity, were introduced as heterogeneous ionic liquids. So far, various methods have appeared in the literature on design and synthesis of efficient SILCs, such as mesoporous silicas [3-5], silica gels [6-8], polymers [9-11] and magnetic nanoparticles [12-14].

Recently, use of carbon nanostructures has attracted enormous attention as one of the most promising candidates as the catalytic substrate due to their unique properties such as high conductivity, high mechanical strength, high surface-to-volume ratio, and good physicochemical properties [15,16]. As a carbon nanomaterial, graphitic carbon nitride (g-C_3N_4) is one of the non-metal substrates, being nontoxic with high chemical and thermal stability, resistant to acidic and basic conditions and various solvents. These unique properties are due to the presence of nitrogen atoms in the carbon architecture of graphitic carbon nitride g-C_3N_4, which can be prepared easily from cheap nitrogen-rich precursors such as thiourea, urea, cyanimide and melamine through pyrolysis [17,18]. Because of these great features, nowadays, g-C_3N_4 is widely applied in different studies such as degradation of pollutants [19-22], water splitting [23,24] and oxidation [25,26] and reduction reactions. However, so far, g-C_3N_4 has not been widely applied as a catalyst support or catalyst in organic syntheses [27-29] Therefore, its use as a catalyst in organic synthesis could be beneficial as the development of new methods for the synthesis of heterocyclic compounds plays a significant role in organic syntheses.

Pyrazolo[3,4-b]pyridines are among the important heterocyclic compounds in organic and medicinal chemistry. They show a wide spectrum of biological and pharmacological activities, such as antiviral [30] and antibacterial [31] activities, and xanthine oxidase and oncogenic Ras inhibitions [32]. On the other hand, some highlighted procedures for the preparation of pyrazolopyridones have disadvantages such as low yields, long reaction times, harsh reaction conditions and use of expensive catalysts and reactants [33]. Thus, more effective and novel methods are desired for the preparation the heterocycles.

Another important heterocyclic compounds are bis(indolyl)methanes and their derivatives. They are significant intermediates in R&D, particularly, in pharmaceutical industry [34,35].

In continuation to our endeavor in the sustainable development using nanocatalysis [36], in this work, preparation and applications of g-C_3N_4-SO_3H (IL) in the syntheses of the above mentioned heterocycles, selected considering their importance in organic and medicinal chemistry, are presented. A cheap raw material, urea, was used for the preparation of IL. Thermal treatment of urea produced g-C_3N_4 in bulk, which was followed by addition of chlorosulfonic acid to obtain the catalyst IL (Scheme 1). Its composition and morphology were analyzed in detail, and then it was applied as an ionic liquid acidic catalyst for one-pot synthesis of pyrazolo[3,4-b]pyridines and bis(indolyl)methanes. The catalyst was proved to be reused at least 5 runs without considerable decrease in its catalytic activity.



Scheme 1. The preparation method of ionic liquid g-C_3N_4-SO_3H (IL)

Experimental

Synthesis of g-C_3N_4/SO_3H

Initially, the graphitic carbon nitride (g-C_3N_4) was prepared by thermal treatment of urea, for which urea powder (10 g) in a Muffle was heated at 550 ºC for 3 h to obtain the crude product. Carbon nitride (0.5 g), without further purification, was dispersed by sonication in dry CH_2Cl_2 (30 mL), after which, applying Zolfigol's method [37], the suspension was placed in an ice bath and $ClSO_3H$ (1 mL) was added dropwise under vigorous stirring at 0-5 ^oC. After that, the reaction mixture was stirred for 12 h at room temperature, and, finally, the product (g-C_3N_4-SO_3H, IL) was collected by filtration, which was washed with ethanol/water (1/1) mixture for several times and dried in an oven at 50 °C for 12 h (0.52 g).

Typical experimental procedure

a) Synthesis of pyrazolo[3,4-b]pyridine derivatives:

To a vigorously stirred mixture of Meldrum's acid (1 mmol), 5-methylpyrazol-3-amine (1 mmol), aldehyde (1 mmol) and g-C_3N_4-SO_3H (10 mg) in ethanol/water (5 mL, 4/1 ratio) at 70 ^oC. The progress of the reaction was checked by thin-layer chromatography (TLC, n-hexane/ethyl acetate, 5:1). After the complete of the reaction, the catalyst was collected by filtration and washed several times with acetone and dried in an oven at 50 °C for 12 h to be used for the next run. The solvent of the filtrate was evaporated under reduced pressure, and the crude product was crystallized from ethanol and dried in a vacuum oven to obtain the title compound. All the products are known compounds in the literature [33].

b) Synthesis of bis(indolyl)methane derivatives:

A mixture of indole (2 mmol), aldehyde (1 mmol) and g-C_3N_4-SO_3H (10 mg) in a mixture of ethanol/water (4/1) was stirred at 70 ^oC until the complete of the reaction (monitored by TLC, n-hexane/ethyl acetate, 5:1). The catalyst was then separated from the reaction mixture by filtration, which was washed several times with acetone and dried in an oven at 50 °C for 12 h to be used for the next run. The solvent of the filtrate was evaporated under reduced pressure, and the crude product was crystallized from ethanol and dried in a vacuum oven to obtain the title compound.

Results and discussion

Characteristics of the g-C_3N_4-SO_3H (IL)

FT-IR

The functionalization of g-C_3N_4 by -SO_3H was explained using FT-IR analyses (Fig. 1). The spectra of g-C_3N_4-SO_3H revealed that, as expected, the original C-N network of g-C_3N_4 remained almost unchanged after the functionalization. The broad peaks between 3000-3500 cm^{-1} were attributed to -NH_2 and N-H stretching vibrations of the both compounds, and the hydrogen bonding interactions of g-C_3N_4. The absorption peaks, observed at 1305 cm^{-1} and 1604 cm^{-1}, are due to the C-N and C=N stretching vibration, respectively, and the peak at 807 cm^{-1} belongs to tri-s-triazine units. After functionalization of g-C_3N_4 with SO_3H, some new peaks appeared, such as the peaks at 1051 cm^{-1} and 1152 cm^{-1} from S=O symmetric and asymmetric stretchings, respectively. The broad peaks at 3000-3500cm^{-1} were attributed to O-H stretching vibration~~,~~ and hydrogen bonding interactions of g-C_3N_4. Overlap of the asymmetric SO_2 and S=O stretching bands with g-C_3N_4 bands makes the peaks not observable, which, as expected, may lead to the conclusion that the functionalization of g-C_3N_4 did not change its C-N network.

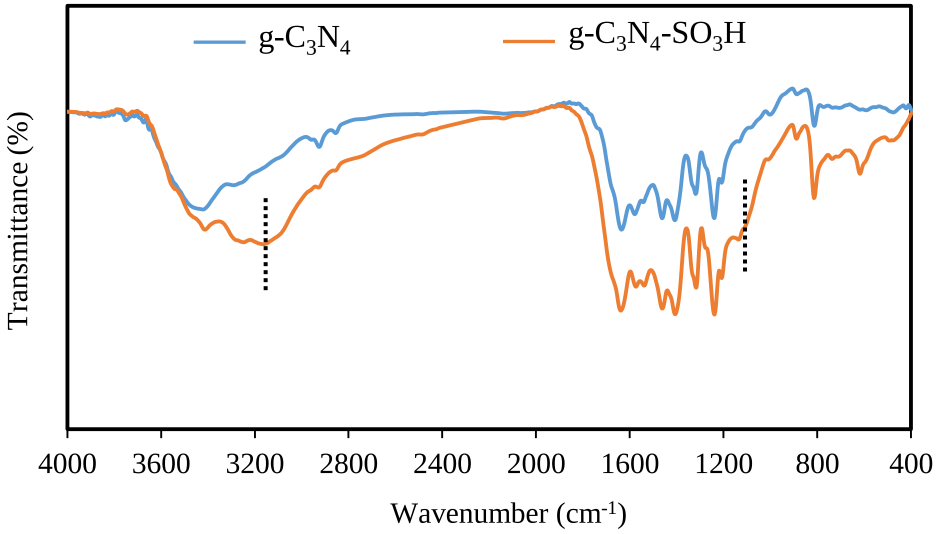


Figure 1. The FTIR of g-C_3N_4 and g-C_3N_4-SO_3H

XRD

In order to investigate the crystalline property of g-C_3N_4-SO_3H, an XRD analysis was conducted (Fig. 2.). A peak with a high intensity at $2\theta = 27.2°$, related to the (002) plane of g-C_3N_4, was attributed to interlayers of g-C_3N_4. Moreover, the peak at $2\theta = 13.1°$ was interpreted to be due to the (100) plane of g-C_3N_4, possessing in-plane structure packing motif of tri-s-triazine units. Thus, the XRD pattern of g -C_3N_4-SO_3H demonstrated that the peak positions of g-C_3N_4 did not change during the functionalization. Therefore, observing the peaks in their positions led to the conclusion that functionalization of g-C_3N_4 did not destruct the C-N crystalline structures.

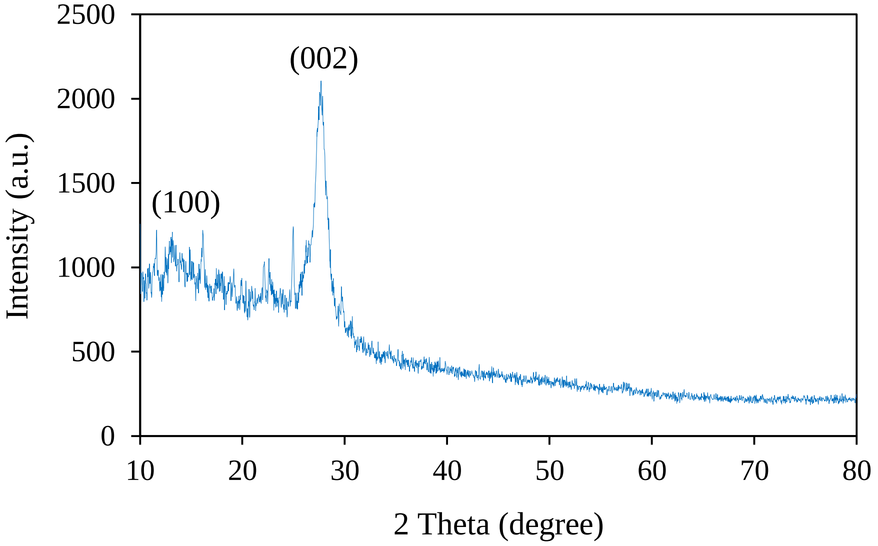


Figure 2. The XRD of g-C_3N_4-SO_3H

FESEM-EDX mapping

The morphology and elemental analysis of g-C_3N_4-SO_3H were performed applying FESEM-EDX mapping, which demonstrated a porous structure with g-C_3N_4-SO_3H. As the structure of g-C_3N_4-SO_3H was agglomerated, its sheets were not observed clearly. This might be due to the electrostatic interactions of g-C_3N_4-SO_3H layers (Fig. 3a). While the EDX analysis of g-C_3N_4-SO_3H confirmed the presence of C, N, S and O atoms (Fig. 3b), its elemental mapping analysis showed the presence of these elements. Moreover, in order to further confirm the presence of the SO_3H groups, CHNS elemental analysis was performed, which indicated the presence of sulfur atom (S= 10.78 %) in good match with EDX analysis. The homogeneity of S, O elements in the mapping was concluded that the functionalization of g-C_3N_4 is successful (Fig. 4).

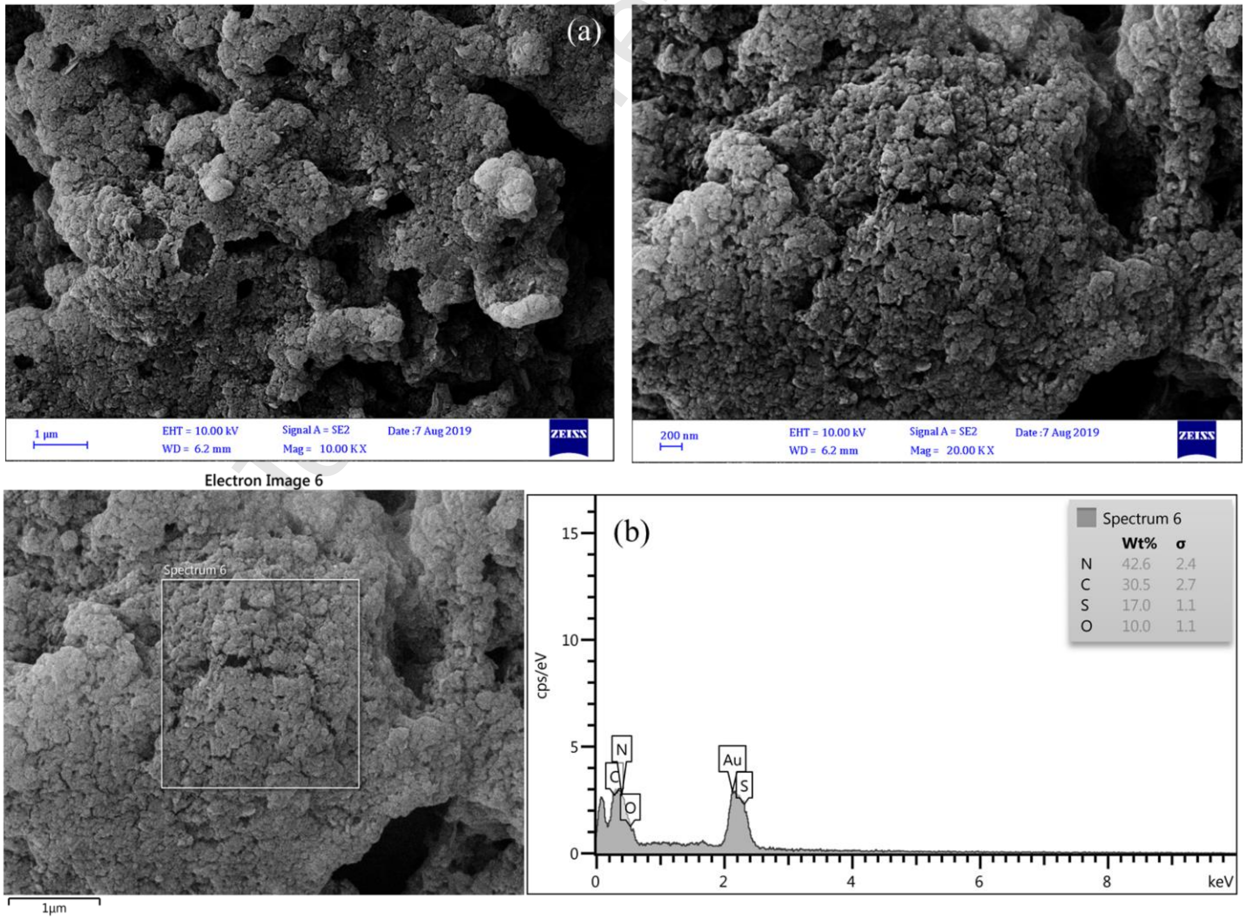


Figure 3. The FESEM-EDX of g-C_3N_4-SO_3H

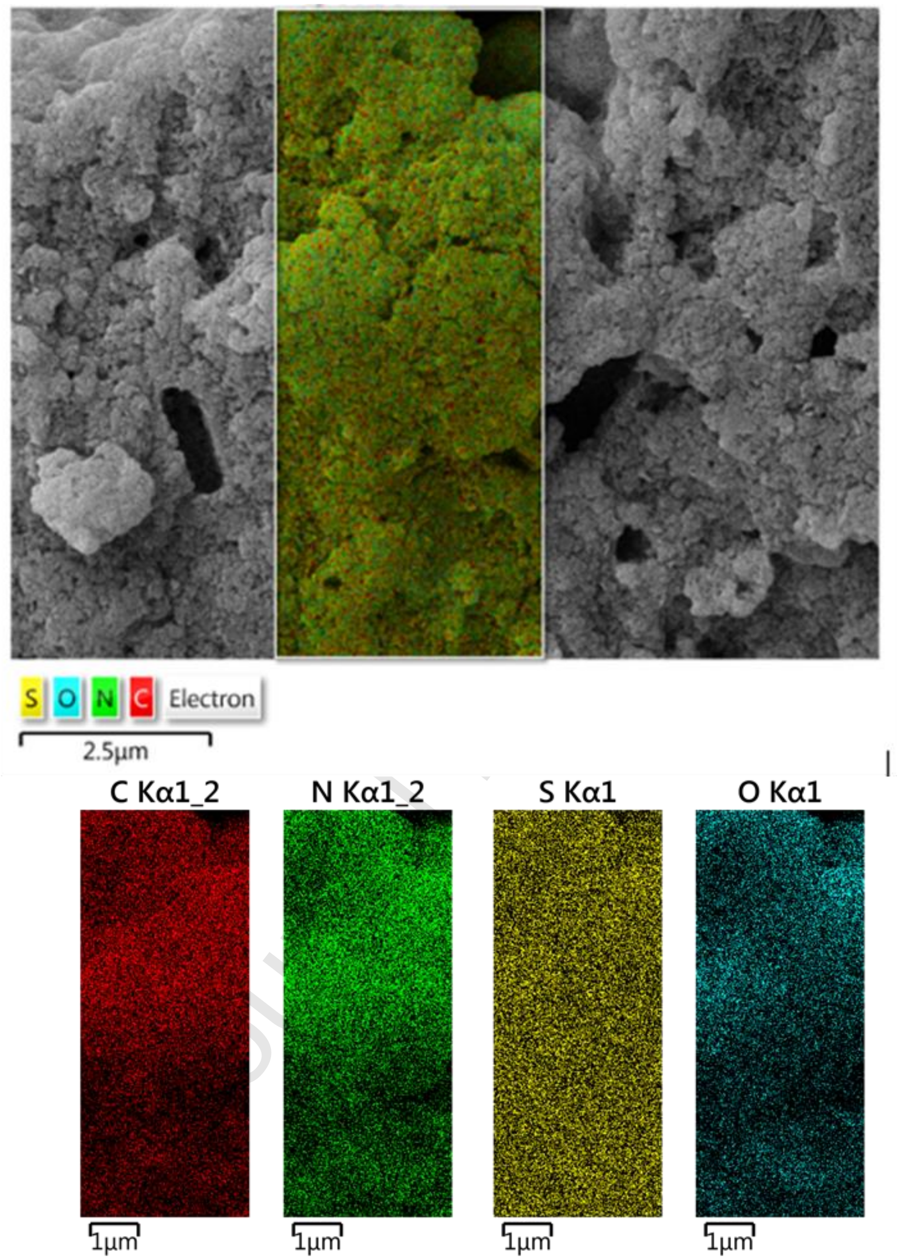


Figure 4. The image mapping of g-C_3N_4-SO_3H

TEM

A TEM image of g-C_3N_4-SO_3H is depicted in Fig. 5. A sheet-like structure with wrinkles was observed with g-C_3N_4-SO_3H. This might be due to the electrostatic interactions between of g-C_3N_4-SO_3H layers.

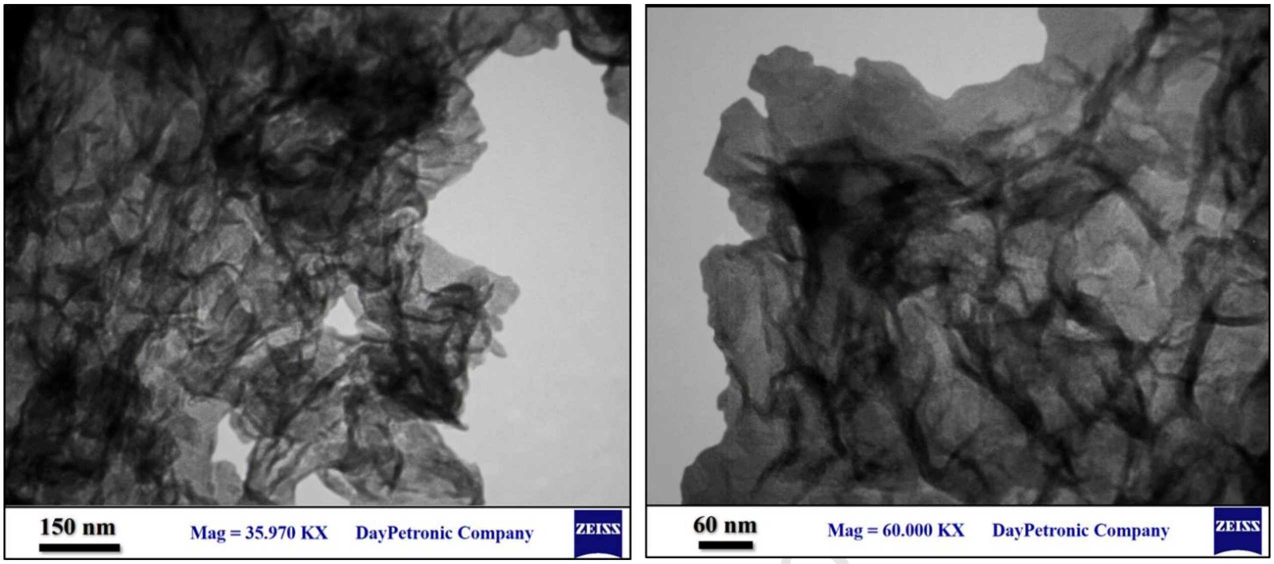


Figure 5. The TEM image of g-C_3N_4-SO_3H

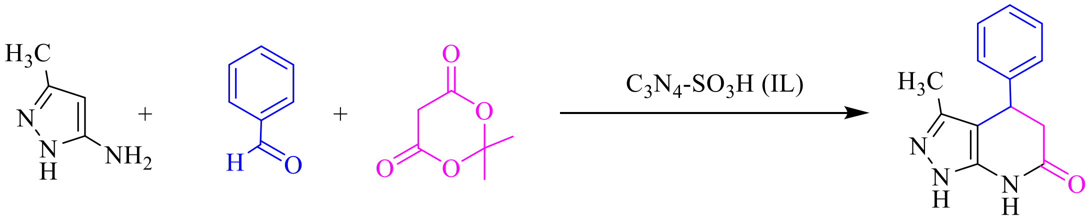
Measurement of the acidic active cites (-SO_3H)

In order to determine the amount of SO_3H groups of g-C_3N_4-SO_3H (IL), a standard acid-base back titration method was applied. The catalyst (0.30 g) was added into NaOH solution (0.01 mol/L, 50 mL) and stirred at room temperature for 1h. Then, it was back titrated with HCl (0.01 mol/L). The total acidity (-SO_3H) of g-C_3N_4-SO_3H (IL) catalyst was obtained to be 3.1 mmol/g. Density of the –SO_3H groups, determined through the back titration method, was found to be in good match with the percentage of S (10.78%), obtained from elemental analysis.

Catalytic activity on the heterogeneous g-C_3N_4-SO_3H

In order to determine the catalytic activity of the catalyst, syntheses of pyrazolo[3,4-b] pyridines and bis(indolyl) methanes as model compounds were performed. Initially, the synthesis of pyrazolo[3,4-b]pyridines was attempted as a model reaction using 5-methylpyrazol-3-amine, Meldrum's acid and benzaldehyde as reactants in the presence of g-C_3N_4-SO_3H to obtain the best reaction conditions. Impacts of different parameters such as temperature, solvent and amount of the catalyst were examined (Table 1). The results indicated that the condition having 15 mg of catalyst, a solvent mixture of EtOH/H_2O (3/1) and 70 ^oC of the reaction temperature is the best to obtain the highest yield (98%) (Table 1, entry 12). The increase of the amount of the catalyst to 20 mg did not change the yield significantly (96%, entry 7). The reaction was also conducted in the absence of the catalyst, which resulted in a very low yield of 12% (entry 10).

Table 1. Optimization of reaction conditions of 3-methyl-4-phenyl-2,4,5,7-tetrahydropyrazolo[3,4-b]pyridine-6-one in the presence of g-C_3N_4-SO_3H .[a]



Entry	Solvent	Catalyst (mg)	Temperature (ºC)	Time (min)	Yield (%)
1	EtOH	15	25	120	79
2	H_2O	15	25	240	42
3	CH_2Cl_2	15	25	120	55
4	Toluene	15	25	120	64
5	CH_3CN	15	25	120	75
6	EtOH/H_2O	15	25	90	95
7	EtOH/H_2O	20	25	90	96
8	EtOH/H_2O	10	25	90	82
9	EtOH/H_2O	5	25	90	62
10	EtOH/H_2O	0	25	180	12
11	EtOH/H_2O	15	50	60	98
12	**EtOH/H_2O**	**15**	**70**	**45**	**98**

[a] Reaction conditions: 5-methylpyrazol-3-amine (1 mmol), aldehyde (1 mmol), Meldrum's acid (1 mmol), and solvent (3 mL).

Applying the determined optimal conditions, various aldehyde derivatives, possessing electron-withdrawing and electron-donating groups, were subjected to the synthesis of a wide range of pyrazolo[3,4-b]pyridines in excellent yields (Table 2). Unusual electronic effect of any substituent was not observed.

Table 2. Synthesis of pyrazolo[3,4-b]pyridines in the presence of g-C_3N_4-SO_3H.[a]

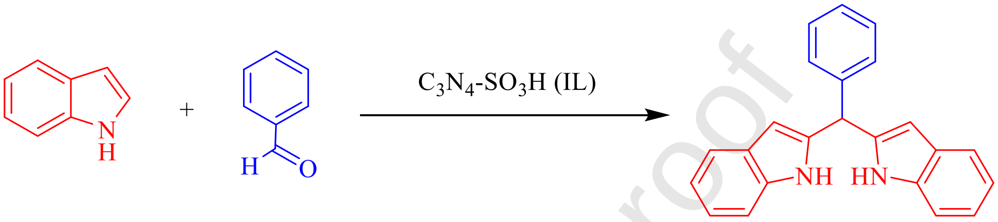
Entry	Aldehyde	Yield (%)[b]	Mp (°C)	Mp (ºC)[ref]
1	C_6H_5CHO	98	303-305	304–306[33]
2	4-Me-C_6H_4CHO	98	>300	>300[33]
3	4-MeO-C_6H_4CHO	96	>300	308–310[33]
4	3-NO_2-C_6H_4CHO	92	266-268	264-266[33]
5	4-Cl-C_6H_4CHO	96	>300	>300[33]
6	3,4,5-$(MeO)_3$-C_6H_2CHO	96	>300	>300[33]
7	2-thienylaldehyde	96	300–302	303–305[33]
8	Butanal	82	258–260	259–260[33]

[a] General procedure: 5-methylpyrazol-3-amine (1 mmol), aldehydes (1 mmol), Meldrum's acid (1 mmol), Fe_3O_4/PEG-SO_3H (10 mg), EtOH (3 mL), 60 minutes at 70 ºC.

[b] Yield based on ^1H NMR data.

After obtaining successful yields with the synthesis of pyrazolo[3,4-b]pyridines, synthesis of bis(indolyl)methanes was attempted. Similarly, optimum reaction conditions were initially determined, which indicated the same reaction conditions of the previous reactions, i.e. 15 mg of catalyst, EtOH/H_2O (4/1) solvent mixture and 70 °C reaction temperature (Table 3).

Table 3. Optimization of reaction conditions of bis(indolyl)methanes in the presence of g-C_3N_4-SO_3H.[a]



Entry	Solvent	Catalyst (mg)	Temperature (°C)	Time (min)	Yield (%)
1	EtOH	15	25	90	81
2	H_2O	15	25	90	47
3	CH_2Cl_2	15	25	90	61
4	Toluene	15	25	90	69
5	CH_3CN	15	25	90	78
6	EtOH/H_2O	15	25	90	94
7	EtOH/H_2O	20	25	80	96
8	EtOH/H_2O	10	25	90	85
9	EtOH/H_2O	5	25	90	68
10	EtOH/H_2O	0	25	120	19
11	EtOH/H_2O	15	50	75	98
12	**EtOH/H_2O**	**15**	**70**	**60**	**98**

[a]Reaction conditions: benzaldehyde (1 mmol), indol (2 mmol), and solvent (3 mL).

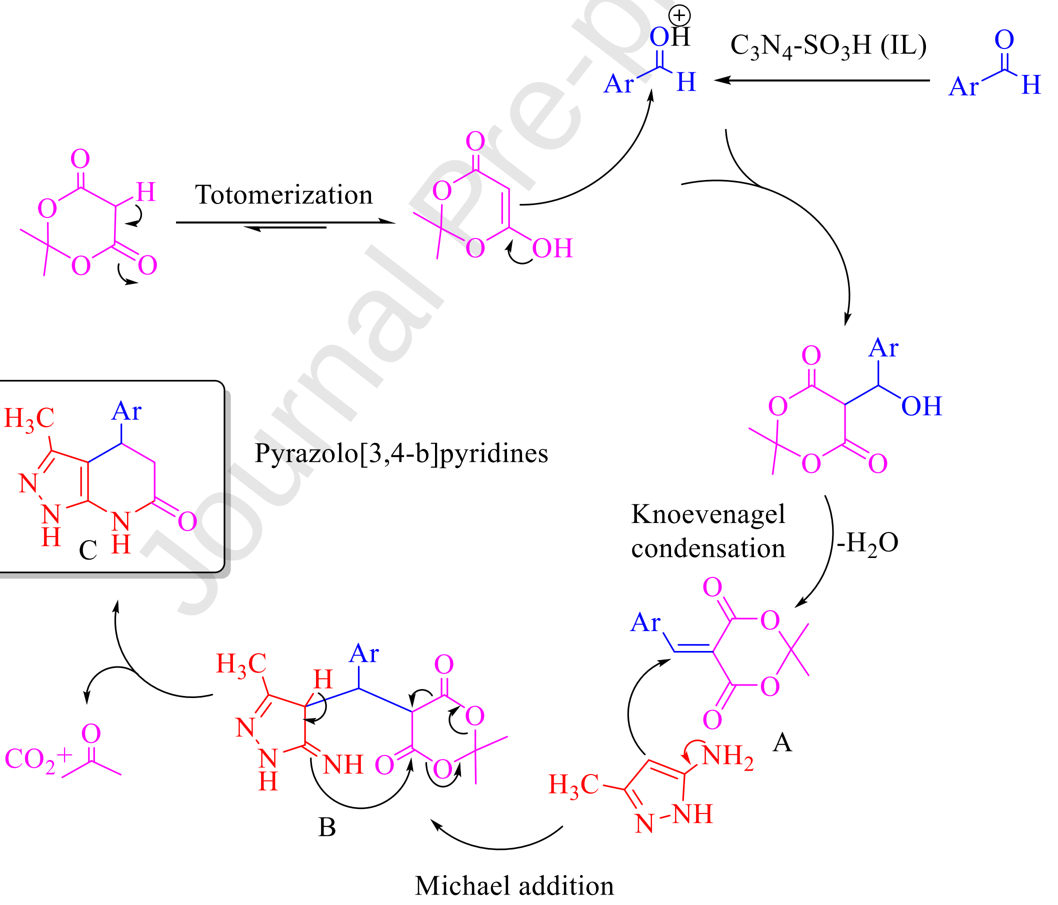
A wide range of bis(indolyl)methane derivatives was then synthesized applying the best reaction conditions to various aldehyde derivatives (Table 4). Contrary to the previous results, better yields were obtained with the aldehydes having electron-withdrawing and electron-donating substituents.

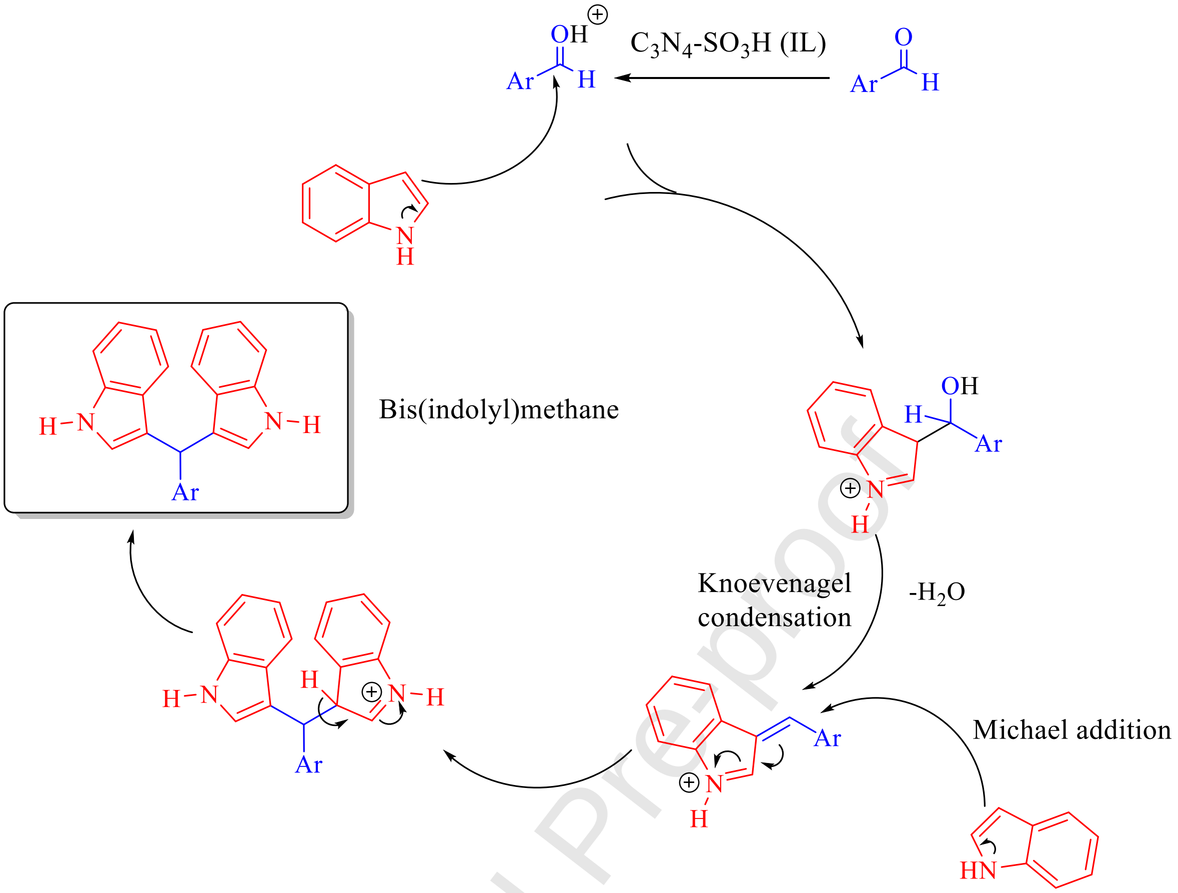
After obtaining successful results with the syntheses of pyrazolo[3,4-b]pyridines and bis(indolyl)methanes in the presence of g-C_3N_4-SO_3H, a possible reaction mechanism was suggested (Scheme 2).

Table 4. Synthesis of bis(indolyl)methane derivatives in the presence of g-C_3N_4-SO_3H.[a]

Entry	Aldehyde	Yield (%)[b]	Mp (°C)	Mp (°C)[ref]
1	C_6H_5CHO	98	123-124	124–125[34]
2	4-Me-C_6H_4CHO	98	92-93	93-94[34]
3	4-MeO-C_6H_4CHO	97	190-192	192–193[34]
4	3-NO_2-C_6H_4CHO	94	266-268	264-266[34]
5	4-Cl-C_6H_4CHO	97	86-88	87-89[34]
6	3,4,5-$(MeO)_3$-C_6H_2CHO	97	225-227	226-227[34]
7	2-thienylaldehyde	96	151–153	152-153[34]
8	Butanal	59	Oil	-

[a] General procedure: aldehydes (1 mmol), indol (2 mmol), g-C_3N_4-SO_3H (15 mg), EtOH (3 mL), 60 minutes at 70 °C.





Scheme 2. The suggested mechanism for synthesis of pyrazolo[3,4-b]pyridines and bis(indolyl)methane by g-C_3N_4-SO_3H were presented

One of the important parameters of the stability of a catalyst is its reusability. Thus, the reusability of the catalyst g-C_3N_4-SO_3H was tested in the presence of 5-methylpyrazol-3-amine, Meldrum's acid and benzaldehyde applying the above optimized reaction conditions (Fig. 6). After the reaction was complete, the catalyst was simply filtered, washed with acetone and dried at 50 ^{o}C. It was then reused for the next reaction. Reusability test was also performed for the synthesis of bis(indolyl)methane in the same optimized reaction conditions. The catalyst was determined to be used at least five times without any considerable decrease in its activity, which was further confirmed by TEM and elemental analyses (Fig. 7). The elemental analyses showed the presence of “S” in 10.24%, which is comparable with the analysis of the original catalyst, i.e. 10.78%. Moreover, TEM image demonstrated the presence of sheet structure of the catalyst without any noticeable change compare with the original one.

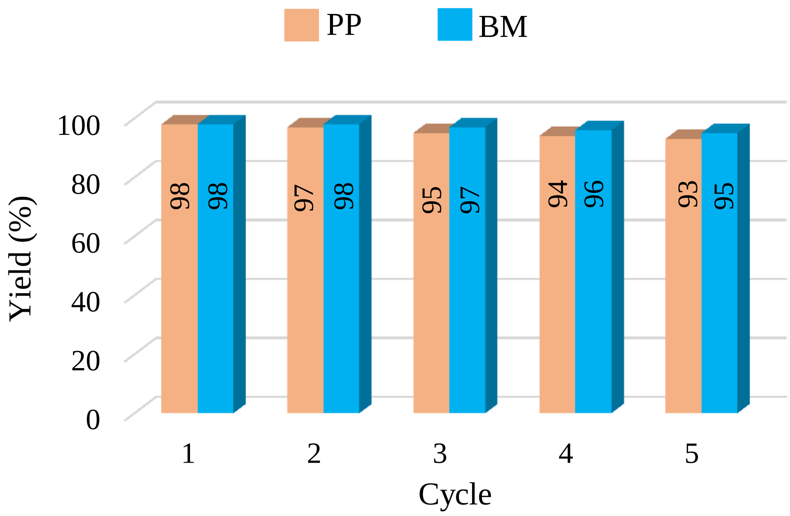


Figure 6. The recyclability of catalyst for synthesis of pyrazolo[3,4-b]pyridines (PP) and bis(indolyl)methanes (BM).

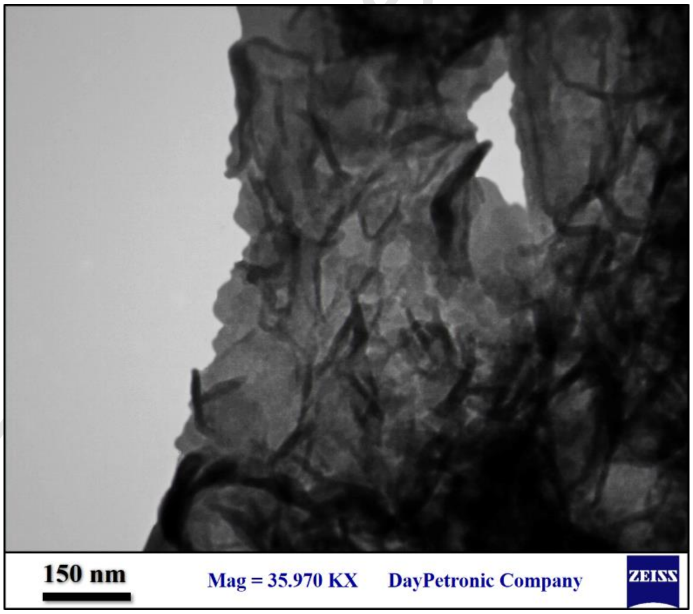


Figure 7. The TEM image of g-C_3N_4-SO_3H after 5 runs.

Conclusions

We have presented the preparation of a recoverable porous ionic liquid catalyst, g-C_3N_4-SO_3H, and its application for the synthesis of a range of pyrazolo[3,4-b] pyridine and bis(indolyl)methane derivatives through a highly effective and environmentally friendly one-pot methodology. The catalyst was proved to be used at least five times without a considerable loss in its activity. Its one-pot reaction resulted in the preparation of the heterocycles in high yields. Therefore, the catalyst demonstrated to produce good to excellent yields, have simple work-up, and could be used many times.

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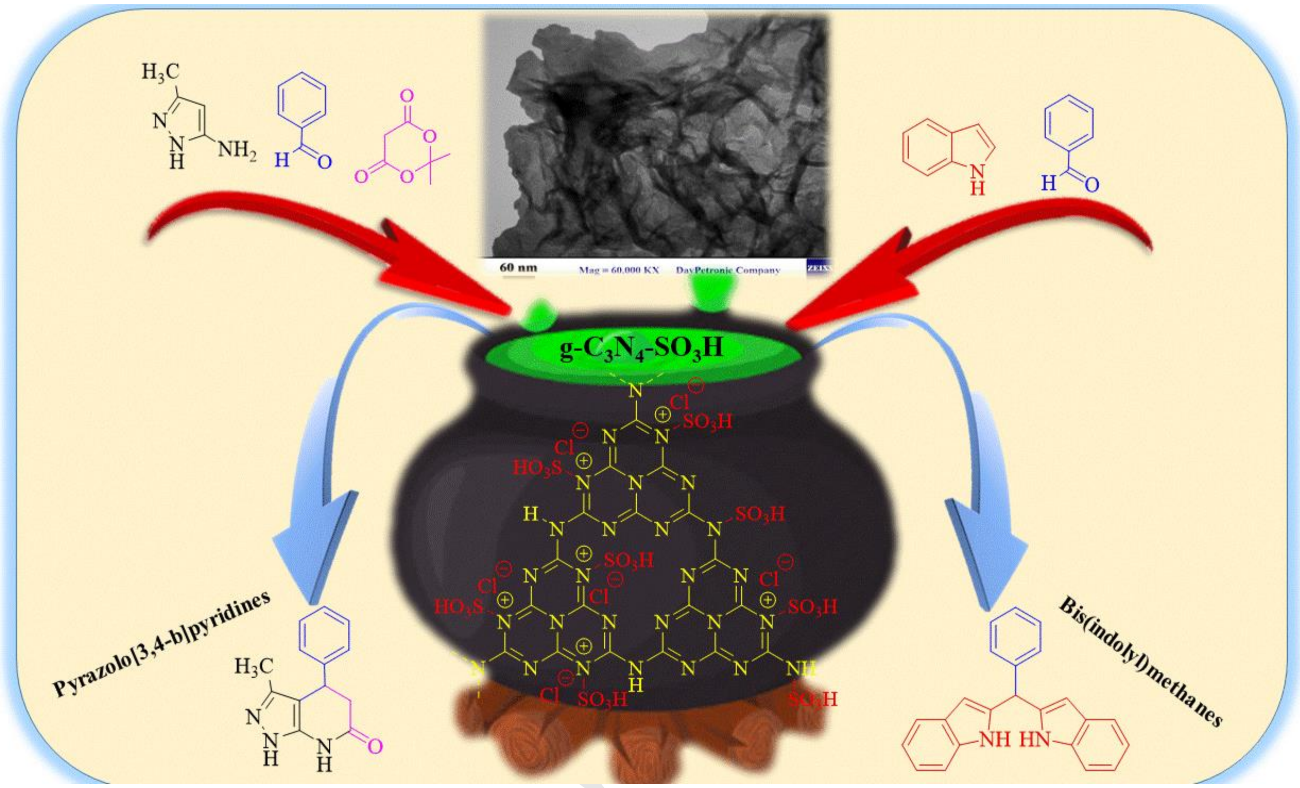
60 nm
Mag = 60.000 KX
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g-C_3N_4-SO_3H
Pyrazolo[3,4-b]pyridines
Bis(indolyl)methanes

Conflict of Interest

The authors report no conflicts of interest in this work.

Highlights

- A novel sulfonic-functionalized ionic liquid of C_3N_4 (C_3N_4-SO_3H (IL)) was prepared.
- The products were produced in excellent yields under mild conditions.
- Low metal loading was used in the reaction.
- The catalyst can be reused several consecutive cycles.