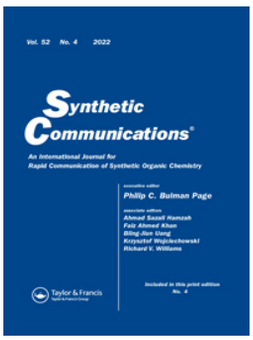

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A facile synthesis of quinoxalines by using SO_4^{2-}/ZrO_2-TiO_2 as an efficient and recyclable heterogeneous catalyst

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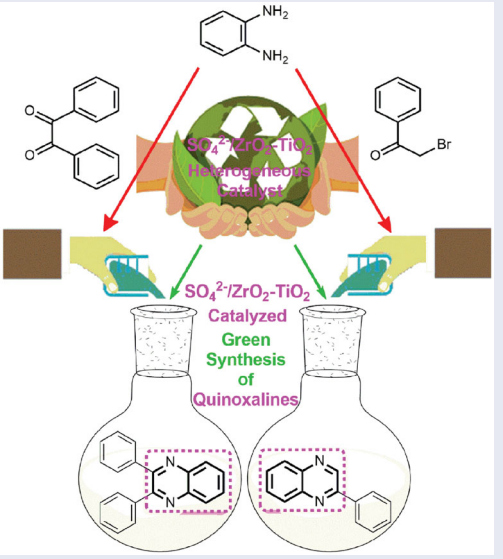
ABSTRACT

Quinoxaline derivatives have been synthesized in good to excellent yields by the cyclocondensation reaction of *o*-pheneylenediamine with substituted phenacyl bromides/benzil in the presence of SO_4^{2-}/ZrO_2-TiO_2 as an efficient and heterogeneous catalyst. The catalyst can be recovered up to five catalytic cycles without significant loss in catalytic activity. The reported SO_4^{2-}/ZrO_2-TiO_2 catalyst has been thoroughly characterized by using infrared spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and powder X-ray diffraction (XRD). Here, we have used ethanol as a green solvent in this cyclocondensation. This new method has several advantages, such as excellent yields, short reaction time, non-toxic, and easily recoverable catalyst.

GRAPHICAL ABSTRACT



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KEYWORDS
SO_4^{2-}/ZrO_2-TiO_2; quinoxalines; recyclable; heterogeneous catalyst; cyclocondensation

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Introduction

Quinoxalines are one of the important classes of nitrogen-containing heterocycles.[1] They are rarely occurred in nature and mostly synthesized by using various synthetic approaches.[2] In a quest to develop sustainable and greener synthetic strategies for quinoxalines, most of the researchers have been developing different greener synthetic approaches that involve recyclable catalysts, mild reactants, and reaction conditions.[3] Over the last few years, quinoxalines have grabbed more attention by researchers as they display a broad range of pharmaceutical as well as biological applications.[4] Various derivatives of quinoxalines have revealed a wide variety of bioactivities, such as antitubercular,[5] anti-inflammatory, antioxidant,[6] antifungal, anticancer, anti-HIV,[7] and antiprotozoan,[8] etc. Most of the clinically used drugs also possess quinoxalinyl moiety in their structural scaffold as an active pharmacophoric unit. Some of them are summarized in Figure 1.

In recent years, focusing on several environmental issues and considering the pharmacological importance of quinoxaline scaffolds there are numerous synthetic methods have been reported. Some of them are the condensation of *o*-phenylenediamine with 1,2-dicarbonyl compounds,[9] oxidation trapping of α-hydroxy ketones,[10] and 1,2-diazenylbutens.[11] Following are the various synthetic protocols involved for the synthesis of quinoxalines, such as heteropoly acid,[12] cellulose sulfuric acid,[13] hypervalent iodine (III) in PEG-400,[14] polyaniline-sulfate salt,[15] $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$,[16] PVPPOTf,[17] and $Ga(ClO_4)_3$.[18]

Among the aforementioned protocols, condensation of *o*-phenylenediamine with phenacyl bromides in the solid phase is highly preferred. This method has involved the use of a catalyst-free approach[19] as well as by using transition metal catalysts[20] and various heterogeneous catalysts like $HClO_4$-SiO_2,[21] silica-supported dodecatungstophosphoric acid,[1] TMSCl,[22] *β*-cyclodextrin,[23] silica-supported phosphomolybdic acid,[24] miceller SDS,[25] T3PDMSO or T3P,[26] *N*-Bromosuccinimide,[27] and ionic liquid.[28]

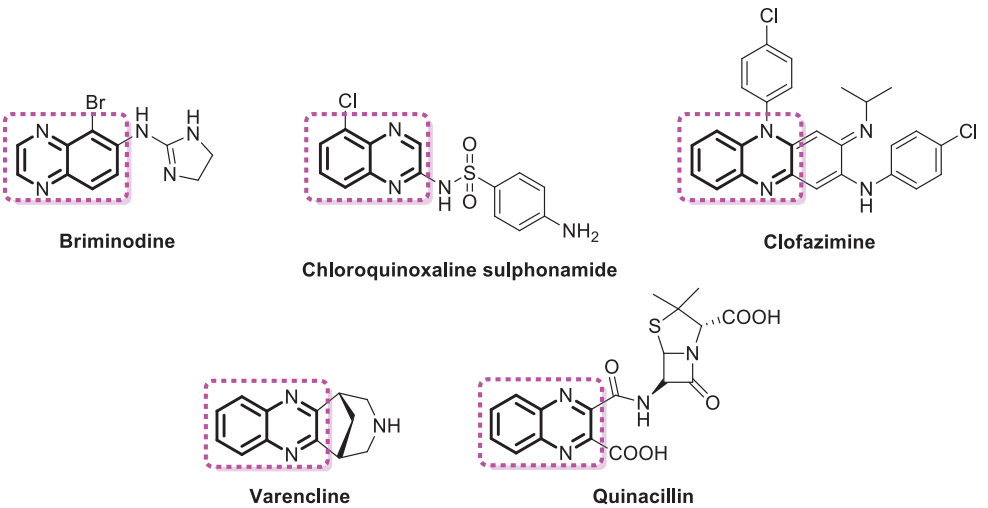


Figure 1. Some clinically used drugs bearing quinoxalinyl moiety.

Among the reported synthetic protocols, there are many synthetic approaches that having some limitations or lacunas, such as the use of $HClO_4$-SiO_2 catalyst is hazardous in nature than its potential application, the reaction catalyzed by TMSCl required higher temperature with low yield, the β-cyclodextrin, and miceller SDS catalyzed reactions were required longer time. Considering these lacunas/limitations with reported synthetic methods and used catalysts, still, there is a need for designing appropriate synthetic methods with the development of new catalysts having acidic strength and recyclability to be environmentally benign.

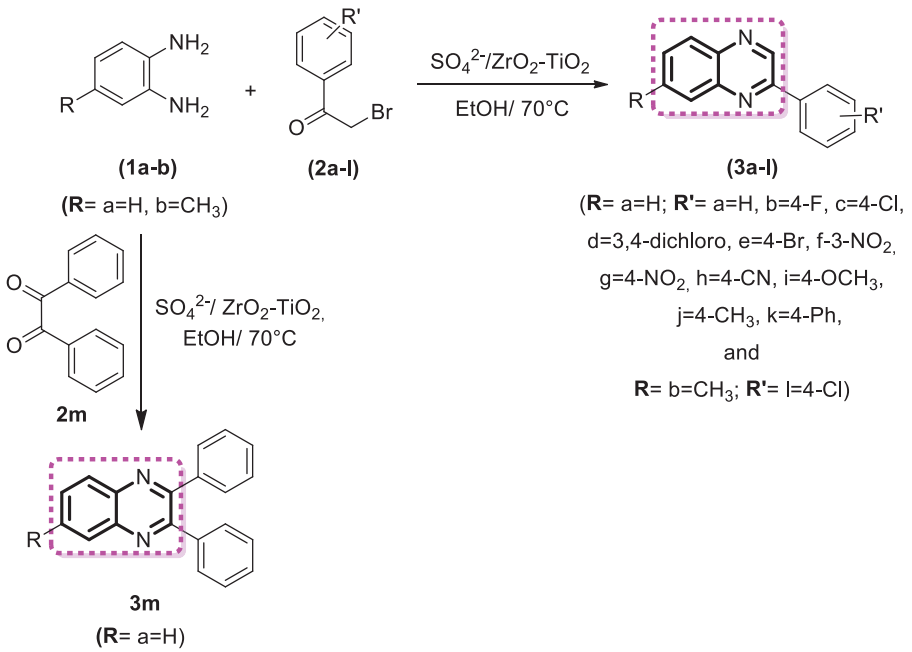
Results and discussion

The synthesis of quinoxalines was carried out by reacting substituted phenacyl bromides/benzil (**2a–m**) (0.001 mol) and *o*-pheneylenediamine (**1a–b**) (0.001 mol) in the presence of SO_4^{2-}/ZrO_2-TiO_2 as a catalyst. Further, the reaction mass was stirred at 70 °C for 50–80 min. afforded quinoxalines (**3a–m**) with excellent yields and high purity. This reaction is outlined in Scheme 1.

The structures of all the synthesized quinoxalines (**3a–m**) are shown in Figure 2.

The model reaction was carried out in presence of *o*-pheneylenediamine (**1a**) and phenacyl bromide (**2a**) as shown in Scheme 2.

The optimization of the reaction was performed by varying the reaction parameters, such as reaction time, solvent, and temperature. It was observed that the quinoxaline formation in ethanol solvent proceeds with an excellent yield at 70 °C for 50 min (Table 1, entry 3). Whereas, no reaction was observed in presence of water as a solvent (Table 1, entry 1).



Scheme 1. Synthesis of quinoxalines (**3a–m**) using SO_4^{2-}/ZrO_2-TiO_2 catalyst.

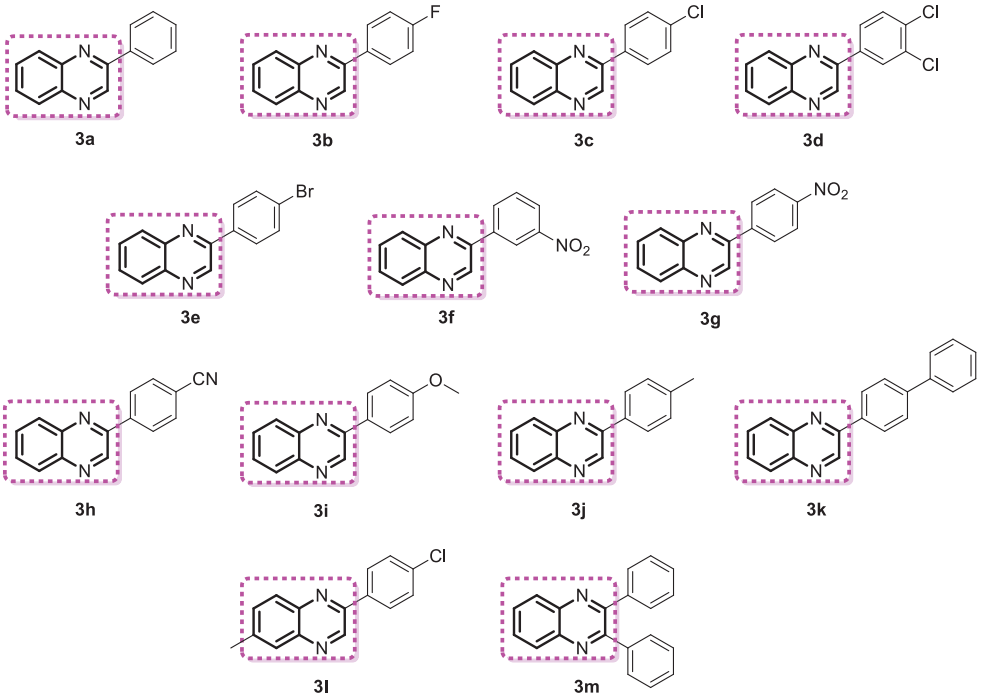
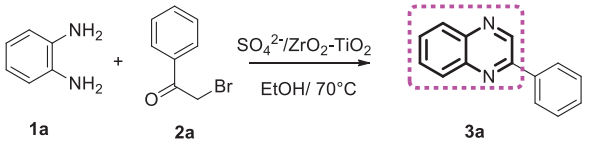


Figure 2. Structures of all the synthesized quinoxalines (**3a–m**).



Scheme 2. Model reaction for the optimization of solvent and catalyst.

Table 1. Screening of reaction condition with respect to solvent and catalyst loading **3a**.[a]

Sr. No.	Solvent	Catalyst	Yield[b] (%)
1	Water	SO_4^{2-}/ZrO_2-TiO_2	NR
2	Methanol	SO_4^{2-}/ZrO_2-TiO_2	82
3	Ethanol	SO_4^{2-}/ZrO_2-TiO_2	94
4	Dichloromethane	SO_4^{2-}/ZrO_2-TiO_2	65
5	Acetonitrile	SO_4^{2-}/ZrO_2-TiO_2	75
6	Dimethylformamide	SO_4^{2-}/ZrO_2-TiO_2	64
7	1,4-Dioxane	SO_4^{2-}/ZrO_2-TiO_2	58
8	Dimethylformamide	SO_4^{2-}/ZrO_2-TiO_2	65
9	EtOH	No catalyst	03

NR: no reaction.
[a]Reaction conditions: Phenacyl bromide (0.001 mol), *o*-phenylenediamine (0.001 mol), 20 SO_4^{2-}/ZrO_2-TiO_2 in 10 ml EtOH, at 70 °C for 50 min.
[b]Isolated yields.

Characterization of SO_4^{2-}/ZrO_2-TiO_2 catalyst

XRD pattern of sulfated TiO_2-ZrO_2 solid acid catalyst is shown in Figure 3. The diffraction pattern confirms the presence of the anatase phase of TiO_2 (JCPDS-211272), and the tetragonal and monoclinic structure of ZrO_2 (JCPDS-897710 and JCPDS-371484).

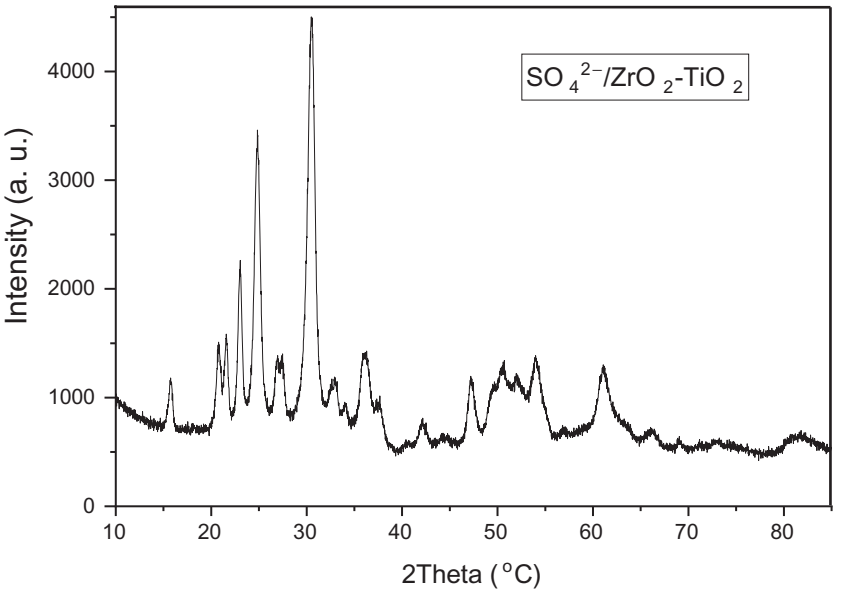


Figure 3. X-ray diffraction pattern of as prepared SO_4^{2-}/ZrO_2-TiO_2 catalyst.

In Figure 3, diffraction peaks are observed due to anatase TiO_2 at 24.83, 36.15, 37.67, 47.20, 53.98, 61.08, and 68.94°, which corresponds to the crystal planes (101), (103), (004), (200), (105), (204), and (116), respectively.[29] However, diffraction peaks are detected due to tetragonal ZrO_2 at the 27.47, 30.49, 32.91, 33.97, 50.57, 59.11, and 75.06° that corresponds to the reflections of crystal planes (−111), (101), (111), (110), (112), (211), and (220), respectively.[30,31]

Figure 4 shows the FT-IR spectra of sulfated TiO_2-ZrO_2 solid acid catalyst. The peaks at 1348, 1440 cm^{-1}, and in the region 1180–1050 cm^{-1}, can be attributed to the asymmetric and symmetric stretching frequency of the O = S = O and O–S–O groups.[32–34] The peaks at lower frequency in the range 500–1100 cm^{-1} are due to M–O stretching, which confirms the presence of metal oxides. Whereas, the peak observed at 1625 cm^{-1} was refers to the bending modes of the –OH groups of water molecules present in the sample.

Figure 5 shows the differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) of sulfated TiO_2-ZrO_2 uncalcinated sample. The TGA measurements agreed fairly well with those expected decompositions of uncalcinated sulfated metal oxide samples. The weight loss events below 600 °C were corresponds to the removal of adsorbed water and the dehydroxylation process. However, the major weight loss in the temperature range is about 600–800 °C, which refers to the decomposition of sulfate groups. Differential scanning calorimetry has shown the endothermic peaks that correspond to the removal of adsorbed water, dihydroxylation process, and decomposition of sulfate groups.

We have also investigated the recyclability of SO_4^{2-}/ZrO_2-TiO_2 catalyst for the model reaction of *o*-phenylenediamine (**1**) and phenacyl bromide (**2a**) in ethanol solvent at 70 °C for 50 min. and observed results were incorporated in Figure 6.

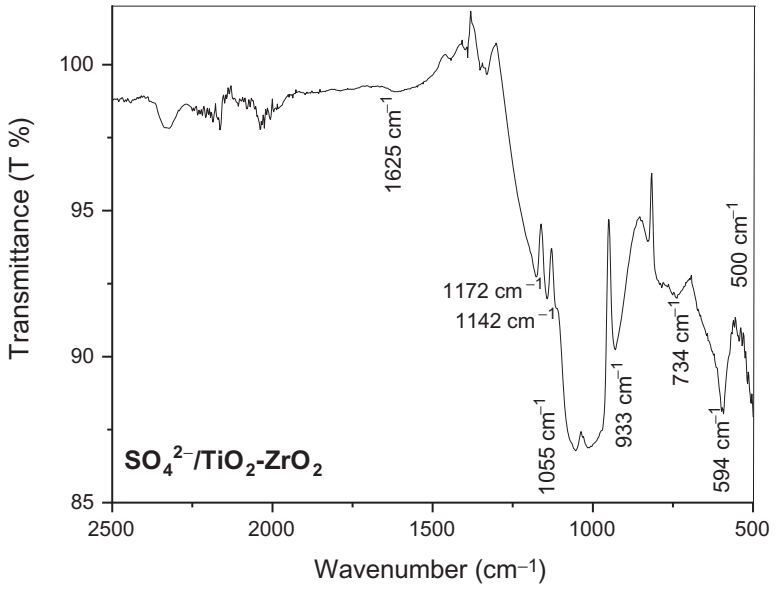


Figure 4. FT-IR spectra of as prepared SO_4^{2-}/TiO_2-ZrO_2 catalyst.

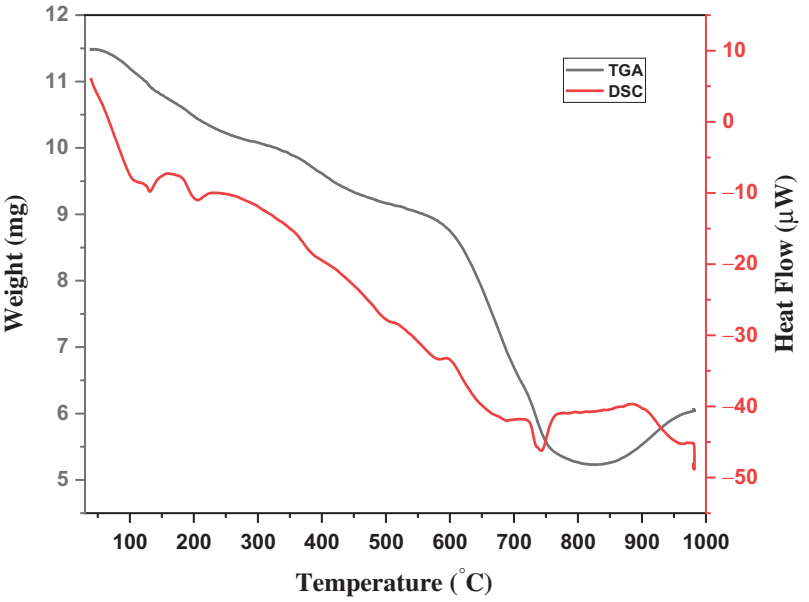


Figure 5. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) pattern of uncalcinated sulfated TiO_2-ZrO_2 sample.

The plausible mechanism for the quinaxolines synthesis was depicted in Scheme 3, which involves the protonation of the carbonyl group of phenacyl bromide over SO_4^{2-}/ZrO_2-TiO_2 catalyst (**A**). Later on, it reacts with *o*-pheneylenediamine that involves dehydration and dehalogenation simultaneously resulting in the formation of cyclic product **B**, which is readily oxidized in air to form desired product **C**.

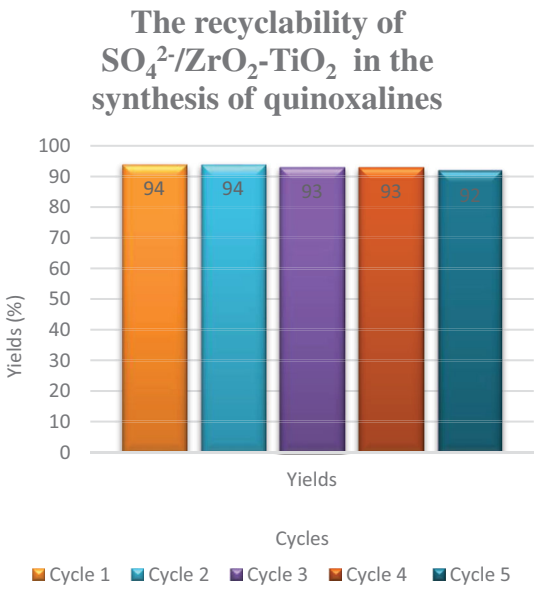


Figure 6. The recyclability of SO_4^{2-}/ZrO_2-TiO_2 catalyst for the synthesis of quinoxalines.

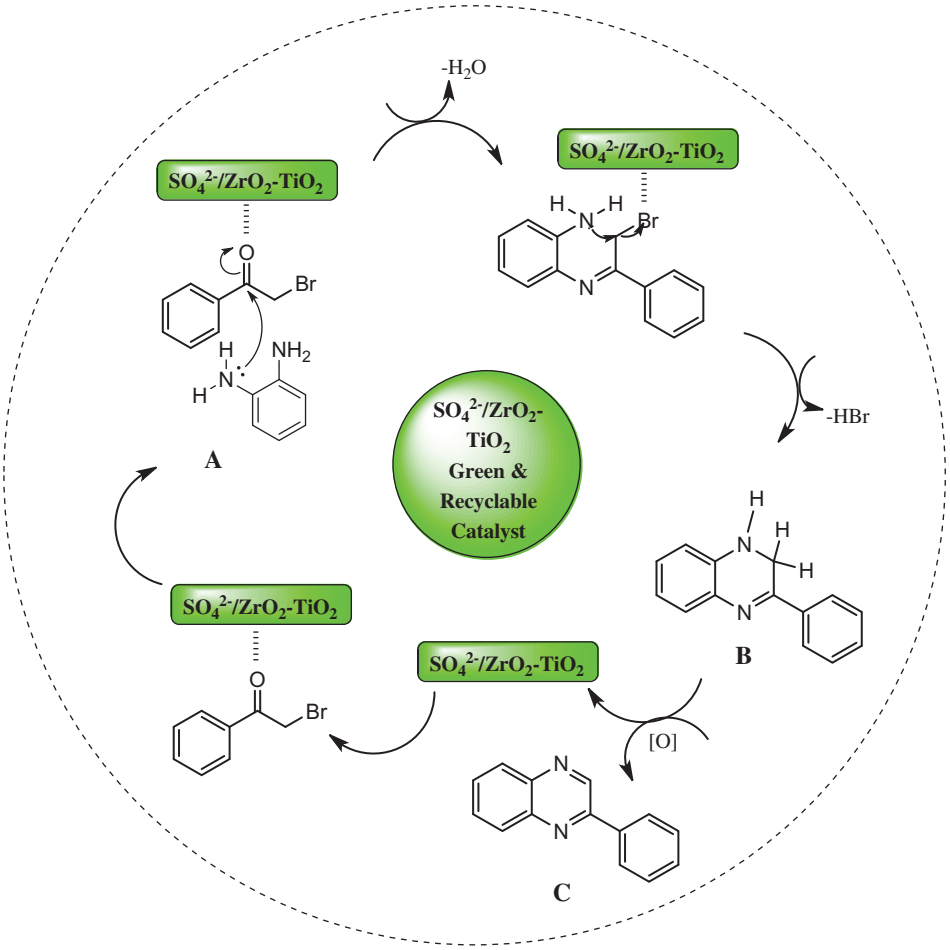
Conclusion

In conclusion, we have developed a mild, efficient, and environmentally benign synthetic protocol for the synthesis of quinoxalines (**3a–m**) from substituted phenacyl bromides/benzil and *o*-pheneylenediamines using SO_4^{2-}/ZrO_2-TiO_2 catalyst. The key feature of the current protocol involves simple reaction conditions, no side reaction with the formation of the desired product in high yield. The present method is an alternative to the conventional processes for the synthesis of quinoxalines. The catalyst could be recovered several times without loss of catalytic activity, which makes the process cost-effective.

Experimental

General procedure for the preparation of SO_4^{2-}/ZrO_2-TiO_2 catalyst

SO_4^{2-}/TiO_2-ZrO_2 solid acid catalyst has been synthesized by sol-gel synthetic method followed by impregnation method. Initially the solution of 50 mL ethyl alcohol, 2 mL conc. HCl and 0.5 mL acetic acid were stirred for 30 min. To this solution, titanium isopropoxide (3.16 mL) and zirconium propoxide (3.35 mL) were added dropwise with constant stirring for 1 h. The solution has been treated at 50 °C for a gel formation and the ethanol has been evaporated. The formed gel has been dried in an oven to form a powder. The formed powder has been used for sulfate impregnation. Here, we have used the 15 mL 0.5 M H_2SO_4 per gram of powder. After this, the formed powder has been added to the H_2SO_4 solution. The water has been evaporated by heating on the sand bath. The formed sulfonated powder has been calcined at 650 °C for 4 h.



Scheme 3. Plausible mechanism for the synthesis of quinoxaline derivatives.

General experimental procedure for synthesis of quinoxalines

Phenacyl bromides/benzil (**2a–m**) (0.001 mol) and SO_4^{2-}/ZrO_2-TiO_2 catalyst (50 mg) were dissolved in EtOH (3 mL) at room temperature for 10 min. Then *o*-phenylenediamine (**1a–b**) (0.001 mol) was added slowly to the reaction mass. The resultant mixture was heated for a stipulated time. The progress of the reaction was monitored by thin-layer chromatography. The reaction mixture was diluted with ethyl acetate (10 mL) and the catalyst was recovered by simple filtration. The crude product was purified by crystallization using ethanol to afford the pure quinoxalines (**3a–m**). The melting points of the desired products were found to be in good agreement with those reported in the literature.[35–41]

2-(Phenyl)quinoxaline (3a)

The compound (**3a**) was obtained by SO_4^{2-}/ZrO_2-TiO_2 catalyzed reaction in between o-pheneylenediamine (**1a**) and phenacyl bromide (**2a**) as bright yellow solid; yield 94%; mp 73–75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.48–7.77 (m, 5H, Ar-H), 8.06–8.14 (m, 4H, Ar-H), 9.38 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 126.42, 128.15,

129.43, 131.32, 135.22, 141.62, 142.15, 143.12, 150.34; HRMS (ESI^+) calcd. for $C_{14}H_{10}N_2$ $(M+H)^+$: 207.0923; found 207.0926.

2,3-Diphenylquinoxaline (3m)

The compound (**3m**) was obtained by SO_4^{2-}/ZrO_2-TiO_2 catalyzed reaction in between o-pheneylenediamine (**1a**) and benzil (**2m**) as white solid; yield 91%; mp 123–125 °C; 7.32–7.54 (m, 5H, Ar-H), 7.74–7.80 (m, 2H, Ar-H), 8.18–8.20 (m, 2H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 128.28, 128.81, 129.21, 129.83, 129.97, 139.06, 141.23, 153.48; HRMS (ESI^+) calcd. for $C_{20}H_{14}N_2$ $(M+H)^+$: 283.1235; found 283.1238.

Disclosure statement

The authors declare no conflict of interest.

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