# Green Chemistry

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# Polythene glycol (PEG) as a Reusable Solvent System for The Synthesis of 1,3,5-triazines *via* Aerobic Oxidative Tandem Cyclization of Benzylamines and *N*-substituted Benzylamines with Amidines under Transition Metal-Free Conditions

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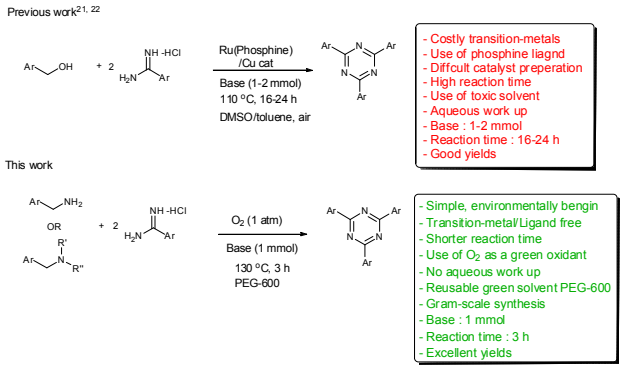
**A green and highly efficient protocol for the syntheis of 1,3,5-triazines from benzylamines and *N*-substituted benzylamines amidines in PEG-600 has been developed firstly. This protocol is transition-metal free, phosphine ligand free and uses inexpensive, easily available molecular oxygen ($O_2$) as an oxidant. A series of 1,3,5-triazines derivatives were synthesized in good to excellent yields in shorter reaction time. The ease of the products separation and resuability of PEG-600 makes it more environmentally benign and economically affordable for the gram-scale synthesis.**

Green Chemistry emphasized on the development of economically feasible, synthetic procedures that avoid the use of toxic transition-metals and the utilization of environmentally benign substances and non-toxic solvents.[1] Recently, transition-metal free reactions have gained prominence in organic synthesis.[2] Not only does it avoids the use of toxic transition-metal, but also reduces the cost of the developed procedure. Oxidation reactions are very important transformations in organic chemistry. Molecular oxygen ($O_2$) is an ideal oxidant as it is inexpensive and easily available.[3] In addition, no toxic by-product makes it a highly attractive reagent from the viewpoint of green sustainable chemistry.[4] The most of organic reactions are affected by solvent as it plays an important role in mixing the ingredients to make the system homogeneous and allow molecular interactions to be more efficient.[5] Thus, selection of solvent is very crucial. The solvent should be inexpensive, non-toxic, non-volatile and easy recyclability. In this context, environmentally benign solvents such as water[6], ionic-liquids[7] has been employed in various organic reactions. However, most of organic moieties have very low solubility in water which results into low yield of products. Further, toxicity and environmental burden data for the most of the ionic-liquids are still unknown. Over the past decade, polythene glycol (PEG) has been used in several organic reactions.[8] PEG and its monomethyl ethers posses unique properties such as thermally stable, commercially available, recyclable, immiscibility with various organic solvents and non-toxic media for phase transfer catalysts.[9] Further, PEG is an inexpensive, completely non-halogenated and complete toxicity profiles are available for a range of polyethylene glycol (PEG) molecular weights, many are approved for internal utilization by the US FDA.[10]

1,3,5-triazines chemistry is of great importance due to their wide applications in biological and medicinal activities such as antimicrobial,[11a] antimalarial,[11b] antitumor agents[11c] antituberculosis[11d] and inhibition of photosynthetic electron transport (PET) and binding.[11e] In addition, they are used as chelating ligands for the preparation of organometallic materials,[12] transition-metal catalysts,[13] liquid crystals,[14] fluorescent brighteners.[15] Although, 1,3,5-trianzines possess extensive functions, but only a few methods for the synthesis of 1,3,5-triazines have been reported. Traditionally, they were synthesized from halogenated 1,3,5-triazines in the presence of transition metal-catalysts,[16] and from the cyclotrimerization reaction of nitriles.[17] However, the former require transition-metal Palladium (Pd), less-environmentally benign halogenated substrates, and produce stoichiometric amounts




**Scheme 1** Synthesis of 1,3,5-triazines

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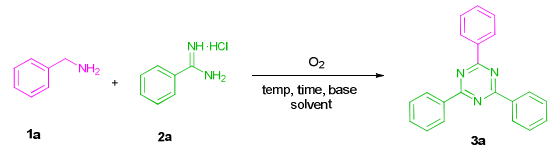
of undesirable waste, and the later usually needs excess of amines as the co-catalysts. Alternatively, these compounds were also obtained by cyclization of aromatic aldehydes with amidines.[18] However, the use of aldehydes have several disadvantages such as aldehydes could undergo a decarbonylation reaction under harsh reaction conditions,[19] oxidation of active aldehyde groups, leading to formation of unwanted by-products, hence require inert conditions.[20] Recently, two methods for synthesis of 1,3,5-triazines from of benzyl alcohol and amidines have been reported (Scheme 1). Nevertheless, these methods require costly ruthenium-complex[21] or less environmentally begin $Cu(OAc)_2$[22] as a catalyst. Moreover, difficult preparation step of Ru-phoshine complex, toxic solvents such as DMSO and toluene, longer reaction time, reflux conditions and aqueous work up has imposed limitations on the applicability of these methods.

In continuation with our ongoing work on transition-metal free approach in organic synthesis.[2h] Herein, we report a transition-metal free method for synthesis of 1,3,5-triazines. Notably, this reaction proceeds *via* aerobic oxidative tandem cyclization of benzylamines with amidines at 130 $^{o}$C for 3h.

**Table 1** Optimization of reaction condition[a]



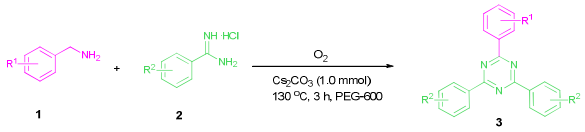

| Entry | Solvent | Temp ($^{o}$C) | Time (h) | Yield[b] (%) |
|---|---|---|---|---|
| 1 | $H_2O$ | 100 | 24 | - |
| 2 | EtOH | 100 | 24 | - |
| 3 | Glycerol | 100 | 24 | - |
| 4 | PEG-600 | 100 | 24 | 70 |
| 5 | PEG-600 | 110 | 24 | 82 |
| 6 | PEG-600 | 120 | 24 | 90 |
| 7 | PEG-600 | 130 | 24 | 95 |
| 8 | PEG-600 | 140 | 24 | 96 |
| 9 | PEG-600 | 130 | 12 | 95 |
| 10 | PEG-600 | 130 | 6 | 95 |
| 11 | PEG-600 | 130 | 3 | 95 |
| 12 | PEG-600 | 130 | 2 | 71 |
| 13 | PEG-600:DMSO (1:1) | 130 | 3 | 64 |
| 14 | PEG-600 | 130 | 3,24 | -,- |
| 15 | PEG-600 | 130 | 3 | 57[c],78[d], 51[e] |

[a] Reaction conditions: benzylamine (**1a**, 0.5 mmol), benzamidine hydrochloride (**2a**, 1.0 mmol), $Cs_2CO_3$ (1.0 mmol) and solvent (2.5 mL). [b] Isolated Yield. [c] $Na_2CO_3$ was used instead of $Cs_2CO_3$. [d] $K_2CO_3$ was used instead of $Cs_2CO_3$. [e] $Cs_2CO_3$ (0.5 mmol).

Initially, the direct reaction between benzylamine (**1a**) and benzamidine hydrochloride (**2a**) was selected as a model reaction to evaluate the feasibility of our system in environment benign solvent at 100 $^{o}$C for 24 h. When the reaction was carried out in $H_2O$, ethanol and glycerol, no formation of the desired product was noted (table 1, entries 1-3). Surprisingly, changing the solvent system to PEG-600 resulted into formation of the desired product **3a** in 70% yield (table 2, entry 4). This surprise result encouraged us to choose this PEG-600 as solvent. To our delight, increasing the temperature has a significant effect on the yield of **3a**, provided 95% yield at 130 $^{o}$C (table 1, entry 5-7). Increasing the reaction temperature above 130 $^{o}$C didn't have significant effect on the yield of **3a** (table 1, entry 8). Reaction time could be reduced to 3 h from 24 h (table 1, entries 9-11). Decreasing the reaction time beyond 3 h leads to significant decrease in the yield of desired product **3a** (table 1, entry 12). Before heating the reaction mixture was transparent but after heating for 3h, it turns into yellow in colour. The addition of DMSO resulted into decrease in the yield of product **3a** (table 2, entry 13). When reaction was carried out in the absence of base, no formation of desired product was observed, even after running the reaction for 24 h (table 1, entry 14). Bases such as $Na_2CO_3$ and $K_2CO_3$ did not give good results for the formation of desired product **3a** (table 1, entry 16). Further, decreasing the amount of base from 1.0 mmol to 0.5 mmol resulted into the formation product **3a** only in 51% (table 1, entry 16). Thus, optimized reaction conditions are: benzylamine (**1a**, 0.5 mmol) amidine hydrochloride (**2a**, 1.0 mmol), $Cs_2CO_3$ (1.0 mmol), PEG-600 (2.5 mL) for 3 h under $O_2$.

Encouraged by these results, we used various benzylamines and amidines to establish the scope and limitations of this protocol. A series of 1,3,5-triazines were synthesized in good to excellent yields under the optimized reaction conditions and representative results are listed in table 2. Firstly, the effect of electron donating group and electron withdrawing on benzylamine with benzamidine was studied (table 2, entries 1-8). It was found that electron donating substituents such as –Me, –OMe, proceeds smoothly and furnished desired products (**3b**-**3c**) in excellent isolated yields (table 2, entries 2 and 3). Subsequently, the reaction of benzylamines bearing strong electron withdrawing groups such as –CN and $–NO_2$ at different position provided corresponding products (**3d**, **3e** and **3f**) in good yields (table 2, entries 5-6). Interestingly, halogen substituents such as –Cl and –F could also be transformed in efficient manner, providing respective products in very good yields (table 2, entries 7-8). Next, heteroatom containing benzylamines such as pyridine-2-yl-2-methanamine, pyridin-3-ylmethanamine (**1i** and **1j**) and furan-2-ylmethanamine (**1k**) were tested. Delightfully, all the reactions progressed efficiently affording products **3i**-**3k** in very good yields (table 2, entries 9-11). These obtained heteroaryl substituted 1,3,5-triazines have potential to be used as C^N or C^N^C ligands in pincer complexes.[23] Next, an apparent substituents effect on amidine was also explored (table 2, entries 12-15). eaction of **1a**, **1c** and **1m** with para-methylbenzamidine (**2b**) progressed very well affording 1,3,5-triazines triazines (**3l**-**3n**) in excellent yields (table 2, entries 12-14). Also, reaction of **1c** with para-bromobenzamidine resulted into the formation of desired product (**3o**) in good yield (table 2, entry 15). Unfortunately, no formation of corresponding products could be observed when the reaction was carried out

**Table 2** Aerobic oxidative cyclization of benzylamines with amidine hydrochlorides[a]




1 2 3

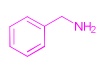
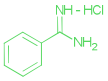
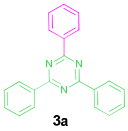
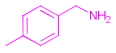
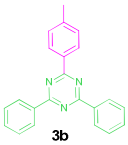
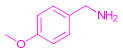
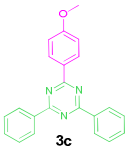
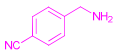
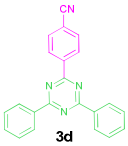
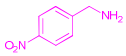
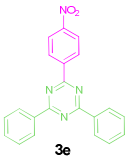
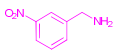
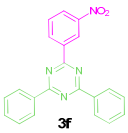
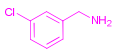
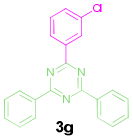
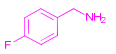
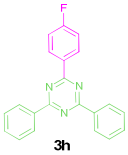
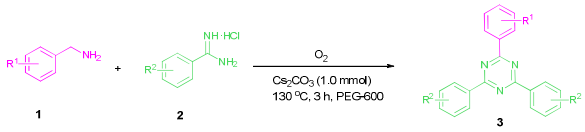
| Entry | Amines (1) | Amidines (2) | Products (3) | Yield[b] (%) |
|---|---|---|---|---|
| 1 |  **1a** |  **2a** |  **3a** | 95 |
| 2 |  **1b** | **2a** |  **3b** | 96 |
| 3 |  **1c** | **2a** |  **3c** | 96 |
| 4 |  **1d** | **2a** |  **3d** | 71 |
| 5 |  **1e** | **2a** |  **3e** | 75 |
| 6 |  **1f** | **2a** |  **3f** | 83 |
| 7 |  **1g** | **2a** |  **3g** | 92 |
| 8 |  **1h** | **2a** |  **3h** | 89 |

**Table 2** *(Contd.)*

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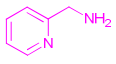
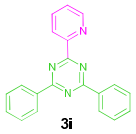
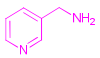
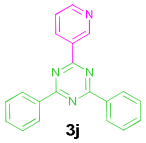
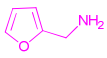
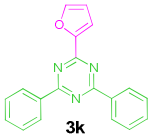
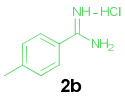
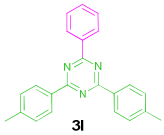
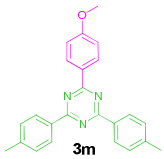
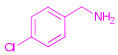
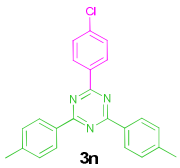
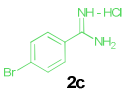
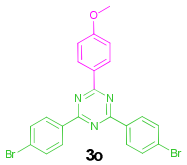
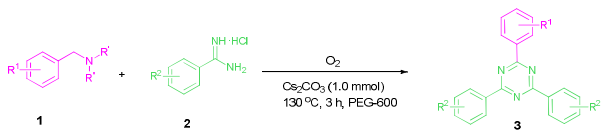
| | | | | |
|---|---|---|---|---|
| 9 |  **1i** | **2a** |  **3i** | 97 |
| 10 |  **1j** | **2a** |  **3j** | 96 |
| 11 |  **1k** | **2a** |  **3k** | 96 |
| 12 | **1a** |  **2b** |  **3l** | 82 |
| 13 | **1c** | **2b** |  **3m** | 85 |
| 14 |  **1m** | **2b** |  **3n** | 87 |
| 15 | **1c** |  **2c** |  **3o** | 80 |

[a] Reaction conditions: benzylamine (**1**, 0.5 mmol), amidine hydrochlorides (**2**, 1.0 mmol), $Cs_2CO_3$ (1.0 mmol), solvent (2.5 mL) for 3 h. [b] Isolated Yield.

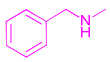
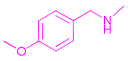
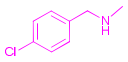
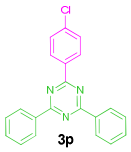
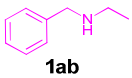
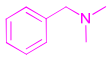
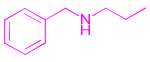
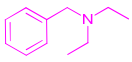
with both aliphatic amines and aliphatic amidines (results are not shown).

Efforts were also made to expand the scope of the method to *N*-mono and *N,N*-di substituted benzylamines and results are summarized in table 3. The reaction proceeded very well for *N*-methylbenzylamines (**1aa**) and *N,N*-dimethylbenzylamine

**Table 3** Aerobic oxidative cyclization of *N*-substituted amines with amidine hydrochlorides[a]




1 2 3

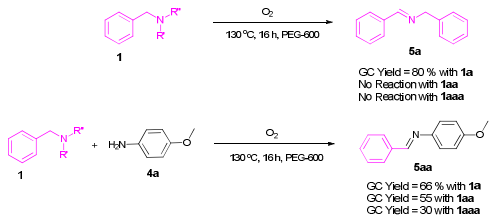
| Entry | Amine (1) | Amidine (2) | Product (3) | Yield[b] (%) |
|---|---|---|---|---|
| 1 |  **1aa** | **2a** | **3a** | 94 |
| 2 |  **1ca** | **2a** | **3c** | 95 |
| 3 |  **1ma** | **2a** |  **3p** | 89 |
| 4 | **1aa** | **2b** | **3m** | 83 |
| 5 | **1ca** | **2b** | **3n** | 84 |
| 6 | **1ma** | **2b** | **3o** | 86 |
| 7 |  **1ab** | **2a** | **3a** | 90 |
| 8 |  **1aaa** | **2a** | **3a** | 78,82[c] |
| 9 | **1aaa** | **2b** | **3m** | 81 |
| 10 |  **1ab'** | **2a** | **3a** | 86 |
| 11 |  **1abb** | **2a** | **3a** | 70[c] |

[a] Reaction conditions: benzylamine (**1**, 0.5 mmol), amidine hydrochlorides (**2**, 1.0 mmol), $Cs_2CO_3$ (1.0 mmol), solvent (2.5 mL) for 3 h. [b] Isolated Yield. [c] Reaction was carried out for 8 h.

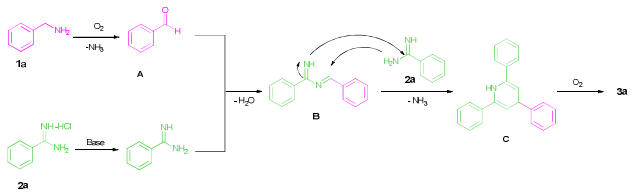
(**1aaa**) providing corresponding products in very good yield (table 3, entries 1-6 and 8). Also, the reactions of N-ethylbenzylamine (**1ab**) and *N*-ethanolbenzylamine (**1ab'**) were found to be effective (table 3, entry 7 and 10). However, reaction of *N,N*-diethylbenzylamine (**1abb**) gave relatively low yield of **3a** than **1aaa** (table 3, entries 8 and 11).

To show the synthetic utility of this protocol, gram-scale reaction were carried out by using substrates **1a** (2 g, 18.87 mmol) with **2a** (5.89 g, 37.74 mmol) and **1c** (2.0 g, 16.53 mmol) with **2a** (5.16 g, 33.06 mmol) under the optimized reaction condition. As per our expectation, reaction preceded well by providing **3c** and **3g** in 91% and 85% isolated yields respectively.

In order to understand the mechanism of these reactions, some control experiments were carried out (Scheme 2). When reaction was carried out in the absence of amidines and $Cs_2CO_3$ formation of imine (**5a**) was noted by self coupling of benzylamine. On the other hand, N-methyl and N,N-dimethylbenzylamine remained unchanged. This is an agreement with the previous report on the synthesis of imines.[24] However, in the presence of para-methoxyaniline (**4a**) formation of imine (**5aa**) was observed form **1a**, **1aa** and **1aaa**. The yields of these imines are very low even after running the reaction for 16 h. This is possibly because **4a** is very less basic than amidines. The formation of these imines (**5a** and **5aa**) was confirmed by GCMS. This proves that the presence of another amine influence the reaction and leads to the formation of aldehyde *via* oxidative cleavage of benzylic carbon and nitrogen bond. Based on the observations of control experiments, a plausible reaction mechanism has been illustrated (Scheme 3). Reaction proceeds with the *in situ*




**Scheme 2** Control experiments




**Scheme 3** A plausible reaction mechanism

generation of aldehyde (**A**). Meanwhile, amidine salt (**2**) is neutralized by $Cs_2CO_3$ from its hydrochloride salt. Consequentially, reacting with **A** to give 1,3,5-tirazine (**3a**) *via* dehydrogenative aromatisation of **C**. This proposed mechanism is consistent with the previous report.[21,22] To the best of our knowledge, there is no report on the synthesis of imines form N-mono substituted benzylamine under transition-metal free condition. This is for the first time we have shown the formation of imine from N-mono and di-substituted benzylamine under transition-metal free conditions. Further, unlike the previous report,[24,25] self coupling reaction of benzylamine does not involve the use of any activating agents such as catalyst or acid.

At last, we attempted to reuse the PEG-600. After completion of the reaction, PEG was recovered and subjected to another run, affording the product in almost same yield. This process was repeated three more times, affording the product in excellent yields (Table 4). It is important to note that weight loss ~10% of PEG was observed for every run due to handling loss. The simple experimental and ease of product separation combined with the easy recovery and reuse of PEG is expected to contribute to the development of a green methodology for the synthesis of 1,3,5-triazines.

**Table 4** Recyclability study of PEG

| Run | 1 | 2 | 3 |
|---|---|---|---|
| Yield[b] (%) | 95 | 95 | 94 |

[a] Reaction conditions: benzylamine (**1**, 0.5 mmol), amidine hydrochlorides (**2**, 1.0 mmol), $Cs_2CO_3$ (1.0 mmol), PEG (2.5 mL) for 3 h. [b] Isolated Yield.

## Conclusions

In conclusion, a highly efficient, transition-metal free synthesis of 1,3,5-triazines has been developed by employing molecular oxygen as a green oxidant in PEG-600. The use of molecular oxygen and non toxic as solvent PEG-600 has made this protocol economical, environmentally benign and potentially viable for commercial and academic applications. Various 1,3,5-triazines were synthesized in good to excellent yields. The developed methodology is suitable for the gram-scale synthesis, owing to its simple non-aqueous work up, shorter reaction time and higher yield. This protocol offers an excellent chance to avoid the toxic solvents, catalysts and use of natural resources than previous reports. Noteworthy, for the first time we have demonstrated the synthesis of imines form *N*-mono and *N,N*-di substituted benzylamines. Moreover, the after extraction of with ether, PEG-600 was recovered and could be reused up to three consecutive cycles.

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