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Triazine-based porous organic polymer: a novel heterogeneous basic organocatalyst for facile one-pot synthesis of 2-amino-4*H*-chromenes

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Abstract

A new triazine-based porous organic polymer TPOP-2 has been synthesized through the reaction between cyanuric chloride and *tris*(2-aminoethyl)amine in anhydrous 1,4-dioxane under N_2 atmosphere. The porous polymer has been characterized by powder X-ray diffraction, N_2 sorption, HR TEM, FE SEM, ^{13}C CPMAS NMR, CO_2-TPD, UV-VIS and FT IR spectroscopic tools. Due to the high density of amine and triazine functional groups, this porous polymer is N-rich and possesses excellent surface basicity, which is utilized as a heterogeneous metal-free basic organocatalyst for the one-pot three-component condensation reaction of aromatic aldehyde, activated phenols (resorcinol and 2-naphthol) and malononitrile for the synthesis of 2-amino-chromenes under solvent-free or aqueous conditions. The ease of catalyst synthesis and its efficient use for five consecutive cycles without noticeable loss in catalytic activity suggests significant future potential of this new N-rich porous organic polymer material for a wide range of base catalyzed reactions.

Keywords: Porous organic polymer; base catalysis; three-component coupling; 2-amino-4H-chromenes; organic frameworks.

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Introduction

Porous organic polymers (POPs)[1] have attracted huge research interest in recent times due to their wide potential to accommodate several reactive functional groups in the framework and these materials are explored in many frontline areas of energy and environmental research, including gas storage and their selective separation from the mixture of gases, heterogeneous catalysis, fabricating the conductive coatings, sensors, optoelectronic devices etc. Unique intrinsic surface properties like high BET surface area, good chemical and thermal stability, and reusability in various catalytic reactions have prompted the researchers to explore organic polycondensation reaction routes for designing these porous polymers.[2] A wide range of synthetic strategies using bottom-up chemistry approach have been employed to design the functional POPs, that are widely used as heterogeneous catalyst. These led to the discovery of novel porous organocatalytic materials such as microporous organic polymers (MOPs),[3] mesoporous poly-melamine-formaldehyde (mPMF),[4] polymeric graphitic carbon nitride materials (g-C_3N_4),[5] conjugated microporous polymers (CMPs),[6] porous aromatic frameworks (PAFs)[7] and related microporous organic polymers.[8] Thus, it is a big challenge for the material chemists to explore new synthetic strategies to design a POP material, which can catalyze the complex chemical reaction in a greener, safer and environment friendly way.

One-pot multicomponent reactions (MCRs) are very exciting class of reactions in the field of medicinal and synthetic organic chemistry.[9] The simplicity of one-pot reaction procedure, conducting the reaction without isolation of intermediates, reduction of reaction time and formation of new C-C, C-O bonds are the main advantages of MCRs compared with traditional reactions. Various heterocyclic compounds such as benzopyrans, benzoxanthene, benzochromene can be synthesized by applying one-pot multicomponent reactions.[10] It has been a matter of great interest in recent years to synthesize these chromene derivatives due to

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their various significant biological and pharmacological activities including antimicrobial,[11] antioxidant,[12] antitumor,[13] central nervous system activity[14] and in vitro study as antibacterial agents.[15] These compounds have been also employed in the field of cosmetics, pigments and potential biodegradable agrochemicals.[16] Owing to these widespread potential biological and pharmacological activities, chromene derivatives are of great interest to the medicinal chemists for many years. 2-amino-4*H*-chromenes were generally prepared by the condensation of aromatic aldehyde, malononitrile and activated phenols in presence of hazardous organic bases such as DBU,[17] piperidine[18] in ethanol and acetonitrile for several hours. There are several reports for the preparation of 2-amino-4*H*-cromenes over various homogeneous catalysts such as NaOH,[19] K_2CO_3,[20] $TiCl_4$,[21] $InCl_3$,[22] Et_3N,[23] tetramethylguanidine,[24] methane sulfonic acid,[25] cetyltrimethylammonium chloride (CTACl),[26] triethylbenzylammonium chloride[27] and *N*,*N*-dimethylaminoethylbenzyl dimethylammonium chloride.[28] Although, most of these catalytic methods showed high activity and selectivity but being homogeneous catalysts their separation from the reaction mixture is major problem associated with their no-reusability after one reaction. Only a few heterogeneous catalysts, such as TAFMC-1,[29] nano-sized magnesium oxide,[30] Mg/Al hydrotalcite,[31] γ-alumina[32] have been developed for the preparation of 2-amino-4*H*-chromenes. However, all of the heterogeneous catalysts are metal based and thus having the possibility of metal leaching in the reaction medium. So, greener reaction pathways, methodologies and easily separable heterogeneous organocatalysts, devoid of metal ions are highly desirable to address these industrial and environmental issues.[33] Recently, our group has reported mesoporous organosilica as an organocatalyst for the synthesis of 2-amino-4*H*-chromenes under solvent-free conditions.[34] But that organocatalyst gives very low yield of desire product in the cases of resorcinol and 2-naphthol. Thus, high yield synthesis of 2-

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amino-4*H*-chromenes under very mild and environment friendly conditions over a tailor-made heterogeneous organocatalyst is highly desirable.

Herein, we report the one-pot three component synthesis of 2-amino-chromene derivatives over a new robust, non-air sensitive heterogeneous metal-free triazine based basic organocatalyst TPOP-2 under solvent-free or aqueous reaction medium. TPOP-2 has been synthesized by the unimolar reaction between cyanuric chloride and *tris*(2-aminoethyl)amine in anhydrous 1,4-dioxane under N_2 atmosphere. The organocatalyst TPOP-2 has been thoroughly characterized by N_2 sorption, HR TEM, FE SEM, CO_2-TPD, FTIR and ^{13}C CPMAS NMR studies. This novel organocatalyst shows excellent catalytic activity in the one-pot three component condensation reaction of aromatic aldehyde, malononitrile and activated phenols for the synthesis of various 2-amino-chromene derivatives in very high yields.

Experimental section

Synthesis of TPOP-2: In a typical synthesis, 1 mmol *tris*(2-aminoethyl)amine (**2**) and 3 mmol anhydrous K_2CO_3 was added in 10 mL anhydrous 1,4-dioxane taken in 50 mL round bottom flask and it was equipped with dropping funnel containing 1 mmol cyanuric chloride (**1**) dissolve in 10 mL anhydrous 1,4-dioxane under N_2 environment (Scheme 1). Cyanuric chloride, dissolved in 1,4-dioxane was added dropwise to the above solution with continuous stirring at 15 ^{o}C for 1 h and it was stirred at 25 ^{o}C for 2 h and then the mixture was kept under stirring conditions for 72 h at 90 ^{o}C. Finally the yellowish white precipitate was filtered and it was washed several times with water, methanol and acetone. Then the organocatalyst was dried under vacuum condition at room temperature. Yield: 82%. The outline for the synthesis of TPOP-2 is depicted in Scheme 1.

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General procedure for the synthesis of 2-amino-chromenes: A mixture of 1 mmol of aromatic aldehyde, 1 mmol of activated phenols (resorcinol or 2-naphthol) and 1 mmol of malononitrile was taken in 25 mL round bottom flask with 40 mg TPOP-2 catalyst and then the mixture was heated under solvent-free conditions (when resorcinol was taken) or aqueous medium (when 2-naphthol was taken) at 80 ^{o}C for appropriate reaction time (4-6 h). After completion of reaction, ethyl acetate was poured into reaction mixture and the catalyst was separated from the reaction mixture by simple filtration. The products were collected from the reaction mixtures by extracting it with ethyl acetate and water. The organic part was dried with anhydrous sodium sulfate and then under vacuum with reduced pressure to obtain the desired crude product. Then it was crystallised from methanol and pure product was characterised by ^{1}H and ^{13}C NMR spectroscopy. The outline for the base catalyzed condensation reaction is illustrated in Scheme 2.

Characterization techniques: Powder X-ray diffraction pattern of TPOP-2 material was recorded on a Bruker D-8 Advance SWAX diffractometer operated at a voltage of 40 kV and a current of 40 mA. The instrument has been calibrated with a standard silicon sample, using Ni-filtered Cu-Kα (λ = 0.15406 nm). FT-IR spectra of the samples were recorded using a Perkin Elmer Spectrum 100. BET surface area and porosity analysis was carried out by using a Quantachrome autosorb-1C at 77 K. JEOL JEM 6700F field emission scanning electron microscope (FE SEM) was used for the determination of morphology of polymer sample. The pore structure was visualized by using a JEOL JEM 2010 high resolution transmission electron microscope (HR TEM) operated at an accelerating voltage of 200 kV. ^{1}H and ^{13}C NMR (solution) experiments were carried out on a Bruker DPX-300 NMR spectrometer. The solid state CP MAS NMR spectra of the samples were taken in Bruker Ascend^{TM} 400 spectrometer. Temperature programmed desorption of carbon dioxide (TPD-CO_2) was carried out in a ChemiSorb 2720 pulse chemisorption system of Micromeritics Instrument

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Corporation, USA. Before purging of CO_2 molecules the sample was activated under He flow for 2 h at 300 ^{0}C followed by cooling to room temperature.

Result and Discussion:

The wide angle powder **X**RD pattern of TPOP-2 polymer is shown in Figure 1. It showed one broad peak around at 2θ value of 20 degrees, which is characteristics diffraction by amorphous polymer, along with a sharp peak centred at 2θ value of 18, which suggests partial crystallinity in the porous polymeric network. The detailed porosity of TPOP-2 is measured using N_2 adsorption-desorption analysis at 77 K and this is shown in Figure 2. The isotherm closely resembles the type IV isotherm with a gradual increase in N_2 uptake in the intermediate region of P/P_o and a noticeable H3 hysteresis loop[35] in the range 0.5 to 0.9 of P/P_o. From N_2 sorption analysis, we get the BET (Brunauer–Emmett–Teller) surface area of TPOP-2 of 105 m^2g^{-1}. Pore size distribution (PSD) of the material has been calculated from non local density functional theory (NLDFT) method. The PSD plot of TPOP-2 (inset, Figure 2) using carbon slit pore model at 77 K shows trimodal porosity with peaks at 1.5 nm, 2.6 nm and 4.5 nm. The micropore surface area and the micro-pore volume of TPOP-2 are 39 m^2g^{-1} and 0.0187 ccg^{-1}, whereas mesopore surface area is 66 m^2g^{-1}, calculated from the *t*-method micropore analysis method. We have analyzed the particle morphology of TPOP-2 material via TEM and SEM analysis. Corresponding results are shown in Figure 3. TEM images (Fig. 3A and 3B) of TPOP-2 suggested that the typical porous network is formed due to the inter-linking of irregular particles. It clearly reveals the existence small micropores along with mesopores. The scanning electron microscopic images (Fig. 3C and 3D) of TPOP-2 clearly suggested that the material is composed of spherical nanoparticles of dimension *ca.* 30-40 nm and they are agglomerated to form bigger particles.

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The FT IR spectrum of TPOP-2 is shown in Figure 4. This spectrum shows stretching frequencies of around 1342 and 1572 cm^{-1} due to the triazine rings.[36] On the other hand peaks at 1423 and 2938 cm^{-1} could be attributed to bending and stretching vibration of sp^3 $-CH_2-$ moiety. The characteristic breathing mode of vibration of triazine units is evident at around 807 cm^{-1}. The absence of C-Cl stretching vibration[37] at 850 cm^{-1} confirms that all three chlorine atoms of cyanuric chloride have been substituted. The elemental analysis of the organocatalyst gave 41.83 wt% C, 6.58 wt% H and 36.27 wt% N. Here nitrogen is the active basic site and thus TPOP-2 can be explored for the base catalyzed condensation reaction. The thermal stability of the porous organocatalyst TPOP-2 is determined from the TG-DTA analysis under continuous flow of N_2 flow. The TGA profile is shown in Figure 5 and it suggests *ca.* 6% weight loss at 60 ^{o}C temperature. This could be due to removal of the adsorbed water from the surface of the porous polymeric network. Then the material is thermally stable up to 340 ^{o}C. Two types of exothermic weight loss are observed in the temperature range 340 to 478 ^{o}C, one is 6% weight loss upto 350 ^{o}C and another is 22% weight loss upto 422 ^{o}C. Both weight losses could be attributed to the decomposition of organic fragments of the polymeric network. Further, endothermic weight loss of *ca.* 26 wt% in the temperature range 486-573 ^{o}C is observed. The framework model structure of the TPOP-2 and its ^{13}C CP-MAS NMR are shown in Figure 6. The ^{13}C CP-MAS NMR spectrum displays characteristic signals for carbon (designated by a) of triazine units at 166.14 ppm. Further, b and c carbons of the TPOP-2 organocatalyst showed the signals at 39.7 and 52.3 ppm, respectively.[38] Temperature programmed desorption of CO_2 has been carried out to understand the nature and the amount of surface basicity of the N-rich TPOP-2 surface. Multiple desorption peaks in the CO_2-TPD profile (Figure 7) suggested weak to moderately strong surface basicity of TPOP-2. Total basicity estimated from this CO_2 desorption plot is 1.13 $mmolg^{-1}$.

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Catalysis

The nitrogen rich TPOP-2 can provide abundant basic sites at the catalyst surface and thus we have employed it for the three-component base catalyzed condensation reaction. The catalytic activity of the TPOP-2 is determined by carrying out the reaction of aromatic aldehyde, activated phenols (resorcinol or 2-naphthol) and malonnonitrile to synthesize 2-amino-chromenes as the model reaction (Table 1). The reaction of aromatic aldehyde, resorcinol and malononitrile is carried out under solvent-free conditions at 80 ^{o}C in the presence of the TPOP-2. Very high yield of the products together with considerably good turn over numbers are observed for all the substrates. But when we had taken 2-naphthol instead of resorcinol as the activated phenol under solvent-free conditions very poor yield of 2-amino-chromenes was formed even at 100 ^{o}C reaction temperature. To find out the optimized conditions, the unimolar reaction between 4-chlorobenzaldehyde, 2-naphthol and malononitrile is carried out under various reaction mediums over the organocatalyst TPOP-2. Among the various solvents used, such as water, ethanol, acetonitrile, DMF, 1,4-dioxane, *n*-hexane; this reaction underwent very smoothly at 80 ^{o}C for 6 h to obtain desired 3-amino-2-cyano-1-(4-chlorophenyl)-1*H*-benzo[f] chromene in aqueous medium with maximum yield of 88% (Table 2, entry 1). When we have used acetonitrile, DMF, 1,4-dioxane or *n*-hexane as a solvent for the above reaction, Knoevenagel condensation adduct was formed as a major product and the desired product 3-amino-chromenes was formed only in 25%, 30%, 15% and 10% yields, respectively (Table 2, entries 3-6). But polar protic solvents such as water and ethanol have improved the yields of the desired product to 88% and 78%, respectively (Table 2, entries 1, 2). So water is the best solvent to obtain maximum yield of 3-amino-2-cyanobenzo-chromenes over TPOP-2 organocatalyst.

To investigate the optimum amount of organocatalyst, the unimolar reaction of 4-chlorobenzaldehyde, resorcinol and malononitrile is carried out under solvent-free conditions

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over different amount of TPOP-2 at 80 ^{o}C for 6 h. When the reaction was carried out at 80^{o}C temperature in the absence of any catalyst, very trace amount of desired product was obtained. With increasing the amount of organocatalyst from 10 mg to 40 mg, the yield of the above reaction was improved (yields are shown in Figure 8). Further increasing of the amount of organocatalyst, there was no significant change in the yield of desired product. From Figure 9, we can conclude that 40 mg of TPOP-2 organocatalyst is optimum to conduct these multicomponent condensation reactions.

The same condensation reaction has been carried out at different temperatures to understand the effect of temperature on the progress of the reactions. As seen in Figure 9 that the yield of the condensation reaction for the synthesis of 2-amino-4*H*-chromenes over the TPOP-2 catalyst under the solvent-free condition increases with increasing the reaction temperature. Figure 9 also suggests that 80 ^{o}C is the optimum temperature to carry out these condensation reactions in good yield. The optimized conditions for the synthesis of 2-amino-chromenes and their yields are summarized in the Table 1.

Similarly we have conducted the condensation reaction of 4-chlorobenzaldehyde, resorcinol and malononitrile using various homogeneous Lewis base such as piperidine, pyridine, imidazole and tris(2-aminoethyl)amine under optimized conditions in order to compare them with the catalytic activity of TPOP-2. Much lower yields of the products are obtained over these homogeneous base catalysts (Table 3, entries 3, 4, 5 and 6, respectively). This result suggested that TPOP-2 is an excellent heterogeneous catalyst for this 3-component coupling reaction.

Effect of substituted groups of aromatic aldehydes: The time required for the completion of these reactions using aromatic aldehydes with electron withdrawing groups (Table 1, entry 6) were somewhat smaller than electron donating groups (Table 1, entries 2, 9 and 14). First

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step of the cyclization reaction is Knoevenagel condensation reaction between aromatic aldehyde and malononitrile. With increasing the electron withdrawing power of substituted groups of aromatic aldehyde, the rate of the first step gets increased. In case of heterocyclic aldehyde also the reaction underwent cleanly with excellent yield (Table 1, entry 7). On the other hand higher reactivity of the *meta*- and *para*- subtituted aromatic aldehydes (Table 1, entries 2-6, 9-12, 14) over *ortho*- substituted aromatic aldehydes (Table 1, entry 13) could be attributed to the steric hindrance.

Plausible reaction mechanism and factors affecting the reaction: The possible reaction pathway for this three component reaction could proceed *via* the Knoevenagel condensation of an aromatic aldehyde and malononitrile. Then the proton of activated phenol is abstracted by N-sites of the organocatalyst and it attacks to the Knoevenagel product through Michael addition. This is followed by intramolecular cyclization to form the 2-amino-chromene derivatives.[34] Since resorcinol is more acidic than 2-naphthol, the phenolic-OH proton of resorcinol can be easily abstracted. Further, due to presence of two hydroxyl groups in resorcinol, it is more electron rich and more nucleophilic than 2-naphthol. So, when we have used resorcinol as an activated phenol the reactions can proceed smoothly under solvent-free conditions with good yields. Whereas, for 2-napthol a solvent is necessary to make a better dispersion of the catalyst in the reaction medium and thus to proceed the reaction. The key factors affecting the process are solvent polarity, temperature and amount of the catalyst. In polar protic solvents, the reaction will be faster compare to non-polar solvents. Hence, water and ethanol could enhanced the rate of the reaction and gave good yields of benzochromenes.

Reusability of the organocatalyst: In order to check the reusability of the organocatalyst TPOP-2 two controlled condensation reactions are carried out: one condensation reaction of 4-bromobenzaldehyde, resorcinol and malononitrile under solvent-free condition and another condensation reaction of 4-chlorobenzaldehyde, 2-naphthol and malononitrile in aqueous

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medium. In both cases after completion of reaction, the catalyst is filtered and washed with ethyl acetate for several times and then dried at 75 ^{o}C for overnight for the next reaction. Total five consecutive cycles have been carried out in each case. In all cases TPOP-2 exhibited consistent catalytic activity (Figure 10). From the Figure 10 it is clear that only very little deviation in the product yield is observed in the consecutive catalytic cycles. Thus, this result suggested high catalytic efficiency of TPOP-2 organocatalyst in the one-pot three component condensation reactions.

Leaching test: In order to check whether any organic group has been leached from the polymer framework of TPOP-2 or not, we have performed in situ filtration technique. In this technique, 0.04 g organocatalyst was stirred in 5 mL dichloromethane for 24 h at room temperature. Then TPOP-2 is separated by filtration and the filtrate was taken in a 50 mL round bottom flask and it is evaporated to dryness. The condensation reaction of 4-chlorobenzaldehyde, malononitrile and resorcinol is conducted similarly in a round bottom flask at 80 ^{o}C temperature for 6 h. Trace amount of desire product (same when the reaction was carried out without any catalyst) has been observed, establishing the fact that no leaching of organic group occurs. The absence of organic triazine moiety or tris(2-aminoethyl)amine group in the filtrate further confirmed by performing UV-vis spectroscopic analysis of the filtrate, where no additional peaks corresponding to the chromophores are observed.

Hot filtration test: We have carried out the condensation reaction of 4-chlorobenzaldehyde, malononitrile and resorcinol under optimized reaction condition. After 3 h the reaction has been stopped, the reaction mixture is cooled and stirred with 5 mL methanol for 6 h at room temperature. Then the catalyst is filtered and the solvent is evaporated to dryness from the reaction mixture. At this stage the yield of the desire product was 55 % (confirmed by ^{1}H NMR). After that the reaction is continued under same reaction condition for another 6 h. Then the reaction is worked-up as done previously. But no increase in the product yield is

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observed (yield 55.2 %). This result clearly confirms the heterogeneous nature of the organocatalyst TPOP-2 and no leaching of organic group from the catalyst to the reaction mixture is occurred during the course of the catalytic reaction.

Characterization of the reused catalyst: We have checked wide angle powder XRD and FT IR spectroscopic data of the reused organocatalyst TPOP-2 after four consecutive catalytic cycles. In the wide angle powder XRD pattern (Fig. S1) of TPOP-2 the characteristic broad peak for amorphous polymer is observed. FT IR spectra of the reused catalyst after fourth catalytic cycle shows two characteristic absorption bands at 1342 cm^{-1} and 1572 cm^{-1} (Figure 4). This is attributed to the triazine rings. Further, absorption bands at 1423 and 2938 cm^{-1} for bending and stretching vibration of sp^3 $-CH_2-$ are observed. Thus the XRD and FT IR results revealed that the framework and bonding of the porous polymer has been retained during the course of successive multicomponent coupling reactions.

Conclusion

In conclusion, we have developed a new protocol to design a triazine based porous organic polymer through the unimolar reaction between cyanuric chloride and *tris*(2-aminoethyl)amine. This porous polymer contains abundance of basic N-sites and it has been employed as a metal-free organocatalyst for the one-pot three component condensation reaction of aromatic aldehyde, malononitrile and activated phenols (resorcinol, 2-naphthol) under solvent-free conditions (for resorcinol) or aqueous medium (for 2-naphthol) to synthesize 2-amino-chromenes. Thus, TPOP-2 organocatalyst has excellent future potential in the environment friendly liquid phase base catalyzed reactions for the synthesis of value added fine chemicals.

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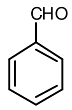
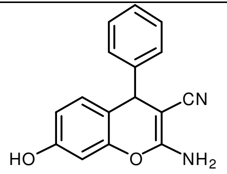
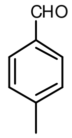
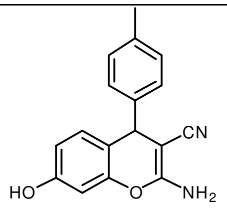
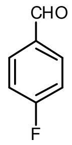
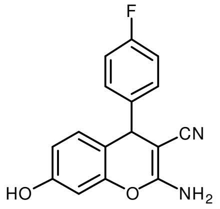
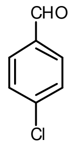
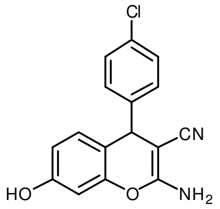
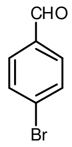
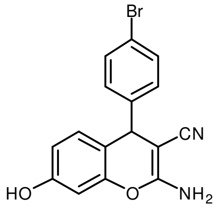
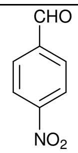
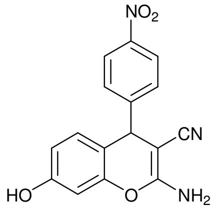
Table 1. Synthesis of 2-amino-4H-chromenes over the organocatalyst TPOP-2.

Entry	Aromatic Aldehyde	Product	Time (h)	Solvent	Yield[a] (%)	TON[b]
1			5	Solvent-free	87	19.2
2			6	Solvent-free	84	18.6
3			5	Solvent-free	88	19.5
4			6	Solvent-free	85	18.8
5			6	Solvent-free	86	19.0
6			4	Solvent-free	85	18.8

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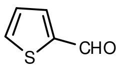
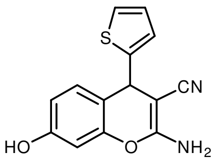
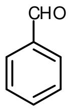
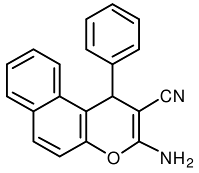
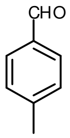
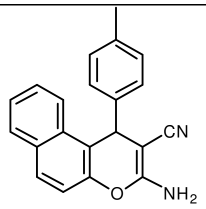
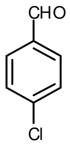
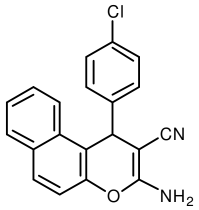
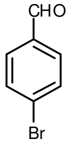
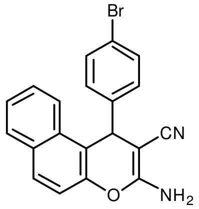
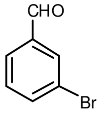
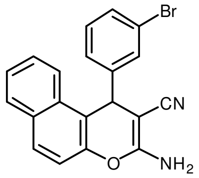
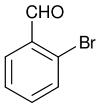
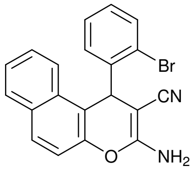
7			5	Solvent-free	86	19.0
8			6	Water	87	19.2
9			6	Water	87	19.2
10			6	Water	88	19.5
11			6	Water	87	19.2
12			6	Water	86	19.0
13			6	Water	82	18.1

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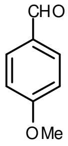
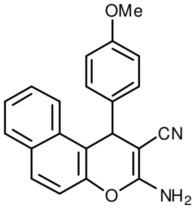
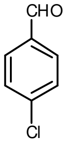
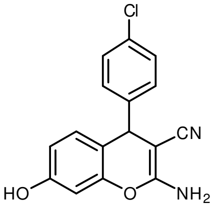
14			6	Water	84	18.6
15			6	Solvent-free	84	18.3[c]

[a] All the reactions are carried out at 80 ^{o}C temperature and isolated yields of products are given. For entries 1-7 and 15 resorcinol was used as reactant whereas for entries 8-14, 2-napthol was used as reactant.

[b] Turn over number (TON) = moles of substrate converted per mole of active site. Total basicity of the TPOP-2 material is 1.13 mmolg^{-1} calculated from CO_2-TPD analysis.

[c] Reaction was carried out in the presence of air.

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Table 2. One-pot condensation reaction of aromatic aldehyde, 2-naphthol and malononitrile in the presence of various solvents over TPOP-2.

Entry	**Solvent**	**Yield[a,b] (%)**
1	Water	88
2	Ethanol	78
3	Acetonitrile	25
4	DMF	30
5	1,4-dioxane	15
6	*n*-hexane	10
7	Solvent-free	Trace

[a] All the reactions were carried out at 80 °C temperature except the reaction where n-hexane was used as a solvent, in case of n-hexane, the reaction temperature was 70 °C . Reaction conditions: 1 mmol 4-chlorobenzaldehyde (140 mg), 1 mmol 2-naphthol (144 mg), 1 mmol malononitrile (66 mg) and 40 mg catalyst. Solvent-free reaction was carried out at 100 °C.

[b] Isolated yields.

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Table 3. Synthesis of 2-amino-4*H*-chromenes under various catalysts and reaction conditions.

Entry	**Catalyst**	**Temperature (°C)**	**Yield[a,b] (%)**
1	No catalyst	25	NR
2	No catalyst	80	Trace
3	Piperidine	80	46
4	Pyridine	80	40
5	Imidazole	80	48
6	*tris*(2-aminoethyl)amine	80	35
7	TPOP-2	80	85

[a] Reaction conditions: 1 mmol 4-chlorobenzaldehyde (140 mg), 1 mmol resorcinol (110 mg), 1 mmol malononitrile (66 mg), 40 mg catalyst TPOP-2 and all the reactions are carried out for 6 h.

[b] Isolated yields

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Caption for figures

Figure 1 Wide angle power XRD pattern of triazine-based porous organic polymer TPOP-2.

Figure 2 N_2 adsorption/desorption isotherm at 77 K and corresponding pore size distribution (shown in inset, employing NLDFT method) plot of TPOP-2. Filled circles represent adsorption points and empty ones represent desorption points.

Figure 3 HR TEM images of TPOP-2 (A and B) and FE SEM images of TPOP-2 (C and D).

Figure 4 FTIR spectrum of TPOP-2 (black line) and the reused organocatalyst after fourth reaction cycle (green line).

Figure 5 TG and DTA profiles of TPOP-2

Figure 6 Network bonding of the porous polymer TPOP-2 and its ^{13}C CP-MAS NMR spectrum. The signals marked by '*' symbol are assigned due to the spinning side bands.

Figure 7 Temperature programmed desorption of CO_2 profile of TPOP-2.

Figure 8 Variation of the amount of catalyst in the one pot three component condensation reaction over TPOP-2.

Figure 9 Effect of temperature on the one-pot three component condensation reaction.

Figure 10 Catalytic activity of TPOP-2 organocatalyst: Reaction 1: reaction of 4-bromobenzaldehyde, resorcinol and malononitrile. Reaction 2 : reaction of 4-chlorobenzaldehyde, 2-naphthol and malononitrile.

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Figure 1 [Kundu and Bhaumik]

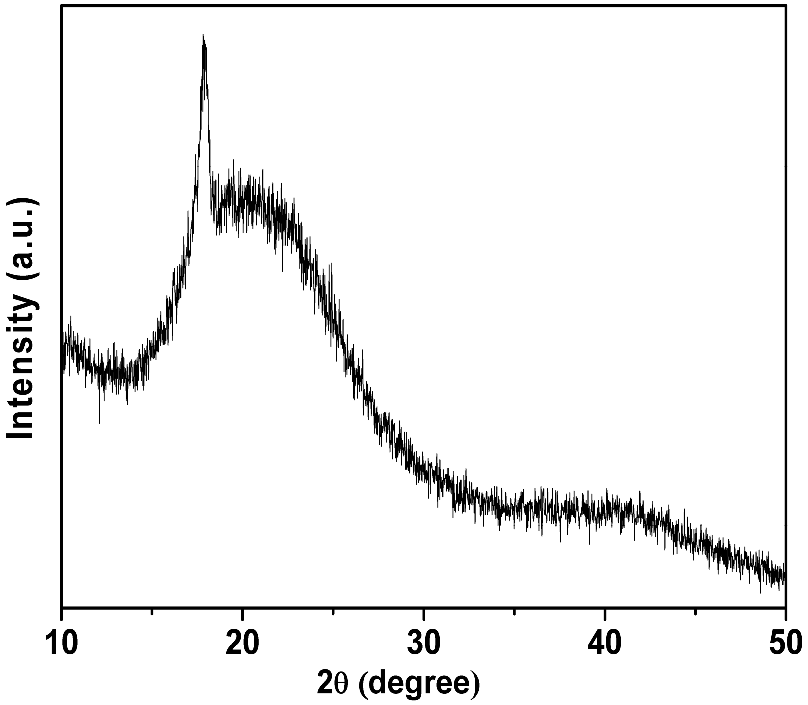

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Figure 2 [Kundu and Bhaumik]

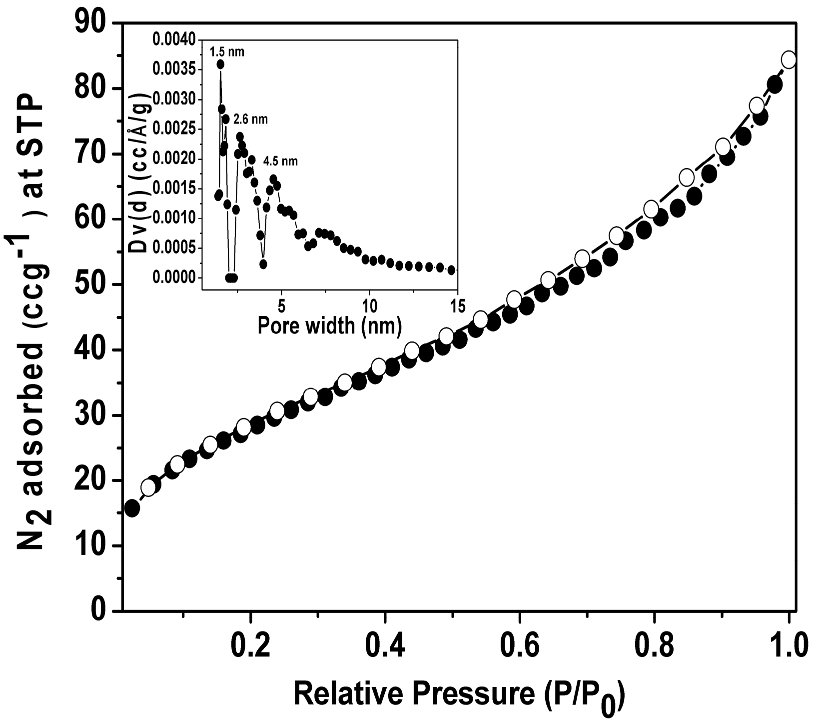

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Figure 3 [Kundu and Bhaumik]

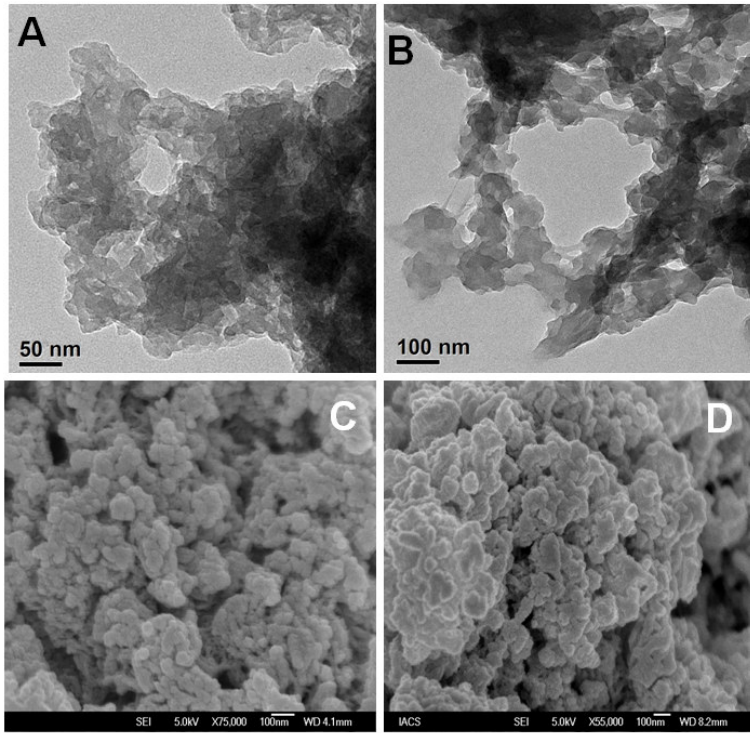

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Figure 4 [Kundu and Bhaumik]

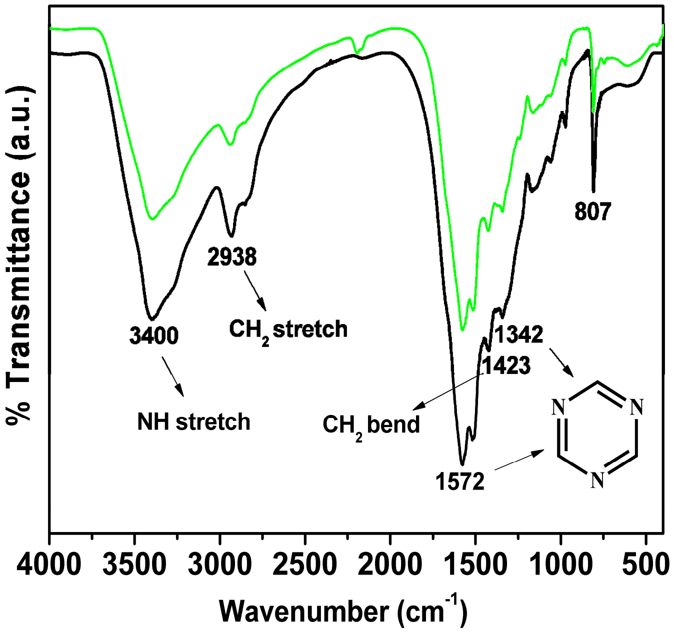

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Figure 5 [Kundu and Bhaumik]

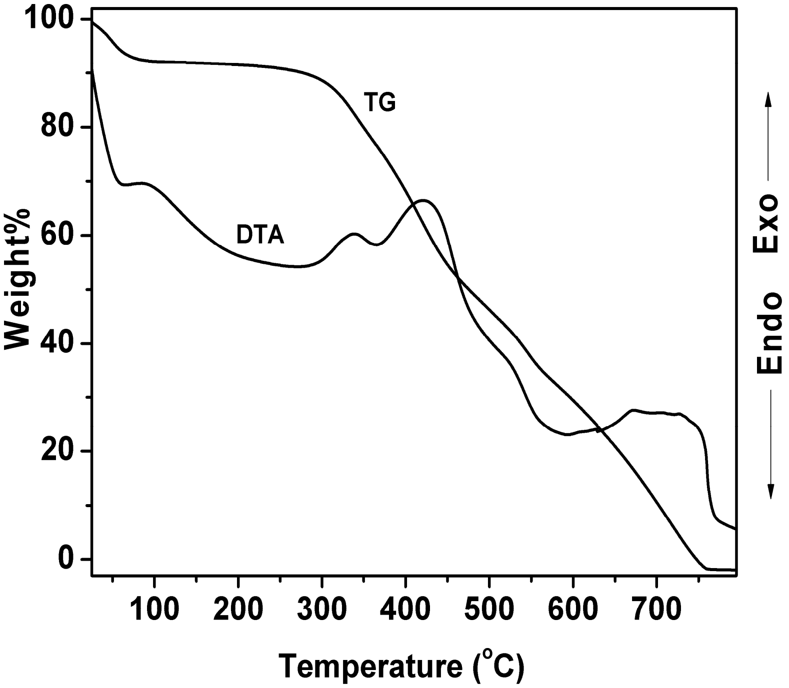

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Figure 6 [Kundu and Bhaumik]

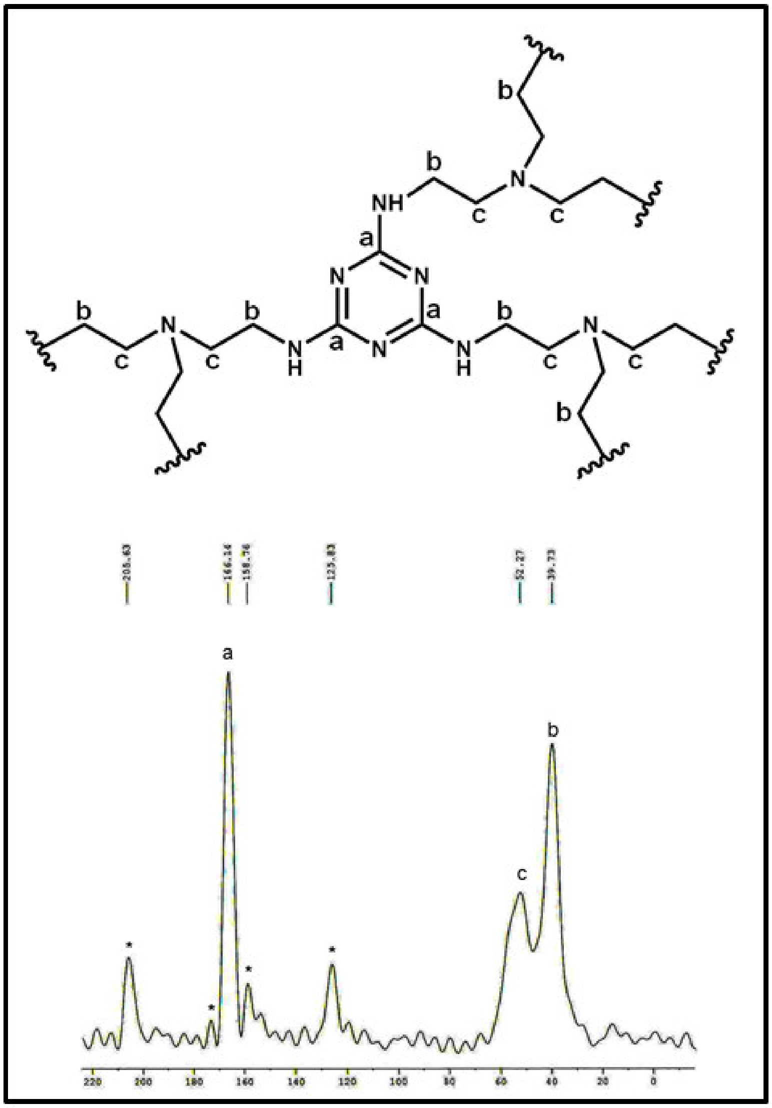

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Figure 7 [Kundu and Bhaumik]

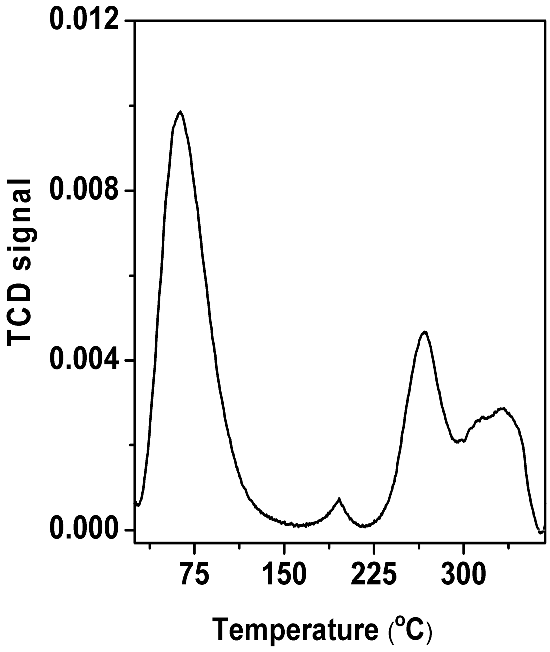

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Figure 8 [Kundu and Bhaumik]

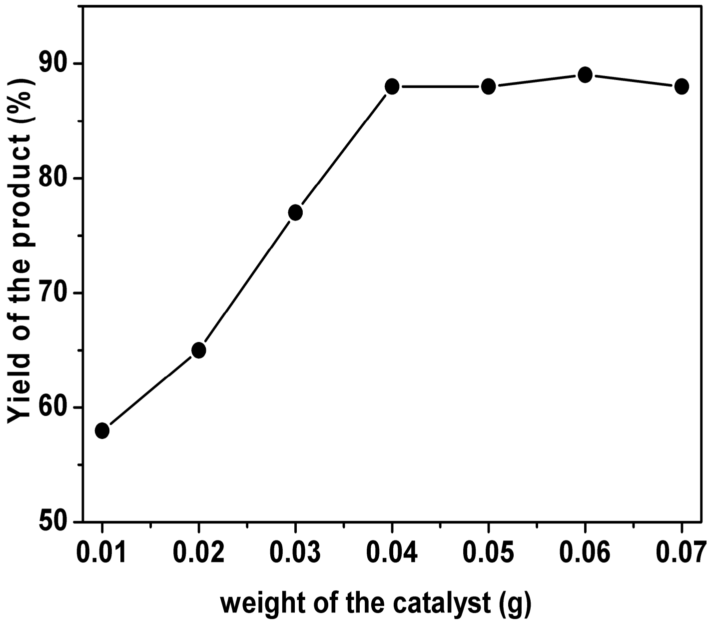

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Figure 9 [Kundu and Bhaumik]

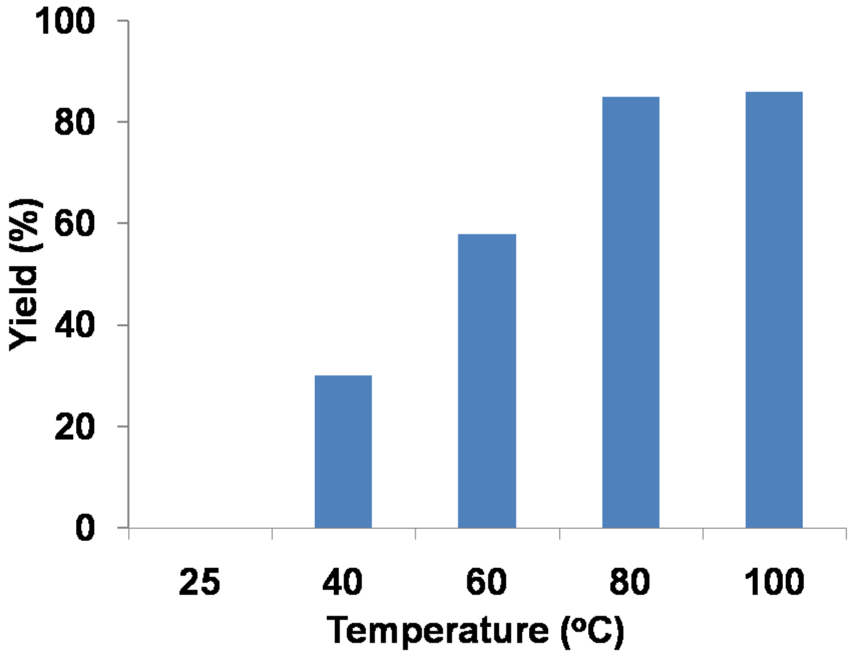

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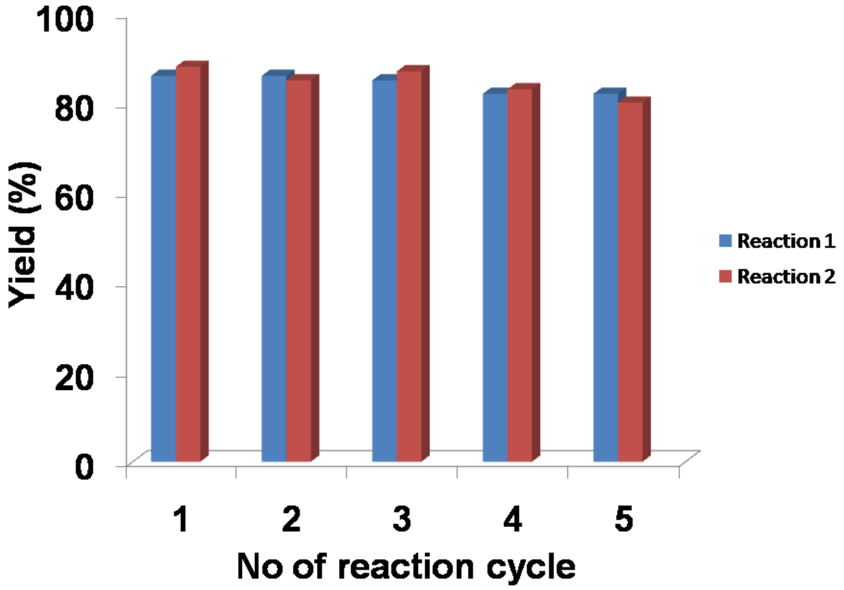
Figure 10 [Kundu and Bhaumik]



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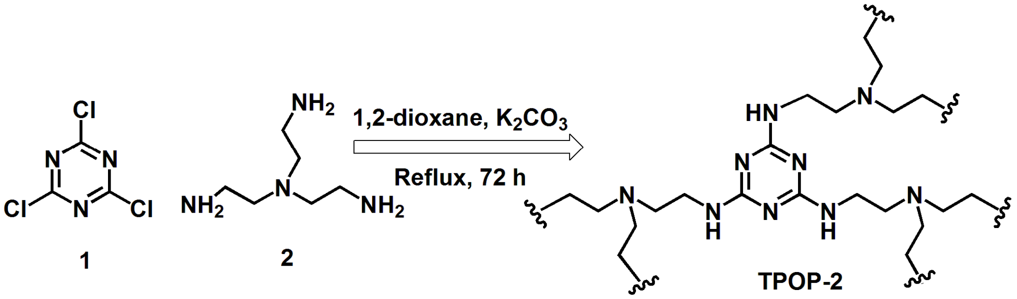
Scheme 1 [Kundu and Bhaumik]



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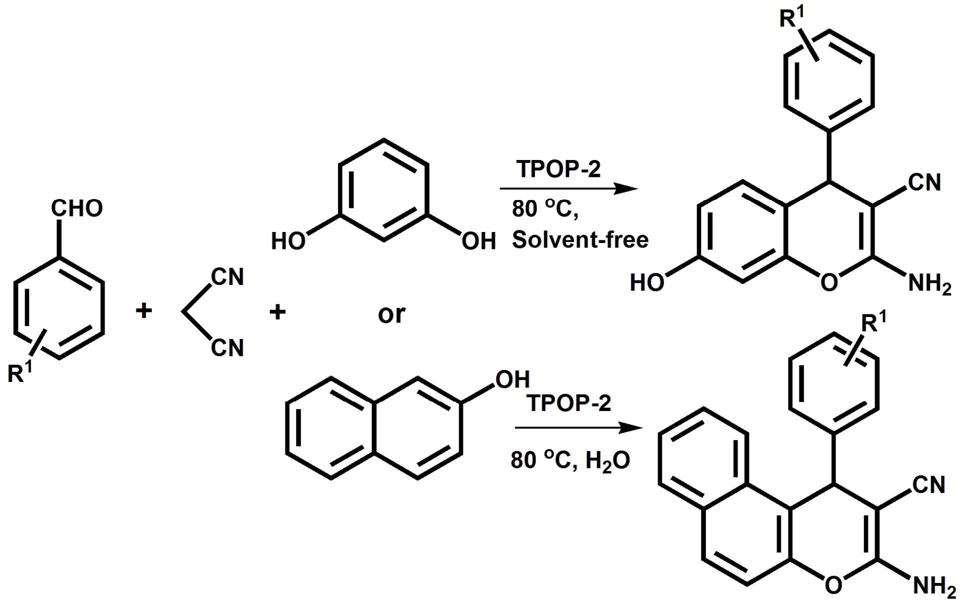
Scheme 2 [Kundu and Bhaumik]



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