Study on the synthesis of 1,3,5-triazinane derivatives on copper-ferrite nanoparticles catalyst

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Abstract. A high efficient method for the synthesis of 1,3,5-triaryltriazinane derivatives is developed by the condensation reaction of amines and formaldehyde followed by spontaneous cyclotrimORIZATION using CuFe₂O₄ NPs as an environmentally benign catalyst at room temperature. The copper ferrite was easily separated, reused in good repetitive catalytic performance by simple filtration or external magnet. This process was efficient and compatible with wide range of amines to afford a direct access to nitrogen containing compounds in excellent yields up to 99% and high selectivity.

1. Introduction
The copper-ferrite nanoparticles are synthesized from inexpensive commercially available materials and characterized by physic-chemical tools as well as SEM, TEM, TGA… [1]. Amongst ferrite nanoparticles CuFe₂O₄ has emerged as a promising materials due to its notable physical and chemical properties such as potential magnetic materials [2], stability and environmentally recycle catalyst in wide range of organic synthesis including biological active molecules [3-5]. The increased interest in nitrogen containing heterocycles has led to the development of novel medicinal agents and new strategies in drugs discovery. The synthesis of nitrogen containing compounds and their derivatives provides unlimited potential for creating novel pharmacologically active lead compounds for use as therapeutics [6]. 1,3,5-triaryl triazinanes have emerged as an important target molecule for chemists due to their therapeutic and pharmacological properties such as antituberculosis [7], antimicrobial [8], antifungal [9] anticancer [10], antioxidant and cytotoxicity [11, 12], anti malarial [13], corrosion inhibitor for oil and gas industry [14]. They also serve as key intermediates for synthesis of α- and β-amino esters, natural alkaloids [15], etc. A number of synthesis methods to prepare these triazinane compounds have been described in the past few years. All of these methods have certain limitations such as tedious procedures, long reaction time, harsh reaction conditions, low yield or microwave activation. Therefore, further studies are still necessary for the versatile, simple, and eco-friendly process. In recent years, the development of efficient and environmentally benign process or methodologies for widely used recycle catalyst is one of the major challenges to chemists in organic synthesis. In continuation of these developments, herein, we wish to report for the first time a highly efficient and green protocol of synthesis of 1,3,5-trisubstituted triazinanes using CuFe₂O₄ NPs as the
recyclable catalyst.

2. Experimental

All reagents were obtained commercially and used without further purification. All reactions have been carried out under a nitrogen atmosphere and dry conditions. The reaction mixtures have been magnetically stirred with teflon stirring bars, and the temperatures were measured externally. All the reactions have been monitored by thin layer chromatography (TLC), carried out on 0.25 mm Merck silica gel plates (60 F254). The eluents used were mixtures of n-pentane and ethyl acetate (EtOAc), with detection by UV light, or a KMnO4 staining solution. Acros silica gel (60, particle size 0.040–0.063 mm) was used for column chromatography. Infrared spectrum has been recorded with Spectrum Two, Perkin Elmer. The nuclear magnetic resonance (NMR) spectra have been recorded with Bruker Avance 500 MHz spectrometers. 1H NMR spectra: δ (H) is given in ppm relative to tetramethylsilane (TMS), using δ (CDCl3) = 7.26 ppm as internal reference. 13C NMR spectra: δ (C) is given in ppm relative to TMS, using δ (CDCl3) = 77.0 ppm as internal reference. Multiplicities were designated as singlet (s), doublet (d), triplet (t), quadruplet (q), quintuplet (q), multiplet (m) or br (broad).

Synthesis of copper-ferrite catalyst. The procedure to prepare CuFe2O4 was similar to that previously reported [16]. In a typical hydrothermal preparation, a solution of Cu(NO3)2 (1 eq) and Fe(NO3)3 (2 eq) in distilled water at room temperature was stirred for 15 minutes for a better homogeneity, adjusting pH to 10 with solution NaOH 0.8 M and introduced in a teflon lined steel autoclave, then kept at 100°C for 24h. The precipitate, a dark brown powder, was filtered then washed with distilled water. The desired copper-ferrite catalyst was obtained after calcining at 800°C for 5h.

General procedure for the synthesis of 1,3,5-triaryl triazinane derivatives (3a-n). A dry 50 mL flask was charged with aromatic amines 1a-n (5.0 mMol, 1eq) and aqueous formaldehyde 2 (15.0 mMol, 3eq) in C2H5OH and the reaction mixture was stirred magnetically at room temperature for the 1h. After completion of the reaction as indicated by (TLC), mixture reaction was filtered to remove catalyst and then cold water (5 ml) was added to solution and stirred for 5 min. The solid precipitate was filtered, washed with water and dried to furnish pure 1,3,5-triaryl triazinanes (3a-n).

(3a) 1,3,5-triphenyl-1,3,5-triazinane. White Solid; (Yield: 98%); mp 143-145°C; IR (cm−1): 3036; 2848; 1594; 1578; 1160; 1H NMR (500 MHz, CDCl3): δ ppm 4.82 (s, 6H), 7.18 – 6.73 (m, 15H); 13C NMR (126 MHz, CDCl3): 148.3, 126.7, 120.1, 112.9, 73.2. HRMS (ESI) m/z: 316.2 [M+H]+.

(3b) 1,3,5-tris(4-methoxyphenyl)-1,3,5-triazinane. White Solid; (Yield: 99%); mp 131-133 °C; IR (cm−1): 3039, 2836, 1602, 1512, 1178, 836, 1602, 1512, 1178, 832, 630; 1H NMR (500 MHz, CDCl3): δ ppm 3.62 (s, 9H), 4.79 (s, 6H), 7.12 – 6.68 (m, 12H); 13C NMR (126 MHz, CDCl3): 149.1, 123.4, 117.6, 114.3, 69.9, 55.2. HRMS (ESI) m/z: 406.2 [M+H]+.

(3c) 1,3,5-tris(4-chlorophenyl)-1,3,5-triazinane. White Solid; (Yield: 96%); mp 132-134 °C; IR (cm−1): 3038, 2842, 1603, 1501, 1147, 824, 632; 1H NMR (500 MHz, CDCl3): δ ppm 4.77 (s, 6H), 7.08 – 6.85 (m, 12H); 13C NMR (126 MHz, CDCl3): 147.1, 129.2, 126.4, 119.6, 68.7.

(3d) 1,3,5-tris(4-bromophenyl)-1,3,5-triazinane. White Solid; (Yield: 95%); mp 168-170 °C; IR (cm−1): 3031, 2834, 1598, 1500, 1157, 832, 630; 1H NMR (500 MHz, CDCl3): δ ppm 4.76 (s, 6H), 7.12 – 6.83 (m, 12H); 13C NMR (126 MHz, CDCl3): 147.3, 132.2, 119.3, 113.7, 68.4.

(3e) 1,3,5-tris(4-fluorophenyl)-1,3,5-triazinane. White Solid; (Yield: 93%); mp 160-162 °C; IR(cm−1): 1609; 1506; 3039; 2862; 1219; 1H NMR (500 MHz, CDCl3) δ ppm 6.92 – 6.83 (m, 12H), 4.70 (s, 6H); 13C NMR (126 MHz, CDCl3): 148.0, 134.3, 119.9, 114.5, 68.7.

(3f) 1,3,5-tri-p-toly1-1,3,5-triazinane. White Solid; (Yield: 96%); mp 130-132 °C; IR (cm−1): 3048, 2973, 2868, 1615, 1517, 1154, 846; 1H NMR (500 MHz, CDCl3) δ ppm 6.97 (d, J = 8, Hz, 6H), 6.86 – 4.69 (m, 12H), 2.18 (s, 9H); 13C NMR (126 MHz, CDCl3): 149.3, 125.4, 119.0; 112.9, 72.1, 20.9.

(3g) 1,3,5-tri-m-toly1-1,3,5-triazinane. White Solid; (Yield: 87%); mp 128-130 °C; IR (cm−1): 3044, 2885, 1598, 1496, 1267, 769, 691; 1H NMR (500 MHz, CDCl3) δ ppm 7.05 – 7.01 (m, 3H), 6.83 – 6.78 (m, 6H), 5.41 (s, 6H), 2.27 (s, 9H); 13C NMR (126 MHz, CDCl3): 149.5, 130.1, 129.8, 128.6, 119.5, 117.1, 114.3, 83.2, 22.1.

(3h) 1,3,5-tri-o-toly1-1,3,5-triazinane. White Solid; (Yield: 76%); mp 118-120 °C; IR (cm−1): 3032, 2934, 1591,
starting materials showed no diffraction peaks.

(3i) 1,3,5-tri(octyl)-1,3,5-triazinane. White Solid; (Yield: 95%); mp 118-120 ºC; IR (cm⁻¹): 2980, 2922, 1087, 726; ¹H NMR (500 MHz, CDCl₃): δ ppm 7.12 – 7.08 (m, 3H), 7.02 – 6.86 (m, 3H), 6.56 – 6.45 (m, 6H), 5.41 (s, 6H), 2.12 (s, 12H); ¹³C NMR (125 MHz, CDCl₃): 151.2, 132.8, 131.4, 126.9, 124.3, 111.3, 84.7, 17.9.

The XRD pattern of the calcined sample is shown that the XRD result match with the literature data.

(3k) 1,3-bis(tert-butylsulfinyl)-5-octyl-1,3,5-triazinane. White Solid; (Yield: 90%); mp 148-150 ºC; IR (cm⁻¹): 2959, 2870, 1061, 724; ¹H NMR (500 MHz, CDCl₃): δ ppm 3.86 (s, 2H), 3.62 (s, 4H), 2.48 (t, J = 7.1 Hz, 2H), 1.36 – 1.28 (m, 28H), 0.89 (J = 7.1 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): 78.5, 76.3, 58.9, 53.2, 31.9, 29.3, 27.8, 27.3, 22.9, 14.1.

(3l) 1-octyl-3,5-bis(phenylsulfonyl)-1,3,5-triazinane. White Solid; (Yield: 92%); mp 168-170 ºC; IR (cm⁻¹): 3031, 2834, 1598, 1500, 1157, 832, 726, 630; ¹H NMR (500 MHz, CDCl₃): δ ppm 7.71 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 4.78 (s, 1H), 4.21 (s, 1H), 0.89 (t, J = 7.1 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃): 143.9, 136.1, 129.9, 129.6, 127.2, 127.0, 65.6, 50.3, 31.9, 31.8, 29.4, 29.3, 27.8, 27.4, 26.9, 22.7, 21.5, 14.2.

(3m) 1-octyl-3,5-ditosyl-1,3,5-triazinane. White Solid; (Yield: 91%); mp 186-188 ºC; IR (cm⁻¹): 3031, 2834, 1598, 1500, 1157, 832, 724, 630; ¹H NMR (500 MHz, CDCl₃): δ ppm 7.87 – 7.80 (m, 4H), 7.61 (t, J = 7.4 Hz, 2H), 7.54 (t, J = 7.6 Hz, 4H), 4.83 (s, 2H), 4.24 (s, 4H), 2.25 – 2.10 (m, 2H), 1.38 – 1.12 (m, 11H), 1.05 (d, J = 7.0 Hz, 2H), 0.89 (t, J = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃): 138.2, 133.1, 129.3, 127.1, 65.6, 60.8, 50.3, 31.8, 29.3, 29.2, 27.4, 26.8, 22.7, 14.1.

(3n) 1,3-bis(4-(tert-butyl)phenylsulfonyl)-5-octyl-1,3,5-triazinane. White Solid; (Yield: 89%); mp 188-190 ºC; IR (cm⁻¹): 3031, 2834, 1598, 1500, 1157, 832, 630; ¹H NMR (500 MHz, CDCl₃): δ ppm 7.76 (d, J = 8.6 Hz, 4H), 7.53 (d, J = 8.5 Hz, 4H), 4.83 (s, 2H), 4.24 (s, 4H), 2.16 (dd, J = 8.7, 6.4 Hz, 2H), 1.35 (s, 19H), 1.29 – 1.10 (m, 12H), 1.00 (d, J = 7.3 Hz, 2H), 0.88 (t, J = 7.1 Hz, 4H); ¹³C NMR (126 MHz, CDCl₃): 156.9, 136.1, 127.0, 126.2, 65.5, 60.9, 50.3, 35.2, 31.8, 31.1, 29.4, 27.5, 26.9, 22.7, 14.1.

3. Results and discussion

3.1. Characterization

Initially, the copper-ferrite was synthesized from Cu(NO₃)₂, Fe(NO₃)₃ and NaOH in distilled water in autoclave by hydrothermal method. The desired dark brown powder was achieved in 80% yield after calcining at 800°C for 5h. This material was characterized by X-ray diffraction, SEM and magnetic property. The XRD pattern of the calcined sample is shown in Figure 1, the mixture of starting materials showed no diffraction peaks in the X-ray powder diffractogram and the reflection planes (111), (200), (311), (222), (400), with Miller indices at 2θ = 19.2°, 30.1°, 35.6°, 37.2° and 42.9° respectively, indicated that crystalline CuFe₂O₄ particles have been established and the XRD pattern of the calcined sample is shown that the mixture of starting materials showed no diffraction peaks and the XRD result match with the data reported in literature [16,17].
Figure 1. XRD pattern of the calcined CuFe$_2$O$_4$

The average particle size was 36 nm determined by using Scherrer formula as follows (Calculated from the main peak (311)):

$$D = \frac{0.9\lambda}{B\cos\theta}$$

Where $D$ is the crystalline size (nm), $B$ in the full width of the diffraction line at half of the maximum intensity, $\lambda$ is the X-ray wavelength of CuK\textit{\alpha} = 0.154 nm and $\theta$ is the Bragg angle.

The SEM image of CuFe$_2$O$_4$ nanocrystallines are shown in Figure 2, the particles were spherical in shape with sizes ranging from 150-250 nm as a porous structure. Therefore, the material could be a promising material with potential activities as a heterogeneous catalyst.

Figure 2. SEM image of CuFe$_2$O$_4$ calcined at 800\degree C

On the other hand, the magnetic moment of the CuFe$_2$O$_4$ NPs increases rapidly in the magnetic field from 0 - 15000 H(Oe) and then slowly increases to about 5000 H(Oe), it is almost saturated. The achievement of saturated magnetic field of the material is relatively high due to the small particle size and the CuFe$_2$O$_4$ sample achieved a magnetization of 28 emu/g at 10000 Oe (Figure 3). This property shows that with high magnetic field intensity, the catalytic nanoparticles are easily dispersed and catalyzed by the external magnetic field.
3.2. Catalytic study

Initial investigation involved developing the condensation reaction between aniline 1a and formaldehyde 2 at the molar ratio of 1:1 as model reaction, with the expected production of triazinane derivatives (Scheme 1). In this regard, we attempted to determine the optimum conditions by examining the influence of molar ratio, concentration of catalyst, reaction time and nature of amine.

Firstly, reaction was carried out in presence of CuFe$_2$O$_4$ at 10 mol% as a catalyst. After stirring in CH$_3$OH at room temperature until disappearance of the starting materials (1.0 hour, monitoring reaction by TLC) the desired product 3a was obtained in 85% yield. Previously, a variety of different catalysts were employed for reaction between aniline 1a and formaldehyde 2 at the identical condition, including Cu(NO$_3$)$_2$, Fe(NO$_3$)$_2$, Fe(NO$_3$)$_3$, CuO, FeO, Fe$_3$O$_4$, Fe$_2$O$_3$ and the mixture of CuO, Fe$_2$O$_3$ (molar ratio 1:1). Unfortunately, in all cases, only imine compound was obtained with no trace amount of the desired product 3a being detected. It should be noted that no reaction occurred in the absence of the CuFe$_2$O$_4$ and the copper-ferrite NPs have been shown the potential and specific catalytic activity for the cyclotrimerization reaction.

Scheme 1. Synthesis of compound 3a

To optimize this reaction, a series of solvents to screen this reaction were investigated such as CH$_3$OH, C$_2$H$_5$OH, i-C$_3$H$_7$OH, n-C$_3$H$_7$OH, acetone, THF, CH$_3$Cl$_2$, EtOAc (Table 1).

| Solvent     | Yield of 3a |
|-------------|-------------|
| CH$_3$OH    | 85%         |
| C$_2$H$_5$OH| 96%         |
| i-C$_3$H$_7$OH| 64%    |
| n-C$_3$H$_7$OH| 68% |
| acetone     | 56%         |
| THF         | 46%         |
| CH$_3$Cl$_2$| 18%         |
| EtOAc       | 30%         |

The results were shown in Table 1, the solvent could accelerate or slow down the reaction, depending on the nature of the solvent and C$_2$H$_5$OH was the best solvent for this reaction at room temperature, triphenyl triazinane was obtained in 96% isolated yield after 1h of reaction. Important factor that should
be seriously addressed when investigating the cyclotrimerization reaction is the effect of the catalyst concentration on the reaction yield. The reaction was then stirred in C$_2$H$_5$OH at room temperature, at the catalyst concentration of 5 mol%, 10 mol% and 15 mol%, respectively.

Table 2. Effect of the catalyst concentration on the cyclotrimerization reaction yield

| Catalyst concentration | 5 mol% | 10 mol% | 15 mol% |
|------------------------|--------|---------|---------|
| Yield of 3a             | 60%    | 96%     | 98%     |

It was found that the yield reaction was significantly affected by the catalyst concentration. The cyclotrimerization reaction using 5 mol% catalyst proceeded difficulty, affording only 60% yield after 1h stirring at room temperature. As expected, increasing the catalyst concentration led to a dramatic enhancement in the reaction rate. A yield of 96% was obtained after 1h for the using 10 mol% catalyst, with this value could be slightly improved to 98% for the case of 15 mol% (Table 2).

On the other hand, the influence of molar ration between amine 1 and formaldehyde 2 was also studied. The reaction was carried out at room temperature in C$_2$H$_5$OH using 10 mol% CuFe$_2$O$_4$ catalyst at the amine: formaldehyde molar ratio of 1:1, 1:2, 1:3 and 1:4 respectively. It was observed that the reagent molar ratio also exhibited a significant effect on the reaction yield. It seems that the reaction gives the best yield up to 96% after stirring 1h at the molar ratio amine: formaldehyde of 1:3 (Table 3).

Table 3. Effect of the amine: formaldehyde molar ratio on the trimerization reaction yield

| Molar ratio | 1:1 | 1:2 | 1:3 | 1:4 |
|-------------|-----|-----|-----|-----|
| Yield of 3a | 78% | 89% | 96% | 94% |

In the view of green chemistry, it would be expected that the solid catalyst should be facilely separated from the mixture reaction and could be recovered and reused several times before decreasing or even losing catalytic activities completely. Therefore, it was decided to investigate the recoverability and reusability of the copper-ferrite in the trimerization reaction. After each run, the catalyst was easily separated from mixture reaction by simple filtration, washed with ethanol then dried at 100°C for 6h and then used it in further reaction under identical conditions to those of the first time. Experimental results showed in the Table 4, it was observed that a conversion of 83% was still achieved in the 5th run, the CuFe$_2$O$_4$ was completely compatible for this reaction and it could be recycled several times with a slight loss of catalytic activity.

Table 4. Effect of reusability CuFe$_2$O$_4$ in catalytic activity on the trimerization reaction

| Time of recycle | 1$^{st}$ | 2$^{nd}$ | 3$^{rd}$ | 4$^{th}$ | 5$^{th}$ |
|-----------------|---------|---------|---------|---------|---------|
| Yield of 3a     | 96%     | 94%     | 90%     | 86%     | 83%     |

The study was then extended to the trimerization reaction of formaldehyde with different aryl amines in the presence of CuFe$_2$O$_4$ 10 mol% as catalyst. The reaction was carried out for 1h at room temperature in C$_2$H$_5$OH, at the amine: formaldehyde molar ratio of 1:3. Experimental results shown that the nature of amine structure exhibited a significant effect on the reaction yield. It is worth noting that excellent results are obtained with aniline and substituted derivatives with electron-withdrawing, as well as electron-donating groups (Table 5). The trimerization reaction of aryl amines could afford up to 99%
yield after stirring 1h at room temperature (entry 2).

Table 5. Synthesis of compound 3a-h

| Entry | Aryl amine 1 | Triaryl triazinane 3 |
|-------|--------------|---------------------|
|       | No. | R | No. | Yield (%) |
| 1     | 1a  | H | 3a  | 98        |
| 2     | 1b  | 4-OMe | 3b | 99        |
| 3     | 1c  | 4-Cl | 3c | 96        |
| 4     | 1d  | 4-Br | 3d | 95        |
| 5     | 1e  | 4-F | 3e | 93        |
| 6     | 1f  | 4-CH₃ | 3f | 96        |
| 7     | 1g  | 3-CH₃ | 3g | 87        |
| 8     | 1h  | 2-CH₃ | 3h | 76        |

Finally, the next step was the extension of this reaction to the other amines and check its scope and limitation. For this purpose, the reaction was carried out at standard condition: amine (1eq), formaldehyde (3eq) with CuFe₂O₄ (10 mol%) stirring for 1h at room temperature in C₂H₅OH. An excellent yield was also obtained with a long-chain alkylamine (3h). Unfortunately, the reaction was not compatible with sulfinamide or sulfonamides, no trace of desired product was observed in stirring mixture of amide, formaldehyde in presence of CuFe₂O₄ 10 mol% as catalyst at room temperature. It should be noted that no reaction occurred in the case of amines with bulky sulfinyl or sulfonyl groups. To further investigate, the mixture of octylamine and sulfinamide (sulfinyl amine) or sulfonamide (sulfonyl amine), molar ratio amine: amide 1:1, was stirring with formaldehyde in presence of CuFe₂O₄ 10 mol% as catalyst for 1h at room temperature in C₂H₅OH. This reaction worked indeed very well, the desired triazinanes were obtained in excellent yields (Scheme 2). This model of reaction is in agreement with the reported data in literature [18], and the CuFe₂O₄ NPs shown potential catalytic activities more efficiently than Mg(ClO₄)₂ in the view of easily work-up, simple purification of desired products, high yield, mild reaction condition, and environmentally benign process.
Scheme 2. Synthesis of triazinanes from formaldehyde, octylamine and sulfinamide or sulfonamides

4. Conclusion

In summary, we have reported a new efficient procedure to synthesis of 1,3,5-triaryl triazinane compounds. Using 10 mol% of CuFe₂O₄ NPs as a catalyst, the methodology was efficient and compatible for versatile arylamines, alkyl amine or mixture of alkyamine with sulfanyl amine or sulfonyl mines as starting materials. We have found that the optimal condition of this reaction is at room temperature, in C₂H₅OH as a solvent and at molar ration of amine: formaldehyde of 1:3, desired products were obtained in excellent yield up to 99%. It was evident that this modified pathway could be continued to extend for this reaction in the future.

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