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ARTICLE

A co-operative effect of visible light photo-catalysis and $CoFe_2O_4$ nanoparticles for green synthesis of furans in water

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A novel approach to poly-functionalized furan synthesis is disclosed via oxidative decarboxylative [3+2] cycloaddition using co-operative catalysis by visible light and $CoFe_2O_4$ nanoparticles at ambient reaction condition in water as solvent. Though, the reported method is efficient without catalyst in presence of visible light (70% yield in 4h at rt), the use of catalyst not only increases the yield (91%) but also accelerates the conversion rate (2h, rt).

One of the areas of green chemistry is the use of renewable energy source and to design a chemical process which reduces the use of hazardous chemicals in multi-step reactions. Photo-catalysis using LED light as visible light source has attracted much attention of synthetic chemists as a renewable energy source to promote chemical reactions involving electron transfers.[1] Selectivity in homogeneous catalysis is better but the difficulty of catalyst separation from the final product creates economic and environmental barriers. Alternatively, organic synthesis via magnetic attraction is more promising as they offer an added advantage of being magnetically separable, thereby eliminating the requirement of catalyst filtration after completion of the reaction. The preface of nanoparticles (NPs) could be a gorgeous to overcome the more than mentioned boundaries due to their exclusive properties of larger and highly reactive surface areas.[2-3] Very recently, metal ferrite NPs have been extensively applied as catalyst because of their Lewis acid and Lewis base nature and also redox properties on the surface.[4]

Polyfunctionalized furans represent an important class of five membered *o*-heterocycles ubiquitous in natural products, pharmaceuticals, agrochemicals and have been used in commercially important pharmaceuticals, drugs and natural products (Fig.1).[5] From chemical viewpoint, they served as building blocks as well as useful intermediates in organic synthesis; especially for preparation of aromatic, alicyclic and acyclic molecules.[6] These unique properties have triggered renewed interest to develop new synthetic methods which enable rapid access to furans.

Since the discovery of conventional Paal–Knorr[7] and Feist–Benary[8] methods, a good number of synthetic protocols have been developed for furan synthesis.[9-14] In most of the cases, construction of the furan ring is based on 3+2 (I),[9,10] 2+2+1 (II),[11] 4+1O (IV),[13] 4+1C (V)[14] intermolecular cycloaddition or intramolecular cycloaddition (III)[12] as represented in figure 2. The [3+2] two component coupling strategy reported for furan synthesis mainly involves acyclic ketones[9,10] and their derivatives, viz., cyclopropenyl ketones,[12c] β-acyloxy acetylenic ketones,[15a] allenyl ketones,[15b] o-alkoxyketones,[15c,d] α-aryloxyketones[15e] and α-diazocarbonyl as substrate.[10a] Furthermore, use of carboxylic acid has several advantages such as its ready availability, easy handling, environmentally benign properties and production of nontoxic CO_2 as the by product.[16] As a consequence, the development of new catalytic route for furan synthesis is still in demand and therefore, decarboxylative annulation using carboxylic acid is its atom economical alternative with reduced waste material.

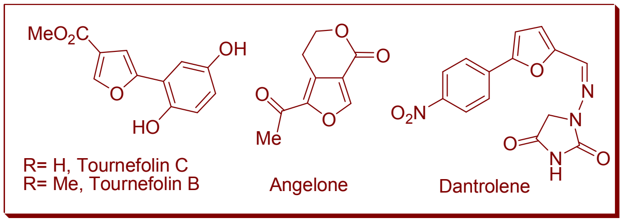

Figure 1. Some drugs and natural products with Furan motif.

Literature records only few reports on furan synthesis through a decarboxylative cyclization between ketones and α,β-unsaturated carboxylic acids.[10f,l] However, all of these reactions undergo from one or more disadvantage such as stoichiometric amount of catalyst, expensive reagents, harsh reaction conditions, high temperature, long reaction time, involved oxidant, lower isolated yields and also sometimes no reusability of catalyst. Due to our interest in developing green chemistry protocols,[17] and new C-C bond forming reaction for

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† Electronic supplementary information (ESI) available: Method for preparation of catalyst and compounds and their characterization details are given.

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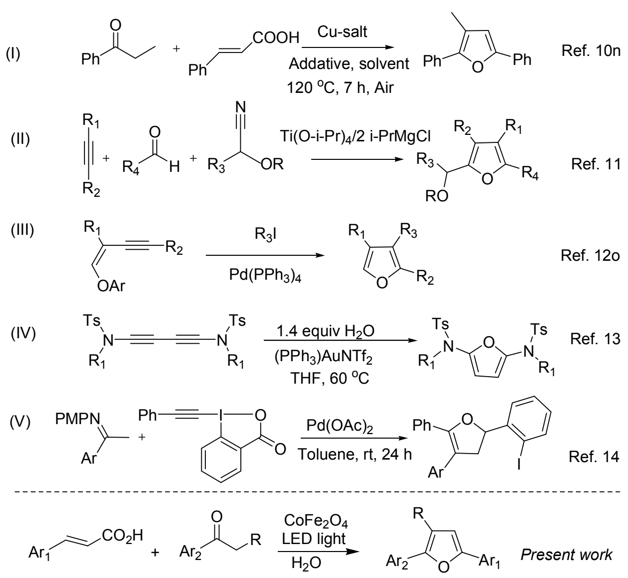
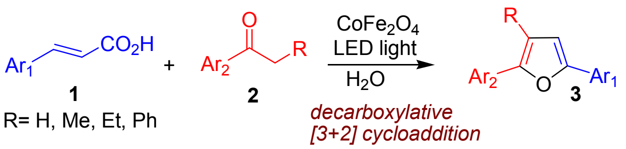


Figure 2. Different synthetic routes reported for synthesis of Furans **3**.



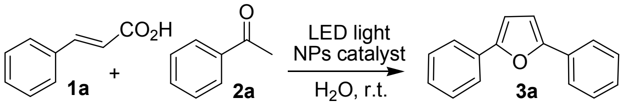
Scheme 1. Photo-catalytic decarboxylative [3+2] cycloaddition route to Furans **3**.

heterocyclic synthesis,[18] we herein, report an unprecedented green synthesis of polyfunctionalized furans via [3+2] cycloaddition between α,β-unsaturated carboxylic acid and ketone. The synthesis of target compound was affected by co-operative catalysis using $CoFe_2O_4$ and LED light as visible light source in the envisaged method (Scheme 1).

Very recently, we have reported the ferrite decorated graphene oxide as peroxide sensing probe.[19] In continuation, we anticipated exploiting the prepared GO/Fe_3O_4 as catalyst for synthesis of target molecule in the present investigation. To our surprise, it afforded the target furan, though the yield was not satisfactory (Table 1, entry 3). Then, we turned our attention to search the most efficient catalyst system for the present reaction and different NPs viz., $CoFe_2O_4$, CuO, $CuFe_2O_4$ and $NiFe_2O_4$ were screened in addition to GO/Fe_3O_4. However, $CoFe_2O_4$ has been found the most efficient catalyst system for the present investigation and was prepared by its reported method.[20]

The formation of $CoFe_2O_4$ NPs was confirmed by UV, XRD, SEM, EDX and TEM screening studies (Figure 3). The powder XRD pattern indicates $CoFe_2O_4$ NPs are single phases and have the cubic spinel structures with reflection planes at (220), (311), (222), (400), (422), (511), (440) (card JCPDS 22-1086) (Figure 3a). The average particle size of $CoFe_2O_4$ NPs was determined to be 28 nm, calculated from full width at half maxima (FWHM) at reflection (311) plane using Debye Scherrer formula. The average particle size was also confirmed by plotting size histogram (Figure 3e). SEM micrograph clearly shows the surface features of prepared $CoFe_2O_4$. Investigated particles are cubic in shape with a narrow size distribution and their particle sizes are 28 nm (calculated from XRD). It can also be seen that the particle agglomeration which indicates a good association between the particles together and further agglomeration was reduced. The increased surface area of $CoFe_2O_4$ is likely to be utilized for further catalysis application (Figure 3b). The EDX analysis showed that the presence of Co, Fe, and O elements (Figure 3d). The formation of cubic $CoFe_2O_4$ NPs was also supported from TEM image (Figure 3c). A UV-Visible spectrum of $CoFe_2O_4$ was taken and no absorption maximum was appeared (Figure 3f).[20b]

Table 1 Optimization reaction conditions for synthesis of furan **3a**.[a]



Entry	Catalyst (NPs)	Mole (%)	Time (h)	Yield (%)[b, c]
1	$CoFe_2O_4$	20	02	91
2	CuO	20	03	72
3	GO/Fe_3O_4	20	03	75
4	$CuFe_2O_4$	20	03	77
5	$NiFe_2O_4$	20	03	71
6	–	–	20	–[d]
7	–	–	04	70[e]
8	$CoFe_2O_4$	20	28	75[f]
9	$CoFe_2O_4$	15	02	82
10	$CoFe_2O_4$	25	02	91

[a] *Reaction conditions:* **1a** (0.5 mmol), **2a** (0.5 mmol), water: 5 mL, rt, in air. [b] Yield of isolated and purified products. [c] All compounds gave C and H analyses within ±0.37%, and spectral (^{1}H NMR, ^{13}C NMR and EIMS: *Electron Ionization Mass Spectroscopy* data). [d] In absence of catalyst and LED light. [e] Only in LED light without catalyst. [f] In the presence of catalyst only without LED light.

In our model experiment, cinnamic acid **1a** (0.5 mmol) and acetophenone **2a** (0.5 mmol) were taken as substrate and different NPs such as $CoFe_2O_4$, CuO, GO/Fe_3O_4, $CuFe_2O_4$ and $NiFe_2O_4$ as catalyst. The reaction mixture was stirred in water under the white LED light (7 W domestic white LED was used as the visible light source) for 2 h and the results are summarized in Table 1. Out of the tested catalysts, 20 mole % of $CoFe_2O_4$ gave the best yield of furan **3a** in 2 h (Table 1, entries 1-5). When the amount of the catalyst decreased from 20% to 15%, the yield of product **3a** reduced (Table 1, entries 1 and 9), but increasing the catalyst loading from 20% to 25% did not increase the yield of product **3a** (Table 1, entries 1 and 10). Next, we turned out attention to check the catalyst-free version of the envisaged reaction. Accordingly, an equimolar mixture of cinnamic acid **1a** and acetophenone **2a** was stirred in water (i) in absence of both i.e. the catalyst as well as LED light (Table 1, entry 6), (ii) only in presence of LED light without catalyst (Table 1, entry 7) and (iii) in the absence of LED light with catalyst only (Table 1, entry 8).

We found that the catalyst as well as LED light individually afforded the desired product, but the reaction required relatively more time with lower yield of final product (Table 1, entries 7 and 8). However, as anticipated, we found the best result when the catalyst was used in conjunction with the LED light in terms of excellent yield of **3a** and reducing the reaction

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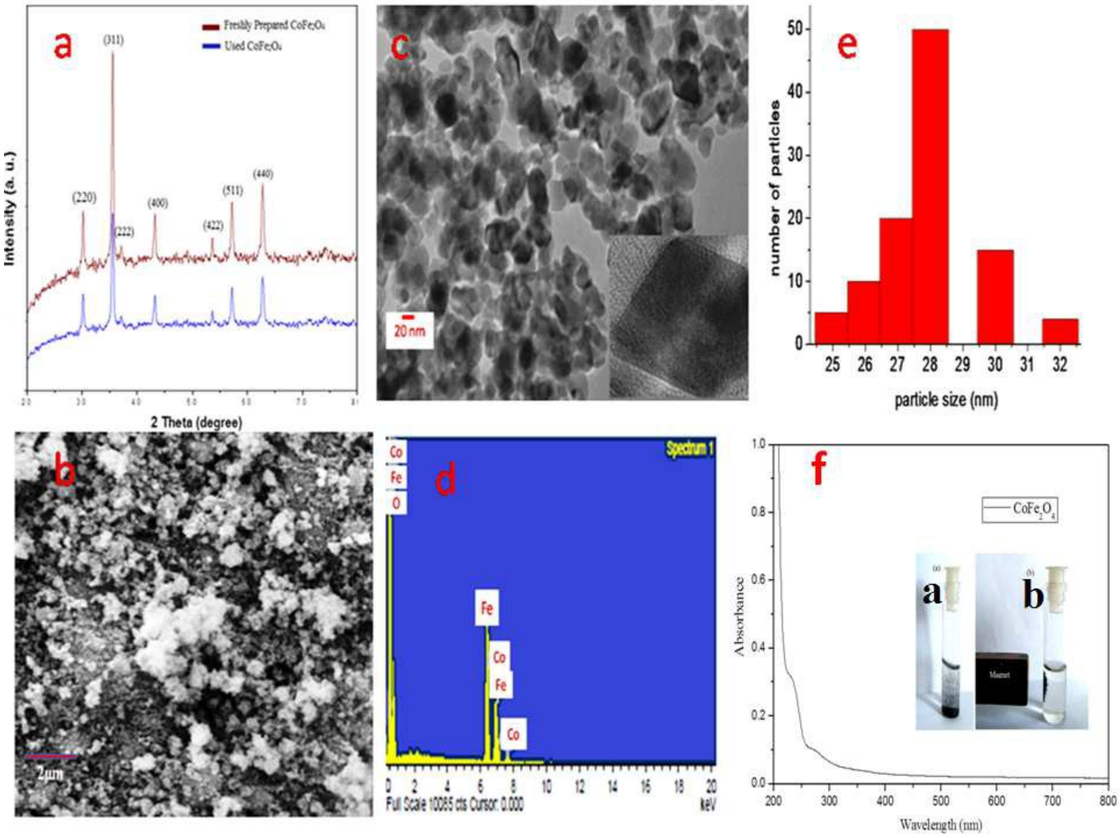

Figure 3. (a) Powder XRD of freshly prepared and after used $CoFe_2O_4$ NPs. (b) SEM image of $CoFe_2O_4$ NPs. (c) HR-TEM image shows cubic structure of $CoFe_2O_4$ NPs. (d) EDX analysis shows elemental compositions of $CoFe_2O_4$ NPs. (e) Particle size histogram. (f) UV-vis spectra of $CoFe_2O_4$ NPs (inset: showing magnetic behaviour).

time as well (Table 1, entry 1). We also performed the envisaged reaction in the dark condition to check the role of light but low yield (62%) of product **3a** was obtained. Next, the same reaction was undertaken in presence of TEMPO (a stable free radical) for confirmation of radical generation, but no product in catalyst-free condition was obtained which led to conclude that visible light is not effective in the presence of TEMPO for formation of **3a**. Thus, we relied upon the combined catalytic effect of $CoFe_2O_4$ and LED light and the present optimized synthesis is proficient by an equimolar mixture of cinnamic acid **1** and acetophenone **2** with $CoFe_2O_4$ (20 mole %) in water, in presence of white LED light for 2-3 h (Table 2). The present optimized synthesis is accomplished by taking different α,β unsaturated carboxylic **1** acids and ketones **2** afforded functionalized furan **3a-q** (Table 2). Total 17 products were synthesized in good to excellent yields with the best yield of **3** as 96% (Table 2, entry 5). The aryl alkyl ketones, such as substituted acetophenone, propiophenone, butyrophenone and 2-phenyl acetophenone reacted smoothly with α,β unsaturated carboxylic acids. However, we have found that substrates tolerated both EWG group (F, Cl, and Br) as well as EDG groups (Me, SMe and OMe) for the formation of **3** within 2-3 h with $CoFe_2O_4$ in mild reaction condition. All the synthesized compounds were characterized by their ^{1}H and ^{13}C NMR spectra.

We have also examined the recyclability and reusability of catalyst $CoFe_2O_4$ for the synthesis of 2,5-diphenylfuran **3a**. After completion of reaction, the $CoFe_2O_4$ was separated by solvent EtOAc (5 mL) was added to the reaction mixture and flask was stirred to completely dissolve the product. The $CoFe_2O_4$ NPs was recovered by attaching the external magnet to the walls of reaction flask, providing the clear solution which was decant to another flask. Then the recovered catalyst was washed carefully with water (2×2 mL) and ethanol (2×1 mL) and reused for subsequent reactions up to seven times without significant loss of catalytic activity (Figure 3a). The cubic morphology of reused catalyst was checked by XRD analysis which showed in morphology and size was not much change (the particles sizes increased from 28 to 35 nm as calculated from FWHM using Debye Scherrer formula), which may presumably be the reason for slightly decrease in yield of the products **3a**.

The formation of furan **3** is explained by tentative mechanism for the photocatalytic role of visible light shown in Scheme 2. Presumably, Co^{2+} is irradiated to excited state of Co^{2+*} using white LED light and this excited state is reductively

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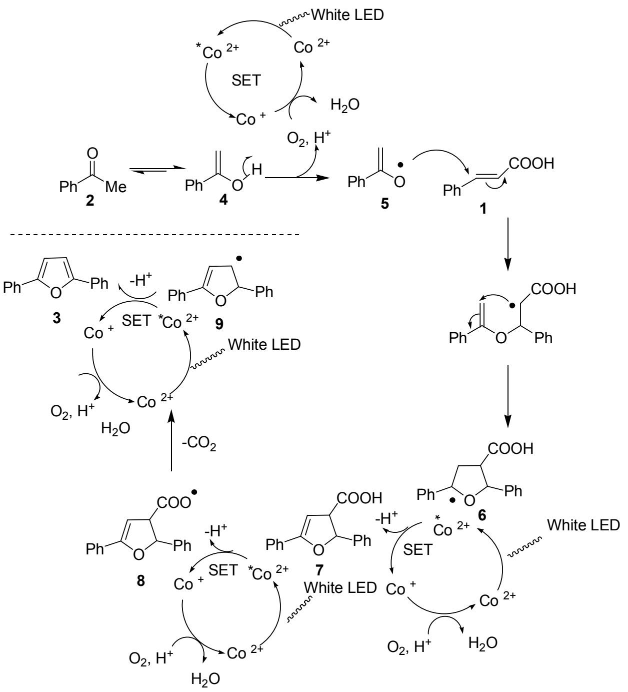
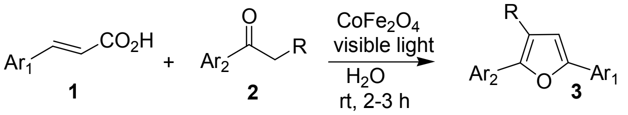


Scheme 2. Plausible mechanism for the photo-catalytic construction of Furan **3**.

Table 2 Optimization reaction conditions for synthesis of furan **3a**.[a]



Product	Ar_1	Ar_2	R	Time	Yield[b,c]
3a	Ph	Ph	H	2	91
3b	4-MeC_6H_4	Ph	H	2.5	89
3c	Ph	4-MeS-C_6H_4	H	3.0	84
3d	4-MeC_6H_4	2-MeC_6H_4	H	2.5	85
3e	Ph	Ph	Me	2.0	96
3f	Ph	4-MeC_6H_4	Me	2.5	85
3g	4-MeC_6H_4	Ph	Me	2.0	93
3h	4-MeOC_6H_4	Ph	Me	3.0	86
3i	4-FC_6H_4	Ph	Me	2.5	88
3j	4-ClC_6H_4	Ph	Me	2.0	91
3k	4-BrC_6H_4	Ph	Me	2.0	92
3l	4-MeC_6H_4	4-MeC_6H_4	Me	3.0	92
3m	Ph	Ph	Et	3.0	91
3n	4-ClC_6H_4	Ph	Et	2.0	89
3o	4-MeC_6H_4	Ph	Et	2.5	88
3p	4-MeC_6H_4	Ph	Ph	3.0	82
3q	4-ClC_6H_4	Ph	Ph	2.5	89

[a] *For detail, please see the experimental section.* [b] Yield of isolated and purified products. [c] All compounds gave C, H and O analyses within ±0.37%, and satisfactory spectral (^1H NMR, ^{13}C NMR and EIMS) data.

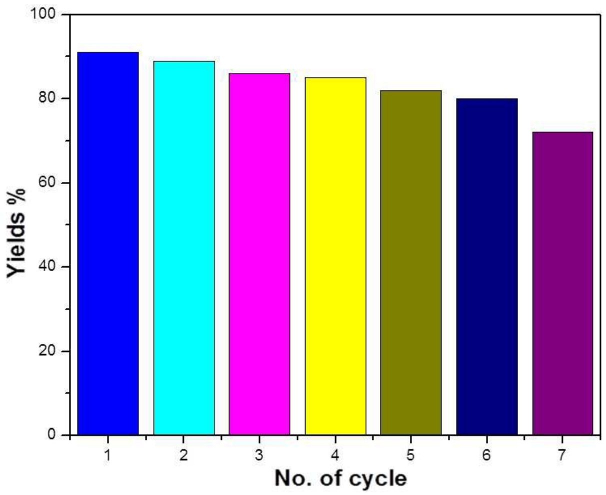


Figure 4. Recyclability of $CoFe_2O_4$ for the synthesis of 2, 5-Diphenylfuran **3a.**

quenched by enol form of acetophenone **4** with the simultaneous generation of vinyloxy radical **5**, which reacts with substrate **1** affording a cyclic radical **6**. Presumably, the sequential reduction **6** to **7** and **7** to **8** by Co^{2+} followed by decarboxylation results the formation of radical **9**. Then the radical **9** further resumes its aromaticity by Co^{2+} induced reductive quenching resulting the target molecule **3**. In the catalytic cycle, SET mechanism involves oxidation of Co^+ into Co^{2+} by molecular O_2. However, the formation of product **3** in absence of catalyst may presumably be explained by photocatalytic path as acetophenone has high triplet energy.[21]

In summary, we have documented an original and efficient route for the synthesis of polyfunctionalized furans using readily available α,β-unsaturated carboxylic acids and ketones and via oxidative decarboxylative [3+2] cycloaddition in presence of visible light. Thus, the envisaged green method has its several advantages, viz., higher yields of products, simple operation, and ambient reaction conditions over the existing procedures for the synthesis of furan and would be a better practical alternative to cater the needs of academia as well as industries.

Preparation of $CoFe_2O_4$:

The preparation of $CoFe_2O_4$ nanoparticles were carried out following reported procedure. Solution of $Co(OAc)_2.7H_2O$ (4.2 g) and anhydrous $FeCl_3$ (4.8 g) was dissolved in distilled water and vigorously mixed under sonication for 3h at 70 ^{0}C. Subsequently, 0.3 M NaOH was added drop by drop into the solutions till the pH is reached up to 11 and black precipitate is formed. Then reaction mixture was centrifuged and rinsed with ethanol and distilled water and was dried in electric oven. The resulting powder is then calcinated at 550 °C in an oven for 4 hours. The magnetic nature of the prepared $CoFe_2O_4$ spinel was checked by using external magnet (inset; Figure 3f).

Synthesis Furan 3:

General

All chemicals were purchased from Aldrich, Sd-fine and HI-MEDIA (India) and used as received, except all solvents which were used after distillation. All reactions were carried out with

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oven-dried glassware under air. Distilled *n*-hexane and ethyl acetate were used for column chromatography. Analytical TLC (Thin Layer Chromatography) was performed on Merck 60F254 silica gel plates (0.25 mm thickness). Column chromatography was performed on silica gel (60-120 mesh size, HI-MEDIA, India).

General method for the preparation of furan 3

A mixture of α,β-unsaturated carboxylic acid (0.5 mmol), ketone (0.5 mmol) and $CoFe_2O_4$ nanoparticles (23 mg) in water (5 mL) was stirred in presence of LED light for 2-3 h. After completion of the reaction (TLC monitored), and an external magnet was used for the separation of the catalyst from the resulting crude reaction mixture. The reaction mixture was extracted with ethyl acetate (20 mL), washed with brine solution (2×5 mL) and distilled water (1×10 mL) and dried over anhydrous sodium sulphate. Solvent was removed under reduced pressure and left the crude solid product which was purified by column chromatography on silica gel (ethyl acetate/n-hexane = 1/9) to provide pure 2,3,5- substituted functionalized product. The product was confirmed by their satisfactory ^{1}H NMR and ^{13}C NMR spectral analysis. However, the spectroscopic data of the representative compound is given. **Compound 3a** Colourless solid, (91%, 100 mg), mp 85–86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (4H, d, *J* = 7.9 Hz), 7.49 (4H, t, *J* = 6.7 Hz), 7.34 (2H, t, *J* = 5.4 Hz), 6.41 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 130.7, 128.7, 127.3, 123.7, 107.2; IR ($CHCl_3$) ν 3061, 3020, 1615, 1593 cm^{-1}. Anal. Calcd for $C_{16}H_{12}O$: C, 87.25; H, 5.49. Found: C, 87.30; H, 5.58. **Compound 3f** Colourless solid (85%, 106 mg), mp 95–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.46–7.43 (m, 2H), 7.32–7.29 (m, 3H), 6.65 (s, 1H), 2.45 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 148.5, 136.5, 131.0, 129.3, 129.1, 128.7, 127.1, 125.3, 123.7, 123.7, 118.0, 110.8, 21.3, 12.1. Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49%. Found: C, 87.43; H, 6.50%. **Compound 3p** Colourless solid (82%, 127 mg), mp 97–99 °C (lit. mp 99–100 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.40–7.37 (m, 2H), 7.32–7.28 (m, 2H), 7.26–7.20 (m, 3H), 7.17–7.13 (m, 3H), 6.68 (s, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 147.6, 137.5, 134.5, 131.3, 129.5, 128.8, 128.7, 128.5, 127.9, 127.5, 127.3, 126.2, 124.6, 123.9, 108.9, 21.4. Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85%; Found: C, 89.32; H, 5.97%.

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TABLE OF CONTENT

A co-operative effect of visible light photo-catalysis and $CoFe_2O_4$ nanoparticles for green synthesis of furans in water

Fooleswar Verma, Puneet K. Singh, Smita R. Bhardiya, Manorama Singh, Ankita Rai, and Vijai K. Rai*

A novel approach to poly-functionalized furan synthesis is disclosed via oxidative decarboxylative [3+2] cycloaddition using co-operative catalysis by visible light and $CoFe_2O_4$ nanoparticles.