Copper Oxide/Reduced Graphene Oxide Nanocomposite-Catalyzed Synthesis of Flavanones and Flavanones with Triazole Hybrid Molecules in One Pot: A Green and Sustainable Approach

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ABSTRACT: An efficient, green, and sustainable synthesis of new hybrid molecules containing flavanone with triazole by merging the Michael addition and Click reaction using a copper oxide/reduced graphene oxide nanocomposite in one pot is reported. The catalyst can easily be recycled and reused in seven consecutive runs without compromising the product yields. Other notable advantages include using water as a reaction medium and obtaining good to excellent yields, low catalyst loading, high atom efficiency, high substrate variation, and good results in the gram scale reaction.

1. INTRODUCTION

The design and preparation of any catalyst with superior catalytic activity has become an important area of research. Nanoparticles as catalysts offer receive much interest due to their higher surface/volume ratio. The major drawback of using bare nanoparticles is agglomeration. Therefore, it needs some stabilizer. At the same time, discovery of graphene oxide has attracted much attention of chemists. Graphene oxide offers interesting electronic, thermal, and mechanical properties† and has a large surface area with various functional groups, which provides for chemical modifications and makes graphene oxide an important candidate in research.‡ Moreover, it also acts as a good catalyst support. Therefore, scientists doped NPs on the GO. Which internally stabilized the NPs with no need for extra stabilizing agent. Metal/graphene oxide nanocomposites play a vital role in several areas of research, such as catalysis,§ sensors,‖ and photocatalysis,¶ for the reduction process in organic synthesis,‖ toxic metal ion removal,‖ cellular imaging,‖ drug delivery,‖ and many other properties reported in the literature.¶† From the brief discussion above, we were inspired to prepare a copper oxide/reduced graphene oxide nanocomposite (CuO/rGO) for catalysis.

Flavanones are basically oxygen-containing heterocycles,‖ having a wide range of biological and pharmaceutical properties. They exhibit antiviral,‖ antitumor,‖ antioxidant,‖ anti-inflammatory,‖ anti-HIV,¶ and antiallergic activities.‖ The flavanone skeleton, also present in many natural products, belongs to the flavonoid group.¶† Some of the important flavanones which show biological activities are shown in Figure 1. Therefore, flavanone is a very attractive target for chemists and biologists. On the other hand, a triazole molecule shows huge biological and pharmaceutical activities. In the literature, it is reported that heterocycles containing a triazole moiety show better biological activity than its mother heterocycles.¶† Along this line, we plan to synthesize flavanones attached to triazole. Various methodologies have been reported for the 

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Figure 1. Some important flavanones showing biological activities.¶†
synthesis of flavanones using a range of catalysts such as Hg(OCOCF₃)₂, iodine, L-proline, ionic liquid EAN, NSSDAIL, silica ferric hydrogensulfate (SFHS), L-alanine in the presence of base, PMA-SiO₂, N-methylimidazole etc. Although each procedure has their own advantages, they also have certain deficiencies, such as the use of toxic organic solvents, harsh conditions, expensive and nonreusable catalysts, etc. However, no method has been reported for the synthesis of flavanone-containing triazole in one step. We herein report a CuO/rGO nanocomposite that is an efficient, green, and sustainable catalyst for flavanone synthesis, and it is also efficient for the construction of flavanones with triazole in one pot.

2. RESULTS AND DISCUSSION

Our investigation progressed with the synthesis of CuO/rGO nanocomposites as was reported by Zhang. Graphite oxide was synthesized according to the modified Hummers method from graphite powder. In the second step, a mixture of GO (30 mg), CuCl₂ (18 mg), and deionized water (200 mL) was taken in a 500 mL round-bottom flask. The mixture was then ultrasonicated (50 Hz) for 1 h at room temperature. Then NaBH₄ (10 mL, 1%) was added dropwise, and the reaction mixture was stirred at 100 °C for 24 h. After that, the reaction mixture was cooled at room temperature, and the CuO/rGO nanocomposites were collected by centrifugation. The resulting CuO/rGO nanocomposites were then dried at 100 °C and characterized by various analytical techniques.

To determine the various functional groups, Fourier transform infrared (FT-IR) spectra of the synthesized CuO/rGO were obtained. The comparative FT-IR spectrum of GO and CuO/rGO nanocomposites is shown in Figure 2. In this spectra, GO shows absorption peaks at 3383, 1732, and 1107 cm⁻¹ due to the presence of hydroxyl, carboxyl, and epoxy functionalities. In the FT-IR spectrum of CuO/rGO nanocomposites, the intensity of −OH stretching was reduced significantly, indicating reduction of GO during the doping process. The absorption peak at 513 cm⁻¹ in CuO/rGO is due to the Cu−O stretching vibrations, and the present results are in close agreement with those reported values. The number of peaks becomes weak or decreases in CuO/rGO due to chemical reduction.

The powder X-ray diffraction (PXRD) pattern of GO (Figure 3A) shows the characteristic diffraction peaks at 2θ ~ 9.33 and 42.20 due to [001] and [100] planes, indicating the oxidation of graphite to GO. In the PXRD pattern of the CuO/rGO nanocomposite (Figure 3B), the disappearance of the [100] plane at 2θ ~ 42.20 and concomitant appearance of a peak at 2θ ~ 24.90 indicated the reduction of GO to rGO during the doping of CuO NPs onto GO. The other diffraction peaks at 2θ ~ 36.45, 42.40, 43.28, 61.48, and 73.57 arise due to Cu₂O, CuO, and Cu particles. These values are very close to the reported ones.

The size and shape of the CuO/rGO were analyzed from transmission electron microscopy (TEM) analysis (Figure 4). Figure 4A represents the low-magnification image of CuO/rGO nanocomposites, which indicates the incorporation of CuO NPs on the surface of rGO. At 5 nm magnification (Figure 4B), it is found that the CuO NPs are 5−15 nm in size. Further, in the high-resolution (HR) TEM image (Figure 4C), the lattice fringes exhibit an interplanar lattice spacing of 0.23 nm, which corresponds to the (111) atomic planes of the facetercentered cubic (fcc) lattice of CuO. The spherical shape of the CuO NPs is clearly visible in the high-magnification TEM image (Figure 4C). The scanning electron microscopy (SEM) analysis was also performed for the present catalytic system. In the SEM image (Figure 4D), we observed that the spherical CuO NPs are embedded on the layers of rGO. We also carried out SEM at lower magnification, which is shown in Supporting Information Figure S1A. The chemical composition and oxidation states of the prepared catalyst were analyzed by energy-dispersive X-ray (EDX) analysis, inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. The EDX spectrum shows the presence of Cu, O, and C species (Figure 4E). Further, the EDX spectrum carried out at
lower magnification is given in Supporting Information Figure S1B,C, indicating the presence of Cu, O, and C species along with other impurities. The low loading of Cu was confirmed by ICP-AES analysis (12.889%). The above discussion indicates the successful preparation of CuO/rGO nanocomposites.

Initially, we investigated the XPS analysis of GO. The presence of oxygen in the XPS survey spectrum of GO confirms the oxidation of graphite to GO (Figure 5A). The C 1s spectrum of GO shows four prominent peaks at 284.6, 286.6, 287.8, and 288.6 eV, corresponding to sp²-hybridized carbon and carbon containing various functionalities such as hydroxyl (C–OH), epoxide (C–O–C), and carboxyl (HO–C=O) groups (Figure 5B). The high-resolution XPS peaks were analyzed using a Voigt function fitting followed by removal of the Shirley background. The XPS survey spectrum (Figure 5C) of the prepared catalyst clearly shows the presence of Cu 2p³/₂, O 1s, and C 1s peaks, indicating the successful preparation of the CuO/rGO nanocomposites. Figure 5D shows the C 1s XPS spectrum of CuO/rGO nanocomposites. In the spectrum, there is a significant decrease in the intensities of the peaks (Figure 5D), which, in turn, prove the reduction of GO to rGO. The Cu 2p spectrum of CuO/rGO
nanocomposites (Figure 5E) shows prominent peaks at 932.4 and 934.4 eV, corresponding to the Cu 2p3/2 peak of Cu+ and Cu2+ species. It also shows peaks corresponding to Cu 2p1/2 at 952.3 and 954.3 eV, which are characteristic of Cu+ and Cu2+ species.32a Further, satellite peaks of Cu 2p3/2 and Cu 2p1/2 were observed at 943.0 and 962.4 eV. The binding energies of core levels are in agreement with those in previous reports.6e,32b The fitting of high-resolution XPS data is used to quantify the atomic percentage32c (Table SI2.).

Figure 6 shows the Raman spectrum of GO (Figure 6A) and CuO/rGO nanocomposites (Figure 6B). In both spectra, two bands are clearly observed, viz. the D band and G band. The \( I_D/I_G \) values for GO and CuO/rGO nanocomposites are found to be 1.06 and 1.64, respectively. In the Raman spectrum of CuO/rGO nanocomposites (Figure 6B), the slightly lower shift of the D band and a slightly higher shift of the G band, along with the higher \( I_D/I_G \) value, prove the reduction of GO due the incorporation of CuO NPs onto GO sheets.

Thermogravimetric analysis (TGA) was performed to study the thermal stability of the prepared catalyst. The TGA thermogram of GO (blue line) shows a characteristic thermal degradation at a temperature of around 180 °C, which is attributed to the degradation of various functional groups.32d On the other hand, the TGA thermogram of CuO/rGO nanocomposites (red line) shows a weight loss (∼48%) at around 335 °C, which can be ascribed to the degradation of various functional group containing oxygen in CuO/rGO. Another weight loss (∼3%) is observed at around 675 °C, which corresponds to the degradation of the C–C skeleton of rGO (Figure 7).33

The prepared CuO/rGO nanocomposite was then employed to show its catalytic activity for the synthesis of flavanones from chalcones. We initiated our study by taking substituted 2-hydroxychalcone (1a, 1.0 mmol) as the model substrate (Scheme 2).

The experiment was performed in the absence of any catalyst, with water (3 mL) as the solvent at room temperature. However, the reaction did not lead to any product even after 3 h of stirring, and only the starting material was revealed by thin layer chromatography (TLC) (Table 1). The same reaction...
was performed in the presence of catalyst (CuO/rGO, 10 mg) under the same condition, and the identical result was encountered (Table 1). Then we applied heat to the reaction, and it was observed that with increasing temperature (50, 60, and 80 °C) the yield of the desired product increased, but the best result (92% yield) was obtained under refluxing conditions for 30 min (Table 1).

To understand the effect of copper in CuO/rGO nanocomposites, the model reaction was setup with graphite oxide (10 mg) and rGO (10 mg), and a trace amount of the product was observed (Table 1, 28 and 20%). Therefore, it was concluded that Cu is an essential component in this reaction. In order to make the procedure more economic, screening of the catalyst concentration was carried out. Seven sets of reactions were performed using 2-hydroxychalcone (1a, 1 mmol) and water (3 mL) with varying catalyst loading under standardized conditions. It was found that the yield of the product increased with increased catalyst loading from 1 to 8 mg. Further increase of the catalyst loading (10 to 12 mg) did not have any impact on the product yield (Figure 8). So, it proved that 8 mg of the catalyst was enough for the conversion of chalcone 1a to flavanone 2a in excellent yield (92%).

Likewise, various polar and nonpolar solvents were tested for the present catalytic process, including water, ethanol, acetonitrile, chloroform, 1,4-dioxane, and toluene. It was found that under refluxing conditions for 30 min the polar aprotic and nonpolar solvents, such as acetonitrile, chloroform, 1,4-dioxane, and toluene, did not have much effect on this catalytic process (Figure 9), but polar protic solvents, such as water and ethanol, showed better conversion (92 and 94%, respectively) of starting material to the desired product within a time frame of 30 min at their refluxing temperature (Figure 9).

Table 1. Reaction Parameters under Various Conditions

| entry | temperature (°C) | catalyst | time (min) | yield (%) |
|-------|------------------|----------|------------|----------|
| 1     | RT no catalyst   |          | 180        | no conversion |
| 2     | RT CuO/rGO (10 mg) |          | 180        | no conversion |
| 3     | 50 °C (water) CuO/rGO (10 mg) | 30 | no conversion |
| 4     | 60 °C (water) CuO/rGO (10 mg) | 30 | 15 |
| 5     | 80 °C (water) CuO/rGO (10 mg) | 30 | 50 |
| 6     | refluxing (water) CuO/rGO (10 mg) | 30 | 92 |
| 7     | 100 °C (neat) CuO/rGO (10 mg) | 180 | 19 |
| 8     | refluxing (water) rGO (10 mg) | 30 | 20 |
| 9     | refluxing (water) graphite oxide (10 mg) | 30 | 28 |

*The reaction was carried out with 1 mmol 1a and 10 mg of catalyst.

*Isolated yield.
Though ethanol showed a slight increase in the product yield, we chose water as the solvent for the present catalytic process as it is environmentally benign, green, sustainable, and easily available. After that, we changed our focus and carried out the reaction under solvent-free reaction conditions (neat condition) in the presence of catalyst (8 mg). The reaction resulted in a lower yield (19%) of the desired product even after prolonged heating for 3 h at 100 °C (Table 1).

After obtaining the excellent result (Table 1, entry 6), we investigated the generality and substrate scope for this reaction (Scheme 3). Likewise, numerous flavanones were prepared from substituted chalcones (1a–1u) containing both electron-withdrawing and electron-donating groups at o-, m-, and p-positions of the aromatic ring (Figure 10). It was found that both electron-donating and electron-withdrawing substituents at different positions of the aromatic ring furnished good to excellent results. Therefore, it was concluded that the nature and position of the substituent have no influence on the product yield. We also prepared a flavanone-containing heterocyclic system (furan ring, 1m) and naphthalene moiety (1l). In both cases, excellent results were encountered (Table 2). We tried to synthesize flavanones containing an aliphatic side chain, but much less chalcone was formed in the case of aliphatic aldehydes, such as butanal and propanal.

Table 3 shows the results of some reported methodologies. From this table, it is clear that these reported procedures suffer some drawbacks such as long reaction time, lower yield, use of toxic, hygroscopic solvents and reagents and use a non-recyclable catalyst. On the other hand, we used green and environmentally friendly solvent (water) and a recyclable catalyst. Moreover, reaction time is short, and product yields are very high. Therefore, the present methodology is superior to other reported procedures.

The plausible mechanism for the present reaction is shown in the Scheme 4. First, the catalyst CuO/rGO increases the electrophilicity of the carbonyl carbon of the conjugated system of 2-hydroxychalcones (1). Then hydroxyl group of the chalcone attacked the β-position of the conjugated part of the molecule according to Michael fashion (1A). Finally, intramolecular proton transfer (1B and 1C) followed by tautomerization furnished the final product 2.

Next we tried to synthesize flavanones containing a 1,2,3-triazole moiety. We constructed the triazole by click reaction using alkyne and azide. For this, chalcone containing an alkyne end was synthesized (1n and 1o) from salicylaldehyde and propargyl bromide (Scheme 5). Then flavanone-enclosed alkyne moieties 2n and 2o were synthesized from chalcones 1n and 1o. In the next step, aryl azide, flavanones 2n and 2o, and catalyst were refluxed in water for 1 h. To our delight,

Figure 10. Scope of substrates.
flavanone with triazoles 4a-4j were formed in excellent yields of 90-97% (Scheme 5 and Table 4).

To make the procedure easier, straightforward, and economically viable, we tried to combine the two steps in a single step. So, chalcone 1n, aryl azide 3g, and CuO/rGO catalyst in water were refluxed for 2 h (Scheme 6). After purification and characterization, it was found that instead of flavanone-containing triazole, open chain triazole 5a was formed.

Then we changed our strategy. First chalcones 1n and 1o were converted to flavanones 2n and 2o, and then in the same pot, alkyl azides (3a-3f) were added and refluxed for 1 h. It was observed that after 1 h of reflux, flavanone-enclosed triazoles 4a-4j were formed nicely and furnished excellent yield (90-97%). In order to show the versatility of the present protocol, we investigated the reaction with both electron-donating and electron-withdrawing substituted phenyl azides (Figure 11). In both cases, good to excellent amounts of the desired products were obtained (Table 4).

We tried to develop an efficient, green, and sustainable catalyst. Therefore, reusability of the catalyst was examined. The model reaction was setup with chalcone 1n (1 mmol), benzyl azide 3a (1 mmol), water (3 mL), and catalyst (8 mg) under the same reflux conditions. After completion of the reaction (TLC), the catalyst was recovered by centrifugation followed by filtration. The recovered catalyst was washed with water, ethanol, and diethyl ether and dried. The recovered catalyst was then used in another seven consecutive runs, and no much decrease in the catalytic activity was observed (Figure 12). Further, the structures of the flavanone and flavanone-containing triazoles 2t, 4e, and 4g were confirmed from X-ray crystallography (Figure 13).

A gram scale reaction was setup with a CuO/rGO nanocomposite catalyst to show industrial application. In our present study, chalcone 1n (4 mmol, 1113 mg) and CuO/rGO (32 mg) were stirred in 15 mL of H2O for 30 min. After that, phenyl azide 3a (4 mmol, 477 mg) was added, and the stirring was further continued for another 1 h. After completion of the reaction (TLC), the catalyst was recovered by centrifugation followed by filtration, and the crude mass was purified by column chromatography. A product yield of 85% (1.35 g) was achieved for the catalytic gram scale reaction (Scheme 7). Thus, this methodology could be efficient for the synthesis of a triazole moiety containing flavanone.

3. CONCLUSIONS

In conclusion, we have developed an easy and efficient method for the synthesis of flavanone-containing triazole moiety in one step using substituted 2'-hydroxy acetophenones, aldehydes,

Scheme 4. Plausible Mechanism for the CuO/rGO Nanocomposite Catalyst To Catalyze the Present Reaction

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Table 2. Various Substituted Flavanone Derivatives (2a–2u)"  

| entry | chalcone | product | time (min) | yield (%)a | melting point (°C) |
|-------|----------|---------|-----------|------------|-------------------|
| 1     | 1a       | 2a      | 30        | 92         | 75–77             |
| 2     | 1b       | 2b      | 30        | 94         | 83–84             |
| 3     | 1c       | 2c      | 30        | 91         | 85–87             |
| 4     | 1d       | 2d      | 30        | 90         | 102–104           |
| 5     | 1e       | 2e      | 30        | 96         | 115–117           |
| 6     | 1f       | 2f      | 30        | 95         | 82–83             |
| 7     | 1g       | 2g      | 30        | 93         | 102–103           |
| 8     | 1h       | 2h      | 30        | 90         | 116–118           |
| 9     | 1i       | 2i      | 30        | 87         | 81–82             |
| 10    | 1j       | 2j      | 30        | 89         | 90–92             |
| 11    | 1k       | 2k      | 30        | 88         | 80–81             |
| 12    | 1l       | 2l      | 30        | 90         | 89–90             |
| 13    | 1m       | 2m      | 30        | 89         | 78–89             |
| 14    | 1n       | 2n      | 30        | 93         | 65–67             |
| 15    | 1o       | 2o      | 30        | 95         | 82–84             |
| 16    | 1p       | 2p      | 30        | 87         | 78–80             |
| 17    | 1q       | 2q      | 30        | 92         | 94–96             |
| 18    | 1r       | 2r      | 30        | 90         | 152–153           |
| 19    | 1s       | 2s      | 30        | 91         | 155–157           |
| 20    | 1t       | 2t      | 30        | 87         | 115–117           |
| 21    | 1u       | 2u      | 30        | 89         | 126–128           |

"The reaction was carried out with 1 mmol 1a–1u, catalyst (8 mg), and water (3 mL) and refluxed (30 min)." Isolated yield, after column chromatography.

Table 3. Catalytic Activity of the Present Catalyst with That Reported in the Literature

| SL no. | catalyst | reaction conditions | time | yield (%)a |
|--------|----------|---------------------|------|------------|
| 1      | iodine   | CH3OH, 40 °C        | 7–24 h | 53–88     |
| 2      | NSSDAI   | neat, 80 °C         | 35–70 min | 71–84   |
| 3      | PMA-SiO2 | EtOH, reflux        | 8–18 h | 52–98     |
| 4      | SFHS     | aniline, EtOH, reflux | 8–17 h | 81–88    |
| 5      | CH3SO3H | acetic acid, reflux | 1.05–3.50 h | 62–89   |
| 6      | CuO/rGO  | H2O, reflux         | 30 min | 87–96 (present method) |

"Isolated yield.

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aryl azides, and CuO/rGO. After completion of the reaction, catalyst was separated easily by centrifugation followed by filtration. Then it was reused in seven consecutive runs. Gram scale reaction was carried out for industrial applications. This protocol avoids the use of toxic and hazardous solvents, costly catalysts, and long reaction times, which in turn satisfies some principles of green chemistry.

4. EXPERIMENTAL SECTION

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a Spectrum BX FT-IR system, PerkinElmer ($\nu_{\text{max}}$ in cm$^{-1}$) on KBr disks. $^1$H NMR and $^{13}$C NMR (400 and 100 MHz, respectively) spectra were recorded using a Bruker Avance II-400 spectrometer, using CDCl$_3$ as the solvent (chemical shifts in $\delta$ with TMS as internal standard). Mass spectra were recorded on a Waters ZQ-4000 system. Transmission electron microscopy analysis was carried out using a JEOL JSM 100CX system. Scanning electron microscopy and energy-dispersive X-ray analysis were carried out using a JSM-6360 (JEOL) system. Thermogravimetric analysis was performed using a Q500 furnace (TA Instruments).

**Scheme 5. General Scheme for 1,2,3-Triazoles**

**Table 4. Various Substituted Triazole Derivatives (4a–4j)**

| entry | chalcone | azide | time (h) | product | yield (%) | melting point ($^\circ$C) |
|-------|----------|-------|----------|---------|-----------|--------------------------|
| 1     | 1n       | 3a    | 1        | 4a      | 97        | 102–104                  |
| 2     | 1n       | 3b    | 1        | 4b      | 95        | 156–158                  |
| 3     | 1n       | 3c    | 1        | 4c      | 97        | 108–110                  |
| 4     | 1n       | 3d    | 1        | 4d      | 95        | 110–112                  |
| 5     | 1n       | 3e    | 1        | 4e      | 90        | 130–132                  |
| 6     | 1n       | 3f    | 1        | 4f      | 96        | 146–148                  |
| 7     | 1o       | 3a    | 1        | 4g      | 94        | 174–176                  |
| 8     | 1o       | 3f    | 1        | 4h      | 97        | 136–138                  |
| 9     | 1o       | 3e    | 1        | 4i      | 92        | 154–156                  |
| 10    | 1o       | 3d    | 1        | 4j      | 93        | 147–149                  |

a The reaction was carried out with 1 mmol 1n and 1o, 1 mmol 3a–3f, catalyst (8 mg), water (3 mL), refluxed (1 h).

b Isolated yield, after column chromatography.

**Figure 11. Substrate scope for 1,2,3-triazoles.**

- Catalysts, and long reaction times, which in turn satisfies some principles of green chemistry.

**Scheme 6**
metric analysis was carried out using a PerkinElmer Precisely STA 6000 simultaneous thermal analyzer. CHN analysis was carried out using a CHN-OS analyzer (PerkinElmer 2400, Series II). Powder XRD analysis was carried out using a Bruker D8 Advance XRD instrument SWAX. Raman analysis was carried out on a Horiba Jobin Vyon, model Lab Ram HR system. X-ray photoelectron spectroscopy was performed using a PHI 5000 Versa Prob II, FEI Inc. system. Inductively coupled plasma atomic emission spectroscopy analysis was carried out on an Arcos simultaneous ICP spectrometer. Silica gel G (E-Merck, India) was used for TLC analysis. Hexane refers to the fraction boiling between 60 and 80 °C.

Procedure for the Synthesis of CuO/rGO Nano-composites. Graphite oxide was synthesized according to a modified Hummers method from graphite powder. In the second step, a mixture of GO (30 mg), CuCl₂ (18 mg), and deionized water (200 mL) was taken in a 500 mL round-bottom flask. The mixture was then ultrasonicated (50 Hz) for 1 h at room temperature. Then NaBH₄ (10 mL, 1%) was added dropwise, and the reaction mixture was stirred at 100 °C for 24 h. After that, the reaction mixture was cooled at room temperature, and the CuO/rGO nanocomposites were collected by centrifugation and filtration and dried at 100 °C.

Procedure for the Cyclization of Chalcones 1a–1u to Flavanones 2a–2u. In a clean round-bottom flask, chalcones 1a–1u (1 mmol) and catalyst (CuO/rGO, 8 mg) were added in water (3 mL) and refluxed for 30 min. Then the catalyst was recovered by filtration with water, ethanol, and diethyl ether and dried. The recovered catalyst was then used in another set of reactions. The filtrate-containing product was then extracted with chloroform (3 × 5 mL), and the organic extract was washed with water (3 × 10 mL) and brine (1 × 10 mL) and dried over anhydrous Na₂SO₄. It was then concentrated under reduced pressure. The crude mass was then purified by column chromatography using ethyl acetate and hexane as eluent.

Procedure for the Synthesis of 1,2,3-Triazoles 4a–4j from Flavanones 2n and 2o. In a clean round-bottom flask flavanones 2n and 2o (1 mmol), aryl azides 3a–3f (1 mmol), catalyst (CuO/rGO, 8 mg), and water (3 mL) were refluxed. After completion (TLC), the catalyst was recovered by centrifugation and filtration, and the recovered catalyst was then washed with water, ethanol, and diethyl ether and dried under reduced pressure and reused for another set of reactions. The filtrate-containing product was then extracted by chloroform (3 × 10 mL), and the combined organic extract was washed with water (3 × 10 mL) and brine (1 × 10 mL) and dried (Na₂SO₄). It was then concentrated under reduced pressure. The crude mass was then purified by column chromatography using ethyl acetate and hexane as eluent to afford the desired product (4a–4j).

Procedure for the Synthesis of 1,2,3-Triazoles 4a–4j from Chalcones 1n and 1o in One Pot. A mixture of chalcones 1n and 1o (1 mmol), catalyst (CuO/rGO, 8 mg), and water (3 mL) was taken in a round-bottom flask and...
reduced pressure. The crude mass was then purified by column chromatography using ethyl acetate and hexane as eluent.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00334.

Experimental procedure; X-ray crystallography data for compounds 2t, 4e, and 4g (CCDC Nos. 1573626, 1580712, and 1580713); analytical and spectral data of compounds 2a–2u, 4a–4j, and 5a; and 1H and 13C spectra of 2a–2u, 4a–4j, and 5a (PDF)

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Notes
The authors declare no competing financial interest.

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