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ARTICLE TYPE

# Lanthanum loaded CuO nanoparticles: Synthesis, characterization and recyclable catalyst for the synthesis of 1, 4- disubstituted 1, 2, 3-triazoles and propargylamines

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The Lanthanum loaded CuO (LCO) nanoparticles (NPs) were successfully synthesized by precipitation-thermal decomposition method and characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive spectra (EDS), diffuse reflectance spectra (DRS), photoluminescence (PL), X-ray photoelectron spectroscopy (XPS) and BET surface area measurements. The synthesized LCO NPs was used as nanocatalyst for the synthesis of 1, 4-disubstituted-1, 2, 3-triazoles by click reaction of substituted benzyl azides and alkynes and synthesis of propargylamines *via* three-component coupling reaction of aldehydes, alkynes and amines under ultrasonication. One-pot operation, atom-economical nature, regioselectivity and good yields are the noteworthy features of this protocol. The reusability of the prepared nanocatalyst was successfully examined six times without any appreciable loss in catalytic activity.

## Introduction

During the last few decades, great attention has been given to click[1] and green chemistry[2] for the development of efficient and environmentally benign protocols. Recently nano-particles and nanoparticles supported on a metal oxide have emerged as a sustainable and competitive alternative to conventional catalysis, and have been extensively studied in the field of medicine for drug delivery systems.[3,4] Mesoporous nano-materials have also gained increasing importance in their use as catalysts in various organic reactions,[5] as sensors for the detection of hydrazine,[6] in optoelectronics[7,8] and as electron transfer mediators in bio-electrochemical systems.[9]

1, 2, 3-Triazoles are important sub-units in heterocyclic chemistry because of their unique structure, chemical and biological properties.[10] Huisgen 1,3-dipolar azide-alkyne cycloaddition is traditionally applied for accessing 1,2,3-triazoles.[11] However, the major limitations of this non-catalyzed process are the requirement of high temperature and poor regioselectively giving a mixture of 1,4- and 1,5-disubstituted triazoles. Up to now, several efforts to control the 1,4- versus 1,5-regioselectivity have been reported.[12] As a prototype for click chemistry,[13] the recent advance in Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) reported by Sharpless[14] and Meldal[15] to access 1,2,3-triazoles in short reaction times under mild conditions and as only one 1,4-regioisomer.[16-19] The major limitations of existing CuAAC protocols realized in terms of homogeneous nature of catalysts, thus creating problem during separation of catalyst/product(s), and the requirement of adding reducing agents and stabilizing ligands limited their utilization for practical processes. Recent research in this area has concentrated on heterogeneous catalytic systems, which have several advantages, such as faster and simpler isolation of the reaction products by filtration, as well as recovery and recycling of the catalyst systems. Thus, the particles of copper[20] or its oxide derivatives,[21] copper salts supported on charcoal[22] or on organic materials,[23] as well as on inorganic supports[24] have been tested for this transformation.

Furthermore, Propargylamines are key intermediates for the synthesis of natural products and nitrogen containing biologically active compounds.[25] Recently, propargylamines are prepared by transition metal-catalyzed A$^3$coupling reactions of aldehydes, alkynes and amines. A$^3$coupling reactions have received much attention due to their simple operation and high efficiency, which employ amines as nitrogen sources. Several homogenous catalysts like nickel[26a] and copper salts,[26b] CuI/ligand,[26c] and heterogeneous systems such as Ag(I),[27a] and Cu(I),[27b] in ionic liquids, silica-immobilized CuI,[27c] Cu(0)-nanoparticles on montmorillonite,[27d] copper ferrite nanoparticles,[27e] CuNPs/MagSilica, [27f] Au-SBA[27g] and Au-$CeO_2$[27h] have been developed for propargylamines synthesis.

On the other hand, ultrasound irradiation has been well established energy source to promote chemical reactions.[28] Many homogeneous and heterogeneous reactions can be conducted smoothly by sonication under milder conditions and shorter reaction times to afford improved yields and increased selectivities.[29] Ultrasound irradiation has some potential effects on a heterogeneous catalytic system like increase of active catalyst surface area, promotion of cavitation bubble formation, and removal of impurities deposited on the catalyst.[30, 31]

Modern research has been focused on finding new catalysts to improve the efficiency of these azide-alkyne cycloaddition and

$A^3$ coupling reactions. As the above mentioned methods are not compatible with heat sensitive substrates and there is a need to develop an effective synthesis of triazoles and propargylamines employing more eco-friendly catalyst. In this view, we wish to describe a heterogeneous lanthanum loaded CuO-catalyzed for the synthesis of 1, 4-disubstituted-1, 2, 3-triazole and propargylamine derivatives under ultrasonication.

## Results and discussion

### Catalyst preparation and characterization

The LCO NPs was prepared by a precipitation thermal decomposition method. Two aqueous solutions of copper nitrate and oxalic acid were separately brought to their boiling points. The oxalic acid solution was added to the copper nitrate solution, copper oxalate was precipitated, then $La(NO_3)_3$ solution was mixed with the copper oxalate suspension and stirred for 1 h at 60−70 °C. After the mixture has cooled to room temperature, La-containing copper oxalate was washed with distilled water, air dried for overnight and dried at 100 °C for 5 h. Calcination of the mixed precipitate at 450 °C for 5 h results in the decomposition of copper oxalate to CuO NPs. The La-loaded CuO NPs was obtained after the sample was cooled to room temperature. The bare CuO NPs was prepared without addition of $La(NO_3)_3$ by the above procedure.

The prepared LCO NPs was characterized by XRD, FE-SEM, EDS, DRS, PL, XPS and BET surface area measurements. The crystalline nature of the bare CuO NPs was identified from their corresponding powder XRD patterns (**Fig. 1a**). All the diffractions were well matched with monoclinic phase of CuO NPs (standard JCPDS File No: 048-1548) and diffraction peaks 2θ are 35.45°, 38.73°, 42.50°, 48.92°, 61.99° and 66.49° corresponding to (002), (111), (200), (202), (220) and (113) plane of monoclinic phase of CuO NPs.[32] In XRD spectrum of LCO NPs (**Fig. 1b**), there was no new peak appearing and the peaks are slightly broadening due to reduction in the particles size when compared to bare CuO NPs. Insert figure (**Fig. 1**) infers that the peak corresponding to LCO NPs was slightly shifted to lower angle, which revealed that the La loaded on the surface of CuO material.[33] The crystalline size of LCO and CuO NPs were determined using Debye-Scherrer equation.

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Where D is the crystal size of the catalyst, K is dimensionless constant, λ is the wavelength of X-ray, β is the full width at half-maximum (FWHM) of the diffraction peak and θ is the diffraction angle. From this equation, we obtained the crystalline size of LCO NPs (19 nm) and was found to be lower than the bare CuO NPs (25 nm).

The FE-SEM images of CuO and LCO NPs represent (**Fig. 2**) that the particles are in nanometer region which is in agreement with grain size based on Scherrer's formula. **Fig. 2(a)** shows the almost uniform formation of spherical shaped CuO (3μm) particle. In addition, it has more gaps between the two spherical shaped CuO NPs. The LCO NPs (3μm) exhibit agglomerate formations (**Fig. 2(b)**) and reveal that the non-uniform formation of spherical shaped nanoparticles. It explains LCO NPs morphology is much better than CuO NPs morphology.

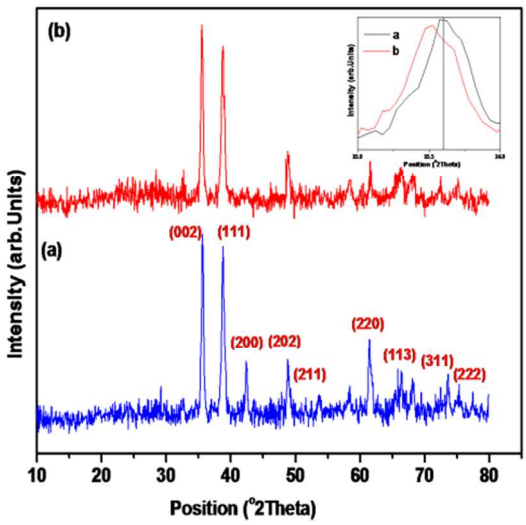



**Figure 1.** XRD patterns of a) bare CuO and b) LCO NPs (The insert figure shows magnification of XRD patterns of (a) bare CuO and (b) LCO NPs)

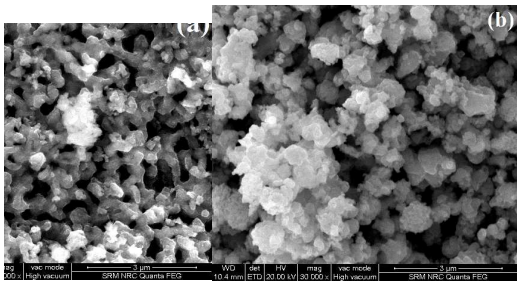



**Figure 2.** FE-SEM images of a) CuO (3μm) and b) LCO NPs (3μm).

The EDS spectra of the bare CuO and LCO NPs were depicted in **Fig. 3**, the presence of Cu and O in the bare CuO and La, Cu, O in the LCO NPs. This indicates clearly that the La ions were successfully loaded on the surface of CuO NPs.

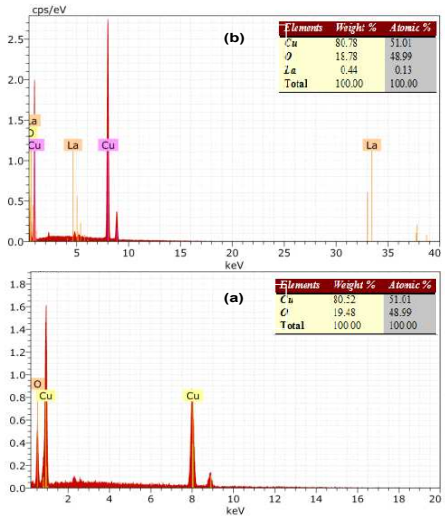



**Figure 3.** EDS of a) bare CuO and b) LCO NPs.

The diffuse reflectance spectra (DRS) of pure CuO and LCO NPs are depicted in **Fig. 4**. $La^{3+}$ might covalently interact with CuO and slightly reduce its band gap of LCO NPs. There is no significant change of absorption in the UV region but LCO NPs have higher absorption than bare CuO NPs in the visible region. Photoluminescence (PL) occurs due to the recombination of electron–hole pair in the semiconductor. PL (**Fig. 5**) spectra reveal that the PL intensity of LCO NPs is less than CuO NPs. This is because of the suppression of recombination of the photo generated electron–hole pairs by the La loaded on CuO. Inhibition of the electron–hole recombination makes this catalyst more active.

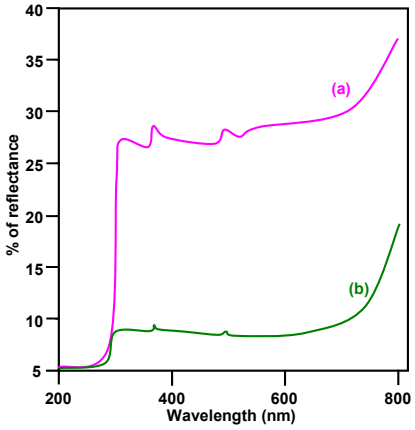



**Figure 4.** DRS of a) bare CuO and b) LCO NPs.

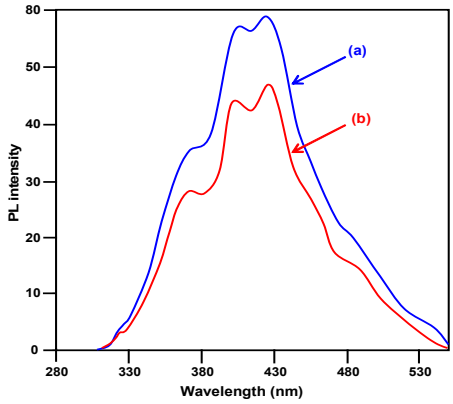



**Figure 5.** Photoluminescence spectra of a) bare CuO and b) LCO NPs.

The elemental composition and oxidation states of the CuO NPs and LCO NPs were analyzed using XPS. The binding energies obtained in the XPS analysis were corrected for specimen by referencing the C 1s to 284.0 eV (**Fig 6a**). A selected area scan for the individual elements in LCO NPs (O 1s, Cu 2p, and La 3d) are shown in **Figure 6b, c, d,** respectively. The Cu 2p core level spectrum (**Fig. 6c**) represents two peaks located at 932.0 and 953.7 eV which corresponds to the Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively. These values match well with the data reported for the Cu 2p in CuO.[34] In addition, the shake-up satellite peaks located at 940.8 eV and 960.5 eV are characteristic of materials having a $d^9$ configuration.[35] The strong shake-up satellites recorded in the LCO NPs confirm the $Cu^{2+}$oxidation state and rule out the possibility of the existence of a $Cu_2O$ phase.[34] The O 1s core level XPS signal is presented in **Fig. 6b**. The peak at binding energy value of 529.0 eV is due to the oxygen in the CuO (The O 1s signal for $Cu_2O$ is generally found at 530.5 ±0.2 eV in the literature).[36] **Fig. 6d** which shows that the binding energy of La $3d_{5/2}$ and La $3d_{3/2}$ are 835.0 and 851.5 eV, respectively.[37] The XPS data revealed that La exist in LCO NPs as $La_2O_3$ only and not as hydroxide or carbonate from the following evidence. The binding energy of O 1s at 529.0 eV which is characteristic for $O^{2-}$ (The O 1s signal for hydroxide and carbonate appeared at 531.6 eV in the literature).[41] The XPS analysis of bare CuO NPs revealed that the oxidation state of Cu is +2.

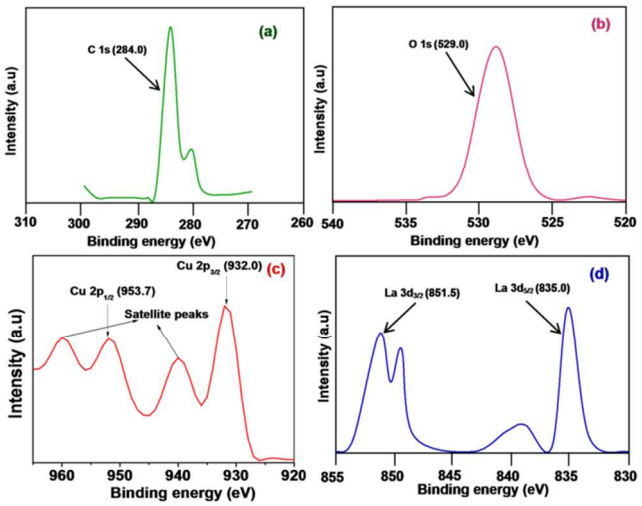



**Fig. 6.** XPS spectrum of LCO NPs: (a) C 1s peak, (b) O 1s peak, (c) Cu 2p peak, and (d) La 3d peak.

In general, the surface area of the catalyst was most important factor influencing the catalytic activity. The BET surface area analysis of bare CuO and LCO NPs were determined by using $N_2$ gas adsorption method. The BET surface area of LCO NPs (4.26 $m^2\ g^{-1}$) was higher than the bare CuO NPs (1.82 $m^2\ g^{-1}$). This is according to the IUPAC classifications of type IV isotherms with type H1 hysteresis. Type H1 hysteresis indicates that for spherical pores, the pore opening was smaller than the diameter of the main cavity. As the desorption portion of the isotherms moves from higher partial pressure to lower partial pressure, a gradual decrease in pore volume was observed. The BET surface and pore volume of bare CuO and LCO NPs are given in **Table 1**.

**Table 1.** Surface properties of the catalysts.

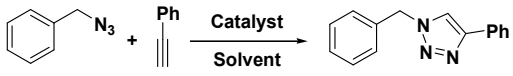
| Properties | Bare CuO | LCO |
|---|---|---|
| BET surface area | 1.82 ($m^2\ g^{-1}$) | 4.26 ($m^2\ g^{-1}$) |
| Total pore volume (single point) | 0.01 ($cm^3\ g^{-1}$) | 0.04 ($cm^3\ g^{-1}$) |

The catalytic activity of synthesized LCO NPs was tested in two different terminal-alkyne transformations: the 1, 3-dipolar cycloaddition of terminal alkynes with azide and the three component synthesis of propargylamines from aldehydes, amines and terminal alkynes ($A^3$ coupling). The optimal reaction conditions were determined independently for both reactions studied.

**Click reaction based synthesis of 1, 4- disubstituted 1, 2, 3-triazole.**

We started our study by examining the model reaction of benzyl azides and phenyl acetylene which afforded 1-benzyl-4-phenyl-1*H*-1, 2, 3-triazole **(3a)**. Initially, the reaction was investigated using various catalysts and solvents **(Table 2)** with a view to finding optimal conditions to maximize the yield of the product. The reaction in the absence of catalyst in water under room temperature and sonication failed to afford the product **(Table 2, entry 1, 2)**. Then we used LCO NPs as heterogeneous catalyst to carry out azide cycloaddition. Under grinding, the triazole was obtained as a sole product with 30% yield **(Table 2, entry 3)** and the product was confirmed by NMR spectrum analysis. When the same reaction was performed using ultrasonic irradiation without solvent that increased the yield up to 40% **(Table 2, entry 4)**. Further optimization was carried out in different organic solvents such as toluene and DMF gave yields of 30% and 15% **(Table 2, entry 5, 6)** respectively. While the reaction proceeded moderately in acetonitrile **(Table 2, entry 7)**, a huge improvement was observed in polar protic solvents (82-85 %), **(Table 2, entry 8-10)** and combination of polar protic solvents with water such as methanol: water, ethanol: water, t-butanol: water and acetonitrile: water gave 93-95% of yield **(Table 2, entry 11-14)**. Inspired by the observed determinant effect of water and polar protic solvents on the reaction, we further investigated the feasibility of using water as the solvent for this reaction. As we expected, the reaction progressed very well and 99% yield was obtained under identical condition **(Table 2, entry 15)**. It should be noted that the model reaction in CuO NPs gave only 65% of yield **(Table 2, entry 20)**, It revealed that the La in La loaded CuO increases the yield of the reaction. Further investigation revealed that the result was affected by the amount of catalyst. The catalyst loading varied from 3 to 30 mg **(Table 2, entry 16-19),** the maximum yield was obtained when 10 mg catalyst was used. Above 10 mg of the catalyst, no significant change in the conversion occurred **(Fig. 7).** Performing model reaction in $H_2O$ not only offers a high reaction yield, but also avoids: (i) generation of toxic wastes (ii) the use of large amount of organic solvent (iii) tedious post treatment. Therefore, our methodology is an attractive strategy for the synthesis of the target compound from the view point of green synthesis.

**Table 2.** Optimization of azide-alkyne cycloaddition.




1a 2a 3a

| Entry | Condition | Catalyst | Weight % of catalyst (mg) | Solvent | Time (min) | Yield (%)[a] |
|---|---|---|---|---|---|---|
| 1 | RT stirring | - | - | Water | 17h | - |
| 2 | Sonication | - | - | Water | 60 | - |
| 3 | Grinding | LCO | 10 | Without solvent | 60 | 30 |
| 4 | Sonication | LCO | 10 | Solvent free | 60 | 40 |
| 5 | Sonication | LCO | 10 | Toluene | 30 | 30 |
| 6 | Sonication | LCO | 10 | Dimethylformamide | 30 | 15 |
| 7 | Sonication | LCO | 10 | Acetonitrile | 30 | 65 |
| 8 | Sonication | LCO | 10 | Methanol | 30 | 85 |
| 9 | Sonication | LCO | 10 | Ethanol | 30 | 85 |
| 10 | Sonication | LCO | 10 | t-butanol | 30 | 82 |
| 11 | Sonication | LCO | 10 | Methanol : water | 15 | 95 |
| 12 | Sonication | LCO | 10 | Ethanol : water | 15 | 95 |
| 13 | Sonication | LCO | 10 | t-butanol : water | 15 | 93 |
| 14 | Sonication | LCO | 10 | Acetonitrile : water | 30 | 95 |
| **15** | **Sonication** | **LCO** | **10** | **Water** | **15** | **99** |
| 16 | Sonication | LCO | 3 | Water | 15 | 94 |
| 17 | Sonication | LCO | 7.5 | Water | 15 | 97 |
| 18 | Sonication | LCO | 15 | Water | 15 | 98 |
| 19 | Sonication | LCO | 30 | Water | 15 | 98 |
| 20 | Sonication | CuO | 10 | Water | 30 | 65 |

[a] Isolated yield

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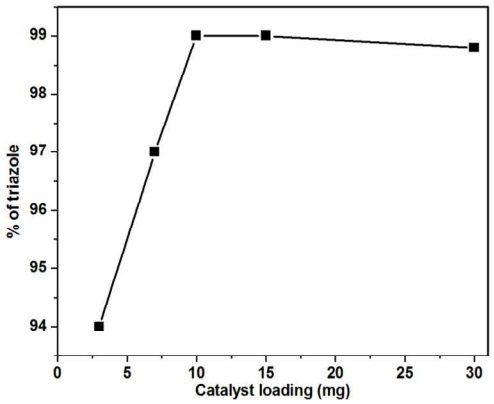



**Fig. 7:** Effect of catalyst loading for the synthesis of 1, 4-disubstitued 1,2,3-triazole under ultrasonication method.

With these results in hand, we further investigate the substrate scope and the results are presented in **Table 3**. Many azides including 4-nitro benzyl, 4-methoxy benzyl, 4-chloro benzyl, 2-thiophenyl methyl, n-octyl and n-hexyl react with various terminal alkynes and afford the corresponding products in good to excellent yields **(Table 3, entry 1-9 and 11-14)**. The reaction condition is also applicable to internal alkyne to afford the corresponding product with moderate yield **(Table 3, entry -10)**. The reusability of the catalyst was checked six times without any treatment (**Table 4**) and found that there is no appreciable loss in the yield (**Fig.8**).

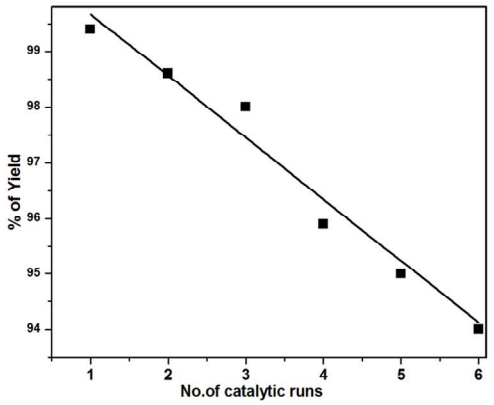
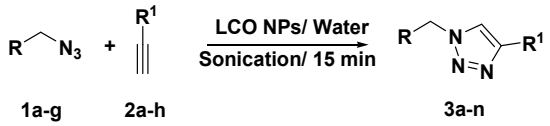
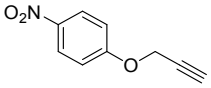
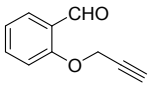
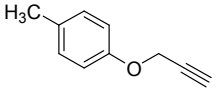
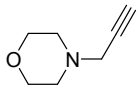
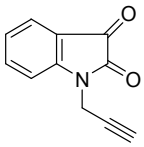



**Fig. 8:** Reusability of catalyst for the synthesis of 1, 4-disubstitued 1, 2, 3-triazole under ultrasonication method.

**Table 3**. Synthesis of 1, 4-disubstituted 1, 2, 3-triazoles with different alkynes and azides.




1a-g 2a-h 3a-n

| Entry | Alkyne | Azide (R) | Product | Yield (%)[a] |
|---|---|---|---|---|
| 1 | Ph—≡—**2a** | $C_6H_5$, **1a** | **3a** | 99 |
| 2 |  **2b** | **1a** | **3b** | 96 |
| 3 |  **2c** | **1a** | **3c** | 97 |
| 4 |  **2d** | **1a** | **3d** | 90 |
| 5 |  **2e** | **1a** | **3e** | 87 |
| 6 |  **2f** | **1a** | **3f** | 89 |
| 7 | **2a** | 4-$NO_2C_6H_4$, **1b** | **3g** | 93 |
| 8 | **2a** | 4-$OCH_3C_6H_4$, **1c** | **3h** | 97 |
| 9 | **2a** | 4-$ClC_6H_4$, **1d** | **3i** | 95 |
| 10 | Ph—≡—Ph **2g** | **1a** | **3j** | 65 |
| 11 | **2a** | 2-thiophenyl, **1e** | **3k** | 82 |
| 12 | **2a** | $CH_3(CH_2)_6$, **1f** | **3l** | 87 |
| 13 | **2a** | $CH_3(CH_2)_4$, **1g** | **3m** | 91 |
| 14 | ≡—COOEt **2h** | **1a** | **3n** | 88 |

[a]Isolated yield

**Table 4.** Reusability of catalyst LCO NPs.[a]

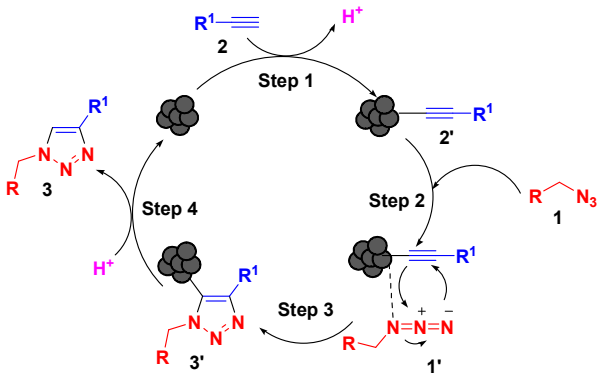
| Run | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Yield[b] | 99.4 | 98.6 | 98.1 | 95.9 | 95.4 | 94.0 |

[a] Reaction condition: benzyl azide (1eqiv.), phenyl acetylene (1.5 eqiv.), LCO NPs (10mg) and 5mL $H_2O$.

[b]Isolated yield.

By analogy with previous reports, the synthesis involves stepwise mechanism **(Scheme 1)**. First step, the LCO NPs coordinate with alkyne **2** to form copper acetylide (**2′**) followed by coordination of the organic azide **1** in the second step. The coordination event

is synergistic for both reactive partners. Coordination of the azide reveals the β-nucleophilic, vinylidene-like properties of the acetylide, whereas the azide's terminus becomes more electrophilic, and a strained copper triazolide (**3′**) is formed. Protonation of the triazole–copper derivative followed by dissociation of the product **3** completes the reaction and regenerates the catalyst.

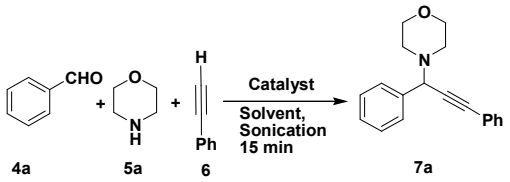



**Scheme 1.** Tentative mechanism for click reaction using LCO NPs catalyst.

**A$^3$ coupling reaction based one-pot synthesis of propargylamines.**

The catalytic activity of the LCO NPs was also examined in the synthesis of propargylamines, the reaction of benzaldehyde, morpholine and phenylacetylene were examined and the results are presented in **Table 5**. Among the various solvents and solvent/co-solvent mixtures, toluene was found to be the most effective medium for this transformation **(Table 5, entry 7)**. After finding the best solvent, amount of catalyst **(Table 5, entry 8-11)** was optimized. The highest yield of propargylamines was achieved when 10 mg catalyst in toluene was used **(Table 5, entry 7).** The low yield was obtained when the bare CuO NPs used as catalyst **(Table 5, entry 12)** and it clearly demonstrates the effect of LCO NPs in this reaction.

**Table 5.** Effect of solvent on A$^3$ coupling reaction.



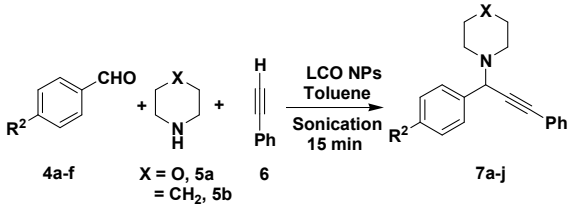

| Entry | Catalyst (mg) | Solvent | Yield (%)[a] |
|---|---|---|---|
| 1 | LCO (10) | Water | 40[b] |
| 2 | LCO (10) | Ethanol | 30 |
| 3 | LCO (10) | Methanol | 45 |
| 4 | LCO (10) | DCM | 40 |
| 5 | LCO (10) | DMF | 15 |
| 6 | LCO (10) | $CH_3CN$ | 58 |
| **7** | **LCO (10)** | **Toluene** | **98** |
| 8 | LCO (3) | Toluene | 93 |
| 9 | LCO (7.5) | Toluene | 95 |
| 10 | LCO (15) | Toluene | 98 |
| 11 | LCO (30) | Toluene | 98 |
| 12 | CuO (10) | Toluene | 60 |

[a] Isolated yield

[b] reaction time 1h

The scope of this LCO NPs catalyzed A$^3$ coupling was further expanded with a variety of aldehydes and amines and these results were summarized in **Table 6**. The reactions proceeded well to obtain products in encouraging yields. Electron donating substituents like methyl, as well as methoxy group at para position **(Table 6, entries 2,3 and 7,8)** and electron withdrawing chlorine and bromine atom at the para position of aldehyde **(Table 6, entries 4,5 and 9,10)** did not induce appreciable changes in the reaction efficiency. In the presence of $NO_2$ group at para position of the aldehyde no product was isolated. **(Table 6, entry 6).**

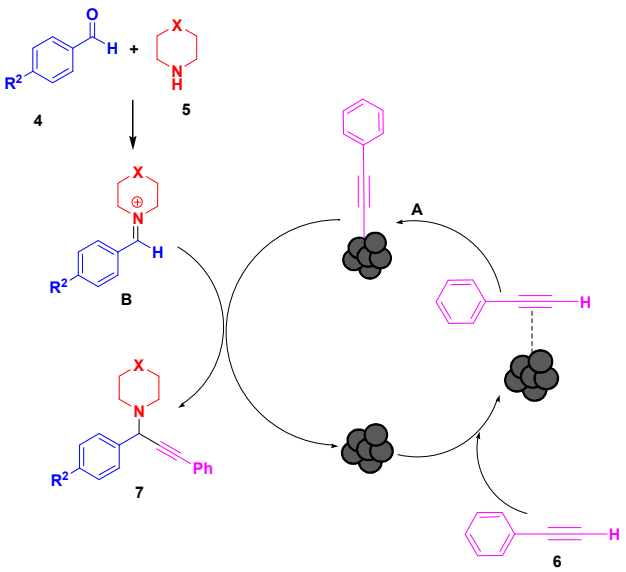
**Table 6**. Substrate scope of different aldehydes and amines.




| Entry | Aldehyde, $R^2$ | Amine | Product | Yield[a] (%) |
|---|---|---|---|---|
| 1 | H, **4a** | **5a** | **7a** | 98 |
| 2 | $CH_3$, **4b** | **5a** | **7b** | 90 |
| 3 | $OCH_3$, **4c** | **5a** | **7c** | 92 |
| 4 | Br, **4d** | **5a** | **7d** | 94 |
| 5 | Cl, **4e** | **5a** | **7e** | 92 |
| 6 | $NO_2$, **4f** | **5a** | **7f** | -[b] |
| 7 | **4b** | **5b** | **7g** | 95 |
| 8 | **4c** | **5b** | **7h** | 89 |
| 9 | **4d** | **5b** | **7i** | 92 |
| 10 | **4e** | **5b** | **7j** | 90 |

[a] Isolated yield.

[b] No reaction.




**Scheme 2.** Tentative mechanism of A$^3$ coupling reaction using LCO catalyst.

A tentative mechanism (**Scheme 2**) is proposed for the probable sequence of events involving the activation of the C-H bond of alkyne **(6)** by LCO NPs. The Cu-acetylide intermediate **(A)**

generated by the reaction of acetylene and LCO reacts with iminium ion **(B)**, formed in situ by condensation of aldehyde with secondary amine to afford desired propargylamines **(7),** and the catalyst is generated.

## Conclusions

We have developed an efficient La loaded CuO nanoparticles as heterogeneous catalyst for the synthesis of 1,4-disubstituted-1,2,3-triazole by click reaction of azide and alkyne and propargyl amine by $A^3$ coupling reaction of aldehyde, secondary amine and terminal alkynes under ultrasonic irradiation. In this method, the catalyst was collected easily by filtration and the reusability of the prepared nanocatalyst was successfully examined over six times and was found to be effective with only a very slight loss of catalytic activity. This protocol is a clean and safe process, and can be used to generate a diverse range of product in good to excellent yields.

## Notes

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† Electronic Supplementary Information (ESI) available: $^1$H and $^{13}$C NMR spectrum of all compounds. See DOI: 10.1039/b000000x/

## Experimental section

All chemicals were obtained from Sigma-Aldrich Company and used as received. All azides were prepared as per the procedure reported earlier.[38] All the solvents and aldehydes were used after distillation. Melting points were measured on Guna melting point apparatus and are uncorrected. NMR spectra were obtained on a Bruker Avance 400 NMR Spectrometer ($^1$H NMR: 400 MHz; $^{13}$C NMR: 100 MHz). Analytical TLC was carried out with Merck plates precoated with silica gel 60 $F_{254}$ (0.25 mm thick). Mass spectra were recorded on a JEOL GC Mate using electron impact ionization (EI) techniques. The mass were analyzed by using a Electrospray Ionisation Method with Thermo Finnigan Mass spectrometer. Elemental analyses were recorded using a Thermo Finnigan FLASH EA 1112 CHN analyzer. Powder X-ray diffraction patterns were obtained using X′Per PRO diffractometer equipped with a CuKα radiation (wavelength 1.5406 Å) at 2.2 kW Max. Peak positions were compared with the standard files to identity the crystalline phase. The morphology of the catalyst was examined using a JEOL JSM-6701F cold field emission scanning electron microscope (FE-SEM). The specific surface areas of the samples were determined through nitrogen adsorption at 77 K on the basis of BET equation using a micrometrics ASAP 2020 V3.00 H. Diffuse reflectance spectra were recorded using Shimadzu UV-2450. Photoluminescence (PL) spectra at room temperature were recorded using a Perkin Elmer LS 55 fluorescence spectrometer. The nanoparticles were dispersed in carbon tetrachloride and excited using light of wavelength 300 nm. X-ray photoelectron spectra of the catalysts were recorded in an ESCA-3 Mark II spectrometer (VG Scientific Ltd., England) using Al Kα (1486.6 eV) radiation as the source. Spectra were referenced to the binding energy of C1s (284 eV).

**Preparation of LCO nano particles.**

The La-loaded CuO NPs was prepared by a precipitation thermal decomposition method. Aqueous solutions consisting of copper nitrate and oxalic acid in deionized water were separately brought to their boiling points. When the oxalic acid solution was added to solution of copper nitrate, copper oxalate was precipitated. Then, $La(NO_3)_3$ solution was mixed with the solution of copper oxalate suspension and then stirred for 1 h at 60−70 °C. After the mixture had cooled to room temperature, La containing copper oxalate was washed with distilled water, air dried overnight, and dried at 100 °C for 5 h. Calcination of the mixed precipitate at 450 °C for 5 h decomposed copper oxalate to CuO. The La-loaded CuO obtained after the sample had cooled to room temperature. The bare CuO was prepared without addition of $La(NO_3)_3$ by the above procedure.

**General Procedure for the Synthesis of 1,4-Disubstituted 1,2,3-Triazoles (3a-j)**

The heterogeneous LCO NPs (10 mg) was added to a mixture of azide (1 mmol) and alkyne (1.5 mmol) in 5ml of water. The solution was subjected to ultrasonic irradiation for particular time duration. The progress of the reaction was monitored by TLC (20% ethyl acetate/hexane). When the reaction was complete, the catalyst was removed by centrifugation. The filtrate was extracted with ethyl acetate (3x 10 ml). The combined organic solutions were dried with $Na_2SO_4$.The pure products were isolated without column purification only by the process of crystallization.

**1-benzyl-4-phenyl-1*H*-1, 2, 3-triazole (3a):**[39a] White solid; Mp = 118-120 °C; $R_f$ = 0.58 (30 % Ethylacetate: n-hexane); $^1$H NMR (400 MHZ, $CDCl_3$): $\delta_H$ 7.80 (d, *J* = 7.6 Hz, 2H), 7.66 (s, 1H), 7.42-7.38 (m, 5H), 7.32-7.30 (m, 3H), 5.58 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δc 149.0, 134.7, 130.5, 129.2, 128.8, 128.2, 128.1, 125.7, 119.5, 54.3.

**4-((4-nitrophenoxy) methyl)-1-benzyl-1*H*-1, 2, 3-triazole (3b):** Yellow solid; Mp = 94-96 °C; $R_f$ = 0.2 (30 % Ethylacetate: n-hexane); $^1$H NMR (400 MHZ, $CDCl_3$): $\delta_H$ 8.19 (d, *J* = 8.8 Hz, 2H), 7.56 (s, 1H), 7.40-7.38 (m, 3H), 7.30-7.26 (m, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 5.55 (s, 2H), 5.27 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δc 163.1, 141.9, 134.2, 129.2, 128.9, 128.2, 125.9, 122.9, 114.9, 62.5, 54.4; HRMS: calculated for $C_{16}H_{14}N_4O_3$ Mw: 310.1066, found: 310.1062.

**2-((1-benzyl-1*H*-1, 2, 3-triazole-4-yl) methoxy) benzaldehyde (3c):** White solid; Mp = 130-132 °C; $R_f$ = 0.23 (30 % Ethylacetate: n-hexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta_H$ 10.42 (s, 1H), 7.83 (d, *J* = 7.6 Hz , 1H), 7.58 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.39-7.37 (m, 3H), 7.29-7.27 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 5.56 (s, 2H), 5.32 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δc 189.6, 160.5, 135.9, 134.3, 129.2, 128.9, 128.7, 128.1, 125.1, 121.4, 113.1, 62.6, 54.4; HRMS: calculated for $C_{17}H_{15}N_3O_2$ Mw: 293.1164, found: 293.1162.

**4-((*p*-tolyloxy)methyl-1-benzyl-1*H*-1, 2, 3-triazole (3d):** White solid; Mp = 96-98 °C; $R_f$ = 0.48 (30 % Ethylacetate: n-hexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta_H$ 7.52 (s, 1H), 7.37-7.35 (m, 3H), 7.27-7.25 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.51 (s, 2H), 5.15 (s, 2H), 2.27 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δc 156.1, 134.5, 130.5, 129.9, 129.2, 128.8, 128.1, 122.7, 114.7, 62.3, 54.3, 20.5; MS m/z = 280 $M^+$+1; Anal. Calcd for $C_{17}H_{17}N_3O$ (279.14): C, 73.10; H, 6.13; N, 15.04. Found: C, 73.18; H, 6.06; N, 15.14.

**4-((1-benzyl-1*H*-1, 2, 3-triazole-4-yl)methyl)morpholine (3e):** Orange solid; Mp = 66-68 °C; $R_f$ = 0.11 (30 % Ethylacetate: n-hexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta_H$ 7.39-7.36 (m, 4H), 7.28-7.26 (m, 2H), 5.51 (s, 2H), 3.70-3.68 (m, 4H), 3.64 (s, 2H), 2.51-2.48 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$): δc 144.5,

134.6, 129.1, 128.8, 128.1, 122.5, 66.8, 54.2, 53.7, 53.4; MS m/z = 259 $M^+$+1; Anal. Calcd for $C_{14}H_{18}N_4O$ (258.15): C, 65.09; H, 7.02; N, 21.69. Found: C, 65.02; H, 7.05; N, 21.75.

**1-((1-benzyl-1*H*-1, 2, 3-triazole-4-yl) methyl) indoline-2,3-dione (3f):** Orange solid; Mp = 134-136 °C; $R_f$ = 0.12 (30 % Ethylacetate: n-hexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta_H$ 7.60-7.56 (m, 2H), 7.52 (s, 1H), 7.37-7.35 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.25-7.23 (m, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 5.48 (s, 2H), 4.99 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δc 183.1, 157.9, 150.2, 142.1, 138.6, 134.0, 129.2, 129.0, 128.3, 125.3, 124.0, 122.8, 117.5, 111.6, 54.4, 35.4. HRMS: calculated for $C_{18}H_{14}N_4O_2$ Mw: 318.1117, found: 318.1115.

**1-(4-nitrobenzyl)-4-phenyl-1*H*-1, 2, 3-triazole (3g):**[39b] White solid; Mp = 114-116 °C; $R_f$ = 0.25 (30 % Ethylacetate: n-hexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta_H$ 8.26-8.23 (m, 2H), 7.82 (d, *J* = 6.8, 2H), 7.75 (s, 1H), 7.46-7.40 (m. 4H), 7.36-7.32 (m, 1H), 5.70 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δc 148.1, 141.7, 130.1, 128.9, 128.6, 128.5, 125.8, 124.4, 119.7, 53.2.

**1-(4-methoxybenzyl)-4-phenyl-1*H*-1, 2, 3-triazole (3h):**[39c] White solid; Mp = 128-130 °C; $R_f$ = 0.45 (30 % Ethylacetate: n-hexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta_H$ 7.78 (d, *J* = 7.2 Hz, 2H), 7.62 (s, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.32-7.25 (m, 3H), 6.90 (d, *J* = 8.8, 2H), 5.49 (s, 2H), 3.80 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δc 159.9, 148.1, 130.6, 129.7, 128.8, 128.1, 126.7, 125.7, 119.3, 114.5, 55.4, 53.8.

**1-(4-chlorobenzyl)-4-phenyl-1*H*-1, 2, 3-triazole (3i):**[39d] White solid; Mp = 132-134 °C; $R_f$ = 0.5 (30 % Ethylacetate: n-hexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta_H$ 7.80 (d, *J* = 7.2 Hz, 2H), 7.67 (s, 1H), 7.42-7.30 (m, 5H), 7.24 (d, *J* = 8.4 Hz, 2H), 5.54 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δc 134.9, 133.2, 130.5, 129.5, 129.4, 129.0, 128.9, 128.3, 125.7, 119.5, 53.5.

**1-benzyl-4,5-diphenyl-1*H*-1, 2, 3-triazole (3j):**[39e] White solid; Mp = 82-86 °C; $R_f$ = 0.5 (30 % Ethylacetate: n-hexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta_H$ 7.55 (d, *J* = 6.8 Hz, 2H), 7.46 (d, *J* = 6.8 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.25-7.22 (m, 6H), 7.14 (d, *J* = 7.2 Hz, 2H), 7.03-7.01 (m, 2H), 5.40 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δc 144.6, 139.4, 135.5, 133.9, 131.0, 130.2, 129.8, 129.3, 128.8, 128.5, 128.2, 127.9, 127.6, 126.8, 52.1.

**4-phenyl-1-(thiophen-2-ylmethyl)-1*H*-1, 2, 3-triazole (3k):**[39f] White solid; Mp = 104-106 °C; $R_f$ = 0.38 (20 % Ethylacetate: n-hexane); $^1$H NMR (400 MHZ, $CDCl_3$): $\delta_H$ 7.71 (d, *J* = 7.2 Hz, 2H), 7.64 (s, 1H), 7.33-7.29 (m, 2H), 7.25-7.22 (m, 2H), 7.05-7.04 (m, 1H), 6.93-6.91(m, 1H), 5.64 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δc 147.2, 135.1, 129.5, 127.8, 127.2, 127.1, 126.3, 126.1, 124.7, 118.2, 47.5.

**1-octyl-4-phenyl-1*H*-1, 2, 3-triazole (3l):**[39g] White solid; Mp = 62-64 °C; $R_f$ = 0.5 (20 % Ethylacetate: n-hexane); $^1$H NMR (400 MHZ, $CDCl_3$): $\delta_H$ 7.75 (d, *J* = 7.6 Hz, 2H), 7.67 (s, 1H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.26-7.22 (m, 1H), 4.29 (t, *J* = 7.6 Hz, 2H), 1.86-1.83 (m, 2H), 1.26-1.18 (m, 10H), 0.79 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δc 147.7, 130.8, 128.8, 128.1, 125.7, 119.4, 50.4, 31.7, 30.4, 29.1, 28.9, 26.5, 22.6, 14.1.

**1-hexyl-4-phenyl-1*H*-1, 2, 3-triazole (3m):**[39f] White solid; Mp = 72-74 °C; $R_f$ = 0.55 (20 % Ethylacetate: n-hexane); $^1$H NMR (400 MHZ, $CDCl_3$): $\delta_H$ 7.75 (d, *J* = 6.8 Hz, 2H), 7.67 (s, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.26-7.22 (m, 1H), 4.30 (t, *J* = 7.2 Hz, 2H), 1.89-1.82 (m, 2H), 1.29-1.21 (m, 6H), 0.81 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δc 146.7, 129.7, 127.8, 127.0, 124.7, 118.3, 49.4, 30.1, 29.3, 25.1, 21.4, 12.9.

**Ethyl-1-benzyl-1H-1,2,3-triazole-4-carboxylate (3n):**[39g] White solid; Mp = 82-86 °C; $R_f$ = 0.15 (20 % Ethylacetate: n-hexane); $^1$H NMR (400 MHZ, $CDCl_3$): $\delta_H$ 8.05 (s, 1H), 7.26-7.19 (m, 5H), 5.83 (s, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δc 157.3, 137.1, 134.0, 127.7, 127.4, 126.9, 126.8, 60.8, 52.3, 13.1.

**General procedure for the synthesis of propargylamine derivatives (7a-j):**

In a 25 mL glass vial, a mixture of benzaldehydes **4a-j** (1mmol), amine **5a, 5b** (1.2 mmol), phenylacetylene **6** (1.5 mmol) and LCO nanoparticles (10 mg) in 5mL toluene, were sonicated for 30 min. The progress of the reaction was monitored by TLC (20% ethyl acetate/hexane). After completion of the reaction, the catalyst was removed by centrifugation. The reaction mixture was extracted with ethyl acetate (3×10 mL). The combined organic phases were dried with $Na_2SO_4$, filtered, concentrated, and the residue was purified by flash chromatography on silica gel (elutant: hexane/ethyl acetate, 3:1, v/v).

**4-(1,3-diphenylprop-2-yn-1-yl)morpholine (7a):**[40a,b] Viscous liquid; $^1$H NMR (400 MHZ, $CDCl_3$): $\delta_H$ 7.64-7.62 (m, 2H), 7.53-7.50 (m, 2H), 7.39-7.24 (m, 6H), 4.79 (s, 1H), 3.78-3.69 (m, 4H), 2.64-2.62 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$): δc 137.8, 131.8, 128.6, 128.3, 128.28, 128.2, 127.8, 123.0, 88.5, 85.1, 67.2, 62.1, 49.9.

**4-(3-phenyl)-1-(*p*-tolyl)prop-2-yn-1-yl)morpholine (7b):**[40c] Viscous liquid; $^1$H NMR (400 MHZ, $CDCl_3$): $\delta_H$ 7.32-7.30 (m, 4H), 7.23-7.21 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 2H), 4.74 (s, 1H), 3.74-3.72 (m, 4H), 2.63-2.61 (m, 4H), 2.35 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δc 137.5, 134.9, 131.8, 128.9, 128.6, 128.3, 128.2, 123.1, 88.3, 85.4, 67.2, 61.8, 49.9, 21.2.

**4-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)morpholine (7c):**[40d] Viscous liquid; $^1$H NMR (400 MHZ, $CDCl_3$): $\delta_H$ 7.51-7.49 (m, 4H), 7.33-7.31(m, 3H), 6.91-6.89 (m, 2H), 4.73(s, 1H) 3.81 (s, 3H), 3.74-3.71 (m, 4H), 2.63-2.59 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$): δc 171.1, 159.2, 131.8, 129.9, 129.7, 128.3, 123.0, 113.6, 88.3, 85.4, 67.2, 61.5, 55.3, 49.8.

**4-(1-(4-bromophenyl)-3-phenylprop-2-yn-1-yl)morpholine (7d):**[40e] Viscous liquid; $^1$H NMR (400 MHZ, $CDCl_3$): $\delta_H$ 7.53-7.47 (m, 6H), 7.34-7.32 (m, 3H), 4.74 (s, 1H), 3.76-3.68 (m. 4H), 2.62-2.59 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$): δc 137.0, 131.8, 131.4, 130.3, 128.5, 128.4, 122.7, 121.8, 88.9, 84.3, 67.1, 61.5, 49.8.

**4-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl)morpholine (7e):**[40e] Viscous liquid; $^1$H NMR (400 MHZ, $CDCl_3$): $\delta_H$ 7.50 (d, *J* = 8.4 Hz, 2H), 7.44-7.41 (m, 2H), 7.26-7.24 (m, 5H), 4.67(s, 1H) 3.66-3.64 (m, 4H), 2.54-2.51 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$): δc 136.5, 133.6, 131.8, 129.9, 128.4, 128.4, 122.7, 88.9, 84.4, 67.1, 61.4, 49.8.

**1-(3-phenyl-1-(*p*-tolyl)prop-2-yn-1-yl)piperidine (7g):**[40f] Viscous liquid; $^1$H NMR (400 MHZ, $CDCl_3$): $\delta_H$ 7.51-7.49 (m, 4H), 7.31-7.30 (m, 3H), 7.17-7.15 (m, 2H), 4.75 (s, 1H), 2.60-2.52 (m, 4H), 2.35 (s, 3H) 1.62-1.53 (m, 4H), 1.44-1.42 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δc 137.1, 135.6, 131.8, 128.8, 128.5, 128.3, 128.0, 123.5, 87.6, 86.4, 62.2, 50.7, 26.2, 24.5, 21.2.

**1-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)piperidine (7h):**[40g] Viscous liquid; $^1$H NMR (400 MHZ, $CDCl_3$): $\delta_H$ 7.54-7.49 (m, 4H), 7.32-7.30 (m, 3H), 6.88 (d, *J* = 7.6 Hz, 2H), 4.78 (s, 1H), 3.80 (s, 3H), 2.59-2.57 (m, 4H), 1.65-1.54 (m, 4H), 1.44-1.42 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δc 159.1 132.0, 131.8, 129.8, 128.3, 128.1, 114.3, 113.4, 87.7, 86.2, 61.7, 55.3, 50.5, 26.0, 24.4.

**1-(1-(4-bromophenyl)-3-phenylprop-2-yn-1-yl)piperidine**

**(7i):**[40h] Viscous liquid; $^1$H NMR (400 MHZ, $CDCl_3$): $\delta_H$ 7.53-7.48 (m, 6H), 7.45-7.32 (m, 3H), 4.73 (s, 1H), 2.54-2.51 (m, 4H), 1-62-1.57 (m, 4H), 1.45-1.44 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δc 137.9, 132.5, 131.9, 131.2, 130.2, 128.5, 123.1, 121.4, 88.3, 85.3, 61.8, 50.7, 26.2, 24.4.

**1-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl)piperidine (7j):**[40i] Viscous liquid; $^1$H NMR (400 MHZ, $CDCl_3$): $\delta_H$ 7.51 (d, *J* = 7.6 Hz, 2H), 7.44-7.42 (m, 2H), 7.26-7.23 (m, 5H), 4.69 (s, 1H), 2.49-2.43 (m, 4H), 1.55-1.49 (m, 4H), 1.38-1.34 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δc 137.4, 133.3, 131.9, 129.9, 128.7, 128.3, 123.2, 121.6, 88.4, 85.5, 61.9, 50.8, 26.3, 24.5.

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## References


1. H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem. Int. Ed*., 2001, **40**, 2004.
2. (a) R. A. Sheldon, I. Arends and U. Hanefeld, *Green Chemistry and Catalysis*, Wiley-VCH, Weinheim, 2007; (b) R. A. Sheldon, *Chem. Commun*., 2008, **29**, 3352–3365; (c) P. Anastas and N. Eghbali, *Chem. Soc. Rev*., 2010, **39**, 301.
3. S. Tan, X. Li, Y. Guo and Z. Zhang, *Nanoscale*., 2013, **5**, 860.
4. K. T. Yong, I. Roy, M. T. Swihart and P. N. Prasad, *J. Mater. Chem*., 2009, **19**, 4655.
5. (a) P. Song, D. Wen, Z. X. Guo and T. Korakianitis, *Phys. Chem. Chem. Phys*., 2008, **10**, 5057; (b) H. Y. Shi, B. Deng, S. L. Zhong, L. Wang and A. W. Xu, *J. Mater. Chem*., 2011, **21**, 12309.
6. (a) Y. Ding, Y. Wang, L. Zhang, H. Zhang, C. M. Li and Y. Lei, *Nanoscale*, 2011, **3**, 1149; (b) O. A. Sadik, A. L. Zhou, S. Kikandi, N. Du, Q. Wang and K. Varner, *J. Environ. Monit*., 2009, **11**, 1782; (c) X. D. Wang, O. S. Wolfbeis and J. R. Meier, *Chem. Soc. Rev*., 2013, **42**, 7834.
7. D. Jariwala, V. K. Sangwan, L. J. Lauhon, T. J. Marks and M. C. Hersam, *Chem. Soc. Rev*., 2013, **42**, 2824.
8. J. Liao, Z. Yang, H. Wu, D. Yan, J. Qiu, Z. Song Y. Yang, D. Zhou, and Z. Yin, *J. Mater. Chem. C*, 2013, **1**, 6541.
9. H. Kang, Y. Zhu, X. Yang, J. Shen, C. Chen and C. Li, *New J. Chem*., 2010, **34**, 2166.
10. (a) H. Wamhoff, *Comprehensive Heterocyclic Chemistry 1*; A. R. Katritzky and C. W. Rees, Eds.; Pergamon: Oxford, 1984, **5**, 669; (b) S. Velazquez, R. Alvarez, C. Perez, F. Gago, C. De, J. Balzarini and M. Camaraza, *J. Antivir. Chem. Chemother.* 1998, **9**, 481; (c) C. Im, S. N. Maiti, R. G. Micetich, M. Daneshtalab, K. Atchison and O. A. Phillips, *J. Antibiot*. 1994**,** **47**, 1030; (d) M. J. Genin, D. A. Allwine, D. J. Anderson, M. R. Barbachyn, D. E. Emmert, S. A. Garmon, D. R. Graber, K. C. Grega, J. B. Hester, D. K. Hutchinson, J. Morris, R. J. Reischer, C.W. Ford, G. E. Zurenko, J. C. Hamel, R. D. Schaadt, D. Stapert and B. H. Yagi, *J. Med. Chem*. 2000, **43,** 953; (e) W. Q. Fan, A. R. Katritzky, *Comprehensive Heterocyclic Chemistry II*; A. R. Katritzky, C. W. Rees and E. F. V. Scriven, Eds.; Elsevier Science: Oxford, 1996, **4**, 1–126.
11. (a) R. Huisgen, *In 1,3-Dipolar Cycloaddition Chemistry*; A. Padwa, Ed.; John Wiley: New York, 1984, 1-176; (b) C.-K. Sha and A. K. Mohanakrishan, *In Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry toward Heterocycles and Natural Products*; A. Padwa and W. H. Pearson, Eds.; Wiley: New York, 2003, 623 - 680.
12. (a) F. Palacios, A. M. Ochoa de Retana, J. Pagalday and J. M. Sanchez, *Org. Prep. Proced. Int*. 1995, **27**, 603-612; (b) D. J. Hlasta and J. H. Ackerman, *J. Org. Chem*. 1994, **59**, 6184-6189; (c) W. L. Mock, T. A. Irra, J. P. Wepsiec and M. Adhya, *J. Org. Chem*. 1989, **54**, 5302-5308; (d) W. Peng and S. Zhu, *Synlett*. 2003, 187-190.
13. (a) K. Wang, X. Bi, S. Xing, P. Liao, Z. Fang, X. Meng, Q. Zhang, Q. Liu and Y. Ji, *Green Chem*. 2011, **13**, 562-565; (b) T. Shamim and S. Paul, *Catal. Lett*. 2010, **136**, 260-265.
14. V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem. Int. Ed*. 2002, **41**, 2596-2599.
15. C. W. Tornoe, C. Christensen and M. Meldal, *J. Org. Chem*. 2002, **67**, 3057-3064.
16. (a) V. D. Bock, H. Hiemstra and J. H. van Maarseveen, *Eur. J. Org. Chem*. 2006, 51–68; (b) M. Medal and C. W. Tornoe, *Chem. Rev*. 2008, **108**, 2952–3015; (c) F. Amblard, J. H. Cho and R. F. Schinazi, *Chem. Rev*. 2009, **109**, 4207–4220; (d) J. E. Hein and V. V. Fokin, *Chem. Soc. Rev*. 2010, **39**, 1302–1315; (e) L. Liang and D. Astruc, *Coord. Chem. Rev*. 2011, **255**, 2933–2945; (f) S. Dıez-Gonzalez, *Catal. Sci. Technol*. 2011, **1**, 166–178; (g) T. Jin, M. Yan and Y. Yamamoto, *Chem. Cat. Chem.*, 2012, **4**, 1217–1229.
17. Q. Wang, S. Chittaboina, H. N. Barnhill, *Lett. Org. Chem*. 2005, **2**, 293-301.
18. F. Himo, T. Lovell, R. Hilgraf, V. V. Rostovtsev, L. Noodleman, K. B. Sharpless and V. V. Fokin, *J. Am. Chem. Soc*. 2005, **127**, 210-216.
19. S. Quader, S. E. Boyd, I. D. Jenkins and T. A. Houston, *J. Org. Chem*. 2007, **72**, 1962-1979.
20. (a) T. Jin, M. Yan, Menggernbateer, T. Minato, M. Bao and Y. Yamamoto, *Adv. Synth. Catal*. 2011, **353**, 3095–3100; (b) T. L. Cook, J. A. Walker and J. Mack, *Green Chem*., 2013, **15**, 617–619.
21. (a) J. Y. Kim, J. C. Park, H. Kang, H. Song and K. H. Park, *Chem. Commun*., 2010, **46**, 439–441; (b) C. Shao, R. Zhu, S. Luo, Q. Zhang, X. Wang and Y. Hu, *Tetrahedron Lett*. 2011, **52**, 3782–3785; (c) F. Alonso, Y. Moglie, G. Radivoy and M. Yus, *Synlett.*, 2012, **23**, 2179–2182; (d) B. S. P. Anil Kumar, K. Harsha Vardhan Reddy, G. Satish, R. Uday Kumar and Y. V. D. Nageswar, *RSC Adv.*, 2014, **4**, 60652-60657.
22. (a) B. H. Lipshutz and B. R. Taft, *Angew. Chem., Int. Ed*. 2006, **45**, 8235–8238; (b) C.-T. Lee, S. Huang and B. H. Lipshutz, *Adv. Synth. Catal*. 2009, **351**, 3139–3142; (c) M. Fuchs, W. Goessler, C. Pilger and C. O. Kappe, *Adv. Synth. Catal*. 2010, **352**, 323–328; (d) F. Alonso, Y. Moglie, G. Radivoy and M. Yus, *Adv. Synth. Catal*. 2010, **352**, 3208–3214; (e) F. Alonso, Y. Moglie, G. Radivoy and M. Yus, *Org. Biomol. Chem*. 2011, **9**, 6385–6395; (f) F. Alonso, Y. Moglie, G. Radivoy and M. Yus, *J. Org. Chem*. 2011, **76**, 8394–8405.
23. (a) Y. Wang, J. Liu and C. Xia, *Adv. Synth. Catal*. 2011, **353**, 1534–1542; (b) M. Liu and O. Reiser, *Org. Lett*. 2011, **13**, 1102–1105; (c) B. Kaboudin, Y. Abedi and T. Yokomatsu, *Org. Biomol. Chem*. 2012, **10**, 4543–4548; (d) A. Kumar, S. Aerry, A. Saxena, A. de and S. Mozumdar, *Green Chem*. 2012, **14**, 1298–1301; (e) Y. M. A. Yamada, S. M. Sarkar and Y. Ouzumi, *J. Am. Chem. Soc*. 2012, **134**, 9285–9290; (f) M. Tajbakhsh, M. Farhang, S. M. Baghbanian, R. Hosseinzadeh and M. Tajbakhsh, *New. J. Chem.*, 2015, **39**, 1827-1839.
24. (a) K. Namitharan, M. Kumarraja and K. Pitchumani, *Chem.–Eur. J*. 2009, **15**, 2755–2758; (b) J. C. Park, A. Y. Kim, J. Y. Kim, S. Park, K. H. Park and H. Song, *Chem. Commun*. 2012, **48**, 8484–8486; (c) M. N. S. Rad, S. Behrouz, M. M. Doroodmand and A. Movahediyan, *Tetrahedron*, 2012, **68**, 7812–7821; (d) S. Mohammed, A. K. Padala, B. A. Dar, B. Singh, B. Sreedhar, R. A. Vishwakarma and S. B. Bharate, *Tetrahedron*, 2012, **68**, 8156–8162; (e) L. Wan and C. Cai, Catal. Lett., 2012, 142, 1134–1140; (f) J.-M. Collinson, J. D. E. T. Wilton-Ely and S. Dıez-Gonzalez, *Chem. Commun*. 2013, **49**, 11358–11360; (g) B. A. Dar, A. Bhowmik, A. Sharma, P. R. Sharma, A. Lazar, A.P. Singh, M. Sharma, B. Singh, Applied Clay Science, 2013; (h) Y. R. Girish, K. S. S. Kumar, U. Muddegowda, N. K. Lokanath, K. S. Rangappa and S. Shashikanth, *RSC Adv.,* 2014, **4**, 55800; (i) J. M. Perez, R. Cano and D. J. Ramon, *RSC Adv.,* 2014, **4**, 23943; (j) V. B.

Purohit, S. C. Karad, K. H. Patel and D. K. Raval, *RSC Adv.,* 2014, **4**, 46002.
25. (a) E-S. Lee, H.-S. Yeom, J-H. Hwang and S. Shin, *Eur. J. Org.Chem*., 2007, 3503-3507; (b) B. Jiang and M. Xu, *Angew. Chem. Int. Ed*., 2004, **43**, 2543-2546.
26. (a) S. Samai, G. C. Nandi and M. S. Singh, *Tetrahedron Lett*. 2010, **51,** 5555–5558; (b) A. Bisai and V. K. Singh, *Org. Lett*., 2006, **8**, 2405-2408; (c) T. Okamura, K. Asano and S. Matsubara, *Synlett*, 2010, 3053-3056.
27. (a) Z. Li, C. Wei, L. Chen, R. S. Varmab and C.-J. Li, *Tetrahedron Lett.* 2004, **45**, 2443– 2446; S. B. Park and H. Alper, *Chem. Commun*. 2005, 1315–1317; (c) P. R. Likhar, S. Roy, M. Roy, M. S. Subhas, M. L. De and R. L. Kantam , *Synlett*, 2007, 2301–2303; (d) B. J -Borah, S. J-Borah, L. Saikia and D. K. Dutta, *Catal. Sci.Technol*., 2014, **4,** 1047-1054; (e) M. L. Kantam, J. Yadav, S. Laha and S. Jha, *Synlett,* 2009, **40** 1791–1794; (f) F. Nador, M. A. Volpe, F. Alonso, A. Feldhoff, A. Kirschning and G. Radivo, *Appl. Catal., A*, 2013, **455,** 39-45; (g) N. Anand, P. Ramudu, K. H. P. Reddy, K. S. R. Rao, B. Jagadeesh, V. S. P. Babu and D. R. Burri, *Appl. Catal., A*, 2013, 45 **454,** 119-126; (f) X. Zhang and A. Corma, *Angew. Chem. Int. Ed*., 2008, **47,** 4358-4361.
28. (a) R. Cella and H. A. Stefani, *Tetrahedron*, 2009, **65**, 2619; (b) G. Cravotto and P. Cintas, *Chem. Soc. Rev*, 2006, **35**, 180; (c) B. Dar, M. Sharma and B. Singh, *Bull. of Chem. React. Eng. & Catal.*, 2012, **7**, 79; (d) M. Driowya, A. Puissant, G. Robert, P. Auberger, R. Benhida, K. Bougrin, *Ultrason. Sonochem*. 2012, **19**, 1132; (e) T. J. Mason, *Chem. Soc. Rev*. 1997, **26**, 443.
29. L. Q. Ding, W. Wang and A.Q. Zhang, *Ultrason. Sonochem*, 2007, **14**, 563.
30. J. K. Kim, F. Martinez and I. S. Metcalfe, *Catal. Today*, 2007, **124**, 224.
31. (a) P. Cintas, A. Barge, S. Tagliapietra, L. Boffa and G. Cravotto, *Nat. Protoc.,* 2010, **5**,607; (b) G. Cravotto, V.V. Fokin, D. Garella, A. Binello, L. Boffa and A. J. Barge, *J. Comb. Chem*. 2010, **12**, 13.
32. (a) R. Srivastava, M. U. A. Prathap and R. Kore, *Colloids Surf. A: Physicochem. Eng. Aspects*. 2011, **392**, 271–282; (b) A. S. Ethiraj and D. J. Kang, *Nanoscale Res. Lett.*. 2012, **7**, 70.
33. A. S. Priya, I. B. S. Banu and M. Chavali, *Arab. J. Sci. Eng.*, 2015, (In press) (DOI 10.1007/s13369-015-1668-z).
34. (a) J. Moulder, W. Sticke, P. Sobol and K. Bomben, *Standard ESCA spectra of the elements and line energy information. In Handbook of X-ray Photoelectron Spectroscopy,* Edited by: J. Chastain, USA, Perkin Elmer Coorporation, Physical Electronics Division; 1992; (b) Z. S. Hong, Y. Cao, J. F. Deng, *Mater. Lett.*, 2002, **52**, 34-38; (c) C. Xu, Y. Lin, G. Xu and G. Wang G *Mater. Res. Bull.* 2002, **37,** 2365-2372; (d) R. A. Zarate, F. Hevia, S. Fuentes, V. M. Fuenzalida, A. Zuniga, J. Solid State Chem., 2007, **180**, 1464-1469; (e) D. Mrabet, A. Abassi, R. Cherizol, T.-O. Do, *Appl. Cata. A-Gen.*, 2012, 447–448, 60–66; (f) M. Pashchanka, R. C. Hoffmann, A. Gurlo, J. C. Swarbrick, J. Khanderi, J. Engstler, A. Issanind and J. J. Schneider, *Dalton Trans.*, 2011, **40**, 4307–4314.
35. (a) J. Ghijsen, L. H. Tjeng, J. V. Elp, H. Eskes, J. Westerink, G. A. Sawatzky and M. T. Czyzyk, *Phys. ReV. B,* 1988, **38**, 11322; (b) C.-K. Wu, M. Yin, S. O'Brien and J. T. Koberstein, *Chem. Mater.* 2006, **18**, 6054-6058.
36. (a) S. Poulston, P. M. Parlett, P. Stone and M. Bowker, *Surf. Interface Anal.,* 1996, **24**, 811–820; (b) A. T. Garcia-Esparza, K. Limkrailassiri, F. Leroy, S. Rasul, W. Yu, L. Lin and K. Takanabe, *J. Mater. Chem. A*, 2014, **2**, 7389–7401.
37. (a) X. Ma, H. Zhang, Y. Ji, J. Xu and D. Yang, *Mater. Lett.* 2004, **58,** 1180–1182; (b) M. Zhou, J. Yuan, W. Yuan, Y. Yin and X. Hong, *Nanotechnology,* 2007, **18**, 405704–405710; (c) M. Salavati-Niasari, G. Hosseinzadeha, F. Davar, *J. Alloy. Compd.,* 2011, **509**, 4098–4103.
38. J. E. Hein and V. V. Fokin, *Chem. Soc. Rev*. 2010, **39**, 1302.
39. (a) K. Kamata, Y. Nakagawa, K. Yamaguchi and N. Mizuno, *J. Am. Chem. Soc.,* 2008, **130**, 15304; (b) P. Appukkuttan, W. Dehaen, V. V. Fokin and E. V. Eycken, *Org. Lett*., 2004, **6**, 4223; (c) C.-Z. Tao, X. Cui, A.-X. Liu, L. Liu and Q.-X. Guo, *Tetrahedron Lett*. 2007, **48**, 3525-3529; (d) C. S. Radatz, L. D. A. Soares, E. R. Vieira, D. Alves, D. Russowsky and P. H. Schneider, *New. J. Chem.* 2014, **38**, 1410-1417; (e) L. Zhang, .X. Chen, P. Xue, H. H. Y. Sun, I. D. Williams, K. B. Sharpless, V. V. Fokin and G. Jia, *J. Am. Chem. Soc.* 2005, **127**, 15998; (f) Z. Chen, Q. Yan, H.Yi, Z. Liu, A. Lei, and Y. Zhang, *Chem. Eur. J*. 2014, **20**, 13692–13697; (g) J. H. Kim and S. Kim, *RSC Adv.,* 2014, **4**, 26516-26523.
40. (a) L. L. Chang, J. Yang, Y. Wei and J. Y. Ying, *Adv. Synth. Catal*. 2009, ***351***, 2887–2896; (b) K.M. Reddy, N.S. Babu, I. Suryanarayana, P.S.S. Prasad and N. Lingaiah, *Tetrahedron Lett*. 2006, **47,** 7563–7566; (c) P. Li and L. Wang, *Tetrahedron*. 2007, **63,** 5455–5459; (d) K. Namitharan and K. Pitchumani, *Eur. J. Org. Chem.* 2010, 411–415; (e) J. Lim, K. Park, A. Byeun, and S. Lee, *Tetrahedron Lett.* 2014, **55**, 4875–4878; (f) N. P. Eagalapatia, A. Rajacka and Y.L.N. Murthy. *J. Mol. Catal. A: Chem.* 2014, **381**,126– 131; (g) S. Samai, G.C. Nandi and M.S. Singh, *Tetrahedron Lett.* 2010, **51**, 5555–5558; (h) K.V.V. Satyanarayana, P. Atchuta Ramaiah, Y.L.N. Murty, M. Ravi Chandra and S.V.N. Pammi, *Catal. Commun*. 2012, **25**, 50–53; (i) C. Wei and C. J. Li, *J. Am. Chem. Soc.* 2003, **125**, 9584–9585.
41. (a) S. N. Shkerin, M. V. Kuznetsov and N. A. Kalashnikova, *Russ. J. Electrochem.* 2003, **39**, 591−599; (b) M. M. Natile, A. Ponzoni, I. Concina and Antonella Glisenti, *Chem. Mater*. 2014, **26**, 1505−1513.