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Regioselective synthesis of 1,4-disubstituted triazoles using *bis*[(L)prolinato-N,O]Zn complex as an efficient catalyst in water as a sole solvent

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A concise, convenient and mild route for one-pot regioselective synthesis of *N*-aryl- and *N*-alkyltriazoles in water as a sole solvent is reported. The methodology involves a three-component reaction comprising aryl/alkyl-alkyne, sodium azide and aryl/alkyl/allyl halide catalyzed by zinc(II) L-prolinate. Prominent features of our protocol are incorporation of transition metal catalyst other than copper, water as the reaction medium, recyclability of catalyst and avoidance of hazardous aryl azide as a reactant. Copyright © 2011 John Wiley & Sons, Ltd.

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Keywords: *bis*[(L)prolinato-N,O]Zn; regioselective; 1,4-disubstituted triazole; water as a sole solvent; recyclability

Introduction

The vast majority of nature's molecules, including proteins, nucleic acid and biologically active compounds, contain nitrogen. There is a growing interest in using specific biologically validated substructures as starting point for library design.[1] The resulting libraries can then be used to address a variety of biological targets.

Triazoles have attracted interest over the past few years as a building block for the synthesis of pharmacologically active compounds and are associated with a wide range of activities including anti-HIVactivity,[2] selective β3-adrenergic receptor inhibition,[3] antibacterial activity,[4] potent antihistamine activity[5–7] and anticancer activity.[8]

These moieties have been widely used in synthetic intermediates and have industrial applications such as for the preparation of dyes, anticorrosive agents, photostabilizers, photographic materials and agrochemicals.[8] These heterocycles are rigid linking units that can mimic the atom placement and electronic properties of a peptide bond without any susceptibility to hydrolytic cleavage.[9]

In 2002, Sharpless *et al*. discovered that Cu(I) catalyzes the 1,3- dipolar cycloaddition of azides and alkynes to form 1,4-disubstituted triazoles, which greatly contributed to the popularization of click chemistry as a highly effective method for functionalization.[10] The conditions used to conduct such reactions can be addition of copper (I) salts in organic or aqueous systems, often in conjunction with a base,[11–13] a copper (II) salts/ascorbic acid system (to generate the copper (I) species *in situ*),[14–16] copper salts adsorbed on zeolites,[17] charcoal[18] or clay,[19] Al_2O_3,[20] copper wire,[21–23] nanoparticles/clusters[24,25] and Cu-based ionic liquid.[26] Use of water as a solvent has also been explored.[27,28] In contrast to the copper-catalyzed version, ruthenium complexes ([Cp*RuCl $(PPh_3)_2$] and [Cp*RuCl]) were found to be efficient catalysts for producing 1,5-disubstituted triazoles regioselectively.[29] Until now no other method has been explored in which a catalyst other than copper has been used. We report for the first time zinc(II) L-prolinate-catalyzed synthesis of 1,4-disubstituted triazole.

The importance of Zn for all kinds of life processes[30–32] is generating new activities in the once-neglected field of Zn coordination chemistry. One aspect of this should be the study of Zn-amino acid and peptide complexes.

Recently, proline and chiral zinc complexes have been shown to act as enantioselective catalysts for aldol reactions.[33,34] *Bis*[(L)prolinato-N,O]Zn complex, i.e zinc(II) L-prolinate, has also been used for the synthesis of 1,5-benzodiazepines.[35] This complex is soluble in water but is not soluble in organic solvents, which allows simple and quantitative recovery of the catalyst. In recent years, organic reactions in aqueous media have attracted a great deal of attention. Water is no doubt cheap, safe and environmentally friendly when compared with organic solvents, and has unique reactivity and selectivity that cannot be obtained in organic solvents. The main advantage of our catalyst is the accessible precursor for the formation of zinc(II) L-prolinate complex.

As part of our ongoing research program to devise greener chemical transformations,[36–38] we reveal herein for the first time a simple, convenient and efficient method for the preparation of triazoles using zinc(II) L-prolinate as a catalyst in water as a solvent.

Experimental Section

All chemicals were purchased from Sigma–Aldrich and Lancaster and were used as received. All reactions and purity of terminal alkynes and halides were monitored by thin-layer chromatography (TLC) using aluminum plates coated with silica gel (Merck) in 30% ethylacetate and 70% hexane. The isolated products were further purified by column chromatography using silica gel

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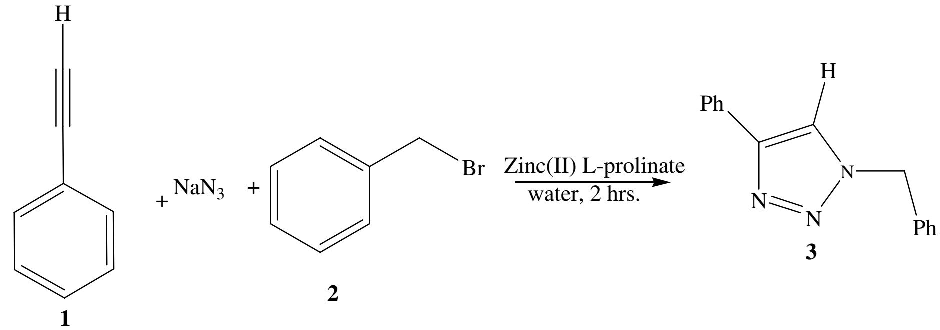


Scheme 1. Model reaction between phenylacetylene, benzylbromide and sodium azide in the presence of zinc(II) L-prolinate in water as a sole solvent.

(Sigma–Aldrich 24, 217–9, 70, 35–70, mesh 40 Å surface area 675 m^2/g). IR spectra were recorded on a Perkin–Elmer FTIR-1710 spectrophotometer using Nujol film and a KBr pellet. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance Spectrospin 300 (300 and 75 MHz) using Tetramethylsilane (TMS) as the internal standard, and chemical shifts are in δ. HR–MS mass spectra were recorded on a Waters LCT Micromass. The melting points of the compounds were measured through a Thomas-Hoover melting point apparatus and are uncorrected. Powder X-ray diffraction (XRD) was done on Bruker D8 Discover at 1600 W. The Transmission electron microscopy (TEM) images were taken on a Technai G2 30 U-TWIN at 300 kV.

Synthesis and Characterization of Zinc(II) L-prolinate

The zinc amino complex was prepared by adding Et_3N (0.6 ml) to the amino acid (4.34 mmol) in MeOH (10 ml), followed, after 10 min, by zinc acetate (2.17 mmol). After stirring for 45 min, a white precipitate was collected by filtration (25–95% yield). Complexes were characterized by ^1H- NMR, IR and ESI-MS.[31]

General Procedure for the Three-component Reactions

An appropriate halide (1.0 mmol), terminal alkyne (1.1 mmol) and sodium azide (1.1 mmol) were added to the round-bottom flask. A 3 ml aliquot of water as solvent and 2 mol% zinc(II) L-prolinate were added and refluxed. The reaction was monitored by TLC. After cooling to room temperature, ethyl ether (2 × 4 ml) was added to the mixture to extract the product. The aqueous part was further used for consecutive runs as the catalyst is water soluble. The combined organic layers were washed with water and brine, dried with anhydrous $MgSO_4$ and evaporated under reduced pressure. The residue was finally purified by column chromatography on silica gel to give the desired product.

Table 1. Model reaction in water catalyzed by various catalysts[a]

Sample no.	Catalyst	Time[b]	Yield[c] (%)
1	$Zn(CH_3COO)_2$	5	40
2	$Zn(OTf)_2$	6	43
3	$Zn\ (ClO_4)_2$	6	40
4	$Zn(NO_3)_2$	5.5	35
6	$ZnSO_4$	12	–
7	$ZnCl_2$	12	–
8	L-Proline	5	38
9	$Zn(Lys)_2$	10	30
10	$Zn(Arg)_2$	6	50
11	$Zn(His)_2$	10	40
12	Zn(L-Pro)$_2$	2	91

[a] Reactions were performed with phenylacetylene (0.01 mol), benzylbromide (0.01 mol), sodium azide (0.01 mol) and various catalysts (2 mol%) in water by refluxing the mixture for *x* h. [b] Reaction progress monitored by TLC. [c] Isolated yield.

Results and Discussion

In an initial endeavor, a blank reaction was carried out using 1 equiv. each of phenylacetylene, benzylbromide and sodium azide. These were refluxed in ethanol. After 20 h only 65% of the expected product was obtained. The same reaction was then carried out using zinc(II) l-prolinate as catalyst in ethanol. Surprisingly, a significant improvement was observed and the yield of product was dramatically increased to 85% after refluxing the mixture in water for only 2 h. After successfully optimizing the reaction conditions for the synthesis of N-aryltriazole 3, we then decided to carry out the reaction using water as the sole solvent (because our catalyst is water-soluble). Water has clear advantages as a solvent because it is cheap, readily available and nontoxic. Moreover, it has been argued that reactants that dislike water tend to come closer (the hydrophobic effect) and complete the reaction faster than in the absence of water. Interestingly, the three-component click chemistry when carried out in water using zinc(II) l-prolinate furnished 3 in a good isolated yield of 90% (Scheme 1).

The catalytic activities for the 1,3-dipolar cycloaddition of **1a** to **2a** in water were also compared with various catalysts. Therefore, the same reaction was initially tested with zinc acetate and proline individually. However, encouraging results were not found. Then, the catalytic abilities of other Zn-(L)-amino acid complexes (2 mol% of catalyst, H_2O) were investigated. The complexes were prepared and isolated as described for Zn-proline. It was found that zinc acetatae is not able to catalyze the reaction efficiently, as the four-membered ring formed by the acetate group on chelation with zinc is not as stable as the five-membered ring formed by the proline group. Moreover only in zinc(II) L-prolinate did the amino acid contain secondary amine, which ultimately enhances the catalytic efficiency of zinc(II) L-prolinate.Other catalysts do not contain any secondary amine. To explain the dominance of our catalyst we tested our model rection with other Zn salts. It was found that the other salts used here were inferior to the zinc(II) L-prolinate. The results are reported in Table 1.

The main point of focus in this reaction is the solubility of the catalyst in the reaction mixture. Since our catalyst is water-soluble,

Table 2. Solvent system for model reaction[a]

Sample no.	Solvent system	Time[b]	Yield[c] (%)
1	Ethanol	4.5	85
2	Ethanol–water	2	92
3	Water	2	91
4	Acetonitrile	2	85
5	THF	3	78
6	Toluene	5	60
7	DMF	5	60
8	DMSO	5	50
9	PEG-400	3.5	80

[a] Reactions were performed with the phenylacetylene (0.01 mol), benzylbromide (0.01 mol), sodium azide (0.01 mol), zinc(II) L-prolinate (2 mol%) as catalyst and solvent system (3 ml) by refluxing the mixture for x h. [b] Reaction progress monitored by TLC. [c] Isolated yield.

Table 3. One-pot synthesis of 1,2,3-triazoles from alkyl/aryl/allyl halides, sodium azide and terminal alkynes[a]

Sample no.	R_1	Halide	Product	Yield[b]	Time (h)
1	Ph	$PhCH_2Br$	3a	91	2
2	Ph	$PhCH_2Cl$	3a	91	2
3	Ph	n-C_4H_9Br	3b	89	2
4	Ph	p-$(NO_2)C_6H_4CH_2Cl$	3c	85	2.5
5	Ph	$CH_2{=}CHCH_2Br$	3d	85	2.5
6	Ph	CH_3I	3e	89	2
7	Ph	n-$C_6H_{13}Br$	3f	82	2.5
8	$COOC_2H_5$	$PhCH_2Br$	3g	90	1.5
9	$COOC_2H_5$	n-C_4H_9Br	3h	88	1.5
10	$COOC_2H_5$	p-$(NO_2)C_6H_4CH_2Cl$	3i	78	2
11	$COOC_2H_5$	$CH_2{=}CHCH_2Br$	3j	87	2
12	$COOC_2H_5$	CH_3I	3k	89	2
13	$COOC_2H_5$	$C_6H_{13}Br$	3l	89	2
14	CH_2OH	$PhCH_2Br$	3m	88	2.5
15	CH_2OH	n-C_4H_9Br	3n	88	3
16	CH_2OH	p-$(NO_2)C_6H_4CH_2Cl$	3o	78	3
17	CH_2OH	$CH_2{=}CHCH_2Br$	3p	85	2.5
18	CH_2OH	CH_3I	3q	88	2.5
19	CH_2OH	$C_6H_{13}Br$	3r	80	3

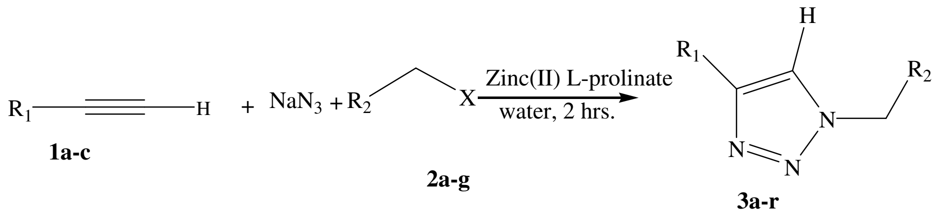
[a] Reactions were performed with the terminal alkyne (0.01 mol), halide (0.01 mol), sodium azide (0.01 mol) and zinc(II) L-prolinate (2 mol%) in water by refluxing the mixture. [b] Isolated yield.

if the reaction were carried out in water as the sole solvent, then the catalyst would be soluble and the catalyst would be homogeneous with the solvent but not with the reactant. On the other hand, if the reaction were carried out in ethanol, then the catalyst would be heterogeneous to the catalyst. Therefore, to investigate the better result, the model reaction was first carried out in water, ethanol and water–ethanol systems individually. When the reaction was carried out in ethanol, the reaction occurred but more slowly. This particular observation explained the lesser selectivity and activity of heterogeneous catalyst as compared with the homogeneous reaction. Other organic solvents were also tested. Although polar solvents such as ethanol and acetonitrile were much better than nonpolar solvents like THF in terms of better yields and shorter reaction times, owing to the enhanced solubility of the reactants. Low yields were observed in the case of nonpolar solvents owing to the failure of the substrate to access the catalyst. Therefore we focused our attention on the aqueous medium. Through these observations, we concluded that reaction in water as the sole solvent would be the preferable option compared with water–ethanol owing to environmental considerations (Table 2).

To further evaluate the scope of this zinc(II) L-prolinate complex-catalyzed process, reactions of benzyl halide with several aliphatic and aromatic terminal alkynes substituted by electron-donating as well as electron-withdrawing groups were carried out. Likewise, the reactivity of phenylacetylene with various alkyl and aryl halides was also studied. In all cases, very good yields of a single regioisomer, namely 1,4-disubstituted 1,2,3-disubstituted triazoles, were obtained (Scheme 2).

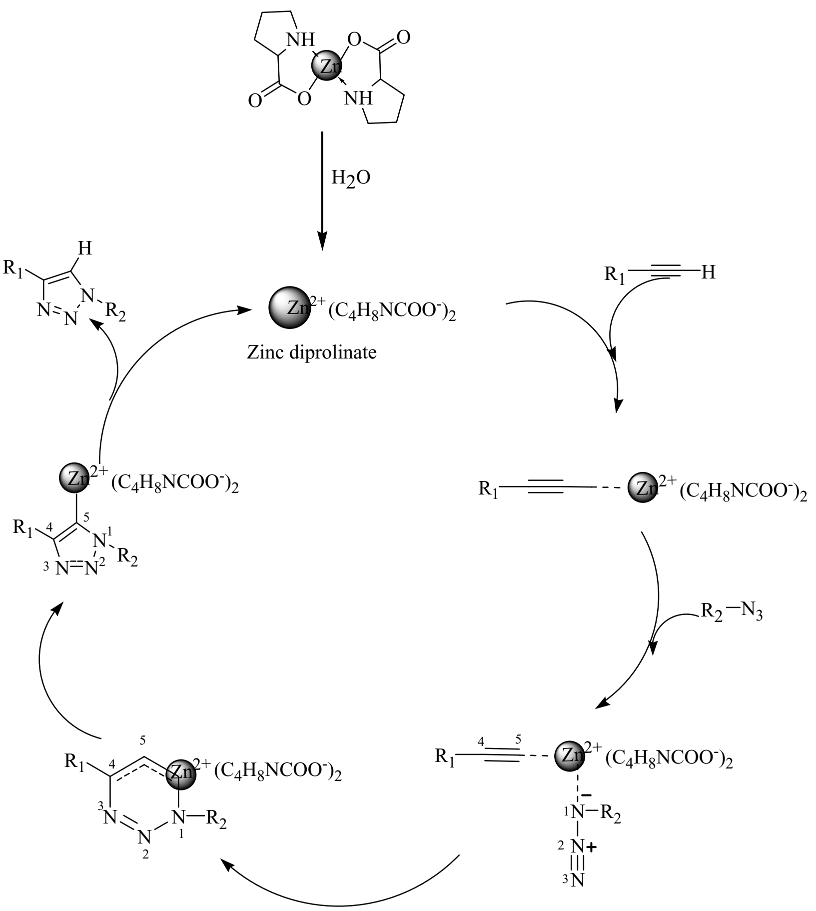
A halide with an electron-withdrawing nitro group [p-$(NO_2)C_6H_4CH_2Cl$] gave a lower yield (Table 3). In our subsequent experiments, we conducted a broader investigation of this reaction in water by utilizing a variety of alkynes and alkyl halides with the aim of synthesizing both N-aryl- and N-alkyltriazoles. The crude N-derivatized triazoles were purified on silica gel column furnishing pure compounds in 80–91% isolated yields.

A proposed mechanism for this transformation is depicted in Scheme 3. Since the reaction is taking place in aqueous medium, *bis*[(L)prolinato-N,O]Zn complex will exist with the metal ion in the form of hydrated cation and the corresponding amino acid in the form of anion as shown in Scheme 3. The *bis*[(L)prolinato-N,O]Zn complex would be transformed into an acetylide by reaction with the alkyne.[39,40] Upon the interaction of acetylide with azide, the reaction would follow the pathway commonly accepted for this transformation to form a triazolide intermediate, which then



R_1, a= Ph, b= $COOC_2H_5$, c= CH_2OH
R_2= Ph, C_3H_7, 4-NO_2-C_6H_4, CH_2CH, H, C_5H_{11}
X= Br, Cl, I

Scheme 2. Reaction between terminal alkynes, halides and sodium azide in the presence of zinc(II) L-prolinate in water as a sole solvent.



Scheme 3. Proposed mechanism.

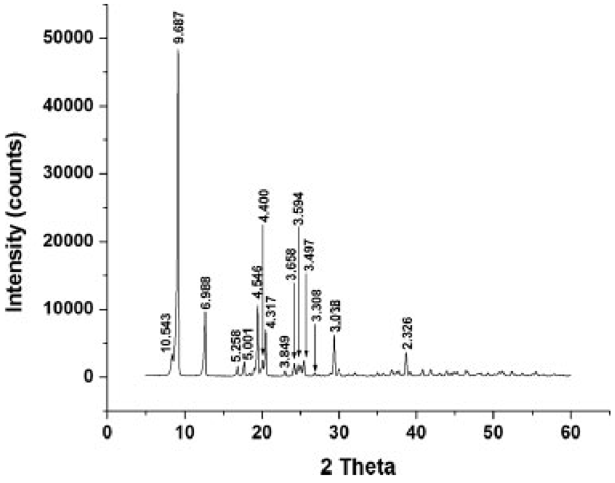


Figure 1. Powder XRD of zinc(II) L-prolinate.

ultimately forms the expected triazole and the regeneration of the catalyst.

Characterization of the Catalyst

Powder X-ray diffraction

X-ray patterns of the zinc(II) L-prolinate complex recorded in the $2\theta = 0-100$ range are shown in Fig. 1. The complex has specific *d* values, which were used for its characterization, and peaks obtained from powder XRD were matched with the data card[41] 47-1919JCDPS. These interpreted peaks revealed that the crystal is orthorhombic in shape.

To check the crystalline nature of the catalyst, TEM images of the catalyst were taken on a carbon-coated grid. By these images it was found that the compound is crystalline in nature. TEM images are given in Fig. 2.

Thermal analysis

To estimate the thermal stability of zinc(II) L-prolinate complex, Thermogravimetric analysis/Differential thermal analysis (TG/DTA) and differential scanning calorimetry (DSC) experiments were carried out and the thermogram is illustrated in Fig. 3. The sample was heated at the rate of 10 K/min in an inert atmosphere. An endothermic peak that was not sharp at 100.62 °C in the DTA curve may be due to the release of adhered solvent molecules. The sharpness of the endothermic peak observed in the DTA curve showed a good degree of crystallinity of the material. The DTA curve gave one sharp endothermic peak at 342.81 °C, which corresponds to the melting point of the complex. The TG curve gives the detailed decomposition of the complex. The DSC study was performed in the temperature range 20–500 °C at a heating rate of 10 K/min in the nitrogen atmosphere (Fig. 3b). The complex underwent an irreversible endothermic transition at 342.81 °C, which corresponds to the melting point of the crystal. The melting point of the substance was confirmed using a melting

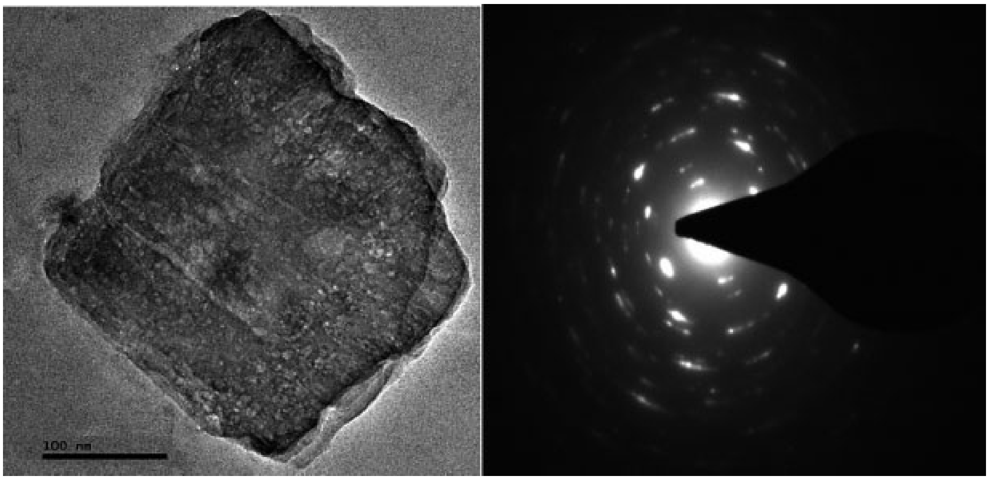


Figure 2. TEM images of zinc(II) L-prolinate.

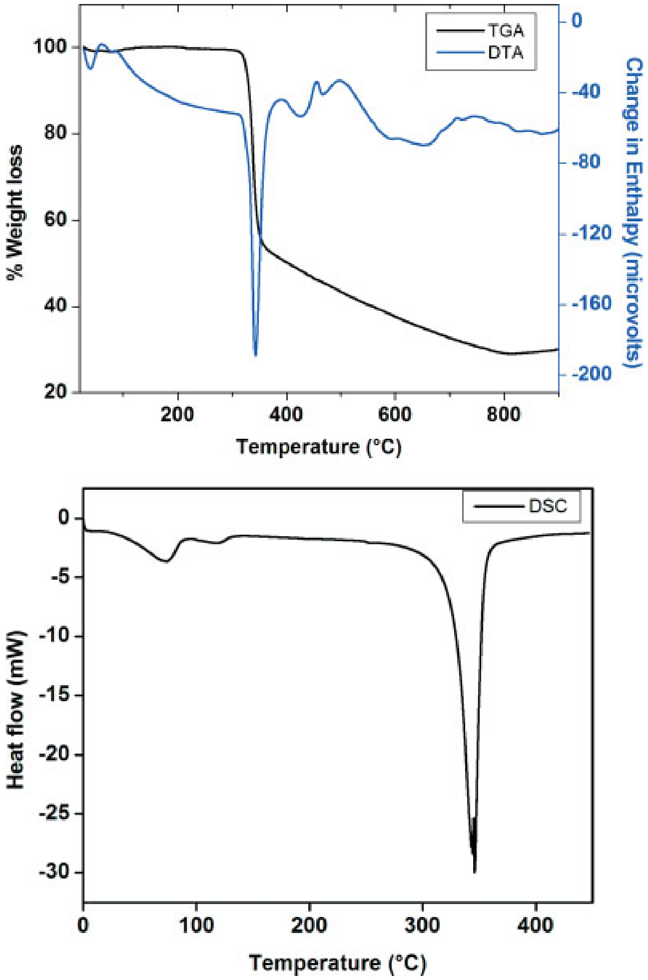


Figure 3. (a) TG/DTA graph of zinc(II) L-prolinate. (b) Differential scanning calorimetry graph of zinc(II) L-prolinate.

point apparatus, and was noted at about 342 °C, almost coinciding with the DTA trace. This is in good agreement with the reported DSC value. Therefore, it is clear that the material is stable up to its melting point, making it suitable for possible applications where the complex is required to withstand high temperatures.

Table 4. Catalyst recycling studies[a]

Catalyst recycle	Yield[b] (%)
1	90
2	87
3	85
4	85
5	70

[a] Reactions were performed with the terminal alkyne (0.01 mol), halide (0.01 mol), sodium azide (0.01 mol) and zinc(II) L-prolinate (2 mol%) in water by refluxing the mixture.
[b] Isolated yield.

FTIR spectral analysis of zinc(II) L-prolinate

The characterization vibration of the complex was compared with that of L-proline and the shift observed confirms the formation of the title compound. The peak at 3422 $\mathrm{cm^{-1}}$ was assigned to the OH stretching vibration of COOH grouping. The very strong peak at 3216 $\mathrm{cm^{-1}}$ occurred owing to NH stretching vibration. The lack of any strong IR band at 1700 $\mathrm{cm^{-1}}$ clearly indicates the existence of the COO^- ion in zwitter ionic form. The peak at 1600 $\mathrm{cm^{-1}}$ was assigned to the COO stretching of the COOH group. The peaks observed between 1330–1450 and 2800–3216 $\mathrm{cm^{-1}}$ were characteristic of L-proline. The COO^- vibrations showed a characteristic peak at 1412 $\mathrm{cm^{-1}}$. The other peaks at 1330 and 1300 $\mathrm{cm^{-1}}$ were assigned to the wagging of CH_2 group of the complex. The twisting NH_2 vibration was well established owing to the peak at 1170 $\mathrm{cm^{-1}}$. The absorption bands owing to the C–N stretch produced peaks at 1076 and 1062 $\mathrm{cm^{-1}}$. CH_2 rocking (937 and 847 $\mathrm{cm^{-1}}$), in-plane deformation of COO^- (784 $\mathrm{cm^{-1}}$), COO^- scissoring (707 $\mathrm{cm^{-1}}$) and rocking COO^- (529 $\mathrm{cm^{-1}}$) vibrations were observed.

Catalyst Recycling Ability

Catalyst recycling ability was checked under the same reaction conditions. The reaction of phenylacetylene, benzylbromide and sodiumazide was considered as a model reaction for recycling studies. The results are reported in Table 4. These results showed that the catalyst exhibits good catalytic ability for up to five cycles.

Conclusions

In conclusion, we have explored a catalyst having Zn as an active metal which can synthesize 1,4-disubstituted triazole (other than that of copper). The mildness of the conversion, experimental simplicity, compatibility with various functional groups, inexpensive reagents, high yields, short reaction times and easy work-up procedure, make this protocol very attractive for synthesis of a variety of these derivatives.

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Supporting information

Supporting information may be found in the online version of this article.

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