Journal of Molecular Catalysis A: Chemical 381 (2014) 126–131

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Nano-size ZnS: A novel, efficient and recyclable catalyst for A^3-coupling reaction of propargylamines

Nageswar Pandit Eagalapati[a,*], Abdul Rajack[a,b], Y.L.N. Murthy[a]

[a] Department of Organic Chemistry, Foods, Drugs & Water, Andhra University, Visakhapatnam 530003, India
[b] Department of Chemistry, MVGR College of Engineering, Vijayanagaram 535005, India

ARTICLE INFO

Article history:
Received 15 August 2013
Received in revised form 13 October 2013
Accepted 16 October 2013
Available online 25 October 2013

Keywords:
Propargylamines
Nano-size ZnS
A^3 coupling reaction
Heterogeneous and recyclable catalyst

ABSTRACT

Nano-size ZnS was prepared by a simple, economic and elegant chemical bath deposition technique and characterized by using SEM, TEM, XRD, and EDAX techniques. Prepared nano-size ZnS was found to be highly efficient novel heterogeneous catalyst for A^3-coupling reaction of Propargylamines (**4a–4l**) using various aldehydes, amines and terminal alkyne groups through C—H activation. The catalyst was recycled more than eight consecutive cycles and reused in the subsequent reactions without any loss in its activity. The developed protocol offers efficient synthesis of diverse propargylamines without using co-catalyst and any other activator, high catalytic activity and short reaction times were obtained when compared to other metal ion and/or metal oxide catalysts.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The assembly of molecular intricacy and diversity from readily available starting materials can be achieved by multi component coupling reactions (MCRs) [1] and this is an attractive synthetic approach for possessing atom economy. Hence, they serve as most powerful tools of synthetic organic chemistry to build up libraries of structurally complex compounds. They are unique and versatile in coupling organic moieties in one step, among the various synthetic methodologies [2]. The three-component one-pot coupling reactions of aldehydes, alkynes, and amines (A^3-coupling) have attracted considerable attention of researchers, because their coupling products, propargylamines are copiously occurring components and versatile building blocks [3e,f] in organic synthesis for the preparation of many nitrogen containing biologically active compounds [3a,b] and natural products [3c,d] such as conformationally restricted peptides, isosteres, oxotremorine analogs, β-lactams, therapeutics drug molecules and many other important structural elements of natural products [4].

There are many transition metal salts which are capable of carrying out multi component A^3 coupling reaction via C—H activation. These include classical methods for the preparation of Propargylamines which have usually been exploited with relatively high acidity of the terminal acetylenic C–H bond to form alkynyl metal reagents by treating with strong bases such as butyl lithium, [5a] organomagnesium compounds, [5b] or LDA [6]. Unfortunately, these reagents are used in stoichiometric ratios, highly moisture-sensitive, and require strictly controlled reaction conditions. In recent years, enormous progress has been made on C–H bond activation reaction on terminal alkynes. The alkyne C–H bond can be activated by employing various homogeneous metal catalysts such as Cu(I) salts [7], Au(I)/Au(III) salts [8], Au(III) salten complexes [9], Silver(I) salts [10], Zinc salts [11], Iron(III) salts [12], $InCl_3$ [13], a $InBr_3$ [13b], Ir-complexes [14], Hg_2Cl_2 [15], and Cu/Ru(II) bimetallic system [16]. Different heterogeneous catalysts such as LDH-$AuCl_4$ [17], AgI [18a–d], Silvernanoparticles [18e], Ag nano particles supported by Ni [18f], Cu(I) complexes [19a–d], CuCl [19], e Silica-immobilized CuI [19f] Ni–Y–zeolite [20], Zn dust [21], Copper ferrite nanoparticles [22], a nano crystalline Copper (II) oxide [22b], Copper-nanoparticles [22c] impregnated Copper on magnetite [22d], Copper–zeolites [22e], and Fe_3O_4 nanoparticles [23] have also been utilized for alkyne C–H activation. These are directly added to carbon–nitrogen double bonds (imines) in one-pot for the synthesis of Propargylamines. In addition, microwave [24a] and ultrasonic radiations [24b] have also been used in the presence of Cu (I) salt.

Most of these reported methodologies have some specific disadvantages such as harsh reaction conditions, prolonged reaction times, use of large amounts of expensive reagents, low yields, use of toxic solvents and tedious separation from the reaction mixture [25]. Hence, there is a scope for efficient synthesis of these biologically active molecules. In the present decade metal sulphide/oxide or metal composites are gaining attention due to their distinct

* Corresponding author. Tel.: +91 9491904419; fax: +91891 2713813.
E-mail addresses: eagalapati@gmail.com (N.P. Eagalapati), abdulrazzack1@gmail.com (A. Rajack).

1381-1169/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molcata.2013.10.009

catalytic activities for various organic transformations. Among the various metal sulphides, ZnS is a magic material because of its wide area of applications and flexibility of preparation in different morphologies with different properties.

Herein, we report nano-size ZnS sphere shaped particles as a new heterogeneous catalysts for the synthesis of Propargylamines. ZnS has been used as a semiconductor material and is often used as a photo catalyst in degradation of contaminated water containing halo benzene derivatives, Organic dyes with toxic metal ions [26,27]. Very recently ZnS has been used as a catalyst for the synthesis of 5-substituted 1*H*-tetrazoles [28].

However there was no report on the usage of nano-size ZnS as a catalyst for the synthesis of Propargylamines by A^3 coupling reaction of aldehydes, alkynes and amines. In this study, we are reporting the synthesis and characterization of Zinc sulphide nano particles along with catalytic activity of nano ZnS for the A^3 coupling reaction to generate propargylamines in the absence of any co-catalyst and/or additive (Scheme 1).

2. Experimental

2.1. General procedure for the synthesis of propargylamines (*4a–4l*)

Zns (10 mol %) was added to a mixture of aldehyde (1 mmol), amine (1.2 mmol) and alkyne (1.5 mmol) in CH_3CN (4 ml) and refluxed at 80 °C for 4–8 h. The reaction was monitored by (thin layer chromatography) TLC. After the completion of reaction, the reaction mixture was centrifuged at 2000–3000 rpm, at 10 °C for 5 min. The organic layer was decanted out and remaining ZnS was reused for further reactions. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude product was subjected to purification through column chromatography using 20% ethyl acetate and 80% petroleum ether as an elutant to obtain the pure Propargylamines (**4a–4l**). The structure of all the synthesized compounds was established by advanced spectral analysis (IR, ^{1}H NMR ^{13}C NMR and EIMS mass spectral data). All the synthesized products are in good agreement with the literature [23,29].

3. Procedure for the preparation of nano-size ZnS

ZnS nano particles [30] were grown from a solution of analytical grade Zn $(CH_3COO)_2$ (Zinc Acetate) as the Zn^{2+} ion source and thiourea as 2^- ion source in an alkaline solution of ammonia. The bath pH was optimized between 10 ± 0.5 by the addition of ammonia solution. The solution was continuously stirred at a constant speed during the growth time with the help of AC motor. The bath temperature was raised to a maximum of 70 ± 2 °C from room temperature using a temperature controller. The ZnS nano particles were washed with methanol ultrasonically to remove the loosely adhered ZnS particles and finally dried in a vacuum. The morphological, chemical composition and optical properties of ZnS nano particles were analyzed with TEM, SEM, and EDAX techniques.

3.1. SEM analysis

Fig. 1(a) and (b) shows the surface morphology of ZnS nano particles studied by SEM analysis with different scales 10 μm and 5 μm, respectively. From the micrographs, it was observed that the grown ZnS nano particles are uniform throughout the entire region, and the small nano-sized grains shows sphere like morphology with diameter around 1 μm which indicates the nanocrystalline nature of ZnS nano particles.

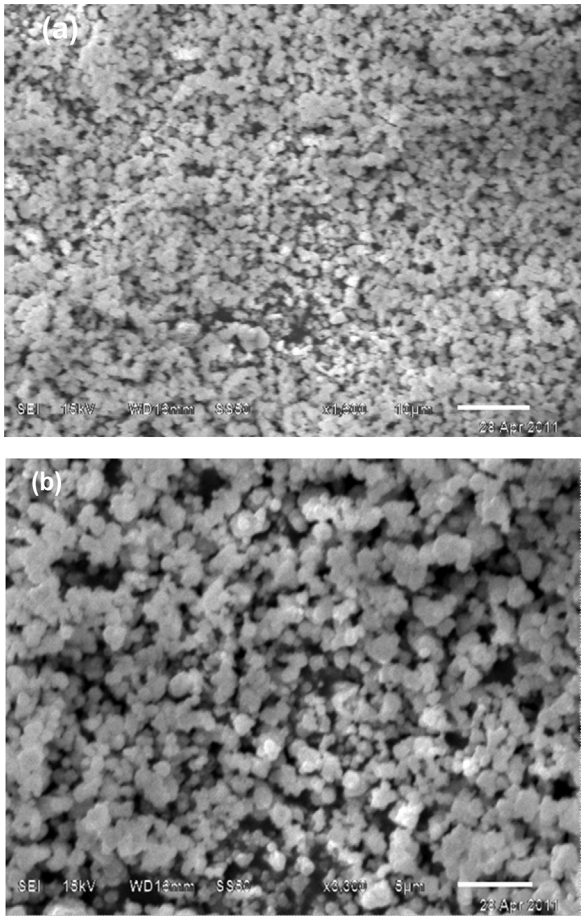


Fig. 1. (a and b) SEM images of nano-size ZnS.

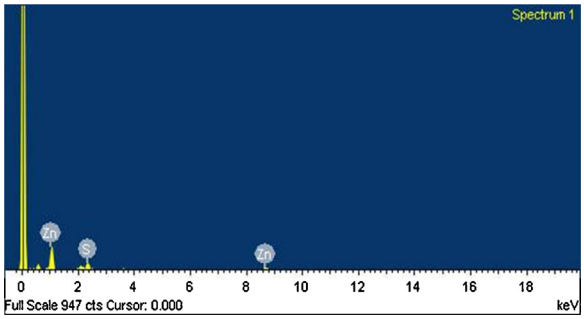


Fig. 2. EDAX analysis results of nano-size ZnS.

3.2. Composition study

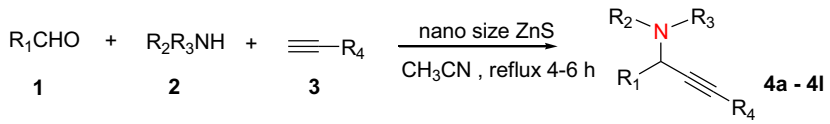
The composition of nano-size ZnS studied by EDAX analysis, indicates that Zn is slightly rich (70.20%) in ZnS nano particles (Fig. 2 and Table 1).

3.3. XRD, TEM analysis

Nano-size ZnS further analyzed by the advanced techniques like TEM, HRTEM, XRD and IR (Fig. 3). FT-IR spectrum of nano-size

Table 1
Composition of nano-size ZnS.

Elements	Weight (%)	Atomic (%)
Zn	70.90	55.44
S	29.10	45.56



Scheme 1. Synthesis of propargylamines catalyzed by nano-size ZnS.

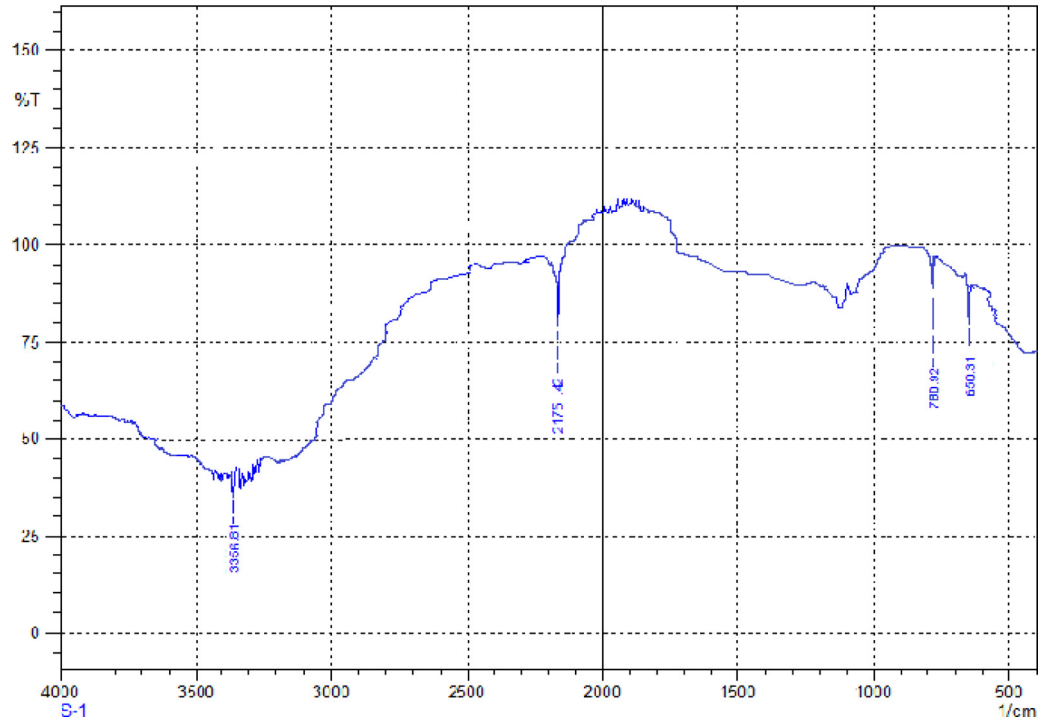


Fig. 3. IR spectrum of nano-size ZnS.

ZnS show the band at 3356.25 cm^{-1} appeared due to O—H stretching vibration of water molecules and the stretching at 2175.70 cm^{-1} (N=N) and at 650 cm^{-1} and 780 cm^{-1} (str) [31]. The nano-size ZnS particles exhibiting hexagonal structure (JCPDS card No. 75–1547) with preferred orientation (0 0 2) along with (1 1 0), and (1 1 2) directions. There were no metal phases detected by XRD (Fig. 4a). From XRD data, we can notice the existence of cubic phase with low intensity, and there is a large similarity in the structures between cubic and hexagonal ZnS. The grain size of ZnS nano particles calculated by the Scherrer formula was about 30 nm. For further investigation on the size of ZnS nano particles, TEM analysis was carried out and presented in (Fig. 4b) the nano particles were composed of 20–30 nm. The interplanar spacing (d-spacing) obtained from HRTEM image (Fig. 4c) is about 0.32 nm corresponding to the (0 0 2) lattice plane of hexagonal ZnS. The surface area of the nano-size ZnS determined by the BET method is 185 $m^2\ g^{-1}$.

4. Results and discussion

We started our study with the nano-size ZnS catalyzed synthesis of Propargylamines (**4a**–**4l**) via terminal C—H activation. The model reaction of benzaldehyde, *p*-methoxy benzyl amine and phenyl acetylene (**4i**) the reaction was optimized by investigating various parameters such as amount of nano-size ZnS, solvent and other conditions. The optimized conditions required reflux conditions with 10 mol% of nano-size ZnS in acetonitrile for 4 h at 80 °C. A summary of the optimized conditions are listed in Table 2. During the optimization, various amounts of nano-size ZnS catalyst were employed in the reaction. Evidently, the reaction with 5 mol% (Table 2, entry 6) of catalyst gave lower product yield (55%) than the one with 10 mol% (Table 2, entry 7) of catalyst (98%), higher loading of catalyst (15%) did not improve the result to a greater extent and leads to decrease (93%) in desired product yield due the formation of unwanted side-product (Table 2, entry 8). The efficiencies of several organic solvents as reaction medium and solvent less system were investigated (Table 2). Polar solvents such as ethanol, methanol, THF, dioxane, and acetonitrile were better organic solvents to effect the reaction, due the solubility limitation of the reagents the non polar solvents such as toluene were unfavorable for this reaction. When water was used as a solvent, trace of product was obtained even after a prolonged reaction time (Table 2 entry 5). However, a significant improvement was observed in acetonitrile (Table 2 entries 6–8).

In order to show the significance of the nano-size ZnS, the efficiency of the reagent compared to various Zinc based catalysts the results were summarized in (Table 3). In this study it was found that

Table 2
Optimization of the nano-size ZnS catalyzed model reaction for synthesis of propargylamines with various solvents and catalyst loading.

Entry	Solvent	Amount (%)	Time (h)	Yield (%)
1	Methanol	10	4	40
2	Ethanol	10	4	46
3	Dioxan	10	4	32
4	THF	10	4	51
5	Water	10	4	Trace
6	Acetonitrile	5	4	55
7	**Acetonitrile**	**10**	**4**	**98**
8	**Acetonitrile**	15	4	93

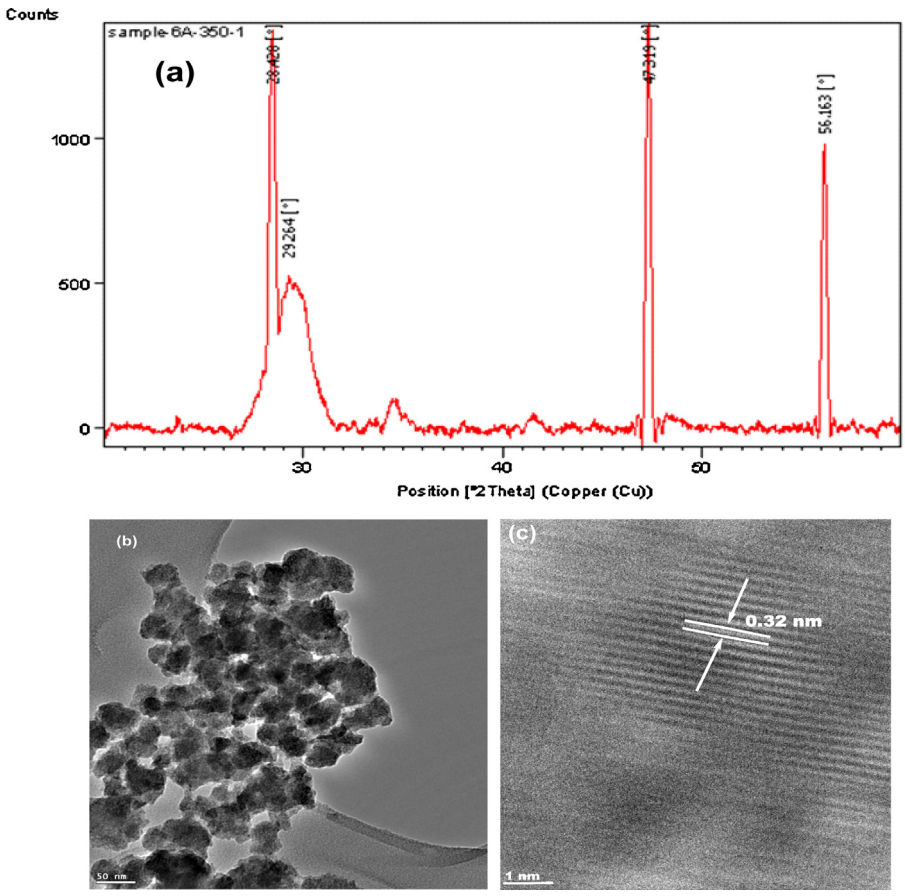


Fig. 4. (a) XRD, (b) TEM and (c) HRTEM patterns of ZnS nano particles respectively.

nano-size ZnS is a more efficient and superior catalyst over other Zinc based catalysts (Table 3 entries 1–9) with respect to reaction time and yield of the desired product (**4i**). It was also observed that the reaction was not moved in the absence of the nano-size ZnS reagent even after 24 h of reaction time (Table 3 entry 5).

It was observed that commercial ZnS afforded low yields, while nano-size ZnS afforded excellent yields. The optimum ratio of aldehyde, amine and alkyne was found to be 1:1.3:1.5. In the A^3 coupling reaction of benzaldehyde, aniline and phenyl acetylene were added along with nano-size ZnS catalyst and stirred at reflux temperature to afford **4i** (Table 3 entry 10) in 98% yield. The catalyst activity of nano-size ZnS was evident as no product was obtained in the absence of a catalyst.

To define the scope and understand the generality of the nano-size ZnS promoted A^3 coupling reaction, the reaction was carried out with various aldehydes and amines possessing wide range of functional groups in the optimized conditions. A variety of propargylamines were prepared by choosing variety of aromatic aldehydes for coupling with piperidine/or morpholine/or various aromatic amines and phenyl acetylene and total of twelve compounds were prepared and the data was summarized in (Table 4). Aromatic aldehydes with electron rich substituents gave excellent results in good yields without undergoing any decomposition or polymerization under the reaction conditions (Table 4 entries 4b, 4c and 4g). Sterically hindered amines and alkynes also afforded the corresponding propargylamines in high yields. (Table 4 entries

Table 3
Comparative study of nano-size ZnS with Zn-based catalysts for the synthesis of Propargylamine (**4i**) in acetonitrile.

Entry	Catalyst[a]	Time (h)	Yield (%)[b]
1	Zn dust	4	19
2	Zn metal	4	15
3	$ZnBr_2$	4	30
4	Zn acetatate	4	26
5	Zn $(NO_3)_2$	4	21
6	$ZnCl_2$	4	35
7	ZnO commercial	4	20
8	ZnO nano	4	52
9	ZnS commercial	4	56
10	**ZnS nano**	**4**	**98**
11	No Catalyst	24	–

(–) No reaction.
[a] Reaction conditions: aldehyde (1 mmol), alkyne (1.5 mmol) and amine (1.2 mmol), ZnS 10 mol%, CH_3CN (4 ml) reflux 4–6 h.
[b] Isolated yields.

Table 4
A^3 Coupling of aldehydes, amines and alkynes by nano-size ZnS as catalyst.[a]

Entry	R^1	Amine (R^2, R^3)	R^4	Product	Time	Yield (%)[b]
1	Ph	Ph	n-$CH_3(CH_2)_2$	**4a**	4.0	89
2	4-$MeOC_6H_4$	n-$CH_3(CH_2)_2$	n-$CH_3(CH_2)_2$	**4b**	4.5	91
3	4-$MeOC_6H_4$	Ph	n-$CH_3(CH_2)_2$	**4c**	4.0	93
4	Ph	Piperidine	Ph	**4d**	4.0	94
5	Ph	Morpholine	Ph	**4e**	4.5	89
6	n-$CH_3(CH_2)_2$	$C_6H_5CH_2$	Ph	**4f**	5.0	91
7	3,4$(MeO)C_6H_3$	4-FC_6H_4	Ph	**4g**	5.0	94
8	n-$CH_3(CH_2)_6$	$C_6H_5CH_2$	Ph	**4h**	6.0	89
9	Ph	Ph	Ph	**4i**	4.0	94
10	Ph	Pyrrolidine	Ph	**4j**	4.5	89
11	Me-Ph	Piperidine	Ph	**4k**	4.5	90
12	Ph	4$(OMe)C_6H_4$	Ph	**4l**	4.2	91

[a] Reaction conditions: aldehyde (1 mmol), alkyne (1.5 mmol) and amine (1.2 mmol), ZnS 10 mol%, CH_3CN (4 ml), reflux.
[b] Isolated yields.

Table 5
The effect of reusability of nano-size ZnS catalyst on the products **4i** yield.[a]

Entry	Cycles[a]	Time (h)	Yield (%)[b]
1	0	4	98
2	2	4.5	95
3	4	5	92
4	6	5	90
5	8	5.5	85

[a] Reaction conditions: benzaldehyde(1 mmol), alkyne (1.2 mmol), amine (1.5 mmol) and 10 mol % ZnS, CH_3CN(4 ml), reflux.
[b] Isolated yield.

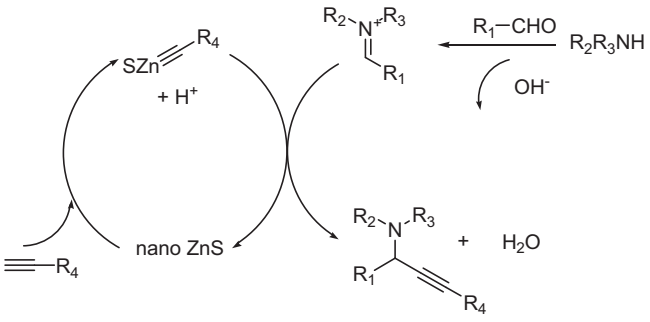


Fig. 5. Plausible mechanism of nano-size ZnS catalyzed A^3 coupling.

4a, 4g and 4i). It was found that piperidine gives better results in term of yield and reaction time than morpholine, pyrrolidine and other aromatic amines.

The catalyst was recovered from the reaction mixture by centrifugation, washed thrice with DCM and dried at 60 °C for period of 1 h and reused. The recovered catalyst can be reused for more than eight times in the subsequent reactions without any significant loss in its activity, results with recyclable nano-size ZnS were summarized in Table 5. The catalytic role of nano-size ZnS was presented in the plausible mechanism involved in the synthesis of 3,4 dihydro pyrimidi-none and *N*-dihydro pyrimidinone-decahydroacridine-1,8-diones in Fig. 5.

5. Plausible mechanism

It is assumed that the A^3 coupling reaction takes place between Zinc acetylide[12] (as Lewis acid (Zn^{+2}) assisted proton transfer with the alkyne, by the C—H bond activation. The Zinc acetylide intermediate, thus generated would react with the iminium ion generated in situ from aldehyde and amine to form the corresponding Propargylamine. A plausible mechanism is presented in Fig. 4.

6. Summary

In conclusion, we have developed a simple and efficient protocol for the synthesis of the propargylamines via C—H activation using nano-size ZnS as the catalyst under mild conditions. Addition of co-catalyst or activator is not required. The reaction is effective for both aliphatic and aromatic aldehydes. The catalyst can be reused for several times, without any appreciable lose in its activity. This procedure is more environmentally benign than the existing procedures.

7. Spectral data

7.1. *N-(1-Phenylhex-2-ynyl) benzenamine (**4a**)*

Yellow oil; IR (neat): ν_{max} 3400 (brs), 3057, 2978, 2943, 1588, 1489, 1330, 756 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.96 (t, J = 6.7 Hz, 3H), 1.46–1.60 (m, 2H), 2.20 (t, J = 6.5 Hz, 2H), 3.90–4.00 (brs, NH, 1H), 5.21 (s, 1H), 6.65–6.75 (m, 3H), 7.10–7.21(m, 2H), 7.45 (m, 1H), 7.50–7.60 (m, 2H), 7.85–7.95 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.2, 20.3, 22.0, 50.2, 79.2, 82.1, 111.5, 116.1, 125.8, 126.8, 127.0, 128.2, 128.6, 141.0, 143.6; ESI-MS (m/z): 249.1353; Elemental Anal. Calcd for $C_{18}H_{19}N$: C, 86.70; H, 7.68; N, 5.62. Found: 86.78; H, 7.65; N, 5.71.

7.2. *N-Butyl-1-(3-methoxyphenyl) non-2-yn-1-amine (**4b**)*

Pale yellow oil; IR (neat): ν_{max} 3440 (brs), 2928, 2848, 1616, 1520, 1456, 1232, 1152, 1024, 736 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.80–1.00 (m, 6H), 1.20–1.40 (m, 12H), 1.50–1.60 (m, 2H), 2.30–2.40 (t, J = 6.5 Hz, 2H), 3.78 (s, 3H), 4.70 (s, 1H), 6.80 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.8, 13.9, 18.9, 20.2, 21.8, 27.2, 28.0, 30.5, 31.8, 43.8, 48.4, 52.9, 73.5, 80.5, 111.0, 113.6, 122.3, 126.2, 142.1, 159.5; ESI-MS (m/z): 301 (M+1); Elemental Anal. Calcd for $C_{20}H_{31}NO$: C, 79.68; H, 10.36; N, 4.65; Found: C, 79.71; H, 10.44; N, 4.72.

7.3. *N-(1-(3-Methoxyphenyl) non-2-ynyl) benzenamine (**4c**)*

Yellow oil; IR (neat): ν_{max} 3408 (brs), 2928, 2864, 1600, 1488, 1424, 1232, 1152, 1008, 832 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.98 (t, J = 6.7 Hz, 3H), 1.30–1.50 (m, 4H), 1.55–1.78 (m,4H), 2.40 (t, J = 6.5 Hz, 2H), 3.78 (s,3H), 4.56 (s, 1H), 6.80 (d, J = 8.0 Hz, 2H), 7.10–7.30 (m, 5H), 7.40 (d, J = 8.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 19.0, 21.2, 26.1, 28.2, 30.5, 50.2, 53.9, 72.5, 80.1, 111.3, 112.3, 113.5, 118.2, 128.6, 146.6, 159.5; ESI-MS (m/z): 321 (M+H); Elemental Anal. Calcd for $C_{22}H_{27}NO$: C, 82.20; H, 8.47; N, 4.36. Found: C, 82.31; H, 8.51; N, 4.42.

7.4. *4-(1,3-Diphenyl-prop-2-ynyl)-morpholine (**4e**)*

Yellow oil; IR (neat): ν_{max} 2930, 2745, 1598, 1500, 1318, 1152, 754, 693 cm^{-1}; ^1H NMR (300 MHz,$CDCl_3$): δ 7.63 (d, J = 6.9 Hz, 2H), 7.50 (d, J = 6.9 Hz, 2H), 7.36–7.31 (m, 6H), 4.78 (s, 1H), 3.71–3.64 (m, 4H), 2.62–2.56 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 46.9, 50.9, 60.2, 81.0, 86.8, 120.6, 126.3, 127.4, 128.5, 128.9, 130.3, 140.1; ESI-MS (m/z): 278 (M+1); Elemental Anal. Calcd. for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.38; H, 6.86; N, 5.10.

7.5. *N-(1-(3,4-Dimethoxyphenyl)-3-phenylprop-2-ynyl)-flouro benzenamine (**4g**)*

Yellow oil; IR (neat): ν_{max} 3342 (brs), 2914, 2842, 1618, 1506, 1264, 1142, 960, 836 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.51 (s, 6H), 4.42–4.50 (brs, NH, 1H), 5.40 (s, 1H), 6.23 (m, 1H), 6.80–6.87 (m, 1H), 6.89–7.00 (m, 3H), 7.28 (m, 3H), 7.35 (m, 2H), 7.68–7.71 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 50.2, 55.2, 81.5, 87.8, 113.2, 116.2, 117.3, 121.3, 123.7, 128.4, 129.1, 131.2, 140.1, 141.2, 148.8, 149.6, 150.3; ESI-MS (m/z): 361 (M+1); Elemental Anal. Calcd. for $C_{23}H_{20}FNO_2$: C, 76.44; H, 5.58; F, 5.26; N, 3.88. Found: C, 76.57; H, 5.67 N, 3.93.

7.6. *N-Benzyl-1-phenyldec-1-yn-3-amine (**4h**)*

Yellow solid, mp. 82 °C; IR (KBr):ν_{max} 3454 (brs), 3086, 2941, 2849, 1601, 1488, 1426, 1051, 887 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.98 (t, J = 6.7 Hz, H), 1.20–1.40 (m, 8H), 1.45–1.55 (m, 2H), 1.65–1.80 (m, 2H), 3.50 (t, J = 6.5 Hz, 1H), 3.80–4.10(m, 2H), 7.20–7.50 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 21.7, 22.7, 28.3, 29.4, 30.9, 35.2, 41.1, 54.1, 80.3, 89.4, 120.7, 126.8, 128.0, 129.1, 129.5, 129.6, 131.0, 135.4; ESI-MS (m/z): 319 (M+1); Elemental Anal. Calcd. for $C_{23}H_{29}N$: C, 86.47; H, 9.15; N, 4.38. Found: C, 86.42; H, 9.11; N, 4.51.

7.7. N-(1,3-Diphenylprop-2-ynyl) benzenamine (**4i**)

Yellow solid, 85 °C mp; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.98–4.05 (brs, NH, 1H),5.42 (s, 1H), 6.64–6.78 (m, 3H), 7.10–7.40 (m, 10H), 7.55–7.60 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 49.9, 81.2, 86.8, 112.6, 119.0, 121.6, 127.0, 127.8, 128.2, 129.3, 129.6, 129.9, 131.6, 145.1, 148.6; ESI-MS (*m*/*z*): 283 (M+1); Elemental Anal. Calcd. for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.91. Found: C, 88.27; H, 6.18; N, 4.95.

7.8. 1-(3-Phenyl-1-(p-tolyl)prop-2-yn-1-yl)piperidine (**4k**)

Yellow oil; IR (neat): ν_{max} 2937, 2744, 1605, 1502, 1320, 1152, 760, 691 cm^{-1};^{1}H NMR (300, MHz, $CDCl_3$): δ 7.51–7.31 (m, 5H), 7.30 (d, *J* = 2.7 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 4.74 (s, 1H), 2.54–2.46 (m, 4H), 2.35 (s, 3H), 1.60–1.56 (m, 4H), 1.45–1.43 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.3, 24.3, 24.9, 51.1, 81.0, 87.8, 121.7, 129.4, 129.9, 130.1, 132.3, 138.9; ESI-MS (*m*/*z*): 290 (M+1); Elemental Anal. Calcd. for $C_{21}H_{23}N$: C, 87.15; H, 8.01; N, 4.84. Found: C, 87.21; H, 8.15; N, 4.91.

7.9. N-(1,3-Diphenylprop-2-ynyl)-4-methoxybenzenamine (**4l**)

Yellow oil; IR (neat): ν_{max} 3342 (brs), 3056, 2929, 2832, 1600, 1504, 1232, 1042, 831 cm^{-1}; ^{1}H NMR (300, MHz, $CDCl_3$): δ 3.69 (s, 3H), 3.65–3.75 (brs, NH, 1H), 5.39 (s, 1H), 6.60–6.79 (m, 4H), 7.20–7.30 (m, 4H), 7.35–7.40 (m,4H), 7.60 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 49.8, 52.9, 81.3, 87.8, 113.2, 116.0, 122.8, 127.1, 127.9, 128.4, 128.8, 129.1, 130.3, 140.1, 142.0 ESI-MS (*m*/*z*): 312.1346 Elemental Anal. Calcd. for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.43; H, 6.18; N, 4.54.

References

[1] (a) A. Domling, W. Wang, K. Wang, Chem. Rev. 112 (2012) 3083;
(b) A. Domling, Y. Huang, Synthesis (2010) 2859;
(c) E. Ruijter, R. Scheffelaar, R. Orru, Angew. Chem. Intl. Ed. 28 (2011) 6234;
(d) R.W. Armstrong, A.P. Combs, P.A. Tempest, S.D. Brown, T. Keating, Acc. Chem. Res. 29 (1996) 123.

[2] (a) A. Domling, I. Ugi, Angew. Chem. 112 (2000) 3300;
(b) I. Ugi, A. Domling, B. Werner, J. Heterocycl. Chem. 37 (2000) 647.

[3] (a) B. Nilsson, H.M. Vargas, B. Ringdahl, U. Hacksell, J. Med. Chem. 35 (1992) 285;
(b) K. Hattori, M. Miyata, H. Yamamoto, J. Am. Chem. Soc. 115 (1993) 1151;
(c) M. Konishi, H. Ohkuma, T. Tsuno, T. Oki, G.D. VanDuyne, J. Clardy, J. Am. Chem. Soc. 112 (1990) 3715;
(d) A.A. Boulton, B.A. Davis, D.A. Durden, L.E. Dyck, A.V. Juorio, X.-M. Li, I.A. Paterson, P.H. Yu, Drug Dev. Res. 42 (1997) 150;
(e) B.M. Trost, Angew. Chem. Int. Ed. Engl. 34 (1995) 259;
(f) E. Bustelo, P.H. Dixneuf, Handbook of C–H Transformations, Wiley-VCH, Weinheim, 2005.

[4] (a) G. Dyker, Angew. Chem. 38 (1999) 1698;
(b) I. Naota, H. Takaya, S.I. Murahashi, Chem. Rev. 98 (1998) 2599.

[5] (a) B.J. Wakefield, Organolithium Methods in Organic Synthesis, Academic Press, London, 1988;
(b) B.J. Wakefield, Organomagnesium Methods in Organic Synthesis, Academic Press, London, 1995.

[6] (a) T. Harada, P. Sharma, T. Fujiwara, K. Iwazaki, A. Oku, Org. Lett. 2 (2000) 1855;
(b) N. Rosas, C. Alvarez, E. Gomez, Y. Gutierrez, M. Mendez, R.A. Toscano, L.A. Maldonado, Tetrahedron Lett. 44 (2003) 8019;
(c) C.H. Ding, D.D. Chen, Z.B. Luo, L.X. Dai, X.L. Hou, Synlett (2006) 1272.

[7] (a) L. Shi, Y.-Q. Tu, M. Wang, F.-M. Zhang, C.-A. Fan, Org. Lett. 6 (2004) 1001;
(b) H.Z. Syad Huma, H. Rajkumar, S.S. Karla, J. Das, J. Iqbal, Tetrahedron Lett. 43 (2002) 6485;
(c) G.W. Kabalka, L. Wang, R.M. Pagni, Synlett (2001) 676;
(d) C. Wei, C.-J. Li, J. Am. Chem. Soc. 124 (2002) 5638;
(e) C. Wei, J.T. Mague, C. Li, J. Proc. Natl. Acad. Sci. U.S.A. 101 (2004) 5749;
(f) N. Gommarman, C. Koradin, K. Polborn, P. Knochel, Angew. Chem. Int. Ed. 42 (2003) 5763;
(g) F. Colombo, M. Benaglia, S. Orlandi, F. Usuelli, J. Mol. Catal. A Chem. 260 (2006) 128;
(h) N. Gommermann, P. Knochel, Chem. Eur. J. 12 (2006) 4380;
(i) A. Bisai, V.K. Singh, Org. Lett. 8 (2006) 2405.

[8] C. Wei, C.J. Li, J. Am. Chem. Soc. 125 (2003) 9584.

[9] V.K.Y. Lo, Y. Liu, M.-K. Wong, C.-M. Che, Org. Lett. 8 (2006) 1529.

[10] C. Wei, Z. Li, C.J. Li, Org. Lett. 5 (2003) 4473.

[11] (a) K.Y. Lee, C.G. Lee, J.E. Na, J.N. Kim, Tetrahedron Lett. 46 (2005) 69;
(b) E. Ramu, V. Ravi, N. Sreelathaa, A.R. Srinivas, Tetrahedron Lett. 48 (2007) 7184.

[12] W.W. Chen, R.V. Nauyen, C.J. Li, Tetrahedron Lett. 50 (2009) 2895.

[13] (a) Y. Zhang, P. Li, M. Wang, L. Wang, J. Org. Chem. 74 (2009) 4364;
(b) J.S. Jadav, B.V.S. Reddy, A.V.H. Gopal, K.S. Patil, Tetrahedron Lett. 50 (2009) 3993.

[14] (a) C. Fischer, E.M. Carreira, Org. Lett. 3 (2001) 4319;
(b) S. Sakaguchi, T. Kubo, Y. Ishii, Angew. Chem. Int. Ed. 40 (2001) 2534;
(c) S. Sakaguchi, T. Mizuta, M. Furuwan, T. Kubo, Y. Ishii, Chem. Commun. (2004) 1638.

[15] L.P. Hua, W. Lei, Chin. J. Chem. 23 (2005) 1076.

[16] C.J. Li, C. Wei, Chem. Commun. (2002) 268.

[17] M.L. Kantam, B.V. Prakash, C.R.V. Reddy, B. Sreedhar, Synlett (2005) 2329.

[18] (a) Z. Li, C. Wei, L. Chen, R.S. Varma, C.J. Li, Tetrahedron Lett. 45 (2004) 2443;
(b) K.M. Reddy, N.S. Babu, P.S.S. Prasad, N. Lingaiah, Tetrahedron Lett. 47 (2006) 7563;
(c) X. Zhang, A. Corma, Angew. Chem. Int. Ed. 47 (2008) 4358;
(d) P. Li, L. Wang, Y. Zhang, M. Wang, Tetrahedron Lett. 49 (2008) 6650;
(e) W. Yan, R. Wang, Z. Xu, J. Xu, L. Lin, Z. Shen, Y. Zhou, J. Mol. Catal. A Chem. 255 (2006) 81;
(f) S. Wang, X. He, L. Song, Z. Wang, Synlett (2009) 447.

[19] (a) P. Li, L. Wang, Tetrahedron 63 (2007) 5455;
(b) S.B. Park, H. Alper, Chem. Commun. (2005) 1315;
(c) B.M. Choudary, C. Sridhar, M.L. Kantam, B. Sreedhar, Tetrahedron Lett. 45 (2004) 7319;
(d) M. Wang, P. Li, L. Wang, Eur. J. Org. Chem. (2008) 2255;
(e) B. Sreedhar, P.S. Reddy, C.S.V. Krishna, P.V. Babu, Tetrahedron Lett. 48 (2007) 7882;
(f) P.R. Likhar, S. Roy, M. Roy, M.S. Subhas, M.L. Kantam, R.L. De, Synlett (2007) 2301.

[20] (a) K. Namitharan, K. Pitchumani, Eur. J. Org. Chem. (2010) 411;
(b) M.L. Kantam, S. Laha, J.S. Yadav, S. Bhargava, Tetrahedron Lett. 49 (2008) 3083.

[21] M.L. Kantam, V. Balasubrahmanyam, K.B.S. Kumar, G.T. Venkanna, Tetrahedron Lett. 48 (2007) 7332.

[22] (a) M.L. Kantam, J.S. Yadav, S. Laha, S. Jha, Synlett (2009) 1791;
(b) M. Kidwai, V. Bansal, N.K. Mishra, A. Kumar, S. Mozumdar, Synlett (2007) 1581;
(c) M.J. Aliaga, D.J. Ramon, M. Yus, Org. Biomol. Chem. 8 (2010) 43;
(d) M.K. Patil, M. Keller, B.M. Reddy, P.J. Pale, Eur. J. Org. Chem. (2008) 4440.

[23] B. Sreedhar, A. Suresh Kumar, P.S. Reddy, Tetrahedron Lett. 51 (2010) 1891.

[24] (a) N.E. Leadbeater, H.M. Torenius, H. Tye, Mol. Divers 7 (2003) 135;
(b) B. Sreedhar, P.S. Reddy, B.V. Prakash, A. Ravindra, Tetrahedron Lett. 46 (2005) 7019.

[25] (a) M.L. Kantam, B.V. Prakash, C.R.V. Reddy, B. Sreedhar, Synlett (2005) 2329;
(b) M. Kidwai, V. Bansal, A. Kumar, S. Mozumdar, Green Chem. 9 (2007) 742;
(c) M. Kidwai, V. Bansal, N.K. Mishra, A. Kumar, S. Mozumdar, Synlett (2007) 1581.

[26] J.S. Hu, L.L. Ren, Y.G. Guo, H.P. Liang, A.M. Cao, L.J. Wang, C.L. Bai, Angew. Chem. Int. Ed. 44 (2005) 1269.

[27] (a) J.H. Bang, R.J. Helmich, K.S. Suslick, Adv. Mater. 20 (2008) 2599;
(b) S. Xiong, B. Xi, C. Wang, D. Xu, X. Feng, Z. Zhu, Y. Qian, Adv. Funct. Mater. 17 (2007) 2728;
(c) H. Fujiwara, K. Hosokawa, Y. Wada, S. Yanagida, Langmuir 14 (1998) 5154;
(d) S. Marinkovic, N. Hoffmann, Eur. J. Org. Chem. (2004) 3102;
(e) A. Kudo, M. Sekizawa, Chem. Commun. (2000) 1371;
(f) O. Hamanoi, A. Kudo, Chem. Lett. (2002) 838.

[28] L. Leiming, L. Baojun, I. We, J. Liu, X. Li, Y.I. Zheng, Chem. Commun. 46 (2010) 448.

[29] (a) T. Mitamura, A. Ogawa, Org. Lett. 11 (2009) 2045;
(b) J.S. Yadav, B.V. Subba Reddy, V.N. Kumar, R. Srinivasa Rao, K. Nagaiah, New J. Chem. 28 (2004) 335.

[30] (a) S.S. Kawar, B.H. Pawar, J. Mater. Sci. Mater. Electron. 21 (2010) 906;
(b) S. Wook Shin, H. Pil Oh, S.M. Pawar, M. Jong-Ha, J. Hyeok, J. Kim, Nanosci. Nanotechnol. 10 (2010) 3686.