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Allylation and propargylation of aldehydes mediated by *in situ* generated zinc from the redox couple of Al and $ZnCl_2$ in 2N HCl†

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A simple one pot allylation and propargylation of aldehydes mediated by zinc(0), which is *in situ* generated from the redox couple of Al and $ZnCl_2$ in 2N HCl, is demonstrated to afford the corresponding homoallyl and homopropargyl alcohols with excellent yields.

Introduction

The construction of a C–C bond is the essence of organic synthesis in building up the backbone of organic compounds. Allylation and Propargylation of carbonyl compounds with allylic and propargylic organometallic reagents are well known processes with a broad spectrum of synthetic applications.[1] For the allylation and propargylation of aldehydes and ketones, various metals *e.g.* Mg, Li, Zn, B, Al, Si, Mn, Ti, Cr, Zr, Cu and Sn are used as metallic reagents.[2] The synthesis of homoallylic and homopropargylic alcohols by allylation and propargylation of carbonyls has attracted significant interest in synthetic organic chemistry because of their use as building blocks in the synthesis of natural products. The addition of allyl, propargyl or allenyl nucleophiles to organic electrophiles like carbonyls, imines, and epoxides is a well-recognized tool for the formation of a carbon–carbon bond in the chemical society.[3] Carbonyls are one of the most useful and versatile substrates in synthetic organic chemistry due to their high reactivity. Several techniques have been reported for the activation of carbonyls with a variety of organometallic nucleophiles. Moreover, a number of methods have been reported for the metal mediated allylation and propargylation of carbonyls. Except a few, all these methods suffer from a lack of efficiency and simplicity. As a result, further scope to test the reactivity of novel reagent systems to bring about efficient and selective allylation and propargylation of carbonyls, epoxides and imines still exists. The development of simple and novel reagents that are more efficient and provide convenient procedures with improved yields remains quite a challenge for synthetic organic chemists.

Metal-mediated allylations and propargylations are well-recognized examples of organic reactions in aqueous media.[4] However, excessive metal is used in most of the cases and the corresponding metal salt is generated as a waste material. Lots of research has been done on developing metal mediated allylation and propargylation reactions in aqueous media. Zinc is very cheap and has low toxicity among the successful metals; it is also less sensitive to air and water due to its highly negative reduction potential (−1.216) receiving special priority both from the economic and scientific points of view to mediate the Barbier-type reactions.[5] There are very few reports where zero or low valent reactive metals are generated from a redox couple followed by the *in situ* generation of reactive nucleophilic organometallic species. Examples include redox reagent systems such as Indium(III)–aluminium, tin(II)–aluminum *etc.*[6] It is hoped that the regeneration of Zn(0) from Zn(II) by aluminum or manganese (combined with TMS-Cl) would be a useful method because they have lower electronegativity than Zn and can easily reduce in principle a divalent zinc to a zero valent one. Aqueous reactions have been extensively considered to avoid flammable, toxic, or carcinogenic organic solvents.[7] Chemists are trying to synthesize various low valent metals preferably having a particular shape and size in nano scale because of their applications as nano catalysts. On the other hand, organozincs also have a huge number of applications in organometallics. Particularly, allylic and propargylic organozincs are extremely important in organic synthesis. So far, to the best of our knowledge, the synthesis of zero valent metallic zinc from a bivalent one followed by the *in situ* generation of allylic and propargylic organozincs is completely unknown (Charts 1 and 2).[8-26] In this work our idea is to generate a zero valent zinc metal from a bivalent, easily available, cheap, moderately stable (to air and moisture) and commercial zinc source. We tried

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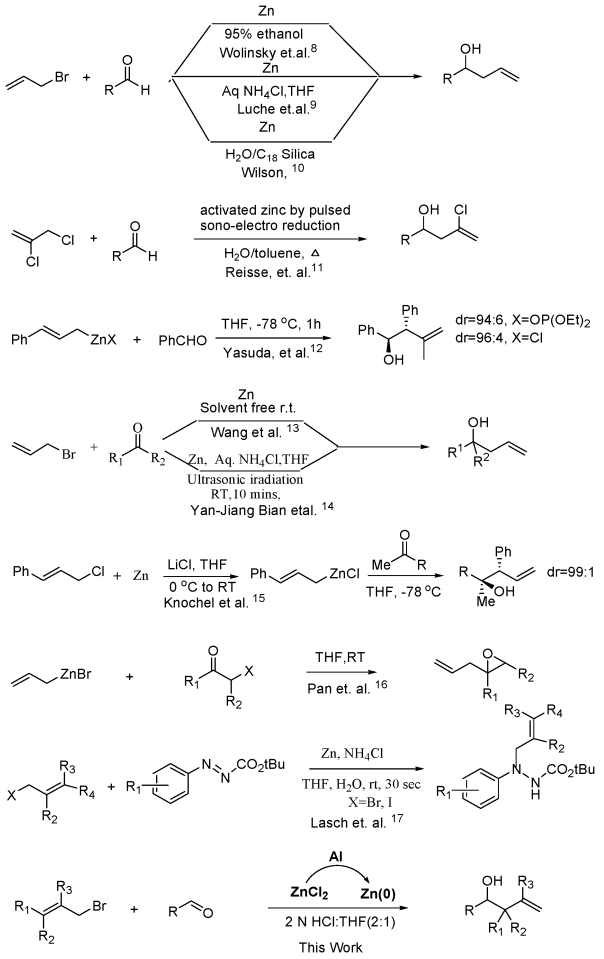


Chart 1 Previous works of allylation reactions using zinc metal.

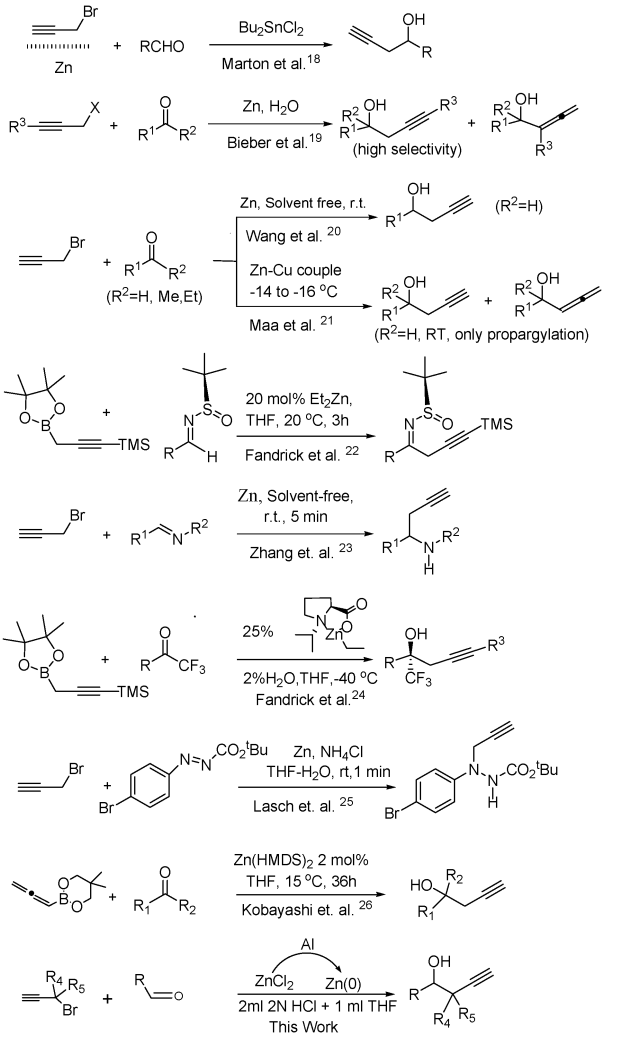


Chart 2 Previous works of propargylation reactions using zinc metal.

a list of reducing agents based on the literature to reduce *in situ* the bivalent, easily available, cheap, moderately stable (to air and moisture) and commercial zinc source in different solvent systems including aqueous medium (neutral/acidic/alkaline). Here, we want to explore a new strategic theme for the nucleophilic allylation and propargylation reactions *via* the insertion of this redox generated zinc(0) *in situ* with allylic and propargylic halides. The strategy involves the oxidative addition of allylic or propargylic halide (RX) across a reactive zero valent metal [M], to form a nucleophilic reagent R–[M]–X. The *in situ* generated nucleophile reacts with suitable electrophile like carbonyls to give homoallylic and homopropargylic alcohols. This process is highly efficient, simple, and convenient to provide homoallylic and homopropargylic alcohols with improved yields. Initial success of the strategy for carbonyl allylation and propargylation prompted us to investigate the process and its mechanism in depth.

Results and discussion

Synthesis and characterization of nano zinc by the redox couple of Al and $ZnCl_2$

We were interested in generating highly active metallic zinc for this purpose and using it *in situ*. We followed the chemical reduction route *i.e.* the bottom up approach for the *in situ* generation of this highly active metallic zinc. To generate an active zero valent zinc *via* chemical redox conditions, the combination of Zinc(II) chloride with a suitable reducing agent was examined. For this purpose, we tried with aluminium powder, manganese, Mn/TMS-Cl, $NaBH_4$, hydrazine hydrate *etc.* as the reducing partner. In a one pot reaction, aluminium powder (1.5 mmol) was added portion wise to a mixture of $ZnCl_2$ (1.5 mmol) in 2 ml of 2 N HCl and the mixture was stirred at room temperature till hydrogen gas liberation ceased. Among the tried methods, this method is most suitable because the *in situ* generated $AlCl_3$ is soluble in hydrochloric acid and reduced metallic zinc is insoluble in the solution. Thus, the metallic zinc can be easily separated for characterization purpose. Metallic lustre of zinc suspension was observed.

XRD analysis

The XRD (Fig. 1) analysis showed that the precipitate from $ZnCl_2$ solutions consisted of pure Zn(0) with a good crystalline structure. The crystal planes of metallic zinc which were

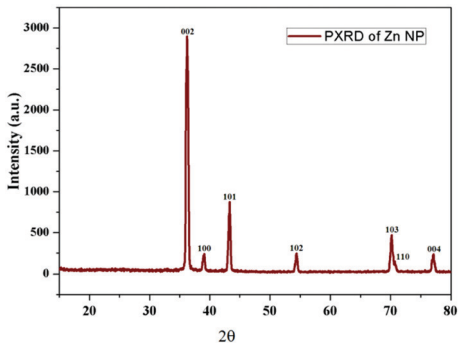


Fig. 1 XRD pattern of the material.

identified included (002), (100), (101), (102), (103), (110) and (004) and perfectly matched with pure Zn metal. Our synthesized Zn nano wire is phase pure. The average crystallite size of the sample is calculated from the broadening of well defined peaks of the sample in the XRD pattern by applying the Debye–Scherrer equation

$$\langle D\rangle = 0.9\lambda/(\beta_{1/2}\cos\theta)$$

where $\langle D\rangle$ is the size of the average crystallite, 'λ' (1.54 Å) is the wavelength of the incident X-ray radiation and 'θ' is the Bragg angle. Here, '$\beta_{1/2}$' is the full-width at half-maximum (FWHM) of the XRD peak (2θ = 36.24°, FWHM = 0.30). The average estimated crystallite size of the sample is ~200 nm which indicates the nanocrystalline nature of the sample.

SEM analysis

The tuned synthesis of highly active metallic zinc for allylation and propargylation reaction was further analyzed by FESEM (field emission scanning electron microscopy) (Fig. 2). The particles show a very uniform spherical morphology. The inset picture shows a selected area scanning.

In situ generation of zinc(0) and its reactivity

To optimize this facile allylation process, we struggled a lot after initial success and performed several experiments. A typical optimization for the allylation of benzaldehyde is described here. Active metallic zinc is a facile reagent for the Barbier-type allylation reactions. We were really interested in finding highly active *in situ* generated metallic zinc for this purpose. We used commercial $ZnCl_2$ salt as the zinc source. We followed the chemical reduction process *i.e.* the bottom up approach for the *in situ* generation of highly active metallic zinc. To generate an active zero-valent zinc *via* chemical redox conditions, the combination of Zinc(II) chloride with a suitable reducing agent was examined (Table 1).

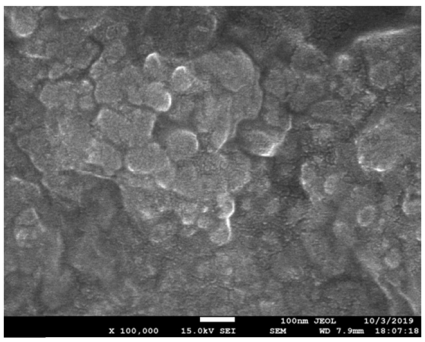


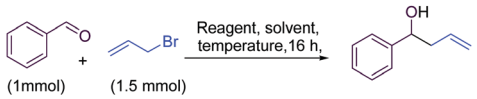
Fig. 2 FESEM image of the material.

For this purpose, we examined aluminium powder, manganese, Mn/TMSCl, $NaBH_4$, hydrazine hydrate *etc.* as the reducing partner. We found that efficient allylation can take place only by reducing $ZnCl_2$ with aluminium powder, and in the first attempt we obtained a 10% yield of homoallyl benzyl alcohol when $ZnCl_2$ (1 mmol) was reduced by Al powder (1 mmol) in water (3 ml) at room temperature (entry 1). The yield of homoallyl alcohol increases by increasing the solubility of the organic reactants by adding a miscible organic solvent. A better yield (20%) of homoallyl benzyl alcohol is obtained when a mixture of H_2O–THF (2 : 1) is used as the solvent (entry 2). The effect of THF addition is more prominent compared to DMF and MeOH (entry 2 *vs.* entries 3 and 4). Saturated NH_4Cl in THF (2 : 1) can act as a better solvent for this type of *in situ* reduction process (entry 5). But, in our study, this solvent system could not give any betterment with respect to the yield of homoallyl benzyl alcohol. We then tried simultaneously a basic and an acidic media for this purpose. HCl medium offers drastic improvement of the yield (entries 8 and 9) while NaOH medium results in a lower yield (entry 7). The effect of organic acid additives like HCO_2H, HOAc and benzoic acid is found to be negative (entries 10–12). Thus, allyl bromide (1 mmol) and benzaldehyde (1 mmol) in the presence of $ZnCl_2$ in an acidic aqueous medium renders a new pathway for homoallyl alcohol synthesis. Trial with a manganese metal powder and Mn/TMS–Cl instead of aluminium decreases the yield (entries 13–15). Reducing agents like $NaBH_4$ and hydrazine hydrate instead of aluminium powder yielded trace amounts of homoallyl alcohol under similar reaction conditions (entries 16 and 17). In a one pot reaction, aluminium powder (1.5 mmol) was added portion wise to a mixture of $ZnCl_2$ (1.5 mmol) in 2 ml of 2 N HCl and the mixture was stirred at room temperature till hydrogen gas liberation ceased. Then THF (1 ml), allyl bromide (1.5 mmol) and benzaldehyde (1 mmol) were added and the reaction mixture was stirred at room temperature to afford the corresponding homoallylic alcohol in good yield (80%). The yield was found to further improve to 86% when the temperature was increased to 70 °C (entries 21 *vs.* 20). Optimized reaction conditions are those given in entry 21.

Generality of the reaction: allylation of aldehyde

A variety of aldehydes and allyl bromides can be used for the allylation reaction using the optimised conditions (Table 1, entry 21). Table 2 summarizes the details of the carbonyl allylation results. Both the aromatic and aliphatic aldehydes can be utilized in this strategy. For the aromatic aldehydes, homoallylic alcohols can be prepared easily in good to excellent yields, and the functionalities including chloro and methoxy groups (entries 1, 7, 9 and 11) are tolerated under these mild conditions. Aliphatic aldehydes are also allylated (entries 3, 5, 8 and 10). Regioselectivity

Table 1 Standardisation of allylation of aldehyde



Sl. no.	Reagents	Solvent	Temp. (°C)	Yield (%)
1	Al (1 eq.), $ZnCl_2$ (1 eq.)	H_2O	40	10
2	Al (1 eq.), $ZnCl_2$ (1 eq.)	H_2O–THF (2 : 1)	40	20
3	Al (1.5 eq.), $ZnCl_2$ (1.5 eq.),	H_2O–DMF (2 : 1)	40	15
4	Al (1.5 eq.), $ZnCl_2$ (1.5 eq.),	H_2O–MeOH (4 : 1)	40	12
5[a]	Al(1.5 eq.), $ZnCl_2$ (1.5 eq.), NH_4Cl	H_2O–THF (2 : 1)	40	20
6	Al (1.5 eq.), $ZnCl_2$ (1.5 eq.), 1N HCl	1N HCl–THF (2 : 1)	40	45
7	Al (1.5 eq.), $ZnCl_2$ (1.5 eq), 1N NaOH	1N NaOH–THF (2 : 1)	40	10
8	Al (1 eq.), $ZnCl_2$ (1 eq.), 2N HCl	2N HCl–THF (2 : 1)	40	75
9	Al (1.5 eq.), $ZnCl_2$ (1.5 eq.), 3N HCl	1N HCl–THF (2 : 1)	40	65
10	Al(1.5 eq.), $ZnCl_2$ (1.5 eq.), HCO_2H (solid, 4 eq.)	H_2O–THF (2 : 1)	40	12
11	Al (1.5 eq.), $ZnCl_2$ (1.5 eq.), 2N HOAc	2N HOAc–THF (2 : 1)	40	10
12	Al (1.5 eq.), $ZnCl_2$ (1.5 eq.), $PhCO_2H$ (solid, 5 eq.)	H_2O–THF (2 : 1)	40	Trace
13	Mn (1.5 eq.), $ZnCl_2$ (1.5 eq.), 2N HCl	2N HCl–THF (2 : 1)	40	10
14	Mn (5 eq.), $ZnCl_2$ (1.5 eq.), 2N HCl	2N HCl–THF (2 : 1)	40	10
15	Mn and TMSCl (5 eq.), $ZnCl_2$ (1.5 eq.), 2N HCl	2N HCl–THF (2 : 1)	40	15
16	$NaBH_4$ (1.5 eq.), $ZnCl_2$ (1.5 eq.), 2N HCl	2N HCl–THF (2 : 1)	40	Trace
17	Hydrazine hydrate (1.5 eq.), $ZnCl_2$ (1.5 eq.), 2N HCl	2N HCl–THF (2 : 1)	40	Trace
18	Al (2 eq.), $ZnCl_2$ (1.5 eq.), 2N HCl,	2N HCl–THF (2 : 1)	40	80
19	Al (1.5 eq.), $ZnCl_2$ (2 eq.), 2N HCl,	2N HCl–THF (2 : 1)	40	80
20	Al (1.5 eq.), $ZnCl_2$ (1.5 eq.), 2N HCl,	2N HCl–THF (2 : 1)	40	80
21	Al (1.5 eq.), $ZnCl_2$ (1.5 eq.), 2N HCl	2N HCl–THF (2 : 1)	70	86

Condition: [a]Sat. NH_4Cl in THF

study using 3-phenyl allyl bromide, crotyl bromide and 3,3-dimethylallyl bromide showed that a γ-substitution product was obtained exclusively (entries 1–4, and 10) with very poor diastereoselectivity.

However, ketones did not undergo allylation under this reaction condition, and negligible conversion of ketone was observed even after 24 h.

Generality of the method: propargylation of aldehydes

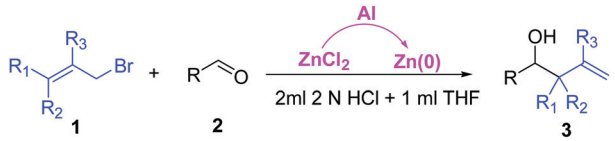
The scope of the reaction was successfully extended to the propargylation of aldehydes. In the following condition model the reaction of 3-bromo-prop-1-yne **4E** and benzyl aldehyde **2F** yielded 72% of 1-phenyl-pent-4-yn-2-ol **5G** (Table 3, entry 7). Complete absence of isomeric allenyl alcohol suggests that under the reaction conditions, metallotropic rearrangement between propargylzinc and allenylzinc is completely arrested.[27] The generality of the method was further tested for the reaction of **2F**, **2A**, and **2G–2L** varying with the corresponding propargyl bromide instead of **4E**, **4A–4D** affording moderate to good yields of the corresponding homopropargyl alcohols **5A–5I** (Table 3).

Methoxy (OMe-) and halide (Br & Cl) groups are tolerated in the reaction conditions. Both the aromatic and aliphatic aldehydes can be utilized in this methodology. For the aromatic aldehydes, homopropargylic alcohols can be prepared easily in good to excellent yields. The functionalities including bromo, chloro, and methoxy groups *etc.* (entries 1, 8 and 9) on aldehydes are tolerated under these mild conditions. Aliphatic aldehydes are also propargylated for the synthesis of homopropargylic alcohols (entries 3, 5 and 6). However, ketones did not undergo propargylation under these reaction conditions, and negligible conversion of ketone was observed even after 24 h.

Comparative reactivity study of different types of zinc depending on surface morphology

The activity of this *in situ* generated Zinc towards the allylation and propargylation of simple aldehydes might be attributed to its special type of metallic Zn(0). A preliminary stoichiometric comparative reactivity study of different types of zinc based on surface morphology was performed using Rieke zinc,[28] commercial zinc powders, granules, foils *etc.* under aqueous acidic conditions (Table 4). To 3 ml of 2 : 1 HCl (2N) : THF, metallic zinc (1.5 mmol, 98 mg), allyl/propargyl bromide (1.5 mmol, 0.15 ml) and benzaldehyde (1 mmol, 106 mg) were added and stirred at 80 °C for 17 hours. The aqueous reaction mixture was extracted twice with diethyl ether (2 × 10 ml). The combined organic layer was washed with brine (10 ml), dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether–ethyl acetate 9 : 1). Our synthesized metallic Zn(0) showed the highest reactivity towards the allylation and propargylation of benzaldehyde in water. Rieke zinc was prepared according to the procedure mentioned in the literature in dry THF using 2 mmol $ZnCl_2$ (supporting information). THF was removed by evaporation from the activated Rieke zinc solution. Then 2N HCl–THF (2 : 1, 3 ml), allyl/propargyl bromide (2 mmol, 0.2 ml) and benzaldehyde (1 mmol, 106 mg) were subsequently added to the residual activated zinc (1.5 mmol) and stirred at 80 °C for 17 h to give the corresponding homoallyl alcohol (yield = 68%). Our synthesized special zero valent metallic zinc

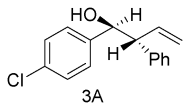
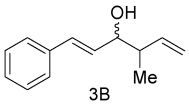
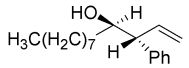
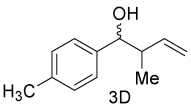
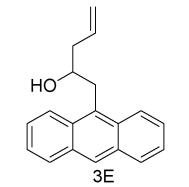
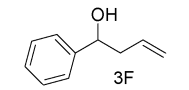
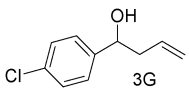
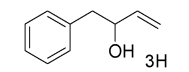
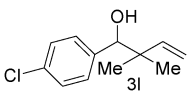
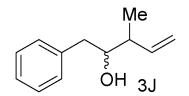
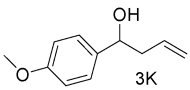
Table 2 Allylation of aldehydes[a]



1A: R_1=R_2=H, R_3=Ph
1B: R_1=R_2=H, R_3=Me
1C: R_1=R_2=R_3=H
1D: R_1=R_2=Me, R_3=H
1E: R_1=Me, R_2=R_3=H

2A: R=4-ClPh-
2B: R=Vinyl-Ph-
2C: R= $H_3C(H_2C)_7$-
2D: R=4-MePh-
2E: R=Anthryl-CH_2-
2F: R=Ph-
2G: R=$PhCH_2$-
2H: R=4-OMePh-

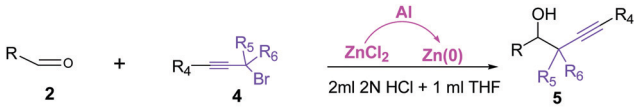
3A-3K

#	Bromide	Aldehyde	Product	Time (h)	Yield%	*Syn*/*anti*[b]
1	**1A**	**2A**	 3A	16	72	00 : 100
2	**1B**	**2B**	 3B	16	77	52 : 48
3	**1A**	**2C**	 3C	16	71	00 : 100
4	**1B**	**2D**	 3D	16	89	46 : 54
5	**1C**	**2E**	 3E	14	83	—
6	**1C**	**2F**	 3F	14	86	—
7	**1C**	**2A**	 3G	16	91	—
8	**1C**	**2G**	 3H	13	65	—
9	**1D**	**2A**	 3I	14	75	—
10	**1E**	**2G**	 3J	16	75	50 : 50
11	**1C**	**2H**	 3K	16	90	—

Conditions: Al 1.5 mmol, $ZnCl_2$ 1.5 mmol, Aldehyde 1 mmol, allyl bromide 1.5 mmol, 2 N HCl 2 ml, 1 ml THF, and 70 °C.

using a cheap zinc salt in combination with a suitable reducing redox partner (Al) showed the highest reactivity towards the

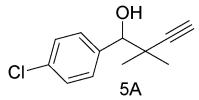
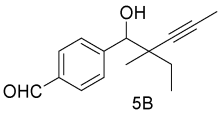
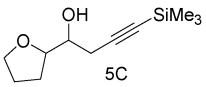
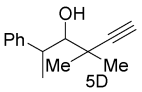
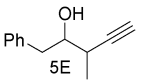
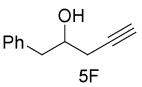
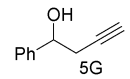
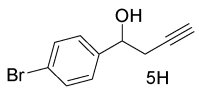
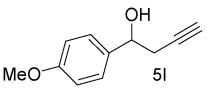
Table 3 Propargylation of aldehydes[a]



2A: R=4-ClPh-
2I: R=CHO-Ph-
2J: R=THF-
2K: R=PhCHMe-
2H: R=$PhCH_2$-
2F: R=Ph-
2L: R=4-BrPh
2G: R=4-OMePh-

4A: R_4=H, R_5=R_6=Me
4B: R_4=R_5=Me, R_6=Et
4C: R_4=$SiMe_3$, R_5=R_6=H
4D: R_4=R_5=H, R_6=Me
4E: R_4=R_5=R_6=H

5A-5I

#	Bromide	Aldehyde	Product	Time (h)	Yield%
1	**4A**	**2A**	 5A	15	81
2	**4B**	**2I**	 5B	16	63
3	**4C**	**2J**	 5C	16	55
4	**4A**	**2K**	 5D	16	48
5	**4D**	**2H**	 5E	15	78
6	**4E**	**2H**	 5F	18	68
7	**4E**	**2F**	 5G	16	72
8	**4E**	**2L**	 5H	14	72
9	**4E**	**2G**	 5I	17	80

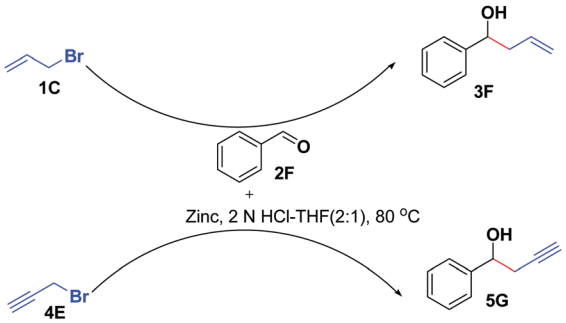
Condition: Al 1.5 mmol, $ZnCl_2$ 1.5 mmol, Aldehyde 1 mmol, propargyl bromide 1.5 mmol, 2 N HCl 2 ml, 1 ml THF, and 70 °C.

allylation and propargylation of benzaldehyde in acidic water–THF (2 : 1).

Plausible reaction pathway

The plausible reaction mechanism is demonstrated schematically in Scheme 1. Allyl bromide oxidatively adds to zero valent zinc which is *in situ* generated by the redox reaction of Al and $ZnCl_2$ in 2N HCl to form reactive allyl zinc(II)bromide. Allyl zinc(II)bromide *in situ* reacts with aldehyde to form homoallyloxyzinc(II) bromide which again hydrolyses under the reaction conditions to form the desired homoallyl alcohol. Metallic zero valent zinc thus generated is more reactive compared to commercial zinc. Plausible mechanistic outcome demands a catalytic cycle for zinc.

Table 4 Comparative reactivity study of different types of zinc depending on surface morphology



Sl. no.	Zinc reagents	Time (h)	Allylation yield (%)	Propargylation yield (%)
1	Rieke zinc synthesized	17	68	60
2	Zinc powder 325 mesh (SRL)	17	53	43
3	Zinc powder 200 mesh (Merck)	17	48	37
4	Zinc granules 30 mesh (Sigma Aldrich)	17	27	15
5	Zinc foil 0.38 mm (commercial)	17	18	trace
6	Zinc(0) by $ZnCl_2$ and Al (this work, condition of Table 1, entry 21)	17	86	72

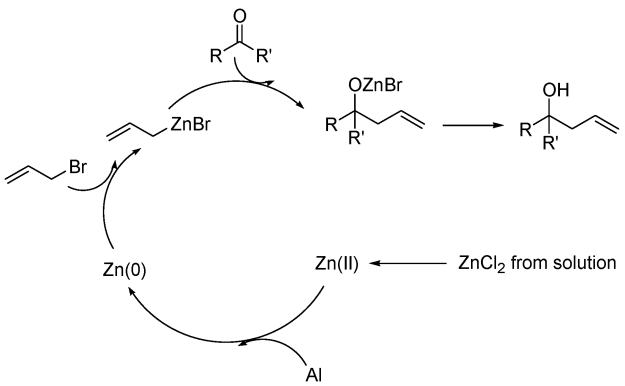
Condition: aldehyde 1 mmol, allyl/propargyl bromide 1.5 mmol, 2N HCl–THF (2 : 1) 3 ml

But in our study zinc is always needed in stoichiometric amount. Significant differences in yield between catalyzed and stoichiometric reaction conditions were observed. In the reaction conditions, the final product is not alcohol but zinc alkoxide, and thus more than stoichiometric amounts of zinc are necessary to mediate the reaction. If the generated zinc(II) alkoxide species *i.e.* homoallyloxyzinc(II) bromide can be reduced to zinc(0) with the formation of alcohol under these conditions by aluminium powder then only catalytic amounts of zinc chloride could do the work. But, this is not happening under our reaction conditions. Aluminium powder cannot reduce zinc(II) alkoxide species to metallic zinc under our reaction conditions.

Similarly propargyl bromide oxidatively adds to zerovalent zinc, *in situ* formed by the redox reaction of Al and $ZnCl_2$ in 2N HCl, to form reactive propargyl zinc(II) bromide which *in situ* reacts with aldehyde to form homopropargyloxyzinc(II) bromide which again hydrolyses under the reaction conditions to form the desired homoproparglyl alcohol.

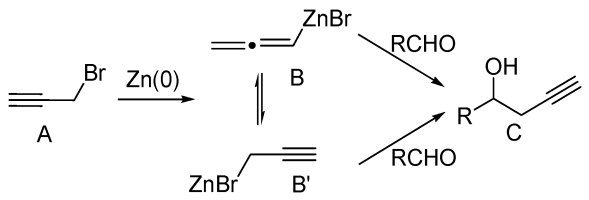
Zinc chloride is reduced to generate metallic zinc. Metallic zero valent zinc thus generated is more reactive compared to commercial zinc. The formation of homopropargylic alcohols as end-organic product suggests that the reaction proceeds *via* the *in situ* generation of propargylic zinc reagent followed by carbonyl addition reaction.

The next issue relates to the metallotropic rearrangement of an organometallic reagent and its nucleophilic reactivity towards an electrophile. In this scenario, the selectivity of the end-organic product is determined by the degree of control in all the reactions occurring in tandem. The selectivity of the addition is determined by the position of equilibrium between the two organometallic intermediates *i.e.* allenylzinc and propargylzinc species. The relative rate of addition to carbonyl compounds by an organometallic species is thus dependent on the steric bulk of the electrophile, substitution pattern on the



Scheme 1

organometallic substrate, solvation and nature of the metal. Deployment of this strategy for the generation of a propargyl or allenyl-metal (Scheme 2) is expected to be complicated by metallotropic rearrangement (B to B′) and selectivity during the reaction with an electrophile (B to C; B′ to C). For the carbonyl compounds as the electrophile, similar to the pathway demonstrated by Tamaru[29] and Marshall[30] A′ → B → C addition of propargylic zinc has been depicted in the scheme for the synthesis of homopropargylic alcohols. Tuning the regioselectivity to homopropargylic alcohol (C) instead of allenic alcohol by



Scheme 2

the same set of metal and other reaction conditions remains a pertinent challenge. Formation of the homopropargylic alcohol as the only product suggests the possible arresting of allenylic-zinc intermediate **B** as major one (Scheme 2).

Experimental

General procedure

The procedures given below for carbonyl propargylation were followed in similar cases. All products showed satisfactory spectral and analytical data.

Allylation of aldehyde

To an opened round bottom flask, aluminium powder (1.5 mmol) was added portion wise to a mixture of $ZnCl_2$ (1.5 mmol) in 2 ml of 2 N HCl. The mixture was stirred at room temperature till hydrogen gas liberation ceased. Then THF (1 ml), allyl bromide (1.5 mmol) and benzaldehyde (1 mmol) were added sequentially and the reaction mixture was stirred at 70 °C to afford the corresponding homoallyl alcohol. The reaction was stopped when the aldehyde had been completely consumed (TLC monitoring, 16 h) and THF was removed by evaporation. The aqueous reaction mixture was extracted twice with diethyl ether (2 × 10 ml). The combined organic layer was washed with brine (10 ml), dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 9 : 1) to afford 65–91% of the corresponding homoallyl alcohol.

Propargylation of aldehydes

To an opened round bottom flask aluminium powder (1.5 mmol) was added portion wise to a mixture of $ZnCl_2$ (1.5 mmol) in 2 ml of 2 N HCl. The mixture was stirred at room temperature till hydrogen gas liberation ceased. Then THF (1 ml), properglyl bromide (1.5 mmol) and benzaldehyde (1 mmol) were added sequentially and the reaction mixture was stirred at 70 °C to afford the corresponding homoallyl alcohol. The reaction was stopped when the aldehyde had been completely consumed (TLC monitoring) and THF was removed by evaporation. The aqueous reaction mixture was extracted twice with diethyl ether (2 × 10 ml). The combined organic layer was washed with brine (10 ml), dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 9 : 1) to afford the corresponding homopropargyl alcohol.

Analytical data

1-(4-Chloro-phenyl)-2-phenyl-but-3-en-1-ol (3A):[31] Using the general procedure but with (1-bromomethyl-vinyl)-benzene **1A** (296 mg, 1.5 mmol), and 4-chloro-benzaldehyde **2A** (141 mg, 1.0 mmol), the title compound **3A** (186 mg, 72%) was obtained as a light yellow oily liquid.

^{1}H NMR ($CDCl_3$): δ 2.32 (brs, 1H), 3.47 (t, 1H, J = 8.46 Hz), 4.80 (d, 1H, J = 7.96 Hz), 5.21–5.31 (m, 2H), 6.14–6.32 (m, 1H), 7.01–7.22 (m, 9H).

^{13}C NMR ($CDCl_3$): δ 59.25, 76.48, 118.68, 126.72, 127.97, 128.21, 128.42, 132.96, 137.49, 140.14, 140.26.

ESI-MS: for $C_{16}H_{15}ClO$ [M], $[M - OH]^+$ = 241.09(^{35}Cl) & 243.09(^{37}Cl).

HRMS calculated for the fragment ion $C_{16}H_{14}Cl$ $[M - OH]^+$ = 241.0784 found 241.0790(^{35}Cl) & 243.0754 found 243.0769(^{37}Cl).

Anal ($C_{16}H_{15}ClO$) calcd, C: 74.27, H: 5.84; found, C: 74.59, H: 5.62.

4-Methyl-1-phenyl-hexa-1,5-dien-3-ol (3B):[32] **(*syn*:*anti* 52 : 48).** Using the general procedure but with 3-bromo-2-methyl-propene **1B** (203 mg, 1.5 mmol), and 3-phenyl-propenal **2B** (132 mg, 1.0 mmol), the title compound **3B** (145 mg, 77%) was obtained as a light yellow oily liquid.

^{1}H NMR ($CDCl_3$): δ 1.06 (d, 3H, J = 5.13 Hz), 1.10 (d, 3H, J = 5.19 Hz), 1.87 (brs, 1H), 2.36–2.51 (m, 1H), 4.06 (t, 1H, J = 6.84 Hz), 4.22 (t, 1H, J = 5.31 Hz), 5.11–5.23 (m, 2H), 5.74–5.95 (m, 1H), 6.16–6.29 (m, 1H), 6.61 (d, 1H, J = 15.97 Hz), 7.21–7.42 (m, 5H).

^{13}C NMR ($CDCl_3$): δ 14.85, 15.97, 43.88, 44.60, 75.79, 76.14, 115.93, 116.54, 126.48, 127.63, 128.55, 130.00, 130.22, 131.17, 131.65, 136.78, 139.94, 140.20.

ESI-MS: for $C_{13}H_{16}O$ [M], $[M - OH]^+$ = 171.09.

HRMS calculated for the fragment ion $C_{13}H_{15}$ $[M - OH]^+$ = 171.1174 found 171.1176.

Anal. ($C_{13}H_{16}O$) calcd, C: 82.94, H: 8.57; found, C: 82.80, H: 8.83.

3-Phenyl-dodec-1-en-4-ol (3C):[33] Using the general procedure but with (1-bromomethyl-vinyl)-benzene **1A** (296 mg, 1.5 mmol), and nonanal **2C** (142 mg, 1.0 mmol), the title compound **3C** (185 mg, 71%) was obtained as a light yellow oily liquid.

^{1}H NMR ($CDCl_3$): δ 0.85 (t, 3H, J = 6.40 Hz), 1.10–1.45 (m, 10H), 1.73 (brs, 1H), 3.26 (t, 1H, J = 8.16 Hz), 3.72–3.80 (m, 1H), 5.15–5.28 (d, 2H), 6.01–6.15 (m, 1H), 7.16–7.35 (m, 5H).

^{13}C NMR ($CDCl_3$): δ 14.03, 22.59, 29.17, 29.47, 31.78, 34.36, 57.30, 73.91, 117.68, 126.53, 127.94, 128.59, 138.31, 141.69.

ESI-MS: for $C_{18}H_{28}O$ [M], $[M - OH]^+$ = 243.22.

HRMS calculated for the fragment ion $C_{18}H_{17}$ $[M - OH]^+$ = 243.2113 found 243.2116.

Anal ($C_{18}H_{28}O$) calcd, C: 83.02, H: 10.84; found, C: 82.95, H: 10.64.

2-Methyl-1-*p*-tolyl-but-3-en-1-ol (3D):[34] **(*syn* : *anti* = 46 : 54).** Using the general procedure but with 3-bromo-2-methyl-propene **1B** (203 mg, 1.5 mmol), and 4-methyl-benzaldehyde **2D** (120 mg, 1.0 mmol), the title compound **3D** (157 mg, 89%) was obtained as a light yellow oily liquid.

^{1}H NMR ($CDCl_3$): δ 0.87 (d, 3H, J = 6.81 Hz), 1.02 (d, 3H, J = 6.82 Hz), 2.07 (brs, 1H), 2.35 (s, 3H), 2.46–2.50 (m, 1H), 4.32 (d, 1H, J = 7.99 Hz), 4.56 (d, 1H, J = 5.64 Hz), 5.01–5.10 (m, 2H), 5.16–5.25 (m, 2H), 5.74–5.78 (m, 1H), 7.12–7.26 (m, 4H).

^{13}C NMR ($CDCl_3$): δ 14.28, 16.49, 21.09, 44.57, 46.10, 77.70, 115.26, 116.48, 126.47, 126.74, 128.71, 128.88, 136.85, 137.17, 139.50, 139.66, 140.43, 140.82.

ESI-MS: for $C_{12}H_{16}O$ [M], $[M - OH]^+$ = 159.12. HRMS calculated for the fragment ion $C_{12}H_{15}$ $[M - OH]^+$ = 159.1174 found 159.1166.

Anal. ($C_{12}H_{16}O$) calcd, C: 81.77, H: 9.15; found, C: 81.53, H: 8.89.

1-Anthrylpent-4-en-2-ol (3E): Using the general procedure but with 3-bromo-2-methyl-propene **1C** (181 mg, 1.5 mmol), and anthracen-9-yl-acetaldehyde **2E** (220 mg, 1.0 mmol), the title compound **3E** (218 mg, 83%) was obtained as a light yellow oily liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ 1.72 (br s, 1H), 2.42–2.48 (m, 2H), 3.79–3.83 (m, 2H), 4.12–4.15 (m, 1H), 5.16–5.26 (m, 2H), 5.84–5.93 (m, 1H), 7.42–7.56 (m, 4H), 7.97–8.02 (m, 2H), 8.28–8.36 (m, 3H).

^{13}C NMR (54.6 MHz, $CDCl_3$): δ 34.74, 41.93, 72.18, 118.40, 124.64, 124.89, 125.71, 126.57, 129.17, 130.53, 130.62, 131.52, 134.74.

ESI-MS: for $C_{19}H_{18}O$ [M], $[M + H]^+$ = 263.14, $[M - OH]^+$= 245.13.

1-Phenyl-but-3-en-1-ol (3F):[35] Using the general procedure but with 3-bromo-propene **1C** (182 mg, 1.5 mmol), and benzaldehyde **2F** (106 mg, 1.0 mmol), the title compound **3F** (127 mg, 86%) was obtained as a light yellow oily liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ 2.12 (s br, 1H), 2.48–2.55 (m, 2H), 4.73 (t, 1H, J = 7.0 Hz), 5.12–5.21 (m, 2H), 5.71–5.92 (m, 1H), 7.23–7.37 (m, 5H); ^{13}C NMR (54.6 MHz, $CDCl_3$): 43.85, 73.34, 118.41, 125.84, 127.57, 128.44, 134.48, 143.9; anal. ($C_{10}H_{12}O$) calcd, C: 81.04, H: 8.16; found, C: 81.09, H: 8.20.

1-(4-Chloro-phenyl)-but-3-en-1-ol (3G):[36] Using the general procedure but with 3-bromo-propene **1C** (182 mg, 1.5 mmol), and 4-chloro-benzaldehyde **2A** (141 mg, 1.0 mmol), the title compound **3G** (166 mg, 91%) was obtained as a light yellow oily liquid.

^{1}H NMR ($CDCl_3$): δ 2.32 (brs, 1H), 3.47 (t, 1H, J = 8.46 Hz), 4.80 (d, 1H, J = 7.96 Hz), 5.21–5.31 (m, 2H), 6.14–6.32 (m, 1H), 7.01–7.22 (m, 9H).

^{13}C NMR ($CDCl_3$): δ 59.25, 76.48, 118.68, 126.72, 127.97, 128.21, 128.42, 132.96, 137.49, 140.14, 140.26.

ESI-MS: for $C_{16}H_{15}ClO$ [M], $[M - OH]^+$ = 241.09(^{35}Cl) & 243.09(^{37}Cl).

HRMS calculated for the fragment ion $C_{16}H_{14}Cl$ $[M - OH]^+$ = 241.0784 found 241.0790(^{35}Cl) & 243.0754 found 243.0769(^{37}Cl).

Anal ($C_{16}H_{15}ClO$) calcd, C: 74.27, H: 5.84; found, C: 74.59, H: 5.62.

1-Phenyl-pent-4-en-2-ol (3H):[37,38] Using the general procedure but with 3-bromo-propene **1C** (182 mg, 1.5 mmol), and phenyl-acetaldehyde **2G** (120 mg, 1.0 mmol), the title compound **3H** (107 mg, 65%) was obtained as a light yellow oily liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ 1.81 (s br, 1H), 2.22–2.35 (m, 2H), 2.67–2.86 (m, 2H), 3.85–3.93 (m, 1H), 5.13–5.21 (m, 2H), 5.78–5.9 (m, 1H), 7.21–7.36 (m, 5H); ^{13}C NMR (54.6 MHz, $CDCl_3$): 41.22, 43.34, 71.75, 118.13, 126.51, 128.57, 129.48, 134.75, 138.46; anal. ($C_{11}H_{14}O$) calcd, C: 81.44, H: 8.70; found, C: 81.38, H: 8.67.

1-(4-Chloro-phenyl)-2,2-dimethyl-but-3-en-1-ol (3I):[39] Using the general procedure but with 1-bromo-3-methyl-but-2-ene **1B** (224 mg, 1.5 mmol), and 4-chloro-benzaldehyde **2A** (141 mg, 1.0 mmol), the title compound **3I** (158 mg, 75%) was obtained as a light yellow oily liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ 0.93 (s, 3H), 0.98 (s, 3H), 4.39 (s, 1H), 5.01–5.17 (m, 2H), 5.8–5.94 (m, 1H), 7.19–7.3 (m, 4H); ^{13}C NMR (54.6 MHz, $CDCl_3$): 20.95, 24.35, 42.27, 79.98, 114.24, 127.66, 129.13, 133.15, 139.25, 144.73; anal. ($C_{12}H_{15}ClO$) calcd, C: 68.40, H: 7.18; found, C: 68.43, H: 7.19.

3-Methyl-1-phenyl-pent-4-en-2-ol (3J):[37,38] **(*syn* : *anti* 42 : 58).** Using the general procedure but with 1-bromo-but-2-ene **1D** (203 mg, 1.5 mmol), and phenyl-acetaldehyde **2G** (120 mg, 1.0 mmol), the title compound **3J** (132 mg, 75%) was obtained as a light yellow oily liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ 1.01–1.04 (d, 3H, J = 6.8 Hz), 1.59 (br s, 1H), 2.17–2.29 (m, 1H), 2.45–2.59 (m, 1H), 2.71–2.83 (m, 1H), 3.54-3.65 (m, 1H), 4.99–5.08 (m, 2H), 5.69–5.86 (m, 1H), 7.08–7.26 (m, 5H); ^{13}C NMR ($CDCl_3$): δ [14.45, 16.20] (*anti* + *syn*), 40.73, [42.95, 43.10] (*anti* + *syn*), [75.52, 75.63] (*anti* + *syn*), [115.03, 115.86] (*anti* + *syn*), 126.57, 128.28, 129.18, 138.87, [139.79, 140.84] (*anti* + *syn*); EIMS *m*/*z* (rel abundance): 176 (M.+, <1), 159 [$(M - OH)^+$, 100], 131 (64), 121 (8) 117 (50), 103 (76), 91 (92), 77 (72), 55 (30), 65 (12).

1-Phenyl-but-3-en-1-ol (3K): Using the general procedure but with 3-bromo-propene **1C** (182 mg, 1.5 mmol), and 4-methoxy benzaldehyde **2G** (136 mg, 1.0 mmol), the title compound **3K** (164 mg, 86%) was obtained as a light yellow oily liquid.

^{1}H NMR (400 MHz, DMSO-d_6): δ 2.27–2.41 (m, 2H), 3.72 (s, 3H), 4.5–4.54 (m, 1H), 4.94–4.96 (m, 2H), 5.68–5.78 (m, 1H); 6.85–6.87 (d, 2H, J = 8.56); 7.21–7.23 (m, 1H);^{13}C NMR (100 MHz, DMSO-d_6): 43.44, 54.45, 71.60, 113.10, 116.35, 136.91, 135.57, 137.50, 157.98; anal. ($C_{11}H_{14}O_2$) calcd, C: 74.13, H: 7.92; found, C: 74.14, H: 7.93.

1-(4-Chloro-phenyl)-2,2-dimethyl-3-butyn-1-ol (5A):[31] Using the general procedure but with 3-bromo-3-methyl-but-1-yne **4A** (221 mg, 1.5 mmol), and 4-chloro-benzaldehyde **2A** (141 mg, 1.0 mmol), the title compound **5A** (169 mg, 81%) was obtained as a light yellow oily liquid.

^{1}H NMR: δ 1.09 (s, 3H), 1.24 (s, 3H), 2.21 (s, 1H), 2.37 (brs, 1H), 4.45 (s, 1H), 7.31 (s, 4H); ^{13}C NMR: 143.23, 133.68, 128.96, 127.73, 88.89, 79.36, 71.04, 37.61, 25.84, 24.32; EIMS *m*/*z* (rel abundance): 208 (1), 166 (2), 141 (100), 113 (21), 77 (75), 68 (75), 51 (15), 39 (9); HRMS calculated for $C_{12}H_{13}OCl$ (*m*/*z*) 208.0655 found (*m*/*z*) 208.0648; anal ($C_{12}H_{13}OCl$) calcd, C: 69.07, H: 6.28; found, C: 69.81, H: 6.13.

1-(4-Formyl-phenyl)-2-ethyl-2-methyl-3-butyn-1-ol (5B): (mixture of 2 diastereomers). Using the general procedure but with 4-bromo-4-methyl-hex-2-yne **4B** (263 mg, 1.5 mmol), and benzene-1,4-dicarbaldehyde **2I** (134 mg, 1.0 mmol), the title compound **5B** (145 mg, 63%) was obtained as a light yellow oily liquid.

^{1}H NMR: δ 0.95–1.73 (m, 8H), 2.26–2.27 (s, 1H), 2.70 (brs, 1H), 4.58, 4.61(s, 1H), 7.51–7.80 (m, 4H), 9.94 (s, 1H); ^{13}C NMR: 191.60, 147.28, 146.80, 135.90, 128.84, 128.49, 127.09, 87.89, 87.33, 78.89, 78.69, 72.69, 42.48, 42.08, 30.58, 29.66, 21.80, 21.00, 9.03; HRMS calculated for $C_{14}H_{16}O_2$ (*m*/*z*) 216.2783 found (*m*/*z*) 216.2775; anal ($C_{14}H_{16}O_2$) calcd, C: 77.75, H: 7.46; found, C: 77.61, H: 7.57.

1-Furan-2-yl-4-trimethylsilanyl-but-3-yn-1-ol (5C): Using the general procedure but with (3-bromo-prop-1-ynyl)-trimethyl-silane **4C** (287 mg, 1.5 mmol), and tetrahydro-furan-2-carbaldehyde **2J** (100 mg,

1.0 mmol), the title compound **5C** (117 mg, 55%) was obtained as a light yellow oily liquid.

^{1}H NMR: δ 0.14 (s, 9H), 2.30 (brs, 1H), 2.78 (d, 2H, J = 6.24 Hz), 4.84 (t, 1H, J = 6.26 Hz), 6.31–6.34 (m, 2H), 7.36–7.38 (m, 1H);

^{13}C NMR: 154.80, 142.09, 110.14, 106.46, 102.48, 88.10, 66.13, 27.69, -0.05; ESI-MS: for $C_{11}H_{16}O_2Si$ [M], $[M + H]^+$ = 209.10, $[M - OH]^+$ = 191.09.

HRMS calculated for the fragment $C_{11}H_{15}OSi$ $[M\text{-}OH]^+$ = 191.0892 found 191.0883; anal ($C_{11}H_{16}O_2Si$) calcd, C: 63.42, H: 7.74; found, C: 63.33, H: 7.57.

3-Methyl-1-phenyl-pent-4-yn-2-ol (5D):[40] Using the general procedure but with 3-bromo-3-methyl-but-1-yne **4A** (221 mg, 1.5 mmol), and 2-phenyl-propionaldehyde **2K** (134 mg, 1.0 mmol), the title compound **5B** (97 mg, 48%) was obtained as a light yellow oily liquid.

^{1}H NMR: δ 1.27 & 1.28 (d, 3H, J = 7.20 Hz and J = 6.94 Hz), 1.84 (brs, 1H), 2.21 (d, 1H, J = 2.43 Hz), 2.55–2.62 (m, 1H), 2.87–2.93 (m, 2H), 3.66–3.74 (m, 1H), 7.19–7.38 (m, 5H);

ESI-MS: for $C_{12}H_{14}O$ [M], $[M + H]^+$ = 175.11, $[M - OH]^+$ = 157.10, HRMS calculated for the quasimolecular ion peak of $C_{12}H_{14}O$ $[M + H]^+$ = 175.1123 found 175.1145 and that of the fragment ion $C_{12}H_{13}$ $[M - OH]^+$ = 157.1017 found 157.1026; anal ($C_{12}H_{14}O$) calcd, C: 82.72, H: 8.10; found, C: 82.95, H: 7.91.

4,4-Dimethyl-2-phenyl-hex-5-yn-3-ol (5E): Using the general procedure but with 3-bromo-but-1-yne **4D** (200 mg, 1.5 mmol), and phenyl-acetaldehyde **2H** (120 mg, 1.0 mmol), the title compound **5E** (136 mg, 78%) was obtained as a light yellow oily liquid.

^{1}H NMR: δ 1.21 (s, 3H), 1.26 (s, 3H), 1.39 (d, 3H, J = 3.53 Hz), 1.86 (brs, 1H), 2.24 (s, 1H), 3.12–3.16 (m, 1H), 3.51 (d, 1H, J = 1.97 Hz), 7.20–7.30 (m, 5H).

ESI-MS: for $C_{14}H_{18}O$ [M], $[M + H]^+$ =203.14, $[M - OH]^+$ = 185.13.

HRMS calculated for the fragment $C_{14}H_{17}$ $[M - OH]^+$ = 185.1330 found 185.1330.

Anal. ($C_{14}H_{18}O$) calcd. C: 83.12, H: 8.97; found, C: 82.91, H: 8.69.

1-Phenyl-pent-4-yn-2-ol (5F):[40,41] Using the general procedure but with 3-bromo-propyne **4E** (179 mg, 1.5 mmol), and Phenyl-acetaldehyde **2H** (120 mg, 1.0 mmol), the title compound **5F** (109 mg, 68%) was obtained as a light yellow oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.96 (d, 1H, J = 4.4 Hz), 2.12 (t, 1H, J = 2.7 Hz), 2.32–2.52 (m, 2H), 2.79–2.96 (m, 2H), 3.87–4.05 (m, 1H), 7.12–7.37 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 26.64, 42.70, 71.03, 71.33, 80.82,126.90, 128.83, 129.61, 137.87; Anal ($C_{11}H_{12}O$) calcd, C: 82.46, H: 7.55; found, C: 82.66, H: 7.47.

1-Phenyl-but-3-yn-1-ol (5G):[42] Using the general procedure but with 3-bromo-propyne **4E** (179 mg, 1.5 mmol) and benzaldehyde **2F** (106 mg, 1.0 mmol), the title compound **5G** (105 mg, 72%) was obtained as a light yellow oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05 (t, 1H, J = 2.8 Hz), 2.37 (s, 1H), 2.68–2.54 (m, 2H), 4.85 (td, 1H, J = 6.5, 2.6 Hz), 7.43–7.20 (m, 5H), ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.42, 70.94, 72.30, 80.62, 125.70, 127.96, 128.45, 142.39, anal. ($C_{10}H_{10}O$) calcd, C: 82.16, H: 8.20, O: 10.94; found, C: 82.17, H: 8.21.

1-(4-Bromo-phenyl)-but-3-yn-1-ol (5H):[43] Using the general procedure but with 3-bromo-propyne **4E** (179 mg, 1.5 mmol) and 4-bromo benzaldehyde **2L** (185 mg, 1.0 mmol), the title compound **5H** (162 mg, 72%) was obtained as a light yellow oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.08–1.98 (m, 1H), 2.38 (br s, 1H), 2.65–2.49 (m, 2H), 4.84–4.71 (m, 1H), 7.28–7.14 (m, 2H), 7.50–7.35 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.64, 71.58, 71.87, 80.34, 122.03, 127.71, 131.78, 141.59; anal. $C_{10}H_9BrO$ calcd, C: 53.36, H: 4.03; found, C: 53.37, H: 4.04.

1-(4-Methoxy-phenyl)-but-3-yn-1-ol (5I):[44,45] Using the general procedure but with 3-bromo-propyne **4E** (179 mg, 1.5 mmol) and 4-methoxy benzaldehyde **2G** (136 mg, 1.0 mmol), the title compound **5I** (141 mg, 80%) was obtained as a light yellow oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.08 (t, 1H, J = 2.6 Hz), 2.31 (br s, 1H), 2.61–2.67 (m, 2H), 3.80 (s, 3H), 4.83 (t, 1H, J = 6.4 Hz), 6.85–6.91 (m, 2H), 7.28–7.34 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.61, 55.51, 71.08, 72.21, 81.03, 114.08, 127.23, 134.87, 159.56; anal. $C_{11}H_{12}O_2$ calcd, C: 74.98, H: 6.86; found, C: 74.99, H: 6.87.

Conclusion

In summary, we have demonstrated a facile strategy for the allylation and propargylation of aldehydes to afford the corresponding homoallyl and homopropargyl alcohols with a two carbon extension. The reaction involves the addition of highly reactive nano Zn(0) species coming from the redox couple of Al & $ZnCl_2$ in THF–H_2O solvent. The process is simple and efficient compared to other processs, and the reagents are easy to handle as they are not sensitive to air and moisture. The reagents are cheap and easily available in an undergraduate laboratory. The yield of the process is good to excellent. The use of aqueous solvent and nontoxic zinc adds to the environmentally friendly nature of the reaction. All of the above features are expected to add to the synthetic utility of the present reaction. Further work is warranted to understand the mechanistic details of the reaction.

Conflicts of interest

There are no conflicts to declare.

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