ISSN 1070-3632, Russian Journal of General Chemistry, 2020, Vol. 90, No. 11, pp. 2189–2196. © Pleiades Publishing, Ltd., 2020.

Indium(I)/$CuFe_2O_4$ Reagent for Allylation of Carbonyls and Epoxide Rearranged Carbonyls

M. Kundu[a], S. P. Mandal[a], B. Mondal[a,b,*], and U. K. Roy[a]

[a] *Department of Chemistry, Kazi Nazrul University, Asansol, 713340 India*
[b] *Department of Chemistry, National Institute of Technology Durgapur, Durgapur, 713209 India*
**e-mail: uroccu@gmail.com*

Received August 13, 2020; revised September 10, 2020; accepted October 2, 2020

Abstract—Indium(I)/$CuFe_2O_4$ reagent for carbonyl allylation and epoxide rearranged carbonyl allylation is proposed for formation of homoallylic alcohols. The In(I) reagent in combination with catalytic amount of $CuFe_2O_4$ support *in situ* formation of nucleophilic allylic indium from allyl halide in THF medium. Nucleophilic allylic indium species react with carbonyls to form homoallyl alcohols in good to excellent yields. Under the presented reaction conditions arylepoxides undergo smooth rearrangement into aldehydes that are also allylated with formation of homoallyl alcohols. The process is highly efficient and tolerates different functional groups.

Keywords: indium(I)chloride, catalyst, copper ferrite, carbonyl allylation, arylepoxides, homoallylic alcohols

DOI: 10.1134/S1070363220110274

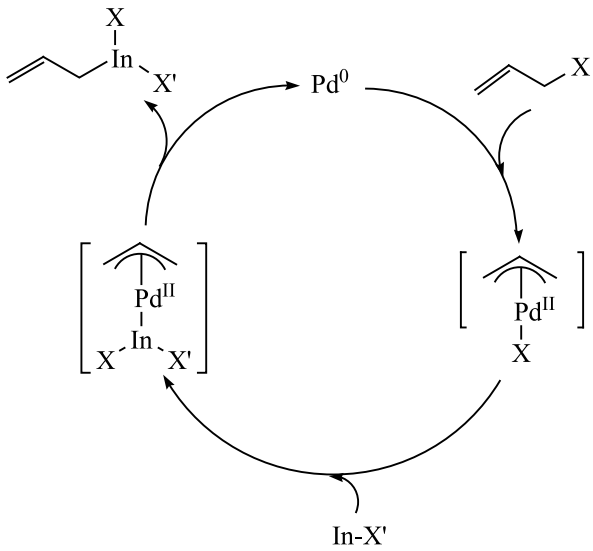
INTRODUCTION

Allyl indium compounds bearing the C-In bond are the most widely used indium compounds in organic synthesis [1]. Among their unique properties is tolerance towards water. Allyl indium derivatives *in situ* were generated by reductive transmetallation of allyl transition metal complexes that could be accumulated from allyl bromide and transition metal catalysts in combination with In(0) and In(III) chloride. These are efficient nucleophilic partners in different multicomponent allylation reactions with a variety of electrophilic reagents [2, 3]. Such reactions lead to the new C–C bonds formation with the desired regio- and stereo-selectivity, that are of particular importance in synthesis of various natural compounds [4–7].

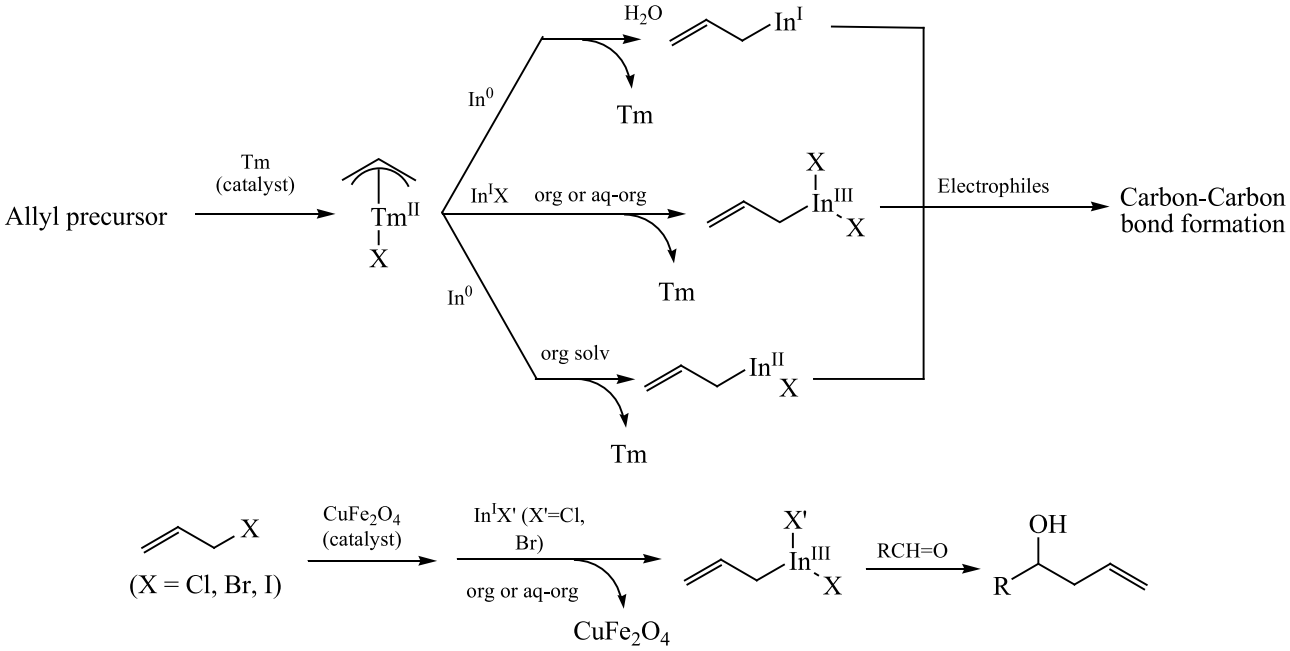
Allyl halides, their derivatives, as well as allenes and dienes are easily activated by a reactive Tm(0) catalyst (Tm = Pd, Ni) to give rise to the corresponding π-allyl-Tm(II) intermediates. Allyl transfer from the latter to In(I) or In(0) generates reactive allylindium intermediates, that are utilized *in situ* for the subsequent C–C bond formation. The allylindium species react with carbonyl compounds to give the corresponding homoallyl alcohols. Oxidative addition of allyl halides, esters, carbonates, ethers, cyclic amines, and alcohols to Pd(0) leads to well-known π-allylpalladium(II) intermediates (Scheme 1). Subsequent insertion of In(I) halides provides the corresponding π-allyl-Pd^{II}–In^{III} intermediates. The follow-up reductive elimination affords allylindium(III) derivatives. The overall reaction may be interpreted as a redox transmetallation. It is noteworthy that indium(I) halide (In-X′) may be used directly or generated *in situ* by mixing indium metal and an indium trihalide.

The above strategy for the Barbier allylation of aldehydes using InI and catalytic amount of $Pd(PPh_3)_4$ in organic solvent leads to formation of homoallylic alcohols with high regioselectivity and varying diastereoselectivity [8, 9]. Such strategy has been extended to the regioselective allylation of aldehydes in aqueous-organic medium using

Scheme 1. Generation of allylindium.



Scheme 2. Generation and reactivity of some allylindium derivatives.



[This work]

in situ generated InCl [10]. We tried other transition metal catalysts, especially copper catalysts, in such processes. Magnetically separable copper ferrite was found to be the most suitable for the Barbier type allylation reactions.

The magnetically separable $CuFe_2O_4$ catalyst was utilized for the *in situ* synthesis of allylindium derivatives (Scheme 2). The transition metal complex "[Tm]" and allyl-moiety were supposed to generate "allyl-[Tm]". The *in situ* generation of allyl-indium may be interpreted as the redox-transmetallation process involving allyl transfer from "allyl-[Tm]" to In(0/I) ensuring catalytic regeneration of the [Tm] reagent (Scheme 2). The "allyl-indium" intermediate generated via the above pathway can act further as a source of allyl-nucleophile in the following carbon-carbon bond formation. For such allyl-nucleophiles a range of electrophiles including epoxides, imines and carbonyls were tested in the carbon-carbon bond formation.

RESULTS AND DISCUSSION

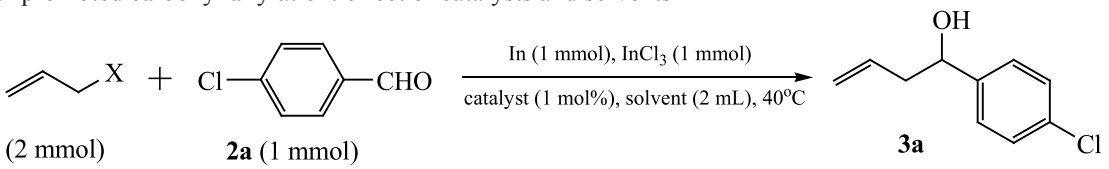
Some carbon-carbon bond forming reactions have been tried with the above synthesized magnetically separable cationic, oxo- and some other complexes of high valence iron and copper. Few commercially available high valence iron and copper salts have also been tried. It was determined that $CuFe_2O_4$ catalyzed allylation of aldehydes as well as arylepoxides rearranged aldehydes was the most efficient in formation of homoallyl alcohol via *in situ* generation of allyl-nucleophile allylindium.

Our study was started with the reaction of allyl bromide and aromatic aldehyde with indium and indium trichloride. Unfortunately, the very first test reaction of 3-bromopropene **1a** and 4-chlorobenzaldehyde **2a** with *in situ* generated InCl from the equivalent amounts of indium and indium trichloride in dry DCM failed to give any product. A mere switch of the solvent system to THF led to less than 25% of the desired homoallylic alcohol **3a**. Use of MeCN solvent resulted in only 15% yield of **3a**. Most remarkably, addition of catalytic amount of $CuCl_2 \cdot 2H_2O$ (1 mol % with respect to the carbonyl) promoted a facile reaction which gave **3a** with 66% yield. The reaction carried out under same conditions but in presence of cationic complex $Cu(OTf)_2$ led to 68% yield of **3a**. The highest yield of **3a** was achieved by using the magnetically separable catalyst $CuFe_2O_4$. These preliminary results clearly supported our view on the efficiency of organometallic processes activation by InCl.

Following the above approach a number of optimization experiments has been carried out (Table 1), and the highlights of those are presented below.

(1) The d^9 and d^{10} metal complexes of copper acted as the most efficient catalysts in THF medium. These catalysts were magnetically separable, thus adding the advantage with respect to green chemistry approach.

Table 1. InCl promoted carbonyl allylation: effect of catalysts and solvents



(2 mmol) **2a** (1 mmol) **3a**

Run no.	X	Catalyst (1 mol %)	Solvent	Time, h	Yield[a], %
1	Br	NIL	DCM	9	Traces
2	Br	NIL	MeCN	9	15
3	Br	NIL	THF	9	25
4	Br	NIL	THF–H_2O (9 : 1)	9	25
5	Br	$CuCl_2 \cdot 2H_2O$	THF	9	66
6	Br	$Cu(OTf)_2$	THF	9	68
7	Br	$CuFe_2O_4$	THF	9	76
8	Br	$Cu_{0.5}Zn_{0.5}Fe_2O_4$	THF	9	73
9	Br	CuCl	THF	9	64
10	Cl	$CuFe_2O_4$	THF	9	54

[a] Isolated yields after chromatography based on aldehydes.

(2) Additives such as QPh_3 (where Q = phosphorus, arsenic, antimony) and dppe did not play any significant role in yield improvement. This suggested that coordinative unsaturation was necessary for initial activation of electrophiles.

(3) Solvents played a very important role in the process. Among the tested solvents, THF was determined as the best choice compared to DCM, MeCN, and THF–H_2O.

The effect of water addition in promoting the reaction was not prominent.

Allyl bromide was much more reactive compared to allyl chloride. Activation of allyl alcohol in the presence of Cu(II) or Cu(I) catalysts was inefficient.

The above data (Table 1) indicated that the optimum conditions were those presented in entry 7. This version of the Barbier reaction was extended to a variety of aldehydes and substituted allyl bromides for generating homoallylic alcohols by the standard conditions (Scheme 3).

Several conclusions could be drawn from the accumulated data (Table 2).

(1) Allylation reaction was 100% γ-regioselective, however the diastereoselectivity (*syn* : *anti* ratio) of the corresponding homoallylic alcohols was achieved (entry 7).

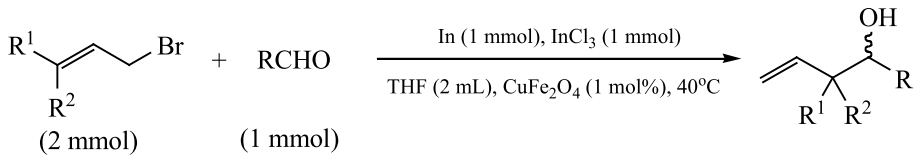
(2) The same method applied to the organometallic substrate **2d** yielded in a ferrocene derivative **3c** with the ene-terminal (entry 3).

(2) Interestingly, in the reaction of benzene-1,4-dicarboxaldehyde **2h** with 2-fold excess of allyl bromide, the mono allylated product **3h** (*syn* : *anti* = 53 : 47) was obtained beside the desired bis allylated derivative **3i**. Compound **3h** was of certain interest due to further allylation at the bare –CHO terminal that could lead to different homoallyl pendants at both sides of the phenyl ring (entry 7).

(4) Attempted application of allyl halides with ketones in the reaction was unsuccessful, thereby suggesting the aldehyde-selectivity of the reagent. Such chemoselectivity was not general for indium mediated carbonyl allylation.

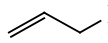
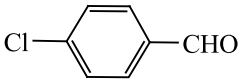
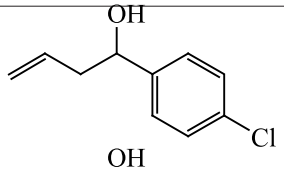
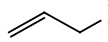
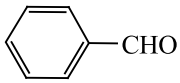
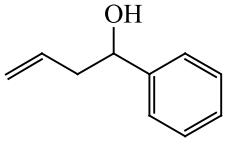
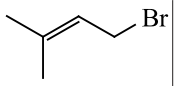
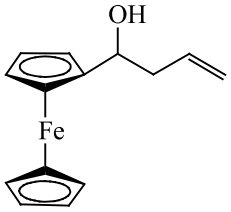
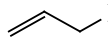
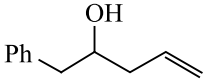
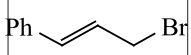
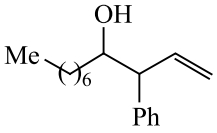
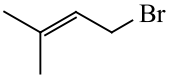
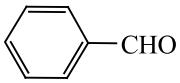
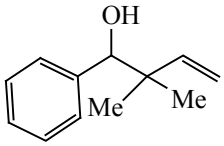
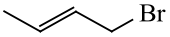
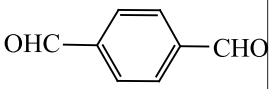
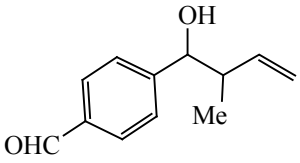
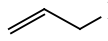
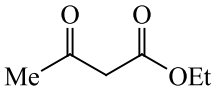
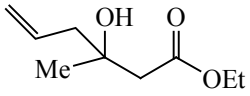
The reaction conditions of carbonyl allylation could be efficient in arylepoxide rearranged carbonyl allylation. Indium chloride was supposed to be the Lewis acid and under Lewis acidic conditions arylepoxides readily underwent rearrangement towards carbonyls. Styrene oxide **4a** demonstrated epoxide rearrangement followed by carbonyl allylation giving homoallyl alcohols **5a**–**5g,**

Scheme 3.



(2 mmol) (1 mmol)

Table 2. Allylation of carbonyls[a]

Run no.	Halide	Carbonyl	Product no.	Product	Yield[b], %	*Syn* : *anti*[c]
1			**3a**		76	–
2			**3b**		75	–
3		FcCHO	**3c**		68	–
4		$PhCH_2CHO$	**3d**		58	–
5		$Me(CH_2)_6CHO$	**3e**		53	–
6			**3f**		74	–
7			**3g**		Mono-ol 27 Diol 42	53 : 47 46 : 54
8			**3h**		70	–

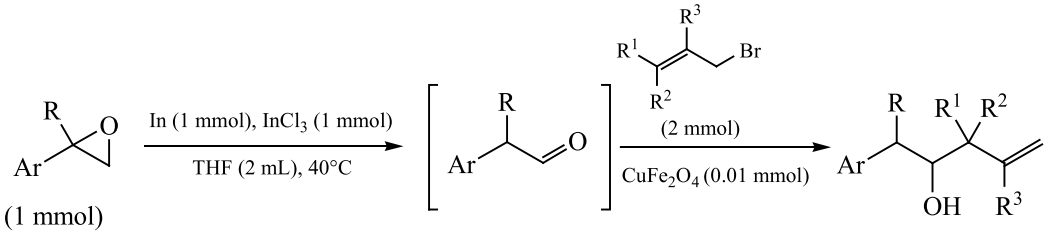
[a] Carbonyl (1 mmol), allyl bromide (2 mmol), In (1 mmol), $InCl_3$ (1 mmol), $CuFe_2O_4$ (1 mol %), THF (2 mL), 40°C.
[b] Isolated yield after column chromatography.
[c] Determined by ^1H NMR.

that corresponded allylation of phenyl acetaldehyde under the above mentioned reaction conditions (Scheme 4).

The above new version of the Barbier reaction was extended to a variety of arylepoxides and substituted allyl bromides for generating homoallylic alcohols under the above standard conditions.

In all cases, homoallylic alcohols were obtained as the exclusive or major products due to the attack of allyl nucleophiles to epoxide rearranged aldehydes. Reactions with substituted allyl bromides demonstrated exclusive γ-regioselectivity (Table 3, entries 3–5, 7). The 1,2-diastereoselectivity (*syn-anti* ratio) was poor and varied from substrate to substrate (Table 3, entries 2, 3).

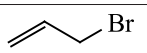
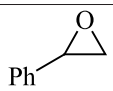
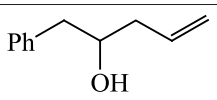
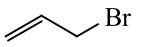
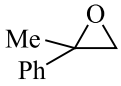
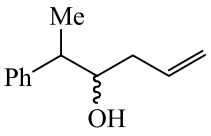
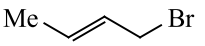
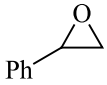
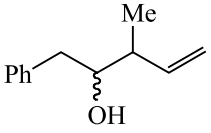
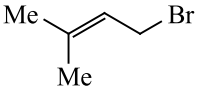
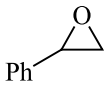
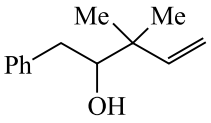
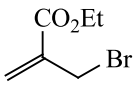
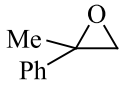
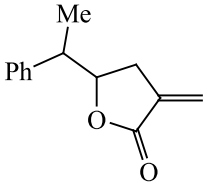
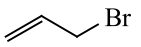
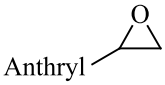
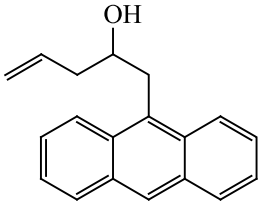
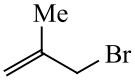
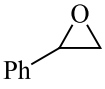
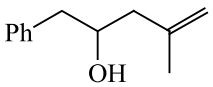
Scheme 4.



EXPERIMENTAL

The chemicals used were either commercial products (Aldrich, Lancaster, Fluka, Merck, SRL, Spectrochem). Those were distilled or recrystallized whenever required, or prepared according to literature procedures. All preparations and manipulations were carried out under the inert atmosphere of Ar using standard vacuum lines and Schlenk techniques. All drying and distillation procedures were carried out according to the standard methods and previously deoxygenated in the vacuum line. Pre-coated

Table 3. Allylation of epoxides[a]

Run no.	Halide	Epoxide	Product no.	Product	Time, h	Yield[b], %	*syn* : *anti*[c]
1			**5a**		11	75	–
2			**5b**		13	78	63 : 37
3			**5c**		13	68	40 : 60
4			**5d**		12	72	–
5			**5e**		3	47	–
6			**5f**		14	85	–
7			**5g**		13	38	–

[a] Conditions: epoxide (1 mmol), allyl bromide (2 mmol), In (1 mmol), $InCl_3$ (1 mmol), $CuFe_2O_4$ (1 mol %), THF (2 mL), 40°C.
[b] Isolated yield after column chromatography.
[c] Determined by ^1H NMR.

silica gel $60F_{254}$ (Merck) plated were used for TLC, and silica gel 60–120 and 100–200 mesh (SRL) was used for column chromatography. ^1H (200 MHz) and ^{13}C NMR (54.6 MHz) spectra were measured on a Brucker-AC 200 MHz spectrometer using TMS as an internal standard and $CDCl_3$ as a solvent. ESI-MS and HRMS spectra were measured on a Waters LCT mass spectrometer. Elemental analyses were performed on a Perkin Elmer 2400 Series II CHNS/O Analyzer and Vario EL, Elementar. Reactions were monitored by TLC.

Synthesis of magnetically separable catalysts. The nanocrystalline $CuFe_2O_4$ and Zn substituted $CuFe_2O_4$ [$Cu_{0.5}Zn_{0.5}Fe_2O_4$] were prepared by the chemical co-precipitation method. $CuCl_2{\cdot}2H_2O$, $FeCl_3$ And $ZnCl_2$ were used as the precursors. For preparing $CuFe_2O_4$ the required amount of $CuCl_2{\cdot}2H_2O$ was mixed with $FeCl_3$ and 200 mL of triple distilled water. The mixture was ultrasonicated for about 2 h. The solution of NaOH in triple distilled water was added drop wise to the solution of salts to make pH of the solution to be ca 10. Ultrasonication was carried on for another 1 h. The co-precipitated particles were rigorously stirred by a magnetic stirrer at 60°C for 2 h then filtered off and washed repeatedly by triple distilled water to reach neutral pH and remove the extra ions. The filtered particles were dried at 80°C for 24 h. For preparing $Cu_{0.5}Zn_{0.5}Fe_2O_4$ the required amount of $CuCl_2{\cdot}2H_2O$ was mixed with iron chloride and zinc chloride followed by addition of 250 mL of triple distilled water. Thus prepared solution of $CuCl_2{\cdot}2H_2O$, $ZnCl_2$ and $FeCl_3$ was ultrasonicated for ca 2 h. Solution of NaOH in triple distilled water was added drop wise to the solution of salts upon ultrasonication to achieve pH 10 and ultrasonication was carried on for another 1 h. The co-precipitated particles were rigorously stirred by a magnetic stirrer at 60°C for 2 h. The co-precipitated particles were then filtered off and washed repeatedly by triple distilled water to neutralize pH and remove the extra ions. The filtered co-precipitated particles were collected by vacuum filtration and dried at 80°C for 24 h.

Allylation of carbonyl compounds using $InCl_3$ and $CuFe_2O_4$ catalysis. To a mixture of a carbonyl compound (1 mmol) with allyl bromide (2 mmol) in THF (2 mL) In (1 mmol), $InCl_3$ (1 mmol) and $CuFe_2O_4$ (1 mol %) were added slowly in the atmosphere of Ar. The mixture was stirred at 40°C for 8–9 h. (TLC monitoring on silica gel, eluent—*n*-hexane : ethyl acetate, 9 : 1). An aqueous solution of ammonium fluoride (15%, 10 mL) was added to the reaction mixture and organic layer was extracted with diethyl ether (3×10 mL), washed with water (2× 10 mL), brine (2×10 mL), and dried over magnesium sulfate. After column chromatography (gradient elution starting from ethyl acetate–hexane, 2 to 10%) the solvent was evaporated to give the corresponding homoallylic alcohols (**3a**–**3h**).

Synthesis of homoallylic alcohols by tandem epoxide rearrangement-allylation. To a stirred solution of epoxide (1 mmol), mmol) in THF (2 mL), In (1 mmol) and $InCl_3$ (1 mmol) were added slowly and the mixture was stirred for 5 min at a 40°C. Then, allyl bromide (2 mmol) and $CuFe_2O_4$ (1 mol %) were added. After completion of the reaction (TLC) water was added to the mixture followed by ammonium fluoride, and it was extracted by ethyl acetate. The combined organic layers were washed with water (4×50 mL), brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the following column chromatography (silica gel 60–120, eluent—2% ethyl acetate in hexane) gave the corresponding allylated product (**5a**–**5g**).

1-(4-Chlorophenyl)but-3-en-1-ol (3a) [11, 12]. Yield 76%. ^1H NMR spectrum, δ, ppm: 2.42–2.51 m (2H), 4.67–4.73 m (1H), 5.09–5.2 m (2H), 5.67–5.88 m (1H), 7.2–7.34 m (1H). ^{13}C NMR spectrum, δ_C, ppm: 43.81, 72.62, 118.76, 127.25, 128.54, 133.15, 134.01, 142.34. Found, %: C 65.69, H 6.03. $C_{10}H_{11}ClO$. Calculated, %: C 65.76, H 6.07.

1-Phenylbut-3-en-1-ol (3b) [12, 13]. Yield 75%. ^1H NMR spectrum, δ, ppm: 2.12 br. s (1H), 2.48–2.56 m (2H), 4.74 t (1H, J = 6.4 Hz), 5.12–5.21 m (2H), 5.72–5.92 m (1H), 7.23–7.38 m (5H). ^{13}C NMR spectrum, δ_C, ppm: 43.85, 73.34, 118.41, 125.84, 127.57, 128.44, 134.48, 143.9. Found, %: C 81.09, H 8.20. $C_{10}H_{12}O$. Calculated, %: C 81.04, H 8.16.

2,2-Dimethyl-1-ferrocenylbut-3-en-1-ol (3c). Yield 68%. ^1H NMR spectrum, δ, ppm: 0.92 s (3H), 0.96 s (3H), 2.15 br. s (1H, OH), 4.00 s (1H), 4.19 s (9H), 4.92–5.04 m (2H), 5.79–5.93 m (1H). ^{13}C NMR spectrum, δ_C, ppm: 22.15, 23.76, 41.37, 65.67, 67.42, 67.61, 68.34, 69.79, 77.15, 112.35, 145.39. EIMS: *m/z*: 284 $[M]^+$. Found, %: C 67.35, H 7.11. $C_{16}H_{20}OFe$. Calculated, %: C 67.61, H: 7.04.

1-Phenylpent-4-en-2-ol (3d) [12, 14, 15]. Yield 58%. ^1H NMR spectrum, δ, ppm: 1.81 br. s (1H), 2.23–2.36 m (2H), 2.67–2.86 m (2H), 3.86–3.93 m (1H), 5.13–5.21 m (2H), 5.78–5.90 m (1H), 7.22–7.37 m (5H). ^{13}C NMR spectrum, δ_C, ppm: 41.22, 43.34, 71.75, 118.13, 126.51,

128.57, 129.48, 134.75, 138.46. Found, %: C 81.38, H 8.67. $C_{11}H_{14}O$. Calculated, %: C 81.44, H 8.70.

Phenyl-1-undecen-4-ol (3e) (*syn* : *anti* = 0 : 100). Yield 53%. ^{1}H NMR spectrum, δ, ppm: 0.85 t (3H, *J* = 5.5 Hz), 1.22–1.42 m (12H), 1.62 br. s (1H, –OH), 3.24 m (1H), 3.78 m (1H), 5.09–5.24 m (2H), 6.03–6.17 m (1H), 7.19–7.42 m (5H). ^{13}C NMR spectrum, δ_C, ppm: 14.06, 22.62, 25.71, 29.22, 29.51, 31.80, 34.46, 57.38, 74.27, 117.76, 126.62, 128.03, 128.55, 138.40, 141.78. Found, %: C 82.75, H 10.69. $C_{17}H_{26}O$. Calculated, %: C 82.87, H 10.64.

2,2 Dimethyl-1-phenylbut-3-en-1-ol (3f) [12, 16]. Yield 74%. ^{1}H NMR spectrum, δ, ppm: 0.97 s (3H), 1.02 s (3H), 4.43 s (1H), 5.04–5.18 m (2H), 5.85–6.00 m (1H), 7.26–7.32 m (5H). ^{13}C NMR spectrum, δ_C, ppm: 21.12, 24.48, 42.28, 80.71, 113.83, 127.44, 127.51, 127.82, 140.84, 145.14. Found, %: C 81.79, H 9.19. $C_{12}H_{16}O$. Calculated, %: C 81.77, H 9.15.

4-(1-Hydroxy-2-methylbut-3-enyl) benzaldehyde (3g) (*syn* : *anti* = 53 : 47). Yield 27%. ^{1}H NMR spectrum (*anti* isomer), δ, ppm: 0.94 d (3H, *J* = 8.0 Hz), 2.29–2.58 m (1H), 4.46 d (1H, *J* = 7.5 Hz), 5.02–5.22 m (2H), 5.72–5.81 m (1H), 7.41–7.52 m (2H), 7.82–7.88 m (2H), 9.99 s (1H). ^{1}H NMR spectrum (*syn* isomer), δ, ppm: 0.98 d (3H, *J* = 8.0 Hz), 2.29–2.58 m (1H), 4.73 d (1H, *J* = 7.5 Hz), 5.02–5.22 m (2H), 5.72–5.81 m (1H), 7.41–7.52 m (2H), 7.82–7.88 m (2H), 9.99 s (1H). ^{13}C NMR spectrum, δ_C, ppm: 13.93, 16.29 (*anti*+*syn*); 44.57, 46.22 (*anti*+*syn*); 76.54, 77.24 (*anti*+*syn*); 116.39, 117.46 (*anti*+*syn*); 127.01, 127.37 129.50, 129.63 (*anti*+*syn*); 139.57, 139.66 (*anti*+*syn*); 149.37, 149.49 (*anti*+*syn*); 191.93. EIMS: *m/z*: 191 $[M]^{+\cdot}$.

1-[4-(1-Hydroxy-2-methylbut-3-enyl) phenyl]-2-methylbut-3-en-1-ol (3g) (*syn* : *anti* = 46 : 54). Yield 42%. ^{1}H NMR spectrum, (*anti* isomer), δ, ppm: 0.86 d (6H, *J* = 6.0 Hz), 1.25 br. s (2H, –OH), 2.40–2.58 m (2H), 4.36 d (2H, *J* = 6.0), 4.99–5.24 m (4H), 5.65–5.79 m (2H), 7.25–7.30 m (4H). 1H NMR spectrum (*syn* isomer), δ, ppm: 1.00 d (6H, *J* = 6.0 Hz), 1.10 br. s (2H, –OH), 2.40–2.58 m (2H), 4.62 d (2H, *J* = 6.0), 4.99–5.24 m (4H), 5.65–5.79 m (2H), 7.25–7.30 m (4H). ^{13}C NMR spectrum, δ_C, ppm: 13.96, 16.45 (*anti*+*syn*); 29.63, 31.15 (*anti*+*syn*); 44.59, 46.23 (*anti*+*syn*), 115.47, 116.76 (*anti*+*syn*); 125.49, 125.67 (*anti*+*syn*); 126.34, 126.51 (*anti*+*syn*); 126.68, 126.79 (*anti*+*syn*); 140.22, 140.57 (*anti*+*syn*). EIMS: *m/z*: 210 $[M - 2H_2O]^+$.

3-Hydroxy-3-methyl-5-hexenoic acid ethyl ester (3h) [17]. Yield 70%. ^{1}H NMR spectrum, δ, ppm: 1.23–1.37 m (6H), 2.26 m (2H) 2.42 m (2H), 3.61 br. s (1H, OH), 4.18 m (2H), 5.02–5.12 m (2H), 5.73–5.90 m (1H). ^{13}C NMR spectrum, δ_C, ppm: 14.09, 26.75, 44.23, 46.43, 60.45, 70.57, 118.40, 133.61, 172.75.

1-Phenylpent-4-en-2-ol (5a) [12, 14, 15]. Yield 75%. ^{1}H NMR spectrum, δ, ppm: 1.75 br. s (1H), 2.15–2.39 m (2H), 2.67–2.88 m (2H), 3.82–3.93 m (1H), 5.12–5.22 m (2H), 5.77–5.94 m (1H), 7.15–7.37 m (5H). ^{13}C NMR spectrum, δ_C, ppm: 41.18, 43.29, 71.68, 118.14, 126.48, 128.53, 129.42, 134.68, 138.37. ESI-MS: 145.108 $[M - OH]^+$. Found, %: C 81.68, H 8.51. $C_{11}H_{14}O$. Calculated, %: C 81.44, H 8.70.

2-Phenylhex-5-en-3-ol (5b) (*syn : anti* = 63 : 37) [18]. Yield 78%. ^{1}H NMR spectrum, δ, ppm: 1.26 d, 1.35 d [3H, *J* = 6.8 Hz each (*anti*+*syn*)], 1.7 br. s (1H), 1.99–2.25 m (2H), 2.75–2.82 m (1H), 3.68–3.77 m (1H), 5.06–5.18 m (2H), 5.73–5.87 m (1H), 7.20–7.36 m (5H). ESI-MS: 159.117 $[M - OH]^+$. Found, %: C 81.69, H 9.20. $C_{12}H_{16}O$. Calculated, %: C 81.77, H 9.15.

3-Methyl-1-phenylpent-4-en-2-ol (5c) [19, 20] **(*syn : anti* = 40 : 60).** Yield 68%. ^{1}H NMR spectrum, δ, ppm: 1.12 d, 1.21 d [3H, *J* = 6.7 Hz each (*anti*+*syn*)], 1.65 br. s (1H), 2.30–2.37 m (1H), 2.55–2.69 m (1H), 2.83–2.93 m (1H), 3.67–3.75 m (1H), 5.09–5.18 m (2H), 5.79–5.96 m (1H), 7.18–7.36 m (5H). ^{13}C NMR spectrum, δ_C, ppm: 14. 54, 16.33 (*anti*+*syn*); 40.76, 40.81 (*anti*+*syn*); 43.01, 43.23 (*anti*+*syn*); 75.64, 75.74 (*anti*+*syn*); 115.24, 116.08 (*anti*+*syn*); 126.31, 126.77 (*anti*+*syn*); 128.43, 128.47 (*anti*+*syn*); 129.28, 129.32 (*anti*+*syn*); 138.88, 138.94 (*anti*+*syn*); 139.87, 140.9 (*anti*+*syn*). ESI-MS: 159.097 $[M - OH]^+$. Found, %: C 81.89, H 9.20. $C_{12}H_{16}O$. Calculated, %: C 81.77, H 9.15.

3,3-Dimethyl-1-phenylpent-4-en-2-ol (5d) [21]. Yield 72%. ^{1}H NMR spectrum, δ, ppm: 1.12 s (6H), 1.58 br. s (1H), 2.4–2.52 m (1H), 2.9 d. d (1H, *J* = 13.7 Hz, *J* = 1.7 Hz), 3.51 d. d (1H, *J* =10.6 Hz, *J* = 1.9 Hz), 5.06–5.15 m (2H), 5.87–6.01 m (1H), 7.21–7.35 m (5H). ^{13}C NMR spectrum, δ_C, ppm: 22.79, 38.38, 41.46, 79.34, 113.05, 126.26, 128.48, 129.3, 139.88, 145.2. ESI-MS: 173.13 $[M - OH]^+$. Found, %: C 81.98, H 9.49. $C_{13}H_{18}O$. Calculated, %: C 82.06, H 9.53.

3-Methylene-5-(1-phenylethyl)-dihydrofuran-2-one (5e) [22] Yield 47%. ^{1}H NMR spectrum, δ, ppm: 1.41–1.44 d (3H, *J* = 7 Hz), 2.49–2.74 m (2H), 2.77–2.92 m (1H), 4.53–4.64 m (1H), 5.49–5.52 m (1H), 6.14–6.17 m (1H), 7.17–7.37 m (5H). ^{13}C NMR spectrum, δ_C, ppm: 17.88, 31.91, 45.54, 81.11, 121.77, 127.10, 127.75, 128.69, 134.51, 141.31, 170.22. EIMS: *m/z*: 202 $[M]^{+\cdot}$.

Found, %: C 76.65, H 7.14. $C_{13}H_{14}O_2$. Calculated, %: C 77.20, H 6.98.

1-Anthrylpent-4-en-2-ol (5f). Yield 85%. ^{1}H NMR spectrum, δ, ppm: 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 spectrum, δ_C, ppm: 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: 263.14 $[M + H]^+$. Found, %: C 86.92, H 6.76. $C_{19}H_{18}O$. Calculated, %: C 86.99, H 6.92.

4-Methyl-1-phenylpent-4-en-2-ol (5g) [23]. Yield 38%. ^{1}H NMR spectrum, δ, ppm: 1.75 s (3H), 1.81 br. s (1H), 2.16–2.29 m (2H), 2.76–2.79 m (2H), 3.93–4.02 m (1H), 4.82–4.95 m (2H), 7.2–7.46 m (5H). ^{13}C NMR spectrum, δ_C, ppm: 22.38, 43.50, 45.43, 69.84, 113.48, 126.4, 127.85, 128.43, 139.90, 142.57. ESI-MS: 159.10 $[M - OH]^+$. Found, %: C 81.81, H 9.26. $C_{12}H_{16}O$. Calculated, %: C 81.77, H 9.15.

CONCLUSIONS

We have demonstrated a facile allylation of carbonyl and arylepoxide compounds using In–$InCl_3$ and $CuFe_2O_4$ catalyst in the synthesis of homoallyl alcohols with two carbon extensions, that is expected to enrich the synthetic application of the reaction. Further study of the mechanism of the process is warranted.

FUNDING

Financial support of this work by SERB-New Delhi, SR/FT/CS-137/2011 dated 12.07.2012, and Science and Technology and Biotechnology-WB, 50(Sanc.)/ST/P/S&T/15G-10/2018 dated 30.01.2019 to UKR is gratefully acknowledged.

CONFLICT OF INTEREST

No conflict of interests was declared by the authors.

REFERENCES

1. Nishimoto, Y., Yi, J., Takata, T., Baba, A., and Yasuda, M., *Molecules*, 2018, vol. 23, p. 1884. https://doi.org/10.3390/molecules23081884
2. Lee, P. H., Seomoon, D., Lee, K., Kim, S., Kim, H., Kim, H., and Sridhar, M., *Adv. Synth. Catal.*, 2004, vol. 346, p. 1641. https://doi.org/10.1002/adsc.200404125
3. Hirashita, T., Sato, Y., Yamada, D., Takahashi, F., and Araki, S., *Chem. Lett.*, 2011, vol. 40, p. 506. https://doi.org/10.1246/cl.2011.506
4. Gintner, M., Denner, C., Schmölzer, C., Fischer, M., Frühauf, P., Kählig, H., and Schmid, W., *Monatsh. Chem,* 2019, vol. 150, p. 849. https://doi.org/10.1007/s00706-019-02438-y
5. Hirashita, T., Takahashi, F., Noda, T., Takagi, Y., and Araki, S., *Molecules*, 2018, vol. 23, p. 1696. https://doi.org/10.3390/molecules23071696
6. Gordon, D.M. and Whitesides, G.M., *J. Org. Chem.*, 1993, vol. 58, p. 7937 https://doi.org/10.1021/jo00079a050
7. Chan, T.H. and Lee, M.C., *J. Org. Chem.*, 1995, vol. 60, p. 4228. https://doi.org/10.1021/jo00118a044
8. Araki, S., Kamei, T., Hirashita, T., Yamamura, H., and Kawai, M., *Org. Lett.*, 2000, vol. 2, p. 847. https://doi.org/10.1021/ol005610i
9. Hirashita, T., Kamei, T., Satake, M., Horie, T., Shimizu, H., and Araki, S., *Org. Biomol. Chem.*, 2003, vol. 1, p. 3799. https://doi.org/10.1039/B306195G
10. Jang, T.S., Keum, G., Kang, S.B., Chung, B.Y., and Kim, Y., *Synthesis*, 2003, p. 775. https://doi.org/10.1055/s-2003-38059
11. Kundu, A., Prabhakar, M., Vairamani, M., and Roy, S., *Organometallics*, 1999, vol. 16, p. 4796. https://doi.org/10.1021/om9704096
12. Sinha, A. K., Mondal, B., Kundu, M., Chakraborty, B., and Roy, U. K. *Org. Chem. Front.*, 2014, vol. 1, p. 1270. https://doi.org/10.1039/c4qo00235k
13. Barczak, N.T., Grote, R.E., and Jarvo, E.R., *Organometallics*, 2007, vol. 26, p. 4863. https://doi.org/10.1021/om700605y
14. Roy, U.K. and Roy, S., *Tetrahedron*, 2006, vol. 62, p. 678. https://doi.org/10.1016/j.tet.2005.10.005
15. Banerjee, M., Roy, U.K., Sinha, P., and Roy, S., *J. Organomet. Chem.*, 2005, vol. 690, p. 1422. https://doi.org/10.1016/j.jorganchem.2004.12.008
16. Hayashi, S., Hirano, K., Yorimitsu, H., and Oshima, K., *Org. Lett.*, 2005, vol. 7, p. 3577. https://doi.org/10.1021/ol0515199
17. Araki, S., Ito, H., and Butsugan, Y., *J. Org. Chem.*, 1988, vol. 53, p. 1831. https://doi.org/10.1021/jo00243a052
18. Jiang, N., Hu, Q., Reid, C.S., Lu, Y., and Li, C.-J., *Chem. Commun.*, 2003, p. 2318. https://doi.org/10.1039/B305161G
19. Collins, S., Kuntz, B.A., and Hong, Y., *J. Org. Chem.*, 1989, vol. 54, p. 4154. https://doi.org/10.1021/jo00278a031
20. Collins, S., Dean, W.P., and Ward, D.G., *Organometallics*, 1988, vol. 7, p. 2289. https://doi.org/10.1021/om00101a007
21. McCluskey, A., Muderawan, I.W., Muntari, and Young, D.J., *J. Org. Chem.*, 2001, vol. 66, p. 7811. https://doi.org/10.1021/jo015904x
22. D'Aniello, F., Mattii, D., and Taddei, M., *Synlett.*, 1993, p. 119. https://doi.org/10.1055/s-1993-22369
23. Kundu, A., Prabhakar, S., Vairamani, M., and Roy, S., *Organometallics*, 1997, vol. 16, p. 4796. https://doi.org/10.1021/om9704096