EurJOC
European Journal of Organic Chemistry

A Journal of
ChemPubSoc Europe

Accepted Article

Title: [bmim][Br] as an Inexpensive and Efficient Medium for the Barbier-type Allylation using a Catalytic Amount of In: Mechanistic Studies

Authors: Papiya Dey, Mrunesh Koli, Dibakar Goswami, Anubha Sharma, and Subrata Chattopadhyay

To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.201800043

Link to VoR: http://dx.doi.org/10.1002/ejoc.201800043

Supported by
ACES Asian Chemical Editorial Society

WILEY-VCH

FULL PAPER WILEY-VCH

[bmim][Br] as an Inexpensive and Efficient Medium for the Barbier-type Allylation using a Catalytic Amount of In: Mechanistic Studies

Papiya Dey, Mrunesh Koli, Dibakar Goswami*, Anubha Sharma and Subrata Chattopadhyay*

[a]Bio-Organic Division, Bhabha Atomic Research Centre, Mumbai - 400 085, India

Fax: +91 22 25505151; e-mail: dibakarg@barc.gov.in; schatt57@gmail.com

Abstract: The Barbier type allylation of aldehydes/ketones can be carried out with both unsubstituted and γ-substituted allyl bromides using only a catalytic amount (0.1 equiv.) of In metal in [bmim][Br], but not in H_2O, organic solvents and other room temperature ionic liquids. The reactions do not require any metal activator, and proceed with chemo- and regio-selectivities. Our temporal ^{1}H NMR studies suggested that besides acting as a solvent, [bmim][Br] also activates In metal surface by electron polarization to generate both CH_2=$CHCH_2$–In (**I**) and CH_2=$CHCH_2$–$InBr_2$ (**II**) from allyl bromide and In. Of the active allylating intermediates, species **II** is regenerated by an *in situ* reduction of $InBr_3$ by an imidazolium-based *N*-heterocyclic carbene, both produced during the process, accounting for the catalytic action of In metal.

Introduction

The Barbier-type allylation, carried out with allylic halides, metals (In, Zn, Sn, Ga etc.) and carbonyl substrates in organic solvents,[1a] H_2O[1b] and room temperature ionic liquids (RTILs),[1c-h] as well as under solvent-free conditions,[1i-k] is widely investigated in organic syntheses due to its convenience and applications in biological and pharmaceutical chemistry.[2] Nevertheless, an ideal version of the reaction involving stoichiometric amounts of the substrates and catalytic amounts of the metal remains elusive. In H_2O, the greenest and cheapest solvent on earth, a majority of the allylmetals are hydrolytically unstable,[3] warranting use of a large excess of the reagents for completion of the reactions. Even the solvent-free synthetic procedures require an excess of reagents.[4] The mechanochemical organic synthesis promises to offer stoichiometric control, but is operationally difficult and is in its infancy.[5] Another limitation of Barbier-type allylation is the need of using toxic metal activators such as metal salts and mineral acids.

We have previously carried out[1f] Barbier-type allylation of carbonyls using sub-stoichiometric (50 mol%) of Ga metal, near stoichiometric amounts of the reactants and the inexpensive RTIL, [bmim][Br], both as the metal activator and solvent. As an imidazolium-based RTIL with small alkyl groups, [bmim][Br] is expected to be safe.[6a] More recently, we reported a highly *syn*-selective Bi-mediated crotylation of aldehydes in [bmim][Br], using near stoichiometric amounts of the reactants.[1h] It is worth mentioning that, although [bmim][Br] is commercially available as a solid, stable existence of a supercooled liquid state of [bmim][Br] could be achieved by cooling down freshly prepared [bmim][Br] below its melting point.[6b,c] Moreover, the chosen RTIL has a very low vapor pressure, dissolves most of the organic substrates and is reusable.[7]

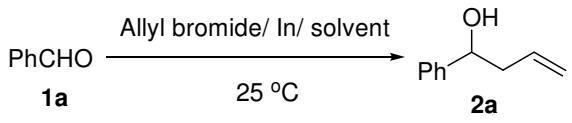
The inertness and low first ionization potential of In metal coupled with the extensive tolerance of organoindium species towards various functional groups make it a popular choice as a metal for Barbier-type allylation.[8] However, most of the previous efforts employed stoichiometric amounts of In metal for the reaction.[8b,9] The carbonyl allylation protocols using catalytic In metal relied on using preformed allyl-metal complexes under strictly anhydrous conditions, and were primarily restricted to limited substrates.[10] Recently, Schneider *et al*. have reported a method for allylation of ketones in water with preformed allylboronates in the presence of In catalyst.[11a] In another report,[11b] Barbier-type allylation of aldehydes and ketones in DMF was accomplished using a catalytic amount of In metal in presence of excess Al metal (foil). Similarly, combination of catalytic amount of $InCl_3$ with stoichiometric amount of Al metal has also been used for this purpose.[11c] Catalytic use of elemental Ga for allylation of acetals, ketals and aminals has also been reported wherein a Ag (I) co-catalyst was used for regeneration of Ga metal.[11d] Thus, these methods[11b,c] could not decrease the total amount of metals, and hence did not reduce the amounts of disposable metallic wastes.

In the present investigation, we explored the possibility of using the In/[bmim][Br] combination for carbonyl allylation using stoichiometric quantities of the substrates. The study also provided new mechanistic insights in the allyl-In chemistry in the chosen RTIL, eventually leading to a protocol with catalytic quantity of In. To the best of our knowledge, catalytic Barbier-type allylation of carbonyls using simple allylic bromides, and without requiring any co-catalyst has never been accomplished.

Results and Discussion

Initially, we carried out the In-mediated reaction between allyl bromide and benzaldehyde (**1a**) in H_2O, THF and three different RTILs, including [bmim][Br], and the results (**Scheme 1**, Table 1) established the efficacy of [bmim][Br] as the best solvent. All the reactions were carried out at 2 mmol scale of **1a** in H_2O/organic solvent (5 mL) or RTIL (4 mL). The reactions in H_2O, THF and THF-H_2O mixture (1:1 v/v) were slow even under ultrasonic activation, affording the product **2a** in 59-69% yields after 18-20 h (Table 1, entries 1-5). Also, a large excess of In (5 equiv.) and allyl bromide (3 equiv.) were required. Reducing their amounts led to poorer yields (data not shown). In contrast, the reaction could be accomplished much faster (4 h) in [bmim][Br] with only 1.5 equiv. of the bromide and 1.2 equiv. of In to obtain **2a** in 89%

yield (Table 1, entry 6). For comparison, we also carried out the allylation of **1a** separately in two other RTILs, [bmim][BF_4], and [bmim][PF_6]. As reported earlier, the reactions in these RTILs took a much longer time.[1c,12a,b] However, we got **2a** in poorer yields than those reported (Table 1, entries 7, 8). This kind of yield variability in different batches of RTIL has been observed previously.[12a]



Scheme 1. In-mediated allylation of benzaldehyde (**1a**) under different conditions.

Table 1. Reaction profile of In-mediated allylation of **1a** in various solvents[a]

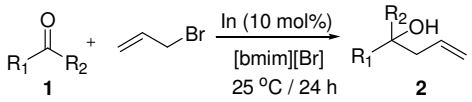
Entry	Allyl bromide (equiv.)	In (equiv.)	Solvent	Time (h)	Yield (%)[b]
1	3	5	H_2O	18	59
2	3	5	H_2O[c]	16	64
3	3	5	THF	18	65
4	3	5	THF[c]	18	69
5	3	5	THF-H_2O[d]	20	61
6	1.5	1.2	[bmim][Br]	4	89
7	1.5	1.2	[bmim][BF_4]	20	64
8	1.5	1.2	[bmim][PF_6]	20	62
9	1.5	0.6	[bmim][Br]	12	89
10	1.5	0.5	[bmim][Br]	16	86
11	1.5	0.1	[bmim][Br]	24	83
12	1.5	0.1	H_2O	72	8
13	1.5	0.1	[bmim][PF_6]	48	9-10
14	1.5	0.1	[bmmim][Br]	72	NR[e]

[a] The reactions were carried out using 2 mmol of **1a**. [b] Isolated yields of the products. [c] Reaction was carried out under ultrasonication. [d] 1:1 (v/v) THF-H_2O was used. [e]NR= No Reaction

Next, we attempted the allylation of **1a** in [bmim][Br] under the above reaction conditions, but using sub-stoichiometric amounts (0.6-0.1 equiv.) of In, and the results are shown in Table 1, entries 9-14. Although the reaction became progressively slower with reduced amounts of In, **2a** was obtained in appreciable yields. Interestingly the reaction could be accomplished even with 0.1 equiv. of In, when **2a** was obtained in 83% yield in 24 h (Table 1, entry 11). However, further reduction of the amount of allyl bromide led to incomplete reactions (data not shown), probably due to the volatility of allyl bromide. Such an allylation protocol using the combination of catalytic amount of In(0) with allyl bromide has never been reported. Use of inexpensive allyl bromide makes the protocol more economical, attractive and amenable for scale-up. The In (0.1 equiv.)-mediated reactions of **1a** and allyl bromide in water and [bmim][PF_6] were very sluggish and produced **2a** in very poor yields (Table 1, entries 12-13). The above reaction in 1-butyl-2,3-dimethylimidazolium bromide ([bmmim][Br]), lacking the imidazole C-2 hydrogen was abortive (Table 1, entry 14). Earlier, allylation of **1a** in [bmim][BF_4] using allyl bromide and sub-stoichiometric amount of Sn proceeded with very poor yield (14%).[12b] This reinforces the importance of our protocol.

The catalytic protocol (0.1 equiv. of In) was equally effective with both aromatic and aliphatic aldehydes/ketones **1b-s** furnishing the products **2b-s** in good yields (Table 2). The nature of the substituents in the aromatic ring or alkyl chain length did not have any appreciable effect on the reaction course. Allylation of ketones proceeded with marginally less, but appreciable (75-87%) yields. The reaction proceeded with complete chemoselectivity with the conjugated aldehyde **1i** and ketone **1q** to furnish the corresponding 1,2-addition products **2i** and **2q** exclusively. Interestingly, allylation of 4-methylcyclohexanone (**1m**) under the above conditions exclusively furnished **2m** with equatorial OH group. This is in sharp contrast with previous reports where allyl indium reagents preferably produced the axial-product.[12c,d] Allylation of the 1,2-diketone **1p** furnished the monoallylated product **2p** only. The ester group was unaffected when ethyl levulinate (**1r**) was allylated to give the product **2r**, further confirming the chemoselectivity and enhancing the scope of the protocol. The reaction with the chiral substrate, (*R*)-cyclohexylideneglyceraldehyde (**1s**) proceeded in good yield, albeit with poor diastereoselectivity. However, reaction with 2-hydroxybenzaldehyde produced a myriad of products, and the desired product was obtained in <20% yield (data not shown). The allylation products could be conveniently isolated by extracting the reaction mixture three times with Et_2O followed by concentration. The reactions were clean without any side-products and/ or starting materials. The RTIL mole fraction was earlier found to govern the reaction yields, which was ascribed to the change in the ionic character of the medium.[13] Hence, we also carried out the reaction using different amounts of [bmim][Br] (1-3 mL/mmol). However, the change in the RTIL mole fractions didn't affect the reaction yields significantly (data not shown). The RTIL, recovered after Et_2O extraction, was reused at least 5 times without any significant yield loss (the yield varied from 83-80% in successive cycles). During the process, although [b2Brmim][Br] is accumulated as a non-metallic bi-product, its amount [b2Brmim][Br] is very small compared to the volume of [bmim][Br] employed as a solvent. More importantly, it does not interfere in the catalytic cycle. Recently we found that the Bi-mediated crotylation of aldehydes can be carried out even with a lesser amount (~1.25 mL/mmol) of [bmim][Br] with marginal yield loss.[1f] Consistent with this, allylation of **1a** at 10 mmol scale could be carried out in [bmim][Br] (12 mL) to obtain **2a** in 86% yield, and the reaction was complete in 26 h, establishing practical feasibility of the protocol (0.1 equiv. of In). Even at 10 mmol scale, the RTIL was used for three cycles without any loss of yield. To avoid even any marginal yield loss, the reaction medium was replenished each time with 2 mL of fresh RTIL, as part of it was consumed during the process (vide infra).

Table 2. Reaction profile of allylation of carbonyls in [bmim][Br] using catalytic amount of In[a]



Entry	Substrate	R_1	R_2	Product	Yield[b] (%)
1	**1b**	2-Cl-C_6H_4	H	**2b**	92
2	**1c**	4-Cl-C_6H_4	H	**2c**	93
3	**1d**	4-F-C_6H_4	H	**2d**	88
4	**1e**	2-Br-C_6H_4	H	**2e**	91
5	**1f**	3-OMe-C_6H_4	H	**2f**	92
6	**1g**	3,5-diOMe-C_6H_3	H	**2g**	90
7	**1h**	C_6F_5	H	**2h**	82
8	**1i**	C_6H_5-CH=CH	H	**2i**	81
9	**1j**	2-furfuryl	H	**2j**	85
10	**1k**	C_9H_{19}	H	**2k**	85
11	**1l**	cyclohexanone		**2l**	88
12	**1m**	4-methylcyclohexanone		**2m**[c]	82
13	**1n**	C_6H_5	CH_3	**2n**	80
14	**1o**	C_6H_5	C_6H_5	**2o**	78
15	**1p**	C_6H_5	C_6H_5-C=O	**2p**	75
16	**1q**	C_6H_5	C_6H_5-CH=CH	**2q**	75
17	**1r**	CH_3	$CH_2CH_2CO_2C_2H_5$	**2r**	87
18	**1s**	(*R*)-cyclohexylideneglyceraldehyde		**2s**	85 (*R*,*R*):(*R*:*S*) :: 37:63[d]

[a] The reactions were carried out using 2 mmol of the carbonyl substrates and 1.5 equiv. of allyl bromide. [b] Isolated yields of the products. [c] The product with equatorial-OH group was obtained. [d] Based on the isolated yields of the individual diastereomers.

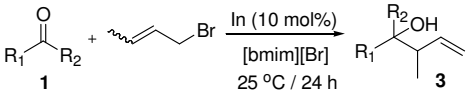
Next, the above protocol was extended for reaction of crotyl bromide with some of the above mentioned aldehydes (**1a**,**1b,1f,1k,1s**), ketones (**1l,1n-p**) and some additional substrates (**1t,1u**). In all the cases, the products **3a-k** were obtained in good yields (72-92%, Table 3). Most of the substrates, except benzil (**1p**) furnished the corresponding γ-adducts exclusively. With **1p** (Table 3, entry 8), an inseparable mixture of the major γ-adduct **3h** along with the α-adduct (*E*/*Z* mixture) was obtained in 67:33 ratio.

Except for **3j** (Table 3, entry 10), the *syn*/*anti* ratios of the products were determined by comparing their ^{1}H NMR spectra with those reported (*vide experimental*). For **3j**, the more downfield doublet in the aliphatic region (δ 0-1.5 ppm) was assigned to the *syn*-isomer by comparing its ^{1}H NMR spectrum with that of **3a**, and the *syn*/*anti* ratio was determined. The exclusive formation of γ-adduct in most of the reactions is in contrast to a previous report[11a] where exclusive α-adducts were obtained using α-methylallyl boronates in presence of catalytic amount of In metal. Overall, the above results clearly established [bmim][Br] as the best RTIL among those chosen for the In-mediated carbonyl allylation. Most importantly, the reaction requires only 0.1 equiv. of In metal. By contrast, a large excess of reagents was required for completion of the reaction in H_2O and THF. The special role of [bmim][Br] in activating In metal, and also ensuring metal recyclability were of interest for further mechanistic studies. Hence, we probed the organometallic species, responsible for the reaction by ^{1}H NMR analyses and the results are disclosed below.

Mechanistic studies: For this, the reactions between In (1 mmol) and allyl bromide (1 mmol) in D_2O / THF-*d*8 (3 mL) were followed by recording the ^{1}H NMR spectra of the aliquots of the reaction mixture over a time period. In case of [bmim][Br], a large excess of allyl bromide (12 mmol) was used in 2 mL of RTIL to mimic the catalytic conditions. The ^{1}H NMR spectra of the reaction mixture carried out in D_2O (*vide SI*, Fig. 2) showed appearance of a new doublet (J = 8.4 Hz) at δ 1.64 ppm at the expense of the –CH_2Br signal at δ 3.9 ppm, after 10 min. The intensity of the peak (δ 1.64 ppm) attained its maximum in 25 min, and thereafter declined gradually to vanish in 2 h. No new olefinic resonances were noticed. The ^{1}H NMR doublet at δ 1.64 ppm was assigned to CH_2=$CHCH_2$–In (**I**), based on an earlier report.[3a] Depletion of the ^{1}H NMR resonances (δ 1.64 ppm) was associated with an increase in the intensity of the resonances at ~ δ 4.37 ppm, suggesting formation of allyl alcohol, as detected earlier.[3a] These results clearly revealed that the active In-species **I** is hydrolytically unstable, and may account for the need of a large excess of In and allyl bromide, when the allylation is carried out in H_2O. Recently, Haddad *et al*. reported formation of a mixture of allylindium intermediates in the reaction of allyl bromide with In metal in D_2O.[1g] They detected species **I**

by recording the ^{1}H NMR spectrum of the reaction mixture in D_2O. Besides **I**, formation of other allylindium intermediates were also suggested.[1g] However, we could not detect any allylindium intermediate other than **I** in D_2O.

Table 3. Reaction profile of allylation of carbonyls in [bmim][Br] using catalytic amount of In[a]



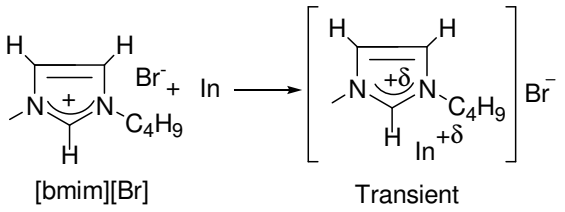
Entry	Substrate	R_1	R_2	Product	Yield[b] (%)	γ (*syn*:*anti*):α (*E*:*Z*)[c]
1	**1a**	C_6H_5	H	**3a**	92	100 (40:60) : 0 (-)
2	**1b**	2-Cl-C_6H_4	H	**3b**	91	100 (48:52) : 0 (-)
3	**1f**	3-OMe-C_6H_4	H	**3c**	87	100 (46:54) : 0 (-)
4	**1k**	C_9H_{19}	H	**3d**	87	100 (49:51) : 0 (-)
5	**1l**	Cyclohexanone		**3e**	82	----
6	**1n**	C_6H_5	CH_3	**3f**	78	100 (65:35) : 0 (-)
7	**1o**	C_6H_5	C_6H_5	**3g**	75	----
8	**1p**	C_6H_5	C_6H_5-C=O	**3h**	72	67 (44:56) : 33 (73:27)
9	**1s**	(*R*)-cyclohexylideneglyceraldehyde		**3i**	85	γ [(2*R*,3*R*,4*R*):(2*R*,3*S*,4*R*):(2*R*,3*S*,4*S*)]:α(*E*:*Z*) :: 100 [9:13:78] : 0(-)[d]
10	**1t**	4-C_2H_5-C_6H_4	H	**3j**	90	100 (50:50) : 0 (-)
11	**1u**	C_6H_{13}	H	**3k**	85	100 (40:60) : 0 (-)

[a] The reactions were carried out using 2 mmol of the carbonyl substrtates and 1.5 equiv. of crotyl bromide. [b] Isolated yields of the products. [c] The regioisomeric and diastereomeric ratios were obtained from the ^{1}H NMR spectra. [d] Based on the isolated yields of the individual diastereomers.

Next, we followed the reaction in THF as above. Due to the overlapping resonances of the solvent in the region of interest (δ 1.5-1.9 ppm), formation of species **I** could not be inferred conclusive (*vide SI*, Fig. 3). But the ^{1}H NMR spectrum recorded after 4 h, showed appearance of the new doublets (J = 8.8 Hz) at δ 1.98 ppm and olefinic multiplets at δ 4.57-4.85 ppm. This suggested formation of some allyl-In species. Although the allyl-In species remained stable up to 6.5 h (*cf.* time-dependent ^{1}H NMR spectra), its formation required a long induction time. Earlier, the reaction of In and allyl bromide in organic media and RTIL produced **I** along with CH_2=$CHCH_2$–$InBr_2$ (**II**), the latter showing a ^{1}H NMR signal at ~ δ 2.01.[12a,14] Keeping these in view, and appearance of the new olefinic resonances at ~ δ 4.5 ppm, formation of the species **II** in THF was inferred.

Previously, Chan *et al.* reported simultaneous formation of **I** and **II** in [emim][BF_4] and [bpy][BF_4].[12a,15] The species **I** is insoluble in $CDCl_3$.[1g] Hence, to detect all the possible allylindium intermediates in [bmim][Br] in the present studies, the reaction mixture aliquots were concentrated in vacuo (~50 Torr), dissolved separately in $CDCl_3$ and D_2O, and their ^{1}H NMR spectra recorded every hour over a period of 8 h. The spectra recorded in $CDCl_3$ (*vide SI*, Fig. 4) showed a new doublet (J = 8.5 Hz) at δ 2.15 ppm along with new olefinic multiplets at δ 6.19 ppm and 4.72 ppm, while that recorded in D_2O (*vide SI*, Fig. 5) showed a doublet (J = 8.5 Hz) at δ 1.67 ppm. As above, the allyl-In species detected in $CDCl_3$ was assigned structure **II**, whereas the species detected in D_2O was assigned structure **I**. Thus, analogous to the observations in other RTILs,[1g] we found that both **I** and **II** are simultaneously generated in [bmim][Br]. The total integration of the signals at δ 2.15 ppm and 1.67 ppm reached a maximum in ~ 3 h, and remained steady up to 8 h. The intensities of the NMR peak due to the CH_2–In protons in the species **I** and **II** were quantified by comparing with that of the N-CH_3 singlet signal originating from the RTIL. Earlier, a rapid conversion of the initially formed species **I** to **II** was reported in [bpy][BF_4],[12a] especially in the presence of [bpy][Br]. However, no such transformation was noticed in [bmim][Br], as their relative ratio remained 1:1 over the entire study period. These results are consistent with the fact that the combination of propargyl bromide and In generated allenylindium and allenylindium dibromide in both aqueous media and THF.[16]

Addition of **1a** (10 fold excess) to the reaction mixture in [bmim][Br] led to the complete disappearance of the ^{1}H NMR signal at δ 1.67 ppm (recorded in D_2O), but no NMR signal of the product **2a** was observed due to its insolubility in D_2O. But when the ^{1}H NMR spectrum of the same aliquot was recorded in $CDCl_3$, the signals due to **2a** along with those of **II** and unreacted **1a** were evident. The temporal profiles (16 h and 24 h) of the ^{1}H NMR spectra of the reaction aliquots recorded in D_2O showed absence of **I** in the reaction mixture. However, the ^{1}H NMR spectrum of aliquot (16 h), recorded in $CDCl_3$ showed the ^{1}H NMR signals of **II** and **2a** (~70% conversion, *cf.* ^{1}H NMR spectrum). Even after 24 h, when the reaction was complete, a significantly intense signal of **II** was observed. Although we are unsure of the relative reactivities of the species **I** and **II** with the carbonyls, the above results suggested that between them, only **II** was regenerated and helped completion of the reaction.

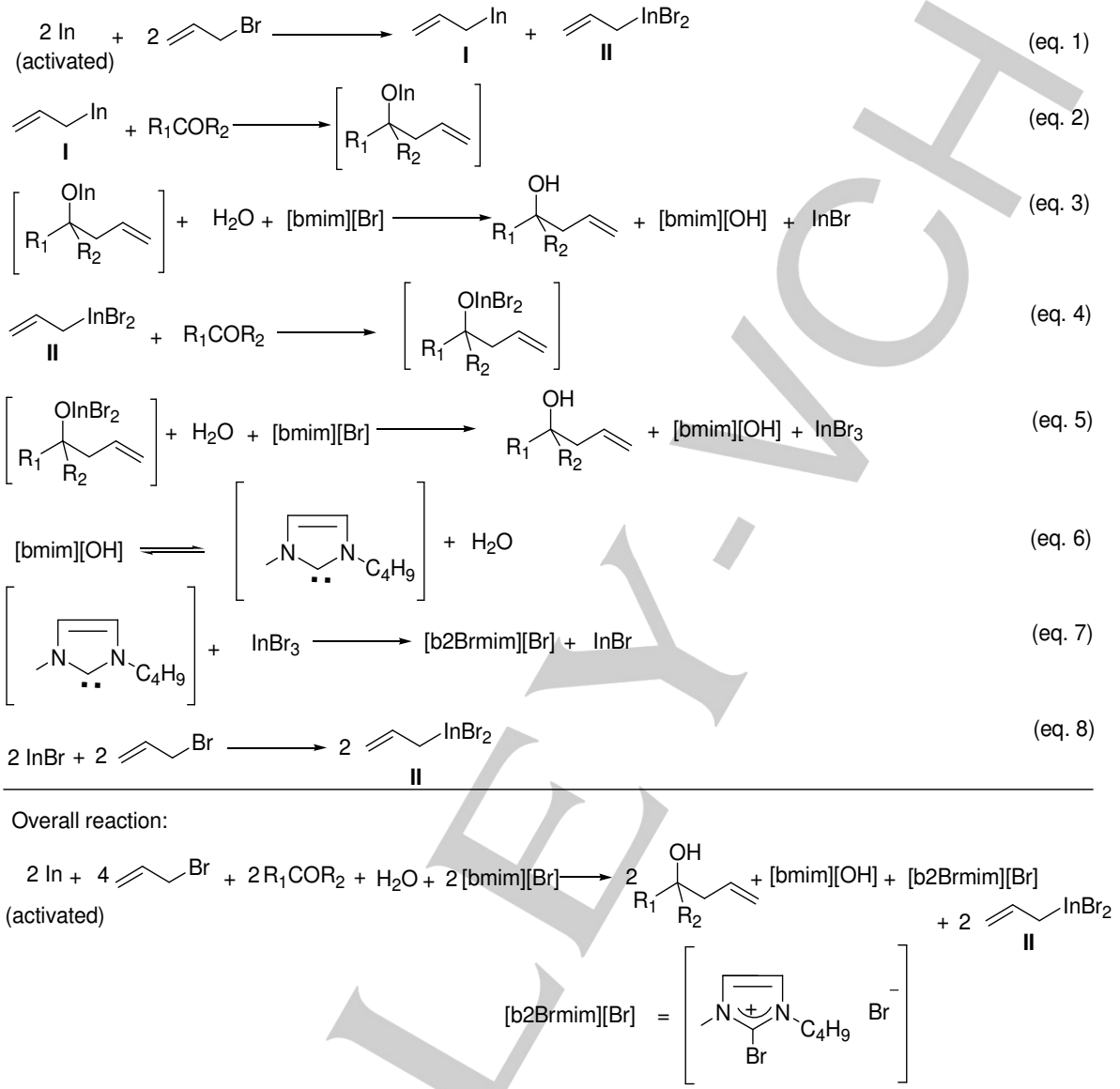


Scheme 2. Activation of In-metal by [bmim][Br].

The above results also suggested activation of In metal specifically by [bmim][Br], but not by other RTILs, chosen for the study. For investigating this, we recorded the ^{1}H NMR spectrum of [bmim][Br] (2 mL) after incubating with In (1.0 mmol) for 0.5 h (*vide SI*, Fig. 6), which showed upfield shifts of its imidazole protons (~ 39 Hz for H-2, H-4 and H-5). The magnitudes of the NMR shifts relates to the charge transfer (CT) process,[17a-c] and the imidazolium-based ILs are known to promote electron-transfer reactions.[17d] Thus, the upfield shift of the ^{1}H NMR resonances suggested electron polarization from In metal to [bmim][Br] that would activate the metal surface via formation of ion-pairs or more complex ion aggregates with a partially charged activated In (**Scheme 2**). Similar activation of Ga and Bi metals in [bmim][Br] were observed earlier by us,[1f,h] and is consistent with higher standard reduction potential of [bmim][Br] (0.641 V, measured against standard calomel electrode as reference)[1f] compared to that of In metal, supporting such a possibility of electron polarization between In and the RTIL. The Barbier type of reactions are known to proceed via formation of radicals on the activated metal surfaces.[18a] Addition of allyl bromide to the above mixture regenerated the RTIL, because the ^{1}H NMR resonances of its imidazole protons were restored. This also confirmed that the proposed electron polarization generated a transient activated In species, facilitating its subsequent reaction with allyl bromide to furnish the active allylating species **I** and **II**. However, similar electron polarization was not evident either in [bmim][BF_4] or in [bmim][PF_6], which unequivocally proved that this kind of metal activation is possible only in [bmim][Br], and not in other similar RTILs used in this study. Possibly, as stated earlier, the reduction potential of the RTILs plays a role in the electron polarization. The reduction potentials of RTILs are reported to be highly dependent on the nature of the anions,[18b,c] particularly the fluorine containing anions are known to enhance their electrochemical stability against reduction.[18c]

The formation of the species **I** and **II** and the catalytic role of In can be rationalized considering the reactions shown in **Scheme 3**. Initially, the activated In metal reacts with allyl bromide to furnish both **I** and **II** (eq. 1). Addition of species **I** to the carbonyl substrate, followed by hydrolysis[19] furnishes the product homoallylic alcohol, along with [bmim][OH] and InBr (eqs. 2-3). On the other hand, a similar reaction course of **II** yields the product along with [bmim][OH] and $InBr_3$ (eqs. 4-5). The [bmim][OH], generated *in situ*, has been reported to be a 1:1 mixture of *N*-heterocyclic carbene (NHC) and water.[20a] *In situ* dissociation of the C-2 hydrogen of the imidazolium ring results in the formation of the carbene. Similar carbene formation was also reported even at pH 8.3 during deuterium exchange of the C-2 proton in D_2O.[20a-c] Such type of unsaturated carbenes are stable[20d] in their monomeric forms. Earlier dimesitylcarbene was used as a reducing agent to produce Au nanoparticles from Au^{+3} solution.[20e] Under the present conditions, the NHC reduces $InBr_3$ to produce InBr along with its oxidized product, 2-bromo-1-butyl-3-methylimidazolium bromide, [b2Brmim][Br] (eqs. 6-7). To confirm this, the crude reaction mixture was successively extracted with Et_2O (to isolate the product alcohol) followed by ice-cold $CHCl_3$, and the residue dried under vacuum to obtain a ~1:1 mixture of [bmim][Br] and[b2Brmim][Br], which was characterized by ^{1}H and ^{13}C NMR spectroscopy. Besides the resonances for [bmim][Br], the ^{1}H NMR spectrum of the mixture showed two doublets (each J = 2.0 Hz) at δ 7.99 ppm and 8.16 ppm, while its ^{13}C NMR spectrum showed resonances at δ 123.3, 124.9 and 130.9 ppm. These suggested formation of [b2Brmim][Br] in the reaction mixture. This was further confirmed by preparing its chloro-analog, [b2Clmim][Cl], according to a reported procedure,[20f] and comparing its ^{1}H and ^{13}C NMR spectra with those for the above mixture. This unambiguously proved the formation of [b2Brmim][Br], and, thus, of the reduction of In(III) to In(I) *in situ*. The InBr produced in eqs. 5-7, subsequently reacts with allyl bromide to furnish **II** (eq. 8), maintaining the catalytic cycle without further addition of In metal. For additional confirmation, commercially available InBr was reacted with allyl bromide in [bmim][Br]. A new ^{1}H NMR doublet at δ 2.12 confirmed formation of the species **II**, as was reported earlier in the reaction of InBr with allyl bromide in [bpy][BF4]/[bpy][Br].[12a]

One limitation of the study is that we could not identify the NHC intermediate, because of its low concentration and also its fast reaction with $InBr_3$. It was also impossible to identify formation of its precursor, [bmim][OH] from the complex reaction mixture. Nevertheless, in an indirect attempt to support our hypothesis, we stirred a mixture of $InBr_3$ (10 mol%), allyl bromide (1 mmol) and [bmim][OH][21] (10 mol%) in [bmim][Br] (2 mL) for 30 min. The ^{1}H NMR spectrum ($CDCl_3$) of an aliquot of the reaction mixture showed the peaks due to the species **II**. This can only happen by the [bmim][OH]-mediated reduction of $InBr_3$ to InBr, followed by its reaction with allyl bromide. Earlier, similar reduction of the group 13-metal halides by an NHC-complex has been reported.[22]



Scheme 3. Plausible mechanism for carbonyl allylation with catalytic In.

Conclusions

Overall, we have developed a catalytic Barbier-type protocol for the indium-mediated allylation of carbonyls achieving excellent yield. The reaction could be accomplished even with 10 mol% of In-metal, thereby reducing the total metallic wastes unlike most of the previous methods of Barbier-type carbonyl allylation. Additionally we have carried out the reactions with only 1.5 equiv. of the allylic halides that would minimize generation of organic wastes. Although a very small amount (1 mmol/mmol of substrate, calculated to be only 1.7% of the RTIL recovered after the reaction) of the non-metallic bi-product, [b2Brmim][Br], is accumulated in the reaction mixture, it does not interfere in the catalytic cycle as evident from the recyclability of the RTIL. The reaction mechanism for the catalytic cycle of In metal and its activation by [bmim][Br] has also been established. Eventual formation of a monomeric NHC, which ultimately reduces In(III) to In(I), has been found to play a pivotal role in maintaining the

catalytic cycle. Overall, the present protocol outscores myriads of previously reported methods of Barbier-type carbonyl allylation, both in terms of procedural advantages and conceptual novelty.

Experimental Section

All chemicals were procured from Sigma Aldrich and used as received. Other reagents were of AR grade. [bmim][Br] and [b2ClMim][Cl] were synthesized following known procedures.[1h,20f] The organic extracts were dried over anhydrous Na_2SO_4. The IR spectra were recorded as films with a BRUKER Tensor II spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded with a Bruker AC-200 (200 MHz) or a Varian 500 MHz NMR spectrometer. For characterization, the NMR spectra were processed using either MestReNova Lite-11.0.4, ACD/1D NMR Processor or Bruker TOPSPIN software. The optical rotations were recorded with a JASCO DIP-360 digital polarimeter. The elemental analyses were carried with an Elementar Vario micro cube. Melting points (mp) were measured in a Büchi B-540 apparatus.

Reaction monitoring by NMR. A mixture of In (1 mmol) and allyl bromide (1 mmol) in D_2O / THF-*d*8 (3 mL) was magnetically stirred at room temperature. Aliquots (35 µL) of reaction mixture were taken at different time intervals, and the ^1H NMR spectra recorded. In case of [bmim][Br], a mixture of In (1 mmol) and allyl bromide (12 mmol) were stirred in [bmim][Br] (2 mL), and the ^1H NMR spectra of the aliquots (35 µL, dried at ~50 Torr) of the reaction mixture recorded separately in $CDCl_3$ and D_2O over a time period.

General procedure for In-mediated allylation of 1a in aqueous or organic media. In metal (1.15 g, 10.0 mmol) was added to a mixture of **1a** (212 mg, 2.0 mmol) and allyl bromide (726 mg, 6.0 mmol) in H_2O or THF or H_2O-THF (1:1 v/v) (5 mL), and stirred magnetically for the time specified in Table 1. Similar reactions were also carried out in H_2O and THF under ultrasonication. The mixture was extracted with Et_2O (2 × 10 mL), dried, concentrated in vacuo, and subjected to column chromatography (silica gel, 0-15% EtOAc/hexane) to obtain pure **2a** (yields in Table 1).

General procedure for In-mediated allylation reactions in RTILs. A mixture of In metal and allyl bromide (quantities specified in Tables 1-3) in the RTIL (2 mL/mmol) was stirred at room temperature for 0.5 h, followed by addition of the aldehyde (2 mmol). After stirring the mixture at room temperature for completion of each reaction (*cf.* TLC), the mixture was extracted with Et_2O (3 × 10 mL), dried, concentrated in vacuo and the residue purified by column chromatography (silica gel, EtOAc/hexane) to give the respective products.

1-Phenylbut-3-en-1-ol (**2a**)[1f]: Colorless liquid; IR: 3419, 918 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.10 (broad s, 1H), 2.50-2.54 (m, 2H), 4.72-4.75 (m, 1H), 5.14-5.19 (m, 2H), 5.78-5.86 (m, 1H), 7.26-7.31 (m, 1H), 7.34-7.37 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 43.8, 73.3, 118.3, 125.8, 127.5, 128.4, 134.5, 143.9.

1-(2-Chlorophenyl)-but-3-en-1-ol (**2b**)[23a]: Colorless liquid; IR: 3385, 918 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.15 (broad s, 1H), 2.36-2.42 (m, 1H), 2.62-2.66 (m, 1H), 5.16-5.21 (m, 3H), 5.83-5.91 (m, 1H), 7.19-7.22 (m, 1H), 7.28-7.34 (m, 2H), 7.56-7.58 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.0, 69.7, 118.6, 127.0, 127.1, 128.4, 129.4, 131.8, 134.2, 141.2.

1-(4-Chlorophenyl)-but-3-en-1-ol (**2c**)[23a]: Yellow liquid; IR: 3416, 914 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.06 (broad s, 1H), 2.36-2.42 (m, 1H), 2.62-2.66 (m, 1H), 5.16-5.22 (m, 3H), 5.83-5.92 (m, 1H), 7.19-7.23 (m, 1H), 7.27-7.34 (m, 2H), 7.56-7.58 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.0, 69.6, 118.6, 127.0, 127.1, 128.4, 129.4, 131.7, 134.2, 141.2.

1-(4-Fluorophenyl)-but-3-en-1-ol (**2d**)[23a]: Yellow liquid; IR: 3385, 919 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.12 (broad s, 1H), 2.45-2.53 (m, 2H), 4.73 (t, *J* = 6.0 Hz, 1H), 5.14-5.18 (m, 2H), 5.75-5.83 (m, 1H), 7.02-7.07 (m, 2H), 7.27-7.34 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 43.9, 72.6, 115.1, 115.3, 118.7, 127.4, 127.5, 134.1, 139.5, 161.2, 163.1.

1-(4-Bromophenyl)-but-3-en-1-ol (**2e**)[1f]: Yellow liquid; IR: 3384, 919 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.25 (broad s, 1H), 2.41-2.50 (m, 2H), 4.67-4.69 (m, 1H), 5.12-5.15 (m, 2H), 5.72-5.80 (m, 1H), 7.20-7.22 (m, 2H), 7.45-7.47 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 43.7, 72.6, 118.8, 121.2, 127.6, 131.4, 133.9, 142.8.

1-(3-Methoxyphenyl)-but-3-en-1-ol (**2f**)[1f]: Colorless liquid; IR: 3417, 917 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.06 (broad s, 1H), 2.46-2.56 (m, 2H), 3.82 (s, 3H), 4.72 (dd, *J* = 7.5 and 5.0 Hz, 1H), 5.14-5.20 (m, 2H), 5.78-5.86 (m, 1H), 6.81-6.84 (m, 1H), 6.93-6.95 (m, 2H), 7.25-7.28 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 43.8, 55.2, 73.2, 111.3, 113.0, 118.1, 118.4, 129.4, 134.4, 145.6, 159.7.

1-(3,5-Dimethoxyphenyl)-but-3-en-1-ol (**2g**)[23b]: Yellow liquid; IR: 3421, 920 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.05 (broad s, 1H), 2.45-2.53 (m, 2H), 3.79 (s, 6H), 4.66 (dd, *J* = 7.5 and 5.0 Hz, 1H), 5.13-5.18 (m, 2H), 5.77-5.85 (m, 1H), 6.36-6.38 (m, 1H), 6.51-6.52 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 43.7, 55.3, 73.3, 99.4, 103.7, 118.3, 134.4, 146.5, 160.8.

1-Pentafluorophenylbut-3-en-1-ol (**2h**)[1f]: Yellow thick liquid; IR: 3384, 968 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.34-2.35 (m, 1H), 2.58-2.64 (m, 1H), 2.75-2.80 (m, 1H), 5.09-5.19 (m, 3H), 5.71-5.79 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 41.3, 65.7, 116.4, 119.5, 132.5, 136.5, 138.5, 139.5, 141.6, 143.7, 145.7, 145.8.

(E)-1-Phenylhexa-1,5-dien-3-ol (**2i**)[1f]: Colorless liquid; IR: 3417, 919 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.86 (broad s, 1H), 2.37-2.47 (m, 2H), 4.35-4.39 (m, 1H), 5.16-5.22 (m, 2H), 5.83-5.91 (m, 1H), 6.25 (dd, *J* = 15.5 and 6.5 Hz, 1H), 6.62 (d, *J* = 15.5 Hz, 1H), 7.23-7.26 (m, 1H), 7.31-7.34 (m, 2H), 7.38-7.40 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.0, 71.7, 118.5, 126.5, 127.6, 128.6, 130.4, 131.6, 134.0, 136.7.

1-(Furan-2-yl)-but-3-en-1-ol (**2j**)[23c]: Brown liquid; IR: 3385, 918 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.14 (broad s, 1H), 2.61-2.64 (m, 2H), 4.74-4.76 (m, 1H), 5.14-5.21 (m, 2H), 5.77-5.85 (m, 1H), 6.26 (t, *J* = 2.5 Hz, 1H), 6.33-6.34 (m, 1H), 7.38-7.39 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 40.1, 66.9, 106.1, 110.1, 118.5, 133.7, 142.0, 156.0.

1-Tridecen-4-ol (**2k**)[1f]: Colorless liquid; IR: 3554, 919 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.0 Hz, 3H), 1.26-1.34 (m, 13H), 1.42-1.48 (m, 3H), 1.61 (broad s, 1H), 2.10-2.16 (m, 1H), 2.28-2.32 (m, 1H), 3.61-3.66 (m, 1H), 5.12-5.15 (m, 2H), 5.79-5.87 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 22.7, 25.7, 29.3, 29.6, 29.7, 31.9, 36.9, 42.0, 70.8, 117.9, 134.9.

1-Allylcyclohexanol (**2l**)[1f]: Colorless liquid; IR: 3405, 912 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.25-1.28 (m, 1H), 1.40-1.61 (m, 10H), 2.20-2.22 (m, 2H), 5.09-5.15 (m, 2H), 5.84-5.93 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.2, 25.8, 37.4, 46.7, 70.9, 118.6, 133.7.

1-Allyl-4-methylcyclohexanol (**2m**):[23d] Colorless liquid; IR: 3385, 919 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.92 (d, *J* = 6.5 Hz, 3H), 1.02-1.10 (m, 2H), 1.39-1.48 (m, 3H), 1.60-1.72 (m merged with broad s, 5H), 2.30 (d, *J* = 7.5 Hz, 2H), 5.12-5.18 (m, 2H), 5.84-5.93 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.2, 31.3, 31.5, 37.2, 42.1, 71.5, 118.6, 133.7.

2-Phenylpent-4-en-2-ol (**2n**)[1f]: Colorless liquid; IR: 3424, 914 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.56 (s, 3H), 2.09 (broad s, 1H), 2.49-2.54 (m, 1H), 2.68-2.72 (m, 1H), 5.12-5.16 (m, 2H), 5.59-5.68 (m, 1H), 7.24-7.27 (m, 1H), 7.34-7.37 (m, 2H), 7.45-7.46 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.9, 48.5, 73.6, 119.5, 124.7, 126.6, 128.1, 133.7, 147.6.

1,1-Diphenylbut-3-en-1-ol (**2o**)[1f]: Colorless liquid; IR: 3416, 914 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.57 (broad s, 1H), 3.09-3.11 (m, 2H), 5.19-5.28 (m, 2H), 5.64-5.73 (m, 1H), 7.22-7.27 (m, 2H), 7.32-7.35 (m, 4H), 7.46-7.48 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 46.7, 76.9, 120.5, 126.0, 126.8, 128.2, 133.4, 146.5.

2-Hydroxy-1,2-diphenylpent-4-en-1-one (**2p**)[23e]: White solid (mp: 90-91 °C); IR: 3453, 1677, 924 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.96-3.00 (m, 1H), 3.12-3.16 (m, 1H), 4.19 (s, 1H), 5.00-5.14 (m, 2H), 5.69-5.78 (m, 1H), 7.27-7.34 (m, 3H), 7.38-7.46 (m, 3H), 7.50-7.51 (m, 2H), 7.72-7.74 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 44.0, 81.4, 120.2, 125.6, 128.0, 128.8, 130.1, 132.3, 132.6, 134.7, 141.8, 200.8.

(E)-1,3-Diphenylhexa-1,5-dien-3-ol (**2q**)[1f]: Colorless thick liquid; IR: 3456, 1640, 969, 918 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.33 (broad s, 1H), 2.77-2.87 (m, 2H), 5.19-5.24 (m, 2H), 5.69-5.77 (m, 1H), 6.54 (d, *J* = 16.0 Hz, 1H), 6.66 (d, *J* = 16.0 Hz, 1H), 7.22-7.33 (m, 4H), 7.36-7.40 (m, 4H), 7.52-7.54 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 47.1, 75.7, 120.0, 125.4, 126.5, 126.9, 127.5, 128.3, 128.4, 128.5, 133.1, 135.3, 136.8, 145.3.

Ethyl 4-Hydroxy-4-methylhept-6-enoate (**2r**):[23f] Colorless liquid; IR: 3443, 1730, 948 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.0 Hz, 3H), 1.40 (s, 3H), 1.66 (broad s, 1H), 1.94-1.98 (m, 1H), 2.12-2.17 (m, 1H), 2.42 (d, *J* = 7.5 Hz, 2H), 2.75 (t, *J* = 6.5 Hz, 2H), 4.13 (q, *J* = 7.0 Hz, 2H), 5.15-5.19 (m, 2H), 5.74-5.83 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 26.1, 28.0, 37.9, 45.2, 60.5, 85.8, 119.6, 132.0, 172.6.

1,2-Cyclohexylidenedioxy-5-hexen-3-ol (**2s**): **(2*R*,3*R*)-isomer**: Colorless liquid; $[\alpha]_D^{24}$ +3.6 (*c* 1.10, $CHCl_3$) (lit.[23g] $[\alpha]_D^{20}$ +3.5 (*c* 1.06, $CHCl_3$)); IR: 3454, 1641, 927 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.39-1.40 (m, 2H), 1.57-1.62 (m, 8H), 2.22-2.32 (m merged with broad s, 3H), 3.55-3.59 (m, 1H), 3.71-3.74 (m, 1H), 3.97-4.04 (m, 2H), 5.09-5.14 (m, 2H), 5.81-5.90 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 23.8, 24.0, 25.1, 34.8, 36.2, 38.3, 65.7, 71.6, 78.0, 109.9, 117.7, 134.0. **(2*R*,3*S*)-isomer**: Colorless liquid; ($[\alpha]_D^{24}$ +7.6 (*c* 1.02, $CHCl_3$) (lit.[23g] $[\alpha]_D^{20}$ +7.4 (*c* 1.15, $CHCl_3$)); IR: 3455, 1642, 926 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.37-1.39 (m, 2H), 1.57-1.61 (m, 8H), 2.13-2.22 (m merged with broad s, 2H), 2.29-2.34 (m, 1H), 3.75-3.77 (m, 1H), 3.88-3.92 (m, 1H), 3.97-4.02 (m, 2H), 5.11-5.16 (m, 2H), 5.79-5.87 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 23.8, 24.0, 25.1, 34.8, 36.2, 37.6, 64.8, 70.5, 77.7, 109.6, 118.2, 134.0.

2-Methyl-1-phenylbut-3-en-1-ol (**3a**)[1h]: Colorless liquid; IR: 3415, 914 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.89 (*anti*) and 1.03 (*syn*) (two d, *J* = 7.0 Hz, 3H), 2.05 (broad s, 1H), 2.48-2.52 (*anti*) and 2.58-2.61 (*syn*) (two m, 1H), 4.37 (*anti*) and 4.62 (*syn*) (two d, *J* = 7.5 and 5.5 Hz, 1H), 5.05-5.08 and 5.18-5.23 (two m, 2H), 5.74-5.86 (m, 1H), 7.27-7.37 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0, 16.5, 44.6, 46.2, 77.3, 77.9, 115.4, 116.6, 126.5, 126.8, 127.3, 127.6, 128.0, 128.2, 140.3, 140.6, 142.5.

2-Methyl-1-(2-chlorophenyl)-but-3-en-1-ol (**3b**)[23h]: Colorless liquid; IR: 3416, 914 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.98 (*syn*) and 1.02 (*anti*) (two d, *J* = 6.5 and 7.0 Hz, 3H), 2.01 (*syn*) and 2.18 (*anti*) (two broad s, 1H), 2.57-2.61 (*anti*) and 2.71-2.75 (*syn*) (two m, 1H), 4.96 (*syn*) (d, *J* = 6.5 Hz, 0.5H), 5.09-5.19 (m, 2.5H), 5.79-5.86 and 5.89-5.96 (two m, 1H), 7.18-7.22 (m, 1H), 7.26-7.35 (m, 2H), 7.47-7.54 (m, 1H); ^{13}C NMR (125 MHz,$CDCl_3$): δ = 12.7, 16.4, 42.5, 45.0, 73.2, 73.5, 115.4, 116.8, 126.6, 128.1, 128.2, 128.4, 129.3, 132.0, 132.6, 139.6, 140.2, 140.4, 140.6.

2-Methyl-1-(3-methoxyphenyl)-but-3-en-1-ol (**3c**)[23c]: Colorless liquid; IR: 3416, 914 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.89 (*anti*) and 1.02 (*syn*) (two d, *J* = 7.0 Hz, 3H), 2.04 (broad s, 1H), 2.46-2.51 (*anti*) and 2.56-2.59 (*syn*) (two m, 1H), 3.82 (s, 3H), 4.34 (*anti*) and 4.59 (*syn*) (two d, *J* = 7.5 and 5.5 Hz, 1H), 5.05-5.09 and 5.17-5.22 (two m, 2H), 5.74-5.85 (m, 1H), 6.80-6.84 (m, 1H), 6.88-6.92 (m, 2H), 7.23-7.27 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 13.9, 16.5, 44.5, 46.0, 55.2, 77.2, 77.8, 112.2, 112.3, 112.7, 113.1, 115.3, 116.6, 118.9, 119.2, 129.0, 129.1, 140.4, 140.6, 144.2, 144.4, 159.6.

3-Methyltridec-1-en-4-ol (**3d**) [23i]: Colorless liquid; IR: 3384, 912 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.0 Hz, 3H), 1.03 and 1.04 (two d, *J* = 5.5 and 5.0 Hz, 3H), 1.27-1.39 (m, 14H), 1.48-1.56 (m merged with broad s, 3H), 2.18-2.24 (*anti*) and 2.26-2.30 (*syn*) (two m, 1H), 3.37-3.41 (*anti*) and 3.48-3.51 (*syn*) (two m, 1H), 5.07-5.13 (m, 2H), 5.73-5.84 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0, 16.3, 22.6, 25.7, 26.1, 29.3, 29.6, 31.9, 34.0, 34.3, 43.4, 44.1, 74.7, 115.1, 116.1, 140.4, 141.1.

1-(1-Methyl-2-propenyl)-cyclohexanol (**3e**)[23j]: Colorless liquid; IR: 3384, 912 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.02 (d, *J* = 7.0 Hz, 3H), 1.16-1.19 (m, 1H), 1.40-1.45 (m, 2H), 1.48-1.56 (m, 5H), 1.57-1.63 (m, 3H), 2.16-2.19 (m, 1H), 5.04-5.08 (m, 2H), 5.79-5.87 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 21.8, 25.8, 34.4, 35.0, 48.3, 72.4, 115.8, 140.4.

3-Methyl-2-phenylpent-4-en-2-ol (**3f**)[23k]: Colorless liquid; IR: 3473, 914 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.89 (*syn*) and 0.99 (*anti*) (two d, *J* = 7.0 and 6.5 Hz, 3H), 1.55 (s, 3H), 2.01 (*syn*) and 2.09 (*anti*) (two broad s, 1H), 2.54-2.58 (*syn*) and 2.59-2.64 (*anti*) (two m, 1H), 5.11-5.15 (m, 2H), 5.70-5.77 (*anti*) and 5.81-5.88 (*syn*) (two m, 1H), 7.24-7.28 (m, 1H), 7.34-7.37 (m, 2H), 7.42-7.47 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 14.8, 25.9, 28.5, 48.8, 49.0, 75.7, 75.8, 116.3, 116.6, 125.2, 125.5, 126.4, 126.6, 127.9, 139.9, 140.0, 147.0.

2-Methyl-1,1-diphenylbut-3-en-1-ol (**3g**)[23l]: White solid (mp: 52-53 °C); IR: 3553, 915 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.16 (d, *J* = 7.0 Hz, 3H), 2.51 (broad s, 1H), 3.66-3.71 (m, 1H), 5.25-5.33 (m, 2H), 6.00-6.07 (m, 1H), 7.28-7.31 (m, 2H), 7.40-7.45 (m, 4H), 7.61-7.72 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.6, 44.4, 79.4, 117.4, 125.8, 126.0, 126.6, 126.7, 128.2, 128.3, 128.4, 130.2, 132.6, 139.4, 145.9, 146.9.

2-Hydroxy-3-methyl-1,2-diphenylpent-4-en-1-one (**3h**) [23m]: White solid (mp: 61-62 °C); IR: 3453, 1719, 919 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.09 (d, *J* = 7.0 Hz, 3H), 2.81-2.85 and 3.09-3.13 (two m, 1H), 3.83 (broad s, 1H), 5.11-5.17 (m, 2H), 5.77-5.84 (m, 1H), 7.26-7.40 (m, 6H), 7.58-7.60 (m, 2H), 7.74-7.77 (m, 2H); *2-Hydroxy-1,2-diphenylhex-4-en-1-one* (Inseparable α-isomer **3h'**)[23n]: ^1H NMR (500 MHz, $CDCl_3$): 1.37 (*Z*) and 1.62 (*E*) (two d, *J* = 7.0 and 6.0 Hz, 3H), 3.51-3.54 (m, 2H), 4.09 (broad s, 1H), 5.32-5.37 and 5.42-5.48 (two m, 2H), 7.26-7.40 (m, 2H), 7.44-7.54 (m, 6H), 7.97-7.99 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.7, 17.9, 36.6, 43.1, 44.6, 81.6, 84.6, 116.9, 123.4, 124.5, 125.5, 125.7, 126.5, 127.6, 127.8, 128.0, 128.4, 128.7, 128.8, 128.9, 129.1, 129.6, 129.8, 130.0, 130.1, 131.4, 132.3, 132.5, 132.6, 133.1, 134.7, 134.9, 135.9, 139.0, 140.9, 142.0, 201.0, 201.8.

1,2-Cyclohexylidenedioxy-4-methyl-5-hexen-3-ol (**3i**): **(2*R*,3*R*,4*R*) isomer**: Colorless oil; $[\alpha]_D^{25}$ +46.2 (*c* 0.96, $CHCl_3$) (lit.[23o] $[\alpha]_D^{24}$ +45.9 (*c* 1.81, $CHCl_3$)); IR: 3486, 927 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.09 (d, *J* = 7.0 Hz, 3H), 1.38-1.40 (m, 2H), 1.55-1.61 (m, 8H), 2.26-2.31 (m, 2H), 3.27-3.30 (m, 1H), 3.70-3.74 (m, 1H), 3.95-4.00 (m, 1H), 4.06-4.15 (m, 1H), 5.02-5.09 (m, 2H), 5.69-5.76 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.7, 23.8, 24.0, 25.1, 34.9, 36.2, 42.3, 66.3, 74.6, 76.7, 109.6, 115.3, 140.5. **(2*R*,3*S*,4*R*) isomer**: Colorless oil; $[\alpha]_D^{25}$ +29.0 (*c* 1.04, $CHCl_3$) (lit.[23o] $[\alpha]_D^{24}$ +29.8 (*c* 1.40, $CHCl_3$)); IR: 3475, 926 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.10 (d, *J* = 6.5 Hz, 3H), 1.38-1.40 (m, 2H), 1.53-1.61 (m, 8H), 2.14 (broad s, 1H), 2.23-2.27 (m, 1H), 3.64-3.66 (m, 1H), 3.86-3.89 (m, 1H), 3.94-3.97 (m, 1H), 4.08-4.11 (m, 1H), 5.03-5.07 (m, 2H), 5.70-5.77 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.5, 23.8, 23.9, 25.1, 34.9, 36.2, 40.7, 64.1, 73.6, 76.3, 109.2, 115.4, 140.1. **(2*R*,3*S*,4*S*) isomer**: Colorless oil; $[\alpha]_D^{25}$ +2.2 (*c* 1.12, $CHCl_3$) (lit.[23o] $[\alpha]_D^{24}$ +2.4 (*c* 1.17, $CHCl_3$)); IR: 3475, 927 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.06 (d, *J* = 7.0 Hz, 3H), 1.36-1.38 (m, 2H), 1.54-1.58 (m, 8H), 2.08 (broad s, 1H), 2.37-2.41 (m, 1H), 3.55-3.57 (m, 1H), 3.85-3.88 (m, 1H), 3.94-3.98 (m, 1H), 4.00-4.04 (m, 1H), 5.07-5.11 (m, 2H), 5.79-5.87 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.5, 23.8, 23.9, 25.1, 34.9, 36.3, 40.3, 65.3, 74.8, 76.8, 109.2, 116.0, 139.3.

2-Methyl-1-(4-ethylphenyl)-but-3-en-1-ol (**3j**): Colorless liquid; IR: 3417, 914 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (*anti*) and 1.04 (*syn*) (two d, *J* = 6.5 Hz each, 3H), 1.25 (t, *J* = 7.5 Hz, 3H), 2.47-2.52 and 2.57-2.61 (m, 1H), 2.64-2.68 (m, 2H), 4.34 (*anti*) and 4.58 (*syn*) (two d, *J* = 8.0 and 6.0 Hz, 1H), 5.05-5.08 and 5.17-5.23 (two m, 2H), 5.73-5.87 (m, 1H), 7.17-7.27 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 14.2, 15.5, 16.5, 28.5, 44.6, 46.1, 77.8, 115.2, 116.4, 125.8, 126.5, 126.8, 127.5, 127.7, 130.3, 139.7,139.9, 140.5, 140.8, 143.3, 143.6. Anal. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.78; H, 9.64.

3-Methyldec-1-en-4-ol (**3k**):[23h] Colorless liquid; IR: 3383, 912 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.0 Hz, 3H), 1.03 and 1.04 (two d merged together, *J* = 5.0 Hz each, 3H), 1.25-1.35 (m, 8H), 1.48-1.57 (m merged with a broad s, 3H), 2.18-2.23 (*anti*) and 2.26-2.30 (*syn*) (two m, 1H), 3.37-3.41 (*anti*) and 3.48-3.50 (*syn*) (two m, 1H), 5.07-5.13 (m, 2H), 5.72-5.84 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 14.0, 16.3, 22.6, 25.7, 26.0, 29.4, 31.8, 34.0, 34.3, 43.4, 44.1, 74.7, 115.1, 116.1, 140.4, 141.1.

Isolation of [b2Brmim][Br]. In a separate experiment of allylation of **1a**, the reaction mixture was extracted with Et_2O to isolate **2a**, thoroughly washed with ice-cold $CHCl_3$ (3 × 5 mL), and the residue dried under vacuum to obtain a product, containing a ~1:1 mixture of both [bmim][Br] and [b2Brmim][Br]. Light red viscous oil; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.91-0.96 (m, 6H), 1.33-1.41 (m, 4H), 1.83-1.90 (m, 4H), 4.06 (s, 3H), 4.09 (s, 3H), 4.28-4.32 (m, 4H), 7.46 (t, *J* = 1.5 Hz, 1H), 7.57 (t, *J* = 1.5 Hz, 1H), 7.99 (d, *J* = 2 Hz, 1H), 8.16 (d, *J* = 2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.3, 13.4, 19.4, 19.5, 31.2, 32.1, 36.9, 37.0, 49.9, 122.1, 123.3, 123.7, 124.9, 128.1, 128.9, 130.9, 137.2.

Synthesis of *1-butyl-2-chloro-3-methylimidazolium chloride* [b2Clmim][Cl][20f]. To a cooled (0 °C) suspension of [bmim][Cl] (873 mg, 5 mmol) in THF (10 mL), dropwise addition of MeMgBr (3 M in Et_2O, 2 mL, 6 mmol), followed by stirring for another 30 min gave a clear solution. It was cooled to -78 °C, and a solution of hexachloroethane (1.66 g, 7 mmol) in THF (10 mL) was dropwise added to it. The reaction mixture was brought to room temperature and stirred further for 18 h. The upper layer was discarded, the bottom phase washed with dry THF (3 × 5 mL), and the residue dried under vacuum to yield pure [b2Clmim][Cl] as a light brown viscous liquid. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.74 (t, *J* = 7.5 Hz, 3H), 1.16-1.23 (m, 2H), 1.64-1.70 (m, 2H), 3.86 (s, 3H), 4.12 (t, *J* = 7.5 Hz, 2H), 7.83 (d, *J* = 1.5 Hz, 1H), 7.90 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.3, 19.3, 31.0, 37.2, 49.8, 123.1, 124.5, 131.0.

Keywords: Allylation, catalytic indium, ionic liquid, [bmim][Br]

[1] a) J. Otera, in *Modern Carbonyl Chemistry* (Eds.: S. E. Denmark, N. G. Almstead) Wiley, **2000**; b) In *Organic Reactions in Water: Principles, Strategies and Applications* (Ed.: U. M. Lindstrom), Blackwell publishing, USA, **2007**, and references cited therein; c) C. M. Gordon, C. Ritchiea, *Green Chem.* **2002**, *4*, 124-128; d) L. Tang, L. Ding, W-X, Chang, J. Li, *Tetrahedron Lett.* **2006**, 47, 303–306; e) R. Slaton, A. Petrone, R. Manchanayakage, *Tetrahedron Lett*. **2011**, 52, 5073–5076; f) D. Goswami, A. Chattopadhyay, A. Sharma, S. Chattopadhyay, *J. Org. Chem.* **2012**, *77*, 11064–11070; g) T. D. Haddad, L. C. Hirayama, B. Singaram, *J. Org. Chem.* **2010**, *75*, 642–649; h) D. Goswami, M. R. Koli, S. Chatterjee, S. Chattopadhyaya, A. Sharma, *Org. Biomol. Chem.* **2017**, *15*, 3756-3774; i) S. Li, J.-X. Wang, X. Wen, X. Ma, *Tetrahedron* **2011**, *67*, 849–855; j) Y. Zhang, X. Jia, J.-X. Wang, *Eur. J. Org. Chem.* **2009**, 2983–2986; k) Y. Z. Jin, N. Yasuda, H. Furuno, J. Inanaga, *Tetrahedron Lett*. **2003**, *44*, 8765–8768.

[2] a) Y. Yamamoto, N. Asao, *Chem. Rev*. **1993**, *93*, 2207-2293; b) J. A. Marshall, *Chem. Rev*. **1996**, *96*, 31–48; c) M. Yus, j. C. G. Gómez, F. Foubelo, *Chem. Rev.* **2011**, *111*, 7774–7854; d) D. Goswami, P. Sur, A. Chattopadhyay, A. Sharma, S. Chattopadhyay, *Synthesis* **2011**, *10*, 1626-1632; e) In *Recent Progress in the Chemical Synthesis of Antibiotics*, *Vol.* **1** (Eds.: G. Lukacs and M. Ohno) Springer: Berlin, **1990**.

[3] a) T. H. Chan, Y. Yang, *J. Am. Chem. Soc.* **1999**, *121*, 3228–3229; b) K. Koszinowski, *J. Am. Chem. Soc.* **2010**, *132*, 6032–6040.

[4] a) S. Wada, N. Hayashi, H. Suzuki, *Org. Biomol. Chem.* **2003**, *1*, 2160–2163; b) X. -H. Yi, J. X. Haberman, C. -J. Li, *Synth. Commun.* **1998**, *28*, 2999–3009.

[5] a) G.-W.Wang, *Chem. Soc. Rev.*, **2013**, *42*, 7668–7700; b) J.-L. Do, T. Fris□c□ić, *ACS Cent. Sci*. **2017**, *3*, 13–19.

[6] a) A. Romero, A. Santos, J. Tojo, A. Rodríguez, *J. Hazard. Mat*. **2008**, *151*, 268–273; b) K. Nishikawa, S. Wang, H. Katayanagi, S. Hayashi, H-o. Hamaguchi, Y. Koga, K. Tozaki, *J. Phys. Chem. B* **2007**, *111*, 4894–4900; (c) H-o. Hamaguchi, R. Ozawa, in *Advances in Chemical Physics*, (Eds. S. A. Rice) John Wiley & sons Inc., USA, **2005**.

[7] In *Thermodynamics, Solubility and Environmental Issues* (Ed.: T. M. Letcher), Elsevier Science, **2007**.

[8] a) J. Burgess, *Chem. Soc. Rev*. **1996,** 25, 85–92; b) D. Kumar, S. R. Vemula, N. Balasubramanian, G. R. Cook, *Acc. Chem. Res.* **2016**, *49*, 2169–2178, and the references cited

therein; c) J. Augé, N. Lubin-Germain, J. Uziel, *Synthesis* **2007**, 1739–1764.

[9] Some selected references: a) V. Nair, S. Ros, C. N. Jayan, B. S. Pillai, *Tetrahedron* **2004**, *60*, 1959–1982; b) T. H. Chan, M. C. Lee, *J. Org. Chem.* **1995**, *60*, 4228–4232; c) L. A. Paquette, T. M. Mitzel, *J. Am. Chem. Soc.* **1996**, *118*, 1931–1937; d) H. Dhanjee, T. G. Minehan, *Tetrahedron Lett.* **2010**, *51*, 5609–5612.

[10] a) For a review see: M. Yus, J. C. González-Gómez, F. Foubelo, *Chem. Rev.* **2011**, *111*, 7774–7854. b) H. –X. Huo, J. R. Duvall, M. –Y. Huang, R. Hong, *Org. Chem. Front.* **2014**, *1*, 303–320; c) J. Lu, M. –L. Hong, S. –J. Ji, Y. –C. Teo, T. –P. Loh, *Chem. Commun.* **2005**, 4217–4218; d) K. M. Waltz, J. Gavenonis, P. J. Walsh, *Angew. Chem., Int. Ed.* **2002**, *41*, 3697–3699; e) S. Yamasaki, K. Fujii, R. Wada, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **2002**, *124*, 6536–6537; f) M. Wadamoto, H. Yamamoto, *J. Am. Chem. Soc.* **2005**, *127*, 14556–14557; g) R. Wada, K. Oisaki, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **2004**, *126*, 8910–8911; h) J. J. Miller, M. S. Sigman, *J. Am. Chem. Soc.* **2007**, *129*, 2752–2753; i) U. Schneider, S. Kobayashi, *Angew. Chem., Int. Ed.* **2007**, *46*, 5909–5912; j) N. Selander, A. Kipke, S. Sebelius, K. J. Szabo´, *J. Am. Chem. Soc.* **2007**, *129*, 13723–13731; k) S. Lou, P. N. Moquist, S. E. Schaus, *J. Am. Chem. Soc.* **2006**, *128*, 12660–12661.

[11] a) U. Schneider, M. Ueno, S. Kobayashi, *J. Am. Chem. Soc.* **2008**, *130*, 13824–13825; b) M. D. Preite, H. A. Jorquera-Geroldi, A. Pérez-Carvajal, *ARKIVOC* **2011**, *vii*, 380-388; c) S. Araki, S. –J. Jin, Y. Idou, Y. Butsugan, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1736–1738; d) B. Qin, U. Schneider, *J. Am. Chem. Soc.* **2016**, *138*, 13119–13122.

[12] a) M. C. Law, T. W. Cheung, K. Y. Wong, T. H. Chan, *J. Org. Chem.* **2007**, *72*, 923–929; b) M. C. Law, K. Y. Wong, T. H. Chan, *Green Chem.* **2002**, *4*, 161–164; c) A. Bellomo, R. Daniellou, D. Plusquellec, *Tetrahedron Lett.* **2010**, *51*, 4934–4936; d) M. T. Reetz, H. Haning, *J. Organomet. Chem.* **1997**, *541*,117–120.

[13] a) H. M. Yau, S. T. Keaveney, B. J. Butler, E. E. L. Tanner, M. S. Guerry, S. R. D. George, M. H. Dunn, A. K. Croft, J. B. Harper, *Pure Appl. Chem.* **2013**, *85*, 1979–1990, and references cited therein; b) F. Hæffner, C. Sun, P. G. Williard, *J. Am. Chem. Soc.* **2000**, *122*, 12542–12546.

[14] S. Araki, H. Ito, Y. Butsugan, *J. Org. Chem.* **1988**, *53*, 1831–1833.

[15] M. C. Law, K. Y. Wong, T. H. Chan, *Green Chem.* **2002**, *4*, 328-330.

[16] W. Miao, L. W. Chung, Y. –D. Wu, T. H. Chan, *J. Am. Chem. Soc.* **2004**, *126*, 13326–13334.

[17] a) M. W. Hanna, A. L. Ashbaugh, *J. Phys. Chem.* **1964**, *68*, 811–816; b) S. Bhattacharya, S. K. Nayak, S. Chattopadhyay, M. Banerjee, A. K. Mukherjee, *J. Phys. Chem. A* **2001**, *105*, 9865–9868; c) S. Bhattacharya, K. Ghosh, A. K. Bauri, S. Chattopadhyay, M. Banerjee, *J. Mol. Struct.* **2006**, *784*, 124–137; d) D. S. Choi, D. H. Kim, U. S. Shin, R. R. Deshmukh, S.-g. Lee, C. E. Song, *Chem. Commun.* **2007**, 3467–3469.

[18] a) T. H. Chan, C. J. Li, M. C. Lee, Z. Y. Wei, *Can. J. Chem.* **1994**, *72*, 1181–1192; b) H. Wang, S. Gu, Y. Bai, S. Chen, N. Zhu, C. Wu, F. Wu, *J. Mater. Chem. A* **2015**, *3*, 22677–22686; c) S. Kazemiabnavi, Z. Zhang, K. Thornton, S. Banerjee, *J. Phys. Chem. B* **2016**, *120*, 5691–5702.

[19] The moisture content in [bmim][Br] was found to be 1200 ppm, as measured by Karl-Fisher titration.

[20] a) A. K. L. Yuen, A. F. Masters, T. Maschmeyer, *Catal. Today* **2013**, *200*, 9–16; b) T. L. Amyes, S. D. Diver, J. P. Richard, F. M. Rivas, K. Toth, *J. Am. Chem. Soc.* **2004**, *126*, 4366–4374; c) R. A. Olofson, W. R. Thompson, J. S. Michelman, *J. Am. Chem. Soc.* **1964**, *86*, 1865–1866; d) A. Poater, F. Ragone, S. Guidice, C. Costabile, R. Dorta, S. P. Nolan, L. Cavallo, *Organometallics* **2008**, *27*, 2679–2681; e) L. Zhao, C. Zhang, L. Zhuo, Y. Zhang, J. Y. Ying, *J. Am. Chem. Soc.* **2008**, *130*, 12586–12587, and references cited therein; f) R. R. Hawker, J. Panchompoo, L. Aldous, J. B. Harper, *ChemPlusChem* **2016**, *81*, 574–583.

[21] B. C. Ranu, S. Banerjee, *Org. Lett.* **2005**, *7*, 3049–3052.

[22] M. L. Cole, A. J. Davies, C. Jones, *J. Chem. Soc., Dalton Trans.*, **2001**, 2451–2452.

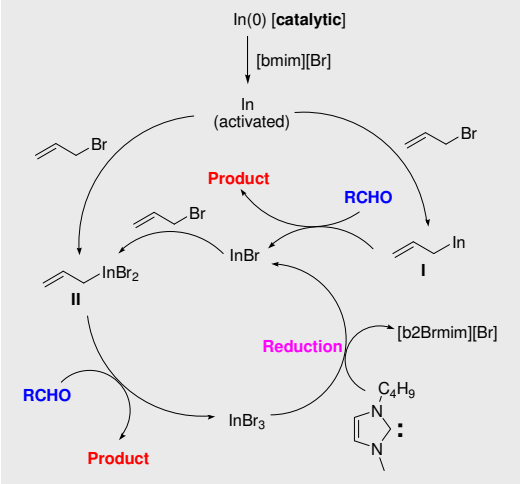
[23] a) L. C. Almenara, C. R. Escrich, L. O. Planes, M. A. Pericàs, *ACS Catal.* **2016**, *6*, 7647–7651; b) J. Chen, D. Liu, D. Fan, Y. Liu, W. Zhang, *Tetrahedron* **2013**, *69*, 8161–8168; c) G-l. Li, G. Zhao, *J. Org. Chem.* **2005**, *70*, 4272–4278; d) P. K. Kalita, S. K. Borthakur, R. Das, C. J. Choudhury, *Syn. Commun.* **2015**, *45*, 2444–2453; e) V. Nair, C. N. Jayan, S. Ros, *Tetrahedron* **2001**, *57*, 9453–9459; f) M. T. Reetz, J. Westermann, R. Steinbach, B. Wenderoth, R. Peter, R. Ostarek, S. Maus, *Chem. Ber.* **1985**, *118*, 1421–1440; g) A. Chattopadhyay, V. R. Mamdapur, *J. Org. Chem.* **1995**, *60*, 585–587; h) Y. Zhou, Z. Zha, Y. Zhang, Z. Wang, *ARKIVOC*, **2008**, *xi*, 142–153; i) W. R. Roush, K. Ando, D. B. Powers, A. D. Palkowitz, R. L. Halterman, *J. Am. Chem. Soc.* **1990**, *112*, 6339; j) K. Takaki, T. Kusudo, S. Uebori, T. Nishiyama, T. Kamata, M. Yokoyama, K. Takehira, Y. Makioka, Y. Fujiwara, *J. Org. Chem.* **1998**, *63*, 4299–4304; k) R.

Wada, K. Oisaki, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **2004**, *126*, 8910–8911; l) M. Kimura, M. Shimizu, S. Tanakab, Y. Tamaru, *Tetrahedron* **2005**, *61*, 3709–3718; m) A. Takuwa, Y. Nishigaichi, T. Yamaoka, K. Lihama, *J. Chem. Soc., Chem. Commun.* **1991**, 1359–1360; n) R. Lebeuf, K. Hirano, F. Glorius *Org. Lett.* **2008**, *10*, 4243–4246; o) D. Goswami, A. Chattopadhyay, S. Chattopadhyay, *Tetrahedron:Asymmetry* **2009**, *20*, 1957–1961.

Table of Contents

FULL PAPER

Barbier type allylation of aldehydes/ketones can be carried out with both unsubstituted and γ-substituted allyl bromides using only a catalytic amount (0.1 equiv.) of In-metal in [bmim][Br].



Catalytic In (10 mol%) , High yield, Reusable

Papiya Dey, Mrunesh Koli, Dibakar Goswami, Anubha Sharma and Subrata Chattopadhyay**

Page No. – Page No.

[bmim][Br] as an Inexpensive and Efficient Medium for the Barbier-type Allylations using a Catalytic Amount of In: Mechanistic Studies