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Indium-assisted aluminium-based stereoselective allylation of prostereogenic α, α-disubstituted cycloalkanones and imines

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Cite this: DOI: 10.1039/xoxxoooooox

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

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Utility of catalytic amount of $InCl_3$ in combination with Al^0 for the allylation of a variety of prostereogenic α, α-disubstituted (hindered) cycloalkanones, 1,2-dione-based systems and various imino systems (C=N functional groups) is reported. The stereoselective $InCl_3$-catalyzed Al-based allylation of various 2-substituted-2-carbethoxycycloalkanones gave the corresponding products with moderate to excellent diastereoselectivity. The allylation and propargylation of imines including α-imino esters using catalytic amount of $InCl_3$ in combination with Al^0 afforded the corresponding allylated and propargylated compounds in moderate to good yields. In the case of addition of γ-substituted allylic halides with imino compounds, low to very good diastereoselectivity was obtained. The allylation of chiral *N*-*tert*-butylsulfinyl imine systems gave the corresponding products in moderate yields with good to excellent diastereoselectivity.

Introduction

The addition of organometallic reagents to carbonyl (C=O) and imino (C=N) functional groups is one of the most important types of organometallic reactions. Especially, the addition of the allylmetals to carbonyl (C=O) and imino (C=N) functional groups considered as an imperative C-C bond forming protocol, which is widely used for assembling functionalized acyclic- or cyclic- homoallylic alcohols/amines having one or more stereocenters with high degree of stereo- and regiocontrol.[1] Notably, the allylation step considered to exhibit immense scope in multistep synthesis; after the allylation reaction, the olefin moiety present in the product can be subjected to a wide range of functional group transformations.

A variety of allylmetal reagents prepared using metals such as Li, Mg, Sn, Zn, Mn, Pb, Ce, Cu, Ti and B, etc have been very well utilized and thoroughly documented for performing, typically, the Grignard-type allylation of the carbonyl (C=O) and imino (C=N) functional groups.[1,2] On the other hand, in recent years, the Barbier-type addition reaction[3-5] of allylmetals involving the some of the above mentioned metals along with other metals[6-11] such as In, Ga and Bi, etc, to carbonyl (C=O) and imino (C=N) functional groups has been widely recognized. This protocol has a benefit as the prior preparation of allylmetal reagents is not necessary and the allylation reaction can be achieved by directly reacting the carbonyl compound or imine, metal powder and allylic halide. Notably, since the report by Araki in 1988,[6a] the indium-based Barbier-type addition of allylic reagents to carbonyl (C=O) and imino (C=N) systems frequently offered very high stereoselectivity and has been applied for the synthesis of a variety of functionalized molecules containing one or more stereocenters.[1,2,6] Generally, stoichiometric amount of allylmetal reagents or metals (e.g. In, Ga, and Bi, etc) are required for performing the Grignard or Barbier-type of allylation reactions.[1-11]

Apart from the utility of indium in organic synthesis, there has been an increased consumption of indium-based materials in information technology industries which are involved in developing liquid crystal display (LCD) and television (TV)

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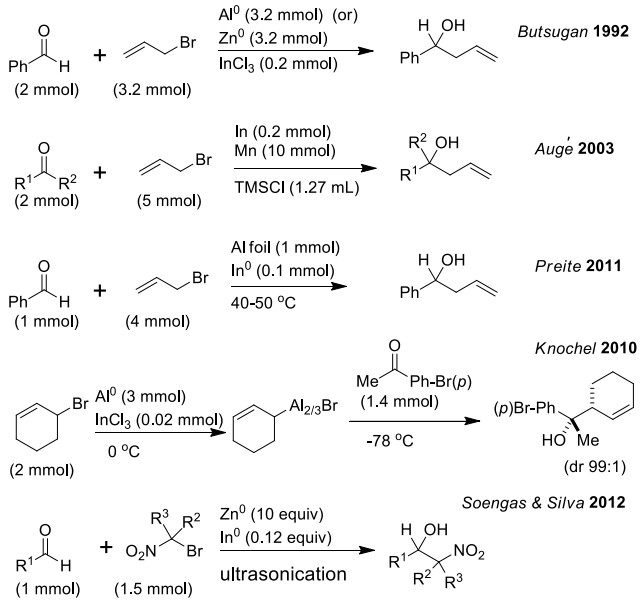
† Electronic Supplementary Information (ESI) available: [Copies of NMR spectra]. See DOI: 10.1039/b000000x/

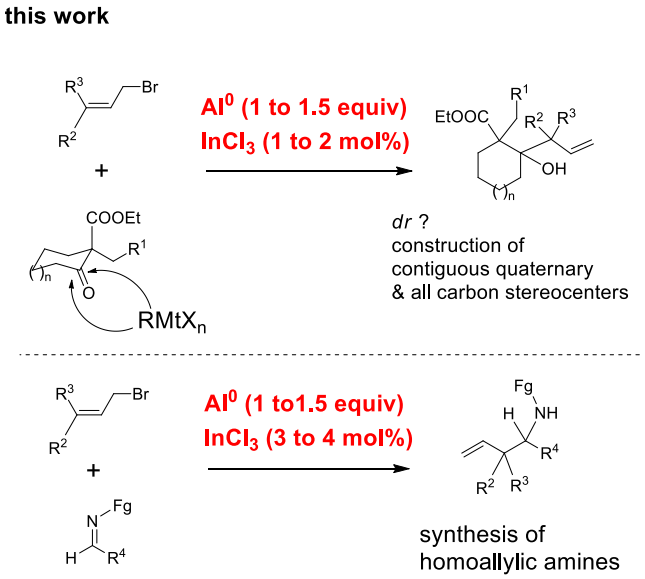
screens, solar energy technology and semiconductors, etc. Due to this reason the cost of indium metal has relatively increased.

In view of the above mentioned points, there is a need for finding alternative, especially, for In and Ga; and if the In-based organic transformations can be performed using catalytic amount of In, then the practicality and adaptability of indium metal in organic synthesis could be remarkably increased.[12] The use of catalytic amount of indium in combination with other metals such as Al or Zn, etc could be an alternative strategy[12,13] and notably, the aluminium metal[14] is relatively very cheap and considered as less toxic when compared to other metals such as In or Ga. Along this line, in recent years, there have been only some remarkable reports dealing with the allylation of carbonyl compounds using catalytic amount of In^0 or In(III) salts in combination with Al or Zn or other metals.[12] Butsugan, Hirashita, Preite and Knochel, Augé, Takai groups have shown the allylation of carbonyl compounds using catalytic amount of In^0 or In(III) salts in combination with Al and other metals (Scheme 1).[12]



Scheme 1 Existing literature reports dealing with the allylation of carbonyl compounds using catalytic amount of In^0 or In(III) salts in combination with Al or Zn or other metals.

Though the aluminium metal belongs to the same group as indium and gallium, however, except the reports by Knochel group on the use of $InCl_3$ in combination with Al, the direct use of Al^0 powder for the stereoselective allylation of carbonyl compounds affording more than one stereocenter has not been considerably explored under Barbier-type reaction.[12-14] Further, to the best of our knowledge the allylation of imino (C=N bond systems) functional groups has not been reported using indium in combination with aluminium metal powder. In continuation of our interest to explore the indium-based stereoselective allylation of carbonyl (C=O) and imino (C=N) functional groups, herein we report our efforts on employing $InCl_3$/Al as an economically alternative bimetallic system for the stereoselective allylation of prostereogenic α, α- disubstituted cycloalkanones[15,16] and various imino compounds (C=N bond systems).[17,18]



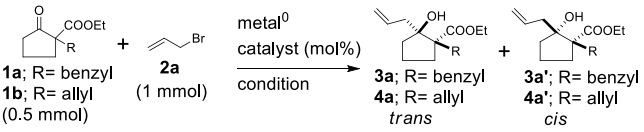
Scheme 2 Theme of this work; $InCl_3$/Al system for the stereoselective allylation of prostereogenic α, α-disubstituted cycloalkanones and imino compounds (C=N systems).

Results and Discussion

Initially, we envisaged to investigate the utility of catalytic amount of $InCl_3$ in combination with Al for the diastereofacial selective allylation of prostereogenic α, α- disubstituted (hindered) cycloalkanones and the stereoselective construction of a stereoarray having consecutively attached tertiary carbinol- and an all carbon-based stereocenters in functionalized carbocyclic compounds.[15,16] In this regard, we performed the optimization reactions using the substrate 2-benzyl-2-carbethoxycyclopentanone (**1a**) or 2-allyl-2-carbethoxycyclopentanone (**1b**), allyl bromide, aluminium metal powder and a catalyst under the Barbier-type reaction conditions (Table 1). The Barbier-type allylation of the substrate 2-benzyl-2-carbethoxycyclopentanone (**1a**) or 2-allyl-2-carbethoxycyclopentanone (**1b**) using Al^0 powder in the absence of any catalyst furnished the respective products **3a** and **4a** in 65 and 20% yields (entries 1 and 2, Table 1). However, the Barbier-type allylation of the substrate **1a** with $InCl_3$ (40 mol%) in the absence of Al^0 powder did not furnish any product (entry 3, Table 1). The

Barbier-type allylation of the substrates **1a** or **1b** using Al^0 powder (0.5-1 mmol) in the presence of catalytic amount of $InCl_3$ or $InBr_3$ (5 or 10 mol%) in anhydrous THF successfully furnished the product **3a** or **4a** (*dr* 98:2, *trans* isomer) in 95% yield, respectively (entries 4-6, Table 1).

Table 1 $InCl_3$/Al-based Barbier-type allylation of substrates **1a**/**1b** and optimization of reaction conditions.



entry	R	$metal^0$ (mmol)	catalyst mol%	solvent (mL)	temp (°C)	t (h)	yield (%) (*dr*)
1	benzyl	Al (0.5)	nil	THF (1.5)	rt	10	65 (98:2)
2	allyl	Al (1)	nil	THF (1.5)	rt	12	20 (N.D.)
3	benzyl	nil	$InCl_3$ (40)	THF (1.5)	rt	10	0 (–)
4	benzyl	Al (0.5)	$InCl_3$ (10)	THF (1.5)	rt	12	95 (98:2)
5	allyl	Al (0.5)	$InCl_3$ (5)	THF (1.5)	rt	15	95 (98:2)
6	benzyl	Al (1)	$InBr_3$ (10)	THF (1.5)	rt	4	95 (98:2)
7	allyl	Al (0.55)	$InCl_3$ (2)	THF (1.5)	rt	1	95 (98:2)
8	allyl	Al (0.5)	$InCl_3$ (2)	DCM (1.5)	rt	2	91 (98:2)
9	allyl	Al (0.5)	$InCl_3$ (3.5)	DMF (1.5)	rt	1.5	<5 (–)
10	allyl	Al (0.5)	$InCl_3$ (2)	MeCN (1.5)	rt	7	90 (98:2)
11	allyl	Al (0.75)	$InCl_3$ (5)	THF (3) / H_2O (1)	rt	9	0 (–)
12	allyl	Al (1)	$SnCl_2$ (5)	THF (1.5)	rt	12	0 (–)
13	allyl	Al (0.75)	$ZnCl_2$ (20)	THF (1.5)	rt	7	0 (–)
14	allyl	Al (0.55)	$Ga(ClO_4)$ (5)	THF (1.5)	rt	2	0 (–)
15	allyl	Al (0.55)	$In(OTf)_3$ (1)	THF (1.5)	rt	1	95 (98:2)
16	allyl	Al (0.55)	$In(OAc)_3$ (1)	THF (1.5)	rt	2	95 (98:2)
17	allyl	Al (0.55)	$BiCl_3$ (8)	THF (1.5)	rt	26	30 (N.D.)
18	benzyl	Al (1)	In (10)	THF (1.5)	rt	9	95 (98:2)
19	allyl	Al (0.5)	Bi (20)	THF (1.5)	rt	7	85 (98:2)
20	allyl	Al (1)	Zn (10)	THF (1.5)	rt	8	40 (N.D.)
21	benzyl	Al (1)	Sn (10)	THF (1.5)	rt	12	0 (–)

All the reactions were carried out under Barbier-type reaction condition. The substrate **1a** or **1b** was treated with allyl bromide, Al^0 and catalytic amount of $InCl_3$ or In^0 or other catalyst in one-pot. N.D. = Not Determined.

Subsequently, the Barbier-type allylation of **1b** using Al^0 powder (0.55 mmol) in the presence of just 2 mol% of $InCl_3$ in anhydrous THF gave the product **4a** (*dr* 98:2, *trans* isomer) in 95% yield (entry 7, Table 1). Further, the allylation of **1b** in other solvents such as DCM or DMF or MeCN gave the product **4a** (*dr* 98:2, *trans* isomer) in 91, <5, 90% yields, respectively (entries 8-10, Table 1). The allylation of **1b** using Al^0 powder in the presence of catalytic amount of $InCl_3$ in THF-water mixture did not afford any product (entries 11, Table 1).

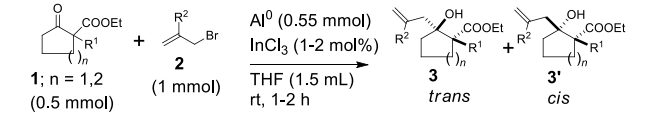
Then, we tried to use different catalysts instead of $InCl_3$ for the Barbier-type allylation of **1b**. We found that the allylation of **1b** using Al^0 powder in the presence of catalytic amount $SnCl_2$ or $ZnCl_2$ or $GaClO_4$ was ineffective (entries 12-14, Table 1). Notably, the allylation of **1b** underwent smoothly when we used Al^0 powder in the presence of catalytic amount $In(OTf)_3$ or $In(OAc)_3$ and furnished the product **4a** (*dr* 98:2, *trans* isomer) in 95% yield (entries 15 and 16, Table 1). When we used $BiCl_3$ (8 mol%) as a catalyst, the product **4a** was obtained in 30% yield (entry 17, Table 1).

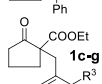
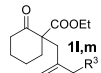
Subsequently, we carried out the Barbier-type allylation of **1a** using Al^0 powder (1 mmol) in the presence of catalytic amount of In^0 powder (10 mol%) in anhydrous THF furnished the product **3a** (95%, *dr* 98:2, *trans* isomer) (entry 18, Table 1). Similarly, the allylation of the substrate **1b** using Al^0 powder (0.5-1 mmol) in the presence of catalytic amount of other metals such as Bi^0 or Zn^0 (10-20 mol%) afforded the product **4a** in 85 and 40% yields, respectively (entries 19 and 20, Table 1). The allylation of **1a** using catalytic amount of Sn^0 powder along with Al^0 powder did not furnish the product **3a** (entry 21, Table 1).

Further, the scope and generality of this allylation protocol using catalytic amount of $InCl_3$ in combination with Al^0 powder was tested with a variety of prostereogenic α, α- disubstituted (hindered) cycloalkanones and the construction of functionalized carbocycles having consecutively attached tertiary carbinol- and an all carbon-based stereocenters is shown in the Table 2. Under the optimized reaction conditions, we carried out the Barbier-type allylation of various prostereogenic 2-benzyl-2-carbethoxycyclopentanones **1a-h** and 2-alkyl-2-carbethoxycyclopentanones **1i,j** with **2a** or **2b** using catalytic amount of $InCl_3$ (1-2 mol%) in combination with Al^0 powder (0.55 mmol) in anhydrous THF. These reactions smoothly gave the corresponding products **3a-i** (*trans* isomers) in 66-95% yields (entries 1-9, Table 2) with very high diastereoselectivity (*dr* 98:2). The Barbier-type allylation of 2-alkyl/aryl-2-carbethoxycyclohexanones **1k-n** using the catalytic amount of $InCl_3$ (1-2 mol%) and Al^0 powder (0.55 mmol) gave the respective products **3j-m** with relatively low diastereoselectivity (entries 10-13, Table 2).

Next, the allylation of the substrate **1b** with 2,3-dibromoprop-1-ene (**2c**) failed to give the expected product **3n** (entry 14). The allylation of 2-allyl-2-carbethoxycyclopentanone (**1b**) and ethyl 2-acetyl-2-benzylpent-4-enoate (**1o**) gave the respective allylated products **4a** (96%, *dr* 98: 2) and **3o** (81%, *dr* 55:45) (entries 15 and 16, Table 2). Consequently, the allylation of ethyl 3-allyl-1-benzyl-4-oxopiperidine-3-carboxylate (**1p**) furnished the piperidine derivative **3p** in 55% yield (*dr* 60:40, entry 17, Table 2).

Table 2 Indium-catalyzed Al-based allylation of α, α- disubstituted cycloalkanones and the construction of functionalized carbocycles.[a]



entry	ketone	allyl bromide	product	yield (%) (*dr*)
1				**3a**: 95 (98:2)
2				**3b**; R^3,R^4=H, R^5=Br, 92 (98:2)
3				**3c**; R^4,R^5=H, R^3=F, 85 (98:2)
4				**3d**; R^3,R^4=H, R^5=Me, 87 (98:2)
5				**3e**; R^3,R^4=H, R^5=NO_2, 76 (98:2)
6				**3f**; R^4,R^5=Cl, R^3=H, 78 (98:2)
7				**3g**; R^3,R^5=Cl, R^4=H, 66 (98:2)
8				**3h**: 78 (98:2)
9				**3i**: 87 (98:2)
10				**3j**: 89 (60:40)
11				**3k**; R^3,R^4=H, R^5=Br, 91 (56:44)
12				**3l**; R^3,R^5=H, R^4=Cl, 89 (60:40)
13				**3m**: 60 (60:40)
14				**3n**: 0
15				**4a**: 96 (98:2)
16				**3o**: 81 (55:45)
17				**3p**: 55 (60:40)
18				**3q**: 87 (95:5)
19[b]				**3a**: 90 (98:2)
20[c]				**3b**; R^3,R^4=H, R^5=Br, 90 (98:2)

[a] All the reactions were carried out under Barbier-type reaction condition. The substrate **1** was treated with allyl bromide, Al^0 and catalytic amount of $InCl_3$ in one pot. N.D. = Not Determined. [b] The reaction was performed using Al^0 (0.55 mmol) and $InCl_3$ (3 mol%) at 35 °C for 15 h. [c] The reaction was performed using Al^0 (0.55 mmol) and $InCl_3$ (3 mol%) at 45 °C for 7 h.

The allylation of a relatively hindered cyclopentanone system ethyl 1-benzhydryl-2-oxocyclopentanecarboxylate (**1q**) was performed and the product **3q** was obtained in 87% yield (*dr* 95:5, entry 18). In the cases of the substrates **1k-p**, the corresponding products **3j-m** and **3o,p** were obtained with low diastereoselectivity than the products **3a-i**, **4a**, and **3q**; this may be due to the involvement of less rigid transition state[16c] under the experimental condition. The Barbier-type allylation of the substrates **1a** and **1c** using allyl chloride, aluminium metal powder and catalytic amount $InCl_3$ (3 mol%) in THF at 35 °C and 45 °C underwent smoothly and afforded the products **3a** and **3b** in 90% yield, respectively (entries 19 and 20, Table 2)

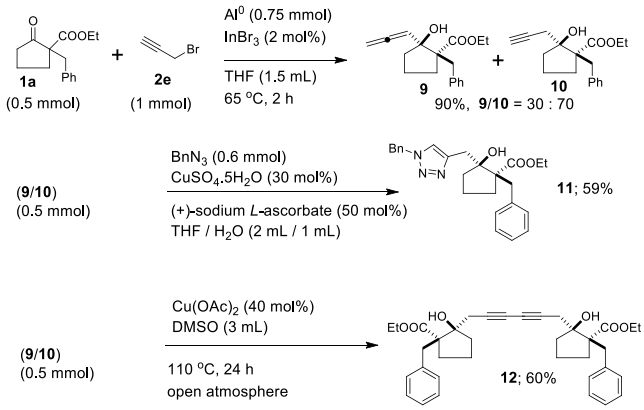
Scheme 3 Indium-catalyzed allylation of ethyl 1-(2-ethoxy-2-oxoethyl)-2-oxocycloalkanecarboxylates **1r,s**. All the reactions were carried out under the Barbier-type reaction condition. The substrate **1r** or **1s** was treated with allyl bromide, Al^0 powder and catalytic amount of $InCl_3$ in one-pot.

Scheme 4 $InCl_3$-catalyzed Al^0-based allylation of 1,2-diones. In all the reactions, the allylmetal was first prepared separately to which the dione **7a** or **7b** was added.

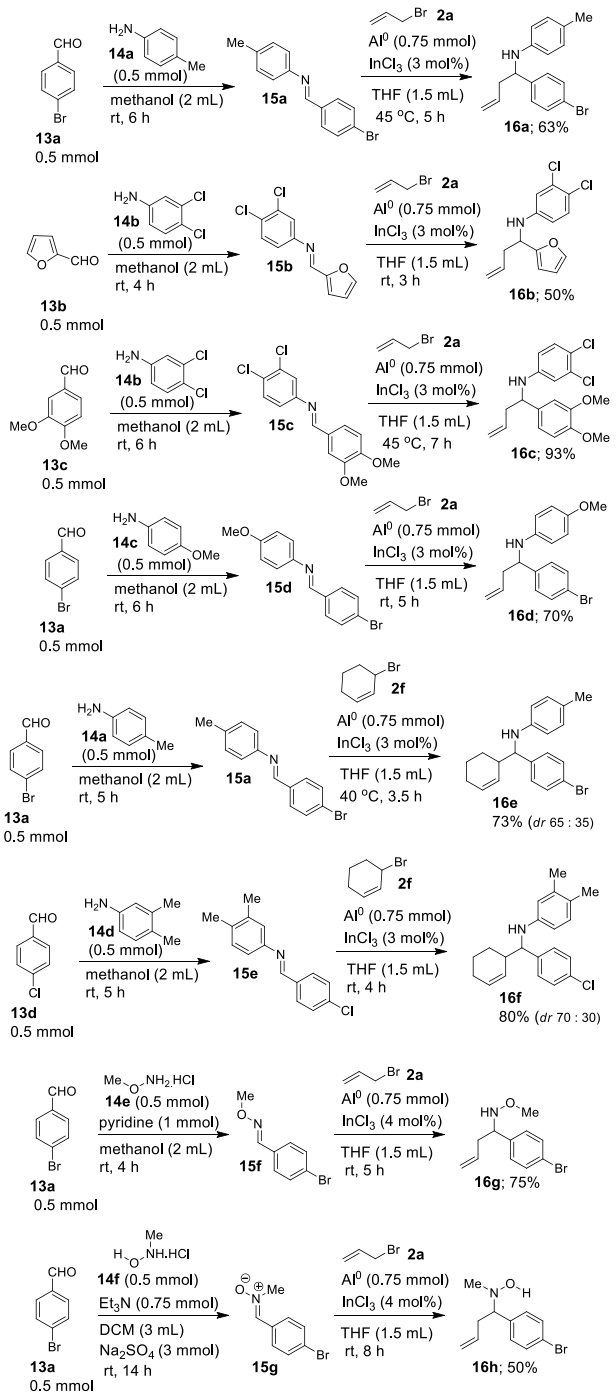
Next, we performed the allylation of prostereogenic ethyl 1-(2-ethoxy-2-oxoethyl)-2-oxocycloalkanecarboxylates, **1r** and **1s** with allyl bromide by using catalytic amount of $InCl_3$ in combination with Al^0 powder in anhydrous THF. The allylation of **1r** and **1s** gave both the allylation products **5a,b** as well as the bicyclic lactones **6a,b**, respectively (eq 1 and 2, Scheme 3).[18a] In these reactions, the bicyclic lactones **6a** (65%) and **6b** (42%) were obtained because the substrates **1r** and **1s** are having an ester group at an appropriate distance and thereby underwent *in situ* lactonization[18a] during the allylation reaction under the experimental condition. In order to increase the yield of the bicyclic lactone **6b**, we used catalytic amount of In^0 instead of $InCl_3$, however, there was no improvement in the yield of the lactone **6b** (eq 3, Scheme 3).

Subsequently, the allylation reactions of the dicarbonyl compound **7a** (*N*-methyl isatin) with allyl bromide and cinnamyl bromide using catalytic amount of $InCl_3$ in combination with Al^0 powder were performed. In these reactions the oxindole products **8a** and **8b** were obtained in 50 and 55% yields, respectively (Scheme 4). The cinnamylation of **7a** afforded the product **8b** with good diastereoselectivity (*dr* 90:10, Scheme 4). The allylation of the dicarbonyl compound **7b** with allyl bromide using catalytic amount of $InCl_3$ in combination with Al^0 gave the bis-allylated compound **8c** (98%, Scheme 4).

Additionally, the scope of this protocol was tested for the propargylation of the substrate **1a** (Scheme 5). The propargylation of cyclic ketone **1a** afforded the allene product **9** and the propargylated product **10** in 90% (combined yield of **9**/**10**). Our efforts to separate these two products were not successful and the products **9**/**10** were isolated as a mixture of compounds. Further, we decided to perform the click reaction[19c] and Glaser-Eglinton-Hay sp-sp coupling[19d] with a mixture of compounds **9**/**10**. Accordingly, the corresponding products **11** (59% yield) and **12** (60% yield) were isolated in pure form after the column chromatography purification (Scheme 5).



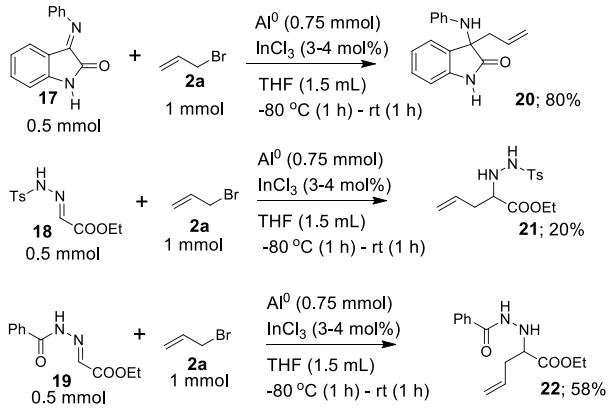
Scheme 5 $InCl_3/Al^0$-based propargylation of **1a** followed by click and Glaser-Eglinton-Hay reactions. The substrate **1a** was treated with propargyl bromide, Al^0 powder and catalytic amount of $InCl_3$ in one-pot.



Scheme 6 $InCl_3$-catalyzed Al^0-based allylation of C=N bond systems **15a-g**. In all the reactions imino compounds **15a-g** and allylmetal were prepared separately and then the corresponding imino compounds **15a-g** were added to the round bottom flask containing the allylmetal reagent obtained from **2a** or **2f**.

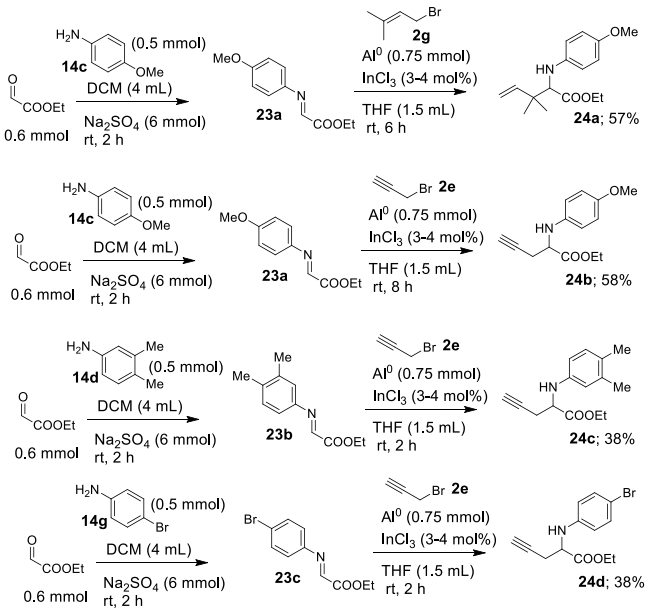
Next, we focused our attention to investigate the C-C bond forming protocol and the synthesis of homoallylic amines via the allylation of imino (C=N) functional groups using catalytic amount of $InCl_3$ in combination with Al^0 metal powder. There

have been some exceptional literature reports on the indium-catalyzed allylation of carbonyl compounds,[12] however, to the best of our knowledge, the allylation of imino (C=N bond systems) functionality has not been explored using catalytic amount of indium in combination with a cheap metal such as aluminium.[6,17,18] To start with, we prepared a series of C=N bond systems, such as the imine compounds **15a-e**, oxime **15f** and nitrone **15g** (Scheme 6). The corresponding imino compounds **15a-g** were added to a THF solution of corresponding allylmetal reagents which were prepared separately from allyl bromide (**2a**) or 3-bromocyclohex-1-ene (**2f**), catalytic amount of $InCl_3$ (3-4 mol%) and Al^0 metal powder (0.75 mmol). All these reactions successfully afforded the respective homoallylic amines **16a-h** in 50-93% yields. In the case of the allylation of substrates **15a** and **15e** with 3-bromocyclohex-1-ene (**2f**), the corresponding products **16e** and **16f** were obtained with moderate diastereoselectivity under the experimental condition.



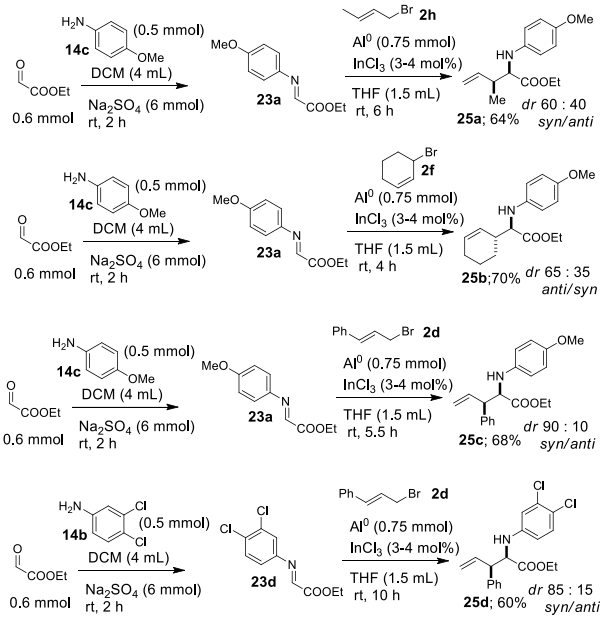
Scheme 7 $InCl_3$-catalyzed Al^0-based allylation of C=N bond systems **17-19**. In all the reactions the imino compounds **17-19** and allylmetals were separately prepared and then the corresponding imino compounds **17-19** were added to the round bottom flask containing the allylmetal reagent.

Successively, we prepared the next series of C=N bond systems such as the isatin-derived imine ((*E*)-3-(phenylimino)indolin-2-one) (**17**) and ethyl glyoxalate-derived imino systems (*E*)-ethyl 2-(2-tosylhydrazono)acetate (**18**) and (*E*)-ethyl 2-(2-benzoylhydrazono)acetate (**19**) (Scheme 7). Then, we added imino compounds **17-19** to a THF solution of allylmetal reagent prepared separately from allyl bromide (**2a**), $InCl_3$ (3-4 mol%) and Al^0 metal powder (0.75 mmol). The allylation of **17** afforded the product 3-allyl-3-(phenylamino)indolin-2-one (**20**) in 80% yield. The product ethyl 2-(2-tosylhydrazinyl)pent-4-enoate (**21**) was obtained in only 20% yield. The allylation of *N*-acylhdrazono ester **19** gave the product ethyl 2-(2-benzoylhydrazinyl)pent-4-enoate (**22**) in 58% yield (Scheme 7). Along this line, we also carried out the indium-catalyzed aluminium-based prenylation of *N*-aryl α-imino ester **23a** and propargylation of a series of *N*-aryl α-imino esters **23a-c** (Scheme 8). These reactions led to the synthesis of γ,δ-unsaturated β,β′-dimethyl *N*-aryl α-amino acid derivative **24a** (57%) and a variety of propargylated products, ethyl 2-((aryl)amino)pent-4-ynoates **24b-d** in 38-58% yields, respectively (Scheme 8).



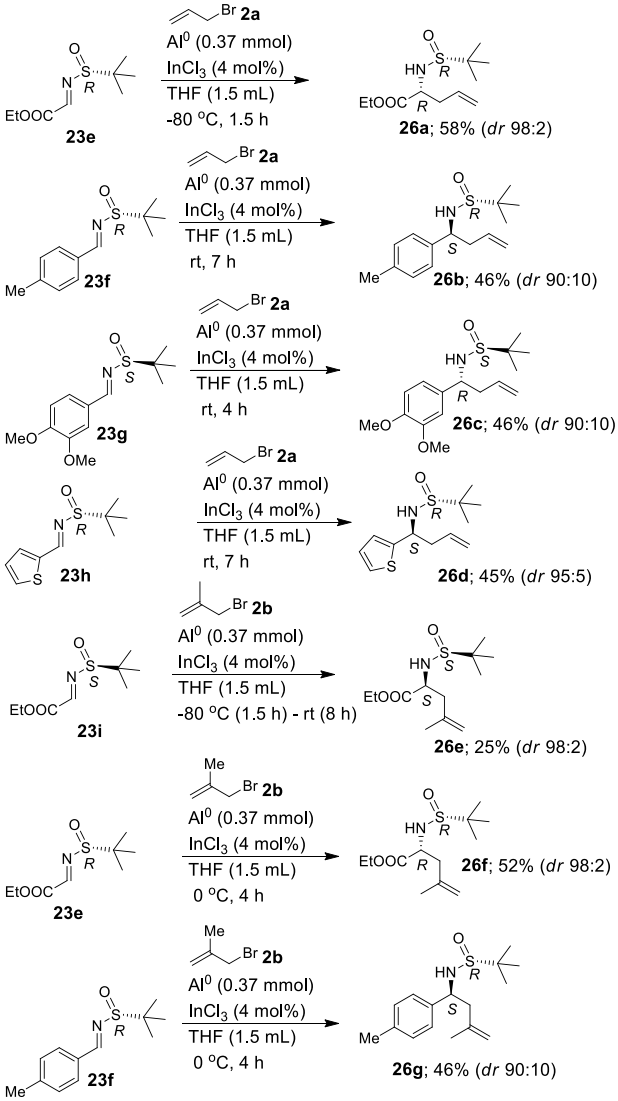
Scheme 8 $InCl_3$-catalyzed Al^0-based propargylation of C=N bond systems. The imino compounds **23a-c** were prepared separately. In the reactions involving the formation of products **24a,b**, imine **23a** was treated with **2g** or **2e**, Al^0 and $InCl_3$ in one-pot. In the reactions involving the formation of products **24c,d**, imines **23b,c** were added to propargylmetal reagents prepared separately.

Then, we attempted the addition of γ-substituted allylic halides to *N*-aryl α-imino esters and the construction of γ,δ-unsaturated β,β′-disubstituted *N*-aryl α-amino acid derivatives bearing two contiguous stereocenters (Scheme 9). The addition of crotyl bromide (**2h**) or cyclohexenyl bromide (**2f**) to α-imino ester **23a** in the presence of $InCl_3$ and Al^0 powder in one-pot gave the respective products, γ,δ-unsaturated β,β′-disubstituted *N*-aryl α-amino acid derivatives **25a** (64%, *dr* 60:40) and **25b** (70%, *dr* 65:35). In these cases, the corresponding products **25a** and **25b** were obtained with low diastereoselectivity and this may be due to the involvement of less rigid transition state (TS) under the present experimental condition involving the combination of $InCl_3$ and Al^0. However, the addition of α-imino esters **23a,d** to cinnamyl bromide (**2d**), $InCl_3$ and Al^0 powder in one-pot gave the respective γ,δ-unsaturated β,β′-disubstituted *N*-aryl α-amino acid derivatives **25c** (68%, *dr* 90:10) and **25d** (60%, *dr* 85:15) with very good diastereoselectivity (Scheme 9).

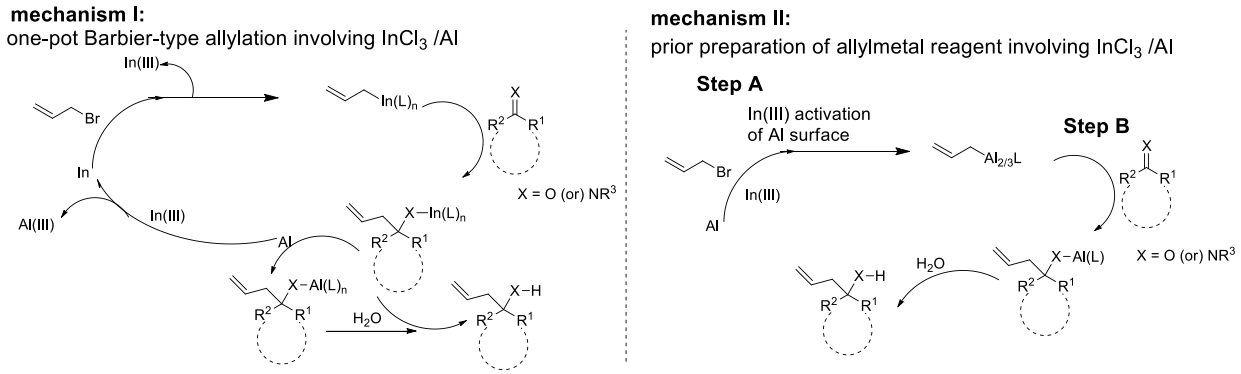


Scheme 9 $InCl_3$-catalyzed Al^0-based stereoselective addition to *N*-aryl α-imino ester **23a,d**. The α-imino esters **23a,d**, were prepared separately and then the corresponding α-imino esters **23a,d** were treated with **2d** or **2f** or **2h**, Al^0 and $InCl_3$ in one-pot.

Additionally, we also tested the combination of $InCl_3$ and Al^0 for the stereoselective addition of allylmetals to a series of chiral *N*-*tert*-butylsulfinyl imino systems **23e-i**, prepared from the condensation of ethyl glyoxal or aromatic aldehydes and (*R*)-*N*-*tert*-butylsulfinyl amine or (*S*)-*N*-*tert*-butylsulfinyl amine. The addition reaction of various chiral imino systems including imino esters **23e-i** to a THF solution of allylmetal reagent prepared separately from allyl bromide and $InCl_3/Al^0$ successfully furnished the respective γ,δ-unsaturated *N*-*tert*-butylsulfinyl α-amino acid derivatives **26a,e,f** and homoallylic amines **26b-d,g** with very high diastereoselectivity (Scheme 10).



Scheme 10 In the reaction involving the preparation of **26a**, the reaction was performed in one-pot by treating **23e** (0.25 mmol), $InCl_3/Al^0$ and **2a** (2 equiv). In the reactions involving the preparation of **26b-g**, the reactions were performed by treating **23e-i** (0.25 mmol) with a THF solution of allylmetal reagent prepared separately.



Scheme 11 Plausible mechanism for the indium-catalyzed Al-based addition to carbonyl- and imino compounds.[12,13,19]

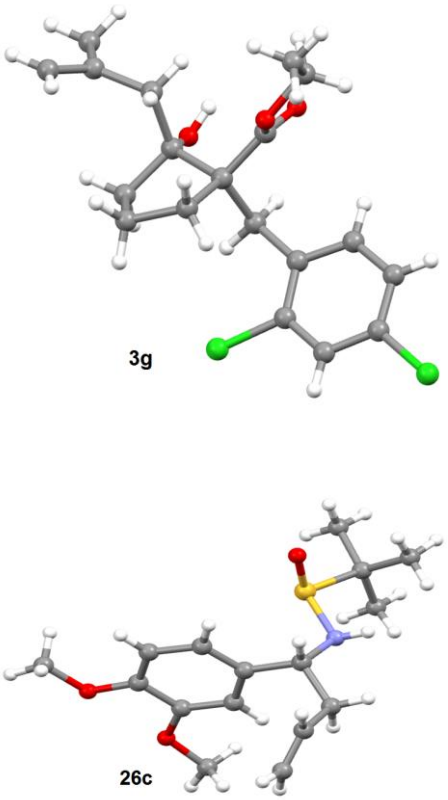
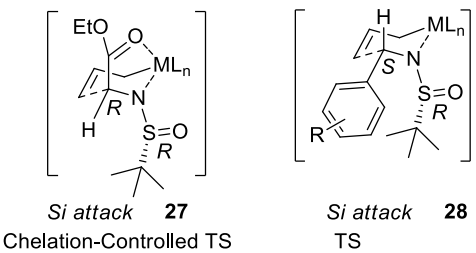


Figure 1 X-ray structures of compounds **3g** and **26c**.



Scheme 12 Plausible Transition States (TS) for the observed stereoselectivity.

Stereochemistry. The stereochemistry of the compound **3g** prepared in this work was unequivocally confirmed based on the X-ray structure analysis (Figure 1). The stereochemistry of other products **3a-l**,[16b] **3p**,[16b] **3q**,[16b] **6a,b**,[16b] **4a**,[16b] and **25a-d**[18a] obtained in this work using Al/$InCl_3$ system was assigned by comparing their spectral data with our previously published work,[16b,18a] where the stereochemistry and structure of various compounds have been already unambiguously confirmed on the basis of X-ray structure analysis.

The compound (*R*)-2-methyl-*N*-((*S*)-1-(p-tolyl)but-3-en-1-yl)propane-2-sulfinamide (**26b)** obtained in this work was reported in the literature.[20f] We have prepared the compound **26b** using the procedure reported by Sun *et al.*[20f] and recorded its specific rotation ($[\alpha]_D^{28}$ = –91.7 (*c* 0.024, DCM). The spectral data of compound **26b** obtained in this work using Al/$InCl_3$ system was found to be similar to the spectral data of **26b** reported in the literature.[20f] Next, we recorded the specific rotation of the compound **26b** prepared using the Al/$InCl_3$ system $[\alpha]_D^{28}$ = –91.7 (*c* 0.024, DCM). Since the spectral data as well as the specific rotation of the compound **26b** prepared using the Al/$InCl_3$ system and the reported method are similar, the stereochemistry of compound **26b** has been assigned as reported in the literature.[20f] Additionally, the compound **26d** also reported in the literature.[20f] Since the compounds **26d** and **26g** were also assembled in a similar manner to **26b** and based on the observed very high diastereoselectivity, the stereochemistry of compounds **26d** and **26g** was assigned after assigning the stereochemistry of **26b**. In this line, the stereochemistry of the product (*S*)-*N*-((*R*)-1-(3,4-dimethoxyphenyl)but-3-en-1-yl)-2-methylpropane-2-sulfinamide (**26c)** which is not reported in the literature was unambiguously established from the single crystal X-ray structure analysis (Figure 1). Similarly, the compound (*(R)-ethyl 2-((R)-1,1-dimethylethylsulfinamido)pent-4-enoate* (**26a)** obtained in this work was reported in the literature by the same group (Sun *et al.*)[20f] as discussed above. The stereochemistry of the compound **26a** has been assigned on the basis of similarity in the spectral data pattern of the compound **26a** obtained using the Al/$InCl_3$ system and the literature method.[20f] Consequently, since the compounds **26e** (starting from (*S*)-ethyl 2-((tert-butylsulfinyl)imino)acetate) and **26f** (starting from (*R*)-ethyl 2-((tert-butylsulfinyl)imino)acetate) were also assembled in a similar manner to **26a** and based on the observed very high diastereoselectivity and similarity in their spectral data pattern, the stereochemistry of compounds **26e** and **26f** was assigned after assigning the stereochemistry of **26a**. Further, the compounds **26e** ($[\alpha]_D^{28}$ = +25.0 (*c* 0.024, DCM) and **26f** ($[\alpha]_D^{26}$ = –25.0 (*c* 0.024, DCM) are enantiomers and their specific rotations values were found to be having opposite sign, which further clearly validated the assigned stereochemistry and revealed that the allylation of the compounds **23i** and **23e** is highly stereoselective.

The preparation as well as stereochemistry of the compounds **26a** and **26b** are reported by Sun *et al.* using the corresponding imines **23e** and **23f**.[20f] Though the imine systems **23e** and **23f** have been prepared using the same chiral amine ((*R*)-*N*-*tert*-butylsulfinyl amine), however, the configuration at the homoallyic chiral carbon in the corresponding products, e.g. **26a** and **26b** are opposite. The reason for this may be the allylation of **23e** is proceeding via a well-known chelation controlled TS model[18a] **27** (Scheme 12) comprising an ester group, thereby affording the compound **26a** having an opposite

stereochemistry when compared to the product **26b** where there would not be a chelation assistance. Presumably, the aryl group being relatively bulky group, which occupies the equatorial position in the six-membered cyclic TS[18a] **28**, thereby affording the compound **26b**.

In concurrence with the literature reports, in which the mechanism of generation of allylmetal reagent from $InCl_3/Al^0$ system is proposed,[12,13,19] plausible mechanisms for the allylation of prostereogenic α, α- disubstituted cycloalkanones and imino compounds using the $InCl_3$/ Al^0 system are proposed in Scheme 11. The involvement of both the types of mechanisms, such as mechanism I and mechanism II is a highly possible.[13] For example, the substrate **1a** or **1b** (Tables 1 and 2) was reacted with allyl bromide, Al^0 and catalytic amount of $InCl_3$ or In^0 in one-pot. Perhaps, in this case, the allylation could be proceeding via allylic indium generated *in situ* involving the mechanism I.[13] On the other hand, in some cases we separately prepared the allylmetal reagent from allyl bromide, Al^0 and catalytic amount of $InCl_3$ and then it was treated with imines. For example, the imino compounds **15a-f** (Schemes 6-10) were treated with a THF solution of allylmetal reagent prepared from allyl bromide, Al^0 and catalytic amount of $InCl_3$. In these cases, perhaps, the allylation could be proceeding via the mechanism II, as in the literature it is also proposed that catalytic amount of $InCl_3$ activates the Al surface thereby leading to the formation of allylmetal reagent.[13a,c,f,k] In view of these points, we also believe that in our reactions, the allylation reaction proceeds through mechanism II by involving an allylic aluminium reagent as an intermediate and $InCl_3$ may be acting as an activator.[12,13a,c,f,k]

Conclusion

In summary, we have shown the utility of catalytic amount of $InCl_3$ in combination with Al^0 powder for the diastereofacial selective allylation of prostereogenic α, α- disubstituted (hindered) cycloalkanones and the stereoselective construction of a stereoarray having consecutively attached tertiary carbinol- and an all carbon-based stereocenters in functionalized carbocyclic compounds. The allylation of various 2-substituted-2-carbethoxycyclopentanones gave the corresponding products with an excellent diastereoselectivity and on the other hand, the allylation of various 2-substituted-2-carbethoxycyclohexanones gave the corresponding products with low diastereoselectivity. We have also reported the C-C bond forming protocol and the synthesis of homoallylic amines via the allylation of imino (C=N) functional groups using catalytic amount of $InCl_3$ in combination with Al^0 powder. In the case of addition of γ-substituted allylic halides to α-imino esters low to very good diastereoselectivity was obtained. The allylation of chiral *N-tert*-butylsulfinyl imino systems including α-imino esters gave the allylated products with an excellent diastereoselectivity. Considering that the aluminium metal is relatively very cheap and less toxic when compared to other metals, further works and developments are anticipated, which will prove that the combination of In and Al as an efficient alternative for performing the Barbier-type allylation reactions.

Experimental Section

General Considerations

Melting points are uncorrected. FT-IR spectra were recorded as thin films or KBr pellets. ^1H and ^{13}C NMR spectra were recorded on 400 MHz and 100 MHz spectrometers respectively. Column chromatography was carried out on silica gel (100-200 mesh) or neutral alumina. TLC was performed on silica plates or neutral alumina and components were visualized by observation under iodine. Anhydrous solvents were prepared using standard drying methods. Reactions were carried out in anhydrous solvents under nitrogen atmosphere where ever required. Solutions were dried using anhydrous sodium sulfate. Reagents were added to the reaction flask with the help of a syringe. Yields were not optimized and ratios of diastereomers were determined from NMR spectra of crude reaction mixtures or after isolation. The ratio of diastereoselectivity (*dr* 98:2) refers to the predominant presence of the major diastereomer and only traces of the corresponding minor isomer in the NMR spectrum of crude reaction mixture. All the starting materials were prepared using standard procedures reported in the literature.

Procedure A: General Procedure for the preparation of compounds **3a-3q, 4a, 5b, 6a,b** and **9/10**. To a solution of cyclic ketone (0.5 mmol) in anhydrous THF (1.5 mL) were added $InCl_3$ (1-2 mol%), Al powder (0.55 mmol) and allyl/propargyl bromide (1.0 mmol) under nitrogen atmosphere and the above reaction mixture was stirred at rt for an appropriate time mentioned in respective Tables/Schemes. After the completion of reaction, the reaction mixture was quenched by adding water (2 mL). The reaction mixture was transferred into a separating funnel and extracted with ethyl acetate (3 X 8 mL). The combined organic layers were dried over anhydrous Na_2SO_4. Then the solvent was evaporated under vacuum. Purification of the resulting crude reaction mixture by column chromatography on silica gel (EtOAc/Hexane as eluent) gave the corresponding product (see the corresponding Tables/Schemes for specific reactions).

Procedure B: General Procedure for the preparation of compounds **24a,b, 25a-d** and **26a**. To a solution of $InCl_3$ (3-4 mol%), Al powder (0.75 mmol) and allyl bromide/prenyl bromide/crotyl bromide/cinnamyl bromide/propargyl bromide/cyclohexenyl bromide (1.0 mmol) in anhydrous THF (1.5 mL), the corresponding imine (0.5 mmol) was added at an appropriate temperature as mentioned in the corresponding Tables/Schemes and reaction mixture was stirred for an appropriate time under nitrogen atmosphere as mentioned in the respective Tables/Schemes. After this period, the reaction mixture was quenched by adding water (2 mL). The reaction mixture was transferred in to a separating funnel and extracted with ethyl acetate (3 X 8 mL). The combined organic layers

were dried over anhydrous Na_2SO_4. Then the solvent was evaporated under vacuum. Purification of the resulting crude reaction mixture by column chromatography on silica gel (EtOAc/Hexane as eluent) gave the corresponding product (see the corresponding Tables/Schemes for specific reactions).

Procedure C: General Procedure for the preparation of compounds **8a-8c, 16a-h, 20, 21, 22, 24c-24d** and **26b-26g**. To a solution of $InCl_3$ (3-4 mol%) and Al powder (0.75 mmol) in anhydrous THF (1.5 mL) was added allyl bromide/prenyl bromide/crotyl bromide/cinnamyl bromide/propargyl bromide/cyclohexenyl bromide (1.0 mmol) under nitrogen atmosphere and the reaction mixture was stirred at rt. After 15 min the corresponding imine/carbonyl compound (0.5 mmol) was added to above reaction mixture at specific temperature for an appropriate time as mentioned in the respective Tables/Schemes. After this period, the reaction mixture was quenched by adding water (2 mL). The reaction mixture was transferred into a separating funnel and extracted with ethyl acetate (3 X 8 mL). The combined organic layers were dried over anhydrous Na_2SO_4. Then the solvent was evaporated under vacuum. Purification of the resulting crude reaction mixture by column chromatography on silica gel (EtOAc/Hexane as eluent) gave the product (see the corresponding Tables/Schemes for specific reactions).

Procedure D: Synthesis of triazole **11**. To the solution of a mixture of compounds **9/10** (0.5 mmol), $CuSO_4.5H_2O$ (30 mol%) and (+)-sodium *L*-ascorbate in THF/H_2O (2 : 1, 6 mL) was added benzyl azide (0.75 mmol) and the reaction mixture was stirred for overnight at rt. After the completion of reaction, the reaction mixture was transferred in to a separating funnel and extracted with ethyl acetate (3 X 8 mL). The combined organic layers were dried over anhydrous Na_2SO_4. Then the solvent was evaporated under vacuum. Purification of the resulting crude reaction mixture by column chromatography on silica gel (EtOAc/Hexane as eluent) gave the product **11**.

Procedure E: Preparation of compound **12**. To the solution of a mixture compounds **9/10** (0.5 mmol) in DMSO (3 mL), was added $Cu(OAc)_2$ (40 mol%) and the reaction mixture was stirred under an open atmosphere for 24 h at 105 ^oC . After completion of the reaction, the solvent was evaporated under vacuum. Purification of the resulting crude reaction mixture by column chromatography on silica gel (EtOAc/Hexane as eluent) gave the product **12**.

Copies of NMR spectra of all the known and unknown compounds reported in this work can be found in ESI. In Table 2, except compounds **3e**, **3g**, **3h**, **3m**, **3o** and **3q**, all other compounds were known in the literature and their spectral data were compared with the spectral data reported in our previous work.[16b] The Spectral data of the known compounds **8a**,[19a] **8b**,[19b] **9/10**,[16b] **16a**,[20a] **16b**,[20b] **16d**,[20c] **22**,[20d] **24a**,[2f] **25a**,[18a] **25b**,[20e] **25c**,[18a] **25d**,[18a] **26a**,[20f] **26b**,[20f] and **26d**[20f] were compared with the spectral data reported in the literature. The compound **5a** could not be isolated in pure form. The compound **8b** was obtained as a mixture of diastereomers (*dr* 90:10).

Ethyl (1*S,2*S**)-2-allyl-2-hydroxy-1-(4-nitrobenzyl)cyclopentanecarboxylate** (**3e**). Following the general procedure A described above, **3e** (*anti*, major isomer) was obtained after purification by silica gel column chromatography (EtOAc : Hexane = 07 : 93) as a semi solid (126 mg, 76%); IR (neat): 3543, 1716, 1519 and 1347 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, 2H, *J* = 8.6 Hz), 7.32 (d, 2H, *J* = 8.6 Hz), 6.00-5.90 (m, 1H), 5.24-5.15 (m, 2H), 4.17-4.09 (m, 2H), 3.51 (d, 1H, *J* = 13.5 Hz), 2.91 (d, 1H, *J* = 13.5 Hz), 2.34-2.23 (m, 2H), 2.14 (br s, 1H), 2.01-1.75 (m, 6H), 1.24 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.7, 146.9, 146.7, 133.5, 130.7, 123.3, 119.4, 83.1, 61.6, 60.8, 42.0, 37.8, 34.8, 29.9, 18.6, 14.2; HRMS: (ESI) calcd for $C_{18}H_{23}NNaO_5$ $[M + Na]^+$ 356.1474, found 356.1441.

Ethyl (1*S,2*S**)-1-(2,4-dichlorobenzyl)-2-hydroxy-2-(2-methylallyl)cyclopentanecarboxylate** (**3g**).[21] Following the general procedure A described above, **3g** (*anti*, major isomer) was obtained after purification by silica gel column chromatography (EtOAc : Hexane = 06 : 94) as a white solid (122 mg, 66%); mp = 80-82 ^oC; IR (KBr): 3500, 1716, 1473 and 889 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, 1H, *J* = 2.2 Hz), 7.14 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.2 Hz), 7.07 (d, 1H, *J* = 8.4 Hz), 4.97 (s, 1H), 4.80 (s, 1H), 4.18 (q, 2H, *J* = 7.1 Hz), 3.37 (d, 1H, *J* = 14.5 Hz), 3.23 (d, 1H, *J* = 14.5 Hz), 2.28 (s, 1H), 2.21 (d, 1H, *J* = 3.8 Hz), 2.07-1.64 (m, 6H), 1.88 (s, 3H), 1.26 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.6, 142.6, 136.0, 135.4, 132.6, 131.5, 129.4, 126.9, 115.3, 83.5, 61.6, 60.8, 44.8, 34.2, 33.6, 28.5, 24.5, 18.6, 14.2; HRMS: (ESI) calcd for $C_{19}H_{25}Cl_2O_3$ $[M + H]^+$ 371.1181, found 371.1001.

Ethyl (1*R,2*S**)-2-hydroxy-2-(2-methylallyl)-1-pentylcyclopentanecarboxylate** (**3h**). Following the general procedure A described above, **3h** (*anti*, major isomer) was obtained after purification by silica gel column chromatography (EtOAc : Hexane = 05 : 95) as a colourless liquid (119 mg, 78%); IR (neat): 3534, 2958, 1721 and 1463 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.90 (s, 1H), 4.73 (s, 1H), 4.23-4.09 (m, 2H), 2.20-2.06 (m, 3H), 2.05 (s, 1H), 1.99-1.84 (m, 2H), 1.82 (s, 3H), 1.77-1.62 (m, 4H), 1.44-1.37 (m, 1H), 1.33-1.24 (m, 5H), 1.28 (t, 3H, *J* = 7.1 Hz), 1.07-1.00 (m, 1H), 0.87 (t, 3H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.9, 142.9, 1144.9, 82.6, 60.9, 60.3, 44.9, 34.5, 32.5, 32.0, 29.8, 25.0, 24.5, 22.5, 18.8, 14.3, 14.0; HRMS: (ESI) calcd for $C_{17}H_{30}NaO_3$ $[M + Na]^+$ 305.2093, found 305.2059.

3-(2-Allyl-2-hydroxy-1-methylcyclohexyl)propanenitrile (**3m**). Following the general procedure A described above, **3m** was obtained as a mixture of diastereomers (*dr* 60:40) after purification by silica gel column chromatography (EtOAc : Hexane = 20 : 80) as a light yellow liquid (62 mg, 60%); IR (neat): 3512, 2939, 2246 and 1462 cm^{-1}; ^1H NMR (400 MHz,

$CDCl_3$): δ 5.91-5.80 (m, 1H), 5.21-5.10 (m, 2H), 2.45-2.19 (m, 4H), 2.07-1.71 (m, 2H), 1.60-1.37 (m, 8H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.8, 133.7, 121.2, 120.8, 119.7, 119.3, 75.0, 74.9, 39.9, 39.7, 39.4, 38.8, 33.6, 32.9, 32.6, 32.6, 32.2, 22.0, 21.5, 21.0, 21.0, 20.6, 18.8, 12.6; HRMS: (ESI) calcd for $C_{13}H_{21}NNaO$ $[M + Na]^+$ 230.1521, found 230.1363. NMR values were given for both the diastereomers.

Ethyl 2-(4-bromobenzyl)-3-hydroxy-2,3-dimethylhex-5-enoate (**3o**). Following the general procedure A described above, **3o** was obtained as a mixture of diastereomers (*dr* 55:45) after purification by silica gel column chromatography (EtOAc : Hexane = 07 : 93) as a colourless liquid (144 mg, 81%); IR (neat): 3486, 1714, 1488 and 1012 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, 2H, *J* = 8.0 Hz), 6.97 (d, 2H, *J* = 8.0 Hz), 6.06-5.91 (m, 1H), 5.17-5.03 (m, 2H), 4.06-3.95 (m, 2H), 3.83 (s, 1H), 3.51 (d, 1H, *J* = 13.2 Hz), 2.58 (d, 1H, 13.2 Hz), 2.34 (dd, 1H, J_1 = 13.9 Hz, J_2 = 8.2 Hz), 2.17-2.09 (m, 1H), 1.18 (s, 3H), 1.12 (t, 3H, *J* = 7.1 Hz), 1.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.2, 176.8, 137.0, 136.8, 134.3, 134.1, 132.0, 132.0, 131.1, 131.1, 120.5, 120.5, 118.0, 117.9, 76.0, 75.3, 61.0, 55.5, 55.0, 43.6, 40.4, 39.3, 38.8, 23.7, 20.9, 17.5, 17.4, 14.0, 13.9; HRMS: (ESI) calcd for $C_{17}H_{23}BrNaO_3$ $[M + Na]^+$ 377.0728, found 377.0696. NMR values were given for both the diastereomers.

Ethyl (1*S,2*S**)-2-allyl-1-benzhydryl-2-hydroxycyclopentanecarboxylate** (**3q**). Following the general procedure A described above, **3q** (*anti*, major isomer) was obtained after purification by silica gel column chromatography (EtOAc : Hexane = 05 : 95) as a white solid (158 mg, 87%); mp = 80-82 ^oC; IR (KBr): 3528, 1722, 1495 and 704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, 2H, *J* = 7.1 Hz), 7.42 (d, 2H, *J* = 7.4 Hz), 7.29-7.13 (m, 6H), 5.97-5.87 (m, 1H), 5.18-5.07 (m, 2H), 5.09 (s, 1H), 3.95-3.86 (m, 2H), 2.79-2.65 (m, 2H), 2.30 (dd, 1H, J_1 = 14.1 Hz, J_2 = 8.1 Hz), 2.21 (s, 1H), 2.18-2.12 (m, 1H), 1.76-1.12 (m, 4H), 0.93 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.8, 143.8, 142.7, 133.8, 130.9, 129.1, 128.1, 128.1, 126.5, 126.1, 118.7, 84.0, 64.2, 60.6, 53.2, 43.0, 34.0, 28.4, 18.7, 13.6; HRMS: (ESI) calcd for $C_{24}H_{28}NaO_3$ $[M + Na]^+$ 387.1936, found 387.1911. This compound was isolated along with its minor isomer.

Ethyl 2-allyl-1-(2-ethoxy-2-oxoethyl)-2-hydroxycyclohexanecarboxylate (**5b**). Following the general procedure A described above, **5b** was obtained as pure compound after purification by silica gel column chromatography (EtOAc : Hexane = 05 : 95) as a colourless liquid (39 mg, 26%); IR (neat): 3512, 1737, 1715 and 1176 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.96-5.86 (m, 1H), 5.12-5.05 (m, 2H), 4.29-4.15 (m, 2H), 4.10 (q, 2H, *J* = 7.2 Hz), 3.86 (s, 1H), 2.79 (d, 1H, *J* = 15.0 Hz), 2.56 (d, 1H, *J* = 15.0 Hz), 2.52 (dd, 1H, J_1 = 13.7 Hz, J_2 = 5.6 Hz), 2.25-2.16 (m, 2H), 1.74-1.34 (m, 7H), 1.30 (t, 3H, *J* = 7.1 Hz), 1.24 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.9, 171.3, 133.8, 117.8, 74.3, 61.1, 60.5, 52.8, 39.4, 38.5, 33.1, 31.6, 21.8, 21.7, 14.1, 14.0; HRMS: (ESI) calcd for $C_{16}H_{26}O_5Na$ $[M + Na]^+$ 321.1678, found 321.1682.

1,2-Diallyl-1,2-dihydroacenaphthylene-1,2-diol (**8c**). Following the general procedure C described above, **8c** was obtained after purification by silica gel column chromatography (EtOAc : Hexane = 20 :80) as a white solid (65 mg, 98%); mp = 143-145 ^oC; IR (KBr): 3362, 1638, 1374 and 1057 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, 2H, *J* = 8.3 Hz), 7.58 (dd, 2H, J_1 = 8.3 Hz, J_2 = 6.9 Hz), 7.42 (d, 2H, *J* = 6.9 Hz), 5.90-5.79 (m, 2H), 5.20-5.14 (m, 4H), 2.88-2.82 (m, 2H), 2.69 (s, 2H), 2.60 (dd, 2H, J_1 = 13.9 Hz, J_2 = 7.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 134.3, 134.1, 130.6, 128.1, 124.6, 119.5, 119.5, 86.4, 43.8; HRMS: (ESI) calcd for $C_{18}H_{17}O_2$ $[M - H]^+$ 265.1229, found 265.1337.

Ethyl (1*S,2*S**)-1-benzyl-2-((1-benzyl-1*H*-1,2,3-triazol-5-yl)methyl)-2-hydroxycyclopentanecarboxylate** (**11**). Following the general procedure D described above, **11** was obtained after purification by silica gel column chromatography (EtOAc : Hexane = 30 : 70) as a brownish yellow solid (124 mg, 59%);); mp = 83-85 ^oC; IR (KBr): 3409, 1716, 1454 and 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (s, 1H,)7.38-7.35 (m, 3H), 7.28-7.19(m, 5H), 7.12-7.10 (m, 2H), 5.52 (s, 2H), 4.14-4.00 (m, 2H), 3.79 (br s, 1H), 3.26 (d, 1H, *J* = 13.5 Hz), 2.98 (d, 1H, *J* = 18.7 Hz), 2.95 (d, 1H, *J* = 18.7 Hz), 2.80 (d, 1H, *J* = 13.5 Hz), 2.06-1.70 (m, 6H), 1.18 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.4, 144.8, 138.6, 134.8, 129.9, 129.1, 128.7, 128.1, 128.0, 126.3, 122.7, 83.2, 61.9, 60.6, 54.1, 38.0, 35.5, 33.2, 30.0, 18.5, 14.1; HRMS: (ESI) calcd for $C_{25}H_{29}N_3NaO_3$ $[M + Na]^+$ 442.2107, found 442.2104. The stereochemistry of the products **9**/**10** was reported[16b] and based on this the stereochemistry of **11** was assigned.

Preparation of compound 12. Following the general procedure E described above, **12** was obtained after purification by silica gel column chromatography (EtOAc : Hexane = 25 : 75) as a white solid (175 mg, 60%); mp = 117-119 ^oC; IR (KBr): 3493, 2979, 1716 and 738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.26-7.22 (m, 6H), 7.14-7.12 (m, 4H), 4.16-4.08 (m, 4H), 3.42 (d, 2H, *J* = 13.6 Hz), 2.81 (d, 2H, *J* = 13.6 Hz), 2.62 (d, 2H, *J* = 16.8 Hz), 2.56 (d, 2H, *J* = 16.8 Hz), 2.41 (s, 2H), 2.11-1.68 (m, 12H), 1.24 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.6, 138.1, 129.9, 128.2, 126.5, 82.5, 74.0, 67.8, 61.1, 60.8, 37.8, 35.8, 29.6, 29.6, 18.1, 14.1; HRMS: (ESI) calcd for $C_{36}H_{42}NaO_6$ $[M + Na]^+$ 593.2879, found 593.2894. The stereochemistry of the products **9**/**10** was reported[16b] and based on this the stereochemistry of **12** was assigned.

3,4-Dichloro-*N*-(1-(3,4-dimethoxyphenyl)but-3-en-1-yl)aniline (**16c**). Following the general procedure C described above, **16c** was obtained after purification by silica gel column chromatography (EtOAc : Hexane = 15 :85) as a light yellow liquid (163 mg, 93%); IR (neat): 3385, 1597, 1514 and 1027

cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (d, 1H, J = 8.7 Hz), 6.89 (dd, 1H, J_1 = 8.4 Hz, J_2 = 1.8 Hz), 6.86-6.84 (m, 2H), 6.60 (d, 1H, J = 2.7 Hz), 6.35 (dd, 1H, J_1 = 8.7 Hz, J_2 = 2.7 Hz), 5.81-5.71 (m, 1H), 5.24-5.17 (m, 2H), 4.30-4.23 (m, 1H), 4.23 (s, 1H), 3.88 (s, 3H), 3.88 (s, 3H), 2.64-2.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 148.1, 146.9, 135.0, 134.3, 132.5, 130.4, 119.9, 118.7, 118.2, 114.8, 113.1, 111.3, 109.1, 56.9, 55.9, 55.9, 43.2; HRMS: (ESI) calcd for $C_{18}H_{20}Cl_2NO_2$ [M + H]$^+$ 352.0871, found 352.0601.

***N*-((4-Bromophenyl)(cyclohex-2-en-1-yl)methyl)-4-methylaniline** (**16e**)**.** Following the general procedure C described above, **16e** was obtained as a mixture of diastereomers (*dr* 70:30) after purification by silica gel column chromatography (EtOAc : Hexane = 05 :95) as a light yellow liquid (129 mg, 73%); IR (neat): 3414, 1618, 1519 and 806 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, 2H, J = 8.5 Hz), 7.26 (d, 2H, J = 8.5 Hz), 6.95 (d, 2H, J = 8.1 Hz), 6.43 (d, 2H, J = 8.1 Hz), 5.98-5.91 (m, 1H), 5.60 (dd, 1H, J_1 = 10.2 Hz, J_2 = 1.5 Hz), 4.30-4.27 (m, 1H), 4.04 (s, 1H), 2.24 (s, 3H), 2.08 (s, 2H), 1.85-1.80 (m, 2H), 1.61-1.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 145.0, 142.0, 141.6, 132.5, 131.5, 131.0, 130.8, 129.7, 129.6, 128.9, 128.8, 128.7, 126.8, 126.3, 125.8, 120.5, 113.7, 113.1, 61.8, 61.2, 43.1, 42.8, 27.6, 25.3, 25.2, 23.7, 21.9, 21.8, 20.4; HRMS: (ESI) calcd for $C_{20}H_{23}BrN$ [M + H]$^+$ 356.1014, found 356.0970. NMR values were given for both the isomers.

***N*-((4-Chlorophenyl)(cyclohex-2-en-1-yl)methyl)-3,4-dimethylaniline** (**16f**). Following the general procedure C described above, **16f** was obtained as a mixture of diastereomers (*dr* 70:30) after purification by silica gel column chromatography (EtOAc : Hexane = 10 : 90) as a reddish brown liquid (130 mg, 80%); IR (neat): 3418, 1617, 1510 and 801 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.35 (m, 4H), 6.92 (d, 1H, J = 7.9 Hz), 6.42 (s, 1H), 6.28-6.27 (m, 1H), 5.98 (d, 1H, J = 9.6 Hz), 5.64-5.57 (m, 1H), 4.34-4.31 (m, 1H), 4.03 (s, 1H), 2.64 (s, 1H), 2.22 (s, 3H), 2.19 (s, 3H), 2.10 (s, 2H), 1.87-1.54 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 145.6, 141.7, 141.2, 137.3, 137.2, 132.3, 131.4, 130.8, 130.3, 130.2, 129.0, 128.6, 128.4, 128.3, 125.9, 125.6, 125.1, 115.6, 114.9, 110.8, 110.3, 61.7, 61.1, 43.2, 42.9, 27.7, 25.3, 25.3, 23.7, 22.0, 21.8, 20.1, 18.7; HRMS: (ESI) calcd for $C_{21}H_{25}ClN$ [M + H]$^+$ 326.1676, found 326.1646. NMR values were given for both the isomers.

***N*-(1-(4-Bromophenyl)but-3-en-1-yl)-O-methylhydroxylamine** (**16g**). Following the general procedure C described above, **16g** was obtained after purification by silica gel column chromatography (EtOAc : Hexane = 07 : 93) as a colourless liquid (96 mg, 75%); IR (KBr): 1639, 1485, 1104 and 739 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, 2H, J = 8.4 Hz), 7.19 (d, 2H, J = 8.4 Hz), 5.81-5.70 (m, 1H), 5.09-5.04 (m, 2H), 4.18-4.14 (m, 1H), 3.23 (s, 3H), 2.60-2.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.8, 134.3, 131.5, 128.5, 121.4, 117.3, 83.0, 56.7, 42.4. NH proton could not be detected in this compound.

***N*-(1-(4-Bromophenyl)but-3-en-1-yl)-N-methylhydroxylamine** (**16h**). Following the general procedure C described above, **16h** was obtained after purification by silica gel column chromatography (EtOAc : Hexane = 10 : 90) as a yellowish brown solid (63 mg, 50%); mp = 72-74 ^{o}C ; IR (KBr): 3224, 1487, 1011 and 739 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, 2H, J = 8.4 Hz), 7.19 (d, 2H, 8.4 Hz), 5.64-5.54 (m, 1H), 5.03-4.96 (m, 2H), 3.57 (dd, 1H, J_1 = 9.2 Hz, J_2 = 5.0 Hz), 2.88-2.81 (m, 1H), 2.57-2.49 (m, 1H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.6, 131.5, 130.4, 121.6, 117.3, 73.3, 46.0, 38.1; HRMS: (ESI) calcd for $C_{11}H_{15}BrNO$ [M + H]$^+$ 256.0337, found 256.0155. OH proton could not be detected in this compound.

3-Allyl-3-(phenylamino)indolin-2-one (**20**). Following the general procedure C described above, **20** was obtained after purification by silica gel column chromatography (EtOAc : Hexane = 20 :80) as white solid (106 mg, 80%); mp = 163-165 ^{o}C; IR (KBr): 3312, 1603, 1716 and 1470 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.60 (s, 1H), 7.29-7.23 (m, 2H), 7.07-6.98 (m, 3H), 6.90 (d, 1H, J = 7.7 Hz), 6.69-6.65 (m, 1H), 6.32 (dd, 1H, J_1 = 8.7 Hz, J_2 = 1.0 Hz), 5.86-5.76 (m, 1H), 5.29-5.22 (m, 2H), 4.73 (s, 1H), 2.80 (dd, 1H, J_1 = 13.3 Hz, J_2 = 7.1 Hz), 2.66 (dd, 1H, J_1 = 13.3 Hz, J_2 = 7.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.0, 145.2, 139.8, 130.3, 129.1, 129.0, 124.0, 123.0, 121.2, 118.8, 114.4, 111.0, 64.3, 44.7; HRMS: (ESI) calcd for $C_{17}H_{16}N_2NaO$ [M + Na]$^+$ 287.1160, found 287.1125.

Ethyl 2-(2-tosylhydrazinyl)pent-4-enoate (**21**). Following the general procedure C described above, **21** was obtained after purification by silica gel column chromatography (EtOAc : Hexane = 30 :70) as yellowish thick liquid (31 mg, 20%); IR (neat): 3300, 3249, 1727 and 738 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, 2H, J = 8.3 Hz), 7.33 (d, 2H, J = 8.0 Hz), 6.36 (s, 1H), 5.71-5.61 (m, 1H), 5.10-5.06 (m, 2H), 4.20 (q, 2H, J = 7.2 Hz), 3.92 (dd, 1H, J_1 = 9.7 Hz, J_2 = 2.9 Hz), 3.64-3.59 (m, 1H), 2.45 (s, 3H), 2.44-2.32 (m, 2H), 1.29 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.4, 144.0, 135.0, 132.6, 129.5, 128.2, 118.5, 62.9, 61.4, 34.8, 21.6, 14.2; HRMS: (ESI) calcd for $C_{14}H_{20}N_2NaO_4S$ [M + Na]$^+$ 335.1041, found 335.1013.

Ethyl 2-((4-methoxyphenyl)amino)pent-4-ynoate (**24b**). Following the general procedure B described above, **24b** was obtained after purification by silica gel column chromatography (EtOAc : Hexane = 20 :80) as reddish black thick liquid (71 mg, 58%); IR (neat): 3286, 1738, 1514 and 1241 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 (d, 2H, J = 9.0 Hz), 6.67 (d, 2H, J = 9.0 Hz), 4.29-4.20 (m, 2H), 4.19 (t, 1H, J = 5.4 Hz), 3.77 (s, 3H), 2.78 (dd, 2H, J_1 = 5.4 Hz, J_2 = 2.6 Hz), 2.11 (t, 1H, J = 2.6 Hz), 1.33 (t, 3H, J = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.2, 153.1, 140.1, 115.7, 114.9, 78.9, 71.6, 61.5, 56.3, 55.7, 22.9, 14.2; HRMS: (ESI) calcd for $C_{14}H_{18}NO_3$ [M + H]$^+$

248.1287, found 248.1268. NH proton could not be detected in this compound.

Ethyl 2-((3,4-dimethylphenyl)amino)pent-4-ynoate (**24c**). Following the general procedure C described above, **24c** was obtained after purification by neutral alumina column chromatography (EtOAc : Hexane = 10 :90) as brownish black thick liquid (46 mg, 38%); IR (neat): 3391, 1738, 1510 and 1209 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.97 (d, 1H, J = 8.0 Hz), 6.53 (d, 1H, J = 2.4 Hz), 6.45 (dd, 1H, J_1 = 8.0 Hz, J_2 = 2.4 Hz), 4.29-4.24 (m, 3H), 2.79 (dd, 2H, J_1 = 5.1 Hz, J_2 = 2.7 Hz), 2,22 (s, 3H), 2.18 (s, 3H), 2.10 (t, 1H, J = 2.7 Hz), 1.31 (t, 3H, J = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.1, 144.1, 137.5, 130.4, 126.9, 115.9, 111.3, 78.9, 71.5, 61.5, 55.4, 22.9, 20.0, 18.8, 14.3; HRMS: (ESI) calcd for $C_{15}H_{20}NO_2$ $[M + H]^+$ 246.1494, found 246.1458. NH proton could not be detected in this compound.

Ethyl 2-((4-bromophenyl)amino)pent-4-ynoate (**24d**). Following the general procedure C described above, **24d** was obtained after purification by neutral alumina column chromatography (EtOAc : Hexane = 10 :90) as a light yellow liquid (59 mg, 40%); IR (neat): 3392, 3295, 1737 and 651 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, 2H, J = 8.9 Hz), 6.55 (d, 2H, J = 8.9 Hz), 4.49 (s, 1H), 4.30-4.21 (m, 3H), 2.79 (dd, 2H, J_1 = 5.2 Hz, J_2 = 2.6 Hz), 2.11 (t, 1H, J = 2.6 Hz), 1.31 (t, 3H, J = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 145.1, 132.1, 115.4, 110.5, 78.6, 71.9, 61.8, 54.9, 22.7, 14.2; HRMS: (ESI) calcd for $C_{13}H_{15}BrNO_2$ $[M + H]^+$ 296.0286, found 296.0265.

(*S*)-*N*-((*R*)-1-(3,4-Dimethoxyphenyl)but-3-en-1-yl)-2-methylpropane-2-sulfinamide (**26c**).[21] Following the general procedure C described above, **26c** was obtained after purification by silica gel column chromatography (EtOAc : Hexane = 90 :10) as white solid (36 mg, 46%); $[\alpha]_D^{28}$ = +54.6 (*c* 0.044, DCM); mp = 103-105 °C; IR (KBr): 3417, 1638, 1421 and 738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.90 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.9 Hz), 6.86 (d, 1H, J = 1.9 Hz), 6.84 (d, 1H, J = 8.0 Hz), 5.81-5.70 (m, 1H), 5.22-5.17 (m, 2H), 4.44-4.40 (m, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.68 (br s, 1H), 2.62-2.41 (m, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9, 148.4, 134.4, 134.1, 119.9, 119.2, 110.8, 110.3, 56.6, 55.8, 55.8, 55.5, 43.6, 22.6; HRMS: (ESI) calcd for $C_{16}H_{26}NO_3S$ $[M + H]^+$ 312.1633, found 312.1607.

Ethyl (*S*)-2-((*S*)-1,1-dimethylethylsulfinamido)-4-methylpent-4-enoate (**26e**). Following the general procedure C described above, **26e** after purification by silica gel column chromatography (EtOAc : Hexane = 70 :30) as a light yellow liquid(16 mg, 25%); $[\alpha]_D^{28}$ = +25.0 (*c* 0.024, DCM); IR (neat): 3402, 1738 and 1056 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.85 (s, 1H), 4.77 (s, 1H), 4.24 (q, 2H, J = 7.2 Hz), 4.11-4.04 (m, 2H), 2.54-2.38 (m, 2H), 1.76 (s, 3H), 1.31 (t, 3H, J = 7.2 Hz), 1.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 140.3, 114.6, 61.7, 56.2, 42.5, 22.6, 22.1, 14.1; HRMS: (ESI) calcd for $C_{12}H_{24}NO_3S$ $[M + H]^+$ 262.1477, found 262.1480.

Ethyl (*R*)-2-((*R*)-1,1-dimethylethylsulfinamido)-4-methylpent-4-enoate (**26f**). Following the general procedure C described above, **26f** was obtained after purification by silica gel column chromatography (EtOAc : Hexane = 65 :30) as a colourless liquid (34 mg, 52%); $([\alpha]_D^{26}$ = –25.0 (*c* 0.024, DCM); IR (neat): 3406, 1738 and 1054 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.85 (s, 1H), 4.77 (s, 1H), 4.24 (q, 2H, J = 7.1 Hz), 4.10-4.04 (m, 2H), 2.54-2.38 (m, 2H), 1.77 (s, 3H), 1.31 (t, 3H, J = 7.1 Hz), 1.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 140.3, 114.6, 61.7, 56.2, 42.5, 22.6, 22.1, 14.1; HRMS: (ESI) calcd for $C_{12}H_{24}NO_3S$ $[M + H]^+$ 262.1477, found 262.1481.

(*R*)-2-methyl-*N*-((*S*)-3-methyl-1-(*p*-tolyl)but-3-en-1-yl)propane-2-sulfinamide (**26g**). Following the general procedure C described above, **26g** was obtained after purification by silica gel column chromatography (EtOAc : Hexane = 60 :40) as white solid (33 mg, 47%); $[\alpha]_D^{28}$ = –87.5 (*c* 0.032, DCM); mp = 51-53 °C; IR (KBr): 3414, 1645, 1063 and 738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, 2H, J = 8.0 Hz), 7.17 (d, 2H, J = 7.8 Hz), 4.95 (s, 1H), 4.89 (s, 1H), 4.51 (dd, 1H, J_1 = 8.2 Hz, J_2 = 5.7 Hz), 3.73 (s, 1H), 2.44-2.35 (m, 2H), 2.36 (s, 3H), 1.81 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 139.2, 137.3, 129.2, 127.4, 114.9, 55.6, 54.2, 48.0, 22.6, 21.8, 21.2; HRMS: (ESI) calcd for $C_{16}H_{26}NOS$ $[M + H]^+$ 280.1735, found 280.1707. This compound was isolated as a mixture of diastereomers and the NMR values were given with respect to major diastereomer.

Acknowledgements

This work was funded by IISER-Mohali. We thank the NMR, X-ray and HRMS facilities of IISER Mohali. We also thank the single crystal X-ray facility of the Department of Chemical Sciences, IISER-Mohali. C. R. and N. A. Aslam thank the CSIR-UGC, New Delhi, for SRF fellowships.

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The allylation of various cyclopentanone systems afforded the respective products with an excellent diastereoselectivity while the allylation of various cyclohexanone systems gave the corresponding products with relatively lower diastereoselectivity. A similar trend was observed in our previous work; see the ref. [16b] Though, we are unable to predict the exact reason for this, however, the conformational flipping in cyclohexane system could be the possible reason for the involvement of a less rigid TS thereby affording the products with relatively low diastereoselectivity when compared to the cyclopentane systems.

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21 Crystallographic data of the X-ray structures of the compounds **3g** (CCDC 1001586) and **26c** (CCDC 1001554) have been deposited at the Cambridge Crystallographic Data Centre.

Table of Contents

Stereoselective allylation of prostereogenic cycloalkanone and imine systems using allylic halides, aluminium powder and catalytic amount of $InCl_3$ is reported.