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Forming Stereogenic Centers in Acyclic Systems from Alkynes[**]

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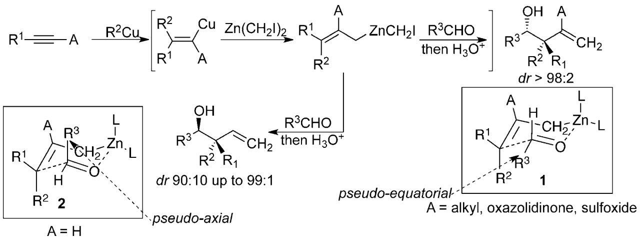
Abstract: *The combined carbometalation/zinc homologation followed by reactions with α-heterosubstituted aldehydes and imines proceed through a chair-like transition structure with the substituent of the incoming aldehyde residue preferentially occupying a pseudo-axial position to avoid the two gauche interactions. The heteroatom in the axial position produces a chelated intermediate (and not a Cornforth–Evans transition structure for α-chloro aldehydes and imines) leading to a face differentiation in the allylation reaction. This method provides access to functionalized products in which three new carbon–carbon bonds and two to three stereogenic centers, including a quaternary one, were created in acyclic systems in a single-pot operation from simple alkynes.*



Scheme 1. Diastereoselectivity in the γ,γ′-allylation reaction of carbonyl groups.

In the past few decades, we have witnessed tremendous achievements in the area of acyclic stereocontrol for the construction of carbon–carbon as well as carbon–heteroatom bonds in a stereoselective manner.[1] However, when structural complexity increases, the difficulty in reaching the desired products usually leads to a single carbon–carbon bond-forming event per chemical step between two components.[2] One element of structure that invariably increases the difficulty of a chemical synthesis is the presence of a quaternary carbon stereogenic center in the target molecule.[3,4] In this context, polyfunctional intermediates[5] such as carbenoids species (Scheme 1)[6] could be used as efficient tools to create consecutively the same number of carbon–carbon bonds as in a multi-step process, including quaternary carbon stereogenic centers, but in a single-pot operation. Particularly interesting is the difference of stereochemical outcome for the reaction of γ,γ′,β-trisubstituted allylzinc (Scheme 1, A = sulfoxide, alkyl, oxazolidinone) and γ,γ′-disubstituted allylzinc (Scheme 1, A = H) with aldehydes. In the former case, the diastereoselectivity of the reaction results from a Zimmerman–Traxler chair-like transition structure in which the incoming aldehyde aryl (alkyl) group occupies a pseudo-equatorial position to avoid potential 1,3-diaxial steric interactions with A as described for **1** (Scheme 1, A = sulfoxide, alkyl, oxazolidinone). However, the diastereoselectivity resulting from the reaction of γ,γ′-disubstituted allylzinc (A = H) with the same aldehydes lead to the opposite diastereoisomer as the same incoming aldehyde group now prefers to occupy a pseudo-axial position to avoid the two gauche interactions with the R^1 and R^2 groups (**2**, Scheme 1).[7] This axial preference in the Zimmerman–Traxler transition structure for the allylation reactions has been successfully extended to the allylation of ketones,[8a] α-alkoxyallylation of aldehydes and ketones.[8b,c]

Beside this interesting mechanistic stereochemical outcome, one potential advantage of having the substituent of the carbonyl group occupying a pseudo-axial position would be the ability to stereocontrol the allylation reactions of α-heterosubstituted aldehydes. Indeed, in the double diastereodifferentiation between chiral aldehydes and achiral allylmetal reagents, the α-heterosubstituted aldehydes tend to display different facial selectivity with either (*Z*)- or (*E*)-substituted allylmetal species.[9] In most cases where the incoming aldehyde residue possessing a stereogenic center occupies a pseudo-equatorial position, the stereochemistry of the final products originates from minimum steric interactions in the transition structure between the allylic partners and the chiral aldehydes.[10] These observations show that the configuration of the allylmetal species and the aldehyde are interdependent in determining the final stereochemical outcome of the reaction and moderate to good diastereoselectivities are obtained (Scheme 2, path A).[11] However, as intramolecular chelation between zinc and heteroatoms (O, S, N)[12] has been successfully used to control the stereochemical outcome of various transformations,[13] and as the incoming aldehyde group occupies a pseudo-axial position, then this α-heteroatom should lead to a chelated transition structure. Such chelation should then promote a face differentiation in the γ,γ′-allylation reaction of prochiral carbonyl

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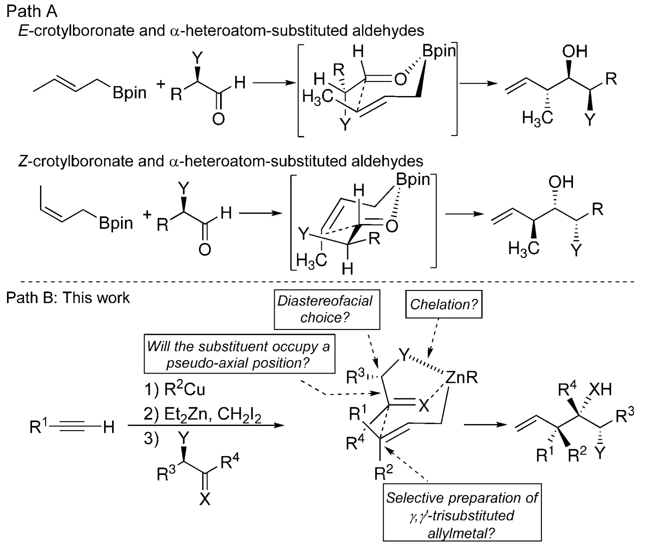
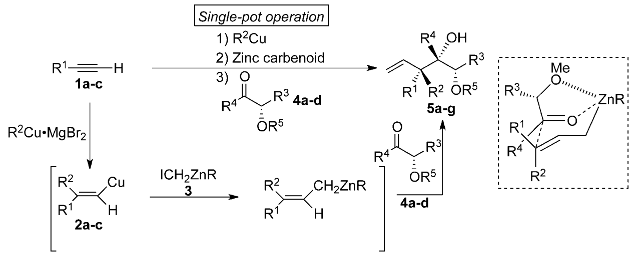


Scheme 2. Known work (path A) and synthetic strategy presented herein (path B).

Table 1: Diastereoselective formation of homoallylic alcohols **5a–g**.



Entry	R	R¹	R²	R³	R⁴	R⁵	d.r.[a]	Yield [%][b]
1	CH_2I	Et (**1a**)	Bu	Ph	H	Me	96:4:0:0	45 (**5a**)
2	CH_2I	Bu (**1b**)	Et	Ph	H	Me	96:4:0:0	45 (**5b**)
3	CH_2I	Bu (**1b**)	Et	Ph	H	TBS	96:4:0:0	42 (**5c**)
4	CH_2I	Bu (**1b**)	Et	Et	H	TBS	96:4:0:0	43 (**5d**)
5	CH_2I	Hex (**1c**)	Et	Ph	Ph	Me	97:3:0:0	53 (**5e**)
6	$OCOCF_3$	Hex (**1c**)	Et	Ph	H	Me	94:6:0:0	58 (**5f**)
7	$OCOCF_3$	Hex (**1c**)	Et	Ph	Ph	Me	95:5:0:0	65 (**5g**)

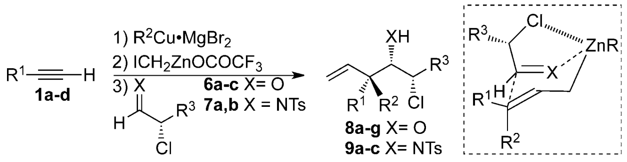
[a] Determined by ^1H NMR analysis of crude reaction mixture. [b] Yields of the major diastereoisomer determined after purification by column chromatography on silica gel.

derivatives as one face is shielded by the alkyl group R^3 as described in Scheme 2 (path B: this work). The proposed Scheme is appealing but the success of this single-pot strategy leading to complex molecular fragments with high diastereoisomeric ratio requires complete control of all parameters summarized in Scheme 2, path B. We started our study by performing a carbocupration reaction[14] on terminal alkyne **1a** leading to vinyl copper species **2a**. A zinc homologation/allylation reaction was performed by successive addition of Et_2Zn and CH_2I_2 [that leads to the in situ formation of the Simmons–Smith–Furukawa zinc carbenoid **3a** $Zn(CH_2I)_2$][5,15] and of the model 2-methoxy-2-phenylacetaldehyde **4a** ($R^3 = Ph$, $R^4 = H$, $R^5 = Me$).

We were pleased to observe the formation of the expected homoallylic alcohol **5a** possessing three stereogenic centers, including the formation of a quaternary carbon stereogenic center, in outstanding diastereoselectivity (d.r. >96:4:0:0) but in moderate 45% yield, although based on three consecutive chemical steps in a single-pot operation (Table 1, entry 1). To have a better mechanistic insight, we then permuted the nature of the alkyl groups R^1 and R^2 present on the alkyne and on the organocopper, respectively, and performed the same combined carbometalation/zinc homologation/allylation reaction. The opposite diastereoisomer **5b** was obtained in identical diastereoisomeric ratio and yield suggesting that the reaction proceeds through a cyclic transition structure (Table 1, entry 2). To make the methodology synthetically more attractive, the methyl group of the ether ($R^5 = Me$, Table 1, entries 1 and 2) was replaced by an easily removable silyl ether ($R^5 = SiMe_2tBu$) and similar diastereoselectivities were observed (Table 1, entry 3). The same type of diastereoselectivity was observed if the α-substituent of the aldehyde was an alkyl group ($R^3 = Et$, Table 1, entry 4) or if a ketone was used ($R^4 = Ph$, Table 1, entry 5). The configuration has been determined by X-ray analysis on **5e** (see the Supporting Information) and suggests that the biggest substituent of the carbonyl derivative occupies a pseudo-axial position in the chair-like transition structure to avoid the two gauche interactions with the γ,γ′-disubstituted allylzinc species. As expected, the alkoxy group chelates intramolecularly the zinc center inducing a differentiation between the two prochiral faces of the carbonyl group as described in the scheme above Table 1.[16] However, despite the excellent diastereoselectivities, yields need to be improved. Therefore, various carbenoid species were tested (i.e. samarium and aluminium carbenoids) in the homologation reaction of vinyl copper and the use of the Shi carbenoid, easily prepared by mixing equimolar amount of Et_2Zn, CH_2I_2, and trifluoroacetic acid (TFA),[17] was found to be the best compromise for good diastereoselectivity and yield. Hence, the addition of the Shi carbenoid $ICH_2ZnOCOCF_3$ to the vinyl copper species **2** in the presence of either α-substituted aldehyde or ketone led to the homoallylic alcohols **5f,g** in better yields (based on three consecutive chemical steps in one-pot reaction) and diastereoselectivities (Table 1, see entries 6 and 7, respectively).

Having in hand an approach for acyclic stereocontrol of several stereogenic centers including the formation of quaternary carbon stereogenic centers such as **5a–g**, we turned our attention to the formation of products that could be easily functionalized by standard chemical reactions. In this context, we were particularly interested to investigate the behavior of α-chloro aldehydes in our reaction sequence. Indeed, the allylation of α-halo carbonyl derivatives is well-known to proceed through a Cornforth–Evans transition structure (non-chelation pathway where dipole-dipole interactions are responsible for the anti-periplanar orientation of the C=O and C-X),[18] as illustrated by the addition of cinnamylzinc chloride to 3-chlorobutan-2-one at low temperature.[19] On the other hand, pioneering studies of Walsh showed that the diastereoselectivity could be reversed through coordination of the C−Cl bond to metals with α-chloro sulfonyl imines.[20] As the incoming carbonyl alkyl group occupies a pseudo-axial position in the allylation reaction of γ,γ′-disubstituted allylzinc, the addition of α-chloro carbonyl species should lead to a chelated chair-like transition structure providing good diastereoselectivity. We were indeed pleased to see that when the combined sequence of carbocupration reaction on terminal alkynes followed by the in situ zinc homologation with the Shi carbenoid $ICH_2ZnOCOCF_3$ and allylation reaction with α-chloro aldehydes **6** and α-chloro imines **7** was performed, the corresponding homoallylic alcohols and amines **8a–g** and **9a–c** were obtained in good overall isolated yields (Table 2). When R^3 was a primary alkyl group (Table 2, entry 1, $R^3 = Et$), the diastereoselectivity of the allylation reaction on the α-chloro aldehyde was rather poor. By increasing the size of the substituent R^3, good to excellent diastereomeric ratios were obtained (Table 2, compare entries 1, 2 and 5). When the two alkyl groups present on the alkyne and on the organocopper are different, the same diastereoisomeric ratio was obtained suggesting that the stereochemistry at the newly formed quaternary all-carbon stereocenter is fully controlled (Table 2, entry 3). When the nature of these two alkyl groups was permuted, similar diastereomeric ratios were obtained implying that the reaction indeed proceeds through a closed transition state (Table 2, compare entries 3 and 4). The same trend was observed for the reactions of α-chloro imines **7** as homoallyl amines **9a–c** were obtained in moderate to good yields as two diastereoisomers ranging from 85:15:0:0 to 100:0:0:0 ratios (Table 2, entries 8–10).

Table 2: Diastereoselective formation of homoallylic alcohols and amines **8** and **9**.

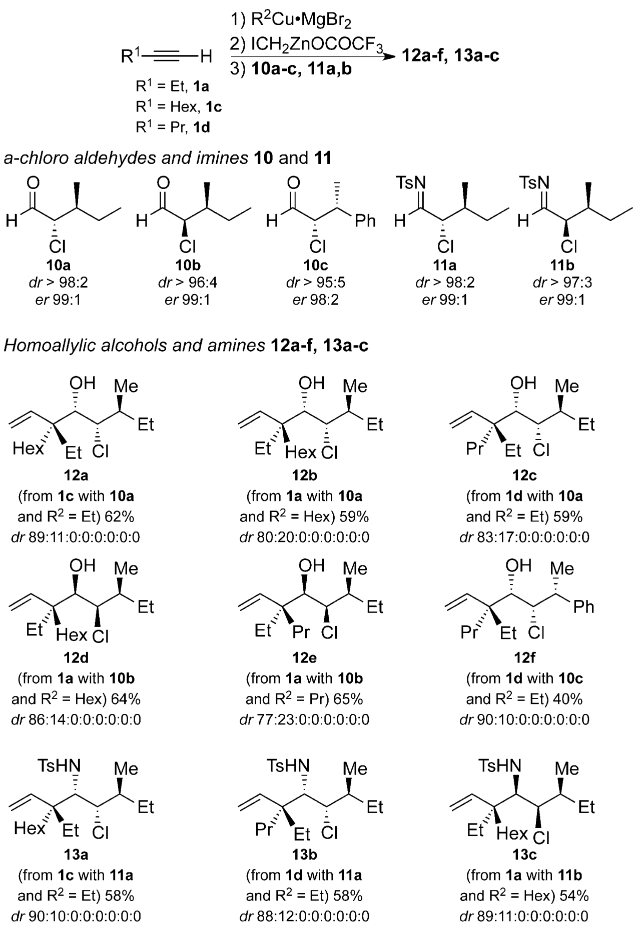


Entry	R^1	R^2	R^3	X	d.r.[a]	Yield [%][b]
1	Et (**1a**)	Et	Et	O (**6a**)	65:35	61 (**8a**)
2	Bu (**1b**)	Bu	*i*Pr	O (**6b**)	87:13	53 (**8b**)
3	Hex (**1c**)	Et	*i*Pr	O (**6b**)	88:12:0:0	64 (**8c**)
4	Et (**1a**)	Hex	*i*Pr	O (**6b**)	83:17:0:0	60 (**8d**)
5	Hex (**1c**)	Et	*t*Bu	O (**6c**)	100:0:0:0	53 (**8e**)
6	Bu (**1b**)	Et	*i*Pr	O (**6b**)	85:15:0:0	59 (**8f**)
7	Pr (**1d**)	Et	*i*Pr	O (**6b**)	80:20:0:0	60 (**8g**)
8	Pr (**1d**)	Et	*t*Bu	NTs (**7a**)	100:0:0:0	70 (**9a**)
9	Hex (**1c**)	Et	*i*Pr	NTs (**7b**)	90:10:0:0	63 (**9b**)
10	Pr (**1d**)	Et	*i*Pr	NTs (**7b**)	85:15:0:0	60 (**9c**)

[a] Determined by ^1H NMR analysis of crude reaction mixture.
[b] Determined after purification by column chromatography on silica gel.

The relative configuration of the products has been determined by X-ray analysis of **9a** (see the Supporting Information) and clearly suggests a transition structure in which the substituent of the aldehyde (or imine) indeed occupies a pseudo-axial position in a chair-like Zimmerman–Traxler transition structure in which the chloride atom chelates intramolecularly the zinc center of the γ,γ′-disubstituted allylzinc species. Although these combined carbocupration/zinc homologation/allylation reactions proceed smoothly with the expected stereochemical outcome, good to excellent diastereoselectivities were restricted to sterically encumbered R^3 groups. To meet this requirement while keeping in mind the goal of preparing several stereogenic centers in acyclic systems, α-chloro aldehydes and imines **10a–c** and **11a–b**, possessing an additional stereogenic center to mimic the required branched alkyl groups, were prepared from known procedures in excellent diastereo and enantiomeric ratios (Figure S1, see the Supporting Information).

When the combined carbometalation/zinc homologation and addition of α-chloro aldehyde **10a** was performed on **1c** ($R^1 = Hex$), the product **12a** was obtained in a good overall yield as two diastereomers in a ratio of 89:11 (Scheme 3), which is very similar to the ratio previously obtained when α-chloro aldehyde **6b** was used (compare Table 2, entry 3 with **12a** in Scheme 3).



Scheme 3. Diastereoselective reaction with α-chloro aldehydes **10** and imines **11**.

Therefore, the additional stereogenic center present in the α-chloro aldehyde does not have a detrimental effect on the stereochemical outcome and indeed mimic an *i*Pr group. The opposite diastereoisomer at the quaternary carbon center **12a** can easily be prepared by permuting the nature of the substituent R^1 and R^2 and this method can be extended to various alkyl groups (**12a** and **12b** respectively, Scheme 3). Interestingly, when the combined reaction was performed on the opposite diastereoisomer **10b** or on differently substituted chiral α-chloro aldehyde (**10c**), similar diastereoselectivity are obtained (formation of **12d–f**). Finally, when chiral α-chloro imines were used (**11a,b**), only two out of the eight possible diastereoisomers were obtained in an approximately 90:10 ratio whatever are the absolute configuration of the starting imines (**11a** or **11b**). In conclusion, the combined carbometalation/zinc homologation and reactions with α-heterosubstituted aldehydes and imines proceed through chair-like transition structures with the substituent of the incoming aldehyde residue preferentially occupying a pseudo-axial position to avoid the two gauche interactions. Moreover, the heteroatom present in the axial position produces a chelated intermediate (and not a Cornforth–Evans transition structure for α-chloro aldehydes and imines) leading to face differentiation in the allylzincation reaction. This method provides access to functionalized adducts in which three new carbon-carbon bonds and two to three stereogenic centers, including a quaternary carbon stereogenic center, were created in acyclic systems in a single-pot operation from simple alkynes.

Keywords: acyclic stereoselection · allylation · chelation · quaternary carbon center · zinc carbenoids

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