DOI: 10.1002/ejoc.200700424

Influence of the Double-Bond Geometry of the Michael Acceptor on Copper-Catalyzed Asymmetric Conjugate Addition

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Keywords: Michael addition / Asymmetric catalysis / Diethylzinc / Copper / Double-bond geometry

Focusing on mechanistic aspects, a study of the influence of the (*E*)/(*Z*) double-bond geometry of the Michael acceptor on the enantioselectivity of copper-catalyzed asymmetric conjugate addition reactions has been realized. In spite of numerous articles concerning copper-catalyzed asymmetric conjugate addition reactions, the major factors of such a reaction are quite difficult to elucidate. Although our experiments have not allowed us to define strict rules, they have highlighted some factors not to be neglected when considering the approach of the copper reagent to the double bond, such as (*E*)/(*Z*) isomerization and steric aspects, which could change the reactive conformation of the substrate. Electronic effects could also modify the polarization of the double bond and influence the nucleophilic attack.

Introduction

The asymmetric conjugate addition (ACA) reaction has received considerable interest over the past decade.[1] Enantioselectivities reaching more than 99% can be obtained with cyclic and acyclic substrates when dialkylzinc species are used. Only a few examples concerning the influence of the double-bond geometry on the enantioselectivity of copper-catalyzed ACA reactions have been reported in the literature. Imamoto and Mukaiyama reported the first instance, in 1980, of a Cu-catalyzed 1,4-addition of methyl Grignard species to (*Z*)- and (*E*)-1,3-diphenylprop-2-en-1-one with a prolinol derivative as the chiral ligand.[2] The authors showed that the same major enantiomer is obtained with the same level of enantioselectivity irrespective of the geometry of the starting material. They also observed that there is an isomerization of the double bond in favour of the thermodynamically more stable (*E*) substrate since, in reactions that do not go to completion, it is recovered at the end of the reaction. Hird and Hoveyda reported the Cu-catalyzed ACA of zinc species to (*Z*)- and (*E*)-α,β-unsaturated *N*-acyloxazolidinone.[3] In this case, the opposite major enantiomer is obtained if the double-bond geometry is modified. This phenomenon means that the face selectivity of the nucleophilic attack remains the same irrespective of the geometry of the double bond. The lower enantioselectivity could be explained by isomerization of the double bond and addition to both isomers. Recently, Loh and co-workers studied the influence of the double-bond geometry during the Cu-catalyzed ACA of Grignard reagents to α,β-unsaturated esters.[4] Changing the double-bond geometry led to the formation of the opposite enantiomer with higher enantioselectivities. This was also the case in a similar study on Cu-catalyzed ACA reactions of Grignard reagents carried out by Feringa and co-workers.[5] An interesting difference between enones and α,β-unsaturated esters concerning the double-bond isomerization rate was revealed. They reported that α,β-unsaturated esters slowly isomerize in contrast to aromatic enones. However, there are not enough instances in the literature to draw conclusions about the influence of the double-bond geometry on the copper-catalyzed asymmetric conjugate addition reactions. Therefore, we decided to investigate this feature in more detail in order to try to determine the general factors that have an important effect on the enantioselectivity of the Cu-catalyzed ACA of diethylzinc.

Results and Discussion

Several (*E*) and (*Z*) Michael acceptors with different steric or electronic properties were used (Figure 1).

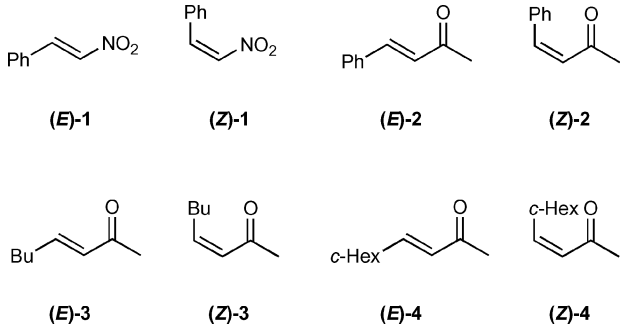

Figure 1. Enones used in this study.

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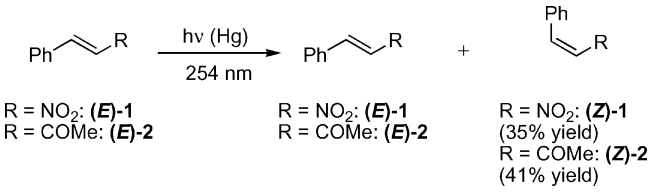
Synthesis of the Substrates

The non-commercially available substrates were prepared according to reported procedures. **(*Z*)-1**[6] and **(*Z*)-2**[7] were isolated as the pure (*Z*) compounds by flash chromatography after photoisomerization of the (*E*) substrates using a mercury-vapour lamp (Scheme 1).



Scheme 1. Isomerization of Michael acceptors.

The pure compounds **(*Z*)-3** and **(*Z*)-4** were prepared by a sequence of carbocupration/carbonation[8a] followed by the reaction of the resulting carboxylic acids with 2 equiv. of methyllithium (Scheme 2). Thus, for **(*Z*)-3**, the reaction of $Bu_2CuLi{\cdot}LiI$ with acetylene in Et_2O gave the bis(vinylic) cuprate which was treated with carbon dioxide (dry ice) in order to generate the pure (*Z*)-carboxylic acid after acidic workup in quantitative yield.[8b] For **(*Z*)-4**, the carbocupration reaction was performed in THF with a cyclohexylmagnesium/copper reagent[8c] followed by carbonation under Normant's conditions[8d] in 45% yield. The reaction of the acids with 2 equiv. of methyllithium in Et_2O generated the desired pure (*Z*)-enones **(*Z*)-3** and **(*Z*)-4** in 80 and 71% yields, respectively. Finally, **(*E*)-4** was prepared by an aldolization/crotonization reaction.[9]

Preliminary Results

Initially, we thought that the nucleophilic attack occurred from the same face irrespective of the geometry of the double bond. If this was generalized, the opposite major enantiomer should be obtained when changing the geometry of the double bond and keeping the same catalytic system (copper salt, ligand, solvent and temperature), as shown in Figure 2.

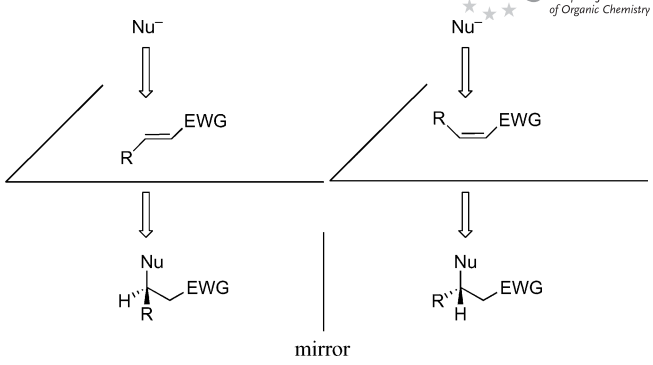
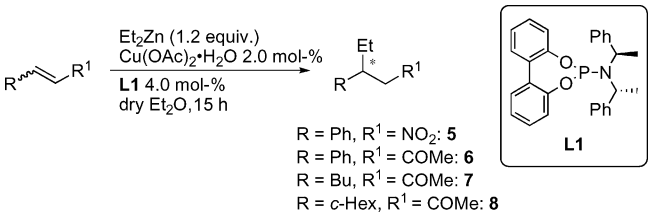


Figure 2. Approaches of the nucleophile in the double-bond attack.

To verify this hypothesis, diethylzinc was added to the (*E*) and (*Z*) substrates in the presence of copper and simple phosphoramidite ligand **L1** under experimental conditions developed by our group (Scheme 3, Table 1).[10] Surprisingly, the opposite major enantiomer was obtained only

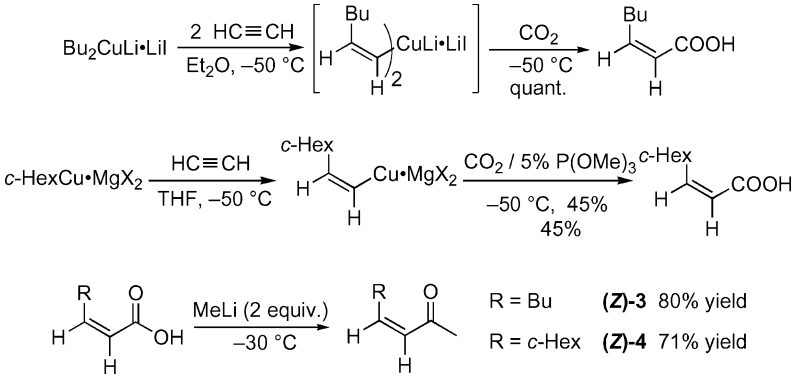


Scheme 3. General procedure used for Cu-catalyzed ACA reactions of Et_2Zn.

Table 1. Cu-catalyzed ACA reactions of Et_2Zn.

Entry	Substrate	T [°C]	Conv.[a] [%]	*ee*[b] [%] (abs. conf.)
1	**(*E*)-1**	–20	>95	64 (*R*)
2	**(*Z*)-1**	–20	>95	44 (*R*)
3	**(*E*)-2**	–30	>95	76 (*R*)
4	**(*Z*)-2**	–30	>95	92 (*R*)
5	**(*E*)-3**	–30	>95	42 (*R*)
6	**(*Z*)-3**	–30	>95	62 (*S*)
7	**(*E*)-4**	–30	>95	82 (*R*)
8	**(*Z*)-4**	–30	>95	76 (*R*)

[a] Conversion determined by GC/MS. [b] *ee* determined by chiral GC.



Scheme 2. Carbocupration reaction to form **(*Z*)-3** and **(*Z*)-4**.

once when the linear substrate **3** was used (Table 1, Entries 5 and 6) and with a better enantioselectivity for the adduct derived from the (*Z*) compound. Other substrates gave the same major enantiomer, irrespective of the geometry of the double bond. The asymmetric induction of the adduct generated from the 4-phenylbut-3-en-2-one (**2**) was higher when the (*Z*) substrate was used (Table 1, Entries 3 and 4), in contrast to nitrostyrene (**1**) for which a lower enantioselectivity was observed (Table 1, Entries 1 and 2). Finally, 4-cyclohexylbut-3-en-2-one (**4**) afforded the 1,4-adduct with similar levels of enantioselectivity (Table 1, Entries 7 and 8). These first results are in contrast to our initial hypothesis except for the oct-3-en-2-one (**3**) for which the nucleophilic attack occurred at the same face of the Michael acceptor.

Study of the Isomerization of the Double Bond During the Cu-Catalyzed ACA of Et_2Zn

The phenomenon of isomerization of the double bond could explain and justify why the same major enantiomer was obtained even though the geometry of the double bond was inverted. This isomerization process was reported by Corey and Boaz in 1985 during the reaction between Gilman reagents and α,β-unsaturated enones.[11a] The isomerization of the double bond is feasible because of the reversible d–π* complexation[11b–11d] which leads to the thermodynamically more stable (*E*) substrate. The isomerization process was studied by applying the general procedure described in Scheme 3 for nitrostyrene (**1**; Table 2) and 4-phenylbut-3-en-2-one (**2**; Table 3).

The asymmetric induction was the same for the entire reaction when **(*E*)-1** was used and no isomerization of the double bond was observed (Table 2, Entry 1). Performing the ACA reaction using **(*Z*)-1** once without diethylzinc and once without the copper salt revealed that no conjugate addition occurred, but an important isomerization phenomenon did occur after only 15 min of reaction (around 70%; Table 2, Entries 2 and 3, respectively). Moreover, when the reaction was carried out with all the reagents, the reaction was complete in less than 15 min and the asymmetric induction was largely inferior (32%; Table 2, Entry 4) to that obtained with **(*E*)-1** (64%; Table 2, Entry 1). It seemed that the double-bond isomerization was the major process in this reaction. As the same major enantiomer was obtained irrespective of the double-bond geometry, the nucleophile could have approached from the same face but at a slower rate than the isomerization process. This could account for the decrease in the enantiomeric excess that was observed when (*Z*)-nitrostyrene [**(*Z*)-1**] was used.

Similarly, the asymmetric induction remained constant during the entire reaction when **(*E*)-2** was used and no isomerization of the double bond was observed (Table 3, Entry 1). However, performing the ACA reaction using **(*Z*)-2** once without diethylzinc and once without the copper salt revealed that no conjugate addition reaction occurred, but that a small amount of isomerization had occurred after only 15 min reaction time (7 and 11%, respectively; Table 3, Entries 3 and 4). If all components took part in the reaction, a small decrease in the asymmetric induction between the beginning (96%) and the end (92%) of the reaction was noticed (Table 3, Entries 2 and 5, respectively). When the reaction was quenched before the complete consumption of the starting materials, a large quantity of isomerized substrate was formed (55% of the remaining substrate), whereas 56% of the 1,4-adduct was generated (Table 3, Entry 5). We could not exclude the isomerization process during the Cu-catalyzed ACA of Et_2Zn to 4-phenylbut-3-en-2-one (**2**), but it did not seem to be the main one. In fact, the isomerization of the double bond could not explain why the enantiomeric excess was largely superior when **(*Z*)-2** was used. In theory, if the nucleophilic approach remained the same and there was an isomerization of the double bond, the asymmetric induction should be, in the best case, equal to that obtained for the opposite isomer. This was not the case and it can be assumed that other effects (steric or elec-

Table 2. Study of the isomerization of nitrostyrene (**1**) at –20 °C.

Entry	Substrate	Et_2Zn [equiv.]	$Cu(OAc)_2·H_2O$ [mol-%]	Ligand [mol-%]	Time	^{1}H NMR proportion [%]			*ee* (%)[a] (abs. conf.)
						(*Z*)-1	**(*E*)-1**	**5**	
1	**(*E*)-1**	1.2	2.0	4.0	48 h	0	0	100	64 (*R*)[b]
2	**(*Z*)-1**	–	2.0	4.0	15 min	31	69	0	n.d.
3	**(*Z*)-1**	1.2	–	4.0	15 min	30	70	0	n.d.
4	**(*Z*)-1**	1.2	2.0	4.0	15 min	0	0	100	32 (*R*)

[a] *ee* was determined by chiral GC. [b] *ee* is constant (determined by chiral GC at different reaction times and conversions).

Table 3. Study of the isomerization of 4-phenylbut-3-en-2-one (**2**) at –20 °C.

Entry	Substrate	Et_2Zn [equiv.]	$Cu(OAc)_2·H_2O$ [mol-%]	Ligand [mol-%]	Time	GC/MS proportion [%]			*ee* [%][a] (abs. conf.)
						(*Z*)-2	**(*E*)-2**	**6**	
1	**(*E*)-2**	1.2	2.0	4.0	48 h	0	0	100	75 (*R*)[b]
2	**(*Z*)-2**	1.2	2.0	4.0	18 h	0	0	100	92 (*R*)
3	**(*Z*)-2**	–	2.0	4.0	15 min	93	7	0	n.d.
4	**(*Z*)-2**	1.2	–	4.0	15 min	89	11	0	n.d.
5	**(*Z*)-2**	1.2	2.0	4.0	15 min	20	24	56	96 (*R*)

[a] *ee* was determined by chiral GC. [b] *ee* is constant (determined by chiral GC at different reaction times and conversions).

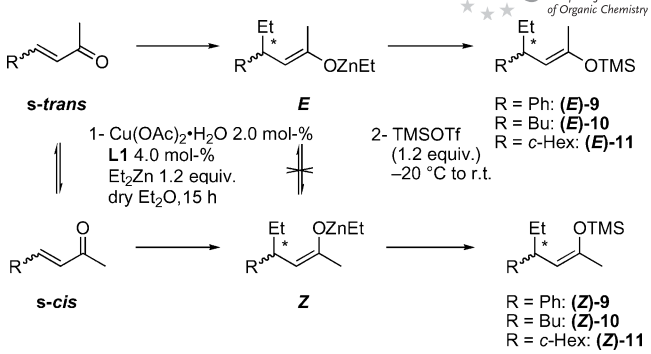
tronic, for instance) influenced the nucleophilic approach to explain the formation of the same major enantiomers. In both cases, the small amount of isomerization that occurred with Et_2Zn or the Cu salt alone could be explained by the Lewis acidity of these metals.

In contrast to previous results, the experimental conditions did not favour the double-bond isomerization of 4-cyclohexylbut-3-en-2-one (**4**) even if the same major enantiomer was generated with similar enantioselectivities. It is noteworthy that **(*Z*)-4** reacted more slowly than the (*E*) compound. When the reaction was quenched at 50% conversion, the (*Z*)/(*E*) ratio of the unreacted starting material was in excess of 95:5.

Determination of the s-*cis*/s-*trans* Conformation of the Enones During the Cu-Catalyzed ACA of Et_2Zn

Another explanation for the results obtained in Table 1 and the formation of the same major enantiomer by using the opposite isomer is that the (*E*) and (*Z*) isomers of the enones could react under different s-*trans* or s-*cis* conformations. The reaction of each isomer in a different conformation could explain the inversion of the nucleophilic approach by changing the steric constraints. To determine the conformation of the enones studied during the copper-catalyzed ACA of Et_2Zn, the previous method developed in our group by Knopff and Alexakis for the formation of enantioenriched silylenol ethers by a tandem ACA/silylation reaction was used.[12] It was demonstrated that the ratio of the (*E*)- and (*Z*)-silylenol ethers synthesized was representative of the ratio of the s-*trans* and s-*cis* forms of the enones used for the Cu-catalyzed ACA of diethylzinc in the presence of a phosphoramidite-type ligand. These conclusions were made because there is no equilibration between the two zinc enolate species generated by the Cu-catalyzed ACA reaction. Moreover, the ratio between the s-*trans* and the s-*cis* conformers of enones did not affect the enantiomeric excess. The ratio of each conformer of each substrate [(*E*) and (*Z*)] during the Cu-catalyzed asymmetric conjugate addition of Et_2Zn in the presence of a phosphoramidite ligand (**L1**) was determined by this methodology (Scheme 4, Table 4). The goal of these attempts was to find out if the modification of the double-bond geometry could affect the conformation of the enone and consequently explain a modification of the facial approach of the nucleophile. The (*E*)/(*Z*) ratio was determined by ^{1}H NMR analysis of the crude mixture by comparison with the results obtained by House et al. for the preparation of trimethylsilylenol ethers.[13] The position of the NMR peak due to the β-vinyl proton of enol ethers allows the assignment of the stereochemistry of silylenol ethers. In the isomer with the β-vinyl proton and the oxygen function *cis* [(*E*) compound], the position of the β-vinyl proton resonance is at a lower field by around 0.2–0.3 ppm than that of the (*Z*) compound.

The conformation of the substrate did not seem influenced by the double-bond geometry except for the sterically hindered 4-cyclohexylbut-3-en-2-one (**4**) for which changing



Scheme 4. Tandem Cu-catalyzed ACA silylation.

Table 4. Formation of silylenol ethers and the (*E*)/(*Z*) ratio.

Entry	Substrate	*T* [°C]	(*E*)/(Z) ratio[a]	Major conformer
1	**(*E*)-2**	–20	81:19	s-*trans*
2	**(*Z*)-2**	–20	71:29	s-*trans*
3	**(*E*)-3**	–20	86:14	s-*trans*
4	**(*Z*)-3**	–20	79:21	s-*trans*
5	**(*E*)-4**	–30	58:42	s-*trans*
6	**(*Z*)-4**	–30	30:70	s-*cis*

[a] (*E*)/(*Z*) ratio was determined by ^{1}H NMR spectroscopy.

the double-bond geometry led to an inversion of the major conformer in favour of the s-*cis* compound for **(*Z*)-4** (Table 4, Entries 5 vs. 6). Other enones preferred to react mainly under an s-*trans* conformation, in accordance with Knopff's results. As (*E*)- and (*Z*)-4-phenylbut-3-en-2-ones (**2**) reacted under the same s-*trans* conformation (Table 4, Entries 1 and 2), a modification of the nucleophilic approach due to steric effects can be excluded. The formation of the same major enantiomer cannot be explained by steric hindrance and/or modification of the major conformer. Oct-3-ene-2-one (**3**) reacted under an s-*trans* conformation irrespective of the geometry of the double bond (Table 4, Entries 3 and 4) although opposite major enantiomers were obtained (Table 1, Entries 5 and 6). This allowed us to confirm that the face selectivity remained the same irrespective of the double-bond geometry. Finally, **(*Z*)-11** was obtained from **(*Z*)-4**, whereas **(*E*)-11** was generated from **(*E*)-4**. Based on Knoppf's results, we can assume that **(*Z*)-4** reacted under an s-*cis* conformation, whereas **(*E*)-4** reacted under an s-*trans* conformation. The same major enantiomer with the same level of enantioselectivity was obtained (Table 1, Entries 7 and 8). By mainly reacting under an s-*cis* conformation, **(*Z*)-4** could prevent the nucleophilic approach at one face due to steric hindrance, and the nucleophilic species has to invert its approach. This modification of conformation could be a key point in the explanation of the formation of the same major enantiomer starting from the substrate with the opposite geometry of the double bond.[14]

Ligand Screening

Finally, it could also be assumed that there is no possible comparison or correlation between the (*E*) and (*Z*) substrates. They could react as different substrates with no

similarities in their structure. That could explain why higher enantioselectivities were obtained when the (*Z*) substrates of **2** and **3** were used. To check this hypothesis ligand screening was performed (Figure 3). If there were similarities between the two isomers of a given substrate, the same trend in enantioselectivity should be observed. For an inefficient ligand, the observed enantiomeric excesses for the two adducts should decrease. In contrast, if there were no similarities, an opposite trend should be noticed. The 4-phenylbut-3-en-2-ones **(*E*)-2** and **(*Z*)-2** (Table 5) and the oct-3-en-2-ones **(*E*)-3** and **(*Z*)-3** (Table 6) were submitted to the Cu-catalyzed ACA of diethylzinc.

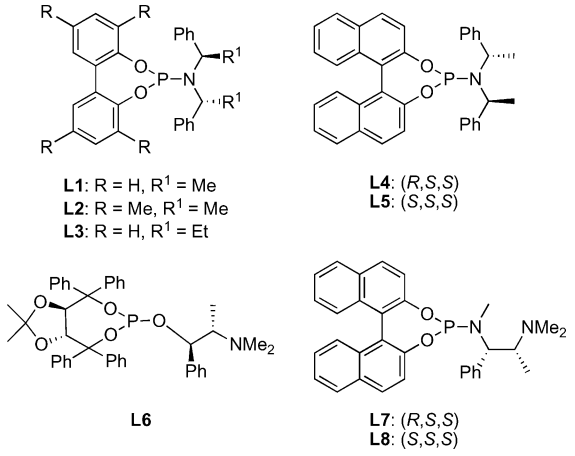
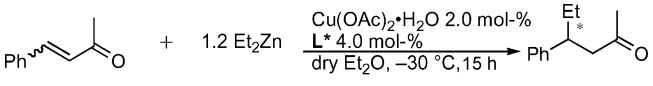


Figure 3. Ligands used in this study.

Table 5. Ligand screening as applied to 4-phenylbut-3-en-2-one (**2**).



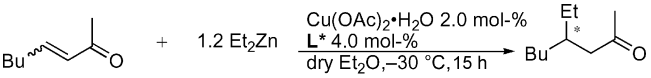
2 **6**

Entry	Substrate	Ligand	Conv.[a] [%]	*ee* [%][b,c]
1	**(*E*)-2**	**L1**	>98	76 (*R*)
2	**(*Z*)-2**	**L1**	>98	96 (*R*)
3	**(*E*)-2**	**L2**	>98	88 (*R*)
4	**(*Z*)-2**	**L2**	>98	94 (*R*)
5	**(*E*)-2**	**L3**	92	82 (*R*)
6	**(*Z*)-2**	**L3**	96	88 (*R*)
7	**(*E*)-2**	**L6**	74	36 (*S*)
8	**(*Z*)-2**	**L6**	86	20 (*S*)
9	**(*E*)-2**	**L7**	94	16 (*S*)
10	**(*Z*)-2**	**L7**	99	88 (*S*)
11	**(*E*)-2**	**L8**	75	34 (*R*)
12	**(*Z*)-2**	**L8**	98	90 (*R*)

[a] Conversion was determined by GC/MS. [b] *ee* was determined by chiral GC. [c] The absolute configuration is given in parentheses.

The (*Z*) substrate **(*Z*)-2** had a slightly higher reactivity than the (*E*) isomer since conversions were similar or superior. In all cases the same major enantiomer was obtained which seems to confirm that the nucleophilic approach is changed by a modification of the double-bond geometry. The asymmetric induction was always higher for the 1,4-adduct **6** derived from **(*Z*)-2** in the presence of a phosphoramidite-type ligand. In contrast, when a TADDOL derivative was used, the enantiomeric excess was higher for the 1,4-adduct derived from **(*E*)-2** (**L6**; Table 5, Entries 7 vs. 8). However, comparison of absolute values of the enantiomeric excesses of adducts derived from **(*E*)-2** and **(*Z*)-2** showed that the enantiomeric excesses did not follow the same trend. For instance, comparison of the results obtained with **L1** and **L2** or **L3** showed an increase in the enantiomeric excess for the adduct derived from the (*E*) substrate [**(*E*)-2**] and a decrease for the (*Z*) one. In contrast, comparison of the results obtained with **L2** and **L7** or **L8** showed a decrease in the enantiomeric excess for the adduct derived from the two substrates the magnitude of which differed depending on the double-bond geometry (Table 5, Entries 1, 2 and 9–12). Since they did not follow the same trend, these two substrates have probably to be studied independently of each other.

Table 6. Ligand screening as applied to oct-3-en-2-one (**3**).



3 **7**

Entry	Substrate	Ligand	Conv.[a] [%]	*ee* [%][b,c]
1	**(*E*)-3**	**L1**	>98	44 (*R*)
2	**(*Z*)-3**	**L1**	>98	60 (*S*)
3	**(*E*)-3**	**L2**	>98	30 (*R*)
4	**(*Z*)-3**	**L2**	95	62 (*S*)
5	**(*E*)-3**	**L3**	>98	32 (*R*)
6	**(*Z*)-3**	**L3**	90	42 (*S*)
7	**(*E*)-3**	**L4**	>98	22 (*S*)
8	**(*Z*)-3**	**L4**	95	55 (*R*)
9	**(*E*)-3**	**L5**	>98	14 (*R*)
10	**(*Z*)-3**	**L5**	96	0
11	**(*E*)-3**	**L6**	>98	0
12	**(*Z*)-3**	**L6**	69	0
13	**(*E*)-3**	**L8**	>98	56 (*S*)
14	**(*Z*)-3**	**L8**	92	14 (*R*)

[a] Conversion was determined by GC/MS. [b] *ee* was determined by chiral GC. [c] The absolute configuration is given in parentheses.

The (*Z*) substrate **(*Z*)-3** was less reactive than the (*E*) isomer since the conversions were worse, except in the case of **L1**. The TADDOL derivative **L6** did not lead to any asymmetric induction in either case (Table 6, Entries 11 and 12). In all cases, the opposite major enantiomer was obtained, which seems to confirm that the nucleophilic approach remains the same. The asymmetric induction was not always higher for the 1,4-adducts derived from the (*Z*) substrate [**(*Z*)-2**; Table 6, Entries 9 vs. 10 and 13 vs. 14]. However, comparison of the absolute values of the enantiomeric excesses of adducts derived from **(*E*)-2** and **(*Z*)-2** showed that the enantiomeric excesses did not follow the same trend. For instance, comparison of the results obtained with **L1** and **L2** showed a decrease in the enantiomeric excess for the adduct derived from the (*E*) substrate **(*E*)-2** and an increase in the enantiomeric excess of the opposite one. Similarly, comparison of the results obtained with **L1** and **L8** showed an increase in the enantiomeric excess of the adduct derived from the (*E*) substrate and a decrease in the opposite one. In contrast, comparison of the

results obtained with **L7** and **L3** showed a decrease in the enantiomeric excess for each adduct of around 30% of the initial value. The same trend was observed between **L1** and **L4** but the enantiomeric excess decreased to a different extent depending on the double-bond geometry. Lastly, the usual matched and mismatched effects of **L4** and **L5** were noticed here (Table 6, Entries 7–10). With regard to oct-3-en-2-one (**3**), ligand screening allowed us to confirm that the nucleophilic approach remained the same irrespective of the geometry of the double bond of the starting material. Since these two substrates did not follow the same tendency on changing the ligand, we can assume that, probably, these two substrates have to be studied independently of each other.

Conclusions

Based on the results of the ligand screening and on the different behaviour of the (*E*) and (*Z*) substrates, it is clear that many reasons have to be considered to account for the results obtained in the copper-catalyzed ACA reactions described herein. In the case of nitrostyrene (**1**) the isomerization of the double bond by a reversible d–π* interaction is the main reason for the results obtained. The same enantioselectivity observed for **4** could be explained by a change in the reactive conformer from s-*trans* to s-*cis*.[14] The results with **3** with a linear aliphatic substituent are in line with those of Hoveyda,[3] Loh[4] and Feringa[5] and their coworkers who also observed a reversal of enantioselectivity. However, when an aromatic substituent is present, such as in **2**, neither an isomerization process nor a change in the reactive conformer can explain the higher enantioselectivity obtained with the (Z) substrate. Therefore, other effects should be considered. One possibility would be to consider the carbon atoms in the α- and β-positions with respect to the EWG and their properties due to the electronic effects of their environment. Their influence could be very important during d–π* interactions. Two possibilities could be envisaged (Figure 4). Duhamel and Plaquevent have already reported these kinds of observations with regard the enantioselective protonation of prochiral enolates.[15] The copper cluster could preferentially "recognize" the carbon atom at the α-position, so there is no influence of the geometry of the double bond, and the opposite major enantiomers should be obtained since the nucleophilic approach should not differ. In this case, it is necessary to work with the pure (*Z*) and (*E*) isomers since products with the opposite configuration are obtained. Similarly, the copper cluster could also "recognize" the carbon atom in the β-position. In this case, modification of the double-bond geometry could modify the facial approach of the nucleophile, leading to the same major enantiomer. It is not necessary to work with the pure (*Z*) and (*E*) isomers since the two pure forms, as well as their mixtures, afford the same enantiomer.

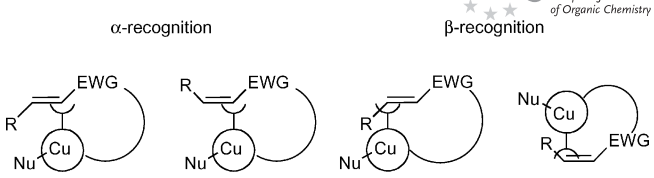


Figure 4. α- and β-recognition patterns in the nucleophilic approach to the vinyl group.

If we consider the studied cases, the EWG is the same in **2** and **3** and the electronic influence on the α-carbon atom in the carbonyl moiety is, thus, the same in both substrates. The only difference is the replacement of a butyl group (**3**) by a phenyl one (**2**) which leads to different electronic effects. The double bond in oct-3-en-2-one (**3**) is subject to the high EWG effects of the ketone on the one hand and to the weak inductive donor effects on the other. It is possible to assume that the copper complex preferentially "recognizes" the α-carbon atom with a high negative polarization during the d–π* interaction. In this case, modification of the double-bond geometry does not influence the nucleophilic approach that occurs at the same face to give opposite enantiomers. The double bond in 4-phenylbut-3-en-2-one (**2**) is subject to the high EWG effects of the ketone on the one hand and to the electronic effects of the phenyl on the other. It is possible to assume that the influence of the phenyl group is stronger than that of the ketone because of π-electron delocalization and that the copper complex preferentially "recognizes" the β-carbon atom just before oxidative addition. Therefore, modification of the double-bond geometry changes the nucleophilic approach which occurs at the opposite face to give the same enantiomer. Changes in the electronic properties of the aromatic group by substitution could shed more light on this aspect. This is, however, beyond the scope of this article.

Experimental Section

General Methods: All reactions were carried out under argon with oven-dried glassware. Solvents were dried by filtration through alumina previously activated at 350 °C under nitrogen for 12 h before use. All solvents were degassed by nitrogen-bubbling before use in all experiments. Diethylzinc [15 wt.-% in hexane (Acros)] and methyllithium [1.6 M in diethyl ether (Acros)] were used without any further purification. $Cu(OAc)_2 \cdot H2O$ (Merck) was purchased and used without any further purification. Evolution of the reaction was monitored by GC/MS with a Hewlett-Packard (EI mode) HP6890-5973 apparatus or by TLC (visualisation by UV and anisaldehyde, $KMnO_4$ or PMA staining). Flash chromatography was performed by using silica gel (32–63 μm, 60 Å). ^1H (300, 400 or 500 MHz) and ^{13}C (75, 100 or 125 MHz) NMR spectra were recorded in $CDCl_3$ with Bruker AMX-300, -400 or -500 spectrometers. Chemical shifts (δ) are given in ppm relative to residual deuteriated solvent. Coupling constants are reported in Hz. Enantiomeric excesses were determined by chiral GC (capillary column, 10 psi H_2) and the temperature programs used are described as follows: initial temperature [°C] – initial time [min] – temperature gradient [°C/min] – final temperature [°C]. Retention times (*Rt*) are given in min. Absolute configurations were assigned by comparison with authentic samples.

(*Z*)-Nitrostyrene [(*Z*)-1]:[6] A solution of (*E*)-nitrostyrene (2.02 g, 13.5 mmol) in cyclohexane (125 mL) was irradiated with a mercury-vapour arc lamp (254 nm) for 16 h. The solvent was removed in vacuo, and the crude mixture was purified by flash chromatography (pentane/Et_2O, 4:1) to afford the desired product as a yellow oil in 35% yield [97% of the (*Z*) isomer]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58–7.26 (m, 5 H, Ar), 6.94 (d, $^1J_{H,H}$ = 9.6 Hz, 1 H, CH), 6.75 (d, $^1J_{H,H}$ = 9.6 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.5, 133.9, 130.6, 130.4, 129.8, 128.5 ppm.

(*Z*)-4-Phenylbut-3-en-2-one [(*Z*)-2]:[7] A solution of (*E*)-4-phenylbut-3-en-2-one (*E*)-**2** (10.34 g, 70.73 mmol) in diethyl ether (125 mL) was irradiated with a mercury-vapour arc lamp (254 nm) for 20 h. The solvent was removed in vacuo, and the crude mixture was purified by flash chromatography (pentane/Et_2O, 4:1) to afford the desired product in 41% yield [97% of the (*Z*) isomer] as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.29 (m, 5 H, Ar), 6.85 (d, $^1J_{H,H}$ = 12.6 Hz, 1 H, CH), 6.14 (d, $^1J_{H,H}$ = 12.6 Hz, 1 H, CH), 2.11 (s, 3 H, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.7, 139.9, 135.2, 129.3, 129.2, 129.1, 128.4, 30.7 ppm.

(*Z*)-Hept-2-enoic Acid:[8b] In a reactor equipped with a mechanical stirrer and under nitrogen, copper iodide (10.55 g, 100.8 mmol) was suspended in dry diethyl ether (250 mL) at room temperature. The solution became grey. At –50 °C, *n*-butyllithium (63.0 mL of a 1.6 M solution in hexane) was added dropwise. The mixture turned black. Acetylene (2.25 L) was bubbled into the mixture. After 30 min of stirring, dry ice (CO_2) was bubbled from a flask into the green solution during 2 h. The crude mixture was quenched with a solution of NH_4Cl/HCl (3:1, v/v) for 30 min. After filtration through Celite and separation, the aqueous layer was extracted three times with diethyl ether. The organic layers were washed with NaOH (1.5 M), and concentrated HCl was added to the aqueous layer until pH = 1. A last extraction of the aqueous layer with diethyl ether was performed (three times). The combined organic layers were dried with Na_2SO_4 and concentrated in vacuo to give 6.47 g of the title compound as a yellow-brown oil in quantitative yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.73 (s, 1 H, OH), 6.32 (dt, $^1J_{H,H}$ = 11.5, $^2J_{H,H}$ = 7.5 Hz, 1 H, CH), 5.75 (dt, $^1J_{H,H}$ = 11.5, $^2J_{H,H}$ = 1.4 Hz, 1 H, CH), 2.64 (ddt, $^1J_{H,H}$ = 7.5, $^2J_{H,H}$ = 7.0, $^3J_{H,H}$ = 1.5 Hz, 2 H, CH_2), 1.46–1.27 (m, 4 H, CH_2), 0.88 (t, $^1J_{H,H}$ = 7.0 Hz, 3 H, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.4, 153.5, 119.1, 31.0, 28.9, 22.3, 13.8 ppm.

(*Z*)-Oct-3-en-2-one [(*Z*)-3]:[16] In a reactor equipped with a mechanical stirrer and under nitrogen, (*Z*)-hept-2-enoic acid (3.32 g, 25.9 mmol) was dissolved in dry diethyl ether (250 mL) at room temperature. The mixture was cooled to –30 °C, and methyllithium (2.0 equiv.) was quickly added. The reaction was exothermic, and a white precipitate was formed. The temperature was increased to 0 °C during 1 h. An aqueous saturated solution of NH_4Cl (150 mL) was added to quench the reaction. The mixture was stirred for 30 min before the aqueous layer was extracted twice with diethyl ether. The combined organic layers were washed with an aqueous saturated solution of $NaHCO_3$ and dried with $MgSO_4$. The solvent was distilled using a Rashig column (4 mm) to give 2.60 g of the title compound as a pale yellow oil in 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.02 (d, $^1J_{H,H}$ = 11.5 Hz, 1 H, CH), 5.96 (dt, $^1J_{H,H}$ = 11.5, $^2J_{H,H}$ = 7.1 Hz, 1 H, CH), 2.49 (dt, $^1J_{H,H}$ = 14.3, $^2J_{H,H}$ = 7.1 Hz, 2 H, CH_2), 2.09 (s, 3 H, Me), 1.33–1.20 (m, 4 H, CH_2), 0.79 (t, $^1J_{H,H}$ = 7.3 Hz, 3 H, Me) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.1, 148.5, 126.8, 31.2, 31.1, 28.9, 22.2, 13.7 ppm.

4-Cyclohexyl-4-hydroxybutan-2-one:[9] Cyclohexanecarbaldehyde (12.0 mL, 100 mmol) was added dropwise over 1 h to a solution of acetone (40 mL), water (30 mL) and pyrrolidine (0.3 mL, 0.36 mmol), while being kept at 30 °C and then stirred at 30 °C for 3 h. After the reaction was complete, the solution was acidified (pH = 4) with concentrated hydrochloric acid and heated to 100 °C to distil the acetone. The remaining residue was cooled to room temperature and extracted twice with dichloromethane. The combined organic layers were concentrated in vacuo. The crude oily product was distilled under reduced pressure (10^{-3} mbar) at 65 °C to give the desired product in 37% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.61 (s, 1 H, CH), 3.47 (s, 1 H, CH), 2.88 (d, $^1J_{H,H}$ = 6.0 Hz, 2 H, CH_2), 1.99 (s, 3 H, Me), 1.67–0.79 (m, 11 H, *c*-Hex) ppm. ^{13}C NMR (70 MHz, $CDCl_3$): δ = 210.1, 71.6, 47.3, 43.1, 28.8, 28.1, 26.4, 26.0 ppm.

(*E*)-4-Cyclohexylbut-3-en-2-one [(*E*)-4]:[9] 4-Cyclohexyl-4-hydroxybutan-2-one (28.0 mmol) and an aqueous hydrochloric acid solution (5 wt.-%, 10 mL) in toluene (25 mL) were heated to reflux for 4 h. After the reaction was complete, the mixture was cooled, and the aqueous layer was separated. The toluene layer was concentrated, and the residue was distilled at 50 °C under reduced pressure (10^{-2} mbar) to give the colourless desired product in 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.70 (dd, $^1J_{H,H}$ = 16.0, $^2J_{H,H}$ = 6.6 Hz, 1 H, CH), 5.99 (dd, $^1J_{H,H}$ = 16.0, $^2J_{H,H}$ = 1.3 Hz, 1 H, CH), 2.22 (s, 3 H, Me), 2.17–2.06 (m, 1 H, CH), 1.75–1.63 (m, 5 H, *c*-Hex), 1.33–1.07 (m, 5 H, *c*-Hex) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.2, 153.4, 128.8, 40.5, 31.7, 26.8, 25.8, 25.6 ppm.

(*Z*)-3-Cyclohexylacrylic Acid:[8b,8d] In a reactor equipped with a mechanical stirrer and under nitrogen, copper iodide (13.84 g, 73 mmol) was suspended in dry THF (220 mL) at room temperature. At –60 °C, cyclohexylmagnesium chloride (63.0 mL of a 1.45 M solution in THF) was added dropwise and the mixture stirred for 45 min. Acetylene (2.0 L) was bubbled into the mixture. After 30 min, the temperature of the mixture was allowed to rise to –20 °C, trimethyl phosphite (ca. 0.6 mL) was added, and dry ice (CO_2) was bubbled from a flask into the solution for 4 h. The crude mixture was stirred at room temperature for 1 h before being quenched with a solution of NH_4Cl/HCl (3:1, v/v) for 30 min. After filtration through Celite and separation, the aqueous layer was extracted three times with diethyl ether. The organic layers were washed with NaOH (1.5 M), and concentrated HCl was added to the aqueous layer until pH = 1. A last extraction of the aqueous layer with diethyl ether was performed (3 times). The combined organic layers were dried with $MgSO_4$, and the solvent was evaporated in vacuo to give 5.0 g (45% yield) of the desired product. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.5 (s, 1 H), 6.15 (dd, $^1J_{H,H}$ = 11.5, $^2J_{H,H}$ = 10.1 Hz, 1 H, CH), 5.68 (dd, $^1J_{H,H}$ = 11.5, $^2J_{H,H}$ = 0.8 Hz, 1 H, CH), 3.34–3.28 (m, 1 H), 1.73–1.03 (m, 10 H, *c*-Hex) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.5, 158.3, 116.9, 37.4, 32.2, 25.9, 25.4 ppm. HRMS (EI): calcd. for $C_9H_{14}O_2$ 154.09938; found 154.09838.

(*Z*)-4-Cyclohexylbut-3-en-2-one [(*Z*)-4]:[16] In a reactor equipped with a mechanical stirrer and under nitrogen, (*Z*)-3-cyclohexylacrylic acid (3.08 g, 20.0 mmol) was dissolved in dry diethyl ether (250 mL) at room temperature. The mixture was cooled to –30 °C, and methyllithium (25 mL, 2.0 equiv.) was added quickly. The reaction was exothermic, and the mixture turned yellow. The temperature was increased to 0 °C over 1 h before saturated NH_4Cl (150 mL) was added. The two layers were stirred for 30 min. The aqueous layer was extracted twice with diethyl ether. The combined organic layers were washed with a saturated solution of $NaHCO_3$, dried with $MgSO_4$ and concentrated in vacuo. The residue was distilled at room temperature under reduced pressure (10^{-2} mbar) to give 2.2 g of a colourless oil in 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.98 (d, $^1J_{H,H}$ = 11.6 Hz, 1 H, CH), 5.82 (dd, $^1J_{H,H}$ =

11.6, $^2J_{H,H}$ = 9.6 Hz, 1 H, CH), 3.22–3.12 (m, 1 H), 1.75–0.97 (2 m, 10 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.0, 153.4, 125.1, 37.3, 32.2, 31.5, 25.8, 25.3 ppm. HRMS (EI): calcd. for $C_{10}H_{16}O$ 152.12012; found 152.12031.

General Procedure for Cu-Catalyzed ACA of Et_2Zn:[10] A solution of $Cu(OAc)_2 \cdot H_2O$ (0.02 mmol) and a phosphoramidite-type ligand (0.04 mmol) in dry diethyl ether (2.5 mL) was stirred at room temperature for 30 min and then cooled to –30 °C. Et_2Zn (1.2 equiv., 1.2 mL of a 1.0 M solution in hexane) was added dropwise in such a way that the temperature did not rise above –30 °C. The solution was stirred for 5 min, and the Michael acceptor (1.0 mmol) in dry diethyl ether (0.5 mL) was added dropwise. The reaction mixture was stirred at –30 °C overnight before the reaction was quenched with a 2 N aqueous solution of HCl.

1-Nitro-2-phenylbutane (5):[10] ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47–7.26 (m, 5 H, Ar), 4.72–4.64 (m, 2 H, CH_2), 3.51–3.45 (m, 1 H, CH), 1.92–1.77 (m, 2 H, CH_2), 0.96 (t, $^1J_{H,H}$ = 7.3 Hz, 3 H, Me) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.2, 128.8, 127.5, 127.4, 80.7, 45.9, 26.1, 11.4 ppm. The enantiomeric excess was measured by chiral GC [100–0–1–170; Rt_1 = 15.3 min, (*S*); Rt_2 = 15.8 min, (*R*); lipodex E].

4-Phenylhexan-2-one (6):[10] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.20 (m, 5 H, Ar), 3.12–3.00 (m, 1 H, CH), 2.76 (d, $^1J_{H,H}$ = 7.3 Hz, 2 H, CH_2), 2.05 (s, 3 H, Me), 1.79–1.53 (m, 2 H, CH_2), 0.82 (t, $^1J_{H,H}$ = 7.3 Hz, 3 H, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 207.9, 144.2, 50.5, 42.9, 30.5, 29.3, 11.9 ppm. The enantiomeric excess was measured by chiral GC [lipodex E; isotherm 75 °C; Rt_1 = 35.05 min, (*S*); Rt_2 = 37.66 min, (*R*)].

4-Ethyloctan-2-one (7):[10] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.20 (d, $^1J_{H,H}$ = 6.8 Hz, 2 H, CH_2), 1.98 (s, 3 H, Me), 1.77–1.67 (m, 1 H, CH), 1.24–1.03 (m, 8 H), 0.74 (t, $^1J_{H,H}$ = 6.8 Hz, 3 H, Me), 0.71 (t, $^1J_{H,H}$ = 7.5 Hz, 3 H, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.7, 48.1, 35.0, 33.0, 28.6, 26.1, 22.7, 13.8, 10.5 ppm. The enantiomeric excess was measured by chiral GC [lipodex E; 60–15–20–170; Rt_1 = 15.8 min, (+)-(*R*); Rt_2 = 16.1 min, (–)-(*S*)].

4-Cyclohexylhexan-2-one (8): ^{1}H NMR (400 MHz, $CDCl_3$):[10] δ = 2.40–2.18 (AB system, 2 H, CH_2), 2.09 (s, 3 H, Me), 1.74–0.85 (2 m, 14 H, *c*-Hex, CH_2), 0.80 (t, $^1J_{H,H}$ = 3.0 Hz, 3 H, Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.5, 45.6, 40.6, 40.0, 30.1, 30.1, 29.1, 29.1, 26.6, 23.9, 11.7 ppm. The enantiomeric excess was measured by chiral GC [lipodex E; isotherm 70 °C; Rt_1 = 34.3 min, (*S*); Rt_2 = 36.3 min, (*R*)].

General Procedure for the Tandem Cu-Catalyzed ACA of Et_2Zn/Silylation Sequence:[12] A solution of $Cu(OAc)_2 \cdot H_2O$ (0.02 mmol) and a phosphoramidite-type ligand (0.04 mmol) in dry diethyl ether (2.5 mL) was stirred at room temperature for 30 min and then cooled to –30 °C. Et_2Zn (1.2 equiv., 1.2 mL of a 1.0 M solution in hexane) was added dropwise so that the temperature did not rise above –30 °C. The solution was stirred for 5 min, and the Michael acceptor (1.0 mmol) in dry diethyl ether (0.5 mL) was added dropwise. The reaction mixture containing the zinc enolate species was stirred at –30 °C overnight. A solution of Et_2Zn (0.1 mL) was added to TMSOTf (0.218 mL, 1.2 mmol) in order to eliminate traces of water. The mixture was added to the solution containing the zinc enolate at –30 °C and stirred overnight. The reaction mixture was diluted with dry diethyl ether (2 mL) and filtered through SiO_2 (2 g) previously neutralized with Et_3N (0.25 mL in 7 mL Et_2O). The solvents were removed in vacuo. The crude mixture was purified by fast flash chromatography on SiO_2 (8 g) previously neutralized with Et_3N (0.25 mL) and with pentane as eluent to give pure silylenol ether as a mixture of (*E*) and (*Z*) compounds.

(*E*)- and (*Z*)-(4-Phenylhex-2-en-2-yloxy)trimethylsilane (9). (*E*)-9:[12] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.24 (m, 2 H, Ar), 7.21–7.12 (m, 3 H, Ar), 4.83 (d, $^1J_{H,H}$ = 9.6 Hz, 1 H, CH), 3.22–3.15 (m, 1 H, CH), 1.76 (s, 3 H, Me), 1.67–1.54 (m, 2 H, CH_2), 0.89 (t, $^1J_{H,H}$ = 7.6 Hz, 3 H, Me), 0.18 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.0, 146.4, 128.2, 127.2, 125.6, 112.7, 45.5, 30.7, 18.2, 12.2 ppm. **(*Z*)-9:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.24 (m, 2 H, Ar), 7.21–7.12 (m, 3 H), 4.63 (d, $^1J_{H,H}$ = 9.9 Hz, 1 H, CH), 3.54–3.47 (m, 1 H, CH), 1.79 (s, 3 H, Me), 1.79–1.67 (m, 2 H, CH_2), 0.85 (t, $^1J_{H,H}$ = 7.3 Hz, 3 H, Me), 0.14 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.6, 146.5, 128.1, 127.5, 125.5, 112.8, 43.4, 30.2, 22.7, 12.3, 0.7 ppm.

(*E*)- and (*Z*)-(4-Ethyloct-2-en-2-yloxy)trimethylsilane (10): IR (neat): $\tilde{\nu}$ = 2958, 2922, 2856, 1670, 1251, 842, 632 cm^{-1}. HRMS (EI): calcd. for $C_{13}H_{28}OSi$ 228.190944; found 228.190840. The enantiomeric excess was measured by chiral GC on deprotected ketone. **(*E*)-10:** ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.36 (d, $^1J_{H,H}$ = 10.1 Hz, 1 H, CH), 1.94–1.85 (m, 1 H, CH), 1.73 (s, 3 H, Me), 1.44–1.11 (m, 6 H), 0.89–0.83 (t, 3 H, Me), 0.19 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.4, 114.1, 39.7, 36.1, 29.7, 22.9, 18.2, 14.1, 11.9, 0.32 ppm. **(*Z*)-10:** ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.15 (d, $^1J_{H,H}$ = 9.5 Hz, 1 H, CH), 2.33–2.23 (m, 1 H, CH), 1.79 (s, 3 H, Me), 1.44–1.11 (m, 6 H), 0.89–0.83 (t, 3 H, Me), 0.19 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.1, 113.9, 36.7, 35.2, 29.7, 28.5, 23.0, 22.7, 14.1, 11.8, 0.8 ppm.

(*Z*)- and (*E*)-(4-Cyclohexylhex-2-en-2-yloxy)trimethylsilane (11): IR (neat): $\tilde{\nu}$ = 2956, 2925, 2853, 1738, 1366, 1217 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{30}OSi$ 254.206594; found 254.206540. The enantiomeric excess was measured by chiral GC on deprotected ketone. **(*E*)-11:** ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.48 (d, $^1J_{H,H}$ = 10.8 Hz, 1 H, CH), 2.22–2.17 (m, 1 H, CH), 1.77 (s, 3 H, Me), 1.74–1.67 (m, 5 H), 1.57–1.43 (m, 1 H), 1.29–1.14 (m, 5 H), 1.10–0.94 (m, 2 H), 0.88 (t, $^1J_{H,H}$ = 7.3 Hz, 3 H, Me), 0.25 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.4, 111.9, 43.0, 42.2, 31.5, 29.4, 26.9, 26.7, 26.1, 22.8, 12.1, 0.4 ppm. **(*Z*)-11:** ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.25 (d, $^1J_{H,H}$ = 9.8 Hz, 1 H, CH), 1.85 (s, 3 H, Me), 1.83–1.80 (m, 1 H, CH), 1.74–1.67 (m, 5 H), 1.57–1.43 (m, 1 H), 1.29–1.14 (m, 5 H), 1.10–0.94 (m, 2 H), 0.88 (t, $^1J_{H,H}$ = 7.3 Hz, 3 H, Me), 0.24 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.7, 111.7, 45.4, 42.2, 31.2, 29.6, 26.9, 26.8, 26.7, 25.2, 18.3, 12.1, 0.9 ppm.

Acknowledgments

The authors thank the Swiss National Research Foundation (No. 20-068095.02 and COST action D24/0003/01 (OFES contract No. c02.0027) for financial support.

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Received: May 12, 2007
Published Online: October 9, 2007

