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Copper-catalyzed Asymmetric Conjugate Addition to Challenging Michael Acceptors and Synthesis of Relevant Target Molecules

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[§]SCS-Metrohm Foundation Award for best oral presentation

Abstract: We report herein the enantioselective Cu-catalyzed conjugate addition of organometallic reagents to sensitive Michael acceptors and their application to the synthesis of relevant target molecules. This is one of the most important methodologies to form a C–C bond in an enantioselective manner. A wide range of α,β-unsaturated aldehydes and β,γ-unsaturated-α-ketoesters has been successfully used. Reactivity, regio- and enantioselectivities were strongly dependent on the reaction conditions, therefore moderate to very good results were obtained. Furthermore, γ-substituted-α-ketoesters were used as chiral building blocks for further derivatization with complete retention of the chiral information to obtain key compounds.

Keywords: Asymmetric conjugate addition · Copper · Organometallic reagents · α,β-Unsaturated aldehydes · β,γ-Unsaturated-α-ketoesters

Introduction

Enantioselective Cu-catalyzed conjugate addition of organometallic reagents to Michael acceptors has been one of the strongest methods to create enantioenriched products through C–C bond formation.[1] In this field, a wide range of nitrodienes, nitroenynes, sulfones, α,β- and β,γ-unsaturated carbonyl compounds has been used successfully. However, the direct asymmetric conjugate addition with organometallic reagents and copper as transition metal catalyst to much more challenging substrates, such as α,β-unsaturated aldehydes or β,γ-unsaturated-α-ketoesters, has not been reported in the literature before our work.[2] Their very high reactivity can easily lead to the formation of an undesired mixture of 1,4- and 1,2-addition products as well as the aldol by-product. The resulting β-substituted aldehydes or γ-substituted-α-ketoesters have valuable properties and can be used, for example, as additives in perfume- or flavor chemistry as well as pharmaceutical drugs for anti-cancer, antimicrobial and bladder disorder treatment in medicinal chemistry. Bräse *et al.* developed the first asymmetric conjugate addition (ACA) to enals through an enantioselective Cu-free 1,4-addition methodology, using [2.2]-paracyclophaneketimine ligands.[3] On the other hand, prior to our work, only indirect methodologies have been developed for Cu-catalyzed ACA to enals. In 2003, Hoveyda *et al.* published the ACA to N-acyloxazolidinones[4] and a few years later, Feringa *et al.* reported on the ACA with thioesters and allylic α-chloroacetate using a one-pot procedure.[5] Finally, in 2008, Palomo *et al.* described the 1,4-addition to α'-oxy enones followed by a reduction–oxidation procedure to obtain the chiral β-substituted aldehydes.[6] Other methods with transition metals, like Pd,[7] Rh,[8] Ir,[9] or organocatalyzed methodologies have been developed to access β-substituted aldehydes.[10] In 2010, based upon the literature results, we developed the challenging ACA to α,β-unsaturated aldehydes. We obtained promising results but unfortunately, we could never achieve high *ee*s and high regioselectivities at the same time.[2a] To obtain β- and γ-substituted compounds with high selectivities, we developed the 1,4-addition to a new class of substrate catalyzed by a transition metal. Following a minor derivatization, the product can then be transformed to access new families of chiral building blocks of β-substituted aldehydes. β,γ-Unsaturated-α-ketoesters pose the same problem as the corresponding aldehyde because the ester functionality activates the α-keto position to generate an undesired mixture of 1,4- and 1,2-addition products. During the last decade, a wide range of organocatalytic additions to β,γ-unsaturated-α-ketoesters were published in the literature.[11] Very recently, Zhang *et al.* developed an enantioselective synthesis of chiral γ-aryl α-ketoesters by ACA to the corresponding β,γ-unsaturated-α-ketoesters catalyzed by copper and using D_2-symmetric biphenyl phosphoroamidite ligands.[12] During the same time, we reported the successful Cu-catalyzed asymmetric conjugate addition to several β,γ-unsaturated-α-ketoesters with trimethylaluminum as organometallic reagent and their derivatization to access natural and unnatural target compounds.[2b] Herein, we report recent progress in Cu-catalyzed asymmetric conjugate addition to challenging Michael acceptors and their derivatization in order to simultaneously access new families of chiral and complex building blocks.

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Results and Discussion

We initially investigated the asymmetric conjugate addition to α,β-unsaturated aldehydes with various types of organometallic reagents. The first attempts were

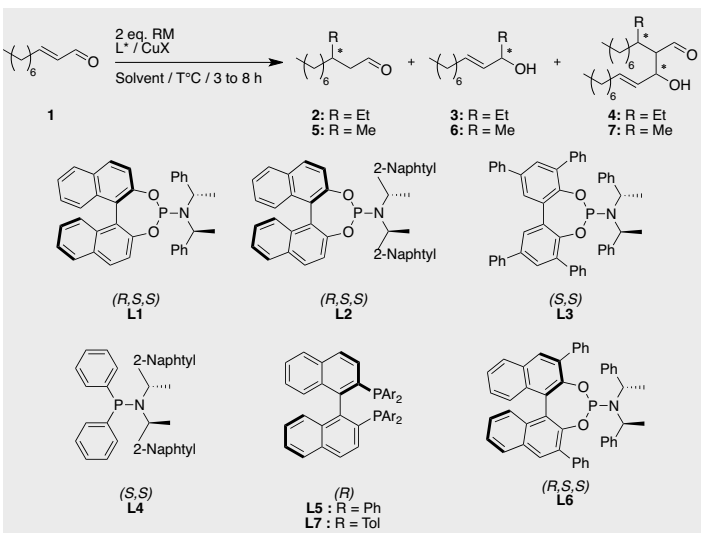
done with *trans*-2-decenal in presence of copper(I) thiophene-2-carboxylate (CuTC) or copper(II) triflate ($Cu(OTf)_2$) and mono- or bidentate phosphorus ligands. As expected, an undesired mixture of 1,4- and 1,2-addition products as well as the aldol by-product were obtained (Table 1). With dialkylzinc reagents only the 1,4-addition products and aldol derivatives were observed. After reductive elimination of the Cu(III) intermediate, the resulting zinc enolate reacted quickly with the highly reactive α,β-unsaturated aldehydes to give undesired byproducts (Table 1, entries 1–7). Due to the high reactivity of Grignard reagents, and the enals themselves, reactions were performed at low temperature with these organometallic reagents. Unfortunately, large amounts of 1,2-addition products were obtained. By addition of trimethylsilyl chloride (TMSCl) as additive the regioselectivity was increased by more than 50% without affecting the enantiomeric excess (Table 1, entry 8–12). Normant *et al.* discovered this beneficial effect in 1980 for the 1,4-addition on enals.[13] Corey and Boaz, Alexakis *et al.* and Nakamura *et al*. confirmed this discovery a few years later.[14] The additive amounts of TMSCl contributed to accelerating cuprate-enone conjugate addition by trapping the copper (III) complex and forcing the conversion towards the β-adduct. The use of trialkylaluminum reagents were also envisaged because they are mild organometallic reagents equally very well known to access methyl-substituted adducts. Unfortunately, the regioselectivity and enanstioselectivity dropped (Table 1, entry 13).

With these experimental conditions in hand, we screened the ACA to various α,β-unsaturated aldehydes. Dialkylzinc reagents are soft organometallic reagents with substantial advantages and one of them is the high tolerance toward functional groups. Thereby, with Et_2Zn or Me_2Zn the regioselectivities were always fully in favor of the 1,4-addition product. No traces of 1,2-addition products or aldol by-products were observed. Diethylzinc enabled full conversion to be obtained with moderate *ees* (Table 2, entries 6–9). However, with dimethylzinc, a poorly reactive organometallic reagent, the reactions must be performed at 0 °C. A small drop in conversions was observed but moderate to good *ee*s were achieved (Table 2, entries 1–5).

The commercial diversity of dialkylzinc remains limited and the self-preparation quite demanding. For these reasons, the use of Grignard reagents was envisaged for the ACA to α,β-unsaturated aldehydes. As mentioned previously, the key factor when using Grignard reagents was the positive effect of TMSCl. Unfortunately, despite the improvement provided with this additive, the regioselectivities were moderate, particularly with aryl derivatives (Table 3, entry 5), with regards to organozinc reagents. However, the enantioselectivities were better, ranging from 74 to 90%, whether with MeMgBr or EtMgBr (Table 3, entries 1–9).

Direct addition of organometallic reagents to α,β-unsaturated aldehydes appears to be a very challenging concept to obtain chiral β-substituted aldehydes with high regio- and enantioselectivities. To achieve this goal, we investigated a new Cu-catalyzed asymmetric conjugate addition of organometallic reagents to β,γ-unsaturated-α-ketoesters. The resulting γ-substituted-α-ketoesters can be easily transformed into the corresponding β-substituted aldehydes by a simple one-

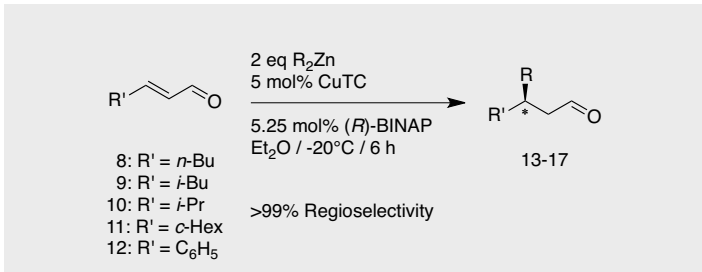
Table 1. Screening of reaction conditions with various organometallic reagents and chiral ligand



Entry	Ligand	RM	Conv. [%][a]	1,4:1,2:aldol[a]	*ee* [%][b]
1[c]	**L1**	Et_2Zn	>99	>99	50
2[c]	**L2**	Et_2Zn	99	>98	57
3[c]	**L3**	Et_2Zn	99	>99	64
4[c]	**L4**	Et_2Zn	99	93:0:7	73
5[c]	**L5**	Et_2Zn	59	87:0:13	72
6[c]	**L5**	Et_2Zn	>99	>99	75
7[d]	**L6**	Et_2Zn	88	95:0:5	79
8[e]	**L1**	EtMgBr	>99	24:76:0	50
9[e]	**L4**	EtMgBr	>99	21:79:0	44
10[e]	**L5**	EtMgBr	98	62:30:0	89
11[e]	**L7**	EtMgBr	99	32:42:26	92
12[f]	**L7**	EtMgBr	>99	85:15:0	90
13[g]	**L5**	Me_3Al	83	65:19:16	66

[a]Determined by ^{1}H NMR. [b]Determined by chiral GC. [c]5 mol% $Cu(OTf)_2$, 10 mol% **L***, Toluene, 0 °C, 3 h. [d]5 mol% CuTC, 5.25 mol% **L***, Et_2O, -20 °C, 6 h. [e]5 mol% $Cu(OTf)_2$, 5.25 mol% **L***, Et_2O, -78 °C, 8 h. [f]1.3 eq TMSCl, 5 mol% $Cu(OTf)_2$, 5.25 mol% **L***, Et_2O, -78 °C, 8h. [g]5 mol% $Cu(OTf)_2$, 5 mol% **L***, THF, -78°C, 13 h.

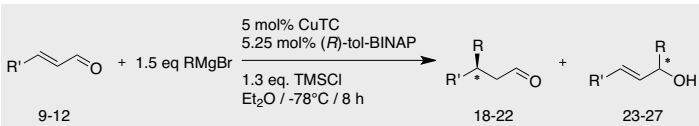
Table 2. Screening of α,β-unsaturated aldehydes with R_2Zn



Entry	R	RM	Conv. [%][a,b]	*ee* [%][c]
1[d]	**1**	Me_2Zn	85(79)	68
2[d]	**8**	Me_2Zn	87	76
3[d]	**10**	Me_2Zn	>99	70
4[d]	**11**	Me_2Zn	87(61)	60
5[d]	**12**	Me_2Zn	50	64
6	**8**	Et_2Zn	>99(60)	64
7	**9**	Et_2Zn	>99	70
8	**10**	Et_2Zn	>99	27
9	**11**	Et_2Zn	>99	52

[a]Determined by ^{1}H NMR. [b]Isolated yield for 1,4-addition product in parentheses. [c]Determined by chiral GC. [d]Reaction performed at 0 °C over 16 h.

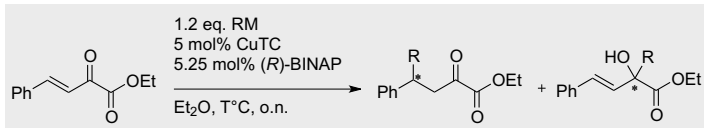
Table 3. Screening of α,β-unsaturated aldehydes with RMgBr



Entry	R	RM	Conv. [%][a,b]	1,4:1,2[a]	*ee* [%][c]
1	**1**	MeMgBr	>99(40)	65:35	81
2	**8**	MeMgBr	>99	40:60	86
3	**10**	MeMgBr	86	43:57	84
4	**11**	MeMgBr	>99(49)	63:37	80
5	**12**	MeMgBr	>99	10:90	n.d.
6	**8**	EtMgBr	>99(46)	60:40	90
7	**9**	EtMgBr	>99(44)	71:29	90
8	**10**	EtMgBr	>99	36:64	74
9	**11**	EtMgBr	>99(51)	63:37	80

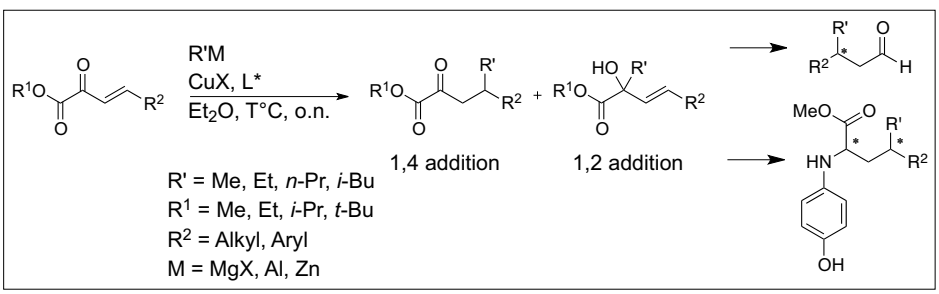
[a]Determined by ^{1}H NMR. [b]Isolated yield for 1,4-addition product in parentheses. [c]Determined by chiral GC.

Table 4. Screening of organometallic reagents to β,γ-unsaturated-α-ketoesters



Entry	RM	T [°C]	Conv. [%][a]	1,4:1,2[a]	*ee* [%][b,c]
1[d]	MeMgBr	-78	>99	1:99	n.d.
2	MeMgBr	-78	>99	1:99	n.d.
3	Me_2Zn	0	0	n.d.	n.d.
4[e]	Me_2Zn	0	>99(14)[f]	99:1	93
5	Me_3Al	-20	>99(40)[f]	43:57	55
6[g]	Me_3Al	-78	>99	70:30	94
7[h]	Me_3Al	-78	>99	>99:1	>99.5

[a]Determined by ^{1}H NMR spectroscopy. [b]Determined by GC analysis using a chiral stationary phase. [c]Enantiomeric excess for 1,4-addition product. [d]Reaction performed with 1.3 equiv TMSCl. [e]Reaction performed with 2 equiv Me_2Zn, 5 mol% CuTC, and (*R*)-binap in THF. [f]Yield of isolated product. [g]Reaction performed with 1.2 equiv Me_3Al, 5 mol% CuTC, and (*R*)-binap in Et_2O. [g]Reaction performed with 2 equiv Me_3Al, 5 mol% CuTC, and (*R*)-binap in THF. binap = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, TMS = trimethylsilyl.



Scheme 1. Cu-catalyzed ACA to β,γ-unsaturated-α-ketoesters.

pot reduction-oxidation or to α-amino acid precursors by reductive amination (Scheme 1).

We initially investigated the ACA with the simplest (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate, **28**. This first attempt was done using the reaction conditions previously developed for α,β-unsaturated aldehydes: 1.2 equivalents of an organometallic reagent, 5mol% of CuTC, 5.25 mol% of (*R*)-binap in diethyl ether (Et_2O) at –78°C (Table 4).

With the Grignard reagent, we obtained full conversion of the substrate, but unfortunately, we observed exclusively the 1,2-addition product as well as in the presence of TMSCl as an additive (Table 4, entries 1,2). The use of the less reactive organometallic reagent Me_2Zn under similar reaction conditions resulted in no conversion. However, under the best reaction conditions developed later, 14% of isolated γ-substituted-α-ketoesters could be isolated with 93% *ee* (Table 4, entries 3,4). The use of trimethylaluminum, a well known mild organometallic reagent to introduce methyl groups, was considered. At –20 °C, full conversion was observed with roughly a 1:1 ratio for the 1,4- and 1,2-adduct selectivity achieving a promising 55% *ee* for the γ-substituted-α-ketoesters (Table 4, entry 5).

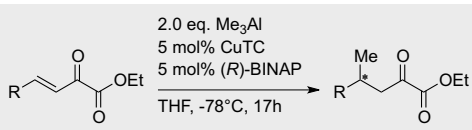
By decreasing the reaction temperature to –78 °C and increasing the reaction time to 17 hours, the regioselectivity was increased in favor of the 1,4-addition adduct and the enantioselectivity could equally be improved (Table 4, entry 6). Various copper salts, solvents and catalyst loadings were screened revealing CuTC, tetrahydrofuran (THF) and 5 mol% of ligand and transition metal catalyst as the reaction conditions of choice. However, an excess of trimethylaluminum (2 equiv.) was required to get full conversion and complete regioselectivity in favor of the γ-substituted-α-ketoesters (Table 4, entry 7).

With these reaction conditions in hand, the substrate scope was investigated with aromatic, aliphatic as well as linear and cyclic β,γ-unsaturated-α-ketoesters. Halogenated, nitro, methoxy aryl and aliphatic derivatives are compatible under the reaction conditions (Table 5). Only strongly electron-donating groups (*o*, *m*, *p*-OMePh) generated lower conversion and yield without furnishing by-products (Table 5, entries 6,8). For R = *o*-OMePh we also noticed an important drop of enantioselectivity to 27% (Table 5, entry 8). It is interesting to notice that β,γ,δ,ε-unsaturated-α-ketoesters, a dienic substrate, provided purely the chiral γ-substituted-α-ketoesters, without any traces of the 1,6-addition adduct (Table 5, entry 15).

The sweeping scope of the ACA was finally explored using various organoaluminum, organozinc and Grignard reagents, but unfortunately a mixture of 1,4- and 1,2-additon products, low yield and/or enantioselectivities were obtained under our reaction conditions.

The ester functionality of β,γ-unsaturated-α-ketoesters gives access to a wide range of chiral building blocks after further small and easy derivatization. As mentioned in the introduction, direct addition of organometallic reagents to aldehydes or alternative methodologies to obtain chiral β-substituted aldehydes left room for improvement. For this reason we developed a one-pot, reduction-oxidation procedure,[15] for the synthesis of (*S*)-Florhydral.[16] With this strategy, we were able to obtain the desired compound with high yield and complete retention of the chiral information (Scheme 2). We can also easily prepare chiral α-amino acid precursors through a one-step procedure. By a simple reductive amination on chiral γ-substituted-α-ketoesters we obtained, under non-optimized reaction conditions, the corresponding unnatural chiral α-amino acid precursors also with complete retention of the chiral information and with a promising diastereoselectivity of up to 3:1 (Scheme 2).

Table 5. Scope of substrate



31-45 46-60

Entry	Sub.	R	Prod.	Yield [%]	*ee* [%][a]
1	**31**	p-FC_6H_4	**46**	68	97
2	**32**	p-ClC_6H_4	**47**	87	97
3	**33**	p-BrC_6H_4	**48**	91	98
4	**34**	m-BrC_6H_4	**49**	85	>99.5
5	**35**	o-BrC_6H_4	**50**	89	99
6	**36**	p-$MeOC_6H_4$	**51**	55	97
7	**37**	m-$MeOC_6H_4$	**52**	35	94
8	**38**	o-$MeOC_6H_4$	**53**	27	27
9	**39**	p-$NO_2C_6H_4$	**54**	88	96
10	**40**	m-$NO_2C_6H_4$	**55**	91	88
11	**41**	o-$NO_2C_6H_4$	**56**	90	92
12	**42**	m-iPrC_6H_4	**57**	93	98
13	**43**	C_7H_{15}	**58**	93	91
14	**44**	cyclohexyl	**59**	90	82
15	**45**	$C_6H_4CH{=}CH$	**60**	92	98

[a]Determined by either GC, SFC or HPLC using chiral stationary phase. [b]No 1,6-addition product was observed.

In conclusion, by direct addition of organometallic reagents to α,β-unsaturated aldehydes we obtained good regio- or enantioselectivities but never both at the same time. With both Grignard reagents and TMSCl as additive to trap the copper (III) complex and forcing conversion to β-adduct, the regioselectivities are not flawless. In contrast, alternative methodologies are complementary and more selective. β,γ-unsaturated-α-ketoesters were shown to be very efficient substrates for the Cu-catalyzed ACA. A wide range of aryl and alkyl derivatives were tolerated under our reaction conditions to give full conversion and regioselectivities up to 99.5% *ee*. However, a strong electronic, steric, and chelating effect with aryl methoxy derivatives was observed, and resulted in a decrease of reactivity and enantioselectivity. Furthermore, γ-substituted-α-ketoesters were used as chiral building blocks for further derivatization. We obtained the corresponding β-substituted aldehydes and unnatural chiral α-amino acid precursors with high yield, complete retention of the chiral information and with promising diastereoselectivity.

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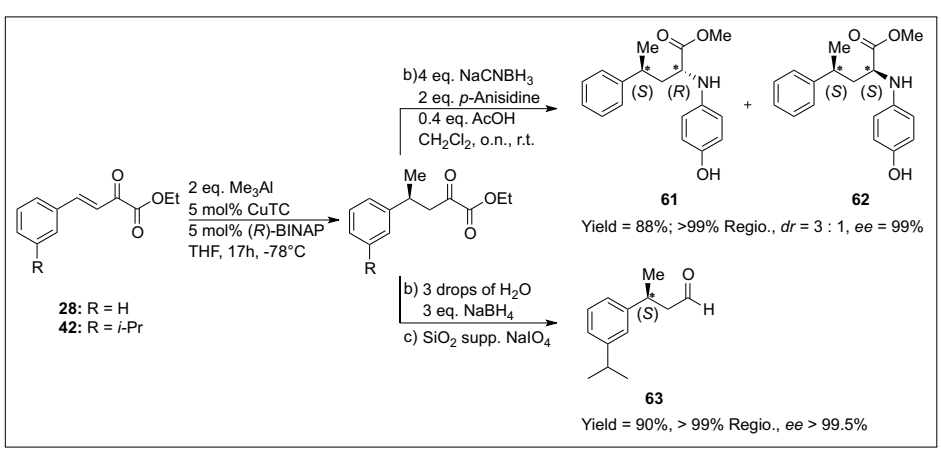

Scheme 2. Synthesis of unnatural α-amino acid precursors and (*S*)-Florhydral.

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