Tetrahedron Letters 55 (2014) 3797–3801

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Chiral Co(II) complex catalyzed asymmetric Michael reactions of β-ketoamides to nitroolefins and alkynones

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ARTICLE INFO

Article history:
Received 26 March 2014
Revised 4 May 2014
Accepted 15 May 2014
Available online 21 May 2014

Keywords:
Asymmetric catalysis
Michael reaction
β-Ketoamides
Nitroolefins
Alkynones

ABSTRACT

The catalytic enantioselective Michael additions of cyclic β-ketoamides to nitroolefins and alkynones were accomplished in the presence of chiral *N,N′*-dioxide–Co(II) complexes. The desired adducts were obtained in high yields (up to 98%) with excellent enantioselectivities (up to 97% ee).

Introduction

In the past decade, the Michael reaction of carbon nucleophiles to α,β-unsaturated compounds has been found to be attractive for the construction of new carbon—carbon bonds.[1,2] A wide variety of β-diketones, β-ketoesters, as well as α-substituted-1,3-dicarbonyls[3] have been extensively and successfully used as the nucleophiles in such reactions. In contrast to the Michael reaction of β-diketones and β-ketoesters, the conjugate addition using β-ketoamides as the nucleophile is interesting.[4] Using α,β-unsaturated aldehydes or ketones as the electrophiles, a Michael-initiated cyclization can occur. For example, Rodriguez and co-workers utilized the electrophilic and nucleophilic property of simple β-ketoamides to realize a multicomponent domino reaction, furnishing highly functionalized 2,6-diazabicylco[2,2,2]octane skeleton.[4a,l] Cooperative participation of the amido group of β-ketoamides can be employed to construct azaspirocyclic derivatives,[4c,m] and spiroaminals.[4g] The modified β-ketoamides containing an acidic methane group and pendant nucleophilic substituent with α,β-unsaturated carbonyl compounds can perform diverse stereodivergent catalytic one-pot addition/cyclization/annulation sequence to synthesize quinolizidine derivatives,[4d,e] oxzaine and oxazolidine derivatives,[4f] as well as other tetracyclic alkaloid derivatives.[4b] In addition, the direct asymmetric addition of α-substituted β-ketoamides with other Michael acceptors provides an easy synthetic route to quaternary stereocenters. Chiral organocatalysts are generally utilized to promote these enantioselective processes. For instance, chiral proline derivatives were used for the β-ketoamide addition to α,β-unsaturated aldehydes,[4d,e] and chiral multifunctional thiourea catalysts were efficient for the cascade reaction between β-ketoamide and α,β-unsaturated ketones[4f,g,l], or formal [3+3] cyclization between amide and α,β-unsaturated acyl cyanides.[4m] Chiral squaramide bearing cinchonine unit promoted the addition between cyclobutanone derivatives with an amide moiety and nitroalkenes in high diastereo- and enantioselectivities.[4i] However, extending the Michael donors and developing the efficient catalyst system for the Michael reactions of β-ketoamides are still desirable.

In recent years, the application of the less expensive and more abundant early transition metals gains momentum for the introduction of asymmetric centers in molecules. Nevertheless, the total number of chiral cobalt complex mediated asymmetric processes still remains small compared to other metals.[5,6j] As excellent chiral ligands, *N,N′*-dioxide-metal complexes have shown powerful catalytic capability in many different types of reactions owing to their easily tunable electronic and steric chiral scaffolds.[6] On our going work, we develop chiral *N,N′*-dioxide–Co(II) complex catalysts for the asymmetric Michael additions of α-substituted β-ketoamides. Both nitroolefins and alkynones are tolerable in the process, furnishing the desired nitro-derivatives with vicinal quartery–tertiary carbon centers and α,β-unsaturated enone derivatives, respectively. High enantioselectivities are obtained for the two kinds of Michael donors, although the diastereoselectivities or *Z*/*E* selectivities are moderate. The *Z*/*E* adducts of alkynones underwent

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http://dx.doi.org/10.1016/j.tetlet.2014.05.067
0040-4039/

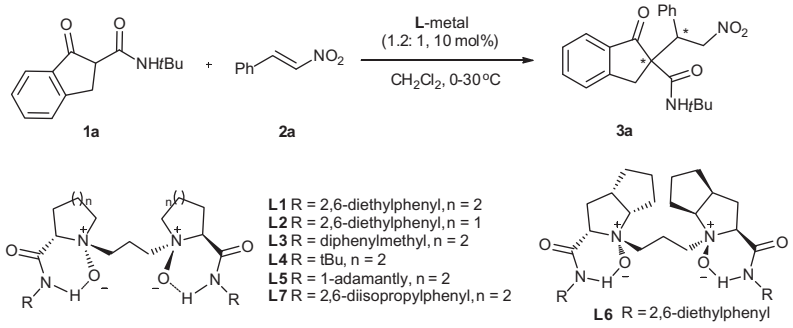
isomerization to afford the *E*-isomers and chloride derivatives by the treatment with HCl. Thermodynamically stable *E*-adduct could be obtained in high enantioselectivity after isomerization with TsOH.

Results and discussion

Initially, we examined various metal salts coordinated with chiral *N*,*N*′-dioxide **L1** in situ to catalyze the Michael reaction of *N*-*tert*-butyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxamide (**1a**) to nitroolefin (**2a**) in CH_2Cl_2 at 0 °C. As shown in Table 1, $Sc(OTf)_3$ did not promote the reaction at all (Table 1, entry 1). Other lanthanides such as $Y(OTf)_3$, $Gd(OTf)_3$, and $Lu(OTf)_3$ could mediate the reaction but in low reactivities and inefficient selectivities (Table 1, entries 2–4). When using $Hf(OTf)_4$ as the metal precursor, the reaction could get 2.0/1 diastereoselectivity, 50%/19% ees, but the yield was very low (Table 1, entry 5). The combination of nickel salts with **L1** could afford the Michael adduct **3a** with delightful yield and enantioselectivity but with poor diastereoselectivity (Table 1, entries 6, 7). And $Ni(BF_4)_2{\cdot}6H_2O$ was superior to $Ni(OTf)_2$ in terms of stereoselectivity. To our delight, the enantioselectivity could be further improved when $Co(BF_4)_2{\cdot}6H_2O$ was used as the center metal, and 89% and 66% ees were obtained for the major and minor diastereomers, respectively (Table 1, entry 8). Encouraged by the initial results, various *N*,*N*′-dioxide ligands were then tested (Table 1, entries 8–15). The screening of chiral amino acids backbone of ligands indicated that **L1** (derived from L-pipecolic acid) gave higher enantioselectivities than the ligand **L2** (derived from L-proline) and the ligand **L6** (derived from L-ramipril) (Table 1, entry 8 vs entry 9, 10). The amide subunits of the ligands also play a crucial role in the enantiocontrol. Comparing to the aryl substituted amide moieties, the introduction of diphenylmethyl group obviously increased the ee value to 97% and 84% ees for the two diastereomeric products (Table 1, entry 11 vs entry 8). Meanwhile, the diastereoselection of the reaction reversed although the dr value was not satisfied in the presence of chiral **L3**–$Co(BF_4)_2{\cdot}6H_2O$ complex. However, both the yield and the enantioselectivity of the reaction significantly decreased when *N*,*N*′-dioxides **L4** and **L5** bearing other sterically hindered alkyl amide moieties were used as the ligands (Table 1, entries 12, 13). Ligand **L7** derived from 2,6-diisopropylaniline accelerated the reaction with satisfied enantioselectivity inferior to that of the ligand **L3** (Table 1, entry 14). Further optimization of the reaction conditions is in vain for the improvement of the diastereoselectivity of the reaction. Other ordinary solvents gave both low yield and enantioselectivity, and CH_2Cl_2 was the most suitable (Table 1, entries 15–19). Thus, the optimized experimental conditions are as follows: 10 mol % of **L3**–$Co(BF_4)_2{\cdot}6H_2O$ (1.2:1) as the catalyst and CH_2Cl_2 as the solvent.

Under the optimized reaction conditions (Table 1, entry 7), the scope of nitroolefins and β-ketoamides was examined and the

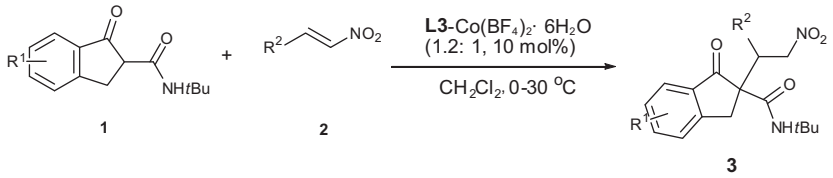
Table 1
Optimization of the Michael addition of β-ketoamide (**1a**) to nitroolefin (**2a**) [a]



Entry	Ligand	Metal	Solvent	Yield[b] (%)	*D.r.*[c]	*ee*[d] (%)
1	**L1**	$Sc(OTf)_3$	CH_2Cl_2	n.r.	n.d.	n.d.
2[e]	**L1**	$Y(OTf)_3$	CH_2Cl_2	50	1/1	27/7
3[e]	**L1**	$Gd(OTf)_3$	CH_2Cl_2	51	1/1.4	0/0
4[e]	**L1**	$Lu(OTf)_3$	CH_2Cl_2	19	1.6/1	44/22
5[e]	**L1**	$Hf(OTf)_4$	CH_2Cl_2	8	2.0/1	50/19
6	**L1**	$Ni(OTf)_2$	CH_2Cl_2	84	1/1	60/77
7	**L1**	$Ni(BF_4)_2{\cdot}6H_2O$	CH_2Cl_2	87	1/1.7	64/85
8	**L1**	$Co(BF_4)_2{\cdot}6H_2O$	CH_2Cl_2	88	1/1.6	66/89
9	**L2**	$Co(BF_4)_2{\cdot}6H_2O$	CH_2Cl_2	84	1/2	37/75
10	**L6**	$Co(BF_4)_2{\cdot}6H_2O$	CH_2Cl_2	57	1/1.9	36/64
11	**L3**	$Co(BF_4)_2{\cdot}6H_2O$	CH_2Cl_2	84	1.7/1	97/84
12	**L4**	$Co(BF_4)_2{\cdot}6H_2O$	CH_2Cl_2	87	4/1	40/50
13	**L5**	$Co(BF_4)_2{\cdot}6H_2O$	CH_2Cl_2	75	1/1	6/60
14	**L7**	$Co(BF_4)_2{\cdot}6H_2O$	CH_2Cl_2	80	1/1.3	94/58
15	**L3**	$Co(BF_4)_2{\cdot}6H_2O$	$CHCl_3$	46	2.1/1	78/51
16	**L3**	$Co(BF_4)_2{\cdot}6H_2O$	THF	81	1/1.2	68/38
17	**L3**	$Co(BF_4)_2{\cdot}6H_2O$	Toluene	33	1/1.2	18/<5
18	**L3**	$Co(BF_4)_2{\cdot}6H_2O$	CH_3OH	64	1/1	58/69
19	**L3**	$Co(BF_4)_2{\cdot}6H_2O$	Et_2O	25	1.8/1	88/52

[a] Unless otherwise noted, the reactions were carried out with the ligand **L** (12 mol %), metal (10 mol %), **1a** (0.1 mmol), and **2a** (0.12 mmol) in solvent (0.6 mL) at 0 °C for 2 days and then at 30 °C for 1 day.
[b] Isolated yield; n.r. = no reaction.
[c] Determined by ^1H NMR analysis, n.d. = not determined.
[d] Determined by chiral HPLC analysis.
[e] The reaction was carried out at 0 °C for 2 days, and the yield was determined by ^1H NMR analysis (using CH_2Br_2 as internal standard).

Table 2
Asymmetric Michael additions of β-ketoamides **1** with nitroolefins **2**[a]

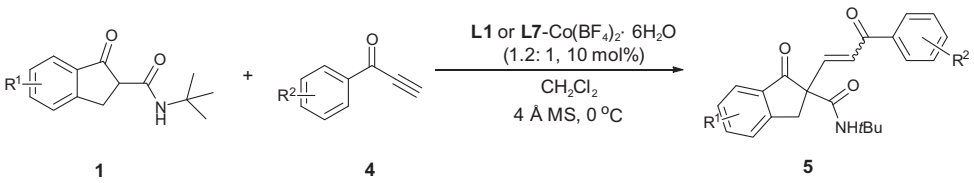


Entry	R^1	R^2	Yield[b] (%)	*D.r.*[c]	*ee*[d] (%)
1	H	Ph	84(**3a**)	63/37	97/84
2	H	4-FC_6H_4	94(**3b**)	62/38	96/77
3	H	4-ClC_6H_4	91(**3c**)	66/34	96/73
4	H	4-BrC_6H_4	82(**3d**)	66/34	97/74
5	H	4-PhC_6H_4	96(**3e**)	65/35	96/77
6	H	3-BrC_6H_4	98(**3f**)	62/38	94/85
7	H	3-ClC_6H_4	96(**3g**)	66/34	96/90
8	H	3,4-$Cl_2C_6H_3$	98(**3h**)	66/34	97/82
9	5-Cl	2-BrC_6H_4	51(**3i**)	54/46	93/72
10	5-Cl	2-Furanyl	84(**3j**)	72/28	86/55
11	5-F	4-BrC_6H_4	97(**3k**)	67/33	96/62
12	5-Cl	4-BrC_6H_4	98(**3l**)	65/35	96/69
13	5-Br	4-BrC_6H_4	94(**3m**)	63/37	96/66
14	5,6-$(OMe)_2$	4-BrC_6H_4	92(**3n**)	69/31	97/70
15	6-F	4-BrC_6H_4	95(**3o**)	67/33	96/71
16	6-Cl	4-BrC_6H_4	98(**3p**)	61/39	93/55
17	6-Me	Ph	92(**3q**)	57/43	94/82

[a] Unless otherwise noted, reactions were carried out with **L3** (12 mol %), $Co(BF_4)_2{\cdot}6H_2O$ (10 mol %), **1** (0.1 mmol), **2** (0.12 mmol) in CH_2Cl_2 (0.6 mL) at 0 °C for 2 days and then at 30 °C for 1 day.
[b] Isolated yield.
[c] Determined by ^1H NMR analysis.
[d] Determined by chiral HPLC analysis.

results are summarized in Table 2. The electron-withdrawing substituents on the β-aryl group of nitroolefins had no obvious effects on the enantioselectivity and reactivity of the reaction (Table 2, entries 2–8). However, 2-bromophenyl substituted nitroalkene suffered moderate reactivity albeit the enantioselectivity was satisfied (93% and 72% ee for the two diastereomers; Table 2, entries 9), probably due to the hindrance of the substituent. 2-(2-Nitrovinyl)furan reacted with 5-chloro-substiuted β-ketoamide smoothly, generating the corresponding product **3j** with improved dr value and slightly decreased enantioselectivity (72:28 dr, 86% and 55% ee; Table 2, entry 10). Next, a variety of dihydro-inden-1-one based β-ketoamides was examined in the reaction. Both electron-withdrawing and electron-donating substituents on the aromatic ring of the indenone scaffold were tolerated with high yields and good enantioselectivities (93–97% ees for the major diastereomer; entries 11–17). The outcome

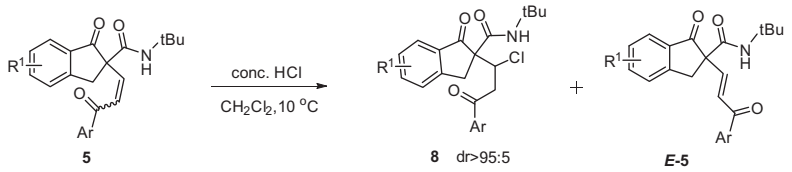
Table 3
Asymmetric Michael additions of β-ketoamides **1** with alkynones **4**[a]



Entry	R^1	R^2	Yield[b] (%)	*Z*/*E*[c]	*ee* of *Z*/*E* isomers[d] (%)
1	H	H	99(98)(**5a**)	74/26(55/45)	90/79(94/96)
2	5-F	H	94(94)(**5b**)	71/29(60/40)	91/80(97/95)
3	5-Br	H	98(97)(**5c**)	69/31(58/42)	90/77(97/94)
4	6-Me	H	99(96)(**5d**)	75/25(64/36)	84/69(97/97)
5	6-Cl	H	97(92)(**5e**)	75/25(68/32)	86/72(96/93)
6	6-F	H	95(80)(**5f**)	78/22(62/38)	89/75(96/95)
7	H	4-Me	94(89)(**5g**)	72/28(47/53)	90/84(97/97)
8	H	3-CF_3	92(98)(**5h**)	65/35(63/37)	84/75(95/92)
9	H	4-CF_3	94(97)(**5i**)	79/21(62/38)	93/80(95/94)
10	H	4-OMe	93(82)(**5j**)	69/31(52/48)	92/85(93/94)

[a] Unless otherwise noted, reactions were carried out with ligand **L1** or **L7** (12 mol %), $Co(BF_4)_2{\cdot}6H_2O$ (10 mol %), **1** (0.1 mmol), **4** (0.12 mmol) and MS (4 Å, 30 mg) in CH_2Cl_2 (1.0 mL) at 0 °C for 24 h. The data in parentheses were the results using the ligand **L7** instead.
[b] Isolated yield.
[c] Determined by ^1H NMR analysis.
[d] Determined by chiral HPLC analysis.

Table 4
Z/*E* adduct in the presence of HCl[a]

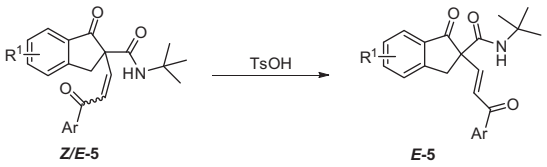


5 8 dr>95:5 *E*-5

Entry	*Z*/*E*-**5** (*ee* %)	R^1	Ar	**8** Yield[b] % (ee %)[c]	***E*-5** Yield[b] % (*ee* %)[c]
1	55/45(94/96)	H	Ph	53(97)(**8a**)	32(94)(***E*-5a**)
2	52/48(93/94)	H	4-$OMeC_6H_4$	38(96)(**8b**)[d]	43(94)(***E*-5j**)
3	64/36(97/97)	6-Me	Ph	60(95)(**8c**)	26(92)(***E*-5d**)

[a] Reaction conditions: HCl (37.5% w/w) (0.2 mL), CH_2Cl_2 (1.0 mL), 10 °C, 24 h.
[b] Isolated yield.
[c] Determined by chiral HPLC analysis.
[d] The absolute configuration was determined by X-ray analysis.

Table 5
Z/*E* adduct in the presence of TsOH[a]



Z/*E*-5 *E*-5

Entry	*Z*/*E*-**5** (*ee* %)	R^1	Ar	Yield[b] (%)	*ee*[c] (%)
1	55/45(94/96)	H	Ph	91(***E*-5a**)	96
2	52/48(93/94)	H	4-$OMeC_6H_4$	94(***E*-5j**)	94
3	64/36(97/97)	6-Me	Ph	87(***E*-5d**)	94

[a] Reaction conditions: TsOH (0.01 mmol), CH_2Cl_2 (1.0 mL), 10 °C, 24 h.
[b] Isolated yield.
[c] Determined by chiral HPLC analysis.

related to the diastereoselectivity is not satisfied in most of the investigated cases.

Compared with nitroolefins, the asymmetric conjugate addition of alkynones is relatively rare.[7–9] Next, we attached the β-ketoamide templates to alkynones in the identified *N*,*N*′-dioxide–$Co(BF_4)_2{\cdot}6H_2O$ complex catalysts. Chiral ligand **L3** bearing alkyl substituted amide subunits were inferior to the aryl substituted partner **L1** related to the enantioselectivity and *Z*/*E*-selectivity. It was found that high yields, moderate *Z*/*E*-selectivity, and high enantioselectivity of *Z*-isomers could be obtained for different alkynones in the presence of *N*,*N*′-dioxide **L1**–$Co(BF_4)_2{\cdot}6H_2O$ catalyst, indicating that electronic effect has no major role in controlling *Z*/*E* and enantioselectivity of the reaction (65:35–79:21 *Z*/*E* ratio, 84–93% ees; Table 3). The thermodynamically unstable *Z*-isomers were produced as the major products. We have also tested other chiral *N*,*N*′-dioxide–$Co(BF_4)_2{\cdot}6H_2O$ complexes, in an attempt to improve the enantioselectivity further. Chiral *N*,*N*′-dioxide **L7**, prepared from L-pipecolic acid and 2,6-diisopropylaniline was subjected to the reaction, exhibiting even higher enantioselectivities compared with the ligand **L3**. Although the *Z*/*E*-selectivity dropped a little, excellent enantioseletivities (92–97% ees) were achieved for each diastereomer (Table 3, data in the parentheses).

The acid mediated isomerization of (*Z*)-enones enables the formation of thermodynamically stable *E*-adduct.[6i,9b] We found that the treatment of the mixture of Michael adducts *Z*/*E*-**5** with concentrated HCl gave another mixture of the chloro addition products **8** and *E*-**5** isomers (Table 4). Considering the isolated yield of the two products, we think that *Z*-isomer preferred to undergo the addition of HCl. Nevertheless, the organic acid such as *p*-toluenesulfonic acid (TsOH) mainly promoted the isomerization process to form the *E*-**5** isomer (Table 5). The optical purity of the resulted *E*-**5** isomer was maintained, indicating that the *Z*/*E*-**5** had a same stereo-arrangement at the quaternary center. Finally, the absolute configuration of the chloro addition products **8b** was unambiguously determined to be (*R*,*R*) by single-crystal X-ray diffraction (Fig. 1) [10]. Therefore, the chiral carbon of the corresponding *Z*/*E*-enone **5** was characterized as (*R*)-configuration.

Conclusions

In summary, we have developed chiral cobalt(II) complexes of *N*,*N*′-dioxides for the enantioselective Michael reaction of cyclic β-ketoamides. The addition of a variety of useful active nitroalkane derivatives underwent the reaction to give nitro-derivatives with vicinal quaternary–tertiary chiral centers in high enantioselectivities. Alkynones also performed the reaction well, affording the enone derivatives donating quaternary carbon centers in high enantioselections for both *Z*- and *E*-isomers. Further application of this catalyst system to other reactions is in progress.

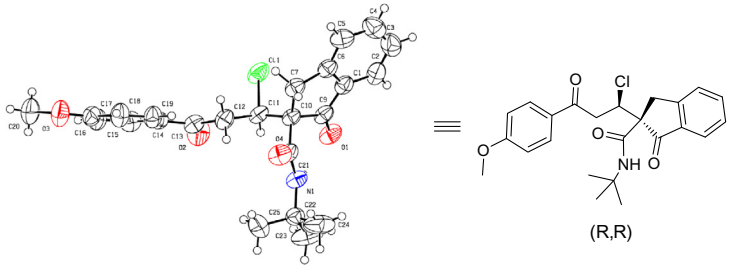


Figure 1. X-ray crystallographic structure of **8b**.

Acknowledgments

We appreciate the National Natural Science Foundation of China (Nos. 21321061, and 21222206) for financial support. We also thank the State Key Laboratory of Biotherapy for HRMS analysis.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.05.067.

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10. CCDC-991899 (**8b**) contains the supplementary crystallographic data of the adduct for this Letter. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.