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A new C_2-symmetric azolium compound for Cu-catalyzed asymmetric conjugate addition of R_2Zn to cyclic enone

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ABSTRACT

A new chiral N-heterocyclic carbene (NHC) ligand was designed. Thus, an efficient synthetic route to C_2-symmetric bis(hydroxyamide)-functionalized benzimidazolium salts from chiral β-amino alcohols was developed. The combination of $Cu(OTf)_2$ and the chiral azolium compound efficiently promoted the conjugate addition reaction of cyclic enone with dialkylzinc to give the corresponding adduct in good yield. Among a series of chiral NHC proligands, the functionalized benzimidazolium chloride possessing a *tert*-butyl group as a stereodirecting group was found to be the best choice of ligand. Under optimized reaction conditions, an excellent enantioselectivity (96% ee) was realized by allowing 2-cyclohepten-1-one to react with Bu_2Zn at room temperature.

1. Introduction

The conjugate addition (1,4-addition) of carbon nucleophiles to α,β-unsaturated carbonyl compounds is one of the most widely used methods for the construction of C–C bonds. Since the reaction often yields a stereogenic center at the β-carbon, considerable efforts have been devoted to the development of its asymmetric versions [1]. The control of stereoselectivity in transition-metal-catalyzed reactions depends on the design of a versatile ligand that would strongly coordinate with the metal center. Chiral N-heterocyclic carbene (NHC) ligands have received considerable interest in recent years because of their strong σ-donating capability to metals and the possibility of varying the substituents on the nitrogen atom [2]. Since NHCs are readily accessible, easily tunable, and form highly stable and efficient NHC–metal catalysts, a rapid elaboration of NHC ligand libraries based on the same scaffold can be envisaged and would enhance the chances of discovering an ideal chiral ligand for a given metal-catalyzed asymmetric transformation [3].

Over the past decade, much attention has been paid to the enantioselective conjugate addition (ECA) reaction catalyzed by a copper salt combined with a functionalized NHC [1]. In 2001, Alexakis and Roland independently reported that monodentate Arduengo-type diaminocarbene ligands afforded moderate enantioselectivity in the 1,4-addition of Et_2Zn to cyclic enones [4,5]. The introduction of a second coordination site at the NHC ligand provided a tightly coordinating polydentate NHC ligand system that is expected to enhance catalyst stability and to offer a key structure for the construction of efficient stereodirecting elements [6–10]. Pioneering work was performed by Arnold et al. in 2004 [6] in which the Cu-catalyzed enantioselective conjugate addition reaction proceeded with moderate enantioselectivity using a chiral anionic tethered bidentate NHC ligand. A breakthrough was achieved by Mauduit and Alexakis et al. who developed various bidentate hydroxyalkyl-NHC precursors for the ECA reaction of cyclic enones with dialkylzincs as well as the 1,4-addition reaction of β-substituted cyclic enones with Grignard reagents [7]. Moreover, Hoveyda et al. introduced chelating anionic hydroxyaryl-NHC ligands which were successfully used not only in asymmetric catalytic allylic alkylations but also in ECA reactions [8,9]. Thus, anionic tethered polydentate NHC chemistry has received considerable attention [11].

Recently, we succeeded in the development of a novel chiral polydentate hydroxyamide-functionalized NHC ligand and its Pd(II) complexes [12]. Note that the Pd(II) complex derived from a chiral β-amino alcohol catalyzes an asymmetric oxidative Heck-type reaction with excellent enantioselectivity. Encouraged by this success, we developed an efficient route to a huge variety of chiral NHC precursors, such as azolium salts and the tridentate, anionic

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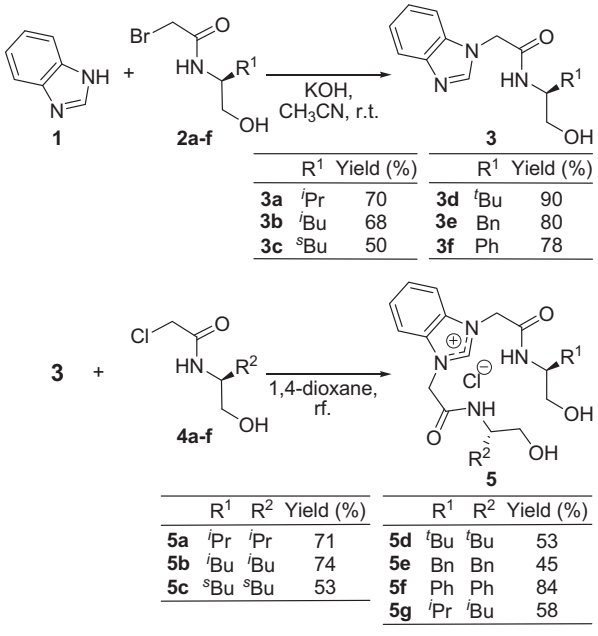
tethered NHC–Pd(II) complexes [13]. Ligand precursors, such as azolium chlorides, have also been tested in the Cu-catalyzed asymmetric conjugate addition of dialkylzincs to cyclic enones. We discovered that reversal of enantioselectivity with the same ligand could be achieved by changing the Cu precatalyst from $Cu(OTf)_2$ to $Cu(acac)_2$ [14].

As part of our continuing efforts to design new catalyst systems for enantioselective C–C bond formation, our interests turned to the design and development of C_2-symmetrical, anionic chelating NHC ligand precursors such as bis(hydroxyamide)-functionalized azolium compounds. It is known that the pincer-type ligands act as tightly coordinating polydentate ligands and that they provide a C_2-symmetric and meridional environment around the metal center. Hence, it is expected that the metal complex having of the pincer ligand becomes a suitable catalyst to distinguish the prochiral face of a substrate [15,16]. Herein, we describe an efficient Cu-catalyzed asymmetric conjugate addition of dialkylzinc to cyclic enones via the new class of chiral C_2-symmetrical ligands based on an NHC scaffold.

2. Results and discussion

A series of benzimidazolium chlorides have been successfully synthesized using commercially available β-amino alcohols as the chiral source (Scheme 1). Reaction of (*S*)-valinol with bromoacetyl bromide or chloroacetyl chloride produced the corresponding α-bromo- or α-chloroacetamide derivative, **2a** or **4a**, in almost quantitative yield, respectively [17]. The hydroxyamide group was introduced into the benzimidazole ring by allowing **2a** to react with benzimidazole (**1**) in the presence of KOH in CH_3CN at room temperature. The resulting N-hydroxyamide-functionalized benzimidazole **3a** was coupled with **4a** to yield the corresponding benzimidazolium salt **5a** in 71% yield. Several azolium compounds **5b**–**5g** could be obtained via the same route from chiral β-amino alcohols such as (*S*)-leucinol, *iso*-leucinol, *tert*-leucinol, phenylalaninol, and phenylglycinol, respectively (Scheme 1). This synthetic approach offers several advantages: (i) the starting materials used, such as chiral β-amino alcohols and reagents are readily available; (ii) all operations in the reaction steps are simple; (iii) the products in each steps could be purified via a simple procedure without employing column chromatographic techniques; (iv) the yields are moderate to good; (v) the azolium compounds **5a**–**5g** are air-stable and easy to handle.



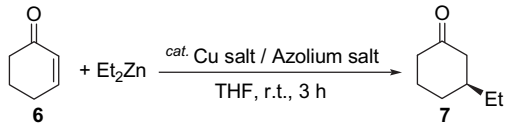
	R1	Yield (%)		R1	Yield (%)
3a	*i*Pr	70	**3d**	*t*Bu	90
3b	*i*Bu	68	**3e**	Bn	80
3c	*s*Bu	50	**3f**	Ph	78

	R1	R2	Yield (%)		R1	R2	Yield (%)
5a	*i*Pr	*i*Pr	71	**5d**	*t*Bu	*t*Bu	53
5b	*i*Bu	*i*Bu	74	**5e**	Bn	Bn	45
5c	*s*Bu	*s*Bu	53	**5f**	Ph	Ph	84
				5g	*i*Pr	*i*Bu	58

Scheme 1. Synthesis of various benzimidazolium salts.

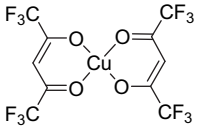
To test the possibility of achieving an asymmetric transformation reaction using the chiral benzimidazolium chlorides **5a**–**5g**, we chose the Cu-catalyzed conjugate addition of Et_2Zn to 2-cyclohexen-1-one (**6**) as a model reaction. First, we screened azolium salts and copper salts for the ECA reaction (Table 1). Treatment of **6** (1 mmol) with Et_2Zn (3 mmol) in THF in the presence of Cu $(OTf)_2$ (2 mol %) and **5a** (3 mol %) at room temperature for 3 h produced the desired adduct, such as 3-ethylcyclohexanone (**7**) in almost quantitative yield and 44% ee (Run 1). The NHC ligand precursor, such as **5b** or **5c** derived from (*S*)-leucinol or (*S*)-*iso*-leucinol, respectively, showed almost the same results (Runs 2 and 3). A sterically hindered substituent such as a *tert*-butyl group in the ligand proved efficient to produce **7** in 62% ee; however, the yield decreased, probably owing to the steric hindrance of the ligand (Run 4). Both **5e** and **5f** resulted in poor enantioselectivities (Runs 5 and 6). When the reaction was carried out using $Cu(OTf)_2$

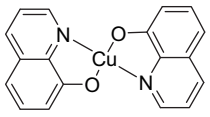
Table 1
ECA reaction of **6** with Et_2Zn catalyzed by Cu salt combined with benzimidazolium salt.[a]

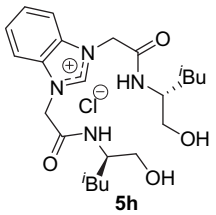


Run	Cu salt	Azolium salt	Yield[b] (%)	Ee[b] (%)
1	$Cu(OTf)_2$	**5a**	>99	44
2	$Cu(OTf)_2$	**5b**	90	54
3	$Cu(OTf)_2$	**5c**	84	51
4	$Cu(OTf)_2$	**5d**	43	62
5	$Cu(OTf)_2$	**5e**	94	25
6	$Cu(OTf)_2$	**5f**	78	30
7[c]	**$Cu(OTf)_2$**	**5d**	**96**	**63**
8[c]	$Cu(NO_3)_2$	**5d**	82	57
9[c]	Cu(II) salt[d]	**5d**	82	42
10[c]	$CuCl_2$	**5d**	70	13
11[c]	$Cu(acac)_2$	**5d**	88	2
12[c]	Cu(II) salt[e]	**5d**	83	5
13	$Cu(OTf)_2$	**5h**[f]	87	*ent*-52

[a] **6** (1 mmol), Et_2Zn (3 mmol), Cu salt (2 mol %), benzimidazolium salt (3 mol %), THF (3 mL), r.t., 3 h.
[b] Yield and ee were determined by GLC analysis. Average of two runs.
[c] Cu salt (4 mol %), **5d** (6 mol %).

d


e


f


(4 mol %) and **5d** (6 mol %), the adduct was obtained in excellent yield with 63% ee (Run 7).

Having established the catalytic activity of $Cu(OTf)_2$ combined with the C_2-symmetrical azolium salt **5d**, we subsequently turned our attention to the effect of copper salt other than $Cu(OTf)_2$ on reactivity and enantioselectivity (Runs 8–12). The result with $Cu(NO_3)_2$ was similar to that with $Cu(OTf)_2$ (Run 8). $CuCl_2$, $Cu(acac)_2$, and bis(8-quinolinolato)copper(II) led to racemic **7**, although moderate to good yields were obtained in each case (Runs 10–12). In the preceding paper, we showed that the conjugate addition of Et_2Zn to **6** catalyzed by $Cu(OTf)_2$ combined with a chiral azolium chloride having both a hydroxyamide group at the N(1) substituent and a methyl group at the N(3) substituent of the azolium ring gave (*S*)-**7**, while use of $Cu(acac)_2$ in combination with the same ligand afforded (*R*)-**7** as the major product [14]. However, the reversal of enantioselectivity by changing the Cu species from $Cu(OTf)_2$ to $Cu(acac)_2$ was not observed in the case of **5d** as a chiral ligand precursor (Run 7 vs. Run 11). (*R*)-**6** was obtained as the major product using **5h** derived from (*R*)-*iso*-leucinol (Run 2 vs. Run 13).

Numerous variations of the reaction conditions were explored for the $Cu(OTf)_2$-catalyzed addition of Et_2Zn to **6** in the presence of **5d** (Table 2). For further reaction optimization, the solvent effect was investigated. The first promising result was achieved with THF, which gave 63% ee and 96% product yield in the ECA reaction by the $Cu(OTf)_2$/**5d** catalytic system (Run 1). Almost the same result was observed for the reaction in 1,4-dioxane, giving **7** in 96% yield and 57% ee (Run 2). Other ethereal solvents such as Et_2O, TBME, and CPME as well as non-polar solvents such as CH_2Cl_2 and toluene did not improve the enantioselectivity, although the conjugate addition took place smoothly to produce **7** in good to excellent yield (Runs 3–7). The reaction in polar solvents such as CH_3CN, DMSO and DMF gave **7** with difficulty (Runs 8–10). However, the stereoselectivity of the conjugate adduct in the reaction using DMA as a solvent was found to be comparable to or better than that obtained using THF (Run 11). The quantity of Et_2Zn in this ECA reaction has a significant effect on the yield of product (Runs 11–13).

Table 2
Solvent effect on ECA reaction of **6** with Et_2Zn catalyzed by $Cu(OTf)_2$ combined with **5d**.[a]

Run	$Cu(OTf)_2$ (mol %)	**5d** (mol %)	Solvent	Yield (%)[b]	Ee[b] (%)
1	**4**	**6**	**THF**	**96**	**63**
2	4	6	1,4-dioxane	96	57
3	4	6	Et_2O	74	25
4	4	6	TBME[c]	95	20
5	4	6	CPME[d]	86	22
6	4	6	CH_2Cl_2	>99	15
7	4	6	toulene	70	9
8	4	6	CH_3CN	46	43
9	4	6	DMSO	43	45
10	4	6	DMF	30	55
11	4	6	DMA[e]	77	67
12[f]	**4**	**6**	**DMA**	**83**	**70**
13[g]	4	6	DMA	27	53
14[f]	4	4	DMA	82	66
15[f]	4	2	DMA	72	68
16[f]	2	5	DMA	73	64
17[f]	2	3	DMA	69	64
18[f]	**4**	**2**	**AcOEt**	**92**	**62**

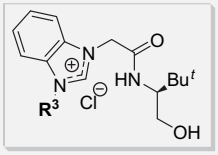
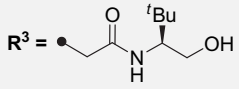
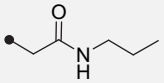
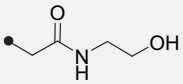
[a] **6** (1 mmol), Et_2Zn (3 mmol), solvent (3 mL), r.t., 3 h.
[b] Yield and ee were determined by GLC analysis. Average of two runs.
[c] *tert*-Butyl methyl ether.
[d] Cyclopentyl methyl ether.
[e] N,N-Dimethyl acetoamide.
[f] Et_2Zn (4 mmol).
[g] Et_2Zn (1.5 mmol).

Then, we examined the influence of the copper/ligand ratio as well as catalyst loading on stereoselectivity in the reaction of **6** with Et_2Zn in DMA (Runs 14–17). The reaction with a $Cu(OTf)_2$/**5d** ratio of 1/1.5, 1/1, and 1/0.5 took place in a similar fashion, affording the corresponding adduct in moderate to good yield and enantioselectivity (Runs 12, 14 and 15). Decreasing the amount of $Cu(OTf)_2$ only slightly reduced the product yield (Runs 16 and 17). In addition, the reaction catalyzed by $Cu(OTf)_2$ (4 mol %) combined with **5d** (2 mol %) in ethyl acetate proceeded in a comparable way to the reaction in THF, giving **7** in 92% yield and 62% ee (Run 1 vs. Run 18).

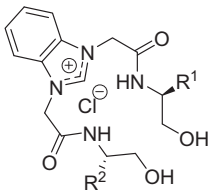
Next, we were interested in the influence of N-functional groups at the azolium ring on the stereoselectivity in the ECA reaction (Table 3). A series of non-C_2-symmetric azolium compounds **8**–**11** having the hydroxyamide-functionality at the N(1) substituent could be synthesized in a route similar to that shown in Scheme 1. These examinations revealed that a bis(hydroxyamide)-substituted azolium compound such as **5d** works more efficiently than azolium salts possessing an alkylamide group or a hydroxyamide group without any stereodirecting elements at the N(3) substituent, such as **8** or **9** (Runs 1–3). The azolium salt **10** that was prepared by the coupling of *N*-methylbenzimidazole with **4d** provided the conjugate addition product **7** in 71% yield and 62% ee (Run 4), while a slightly better result was obtained using the chiral NHC precursor **11** bearing an N-benzyl group at the azolium ring (Run 5). The ECA reaction using **10** or **11** as a chiral ligand is currently under investigation [14b].

Moreover, the easy access to N-functionalized NHC precursors allowed us to investigate the synergetic effect of the stereodirecting groups on the ligands (Scheme 2). With **5a** and **5b**, **6** reacted with

Table 3
Influence of N(3) substituent at benzimidazolium ring on the ECA reaction of **6** with Et_2Zn catalyzed by $Cu(OTf)_2$.[a]

Run	Azolium salt		Yield[b] (%)	Ee[b] (%)
				
1		**5d**	72	68
2		**8**	95	46
3		**9**	63	35
4		**10**	71	62
5		**11**	83	70

[a] **6** (1 mmol), Et_2Zn (4 mmol), DMA (3 mL), $Cu(OTf)_2$ (4 mol %), benzimidazolium salt (2 mol %), r.t., 3 h.
[b] Yield and ee were determined by GLC analysis. Average of two runs.

Azolium salt		Yield (%)	Ee (%)
	**5a** (R^1, R^2 = ^{i}Pr)	36	42
	5b (R^1, R^2 = ^{i}Bu)	59	47
	5g (R^1, R^2 = ^{i}Pr, ^{i}Bu)	80	53

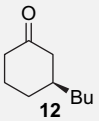
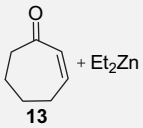
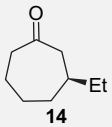
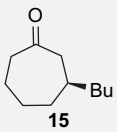
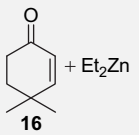
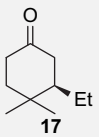
Reaction contions: **6** (1 mmol), Et_2Zn (4 mmol), $Cu(OTf)_2$ (4 mol %), benzimidazolium salt (2 mol %), DMA (3 mL), r.t., 3 h.

Scheme 2. Synergetic effect of the stereodirecting groups on the benzimiazolium salt in the ECA reaction of **6** with Et_2Zn catalyzed by $Cu(OTf)_2$.

Et_2Zn in DMA under the influence of $Cu(OTf)_2$ to produce the conjugate adduct **7** in low yield and enantioselectivity, respectively. However, it was found that the reaction with non-C_2-symmetric bis (hydroxyamide)-functionalized benzimidazolium salt **5g** was more efficient (80% yield) as well as slightly more enantioselective (53% ee) than that with the C_2-symmetric azolium salts **5a** or **5b**. The reason for this synergetic effect is unclear, but one possibility is that a suitable site for coordination of the enone **6** might be generated in the catalytic-active species derived from $Cu(OTf)_2$ and **5g** having both *iso*-propyl and *iso*-butyl groups.

With the optimal catalyst combination and reaction conditions in hand, we finally investigated the scope of the ECA reaction of different cyclic enones with dialkylzincs (Table 4). These reactions were performed in the presence of catalytic amounts of $Cu(OTf)_2$ and **5d** at room temperature for 3 h with either THF or DMA as a solvent. Replacement of Et_2Zn by Bu_2Zn in the reaction of **6** in THF led to a slight improvement in the enantioselectivity (76% ee) of the corresponding adducts (*S*)-**12** (Run 1). Treatment of **6** with Bu_2Zn in DMA gave (*S*)-**12** with a somewhat lower ee value (Run 2). Reaction of a cyclic enone consisting of a seven-membered ring such as 2-cyclohepten-1-one (**13**) increased the stereoselectivity (Runs 3–6). For example, cyclic enone **13** efficiently underwent 1,4-addition with Et_2Zn in DMA to afford (*S*)-3-ethylcycloheptanone (**14**) in 96% yield and 85% ee (Run 4). An excellent ee value of 96% was obtained by allowing **13** to react with Bu_2Zn in DMA to produce (*S*)-3-butylcycloheptanone (**15**) (Run 6). 4,4-Dimethyl-2-cyclohexen-1-one (**16**) also reacted smoothly with Et_2Zn to form (*R*)-3-ethyl-4, 4-dimethylcyclohexanone (**17**) in good yield (Runs 7–8). A better result was obtained by using DMA as a solvent than that obtained using THF.

Table 4
ECA reaction of several cyclic enones with R_2Zn catalyzed by $Cu(OTf)_2$ combined with **5d**.[a]

Run	Substrate	Solvent	Product	Yield[b] (%)	Ee[c] (%)
1	**6**+Bu_2Zn	THF	 **12**	78	76
2		DMA		84	66
3	 + Et_2Zn **13**	THF	 **14**	65	74
4		DMA		96	85
5	**13**+Bu_2Zn	THF	 **15**	91	84
6		DMA		83	96
7	 + Et_2Zn **16**	THF	 **17**	86	58
8		DMA		78	71

[a] Enone (1 mmol), R_2Zn (3 mmol for THF or 4 mmol for DMA), solvent (3 mL), $Cu(OTf)_2$ (4 mol %), **5d** (6 mol %), r.t., 3 h.
[b] Isolated yield. Average of two runs.
[c] Ee was determined by GLC analysis.

3. Conclusion

We have demonstrated that a C_2-symmetric bis(hydroxyamide)-functionalized benzimidazolium salt efficiently performs a copper-catalyzed asymmetric conjugate addition of dialkylzinc reagents to cyclic enones, with up to 96% ee. These air-stable, chiral ligands are especially useful because of the operational simplicity of their preparation. In addition, the ECA reaction could be carried out at ambient temperature without controlling the temperature of the solution. The applications of the chiral chelating polydentate NHC catalysts as well as the design and development of a new class of chiral ligand based on an NHC scaffold for efficient catalytic enantioselective transformations is the subject of ongoing research in our laboratory.

4. Experimental

4.1. General procedure for the preparation of *3* and *5*

To CH_3CN were added KOH (0.48 M), benzimidazole (**1**) (0.32 M) and α-bromoacetamide derivative **2** (0.32 M) derived from bromoacetyl bromide and β-amino alcohol. After stirring the reaction mixture at room temperature for 16 h, H_2O was added to form a white precipitate. The white product was separated from the solution by filtration under reduced pressure, and then the solid was dissolved in methanol. The resulting solution was dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure to obtain the desired product such as N-hydroxyamide substituted benzimidazole derivative **3**. The product **3** could be used without further purification in the next step.

Then, to 1,4-dioxane were added **3** (0.293 M) and α-chloroacetamide **4** (0.267 M) derived from chloroacetyl chloride and β-amino alcohol. After stirring the reaction mixture at 110 °C for 16 h, the solvent was removed under reduced pressure. The residue was dissolved in methanol, and then activated carbon was added. After 16 h, the activated carbon was removed by filtration. The filtrate was concentrated under reduced pressure to obtain a solid, which was purified by reprecipitation using ethyl acetate and methanol to afford the corresponding coupling product **5** as a solid.

4.2. Analytical data

4.2.1. Compound *3a*

^{1}H-NMR (CD_3OD): δ 8.16 (s, 1H), 7.68–7.65 (m, 1H), 7.51–7.47 (m, 1H), 7.34–7.23 (m, 2H), 5.05 (d, J = 16.3 Hz, 1H), 4.98 (d, J = 16.3 Hz, 1H), 3.75–3.67 (m, 1H), 3.67–3.52 (m, 2H), 1.94–1.80 (m, 1H), 0.93 (d, J = 4.7 Hz, 3H), 0.90 (d, J = 4.7 Hz, 3H); ^{13}C-NMR: δ 169.1, 145.7, 124.4, 123.7, 120.0, 111.3, 63.0, 58.4, 48.2, 30.0, 20.0, 18.8.

4.2.2. Compound *3b*

^{1}H-NMR ($(CD_3)_2SO$): δ 8.15 (s, 1H), 8.13 (d, J = 12.0 Hz, 1H), 7.65–7.63 (m, 1H), 7.42–7.41 (m, 1H), 7.24–7.17 (m, 2H), 4.93 (d,

J = 16.0 Hz, 1H), 4.87 (d, J = 16.0 Hz, 1H), 4.75 (br, 1H), 3.84–3.75 (m, 1H), 3.37–3.26 (m, 2H), 1.64–1.54 (m, 1H), 1.33–1.30 (m, 2H), 0.87 (d, J = 4.0 Hz, 3H), 0.80 (d, J = 4.0 Hz, 3H); ^{13}C-NMR: δ 166.1, 144.9, 143.3, 134.2, 122.3, 121.5, 119.4, 110.2, 63.7, 49.2, 48.6, 47.0, 24.3, 23.4, 21.8.

4.2.3. Compound ***3c***

^{1}H-NMR ($(CD_3)_2SO$): δ 8.15 (s, 1H), 8.12 (d, J = 9.0 Hz, 1H), 7.65–7.63 (m, 1H), 7.45–7.43 (m, 1H), 7.24–7.17 (m, 2H), 4.96 (d, J = 16.1 Hz, 1H), 4.89 (d, J = 16.1 Hz, 1H), 4.64 (br, 1H), 3.64–3.57 (m, 1H), 3.48–3.41 (m, 2H), 1.66–1.55 (m, 1H), 1.46–1.40 (m, 1H), 1.10–1.03 (m, 1H), 0.83–0.78 (m, 6H); ^{13}C-NMR: δ 166.2, 144.9, 143.2, 134.2, 122.2, 121.5, 119.3, 110.2, 60.9, 55.0, 47.0, 34.8, 24.7, 15.5, 11.2.

4.2.4. Compound ***3d***

^{1}H-NMR ($(CD_3)_2SO$): δ 8.16 (s, 1H), 8.02 (br, 1H), 7.65–7.63 (m, 1H), 7.47–7.45 (m, 1H), 7.24–7.16 (m, 2H), 5.00 (d, J = 16.4 Hz, 1H), 4.92 (d, J = 16.4 Hz, 1H), 4.52 (br, 1H), 3.62–3.57 (m, 2H), 3.38–3.32 (m, 1H), 0.85 (s, 9H); ^{13}C-NMR: δ 166.9, 144.9, 143.2, 134.2, 122.2, 121.4, 119.3, 110.3, 60.4, 59.2, 47.0, 33.7, 26.9.

4.2.5. Compound ***3e***

^{1}H-NMR ($(CD_3)_2SO$): δ 8.34 (d, J = 8.0 Hz, 1H), 8.08 (s, 1H), 7.62–7.60 (m, 1H), 7.26–7.14 (m, 8H), 4.94 (t, J = 6.0 Hz, 1H), 4.89 (d, J = 16.0 Hz, 1H), 4.79 (d, J = 16.0 Hz, 1H), 3.97–3.89 (m, 1H), 3.47–3.33 (m, 2H), 2.89–2.85 (m, 1H), 2.66–2.49 (m, 1H); ^{13}C-NMR: δ 166.0, 144.9, 143.2, 139.0, 134.1, 129.2, 128.2, 126.1, 122.4, 121.5, 119.3, 110.3, 62.7, 52.8, 46.9, 36.6.

4.2.6. Compound ***3f***

^{1}H-NMR ($(CD_3)_2SO$): δ 8.85 (d, J = 8.2 Hz, 1H), 8.15 (s, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.32–7.16 (m, 7H), 5.01–4.98 (m, 3H), 4.86–4.84 (m, 1H), 3.64–3.54 (m, 2H); ^{13}C-NMR: δ 166.3, 144.9, 143.2, 140.7, 134.2, 128.1, 126.9, 122.2, 121.5, 119.3, 110.3, 64.6, 55.4, 46.9.

4.2.7. Compound ***5a***

White solid; mp 212.7–214.5 °C. ^{1}H-NMR (CD_3OD): δ 9.62 (s, 1H), 7.93–7.87 (m, 2H), 7.74–7.67 (m, 2H), 5.42 (d, J = 16.4 Hz, 2H), 5.35 (d, J = 16.4 Hz, 2H), 3.78–3.55 (m, 6H), 1.96–1.81 (m, 2H), 0.96 (d, J = 6.4 Hz, 6H), 0.94 (d, J = 6.4 Hz, 6H); ^{13}C-NMR: δ 166.6, 145.0, 133.0, 128.5, 114.4, 63.0, 59.0, 49.8, 30.2, 20.0, 18.9. Anal. Calc. for $C_{21}H_{33}ClN_4O_4 \cdot 0.75H_2O$: C, 55.50; H, 7.65; N, 12.33. Found: C, 55.14; H, 7.24; N, 12.18%.

4.2.8. Compound ***5b***

White solid; mp 167.4–168.3 °C. ^{1}H-NMR ($(CD_3)_2SO$): δ 9.82 (s, 1H), 8.57 (d, J = 8.8 Hz, 2H), 7.93–7.90 (m, 2H), 7.71–7.67 (m, 2H), 5.42 (d, J = 16.4 Hz, 2H), 5.35 (d, J = 16.4 Hz, 2H), 4.84 (t, J = 5.6 Hz, 2H), 3.84–3.78 (m, 2H), 3.41–3.46 (m, 4H), 1.71–1.58 (m, 2H), 1.34–1.28 (m, 4H), 0.88 (d, J = 6.8 Hz, 6H), 0.81 (d, J = 6.8 Hz, 6H); ^{13}C-NMR: δ 164.0, 144.3, 131.2, 126.7, 113.6, 63.5, 49.6, 48.7, 24.3, 23.3, 21.9. Anal. Calc. for $C_{23}H_{37}ClN_4O_4 \cdot 1.5H_2O$: C, 55.69; H, 8.13; N, 11.29. Found: C, 55.37; H, 7.65; N, 11.22%.

4.2.9. Compound ***5c***

White solid; mp 222.7–223.1 °C. ^{1}H-NMR ($(CD_3)_2SO$): δ 9.81 (s, 1H), 8.52 (d, J = 8.5 Hz, 2H), 7.93–7.90 (m, 2H), 7.71–7.68 (m, 2H), 5.44 (d, J = 16.1 Hz, 2H), 5.36 (d, J = 16.1 Hz, 2H), 4.73 (t, J = 5.4 Hz, 2H), 3.68–3.60 (m, 2H), 3.48–3.46 (m, 4H), 1.65–1.58 (m, 2H), 1.49–1.43 (m, 2H), 1.19–1.06 (m, 2H), 0.86–0.81 (m, 12H); ^{13}C-NMR: δ 164.1, 144.3, 131.2, 126.7, 113.5, 60.8, 55.5, 48.7, 34.9, 24.7, 15.5, 11.2. Anal. Calc. for $C_{23}H_{37}ClN_4O_4 \cdot 0.5H_2O$: C, 57.79; H, 8.01; N, 11.72. Found: C, 57.49; H, 7.84; N, 11.73%.

4.2.10. Compound ***5d***

White solid; mp 116.2–117.1 °C. ^{1}H-NMR ($(CD_3)_2SO$): δ 9.86 (s, 1H), 8.45 (d, J = 9.2 Hz, 2H), 7.98–7.95 (m, 2H), 7.70–7.67 (m, 2H), 5.52 (d, J = 16.4 Hz, 2H), 5.42 (d, J = 16.4 Hz, 2H), 4.64 (t, J = 5.6 Hz, 2H), 3.78–3.60 (m, 4H), 3.43–3.40 (m, 2H), 0.89 (s, 18H); ^{13}C-NMR: δ 164.7, 144.3, 131.2, 126.7, 113.6, 60.3, 59.8, 48.7, 33.6, 26.8. Anal. Calc. for $C_{23}H_{37}ClN_4O_4 \cdot 3H_2O$: C, 52.81; H, 8.29; N, 10.71. Found: C, 52.42; H, 7.76; N, 10.57%.

4.2.11. Compound ***5e***

White solid; mp 215.6–216.6 °C. ^{1}H-NMR ($(CD_3)_2SO$): δ 9.63 (s, 1H), 8.76 (d, J = 8.0 Hz, 2H), 7.58–7.51 (m, 4H), 7.24–7.18 (m, 10H), 5.31 (d, J = 16.0 Hz, 2H), 5.22 (d, J = 16.0 Hz, 2H), 5.00 (br, 2H), 3.97–3.89 (m, 2H), 3.47–3.33 (m, 4H), 2.89–2.84 (m, 2H), 2.68–2.63 (m, 2H); ^{13}C-NMR: δ 163.9, 144.1, 138.9, 131.0, 129.2, 128.2, 126.7, 126.1, 113.4, 62.6, 53.3, 48.6, 36.6. Anal. Calc. for $C_{29}H_{33}ClN_4O_4 \cdot 2.25H_2O$: C, 60.30; H, 6.54; N, 9.70. Found: C, 60.31; H, 6.16; N, 9.74%.

4.2.12. Compound ***5f***

Light yellow solid; mp 215.3–216.0 °C. ^{1}H-NMR ($(CD_3)_2SO$): δ 9.81 (s, 1H), 9.38 (d, J = 8.1 Hz, 2H), 7.96–7.93 (m, 2H), 7.67–7.63 (m, 2H), 7.38–7.21 (m, 10H), 5.49 (s, 4H), 5.12 (t, J = 5.7 Hz, 2H), 4.89–4.81 (m, 2H), 3.64–3.56 (m, 4H); ^{13}C-NMR: δ 164.2, 144.3, 140.4, 131.2, 128.1, 127.0, 126.9, 126.6, 113.6, 64.6, 55.9, 48.6. Anal. Calc. for $C_{27}H_{29}ClN_4O_4 \cdot 2.3H_2O$: C, 58.92; H, 6.15; N, 10.18. Found: C, 58.83; H, 5.37; N, 10.18%.

4.2.13. Compound ***5g***

White solid; mp 198.7–199.3 °C. ^{1}H-NMR ($(CD_3)_2SO$): δ 9.85 (s, 1H), 8.59 (d, J = 8.4 Hz, 1H), 8.55 (d, J = 8.8 Hz, 1H), 7.97–7.91 (m, 2H), 7.70–7.68 (m, 2H), 5.48 (d, J = 16.4 Hz, 1H), 5.43 (d, J = 11.2 Hz, 1H), 5.39 (d, J = 11.2 Hz, 1H), 5.36 (d, J = 16.4 Hz, 1H), 4.84 (t, J = 10.0 Hz, 1H), 4.78 (t, J = 10.0 Hz, 1H), 3.82–3.80 (m, 1H), 3.61–3.57 (m, 1H), 3.46–3.44 (m, 4H), 1.88–1.83 (m, 1H), 1.64–1.61 (m, 1H), 1.39–1.32 (m, 2H), 0.88–0.81 (m, 12H); ^{13}C-NMR: δ 164.3, 163.9, 144.3, 131.2, 126.7, 126.6, 113.6, 63.5, 61.1, 56.6, 49.6, 48.6, 28.3, 24.2, 23.2, 21.8, 19.6, 18.2. Anal. Calc. for $C_{22}H_{35}ClN_4O_4 \cdot H_2O$: C, 55.86; H, 7.88; N, 11.84. Found: C, 55.69; H, 7.51; N, 11.76%.

4.2.14. Compound ***5h***

White solid; mp 172.5–173.3 °C. ^{1}H-NMR ($(CD_3)_2SO$): δ 9.79 (s, 1H), 8.52 (d, J = 8.0 Hz, 2H), 7.90–7.88 (m, 2H), 7.69–7.67 (m, 2H), 5.40 (d, J = 16.0 Hz, 2H), 5.33 (d, J = 16.0 Hz, 2H), 4.83 (t, J = 8.0 Hz, 2H), 3.84–3.76 (m, 2H), 3.46–3.41 (m, 4H), 1.66–1.56 (m, 2H), 1.38–1.27 (m, 4H), 0.87 (d, J = 6.8 Hz, 6H), 0.80 (d, J = 6.8 Hz, 6H); ^{13}C-NMR: δ 164.0, 144.3, 131.2, 126.7, 113.6, 63.5, 49.6, 48.7, 24.2, 23.3, 21.8. Anal. Calc. for $C_{23}H_{37}ClN_4O_4 \cdot 1.125H_2O$: C, 56.46; H, 8.09; N, 11.45. Found: C, 56.13; H, 7.89; N, 11.33%.

4.2.15. Compound ***8***

White solid; mp 119.2–121.3 °C. ^{1}H-NMR ($(CD_3)_2SO$): δ 9.78 (s, 1H), 8.62 (br, 1H), 8.31 (br, 1H), 7.92–7.89 (m, 2H), 7.69–7.67 (m, 2H), 5.47 (d, J = 16.0 Hz, 1H), 5.37 (s, 2H), 5.36 (d, J = 16.0 Hz, 1H), 4.59 (t, J = 4.0 Hz, 1H), 3.64–3.58 (m, 2H), 3.46–3.45 (m, 1H), 3.11–3.07 (m, 2H), 1.49–1.41 (m, 2H), 0.88 (s, 9H), 0.87 (t, J = 8.0 Hz, 3H); ^{13}C-NMR: δ 164.6, 164.3, 144.3, 131.3, 131.2, 126.7, 126.7, 113.7, 113.6, 60.3, 59.8, 48.8, 48.5, 40.8, 33.7, 26.8, 22.2, 11.4. Anal. Calc. for $C_{20}H_{31}ClN_4O_3 \cdot 1.125H_2O$: C, 55.71; H, 7.77; N, 12.99. Found: C, 55.32; H, 7.46; N, 12.82%.

4.2.16. Compound ***9***

White solid; mp 160.2–160.9 °C. ^{1}H-NMR ($(CD_3)_2SO$): δ 9.80 (s, 1H), 8.75 (br, 1H), 8.40 (br, 1H), 7.94–7.91 (m, 2H), 7.69–7.66 (m, 2H),

5.48 (d, $J = 16.0$ Hz, 1H), 5.37 (s, 2H), 5.37 (d, $J = 16.0$ Hz, 1H), 4.85 (t, $J = 8.0$ Hz, 1H), 4.63 (t, $J = 8.0$ Hz, 1H), 3.69–3.58 (m, 2H), 3.46–3.45 (m, 1H), 3.21–3.19 (m, 2H), 0.87 (s, 9H); ^{13}C-NMR: δ 164.7, 164.6, 144.3, 131.3, 131.2, 126.7, 126.7, 113.8, 113.7, 60.3, 59.9, 59.5, 48.8, 48.6, 42.0, 33.7, 26.9. Anal. Calc. for $C_{19}H_{29}ClN_4O_4 \cdot 0.5CH_2Cl_2$: C, 51.43; H, 6.64; N, 12.30. Found: C, 51.29; H, 6.69; N, 12.57%.

4.3. General procedure for the Cu(OTf)$_2$-catalyzed ECA of enone with R_2Zn

To a solution of azolium salt (0.04 mmol) in THF (3 mL) were added Cu(OTf)$_2$ (0.06 mmol) and enone (1 mmol). After the mixture was cooled to 0 °C, Et_2Zn (3 mmol, 1 mol/L in hexanes) was added to the reaction vessel. The color immediately changed from yellow to dark brown. After stirring at room temperature for 3 h, the reaction was quenched with 10% HCl aq. The resulting mixture was extracted with diisopropyl ether and dried over Na_2SO_4. The product was purified by silica gel column chromatography (hexane/EtOAc). The ee was measured by chiral GLC.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.jorganchem.2010.07.038.

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