Asymmetric Catalysis

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Catalytic Asymmetric Homologation of α-Ketoesters with α-Diazoesters: Synthesis of Succinate Derivatives with Chiral Quaternary Centers**

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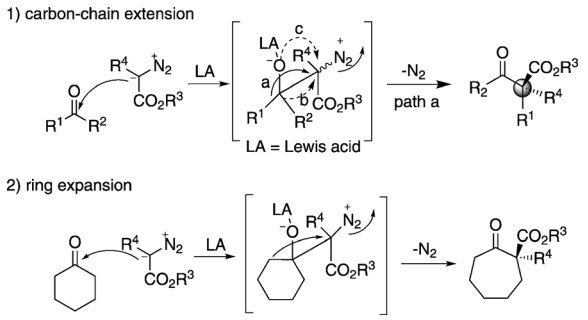
The one-carbon homologation of carbonyl compounds using diazo compounds is a frequently encountered synthetic objective.[1] Several related reactions have been developed and are known as the Arndt–Eistert reaction,[2] Buchner–Curtius–Schlotterbeck reaction,[3] Tiffeneau–Demjanov rearrangement,[4] and Roskamp–Feng reaction.[5] Among these reactions, Lewis acid catalyzed homologation of aldehydes or ketones with diazo compounds results in a carbon-chain extension or ring expansion at a carbonyl group, thus producing a synthetically useful carbonyl-containing backbone (Scheme 1).[6,7] Remarkably, the reactions found successful applications in natural product synthesis in recent years.[8]



Scheme 1. Lewis acid (LA) catalyzed homologation of carbonyl compounds using α-diazoesters.

Intriguingly, a catalytic asymmetric variant of this transformation by using α-substituted α-diazo compounds will incorporate a chiral tertiary (for aldehydes) or quaternary (for ketones) carbon center[9] at the position adjacent to the carbonyl group (Scheme 1). Recently, innovative studies by several groups have been extended to the asymmetric reaction of aldehydes and cyclic carbonyl compounds. Asymmetric homologation of aldehydes with α-alkyl-α-diazo compounds were documented by Maruoka and co-workers,[10] ourselves,[11] and Ryu and co-workers.[12] Stereoselective construction of seven-membered rings from cyclohexanones was accomplished by the group of Maruoka by using a chiral aluminum complex of a binol derivative.[13] An asymmetric ring expansion of cycloalkanones with terminal diazoalkanes was reported by Kingsbury and co-workers by using chiral scandium complexes of oxazoline ligands.[14] We realized the corresponding ring-expansion reaction of isatins.[11c] Nevertheless, daunting challenges remain in the asymmetric carbon-chain extention of acyclic ketones. Compared with the asymmetric homologation of cycloalkanones, the control of the enantioselectivity and regioselectivity of acyclic ketones (Scheme 1, path a) is more complex without the ring system. Additionally, acyclic ketones receive more steric hindrance than the relatively bare carbonyl group on a cyclic ring, which reduces the reactivity. Otherwise, the formation of epoxides from acyclic ketones is highly competitive relative to aldehydes and cyclic ketones.[1a,b] Continued improvement of asymmetric homologation of ketones achieved by new Lewis acid catalysts under mild reaction conditions is significantly desired. We report herein a breakthrough by using chiral *N*,*N*′-dioxide-yttrium(III) complexes. Asymmetric homologation of α-ketoesters with α-alkyl-α-diazoesters was achieved, thus generating enantiomeric enriched succinate derivatives with chiral all-carbon quaternary centers.

After preliminary screening, we chose the α-ketoester **1a** and α-methyl-α-diazoester **2a** as the model substrates for catalysis using chiral *N*,*N*′-dioxide/metal complexes[15] (Table 1). Surprisingly, the catalyst **L1**/$Sc(OTf)_3$, which was efficient in our previous study,[11] could not promote the reaction of the α-ketoester (entry 1). The complexes of $Ni(OTf)_2$ and $Zn(OTf)_2$ also failed to catalyze the reaction (entries 2 and 3). To our delight, the complex **L1**/$Yb(OTf)_3$ gave the desired product in 38% yield and 87% *ee* (entry 4). The carbon-chain extension at the carbonyl group occurred by 1,2-aryl migration, thus producing the succinate derivative **3aa** with a chiral all-carbon quaternary center. Better outcomes were obtained when $Y(OTf)_3$ was used as the metal precursor (44% yield and 92% *ee*; entry 5). Other metal sources were also tested, but no further improvement was observed. The amino acid backbone of the ligand was then probed. Using the L-pipecolic-acid-derived *N*,*N*′-dioxide **L2** gave lower reactivity and enantioselectivity (entry 5 versus entry 6). Comparatively, the ligand **L3** derived from L-proline showed slightly superior outcomes with 45% yield and 92% *ee* (entry 7). Steric hindrance on the phenyl ring of the ligand plays a key role in promoting both the enantioselectivity and

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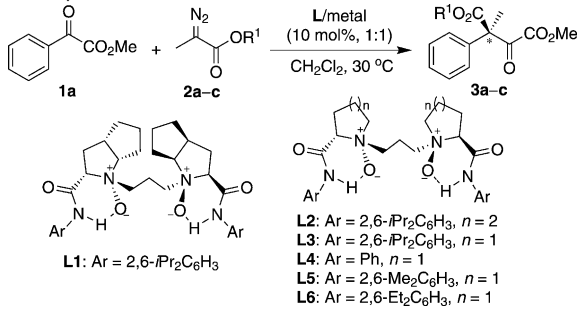
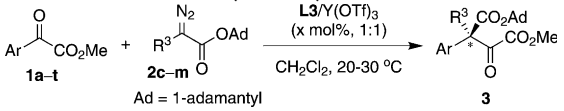
Table 1: Optimization of the reaction conditions.[a]

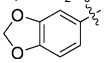


Entry	L	Metal	R^1	Yield [%][b]	*ee* [%][c]
1	**L1**	$Sc(OTf)_3$	Et (**2a**)	0	–
2	**L1**	$Ni(OTf)_2$	Et (**2a**)	0	–
3	**L1**	$Zn(OTf)_2$	Et (**2a**)	0	–
4	**L1**	$Yb(OTf)_3$	Et (**2a**)	38 (**3aa**)	87
5	**L1**	$Y(OTf)_3$	Et (**2a**)	44 (**3aa**)	92
6	**L2**	$Y(OTf)_3$	Et (**2a**)	29 (**3aa**)	81
7	**L3**	$Y(OTf)_3$	Et (**2a**)	45 (**3aa**)	92
8	**L4**	$Y(OTf)_3$	Et (**2a**)	8 (**3aa**)	5
9	**L5**	$Y(OTf)_3$	Et (**2a**)	15 (**3aa**)	76
10	**L6**	$Y(OTf)_3$	Et (**2a**)	40 (**3aa**)	88
11	**L3**	$Y(OTf)_3$	*t*Bu (**2b**)	65 (**3ab**)	92
12	**L3**	$Y(OTf)_3$	1-adamantyl (**2c**)	73 (**3ac**)	92
13[d]	**L3**	$Y(OTf)_3$	1-adamantyl (**2c**)	73 (**3ac**)	92
14[e]	**L3**	$Y(OTf)_3$	1-adamantyl (**2c**)	69 (**3ac**)	90

[a] Unless specified, all reactions were performed with **1a** (0.10 mmol), **2** (0.15 mmol), **L**/metal (10 mol%, 1:1), and CH_2Cl_2 (0.5 mL) at 30°C for 24 h. [b] Yield of isolated product. [c] Determined by HPLC analysis using a chiral stationary phase. [d] The reaction was performed with **1a** (0.20 mmol), **2c** (0.30 mmol), **L3**/$Y(OTf)_3$ (2 mol%, 1:1), and CH_2Cl_2 (0.5 mL) at 30°C for 48 h. [e] Using 0.5 mol% of the catalyst in CH_2Cl_2 (0.1 mL) at 30°C for 48 h. Tf = trifluoromethanesulfonyl.

Table 2: Substrate scope of the catalytic asymmetric homologation of aryl-substituted α-ketoesters by a 1,2-aryl shift.[a]



Entry	Ar	R^3	x	Yield [%][b]	*ee* [%][c]
1	Ph	Me	2	73 (**3ac**)	92
2	3-MeC_6H_4	Me	2	73 (**3bc**)	95
3	3-*i*PrC_6H_4	Me	2	70 (**3cc**)	95
4	3-CH_2=CHC_6H_4	Me	2	69 (**3dc**)	93
5	3-$MeOC_6H_4$	Me	2	60 (**3ec**)	94
6	3-FC_6H_4	Me	2	65 (**3fc**)	92
7	3-ClC_6H_4	Me	2	70 (**3gc**)	93
8	3-$CF_3C_6H_4$	Me	2	62 (**3hc**)	91
9	4-MeC_6H_4	Me	2	76 (**3ic**)	93
10	4-*t*BuC_6H_4	Me	2	70 (**3jc**)	91
11	4-CH_2=CHC_6H_4	Me	2	71 (**3kc**)	92
12	4-PhC_6H_4	Me	2	73 (**3lc**)	92
13	4-$MeOC_6H_4$	Me	5	55 (**3mc**)	92
14	4-FC_6H_4	Me	2	65 (**3nc**)	92
15	4-ClC_6H_4	Me	2	69 (**3oc**)	90
16	4-BrC_6H_4	Me	2	59 (**3pc**)	91
17[d]	4-$CF_3C_6H_4$	Me	5	55 (**3qc**)	83
18	3,5-$Me_2C_6H_3$	Me	2	75 (**3rc**)	94
19		Me	5	65 (**3sc**)	92
20	2-naphthyl	Me	2	76 (**3tc**)	92
21	3-MeC_6H_4	Et	5	53 (**3bd**)	90
22	3-MeC_6H_4	*n*Pr	5	64 (**3be**)	90
23	3-MeC_6H_4	*n*Bu	5	61 (**3bf**)	88
24	3-MeC_6H_4	*n*-hexyl	5	63 (**3bg**)	92
25	3-MeC_6H_4	$(CH_2)_9CH_3$	5	60 (**3bh**)	87
26	3-MeC_6H_4	isopentyl	5	63 (**3bi**)	85
27	3-MeC_6H_4	CH_2CH=CH_2	5	55 (**3bj**)	86
28	3-MeC_6H_4	CH_2C≡CH	5	65 (**3bk**)	91
29	3-MeC_6H_4	$(CH_2)_3OTBS$	5	77 (**3bl**)	90
30	3-MeC_6H_4	$(CH_2)_4Cl$	5	56 (**3bm**)	86

[a] Unless specified, all reactions were performed with **1** (0.20 mmol), **2** (0.30–0.36 mmol), **L3**/$Y(OTf)_3$ (2–5 mol%, 1:1), and CH_2Cl_2 (0.4–0.5 mL) at 20–30°C for the indicated times (see the Supporting Information). [b] Yield of the isolated product. [c] Determined by HPLC analysis using a chiral stationary phase. [d] The reaction was carried out at 0°C. TBS = *tert*-butyldimethylsilyl.

reactivity. Poor results were observed by using the aniline-derived ligand **L4** (entry 8). Enhancing steric hindrance on the 2,6-positions of the phenyl ring improved the enantioselectivity and reactivity greatly (entries 7, 9, and 10 versus entry 8). It is noteworthy that the 1,2-ester migration product, epoxide product, and other unknown byproducts are present in this reaction system, and results in low yield of the desired product **3**.[16] We presumed that more sterically hindered ester moiety on α-diazoesters might improve the yield of **3aa** by suppressing the ester/oxygen shift, as well as other side reactions. Luckily, when changing ethyl ester into a *tert*-butyl ester, the yield was enhanced to 65% with and the enantioselectivity maintained (entry 11). The more-bulky 1-adamantyl α-diazoester **2c** gave even better yield of 73% (entry 12). Furthermore, the catalyst loading could be reduced to 2.0 mol%, thus giving the similar enantioselectivity and yield after a prolonged reaction time (entry 13). The reaction could even be performed in the presence of 0.5 mol% of the catalyst, albeit with a slight reduction of yield and *ee* value (entry 14). Notably, the reaction system is insensitive to air and moisture, and makes the process practical and facile.

With the optimized reaction conditions in hand (Table 1, entry 13), we firstly investigated the reactions between various α-aryl-substituted α-ketoesters (**1**) and α-alkyl-α-diazoesters (**2**; Table 2). The corresponding products from the 1,2-aryl shift were obtained in moderate to good yields with satisfactory enantioselectivities. When **2c** was used as the reactant, it was found that electronic nature and steric bulk of the substituents on the α-aryl group of the α-ketoesters had a slight influence on the enantioselectivity (entries 1–17). Meanwhile, methoxy- and trifluoromethyl-substituted ones gave lower yields (entries 5, 8, 13, and 17). Multisubstituted and fused-ring-substituted α-ketoesters also proceeded well, thus providing the corresponding succinate derivatives with up to 76% yield and 94% *ee* (entries 18–20). Next, the utility of this approach was extended to a range of α-alkyl-α-diazoesters. The length of the α-alkyl chain attached to α-diazoesters had a slight effect on the enantioselectivities (entries 21–26). The reactivities of such substrates were lower than those of **2c**, even when the catalyst loading was increased to 5 mol%. Pleasingly, important functional groups, such as allyl, propargyl, silyl ethers, and halogens, were tolerable under the mild reaction conditions, thus giving the function-

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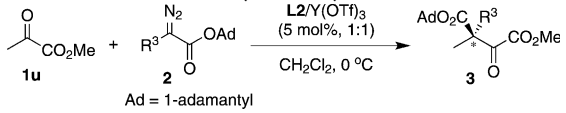
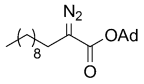
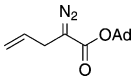
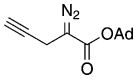
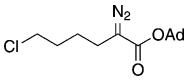
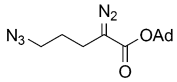
alized succinate derivatives with up to 77% yield and 91% *ee* (entries 27–30).

To test whether a 1,2-alkyl shift of a C(sp^3) center was efficient, the reactions between methyl 2-oxopropanoate (**1u**) and α-alkyl-α-diazoesters were carried out. After some investigation on the reaction conditions, the desired homologation reaction proceeded by using **L2**/Y(OTf)$_3$ as the catalyst at 0°C (Table 3). Moreover, a variety of α-diazoesters with saturated or unsaturated carbon chains, including chloro- and azide-substituted side chains, was found to be suitable, thus giving the corresponding 1,2-methyl migration products with 70–81% yields in 88–94% *ee* values.

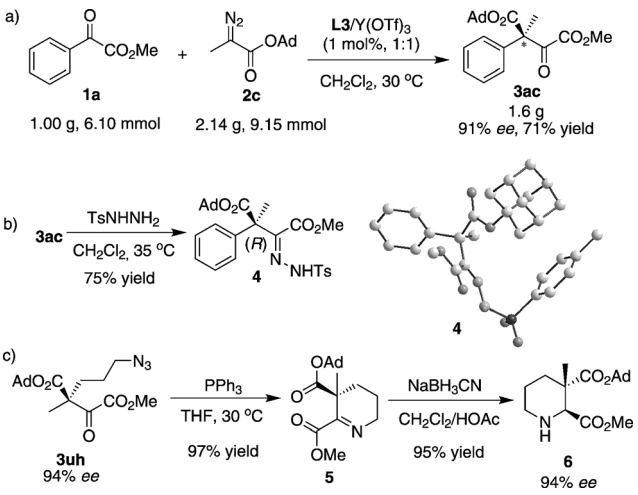
Table 3: Substrate scope of the catalytic asymmetric homologation of alkyl-substituted α-ketoesters by a 1,2-alkyl shift.[a]



Entry	**2**	Yield [%][b]	*ee* [%][c]
1		72 (**3uh**)	>92
2		81 (**3uj**)	>92
3		75 (**3uk**)	88
4		76 (**3um**)	94
5		70 (**3un**)	94

[a] All reactions were performed with **1u** (0.20 mmol), **2** (0.26 mmol), **L2**/Y(OTf)$_3$ (5 mol%, 1:1), CH_2Cl_2 (0.4 mL) at 0°C for the indicated times (for details, see the Supporting Information). [b] Yield of the isolated product. [c] Determined by HPLC analysis using a chiral stationary phase.

The synthetic value of the homologation reaction is demonstrated in Scheme 2. Because of the potential danger (potential toxicity and unpredictable explosive behavior) of diazo compounds,[17] it was vital to perform a scaled-up version of this process. As expected, by using 1 mol% of the catalyst, **2c** reacted with **1a** smoothly on a gram scale, thus generating the product **3ac** with 91% *ee* and 71% yield (Scheme 2a). After a simple transformation, the corresponding hydrazone compound **4** was obtained as a solid in 75% yield (Scheme 2b). Therefore, the absolute configuration of **3ac** was determined to be *R* by the X-ray crystallographic analysis of **4**.[18] Moreover, the product **3un**, bearing an azide group, could easily undergo an intramolecular Staudinger/aza-Wittig reaction[19] using PPh_3, thus affording the cyclic imine compound **5** in particularly high yield (Scheme 2c). Following a reduction of the imine with $NaBH_3CN$ gave the useful chiral piperidine derivative **6** in 95% yield. It is worth pointing out that the chiral compound **6** was considered as a promising synthetic intermediate for the total synthesis of

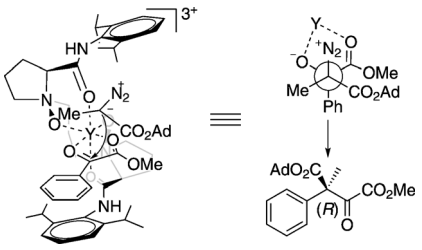


Scheme 2. Scaled-up version of the asymmetric homologation reaction and further transformations of the products. Ts = 4-toluenesulfonyl.

a vincamine analogue.[20] In the above transformations, the enantioselectivity of the derivatives were maintained.

In light of the experimental results and our previous work,[15a] a proposed stereochemical model was described in Scheme 3. The α-ketoester is activated through coordination to the Y^{III} in a bidentate fashion by its dicarbonyl group. The α-diazoester would attack from the *Re* face of the α-ketoester, because the *Si* face is blocked by the neighboring amide group of the ligand. The prochiral face of the α-diazoester **2c** was distinguished by the repulsive interaction between the ester group of α-diazoester and the other amide moiety of the ligand. The arrangement meets the demand of antiperiplanar rearrangement for the 1,2-aryl shift/dinitrogen extrusion process. Thus, simultaneous discrimination of the prochiral faces of both the α-ketoester and α-diazoester results in the generation of the *R*-configured product.

In summary, we have demonstrated the catalytic asymmetric homologation of acyclic ketones by using α-ketoesters with a series of α-alkyl-α-diazoesters. In the presence of the *N*,*N*′-dioxide/Y(OTf)$_3$ catalysts, both aryl- and alkyl-substituted α-ketoesters underwent the reaction smoothly, thus providing the corresponding 1,2-aryl/alkyl-shift products with all-carbon quaternary centers in good yields (up to 81%) and excellent enantioselectivities (up to 95% *ee*). Also important is the functional-group tolerance as well as the mild reaction conditions. Additional studies of α-diazoesters are currently ongoing.



Scheme 3. Proposed stereochemical model.

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Experimental Section

The **L** (0.004–0.020 mmol), $Y(OTf)_3$ (0.004–0.020 mmol), and CH_2Cl_2 (0.4–0.5 mL) were added to a dry reaction tube. After stirring for 0.5 h at 30 °C, the α-ketoester **1** (0.20 mmol) and α-diazoester **2** (0.26–0.36 mmol) were added, and the mixture was stirred at 0–30 °C for the indicated time. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/dichloromethane = 2:1) to afford the desired product **3**.

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[1] For selected reviews, see: a) C. D. Gutsche, *Org. React.* **1954**, *8*, 364–429; b) T. Ye, M. A. McKervey, *Chem. Rev.* **1994**, *94*, 1091–1160; c) M. P. Doyle, M. A. McKervey, T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*, Wiley, New York, **1998**; d) Z. Zhang, J. Wang, *Tetrahedron* **2008**, *64*, 6577–6605; e) Y. Zhang, J. Wang, *Chem. Commun.* **2009**, 5350–5361.

[2] a) F. Arndt, B. Eistert, *Ber. Dtsch. Chem. Ges. B* **1935**, *68*, 200–208; b) W. E. Bachmann, W. S. Struve, *Org. React.* **1942**, *1*, 38–62; c) W. Kirmse, *Eur. J. Org. Chem.* **2002**, 2193–2256.

[3] a) E. Buchner, T. Curtius, *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 2371–2377; b) J. J. Li in *Name Reactions: A Collection of Detailed Reaction Mechanism*, Springer, Berlin, **2003**, p. 58.

[4] a) M. Tiffeneau, B. Tchoubar, *Compt. Rend.* **1937**, *205*, 1411–1413; b) P. A. S. Smith, D. R. Baer, *Org. React.* **1960**, *11*, 157–188.

[5] a) C. R. Holmquist, E. J. Roskamp, *J. Org. Chem.* **1989**, *54*, 3258–3260; b) C. R. Holmquist, E. J. Roskamp, *Tetrahedron Lett.* **1992**, *33*, 1131–1134; c) A. Hassner, I. Namboothiri in *Organic Syntheses Based on Name Reactions*, 3rd ed., Elsevier, Oxford, **2011**, p. 408.

[6] For selected Roskamp reaction with aldehydes and diazo compounds, see: a) A. Padwa, S. F. Hornbuckle, Z. Zhang, L. Zhi, *J. Org. Chem.* **1990**, *55*, 5297–5299; b) K. Nomura, T. Iida, K. Hori, E. Yoshii, *J. Org. Chem.* **1994**, *59*, 488–490; c) H. Murata, H. Ishitani, M. Iwamoto, *Tetrahedron Lett.* **2008**, *49*, 4788–4791; d) T. Hashimoto, Y. Naganawa, K. Maruoka, *J. Am. Chem. Soc.* **2008**, *130*, 2434–2435; e) H. E. Bartrum, D. C. Blakemore, C. J. Moody, C. J. Hayes, *J. Org. Chem.* **2010**, *75*, 8674–8676; f) B. Morandi, E. M. Carreira, *Angew. Chem.* **2011**, *123*, 9251–9254; *Angew. Chem. Int. Ed.* **2011**, *50*, 9085–9088.

[7] For selected examples of ketone homologation reactions with diazo compounds, see: a) E. Mosettig, A. Burger, *J. Am. Chem. Soc.* **1930**, *52*, 3456–3463; b) H. O. House, E. J. Grubbs, W. F. Gannon, *J. Am. Chem. Soc.* **1960**, *82*, 4099–4106; c) W. L. Mock, M. E. Hartman, *J. Am. Chem. Soc.* **1970**, *92*, 5767–5768; d) K. Maruoka, A. B. Concepcion, H. Yamamoto, *J. Org. Chem.* **1994**, *59*, 4725–4726; e) K. Maruoka, A. B. Concepcion, H. Yamamoto, *Synthesis* **1994**, 1283–1290; f) D. C. Moebius, J. S. Kingsbury, *J. Am. Chem. Soc.* **2009**, *131*, 878–879; g) J. A. Dabrowski, D. C. Moebius, A. J. Wommack, A. F. Kornahrens, J. S. Kingsbury, *Org. Lett.* **2010**, *12*, 3598–3601; h) T. Hashimoto, Y. Naganawa, K. Maruoka, *J. Am. Chem. Soc.* **2009**, *131*, 6614–6617; i) T. Hashimoto, Y. Naganawa, K. Maruoka, *Chem. Commun.* **2010**, *46*, 6810–6812; j) A. Gioiello, F. Venturoni, M. Marinozzi, B. Natalini, R. Pellicciari, *J. Org. Chem.* **2011**, *76*, 7431–7437; k) B. Alcaide, P. Almendros, C. Aragoncillo, G. Gómez-Campillos, M. Arnó, L. R. Domingo, *ChemPlusChem* **2012**, *77*, 563–569, and reference [6f].

[8] For selected examples in natural product synthesis, see: a) D. A. Evans, D. J. Adams, *J. Am. Chem. Soc.* **2007**, *129*, 1048–1049; b) J. Toueg, J. Prunet, *Org. Lett.* **2008**, *10*, 45–48; c) J. A. Marshall, P. M. Eidam, *Org. Lett.* **2008**, *10*, 93–96; d) K. L. Jackson, J. A. Henderson, H. Motoyoshi, A. J. Phillips, *Angew. Chem.* **2009**, *121*, 2382–2386; *Angew. Chem. Int. Ed.* **2009**, *48*, 2346–2350; e) J. Li, J. M. Suh, E. Chin, *Org. Lett.* **2010**, *12*, 4712–4715; f) G. Kumaraswamy, N. Jayaprakash, *Tetrahedron Lett.* **2010**, *51*, 6500–6502; g) H. Xue, J. Yang, P. Gopal, *Org. Lett.* **2011**, *13*, 5696–5699; h) M. Iqbal, R. J. G. Black, J. Winn, A. T. Reeder, A. J. Blake, P. A. Clarke, *Org. Biomol. Chem.* **2011**, *9*, 5062–5078; i) J. Yin, C. Wang, L. Kong, S. Cai, S. Gao, *Angew. Chem.* **2012**, *124*, 7906–7909; *Angew. Chem. Int. Ed.* **2012**, *51*, 7786–7789; j) D. A. Evans, D. J. Adams, E. E. Kwan, *J. Am. Chem. Soc.* **2012**, *134*, 8162–8170; k) J. S. Yadav, A. Haldar, T. Maity, *Eur. J. Org. Chem.* **2013**, 3076–3085; l) W. P. Unsworth, K. A. Gallagher, M. Jean, J. P. Schmidt, L. J. Diorazio, R. J. K. Taylor, *Org. Lett.* **2013**, *15*, 262–265; m) E. J. Corey, M. Ohno, R. B. Mitra, P. A. Vatakencherry, *J. Am. Chem. Soc.* **1964**, *86*, 478–485; n) Z.-L. Song, C.-A. Fan, Y.-Q. Tu, *Chem. Rev.* **2011**, *111*, 7523–7556.

[9] For selected reviews on construction of chiral quaternary carbon centers, see: a) K. Fuji, *Chem. Rev.* **1993**, *93*, 2037–2066; b) E. J. Corey, A. Guzman-Perez, *Angew. Chem.* **1998**, *110*, 402–415; *Angew. Chem. Int. Ed.* **1998**, *37*, 388–401; c) J. Christoffers, A. Mann, *Angew. Chem.* **2001**, *113*, 4725–4732; *Angew. Chem. Int. Ed.* **2001**, *40*, 4591–4597; d) C. J. Douglas, L. E. Overman, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5363–5367; e) J. Christoffers, A. Baro, *Adv. Synth. Catal.* **2005**, *347*, 1473–1482; f) B. M. Trost, C. Jiang, *Synthesis* **2006**, 369–396; g) M. Bella, T. Gasperi, *Synthesis* **2009**, 1583–1614; h) C. Hawner, A. Alexakis, *Chem. Commun.* **2010**, *46*, 7295–7306; i) J. P. Das, I. Marek, *Chem. Commun.* **2011**, *47*, 4593–4623.

[10] T. Hashimoto, H. Miyamoto, Y. Naganawa, K. Maruoka, *J. Am. Chem. Soc.* **2009**, *131*, 11280–11281.

[11] a) W. Li, J. Wang, X. L. Hu, K. Shen, W. T. Wang, Y. Y. Chu, L. L. Lin, X. H. Liu, X. M. Feng, *J. Am. Chem. Soc.* **2010**, *132*, 8532–8533; b) W. Li, X. H. Liu, X. Y. Hao, X. L. Hu, Y. Y. Chu, W. D. Cao, S. Qin, C. W. Hu, L. L. Lin, X. M. Feng, *J. Am. Chem. Soc.* **2011**, *133*, 15268–15271; c) W. Li, X. H. Liu, X. Y. Hao, Y. F. Cai, L. L. Lin, X. M. Feng, *Angew. Chem.* **2012**, *124*, 8772–8775; *Angew. Chem. Int. Ed.* **2012**, *51*, 8644–8647, and reference [5c].

[12] L. Gao, B. C. Kang, G.-S. Hwang, D. H. Ryu, *Angew. Chem.* **2012**, *124*, 8447–8450; *Angew. Chem. Int. Ed.* **2012**, *51*, 8322–8325.

[13] T. Hashimoto, Y. Naganawa, K. Maruoka, *J. Am. Chem. Soc.* **2011**, *133*, 8834–8837.

[14] V. L. Rendina, D. C. Moebius, J. S. Kingsbury, *Org. Lett.* **2011**, *13*, 2004–2007.

[15] For reviews, see: a) X. H. Liu, L. L. Lin, X. M. Feng, *Acc. Chem. Res.* **2011**, *44*, 574–587; b) A. V. Malkov, P. Kočovský, *Eur. J. Org. Chem.* **2007**, 29–36.

[16] The byproducts of the 1,2-ester shift and the epoxide were detected by NMR and HRMS analysis. However, it was hard to purify them for yield and *ee* value analysis.

[17] J. R. Fulton, V. K. Aggarwal, J. de Vicente, *Eur. J. Org. Chem.* **2005**, 1479–1492.

[18] CCDC 944066 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[19] For recent reviews, see: a) G. Hajós, I. Nagy, *Curr. Org. Chem.* **2008**, *12*, 39–58; b) F. Palacios, C. Alonso, D. Aparicio, G. Rubiales, J. M. de Los Santos, *Tetrahedron* **2007**, *63*, 523–573.

[20] a) P. Gmeiner, P. L. Feldman, M. Y. Chu-Moyer, H. Rapoport, *J. Org. Chem.* **1990**, *55*, 3068–3074; b) P. L. Feldman, H. Rapoport, *J. Am. Chem. Soc.* **1987**, *109*, 1603–1604.

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