DOI: 10.1002/adsc.200505156

Mannich-Type Reaction Using Alkenyl Trichloroacetates Catalyzed by Dibutyltin Dimethoxide

Akira Yanagisawa,[a,]* Hironao Saito,[b] Masanori Harada,[a] Takayoshi Arai[a]

[a] Department of Chemistry, Faculty of Science, Chiba University, Inage, Chiba 263-8522, Japan
Fax: (+81)-43-290-2789, e-mail: ayanagi@faculty.chiba-u.jp
[b] Graduate School of Science and Technology, Chiba University, Inage, Chiba 263-8522, Japan

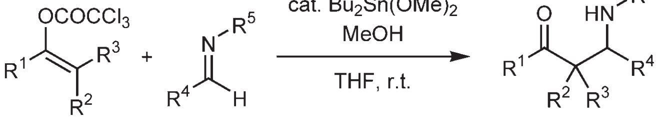
Received: April 18, 2005; Accepted: July 16, 2005

Abstract: A novel Mannich-type reaction of alkenyl trichloroacetates with aldimines has been realized by using dibutyltin dimethoxide as a catalyst, which is regenerated by addition of methanol. A three-component coupling reaction of aldehydes, primary amines, and alkenyl trichloroacetates has been also efficiently achieved. These procedures can provide a variety of β-amino ketones not only from aromatic aldehydes but also from α,β-unsaturated aldehydes mainly with *syn*-selectivity in high yields up to 99%.

Keywords: alcohols; alkenyl esters; homogeneous catalysis; imines; Mannich reaction; tin

The Mannich-type reaction of enolates with imines and related compounds provides a beneficial route to β-aminocarbonyl compounds including β-amino esters, which can further be transformed into β-lactams or other useful organic molecules.[1] In order to obtain these Mannich products in high yield and purity, various methods have so far been developed.[2,3] One promising method for this purpose is the reaction using silyl enolates catalyzed by Lewis acids;[3b–3e] however, the method has an innate disadvantage in that the Lewis acids are deactivated by the polar Mannich products. Here we describe a novel Mannich-type reaction of alkenyl trichloroacetates with imines catalyzed by dibutyltin dimethoxide (Scheme 1).

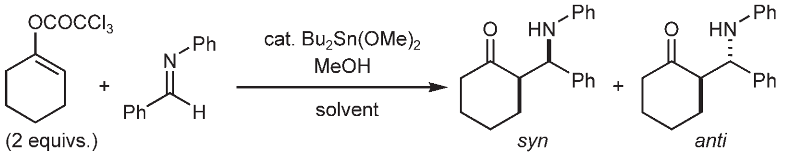
We have previously shown that tin dimethoxide behaves as a catalyst in the aldol reaction of alkenyl trichloroacetates with aldehydes.[4] The tin compound is effectively regenerated from the aldol adduct under the action of MeOH and thus the reaction proceeds catalytically. We anticipated that $Bu_2Sn(OMe)_2$ could also catalyze the addition of alkenyl trichloroacetates to imines avoiding the product inhibition which is often seen in the Lewis acid-promoted Mukaiyama-type aldol reaction of silyl enolates or ketene silyl acetals.[5] First, we examined catalytic activity of $Bu_2Sn(OMe)_2$ in the reaction of 1-trichloroacetoxycyclohexene (2 equivs.) with *N*-phenylbenzaldimine (1 equiv.), and, gratifyingly, found that the targeted β-amino ketone was obtained in 81% yield with a *syn/anti* ratio of 65:35 in the presence of 10 mol % of the catalyst and 20 equivs. of MeOH in THF at room temperature (22 °C) for 1 h (entry 1, Table 1). We then optimized the reaction conditions to reduce the catalyst loading and to obtain higher yields of the product. The results are summarized in Table 1. We tried the reaction employing less than 0.1 equiv. of $Bu_2Sn(OMe)_2$ and found that the 84% yield of the product was still formed under the influence of 2 mol % of the catalyst with 20 equivs. of MeOH (entry 5). Among the various conditions, use of 5 mol % of the catalyst and 20 equivs. of MeOH at room temperature gave the most satisfactory results in the terms of product yield and *syn/anti* selectivity (entry 3). The reactivity of $Bu_2Sn(OMe)_2$ was higher than that demonstrated by Bu_3SnOMe[4a,6] (entries 3 *vs.* 6). Although less polar and more polar solvents including MeOH were also usable in the present Mannich-type reaction, THF was the solvent of choice (entries 3 and 7–10). We also examined several reaction temperatures (entries 11–14) and the reaction at 10 °C gave the highest yield (entry 12).



Scheme 1. Mannich-type reaction of alkenyl trichloroacetates with aldimines catalyzed by $Bu_2Sn(OMe)_2$.

We next performed the catalytic Mannich-type reaction of 1-trichloroacetoxycyclohexene with various aldimines under the optimized reaction conditions (Table 2). From aromatic aldimines, the corresponding Mannich products were *syn*-selectively produced in good yield (entries 1–4). With (*E*)-cinnamaldimine, exclusive 1,2-addition took place (entry 5). We further carried out a screening of the R^2 substituent of imines and found that arylamine-derived imines showed remarka-

Table 1. Optimization of Mannich-type reaction of an alkenyl trichloroacetate of cyclohexanone with *N*-phenylbenzaldimine catalyzed by $Bu_2Sn(OMe)_2$.[a]



Entry	$Bu_2Sn(OMe)_2$ [equivs.]	MeOH [equivs.]	Solvent	Temp. [°C]	Time [h]	Yield[b] [%]	*syn/anti*[c]
1	0.1	20	THF	rt	1	81	65/35
2	0.05	15	THF	rt	1	80	80/20
3	0.05	20	THF	rt	1	88	84/16
4	0.05	25	THF	rt	1	77	64/36
5	0.02	20	THF	rt	1	84	71/29
6[d]	0.05	20	THF	rt	2.5	29	78/22
7	0.05	20	CH_2Cl_2	rt	1	76	81/19
8	0.05	20	MeOH	rt	1	72	56/44
9	0.05	20	toluene	rt	1	70	84/16
10	0.05	20	DMF	rt	1	65	55/45
11	0.05	20	THF	30	1	88	76/24
12	0.05	20	THF	10	1	92	80/20
13	0.05	20	THF	2	6	91	80/20
14	0.05	20	THF	−40	24	5	74/26

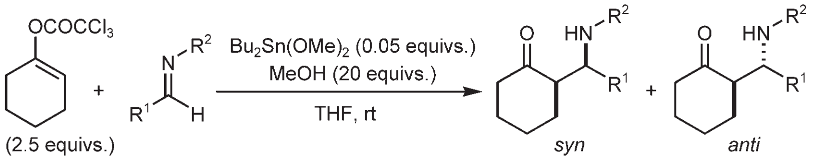
[a] Unless otherwise noted, the reaction was performed using $Bu_2Sn(OMe)_2$ (0.02–0.1 equivs.), 1-trichloroacetoxycyclohexene (2 equivs.), and *N*-phenylbenzaldimine (1 equiv.) in a dry solvent containing MeOH (15–25 equivs.) at the specified temperature for 1–24 h. Room temperature is 22–24 °C.

[b] Yield of isolated product.

[c] Determined by ^1H NMR analysis.

[d] Bu_3SnOMe was used as a catalyst instead of $Bu_2Sn(OMe)_2$. 2.5 equivs. of 1-trichloroacetoxycyclohexene were used.

Table 2. $Bu_2Sn(OMe)_2$-catalyzed Mannich-type reaction of various aldimines.[a]



Entry	R^1	R^2	Time [h]	Yield [%] [b]	*syn/anti*[c]
1	Ph	Ph	3	94	81/19
2	4-MeOC_6H_4	Ph	2.5	92	79/21
3	4-BrC_6H_4	Ph	2.5	88	77/23
4	$4\text{-NO}_2C_6H_4$	Ph	3	68	74/26
5	(*E*)-PhCH=CH	Ph	2.5	93[d]	N. D.[e]
6	Ph	2-MeOC_6H_4	2	>99	63/37
7	Ph	4-MeOC_6H_4	3.5	86	73/27
8	Ph	4-BrC_6H_4	3.5	87	81/19
9	Ph	$4\text{-NO}_2C_6H_4$	3	66	83/17
10[f]	Ph	$PhCH_2$	1.5	<1[g]	–
11[f]	Ph	$c\text{-}C_6H_{11}$	5	<1[h]	–

[a] Unless otherwise noted, the reaction was performed using $Bu_2Sn(OMe)_2$ (0.05 equivs.), 1-trichloroacetoxycyclohexene (2.5 equivs.), and aldimine (1 equiv.) in dry THF containing MeOH (20 equivs.) at room temperature (22–24 °C) for 1.5–5 h.

[b] Yield of isolated product.

[c] Determined by ^1H NMR analysis.

[d] A 1,2-adduct was formed exclusively.

[e] The *syn/anti* ratio was not determined.

[f] 2 equivs. of 1-trichloroacetoxycyclohexene were used.

[g] An enone was formed in 42% yield.

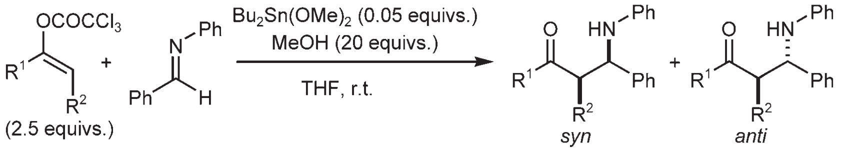
[h] An enone was formed in 22% yield.

ble reactivity (entries 6–9), while use of benzyl and cyclohexyl groups led to totally unsatisfactory results (entries 10 and 11).

The utility of the present $Bu_2Sn(OMe)_2$-catalyzed Mannich-type reaction was then demonstrated by using alkenyl trichloroacetates prepared from diverse ketones (Table 3). In addition to cyclic substrates, acyclic substrates also added to *N*-phenylbenzaldimine, although longer reaction times were indispensable to get good yields (entries 4 and 5). Cyclic alkenyl trichloroacetates showed moderate *syn*-selectivity (entries 1–3). In contrast, the reaction of acyclic ketone derivatives proceeded with almost no diastereoselectivity (entries 4 and 5).

We further attempted a three-component coupling reaction[7] of 1-trichloroacetoxycyclohexene, aldehydes, and amines, and the results are listed in Table 4. All re-

Table 3. $Bu_2Sn(OMe)_2$-catalyzed Mannich-type reaction of various alkenyl esters.[a]



Entry	R^1	R^2	Time [h]	Yield [%] [b]	*syn/anti*[c]
1	$-(CH_2)_3-$		1.5	91	79/21
2	$-(CH_2)_4-$		3	94	81/19
3	$-(CH_2)_5-$ [d]		5	91	75/25
4	Et	Me[e]	68	68	45/55
5	Ph	Me[f]	71	58	53/47

[a] Unless otherwise noted, the reaction was performed using $Bu_2Sn(OMe)_2$ (0.05 equivs.), alkenyl trichloroacetate (2.5 equivs.), and *N*-phenylbenzaldimine (1 equiv.) in dry THF containing MeOH (20 equivs.) at room temperature (22–24 °C) for 1.5–71 h.

[b] Yield of isolated product.

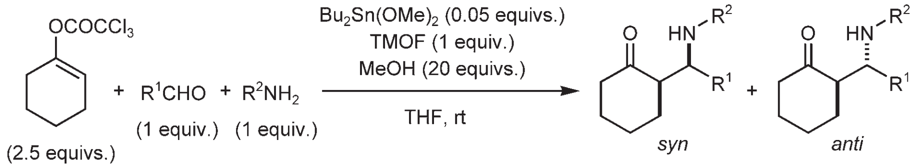
[c] Determined by ^1H NMR analysis.

[d] 2 equivs. of 1-trichloroacetoxycycloheptene were used.

[e] The *E/Z* ratio was 17/83.

[f] The *E/Z* ratio was 84/16.

Table 4. $Bu_2Sn(OMe)_2$-catalyzed three-component coupling reaction.[a]



Entry	R^1	R^2	Time [h]	Yield [%] [b]	*syn/anti*[c]
1	Ph	Ph	3	84 (77)[d]	77/23
2	$4\text{-}MeOC_6H_4$	Ph	3	88	72/28
3	$4\text{-}BrC_6H_4$	Ph	3	87	74/26
4	$4\text{-}NO_2C_6H_4$	Ph	3.5	85	68/32
5	(*E*)-PhCH=CH	Ph	3	90[e]	N. D.[f]
6	Ph	$2\text{-}MeOC_6H_4$	3	81	58/42
7	Ph	$4\text{-}MeOC_6H_4$	3	53[g]	67/33
8	Ph	$4\text{-}BrC_6H_4$	3	84	78/22

[a] Unless otherwise noted, the reaction was performed using $Bu_2Sn(OMe)_2$ (0.05 equivs.), 1-trichloroacetoxycyclohexene (2.5 equivs.), aldehyde (1 equiv.), amine (1 equiv.), and trimethyl orthoformate (TMOF, 1 equiv.) in dry THF containing MeOH (20 equivs.) at room temperature (21–24 h) for 3 or 3.5 h.

[b] Yield of isolated product.

[c] Determined by ^1H NMR analysis.

[d] Without TMOF.

[e] A 1,2-adduct was formed exclusively.

[f] The *syn/anti* ratio was not determined.

[g] An enone was formed in 19% yield.

actions provided the desired β-amino ketones in moderate to high yields under the influence of 5 mol % of $Bu_2Sn(OMe)_2$ at room temperature. Employment of trimethyl orthoformate (TMOF) as an additive was effective for suppressing the concomitant β-elimination of the product and for obtaining better product yields. In the present three-component system no aldol reaction took place and the corresponding β-hydroxy ketones were not obtained at all.

A probable catalytic cycle is illustrated in Figure 1. First of all, $Bu_2Sn(OMe)_2$ reacts with an alkenyl trichloroacetate to yield a tin enolate accompanied by methyl trichloroacetate. The enolate is then allowed to add to an imine, affording a tin amide of the Mannich adduct. Finally, protonation of the tin amide with MeOH results in the formation of the β-amino ketone and regeneration of the tin dimethoxide. Rapid methanolysis of the amide completes the catalytic cycle.

From the aforementioned catalytic cycle and the fact that cyclic alkenyl trichloroacetates reacted with aldimines *syn*-selectively, the cyclic transition-state structures **A** and **B** shown in Figure 2 can be postulated as models for the Mannich-type reaction of the cyclic substrates. In these models, the imine coordinates to a tin atom of the enolate to form a six-membered cyclic structure. Thus, from the cyclic enolate (*E*-enolate), the *syn*-Mannich adduct is formed *via* a chair-type transition-state structure **A**, whereas model **B** possessing a boat conformation connects the *E*-enolate to the *anti* product.[8] Among these transition-state structures, model **A** is estimated to be more stable than model **B**, since the latter has a thermodynamically less favored boat form.

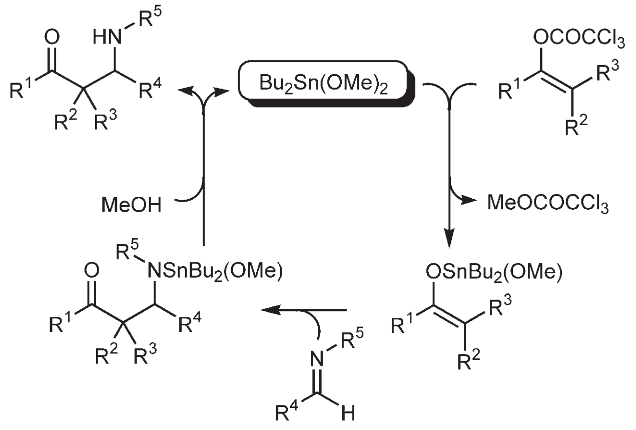
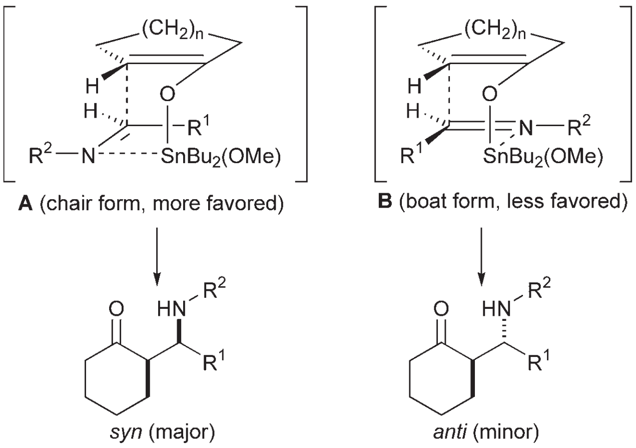


Figure 1. A plausible catalytic mechanism for the Mannich-type reaction catalyzed by $Bu_2Sn(OMe)_2$.



A (chair form, more favored)

B (boat form, less favored)

syn (major)

anti (minor)

Figure 2. Probable cyclic transition-state structures.

In summary, we have presented a successful application of $Bu_2Sn(OMe)_2$ as a catalyst for the Mannich-type reaction between alkenyl trichloroacetates and aldimines. The catalytic reaction proceeded with good to high yields and mainly *syn*-selectivity, when cycloalkanone-derived alkenyl trichloroacetates and *N*-aryl aromatic aldimines were employed. A $Bu_2Sn(OMe)_2$-catalyzed three-component coupling process has been also developed as a more efficient alternative. To the best of our knowledge, this is the first example of a Mannich reaction variant using alkenyl esters. Current efforts in our laboratory are directed towards the application of the present catalytic system to other reactions, as well as the development of an asymmetric version of this reaction.

Experimental Section

General Remarks

Analytical TLC was done on precoated (0.25 mm) silica gel plates. Column chromatography was conducted with 70–230 mesh silica gel (neutral). Infrared (IR) spectra were recorded on an FTIR spectrometer. ^1H NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts of ^1H NMR spectra were reported relative to tetramethylsilane ($\delta = 0$). Splitting patterns are indicated as s, singlet; d, doublet; m, multiplet; br, broad. ^{13}C NMR spectra were recorded on a 100 MHz spectrometer. Chemical shifts of ^{13}C NMR spectra were reported relative to $CDCl_3$ ($\delta = 77.0$). All experiments were carried out under an atmosphere of standard grade argon gas (oxygen < 10 ppm). Alkenyl trichloroacetates were prepared by treatment of the corresponding ketones with trichloroacetic anhydride in the presence of a catalytic amount of *p*-toluenesulfonic acid and purified by distillation before use.[9] Aldimines were prepared from the corresponding aldehydes and amines in the presence of anhydrous $MgSO_4$ in dry THF. Other chemicals were used as purchased.

Typical Experimental Procedure for the Mannich-Type Reaction: Synthesis of 2-[Phenylamino(phenyl)methyl]cyclohexanone (Entry 1 in Table 2, Entry 2 in Table 3)

1-Trichloroacetoxycyclohexene (608 mg, 2.50 mmol) and *N*-phenylbenzaldimine (181 mg, 1.00 mmol) were dissolved in dry THF (5 mL) under an argon atmosphere and then dibutyltin dimethoxide (14.8 mg, 0.050 mmol) was added to the resulting solution at room temperature (22 °C). To the mixture was added dropwise MeOH (0.81 mL, 20.0 mmol). After being stirred for 3 h at this temperature, the mixture was treated with Et_3N (1 mL), MeOH (2 mL), brine (2 mL), and solid KF (*ca.* 1 g) at ambient temperature for 30 min. The resulting precipitate was filtered off and the filtrate was dried over Na_2SO_4 and concentrated under vacuum after filtration. The residual crude product was purified by column chromatography on silica gel (neutral) to give a mixture of the Mannich adducts as crystals; yield: 263.0 mg (94%). The *syn/anti* ratio was determined to be 81/19 by ^1H NMR analysis. Physical and spectral data of a 71/29 mixture of the *syn* and *anti* isomers: TLC $R_f = 0.36$ (1:4 ethyl acetate/hexane); IR (neat): $\nu = 3382$, 2930, 2850, 1693, 1602 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.58-2.06$ (m, 6H, 3 CH_2), 2.29–2.43 (m, 2H, CH_2), 2.77 (m, 1H, CH), 4.4–4.7 (br s, 1H, NH), 4.62 (d, 0.29H, $J = 7.0$ Hz, CH), 4.80 (d, 0.71H, $J = 4.3$ Hz, CH), 6.52–6.65 (m, 3H, aromatic), 7.04–7.08 (m, 2H, aromatic), 7.18–7.37 (m, 5H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$, *syn* isomer): $\delta = 24.8$, 27.0, 28.6, 42.4, 56.6, 57.4, 114.0 (2 C), 117.6, 126.9, 127.4 (2 C), 128.3 (2 C), 128.9 (2 C), 141.5, 147.4, 211.3; (*anti* isomer) $\delta = 23.6$, 27.9, 31.2, 41.7, 57.1, 57.9, 113.5 (2 C), 117.4, 127.1, 127.2 (2 C), 128.4 (2 C), 129.0 (2 C), 141.6, 147.1, 212.8. The above-mentioned spectral data exhibited good agreement with reported data.[7i,7j,10]

Acknowledgements

We gratefully acknowledge financial support from the Ministry of Education, Science, Sports, Culture and Technology of the Japanese Government and the Uehara Memorial Foundation.

References and Notes

[1] Reviews: a) E. F. Kleinman, in: *Comprehensive Organic Synthesis*, Vol. 2, (Eds.: B. M. Trost, I. Fleming, C. H. Heathcock), Pergamon, Oxford, **1991**, p. 893; b) L. E. Overman, D. J. Ricca, in: *Comprehensive Organic Synthesis*, Vol. 2, (Eds.: B. M. Trost, I. Fleming, C. H. Heathcock), Pergamon, Oxford, **1991**, p. 1007.

[2] Reviews: a) M. Arend, B. Westermann, N. Risch, *Angew. Chem.* **1998**, *110*, 1096; *Angew. Chem. Int. Ed.* **1998**, *37*, 1044; b) S. Kobayashi, H. Ishitani, *Chem. Rev.* **1999**, *99*, 1069; c) S. E. Denmark, O. J.-C. Nicaise, in: *Comprehensive Asymmetric Catalysis*, Vol. 2, (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Heidelberg, **1999**, p. 923; d) A. Córdova, *Acc. Chem. Res.* **2004**, *37*, 102; e) K. Hatanaka, H. Yamamoto, in: *Comprehensive Asymmetric Catalysis*, Supplement 1, (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Heidelberg, **2004**, p. 107; f) S. Kobayashi, M. Ueno, in: *Comprehensive Asymmetric Catalysis*, Supplement 1, (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Heidelberg, **2004**, p. 143.

[3] For recent notable examples of two-component Mannich-type reactions, see: a) B. M. Trost, L. R. Terrell, *J. Am. Chem. Soc.* **2003**, *125*, 338; b) S. Kobayashi, R. Matsubara, Y. Nakamura, H. Kitagawa, M. Sugiura, *J. Am. Chem. Soc.* **2003**, *125*, 2507; c) S. Kobayashi, H. Kiyohara, Y. Nakamura, R. Matsubara, *J. Am. Chem. Soc.* **2004**, *126*, 6558; d) T. Hamada, K. Manabe, S. Kobayashi, *J. Am. Chem. Soc.* **2004**, *126*, 7768; e) S. Kobayashi, K. Arai, H. Shimizu, Y. Ihori, H. Ishitani, Y. Yamashita, *Angew. Chem.* **2005**, *117*, 771; *Angew. Chem. Int. Ed.* **2005**, *44*, 761; f) S. Matsunaga, N. Kumagai, S. Harada, M. Shibasaki, *J. Am. Chem. Soc.* **2003**, *125*, 4712; g) S. Matsunaga, T. Yoshida, H. Morimoto, N. Kumagai, M. Shibasaki, *J. Am. Chem. Soc.* **2004**, *126*, 8777; h) A. G. Wenzel, M. P. Lalonde, E. N. Jacobsen, *Synlett* **2003**, 1919; i) H. Fujisawa, E. Takahashi, T. Nakagawa, T. Mukaiyama, *Chem. Lett.* **2003**, 1036; j) E. Takahashi, H. Fujisawa, T. Mukaiyama, *Chem. Lett.* **2004**, 936; k) E. Takahashi, H. Fujisawa, T. Mukaiyama, *Chem. Lett.* **2004**, 1426; l) E. Takahashi, H. Fujisawa, T. Mukaiyama, *Chem. Lett.* **2005**, 84; m) E. Takahashi, H. Fujisawa, T. Yanai, T. Mukaiyama, *Chem. Lett.* **2005**, 216; n) W. Notz, F. Tanaka, S. Watanabe, N. S. Chowdari, J. M. Turner, R. Thayumanavan, C. F. Barbas III, *J. Org. Chem.* **2003**, *68*, 9624; o) N. S. Chowdari, J. T. Suri, C. F. Barbas III, *Synlett* **2004**, 2507; p) T. Akiyama, J. Itoh, K. Yokota, K. Fuchibe, *Angew. Chem.* **2004**, *116*, 1592; *Angew. Chem. Int. Ed.* **2004**, *43*, 1566; q) T. Akiyama, K. Matsuda, K. Fuchibe, *Synlett* **2005**, 322; r) T. Akiyama, A. Suzuki, K. Fuchibe, *Synlett* **2005**, 1024; s) A. J. A. Cobb, D. M. Shaw, S. V. Ley, *Synlett* **2004**, 558; t) D. Uraguchi, M. Terada, *J. Am. Chem. Soc.* **2004**, *126*, 5356; u) W. Zhuang, S. Saaby, K. A. Jørgensen, *Angew. Chem.* **2004**, *116*, 4576; *Angew. Chem. Int. Ed.* **2004**, *43*, 4476; v) Y. Hamashima, N. Sasamoto, D. Hotta, H. Somei, N. Umebayashi, M. Sodeoka, *Angew. Chem.* **2005**, *117*, 1549; *Angew. Chem. Int. Ed.* **2005**, *44*, 1525.

[4] a) A. Yanagisawa, T. Sekiguchi, *Tetrahedron Lett.* **2003**, *44*, 7163; b) A. Yanagisawa, R. Goudu, T. Arai, *Org. Lett.* **2004**, *6*, 4281.

[5] Reviews: a) C. Gennari, in: *Comprehensive Organic Synthesis*, Vol. 2, (Eds.: B. M. Trost, I. Fleming, C. H. Heathcock), Pergamon, Oxford, **1991**, p. 629; b) M. Braun in: *Houben-Weyl: Methods of Organic Chemistry*, Vol. E 21, (Eds.: G. Helmchen, R. W. Hoffmann, J. Mulzer, E. Schaumann), Georg Thieme Verlag, Stuttgart, **1995**, p. 1730; c) R. Mahrwald, *Chem. Rev.* **1999**, *99*, 1095; d) E. M. Carreira, in: *Modern Carbonyl Chemistry*, (Ed.: J. Otera), Wiley-VCH, Weinheim, **2000**, p. 227; e) *Modern Aldol Reactions*, Vols. 1 and 2 (Ed.: R. Mahrwald), Wiley-VCH, Weinheim, **2004**; see also: f) *Lewis Acids in Organic Synthesis*, Vols. 1 and 2 (Ed.: H. Yamamoto), Wiley-VCH, Weinheim, **2000**.

[6] a) A. Yanagisawa, Y. Matsumoto, K. Asakawa, H. Yamamoto, *J. Am. Chem. Soc.* **1999**, *121*, 892; b) A. Yanagisawa, Y. Matsumoto, K. Asakawa, H. Yamamoto, *Tetrahedron* **2002**, *58*, 8331.

[7] For recent notable examples of three-component Mannich-type reactions, see: a) S.-L. Chen, S.-J. Ji, T.-P. Loh, *Tetrahedron Lett.* **2003**, *44*, 2405; b) Y. Hayashi, W. Tsuboi, I. Ashimine, T. Urushima, M. Shoji, K. Sakai,

Angew. Chem. **2003**, *115*, 3805; *Angew. Chem. Int. Ed.* **2003**, *42*, 3677; c) Y. Hayashi, W. Tsuboi, M. Shoji, N. Suzuki, *J. Am. Chem. Soc.* **2003**, *125*, 11208; d) S. Iimura, D. Nobutou, K. Manabe, S. Kobayashi, *Chem. Commun.* **2003**, 1644; e) A. Córdova, *Synlett* **2003**, 1651; f) A. Córdova, *Chem. Eur. J.* **2004**, *10*, 1987; g) I. Ibrahem, J. Casas, A. Córdova, *Angew. Chem.* **2004**, *116*, 6690; *Angew. Chem. Int. Ed.* **2004**, *43*, 6528; h) I. Ibrahem, A. Córdova, *Tetrahedron Lett.* **2005**, *46*, 2839; i) Y.-S. Wu, J. Cai, Z.-Y. Hu, G.-X. Lin, *Tetrahedron Lett.* **2004**, *45*, 8949; j) T. Olevier, E. Nadeau, *J. Org. Chem.* **2004**, *69*, 9292; see also refs.[3n,3q,3r,3v]

[8] D. A. Evans, J. V. Nelson, T. R. Taber, *Top. StereoChem.* **1982**, *13*, 1; see also ref.[1a] (pp. 918–919).

[9] J. Libman, M. Sprecher, Y. Mazur, *Tetrahedron* **1969**, *25*, 1679.

[10] a) S. Kobayashi, S. Nagayama, *J. Am. Chem. Soc.* **1997**, *119*, 10049; b) B. C. Ranu, S. Samanta, S. K. Guchhait, *Tetrahedron* **2002**, *58*, 983; c) T. Akiyama, J. Takaya, H. Kagoshima, *Adv. Synth. Catal.* **2002**, *344*, 338.