High Atom Efficiency in $Sc(OTf)_3$-Catalyzed Allylation of Aldehydes with Tetraallyltin

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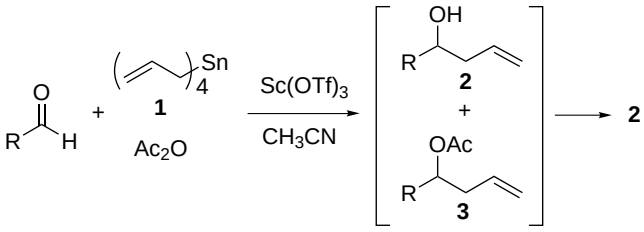
Abstract: The high atom efficiency was achieved through addition of Ac_2O in the $Sc(OTf)_3$-catalyzed allylation of aldehyde with tetraallytin in a 4:1 molar ratio.

Keywords: acylation; allylation; Lewis acids; scandium; stannanes



"Atom efficiency" is a central keyword in green chemistry.[1] Of great importance for access to this end is realization of a 100% yield by use of reactants just in the theoretical stoichiometry. The employment of the least possible amount of catalyst as well as minimization of undesired side-products is also indispensable. In this sense, the reaction of carbonyls with tetraallyltin (**1**), that is a useful method to provide homoallylic alcohols, is attractive because all four allyl residues of **1** can be utilized. This is much more advantageous than more popular protocols using allyltrialkylsilyl or alkyltrialkylstannyl reagents which transfer only one allyl moiety out of four organic groups on the silicon or tin. The reaction between **1** and an aldehyde in a 1:4 molar ratio was reported to be promoted by HCl[2] or methanol,[3] yet the yields of desired homoallyl alcohols were not constantly high: more than 90% in some cases but less in others. Ionic liquids were employed as reaction media in which the yields were 70–93%.[4] Phenol was found to be an effective promoter for reaction with ketone affording 87–99% yields.[5] Lewis acids are potentially useful as well, yet only brief mention was made of $Sc(OTf)_3$[6] and $Cu(OTf)_2$[7] catalysts for reaction between **1** and PhCHO to furnish 84 and 90% yields, respectively.[8] As part of our project to explore highly atom-efficient processes catalyzed by Lewis acid,[9] we have disclosed that the yield of $Sc(OTf)_3$-catalyzed allylation of aldehydes with **1** is intensively improved simply by addition of acetic anhydride (Ac_2O) (Equation 1).

Obviously, the primary purpose of this study is the attainment of high yield through employment of **1** and aldehyde in a strict 1:4 ratio. Moreover, reduction of the catalyst concentration to a minimum level is equally important for the high atom efficiency. Along this line, the reaction between **1** and PhCHO with a 1:4 molar ratio in CH_3CN at 0 °C was investigated (Table 1). With a 5 mol % catalyst concentration relative to the aldehyde that is the most common level in various $Sc(OTf)_3$-catalyzed reactions, the yield was 80% (entry 1), a figure comparable with that obtained in aqueous media.[6] Upon gradual reduction of the catalyst concentration, it turned out that the yield was not significantly decreased until the 0.1 mol % level where an 82% yield was obtained (entry 2). This may be a rather surprising outcome with such a low level of catalyst concentration; nevertheless the attained figure is unsatisfactory from the standpoint of atom efficiency. Since we had become aware of the potential efficacy of Ac_2O to accelerate the reaction rate in a similar system,[10] we decided to scrutinize the effect of this additive in more detail. As we expected, the yield was improved by adding Ac_2O and an almost perfect allylation was achieved when the additive was used in an equimolar amount to aldehyde (entry 3). Although the products were composed of homoallyl alcohol **2a** and acetate **3a**, the single product **2a** was obtained simply by subjecting the reaction mixture to alkaline hydrolysis while addition of Ac_2O/pyridine to the reaction mixture furnished **3a** in 97% yield (Scheme 1). It should be noted that such an improvement of yield was not induced by other anhydrides under the same conditions but rather a decrease in the yield compared to the blank experiment was observed: 82% (blank); 67% with hexanoic anhydride; 42% with benzoic anhydride; 65% with methanesulfonic anhydride; 76% with toluenesulfonic anhydride. Needless to say, Ac_2O itself cannot work as a promoter. When a mixture of **1** and PhCHO was exposed to Ac_2O in the absence of $Sc(OTf)_3$, no reaction took place.

Then, other Lewis acids were screened in the same reaction (Table 2). The similar increase in the yield was attained with benzaldehyde (entries 1–4) but virtually

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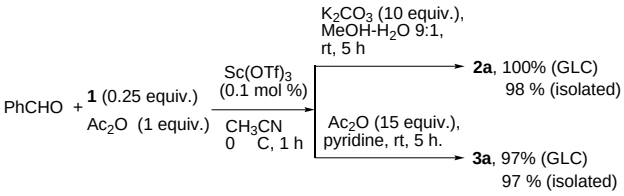
Table 1. Screening of the amount of $Sc(OTf)_3$ and the effect of Ac_2O.[a]

Entry	$Sc(OTf)_3$	Ac_2O	Yield [%]		
			2a	**3a**	**2a + 3a**
1[b]	5 mol %	–	80	–	80
2[c]	0.1 mol %	–	82	–	82
3[c]	0.1 mol %	1 equiv.	39	59	98

[a] Reaction conditions: aldehyde (3 mmol), **1** (0.75 mmol), $Sc(OTf)_3$ (0.15 mmol, 5 mol % or 0.003 mmol, 0.1 mol %), 0 °C; yields determined by GLC.
[b] Reaction time: 30 min.
[c] Reaction time: 1 h.



Scheme 1.

no improvement was observed for nonanal with these Lewis acids (entries 5 – 8) in contrast to a high yield with $Sc(OTf)_3$ (entry 9). Evidently, this catalyst is superior to the other Lewis acids in terms of generality.

Armed with these results, a variety of aldehydes was subjected to the allylation as shown in Table 3, from which the effectiveness of Ac_2O to increase the yield is apparent. The following comments are further worthy of note.

(1) The reaction proceeded smoothly with α,β-unsaturated, sterically bulky, and both aliphatic and aromatic aldehydes. Even acid-sensitive substrates are employable.
(2) In general, the yield is higher than 90%.
(3) Since the reaction is clean and virtually free from contaminants, isolation of the desired product is simple.

The analogous increase of yield by adding Ac_2O was reported for the $Sc(OTf)_3$-catalyzed allylation of electron-rich aldehydes with allyltrimethylsilane.[11] In this case, the coexisting Ac_2O serves for suppressing the secondary reactions (like double allylation or ether formation) of the resulting homoallyl alcohols through *in situ* acetylation to furnish homoallyl acetates. Apparently, our reaction is totally different because the homoallyl alcohols remained in the final reaction mixture. Recently, the utility of the combination of Lewis acids with Brønsted[12] or carboxylic[13] acids as well as phenol[5] was well recognized. Thus, we checked the possibility of activation by acetic acid that was *in situ* produced as the reaction had proceeded. However, addition of this acid in our protocol led to no increase in the yield but the ether derived from the resulting homoallyl alcohol was formed to some extent.

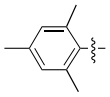
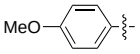
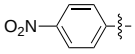
When the reaction was conducted in the presence of a catalytic amount (0.1 mol %) of triflic acid or triflic anhydride but in the absence of metal triflate, the yields of the nonanal adduct were 75% and 79%, respectively, nearly comparable to that in the $Sc(OTf)_3$-catalyzed reaction. However, when one equivalent of Ac_2O was added in the presence of triflic acid or triflic anhydride, the yield was not increased so much, only up to 88% and 83%, respectively. In the $Sc(OTf)_3$-catalyzed reaction, the addition of one equivalent of Ac_2O resulted in an increase in the yield of the nonanal adduct to 96% yield (see Table 2, entry 9). Apparently, the triflic acid or anhydride that may possibly arise *in situ* from the metal triflate plays no pivotal role in the present protocol.

Table 2. Comparison of various Lewis acids.[a]

Entry	R	Lewis acid	Yield [%]	
			Total yield (**2** + **3**)[b]	**2**[c]
1	Ph	$Bi(OTf)_3$	97 (**2a**, 33; **3a**, 64)	**2a**, 80
2	Ph	$Cu(OTf)_2$	99 (**2a**, 29; **3a**, 70)	**2a**, 75
3[d]	Ph	TMSOTf	86 (**2a**, 35; **3a**, 51)	**2a**, 51
4	Ph	BF_3OEt_2	93 (**2a**, 42; **3a**, 51)	**2a**, 61
5	C_8H_{17}	$Bi(OTf)_3$	83 (**2b**, 43; **3b**, 40)	**2b**, 81
6	C_8H_{17}	$Cu(OTf)_2$	89 (**2b**, 60; **3b**, 29)	**2b**, 81
7	C_8H_{17}	TMSOTf	86 (**2b**, 60; **3b**, 26)	**2b**, 84
8	C_8H_{17}	BF_3OEt_2	75 (**2b**, 62; **3b**, 13)	**2b**, 73
9	C_8H_{17}	$Sc(OTf)_3$	96[e] (**2b**, 37; **3b**, 59)	**2b**, 71

[a] Reaction conditions: aldehyde (3 mmol), **1** (0.75 mmol), Lewis acid (0.003 mmol), 0 °C, 1 h; yields determined by GLC.
[b] With Ac_2O (3 mmol).
[c] Without Ac_2O.
[d] Reaction time: 2 h.
[e] A 94% yield of **2** was obtained after hydrolysis: Reaction conditions: 5.0 equiv. NaOMe in MeOH, rt, 5 h.

Table 3. Ac_2O-preomoted $Sc(OTf)_3$-catalyzed allylation of various aldehydes.[a]

Entry	R	Yield [%]	
		Total yield (**2** + **3**)[b]	**2**[c,d]
1[e]		97 (**2c**, 62; **3c**, 35)[f]	**2c**, 96[f] (82)[f]
2[g]		90 (**2d**, 42; **3d**, 48)[h]	**2d**, 90[h] (65)[h]
3[g]		96 (**2e**, 33; **3e**, 63)[f]	**2e**, 96[f] (74)[f]
4[i]		94 (**2f**, 25; **3f**, 69)[h]	**2f**, 95[h,j] (89)[h]
5[e]		90 (**2g**, 47; **3g**, 43)[f]	**2g**, 90[f,k] (64)[f]
6[e]		95 (**2h**, 27; **3h**, 68)[f]	**2h**, 98[f,k] (91)[f]
7[e]		94 (**2i**, 47; **3i**, 47)[l]	**2i**, 92[l] (71)[l]
8[i]		92 (**2j**, 68; **3j**, 24)[l]	**2j**, 92[h] (66)[h]

[a] Reaction conditions: 3 mmol aldehyde, 0.25 equiv. **1**, 0.1 mol % $Sc(OTf)_3$, 0 °C.
[b] With 1 equiv. Ac_2O.
[c] After hydrolysis: Reaction conditions: 5.0 equiv. NaOMe in MeOH, rt, 5 h.
[d] Yield of **2** without Ac_2O in parentheses.
[e] Reaction time: 1 h.
[f] Determined by GLC.
[g] Reaction time: 3 h.
[h] Isolated yields.
[i] Reaction time: 2 h.
[j] Reaction temp.: 40 °C, Reaction time: 12 h.
[k] Reaction conditions: 10 equiv. K_2CO_3 in MeOH/water (9:1), rt, 5 h.
[l] Determined by ^1H NMR.

Upon addition of Ac_2O (1 equiv.) to $Sc(OTf)_3$ (1 equiv.) in CH_3CN, the color of the solution turned faintly yellow indicative of interaction between these two components. While a ^{13}C NMR spectrum of the solution exhibited no change from free Ac_2O, an IR spectrum gave rise to low wavenumber shifts of carbonyl stretching bands in the presence of $Sc(OTf)_3$.[14] As such, it is deduced that an $Sc(OTf)_3$ species that is weekly coordinated by Ac_2O is responsible for increasing the allylation yield.

In summary, we have arrived at a considerably high level of atom efficiency. All of the four allyl residues together with an aldehyde component are consumed and hence, no organotin species remains. Another notable feature is the use of a tiny amount of the catalyst. In the reaction using 3 mmol of aldehyde, the necessary amount of $Sc(OTf)_3$ is only 1.5 mg. This is extremely economical and, in addition, advantageous in separation of the catalyst residue from the product. As a whole, the present protocol offers a highly atom-efficient process for synthesis of homoallyl alcohols.

Experimental Section

General Methods

All reactions were carried out under an atmosphere of argon with freshly distilled solvents, unless otherwise noted. All the solvents such as acetonitrile and pyridine were distilled from CaH_2. Metal triflates such as $Sc(OTf)_3$, $Cu(OTf)_2$ and Me_3SiOTf and $BF_3 \cdot OEt_2$ were purchased and used without purification. All the products were characterized by comparing their spectral and physical data with the literature values: **2a**,[15] **2b**,[16] **2c**,[15] **2e**,[17] **2f**,[18] **2 g**,[19] **2 h**,[15] **2i**,[20] **3a**,[21] **3b**,[22] **3c**,[21] **3g**,[21] **3h**,[21] and **3i**.[23]

Representative Procedure for Allylation

To a mixture of PhCHO (318 mg, 3.0 mmol) and $Sc(OTf)_3$ (1.5 mg, 0.003 mmol) in CH_3CN (4 mL) was added tetraallyltin (180 μL, 0.75 mmol) and Ac_2O (0.28 mL, 3.0 mmol) in CH_3CN (1 mL) at 0 °C under Ar. The mixture was stirred for 1 h and saturated aqueous $NaHCO_3$ solution (10 mL) was added. After usual work-up (AcOEt/H_2O), the organic layer was washed with brine. The organic layer was dried (Na_2SO_4) and filtered. The filtrate was evaporated. GLC analysis of the crude mixture showed the formation of **2a** (39% yield) and **3a** (59% yield).

Representative Procedure for Homoallyl Alcohols in One Pot

To a mixture of PhCHO (318 mg, 3.0 mmol) and $Sc(OTf)_3$ (1.5 mg, 0.003 mmol) in CH_3CN (4 mL) was added tetraallyltin (180 μL, 0.75 mmol) and Ac_2O (0.28 mL, 3.0 mmol) in CH_3CN (1 mL) at 0 °C under Ar, and the mixture was stirred for 1 h. To the mixture were added K_2CO_3 (4.14 g, 30 mmol), MeOH (4.5 mL) and H_2O (0.5 mL) at 0 °C, and the mixture was stirred at room temperature for 5 h. To this mixture, 1 N aqueous HCl was added until the solution turned to pH 7. After usual work-up (AcOEt/H_2O), the organic layer was washed with brine. The organic layer was dried (Na_2SO_4) and filtered. The filtrate was evaporated. GLC analysis of the crude mixture showed the formation of **2a** (100% yield). Subjection of the crude mixture to column chromatography on silica gel (15% AcOEt/hexane) provided **2a** in a 98% yield (435 mg).

Representative Procedure for Homoallyl Acetates in One Pot

To a mixture of PhCHO (318 mg, 3.0 mmol) and $Sc(OTf)_3$ (1.5 mg, 0.003 mmol) in CH_3CN (4 mL) was added tetraallyltin (180 μL, 0.75 mmol) and Ac_2O (0.28 mL, 3.0 mmol) in CH_3CN (1 mL) at 0 °C under Ar, and the mixture was stirred for 1 h. To the mixture were added pyridine (5 mL) and Ac_2O (4.25 mL, 45 mmol) at 0 °C, and the mixture was stirred at room temperature for 5 h. After addition of aqueous 1 N HCl (10 mL) at 0 °C and usual work-up (AcOEt/H_2O), the organic layer was washed with aqueous $NaHCO_3$ and brine. The organic layer was dried (Na_2SO_4) and filtered. The filtrate was evaporated. GLC analysis of the crude mixture showed the formation of **3a** (97% yield). Subjection of the crude mixture to

column chromatography on silica gel (5% AcOEt/hexane) provided **3a** in a 97% yield (551 mg).

1-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)but-3-enol (2d) (53:47 mixture of diastereomers): ^{1}H NMR ($CDCl_3$): δ = 0.83, 0.85 (2 s, 3H), 1.15, 1.17 (2 d, J = 8.6, 8.4 Hz, 1H), 1.30 (s, 3H), 1.55 (br, 1H), 2.07 – 2.46 (m, 7H), 4.05 (dd, J = 5.6, 6.9 Hz, 1H), 5.09 – 5.18 (m, 2H), 5.47 (br, 1H), 5.72 – 5.89 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 21.3, 26.0, 26.1, 30.9, 31.5, 31.6, 37.6, 37.7, 39.3, 39.4, 40.8, 42.0, 73.47, 73.53, 117.36, 117.45, 117.54, 117.6, 134.8, 134.9, 149.3, 149.7; HRMS (EI): calcd. for $C_{13}H_{20}O$: 192.1514; found: 192.1517.

1-(8-Perhydro-2*H*-pyran-2-yloxyoctyl)but-3-enol (2j): ^{1}H NMR ($CDCl_3$): δ = 1.31 – 1.87 (m, 21H), 2.08 – 2.18 (m, 1H), 2.28 – 2.35 (m, 1H), 3.38 (dt, J = 6.7, 9.5 Hz, 1H), 3.47 – 3.54 (m, 1H), 3.60 – 3.68 (m, 1H), 3.73 (dt, J = 7.0, 9.5 Hz, 1H), 3.84 – 3.91 (m, 1H), 4.58 (dd, J = 2.6, 4.4 Hz, 1H), 5.11 – 5.17 (m, 2H), 5.76 – 5.90 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 19.6, 25.4, 25.6, 26.1, 29.3, 29.46, 29.52, 29.7, 30.7, 36.7, 41.9, 62.3, 67.6, 70.6, 98.8, 118.0, 134.9; HRMS (EI): calcd. for $C_{17}H_{32}O_3$: 284.2351; found: 284.2341.

1-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)but-3-enyl Acetate (3d) (52:48 mixture of diastereomers): ^{1}H NMR ($CDCl_3$): δ = 0.78, 0.82 (2 s, 3H), 1.12, 1.13 (2 d, J = 8.6 Hz, 1H), 1.29 (s, 3H), 2.01, 2.02 (2 s, 3H), 2.05 – 2.12 (m, 1H), 2.18 – 2.43 (m, 6H), 5.02 – 5.10 (m, 2H), 5.17 – 5.24 (m, 1H), 5.48 – 5.52 (m, 1H), 5.62 – 5.80 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 21.1, 21.2, 21.3, 26.1, 26.2, 31.0, 31.1, 31.4, 31.5, 36.7, 37.0, 37.8, 37.9, 40.7, 41.8, 42.4, 75.4, 75.6, 117.2, 117.3, 119.5, 121.0, 133.7, 133.9, 145.2, 145.9, 170.1, 170.2; HRMS (EI): calcd. for $C_{15}H_{22}O_2$: 234.1620; found: 234.1633.

1-(Diphenylmethyl)but-3-enyl Acetate (3e): ^{1}H NMR ($CDCl_3$): δ = 1.81 (s, 3H), 2.15 – 2.25 (m, 1H), 2.34 – 2.42 (m, 1H), 4.10 (d, J = 9.7 Hz, 1H), 4.95 – 5.07 (m, 2H), 5.70 – 5.84 (m, 2H), 7.14 – 7.33 (m, 10H); ^{13}C NMR ($CDCl_3$): δ = 20.8, 37.5, 55.5, 74.1, 118.0, 126.5, 126.8, 128.2, 128.3, 128.4, 128.7, 133.4, 141.2, 141.3, 170.4; HRMS (EI): calcd. for $C_{19}H_{20}O_2$: 280.1463; found: 280.1469.

1-(2,4,6-Trimethylphenyl)but-3-enyl Acetate (3f): ^{1}H NMR ($CDCl_3$): δ = 2.04 (s, 3H), 2.24 (s, 3H), 2.42 (s, 6H), 2.51 – 2.60 (m, 1H), 2.74 – 2.84 (m, 1H), 5.02 – 5.13 (m, 2H), 5.64 – 5.78 (m, 1H), 6.18 (dd, J = 6.4, 8.8 Hz, 1H), 6.81 (s, 2H); ^{13}C NMR ($CDCl_3$): δ = 20.6, 20.8, 21.0, 38.2, 72.3, 117.6, 129.9, 132.9, 133.9, 136.3, 137.1, 170.2; HRMS (EI): calcd. for $C_{15}H_{20}O_2$: 232.1463; found: 232.1478.

1-(8-Perhydro-2*H*-pyran-2-yloxyoctyl)but-3-enyl Acetate (3j): ^{1}H NMR ($CDCl_3$): δ = 1.28 – 1.87 (m, 20H), 2.03 (s, 3H), 2.22 – 2.37 (m, 2H), 3.38 (dt, J = 6.7, 9.5 Hz, 1H), 3.46 – 3.53 (m, 1H), 3.73 (dt, J = 6.9, 9.5 Hz, 1H), 3.83 – 3.91 (m, 1H), 4.57 (dd, J = 2.8, 4.2 Hz, 1H), 4.91 (quin, J = 6.2 Hz, 1H), 5.04 – 5.10 (m, 2H), 5.68 – 5.82 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 19.6, 21.2, 25.2, 25.4, 26.1, 29.3, 29.4, 29.7, 30.7, 33.5, 38.6, 62.3, 67.6, 73.3, 98.8, 117.5, 133.7, 170.7; HRMS (EI): calcd. for $C_{19}H_{34}O_4$: 326.2457; found: 326.2453.

References and Notes

[1] a) B. M. Trost, *Science* **1991**, *254*, 1471; b) R. A. Sheldon, *Chem. Ind. (London)* **1997**, 12.

[2] A. Yanagisawa, H. Inoue, M. Morodome, H. Yamamoto, *J. Am. Chem. Soc.* **1993**, *115*, 10356.

[3] a) T. M. Cokley, P. J. Harvey, R. L. Marshall, A. McCluskey, D. J. Young, *J. Org. Chem.* **1997**, *62*, 1961; b) A. McCluskey, I. W. Muderawan Muntari, D. J. Young, *J. Org. Chem.* **2001**, *66*, 7811.

[4] C. M. Gordon, A. McCluskey, *Chem. Commun.* **1999**, 1431.

[5] a) M. Yasuda, N. Kitahara, T. Fujibayashi, A. Baba, *Chem. Lett.* **1998**, 743; b) M. Yasuda, T. Fujibayashi, A. Baba, *J. Org. Chem.* **1998**, *63*, 6401.

[6] I. Hachiya, S. Kobayashi, *J. Org. Chem.* **1993**, *58*, 6958.

[7] S. Kobayashi, S. Nagayama, T. Busujima, *Chem. Lett.* **1997**, 959.

[8] For other relevant papers on the use of tetraallyltin in excess, see: a) D. N. Harpp, M. Gingras, *J. Am. Chem. Soc.* **1988**, *110*, 7737; b) S. Fukuzawa, K. Sato, T. Fujinami, S. Sakai, *J. Chem. Soc. Chem. Commun.* **1990**, 939; c) S. Kobayashi, S. Nagayama, *J. Org. Chem.* **1996**, *61*, 2256; d) N. Asao, S. Kii, H. Hanawa, K. Maruoaka, *Tetrahedron Lett.* **1998**, *39*, 3729; e) H. C. Aspinall, N. Greeves, E. G. McIver, *Tetrahedron Lett.* **1998**, *39*, 9238; f) S. Casolari, D. D'Addario, E. Tagliavini, *Org. Lett.* **1999**, *7*, 1061; g) R. Hamasaki, Y. Chounan, H. Horino, Y. Yamamoto, *Tetrahedron Lett.* **2000**, *41*, 9883.

[9] a) J. Xiang, S. Toyoshima, A. Orita, J. Otera, *Angew. Chem. Int. Ed.* **2001**, *40*, 3670; b) J. Xiang, A. Orita, J. Otera. *Adv. Synth. Cat.* **2002**, *344*, 84.

[10] A. Orita, Y. Nagano, K. Nakazawa, J. Otera, *Synlett* **2000**, 599.

[11] V. K. Aggarwal, G. P. Vennall, *Synthesis* **1998**, 1823.

[12] a) K. Ishihara, S. Nakamura, M. Kaneeda, H. Yamamoto, *J. Am. Chem. Soc.* **1996**, *118*, 12854; b) A. G. M. Barrett, D. C. Braddock, J. P. Henschke, E. R. Walker, *J. Chem. Soc. Perkin Trans. 1* **1999**, 873; c) K. Manabe, S. Kobayashi, *Tetrahedron Lett.* **1999**, *40*, 3773.

[13] a) M. V. Deaton, M. A. Ciufolini, *Tetrahedron Lett.* **1993**, *34*, 2409; b) M. A. Ciufolini, M. V. Deaton, S. Zhu, M. Chen, *Tetrahedron* **1997**, *53*, 16299; c) H. C. Aspinall, J. S. Bissett, N. Greeves, D. Levin, *Tetrahedron Lett.* **2002**, *43*, 319.

[14] $\nu_{(C=O)}$ bands in CH_3CN: 1825 and 1755 cm^{-1} for free Ac_2O; 1806, 1754, 1671, 1625, 1597 cm^{-1} in the presence of $Sc(OTf)_3$.

[15] A. Hosomi, S. Kohra, K. Ogata, T. Yanagi, Y. Tomonaga, *J. Org. Chem.* **1990**, *55*, 2415.

[16] K. Yamada, T. Tozawa, M. Nishida, T. Mukaiyama, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2301.

[17] T. Harada, T. Mukaiyama, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 882.

[18] H. Yamataka, K. Nishikawa, T. Hanafusa, *Chem. Lett.* **1990**, 1711.

[19] X-H. Yi, J. X. Haberman, C-J. Li, *Synth. Commun.* **1998**, *28*, 2999.

[20] M. Kira, K. Sato, H. Sakurai, *J. Am. Chem. Soc.* **1988**, *110*, 4599.

[21] J. S. Yadav, B. V. Subba Reddy, G. S. Kiran Kumar Reddy, *Tetrahedron Lett.* **2000**, *41*, 2695.

[22] G. A. Kraus, M. Silveira, S. J. Danko, *J. Agric. Food Chem.* **1984**, *32*, 1265.

[23] C. Tanyeli, A. S. Demir, A. H. Arkin, I. M. Akhmedov, *Enantiomer* **1997**, *2*, 433.

