Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Fluorine Chemistry 125 (2004) 67–71
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/jfluchem

Synthetic applications of the carbanion generated from 4,4,4-trifluorobutan-2-one

Tsuneyoshi Tominaga, Kouji Nishi, Tomoya Kitazume*

Graduate School of Bioscience and Biotechnology, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku Yokohama 226-8501, Japan

Received 10 September 2003; received in revised form 11 October 2003; accepted 16 October 2003

Abstract

Synthetic routes for α-trifluoromethylated carbonyl compounds based on the aldol reaction of silylenol ether and the palladium(0) catalyzed reaction using by 4,4,4-trifluorobutan-2-one are described.

Keywords: α-Trifluoromethylated carbonyl compounds; β-Fluorocarbanion; Palladium(0)

1. Introduction

While we have reported the methodology and/or reagents suitable for the regio- or stereoselective introduction of fluoroalkyl group onto the specific position of the molecules [1], several problems remain to be solved in the field of fluorinated materials [2–8]. In particular, the stereoselective introduction of fluoromethyl groups onto the sequential carbon atoms has not been studied in detail. Moreover, the chemistry of β-fluorocarbanions, which do not undergo elimination to form fluoroolefins, has not been studied for the construction of regio- and stereocontrolled fluorinated materials [9–13], except for indium-mediated allylation [14]. Further, except for diastereoselective perfluoroalkylation of chiral *N*-acyloxazolidinones [15], no other examples of highly diastereocontrolled difluoromethylation [16] have been reported to our knowledge. Recently, we have reported the chemistry of β-fluorocarbanions such as the palladium-catalyzed allylation reactions [17] and highly stereocontrolled synthesis with trifluoromethylated allyl zinc and allenyl zinc reagents [18]. Obviously, practical generation for β-fluorocarbanions remains an important synthetic challenge. Although palladiym-catalyzed allylation reactions under neutral condition have been recognized to be useful for organic synthesis [19], their synthetic value in fluorine chemistry still appears to be grossly underestimated [20].

In this paper, we describe the synthetic utilities of 4,4,4-trifluorobutan-2-one, producing α-trifluoromethylated carbonyl compounds.

2. Results and discussion

To construct the sequential stereoselction with a fluoromethyl group, we have designed a facile synthetic route based on the synthesis and applications of activated α-trifluoromethylated carbinols derived from silylenol ether of 4,4,4-trifluorobutan-2-one (**1**). Initially, we carried out the reaction of benzaldehyde dimethylacetal with silylenol ether (**2**) derived from 4,4,4-trifluorobutan-2-one in the presence of trimethylsilyl trifluoromethanesulfonate ($CF_3SO_3SiMe_3$) and triethylamine at room temperature, however the mixture of compounds **3a** and **4a** were obtained with regioselectivity (58:38). Therefore, silylenol ether (**2**) was prepared at room temperature, and then the corresponding acetal was added to the above mixture solution at −78 °C. The reaction produces the construction of sequential stereoselction with a CF_3 group as shown in Table 1. Nakai and co-workers [12] have reported that silylenol ethers of phenyl 2,2,2-trifluoroethyl ketone and 3,3,3-trifluoropropanate reacted with the electrophiles such as aromatic acetals, acid chlorides, and chloromethyl ethers. However, it was impossible to react with aliphatic acetals. In the case of silylenol ether of 4,4,4-trifluorobutan-2-one, it is possible to proceed the reaction with aromatic and aliphatic acetals with high regioselectivity, giving the compounds **3** with a diastereoselectivity shown in Table 1.

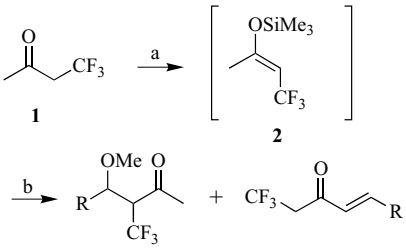
* Corresponding author. Tel.: +81-45-924-5754; fax: +81-45-924-5780.
E-mail address: tkitazum@bio.titech.ac.jp (T. Kitazume).

0022-1139/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2003.10.005

Table 1
Preparation of compound **3**

Entry	R	Yield (%)	
		3	d.r.
1	Ph	95	78:22
2	4-$MeOC_6H_4$	77	80:20
3	C_5H_{11}	37[a]	45:55
4	C_7H_{15}	42[a]	43:57

[a] Yield was determined by ^{19}F NMR.



[a] $CF_3SO_3SiMe_3$, CH_2Cl_2, Et_3N, rt
[b] $RCH(OMe)_2$, -78 °C

Scheme 1.

However, when the corresponding aldehydes as a substrate were used in this reaction type, it was impossible to proceed the reaction. The diastereomeric ratio was determined by ^1H NMR chemical shift of methyl signals in CH_3CO group which appeared at $\delta = 1.80-1.85$ and 2.30−2.40 ppm (see Section 3). The relative conformation of the above compounds (**3a** and **3b**) was determined from ^1H NMR chemical shift. From the comparison of the conformations (*syn* and *anti*), we have found that phenyl group of *syn*-isomer affects the methyl proton of CH_3CO group more than those of *anti*-isomer. Therefore, the ^1H NMR chemical shift indicates a *syn* conformation for the down field (Scheme 1).

In the next step, $Pd(PPh_3)_4$ was used at 50–60 °C (oil bath temperature) under neutral conditions in the reaction of 4,4,4-trifluorobutan-2-one with cinnamyl carbonate in tetrahydrofuran to obtain (*E*)-3-trifluoromethyl-5-hepten-2-one in 74% yield. The temperature (oil bath temperature: 50−60 °C) and Pd(0) catalyst system increased the chemical yield. The mechanism of the above palladium(0)-catalyzed allylation reaction is explained as follows. In the case of neutral condition, alkoxide anion in the possible intermediate **Int-A** reacts with the activated methylene group in substrate ($CF_3CH_2C(O)CH_3$), resulting in the formation of intermediate **Int-B** (Fig. 1). In this reaction step, it appears that free β-carbanion with a trifluoromethyl group, such as $-CH(CF_3)C(O)CH_3$, is not generated and that the EtO ligand on the palladium atom is replaced by $CH(CF_3)C(O)CH_3$. Finally, reductive elimination from **Int-B** produces the S_N2 and/or S_N2' allylation product as products **6–8** (Table 2).

In the case of the butane monoxide system shown in Fig. 2, the formation of 3-trifluoro-methyl-7-hydroxy-5-hepten-2-one (**9**) (70% yield) can be rationalized via reductive elimination from an intermediate such as **Int-D**.

In conclusion, we have found a convenient procedure for construction of the stereocenter on the carbon atom attached to a fluoromethyl group.

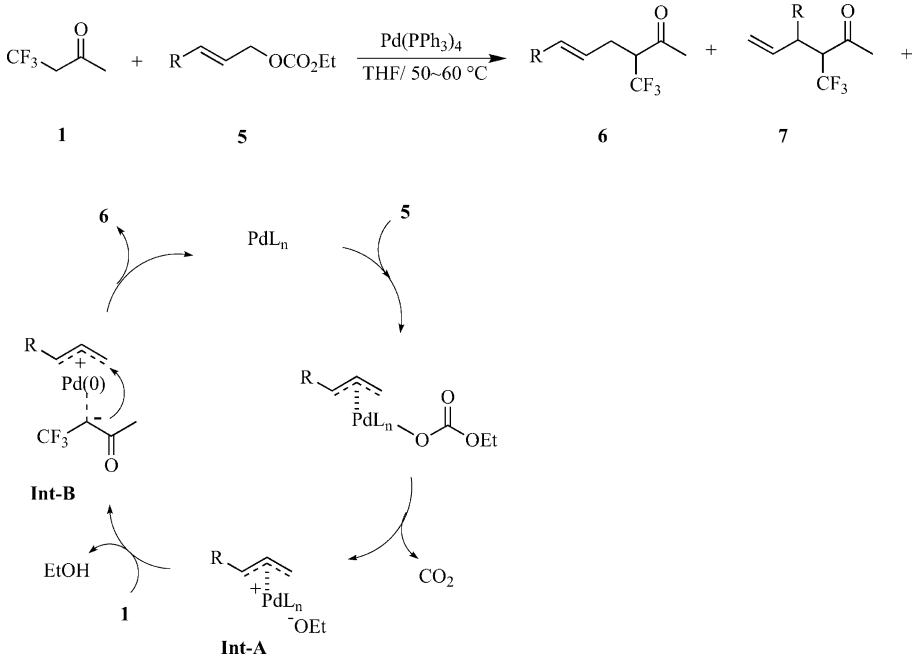


Fig. 1. Pd(0)-catalyzed reaction system.

Table 2
Preparation of compounds **6** and **8**

Entry	R	Yield (%)		
		6	**7**	**8**
1[c]	H	28		8
2[d,e]	H	59		3
3[c]	Me	17	6[a]	2
4[d,e]	Me	39	17[b]	1
5[c]	Ph	46		12
6[d]	Ph	74		12

[a] Diastereomeric ratio (54/46).
[b] Diastereomeric ratio (56/44).
[c] Molar ratio (**1/5** = 1.5/1).
[d] Molar ratio (**1/5** = 4/1).
[e] Molecular sieves were used.

3. Experimental

3.1. General

All commercially available reagents were used without further purification. Chemical shifts of ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in ppm (δ) downfield from the following internal standard (Me_4Si, δ 0.00) in $CDCl_3$. The ^{19}F (282 MHz) NMR spectra were recorded in ppm (δ) downfield from internal standard C_6F_6 in $CDCl_3$ using a VXR 300 instrument.

General procedure of the aldol reaction.

3.2. 4-Methoxy-4-phenyl-3-trifluoromethylbutan-2-one (*3a*)

To a mixture solution of 4,4,4-trifluorobutan-2-one (**1**) (139 mg, 1.1 mmol) and triethylamine (111 mg, 1.1 mmol) in dichloromethane (2 ml), trimethylsilyl trifluoromethanesulfonate (289 mg, 1.3 mmol) was added at room temperature under a nitrogen atmosphere. After the whole was stirred for 2 h at that temperature, the corresponding acetal was added to the mixture of benzaldehyde dimethyl acetal (1 mmol) in CH_2Cl_2 (2 ml) at −78 °C. The whole was stirred at −78 °C overnight, and then the mixture was quenched with 3N HCl. Oily materials were extracted with diethyl ether, and the extract was dried over $MgSO_4$. On removal of the solvent, the resultant crude product was purified by column chromatography on silica gel using a mixture of hexane and ethyl acetate.

Major isomer. ^{1}H NMR ($CDCl_3$): δ 1.80 (3 H, s), 3.20 (3 H, s), 3.71 (1 H, dq, J = 10.01, 8.06 Hz), 4.61 (1 H, d, J = 10.01 Hz), 7.25–7.30 (Ar–H). ^{13}C NMR ($CDCl_3$): δ 27.970 (minor: 27.995), 51.904, 57.271 (qd, J = 24.3, 1.15 Hz), 75.566 (q, J = 2.57 Hz), 119.110 (CF_3, q, J = 281.42 Hz), 122.876, 124.147, 124,303 132.220, 195.575 (minor: 195.564). ^{19}F NMR ($CDCl_3$): δ 98.6 (d, J = 7.63 Hz), IR (neat): 1728 (C=O) cm^{-1}. Minor isomer: ^{1}H NMR ($CDCl_3$): δ 2.38 (3 H, s), 3.64 (1 H, dq, J = 9.52, 8.55 Hz), 4.65 (1 H, d, J = 9.77 Hz), 7.25–7.30 (Ar–H). ^{19}F NMR ($CDCl_3$): δ 98.64 (d, J = 8.4 Hz) ppm from C_6H_6. Anal. calcd. for $C_{12}H_{13}O_2F_3$: C, 58.54; H, 5.32. Found: C, 58.43; H, 5.52.

3.3. 4-Methoxy-4-(4-methoxyphenyl)-3-trifluoromethylbutan-2-one (*3b*)

Major isomer. ^{1}H NMR ($CDCl_3$): δ 1.82 (3 H, s), 3.18 (3 H, s), 3.70 (1 H, dq, J = 10.0, 7.81 Hz), 3.81 (3 H, s), 4.56 (1 H, d, J = 10.0 Hz), 6.85–7.25 (Ar–H). ^{13}C NMR ($CDCl_3$): δ 32.511 (m), 55.182, 56.165, 61.869 (q, J = 24.3 Hz), 79.650 (q, J = 2.57 Hz), 114.068, 123.735 (q, J = 281.1 Hz), 128.579, 128.727, 159.790, 200.181 (q, J = 2.29 Hz). ^{19}F NMR ($CDCl_3$): δ 98.5 (d, J = 7.63 Hz) ppm from C_6H_6. IR (neat): 1728 (C=O) cm^{-1}. Minor isomer ^{1}H NMR ($CDCl_3$): δ 2.37 (3 H, s), 3.09 (3 H, s), 3.61 (1 H, dq, J = 9.52, 8.55 Hz), 3.82 (3 H, s), 4.59 (1 H, d, J = 10.0 Hz), 6.90–7.30 (Ar–H). ^{13}C NMR ($CDCl_3$): δ 31.961 (m), 55.171, 56.195, 62.146 (q, J = 23.5 Hz), 80.335 (q, J = 2.29 Hz), 113.848, 123.065 (q, J = 279.7 Hz), 128.571, 128.818, 159.797, 200.500. ^{19}F NMR ($CDCl_3$): δ 98.7 (d, J = 8.39 Hz) ppm from ext. C_6H_6. Anal. calcd. for $C_{13}H_{15}O_3F_3$: C, 56.52; H, 5.47. Found: C, 56.25; H, 5.80.

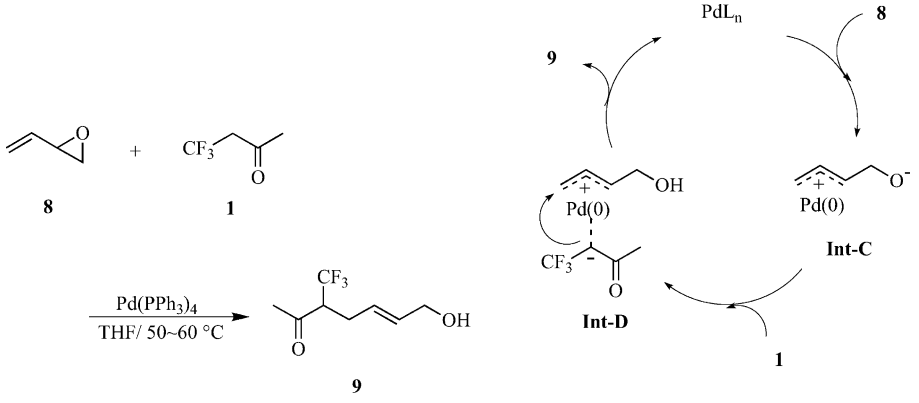


Fig. 2. Butadiene monooxide system.

3.4. 4-Methoxy-3-trifluoromethylnonen-2-one (**3c**)

Major isomer: ^{1}H NMR ($CDCl_3$): δ 0.89 (3 h, t, 7.08 Hz), 1.25–1.75 (8 H, m), 2.29 (3 H, s), 3.43 (3 H, s), 3.36 (1 H, qd, $J = 9.28, 9.03$ Hz), 3.67 (1 H, ddd, $J = 8.30, 6.10, 3.05$ Hz). ^{19}F NMR ($CDCl_3$): δ 98.0 (d, $J = 9.15$ Hz) ppm from ext. C_6H_6. Minor isomer: ^{1}H NMR ($CDCl_3$): δ 0.90 (3 H, t, $J = 5.98$ Hz), 1.25–1.75 (8 H, m), 2.30 (3 H, s), 3.31 (3 H, s), 3.50 (1 H, qd, $J = 8.79$, 6.22 Hz), 3.76 (1 H, ddd, $J = 7.57$, 4.76, 5.86 Hz). ^{19}F NMR ($CDCl_3$): δ 97.5 (d, $J = 9.15$ Hz) ppm from ext. C_6H_6. ^{13}C NMR ($CDCl_3$): δ diastereomeric mixture: ^{13}C NMR ($CDCl_3$): δ 14.036, 14.047, 22.572, 22.591, 23.661, 25.004, 31.608, 31.791, 31.950 (q, $J = 2.01$ Hz), 32.219 (q, $J = 1.14$ Hz), 58.001, 58.035, 58.667 (q, $J = 23.76$ Hz), 58.906 (q, $J = 24.33$ Hz), 78.294 (q, $J = 2.29$ Hz), 78.379 (q, $J = 2.00$ Hz), 123.953 (q, $J = 279.7$ Hz), 124.082 (q, $J = 280.3$ Hz), 200.697, 200.834. IR (neat): 1729 cm^{-1}.

3.5. 4-Methoxy-3-trifluoromethylundecan-2-one (**3d**)

Diastereomer mixture: ^{1}H NMR ($CDCl_3$): δ 0.880 (3 H, t, $J = 7.08$ Hz), 0.889 (3 H, t, $J = 7.08$ Hz), 1.23–1.40 (24 H, m), 2.293 (3 H, s), 2.299 (3 H, s), 3.306 (3 H, s), 3.315 (3 H, s), 3.33–3.39 (1 H, m), 3.425 (3 H, s), 3.512 (1 H, qd, $J = 8.71, 6.10$ Hz), 3.67 (1 H, m), 3.76 (1 H, m). ^{13}C NMR ($CDCl_3$): δ 9.536, 18.068, 18.087, 19.381, 20.731, 24.593, 24.608, 24.798, 24.972, 26.942 (q, $J = 1.14$ Hz), 26.941, (q, $J = 1.15$ Hz), 27.180, 27.192, 27.336 (m), 27.651 (q, $J = 1.15$ Hz), 53.387, 53.425, 53.998 (q, $J = 24.05$ Hz), 54.283 (q, $J = 24.62$ Hz), 73.680 (q, $J = 2.29$ Hz), 73.767 (q, $J = 1.72$ Hz), 119.339 (q, $J = 279.7$ Hz), 119.464 (q, $J = 280.27$ Hz), 196.089 (q, $J = 2.0$ Hz), 196.222 (q, $J = 2.0$ Hz), 196.087, 196.212. ^{19}F NMR ($CDCl_3$): δ 97.5 (minor: d, $J = 7.17$ Hz), 98.1 (major: d, $J = 7.63$ Hz) from ext. C_6H_6. IR (neat): 1733 cm^{-1}.

Palladium catalyzed allylation reaction: typical procedure is as follows.

3.6. 3-Trifluoromethyl-6-phenyl-5-hexen-2-one (**6c**)

A mixture of 4,4,4-trifluorobutan-2-one (761 mg, 6 mmol) and cinnamyl carbonate (416 mg, 2 mmol) was added to a solution of $Pd(PPh_3)_4$ (0.2 mmol, 10 mol%) in THF (20 ml) under an argon atmosphere. After the reaction mixture was stirred for 5.5 h at 50−60 °C (oil bath temperature), the mixture was diluted with diethyl ether and then passed through a pad of celite. On removal of the solvent, the yields were determined by ^{19}F NMR integral intensities using CF_3Ph as an internal standard, giving 3-trifluoromethyl-6-phenyl-5-hexen-2-one (74%) and 1,1,1-trifluoro-2-bis(3-phenyl-2-propenyl)butan-3-one (12%). The residue was purified by column chromatography on silica gel, eluting with a mixture solution of hexane-ethyl acetate (30:1) to give 3-trifluoromethyl-6-phenyl-5-hexen-2-one (**6c**).

3-Trifluoromethyl-6-phenyl-5-hexen-2-one (**6c**): ^{1}H NMR ($CDCl_3$): δ 2.29 (3 H, s), 2.64–2.85 (2 H, m), 3.37 (1 H, qdd, $J = 9.06$, 9.06, 4.67 Hz), 6.06 (1 H, m), 6.49 (1 H, dt, $J = 15.9$, 1.38 Hz), 7.20–7.40 (Ar–H).^{13}C NMR ($CDCl_3$): δ 29.302 (q, $J = 2.57$ Hz), 30.870 (q, $J = 2.0$ Hz), 56.209 (q, $J = 25.19$ Hz), 123.621, 124.457 (q, $J = 280.28$ Hz), 126.098, 127.596, 128.454, 133.621, 136.383, 200.916 (q, $J = 2.00$ Hz). ^{19}F NMR ($CDCl_3$): δ 95.0 (d, $J = 9.16$ Hz) from ext. C_6H_6.

3.7. 3-Trifluoromethyl-5-hexen-2-one **6a** and 1,1,1-trifluoro-2-bis(2-propenyl)butan-3-one

Mixture: ^{1}H NMR ($CDCl_3$): δ 2.28 (3 H, m), 2.52 (2 H, dd, $J = 14.6$, 7.69 Hz), 2.62 (2 H, dd, $J = 14.6$, 6.87 Hz), 3.29 (1 H, qdd, $J = 8.79, 8.79, 4.94$ Hz), 5.10–5.18 (4 H, m), 5.61–5.76 (2 H, m). ^{13}C NMR ($CDCl_3$): δ 20.963, 27.889 (q, $J = 2.58$ Hz), 60.285, 119.395, 126.305 (q, $J = 284.28$ Hz), 131.242, 202.127. ^{19}F NMR ($CDCl_3$): δ 94.8 (**6a**: d, $J = 8.61$ Hz): 95.3 (s) from ext. C_6H_6.

3.8. 3-Trifluoromethyl-5-hepten-2-one (**6b**)

^{1}H NMR ($CDCl_3$): δ 1.65 (3 H, dd, $J = 6.35$, 1.37 Hz), 2.25 (3 H, s), 2.43–2.58 (2 H, m), 3.24 (1 H, qdd, $J = 8.79$, 8.79, 4.64 Hz), 5.30 (1 H, m), 5.50–5.60 (1 H, m). ^{13}C NMR ($CDCl_3$): δ 17.773, 28.989 (q, $J = 2.58$ Hz), 30.555 (q, $J = 2.00$ Hz), 56.353 (q, $J = 24.91$ Hz), 124.514 (q, $J = 280.27$ Hz), 124.797, 129.323, 201.179. ^{19}F NMR ($CDCl_3$): δ 94.8 (d, $J = 9.16$ Hz) from ext. C_6H_6.

3.9. 3-Trifluoromethyl-7-hydroxy-5-hepten-2-one (**9**)

A mixture of 4,4,4-trifluorobutan-2-one (766 mg, 6.1 mmol) and 1,3-butadiene monoepoxide (150 mg, 2.1 mmol) was added to a solution of $Pd(PPh_3)_4$ (10 mol%) in THF (20 ml) under an argon atmosphere. After the reaction mixture was stirred for 6 h at 60 °C (oil bath temperature), the mixture was diluted with diethyl ether and then passed through a pad of celite. On removal of the solvent, the residue was purified by column chromatography on silica gel, eluting with a mixture solution of hexane-ethyl acetate (5:2) to give 3-trifluoromethyl-7-hydroxy-5-hepten-2-one.

^{1}H NMR ($CDCl_3$): δ 2.28 (Me, s), 2.48–2.70 (2 H, m), 3.28 (1 H, qdd, $J = 9.07$, 9.07, 4.94 Hz), 4.08 (2 H, d, $J = 5.50$ Hz), 5.58 (1 H, m), 5.75 (1 H, m). ^{19}F NMR ($CDCl_3$): δ 94.94 (d, $J = 8.61$ Hz) ppm from ext. C_6F_6. ^{13}C NMR ($CDCl_3$): δ 28.359 (q, $J = 2.58$ Hz), 30.476 (q, $J = 2.00$ Hz), 55.862 (q, $J = 25.2$ Hz), 62.383, 124.334 (q, $J = 280.28$ Hz), 125.442, 133.086, 201.391.

References

[1] (a) T. Kitazume, T. Yamazaki, Topics in Current Chemistry, vol. 193, Springer, Berlin, Germany, 1997, p. 91, and references cited therein;

(b) T. Kitazume, K. Mizutani, T. Yamazaki, Biomedical Frontiers of Fluorine Chemistry, Symposium Series No. 639, American Chemical Society, Washington, DC, 1996, Chapter 8, p. 105;
(c) T. Kitazume, T. Yamazaki, Selective Fluorination in Organic and Bioorganic Chemistry, Symposium Series No. 456, American Chemical Society, Washington, DC, Chapter 12, p. 175.

[2] R. Filler, Y. Kobayashi, Biomedicinal Aspects of Fluorine Chemistry, Kodansha/Elsevier Biomedical, Tokyo, 1982.

[3] J.T. Welch, S. Eswarakrishnan, Fluorine in Bioorganic Chemistry, Wiley, New York, 1991.

[4] M. Hudlicky, A.E. Pavlath, Chemistry of Organic Fluorine Compounds. II. Critical Review ACS, Washington, DC, 1995.

[5] I. Ojima, J.R. McCarthy, J.T. Welch, Biomedical Frontiers of Fluorine Chemistry, ACS Symposium Series 639, Washington, DC, 1996.

[6] T. Kitazume, T. Yamazaki, Experimental Methods in Organic Fluorine Chemistry, Kodansha/Gordon and Breach Science, Tokyo, 1998.

[7] V.A. Soloshonok, Enantiocontrolled Synthesis of Fluoro-organic Compounds, Wiley, New York, 1999.

[8] P.V. Ramachandran, Asymmetric Fluoroorganic Chemistry, ACS Symposium Series 746, Washington, DC, 1999.

[9] D. Seebach, A.K. Beck, P. Renaud, Angew. Chem. 98 (1986) 96–97.

[10] N. Ishikawa, T. Yokozawa, Bull. Chem. Soc. Jpn. 56 (1983) 724–726.

[11] T.S. Everett, S.T. Purrington, C.L. Bumgardner, J. Org. Chem. 49 (1984) 3702–3706.

[12] (a) T. Yokozawa, M. Yamaguchi, T. Nakai, N. Ishikawa, Nippon Kagakukaish (1985) 2202–2204;
(b) T. Yokozawa, T. Nakai, N. Ishikawa, Tetrahedron. Lett. 25 (1984) 3987–3990;
(c) T. Yokozawa, T. Nakai, N. Ishikawa, Tetrahedron. Lett. 25 (1984) 3991–3994.

[13] (a) M. Kuroboshi, T. Ishihara, Bull. Chem. Soc. Jpn. 63 (1990) 1191–1195;
(b) T. Ishihara, M. Kuroboshi, K. Yamaguchi, Chem. Lett. (1990) 211–214;
(c) C.-P. Qian, T. Nakai, Tetrahedron. Lett. 31 (1990) 7043–7046.

[14] T.-P. Loh, X.-R. Li, Tetrahedron Lett. 38 (1997) 869–872.

[15] (a) K. Iseki, N. Nagai, Y. Kobayashi, Tetrahedron Lett. 34 (1993) 2169–2172;
(b) K. Iseki, N. Nagai, Y. Kobayashi, Tetrahedron: Asym. 5 (1994) 961–964;
(c) K. Iseki, D. Asada, M. Takahashi, N. Nagai, Y. Kobayashi, Tetrahedron Lett. 36 (1995) 3711–3714.

[16] K. Iseki, D. Asada, M. Takahashi, N. Nagai, Y. Kobayashi, Tetrahedron Lett. 35 (1994) 7399–7402.

[17] Y. Komatsu, T. Sakamoto, T. Kitazume, J. Org. Chem. 64 (1999) 8369–8374.

[18] T. Sakamoto, T. Takahashi, T. Yamazaki, T. Kitazume, J. Org. Chem. 64 (1999) 9467–9474.

[19] (a) B.H. Lipshutz, S. Sengupta, in: L.A. Paquette (Ed.), Organic Reactions, vol. 41, Wiley, New York, 1992, p. 135;
(b) J. Tsuji, Palladium Reagents and Catalysts, Wiley, New York, 1996.

[20] (a) T. Fuchikami, Y. Shibata, H. Urata, Chem. Lett. (1987) 521;
(b) P.L. Heimze, D.J. Burton, J. Org. Chem. 23 (1988) 2714.