# (*E*)-Selective Horner–Wadsworth–Emmons reaction of aldehydes with *bis*-(2,2,2-trifluoroethyl)phosphonoacetic acid

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**Dedicated to Professor Keiichiro Fukumoto on his 70th birthday**
**(received 29 May 03; accepted 30 June 03; published on the web 14 July 03)**

**Abstract**
The stereoselective Horner–Wadsworth–Emmons reaction of aldehydes with *bis*-(2,2,2-trifluoroethyl)phosphonoacetic acid utilizing *i*-PrMgBr afforded (*E*)-α,β-unsaturated carboxylic acids as the major products. *bis*-(2,2,2-Trifluoroethyl)phosphonoacetic acid was prepared by enzymatic hydrolysis of the corresponding methyl ester with porcine liver esterase.

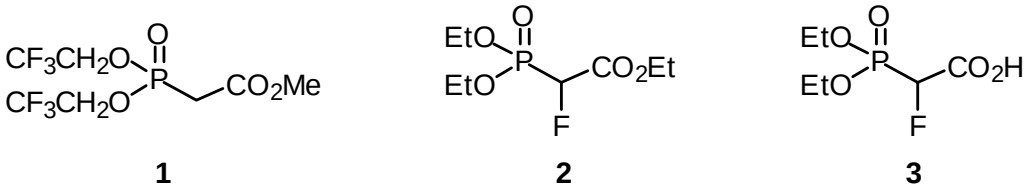
**Keywords:** Horner–Wadsworth–Emmons reaction, olefination, magnesium, α,β-unsaturated carboxylic acid, α,β-unsaturated ester

## Introduction

One of the most powerful methods for the stereoselective preparation of α,β-unsaturated esters is the Horner–Wadsworth–Emmons (HWE) reaction of aldehydes.[1] The HWE reaction of aldehydes with methyl *bis*-(2,2,2-trifluoroethyl)phosphonoacetate (**1**) is a convenient method for the *Z*-selective synthesis of α,β-unsaturated esters.[2] It is also known that ethyl 2-fluoro-2-diethylphosphonoacetate (**2**) is an efficient HWE reagent for bringing about *E*-selective fluoro-olefination.[3] According to the Cahn–Ingold–Prelog (CIP) convention, (*Z*)-α,β-unsaturated esters from phosphonoacetate **1**, and (*E*)-α-fluoro-α,β-unsaturated esters from phosphonoacetate **2** have the same geometric arrangement about their double bonds. Recently, we have reported the Mg(II)-promoted *Z*-selective HWE reaction of aldehydes with 2-fluoro-2-diethylphosphonoacetic acid (**3**) for the stereoselective synthesis of (*Z*)-α-fluoro-α,β-unsaturated esters.[4] That is to say, the *Z*-selectivity of the resulting α-fluoro-α,β-unsaturated carboxylic acids was achieved by utilizing phosphonoacetic acid **3** and *i*-PrMgBr in the HWE reaction of various aldehydes in THF under reflux conditions. In an effort to understand the origin of the stereoselectivities in the HWE reaction, we investigated the HWE reaction of *bis*-(2,2,2-

trifluoroethyl)phosphonoacetic acid (**4**) with various aldehydes **7a**–**d** utilizing *i*-PrMgBr. We now report on phosphonoacetic acid **4** with an *E*-selective HWE reagent for the preparation of α,β-unsaturated esters.

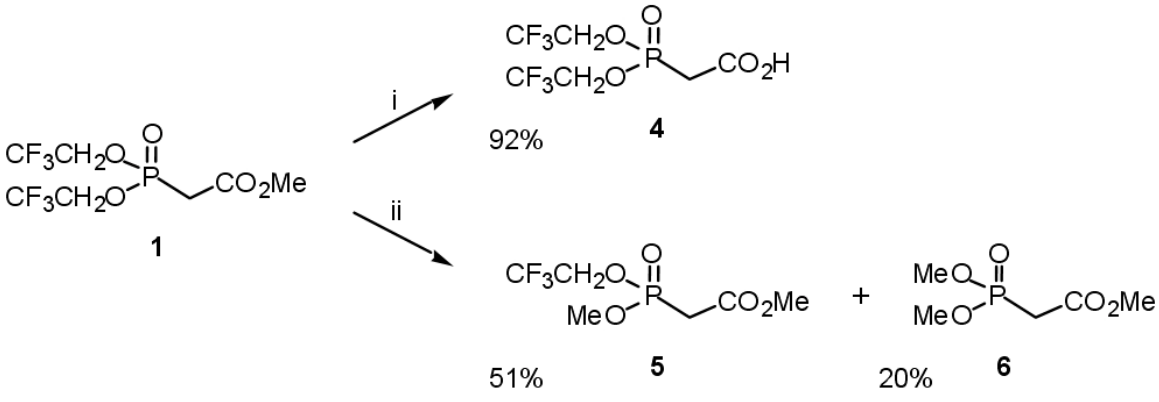



**1** **2** **3**

**Figure 1**

## Results and Discussion

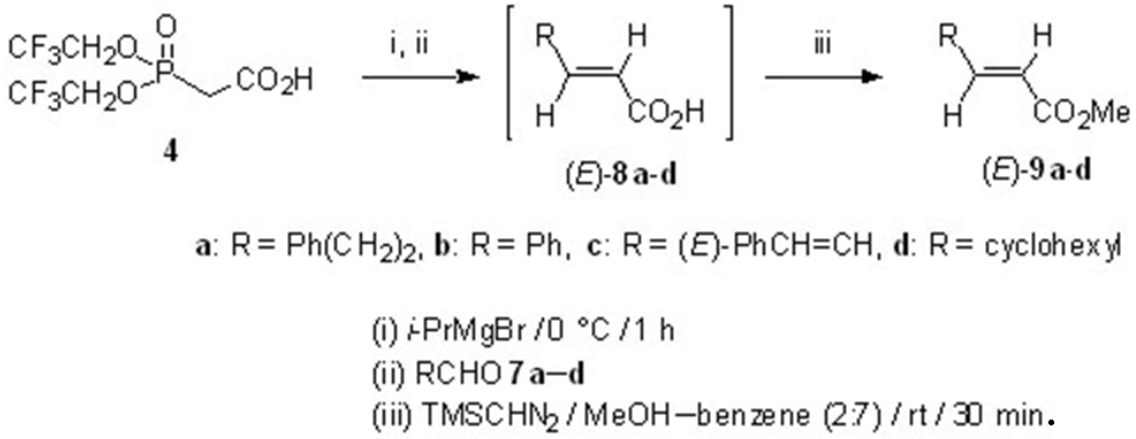
The HWE reagent, *bis*-(2,2,2-trifluoroethyl)phosphonoacetic acid (**4**) was prepared by enzymatic hydrolysis of methyl *bis*-(2,2,2-trifluoroethyl)phosphonoacetate (**1**) with porcine liver esterase (PLE, Sigma; E-2884) in 92% yield, as shown in Scheme 1. Attempts to hydrolyze the phosphonoacetate **1** under aqueous alkaline conditions were unsuccessful, even though methyl methyl-(2,2,2-trifluoroethyl)phosphonoacetate (**5**) and methyl dimethylphosphonoacetate (**6**) were obtained in 51 and 20% yields, respectively. Ghosh *et al*. reported a non-enzymatic procedure for the synthesis of phosphonoacetic acid **4** from 2,2,2-trifluoroethanol, methylphosphonic dichloride, and benzyl chloroformate.[5]




(i) PLE / 0.1 *M*phosphate buffer (pH 7.4 )–acetone (9:1) / rt / 2h .
(ii) 1 *M*NaOH–MeOH (1:1) / 0 °C / 45 min .

**Scheme 1**

The HWE reaction of the substituted phosphonoacetic acid **4** with the aldehydes **7a**–**d** in the presence of *i*-PrMgBr afforded the α,β-unsaturated carboxylic acids **8a**–**d**. Esterification of **8a**–**d** with an excess amount of trimethylsilyldiazomethane ($TMSCHN_2$)[6] provided the desired α,β-unsaturated esters **9a**–**d**, without the isolation of **8a**–**d**, as shown in Scheme 2. All the results of the HWE reactions employing the phosphonoacetic acid **4** are summarized in the following Tables 1 and 2. Under reflux conditions in THF, utilizing *i*-PrMgBr, the reaction of the phosphonoacetic acid **4** with 3-phenylpropionaldehyde (**7a**) proceeded in a *E*-selective manner (*E*:*Z* = 87:13), while under 0 °C conditions, the *E*:*Z* ratio was 77:23 (Table 1, entries 3 and 4). A temperature-dependent improvement of *E*-selectivity up to 95:5 (*E*:*Z*) was found in the reaction of **4** with **7a** under reflux conditions in toluene (Table 1, entry 1). The HWE reactions of **4** with **7a** using *n*-BuLi resulted in low yields (18–52%) (Table 1, entries 5–7). In the HWE reactions of the phosphonoacetate **1** with **7a** employing *i*-PrMgBr (1.25 mol eq) under reflux conditions in toluene, the *E*:*Z* stereoselectivity of the products **9a** was moderate, with a ratio of 78:22, in 77% yield.




**Scheme 2**

In the HWE reaction of the phosphonoacetic acid **4** with aldehydes **7b**–**d**, α,β-unsaturated carboxylic acids **8b**–**d** were obtained in a fairly good diastereomer ratio up to >99:<1 (*E*:*Z*), as shown in Table 2. A lowering of the reaction temperature did not result in lowering of the stereoselectivity in the HWE reactions of **4** with benzaldehyde (**7b**), and the α,β-unsaturated ester (*E*)-**9b** was obtained as a sole product in each reaction (Table 2, entries 1–3). The geometry and the diastereomer ratios of **9a**–**d** were confirmed on the basis of the coupling constants between the olefinic protons, and integration of the appropriate proton absorptions determined by $^1H$ NMR (400 MHz, $CDCl_3$) analysis.

**Table 1.** Horner–Wadsworth–Emmons reactions of phosphonoacetic acid **4** with aldehyde **7a**[a]

| Entry | Base | Solvent | Temperature | Time (h) | Yield of **9a** (%) [b] | *E*-**8a** : *Z*-**8a** [c] |
|---|---|---|---|---|---|---|
| **1** | *i*-PrMgBr | toluene | reflux | 1 | 82 | 95 : 5 |
| **2** | *i*-PrMgBr | dioxane | reflux | 1 | 93 | 90 : 10 |
| **3** | *i*-PrMgBr | THF | reflux | 1 | 96 | 87 : 13 |
| **4** | *i*-PrMgBr | THF | 0 °C | 2.5 | 74 | 77 : 23 |
| **5** | *n*-BuLi | toluene | reflux | 1 | 18 | 91 : 9 |
| **6** | *n*-BuLi | THF | reflux | 1 | 33 | 42 : 58 |
| **7** | *n*-BuLi | THF | 0 °C | 17 | 52 | 41 : 59 |

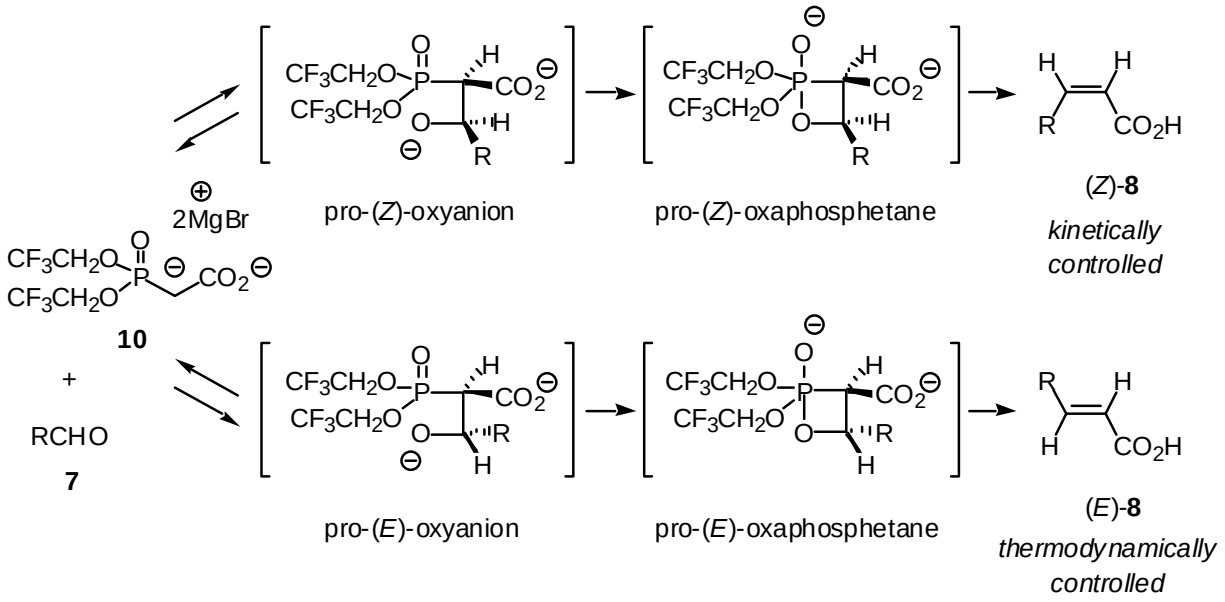
[a] **4** / *i*-PrMgBr or *n*-BuLi / **7a** (1.2:2.5:1 molar ratio). [b] Isolated yields. [c] Determined by $^1$H NMR (400 MHz, $CDCl_3$) analysis.

**Table 2.** Mg(II)-promoted Horner–Wadsworth–Emmons reactions of phosphonoacetic acid **4** with aldehydes **7b**–**d**[a]

| Entry | Aldehyde | Solvent | Temperature | Time (h) | Yield (%) [b] | *E* : *Z* [c] |
|---|---|---|---|---|---|---|
| **1** | **7b** | toluene | reflux | 1 | 61 (**9b**) | >99 : <1 (**8b**) |
| **2** | **7b** | THF | reflux | 1 | 95 (**9b**) | >99 : <1 (**8b**) |
| **3** | **7b** | THF | 0 °C | 4 | 90 (**9b**) | >99 : <1 (**8b**) |
| **4** | **7c** | toluene | reflux | 1 | 58 (**9c**) | 96 : 4 (**8c**) |
| **5** | **7c** | THF | reflux | 1 | 88 (**9c**) | 95 : 5 (**8c**) |
| **6** | **7d** | toluene | reflux | 1 | 72 (**9d**) | 97 : 3 (**8d**) |
| **7** | **7d** | THF | reflux | 1 | 93 (**9d**) | 93 : 7 (**8d**) |

[a] **4** / *i*-PrMgBr / **7** (1.2:2.5:1 molar ratio). [b] Isolated yields. [c] Determined by $^1$H NMR (400 MHz, $CDCl_3$) analysis.

A plausible mechanism for the HWE reactions of phosphonoacetic acid **4** with aldehyde **7** is shown in Scheme 3. On the basis of the experimental results described above, the stereoselective outcome with *E*-selectivity in the Mg(II)-promoted HWE reactions of **4** with **7** can be rationalized in terms of thermodynamic control in a manner similar to that proposed by us in the Mg(II)-promoted HWE reactions of phosphonoacetic acid **3** with **7**.[4a,7] The step involving the nucleophilic addition of dianion **10** to **7** toward the *pro*-(*E*)- or *pro*-(*Z*)-oxyanion must be effectively reversible because of the oxophilicity of Mg(II).[8] Also, a repulsive interaction between the carboxylate anion of **10** and R of **7** may be unfavorable for occupying a pro-(*Z*)-transition state. Consequently, the (*E*)-α,β-unsaturated carboxylic acid (*E*)-**8** was obtained as the thermodynamically controlled major product.




**Scheme 3**

## Conclusions

We were able to demonstrate that (*E*)-α,β-unsaturated esters **9a**–**d** were obtained by the HWE reaction of aldehydes **7a**–**d** with *bis*-(2,2,2-trifluoroethyl)phosphonoacetic acid (**4**), readily prepared by the enzymatic hydrolysis of methyl *bis*-(2,2,2-trifluoroethyl)phosphonoacetate (**1**). In light of the well-known fact that the phosphonoacetate **1** is a powerful HWE reagent for the preparation of (*Z*)-α,β-unsaturated esters, the *E*-selective HWE reaction of aldehydes **7a**–**d** with the substituted phosphonoacetic acid **4** provides significant information on the mechanisms of the HWE reaction.

## Experimental Section

**General Procedures.** All melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were obtained using a JASCO FT/IR-420 IR Fourier transform spectrometer. $^{1}$H-NMR (400 MHz) and $^{13}$C-NMR (75 MHz) spectra were recorded on JEOL JNM-AL400 and JEOL JNM-AL300 spectrometers, respectively. Chemical shifts are given in δ values (ppm) using tetramethylsilane (TMS) as an internal standard. Electron impact (EI)- MS were recorded on a JEOL JMS SX-102A spectrometer. Elemental combustion analyses were performed using a Yanagimoto CHN CORDER MT-5. All reactions were monitored by TLC employing 0.25-mm silica gel plates (Merck 5715; 60 $F_{254}$). Preparative TLC (PTLC) was

performed on 0.5-mm silica gel plates (Merck 5744; 60 $F_{254}$). Column chromatography was carried out on silica gel [Nacalai Tesque 75SL-II-PREP; 70–300 mesh, Kanto Chemical N60 (spherical, neutral); 63–210 μm]. "The usual workup" refers to washing an organic portion with brine, drying over anhydrous $MgSO_4$, filtration, and concentration *in vacuo*. Anhydrous THF, 1,4-dioxane, and toluene were used as purchased from Kanto Chemical. All aldehydes were distilled prior to use. All other reagents were used as purchased.

**Bis-(2,2,2-trifluoroethyl)phosphonoacetic acid (4).** PLE (Sigma; E-2884, 800 units/mmol) was added to a stirred solution of methyl *bis*-(2,2,2-trifluoroethyl)phosphonoacetate (**1**) (228 μL, 1.08 mmol) in 0.1*M* phosphate buffer (pH 7.4)–acetone (9:1) (30 mL) at room temperature. After being stirred at room temperature for 2 h, the reaction mixture was treated with 10% HCl and then extracted with AcOEt (70 mL x5). The extract was subjected to the usual workup to give an oily residue, which was purified by silica gel (Nacalai Tesque 75SL-II-PREP) column chromatography [$CHCl_3$/MeOH (9:1)] to afford **4** (303 mg, 92%) as colorless plates, mp 44.5–46.5 °C ($Et_2O$–*n*-hexane); $^1$H NMR (400 MHz, $CDCl_3$) δ 3.22 (2H, d, $^2J_{H,P}$ = 21.2 Hz), 4.40–4.60 (4H, m), 5.45 (1H, bs); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 33.7 (d, $^1J_{C,P}$ = 144.5 Hz), 63.0 (quart d, $^2J_{C,F}$ = 38.6 Hz, $^2J_{C,P}$ = 5.6 Hz), 122.4 (quart d, $^1J_{C,F}$ = 277.2 Hz, $^3J_{C,P}$ = 8.1 Hz), 167.0 (d, $^2J_{C,P}$ = 4.4 Hz); IR (KBr) 2981, 1730, 1295, 1184, 1075 cm$^{-1}$; EI-MS calcd for $C_6H_7O_5F_6P$ MW 303.9935, found m/e 303.9936 ($M^+$); Anal. calcd for $C_6H_7O_5F_6P$: C, 23.70; H, 2.32. Found: C, 23.75; H, 2.32%.

**Methyl methyl-(2,2,2-trifluoroethyl) phosphonoacetate (5) and methyl dimethylphosphonoacetate (6).** To a solution of methyl *bis*-(2,2,2-trifluoroethyl)phosphonoacetate (**1**) (324 mg, 1.02 mmol) in MeOH (1 mL) was added aqueous 1*M* NaOH (1 mL) at 0 °C. After being stirred at 0 °C for 45 min, the reaction mixture was treated with 5% HCl and then extracted with AcOEt (20 mL x5). The extract was submitted to the usual workup to give an oily residue, which was purified by column chromatography on silica gel (Kanto Chemical N60) [*n*-hexane/AcOEt (1:4) to $CHCl_3$/MeOH (20:1)] to afford **5** (130 mg, 51%) and **6** (36 mg, 20%). **5**; Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 3.07 (2H, d, $^2J_{H,P}$ = 21.5 Hz), 3.77 (3H, s), 3.84 (3H, d, $^3J_{H,P}$ = 11.7 Hz), 4.43 (1H, d quint, $^2J_{H,H}$ = 12.2 Hz, $^3J_{H,F}$ = $^3J_{H,P}$ = 8.3 Hz), 4.51 (1H, d quint, $^2J_{H,H}$ = 12.2 Hz, $^3J_{H,F}$ = $^3J_{H,P}$ = 8.3 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 33.6 (d, $^1J_{C,P}$ = 140.8 Hz), 52.9 (s), 53.1 (d, $^2J_{C,P}$ = 6.9 Hz), 62.9 (qd, $^2J_{C,F}$ = 37.7 Hz, $^2J_{C,P}$ = 5.3 Hz), 122.8 (qd, $^1J_{C,F}$ = 277.4 Hz, $^3J_{C,P}$ = 8.1 Hz), 165.7 (d, $^2J_{C,P}$ = 5.0 Hz); IR (neat) 2964, 1743, 1264, 1174, 1094, 1041 cm$^{-1}$; EI-MS calcd for $C_6H_{10}O_5F_3P$ MW 250.0218, found *m/e* 250.0216 ($M^+$); Anal. calcd for $C_6H_{10}O_5F_3P$: C, 28.81; H, 4.03. Found: C, 28.85; H, 3.98%. **6**;[9] Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 3.00 (2H, d, $^2J_{H,P}$ = 21.7 Hz), 3.76 (3H, s), 3.82 (6H, d, $^3J_{H,P}$ = 11.2 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 33.2 (d, $^1J_{C,P}$ = 135.1 Hz), 52.7 (s), 53.2 (d, $^2J_{C,P}$ = 6.2 Hz), 166.1 (d, $^2J_{C,P}$ = 6.2 Hz).

**Typical procedure for the HWE reaction of *bis*-(2,2,2-trifluoroethyl)phosphonoacetic acid (4) with *i*-PrMgBr**

A 0.76*M* solution of *i*-PrMgBr (1.96 mL, 1.49 mmol) in THF was added to a stirred solution of *bis*-(2,2,2-trifluoroethyl)phosphonoacetic acid (**4**) (218 mg, 0.72 mmol) in anhydrous toluene (10 mL) at 0 °C under argon. The mixture was stirred at 0°C for 1 h and then heated at reflux. 3-Phenylpropionaldehyde (**7a**) (80 μL, 0.60 mmol) was added to the refluxing solution. After being heated at reflux for 1 h, the reaction mixture was treated with 5% HCl and then extracted with AcOEt (70 mL x3). The extract was submitted to the usual workup to afford a crude product **8a** (*E*:*Z* = 95:5). To the solution of **8a** in MeOH (2 mL) and benzene (7 mL) was added an excess amount of $TMSCHN_2$ (2.0*M* solution in *n*-hexane, *ca*. 1 mL, *ca*. 2 mmol). After being stirred at room temperature for 30 min, the reaction mixture was evaporated *in vacuo* to afford a crude product, which was purified by chromatography on a silica gel (Kanto Chemical N60) column [*n*-hexane/AcOEt/acetone (50:2:1)] to afford (*E*)-**9a** (89 mg, 78%) and (*Z*)-**9a** (4.7 mg, 4%) as colorless oils.

**Methyl (*E*)-5-phenyl-2-pentenoate [(*E*)-9a].**[2b,10] Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 2.48–2.57 (2H, m), 2.77 (2H, t, *J* = 7.7 Hz), 3.72 (3H, s), 5.85 (1H, td, *J* = 1.5, 15.6 Hz), 7.01 (1H, td, *J* = 6.8, 15.6 Hz), 7.16–7.24 (3H, m), 7.24–7.32 (2H, m); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 33.9, 34.3, 51.4, 121.4, 126.2, 128.3, 128.5, 140.7, 148.4, 167.0.

**Methyl (*Z*)-5-phenyl-2-pentenoate [(*Z*)-9a].**[2b,10] Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 2.77 (2H, t, *J* = 7.6 Hz), 2.96–3.03 (2H, m), 3.70 (3H, s), 5.79 (1H, td, *J* = 1.5, 11.5 Hz), 6.25 (1H, td, *J* = 7.4, 11.5 Hz), 7.16–7.32 (5H, m); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 30.5, 35.0, 51.1, 119.9, 126.0, 128.4, 128.5, 141.1, 149.4, 166.7.

**Methyl (*E*)-3-phenyl-2-propenoate [(*E*)-9b].**[2b,11] Colorless plates (*n*-hexane), mp 32.5–33 °C (lit.[10a] 34–34.5 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 3.81 (3H, s), 6.44 (1H, d, *J* = 16.0 Hz), 7.36–7.42 (3H, m), 7.50–7.56 (2H, m), 7.70 (1H, d, *J* = 16.0 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 51.7, 117.8, 128.1, 128.9 130.3, 134.4, 144.9, 167.4.

**Methyl (2*E*,4*E*)-5-phenyl-2,4-pentadienoate [(*E*)-9c].**[12] White powder ($Et_2O$–*n*-hexane), mp 71 °C (lit.[11b] 68–70 °C); $^1$H NMR (400 MHz, $CDCl_3$) δ 3.78 (3H, s), 6.00 (1H, d, *J* = 15.4 Hz), 6.83–6.95 (2H, m), 7.28–7.40 (3H, m), 7.42–7.50 (3H, m); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 51.6, 120.8, 126.2, 127.2, 128.8, 129.1, 136.0, 140.5, 144.8, 167.5.

**Methyl (2*Z*,4*E*)-5-phenyl-2,4-pentadienoate [(*Z*)-9c].**[12a] Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 3.77 (3H, s), 5.74 (1H, d, *J* = 11.0 Hz), 6.71–6.80 (1H, m), 6.83 (1H, d, *J* = 15.6 Hz), 7.27–7.39 (3H, m), 7.50–7.56 (2H, m), 8.14 (1H, dd, *J* = 11.5, 15.6 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 51.2, 116.9, 124.8, 127.5, 128.7, 129.0, 136.3, 141.4, 145.0, 167.0.

**Methyl (*E*)-3-cyclohexyl-2-propenoate [(*E*)-9d].**[13a,b] Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 1.07–1.38 (5H, m), 1.62–1.82 (5H, m), 2.08–2.20 (1H, m), 3.73 (3H, s), 5.77 (1H, dd, *J* = 1.3, 15.9 Hz), 6.92 (1H, dd, *J* = 6.8, 15.9 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 25.7, 25.9, 31.7, 40.4, 51.4, 118.5, 154.7, 167.6.

**Methyl (*Z*)-3-cyclohexyl-2-propenoate [(*Z*)-9d].**[13c] Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 1.02–1.42 (5H, m), 1.65–1.76 (5H, m), 3.24–3.36 (1H, m), 3.70 (3H, s), 5.67 (1H, *J* = 11.4

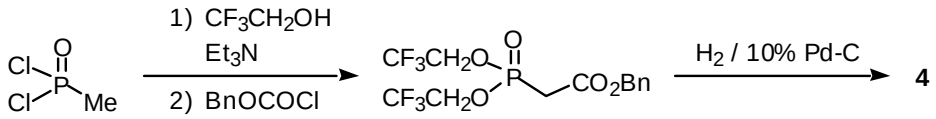
Hz), 6.04 (1H, dd, *J* = 10.1, 11.4 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 25.5, 25.9, 32.3, 37.3, 51.0, 117.1, 156.1, 166.8.

## Acknowledgments

This work was partially supported by a Grant-in-Aid for Scientific Research (C) from the Japan Society for the Promotion of Science.

## References

1. (a) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863. (b) Rein, T.; Reiser, O. *Acta Chem. Scand.* **1996**, *50*, 369. (c) Sano, S. *Yakugaku Zasshi* **2000**, *120*, 432. (d) Rein, T.; Pedersen, T. M. *Synthesis* **2002**, 579.
2. (a) Still, W. C.; Gennari, C. *Tetrahedron Lett.* **1983**, *24*, 4405. (b) Sano, S.; Yokoyama, K.; Fukushima, M.; Yagi, T., Nagao, Y. *Chem. Commun.* **1997**, 559. (c) Sano, S.; Takehisa, T.; Ogawa, S.; Yokoyama, K.; Nagao, Y. *Chem. Pharm. Bull.* **2002**, *50*, 1300.
3. (a) Machleidt, H.; Wessendorf, R. *Liebigs Ann. Chem.* **1996**, *674*, 1. (b) Burton, D. J.; Yang, Z. -Y.; Qin, W. *Chem. Rev.* **1996**, *96*, 1641. (c) Sano, S.; Ando, T.; Yokoyama, K.; Nagao, Y. *Synlett* **1989**, 777. (d) Sano, S.; Yokoyama, K.; Shiro, M.; Nagao, Y. *Chem. Pharm. Bull.* **2002**, *50*, 706.
4. (a) Sano, S.; Teranishi, R.; Nagao, Y. *Tetrahedron Lett.* **2002**, *43*, 9183. (b) Sano, S.; Saito, K.; Nagao, Y. *Tetrahedron Lett.* **2003**, *44*, 3987.
5. Supporting information available, see: Ghosh, A. K. *J. Org. Chem.* **2001**, *66*, 8973.




6. Shioiri, T.; Aoyama, T. *J. Synth. Org. Chem. Jpn.* **1986**, *44*, 149.
7. Shen, Y.; Wang, G.; Sun, J. *J. Chem. Soc., Perkin Trans. 1* **2001**, 519.
8. (a) Sano, S.; Kobayashi, Y.; Kondo, T.; Takebayashi, M.; Maruyama, S.; Fujita, T.; Nagao, Y. *Tetrahedron Lett.* **1995**, *36*, 2097. (b) Sano, S.; Liu, X-K.; Takebayashi, M.; Kobayashi, Y.; Tabata, K.; Shiro, M.; Nagao, Y. *Tetrahedron Lett.* **1995**, *36*, 4101. (c) Hayashi K.; Kogiso, H.; Sano, S.; Nagao, Y. *Synlett* **1996**, 1203. (d) Sano, S.; Miwa, T.; Liu, X.-K.; Ishii T.; Takehisa, T.; Shiro, M.; Nagao, Y. *Tetrahedron: Asymmetry* **1998**, *9*, 3615. (e) Sano, S.; Ishii, T.; Miwa, T.; Nagao, Y. *Tetrahedron Lett.* **1999**, *40*, 3013. (f) Sano, S.; Nagao, Y. *J. Synth. Org. Chem. Jpn.* **2000**, *58*, 756.
9. Fieser, M.; Fieser, L. In *Reagents for Organic Synthesis*; John Wiley Sons: New York, 1969; Vol. 2, p 442.
10. Hon, Y.-S.; Lee, C.-F. *Tetrahedron* **2000**, *56*, 7893.

11. (a) Kunishima, M.; Kawachi, C.; Morita, J.; Terao, K.; Iwasaki, F.; Tani, S. *Tetrahedron* **1999**, *56*, 13159. (b) Keck, G. E.; McLaws, M. D.; Wager, T. T. *Tetrahedron* **2000**, *56*, 9875.
12. (a) Nakamura, S.; Hayakawa, T.; Nishi, T.; Watanabe, Y.; Toru, T. *Tetrahedron* **2001**, *57*, 6703. (b) O'Donnell, M. E.; Sanvoisin, J.; Gani, D. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1696.
13. (a) Huang, Y.-Z.: Shi, L.-L.; Li, S.-W.; Wen, X.-Q. *J. Chem. Soc., Perkin Trans. 1* **1989**, 2397. (b) Zhou, Z.-L.; Huang, Y.-Z.; Shi, L.-L. *Tetrahedron* **1993**, *49*, 6821. (c) Ando, K. *J. Org. Chem.* **1999**, *64*, 8406.