Stereocontrol in radical-mediated allylation of acyclic α-bromo-β-siloxy esters by complexation with lanthanide shift reagents Ln(fod)$_3$[1]

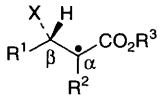
Hajime Nagano,* Yukie Kuno, Yuriko Omori and Mayumi Iguchi

Department of Chemistry, Faculty of Science, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112, Japan

Stereoselectivity in the radical-mediated allylation of α-bromo-β-siloxy esters 2 yielding α-allyl-β-siloxy esters 3 (*syn*) and 4 (*anti*) was remarkably affected when the reaction was conducted in the presence of Ln(fod)$_3$ [= tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato)lanthanide]. In the allylation of α-bromo-β-siloxysuccinate esters 2c and 2d affording preferentially *syn*-diastereoisomers 3c and 3d through chelated transition states a stoichiometric amount of the Lewis acid [Eu(fod)$_3$ or La(fod)$_3$] was required in order to maximize the stereoselectivities, whereas in the reaction of α-bromo-β-siloxybutanoate esters 2g and 2h and α-bromo-β-siloxy-β-phenylpropanoate ester 2i the effect induced by the coordination of Eu(fod)$_3$ to the ester group was catalytic.

Introduction

A current interest in radical chemistry is the control of acyclic stereochemistry. In particular, attention has focused on chirality transfer using a stereogenic centre adjacent to the radical carbon atom (1,2-stereoinduction),[2] and, recently, stereoselective trapping of radicals **1** bearing a carbonyl group

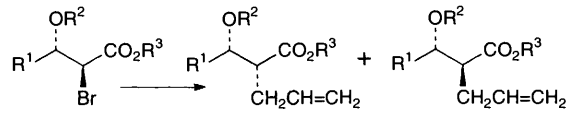


1

and a stereogenic centre has been demonstrated by Hart,[3] Guindon,[4,5f] Giese,[5] Curran,[6] and others.[7] However, little is known about controlling the stereochemistry by complexation of radical intermediates (whether cyclic or acyclic) with Lewis acids,[3c,4c,8] except for the case of α-sulfinyl radicals (strong Lewis bases) showing promise for stereocontrol.[9] We now report that the stereoselectivity in the radical-mediated allylation of α-bromo-β-siloxy esters **2** yielding α-allyl-β-siloxy esters **3** and **4** was significantly affected when the reaction was conducted in the presence of Ln(fod)$_3$ [= tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato)lanthanide] (Scheme 1).

Results and discussion

Bromides **2c–2e** were prepared by standard silylation of hydroxy diester **2a**, which was derived from diethyl (2*R*,3*R*)-tartrate *via* acetate **2b**.[10] Bromide **2f** was prepared similarly from diisopropyl (2*R*,3*R*)-tartrate. Bromides **2i** and **2j** were obtained by standard silylation of the corresponding known alcohols.[6c] Authentic products **4b–4d** were prepared by allylation of the dianion of diethyl malate,[11] and subsequent standard acetylation or silylation. The 3-H doublet signals of compounds **3b–3d** in their ^{1}H NMR spectra were observed consistently at lower field than those of **4b–4d**, and the stereochemistry of compounds **3e**, **4e**, **3f** and **4f** was assigned based on the chemical shifts of their 3-H signals (**3e**: 4.54; **4e**: 4.44; **3f**: 4.47; **4f**: 4.29). Allylation of **2g** and **2h** has already been reported.[6c] The stereochemistry of the ethyl esters **3j** and **4j** was assigned by comparison of their ^{1}H NMR spectral data with



2 **3** (*syn*) **4** (*anti*)

a; R^1 = CO_2Et, R^2 = H, R^3 = Et
b; R^1 = CO_2Et, R^2 = Ac, R^3 = Et
c; R^1 = CO_2Et, R^2 = $SiMe_3$, R^3 = Et
d; R^1 = CO_2Et, R^2 = $SiMe_2Bu^t$, R^3 = Et
e; R^1 = CO_2Et, R^2 = $SiPh_2Bu^t$, R^3 = Et
f; R^1 = CO_2Pr^i, R^2 = $SiMe_2Bu^t$, R^3 = Pr^i
g; R^1 = Me, R^2 = $SiMe_2Bu^t$, R^3 = Et
h; R^1 = Me, R^2 = $SiPh_2Bu^t$, R^3 = Et
i; R^1 = Ph, R^2 = $SiMe_2Bu^t$, R^3 = Me
j; R^1 = Ph, R^2 = $SiMe_2Bu^t$, R^3 = Et

Scheme 1 Radical-mediated allylation of bromides **2** with CH_2=CH-CH_2SnBu_3. The *syn-anti* designation indicates here the relative configuration of substituents OR^2 and CH_2CH=CH_2 (main chain R^{1}CHCHCO$_2$R^3). *Reagents and conditions:* CH_2=$CHCH_2SnBu_3$, AIBN, Ln(fod)$_3$, *hv*.

those of the methyl esters **3i** and **4i**, which were desilylated to the corresponding known alcohols.[3c]

Diastereoisomeric ratios of the inseparable mixtures of compounds **3** and **4** were determined by integration of resonances in ^{1}H NMR or ^{13}C NMR spectra (see Experimental section).[12]

Allylation of bromides **2** was conducted with 2 mol equiv. of allyltributyltin and a catalytic amount of azoisobutyronitrile (AIBN) in CH_2Cl_2 (0.07–0.08 mol dm^{-3}) under irradiation with a 100 W tungsten-filament lamp or 400 W Xe lamp in the presence (or absence) of Ln(fod)$_3$.† A summary of the allylation results is given in Table 1.

Allylation of bromides **2a–2j** showed modest to poor stereoselectivities in the absence of Lewis acid (entries 1, 3, 5, 8, 19, 25, 27 and 30). Addition of 1.1 mol equiv. of Eu(fod)$_3$ reversed the stereoselectivity in the reaction of compound **2a**,

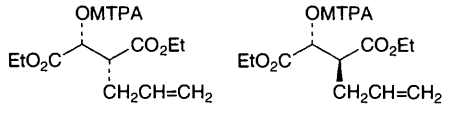
† Reactions under irradiation with a Xe lamp were more reproducible than those under irradiation with a tungsten-filament lamp, especially in the case of bromides **2g–2j**.

Table 1 Radical-mediated allylation of bromides **2** with CH_2=$CHCH_2SnBu_3$ in CH_2Cl_2 [a] (Scheme 1 applies)

Entry	Bromide **2**	$Ln(fod)_3$ (mol equiv.)	Temp. (θ/°C)	Yield of stereoisomers **3** and **4** (%) [b]	Ratio **3**:**4**
1	**a**		reflux	85	1:1.9
2	**a**	$Eu(fod)_3$ (1.1)	reflux	63	1.7:1
3	**b**		reflux	56	1.8:1
4	**b**	$Eu(fod)_3$ (1.1)	reflux	72	3.4:1
5	**c**		reflux	63	1.3:1
6	**c**	$Eu(fod)_3$ (0.1)	reflux	45	3.0:1
7	**c**	$Eu(fod)_3$ (1.1)	reflux	62	8.6:1
8	**d**		reflux	57	1.1:1
9	**d**	$Eu(fod)_3$ (0.1)	reflux	81	2.7:1
10	**d**	$Eu(fod)_3$ (0.1)	32	73	4.9:1
11	**d**	$Eu(fod)_3$ (0.3)	reflux	61	4.1:1
12	**d**	$Eu(fod)_3$ (1.1)	reflux	67	5.7:1
13	**d**	$La(fod)_3$ (0.1)	32	63	5.4:1
14	**d**	$La(fod)_3$ (0.1)	3	68	8.6:1
15	**d**	$La(fod)_3$ (0.1)	−10	71	4.3:1
16	**d**	$La(fod)_3$ (1.1)	3	63	10.9:1
17	**e**	$Eu(fod)_3$ (1.1)	reflux	66	1.5:1
18	**f**	$Eu(fod)_3$ (1.1)	reflux	77	1.7:1
19	**g**		32	94	1:2.2 [c]
20	**g**	$Eu(fod)_3$ (0.1)	32	91	1:4.0
21	**g**	$Eu(fod)_3$ (1.1)	32	81	1:4.1
22	**g**	$Pr(fod)_3$ (0.1)	32	58	1:3.3
23	**g**	$La(fod)_3$ (0.1)	32	67	1:3.4
24	**g**	$La(fod)_3$ (0.5)	32	62	1:3.4
25	**h**		reflux	66	1:1.2 [c]
26	**h**	$Eu(fod)_3$ (0.1)	32	94	1:1.7
27	**i**		32	100	3.4:1
28	**i**	$Eu(fod)_3$ (0.1)	32	88	4.0:1
29	**i**	$Eu(fod)_3$ (1.1)	32	77	4.0:1
30	**j**		32	100	3.0:1
31	**j**	$Eu(fod)_3$ (0.1)	32	91	4.1:1
32	**j**	$Eu(fod)_3$ (1.1)	32	94	4.8:1

[a] Allylation of bromides **2** was conducted with 2 mol equiv. of allyltributyltin and a catalytic amount of AIBN in CH_2Cl_2 (0.07–0.08 mol dm^{-3}) under irradiation from a 100 W tungsten-filament lamp (entries 1–9, 11, 12, 17, 18 and 25) or 400 W Xe lamp (entries 10, 13–16, 19–24 and 26–32) in the presence (or absence) of $Ln(fod)_3$. [b] Isolated yield. [c] See ref. 6*c*. **3g**:**4g** = 1:1.5 and **3h**:**4h** = 1:1 (at 80 °C).

but the stereoselectivity enhancement induced by complexation was not large (entry 2). In the case of substrates **2b**, **2c** and **2d** the addition of $Eu(fod)_3$ (1.1 mol equiv.) led to high stereoselectivity enhancement (entries 4, 7 and 12). Racemization of compounds **3d** and **4d** was not observed after HPLC analysis of the (*R*)-MTPA ["α-methoxy-α-(trifluoromethyl)-phenylacetate"] esters (**3k** and **4k**) and (*S*)-MTPA esters (**3l** and **4l**) derived from silyl ethers **3d** and **4d**.[13] The stereoselectivity induced by the coordination of the ester groups to $Eu(fod)_3$ in the reaction of bromides **2c** and **2d** decreased as the molar ratio of $Eu(fod)_3$ was decreased (entries 6, 9 and 11), but further improvement of stereoselectivity was not attained even in the presence of 2.0 mol equiv. of $Eu(fod)_3$. The reaction may proceed through the 1:1 complex [**2**•$Ln(fod)_3$] rather than the 1:2 complex [**2**•2$Ln(fod)_3$] in spite of the presence of two ester groups in bromides **2**. The diastereoisomer ratio depended on the irradiation conditions when a catalytic amount of $Eu(fod)_3$ was used (entries 9 and 10), whereas in the presence of 1.1 mol equiv. of the Lewis acid the ratio was not influenced (entry 12). Allylation of bromides **2e** and **2f** showed poor stereoselectivity in the presence of $Eu(fod)_3$ (entries 17 and 18).



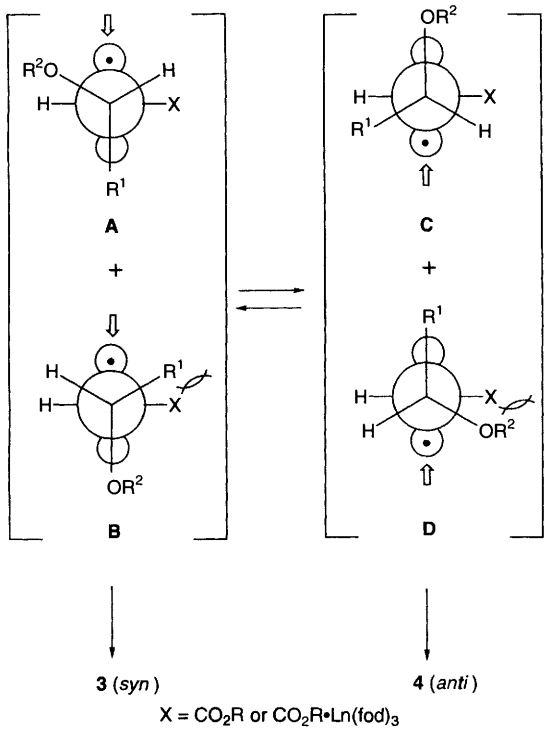
3k, **3l** **4k**, **4l**

k = (*R*)-MTPA esters
l = (*S*)-MTPA esters

The weaker Lewis acid $Eu(tfc)_3$ {= tris-[3-(trifluoromethylhydroxymethylene)-(−)-camphorato]europium} was less effective (**3d**:**4d** = 2.2:1). $Pr(thd)_3$ [= tris-(2,2,6,6-tetramethylheptane-3,5-dionato)praseodymium] and $Yb(thd)_3$ had no effect on the stereoselectivity in the reaction of bromide **2d**. Although Renaud and Curran have recently reported the efficient stereocontrol in the radical-mediated allylation by complexation of $Eu(thd)_3$ with a sulfinyl group (strong Lewis base),[9b,9e] weaker Lewis bases **2c** and **2d** required stronger Lewis acids such as $Ln(fod)_3$ to achieve effective stereocontrol.

The diastereoisomer ratios **3d**:**4d** in the allylation of bromide **2d** performed in the presence of 1.1 mol equiv. of $Ln(fod)_3$ under irradiation with a 100 W tungsten-filament lamp decreased in the order of $Pr(fod)_3$ (6.3:1; 56% yield), $Eu(fod)_3$ (5.7:1; 67%), $Gd(fod)_3$ (4.2:1; 81%), $Dy(fod)_3$ (3.4:1; 84%), $Er(fod)_3$ (2.2:1; 77%) and $Ho(fod)_3$ (2.1:1; 96%). This result shows that the selectivity depends on the formation constants which decrease from large, lighter Ln^{3+} to small, heavier Ln^{3+}.[14] In fact, $La(fod)_3$, possessing the largest metal ion radius of the lanthanide elements, was highly efficient and improved the *syn* diastereoselectivity to 5.4:1 in the presence of 0.1 mol equiv. of the Lewis acid (entry 13; *cf.* entry 10). Furthermore, the diastereoisomer ratio **3d**:**4d** increased to 10.9:1 and 8.6:1 when the reaction was conducted at 3 °C in the presence of 1.1 and 0.1 mol equiv. of $La(fod)_3$, respectively (entries 14 and 16; in the absence of the Lewis acid the ratio **3d**:**4d** was 1.2:1 at 3 °C). However, the stereoselectivity was lower when the reaction was conducted at −10 °C (entry 15).

The stereocontrol observed in the reaction of compounds **2c** and **2d** is referred to the coordination of the ester groups

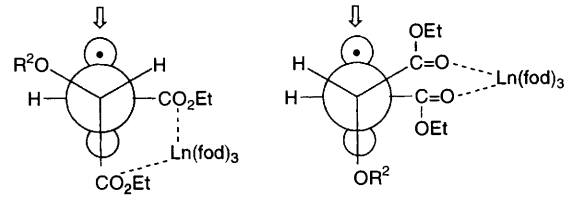


Scheme 2 Transition-state models **A**–**D**. Large arrow ⇩ shows the approach of allyltributyltin.

C^{α}–CO_2Et and/or C^{β}–CO_2Et to $Ln(fod)_3$. To reveal the participation of the C^{α}–CO_2Et moiety in the stereocontrol, allylation of bromides **2g**–**2j** possessing an ester group adjacent to the radical centre was carried out. Very interestingly, in the case of compounds **2g**–**2i** the effect of $Ln(fod)_3$ was catalytic (entries 20–24, 26, 28 and 29). $Pr(fod)_3$ and $La(fod)_3$ were slightly less effective than $Eu(fod)_3$ (entries 20, 22 and 23), in contrast to the allylation of compounds **2c** and **2d**. These results show that in the reactions of bromides **2c** and **2d** coordination of the two ester groups, C^{α}–CO_2Et and C^{β}–CO_2Et, to $Ln(fod)_3$ contributes to the stereocontrol and that 1 mol equiv. of $Ln(fod)_3$ is required to maximize the stereoselectivity.

Steric and electronic effects governing stereoselectivity of intermolecular radical reactions of acyclic systems are fairly well understood.[2] Reduction of compounds **2g** and **2h** with Bu_3SnD, affording preferentially the *anti* diastereoisomers, has been reported to proceed through transition-state model **C** (X = CO_2Et, R^1 = Me, R^2 = $SiMe_2Bu^t$ or $SiPh_2Bu^t$) rather than model **A**. In model **C** both the $\Delta^{1,3}$ allylic strain and the dipole–dipole interaction due to the polar groups, CO_2Et and OR^2, are minimized (Scheme 2). In the allylation of compounds **2g** and **2h** with the large reagent allyltributyltin, however, high-energy transition-state models **B** and **D** (X = CO_2Et, R^1 = Me, R^2 = $SiMe_2Bu^t$ or $SiPh_2Bu^t$) also participate. Decreasing the stereoselectivity in allylation by increasing the size of the silyl groups (entries 19 and 25) is opposite to the stereocontrol in reduction with the small reagent Bu_3SnD.[6c] As the size of the silyl group increases, transition-state model **D**, where large steric repulsion between CO_2Et and the siloxy group exists, rises in energy. In the case of compound **2g** coordinated to $Ln(fod)_3$,‡ the transition-state models **B** and **D** (X = CO_2Et•$Ln(fod)_3$, R^1 = Me, R^2 = $SiMe_2Bu^t$) must be disfavoured because of the large $\Delta^{1,3}$ allylic strains between the bulky CO_2Et•$Ln(fod)_3$ group and Me and between CO_2Et•$Ln(fod)_3$ and $OSiMe_2Bu^t$. Approach of the large reagent allyltributyltin between H and $OSiMe_2Bu^t$ in model **A** is probably prohibited. Allylation would consequently proceed through the complexed transition-state model **C** (X = CO_2Et•$Ln(fod)_3$, R^1 = Me, R^2 = $SiMe_2Bu^t$) to afford compound **4g** (entry 20).§

Allylation of compounds **2i** and **2j** may proceed preferentially through the transition-state models **A** and **B** [R^1 = Ph; R^2 = $OSiMe_2Bu^t$, X = CO_2Me or CO_2Et] to yield *syn* products **3i** and **3j**, respectively. Poor stereoselectivity enhancement induced by coordination of $Eu(fod)_3$ is referred to the diminution of conformer **B** because of large steric repulsion between Ph and CO_2Et•$Eu(fod)_3$.[4b] Association-dissociation of $Ln(fod)_3$ probably is faster than the allylation reaction and therefore the reaction is catalytic. Allyltributyltin is nucleophilic in character, and an increase of reactivity by complexation is expected. However, although a catalytic amount of $Eu(fod)_3$ did not affect the reaction rate, as the amount of the Lewis acid was increased the reactivity decreased and the reaction was about 5 times slower when 1.1 mol equiv. of $Eu(fod)_3$ was used (*vide infra*).



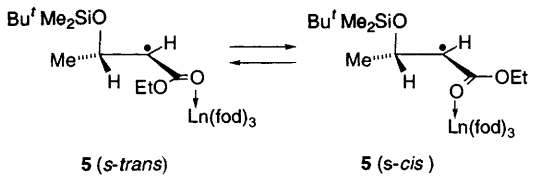
Allylations of bromides **2c**–**2e** in the presence of 1 mol equiv. of $Ln(fod)_3$ may proceed through the chelated transition-state model **E** to afford compounds **3c**–**3e** as the major products. The stereoselectivity decreased as the bulk of silyl groups was increased (entries 7, 12 and 17). This excludes the alternative transition-state model **F**,[4c] since the stereoselectivity in the reaction proceeding through **F** is independent of the size of R^2. To avoid $\Delta^{1,3}$ allylic strain and the electrostatic repulsion between the polar ester groups, the seven-membered chelated radical intermediate would adopt conformation **E** rather than **F**.¶

The lower stereoselectivity in the reaction of bromide **2d** conducted at −10 °C (entry 15) compared with that at 3 °C (entry 14) shows that the association–dissociation of $La(fod)_3$ is probably slower at −10 °C and the proportion of the allylation proceeding through the complexed intermediates may be diminished. Apparent acceleration of the allylation reaction of bromide **2d** by chelate formation was observed when the reaction was conducted at 3 °C in the presence of 1.1 mol equiv. of $La(fod)_3$ (*vide supra*). The reaction proceeded faster (~twice) than that performed without the Lewis acid.

In the reaction of bromide **2f** the bulky isopropyl groups may prevent the coordination of $Eu(fod)_3$, and consequently

‡ Coordination to the *tert*-butyldimethylsiloxy group is not included because lanthanide-induced shift of the bis-*tert*-butyldimethylsilyl ether of decane-1,10-diol was not observed when the ^1H NMR spectrum of a mixture of ethyl acetate and the bissilyl ether was measured in the presence of $Eu(fod)_3$.

§ In these transition-state models **A**–**D**, stereoisomers **5** (*s-trans*) and **5** (*s-cis*) and the coordination geometry of $Ln(fod)_3$ are not taken into account.[6c]



¶ Transition-state model **E** resembles model **A** and a rapid equilibrium between transition-state models **A** [R^1 = CO_2Et•$Ln(fod)_3$, X = CO_2Et and R^1 = CO_2Et, X = CO_2Et•$Ln(fod)_3$] cannot be neglected.

only slight stereoselectivity enhancement was observed (entry 18; in the absence of the Lewis acid, **3f**:**4f** = 1:1.1). The low efficiency observed in the reactions of substrates **2a** and **2b** may be referred to the chelation of $Eu(fod)_3$ with the OH or OAc group as well as with the ester groups (entries 2 and 4).

In conclusion we have demonstrated that the diastereoselectivity in the radical-mediated allylations of bromides **2** was highly affected by the complexation with the lanthanide shift reagents $Ln(fod)_3$. The chelation-controlled allylation of bromides **2c** and **2d** performed in the presence of $Eu(fod)_3$ or $La(fod)_3$ gave the *syn* isomers **3c** and **3d**, respectively, with high diastereoselectivity. Chelation-controlled allylation of the dianion derived from diethyl malate gives *anti*-isomer **4a** with extremely high stereoselectivity,[11] and alkylation of diethyl 2,3-epoxysuccinate derived from optically active diethyl tartrate gives diethyl *anti*-3-alkyl-2-hydroxysuccinates.[10] This work and ours are complementary.

Experimental

Mps were determined on a Yanaco micro melting point apparatus and are uncorrected. IR spectra were taken on a JASCO A-3 spectrometer. ^1H NMR spectra were recorded on a JEOL GX-270 or GSX-270 spectrometer operating at 270 MHz with [^2H]chloroform (unless otherwise stated) as solvent and tetramethylsilane as internal standard. *J* Values are given in Hz. ^{13}C NMR spectra were recorded on the instruments operating at 67.8 MHz with [^2H]chloroform as solvent and internal standard (δ_C 77.05). Mass spectra were obtained on a JEOL DX-300 mass spectrometer using the electron-impact mode (70 eV). Accurate mass measurements were recorded on the same mass spectrometer. HPLC was carried out with a JASCO TRIROTAR-IV apparatus using UV detector UVIDEC-100-VI. Dichloromethane was dried by distillation from calcium hydride. $La(fod)_3$ was prepared from lanthanum nitrate hexahydrate and 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dione following the reported procedures.[15] Other lanthanide shift reagents were purchased from Aldrich. Silica gel (Wakogel C-300) was used for flash column chromatography. Elimination of $Ln(fod)_3$ was carried out with Merck aluminium oxide 90 active neutral (activity I).

Diethyl (2*S*,3*S*)-2-bromo-3-(trimethylsiloxy)succinate 2c

To a solution of diethyl (2*S*,3*S*)-2-bromo-3-hydroxysuccinate **2a**[10] (206 mg, 0.77 mmol) in dry tetrahydrofuran (THF) (12 cm^3) were added triethylamine (0.5 cm^3, 3.6 mmol) and trimethylsilyl chloride (0.15 cm^3, 1.2 mmol) and the mixture was stirred overnight at room temperature. After dilution with hexane the mixture was washed successively with saturated aq. sodium hydrogen carbonate and saturated brine, and dried over anhydrous sodium sulfate. Evaporation off of the solvent gave an oil, which was purified by flash column chromatography (hexane–ethyl acetate, 10:1) to give title compound **2c** (154 mg, 59%) as a pale yellow oil; ν_{max}(film)/cm^{-1} 1748, 1300, 1255, 1155, 1097, 1025, 980 and 950; δ_H 4.58 (1 H, d, *J* 8.3, 2- or 3-H), 4.46 (1 H, d, *J* 8.3, 3- or 2-H), 4.25 (4 H, m, 2 × CO_2CH_2Me), 1.32 (3 H, t, *J* 7.1, $CO_2CH_2CH_3$), 1.30 (3 H, t, *J* 7.1, $CO_2CH_2CH_3$) and 0.14 (9 H, s, $SiMe_3$); δ_C 169.5, 167.4, 74.1, 62.3, 61.7, 44.6, 14.1, 14.0 and −0.3; *m*/*z* 327 (M^+ − Me, 8%), 325 (M^+ − Me, 8), 269 (18), 267 (14), 197 (45), 75 (100) and 73 (89) [Found (HRMS): *m*/*z*, 325.0124. $C_{10}H_{18}BrO_5Si$ requires (M^+ − Me), 325.0107].

Diethyl (2*S*,3*S*)-2-bromo-3-(*tert*-butyldimethylsiloxy)succinate 2d

To a solution of diethyl (2*S*,3*S*)-2-bromo-3-hydroxysuccinate **2a** (501 mg, 1.86 mmol) in dry dimethylformamide (DMF) (2 cm^3) cooled to 0 °C were added imidazole (456 mg, 6.69 mmol) and *tert*-butyldimethylsilyl chloride (364 mg, 2.42 mmol). The mixture was stirred at room temperature for 3 h and then extracted with pentane. The pentane extract was washed with water and dried over anhydrous sodium sulfate. The crude oily product was purified by flash column chromatography (hexane–ethyl acetate, 10:1) to give compound **2d** (608 mg, 85%) as an oil; ν_{max}(film)/cm^{-1} 1749, 1260, 1155, 1103, 1025, 840 and 780; δ_H 4.57 (1 H, d, *J* 8.3, 2- or 3-H), 4.45 (1 H, d, *J* 8.5, 3- or 2-H), 4.23 (4 H, m, 2 × CO_2CH_2Me), 1.30 (3 H, t, *J* 7.1, $CO_2CH_2CH_3$), 1.28 (3 H, t, *J* 7.1, $CO_2CH_2CH_3$), 0.84 (9 H, s, $SiCMe_3$) and 0.08 (6 H, s, $SiMe_2$); δ_C 169.5, 167.3, 74.5, 62.3, 61.5, 44.9, 25.5, 18.1, 14.1, 13.9, −5.1 and −5.4; *m*/*z* 369 (M^+ − Me, 0.8%), 367 (M^+ − Me, 1), 327 (M^+ − C_4H_9, 31), 325 (M^+ − C_4H_9, 31), 181 (30), 179 (30), 75 (100) and 73 (69) [Found (HRMS): *m*/*z*, 325.0082. $C_{10}H_{18}BrO_5Si$ requires (M^+ − C_4H_9), 325.0107].

Diethyl (2*S*,3*S*)-2-bromo-3-(*tert*-butyldiphenylsiloxy)succinate 2e

Following the procedure for its analogue **2d**, compound **2e** was prepared from diethyl (2*S*,3*S*)-2-bromo-3-hydroxysuccinate **2a** (450 mg, 1.67 mmol), imidazole (250 mg, 3.8 mmol) and *tert*-butyldiphenylsilyl chloride (0.5 cm^3, 1.9 mmol) in dry DMF (2 cm^3). Purification by flash column chromatography (hexane–ethyl acetate, 100:1) gave compound **2e** (529 mg, 62%) as prisms, mp 59–60 °C (from ethyl acetate); ν_{max}(KBr)/cm^{-1} 1744, 1300, 1172, 1112, 1095 and 1020; δ_H 7.66 (4 H, m, $SiPh_2$), 7.39 (6 H, m, $SiPh_2$), 4.63 (1 H, d, *J* 8.1, 2- or 3-H), 4.52 (1 H, d, *J* 8.1, 3- or 2-H), 4.17 (2 H, m, CO_2CH_2Me), 3.97–3.72 (2 H, m, CO_2CH_2Me), 1.25 (3 H, t, *J* 7.1, $CO_2CH_2CH_3$), 1.04 (9 H, s, $SiCMe_3$) and 1.02 (3 H, t, *J* 7.1, $CO_2CH_2CH_3$); δ_C 168.8, 167.2, 136.1, 136.0, 132.4, 132.0, 130.2, 130.0, 127.7, 127.5, 74.5, 62.4, 61.3, 45.7, 26.8, 19.5, 13.9 and 13.7; *m*/*z* 451 (M^+ − C_4H_9, 58%), 449 (M^+ − C_4H_9, 58), 227 (94) and 199 (100) [Found (HRMS): *m*/*z*, 449.0420. $C_{20}H_{22}BrO_5Si$ requires (M^+ − C_4H_9), 449.0420].

Diisopropyl (2*S*,3*S*)-2-bromo-3-(*tert*-butyldimethyl)siloxysuccinate 2f

Diisopropyl (2*S*,3*S*)-2-bromo-3-hydroxysuccinate, prepared from diisopropyl (2*R*,3*R*)-tartrate following the procedures reported in ref. 10, was transformed into title compound **2f** as described above. Product **2f** showed ν_{max}(film)/cm^{-1} 1740; δ_H 5.07 (2 H, sept, *J* 6.3, CO_2CHMe_2), 4.55 (1 H, d, *J* 8.1, 2- or 3-H), 4.44 (1 H, d, *J* 8.1, 3- or 2-H), 1.29 [6 H, *J* 6.4, $CO_2CH(CH_3)_2$], 1.27 [6 H, d, *J* 6.4, $CO_2CH(CH_3)_2$], 0.87 (9 H, s, $SiCMe_3$) and 0.10 (6 H, s, $SiMe_2$); δ_C 169.1, 166.8, 74.6, 70.2, 69.3, 45.5, 25.5, 21.75, 21.66, 21.60, 21.46, 18.1, −5.0 and −5.4; *m*/*z* 413 (M^+ + H, 7%), 411 (M^+ + H, 7), 313 (26), 311 (27), 271 (100), 269 (98), 75 (93) and 73 (64) [Found (HRMS): *m*/*z*, 411.1194. $C_{16}H_{32}BrO_5Si$ requires (M^+ + H), 411.1203].

Methyl 2-bromo-3-(*tert*-butyldimethylsiloxy)-3-phenylpropanoate 2i

Following the procedures for **2d**, compound **2i** was prepared from methyl 2-bromo-3-hydroxy-3-phenylpropanoate (289 mg, 1.1 mmol),[6c] imidazole (680 mg, 10 mmol) and *tert*-butyldimethylsilyl chloride (505 mg, 3.4 mmol) in DMF (3 cm^3). Purification by flash column chromatography (hexane–ethyl acetate, 50:1) gave compound **2i** (361 mg, 87%) as needles, mp 35–36 °C; ν_{max}(KBr)/cm^{-1} 1745, 1268, 1072, 1018, 870, 830 and 775; δ_H 7.35 (5 H, m, Ph), 4.98 (1 H, d, *J* 9.8, 3-H), 4.21 (1 H, d, *J* 9.8, 2-H), 3.82 (3 H, s, CO_2Me), 0.79 (9 H, s, $SiCMe_3$), 0.01 (3 H, s, SiMe) and −0.29 (3 H, s, SiMe); δ_C 169.5, 140.0, 128.6, 128.2, 127.6, 76.6, 52.8, 49.3, 25.4, 17.9, −4.8 and −5.5; *m*/*z* 359 (M^+ − Me, 0.5%), 357 (M^+ − Me, 0.5), 317 (27), 315 (26), 199 (19), 197 (19) and 89 (100) [Found (HRMS): *m*/*z*, 315.0034. $C_{12}H_{16}BrO_3Si$ requires (M^+ − C_4H_9), 315.0052].

Ethyl 2-bromo-3-(*tert*-butyldimethylsiloxy)-3-phenylpropanoate 2j

Compound **2j** was prepared from ethyl 2-bromo-3-hydroxy-3-phenylpropanoate (300 mg, 1.1 mmol),[6c] imidazole (279 mg, 4.1 mmol) and *tert*-butyldimethylsilyl chloride (227 mg, 1.5 mmol) in DMF (1 cm^3). Purification by flash column chromatography (hexane–ethyl acetate, 30:1) gave compound **2j** (330 mg, 77%) as an oil, ν_{max}(film)/cm^{-1} 1749, 1260, 1180, 1140, 1080, 862, 840, 780 and 700; δ_H 7.35 (5 H, m, Ph), 4.99 (1 H, d, *J* 9.8, 3-H), 4.30 (2 H, m, CH_2Me), 4.20 (1 H, m, *J* 9.8, 2-H), 1.34 (3 H, t, *J* 7.1, CH_2CH_3), 0.79 (9 H, s, $SiCMe_3$), 0.02 (3 H, s, SiMe) and −0.29 (3 H, s, SiMe); δ_C 169.1, 140.1, 128.5, 128.1, 127.6, 76.5, 61.9, 49.6, 25.5, 17.9, 13.9, −4.8 and −5.4; *m/z* 331 ($M^+ - C_4H_9$, 28%), 329 ($M^+ - C_4H_9$, 28) and 177 (100) [Found (HRMS): *m/z*, 329.0237. $C_{13}H_{18}BrO_3Si$ requires ($M^+ - C_4H_9$), 329.0208].

Allylation of compound 2d with allyltributyltin in the presence of La(fod)$_3$, a typical procedure of allylation

To a solution of bromide **2d** (31 mg, 0.080 mmol), La(fod)$_3$ (88 mg, 0.086 mmol) and a catalytic amount of AIBN in dry dichloromethane (0.8 cm^3) was added a solution of allyltributyltin (49 mm^3, 0.15 mmol) in dry dichloromethane (0.4 cm^3). The solution was irradiated with a 400 W Xe lamp at 3 °C for 2 h under nitrogen. After treatment of the mixture with aq. potassium fluoride, the reaction mixture was chromatographed on alumina [5 g; hexane and then hexane–ethyl acetate (100:1)] to give an inseparable mixture of diastereoisomers **3d** and **4d** (17 mg, 63%) as an oil; ν_{max}(film)/cm^{-1} 1737, 1640, 1255, 1148, 1025, 837 and 778; *m/z* 345 (M^+ + H, 0.7%), 329 (M^+ − Me, 3), 287 ($M^+ - C_4H_9$, 95), 75 (100) and 73 (74) [Found (HRMS): *m/z*, 329.1761. $C_{16}H_{29}O_5Si$ requires (M^+ − Me), 329.1784].

Diethyl (2*R*,3*R*)-2-allyl-3-(*tert*-butyldimethylsiloxy)succinate 3d. δ_H 5.76 (1 H, m, C*H*=CH_2), 5.03 (2 H, m, CH=CH_2), 4.52 (1 H, d, *J* 5.4, 3-H), 4.14 (4 H, m, 2 × CO_2CH_2Me), 2.92 (1 H, m, 2-H), 2.51 (1 H, m, C*H*CH=CH_2), 2.37 (1 H, m, C*H*CH=CH_2), 1.27 (3 H, t, *J* 7.1, $CO_2CH_2CH_3$), 1.25 (3 H, t, *J* 7.1, $CO_2CH_2CH_3$), 0.89 (9 H, s, $SiCMe_3$), 0.08 (3 H, s, SiMe) and 0.03 (3 H, s, SiMe); δ_C 172.3, 172.1, 135.5, 116.8, 73.0, 61.0, 60.7, 49.8, 31.1, 25.7, 18.2, 14.2, 14.1, −4.8 and −5.4.

Diethyl (2*S*,3*R*)-2-allyl-3-(*tert*-butyldimethylsiloxy)succinate 4d. δ_H 5.76 (1 H, m, C*H*=CH_2), 5.03 (2 H, m, CH=CH_2), 4.33 (1 H, d, *J* 5.6, 3-H), 4.14 (4 H, m, 2 × CO_2CH_2Me), 2.92 (1 H, m, 2-H), 2.45 (1 H, m, C*H*CH=CH_2), 2.24 (1 H, m, C*H*CH=CH_2), 1.29 (3 H, t, *J* 7.1, $CO_2CH_2CH_3$), 1.23 (3 H, t, *J* 7.1, $CO_2CH_2CH_3$), 0.89 (9 H, s, $SiCMe_3$), 0.06 (3 H, s, SiMe) and 0.03 (3 H, s, SiMe); δ_C 172.0, 171.7, 135.1, 117.1, 73.0, 61.0, 60.6, 50.0, 31.9, 25.6, 18.2, 14.2, 14.1, −4.8 and −5.4.

HPLC analysis of MTPA esters 3k, 4k, 3l and 4l

A mixture of diastereoisomers **3d** and **4d**, prepared in the presence of Eu(fod)$_3$ and purified by column chromatography on alumina, was treated with tetrabutylammonium fluoride in THF to give a mixture of alcohols **3a** and **4a**. Following the reported procedures,[13] the mixture was treated with "(*R*)- or (*S*)-methoxy(trifluoromethyl)phenylacetic acid" (MTPA), 1,3-dicyclohexylcarbodiimide and 4-(dimethylamino)pyridine in dry dichloromethane and then chromatographed on silica gel to give mixtures (**3k** and **4k**) and (**3l** and **4l**), respectively. Column: FINPAK SIL (JASCO, 4.6 mm × 250 mm); eluent: hexane–ethyl acetate (20:1); flow rate: 1.0 cm^3 min^{-1}; detection: λ 250 nm: t_R (**3k**) 26.7 min; t_R (**4k**) 31.0 min; t_R (**3l**) 27.7 min; t_R (**4l**) 32.4 min.

Determination of the diastereoisomer ratios of 3 and 4

The diastereoisomer ratios of the inseparable mixtures (**3b/4b**, **3d/4d**–**3f/4f**) were determined by the ^{1}H NMR integration of the signals for 3-H. The ratio of isomers **3a** and **4a** was determined after acetylation with acetic anhydride and pyridine. Compounds **3c** and **4c** were found to be decomposed on alumina. Therefore, when the allylation of compound **2c** was conducted in the presence of Eu(fod)$_3$, the crude mixture of diastereoisomers **3c** and **4c** was successively desilylated and acetylated, and then purified by flash column chromatography to obtain the yield (for three steps) and the diastereoisomer ratio (entries 6 and 7). Resonances for the mixture (**3g** + **4g**) were not resolved in the ^{1}H NMR spectrum recorded in $CDCl_3$ and therefore the ratio was determined by integration of the SiMe signals recorded in C_6D_6. Determination of the **3h/4h** ratio was performed using the integration of CH_2CH=CH_2 signals in their ^{13}C NMR spectrum.[6c,12] The ratios of isomers **3i/4i** and **3j/4j** were obtained by the ^{1}H NMR integrations of CO_2Me and $SiMe_2$ signals, respectively.

Diethyl (2*R*,3*R*)-2-acetoxy-3-allylsuccinate 3b and diethyl (2*R*,3*S*)-2-acetoxy-3-allylsuccinate 4b. An oil; ν_{max}(film)/cm^{-1} 1750, 1644 and 1210; *m/z* 273 (M^+ + H, 47%), 227 (47), 166 (36), 157 (46), 139 (100), 127 (72) and 83 (61) [Found (HRMS): *m/z*, 273.1340. $C_{13}H_{21}O_6$ requires (M^+ + H), 273.1338]. Isomer **3b**: δ_H 5.73 (1 H, m, C*H*=CH_2), 5.43 (1 H, d, *J* 5.4, 2-H), 5.04 (2 H, m, CH=CH_2), 4.20 (4 H, m, 2 × CO_2CH_2Me), 3.03 (1 H, m, 3-H), 2.55 [1 H, m, CH(*H*)CH=CH_2], 2.37 [1 H, m, C(*H*)HCH=CH_2], 2.14 (3 H, s, $MeCO_2$), 1.28 (3 H, t, *J* 7.1, $CO_2CH_2CH_3$) and 1.26 (3 H, t, *J* 7.1, $CO_2CH_2CH_3$); δ_C 171.1, 169.8, 168.3, 134.5, 117.5, 71.6, 61.6, 61.0, 46.6, 31.6, 20.4, 14.1 and 14.0. Isomer **4b**: δ_H 5.73 (1 H, m, C*H*=CH_2), 5.25 (1 H, d, *J* 4.9, 2-H), 5.12 [1 H, m, CH=CH(*H*)], 5.07 [1 H, m, CH=C(*H*)H], 4.20 (4 H, m, 2 × CO_2CH_2Me), 3.10 (1 H, m, 3-H), 2.55 [1 H, m, CH(*H*)CH=CH_2], 2.30 [1 H, m, C(*H*)HCH=CH_2], 2.13 (3 H, s, $MeCO_2$), 1.29 (3 H, t, *J* 7.1, $CO_2CH_2CH_3$) and 1.25 (3 H, t, *J* 7.1, $CO_2CH_2CH_3$); δ_C 170.6, 170.0, 168.5, 134.2, 118.0, 71.5, 61.6, 61.0, 46.2, 31.8, 20.4, 14.1 and 14.0.

Diethyl (2*R*,3*R*)-2-allyl-3-(trimethylsiloxy)succinate 3c and diethyl (2*S*,3*R*)-2-allyl-3-(trimethylsiloxy)succinate 4c. An oil, ν_{max}(film)/cm^{-1} 1740, 1642, 1252, 1150, 1025 and 842; *m/z* 302 (M^+, 0.7%), 287 (M^+ − Me, 16), 229 (39), 147 (29), 75 (46) and 73 (100) [Found (HRMS): *m/z*, 287.1314. $C_{13}H_{23}O_5Si$ requires (M^+ − Me), 287.1315]. Compound **3c**: δ_H 5.75 (1 H, m, C*H*=CH_2), 5.05 (2 H, m, CH=CH_2), 4.46 (1 H, d, *J* 6.6, 3-H), 4.16 (4 H, m, 2 × CO_2CH_2Me), 2.92 (1 H, m, 2-H), 2.53–2.15 (2 H, m, CH_2CH=CH_2), 1.27 (3 H, t, *J* 7.1, $CO_2CH_2CH_3$), 1.25 (3 H, t, *J* 7.1, $CO_2CH_2CH_3$) and 0.13 (9 H, s, $SiMe_3$); δ_C 172.4, 172.2, 135.2, 117.0, 72.3, 61.2, 60.7, 49.4, 31.6, 14.2, 14.1 and −0.2. Compound **4c**: δ_H 5.75 (1 H, m, C*H*=CH_2), 5.05 (2 H, m, CH=CH_2), 4.31 (1 H, d, *J* 6.6, 3-H), 4.16 (4 H, m, 2 × CO_2CH_2Me), 2.92 (1 H, m, 2-H), 2.53–2.15 (2 H, m, CH_2CH=CH_2), 1.29 (3 H, t, *J* 7.1, $CO_2CH_2CH_3$), 1.23 (3 H, t, *J* 7.1, $CO_2CH_2CH_3$) and 0.11 (9 H, s, $SiMe_3$); δ_C 172.1, 171.9, 135.0, 117.3, 72.7, 61.1, 60.6, 49.6, 31.9, 14.2, 14.1 and −0.1.

Diethyl (2*R*,3*R*)-2-allyl-3-(*tert*-butyldiphenylsiloxy)succinate 3e and diethyl (2*S*,3*R*)-2-allyl-3-(*tert*-butyldiphenylsiloxy)succinate 4e. An oil, ν_{max}(film)/cm^{-1} 1740, 1648, 1600, 1115, 1033, 820, 740 and 703; *m/z* 411 ($M^+ - C_4H_9$, 100%), 339 (20), 227 (72), 199 (78), 183 (47), 135 (36) and 68 (53) [Found (HRMS): *m/z*, 411.1591. $C_{23}H_{27}O_5Si$ requires ($M^+ - C_4H_9$), 411.1628]. Compound **3e**: δ_H 7.70–7.60 (4 H, m, Ph), 7.45–7.30 (6 H, m, Ph), 5.70 (1 H, m, C*H*=CH_2), 5.02 (2 H, m, CH=CH_2), 4.54 (1 H, d, *J* 4.9, 3-H), 4.10 (2 H, m, CO_2CH_2Me), 3.84 (2 H, m, CO_2CH_2Me), 2.92 (1 H, m, 2-H), 2.70–2.20 (2 H, m, CH_2CH=CH_2), 1.18 (3 H, t, *J* 7.1, $CO_2CH_2CH_3$), 1.08 (9 H, s, $SiCMe_3$) and 0.99 (3 H, t, *J* 7.1, $CO_2CH_2CH_3$); δ_C 172.2, 171.3, 136.0, 135.4, 133.1, 132.9, 129.9, 127.4, 116.9, 73.2, 60.8, 60.7, 50.1, 31.2, 26.9, 19.6, 14.1 and 13.8. Compound **4e**: δ_H 7.70–7.60 (4 H, m, Ph), 7.45–7.30 (6 H, m, Ph), 5.70 (1 H, m, C*H*=CH_2), 5.02 (2 H, m, CH=CH_2), 4.44 (1 H, d, *J* 5.6, 3-H), 4.10 (2 H, m, CO_2CH_2Me), 3.84 (2 H, m, CO_2CH_2Me), 2.92 (1 H, m, 2-H), 2.70–2.20 (2 H, m, CH_2CH=CH_2), 1.23 (3 H, t, *J* 7.1, $CO_2CH_2CH_3$), 1.07 (9 H, s, $SiCMe_3$) and 1.01 (3 H, t, *J* 7.1, $CO_2CH_2CH_3$); δ_C 171.6, 171.1, 136.0, 135.2, 133.0, 132.8, 129.7,

127.6, 117.0, 73.7, 60.8, 60.7, 50.3, 31.6, 26.8, 19.6, 14.1 and 13.8.

Diisopropyl (2*R*,3*R*)-2-allyl-3-(*tert*-butyldimethylsiloxy)succinate 3f and diisopropyl (2*S*,3*R*)-2-allyl-3-(*tert*-butyldimethylsiloxy)succinate 4f. An oil; ν_{max}(film)/cm^{-1} 1735, 1644, 1260, 1105 and 840; *m*/*z* 373 (M^+ + H, 3%), 315 ($M^+ - C_4H_9$, 12), 185 (86), 75 (100) and 73 (64) [Found (HRMS): *m*/*z*, 373.2399. $C_{19}H_{37}O_5Si$ requires (M^+ + H), 373.2410]. Compound **3f**: δ_H 5.77 (1 H, m, C*H*=CH$_2$), 5.15–4.95 (4 H, m, CH=C*H*$_2$ and 2 × CO$_2$C*H*Me$_2$), 4.47 (1 H, d, *J* 5.4, 3-H), 2.90 (1 H, m, 2-H), 2.55–2.15 (2 H, m, C*H*$_2$CH=CH$_2$), 1.30–1.20 [12 H, m, 2 × CH(C*H*$_3$)$_2$], 0.90 (9 H, s, SiCMe$_3$), 0.09 (3 H, s, SiMe) and 0.05 (3 H, s, SiMe). Compound **4f**: δ_H 5.77 (1 H, m, C*H*=CH$_2$), 5.15–4.95 (4 H, m, CH=C*H*$_2$ and 2 × CO$_2$C*H*Me$_2$), 4.29 (1 H, d, *J* 5.1, 3-H), 2.90 (1 H, m, 2-H), 2.55–2.15 (2 H, m, C*H*$_2$CH=CH$_2$), 1.30–1.20 [12 H, m, 2 × CH(C*H*$_3$)$_2$], 0.89 (9 H, s, SiCMe$_3$), 0.08 (3 H, s, SiMe) and 0.05 (3 H, s, SiMe).

Ethyl (*syn*)-2-allyl-3-(*tert*-butyldimethylsiloxy)butanoate 3g and ethyl (*anti*)-2-allyl-3-(*tert*-butyldimethylsiloxy)butanoate 4g. An oil; ν_{max}(film)/cm^{-1} 1739, 1642, 1258, 1180, 1100, 838 and 775; *m*/*z* 271 (M^+ − Me, 2%), 229 ($M^+ - C_4H_9$, 52), 157 (28), 103 (43), 75 (100) and 73 (43) [Found (HRMS): *m*/*z*, 271.1710. $C_{14}H_{27}O_3Si$ requires (M^+ − Me), 271.1730]. Compound **3g**: δ_H(C_6D_6) 5.87 (1 H, m, C*H*=CH$_2$), 5.20–4.95 (2 H, m, CH=C*H*$_2$), 4.05 (1 H, m, 3-H), 4.00 (2 H, q, *J* 7.1, CO$_2$C*H*$_2$Me), 2.55 (3 H, m, 2-H and C*H*$_2$CH=CH$_2$), 1.20 (3 H, d, *J* 6.3, Me), 1.01 (3 H, t, *J* 7.1, CO$_2$CH$_2$C*H*$_3$), 0.96 (9 H, s, SiCMe$_3$), 0.04 (3 H, s, SiMe) and 0.02 (3 H, s, SiMe). Compound **4g**: δ_H(C_6D_6) 5.87 (1 H, m, C*H*=CH$_2$), 5.20–4.95 (2 H, m, CH=C*H*$_2$), 4.05–4.00 (3 H, m, 3-H and CO$_2$C*H*$_2$Me), 2.55 (3 H, m, 2-H and C*H*$_2$CH=CH$_2$), 1.08 (3 H, d, *J* 6.1, Me), 0.98 (9 H, s, SiCMe$_3$), 0.96 (3 H, t, *J* 7.1, CO$_2$CH$_2$C*H*$_3$), 0.10 (3 H, s, SiMe) and 0.07 (3 H, s, SiMe).

Methyl (*syn*)-2-allyl-3-(*tert*-butyldimethylsiloxy)-3-phenylpropanoate 3i and methyl (*anti*)-2-allyl-3-(*tert*-butyldimethylsiloxy)-3-phenylpropanoate 4i. An oil; ν_{max}(film)/cm^{-1} 1740, 1642, 1260, 1087, 840, 787 and 700; *m*/*z* 277 ($M^+ - C_4H_9$, 53%) and 89 (100) [Found (HRMS): *m*/*z*, 277.1264. $C_{15}H_{21}O_3Si$ requires ($M^+ - C_4H_9$), 277.1260]. Compound **3i**: δ_H 7.40–7.12 (5 H, m, Ph), 5.84–5.65 (1 H, m, C*H*=CH$_2$), 5.12–4.85 (2 H, m, CH=C*H*$_2$), 4.82 (1 H, d, *J* 7.6, 3-H), 3.44 (3 H, s, CO$_2$Me), 2.85–2.36 (3 H, m, 2-H and C*H*$_2$CH=CH$_2$), 0.87 (9 H, s, SiCMe$_3$), 0.02 (3 H, s, SiMe) and −0.24 (3 H, s, SiMe); δ_C 173.4, 142.8, 135.8, 128.0, 127.5, 126.5, 116.4, 75.8, 55.6, 51.2, 32.6, 25.7, 18.1, −4.6 and −5.2. Compound **4i**: δ_H 7.40–7.12 (5 H, m, Ph), 5.84–5.65 (1 H, m, C*H*=CH$_2$), 5.12–4.85 (2 H, m, CH=C*H*$_2$), 4.72 (1 H, d, *J* 9.5, 3-H), 3.70 (3 H, s, CO$_2$Me), 2.85–2.35 (3 H, m, 2-H and C*H*$_2$CH=CH$_2$), 0.80 (9 H, s, SiCMe$_3$), −0.01 (3 H, s, SiMe) and −0.32 (3 H, s, SiMe); δ_C 174.4, 142.2, 134.8, 128.2, 128.1, 127.1, 116.6, 77.2, 55.3, 51.4, 33.3, 25.5, 17.9, −4.7 and −5.5.

Ethyl (*syn*)-2-allyl-3-(*tert*-butyldimethylsiloxy)-3-phenylpropanoate 3j and ethyl (*anti*)-2-allyl-3-(*tert*-butyldimethylsiloxy)-3-phenylpropanoate 4j. An oil; ν_{max}(film)/cm^{-1} 1740, 1647, 1260, 1177, 1090, 840, 780 and 703; *m*/*z* 333 (M^+ − Me, 2%), 291 ($M^+ - C_4H_9$, 98), 221 (38), 157 (34), 103 (70), 75 (100) and 73 (62) [Found (HRMS): *m*/*z*, 291.1408. $C_{16}H_{23}O_3Si$ requires ($M^+ - C_4H_9$), 291.1416]. Compound **3j**: δ_H 7.41–7.19 (5 H, m, Ph), 5.84–5.49 (1 H, m, C*H*=CH$_2$), 5.08–4.86 (2 H, m, CH=C*H*$_2$), 4.77 (1 H, d, *J* 8.1, 3-H), 3.88 (2 H, q, *J* 7.1, CO$_2$C*H*$_2$Me), 2.81–2.38 (3 H, m, 2-H and C*H*$_2$CH=CH$_2$), 0.98 (3 H, t, *J* 7.1, CO$_2$CH$_2$C*H*$_3$), 0.87 (9 H, s, SiCMe$_3$), 0.02 (3 H, s, SiMe) and −0.25 (3 H, s, SiMe); δ_C 172.9, 142.8, 135.8, 127.9, 127.5, 126.7, 116.3, 76.0, 60.0, 55.6, 33.0, 25.7, 18.1, 14.0, −4.6 and −5.2. Compound **4j**: δ_H 7.41–7.19 (5 H, m, Ph), 5.84–5.49 (1 H, m, C*H*=CH$_2$), 5.08–4.86 (2 H, m, CH=C*H*$_2$), 4.72 (1 H, d, *J* 9.3, 3-H), 4.15 (2 H, q, *J* 7.1, CO$_2$C*H*$_2$Me), 2.81–2.38 (3 H, m, 2-H and C*H*$_2$CH=CH$_2$), 1.27 (3 H, t, *J* 7.1, CO$_2$CH$_2$C*H*$_3$), 0.80 (9 H, s, SiCMe$_3$), −0.03 (3 H, s, SiMe) and −0.32 (3 H, s, SiMe); δ_C 174.0, 142.2, 134.8, 128.2, 128.1, 127.1, 116.5, 76.9, 60.3, 55.2, 33.4, 25.6, 17.9, 14.3, −4.8 and −5.5.

References

1 Preliminary communication: H. Nagano and Y. Kuno, *J. Chem. Soc., Chem. Commun.*, 1994, 987.
2 N. A. Porter, B. Giese and D. P. Curran, *Acc. Chem. Res.*, 1991, **24**, 296; W. Smadja, *Synlett*, 1994, 1.
3 (*a*) D. J. Hart, H.-C. Huang, R. Krishnamurthy and T. Schwartz, *J. Am. Chem. Soc.*, 1989, **111**, 7507; (*b*) D. J. Hart and R. Krishnamurthy, *Synlett*, 1991, 412; (*c*) *J. Org. Chem.*, 1992, **57**, 4457.
4 (*a*) Y. Guindon, C. Yoakim, R. Lemieux, L. Boisvert, D. Delorme and J.-F. Lavallée, *Tetrahedron Lett.*, 1990, **31**, 2845; (*b*) Y. Guindon, J.-F. Lavallée, L. Boisvert, C. Chabot, D. Delorme, C. Yoakim, D. Hall, R. Lemieux and B. Simoneau, *Tetrahedron Lett.*, 1991, **32**, 27; (*c*) Y. Guindon, J.-F. Lavallée, M. Llinas-Brunet, G. Horner and J. Rancourt, *J. Am. Chem. Soc.*, 1991, **113**, 9701; (*d*) K. Durkin, D. Liotta, J. Rancourt, J.-F. Lavallée, L. Boisvert and Y. Guindon, *J. Am. Chem. Soc.*, 1992, **114**, 4912; (*e*) Y. Guindon, A. Slassi, J. Rancourt, G. Bantle, M. Bencheqroun, L. Murtagh, E. Ghiro and G. Jung, *J. Org. Chem.*, 1995, **60**, 288.
5 (*a*) M. Bulliard, H.-G. Zeitz and B. Giese, *Synlett*, 1991, 423; (*b*) B. Giese, M. Bulliard and H.-G. Zeitz, *Synlett*, 1991, 425; (*c*) M. Bulliard, M. Zehnder and B. Giese, *Helv. Chim. Acta*, 1991, **74**, 1600; (*d*) B. Giese, W. Damm, F. Wetterich and H.-G. Zeitz, *Tetrahedron Lett.*, 1992, **33**, 1863; (*e*) P. Erdmann, J. Schäfer, R. Springer, H.-G. Zeitz and B. Giese, *Helv. Chim. Acta*, 1992, **75**, 638; (*f*) B. Giese, W. Damm, F. Wetterich, H.-G. Zeitz, J. Rancourt and Y. Guindon, *Tetrahedron Lett.*, 1993, **34**, 5885; (*g*) B. Giese, M. Bulliard, J. Dickhaut, R. Halbach, C. Hassler, U. Hoffmann, B. Hinzen and M. Senn, *Synlett*, 1995, 116.
6 (*a*) D. P. Curran, A. C. Abraham and H. T. Liu, *J. Org. Chem.*, 1991, **56**, 4335; (*b*) D. P. Curran and A. C. Abraham, *Tetrahedron*, 1993, **49**, 4821; (*c*) D. P. Curran and P. S. Ramamoorthy, *Tetrahedron*, 1993, **49**, 4841.
7 A. L. J. Beckwith, R. Hersperger and J. M. White, *J. Chem. Soc., Chem. Commun.*, 1991, 1151; M. Hamdani, B. De Jeso, H. Deleuze, A. Saux and B. Maillard, *Tetrahedron: Asymmetry*, 1993, **4**, 1233; A. De Mesmaeker, A. Waldner, P. Hoffmann and T. Mindt, *Synlett*, 1993, 871.
8 Y. Yamamoto, S. Onuki, M. Yumoto and N. Asao, *J. Am. Chem. Soc.*, 1994, **116**, 421; M. Nishida, E. Ueyama, H. Hayashi, Y. Ohtake, Y. Yamaura, E. Yanaginuma, O. Yonemitsu, A. Nishida and N. Kawahara, *J. Am. Chem. Soc.*, 1994, **116**, 6455; M. Nishida, H. Hayashi, Y. Yamaura, E. Yanaginuma, O. Yonemitsu, A. Nishida and N. Kawahara, *Tetrahedron Lett.*, 1995, **36**, 269; M. Murakata, H. Tsutsui and O. Hoshino, *J. Chem. Soc., Chem. Commun.*, 1995, 481; H. Urabe, K. Kobayashi and F. Sato, *J. Chem. Soc., Chem. Commun.*, 1995, 1043; P. Renaud and M. Gerster, *J. Am. Chem. Soc.*, 1995, **117**, 6607; Y. Guindon, B. Guérin, C. Chabot, N. Mackintosh and W. W. Ogilvie, *Synlett*, 1995, 449.
9 (*a*) A. Waldner, A. De Mesmaeker, P. Hoffmann, T. Mindt and T. Winkler, *Synlett*, 1991, 101; (*b*) P. Renaud and M. Ribezzo, *J. Am. Chem. Soc.*, 1991, **113**, 7803; (*c*) T. Toru, Y. Watanabe, M. Tsusaka and Y. Ueno, *J. Am. Chem. Soc.*, 1993, **115**, 10464; (*d*) D. P. Curran and L. H. Kuo, *J. Org. Chem.*, 1994, **59**, 3259; (*e*) P. Renaud, N. Moufid, L.-H. Kuo and D. P. Curran, *J. Org. Chem.*, 1994, **59**, 3547; (*f*) P. Renaud, T. Bourquard, M. Gerster and N. Moufid, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1601.
10 K. Mori and H. Iwasaki, *Tetrahedron*, 1980, **36**, 87.
11 D. Seebach and D. Wasmuth, *Helv. Chim. Acta*, 1980, **63**, 197.
12 H. Nagano, M. Ohno, Y. Miyamae and Y. Kuno, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 2814.
13 T. Kusumi, *Yuki Gosei Kagaku Kyokaishi*, 1993, **51**, 462 (*Chem. Abstr.*, 1993, **119**, 180080h).
14 R. Porter, T. J. Marks and D. F. Shriver, *J. Am. Chem. Soc.*, 1973, **95**, 3548.
15 C. S. Springer, Jr., D. W. Merck and R. E. Sievers, *Inorg. Chem.*, 1967, **6**, 1105.

Paper 5/04260G
Received 3rd *July* 1995
Accepted 15th *August* 1995