Chemistry of Silylketenes: a Simple Preparation of α-Silyl-α-stannylacetic Esters and Their Stereoselective Reformatsky-type Reaction with Aldehydes or Aldimines

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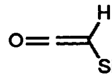
Silylketenes **1a, b** reacted smoothly with alkoxystannanes **3** to give the corresponding α-silyl-α-stannylacetates **4** almost quantitatively. Treatment of **4** with $TiCl_4$ caused selective cleavage of the C–Sn bond to bring about Reformatsky-type reaction with aldehydes **6** giving β-hydroxy-α-silyl esters **7**. These two steps were carried out by one-pot operation, and variously substituted compounds **7** were obtained with high *syn*-selectivity (52–≥96% d.e.) in 41–89% yields. A similar one-pot procedure starting from **1a–c**, **3**, and aldimines **11** also provided the corresponding β-amino-α-silyl esters **12** with excellent *syn*-selectivity (≥96% d.e.) in 64–94% yields. Stereocontrolled preparation of both (*E*)- and (*Z*)-α,β-unsaturated esters **8** and a *syn*-amino diol derivative **17** from *syn*-**7** and *syn*-**12**, respectively, is also described.

Since the first preparation of (trimethylsilyl)ketene **1a** (R^1 = Me) in 1965,[1] silylketenes **1** have attracted much attention because of their unique characteristics [as well as (trimethylsilyl)ketene,[2] diethylmethylsilyl-,[2f,m] triethylsilyl-,[2c,f,i,3,4] *tert*-butyldimethylsilyl-,[2j,p,3] *tert*-butyldiphenylsilyl-,[2p] dimethylphenylsilyl-,[2f,5] and (methyldiphenylsilyl)-ketene[5] have been prepared]. They are easy to handle, distillable liquid monomers, and can be stored for a long time without polymerization, which is in remarkable contrast to the parent ketene and alkylketenes. Although fundamental studies on the reaction of silylketenes **1** with various nucleophiles have been extensively developed,[2–5] their inherent silyl groups have scarcely been utilized positively.[2h,o] Being interested in practical applications of silylketenes, we have communicated simple and regiocontrolled syntheses of α-silylacetates bearing various functional groups[3] and unsymmetrical α-silylketones.[6] The latter synthesis was achieved by a one-pot operation through the addition of carbon nucleophiles to **1** and the subsequent reaction of the intermediate metal enolates with alkyl halides (eqn. 1). We have extended this methodology to a one-pot coupling of silylketenes **1**, alkoxyanions **A**, and aldehydes or aldimines as illustrated in eqn. 2 (Scheme 1). Addition of **A** to **1** would generate the enolates **B**, which would react with aldehydes or aldimines to give the adducts **C** bearing a silyl group at the α-position. Recently we have published a preliminary communication showing that the use of alkoxystannanes **3** as alkoxyanions **A** accomplished the desired reactions with aldehydes **6** to give the corresponding adducts, β-hydroxy-α-silyl esters **7** with high *syn*-selectivity.[7] Here we describe the full account of our results along with the successful extension of this methodology to the reaction with aldimines **11** leading to stereospecific preparation of *syn*-β-amino-α-silyl esters **12**. The usefulness of the esters **7** and **12** is presented in their stereocontrolled conversion into (*E*)- and (*Z*)-α,β-unsaturated esters **8** and a *syn*-amino diol derivative **17**, respectively.



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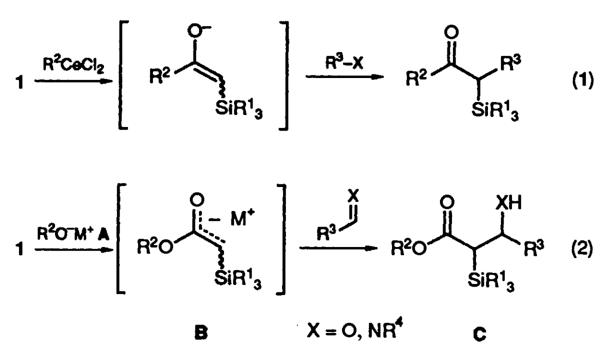

Scheme 1

Results and Discussions

First we examined the reaction of metal alkoxides or a silyl ether with the silylketenes **1a**, **b**: (a) **1a** or **1b** was slowly added to a solution of $PhCH_2OLi$ or $PhCH_2OLi–CeCl_3$ in tetrahydrofuran (THF) at −78 °C and the reaction mixture was quenched with Me_3SiCl; and (b) a mixture of **1a** or **1b** and $PhCH_2OSiMe_3$ was treated with various Lewis acids in dichloromethane or acetonitrile. These methods, however, could not provide the desired *O*-silyl ketene acetal **2** and resulted in complex mixtures. Addition of cyclohexanone to the above reaction mixture also failed to give the desired addition product **C**. On the other hand, reaction of **1a** or **1b** with the ethoxystannane **3** (R^2 = Et) proceeded smoothly in dry dichloromethane at −30 °C to give the corresponding adduct, ethyl α-silyl-α-(tributylstannyl)acetates **4a, b** (R^2 = Et) in nearly quantitative yields (Scheme 2).[8,†] The structures of **4a, b** were confirmed unambiguously by IR, ^1H NMR and ^{13}C NMR spectroscopy. Furthermore, the ^1H NMR spectrum of **4** in [$^2H_2$]-dichloromethane revealed that it exists in the ester form under the conditions used for its generation (−30 °C) (see Experimental section) and no signal for the corresponding *O*-stannylketene acetal **5** was observed.

The reaction of **4** with aldehydes **6** in the presence of $TiCl_4$ caused selective cleavage of the C–Sn bond to bring about Reformatsky-type reaction. Thus, to a solution of the α-(*tert*-butyldimethylsilyl)acetate **4b** in dichloromethane were successively added benzaldehyde **6** (R^3 = Ph) and $TiCl_4$ (0.5 equiv.) at −78 °C and the reaction mixture was stirred for 1 h to give

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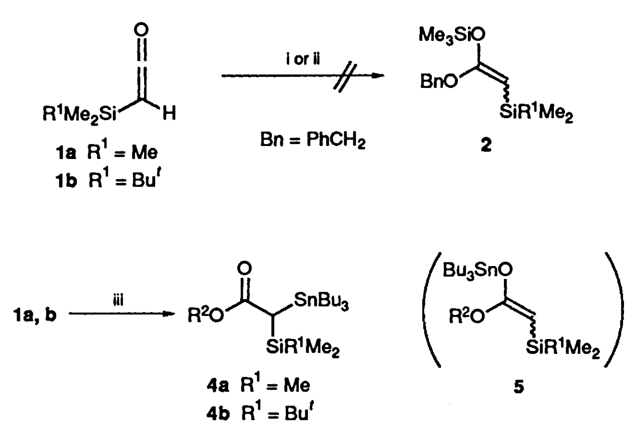
[†] Similar preparation of α-trimethyl- or triethylsilyl-α-stannylacetates from the corresponding silylketenes and alkoxystannanes in pentane was concurrently reported by Russian chemists.[2n] Another preparation of an α-silyl-α-stannylacetate was reported by stannylation of a lithium enolate of *tert*-butyl α-(trimethylsilyl)acetate.[9]

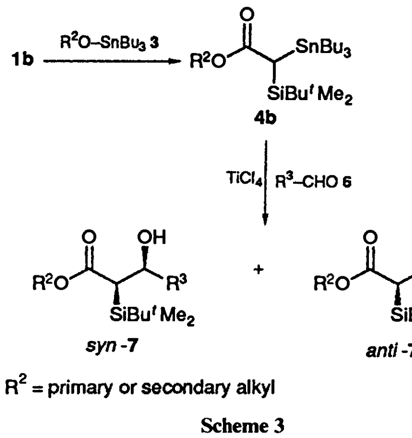


Scheme 2 *Reagents:* i, BnOLi or BnOLi–$CeCl_3$ then Me_3SiCl; ii, $BnOSiMe_3$, Lewis acids; iii, $R^2O–SnBu_3$ **3**

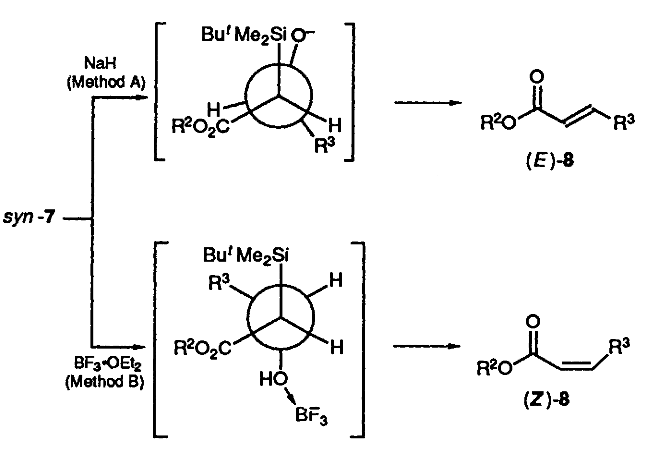
the ethyl β-hydroxy-α-silyl ester **7a** as a mixture (80:20) of *syn*- and *anti*-isomers in 66% yield. Use of other Lewis acids such as $SnCl_4$, $CF_3SO_3SiMe_3$, BF_3•OEt_2 and $ZnCl_2$ was not effective, giving complicated products from which ethyl α-(*tert*-butyldimethylsilyl)acetate was obtained as the major by-product. Without any catalyst, the reaction did not proceed at all even after warming at 60 °C for 10 h. Use of the α-(trimethylsilyl)acetate **4a** instead of **4b** decreased the yield of the adduct and ethyl (*E*)-cinnamate was obtained probably through the elimination of silanol from the adduct (Peterson olefination).[10]

More conveniently, the above two steps could be carried out by one-pot operation without isolation of **4**, and a 77:23 mixture of *syn*- and *anti*-**7a** was obtained from **1b** in 78% yield. By this procedure, coupling of three components, **1b**, primary and secondary alkoxystannanes **3**, and aliphatic and aromatic aldehydes **6** readily provided the corresponding adducts **7** in moderate to high yields (Scheme 3 and Table 1).* In every case the *syn*-isomer was obtained predominantly. In particular, use of alkoxystannanes **3** bearing bulky neopentyl (entry 5) or secondary alkyl groups for R^2 (entries 8, 10–14) achieved complete *syn*-selectivity. When the reaction of **1** and **3** was sluggish even at room temperature, addition of ZnI_2 (about 0.01 equiv.) solved this problem (entries 4–14). The stereochemistry of adducts **7** was determined based on their ^1H NMR spectroscopic data [the vicinal coupling constants between α- and β-H for *syn*-**7** are larger (5.6–9.9 Hz) than those for *anti*-**7** (2.3–3.3 Hz), which are in agreement with those for the similar compounds[11,12]], and was confirmed by the following transformations.

Formation of the *syn*-adducts **7** by the present method gave a promising entry to either (*E*)- or (*Z*)-α,β-unsaturated esters **8**, depending on the conditions used (Scheme 4). Typical procedures are shown in the following reactions of *syn*-**7j**. Treatment of *syn*-**7j** with one equivalent of NaH in THF at room temperature (Method A) for 1.5 h gave exclusively (*E*)-**8j** in 95% yield through the *syn*-elimination of silanol. On the other hand, the corresponding (*Z*)-**8j** was obtained from *syn*-**7j** by treatment with one equivalent of BF_3•OEt_2 in dichloromethane at −20 °C (Method B) for 4 h in 97% yield (*E*:*Z* = 2:98) through the *anti*-elimination. [The reaction should be carried out at low temperature, since treatment of *syn*-**7j** with BF_3•OEt_2 at 0 °C to room temperature resulted in poor selectivity (*E*:*Z* = 3:7).] Similarly stereospecific formation of (*Z*)-**8c, d, h, k, n** from *syn*-**7c, d, h, k, n** was performed under the same conditions in almost quantitative yields (Table 1).

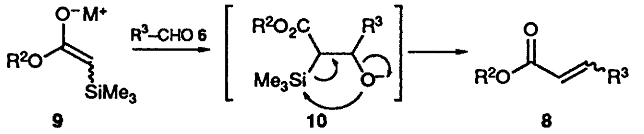


Scheme 3



Scheme 4

Over the last two decades, reactions of enolates **9**, generated from α-silylacetates, and aldehydes **6** have been studied well, since they directly provide α,β-unsaturated esters **8** in high yields through facile elimination of silanol from initial adducts **10** (Scheme 5).[10–13] However, this method often suffers from formation of mixtures of (*E*)- and (*Z*)-**8** in variable ratios depending on the substrates and the reaction conditions. Although selective preparations of more stable (*E*)-**8** have been elaborated,[11,14] effective methods for (*Z*)-**8** are quite few.[12] Since the present method features a one-pot and convenient preparation of *syn*-**7** by the coupling of three components, **1**, **3** and **6**, we believe that this overall method provides an effective preparation of (*Z*)-**8** as well as (*E*)-**8**.



Scheme 5

Next, we extended our one-pot methodology to the reaction with aldimines **11**. Into a solution of **4** in dichloromethane, prepared *in situ* from **1** and **3**, were added **11** and $TiCl_4$ (1 equiv.)

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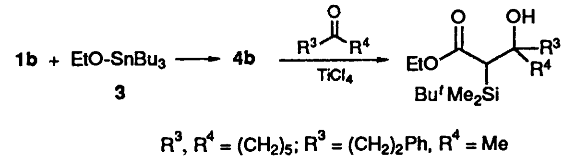
* The present method is also applicable to the reaction with ketones. Coupling of **1b**, $EtOSnBu_3$ **3**, and cyclohexanone or 4-phenylbutan-2-one gave the adducts in 95 and 83% (as a 53:47 diastereoisomeric mixture) yields, respectively.



R^3, R^4 = $(CH_2)_5$; R^3 = $(CH_2)_2Ph$, R^4 = Me

Table 1 Preparation of α-(*tert*-butyldimethylsilyl)-β-hydroxy esters **7** and their conversion into (*E*)- and (*Z*)-α,β-unsaturated esters **8**

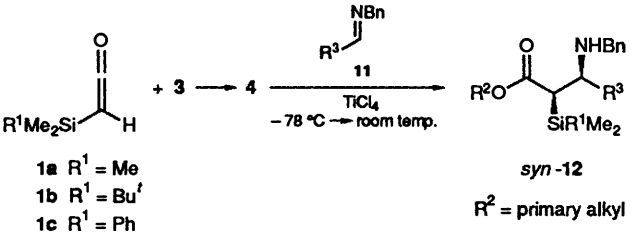
					% Yield of **8**[c] (*E*:*Z*)[b]	
Entry	R^2	R^3	% Yield of **7**[a] (*syn*:*anti*)[b]		Method A	Method B
1	Et	Ph	**7a** 78 (77:23)			
2	Et	$(CH_2)_2Ph$	**7b** 54 (91:9)			
3	Me	Ph	**7c** 68 (76:24)	**8c**[e]	95 (>99:1)	99 (3:97)
4	CH_2Bu^t	Ph	**7d**[d] 77 (89:11)	**8d**[f]	87 (>99:1)	98 (7:93)
5	CH_2Bu^t	Pr^i	**7e**[d] 58 (≥98:2)			
6	Pr^i	Ph	**7f**[d] 89 (85:15)			
7	Pr^i	$(CH_2)_2Ph$	**7g**[d] 56 (91:9)			
8	$CHEt_2$	Ph	**7h**[d] 59 (≥98:2)	**8h**		98 (2:98)
9	c-C_5H_9	Ph	**7i**[d] 68 (89:11)			
10	c-C_6H_{11}	Ph	**7j**[d] 60 (≥98:2)	**8j**	95 (>99:1)	97 (2:98)
11	c-C_6H_{11}	$(CH_2)_2Ph$	**7k**[d] 42 (≥98:2)	**8k**		99 (4:96)
12	c-C_6H_{11}	$(CH_2)_3Me$	**7l**[d] 74 (≥98:2)			
13	c-C_6H_{11}	Bu^t	**7m**[d] 84 (≥98:2)			
14	c-C_6H_{11}	Pr^i	**7n**[d] 41 (≥98:2)	**8n**		82 (4:96)

[a] Isolated yields based on **6**. [b] The ratios determined by 250 MHz ^1H NMR analysis. [c] Isolated yields based on *syn*-**7**. [d] ZnI_2 (*ca.* 0.01 equiv.) was added for the reaction of **1** and **3**. [e] Pure *syn*-**7c** obtained by column chromatography purification was used. [f] Pure *syn*-**7d** obtained by one recrystallization from hexane of an 89:11 mixture was used.

Table 2 Preparation of β-amino-α-silyl esters **12**

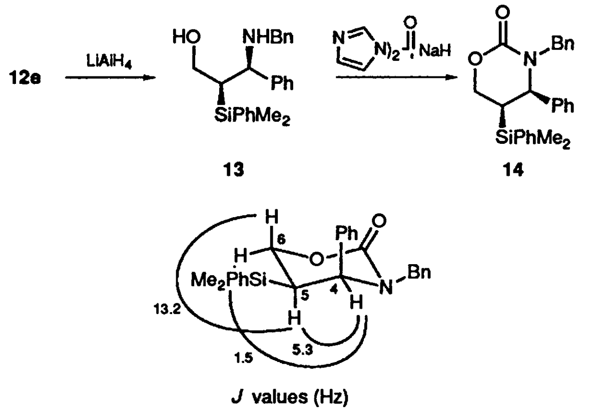
Entry	R^1	R^2	R^3	% Yield of **12**[a]
1	Me	Me	Ph	**12a** 84
2	Bu^t	Me	Ph	**12b** 81
3	Bu^t	Me	Pr^i	**12c** 67
4	Bu^t	Et	Ph	**12d** 85
5	Ph	Me	Ph	**12e** 94
6	Ph	Et	Pr^i	**12f** 64

[a] Isolated yields based on **11**. A single isomer (≥96% d.e.) was obtained in every case based on 250 MHz ^1H NMR analysis.



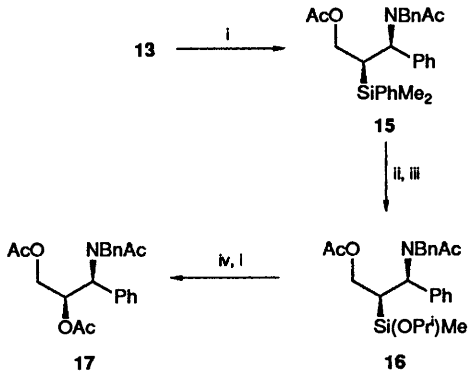
Scheme 6

at −78 °C. The reaction mixture was gradually allowed to warm to room temperature overnight, giving the expected adduct, β-amino-α-silyl ester **12** in moderate to high yields (Scheme 6 and Table 2). In these reactions, two features are noteworthy. (a) In every case, single *syn*-product **12** (≥96% d.e. based on 250 MHz ^1H NMR analysis) was obtained from the most simple alkoxystannanes **3** (R^2 = Me, Et); and (b) use of trimethylsilyl- **1a** (entry 1) and (dimethylphenylsilyl)-ketene **1c** (entries 5 and 6) afforded satisfactory results equal to those of **1b**. The stereochemistry of **12** was determined as follows: Reduction of **12e** with $LiAlH_4$ gave the alcohol **13**, which was treated with *N*,*N'*-carbonyldiimidazole to give the cyclic carbamate **14** in 59% overall yield. ^1H NMR spectroscopic study of **14** showed a relatively small coupling constant (5.3 Hz) between 4- and 5-H, a large coupling constant (13.2 Hz) between 5- and 6-axH, and a long range coupling between 4- and 6-eqH. These results are unambiguously compatible with the chair form in which the relation between the silyl and phenyl groups is *cis* (Scheme 7), and hence **12e** has the *syn* configuration. All other β-amino-α-silyl esters **12** were deduced also to be *syn* from the fact that the coupling constants between α- and β-H for all **12** are within the range of 10.0–11.6 Hz.



Scheme 7

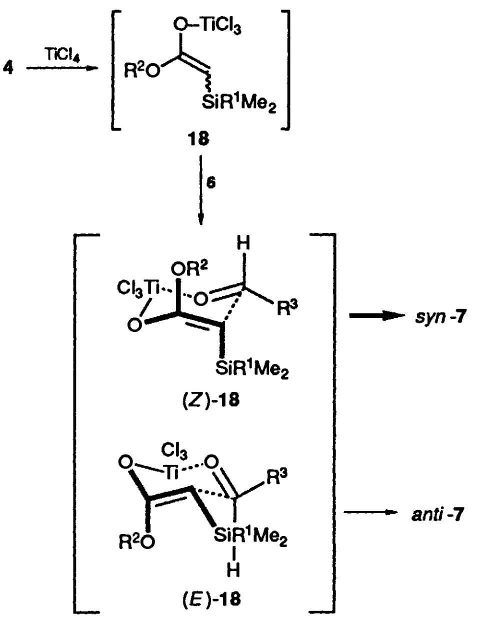
The usefulness of this method is shown in a transformation of the silyl group into a hydroxy group according to Tamao and Fleming's method.[15] Thus, the alcohol **13** derived from **12e** was converted to the *syn*-amino diol derivative **17**[16] by a series of reactions (**13** ⟶ **15** ⟶ **16** ⟶ **17**) (Scheme 8).



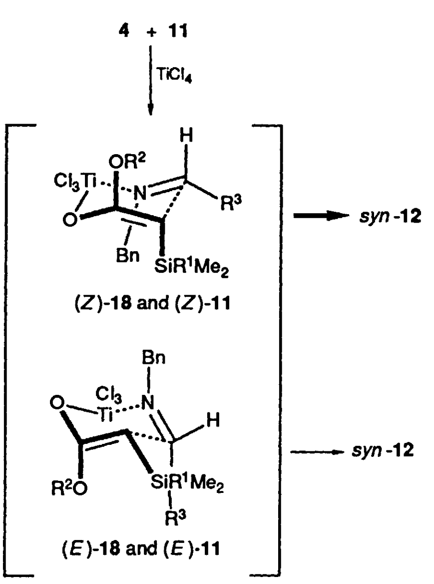
Scheme 8 *Reagents:* i, AcCl; ii, Br_2; iii, Pr^iOH, Et_3N; iv, H_2O_2, KF, $KHCO_3$

For the present stereoselective Reformatsky-type reaction, the following mechanism may be presumed. In analogy with the tin–titanium exchange reaction of β-stannyl esters and $TiCl_4$[17] and the formation of *O*-titanium ketene acetals from esters upon treatment with base,[18] **4** initially reacts with $TiCl_4$ to generate

O-titanium ketene acetal **18**, which gives **7** or **12** *via* usual titanium-mediated cyclic transition states with aldehydes **6** or aldimines **11**. When **4b** (R^2 = Et) was treated with one equivalent of $TiCl_4$ in dichloromethane at −78 °C for 10 min, its spot turned into that of ethyl α-(*tert*-butyldimethylsilyl)acetate based on TLC analysis. To this reaction mixture was added benzaldehyde **6** (R^3 = Ph) to give **7a**, which is similar to the result shown in Table 1. On the other hand, reaction of cyclohexyl α-(*tert*-butyldimethylsilyl)acetate and **6** (R^3 = Ph) in the presence of one equivalent of $TiCl_4$ in dichloromethane at −78 °C and warming to room temperature resulted in no reaction. These results are compatible with this mechanism. Taking account of both possibilities of (*Z*)- and (*E*)-**18**, the most plausible transition state for the reaction with **6** for each geometry is presented in Scheme 9. The fact that **4** bearing a bulky R^2 group attains complete *syn*-selectivity suggests the favourable formation of (*Z*)-**18** leading to *syn*-**7**. In the reaction with aldimines **11**, (*Z*)-**18** presumably reacts with more reactive (*Z*)-**11** to give *syn*-**12** (Scheme 10).[19] If (*E*)-**18** is formed as a minor isomer in the case of small R^2, it may react with (*E*)-**11** also leading to *syn*-**12**.



Scheme 9



Scheme 10

In conclusion, we have elucidated a one-pot coupling of **1**, **3**, and **6** or **11** to give the corresponding adducts, α-silyl esters, **7** and **12**, with high stereoselectivity. α-Silyl esters are valuable nucleophiles for carbon–carbon bond formation with carbonyl compounds[13,20] and also are versatile substrates for the syntheses of olefins and α-silyl ketones.[21] The present method is convenient in operation and provides a novel and useful entry to functionalized α-silyl esters and their derivatives.

Experimental

All boiling and melting points are uncorrected. IR spectra were recorded on a JASCO HPIR-102 spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian VXR-200, a Hitachi R-250HT, and a JEOL JNM-EX270 spectrometer. Low temperature spectra were recorded on a JEOL JNM-GX500. All NMR spectra were measured with $SiMe_4$ or $CHCl_3$ as internal standards and *J* values are given in Hz. High resolution mass spectra (MS) were recorded at 70 or 20 eV with a direct inlet system on a JEOL JMS-HX100 spectrometer. E. Merck silica gel 60 (0.063–0.200 nm, 70–230 mesh ASTM) and E. Merck pre-coated TLC plates, silica gel 60 F_{254} were used for column chromatography and for preparative TLC, respectively. Organic layers were dried with anhydrous Na_2SO_4. Silylketenes **1a**,[3] **b**[3] and **c**,[5] alkoxystannanes **3**,[22] and an imine **11** (R^3 = Pr^i)[23] were prepared according to the reported methods. All other compounds are commercially available.

Ethyl α-(Tributylstannyl)-α-(trimethylsilyl)acetate **4a** (R^2 = Et).—Under a nitrogen atmosphere, a mixture of **1a** (0.30 cm^3, 2.10 mmol) and **3** (R^2 = Et) (0.64 g, 1.90 mmol) was stirred in dry CH_2Cl_2 (4 cm^3) at −30 °C for 1 h. The reaction mixture was allowed to warm to room temperature and concentrated under reduced pressure (finally under 0.2 mmHg at 40 °C for 30 min) to give the *title compound* **4a** (R^2 = Et) (0.86 g, quant.), which was more than 90% pure by 250 MHz ^1H NMR spectroscopic analysis. Distillation of this product gave analytically pure **4a** (R^2 = Et) (0.61 g) as a colourless oil; b.p. 105–109 °C/0.15 mmHg; $\nu_{max}(CHCl_3)/cm^{-1}$ 1670; δ_H(250 MHz; $CDCl_3$), 0.09 (9 H, s), 0.89 (9 H, t, *J* 7.0), 0.92–1.00 (6 H, m), 1.22 (3 H, t, *J* 7.0), 1.24–1.38 (6 H, m), 1.42–1.53 (6 H, m), 1.67 (1 H, s) and 3.96–4.10 (2 H, m); δ_C(67.5 MHz; $CDCl_3$) 0.1 (q), 11.0 (t), 13.6 (q), 14.5 (d), 23.2 (q), 27.3 (t), 28.8 (t), 59.5 (t) and 176.0 (s) (Found: C, 50.5; H, 9.25. $C_{19}H_{42}O_2SiSn$ requires C, 50.82; H, 9.43%).

*Ethyl α(*tert*-butyldimethylsilyl)-α-(tributylstannyl)acetate* **4b** (R^2 = Et). Similarly to the preparation of **4a**, the *title compound* **4b** (R^2 = Et) (0.61 g, quant.) was obtained from **1b** (0.25 cm^3, 1.4 mmol) and **3** (R^2 = Et) (0.39 g, 1.15 mmol). This product was about 90% pure, and was subjected to distillation to give analytically pure **4b** (R^2 = Et) (0.42 g) as a colourless oil; b.p. 114–120 °C/0.1 mmHg; $\nu_{max}(CHCl_3)/cm^{-1}$ 1675; δ_H(250 MHz; $CDCl_3$) 0.03 (3 H, s), 0.15 (3 H, s), 0.86–1.00 (6 H, m), 0.87 (9 H, s), 0.89 (9 H, t, *J* 7.0), 1.22 (3 H, t, *J* 7.0), 1.24–1.38 (6 H, m), 1.42–1.52 (6 H, m), 1.80 (1 H, s) and 4.03 (2 H, d, *J* 7.0); δ_C(67.5 MHz; $CDCl_3$) −4.9 (q), −3.7 (q), 11.3 (t), 13.6 (q), 14.4 (d), 18.8 (s), 19.7 (q), 26.5 (q), 27.3 (t), 28.8 (t), 59.5 (t) and 176.3 (s) (Found: C, 53.95; H, 9.75. $C_{22}H_{48}O_2SiSn$ requires C, 53.77; H, 9.85%).

Low temperature ^1H *NMR Study of* **4b** (R^2 = Et).—To a solution of **3** (R^2 = Et) (10 mg, 0.030 mmol) in dry CD_2Cl_2 (0.7 cm^3) in an NMR tube was added **1b** (7 mg, 0.045 mmol) at −70 °C. The reaction mixture was quickly subjected to ^1H NMR measurement at −30 °C then allowed to warm to room temperature; δ_H(500 MHz; CD_2Cl_2; −30 °C) −0.06 (3 H, s), 0.12 (3 H, s), 0.83 (9 H, s), 0.87 (9 H, t, *J* 7.3), 0.90–0.96 (6 H, m), 1.18 (3 H, t, *J* 7.3), 1.24–1.32 (6 H, m), 1.38–1.52 (6 H, m), 1.75 (1 H, s) and 3.90–3.97 (2 H, m).

General One-pot Procedure for the Preparation of α-(tert-*Butyldimethylsilyl*)-β-*hydroxy Esters* **7**.—Similarly to the preparation of **4a**, **1b** (1.3 mmol) and an alkoxystannane **3** (1.2 mmol) [anhydrous ZnI_2 (*ca.* 0.01 mmol) was added for entries 4–14 in Table 1] were stirred in dry CH_2Cl_2 (8 cm^3) at −30 °C for 2 h. The reaction mixture was cooled to −78 °C, and then an aldehyde **6** (1.0 mmol) and $TiCl_4$ (0.6 mmol) were successively added. The whole was stirred at −78 °C for 1 h, saturated aqueous $NaHCO_3$ solution (10 cm^3) was added and the mixture extracted with diethyl ether (2 × 15 cm^3). The combined organic layer was filtered through Celite pad with diethyl ether as an eluent. The filtrate was washed with brine, dried, and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate–hexane) to give the *ester* **7**. The diastereomeric ratio of **7** was determined by 250 MHz ^1H NMR analysis of both the crude and purified product. Analytically pure *syn*-**7** (except for **7a**) was obtained by column chromatography and/or recrystallization.

Ethyl (2R*,3S*)-2-(tert-*butyldimethylsilyl*)-3-*hydroxy*-3-*phenylpropionate* syn-**7a** *and its* (2R*,3R*)-*isomer* anti-**7a**. A 77:23 mixture was obtained as a colourless oil; ν_{max}($CHCl_3$)/cm^{-1} 3500, 1695 and 1600; δ_H(500 MHz; $CDCl_3$) 0.06 and 0.23 (3 H in total, 77:23 ratio, s each), 0.12 (3 H, s), 0.93 and 0.97 (9 H in total, 77:23 ratio, s each), 1.10 and 1.21 (3 H in total, 77:23 ratio, t, *J* 7.1 each), 2.72 (23/100 H, d, *J* 3.1), 2.74 (77/100 H, d, *J* 8.6), 3.95 and 3.97 (2 H in total, 77:23 ratio, q, *J* 7.1 each), 4.98 (23/100 H, dd, *J* 10.5 and 3.1), 5.16 (77/100 H, dd, *J* 8.6 and 3.1) and 7.20–7.35 (5 H, m) [Found: 251.1123. $C_{13}H_{19}O_3Si$ (M^+ − Bu^t) requires 251.1104].

Ethyl (2R*,3S*)-2-(tert-*butyldimethylsilyl*)-3-*hydroxy*-5-*phenylpentanoate* syn-**7b**. A colourless oil: ν_{max}($CHCl_3$)/cm^{-1} 3500, 1700 and 1600; δ_H(250 MHz; $CDCl_3$) 0.03 (3 H, s), 0.20 (3 H, s), 0.92 (9 H, s), 1.24 (3 H, t, *J* 7.0), 1.69–1.98 (2 H, m), 2.37 (1 H, d, *J* 6.0), 2.58–3.01 (2 H, m), 4.07 (2 H, q, *J* 7.0), 4.02–4.17 (1 H, m) and 7.15–7.34 (5 H, m) [Found: 279.1434. $C_{15}H_{23}O_3Si$ (M^+ − Bu^t) requires 279.1416].

Characteristic ^1H NMR spectroscopic data for *anti*-**7b**; δ_H(250 MHz; $CDCl_3$) 2.30 (1 H, d, *J* 3.1).

Methyl (2R*,3S*)-2-(tert-*butyldimethylsilyl*)-3-*hydroxy*-3-*phenylpropionate* syn-**7c**. A colourless oil: ν_{max}($CHCl_3$)/cm^{-1} 3550 and 1700; δ_H(250 MHz; $CDCl_3$) 0.04 (3 H, s), 0.13 (3 H, s), 0.92 (9 H, s), 2.76 (1 H, d, *J* 8.5), 3.48 (3 H, s), 5.16 (1 H, d, *J* 8.5) and 7.23–7.39 (5 H, m) [Found: 237.0962. $C_{12}H_{17}O_3Si$ (M^+ − Bu^t) requires 237.0947].

Characteristic ^1H NMR spectroscopic data for *anti*-**7c**; δ_H(250 MHz; $CDCl_3$) 0.11 (3 H, s), 0.22 (3 H, s), 0.96 (9 H, s), 2.74 (1 H, d, *J* 3.3), 3.53 (3 H, s) and 4.98 (1 H, d, *J* 3.3).

Neopentyl (2R*,3S*)-2-(tert-*butyldimethylsilyl*)-3-*hydroxy*-3-*phenylpropionate* syn-**7d**. White crystals: m.p. 71–71.5 °C (from hexane); ν_{max}($CHCl_3$)/cm^{-1} 3500 and 1695; δ_H(250 MHz; $CDCl_3$) 0.07 (3 H, s), 0.19 (3 H, s), 0.81 (9 H, s), 0.93 (9 H, s), 2.78 (1 H, d, *J* 8.8), 3.35 (1 H, d, *J* 10.5), 3.69 (1 H, d, *J* 10.5), 5.16 (1 H, d, *J* 8.8) and 7.23–7.38 (5 H, m) (Found: C, 68.65; H, 9.85. $C_{20}H_{34}O_3Si$ requires C, 68.57; H, 9.71%).

Characteristic ^1H NMR spectroscopic data for *anti*-**7d**; δ_H(250 MHz; $CDCl_3$) 0.14 (3 H, s), 0.24 (3 H, s), 0.76 (9 H, s), 0.96 (9 H, s), 2.74 (1 H, d, *J* 2.8) and 5.00 (1 H, d, *J* 2.8).

Neopentyl (2R*,3S*)-2-(tert-*butyldimethylsilyl*)-3-*hydroxy*-4-*methylpentanoate* syn-**7e**. White crystals: m.p. 45.5–46 °C (from hexane); ν_{max}($CHCl_3$)/cm^{-1} 3500 and 1695; δ_H(250 MHz; $CDCl_3$) 0.04 (3 H, s), 0.20 (3 H, s), 0.89 (3 H, d, *J* 7.0), 0.93 (9 H, s), 0.94 (3 H, d, *J* 7.0), 0.95 (9 H, s), 1.68–1.87 (1 H, m), 2.47 (1 H, d, *J* 9.5), 3.57 (1 H, d, *J* 10.8), 3.78 (1 H, d, *J* 10.8) and 3.91–4.01 (1 H, m) (Found: C, 64.4; H, 11.6. $C_{17}H_{36}O_3Si$ requires C, 64.60; H, 11.40%).

Isopropyl (2R*,3S*)-2-(tert-*butyldimethylsilyl*)-3-*hydroxy*-3-*phenylpropionate* syn-**7f**. White crystals; m.p. 72–72.5 °C (from hexane); ν_{max}($CHCl_3$)/cm^{-1} 3400 and 1695; δ_H(250 MHz; $CDCl_3$) 0.08 (3 H, s), 0.13 (3 H, s), 0.93 (9 H, s), 0.99 (3 H, d, *J* 5.8), 1.06 (3 H, d, *J* 5.8), 2.70 (1 H, d, *J* 8.5), 4.79 (1 H, septet, *J* 5.8), 5.13 (1 H, d, *J* 8.5) and 7.26–7.38 (5 H, m) (Found: C, 66.85; H, 9.35. $C_{18}H_{30}O_3Si$ requires C, 67.08; H, 9.32%).

Characteristic ^1H NMR spectroscopic data for *anti*-**7f**; δ_H(250 MHz; $CDCl_3$) 2.66 (1 H, d, *J* 2.8) and 4.97 (1 H, d, *J* 2.8).

Isopropyl (2R*,3S*)-2-(tert-*butyldimethylsilyl*)-3-*hydroxy*-5-*phenylpentanoate* syn-**7g**. A colourless oil; ν_{max}($CHCl_3$)/cm^{-1} 3500 and 1695; δ_H(250 MHz; $CDCl_3$) 0.05 (3 H, s), 0.19 (3 H, s), 0.90 (9 H, s), 1.22 (6 H, d, *J* 6.3), 1.75–1.95 (2 H, m), 2.32 (1 H, d, *J* 6.3), 2.59–2.94 (2 H, m), 4.04–4.17 (1 H, m), 4.97 (1 H, septet, *J* 6.3) and 7.14–7.35 (5 H, m) [Found: 277.1623. $C_{16}H_{25}O_2Si$ (M^+ − Bu^t) requires 277.1623].

Characteristic ^1H NMR spectroscopic data for *anti*-**7g**; δ_H(250 MHz; $CDCl_3$) 2.27 (1 H, d, *J* 2.3).

3-*Pentyl* (2R*,3S*)-2-(tert-*butyldimethylsilyl*)-3-*hydroxy*-3-*phenylpropionate* syn-**7h**. White crystals; m.p. 101.5–102 °C (from hexane); ν_{max}($CHCl_3$)/cm^{-1} 3500 and 1695; δ_H(250 MHz; $CDCl_3$) 0.07 (3 H, s), 0.17 (3 H, s), 0.54 (3 H, t, *J* 7.5), 0.78 (3 H, t, *J* 7.5), 0.96 (9 H, s), 1.25–1.45 (4 H, m), 2.72 (1 H, d, *J* 8.8), 4.52 (1 H, quintet, *J* 7.5), 5.13 (1 H, d, *J* 8.8) and 7.22–7.33 (5 H, m) (Found: C, 68.6; H, 9.75. $C_{20}H_{34}O_3Si$ requires C, 68.57; H, 9.71%).

Cyclopentyl (2R*,3S*)-2-(tert-*Butyldimethylsilyl*)-3-*hydroxy*-3-*phenylpropionate* syn-**7i**. White crystals; m.p. 84–84.5 °C (from hexane); ν_{max}($CHCl_3$)/cm^{-1} 3500 and 1695; δ_H(250 MHz; $CDCl_3$) 0.07 (3 H, s), 0.13 (3 H, s), 0.92 (9 H, s), 1.46–1.69 (8 H, m), 2.69 (1 H, d, *J* 8.5), 4.92–5.03 (1 H, m), 5.13 (1 H, d, *J* 8.5) and 7.23–7.41 (5 H, m) (Found: C, 68.9; H, 9.2. $C_{20}H_{32}O_3Si$ requires C, 68.97; H, 9.20%).

Characteristic ^1H NMR spectroscopic data for *anti*-**7i**; δ_H(250 MHz; $CDCl_3$) 2.65 (1 H, d, *J* 3.0).

Cyclohexyl (2R*, 3S*)-2-(tert-*butyldimethylsilyl*)-3-*hydroxy*-3-*phenylpropionate* syn-**7j**. White crystals; m.p. 97–97.5 °C (from hexane); ν_{max}($CHCl_3$)/cm^{-1} 3500 and 1695; δ_H(250 MHz; $CDCl_3$) 0.07 (3 H, s), 0.17 (3 H, s), 0.93 (9 H, s), 1.21–1.68 (10 H, m), 2.69 (1 H, d, *J* 8.6), 4.42–4.70 (1 H, m), 5.11 (1 H, d, *J* 8.6) and 7.22–7.34 (5 H, m) (Found: C, 69.5; H, 9.35. $C_{21}H_{34}O_3Si$ requires C, 69.61; H, 9.39%).

Cyclohexyl (2R*,3S*)-2-(tert-*butyldimethylsilyl*)-3-*hydroxy*-5-*phenylpentanoate* syn-**7k**. A colourless oil; ν_{max}($CHCl_3$)/cm^{-1} 3500, 1695 and 1600; δ_H(250 MHz; $CDCl_3$) 0.06 (3 H, s), 0.21 (3 H, s), 0.94 (9 H, s), 1.23–1.45 (10 H, m), 1.60–1.94 (2 H, m), 2.35 (1 H, d, *J* 5.6), 2.59–3.01 (2 H, m), 4.07–4.18 (1 H, m), 4.69–4.81 (1 H, m) and 7.18–7.34 (5 H, m) [Found: 258.1624. $C_{17}H_{22}O_2$ (M^+ − Bu^tMe_2SiOH) requires 258.1620].

Cyclohexyl (2R*,3S*)-2-(tert-*butyldimethylsilyl*)-3-*hydroxyheptanoate* syn-**7l**. A colourless oil; ν_{max}($CHCl_3$)/cm^{-1} 3500 and 1690; δ_H(250 MHz; $CDCl_3$) 0.05 (3 H, s), 0.21 (3 H, s), 0.90 (3 H, t, *J* 7.0), 0.94 (9 H, s), 1.18–1.91 (16 H, m), 2.30 (1 H, d, *J* 6.6), 3.98–4.10 (1 H, m) and 4.68–4.82 (1 H, m) (Found: C, 66.35; H, 11.1. $C_{19}H_{38}O_3Si$ requires C, 66.61; H, 11.18%).

Cyclohexyl (2R*,3S*)-2-(tert-*butyldimethylsilyl*)-3-*hydroxy*-4,4-*dimethylpentanoate* syn-**7m**. White crystals; m.p. 85–86 °C (from hexane); ν_{max}($CHCl_3$)/cm^{-1} 3500 and 1695; δ_H(250 MHz; $CDCl_3$) 0.03 (3 H, s), 0.17 (3 H, s), 0.89 (9 H, s), 0.93 (9 H, s), 1.30–1.88 (10 H, m), 2.48 (1 H, d, *J* 9.9), 4.02 (1 H, d, *J* 9.9) and 4.62–4.76 (1 H, m) (Found: C, 66.3; H, 11.2. $C_{19}H_{38}O_2Si$ requires C, 66.61; H, 11.18%).

Cyclohexyl (2R*,3S*)-2-(tert-*butyldimethylsilyl*)-3-*hydroxy*-4-*methylpentanoate* syn-**7n**. White crystals; m.p. 48.5–49 °C (from hexane); ν_{max}($CHCl_3$)/cm^{-1} 3500 and 1695; δ_H(250 MHz; $CDCl_3$) 0.05 (3 H, s), 0.20 (3 H, s), 0.94 (3 H, d, *J* 6.5), 0.94 (9 H, s), 0.95 (3 H, d, *J* 6.5), 1.25–1.88 (11 H, m), 2.41 (1 H, d, *J* 8.8), 3.87–3.96 (1 H, m) and 4.67–4.78 (1 H, m) (Found: C, 65.8; H, 11.05. $C_{18}H_{36}O_3Si$ requires C, 65.44; H, 11.08%).

Cyclohexyl (E)-*Cinnamate* (E)-**8j**. *Typical Procedure for the Preparation of* (E)-α,β-*Unsaturated Esters* (E)-**8**.—Under a nitrogen atmosphere, a solution of *syn*-**7j** (45 mg, 0.124 mmol) in dry THF (1 cm^3) was added into the suspension of NaH [5.0 mg of 60% oil suspension, 0.125 mmol, washed with dry pentane (2 × 1 cm^3) before use] in dry THF (1 cm^3) at room temperature. After being stirred for 1.5 h, saturated aqueous NH_4Cl (4 cm^3) was added and extracted with diethyl ether (2 × 5 cm^3). The combined organic layer was washed with brine, dried, and concentrated under reduced pressure. The residue was purified by preparative TLC (ethyl acetate–hexane, 1:9) to give the (*E*)-α,β-*unsaturated ester* (*E*)-**8j** (27 mg, 95%) as a colourless oil. Its geometric purity was judged to be more than 99% by 250 MHz ^{1}H NMR analysis of both crude and purified **8j**; ν_{max}(CHCl$_3$)/cm^{-1} 1690, 1640 and 1600; δ_H(250 MHz; CDCl$_3$) 1.35–1.95 (10 H, m), 4.72–4.91 (1 H, m), 6.43 (1 H, d, *J* 16.0), 7.34–7.54 (5 H, m) and 7.67 (1 H, d, *J* 16.0) (Found: C, 77.95; H, 8.05. $C_{15}H_{18}O_2$ requires C, 78.23; H, 7.88%).

Methyl (E)-*cinnamate* (E)-**8c**. A colourless oil; ν_{max}(CHCl$_3$)/cm^{-1} 1700, 1640 and 1600; δ_H(250 MHz; CDCl$_3$) 3.81 (3 H, s), 6.45 (1 H, d, *J* 16.5), 7.33–7.54 (5 H, m) and 7.69 (1 H, d, *J* 16.5).

Neopentyl (E)-*cinnamate* (E)-**8d**. A colourless oil; ν_{max}(CHCl$_3$)/cm^{-1} 1700, 1640 and 1600; δ_H(250 MHz; CDCl$_3$) 1.00 (9 H, s), 3.91 (2 H, s), 6.47 (1 H, d, *J* 16.3), 7.35–7.56 (5 H, m) and 7.69 (1 H, d, *J* 16.3) (Found: M$^+$, 218.1307. $C_{14}H_{18}O_2$ requires *M*, 218.1307).

Cyclohexyl (Z)-*Cinnamate* (Z)-**8j**. *Typical Procedure for the Preparation of* (Z)-α,β-*Unsaturated Esters* (Z)-**8**.—Under a nitrogen atmosphere, $BF_3\cdot OEt_2$ (27 mg, 0.19 mmol) was added into a solution of *syn*-**7j** (61 mg, 0.17 mmol) in dry CH_2Cl_2 (2 cm^3) at −20 °C. After being stirred for 4 h at the same temperature, the reaction mixture was quenched with saturated $NaHCO_3$ (5 cm^3). Similar extractive work-up to the preparation of (*E*)-**8j** and the subsequent purification gave the (*Z*)-α,β-*unsaturated ester* (*Z*)-**8j** (38 mg, 97%) as a colourless oil. Its geometric ratio (*E*:*Z* = 2:98) was determined by 250 MHz ^{1}H NMR analysis; ν_{max}(CHCl$_3$)/cm^{-1} 1705, 1625 and 1600; δ_H(250 MHz; CDCl$_3$) 1.17–1.89 (10 H, m), 4.70–4.85 (1 H, m), 5.94 (1 H, d, *J* 12.5), 6.92 (1 H, d, *J* 12.5) and 7.28–7.58 (5 H, m) (Found: C, 78.05; H, 8.0. $C_{15}H_{18}O_2$ requires C, 78.23; H, 7.88%).

Methyl (Z)-*cinnamate* (Z)-**8c**. A colourless oil; ν_{max}(CHCl$_3$)/cm^{-1} 1710, 1630 and 1600; δ_H(250 MHz; CDCl$_3$) 3.71 (3 H, s), 5.95 (1 H, d, *J* 12.8), 6.95 (1 H, d, *J* 12.8) and 7.31–7.60 (5 H, m).

Neopentyl (Z)-*cinnamate* (Z)-**8d**. A colourless oil; ν_{max}(CHCl$_3$)/cm^{-1} 1700, 1620 and 1600; δ_H(250 MHz; CDCl$_3$) 0.87 (9 H, s), 3.81 (2 H, s), 5.98 (1 H, d, *J* 12.8), 6.69 (1 H, d, *J* 12.8) and 7.29–7.58 (5 H, m) (Found: C, 76.7; H, 8.45. $C_{14}H_{18}O_2Si$ requires C, 77.03; H, 8.31%).

Pentan-3-*yl* (Z)-*cinnamate* (Z)-**8h**. A colourless oil; ν_{max}(CHCl$_3$)/cm^{-1} 1710, 1630 and 1600; δ_H(250 MHz; CDCl$_3$) 0.85 (6 H, t, *J* 6.3), 1.50–1.62 (4 H, m), 4.80 (1 H, quintet, *J* 6.3), 5.96 (1 H, d, *J* 12.5), 6.94 (1 H, d, *J* 12.5) and 7.30–7.60 (5 H, m) (Found: M$^+$, 218.1297. $C_{14}H_{18}O_2$ requires *M*, 218.1304).

Cyclohexyl (Z)-5-*phenylpent*-2-*enoate* (Z)-**8k**. A colourless oil; ν_{max}(CHCl$_3$)/cm^{-1} 1710, 1640 and 1600; δ_H(250 MHz; CDCl$_3$) 1.24–1.90 (10 H, m), 2.73–2.79 (2 H, m), 2.93–3.04 (2 H, m), 4.75–4.85 (1 H, m), 5.76 (1 H, dt, *J* 11.8 and 1.8), 6.20 (1 H, dt, *J* 11.8 and 7.5) and 7.14–7.32 (5 H, m) (Found: C, 78.65; H, 8.75. $C_{17}H_{22}O_2$ requires C, 79.03; H, 8.59%).

Cyclohexyl (Z)-4-*methylpent*-2-*enoate* (Z)-**8n**. A colourless oil; ν_{max}(CHCl$_3$)/cm^{-1} 1710 and 1640; δ_H(500 MHz; CDCl$_3$) 1.02 (6 H, d, *J* 6.7), 1.22–1.90 (10 H, m), 3.52–3.62 (1 H, m), 4.77–4.85 (1 H, m), 5.62 (1 H, d, *J* 11.6) and 5.96 (1 H, dd, *J* 11.6 and 9.8) (Found: M$^+$, 196.1471. $C_{12}H_{20}O_2$ requires *M*, 196.1464).

General Procedure for the One-pot Preparation of β-*Amino*-α-*silylesters* **12**. Similarly to the preparation of **7**, **1** (1.0 mmol) and **3** (1.05 mmol) were stirred at −40 °C and then cooled to −78 °C. To the reaction mixture were successively added **11** (0.85 mmol) and $TiCl_4$ (1.0 mmol). After being stirred at −78 °C for 1 h, the whole was allowed to gradually warm to room temperature overnight. Saturated $NaHCO_3$ (10 cm^3) was added, and the mixture was worked up and purified by column chromatography (ethyl acetate–hexane) similarly to the preparation of **7** to give the syn-β-*amino*-α-*silylester* **12**. Its diastereoisomeric purity (*syn*:*anti* = ≥98:2) was determined by 250 MHz ^{1}H NMR analysis of both the crude and purified product.

Methyl (2R*,3S*)-3-*benzylamino*-3-*phenyl*-2-(*trimethylsilyl*)-*propionate* syn-**12a**. White crystals: m.p. 97.5–98 °C (from hexane); ν_{max}(CHCl$_3$)/cm^{-1} 3400, 1710 and 1600; δ_H(270 MHz; CDCl$_3$) 0.18 (9 H, s), 2.47 (1 H, d, *J* 11.6), 3.40 (3 H, s), 3.48 (2 H, s), 4.03 (1 H, d, *J* 11.6) and 7.20–7.34 (10 H, m) (Found: C, 70.15; H, 7.7; N, 4.23. $C_{20}H_{27}NO_2Si$ requires C, 70.33; H, 7.97; N, 4.10%).

Methyl (2R*,3S*)-3-*benzylamino*-2-(tert-*butyldimethylsilyl*)-3-*phenylpropionate* syn-**12b**. White crystals; m.p. 87.5–88 °C (from hexane); ν_{max}(CHCl$_3$)/cm^{-1} 3400, 1710 and 1600; δ_H(200 MHz; CDCl$_3$) 0.06 (3 H, s), 0.25 (3 H, s), 0.95 (9 H, s), 2.62 (1 H, d, *J* 11.4), 3.34 (3 H, s), 3.43 (1 H, d, *J* 12.0), 3.50 (1 H, d, *J* 12.0), 4.00 (1 H, d, *J* 11.4) and 7.20–7.39 (10 H, m) (Found: C, 71.95; H, 8.55; N, 3.7. $C_{23}H_{33}NO_2Si$ requires C, 72.01; H, 8.67; N, 3.65%).

Methyl (2R*,3S*)-3-*benzylamino*-2-(tert-*butyldimethylsilyl*)-4-*methylpentanoate* syn-**12c**. A colourless oil; ν_{max}(CHCl$_3$)/cm^{-1} 3400, 1705 and 1600; δ_H(200 MHz; CDCl$_3$) 0.09 (3 H, s), 0.17 (3 H, s), 0.88 (9 H, s), 0.99 (3 H, d, *J* 6.8), 1.02 (3 H, d, *J* 6.8), 1.91–2.09 (1 H, m), 2.38 (1 H, d, *J* 10.0), 3.16 (1 H, dd, *J* 10.0 and 2.6), 3.62 (3 H, s), 3.88 (1 H, d, *J* 12.2), 3.90 (1 H, d, *J* 12.2) and 7.21–7.38 (5 H, m) (Found: C, 68.7; H, 10.1; N, 4.2. $C_{20}H_{35}NO_2Si$ requires C, 68.71; H, 10.09; N, 4.01%).

Ethyl (2R*, 3S*)-3-*benzylamino*-2-(tert-*butyldimethylsilyl*)-3-*phenylpropionate* syn-**12d**. White crystals; m.p. 50.5–51 °C (from hexane); ν_{max}(CHCl$_3$)/cm^{-1} 3500, 1705 and 1600; δ_H(250 MHz; CDCl$_3$) 0.07 (3 H, s), 0.25 (3 H, s), 0.95 (9 H, s), 0.95 (3 H, t, *J* 7.3), 2.53 (1 H, d, *J* 11.3), 3.41 (1 H, d, *J* 13.0), 3.48 (1 H, d, *J* 13.0), 3.68–3.85 (2 H, m), 3.96 (1 H, d, *J* 11.3) and 7.19–7.31 (10 H, m) (Found: C, 72.5; H, 8.95; N, 3.5. $C_{24}H_{35}NO_2Si$ requires C, 72.49; H, 8.87; N, 3.52%).

Methyl (2R*,3S*)-3-*benzylamino*-2-(*dimethylphenylsilyl*)-3-*phenylpropionate* syn-**12e**. White crystals; m.p. 83.5–84 °C (from hexane); ν_{max}(CHCl$_3$)/cm^{-1} 3430, 1730 and 1600; δ_H(250 MHz; CDCl$_3$) 0.43 (3 H, s), 0.49 (3 H, s), 2.69 (1 H, d, *J* 11.6), 3.23 (3 H, s), 3.29 (1 H, d, *J* 12.9), 3.36 (1 H, d, *J* 12.9), 4.00 (1 H, d, *J* 11.6) and 7.06–7.61 (15 H, m) (Found: C, 74.6; H, 7.35; N, 3.45. $C_{23}H_{33}NO_2Si$ requires C, 74.40; H, 7.23; N, 3.47%).

Ethyl (2R*,3S*)-3-*benzylamino*-2-(*dimethylphenylsilyl*)-4-*methylpentanoate* syn-**12f**. A colourless oil; ν_{max}(CHCl$_3$)/cm^{-1} 3500, 1705 and 1600; δ_H(270 MHz; CDCl$_3$) 0.36 (3 H, s), 0.42 (3 H, s), 0.85 (3 H, d, *J* 6.8), 0.90 (3 H, d, *J* 6.8), 1.13 (3 H, t, *J* 7.5), 2.00–2.10 (1 H, m), 2.47 (1 H, d, *J* 10.8), 3.25 (1 H, dd, *J* 10.8 and 2.8), 3.48 (1 H, d, *J* 12.0), 3.81 (1 H, d, *J* 12.0), 3.69–3.90 (2 H, m) and 7.10–7.38 (10 H, m) [Found: 142.0993. $C_8H_{14}O_2$ (M$^+$ − PhMe$_2$SiNHBn) requires 142.0993].

(2R*,3S*)-3-*Benzylamino*-2-(*dimethylphenylsilyl*)-3-*phenylpropan*-1-*ol* **13**.—Under a nitrogen atmosphere, a solution of **12e** (143 mg, 0.35 mmol) in dry diethyl ether (14 cm^3) was added to an ice-cooled suspension of $LiAlH_4$ (54 mg, 1.4 mmol) in dry diethyl ether (2 cm^3), and the reaction mixture was stirred at 0 °C for 10 min and then at room temperature for 30 min. The whole was poured portionwise into a mixture of water and diethyl ether. Usual extractive work-up with diethyl ether and the subsequent purification by column chromatography (ethyl acetate–hexane, 3:1) gave **13** (117 mg, 89%) as a colourless gum; ν_{max}(CHCl$_3$)/cm^{-1} 3300 and 1600; δ_H(200 MHz; CDCl$_3$) 0.06 (3 H, s), 0.10 (3 H, s), 1.95 (1 H, ddd, *J* 9.6, 4.4 and 3.2), 3.58 (1 H, d, *J* 12.9), 3.66 (1 H, d, *J* 12.9), 3.75 (1 H, dd, *J* 11.4 and 3.2), 4.00 (1 H, dd, *J* 11.4 and 9.6), 4.14 (1 H, d, *J* 4.4) and 7.14–7.48 (15 H, m) (Found: M$^+$, 375.2032. $C_{24}H_{29}NOSi$ requires *M*, 375.2109).

(4S*,5R*)-3-*Benzyl*-5-(*dimethylphenylsilyl*)-4-*phenyltetrahydro*-1,3-*oxazin*-2-*one* **14**.—Under a nitrogen atmosphere, a solution of **13** (11.3 mg, 0.030 mmol) in dry THF (0.2 cm^3) was added to a suspension of NaH (2 mg of 60% oil suspension, 0.060 mmol, washed with dry pentane before use) in dry THF (0.3 cm^3) at −20 °C. *N,N'*-Carbonyldiimidazole (26 mg, 0.16 mmol) was added, and the whole was stirred at room temperature for 30 min and then at 75 °C for 5 h. After being cooled, the reaction mixture was poured into ice-cooled saturated NH_4Cl, and extracted with diethyl ether (2 × 5 cm^3). The combined organic layer was washed with brine, dried, and concentrated under reduced pressure. Purification of the residue by preparative TLC (ethyl acetate–CH_2Cl_2, 1:30) gave the *title compound* **14** (7.1 mg, 59%) as a pale yellow gum; $\nu_{max}(CHCl_3)/cm^{-1}$ 1675 and 1600; δ_H(270 MHz; $CDCl_3$) −0.18 (3 H, s), −0.14 (3 H, s), 2.10 (1 H, ddd, *J* 13.2, 5.3 and 4.3), 3.46 (1 H, d, *J* 15.2), 4.27 (1 H, ddd, *J* 11.6, 4.3 and 1.5), 4.35 (1 H, dd, *J* 5.3 and 1.5), 4.60 (1 H, dd, *J* 13.2 and 11.6), 5.20 (1 H, d, *J* 15.2), 6.95–7.00 (2 H, m) and 7.17–7.41 (13 H, m) (Found: M$^+$, 401.1791. $C_{25}H_{27}NO_2Si$ requires *M*, 401.1811).

(2R*,3S*)-1-*Acetoxy*-3-(N-*benzylacetamido*)-2-(*dimethylphenylsilyl*)-3-*phenylpropane* **15**.—Under a nitrogen atmosphere, acetyl chloride (0.16 cm^3, 2.2 mmol) and pyridine (0.35 cm^3, 4.4 mmol) were added to an ice-cooled solution of **13** (83.5 mg, 0.22 mmol) in dry CH_2Cl_2 (2.5 cm^3). The whole was stirred at 0 °C for 2 h, and ice–water was added. Usual extractive work-up with CH_2Cl_2 and the purification by column chromatography (ethyl acetate–hexane, 1:3) gave the *title compound* **15** (93 mg, 95%) as white crystals; m.p. 163–163.5 °C (from hexane); $\nu_{max}(CHCl_3)/cm^{-1}$ 1725, 1635 and 1600; δ_H(270 MHz; $CDCl_3$) 0.38 (3 H, s), 0.60 (3 H, s), 1.50 (3 H, s), 2.00 (3 H, s), 2.23 (1 H, ddd, *J* 12.5, 3.3 and 2.6), 3.03 (1 H, d, *J* 18.5), 3.97 (1 H, dd, *J* 11.6 and 2.6), 4.03 (1 H, d, *J* 18.5), 4.27 (1 H, dd, *J* 11.6 and 3.3), 6.11 (2 H, d, *J* 7.3), 6.33 (1 H, d, *J* 12.5) and 6.82–7.63 (13 H, m) (Found: C, 73.1; H, 7.3; N, 2.95. $C_{28}H_{33}NO_3Si$ requires C, 73.16; H, 7.23; N, 3.05%).

(2R*,3S*)-1,2-*Diacetoxy*-3-(N-*benzylacetamido*)-3-*phenylpropane* **17**.—Under a nitrogen atmosphere, bromine (40 mg, 0.25 mmol) was added to a solution of **15** (20 mg, 0.044 mmol) in dry CH_2Cl_2 (1 cm^3) at room temperature. After being stirred for 2 h, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in THF (1 cm^3), and isopropyl alcohol (0.04 cm^3, 0.5 mmol) and Et_3N (0.015 cm^3, 0.1 mmol) were added. The whole was stirred at room temperature for 1 h, and water (2 cm^3) and CH_2Cl_2 (3 cm^3) were added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 cm^3). The combined organic layer was washed with brine, dried, and concentrated under reduced pressure to give the crude (isopropoxy)silane **16** (25 mg) as a colourless oil: δ_H(270 MHz; $CDCl_3$) 0.26 (3 H, s), 0.31 (3 H, s), 1.21 (3 H, d, *J* 6.0), 1.24 (3 H, d, *J* 6.0), 1.85 (3 H, s), 1.97 (3 H, s), 2.06–2.20 (1 H, m), 3.88 (1 H, dd, *J* 11.3 and 1.5), 4.09 (1 H, septet, *J* 6.0), 4.25 (1 H, dd, *J* 11.3 and 3.1), 4.63 (2 H, br s), 6.27 (1 H, d, *J* 12.8) and 6.97–7.48 (10 H, m).

The above crude **16** (25 mg) was dissolved in THF–MeOH (1:1, 0.6 cm^3), to which were added KF (8 mg, 0.14 mmol), $KHCO_3$ (14 mg, 0.14 mmol), and 30% H_2O_2 (0.05 cm^3). The reaction mixture was stirred overnight and quenched with aqueous $Na_2S_2O_3$ (2 cm^3). The usual extractive work-up with CH_2Cl_2 gave a crude product, which was dissolved in dry CH_2Cl_2 (1 cm^3). Pyridine (0.07 cm^3, 0.90 mmol), Ac_2O (0.04 cm^3, 0.45 mmol) and 4-(*N,N*-dimethylamino)pyridine (6 mg, 0.045 mmol) were added, and the whole was stirred overnight and then concentrated under reduced pressure. The residue was purified by preparative TLC (ethyl acetate–hexane, 2:1) to give the *title compound* **17** (11 mg, 64%) as a colourless gum; $\nu_{max}(CHCl_3)/cm^{-1}$ 1740, 1640 and 1600; δ_H(270 MHz; $CDCl_3$) 1.96 (3 H, s), 2.01 (3 H, s), 2.07 (3 H, s), 3.84 (1 H, dd, *J* 12.2 and 6.3), 4.36 (1 H, dd, *J* 12.2 and 2.3), 4.43 (1 H, d, *J* 17.8), 4.58 (1 H, d, *J* 17.8), 5.92 (1 H, ddd, *J* 10.5, 6.3 and 2.3), 6.09 (1 H, d, *J* 10.5), 6.76–6.80 (2 H, m), 7.04–7.13 (3 H, m) and 7.21–7.41 (5 H, m) (Found: M$^+$, 383.1733. $C_{22}H_{25}NO_5$ requires *M*, 383.1733).

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