

Synthesis of Enantiopure β - and γ -Amino Alcohols from Homochiral α - and β -Aminoacylsilanes as Stable Synthetic Equivalents of α - and β -Amino Aldehydes

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A practical route is described for the synthesis of enantiopure β - and γ -amino alcohols with two stereocenters, starting from homochiral α - (**1** and **5**) and β - (**13** and **16**) -aminoacylsilanes, and involving stereoselective addition of allylmethyl compounds and subsequent stereospecific protidesilylation of the adducts. The degree of diastereoselectivity achieved in the nucleophilic addition step depends on both the nitrogen-protecting group and the reagents used. Diastereomeric excess (*de*) values equal to or higher than 98% were obtained in the TiCl_4 -promoted allylation of the *N*-Pht-

aminoacylsilanes **1** and **13** and of the *N*-Ts-aminoacylsilane **5** with allyltrimethylsilane. Lower *de* values were obtained in the $\text{Sc}(\text{OTf})_3$ -catalyzed allylation of **5** with tetraallyltin and in the additions of both allyltrimethylsilane and tetraallyltin to the *N*-Ts- β -aminoacylsilane **16**. Protidesilylation of the adducts, leading to the β - and γ -amino alcohols, was accomplished with TBAF, except in the case of the adducts obtained from **5**. For these, a preliminary removal of the tosyl group was necessary, which was accomplished with simultaneous desilylation by treatment with Na in liquid ammonia.

Much effort has been directed towards the synthesis of enantiopure β -amino alcohols with two stereocenters due to their numerous and important applications as peptidomimetics,^[1,2] as building blocks in the synthesis of pharmaceuticals,^[1,3] and as ligands for asymmetric catalysis.^[4–7] One of the most straightforward methodologies for the synthesis of optically active β -amino alcohols involves the diastereoselective addition of organometallic reagents to *N*-protected α -amino aldehydes, which, in turn, are accessible from the corresponding α -amino acids.^[1,8–11] However, it is well known^[1] that most *N*-protected α -amino aldehydes are relatively unstable, both chemically and configurationally, and must be used immediately after their preparation. Another problem is the low degree of stereoselectivity often associated with the addition step.^[1,12] Specific variations of the protecting groups and reagents have been partly successful in overcoming these problems.^[9,10]

Enantiopure γ -amino alcohols containing two stereocenters, a structural motif quite commonly encountered in natural products,^[13,14] are important compounds in the pharmacological field^[15,16] and have recently found widespread use as chiral catalysts.^[17] Many methods are known for their synthesis. The most commonly used procedure involves the reduction of β -amino carbonyl compounds^[13,18]

or of heterocycles such as 2-isoxazolines.^[19] To the best of our knowledge, a synthetic protocol analogous to that used for β -amino alcohols, starting in this case from β -amino aldehydes, has never been reported, probably because of the highly unstable nature of these precursors.^[20]

We have previously reported^[21] that homochiral α - and β -aminoacylsilanes, obtained from natural α -amino acids, can be used as stable synthetic equivalents of α - and β -amino aldehydes in the diastereoselective synthesis of optically active β - and γ -amino alcohols, respectively. This approach is based on the possibility of stereospecifically replacing the silyl group with a proton in the initially formed α -hydroxysilanes. Moreover, the use of acylsilanes as synthetic equivalents of the corresponding aldehydes has the advantage of increasing the degree of stereoselectivity in the nucleophilic addition step, due to the bulkiness of the silyl group.^[22–24]

In this paper we wish to report the results of a more extensive study on the synthesis of β - and γ -amino alcohols by the reaction of homochiral α - and β -aminoacylsilanes bearing different protecting groups at the nitrogen atom with allylmethyl compounds, which, among the various organometallics, have a prominent position due to the various possibilities for further transformation of the homoallylic function.^[25]

Results and Discussion

Synthesis of β -Amino Alcohols

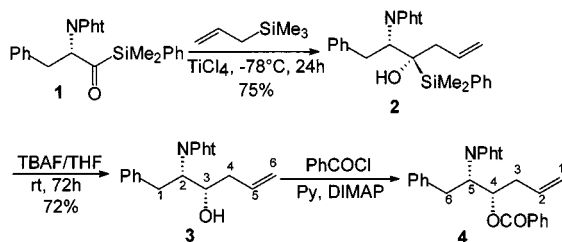
The α -aminoacylsilanes selected for study were (*S*)-dimethyl(phenyl)(3-phenyl-2-phthalimidopropanoyl)silane (**1**)^[26] and (*S*)-dimethyl(phenyl)(3-phenyl-2-tosylamidopro-

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panoyl)silane (**5**), both of which are stable compounds that can be purified and stored. In our preliminary communication^[21] we reported the allylation of **1** by treatment with allyltrimethylsilane in the presence of 1 equiv. of titanium tetrachloride in CH₂Cl₂ for 24 h at –78 °C. Under these conditions, the allylated α -hydroxysilane **2** was obtained in 75% yield. The ¹H- and ¹³C-NMR spectra of **2** showed the presence of a single diastereoisomer, thus suggesting *de* values equal to or higher than 98% (see General in the Experimental Section) (Scheme 1).



Scheme 1. Synthesis of (2*S*,3*S*)-1-phenyl-2-phthalimido-5-hexen-3-ol **3** and its conversion into the benzoyl derivative **4**

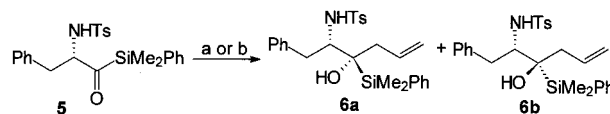
Subsequent protidesilylation of **2** with tetrabutylammonium fluoride (TBAF) in THF gave stereospecifically the *syn*-amino alcohol, viz. (2*S*,3*S*)-1-phenyl-2-phthalimido-5-hexen-3-ol (**3**), in 60% yield (Scheme 1). The (*S*) configuration at C-3 was determined, after conversion to (4*S*,5*S*)-4-benzoyloxy-6-phenyl-5-phthalimido-1-hexene (**4**) (Scheme 1), from the sign of the exciton Cotton effect resulting from the coupling of the π - π^* transitions of the phthalimide and benzoate chromophores (see Supporting Information).

Having established that the *syn*-amino alcohol **3** had been formed, we tentatively assigned the *syn* configuration to compound **2** as well. In fact, it is known^[22] that TBAF-induced protidesilylation of α -hydroxysilanes, derived from acylsilanes bearing an α -chiral carbon atom, proceeds with retention of configuration. Moreover, the presence of TiCl₄ should favour a chelation-controlled addition^[9] leading to the *syn* diastereoisomer.

Next, we attempted the scandium triflate catalyzed allylation of acylsilane **1** with tetraallyltin according to the Kobayashi methodology,^[27] but in the case at hand the procedure failed and **1** was recovered almost quantitatively. Since this protocol has proved to be successful in the allylation of aliphatic and aromatic acylsilanes,^[28] we inferred that its failure might have been due to some incompatibility between the Lewis acid and the phthaloyl protecting group in **1**. Indeed, a change of the *N*-protecting group from phthaloyl to tosyl allowed successful allylation using both of the aforementioned methodologies.

The reaction of acylsilane **5** with tetraallyltin (0.5 equiv.) in the presence of Sc(OTf)₃ (7 mol-%) was investigated with regard to the optimal conditions of temperature and time. From these experiments, it was established that the best results were achieved at 20 °C with a reaction time of 90 min. Under these conditions, a 75:25 mixture of (2*S*,3*R*)-3-dimethylphenylsilyl-1-phenyl-2-tosylamido-5-hexen-3-ol (**6a**) and (2*S*,3*S*)-3-dimethylphenylsilyl-1-phenyl-2-tosylamido-

5-hexen-3-ol (**6b**) was obtained in 88% yield (Scheme 2, path a).

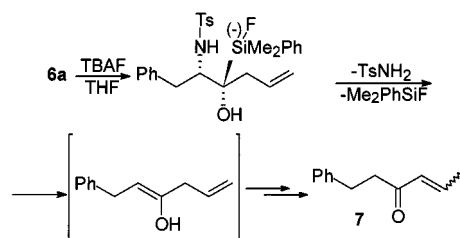


Scheme 2. a) tetraallyltin (0.5 equiv.), Sc(OTf)₃ (7 mol-%), 20 °C, 90 min, **6a**/**6b** = 75:25, 88%; b) allyltrimethylsilane (2 equiv.), TiCl₄ (1 equiv.), –78 °C, 8 h, only **6a**, 60%

Compounds **6a** and **6b** were separated on silica gel plates (eluent: CH₂Cl₂) and were assigned the *syn* (2*S*,3*R*) and the *anti* (2*S*,3*S*) relative configurations, respectively, with the aid of NOE techniques (see Experimental Section).

Allylation of the same acylsilane **5** with allyltrimethylsilane in the presence of 1 equiv. of TiCl₄ for 8 h at –78 °C gave the *syn* adduct **6a** in 60% yield as a single diastereoisomer, as was apparent from analysis of its NMR spectra, thus suggesting a *de* value equal to or higher than 98% (Scheme 2, path b). The high *syn* selectivity observed in this reaction can be attributed, in terms of a “Cram chelating model”, to the presence of TiCl₄, which is known to give very constrained chelated transition states.^[9] The lower diastereoselectivity observed in the reaction of **5** with tetraallyltin and Sc(OTf)₃ can probably be attributed to a reduced chelation ability of this Lewis acid owing to both its greater size and the lower charge on scandium, which allows an increase in the degrees of freedom.

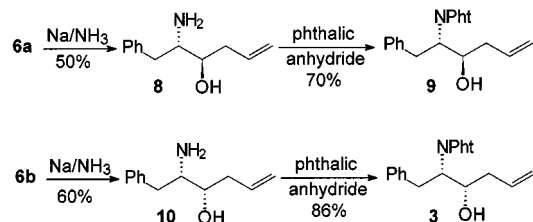
In order to complete our protocol for the synthesis of β -amino alcohols, the replacement of the silyl group by a proton was investigated. Treatment of **6a** with TBAF in THF led to 1-phenyl-4-hexen-3-one (**7**) in 30% yield, besides other unidentified products, rather than to the expected desilylated amino alcohol. The formation of this compound can be rationalized in terms of a facile β -elimination reaction, favoured by the good leaving group ability of tosylamido, occurring in the initial intermediate formed by attack of the fluoride ion on the silicon atom, followed by isomerization (Scheme 3).



Scheme 3. Reaction of **6a** with TBAF

Removal of the tosyl group prior to desilylation was therefore investigated. Treatment of compound **6a** with Na in liquid ammonia led to both deprotection of the amino group and to desilylation, with the formation of the *anti*-amino alcohol (2*S*,3*R*)-2-amino-1-phenyl-5-hexen-3-ol (**8**) as a single diastereoisomer in 50% yield. The *anti* relative stereochemistry in **8** was assigned through its conversion to the *N*-phthaloyl derivative **9**, which turned out to be the

diastereoisomer of the corresponding *syn* derivative **3** (Scheme 4).



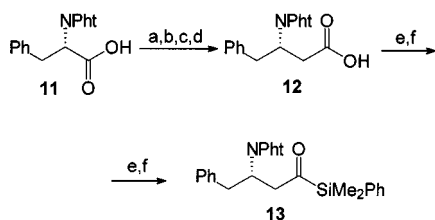
Scheme 4. Deprotection and desilylation of **6a** and **6b**, followed by transformation of **8** and **10** into the phthaloyl derivatives **9** and **3**

Analogous treatment with Na in liquid ammonia of the *anti*- α -hydroxysilane **6b** gave the *syn*-(2*S*,3*S*)-amino alcohol **10** in 60% yield, and indeed, its reaction with phthalic anhydride gave the *syn* derivative **3** (Scheme 4). Under these basic conditions, the desilylation of **6a** and **6b** most probably occurs by a Brook rearrangement^[29] with inversion of configuration at C-3, followed by hydrolysis.

Synthesis of γ -Amino Alcohols

As starting β -aminoacylsilanes, we used homologues of **1** and **5**, specifically (*S*)-dimethyl(phenyl)(4-phenyl-3-phthalimidobutanoyl)silane (**13**) and (*S*)-dimethyl(phenyl)(4-phenyl-3-tosylamidobutanoyl)silane (**16**), both of which were derived from L-phenylalanine.

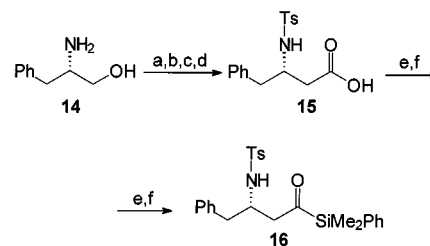
For the synthesis of **13**, *N*-Pht-L-phenylalanine^[30] (**11**) was homologated by means of the Arndt–Eistert reaction to give (*S*)-4-phenyl-3-phthalimidobutanoic acid (**12**), from which **13** was obtained following sequential chlorination–silylcupration^[21] (Scheme 5).



Scheme 5. a) ref.^[30], 90%; b) CH₂N₂, Et₂O/THF, r.t., 1 h, 94%; c) Ag₂O, MeOH, 50°C, 40 min, 87%; d) HCl, H₂O, acetone, reflux, 150 min, 81%; e) SOCl₂, 55°C, 4 h, 93%; f) (PhMe₂Si)₂CuCN(Li)₂, –78°C, 1 h, 55%

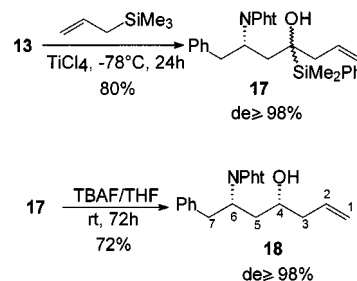
For the synthesis of **16**, we started from commercially available L-phenylalaninol (**14**), derived from L-phenylalanine, which, by tosylation, iodination, cyanide displacement, and hydrolysis, was converted to (*S*)-4-phenyl-3-tosylamidobutanoic acid (**15**). Sequential chlorination–silylcupration was again used to convert **15** to **16** (Scheme 6).

The *N*-Ts- β -aminoacylsilane **16**, as well as the corresponding *N*-Pht derivative **13**, proved to be stable compounds.^[21] As previously reported,^[21] the TiCl₄-mediated addition of allyltrimethylsilane to the β -aminoacylsilane **13** by reaction at –78°C for 24 h gave the α -hydroxysilane **17** in 80% yield and with a *de* value equal to or higher than 98%. Subsequent protidesilylation of **17** with TBAF in



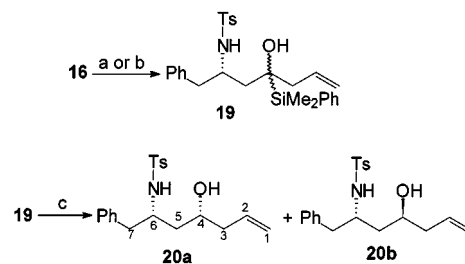
Scheme 6. a) TsCl, THF/H₂O, r.t., 9 h, 98%; b) Ph₃P, I₂, imidazole, CH₃CN, 95–100°C, 1 h, 90%; c) Bu₄CN, CH₃CN, 70°C, 4 h, 65%; d) H₂SO₄, CH₃COOH, H₂O, 110°C, 9 h, 70%; e) SOCl₂, 55–60°C, 6 h, 95%; f) (PhMe₂Si)₂CuCN(Li)₂, –78°C, 1 h, 50%

THF gave stereospecifically the (4*R*,6*R*)-7-phenyl-6-phthalimido-1-hepten-4-ol (**18**) in 72% yield (Scheme 7). In this case, the absolute stereochemistry of the newly formed stereogenic center (C-4) was assigned using the Mosher method,^[31] as already reported in our preliminary communication.^[21]



Scheme 7. Synthesis of (4*R*,5*R*)-7-phenyl-6-phthalimido-1-hepten-4-ol **18**

When the β -aminoacylsilane **16** was allylated under the same conditions, the α -hydroxysilane **19** was obtained in 62% yield and with 64% *de* (Scheme 8, path a). The allylation of **16** was also performed with 0.5 equiv. of tetraallyltin in the presence of 7 mol-% Sc(OTf)₃ by reaction at 20°C for 24 h, which afforded **19** in 96% yield and with 50% *de* (Scheme 8, path b).



Scheme 8. a) allyltrimethylsilane, TiCl₄ (1 equiv.), –78°C, 24 h, *de* 64%, 62%; b) tetraallyltin (0.5 equiv), Sc(OTf)₃ (7 mol-%), 20°C, 24 h, *de* 50%, 96%; c) TBAF, THF, r.t., 72 h, starting from **19** *de* 50%, 72%

The α -hydroxysilane **19** (*de* 50%) was subsequently treated with TBAF in THF, giving a 75:25 mixture of the two diastereoisomers (4*R*,6*R*)-7-phenyl-6-tosylamido-1-hepten-4-ol (**20a**) and (4*S*,6*R*)-7-phenyl-6-tosylamido-1-hepten-4-ol (**20b**) in 72% yield (Scheme 8, path c). The isomers **20a** and **20b** were separated on silica gel plates (eluent: dichloromethane/light petroleum ether, 5:1). The absolute

stereochemistry of the newly formed stereogenic center (C-4) was determined for the major diastereoisomer **20a** by ^1H -NMR analysis of the corresponding esters of the Mosher's acids (*R*)-MTPA and (*S*)-MTPA. From the differences in the chemical shifts, the configuration at C-4 could be assigned as *R*^[31] (Table 1).

Table 1. Determination of the absolute configuration of **20a**

	δ_{H} C(1)	δ_{H} C(3)	δ_{H} C(5)	δ_{H} C(7)
(<i>R</i>)-MTPA ester of 20a	4.862	5.508	1.816	2.709
(<i>S</i>)-MTPA ester of 20a	4.966	5.625	1.746	2.591
$\Delta\delta_{\text{H}} = \delta_{(\text{R})} - \delta_{(\text{S})}$	-0.104	-0.117	+0.070	+0.118

Concluding Remarks

The results reported herein illustrate a means of obtaining enantiopure β - and γ -amino alcohol units, starting from the α -amino acids of the chiral pool, that avoids the problems associated with the use of α - and β -amino aldehydes. In fact, the α -aminoacylsilanes **1** and **5** and the β -aminoacylsilanes **13** and **16** used as precursors are stable compounds that can be purified, handled, and stored without any problems. The degree of stereoselectivity achieved in the addition step is strongly dependent on both the type of protecting groups and the reagents, as previously reported by Reetz^[9] for the reactions of α -amino aldehydes. In fact, with the bulky phthaloyl *N*-protecting group, a very high diastereoselectivity is obtained with both the α - and β -aminoacylsilanes **1** and **13**.

With the tosyl group, a high degree of diastereoselectivity is achieved only under conditions which allow the formation of a constrained five-membered ring chelate, as in the reaction of the α -aminoacylsilane **13** with allyltrimethylsilane in the presence of TiCl_4 . In other cases, mixtures of two diastereoisomers are formed, which can be separated either at the α -hydroxysilane stage, with subsequent stereospecific protidesilylation of the two isomers, or at the stage of the protidesilylated compounds, thereby furnishing enantiopure *syn*- and *anti*- β - and γ -amino alcohols.

Experimental Section

General: Melting points, determined using a capillary apparatus, are uncorrected. — ^1H - and ^{13}C -NMR spectra were recorded using CDCl_3 solutions at 200 and 50.3 MHz, respectively, with a Varian Gemini 200, or at 300 and 75.4 MHz, respectively, with a Varian Gemini 300. Chemical shifts are reported in ppm relative to CHCl_3 ($\delta = 7.23$ for ^1H and $\delta = 77.0$ for ^{13}C). — IR spectra were recorded with a Perkin-Elmer 257 spectrometer. — Mass spectra were obtained with a VG 7070E spectrometer at an ionizing voltage of 70 eV. — $[\alpha]_{\text{D}}$ values were determined with a Jasco Dip-360 polarimeter. — UV spectra were recorded with a Shimadzu 160 spectrophotometer. — CD spectra were obtained with a Jobin-Yvon dichrograph III. — Moisture-sensitive reactions were carried out in oven-dried (120°C) glassware under Ar. Transfers of anhydrous solvents or of mixtures were accomplished using standard syringe/

septum techniques. THF was distilled immediately prior to use from sodium/benzophenone ketyl under Ar. CH_2Cl_2 was passed through basic alumina and distilled from CaH_2 prior to use. Other solvents were purified by standard procedures. Light petroleum ether refers to the fraction with b.p. $40\text{--}60^\circ\text{C}$. The reactions were monitored by TLC on Baker-flex IB2-F silica gel plates. Column chromatography was performed with Merck 70–230 mesh silica gel 60. Preparative TLC was carried out on glass plates using a 1 mm layer of Merck silica gel Pf_{254} . — (*S*)-Dimethyl(phenyl)(3-phenyl-2-phthalimidopropanoyl)silane (**1**) was obtained as described previously.^[26] — The diastereoisomer ratios of the diastereomeric mixtures were determined from the ^1H -NMR spectra of the crude products by integration of well-separated signals. In cases where the NMR spectra were indicative of the presence of a single diastereoisomer (**2**, **3**, **6a** obtained from **5** and allyltrimethylsilane/ TiCl_4 , **17** and **18**), the *de* values were estimated from a measure of the signal-to-noise ratio of the NMR spectra of the crude products.

Reaction of 1 with Allyltrimethylsilane: To a stirred solution of the acylsilane **1** (0.40 g, 0.97 mmol) in CH_2Cl_2 (1.5 mL) at -78°C , allyltrimethylsilane (0.22 g, 1.94 mmol) was added, followed by a 1.0 M solution of TiCl_4 (0.97 mL, 0.97 mmol) in CH_2Cl_2 . The reaction mixture was stirred under Ar at -78°C until the starting material **1** was no longer detectable by TLC analysis (24 h). Saturated aqueous NH_4Cl solution (10 mL) and CH_2Cl_2 (10 mL) were then added and the mixture was allowed to warm to room temperature (r.t.). The organic layer was separated, washed with saturated aqueous NH_4Cl solution, and dried with MgSO_4 . After removal of the solvent in vacuo, the crude residue was submitted to ^1H - and ^{13}C -NMR analysis, which showed the presence of a single diastereoisomer. The product was then purified by column chromatography on silica gel (light petroleum ether/ Et_2O , 3:1), affording 0.35 g (75% yield) of pure (2*S*,3*R*)-3-(dimethylphenylsilyl)-1-phenyl-2-phthalimido-5-hexen-3-ol (**2**) as a white crystalline solid; m.p. $128\text{--}130^\circ\text{C}$. — $[\alpha]_{\text{D}} = -7.3$ ($c = 2.14$, C_6H_6). — ^1H NMR (200 MHz, CDCl_3): $\delta = 7.87\text{--}7.39$ (m, 9 H), $7.10\text{--}6.86$ (m, 5 H), $5.80\text{--}5.60$ (m, 1 H), $4.90\text{--}4.70$ (m, 3 H), 4.45 (s, 1 H), 3.29 (dd, $J = 13.9$, 11.7 Hz, 1 H), 2.94 (dd, $J = 13.9$, 3.9 Hz, 1 H), $2.55\text{--}2.23$ (m, 2 H), 0.55 (s, 6 H). — ^{13}C NMR (50.3 MHz, CDCl_3): $\delta = 171.76$, 167.58 , 137.74 , 137.32 , 134.73 , 134.08 , 133.91 , 133.16 , 131.21 , 129.35 , 128.82 , 128.12 , 127.82 , 126.83 , 123.27 , 123.16 , 117.64 , 70.97 , 59.58 , 43.73 , 34.97 , -3.50 , -3.91 . — IR (CCl_4): $\tilde{\nu} = 3440\text{ cm}^{-1}$, 1770 , 1715 . — MS; m/z : 455 [M^+], 440 , 414 , 364 , 308 , 135 . — $\text{C}_{28}\text{H}_{29}\text{NO}_3\text{Si}$ (455.63): calcd. C 73.82, H 6.42, N 3.08; found C 73.41, H 6.39, N 3.05.

(2*S*,3*S*)-1-Phenyl-2-phthalimido-5-hexen-3-ol (3): To a stirred solution of the α -hydroxysilane **2** (100 mg, 0.22 mmol) in dry THF (3 mL) at r.t. was added a 1.0 M solution of TBAF (0.24 mL, 0.24 mmol) in THF and the reaction mixture was stirred under Ar at r.t. for 72 h. A saturated aqueous NH_4Cl solution (5 mL) followed by Et_2O (20 mL) was then added. The organic layer was separated, washed three times with water, and dried with MgSO_4 . After evaporation of the solvent in vacuo, the crude residue was submitted to ^1H -NMR analysis, which showed the presence of a single diastereoisomer. The product was then purified by column chromatography on silica gel (light petroleum ether/ Et_2O , 3:1), affording 42 mg (60%) of pure **3** as a white crystalline product; m.p. $110\text{--}112^\circ\text{C}$. — $[\alpha]_{\text{D}} = -37.8$ ($c = 1.14$, CH_2Cl_2). — ^1H NMR (300 MHz, CDCl_3): $\delta = 7.80\text{--}7.60$ (m, 4 H), $7.15\text{--}7.05$ (m, 5 H), $5.90\text{--}5.70$ (m, 1 H), $5.05\text{--}4.95$ (m, 2 H), $4.60\text{--}4.50$ (m, 1 H), $4.02\text{--}3.95$ (m, 1 H), 3.65 (br. d, $J = 9.4$ Hz, 1 H), 3.20 (dd, $J = 7.9$, 3.1 Hz, 2 H), 2.20 (t, $J = 6.9$ Hz, 2 H). — ^{13}C NMR (75.4 MHz, CDCl_3): $\delta = 169.53$, 137.35 , 134.18 , 133.79 , 131.45 , 129.07 , 128.44 , 126.63 , 123.42 , 117.96 , 71.09 , 57.47 , 39.82 , 35.44 . — IR (CCl_4): $\tilde{\nu} = 3460$

cm^{-1} , 1775, 1745, 1705. – MS; (m/z): 321 [M^+], 280, 262, 133. – $\text{C}_{20}\text{H}_{19}\text{NO}_3$ (321.38): calcd. C 74.73, H 5.96, N 4.36; found C 74.38, H 5.92, N 4.33.

(4S,5S)-4-Benzoyloxy-6-phenyl-5-phthalimido-1-hexene (4): Alcohol **3** (20 mg, 0.06 mmol) was dissolved in dichloromethane (0.8 mL) and treated with benzoyl chloride (0.02 mL), pyridine (0.1 mL), and 4-(dimethylamino)pyridine (5 mg). After 4 h at room temperature, the mixture was diluted with ethyl acetate and extracted with 2 M aq. HCl, 1 M aq. Na_2CO_3 solution, and water. The organic phase was dried (MgSO_4), the solvent was evaporated, and the residue was purified by short-column chromatography (hexane/dichloromethane, 1:1) to give 21 mg (79%) of the benzoate **4** as a white crystalline product; m.p. 113–114°C (from MeOH). – ^1H NMR (CDCl_3): δ = 8.00–7.05 (m, 14 H), 6.00–5.80 (m, 2 H), 5.30–5.10 (m, 2 H), 4.84 (ddd, J = 12.1, 8.2, 4.9 Hz, 1 H), 3.55 (dd, 1 H, J = 13.7, 11.8 Hz), 3.19 (dd, J = 13.7, 4.8 Hz, 1 H), 2.77–2.70 (m, 1 H), 2.55–2.50 (m, 1 H). – CD (MeCN): $\Delta\epsilon$ = –1.6 (241 nm), +2.8 (230 nm), –12.6 (218 nm). – UV (MeCN): λ_{max} (ϵ) = 220 nm (45200).

(S)-Dimethyl(phenyl)(3-phenyl-2-tosylamidopropanoyl)silane (5): To a 0.4 M solution of bis(dimethylphenylsilyl)lithium cyanocuprate^[32] (11.5 mL, 4.6 mmol) in THF at –78°C was added a solution of *N*-tosyl-L-phenylalanyl chloride^[33] (1.55 g, 4.6 mmol) in THF (9 mL). The reaction mixture was stirred under Ar at –78°C for 1 h. Saturated aqueous NH_4Cl solution (10 mL) was then added, the mixture was allowed to warm to r.t., whereupon it was extracted three times with diethyl ether. The combined organic extracts were dried with Na_2SO_4 . After removal of the solvent in vacuo, the crude residue was purified by column chromatography on silica gel (light petroleum ether/ Et_2O , 5:1), affording 0.96 g (48%) of pure **5** as a pale-yellow solid; m.p. 107–109°C. – $[\alpha]_{\text{D}}^{25}$ = 93.6 (c = 1.79, CHCl_3). – ^1H NMR (200 MHz, CDCl_3): δ = 7.50–7.40 (m, 8 H), 7.15–7.00 (m, 4 H), 6.70–6.60 (m, 2 H), 5.25 (d, J = 7.6 Hz, 1 H), 4.25–4.15 (m, 1 H), 2.75 (dd, J = 15.2, 4.8 Hz, 1 H), 2.40–2.25 (m + s, 4 H), 0.42 (s, 3 H), 0.34 (s, 3 H). – ^{13}C NMR (50.3 MHz, CDCl_3): δ = 240.59, 170.30, 143.19, 134.98, 134.16, 126.75–130.38, 65.97, 36.24, 21.44, –4.6. – IR (CCl_4): $\tilde{\nu}$ = 3300 cm^{-1} , 1650, 1350, 1175. – MS; (m/z): 437 [M^+], 422, 274, 135, 91. – $\text{C}_{24}\text{H}_{27}\text{NO}_3\text{SSi}$ (437.15): calcd. C 65.88, H 6.22, N 3.20; found C 65.10, H 6.05, N 3.12.

Reaction of Acylsilane 5 with Tetraallyltin: To a stirred suspension of scandium(III) triflate (7.9 mg, 0.016 mmol) and tetraallyltin (33 mg, 0.115 mmol) in CH_2Cl_2 (3 mL) at r.t. was added a solution of **5** (100 mg, 0.23 mmol) in CH_2Cl_2 . After 90 min, saturated aqueous NH_4Cl solution (10 mL) was added and the mixture was extracted three times with diethyl ether. The combined organic extracts were dried with Na_2SO_4 and the solvent was evaporated in vacuo. The crude residue was submitted to ^1H -NMR analysis, which showed the presence of both the *syn* and the *anti* isomer **6a** and **6b** in a 75:25 ratio. The two isomers were separated on silica gel plates (CH_2Cl_2 as eluent) giving, as the slower moving compound, 73 mg (67%) of (2S,3R)-3-[dimethyl(phenyl)silyl]-1-phenyl-2-tosylamido-5-hexen-3-ol (**6a**), and, as the faster moving compound, 23 mg (21%) of (2S,3S)-3-[dimethyl(phenyl)silyl]-4-phenyl-2-tosylamido-5-hexen-3-ol (**6b**).

6a: Major isomer; light-yellow oil. – $[\alpha]_{\text{D}}^{25}$ = –44.0 (c = 2.78, CHCl_3). – ^1H NMR (300 MHz, CDCl_3): δ = 7.75–7.65 (m, 2 H), 7.50–7.35 (m, 3 H), 7.00–6.90 (m, 3 H), 6.89–6.70 (m, 4 H), 6.30–6.10 (m, 3 H), 5.25–5.15 (m, 2 H), 4.45 (d, J = 8.5 Hz, 1 H), 3.65 (s, 1 H), 3.45–3.30 (m, 1 H), 2.70–2.65 (dd, J = 13.6, 2.7 Hz, 1 H), 2.55–2.40 (m, 2 H), 2.30 (s, 3 H), 2.15–2.05 (dd, J = 13.6, 10.2 Hz, 1 H), 0.48 (s, 3 H), 0.42 (s, 3 H). – ^{13}C NMR (75.4

MHz, CDCl_3): δ = 142.42, 136.64, 136.20, 135.70, 135.60, 134.98, 134.57, 129.34, 129.10, 128.37, 127.84, 125.56, 125.68, 117.14, 69.85, 62.72, 38.46, 37.61, 21.26, –3.89, –2.92. – IR (CCl_4): $\tilde{\nu}$ = 3470 cm^{-1} , 3720, 1430, 1175. – MS; (m/z): 479 [M^+], 438, 309, 274, 230, 217, 155, 135, 91. – $\text{C}_{27}\text{H}_{33}\text{NO}_3\text{SSi}$ (479.71): calcd. C 67.61, H 6.94, N 2.92; found C 67.20, H 6.75, N 2.80.

6b: Minor isomer; m.p. 45–50°C. – $[\alpha]_{\text{D}}^{25}$ = 11.0 (c = 2.78, CHCl_3). – ^1H NMR (300 MHz, CDCl_3): δ = 7.75–7.65 (m, 2 H), 7.50–7.40 (m, 3 H), 7.05–6.80 (m, 7 H), 6.50–6.40 (m, 2 H), 6.20–6.00 (m, 1 H), 5.25–5.05 (m, 2 H), 4.00 (d, J = 7.5 Hz, 1 H), 3.57 (s, 1 H), 3.45–3.35 (m, 1 H), 2.78–2.65 (m, 2 H), 2.40–2.25 (s + m, 4 H), 1.85 (dd, J = 13.1, 11.2 Hz, 1 H), 0.60 (s, 3 H), 0.45 (s, 3 H). – ^{13}C NMR (75.4 MHz, CDCl_3): δ = 142.60, 137.40, 136.84, 134.12, 132.99, 129.75, 129.26, 128.26, 126.99, 126.67, 126.08, 118.29, 71.37, 63.77, 40.50, 37.48, 21.36, –3.46. – IR (CCl_4): $\tilde{\nu}$ = 3470 cm^{-1} , 3720, 1430, 1175. – MS; (m/z): 479 [M^+], 438, 309, 274, 230, 217, 155, 135, 91. – $\text{C}_{27}\text{H}_{33}\text{NO}_3\text{SSi}$ (**mol. mass?**): calcd. C 67.61, H 6.94, N 2.92; found C 67.30, H 6.80, N 2.78.

The relative configurations of **6a** and **6b** were elucidated from NOE experiments: In the major isomer **6a**, saturation of the signals of the two methyl groups bonded to the silicon atom at δ = 0.42 and δ = 0.48 produced an increase in the intensity of the 5-H signal at δ = 3.45–3.30 (3.5%) and no increase in the intensity of the NH signal at δ = 4.45. In the minor isomer **6b**, saturation of the signals of the two methyl groups bonded to the silicon atom at δ = 0.45 and δ = 0.60 produced an increase in the intensity of the NH signal at δ = 4.00 (2.8%) and no increase in the intensity of the 5-H signal at δ = 3.45–3.35.

Reaction of 5 with Allyltrimethylsilane: The reaction was performed under the same conditions as used for the reaction of acylsilane **1**, starting from acylsilane **5** (0.44 g, 1 mmol) in CH_2Cl_2 (1.5 mL), allyltrimethylsilane (0.23 g, 2 mmol), and a 1.0 M solution of TiCl_4 (1 mL, 1.0 mmol) in CH_2Cl_2 . The crude product was submitted to ^1H - and ^{13}C -NMR analysis, which showed the presence of a single diastereoisomer. The material was then purified on a silica gel column (eluent: light petroleum ether/ Et_2O , 5:1) affording 0.24 g (60%) of pure **6a**.

Attempted Protodesilylation of 6a with TBAF: To a stirred solution of **6a** (0.23 g, 0.48 mmol) in THF (3 mL) at r.t., a 1 M solution of TBAF (0.53 mL, 0.53 mmol) in THF was added. After 16 h, saturated aqueous NH_4Cl solution (5 mL) and Et_2O (10 mL) were added. The organic layer was separated, washed with water, and dried with MgSO_4 . After removal of the solvent in vacuo, the crude residue was purified by preparative TLC on silica gel plates (ethyl acetate/ Et_2O , 1:1), giving 25 mg (30%) of 1-phenyl-4-hexen-3-one (**7**) as a colorless oil. – ^1H NMR (200 MHz, CDCl_3): δ = 7.37–7.15 (m, 5 H), 6.95–6.75 (m, 1 H), 6.20–6.06 (m, 1 H), 3.01–2.80 (m, 4 H), 1.95–1.88 (m, 3 H). – IR (CCl_4): $\tilde{\nu}$ = 2960 cm^{-1} , 1660. – MS; (m/z): 174 [M^+], 159, 105, 69.

(2S,3R)-2-Amino-1-phenyl-5-hexen-3-ol (8): A solution of **6a** (0.479 g, 1 mmol) in THF (5 mL) was added with stirring to liquid ammonia (30 mL) at –78°C. Stirring was continued and clean sodium was added in small pieces until the blue color, which developed on dissolution of the metal and disappeared during the reaction, persisted for about 1 min. Approximately 0.14 g (6 mmol) of sodium was required. Ethanol was then added and the ammonia was allowed to evaporate at r.t. The residual ammonia and the THF were removed in vacuo. The residue was then purified on a silica gel column ($\text{CHCl}_3/\text{MeOH}$, 2:1) giving 96 mg (50%) of **8** as a colorless oil. – ^1H NMR (200 MHz, CDCl_3): δ = 7.35–7.00 (m, 5 H), 5.95–5.40 (m, 4 H), 5.20–4.90 (m, 2 H), 4.00–3.95 (m, 1 H),

3.50–3.35 (m, 1 H), 3.10–2.70 (m, 2 H), 3.15–2.25 (m, 2 H). – ^{13}C NMR (75.4 MHz, CDCl_3): δ = 136.46, 133.95, 129.35, 128.82, 127.08, 118.03, 70.02, 57.07, 37.17, 33.55. – IR (CCl_4): $\tilde{\nu}$ = 3650–3200 (br.) cm^{-1} . – MS; m/z : 181 [M^+], 150, 120, 91.

(2S,3R)-1-Phenyl-2-phthalimido-5-hexen-3-ol (9): A mixture of **8** (50 mg, 0.26 mmol) and phthalic anhydride (46 mg, 0.31 mmol) was stirred at 150 °C for 30 min. After cooling to r.t., the reaction mixture was extracted with CHCl_3 . After removal of the solvent in vacuo from the combined organic extracts, the residue was chromatographed on silica gel plates giving 59 mg (70%) of pure **9** as a white solid; m.p. 71–72 °C. – $[\alpha]_{\text{D}} = -64.5$ (c = 0.69, CHCl_3). – ^1H NMR (300 MHz, CDCl_3): δ = 7.80–7.60 (m, 4 H), 5.90–5.75 (m, 1 H), 5.20–5.15 (m, 2 H), 4.65–4.45 (m, 1 H), 4.30–4.20 (m, 1 H), 3.39–3.20 (m, 3 H), 2.45–2.30 (m, 2 H). – ^{13}C NMR (75.4 MHz, CDCl_3): δ = 168.45, 137.85, 131.37, 134.09, 133.96, 128.94, 128.38, 126.47, 123.31, 118.69, 71.94, 57.40, 39.20, 33.08. – IR (CCl_4): $\tilde{\nu}$ = 3460 cm^{-1} , 1770, 1750, 1705. – MS; m/z : 321 [M^+], 280, 262, 133. – $\text{C}_{20}\text{H}_{19}\text{NO}_3$ (321.38): calcd. C 74.75, H 5.96, N 4.36; found C 74.09, H 5.88, N 4.28.

(2S,3S)-2-Amino-1-phenyl-5-hexen-3-ol (10): The reaction was performed under the same conditions as used for **6a**, starting from **6b** (0.14 g, 0.29 mmol), liquid ammonia (9 mL), and sodium (40 mg, 1.74 mmol). Chromatography of the crude product on silica gel plates ($\text{CHCl}_3/\text{MeOH}$, 2:1) gave 33 mg (60%) of **10**. – ^1H NMR (200 MHz, CDCl_3): δ = 7.50–7.20 (m, 5 H), 6.10–5.70 (m, 4 H), 5.30–5.10 (m, 2 H), 3.95–3.80 (m, 1 H), 3.45–3.40 (m, 1 H), 3.30–2.90 (m, 2 H), 2.40–2.00 (m, 2 H). – ^{13}C NMR (75.4 MHz, CDCl_3): δ = 137.60, 133.63, 129.75, 129.05, 127.15, 118.39, 69.17, 56.92, 36.36, 29.68. – IR (CCl_4): $\tilde{\nu}$ = 3690–3220 (br.) cm^{-1} . – MS; m/z : 150 [$\text{M}^+ - 41$], 120, 100, 91, 77. – Compound **10** was *N*-protected with phthalic anhydride (29.6 mg, 0.2 mmol) under the same conditions as used for the protection of **8**, giving 48 mg (86%) of (2S,3S)-1-phenyl-2-phthalimido-5-hexen-3-ol (**3**).

(S)-4-Phenyl-3-phthalimidobutanoic Acid (12): To a stirred 0.3 M solution of diazomethane (90 mL, 27 mmol) in diethyl ether at 0 °C, was added a solution of *N*-phthaloyl-L-phenylalanyl chloride^[30] (2.5 g, 8 mmol) in THF (10 mL). After 1 h, the excess diazomethane was removed by bubbling Ar through the solution. Concentration of the reaction mixture under reduced pressure gave 2.4 g (94%) of (S)-1-diazo-3-phthalimido-4-phenyl-2-butanone; m.p. 129–131 °C (dec.). – $[\alpha]_{\text{D}} = -210.8$ (c = 0.66, CHCl_3). – ^1H NMR (200 MHz, CDCl_3): δ = 7.85–7.60 (m, 4 H), 7.05–7.10 (m, 5 H), 5.35 (s, 1 H), 5.10 (dd, J = 9.3, 5.8 Hz, 1 H), 3.55–3.45 (m, 2 H). – ^{13}C NMR (50.3 MHz, CDCl_3): δ = 189.27, 167.55, 136.64, 134.27, 131.34, 128.80, 128.57, 126.83, 123.51, 58.29, 54.23, 33.89. – IR (CCl_4): $\tilde{\nu}$ = 2113 cm^{-1} , 1775, 1715, 1650. – MS; m/z : 291 [$\text{M}^+ - \text{N}_2$], 250, 200. – To a stirred solution of (S)-1-diazo-3-phthalimido-4-phenyl-2-butanone (3.19 g, 10 mmol) in methanol (90 mL) was added silver oxide (0.28 g, 1.2 mmol) and the mixture was warmed to 50 °C for 40 min. After cooling to r.t., the reaction mixture was filtered through Celite and the filtrate was concentrated in vacuo. The crude residue was purified on a silica gel column (eluent: light petroleum ether/diethyl ether, 1:2) giving 2.8 g (87%) of methyl(S)-4-phenyl-3-phthalimidobutanoate; m.p. 73–75 °C. – $[\alpha]_{\text{D}} = -1.3$ (c = 1.00, CHCl_3). – ^1H NMR (200 MHz, CDCl_3): δ = 7.85–7.63 (m, 4 H), 7.28–7.15 (m, 5 H), 5.15–4.95 (m, 1 H), 3.62 (s, 3 H), 3.40–3.13 (m, 3 H), 2.95–2.80 (dd, J = 15.8, 5.3 Hz, 1 H). – ^{13}C NMR (50.3 MHz, CDCl_3): δ = 170.15, 168.01, 137.55, 134.03, 131.98, 129.13, 128.66, 126.92, 123.31, 51.98, 49.02, 38.56, 36.22. – IR (CCl_4): $\tilde{\nu}$ = 1770 cm^{-1} , 1720, 1745. – MS; m/z : 323 [M^+], 292, 250, 176. – $\text{C}_{19}\text{H}_{17}\text{NO}_4$ (323.35): calcd. C 70.58, H 5.30, N 4.33; found C 70.30, H 5.26, N

4.30. – A suspension of methyl (S)-4-phenyl-3-phthalimidobutanoate (1.0 g, 3.1 mmol) in acetone (13 mL), water (10 mL), and concentrated hydrochloric acid (4 mL) was heated under reflux for 3 h. The reaction mixture was then concentrated to dryness in vacuo. The residue was dissolved in 12% aqueous potassium hydrogen carbonate solution, the solution was filtered to eliminate impurities, and then acidified with hydrochloric acid. The resulting precipitate was filtered off and crystallized from $\text{MeOH}/\text{H}_2\text{O}$, giving 0.77 g (81%) of **12** as a white solid; m.p. 123–125 °C. – $[\alpha]_{\text{D}} = -118.2$ (c = 1.01, CHCl_3). – ^1H NMR (200 MHz, CDCl_3): δ = 7.81–7.62 (m, 4 H), 7.25–7.12 (m, 5 H), 5.00–4.85 (m, 1 H), 3.40–3.08 (m, 3 H), 2.98–2.82 (dd, J = 17.5, 5.0 Hz, 1 H). – ^{13}C NMR (50.3 MHz, CDCl_3): δ = 176.53, 168.01, 136.99, 133.89, 131.40, 128.92, 128.48, 126.77, 123.18, 48.78, 38.34, 35.98. – IR (CCl_4): $\tilde{\nu}$ = 3500 cm^{-1} , 1780, 1720. – MS; m/z : 309 [M^+], 291, 218, 200, 162. – $\text{C}_{18}\text{H}_{15}\text{NO}_4$ (309.10): calcd. C 69.89, H 4.89, N 4.53; found C 69.80, H 4.86, N 4.50.

(S)-(4-Phenyl-3-phthalimidobutanoyl)dimethylphenylsilane (13): A mixture of the acid **12** (2.0 g, 6.4 mmol) and SOCl_2 (20 mL) was warmed to 55–60 °C for 6 h. After work-up according to the standard procedures, 1.96 g (93%) of (S)-4-phenyl-3-phthalimidobutanoyl chloride was obtained as a white solid, which was used in the next step without further purification; m.p. 93–95 °C. – ^1H NMR (200 MHz, CDCl_3): δ = 7.84–7.65 (m, 4 H), 7.30–7.15 (m, 5 H), 5.05–4.90 (m, 1 H), 3.92 (dd, J = 17.5, 10 Hz, 1 H), 3.45–3.05 (m, 3 H). – IR (CCl_4): $\tilde{\nu}$ = 1800 cm^{-1} , 1780, 1720. – MS; m/z : 327 [M^+], 292, 250. – Compound **13** was prepared using the same procedure as that described for acylsilane **5**, by reaction of a 0.4 M solution of bis(dimethylphenylsilyl)lithium cyanocuprate^[32] (7.5 mL, 3 mmol) in THF with (S)-4-phenyl-3-phthalimidobutanoyl chloride (1.0 g, 3 mmol) in THF (10 mL). The crude product was purified on a silica gel column (eluent: light petroleum ether/ Et_2O , 10:1), giving 0.72 g (55%) of pure **13** as a white solid; m.p. 60–61 °C. – $[\alpha]_{\text{D}} = -45.2$ (c = 2.76, C_6H_6). – ^1H NMR (200 MHz, CDCl_3): δ = 7.80–7.10 (m, 14 H), 5.05–4.95 (m, 1 H), 3.52 (dd, 1 H, J = 17.5, 7.5 Hz), 3.20–3.05 (m, 2 H), 2.95 (dd, J = 17.5, 6.0 Hz, 1 H), 0.48 (s, 3 H), 0.43 (s, 3 H). – ^{13}C NMR (50.3 MHz, CDCl_3): δ = 243.47, 168.07, 137.49, 134.95, 133.97, 133.71, 131.55, 129.99, 128.94, 128.37, 128.20, 126.58, 123.04, 50.07, 47.48, 38.84, –4.69, –4.05. – IR (CCl_4): $\tilde{\nu}$ = 1780 cm^{-1} , 1720, 1650, 1250. – MS; m/z : 427 [M^+], 399, 336, 292, 135. – $\text{C}_{26}\text{H}_{25}\text{NO}_3\text{Si}$ (427.57): calcd. C 73.04, H 5.89, N 3.28; found C 72.75, H 5.85, N 3.26.

Reaction of 13 with Allyltrimethylsilane: The reaction was performed under the same conditions as used for the reaction of acylsilane **1**, starting from **13** (0.49 g, 1.15 mmol) in CH_2Cl_2 (4 mL), allyltrimethylsilane (0.26 g, 2.3 mmol), and a 1.0 M solution of TiCl_4 (1.15 mL, 1.15 mmol) in CH_2Cl_2 . The crude product was submitted to ^1H - and ^{13}C -NMR analysis, which showed the presence of a single diastereoisomer. The material was then purified on a silica gel column (eluent: light petroleum ether/ Et_2O , 5:1), affording 0.43 g (80%) of pure (S)-4-(dimethylphenylsilyl)-7-phenyl-6-phthalimido-1-hepten-4-ol (**17**) as a colorless oil. – $[\alpha]_{\text{D}} = -63.3$ (c = 1.98, C_6H_6). – ^1H NMR (200 MHz, CDCl_3): δ = 7.75–7.58 (m, 6 H), 7.45–7.35 (m, 3 H), 7.20–7.05 (m, 5 H), 5.70–5.50 (m, 1 H), 5.15–4.95 (m, 2 H), 4.85–4.65 (m, 1 H), 3.28 (dd, J = 14.1, 9.8 Hz, 1 H), 3.04 (dd, J = 14.1, 6.5 Hz, 1 H), 2.75 (dd, J = 15.2, 9.8 Hz, 1 H), 2.48–2.35 (m, 2 H), 1.85 (dd, J = 15.2, 2.6 Hz, 1 H), 1.09 (s, 1 H), 0.39 (s, 6 H). – ^{13}C NMR (50.3 MHz, CDCl_3): δ = 168.62, 138.01, 134.59, 133.83, 133.67, 133.53, 131.88, 129.40, 128.94, 128.34, 127.85, 126.43, 122.91, 118.75, 68.01, 48.37, 41.81, 39.87, 36.34, –4.68, –4.98. – IR (CCl_4): $\tilde{\nu}$ = 3571 cm^{-1} , 1770, 1708. – MS; m/z : 469 [M^+], 428, 378, 321, 135. – $\text{C}_{29}\text{H}_{31}\text{NO}_3\text{Si}$

(469.21): calcd. C 74.16, H 6.65, N 2.98; found C 73.85, H 6.61, N 2.26.

(4R,6R)-7-Phenyl-6-phthalimido-1-hepten-4-ol (18): Prepared using the same procedure as that used for compound **3**, starting from **17** (80 mg, 0.17 mmol) in THF (3 mL) and 0.19 mL (0.19 mmol) of a 1.0 M solution of TBAF in THF. ^1H - and ^{13}C -NMR analysis of the crude product showed the presence of a single diastereoisomer. Subsequent purification on a silica gel column (eluent: light petroleum ether/Et₂O, 3:1) gave 41 mg (72%) of pure **18** as a colorless oil. – $[\alpha]_{\text{D}} = -57.3$ ($c = 1.74$, C₆H₆). – ^1H NMR (200 MHz, CDCl₃): $\delta = 7.80\text{--}7.65$ (m, 4 H), $7.25\text{--}7.10$ (m, 5 H), $5.85\text{--}5.75$ (m, 1 H), $5.15\text{--}5.05$ (m, 2 H), $4.90\text{--}4.70$ (m, 1 H), $3.50\text{--}3.35$ (m, 1 H), $3.15\text{--}3.05$ (dd, $J = 13.8$, 5.75 Hz, 1 H), $2.48\text{--}2.35$ (m, 1 H), $2.28\text{--}2.15$ (m, 3 H), $1.85\text{--}1.70$ (m, 1 H). – ^{13}C NMR (50.3 MHz, CDCl₃): $\delta = 168.84$, 137.88 , 134.42 , 133.92 , 131.52 , 128.84 , 128.44 , 126.51 , 123.18 , 118.08 , 67.46 , 50.80 , 41.77 , 39.06 , 38.58 . – IR (CCl₄): $\tilde{\nu} = 3515$ cm^{–1}, 1770 , 1715 . – MS; m/z : 335 [M⁺], 317 , 294 , 250 , 244 . – C₂₁H₂₁NO₃ (335.40): calcd. C 75.20, H 6.31, N 4.18; found C 74.91, H 6.27, N 4.15.

MTPA Esters of Alcohol 18: These esters (**18**) were obtained under standard conditions (see ref.^[31]).

(R)-MTPA Ester of 18: Purified by preparative TLC (eluent: light petroleum ether/Et₂O, 3:1). – ^1H NMR (300 MHz, CDCl₃): $\delta = 8.20\text{--}6.90$ (m, 14 H), $5.46\text{--}5.30$ (m, 1 H), $5.05\text{--}4.90$ (m, 3 H), 4.52 (m, 1 H), 3.60 (s, 3 H), 3.20 (dd, 1 H), 2.97 (dd, 1 H), $2.66\text{--}2.50$ (m, 1 H), $2.29\text{--}2.25$ (m, 2 H), 1.98 (m, 1 H).

(S)-MTPA Ester of 18: Purified as in the case of the (R)-MTPA ester. – ^1H NMR (300 MHz, CDCl₃): $\delta = 8.10\text{--}7.00$ (m, 14 H), 5.62 (m, 1 H), $5.10\text{--}4.90$ (m, 3 H), $4.44\text{--}4.40$ (m, 1 H), 3.60 (s, 3 H), 3.18 (dd, 1 H), 2.95 (dd, 1 H), $2.65\text{--}2.60$ (m, 1 H), $2.42\text{--}2.38$ (m, 2 H), $1.96\text{--}1.85$ (m, 1 H).

(S)-4-Phenyl-3-tosylamidobutanoic Acid (15): A mixture of L-phenylalaninol (7.6 g, 0.05 mol), *p*-toluenesulfonyl chloride (11 g, 0.06 mol), water (50 mL), and THF (75 mL) was stirred at r.t. for 9 h, then extracted with diethyl ether. The organic phase was washed with water, dried with MgSO₄, and the solvent was evaporated in vacuo. The crude residue was purified by chromatography on a silica gel column (eluent: light petroleum ether/diethyl ether, 1:2), giving 15 g (98%) of *N*-tosyl-L-phenylalaninol as a white product; m.p. $28\text{--}30^\circ\text{C}$. – $[\alpha]_{\text{D}} = -32.5$ ($c = 5.38$, CHCl₃). – ^1H NMR (200 MHz, CDCl₃): $\delta = 7.65\text{--}7.60$ (m, 2 H), $7.30\text{--}7.10$ (m, 5 H), $7.10\text{--}6.95$ (m, 2 H), 5.90 (d, $J = 7.8$ Hz, 1 H), $3.80\text{--}3.40$ (m, 4 H), $2.90\text{--}2.60$ (m, 2 H), 2.40 (s, 3 H). – IR (CCl₄): $\tilde{\nu} = 3500$ cm^{–1}, 3260 , 1160 . – MS; m/z : 305 [M⁺], 274 , 242 , 155 . – C₁₆H₁₉NO₃S (305.39): calcd. C 62.93, H 6.27, N 4.59; found C 62.86, H 6.22, N 4.56. – To a stirred solution of *N*-tosyl-L-phenylalaninol (10 g, 33 mmol) in dry CH₃CN (135 mL), were added triphenylphosphane (13 g, 49.5 mmol), imidazole (3.3 g, 49.5 mmol), and iodine (12.6 g, 49.5 mmol) and the mixture was warmed to $95\text{--}100^\circ\text{C}$ for 2 h. After cooling to r.t., the excess iodine was removed by the addition of a 40% aqueous sodium thiosulfate solution. The reaction mixture was then extracted with diethyl ether, the combined organic phases were washed with water, dried with MgSO₄, and concentrated in vacuo. The residue was purified on a silica gel column (eluent: light petroleum ether/Et₂O, 2:1) giving 12.2 g (90%) of (S)-1-iodo-3-phenyl-2-tosylamidopropane as a white product; m.p. $86\text{--}87^\circ\text{C}$. – $[\alpha]_{\text{D}} = -11.0$ ($c = 4.81$, CHCl₃). – ^1H NMR (300 MHz, CDCl₃): $\delta = 7.70\text{--}7.60$ (m, 2 H), $7.20\text{--}7.10$ (m, 5 H), $7.10\text{--}7.00$ (m, 2 H), 5.25 (d, $J = 7.8$ Hz, 1 H), $3.30\text{--}3.10$ (m, 3 H), 2.85 (dd, $J = 14.2$, 6.8 Hz, 1 H), 2.70 (dd, $J = 14.3$, 6.4 Hz, 1 H), 2.40 (s, 3 H). – MS; m/z : 415 [M⁺], 324 , 288 , 274 , 155 , 91 . – C₁₆H₁₈NO₂S (415.01): calcd. C 46.26, H 4.37, N 3.37; found C

46.10, H 4.20, N 3.31. – A mixture of (S)-1-iodo-3-phenyl-2-tosylamidopropane (6.5 g, 15.7 mmol), tetrabutylammonium cyanide (10 g, 37.3 mmol, previously dried in vacuo over P₂O₅), and dry CH₃CN (35 mL), was stirred at 70°C for 4 h. The solvent was then removed under reduced pressure and the residue was extracted with chloroform. The combined organic phases were washed with water, dried with MgSO₄, and concentrated in vacuo. The residue was purified on a silica gel column (eluent: CHCl₃), affording 3.2 g (65%) of (S)-3-phenyl-2-tosylamido-1-butanonitrile as a light-yellow oil. – $[\alpha]_{\text{D}} = +58.6$ ($c = 4.00$, CHCl₃). – ^1H NMR (300 MHz, CDCl₃): $\delta = 7.60\text{--}7.50$ (m, 2 H), $7.20\text{--}7.10$ (m, 5 H), $7.00\text{--}6.90$ (m, 2 H), 5.35 (d, $J = 6.5$ Hz, 1 H), 3.60 (m, 1 H), 2.85 (dd, $J = 14.1$, 6.4 Hz, 1 H), 2.75 (dd, $J = 14.1$, 7.7 Hz, 1 H), 2.65 (dd, $J = 16.7$, 5.4 Hz, 1 H), 2.50 (dd, $J = 16.7$, 3.85 Hz, 1 H), 2.40 (s, 3 H). – ^{13}C NMR (75.4 MHz, CDCl₃): $\delta = 143.04$, 136.01 , 135.02 , 129.26 , 128.48 , 128.25 , 126.52 , 126.30 , 116.70 , 51.18 , 39.16 , 23.84 , 20.97 . – IR (CCl₄): $\tilde{\nu} = 3310$ cm^{–1}, 1660 , 1175 . – MS; m/z : 314 [M⁺], 274 , 223 , 155 , 91 . – C₁₇H₁₈N₂O₂Si (314.11): calcd. C 64.95, H 5.78, N 8.92; found C 64.81, H 5.60, N 8.64. – A mixture of (S)-3-phenyl-2-tosylamido-1-butanonitrile (3.14 g, 10 mmol), glacial acetic acid (10 mL), water (10 mL), and concentrated sulfuric acid (10 mL) was stirred at 110°C for 9 h. After cooling, the reaction mixture was poured into iced water and the precipitated solid was washed with water until a neutral pH was reached. The residue was dissolved in a 20% aqueous potassium hydrogen carbonate solution and the resulting solution was filtered in order to eliminate impurities. Acidification with concentrated hydrochloric acid led to clouding of the solution, which was then extracted three times with diethyl ether. The combined organic phases were dried with MgSO₄ and the solvent was evaporated in vacuo, leaving 2.3 g (70%) of **15** as a white solid (MeOH/H₂O, 1:1); m.p. $91\text{--}93^\circ\text{C}$. – ^1H NMR (300 MHz, CDCl₃): $\delta = 10.0$ (br. s, 1 H), $7.70\text{--}7.50$ (m, 2 H), $7.30\text{--}7.10$ (m, 5 H), $7.10\text{--}6.90$ (m, 2 H), $5.90\text{--}5.70$ (m, 1 H), $3.90\text{--}3.70$ (m, 1 H), $2.90\text{--}2.70$ (m, 2 H), $2.60\text{--}2.45$ (m, 2 H), 2.40 (s, 3 H). – ^{13}C NMR (75.4 MHz, CDCl₃): $\delta = 176.12$, 143.17 , 136.95 , 136.64 , 129.48 , 129.08 , 128.42 , 126.76 , 126.57 , 51.76 , 40.48 , 38.13 , 21.30 . – IR (CCl₄): $\tilde{\nu} = 3480$ cm^{–1}, 3380 , 1720 , 1175 . – MS; m/z : 333 [M⁺], 274 , 242 , 155 , 91 . – C₁₇H₁₉NO₄S (333.10): calcd. C 61.24, H 5.75, N 4.20; found C 61.00, H 5.64, N 4.01.

(S)-(4-Phenyl-3-tosylamidobutanoyl)dimethylphenylsilane (16): A mixture of the acid **15** (2.0 g, 6.0 mmol) and SOCl₂ (20 mL) was warmed to $55\text{--}60^\circ\text{C}$ for 6 h. After work-up according to standard procedures, 2.0 g (95%) of (S)-4-phenyl-3-tosylamidobutanoyl chloride was obtained as a light-yellow solid, which was used in the next step without further purification; m.p. $84\text{--}86^\circ\text{C}$. – $[\alpha]_{\text{D}} = -36.0$ ($c = 2.43$, CHCl₃). – ^1H NMR (300 MHz, CDCl₃): $\delta = 7.60\text{--}7.50$ (m, 2 H), $7.30\text{--}7.10$ (m, 5 H), $7.00\text{--}6.90$ (m, 2 H), 4.80 (d, $J = 7.5$ Hz, 1 H), 3.75 (m, 1 H), $3.15\text{--}3.00$ (m, 2 H), $2.80\text{--}2.60$ (m, 2 H), 2.40 (s, 3 H). – IR (CCl₄): $\tilde{\nu} = 3260$ cm^{–1}, 1800 , 1175 . – Compound **16** was prepared using the same procedure as that described for **5**, by reaction of a 0.4 M solution of bis(dimethylphenylsilyl)lithium cyanocuprate^[32] (14.25 mL, 5.7 mmol) in THF with (S)-4-phenyl-3-tosylamidobutanoyl chloride (2.0 g, 5.7 mmol) in THF (12 mL). The crude product was purified on a silica gel column (eluent: light petroleum ether/Et₂O, 3:1), giving 1.28 g (50%) of pure **16** as a colorless oil. – $[\alpha]_{\text{D}} = -21.0$ ($c = 3.00$, CHCl₃). – ^1H NMR (300 MHz, CDCl₃): $\delta = 7.60\text{--}7.55$ (m, 2 H), $7.50\text{--}7.30$ (m, 5 H), $7.20\text{--}7.00$ (m, 5 H), $7.75\text{--}7.70$ (m, 2 H), 5.10 (d, $J = 8.2$ Hz, 1 H), $3.70\text{--}3.55$ (m, 1 H), 2.75 (dd, $J = 18.2$, 4.1 Hz, 1 H), $2.65\text{--}2.50$ (m, 3 H), 2.40 (s, 3 H), 0.40 (s, 6 H). – ^{13}C NMR (75.4 MHz, CDCl₃): $\delta = 245.59$, 143.06 , 137.55 , 137.17 , 133.92 , 130.10 , 129.54 , 129.02 , 128.51 , 128.26 , 127.98 , 126.90 , 126.55 , 51.11 , 50.59 , 40.29 , 21.46 , -5.20 . – IR (CCl₄): $\tilde{\nu} = 3300$

cm^{-1} , 1650, 1175. – MS; m/z : 451 $[\text{M}^+]$, 360, 274, 155, 135, 91. – $\text{C}_{25}\text{H}_{29}\text{NO}_3\text{SSi}$ (451.16): calcd. C 66.49, H 6.48, N 3.10; found C 66.49, H 6.31, N 2.90.

Reaction of 16 with Allyltrimethylsilane: The reaction was performed under the same conditions as used for the reaction of acylsilane **1**, starting from acylsilane **16** (0.3 g, 0.66 mmol) in CH_2Cl_2 (1.5 mL), allyltrimethylsilane (0.15 g, 1.32 mmol), and a 1.0 M solution of TiCl_4 (0.66 mL, 0.66 mmol) in CH_2Cl_2 . (S)-4-[Dimethyl(phenyl)silyl]-7-phenyl-6-tosylamido-1-hepten-4-ol (**19**) was obtained as an 82:18 mixture of two diastereoisomers. Purification of the crude product on a silica gel column (eluent: light petroleum ether/ CH_2Cl_2 , 1:5) gave 0.2 g (62%) of pure **19** as a light-yellow oil containing both diastereoisomers in the same 82:18 ratio. – ^1H NMR (200 MHz, CDCl_3): major stereoisomer: δ = 0.231 (s, 3 H), 0.243 (s, 3 H); minor stereoisomer: δ = 0.098 (s, 3 H), 0.185 (s, 3 H). – ^{13}C NMR (50.3 MHz, CDCl_3): major stereoisomer: δ = –5.12 (CH_3Si); minor stereoisomer: δ = –4.98 (CH_3Si). – IR (CCl_4): $\tilde{\nu}$ = 3520 cm^{-1} , 3280, 1350, 1175. – MS; m/z : 493 $[\text{M}^+]$, 478, 452.

Reaction of 16 with Tetraallyltin: The reaction was performed under the same conditions as used in the reaction of **5**, starting from acylsilane **16** (180 mg, 0.4 mmol) in CH_2Cl_2 (2.0 mL), tetraallyltin (57 mg, 0.2 mmol), and $\text{Sc}(\text{OTf})_3$ (14 mg, 0.028 mmol) in CH_2Cl_2 (1.0 mL). Compound **19** was obtained as a 75:25 mixture of two diastereoisomers, the ratio of which was maintained after purification on a silica gel column, which furnished 188 mg (96%) of pure **19**.

(4R,6R)- (20a) and (4S,6R)-7-Phenyl-6-tosylamido-1-hepten-4-ol (20b): Prepared using the same procedure as that used for compound **3**, starting from **19** (0.1 g, 0.2 mmol, 75:25 mixture of two diastereoisomers) in THF (4 mL) and 0.28 mL (0.28 mmol) of a 1.0 M solution of TBAF in THF. The crude product was submitted to ^1H -NMR analysis, which showed the presence of **20a** and **20b** in a 75:25 ratio. The two isomers were separated on silica gel plates. A double elution with CH_2Cl_2 /light petroleum ether, 5:1, gave, as the slower moving product, 39 mg (54%) of **20a** and, as the faster moving product, 13 mg (18%) of **20b**.

20a (major): $[\alpha]_D$ = 8.1 (c = 2.5, CHCl_3). – ^1H NMR (200 MHz, CDCl_3): δ = 7.70–7.60 (m, 2 H), 7.29–7.15 (m, 5 H), 6.95–6.85 (m, 2 H), 5.82–5.60 (m, 1 H), 5.07–4.88 (m, 3 H), 4.00–3.81 (m, 1 H), 3.78–3.61 (m, 1 H), 2.68–2.49 (m, 3 H), 2.40 (s, 3 H), 2.15–2.03 (m, 2 H), 1.55–1.30 (m, 2 H). – ^{13}C NMR (50.3 MHz, CDCl_3): δ = 143.29, 137.70, 136.89, 134.57, 129.69, 128.52, 126.95, 126.58, 117.80, 66.89, 52.20, 41.72, 41.53, 40.72, 21.51. – IR (CCl_4): $\tilde{\nu}$ = 3510 cm^{-1} , 3280, 1175. – MS; m/z : 359 $[\text{M}^+]$, 318, 268, 198, 155, 91. – $\text{C}_{20}\text{H}_{25}\text{NO}_3\text{S}$ (359.48): calcd. C 66.82, H 7.02, N 3.90; found C 66.58, H 6.88, N 3.77.

20b (minor): $[\alpha]_D$ = –4.5 (c = 0.81, CHCl_3). – ^1H NMR (300 MHz, CDCl_3): δ = 7.71–7.62 (m, 2 H), 7.29–7.10 (m, 5 H), 7.05–6.98 (m, 2 H), 5.69–5.58 (m, 1 H), 5.38 (d, J = 7.0 Hz, 1 H), 5.12–4.98 (m, 2 H), 3.50–3.38 (m, 2 H), 2.85 (dd, J = 14.0, 5.0 Hz, 1 H), 2.65 (dd, J = 14.0, 6.5 Hz, 1 H), 2.40 (s, 3 H), 2.19–1.92 (m, 3 H), 1.60–1.40 (m, 2 H). – ^{13}C NMR (50.3 MHz, CDCl_3): δ = 143.17, 137.32, 133.68, 128.49, 128.40, 127.92, 127.22, 127.14, 126.56, 119.05, 69.08, 54.49, 42.34, 41.96, 39.99, 21.54. – IR (CCl_4): $\tilde{\nu}$ = 3510 cm^{-1} , 3280, 1175. – MS; m/z : 359 $[\text{M}^+]$, 318, 268, 198, 155, 91. – $\text{C}_{20}\text{H}_{25}\text{NO}_3\text{S}$ (359.48): calcd. C 66.82, H 7.02, N 3.90; found C 66.78, H 6.94, N 3.78.

MTPA Esters of Alcohol (20a): These esters were obtained under standard conditions (see ref.^[31]).

(R)-MTPA Ester of 20a: Purified by preparative TLC ($\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$, 1:1). – ^1H NMR (300 MHz, CDCl_3): δ = 7.62–7.60 (m, 2

H), 7.58–7.52 (m, 2 H), 7.50–7.40 (m, 3 H), 7.30–7.15 (m, 5 H), 6.98–6.90 (m, 2 H), 5.53–5.39 (m, 1 H), 5.18–5.06 (m, 1 H), 4.94–4.82 (m, 2 H), 4.78 (d, J = 7.5 Hz, 1 H), 3.60–3.44 (m, 1 H), 3.42 (s, 3 H), 2.71–2.52 (m, 2 H), 2.39 (s, 3 H), 2.22–2.17 (m, 2 H), 1.82–1.55 (m, 2 H).

(S)-MTPA Ester of 20a: Purified as in the case of the (R)-MTPA ester. – ^1H NMR (300 MHz, CDCl_3): δ = 7.63–7.60 (m, 2 H), 7.56–7.48 (m, 2 H), 7.42–7.37 (m, 2 H), 7.28–7.15 (m, 6 H), 6.90–6.80 (m, 2 H), 5.65–5.51 (m, 1 H), 5.05–4.90 (m, 2 H), 3.53–3.40 (s + m, 3 H), 2.59–2.40 (m, 2 H), 2.39 (s, 3 H), 1.75–1.49 (m, 2 H), 0.97–0.81 (m, 2 H).

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