Benzotriazole-Mediated Stereoselective Olefination of Carboxylic Esters: Transformation of α-Amino Acid Esters into Chiral Allylamines

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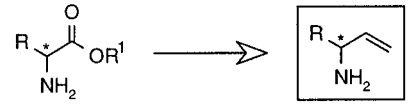
Diastereoselective trans-olefinations of carboxylic esters **3a**−**h** have been accomplished using benzylic or allylic benzotriazole derivatives **1a**−**e** to prepare α-(benzotriazol-1-yl) ketones **4a**−**i**, for the subsequent reduction of **4a**−**i**, and finally for low-valent titanium-effected dehydroxybenzotriazolylation.[1] N-Protected α-amino acid esters **9a**−**c** and **15** thus give allylamines **13a**−**e** and **19** with virtually full retention of chirality. Mechanistic aspects of the dehydroxybenzotriazolylation are discussed.

Introduction

Constructive olefination of carbonyl compounds is an important transformation in organic synthesis. Wittig, Peterson, and Julia reactions are the three most frequently used procedures.[2] During the past two decades, low-valent titanium-induced coupling of carbonyl compounds has received wide application in intramolecular cyclizations,[3] while the unsymmetrical intermolecular variant generally suffers from statistical crossovers. Recently, Horikawa et al. reported that unsymmetric intermolecular coupling between carbonyl compounds and dithioacetals with low-valent titanium generally gave mixed cis- and trans-isomers with little stereoselectivity.[4] Our recently published procedure of low-valent titanium-effected dehydroxybenzotriazolylation[1] has the advantages of high stereoselectivity for trans-isomers and a simple procedure. It constitutes an alternative to the Julia reaction, especially for benzylic and allylic substrates.

Most olefination methods construct double bonds from aldehydes and ketones. However, carboxylic esters have been used in Horner−Wittig reactions to obtain selectively (via selective reduction) threo-diastereomers of the *β*-hydroxyphosphine oxides, which upon elimination led stereospecifically to *trans*-alkenes.[5] Julia reactions have been applied to construct double bonds from carboxylic esters in some natural product syntheses.[2c,6] Despite this, little effort appears to have been made to study systematically the olefination of carboxylic esters, although carboxylic esters are frequently more easily available than the corresponding aldehydes. For example, the naturally occurring chiral α-amino acids are easily converted to esters. In today's era of asymmetric synthesis, it is of great interest to explore these readily available and enantiomerically pure compounds as building blocks and/or to introduce chiral centers.[7,8]

Scheme 1



Successful olefinations of such compounds would lead to allylamines (Scheme 1) which are of great synthetic[9] and biological importance.[10] Recent syntheses of chiral allylamines include the following: (i) asymmetric allylic amination;[11] (ii) modification of enantiomerically pure α-amino aldehydes;[12] (iii) asymmetric addition to alkynes;[13] and (iv) asymmetric nucleophilic addition to carbon−nitrogen double bonds.[14] However, most previous synthetic transformations of the carboxyl groups of α-amino acids have involved conversion into N-protected α-amino aldehydes.[15] Subsequent olefinations via Wittig-type reactions suffer from a lack of general control of diastereoselectivity in the formation of the double bond and

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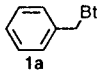
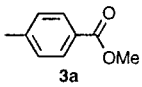
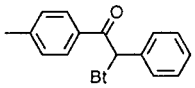
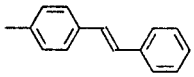
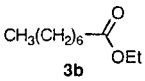
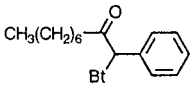
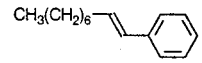
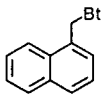
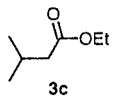
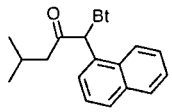
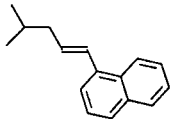
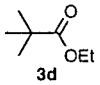
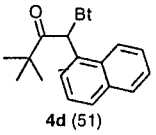
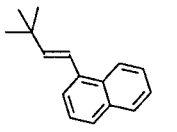
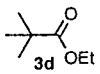
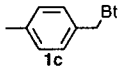
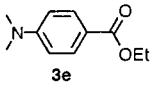
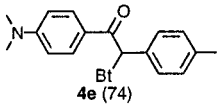
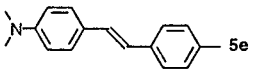
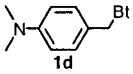
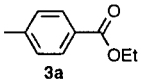
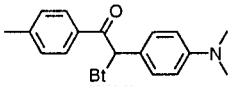
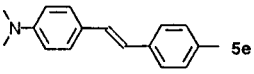
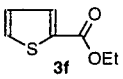
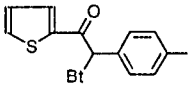
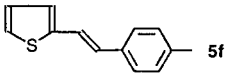
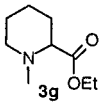
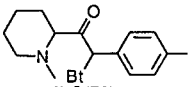
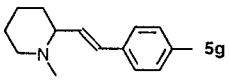
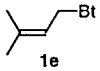
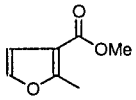
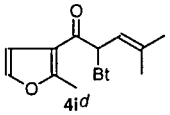
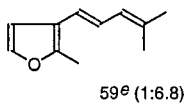
Table 1. Preparation of α-Bt Ketones 4a–i and Olefins 5a–h

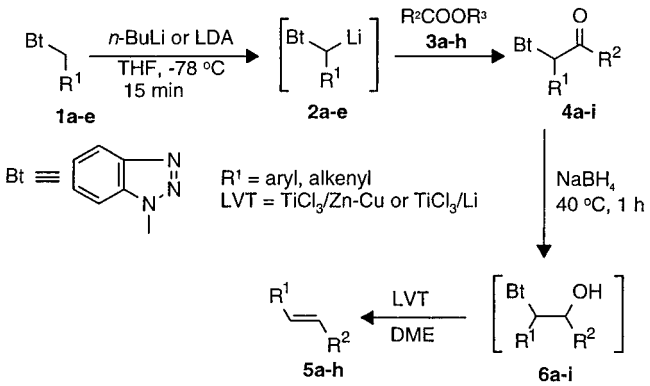
entry	Bt-deriv. 1	ester 3	temperature (°C)	ketones 4 (yield, %)	5 yield (%) and selectivity[a] (*cis:trans*) $TiCl_3$/Li	$TiCl_3$/Zn-Cu
1	 1a	 3a	-78	 4a (96)	 5a 63 (1:28.5)	—
2	1a	 3b	-78	 4b (70)	 5b 14 (1:35)	32 (1:17.8)
3	 1b	 3c	-78	 4c (63)	 5c 20 (1:23.8)	64 (1:17.2)
4	1b	 3d	-78 to 60	 4d (51)	 5d	
5	1b	 3d	-78 to 60	4d (90)[b]	70 (*trans*- only)	77 (*trans*- only)
6	 1c	 3e	-78	 4e (74)	 5e —	57 (*trans*- only)
7	 1d	 3a	-78	 4f (92)	 5e —	88 (*trans*- only)
8	1c	 3f	-78	 4g (95)	 5f —	76 (1:19.2)
9	1c	 3g	-78 to -40	 4h[c] (72)	 5g —	33 (1:3.4)
10	 1e	 3h	-78	 4i[d]	 5h	59[e] (1:6.8)

[a] Overall yield starting from **4**; selectivity ratios determined by ^{1}H NMR. [b] 2 equiv of LDA for entry 5; 1 equiv of BuLi for other entries. [c] Two diastereomers without separation. [d] Not isolated. [e] Overall yield based on **1e**.

racemization at the chiral centers.[12a,15] N-Protected α-amino aldehydes are relatively unstable, both chemically and configurationally,[15] and their preparation from the corresponding acids via esters or active amides is lengthy.[15,16]

We now report a method for the stereoselective preparation of *trans*-alkenes **5a–h** from carboxylic esters **3a–h** and benzylic or allylic benzotriazole derivatives **1a–e** (Scheme 2 and Table 1). This comprises the preparation of α-(benzotriazol-1-yl) ketones **4a–i** from benzylic or allylic benzotriazole derivatives **1a–e** and carboxylic esters **3a–h**, subsequent reduction of **4a–i** to hydroxy analogues **6a–i**, and finally low-valent titanium-promoted dehydroxybenzotriazolylation to give **5a–h**. After N-protection, α-amino acid esters **7a–c** and **14** were similarly converted into allylamines **13a–e** and **19** with

Scheme 2[a]



[a] For designation of individual compounds, see Table 1.

virtually full retention of the configuration of the chiral centers (Schemes 4 and 5 and Table 2).

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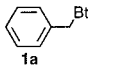
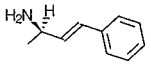
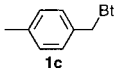
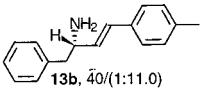
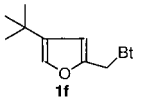
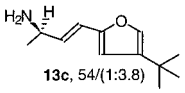
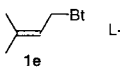
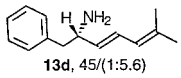
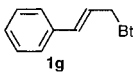
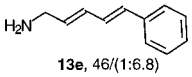
Table 2. Preparation of Allylamines 13a−e

entry	Bt-deriv. 1	ester 7	allyl amine 13 yield(%)/selectivity (*cis:trans*)[a]
1	 1a	D-alanine	 13a, 41/(1:13.1)
2	 1c	L-phenylalanine	 13b, 40/(1:11.0)
3	 1f	D-alanine	 13c, 54/(1:3.8)
4	 1e	L-phenylalanine	 13d, 45/(1:5.6)
5	 1g	glycine	 13e, 46/(1:6.8)

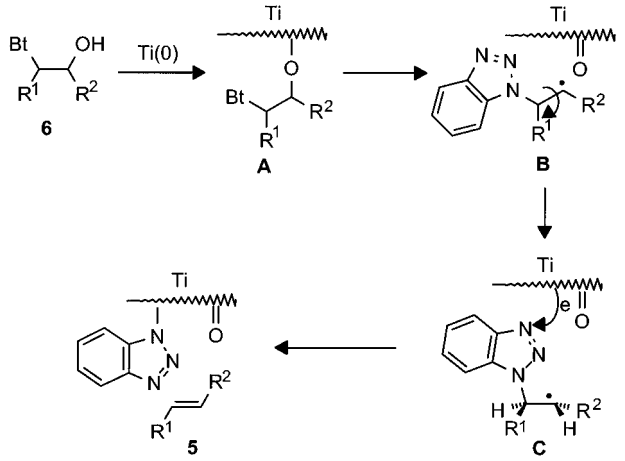
[a] Overall yield based on **1**.

Results and Discussion

Preparation of the Starting Materials 1a−g. 1-Benzyl- and 1-allylbenzotriazoles **1** were readily prepared either by refluxing of arylmethyl halides with benzotriazole in toluene (for compounds **1a**,**b**, Table 1)[17] or by reacting the corresponding halides with benzotriazole in the presence of sodium hydroxide (for compounds **1c**, **1e**, and **1g**, Tables 1 and 2).[1,18] 1-[4-(*N*,*N*-Dimethylamino)benzyl]benzotriazole (**1d**) (Table 1) was obtained from the reaction of 1-(hydroxymethyl)benzotriazole with *N*,*N*-dimethylaniline under acidic conditions.[19] 2-[(Benzotriazol-1-ylmethyl)-4-*tert*-butylfuran (**1f**) (Table 2) was prepared by a previously reported[20] ring construction method.

Olefination of Carboxylic Esters 3a−h with 1-Benzyl- and 1-Allylbenzotriazoles 1a−e. Due to the anion-stabilizing ability of the benzotriazolyl group,[21] 1-benzylbenzotriazoles **1a−e** readily underwent lithiation to generate the lithio derivatives **2a−e**, which reacted with carboxylic esters **3a−h** to give α-(benzotriazol-1-yl) ketones **4a−i** in moderate to excellent yields (Scheme 2 and Table 1), in agreement with previously reported methodology.[22] The reactions of **2a** and **2c**,**d** with aromatic esters **3a** and **3f** took place rapidly to give **4a** and **4f**,**g**, in excellent yields. Slightly lower yields were obtained for compounds **4b**,**c**,**e**, and **h**. For compound **4e**, this was probably due to already formed **4e** being lithiated by some of the **2c** and also by double addition of **2c** to **3e**. The lower yields for compounds **4b**,**c**,**h** were probably due to lithiation at the α-position of esters **3b**,**c**,**g**, by the lithiated benzotriazole derivatives in place of the desired addition reactions. In all cases, the yield could probably be increased by exchanging the lithium reagent with cerium chloride.[23] The reaction corresponding to entry 4 of Table 1 required an elevated temperature because of steric hindrance in ester **3d**, and the higher temperature caused proton-exchange of product **4d** with **2b**, which caused almost half of the starting material to be recovered. However, this problem was solved by using 2 equiv of LDA as shown in entry 5 of Table 1. 1-Allylbenzotriazole (**1e**) reacted with ester **3h** similarly to give product **4i**, which was unstable and used immediately for further reaction after aqueous workup.

Scheme 3



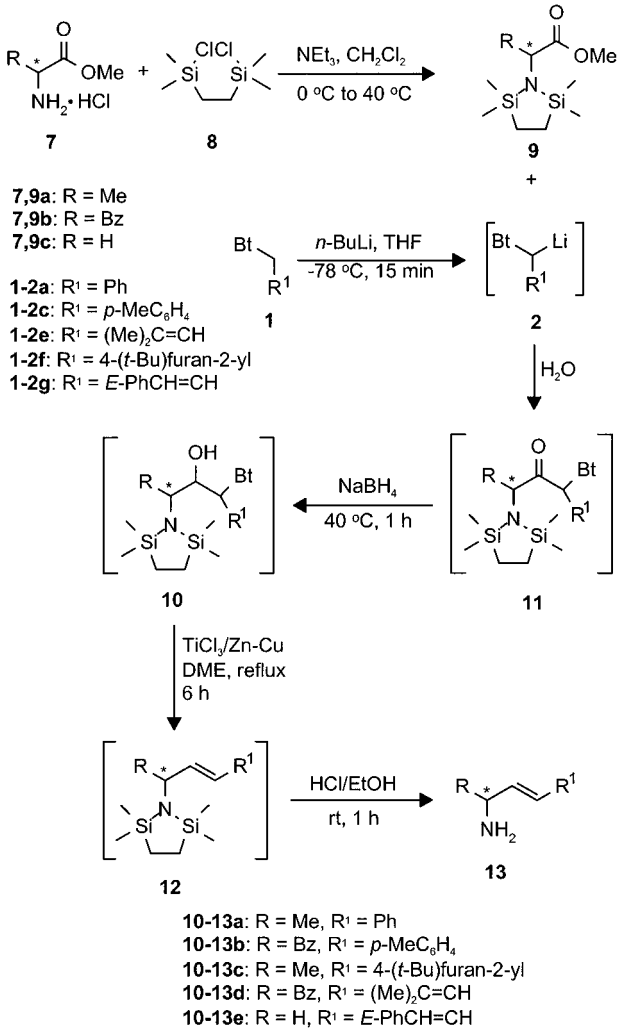
The reduction of ketones **4a−i** to hydroxy compounds **6a−i** as mixtures of diastereomers was achieved in virtually quantitative yields by using $NaBH_4$ in ethanol or a mixture of water and THF at 40 °C for 1 h. According to ^1H NMR, no ketones **4a−i** were detected in the crude intermediates **6a−i**. The ratios of the two possible diastereomers of **6a−i** varied among different substrates, but no high preferences and no obvious pattern was found. The diastereomers of **6a−i** were not separated, and each pair of diastereomers was used directly for the olefination step (Scheme 2).

In our preliminary study,[1] we found that the low-valent titanium reagent, generated from the reduction of $TiCl_3$ with lithium in THF or DME, effectively promoted dehydroxybenzotriazolylation from *N*-(β-hydroxyalkyl)-benzotriazoles to form an olefinic bond with the trans-isomer predominating. In the present work, treatment of the corresponding intermediates **6a−d** with $TiCl_3$/Li in DME under reflux gave the expected alkenes **5a−d** (Scheme 2, Table 1). However, the yields of **5b**,**c** by this procedure were low, although the trans-selectivities were excellent. We assumed that the low yields were probably due to the poor reproducibility involved in the preparation of the $TiCl_3$/Li system as McMurry and co-workers reported.[3a] Therefore, the reagent $TiCl_3$/Zu−Cu, reported by McMurry and co-workers to be more reproducible,[24] was employed, and this gave products **5a−h** in moderate to good yields. As shown in Table 1, the yields of **5b−d** were all considerably improved; however, it has to be noted that selectivities were slightly lower with $TiCl_3$/Zn−Cu than with $TiCl_3$/Li.

We tentatively assume that the dehydroxybenzotriazolylation follows a mechanism similar to that of the McMurry coupling[3a] as shown in Scheme 3. The diastereomeric intermediates **6** on treatment with low-valent titanium undergo sequential reductive cleavages to form

(17) (a) Katritzky, A. R.; Wu, J. *Synthesis* **1994**, 597. (b) Katritzky, A. R.; Zhang, G.; Xie, L. *J. Org. Chem.* **1997**, *62*, 721.
(18) (a) Gibson, M. S. *J. Chem. Soc.* **1956**, 1076. (b) Katritzky, A. R.; Xie, L.; Toader, D.; Serdyuk, L. *J. Am. Chem. Soc.* **1995**, *117*, 12015.
(19) Katritzky, A. R.; Lan, X.; Lam, J. N. *Synthesis* **1990**, 341.
(20) Katritzky, A. R.; Li, J. *J. Org. Chem.* **1995**, *60*, 638.
(21) Katritzky, A. R.; Yang, Z.; Cundy, D. J. *Aldrichim. Acta* **1994**, *27*, 31.
(22) Katritzky, A. R.; Wang, J.; Karodia, N.; Li, J. *J. Org. Chem.* **1997**, *62*, 4142.
(23) Lequeux, T. P.; Percy, J. M. *J. Chem. Soc., Chem. Commun.* **1995**, 2111.
(24) McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krepski, L. R. *J. Org. Chem.* **1978**, *43*, 3255.

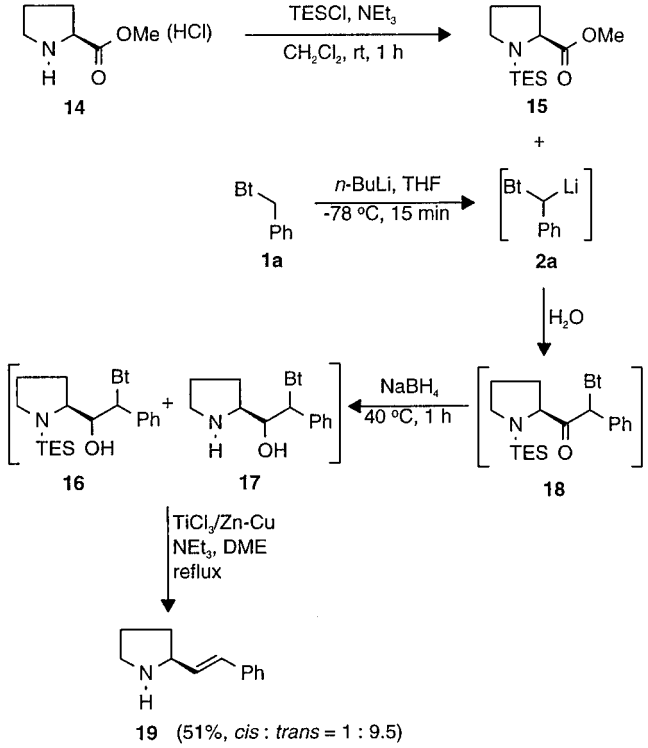
Scheme 4



first metal-attached species **A** and then radical **B**. The radical intermediate **B** rotates to the thermodynamically favored configuration, from which elimination of the benzotriazolyl group forms *trans*-alkenes **5**. This proposed mechanism explains the *trans*-alkene predominance and is supported by our experimental results and by literature evidence.[3a,24] On the basis of this mechanism, the diastereoselectivity of the double-bond formation should depend on the rate at which the Bt group is cleaved: the more slowly, the more time the radical intermediate has available to rotate to the thermodynamically favored configuration and the higher the selectivity for the trans-isomers. Since Zn^{2+} cations, generated from the reaction of $TiCl_3$ with Zn−Cu couple, assist the benzotriazolyl group to leave,[25] higher yields and lower selectivities are expected as compared with $TiCl_3$/Li in the cases of **5b**,**c**. The selectivities also depend on the bulkiness of the substituents R^1 and R^2 as can be seen in Table 1.

Synthesis of Allylamines 13a−e and 19 from α-Amino Acid Esters 7a−c and 14. The above olefination method was successfully applied to commercially available α-amino acid methyl ester hydrochlorides **7a−c** as shown in Schemes 4 and 5 and Table 2. Thus, the amino groups of **7a−c** were readily protected with bis(chlorodimethylsilyl)ethane (**8**) in the presence of NEt_3 in CH_2Cl_2, to give **9a−c** in almost quantitative yields.[26] The N-protected α-amino esters **9a−c** reacted with lithium derivatives **2** to give ketones **11a−e**, which were reduced in situ with $NaBH_4$ to form intermediates **10a−e**. After aqueous workup, the mixed diastereomeric pairs of compounds **10a−e** were each treated with low-valent titanium followed by deprotection to afford allylamines **13a−e** with trans-isomers predominating, in 40−54% overall yields based on benzotriazole derivatives **1**.

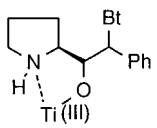
Scheme 5



19 (51%, *cis* : *trans* = 1 : 9.5)

For L-proline **14**, protection for the amino group was effected with triethylsilyl chloride. This N-protected L-proline **15** underwent the desired reaction with lithiated 1-benzylbenzotriazole (**2a**) and subsequent reduction of ketone **18** to give, according to the ^1H NMR spectrum of the crude mixture, a mixture of **16** and **17**. Surprisingly, treatment of the mixture of **16** and **17** with low-valent titanium under the same reaction conditions as above resulted in 25% conversion to the product **19** (based on ^1H NMR of the reaction mixture), after refluxing in DME for 6 h; prolonging the heating time did not increase the conversion. However, in the presence of NEt_3, dehydroxybenzotriazolylation proceeded smoothly to give the product **19** in 51% isolated yield. We believe that the low conversion in the absence of NEt_3 is probably due to the formation of the metal complex as shown in Chart 1.

Chart 1



This type of complex is relatively stable under low-valent titanium conditions as reported previously.[27] NEt_3 per-

(25) Katritzky, A. R.; Lan, X.; Fan, W.-Q. *Synthesis* **1994**, 445.

(26) Djuric, S.; Venit, J.; Magnus, P. *Tetrahedron Lett.* **1981**, *22*, 1787.

(27) Newkome, G. R.; Roper, J. M. *J. Org. Chem.* **1979**, *44*, 502.

haps decomposed this complex so that dehydroxybenzotriazolylation proceeded in the normal way. The conversion of the N-protected intermediates **10a**−**e** under normal low-valent titanium conditions without NEt_3 is probably due to the bulky protecting group that makes a five-membered-ring complex unfavorable.

Determination of Enantiomeric Excess. Two experiments were conducted to determine the preservation of chirality of this procedure. The trans-isomer of allylamine **13d** (homogeneous according to ^{1}H and ^{13}C NMR) was converted into the corresponding amide with the enantiomerically pure (*S*)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetic acid. Only a single diastereomer was observed in the ^{1}H NMR spectrum of the crude product and in the ^{13}C NMR spectrum of the purified product. Second, the trans-isomer of **13a**, containing less than 2% of the cis-isomer according to the ^{1}H NMR ratio, had an optical rotation of $[\alpha]^{22}_D = +25.8$ (*c* 1.16, $CHCl_3$), which is in agreement with the literature value of +25.9 (*c* 0.9, $CHCl_3$) for 97% (*R*).[14a] Therefore, we conclude that the transformations of α-amino acid esters **7a**,**b** and **14** to chiral allylamines **13a**−**d** and **19** proceeded with full retention of the configuration at the chiral centers.

Conclusion

In conclusion, we have described a method that links carboxylic esters with benzyl or allyl groups to form carbon−carbon double bonds with generally good selectivity for trans-isomers. It has also been demonstrated that this procedure can be used on N-protected α-amino acid esters to synthesize allylamines with retention of the chirality. The present constructive method constitutes a novel route featuring cheap starting materials and reagents, a simple experimental procedure, satisfactory overall yields, a general preference for trans-olefination, and virtually full retention of the chirality.

Experimental Section

THF and DME were distilled prior to use from a purple solution resulting from benzophenone and sodium. CH_2Cl_2 for N-protection was distilled after refluxing for 24 h in the presence of P_2O_5 and was stored over molecular sieves. The Zn−Cu couple was prepared and stored according to the literature method.[24] The HCl/ethanol solution was prepared by passing HCl gas through absolute alcohol and the concentration calculated according to the weight difference. Column chromatography was carried out on MCB silica gel (230−400 mesh). Other chemicals were used as obtained from commercial sources. The (*S*)-(−)-α-methoxy-α-(trifluoromethyl)-phenylacetic acid was >98.5% enantiomerically pure according to the commercial source.

Reactions were routinely carried out under dry nitrogen or argon atmosphere with magnetic stirring.

Melting points were determined on a hot-stage apparatus without correction. NMR spectra were obtained with a Varian Gemini-300 spectrometer at 75 MHz for ^{13}C and 300 MHz for ^{1}H. Both ^{13}C and ^{1}H NMR spectra were obtained in chloroform-*d*, and chemical shift values are reported as δ downfield from TMS as an internal standard. The ^{13}C chemical shifts are given to one decimal place unless this would involve two resolved peaks being reported with identical chemical shifts. The NMR spectra reported are the peaks assigned to the trans-isomers. Some spectra also contain small peaks for the cis-isomers unresolved by column chromatography. High-resolution mass spectra and elemental analyses were performed within the department. Optical rotation values reported for **13b**−**d** and **19** were of the mixtures of cis- and trans-isomers and for **13a** of the purified trans-isomer and were measured with a Perkin-Elmer 341 polarimeter with the use of the sodium D line.

Preparation of 2-[(Benzotriazol-1-yl)methyl]-4-*tert*-butyl)furan (1f). A solution of *n*-BuLi (37.5 mL of 1.6 M in hexane, 60 mmol) was added dropwise with stirring to a solution of 1-propargylbenzotriazole[20] (9.6 g, 60 mmol) in THF (100 mL) at −78 °C. The mixture was stirred at this temperature for 1 h, and bromomethyl *tert*-butyl ketone (10.74 g, 60 mmol) was added slowly. The mixture was stirred for 4 h, and *t*-BuOK (6.7 g, 60 mmol) in *t*-BuOH (30 mL) was added. The reaction was warmed to room temperature and heated at 50 °C overnight. Water (100 mL) and EtOAc (100 mL) were added, and the organic phase was washed with ammonium chloride solution (3 × 100 mL) and dried with $MgSO_4$. After removal of the solvents, the residue was subjected to silica gel column chromatography using ether/hexane (1:3) as eluent to give **1f** (11.48 g, 75%) as a white powder: mp 63−65 °C; ^{1}H NMR δ 1.54 (s, 9 H), 5.77 (s, 2 H), 6.39 (s, 1 H), 7.12 (s, 1 H), 7.37 (t, J = 7.7 Hz, 1 H), 7.48 (t, J = 7.7 Hz, 1 H), 7.59 (d, J = 8.3 Hz, 1 H), 8.06 (d, J = 8.3 Hz, 1 H); ^{13}C NMR δ 29.8, 30.6, 45.2, 109.2, 109.8, 119.8, 123.8, 127.4, 132.8, 137.2, 137.3, 146.1, 147.8. Anal. Calcd for $C_{15}H_{17}N_3O$: C, 70.56; H, 6.71; N, 16.46. Found: C, 70.62; H, 7.07; N, 16.58.

General Procedure for Preparation of α-(Benzotriazol-1-yl) Ketones 4a−h. To a THF (40 mL) solution of **1** (8 mmol) in a lithiation bottle at −78 °C and protected with nitrogen or argon was added the base (Table 1) dropwise. The resulting dark blue solution was stirred at −78 °C for 15 min. The corresponding ester **3** (8.4 mmol) was added dropwise as a solution in dry THF (5 mL) and the temperature raised if necessary (Table 1). After the dark color disappeared, saturated NH_4Cl solution (20 mL) was added. After the mixture reached room temperature, it was diluted with CH_2Cl_2 (80 mL) and water (50 mL). The organic phase was separated, washed with water (80 mL), and dried with $MgSO_4$. Evaporation of the solvent under reduced pressure followed by separation (see each compound) gave the product **4**.

α-Phenyl-α-(benzotriazol-1-yl)methyl 4-Methylphenyl Ketone (4a). Crystallization of the reaction mixture from ether: mp 161−163 °C; ^{1}H NMR δ 2.40 (s, 3 H), 7.20−7.40 (m, 10 H), 7.86 (s, 1 H), 7.91 (d, J = 8.1 Hz, 2 H), 8.00−8.05 (m, 1 H); ^{13}C NMR δ 21.7, 68.1, 111.6, 120.0, 123.8, 127.4, 129.1, 129.26, 129.34, 129.7, 132.1, 133.2, 133.3, 145.4, 146.7, 192.2. Anal. Calcd for $C_{21}H_{17}N_3O$: C, 77.04; H, 5.23; N, 12.84. Found: C, 76.91; H, 5.25; N, 12.95.

α-Phenyl-α-(benzotriazol-1-yl)methyl *n*-Heptyl Ketone (4b). Silica gel column chromatography with hexane/ethyl acetate (1:1) as eluent followed by evaporation of the solvents gave the solid product: mp 88−89 °C; ^{1}H NMR δ 0.84 (t, J = 6.5 Hz, 3 H), 1.12−1.32 (m, 8 H), 1.60−1.66 (m, 2 H), 2.61 (t, J = 7.3 Hz, 2 H), 6.78 (s, 1 H), 7.20−7.40 (m, 8 H), 8.04 (d, J = 7.8 Hz, 1 H); ^{13}C NMR δ 14.0, 22.5, 23.6, 28.8, 31.5, 40.8, 71.3, 110.7, 120.0, 123.9, 127.5, 129.0, 129.2, 129.4, 132.5, 133.0, 146.3, 203.1. Anal. Calcd for $C_{21}H_{25}N_3O$: C, 75.19; H, 7.52; N, 12.53. Found: C, 75.01; H, 7.92; N, 12.60.

α-1-Naphthyl-α-(benzotriazol-1-yl)methyl Isobutyl Ketone (4c). Crystallization of the reaction mixture from hexane/ethyl acetate (1:1): mp 124−125 °C; ^{1}H NMR δ 0.97−1.01 (m, 6 H), 2.27−2.37 (m, 1 H), 2.62 (d, J = 6.9 Hz, 2 H), 7.10−7.15 (m, 1 H), 7.20−7.27 (m, 2 H), 7.50−7.63 (m, 5 H), 7.80−8.11 (m, 4 H); ^{13}C NMR δ 22.4, 22.6, 24.9, 68.7, 111.1, 120.0, 122.7, 123.7, 124.8, 126.6, 127.2, 127.4, 127.5, 127.7, 129.2, 130.9, 132.1, 133.3, 134.3, 146.5, 203.4. Anal. Calcd for $C_{22}H_{21}N_3O$: C, 76.93; H, 6.17; N, 12.24. Found: C, 76.81; H, 6.20; N, 12.21.

α-1-Naphthyl-α-(benzotriazol-1-yl)methyl *tert*-Butyl Ketone (4d). Crystallization of the reaction mixture from hexane/ethyl acetate (1:1): mp 188−189 °C; ^{1}H NMR δ 1.31 (s, 9 H), 7.16−7.28 (m, 3 H), 7.48−7.52 (m, 2 H), 7.59 (t, J = 7.5 Hz, 1 H), 7.66 (d, J = 6.9 Hz, 1 H), 7.87−7.92 (m, 1 H), 7.93−8.01 (m, 2 H), 8.12−8.18 (m, 2 H); ^{13}C NMR δ 26.7, 44.9, 63.7, 111.9, 119.8, 122.5, 123.6, 124.6, 126.6, 127.0, 127.2, 127.5, 127.8, 129.2, 131.1, 131.7, 133.5, 134.4, 146.7, 209.7. Anal. Calcd for $C_{22}H_{21}N_3O$: C, 76.93; H, 6.17; N, 12.24. Found: C, 76.67; H, 6.32; N, 12.15.

α-(4-Methylphenyl)-α-(benzotriazol-1-yl)methyl 4-(Dimethylamino)phenyl Ketone (4e). Silica gel column chromatography with ethyl acetate as eluent followed by evaporation of the solvents gave the solid product: mp 217−219 °C; ^{1}H NMR δ 2.33 (s, 3 H), 3.06 (s, 6 H), 6.63 (d, J = 9.0 Hz, 2 H), 7.16, (d, J = 7.5 Hz, 2 H), 7.28−7.31 (m, 5 H), 7.83 (s, 1 H), 7.92 (d, J = 9.0 Hz, 2 H), 8.00−8.04 (m, 1H); ^{13}C NMR δ 21.2, 39.9, 67.5, 110.9, 112.2, 119.7, 123.6, 127.1, 128.4, 129.0, 129.8, 131.1, 131.3, 133.4, 139.0, 146.7, 153.9, 190.2. Anal. Calcd for $C_{23}H_{22}N_4O$: C, 74.56; H, 5.99; N, 15.13. Found: C, 74.38; H, 6.02; N, 15.18.

α-[4-(Dimethylamino)phenyl]-α-(benzotriazol-1-yl)-methyl 4-Methylphenyl Ketone (4f). Crystallization of the reaction mixture from hexane/ethyl acetate (1:1): mp 164−165 °C; ^{1}H NMR δ 2.41 (s, 3 H), 2.96 (s, 6 H), 6.67 (d, J = 9.0 Hz, 2 H), 7.21−7.32 (m, 7 H), 7.80 (s, 1 H), 7.93 (d, J = 8.1 Hz, 2 H), 8.02−8.05 (m, 1 H); ^{13}C NMR δ 21.7, 40.0, 68.5, 112.0, 112.4, 119.6, 119.8, 123.5, 127.1, 129.1, 129.6, 130.3, 132.3, 133.5, 144.9, 146.7, 150.8, 192.9. Anal. Calcd for $C_{23}H_{22}N_4O$: C, 74.56; H, 5.99; N, 15.13. Found: C, 74.47; H, 6.18; N, 15.02.

α-(4-Methylphenyl)-α-(benzotriazol-1-yl)methyl 2-Thiopheneyl Ketone (4g). Crystallization of the reaction mixture from hexane/ethyl acetate (1:1): mp 104−107 °C; ^{1}H NMR δ 2.34 (s, 3 H), 7.11 (t, J = 4.5 Hz, 1 H), 7.20 (d, J = 7.8 Hz, 2 H), 7.28−7.40 (m, 5 H), 7.67 (s, 1 H), 7.70−7.68 (m, 2 H), 8.00−8.08 (m, 1 H); ^{13}C NMR δ 21.2, 68.6, 111.6, 120.0, 123.9, 127.5, 128.6, 128.9, 130.0, 133.1, 133.9, 135.5, 139.6, 141.4, 146.7, 185.7. Anal. Calcd for $C_{19}H_{15}N_3OS$: C, 68.45; H, 4.54; N, 12.61. Found: C, 68.22; H, 4.38; N, 12.58.

α-(4-Methylphenyl)-α-(benzotriazol-1-yl)methyl 2-(*N*-Methylpiperidinyl) Ketone (4h) (a Mixture of Two Diastereomers). Silica gel column chromatography with CH_2Cl_2/MeOH (100:5) as eluent followed by evaporation of the solvents gave the solid product: mp 151−2 °C; ^{1}H NMR δ 1.21−1.99 (m, 6 H), 2.01−2.42 (m, 7 H), 2.91−3.10 (m, 2 H), 7.02−7.42 (m, 8 H), 8.00−8.06 (m, 1 H). Anal. Calcd for $C_{21}H_{24}N_4O$: C, 72.37; H, 6.95; N, 16.09. Found: C, 72.31; H, 7.09; N, 16.05.

General Procedure for Generating the Low-Valent Titanium. To a 250 mL three-neck flask under argon protection was added Zn−Cu (5.4 g), and the system was degassed and protected with argon. $TiCl_3$ (3.85 g 15 mmol) was quickly weighed and added to the flask, which was again degassed and protected with argon. Under stirring, dry DME (40 mL) was added with a syringe, and the mixture was refluxed for 5 h and cooled to room temperature (with $TiCl_3$/Li, see ref 1).

General Procedure for Olefination 5a−g. α-(Benzotriazol-1-yl) ketone **4a**−**h** (5 mmol) was heated at 40 °C for 15 min with $NaBH_4$ (0.5 g) in ethanol (40 mL), and the reaction mixture was then cooled to room temperature. The reaction mixture was then slowly poured into saturated NH_4Cl solution (50 mL). CH_2Cl_2 (100 mL) was added, and the mixture was stirred vigorously for 5 min. The organic phase was separated, washed with 5% NaCl solution (50 mL) and water (50 mL), and dried with $MgSO_4$. Hexane (20 mL) was added, the solution was rotovapored, and the residue was dried under vacuum to give the corresponding intermediate **6** as a mixture of diastereomers. Mixture **6** was dissolved in DME (20 mL) and then added to the low-valent titanium mixture (generated as described above), and the mixture was refluxed overnight. It was then cooled to room temperature and filtered, and the solid residue was extracted with CH_2Cl_2 (2 × 100 mL). The combined organic phase was washed with saturated NH_4Cl (100 mL), 10% Na_2CO_3 solution (100 mL), and water (100 mL) and dried with $MgSO_4$. Evaporation of the solvent followed by column chromatography (for eluents, see each compound below) gave **5a**−**g**.

***trans*-1-Phenyl-2-(*p*-toluyl)ethylene (5a).** Hexanes as eluent followed by evaporation gave the solid product: mp 119−120 °C (lit.[28] mp 119−120 °C); ^{1}H NMR δ 2.35 (s, 3 H), 7.07 (s, 2 H), 7.16 (d, J = 8.1 Hz, 2 H), 7.22−7.27 (m, 1 H), 7.34 (t, J = 7.8 Hz, 2 H), 7.41 (d, J = 8.1 Hz, 2 H), 7.49 (d, J = 7.8 Hz, 2 H); ^{13}C NMR δ 21.2, 126.4, 127.4, 127.8, 128.3, 128.4, 128.6, 129.4, 134.6, 137.5, 137.6.

***trans*-1-Pheny1-1-nonene (5b).**[29] Hexanes as eluent followed by evaporation gave the product: oil; ^{1}H NMR δ 0.89 (t, J = 6.5 Hz, 3 H), 1.15−1.55 (m, 10 H), 2.20 (q, J = 7.0 Hz, 2 H), 6.22 (dt, J = 6.6, 15.9 Hz, 1 H), 6.38 (d, J = 15.9 Hz, 1 H), 7.14−7.35 (m, 5 H); ^{13}C NMR δ 14.1, 22.7, 29.2, 29.4, 31.9, 33.1, 125.9, 126.7, 128.4, 129.7, 131.2, 138.0.

***trans*-1-(1-Naphthyl)-4-methyl-1-pentene (5c).** Hexanes as eluent followed by evaporation gave the product: oil; ^{1}H NMR δ 0.99 (d, J = 6.6 Hz, 6 H), 1.70−1.90 (m, 1 H), 2.15−2.25 (m, 2 H), 6.21 (dt, J = 15.5, 7.4 Hz, 1 H), 7.08 (d, J = 15.5 Hz, 1 H), 7.35−7.60 (m, 4 H), 7.73 (d, J = 8.4 Hz, 1 H), 7.80−7.90 (m, 1 H), 8.12 (d, J = 7.5 Hz, 1 H); ^{13}C NMR δ 22.4, 28.6, 42.8, 123.6, 124.0, 125.6, 125.7, 125.8, 127.2, 128.1, 128.4, 131.2, 133.2, 133.6, 135.9. Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.60; H, 9.01.

***trans*-1-Naphthyl-3,3-dimethyl-1-butene (5d).** Hexanes as eluent followed by evaporation gave the product: oil; ^{1}H NMR δ 1.21 (s, 9 H), 6.26 (d, J = 15.9 Hz, 1 H), 7.04 (d, J = 15.9 Hz, 1 H), 7.25−7.56 (m, 4 H), 7.73 (d, J = 8.4 Hz, 1 H), 7.81−7.85 (m, 1 H), 8.10−8.14 (m, 1 H); ^{13}C NMR δ 29.7, 33.8, 121.9, 123.5, 124.0, 125.6, 125.7, 125.7, 127.1, 128.5, 131.4, 133.7, 136.0, 145.3. Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.61; H, 9.03.

***trans*-*p*-Methyl-*p*′-(dimethylamino)stilbene (5e).** CH_2Cl_2/hexane (1:1) as eluent followed by evaporation gave the solid product: mp 163−165 °C; ^{1}H NMR δ 2.34 (s, 3 H), 2.97 (s, 6 H), 6.71 (d, J = 9.0 Hz, 2 H), 6.88 (d, J = 16.2 Hz, 1 H), 7.00 (d, J = 16.2 Hz, 1 H), 7.13 (d, J = 8.1 Hz, 2 H), 7.30−7.42 (m, 4 H); ^{13}C NMR δ 21.2, 40.5, 112.5, 124.4, 125.9, 126.0, 127.4, 127.8, 129.3, 135.4, 136.4, 150.0. Anal. Calcd for $C_{17}H_{19}N$: C, 86.02; H, 8.07; N, 5.90. Found: C, 86.11; H, 8.45; N, 6.10.

***trans*-1-(4-Methylphenyl)-2-thiopheneylethene (5f).** Hexanes as eluent followed by evaporation gave the solid product: mp 104−107 °C (lit.[30] mp 115−6 °C); ^{1}H NMR δ 2.36 (s, 3 H), 6.91 (d, J = 16.2 Hz, 1 H), 6.99−7.02 (m, 1 H), 7.04−7.08 (m, 1 H), 7.14−7.19 (m, 3 H), 7.20−7.26 (m, 1 H), 7.37 (d, J = 8.1 Hz, 2 H); ^{13}C NMR δ 21.2, 120.9, 124.0, 125.7, 126.2, 127.5, 128.4, 129.4, 134.2, 137.5, 143.2. Anal. Calcd for $C_{13}H_{12}S$: C, 77.97; H, 6.04. Found: C, 77.71; H, 6.19.

1-*p*-Tolyl-2-[2-(*N*-methylpiperidinyl)]ethene (5g). Aluminum oxide (activated, neutral, 50−200 μm) with hexane/ethyl acetate (1:1) as eluent followed by evaporation gave the product: oil; ^{1}H NMR (cis- and trans-isomers) δ 1.20−1.83 (m, 6 H, cis and trans), 1.90−2.08 (m, 1 H, cis and trans), 2.20 (s, 3 H, cis), 2.24 (s, 3 H, trans), 2.33 (s, 3 H, trans), 2.35 (s, 3 H, cis), 2.40−2.50 (m, 1 H, cis and trans), 2.80−3.00 (m, 1 H, cis and trans), 5.6 (dd, J = 12, 9.8 Hz, 1 H, cis), 6.1 (dd, J = 15.9, 8.7 Hz, 1 H, trans), 6.40−6.50 (m, 1 H, cis and trans), 7.0−7.3 (m, 4 H, cis and trans); ^{13}C NMR δ (cis- and trans-isomers) 21.1, 23.8, 24.0, 26.0, 29.7, 32.5, 33.5, 44.3, 44.6, 44.7, 56.3, 56.5, 61.8, 68.1, 126.1, 128.6, 128.8, 129.2, 129.4, 130.4, 132.7, 134.4, 134.6, 135.6, 136.3, 137.0. Anal. Calcd for $C_{15}H_{21}N$: N, 6.51. Found: N, 6.72.

Procedure for the Preparation of 5h. 1-(Benzotriazol-1-yl)-3-methyl-2-butene (**1e**) (0.90 g, 4.8 mmol) was dissolved in dry THF (30 mL) in a lithiation bottle protected under argon or nitrogen, and the mixture was cooled to −78 °C. A solution of *n*-BuLi (3.3 mL of 1.6 M in hexane, 5.3 mmol) was added. After 15 min, methyl 2-methyl-3-furancarboxylate (**3h**) (0.74 g, 5.3 mmol) in dry THF (4 mL) was added dropwise. After the color disappeared (within about 5 min), the reaction was quenched with water (30 mL) followed by addition of $NaBH_4$ (0.8 g). The mixture was warmed and maintained at 40 °C for 1 h. Ether (100 mL) was added, and the organic phase was separated and dried with $MgSO_4$. After evaporation of the solvents, the residue was dried in a vacuum, protected under argon, and transferred with a syringe using dry DME (2 × 15 mL) to the low-valent titanium mixture. The reaction

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mixture was refluxed for 2 h, cooled to room temperature, and filtered, and the solid residue was extracted with ether (2 × 100 mL). The combined organic phase was washed with saturated $NaHCO_3$ (2 × 100 mL), brine (100 mL), and water (100 mL) and dried with $MgSO_4$. Evaporation of the solvent followed by silica gel column chromatography with hexane/ethyl acetate (1:1) as the eluent gave the product **5h** as an oil: ^{1}H NMR δ 1.84 (s, 6 H), 2.31 (s, 3 H), 5.96 (d, J = 10.8 Hz, 1 H), 6.24 (d, J = 15.3 Hz, 1 H), 6.50 (d, J = 1.5 Hz, 1 H), 6.60 (dd, J = 10.8, 15.3 Hz, 1 H), 7.24 (d, J = 1.8 Hz, 1 H); ^{13}C NMR δ 11.7, 18.4, 26.1, 107.8, 119.2, 119.7, 124.3, 125.5, 134.4, 140.7, 148.9. Anal. Calcd for $C_{11}H_{14}O$: C, 81.43; H, 8.70. Found: C, 81.66; H, 9.10.

General Procedure for Preparation of N-Protected Esters 9a−c. To α-amino acid methyl ester hydrochloride **7a−c** (20 mmol) in a three-neck round-bottom flask under argon was added NEt_3 (6.16 g, 61 mmol) with dry CH_2Cl_2 (15 mL), and the mixture was cooled to 0 °C. 1,2-Bis(chlorodimethylsilyl)ethane (**8**) (4.73 g, 22 mmol, 96%) was added dropwise with dry CH_2Cl_2 (15 mL). The mixture was stirred at 40 °C for 1 h, diluted with hexane, and filtered. The filtrate was evaporated and dried in a vacuum. Hexane was added to the residue followed by filtration with a fine sintered glass filter to obtain a clear solution that was then subjected to evaporation under vacuum to give a clear oil **9a−c** (>92%).

General Procedure for Preparation of Primary Allylamines 13a−e. Compound **1** (6.4 mmol) was dissolved in dry THF (30 mL) in a lithiation bottle protected under argon or nitrogen, and the mixture was cooled to −78 °C. A solution of *n*-BuLi (4.4 mL of 1.6 M in hexane, 7.0 mmol) was added. After 15 min, the N-protected ester **9** (7.0 mmol) (prepared as described above) in dry THF (4 mL) was added dropwise (and then the temperature was raised to about 0 °C for entry 5, Table 2). After the color disappeared, the reaction mixture was quenched with water (30 mL), followed by addition of $NaBH_4$ (0.9 g). The mixture was warmed and maintained at 40 °C for 1 h. Ether (100 mL) was added, and the organic phase was separated and dried with K_2CO_3. After evaporation of the solvents, the residue was dried in a vacuum, protected under argon, and transferred with dry DME (2 × 15 mL) to the low-valent titanium mixture. The reaction mixture was refluxed for 2 h and decanted to a sintered glass filter. Both the filtrate and the solid residue were quenched with 15% KOH solution (100 mL), and the aqueous mixture was extracted with solvents (100 mL, 2 × 50 mL, 1:1 ethyl acetate and ether for the DME filtrate; ether for the solid residue). (Moderate stirring for 10−15 min is recommended for extraction instead of vigorous shaking to obtain good separation. In case phase separation is hard to complete, filtration can be used to solve the problem.) The organic phases were combined, dried with K_2CO_3, and subjected to evaporation. The residue was diluted with ether (20 mL) and treated with 1 M HCl ethanol solution (20 mL). After being stirred for 1 h, the mixture was basified with saturated K_2CO_3 solution (50 mL). CH_2Cl_2 (100 mL) was added, and the organic phase was separated and dried with K_2CO_3. Column chromatography of the residue (first 100:5 CH_2Cl_2 and MeOH to elute other fractions and then 100:5:1 CH_2Cl_2, MeOH, and NEt_3 to fully rinse out the products) gave products **13a−e**.

***R-trans*-1-Phenyl-3-amino-1-butene (13a):** oil; $[\alpha]^{22}_D$ +25.8° (*c* 1.16, $CHCl_3$) [lit.[14a] $[\alpha]^{22}_D$ +25.9° (*c* 0.9, $CHCl_3$)]; ^{1}H NMR δ 1.22 (d, J = 6.3 Hz, 3 H), 1.92 (br s, 2 H), 3.60−3.66 (m, 1 H), 6.17 (dd, J = 6.6, 15.9 Hz, 1 H), 6.43 (d, J = 15.9 Hz, 1 H), 7.10−7.40 (m, 5 H); ^{13}C NMR δ 23.7, 49.3, 126.2, 127.2, 128.0, 128.5, 135.7, 137.0.

***S-trans*-1-*p*-Tolyl-3-amino-4-phenyl-1-butene (13b):** oil; $[\alpha]^{22}_D$ +37.9° (*c* 1.01, $CHCl_3$); ^{1}H NMR δ 1.40 (br s, 2 H), 2.32 (s, 3 H), 2.68 (dd, J = 8.1, 13.5 Hz, 1 H), 2.90 (dd, J = 5.1, 13.5 Hz, 1 H), 3.72−3.76 (m, 1 H), 6.21 (dd, J = 6.9, 15.8 Hz, 1 H), 6.46 (d, J = 15.8 Hz, 1 H), 7.00−7.40 (m, 9 H); ^{13}C NMR δ 21.1, 44.6, 55.1, 126.1, 126.3, 128.3, 128.8, 129.2, 129.4, 132.9, 134.2, 137.0, 138.6; HRMS calcd for $C_{17}H_{19}N$ *m/e* 237.1517, found 237.1496.

***R-trans*-1-(4-*tert*-Butylfuran-2-yl)-3-amino-1-butene (13c):** oil; $[\alpha]^{22}_D$ +3.2° (*c* 1.21, $CHCl_3$); ^{1}H NMR δ 1.16−1.23 (m, 12 H), 1.69 (br s, 2 H), 3.55−3.65 (m, 1 H), 6.11 (dd, J = 6.3, 15.9 Hz, 1 H), 6.17 (s, 1 H), 6.24 (d, J = 15.9 Hz, 1 H), 7.07 (s, 1 H); ^{13}C NMR δ 23.8, 30.7, 45.2, 48.9, 106.9, 116.6, 134.6, 135.9, 137.8, 152.6. Anal. Calcd for $C_{12}H_{19}NO$: N, 7.25. Found: N, 7.64.

***S-trans*-2-Methyl-6-amino-7-phenyl-2,4-heptadiene (13d):** oil; $[\alpha]^{22}_D$ +36.6° (*c* 0.99, $CHCl_3$); ^{1}H NMR δ 1.20 (br s, 2 H), 1.75 (s, 3 H), 1.78 (s, 3 H), 2.61 (dd, J = 8.3, 13.4 Hz, 1 H), 2.87 (dd, J = 5.1, 13.2 Hz, 1 H), 3.60−3.70 (m, 1 H), 5.60 (dd, J = 6.9, 15.0 Hz, 1 H), 5.82 (d, J = 10.5 Hz, 1 H), 6.37 (dd, J = 10.8, 15.0 Hz, 1 H), 7.20−7.40 (m, 5 H); ^{13}C NMR δ 18.2, 25.9, 44.8, 54.9, 124.5, 125.7, 126.2, 128.3, 129.3, 134.8, 138.9; HRMS calcd for $C_{14}H_{19}N$ *m/e* 201.1517, found 201.1543.

***trans,trans*-1-Phenyl-5-amino-1,3-pentadiene (13e):** oil; ^{1}H NMR δ 1.53 (br s, 2 H), 3.41 (d, J = 5.7 Hz, 2 H), 5.92 (dt, J = 15.3, 6.0 Hz, 1 H), 6.32 (dd, J = 10.5, 15.3 Hz, 1 H), 6.50 (d, J = 15.6 Hz, 1 H), 6.79 (dd, J = 10.5, 15.6 Hz, 1 H), 7.15−7.45 (m, 5 H); ^{13}C NMR δ 44.0, 126.2, 127.3, 128.5, 128.6, 130.0, 131.5, 135.5, 137.3. Anal. Calcd for $C_{11}H_{13}N$: N, 8.80. Found: N, 8.53.

Preparation of L-*trans*-1-(2-Pyrrolidinyl)-2-phenylethene (19). Ester **15** was prepared in a similar way to **9** except that only 2.05 equiv of NEt_3 was used. The procedure for the preparation of **19** is similar to that of **13** except that NEt_3 (2 mL, corresponding to 6.6 mmol scale) was present in the low-valent titanium mixture and there was no HCl/ethanol treatment: oil; $[\alpha]^{22}_D$ −64.5° (*c* 1.28, $CHCl_3$); ^{1}H NMR δ 1.50−1.70 (m, 1 H), 1.71−1.95 (m, 2 H), 1.96−2.15 (m, 1 H), 2.50 (br s, 1 H), 2.85−3.04 (m, 1 H), 3.06−3.20 (m, 1 H), 3.60−3.80 (m, 1 H), 6.23 (dd, J = 7.2, 15.9 Hz, 1 H), 6.53 (d, J = 15.9 Hz, 1 H), 7.10−7.50 (m, 5 H); ^{13}C NMR δ 25.2, 32.3, 46.4, 60.9, 126.2, 127.2, 128.4, 129.7, 132.4, 137.1; HRMS calcd for $C_{12}H_{15}N$ *m/e* 173.1205, found 173.1206.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **5g**, **13a−e**, and **19** are provided (24 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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