Enantioselective Lithiation and Substitution of (*E*)-Cinnamyl *N*,*N*-Diisopropylcarbamate through Use of (–)-Sparteine Complexes☆

Karin Behrens, Roland Fröhlich, Oliver Meyer, and Dieter Hoppe*

Organisch-Chemisches Institut der Universität,
Corrensstraße 40, D-48149 Münster, Germany
Fax: (internat.) +49 (0)251/8339772

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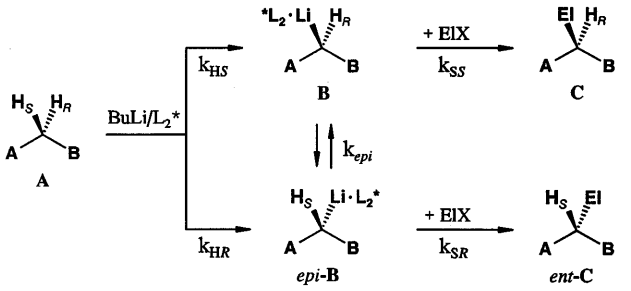
The title reaction leads to diastereomeric lithium carbanion pairs that are configurationally unstable and equilibrate even at temperatures below –50 °C. The initially formed epimer (1*S*)-*epi*-**10** is rapidly converted to the thermodynamically more stable (1*R*)-**10** (in toluene solution). Carboxylation, acylation with acid chlorides, stannylation, and silylation take place at the α-position with stereoinversion (79–86% *ee*). Methylating agents attack the γ-position; here, the stereochemical course depends on the leaving group, *anti*-$S_{E'}$ for the iodide (50% *ee*) and *syn*-$S_{E'}$ (48% *ee*) for the tosylate.

Chiral lithium/(−)-sparteine carbanion pairs **B** and *epi*-**B**, which are accessible by deprotonation of prochiral precursors **A**, are valuable tools in enantioselective synthesis[1][2]. Once produced, each of the epimeric ion pairs reacts stereospecifically with electrophiles to yield the enantioenriched products **C** or *ent*-**C**, respectively. The direction of stereospecificity may differ depending on the nature of the carbanionic species and the electrophile. In Scheme 1, a reaction proceeding with stereoretention is illustrated.

Three different mechanisms can be operative in the step responsible for the stereoselection (Scheme 1):

Scheme 1. Pathways of chiral induction in lithium carbanion pairs



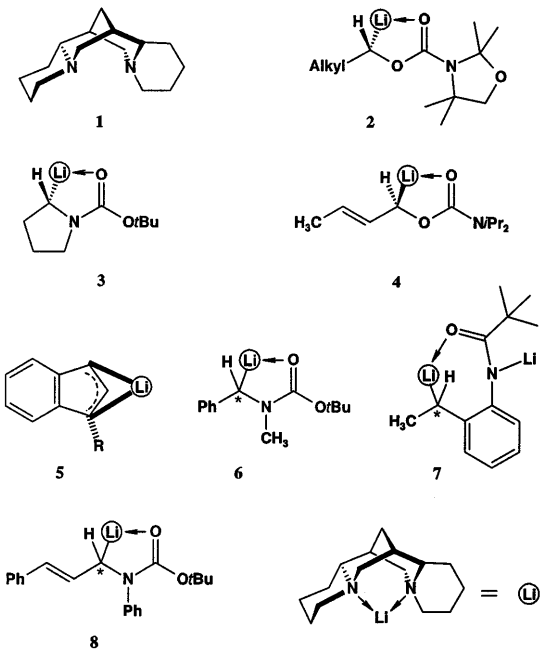
1. The chiral base alkyllithium/(−)-sparteine (**1**) differentiates between the enantiotopic protons H_S and H_R of the carbon acid **A** and the resulting ion pairs **B** and *epi*-**B** do not interconvert under the reaction conditions. The ratio of enantiomers **C** and *ent*-**C** thus reflects the rate ratio k_{HR}/k_{HS}.

2. The ion pairs **B** and *epi*-**B** are able to equilibrate and are then trapped by the electrophile ElX. If k_{SS} and k_{SR} are much greater than k_{epi}, the enantiomeric ratio reflects the (thermodynamically determined) equilibrium. The position of the equilibrium may be further shifted to one side or other by the preferential crystallization of one epimer[3].

3. In case 3, a kinetic resolution of the diastereomers **B** and *epi*-**B** by very different rates k_{SS} and k_{SR} in the substitution step is responsible for the ratio of enantiomers. This typical Curtin-Hammett situation applies, e.g. if $k_{SS} > k_{SR} << k_{epi}$.

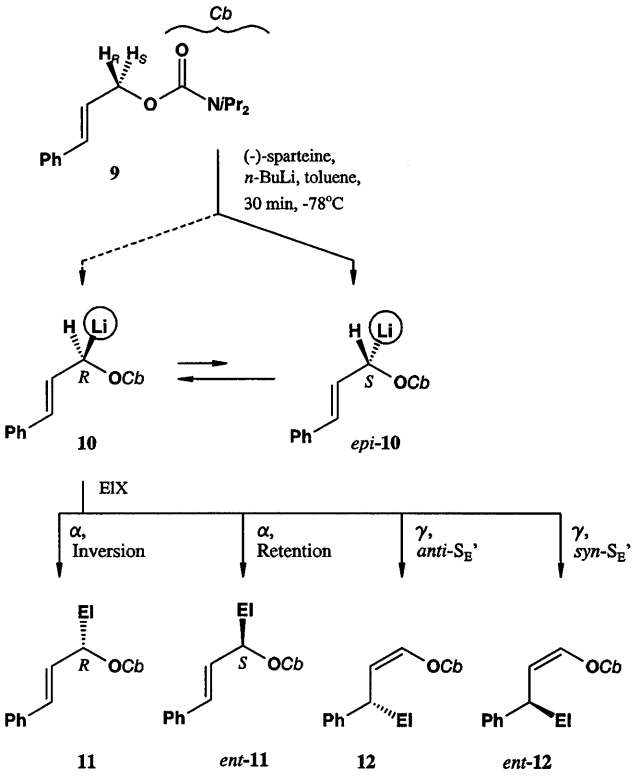
Case 1 was found to be valid for lithiated alkyl carbamates **2**[4], *N*-Boc-pyrrolidine **3**[5], and the cinnamyl amine **8**[6] (Scheme 2), while route 2 was found to be operative in the case of lithiated crotyl carbamate **4**[7], alkylindenides **5**[8], and *N*-Boc-benzylamines **6**[9]. Markedly different reaction rates for the two epimers were observed by Beak et al.[10] in the case of the benzyllithium derivatives **7**.

Scheme 2. Examples of chiral lithium/(−)-sparteine complexes of carbamates



  1434−193X/98/1111−2397 $ 17.50+.50/0

Scheme 3. (−)-Sparteine-mediated lithiation and substitution of carbamate **9** under standard conditions



11-12	a	b	c	d	e	f
El	CH_3	Me_3Si	Me_3Sn	Bu_3Sn	*t*BuC(=O)	CO_2Me[a]

[a] Obtained by substitution with CO_2 as electrophile, followed by *O*-methylation with diazomethane.

Results and Discussion

In view of the configurational instability of the allyllithium derivative **4** and, surprisingly, the configurational stability of the lithiated *N*-cinnamyl amide **8**[6], we investigated the asymmetric lithiation and substitution of the cinnamyl *N*,*N*-diisopropylcarbamate **9** (Scheme 3). The rapid deprotonation of the latter by means of *n*-butyllithium/TMEDA was recognized several years ago[11].

Under standard conditions, to a solution of (−)-sparteine (1.5 equiv.) in toluene (4 ml/mmol), *n*-butyllithium in hexane (1.3 equiv.) followed by a 0.25 M solution of the carbamate **9** were added dropwise at −78°C. The reaction mixture was allowed to stir for 30 min., and then the appropriate electrophile was added at this temperature (Scheme 3, Table 1). Trimethylsilyl chloride, trimethyltin chloride, tributyltin chloride, and pivaloyl chloride (entries 1−4) reacted with complete α-regioselectivity to afford the products **11b**/*ent*-**11b**, **11c**/*ent*-**11c**, **11d**/*ent*-**11d**, and **11e**/*ent*-**11e**, respectively, in enantiomeric ratios of 90:10 to 93:7 (79−86% *ee*). On the other hand, methyl iodide (entry 6) yielded solely the γ-adduct **12a**/*ent*-**12a** with only 50% *ee* (*er* = 75:25). The enantiomeric ratio was reversed when methyl tosylate (entry 7) was used as the methylating reagent; similar observations for a few benzylic systems were reported by Beak et al.[12]. Carboxylation of **10**/*epi*-**10**, followed by *O*-methylation with diazomethane, furnished a mixture of the regioisomeric esters **11f** and **12f** in a 75:25 ratio (entry 5), with *er* values 91:9 (82% *ee*) and 59:41 (18% *ee*).

The absolute configurations of the products **11b**, **11c**, **11e**, **11f**, and **12a** were determined by the following transformations (Scheme 4):

Ozonolysis of the product (+)-**12a**, derived from **10**/*epi*-**10** by reaction with methyl iodide, followed by reductive work-up, afforded the known[13] alcohol (+)-(*R*)-**13** and thus this product is assigned the (*S*)-configuration. Upon hydrogenation of their double bonds, the alkenes **11c**,**e**,**f** gave the same enantiomers as were obtained by the *sec*-butyllithium/(−)-sparteine-mediated deprotonation of the 3-phenylpropyl carbamate **15**. This protocol, proceeding via non-mesomerically stabilized lithium carbanion pairs, is known for its high reliability in the replacement of the *pro-S*−H in the starting material by any electrophile[1]. The silane (*S*)-**14b**, prepared from **15**, exhibited a specific rotation of $[\alpha]_D^{22} = 0$, and this value did not change significantly at longer wavelengths. Fortunately, the allylsilane **11b** provided suitable crystals for an X-ray analysis[14] with anomalous dispersion (Figure 1) clearly demonstrating its (*S*)-configuration [enantiopole parameter = 0.07(4)].

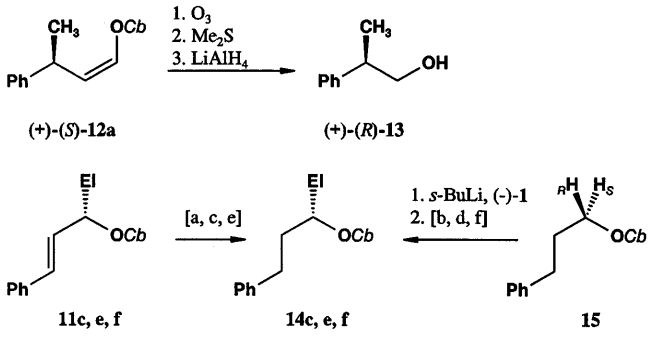
The following experiments were devised in order to elucidate the configuration of the predominant diastereomer in

Table 1. Products **11** and **12** obtained by substitution of carbamate **9**

Entry	Products	El	ElX	Yield (**11** + **12**)	Ratio **11**/**12**	*er* (*ee*) **11** (configuration)	*er* (*ee*) **12** (configuration)	$[\alpha]_D^{22}$ [a]
1	**11b**/*ent*-**11b**	Me_3Si	Me_3SiCl	88	100:0	93:7 (86, *S*)	−	−7.8
2	**11c**/*ent*-**11c**	Me_3Sn	Me_3SnCl	71	100:0	90:10 (80, *S*)	−	−48.1
3	**11d**/*ent*-**11d**	Bu_3Sn	Bu_3SnCl	85	100:0	[b]	−	−49.6
4	**11e**/*ent*-**11e**	*t*BuCO	*t*BuCOCl	86	100:0	90:10 (80, *R*)	−	−143
5	**11f**/*ent*-**11f**	CO_2Me	CO_2[c]	92	75:25	91:9 (82, *R*)	59:41 (18)[b]	−57.9
	12f/*ent*-**12f**							+19.1
6	**12a**/*ent*-**12a**	Me	MeI	85	0:100	−	75:25 (50, *S*)	+85.1
7	**12a**/*ent*-**12a**	Me	MeOTs	79	0:100	−	74:26 (48, *R*)	−81.7

[a] *c* = 1.0−1.2 (CH_2Cl_2). − [b] Configuration and/or *ee* unknown. − [c] Followed by *O*-methylation with diazomethane.

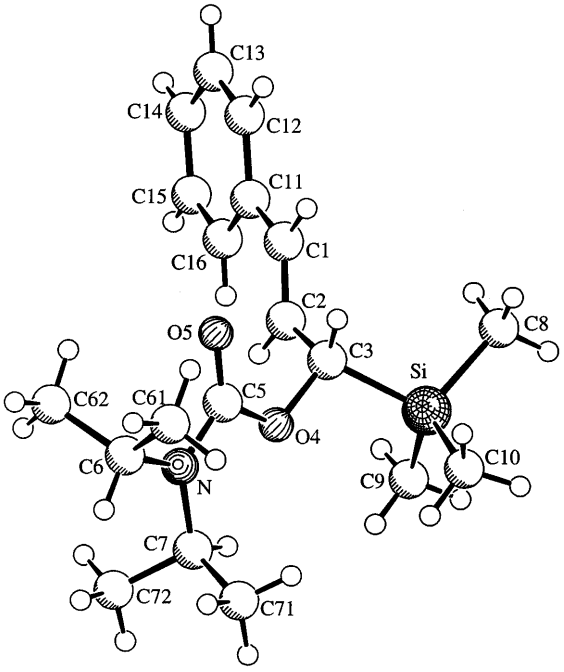
Scheme 4. Determination of the configurations of products **11** and **12**



11, 14	c	e	f
El	Me_3Sn	*t*BuC(=O)	CO_2Me

[a] (−)-(*S*)-**11c**, $KO_2C-N=N-CO_2K$, HOAc → (+)-(*S*)-**14c**, 41%. − [b] Me_3SnCl → (+)-(*S*)-**14c**, 30%. − [c] (−)-(*R*)-**11e**, H_2, 10% $Pd(OH)_2/C$ → (−)-(*R*)-**14e**, 78%. − [d] $^tBuC(=O)Cl$ → (−)-(*R*)-**14e**, 46%. − [e] (−)-(*R*)-**11f**, H_2, 10% $Pd(OH)_2/C$ → (−)-(*R*)-**14f**, 91%. − [f] CO_2/CH_2N_2 → (−)-(*R*)-**14f**, 30%.

Figure 1. SCHAKAL plot of **11b**

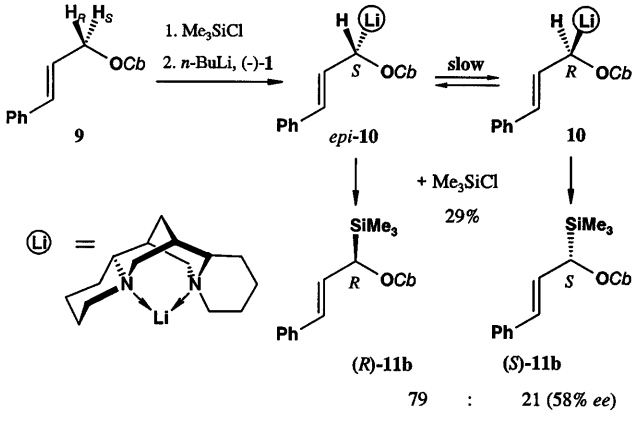


the ion pairs **10**/*epi*-**10** and to allow a distinction to be made between the possible mechanisms of stereoinduction.

The cinnamyl carbamate **9** was lithiated with *n*-butyllithium at −78°C in the presence of trimethylsilyl chloride (Scheme 5). To our surprise, (+)-(*R*)-*ent*-**11b** with 58% *ee* ($[\alpha]_D^{22}$ = +6.0) was the major enantiomer obtained. This is in contrast to the result obtained applying the standard procedure, which led to (−)-(*S*)-**11b** with 86% *ee* ($[\alpha]_D^{22}$ = −7.8).

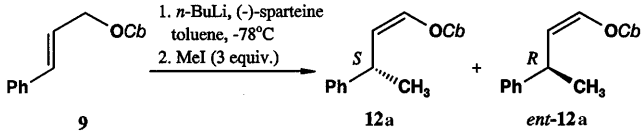
The "in situ trapping" experiment clearly reveals that the diastereomer that is initially formed in excess is the thermodynamically less stable one, and hence, it undergoes moderately rapid epimerization. Considering the high *pro-S* preference of the *sec*-butyllithium/(−)-sparteine reagent, we assign the (*S*)-configuration to *epi*-**10** and the (*R*)-configuration to **10**.

Scheme 5. Trapping of the kinetically determined intermediate *epi*-**10**



Further evidence for epimerization of *epi*-**10** to form **10**, even at temperatures of −78°C and below, comes from a series of experiments in which the standard conditions were altered with regard to the temperature of deprotonation and the length of time for which the reaction mixture was allowed to stand prior to quenching with methyl iodide. The results, collected in Table 2, demonstrate that equilibration occurs and that it is essentially complete after 0.5 h at −78°C.

Scheme 6. Deprotonation and methylation of **9** with methyl iodide under different conditions



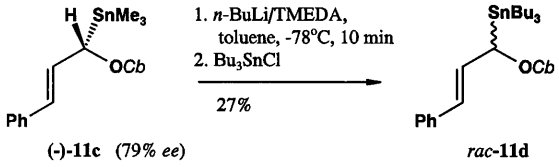
The stereochemical courses of the substitution reactions, deduced from the configurations of the predominant lithium complex (*R*)-**10** and the products, are as follows: Inversion for the α-selective reactions such as silylation, stannylation, acylation with acid chlorides, and α-carboxylation; *anti*-$S_{E'}$ for the alkylation with methyl iodide. The results are in good agreement with the limited number of substantiated reports on the stereochemistry of these reactions with benzylic[7d][7e][15][16] and allylic lithium compounds[17].

A further experiment underlines the configurational lability of lithium compounds of type **10**. The lithiodestannylation of the trimethylstannane (−)-**11c** (79% *ee*) in tolene with *n*-butyllithium/TMEDA and restannylation with tributyltin chloride afforded a completely racemic stannane *rac*-**11d** (Scheme 7). As we[15b] and others[7d][7e][16] have demonstrated, the destannylation of enantioenriched carbanions proceeds with strict stereoretention and the restannylation takes place at the benzylic position with inversion. Thus, if it was configurationally stable, *ent*-**11d** is expected to be the major product.

Table 2. Trapping of ion pairs **10**/*epi*-**10** by methyl iodide at different temperatures

Entry	Temperature [°C]	Time [h]	Yield [%]	Ratio **12a**/*ent*-**12a** (% *ee*)	
1	−110	0.5	80	58:42	(16)
2	−96	0.5	73	64:36	(28)
3	−78	0.1	80	67:33	(34)
4	−78	0.5	85	75:25	(50)
5	−78 → −28 → −78	3.5	77	78:22	(56)

Scheme 7. Lithiodestannylation of **11c**

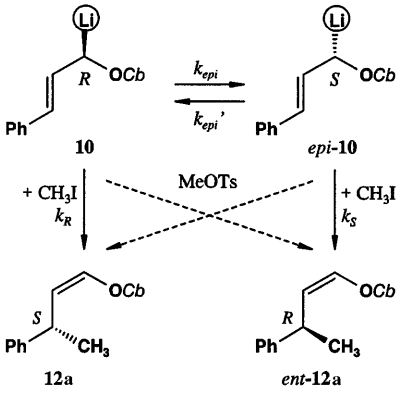


(-)-**11c** (79% *ee*) *rac*-**11d**

The stereochemistry of the methylation is completely reversed to *syn*-$S_{E'}$ when methyl tosylate is employed. There is some precedence for this behaviour, e.g. in the observations of Beak et al.[10] concerning the benzyllithium compound **7**[12].

At this stage of the investigation, one discrepancy remains. If the substitution reactions are stereospecific, why is the magnitude of chiral transmission different when the electrophile is changed? (It is particularly low for the methylation at the γ position). We assume that case 3 in Scheme 1, i.e. a dynamic kinetic resolution in the electrophilic substitution step, was responsible. In the present case, the experimental results can be explained if the minor diastereomer *epi*-**10** is the more reactive one (Scheme 8), i.e. $k_{SS} > k_{SR}$, and the rate of epimerization k_{epi} is greater than k_{SR}. In such a situation, the *er* must be further reduced when less of the electrophilic reagent is used. As indicated in Scheme 8, the enantiomeric excess drops to 6% *ee* when only 0.2 equiv. of methyl iodide is added.

Scheme 8. Divergent reaction courses in the methylation of **10** and *epi*-**10**



equiv. of CH_3I	3.0	0.6	0.2
ratio **12**/*ent*-**12**	75:25	69:31	53:47
yield [a]	85	50	16

[a] Based on **9**.

The same is true, albeit to a lesser extent, for substitution reactions at the α-position. The tributylstannane **11d** is formed with $[\alpha]_D^{22} = -49.6$ ($c = 1.0$ in CH_2Cl_2, approx. 79% *ee*) by addition of three equivalents of tributyltin chloride, whereas only $[\alpha]_D^{22} = -41.9$ ($c = 1.0$ in CH_2Cl_2, approx. 67% *ee*) was achieved by employing 0.5 equivalents of the reagent.

Attempts to determine the ratio of **10** and *epi*-**10** and the barrier of interconversion by temperature-dependent ^{1}H-NMR studies (600 MHz, in [D_8]toluene) failed. The difficulties arise in the interpretation of the experimental results, since already in the starting materials **9** four conformational diastereomers are recognized at low temperature resulting from frozen rotations of the amide bond (below 20°C) and of the isopropyl groups (below −40°C)[18][19].

Conclusions

The two epimeric lithium/(−)-sparteine complexes **10**/*epi*-**10**, derived from the cinnamyl carbamate **9**, are not configurationally stable at −78°C in toluene, in contrast to the corresponding lithium carbanion pairs derived from cinnamyl amine **8**[6]. The configuration of the major isomer, *epi*-**10**, produced by kinetically-controlled deprotonation with *n*-butyllithium/(−)-sparteine, is opposite to that of the major isomer **10** originating by equilibration. For the first time it is demostrated that the *pro-S* preference in the selection between enantiotopic protons by (−)-sparteine/butyllithium bases is also valid for allyl carbamates. Further, indubitable evidence for the stereochemical course of substitution of chiral aryl substituted allyllithium ion pairs is provided. Reactions with several electrophiles proceed regioselectively and stereospecifically at the α- or γ-position, but some levelling out reduces the initially achieved, thermodynamically-controlled stereoselectivity. The reason for this is assumed to be a "negative dynamic kinetic resolution" owing to the enhanced reactivity of the minor diastereomer. Nevertheless, the method provides an attractive route to optically active α-substituted cinnamyl alcohols, since a carbamate group, removable under mild conditions, is available[15a].

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Experimental Section

General: All organometallic reactions were performed under Ar with exclusion of air and moisture. Toluene was dried with Na be-

fore use. LC separations were carried out at 0.5−1.5 bar on silica gel 40−63 μm (Merck, Darmstadt). − IR: Perkin-Elmer 298. − Optical rotations: Perkin-Elmer polarimeter 241. − NMR: Bruker WM 300 (300 MHz and 75.5 MHz for ^1H and ^{13}C NMR, respectively). For ^1H NMR, $CDCl_3$ as solvent, TMS as internal standard; for ^{13}C NMR, $CDCl_3$ δ_C = 77.0. The ^1H-NMR shift experiments were performed by addition of +Eu(hfc)$_3$ or +Pr(hfc)$_3$, respectively, to a solution of the enantioenriched product (20 mg) in $CDCl_3$ (0.8 ml). − Combustion analysis: Perkin-Elmer 240, Institute of Organic Chemistry, University of Münster.

(E)-3-Phenyl-2-propenyl N,N-Diisopropylcarbamate (**9**): To (*E*)-3-phenyl-2-propen-1-ol (14.1 g, 105 mmol) and dry pyridine (11.8 g, 150 mmol), *N,N*-diisopropylcarbamoyl chloride[11][20] (16.4 g, 100 mmol) was added portionwise at room temp. After refluxing for 18 h and then cooling to room temp., the reaction mixture was poured onto a mixture of ice (50 g), conc. aq. HCl (20 ml), and Et_2O (50 ml). After separation of the phases, the aq. solution was extracted with further Et_2O (3 × 80 ml). The combined ethereal extracts were dried with anhydrous $Na_2SO_4/NaHCO_3$ (2:1) and the solvent was removed in vacuo. The residue was purified by flash chromatography on silica gel (400 g) with petroleum ether/Et_2O (8:1) as eluent, to yield 25.0 g of **9** (91%), colourless oil, R_f (PE/Et_2O, 2:1) = 0.56. − IR (film): $\tilde{\nu}$ = 1680 cm^{-1} (C=O), 1600, 1570 (C=C), 1380, 1360 [C(CH$_3$)$_2$]. − ^1H NMR ($CDCl_3$): δ = 1.23 (d, $J_{2,1}$ = 6.9 Hz, 2-H$_3$), 3.92 (m$_c$, 2 H, 1-H), 4.75 (dd, $J_{1',2'}$ = 6.2, $^4J_{1',3'}$ = 1.4 Hz, 1′-H$_2$), AB signal [δ_A = 6.33, δ_B = 6.63, J_{AB} = 16.0 Hz (= J_{trans}), additionally split by $J_{A,1'}$ = 6.2 Hz, 2′-H and 3′-H], 7.20−7.41 (m, 5 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 20.96 (C-2), 45.83 (C-1), 65.07 (C-1′), 124.65, 126.50, 127.72, 128.46 and 132.87 (Ar-C and C-2′, C-3′), 136.54 (*ipso*-C of Ph), 155.31 (C=O). − $C_{16}H_{23}NO_2$ (261.36): calcd. C 73.53, H 8.87, N 5.36; found C 73.62, H 8.89, N 5.55.

Deprotonation of **9** *and Substitution with Electrophiles. − General Procedure:* To a solution of (−)-sparteine (352 mg, 1.50 mmol) in dry toluene (4 ml) at −78°C under argon, *n*-butyllithium in hexane (1.6 M, 0.81 ml, 1.30 mol) followed after 10 min. by a solution of the carbamate **9** (261 mg, 1.00 mmol) in toluene (3 ml), were slowly introduced by means of syringes. The orange-green solution was stirred for 30 min. at −78°C (no crystallization occurred), and then the electrophile (3.00 mmol) was added dropwise. For carboxylations, gaseous CO_2 (liberated from dry ice) was introduced via a gas inlet. Stirring was continued for 2 h at −78°C, and then a mixture of glacial acetic acid (0.2 ml) and diethyl ether (4 ml), followed by 2 N aq. HCl (5 ml), were added. The aq. phase was extracted with diethyl ether (3 × 30 ml), washed with sat. aq. $NaHCO_3$, and dried with $Na_2SO_4/NaHCO_3$ (2:1). After evaporation of the solvent in vacuo, the residue was purified by flash chromatography on silica gel. In contrast to the standard procedure, carboxylation reactions were quenched directly with 2 N aq. HCl and washing with sat. aq. $NaHCO_3$ was omitted. The esterification of the crude product was performed by addition of diazomethane. Samples of the racemic products were produced by using *N,N,N′,N′*-tetramethylethylenediamine (TMEDA, 174 mg, 1.50 mmol) instead of (−)-sparteine. For variations of reaction temperatures and times, see Table 2.

(2E,1S)-3-Phenyl-1-trimethylsilyl-2-propenyl N,N-Diisopropylcarbamate (**11b**): Deprotonation and addition of trimethylsilyl chloride (0.33 g, 3.0 mmol) yielded 292 mg of **11b** (88%); colourless crystals, m.p. 67°C (*n*-hexane)[21]; shift experiment: *er* = 93:7 (86% *ee*), 10 mg +Eu(hfc)$_3$, $\Delta\delta$ (SiCH_3) = 0.03 ppm; R_f (PE/Et_2O, 1:1) = 0.63. − IR (KBr): $\tilde{\nu}$ = 1680 cm^{-1} (C=O), 1380, 1360 [C(CH$_3$)$_2$]. − ^1H NMR ($CDCl_3$): δ = 0.12 (s, $SiMe_3$), 1.25 (m$_c$, 12 H, 2-H$_3$), 3.96 (br. s, 1-H), 5.31 (dd, $J_{1',2'}$ = 6.3, $^4J_{1',3'}$ = 1.3 Hz, 1′-H), AB signal [δ_A = 6.28, δ_B = 6.38, J_{AB} (= J_{trans}) = 16.0 Hz, additionally split by $J_{A,1'}$ = 6.2, $^4J_{B,1'}$ = 1.2 Hz, 2′-H and 3′-H], 7.14−7.35 (m, 5 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = −3.02 ($SiMe_3$), 21.10 (C-2), 45.79 (C-1), 70.49 (C-1′), 126.09, 126.84, 126.91, 128.21 and 128.36 (Ar-C, C-2′, C-3′), 137.49 (*ipso*-C of Ph), 155.55 (C=O). − $C_{19}H_{31}NO_2Si$ (333.54): calcd. C 68.42, H 9.37, N 4.20; found C 68.60, H 9.25, N 4.25.

In Situ Trapping of the Ion Pairs **10***/epi-***10** *with Trimethylsilyl Chloride:* To a mixture of **9** (392 mg, 1.50 mmol), (−)-sparteine (527 mg, 2.25 mmol), and trimethylsilyl chloride (1.0 g, 9.5 mmol) in toluene (4 ml), *n*-butyllithium in hexane (1.6 M, 1.2 ml, 2.0 mmol) was added at −78°C. The reaction mixture was stirred for 2.5 h at −78°C, and then the standard work-up procedure was performed. Yield 144 mg of **11b** (29%), $[\alpha]_D^{22}$ = +6.0 (*c* = 1.1 in CH_2Cl_2); shift experiment: *er* = 21:79 (58% *ee*).

(2E,1S)-3-Phenyl-1-trimethylstannyl-2-propenyl N,N-Diisopropylcarbamate (**11c**): Deprotonation and addition of trimethyltin chloride (3.0 ml of a 1.0 M solution in hexane, 3.0 mmol) yielded 301 mg of **11c** (71%); colourless crystals, m.p. 26°C (Et_2O/PE)[21]; shift experiment: *er* = 90[22]:10 (79% *ee*), 5 mg +Eu(hfc)$_3$, $\Delta\delta$ (SnCH_3) = 0.02 ppm. − R_f (PE/Et_2O, 2:1) = 0.59. − IR (film): $\tilde{\nu}$ = 1670 cm^{-1} (C=O), 1370, 1350 [C(CH$_3$)$_2$]. − ^1H NMR ($CDCl_3$): δ = 0.16 (s, $SnMe_3$), 1.25 (d, $J_{2,1}$ = 6.5 Hz, 2-H$_3$), 3.93 (br. s, 1-H), 5.22 (dd, $J_{1',2'}$ = 6.2, $^4J_{1',3'}$ = 1.7 Hz, 1′-H), AB signal [δ_A = 6.33, δ_B = 6.47, J_{AB} (= J_{trans}) = 15.8 Hz, additionally split by $^4J_{A,1'}$ = 1.6, $J_{B,1'}$ = 6.2 Hz, 3′-H and 2′-H], 7.13−7.19 and 7.25−7.35 (2 m, 1 H, 4 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = −8.50 ($SnMe_3$), 20.98 and 22.61 (C-2), 46.00 (C-1), 72.82 (C-1′), 122.67, 125.83, 126.47, 128.46, 130.82 (Ar-C and C-2′, C-3′), 137.86 (*ipso*-C of Ph), 155.82 (C=O). − $C_{19}H_{31}NO_2Sn$ (424.15): calcd. C 53.80, H 7.37, N 3.30; found C 53.57, H 7.37, N 3.55.

(E)-3-Phenyl-1-tributylstannyl-2-propenyl N,N-Diisopropylcarbamate (**11d**): Deprotonation and addition of tributyltin chloride (976 mg, 3.0 mmol) yielded 469 mg of **11d** (85%); colourless oil; R_f (PE/Et_2O, 2:1) = 0.69. − IR (film): $\tilde{\nu}$ = 1670 cm^{-1} (C=O), 1380, 1370 [C(CH$_3$)$_2$]. − ^1H NMR ($CDCl_3$): δ = 0.87 (t, $J_{1'',2''}$ = 7.3 Hz, 1″-H$_2$), 0.92−0.99, 1.24−1.36 and 1.46−1.58 (3 m, 6 H, 21 H, 6 H, 2-H$_3$, 2″-H$_2$, 3″-H$_2$ and 4″-H$_3$), 3.96 (br. s, 1-H), 5.45 (dd, $J_{1',2'}$ = 6.1, $^4J_{1',3'}$ = 1.8 Hz, 1′-H), AB signal [δ_A = 6.29, δ_B = 6.46, J_{AB} (= J_{trans}) = 15.9 Hz, additionally split by $^4J_{A,1'}$ = 1.8, $J_{B,1'}$ = 6.1 Hz, 3′-H, 2′-H], 7.11−7.18 and 7.24−7.32 (2 m, 1 H, 4 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 10.58 (C-1″), 13.65 (C-4″), 20.90 (C-2), 27.43 and 29.01 (C-2″ and C-3″), 45.94 (C-1), 72.21 (C-1′), 122.05, 125.73, 126.27, 128.39 and 131.49 (Ar-C and C-2′, C-3′), 138.03 (*ipso*-C of Ph), 155.45 (C=O). − $C_{28}H_{49}NO_2Sn$ (550.39): calcd. C 61.10, H 8.97, N 2.54; found C 61.00, H 9.04, N 2.82.

(1R)-3,3-Dimethyl-2-oxo-1-[(E)-styryl]butyl N,N-Diisopropylcarbamate (**11e**): Deprotonation and addition of 2,2-dimethylpropanoyl chloride (0.36 g, 3.0 mmol) yielded 298 mg of **11e** (86%); colourless crystals, m.p. 141°C (Et_2O/PE)[21], ≥ 80% *ee*[23]; R_f (PE/Et_2O, 1:1) = 0.50. − IR (KBr): $\tilde{\nu}$ = 1710 cm^{-1} (CC=O), 1690 (NC=O), 1380, 1360 [C(CH$_3$)$_2$]. − ^1H NMR ($CDCl_3$): δ = 1.24 (s, 2-H$_3$ and CH$_3$ of *t*Bu), 3.87 (br. s, 1-H), 6.04 (dd, $J_{1',1''}$ = 8.4, $^4J_{1',2''}$ = 0.4 Hz, 1′-H), AB signal [δ_A = 6.21, δ_B = 6.81, J_{AB} (= J_{trans}) = 15.7 Hz, additionally split by $J_{A,1'}$ = 8.3 Hz, 1″-H and 2″-H], 7.20−7.43 (m, 5 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 20.63 and 21.21 (C-2), 27.03 (CH$_3$ of *t*Bu), 43.66 (C$_{quat.}$ of *t*Bu), 45.43 and 46.53 (C-1), 74.89 (C-1′), 122.58 (C-1″), 126.79, 128.48 and 128.68 (Ar-C), 136.05 (*ipso*-C of Ph), 136.56 (C-2″), 154.39 (NC=O), 210.52 (CC=O). − $C_{21}H_{31}NO_3$ (345.48): calcd. C 73.01, H 9.04, N 4.05; found C 72.73, H 9.12, N 4.25.

Methyl (3E,2R)-2-(N,N-Diisopropylcarbamoyloxy)-4-phenyl-3-butenoate (**11f**) *and Methyl (Z)-4-(N,N-Diisopropylcarbamoyloxy)-2-phenyl-3-butenoate* (**12f**): Deprotonation and addition of CO_2 (in excess) followed by *O*-methylation with diazomethane yielded 219 mg of **11f** (69%) and 73 mg of **12f** (23%).

11f: Colourless crystals, m.p. 59°C (Et_2O/PE)[21]; shift experiment: *er* = 91[22]:9 (82% *ee*), 7 mg +Eu(hfc)$_3$, Δδ (OCH_3) = 0.07 ppm; R_f (PE/Et_2O, 2:1) = 0.53. − IR (KBr): $\tilde{\nu}$ = 1760 cm^{-1} (OC=O), 1690 (NC=O). − ^{1}H NMR ($CDCl_3$): δ = 1.24−1.31 (m, 12 H, 2′-H_3), 3.77 (s, OCH_3), 3.97 (br. s, 2 H, 1′-H), 5.66 (dd, $J_{2,3}$ = 7.0, $^4J_{2,4}$ = 1.3 Hz, 2-H), AB signal [δ_A = 6.30, δ_B = 6.80, J_{AB} (= J_{trans}) = 16.0 Hz, additionally split by $J_{A,2}$ = 6.9, $^4J_{B,2}$ = 1.2 Hz, 3-H and 4-H], 7.24−7.42 (m, 5 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 20.66 and 22.62 (C-2′), 45.48 (C-1′), 52.32 (OCH_3), 73.47 (C-2), 121.96 (C-3), 126.78, 128.33 and 128.60 (Ar-C), 134.61 (C-4), 135.88 (*ipso*-C of Ph), 154.28 (NC=O), 170.08 (OC=O). − $C_{18}H_{25}NO_4$ (319.40): calcd. C 67.69, H 7.89, N 4.39; found C 67.85, H 8.08, N 4.52.

12f: Colourless crystals, m.p. 57°C (Et_2O/PE)[21]; shift experiment: *er* = 59:41[22] (17% *ee*), 14 mg +Eu(hfc)$_3$, Δδ (OCH_3) = 0.03 ppm. − R_f (PE/Et_2O, 2:1) = 0.67. − IR (KBr): $\tilde{\nu}$ = 1740−1700 cm^{-1} (NC=O, OC=O). − ^{1}H NMR ($CDCl_3$): δ = 1.22 and 1.24 (2 d, $J_{2',1'}$ = 6.7 Hz, 2′-H_3), 3.69 (s, OCH_3), 3.84 and 3.97 (2 br. s, 1′-H), 4.78 (dd, $J_{2,3}$ = 9.2, $^4J_{2,4}$ = 1.1 Hz, 2-H), AB signal [δ_A = 5.31, δ_B = 7.21, J_{AB} (= J_{cis}) = 6.4 Hz, additionally split by $J_{A,2}$ = 9.1, $^4J_{B,2}$ = 1.2 Hz, 3-H, 4-H), 7.23−7.35 (m, 5 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 20.39 and 21.33 (C-2′), 46.11 and 46.74 (C-1′), 47.80 (C-2), 52.29 (OCH_3), 107.49 (C-3), 127.30, 127.73 and 128.69 (Ar-C), 136.43 (C-4), 138.55 (*ipso*-C of Ph), 151.99 (NC=O), 172.69 (OC=O). − $C_{18}H_{25}NO_4$ (319.40): calcd. C 67.69, H 7.89, N 4.39; found C 67.81, H 8.03, N 5.58.

(1Z,3S)-3-Phenyl-1-butenyl N,N-Diisopropylcarbamate (**12a**): Deprotonation and addition of methyl iodide (0.43 g, 3.0 mmol) yielded 234 mg of **12a** (85%); colourless oil, shift experiment: *er* = 75[22]:25 (50% *ee*), 31 mg +Pr(hfc)$_3$, Δδ (2′-H) = 0.09 ppm; R_f (PE/Et_2O, 2:1) = 0.52. − IR (film): $\tilde{\nu}$ = 1710 cm^{-1} (C=O). − ^{1}H NMR ($CDCl_3$): δ = 1.23 and 1.25 (2 d, $J_{2,1}$ = 6.9 Hz, 2-H_3), 1.38 (d, $J_{4',3'}$ = 7.2 Hz, 4′-H_3), 3.80 and 4.06 (2 br. s, 1-H), superimposed by: 3.97 (dq, $J_{3',2'}$ = $J_{3',4'}$ = 7.6 Hz, 3′-H), 4.91 [dd, $J_{2',3'}$ = 9.3, $J_{2',1'}$ (= J_{cis}) = 6.4 Hz, 2′-H], 7.05 [dd, $J_{1',2'}$ (= J_{cis}) = 6.4, $^4J_{1',3'}$ = 1.0 Hz, 1′-H], 7.14−7.32 (m, 5 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 20.42 and 21.41 (C-2), 22.29 (C-4′), 35.58 (C-3′), 45.82 and 46.68 (C-1), 115.69 (C-2′), 125.98, 126.81 and 128.38 (Ar-C), 134.00 (C-1′), 146.06 (*ipso*-C of Ph), 152.73 (C=O). − $C_{17}H_{25}NO_2$ (275.39): calcd. C 74.14, H 9.15, N 5.09; found C 74.24, H 9.04, N 5.29.

Experiments to Determine the Stereochemical Correlations − 3-Phenylpropyl N,N-Diisopropylcarbamate (**15**): Prepared from 3-phenylpropanol (3.50 g, 25.7 mmol) according to the procedure given for the synthesis of **9**. Yield 6.14 g of **15** (95%), colourless oil, R_f (PE/Et_2O, 1:1) = 0.44. − IR (film): $\tilde{\nu}$ = 1680 cm^{-1} (C=O), 1380, 1360 [C(CH_3)$_2$]. − ^{1}H NMR ($CDCl_3$): δ = 1.22 (d, $J_{2,1}$ = 6.9 Hz, 2-H_3), 1.98 (m_c, 2 H, 2′-H_2), 2.71 (m_c, 2 H, 3′-H_2), 3.90 (br. s, 1-H), 4.12 (t, $J_{1',2'}$ = 6.4 Hz, 1′-H_2), 7.14−7.31 (m, 5 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 20.98 (C-2), 30.83 (C-2′), 32.49 (C-3′), 45.70 (C-1), 63.93 (C-1′), 125.83 and 128.30 (Ar-C), 141.47 (*ipso*-C of Ph), 155.68 (C=O). − $C_{16}H_{25}NO_2$ (263.38): calcd. C 72.97, H 9.57, N 5.32; found C 72.79, H 9.70, N 5.60.

Methyl (R)-2-(N,N-Diisopropylcarbamoyloxy)-4-phenylbutanoate (**14f**) *(Typical Procedure):* To a solution of (−)-sparteine (**1**) (509 mg, 2.18 mmol) in toluene (5 ml), was added *sec*-butyllithium in cyclohexane/hexane (1.34 M, 1.57 ml, 2.10 mmol) followed by **15** (395 mg, 1.50 mmol). The reaction mixture was stirred for 4.5 h at −78°C, and then CO_2 was introduced. Aqueous work-up and esterification as described for **9** yielded 147 mg of **14f** (30%), colourless oil, $[\alpha]_D^{22}$ = −17.3 (*c* = 1.2 in CH_2Cl_2), R_f (PE/Et_2O, 2:1) = 0.55. − IR (film): $\tilde{\nu}$ = 1750 cm^{-1} (OC=O), 1690 (NC=O), 1380, 1360 [C(CH_3)$_2$]. − ^{1}H NMR ($CDCl_3$): δ = 1.27 (br. s, 2′-H_3), 2.13−2.22 (m, 2 H, 3-H_2), 2.76 (m_c, 2 H, 4-H_2), 3.72 (s, OCH_3), 3.88 and 4.07 (2 br. s, 1′-H), 5.08 (t, $J_{2,3}$ = 6.3 Hz, 2-H), 7.16−7.32 (m, 5 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 20.65 and 21.62 (C-2′), 31.74 (C-3), 33.23 (C-4), 45.61 and 46.62 (C-1′), 52.00 (OCH_3), 72.05 (C-2), 126.16, 128.36 and 128.49 (Ar-C), 140.79 (*ipso*-C of Ph), 154.77 (NC=O), 171.56 (OC=O). − $C_{18}H_{27}NO_4$ (321.42): calcd. C 67.26, H 8.47, N 4.36; found C 67.18, H 8.38, N 4.17.

14f *by Hydrogenation of* **11f**: A mixture of ester (−)-**11f** (113 mg, 0.35 mmol, 85% *ee*) and palladium(II) hydroxide (11 mg, 10% *w/w*) in MeOH (3 ml) was stirred under a H_2 atmosphere at room temp. for 2 h. Standard work-up afforded 104 mg of **14f** (91% yield, 72% *ee*), $[\alpha]_D^{22}$ = −12.4 (*c* = 1.2 in CH_2Cl_2).

The following were prepared analogously:

(R)-3,3-Dimethyl-2-oxo-1-(2-phenylethyl)-butyl N,N-Diisopropylcarbamate (**14e**): Deprotonation and addition of 2,2-dimethylpropanoyl chloride (0.54 g, 4.5 mmol) yielded 240 mg of **14e** (46%); colourless oil, $[\alpha]_D^{22}$ = −23.3 (*c* = 1.0 in CH_2Cl_2), R_f (PE/Et_2O, 1:1) = 0.52. − IR (film): $\tilde{\nu}$ = 1680 cm^{-1} (C=O), 1380, 1360 [C(CH_3)$_2$]. − ^{1}H NMR ($CDCl_3$): δ = 1.18 (s, *t*Bu), 1.25 (m_c, 12 H, 2-H_3), 1.97−2.06 (m, 2 H, 1′′-H_2), 2.65−2.84 (m, 2 H, 2′′-H_2), 3.81 and 4.01 (2 br. s, 1-H), 5.45 (m_c, 1 H, 1′-H), 7.14−7.32 (m, 5 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 20.85 (C-2), 26.95 (CH_3 of *t*Bu), 32.04 (C-1′′), 33.12 (C-2′′), 43.32 ($C_{quat.}$ of *t*Bu), 46.55 (C-1), 73.28 (C-1′), 126.18, 128.37 and 128.54 (Ar-C), 140.98 (*ipso*-C of Ph), 154.70 (NC=O), 212.48 (CC=O). − $C_{21}H_{33}NO_3$ (347.50): calcd. C 72.59, H 9.57, N 4.36; found C 72.58, H 9.86, N 4.37.

Hydrogenation of **11e** (76 mg, 0.22 mmol) afforded 60 mg of **14e** (78%), $[\alpha]_D^{22}$ = −18.7 (*c* = 1.0 in CH_2Cl_2), ≥ 80% *ee*.

(S)-3-Phenyl-1-(trimethylsilyl)propyl N,N-Diisopropylcarbamate (**14b**): Deprotonation and addition of trimethylsilyl chloride (1.0 g, 9.5 mmol) yielded 216 mg of **14b** (43%); colourless oil, $[\alpha]_D^{22}$ = ±0.0, $[\alpha]_{365}^{22}$ = −4.6 (*c* = 1.1 in CH_2Cl_2), R_f (PE/Et_2O, 1:1) = 0.66. − IR (film): $\tilde{\nu}$ = 1680 cm^{-1} (C=O), 1380, 1360 [C(CH_3)$_2$]. − ^{1}H NMR ($CDCl_3$): δ = 0.06 (s, $SiMe_3$), 1.25 (m_c, 12 H, 2-H_3), 1.77−2.03 (m, 2 H, 2′-H_2), AB signal (δ_A = 2.61, δ_B = 2.74, J_{AB} = 13.6 Hz, additionally split by $J_{A,2'\text{-}H(1)}$ = 10.6, $J_{A,2'\text{-}H(2)}$ = 6.1, $J_{B,2'\text{-}H(2)}$ = 10.9, $J_{B,2'\text{-}H(1)}$ = 5.1 Hz, 3′-H_2), 2.80 and 4.11 (2 br. s, 1-H), 4.79 (dd, $J_{1',2'\text{-}H(1)}$ = 10.5*, $J_{1',2'\text{-}H(2)}$ = 3.8 Hz*, 1′-H), 7.14−7.31 (m, 5 H, aromatic H); *assignments interchangeable. − ^{13}C NMR ($CDCl_3$): δ = −3.22 ($SiMe_3$), 21.58 (C-2), 33.76 and 33.87 (C-2′, C-3′), 46.39 (C-1), 68.57 (C-1′), 125.73 and 128.32 (Ar-C), 142.44 (*ipso*-C of Ph), 156.26 (C=O). − $C_{19}H_{33}NO_2Si$ (335.56): calcd. C 68.01, H 9.91, N 4.17; found C 68.00, H 10.00, N 4.64.

(S)-3-Phenyl-1-(trimethylstannyl)propyl N,N-Diisopropylcarbamate (**14c**): Deprotonation and addition of 1.0 M trimethyltin chloride (3.0 ml, 3.0 mmol) in toluene yielded 213 mg of **14c** (32%); colourless oil, $[\alpha]_D^{22}$ = +38.6 (*c* = 1.0 in CH_2Cl_2), R_f (PE/Et_2O, 2:1) = 0.61. − IR (film): $\tilde{\nu}$ = 1660 cm^{-1} (C=O), 1380, 1360 [C(CH_3)$_2$]. − ^{1}H NMR ($CDCl_3$): δ = 0.10 (s, $SnMe_3$), 1.22 (d, $J_{2,1}$ = 6.4 Hz, 2-H_3), 2.03−2.31 (m, 2 H, 2′-H_2), AB signal (δ_A = 2.67, δ_B = 2.78, J_{AB} = 13.6 Hz, additionally split by $J_{A,2'\text{-}H(1)}$ = 10.2, $J_{A,2'\text{-}H(2)}$ = 6.3, $J_{B,2'\text{-}H(2)}$ = 10.4, $J_{B,2'\text{-}H(1)}$ = 5.3 Hz, 3′-H_2), 3.73 and 4.08 (2 br. s, 1-H), 4.49 (dd, $J_{1',2'\text{-}H(1)}$ = 9.1*, $J_{1',2'\text{-}H(2)}$ = 5.2 Hz*, 1′-H), 7.17−7.32 (m, 5 H, aryl-H); *assignments inter-

changeable. – ^{13}C NMR ($CDCl_3$): δ = −8.93 ($SnMe_3$), 21.19 (C-2), 34.48 (C-2′), 36.12 (C-3′), 45.27 (C-1), 71.51 (C-1′), 125.80 and 128.36 (Ar-C), 142.00 (*ipso*-C of Ph), 156.46 (C=O). – $C_{19}H_{33}NO_2Sn$ (426.17): calcd. C 53.55, H 7.80, N 3.29; found C 53.82, H 7.89, N 3.62.

Preparation of **14c** *by Hydrogenation of* **11c**: To stannane (−)-**11c** (130 mg, 0.31 mmol, 79% *ee*) and dipotassium azodicarboxylate[24] (2.98 g, 15.3 mmol) in MeOH (6 ml), CH_3CO_2H (1.84 g, 30.6 mmol) was slowly added at 0°C. The reaction mixture was allowed to warm to room temp. and was stirred overnight until the yellow colour had disappeared. Aqueous work-up and purification by LC yielded 54 mg of **14c** (42% yield, 75% *ee*), $[\alpha]_D^{22}$ = +28.9 (*c* = 1.0 in CH_2Cl_2).

(R)-2-Phenylpropan-1-ol (**13**) *from* **12a**: A stream of ozone was bubbled through a solution of carbamate **12a** (434 mg, 1.58 mmol, 54% *ee*) in CH_2Cl_2 (15 ml) at −78°C until a blue colour persisted (15 min.). Excess O_3 was then removed with a stream of argon. Dimethyl sulfide (0.29 g, 4.7 mmol) was added and the reaction mixture was allowed to warm to room temp. (3 h). The volatiles were then removed in vacuo. The residue was dissolved in THF (6 ml) and this solution was added dropwise to a chilled suspension of $LiAlH_4$ (120 mg, 3.16 mmol) in THF (5 ml). After stirring the reaction mixture for 12 h at room temp., Fieser work-up[25] [H_2O (0.12 ml), 15% aq. NaOH (0.12 ml), followed by H_2O (0.36 ml)] followed by LC (silica gel, PE/Et_2O, 4:1) afforded 170 mg of **13** (79%), $[\alpha]_D^{22}$ = +2.8 (*c* = 1.1 in $CHCl_3$) approx. 20% *ee*; {ref.[13] $[\alpha]_D^{22}$ = +13.6 (*c* = 1.1 in $CHCl_3$)}.

☆ Dedicated to Professor *Bernt Krebs* on the occasion of his 60th birthday.

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