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Asymmetric Induction in the Wittig-Still Rearrangement of Ethers Containing an Allylic Stereocenter – Diastereocontrol by Allylic Nitrogen

Henning Priepke, Reinhard Brückner*, Klaus Harms [+]

Fachbereich Chemie der Philipps-Universität,
Hans-Meerwein-Straße, D-3550 Marburg

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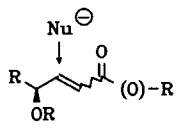
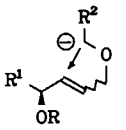
The stereochemistry of Wittig-Still rearrangements under the influence of an allylic stereogenic center attached to Bn_2N or RNBoc groups is studied. Rearrangements are subject to stereocontrol through asymmetric induction. Stannylated allyl ethers **13** with *Z* double bonds give *syn*-configuration amino alcohols **15** exclusively (ds >95: <5 – >99.8: <0.2). Stannanes of *E* configuration **14** lead to **15** less selectively (*syn*:*anti* = 46:54 – 92:8). X-ray structural data are provided for amino alcohol *syn*-**15b** and for the bis(carbamate) **17**.

In an allylic system the faces of the C=C bond become diastereotopic if the allylic carbon represents a stereogenic center ("stereocenter"). Hence, reactions with this double bond can – in principle – exhibit facial selectivity. In fact, such facial selectivity abounds, as shown by an ever increasing number of examples [1].



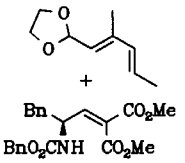
E-**1**: *top or bottom face attack*



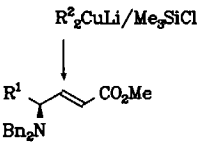
E-, *Z*-**2**: *bottom face attack*

Z-**1**: *top face attack*

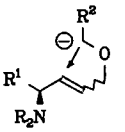
For instance, nucleophiles ("Nu") add preferentially to *one* face of allylically oxygenated electron-deficient olefins. Top face selectivity was found in additions to enones/enoates **1** with *Z* configuration for Nu = $BnNH_2$ [2], $BuCu \cdot BF_3$ [3], $Ph_3P=CMe_2$ [4], $Ph_2S=CMe_2$ [5], or cyclopentadiene [6]. Nucleophilic additions to *E*-configurated enones/enoates **1** exhibited top face selectivies for Nu = $MeO^{\ominus}$ [7], $BnNH_2$ [2], $(methallyl)_2CuLi$ [8], $Ph_2S=CMe_2$ [5], and cyclopentadiene [6]. Bottom face selectivity was reported for reactions between *E*-**1** and Nu = $BuCu \cdot BF_3$ [3], Bu_2CuLi [8], $(vinyl)_2CuLi$ [9], $Bu_2Cu(CN)Li_2$ [10], $Ph_3P=CMe_2$ [4,11], cyclopentadiene [12], or an *o*-quinone dimethide [13,14]. That these *intermolecular* nucleophilic reactions are stereoselective inspired us to study the steric course of [2,3] Wittig rearrangements under the influence of a similar stereocenter, i.e. rearrangements of allylically oxygenated ether anions **2**. We were led by the idea that a [2,3] Wittig rearrangement – simplified – constitutes an *intramolecular* nucleophilic reaction, i.e. an S_N2' type substitution, in a sense. This common feature of nucleophilic double bond attack was the basis of our hope that the Wittig rearrangement of **2** would experience as much stereocontrol as the cited additions to enones/enoates **1** [15]. In fact, asymmetric induction governs the stereochemistry of such Wittig rearrangements quite efficiently: The anion moiety of the lithiated ether **2** attacks the C=C bond preferentially or exclusively from the bottom face [16].



3: *bottom face attack*



4: *top face attack (?)*



5: *facial selectivity?*

Bn = Benzyl

Stereoselective olefin reactions under the influence of an allylic stereocenter bearing a heteroatom *other* than oxygen have not been studied systematically. As to stereodirecting effects of allylic nitrogen, we are aware of only two reports: Tamm et al. [17] isolated (51%) exclusively a compound derived from a Diels-Alder reaction of carbamate **3** at its bottom face, and Reetz [18] found >96: <4 diastereoselectivities for the conjugate additions of lower-order cuprates to amino acrylic esters **4** [19]. Scattered as these findings are, they demonstrate that allylic nitrogen *can* determine the facial selectivity of nucleophilic reactions at an adjacent double bond.

[+] To whom inquiries concerning the X-ray structural analyses should be addressed.

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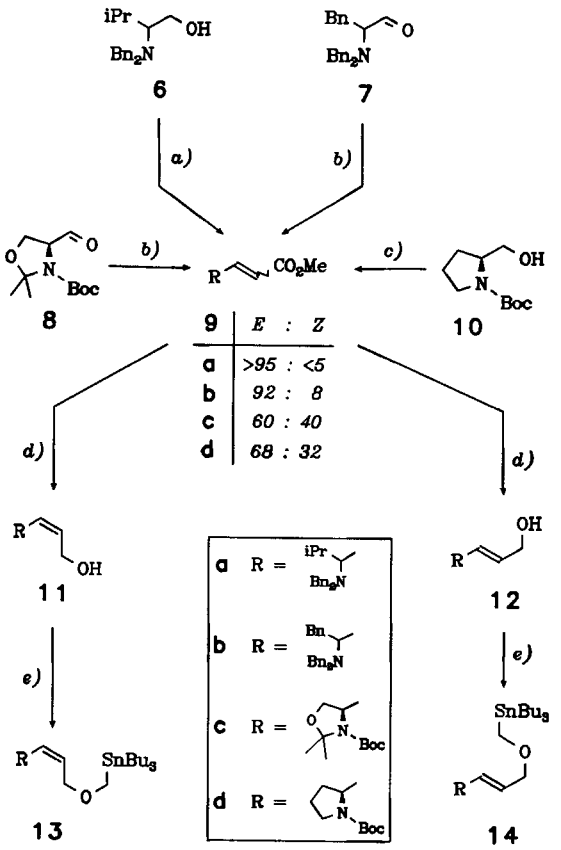
Would a nitrogen atom – when attached to the allylic stereocenter of an ether anion **5** – steer the faciality of a [2,3] Wittig rearrangement, too? As will be shown in this communication for Wittig-Still rearrangements[20], i.e. [2,3] rearrangements of **5** with R^2 = H, it *does*.

Scheme 1



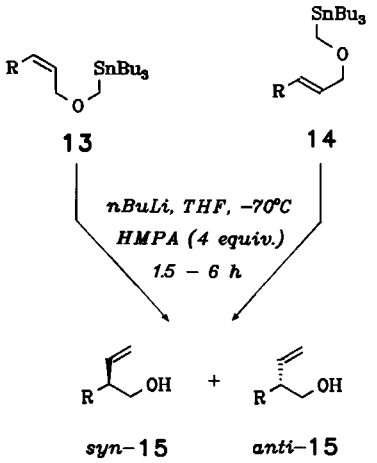
a) $(COCl)_2$, DMSO, NEt_3; NaH, $(EtO)_2(P{=}O)CH_2CO_2Me$, THF.– b) $Ph_3P{=}CHCO_2Me$, MeOH.– c) $(COCl)_2$, DMSO, NEt_3; $Ph_3P{=}CHCO_2Me$, MeOH.– d) DIBAH[22].– e) KH, $Bu_3Sn{-}CH_2{-}I$.

% Yield	9	11	12	13	14
a	60	–	95	–	76
b	93	a)	100	48 b)	81
c	91	72	30	77	54
d	77	56	65	32	71

a) Not isolated.– b) Yield over 2 steps.

Wittig-Still intermediates are usually[21] generated from stannanes by tin/lithium exchange. Hence, our first objective was to prepare the stannylated ethers *Z*-**13b–d** and *E*-**14a–d** (Scheme 1). These compounds resulted from the DIBAH reduction[22] of γ-amino acrylic esters **9** to allylic alcohols **11/12**, followed by etherification with KH/Bu_3SnCH_2I (method: ref.[20]). If possible, the ester precursors **9** were prepared as mixtures of *E* and *Z* isomers. Since these isomers were readily separable by flash chromatography[23], *one* batch of ester could be conveniently converted into *both* configurational series of stannanes (*Z*-**13**, *E*-**14**). *E*/*Z* mixtures of esters **9b–d** were obtained by Wittig reactions of the precursor α-amino aldehydes with $Ph_3P{=}CH{-}CO_2Me$ *in methanol*. These conditions were first described by Tronchet and Gentile, who obtained a *Z*-configuration α,β-unsaturated ester (*Z*:*E* = 92:8) from a tetrahydro-2-furancarbaldehyde; they have since proven a versatile tool for the synthesis of α,β-unsaturated esters with *Z* configuration from α-alkoxy aldehydes in general[24]. Even though in the case at hand – the condensation of $Ph_3P{=}CH{-}CO_2Me$ with α-amino aldehydes in methanol – *E* isomers prevailed, the Tronchet-Gentile method concomitantly delivered 8, 40, and 32 rel-% of the *Z*-configuration esters **9b**, **c**, and **d** (Scheme 1). The only ester prepared by Wittig-Horner olefination was **9a**. It was obtained with >95:<5 *E* selectivity[25]. α-Amino aldehydes were the starting materials for all synthetic sequences of Scheme 1. They were used as

Scheme 2. Diastereoselective Wittig-Still rearrangements [*syn*:*anti* ratios determined by ^1H NMR spectroscopy (**a**, **b**) or capillary GLC (**c**, **d**)]



	R	From Z stannane % Yield	From Z stannane syn:anti	From E stannane % Yield	From E stannane syn:anti
a	iPr Bn2N a)	–	–	90	46:54
b	Bn Bn2N a)	45 b)	>95:<5	82	78:22
c	O N Boc	75 c)	>99.8:<0.2	79 c)	92:8
d	N Boc	88	>99.8:<0.2	77	70:30

a) Racemic material; one enantiomer depicted.– b) 40% of **11b** *was recovered.– c) No HMPA was added.*

such (**8**[26], **7**[27]) or generated by in situ Swern oxidation[28] of amino alcohols **6**[27] and **10**[29].

Wittig-Still rearrangements[20] of the stannylated ethers **13b–d** and **14a–d** were performed in THF by treatment with 1.2–2.3 equivalents of *n*-BuLi. Usually, 4 equivalents of HMPA were added to the reaction mixture beforehand (Scheme 2). HMPA was added to improve the yield of rearrangement product, in analogy to our experience with Wittig-Still rearrangements of oxygenated ethers **2**[16f]. Indeed, when stannane **14d** was rearranged in the absence of HMPA, the yield dropped from 77% to 45%[30].

In general, the rearrangements were high-yielding, delivering 75–90% of homoallylic alcohols **15** (Scheme 2). A lower yield resulted from the rearrangement of amino ether *Z*-**13b**, where about as much fragmentation to allyl alcohol **11b**[31] (40%) as [2,3] shift to **15b** (45%) occurred. When mixtures of *syn* and *anti* isomers were produced, they were not separated.

The *syn*/*anti* assignment of rearrangement product **15a** is based on the low-field shift of the olefinic –CH= proton in *syn* (δ = 5.88) vs. *anti* epimer (δ = 5.52). Comparably spaced ^{1}H NMR shifts – δ_{syn} = 5.90, δ_{anti} = 5.76 and δ_{syn} = 5.84, δ_{anti} = 5.63 – are found in alcohols where the Bn_2N group is replaced by BnO and OH groups, respectively[16f]. Similar favored conformations – a prerequisite for the homology of δ_{syn} and δ_{anti} values – may be assumed. Intramolecular H-bonds in the BnO and OH containing reference compounds were inferred from their ^{1}H NMR spectra[16f], and H-bonding in **15a** is made very likely by the occurrence of a H-bond in the structurally related rearrangement product **15b** (vide infra).

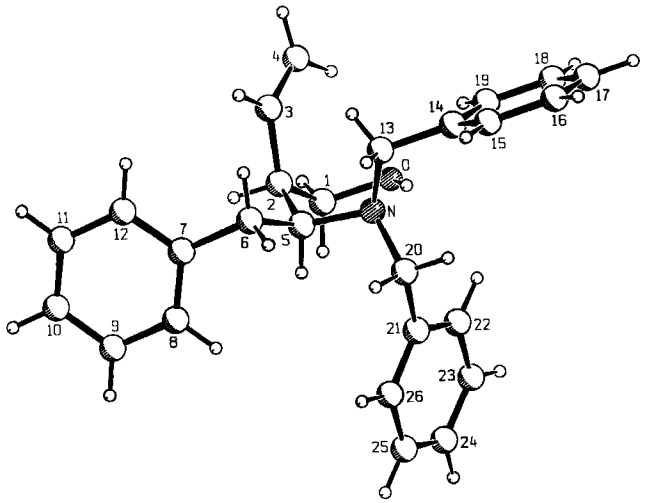
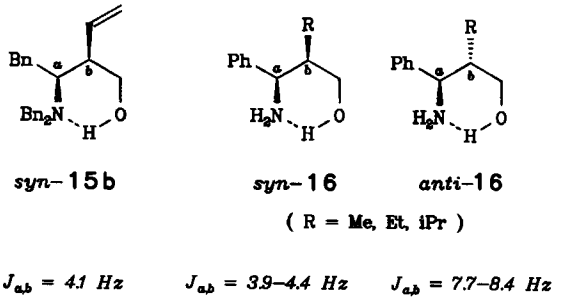


Figure 1. SCHAKAL plot of the solid-state structure of one of the enantiomers of amino alcohol **15b**[32]

The stereostructure of the rearrangement product *syn*-**15b** was determined by X-ray diffractometry (Figure 1). The existence of a hydrogen bond between the hydroxy (H donor) and dibenzylamino groups (H acceptor) emerges from the short N···H bond length (1.89 Å) as compared to a distance of ca. 2.80 Å expected for *inter*molecular association[33]. Also, oxygen and nitrogen come as close to each other (N···O = 2.84 Å) as a hydrogen bond permits (2.6–2.9 Å[34]).

Scheme 3



In the H-bonded 6-membered substructure of amino alcohol *syn*-**15b**, the heavy atoms are located at positions corresponding to a chair conformation (Figure 1). Accordingly, the substituents at these atoms can be staggered *perfectly*. As expected, then, the dihedral angle ("φ") between the allylic hydrogen (H21 in Figure 1) and the hydrogen α to the Bn_2N group (H51) measures 63° in the solid state. Presumably, the same angle φ – in formula *syn*-**15b** (Scheme 3) between *a*-H and *b*-H – is preferred in solution. This follows from the relatively small *J*-value between *a*-H and *b*-H (4.1 Hz) in conjunction with a Karplus-type dependence of $J_{a,b}$ from φ. $J_{a,b}$ = 4.1 Hz is also indicative of the shown stereochemistry of *syn*-**15b** because this value fits better with the 3.9–4.4 Hz range of $J_{a,b}$ values reported for the *syn* vs. the 7.7–8.4 Hz range found for the *anti* γ-amino alcohols **16**[35].

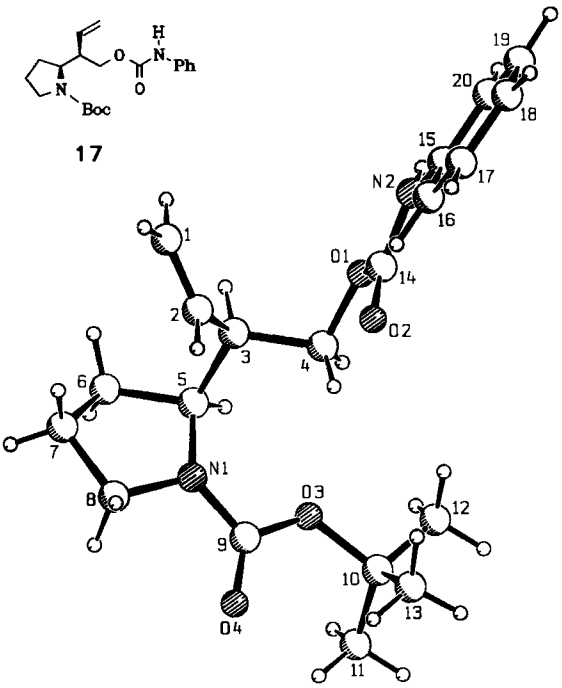


Figure 2. SCHAKAL plot of the solid-state structure of carbamate **17**[32]

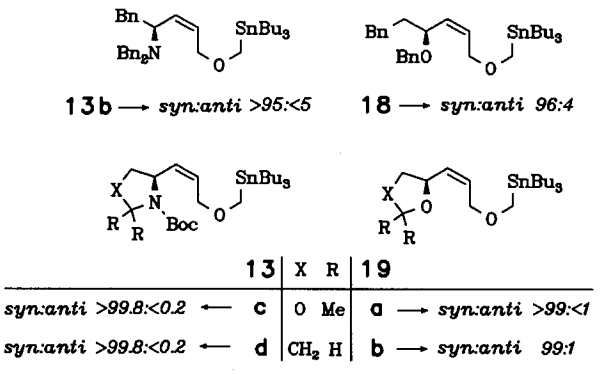
The configuration of the rearranged pyrrolidine **15d** was established after derivatization of **15d** (*syn*:*anti* ≈ 10:1) with Ph–NCO. The resulting carbamate **17** was recrystallized several times from hexane and subsequently X-rayed (Figure 2). The identity of the X-rayed crystal with the *syn* epimer of carbamate **17** was secured by comparison with HPLC.

The configurations of oxazolidines *syn*/*anti* **15c** obtained from stannanes **13c** and **14c** could not be deduced from their ^{1}H NMR spectra. Here, *syn*/*anti* assignments are based on the plausible assumption that asymmetric inductions in the Wittig-Still rearrangements of serine derivatives **13c** (**14c**) and proline derivatives **13d** (**14d**) are pairwise identical (cf. Scheme 2).

Scheme 2 reveals for the first time that allylic stereocenters bearing NR_2 or N(Boc) groups exert stereocontrol through asymmetric induction in the Wittig-Still rearrangement. The seven model compounds examined lead to epimer *syn*-**15** as the preferred rearrangement product. The *syn* fraction comprised 46–92% of the rearrangement product starting from *E*-configuration stannylated ethers **14**. Considerably higher *syn* selectivities were observed when stannanes **13** with *Z* double bonds served as starting materials[36]. In these reactions, the content of contaminating *anti* epimer remained below the limit of detection [< 5% for **b** (^{1}H NMR); < 0.2% for **c** and **d** (capillary GLC)].

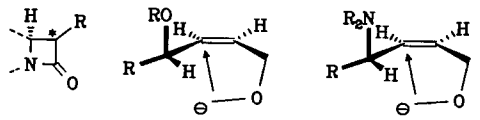
By using Wittig-Still rearrangements of *Z*-configuration stannanes **13**, we have converted enantiomerically pure amino acids into amino alcohols *syn*-**15** stereoselectively. Such amino alcohols look like promising precursors of optically active β-lactams **20**.

Scheme 4



Scheme 4 shows that in Wittig-Still rearrangements allylic nitrogen is a comparably efficient inducer of chirality as allylic oxygen was in the reference compounds **18** and **19**[16f]. Both nitrogen *and* oxygen induce the preferential formation of *syn*-configuration products, the *syn* preference being higher starting from *Z* olefins (shown) than from *E* olefins (not shown).

Chirally oxygenated ethers like **18**/**19** are believed to rearrange via transition state **21**. Transition state **21** is marked by the possibility of overlap between the anionic lone pair, the $\pi^*_{C=C}$ and the low-lying σ^*_{C-O} orbital aligned parallel. Such overlap would engender maximum charge delocalization, i.e. maximum stabilization (cf. ref.[16c–e] for a detailed discussion). Analogously the favored transition state for the rearrangement of the *aminated* intermediates of the present communication should be **22**. Of course, nitrogen is less electronegative than oxygen, and one would therefore ascribe *less* charge delocalizing ability to the σ^*_{C-N} orbital of transition state **22** than to the σ^*_{C-O} orbital of transition state **21**. Hence, *less* stabilization should be provided to transition state **22**, and more "stereochemical failure" furnishing *anti* product should occur. However, the *comparably* high *syn* selectivities caused by allylic nitrogen vs. oxygen (Scheme 4) implies that transition state **22** (containing N) is as much stabilized as **21** (containing O). We believe that transition state **22** – unlike **21** – is also favored sterically. Repulsive interactions between the allylic amino group (conformational *A* value of NMe_2[37]: 2.1 kcal/mol) need to be avoided more strictly than interactions with allylic oxygen (*A* value of OMe[37]: 0.6 kcal/mol).



20 **21** **22**

Clearly, the electronic status of the stereodirecting entity differs in rearrangement substrates **13b** and **14a–b** (amino nitrogen) from that in **13c–d** and **14c–d** (carbamate nitrogen). Our data do not allow to recognize *differential* effects of these substituents on the magnitude of asymmetric induction in the Wittig-Still rearrangement. We cannot, therefore, exclude the possibility that the preference for transition state **22** is preponderantly – or may be even exclusively – steric in nature.

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Experimental

^{1}H NMR: Bruker AC 300, tetramethylsilane as internal standard in $CDCl_3$ unless indicated differently; Bruker WH 400, $C_6HD_4NO_2$ as internal standard for the high-temperature (100°C) spectra in $C_6D_5NO_2$; integrals in accord with assignments; coupling constants in Hz; coupling constants $J_{H,^{117}Sn}$ and $J_{H,^{119}Sn}$ abbreviated as $J_{H,Sn}$. – Capillary gas chromatography: Siemens Sichromat 3, glass capillary coated with Supelcowax-10 (30 m × 0.32 mm). – All reactions were performed in oven-dried (100°C) glassware under dry N_2. – Compounds were purified by flash chromatography[23] on Merck silica gel 60 (particle size 0.040–0.063 mm, 230–400 mesh ASTM). – Yields refer to analytically pure samples.

Methyl (E)-4-(Dibenzylamino)-5-methyl-2-hexenoate (*E*-**9a**): Oxalyl chloride (0.869 g, 6.85 mmol, 1.2 equiv.) in CH_2Cl_2 (12 ml) was treated with DMSO (0.71 ml, 0.78 g, 10.0 mmol, 1.8 equiv.) for 7 min at –70°C. *N,N-Dibenzylvalinol*[27] (**6**) (1.59 g, 5.60 mmol) in CH_2Cl_2 (2.5 ml) was added, followed 1 h later by triethylamine (1.20 g, 11.8 mmol, 2.1 equiv.). After another 15 min at –70°C the mixture was warmed to room temp., washed with 1.5% HCl (20 ml)

and satd. aqueous Na_2CO_3 (2 × 20 ml), and dried with $MgSO_4$. Removal of the solvent left the crude aldehyde which was dissolved in THF (5 ml) and added to a previously prepared solution (0°C → room temp.; 2 h) of methyl (diethylphosphono)acetate (1.46 g, 6.94 mmol, 1.2 equiv.), NaH (0.25 g, 10.2 mmol, 1.8 equiv.), and THF (35 ml). After 2 h the mixture was diluted with H_2O (50 ml) and extracted with diethyl ether (2 × 50 ml). The combined organic layers were washed with 1% HCl (2 × 50 ml) and dried with $MgSO_4$. Flash chromatography [petroleum ether/ether (10:1)] yielded *E*-**9a** (1.13 g, 60%). – ^{1}H NMR: δ = 0.72 and 1.09 [2 d, J_{vic} = 6.6, $(CH_3)_2CH$], 1.95 (dsept, $J_{5,4}$ = 10.3, J_{vic} = 6.6, 5-H), 2.62 (dd, $J_{4,5}$ = $J_{4,3}$ = 10.3, 4-H), two superimposing AB signals [δ_A = 3.28, δ_B = 3.92, $J_{A,B}$ = 13.8, $N(CH_2Ph)_2$], 3.80 (s, OMe), 5.75 (d, J_{trans} = 15.6, 2-H), 6.89 (dd, J_{trans} = 15.7, $J_{3,4}$ = 10.4, 3-H), 7.20–7.40 (m, 2 C_6H_5).

$C_{22}H_{27}NO_2$ (337.5) Calcd. C 78.30 H 8.06 N 4.15
Found C 78.12 H 8.04 N 4.12

Methyl (E)- and (Z)-4-(Dibenzylamino)-5-phenyl-2-pentenoates (*E*-**9b**, *Z*-**9b**): *E*-**9b** (1.45 g, 85%) and *Z*-**9b** (0.132 g, 8%) were prepared from *N,N*-dibenzylphenylalaninal[27] (7; 1.45 g, 4.41 mmol) according to the procedure given for the preparation of *E*-**9c** and *Z*-**9c** from **8**. – *Z*-**9b**: ^{1}H NMR: δ = AB signal (δ_A = 2.82, δ_B = 2.94, $J_{A,B}$ = 13.9, in addition split by $J_{A,4}$ = 6.1, $J_{B,4}$ = 9.1, 5-H_2), 3.41 [d, J_{gem} = 13.9, $N(CH^1H^2Ph)_2$], 3.44 (s, OMe), 3.90 [d, J_{gem} = 13.9, $N(CH^1H^2Ph)_2$], 4.72 (m_c, 4-H), 5.97 (dd, J_{cis} = 11.8, $J_{2,4}$ = 1.0, 2-H), 6.40 (dd, J_{cis} = 11.7, $J_{3,4}$ = 10.1, 3-H), 7.06–7.30 (m, 3 C_6H_5).

$C_{26}H_{27}NO_2$ (385.5) Calcd. C 81.01 H 7.06 N 3.63
Found C 80.60 H 7.25 N 3.86

^{1}H NMR and combustion analytical data of ester *E*-**9b** have been described recently[38].

Methyl (Z)- and (E)-3-[(4R)-3-(tert-Butoxycarbonyl)-2,2-dimethyl-1,3-oxazolidin-4-yl]propenoates (*Z*-**9c**, *E*-**9c**): At 0°C [(methoxycarbonyl)methylene]triphenylphosphorane (6.50 g, 19.4 mmol, 1.5 equiv.) and (4*S*)-3-(*tert*-butoxycarbonyl)-2,2-dimethyl-1,3-oxazolidine-4-carbaldehyde (**8**) [2.96 g, 12.9 mmol; $[\alpha]_D^{21}$ = −81 (*c* = 4.9, CH_2Cl_2); ref.[26]: $[\alpha]_D$ = −91.7 (*c* = 1.34, $CHCl_3$)] were allowed to react in dry methanol (40 ml) for 17 h. The mixture was diluted with H_2O (70 ml), extracted with diethyl ether (150 + 80 + 80 ml), and dried with Na_2SO_4. Flash chromatography [petroleum ether/diethyl ether (5:1)→diethyl ether] gave *Z*-**9c** in the first fractions (1.33 g, 36%) and *E*-**9c** (2.02 g, 55%) in the last ones.

Z-**9c**: $[\alpha]_D^{21}$ = −37 (*c* = 4.5, CH_2Cl_2). – ^{1}H NMR ($C_6D_5NO_2$): δ = 1.49 [s, $C(CH_3)_3$], 1.59 and 1.68 [2 s, 2′-$(CH_3)_2$], 3.70 (s, OCH_3), 3.78 (dd, J_{gem} = 9.1, $J_{5'\text{-}H^1,4'}$ = 3.5, 5′-H^1), 4.27 (dd, J_{gem} = 8.9, $J_{5'\text{-}H^2,4'}$ = 7.1, 5′-H^2), 5.52 (m_c, 4′-H), 5.87 (d, J_{cis} = 11.5, 2-H), 6.34 (dd, J_{cis} = 11.4, $J_{3,4'}$ = 8.0, 3-H).

$C_{14}H_{23}NO_5$ (285.3) Calcd. C 58.93 H 8.12 N 4.91
Found C 59.13 H 8.26 N 4.87

E-**9c**: $[\alpha]_D^{21}$ = −65 (*c* = 4.2, CH_2Cl_2). – ^{1}H NMR ($C_6D_5NO_2$): δ = 1.50 [s, $C(CH_3)_3$], 1.59 and 1.67 [2 s, 2′-$(CH_3)_2$], 3.71 (s, OCH_3), 3.83 (dd, J_{gem} = 9.1, $J_{5'\text{-}H^1,4'}$ = 2.5, 5′-H^1), 4.15 (dd, J_{gem} = 9.1, $J_{5'\text{-}H^2,4'}$ = 6.5, 5′-H^2), 4.59 (m_c, 4′-H), 6.07 (d, J_{trans} = 15.6, 2-H), 6.99 (dd, J_{trans} = 15.7, $J_{3,4'}$ = 6.8, 3-H).

$C_{14}H_{23}NO_5$ (285.3) Calcd. C 58.93 H 8.12 N 4.91
Found C 59.00 H 8.15 N 4.78

Methyl (E)- and (Z)-3-[(2S)-1-(tert-Butoxycarbonyl)pyrrolidin-2-yl]propenoates (*E*-**9d**, *Z*-**9d**): Oxalyl chloride (0.63 ml, 0.91 g, 7.1 mmol, 1.1 equiv.) in THF (5 ml) was treated with DMSO (1.06 ml, 1.17 g, 15.0 mmol, 2.3 equiv.) for 7 min at −70°C. (2*S*)-*N*-(*tert*-butoxycarbonyl)prolinol (**10**; 1.31 g, 6.52 mmol) in THF (5 ml) was added, followed 2 h later by triethylamine (2.73 ml, 1.98 g, 19.6 mmol, 3.0 equiv.). The mixture was kept at −70°C for 15 min, warmed to room temp., diluted with 30 ml MeOH, and transferred via cannula to (methoxycarbonyl)triphenylphosphorane (3.27 g, 9.78 mmol, 1.5 equiv.) in MeOH (50 ml). After 40 min the mixture was poured into ether (200 ml) and washed with 1% HCl (100 ml) and 5% aqueous Na_2CO_3 (100 ml). The crude product – purified by flash chromatography [petroleum ether/ether (7:1 → 3:1)] – gave *Z*-**9d** (0.409 g, 25%) and *E*-**9d** (0.862 g, 52%).

Z-**9d**: $[\alpha]_D^{20}$ = +71 (*c* = 1.1, CH_2Cl_2). – ^{1}H NMR ($C_6D_5NO_2$): δ = 1.50 [s, $C(CH_3)_3$], 1.65–1.97 (m, 3′-H_2, 4′-H^1), 2.28 (m_c, 4′-H^2), AB signal (δ_A = 3.45, δ_B = 3.55, $J_{A,B}$ = 10.7, in addition split by $J_{A,4'}$ = 6.9, $J_{B,4'}$ ≈ 7.0, 5′-H_2), 3.70 (s, OMe), 5.41 (m_c, 2′-H), 5.77 (dd, J_{cis} = 11.5, $J_{2,2'}$ = 1.4, 2-H), 6.23 (dd, J_{cis} = 11.5, $J_{3,2'}$ = 8.2, 3-H).

$C_{13}H_{21}NO_4$ (255.3) Calcd. C 61.16 H 8.29 N 5.49
Found C 61.07 H 8.42 N 5.62

E-**9d**: $[\alpha]_D^{20}$ = +78 (*c* = 1.5, CH_2Cl_2). – ^{1}H NMR ($C_6D_5NO_2$): δ = 1.51 [s, $C(CH_3)_3$], 1.72–1.87 (m, 3′-H_2, 4′-H^1), 2.08 (dq, J_{gem} = 11.9, J_{vic} = 8.1, 4′-H^2), AB signal (δ_A = 3.42, δ_B = 3.47, $J_{A,B}$ = 10.8, in addition split by $J_{A,a}$ = 7.3, $J_{A,b}$ = 5.2, $J_{B,4'}$ = 7.5, 5′-H_2), 3.71 (s, OMe), 4.49 (m_c, 2′-H), 5.95 (dd, J_{trans} = 15.6, $J_{2,2'}$ = 1.3, 2-H), 6.94 (dd, J_{trans} = 15.6, $J_{3,2'}$ = 6.0, 3-H). – ^{1}H NMR (−60°C in $CDCl_3$, 400 MHz): Major conformer (ca. 55% of the mixture): δ = 1.42 [s, $C(CH_3)_3$], 3.78 (s, OMe), 4.44 (m_c, 2′-H), 5.84 (d, J_{trans} = 15.8, 2-H), 6.87 (dd, J_{trans} = 15.4, $J_{3,2'}$ = 5.5, 3-H); minor conformer: δ = 1.47 [s, $C(CH_3)_3$], 3.75 (s, OMe), 4.54 (m_c, 2′-H), 5.88 (d, J_{trans} = 16.9, 2-H), 6.93 (dd, J_{trans} = 15.5, $J_{3,2'}$ = 5.2, 3-H); superimposing multiplets of both conformers: 1.80–2.13 (3′-H_2, 4′-H_2), 3.34–3.52 (5′-H_2).

$C_{13}H_{21}NO_4$ (255.3) Calcd. C 61.16 H 8.29 N 5.49
Found C 60.87 H 8.44 N 5.64

(2S)-N-(tert-Butoxycarbonyl)prolinol[29] (**10**): At 0°C 2.15 g (10.0 mmol) *N*-(*tert*-butoxycarbonyl)proline and borane dimethyl sulfide adduct (2 ml, ca. 20 mmol) in THF (10 ml) were allowed to react for 20 h. The mixture was treated with methanolic 10% HOAc (20 ml) and the solvent was removed under reduced pressure. The crude product was dissolved in AcOEt (50 ml). Successive washings with 1 N HCl (50 ml), H_2O (100 ml) and satd. aqueous NH_4HCO_3 (2 × 50 ml) and removal of the solvent yielded **10** (1.48 g, 73%). – $[\alpha]_D^{20}$ = +48 (*c* = 1.1, CH_2Cl_2). – M.p. 57–59°C. – ^{1}H NMR: δ = 1.47 [s, $C(CH_3)_3$], 1.54–2.07 (m, 3-H_2, 4-H_2), 3.25–3.70 (m, 4H), 3.96 (m_c, 1H), 4.79 (m_c, 1H).

$C_{10}H_{19}NO_3$ (201.3) Calcd. C 59.68 H 9.52 N 6.96
Found C 59.41 H 9.43 N 6.68

(Z)-4-(Dibenzylamino)-5-phenyl-2-penten-1-ol (**11b**) was prepared from *Z*-**9b** by the procedure described for *Z*-**9c** → **11c**. The procedure was carried on towards the stannylated ether **13b** without purification. – A spectroscopically pure sample of **11b** (0.014 g, 40%) was isolated upon attempted Wittig-Still rearrangement of **13b** (0.067 g, 0.10 mmol). – ^{1}H NMR: δ = 2.68 (dd, J_{gem} = 13.0, $J_{5\text{-}H^1,4}$ = 9.8, 5-H^1), 3.14 (dd, J_{gem} = 12.9, $J_{5\text{-}H^2,4}$ = 4.9, 5-H^2), AB signal (δ_A = 3.44, δ_B = 3.61, $J_{A,B}$ ≈ 13, in addition split by $J_{A,2}$ = 7.3, $J_{B,2}$ = 6.4, 1-H_2), two superimposing AB signals [δ_A = 3.58, δ_B = 3.82, $J_{A,B}$ = 13.7, $N(CH_2Ph)_2$], 3.68, partly superimposed (ddd, $J_{4,3}$ = $J_{4,5\text{-}H^1}$ ≈ 9, $J_{4,5\text{-}H^2}$ ≈ 5, 4-H), AB signal (δ_A = 5.63, δ_B = 5.78, $J_{A,B}$ = 11.1, in addition split by $J_{A,4}$ = 9.4, $J_{B,1}$ ≈ 7, A: 3-H, B: 2-H), 7.01–7.27 (m, 3 C_6H_5); OH not observed.

(Z)-3-[(4R)-3-(tert-Butoxycarbonyl)-2,2-dimethyl-1,3-oxazolidin-4-yl]-2-propen-1-ol (**11c**): At −70°C, $F_3B{-}OEt_2$ (0.50 ml, 0.58 g, 4.1 mmol, 1.2 equiv.) and DIBAH (1.0 mol/l in hexane; 8.9 ml, 8.9 mmol, 2.6 equiv.) were added successively to *Z*-**9c** (0.971 g, 3.40 mmol) in CH_2Cl_2 (10 ml). After 6 h, 50% HOAc (8 ml)

and 10% tartaric acid (67 ml) were added. Extraction with CH_2Cl_2 (3 × 80 ml), washing of the combined organic phases with satd. aqueous Na_2CO_3 (80 ml) and brine (80 ml) and flash chromatography [petroleum ether/diethyl ether (4:1) → (1:3)] led to 0.631 g (72%) **11c**. – $[\alpha]_D^{20}$ = +40 (*c* = 3.5, CH_2Cl_2). – ^{1}H NMR ($C_6D_5NO_2$): δ = 1.50 [s, $C(CH_3)_3$], 1.56 and 1.64 [2 s, 2′-$(CH_3)_2$], 3.70 (d, J_{gem} = 8.9, 5′-H^1), 4.09, 4.17, 4.50, and 4.93 (4 m_c, 1-H_2, 4′-H, 5′-H^2), 5.57 (dd, $J_{cis} = J_{3,4'}$ = 10.4, 3-H), 5.83 (dt, J_{cis} = 10.8, $J_{2,1}$ = 6.5, 2-H); OH signal not observed.

$C_{13}H_{23}NO_4$ (257.3) Calcd. C 60.68 H 9.01 N 5.44
Found C 60.57 H 9.01 N 5.36

(Z)-3-[(2S)-1-(tert-Butoxycarbonyl)pyrrolidin-2-yl]-2-propen-1-ol (**11d**) (0.258 g, 76%) was obtained from *Z*-**9d** (0.382 g, 1.50 mmol) by the procedure described for the preparation of **11c** from *Z*-**9c**. – $[\alpha]_D^{20}$ = +36 (*c* = 0.9, CH_2Cl_2). – ^{1}H NMR: δ = 1.44 [s, $C(CH_3)_3$], 1.62–2.11 (m, 3′-H_2, 4′-H_2), 3.37 (m_c, 5′-H_2), 3.85 (m_c, OH), 4.30–4.60 (m, 1-H_2), 4.78 (m_c, 2′-H), 5.37 (dd, $J_{cis} = J_{3,2'}$ = 10.3, 3-H), 5.82 (m, 2-H).

No correct C,H,N analysis could be obtained.

(E)-4-(Dibenzylamino)-5-methyl-2-hexen-1-ol (**12a**): *E*-**9a** (1.16 g, 3.44 mmol) in THF (15 ml) was treated with DIBAH (1.0 mol/l in hexane; 11.3 ml, 11.3 mmol, 3.3 equiv.) for 1 h at −70°C and 1 h at 0°C. The reaction was quenched at −70°C with 5 ml of MeOH. The resulting mixture was poured into aqueous K,Na tartrate (ca. 1 mol/l; 20 ml) and extracted with ether (4 × 20 ml). Purification by flash chromatography [petroleum ether/ether (2:1)] yielded 1.11 g **12a** (95%). – ^{1}H NMR: δ = 0.74 and 1.07 [2 d, J_{vic} = 6.6, $(CH_3)_2CH$], 1.33 (t, $J_{OH,1}$ = 5.9, OH), 1.87 (dsept, $J_{5,4}$ = 10.0, J_{vic} = 6.6, 5-H), 2.51 (m_c, 4-H), two superimposing AB signals [δ_A = 3.28, δ_B = 3.85, $J_{A,B}$ = 13.8, $N(CH_2Ph)_2$], 4.25 (dd, $J_{1,OH}$ = 5.9, $J_{1,2}$ = 3.8, 1-H_2), 5.58–5.61 (m, 2-H, 3-H), 7.18–7.41 (m, 2 C_6H_5).

$C_{21}H_{27}NO$ (309.5) Calcd. C 81.51 H 8.79 N 4.53
Found C 81.42 H 8.84 N 4.50

(E)-4-(Dibenzylamino)-5-phenyl-2-penten-1-ol (**12b**) (1.96 g, 100%) was obtained from *E*-**9b** (2.102 g, 5.45 mmol) by the procedure described for the preparation of **12a** from *E*-**9a**. – ^{1}H NMR: δ = 1.25 (t, $J_{OH,1}$ = 5.9, OH), AB signal (δ_A = 2.77, δ_B = 3.03, $J_{A,B}$ = 13.7, in addition split by $J_{5A,4}$ = 7.5, $J_{5B,4}$ = 7.6, 5-H_2), 3.42 (m_c, 4-H), superimposing two superimposing AB signals [δ_A = 3.46, δ_B = 3.81, $J_{A,B}$ = 13.9, $N(CH_2Ph)_2$], 4.16 [br. dd, $J_{1,OH}$ = $J_{1,2}$ = 5.2, 1-H_2], AB signal (δ_A = 5.65, δ_B = 5.76, $J_{A,B}$ = 15.5, in addition split by $J_{A,1}$ = 5.1, $J_{B,4}$ = 7.8, A: 2-H, B: 3-H), 7.01–7.27 (m, 3 C_6H_5).

$C_{25}H_{27}NO$ (357.5) Calcd. C 83.99 H 7.61 N 3.92
Found C 84.19 H 7.63 N 3.96

(E)-3-[(4R)-3-(tert-Butoxycarbonyl)-2,2-dimethyl-1,3-oxazolidin-4-yl]-2-propen-1-ol (**12c**) (0.501 g, 30%) was obtained from *E*-**9c** (1.85 g, 6.49 mmol) by the procedure described for the preparation of **11c** from *Z*-**9c**. – $[\alpha]_D^{20}$ = −13 (*c* = 3.9, CH_2Cl_2). – ^{1}H NMR ($C_6D_5NO_2$): δ = 1.52 [s, $C(CH_3)_3$], 1.58 and 1.67 [2 s, 2′-$(CH_3)_2$], 2.04 (s, OH), 3.77 (br. d, J_{gem} = 8.9, 5′-H^1), 4.07 (br. dd, $J_{gem} \approx J_{5'\text{-}H^2,4'} \approx$ 7.5, 5′-H^2), 4.24 (m_c, 1-H_2), 4.46 (m_c, 4′-H), AB signal (δ_A = 5.87, δ_B = 5.95, $J_{A,B}$ = 15.5, in addition split by $J_{A,4'}$ = 7.1, $J_{B,1} \approx$ 5, A: 3-H, B: 2-H).

$C_{13}H_{23}NO_4$ (257.3) Calcd. C 60.68 H 9.01 N 5.44
Found C 60.21 H 9.02 N 5.38

(E)-3-[(2S)-1-(tert-Butoxycarbonyl)pyrrolidin-2-yl]-2-propen-1-ol (**12d**) (0.428 g, 65%) was prepared from *E*-**9d** (0.743 g, 2.91 mmol) as described for the conversion of *Z*-**9c** into **11c**. – $[\alpha]_D^{20}$ = +35 (*c* = 2.2, CH_2Cl_2). – ^{1}H NMR: δ = 1.44 and 1.46 [2 s, $C(CH_3)_3$ of two conformers], 1.50–2.09 (m, 3′-H_2, 4′-H_2), 3.28–3.44 (m, 5′-H_2), 4.13–4.37 (m, 2′-H, 1-H_2), 5.50–5.73 (m, 2-H, 3-H); OH signal not observed.

$C_{12}H_{21}NO_3$ (227.3) Calcd. C 63.41 H 9.31 N 6.16
Found C 63.22 H 9.43 N 6.11

Stannylated Ethers **13** *and* **14**: **13d** (0.155 g, 32%), **14a** (1.21 g, 76%), **14b** (1.34 g, 81%), **14c** (0.493 g, 54%), and **14d** (0.665 g, 71%) were prepared from the corresponding allylic alcohols **11d** (0.210 g, 0.92 mmol), **12a** (0.831 g, 2.68 mmol), **12b** (0.856 g, 2.39 mmol), **12c** (0.420 g, 1.63 mmol), and **12d** (0.401 g, 1.77 mmol) according to the procedure described for the preparation of **13c** from **11c**. Stannane **13b** (0.080 g) was obtained similarly from allylic alcohol **11b** prepared by DIBAH reduction of *Z*-**9b** (0.097 g, 0.25 mmol); yield: 48% for the two steps.

(Z)-4-(Dibenzylamino)-5-phenyl-1-[(tributylstannyl)methoxy]-2-pentene (**13b**): ^{1}H NMR: δ = 0.84 (m_c, 3 × $SnCH_2$-CH_2), superimposed by 0.88 (t, *J* = 7.3, 3 × CH_2-CH_3), 1.29 (qt, both *J* values 7.3, 3 × CH_2-CH_2-CH_3), 1.46 (m_c, 3 × CH_2-CH_2-CH_2), AB signal (δ_A = 2.70, δ_B = 3.05, $J_{A,B}$ = 13.4, in addition split by $J_{A,4}$ = 7.9, $J_{B,4}$ = 6.8, 5-H_2), AB signal (δ_A = 3.20, δ_B = 3.55, $J_{A,B}$ = 12.8, in addition split by $J_{A,2}$ = 4.8, $J_{B,2} \approx$ 6.6, 1-H_2), AB signal (δ_A = 3.37, δ_B = 3.40, $J_{A,B}$ = 10.3, each signal branch superimposed by d caused by $^2J_{H,Sn} \approx$ 15, OCH_2Sn), two superimposing AB signals [δ_A = 3.43, δ_B = 3.85, $J_{A,B}$ = 13.9, $N(CH_2Ph)_2$], 3.62 (m_c, 4-H), AB signal (δ_A = 5.63, δ_B = 5.70, $J_{A,B}$ = 11.0, in addition split by $J_{A,4}$ = 9.4, $J_{B,1}$ = 5.9, A: 3-H, B: 2-H), 7.00–7.28 (m, 3 C_6H_5).

$C_{38}H_{55}NOSn$ (660.6) Calcd. C 69.10 H 8.39 N 2.12
Found C 69.02 H 8.43 N 2.20

(Z)-1-[(4R)-3-(tert-Butoxycarbonyl)-2,2-dimethyl-1,3-oxazolidin-4-yl]-3-[(tributylstannyl)methoxy]-1-propene (**13c**): KH (0.292 g, 7.27 mmol, 3.7 equiv.), tributyl(iodomethyl)stannane (1.27 g, 2.95 mmol, 1.5 equiv.), and **11c** (0.505 g, 1.96 mmol) were stirred in THF (20 ml) overnight. Quenching with satd. aqueous NH_4Cl (10 ml), extraction with H_2O (20 ml) and diethyl ether (4 × 30 ml), and flash chromatography [petroleum ether/diethyl ether (10:1)→(7:1)] gave 0.845 g (77%) of **13c**. – $[\alpha]_D^{19}$ = +58 (*c* = 3.3, CH_2Cl_2). – ^{1}H NMR ($C_6D_5NO_2$): δ = 0.93 (t, *J* = 7.2, 3 × CH_2-CH_3), 1.00 (t, *J* = 7.9, 3 × $SnCH_2$-CH_2), 1.37 (tq, both J_{vic} values = 7.2, 3 × CH_2-CH_2-CH_3), 1.54 [s, $C(CH_3)_3$], 1.49–1.74 (m, 3 × CH_2-CH_2-CH_2), superimposing 1.61 and 1.68 [2 s, 2′-$(CH_3)_2$], 3.73 (dd, J_{gem} = 8.7, $J_{5'\text{-}H^1,4'}$ = 3.2, 5′-H^1), 3.87 (s with superimposing d caused by $J_{H,Sn}$ = 14.6, OCH_2Sn), 4.12–4.18 (m, 3-H_2, 5′-H^2), 4.80 (m_c, 4′-H), AB signal (δ_A = 5.60, δ_B = 5.67, $J_{A,B}$ = 11.2, in addition split by $J_{A,4'} \approx$ 10, $J_{B,3}$ = 5.7, A: 1-H, B: 2-H).

$C_{26}H_{51}NO_4Sn$ (560.4) Calcd. C 55.73 H 9.17 N 2.50
Found C 56.00 H 9.07 N 2.31

(Z)-1-[(2S)-1-(tert-Butoxycarbonyl)pyrrolidin-2-yl]-3-[(tributylstannyl)methoxy]-1-propene (**13d**): $[\alpha]_D^{20}$ = +50 (*c* = 1.7, CH_2Cl_2). – ^{1}H NMR ($C_6D_5NO_2$): δ = 0.94 (t, *J* = 7.3, 3 × CH_2-CH_3), 1.02 (t, *J* ≈ 8, 3 × $SnCH_2$-CH_2), 1.38 (qt, both *J* values 7.3, 3 × CH_2-CH_2-CH_3), 1.54 [s, $C(CH_3)_3$], 1.62 (m_c, 3 × CH_2-CH_2-CH_2), superimposed by 1.62–1.71 (m, 4′-H^1), 1.84 (m_c, 3′-H_2), 2.12 (m_c, 4′-H^2), AB signal (δ_A = 3.44, δ_B = 3.52, $J_{A,B}$ = 10.6, in addition split by $J_{A,a}$ = 7.4, $J_{A,b}$ = 5.5, $J_{B,4'}$ = 7.2, 5′-H_2), 3.90 (s, with superimposing d caused by $^2J_{H,Sn}$ = 14.9, OCH_2Sn), 4.19 (dd, $J_{3,2}$ = 5.9, $J_{3,1}$ = 1.1, 3-H_2), 4.66 (dt, $J_{2',1}$ = 8.0, $J_{2',3'}$ = 4.8, 2′-H), 5.52 (dd, J_{cis} = 11.2, $J_{1,2'}$ = 8.5, 1-H), 5.61 (dt, J_{cis} = 11.4, $J_{2,3}$ = 5.8, 2-H).

$C_{25}H_{49}NO_3Sn$ (530.4) Calcd. C 56.62 H 9.31 N 2.64
Found C 56.98 H 9.46 N 2.89

(E)-4-(Dibenzylamino)-5-methyl-1-[(tributylstannyl)methoxy]-2-hexene (**14a**): ^{1}H NMR: δ = 0.74 and 1.07 [2 d, J_{vic} = 6.6 and 6.5, $(CH_3)_2CH$], 0.89 (t, *J* = 7.2, 3 × CH_2-CH_3), superimposing 0.93

(m_c, 3 × $SnCH_2$-CH_2), 1.32 (qt, both J values 7.2, 3 × CH_2-CH_2-CH_3), 1.53 (m_c, 3 × CH_2-CH_2-CH_2), 1.85 (dsept, $J_{5,4}$ = 10.1, J_{vic} = 6.7, 5-H), 2.49 (dd, $J_{4,3}$ = $J_{4,5}$ = 9.7, 4-H), two superimposing AB signals [δ_A = 3.27, δ_B = 3.84, $J_{A,B}$ = 13.7, $N(CH_2Ph)_2$], AB signal (δ_A = 3.76, δ_B = 3.79, $J_{A,B}$ = 10.4, each signal branch superimposed by d caused by $^2J_{H,Sn}$ = 14.5, OCH_2Sn), 3.95 (br. d, $J_{1,2}$ = 4.8, 1-H_2), AB signal (δ_A = 5.45, δ_B = 5.54, $J_{A,B}$ = 15.5, in addition split by $J_{A,1}$ = 5.2, $J_{B,4}$ = 9.3, A: 2-H, B: 3-H), 7.18–7.40 (m, 2 C_6H_5).

$C_{34}H_{55}NOSn$ (612.5) Calcd. C 66.67 H 9.05 N 2.29
Found C 66.40 H 9.02 N 2.25

(E)-4-(Dibenzylamino)-5-phenyl-1-[(tributylstannyl)methoxy]-2-pentene (**14b**): ^{1}H NMR: δ = 0.90 (t, J = 7.3, 3 × CH_2-CH_3), superimposed by 0.92 (m_c, 3 × $SnCH_2$-CH_2), 1.31 (qt, both J values 7.2, 3 × CH_2-CH_2-CH_3), 1.52 (m_c, 3 × CH_2-CH_2-CH_2), AB signal (δ_A = 2.78, δ_B = 3.01, $J_{A,B}$ = 13.8, in addition split by $J_{A,4}$ = 7.2, $J_{B,4}$ = 7.8, 5-H_2), 3.40 (m_c, 4-H), superimposed by part of the following pair of superimposing AB signals [δ_A = 3.43, δ_B = 3.82, $J_{A,B}$ = 13.8, $N(CH_2Ph)_2$], AB signal (δ_A = 3.67, δ_B = 3.71, $J_{A,B}$ = 10.3, each signal branch superimposed by d caused by $^2J_{H,Sn}$ = 14.2, OCH_2Sn), 3.89 (br. d, $J_{1,2}$ = 5.5, 1-H_2], AB signal (δ_A = 5.51, δ_B = 5.73, $J_{A,B}$ = 15.5, in addition split by $J_{A,1}$ = 5.6, $J_{B,4}$ = 8.3, A: 2-H, B: 3-H), 7.01–7.26 (m, 3 C_6H_5).

$C_{38}H_{55}NOSn$ (660.6) Calcd. C 69.10 H 8.39 N 2.12
Found C 68.99 H 8.37 N 2.29

(E)-1-[(4R)-3-(tert-Butoxycarbonyl)-2,2-dimethyl-1,3-oxazolidin-4-yl]-3-[(tributylstannyl)methoxy]-1-propene (**14c**): $[\alpha]_D^{19}$ = −14 (c = 4.7, CH_2Cl_2). – ^{1}H NMR ($C_6D_5NO_2$): δ = 0.92 (t, J = 7.2, 3 × CH_2-CH_3), 0.99 (t, J = 7.8, 3 × $SnCH_2$-CH_2), 1.36 (tq, both J_{vic} values = 7.1, 3 × CH_2-CH_2-CH_3), 1.54–1.67 (m, 3 × CH_2-CH_2-CH_2), superimposing in part 1.54 [s, $C(CH_3)_3$], also superimposing in part 1.59 and 1.70 [2 s, 2′-$(CH_3)_2$], 3.77 (br. d, J_{gem} = 8.6, 5′-H^1), 3.87 (m_c, OCH_2Sn), 3.98 (m_c, 3-H_2), 4.08 (dd, J_{gem} ≈ $J_{5'\text{-}H^2,4'}$ ≈ 7.5, 5′-H^2), 4.45 (m_c, 4′-H), 5.85 (m_c, 1-H, 2-H).

$C_{26}H_{51}NO_4Sn$ (560.4) Calcd. C 55.73 H 9.17 N 2.50
Found C 55.46 H 9.22 N 2.31

(E)-1-[(2S)-1-(tert-Butoxycarbonyl)pyrrolidin-2-yl]-3-[(tributylstannyl)methoxy]-1-propene (**14d**): $[\alpha]_D^{20}$ = +24 (c = 2.9, CH_2Cl_2). – ^{1}H NMR ($C_6D_5NO_2$): δ = 0.94 (t, J = 7.3, 3 × CH_2-CH_3), 1.02 (m_c, 3 × $SnCH_2$-CH_2), 1.38 (qt, both J values 7.3, 3 × CH_2-CH_2-CH_3), 1.55 [s, $C(CH_3)_3$], 1.63 (m_c, 3 × CH_2-CH_2-CH_2), superimposed by 1.68–2.05 (m, 3′-H_2, 4′-H_2), 3.43 (m_c, 5′-H_2), 3.88 (s with superimposing d caused by $^2J_{H,Sn}$ = 14.4, OCH_2Sn), 3.97 (d, $J_{3,2}$ = 3.5, 3-H_2), 4.40 (m_c, 2′-H), 5.70–5.80 (m, 1-H, 2-H).

$C_{25}H_{49}NO_3Sn$ (530.4) Calcd. C 56.62 H 9.31 N 2.64
Found C 56.66 H 9.47 N 2.84

Wittig-Still Rearrangements[20] of **13c** (0.346 g, 0.62 mmol), **13d** (0.088 g, 0.17 mmol), **14a** (0.215 g, 0.35 mmol), **14b** (0.330 g, 0.50 mmol), **14c** (0.283 g, 0.51 mmol), and **14d** (0.106 g, 0.20 mmol) were performed according to the procedure given for the rearrangement of **13b** (**13c** and **14c** were rearranged in the absence of HMPA). Isolated were **15c** [0.126 g, 75%, >99.8% *syn* (GLC)], **15d** [0.036 g, 88%, >99.8% *syn* (GLC)], **15a** [0.102 g, 90%, *syn*:*anti* = 46:54 (^{1}H NMR)], **15b** [0.152 g, 82%, *syn*:*anti* = 78:22 (^{1}H NMR)], **15c** [0.108 g, 79%, *syn*:*anti* = 92:8 (GLC)], and **15d** [0.037 g, 77%, *syn*:*anti* = 70:30 (GLC)], respectively. A crystal obtained from the 78:22 mixture of *syn*- and *anti*-**15b** was cut into two pieces. One piece was X-rayed. The other piece – by ^{1}H NMR spectroscopy – was shown to be identical with the *major* epimer of the original 78:22 mixture of diastereomers.

Wittig-Still Rearrangement of **13b**: At −70°C, *n*-BuLi (1.5 mol/l in hexane; 0.12 ml, 0.18 mmol, 1.8 equiv.) was added to **13b** (0.067 g, 0.10 mmol) in THF (2 ml) and HMPA (0.07 ml, 0.4 mmol, 4 equiv.). Since after 2 h **13b** was still detected by TLC, additional *n*-BuLi (0.12 ml, 0.18 mmol, 1.8 equiv.) was added. After 1.5 h the reaction was quenched with satd. aqueous NH_4Cl (5 ml). Dilution with H_2O (2 ml), extraction with ether (4 × 10 ml), and flash chromatography [petroleum ether/ether (3:1 → 1:1)] led to **15b** [0.017 g, 45%; >95% syn, (^{1}H NMR)] along with **11b** (0.015 g, 40%).

(2R,3S*)- and (2S*,3S*)-3-(Dibenzylamino)-4-methyl-2-vinyl-1-pentanol* (*syn*-**15a**, *anti*-**15a**): The 46:54 (i.e. nearly 1:1) ratio of these epimers in the obtained mixture precluded – in general – an unambiguous assignment of the ^{1}H NMR signals to major and minor isomers, respectively. ^{1}H NMR of *syn*-**15a**: δ = two superimposing AB signals [δ_A = 3.48, δ_B = 3.87, $J_{A,B}$ = 13.0, $N(CH_2Ph)_2$], 5.88 (ddd, J_{trans} = 18.2, J_{cis} = $J_{1',2}$ = 9.2, 1′-H). – *anti*-**15a**: δ = two superimposing AB signals [δ_A = 3.65, δ_B = 3.85, $J_{A,B}$ = 13.3, $N(CH_2Ph)_2$], 5.52 (ddd, J_{trans} = 17.2, J_{cis} = $J_{1',2}$ = 9.7, 1′-H). – Unassigned: δ = 0.98, superimposing 0.98, 1.07 and 1.15 [4 d, J_{vic} = 7.0, J_{vic} = 7.0, J_{vic} = 6.9, J_{vic} = 6.8, 2 × $CH(CH_3)_2$], 1.66 (dd, J_a = 8.4, J_b = 4.0, OH), 2.22 (m_c, 2-H), 2.48 (m_c, 2-H), 2.56 (dd, J_a = 9.6, J_b = 5.0, 3-H), 2.61 (dd, J_a = 9.8, J_b = 2.2, 3-H), 2.85 (m_c, 2-H), 3.29 (ddd, J_a = 10.4, J_b = 6.4, J_c = 4.0, 1-H^1), 3.44–3.55 (m, 1-H_2, 1-H^2), 4.15 (br. t, J = 6.0, OH), 5.09–5.17 (m, *E*-2′-H, *Z*-2′-H).

$C_{22}H_{29}NO$ (323.5) Calcd. C 81.69 H 9.04 N 4.33
Found C 81.73 H 9.14 N 4.19

(2R,1′S*)-2-[1-(Dibenzylamino)-2-phenylethyl]-3-buten-1-ol* (*syn*-**15b**): ^{1}H NMR (300 MHz, C_6D_6, C_6D_5H as internal standard): δ = 2.09 (dddd, $J_{2,3}$ = 9.4, $J_{2,1\text{-}H^1}$ = $J_{2,1\text{-}H^2}$ = $J_{2,1'}$ ≈ 4, 2-H), 2.54 (dd, J_{gem} = 13.6, $J_{2'\text{-}H^1,1'}$ = 10.2, 2′-H^1), 2.71 (m_c, OH), 2.92 (dd, J_{gem} = 13.6, $J_{2'\text{-}H^2,1'}$ = 3.8, 2′-H^2), 3.23 [d, J_{gem} = 13.4, $N(CH^1HPh)_2$], 3.27 (ddd, $J_{1',2'\text{-}H^1}$ = 10.1, $J_{1',2'\text{-}H^2}$ = $J_{1',2}$ = 4.1, 1′-H), 3.34 (dd, J_{gem} = 10.8, $J_{1\text{-}H^1,2}$ = 4.7, 1-H^1), 3.54 (m_c, 1-H^2), 3.90 [d, J_{gem} = 13.6, $N(CH^2HPh)_2$], 5.09 (dd, J_{cis} = 10.3, J_{gem} = 2.2, *E*-4-H), 5.11 (dd, J_{trans} = 17.3, J_{gem} = 2.2, *Z*-4-H), 6.13 (ddd, J_{trans} = 17.2, J_{cis} = 10.3, $J_{3,2}$ = 9.4, 3-H), 7.00–7.44 (m, 3 C_6H_5).

(2S,1′S*)-2-[1-(Dibenzylamino)-2-phenylethyl]-3-buten-1-ol* (*anti*-**15b**): ^{1}H NMR: (300 MHz, C_6D_6, C_6D_5H as internal standard): δ = 2.73 (dd, J_{gem} ≈ 14, $J_{2'\text{-}H^2,1'}$ ≈ 7, low field 2′-H), 3.66 [d, J_{gem} = 13.3, low field $N(CHHPh)_2$], 4.75 (dd, J_{cis} = 10.1, J_{gem} = 2.1, *E*-4-H), 4.86 (dd, J_{trans} = 17.3, J_{gem} = 2.1, *Z*-4-H), 5.13 (ddd, J_{trans} = 17.2, J_{cis} = $J_{3,2}$ = 9.5, 3-H); residual signals superimposed by those of *syn*-**15b**.

$C_{26}H_{29}NO$ (371.5) Calcd. C 84.06 H 7.87 N 3.77
Found C 83.72 H 7.81 N 3.89

(2R)-2-[(4R)-3-(tert-Butoxycarbonyl)-2,2-dimethyl-1,3-oxazolidin-4-yl]-3-buten-1-ol (*syn*-**15c**): $[\alpha]_D^{19}$ = −7.5 (c = 4.0, CH_2Cl_2). – ^{1}H NMR ($C_6D_5NO_2$): δ = 1.53 [s, $C(CH_3)_3$], superimposes 1.53 [s, 2′-$(CH_3)_a$], 1.66 [s, 2′-$(CH_3)_b$], 2.68 (m_c, 2-H), 3.73 and 3.99 (2 m_c, 1-H_2, 5′-H_2), 4.25 (m_c, 4′-H), 5.16 (d, J_{cis} = 10.6, *E*-4-H), 5.19 (d, J_{trans} = 17.9, *Z*-4-H), 5.94 (ddd, J_{trans} = 18.0, J_{cis} = $J_{3,2}$ = 9.5, 3-H).

$C_{14}H_{25}NO_4$ (271.4) Calcd. C 61.97 H 9.29 N 5.16
Found C 61.80 H 9.52 N 5.04

(2S)-2-[(4R)-3-(tert-Butoxycarbonyl)-2,2-dimethyl-1,3-oxazolidin-4-yl]-3-buten-1-ol (*anti*-**15c**): ^{1}H NMR ($C_6D_5NO_2$): δ = 1.51 (m_c, 2-H), 3.82 (m_c), 4.14 (m_c), 4.74 (m_c or impurity), ca. 6.0 (m_c, 3-H); residual signals superimposed by *syn*-**15c**.

(2R,2′S)-2-[1-(tert-Butoxycarbonyl)pyrrolidin-2-yl]-3-buten-1-ol (*syn*-**15d**): $[\alpha]_D^{20}$ = +60 (c = 0.6, CH_2Cl_2). – ^{1}H NMR ($C_6D_5NO_2$): δ = 1.53 [s, $C(CH_3)_3$], 1.67–2.07 (m, 3′-H_2, 4′-H_2, OH), 2.52 (m_c, 2-H), 3.23 (ddd, J_a = 11.0, J_b = 7.9, J_c = 5.1, 1H), 3.53–3.60 (m, 2H), 3.69 (dd, J_a = 11.0, J_b = 8.2, 1H), 4.27 (m_c, 2′-

H), 5.12 (dd, J_{cis} = 10.3, J_{gem} = 2.1, *E*-4-H), 5.16 (ddd, J_{trans} = 17.3, J_{gem} = 2.1, $J_{Z\text{-}4\text{-}H,2}$ = 0.8, *Z*-4-H), 5.73 (ddd, J_{trans} = 17.3, J_{cis} = 10.0, $J_{3,2}$ = 9.3, 3-H).

(2S,2'S)-2-[N-(tert-Butoxycarbonyl)pyrrolidin-2-yl]-3-buten-1-ol (*anti*-**15d**): ^{1}H NMR ($C_6D_5NO_2$): δ = 1.53 [s, $C(CH_3)_3$], 2.29 (m_c, 2-H), 3.81 (dd, J_a = 11.5, J_b = 4.0, 1 H), 4.10 (m_c, 2'-H), 5.97 (ddd, J_{trans} = 17.4, J_{cis} = 10.5, $J_{3,2}$ = 9.5, 3-H); residual signals superimposed by those of *syn*-**15d**.

$C_{13}H_{23}NO_3$ (241.3) Calcd. C 64.70 H 9.61 N 5.80
Found C 64.67 H 9.84 N 5.71

(2R,2'S)-3-[1-(tert-Butoxycarbonyl)pyrrolidin-2-yl]-4-[(phenylcarbamoyl)oxy]-1-butene (*syn*-**17**) {contaminated with ca. 9% of *(2S,2'S)-3-[1-(tert-butoxycarbonyl)pyrrolidin-2-yl]-4-[(phenylcarbamoyl)oxy]-1-butene* (*anti*-**17**)}: **15d** (ca. 0.07 g, *syn*:*anti* ≈ 10:1) and phenyl isocyanate (0.3 ml) were allowed to react for 3 h at 140°C and 3 d at room temp. The crude carbamates were isolated by flash chromatography. Several recrystallizations from petroleum ether/diethyl ether (3:1) by slow evaporation of the solvent delivered a crop of crystals. One of them was cut into halves. One half was used for X-ray analysis (*syn*-**17**) the other half was the *major* epimer of the original *syn*/*anti*-**17** mixture as shown by HPLC comparison [Beckman 163 Variable Wavelength Detector, Nucleosil 120–7 C 18 column, MeOH/H_2O (65:35), flow rate: 1 ml/min]. – Too little material was available to determine the m.p. – ^{1}H NMR ($C_6D_5NO_2$): *syn*-**17**: δ = 1.56 [s, $C(CH_3)_3$], 1.57–1.97 (m, 3'-H_2, 4'-H_2), 3.02 (m_c, 3-H), 3.29 (m_c, 1 H), 3.59 (m_c, 1 H), 4.11 (m_c, 1 H), 4.37 (m_c, 4-H_2), 5.14 (br. d, J_{cis} ≈ 10, *E*-1-H), 5.20 (br. d, J_{trans} = 16.8, *Z*-1-H), 5.89 (ddd, J_{trans} = 17.2, J_{cis} = 10.2, $J_{2,3}$ = 8.3, 2-H), 7.05–7.65 (m, C_6H_5). – *anti*-**17**: δ = 3.17 (m_c, 3-H), 5.80 (ddd, J_{trans} = 17.4, J_{cis} = 11.0, $J_{3,2}$ = 8.4, 3-H); residual signals superimposed by those of *syn*-**17**.

$C_{20}H_{28}N_2O_3$ (360.5) Calcd. C 66.64 H 7.83 N 7.77
Found C 66.63 H 7.90 N 7.59

Table 1. Crystal data of **15b** and **17**[32]

	15b	**17**
Emp. Formula	$C_{26}H_{29}ON$	$C_{20}H_{28}O_4N_2$
M_r	371.52	360.45
Size [mm]	0.3 × 0.2 × 0.4	0.4 × 0.1 × 0.5
crystal system	monoclinic	orthorhombic
space group	$P1$ (Nr. 2)	$P2_12_12_1$ (Nr. 19)
a [Å]	9.425(2)	9.939(2)
b [Å]	9.490(2)	8.520(2)
c [Å]	12.386(1)	23.674(4)
α [°]	94.74(1)	
β [°]	97.68(1)	
γ [°]	102.49(1)	
V [Å^3]	1064.8(3)	2004.7(6)
Z	2	4
D_c [g/cm^3]	1.159	1.194
μ(Cu-K_α) [cm^{-1}]	5.0	6.4
F(000) [e]	400	776
T	room temp.	room temp.
Diffractometer	Enraf-Nonius CAD4	
Radiation	Cu-K_α (1.54184 Å), graphite monochromator	
Scan	ω, Δω = [0.8 + 0.14tg(Θ)]°	
Measured reflections	3332	3777
Unique reflections	2930	2826
R_{int}	0.032	0.034
Observed reflections	2711 [$F_o \geq 5\sigma(F_o)$]	2629 [$F_o \geq 5\sigma(F_o)$]
Solution	direct methods	
Refinement	full matrix least squares	
R/R_w ($w = 1/\sigma^2$)	0.072/0.070	0.043/0.040
Hydrogens	calculated; vinylic, *O*-,*N*-bonded found	
Refined parameters	263	245
Programs used	SHELXS-86[39], SHELX-76[40], PLATON89[41], SCHAKAL-88B[42]	

Table 2. Coordinates and equivalent isotropic temperature factors of **15b**; $U_{eq} = 1/3\ \Sigma_{ij}(U_{ij} \cdot a_i^* \cdot a_j^* \cdot a_i \cdot a_j)$

Atom	x/a	y/b	z/c	U_{eq}
O	0.2971(3)	0.9534(3)	0.2203(2)	0.080(1)
N	0.0618(2)	0.7648(2)	0.2945(2)	0.0428(8)
C1	0.3827(4)	0.9138(4)	0.3118(3)	0.063(1)
C2	0.3036(3)	0.8935(3)	0.4100(3)	0.046(1)
C3	0.2668(4)	1.0273(3)	0.4609(3)	0.062(1)
C4	0.2883(6)	1.1551(5)	0.4252(5)	0.095(2)
C5	0.1753(3)	0.7563(3)	0.3870(2)	0.042(1)
C6	0.1136(3)	0.7107(3)	0.4917(3)	0.050(1)
C7	0.2254(3)	0.6683(3)	0.5739(3)	0.047(1)
C8	0.2872(3)	0.5532(4)	0.5476(3)	0.059(1)
C9	0.3878(4)	0.5135(4)	0.6238(4)	0.079(2)
C10	0.4289(5)	0.5889(5)	0.7264(4)	0.089(2)
C11	0.3702(5)	0.7035(5)	0.7531(3)	0.088(2)
C12	0.2682(4)	0.7430(4)	0.6779(3)	0.066(1)
C13	-0.0516(3)	0.8400(3)	0.3264(3)	0.051(1)
C14	-0.1378(3)	0.8865(3)	0.2301(3)	0.049(1)
C15	-0.2874(3)	0.8361(4)	0.2046(3)	0.057(1)
C16	-0.3676(4)	0.8795(4)	0.1166(3)	0.070(2)
C17	-0.2979(5)	0.9727(5)	0.0525(3)	0.078(2)
C18	-0.1486(5)	1.0239(5)	0.0770(3)	0.087(2)
C19	-0.0694(4)	0.9822(4)	0.1644(3)	0.075(2)
C20	-0.0126(3)	0.6187(3)	0.2366(3)	0.053(1)
C21	0.0870(3)	0.5507(3)	0.1745(3)	0.049(1)
C22	0.1497(4)	0.6173(4)	0.0925(3)	0.065(1)
C23	0.2356(5)	0.5507(5)	0.0315(3)	0.083(2)
C24	0.2584(4)	0.4179(5)	0.0524(4)	0.084(2)
C25	0.1967(5)	0.3507(4)	0.1321(4)	0.083(2)
C26	0.1112(4)	0.4157(4)	0.1936(3)	0.065(1)

Table 3. Coordinates and equivalent isotropic temperature factors of **17**; $U_{eq} = 1/3\ \Sigma_{ij}(U_{ij} \cdot a_i^* \cdot a_j^* \cdot a_i \cdot a_j)$

Atom	x/a	y/b	z/c	Ueq
O1	0.1463(2)	0.6733(3)	0.04759(8)	0.0581(8)
O2	-0.0729(2)	0.6038(3)	0.05573(8)	0.0623(8)
O3	0.0619(2)	0.8227(2)	-0.12631(7)	0.0504(7)
O4	-0.1310(2)	0.9428(3)	-0.15368(7)	0.0559(7)
N1	-0.0148(2)	1.0265(3)	-0.0772(1)	0.0474(8)
N2	0.0863(2)	0.5350(3)	0.1215(1)	0.052(1)
C1	0.0264(5)	1.0258(5)	0.1038(1)	0.110(2)
C2	0.0028(4)	0.9748(4)	0.0520(1)	0.075(1)
C3	0.1098(3)	0.9351(4)	0.0113(1)	0.052(1)
C4	0.1163(3)	0.7621(4)	-0.0029(1)	0.051(1)
C5	0.1096(3)	1.0363(4)	-0.0434(1)	0.050(1)
C6	0.1181(4)	1.2140(4)	-0.0316(1)	0.073(1)
C7	-0.0265(4)	1.2723(4)	-0.0313(2)	0.091(2)
C8	-0.0969(3)	1.1685(4)	-0.0734(1)	0.076(1)
C9	-0.0346(3)	0.9303(4)	-0.1215(1)	0.047(1)
C10	0.0500(4)	0.6934(4)	-0.1676(1)	0.060(1)
C11	0.0548(4)	0.7583(5)	-0.2271(1)	0.072(1)
C12	0.1747(4)	0.5973(5)	-0.1549(2)	0.089(2)
C13	-0.0768(4)	0.5986(4)	-0.1559(1)	0.080(2)
C14	0.0421(3)	0.6030(4)	0.0737(1)	0.052(1)
C15	0.0106(3)	0.4434(4)	0.1597(1)	0.045(1)
C16	-0.1288(3)	0.4451(4)	0.1615(1)	0.062(1)
C17	-0.1947(3)	0.3537(5)	0.2006(1)	0.071(1)
C18	-0.1264(4)	0.2620(5)	0.2386(1)	0.074(2)
C19	0.0121(4)	0.2635(5)	0.2369(1)	0.078(2)
C20	0.0798(3)	0.3527(4)	0.1980(1)	0.063(1)

CAS Registry Numbers

(±)-**6**: 123808-73-1 / (±)-**7**: 123808-74-2 / (*R*)-**8**: 102308-32-7 / (*E*)-**9a**: 123751-06-4 / (*E*)-**9b**: 123751-07-5 / (*Z*)-**9b**: 123751-08-6 / (*E*)-**9c**: 123751-09-7 / (*Z*)-**9c**: 123751-10-0 / (*E*)-**9d**: 123751-11-1 / (*Z*)-**9d**: 123751-12-2 / (*S*)-**10**: 69610-40-8 / (±)-**11b**: 123751-13-3 / **11c**:

123751-14-4 / **11d**: 123751-15-5 / (±)-**12a**: 123751-16-6 / (±)-**12b**: 123751-17-7 / **12c**: 123751-18-8 / **12d**: 104700-47-2 / (±)-**13b**: 123751-19-9 / **13c**: 123774-93-6 / **13d**: 123751-20-2 / (±)-**14a**: 123751-21-3 / (±)-**14b**: 123751-22-4 / **14c**: 123751-23-5 / **14d**: 123751-24-6 / (±)-(*syn*)-**15a**: 123751-25-7 / (±)-(*anti*)-**15a**: 123751-26-8 / (±)-(*syn*)-**15b**: 123751-27-9 / (±)-(*anti*)-**15b**: 123751-28-0 / (*syn*)-**15c**: 123751-29-1 / (*anti*)-**15c**: 123751-30-4 / (*syn*)-**15d**: 123751-31-5 / (*anti*)-**15d**: 123751-32-6 / (*syn*)-**17**: 123751-33-7 / (*anti*)-**17**: 123751-34-8 / Bu_3SnCH_2I: 66222-29-5 / PhNCO: 103-71-9 / $(EtO)_2P(O)CH_2CO_2Me$: 1067-74-9 / $Ph_3P{=}CHCO_2Me$: 2605-67-6 / (*S*)-*N*-(*tert*-butoxycarbonyl)proline: 15761-39-4

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[28] Method: R. E. Ireland, D. W. Norbeck, *J. Org. Chem.* **50** (1985) 2198.

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[30] The *syn*:*anti* ratio in **15d** was 70:30 with HMPA and 68:32 without. Similarly, a 78:22 mixture of *syn*- and *anti*-**15b** resulted from the Wittig-Still rearrangement of **14b** whether HMPA was present or not (yield: 80%). For a discussion of the mechanistic implications of the invariance of *syn*:*anti* ratios vs. the presence or absence of HMPA in the related Wittig-Still rearragements of lithio ethers **2** cf. ref.[16f].

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