Chiral Carbanions, III[+]

Configurational Stability and Stannylation of Dipole-Stabilised Cyclic Tertiary Benzylic α-Oxycarbanions, which Occurs with Retention or Inversion of Configuration Depending on R and X of R_3SnX Used

Friedrich Hammerschmidt,*[a] Achim Hanninger,[a] Biljana Peric Simov,[a] Horst Völlenkle,[b] and Andreas Werner[†][a]

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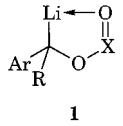
2,4,6-Triisopropylbenzoates of 1-indanol and 1-tetralol (ee 98%) are deprotonated at –78 °C in hexane by *s*BuLi/TMEDA to give partly configurationally labile organolithium intermediates **5a** and **5b**, which are deuterated by MeOD with retention of configuration. These intermediates are stannylated by trimethyltin chloride with inversion as determined by lithiodestannylation followed by addition of MeOD to produce deuterated esters of low ee. Stannylation of (*S*)-**5b** with (–)-menthyldimethyltin bromide affords stannane **7** (de ≥ 95%) with inversion. The carbanion derived from (*S*)-1-indanyl *N*,*N*-diisopropylcarbamate (**9**) is configurationally stable. It reacts with trimethyltin chloride favouring inversion of configuration (ee up to 17%). Tributyltin chloride and tributyltin triflate yield stannanes **11b** of opposite stereochemistry, the latter giving retention of configuration. Tributyltin bromide behaves similarly to the chloride, but the ee of the reaction product is only about 30%.

Introduction

α-Hetero-substituted alkylmetal compounds are valuable reagents in organic chemistry.[1] The preparation[2] and reaction of chiral, nonracemic alkyllithium compounds with electrophiles, their configurational stability[3] and their mechanism[4] of inversion of configuration have attracted much interest in recent years. This development was initiated by Still′s discovery of configurational stability of α-oxyalkyllithium compounds in 1980.[5] Dipole-stabilised α-oxybenzyllithium compounds of type **1a**[6] and **1b**[7] have been shown to be macroscopically stable only if R is an alkyl group such as methyl, but not for R = H. The dialkoxyphosphoryloxy-substituted carbanions of type **1c**[8a] are configurationally stable, even[8b] for R = H, for their short life-time before isomerisation (phosphate-phosphonate rearrangement)[8] to the corresponding phosphonates. The stereochemical outcome of the reaction of tertiary carbanions of types **1a** and **1b** (Ar = Ph, R = Me, X = iPr$_2$NC or 2,4,6-iPr$_3$C$_6$H$_2$C) is delicately influenced by the added electrophiles and the nature of X. Beak et al. reported on the reaction of two different secondary, nitrogen-substituted benzylic organolithium compounds in the presence of (−)-sparteine with a variety of electrophiles. In the case of the configurationally unstable carbanion the stereochemistry with alkyl tosylates as electrophiles was opposite to the one obtained with alkyl halides, trimethylsilyl and trimethyltin chloride.[9] The second organolithium compound, containing a configurationally stable carbanion, reacts with alkyl triflates and trimethyltin chloride with inversion of configuration.[10]



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1	X
a	CNR_2
b	$CC_6H_2iPr_3$
c	$P(OR)_2$

Figure 1. Dipole-stabilised α-oxybenzyllithium compounds

In the preceding paper, we proved by use of an X-ray structure analysis of a stannane, obtained by the reaction of **1b** with a trialkyltin bromide, that stannylation occurs with inversion of configuration,[11] first postulated[12] by Hoppe et al. for **1a** on the basis of plausible arguments. Carbamoyloxy-substituted carbanions derived from primary alcohols are stannylated with retention of configuration.[13]

This work deals with the configurational stability and the stereochemistry of stannylation of benzylic carbanions being part of a five- or six-membered ring and having a 2,4,6-triisopropylbenzoyloxy or *N*,*N*-diisopropylcarbamoyloxy substituent with various trialkyltin halides and tributyltin triflate.

[+] Part 2: Ref.[11]. For a related study see: C. Derwing, H. Frank, D. Hoppe, *Eur. J. Org. Chem.* **1999**, 3519−3524, following paper.

[†] Deceased August 23, 1999
[a] Institut für Organische Chemie der Universität Wien, Währingerstraße 38, A-1090 Wien, Austria
Fax: (internat.) + 43-1/31367-2280
E-mail: frha@felix.orc.univie.ac.at
[b] Institut für Mineralogie, Kristallographie und Strukturchemie, Technische Universität Wien, Getreidemarkt 9, A-1060 Wien, Austria

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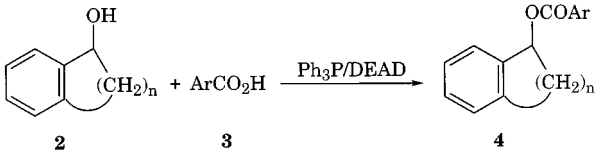
Synthesis of 2,4,6-Triisopropylbenzoates of 1-Indanol and 1-Tetralol, Their Deuteration and Stannylation

2,4,6-Triisopropylbenzoates **4** used for the generation of benzylic carbanions by deprotonation were prepared by Mitsunobu reaction of representative cyclic benzylic alcohols (±)-**2a**, (*S*)-(+)-**2a**, (*R*)-(−)-**2b** and (*S*)-(+)-**2b**, occuring with inversion of configuration (Scheme 1).[14] Ester (±)-**4a**, but not (±)-**4b**, could be resolved on a HPLC column with a chiral stationary phase (Chiracel OD). So the enantiomeric excesses of samples of **4a** could be determined easily [(*R*)-**4a** is less retained than (*S*)-**4a**, see Table 1]. This was very important as the specific optical rotation of ester (*R*)-**4a** having 98% ee as determined by HPLC is very small $\{[\alpha]_D^{20} = +1.91\}$ and cannot be used to evaluate the ee of chiral, nonracemic samples of **4a**.



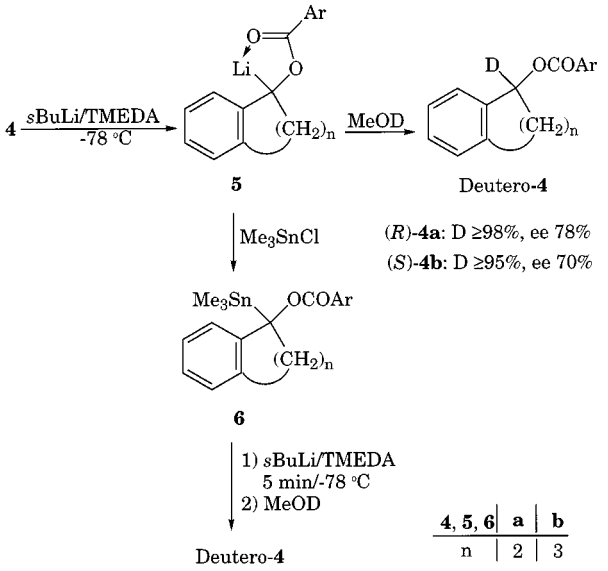
2 **3** **4**

$ArCO_2H$ = 2,4,6-*i*$Pr_3C_6H_2CO_2H$ **2a/4a**: n = 2 **2b/4b**: n = 3

2	(±)-**2a**	(*S*)-(+)-**2a**	(*R*)-(−)-**2b**	(*S*)-(+)-**2b**
4	(±)-**4a**	(*R*)-(+)-**4a**	(*S*)-(−)-**4b**	(*R*)-(+)-**4b**
yield of **4**	64%	76%	85%	69%

Scheme 1. Synthesis of 2,4,6-triisopropylbenzoates **4** by Mitsunobu reaction

Deprotonation of (±)-**4a** was tried in two different solvents at −78°C. When organolithium compound **5a** was generated with 2 equiv. of *s*BuLi in toluene/diethyl ether (20%) and quenched after 45 min with MeOD, deuterated ester (±)-**6a** (65% D, ^{1}H NMR) was isolated (Scheme 2). A mixture of toluene/diethyl ether (20%) proved ideal for the generation of configurationally stable carbanions derived from optically active 1-phenylethyl 2,4,6-triisopropylbenzoates with *s*BuLi without TMEDA as complexing agent.[7] In hexane on the contrary metallation of ester (±)-**4a** was virtually finished in 2 min by 1.2 equiv. of *s*BuLi/TMEDA. The yield of racemic deutero-**4a** was 80% and had a deuterium content of ≥ 95%. When 2 equiv. of *s*BuLi/TMEDA were used for deprotonation and the intermediate organolithium compound **5** was again quenched with MeOD, the deuterium content of the isolated ester (80% yield) increased to 98%. Ester (*R*)-(+)-**4a** furnished under the same conditions deutero-(*R*)-(+)-**4a** (63% yield, D ≥ 98%) with an ee of 78% as determined by HPLC (see Table 1). Increasing the amount of *s*BuLi/TMEDA from 1.2 equiv. used for the metallation of 2,4,6-triisopropylbenzoates **4** under standard conditions (reaction time: 2 min; solvent: hexane) to 2 equiv. caused the formation of side products. Benzyllithium compound **5a**, obtained by metallation of ester (*R*)-**4a**, is only partially configurationally stable and is deuterated with net retention of configuration.



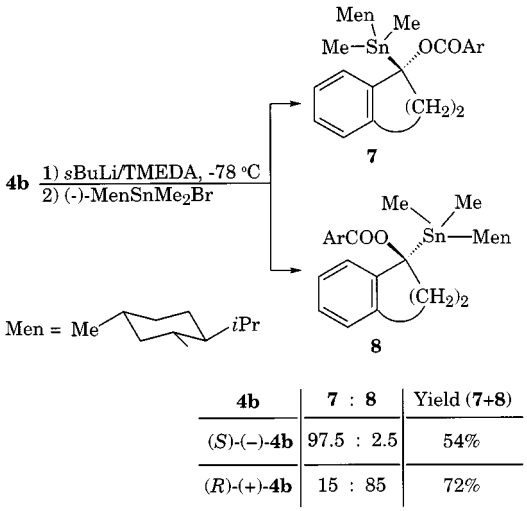
Scheme 2. Deuteration and stannylation of esters **4a** and **4b**

Next, the carbanion generated from ester (*R*)-(+)-**4a** was treated with trimethyltin chloride to furnish stannane (+)-**6a** $\{[\alpha]_D^{20} = +2.83\}$ in 44% yield. To assign the configuration, it was lithiodestannylated with 3 equiv. of *s*BuLi/TMEDA in hexane at −78°C for 5 min and then treated with MeOD to give deutero-(+)-**4a** {58% yield, 98% D, $[\alpha]_D^{20} = +0.12$; 5% ee by HPLC}, in which the (*R*) antipode is slightly favoured. Therefore, stannylation occurs with retention of configuration assuming that transmetallation here and in the following cases does not change the stereochemistry. Consequently, stannane (+)-**6a** has (*S*) configuration. The low enantiomeric excess is in part attributed to the configurational instability of the organolithium compound **5a** and very likely also to the low ee of stannane (+)-**6a**, which could not be resolved by HPLC on Chiracel OD (see Table 1). This result will be discussed in more detail later. To obtain more stereochemical information on the stannylation of (*R*)-**5a**, we tried to treat it with (−)-menthyldimethyltin bromide to produce diastereomeric stannanes, but we could not isolate the desired compounds.

2,4,6-Triisopropylbenzoate (*S*)-(−)-**4b**, derived from (*R*)-(−)-1-tetralol by Mitsunobu reaction, was deprotonated for 2 min in hexane with 1.2 equiv. of *s*BuLi/TMEDA and the carbanion **5b** formed was quenched with MeOD. Deuterated ester (*S*)-(−)-**4b** was isolated in 83% yield (D ≥ 95%; ee 70% on the basis of specific rotation). The configurational stability of the two cyclic α-oxycarbanions **5a** and **5b** is very similar as deduced from ee (78% versus 70%) of deutero-**4a**,**b** obtained by deuteration with MeOD. Carbanion **5b**, generated from ester (*S*)-(−)-**4b**, was smoothly transformed into stannane (+)-**6b** {74% yield, $[\alpha]_D^{20} = +6.10$} with Me_3SnCl. The ee of (+)-**6b** could not be determined directly, as it was not resolved on Chiracel OD. Lithiodestannylation of stannane (+)-**6b**, followed by addition

of MeOD, produced with net inversion deutero-(*R*)-(+)-**4b** in 80% yield with an enantiomeric excess of merely 16% as deduced from optical rotation. This implies that stannylation of **5b** occured with inversion of configuration to give stannane (+)-**6b** having (*S*) configuration.

Organolithium compound (*S*)-**5b** reacted with (−)-menthyldimethyltin bromide to produce stannanes **7** and **8** (54% yield, **7**/**8** = 97.5:2.5) (Scheme 3). Stannane **7** could be purified by crystallisation, but it could not be lithiodestannylated neither according to the general procedure nor by increasing the amount of *s*BuLi/TMEDA to 10 equiv. to determine its structure. Therefore, an X-ray structure analysis of a single crystal was carried out to show that **7** had the configuration given in Scheme 3 (Figure 2). Similarly, organolithium compound (*R*)-**5b** was treated with (−)-menthyldimethyltin bromide. The mixture of the two diastereomeric stannanes **7** and **8** formed in 72% yield in a ratio of 15:85 could not be separated by chromatography. The NMR spectra revealed that stannane **8** was the main product in this case. This result is expected if racemisation of (*S*)- and (*R*)-**5b** is slow compared to stannylation. Therefore, stannylation of partially configurationally stable (*S*)- and (*R*)-**5b** with (−)-menthyldimethyltin bromide occurs with inversion of configuration. The results will be discussed in the context of all experiments at the end.



4b	7 : 8	Yield (7+8)
(*S*)-(−)-**4b**	97.5 : 2.5	54%
(*R*)-(+)-**4b**	15 : 85	72%

Scheme 3. Stannylation of esters (*S*)-(−)- and (*R*)-(+)-**4b** with (−)-menthyldimethyltin bromide

Synthesis of (*S*)-(+)-1-Indanyl *N*,*N*-Diisopropylcarbamate, Its Deuteration and Stannylation

To increase the configurational stability of the cyclic α-oxyorganolithium compound **5a** derived from indanol, we replaced the 2,4,6-triisopropylbenzoyl group by the *N*,*N*-diisopropylcarbamoyl group. This will reduce or even eliminate the interferring partial racemisation in the stereochemical studies of deuteration and stannylation. Esterification of (*S*)-(+)-indanol with *N*,*N*-diisopropylcarbamoyl chloride

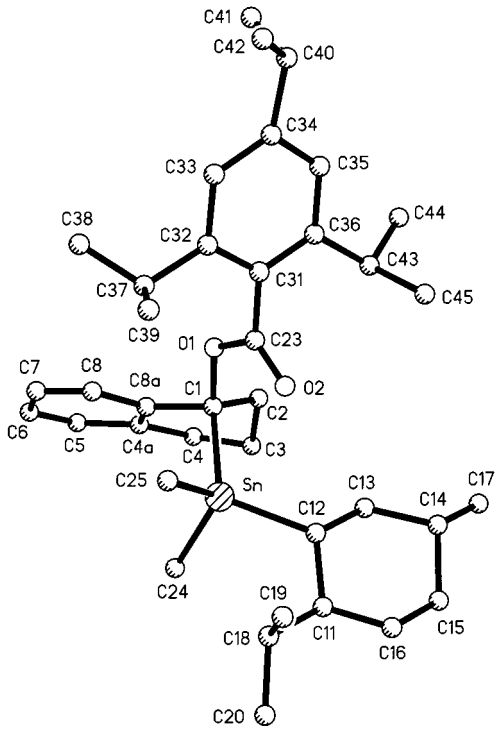
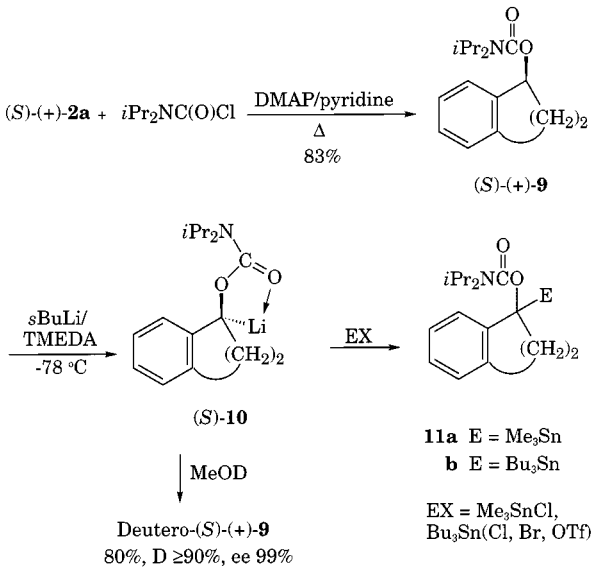


Figure 2. Crystal structure of stannane **7**; H atoms are omitted for the sake of clarity: selected distances [Å] and angles [°]: Sn−C1 2.24(2), Sn−$C_{menthyl}$ 2.15(2), C1−C2 1.48(3), C1−C10 1.58(3), C1−O 1.44(3), O−C(O) 1.36(2), C=O 1.21(2); C1−Sn−$C_{menthyl}$ 118.0(8), Me−Sn−Me 114.6(9), Sn−C1−O 115.6(13), C2−C1−C10 108(2)

in refluxing pyridine containing DMAP gave the corresponding carbamate (*S*)-(+)-**9** in 83% yield (Scheme 4).[6] Its deprotonation with 1.2 equiv. of *s*BuLi/TMEDA in hexane for 5 min, followed by quenching with MeOD gave in 80% yield deutero-(*S*)-(+)-**9** (90% D) and an enantiomeric excess of 99% [by HPLC; (*R*)-**9** is the less retained enantiomer, see Table 1]. When the reaction was quenched after 30 min, the enantiomeric excess was unchanged. Lithium-complexed dipole-stabilised α-oxycarbanion (*S*)-**10** is macroscopically configurationally stable, supported by a recent report by Hoppe et al.[6b] on a compound with a different carbamoyl group. Metallated carbamate **10** is configurationally more stable than metallated ester **5a**, because the *N*,*N*-diisopropylcarbamoyl group forms a stronger chelate complex than the 2,4,6-triisopropylbenzoyl group.

Organolithium intermediate (*S*)-**10** was stannylated with a variety of trialkyltin halides. Trimethyltin chloride gave stannane (+)-**11a** {$[\alpha]_D^{20}$ = +3.61} in 57% yield. When 1.75 equiv. of *s*BuLi/TMEDA was used instead of 1.2 equiv. for the generation of the carbanion, the yield (61%) remained virtually constant, but the sign of optical rotation changed and the value dropped significantly {$[\alpha]_D^{20}$ = −0.78}.

Compound **11a** could be resolved on an HPLC column with a chiral stationary phase [Chiracel OD; the (*R*) enanti-



Scheme 4. Synthesis, deuteration and stannylation of carbamate (*S*)-(+)-**9**

Scheme 5. Lithiodestannylation and deuteration of stannanes **11a** and **11b**

omer is less retained]. Although the two peaks were not base-line separated, the ee values could be estimated to be 17% and 2%, respectively. Lithiodestannylation and deuteration with MeOD produced deutero-(*R*)-(−)-**9** {$[\alpha]_D^{20}$ = −0.62; ee 11% by HPLC} and deutero-(*S*)-(+)-**9** {$[\alpha]_D^{20}$ = +0.21; ee 2% by HPLC} for the two different samples of stannanes. Stannylation of (*S*)-**10** with trimethyltin chloride occurs mainly with inversion of configuration and the proportion of molecules following retention approaches virtually 50%.

At last, organolithium compound (*S*)-**10** was stannylated with tributyltin chloride, bromide and triflate. The yields of stannanes **11b** are 56%, 57% and 37%. The low yield with tributyltin triflate is possibly caused by an incomplete transformation because of its low solubility at −78°C in the reaction mixture and starting material was present in the crude product. The specific optical rotations for the three stannanes were $[\alpha]_D^{20}$ = +14.64, +5.33, and −13.96. This result is very interesting, as it demonstrates the strong influence of the leaving group on tin on the stereochemical outcome of the substitution process. Stannylation with tributyltin chloride and triflate gave products of opposite stereochemistry. Although the ee of the reaction products could not be determined by HPLC on Chiracel OD, we assume that the two specific rotations of about 14 correspond to high ee, possibly 90−98%. If so, the reaction product with tributyltin bromide would correspond to an ee of about 30%. Lithiodestannylation of (−)-**11b** could not be effected by treatment at −78°C with 10 equiv. of *s*BuLi/TMEDA for 15 min in hexane, with 5 equiv. of *s*BuLi/TMEDA in diethyl ether. Tributylstannane **11b** was transmetallated in THF by 3 equiv. of *s*BuLi without TMEDA for 5 min at −78°C and deuterated with MeOD to produce racemic deutero-**9** in 65% yield. The reaction conditions could be optimised to deuterate the carbanion before it racemised completely. Stannane (−)-**11b** {$[\alpha]_D^{20}$ = −13.96} was still smoothly lithiodestannylated by 3 equiv. of *n*BuLi in THF for 30 s at −90°C. The carbanion formed was quenched with MeOD to afford carbamate deutero-(*S*)-(+)-**9** {$[\alpha]_D^{20}$ = +1.85; ee by HPLC 29%} in 75% yield. It is very likely that under these conditions the racemisation still accounts for the loss in ee from possibly 98% to 29%. The increased configurational instability by going from diethyl ether to THF is in agreement with findings of Hoppe et al.[6a] and our previous results[11] with the carbanion derived from chiral, nonracemic 1-phenylethyl 2,4,6-triisopropylbenzoate. Furthermore, it is unequivocally proven that (−)-**11b** has (*S*) configuration and the reaction with tributyltin triflate occurs with retention and with tributyltin chloride with inversion of configuration. Stannylation of (*S*)-**10** by tributyltin bromide follows an inversion process, but the retention process is contributing significantly to the stereochemical outcome.

Hoppe et al. report in the accompanying paper among other studies their results on the trimethyl- and tributylstannylation of carbamate (*R*)-(−)-**9**. Their higher yields and higher enantiomeric excesses can be explained by the different reaction conditions. Most noteworthy is their use of diethyl ether compared to hexane in our experiments. Their conclusions agree with ours.

Discussion of Results

Two mechanistic extremes for the stannylation of dipole-stabilised carbanions are known, retention of configuration for compounds of type **1a** (R = alkyl, Ar is replaced by H) and inversion for tertiary benzylic α-oxyanions of type **1a** and **1b** (R = Me, Ar = Ph). Cyclic benzylic organolithium compound (*S*)-**10** with a carbamoyloxy substituent is configurationally stable like the open-chain counterpart derived from 1-phenylethyl *N*,*N*-diisopropylcarbamate. The five- and six-membered 2,4,6-triisopropylbenzoyl-substituted benzyllithium compounds **5a** and **5b** are configurationally labile and racemise partly. Deprotonation for 2 min using *s*BuLi/TMEDA in hexane at −78°C results in an about 30% decrease of ee relative to the starting material. Organolithium compound **10** is stannylated with trimethyltin chloride with inversion of configuration (ee 17%), starting with an ester with 98% ee. The configuration was determined by lithiodestannylation and deuteration and assuming retention[11] for both steps. In a second experiment the product was virtually racemic (2% ee if at all, retention being slightly favoured). We assume that the stannylation of benzyllithium compounds **5a** and **5b** with trimethyltin chloride afforded stannanes **6a** and **6b** of low enantiomeric excess. This was in part caused by the configurational instability of the respective carbanions **5a**,**b** and a competing inversion/retention mechanism for stannylation. The re-

sulting stannane **6a** is virtually racemic (5% ee, marginally favouring retention of configuration) and **6b** is chiral, nonracemic (16% ee, inversion of configuration is predominating). Both enantiomeric excesses were determined after lithiodestannylation and deuteration, which additionally lowered the ee. (−)-Menthyldimethyltin bromide reacted with organolithium intermediate (*S*)-**5b** with inversion (de ≥ 95%) as proven by a single-crystal X-ray structure analysis.

The reaction mechanism of Bu_3SnX with α-carbamoyloxy-substituted benzyllithium compound (*S*)-**10** was dramatically influenced by the nature of X. The reactions resulted in opposite stereochemistry for X = Cl and TfO, being retention for the latter. The reaction with tributyltin bromide favoured inversion of configuration.

Interestingly, Beak et al. found that a configurationally labile, nitrogen-substituted benzylic carbanion was alkylated in the presence of (−)-sparteine by alkyl chloride with retention and by alkyl triflates with inversion of configuration.[10] More experiments are necessary to unravel the subtleties of electrophilic substitution at benzylic carbanions, being prone to significant changes in mechanism on little changes of reaction parameters. At present one has to be very cautious in generalizing observations. Each compound has to be treated individually.

Experimental Section

General: TLC: Merck precoated TLC plates (0.25 mm), silica gel 60, F_{254}; detection: UV and/or spraying with a 2% solution of $CeIVSO_4{\cdot}4H_2O$ in 2 N H_2SO_4 and heating on a hot plate. − Flash chromatography: Merck silica gel 60, 0.040−0.063 mm; eluents: petroleum ether (PE, boiling range 60−95°C), ethyl acetate (EA). − IR: Perkin-Elmer FT 1600 IR-Spectrometer, (Si[15]: a solution of the sample in Uvasol $CHCl_3$ was applied to an Si plate and the solvent was allowed to evaporate). − ^1H NMR and ^{13}C NMR (*J*-modulated): Bruker spectrometers AC 250F or AM 400 WB; TMS as internal standard. Satellite signals of ^1H and ^{13}C resonances for tin isotopes 117/119 are only given if they are clearly visible and assignable. − Optical rotation: Perkin-Elmer polarimeter 241 (1-dm cell). − Melting points were measured with a Reichert Thermovar instrument and are uncorrected. − The liquid chromatographic system consisted of a Hewlett Packard *hp* 1090 M instrument used in isocratic mode, equipped with a diode array detector. Integration was performed at 250 nm, bandwidth 40 nm or at 260 nm, bandwidth 20 nm, respectively. The column oven was kept at constant temperature by an external thermostatted bath to achieve working temperatures down to 7°C. A Chiralcel OD analytical column (250 × 4.6 mm; particle diameter 10 μm) from Daicel (Japan) was used with flow rates of 0.25 or 0.5 ml/min. Depending on the separation the temperature was kept at 15 or 7°C. The mobile phase contained hexane with 0.25 vol-% 2-propanol and 0.1 vol-% diethylamine freshly distilled. The mobile phase was premixed in portions of 500 ml and used in isocratic mode. − Reactions were carried out in dry solvents. THF was distilled from potassium and diethyl ether from lithium aluminum hydride. Hexane was dried over molecular sieve (4 Å). TMEDA was refluxed for 5 h with CaH_2, distilled and stored over molecular sieve (4 Å). The commercially available *s*BuLi (1.3 M solution in cyclohexane) was titrated with diphenylacetic acid in dry THF. If 2 equiv. was used for deprotonation, the concentration of *s*BuLi was assumed to be 1.3 M. For reactions with 1.2 equiv. the concentration determined by titration was used for the calculation of the amount needed. − Optically active alcohols (ee ≥ 98%) were prepared by enzymatic resolution[16] of their esters using lipase SAM II (from *Pseudomonas sp.*; *Amano*). The hydrolyses were stopped at conversions of 45%. Ester and alcohol were separated by flash chromatography. The ester was again hydrolysed enzymatically until the consumption of base ceased. The ester was isolated and hydrolysed with KOH in methanol. Optically active indanol was crystallised.

Determination of Enantiomeric Excess: The enantiomeric excess was determined by HPLC on an analytical column containing chiral cellulose tribenzoate[17] (Chiralcel OD) or by measurement of optical rotation. HPLC on other phases like Chiralcel OA, OB, OC gave no separation. − Ester (±)-**4a** was separated into enantiomers on Chiralcel OD, ester (±)-**4b** was not (see Table 1). Separation parameters of deuterated compounds were within the variation of those of corresponding unlabelled compounds. The enantiomers of trimethylstannane **11a** were separated on Chiralcel OD, whereas the enantiomers of tributylstannane **11b** were not, probably because of the larger substituents, also indicated by the low retention (Table 1).

Table 1. Data of HPLC of compounds **4a**, **4b**, **6a**, **9**, **11a** and **11b**

Compound	k_1	k_2	α	R_S	*T* [°C]
4a	0.315	0.383	1.215	1.453	15
4b	0.212	0.212	1	0	15
6a	0.076	0.076	1	0	15
9	1.336	1.546	1.157	1.675	7
11a	0.168	0.213	1.266	1.039	7
11b	0.081	0.081	1	0	7

Calculations: The parameter used in the evaluation of retention and stereoselectivity are capacity factor *k* (according to IUPAC nomenclature for chromatography), separation factor α and peak resolution R_S.

$$k = (t_R - t_0)/t_0$$

$$\alpha = k_2/k_1$$

where t_R is the retention time and t_0 is the retention time for the interstitial volume (2.8 ml at 25°C, 2.9 ml at 7°C) which was measured for 1,3,5-tri-*tert*-butylbenzene.

$$R_S = 2(t_{R2} - t_{R1})/(W_{b1} + W_{b2})$$

where W_b is the peak width at base. Enantiomeric excess is determined from $ee_{(R)}$ = area-%$_{peak(R)}$ − area-%$_{peak(S)}$ as given from the integration of the two peaks.

Deuteration and Stannylation of Esters 4 and Carbamate 9 (General Procedure A): *s*BuLi (1.2 mmol, of titrated commercially available 1.3 M solution in cyclohexane; if 2 equiv. of *s*BuLi was taken 1.54 ml ot the 1.3 M solution was used) was added dropwise to a stirred solution of substrate (1 mmol) and an equal molar amount of dry TMEDA (0.139 g, 0.18 ml, 1.2 mmol or 0.232 g, 0.3 ml, 2 mmol) in dry hexane (10 ml) at −78°C under argon. MeOD (0.5 ml) or trialkyltin compound [2 mmol, dissolved in 5 ml of dry hexane; dry diethyl ether/hexane (1:1) for tributyltin bromide and triflate] was added to the colored solution after 2 min for esters **4a** and **4b** and 5 min for carbamate **9**. Stirring was continued for 30 min at −78°C for MeOD and trialkyltin derivatives, and for 18 h with gradual warming up from −78°C to room temperature for (−)-menthyldimethyltin bromide. Petroleum ether (20 ml) and 2 N HCl (10 ml)

were added. The organic phase was separated and the aqueous phase was extracted with petroleum ether (20 ml). The combined organic layers were washed with water and a saturated solution of $NaHCO_3$, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash chromatography [for deuterated compounds with eluents as used for **4** or **9**, respectively; for stannanes with PE/diethyl ether (40:1), for R_f see respective compounds].

Lithiodestannylation of Stannanes 6, 11a and 11b Followed by Addition of MeOD (General Procedure B): A stirred solution of stannane (usually 0.2−0.5 mmol), 3 equiv. of dry TMEDA in dry hexane (1 ml for each 0.1 mmol) was cooled under argon to −78°C. 3 equiv. of *s*BuLi (1.3 M solution in cyclohexane, not titrated; sometimes *n*BuLi was used instead of *s*BuLi) was added dropwise. After 5 min, MeOD (0.25 ml, in 1 ml of dry hexane) was added. Stirring was continued for 30 min. The cooling bath was removed. Petroleum ether (20 ml) and 2 N HCl (10 ml) were added. The organic phase was separated and the aqueous phase was extracted with petroleum ether (20 ml). The combined organic layers were washed with water and a saturated solution of $NaHCO_3$, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash chromatography with the eluents used for the nondeuterated compounds. The individual reactions are described after the respective stannanes.

(±)- and (*R*)-(+)-(1-Indanyl) 2,4,6-Triisopropylbenzoate [(±)- and (*R*)-(+)-4a]: Diethyl azodicarboxylate (1.045 g 0.94 ml, 6 mmol) was added dropwise to a stirred and cooled (ice/water) mixture of (±)-1-indanol (0.671 g, 5 mmol), triphenylphosphane (1.57 g, 6 mmol), and 2,4,6-triisopropylbenzoic acid (1.24 g, 5 mmol) in dry toluene (20 ml) under argon. Stirring was continued for 1 hr at 0°C and 4 h at ambient temperature. Then the toluene was removed in vacuo and the residue was taken up in petroleum ether. After 2 h, the crystalline material (Ph_3PO and hydrazo ester) was filtered off. The mother liquor was concentrated in vacuo and purified twice by flash chromatography [PE/Et_2O (40:1); R_f = 0.42 with PE/Et_2O (20:1)] to yield (±)-**4a** as a viscous, colorless oil (1.17 g, 64%). − (*S*)-(+)-**2a** (0.671 g, 5 mmol) was esterified similarly to give (*R*)-(+)-**4a** {1.39 g (76%); $[\alpha]_D^{20}$= +1.91 (*c* = 5.71, $CHCl_3$)}. − IR (Si): $\tilde{\nu}$ = 2962 cm^{-1}, 1723, 1461, 1249, 1136, 1075. − ^1H NMR (400 MHz, $CDCl_3$): δ = 1.14 (d, *J* = 6.9 Hz, 6 H, *Me*$_2$CH), 1.20 (d, *J* = 6.9 Hz, 12 H, *Me*$_2$CH), 2.23 (dddd, *J* = 3.0, 3.9, 7.4, 14.3 Hz, 1 H, 2-H_b), 2.55 (ddt, *J* = 7.4, 8.4, 14.3 Hz, 1 H, 2-H_a), 2.84 (sept, *J* = 6.9 Hz, 3 H, Me$_2$C*H*), 2.90 (ddd, *J* = 3.9, 8.4, 16.0 Hz, 1 H, 3-H_a), 3.11 (dt, *J* = 7.4, 16.0 Hz, 1 H, 3-H_b), 6.46 (dd, *J* = 3.0, 7.4 Hz, 1 H, 1-H), 6.95 (s, 2 H, H_{arom}), 7.24 (m, 3 H, H_{arom}), 7.50 (d, *J* = 7.4 Hz, 1 H, H_{arom}). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 23.93 (2 C, *Me*$_2$CH), 24.04 (4 C, *Me*$_2$CH), 30.35 (CH_2), 31.26 (2 C, Me$_2$*C*H), 32.24 ($PhCH_2$), 34.41 (Me$_2$*C*H), 79.02 (CHO), 120.75 (2 C, HC_{arom}), 124.78, 125.76, 126.58 and 129.04 (4 C, HC_{arom}), 130.47 and 140.81 (2 C, C_{arom}), 144.66 (2 C, *i*Pr*C*$_{arom}$), 150.04 (OC*C*arom), 170.72 (C=O). − $C_{25}H_{32}O_2$ (364.53): calcd. C 82.37, H 8.84; found C 82.74, H 8.89.

(*S*)-(−)- and (*R*)-(+)-(1,2,3,4-Tetrahydro-1-naphthyl) 2,4,6-Triisopropylbenzoate [(*S*)-(−)- and (*R*)-(+)-4b]: (*R*)-(−)-1-Tetralol (0.741 g, 5 mmol) was esterified by the procedure used for the preparation of (±)-**4a**. Flash chromatography [PE/Et_2O (40:1); R_f = 0.45 with PE/Et_2O (20:1)] gave ester (*S*)-(−)-**4b** (1.617 g, 85%) as viscous oil, which contained possibly some anhydride and gradually solidified; m.p. 55−65°C; $[\alpha]_D^{20}$= −3.56 (*c* = 5.2, $CHCl_3$), $[\alpha]_{436}^{20}$= −10.06 (*c* = 5.2, $CHCl_3$). − (*S*)-(+)-1-Tetralol (0.741 g, 5 mmol) was esterified similarly to give (*R*)-(+)-**4b** (1.31 g, 69%); $[\alpha]_D^{20}$= +3.84 (*c* = 4.3, $CHCl_3$), $[\alpha]_{436}^{20}$= +11.09 *c* = 4.3, $CHCl_3$). − IR (Si): $\tilde{\nu}$ = 2961 cm^{-1}, 1721, 1460, 1250, 1075, 1058. − ^1H NMR (400 MHz, $CDCl_3$): δ = 1.18, 1.23 and 1.26 (3 × d, *J* = 6.9 Hz, each 6 H, *Me*$_2$CH), 1.87 (m, 1 H, CH_2), 2.01 (m, 1 H, CH_2), 2.11 (m, 1 H, CH_2), 2.22 (m, 1 H, CH_2), 2.81 (2 overlapping m, 3 H, 4-H, Me$_2$C*H*), 2.91 (sept, *J* = 6.9 Hz, 2 H, Me$_2$C*H*), 6.31 (t, *J* = 3.9 Hz, 1 H, CHO), 6.98 (s, 2 H, H_{arom}), 7.11 (m, 1 H, H_{arom}), 7.20 (m, 2 H, H_{arom}), 7.41 (m, 1 H, H_{arom}). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.53 (CH_2), 23.92, 24.08 and 24.16 (each 2 C, *Me*$_2$CH), 28.88 (CH_2), 29.06 (CH_2), 31.30 (2 C, Me$_2$*C*H), 34.39 (Me$_2$*C*H), 70.78 (CHO), 120.74 (2 C, HC_{arom}), 125.90, 128.19, 129.04 and 129.89 (4 C, HC_{arom}), 130.60, 134.06, 137.99, 144.61 (2 C) and 149.95 (C_{arom}), 170.42 (C=O). − $C_{26}H_{34}O_2$ (378.56): calcd. C 82.49, H 9.05; found C 82.75, H 9.31.

(*S*)-(+)-(1-Trimethylstannyl-1-indanyl) 2,4,6-Triisopropylbenzoate [(*S*)-(+)-6a]: Ester (*R*)-(+)-**4a** (0.365 g, 1 mmol) was stannylated according to General Procedure A. The product was purified by flash chromatography [PE/Et_2O (40:1); for TLC: PE/Et_2O (20:1), R_f = 0.64) to give 0.232 g (44%) of stannane (*S*)-(+)-**6a** as a viscous oil which eventually crystallized, m.p. 50−60°C, $[\alpha]_D^{20}$= +2.83 (*c* = 1.8, $CHCl_3$). − IR (Si): $\tilde{\nu}$ = 2962 cm^{-1}, 1699, 1607, 1461, 1255, 1138, 1080. − ^1H NMR (400 MHz, $CDCl_3$): δ = 0.08 [s, 9 H, $SnMe_3$; $J(^{117/119}Sn)$ = 51.2, 53.2 Hz], 1.21 (d, *J* = 6.9 Hz, 12 H, *Me*$_2$CH), 1.24 (d, *J* = 6.4 Hz, 6 H, *Me*$_2$CH), 2.26 [dt, *J* = 8.6, 12.2 Hz, 1 H, 2-H_a; $J(^{117/119}Sn)$ = 58.0, 60.1 Hz], 2.71 (dt, *J* = 8.6, 15.3 Hz, 1 H, 3-H_b), 2.85 (m, 2 H, Me$_2$C*H*, 2-H_b), 2.96 (sept, *J* = 6.9 Hz, 2 H, Me$_2$C*H*), 3.06 (ddd, *J* = 2.5, 8.6, 15.3 Hz, 1 H, 3-H_b), 6.97 (s, 2 H, H_{arom}), 7.17 (m, 4 H, H_{arom}). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = −7.36 [Me_3Sn; $J(^{117/119}Sn)$ = 330.4, 338.0 Hz], 23.91, 24.24 and 24.28 (each 2 C, *Me*$_2$CH), 30.46 (CH_2), 31.16 (2 C, Me$_2$*C*H), 34.36 (Me$_2$*C*H), 38.40 [Sn*C*H_2; $J(^{117/119}Sn)$ = 20.0 Hz], 87.74 (SnCO), 120.80 (2 C, CH_{arom}), 123.18, 124.66 126.73 and 126.79 (4 C, HC_{arom}), 130.03 (C_{arom}), 140.56 [C_{arom}; $J(^{117/119}Sn)$ = 20.6 Hz], 145.02, 146.56 (2 C) and 150.07 (C_{arom}), 172.00 (C=O). − $C_{28}H_{40}O_2Sn$ (527.23): calcd. C 63.77, H 7.65; found C 64.06, H 7.95. − Stannane (+)-**6a** (0.092 g, 0.175 mmol) was transformed into 0.037 g (58%) of deutero-(*R*)-(+)-**4a** {$[\alpha]_D^{20}$= +0.12 (*c* = 0.95, $CHCl_3$); ee 5% by HPLC} according to General Procedure B using *s*BuLi.

(*S*)-(+)-(1,2,3,4-Tetrahydro-1-trimethylstannyl-1-naphthyl) 2,4,6-Triisopropylbenzoate [(*S*)-(+)-6b]: Ester (*S*)-(−)-**4b** (0.757 g, 2 mmol) was stannylated in hexane (15 ml) according to General Procedure A. The residue was purified by flash chromatography [PE/Et_2O (40:1), R_f = 0.51] to give crystalline (*S*)-(+)-**6b** (1.083 g, 74%); $[\alpha]_D^{20}$= +9.16 (*c* = 36.1, $CHCl_3$). − IR (Si): $\tilde{\nu}$ = 2962 cm^{-1}, 1698, 1461, 1288, 1257. − ^1H NMR (400 MHz, $CDCl_3$): δ = 0.08 [s, 9 H, $SnMe_3$; $J(^{117/119}Sn)$ = 49.7, 51.7 Hz], 1.22, 1.25 and 1.29 (3d, *J* = 6.9 Hz, each 6 H, *Me*$_2$CH), 1.81 and 1.98 (2m, each 1 H, 3-H), 2.19 [ddd, 1 H, *J* = 3.0, 11.3, 12.8 Hz, 2-H_a; $J(^{117/119}Sn)$ = 69.0, 71.4 Hz], 2.62 [ddd, *J* = 3.0, 6.6, 12.8 Hz, 1 H, 2-H_b; $J(^{117/119}Sn)$ = 30.0, 33.3 Hz], 2.74 (B part of ABXY system, dt, *J* = 4.9, 16.7 Hz, 4-H_a), 2.87 (A part of ABXY system overlapping with sept, *J* = 6.9 Hz, 2 H, 4-H_b, Me$_2$C*H*), 3.03 (sept, *J* = 6.9 Hz, 2 H, Me$_2$C*H*), 6.99 (s, 2 H, H_{arom}), 7.05 (m, 2 H, H_{arom}), 7.12 (m, 1 H, H_{arom}), 7.20 (m, 1 H, H_{arom}). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = −6.67 [Me_3Sn; $J(^{117/119}Sn)$ = 325.8, 340.3 Hz], 20.27 [CH_2; $J(^{117/119}Sn)$ = 13.0 Hz], 23.91 and 23.93 (each 1 C, *Me*$_2$CH), 24.23 and 24.44 (each 2 C, *Me*$_2$CH), 29.22 (CH_2), 31.24 (2 C, Me$_2$*C*H), 33.60 [CH_2; $J(^{117/119}Sn)$ = 10.6 Hz], 34.36 (Me$_2$*C*H), 82.73 (OCSn), 120.81 (2 C, HC_{arom}), 125.77 [HC_{arom}; $J(^{117/119}Sn)$ = 9.9 Hz], 126.06 [HC_{arom}; $J(^{117/119}Sn)$ = 8.4 Hz], 126.55 [HC_{arom}; $J(^{117/119}Sn)$ = 19.1 Hz], 129.03 (HC_{arom}), 130.17 (C_{arom}), 135.03 [C_{arom}; $J(^{117/119}Sn)$ = 9.8 Hz], 140.44 (C_{arom}), 144.89 (2 C_{arom}), 150.01 (C_{arom}), 172.07 (C=O). − $C_{29}H_{42}O_2Sn$ (541.34): calcd. C 64.34, H 7.84; found C 64.40, H 7.99. − Stannane (+)-**6b** (0.391

g, 0.72 mmol) was transformed using TMEDA (0.174 g, 023 ml, 1.5 mmol) and *n*BuLi (0.94 ml of a 1.6 M solution in hexane, 1.5 mmol) into 0.219 g (80%) of deutero-(*R*)-(+)-**4b** {$[\alpha]_D^{20}$= +0.58 (*c* = 9.88, $CHCl_3$), 16% ee; $[\alpha]_{436}^{20}$ = +1.70 (*c* = 9.88, $CHCl_3$), 17% ee} according to General Procedure B.

Synthesis of Stannanes 7 and 8 from (*S*)-(−)-4b: Ester (*S*)-(−)-**4b** (0.379 g, 1 mmol) was stannylated with (−)-menthyldimethyltin bromide[18] according to General Procedure A. The residue was purified by flash chromatography [PE/Et_2O (40:1); R_f = 0.67 in PE/Et_2O (20:1)] to give 0.359 g (54%, de ≥ 95% by ^1H NMR) of stannanes **7** and **8** in a ratio of 97.5:2.5. Crystallisation of the crude product from methanol furnished diastereomerically pure stannane **7**; m.p. 118°C; $[\alpha]_D^{20}$= −2.74 (*c* = 6.87, $CHCl_3$). − IR (Si): $\tilde{\nu}$ = 2960 cm^{-1}, 1697, 1461, 1288, 1257. − ^1H NMR (400 MHz, $CDCl_3$): δ = −0.11 [s, 3 H, $SnMe_2$; $J(^{117/119}Sn)$ = 42.8, 44.8 Hz], 0.09 [s, 3 H, $SnMe_2$; $J(^{117/119}Sn)$ = 44.3, 46.3 Hz], 0.76 (d, *J* = 6.9 Hz, 3 H, $Me_{menthyl}$), 0.79 (d, *J* = 6.4 Hz, 3 H, $Me_{menthyl}$), 0.81 (d, *J* = 6.4 Hz, 3 H, $Me_{menthyl}$), 0.86 (m, 1 H), 0.97 (dq, *J* = 3.0, 12.8 Hz, 1 H), 1.19 (m, 3 H), 1.22, 1.25 and 1.28 (3d, *J* = 6.9 Hz, each 6 H, Me_2CH), 1.33 (m, 1 H), 1.65 (m, 3 H), 1.92 (m, 2 H, 3-H), 2.03 (m, 1 H), 2.24 [ddd, *J* = 2.7, 10.8, 12.8 Hz, 1 H, 2-H_a; $J(^{117/119}Sn)$ = 60.8, 64.0 Hz], 2.61 [ddd, *J* = 2.6, 6.4, 12.8 Hz, 1 H, 2-H_b; $J(^{117/119}Sn)$ = 27.7, 30.8 Hz], 2.75 (B part of ABXY system, dt, *J* = 4.9, 16.7 Hz, $ArCH_2$), 2.87 [sept (*J* = 6.9 Hz) and A part of ABXY system, 2 H, Me_2CH, $ArCH_2$], 3.06 (sept, *J* = 6.9 Hz, 2 H, Me_2CH), 6.99 (s, 2 H, H_{arom}), 7.04 (m, 2 H, H_{arom}), 7.09 (m, 1 H, H_{arom}), 7.20 (m, 1 H, H_{arom}). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = −7.43 and −6.33 (Me_2Sn), 16.03 ($Me_{menthyl}$), 20.22 [CH_2; $J(^{117/119}Sn)$ = 12.2 Hz], 21.91 ($Me_{menthyl}$), 22.62 ($Me_{menthyl}$), 23.93, 24.23 and 24.53 (each 2 C, Me_2CH), 26.90 ($CH_{2menthyl}$), 29.15 (CH_2), 31.28 (2 C, Me_2CH), 32.72 [$CH_{menthyl}$; $J(^{117/119}Sn)$ = 16.8 Hz], 34.22 (CH_2), 34.38 (Me_2CH), 35.19 [$CH_{menthyl}$; $J(^{117/119}Sn)$ = 70.2 Hz], 35.31 ($CH_{2menthyl}$), 36.61 [$SnCH_{menthyl}$; $J(^{117/119}Sn)$ = 403.9, 423.0 Hz], 41.23 [$CH_{2menthyl}$; $J(^{117/119}Sn)$ = 21.4 Hz], 45.58 [$CH_{menthyl}$; $J(^{117/119}Sn)$ = 13.7 Hz], 84.07 (OCSn), 120.90 (2 C, HC_{arom}), 125.41 [HC_{arom}; $J(^{117/119}Sn)$ = 7.0 Hz], 125.75 [CH_{arom}; $J(^{117/119}Sn)$ = 7.1 Hz], 126.90 [CH_{arom}; $J(^{117/119}Sn)$ = 17.5 Hz], 128.93 (CH_{arom}), 130.29 (C_{arom}), 134.99 (C_{arom}; $J(^{117/119}Sn)$ = 16.3 Hz], 140.57 (C_{arom}), 144.91 (2 C, C_{arom}), 150.02 (C_{arom}), 172.06 (C=O). − $C_{38}H_{58}O_2Sn$ (665.57): calcd. C 68.58, H 8.78; found C 68.41, H 8.86.

Synthesis of Stannanes 7 and 8 from (*R*)-(+)-4b: Ester (*R*)-(+)-**4b** (0.379 g, 1 mmol) was stannylated with (−)-menthyldimethyltin bromide[18] according to General Procedure A. The residue was purified by flash chromatography [PE/Et_2O (40:1); R_f = 0.75 in PE/Et_2O (20:1)] to give 0.479 g (72%, de 70% by ^1H NMR) of an inseparable mixture of stannanes **7** and **8** in a ratio of 15:85; $[\alpha]_D^{20}$= −42.10 (*c* = 1.05, $CHCl_3$). − IR (Si): $\tilde{\nu}$ = 2959 cm^{-1}, 1697, 1461, 1288, 1256. − ^1H NMR (400 MHz, $CDCl_3$, only signals for **8** are given): δ = −0.01 [s, 3 H, $SnMe_2$; $J(^{117/119}Sn)$ = 43.3, 45.3 Hz], 0.09 [s, 3 H, $SnMe_2$; $J(^{117/119}Sn)$ = 44.3, 46.3 Hz], 0.68 (d, *J* = 6.9 Hz, 3 H, $Me_{menthyl}$), 0.79 (d, *J* = 6.4 Hz, 3 H, $Me_{menthyl}$), 0.88 (d, *J* = 6.9 Hz, 3 H, $Me_{menthyl}$), 0.80 − 1.25 (m, 4 H, $H_{menthyl}$), 1.22 (d, *J* = 6.9 Hz, 6 H, Me_2CH), 1.25 (d, *J* = 6.9 Hz, 6 H, Me_2CH), 1.26 (d, *J* = 6.4 Hz, 6 H, Me_2CH), 1.61 (m, 5 H, $H_{menthyl}$), 1.89 (m, 3 H, $H_{menthyl}$, 3-H), 2.33 (ddd, *J* = 3.0, 9.9, 13.0 Hz, 1 H, 2-H_a), 2.52 (ddd, *J* = 3.0, 7.8, 12.8 Hz, 1 H, 2-H_b), 2.74 (B part of ABXY system, dt, *J* = 6.4, 16.5 Hz, $ArCH_2$), 2.85 (m, 2 H, B part of ABXY system, Me_2CH), 3.03 (sept, *J* = 6.9 Hz, 2 H, Me_2CH), 6.98 (s, 2 H, H_{arom}), 7.04 (m, 2 H, H_{arom}), 7.09 (m, 1 H, H_{arom}), 7.20 (m, 1 H, H_{arom}). − ^{13}C NMR (100.6 MHz, $CDCl_3$, only signals for **8** are given): δ = −7.68 and −5.83 (Me_2Sn), 15.76 ($Me_{menthyl}$), 20.03 [CH_2; $J(^{117/119}Sn)$ = 11.8 Hz], 22.01 ($Me_{menthyl}$), 22.58 ($Me_{menthyl}$), 23.93, 24.25 and 24.43 (each 2 C, Me_2CH), 26.48 ($CH_{2menthyl}$), 29.44 (CH_2), 31.16 (2 C, Me_2CH), 33.17 [$CH_{menthyl}$; $J(^{117/119}Sn)$ = 18.3 Hz], 34.37 (Me_2CH), 34.44 (CH_2), 35.15 [$CH_{menthyl}$; $J(^{117/119}Sn)$ = 71.7 Hz], 35.28 ($CH_{2menthyl}$), 36.85 ($CH_{menthyl}$), 41.18 [$CH_{2menthyl}$; $J(^{117/119}Sn)$ = 19.8 Hz], 45.99 [$CH_{menthyl}$; $J(^{117/119}Sn)$ = 13.7 Hz], 83.57 (OCSn), 120.89 (2 C, HC_{arom}), 125.68 [HC_{arom}; $J(^{117/119}Sn)$ = 6.3 Hz], 125.95 [CH_{arom}; $J(^{117/119}Sn)$ = 8.4 Hz], 127.82 [CH_{arom}; $J(^{117/119}Sn)$ = 16.3 Hz], 128.99 (CH_{arom}), 130.32 (C_{arom}), 133.39 (C_{arom}; $J(^{117/119}Sn)$ = 18.0 Hz], 140.47 (C_{arom}), 144.98 (2 C, C_{arom}), 149.97 (C_{arom}), 171.68 (C=O).

Crystal-Structure Analysis of 7: Crystal data[19] and structure Refinement: $C_{38}H_{58}O_2Sn$; *M* = 665.5 g/mol; temperature: 293(2) K, wavelenth: 0.71073 Å; crystal system: orthorhombic; space group: *P*2(1)2(1)2(1); unit cell dimensions: *a* = 9.327(2) Å, *b* = 11.035(3) Å, *c* = 35.600(10) Å; volume: 3669(2) $Å^3$, *Z* = 4; density(calcd.): 1.205 Mg/m^3; absorption coefficient: 0.725 mm^{-1}; F(000): 1408; crsytal size: 0.5 × 0.5 × 0.3 mm; θ range for data collection: 2.26−24.93°, limiting indices: $0 \le h \le 11$, $0 \le k \le 13$, $0 \le l \le 42$; reflections collected: 3630; independent reflections: 3630 [*R*(int) = 0.0000], refinement method: full-matrix least squars on F^2; data/restraints/parameters: 3630/96/372: goodness of fit on F^2: 1.090; final *R* indices [$I > 2\sigma(I)$]: *R*1 = 0.0953, *wR*2 = 0.2583, *R* indices (all data): *R*1 = 0.1201, *wR*2 = 0.2773; absolute structure parameter: −0.04(14); largest difference peak and hole: 1.736 and −1.760 $e \cdot Å^{-3}$.

(*S*)-(+)-1-Indanyl *N*,*N*-Diisopropylcarbamate [(*S*)-(+)-9]: A solution of (*S*)-(+)-1-indanol (**4a**) (0.671 g, 5 mmol), *N*,*N*-diisopropylcarbamoyl chloride (0.982 g, 6 mmol), and 4-dimethylaminopyridine (0.855 g, 7 mmol) in dry pyridine (10 ml) were refluxed under argon for 15 h. Water (0.5 ml) was added to the cooled solution and the mixture was heated under reflux for 15 min. The solvent was removed in vacuo. The residue was taken up in diethyl ether, washed with 2 N HCl, water, a saturated solution of $NaHCO_3$, dried ($MgSO_4$) and concentrated in a rotary evaporator. The residue was purified by flash chromatography [PE/EA (15:1); for TLC: PE/EA (5:1), R_f = 0.37] and bulb-to-bulb distillation (145−150°C/0.5 Torr) to yield 1.09 g (83%) of (*S*)-(+)-**9** as an oil which eventually crystallized; m.p. 27°C, $[\alpha]_D^{20}$= +6.63 (*c* = 4.57, $CHCl_3$). − IR (Si): $\tilde{\nu}$ = 2970 cm^{-1}, 1688, 1439, 1290, 1151, 1133, 1054. − ^1H NMR (400 MHz, $CDCl_3$): δ = 1.16 (2 br. overlapping d, *J* = 6.4 Hz, 12 H, Me_2CH), 2.08 (dddd, *J* = 4.4, 5.9, 8.4, 13.8 Hz, 1 H, 2-H_a), 2.52 (dddd, *J* = 5.4, 6.9, 8.4, 13.8 Hz, 1 H, 2-H_b), 2.95 (AB system, J_{AB} = 16.0 Hz; *J* = 5.9, 8.4; 5.4, 8.4 Hz, 3-H), 3.67 and 4.12 (2 br.s, each 1 H, Me_2CH), 6.16 (dd, *J* = 4.4, 6.9 Hz, 1 H, 1-H), 7.22 (m, 3 H, H_{arom}), 7.42 (d, *J* = 6.4 Hz, 1 H, H_{arom}). − ^{13}C NMR (100.6 MHz, [D_8]toluene, 87°C): δ = 22.35 (4 C, Me_2CH), 31.53 (CH_2), 34.17 (CH_2), 47.52 (2 C, Me_2CH), 79.81 (CHO), 125.91, 127.05, 127.92 and 129.75 (4 C, HC_{arom}), 144.06 and 145.28 (2 C, C_{arom}), 156.54 (C=O). − $C_{16}H_{23}NO_2$ (261.37): calcd. C 73.53, H 8.87, N 5.36; found C 73.28, H 9.08, 5.26.

(*S*)-(+)- and (*R*)-(−)-(1-Trimethylstannyl-1-indanyl) *N*,*N*-Diisopropylcarbamate [(*S*)-(+)- and (*R*)-(−)-11a]: Carbamate (*S*)-(+)-**9** (0.13 g, 0.5 mmol) was stannylated with trimethyltin chloride according to General Procedure A. The product was purified by flash chromatography [PE/Et_2O (40:1); for TLC: PE/Et_2O (20:1), R_f = 0.56] to give 0.12 g (57%) of crystalline stannane (*S*)-(+)-**11a** {$[\alpha]_D^{20}$= +3.61 (*c* = 0.72, $CHCl_3$); ee 17% by HPLC}. When carbamate (*S*)-(+)-**9** (0.261 g, 1 mmol) was stannylated using 1.75 mmol of *s*BuLi (1.35 ml of 1.3 M solution in cyclohexane) and trimethyltin chloride (0.598 g, 3 mmol, dissolved in 5 ml of hexane) according to General Procedure A, 0.26 g (61%) of crystalline (*R*)-

(−)-**11a** {$[\alpha]_D^{20}$= −0.78 (*c* = 1.03, $CHCl_3$); m.p. 63°C; ee 2% by HPLC} was obtained. − IR (Si): $\tilde{\nu}$ = 2970 cm^{-1}, 1669, 1438, 1334, 1311, 1135, 1055. − ^1H NMR (400 MHz, $CDCl_3$): δ = 0.10 [s, 9 H, Me_3Sn; $J(^{117/119}Sn)$ = 50.2, 52.7 Hz], 1.18 (d, *J* = 6.9 Hz, 9 H, Me_2CH), 1.28 (br. s, 3 H, Me_2CH), 2.08 [dt, *J* = 8.7, 11.4 Hz, 1 H, 2-H_a; $J(^{117/119}Sn)$ = 73.6, 76.8 Hz], 2.59 (ddd, *J* = 7.4, 11.4, 15.6 Hz, 1 H, 3-H_a), 2.81 [ddd, *J* = 1.5, 7.4, 11.4 Hz, 1 H, 2-H_b; $J(^{117/119}Sn)$ = 40.0, 41.5 Hz], 2.97 (ddd, *J* = 1.5, 8.7, 15.6 Hz, 1 H, 3-H_b), 3.65 (br. s, 1 H, Me_2CH), 4.21 (br. s, 1 H, Me_2CH), 7.08 (m, 1 H, H_{arom}), 7.18 (m, 3 H, H_{arom}). − ^{13}C NMR (100.6 MHz, [D_8]toluene, 87°C): δ = −6.09 [Me_3Sn; $J(^{117/119}Sn)$ = 327.8, 340.0 Hz], 22.22 (2 C, Me_2CH), 22.31 (2 C, Me_2CH), 31.52 (C-3), 40.56 [C-2; $J(^{117/119}Sn)$ = 24.8 Hz], 47.65 (Me_2CH), 88.71 (SnCO), 124.22 [CH_{arom}; $J(^{117/119}Sn)$ = 14.5 Hz], 126.09 [CH_{arom}; $J(^{117/119}Sn)$ = 8.7 Hz], 127.69 [CH_{arom}; $J(^{117/119}Sn)$ = 10.9 Hz], 128.08 [HC_{arom}; $J(^{117/119}Sn)$ = 9.4 Hz], 141.53 and 149.48 (2 C, C_{arom}), n. d. (C=O). − $C_{19}H_{31}NO_2Sn$ (424.15): calcd. C 53.80, H 7.36, N 3.30; found C 54.08, H 7.40, N 3.41. − Stannane (−)-**11a** {0.212 g, 0.5 mmol, $[\alpha]_D^{20}$= −0.78, (*c* = 1.03, $CHCl_3$)} was transformed into 0.077 g (59%) of deutero-(*S*)-(+)-**9** {$[\alpha]_D^{20}$= +0.21 (*c* = 2.8, $CHCl_3$), 2% ee by HPLC}. Stannane (+)-**11a** {0.212 g, 0.5 mmol, $[\alpha]_D^{20}$= +3.61 (*c* = 0.72, $CHCl_3$)} was transformed by General Procedure B into 0.029 g (51%) of deutero-(*R*)-(−)-**9** {$[\alpha]_D^{20}$= −0.62 (*c* = 1.45, $CHCl_3$), 11% ee by HPLC}.

(*R*)-(−)- and (*S*)-(+)-(1-Tributylstannyl-1-indanyl) *N*,*N*-Diisopropylcarbamate [(*R*)-(+)-and (*S*)-(−)-11b]: Cabamate (*S*)-(+)-**9** (0.261 g, 1 mmol) was stannylated according to General Procedure A using tributyltin chloride. The crude product was purified by flash chromatography [PE/Et_2O (40:1); for TLC: PE/Et_2O (20:1), R_f = 0.60] to give 0.307 g (56%) of (*S*)-(+)-**11b** as an oil; $[\alpha]_D^{20}$= +14.64 (*c* = 2.11, $CHCl_3$). − Similarly, 1 mmol of carbamate (*S*)-(+)-**9** was stannylated using tributyltin bromide to give 0.312 g (57%) of (*S*)-(+)-**11b**; $[\alpha]_D^{20}$= +5.33 (*c* = 3.0, $CHCl_3$). − Similarly, 0.5 mmol of carbamate (*S*)-(+)-**9** was stannylated using tributyltin triflate to give 0.101 g (37%) of (*R*)-(−)-**11b**; $[\alpha]_D^{20}$= −13.96 (*c* = 2.85, $CHCl_3$). − IR (Si): $\tilde{\nu}$ = 2956 cm^{-1}, 2926, 1701, 1671, 1458, 1438, 1333, 1310, 1053. − ^1H NMR (400 MHz, $CDCl_3$): δ = 0.68 (m, 6 H, CH_2Sn), 0.80 [t, *J* = 7.4 Hz, 9 H, $Me(CH_2)_3$], 1.17 and 1.18 (2 × d, *J* = 6.8 Hz, each 6 H, Me_2CH), 1.25 (m, 12 H, CH_2CH_2Me), 2.01 [dt, *J* = 8.9, 11.4 Hz, 1 H, 2-H_a; $J(^{117/119}Sn)$ = 67.0, 70.0 Hz], 2.63 (ddd, *J* = 7.4, 11.4, 15.7 Hz, 1 H, 3-H_a), 2.84 [ddd, *J* = 1.0, 7.4, 11.4 Hz, 1 H, 2-H_b; $J(^{117/119}Sn)$ = 34.0, 37.0 Hz], 2.95 (ddd, *J* = 1.0, 8.9, 15.7 Hz, 1 H, 3-H_b), 3.65 (br. s, 1 H, Me_2CH), 4.21 (br. s, 1 H, Me_2CH), 7.06 (m, 1 H, H_{arom}), 7.17 (m, 3 H, H_{arom}). − ^{13}C NMR (100.6 MHz, [D_8]toluene, 87°C): δ = 13.80 [$SnCH_2$; $J(^{117/119}Sn)$ = 308.1, 322.6 Hz], 14.81 ($MeCH_2$), 22.32 (very br., Me_2CH), 29.07 [$SnCH_2CH_2$; $J(^{117/119}Sn)$ = 56.3 Hz], 30.71 [$SnCH_2CH_2CH_2$; $J(^{117/119}Sn)$ = 19.6 Hz], 31.61 (C-3), 41.22 [C-2; $J(^{117/119}Sn)$ = 22.6 Hz], 47.64 (Me_2CH), 90.14 (SnCO), 124.68 [CH_{arom}; $J(^{117/119}Sn)$ = 12.4 Hz], 126.13 [CH_{arom}; $J(^{117/119}Sn)$ = 7.3 Hz], 127.64 [CH_{arom}; $J(^{117/119}Sn)$ = 9.7 Hz], 128.03 [HC_{arom}; $J(^{117/119}Sn)$ = 8.7 Hz], 141.69 and 149.92 (2 C, C_{arom}), n. d. (C=O). − $C_{28}H_{49}NO_2Sn$ (554.72): calcd. C 60.66, H 8.91, N 2.53; found C 60.27, H 9.31, N 2.00. − Stannane (−)-**11b** {0.11 g, 0.2 mmol; $[\alpha]_D^{20}$= −13.96 (*c* = 0.45, $CHCl_3$)} was transmetallated in dry THF at −90°C (bath temperature, acetone/liquid nitrogen) using *n*BuLi (0.37 ml, 0.6 mmol, 1.6 M solution in hexane) without TMEDA according to General Procedure B. After 30 s, MeOD (0.25 ml, in 1 ml of dry THF) was added. The crude product was purified by flash chromatography to give 0.039 g (75%) of deutero-(*S*)-(+)-**9** {$[\alpha]_D^{20}$= +1.58 (*c* = 1.95, $CHCl_3$); ee 29% by HPLC}.

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[19] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102461. A copy of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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