Synthesis of Novel Optically Active Tin Hydrides Containing Chiral Ligands

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The synthesis of the chiral tin bromides **1**–**4** and hydrides **5**–**8**, containing the potentially bidentate, optically active 2-[(1*S*/*R*)-1-dimethylaminoethyl]phenyl and 2-[(1*S*)-1-dimethylamino-2,2-dimethylpropyl]phenyl ligands, is reported. The tin hydrides **5**–**8**, with the tin atom as the stereogenic centre, were isolated as diastereomeric mixtures with diastereomeric ratios of dr = 50:50 up to dr = 80:20. The absolute configuration of (–)-(1*S*)-1-(2-bromophenyl)-2,2-dimethylpropylamine [(*S*)-**10**] was determined by single-crystal X-ray structure analysis.

Introduction

Chiral organotin compounds have received considerable attention both from a stereochemical point of view and as reagents in asymmetric synthesis[1][2]. Tin compounds containing both chiral ligands and a stereogenic tin atom have already been investigated[3]. Triorganotin halides are configurationally unstable in solution. Optically active triorganotin hydrides, with the tin atom as the stereogenic centre, are reported to be configurationally stable, but they are racemized under free-radical or polar reaction conditions[4].

Optically active tin bromides containing the intramolecular coordinating chiral 2-[(1*S*)-1-dimethylaminoethyl]phenyl ligand were first synthesized by van Koten[5]. An optically active tin hydride with a stereogenic tin atom containing a potentially bidental 8-(dimethylamino)naphthyl ligand and a chiral (–)-menthyl substituent was synthesized by Schumann[6] and assumed to be configurationally stable.

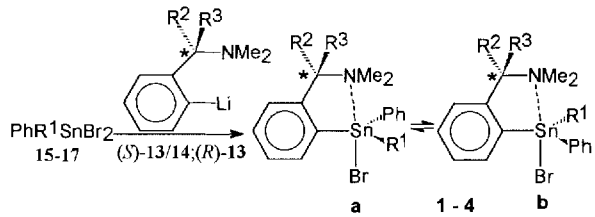
Tin hydrides with chiral ligands are chiral radical-reducing agents which could possibly be used to trap enantioselectively prochiral radicals without loss of chiral information under free-radical conditions[7]. For this reason we synthesized, for the first time, the tin hydrides **5**–**8** with potentially bidental chiral 2-(1-dimethylaminoalkyl)phenyl ligands (DAAP).

Results

Starting from *tert*-butyl(phenyl)tin dibromide (**15**) and diphenyltin dibromide (**17**)[8], which were prepared by adopted procedures[6], the slow 1:1 addition of highly diluted lithium compounds (*S*)-**13** and (*R*)-**13** gave the tin bromides (S_C)-**1**, (R_C)-**1** and (*S*)-**2**, respectively. The tin bromides **1** were obtained as mixtures of diastereomers consistent with the results of van Koten[9] (Table 1).

Lithiation of amine (*S*)-**12** with butyllithium and reaction of the resulting lithium compound (*S*)-**14** with tin dibromides **15** and **16** gave diastereomeric mixtures of tin bromides (S_C)-**3** and (S_C)-**4** (Table 1). The ratios of the diastereomers were modest in the case of (S_C)-**3** and better for (S_C)-**4**.

Scheme 1. Synthesis of the intramolecularly coordinated tin bromides **1**–**4**



	R^1	R^2	R^3
(S_C)-**1a,b**	*t*Bu	Me	H
(R_C)-**1a,b**	*t*Bu	H	Me
(*S*)-**2**	Ph	Me	H
(S_C)-**3a,b**	*n*Bu	*t*Bu	H
(R_C)-**4**	*t*Bu	*t*Bu	H
(*S*)-**13**	-	Me	H
(*R*)-**13**	-	H	Me
(*S*)-**14**	-	*t*Bu	H
15	*t*Bu	-	-
16	*n*Bu	-	-
17	Ph	-	-

Table 1. Diastereomeric ratios of the tin bromides **1**, **3**, **4** and of the tin hydrides **5**, **7**, and **8**

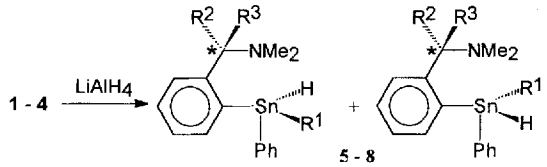
	(S_C)-**1**	(R_C)-**1**	(S_C)-**3**	(S_C)-**4**
dr	69:31[a]	30:70[a]	75:25[a]	84:16[a]
	(S_C)-**5**	(R_C)-**5**	(S_C)-**7**	(S_C)-**8**
dr	58:42[b]	80:20[c]	66:34[c]	51:49[c]

[a] [S_{Sn}]/[R_{Sn}], ([**a**]/[**b**]). – [b] Reduction was carried out in THF. – [c] Reduction was carried out in Et_2O.

  0009–2940/97/1010–1539 $ 17.50–.50/0

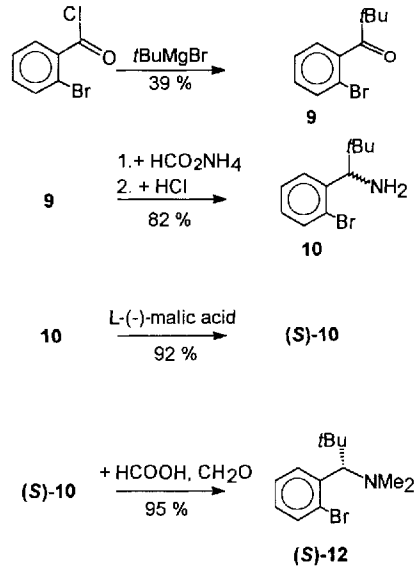
In the final step, the reduction of the tin bromides **1**–**4** with lithium aluminium hydride afforded the tin hydrides (S_C)-**5**, (R_C)-5, (*S*)-**6**, (S_C)-**7**, and (S_C)-**8**. The tin hydrides **5**, **7**, and **8** were isolated as diastereomeric mixtures (Table 1). For the reduction of the tin bromide (R_C)-**1**, two different diastereomeric mixtures of (R_C)-**5** were obtained depending on the choice of solvent. Using THF as the solvent at room temperature, the reduction gave a diastereomeric mixture of dr = 58:42; using diethyl ether as the solvent and a reaction

Scheme 2. Synthesis of the tin hydrides **5**–**8**



	R1	R2	R3
(S_C)-**5**	*t*Bu	Me	H
(R_C)-**5**	*t*Bu	H	Me
(*S*)-**6**	Ph	Me	H
(S_C)-**7**	*n*Bu	*t*Bu	H
(S_C)-**8**	*t*Bu	*t*Bu	H

Scheme 3. Synthesis of the amine (**5**)–**12**



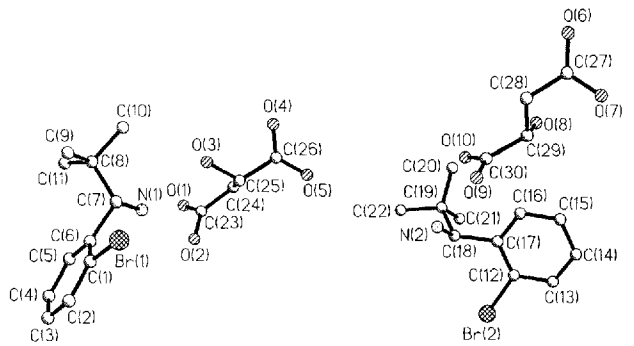
temperature of 0°C, a mixture of dr = 80:20 was obtained.

The ratios of both diastereomeric mixtures of (R_C)-**5** were stable for weeks. This shows that the stereogenic tin centre is configurationally stable and the two diastereomers are not in a dynamic equilibrium like the corresponding tin bromides. A solution of the tin hydride (R_C)-**5** (dr = 80:20) in THF also showed no epimerisation process. However, epimerisation was observed when a solution of the tin hydride (R_C)-**5** (dr = 80:20) in THF was treated with an excess of lithium aluminium hydride at room temperature to give dr = 70:30 after 2 h.

Reduction of the tin bromides (S_C)-**3** and (S_C)-**4** with lithium aluminium hydride in diethyl ether at 0°C gave the corresponding tin hydrides (S_C)-**7** and (S_C)-**8** as diastereomeric mixtures with dr = 66:34 and dr = 51:49, respectively. The almost nonselective formation of the tin hydride (S_C)-**8** is remarkable. This shows that the reduction occurs stereospecifically and that the minor diastereomer **4b** is reduced faster than the major diastereomer **4a** which is epimerised because of its configurational instability[3].

We synthesized the chiral DAAP ligand for the tin hydrides (S_C)-**7** and (S_C)-**8** in an enantiomerically pure form, hoping that a strong repulsive steric interaction of the ligands bound to the tin centre with the *tert*-butyl group of the DAAP ligand would lead exclusively to one diastereomer of the respective tin hydride. This was unfortunately not the case. Starting from 2-bromobenzoyl chloride the alkylation with *t*BuMgCl gave the ketone **9**[10]. Reductive amination by adopted procedures afforded amine **10**[11], which could be separated into its enantiomers by crystallisation with malic acid. The absolute configuration of the amine (*S*)-**10** was determined by X-ray structure analysis of the salt **11**, which showed a 1:1 pair of two salt molecules.

Figure 1. SCHAKAL plot of (−)-(1*S*)-1-(2-bromophenyl)-2,2-dimethylpropylammonium malate (**11**)[a]



[a]Selected bond lengths [pm] and angles [°]: C(1)–Br(1) 187.4(3), C(6)–C(7) 154.9(5), C(7)–N(1) 149.8(6), C(7)–C(8) 155.4(8), C(12)–Br(2) 188.5(3), C(17)–C(18) 154.5(6), C(18)–N(2) 149.3(7), C(18)–C(19) 155.0(8); C(6)–C(7)–N(1) 108.5(4), N(1)–C(7)–C(8) 111.9(4), C(8)–C(7)–C(6) 116.3(4), C(17)–(18)–N(2) 109.0(4), N(2)–C(18)–C(19) 112.0(4), C(19–C(18)–C(17) 116.5(4).

In both pairs of **11** the amine **10** was (*S*)-configured. The main structure element consists of two independent chains of malate ions of contrary orientation in the crystal structure showing a short hydrogen bond of 251.0(7) pm (O2–O5) and 251.3(7) pm (O7–O10). Both chains are connected by hydrogen bonding to the two independent ammonium ions. Interestingly, the N···(H)···O distances for N1–O3 [285.4(7) pm] and N1–O4 [282.0(7) pm] are almost the same while the distance N1–O6 [274.8(7) pm] is shorter. Comparable hydrogen bond distances were found for the second ammonium ion with two larger distances of N2–O8 [285.9(7) pm] and N2–O9 (280.2 pm) and one shorter distance for N2–O1 [275.3(7) pm].

(*S*)-**10** was liberated from the salt **11** and the enantiomeric purity was determined by using the chiral shift reagent Eu(facam)$_3$ showing an ee of 96 %. Reductive methylation of amine (*S*)-**10** gave amine (*S*)-**12**.

Discussion

The structures of tin bromides containing ligands with an amino group suited for intramolecular coordination have in the past been investigated by van Koten[9]. ^{1}H- and ^{119}Sn-NMR spectroscopy have also been used to distinguish between coordinated and noncoordinated tin bromides[5]. There is clear evidence that each of the new tin bromides **1**–**4** investigated in this study is intramolecularly coordinated by the amino group of the DAAP ligands. All methyl groups of the amino function show broaded signals in the ^{1}H and ^{13}C NMR showing coalescence of the NMe_2 resonances at 30°C comparable to the results of van Koten.[9] This can be explained in terms of a dynamic Sn–N dissociation/association process, which is fast compared to the NMR time scale.[9]

Table 2. ^{119}Sn-NMR chemical shifts of the tin bromides **1**, **2**, and **3**

	(S_C)-**1**	(*S*)-**2**	(S_C)-**3**
solvent	$CDCl_3$	[D_8]toluene	$CDCl_3$
major diastereomer **a** (S_{Sn})	−103.2	−121.7	−100.3
minor diastereomer **b** (R_{Sn})	−98.2		−93.1

Comparison of the ^{119}Sn-NMR data of the tin bromides (S_C)-**1a** and **b** and (S_C)-**3a** and **b** in Table 2, with the equivalent data for diphenyl(neomenthyl)tin bromide[12] (δ = −2.67), and diphenyl(menthyl)tin bromide[12] (δ = −5.91), which have the same substituent model of one alkyl and two aryl groups, shows a large high-field shift of approximately 100 ppm. A high-field shift of about 120 ppm was also observed for the tin bromide (S_C)-**2** which has three phenyl substituents. These data clearly show the presence of a coordinative interaction between the dimethylamino group of the chiral DAAP ligand and the tin centre[5]. It is understood from theory and known from many examples that the bromine atom occupies the axial position *anti* to the coordinating amino group[9]. Comparison of the ^{1}H- and ^{13}C-NMR data of the hydrogen and carbon atoms at the stereogenic centre of the DAAP ligand of (S_C)-**2** (^{13}C: δ = 63.4; ^{1}H: δ = 3.7), which has two phenyl groups in the equatorial position, and (S_C)-**1** [major diastereomer (S_C,S_{Sn})-**1**: ^{13}C: δ = 62.5; ^{1}H: δ = 3.6; minor diastereomer (S_C,R_{Sn})-**1**: ^{13}C: δ = 65.8; ^{1}H: δ = 3.4) shows that in the major diastereomer the large *tert*-butyl group points away from the methyl group at the stereogenic centre of the DAAP ligand while the smaller phenyl group lies on the same side. It is most likely that in solution the most abundant diastereomers are (S_C,S_{Sn})-**3** and (S_C,S_{Sn})-**4** respectively, consistent with the results of van Koten[9].

The effects that control the stereochemistry of comparable tin hydrides are not well understood and have been investigated in one only example by Schumann[6].

The tin hydrides **5**, **6**, **7**, and **8** show, in general, a chemical shift for ^{119}Sn of $\delta \leq -130$ (Table 3).

The tin hydride **6** shows an extremely high field shift (δ = −188.8) as a result of the two phenyl groups at the tin centre. This shift is significantly larger than that expected when compared to other tin compounds with a comparable substituent pattern[12]. This can be explained by a slightly stronger coordinative interaction of the DAAP ligand in the tin hydride **6**, as a result of the negative inductive effect of the phenyl substituent.

Table 3. ^{119}Sn-NMR chemical shifts and ^1J(Sn,H) coupling constants of the tin hydrides **5**–**8**[a]

	(R_C)-**5**	(*S*)-**6**	(S_C)-**7**	(S_C)-**8**
major diastereomer	−134.9	−188.8	−139.1	−137.6
$^1J(^{119}Sn,H)$	1920 Hz		1832 Hz	1806 Hz
$^1J(^{117}Sn,H)$	1836 Hz		1750 Hz	1737 Hz
minor diastereomer	−134.7		−148.7	−138.8
$^1J(^{119}Sn,H)$	1879 Hz			
$^1J(^{117}Sn,H)$	1795 Hz			

[a]Solvent [D_8]toluene.

The chemical ^{119}Sn-NMR shifts of the tin hydrides **5**–**8** are in the region of the values that were found for tin hydrides with comparable substituent patterns diaryl(monoalkyl)tin hydrides] and which have no bidental ligand containing a potentially coordinating amino group[12]. This is consistent with the results of Schumann[6], who found a small intramolecular coordinative interaction for one of his tin hydrides but found no significant shift in the ^{119}Sn-NMR signal. This reflected the absence of a significant donor-acceptor interaction between the tin and nitrogen atoms. The weaker coordination of the tin hydrides when compared to the tin bromides is the result of the reduced Lewis acidity of the tin atom. From these ^{119}Sn-NMR data it cannot be concluded directly that there is no coordinative interaction.

The coordination also influences the hybridisation of the tin centre. It is known that with increasing s-character in the equatorial position, a larger $^1J(^1H, ^{119/117}Sn)$ coupling constant is found[13][14][15]. It can be seen from Table 3 that all $^1J(^1H, ^{119/117}Sn)$ coupling constants are large compared to noncoordinated tin hydrides with similar substituent patterns[12], showing the trend towards an intramolecular coordination at the tin atom. These values also show that the hydrogen atom bound to the tin centre occupies the equatorial position. This is consistent with the only X-ray structure analysis that exists for a tin hydride with an intramolecularly coordinating ligand[6]. Interestingly, the $^1J(^1H, ^{117/119}Sn)$ coupling constants of both diastereomers of the tin hydride (S_C)-**5** are large. That means that the hydrogen atom is in both cases in the equatorial position.

Unfortunately, to date, we have not been able to determine the absolute configuration of the tin atom of the diastereomeric tin hydrides.

Conclusion

Chiral tin hydrides **5**–**8** were synthesized by reduction of the respective tin bromides **1**–**4**. By using different reaction conditions for the reduction of the tin bromide (S_C)-**1** and (R_C)-**1** we obtained two different diastereomeric mixtures of the tin hydrides (S_C)-**5** and (R_C)-**5**. The diastereomeric ratios of the obtained mixtures remained constant over weeks

showing the configurational stability of the tin centre in the new tin hydrides. Epimerisation of the tin hydride (R_C)-**5** was observed using an excess of $LiAlH_4$ in THF. It can be concluded from our results that the diastereomeric ratios of the tin hydrides are the result of a kinetically controlled and stereospecific reduction of the corresponding tin bromides. The NMR investigations have shown that there may be a small contribution from a trigonal bipyramidal structure

Experimental Section

General: Melting points: Büchi Melt-Temp apparatus. – ^1H (300.1 MHz), ^{13}C (75.47 MHz), and ^{119}Sn (111.9 MHz, inverse gated, 10-mm tubes) NMR: Bruker AM 300, internal standard for ^1H NMR tetramethylsilane (TMS); ^{13}C NMR solvent signals; ^{119}Sn NMR tetramethyltin with positive shifts referring to lower field; measuring temperature for all NMR spectra is 28°C. – MS: Finnigan MAT 212; MAT 95 for HRMS. – IR: Philips PU 9706. – Elementary analysis of organometallic compounds: Analytische Laboratorien Lindlar; others with FA 1108 CHNS-O Fison Instr. – Optical Rotations: 343 Polarimeter Perkin Elmer. – All reactions with organometallic compounds were carried out using standard Schlenk techniques under dry, oxygen-free argon. The (–)-dimethyl[(1*S*)-1-phenylethyl]amine and (+)-dimethyl[(1*R*)-1-phenylethyl]-amine used, had an enantiomeric purity of er = 98:2.

tert-Butyl{2-[(1S)-1-dimethylaminoethyl]phenyl}phenyltin Bromide [(S_C)-**1a** and **b**]: A solution of 1.97 g (14 mmol) of the lithium compound (*S*)-**13** in 47 ml of ether was added slowly at –20°C to a stirred solution of 6.90 g (14.09 mmol) of freshly distilled **15** in 100 ml of THF. The solution was stirred overnight at room temp. The solvent was removed in vacuo and the residue extracted with a mixture of 50 ml of benzene and 50 ml of toluene at 50°C. The solvent was removed in vacuo and the residue was dissolved in 25 ml of toluene. Dropwise addition of pentane at 0°C gave a yellow precipitate which was filtered off at –30°C, washed with pentane at the same temperature and dried under high vacuum to give 3.52 g (52 %) of (S_C)-**1** – **[1a]/[1b]** = 69:31 (^1H NMR). – M. p. 96–98°C. – $[\alpha]_D^{21}$ = –3.5 (*c* = 0.75, THF). – $[\alpha]_D^{20}$ = –3.7 (*c* = 1, benzene). – ^1H NMR ($CDCl_3$): **1a**: δ = 8.43–8.31 (m, 1 H, 6-H), 7.57–7.47 (m, 2 H, aromatic H), 7.40–7.05 (m, 6 H, aromatic H), 3.60 [br. m, 1 H, C*H*–CH_3, ^3J(CH,CH_3) = 6.6 Hz], 1.92 [br. s, 6 H, $N(CH_3)_2$], 1.54 [s, 9 H, $C(CH_3)_3$], 1.19 (d, 3 H, CH–CH_3); **1b**: δ = 7.60–7.57 (m, 2 H, 6-H), 7.40–7.05 (m, 6 H, aromatic H), 3.40 [q, 1 H, C*H*–CH_3, ^3J(CH,CH_3) = 7.0 Hz], 1.96 [br. s, 6 H, $N(CH_3)_2$], 1.48 [s, 9 H, $C(CH_3)_3$]. – ^{13}C NMR ($CDCl_3$): **1a**: δ = 147.49, 143.98, 139.84, 136.10, 129.90, 128.95, 128.47, 127.50, 125.53, 62.54 (*C*H-CH_3), 41.70 [br., $N(CH_3)_2$], 38.47 [*C*$(CH_3)_3$], 31.54 [C(*C*$H_3)_3$], 10.40 (br., CH–*C*H_3); **1b**: δ = 136.90, 65.78 (*C*H–CH_3), 42.95 [br., $N(CH_3)_2$], 31.94 [C(*C*$H_3)_3$], 37.50 [*C*$(CH_3)_3$], 31.88 [C(*C*$H_3)_3$], 13.80 (br., CH–*C*H_3). – ^{119}Sn NMR ($CDCl_3$): **1a**: δ = –103.22; **1b**: δ = –98.20. – MS/CI (isobutane); *m/z* (%): 482 (3) [MH^-], 402 (100) [M^+ – Br]. – Isotopic pattern of $C_{20}H_{29}BrNSn$ [MH^+]: calcd. 488 (10), 487 (4), 486 (18), 485 (14), 484 (66), 483 (36), 482 (100), 481 (42), 480 (67), 479 (20), 478 (25), 477 (1), 476 (2), 474 (1); found 488 (9), 487 (6), 486 (23), 485 (20), 484 (66), 483 (44), 482 (100), 481 (53), 480 (68), 479 (23), 478 (27), 477 (1), 476 (2), 474 (1). – $C_{20}H_{29}BrNSn$: calcd. 482.0505; found 482.0505 (HRMS/CI, isobutane [MH^-]).

tert-Butyl{2-[(1R)-1-dimethylaminoethyl]phenyl}phenyltin Bromide [(R_C)-**1a** and **b**]: A solution of 0.99 g (6.38 mmol) of the lithium compound (*R*)-**13** in 15 ml of diethyl ether was added dropwise to a stirred solution of 2.63 g (6.38 mmol) of **15** in 120 ml of diethyl ether at 0°C. A prepicitate formed at the beginning of the addition but faded with further addition of the solution of the lithium compound (*R*)-**13**. After the addition, the reaction mixture was stirred overnight. The solvent was removed in vacuo and the residue was extracted with 200 ml of benzene at 50°C. The solvent was removed in vacuo and the residue was dissolved in 5 ml of toluene. Dropwise addition of pentane at –30°C gave a slightly yellow prepicitate which was filtered off at the same temperature, washed with pentane at –30°C and dried in vacuo to give 2.98 g (97 %) of (R_C)-**1** – **[1a]/[1b]** = 70:30 (^1H NMR) – M. p. 98–101°C. – $[\alpha]_D^{21}$ = +3.8 (*c* = 0.65, THF). – NMR and MS data correspond to (S_C)-**1**. – $C_{20}H_{29}BrNSn$: calcd. 482.0505; found 482.0501 (HRMS/CI, isobutane [MH^-]).

{2-[(1S)-1-Dimethylaminoethyl]phenyl}diphenyltin Bromide [(*S*)-**2**]: A solution of 2.1 g (13.5 mmol) of (*S*)-**13** in 10 ml of diethyl ether was added dropwise to a stirred solution of 5.84 g (13.5 mmol) diphenyltin dibromide (**17**)[18] in 20 ml of diethyl ether at 10°C. During the addition, 20 ml of THF was added to dissolve the prepicitate that was formed during the addition. After complete addition, the solution was stirred for 3 d at room temp. The work-up procedure followed the synthesis of (R_C)-**1**. Crystallisation from toluene/pentane at –35°C gave 3.0 g (53 %) colourless crystals of (*S*)-**2**. – M. p. 170–172°C. – $[\alpha]_D^{21}$ = –26.4 (*c* = 0.5, THF). – ^1H NMR ($CDCl_3$): δ = 8.58 [dd, 1 H, 6-H, ^3J(6-H,5-H) = 7.02 Hz, ^4J(6-H,4-H) = 1.90 Hz], 7.73 (dd, 2 H, aromatic H, ^3J = 7.65 Hz, ^4J = 1.56 Hz), 7.66 (dd, 2 H, aromatic H, ^3J = 7.51 Hz, ^4J = 2.12 Hz), 7.5–7.1 (m, 9 H, aromatic H), 3.73 [q, 1 H, C*H*–$N(CH_3)_2$], 2.0 (br. s, 3 H, NCH_3), 1.62 (br. s, 3 H, NCH_3'), 1.21 [d, 3 H, CH–CH_3, ^3J(CH,CH_3) = 6.75 Hz]. – ^{13}C NMR ($CDCl_3$): δ = 147.33 (C-2), 143.15, 141.58, 139.40 (C-6), 135.72, 135.67, 130.23, 129.43, 129.28, 128.92, 128.76, 127.93, 125.93, 63.43 [*C*H–$N(CH_3)_2$], 44.72 [br., $N(CH_3)$], 38.33 [br., $N(CH_3')$], 11.70 (CH–*C*H_3). – ^{119}Sn NMR (toluene/[D_8]toluene): δ = –121.69. – MS/CI (isobutane); *m/z*: 422 [M^+ – Br]. – MS/EI (70 eV); *m/z* (%) = 422 (0.3) [M^+ – Br], 353 (1) [Br – $SnPh_2^+$], 331 (3) [$HSnPh_2Br^-$], 275 (3), 91 (100) [$C_6H_7^+$], 57 (66). – $C_{22}H_{24}NSn$: calcd. 422.0930; found 422.0931 (HRMS/CI, isobutane [M^+ – Br]).

Butyl{2-[(1S)-1-dimethylamino-2,2-dimethylpropyl]phenyl}-phenyltin Bromide [(S_C)-**3a,b**]: Analogously to the synthesis of (R_C)-**1**, the reaction of 2.77 g (14.05 mmol) of the lithium compound **14** and 5.76 g (14 mmol) of tin dibromide **16** in diethyl ether at 0°C gave 6.1 g (83 %) of the product as a white solid – **[3a]/[3b]** = 75:25 (^1H NMR). – M. p. 70–72°C. – $[\alpha]_D^{21}$ = +51.3 (*c* = 1.6, THF). – ^1H NMR ($CDCl_3$): **3a**: δ = 8.72 [dd, 1 H, 6-H, ^3J(6-H,5-H) = 7.53 Hz, ^4J(6-H,4-H) = 0.71 Hz], 7.7–7.05 (m, 8 H, aromatic H), 3.13 [s, 1 H, C*H*–$N(CH_3)_2$], 2.9–2.4 (br. s, 3 H, NCH_3), 2.5–2.2 (br. s, 3 H, NCH_3), 2.75–1.8 (m, 4 H, Sn–CH_2CH_2), 1.5 (qt, 2 H, CH_2CH_3), 1.04 [s, 9 H, $C(CH_3)_3$], 0.98 [t, 3 H, CH_3, ^3J(CH_2,CH_3) = 7.39 Hz]; **3b**: δ = 8.58 [dd, 1 H, 6-H, ^3J(6-H,5-H) = 6.64 Hz], 0.82 [s, 9 H, C(C$H_3)_3$]. – ^{13}C NMR ($CDCl_3$): **3a**: δ = 145.65, 144.59, 138.96, 134.99 [^2J(Sn,C) = 20.45 Hz], 131.56, 128.64, 128.33, 128.07, 127.75, 82.52 (*C*H–N), 53.7–51.76 (N–*C*H_3), 47.3–43.9 (N–*C*H_3), 35.35 [*C*$(CH_3)_3$], 30.18 [C(*C*$H_3)_3$], 29.02 (*C*H_2), 27.03 (*C*H_2), 22.70 (*C*H_2), 13.678 (CH_2*C*H_3); **3b**: δ = 137.80, 136.39, 128.23, 127.96, 30.58 [*C*$(CH_3)_3$], 29.1 (CH_2), 13.46 (CH_2*C*H_3). – ^{119}Sn NMR ($CDCl_3$): **3a**: δ = –100.33; **3b**: δ = –93.14. – MS/CI (isobutane); *m/z* (%): 524 (10) [MH^+], 444 (100) [M^+ – Br]. – $C_{23}H_{35}BrNSn$: calcd. 524.0975; found 524.1015 (HRMS/CI, NH_3 [MH^-]).

tert-Butyl{2-[(1S)-1-Dimethylamino-2,2-dimethylpropyl]-phenyl}phenyltin Bromide [(S_C)-**4a,b**]: Analogously to the synthesis of (R_C)-**1**, 1.89 g (9.6 mmol) of the lithium compound **14** and 3.95

g (9.6 mmol) of tin dibromide **15** gave 3.9 g (75 %) of the product as a white solid. – **[4a]/[4b]** = 84:16 (^{1}H NMR). – M. p. 85°C. – $[\alpha]_D^{21}$ = +20.2 (*c* = 0.5, THF). – ^{1}H NMR ($CDCl_3$): **4a**: δ = 7.95–6.94 (m, 9 H, aromatic H), 3.23 [br. s, 1 H, C*H*–N$(CH_3)_2$], 2.21 [br. s, 6 H, N$(CH_3)_2$], 1.45 [s, 9 H, Sn–C(C*H*$_3)_3$], 1.15–0.75 [m, 9 H, CH–C$(CH_3)_3$]; **4b**: δ = 1.47 [s, 9 H, C$(CH_3)_3$]. – ^{13}C NMR ($CDCl_3$): **4a**: δ = 137.33, 136.76, 136.48, 136.25, 135.90, 129.80, 128.96, 128.27, 128.01, 80.23 [*C*H-N$(CH_3)_2$], 46.00 [br., N(*C*H$_3)_2$], 35.88 [*C*$(CH_3)_3$], 30.18 [C(*C*H$_3')_3$], 29.57 [C(*C*H$_3'')_3$], 29.08 [C(*C*H$_3''')_3$]. – MS/CI (isobutane); *m/z* (%): 524 (44) [MH$^+$], 466 (10) [M$^+$ – C_4H_9], 444 (100) [M$^+$ – Br]. – Isotopic pattern of $C_{23}H_{35}BrNSn$ [MH$^+$]: calcd. 530 (9), 529 (4), 528 (24), 527 (17), 526 (65), 525 (39), 524 (100), 523 (43), 522 (66), 521 (20), 520 (25), 518 (2); found 530 (8), 529 (3), 528 (14), 527 (16), 526 (66), 525 (26), 524 (100), 523 (36), 522 (74), 521 (19), 520 (31), 518 (2). – $C_{23}H_{35}BrNSn$: calcd. 524.0975; found 524.0966 (HRMS/CI, NH_3 [MH$^+$]).

tert-Butyl{2-[(1S)-1-Dimethylaminoethyl]phenyl}phenyltin Hydride [(S_C)-**5**]: A solution of 3.52 g (7.32 mmol) of the tin bromide (S_C)-**1** in 50 ml of THF was slowly added at room temp. to a stirred suspension of 1.5 g (39.56 mmol) of $LiAlH_4$ in 20 ml of THF. The addition was complete after 5 h and the solution was stirred overnight. The mixture was treated with a mixture of THF/water (1:5, v/v) until no more gas evolution could be detected. The suspension was stirred for 30 min and dried with Na_2SO_4 followed by the addition of 70 ml of diethyl ether. The suspension was filtered and the solvent removed in vacuo. 1.76 g (60 %) of (S_C)-**5** were obtained as a slightly yellow viscous oil. – dr = 58:42 (^{1}H NMR). – $[\alpha]_D^{20}$ = –3.9 (*c* = 1, benzene). – IR (NaCl): $\tilde{\nu}$ = 1795 cm^{-1} (Sn–H). – ^{1}H NMR ([D$_8$]toluene): major diastereomer: δ = 7.9–6.95 (8 H, aromatic H), 6.53 (Sn–H), 3.21 [q, 1 H, CH–C*H*$_3$, ^3J(CH,CH$_3$) = 6.72 Hz], 1.72 [s, 6 H, N(C*H*$_3)_2$], 1.34 [s, 9 H, C(C*H*$_3)_3$], 1.1 (d, 1 H, N–C*H*–CH$_3$); minor diastereomer: δ = 7.9–6.95 (8 H, aromatic H), 6.34 (Sn–H), 3.46 [q, 1 H, CH–C*H*$_3$, ^3J(CH,CH$_3$) = 6.76 Hz], 1.64 [s, 6 H, N(C*H*$_3)_2$], 1.344 [s, 9 H, C(C*H*$_3)_3$], 0.98 (d, 1 H, N–C*H*–CH$_3$). – ^{13}C NMR ([D$_8$]toluene): major diastereomer: δ = 152.00, 141.98, 138.4, 137.25, 65.27 (N–*C*–CH$_3$), 41.24 [N(*C*H$_3)_2$], 31.39 [C(*C*H$_3)_3$], 26.69 [Sn–*C*(CH$_3)_3$], 15.72 (HC–*C*H$_3$); minor distereomer: δ = 150.89, 141.86, 137.94, 136.94, 63.12 (N–*C*–CH$_3$), 39.42 [N(*C*H$_3)_2$], 31.39 [C(*C*H$_3)_3$], 24.89 [Sn–*C*(CH$_3)_3$], 10.75 (HC–*C*H$_3$). – ^{119}Sn NMR ([D$_8$]toluene): major diastereomer: δ = –134.92; minor diastereomer: δ = –134.74. – MS/CI (isobutane); *m/z*: 402 [M$^+$ – H]. – MS/EI (70 eV); *m/z* (%): 351 (24), 197 (43) [$SnC_6H_4^+$], 120 (69) [Sn$^+$], 43 (100) [$C_3H_7^+$]. – $C_{20}H_{28}NSn$: calcd. 402.1243; found 402.1243 (HRMS/CI, isobutane [M$^+$ – H]). – Isotopic pattern of $C_{20}H_{28}NSn$ [M$^+$ – H]: calcd. 406 (17), 403 (22), 402 (100), 401 (41), 400 (75), 399 (31), 398 (42); found 406 (18), 403 (36), 402 (100), 401 (41), 400 (68), 399 (23), 398 (27). – $C_{20}H_{29}NSn$ (401.91): calcd. C 59.73 H 7.27 N 3.48; found C 57.62 H 6.74 N 3.81.

tert-Butyl{2-[(1R)-1-Dimethylaminoethyl]phenyl}phenyltin Hydride [(R_C)-**5**]: A solution of 6.57 g (13.66 mmol) of tin bromide (R_C)-**1** in 100 ml of diethyl ether was added within 1 h to a 0°C cold stirred suspension of 531 mg (14 mmol) of $LiAlH_4$ in 50 ml of diethyl ether. After completion of the addition, the reaction mixture was stirred for 18 h at room temp.; 0.98 ml of water, diluted in 4 ml of dioxane, was added under ice cooling and the stirring was continued for 30 min; 2 g of Na_2SO_4 was then added and the suspension was filtered off after 1 h. The solvent was removed in vacuo and the residue extracted with 100 ml of hot benzene. The benzene was evaporated and the residue extracted with –30°C cold pentane. After evaporation, 5.16 g (94 %) of the product was isolated as a viscous oil. – dr = 80:20 (^{1}H NMR). – n_D^{20} = 1.6144. – $[\alpha]_D^{20}$ = +2.9 (*c* = 1, THF). – IR (NaCl): $\tilde{\nu}$ = 1795 cm^{-1} (Sn–H). – ^{1}H NMR ([D$_6$]benzene): major diastereomer: δ = 7.91 [dd, 1 H, 6-H, ^3J(6-H,5-H) = 5.54 Hz], 7.58–7.49 (m, 2 H, aromatic H), 7.35–6.90 (m, 5 H, arom.), 6.60 [Sn–H, $^1J(^{119}Sn,H)$ = 1920.0 Hz, $^1J(^{117}Sn,H)$ = 1836.4 Hz], 3.24 [q, 1 H, CH–C*H*$_3$, ^3J(CH,CH$_3$) = 6.90 Hz], 1.74 [s, 6 H, N$(CH_3)_2$], 1.38 [s, 9 H, C(C*H*$_3)_3$], 1.11 (d, 1 H, C*H*–CH$_3$); minor diastereomer: δ = 7.91 (dd, 1 H, 6-H), 7.58–7.49 (m, 2 H, aromatic H), 7.35–6.90 (5 H, aromatic H), 6.41 [Sn–H, $^1J(^{119}Sn,H)$ = 1878.6 Hz, $^1J(^{117}Sn,H)$ = 1795.0 Hz], 3.48 [q, 1 H, CH–C*H*$_3$, ^3J(CH,CH$_3$) = 6.76 Hz], 1.66 [s, 6 H, N$(CH_3)_2$], 1.39 [s, 9 H, C(C*H*$_3)_3$], 0.98 (d, 1 H, C*H*–CH$_3$). – ^{13}C NMR ([D$_6$]benzene): major diastereomer: δ = 152.00, 145.56, 142.01, 138.45, 137.30, 66.22 (N-*C*H-CH$_3$), 41.25 [N(*C*H$_3)_2$], 31.38 [C(*C*H$_3)_3$], 26.74 [Sn–*C*(CH$_3)_3$], 15.77 (HC–*C*H$_3$); minor diastereomer: δ = 137.99, 137.01, 63.17 (N–*C*–CH$_3$), 39.47 [N(*C*H$_3)_2$], 31.38 [C(*C*H$_3)_3$], 24.77 [Sn–*C*(CH$_3)_3$], 10.95 (HC–*C*H$_3$). – $C_{20}H_{28}NSn$: calcd. 402.1243; found 402.1244 (HRMS/CI, isobutane [M$^+$ – H]). – $C_{20}H_{29}NSn$ (401.91): calcd. C 59.73 H 7.27 N 3.48; found C 57.80 H 6.78 N 3.82.

Epimerisation of (R_C)-**5**: 300 mg (0.75 mmol) of the tin hydride (R_C)-**5** (dr = 80:20) was added to a suspension of 265 mg (7 mmol) of $LiAlH_4$ in 4.5 ml of THF at room temp. The suspension was stirred for 2 h at room temp.; 30 mg of water was added and stirring was continued for 30 min; 10 ml of ether and Na_2SO_4 were then added to the reaction mixture. Filtration and removal of the solvent gave 294 mg (89 %) of the product as a viscous oil. – dr = 70:30 (^{1}H NMR).

{2-[(1S)-1-Dimethylaminoethyl]phenyl}diphenyltin Hydride [(*S*)-**6**]: A solution of 1 g (2 mmol) of the tin bromide (*S*)-**2** in 30 ml of diethyl ether and 20 ml of THF were added slowly at room temp. to a stirred suspension of 0.152 g (4 mmol) of $LiAlH_4$ in 20 ml of THF. After complete addition, the reaction mixture was stirred for 24 h at room temp. followed by the addition of 0.8 ml of water under ice cooling. After 30 min, 0.5 g of Na_2SO_4 and 30 ml of ether were added. Filtration and evaporation of the solvent gave a slurry that was extracted with 100 ml of boiling pentane. After the evaporation of the solvent, the crude product mixture was dissolved in hexane and the starting compound (*S*)-**2** was crystallized selectively at –10°C. Filtration and evaporation of the solvent gave 0.56 g (81 %) of the product as colourless viscous oil. – n_D^{20} = 1.6218. – $[\alpha]_D^{20}$ = –14.1 (*c* = 0.4, THF). – IR (NaCl): $\tilde{\nu}$ = 1820 cm^{-1} (Sn–H). – ^{1}H NMR ([D$_6$]benzene): δ = 8.00–6.85 (m, 15 H, aromatic H, H–Sn), 3.33 [q, 1 H, *H*C–CH$_3$, ^3J(HC,CH$_3$) = 6.71 Hz], 1.66 [s, 6 H, N$(CH_3)_2$], 1.02 (d, 1 H, H_3C–CH). – ^{13}C NMR ([D$_6$]benzene): δ = 150.93, 150.76, 142.57, 137.36, 137.30, 137.07, 129.35, 128.51, 128.24, 128.08, 127.05, 126.87, 126.50, 64.19 (N–C*H*–CH$_3$), 40.62 [N(CH$_3$)], 40.52 [N(CH$_3$)'], 14.08 (CH–*C*H$_3$). – ^{119}Sn NMR (toluene/[D$_8$]toluene): δ = –188.82. – MS/CI (isobutane); *m/z* (%): 422 (100) [M$^+$ – H], 346 (49) [M$^+$ – C_6H_6]. – MS/EI (70 eV); 134 (100), 105 (21), 72 (45). – $C_{22}H_{24}NSn$: calcd. 422.0930; found 422.0930 (HRMS/CI, isobutane [M$^+$ – H]). – Isotopic pattern of $C_{22}H_{24}NSn$ [M$^+$ – H]: calcd. 427 (4), 426 (16), 425 (4), 424 (16), 423 (27), 422 (100), 421 (44), 420 (76), 419 (33), 418 (42); found 427 (5), 426 (16), 425 (4), 424 (16), 423 (24), 422 (100), 421 (42), 420 (76), 419 (33), 418 (44).

Butyl{2-[(1S)-1-Dimethylamino-2,2-dimethylpropyl]phenyl}-phenyltin Hydride [(S_C)-**7**]: Analogously to the synthesis of (R_C)-**5**, 6 g (11.78 mmol) of the tin bromide (S_C)-**3** was treated with 0.6 g (15.8 mmol) of $LiAlH_4$ in diethyl ether at room temp.; 4.9 g (94 %) of the product was isolated as a viscous oil. – dr = 66:34 (^{1}H NMR). – n_D^{20} = 1.6025. – $[\alpha]_D^{20}$ = +10.8 (*c* = 1, THF). – IR

(NaCl): $\tilde{\nu}$ = 1815 cm^{-1} (Sn−H). − ^1H NMR ([D$_8$]toluene): major diastereomer: δ = 7.7−7.35 (m, 3 H, aromatic H), 7.2−7.0 (m, 5 H, aromatic H), 6.56 [s, 1 H, Sn−H, $^1J(^{119}Sn,H)$ = 1831.7 Hz, $^1J(^{117}Sn,H)$ = 1750.4 Hz], 3.33 [s, 1 H, C*H*−N(CH$_3$)$_3$], 2.16 [s, 6 H, N(CH$_3$)$_2$], 1.67−1.55 (m, 2 H, CH$_2$−C*H*$_2$−CH$_2$), 1.41−1.24 (m, 2 H, C*H*$_2$CH$_3$), 1.13−1.05 (m, 2 H, Sn−CH$_2$), 1.04−1.03 [br., 9 H, C(C*H*$_3$)$_3$], 0.89−0.77 (m, 3 H, CH$_3$); minor diastereomer: δ = 7.7−7.35 (m, 3 H, aromatic H), 7.2−7.0 (m, 5 H, aromatic H), 3.05 [s, 1 H, C*H*−N(CH$_3$)$_3$], 2.15 [s, 6 H, N(CH$_3$)$_2$], 0.99 [s, 9 H, C(C*H*$_3$)$_3$], 0.89−0.77 (m, 3 H, CH$_3$). − ^{13}C NMR ([D$_8$]toluene): major diastereomer: δ = 147.28, 142.60, 137.51, 137.41, 128.69, 128.2, 127.59, 81.31 (N−CH), 45.94 [N(CH$_3$)$_2$], 36.63 [*C*(CH$_3$)$_3$], 29.72 [C(*C*H$_3$)$_3$], 29.85 (CH$_2$), 27.33 (CH$_2$), 13.73 (CH$_3$), 11.65 (Sn−CH$_2$); minor diastereomer: δ = 128.79, 79.41 (N-CH), 44.92 [N(CH$_3$)$_2$], 36.57 [C(CH$_3$)$_3$], 29.90 (CH$_2$), 29.12 [C(*C*H$_3$)$_3$], 27.39 (CH$_2$), 13.73 (CH$_3$), 12.05 (Sn−CH$_2$). − ^{119}Sn NMR ([D$_8$]tolune): major diastereomer δ = −139.1; minor diastereomer δ = −148.7. − MS/CI (isobutane); *m/z*: 444 [M$^+$ − H]. − C$_{23}$H$_{34}$NSn: calcd. 444.1712; found 444.1723 (HRMS/CI, isobutane [M$^+$ − H]). − Isotopic pattern of C$_{23}$H$_{34}$NSn [M$^+$ − H]: calcd. 448 (17), 445 (25), 444 (100), 443 (43), 442 (75), 441 (32), 440 (41); found 448 (18), 445 (37), 444 (100), 443 (44), 442 (68), 441 (19), 440 (23). − C$_{23}$H$_{35}$NSn (444.23): calcd. C 62.19 H 7.94 N 3.15; found C 59.90 H 7.78 N 3.18.

tert-Butyl-[2-(1-(S)-Dimethylamino-2,2-dimethylpropyl)phenyl]-phenyltin Hydride [(*S*$_C$)-**8**]: Analogous to the synthesis of (*R*$_C$)-**5**, 3.7 g (7.07 mmol) of tin bromide (*S*$_C$)-**4a** and **b** and 0.28 g (7.37 mmol) of LiAlH$_4$ in diethyl ether at −5°C gave 2.9 g (92 %) of the product as a slighthly yellow oil. − dr = 51:49 (^1H NMR). − n_D^{20}: 1.6017. − $[\alpha]_D^{20}$: +7.3 (*c* = 1, THF). − IR (NaCl): $\tilde{\nu}$ = 1815 cm^{-1} (Sn−H). − ^1H NMR ([D$_8$]toluene): major diastereomer: δ = 7.65−7.39 (m, 3 H, aromatic H), 7.23−7.04 (m, 6 H, aromatic H), 6.76 (s, 1 H, Sn-H), 3.67 [1 H, C*H*-N(CH$_3$)$_2$], 2.13 [s, 6 H, N(CH$_3$)$_2$], 1.32 {s, 9 H, Sn-C(CH$_3$)$_3$, $^3J[^{119}Sn,C(CH_3)_3]$ = 72.45 Hz, $^3J[^{117}Sn,C(CH_3)_3]$ = 70.14 Hz}, 0.98 [s, 9 H, NC-C(CH$_3$)$_3$]; minor diastereomer: δ = 7.65−7.39 (m, 3 H, aromatic H), 7.23−7.04 (m, 6 H, aromatic H), 6.72 (s, 1 H, Sn-H), 3.05 [1 H, C*H*-N(CH$_3$)$_2$], 2.15 [s, 6 H, N(CH$_3$)$_2$], 1.30 [s, 9 H, Sn-C(CH$_3$)$_3$], 1.09 {s, 9 H, NC-C(CH$_3$)$_3$, $^3J[^{119}Sn,C(CH_3)_3]$ = 73.81 Hz, $^3J[^{117}Sn,C(CH_3)_3]$ = 70.99 Hz}. − ^{13}C NMR ([D$_8$]toluene): both diastereomers: 146.71, 143.79, 137.64, 137.41, 130.77, 129.67, 129.13, 128.67, 128.14, 127.70, 126.84, 126.51, 79.70/79.41(*C*H-N(CH$_3$)$_3$), 45.84/45.52 [N(CH$_3$)$_2$], 36.86/36.55 [CH-*C*(CH$_3$)$_3$], 31.61/31.55 [Sn-C(*C*H$_3$)$_3$], 29.68/29.52 [CH-C(*C*H$_3$)$_3$], 27.61/24.82 [Sn-*C*(CH$_3$)$_3$]. − ^{119}Sn NMR ([D$_8$]toluene): major diastereomer: δ = −137.56; minor diastereomer: δ = −138.8. − MS/CI (isobutane); *m/z*: 444 [M$^+$ − H]. − C$_{23}$H$_{34}$NSn: calcd. 444.1713; found 444.1718 (HRMS/CI, isobutane [M$^+$ − H]). − Isotopic pattern of C$_{23}$H$_{34}$NSn: calcd. 448 (17), 445 (25), 444 (100), 443 (43), 442 (75), 441 (32), 440 (41); found 448 (19), 445 (41), 444 (100), 443 (45), 442 (66), 441 (18), 440 (23). − C$_{23}$H$_{35}$NSn (444.22): calcd. C 62.19 H 7.94 N 3.15; found C 60.18 H 7.84 N 3.16.

1-(2-Bromophenyl)-2,2-dimethylpropan-1-one (**9**): A Grignard solution prepared from 98 ml (0.91 mol) of *tert*-butyl bromide and 24.3 g (1 mol) of magnesium in 400 ml of diethyl ether was filtered through a plug of glas wool into a 500-ml dropping funnel. The Grignard solution was added within 16 h to a stirred solution of 100 ml (0.761 mol) of 2-brombenzoyl chloride in 400 ml of diethyl ether at −60°C through a glass tube with cooling jacket which was cooled to −78°C. After the addition of the Grignard solution, the reaction mixture was stirred at room temp. overnight. The solution was carefully hydrolysed with iced water and 50 ml of half-concentrated hydrochloric acid. The organic layer was separated and the aqueous layer extracted with diethyl ether. The combined organic layers were dried with MgSO$_4$, the solvent removed and the residue distilled at reduced pressure through a 30-cm Vigreux column. 71.6 g (39 %) of **9** were isolated as a colourless liquid. − B. p. 139−140°C/13 Torr. − n_D^{20} = 1.5334. − ^1H NMR (CDCl$_3$): δ = 7.48 (dd, 1 H, aromatic H), 7.28−7.10 (m, 2 H, aromatic H), 7.04 (dd, 1 H, aromatic H), 1.2 [s, 9 H, C(C*H*$_3$)$_3$]. − ^{13}C NMR (CDCl$_3$): δ = 211.89 (C=O), 142.52 (C-1), 132.93 (C-4), 129.81 (C-3), 126.69 (C-6), 125.96 (C-5), 117.73 (C-2), 44.88 [*C*(CH$_3$)$_3$], 27.02 [C(*C*H$_3$)$_3$]. − MS/CI (isobutane); *m/z* (%): 243/241 (100/98) [MH$^+$]. − MS/EI (70 eV); *m/z* (%): 185/183 (100/98) [M$^+$ − C$_4$H$_9$], 57 (99) [C$_4$H$_9^+$]. − C$_{11}$H$_{14}$BrO: calcd. 241.0290; found 241.0345 (HRMS/CI, isobutane [MH$^+$]).

(±)-1-(2-Bromophenyl)-2,2-dimethylpropylamine (**10**): 71.55 g (0.297 mol) of **9** and 97.35 g (1.54 mol) of ammonium formate were heated at reflux (180°C bath temperature) for 24 h, followed by the addition of another 80 g (1.27 mol) of ammonium formate. The reflux condenser was replaced by a 30-cm Vigreux column with Liebig condenser. The reaction mixture was heated for another 24 h (190°C bath temperature). The distillate was collected in portions of 10 ml and extracted with little portions of dichloromethane. After the removal of the dichloromethane, the residue was returned to the reaction vessel through the column. After another 12 h, the mixture was cooled to room temp. and 103 ml of conc. HCl was added. The resulting suspension was then heated for 12 h at reflux. Another 120 ml of conc. HCl was added and the reaction mixture was heated at reflux for another 36 h. The resulting mixture was cooled to room temp. and poured into 400 ml of water. The acidic aqueous layer was extracted with two 200-ml portions of hexane. The aqueous phase was treated with NaOH with intensive stirring and ice cooling until a pH of 10 was reached. The aqueous layer was extracted five times with 100 ml of diethyl ether. The combined organic extracts were dried with K$_2$CO$_3$. After removal of the solvent, the residue was distilled at reduced pressure yielding 58.9 g (82 %) of **10**. − B.p. 77°C/0.06 Torr. − n_D^{20} = 1.5472. − ^1H NMR (CDCl$_3$): δ = 7.55−7.00 (m, 4 H, aromatic H), 4.36 (s, 1 H, C*H*−NH$_2$), 1.41 (s, 2 H, N*H*$_2$), 0.97 [s, 9 H, C(C*H*$_3$)$_3$]. − ^{13}C NMR (CDCl$_3$): δ = 138.65 (C-1), 132.66 (C-3), 129.33 (C-6), 128.09 (C-4), 126.88 (C-5), 125.15 (C-2), 61.54 (*C*-NH$_2$), 36.35 [*C*(CH$_3$)$_3$], 26.41 [C(*C*H$_3$)$_3$]. − MS/CI (isobutane); *m/z* (%): 244/242 (100/90) [MH$^+$]. − MS/EI (70 eV); *m/z* (%): 226/224 (100/98) [M$^+$ − NH$_3$], 89 (58) [C$_7$H$_5^+$], 77 (30) [C$_6$H$_5^+$]. − C$_{11}$H$_{17}$BrN: calcd. 242.0718; found 242.0719 (HRMS/CI, isobutane [MH$^+$]).

(−)-(1S)-1-(2-Bromophenyl)-2,2-dimethylpropylamine [(*S*)-**10**]: 48.96 g (0.202 mol) of (±)-1-(2-Bromophenyl)-2,2-dimethyl-propyl amine (**10**) was added under argon to a solution of 20.33 g (0.152 mol) of L-(−)-malic acid in 378 ml of CO$_2$-free water at 70°C. After the addition, the resulting slurry was heated to 95°C until the solution cleared. The solution was allowed to cool down slowly within 24 h. The salt **11** was filtered off by a Büchner funnel and washed with little portions of ice-cold water yielding 34 g (92 %) of **11**. − M. p. 186°C. − $[\alpha]_D^{20}$ = −22.1 (*c* = 0.3, water).

X-ray Crystal Structure Analysis of **11**: Data collection was carried out with a Siemens AED 2 diffractometer using Mo-K_α radiation and a graphite monochromator. − Size of single crystal: 0.48 × 0.42 × 0.23 mm. − θ range: 1.50−25.98 °. − Number of reflections measured: 3528. − Number of symmetry-independent reflections: 3528 measured, 3096 [$I > 2\sigma(I)$] were used in all calculations. − Absorption coefficient: 2.501 mm^{-1}. Empirical correction for absorption was applied (ψ scan). The structure was solved by direct methods using the programm SHELXTL PLUS (VMS) and the solution developed using full-matrix least-squares refinement on F^2

and difference Fourier synthesis. Displacement parameters were refined for non-H atoms, H atoms were included in fixed calculated positions (SHELXL93). The aromatic rings were refined as regular hexagons. At convergence, $R = 0.0408$, $wR2 = 0.0961$, GOF = 1.048 for 374 parameters. $F(000) = 388$. Flack, $X = -0.006$ with e.s.d/0.010 (expected are 0 for correct and 1 for inverted absolute structure). Crystal data: Formula $C_{30}H_{44}Br_2N_2O_{10}$, crystal system and space group: triclinic $P1$, unit cell dimension (pm): a = 719.3(1), b = 849.8(1), c = 1386.6(2) Å, α = 98.67(2), β = 98.14(2), γ = 90.61(2)°, V = 0.8290(2) nm^3, $Z = 1$, $\rho = 1.507$ g·cm^{-3}. Reciprocal lattice segment $0 \le h \le 8$, $-10 \le k \le 10$, $-17 \le l \le 16$. Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-405945, the names of the authors, and the journal citation.

The salt **11** was diluted in 100 ml of ice-cold 4 N NaOH. The separating amine, (*S*)-**10**, was isolated and the aqueous layer extracted with five 40-ml portions of diethyl ether. The combined organic layers were dried with K_2CO_3. The amine (*S*)-**10** was used for the next steps without further purification after the evaporation of the solvent at reduced pressure. – Yield: 22.56 g (100 %). – $[\alpha]_D^{20} = -36.5$ (c = 1.08, $CHCl_3$).

Determination of the Enantiomeric Purity of (*S*)-**10**: 134 mg (0.15 mmol) of tris[3-(trifluoromethylhydroxymethylene)-D-camphorato]europium(III) [Eu(facam)$_3$] was dissolved in 1 ml of $CDCl_3$. The filtered solution of Eu(facam)$_3$ was added in portions of 15 µl to a solution of 36.3 mg of amine (*S*)-**10** in 0.3 ml of $CDCl_3$. After every addition, a ^{1}H-NMR spectrum was measured. The signals of the *tert*-butyl group could be separated. The signal for the (*S*) enantiomer was shifted downfield. Integration of the separated signals gave a ratio of [(*S*)-**10**]/[(*R*)-**10**] = 96.5:3.5.

(–)-[(1S)-1-(2-Bromophenyl)-2,2-dimethylpropyl]dimethylamine [(*S*)-**12**]: 40 g (0.869 mol) of formic acid and 16.9 ml of formalin (36 % in water) were added to 22.56 g (93.2 mmol) of amine (*S*)-**10** under ice cooling. The reaction mixture was heated for 12 h under reflux until no further evolution of gas was observed. After cooling to room temp., 8 ml of half-concentrated HCl was added and the mixture was concentrated in a rotary evaporator at 70°C (bath Temp.)/60 mbar. The residue was poured into 40 ml of water and extracted with small portions of pentane. The aqueous phase was treated with KOH to give a pH of 10. The amine was extracted with several portions of 20 ml of diethyl ether. The combined organic phases were dried with K_2CO_3. After the evaporation of the solvent, the amine was distilled under reduced pressure to yield 24 g (95 %) of (*S*)-**10**. – B. p. 129–130°C/5.6 Torr. – $n_D^{20} = 1.5361$. – $[\alpha]_D^{20} = -39.0$ (c = 1,02, $CHCl_3$). – ^{1}H NMR ($CDCl_3$): δ = 7.59 [dd, 1 H, 3-H, ^3J(3-H,4-H) = 7.85 Hz, ^4J(3-H,5-H) = 1.46 Hz], 7.47 [dd, 1 H, 6-H, ^3J(6-H,5-H) = 7.8 Hz, ^4J(6-H,4-H) = 1.69 Hz], 7.26 [ddd, 1 H, 5-H, ^3J(5-H,4-H) = 7.3 Hz], 7.08 (ddd, 1 H, 4-H), 4.02 [s, 1 H, C*H*–N(CH$_3$)$_2$], 2.29 [s, 6 H, N(C*H*$_3$)$_2$], 1.04 [s, 9 H, C(C*H*$_3$)$_3$]. – ^{13}C NMR ($CDCl_3$): δ = 138.46, 133.06, 130.26, 127.91, 127.75, 126.18, 74.34 [*C*–N(CH$_3$)$_2$], 44.97 [N(*C*H$_3$)$_2$], 36.50 [*C*(CH$_3$)$_3$], 28.79 [C(*C*H$_3$)$_3$]. – MS/CI (isobutane); *m/z*: 270/272 (100/98) [MH$^+$]. – MS/EI (70 eV); *m/z* (%): 256/254 (7/7) [M$^+$ – CH$_3$], 214/212 (100/98) [M$^+$ – C$_4$H$_9$], 132 (89) [M$^+$ – C$_4$H$_{10}$Br], 91 (40) [C$_7$H$_7^+$]. – $C_{13}H_{21}BrN$: calcd. 270.0732; found 270.0732 (HRMS/CI, isobutane [MH$^+$]).

2-(1-Dimethylaminoethyl)phenyllithium [(*S*)/(*R*)-**13**]: In a typical reaction a solution of 1 g (6.7 mmol) of (*S*)/(*R*)-dimethyl(1-phenylethyl)amine in 20 ml of pentane was treated dropwise with 4.2 ml (6.7 mmol) of *tert*-butyllithium (1.6 M in hexane) at 0°C. After 1 h, the solution was cooled to –30°C and the solvent was decanted from the solid lithium compound. The lithium compound (*S*)/(*R*)-**13** was washed with 10 ml of pentane at –30°C and the solvent was decanted. The solid was freeze-dried to yield 0.8–1.0 g (87–96 %) of (*S*)/(*R*)-**13** as pyrophoric colourless crystals.

2-[(1S)-1-Dimethylamino-2,2-dimethylpropyl]phenyllithium (**14**): In a typical reaction a solution of 5 g (18.5 mmol) of amine (*S*)-**12** in 20 ml of pentane was treated with 11.6 ml (18.5 mmol) of *n*-butyllithium (1.6 M in hexane). After 2 h, the resulting suspension was cooled to –30°C and the remaining solution was decanted from the precipitate. The precipitate was washed with 10 ml pentane at –30°C and the solvent was decanted. The solid was freeze-dried yielding 2.5–3 g (69–82 %) of **14** as pyrophoric colourless crystals.

tert-Butyl(phenyl)tin Dibromide (**15**): 2.53 ml (49.18 mmol) of bromine was added slowly under the exclusion of light to a stirred solution of 10 g (24.59 mmol) *tert*-butyltriphenyltin[16] in 750 ml of methanol at –10°C. After completion of the addition, the solution was stirred overnight. The solvent was removed in vacuo and the residue was filtered to give a yellow oil, which was distilled twice at reduced pressure to yield 6.3 g (62 %) of **15**. – B.p. 124–126°C/0.2 Torr. – $n_D^{20} = 1.6033$. – ^{1}H NMR ($CDCl_3$): δ = 7.8–7.4 (m, 5 H, aromatic H), 1.47 [s, 9 H, C(C*H*$_3$)$_3$, $^3J(^{119}Sn,CH_3)$ = 70.38 Hz, $^3J(^{117}Sn,CH_3)$ = 67.14 Hz]. – ^{13}C NMR ($CDCl_3$): δ = 138.60 (C-1), 135.19 [C-2, $^2J(^{119,117}Sn,C\text{-}2)$ = 28.3 Hz], 131.18 (C-4), 129.41 (C-3), 43.64 (Sn–*C*), 28.51 (*C*H$_3$). – ^{119}Sn NMR ($CDCl_3$): δ = 8.124. – MS/CI (isobutane); *m/z* (%): 355 (29) [M$^+$ – C$_4$H$_9$], 333 (100) [M$^+$ – Br], 199 (22) [SnBr$^+$]. – MS/EI (70 eV); *m/z* (%): 355 (2) [M$^+$ – C$_4$H$_9$], 199 (3) [SnBr$^+$], 276 (1) [SnBrC$_6$H$_5^+$], 57 (100) [C$_4$H$_9^+$]. – $C_{10}H_{14}Br_2Sn$ (412.72): calcd. C 29.10 H 3.42; found C 30.94 H 3.35.

n-Butyl(phenyl)tin Dibromide (**16**): 6.83 ml (132.79 mmol) of bromine in 70 ml of methanol was added slowly and under the exclusion of light to a stirred solution of 27 g (66.39 mmol) of *n*-butyltriphenyltin[15] in 950 ml of methanol at –30°C. Stirring was continued overnight at 0°C. The solvent was removed in vacuo and the residue distilled at 0.08 Torr to give 20.6 g (75 %) of **16** as a colourless oil. – B. p. 115–120°C/0.08 Torr. – $n_D^{20} = 1.6041$. – ^{1}H NMR ($CDCl_3$): δ = 7.7–7.4 (m, 5 H, aromatic H), 2.15–1.90 [m, 2 H, Sn–C*H*$_2$, ^3J(SnC*H*$_2$, H′) = 7.3 Hz], 1.90–1.7 [m, 2 H, CH$_2$–C*H*$_2$′–CH$_2$, ^3J(H′,H″) = 7.9 Hz], 1.55–1.40 (m, 2 H, C*H*$_2$″–CH$_3$), 0.99–0.90 [t, 3 H, C*H*$_3$, ^3J(CH$_3$,H″) = 7.1 Hz]. – ^{13}C NMR ($CDCl_3$): δ = 139.21 (C-1), 134.56 (C-2), 131.24 (C-4), 129.37 (C-3), 27.61(CH$_2$), 26.26 (CH$_2$), 25.99 (CH$_2$), 13.46 (CH$_3$). – ^{119}Sn NMR ($CDCl_3$): δ = 6.52. – MS/EI (70 eV); *m/z* (%): 357 (100) [M$^+$ – C$_4$H$_9$], 277 (20) [SnBrC$_6$H$_5^+$],199 (59) [SnBr$^+$], 77 (59) [C$_6$H$_5^+$]. – MS/CI (isobutane): *m/z* (%): 413 (3) [MH$^+$], 333 (100) [M$^+$ – Br], 133 (89). – $C_{10}H_{14}Br_2Sn$ (412.72): calcd. C 29.10 H 3.42; found C 28.97 H 3.33.

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