phospholane **23**. Toluene solvent (3 mL) was added, and the resulting mixture allowed to stir at 80 °C (48 h). ^{13}C and ^{31}P NMR analyses indicated only the dioxyphosphorane, and this sample was allowed to stir at 90 °C for a week. Reexamination of the solution indicated approximately 50% phosphorane and 50% diol. The latter apparently resulting from hydrolysis of phosphorne **23**. Additional Ph_3P (222 mg, 0.85 mmol) and diethyl peroxide (80 mg, 0.9 mmol) were added to the mixture of phosphorane **23** and diol **18** and the mixture was stirred at 80 °C for 48 h. ^{13}C and ^{31}P NMR confirmed that all the diol had been quantitatively converted to 1,3,2-dioxaphospholane **23**. Quantitative flash thermolysis (250 °C; 15–25 torr) of 1,3,2-dioxaphospholane **23** gave 57.5% 3-methylcyclohexanone and 42.5% 2-methylcyclohexanone by ^{13}C NMR analysis.

Reaction of *cis*-Cyclohexane-1,2-diol (3) with DTPP. Diethyl peroxide (495 mg, 5.5 mmol) in CH_2Cl_2 (5 mL) was added to Ph_3P (1.44 g, 5.5 mmol). *cis*-Cyclohexane-1,2-diol (0.58 g, 5.0 mmol) was added, and the reaction mixture was refluxed for 72 h. ^{13}C and ^{31}P NMR analyses indicated the presence of phosphorane **4** as the major product (>90%) which was distilled (bp 150 °C, 0.05 torr) with minor decomposition. Flash thermolysis (330 °C, 15–23 torr) gave cyclohexanone (>80%).

Acknowledgment is made to the National Science Foundation (CHE-78-05921) and the National Research Council's Senior Postdoctoral Fellowship Program (to S.A.E.) for support of this research. We are grateful to Mr. Jeffery W. Kelly for recording the ^{31}P NMR spectra of the dioxyphosphoranes, and we are pleased to acknowledge M & T Chemicals, Inc., for generous samples of triphenylphosphine.

Enantioselective Synthesis of α-Functionally Substituted Cyclic Ketones via Chiral Organotin Enamines

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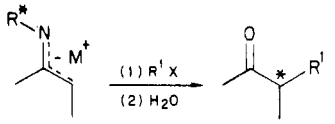
Chiral organotin enamines **1a–f** are easily prepared from cyclic ketones, chiral amino alcohols **5a–c** (derived from amino acids), and an organotin precursor. Nucleophilic addition of these compounds to electrophilic alkenes followed by hydrolysis leads to the title compounds **2a–d** in 10–98% ee. The determination of the enantiomeric excess was carried out by using ^{13}C NMR spectroscopy on the diastereoisomeric ketals. ^{119}Sn spectra of chiral organotin enamines exhibit two high-field singlets. These signals are indicative of associated species.

The alkylation of metallo enamines[3] has been used in the enantioselective synthesis of α-alkylcarbonyl compounds as shown initially by Horeau.[4]

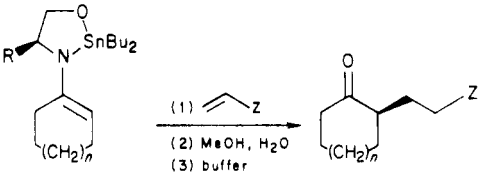


72% ee

Some years later, Meyers[5] and Whitesell[6] proposed an important improvement by using intramolecularly bonded lithium or magnesium salts, resulting in optical yields that were sometimes better than 90%.

In a preliminary paper we have reported the first results concerning enantioselective addition of chiral organotin enamines to electrophilic alkenes leading to optically active α-substituted cyclohexanones.[7] This paper deals with the scope and limitations of this reaction (Scheme I). Chiral organotin enamines were synthesized according to the reactions reported in Scheme II.

Scheme I



90% ee

The key step of the cyclization can be explained by the existence of a ring–chain tautomerism of the 1,3-oxazolidine[8] and by reaction of the open-chain tautomer with the aminotin compound. This leads to the formation of an imino alkoxy organotin compound which is itself in tautomeric equilibrium with a secondary enamine.[9] The secondary enamine is acidic enough to effect an intramolecular transamination. The reaction is monitored by ^1H NMR spectroscopy: the singlet (δ_{N-Me} 2.6) corresponding to the organotin amine decreases sharply leading to two singlets (δ 2.1–2.2), one from each of the two nonequivalent dimethylamino groups of the transient secondary enamine (Scheme II). As the reaction proceeds, these signals decrease while a broad triplet (δ 4.5) due to the olefinic proton of the chiral metallo enamine (**1a–f**) increases. Because of their thermal instability, organotin enamines

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(2) Centre de Recherche de la Cellulose du Pin, Institut du Pin, 33405 Talence Cedex, France.
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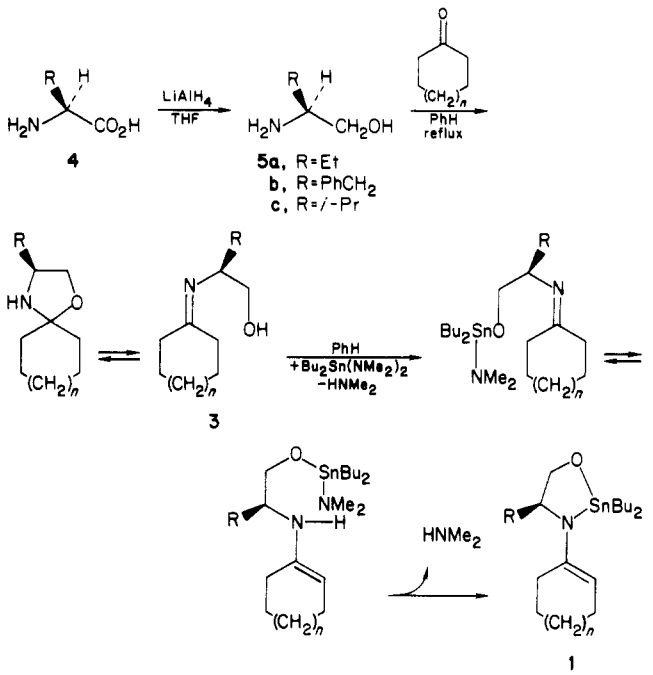
Table I. Enantioselective Synthesis of α-Functionally Substituted Ketones

organotin enamine	n	R[a]	Z	solv	T, °C	yield[b] of 2, %	$[\alpha]^{20}_{436}$ (c, MeOH)	ee, %
1a	1	Et	CO_2Me	C_5H_{12}	20	52	−16.34 (5.1)	94
1a	1	Et	CN	C_6H_6	20	16	+1.19 (5.0)	10
1b	1	$PhCH_2$	CO_2Me	C_5H_{12}	20	39	+17.13 (5.1)	97
1b	1	$PhCH_2$	CN	C_5H_{12}	20	23	−5.58 (4.8)	36
1c	1	*i*-Pr	CO_2Me	C_5H_{12}	20	41	+16.35 (4.8)	93
1c	1	*i*-Pr	CN	C_6H_6	80	50	−6.70 (5.1)	44
1d	2	Et	CO_2Me	C_5H_{12}	20	53	−81.92 (5.2)	84
1d	2	Et	CN	C_6H_6	80	68	−63.16 (5.0)	19
1e	2	$PhCH_2$	CO_2Me	C_6H_6	80	26	+97.36 (4.8)	98
1e	2	$PhCH_2$	CN	C_6H_6				*c*
1f	2	*i*-Pr	CO_2Me	C_5H_{12}	20	28	+92.75 (4.7)	95
1f	2	*i*-Pr	CN	C_6H_6	80	52	+49.09 (4.8)	14

[a] From (*R*)-(−)-aminobutanol, (*S*)-(+)-phenylalaninol, and (*S*)-(+)-valinol. [b] Overall buffer, KH_2PO_4, 1 M, except for compounds 1c and 1f, buffer, CH_3CO_2Na/CH_3CO_2H, 1 M. [c] No reaction observed.

Scheme II



were used without further purification.

According to the Scheme II a chiral amino alcohol leads to a chiral enamine of the same optical purity. The nucleophilic addition (Scheme I) was performed under various conditions as reported in Table I. We can observe that the addition is much less selective with nitriles, ee 10–44%, than with esters, ee 84–98%.

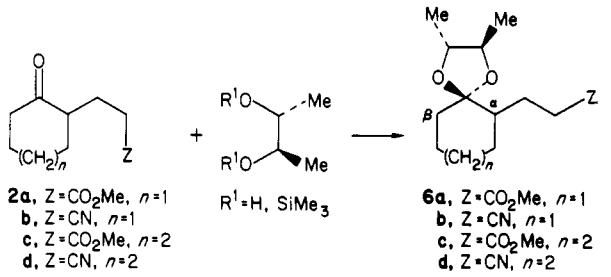
Solvent effects on the asymmetric induction were examined by allowing organotin enamine **1a** to react with 1 equiv of acrylic acid methyl ester at room temperature for 1.5 h. This was followed by the usual hydrolysis procedure for obtaining optically active substituted ketones. As shown in Table II, the best ee was obtained in pentane.

The recovery of optically active ketone is the key step in the synthesis. The first hydrolysis (Scheme I, step 2) leads to dibutyltin oxide (an amorphous powder easily eliminated by filtration) and to the alkylated imino alcohol (in equilibrium with the tautomeric oxazolidine). The hydrolysis rate of such compounds is pH dependent[10] as is the enolization (and racemization) of the alkylated ketone. It is therefore necessary to perform the second hydrolysis (Scheme I, step 3) with a buffer (Table I, ref *b*). Under such conditions the racemization is very low, as

Table II. Solvent Effects on Enantiomeric Excess of 3-(2-Oxocyclohexyl)propionic Acid Methyl Ester Prepared with Benzyloxazolidine

solv	chem yield, %	ee, %
C_6H_6	30	61
C_5H_{12}	39	97
HMPA	26	47
THF	38	20

Scheme III



shown by Yamada[11] (see Experimental Section), and the ketone can be obtained with a minimum loss of optical activity.

It is noteworthy that the starting chiral amino alcohol can be recovered unchanged by liquid–liquid extraction of the aqueous phase.

The main experimental problem was related to the determination of the enantiomeric excess of the products. This was most easily achieved by ^{13}C NMR spectroscopy following the derivatization[12,13,5c] to form ketals as shown in Scheme III and Table III.

A racemic mixture gives two signals of equal intensity for the carbons α and β. Integration of these two signals therefore gives the ee directly.

The accuracy of the NMR method for measuring ee was confirmed for compound **2a** by measuring its optical rotation since, for this compound, the specific rotation is known[11] (% optical purity = % ee determined by ^{13}C NMR).

Before proposing a mechanism for any reaction it is wise to know the structure of the reacting compounds. In the present case the exact structure of the tin enamine was unknown, and so the reason for the observed asymmetric induction is rather difficult to define. We therefore tried to investigate the possible states in which the starting enamine exists during the course of the reaction. It is well recognized that organotin alkoxides are associated by co-

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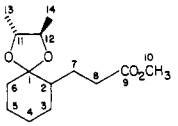
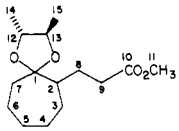
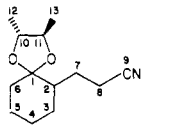
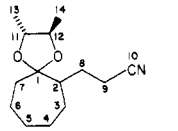
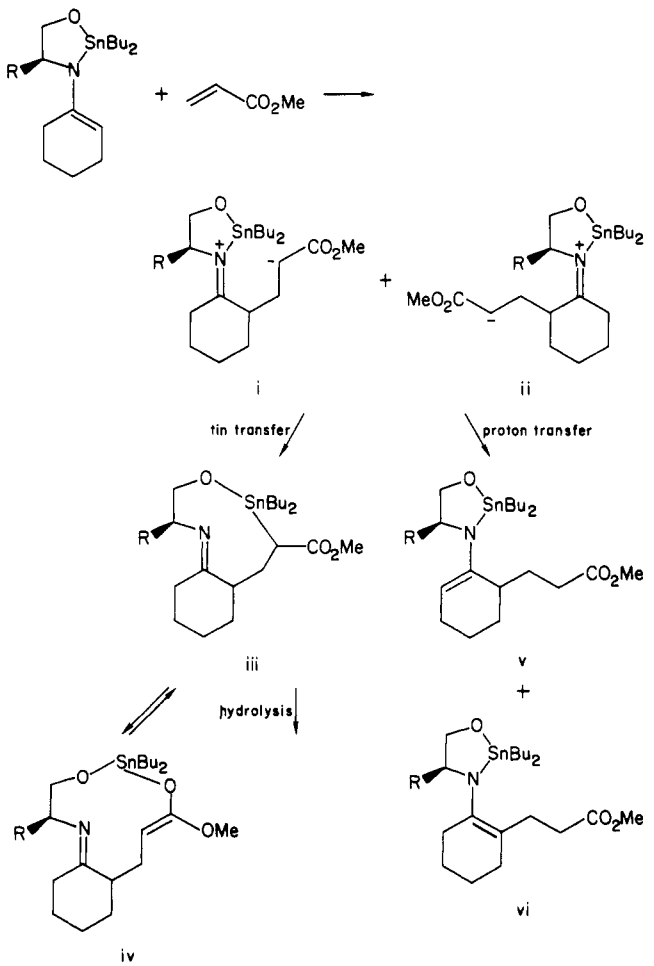
Table III. ^{13}C Chemical Shifts (δ) of Ketals 6[a]

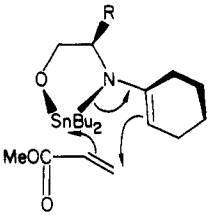
	C_1	C_2	others
	109.5, 109.2	44.5, 43.8	C_9, 174.0; C_{11}, C_{12}, 78.7, 76.9; C_{10}, 50.9; C_6, 36.6, 36.0; C_8, 32.0; C_3, C_4, C_5, C_7, 28.6–28.4, 24.2, 23.4, 23, C_{13}, C_{14}, 17.5, 15.8
	112.7, 112.0	47.1, 46.8	C_{10}, 173.6; C_{12}, C_{13}, 78.6–78.2, 77.3–76.5; C_{11}, 50.6; C_7, 28.6–27.3; C_9, 36.4; C_3, C_4, C_5, C_6, C_8, 26.6–26.3, 24.9–24.5, 21.5, 20.4, 17.2; C_{14}, C_{15}, 15.8, 15.5
	109.6, 109.4	44.4, 43.7	C_9, 120.1; C_{10}, C_{11}, 79.3, 77.7; C_6 36.8–36.2; C_8, 29.0–28.7; C_3, C_4, C_5, C_7, 25.0–24.8, 24.5–23.7, 18.0, 16.31; C_{15}, 15.6; C_{16}, 15.4
	112.4, 112.0	46.7, 46.5	C_{10}, 119.7; C_{11}, C_{12}, 79.0–78.5, 77.5–76.9; C_7, 38.3; C_9, 28.4; C_3, C_4, C_5, C_7, C_8, 27.0–26.4, 25.5–24.9, 21.4, 20.3, 17.3; C_{13}, C_{14}, 15.9, 15.7

[a] From optically active compounds 2.

Scheme IV



Scheme V



ordination bonds. Thus a crystallographic study of cyclic organotin alkoxides has shown a polymeric structure, whereas in solution, these compounds are dimeric.[14] In our case, ^{119}Sn NMR spectroscopy of optically pure organotin enamines in benzene from 30 to 60 °C shows a singlet (δ −120). This large upfield shift indicates the presence of associated species (5- or 6-coordinated tin). The same experiment performed with racemic mixtures or with partly resolved organotin enamines showed two singlets and in the latter case with an integration ratio compatible with an associated structure. The spectra showed no change with temperature. Moreover, when recorded in good complexing solvents (THF, Me_2SO) it did not show any differences from those obtained in benzene, indicating strong association of the tin enamine molecules. This finding indicates that the previously mentioned solvent effects (Table II) on the ee cannot be accounted for by a specific chelation of the tin atom by the solvent. Attempts to study the structure of chiral organotin enamines by X-ray crystallography were unsuccessful because removal of solvent led only to brown viscous oils or amorphous powders. We believe that chiral organotin enamines probably exist as dimers in benzene.

From another point of view we showed previously[15] that during the addition step the first formed product is an α-organotin ester (Scheme IV).

In nonpolar solvents, zwitterions i or ii revert back to neutral species by tin transfer instead of proton transfer, leading to iii in equilibrium with a tautomeric O-structure iv.[16] So a six-membered transition state may be proposed (Scheme V). But, as we pointed out previously, the tin atom would be aggregated providing a steric inhibition, and without further information concerning the structure of organotin enamine it would be unwise to predict the steric course of the asymmetric synthesis.

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(16) Lutsenko, I. F.; Baukov, Yu. I.; Belavin, I. Yu. *J. Organomet. Chem.* **1970**, *24*, 359.

In summary, our reaction leads to functionally substituted ketones in high yields with a high enantiomeric excess (up to 98%). The detailed mechanism by which asymmetric induction occurs remains to be determined.

Experimental Section[17]

(*R*)-(−)-2-Amino-1-butanol (5a) was purchased from Fluka A.G.: $[\alpha]^{20}_D$ −6.81° (neat, c = 1), $[\alpha]^{20}_D$ (max) −10.1°.[18]

(*S*)-(−)-Phenylalaninol (5b). (*S*)-(−)-Phenylalanine (55.7 g, 0.35 mol, $[\alpha]^{20}_D$ 34.1° (c = 2, H_2O) was added to a suspension of lithium aluminum hydride (22.8 g, 0.6 mol) in dry tetrahydrofuran (700 mL) with mechanical stirring. The hot solution was refluxed for 1 h and cooled overnight to room temperature. After the mixture was cooled in an ice bath, H_2O was added with vigorous stirring. Lithium salts were filtered off, and the organic layer was dried over anhydrous $MgSO_4$, the solvent removed under vacuum, the residue distilled under vacuum, providing 34.9 g (66%) of (S)-(−)-phenylalaninol: bp 135 °C (0.2 mm); $[\alpha]^{20}_D$ −25.4° (c 1.15, EtOH); mp 88 °C.[19]

(*S*)-(+)-Valinol (5c) was prepared according to the procedure for **5b**: yield, 24.5 g (68%); bp 80 °C (0.2 mm); $[\alpha]^{20}_D$ +18.6° (c 8, EtOH).[19]

Cyclanones, oxazolidines, and **chiral imino alcohols** were prepared according to Bergmann's procedure.[8a] **3a**: bp 87 °C (0.2 mm); NMR (CCl_4) δ 1.0 (t, 3). **3b**: bp 132 °C (0.2 mm); NMR (CCl_4) δ 7.1 (m, 5), 0.95 (m, 6). **3c**: bp 85 °C (0.2 mm); NMR (CCl_4) δ 3.8 (t, 1), 3.1 (m, 2), 1–0.95 (d, 6). **3d**: bp 82 °C (0.2 mm); NMR (CCl_4) δ 3.75 (m, 1), 3.05 (m, 2). **3e**: bp 155 °C (0.2 mm); NMR (CCl_4) δ 7.1 (m, 5). **3f**: bp 95 °C (0.2 mm); NMR (CCl_4) δ 1–0.95 (d, 6).

Chiral Organotin Enamines 1. In an oven-dried 100-mL flask equipped with a magnetic stir bar under an argon atmosphere, oxazolidine/imino alcohol (25 mM) and benzene (20 mL) were added via a syringe to a solution of bis(dimethylamino)-di-*n*-butylstannane[20] (25 mM) in dry benzene (40 mL). The solution was stirred under reflux for 1–6 h.

2,2-Dibutyl-3-cyclohexenyl-4-ethyl-1-oxa-3-aza-2-stannacyclopentane (1a): reflux, 5 h; NMR (C_6H_6) δ 4.55 (t, 1).

2,2-Dibutyl-3-cyclohexenyl-4-benzyl-1-oxa-3-aza-2-stannacyclopentane (1b): reflux, 4 h; NMR (C_6H_6) δ 4.9 (t, 1).

2,2-Dibutyl-3-cyclohexenyl-4-isopropyl-1-oxa-3-aza-2-stannacyclopentane (1c): reflux, 6 h; NMR (C_6H_6) δ 4.75 (t, 1).

2,2-Dibutyl-3-cycloheptenyl-4-ethyl-1-oxa-3-aza-2-stannacyclopentane (1d): reflux, 2 h; NMR (C_6H_6) δ 4.6 (t, 1).

2,2-Dibutyl-3-cycloheptenyl-4-benzyl-1-oxa-3-aza-2-stannacyclopentane (1e): reflux, 1.5 h; NMR (C_6H_6) δ 4.95 (t, 1).

2,2-Dibutyl-3-cycloheptenyl-4-isopropyl-1-oxa-3-aza-2-stannacyclopentane (1f): reflux, 1 h; NMR (C_6H_6) δ 4.1 (t, 1).

Michael Addition of Organotin Enamines. Asymmetric Synthesis of 2-Functionally Substituted Cyclic Ketones (2). If necessary the solvent was removed by evaporation with a vacuum pump (0.2 mm). The new freshly distilled solvent was added on the viscous liquid. Then 26 mM of electrophilic alkene was added via a syringe to the organotin enamine. The mixture was heated from 20 °C to reflux for 1–2.5 h as shown in Table I. After cooling the solution to room temperature the addition of 50 mL of ether, methanol (1 mL) and water (1 mL) were added. Stirring was continued for 20 h. Dibutyltin oxide was filtered off, and the residual mixture was treated with a buffer[21] (KH_2PO_4, 1 M, 35 mL) for 4 h. The phases were separated. The aqueous phase was extracted twice with ether (20 mL), the combined organic phases were washed and dried ($MgSO_4$), and ether was evaporated. The crude mixture was distilled in vacuo. The product was free of impurities (VPC, IR, ^1H NMR, microanalysis).

3-(2-Oxocyclohexyl)propionic acid methyl ester (2a): bp 100 °C (0.1 mm); NMR (CCl_4) δ 3.6 (s, 3); IR (film) 1745, 1715 cm^{-1}; VPC shows 99% purity. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.21; H, 8.69. Found: C, 65.29; H, 8.65.

3-(2-Oxocyclohexyl)propionitrile (2b): bp 95 °C (0.1 mm); IR (film) 2260, 1720 cm^{-1}; VPC shows 99% purity. Anal. Calcd for $C_9H_{13}NO$: C, 71.52; H, 8.60; N, 9.45. Found: C, 71.49; H, 8.64; N, 9.40.

3-(2-Oxocycloheptyl)propionic acid methyl ester (2c): bp 138 °C (0.5 mm); NMR (CCl_4) δ 3.6 (s, 3); IR (film) 1720, 1740 cm^{-1}; VPC shows 99% purity. Anal. Calcd for $C_{11}H_{17}O_3$: C, 67.00; H, 8.62. Found: C, 66.94; H, 8.65.

3-(2-Oxocycloheptyl)propionitrile (2d): bp 90 °C (0.05 mm); IR (film) 2260, 1720 cm^{-1}; VPC shows 99% purity. Anal. Calcd for $C_{10}H_{15}NO$: C, 72.72; H, 9.09; N, 8.48. Found: C, 72.71; H, 9.12; N, 8.50.

Control Experiment of Racemization Rate of α-Substituted Ketones 2a–d. Optically active α-substituted ketones of known optical purity (10 mM) in ether (25 mL) were treated by the buffer for 4 h. The phases were separated. The aqueous phase was extract twice with ether (20 mL), the combined organic phases were washed and dried ($MgSO_4$), and ether was evaporated. The crude product was free of impurities. Optical yield was larger than 95%, showing that products were rather stable in these conditions.

Cyclic Ketals of Cyclic Ketones 6a–d. These compounds were prepared according to Meyers and Noyori.[5c,12] α-Substituted ketone (2.5 mM), (2*R*,3*R*)-2,3-butanediol (5 mM), methylene chloride (5 mL), and *p*-toluenesulfonic acid (1–2 mg) were heated under reflux. The reaction was followed by VPC until all the ketone had gone. The product was used without purification.

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Registry No. **1a**, 97806-86-5; **1b**, 97806-87-6; **1c**, 97806-88-7; **1d**, 97806-89-8; **1e**, 97806-90-1; **1f**, 97806-91-2; (*R*)-**2a**, 77397-55-8; (*S*)-**2a**, 24738-84-9; (*R*)-**2b**, 58800-16-1; (*S*)-**2b**, 24773-62-4; (*R*)-**2c**, 97806-92-3; (*S*)-**2c**, 97807-10-8; (*R*)-**2d**, 97806-93-4; (*S*)-**2d**, 97807-11-9; **3a**, 97806-94-5; **3b**, 97806-95-6; **3c**, 97806-96-7; **3d**, 97806-97-8; **3e**, 97806-98-9; **3f**, 97806-99-0; **5a**, 5856-63-3; **5b**, 3182-95-4; **5c**, 2026-48-4; (2*R*)-**6a**, 97807-00-6; (2*S*)-**6a**, 97859-88-6; (2*R*)-**6b**, 97807-01-7; (2*S*)-**6b**, 97859-89-7; (2*R*)-**6c**, 97807-02-8; (2*S*)-**6c**, 97859-90-0; (2*R*)-**6d**, 97807-03-9; (2*S*)-**6d**, 97859-91-1; CH_2=CHC(O)OMe, 96-33-3; CH_2=CHCN, 107-13-1; $Bu_2Sn(Me_2N)_2$, 1067-16-9; (*S*)-(−)-phenylalanine, 63-91-2; (2*R*,3*R*)-2,3-butanediol, 24347-58-8; (3*S*)-3-ethyl-4-aza-1-oxaspiro[4.5]decane, 97807-04-0; (3*S*)-3-benzyl-4-aza-1-oxaspiro[4.5]decane, 97807-05-1; (3*S*)-3-isopropyl-4-aza-1-oxaspiro[4.5]decane, 97807-06-2; (3*S*)-3-ethyl-4-aza-1-oxaspiro[4.6]undecane, 97807-07-3; (3*S*)-3-benzyl-4-aza-1-oxaspiro[4.6]undecane, 97807-08-4; (3*S*)-3-isopropyl-4-aza-1-oxaspiro[4.6]undecane, 97807-09-5.

(17) Microanalyses were performed by Service Central d'Analyses du CNRS. Optical rotations taken on a Perkin-Elmer Model 141 polarimeter. ^1H NMR were taken on a Perkin-Elmer R 12, ^{13}C on a Bruker WP 60 operating at 15.08 MHz, and ^{119}Sn on a Bruker WP 90 operating at 33.54 MHz.

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(19) Meyers, A. I.; Poindexter, G. S.; Brich, Z. *J. Org. Chem.* **1978**, *43*, 892.

(20) Prepared according to: Jones, K.; Lappert, M. F. *J. Organomet. Chem.* **1965**, *3*, 295.

(21) For compounds **1c** and **1f** (R = *i*-Pr), the best result was obtained with CH_3CO_2H/CH_3CO_2Na buffer.