

SUPPORTING INFORMATION (13 pages)

N-Boc-2-Stannyloxazolidines Derived from (*R*)-Phenylglycinol: Preparation, Transmetalation and Use as Precursors of Enantioenriched α -Aminoalkyltriorganostannanes

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1. Preparation of *N*-Boc-2-triorganostannyloxazolidines

Method A

A solution of diethoxymethyltributyltin **1a** (2.76 g, 7 mmol) or diethoxymethyltrimethyltin **1b** (1.87 g, 7 mmol), *N*-Boc-(*R*)-phenylglycinol **2** (1.67 g, 7 mmol) and camphor sulphonic acid (232 mg, 1 mmol) in CH₂Cl₂ (50 mL) was stirred at room temperature on a bed of molecular sieves 4Å. After stirring for 20h, the mixture was neutralized with K₂CO₃, filtrated through neutral alumina using diethyl ether as eluent, concentrated by evaporation and purified by flash chromatography on silica gel (eluent : hexanes/diethyl ether/ Et₃N : 95/3/2) to yield in the best cases 2.5 g of **3a-trans/cis** (66%) or 0.75 g of **3b-trans/cis** (26%).

This initial experimental procedure was problematic because sometimes the reaction stops at level of the true transacetalisation step (exchange of the alcohol function of the *N*-Boc phenylglycinol only). We have explored possible reasons (quantity of acid, quality of molecular sieves, activation mode of the molecular sieves....). Finally, we thought that problems were due to the irregular quality of molecular sieves (in terms of activation) and also to the quantity of acid. For further studies we changed method A to method B which gives reproducible results without using molecular sieves

Method B

Camphor sulphonic acid (8.14 g, 35 mmol) in cyclohexane (50 mL) was refluxed for 2h in a 100 mL flask equipped with a Dean & Stark apparatus. After cooling the solution at room temperature, diethoxymethyltributyltin **1a** (2.76 g, 7 mmol) and *N*-Boc-(*R*)-phenylglycinol (1.67 g, 7 mmol) were added. After stirring for 15 min, the mixture was neutralized with K₂CO₃, filtrated through neutral alumina using diethyl ether as eluent, concentrated by

evaporation and purified by flash chromatography on silica gel (eluent : hexanes/diethyl ether/Et₃N : 95/3/2) to yield 2.6 g of **3a-trans/cis** (69%).

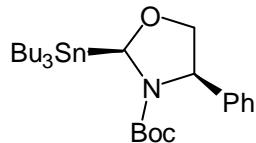
Characterization of the obtained products: ¹H and ¹³C NMR chemical shifts are given related to tetramethylsilane. ¹¹⁹Sn NMR chemical shift are given related to tetramethylstannane. For MS spectra the stannylylated fragments are given for ¹²⁰Sn.

N-t-butylcarbamate-2-tributylstannylyl-(4R)-phenyl-1,3-oxazolidine 3a

C₂₆H₄₅NO₃Sn (538.35): Calcd. C 58.01; H 8.43; N 2.60 ; found 57.65; H 8.37 ; N. 2.53

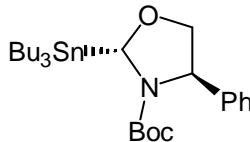
IR (n cm⁻¹): 1726, 1685, 1417, 1162, 699. **MS (70 eV, EI): m/z (%): Stannylylated fragments:** 482(6), 426(20), 291(4), 233(9), 179(15); **Organic fragments:** 248(18), 192(100), 148(94), 120(19), 69(12).

3a-cis



¹H NMR (C₆D₆, 340 K): 0.7-1.8 (m, 27H, (CH₃CH₂CH₂CH₂)₃Sn), 1.25 (s, 9H, C(CH₃)₃), 3.59 (dd, 1H, OCH₂, ²J(H,H) = 8.5 Hz, ³J(H,H) = 6.5 Hz), 3.87 (dd, 1H, OCH₂, ²J(H,H) = 8.5 Hz, ³J(H,H) ~ 2 Hz), 4.27 (dd, 1H, CHC₆H₅, ³J(H,H) = 6.5 Hz, ³J(H,H) ~ 2 Hz), 5.27 (1H, SnCH₂, ²J(Sn,H) = 66.9 Hz), 6.8-7.2 (m, 5H, C₆H₅). **¹³C NMR (C₆D₆, 340 K):** 11.6 (3C, (CH₃CH₂CH₂CH₂)₃Sn, ¹J(Sn,C) = 313-320 Hz), 13.7 (3C, (CH₃CH₂CH₂CH₂)₃Sn), 27.8 (3C, (CH₃CH₂CH₂CH₂)₃Sn, ³J(Sn,C) = 54.6 Hz), 28.3 (3C, (CH₃)₃C), 29.5 (3C, (CH₃CH₂CH₂CH₂)₃Sn, ²J(Sn,C) = 19.8 Hz), 59.9 (1C, CHC₆H₅, ³J(Sn,C) = 10.2 Hz), 77.3 (1C, CH₂, ³J(Sn,C) = 37.3 Hz), 79.4 (1C, (CH₃)₃C), 89.6 (1C, SnCH₂, ¹J(Sn,C) = 409-428 Hz), 127-129 (5C, C₆H₅), 143.4 (1C, C₆H₅), 152.3 (1C, C=O). **¹¹⁹Sn NMR (CDCl₃, 300 K):** -43.3. [a]_D²⁰ = +58.3 (c = 0.9, CHCl₃).

3a-trans



¹H NMR (C₆D₆, 300 K): 0.8-1.9 (m, 27H, (CH₃CH₂CH₂CH₂)₃Sn), 1.20 (s, 9H, C(CH₃)₃), 3.5 (dd, 1H, OCH₂, ²J(H,H) = ³J(H,H) ~ 8.4 Hz), 4.2 (dd, 1H, OCH₂, ²J(H,H) = 8.4 Hz, ³J(H,H) = 7.3 Hz), 4.6 (m, 1H, CHC₆H₅, ³J(H,H) ~ 7.8 Hz), 5.37 (s, SnCH₂, ²J(Sn,H) = 61.6 Hz), 7.1 (m, 5H, C₆H₅). **¹³C NMR (C₆D₆, 300 K):** 10.9 (3C, (CH₃CH₂CH₂CH₂)₃Sn, ¹J(Sn,C) = 324-338 Hz), 13.5 (3C, (CH₃CH₂CH₂CH₂)₃Sn), 27.4 (3C, (CH₃CH₂CH₂CH₂)₃Sn, ³J(Sn,C) = 55.1 Hz), 27.6 (3C, (CH₃)₃C), 29.0 (3C, (CH₃CH₂CH₂CH₂)₃Sn, ²J(Sn,C) = 17.1 Hz), 60.5 (1C, CHC₆H₅, ³J(Sn,C) = 9.1 Hz), 77.4 (1C, CH₂, ³J(Sn,C) = 34.3 Hz), 78.9 (1C, (CH₃)₃C), 88.8 (1C, SnCH₂, ¹J(Sn,C) = 382-400 Hz), 126-128 (5C, C₆H₅), 141.4 (1C, C₆H₅), 152.8 (1C, C=O). **¹¹⁹Sn NMR (CDCl₃, 300 K):** -40.1 [a]_D^{po} = -144.1 (c = 1.1, CHCl₃).

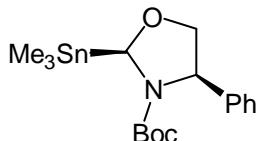
N-t-butylcarbamate-2-trimethylstannylyl-(4R)-phenyl-1,3-oxazolidine 3b

C₁₇H₂₇NO₃Sn (412.11): calcd. C. 49.55, H. 6.60, N 3.40; found: C. 49.60; H. 6.77; N. 3.61

IR (n cm⁻¹): 2972, 2907, 2842, 1805, 1648, 1398, 1157, 750. **MS (70 eV, EI): m/z (%):**

Stannylated fragments: 342 (5), 312(7), 165(32); **Organic fragments:** 248(11), 192(70), 148(63), 120(43), 104(20), 57(100), 41(21); 29(10).

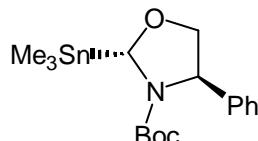
3b-cis



¹H NMR (C₆D₆, 300 K): 0.36 (s, 9H, (CH₃)₃Sn, ²J(Sn,H) = 54 Hz), 1.22 (s, 9H, (CH₃)₃C), 3.68 (dd, 1H, OCH₂, ²J(H,H) = 8.3 Hz, ³J(H,H) = 6.3 Hz), 3.89 (dd, 1H, OCH₂, ²J(H,H) = 8.3 Hz, ³J(H,H) = 2 Hz), 4.43 (dd, 1H, CHC₆H₅, ³J(H,H) = 6.3 Hz, ³J(H,H) = 2 Hz), 5.05 (s, 1H, SnCH₂, ²J(Sn,H) = 75 Hz), 7.0-7.2 (m, 5H, C₆H₅). **¹³C NMR (C₆D₆, 300 K):** -8.6 (3C, (CH₃)₃Sn, ¹J(Sn,C) = 343 Hz), 28.0 (3C, (CH₃)₃C), 59.7 (1C, CHC₆H₅, ³J(Sn,C) = 12 Hz), 77.8

(1C, OCH₂, ³J(Sn,C) = 39 Hz), 79.4 (1C, (CH₃)₃C), 88.3 (1C, SnCH, ¹J(Sn,C) = 329-346 Hz), 126.5 (2C, CHC₆H₅), 127.2 (1C, CHC₆H₅), 128.3 (2C, CHC₆H₅), 143.6 (1C, CHC₆H₅), 152.2 (1C, C=O). ¹¹⁹Sn NMR (C₆D₆, 340 K): -23.0. [a]_D²⁰ = +33.6 (c = 0.9, CHCl₃).

3b-trans



¹H NMR (C₆D₆, 340 K): 0.44 (s, 9H, (CH₃)₃C, ²J(Sn,H) = 54.0), 1.18 (s, 9H, (CH₃)₃C), 3.53 (dd, 1H, OCH₂, ²J(H,H) = 8.7 Hz, ³J(H,H) = 7.2 Hz), 4.14 (dd, 1H, OCH₂, ²J(H,H) = 8.7 Hz, ³J(H,H) = 7.2 Hz), 4.57 (~t, 1H, CHC₆H₅, ³J(H,H) = 7.2 Hz), 5.19 (s, 1H, SnCH, ²J(Sn,H) = 69.1 Hz), 7.0-7.2 (m, 5H, C₆H₅). ¹³C NMR (C₆D₆, 300 K): -8.4 (3C, (CH₃)₃Sn, ¹J(Sn,C) = 336-351 Hz), 28.2 (3C, (CH₃)₃C), 61.2 (1C, CHC₆H₅, ³J(Sn,C) = 11 Hz), 77.6 (1C, OCH₂, ³J(Sn,C) = 39 Hz), 79.7 (1C, (CH₃)₃C), 89.3 (1C, SnCH, ¹J(Sn,C) = 457-479 Hz), 126.7 (2C, CHC₆H₅), 127.4 (1C, CHC₆H₅), 128.5 (2C, CHC₆H₅), 142.0 (1C, CHC₆H₅), 153.5 (1C, C=O). ¹¹⁹Sn NMR (C₆D₆, 340 K): -25.0. [a]_D²⁰ = -140.5 (c = 1.1, CHCl₃).

2. Transmetalation of N-Boc-2-tributylstannyloxazolidines

A solution of *N*-Boc-tributylstannyloxazolidine **3a-cis** or **3a-trans** (539 mg, 1 mmol) in THF (20 mL) was cooled at -78°C and degassed before dropwise addition of *n*-butyllithium (1.2 mmol, 0.80 mL, 1.5 M in hexane). After 30 min stirring, a solution of trimethyltin chloride (219 mg, 1.1 mmol), triphenyltin chloride (424 mg, 1.1 mmol) or cyclohexanone (108 mg, 114 μL, 1.1 mmol) in THF (2 mL) was added dropwise at -78°C. After 30 min additional stirring the hydrolysis was achieved with an aqueous NH₄Cl solution. The products were subsequently extracted with ether (2x50mL) and the organic layer dried on magnesium sulfate. After filtration and evaporation of the solvent, the crude compounds were purified on silica gel

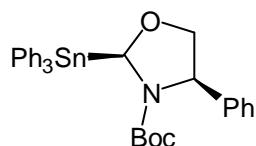
(eluent = hexanes/diethyl ether/ Et₃N : 95/3/2 for **3b**, 70/28/2 for **3c**, 90/10/0 for **3d**) to afford 239 mg (58%) of **3b-trans**, 239 mg (58%) of **3b-cis**, 497 mg (83%) of **3c-trans**, 401 mg (67%) of **3c-cis**, 240 mg (69%) of **3d-trans** or 261 mg (75%) of **3d-cis**.

N-t-butylcarbamate-2-triphenylstannylyl-(4R)-phenyl-1,3-oxazolidine 3c

C₃₂H₃₃NO₃Sn (598.32): C 64.24; H 5.56; N 2.34; Calcd. 64.21; H. 5.51; N. 2.32

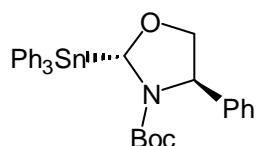
IR (n cm⁻¹): 1669, 1408, 1165, 731, 695, 1480, 1454. **MS (70 eV, EI): m/z (%): Stannylated fragments:** 498 (3), 466 (1), 351 (28), 197(20); **Organic fragments:** 248 (8); 192(90); 148(100); 120(51), 57(100); 41(16), 20(6)

3c-cis



¹H NMR (CDCl₃, 300 K): 1.18 (s, 9H, (CH₃)₃C), 3.82 (dd, 1H, OCH₂, ²J(H,H) = 8.5 Hz, ³J(H,H) = 6.9 Hz), 3.97 (dd, 1H, OCH₂, ²J(H,H) = 8.5 Hz, ³J(H,H) = 2.5 Hz), 4.55 (dd, 1H, CHC₆H₅, ³J(H,H) = 2.5 Hz, ³J(H,H) = 6.9 Hz), 5.78 (s, 1H, SnCH₂, ²J(Sn,H) = 88-93 Hz), 7.1-7.4 (m, 14H, (C₆H₅)₃Sn and CHC₆H₅), 8.0 (m, 6H, (C₆H₅)₃Sn, ³J(Sn,H) = 50 Hz). **¹³C NMR (CDCl₃, 300 K):** 28.4 (3C, (CH₃)₃C), 60.0 (1C, CHC₆H₅, ³J(Sn,C) = 13 Hz), 77.4 (1C, OCH₂, ³J(Sn,C) = 45 Hz), 79.2 (1C, (CH₃)₃C), 91.1 (1C, SnCH₂, ¹J(Sn,C) = 557-583 Hz), 127.2-129.4 (14C, (C₆H₅)₃Sn and CHC₆H₅), 138.4 (6C, (C₆H₅)₃Sn, ³J(Sn,C) = 36 Hz), 140.5 (3C, (C₆H₅)₃Sn, ¹J(Sn,C) = 502-520 Hz), 142.4 (1C, CHC₆H₅), 152.7 (1C, C=O). **¹¹⁹Sn NMR (CDCl₃, 300 K):** -158.7 (90) and -136.2 (10). [a]_D²⁰ = +40.2 (c = 1.06, CHCl₃).

3c-trans



¹H NMR (CDCl₃, 300 K): 1.16 (s, 9H, (CH₃)₃C), 3.97 (dd, 1H, OCH₂, ²J(H,H) = 8.7 Hz, ³J(H,H) = 7.1 Hz), 4.61 (dd, 1H, OCH₂, ²J(H,H) = 8.7 Hz, ³J(H,H) = 7.0 Hz), 4.75 (dd, 1H,

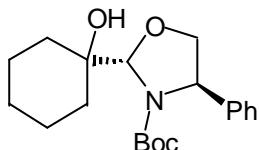
$\underline{\text{CHC}_6\text{H}_5}$, $^3\text{J}(\text{H},\text{H}) = 7.0$ Hz, $^3\text{J}(\text{H},\text{H}) = 7.1$ Hz), 5.91 (s, 1H, $\underline{\text{CHSn}}$, $^2\text{J}(\text{Sn},\text{H}) = 83\text{-}87$ Hz), 7.15-7.32 (m, 14H, $(\text{C}_6\underline{\text{H}}_5)_3\text{Sn}$ and $\text{CHC}_6\underline{\text{H}}_5$), 7.62 (m, 6H, $(\text{C}_6\underline{\text{H}}_5)_3\text{Sn}$, $^3\text{J}(\text{Sn},\text{H}) = 45$ Hz). **$^{13}\text{C NMR}$** (CDCl_3 , 300 K): 27.8 (3C, $(\underline{\text{CH}_3})_3\text{C}$), 60.2 (1C, $\underline{\text{CHC}_6\text{H}_5}$, $^3\text{J}(\text{Sn},\text{C}) = 12$ Hz), 77.4 (1C, $\underline{\text{OCH}_2}$, $^3\text{J}(\text{Sn},\text{C}) = 37$ Hz), 84.8 (1C, $(\text{CH}_3)_3\underline{\text{C}}$), 90.3 (1C, $\underline{\text{SnCH}}$, $^1\text{J}(\text{Sn},\text{C}) = 535\text{-}559$ Hz), 126.4 (2C, $\underline{\text{CHC}_6\text{H}_5}$), 127.3 (1C, $\underline{\text{CHC}_6\text{H}_5}$), 128.3 (6C, $(\underline{\text{C}_6\text{H}}_5)_3\text{Sn}$, $^3\text{J}(\text{Sn},\text{C}) = 54$ Hz), 128.3 (3C, $(\underline{\text{C}_6\text{H}}_5)_3\text{Sn}$), 128.4 (2C, $\underline{\text{CHC}_6\text{H}_5}$), 137.4 (6C, $(\underline{\text{C}_6\text{H}}_5)_3\text{Sn}$, $^2\text{J}(\text{Sn},\text{C}) = 37$ Hz), 140.2 (3C, $(\underline{\text{C}_6\text{H}}_5)_3\text{Sn}$, $^1\text{J}(\text{Sn},\text{C}) = 500\text{-}523$ Hz), 140.9 (1C, $\underline{\text{CHC}_6\text{H}_5}$), 153.2 (1C, $\underline{\text{C=O}}$). **$^{119}\text{Sn NMR}$** (CDCl_3 , 300 K): -161.5. $[\alpha]_D^{20} = -136.5$ (c = 0.86, CHCl_3).

N-t-butylcarbamate-2-[1-hydroxycyclohex-1-yl]-(4*R*)-phenyl-1,3-oxazolidine

$\text{C}_{20}\text{H}_{29}\text{NO}_4$ (347.45): Calcd. C 69.14; H 8.41; N 4.03; found: C 69.23; H. 8.43; N 3.94

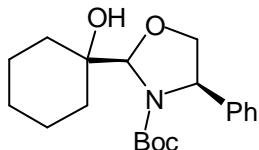
IR (n cm⁻¹): 3480, 2935, 1670, 1395, 1367, 1310, 1256, 1164, 699. **MS (70 eV, EI): m/z (%):** 292(3), 274(2), 248(19), 192(68), 148(100), 120(48), 104(20), 81(14), 57(71), 41(16), 29(10).

3d-trans



$^1\text{H NMR}$ (C_6D_6 , 340 K): 1.06 (s, 9H, $(\text{CH}_3)_3\text{C}$), 1.2-2.1 (m, 10H, $\underline{\text{CH}_2}$), 3.50 (dd, 1H, $\underline{\text{OCH}_2}$, $^3\text{J}(\text{H},\text{H}) = 3.8$ Hz, $^2\text{J}(\text{H},\text{H}) = 8.4$ Hz), 4.1 (dd, 1H, $\underline{\text{OCH}_2}$, $^3\text{J}(\text{H},\text{H}) = 6.8$ Hz, $^2\text{J}(\text{H},\text{H}) = 8.4$ Hz), 4.47 (dd, 1H, $\underline{\text{CHC}_6\text{H}_5}$, $^3\text{J}(\text{H},\text{H}) = 6.8$ Hz, $^3\text{J}(\text{H},\text{H}) = 3.8$ Hz), 4.81 (bs, 1H, $\underline{\text{OH}}$), 5.45 (1H, s, $\underline{\text{CH}}$), 7.0-7.11 (m, 5H, $\text{C}_6\underline{\text{H}}_5$). **$^{13}\text{C NMR}$ (C_6D_6 , 340 K):** 21.7 (1C, $(\underline{\text{CH}_2})_5$), 22.1 (1C, $(\underline{\text{CH}_2})_5$), 26.7 (1C, $(\underline{\text{CH}_2})_5$), 27.9 (3C, $(\underline{\text{CH}_3})_3\text{C}$), 32.2 (1C, $(\underline{\text{CH}_2})_5$), 35.4 (1C, $(\underline{\text{CH}_2})_5$), 62.6 (1C, $\underline{\text{CHC}_6\text{H}_5}$), 74.4 (1C, $\underline{\text{OCH}_2}$), 74.6 (1C, $\underline{\text{COH}}$), 80.9 (1C, $(\text{CH}_3)_3\underline{\text{C}}$), 97.1 (1C, $\underline{\text{OCHN}}$), 126.5 (2C, $\underline{\text{CHC}_6\text{H}_5}$), 127.6 (1C, $\underline{\text{CHC}_6\text{H}_5}$), 128.7 (2C, $\underline{\text{CHC}_6\text{H}_5}$), 143.4 (1C, $\underline{\text{CHC}_6\text{H}_5}$), 155.3 (1C, $\underline{\text{C=O}}$). $[\alpha]_D^{20} = -86.4$ (c = 0.46, CHCl_3). m.p. = 160°C.

3d-cis



¹H NMR (C₆D₆, 340 K): 1.23 (s, 9H, (CH₃)₃C), 1.3-2.1 (m, 10H, CH₂), 3.81 (dd, 1H, OCH₂, ³J(H,H) = 7.5 Hz, ²J(H,H) = 8.5 Hz), 3.92 (dd, 1H, OC₆H₅, ³J(H,H) = 6.8 Hz, ²J(H,H) = 8.5 Hz), 4.00 (s, 1H, OH), 4.69 (dd, 1H, CHC₆H₅, ³J(H,H) = 7.5 Hz, ³J(H,H) = 6.8 Hz), 5.13 (s, 1H, CH), 7.0-7.35 (m, 5H, C₆H₅). **¹³C NMR (C₆D₆, 340 K):** 21.7 (1C, (CH₂)₅), 21.8 (1C, (CH₂)₅), 26.5 (1C, (CH₂)₅), 28.1 (3C, (CH₃)₃C), 32.1 (1C, (CH₂)₅), 35.3 (1C, (CH₂)₅), 61.8 (1C, CHC₆H₅), 73.1 (1C, OCH₂), 73.6 (1C, COH), 81.1 (1C, (CH₃)₃C), 97.3 (1C, OCHN), 127.0 (2C, CHC₆H₅), 127.5 (1C, CHC₆H₅), 128.5 (2C, CHC₆H₅), 141.4 (1C, CHC₆H₅), 156.4 (1C, C=O). [α]_D²⁰ = -16.4 (c = 0.98, CHCl₃).

3. Reaction of *N*-Boc-2-triorganostannyloxazolidines with lithium dimethylcuprate in the presence of boron trifluoride

Cuprous iodide (571.4 mg, 3 mmol) was placed in a Schlenk tube and dried under vacuum upon heating with a flame. Dry diethyl ether (25 mL) was subsequently added and the suspension obtained was cooled to -50°C before dropwise addition of methylolithium (6 mmol, 4 mL, 1.5M in diethyl ether). After being stirred at -30°C for 30 min, the clear solution of lithium dimethylcuprate was cooled to -78°C and freshly distilled boron trifluoride etherate (370 µL, 3 mmol) was added. After 10 min stirring, a solution of 2-stannyloxazolidine (1 mmol in 5 mL of diethyl ether) was added dropwise (addition in 2 min using syringe method) to the reaction mixture. Further stirring for 2 h and subsequent hydrolysis with aqueous NH₄Cl afforded after extraction and usual treatments the crude mixture of diastereomers **4** and **5** which were purified on silica gel (eluent : hexanes/diethyl ether : 80/20) to afford 382 mg (69% yield)

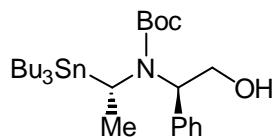
for **4a/5a** (84/16) or 201 mg (47%) for **4b/5b** (55/45). Compound **4a** was eluted before **5a** and compound **4b** before **5b** using this eluent

N-[1-(Tributylstannyl)ethyl]-N-[(2-hydroxy-(1*R*)-phenyl)ethyl]-*t*-butylcarbamate

C₂₇H₄₉NO₃Sn (554.39): C 58.49; H 8.91; N 2.53; found: C 58.21; H. 8.72; N 2.72

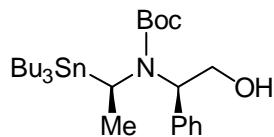
IR (n cm⁻¹): 3436, 1675, 1453, 1420, 1312, 1069, 699. **MS (70 eV, EI): m/z (%): Stannylated fragments:** 498(12), 442(37, 422(5), 322(2), 291(3), 282(4), 276(3), 235(10), 179(14), 177(15), 121(18); **Organic fragments:** 264(1), 164(100), 121(18), 105(5), 103(8), 57(29), 44(25), 41(10), 29(9).

4a



¹H NMR (C₆D₆, 340 K): 0.9-1.85 (m, 28H, (CH₃CH₂CH₂CH₂)₃Sn + OH), 1.2 (d, 3H, CH₃CH, ³J(H,H) = 7.1 Hz), 1.45 (s, 9H, (CH₃)₃C), 3.08 (q, SnCH₂, ³J(H,H) = 7.1 Hz, ²J(Sn,H) = 49.1 Hz), 3.87-4.13 (m, 2H, CH₂OH), 5.1 (dd, 1H, CHC₆H₅, ³J(H,H) = 7 Hz, ³J(H,H) = 6.8 Hz), 7.1-7.4 (m, 5H, C₆H₅). **¹³C NMR (C₆D₆, 340 K):** 11.3 (3C, (CH₃CH₂CH₂CH₂)₃Sn, ¹J(Sn,C) = 307-321 Hz), 13.8 (3C, (CH₃CH₂CH₂CH₂)₃Sn), 18.9 (1C, CH₃CH), 27.9 (3C, CH₃CH₂CH₂CH₂)₃Sn, ³J(Sn,C) = 53.8-56.1 Hz), 28.6 (1C, (CH₃)₃C), 29.7 (3C, (CH₃CH₂CH₂CH₂)₃Sn, ²J(Sn,C) = 19.1 Hz), 42.0 (1C, CH₃CH, ¹J(Sn,C) = 375-393 Hz), 63.3 (1C, CH₂OH), 63.7 (1C, CHC₆H₅, ³J(Sn,C) = 15.3 Hz), 80.0 (1C, (CH₃)₃C), 127.5 (2C, C₆H₅), 127.7 (1C, C₆H₅), 128 (2C, C₆H₅), 139.7 (1C, C₆H₅), 156.1 (1C, C=O). **¹¹⁹Sn NMR (CDCl₃, 300 K):** -24.0 (83%) and -16.7 (17%). [a]_D¹⁹ = -42.8 (c = 1.3, CHCl₃).

5a



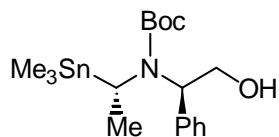
¹H NMR (C₆D₆, 340 K): 0.8-1.5 (m, 21H, (CH₃CH₂CH₂CH₂)₃Sn), 1.52 (s, 9H, (CH₃)₃C), 1.63 (d, 3H, CH₃CH, ³J(H,H) = 7.2 Hz), 1.55-1.72 (m, 7H, (CH₃CH₂CH₂CH₂)₃Sn, + OH), 2.93 (q,

1H, CHCH₃, ³J(H,H) = 7.2 Hz, ²J(Sn,H) = 50.1 Hz), 3.95-4.15 (m, 2H, CH₂OH), 5.4 (t, 1H, CHC₆H₅, ³J(H,H) = 6.5 Hz), 7.15-7.25 (m, 5H, C₆H₅). **¹³C NMR (C₆D₆, 340K):** 11.1 (3C, (CH₃CH₂CH₂CH₂)₃Sn, ¹J(Sn,C) = 307-320 Hz), 13.9 (3C, (CH₃CH₂CH₂CH₂)₃Sn), 20.0 (1C, CH₃CH), 28.0 (3C, (CH₃CH₂CH₂CH₂)₃Sn, ³J(Sn,C) = 56.2 Hz), 28.7 (3C, (CH₃)₃C), 29.7 (3C, (CH₃CH₂CH₂CH₂)₃Sn, ²J(Sn,C) = 17.7 Hz), 40.2 (1C, SnCH, ¹J(Sn,C) = 373-389 Hz), 62.6 (1C, CHC₆H₅), 62.7 (1C, CH₂OH), 80.0 (1C, (CH₃)₃C), 127.8-128.3 (5C, C₆H₅), 139.3 (1C, C₆H₅), 156.3 (1C, C=O). **¹¹⁹Sn NMR (CDCl₃, 300K):** -20.0 (76%), -15.0 (24%). [a]_D¹⁹ = +2 (c = 0.6, CHCl₃).

N-[1-(Trimethylstannylyl)ethyl]-N-[(2-hydroxy-(1*R*)-phenyl)ethyl]-*t*-butylcarbamate

C₁₈H₃₁NO₃Sn (428.15): C 50.49; H 7.30; N 3.27; found: C 50.24; H 7.25; N 3.21
IR (n cm⁻¹): 3425, 2980, 2920, 2850, 1675, 1420, 1360, 1150, 750, 690. **MS (70 eV, EI): m/z (%):** **Stannylated fragments:** 414(2), 358(8), 340(4), 328(4), 298(1), 282(2), 252(2), 238(3), 220(3), 208(9), 192(5), 165(57), 150(6), 135(12); **Organic fragments:** 190(14), 164(100); 146(17); 132(20), 121(23), 105(19), 104(26), 103(29), 91(17), 77(14), 59(14), 57(83), 44(60), 41(29), 29(12).

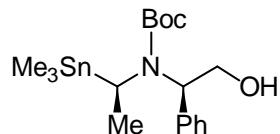
4b



¹H NMR (C₆D₆, 340K): 0.22 (s, 9H, (CH₃)₃Sn, ²J(Sn,H) = 50.6-52.7 Hz), 1.12 (d, 3H, CH₃CH, ³J(H,H) = 7.3 Hz, ³J(Sn,H) = 59.2-61.9 Hz), 1.38 (s, 9H, (CH₃)₃C), 2.86 (q, 1H, CH₃CH, ³J(H,H) = 7.3 Hz, ²J(Sn,H) = 47.0 Hz), 3.8 (dd, 1H, CH₂OH, ²J(H,H) = 10.9 Hz, ³J(H,H) = 6.2 Hz), 3.9 (dd, 1H, CH₂OH, ²J(H,H) = 10.9 Hz, ³J(H,H) = 7.8 Hz), 5.13 (dd, CHC₆H₅, ³J(H,H) = 6.2 Hz, ³J(H,H) = 7.8 Hz), 7.1-7.2 (m, C₆H₅). **¹³C NMR (C₆D₆, 300K):** -7.3 (3C, (CH₃)₃Sn, ¹J(Sn,C) = 318 Hz), 18.6 (1C, CH₃CH), 29.1 (3C, (CH₃)₃C), 42.4 (1C, CH₃CH), 62.9 and 63.1 (2C, CH₂OH and CHC₆H₅), 80.4 (1C, (CH₃)₃C), 126.4-129.1 (5C, C₆H₅), 139.9 (1C, C₆H₅),

156.5 (1C, C=O). **¹¹⁹Sn NMR (C₆D₆, 300 K):** -9.5. [a]_D¹⁹ = -72.2 (c = 1.03, CHCl₃). m.p. = 64°C.

5b



¹H NMR (C₆D₆, 340K): 0.04 (s, 9H, (CH₃)₃Sn), ²J(Sn,H) = 52.5 Hz), 1.40 (s, 9H, (CH₃)₃C), 1.45 (d, 3H, CH₃CH, ³J(H,H) = 7.3 Hz, ³J(Sn,H) = 58.8-61.6 Hz), 2.66 (q, 1H, CH₃CH₂, ³J(H,H) = 7.3 Hz), 3.88 (m, 2H, CH₂OH), 5.31 (m, 1H, CHC₆H₅), 7.15 (m, 5H, C₆H₅). **¹³C NMR (C₆D₆, 340K):** -7.6 (3C, (CH₃)₃Sn), 19.6 (1C, CH₃CH), 30.8 (3C, (CH₃)₃C), 41.2 (1C, CH₃CH), 62.6 (2C, CHC₆H₅ and CH₂OH), 80.3 (1C, (CH₃)₃C), 128.3-129.2 (5C, C₆H₅), 139.7 (1C, C₆H₅), 156.6 (1C, C=O). **¹¹⁹Sn NMR (C₆D₆, 300 K):** -5.4. [a]_D¹⁹ = +7.5 (c = 1.06, CHCl₃).

4. X-ray analysis of the compound 3d-trans

$C_{20}H_{29}NO_4$, Mr = 347.44, monoclinic, $P\bar{2}_1$, $a = 5.7052(1)$, $b = 18.4464(6)$, $c = 8.8758(3) \text{ \AA}$, $\beta = 97.681(1)^\circ$, $V = 925.71(5) \text{ \AA}^3$, $Z = 2$, $D_x = 1.246 \text{ Mg.m}^{-3}$, $\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$, $\mu = 0.86 \text{ cm}^{-1}$, $F(000) = 376$, $T = 120 \text{ K}$. The sample (0.45*0.12*0.12 mm) is studied on a NONIUS Kappa CCD with graphite monochromatized MoK α radiation. The cell parameters are obtained with Denzo and Scalepack (Otwinowski & Minor, 1997) with 10 frames (psi rotation : 1° per frame). The data collection (Nonius, 1999) ($2\theta_{\max} = 54^\circ$, 164 frames via 1.9° omega rotation and 15 s per frame, range HKL : H 0.7 K 0.23 L -11.11) gives 12154 reflections. The data reduction with Denzo and Scalepack (Otwinowski & Minor, 1997) leads to 4217 independent reflections from which 3579 with $I > 2.0\sigma(I)$. The structure was solved with SIR-97 (Altomare & al., 1998) which reveals the non hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms may be found with a Fourier Difference. The whole structure was refined with SHELXL97 (Sheldrick, 1997) by the full-matrix least-square techniques (use of F square magnitude ; x, y, z, β_{ij} for C, O and N atoms, x, y, z in riding mode for H atoms ; 227 variables and 3579 observations with $I > 2.0\sigma(I)$; calc w=1/[$\sigma^2(Fo^2) + (0.077P)^2 + 0.028P$] where $P=(Fo^2+2Fc^2)/3$ with the resulting $R = 0.057$, $R_w = 0.111$ and $S_w = 0.997$, $\Delta\rho < 0.24 \text{ e\AA}^{-3}$.

Atomic scattering factors from International Tables for X-ray Crystallography (1992). Ortep views realized with PLATON98 (Spek, 1998).

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5. X-ray analysis of the compound 4b

$C_{18}H_{31}NO_3Sn$, Mr = 428.13, orthorhombic, P 2₁2₁2₁, a = 10.696(6), b = 12.306(3), c = 16.009(8) Å, V = 2107(2) Å³, Z = 4, D_x = 1.350 Mg.m⁻³, $\lambda(MoK\alpha)$ = 0.71073 Å, μ = 12.25 cm⁻¹, F(000) = 880, T = 293 K. The sample (0.28*0.25*0.08 mm) is studied on an automatic diffractometer CAD4 NONIUS with graphite monochromatized MoK α radiation (Fair, 1990). The cell parameters are obtained by fitting a set of 25 high-theta reflections. The data collection ($2\theta_{max}$ = 54°, scan $\omega/2\theta$ = 1, t_{max} = 60 s, range HKL : H 0.10 K 0.14 L 0.19, intensity controls without appreciable decay (0.6%) gives 2281 reflections from which 2143 with $I > 2.0\sigma(I)$. After Lorenz and polarization corrections, absorption corrections with psi scan (Spek, 1997) the structure was solved with SIR-97 (Altomare & al., 1998) which reveals the non hydrogen atoms of the structure. After anisotropic refinement, all the hydrogène atoms are found with a Fourier Difference. The whole structure was refined with SHELXL97 (Sheldrick, 1993) by the full-matrix least-square techniques (use of F magnitude ; x, y, z, β_{ij} for Sn, C, N and O atoms, x, y, z in riding mode for H atoms ; 209 variables and 2281 observations with $I > 2.0\sigma(I)$; calc w = 1/[$\sigma^2(Fo^2)$ + (0.0548P)² + 0.1911P] where P = (Fo²+2Fc²)/3 with the resulting R = 0.024, R_w = 0.065 and S_w = 0.986 (residual $\Delta\rho$ = 0.55 eÅ⁻³). Absolute configuration was verified with the Flack parameter (Flack, 1983) 0.1(2). Atomic scattering factors from International Tables for X-ray Crystallography (1974). Ortep views realized with PLATON98 (Spek, 1998). All the calculations were performed on a Silicon Graphics Indy computer.

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Table 1. Crystallographic Data for compounds **3d-trans** and **4b**

	3d-trans	4b
Empirical formula	C ₂₀ H ₂₉ NO ₄	C ₁₈ H ₃₁ NO ₃ Sn
Formula weight	347.44	428.13
Temperature (K)	120(1)	293(2)
Diffractometer	Kappa CCD	CAD4
Wavelength (Å)	0.71069	0.71069
Crystal size (mm)	0.45 x 0.12 x 0.12	0.28 x 0.25 x 0.08
Cryst syst	monoclinic	orthorhombic
Space group	P 2 ₁	P 2 ₁ 2 ₁
a (Å)	5.70520(10)	10.696(6)
b (Å)	18.4464(6)	12.306(3)
c (Å)	8.8758(3)	16.009(8)
β (deg)	97.6810(10)	
Volume (Å ³)	925.71(5)	2107.2(17)
Z	2	4
Density (calculated) (Mg.m ⁻³)	1.246	1.350
Absorption coefficient (mm ⁻¹)	0.086	1.225
F(000)	376	880
Theta range for data collection (deg)	2.32 to 27.47	2.09 to 26.95
Index ranges		
<i>H</i>	-7 to 7	0 to 10
<i>K</i>	-23 to 23	0 to 14
<i>L</i>	-11 to 11	0 to 19
Reflections collected	4217	2281
Independent reflections	4217 [R(int) = 0.0000]	2281 [R(int) = 0.0000]
Reflections observed [I>2 σ(I)]	3579	2143
Data Completeness	0.999	0.999
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	4217 / 1 / 227	2281 / 0 / 209
Goodness-of-fit on <i>F</i> ²	1.019	0.986
Final R indices [I>2 σ(I)]	R1 ^a = 0.0440 wR2 ^b = 0.1112	R1 ^a = 0.0241, wR2 ^b = 0.0655
R indices (all data)	R1 ^a = 0.0579 wR2 ^b = 0.1227	R1 ^a = 0.0281, wR2 ^b = 0.0675
Absolute structure parameter	0.6(9)	0.03(3)
Flack parameter	-	0.1(2)
Extinction coefficient	0.049(7)	0.0011(4)
Largest diff. peak and hole (e.Å ⁻³)	0.239 and -0.248	0.552 and -0.352

^a R1 = $\sum(|F_o| - |F_c|) / \sum |F_o|$. ^b wR2 = $[\sum w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$ where $w=1/[\sigma^2(F_o)^2 + (uP)^2 + vP]$ where $P = (F_o^2 + 2F_c^2)/3$, $u = 0.0771$ and $v = 0.0278$; for **3d-trans** and $u = 0.055$ and $v = 0.191$; for **4b**.