Addition of Bu_3SnLi to *t*-Butanesulfinimines as an Efficient Route to Chiral, Non-racemic α-Aminoorganostannanes

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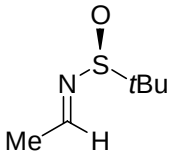
Supporting Information

General Experimental

All reactions were performed using flame-dried glassware under an argon atmosphere. Diethyl ether and THF were freshly distilled from Na/benzophenone. (*R*)- and (*S*)-*t*-butanesulfinamide were prepared from the appropriate *cis*-1-amino-2-indanol as reported by the Sepracor group.[1] ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 and 75 MHz, respectively. Optical rotations were recorded in cells with 10 cm path length on a Perkin-Elmer 241 digital polarimeter.

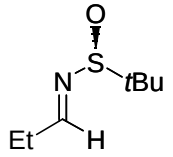
General procedure for synthesis of enantiomerically pure sulfinimines 4. t-Butanesulfinimines were prepared by condensation of (*R*)- or (*S*)-*t*-butanesulfinamide with aldehydes as described by Ellman.[2] Our (*R*)-*t*-butanesulfinamide showed $[\alpha]_D$ = +4.6 (c 0.8, $CHCl_3$); lit[2]: $[\alpha]_D$ = +4.9 (c 1.0, $CHCl_3$). Our (*S*)-*t*-butanesulfinamide showed $[\alpha]_D$ = -5.1 (c 0.6, $CHCl_3$). Spectral data are as follows:

(S_S)-*N*-(Ethylidene)-*t*-butanesulfinamide (4a)[3]



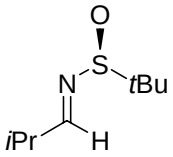
$[\alpha]_D$ = -94.8 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ7.94 (1H, q, J = 5.1 Hz), 2.34 (3H, d, J = 5.1 Hz), 1.09 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ165.8, 56.3, 55.0, 22.1.

(S_S)-*N*-(Propylidene)-*t*-butanesulfinamide (4b)



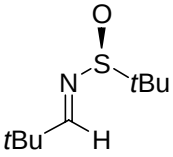
$[\alpha]_D$ = +294.6 (c 1.0, $CHCl_3$), lit for (R_S)-**4b**[2] $[\alpha]_D$ = -328.5 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ7.94 (1H, t, J = 4.2 Hz), 2.39 (2H, dq, J = 7.4, 4.2 Hz), 1.04 (9H, s), 1.03 (3H, t, J = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ169.9, 56.1, 29.2, 22.0, 9.3.

(S_S)-*N*-(Isobutylidene)-*t*-butanesulfinamide (4c)



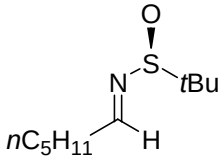
$[\alpha]_D$ = +299.9 (c1.0, $CHCl_3$), lit[2] for (R_S)-**4c**: $[\alpha]_D$ = -259.4 (c1.0, $CHCl_3$); ; ^{1}H NMR (300 MHz, $CDCl_3$) δ7.91 (1H, d, J = 4.4 Hz), 2.64 (1H, dsept, J = 6.9, 4.4 Hz), 1.11 (9H, s), 1.05 (3H, d, J = 6.9 Hz), 1.04 (3H, d, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ173.4 56.3, 34.7, 22.2, 18.8.

(S_S)-*N*-(Neopentylidene)-*t*-butanesulfinamide (4d)



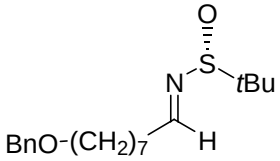
$[\alpha]_D$ = +104.3 (c 1.0, $CHCl_3$), lit[3] for (R_S)-**4d**: $[\alpha]_D$ = -285 (c1.0, $CHCl_3$); ; ^{1}H NMR (300 MHz, $CDCl_3$) δ7.89 (1H, s), 1.15 (9H, s), 1.13 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ175.6, 56.5, 37.9, 26.7, 22.3.

(S_S)-*N*-(Hexylidene)-*t*-butanesulfinamide (4e)



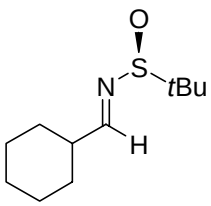
$[\alpha]_D$ = +240.3 (c = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ8.00 (1H, t, J = 4.7 Hz), 2.45 (2H, dt, J = 7.4, 4.7 Hz), 1.57 (2H, m), 1.28 (4H, m), 1.13 (9H, s), 0.83 (3H, m); ^{13}C NMR (300 MHz, $CDCl_3$) δ169.7, 56.4, 36.0, 31.3, 25.1, 22.3, 22.2, 13.8

(R_S)-*N*-(8-Benzyloxyoctylidene)-*t*-butanesulfinamide (4f)



$[\alpha]_D$ = -142.0 (c = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ8.03 (1H, t, J = 4.7 Hz), 7.30 (5H, m), 4.46 (2H, s), 3.43 (2H, t, J = 6.5 Hz), 2.47 (2H, dt, J = 7.3, 4.7 Hz), 1.58 (4H, m), 1.41-1.27 (6H, m), 1.16 (9H, s); ^{13}C NMR (300 MHz, $CDCl_3$) δ169.6, 138.5, 128.2, 127.5, 127.4, 72.8, 70.2, 56.4, 36.0, 29.6, 29.1, 25.9, 25.3, 22.2 (2C); IR (neat) 1721, 1622, 1363, 1086 cm^{-1}; MS (ESI) *m/z* 338 (M+H), 355 (M+NH_4), 360 (M+Na); Anal. Calcd for $C_{19}H_{31}NO_2S$: C, 67.61; H, 9.26; N, 4.15. Found: C, 67.36; H, 9.32; N, 4.00.

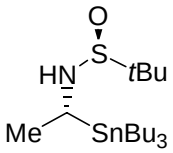
(S_S)-*N*-(Cyclohexylmethylidene)-*t*-butanesulfinamide (4g)[4]



$[\alpha]_D$ = -173.8 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ7.93 (1H, d, J = 4.5 Hz), 2.43 (1H, m), 1.96-1.55 (5H, m), 1.45-1.23 (5H, m), 1.16 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ172.5, 56.3, 43.8, 29.1, 25.7, 25.2, 22.1.

General procedure for the synthesis of α-sulfinamidostannanes 5. A flame dried round bottom flask equipped with a stir bar and septum was charged with dry THF (10 mL) while being kept under argon. Upon cooling the solution to 0 °C, diisopropylamine (4.0 mmol, 1.3 eq) was added via syringe, followed by *n*-butyllitihium (1.6 M, 4.0 mmol, 1.3 eq). The solution was stirred for 15 min. at 0 °C. Tributyltin hydride (4.0 mmol, 1.3 eq) was then added via syringe and the solution stirred for another 15 min. at 0 °C before cooling to –78 °C. The sulfinimine (3.64 mmol) was dissolved in dry THF (1 mL) and added dropwise to the stirring solution. Upon completion of the addition, the solution was stirred at –78 °C for 1 h. The reaction was quenched cold with methanol (2 mL), then saturated aqueous ammonium chloride (5 mL), and allowed to warm to room temperature. The mixture was diluted with diethyl ether (100 mL) and water (15 mL), and the ether layer washed with brine (20 mL), dried with sodium sulfate, and filtered through a pad of Celite®. The ether layer was evaporated under reduced pressure to afford a clear colorless oil, which was purified via flash column chromatography (30 g of silica/g of crude material, 5:1 hexane:ethyl acetate) to provide sulfinamides **5** in the yields reported in Table 1.

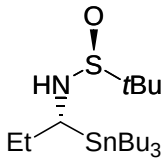
(*S*$_S$,*R*)-*N*-(1-Tributylstannylethyl)-*t*-butanesulfinamide (5a)



$[\alpha]_D$ = +51.2 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ3.32 (1H, dq, J = 7.4, 8.4 Hz), 3.02 (1H, d, J = 8.4 Hz), 1.60-1.33 (6H, m), 1.49 (3H, d, J = 7.4 Hz), 1.33-1.18 (6H, m), 1.14 (9H, s), 0.97-0.75 (15H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ55.7 42.2 (^{1}J = 347 Hz), 29.1 (^{2}J = 20 Hz), 27.4 (^{3}J = 54 Hz),

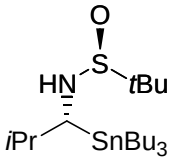
23.1, 22.6, 13.6, 8.9 (^{1}J = 315, 301 Hz); IR (neat) 3436, 3195, 1464, 1056 cm^{-1}; MS (ESI) *m/z* 440 (M+H), 462 (M+Na); Anal. Calcd for $C_{18}H_{41}NOSSn$: C, 49.33; H, 9.43; N, 3.20. Found: C, 49.60; H, 9.24; N, 3.50.

(S_S,*R*)-*N*-(1-Tributylstannylpropyl)-*t*-butanesulfinamide (5b)



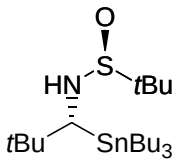
$[\alpha]_D$ = +35.1 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ3.27 (1H, m), 3.14 (1H, d, J = 8.5 Hz), 1.83 (2H, m), 1.55-1.32 (6H, m), 1.30-1.17 (6H, m), 1.12 (9H, s), 0.92-0.78 (18H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ55.8 49.9 (^{1}J = 344 Hz), 29.6, 29.1 (^{2}J = 20 Hz), 27.4 (^{3}J = 57 Hz), 22.6, 13.5, 12.4, 9.4 (^{1}J = 314, 300 Hz); IR (neat) 3198, 1464, 1056 cm^{-1}; MS (ESI) *m/z* 454 (M+H), 476 (M+Na); Anal. Calcd for $C_{19}H_{43}NOSSn$: C, 50.45; H, 9.58; N, 3.10. Found: C, 50.23; H, 9.36; N, 3.12.

(S_S,*R*)-*N*-(1-Tributylstannyl-2-methylpropyl)-*t*-butanesulfinamide (5c)



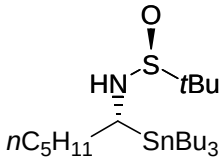
$[\alpha]_D$ = +18.0 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ3.30 (2H, m), 2.26 (1H, dsept, J = 3.0, 6.7 Hz), 1.45-1.42 (6H, m), 1.30-1.23 (6H, m), 1.15 (9H, s), 0.93 (3H, d, J = 6.7 Hz), 0.90-0.81 (18H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ57.2 56.0, 34.1, 29.1, 27.4, 22.6, 21.0, 20.6, 13.6, 10.3; IR (neat) 3226, 1464, 1073 cm^{-1}; MS (ESI) *m/z* 468 (M+H), 490 (M+Na); Anal. Calcd for $C_{20}H_{45}NOSSn$: C, 51.51; H, 9.73; N, 3.00. Found: C, 51.71; H, 9.52; N, 3.05.

(S_S,*R*)-*N*-(1-Tributylstannyl-2,2-dimethylpropyl)-*t*-butanesulfinamide (5d)



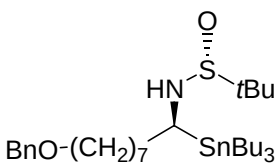
$[\alpha]_D$ = +7.3 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ3.26 (1H, d, J = 8.6 Hz), 3.19 (1H, d, J = 8.6 Hz), 1.55-1.32 (6H, m), 1.36-1.20 (6H, m), 1.18 (9H, s), 0.97 (9H, s), 0.92-0.82 (15H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ62.5 (^{1}J = 361 Hz), 56.3, 36.0, 29.0 (^{2}J = 28 Hz), 28.8, 27.4 (^{3}J = 59 Hz), 22.7, 13.5, 11.2 (^{1}J = 308, 294 Hz); IR (neat) 3251, 1464, 1072 cm^{-1}; MS (ESI) *m/z* 482 (M+H), 504 (M+Na); Anal. Calcd for $C_{21}H_{47}NOSSn$: C, 52.51; H, 9.86; N, 2.92. Found: C, 52.37; H, 9.91; N, 2.98.

(S_S,*R*)-*N*-(1-Tributylstannylhexyl)-*t*-butanesulfinamide (5e)



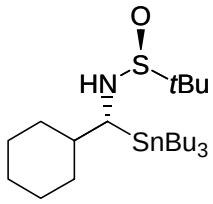
$[\alpha]_D$ = +31.0 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ3.34 (1H, dt, J = 6.42, 8.4 Hz), 3.15 (1H, d, J = 8.4 Hz), 1.90-1.75 (2H, m), 1.55-1.42 (6H, m), 1.35-1.20 (12H, m), 1.16 (9H, s), 0.92-0.82 (18H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ55.6, 48.2 (^{1}J = 346, 331 Hz), 36.7, 31.6, 29.0 (^{2}J = 20 Hz), 27.6 (^{2}J = 23 Hz), 27.3 (^{3}J = 56 Hz), 22.5, 22.4, 13.8, 13.4, 9.4 (^{1}J = 313, 299 Hz); IR (neat) 3192, 1464, 1056 cm^{-1}; MS (ESI) *m/z* 496 (M+H), 518 (M+Na); Anal. Calcd for $C_{22}H_{49}NOSSn$: C, 53.44; H, 9.99; N, 2.83. Found: C, 53.42; H, 9.86; N, 2.76.

(R_S,*S*)-*N*-(8-Benzyloxy-1-tributylstannyloctyl)-*t*-butanesulfinamide (5f)



$[\alpha]_D$ = -23.4 (c 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ7.30 (5H, m), 4.45 (2H, s), 3.42 (2H, t, J = 6.6 Hz), 3.33 (1H, dt, J = 6.3, 8.4 Hz), 3.15 (1H, d, J = 8.4 Hz), 1.90-1.75 (2H, m), 1.63-1.40 (8H, m), 1.41-1.20 (14H, m), 1.16 (9H, s), 0.91-0.83 (15H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ138.6, 128.2, 127.5, 127.3, 72.7, 70.2, 55.7, 48.3, 36.8, 29.6, 29.4, 29.2, 29.1, 28.0, 27.4 (^3J = 55 Hz), 22.6, 22.2, 13.6, 9.5 (^1J = 313, 299 Hz); IR (neat) 3196, 1455, 1362, 1073 cm^{-1}; MS (ESI) *m/z* 630 (M+H), 652 (M+Na); Anal. Calcd for $C_{31}H_{59}NO_2SSn$: C, 59.23; H, 9.46; N, 2.23. Found: C, 59.22; H, 9.23; N, 2.15.

(*S*$_S$,*R*)-*N*-(1-Tributylstannyl-1-cyclohexylmethyl)-*t*-butanesulfinamide (5g)



$[\alpha]_D$ = -2.6 (c 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ3.28 (2H, s), 1.92-1.18 (23H, m), 1.14 (9H, s), 1.00-0.79 (15H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ56.2, 55.9, 44.2, 32.0 (^2J = 30 Hz), 31.1, 29.1 (^2J = 19 Hz), 27.4 (^3J = 58 Hz), 26.2, 26.1, 22.6, 13.5, 10.3 (^1J = 311, 298 Hz); IR (neat) 3234, 1449, 1072 cm^{-1}; MS (ESI) *m/z* 508 (M+H), 530 (M+Na); Anal. Calcd for $C_{23}H_{49}NOSSn$: C, 54.55; H, 9.75; N, 2.77. Found: C, 54.70; H, 9.50; N, 2.74.

General procedure for the synthesis of enantiomerically enriched α-benzamidostannanes 6. Into a flame dried round bottom flask equipped with a stir bar was weighed the sulfinamide **5** (0.18 mmol). The flask was then charged with dry THF (3 mL) while being kept under argon, and then cooled to –78 °C. *n*-Butyllithium (1.6 M, 0.27 mmol, 1.5 eq) was then added via syringe, and the solution stirred for 15 min. Benzoic anhydride (0.54 mmol, 3 eq) was dissolved in dry THF (0.5 mL) and added rapidly to the sulfinamide solution. The solution was allowed to warm to room temperature, and then stirred for 1 h. The reaction was quenched with saturated aqueous sodium bicarbonate (3 mL), diluted

with diethyl ether (30 mL) and water (5 mL), and the ether layer washed with 1 M sodium hydroxide solution (10 mL) and then brine (10 mL). The ether layer was then dried with sodium sulfate, and filtered through a pad of Celite®. The ether layer was evaporated under reduced pressure to afford the *N*-benzoyl α-sulfinamidostannanes as a clear colorless oil, which was purified via flash column chromatography (30 g of silica/g of crude material, 10:1 hexane:ethyl acetate).

The acyl sulfinamide (0.20 mmol) was weighed into a round bottom flask equipped with a stir bar and argon line and dissolved in dry methanol (2.5 mL). Concentrated HCl (0.5 mL) was added dropwise, and the solution stirred at room temperature for 30 min. The reaction was quenched with saturated sodium bicarbonate (10 mL), and diluted with CH_2Cl_2 (30 mL) and water (5 mL). The CH_2Cl_2 layer was washed with saturated sodium bicarbonate (10 mL) and then brine (10 mL), dried with sodium sulfate, and filtered through a pad of Celite®. The CH_2Cl_2 was evaporated under reduced pressure to afford a clear colorless oil which was purified via flash column chromatography (30 g of silica/g of crude material, 10:1 hexane:ethyl acetate).

General procedure for the synthesis of racemic α-benzamidostannanes (±)-6. To a cooled (0 ^oC) 0.5 M solution of diisopropylamine (1 mmol, 1 eq) in THF was added *n*BuLi (1 mmol, 1 eq) dropwise, and the resulting solution was stirred for 15 min. Bu_3SnH (1 mmol, 1 eq) was then added dropwise, and the solution was stirred for another 15 min. The resulting slightly yellowish solution of Bu_3SnLi was then cooled to -78 ^oC and the appropriate aldehyde (1 mmol, 1 eq) was added dropwise. The reaction was stirred at -78 ^oC for 30 min., quenched with saturated aqueous NH_4Cl (20 mL), and allowed to warm to room temperature. The solution was diluted with 50 mL of Et_2O, the layers were separated, and the aqueous layer washed with 20 mL of Et_2O. The organic layers were washed with brine (20 mL), dried with $MgSO_4$, filtered, and concentrated *in vacuo* (room temperature water bath) to afford the crude α-hydroxystannane as a colorless oil.

The crude hydroxystannane was made as a 0.5 M solution in THF, and cooled to 0 ^{o}C. To the cooled solution was added phthalimide (1.3 mmol, 1.3 eq), and triphenylphosphine (1.3 mmol, 1.3 eq). A 3 M solution of DEAD (1.3 mmol, 1.3 eq) in THF was then added dropwise slowly to the stirring solution through a dropping funnel. The cooling bath was removed and the solution stirred at room temperature for 30 min. The THF was removed *in vacuo* and the resulting yellow oil extracted 4 times with 30 mL each of hexanes. The combined hexanes extracts were washed with a small amount (10 mL) of acetonitrile and then concentrated *in vacuo* to give the stannyl phthalimide as a yellow oil which was purified via flash column chromatography (20 g silica/ g substrate, 2-10% diethyl ether/hexanes).[5]

The appropriate phthalimide (0.30 mmol) was weighed into a round bottom flask equipped with a stir bar and argon line, and dissolved in ethanol (7 mL). Water (3 drops) was added to the solution, followed by hydrazine monohydrate (9.0 mmol, 30 eq), and the solution was refluxed for 4 hours. The ethanol was evaporated under reduced pressure and the residue dissolved in diethyl ether (40 mL). The ether layer was washed with brine (10 mL), dried with sodium sulfate, filtered through a pad of Celite® and evaporated under reduced pressure to afford the crude α-aminostannane as a clear colorless oil.

The crude α-aminostannane was dissolved in dry CH_2Cl_2 (5 mL) and added to a dry round bottom flask equipped with a stir bar and argon line. The solution was cooled to 0 ^{o}C and triethylamine (0.60 mmol, 2 eq) was added, followed by benzoyl chloride (0.45 mmol, 1.5 eq), and finally DMAP (0.03 mmol, 0.1 eq). The solution was allowed to warm to room temperature and stirred overnight. The reaction was quenched with saturated sodium bicarbonate (2 mL). The solution was diluted with CH_2Cl_2 (20 mL), and the CH_2Cl_2 layer was washed with 1 M NaOH (10 mL) and then brine (10 mL), dried with sodium sulfate, and filtered through a pad of Celite®. The CH_2Cl_2 was evaporated under reduced pressure to afford a clear orange oil which was purified via

flash column chromatography (30 g of silica/g of crude material, 10:1 hexane:ethyl acetate) to afford a clear colorless oil.

These racemic benzamides were analyzed by HPLC (4.6 x 250 mm ChiralCel OD, 0.25 – 2.5% *i*PrOH/Hexane) in order to separate the two enantiomers. Details are shown in the following Table.

R	**Solvent (% *i*PrOH/Hexane)[a]**	**Flow rate (mL/min)**	**Retention time of 1st enantiomer eluted (min)**	**Retention time of 2nd enantiomer eluted (min)**
Me (**6a**)	1.0	1.0	10.34 (*S*)	17.16 (*R*)
Et (**6b**)	1.0	1.0	8.59 (*S*)	9.53 (*R*)
i-Pr (**6c**)	1.0	1.0	6.83 (*R*)	7.81 (*S*)
n-C_5H_{11} (**6e**)	1.0	1.0	7.19 (*S*)	8.66 (*R*)
$BnO(CH_2)_7$ (**6f**)	2.5	1.0	12.05 (*S*)	14.76 (*R*)
c-C_6H_{11} (**6g**)	0.25	0.5	20.18 (*S*)	21.58 (*R*)

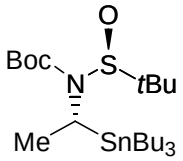
Authentic samples of enantiomerically enriched **6b**, **6c**, and **6e** of known absolute configuration[5] were prepared and co-injected with racemic mixtures to determine the order of elution. In all cases, except R = *i*-Pr, the *R*-enantiomer eluted second. Absolute configurations were assigned on the basis of relative elution times. The rotations of the sulfinamides **5** and of the final N-Boc aminostannanes **8** are also internally consistent with the assigned configurations (See Table below). Only the cyclohexyl series, which shows low rotations, is anomalous.

R	**Optical Rotation $[\alpha]_D$ (c 1.0, $CHCl_3$)**	
	Sulfinamide 5	***N*-Boc Aminostannane 8**
Me	+ 51.2 (S_S,*R*)	+37.0 (*R*)
Et	+ 35.1 (S_S,*R*)	+21.4 (*R*)
i-Pr	+18.0 (S_S,*R*)	+5.6 (*R*)
n-C_5H_{11}	+31.0 (S_S,*R*)	+23.3 (*R*)
c-C_6H_{11}	-2.6 (S_S,*R*)	-1.9 (*R*)
$BnO(CH_2)_7$	-23.4 (R_S,*S*)	-18.2 (*S*)

General procedure for the synthesis of *N*-Boc α-sulfinamidostannanes 7. Into a flame dried round bottom flask equipped with a stir bar was weighed di-*tert*-butyl dicarbonate (1.77 mmol, 3 eq). The flask was then charged with dry THF (2.5 mL) while being kept under argon. The solution was cooled to 0 ^{o}C, following which DMAP (1.77 mmol, 3 eq) was added to the solution. The ice bath was removed and the solution allowed to stir at room temperature for 30 min.

Into a flame dried round bottom flask equipped with a stir bar was weighed sulfinamide **5** (0.59 mmol). The flask was then charged with dry THF (5 mL) while being kept under argon, and then cooled to –78 ^{o}C. *n*-Butyllithium (1.6 M, 1.77 mmol, 3 eq) was then added via syringe, and the solution stirred for 15 min. The Boc_2O/DMAP solution was drawn into a syringe, and added rapidly to the sulfinamide solution, following which the –78 ^{o}C bath was removed immediately. The solution was allowed to stir at room temperature for 1 h, and then quenched with saturated aqueous ammonium chloride (3 mL). The mixture was diluted with diethyl ether (50 mL) and water (10 mL), and the ether layer washed with brine (10 mL), dried with sodium sulfate, and filtered through a pad of Celite®. The ether layer was evaporated under reduced pressure yielding a clear orange oil, which was purified via flash column chromatography (30 g of silica/g of crude material, 5-10% diethyl ether/hexane) to afford a clear colorless oil.

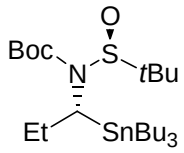
(*S*$_S$,*R*)-*N*-Boc-*N*-(1-tributylstannylethyl)-*t*-butanesulfinamide (7a)



$[\alpha]_D$ = -33.6 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ3.52 (1H, q, J = 7.5 Hz), 1.56-1.36 (9H, m), 1.41 (9H, s), 1.35-1.20 (6H, m), 1.17 (9H, s), 0.93-0.72 (15H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ154.3, 81.8, 58.9, 32.0, 28.9, 28.2, 27.5, 22.7, 18.5, 13.6, 9.8; IR (neat) 1698, 1457, 1093 cm^{-1}; MS

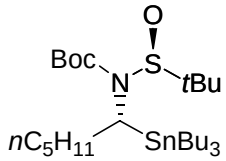
(ESI) *m/z* 540 (M+H), 562 (M+Na); Anal. Calcd for $C_{23}H_{49}NO_3SSn$: C, 51.31; H, 9.17; N, 2.60. Found: C, 51.50; H, 9.31; N, 2.64.

(S_S,*R*)-*N*-Boc-*N*-(1-tributylstannylpropyl)-*t*-butanesulfinamide (7b)



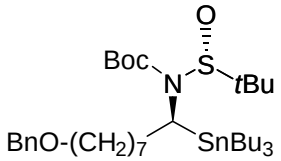
$[\alpha]_D$ = -35.2 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ3.26 (1H, dd, J = 12.5, 3.1 Hz), 2.21 (1H, m), 1.65-1.36 (7H, m), 1.42 (9H, s), 1.35-1.19 (6H, m), 1.16 (9H, s), 0.92-0.74 (18H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ154.4, 81.8, 59.0, 40.0, 29.0, 28.2, 27.5, 25.9, 22.6, 13.6, 12.3, 10.1; IR (neat) 1698, 1458, 1092 cm^{-1}; MS (ESI) *m/z* 554 (M+H), 576 (M+Na); Anal. Calcd for $C_{24}H_{51}NO_3SSn$: C, 52.18; H, 9.31; N, 2.54. Found: C, 51.98; H, 9.34; N, 2.55.

(S_S,*R*)-*N*-Boc-*N*-(1-tributylstannylhexyl)-*t*-butanesulfinamide (7e)



$[\alpha]_D$ = -53.2 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ3.35 (1H, dd, J = 12.5, 3.1 Hz), 2.23 (1H, m), 1.61-1.36 (7H, m), 1.43 (9H, s), 1.37-1.20 (12H, m), 1.17 (9H, s), 0.95-0.72 (18H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ154.5, 81.8, 59.1, 38.4, 33.0, 31.8, 29.0, 28.3, 27.7, 27.5, 22.7, 22.6, 13.9, 13.6, 10.2; IR (neat) 1698, 1458, 1093 cm^{-1}; MS (ESI) *m/z* 596 (M+H), 618 (M+Na); Anal. Calcd for $C_{27}H_{57}NO_3SSn$: C, 54.55; H, 9.66; N, 2.36. Found: C, 54.74; H, 10.00; N, 2.40.

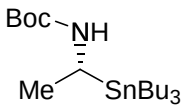
(R_S, *S*)-*N*-Boc-*N*-(8-Benzyloxy-1-tributylstannyloctyl)-*t*-butanesulfinamide (7f)



$[\alpha]_D$ = +36.3 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ7.30 (5H, m), 4.48 (2H, s), 3.44 (2H, t, J = 6.6 Hz), 3.36 (1H, dd, J = 12.6, 2.7 Hz), 2.24 (1H, m), 1.67-1.39 (9H, m), 1.45 (9H, s), 1.38-1.22 (14H, m), 1.19 (9H, s), 0.94-0.75 (15H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ154.5, 138.6, 128.3, 127.6, 127.4, 81.8, 72.8, 70.4, 59.1, 38.3, 33.0, 29.7, 29.6, 29.5, 29.0, 28.3, 28.0, 27.5, 26.1, 22.7, 13.7, 10.2; IR (neat) 1697, 1456, 1092 cm^{-1}; MS (ESI) *m/z* 730 (M+H), 752 (M+Na); Anal. Calcd for $C_{36}H_{67}NO_4SSn$: C, 59.34; H, 9.27; N, 1.92. Found: C, 59.52; H, 9.10; N, 1.92.

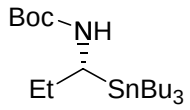
General procedure for the synthesis of *N*-Boc α-aminostannanes 8 from sulfinamides 7. Into a flame dried round bottom flask equipped with a stir bar was weighed the Boc-protected sulfinamide **7** (0.17 mmol). The flask was then charged with dry THF (3 mL) while being kept under argon, and then cooled to –78 ^{o}C. Methyllithium (1.6 M, 0.34 mmol, 2 eq) was then added dropwise via syringe, and the solution was stirred for 15 min. The reaction was quenched cold with saturated aqueous ammonium chloride (2 mL), and allowed to warm to room temperature. The mixture was diluted with diethyl ether (20 mL) and water (5 mL), and the ether layer washed with brine (5 mL), dried with sodium sulfate, and filtered through a pad of Celite®. The ether layer was evaporated under reduced pressure to afford a clear colorless oil, which was purified via flash column chromatography (30 g of silica/g of crude material, 2-5% diethyl ether/hexane) to afford carbamates **8** in the yields reported in Table 2.

(*R*)-*t*-Butyl *N*-(1-tributylstannylethyl)carbamate (8a)



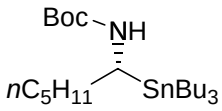
$[\alpha]_D$ = +37.0 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ4.59 (1H, d, J = 7.5 Hz), 3.25 (1H, dq, J = 7.5, 7.5 Hz), 1.58-1.38 (6H, m), 1.40 (9H, s), 1.36-1.20 (9H, m), 0.96-0.74 (15H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ155.7, 78.7, 35.0, 29.1, 28.4, 27.5, 20.7, 13.7, 9.4; IR (neat) 3352, 1702, 1500, 1366 cm^{-1}; MS (ESI) *m/z* 436 (M+H), 458 (M+Na); Anal. Calcd for $C_{19}H_{41}NO_2Sn$: C, 52.55; H, 9.52; N, 3.23. Found: C, 52.71; H, 9.65; N, 3.01.

(*R*)-*t*-Butyl *N*-(1-tributylstannylpropyl)carbamate (8b)[6]



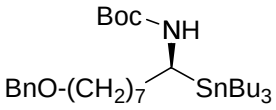
$[\alpha]_D$ = +21.4 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ4.64 (1H, d, J = 7.5 Hz), 3.13 (1H, dt, J = 7.5, 7.5 Hz), 1.76-1.57 (2H, m), 1.57-1.38 (6H, m), 1.40 (9H, s), 1.35-1.20 (6H, m), 0.96-0.73 (18H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ155.9, 78.6, 42.7, 29.2, 28.4, 27.5, 27.2, 13.7, 12.7, 9.6

(*R*)-*t*-Butyl *N*-(1-tributylstannylhexyl)carbamate (8e)[6]



$[\alpha]_D$ = +23.3 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ4.61 (1H, d, J = 7.6 Hz), 3.20 (1H, dt, J = 7.2, 7.6 Hz), 1.70-1.42 (8H, m), 1.39 (9H, s), 1.35-1.16 (12H, m), 0.95-0.73 (18H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ155.9, 78.6, 40.9, 34.9, 31.6, 29.2, 28.4, 27.8, 27.5, 22.6, 14.0, 13.7, 9.7

(*R*)-*t*-Butyl *N*-(8-benzyloxy-1-tributylstannyloctyl)carbamate (8f)

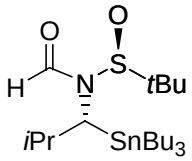


$[\alpha]_D$ = -18.2 (c = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ7.30 (5H, m), 4.62 (1H, d, J = 7.8 Hz), 4.48 (2H, s), 3.44 (2H, t, J = 6.6 Hz), 3.20 (1H, dt, J = 7.8, 7.1 Hz), 1.73-1.40 (10H, m), 1.41 (9H, s),

1.38-1.19 (14H, m), 0.96-0.73 (15H, m); ^{13}C NMR (300 MHz, $CDCl_3$) δ156.0, 138.8, 128.4, 127.7, 127.5, 78.7, 72.9, 70.6, 40.9, 35.0, 29.8, 29.5 (2C), 29.3, 28.5, 28.2, 27.6, 26.3, 13.8, 9.8; IR (neat) 3345, 1698, 1498, 1366 cm^{-1}; MS (ESI) *m/z* 626 (M+H), 648 (M+Na); Anal. Calcd for $C_{32}H_{59}NO_3Sn$: C, 61.54; H, 9.52; N, 2.24. Found: C, 61.60; H, 9.33; N, 2.19.

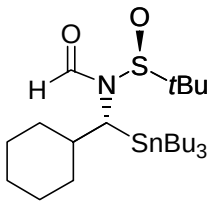
General procedure for the synthesis of *N*-formyl α-sulfinamidostannanes 9. Into a flame dried round bottom flask equipped with a stir bar was weighed the sulfinamide **5** (0.40 mmol). The flask was then charged with dry THF (3 mL) while being kept under argon, and then cooled to –78 °C. *n*-Butyllithium (1.6 M, 1.2 mmol, 3 eq) was then added via syringe, and the solution was stirred for 15 min. Methyl formate (1.2 mmol, 3 eq) was then added as quickly as possible and the solution was stirred for 2 h at –78 °C. The reaction was quenched with saturated aqueous ammonium chloride (3 mL), diluted with diethyl ether (30 mL) and water (5 mL), and the ether layer washed with brine (10 mL). The ether layer was then dried with sodium sulfate, and filtered through a pad of Celite®. The ether layer was evaporated under reduced pressure to afford a clear colorless oil, which was purified via flash column chromatography (30 g of silica/g of crude material, 10:1 hexane:ethyl acetate).

(S_S,*R*)-*N*-Formyl-*N*-(1-tributylstannyl-2-methylpropyl)-*t*-butanesulfinamide (9c)



$[\alpha]_D$ = -53.0 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ8.57 (1H, s), 2.54 (1H, d, J = 9.4 Hz), 2.31 (1H, m), 1.43 (6H, m), 1.41-1.22 (6H, m), 1.23 (9H, s), 1.02 (3H, d, J = 6.6 Hz), 0.95-0.79 (18H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ161.9, 59.7, 53.6, 30.9, 29.0, 27.5, 21.8, 21.4, 21.0, 13.6, 11.9; IR (neat) 1660, 1463, 1098 cm^{-1}; MS (ESI) *m/z* 496 (M+H), 518 (M+Na); Anal. Calcd for $C_{21}H_{45}NO_2SSn$: C, 51.02; H, 9.17; N, 2.83. Found: C, 50.93; H, 9.05; N, 2.76.

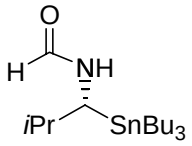
(S_S,*R*)-*N*-Formyl-*N*-(1-tributylstannyl-1-cyclohexylmethyl)-*t*-butanesulfinamide (9g)



$[\alpha]_D$ = +52.2 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ8.56 (1H, s), 2.56 (1H, d, J = 9.5 Hz), 1.92 (2H, m), 1.80-1.36 (11H, m), 1.35-1.22 (10H, m), 1.22 (9H, s), 0.94-0.76 (15H, m); ^{13}C NMR (300 MHz, $CDCl_3$) δ161.9, 59.6, 52.8, 40.0, 32.2, 31.5, 29.0, 27.4, 26.4, 26.2, 26.0, 21.8, 13.6, 11.9; IR (neat) 1659, 1461, 1099 cm^{-1}; MS (ESI) *m/z* 536 (M+H), 558 (M+Na); Anal. Calcd for $C_{24}H_{49}NO_2SSn$: C, 53.94; H, 9.24; N, 2.62. Found: C, 54.04; H, 9.15; N, 2.64.

General procedure for the synthesis of α-formamidostannanes 10. The formyl sulfinamide **9** (0.22 mmol) was weighed into a round bottom flask equipped with a stir bar and argon line and dissolved in dry methanol (2.5 mL). Concentrated HCl (0.5 mL) was added dropwise, and the solution was stirred at room temperature for 4 h. The reaction was quenched with saturated sodium bicarbonate (5 mL), and diluted with CH_2Cl_2 (30 mL) and water (5 mL). The CH_2Cl_2 layer was washed with saturated sodium bicarbonate (10 mL) and then brine (10 mL), dried with sodium sulfate, and filtered through a pad of Celite®. The CH_2Cl_2 was evaporated under reduced pressure to afford a clear colorless oil which was purified via flash column chromatography (30 g of silica/g of crude material, 5:1 hexane:ethyl acetate).

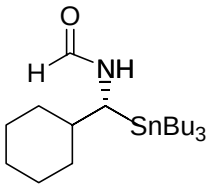
(*R*)-*N*-(1-Tributylstannyl-2-methylpropyl)formamide (10c)



$[\alpha]_D$ = +44.8 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ8.09 (1H, s), 5.98 (1H, d, J = 8.1 Hz), 3.30 (1H, dd, J = 8.0, 8.1 Hz), 2.00 (1H, m), 1.57-1.13 (15H, m), 0.95-0.76 (18H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ160.4, 46.7, 31.8, 29.1, 27.5, 21.6, 20.8, 13.6, 10.3; IR (neat) 3251, 1649, 1375 cm^{-1}; MS

(ESI) *m/z* 414 (M+Na); Anal. Calcd for $C_{17}H_{37}NOSn$: C, 52.33; H, 9.56; N, 3.59. Found: C, 52.48; H, 9.38; N, 3.56.

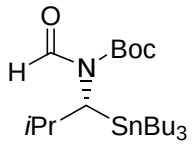
(*R*)-*N*-(1-Tributylstannyl-1-cyclohexylmethyl)formamide (10g)



$[\alpha]_D$ = -29.7 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ8.11 (1H, s), 5.69 (1H, d, J = 8.3 Hz), 3.35 (1H, dd, J = 8.1, 8.1 Hz), 1.81-1.03 (23H, m), 0.97-0.76 (15H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ160.4, 45.8, 41.4, 32.4, 31.6, 29.2, 27.5, 26.3, 26.1, 13.7, 10.4; IR (neat) 3248, 1649, 1376 cm^{-1}; MS (ESI) *m/z* 454 (M+Na); Anal. Calcd for $C_{20}H_{41}NOSn$: C, 55.83; H, 9.60; N, 3.26. Found: C, 58.15; H, 10.00; N, 3.11.

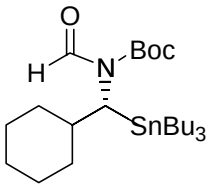
General procedure for the synthesis of *N*-Boc α-formamidostannanes 11. Into a flame dried round bottom flask equipped with a stir bar was weighed the formamidostannane **10** (0.24 mmol). The flask was then charged with dry acetonitrile (10 mL) while being kept under argon, and cooled to 0 ^oC. Boc_2O (0.48 mmol, 2 eq) was added to the solution, followed by triethylamine (0.72 mmol, 3 eq) and finally DMAP (0.024 mmol, 0.1 eq). The ice bath was removed and the solution was stirred at room temperature overnight. The mixture was extracted 3 times with hexane (15 mL, 45 mL in total), and the combined hexane layers were washed with brine (10 mL), dried with sodium sulfate, and filtered through a pad of Celite®. The solvent was evaporated under reduced pressure to afford a clear yellowish oil, which was purified via flash column chromatography (30 g of silica/g of crude material, 10% diethyl ether/hexane).

(*R*)-*N*-Boc-*N*-(1-Tributylstannyl-2-methylpropyl)formamide (11c)



$[\alpha]_D$ = -45.3 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ9.19 (1H, s), 2.22 (1H, m), 1.65-1.37 (7H, m), 1.51 (9H, s), 1.35-1.19 (6H, m), 1.11-0.72 (21H, m); ^{13}C NMR (300 MHz, $CDCl_3$) δ163.4, 153.2, 83.6, 29.1, 28.0, 27.9, 27.5, 21.6, 20.2, 13.7, 10.7, 10.1; IR (neat) 2115, 1733, 1679 cm^{-1}; MS (ESI) *m/z* 492 (M+H), 514 (M+Na); Anal. Calcd for $C_{22}H_{45}NO_3Sn$: C, 53.89; H, 9.25; N, 2.86. Found: C, 54.01; H, 9.14; N, 2.91.

(*R*)-*N*-Boc-*N*-(1-Tributylstannyl-1-cyclohexylmethyl)formamide (11g)

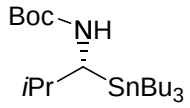


$[\alpha]_D$ = +47.4 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ9.18 (1H, s), 2.00-0.96 (24H, m), 1.50 (9H, s), 0.96-0.68 (15H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ163.4, 153.2, 83.6, 38.3, 32.4, 30.8, 28.9, 28.0, 27.4, 26.5, 26.2, 25.8, 13.7, 10.7, 10.1; IR (neat) 2114, 1732, 1682 cm^{-1}; MS (ESI) *m/z* 532 (M+H), 554 (M+Na); Anal. Calcd for $C_{25}H_{49}NO_3Sn$: C, 56.61; H, 9.31; N, 2.64. Found: C, 56.81; H, 9.17; N, 2.74.

General procedure for the synthesis of *N*-Boc α-aminostannanes 8 from formamides 11. Into a round bottom flask equipped with a stir bar was weighed the Boc-protected formamide **11** (0.10 mmol), which was then dissolved in ethanol (5 mL). A few drops of water were added to the solution, followed by hydrazine monohydrate (3.0 mmol, 30 eq). The solution was refluxed under argon for 2 h. The ethanol was evaporated under reduced pressure, and the residue dissolved in diethyl ether (30 mL). The ether layer was washed with water (10 mL), saturated ammonium chloride (10 mL), and then brine (10 mL). The ether was dried with sodium sulfate and filtered through a pad of Celite®,

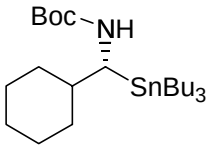
and then evaporated under reduced pressure to afford a clear colorless oil, which was purified via flash column chromatography (30 g of silica/g of crude material, 2-5% diethyl ether/hexane).

(*R*)-*t*-Butyl *N*-(1-tributylstannyl-2-methylpropyl)carbamate (8c)[5]



$[\alpha]_D$ = +5.6 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ4.69 (1H, d, J = 8.4 Hz), 3.08 (1H, dd, J = 7.5, 8.4 Hz), 1.95 (1H, m), 1.59-1.39 (6H, m), 1.40 (9H, s), 1.36-1.21 (9H, m), 1.10-0.72 (18H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ156.0, 78.6, 49.0, 32.7, 29.2, 28.4, 27.6, 21.5, 20.8, 13.7, 10.2

(*R*)-*t*-Butyl *N*-(tributylstannylcyclohexylmethyl)carbamate (8g)[6]



$[\alpha]_D$ = -1.9 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ4.68 (1H, d, J = 7.6 Hz), 3.11 (1H, dd, J = 7.6, 8.2 Hz), 1.82-1.05 (23H, m), 1.40 (9H, s), 0.96-0.73 (15H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ156.1, 78.7, 48.2, 42.4, 32.4, 31.6, 29.3, 28.5, 27.6, 26.6, 26.5, 26.3, 13.8, 10.4

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