Supporting Information

Chiral α,β-Dialkoxy- and α-Alkoxy-β-aminostannanes: Preparation and Copper Mediated Cross-Coupling

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Preparation of α,β-Dialkoxy- and α-Alkoxy-β-aminostannanes: General Procedure

n-Buli (3.8 mL, 9.61 mmol, 2.5 M in THF) was added dropwise to a 0°C solution of (*i*-Pr)$_2$NH (1.34 mL, 9.61 mmol) in anhydrous THF (3 mL) under an argon atmosphere. After 0.5 h, *n*-Bu$_3$SnH (2.79 mL, 9.61 mmol) was added neat over 10 min followed after another 0.5 h by dry $ZnBr_2$ (1.08g, 4.8 mmol) in THF (2 mL). The reaction mixture was maintained at 0ºC for 0.5 h, then cooled to -78ºC, and a prochiral aldehyde (3.84 mmol) in THF (2 mL) was added. After 4 h, the reaction mixture was quenched with saturated aq. NH_4Cl and extracted with Et_2O (3 × 8 mL). The combined ethereal extracts were washed with water, brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was purified by flash SiO_2 chromatography to give the α-hydroxyalkylstannane adduct in 68-77% yield (Table 1). Adducts are somewhat labile and were generally used immediately in the next reaction.

Cross-Coupling: General Procedure

To a stirring, room temperature solution of α,β-dialkoxystannane or α-alkoxy-β-aminostannane (1.0 mmol) and CuI (7-10 mole %) in anhydrous THF (5 ml) was added an organic halide (1.1 mmol) in THF (1 mL) under an argon atmosphere. Larger quantities of CuI encouraged β-elimination. The resulting mixture was heated at 50°C for 3-4 h. After cooling, Et_2O (10 mL) was added and the mixture was filtered. Evaporation of the filtrate under reduced pressure and SiO_2 chromatographic purification of the residue gave the cross-coupled adduct in the indicated yield (Table 2).

Adduct 3

Addition of Zn(*n*-Bu$_3$Sn)$_2$ to (*R*)-2,3-isopropylidene-**D**-glyceradehyde according to the general procedure gave adduct **3** in the indicated yield. TLC (SiO_2): EtOAc/hexane (1:9), R_f = 0.25; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.87-0.96 (m, 15H), 1.28-1.35 (m, 6H), 1.39 (s, 3H), 1.43 (s, 3H), 1.48-1.54 (m, 6H), 1.99-2.01 (m, 1H), 3.83-3.88 (m, 1H), 3.92-3.97 (m, 1H), 4.19-4.21 (m, 1H), 4.30-4.36 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.14, 13.88, 25.86, 26.58, 27.62, 29.29, 65.37, 65.59, 81.21, 108.92; MS *m/z* 422 (M^+); $[\alpha]^{23}_D$ = 11.9º (*c* 1.65, $CHCl_3$).

Adduct **3** (0.025 g, 0.008 mmol) was immediately converted to the Mosher's ester using S-(-)Mosher's acid (0.023 g, 0.009 mmol), DCC (0.02 g, 0.009 mmol), and a catalytic amount of DMAP in CH_2Cl_2 (1 mL) at room temperature for 24 h. The solvent

was removed under reduced pressure and the residue was purified by column chromatography to afforded the Mosher's ester derivative of **3** (98%, ee > 98%). TLC (SiO_2): EtOAc/hexane (1:9), R_f = 0.66; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.86-0.95 (m, 15H), 1.26-1.48 (m, 18H), 3.50 (s, 3H), 3.61 (t, 1H, J = 7.9 Hz), 3.96 (t, 1H, J = 7.9 Hz), 4.33 (q, 1H, J = 6.1 Hz), 5.23 (d, 1H, J = 5.8 Hz), 7.40-7.42 (m, 3H), 7.51-7.52 (m, 2H).

Adduct 5

Addition of Zn(*n*-$Bu_3Sn)_2$ to (*R*)-2,3-*O*-cyclohexylidene-**D**-glyceraldehyde according to the general procedure gave adduct **5** in the indicated yield. TLC (SiO_2): EtOAc/hexane (3:7), R_f = 0.60; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.87-0.94 (m, 15H), 1.29-1.63 (m, 22H), 2.01-2.12 (m, 1H), 3.84 (t, 1H, J = 7.4 Hz), 3.94 (t, 1H, J = 7.35 Hz), 4.17-4.25 (m, 1H), 4.30-4.36 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.14, 13.88, 23.99, 24.88, 25.86, 26.89, 27.62, 28.46, 29.29, 63.66, 64.12, 65.59, 108.92; MS *m/z* 462 (M^+).

As described above for adduct **3**, adduct **5** was immediately converted to the Mosher's ester derivative (95%, ee > 98%); TLC (SiO_2): EtOAc/hexane (1:9), R_f = 0.45; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.86-0.97 (m, 15H), 1.24-1.60 (m, 22H), 3.50 (s, 3H), 3.56 (t, 1H, J = 7.3 Hz), 3.94-3.99 (m, 1H), 4.34 (q, 1H, J = 7.0 Hz), 5.15-5.20 (m, 1H), 7.37-7.42 (m, 3H), 7.50-7.55 (m, 2H).

Adduct 7

Addition of Zn(*n*-$Bu_3Sn)_2$ to (*S*)-N-*tert*-butoxycarbonyl **L**-serinal acetonide according to the general procedure gave adduct **7** in the indicated yield. TLC (SiO_2): EtOAc/hexane (1:9), R_f = 0.29; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.87-1.05 (m, 15H), 1.15-1.60 (m, 27H), 1.99-2.02 (m, 1H), 3.84-3.89 (m, 1H), 3.93-3.99 (m, 1H), 4.20-4.22 (m, 1H), 4.30-4.35 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 10.17, 13.92, 23.99, 27.34, 27.67, 28.05, 28.48, 30.84, 63.70, 64.17, 64.93, 109.5, 199.72; MS *m/z* 521 (M^+).

As described above for adduct **3**, adduct **7** was immediately converted to the Mosher's ester derivative (98%, ee > 98%); TLC (SiO_2): EtOAc/hexane (1:9), R_f = 0.65; ^{1}H NMR (C_6D_6, 60ºC, 400 MHz) δ 0.92-1.12 (m, 15H), 1.32-1.70 (m, 27H), 3.53 (s, 3H), 3.97-4.01 (m, 2H), 4.38-4.40 (m, 1H), 5.82-5.85 (m, 1H), 6.96-7.05 (m, 2H), 7.35-7.37 (m, 1H), 7.61-7.80 (m, 2H).

Adduct 9

Addition of Zn(*n*-$Bu_3Sn)_2$ to N-(*tert*-butoxycarbonyl)-**D**-prolinal according to the general procedure gave adduct **9** in the indicated yield. TLC (SiO_2): EtOAc/hexane (3:7), R_f = 0.57; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.81-0.95 (m, 15H), 1.21-1.60 (m, 21H), 1.65-1.85 (m, 4H), 1.98-2.10 (m, 1H), 3.19-3.27 (m, 1H), 3.48-3.61 (m, 1H), 4.10-4.12 (m, 1H), 4.98-5.02 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.13, 13.28, 23.6, 25.66, 26.44, 28.4, 28.50, 47.19, 60.05, 80.10, 109.02, 156.4; MS *m/z* 491 (M^+).

As described above for adduct **3**, adduct **9** was immediately converted to the Mosher's ester derivative (98%, ee > 95%); TLC (SiO_2): EtOAc/hexane (1:4), R_f = 0.65; ^{1}H NMR (C_6D_6, 400 MHz) δ 0.92-1.11 (m, 15H), 1.34-1.42 (m, 6H), 1.49 (s, 9H), 1.60-1.92 (m, 10H), 2.95-3.01 (m, 1H), 3.25-3.40 (m, 1H), 3.46 (s, 3H), 4.05-4.10 (m, 1H), 6.12 (d, 1H, J = 2.1 Hz), 7.08-7.24 (m, 3H), 7.69 (d, 2H, J = 7.6 Hz).

Adduct 11

To a stirring, 0 °C solution of commercial ethyl (R)-2-hydroxy-4-phenylbutyrate (1 g, 4.8 mmol) in anhydrous CH_2Cl_2 (10 mL) under an argon atmosphere was added diisopropylethylamine (2.5 mL, 14.4 mmol) followed by MOMCl (0.73 mL, 9.6 mmol). After 24 h at rt, the reaction mixture was quenched with water, extracted with CH_2Cl_2 (3 × 8 mL). The combined organic extracts were washed with water, brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was purified by flash SiO_2 chromatography to give the corresponding MOM ether (95%). TLC (SiO_2): EtOAc/hexane (1:4), R_f = 0.53; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.30 (t, 3H, J = 6.8 Hz), 2.05-2.19 (m, 2H), 2.61-2.73 (m, 2H), 3.42 (s, 3H), 4.09-4.24 (m, 3H), 4.75 (q, 2H, J = 6.7 Hz), 7.21-7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ15.46, 30.63, 58.20, 61.08, 75.24, 95.56, 126.37, 128.44, 128.56, 140.30, 173.65.

The above MOM protected ester was reduced to the aldehyde (82%) according to literature method.[1] TLC (SiO_2): EtOAc/hexane (3:7), R_f = 0.35; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.98-2.00 (m, 2H), 2.74-2.77 (m, 2H), 3.44 (s, 3H), 3.88-3.91 (m, 1H), 4.68-4.77 (m, 2H), 7.21-7.42 (m, 5H), 9.60 (d, 1H, J = 2.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 30.12, 58.24, 66.70, 71.43, 95.25, 125.64, 127.77, 127.98, 140.1, 201.99.

The above aldehyde was converted to adduct **11** according to the general procedure in the indicated yield. TLC (SiO_2): EtOAc/hexane (1:4), R_f = 0.36; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.85-0.94 (m, 15H), 1.25-1.34 (m, 6H), 1.44-1.51 (m, 6H), 1.85-2.00 (m, 2H), 2.60-2.80 (m, 2H), 3.42 (s, 3H), 3.75-3.80 (m, 1H), 4.08 (dd, 1H, J = 1.9, 6.3 Hz), 4.60 (dd, 1H, J = 1.95, 6.3 Hz), 4.77 (dd, 1H, J = 2.0, 6.4 Hz), 7.21-7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.10, 12.98, 26.60, 32.20, 33.35, 57.99, 68.25, 71.12, 99.10, 108.56, 126.44, 127.30, 128.21, 141.26; MS m/z 500 (M^+).

As described above for adduct **3**, adduct **11** was immediately converted to the Mosher's ester derivative (95%, ee > 98%). TLC (SiO_2): EtOAc/hexane (1:4), R_f = 0.65; ^{1}H NMR (CDCl3, 400 MHz) δ 0.80-0.87 (m, 15H), 1.20-1.48 (m, 12H), 1.62-1.70 (m, 1H), 1.96-2.03 (m, 1H), 2.63-2.70 (m, 1H), 2.79-2.87 (m, 1H), 3.36 (s, 3H), 3.58 (s, 3H), 3.83-3.87 (m, 1H), 4.57 (d, 1H, J = 7.0 Hz), 4.72 (d, 1H, J = 7.0 Hz), 5.50 (d, 1H, J = 1.5 Hz), 7.19 (t, 3H, J = 6.5 Hz), 7.24-7.38 (m, 3H), 7.38-7.42 (m, 2H), 7.58-7.63 (m, 2H).

Adduct 13

Commercial ethyl (R)-2-hydroxy-4-phenylbutyrate was converted to the corresponding MEM ether (87%) using MEMCl as described above. TLC (SiO_2): EtOAc/hexane (3:7), R_f = 0.22; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.27 (t, 3H, J = 7.3 Hz), 2.22-2.34 (m, 2H), 2.68-2.82 (m, 2H), 3.37 (s, 3H), 3.52-3.56 (m, 2H), 3.68-3.77 (m, 2H), 4.11-4.22 (m, 3H), 4.77-4.88 (m, 2H), 7.17-7.30 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.44, 31.63, 34.75, 59.20, 61.08, 67.78, 71.87, 75.28, 95.46, 126.27, 128.64, 128.66, 141.30, 172.69.

The above MEM protected ester was reduced as reported above to the corresponding aldehyde (88%). TLC (SiO2): EtOAc/hexane (2:3), R_f = 0.35; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.96-2.04 (m, 2H), 2.68-2.84 (m, 2H), 3.37 (s, 3H), 3.52-3.56 (m, 2H), 3.68-3.84 (m, 2H), 3.92-3.97 (m, 1H), 4.78-4.89 (m, 2H), 7.17-7.30 (m, 5H), 9.60 (d, 1H, J = 1.50 Hz); ^{13}C NMR (CDCl3, 75 MHz) δ 31.15, 31.91, 59.26, 67.99, 71.84, 82.01, 96.06, 126.44, 128.67, 128.75, 141.06, 202.90.

The aldehyde above was converted to adduct **13** according to the general procedure above in the indicated yield. TLC (SiO_2): EtOAc/hexane (1:4), R_f = 0.30; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.85-0.94 (m, 15H), 1.25-1.34 (m, 6H), 1.44-1.51 (m, 6H), 1.85-

2.00 (m, 2H), 2.60-2.80 (m, 2H), 3.42 (s, 3H), 3.75-3.80 (m, 2H), 4.08 (dd, 2H, J = 1.9, 6.3 Hz), 4.60 (dd, 2H, J = 1.95, 6.3 Hz), 4.77 (dd, 2H, J = 2.0, 6.4 Hz), 7.21-7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.12, 13.68, 25.66, 26.68, 31.00, 31.95, 59.16, 67.68, 72.14, 82.00, 97.16, 108.56, 126.54, 128.37, 128.35, 140.96; MS *m/z* 544 (M^+).

As described above for adduct **3**, the adduct **13** was immediately converted to the Mosher's ester derivative (97%, ee > 98%). TLC (SiO_2): EtOAc/hexane (1:9), R_f = 0.43; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.79-0.87 (m, 15H), 1.19-1.28 (m, 6H), 1.34-1.44 (m, 6H), 1.60-1.68 (m, 1H), 1.96-2.08 (m, 1H), 2.61-2.69 (m, 1H), 2.79-2.86 (m, 1H), 3.37 (s, 3H), 3.49-3.52 (m, 2H), 3.57 (s, 3H), 3.62-3.76 (m, 2H), 3.84-3.89 (m, 1H), 4.69 (d, 1H, J = 7.3 Hz), 4.83 (d, 1H, J = 7.3 Hz), 5.55-5.62 (m, 1H), 7.16-7.30 (m, 5H), 7.35-7.37 (m, 3H), 7.38-7.42 (m, 2H), 7.58-7.63 (m, 2H).

Adduct 15

Adduct **15** was prepared from the known 2-benzoyloxyaldehyde [2] according to the general procedure in the indicated yield. TLC (SiO_2): EtOAc/hexane (1:4), R_f = 0.30; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.78-0.97 (m, 18H), 1.21-1.52 (m, 16H), 1.68-1.85 (m, 2H), 4.08 (dd, 1H, J = 1.9, 6.3 Hz), 5.60 (m, 1H), 7.21-7.42 (m, 5H); MS *m/z* 512 (M^+).

As described above for adduct **3**, adduct **15** was immediately converted to the Mosher's ester derivative (95%, ee > 92%). TLC (SiO_2): EtOAc/hexane (1:4), R_f = 0.63; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.78-0.97 (m, 18H), 1.21-1.52 (m, 16H), 1.68-1.85 (m, 2H), 3.51 (s, 3H), 4.95-5.08 (m, 1H), 5.32-5.37 (m, 1H), 7.32-7.60 (m, 8H), 8.02-8.06 (m, 2H).

Benzoate 16

DIAD (0.07g, 0.35 mmol) in benzene (2 mL) was added to a stirring, room temperature solution of **3** (0.1 g, 0.23 mmol), TPP (0.09 g, 0.35 mmol), and benzoic acid (0.03 g, 0.23 mmol) in anhydrous benzene (3 mL) under an argon atmosphere. After 24 h, the precipitate was removed by filtration and the filtrate was concentrated under reduced pressure. The residue was purified by flash SiO_2 column chromatography to give **16** (95%). TLC (SiO_2): EtOAc/hexane (1:4), R_f = 0.60; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.85-0.98 (m, 15H), 1.21-1.62 (m, 18H), 3.77 (t, 1H, J = 7.9 Hz), 3.97 (t, 1H, J = 6.4 Hz), 4.41-4.49 (m, 1H), 5.12-5.21 (m, 1H), 7.40-7.58 (m, 3H), 8.04 (d, 2H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.10, 13.44, 25.40, 25.90, 26.89, 28.99, 65.00, 63.53, 82.10, 110.58, 125.64, 127.77, 127.98, 140.1, 184.58. MS *m/z* 526 (M^+); Anal. calcd. for $C_{25}H_{42}O_4Sn$: C, 57.16; H, 8.06; found: C, 57.30; H, 8.29.

Alcohol 17

A solution of **16** (0.1 g, 0.24 mmol) and K_2CO_3 (4 equiv.) in anhydrous methanol (6 mL) was heated at 45°C. After 6 h, the reaction mixture was cooled to room temperature, neutralized to pH 7 using 1N HCl, and extracted with Et_2O (2 × 25 mL). The combined ethereal extracts were washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by flash SiO_2 column chromatography to give **17** (85%). TLC (SiO_2): EtOAc/hexane (1:9), R_f = 0.20; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.89-0.97 (m, 15H), 1.30-1.36 (m, 6H), 1.37 (s, 3H), 1.44 (s, 3H), 1.48-1.55 (m, 6H), 1.82 (d, 1H, J = 6.7 Hz), 3.75 (t, 1H, J = 7.30 Hz), 3.91-3.96 (m, 2H), 4.39 (q, 1H, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.11, 13.84, 25.82, 26.55, 27.59, 29.26, 65.36, 65.58, 81.18, 108.89; MS *m/z* 422 (M^+).

Thiocarbamate 19

1,1'-Thiocarbonyldiimidazole (1.1 mmol) was added to a stirring solution of alcohol **3** (1 mmol) in dry CH_2Cl_2 (5 mL) containing DMAP (0.1 mmol) under an argon atmosphere. After 8 h, the reaction mixture was filtered through a small pad of silica gel and the filter cake was washed with EtOAc (5 mL). The combined filtrate was concentrated under reduced pressure and the residue was dissolved in pyrrolidine (2 mL). After 2-4 h, all volatiles were removed *in vacuo* and the residue was chromatographed over silica gel affording the thiocarbamate **19** (89%). TLC (SiO_2): EtOAc/hexane (1:4), R_f = 0.65; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.80-1.00 (m, 15H), 1.27-1.35 (m, 9H), 1.42 (s, 3H), 1.48-1.56 (m, 6H), 1.90-2.01 (m, 4H), 3.47-3.64 (m, 2H), 3.70-3.74 (m, 3H), 3.90-3.94 (m, 1H), 4.38-4.42 (m, 1H), 5.73-5.79 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 10.87, 13.78, 24.66, 25.20, 25.84, 26.64, 27.52, 29.10, 47.77, 52.13, 65.08, 76.65, 79.10, 108.13, 185.51; HRMS (CI, CH_4) calcd for $C_{19}H_{37}NO_3SSn$ (M^++1-Bu) *m/z* 479.1516, found 479.1512.

DMTC 20

1,1'-Thiocarbonyldiimidazole (1.1 mmol) was added to a stirring solution of alcohol **3** (1 mmol) in dry CH_2Cl_2 (5 mL) containing DMAP (0.1 mmol) under an argon atmosphere. After 2-10 h, the reaction mixture was filtered through a small pad of silica gel and the filter cake was washed with EtOAc (5 mL). The combined filtrate was concentrated under reduced pressure and the residue was dissolved in a 2 M THF solution of dimethylamine (4 mL). After 2-4 h, all volatiles were removed *in vacuo* and the residue was chromatographed over silica gel affording the DMTC protected alcohol **20** (93%). TLC (SiO_2): EtOAc/hexane (1:4), R_f = 0.55; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.87 (t, 9H, J = 7.3 Hz), 0.95 (t, 6H, J = 7.5 Hz), 1.24-1.34 (m, 9H), 1.39 (s, 3H), 1.42-1.54 (m, 6H), 3.10 (s, 3H), 3.35 (s, 3H), 3.62-3.66 (m, 1H), 4.07-4.11 (m, 1H), 4.44-4.54 (m, 1H), 4.64-5.72 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 10.79, 13.89, 25.32, 26.79, 27.64, 29.27, 37.86, 43.09, 67.21, 79.06, 79.21, 109.29, 188.71; $[\alpha]^{25}_D$ = 25.75° (*c* 2.36, $CHCl_3$); HRMS (CI, CH_4) calcd for $C_{17}H_{35}NO_3SSn$ (M^++1-Bu) *m/z* 453.1360, found 453.1365.

Adduct 22

Stannane **19a** was converted to **22** according to the general cross-coupling procedure in the indicated yield (Table 2). TLC (SiO_2): EtOAc/hexane (3:7), R_f = 0.51; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.34 (s, 3H), 1.42 (s, 3H), 1.92-2.01 (m, 4H), 2.51 (t, 2H, J = 6.5 Hz), 3.43-3.58 (m, 2H), 3.72 (t, 2H, J = 6.7 Hz), 3.91 (t, 1H, J = 6.7 Hz), 4.01 (t, 1H, J = 6.7 Hz), 4.31 (q, 1H, J = 6.1 Hz), 4.95-5.10 (m, 2H), 5.67 (q, 1H, J = 5.4 Hz), 5.79-5.91 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.70, 25.33, 25.77, 26.63, 35.23, 47.98, 52.32, 66.41, 76.34, 79.24, 109.75, 118.23, 133.47, 184.61; Anal. calcd. for $C_{14}H_{23}NO_3S$: C, 58.92; H, 8.12; found: C, 59.09; H, 8.30.

Adduct 23

Stannane **19b** was converted to **23** according to the general cross-coupling procedure in the indicated yield (Table 2). TLC (SiO_2): EtOAc/hexane (3:7), R_f ~ 0.40; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.87-1.45 (m, 15H), 1.90-2.01 (m, 4H), 2.49 (t, 2H, J = 5.5 Hz), 3.40-3.52 (m, 2H), 3.70 (t, 2H, J = 6.5 Hz), 3.87-3.93 (m, 1H), 4.15 (t, 1H, J = 6.5 Hz),

4.22-4.44 (m, 1H), 5.13-5.35 (m, 2H), 5.63 (q, 1H, J = 4.4 Hz), 5.78-5.93 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.80, 24.70, 25.80, 26.70, 28.3, 36.20, 48.08, 52.32, 64.78, 66.40, 76.24, 79.34, 81.1, 94.5, 108.75, 117.93, 132.40, 152.01, 184.61; Anal. calcd. for $C_{14}H_{23}NO_3S$: C, 58.92; H, 8.12; found: C, 59.09; H, 8.30.

Adduct 24

Stannane **20** was converted to **24** according to the general cross-coupling procedure in the indicated yield (Table 2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.33 (s, 3H), 1.41 (s, 3H), 2.47-2.51 (m, 2H), 3.09 (s, 3H), 3.35 (s, 3H), 3.88 (dd, 1H, J = 6.0, 8.4 Hz), 4.03 (dd, 1H, J = 6.8, 8.4 Hz), 4.26-4.31 (m, 1H), 5.05-5.13 (m, 2H), 5.63-5.68 (m, 1H), 5.75-5.86 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.33, 26.61, 35.16, 37.93, 43.09, 66.40, 76.31, 80.11, 109.82, 118.29, 133.40, 187.74; MS *m/z* 259 (M^+); $[\alpha]^{25}_D$ = -17.56° (*c* 1.97, $CHCl_3$); HRMS (CI, CH_4) calcd for $C_{12}H_{22}NO_3S$ (M^++1) *m/z* 260.1320, found 260.1322.

Adduct 26

Stannane **19a** was converted to **26** according to the general cross-coupling procedure in the indicated yield (Table 2). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.35 (s, 3H), 1.44 (s, 3H), 1.84-1.94 (m, 4H), 2.67 (t, 2H, J = 7.0 Hz), 3.48-3.56 (m, 2H), 3.64-3.74 (m, 2H), 3.91-3.96 (m, 1H), 4.03-4.09 (m, 1H), 4.33 (q, 1H J = 6.1 Hz), 5.72 (q, 1H, J = 6.1 Hz), 6.17-6.27 (m, 1H), 6.45 (d, 1H, J = 15.8 Hz), 7.25-7.37 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.68, 25.40, 25.80, 26.72, 34.60, 48.06, 52.35, 66.55, 76.35, 79.50, 109.85, 125.20, 126.34, 127.45, 128.74, 133.21, 137.57, 184.58; MS *m/z* 361(M^+); Anal. calcd. for $C_{20}H_{27}NO_3S$: C, 66.45; H, 7.53; found: C, 66.50; H, 7.31.

Adduct 28

Stannane **19a** was converted to **28** according to the general cross-coupling procedure in the indicated yield (Table 2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.36 (s, 3H), 1.46 (s, 3H), 1.61-1.73 (m, 2H), 1.90-1.98 (m, 2H), 2.05-2.12 (m, 2H), 2.28-2.34 (m, 2H), 2.38-2.61 (m, 2H), 2.79 (t, 2H, J = 4.5 Hz), 3.49-3.63 (m, 2H), 3.62 (s, 3H), 3.66-3.67 (m, 3H), 3.70-3.75 (m, 2H), 3.90-4.20 (m, 2H), 4.26-4.36 (m, 1H), 5.01-5.15 (m, 1H), 5.60-5.72 (m, 1H), 5.81-5.83 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.71, 24.98, 25.86, 26.54, 26.88, 27.44, 28.56, 28.99, 35.10, 46.24, 47.40, 51.63 69.63, 74.29, 109,76, 123.75, 126.06, 174.45, 207.58; MS *m/z* 399 (M^+); Anal. calcd. for $C_{19}H_{31}NO_5S$: C, 59.19; H, 8.10; found: C, 59.25; H, 8.18.

Adduct 30

Stannane **19a** was converted to **30** according to the general cross-coupling procedure in the indicated yield (Table 2). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.37 (s, 3H), 1.44 (s, 3H), 1.89-2.00 (m, 4H), 2.85 (dd, 1H, J = 4.4, 17.3 Hz), 3.02 (dd, 1H, J = 5.1, 17.3 Hz), 3.50-3.67 (m, 2H), 3.70-3.76 (m, 2H), 4.05 (dd, 1H, J = 5.6, 8.5 Hz), 4.10 (dd, 1H, J = 6.6, 8.5 Hz), 4.51 (q, 1H, J = 6.3 Hz), 5.61-5.67 (m, 1H), 7.26-7.31 (m, 3H), 7.36-7.40 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.06, 24.73, 25.44, 25.81, 26.82, 48.18, 52.37, 66.61, 75.70, 77.55, 82.86, 85.16, 109.90, 123.74, 128.09, 128.46, 131.77, 184.11; MS *m/z* 345 (M+); Anal. calcd. for $C_{20}H_{25}NO_5S$: C, 66.82; H, 7.01; found: C, 66.77; H,7.20.

Adduct 32

Stannane **19a** was converted to **32** according to the general cross-coupling procedure in the indicated yield (Table 2). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.37 (s, 3H), 1.42 (s, 3H), 1.85-1.96 (m, 4H), 2.31-2.35 (m, 2H), 2.34 (t, 2H, J = 6.7 Hz), 3.50 (t, 2H, J = 6.5 Hz), 3.70-3.74 (m, 1H), 4.11-4.14 (m, 1H), 4.65 (q, 1H, J = 7.0 Hz), 5.31-5.34 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.81, 14.22, 18.93, 21.34, 22.44, 24.74, 25.41, 25.79, 26.76, 28.84, 31.25, 48.07, 52.28, 66.44, 75.64, 77.79, 82.83, 109.72, 184.20; MS *m/z* 339 (M+); Anal. calcd. for $C_{19}H_{31}NO_5S$: C, 64.55; H, 8.84; found: C, 64.66; H, 8.93.

Adduct 34

Stannane **19a** was converted to **34** according to the general cross-coupling procedure in the indicated yield (Table 2). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.34 (s, 3H), 1.38 (s, 3H), 1.90-1.97 (m, 4H), 2.35-2.42 (m, 2H), 2.71 (t, 2H, J = 7.8 Hz), 3.46-3.63 (m, 2H), 3.69-3.82 (m, 3H), 3.99 (dd, 1H, J = 6.0, 8.4 Hz), 4.23-4.31 (m, 1H), 5.44-5.53 (m, 1H), 5.79-5.89 (m, 1H), 6.01-6.05 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.74, 25.44, 25.82, 26.54, 34.42, 35.49, 48.06, 52.37, 66.08, 77.68, 80.03, 109.98, 125.17, 126.07, 128.51, 128.75, 135.52, 141.75, 184.44; $[\alpha]_{25}^{D}$ = -11.93º (*c* 0.62, $CHCl_3$); HRMS (CI, CH_4) calcd for $C_{22}H_{32}NO_3S$ (M^++1) *m/z* 390.2103, found 390.2107.

Adduct 36

Stannane **20** was converted to **36** according to the general cross-coupling procedure in the indicated yield (Table 2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.36 (s, 3H), 1.41 (s, 3H), 1.79-1.87 (m, 2H), 2.34-2.40 (m, 2H), 2.64 (t, 2H, J = 8.0 Hz), 2.97 (s, 6H), 3.72 (dd, 1H, J = 6.8, 8.0 Hz), 4.12 (dd, 1H, J = 6.4, 8.0 Hz), 4.62-4.68 (m, 1H), 5.33-5.40 (m, 1H), 7.14-7.20 (m, 3H), 7.23-7.28 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.07, 26.89, 29.79, 34.79, 35.43, 37.03, 69.62, 74.20, 91.90, 98.10, 109.83, 125.95, 128.50, 128.73, 142.38, 166.36, 207.79; $[\alpha]_{25}^{D}$ = -5.32º (*c* 2.05, $CHCl_3$); HRMS (CI, CH_4) calcd for $C_{20}H_{28}NO_3S$ (M^++1) *m/z* 362.1790, found 362.1788.

Adduct 38

Stannane **19a** was converted to **38** according to the general cross-coupling procedure in the indicated yield (Table 2). IR (neat) 1733, 1663, 1366, 1250, 1216, 1163, 1056 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.24-1.32 (m, 4H), 1.35 (s, 3H), 1.40 (s, 3H), 1.42-1.53 (m, 2H), 1.54-1.62 (m, 2H), 1.81-1.97 (m, 4H), 2.24-2.34 (m, 4H), 3.32 (t, 2H, J = 6.8 Hz), 3.48 (t, 2H, J = 6.8 Hz), 3.62 (s, 3H), 3.70 (dd, 1H, J = 6.8, 8.4 Hz), 4.10 (dd, 1H, J = 6.0, 8.4 Hz), 4.59-4.65 (m, 1H), 5.28-7.32 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.74, 25.10, 25.88, 26.04, 26.88, 27.74, 28.76, 29.10, 34.26, 35.11, 46.24, 47.40, 51.63 69.63, 74.29, 91.68. 98.23, 109,76, 163.76, 163.87, 174.45, 207.58; $[\alpha]^{25}_{D}$ = -11.60º (*c* 1.5, $CHCl_3$); HRMS (CI, CH_4) calcd for $C_{21}H_{34}NO_5S$ (M^++1) *m/z* 412.2158, found 412.2153.

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