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Preparation of Monoorganotin Compounds

Bis(N,N-bistrimethylsilylamino) stannylene **1** (1.00 g, 2.27 mmol) and organic halide (1 eq) are mixed in anhydrous solvent (10 ml) under an inert atmosphere at T°C, until the reaction mixture turns pale yellow. The reaction is quantitative and **2a-c** and **5-13** are used without further purification.

Compound **2a**

Solvent : Benzene Temperature : 20°C reaction time : immediate

^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.18 (bs, 1H; $^4J_{Sn-H}$ 20.9 Hz), 5.69 (bs, 1H; $^4J_{Sn-H}$ 34.6 Hz), 4.25 (q, 2H, *J* 7.2 Hz), 2.64 (bs, 2H; $^2J_{Sn-H}$ 98.5 Hz), 1.31, (t, 3H, *J* 7.2 Hz), 0.22 (36H, s); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 169.3 ($^3J_{Sn-C}$ 29 Hz), 135.3 ($^2J_{Sn-C}$ 76 Hz), 125.3 ($^3J_{Sn-C}$ 76 Hz), 62.3, 34.4 ($^1J_{Sn-C}$ 650 Hz), 14.2, 5.8; ^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ -129.1; IR (KBr): 1661, 1613, 1336, 1249, 1202, 898, 867, 840, 678 cm^{-1}; SMHR : calcd for $C_{18}H_{45}N_2O_2BrSi_4Sn$: 617.0529, found : 617.0589.

Compound **2b**

Solvent : Benzene Temperature : 20°C reaction time : immediate

^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.03 (s, 1H; $^4J_{Sn-H}$ 35.3 Hz), 5.97 (s, 1H; $^4J_{Sn-H}$ 29.4 Hz), 2.53 (bs, 2H; $^2J_{Sn-H}$ 81.4 Hz), 0.23 (36H, s); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 156.2 ($^3J_{Sn-C}$ 77 Hz), 117.7 ($^2J_{Sn-C}$ 26 Hz), 106.6 ($^3J_{Sn-C}$ 78 Hz), 34.3 ($^1J_{Sn-C}$ 579 Hz), 6.4 (12C); ^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ -81.8. IR (KBr) 3035, 2964, 2218, 1645, 1465, 1403, 1252, 1093, 843 cm^{-1}.

Compound **2c**

Solvent : Benzene Temperature : 25°C reaction time : immediate

^{1}H NMR ($CDCl_3$, 250 MHz) δ 5.19 (bs, 1H; $^4J_{Sn-H}$ 40.9 Hz), 5.17 (d, 1H; *J* 1.5 Hz, $^4J_{Sn-H}$ 39.6 Hz), 2.86 (bs, 2H; $^2J_{Sn-H}$ 103.0 Hz), 0.23 (36H, s); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 137.3, 113.9 ($^3J_{Sn-C}$ 81 Hz), 42.4 ($^1J_{Sn-C}$ 532 Hz), 6.3 (12C); ^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ -194.0. IR (KBr) 3033, 2955, 1615, 1403, 1252, 899, 858 cm^{-1}.

Compound **5**

Solvent : THF Temperature : 20°C reaction time : 1 h

^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.63-1.57 (m, 5H), 0.93 (d, 6H, *J* 6.1 Hz), 0.27 (s, 36H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 34.5 ($^2J_{Sn-C}$ 22 Hz), 31.2 ($^3J_{Sn-C}$ 139 Hz), 28.7 ($^1J_{Sn-C}$ 611 Hz), 22.0 (2C), 5.8 (12C), ^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ -54.5.

Compound **6**

Solvent : Benzene Temperature : 20°C reaction time : immediate

^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.65 (t, 2H, *J* 7.0 Hz, $^2J_{Sn-H}$ 83.6 Hz), 1.51-1.40 (m, 16H), 0.98 (t, 3H, *J* 5.1 Hz), 0.23 (s, 36H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 33.6 ($^3J_{Sn-C}$ 87 Hz), 32.1, 31.7 ($^1J_{Sn-C}$ 583 Hz), 29.7, 29.6, 29.5, 28.7, 26.7 ($^2J_{Sn-C}$ 36 Hz), 22.8, 14.3, 6.1 (12C); ^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ -141.1.

Compound **7**

Solvent : Benzene Temperature : 20°C reaction time : immediate

^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.03-5.85 (m, 1H), 5.17-5.07 (m, 2H), 2.58 (bd, 2H, *J* 8.3 Hz), 0.29 (s, 36H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 132.4 ($^{2}J_{Sn-C}$ 84 Hz), 116.9 ($^{3}J_{Sn-C}$ 107 Hz), 36.7($^{1}J_{Sn-C}$ 584 Hz), 5.6 (12C); ^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ -84.1.

Compound **8**

Solvent : Benzene Temperature : 20°C reaction time : immediate

^{1}H NMR ($CDCl_3$, 250 MHz) δ 5.63-5.47 (m, 2H), 2.65-2.57 (m, 2H, $^{2}J_{Sn-H}$ 84.8 Hz), 1.74-1.71 (m, 3H), 0.29 (s, 36H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 127.5 ($^{3}J_{Sn-C}$ 111 Hz), 125.46 ($^{2}J_{Sn-C}$ 85 Hz), 36.6 ($^{1}J_{Sn-C}$ 541 Hz), 18.1 ($^{4}J_{Sn-C}$ 28 Hz), 6.0 (12C); ^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ -163.0.

Compound **9**

Solvent : Benzene Temperature : 20°C reaction time : immediate

^{1}H NMR ($CDCl_3$, 250 MHz) δ 5.34 (bt, 1H, *J* 8.6 Hz, $^{3}J_{Sn-H}$ 41.8 Hz), 2.53 (d, 2H, *J* 8.6 Hz, $^{2}J_{Sn-H}$ 90.0 Hz), 1.77 (bs, 3H, $^{5}J_{Sn-H}$ 52.0 Hz), 1.71 (bs, 3H, $^{5}J_{Sn-H}$ 38.6 Hz), 0.28 (s, 36H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 133.8, 118.1 ($^{2}J_{Sn-C}$ 88 Hz), 32.1 ($^{1}J_{Sn-C}$ 598 Hz), 26.1 ($^{4}J_{Sn-C}$ 29 Hz), 18.5 ($^{4}J_{Sn-C}$ 26 Hz), 5.9 (12C); ^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ -86.5.

Compound **10**

Solvent : Pentane Temperature : - 40°C reaction time : 0.5 h

^{1}H NMR ($CDCl_3$, 250 MHz) δ 5.44 (t, 1H, *J* 6.9 Hz, $^{2}J_{Sn-H}$ 54.6 Hz), 4.7 (d, 2H, *J* 6.9 Hz, $^{4}J_{Sn-H}$ 79.4 Hz), 0.23 (s, 36H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 211.3, 87.0 ($^{1}J_{Sn-C}$ 818 Hz), 71.2 ($^{3}J_{Sn-C}$ 94 Hz), 5.5 (12C); ^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ -133.4.

Compound **11**

Solvent : Benzene Temperature : 20°C reaction time : 0.25 h

^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.23 (t, 2H, *J* 6.9 Hz), 1.47-1.40 (m, 4H), 0.85 (t, 3H, *J* 6.9 Hz), 0.27 (s, 36H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 111.3 ($^{1}J_{Sn-C}$ 198 Hz), 86.9, 30.2, 21.9, 19.5, 13.5, 5.9 (12C); ^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ -371.

Compound **12**

Solvent : Benzene Temperature : 20°C reaction time : 24 h

THF 20°C 3 h

characterized in Lappert's original paper

Compound **13**

Solvent : Benzene Temperature : 80°C reaction time : 24 h

^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.53-7.33 (m, 5H), 7.18 (d, 1H, *J* = 18.3 Hz), 6.81 (d, 1H, *J* 18.3 Hz, $^{2}J_{Sn-H}$ 127.0 Hz), 0.37 (s, 36H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 148.3 ($^{2}J_{Sn-C}$ 26 Hz), 137.7 ($^{3}J_{Sn-C}$ 133 Hz), 132.8 ($^{1}J_{Sn-C}$ 793 Hz)), 130.0, 129.7, 127.9, 5.1 (12C); ^{119}Sn NMR ($CDCl_3$, 74.6 MHz) δ -212.2.

Coupling procedure A

Bis(N,N-bistrimethylsilylamino) stannylene (800 mg, 1.82 mmol) and allyl halide (1.82 mmol) are mixed in anhydrous toluene (5 ml) under nitrogen. After stirring for 15 minutes at 25°C, the resulting yellow solution was added to a solution of Pd_2dba_3 (32 mg, 0.035 mmol) and triphenylphosphine (36 mg, 0.14 mmol) in toluene (3 ml), and the reaction mixture is heated to 90 or 110°C. Benzylic bromide (1.13 mmol) is added and the reaction allowed to stir until catalyst has precipitated. The mixture was then cooled, concentrated and the residual oil purified by flash chromatography on silica gel (elution with petrol-ether 9:1), providing **3a-e** as a colourless oils.

Compound **3a**

^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.19-7.04 (m, 5H), 6.00 (d, 1H, *J* 1.3 Hz), 5.36 (q, 1H, *J* 1.2 Hz), 4.07 (q, 2H, *J* 7.1 Hz), 3.80 (dd, 1H, *J* 8.6, 6.7 Hz), 3.50 (s, 3H), 2.95 (ddd, 1H, *J* 14.2, 8.6, 0.9 Hz), 2.59 (dd, 1H, *J* 14.2, 6.7, 1.1 Hz), 1.16 (t, 3H, *J* 7.1 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 173.7, 166.7, 138.5, 137.5, 128.7 (2C), 128.0 (2C), 127.5, 127.4, 60.8, 52.0, 50.4, 36.2, 14.2. MS *m/z* : 262, 230 (82), 202 (20), 189 (11), 173 (53), 157 (23), 149 (11), 129 (100), 128 (25), 121 (34); HRMS: calcd for $C_{15}H_{18}O_4$: 262.1205 found : 262.1206.

Compound **3b**

^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.30-7.18 (m, 5H), 5.74 (bs, 1H), 5.60 (bs, 1H), 3.82 (dd, 1H, *J* 8.0, 7.6 Hz), 3.59 (s, 3H), 2.97 (dd, 1H, *J* 14.4, 8.0 Hz), 2.59 (dd, 1H, *J* 14.4, 7.6 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 172.6, 136.9, 133.0, 128.9 (2C), 127.9, 127.8 (2C), 119.9, 118.0, 52.3, 49.5, 38.1. MS *m/z* : 215, 188 (91), 156 (81), 155 (31), 149 (52), 129 (100), 128 (36), 121 (56); HRMS: calcd for $C_{13}H_{13}NO_2$: 215.0946 found : 215.0937.

Compound **3c**

^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.33-7.21 (m, 5H), 5.05 (d, 1H, *J* 1.3 Hz), 5.00 (d, 1H, *J* 1.3 Hz), 3.93 (dd, 1H, *J* 7.9, 7.3 Hz), 3.59 (s, 3H), 3.07 (dd, 1H, *J* 14.6, 7.9 Hz), 2.96 (dd, 1H, *J* 14.6, 7.3 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 173.3, 139.2, 137.7, 128.8 (2C), 127.9 (2C), 127.7, 114.8, 52.2, 49.2, 42.9. MS (CI, NH_3)*m/z* : 242 (100), 225 (14), 189 (31), 149 (11), 129 (13), 121 (22);

Compound **3d**

^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.33-7.17 (m, 5H), 6.18 (d, 1H, *J* 0.6 Hz), 5.51 (d, 1H, *J* 0.6 Hz), 4.24 (q, 2H, *J* 7.1 Hz), 2.84-2.18 (m, 4H), 1.33 (t, 3H, *J* 7.1 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 167.2, 141.5, 139.2, 128.5 (2C), 128.4 (2C), 126.0, 125.2, 60.7, 35.0, 34.0, 14.3

Compound **3e**

^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.41-7.12 (m, 5H), 6.13 (d, 1H, *J* 1.5 Hz), 5.39 (q, 1H, *J* 1.5 Hz), 4.22 (q, 2H, *J* 7.1 Hz), 3.03 (m, 1H), 2.67 (dd, 1H, *J* 13.8, 7.2 Hz), 2.56 (dd, 1H, *J* 13.8, 7.6 Hz), 1.32 (t, 3H, *J* 7.1 Hz), 1.29 (d, 3H, *J* 6.9 Hz) ; ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ, 167.3, 146.6, 139.2, 128.4 (2C), 127.1 (2C), 126.4, 126.1, 60.6, 41.0, 38.8, 21.4, 14.3.

Coupling procedure B

Monoorganotin reagent **5** to **13** (1.85 mmol) are prepared following the above procedure. TBAF (5.9 ml, 1M) is then added *in situ* and after concentration anhydrous solvent (8 ml), halogenated substrate (1.23 mmol) and tetrakis(triphenylphosphine)palladium (0.015 mmol) are added and the reaction mixture is heated at T°C for t h. After cooling and removal of the solvent, purification on silica gel afforded the coupling product **14** to **23**.

Compound **14**

Solvent : dioxane Temperature : 101°C reaction time : 12 h

^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.52 (d, 2H, *J* 8.2 Hz), 7.34 (d, 2H, *J* 8.2 Hz), 2.81 (bt, 2H, *J* 7.9 Hz), 1.78-1.62 (m, 3H), 1.54 (s, 9H), 1.17 (d, 6H, *J* 6.3 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 148.4, 140.2, 128.2 (2C), 125.4 (2C), 41.1, 34.5, 33.5, 31.7 (3C), 28.0, 22.8 (2C).

Compound **15**

Solvent : dioxane Temperature : 101°C reaction time : 12 h

^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.43-7.26 (m, 5H), 2.73 (t, 2H, *J* 6.0 Hz), 1.78-1.72 (m, 2H), 1.52-1.41 (m, 14H), 1.03 (t, 3H, *J* 5.2 Hz); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 143.0, 128.5 (2C), 128.3 (2C), 125.7, 36.2, 32.1, 31.7, 29.8, 29.7, 29.5 (2C), 22.9, 14.3 (2C).

Compound **16**

Solvent : dioxane Temperature : 80°C reaction time : 0.5 h

^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.62 (d, 2H, *J* 8.3 Hz), 7.43 (d, 2H, *J* 8.1 Hz), 6.26 (ddt, 1H, *J* 17.2, 8.4, 7.6 Hz), 5.39 (bd, 1H, *J* 17.2 Hz), 5.36 (bd, 1H, *J* 8.4 Hz), 3.66 (bd, 2H, *J* 6.8 Hz), 1.63 (s, 9H); ^{13}C NMR ($CDCl_3$, 50,3 MHz) δ 148.9, 137.7, 137.1, 128.4 (2C), 125.4 (2C), 115.3, 39.9, 34.5, 31.6 (3C).

Compound **17**

Solvent : dioxane Temperature : 75°C reaction time : 0.5 h

^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.47 (d, 2H, *J* 8.4 Hz), 7.29 (d, 2H, *J* 8.3 Hz), 6.15 (ddd, 1H, *J* 17.0, 10.3, 6.6 Hz), 5.21 (dt, 1H, 17.0, 1.2 Hz), 5.15 (dt, 1H, 10.3, 1.2 Hz), 3.59 (m, 1H), 1.48 (d, 3H, *J* 5.6 Hz), 1.46 (s, 9H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 149.0, 143.6, 142.6, 127.0 (2C), 125.4 (2C), 113.0, 42.9, 34.5, 31.6 (3C), 20.8.

Compound **18**

Solvent : THF Temperature : 65°C reaction time : 12 h

^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.41-7.33 (m, 4H), 6.12 (dd, 1H, *J* 17.4, 11.6 Hz), 5.13 (dd, 1H, *J* 17.4, 1.4 Hz), 5.10 (dd, 1H, *J* 11.6, 1.4 Hz), 1.48 (s, 6H), 1.40 (s, 9H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 149.4, 148.5, 145.6, 125.9 (2C), 125.1 (2C), 110.5, 40.8, 34.4, 31.5 (3C), 28.4 (2C).

Compound **19**

Solvent : THF Temperature : 35°C reaction time : 3 h

^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.42-7.25 (m, 5H), 6.21 (t, 1H, *J* 6.7 Hz), 5.18 (d, 2H, 6.7 Hz), 1.37 (s, 9H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 209.9, 150.1, 131.0, 126.5 (2C), 125.7 (2C), 94.0, 78.7, 34.6, 31.4 (3C).

Compound **20**

Solvent : dioxane Temperature : 101°C reaction time : 2 h

^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.51-7.43 (m, 2H), 7.39-7.26 (m, 3H), 2.48 (t, 2H, *J* 6.9 Hz), 1.74-1.50 (m, 4H), 1.03 (t, 3H, *J* 7.0 Hz); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 131.6 (2C), 128.3 (2C), 127.5, 124.3, 90.4, 80.7, 31.0, 22.1, 19.2, 13.3.

Compound **21**

Solvent : dioxane Temperature : 101°C reaction time : 12 h

^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.61-7.27 (m, 10H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 141.2 (2C), 128.7 (4C), 127.2 (4C), 127.1 (2C).

Compound **22**

Solvent : dioxane Temperature : 101°C reaction time : 12 h

^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.28-7.08 (m, 5H), 6.31 (bd, 1H, *J* 15.8 Hz), 6.15 (dt, 1H, *J* 15.8, 6.5 Hz), 2.29-2.22 (m, 2H), 1.47-1.10 (m, 4H), 1.04-0.76 (m, 3H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 138.1, 128.9 (2C), 128.5, 127.4, 127.3 (2C), 125.4, 32.7, 31.5, 22.2, 13.9.

Compound **23**

Solvent : dioxane Temperature : 101°C reaction time : 12 h

^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.43-7.21 (m, 5H), 6.85 (dd, 1H, *J* 15.7, 10.3 Hz), 6.52 (d, 1H, *J* 15.7 Hz), 6.29 (ddt, 1H, *J* 15.1, 10.3, 1.1 Hz), 5.91 (dt, 1H, *J* 15.1, 6.9 Hz), 2.26 (m, 2H), 1.51 (m, 4H), 1.05 (t, 3H, *J* 7.1 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 137.8, 136.0, 130.6, 130.0, 129.6, 128.6 (2C), 127.1, 126.2 (2C), 32.7, 31.6, 22.4, 14.1.