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**5-Methoxy-7-methyl-1,4-naphthoquinone (19):**

To a solution of diene **6**<sup>18,19</sup> (0.502 mg, 2.70 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> under an argon atmosphere at room temperature, was added solid benzoquinone **16** (379 mg, 3.51 mmol) in one portion. The resulting dark greenish solution was stirred at room temperature for 12 h. Then, the solvent was evaporated under reduced pressure and the residue redissolved in 10 mL of a MeOH and 1 mL of 1N HCl was added at 0 °C. The mixture was stirred for 1 h at 0 °C, during which time an orange-red solid precipitated. The solid was collected by filtration to give 0.21 g (41%) of **19**, identical with an authentic<sup>24</sup> sample. Because of the near simultaneous development of a procedure that gives **20** directly, this procedure was not optimized.

**2,2'-Bis(1-acetoxy-8-methoxy-6-methyl-4-tributylstannyl)naphthalene (27a):**

A mixture of 79 mg (0.09 mmol) of ditriflate **26**, 0.28 mL (0.02 mmol) of hexabutyliditin, 15 mg (0.02 mmol) of bis(triphenylphosphine)palladium(II) chloride and 8.00 mg (0.19 mmol) of anhydrous lithium chloride was heated at 60 °C for 1 h under vacuum. Then, 3 mL of dry dioxane was added and the reaction was heated at reflux under argon for 28 h. Solvent was removed *in vacuo* and the residue was chromatographed on silica gel eluting with 15:1 petroleum ether/ethyl acetate to give 75.0 mg (76%) of the distannane **27a** as a light yellow liquid. IR (film)  $\nu$  2960, 2930, 2850, 1760, 1625 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200.1 MHz)  $\delta$  0.83-1.69 (54H, m), 2.01 (6H, s), 2.49 (6H, s), 3.88 (6H, s), 6.70 (2H, s), 7.19 (2H, s), 7.46 (2H, s); Anal. Calcd for C<sub>52</sub>H<sub>78</sub>O<sub>6</sub>Sn<sub>2</sub>: C, 60.25; H, 7.58. Found: C, 59.66; H, 7.85.

**2,2'-Bis(1-acetoxy-8-methoxy-6-methyl-4-trimethylstannyl)naphthalene (27b):**

In a screw-cap Carius tube, ditriflate **26** (0.15 g, 0.20 mmol) was dissolved in anhydrous dioxane (10 mL). Bis(triphenylphosphine)palladium(II) chloride (0.028 g, 0.040 mmol),

anhydrous lithium chloride (0.034 g, 0.80 mmol) and hexamethylditin (0.20 g, 0.60 mmol) were added sequentially. The mixture was deaerated via sonication under nitrogen for 20 min. The tube was flushed with nitrogen, sealed, and heated to 110 °C at which temperature the mixture was magnetically stirred for 12 h. All volatiles were removed *in vacuo* and the residue was purified by flash column chromatography (silica gel, 9:1 petroleum ether/ethyl acetate) to yield 0.12 g (73%) of **27b** as a beige solid mp 228-230 °C (dec.). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.40 (18H, apparent t, *J* = 26.8 Hz), 2.03 (6H, s), 2.50 (6H, s), 3.89 (6H, s), 6.72 (2H, s), 7.21 (2H, s), 7.51 (2H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -8.1, 21.0, 22.4, 56.4, 108.6, 122.8, 128.8, 132.3, 132.4, 136.3, 156.1; HRMS: Calcd for C<sub>34</sub>H<sub>42</sub>O<sub>6</sub>Sn<sub>2</sub>: 787.1104. Found: 787.1100.

### 2,2'-Bis(1-acetoxy-4-iodo-8-methoxy-6-methylnaphthalene) (**28**):

Distannane **27b** (50 mg, 0.064 mmol) was dissolved in distilled CH<sub>2</sub>Cl<sub>2</sub> (5 mL) with stirring at ambient temperature under nitrogen. Iodine crystals (49 mg, 0.19 mmol) were added, and the solution was stirred 30 min at room temperature. The reaction mixture was poured into saturated aqueous sodium thiosulfate (5 mL). The organic layer was separated, washed with additional aqueous sodium thiosulfate (5 mL), water and brine, and dried over anhydrous magnesium sulfate. Concentration to dryness *in vacuo* afforded **28** as a scarlet solid (42 mg, 93%). An analytical sample of **28** was obtained as a white, crystalline solid by preparative TLC purification (silica gel, 1:4 ethyl acetate/petroleum ether) mp 247-248 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 2.08 (6H, s), 2.54 (6H, s), 3.91 (6H, s), 6.79 (2H, s), 7.56 (2H, s), 8.01 (2H, br s); HRMS: Calcd for C<sub>28</sub>H<sub>24</sub>I<sub>2</sub>O<sub>6</sub>: 710.9741. Found: 710.9747.

### 2-Bromo-3,5-di(benzyloxy)toluene (**29b**):

To a stirred mixture of 14.6 g (106 mmol) of K<sub>2</sub>CO<sub>3</sub> and 5.00 g (35.2 mmol) of orcinol monohydrate in 200 mL of dry acetone was added 16.7 mL (141 mmol) of benzyl bromide. The stirred suspension was heated at reflux for 20 h under an argon atmosphere, during which time the

color of the suspension changed from rose to pale yellow. The insoluble material ( $K_2CO_3$  and  $KBr$ ) was filtered off and washed with acetone. The combined filtrate and wash were concentrated on a rotary evaporator, and remaining benzyl bromide was evaporated at room temperature under high vacuum. The residual light yellow oil was filtered through a G3 glass frit which was rinsed with acetone and again further impurities were distilled off under high vacuum ( $4 \times 10^{-4}$  torr) and a head temperature  $>176$  °C. The residual 3,5-di(benzyloxy)toluene (10.7g; approx. 100 %) was a yellow-orange colored oil that contained (NMR) only minor amounts of impurities and solidified in the refrigerator. It was converted to 2-bromo-3,5-di(benzyloxy)toluene (**29b**) without further purification.  $^1H$  NMR ( $CDCl_3$ , 200 MHz):  $\delta$  2.35 (s, 3H), 5.05 (s, 4H), 6.50 (s, 3H) 7.20-7.50 (m, 10H).

To a solution of 5.09 g (16.7 mmol) of 3,5-di(benzyloxy)toluene in 50 mL of  $CH_2Cl_2$  was slowly added dropwise over 2 h with stirring 850  $\mu$ l (16.7 mmol)  $Br_2$  in 50 mL of  $CH_2Cl_2$ . The reaction was monitored by TLC (1:1 petroleum ether/diethyl ether).  $HBr$  and  $Br_2$  vapors were absorbed using an aqueous  $NaOH/Na_2S_2O_3$  trap. The reaction mixture was allowed to warm to room temperature over 2 h with stirring, and, after standing 15 h, was treated with 100 mL of 2N  $NaOH$ . The phases were separated and the aqueous phase extracted twice with 25 mL portions of  $CH_2Cl_2$ . The combined organic phases were washed twice with 25 mL portions of water, dried over  $MgSO_4$ , filtered, and the solvent removed under vacuum to give 5.3 g of brown oil. The oil was dissolved in 5 mL of petroleum ether and overlaid with 5-10 mL of methanol. At  $-18$  °C fine colorless crystals separated which were collected to give 2.38 g (37%) of **29b**, mp  $68-69$  °C. IR (KBr):  $\nu$  3040, 3010, 2900, 1575, 1160  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$  2.49 (3H, s), 5.01 (2H, s), 5.15 (2H, s), 6.56 (1H, d,  $J=3.4$  Hz), 6.61 (1H, d,  $J=3.4$  Hz), 7.39-7.57 (10H, m). Anal. Calcd for  $C_{21}H_{19}BrO_2$ : C, 65.81; H, 5.00. Found: C, 65.95; H, 5.06.

**2,4-Dimethoxy-6-methyl-1-(tributylstannyl)benzene (30a):**

To a solution of 5.00 g (21.6 mmol) of 1-bromo-2,4-dimethoxy-6-methylbenzene\* (**29a**) in 10 mL of dry THF and 5 mL of dry diethyl ether at -78 °C under argon was added dropwise over 30 min 12.7 mL (21.6 mmol) of a 1.70 M *n*-BuLi solution in hexanes. After 30 min of stirring at -78 °C 6.00 mL (21.6 mmol) of tributyltin chloride was added over 20 min. After stirring for 5 h the reaction was warmed to room temperature and washed with saturated NH<sub>4</sub>Cl solution. The organic phase was separated, washed with water and dried over MgSO<sub>4</sub>. The solvent was evaporated *in vacuo* to give 7.13 g (75%) of **30a** as a clear, light yellow oil. IR (film)  $\nu$  2980, 2940, 2900, 2840, 2830, 1580, 1450 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200.1 MHz)  $\delta$  0.88 (9H, t, *J*=7.5 Hz), 1.10-1.71 (18H, m), 2.33 (3H, s), 3.73 (3H, s), 3.80 (3H, s), 6.25 (1H, d, *J*=2.0 Hz), 6.38 (1H, d, *J*=2.0 Hz); Anal. Calcd for C<sub>21</sub>H<sub>38</sub>O<sub>2</sub>Sn: C, 57.17; H, 8.68. Found: C, 56.71; H, 8.60.

#### 2,4-Di(benzyloxy)-6-methyl-1-(tributylstannyl)benzene (**30b**):

To a solution of 2.00 g (5.22 mmol) of 1-bromo-2,4-dibenzyloxy-6-methylbenzene\* (**29b**) in 20 mL of dry THF under argon cooled to -78 °C was added dropwise over 30 min 3.07 mL (5.22 mmol) of a 1.70 M solution of *n*-BuLi in hexanes. Then, 1.70 g (5.22 mmol) of tributyltin chloride was added over 30 min at -78 °C. After stirring for 45 min the reaction was slowly warmed to room temperature and 20 mL of saturated NH<sub>4</sub>Cl solution was added. The organic solvent was removed *in vacuo* and the aqueous phase twice extracted with 20 mL of ether. The extracts were combined, washed several times with saturated NH<sub>4</sub>Cl solution and with water, and dried over MgSO<sub>4</sub>. Solvent was removed under vacuum to give 2.59 g (84%) of **30b** as a clear liquid. IR (film)  $\nu$  3010, 2920, 2880, 2840, 1570 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200.1 MHz)  $\delta$  0.90 (9H, t, *J*=7.4 Hz), 1.10-1.71 (18H, m), 2.34 (3H, s), 4.96 (2H, s), 5.01 (2H, s), 6.38 (1H, d, *J*=2.0 Hz), 6.48 (1H, d, *J*=2.0 Hz), 7.35-7.41 (10H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 62.9 MHz)  $\delta$  12.1, 13.9, 27.7, 28.1, 29.5, 70.2, 70.6, 108.0, 127.7, 127.8, 128.2, 128.3, 128.7, 128.8, 137.2,

\* Cannon, J. R.; Cresp, T. M.; Metcalf, B. W.; Sargent, M. V.; Vinciguerra, G. *J. Chem. Soc. (C)* **1971**, 3495.

137.5, 160.9, 164.6; Anal. Calcd for  $C_{33}H_{46}O_2Sn$ : C, 66.79; H, 7.81. Found: C, 66.48; H, 7.81.

### 2,4-Dimethoxy-6-methylphenylboronic acid (**31a**):

In a dry Schlenk tube under argon, 300 mg (1.30 mmol) of 1-bromo-2,4-dimethoxy-6-methylbenzene<sup>37</sup> (**29a**) was dissolved in 8 mL of dry THF and cooled to -78 °C. Over 15 min, 0.90 mL (1.35 mmol) of 1.5 M *n*-BuLi in hexanes was added and the reaction mixture was allowed to stir for 50 min at -78 °C. Triisopropyl borate, freshly distilled from sodium (0.89 mL, 6.50 mmol) was added at -78 °C and the mixture was stirred at that temperature for 30 min before allowing it to warm to room temperature. Five mL of water was added and, after stirring for 10 min, the reaction mixture was thoroughly extracted with diethyl ether. The combined organic extracts were dried over  $MgSO_4$  and the solvent evaporated *in vacuo* to give 230 mg (91%) of boronic acid **31a** as a white solid which could be recrystallized from ethanol to give analytically pure material, mp 96-97 °C. IR (KBr)  $\nu$  3350-3050, 2940, 1590  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  2.55 (3H, s), 3.83 (3H, s), 3.86 (3H, s), 5.85 (2H, s), 6.32 (1H, d,  $J = 2.4$  Hz), 6.41 (1H, d,  $J = 2.4$  Hz);  $^{13}C$  NMR ( $CDCl_3$ , 62.9 MHz)  $\delta$  26.8, 55.7, 55.9, 95.7, 108.2, 109.0, 149.5, 162.3, 166.7; Anal. Calcd for  $C_9H_{13}BO_4$ : C, 55.15; H, 6.69. Found: C, 55.09; H, 6.83.

### 2,4-Di(benzyloxy)-6-methylphenylboronic acid (**31b**):

Prepared starting from **29b** in 87% yield using the procedure described for the preparation of **31a**. A small sample of **31b** was purified by recrystallization from petroleum ether/ethyl acetate as a white solid, mp 78-81 °C. IR ( $CH_2Cl_2$ )  $\nu$  3367, 3216  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$  2.55 (3H, s), 5.06 (4H, s), 5.81 (2H, s), 6.47 (1H, d,  $J = 2.2$  Hz), 6.51 (1H, d,  $J = 2.2$  Hz), 7.30-7.48 (10H, m);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz)  $\delta$  24.7, 70.6, 71.8, 98.2, 109.1, 110.8, 128.2, 128.4, 128.8, 129.2, 129.3, 129.6, 136.7, 137.4, 149.9, 161.9, 166.3.

**2,2'-Bis[1-acetoxy-4-(2,4-dimethoxy-6-methylphenyl)-8-methoxy-6-methylnaphthalene] (32a):**

Under argon were dissolved 20.0 mg (0.10 mmol) of 2,4-dimethoxy-6-methylboronic acid (**31a**), 34 mg (0.46 mmol) of ditriflate **26**, 3.0 mg (0.01 mmol) of tetrakis(triphenylphosphine)-palladium(0) and 26.0 mg (0.15 mmol) of barium hydroxide in a mixture of 1 mL of dimethoxyethane and 0.5 mL of degassed water. The reaction mixture was heated for 4 h at 80 °C, evaporated *in vacuo*, and the residue dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> and washed with H<sub>2</sub>O. The solvent was evaporated, and the residue chromatographed on silica gel that had been deactivated<sup>36b</sup> with 7.5% NH<sub>3</sub>, eluting with 1:1 petroleum ether/ethyl acetate. One obtains therefrom, after recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether, 33 mg (94%) of **32a** as pale red crystals. IR (KBr)  $\nu$  2910, 2840, 1720, 1580 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200.1 MHz)  $\delta$  1.55 (6H, s), 2.04 (6H, br s), 2.34 (6H, s), 3.60 (6H, br s), 3.87 (6H, s), 3.89 (6H, s), 6.44 (2H, s), 6.46 (2H, s), 6.66 (2H, s), 6.78 (2H, s), 7.21 (2H, br s); Anal. Calcd for C<sub>46</sub>H<sub>46</sub>O<sub>10</sub>: C, 72.81; H, 6.11. Found: C, 73.07; H, 5.91.

**2,2'-Bis[1-acetoxy-4-(2,4-dibenzyloxy-6-methylphenyl)-8-methoxy-6-methylnaphthalene] (32b):**

Into a sealable tube were introduced ditriflate **26** (71.7 mg, 0.095 mmol), boronic acid **31b** (66.2 mg, 0.19 mmol), tetrakis(triphenylphosphine)palladium(0) (22.0 mg, 0.019 mmol), barium hydroxide octahydrate (72 mg, 0.23 mmol), anhydrous ethylene glycol dimethyl ether (DME, 6.0 mL) and distilled water (2.0 mL). The tube was sealed under argon and heated at 80 °C for 3 h. The mixture was filtered through Celite and the Celite washed with CH<sub>2</sub>Cl<sub>2</sub>. Water was added to the combined filtrate and wash and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The extract was dried over sodium sulfate and evaporated to dryness. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 3:2) affording 88.9 mg (88%) of **32b** as a gum. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  1.80-2.20 (12H, br s), 2.35 (6H, s), 3.91 (6H, br s), 4.90 (4H, br s), 5.09 (4H, br s), 6.54 (2H, s), 6.60 (2H, s), 6.68 (2H, s), 6.81 (2H, s), 6.88 (2H, s), 6.94 (4H, br s), 7.1-7.5 (16H, m).