Supplementary Material (ESI) for Chemical Communications

Palladium-catalysed dimerisation-distannylation of arynes: synthesis and reaction of 2,2'-distannylbiaryls

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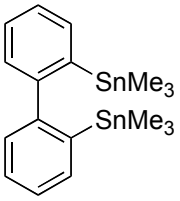
Supplementary Information

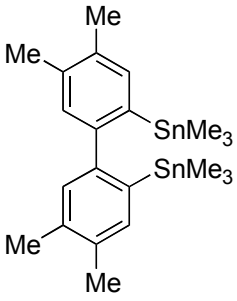
General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL EX-270 (^{1}H, 270 MHz; ^{13}C, 67.8 MHz) spectrometer or a JEOL Lambda-400 (^{1}H, 400 MHz; ^{13}C, 99.5 MHz; ^{119}Sn, 147.5 MHz) spectrometer using residual chloroform (^{1}H) or $CDCl_3$ (^{13}C) as an internal standard and tetramethyltin (^{119}Sn) as an external standard. The preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L columns (chloroform as an eluent). Column chromatography was carried out using Merck Aluminium oxide 90, activated, neutral. Unless otherwise noted, commercially available reagents were used without purification. 18-Crown-6 was recrystallized from distilled MeCN. KF (spray-dried) was vacuum dried at 100 °C for 12 h. THF was distilled from sodium/benzophenone ketyl. MeCN was distilled from phosphorus pentoxide. 2-(Trimethylsilyl)phenyl triflate (**1a**),[1] 4,5-dimethyl-2-(trimethylsilyl)phenyl triflate (**1b**),[2] 3-(trimethylsilyl)-5,6,7,8-tetrahydro-2-naphthyl triflate (**1d**),[3] 6-(trimethylsilyl)-5-indanyl triflate (**1e**),[2] 3-(trimethylsilyl)-2-naphthyl triflate (**1h**),[3] 3,6-dimethyl-2-(trimethylsilyl)phenyl triflate (**1i**),[3] 3,6-dimethoxy-2-(trimethylsilyl)phenyl triflate (**1j**),[2] 5-methyl-2-(trimethylsilyl)phenyl triflate (**1k**),[4] and 3-methoxy-2-(trimethylsilyl)phenyl triflate (**1l**)[5] were prepared according to literature procedures. 4,5-diethyl-2-(trimethylsilyl)phenyl triflate (**1c**), 4,5-dibutyl-2-(trimethylsilyl)phenyl triflate (**1f**) and 4,5-dihexyl-2-(trimethylsilyl)phenyl triflate (**1g**) were prepared from the respective 3,4-dialkylphenols in a similar manner as the preparation of **1b**. The 3,4-dialkylphenols were readily obtained from 3,4-dialkylphenyl methoxymethyl ether, which could be synthesized through the nickel-catalyzed cross-coupling of alkyl Grignard reagents with 3,4-dichlorophenyl methoxymethyl ether.[6]

Dimerisation-Distannylation of Arynes. ***A General Procedure.*** To a THF solution (2.0 mL) of 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (3.6 mg, 0.022 mmol), $Pd(OAc)_2$ (1.0 mg, 4.4 μmol), 18-crown-6 (0.349 g, 1.32 mmol), KF (0.077 g, 1.32 mmol) and **2** (0.22 mmol) was added **1** (0.66 mmol), and the resulting mixture was stirred at 20 °C. After the time specified in Table 2 or Scheme 1, the mixture was diluted with ethyl acetate, filtered

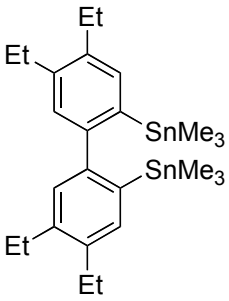
through a Celite plug, and concentrated. Alumina column chromatography (hexane as an eluent, activity IV) followed by gel permeation chromatography (chloroform as an eluent) gave the corresponding product.



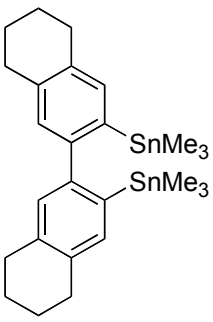
2,2'-Bis(trimethylstannyl)biphenyl (3a). Isolated in 62% yield as a colorless oil; ^{1}H NMR ($CDCl_3$) δ -0.08 (s, $J_{H–Sn}$ = 53.6 Hz, 18 H), 7.21-7.24 (m, 2 H), 7.30-7.36 (m, 4 H), 7.46-7.59 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -8.5 ($J_{C–Sn^{119}}$ = 351.1 Hz, $J_{C–Sn^{117}}$ = 336.3 Hz), 126.6 ($J_{C–Sn}$ = 45.9 Hz), 127.9, 128.8 ($J_{C–Sn}$ = 35.3 Hz), 135.8 ($J_{C–Sn}$ = 37.7 Hz), 142.7, 152.4 ($J_{C–Sn}$ = 30.4, 18.9 Hz); ^{119}Sn NMR ($CDCl_3$) δ -43.1; Anal. Calcd for $C_{18}H_{26}Sn_2$: C, 45.06; H, 5.46. Found: C, 45.33; H, 5.44.



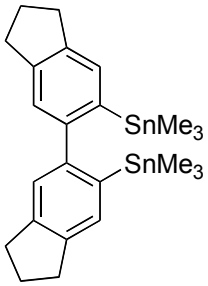
4,4',5,5'-Tetramethyl-2,2'-bis(trimethylstannyl)biphenyl (3b). Isolated in 53% yield as a white solid; ^{1}H NMR ($CDCl_3$) δ -0.08 (s, $J_{H–Sn^{119}}$ = 54.6 Hz, $J_{H–Sn^{117}}$ = 52.2 Hz, 18 H), 2.27 (s, 6 H), 2.31 (s, 6 H), 7.02 (s, 2 H), 7.25 (s, $J_{H–Sn}$ = 48.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ -8.4 ($J_{C–Sn^{119}}$ = 349.5 Hz, $J_{C–Sn^{117}}$ = 333.9 Hz), 19.4, 19.6, 130.5 ($J_{C–Sn}$ = 38.6 Hz), 134.4 ($J_{C–Sn}$ = 47.6 Hz), 136.1, 137.0 ($J_{C–Sn}$ = 39.4 Hz), 139.0, 150.2 ($J_{C–Sn}$ = 32.0, 18.9 Hz); ^{119}Sn NMR ($CDCl_3$) δ -33.9; Anal. Calcd for $C_{22}H_{34}Sn_2$: C, 49.30; H, 6.39. Found: C, 49.52; H, 6.42.



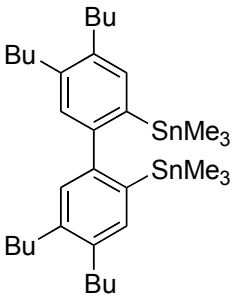
4,4',5,5'-Tetraethyl-2,2'-bis(trimethylstannyl)biphenyl (3c). Isolated in 52% yield as a white solid; ^{1}H NMR ($CDCl_3$) δ-0.07 (s, $J_{H–Sn^{119}}$ = 54.6 Hz, $J_{H–Sn^{117}}$ = 52.2 Hz, 18 H), 1.24 (t, J = 7.5 Hz, 6 H), 1.28 (t, J = 7.5 Hz, 6 H), 2.69 (q, J = 7.5 Hz, 4 H), 2.72 (q, J = 7.5 Hz, 4 H), 7.08 (s, $J_{H–Sn}$ = 17.4 Hz, 2 H), 7.29 (s, $J_{H–Sn}$ = 50.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ-8.5 ($J_{C–Sn^{119}}$ = 351.2 Hz, $J_{C–Sn^{117}}$ = 336.4 Hz), 15.2, 15.7, 25.3, 25.5, 128.9, 135.9, 139.3, 139.7, 141.2, 150.3; ^{119}Sn NMR ($CDCl_3$) δ -34.0; Anal. Calcd for $C_{26}H_{42}Sn_2$: C, 52.75; H, 7.15. Found: C, 52.68; H, 7.11.



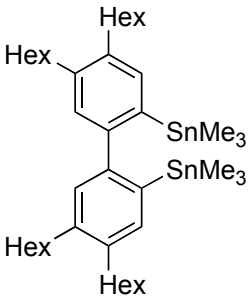
3,3'-Bis(trimethylstannyl)-5,5',6,6',7,7',8,8'-octahydro-2,2'-binaphthyl (3d). Isolated in 54% yield as a white solid; ^{1}H NMR ($CDCl_3$) δ-0.06 (s, $J_{H–Sn^{119}}$ = 54.6 Hz, $J_{H–Sn^{117}}$ = 52.2 Hz, 18 H), 1.84 (br, 8 H), 2.77 (br, 4 H), 2.82 (br, 4 H), 6.96 (s, $J_{H–Sn}$ = 17.4 Hz, 2 H), 7.19 (s, $J_{H–Sn}$ = 49.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ-8.4 ($J_{C–Sn^{119}}$ = 348.7 Hz, $J_{C–Sn^{117}}$ = 333.1 Hz), 23.3, 23.4, 29.1, 29.3, 129.7 ($J_{C–Sn}$ = 37.7 Hz), 135.1 ($J_{C–Sn}$ = 47.6 Hz), 136.3 ($J_{C–Sn}$ = 37.7 Hz), 136.8, 138.3, 149.7 ($J_{C–Sn}$ = 32.8, 18.0 Hz); ^{119}Sn NMR ($CDCl_3$) δ -34.0; Anal. Calcd for $C_{26}H_{38}Sn_2$: C, 53.11; H, 6.51. Found: C, 53.23; H, 6.29.



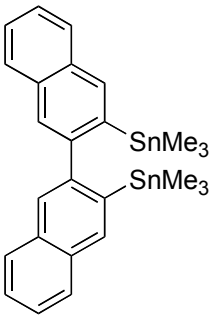
6,6'-Bis(trimethylstannyl)-5,5'-biindanyl (3e). Isolated in 45% yield as a white solid; ^{1}H NMR ($CDCl_3$) δ-0.08 (s, $J_{H–Sn^{119}}$ = 54.4 Hz, $J_{H–Sn^{117}}$ = 52.2 Hz, 18 H), 2.12 (quintet, J = 7.5 Hz, 4 H), 2.91-2.99 (m, 8 H), 7.13 (s, $J_{H–Sn}$ = 15.7 Hz, 2 H), 7.39 (s, $J_{H–Sn}$ = 48.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ-8.3 ($J_{C–Sn^{119}}$ = 348.7 Hz, $J_{C–Sn^{117}}$ = 333.1 Hz), 25.4, 32.5, 32.8, 125.4 ($J_{C–Sn}$ = 41.8 Hz), 131.5 ($J_{C–Sn}$ = 39.4 Hz), 139.9, 142.2 ($J_{C–Sn}$ = 48.4 Hz), 144.2, 150.7; ^{119}Sn NMR ($CDCl_3$) δ -32.8; Anal. Calcd for $C_{24}H_{34}Sn_2$: C, 51.48; H, 6.12. Found: C, 51.22; H, 6.13.



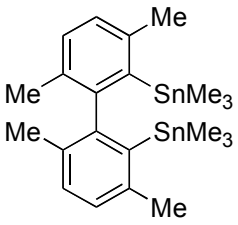
4,4',5,5'-Tetrabutyl-2,2'-bis(trimethylstannyl)biphenyl (3f). Isolated in 41% yield as a colorless oil; ^{1}H NMR ($CDCl_3$) δ -0.08 (s, $J_{H–Sn^{119}}$ = 54.6 Hz, $J_{H–Sn^{117}}$ = 52.2 Hz, 18 H), 0.93-1.01 (m, 12 H), 1.38-1.49 (m, 8 H), 1.55-1.65 (m, 8 H), 2.55-2.73 (m, 8 H), 7.05 (s, $J_{H–Sn}$ = 17.6 Hz, 2 H), 7.25 (s, $J_{H–Sn}$ = 50.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ -8.5 ($J_{C–Sn^{119}}$ = 347.8 Hz, $J_{C–Sn^{117}}$ = 332.2 Hz), 14.00, 14.05, 22.8, 23.0, 32.3, 32.5, 33.5, 33.8, 129.7 ($J_{C–Sn}$ = 39.4 Hz), 136.7 ($J_{C–Sn}$ = 39.4 Hz), 138.4 ($J_{C–Sn}$ = 46.8 Hz), 139.1, 140.2, 150.2; ^{119}Sn NMR ($CDCl_3$) δ -34.6; Anal. Calcd for $C_{34}H_{58}Sn_2$: C, 57.99; H, 8.30. Found: C, 57.85; H, 8.32.



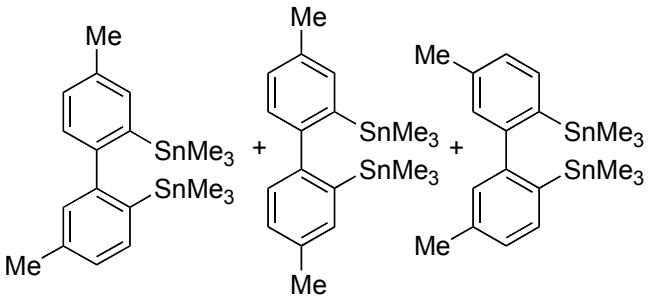
4,4',5,5'-Tetrahexyl-2,2'-bis(trimethylstannyl)biphenyl (3g). Isolated in 36% yield as a colorless oil; ^{1}H NMR ($CDCl_3$) δ -0.09 (s, $J_{H–Sn^{119}}$ = 54.4 Hz, $J_{H–Sn^{117}}$ = 52.2 Hz, 18 H), 0.88-0.94 (m, 12 H), 1.27-1.65 (m, 32 H), 2.53-2.72 (m, 8 H), 7.04 (s, $J_{H–Sn}$ = 17.6 Hz, 2 H), 7.24 (s, $J_{H–Sn}$ = 49.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ -8.5 ($J_{C–Sn^{119}}$ = 347.8 Hz, $J_{C–Sn^{117}}$ = 332.2 Hz), 14.09, 14.12, 22.6, 22.7, 29.3, 29.7, 31.3, 31.5, 31.74, 31.79, 32.4, 32.8, 129.7 ($J_{C–Sn}$ = 38.6 Hz), 136.7 ($J_{C–Sn}$ = 38.6 Hz), 138.4, 139.0, 140.3, 150.2; ^{119}Sn NMR ($CDCl_3$) δ -34.5; Anal. Calcd for $C_{42}H_{74}Sn_2$: C, 61.79; H, 9.14. Found: C, 62.09; H, 9.01.



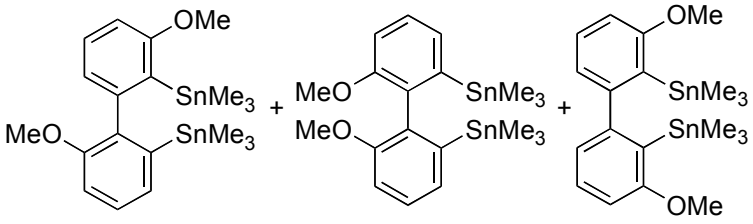
3,3'-Bis(trimethylstannyl)-2,2'-binaphthyl (3h). Isolated in 31% yield as an orange solid; ^{1}H NMR ($CDCl_3$) δ -0.04 (s, $J_{H–Sn^{119}}$ = 54.9 Hz, $J_{H–Sn^{117}}$ = 52.4 Hz, 18 H), 7.45-7.54 (m, 4 H), 7.75 (s, $J_{H–Sn}$ = 15.2 Hz, 2 H), 7.81-7.91 (m, 4 H), 8.06 (s, $J_{H–Sn}$ = 53.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ -8.2 ($J_{C–Sn^{119}}$ = 353.6 Hz, $J_{C–Sn^{117}}$ = 337.2 Hz), 125.9, 126.5, 127.2 ($J_{C–Sn}$ = 32.8 Hz), 127.6, 127.7, 132.1 ($J_{C–Sn}$ = 50.9 Hz), 132.9 ($J_{C–Sn}$ = 8.2 Hz), 136.3 ($J_{C–Sn}$ = 36.1 Hz), 141.8, 149.1 ($J_{C–Sn}$ = 33.6, 15.6 Hz); ^{119}Sn NMR ($CDCl_3$) δ -29.2; Anal. Calcd for $C_{26}H_{30}Sn_2$: C, 53.85; H, 5.21. Found: C, 53.63; H, 5.14.



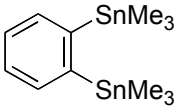
3,3',6,6'-Tetramethyl-2,2'-bis(trimethylstannyl)biphenyl (3i). Isolated in 16% yield as an orange solid; ^{1}H NMR ($CDCl_3$) δ -0.14 (s, $J_{H–Sn^{119}}$ = 53.8 Hz, $J_{H–Sn^{117}}$ = 51.8 Hz, 18 H), 1.78 (s, 6 H), 2.44 (s, 6 H), 7.03 (d, J = 7.8 Hz, 2 H), 7.08 (d, J = 7.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ -6.8 ($J_{C–Sn^{119}}$ = 340.6 Hz, $J_{C–Sn^{117}}$ = 324.7 Hz), 20.5, 24.5 ($J_{C–Sn}$ = 31.7 Hz), 128.5 ($J_{C–Sn}$ = 42.7 Hz), 130.6, 132.6 ($J_{C–Sn}$ = 36.1 Hz), 142.3 ($J_{C–Sn}$ = 28.2 Hz), 150.6 (1 x C resonance is absent as a result of overlapping); ^{119}Sn NMR ($CDCl_3$) δ -54.5; Anal. Calcd for $C_{22}H_{34}Sn_2$: C, 49.30; H, 6.39. Found: C, 49.25; H, 6.30.



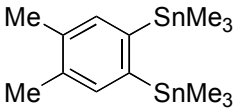
A mixture of 4,5'-dimethyl-2,2'-bis(trimethylstannyl)biphenyl (3k), 4,4'-dimethyl-2,2'-bis(trimethylstannyl)biphenyl (3k') and 5,5'-dimethyl-2,2'-bis(trimethylstannyl)biphenyl (3k''). Isolated in 52% yield as a white solid; ^{1}H NMR ($CDCl_3$) δ -0.064 (s), -0.059 (s), 2.380 (s), 2.382 (s), 2.407 (s), 7.07-7.17 (m), 7.33-7.49 (m); ^{13}C NMR ($CDCl_3$) δ -8.51, -8.48, -8.42, -8.38, 21.19, 21.2, 127.2, 127.3, 128.6, 128.9, 129.8, 130.2, 135.71, 135.74, 135.75, 136.40, 136.43, 137.59, 137.62, 138.6, 138.8, 142.4, 142.6, 149.5, 149.7, 152.4, 152.5; ^{119}Sn NMR ($CDCl_3$) δ -32.7, -32.7, -32.20, -32.16; Anal. Calcd for $C_{20}H_{30}Sn_2$: C, 47.30; H, 5.95. Found: C, 47.46; H, 5.88.



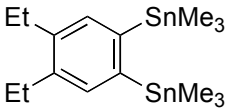
A mixture of 3,6'-dimethoxy-2,2'-bis(trimethylstannyl)biphenyl (3l), 6,6'-dimethoxy-2,2'-bis(trimethylstannyl)biphenyl (3l') and 3,3'-dimethoxy-2,2'-bis(trimethylstannyl)biphenyl (3l''). Isolated in 19% yield as a colorless oil; ^{1}H NMR ($CDCl_3$) δ -0.14 (s, 18 H), -0.15 (s), -0.13 (s), -0.07 (s), 3.68 (s), 3.68 (s), 3.82 (s), 6.72-6.87 (m), 7.10-7.13 (m), 7.25-7.36 (m); ^{13}C NMR ($CDCl_3$) δ -8.7, -8.2, -7.9, -7.6, 55.1, 55.5, 108.3, 110.5, 110.6, 110.8, 123.7, 127.5, 127.7, 127.9, 128.2, 129.6, 144.7, 149.0, 156.6, 163.1; ^{119}Sn NMR ($CDCl_3$) δ -44.5, -33.0, -32.9; Anal. Calcd for $C_{20}H_{30}O_2Sn_2$: C, 44.49; H, 5.60. Found: C, 44.51; H, 5.72.



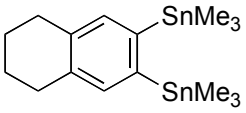
1,2-Bis(trimethylstannyl)benzene (4a).[7] Isolated in 15% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.32 (s, $J_{H–Sn}$ = 52.2 Hz, 18 H), 7.25-7.28 (m, 2 H), 7.50-7.54 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -7.1 ($J_{C–Sn^{119}}$ = 338.1 Hz, $J_{C–Sn^{117}}$ = 321.2 Hz), 127.6 ($J_{C–Sn}$ = 47.6, 12.8 Hz), 136.9 ($J_{C–Sn}$ = 62.3, 46.6 Hz), 151.9; ^{119}Sn NMR ($CDCl_3$) δ -32.6.



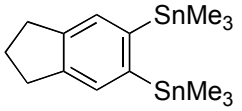
4,5-Dimethyl-1,2-bis(trimethylstannyl)benzene (4b). Isolated in 19% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.31 (s, $J_{H–Sn^{119}}$ = 53.1 Hz, $J_{H–Sn^{117}}$ = 51.1 Hz, 18 H), .2.25 (s, 6 H), 7.29 (s, $J_{H–Sn}$ = 46.7, 12.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ -7.1 ($J_{C–Sn^{119}}$ = 338.1 Hz, $J_{C–Sn^{117}}$ = 323.5 Hz), 19.4, 135.9, 138.3, 148.4; ^{119}Sn NMR ($CDCl_3$) δ -33.4; HRMS Calcd for $C_{14}H_{26}{}^{118}Sn_2$: M^+-Me, 417.9832. Found: *m/z* 414.9822.



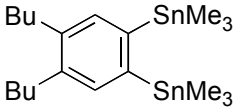
4,5-Diethyl-1,2-bis(trimethylstannyl)benzene (4c). Isolated in 17% yield as a white solid; ^{1}H NMR ($CDCl_3$) δ 0.32 (s, $J_{H–Sn^{119}}$ = 53.2 Hz, $J_{H–Sn^{117}}$ = 51.0 Hz, 18 H), 1.24 (t, *J* = 7.5 Hz, 6 H), 2.65 (q, *J* = 7.5 Hz, 4 H), 7.32 (s, $J_{H–Sn}$ = 44.9, 11.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ-7.1 ($J_{C–Sn}$ = 340.2 Hz), 15.4, 25.4, 137.1, 140.9, 148.5; ^{119}Sn NMR ($CDCl_3$) δ -33.1; Anal. Calcd for $C_{16}H_{30}Sn_2$: C, 41.79; H, 6.58. Found: C, 41.59; H, 6.53.



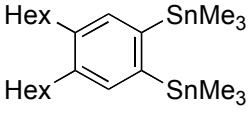
2,3-Bis(trimethylstannyl)-5,6,7,8-tetrahydronaphthalene (4d). Isolated in 18% yield as a colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.30 (s, $J_{H–Sn^{119}}$ = 53.1 Hz, $J_{H–Sn^{117}}$ = 51.1 Hz, 18 H), 1.79 (br, 4 H), 2.75 (br, 4 H), 7.22 (s, $J_{H–Sn}$ = 47.9, 11.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ -7.0 ($J_{C–Sn^{119}}$ = 339.0 Hz, $J_{C–Sn^{117}}$ = 327.7 Hz), 55.9, 61.9, 161.7, 169.5, 170.9; ^{119}Sn NMR ($CDCl_3$) δ -33.2; HRMS Calcd for $C_{16}H_{28}{}^{120}Sn_2$: M^+-Me, 445.0000. Found: *m/z* 444.9991.



5,6-Bis(trimethylstannyl)indan (4e). Isolated in 29% yield as a colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.32 (s, $J_{H–Sn^{119}}$ = 53.1 Hz, $J_{H–Sn^{117}}$ = 50.8 Hz, 18 H), 2.05 (quintet, *J* = 7.4 Hz, 2 H), 2.92 (t, *J* = 7.4 Hz, 4 H), 7.46 (s, $J_{H–Sn}$ = 46.0, 10.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ -6.9 ($J_{C–Sn^{119}}$ = 338.1 Hz, $J_{C–Sn^{117}}$ = 322.3 Hz), 24.9, 32.8, 133.2, 143.8, 148.3; ^{119}Sn NMR ($CDCl_3$) δ -31.4; HRMS Calcd for $C_{15}H_{26}{}^{120}Sn_2$: M^+-Me, 430.9844. Found: *m/z* 430.9822.

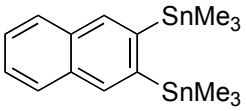


4,5-Dibutyl-1,2-bis(trimethylstannyl)benzene (4f). Isolated in 19% yield as a colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.31 (s, $J_{H–Sn^{119}}$ = 53.1 Hz, $J_{H–Sn^{117}}$ = 51.1 Hz, 18 H), 0.96 (t, *J* = 7.1 Hz, 6 H), 1.38-1.60 (m, 8 H), 2.58 (t, *J* = 7.8 Hz 4 H), 7.28 (s, $J_{H–Sn}$ = 47.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ -7.1 ($J_{C–Sn^{119}}$ = 338.2 Hz, $J_{C–Sn^{117}}$ = 323.5 Hz), 13.9, 22.9, 32.3, 33.5, 137.9 ($J_{C–Sn}$ = 65.9, 50.0 Hz), 139.8, 148.2; ^{119}Sn NMR ($CDCl_3$) δ -33.6; HRMS Calcd for $C_{20}H_{38}{}^{120}Sn_2$: M^+-Me, 503.0783. Found: *m/z* 503.0784.

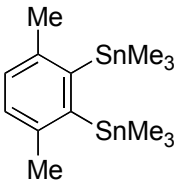


4,5-Dihexyl-1,2-bis(trimethylstannyl)benzene (4g). Isolated in 20% yield as a colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.31 (s, $J_{H–Sn}$ = 53.1 Hz, 18 H), 0.91 (br, 6 H), 1.33-159 (m, 16 H), 2.58 (t, *J* = 7.8 Hz 4 H), 7.28

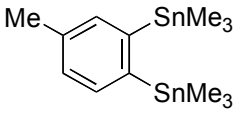
(s, $J_{H–Sn}$ = 48.1, 12.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ -7.1 ($J_{C–Sn^{119}}$ = 338.2 Hz, $J_{C–Sn^{117}}$ = 322.3 Hz), 14.1, 22.7, 29.6, 31.3, 31.7, 32.6, 137.9 ($J_{C–Sn}$ = 65.9, 48.8 Hz), 139.9, 148.2; ^{119}Sn NMR ($CDCl_3$) δ -33.6; HRMS Calcd for $C_{24}H_{46}{}^{118}Sn^{120}Sn$: M^+-Me, 557.1403. Found: *m/z* 557.1431.



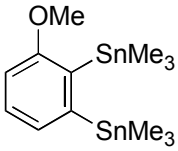
2,3-Bis(trimethylstannyl)naphthalene (4h).[7] Isolated in 26% yield as a yellow solid; ^1H NMR ($CDCl_3$) δ 0.39 (s, $J_{H–Sn^{119}}$ = 53.4 Hz, $J_{H–Sn^{117}}$ = 51.2 Hz, 18 H), 7.46-7.48 (m, 2 H), 7.76-7.79 (m, 2 H), 7.98 (s, $J_{H–Sn}$ = 53.2, 10.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ -7.0 ($J_{C–Sn^{119}}$ = 340.6 Hz, $J_{C–Sn^{117}}$ = 325.9 Hz), 126.2, 127.4, 132.5, 136.4 ($J_{C–Sn}$ = 59.9, 45.1 Hz), 147.7; ^{119}Sn NMR ($CDCl_3$) δ -29.1.



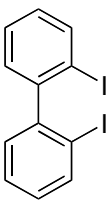
2,3-Bis(trimethylstannyl)-*p*-xylene (4i). Isolated in 4% yield as a colorless oil; ^1H NMR ($CDCl_3$) δ 0.35 (s, $J_{H–Sn}$ = 51.1 Hz, 18 H), 2.40 (s, 6 H), 7.02 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ -3.8 ($J_{C–Sn^{119}}$ = 351.6 Hz, $J_{C–Sn^{117}}$ = 325.7 Hz), 25.4, 129.2, 142.1, 153.5; ^{119}Sn NMR ($CDCl_3$) δ -48.7; HRMS Calcd for $C_{14}H_{26}{}^{116}Sn^{120}Sn$: M^+-Me, 414.9839. Found: *m/z* 414.9822.



3,4-Bis(trimethylstannyl)toluene (4k).[7] Isolated in 24% yield as a colorless oil; ^1H NMR ($CDCl_3$) δ 0.31 (s, $J_{H–Sn^{119}}$ = 53.5 Hz, $J_{H–Sn^{117}}$ = 51.5 Hz, 9 H), 0.32 (s, $J_{H–Sn^{119}}$ = 53.5 Hz, $J_{H–Sn^{117}}$ = 51.1 Hz, 9 H), 2.33 (s, 3 H), 7.11 (dd, *J* = 7.6, 1.7 Hz, 1 H), 7.35 (d, *J* = 1.7 Hz, 1 H), 7.43 (d, *J* = 7.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ -7.1 ($J_{C–Sn^{119}}$ = 339.4 Hz, $J_{C–Sn^{117}}$ = 324.7 Hz), 21.3, 128.4 ($J_{C–Sn}$ = 48.9 Hz), 136.8, 137.1, 137.8 ($J_{C–Sn}$ = 66.0, 47.6 Hz), 147.7, 151.6 (1 x C resonance is absent as a result of overlapping); ^{119}Sn NMR ($CDCl_3$) δ -32.9, -32.2.



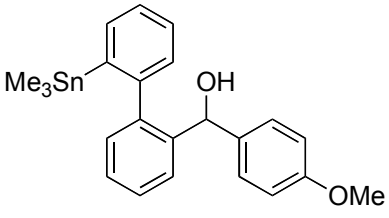
2,3-Bis(trimethylstannyl)anisole (4l). Isolated in 16% yield as a colorless oil; ^1H NMR ($CDCl_3$) δ 0.28 (s, $J_{H–Sn^{119}}$ = 54.8 Hz, $J_{H–Sn^{117}}$ = 52.8 Hz, 9 H), 0.32 (s, $J_{H–Sn^{119}}$ = 53.5 Hz, $J_{H–Sn^{117}}$ = 51.1 Hz, 9 H), 3.77 (s, 3 H), 6.79 (dd, *J* = 8.4, 1.0 Hz, 1 H), 7.16 (dd, *J* = 7.2, 1.0 Hz, 1 H), 7.28 (dd, *J* = 8.4, 7.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ -6.4 ($J_{C–Sn^{119}}$ = 344.2 Hz, $J_{C–Sn^{117}}$ = 329.6 Hz), -5.9 ($J_{C–Sn^{119}}$ = 351.6 Hz, $J_{C–Sn^{117}}$ = 335.7 Hz), 55.3, 109.4, 128.8, 129.9, 140.3, 152.8, 163.4; ^{119}Sn NMR ($CDCl_3$) δ -46.6, -31.6; HRMS Calcd for $C_{13}H_{24}O^{116}Sn^{120}Sn$: M^+-Me, 418.9630. Found: *m/z* 418.9629.



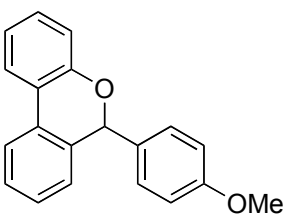
2,2'-Diiodobiphenyl (8).[8] To a CH_2Cl_2 solution (2 mL) of **3a** (46.0 mg, 0.096 mmol) was added iodine (51.3 mg, 0.202 mmol), and the mixture was stirred at room temperature for 1.5 h before dilution with ether. The organic layer was washed with water and dried over $MgSO_4$. Evaporation of the solvent followed by gel permeation chromatography (chloroform as an eluent) gave 2,2'-

diiodobiphenyl (**8**) in 89% yield as a white solid. ^{1}H NMR ($CDCl_3$) δ 6.96-7.56 (m, 6 H), 7.95 (d, J = 7.9, Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 99.6, 127.9, 129.3, 129.8, 138.8, 148.8.

9,9-Dimethyl-9-stannafluorene (9).[9] To a THF solution (1 mL) of **3a** (34.4 mg, 0.071 mmol) was added MeLi (0.90 M in ether, 0.12 mL, 0.108 mmol) dropwise and the mixture was stirred at 0 °C for 1.5 h. After the mixture was diluted with ether, the organic layer was washed with water and dried over $MgSO_4$. Evaporation of the solvent followed by gel permeation chromatography (chloroform as an eluent) gave 9,9-dimethyl-9-stannafluorene (**9**) in 73% yield as a white solid. ^{1}H NMR ($CDCl_3$) δ 0.54 (s, $J_{H–Sn}$ = 59.4 Hz, 6 H), 7.25-7.45 (m, 4 H), 7.68 (d, J = 6.9 Hz, $J_{H–Sn}$ = 37.5 Hz, 2 H), 7.96 (d, J = 7.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ -8.6 ($J_{C–Sn^{119}}$ = 362.6 Hz, $J_{C–Sn^{117}}$ = 346.7 Hz), 122.5 ($J_{C–Sn}$ = 37.9 Hz), 127.5 ($J_{C–Sn}$ = 42.7 Hz), 129.1, 136.3 ($J_{C–Sn}$ = 43.9 Hz), 140.9, 148.2; ^{119}Sn NMR ($CDCl_3$) δ -31.0.



4-Methoxy-2'-[2-(trimethylstannyl)phenyl]benzhydrol (10). A solution of **3a** (97.0 mg, 0.202 mmol) in THF (1 mL) was treated with MeLi (0.90 M in ether, 0.34 mL, 0.303 mmol) at –78 °C, and the resulting mixture was stirred at –78 °C for 1 h before addition of 4-methoxybenzaldehyde (82.5 mg, 0.606 mmol). Then the mixture was diluted with ether, washed with water and dried over $MgSO_4$. Evaporation of the solvent followed by gel permeation chromatography (chloroform as an eluent) gave 4-methoxy-2'-[2-(trimethylstannyl)phenyl]benzhydrol (**10**) as a mixture of diastereomers (diastereomeric ratio = *ca.* 59:41) in 71% yield as a colorless oil. ^{1}H NMR ($CDCl_3$) δ -0.31 (s, $J_{H–Sn^{119}}$ = 54.9 Hz, $J_{H–Sn^{117}}$ = 52.6 Hz, 9 H, *minor*), -0.01 (s, $J_{H–Sn^{119}}$ = 54.8 Hz, $J_{H–Sn^{117}}$ = 52.4 Hz, 9 H, *major*), 1.87 (s, 1 H, *major*), 2.04 (s, 1 H, *minor*), 3.73 (s, 3 H, *minor*), 3.78 (s, 3 H, *major*), 5.57 (s, 1 H, *major*), 5.90 (s, 1 H, *minor*), 6.66-6.85 (m), 7.01-7.16 (m), 7.25-7.58 (m), 7.71-7.74 (m); ^{13}C NMR ($CDCl_3$) δ -8.7 ($J_{C–Sn}$ = 343.0 Hz), -8.5 ($J_{C–Sn}$ = 343.0 Hz), 29.7, 55.2, 72.4, 72.6, 113.4, 113.6, 125.7, 126.2, 126.5, 126.7, 126.9, 127.1, 127.5, 127.6, 127.76, 127.87, 127.96, 128.8, 128.9, 129.7, 129.9, 130.2, 135.4, 135.88, 135.9, 136.5, 141.7, 141.8, 142.3, 142.8, 143.2, 147.7, 147.8, 158.9; ^{119}Sn NMR ($CDCl_3$) δ -32.5, -31.0; Anal. Calcd for $C_{23}H_{26}O_2Sn$: C, 60.69; H, 5.78. Found: C, 60.83; H, 5.76.



2-(4-Methoxyphenyl)-2*H*-benzo[*c*]chromene (11). To a DMSO solution (1 mL) of **7** (28.9 mg, 0.064 mmol) was added $CuCl_2$ (8.6 mg, 0.064 mmol), and the mixture was stirred at 50 °C for 8 h. The mixture was diluted with ether, washed with water and dried over $MgSO_4$. Evaporation of the solvent followed by gel permeation chromatography (chloroform as an eluent) gave 2-(4-methoxyphenyl)-2*H*-benzo[*c*]chromene (**11**) in 51% yield as a colorless oil. ^{1}H NMR ($CDCl_3$) δ 3.80 (s, 3 H), 6.13 (s, 1 H), 6.86-

7.06 (m, 3 H), 6.88 (d, *J* = 8.7 Hz, 2 H), 7.20-7.42 (m, 3 H), 7.30 (d, *J* = 8.7 Hz, 2 H) 7.75-7.78 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 55.3, 79.3, 113.8, 117.9, 122.00, 122.03, 122.8, 123.1, 126.2, 127.6, 128.4, 129.5, 129.6, 130.1, 131.7, 134.2, 153.6, 159.6; Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.15; H, .5.50.

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