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Supporting Information for Palladium-Catalyzed Dimerization-Carbostannylation of Alkynes: Synthesis of Highly Conjugated Alkenylstannanes

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General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere (deoxygenated by passing through BASF-Catalyst R3-11 column at 80 °C). Nuclear magnetic resonance spectra were taken on a JEOL EX-270 (^{1}H, 270 MHz; ^{13}C, 67.8 MHz; ^{119}Sn, 101 MHz) spectrometer or a Varian Mercury 200 (^{1}H, 200 MHz) spectrometer using tetramethylsilane (^{1}H) as an internal standard and tetramethyltin (^{119}Sn) as an external standard. The preparative recycling gel permeation chromatography was performed with JAI LC-908 equipped with JAIGEL-1H and -2H columns (chloroform as an eluent). Unless otherwise noted, reagents commercially available were used without purification. Solvents were distilled from a suitable drying reagent as follows: sodium/benzophenone ketyl for Toluene, THF, dioxane and DME; phosphorus pentoxide for chloroform; calcium hydride for DMF. Tributyl(phenylethynyl)tin,[1] tributyl(1-hexyn-1-yl)tin,[1] tributyl(trimethylsilylethynyl)tin,[1] tributyl(vinyl)tin,[2] tributyl((*E*)-β-styryl)tin,[3] and tributyl((*E*)-1-octen-1-yl)tin[4] were prepared according to literature procedures.

Dimerization-Carbostannylation of Alkynes. ***A General Procedure.*** A solution of bis(phenylimino)acenaphthene (**2a**) (5.5 mg, 16 μmol), $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (3.0 mg, 8.2 μmol) and an alkyne (1.0 mmol) in toluene (3 mL) was degassed by four freeze-thaw cycles. To this solution was added an organostannane (0.34 mmol), and the mixture was stirred at the temperature indicated in Table 2. After the time specified in Table 2, the solvent was evaporated. Gel permeation chromatography of the residue gave a corresponding dimerization-carbostannylation product. Yields are listed in Table 2.

Diethyl (1*Z*,3*E*)-6-Phenyl-1-tributylstannylhexa-1,3-dien-5-yne-1,4-dicarboxylate (5a). A brown oil: ^{1}H NMR ($CDCl_3$) δ 0.70–1.83 (m, 33 H), 4.24 (q, J = 7.2 Hz, 2 H), 4.32 (q, J = 7.2 Hz, 2 H), 7.15–7.74 (m, 6 H), 8.30 (d, J = 12.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.9, 13.6, 14.2, 14.3, 27.2, 28.9, 61.0, 61.8, 83.4, 100.8, 121.3, 122.6, 128.4, 129.0, 131.8, 144.3, 147.8, 153.0, 164.5, 171.3; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -42.8; Anal. Calcd for $C_{30}H_{44}O_4Sn$: C, 61.34; H, 7.55. Found: C, 61.60; H, 7.60.

Diethyl (1*Z*,3*E*)-1-Tributylstannyldeca-1,3-dien-5-yne-1,4-dicarboxylate (5b). A brown oil: ^{1}H NMR ($CDCl_3$) δ 0.72–1.72 (m, 40 H), 2.49 (t, J = 6.9 Hz, 2 H), 4.08–4.36 (m, 4 H), 7.53 (d, J = 11.9 Hz, 1 H), 8.17 (d, J = 11.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.9, 13.59, 13.64, 14.2, 14.3, 19.6, 21.9, 27.2, 28.9, 30.5, 60.9, 61.6, 74.6,

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102.8, 121.8, 143.6, 148.0, 151.8, 164.9, 171.4; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -43.3; Anal. Calcd for $C_{28}H_{48}O_4Sn$: C, 59.27; H, 8.53. Found: C, 59.12; H, 8.31.

Diethyl (1*Z*,3*E*)-1-Tributylstannyl-6-trimethylsilylhexa-1,3-dien-5-yne-1,4-dicarboxylate (5c). A brown oil: ^1H NMR ($CDCl_3$) δ 0.26 (s, 9 H), 0.71–1.73 (m, 33 H), 4.22 (q, *J* = 7.1 Hz, 2 H), 4.27 (q, *J* = 7.1 Hz, 2 H), 7.59 (d, *J* = 12.1 Hz, 1 H), 8.18 (d, *J* = 12.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ -0.2, 11.9, 13.6, 14.1, 14.3, 27.2, 28.9, 61.0, 61.7, 98.1, 107.1, 121.1, 145.7, 147.7, 153.6, 164.3, 171.2; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -42.8; Anal. Calcd for $C_{27}H_{48}O_4SiSn$: C, 55.58; H, 8.29. Found: C, 55.66; H, 8.55.

Diethyl (1*Z*,3*E*)-1-Tributylstannylhexa-1,3,5-triene-1,4-dicarboxylate (5d). A brown oil: ^1H NMR ($CDCl_3$) δ 0.82–1.74 (m, 33 H), 4.21 (q, *J* = 7.1 Hz, 2 H), 4.27 (q, *J* = 7.1 Hz, 2 H), 5.54 (dd, *J* = 11.5, 1.6 Hz, 1 H), 5.74 (dd, *J* = 17.6, 1.6 Hz, 1 H), 6.71 (dd, *J* = 17.6, 11.5 Hz, 1 H), 7.24 (d, *J* = 12.7 Hz, 1 H), 8.15 (d, *J* = 12.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.8, 13.6, 14.25, 14.29, 27.2, 29.0, 60.9, 61.0, 122.7, 128.9, 134.7, 136.9, 146.6, 149.7, 166.6, 171.4; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -44.4; Anal. Calcd for $C_{24}H_{42}O_4Sn$: C, 56.16; H, 8.25. Found: C, 56.27; H, 8.22.

Diethyl (1*Z*,3*E*)-1-Tributylstannylhexa-1,3,5-triene-1,3-dicarboxylate (6d). A brown oil: ^1H NMR ($CDCl_3$) δ 0.69–1.78 (m, 33 H), 4.22 (q, *J* = 7.1 Hz, 2 H), 4.24 (q, *J* = 7.1 Hz, 2 H), 5.50 (d, *J* = 10.1 Hz, 1 H), 5.67 (d, *J* = 17.6, 1 H), 6.63 (ddd, *J* = 17.6, 11.2, 10.1 Hz, 1 H), 7.24 (d, *J* = 11.2 Hz, 1 H), 7.89 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.3, 13.6, 14.3, 27.3, 29.0, 60.9, 61.0, 126.5, 130.9, 132.9, 141.0, 144.2, 148.1, 166.3, 170.6; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -47.3.

Diethyl (1*Z*,3*E*,5*E*)-6-Phenyl-1-tributylstannylhexa-1,3,5-triene-1,4-dicarboxylate (5e). A brown oil: ^1H NMR ($CDCl_3$) δ 0.74–1.76 (m, 33 H), 4.23 (q, *J* = 7.1 Hz, 2 H), 4.32 (q, *J* = 7.1 Hz, 2 H), 7.15–7.60 (m, 8 H), 8.29 (d, *J* = 11.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.8, 13.7, 14.3, 27.2, 29.0, 60.9, 61.1, 120.5, 127.0, 128.4, 128.6, 134.3, 136.1, 136.5, 137.0, 146.5, 149.3, 166.8, 171.5; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -44.1; Anal. Calcd for $C_{30}H_{46}O_4Sn$: C, 61.13; H, 7.87. Found: C, 60.87; H, 7.80.

Diethyl (1*Z*,3*E*,5*E*)-6-Phenyl-1-tributylstannylhexa-1,3,5-triene-1,3-dicarboxylate (6e). A brown oil: ^1H NMR ($CDCl_3$) δ 0.68–1.50 (m, 33 H), 4.26 (q, *J* = 7.1 Hz, 4 H), 6.95–7.02 (m, 2 H), 7.28–7.50 (m, 6 H), 8.00 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.4, 13.6, 14.3, 27.3, 29.0, 60.90, 60.95, 124.2, 127.4, 128.7, 129.2, 129.8, 136.0, 141.3, 141.5, 144.0, 148.6, 166.4, 170.7; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -47.3.

Diethyl (1*Z*,3*E*,5*E*)-1-Tributylstannyldodeca-1,3,5-triene-1,4-dicarboxylate (5f). A brown oil: ^1H NMR ($CDCl_3$) δ 0.74–1.77 (m, 44 H), 2.22 (q, *J* = 6.8 Hz, 2 H), 4.21 (q, *J* = 7.1 Hz, 2 H), 4.26 (q, *J* = 7.1 Hz, 2 H), 6.21 (dt, *J* = 15.7, 6.8 Hz, 1 H), 6.40 (d, *J* = 15.7 Hz, 1 H), 7.11 (d, *J* = 11.9 Hz, 1 H), 8.17 (d, *J* = 11.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.7, 13.6, 14.1, 14.2, 14.3, 22.6, 27.2, 28.89, 28.94, 29.0, 31.6, 33.9, 60.8, 60.9, 122.0, 134.8, 135.1, 140.7, 147.3, 147.7, 167.0, 171.5; $^{119}Sn\{^1H\}$

NMR ($CDCl_3$) δ -45.0; Anal. Calcd for $C_{30}H_{54}O_4Sn$: C, 61.13; H, 7.87. Found: C, 60.87; H, 7.80.

Diethyl (1*Z*,3*E*,5*E*)-1-Tributylstannyldodeca-1,3,5-triene-1,3-dicarboxylate (6f). A brown oil: ^1H NMR ($CDCl_3$) δ 0.69–1.75 (m, 44 H), 2.17 (q, *J* = 6.8 Hz, 2 H), 4.22 (q, *J* = 7.2 Hz, 2 H), 4.23 (q, *J* = 7.1 Hz, 2 H), 6.18 (dt, *J* = 15.2, 6.6 Hz, 1 H), 6.33 (dd, *J* = 15.2, 10.3 Hz, 1 H), 7.23 (d, *J* = 10.3 Hz, 1 H), 7.91 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.3, 13.6, 14.0, 14.3, 22.6, 27.3, 28.9, 29.0, 31.7, 33.5, 60.8, 126.6, 127.7, 141.7, 143.1, 146.4, 148.8, 166.6, 170.8; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -47.9.

Tetramethyl (1*E*,3*Z*)-6-Phenyl-1-tributylstannylhexa-1,3-dien-5-yne-1,2,3,4-tetracarboxylate (5g). A brown oil: ^1H NMR ($CDCl_3$) δ 0.73–1.83 (m, 27 H), 3.71 (s, 3 H), 3.77 (s, 3 H), 3.86 (s, 3 H), 3.93 (s, 3 H), 7.16–7.65 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.1, 13.5, 27.2, 28.6, 51.6, 52.7, 53.2, 84.1, 104.9, 121.4, 128.4, 129.5, 129.9, 132.0, 132.5, 135.0, 137.1, 161.0, 163.0, 164.7, 172.5; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -26.1; Anal. Calcd for $C_{32}H_{44}O_8Sn$: C, 56.91; H, 6.57. Found: C, 56.92; H, 6.63.

Tetramethyl (1*E*,3*Z*)-1-Tributylstannyldeca-1,3-dien-5-yne-1,2,3,4-tetracarboxylate (5h). A brown oil: ^1H NMR ($CDCl_3$) δ 0.71–1.72 (m, 34 H), 2.32 (t, *J* = 7.1 Hz, 2 H), 3.68 (s, 3 H), 3.71 (s, 3 H), 3.77 (s, 3 H), 3.83 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 12.4, 13.5, 13.7, 19.7, 22.0, 27.2, 28.8, 30.1, 51.4, 52.5, 52.9, 75.3, 105.8, 127.9, 135.8, 136.0, 162.4, 164.9, 165.5, 166.7, 171.2; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -35.0; Anal. Calcd for $C_{30}H_{48}O_8Sn$: C, 54.98; H, 7.38. Found: C, 55.04; H, 7.46.

Tetramethyl (1*E*,3*Z*)-1-Tributylstannyl-6-trimethylsilylhexa-1,3-dien-5-yne-1,2,3,4-tetracarboxylate (5i). A brown oil: ^1H NMR ($CDCl_3$) δ 0.19 (s, 9 H), 0.81–1.73 (m, 27 H), 3.70 (s, 3 H), 3.75 (s, 3 H), 3.80 (s, 3 H), 3.88 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ -0.7, 11.1, 13.6, 27.2, 28.6, 51.4, 52.5, 52.7, 53.1, 97.7, 112.3, 129.0, 134.7, 139.2, 160.6, 162.5, 164.4, 172.3; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -27.4; Anal. Calcd for $C_{29}H_{48}O_8SiSn$: C, 51.87; H, 7.21. Found: C, 51.86; H, 7.00.

Tetramethyl (1*E*,3*Z*)-1-Tributylstannylhexa-1,3,5-triene-1,2,3,4-tetracarboxylate (5j). A brown oil: ^1H NMR ($CDCl_3$) δ 0.80–1.82 (m, 27 H), 3.70 (s, 3 H), 3.74 (s, 3H), 3.83 (s, 3 H), 3.92 (s, 3 H), 5.54 (d, *J* = 17.4 Hz, 1 H), 5.60 (d, *J* = 10.8 Hz, 1 H), 6.96 (dd, *J* = 17.4, 10.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.8, 13.6, 27.2, 28.6, 51.7, 52.5, 52.7, 125.2, 127.6, 130.9, 134.6, 145.5, 161.1, 163.3, 165.2, 167.4, 172.4; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -26.5; Anal. Calcd for $C_{26}H_{42}O_8Sn$: C, 51.93; H, 7.04. Found: C, 51.82; H, 7.11.

Tetramethyl (1*E*,3*Z*,5*E*)-6-Phenyl-1-tributylstannylhexa-1,3,5-triene-1,2,3,4-tetracarboxylate (5k). A brown oil: ^1H NMR ($CDCl_3$) δ 0.70–1.58 (m, 27 H), 3.69 (s, 3 H), 3.73 (s, 3 H), 3.85 (s, 3 H), 3.97 (s, 3 H), 6.75 (d, *J* = 16.2 Hz, 1 H), 6.96 (d, *J* = 16.2 Hz, 1 H), 7.20–7.54 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.8, 13.5, 27.1, 28.6, 51.7, 52.4, 52.6, 52.7, 122.0, 126.4, 127.7, 128.8, 129.7, 134.9, 135.2, 139.5, 145.9,

161.3, 163.5, 165.4, 168.0, 172.6; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -30.3; Anal. Calcd for $C_{32}H_{46}O_8Sn$: C, 56.74; H, 6.84. Found: C, 56.62; H, 7.04.

Tetramethyl (1*E*,3*Z*,5*E*)-1-Tributylstannyldodeca-1,3,5-triene-1,2,3,4-tetracarboxylate (5l). A brown oil: ^1H NMR ($CDCl_3$) δ 0.78–1.64 (m, 38 H), 2.16 (q, *J* = 7.0 Hz, 2 H), 3.67 (s, 3 H), 3.70 (s, 3 H), 3.81 (s, 3 H), 3.89 (s, 3 H), 6.00 (dt, *J* = 15.9, 6.8 Hz, 1 H), 6.23 (d, *J* = 15.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.8, 13.6, 14.0, 22.5, 27.2, 28.5, 28.6, 28.9, 31.5, 33.7, 51.6, 52.3, 52.4, 52.6, 124.5, 134.9, 144.6, 146.1, 160.7, 163.5, 165.5, 168.0, 172.5; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -27.7; Anal. Calcd for $C_{32}H_{54}O_8Sn$: C, 56.07; H, 7.94. Found: C, 55.88; H, 7.98.

Tetramethyl (1*E*,3*Z*,6*E*)-7-Phenyl-1-tributylstannylhepta-1,3,6-triene-1,2,3,4-tetracarboxylate (5m). A brown oil: ^1H NMR ($CDCl_3$) δ 0.82–1.67 (m, 27 H), 3.60 (s, 3 H), 3.73 (s, 3 H), 3.82 (s, 3 H), 3.83 (s, 3 H), 6.04 (dt, *J* = 15.7, 7.0 Hz, 1 H), 6.43 (d, *J* = 15.7 Hz, 1 H), 7.14–7.39 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.0, 13.5, 27.2, 28.6, 35.6, 51.6, 52.3, 52.45, 52.54, 122.7, 126.2, 127.5, 128.4, 130.3, 133.5, 135.0, 136.8, 145.4, 159.7, 163.3, 165.4, 168.6, 172.3; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -28.3; Anal. Calcd for $C_{33}H_{48}O_8Sn$: C, 57.32; H, 7.00. Found: C, 57.07; H, 7.27.

Dimerization-Carbostannylation of Alkynes with (*E*)-1,2-Bis(tributylstannyl)ethene. A solution of bis(phenylimino)acenaphthene (**3a**) (5.5 mg, 16 μmol), $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (3.0 mg, 8.2 μmol) and an alkyne (1.0 mmol) in toluene (3 mL) was degassed by four freeze-thaw cycles. To this solution was added (*E*)-1,2-bis(tributylstannyl)ethene (0.17 mmol), and the mixture was stirred at 50 °C. After the time specified in eq 3, the solvent was evaporated. Gel permeation chromatography of the residue gave a corresponding dimerization-carbostannylation product.

Tetraethyl (1*Z*,3*E*,5*E*,7*E*,9*Z*)-1,10-Bis(tributylstannyl)deca-1,3,5,7,9-pentaene-1,4,7,10-tetracarboxylate (9a). A brown solid: ^1H NMR ($CDCl_3$) δ 0.74–1.81 (m, 66 H), 4.20 (q, *J* = 7.1 Hz, 4 H), 4.31 (q, *J* = 7.1 Hz, 4 H), 7.26 (d, *J* = 12.1 Hz, 2 H), 7.32 (s, 2 H), 8.17 (d, *J* = 12.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 11.8, 13.7, 14.25, 14.29, 27.2, 29.0, 60.9, 61.2, 127.8, 134.0, 138.0, 145.9, 151.0, 166.5, 171.3; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -44.0; Anal. Calcd for $C_{46}H_{80}O_8Sn_2$: C, 55.33; H, 8.08. Found: C, 55.35; H, 7.88.

Octamethyl (1*E*,3*Z*,5*E*,7*Z*,9*E*)-1,10-Bis(tributylstannyl)deca-1,3,5,7,9-pentaene-1,2,3,4,7,8,9,10-octacarboxylate (9b). A brown solid: ^1H NMR ($CDCl_3$) δ 0.69–1.93 (m, 54 H), 3.67 (s, 6 H), 3.73 (s, 6 H), 3.82 (s, 6 H), 3.94 (s, 6 H), 6.54 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 10.8, 13.6, 27.1, 28.6, 51.6, 52.6, 52.7, 52.8, 130.7, 131.9, 134.3, 144.5, 162.1, 162.9, 164.8, 166.5, 172.1; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -25.9; Anal. Calcd for $C_{50}H_{80}O_{16}Sn_2$: C, 51.13; H, 6.86. Found: C, 50.93; H, 6.89.

Coupling of 5a with 4-iodonitrobenzene. A solution of **5a** (50 mg, 85 μmol) in DMF (1.5 mL) was degassed by three freeze-thaw cycles. To this solution was added 4-

iodonitrobenzene (21 mg, 85 μmol), $Pd(PPh_3)_4$ (9.8 mg, 8.5 μmol) and CuI (12 mg, 64 μmol). The mixture was stirred at 50 °C for 18 h, and then diluted with diethyl ether (25 mL). The organic layer was washed with water, dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The residue was diluted with diethyl ether (10 mL) and stirred for 30 min with a 1 M KF aqueous solution (2 mL). Filtration through a Celite plug was followed by extraction with diethyl ether (20 mL). The organic layer was washed successively with water and brine, and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by gel permeation chromatography gave diethyl (1*E*,3*E*)-1-(4-nitrophenyl)-6-phenylhexa-1,3-dien-5-yne-1,4-dicarboxylate (**10**) (25 mg, 70%) as a yellow solid: ^{1}H NMR ($CDCl_3$) δ 1.26 (t, *J* = 7.1 Hz, 3 H), 1.27 (t, *J* = 7.1 Hz, 3 H), 4.21 (q, *J* = 7.1 Hz, 2 H), 4.24 (q, *J* = 7.1 Hz, 2 H), 7.09–7.75 (m, 8 H), 8.11 (d, *J* = 12.3 Hz, 1 H), 8.22 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.09, 14.13, 61.9, 62.1, 83.4, 102.1, 122.2, 123.3, 123.5, 128.5, 129.4, 131.3, 131.9, 136.5, 137.5, 138.9, 140.9, 147.8, 164.0, 165.6.

Coupling of 5a with bromo(phenyl)ethyne. A solution of **5a** (65 mg, 0.11 mmol) in DMF (1.5 mL) was degassed by three freeze-thaw cycles. To this solution was added bromo(phenyl)ethyne (20 mg, 0.11 mmol), $Pd(PPh_3)_4$ (13 mg, 11 μmol) and CuI (2.1 mg, 11 μmol). The mixture was stirred at 50 °C for 5 h, and then diluted with diethyl ether (25 mL). The organic layer was washed with water and dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The residue was diluted with diethyl ether (10 mL) and stirred for 30 min with a 1 M KF aqueous solution (2 mL). Filtration through a Celite plug was followed by extraction with diethyl ether (20 mL). The organic layer was washed successively with water and brine, and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by gel permeation chromatography gave diethyl (3*E*,5*E*)-1,8-diphenylocta-3,5-diene-1,7-diyne-3,6-dicarboxylate (**11**) (24 mg, 54%) as a red solid: ^{1}H NMR ($CDCl_3$) δ 0.91 (t, *J* = 7.1 Hz, 6 H), 4.02 (q, *J* = 7.1 Hz, 4 H), 6.82 (s, 2 H), 7.13–7.45 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 13.8, 60.5, 117.3, 125.4, 127.8, 129.2, 131.2, 154.4, 154.8, 165.1.

Coupling of 5a with 1,4-diiodobenzene. A solution of **5a** (48 mg, 81 μmol) in DMF (1.5 mL) was degassed by three freeze-thaw cycles. To this solution was added 1,4-diiodobenzene (13 mg, 41 μmol), $Pd(PPh_3)_4$ (9.4 mg, 8.1 μmol) and CuI (7.7 mg, 41 μmol). The mixture was stirred at 50 °C for 8 h, and then diluted with diethyl ether (25 mL). The organic layer was washed with water, dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The residue was diluted with diethyl ether (10 mL) and stirred for 30 min with a 1 M KF aqueous solution (2 mL). Filtration through a Celite plug was followed by extraction with diethyl ether (20 mL). The organic layer was washed successively with water and brine, and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by gel permeation chromatography gave 1,4-bis[(1*E*,3*E*)-1,4-bis(ethoxycarbonyl)-6-phenylhexa-1,3-dien-5-yn-1-yl]benzene (**12**) (17 mg, 62%) as an orange solid: ^{1}H NMR ($CDCl_3$) δ 1.33 (t, *J* = 7.2 Hz, 6 H), 1.36 (t, *J* = 7.1 Hz, 6 H), 4.29 (q, *J* = 7.2 Hz, 4 H),

4.33 (q, J = 7.1 Hz, 4 H), 7.15–7.73 (m, 16 H), 8.12 (d, J = 12.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 14.2, 61.6, 61.9, 83.8, 101.3, 122.1, 122.5, 128.4, 129.1, 130.1, 131.8, 134.5, 135.2, 139.2, 140.6, 164.3, 166.6.

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