

Supporting information

Synthesis of Bicyclic *p*-Diiodobenzenes via Silver-Catalyzed *C*_{sp}-H Iodination and Ruthenium-Catalyzed Cycloaddition

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General Considerations. Column chromatography were performed on silica gel (Cica silica gel 60N) with mixed solvents [hexane / ethyl acetate]. ¹H and ¹³C NMR spectra were obtained for samples in CDCl₃ solution at 25 °C. ¹H NMR chemical shifts are reported in terms of chemical shift (δ, ppm) relative to the singlet at 7.26 ppm for chloroform. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; sept, septet; m, multiplet. Coupling constants are reported in Hz. ¹³C NMR spectra were fully decoupled and are reported in terms of chemical shift (δ, ppm) relative to the triplet at δ = 77.0 ppm for CDCl₃. Elemental analyses were performed by the Instrumental Analysis Facility of Nagoya University. Melting points were obtained in capillary tubes and are uncorrected. 1,2-Dichloroethane and toluene were distilled from CaH₂, and degassed before use. Dry DMF was purchased and used directly as received. Cp*RuCl(cod) was prepared according to the literature procedures (Oshima, N., Suzuki, H. Moro-oka, Y. *Chem. Lett.* **1984**, 1161-1164.).

General Procedure for Silver-Catalyzed Iodination (Bromination) of Diynes: Synthesis of

diiododiene 3a-I. A solution of dimethyl dipropargylmalonate (**2a**) (208.3 mg, 1.0 mmol), *N*-iodosuccinimide (675.2 mg, 3.0 mmol), and AgNO₃ (16.8 mg, 0.099 mmol) in dry DMF (6.0 mL) was stirred for 3 h at room temperature in the dark. The reaction mixture was then quenched with sat. Na₂S₂O₃ (50 mL), and extracted with AcOEt (20 mL × 3). The combined organic layer was washed with distilled water (40 mL × 2) and brine (40 mL × 2), and dried with MgSO₄. The solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel eluted with hexane/AcOEt (20:1 ~ 10:1) to give **3a-I** (422.7 mg, 92%) as colorless solids (mp. 94.9-95.1 °C): IR (CHCl₃) 2253 (C≡C), 1739 (C=O) cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 3.13 (s, 4 H), 3.76 (s, 6 H); ¹³C NMR (75 MHz, CDCl₃): δ -2.0, 25.2, 53.3, 56.8, 88.2, 168.6; MS (EI): *m/z* (%): 460 (8) [M⁺], 429 (20) [M⁺ - OCH₃], 401 (15) [M⁺ - CO₂Me], 301 (100) [M⁺ - HOCH₃ - I]; EA calcd (%) for C₁₁H₁₀I₂O₄ (460.00): C 28.72, H 2.19; found: C 28.89, H 2.22.

3a-Br: oil; IR (CHCl₃) 2253 (C≡C), 1736 (C=O) cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 2.95 (s, 4 H), 3.73 (s, 6 H); ¹³C NMR (75 MHz, CDCl₃): δ 24.0, 42.2, 53.2, 56.3, 74.2, 168.5; MS (EI): *m/z* (%): 366 (4) [M⁺], 334 (100) [M⁺ - HOCH₃], 306 (48) [M⁺ - H - CO₂Me], 227 (86) [M⁺ - H - CO₂Me - Br]; EA calcd (%) for C₁₁H₁₀Br₂O₄ (366.00): C 36.10, H 2.75; found: C 36.02, H 2.83.

3b: mp. 120.0-120.3 °C; IR (CHCl₃) 2200 (C≡C) cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 3.20 (s, 4 H); ¹³C NMR (75 MHz, CDCl₃): δ 5.3, 29.4, 36.1, 83.6, 113.1; MS (EI): *m/z* (%): 394 (2) [M⁺], 267 (100) [M⁺ - I], 240 (24) [M⁺ - I - HCN]; EA calcd (%) for C₉H₄I₂N₂ (393.95): C 27.44, H 1.02, N 7.11; found: C 27.61, H 0.78, N 6.84.

3c: mp. 63.8-64.1 °C; IR (CHCl₃) 2189 (C≡C) cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 4.39 (s, 4 H); ¹³C NMR (75 MHz, CDCl₃): δ 4.0, 58.2, 89.5; MS (EI): *m/z* (%): 345 (4) [M⁺], 317 (18) [M⁺ - CO], 190 (100) [M⁺ - CO - I]; EA calcd (%) for C₆H₄I₂O (345.90): C 20.83, H 1.17; found: C 20.99, H 1.22.

3d: mp. 138.0-138.6 °C; IR (CHCl₃) 2253 (C≡C), 1354 (SO₂N), 1164 (SO₂N) cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 2.44 (s, 3 H), 4.26 (s, 4 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 7.69 (d, *J* = 8.1 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ 2.7, 21.7, 38.6, 86.3, 127.8, 129.6, 134.6, 144.0; MS (EI): *m/z* (%): 499 (2) [M⁺], 372 (8) [M⁺ - I], 343 (100) [M⁺ - H - SO₂C₆H₄Me]; EA calcd (%) for C₁₃H₁₁I₂NO₂S (499.11): C 31.28, H 2.22, N 2.81; found: C 31.33, H 1.96, N 2.52.

3e: mp. 124.1-124.5 °C; IR (CHCl₃) 2252 (C≡C) cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 1.40 (s, 6 H), 2.57 (s, 4 H), 3.72 (s, 4 H); ¹³C NMR (75 MHz, CDCl₃): δ -3.3, 23.8, 25.2, 36.1, 65.8, 89.8, 98.2; MS (EI): *m/z* (%): 445 (6) [M⁺], 429 (100) [M⁺ - CH₃], 355 (15) [M⁺ - OC(Me)₂O]; EA calcd (%) for C₁₂H₁₄I₂O₂ (444.05): C 32.46, H 3.18; found: C 32.64, H 3.16.

3f: mp. 49.7-49.8 °C; IR (CHCl₃) 2251 (C≡C) cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 2.58 (s, 4 H), 3.44 (s, 4 H), 4.51 (s, 4 H), 7.29-7.37 (m, 10 H); ¹³C NMR (75 MHz, CDCl₃): δ -4.6, 24.5, 42.9, 71.0, 73.6, 90.8, 127.2, 127.3, 128.2, 138.2; MS (EI): *m/z* (%): 584 (100) [M⁺], 493 (51) [M⁺ - CH₂Ph], 457 (56) [M⁺ - I]; EA calcd (%) for C₂₃H₂₂I₂O₂ (584.23): C 47.28, H 3.80; found: C 47.31, H 3.77.

3g: mp. 156.5-156.9 °C; IR (CHCl₃) 2252 (C≡C) cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 2.97 (s, 4 H), 7.34 (dt, *J* = 7.5, 1.5 Hz, 2 H), 7.41 (dt, *J* = 7.5, 1.2 Hz, 2 H), 7.66 (ddd, *J* = 6.9, 1.5, 0.6 Hz, 2 H), 7.73 (ddd, *J* = 6.9, 1.2, 0.9 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ -3.5, 29.7, 50.6, 91.4, 119.9, 123.8, 127.3, 128.0, 139.6, 147.9; MS (EI): *m/z* (%): 494 (19) [M⁺], 329 (35) [M⁺ - CH₂C≡CI], 202 (100) [M⁺ - CH₂C≡CI - I]; EA calcd (%) for C₁₉H₁₂I₂ (494.11): C 46.18, H 2.45; found: C 46.26, H 2.56.

3h: mp. 47.3-47.5 °C; IR (CHCl₃) 2252 (C≡C), 2181 (C≡C) cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 1.83 (t, *J* = 2.4 Hz, 3 H), 4.16 (q, *J* = 2.4 Hz, 2 H), 4.34 (s, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ 3.5, 3.7, 57.2, 57.8, 74.1, 83.3, 89.8; MS (EI): *m/z* (%): 234 (100) [M⁺], 179 (74) [M⁺ - 2H - CH₂C≡CMe]; EA calcd (%) for C₇H₇IO (234.03): C 35.92, H 3.01; found: C 35.98, H 2.94.

3i: oil; IR (CHCl₃) 2237 (C≡C), 2184 (C≡C) cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 4.47 (s, 2

H), 4.48 (s, 2 H), 7.30-7.35 (m, 3 H), 7.45-7.49 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3): δ 4.0, 57.4, 58.0, 84.0, 86.8, 89.7, 122.1, 128.1, 128.4, 131.6; MS (EI): m/z (%): 296 (4) [M^+], 267 (18) [$\text{M}^+ - \text{H} - \text{CO}$], 139 (100) [$\text{M}^+ - 2\text{H} - \text{CO} - \text{I}$]; EA calcd (%) for $\text{C}_{12}\text{H}_9\text{IO}$ (296.10): C 48.67, H 3.06; found: C 48.40, H 2.98.

3j: mp. 47.3-47.5 °C; IR (CHCl_3) 2253 ($\text{C}\equiv\text{C}$), 2189 ($\text{C}\equiv\text{C}$), 1715 (CO_2Me) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 3.78 (s, 3 H), 4.37 (s, 2 H), 4.40 (s, 2 H); ^{13}C NMR (75 MHz, CDCl_3): δ 4.8, 52.9, 56.2, 58.5, 78.2, 82.5, 88.9, 153.2; MS (EI): m/z (%): 278 (13) [M^+], 263 (28) [$\text{M}^+ - \text{CH}_3$], 254 (100) [$\text{M}^+ - \text{C}\equiv\text{C}$], 219 (10) [$\text{M}^+ - \text{CO}_2\text{Me}$]; EA calcd (%) for $\text{C}_8\text{H}_7\text{IO}_3$ (278.04): C 34.56, H 2.54; found: C 34.50, H 2.49.

7: mp. 72.5-72.9 °C; IR (CHCl_3) 2252 ($\text{C}\equiv\text{C}$), 2187 ($\text{C}\equiv\text{C}$) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 4.26 (s, 4 H), 4.36 (s, 4 H); ^{13}C NMR (75 MHz, CDCl_3): δ 4.2, 56.8, 58.0, 82.0, 89.4; MS (EI): m/z (%): 414 (13) [M^+]; EA calcd (%) for $\text{C}_{10}\text{H}_8\text{I}_2\text{O}_2$ (413.98): C 29.01, H 1.95; found: C 29.00, H 1.96.

15: mp. 109.0-109.5 °C; IR (CHCl_3) 1740 (CO_2Me) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 3.01 (s, 4 H), 3.09 (s, 4 H), 3.74 (s, 6 H); ^{13}C NMR (75 MHz, CDCl_3): δ -1.6, 23.7, 25.2, 53.3, 56.5, 68.0, 72.1, 88.0, 168.4; MS (EI): m/z (%): 667 (6) [M^+], 607 (10) [$\text{M}^+ - \text{H} - \text{CO}_2\text{Me}$], 546 (94) [$\text{M}^+ - 3\text{H} - 2\text{CO}_2\text{Me}$], 487 (78) [$\text{M}^+ - 3\text{H} - 3\text{CO}_2\text{Me}$], 419 (100) [$\text{M}^+ - 3\text{H} - 2\text{CO}_2\text{Me} - \text{I}$]; EA calcd (%) for $\text{C}_{22}\text{H}_{20}\text{I}_2\text{O}_8$ (666.20): C 39.66, H 3.03; found: C 39.78, H 3.10.

General Procedure for Ruthenium-Catalyzed Cycloaddition with Acetylene: Synthesis of Diiodobenzene 4a-I. To a solution of $\text{Cp}^*\text{RuCl}(\text{cod})$ (5.7 mg, 0.015 mmol) in dry degassed 1,2-dichloroethane (1.5 mL) was added a solution of diiododiyne **3a-I** (138.2 mg, 0.30 mmol) in dry degassed 1,2-dichloroethane (2.0 mL) over 15 min at room temperature under acetylene atmosphere and the solution was stirred for 30 min. The solvent was removed in vacuo, and the residue was purified by flash column chromatography on silica gel eluted with hexane/AcOEt 20:1) to give **4a-I** (120.0 mg, 83%) as colorless solids (mp. 131.9-132.2 °C): IR (CHCl_3) 1735 (CO_2Me) cm^{-1} ; ^1H

NMR (300 MHz, CDCl₃): δ 3.70 (s, 4 H), 3.79 (s, 6 H), 7.25 (s, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ 47.03, 53.29, 56.57, 92.44, 137.71, 144.63, 171.13; MS (EI): *m/z* (%): 486 (72) [M⁺], 426 (100) [M⁺ - H - CO₂Me], 395 (20) [M⁺ - H - CO₂Me - OMe], 367 (30) [M⁺ - H - 2CO₂Me]; EA calcd (%) for C₁₃H₁₂I₂O₄ (486.04): C 32.12, H 2.49; found: C 32.08, H 2.53.

4a-Br: mp. 133.4-133.6 °C: IR (CHCl₃) 1736 (CO₂Me) cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 3.69 (s, 2 H), 3.78 (s, 6 H), 7.19 (s, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ 42.96, 53.29, 57.72, 117.96, 131.62, 141.64, 171.15; MS (EI): *m/z* (%): 392 (32) [M⁺], 332 (100) [M⁺ - H - CO₂Me], 301 (12) [M⁺ - H - CO₂Me - OMe], 273 (36) [M⁺ - H - 2CO₂Me]; EA calcd (%) for C₁₃H₁₂Br₂O₄ (392.04): C 39.83, H 3.09; found: C 39.86, H 3.16.

4b: mp. 176.6-177.0 °C: ¹H NMR (300 MHz, CDCl₃): δ 3.86 (s, 4 H), 7.26 (s, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ 30.4, 50.6, 92.1, 115.5, 139.3, 141.3; MS (EI): *m/z* (%): 420 (100) [M⁺], 293 (4) [M⁺ - I], 266 (4) [M⁺ - I - HCN]; EA calcd (%) for C₁₁H₆I₂N₂ (419.99): C 31.46, H 1.44, N 6.67; found: C 31.48, H 1.21, N 6.50.

4c: mp. 117.2-117.5 °C: ¹H NMR (300 MHz, CDCl₃): δ 5.12 (s, 4 H), 7.29 (s, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ 79.2, 86.9, 137.7, 144.4; MS (EI): *m/z* (%): 372 (78) [M⁺], 344 (24) [M⁺ - CO], 217 (100) [M⁺ - CO - I]; EA calcd (%) for C₈H₆I₂O (371.94): C 25.83, H 1.63; found: C 25.77, H 1.71.

4d: mp. 217.5-218.0 °C: IR (CHCl₃) 1350 (SO₂N), 1166 (SO₂N) cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 2.43 (s, 3 H), 4.63 (s, 4 H), 7.28 (s, 2 H), 7.36 (d, *J* = 8.5 Hz, 2 H), 7.80 (d, *J* = 8.5 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ 21.7, 59.6, 89.2, 127.4, 129.9, 133.4, 138.2, 141.5, 143.9; MS (EI): *m/z* (%): 525 (30) [M⁺], 370 (100) [M⁺ - SO₂C₆H₄Me], 243 (29) [M⁺ - SO₂C₆H₄Me - I]; EA calcd (%) for C₁₅H₁₃I₂NO₂S (525.14): C 34.31, H 2.50, N 2.67; found: C 34.42, H 2.20 N 2.42.

4e: mp. 149.9-150.2 °C: ¹H NMR (300 MHz, CDCl₃): δ 1.48 (s, 6 H), 2.99 (s, 4 H), 3.75 (s, 4 H), 7.24 (s, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ 23.9, 38.9, 46.9, 68.7, 93.9, 98.0, 137.4, 146.3; MS (EI): *m/z* (%): 470 (25) [M⁺], 455 (100) [M⁺ - CH₃], 395 (39) [M⁺ - OC(Me)₂O]; EA calcd (%) for

C₁₄H₁₆I₂O₂ (470.08): C 35.77, H 3.43; found: C 35.95, H 3.44.

4f: mp. 91.2-91.7 °C: ¹H NMR (300 MHz, CDCl₃): δ 2.99 (s, 4 H), 3.48 (s, 4 H), 4.53 (s, 4 H), 7.20 (s, 2 H), 7.27-7.36 (m, 10 H); ¹³C NMR (75 MHz, CDCl₃): δ 45.2, 46.0, 73.1, 73.2, 93.8, 127.3, 127.4, 128.2, 137.0, 138.3, 147.1; MS (EI): *m/z* (%): 610 (11) [M⁺], 519 (67) [M⁺ - CH₂Ph], 502 (39) [MH⁺ - OCH₂Ph], 381 (100) [MH⁺ - OCH₂Ph - CH₂OCH₂Ph]; EA calcd (%) for C₂₅H₂₄I₂O₂ (610.27): C 49.20, H 3.96; found: C 49.23, H 3.90.

4g: mp. 273.2-273.6 °C: ¹H NMR (300 MHz, CDCl₃): δ 3.56 (s, 4 H), 7.25-7.27 (m, 4 H), 7.33-7.41 (m, 4 H), 7.72-7.75 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ 52.1, 53.9, 93.2, 119.9, 122.2, 127.6, 127.7, 137.6, 139.4, 147.7, 151.5; MS (EI): *m/z* (%): 520 (100) [M⁺], 392 (4) [MH⁺ - I], 265 (56) [MH⁺ - 2I]; EA calcd (%) for C₂₁H₁₄I₂ (520.14): C 48.49, H 2.71; found: C 48.56, H 2.63.

4h: mp. 31.3-31.8 °C: ¹H NMR (300 MHz, CDCl₃): δ 2.18 (s, 3 H), 5.01 (s, 2 H), 5.20 (s, 2 H), 6.79 (d, *J* = 7.5 Hz, 1 H), 7.49 (d, *J* = 7.5 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃): δ 18.4, 74.6, 78.1, 83.4, 130.1, 131.1, 136.2, 139.0, 142.9; MS (EI): *m/z* (%): 260 (74) [M⁺], 245 (26) [M⁺ - CH₃], 231 (34) [MH⁺ - CO], 217 (65) [M⁺ - CH₃ - CO], 105 (100) [M⁺ - CO - I]; EA calcd (%) for C₉H₉IO (260.07): C 41.56, H 3.49; found: C 41.67, H 3.38.

4i: mp. 81.2-81.6 °C: ¹H NMR (300 MHz, CDCl₃): δ 5.08 (br s, 2 H), 5.34 (br s, 2 H), 7.06 (d, *J* = 7.8 Hz, 1 H), 7.35-7.47 (m, 5 H), 7.70 (d, *J* = 7.8 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃): δ 75.0, 77.9, 86.1, 127.5, 127.7, 128.7, 129.2, 135.8, 136.8, 137.8, 138.9, 144.1; MS (EI): *m/z* (%): 322 (100) [M⁺], 293 (9) [M⁺ - H - CO], 245 (2) [M⁺ - C₆H₅], 195 (9) [M⁺ - I], 165 (94) [M⁺ - 2H - CO - I]; EA calcd (%) for C₁₄H₁₁IO (322.14): C 52.20, H 3.44; found: C 52.14, H 3.45.

4j: mp. 94.8-95.1 °C: IR (CHCl₃) 1718 (CO₂Me) cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 3.90 (s, 3 H), 5.01-5.02 (m, 2 H), 5.50-5.52 (m, 2 H), 7.61 (d, *J* = 8.4 Hz, 1 H), 7.71 (d, *J* = 8.4 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃): δ 52.3, 76.5, 93.7, 124.1, 130.1, 136.7, 142.0, 145.1, 165.9; MS (EI): *m/z* (%): 304 (58) [M⁺], 289 (100) [M⁺ - CH₃], 244 (17) [M⁺ - H - CO₂Me]; EA calcd (%) for

C₁₀H₉IO₃ (304.08): C 39.50, H 2.98; found: C 39.50, H 2.97.

16: mp. 139.4-139.9 °C; IR (CHCl₃) 1734 (CO₂Me) cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 3.49 (s, 4 H), 3.62 (s, 4 H), 3.73 (s, 12 H), 6.76 (d, *J* = 8.1 Hz, 2 H), 7.61 (d, *J* = 8.1 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ 41.0, 45.9, 53.1, 58.12, 91.9, 128.8, 135.8, 136.5, 138.5, 144.6, 171.2; MS (EI): *m/z* (%): 720 (100) [MH₂⁺], 658 (10) [M⁺ - H - CO₂Me], 626 (40) [M⁺ - 2H - CO₂Me - OMe]; EA calcd (%) for C₂₆H₂₄I₂O₈ (718.27): C 43.48, H 3.37; found: C 43.34, H 3.51.

General Procedure for Ruthenium-Catalyzed Cycloaddition with Monoalkynes: Synthesis of

Diiodobenzene 5a. To a solution of Cp^{*}RuCl(cod) (5.8 mg, 0.015 mmol) and 1-hexyne (37.0 mg, 0.45 mmol) in dry degassed 1,2-dichloroethane (1.5 mL) was added a solution of diiododiyne **3c** (103.7 mg, 0.30 mmol) in dry degassed 1,2-dichloroethane (2.0 mL) over 15 min at room temperature under argon atmosphere and the solution was stirred for 4 h. The solvent was removed in vacuo, and the residue was purified by flash column chromatography on silica gel eluted with hexane/AcOEt 50:1 ~ 20:1) to give **5a** (106.7 mg, 83%) as colorless solids (mp. 60.5-60.7 °C): ¹H NMR (300 MHz, CDCl₃): δ 0.96 (t, *J* = 7.2 Hz, 3 H), 1.34-1.59 (m, 4 H), 2.65 (t, *J* = 7.5 Hz, 2 H), 5.12 (s, 4 H), 7.40 (s, 1 H); ¹³C NMR (75 MHz, CDCl₃): δ 14.0, 22.5, 32.5, 39.1, 79.2, 80.3, 87.0, 93.2, 136.5, 141.4, 145.2, 146.3; MS (EI): *m/z* (%): 428 (100) [M⁺], 399 (25) [M⁺ - C₂H₅], 385 (21) [M⁺ - C₃H₇], 357 (41) [M⁺ - C₃H₇ - CO], 301 (25) [M⁺ - I], 273 (82) [M⁺ - CO - I]; EA calcd (%) for C₁₂H₁₄I₂O (428.05): C 33.67, H 3.30; found: C 33.58, H 3.39.

5b: mp. 135.2-135.4 °C; ¹H NMR (300 MHz, CDCl₃): δ 5.21 (s, 4 H), 7.29-7.32 (m, 2 H), 7.39-7.44 (m, 3 H), 7.55 (s, 1 H); ¹³C NMR (75 MHz, CDCl₃): δ 79.3, 80.5, 86.9, 91.6, 127.9, 128.0, 129.1, 137.3, 141.7, 142.7, 145.3, 147.2; MS (EI): *m/z* (%): 448 (100) [M⁺], 419 (15) [M⁺ - H - CO], 293 (36) [M⁺ - CO - I], 165 (72) [M⁺ - H - CO - 2I]; EA calcd (%) for C₁₄H₁₀I₂O (448.04): C 37.53, H 2.25; found: C 37.70, H 2.25.

5c: mp. 195.8-196.2 °C; ¹H NMR (300 MHz, CDCl₃): δ 5.29 (s, 4 H), 6.93-6.96 (m, 4 H), 7.13-7.21 (m, 6 H); ¹³C NMR (75 MHz, CDCl₃): δ 80.8, 94.0, 127.1, 127.4, 129.7, 143.1, 143.7,

145.4; MS (EI): m/z (%): 524 (100) [M^+], 495 (15) [$M^+ - H - CO$], 397 (9) [$M^+ - I$], 369 (26) [$M^+ - CO - I$], 269 (5) [$M^+ - H - 2I$], 239 (84) [$M^+ - H - CO - 2HI$]; EA calcd (%) for $C_{20}H_{14}I_2O$ (524.13): C 45.83, H 2.69; found: C 45.88, H 2.64.

5d/5d': oil (6:4 mixture); 1H NMR (300 MHz, $CDCl_3$): δ 0.95 and 0.97 (t, $J = 7.2$ Hz, 3 H), 1.33-1.61 (m, 4 H), 2.10 and 2.17 (s, 3 H), 2.55 and 2.68 (t, $J = 7.8$ Hz, 2 H), 4.99-5.02 (m, 2 H), 5.20-5.21 (m, 2 H), 6.89 and 7.40 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1 and 15.3, 18.2, 22.6 and 22.7, 32.2 and 32.8, 32.7 and 39.3, 74.8 and 75.0, 78.1 and 79.2, 83.5 and 89.4, 129.0 and 129.2, 130.0 and 142.6, 136.1 and 136.6, 139.5 and 140.4, 143.9 and 144.2; MS (EI): m/z (%): 316 (100) [M^+], 287 (20) [$M^+ - CH_2CH_3$], 189 (12) [$M^+ - I$], 161 (57) [$M^+ - CH_2=CH_2 - I$]; EA calcd (%) for $C_{13}H_{17}IO$ (316.18): C 49.38, H 5.42; found: C 49.14, H 5.27.

Procedure for Ruthenium-Catalyzed Cyclization of Diiodotriyne 7. To a solution of $Cp^*RuCl(cod)$ (17.1 mg, 0.045 mmol) in dry degassed 1,2-dichloroethane (1.5 mL) was added a solution of diiodotriyne **7** (124.1 mg, 0.30 mmol) in dry degassed 1,2-dichloroethane (2.0 mL) over 15 min at room temperature under argon atmosphere and the solution was stirred for 24 h. The solvent was removed in vacuo, and the residue was purified by flash column chromatography on silica gel eluted with hexane/AcOEt 20:1 ~ 5:1) to give **8** (72.5 mg, 60%) as brown solids (mp. 219.8-220.4 °C): 1H NMR (300 MHz, $CDCl_3$): δ 5.00 (s, 4 H), 5.14 (s, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 73.6, 79.9, 80.3, 99.4, 132.4, 145.8; MS (EI): m/z (%): 414 (100) [M^+], 287 (12) [$M^+ - I$]; EA calcd (%) for $C_{10}H_8I_2O_2$ (413.98): C 29.01, H 1.95; found: C 29.14, H 1.92.

Procedure of Mizoroki-Heck Reaction of 4e. A solution of $Pd_2(dba)_3 \cdot CHCl_3$ (7.8 mg, 0.0075 mmol), SPhos (13.6 mg, 0.033 mmol), **4e** (141.0 mg, 0.30 mmol), and styrene (125.0 mg, 1.20 mmol) in degassed mixed solvent (DMF 5 mL / Et_3N 1 mL) was stirred at 85 °C for 24 h. The reaction mixture was quenched with 1 N HCl (50 mL) and extracted with AcOEt (20 mL \times 3). The combined organic layer was then washed with brine (50 mL \times 2) and dried with $MgSO_4$. After removing the solvent in vacuo, the residue was purified by flash column chromatography on silica gel eluted with hexane/AcOEt 50:1 ~ 10:1) to give **9** (84.8 mg, 67%) as pale-yellow solids (mp.

205.7-205.8 °C): ¹H NMR (300 MHz, CDCl₃): δ 1.53 (s, 6 H), 3.06 (s, 4 H), 3.83 (s, 4 H), 7.09 (d, *J* = 16.5 Hz, 2 H), 7.17 (d, *J* = 16.5 Hz, 2 H), 7.25-7.42 (m, 7 H), 7.51-7.55 (m, 5 H); ¹³C NMR (75 MHz, CDCl₃): δ 24.0, 39.3, 41.4, 69.1, 98.0, 123.6, 125.9, 126.4, 127.6, 128.6, 129.4, 132.9, 137.4, 139.9; MS (EI): *m/z* (%): 422 (100) [M⁺]; EA calcd (%) for C₃₀H₃₀O₂ (422.56): C 85.27, H 7.16; found: C 85.25, H 7.18.

Procedure of Sonogashira Reaction of 4e. A solution of Pd(PPh₃)₄ (17.4 mg, 0.015 mmol), CuI (5.7 mg, 0.030 mmol), **4e** (141.1 mg, 0.30 mmol), and ethynylbenzene (92.9 mg, 0.91 mmol) in degassed ^tPr₂NH (5 mL) was stirred at room temperature for 2 h. The reaction mixture was quenched with 1 N HCl (40 mL) and extracted with AcOEt (20 mL × 3). The combined organic layer was then washed with distilled water (50 mL) and dried with MgSO₄. After removing the solvent in vacuo, the residue was purified by flash column chromatography on silica gel eluted with hexane/AcOEt 50:1 ~ 5:1) to give **10** (121.1 mg, 97%) as colorless solids (mp. 161.6-162.0 °C): ¹H NMR (300 MHz, CDCl₃): δ 1.51 (s, 6 H), 3.10 (s, 4 H), 3.82 (s, 4 H), 7.33 (s, 2 H), 7.34-7.39 (m, 6 H), 7.53-7.56 (m, 4 H); ¹³C NMR (75 MHz, CDCl₃): δ 23.9, 40.3, 40.9, 68.8, 87.5, 94.1, 97.9, 119.9, 123.0, 128.2, 128.3, 129.5, 131.4, 143.6; MS (EI): *m/z* (%): 418 (100) [M⁺], 343 (29) [M⁺ - H - OC(CH₃)₂O]; EA calcd (%) for C₃₀H₂₆O₂ (418.53): C 86.09, H 6.26; found: C 85.99, H 6.23.

Procedure of Suzuki-Miyaura Coupling of 4e. A solution of Pd₂(dba)₃•CHCl₃ (7.8 mg, 0.0075 mmol), SPhos (13.7 mg, 0.033 mmol), **4e** (141.1 mg, 0.30 mmol), phenylboronic acid (146.6 mg, 1.20 mmol), and K₃PO₄ (254.8 mg, 1.20 mmol) in degassed toluene (1 mL) was stirred at 110 °C for 24 h. The reaction mixture was quenched with sat. NH₄Cl (40 mL) and extracted with AcOEt (20 mL × 3). The combined organic layer was then washed with brine (50 mL) and dried with MgSO₄. After removing the solvent in vacuo, the residue was purified by flash column chromatography on silica gel eluted with hexane/AcOEt 20:1 ~ 5:1) to give **11** (95.5 mg, 87%) as pale-yellow solids (mp. 186.5-186.7 °C): ¹H NMR (300 MHz, CDCl₃): δ 1.42 (s, 6 H), 3.06 (s, 4 H), 3.75 (s, 4 H), 7.34 (s, 2 H), 7.35-7.40 (m, 2 H), 7.43-7.52 (m, 8 H); ¹³C NMR (75 MHz, CDCl₃): δ 23.8, 40.4,

41.9, 68.8, 97.9, 126.9, 127.7, 128.2, 128.5, 137.7, 139.5, 140.6; MS (EI): m/z (%): 370 (73) [M^+], 355 (38) [$M^+ - CH_3$], 295 (100) [$M^+ - H - OC(CH_3)_2O$]; EA calcd (%) for $C_{26}H_{26}O_2$ (370.48): C 84.29, H 7.07; found: C 84.37, H 7.02.

Procedure for Synthesis of Penta-*p*-phenylene 13. A solution of $Pd_2(dba)_3 \cdot CHCl_3$ (15.6 mg, 0.015 mmol), SPhos (27.2 mg, 0.066 mmol), **4e** (141.4 mg, 0.30 mmol), **12** (278.0 mg, 0.90 mmol), and K_3PO_4 (255.5 mg, 1.2 mmol) in degassed mixed solvent (toluene 1 mL / H_2O 10 μ L) was stirred at 110 °C for 15 h. The reaction mixture was quenched with sat. NH_4Cl (50 mL) and extracted with AcOEt (20 mL \times 3). The combined organic layer was then washed with brine (50 mL) and dried with $MgSO_4$. After removing the solvent in vacuo, the residue was purified by flash column chromatography on silica gel eluted with hexane/AcOEt 50:1 \sim 5:1) to give **13** (90.8 mg, 50%) as colorless solids (mp. 224.5-225.0 °C): 1H NMR (300 MHz, $CDCl_3$): δ 1.42 (s, 6 H), 2.91 (s, 4 H), 3.75 (s, 4 H), 5.11 (s, 4 H), 5.29 (s, 4 H), 7.17 (s, 2 H), 7.33 (d, $J = 7.5$ Hz, 2 H), 7.42 (d, $J = 7.5$ Hz, 2 H), 7.35-7.51 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.8, 40.0, 41.8, 68.7, 73.6, 73.8, 98.0, 126.9, 127.4, 127.6, 127.7, 128.5, 128.6, 133.5, 134.9, 136.1, 137.5, 138.3, 139.8, 140.0; MS (EI): m/z (%): 606 (91) [M^+], 591 (47) [$M^+ - CH_3$], 548 (100) [$M^+ - OC(CH_3)_2$]; EA calcd (%) for $C_{42}H_{38}O_4$ (606.75): C 83.14, H 6.31; found: C 82.90, H 6.55.

Procedure for Synthesis of Hexa-*p*-phenylene 17. A solution of $Pd_2(dba)_3 \cdot CHCl_3$ (15.4 mg, 0.015 mmol), SPhos (27.2 mg, 0.066 mmol), **16** (215.5 mg, 0.30 mmol), **12** (277.6 mg, 0.90 mmol), and K_3PO_4 (254.7 mg, 1.2 mmol) in degassed mixed solvent (toluene 1 mL / H_2O 10 μ L) was stirred at 110 °C for 24 h. The reaction mixture was quenched with sat. NH_4Cl (40 mL) and extracted with AcOEt (20 mL \times 3). The combined organic layer was then washed with brine (50 mL) and dried with $MgSO_4$. After removing the solvent in vacuo, the residue was purified by flash column chromatography on silica gel eluted with hexane/AcOEt 50:1 \sim 1:1) to give **17** (94.4 mg, 37%) as pale-yellow solid (sublimation around 167 °C): 1H NMR (300 MHz, $CDCl_3$): δ 3.55 (s, 4 H), 3.59 (s, 4 H), 3.74 (s, 12 H), 5.14 (s, 4 H), 7.18 (d, $J = 8.1$ Hz, 2 H), 7.22 (d, $J = 8.1$ Hz, 2 H), 7.34-7.49 (m, 14 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.1, 40.3, 53.0, 60.1, 109.1, 127.2, 127.4, 127.7, 127.8,

127.9, 128.5, 128.6, 133.3, 135.0, 135.4, 136.1, 137.5, 138.4, 138.7, 139.8, 171.7; MS (EI): m/z (%) : 857 (91) $[\text{MH}_2^+]$; EA calcd (%) for $\text{C}_{54}\text{H}_{46}\text{O}_{10}$ (854.94): C 75.86, H 5.42; found: C 75.85, H 5.43.