Supporting Information for Formation of Linear Tetramers of Diarylalkynes by Zr/Cr System

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Experimental Section

All reactions involving organometallic compounds were carried out using standard Schlenk technique under nitrogen. Tetrahydrofuran (THF) was dried over sodium and benzophenone. Zirconocene dichloride was purchased from Aldrich Chemical Co., Inc. and Nichia Co. *n*-Butyllithium (1.6 M solution in hexane) was purchased from Kanto Chemical Co.

¹H and ¹³C NMR spectra were recorded for CDCl₃ (containing 1% TMS) solutions at 25 °C on Bruker ARX-400 spectrometer. GC analysis was performed on SHIMADZU GC-14A equipped with fused silica capillary column SHIMADZU CBP1-M25-O25 and SHIMADZU C-R6A-Chromatopac integrator.

Representative procedure of the synthesis of octaaryloctatetraenes: Synthesis of 1,2,3,4,5,6,7,8-octaphenyl-(1*E*,3*E*,5*E*,7*E*)-octatetraene (2a)

In a 20 mL Schlenk tube, a solution of Cp₂ZrCl₂ (292 mg, 1.00 mmol) in 10 mL of THF was cooled to -78 °C, and added *n*-BuLi (1.59 M hexane solution, 1.3 mL, 2.0 mmol) dropwise via a syringe. After 1 h, diphenylacetylene (356 mg, 2.00 mmol) was added to the solution, and stirred at rt for 3 h. To the resulting solution, CrCl₃ (158 mg, 1.00 mmol) was added and heated to 50 °C for 5 d. The reaction course was monitored by TLC. After cooling to rt, the mixture was quenched with 3 N HCl, and extracted with ether or chloroform, washed with water, saturated sodium bicarbonate aqueous solution, and brine. After removal of the solvent the residue was purified by flash chromatography to afford pale-yellow powder. It was purified by recrystallization. White crystals were obtained. (227 mg, isolated yield 64%; NMR yield 84%). ¹H NMR (C₆D₆, Me₄Si) δ 6.40 (s, 2 H), 6.41 – 6.77 (m, 28 H), 7.06 (d, 4 H, *J* = 7.5 Hz), 7.14 (d, 4 H, *J* = 7.5 Hz), 7.68 (d, 4 H, *J* = 7.5 Hz); ¹³C NMR (C₆D₆, Me₄Si) δ 126.84, 127.02, 127.09, 127.22, 127.68, 127.90, 128.21 (2C), 129.45, 130.21, 130.42, 130.64, 134.49, 138.09, 139.71, 141.92, 142.56, 143.12, 143.28, 146.15.

Figure 1. Perspective view of Compound **2a**.

1,2,3,4,5,6,7,8-Octa-*m*-tolyl-(1*E*,3*E*,5*E*,7*E*)-octatetraene (2b)

Yellow powder; GC yield, 35%; ^1H NMR (CDCl_3 , Me_4Si) δ 2.08 (s, 6 H), 2.10 (s, 6 H), 2.12 (s, 6 H), 2.16 (s, 6 H), 6.22 (s, 2 H), 6.50 – 6.65 (m, 4 H), 6.67 – 6.98 (m, 24 H), 7.04 – 7.12 (m, 4 H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 21.25 (2C), 21.30, 21.62, 125.98, 126.50, 126.80, 126.86 (2C), 126.91, 126.97, 127.02, 127.11, 127.18, 127.31, 127.46, 129.85, 130.13, 130.99, 131.12, 133.08, 135.82, 136.21, 136.60, 137.04, 137.98, 139.54, 141.76, 142.54, 143.09, 143.12, 145.20; MS m/z (%) 826 (M^+ , 100), 721 (59), 629 (58), 539 (36), 423 (51), 333 (28), 309 (53), 279 (22), 219 (51), 195 (78), 105 (36); HRMS calcd for $\text{C}_{64}\text{H}_{58}$: 826.4538, found: 826.4543.

1,2,3,4,5,6,7,8-Octa-(2-thienyl)-(1*E*,3*E*,5*E*,7*E*)-octatetraene (2c)

Yellow-orange powder; NMR yield, 71%; isolated yield 57%; ^1H NMR (C_6D_6 , Me_4Si) δ 6.17 (dd, 2 H, $J = 5.1, 3.9$ Hz), 6.23 (dd, 2 H, $J = 5.1, 3.6$ Hz), 6.25 – 6.32 (m, H), 6.39 (dd, 2 H, $J = 5.1, 1.0$ Hz), 6.40 (dd, 2 H, $J = 5.1, 1.0$ Hz), 6.46 (dd, 2 H, $J = 5.1, 1.2$ Hz), 6.59 (d, 2 H, $J = 3.3$ Hz), 6.85 – 6.89 (m, 4 H), 7.17 (dd, 2 H, $J = 3.9, 1.0$ Hz); ^{13}C NMR (C_6D_6 , Me_4Si) δ 126.61, 126.71, 126.79 (2C), 127.04, 127.10, 127.12, 127.33, 128.18, 128.55, 129.34, 130.04, 130.46, 133.35, 133.85, 135.08, 139.51, 139.96, 143.03, 143.32; MS m/z (%) 762 (M^+ , 6), 307 (32), 289 (15), 179 (9), 154 (100), 136 (68), 107 (17); HRMS calcd for $\text{C}_{40}\text{H}_{26}\text{S}_8$: 761.9800, found: 761.9777.

1,2,3,4,5,6,7,8-Octa-(3-thienyl)-(1*E*,3*E*,5*E*,7*E*)-octatetraene (2d)

Yellow-orange powder; NMR yield, 59%; isolated yield 45%; ^1H NMR (C_6D_6 , Me_4Si) δ 6.10 (s, 2 H), 6.26 – 6.32 (m, 10 H), 6.33 – 6.36 (m, 2 H), 6.41 (dd, 2 H, $J = 5.1, 1.2$ Hz), 6.53 (dd, 2 H, $J = 3.0, 1.2$ Hz), 6.61 (dd, 2 H, $J = 2.7, 1.2$ Hz), 6.64 (dd, 2 H, $J = 4.8, 1.2$ Hz), 7.00 (dd, 2 H, $J = 3.0, 1.5$ Hz), 7.05 (dd, 2 H, $J = 5.1, 1.2$ Hz); ^{13}C NMR (C_6D_6 , Me_4Si) δ 124.1, 124.2,

124.4, 124.5, 124.7 (2C), 125.1, 125.2, 125.8, 128.0, 128.8, 129.0, 129.2, 135.6, 137.0, 138.2, 138.8, 140.2, 142.4, 142.5; MS m/z (%) 762 (M^+ , 14), 460 (38), 307 (100), 289 (97), 155 (98), 138 (99), 107 (97), 89 (80), 77 (67); HRMS calcd for $C_{40}H_{26}S_8$: 761.9800, found: 761.9810.

Structure of 2d

X-ray analysis of **2d** was carried out. However, the analysis was not completed. Only preliminary result was obtained. The result showed the stereochemistry of the tetraene was the same as **2a** and **2c**.

Synthesis of 1,2,3,4,5,6,7,8-octaphenyl-(1E,3Z,5Z,7E)-octatetraene 4a

To a 20 mL Schlenk tube Cp_2ZrCl_2 and 5 mL of dry THF was added and cooled to -78 °C. To the solution n-BuLi (1.59 M hexane solution, 0.64 mL, 1.0 mmol) was added dropwise via a syringe, and stirred for 1 h. The mixture was added diphenylacetylene (178 mg, 1.00 mmol) and warmed to rt. After 3 h t-BuOH was added and stirred for 1 h. 1H NMR analysis of the solution revealed that the corresponding butadienylzirconocene complex was formed in 85% yield. To the solution, 1-iodo-2,3,4,5-tetraphenyl-(1Z, 3Z)-butadiene (242 mg, 0.50 mmol) and CuCl (52 mg, 0.53 mmol), and $Pd(PPh_3)_4$ (55 mg) were added and the mixture was heated to 50 °C with stirring. After 1 day, the mixture was quenched with 3 N HCl and extracted with ether. After removal of the solvent the residue was purified by flash chromatography to afford yellow viscous solid. The solid was washed with EtOH to afford yellow powder (80 mg, 22% yield). 1H NMR ($CDCl_3$, Me_4Si) δ 6.21 – 6.43 (m, 16 H), 6.50 – 6.75 (m, 20 H), 7.19 (d, 4 H, J = 7.2 Hz), 7.48 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 125.66, 126.06, 126.33, 126.64, 126.97, 127.12, 127.22, 127.60, 130.04, 130.10, 131.12, 132.31, 132.40, 137.23, 138.90, 141.29, 143.94, 144.15, 144.20, 145.61; Anal. Calcd for $C_{56}H_{42}$: C, 94.08; H, 5.92. Found: C, 93.95; H, 6.14.

1,2,3,4,5,6,7,8-Octa-m-tolyl-(1E,3Z,5Z,7E)-octatetraene (4b)

Yellow powder, yield 20%. 1H NMR ($CDCl_3$, Me_4Si) δ 1.985 (s, 6 H), 1.993 (s, 6 H), 2.02 (s, 6 H), 2.05 (s, 6 H), 6.16 (s, 2 H), 6.34 (d, 2 H, J = 7 Hz), 6.51 – 7.31 (m, 30 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 21.11, 21.16, 21.18, 21.22, 126.48, 126.55, 126.73, 126.80 (2C), 127.13 (2C), 127.29, 127.37, 128.35, 129.46 (2C), 130.49, 130.91, 131.91, 132.23, 133.36, 135.94, 135.97, 136.30, 136.81, 137.50, 139.09, 141.42, 143.96, 143.99, 144.16, 145.35. MS m/z (%) 826 (M^+ , 100), 721 (34), 629 (34), 539 (22), 423 (26), 309 (33), 219 (30), 195 (47); HRMS calcd for $C_{64}H_{58}$: 826.4538, found: 826.4562.

2,3,4,5,6-Pentapropylpyridine (6a)

Yield 62%. 1H NMR ($CDCl_3$, Me_4Si) δ 0.97-1.07 (m, 15H), 1.45-1.54 (m, 6H), 1.67-1.74 (m, 4H), 2.48-2.54(m, 6H), 2.65-2.70(m, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.42, 14.86, 14.98, 23.56, 24.49, 24.56, 30.92, 31.43, 37.33, 130.75, 147.51, 156.77. HRMS(EI) calcd for $C_{20}H_{35}N$ 289.2769, found 289.2769

2-(4'-Fluorophenyl)-3,4,5,6-tetrapropylpyridine (6b)

1H NMR ($CDCl_3$, Me_4Si) δ 0.79(t, J = 7.3 Hz, 3H), 0.99 (t, J = 7.3 Hz, 3H), 1.08 (t, J = 7.2 Hz, 6H), 1.32-1.39 (m, 2H), 1.50-1.61(m, 4H), 1.69-1.76(m, 2H), 2.43-2.49(m, 2H), 2.57-2.62 (m, 4H), 2.71-2.76 (m, 2H), 7.07 (t, J = 8.8Hz, 2H), 7.34(d, J = 5.5Hz, 1H), 7.37(d, J = 5.7 Hz, 1H).

^{13}C NMR (CDCl_3 , Me_4Si) δ 14.42, 14.56, 14.90, 15.00, 23.66, 24.55(3C), 30.99, 31.39, 31.48, 37.48, 114.69, 114.99, 130.55, 130.66, 131.28, 132.58, 138.50, 138.54, 148.33, 155.48, 157.26, 160.59, 163.84. HRMS calcd for $\text{C}_{23}\text{H}_{32}\text{FN}$ 341.2519, Found 341.2529.

6,7-Dihydro-1,4-dipropyl-3-methyl-5H-cyclopenta[c]pyridine (6c)

^1H NMR (CDCl_3 , Me_4Si) δ 0.94-1.01 (m, 7H), 1.48-1.56 (m, 2H), 1.61-1.72 (m, 2H), 2.01-2.11 (m, 2H), 2.49-2.56 (m, 5H), 2.61-2.67 (m, 2H), 2.82-2.90 (m, 3H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.26, 14.44, 21.56, 22.57, 22.68, 24.63, 30.68, 31.62, 32.06, 38.09, 129.38, 134.96, 152.51, 153.29, 153.96. HRMS(EI) calcd for $\text{C}_{15}\text{H}_{23}\text{N}$: 217.1830, found 217.1826

6,7-Dihydro-1,3,4-tripropyl-5H-cyclopenta[c]pyridine (6d)

^1H NMR (CDCl_3 , Me_4Si) δ 0.94-1.02 (m, 9H), 1.48-1.56 (m, 2H), 1.64-1.73 (m, 4H), 12.01-2.11 (m, 2H), 2.51-2.56 (m, 2H), 2.62-2.75 (m, 4H), 2.82-2.89 (m, 4H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.19, 14.36, 14.54, 22.62, 23.47, 23.95, 24.59, 30.67, 31.72, 36.72, 38.01, 128.91, 134.78, 152.60, 154.11, 157.17. HRMS(EI) calcd for $\text{C}_{17}\text{H}_{27}\text{N}$: 245.2143, found 245.2147

1-Tolyl-3,4,5,6-tetrapropylpyrid-2-one (7a)

^1H NMR (CDCl_3 , Me_4Si) δ 0.70 (t, J = 7.3 Hz, 3H), 0.97(t, J = 7.3Hz, 3H), 1.02(t, J = 7.2 Hz, 3H), 1.07(t, J = 7.3 Hz, 3H), 1.30-1.62(m, 8H), 2.22-2.28(m, 2H), 2.30-2.42(m, 2H), 2.38(s, 3H), 2.46-2.53(m, 4H), 7.04(d, J = 8.0Hz, 2H), 7.24-7.27(m, 2H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.21, 14.61, 14.63, 14.81, 21.08, 22.25, 22.75, 23.91, 24.85, 29.79, 30.42, 31.98, 32.17, 116.61, 128.02(2C), 128.42, 129.73(2C), 137.10, 137.70, 143.14, 150.23, 163.00. HRMS calcd for $\text{C}_{24}\text{H}_{35}\text{NO}$ 353.2719, Found 353.2719.

1-(2'-Trifluoromethyl)-3,4,5,6-tetrapropylpyrid-2-one (7b)

^1H NMR (CDCl_3 , Me_4Si) δ 0.69(t, J = 7.3 Hz, 3H), 0.96(t, J = 7.4Hz, 3H), 1.01(t, J = 7.4 Hz, 3H), 1.07(t, J = 7.3 Hz, 3H), 1.33-1.56(m, 8H), 2.33-2.66(m, 8H), 7.31(d, J = 7.8 Hz, 1H), 7.55 (t, J = 7.7 Hz, 1H), 7.68(t, J = 7.5 Hz, 1H), 7.79(d, J = 7.7 Hz, 1H). ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.16, 14.32(2C), 14.65, 21.99, 22.62, 23.87, 24.57, 29.39, 29.96, 31.81, 32.52, 116.72, 118.71, 121.44, 124.16, 126.87, 127.17, 127.21, 127.26, 127.31, 127.36, 127.48, 127.78, 128.40, 128.60, 130.90, 132.61, 137.79, 137.80, 142.88, 150.88, 162.88. HRMS calcd for $\text{C}_{24}\text{H}_{32}\text{F}_3\text{NO}$ 407.2436, Found 407.2428.

2-(*n*-Butyl)-1,4-diethyl-5,6,7,8-tetrahydrobenzopyrid-3-one (7d)

GC yield: 66%; Isolated yield: 33%; ^1H NMR (CDCl_3 , Me_4Si) δ 0.91 (t, J = 7.2 Hz, 3H), 1.01 (t, J = 7.4 Hz, 3H), 1.11 (t, J = 7.5 Hz, 3H), 1.31-1.44 (m, 2H), 1.55-1.68 (m, 6H), 2.46-2.63 (m, 8H), 4.00 (t, J = 7.8 Hz, 2H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 12.25, 12.56, 13.64, 19.73, 20.35, 21.77, 22.37, 22.92, 25.35, 26.87, 31.38, 44.17, 112.91, 128.09, 143.43, 145.59, 161.49, HRMS(FAB) calcd for $\text{C}_{17}\text{H}_{28}\text{NO}$ $[\text{MH}]^+$ 262.2173, found 262.2171.

2-Naphthyl-1,4-diethyl-5,6,7,8-tetrahydrobenzopyrid-3-one (7c)

GC yield: 85%; Isolated yield: 74%; ^1H NMR (CDCl_3 , Me_4Si) δ 0.80 (t, $J=7.4$ Hz, 3H), 1.11 (t, $J=7.4$ Hz, 3H), 1.69 (m, 4H), 1.80-1.99 (m, 5H), 2.30-2.42 (m, 1H), 2.60-2.67 (m, 4H), 2.78 (m, 2H), 7.31-7.57 (m, 5H), 7.88 (dd, 2H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 12.39, 12.82, 19.73, 22.55, 22.90, 23.09, 25.30, 27.18, 113.24, 122.46, 125.40, 126.23, 126.37, 127.29, 128.33, 128.73, 129.08, 130.46, 134.35, 136.46, 144.48, 147.21, 162.26, HRMS calcd for $\text{C}_{23}\text{H}_{25}\text{NO}$ 331.1925, found 331.1936

Synthesis of 1,4-Diethyl-2-cyano-2,3,5,6,7,8-hexahydronaphthalene (8)

In a 20 mL Schlenk tube, a solution of Cp_2ZrCl_2 (292 mg, 1.00 mmol) in 10 mL of THF was cooled to -78°C , and to this solution $n\text{-BuLi}$ (1.59 M hexane solution, 1.3 mL, 2.0 mmol) was added dropwise via a syringe. After 1 h, 3,9-dodecadiyne (200 μL , 1.0 mmol) was added to the solution, and stirred at rt for 3 h. To the resulting solution, CrCl_3 (158 mg, 1.00 mmol) and acrylonitrile (0.2 mL, 3 mmol) were added and heated to 50°C for 3 h. After cooling to rt, the mixture was quenched with 3 N HCl , and extracted with ethyl acetate, washed with water, saturated sodium bicarbonate aqueous solution, and brine. After removal of the solvent the residue was purified by flash chromatography to afford a colorless oil (100 mg, 46%; GC yield 51%).

^1H NMR (CDCl_3 , Me_4Si) δ 1.03 (t, 3 H, $J = 7.5$ Hz), 1.06 (t, 3 H, $J = 7.5$ Hz), 1.43 – 1.73 (m, 4 H), 1.97 – 2.39 (m, 8 H), 2.40 – 2.55 (m, 2 H), 3.12 (t, 1 H, $J = 6.0$ Hz); ^{13}C NMR (CDCl_3 , Me_4Si) δ 12.29, 13.00, 23.49, 23.61, 24.77, 25.53, 25.72, 26.31, 29.54, 31.28, 121.47, 124.37, 128.73, 129.65, 132.44; MS m/z (%) 215 (M^+ , 85), 213 (34), 200 (26), 186 (100), 184 (74), 158 (35), 144 (39). HRMS calcd for $\text{C}_{15}\text{H}_{21}\text{N}$: 215.1674, found: 215.1678.