Supporting Information

Palladium-Catalyzed Intermolecular Three-Component Coupling of Aryl Iodides, Alkynes, and Alkenes to Produce 1,3- Butadiene Derivatives

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Di(4-methylphenyl)acetylene (**2b**), di(4-chlorophenyl)acetylene (**2c**), and di(2-thienyl)acetylene (**2d**) were prepared by the method reported previously.¹ Other reagents used in the present study are commercially available. DMF and 1-propanol were distilled before use. Mizoroki-Heck type products **5**, **8**, and **10** are known and were compared with those authentic specimens. The following experimental details given below may be regarded as typical in methodology and scale.

Reaction of 4-Iodotoluene (1a) with Diphenylacetylene (2a) and Butyl Acrylate (3a). A mixture of **1a** (1 mmol, 218 mg), **2a** (4 mmol, 712 mg), **3a** (1 mmol, 128 mg), Pd(OAc)₂ (0.05 mmol, 11 mg), LiCl (0.7 mmol, 30 mg), and NaHCO₃ (2 mmol, 168 mg) was stirred in DMF/H₂O (5 mL, 9:1) under nitrogen at 130 °C. After 1 h, the reaction mixture was poured into ether (70 mL), washed by

water (100 mL, three times), and dried over sodium sulfate. GC and GC-MS analyses confirmed the formation of **4a** and **5a** in 72 and 12% yields, respectively. The product **4a** (197 mg, 50%) was isolated by column chromatography on silica gel using hexane-ethyl acetate (99.5:0.5, v/v) as eluant. Although the NMR spectra of **4a** indicated that it consists of two geometrical isomers ((*2E*, *4E*):(*2E*, *4Z*) = 1.2:1), the minor isomer could be isolated by recrystallization from hexane after the column chromatographic separation and was determined to possess (*2E*, *4Z*)-geometry by NOE experiments as shown below.

The characterization data of three-component coupling products **4**, **6**, **7**, and **9** are given below.

Butyl 5-(4-methylphenyl)-4,5-diphenyl-2,4-pentadienoate (4a, 4E:4Z = 1.2:1). Oil; ^1H NMR (400 MHz, CDCl_3) δ 0.87-0.91 (m, 3H), 1.25-1.36 (m, 2H), 1.53-1.58 (m, 2H), 2.20 (s, 3H, 4Z), 2.39 (s, 3H, 4E), 4.04-4.09 (m, 2H), 5.59 (d, $J = 15.4$ Hz, 1H, 4Z), 5.61 (d, $J = 15.4$ Hz, 1H, 4E), 6.76 (d, $J = 8.1$ Hz, 2H, 4Z), 6.83 (d, $J = 8.1$ Hz, 2H, 4Z), 6.88-6.90 (m, 2H, 4E), 7.01-7.04 (m, 2H, 4E), 7.08-7.37 (m, 10H), 7.70 (d, $J = 15.4$ Hz, 1H, 4Z), 7.76 (d, $J = 15.4$ Hz, 1H, 4E); ^{13}C NMR (100 MHz, CDCl_3) δ 13.71 (overlapped), 19.12 (4Z), 19.15 (4E), 21.15 (4Z), 21.31 (4E), 30.68 (4Z), 30.71 (4E), 64.03

(overlapped), 121.33 (4Z), 121.38 (4E), 126.93 (4Z), 127.03 (4E), 127.37 (4E), 128.03 (4Z), 128.10 (4E), 128.12 (4Z), 128.15 (4Z), 128.18(4Z), 128.77 (4E), 130.98 (4Z), 131.03 (overlapped), 131.08 (overlapped), 131.14 (4E), 136.56 (4Z), 136.68 (4E), 136.97 (4Z), 138.17 (4E), 138.47 (4E), 138.98 (4Z), 139.51 (4E), 139.54 (4Z), 141.59 (4Z), 142.12 (4E), 146.42 (4Z), 146.48 (4E), 149.57 (4Z), 149.68 (4E), 167.64 (4Z), 167.71 (4E); MS m/z 396 (M^+). Anal. Calcd for $C_{28}H_{28}O_2$: C, 84.81, H, 7.12. Found: C, 84.67, H, 7.16.

Butyl 4,5,5-triphenyl-2,4-pentadienoate (6a). Mp 108.5-110 °C; 1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, $J = 7.3$ Hz, 3H), 1.31 (m, 2H), 1.56 (m, 2H), 4.07 (t, $J = 6.6$ Hz, 2H), 5.61 (d, $J = 15.4$ Hz, 1H), 6.88-6.90 (m, 2H), 7.02-7.09 (m, 3H), 7.09 (dd, $J = 2.2$ Hz, 2H), 7.18-7.25 (m, 5H), 7.35-7.40 (m, 3H), 7.72 (d, $J = 15.4$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.69, 19.13, 30.69, 64.08, 121.81, 127.02, 127.08, 127.42, 128.08, 128.14, 128.19, 130.97, 131.04, 131.10, 137.04, 139.33, 141.35, 141.96, 146.16, 149.52, 167.57; MS m/z 382 (M^+). Anal. Calcd for $C_{27}H_{26}O_2$: C, 84.78, H, 6.85. Found: C, 84.66, H, 6.81.

Butyl 4,5,5-tri(4-methylphenyl)-2,4-pentadienoate (6b). Mp 99-102 °C; 1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, $J = 7.3$ Hz, 3H), 1.31 (m, 2H), 1.55 (m, 2H), 2.21 (s, 3H), 2.30 (s, 3H), 2.38 (s, 3H), 4.06 (t, $J = 6.9$ Hz, 2H), 5.59 (d, $J = 15.6$ Hz, 1H), 6.77 (d, $J = 8.3$ Hz, 2H), 6.84 (d, $J = 8.0$ Hz, 2H), 6.98 (d, $J = 8.3$ Hz, 2H), 7.02 (d, $J = 8.0$ Hz, 2H), 7.09 (d, $J = 8.0$ Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 7.71 (d, $J = 15.6$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.70, 19.14,

21.17, 21.21, 21.29, 30.71, 63.95, 120.81, 128.11, 128.69, 128.86, 130.95, 131.04, 131.07, 136.19, 136.40, 136.62, 136.76, 137.96, 138.89, 139.30, 146.99, 149.40, 167.83; MS m/z 424 (M^+). Anal. Calcd for $C_{30}H_{32}O_2$: C, 84.87, H, 7.60. Found: C, 84.74, H, 7.55

Butyl 4,5,5-tri(4-chlorophenyl)-2,4-pentadienoate (6c). Mp 150-152°C; 1H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, $J = 7.3$ Hz, 3H), 1.33 (m, 2H), 1.57 (m, 2H), 4.09 (t, $J = 6.6$ Hz, 2H), 5.61 (d, $J = 15.4$ Hz, 1H), 6.79 (d, $J = 8.4$ Hz, 2H), 7.02 (d, $J = 8.8$ Hz, 2H), 7.06 (d, $J = 8.4$ Hz, 2H), 7.13 (d, $J = 8.8$ Hz, 2H), 7.23 (d, $J = 8.8$ Hz, 2H), 7.37 (d, $J = 8.8$ Hz, 2H), 7.62 (d, $J = 15.4$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.68, 19.14, 30.64, 64.35, 122.88, 128.10, 128.58, 128.75, 132.21, 132.28 (overlapped), 133.45, 133.60, 134.76, 136.59, 137.27, 139.08, 139.64, 145.03, 147.00, 167.14; MS m/z 484, 486, 488 (M^+). Anal. Calcd for $C_{27}H_{25}O_2Cl_3$: C, 77.78, H, 6.04, Cl, 8.50. Found: C, 77.65, H, 5.92, Cl, 8.52. Anal. Calcd for $C_{27}H_{23}O_2Cl_3$: C, 66.75, H, 4.77, Cl, 21.89. Found: C, 66.69, H, 4.61, Cl, 21.77.

Butyl 4,5,5-tri(2-thienyl)-2,4-pentadienoate (6d). Oil: 1H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, $J = 7.3$ Hz, 3H), 1.34 (m, 2H), 1.58 (m, 2H), 4.08 (t, $J = 6.6$ Hz, 2H), 5.74 (d, $J = 15.4$ Hz, 1H), 6.78 (dd, $J = 1.1, 3.7$ Hz, 1H), 6.83 (dd, $J = 3.7, 5.1$ Hz, 1H), 6.97 (dd, $J = 1.1, 3.3$ Hz, 1H), 7.08 (dd, $J = 3.3, 5.1$ Hz, 1H), 7.12 (dd, $J = 3.7, 5.1$ Hz, 1H), 7.18 (dd, $J = 1.1, 3.7$ Hz, 1H), 7.27 (dd, $J = 1.1, 5.1$ Hz, 1H), 7.44 (dd, $J = 1.1, 5.1$ Hz, 1H), 7.49 (dd, $J = 1.1, 5.1$ Hz, 1H), 7.78 (d, $J = 15.4$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.70, 19.13, 30.66, 64.18, 121.99, 126.14, 126.90, 127.49, 127.65, 127.97, 129.64,

129.70, 129.73, 130.74, 132.00, 136.59, 138.90, 141.47, 143.87, 145.78, 167.32; MS m/z 400 (M^+). Anal. Calcd for $C_{21}H_{20}O_2S_3$: C, 62.97, H, 5.03, S, 24.01. Found: C, 62.94, H, 4.92, S, 23.85.

Ethyl 4,5,5-triphenyl-2,4-pentadienoate (7a). Mp 181-182 °C; 1H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, J = 7.3 Hz, 3H), 4.13 (q, J = 7.3 Hz, 2H), 5.62 (d, J = 15.4 Hz, 1H), 6.87-6.90 (m, 2H), 7.02-7.05 (m, 3H), 7.09-7.12 (m, 2H), 7.17-7.20 (m, 2H), 7.21-7.25 (m, 3H), 7.26-7.39 (m, 3H), 7.73 (d, J = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.22, 60.16, 121.83, 127.01, 127.07, 127.41, 128.10, 128.13, 128.23, 130.97, 131.06, 131.10, 137.01, 139.37, 141.31, 141.99, 146.20, 149.55, 167.52; MS m/z 354 (M^+). Anal. Calcd for $C_{25}H_{22}O_2$: C, 84.72, H, 6.26. Found: C, 84.61, H, 6.14.

N,N-Dimethyl-4,5,5-triphenyl-2,4-pentadienamide (7b). Mp 178-179 °C; 1H NMR (400 MHz, $CDCl_3$) δ 2.85 (s, 3H), 2.94 (s, 3H), 6.04 (d, J = 15.0 Hz, 1H), 6.87-6.89 (m, 2H), 7.01-7.04 (m, 3H), 7.12-7.19 (m, 2H), 7.17-7.19 (m, 2H), 7.21-7.24 (m, 3H), 7.31-7.38 (m, 3H), 7.67 (d, J = 15.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.59, 37.18, 121.71, 126.77, 126.84, 127.36, 127.97, 127.99, 128.10, 130.94, 130.98, 131.18, 137.36, 140.08, 141.19, 142.33, 143.73, 148.05, 167.30; MS m/z 353 (M^+). Anal. Calcd for $C_{25}H_{23}ON$: C, 84.95, H, 6.56, N, 3.96. Found: C, 84.81, H, 6.38, N, 3.94.

4,5,5-Triphenyl-2,4-pentadienenitrile (7c). Mp 136-138 °C; 1H NMR (400 MHz, $CDCl_3$) δ 5.08 (d, J = 16.5 Hz, 1H), 6.86-6.88 (m, 2H), 7.02-8.07 (m, 3H), 7.08-7.11 (m, 2H), 7.20-7.25 (m, 5H), 7.39-

7.44 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 99.17, 118.98, 127.55, 127.57, 127.60, 128.38, 128.49, 128.70, 130.88 (overlapped), 131.05, 136.44, 137.81, 140.75, 141.21, 150.56, 151.75; MS m/z 307 (M^+). Anal. Calcd for $\text{C}_{23}\text{H}_{17}\text{N}$: C, 89.87, H, 5.57, N, 4.56. Found: C, 89.64, H, 5.57, N, 4.58.

1,1,2,4-Tetraphenyl-1,3-butadiene (9a). Mp 145-146 °C (lit.² mp 144-145 °C); ^1H NMR (400 MHz, CDCl_3) δ 6.26 (d, $J = 16.1$ Hz, 1H), 6.89-6.91 (m, 2H), 7.00-7.03 (m, 3H), 7.15-7.23 (m, 12H), 7.30-7.40 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 126.22, 126.47, 126.66, 127.28, 127.31, 127.35, 127.87, 127.95, 128.52, 131.10, 131.16, 131.26, 131.50, 132.62, 137.75, 138.94, 140.49, 142.48, 142.75, 142.87; MS m/z 358 (M^+).

1,1,2-triphenyl-4-(4-methylphenyl)-1,3-butadiene (9b). Mp 133-134 °C (lit.³ 131-132 °C); ^1H NMR (400 MHz, CDCl_3) δ 2.29 (s, 3H), 6.23 (d, $J = 16.12$ Hz, 1H), 6.88-6.91 (m, 2H), 6.99-7.05 (m, 5H), 7.09-7.11 (m, 2H), 7.18-7.22 (m, 5H), 7.30-7.39 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.19, 126.13, 126.39, 126.61, 127.25, 127.28, 127.82, 127.91, 129.23, 130.25, 131.10, 131.27, 131.51, 132.60, 134.97, 137.19, 139.07, 140.58, 142.20, 142.56, 142.97; MS m/z 372 (M^+).

1,1,2-triphenyl-4-(4-chlorophenyl)-1,3-butadiene (9c). Mp 167-169 °C; ^1H NMR (400 MHz, CDCl_3) δ 6.20 (d, $J = 16.1$ Hz, 1H), 6.88-6.90 (m, 2H), 7.00-7.03 (m, 3H), 7.10-7.12 (m, 2H), 7.17-7.23 (m, 8H), 7.29-7.31 (m, 2H), 7.34-7.40 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 126.34, 126.75, 127.34, 127.47, 127.58, 127.94, 128.00,

128.66, 131.06, 131.21 (overlapped), 131.43, 131.74, 132.80, 136.28, 138.70, 140.29, 142.36, 142.73, 143.32; MS m/z 392, 394 (M^+). Anal. Calcd for $C_{28}H_{21}Cl$: C, 85.59, H, 5.39, Cl, 9.02. Found: C, 85.53, H, 5.47, Cl, 8.95.

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