Supporting Information

Selective *cis*-Addition of Aromatic C–H Bonds to Alkynes Catalyzed Dinuclear Palladium Complexes

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General. Alkynes and THF solutions of boranes were purchased from Aldrich and TCI and used without further purification. Arenes were distilled from CaH_2 under nitrogen before use. The complexes **1c**,¹ $\text{PdMe}(\text{dpfam})$,¹ $[\text{PdPh}(\text{PPh}_3)(\text{CH}_2\text{OH})]_2$,² and **10b**¹ were prepared according to literature methods.

$\text{Pd}_2(p\text{-Tol})_2(\text{CH}_2\text{OH})(\text{CH}_2\text{dpfam})$ 1a. To a suspension of **1c** (0.50 mmol, 0.54 g) in THF (5 ml) and H_2O (2.5 ml) was added *t*-BuOK (2.5 mmol, 0.28 g). The mixture was refluxed for 2 h. Tetrahydrofuran was removed under reduced pressure, and the resulted aqueous layer was extracted with dichloromethane (2 x 20 ml). The combined extracts were dried over anhydrous Na_2SO_4 and evaporate to give a pale yellow powder, which was washed with ether (2 x 20 ml), filtered, and dried. Yield: 0.47 g, 96%. ^1H NMR (400 MHz, CDCl_3) δ 8.38 (s, 1H), 7.52–7.43 (m, 8H), 7.42–7.27 (m, 14H), 7.25–7.17 (m, 2H), 7.12–7.06 (m, 2H), 6.97 (t, $J = 7.4$ Hz, 2H), 6.92 (dd, $J = 7.9$, $^4J(\text{P,H}) = 1.9$ Hz, 4H), 6.49 (d, $J = 7.9$ Hz, 4H), 2.06 (s, 6H), 0.58 (t, $^3J(\text{P,H}) = 1.6$ Hz, 1H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 36.16. Anal. Calcd for

$C_{51}H_{44}N_2OP_2Pd_2$: C, 62.78; H, 4.55; N, 2.87. Found: C, 62.76; H, 4.79; N, 2.85.

$Pd_2Me_2(\text{Hdpfam})$ 1b. To a solution of Hdpfam (0.5 mmol, 0.28 g) in acetone (17.5 ml) and H_2O (2.5 ml) was added $PdMe_2(tmeda)$ (1.0 mmol, 0.26 g). The mixture was stirred overnight to give a white precipitate, which was collected by filtration, washed with a small amount of cold acetone, and dried. Yield: 0.38 g, 92%. 1H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.64–7.57 (m, 8H), 7.46–7.34 (m, 12H), 7.29–7.24 (m, 2H), 7.15–7.09 (m, 2H), 7.02–6.97 (m, 2H), 6.93–6.88 (m, 2H), 0.39 (d, $^3J(P,H) = 1.9$ Hz, 6H), 0.14 (s, 1H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 40.81. Anal. Calcd for $C_{39}H_{36}N_2OP_2Pd_2$: C, 56.88; H, 4.41; N, 3.40. Found: C, 57.00; H, 4.62; N, 3.53.

General procedure for the hydroarylation of alkynes with arenes. To a solution of **1a** (0.01 mmol, 10 mg) in arene (2 ml) was added a THF solution (1.0 M) of tri(*n*-butyl)borane (0.15 mmol, 0.15 ml) and then alkyne (0.5 mmol) under nitrogen atmosphere in a pressure vial. After heating at 100°C for 4 h, the mixture was filtered through a short column using ether as an eluent. Solvents were removed under reduced pressure, and the product was purified by silica gel column chromatography.

Product Characterization. The structures of the products **3a**,³ **3b**,³ **3c**,⁴ **3d**,⁵ **4**,⁶ and **5**⁷ were determined by comparing their 1H NMR spectra and those in the literature.

(*E*)-3-Tolyl-3-hexene 6. Since the aromatic region in the 1H NMR spectrum of the isomer mixture was intricate, the structures of **6a** and **6b** were determined by comparing the 1H NMR spectrum of the mixture to those of authentic samples prepared by Suzuki–Miyaura couplings⁸ of 2-(*cis*-1-ethyl-1-butenyl)benzo[1,3,2]dioxaborole and *m*- and *p*-bromotoluenes, and by co-injection with the authentic samples using GC and GC-MS. No *o*-isomer was observed in the NMR spectrum of the mixture and GC.

6a. ^1H NMR (500 MHz, CDCl_3) δ 7.18 (t, $J = 7.5$ Hz, 1H), 7.16 (s, 1H), 7.14 (d, $J = 7.5$ Hz, 1H), 7.03 (d, $J = 7.5$ Hz, 1H), 5.61 (t, $J = 7.3$ Hz, 1H), 2.49 (q, $J = 7.5$ Hz, 2H), 2.34 (s, 3H), 2.20 (dq, $J = 7.5, 7.3$ Hz, 2H), 1.05 (t, $J = 7.5$ Hz, 3H), 0.98 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.1, 141.1, 137.6, 129.8, 128.0, 127.2, 127.0, 123.4, 22.9, 21.7, 21.5, 14.5, 13.7. HRMS (EI) m/z calcd for $[\text{C}_{13}\text{H}_{18}]^+$: 174.1404, found 174.1403. The *E*-configuration was confirmed by an NOE experiment.

6b. ^1H NMR (400 MHz, CDCl_3) δ 7.25 (d, $J = 8.0$ Hz, 2H), 7.11 (d, $J = 8.0$ Hz, 2H), 5.60 (t, $J = 7.3$ Hz, 1H), 2.49 (q, $J = 7.5$ Hz, 2H), 2.33 (s, 3H), 2.19 (dq, $J = 7.5, 7.3$ Hz, 2H), 1.05 (t, $J = 7.5$ Hz, 3H), 0.97 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.7, 140.1, 136.0, 129.2, 128.8, 126.1, 22.8, 21.7, 21.0, 14.5, 13.7. HRMS (EI) m/z calcd for $[\text{C}_{13}\text{H}_{18}]^+$: 174.1704, found 174.1403. The *E*-configuration was confirmed by an NOE experiments.

(*E*)-3-(Methoxyphenyl)-3-hexene 7. The structures of **7a** and **7b** were determined by ^1H NMR spectrum of the mixture. No *o*-isomer was observed. ^1H NMR (400 MHz, CDCl_3) for **7a**; δ 7.22 (t, $J = 8.0$ Hz, 1H), 6.95 (ddd, $J = 8.0, 1.6, 0.9$ Hz, 1H), 6.89 (dd, $J = 2.6, 1.6$ Hz, 1H), 6.77 (ddd, $J = 8.0, 2.6, 0.9$ Hz, 1H), 5.64 (t, $J = 7.2$ Hz, 1H), 3.82 (s, 3H), 2.49 (q, $J = 7.5$ Hz, 2H), 2.20 (dq, $J = 7.5, 7.2$ Hz, 2H), 1.05 (t, $J = 7.5$ Hz, 3H), 0.98 (t, $J = 7.5$ Hz, 3H); for **7b**; δ 7.28 (d, $J = 8.8$ Hz, 2H), 6.84 (d, $J = 8.8$ Hz, 2H), 5.56 (t, $J = 7.2$ Hz, 1H), 3.80 (s, 3H), 2.48 (q, $J = 7.5$ Hz, 2H), 2.18 (dq, $J = 7.5, 7.2$ Hz, 2H), 1.05 (t, $J = 7.5$ Hz, 3H), 0.97 (t, $J = 7.5$ Hz, 3H). HRMS (EI) m/z calcd for $[\text{C}_{13}\text{H}_{18}\text{O}]^+$: 190.1353, found 190.1352. The *E*-configurations were

confirmed by NOE experiments.

(*E*)-3-(Methoxycarbonyl)-3-hexene 8. The structures of **8a** and **8b** were determined by ^1H NMR spectrum of the mixture. No *o*-isomer was observed. ^1H NMR (400 MHz, CDCl_3) for ***m*-9c**: δ 8.02 (dd, $J = 1.9, 1.5$ Hz, 1H), 7.89 (ddd, $J = 7.8, 1.5, 1.2$ Hz, 1H), 7.53 (ddd, $J = 7.8, 1.9, 1.2$ Hz, 1H), 7.37 (t, $J = 7.8$ Hz, 1H), 5.68 (t, $J = 7.2$ Hz, 1H), 3.92 (s, 3H), 2.53 (q, $J = 7.5$ Hz, 2H), 2.22 (dq, $J = 7.5, 7.2$ Hz, 2H), 1.07 (t, $J = 7.5$ Hz, 3H), 0.97 (t, $J = 7.5$ Hz, 3H); for ***p*-9c**: δ 7.97 (d, $J = 8.6$ Hz, 2H), 7.41 (d, $J = 8.6$ Hz, 2H), 5.75 (t, $J = 7.2$ Hz, 1H), 3.91 (s, 3H), 2.52 (q, $J = 7.5$ Hz, 2H), 2.23 (dq, $J = 7.5, 7.2$ Hz, 2H), 1.07 (t, $J = 7.5$ Hz, 3H), 0.98 (t, $J = 7.5$ Hz, 3H). HRMS (EI) m/z calcd for $[\text{C}_{14}\text{H}_{18}\text{O}_2]^+$: 218.1302, found 218.1301. The *E*-configurations were confirmed by NOE experiments.

(*E*)-3-(Chlorophenyl)-3-hexene 9. Since the aromatic region in the ^1H NMR spectrum of the isomer mixture was intricate, the structures of **9a** and **9b** were determined by comparing the ^1H NMR spectrum of the mixture to those of authentic samples prepared by Suzuki–Miyaura couplings⁸ of 2-(*cis*-1-ethyl-1-butenyl)benzo[1,3,2]dioxaborole and *m*- and *p*-bromochlorobenzenes, and by co-injection with the authentic samples using GC and GC-MS. No *o*-isomer was observed in the NMR spectrum of the mixture and GC.

9a. ^1H NMR (400 MHz, CDCl_3) δ 7.33–7.32 (m, 1H), 7.23–7.17 (m, 3H), 5.64 (t, $J = 7.2$ Hz, 1H), 2.48 (q, $J = 7.5$ Hz, 2H), 2.20 (dq, $J = 7.5, 7.2$ Hz, 2H), 1.06 (t, $J = 7.5$ Hz, 3H), 0.98 (t, $J =$

7.5 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 145.0, 139.9, 134.1, 131.2, 129.3, 126.5, 126.4, 124.4, 22.8, 21.7, 14.4, 13.6. Anal. Calcd for $\text{C}_{12}\text{H}_{15}\text{Cl}$: C, 74.03; H, 7.77; Cl, 18.21. Found: C, 74.03; H, 7.96; Cl, 18.14. The *E*-configuration was confirmed by an NOE experiment.

9b. ^1H NMR (100 MHz, CDCl_3) δ 7.29–7.24 (m, 4H), 5.61 (t, $J = 7.2$ Hz, 2H), 2.47 (q, $J = 7.5$ Hz, 2H), 2.20 (dq, $J = 7.5, 7.2$ Hz, 2H), 1.05 (t, $J = 7.5$ Hz, 2H), 0.96 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 141.5, 139.9, 132.1, 130.5, 128.2, 127.6, 22.7, 21.7, 14.4, 13.6. HRMS (EI) m/z calcd for $[\text{C}_{12}\text{H}_{15}\text{Cl}]^+$: 194.0857, found: 194.0857. The *E*-configuration was confirmed by an NOE experiment.

$\text{Pt}_2\text{Me}_2(\text{[7-OH]})(\text{[7-dpfam]})$ 10a. To a suspension of **10b**¹ (0.05 mmol, 51 mg) in THF (2.5 ml) and H_2O (1.0 ml) was added *t*-BuOK (0.25 mmol, 28 mg). The mixture was refluxed for 3 h. Tetrahydrofuran was removed under reduced pressure, and the resulted aqueous layer was extracted with dichloromethane (2 x 5 ml). The combined extracts were dried over anhydrous Na_2SO_4 and evaporate to give a white powder, which was washed with ether (2 x 5 ml), filtered, and dried. Yield: 39 mg, 79%. ^1H NMR (400 MHz, CDCl_3) δ 8.58 (s, $^3J(\text{Pt},\text{H}) = 24$ Hz, 1H), 7.70–7.63 (m, 8H), 7.46–7.34 (m, 12H), 7.31–7.27 (m, 2H), 7.23–7.16 (m, 2H), 7.14–7.09 (m, 2H), 6.95 (t, $J = 7.5$ Hz, 2H), 1.41 (s, 1H), 0.51 (d, $^3J(\text{P},\text{H}) = 1.7$ Hz, $^2J(\text{Pt},\text{H}) = 70$ Hz, 6H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 15.72 ($^1J(\text{Pt},\text{P}) = 4576$ Hz). Anal. Calcd for $\text{C}_{39}\text{H}_{36}\text{N}_2\text{OP}_2\text{Pt}_2$: C, 46.80; H, 3.63; N, 2.80. Found: C, 47.07; H, 3.71; N, 2.96.

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