Supporting Information

Oxygen Promoted Palladium(II) Catalysis: Facile C(sp²)-C(sp²) Bond Formation via Cross Coupling of
Alkenylboronic Compounds and Olefins**

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General Procedure for the Boron-Heck Reaction of Alkenylboronic Compounds and Olefins

A. One Pot Reaction Conditions (Condition A): Olefin (1.5 mmol) was dissolved in *N,N*-dimethylacetamide (2.5 mL, 0.2 M solution), and stirred at room temperature. To the clear solution, was added pinacol boronic ester (0.5 mmol) followed by a single addition of Na₂CO₃ (1.0 mmol) and Pd(OAc)₂ (0.05 mmol). The reaction flask was fitted with an oxygen balloon and stirred for 3 hours. The mixture was then diluted with ethyl acetate (20 mL), and washed with water (2 X 10 mL). The organic layer was dried over anhydrous Na₂SO₄ and filtered. The filtrate was concentrated *in vacuo*, and subjected to flash chromatography affording the cross-coupling compound.

B. Slow Addition Reaction Conditions (Condition B): To a solution of olefin (1.5 mmol) in *N,N*-dimethylacetamide (2.5 mL, 0.2 M solution), was added palladium acetate (0.01 mmol) followed by a single addition of Na₂CO₃ (1.0 mmol). The two neck round flask was fitted with an oxygen balloon. The solution of pinacol boronic ester (0.5 mmol) in *N,N*-dimethylacetamide (1 mL) was slowly added into the reaction mixture via syringe pump over 6 hours at room temperature. After completion of addition, the reaction mixture was stirred for an additional hour, diluted with ethyl acetate (20 mL), and washed with water (2 X 10 mL). The organic layer was dried over anhydrous Na₂SO₄ and filtered. The filtrate was concentrated *in vacuo*, and subjected to flash chromatography affording the cross-coupling compound.

(1E)-2-Hex-1-enyl-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (1): The mixture of 1-hexyne (1 g, 12.2 mmol) and catechol borane (1.4 mL, 13.4 mmol) was heated to 70 °C with stirring for 2 hours. After cooled to room temperature, pinacol (1.7 g, 14.6 mmol) was added to the reaction and the resulting mixture was stirred for 3 hours, which was chromatographed on silica gel to afford **1** as colorless oil; ¹H NMR (250 MHz, CDCl₃): δ = 6.61 (dt, *J* = 6.5, 17.9 Hz, 1 H), 5.40, (d, *J* = 17.9 Hz, 1 H), 2.13 (dt, *J* = 6.5, 6.6 Hz, 2 H), 1.34 (m, 4 H), 1.24 (s, 12 H), 0.86 (t, *J* = 6.9 Hz, 3 H).

(2E,4E)-Nona-2,4-dienoic acid *tert*-butyl ester (2): Cross coupling reaction of boronic ester **1** with *tert*-butyl acrylate afforded diene **2** (90%) at room temperature under the slow addition conditions; ¹H NMR (250 MHz, CDCl₃): δ = 7.13 (dd, *J* = 25.4, 15.4 Hz, 1 H), 6.10 (m, 2 H), 5.68 (d, *J* = 15.4 Hz, 1 H), 2.12 (m, 2 H), 1.45 (s, 9 H), 1.32 (m, 4 H), 0.87 (t, *J* = 6.9 Hz, 3 H); ¹³C NMR (63 MHz, CDCl₃): δ = 166.7, 144.1, 144.0, 128.3, 121.0, 80.0, 32.6, 30.8, 28.1, 22.2, 13.8.

(1E,3E)-Octa-1,3-dienyl-benzene (3): Cross coupling reaction of boronic ester **3** with styrene afforded diene **3** (92%) at room temperature under the slow addition conditions; ¹H NMR (250 MHz, CDCl₃): δ = 7.27 (m, 5 H, Ph), 6.73 (dd, *J* = 15.6, 10.3 Hz, 1 H), 6.41 (d, *J* = 15.6 Hz, 1 H), 6.18 (dd, *J* = 15.1, 10.3 Hz, 1 H), 5.80 (dt, *J* = 15.1, 7.5 Hz, 1 H), 2.12 (m, 2 H), 1.34 (m, 4 H), 0.88 (t, *J* = 6.9 Hz, 3 H); ¹³C NMR (63 MHz, CDCl₃): δ = 137.6, 136.0, 130.4, 129.9, 129.4, 128.5, 127.0, 126.1, 32.6, 31.4, 22.3, 14.0.

(2E,4E)-Nona-2,4-dienyloxymethyl-benzene (4): Cross coupling reaction of boronic ester **1** with allyl benzyl ether afforded diene **4** (81%) and homo coupling compound (17%) at room temperature under the slow addition conditions. For **4**; ¹H NMR (250 MHz, CDCl₃): δ = 7.28 (m, 5 H, Ph), 6.21 (dd, *J* = 15.2, 10.5 Hz, 1 H), 6.03 (dd, *J* = 15.2, 10.2 Hz, 1 H), 5.68 (m, 2 H), 4.48 (s, 2 H), 4.02 (d, *J* = 6.3 Hz, 2 H), 2.11 (m, 2 H), 1.31 (m, 4 H), 0.87 (t, *J* = 6.8 Hz, 3 H); ¹³C NMR (63 MHz, CDCl₃): δ = 138.3, 135.7, 133.5, 129.4, 128.3, 127.8, 127.5, 126.8, 71.9, 70.6, 32.3, 31.3, 22.2, 13.9.

(2E,4E)- and (2Z,4E)-Nona-2,4-dienitrile (5): Cross coupling reaction of boronic ester **1** with acrylonitrile afforded an inseparable mixture of (2E,4E)- and (2Z,4E)-diene **5** (85%) at room temperature under the one-pot conditions. For **(2E,4E)**; ¹H NMR (250 MHz, CDCl₃): δ 6.84 (m, 1 H), 6.04-6.21 (m, 2 H), 5.21 (d, *J* = 16.0 Hz, 1 H), 2.18 (m, 2 H), 1.34 (m, 4 H), 0.88 (t, *J* = 7.0 Hz, 3 H), For **(2Z,4E)**; ¹H NMR (250 MHz, CDCl₃): δ 6.77 (dd, *J* = 10.9, 10.9 Hz, 1 H), 6.47-6.58 (m, 1 H), 6.04-6.21 (m, 1 H), 5.07 (d, *J* = 10.9 Hz, 1 H), 2.18 (m, 2 H), 1.34 (m, 4 H), 0.89 (t, *J* = 7.0 Hz, 3 H).

(2E,4E)-3-Methyl-nona-2,4-dienoic acid ethyl ester (6): Cross coupling reaction of boronic ester **1** with ethyl crotonate afforded diene **6** (79%) and homo coupling compound (17%) at room temperature under the slow addition conditions. ¹H NMR (250 MHz, CDCl₃): δ 6.08 (m, 1 H), 5.66 (s, 1 H), 4.13 (q, 2 H, *J* = 7.2 Hz), 2.24 (s, 3 H), 2.15 (m, 2 H), 1.31 (m, 4 H), 1.25 (t, 3 H, *J* = 7.2 Hz), 0.87 (t, 3 H, *J* = 7.0 Hz); ¹³C NMR (63 MHz, CDCl₃): δ 167.3, 152.7, 137.5, 133.5, 117.5, 59.6, 32.7, 31.1, 22.2, 14.3, 13.9, 13.8.

(2E,4E)-2-Methyl-nona-2,4-dienoic acid *tert*-butyl ester (7): Cross coupling reaction of boronic ester **1** with *tert*-butyl methacrylate afforded diene **7** (81%) and homo coupling compound (15%) at room temperature under the slow addition conditions; ¹H NMR (250 MHz, CDCl₃): δ = 7.04 (d, *J* = 11.3 Hz,

1 H), 6.29 (dd, $J = 14.8, 11.4$ Hz, 1 H), 5.92 (m, 1 H), 2.18 (m, 2 H), 1.85 (s, 3 H), 1.46 (s, 9 H), 1.33 (m, 4 H), 0.88 (t, $J = 7.0$ Hz, 3 H); ^{13}C NMR (63 MHz, CDCl_3): $\delta = 167.9, 142.5, 137.8, 126.5, 126.1, 79.9, 32.9, 31.1, 28.1, 22.2, 13.8, 12.5$.

(1E,3E)- and (1Z,3E)-(2-Methyl-octa-1,3-dienyl)-benzene (8) and (9): Cross coupling reaction of boronic ester **1** with *trans*- β -methylstyrene afforded an inseparable mixture of dienes **8** and **9** (88%) and homo coupling compound (11%) at 50 °C under the slow addition conditions; ^1H NMR (250 MHz, CDCl_3): $\delta = 7.24$ (m, 5 H, Ph), 6.57 (for **9**, d, $J = 15.7$ Hz) and 6.22 (for **8**, dd, $J = 15.5, 1.1$ Hz), 6.40 (for **8**, s) and 6.33 (for **9**, s), 5.77 (dt, $J = 15.5, 7.1$ Hz, 2 H), 2.15 (m, 2 H), 1.97 (d, $J = 1.1$ Hz, 3 H), 1.35 (m, 4 H), 0.89 (t, $J = 7.0$ Hz, 3 H).

(1E,3E)-(1-Methyl-octa-1,3-dienyl)-benzene (10) and (3E)-(1-Methylene-oct-3-enyl)-benzene (11): Cross coupling reaction of boronic ester **1** with α -methylstyrene afforded an inseparable mixture of dienes **10** and **11** (88%) and homo coupling compound (7%) at 50 °C under the slow addition conditions; ^1H NMR (250 MHz, CDCl_3): $\delta = 7.21\text{--}7.45$ (m, 5 H, Ph), 6.42 (for **10**, m), 5.84 (for **10**, m), 5.49 (for **11**, m), 5.34 (for **11**, br s), 5.07 (for **11**, d, $J = 1.4$ Hz), 2.14 (for **10**, s), 1.99 (m, 2 H), 1.29 (m, 4 H), 0.88 (m, 3 H).

(1E)-3-Hex-1-enyl-cyclohex-2-enone (12): Cross coupling reaction of boronic ester **1** with cyclohexenone afforded diene **12** (76%) and homo coupling compound (17%) at room temperature under the slow addition conditions; ^1H NMR (250 MHz, CDCl_3): $\delta = 6.19$ (m, 2 H), 5.85 (s, 1 H), 2.41 (m, 4 H), 2.16 (m, 2 H), 2.00 (m, 2 H), 1.35 (m, 4 H), 0.89 (t, $J = 7.0$ Hz, 3 H); ^{13}C NMR (63 MHz, CDCl_3): $\delta = 200.5, 157.7, 139.2, 131.3, 126.4, 37.7, 32.9, 31.0, 25.0, 22.3, 22.2, 13.9$.

(1Z)-2-Hex-1-enyl-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (13): A two neck flask was charged with $[\text{Rh}(\text{cod})\text{Cl}_2]_2$ (43 mg, 0.015 eq) and then flushed with nitrogen. Cyclohexane, Pi-Pr_3 (67 μL , 0.06 eq.), TEA (0.82 mL, 1 eq.), and catechol borane (0.65 mL, 5.8 mmol) were successively added and the mixture was stirred for 30 minutes at room temperature. 1-Hexyne (0.58 g, 1.2 eq.) was added and the reaction mixture was stirred for 4 hours at room temperature. After addition of pinacol (1.0 g, 1.5 eq.), the resulting reaction mixture was stirred for an additional 12 hours, concentrated *in vacuo* and chromatographed on silica gel to give *cis*-pinacol boronic ester **13** as colorless oil; ^1H NMR (250 MHz,

CDCl₃): δ = 6.40 (dt, J = 13.4, 6.6 Hz, 1 H), 5.30 (dt, J = 13.4, 1.1 Hz, 1 H), 2.38 (m, 2 H), 1.31 (m, 4 H), 1.24 (s, 12 H), 0.87 (t, J = 7.0 Hz, 3 H).

(2E,4Z)-Nona-2,4-dienoic acid *tert*-butyl ester (14): Cross coupling reaction of boronic ester **13** with *tert*-butyl acrylate afforded diene **14** (86%) and homo coupling compound (17%) at room temperature under the slow addition conditions; ¹H NMR (250 MHz, CDCl₃): δ = 7.50 (ddd, J = 15.3, 11.5, 0.7 Hz, 1 H), 6.06 (dd, J = 11.0, 10.9 Hz, 1 H), 5.79 (m, 1 H), 5.77 (d, J = 15.3 Hz, 1 H), 2.25 (m, 2 H), 1.46 (s, 9 H), 1.34 (m, 4 H), 0.89 (t, J = 7.0 Hz, 3 H); ¹³C NMR (63 MHz, CDCl₃): δ = 166.8, 141.0, 138.5, 126.3, 122.9, 80.1, 31.5, 28.1, 27.9, 22.3, 13.9.

***trans*-2-phenyvinyl pinacol boronic ester (15):** Pinacol was added to a solution of commercial available *trans*-2-phenyl boronic acid (**17**) in THF at room temperature. After stirred for 3 hours, the reaction mixture was concentrated *in vacuo* and chromatographed on silica gel to afford pinacol boronic ester (**15**) as colorless oil in quantitative yield; ¹H NMR (250 MHz, CDCl₃): δ = 7.24-7.49 (m, 6 H), 6.15 (d, J = 18.4 Hz, 1 H), 1.30 (s, 12 H).

(2E,4E)-5-Phenyl-penta-2,4-dienoic acid *tert*-butyl ester (16): Cross coupling reaction of boronic ester **15** with *tert*-butyl acrylate afforded diene **16** (89%) at room temperature under the slow addition conditions; ¹H NMR (250 MHz, CDCl₃): δ = 7.21-7.39 (m, 6 H), 6.77 (m, 2 H), 5.85 (d, J = 15.2 Hz, 1 H), 1.44 (s, 9 H); ¹³C NMR (63 MHz, CDCl₃): δ = 166.4, 143.5, 139.7, 136.1, 128.9, 128.8, 127.1, 126.3, 123.3, 80.3, 28.2.

2-Isopropenyl pinacol boronic ester (18): Following the known procedure¹, isopropenyl bromide was converted to 2-isopropenyl boronic acid, which was transformed to the corresponding pinacol boronic ester **18** by following the same procedure for the *trans*-2-phenyvinyl pinacol boronic ester (**15**); ¹H NMR (250 MHz, CDCl₃): δ = 5.7 (br s, 1 H), 5.61 (br s, 1 H), 1.79 (dd, J = 1.31, 1.26 Hz, 3 H), 1.25 (s, 12 H).

(2E)-4-Methyl-penta-2,4-dienoic acid *tert*-butyl ester (19): Cross coupling reaction of boronic ester **18** with *tert*-butyl acrylate afforded diene **19** (91%) at room temperature under the slow addition conditions; ¹H NMR (250 MHz, CDCl₃): δ = 7.24 (d, J = 15.7 Hz, 1 H), 5.78 (d, J = 15.7 Hz, 1 H), 5.28

(1) C. E. Tucker, J. Davidson, P. Knochel, *J. Org. Chem.* **1992**, 57, 3482.

(m, 2 H), 1.85 (s, 3 H), 1.48 (s, 9 H); ^{13}C NMR (63 MHz, CDCl_3): δ = 166.5, 145.9, 140.5, 123.6, 120.6, 80.3, 46.3, 30.9, 28.1, 18.1.

(2E,4E)-6-(tert-Butyl-diphenyl-silanyloxy)-hexa-2,4-dienoic acid tert-butyl ester (21): Cross coupling reaction of boronic ester **20**, prepared from propargyl alcohol through TBDPS protection, hydroboration with catechol borane, and pinacol esterification, with *tert*-butyl acrylate afforded diene **21** (87%) at room temperature under the slow addition conditions; ^1H NMR (250 MHz, CDCl_3): δ = 7.65-7.34 (m, 10 H, Ph), 7.19 (dd, J = 15.3, 11.4 Hz, 1 H), 6.46 (dd, 15.2, 11.4 Hz, 1 H), 6.10 (dt, J = 15.2, 2.4 Hz, 1 H), 4.29 (d, J = 2.4 Hz, 2 H), 1.47 (s, 9 H), 1.04 (s, 9 H); ^{13}C NMR (63 MHz, CDCl_3): δ = 166.5, 143.0, 140.6, 135.4, 133.2, 129.7, 127.7, 126.8, 122.7, 80.2, 63.6, 28.1, 26.7, 19.2.

(2E,4E)-7-Hydroxy-octa-2,4-dienoic acid tert-butyl ester (23): Cross coupling reaction of boronic ester **22**, prepared from 4-pentyn-2-ol through TMS protection, hydroboration with catechol borane, and pinacol esterification, with *tert*-butyl acrylate afforded diene **23** (91%) at room temperature under the slow addition conditions; ^1H NMR (250 MHz, CDCl_3): δ = 7.14 (dd, J = 15.3, 10.5 Hz, 1 H), 6.20 (dd, J = 15.1, 10.5 Hz, 1 H), 6.06 (dt, J = 15.1, 7.0 Hz, 1 H), 5.73 (d, J = 15.3 Hz, 1 H), 3.88 (m, 1 H), 2.30 (m, 2 H), 1.46 (s, 9 H), 1.20 (d, J = 6.2 Hz, 3 H); ^{13}C NMR (63 MHz, CDCl_3): δ = 166.4, 143.2, 138.8, 131.1, 122.2, 80.2, 67.1, 42.6, 28.1, 23.0.