Stereoselective Synthesis of Trisubstituted Alkenylboranes by Palladium-Catalysed Reaction of Alkynyltriarylborates with Aryl Halides

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General. NMR spectra were recorded on a Varian Gemini 2000 (¹H at 300 MHz and ¹³C at 75 MHz) or Varian Mercury-400 (¹H at 400 MHz and ¹¹B at 128 MHz) spectrometers. Unless otherwise noted, CDCl₃ was used as a solvent. Me₄Si (¹H, δ =0.00), residual H of CD₃CN (¹H in CD₃CN, δ =1.94), CDCl₃ (¹³C, δ =77.0), CD₃CN (¹³C, δ =1.32), and BF₃·OEt₂ (¹¹B, δ =0.00) were used as standard. High-resolution mass spectra were recorded on a JEOL JMS-SX102A spectrometer. UV-vis spectra were recorded on a JASCO V-550S. All reactions were carried out under an argon atmosphere. Column chromatography was performed with silica gel 60 N (Kanto). Preparative thin-layer chromatography was performed with silica gel 60 PF₂₅₄ (Merck). Gel permeation chromatography (GPC) was carried out with Japan Analytical Industry LC-908.

Materials. Unless otherwise noted, all chemicals and anhydrous solvents were obtained from commercial suppliers and used as received. CH_2Cl_2 was purchased from Kanto chemicals. $(CH_2Cl)_2$ was dried over CaH₂. Pd_2dba_3 ·CHCl₃ was prepared according to the reported procedures.¹ AcOH and AcOD were degassed by sonication. Ar₃B·Py were prepared from thermolysis of Ar₄B·HPy, which is prepared from ArLi and BF₃·OEt₂² or ArMgBr and B(OMe)₃,³ followed by cation exchange with Py·HCl in water. Aryl iodide **4** was prepared according to reported procedures.⁴

Preparation of alkynyltriarylborate 1a. A typical procedure for the preparation of alkynyltriarylborates.

$${}^{n}C_{5}H_{11} \longrightarrow \xrightarrow{n}{} {}^{n}BuLi \xrightarrow{Ph_{3}B\cdotPy} \xrightarrow{[Me_{4}N]CI} [Me_{4}N][{}^{n}C_{5}H_{11} \longrightarrow BPh_{3}]$$

To a stirred solution of hept-1-yne (580 mg, 6.0 mmol) in THF (20 ml) at -78 °C was added *n*-BuLi (1.6M in hexane, 3.4 ml, 5.5 mmol). After 30 minutes at this temperature, Ph₃B·Py (1.61 g, 5.0 mmol) was added and the cooling bath was removed. After being stirred for 1 h at room temperature, the reaction was quenched by adding a small amount of MeOH. Volatile materials were removed under reduced pressure and the residue was dissolved in MeOH. Me₄NCl (1.1g, 10 mmol) was added with stirring, resulting white solid. It was collected by filtration and was washed with cold MeOH to give alkynyltriarylborate **1a** (1.95 g, 4.7 mmol, 95% yield).

Tetramethylammonium hept-1-ynyltriphenylborate (1a)



¹H NMR (CD₃CN): $\delta = 0.97$ (t, J = 7.2 Hz, 3H), 1.40-1.43 (m, 2H), 1.52-1.59 (m, 4H), 2.28 (t, J = 6.6 Hz, 2H), 2.89-2.95 (m, 12H), 6.89 (t, J = 6.4 Hz, 3H), 7.01-7.05 (m, 6H), 7.41 (br, 6H); ¹³C NMR (CD₃CN): $\delta = 14.5$, 21.1, 23.1, 31.3, 32.1, 56.0, 94.6, 107.1 (q, $J_{B-C} = 65.9$ Hz), 123.1, 126.6, 135.4, 162.9 (q, $J_{B-C} = 49.8$ Hz); ¹¹B NMR (CD₃CN): $\delta = -7.1$; HRMS (FAB⁻) Calcd for C₂₅H₂₆B [M-(NMe₄)]⁻ 337.2128. Found 337.2123.

Tetramethylammonium (3,3-dimethylbut-1-ynyl)triphenylborate (1b)



¹H NMR (CD₃CN): δ = 1.31 (s, 9H), 2.84-2.87 (m, 12H), 6.89 (t, *J* = 7.2 Hz, 3H), 7.03 (pseudo t, *J* = 7.4 Hz, 6H), 7.42 (br, 6H); ¹³C NMR (CD₃CN): δ = 28.8, 33.1, 55.9, 104.2 (q, *J*_{B-C} = 64.8 Hz), 104.3, 123.0, 126.5, 135.3, 162.9 (q, *J*_{B-C} = 49.5 Hz); ¹¹B NMR (CD₃CN): δ = -7.3; HRMS (FAB⁻) Calcd for C₂₄H₂₄B [M-(NMe₄)]⁻ 323.1971. Found 323.1965.

Tetramethylammonium triphenyl(4-phenylbut-1-ynyl)borate (1c)



¹H NMR (CD₃CN): $\delta = 2.60$ (t, J = 7.4 Hz, 2H), 2.74 (s, 12H), 2.91 (t, J = 7.4 Hz, 2H), 6.93 (tt, J = 7.2, 1.6 Hz, 3H), 7.05-7.09 (m, 6H), 7.24 (tt, J = 7.2, 1.6 Hz, 1H), 7.31-7.35 (m, 2H), 7.39-7.44 (m, 8H); ¹³C NMR (CD₃CN): $\delta = 23.6$, 37.8, 55.8, 94.1, 107.7 (q, $J_{B-C} = 64.1$ Hz), 123.1, 126.5, 128.9, 129.6, 135.4, 143.1, 162.6 (q, $J_{B-C} = 49.5$ Hz); ¹¹B NMR (CD₃CN): δ = -7.0; HRMS (FAB⁻) Calcd for C₂₈H₂₄B [M-(NMe₄)]⁻ 371.1971. Found 371.1957.

Tetramethylammonium tris(4-methoxyphenyl)hept-1-ynylborate (1d)



¹H NMR (CD₃CN): $\delta = 0.93$ (t, J = 7.2 Hz, 3H), 1.34-1.39 (m, 2H), 1.46-1.54 (m, 4H), 2.22 (t, J = 6.6 Hz, 2H), 2.98-3.00 (m, 12H), 3.68 (s, 9H), 6.60 (d, J = 8.4 Hz, 6H), 7.22 (br d, J = 7.6 Hz, 6H); ¹³C NMR (CD₃CN): $\delta =$ 14.6, 21.2, 23.1, 31.3, 32.1, 55.3, 55.8, 94.4, 107.7 (q, $J_{B-C} = 63.6$ Hz), 112.2, 135.9, 154.3 (q, $J_{B-C} = 48.5$ Hz), 156.6; ¹¹B NMR (CD₃CN): $\delta = -7.9$; HRMS (FAB⁻) Calcd for C₂₈H₃₂BO₃ [M-(NMe₄)]⁻ 427.2445. Found 427.2441.

Tetramethylammonium but-1-ynyltriphenylborate (1e)



¹H NMR (CD₃CN): δ = 1.18 (t, *J* = 7.4 Hz, 3H), 2.27 (q, *J* =7.4 Hz, 2H), 2.92 (s, 12H), 6.87 (tt, *J* = 7.2, 1.6 Hz, 3H), 7.01 (pseudo t, *J* = 7.2 Hz, 6H), 7.37 (br, 6H); ¹³C NMR (CD₃CN): δ = 14.7, 16.5, 55.9, 96.2, 106.2 (q, *J*_{B-C} = 65.5 Hz), 123.0, 126.5, 135.3, 162.8 (q, *J*_{B-C} = 49.5 Hz); ¹¹B NMR (CD₃CN): δ = -7.1; HRMS (FAB⁻) Calcd for C₂₂H₂₀B [M-(NMe₄)]⁻ 295.1658. Found 295.1652.

Tetramethylammonium 4-methylpent-1-ynyltriphenylborate (1f)



¹H NMR (CD₃CN): δ = 1.05 (d, *J* = 6.8 Hz, 6H), 1.78 (pseudo sept., *J* = 6.6 Hz, 1H), 2.14 (d, *J* = 6.0 Hz, 2H), 2.96-2.99 (br, 12H), 6.83-6.88 (m, 3H), 6.98-7.01 (m, 6H), 7.36 (br, 6H); ¹³C NMR (CD₃CN): δ = 22.6, 30.4, 30.7, 56.0, 93.4, 108.0 (q, *J*_{B-C} = 65.3 Hz), 123.2, 126.7, 135.5, 163.1 (q, *J*_{B-C} = 50.0 Hz); ¹¹B NMR (CD₃CN): δ = -7.0; HRMS (FAB⁻) Calcd for C₂₄H₂₄B [M-(NMe₄)]⁻ 323.1971. Found 323.1964.

Tetramethylammonium 3-methylbutyn-1-yltriphenylborate (1g)



¹H NMR (CD₃CN): $\delta = 1.23$ (d, J = 6.8 Hz, 6H), 2.65 (sept., J = 6.8 Hz, 1H), 2.88 (s, 12H), 6.88 (tt, J = 7.2, 1.6 Hz, 3H), 7.00-7.04 (m, 6H), 7.39 (br, 6H); ¹³C NMR (CD₃CN): $\delta = 22.7$, 25.4, 55.9, 123.0, 126.5, 135.3, 162.8 (q, $J_{B-C} = 49.8$ Hz); ¹¹B NMR (CD₃CN): $\delta = -7.2$; HRMS (FAB⁻) Calcd for C₂₃H₂₂B [M-(NMe₄)]⁻ 309.1815. Found 309.1806.

Tetramethylammonium hept-1-ynyltris(4-methylphenyl)borate (1h)



¹H NMR (CD₃CN): δ = 0.97 (t, *J* = 7.2 Hz, 3H), 1.36-1.45 (m, 2H), 1.49-1.59 (m, 4H), 2.23-2.29 (m, 11H), 2.80 (s, 12H), 6.85 (d, *J* = 7.6 Hz, 6H), 7.27 (d, *J* = 7.2 Hz, 6H); ¹³C NMR (CD₃CN): δ = 14.6, 21.2, 23.1, 31.3, 32.1, 55.8, 94.2, 107.6 (q, *J*_{B-C} = 63.8 Hz), 127.3, 131.5, 135.4, 159.5 (q, *J*_{B-C} = 49.0 Hz); ¹¹B NMR (CD₃CN): δ = -7.5; HRMS (FAB⁻) Calcd for C₂₈H₃₂B [M-(NMe₄)]⁻ 379.2597. Found 379.2582.

Tetramethylammonium hept-1-ynyltris(3-methylphenyl)borate (1i)



¹H NMR (CD₃CN): δ = 0.98 (t, *J* = 7.4 Hz, 3H), 1.39-1.45 (m, 2H), 1.57-1.58 (m, 4H), 2.22 (s, 9H), 2.28 (m, 2H), 2.80-2.83 (m, 12H), 6.71-6.73 (m, 3H), 6.90-6.94 (m, 3H), 7.16 (br, 3H), 7.28 (br, 3H); ¹³C NMR (CD₃CN): δ = 14.6, 21.2, 22.0, 23.2, 31.3, 32.1, 55.8, 94.5, 107.5 (q, *J*_{B-C} = 63.4 Hz), 123.7, 126.4, 132.6, 134.8, 136.3, 162.8 (q, *J*_{B-C} = 49.0 Hz); ¹¹B NMR

 (CD_3CN) : $\delta = -7.2$; HRMS (FAB⁻) Calcd for $C_{28}H_{32}B [M-(NMe_4)]^-$ 379.2597. Found 379.2600.

Tetramethylammonium tris(4-fluorophenyl)hept-1-ynylborate (1j)



¹H NMR (CD₃CN): $\delta = 0.95$ (t, J = 7.2 Hz, 3H), 1.36-1.41 (m, 2H), 1.48-1.58 (m, 4H), 2.26 (t, J = 6.8 Hz, 2H), 2.97 (s, 12H), 6.75-6.81 (m, 6H), 7.32 (br, 6H); ¹³C NMR (CD₃CN): $\delta = 14.5$, 21.0, 23.1, 31.1, 32.1, 56.0, 95.0, 106.3 (q, $J_{B-C} = 64.8$ Hz), 112.8 (d, $J_{C-F} = 18.2$ Hz), 136.2 (d, $J_{C-F} = 5.8$ Hz), 157.7 (q, $J_{B-C} = 50.7$ Hz), 160.9 (d, $J_{C-F} = 235.1$ Hz); ¹¹B NMR (CD₃CN): $\delta = -7.8$; HRMS (FAB⁻) Calcd for C₂₅H₂₃BF₃ [M-(NMe₄)]⁻ 391.1845. Found 391.1828.

Tetramethylammonium hept-1-ynyltri(2-thienyl)borate (1k)



¹H NMR (CD₃CN): δ = 0.97 (t, *J* = 7.2 Hz, 3H), 1.38-1.44 (m, 2H), 1.52-1.62 (m, 4H), 2.25-2.28 (m, 2H), 2.77 (s, 12H), 6.89-6.93 (m, 6H), 7.12 (d, *J* = 4.4 Hz, 3H); ¹³C NMR (CD₃CN): δ = 14.5, 20.9, 23.1, 30.8, 32.0, 55.8, 94.5 (q, *J*_{B-C} = 13.1 Hz), 103.1 (q, *J*_{B-C} = 68.2 Hz), 124.2, 127.0, 128.3, 164.7 (q, *J*_{B-C} = 54.6 Hz); ¹¹B NMR (CD₃CN): δ = -12.6; HRMS (FAB⁻) Calcd for C₁₉H₂₀BS₃ [M-(NMe₄)]⁻ 355.0820. Found

355.0819.

Palladium-catalysed reaction of alkynyltriarylborate 1a with 4-bromotoluene. A typical procedure for the palladium-catalysed reaction of alkynyltriarylborates with aryl halides.

Under an argon atmosphere, a CH₂Cl₂ solution (0.5 ml) of alkynyltriarylborate **1a** (82.2 mg, 0.20 mmol), Pd₂dba₃·CHCl₃ (5.2 mg, 2.5 µmol), and P(*o*-tol)₃ (3.6 mg, 6.0 µmol) was stirred for 30 minutes at room temperature. To the solution was added 4-bromotoluene (34.2 mg, 0.20 mmol) in CH₂Cl₂ (0.5 ml). After being stirred for 3 h, AcOH (1 ml) was added. After 3 h, the reaction mixture was neutralized with Na₂CO₃ solution. The aqueous layer was extracted with Et₂O (3 times), washed with water (once), brine (once), dried over MgSO₄ and concentrated. The residue was purified by preparative thin-layer chromatography on silica gel (hexane) to afford the trisubstituted alkene **3a** with a small amount of impurities. Further purification was performed by GPC, affording the alkene **3a** (46.9 mg, 0.18 mmol, 89% yield, E/Z = 7/93).

(Z)-2-(4-Methylphenyl)-1-phenylhept-1-ene (3a)



¹H NMR: $\delta = 0.86$ (t, J = 6.9 Hz, 3H), 1.23-1.43 (m, 6H), 2.33 (s, 3H), 2.45 (t, J = 6.9 Hz, 2H), 6.40 (s, 1H), 6.92-6.95 (m, 2H), 7.00-7.21 (m, 7H); ¹³C NMR: $\delta = 14.2$, 21.3, 22.6, 27.7, 31.5, 40.8, 125.7, 125.8, 127.7, 128.3, 128.8, 129.1, 136.2, 137.6, 138.2, 143.4; HRMS (CI⁺) Calcd for C₂₀H₂₄ (M⁺) 264.1878. Found 264.1884; UV-Vis (CHCl₃), λ /nm: 240, 269.

Preparation of trisubstituted alkenylborane 2b

Under an argon atmosphere, a $(CH_2Cl)_2$ solution (0.5 ml) of alkynyltriarylborate **1b** (79.5 mg, 0.20 mmol), Pd₂dba₃·CHCl₃ (5.1 mg, 2.5 µmol), and P(*o*-tol)₃ (3.7 mg, 6.0 µmol) was stirred for 30 minutes at room temperature. To the solution was added 4-bromotoluene (35.0 mg, 0.20 mmol) in $(CH_2Cl)_2$ (0.5 ml). After being stirred at reflux for 3 h, water was added. The aqueous later was extracted with AcOEt (3 times), washed with water (once), brine (once), dried over MgSO₄ and concentrated. The residue was purified by preparative thin-layer chromatography on silica gel (hexane) to afford the trisubstituted alkenylborane **2b** (76.0 mg, 0.18 mmol, 92% yield).

(Z)-3,3-Dimethyl-2-(4-methylphenyl)-1-phenyl -1-diphenylborylbut-1-ene (2b)



¹H NMR (CD₃CN): δ = 1.13 (s, 9H), 2.18 (s, 3H), 6.74-6.81 (m, 5H), 6.88 (d, J = 8.1 Hz, 2H), 6.99 (d, J = 8.1 Hz, 2H), 7.43-7.49 (m, 6H) 7.95 (d, J = 7.8 Hz, 4H); ¹³C NMR: δ = 21.1, 31.8, 37.8, 124.7, 127.1, 127.2, 127.5, 130.9, 131.1, 131.4, 134.4, 138.1, 139.0, 140.2, 141.2, 152.7; ¹¹B NMR: δ = 63.7; HRMS (CI⁺) Calcd for C₃₁H₃₁B (M⁺) 414.2519. Found 414.2526; UV-Vis (CHCl₃), λ /nm: 244, 275.

(Z)-2-(4-Methylphenyl)-1,4-diphenylbut-1-ene (3c)



¹H NMR: $\delta = 2.35$ (s, 3H), 2.68-2.79 (m, 4H), 6.37 (s, 1H), 6.90-6.92 (m, 2H), 7.01-7.30 (m, 12H); ¹³C NMR: $\delta = 21.3$, 34.6, 42.6, 125.7, 126.0, 126.4, 127.7, 128.2, 128.38, 128.45, 128.9, 129.2, 136.5, 137.4, 137.7, 141.8, 142.1; HRMS (CI⁺) Calcd for C₂₃H₂₂ (M⁺) 298.1721. Found 298.1720.

(Z)-1-(4-Methoxyphenyl)-2-(4-methylphenyl)hept-1-ene (3d)



¹H NMR: $\delta = 0.86$ (t, J = 6.9 Hz, 3H), 1.26-1.40 (m, 6H), 2.34 (s, 3H), 2.43 (t, J = 7.1 Hz, 2H), 3.71 (s, 3H), 6.33 (s, 1H), 6.63 (d, J = 9.0 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 7.04 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.1 Hz, 2H); ¹³C NMR: $\delta = 14.2$, 21.3, 22.6, 27.7, 31.5, 40.8, 55.1, 113.1, 125.1, 128.3, 129.1, 129.9, 130.2, 136.1, 138.4, 141.4, 157.6; HRMS (CI⁺) Calcd for C₂₁H₂₆O (M⁺) 294.1984. Found 294.1988; UV-Vis (CHCl₃), λ /nm: 240, 276.

(Z)-1,2-Diphenylhept-1-ene (3e)



¹H NMR: $\delta = 0.87$ (t, J = 7.1 Hz, 3H), 1.26-1.45 (m, 6H), 2.48 (t, J = 7.1 Hz, 2H), 6.42 (s, 1H), 6.89-6.92 (m, 2H), 7.03-7.32 (m, 8H); ¹³C NMR: $\delta = 14.2, 22.6, 27.6, 31.5, 40.7, 125.92, 125.95, 126.7, 127.7, 128.35, 128.43, 128.9, 137.4, 141.3, 143.4; HRMS (CI⁺) Calcd for C₁₉H₂₂ (M⁺) 250.1721. Found 250.1722.$

(Z)-2-(4-Methoxyphenyl)-1-phenylhept-1-ene (3f)



¹H NMR: $\delta = 0.87$ (t, J = 7.2 Hz, 3H), 1.26-1.41 (m, 6H), 2.45 (t, J = 6.9 Hz, 2H), 3.80 (s, 3H), 6.39 (s, 1H), 6.81-6.84 (m, 2H), 6.92-6.96 (m, 2H), 7.03-7.09 (m, 5H); ¹³C NMR: $\delta = 14.2$, 22.6, 27.7, 31.5, 40.7, 55.1, 113.7, 125.7, 125.8, 127.7, 128.8, 129.5, 133.3, 137.7, 143.0, 158.3; HRMS (CI⁺) Calcd for C₂₀H₂₄O (M⁺) 280.1827. Found 280.1823; UV-Vis (CHCl₃), λ /nm: 240, 274.

(Z)-2-(4-Trifluoromethylphenyl)-1-phenylhept-1-ene (3g)



¹H NMR: $\delta = 0.87$ (t, J = 7.1 Hz, 3H), 1.26-1.43 (m, 6H), 2.49 (t, J = 6.9 Hz, 2H), 6.51 (s, 1H), 6.84-6.93 (m, 2H), 7.06-7.14 (m, 3H), 7.26 (d, J = 7.8 Hz, 2H), 7.52 (d, J = 8.1 Hz, 2H); ¹³C NMR: $\delta = 14.2$, 22.6, 27.6, 31.4, 40.3, 124.1 (q, $J_{C-F} = 270.2$ Hz), 125.3 (q, $J_{C-F} = 3.7$ Hz), 126.4, 127.2, 127.9, 128.4 (q, $J_{C-F} = 24.1$ Hz), 128.91, 128.93, 136.8, 141.9, 145.2; HRMS (CI⁺) Calcd for C₂₀H₂₁F₃ (M⁺) 318.1595. Found 318.1597; UV-Vis (CHCl₃), λ /nm: 240.

(Z)-2-(4-Ethoxycarbonylphenyl)-1-phenylhept-1-ene (3h)



¹H NMR: $\delta = 0.86$ (t, J = 7.1 Hz, 3H), 1.27-1.43 (m, 9H), 2.49 (t, J = 7.1 Hz, 2H), 4.37 (q, J = 7.1 Hz, 2H), 6.49 (s, 1H), 6.88-6.91 (m, 2H), 7.05-7.12 (m, 3H), 7.22 (d, J = 8.7 Hz, 2H), 7.97 (d, J = 8.1 Hz, 2H); ¹³C NMR: $\delta = 14.1$, 14.4, 22.5, 27.6, 31.4, 40.3, 60.9, 126.2, 126.9, 127.8, 128.6, 128.7, 128.9, 129.6, 136.9, 142.4, 146.3, 166.4; HRMS (CI⁺) Calcd for C₂₂H₂₆O₂ (M⁺) 322.1933. Found 322.1925.

(Z)-1-Phenyl-2-(4-phthalimidophenyl)hept-1-ene (3i)



¹H NMR: $\delta = 0.89$ (t, J = 6.9 Hz, 3H), 1.26-1.47 (m, 6H), 2.50 (t, J = 7.4 Hz, 2H), 6.48 (s, 1H), 6.96-6.99 (m, 2H), 7.04-7.15 (m, 3H), 7.27-7.31 (m, 2H), 7.38-7.42 (m, 2H), 7.75-7.81 (m, 2H), 7.92-7.98 (m, 2H); ¹³C NMR: $\delta = 14.2, 22.5, 27.7, 31.5, 40.5, 123.6, 126.1, 126.7, 127.8, 128.9, 129.1, 130.2, 131.6, 134.3, 137.1, 141.0, 142.3, 167.1; HRMS (CI⁺) Calcd for C₂₇H₂₅NO₂ (M⁺) 395.1885. Found 395.1884; UV-Vis (CHCl₃), <math>\lambda$ /nm: 241.

(Z)-2-(4-Chlorophenyl)-1-phenylhept-1-ene (3j)



¹H NMR: $\delta = 0.87$ (t, J = 7.1 Hz, 3H), 1.25-1.39 (m, 6H), 2.45 (t, J = 7.4 Hz, 2H), 6.44 (s, 1H), 6.91 (m, 2H), 7.07-7.11 (m, 5H), 7.25 (m, 2H); ¹³C NMR: $\delta = 14.2$, 22.6, 27.6, 31.4, 40.4, 126.2, 126.6, 127.8, 128.6, 128.9, 129.9, 132.4, 137.1, 139.6, 142.0; HRMS (CI⁺) Calcd for C₁₉H₂₁Cl (M⁺) 284.1332. Found 284.1328.

(Z)-2-(3-Methylphenyl)-1-phenylhept-1-ene (3k)



¹H NMR: $\delta = 0.87$ (t, J = 7.1 Hz, 3H), 1.26-1.42 (m, 6H), 2.30 (s, 3H), 2.45 (t, J = 7.4 Hz, 2H), 6.39 (s, 1H), 6.90-7.08 (m, 8H), 7.17 (t, J = 7.5 Hz, 1H); ¹³C NMR: $\delta = 14.2$, 21.6, 22.6, 27.7, 31.5, 40.9, 125.5, 125.7, 125.9, 127.4, 127.7, 128.2, 128.8, 137.4, 137.9, 141.3, 143.6; HRMS (CI⁺) Calcd for C₂₀H₂₄ (M⁺) 264.1878. Found 264.1879.

(Z)-2-(4-Methylphenyl)-1-phenylbut-1-ene (3l)



¹H NMR: $\delta = 1.06$ (t, J = 7.5 Hz, 3H), 2.34 (s, 3H), 2.50 (q, J = 7.4 Hz, 2H), 6.40 (s, 1H), 6.91-6.96 (m, 2H), 7.01-7.11 (m, 7H); ¹³C NMR: $\delta = 13.0, 21.3, 33.6, 124.7, 125.8, 127.7, 128.3, 128.9, 129.1, 136.3, 137.6, 138.3, 144.8; HRMS (CI⁺) Calcd for C₁₇H₁₈ (M⁺) 222.1409. Found 222.1406.$

(Z)-4-Methyl-2-(4-methylphenyl)-1-phenylpent-1-ene (3m)



¹H NMR: $\delta = 0.90$ (d, J = 6.3 Hz, 6H), 1.56 (pseudo sept. J = 6.8 Hz, 1H), 2.33-2.36 (m, 5H), 6.38 (s, 1H), 6.93-6.95 (m, 2H), 7.02-7.11 (m, 7H); ¹³C NMR: $\delta = 21.3$, 22.4, 25.9, 50.5, 125.9, 127.0, 127.7, 128.4, 128.9, 129.1, 136.3, 137.6, 138.0, 142.3; HRMS (CI⁺) Calcd for C₁₉H₂₂ (M⁺) 250.1721. Found 250.1728.

(Z)-3-Methyl-2-(4-methylphenyl)-1-phenylbut-1-ene (3n)



¹H NMR: $\delta = 1.10$ (d, J = 6.9 Hz, 6H), 2.35 (s, 3H), 2.69 (sept., J = 6.8 Hz, 1H), 6.37 (s, 1H), 6.87 (dd, J = 8.8, 1.4 Hz, 2H), 7.01-7.12 (m, 7H); ¹³C NMR: $\delta = 21.3$, 21.9, 37.5, 123.9, 125.8, 127.6, 128.7, 128.9, 129.0, 136.1, 137.6, 138.0, 149.3; HRMS (CI⁺) Calcd for C₁₈H₂₀ (M⁺) 236.1565. Found 236.1562; UV-Vis (CHCl₃), λ /nm: 240, 260.

(Z)-1,2-Bis(4-methylphenyl)hept-1-ene (30)



¹H NMR: $\delta = 0.86$ (t, J = 7.2 Hz, 3H), 1.26-1.43 (m, 6H), 2.22 (s, 3H), 2.34 (s, 3H), 2.44 (t, J = 6.8 Hz, 2H), 6.36 (s, 1H), 6.82 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H); ¹³C NMR: $\delta = 14.2$, 21.1, 21.3, 22.6, 27.7, 31.5, 40.8, 125.6, 128.3, 128.4, 128.7, 129.1, 134.7, 135.4, 136.1, 138.4, 142.5; HRMS (CI⁺) Calcd for C₂₁H₂₆ (M⁺) 278.2034. Found 278.2035.

(Z)-1-(3-Methylphenyl)-2-(4-methylphenyl)hept-1-ene (3p)



¹H NMR: $\delta = 0.87$ (t, J = 6.9 Hz, 3H), 1.28-1.43 (m, 6H), 2.12 (s, 3H), 2.33 (s, 3H), 2.45 (t, J = 7.4 Hz, 2H), 6.36 (s, 1H), 6.68 (d, J = 7.5 Hz, 1H), 6.79 (s, 1H), 6.85 (d, J = 7.5 Hz, 1H), 6.94 (dd, J = 7.8, 7.2 Hz, 1H), 7.03 (d, J = 7.8 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H); ¹³C NMR: $\delta = 14.2$, 21.3, 21.4, 22.6, 27.7, 31.5, 40.8, 125.77, 125.82, 126.6, 127.5, 128.3, 129.0, 129.8, 136.1, 137.1, 137.5, 138.3, 143.2; HRMS (CI⁺) Calcd for

 $C_{21}H_{26}$ (M⁺) 278.2034. Found 278.2042.

(Z)-1-(4-Fluorophenyl)-2-(4-methylphenyl)hept-1-ene (3q)



¹H NMR: $\delta = 0.86$ (t, J = 7.1 Hz, 3H), 1.26-1.43 (m, 6H), 2.34 (s, 3H), 2.44 (t, J = 7.2 Hz, 2H), 6.35 (s, 1H), 6.72-6.80 (m, 2H), 6.85-6.91 (m, 2H), 7.01 (d, J = 7.8 Hz, 2H), 7.09 (d, J = 7.5 Hz, 2H); ¹³C NMR: $\delta =$ 14.2, 21.3, 22.6, 27.7, 31.5, 40.7, 114.5 (d, $J_{C-F} = 21.2$ Hz), 124.5, 128.3, 129.2, 130.3 (d, $J_{C-F} = 7.3$ Hz), 133.6 (d, $J_{C-F} = 2.9$ Hz), 136.4, 137.9, 143.2, 160.9 (d, $J_{C-F} = 243.2$ Hz); HRMS (CI⁺) Calcd for

C₂₀H₂₃F (M⁺) 282.1784. Found 282.1776; UV-Vis (CHCl₃), λ/nm: 239, 266.

(Z)-2-(4-Methylphenyl)-1-(2-thienyl)hept-1-ene (3r)



¹H NMR: $\delta = 0.87$ (t, J = 6.9 Hz, 3H), 1.28-1.45 (m, 6H), 2.36-2.42 (m, 5H), 6.58 (s, 1H), 6.73 (d, J = 3.3 Hz, 1H), 6.80 (dd, J = 5.1, 3.6 Hz, 1H), 6.92 (d, J = 5.1 Hz, 1H), 7.08 (d, J = 7.8 Hz, 2H), 7.21 (d, J = 7.5 Hz, 2H); ¹³C NMR: $\delta = 14.2$, 21.4, 22.6, 27.5, 31.5, 40.9, 119.5, 124.5, 125.8, 126.6, 128.4, 129.5, 137.0, 137.8, 141.1, 142.2; HRMS (CI⁺) Calcd for C₁₈H₂₂S (M⁺) 270.1442. Found 270.1445; UV-Vis (CHCl₃), λ /nm: 241, 290.

Preparation of (E)-Tamoxifen (5)

Under an argon atmosphere, a CH_2Cl_2 solution (0.5 ml) of alkynyltriarylborate **1e** (75.5 mg, 0.20 mmol), $Pd_2dba_3 \cdot CHCl_3$ (5.2 mg, 2.5 µmol), and $P(o-tol)_3$ (3.6 mg, 6.0 µmol) was stirred for 30 minutes at room temperature. To the solution was added bromobenzene (33.0 mg, 0.20 mmol) in CH_2Cl_2 (0.5 ml). After being stirred for 3 h, 4-(Me_2NCH_2CH_2O)C_6H_4I (**4**, 178 mg, 0.60 mmol) in CH_2Cl_2 (0.5 ml), powdered NaOH (78 mg, 1.8 mmol), and water (100 µl) were added. After 24 h, water was added to the reaction mixture. The aqueous later was extracted with CH_2Cl_2 (3 times),

washed with water (once), brine (once), dried over Na₂SO₄ and concentrated. The residue was purified by preparative thin-layer chromatography on silica gel (benzene:AcOEt:NEt₃ = 100:40:1) to afford Tamoxifen (**5**, 58.4 mg, 0.16 mmol, 79% yield, E/Z = 97/3). The spectral data was identical to that reported.⁵

Preparation of alkenyl iodide 6

Under an argon atmosphere, a CH₂Cl₂ solution (0.5 ml) of alkynyltriarylborate **1e** (75.9 mg, 0.20 mmol), Pd₂dba₃·CHCl₃ (5.2 mg, 2.5 µmol), and P(o-tol)₃ (3.6 mg, 6.0 µmol) was stirred for 30 minutes at room temperature. To the solution was added bromobenzene (33.2 mg, 0.20 mmol) in CH₂Cl₂ (0.5 ml). After being stirred for 3 h, aqueous ammonia (1 ml) was added. The aqueous later was extracted with Et₂O (3 times), washed with water (once), brine (once), dried over Na₂SO₄ and concentrated. The residue was dissolved in acetone and treated with NIS (225 mg, 1.0 mmol) at 0 °C for 1 h. The reaction mixture was purified by preparative thin-layer chromatography on silica gel (hexane), followed by GPC to afford alkenyl iodide **6** (39.2 mg, 0.12 mmol, 59% yield, E/Z = 96/4). The spectral data was identical to that reported.⁶

Preparation of ketone 7

Under an argon atmosphere, a CH_2Cl_2 solution (0.5 ml) of alkynyltriarylborate **1e** (75.9 mg, 0.20 mmol), $Pd_2dba_3 \cdot CHCl_3$ (5.2 mg, 2.5 µmol), and $P(o-tol)_3$ (3.6 mg, 6.0 µmol) was stirred for 30 minutes at room temperature. To the solution was added bromobenzene (33.2 mg, 0.20 mmol) in CH_2Cl_2 (0.5 ml). After being stirred for 3 h, trimethylamine-*N*-oxide (75.1 mg, 1.0 mmol) was added. After 3 h, water was added to the reaction mixture. The aqueous later was extracted with AcOEt (3 times), washed with water (once), brine (once), dried over MgSO₄ and concentrated. The residue was purified by preparative thin-layer chromatography on silica gel (hexane:AcOEt = 50:1) to afford ketone **7** (40.8 mg, 0.18 mmol, 91% yield). The spectral data was identical to that reported.⁷

Preparation of diboranyl compound 8

Under an argon atmosphere, a $(CH_2Cl)_2$ solution (0.5 ml) of alkynyltriarylborate **1b** (79.5 mg, 0.20 mmol), Pd₂dba₃·CHCl₃ (2.5 mg, 1.2 µmol), and P(*o*-tol)₃ (2.9 mg, 3.0 µmol) was stirred for 30 minutes at room temperature. To the solution was added 1,4-dibromobenzene (23.7 mg, 0.10 mmol) in $(CH_2Cl)_2$ (0.5 ml). After being stirred at reflux for 1 h, water was added. The aqueous later was extracted with AcOEt (3 times), washed with water (once), brine (once), dried over MgSO₄ and concentrated. The residue was purified by preparative thin-layer chromatography on silica gel (hexane:AcOEt = 10:1) to afford the diboranyl compound **8** (44.9 mg, 0.062 mmol, 62% yield).

1,4-Bis[(Z)-1-*tert*-butyl-2-phenyl-2-(diphenylboryl)ethenyl]benzene (8)



¹H NMR: $\delta = 0.98$ (s, 18H), 6.71-6.76 (m, 14H), 7.40-7.48 (m, 12H), 7.91 (d, *J* = 6.8 Hz, 8H); ¹³C NMR: $\delta = 31.7$, 37.6, 124.6, 127.0, 127.5, 129.5, 130.9, 131.3, 138.1, 139.1, 140.5, 141.3, 143.9, 153.3; ¹¹B NMR: $\delta = 59.6$; HRMS (CI⁺) Calcd for C₅₄H₅₂B₂ (M⁺) 722.4255. Found 722.4252; UV-Vis (CHCl₃), λ /nm: 248.

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