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Copper(I)-Catalysed Stereoselective Debromoborylation of Aliphatic 1,1-Dibromo-1-Alkenes with Bis(pinacolato)diboron

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1. Instrumentation and Chemicals

Materials were obtained from commercial suppliers and purified by standards procedures unless otherwise noted. Solvents (Tetrahydrofuran, dehydrated –super–, 41001-05, Kanto Chemical Co., Inc.) for reactions were purchased from commercial suppliers, degassed via three freeze-pump-thaw cycles, and further dried over molecular sieves (MS 4Å). NMR spectra were recorded on JEOL JNM-ECX400P and JNM-ECS400 spectrometers (¹H: 392 or 396 MHz, ¹³C: 99 MHz and ¹¹B: 127 MHz). Tetramethylsilane (¹H) CDCl₃ (¹³C) and BF3·OEt₂ (¹¹B) were employed as external standards, respectively. Multiplicity was recorded as follows: s = singlet, brs = broad singlet, d = doublet, t= triplet, q= quartet, m = multiplet. CuCl (ReagentPlus® grade, 224332-25G, \geq 99%) was purchased from Sigma-Aldrich Co., and used as received. Mesitylene was used as an internal standard to determine NMR yields. GLC analyses were conducted with a Shimadzu GC-2014 or GC-2025 equipped with ULBON HR-1 glass capillary column (Shinwa Chemical Industries) and a FID detector. High-resolution mass spectra were recorded at the Global Facility Center, Hokkaido

University.

2. Substrate Preparations

All 1,1-dibromo-1-alkenes were synthesized from corresponding aldehydes through Wittig reaction by using PPh₃ and CBr₄.¹ If aldehydes were not commercially available materials, the aldehydes were synthesized from the corresponding alcohols by Swern oxidation.² The synthesized 1,1dibromo-1-alkenes were subjected to purification by Kugelrohr distillation prior to use. The 1,1dibromo-1-alkenes (**1c**, **1d**, **1k**, **1l**) were unknown compounds and the other 1,1-dibromo-1-alkenes (**1a**^{3a}, **1b**^{3b}, **1e**^{3c}, **1f**^{3d}, **1g**^{3e}, **1h**^{3f}, **1i**^{3g}, **1j**^{3f}, **1m**^{3h}, **1n**³ⁱ) were known compounds.

3. Characterizations of 1,1-Dibromo-1-Alkenes Substrates

1-(4,4-Dibromobut-3-en-1-yl)-3-(trifluoromethyl)benzene (1c).



The product **1c** was obtained from corresponding alcohol in 98% yield (two steps, 1.72 g, 4.8 mmol) as a colorless oil.

¹H NMR (392 MHz, CDCl₃, δ): 2.43 (dd, *J* = 15.1, 7.6 Hz, 2H), 2.79 (t, *J* = 7.6 Hz, 2H), 6.40 (t, *J* = 7.4 Hz, 1H), 7.34–7.51 (m, 4H). ¹³C NMR (99 MHz, CDCl₃, δ): 33.6 (CH₂), 34.3 (CH₂), 90.2 (C), 123.2 (d, *J*_{C-F} = 3.8 Hz, CH), 124.2 (d, *J*_{C-F} = 272.8 Hz, C), 125.1 (d, *J*_{C-F} = 3.8 Hz, CH), 129.0 (CH), 130.8 (q, *J*_{C-F} = 32.4 Hz, C), 131.8 (CH), 136.8 (CH), 141.3 (C). HRMS-EI (*m*/*z*): [M]⁺ calcd for C₁₁H₉Br₂F₃, 355.90231; found, 355.90137.

1-Bromo-4-(4,4-dibromobut-3-en-1-yl)benzene (1d).



The product **1d** was obtained from corresponding alcohol in 99% yield (two steps, 3.42 g, 9.3 mmol) as a colorless oil.

¹H NMR (392 MHz, CDCl₃, δ): 2.39 (q, J = 7.7 Hz, 2H), 2.69 (t, J = 7.6 Hz, 2H), 6.38 (t, J = 7.3

Hz, 1H), 7.06 (d, J = 7.8 Hz, 2H), 7.38–7.47 (m, 2H). ¹³C NMR (99 MHz, CDCl₃, δ): 33.2 (*C*H₂), 34.4 (*C*H₂), 89.9 (*C*), 120.0 (*C*), 130.1 (*C*H), 131.6 (*C*H), 137.1 (*C*H), 139.4 (*C*). HRMS-EI (*m/z*): [M]⁺ calcd for C₁₀H₉Br₃, 365.82544; found, 365.82554.

1,1-Dibromo-7-chlorohept-1-ene (1k).



The product **1k** was obtained from corresponding alcohol in 65% yield (two steps, 2.35 g, 8.1 mmol) as a colorless oil.

¹H NMR (392 MHz, CDCl₃, δ): 1.41–1.53 (m, 4H), 1.74–1.84 (m, 2H), 2.07–2.17 (m, 2H), 3.54 (t, J = 6.5 Hz, 2H), 6.39 (t, J = 6.9 Hz, 1H). ¹³C NMR (99 MHz, CDCl₃, δ): 26.3 (*C*H₂), 27.1 (*C*H₂), 32.3 (*C*H₂), 32.8 (*C*H₂), 44.8 (*C*H₂), 89.0 (*C*), 138.3 (*C*H). HRMS-EI (*m*/*z*): [M]⁺ calcd for C₇H₁₁Br₂Cl, 287.89160; found, 287.89205.

1,1-Dibromoundeca-1,10-diene (11).



The product **11** was obtained from corresponding alcohol in 85% yield (two steps, 2.86 g, 9.2 mmol) as a colorless oil.

¹H NMR (392 MHz, CDCl₃, δ): 1.25–1.46 (m, 10H), 2.00–2.13 (m, 4H), 4.93 (ddt, *J* = 9.8, 2.4, 0.8 Hz, 1H), 5.00 (dq, *J* = 17.6, 2.0 Hz, 1H), 5.81 (ddt, *J* = 16.9, 13.3, 6.7 Hz, 1H), 6.38 (t, *J* = 7.3 Hz, 1H). ¹³C NMR (99 MHz, CDCl₃, δ): 27.8 (*C*H₂), 28.8 (*C*H₂), 29.0 (*C*H₂), 29.2 (*C*H₂), 33.0 (*C*H₂), 33.8 (*C*H₂), 88.4 (*C*), 114.2 (*C*H₂), 138.9 (*C*H), 139.1 (*C*H). HRMS-EI (*m/z*): [M]⁺ calcd for C₁₁H₁₈Br₂, 307.97753; found, 307.97750.

4. General Debromoborylation Procedures

Copper chloride (1.3 mg, 0.013 mmol), Xantphos (7.3 mg, 0.013 mmol), bis(pinacolato)diboron (76.2 mg, 0.30 mmol) were placed in an oven-dried reaction vial. And then, the vial was transferred to the glove box and NaOMe (27.0 mg, 0.50 mmol) was added to the vial under argon atmosphere. After the vial was sealed with a screw cap containing a Teflon-coated rubber septum, the vial was removed from the glove box and connected to a vacuum/nitrogen manifold through a needle. After dry THF (1 mL) was added to the reaction mixture, **1a** (69.1 mg, 0.24 mmol) was added dropwise to the reaction mixture at 30°C. After the reaction was complete, the mixture was passed through a short silica gel column eluting with Et_2O . The crude material was purified by flash chromatography (SiO₂, hexane/ethyl acetate, 20:1) to give the corresponding debromoborylation product (*Z*)-**3a** (46.1 mg, 0.14 mmol, 55%) as a slightly yellow oil.

5. Characterizations of Debromoborylation Products

(Z)-2-(1-Bromo-4-phenylbut-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(Z)-3a].



The reaction was conducted with 69.1 mg (0.24 mmol) of **1a**. The product (*Z*)-**3a** was obtained in 55% yield (46.1 mg, 0.14 mmol) as a slightly yellow oil by flash chromatography (SiO₂, hexane/ethyl acetate, 20:1).

¹H NMR (392 MHz, CDCl₃, δ): 1.30 (s, 12H), 2.58–2.66 (m, 2H), 2.77 (t, *J* = 7.8 Hz, 2H), 6.91 (t, *J* = 6.7 Hz, 1H), 7.17–7.24 (m, 3H), 7.27–7.33 (m, 2H). ¹³C NMR (99 MHz, CDCl₃, δ): 24.6 (*C*H₃), 33.7 (*C*H₂), 34.0 (*C*H₂), 84.6 (*C*), 126.0 (*C*H), 128.2 (*C*H), 128.3 (*C*H), 141.0 (*C*), 148.0 (*C*H). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation.^{4,5} ¹¹B NMR (127 MHz, CDCl₃, δ): 28.0. HRMS-EI (*m*/*z*): [M]⁺ calcd for C₁₆H₂₂BBrO₂, 335.09325; found, 335.09292.

(*Z*)-2-[1-Bromo-4-(4-methoxyphenyl)but-1-en-1-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*Z*)-3b].



The reaction was conducted with 80.0 mg (0.25 mmol) of **1b**. The product (*Z*)-**3b** was obtained in 52% yield (47.2 mg, 0.13 mmol) as a colorless oil by flash chromatography (SiO₂, hexane/ethyl acetate, 20:1).

¹H NMR (392 MHz, CDCl₃, δ): 1.29 (s, 12H), 2.54–2.63 (m, 2H), 2.71 (dd, *J* = 9.4, 6.3 Hz, 2H), 3.79 (s, 3H), 6.84 (dd, *J* = 6.7, 2.0 Hz, 2H), 6.90 (t, *J* = 6.5 Hz, 1H), 7.13 (dt, *J* = 9.3, 2.6 Hz, 2H). ¹³C NMR (99 MHz, CDCl₃, δ): 24.7 (*C*H₃), 32.8 (*C*H₂), 34.4 (*C*H₂), 55.2 (*C*H₃), 84.6 (*C*), 113.8 (*C*H), 129.2 (*C*H), 133.2 (*C*), 148.2 (*C*H), 157.9 (*C*). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation.^{4,5} ¹¹B NMR (127 MHz, CDCl₃, δ): 27.9. HRMS-EI (*m*/*z*): [M]⁺ calcd for C₁₇H₂₄BBrO₃, 365.10382; found, 365.10351.

(*Z*)-2-{1-Bromo-4-[3-(trifluoromethyl)phenyl]but-1-en-1-yl}-4,4,5,5-tetramethyl-1,3,2dioxaborolane [(*Z*)-3c].



The reaction was conducted with 85.0 mg (0.24 mmol) of **1c**. The product (*Z*)-**3c** was obtained in 58% yield (55.3 mg, 0.14 mmol) as a colorless oil by flash chromatography (SiO₂, hexane/ethyl acetate, 25:1).

¹H NMR (392 MHz, CDCl₃, δ): 1.30 (s, 12H), 2.59–2.67 (m, 2H), 2.83 (dd, *J* = 9.0, 6.7 Hz, 2H), 6.87 (t, *J* = 6.7 Hz, 1H), 7.38–7.49 (m, 4H). ¹³C NMR (99 MHz, CDCl₃, δ): 24.6 (*C*H₃), 33.5 (*C*H₂), 33.7 (*C*H₂), 84.8 (*C*), 123.0 (d, *J*_{C-F} = 3.8 Hz, *C*H), 124.2 (d, *J*_{C-F} = 273.8 Hz, *C*), 125.1 (d, *J*_{C-F} = 3.8 Hz, *C*H), 128.8 (*C*H), 130.6 (d, *J*_{C-F} = 32.1 Hz, *C*), 131.7 (*C*H), 141.9 (*C*), 147.1 (*C*H). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation.^{4,5} ¹¹B NMR (127 MHz, CDCl₃, δ): 28.0. HRMS-EI (*m*/*z*): [M]⁺ calcd for C₁₇H₂₁BBrF₃O₂, 403.08064; found, 403.07908. (*Z*)-2-[1-Bromo-4-(4-bromophenyl)but-1-en-1-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*Z*)-3d].



The reaction was conducted with 88.5 mg (0.24 mmol) of **1d**. The product (*Z*)-**3d** was obtained in 62% yield (61.3 mg, 0.15 mmol) as a white solid (m.p. = 64–65°C) by flash chromatography (SiO₂, hexane/ethyl acetate, 20:1).

¹H NMR (392 MHz, CDCl₃, δ): 1.30 (s, 12H), 2.55–2.63 (m, 2H), 2.68–2.76 (m, 2H), 6.86 (t, J = 6.9 Hz, 1H), 7.09 (d, J = 8.2 Hz, 2H), 7.38–7.43 (m, 2H). ¹³C NMR (99 MHz, CDCl₃, δ): 24.7 (*C*H₃), 33.1 (*C*H₂), 33.8 (*C*H₂), 84.8 (*C*), 119.8 (*C*), 130.1 (*C*H), 131.4 (*C*H), 140.0 (*C*), 147.5 (*C*H). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation.^{4,5} ¹¹B NMR (127 MHz, CDCl₃, δ): 27.9. HRMS-EI (m/z): [M]⁺ calcd for C₁₆H₂₁BBr₂O₂, 413.00377; found, 413.00367.

(Z)-2-(1-Bromo-3-phenylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(Z)-3e].



The reaction was conducted with 70.5 mg (0.26 mmol) of **1e**. The product (*Z*)-**3e** was obtained in 55% yield (44.6 mg, 0.14 mmol) as a yellow oil by flash chromatography (SiO₂, hexane/ethyl acetate, 25:1).

¹H NMR (396 MHz, CDCl₃, δ): 1.29 (s, 12H), 3.66 (d, *J* = 6.7 Hz, 2H), 6.99 (t, *J* = 6.9 Hz, 1H), 7.20–7.25 (m, 3H), 7.27–7.33 (m, 2H). ¹³C NMR (99 MHz, CDCl₃, δ): 24.6 (*C*H₃), 38.7 (*C*H₂), 84.7 (*C*), 126.4 (*C*H), 128.5 (*C*H), 128.6 (*C*H), 138.2 (*C*), 147.3 (*C*H). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation.^{4,5} ¹¹B NMR (127 MHz, CDCl₃, δ): 28.1. HRMS-EI (*m*/*z*): [M]⁺ calcd for C₁₅H₂₀BBrO₂, 321.07760; found, 321.07687. (*Z*)-2-[1-Bromo-4-(5-methylfuran-2-yl)but-1-en-1-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*Z*)-3f].



The reaction was conducted with 75.8 mg (0.26 mmol) of **1f**. The product (*Z*)-**3f** was obtained in 62% yield (55.0 mg, 0.16 mmol) as a slightly yellow oil by flash chromatography (SiO₂, hexane/ethyl acetate, 25:1).

¹H NMR (396 MHz, CDCl₃, δ): 1.30 (s, 12H), 2.25 (s, 3H), 2.59–2.66 (m, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 5.85 (dd, *J* = 2.9, 1.0 Hz, 1H), 5.90 (d, *J* = 2.7 Hz, 1H), 6.88 (t, *J* = 6.3 Hz, 1H). ¹³C NMR (99 MHz, CDCl₃, δ): 13.5 (CH₃), 24.7 (CH₃), 26.1 (CH₂), 30.9 (CH₂), 84.7 (C), 105.7 (CH), 105.8 (CH), 147.8 (CH), 150.5 (C), 152.9 (C). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation.^{4,5} ¹¹B NMR (127 MHz, CDCl₃, δ): 27.9. HRMS-EI (*m*/*z*): [M]⁺ calcd for C₁₅H₂₂BBrO₃, 339.08817; found, 339.08676.

(Z)-2-(1-Bromopent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(Z)-3g].



The reaction was conducted with 56.6 mg (0.25 mmol) of **1g**. The product (*Z*)-**3g** was obtained in 59% yield (40.0 mg, 0.15 mmol) as a slightly yellow oil by flash chromatography (SiO₂, hexane/ethyl acetate, 25:1).

¹H NMR (392 MHz, CDCl₃, δ): 0.96 (t, *J* = 7.4 Hz, 3H), 1.30 (s, 12H), 1.49 (sxt, *J* = 7.4 Hz, 2H), 2.28 (dd, *J* = 14.5, 7.4 Hz, 2H), 6.85 (t, *J* = 6.7 Hz, 1H). ¹³C NMR (99 MHz, CDCl₃, δ): 13.9 (*C*H₃), 21.0 (*C*H₂), 24.7 (*C*H₃), 34.4 (*C*H₂), 84.6 (*C*), 149.3 (*C*H). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation.^{4,5} ¹¹B NMR (127 MHz, CDCl₃, δ): 28.0. HRMS-EI (*m/z*): [M]⁺ calcd for C₁₁H₂₀BBrO₂, 273.07760; found, 273.07773. (Z)-2-(1-Bromonon-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(Z)-3h].



The reaction was conducted with 68.5 mg (0.24 mmol) of **1h**. The product (*Z*)-**3h** was obtained in 62% yield (49.1 mg, 0.15 mmol) as a slightly yellow oil by flash chromatography (SiO₂, hexane/ethyl acetate, 25:1).

¹H NMR (392 MHz, CDCl₃, δ): 0.88 (t, *J* = 6.9 Hz, 3H), 1.24–1.35 (m, 20H), 1.40–1.50 (m, 2H), 2.30 (q, *J* = 7.1 Hz, 2H), 6.84 (t, *J* = 6.9 Hz, 1H). ¹³C NMR (99 MHz, CDCl₃, δ): 14.0 (CH₃), 22.6 (CH₂), 24.7 (CH₃), 27.7 (CH₂), 29.0 (CH₂), 29.2 (CH₂), 31.7 (CH₂), 32.4 (CH₂), 84.5 (C), 149.5 (CH). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation.^{4,5 11}B NMR (127 MHz, CDCl₃, δ): 28.0. HRMS-EI (*m*/*z*): [M]⁺ calcd for C₁₅H₂₈BBrO₂, 329.14020; found, 329.14013.

(Z)-2-(1-Bromo-4-cyclohexylbut-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(Z)-3i].



The reaction was conducted with 75.5 mg (0.26 mmol) of **1i**. The product (*Z*)-**3i** was obtained in 57% yield (49.6 mg, 0.14 mmol) as a slightly yellow oil by flash chromatography (SiO₂, hexane/ethyl acetate, 25:1).

¹H NMR (392 MHz, CDCl₃, δ): 0.82–0.95 (m, 2H), 1.17–1.37 (m, 18H), 1.60–1.78 (m, 5H), 2.30 (dd, *J* = 15.9, 6.9 Hz, 2H), 6.83 (t, *J* = 6.7 Hz, 1H). ¹³C NMR (99 MHz, CDCl₃, δ): 24.7 (*C*H₃), 26.2 (*C*H₂), 26.6 (*C*H₂), 29.9 (*C*H₂), 33.1 (*C*H₂), 35.2 (*C*H₂), 37.2 (*C*H), 84.6 (*C*), 149.8 (*C*H). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation.^{4,5} ¹¹B NMR (127 MHz, CDCl₃, δ): 28.0. HRMS-EI (*m*/*z*): [M]⁺ calcd for C₁₆H₂₈BBrO₂, 341.14020; found, 341.14006.

(Z)-2-(1-Bromo-3-cyclohexylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(Z)-3j].



The reaction was conducted with 69.5 mg (0.25 mmol) of **1j**. The product (*Z*)-**3j** was obtained in 58% yield (46.6 mg, 0.14 mmol) as a pink oil by flash chromatography (SiO₂, hexane/ethyl acetate, 25:1).

¹H NMR (392 MHz, CDCl₃, δ): 0.92–1.04 (m, 2H), 1.12–1.25 (m, 3H), 1.30 (s, 12H), 1.40–1.52 (m, 1H), 1.58–1.78 (m, 5H), 2.20 (t, *J* = 7.1 Hz, 2H), 6.86 (t, *J* = 6.9 Hz, 1H). ¹³C NMR (99 MHz, CDCl₃, δ): 24.7 (*C*H₃), 26.2 (*C*H₂), 26.3 (*C*H₂), 33.1 (*C*H₂), 37.1 (*C*H), 40.0 (*C*H₂), 84.6 (*C*), 148.3 (*C*H). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation.^{4,5 11}B NMR (127 MHz, CDCl₃, δ): 28.0. HRMS-EI (*m*/*z*): [M]⁺ calcd for C₁₅H₂₆BBrO₂, 327.12455; found, 327.12477.

(Z)-2-(1-Bromo-7-chlorohept-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(Z)-3k].



The reaction was conducted with 70.0 mg (0.24 mmol) of **1k**. The product (*Z*)-**3k** was obtained in 57% yield (46.4 mg, 0.14 mmol) as a slightly yellow oil by flash chromatography (SiO₂, hexane/ethyl acetate, 25:1).

¹H NMR (396 MHz, CDCl₃, δ): 1.30 (s, 12H), 1.45–1.52 (m, 4H), 1.75–1.85 (m, 2H), 2.29–2.36 (m, 2H), 3.54 (t, *J* = 6.7 Hz, 2H), 6.83 (t, *J* = 6.9 Hz, 1H). ¹³C NMR (99 MHz, CDCl₃, δ): 24.7 (*C*H₃), 26.5 (*C*H₂), 26.9 (*C*H₂), 32.1 (*C*H₂), 32.3 (*C*H₂), 44.9 (*C*H₂), 84.6 (*C*), 148.7 (*C*H). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation.^{4,5} ¹¹B NMR (127 MHz, CDCl₃, δ): 28.0. HRMS-EI (*m*/*z*): [M]⁺ calcd for C₁₃H₂₃BBrClO₂, 335.06993; found, 335.07008.

(Z)-2-(1-Bromoundeca-1,10-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(Z)-3l].



The reaction was conducted with 79.8 mg (0.26 mmol) of **11**. The product (*Z*)-**31** was obtained in 54% yield (49.1 mg, 0.14 mmol) as a salmon pink oil by flash chromatography (SiO₂, hexane/ethyl acetate, 25:1).

¹H NMR (392 MHz, CDCl₃, δ): 1.28–1.49 (m, 22H), 2.04 (dd, *J* = 13.7, 7.1 Hz, 2H), 2.30 (q, *J* = 7.2 Hz, 2H), 4.91–4.96 (m, 1H), 4.96–5.03 (m, 1H), 5.81 (ddt, *J* = 17.2, 13.7, 6.7 Hz, 1H), 6.84 (t, *J* = 6.7 Hz, 1H). ¹³C NMR (99 MHz, CDCl₃, δ): 24.7 (CH₃), 27.7 (CH₂), 28.8 (CH₂), 29.0 (CH₂), 29.2 (CH₂), 32.4 (CH₂), 33.8 (CH₂), 84.6 (C), 114.1 (CH₂), 139.1 (CH), 149.5 (CH). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation.^{4,5 11}B NMR (127 MHz, CDCl₃, δ): 28.0. HRMS-EI (*m*/*z*): [M]⁺ calcd for C₁₇H₃₀BBrO₂, 355.15585; found, 355.15485.

Tert-butyl-(*Z*)-4-[3-bromo-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl]piperidine-1carboxylate [(*Z*)-3m].



The reaction was conducted with 95.0 mg (0.25 mmol) of **1m**. The product (*Z*)-**3m** was obtained in 51% yield (54.0 mg, 0.13 mmol) as a white solid (m.p. = $82-83^{\circ}$ C) by flash chromatography (SiO₂, hexane/ethyl acetate, 10:1).

¹H NMR (392 MHz, CDCl₃, δ): 1.12–1.25 (m, 2H), 1.30 (s, 12H), 1.45 (s, 9H), 1.56–1.73 (m, 3H), 2.28 (t, *J* = 6.9 Hz, 2H), 2.58–2.78 (m, 2H), 4.08 (brs, 2H), 6.85 (t, *J* = 6.9 Hz, 1H). ¹³C NMR (99 MHz, CDCl₃, δ): 24.6 (*C*H₃), 28.4 (*C*H₃), 31.8 (*C*H₂), 35.3 (*C*H), 38.9 (*C*H₂), 43.4 (*C*H₂), 44.1 (*C*H₂), 79.2 (*C*), 84.6 (*C*), 146.7 (*C*H), 154.7 (*C*). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation.^{4,5} ¹¹B NMR (127 MHz, CDCl₃, δ): 28.0. HRMS-EI (*m*/*z*): [M]⁺ calcd for C₁₉H₃₃BBrNO₄, 428.17223; found, 427.17182. (*Z*)-2-[4-Bromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl]isoindoline-1,3dione [(*Z*)-3n].



The reaction was conducted with 92.0 mg (0.26 mmol) of **1n**. The product (*Z*)-**3n** was obtained in 50% yield (51.1 mg, 0.13 mmol) as a white solid (m.p. = $126-127^{\circ}$ C) by flash chromatography (SiO₂, hexane/ethyl acetate, 10:1).

¹H NMR (392 MHz, CDCl₃, δ): 1.29 (s, 12H), 2.71 (dd, *J* = 14.3, 7.3 Hz, 2H), 3.84 (t, *J* = 7.1 Hz, 2H), 6.88 (t, *J* = 6.7 Hz, 1H), 7.69–7.75 (m, 2H), 7.81–7.88 (m, 2H). ¹³C NMR (99 MHz, CDCl₃, δ): 24.6 (*C*H₃), 31.6 (*C*H₂), 35.7 (*C*H₂), 84.7 (*C*), 123.2 (*C*H), 132.0 (*C*), 133.9 (*C*H), 144.2 (*C*H), 168.1 (*C*). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation.^{4,5} ¹¹B NMR (127 MHz, CDCl₃, δ): 27.9. HRMS-EI (*m/z*): [M]⁺ calcd for C₁₈H₂₁BBrNO₄, 404.07833; found, 404.07791.

6. Information on Single Crystal X-ray Diffraction Analysis

CCDC 1835168 contains the supplementary crystallographic data for compound (Z)-**3n**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

7. References

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