Stereoselective Cross-coupling Reaction of 1,1-Diboryl-1-alkenes with Electrophiles: A Highly Stereocontrolled Approach to 1,1,2-Triaryl-1-alkenes

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General:

Melting points were determined using a Yanagimoto Micro Melting Point Apparatus. ¹H NMR spectra were measured on a Varian Mercury 200 (200 MHz) and 400 (400 MHz) spectrometers. The chemical shifts of ¹H NMR are expressed in parts per million downfield relative to the internal tetramethylsilane (δ = 0 ppm) or chloroform (δ = 7.26 ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. ¹³C NMR spectra were measured on a Varian Mercury 400 (100 MHz), and JEOL EX-270 (67.8 MHz) spectrometers with tetramethylsilane as an internal standard (δ = 0 ppm) or chloroform-*d* (δ = 77.0 ppm). ¹⁹F NMR spectra were measured on a Varian Mercury 200 (188 MHz) spectrometer with CFCl₃ as an internal standard (δ = 0 ppm). Chemical shift values are given in parts per million downfield relative to the internal standard. Infrared spectra (IR) were recorded on a Shimadzu FTIR-8400 spectrometer. GC-MS analyses were performed with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. Elemental analyses were carried out with a YANAKO MT2 CHN CORDER machine at Elemental Analysis Center of Kyoto University. TLC analyses were performed by means of Merck Kieselgel 60 F₂₅₄ and column chromatography was carried out using Merck Kieselgel 60 (230-400 mesh). Preparative HPLC was carried out with a Japan Analytical Industry Co., Ltd, LC-908 chromatograph using a JAIGEL-1H and -2H GPC columns. Tetrahydrofuran was distilled from benzophenone and sodium before use under an argon atmosphere. All reactions were carried out under an argon atmosphere.

Preparation of 1,1-diboryl-1-alkenes 2:

2-Aryl-1,1-diboryl-1-alkenes were prepared by *gem*-diborylation of 2-aryl-1,1-dibromo-1-alkenes with bis(pinacolato)diboron (method A) or ketone addition of tris(pinacolato)borylmethyl lithium (method B) as reported in the following references.

Method A: Hata, T.; Kitagawa, H.; Masai, H.; Kurahashi, T.; Shimizu, M.; Hiyama, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 790-792; Kurahashi, T.; Hata, T.; Masai, H.; Kitagawa, H.; Shimizu, M.; Hiyama, T. *Tetrahedron* **2002**, *58*, 6381-6395.

Method B: Matteson, D. S.; Tripathy, P. B. *J. Organomet. Chem.* **1974**, *69*, 53-62.

1,1-Bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-2-phenyl-1-butene (2a)

Prepared by method A.

Yield: 72%, colorless solid.

Mp. 80.6 °C (hexane).

TLC: R_f 0.33(hexane/ethyl acetate = 10 : 1).

¹H NMR (400 MHz, CDCl₃, δ): 0.92 (t, *J* = 7.2 Hz, 3H), 1.03 (s, 12H), 1.28 (s, 12H), 2.71 (q, *J* = 7.2 Hz, 2H), 7.21-7.25 (m, 5H).

¹³C NMR (67.8 MHz, CDCl₃, δ): 13.8, 24.4, 24.8, 32.1, 82.8, 82.9, 126.9, 127.6, 144.3, 170.8.

IR (KBr): 2976, 2932, 1595, 1354, 1323, 1144, 854, 775, 706 cm⁻¹.

EIMS (70 eV) *m/z*: 386 (3, M⁺+2), 385 (22, M⁺+1), 384 (87, M⁺), 327 (100).

Anal. Calcd for C₂₂H₃₄B₂O₄: C, 68.79; H, 8.92. Found: C, 68.73; H, 8.62.

1,1-Bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-2-(4''-methylphenyl)-1-butene (2b)

Prepared by method A.

Yield: 67%, colorless solid.

Mp. 104.0 °C (hexane).

TLC: R_f 0.38 (hexane/ethyl acetate = 10 : 1).

¹H NMR (400 MHz, CDCl₃, δ): 0.91 (t, *J* = 7.6 Hz, 3H), 1.06 (s, 12H), 1.27 (s, 12H), 2.31 (q, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H).

¹³C NMR (67.8 MHz, CDCl₃, δ): 14.0, 21.2, 24.5, 24.9, 32.0, 82.7, 82.8, 127.4, 128.1, 136.4, 142.2, 170.6.

IR (KBr): 2978, 2923, 1599, 1508, 1464, 1321, 1292, 1142, 854, 824 cm⁻¹.

EIMS (70 eV) *m/z*: 400 (3.3, M⁺+2), 399 (22, M⁺+1), 398 (83, M⁺), 84 (100).

Anal. Calcd for C₂₃H₃₆B₂O₄: C, 69.38; H, 9.11. Found: C, 69.10; H, 8.92.

1,1-Bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-2-(4''-trifluoromethylphenyl)-1-butene (2c)

Prepared by method A.

Yield: 88%, colorless solid.

Mp. 138.5 °C (hexane).

TLC: R_f 0.43 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 0.92 (t, J = 7.6 Hz, 3H), 1.01 (s, 12H), 1.29 (s, 12H), 2.70 (q, J = 7.6 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 7.53 (d, J = 7.8 Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 13.6, 24.3, 24.8, 32.1, 83.1, 124.3 (q, J = 270.0 Hz), 124.6 (q, J = 3.8 Hz), 128.0, 129.0 (q, J = 32.1 Hz), 148.8, 168.9.

^{19}F NMR (200 MHz, CDCl_3 , δ): -62.9.

IR (KBr): 2980, 2341, 1605, 1323, 1298, 1163, 1146, 1121, 854 cm^{-1} .

EIMS (70 eV) m/z : 454 (3.3, $\text{M}^+ + 2$), 453 (20, $\text{M}^+ + 1$), 452 (77, M^+), 84 (100).

Anal. Calcd for $\text{C}_{23}\text{H}_{33}\text{B}_2\text{F}_3\text{O}_4$: C, 61.10; H, 7.36. Found: C, 60.95; H, 7.30.

1,1-Bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-2-phenyl-1-propene (2d)

Prepared by method A.

Yield: 61%, colorless solid.

Mp. 71.7 °C (hexane).

TLC: R_f 0.33 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 1.06 (s, 12H), 1.29 (s, 12H), 2.34 (s, 3H), 7.22-7.32 (m, 5H).

^{13}C NMR (67.8 MHz, CDCl_3 , δ): 24.3, 24.7, 25.2, 82.7, 82.8, 126.8, 127.0, 127.6, 146.6, 164.4.

IR (KBr): 2980, 2930, 1614, 1441, 1354, 1298, 1142, 980, 854, 698 cm^{-1} .

EIMS (70 eV) m/z : 372 (5.3, $\text{M}^+ + 2$), 371 (30, $\text{M}^+ + 1$), 370 (97, M^+), 369 (62, $\text{M}^+ - 1$), 368 (7.3, $\text{M}^+ - 2$), 313 (100).

Anal. Calcd for $\text{C}_{21}\text{H}_{32}\text{B}_2\text{O}_4$: C, 68.15; H, 8.72. Found: C, 67.89; H, 8.61.

1,1-Bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-3-methyl-2-phenyl-1-butene (2e)

Prepared by method B.

Yield: 48%, colorless solid.

Mp. 107.0 °C (hexane).

TLC: R_f 0.30 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 0.91 (s, 12H), 0.95 (d, J = 6.8 Hz, 6H), 1.27 (s, 12H), 3.35 (dq, J = 6.8, 6.8 Hz, 1H), 7.08-7.22 (m, 5H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 21.7, 24.1, 24.7, 36.2, 82.6, 82.7, 126.1, 126.8, 128.6, 142.6, 173.8.

IR (KBr): 2976, 1593, 1371, 1329, 1288, 1144, 971, 851, 706 cm^{-1} .

EIMS (70 eV) m/z : 400 (0.1, $\text{M}^+ + 2$), 399 (0.5, $\text{M}^+ + 1$), 398 (2.0, M^+), 84 (100).

Anal. Calcd for $\text{C}_{23}\text{H}_{36}\text{B}_2\text{O}_4$: C, 69.38; H, 9.11. Found: C, 69.22; H, 8.95.

1,1-Bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-3,3-dimethyl-2-phenyl-1-butene (2f)

Prepared by method B.

Yield: 64%, colorless solid.

Mp. 146.0 °C (hexane).

TLC: R_f 0.30 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 0.87 (s, 12H), 1.13 (s, 9H), 1.29 (s, 12H), 7.08-7.18 (m, 5H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 24.3, 24.8, 30.4, 38.9, 82.8, 83.3, 125.8, 126.6, 129.3, 144.7, 171.4.

IR (KBr): 2978, 2932, 2359, 1589, 1371, 1329, 1302, 1140, 966, 854, 702, 669 cm^{-1} .

EIMS (70 eV) m/z : 414 (1.0, $\text{M}^+ + 2$), 413 (5, $\text{M}^+ + 1$), 412 (17, M^+), 284 (100).

Anal. Calcd for $\text{C}_{24}\text{H}_{38}\text{B}_2\text{O}_4$: C, 69.94; H, 9.29. Found: C, 69.76; H, 9.15.

1,1-Bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-3,3,3-trifluoro-2-phenyl-1-propene (2g)

Prepared by method B.

Yield: 72%, colorless solid.

Mp. 104.5 °C (hexane).

TLC: R_f 0.45 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 1.01 (s, 12H), 1.32 (s, 12H), 7.26-7.31 (m, 5H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 24.3, 24.6, 83.9, 84.3, 123.0 (q, J = 275.2 Hz), 127.7, 128.4, 129.2, 136.5, 147.0 (q, J = 29.7 Hz).

^{19}F NMR (200 MHz, CDCl_3 , δ): -64.2.

IR (KBr): 2980, 1373, 1321, 1138, 1126, 962, 849, 708 cm^{-1} .

EIMS (70 eV) m/z : 425 (7.8, $\text{M}^+ + 1$), 424 (32, M^+), 83 (100).

Anal. Calcd for $\text{C}_{21}\text{H}_{29}\text{B}_2\text{F}_3\text{O}_4$: C, 59.48; H, 6.89. Found: C, 59.31; H, 6.87.

Typical procedure for Pd-catalyzed cross-coupling reaction of 2 with an aryl iodide:

A mixture of **2a** (38 mg, 0.10 mmol), iodobenzene (21 mg, 0.10 mmol), $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 5.0 μmol), PrBu_3 (4.0 mg,

0.020 mmol) and 3 M KOH aqueous solution (0.10 mL, 0.30 mmol) in THF (1 mL) was stirred at room temperature for 5 h before quenching with saturated aq. NH_4Cl (1 mL). The resulting mixture was diluted with diethyl ether (10 mL) and washed with water (3 mL). The organic layer was separated, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The crude product was purified by preparative TLC (hexane/ethyl acetate 10:1) to give **3a** as colorless oil (27 mg, 83% yield).

(E)-1-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-1,2-diphenyl-1-butene (3a)

Yield: 83%, colorless oil.

TLC: R_f 0.32 (hexane/ethyl acetate = 10 : 1).

^1H NMR (200 MHz, CDCl_3 , δ): 0.86 (t, J = 5.8 Hz, 3H), 1.00 (s, 12H), 2.41 (q, J = 5.8 Hz, 2H), 7.22-7.38 (m, 10H).

^{13}C NMR (67.8 MHz, CDCl_3 , δ): 13.8, 24.5, 27.2, 83.3, 125.8, 126.9, 127.8, 128.0, 128.3, 128.4, 141.4, 143.5, 153.6.

IR (neat): 2976, 2932, 2872, 1597, 1493, 1356, 1300, 1269, 1215, 1103, 1030, 978, 905, 854, 702 cm^{-1} .

EIMS (70 eV) m/z : 336 (8, $\text{M}^+ + 2$), 335 (22, $\text{M}^+ + 1$), 334 (100, M^+).

Anal. Calcd for $\text{C}_{22}\text{H}_{27}\text{BO}_2$: C, 79.05; H, 8.14. Found: C, 79.22; H, 8.13.

(E)-1-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-1-(4''-fluorophenyl)-2-phenyl-1-butene (3b)

Yield: 86%, colorless solid.

Mp. 67.2 °C (hexane).

TLC: R_f 0.50 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 0.84 (t, J = 7.6 Hz, 3H), 0.99 (s, 12H), 2.40 (q, J = 7.6 Hz, 2H), 7.01-7.33 (m, 9H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 13.3, 24.3, 27.1, 83.3, 115.0 (d, J = 21.4 Hz), 127.1, 127.9, 128.4, 129.9 (d, J = 7.6 Hz), 137.3 (d, J = 3.0 Hz), 143.4, 154.3, 161.3 (d, J = 242.5 Hz).

^{19}F NMR (200 MHz, CDCl_3 , δ): -117.7.

IR (KBr): 2976, 2936, 1614, 1597, 1506, 1358, 1308, 1217, 1146, 978, 849, 777, 702 cm^{-1} .

EIMS (70 eV) m/z : 354 (3.4, $\text{M}^+ + 2$), 353 (27, $\text{M}^+ + 1$), 352 (100, M^+), 351 (27, $\text{M}^+ - 1$).

Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{BFO}_2$: C, 75.01; H, 7.44. Found: C, 75.07; H, 7.65.

(E)-1-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-1-(4''-trifluoromethylphenyl)-2-phenyl-1-butene (3c)

Yield: 75%, colorless solid.

Mp. 81.5 °C (hexane).

TLC: R_f 0.45 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 0.85 (t, J = 7.2 Hz, 3H), 1.00 (s, 12H), 2.37 (q, J = 7.2 Hz, 2H), 7.33-7.35 (m, 9H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 13.1, 24.3, 27.3, 83.5, 124.4 (q, J = 270.7 Hz), 125.1 (q, J = 3.8 Hz), 127.3, 127.9, 128.0 (q, J = 32.0 Hz), 128.3, 128.7, 143.1, 145.4, 155.4.

^{19}F NMR (200 MHz, CDCl_3 , δ): -62.7.

IR (KBr): 2978, 2932, 1614, 1356, 1325, 1144, 1105, 1065, 856, 702 cm^{-1} .

EIMS (70 eV) m/z : 404 (3.4, $\text{M}^+ + 2$), 403 (24, $\text{M}^+ + 1$), 402 (89, M^+), 345 (100).

Anal. Calcd for $\text{C}_{23}\text{H}_{26}\text{BF}_3\text{O}_2$: C, 68.67; H, 6.51. Found: C, 68.78; H, 6.57.

(E)-1-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-1-(4''-ethoxycarbonylphenyl)-2-phenyl-1-butene (3d)

Yield: 74%, colorless oil.

TLC: R_f 0.35 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 0.85 (t, J = 7.6 Hz, 3H), 1.00 (s, 12H), 1.40 (t, J = 7.2 Hz, 3H), 2.38 (q, J = 7.6 Hz, 2H), 4.37 (q, J = 7.2 Hz, 2H), 7.30-8.02 (m, 9H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 13.2, 14.4, 24.3, 27.3, 60.8, 83.4, 127.2, 127.9, 128.1, 128.3, 128.5, 129.5, 143.2, 146.7, 155.0, 166.7.

IR (neat): 2976, 2932, 2874, 1715, 1605, 1443, 1352, 1271, 1144, 1101, 1022, 854, 758, 702 cm^{-1} .

EIMS (70 eV) m/z : 408 (4.3, $\text{M}^+ + 2$), 407 (27, $\text{M}^+ + 1$), 406 (98, M^+), 306 (100).

Anal. Calcd for $\text{C}_{25}\text{H}_{31}\text{BO}_4$: C, 73.90; H, 7.69. Found: C, 74.16; H, 7.56.

(E)-1-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-1-(4''-aminophenyl)-2-phenyl-1-butene (3e)

Yield: 61%, colorless solid.

Mp. 81.5 °C (hexane).

TLC: R_f 0.18 (hexane/ethyl acetate = 4 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 0.85 (t, J = 7.6 Hz, 3H), 1.00 (s, 12H), 2.42 (q, J = 7.6 Hz, 2H), 6.90 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H), 7.27-7.35 (m, 5H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 13.3, 24.4, 27.0, 83.1, 115.1, 126.8, 127.8, 128.5, 129.4, 131.9, 143.9, 144.3, 152.8.

IR (KBr): 3362, 2968, 1607, 1512, 1356, 1288, 1146, 1103, 1022, 856, 806, 704 cm^{-1} .

EIMS (70 eV) m/z : 350 (24, $\text{M}^+ + 1$), 349 (100, M^+), 348 (26, $\text{M}^+ - 1$).

Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{BNO}_2$: C, 75.65; H, 8.08. Found: C, 75.70; H, 7.97.

(E)-1-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-1-(4''-methoxyphenyl)-2-phenyl-1-butene (3f)

Yield: 60%, colorless oil.

Mp. 66.5 °C (hexane).

TLC: R_f 0.43 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 0.86 (t, $J = 7.6$ Hz, 3H), 1.00 (s, 12H), 2.42 (q, $J = 7.6$ Hz, 2H), 3.82 (s, 3H), 6.90 (d, $J = 9.0$ Hz, 2H), 7.15 (d, $J = 9.0$ Hz, 2H), 7.27-7.36 (m, 5H).

^{13}C NMR (67.8 MHz, CDCl_3 , δ): 13.4, 24.5, 27.1, 55.2, 83.2, 113.5, 126.8, 127.7, 128.4, 129.4, 133.7, 143.6, 153.2, 157.7.

IR (KBr): 2976, 2932, 2872, 1607, 1508, 1462, 1441, 1354, 1285, 1244, 1144, 1036, 854, 702 cm^{-1} .

EIMS (70 eV) m/z : 366 (3.7, M^{+2}), 365 (24, M^{+1}), 364 (100, M^{+}), 363 (27, M^{+1}).

Anal. Calcd for $\text{C}_{23}\text{H}_{29}\text{BO}_3$: C, 75.83; H, 8.02. Found: C, 75.56; H, 7.95.

(Z)-1-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-1-[4''-(2'''-dimethylaminoethoxy)phenyl]-2-phenyl-1-butene (3g)

Yield: 55%, colorless oil.

TLC: R_f 0.41 (hexane/ethyl acetate/ Et_3N = 10 : 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 0.85 (t, $J = 5.8$ Hz, 3H), 1.00 (s, 12H), 2.42 (s, 6H), 2.43 (q, $J = 5.8$ Hz, 2H), 2.80 (t, $J = 4.2$ Hz, 2H), 4.11 (t, $J = 4.2$ Hz, 2H), 6.89 (d, $J = 7.2$ Hz, 2H), 7.14 (d, $J = 7.2$ Hz, 2H), 7.25-7.32 (m, 5H).

^{13}C NMR (67.8 MHz, CDCl_3 , δ): 13.4, 24.5, 27.1, 45.8, 58.2, 65.6, 83.2, 114.1, 126.8, 127.7, 128.3, 129.4, 133.9, 143.6, 153.2, 156.8.

IR (neat): 2974, 2932, 2872, 2770, 1604, 1506, 1356, 1298, 1240, 1143, 1036, 978, 854 cm^{-1} .

EIMS (70 eV) m/z : 423 (3, M^{+2}), 422 (15, M^{+1}), 421 (39, M^{+}), 58 (100).

HRMS Calcd for $\text{C}_{26}\text{H}_{36}\text{BNO}_3$: M^{+} , 421.2788. Found: m/z 421.2786.

(E)-1-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-1-(4''-methylphenyl)-2-phenyl-1-butene (3h)

Yield: 87%, colorless oil.

TLC: R_f 0.53 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 0.85 (t, $J = 7.6$ Hz, 3H), 1.00 (s, 12H), 2.35 (s, 3H), 2.42 (q, $J = 7.6$ Hz, 2H), 7.13-7.34 (m, 9H).

^{13}C NMR (67.8 MHz, CDCl_3 , δ): 13.4, 21.3, 24.5, 27.2, 83.2, 126.8, 127.7, 128.2, 128.4, 128.8, 135.2, 138.4, 143.6, 153.4.

IR (neat): 2976, 2930, 2872, 1597, 1508, 1354, 1298, 1144, 854, 700 cm^{-1} .

EIMS (70 eV) m/z : 350 (3.8, M^{+2}), 349 (24, M^{+1}), 348 (100, M^{+}), 347 (25, M^{+1}).

Anal. Calcd for $\text{C}_{23}\text{H}_{29}\text{BO}_2$: C, 79.32; H, 8.39. Found: C, 79.16; H, 8.34.

(E)-1-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-1-(2''-methylphenyl)-2-phenyl-1-butene (3i)

Yield: 78%, colorless solid.

Mp. 51.6 °C (hexane).

TLC: R_f 0.50 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 0.75 (t, $J = 7.4$ Hz, 3H), 0.97 (s, 12H), 2.18 (q, $J = 7.4$ Hz, 2H), 2.31 (s, 3H), 7.10-7.38 (m, 9H).

^{13}C NMR (67.8 MHz, CDCl_3 , δ): 12.6, 20.2, 24.4, 27.5, 83.0, 125.4, 125.9, 126.8, 127.7, 128.3, 128.6, 129.5, 135.6, 141.1, 143.3, 153.9.

IR (KBr): 2974, 2932, 1597, 1481, 1354, 1306, 1146, 1115, 980, 854, 770, 737, 704 cm^{-1} .

EIMS (70 eV) m/z : 350 (18, M^{+2}), 349 (97, M^{+1}), 348 (100, M^{+}), 347 (93, M^{+1}).

Anal. Calcd for $\text{C}_{23}\text{H}_{29}\text{BO}_2$: C, 79.32; H, 8.39. Found: C, 79.02; H, 8.37.

(E)-1-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-1-(4''-fluorophenyl)-2-(4'''-methylphenyl)-1-butene (3j)

Yield: 67%, colorless solid.

Mp. 68.3 °C (hexane).

TLC: R_f 0.53 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 0.84 (t, $J = 7.2$ Hz, 3H), 1.01 (s, 12H), 2.35 (s, 3H), 2.39 (q, $J = 7.2$ Hz, 2H), 7.02-7.26 (m, 8H).

^{13}C NMR (67.8 MHz, CDCl_3 , δ): 13.3, 21.2, 24.4, 27.1, 83.3, 114.9 (d, $J = 21.2$ Hz), 128.1, 128.4, 129.8 (d, $J = 7.8$ Hz), 136.6, 137.4 (d, $J = 3.3$ Hz), 140.3, 154.1, 161.2 (d, $J = 243.2$ Hz).

^{19}F NMR (200 MHz, CDCl_3 , δ): -117.8.

IR (KBr): 2970, 2936, 1597, 1502, 1356, 1300, 1215, 1155, 1144, 1103, 976, 853, 820 cm^{-1} .

EIMS (70 eV) m/z : 368 (3.9, M^{+2}), 367 (31, M^{+1}), 366 (100, M^{+}), 365 (32, M^{+1}).

Anal. Calcd for $\text{C}_{23}\text{H}_{28}\text{BFO}_2$: C, 75.42; H, 7.71. Found: C, 75.48; H, 7.72.

(E)-1-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-2-(4''-fluoromethylphenyl)-1-(4'''-trifluorophenyl)-1-butene (3k)

Yield: 66%, colorless solid.

Mp. 84.4 °C (hexane).

TLC: R_f 0.50 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 0.84 (t, $J = 7.2$ Hz, 3H), 0.98 (s, 12H), 2.39 (q, $J = 7.2$ Hz, 2H), 7.04-7.18 (m, 4H), 7.45 (d, $J = 7.8$ Hz, 2H), 7.58 (d, $J = 7.8$ Hz, 2H).

^{13}C NMR (67.8 MHz, CDCl_3 , δ): 13.1, 24.4, 27.3, 83.5, 115.0 (d, $J = 21.2$ Hz), 124.2 (q, $J = 271.1$ Hz), 124.7 (q, $J = 271.1$ Hz), 128.7, 129.2 (q, $J = 32.3$ Hz), 129.7 (d, $J = 7.8$ Hz), 136.7 (d, $J = 3.3$ Hz), 147.1, 153.2, 161.4 (d, $J = 244.4$ Hz).

^{19}F NMR (200 MHz, CDCl_3 , δ): -62.9, -117.2.

IR (KBr): 2978, 2934, 2874, 1601, 1506, 1350, 1325, 1310, 1223, 1167, 1140, 1117, 1067, 851 cm^{-1} .

EIMS (70 eV) m/z : 421 (6.3, $\text{M}^+ + 1$), 420 (25, M^+), 101 (100).

Anal. Calcd for $\text{C}_{23}\text{H}_{25}\text{BF}_4\text{O}_2$: C, 65.73; H, 6.00. Found: C, 65.59; H, 6.29.

(*E*)-1-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-1,2-diphenyl-1-propene (3l)

Yield: 69%, colorless solid.

Mp. 48.5 °C (hexane).

TLC: R_f 0.50 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 1.03 (s, 12H), 2.05 (s, 3H), 7.23-7.41 (m, 10H).

^{13}C NMR (67.8 MHz, CDCl_3 , δ): 21.6, 24.5, 83.3, 125.8, 127.0, 127.7, 127.9, 128.0, 128.7, 141.6, 145.3, 147.6.

IR (KBr): 2978, 2926, 1491, 1373, 1340, 1294, 1146, 854, 702 cm^{-1} .

EIMS (70 eV) m/z : 322 (4.5, $\text{M}^+ + 2$), 321 (34, $\text{M}^+ + 1$), 320 (100, M^+), 319 (32, $\text{M}^+ - 1$).

Anal. Calcd for $\text{C}_{23}\text{H}_{25}\text{BO}_2$: C, 78.76; H, 7.87. Found: C, 78.64; H, 7.85.

(*E*)-1-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-1-(4''-trifluoromethylphenyl)-2-phenyl-1-propene (3m)

Yield: 66%, colorless solid.

Mp. 145.0 °C (hexane).

TLC: R_f 0.48 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 1.03 (s, 12H), 2.09 (s, 3H), 7.29-7.59 (m, 9H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 21.6, 24.4, 83.5, 124.4 (q, $J = 270.7$ Hz), 125.1 (q, $J = 3.9$ Hz), 127.4, 127.7, 128.0 (q, $J = 32.0$ Hz), 128.1, 129.0, 144.9, 145.6, 149.5.

^{19}F NMR (200 MHz, CDCl_3 , δ): -62.7.

IR (KBr): 2984, 1611, 1346, 1321, 1165, 1123, 1063, 856, 773, 706 cm^{-1} .

EIMS (70 eV) m/z : 390 (1.3, $\text{M}^+ + 2$), 389 (9.1, $\text{M}^+ + 1$), 388 (38, M^+), 331 (100).

Anal. Calcd for $\text{C}_{22}\text{H}_{24}\text{BF}_3\text{O}_2$: C, 68.06; H, 6.23. Found: C, 68.29; H, 6.23.

(*E*)-1-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-1-(4''-methoxyphenyl)-2-phenyl-1-propene (3n)

Yield: 66%, colorless solid.

Mp. 75.8 °C (hexane).

TLC: R_f 0.45 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 1.03 (s, 12H), 2.06 (s, 3H), 3.82 (s, 3H), 6.90 (d, $J = 8.8$ Hz, 2H), 7.16 (d, $J = 8.8$ Hz, 2H), 7.28-7.40 (m, 5H).

^{13}C NMR (67.8 MHz, CDCl_3 , δ): 21.6, 24.5, 55.2, 83.3, 113.5, 126.9, 127.7, 127.9, 129.8, 133.9, 145.5, 147.1, 157.7.

IR (KBr): 2980, 2932, 1607, 1510, 1371, 1354, 1300, 1248, 1146, 1028, 856, 702 cm^{-1} .

EIMS (70 eV) m/z : 352 (3.6, $\text{M}^+ + 2$), 351 (21, $\text{M}^+ + 1$), 350 (86, M^+), 349 (19, $\text{M}^+ - 1$), 149 (100).

Anal. Calcd for $\text{C}_{22}\text{H}_{27}\text{BO}_3$: C, 75.44; H, 7.77. Found: C, 75.32; H, 7.84.

(*E*)-1-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-1-(4''-trifluoromethylphenyl)-3-methyl-2-phenyl-1-butene (3o)

Yield: 68%, colorless solid.

Mp. 125.7 °C (hexane).

TLC: R_f 0.53 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 0.88 (s, 12H), 0.89 (d, $J = 6.8$ Hz, 6H), 2.91 (dq, $J = 6.8, 6.8$ Hz, 1H), 7.23-7.31 (m, 5H), 7.39 (d, $J = 8.2$ Hz, 2H), 7.61 (d, $J = 8.2$ Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 21.2, 24.2, 30.7, 83.3, 124.5 (q, $J = 270.7$ Hz), 125.1 (q, $J = 3.8$ Hz), 126.7, 127.2, 128.0 (q, $J = 32.0$ Hz), 128.7, 130.0, 140.2, 144.7, 157.9.

^{19}F NMR (200 MHz, CDCl_3 , δ): -62.7.

IR (KBr): 2974, 2330, 1614, 1362, 1329, 1302, 1117, 1067, 851, 700 cm^{-1} .

EIMS (70 eV) m/z : 418 (6.6, $\text{M}^+ + 2$), 417 (43, $\text{M}^+ + 1$), 416 (100, M^+).

Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{BF}_3\text{O}_2$: C, 69.25; H, 6.78. Found: C, 69.19; H, 6.78.

(*E*)-1-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-1-(4''-methoxyphenyl)-3-methyl-2-phenyl-1-butene (3p)

Yield: 71%, colorless solid.

Mp. 90.0 °C (hexane).

TLC: R_f 0.33 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 0.88 (s, 12H), 0.90 (d, J = 6.8 Hz, 6H), 3.06 (dq, J = 6.8, 6.8 Hz, 1H), 3.82 (s, 3H), 6.88 (d, J = 8.8 Hz, 2H), 7.18 (d, J = 8.8 Hz, 2H), 7.23-7.29 (m, 5H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 21.4, 24.2, 30.2, 55.1, 83.0, 113.6, 126.4, 127.1, 129.5, 130.2, 132.8, 140.8, 156.1, 157.8.

IR (KBr): 2966, 1508, 1358, 1296, 1250, 1144, 970, 839, 702 cm^{-1} .

EIMS (70 eV) m/z : 380 (4, $\text{M}^+ + 2$), 379 (27, $\text{M}^+ + 1$), 378 (100, M^+).

Anal. Calcd for $\text{C}_{24}\text{H}_{31}\text{BO}_3$: C, 76.20; H, 8.26. Found: C, 76.46; H, 8.14.

(*E*)-1-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-1-(4''-trifluoromethylphenyl)-3,3-dimethyl-2-phenyl-1-butene (3q)

Yield: 54%, colorless solid.

Mp. 138.8 °C (hexane).

TLC: R_f 0.55 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 0.77 (s, 12H), 0.91 (s, 9H), 7.27-7.39 (m, 5H), 7.41 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 24.0, 31.7, 38.2, 83.3, 124.5 (q, J = 270.6 Hz), 124.6 (q, J = 3.1 Hz), 126.5, 127.2, 127.9 (q, J = 32.0 Hz), 128.7, 129.9, 143.5, 146.0, 157.4.

^{19}F NMR (200 MHz, CDCl_3 , δ): -62.6.

IR (KBr): 2978, 2330, 1616, 1373, 1323, 1163, 1119, 1067, 966, 858, 702, 685 cm^{-1} .

EIMS (70 eV) m/z : 432 (4.7, $\text{M}^+ + 2$), 431 (29, $\text{M}^+ + 1$), 430 (100, M^+).

Anal. Calcd for $\text{C}_{25}\text{H}_{30}\text{BF}_3\text{O}_2$: C, 69.78; H, 7.03. Found: C, 69.78; H, 7.00.

(*E*)-1-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-1-(4''-methoxyphenyl)-3,3-dimethyl-2-phenyl-1-butene (3r)

Yield: 39%, colorless solid.

Mp. 123.2 °C (hexane).

TLC: R_f 0.43 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 0.78 (s, 12H), 0.92 (s, 9H), 3.81 (s, 3H), 6.82 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 7.19-7.27 (m, 5H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 24.0, 31.7, 37.9, 55.1, 83.0, 113.1, 126.2, 127.1, 129.4, 130.1, 133.8, 144.2, 156.6, 157.6.

IR (KBr): 2951, 1603, 1504, 1464, 1339, 1238, 1144, 1034, 968, 856, 704 cm^{-1} .

EIMS (70 eV) m/z : 394 (5, $\text{M}^+ + 2$), 393 (27, $\text{M}^+ + 1$), 392 (100, M^+).

Anal. Calcd for $\text{C}_{25}\text{H}_{33}\text{BO}_3$: C, 76.53; H, 8.48. Found: C, 76.40; H, 8.53.

(*Z*)-1-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-3,3,3-trifluoro-1,2-diphenylpropene (3s)

Yield: 72%, colorless solid.

Mp. 72.7 °C (hexane).

TLC: R_f 0.60 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 0.92 (s, 12H), 7.28-7.45 (m, 10H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 24.2, 84.2, 122.8 (q, J = 276.0 Hz), 127.0 (q, J = 1.5 Hz), 127.2, 128.0, 128.0, 128.5, 130.1, 136.0, 136.4 (q, J = 29.0 Hz), 137.6.

^{19}F NMR (200 MHz, CDCl_3 , δ): -57.5.

IR (KBr): 2978, 1445, 1373, 1300, 1165, 1115, 962, 849, 706 cm^{-1} .

EIMS (70 eV) m/z : 376 (3.9, $\text{M}^+ + 2$), 375 (28, $\text{M}^+ + 1$), 374 (99, M^+), 189 (100).

Anal. Calcd for $\text{C}_{21}\text{H}_{22}\text{BF}_3\text{O}_2$: C, 67.40; H, 5.93. Found: C, 67.13; H, 5.96.

Typical procedure for the preparation of 4 from 3: A mixture of **3h** (18 mg, 0.054 mmol), iodobenzene (17 mg, 0.081 mmol), $\text{Pd}[\text{P}(t\text{Bu})_3]_2$ (1.4 mg, 2.7 μmol), and 3 M NaOH aqueous solution (0.054 mL, 0.16 mmol) in THF (1 mL) was stirred at 60 °C for 24 h before quenching with saturated aq. NH_4Cl (1 mL). The resulting mixture was diluted with diethyl ether (10 mL) and washed with water (3 mL). The organic layer was separated, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The crude product was purified by column chromatography (hexane/ethyl acetate 10:1) to give **4f** as colorless solid (14 mg, 89% yield).

CAS numbers of products **4** are listed below:

(*Z*)-Tamoxifen (**4a**): [10540-29-1]

(*Z*)-1-4-Fluorophenyl-1-4-methoxyphenyl-2-phenyl-1-butene (**4b**): [97732-60-0]

(*E*)-1-4-Trifluoromethylphenyl-1-4-methoxyphenyl-2-phenyl-1-butene (**4c**): [624731-47-1]

(*E*)-1-4-Methoxyphenyl-1-4-methylphenyl-2-phenyl-1-butene (**4d**): [185223-87-4]

(*E*)-Tamoxifen (**4e**): [7728-73-6]

(*E*)-1-4-Methylphenyl-1,2-diphenyl-1-butene (**4f**): [116454-41-2]

(*E, Z*)-1-Phenyl-3-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-4-phenyl-1,3-hexadiene (5**)**

Prepared by the same procedure for the preparation of **3** except for use of Pd(PPh₃)₄ as the catalyst.

Yield: 73%, colorless solid.

Mp. 93.9 °C (hexane).

TLC: R_f 0.50 (hexane/ethyl acetate = 10 : 1).

¹H NMR (400 MHz, CDCl₃, δ): 1.00 (t, *J* = 7.6 Hz, 3H), 1.10 (s, 12H), 2.19 (q, *J* = 7.6 Hz, 2H_c), 6.19 (d, *J* = 16.0 Hz, H_a), 7.19-7.43 (m, 10H), 7.26 (d, *J* = 16.0 Hz, H_b).

¹³C NMR (67.8 MHz, CDCl₃, δ): 13.3, 24.7, 27.2, 83.5, 126.2, 127.0, 127.1, 127.9, 128.4, 128.5, 128.6, 131.5, 138.3, 144.5, 154.4.

IR (KBr): 3028, 2974, 2930, 2870, 1579, 1488, 1371, 1298, 1139, 959, 843, 768, 696 cm⁻¹.

EIMS (70 eV) *m/z*: 362 (8, M⁺+2), 361 (57, M⁺+1), 360 (100, M⁺), 260 (66), 232 (87), 101 (64), 91 (46).

Anal. Calcd for C₂₄H₂₉BO₂: C, 80.01; H, 8.11. Found: C, 80.01; H, 8.25.

(*Z,Z*)-1,4-Diphenyl-3-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-1,3-hexadiene (6**)**

Yield: 72%, colorless solid.

Mp. 92.0 °C (hexane).

TLC: R_f 0.50 (hexane/ethyl acetate = 10 : 1).

¹H NMR (400 MHz, CDCl₃, δ): 0.72 (s, 12H), 0.92 (t, *J* = 7.6 Hz, 3H), 2.55 (q, *J* = 7.6 Hz, 2H_c), 6.55 (s, H_a and H_b), 7.15-7.42 (m, 10 H).

¹³C NMR (67.8 MHz, CDCl₃, δ): 11.9, 24.4, 28.9, 82.9, 126.8, 126.8, 127.7, 128.1, 128.4, 129.4, 130.4, 130.4, 138.0, 143.7, 156.9

IR (KBr): 3051, 2974, 2929, 2869, 1587, 1490, 1353, 1301, 1145, 1118, 1030, 964, 790, 698, 648 cm⁻¹.

EIMS (70 eV) *m/z*: 361 (36, M⁺+1), 360 (100, M⁺), 359 (30, M⁺-1), 232 (79), 231(50), 101(59), 91(25).

Anal. Calcd for C₂₄H₂₉BO₂: C, 80.01; H, 8.11. Found: C, 79.77; H, 8.08.

(*Z,Z*)-1,4-Diphenyl-3-((*E*)-1'-octenyl)-1,3-hexadiene (7**)**

A DME (1 mL) solution of **5** (15 mg, 0.041 mmol), 1-iodo-1-octene (10.7 mg, 0.053 mmol), PdCl₂(dppf) (1.7 mg, 2.0 μmol), 3 M KOH aqueous solution (41 μL, 0.12 mmol) was stirred at 40 °C for 4 h before quenching with saturated aq. NH₄Cl (1 mL). The resulting mixture was diluted with ethyl acetate (10 mL). The aqueous layer was extracted with ethyl acetate (twice). The combined organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The crude product was purified by preparative TLC (hexane/ethyl acetate 10:1) to give **7** (12 mg, 81% yield) as colorless oil.

Yield: 81%, colorless oil.

TLC: R_f 0.75 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 0.86 (t, $J = 7.2$ Hz, 3 H), 0.97 (t, $J = 7.2$ Hz, 3 H), 1.19-1.27 (m, 8 H), 1.96 (q, $J = 7.2$ Hz, 2 H), 2.62 (q, $J = 7.2$ Hz, 2H), 5.62 (dt, $J = 16.0, 7.2$ Hz, 1H), 5.92 (d, $J = 16.0$ Hz, 1H), 6.70 (d, $J = 16.4$ Hz, 1H), 7.00 (d, $J = 16.4$ Hz, 1H), 7.18-7.49 (m, 10H)

^{13}C NMR (67.8 MHz, CDCl_3 , δ): 13.5, 14.1, 22.6, 28.4, 28.8, 29.3, 31.7, 33.1, 126.3, 126.4, 127.0, 127.3, 127.8, 128.6, 129.1, 129.4, 129.4, 132.5, 134.0, 137.9, 142.1, 142.6.

IR (neat): 2959, 2926, 2854, 1598, 1491, 1448, 1375, 1261, 968, 700 cm^{-1} .

EIMS (70 eV) m/z : 346 (3, $\text{M}^+ + 2$), 345 (23, $\text{M}^+ + 1$), 344 (80, M^+), 259 (100), 217(20), 181(20), 91(57).

HRMS Calcd for $\text{C}_{26}\text{H}_{32}$: M^+ , 344.2504 Found: 344.2501.

(*Z,Z*)-1,3,4-Triphenyl-1,3-hexadiene (8)

Yield: 81%, colorless solid.

Mp. 58.6°C (hexane).

TLC: R_f 0.60 (hexane/ethyl acetate = 10 : 1).

^1H NMR (400 MHz, CDCl_3 , δ): 1.15 (t, $J = 7.6$ Hz, 3H), 2.83 (q, $J = 7.6$ Hz, 2H), 6.19 (d, $J = 16.0$ Hz, 1 H), 6.98-7.40 (m, 15H), 7.53 (d, $J = 16.0$ Hz, 1H)

^{13}C NMR (67.8 MHz, CDCl_3 , δ): 13.7, 27.7, 125.8, 126.0, 126.4, 127.3, 127.4, 127.5, 128.1, 128.5, 129.4, 131.2, 132.3, 136.5, 137.9, 140.2, 143.0, 144.2

IR (KBr): 3039, 3024, 2959, 2924, 1597, 1571, 1489, 1442, 1070, 960, 694 cm^{-1} .

EIMS (70 eV) m/z : 312 (3, $\text{M}^+ + 2$), 311 (20, $\text{M}^+ + 1$), 310 (78, M^+), 281 (100), 219 (43), 203 (26), 91(27).

HRMS Calcd for $\text{C}_{24}\text{H}_{22}$: M^+ , 310.1722 Found: 310.1724.

ORTEP drawings:

3b: A (pinacolato)boryl group was disordered.

Empirical formula	C ₂₂ H ₂₆ B F O ₂	
Formula weight	352.24	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.1960(16) Å	α = 90°.
	b = 13.885(2) Å	β = 101.995(2)°.
	c = 13.677(2) Å	γ = 90°.
Volume	2079.7(5) Å ³	
Z	4	
Density (calculated)	1.125 Mg/m ³	
Absorption coefficient	0.075 mm ⁻¹	
F(000)	752	
Crystal size	0.4 x 0.3 x 0.2 mm ³	
Theta range for data collection	1.86 to 25.50°.	
Index ranges	-9 ≤ h ≤ 13, -16 ≤ k ≤ 16, -16 ≤ l ≤ 16	
Reflections collected	11199	
Independent reflections	3866 [R(int) = 0.0239]	
Completeness to theta = 25.50°	99.7 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3866 / 0 / 241	
Goodness-of-fit on F ²	1.659	
Final R indices [I > 2σ(I)]	R1 = 0.1143, wR2 = 0.4019	
R indices (all data)	R1 = 0.1457, wR2 = 0.4302	
Largest diff. peak and hole	0.514 and -0.394 e.Å ⁻³	

3j:

Empirical formula	C ₂₃ H ₂₈ B F O ₂	
Formula weight	325.57	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 12.627(2) Å	α = 90°.
	b = 18.210(3) Å	β = 90°.
	c = 18.636(4) Å	γ = 90°.
Volume	4285.1(14) Å ³	
Z	9	
Density (calculated)	1.135 Mg/m ³	
Absorption coefficient	0.076 mm ⁻¹	
F(000)	1568	
Crystal size	0.5 x 0.5 x 0.1 mm ³	
Theta range for data collection	1.56 to 27.03°.	
Index ranges	-16 ≤ h ≤ 9, -23 ≤ k ≤ 21, -22 ≤ l ≤ 23	
Reflections collected	24570	
Independent reflections	9310 [R(int) = 0.0550]	
Completeness to theta = 27.03°	99.3 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9310 / 0 / 499	
Goodness-of-fit on F ²	1.011	
Final R indices [I > 2σ(I)]	R1 = 0.0641, wR2 = 0.1353	
R indices (all data)	R1 = 0.1411, wR2 = 0.1656	
Absolute structure parameter	-0.3(11)	
Largest diff. peak and hole	0.258 and -0.129 e.Å ⁻³	

3k: A CF₃ group was disordered.

Empirical formula	C ₂₃ H ₂₅ B F ₄ O ₂	
Formula weight	420.24	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.5318(12) Å	α = 90°.
	b = 9.9623(12) Å	β = 94.592(2)°.
	c = 21.543(3) Å	γ = 90°.
Volume	2253.0(5) Å ³	
Z	4	
Density (calculated)	1.239 Mg/m ³	
Absorption coefficient	0.099 mm ⁻¹	
F(000)	880	
Crystal size	0.5 x 0.4 x 0.3 mm ³	
Theta range for data collection	1.90 to 27.04°.	
Index ranges	-13 ≤ h ≤ 12, -11 ≤ k ≤ 12, -20 ≤ l ≤ 27	
Reflections collected	13274	
Independent reflections	4913 [R(int) = 0.0235]	
Completeness to theta = 27.04°	99.3 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4913 / 0 / 304	
Goodness-of-fit on F ²	1.030	
Final R indices [I > 2σ(I)]	R1 = 0.0513, wR2 = 0.1392	
R indices (all data)	R1 = 0.0789, wR2 = 0.1564	
Largest diff. peak and hole	0.176 and -0.144 e.Å ⁻³	

3n: A (pinacolato)boryl group was disordered.

Empirical formula	C ₂₂ H ₂₇ B O ₃	
Formula weight	350.25	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 15.128(10) Å	α = 90°.
	b = 7.230(5) Å	β = 97.048(12)°.
	c = 18.994(12) Å	γ = 90°.
Volume	2062(2) Å ³	
Z	4	
Density (calculated)	1.128 Mg/m ³	
Absorption coefficient	0.073 mm ⁻¹	
F(000)	752	
Crystal size	0.5 x 0.5 x 0.5 mm ³	
Theta range for data collection	2.16 to 26.92°.	
Index ranges	-18 ≤ h ≤ 19, -9 ≤ k ≤ 9, -24 ≤ l ≤ 12	
Reflections collected	11757	
Independent reflections	4402 [R(int) = 0.0229]	
Completeness to theta = 26.92°	98.6 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4402 / 0 / 222	
Goodness-of-fit on F ²	1.384	
Final R indices [I > 2σ(I)]	R1 = 0.1562, wR2 = 0.4219	
R indices (all data)	R1 = 0.1768, wR2 = 0.4453	
Largest diff. peak and hole	0.944 and -0.630 e.Å ⁻³	

3o: A (pinacolato)boryl group was disordered.

Empirical formula	C ₂₄ H ₂₈ B F ₃ O ₂	
Formula weight	416.27	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.2470(6) Å	α = 79.4000(10)°.
	b = 13.0195(11) Å	β = 85.3480(10)°.
	c = 14.7090(13) Å	γ = 88.5050(10)°.
Volume	1171.96(18) Å ³	
Z	2	
Density (calculated)	1.180 Mg/m ³	
Absorption coefficient	0.089 mm ⁻¹	
F(000)	440	
Crystal size	0.5 x 0.5 x 0.2 mm ³	
Theta range for data collection	1.41 to 25.50°.	
Index ranges	-7 ≤ h ≤ 7, -15 ≤ k ≤ 15, -17 ≤ l ≤ 17	
Reflections collected	11947	
Independent reflections	4353 [R(int) = 0.0195]	
Completeness to theta = 25.50°	99.6 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4353 / 100 / 324	
Goodness-of-fit on F ²	1.859	
Final R indices [I > 2sigma(I)]	R1 = 0.1135, wR2 = 0.4105	
R indices (all data)	R1 = 0.1388, wR2 = 0.4412	
Largest diff. peak and hole	0.491 and -0.380 e.Å ⁻³	

3r: *tert*-Butyl and (pinacolato)boryl groups were disordered.

Empirical formula	C ₂₅ H ₃₃ B O ₃	
Formula weight	392.32	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.8505(6) Å	α = 82.2570(10)°.
	b = 15.3778(10) Å	β = 79.4000(10)°.
	c = 16.1829(10) Å	γ = 80.5940(10)°.
Volume	2363.3(3) Å ³	
Z	4	
Density (calculated)	1.103 Mg/m ³	
Absorption coefficient	0.070 mm ⁻¹	
F(000)	848	
Crystal size	0.5 x 0.5 x 0.5 mm ³	
Theta range for data collection	1.76 to 25.50°.	
Index ranges	-10 ≤ h ≤ 11, -18 ≤ k ≤ 18, -19 ≤ l ≤ 18	
Reflections collected	12971	
Independent reflections	8652 [R(int) = 0.0153]	
Completeness to theta = 25.50°	98.4 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8652 / 0 / 601	
Goodness-of-fit on F ²	1.096	
Final R indices [I > 2σ(I)]	R1 = 0.0645, wR2 = 0.1898	
R indices (all data)	R1 = 0.0896, wR2 = 0.2069	
Largest diff. peak and hole	0.487 and -0.245 e.Å ⁻³	