Supporting Information

Palladium-Catalyzed Oxidative Allylation of Bis[(pinacolato)boryl]methane: Synthesis of Homoallylicboronic Esters

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A. General Information

$^1$H and $^{13}$C NMR spectra were recorded using a 400 MHz NMR spectrometer. Chemical shifts were reported in ppm from the solvent resonance as the internal reference (CDCl$_3$, $\delta_H = 7.26$ ppm, downfield from TMS, $\delta_C = 77.16$ ppm. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). IR spectra were obtained as potassium bromide pellets between two potassium bromide pellets with a spectrometer. GC-MS was obtained using electron ionization. HRMS was obtained with a LCMS-IT-TOF mass spectrometer or recorded on an EI-ion trap High Resolution mass spectrometer. TLC was performed by using commercially prepared 100-400 mesh silica gel plates and visualization was effected at 254 nm. X-ray structural analyses were conducted on an x-ray analysis instrument.

Materials. Toluene and tetrahydrofuran were distilled from sodium/benzophenone. Acetonitrile was distilled from phosphorus pentoxide. Other commercially available reagents were purchased and used without further purification. Analytical thin-layer chromatography was performed on 0.20 mm silica gel plates (GF$_{254}$) using UV light as a visualizing agent. Flash column chromatography was conducted using silica gel (200–300 mesh) with the indicated solvent system. All the reaction temperatures reported are oil bath temperatures. Bis[(pinacolato)boryl]methane were commercially available.

B. Typical Procedures for the Synthesis of Substrates

(a). General Procedure for the Synthesis of Allylbenzenes

\[
\begin{align*}
\text{ArH} & \quad (5 \text{ mmol}) \quad \xrightarrow{\text{Mg (1.2 equiv)}} \quad \text{Ar}^+ \quad \xrightarrow{\text{THF, r.t., I$_2$}} \quad \text{Ar}^+\text{MgBr}^- \quad \xrightarrow{\text{THF solution of allyl bromide}} \quad \text{Ar}^+\text{MgBr}^- \quad \xrightarrow{\text{NH$_4$Cl (aq.)}} \quad \text{ArH}
\end{align*}
\]

Aryl bromide (5 mmol) was reacted with magnesium (1.2 equiv) in 10 mL anhydrous THF using I$_2$ as initiator at room temperature. After the reaction was finished, the combined organics was added to the anhydrous THF solution of allyl bromide. After stirring for 1 h, NH$_4$Cl (aq.) was added to the reaction mixture, washing with water and then concentrated for further purification. Purification by column chromatography over silica gel (230-400 mesh) using petroleum ether as eluent afforded 1c, 1d, 1g, 1j, 1m, 1n, 1o, 1q, 1t as a colorless oil.

(b). General Procedure for Synthesis of $\alpha$-Methyl Styrenes

\[
\begin{align*}
\text{ArH} & \quad (1.0 \text{ equiv}) \quad \xrightarrow{\text{Ph$_3$P$^+CH_2Br$ (1.2 equiv)}} \quad \text{ArH} & \quad \xrightarrow{\text{Anhydrous THF}} \quad \text{ArH}
\end{align*}
\]

In an oven dried flask, methyl triphenylphosphonium bromide (1.2 equiv) in THF (1.6 mL/mmol) was added. The suspension was cooled to 0 °C, KO'Bu (1.2 equiv) was added and the resulting yellow suspension was stirred at 0 °C for 45 min. To this suspension, a solution of acetophenone (1.0 equiv) in THF (0.7 mL/mmol) was added dropwise and the resulting mixture was warmed
gradually to r.t. and stirred at r.t. for 16 h. Reaction mixture was concentrated under reduced pressure and filtered. The filtrate was concentrated under reduced pressure to yield a yellow oil. Purification by column chromatography over silica gel (230-400 mesh) using petroleum ether as eluent afforded 4b, 4c, 4d, 4e, 4f, 4g, 4h as a colorless oil.

C. Optimization of Reaction Conditions

In a 25 mL sealed test tube, a mixture of allylbenzene 1a (0.25 mmol), bis[(pinacolato)boryl]methane 2a (0.1 mmol), catalyst (10 mol %), ligand (15 mol %), base (2 equiv), additive (20 mol %), oxidant (2 equiv) in 2 mL solvent was vigorously stirred together for 24 h. After completion of the reaction and quenched by saturated brines, the mixture was extracted with ethyl acetate (3 × 10 mL). The combined ethyl acetate layer was then dried over anhydrous sodium sulfate and concentrated in vacuum. Further purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded the pure product 3a, and calculated the isolated yield.

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<th>oxidant</th>
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<td>NQ</td>
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</table>
a A mixture of 1a (0.25 mmol, 2.5 equiv), 2a (0.1 mmol, 1 equiv), base (0.2 mmol, 2 equiv), catalyst (10 mol %), additive (20 mol %), ligand (15 mol %), oxidant (2 equiv) and solvent (2 mL) was sealed in a 25 mL Schlenk tube at 50°C for 24 h. N.D. = not detected. L1: PPh3. L2: dppf. L3: 4,4'-bipyridine. L4: 1,2-bis(phenylsulphonyl)ethane. L5: 1,2-bis(phenylsulfanyl)ethane. Isolated yields based on 2a. BQ:DDQ=2:1; BQ:DDQ=4:1. The reaction was at room temperature. The temperature was 100°C.

D. General Procedure for the Synthesis of Homoallylic Organoboronic Esters

In a 25 mL sealed test tube, a mixture of olefins 1 (0.25 mmol), bis[(pinacolato)boryl]methane 2a (0.1 mmol), Pd(OAc)2 (10 mol %), AgBF4 (20 mol %), KH2PO4 (2 equiv), NQ (2 equiv), 1,2-bis(phenylsulfanyl)ethane (10 mol %) and 2 mL of anhydrous 1,4-dioxane was vigorously stirred together at 50°C for 24 h. After completion of the reaction and quenched by saturated brine, the mixture was extracted with ethyl acetate (3 × 10 mL). The combined ethyl acetate layer was then dried over anhydrous sodium sulfate and concentrated in vacuum. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) afforded the pure product 3.

E. Possible Reaction Mechanism

In light of the previous literature, a plausible mechanism is outlined in the manuscript. In this
catalytic cycle, KH$_2$PO$_4$ represents an important additive in this oxidative allylic alkylation reaction. When screening for the optimal reaction conditions, various bases were surveyed and KH$_2$PO$_4$ was found to be the most effective base for this reaction. Based on these results and the literatures (Angew. Chem. Int. Ed. 2011, 50, 12236, Chem. Eur. J. 2011, 17, 14371, Chem. Commun. 2017, 53, 8316), we supposed that KH$_2$PO$_4$ behaved as an important additive in the step of allylic C-H activation. Furthermore, 1,1-bis[(pinacolato)boryl]methane underwent a deborylative transmetallation process to form an alkyl silver species III. In this process, ‘PinB-X’ should be appended as a releasing byproduct in the smaller catalytic cycle. Unfortunately, we are not able to detect or isolate this byproduct in our reaction.

F. Analysis Data for the Products

**(**E**)-4,4,5,5-Tetramethyl-2-(4-phenylbut-3-en-1-yl)-1,3,2-dioxaborolane (3a)**

![Structure of 3a](image)

21.4 mg, 83% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): $R_f$ = 0.23; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 - 7.28 (m, 3H), 7.25 (s, 1H), 7.19 - 7.14 (m, 1H), 6.38 (d, $J$ = 16.0 Hz, 1H), 6.27 (dt, $J$ = 16.0, 6.0 Hz, 1H), 2.33 (dd, $J$ = 15.2, 7.6 Hz, 2H), 1.24 (s, 12H), 0.98 (t, $J$ = 8.0 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.0, 132.8, 128.8, 128.4, 126.6, 125.9, 83.1, 27.3, 24.8; IR (KBr): 3883, 3606, 3296, 2924, 1736, 1456, 1145, 801, 694 cm$^{-1}$; HRMS (EI, m/z): [M]$^+$ Calcd. for C$_{16}$H$_{23}$NaO$_2$, 281.1683, found, 281.1684.

**(**E**)-4,4,5,5-Tetramethyl-2-(4-(p-tolyl)but-3-en-1-yl)-1,3,2-dioxaborolane (3b)**

![Structure of 3b](image)

23.9 mg, 88% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): $R_f$ = 0.25; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.22 (d, $J$ = 8.0 Hz, 2H), 7.09 (d, $J$ = 8.0 Hz, 2H), 6.35 (d, $J$ = 16.0 Hz, 1H), 6.22 (dt, $J$ = 16.0, 6.0 Hz, 1H), 2.38 - 2.27 (m, 5H), 1.24 (s, 12H), 0.98 (t, $J$ = 8.0 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.3, 135.2, 131.7, 129.1, 128.6, 125.8, 83.0, 27.3, 24.8, 21.1; IR (KBr): 3883, 3593, 3297, 2920, 1736, 1371, 1144, 797, 712 cm$^{-1}$; HRMS (ESI, m/z): [M+Na]$^+$ Calcd. for C$_{17}$H$_{25}$NaO$_2$, 295.1840, found, 295.1847.

**(**E**)-2-(4-(4-Ethylphenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)**

![Structure of 3c](image)

24.3 mg, 85% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): $R_f$ = 0.18; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.24 (d, $J$ = 8.0 Hz, 2H), 7.11 (d, $J$ = 8.0 Hz, 2H), 6.35 (d, $J$ = 16.0 Hz, 1H), 6.22 (dt, $J$ = 16.0, 6.0 Hz, 1H), 2.61 (q, $J$ = 8.0 Hz, 2H), 2.32 (q, $J$ = 8.0 Hz, 2H), 1.24 (s, 12H), 1.20 (d, $J$ = 8.0 Hz, 3H), 0.97 (t, $J$ = 8.0 Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 142.8, 135.5, 131.8, 128.7, 127.9, 125.9, 83.0, 28.5, 27.3, 24.8, 15.6; IR (KBr): 3881, 3729, 3610, 2928, 1745, 1370, 1143, 803, 707 cm$^{-1}$; HRMS (ESI, m/z): [M+Na]$^+$ Calcd. for C$_{18}$H$_{27}$NaO$_2$, 309.1996, 309.1997.
(E)-2-(4-(4-(tert-Butyl)phenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d)

\[
\begin{align*}
\text{Bu} & \\
\text{Bpin} &
\end{align*}
\]

19.2 mg, 79% yield; yellow oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R\text{f} = 0.25; \^H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.32 - 7.23 (m, 4H), 6.35 (d, J = 16.0 Hz, 1H), 6.23 (dt, J = 16.0, 6.4 Hz, 1H), 2.32 (q, J = 8.0 Hz, 2H), 1.30 (s, 9H), 1.24 (s, 12H), 0.97 (t, J = 8.0 Hz, 2H); \^C NMR (100 MHz, CDCl\textsubscript{3}) δ 149.6, 135.2, 132.0, 128.5, 125.6, 125.3, 83.0, 34.4, 31.3, 27.3, 24.8; IR (KBr): 3893, 3611, 3296, 2949, 1744, 1462, 1141, 803, 707 cm\textsuperscript{-1}; HRMS (ESI, m/z): [M+Na]\textsuperscript{+} Calcd. for C\textsubscript{20}H\textsubscript{31}BNaO\textsubscript{2}, 337.2313, found, 337.2310.

(\textit{E})-2-(4-(4-Methoxyphenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e)

\[
\begin{align*}
\text{MeO} & \\
\text{Bpin} &
\end{align*}
\]

In a 25 mL sealed test tube, a mixture of olefins 1a (0.25 mmol), bis[(pinacolato)boryl]methane 2a (0.1 mmol), Pd(OAc)\textsubscript{2} (10 mol %), AgBF\textsubscript{4} (20 mol %), KH\textsubscript{2}PO\textsubscript{4} (2 equiv), BQ (4 equiv), DDQ (1 equiv), 1,2-bis(phenylsulfinyl)ethane (10 mol %) and 2 mL of anhydrous dioxane was vigorously stirred together at 50 °C for 24 h. After completion of the reaction and quenched by saturated brines, the mixture was extracted with ethyl acetate (3 × 10 mL). The combined ethyl acetate layer was then dried over anhydrous sodium sulfate and concentrated in vacuum. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) afforded the pure product 3e.

22.2 mg, 88% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R\text{f} = 0.31; \^H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.25 (t, J = 4.0 Hz, 2H), 6.83 - 6.78 (m, 2H), 6.32 (d, J = 16.0 Hz, 1H), 6.13 (dt, J = 16.0, 6.4 Hz, 1H), 3.79 (s, 3H), 2.31 (dd, J = 14.0, 6.4 Hz, 2H), 1.24 (s, 12H), 0.97 (t, J = 8.0 Hz, 2H); \^C NMR (100 MHz, CDCl\textsubscript{3}) δ 158.6, 130.9, 130.7, 128.2, 127.0, 113.9, 83.1, 55.3, 27.3, 24.9; IR (KBr): 3885, 3607, 3295, 2924, 1520, 1370, 1238, 803, 705 cm\textsuperscript{-1}; HRMS (ESI, m/z): [M+Na]\textsuperscript{+} Calcd. for C\textsubscript{17}H\textsubscript{25}BNaO\textsubscript{3}, 311.1789, found, 311.1794.

(\textit{E})-2-(4-(4-Fluorophenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)

\[
\begin{align*}
\text{F} & \\
\text{Bpin} &
\end{align*}
\]

19.6 mg, 71% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R\text{f} = 0.17; \^H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.31 - 7.23 (m, 2H), 6.99 - 6.93 (m, 2H), 6.33 (d, J = 16.0 Hz, 1H), 6.18 (dt, J = 16.0, 6.4 Hz, 1H), 2.32 (q, J = 8.0 Hz, 2H), 1.24 (s, 12H), 0.97 (t, J = 8.0 Hz, 2H); \^C NMR (100 MHz, CDCl\textsubscript{3}) δ 161.8 (d, J = 245.2 Hz), 134.1 (d, J = 3.0 Hz), 132.5 (d, J = 3.0 Hz), 127.7, 127.3 (d, J = 8.0 Hz), 115.2 (d, J = 21.5 Hz), 83.1, 27.2, 24.8; IR (KBr): 3882, 3614, 3205, 2924, 1756, 1372, 1144, 799, 703 cm\textsuperscript{-1}; HRMS (ESI, m/z): [M+Na]\textsuperscript{+} Calcd. for C\textsubscript{16}H\textsubscript{23}BFNaO\textsubscript{2}, 299.1589, found, 299.1587.
(E)-2-(4-(4-Chlorophenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)

Cl

Bpin

22.2 mg, 76% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): Rf = 0.38; 1H NMR (400 MHz, CDCl3) δ 7.24 (s, 4H), 6.32 (d, J = 16.0 Hz, 1H), 6.25 (dt, J = 16.0, 6.4 Hz, 1H), 2.33 (q, J = 8.0 Hz, 2H), 1.24 (s, 12H), 0.97 (t, J = 8.0 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ 136.5, 133.5, 132.2, 128.5, 127.7, 127.1, 83.1, 27.3, 24.8; IR (KBr): 3886, 3618, 2924, 1742, 1372, 1322, 1145, 839, 681 cm⁻¹; HRMS (ESI, m/z): [M+Na]⁺ Calcd. for C16H22BClNaO2, 315.1294, found, 315.1294.

(E)-4,4,5,5-Tetramethyl-2-(4-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)-1,3,2-dioxaborolane (3h)

F₃C

Bpin

22.8 mg, 70% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): Rf = 0.31; 1H NMR (400 MHz, CDCl3) δ 7.52 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 6.40 - 6.38 (m, 2H), 2.39 - 2.34 (m, 2H), 1.24 (s, 12H), 0.99 (t, J = 8.0 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ 141.5, 135.6, 128.5 (q, J = 32.0 Hz), 127.7, 126.0, 125.4 (q, J = 3.8 Hz), 123.0, 83.1, 27.3, 24.8; IR (KBr): 3884, 3296, 2980, 1616, 1323, 1133, 843, 803, 711 cm⁻¹; HRMS (ESI, m/z): [M+Na]⁺ Calcd. for C17H22BF3NaO2, 349.1555, found, 349.1560.

(E)-4,4,5,5-Tetramethyl-2-(4-(m-tolyl)but-3-en-1-yl)-1,3,2-dioxaborolane (3i)

Bpin

22.6 mg, 83% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): Rf = 0.19; 1H NMR (400 MHz, CDCl3) δ 7.21 - 7.11 (m, 3H), 7.00 (d, J = 8.0 Hz, 1H), 6.36 (d, J = 16.0 Hz, 1H), 6.27 (dt, J = 16.0, 6.0 Hz, 1H), 2.38 - 2.27 (m, 5H), 1.26 (s, 12H), 0.99 (t, J = 8.0 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ 137.9, 137.9, 132.6, 128.9, 128.3, 127.4, 126.7, 123.1, 83.0, 27.3, 24.8, 21.4; IR (KBr): 3916, 3261, 3298, 2922, 1748, 1371, 1143, 796, 705 cm⁻¹; HRMS (ESI, m/z): [M+Na]⁺ Calcd. for C17H25BNaO2, 295.1840, found, 294.1842.

(E)-2-(4-(3-Fluorophenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)

Bpin

17.4 mg, 63% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): Rf = 0.21; 1H NMR (400 MHz, CDCl3) δ 7.25 - 7.19 (m, 1H), 7.10 - 6.97 (m, 2H), 6.89 - 6.82 (m, 1H), 6.38 - 6.24 (m, 2H), 2.33 (td, J = 8.0, 5.6 Hz, 2H), 1.24 (s, 12H), 0.98 (t, J = 8.0 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ 163.1 (d, J = 243.0 Hz), 140.4 (d, J = 8.0 Hz), 134.2, 129.8 (d, J = 8.0 Hz), 127.9
(d, \( J = 3.0 \) Hz), 121.8 (d, \( J = 3.0 \) Hz), 113.4 (d, \( J = 21.0 \) Hz), 112.3 (d, \( J = 22.0 \) Hz), 83.1, 27.3, 24.8; IR (KBr): 3882, 3620, 3296, 2922, 1754, 1372, 1143, 798, 679 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]\(^+\) Calcd. for C\(_{16}\)H\(_{22}\)BFNaO\(_2\), 299.1589, found, 299.1589.

(E)-4,4,5,5-Tetramethyl-2-(4-(o-tolyl)but-3-en-1-yl)-1,3,2-dioxaborolane (3k)

\[
\begin{align*}
&\text{(E)-4,4,5,5-Tetramethyl-2-(4-(o-tolyl)but-3-en-1-yl)-1,3,2-dioxaborolane (3k)} \\
&\text{Bpin} \\
&21.2 \text{ mg, 78% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): } R_f = 0.23; \text{ } ^1H \text{ NMR (400 MHz, CDCl}_3\text{)} \delta 7.41 (d, \( J = 7.2 \) Hz, 1H), 7.18 - 7.08 (m, 3H), 6.59 (d, \( J = 16.0 \) Hz, 1H), 6.16 (dt, \( J = 16.0, 6.0 \) Hz, 1H), 2.41 - 2.35 (m, 2H), 2.33 (s, 3H), 1.26 (s, 12H), 1.01 (t, \( J = 8.0 \) Hz, 2H); \text{ } ^13C \text{ NMR (100 MHz, CDCl}_3\text{)} \delta 137.0, 134.9, 134.1, 130.1, 126.6, 126.6, 125.9, 125.4, 83.0, 27.6, 24.8, 19.8; IR (KBr): 3886, 3601, 3294, 2922, 1641, 1371, 1145, 795, 709 cm\(^{-1}\); HRMS (ESI, m/z): [M+Na]\(^+\) Calcd. for C\(_{17}\)H\(_{25}\)BNaO\(_2\), 295.1840; found, 295.1847.
\end{align*}
\]

(E)-4,4,5,5-tetramethyl-2-(3-methyl-4-phenylbut-3-en-1-yl)-1,3,2-dioxaborolane (3l)

\[
\begin{align*}
&\text{(E)-4,4,5,5-tetramethyl-2-(3-methyl-4-phenylbut-3-en-1-yl)-1,3,2-dioxaborolane (3l)} \\
&\text{Bpin} \\
&19.6 \text{ mg, 72% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): } R_f = 0.30; \text{ } ^1H \text{ NMR (400 MHz, CDCl}_3\text{)} \delta 7.29 (t, \( J = 6.0 \) Hz, 3H), 7.24 (d, \( J = 12.0 \) Hz, 3H), 7.21 - 7.13 (m, 5H), 6.28 (s, 1.2H), 4.85 (s, 1H), 4.68 (s, 1H), 3.35 (s, 2H), 2.29 (t, \( J = 8.0 \) Hz, 2.4H), 2.18 - 2.05 (m, 2H), 1.85 (s, 3H), 1.24 (s, 14.4H), 1.22 (s, 12H), 1.06 - 1.00 (m, 2.4H), 0.97 - 0.92 (m, 2H); \text{ } ^13C \text{ NMR (100 MHz, CDCl}_3\text{)} \delta 150.7, 140.9, 140.0, 138.8, 129.0, 128.8, 128.2, 127.9, 125.9, 125.6, 123.6, 110.0, 83.0, 82.9, 43.0, 34.6, 29.6, 24.8, 24.8, 17.7; IR (KBr): 3885, 3614, 3296, 2921, 1646, 1370, 1144, 797, 704 cm\(^{-1}\); HRMS (ESI, m/z): [M+Na]\(^+\) Calcd. for C\(_{17}\)H\(_{25}\)BNaO\(_2\), 295.1840; found, 295.1841.
\end{align*}
\]

(E)-2-(4-(3,5-Dimethylphenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m)

\[
\begin{align*}
&\text{(E)-2-(4-(3,5-Dimethylphenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m)} \\
&\text{Bpin} \\
&23.5 \text{ mg, 82% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): } R_f = 0.28; \text{ } ^1H \text{ NMR (400 MHz, CDCl}_3\text{)} \delta 6.96 (s, 2H), 6.83 (s, 1H), 6.33 (d, \( J = 16.0 \) Hz, 1H), 6.25 (dt, \( J = 16.0, 6.4 \) Hz, 1H), 2.40 - 2.21 (m, 8H), 1.26 (s, 12H), 0.98 (t, \( J = 8.0 \) Hz, 2H); \text{ } ^13C \text{ NMR (100 MHz, CDCl}_3\text{)} \delta 137.9, 137.8, 132.4, 128.9, 128.4, 123.9, 123.9, 83.1, 27.4, 24.9, 21.3; IR (KBr): 3889, 3618, 3425, 2922, 1736, 1371, 1144, 801, 704 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]\(^+\) Calcd. for C\(_{18}\)H\(_{27}\)BNaO\(_2\), 309.1996, found, 309.2004.
\end{align*}
\]

(E)-2-(4-(2,4-Dimethylphenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3n)

\[
\begin{align*}
&\text{(E)-2-(4-(2,4-Dimethylphenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3n)} \\
&\text{Bpin} \\
&23.5 \text{ mg, 82% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): } R_f = 0.28; \text{ } ^1H \text{ NMR (400 MHz, CDCl}_3\text{)} \delta 6.96 (s, 2H), 6.83 (s, 1H), 6.33 (d, \( J = 16.0 \) Hz, 1H), 6.25 (dt, \( J = 16.0, 6.4 \) Hz, 1H), 2.40 - 2.21 (m, 8H), 1.26 (s, 12H), 0.98 (t, \( J = 8.0 \) Hz, 2H); \text{ } ^13C \text{ NMR (100 MHz, CDCl}_3\text{)} \delta 137.9, 137.8, 132.4, 128.9, 128.4, 123.9, 123.9, 83.1, 27.4, 24.9, 21.3; IR (KBr): 3889, 3618, 3425, 2922, 1736, 1371, 1144, 801, 704 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]\(^+\) Calcd. for C\(_{18}\)H\(_{27}\)BNaO\(_2\), 309.1996, found, 309.2004.
\end{align*}
\]
23.5 mg, 81% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.44; ^1H NMR (400 MHz, CDCl_3) δ 7.29 (d, J = 8.0 Hz, 1H), 6.94 (d, J = 8.0 Hz, 2H), 6.53 (d, J = 16.0 Hz, 1H), 6.10 (dt, J = 16.0, 6.4 Hz, 1H), 2.35 - 2.31 (m, 2H), 2.28 (s, 6H), 1.24 (s, 12H), 0.98 (t, J = 8.0 Hz, 2H); ^13C NMR (100 MHz, CDCl_3) δ 136.2, 134.7, 134.2, 133.2, 130.8, 126.7, 126.4, 125.4, 83.0, 27.6, 24.8, 21.0, 19.7; IR (KBr): 3887, 3620, 2921, 1748, 1545, 1370, 1141, 801, 709 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]^+ Calcd. for C_{18}H_{27}BNaO_2, 309.1996, found, 309.2002.

\((E)-2-(4-(2,5-Dimethylphenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o)\)

\(\begin{align*}
\text{Bpin} \\
\end{align*}\)

24.3 mg, 85% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.33; ^1H NMR (400 MHz, CDCl_3) δ 7.22 (s, 1H), 6.99 (d, J = 8.0 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 6.54 (d, J = 16.0 Hz, 1H), 6.13 (dt, J = 16.0, 6.4 Hz, 1H), 2.35 (q, J = 8.0 Hz, 2H), 2.29 (s, 3H), 2.27 (s, 3H), 1.25 (s, 12H), 0.99 (t, J = 8.0 Hz, 2H); ^13C NMR (100 MHz, CDCl_3) δ 136.8, 135.2, 133.8, 131.8, 130.0, 127.4, 126.7, 126.1, 83.0, 27.6, 24.8, 21.0, 19.3; IR (KBr): 3914, 3727, 3065, 2927, 1617, 1371, 1321, 1144, 825 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]^+ Calcd. for C_{18}H_{27}BNaO_2, 309.1996, found, 309.2002.

\((E)-2-(4-(3,4-Dimethoxyphenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3p)\)

\(\begin{align*}
\text{Bpin} \\
\end{align*}\)

15.3 mg, 48% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 10/1, v/v): R_f = 0.21; ^1H NMR (400 MHz, CDCl_3) δ 6.90 (d, J = 4.0 Hz, 1H), 6.85 (dd, J = 8.0, 2.0 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.31 (d, J = 16.0 Hz, 1H), 6.14 (dt, J = 16.0, 6.4 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 2.37 - 2.26 (m, 2H), 1.24 (s, 12H), 0.98 (t, J = 8.0 Hz, 2H); ^13C NMR (100 MHz, CDCl_3) δ 149.0, 148.2, 131.2, 130.9, 128.5, 118.8, 111.2, 108.6, 83.1, 55.9, 55.8, 27.2, 24.8, 21.0, 19.3; IR (KBr): 3986, 3623, 3418, 2923, 1731, 1371, 1321, 1144, 825 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]^+ Calcd. for C_{18}H_{27}BNaO_4, 341.1895, found, 341.1895.

\((E)-2-(4-Mesitylbut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3q)\)

\(\begin{align*}
\text{Bpin} \\
\end{align*}\)

23.7 mg, 79% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.38; ^1H NMR (400 MHz, CDCl_3) δ 6.86 (s, 2H), 6.29 (d, J = 16.0 Hz, 1H), 5.73 (dt, J = 16.0, 6.4 Hz, 1H), 2.37 (q, J = 8.0 Hz, 2H), 2.27 (s, 9H), 1.27 (s, 12H), 1.01 (t, J = 8.0 Hz, 2H); ^13C NMR (100 MHz, CDCl_3) δ 137.3, 135.8, 135.4, 134.7, 128.3, 126.0, 83.0, 27.7, 24.8, 20.8; IR (KBr): 3886, 3608, 3295, 2923, 1732, 1372, 1144, 797, 703 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]^+ Calcd. for C_{19}H_{30}BNaO_2, 323.2153, found, 323.2158.
(E)-4,4,5,5-Tetramethyl-2-(4-(perfluorophenyl)but-3-en-1-yl)-1,3,2-dioxaborolane (3r)

32.4 mg, 93% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.41; ^1H NMR (400 MHz, CDCl_3) δ 6.63 (dt, J = 16.0, 6.4 Hz, 1H), 6.27 (d, J = 16.0 Hz, 1H), 2.39 (q, J = 8.0 Hz, 2H), 1.25 (s, 12H), 0.99 (t, J = 8.0 Hz, 2H); ^13C NMR (100 MHz, CDCl_3) δ 144.5 (dm, J = 249.1 Hz), 142.7 (td, J = 7.4, 2.0 Hz), 139.2 (dm, J = 252.7 Hz), 137.6 (dm, J = 251.3 Hz), 113.18 (t, J = 1.0 Hz), 112.62 (td, J = 14.3, 4.0 Hz), 83.2, 28.6, 24.7; IR (KBr): 3850, 3620, 2982, 2925, 1647, 1376, 1144, 842, 669 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]^+ Calcd. for C_{16}H_{18}BF_5NaO_2, 371.1212, found, 371.1210.

(E)-4,4,5,5-Tetramethyl-2-(4-(naphthalen-1-yl)but-3-en-1-yl)-1,3,2-dioxaborolane (3s)

21.3 mg, 78% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.14; ^1H NMR (400 MHz, CDCl_3) δ 8.17 - 8.10 (m, 1H), 7.82 (dd, J = 6.4, 2.8 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 7.2 Hz, 1H), 7.49 - 7.36 (m, 3H), 7.12 (d, J = 16.0 Hz, 1H), 6.30 (dt, J = 16.0, 6.4 Hz, 1H), 2.49 - 2.42 (m, 2H), 1.25 (s, 12H), 1.07 (t, J = 8.0 Hz, 2H); ^13C NMR (100 MHz, CDCl_3) δ 136.0, 135.8, 133.6, 131.2, 128.4, 127.1, 125.9, 125.6, 125.5, 124.0, 123.4, 83.1, 27.7, 24.9; IR (KBr): 3876, 3607, 3296, 2925, 1471, 1372, 1144, 828, 680 cm\(^{-1}\); HRMS (ESI, m/z): [M+H]^+ Calcd. for C_{20}H_{25}BNaO_2, 331.1840, found, 331.1846.

(E)-2-(4-(Dibenzo[b,d]furan-2-yl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3t)

24.4 mg, 70% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.23; ^1H NMR (400 MHz, CDCl_3) δ 7.94 - 7.87 (m, 2H), 7.53 (d, J = 8.0 Hz, 1H), 7.43 (ddd, J = 8.0, 4.4, 2.0 Hz, 3H), 7.32 (td, J = 8.0, 0.8 Hz, 1H), 6.52 (d, J = 16.0 Hz, 1H), 6.32 (dt, J = 16.0, 6.4 Hz, 1H), 2.38 (td, J = 8.0, 1.2 Hz, 2H), 1.25 (s, 12H), 1.03 (t, J = 8.0 Hz, 2H); ^13C NMR (100 MHz, CDCl_3) δ 156.6, 155.4, 133.1, 132.0, 128.7, 127.0, 125.4, 124.4, 124.3, 122.6, 120.6, 117.7, 111.6, 111.4, 83.1, 27.4, 24.8; IR (KBr): 3066, 2973, 1672, 1590, 1463, 1369, 1189, 964, 747, 664 cm\(^{-1}\); HRMS (ESI, m/z): [M+Na]^+ Calcd. for C_{22}H_{25}BNaO_3, 371.1789, found, 371.1790.

4,4,5,5-Tetramethyl-2-(3-phenylbut-3-en-1-yl)-1,3,2-dioxaborolane (5a)

---

S10
23.2 mg, 90% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.20; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.42 - 7.38 (m, 2H), 7.32 - 7.28 (m, 2H), 7.26 - 7.21 (m, 1H), 5.23 (s, 1H), 5.07 (d, \(J = 1.2\) Hz, 1H), 2.63 - 2.58 (m, 2H), 1.23 (s, 12H), 1.02 - 0.95 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 150.4, 141.7, 128.1, 127.1, 126.2, 111.0, 83.0, 29.3, 24.8; IR (KBr): 3835, 3742, 3620, 2923, 1691, 1533, 1142, 793, 707 cm\(^{-1}\); HRMS (ESI, m/z): [M+Na]\(^+\) Calcd. for C\(_{16}\)H\(_{23}\)BNaO\(_2\), 281.1683, found, 281.1682.

2-(3-(4-\textit{iso}Butylphenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5b)

\begin{center}
\includegraphics{image}
\end{center}

25.5 mg, 81% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.47; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.32 (d, \(J = 8.0\) Hz, 2H), 7.08 (d, \(J = 8.0\) Hz, 2H), 5.22 (s, 1H), 5.03 (d, \(J = 1.2\) Hz, 1H), 2.62 - 2.56 (m, 2H), 2.45 (d, \(J = 8.0\) Hz, 2H), 1.85 (dt, \(J = 13.2,\) 6.8 Hz, 1H), 1.23 (s, 12H), 1.02 - 0.96 (m, 2H), 0.90 (d, \(J = 8.0\) Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 150.1, 140.7, 138.9, 128.9, 125.8, 110.2, 83.0, 45.1, 30.2, 29.3, 24.8, 22.4; IR (KBr): 3894, 3457, 3293, 2924, 1743, 1371, 1142, 800, 712 cm\(^{-1}\); HRMS (ESI, m/z): [M+Na]\(^+\) Calcd. for C\(_{20}\)H\(_{31}\)BNaO\(_2\), 337.2309, found, 337.2317.

2-(3-(4-Fluorophenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5c)

\begin{center}
\includegraphics{image}
\end{center}

19.6 mg, 71% yield; light yellow oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): R_f = 0.20; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.39 - 7.33 (m, 2H), 6.98 (t, \(J = 8.0\) Hz, 2H), 5.18 (s, 1H), 5.01 (d, \(J = 1.2\) Hz, 1H), 2.60 - 2.53 (m, 2H), 1.23 (s, 12H), 1.01 - 0.92 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.2 (d, \(J = 245.0\) Hz), 149.3, 137.7 (d, \(J = 3.0\) Hz), 127.7 (d, \(J = 8.0\) Hz), 114.9 (d, \(J = 21.0\) Hz), 111.0, 83.1, 29.5, 24.8; IR (KBr): 3887, 3800, 3459, 2924, 1743, 1371, 1142, 800, 712 cm\(^{-1}\); HRMS (ESI, m/z): [M+Na]\(^+\) Calcd. for C\(_{16}\)H\(_{22}\)BFNaO\(_2\), 299.1589, found, 299.1590.

2-(3-(4-Chlorophenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5d)

\begin{center}
\includegraphics{image}
\end{center}

24.2 mg, 83% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50:1, v/v): R_f = 0.38; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.35 - 7.31 (m, 2H), 7.29 - 7.27 (m, 2H), 5.22 (s, 1H), 5.08 (d, \(J = 1.2\) Hz, 1H), 2.61 - 2.51 (m, 2H), 1.23 (s, 12H), 1.01 - 0.91 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 149.2, 140.1, 132.9, 128.3, 127.5, 111.6, 83.1, 29.3, 24.8; IR (KBr): 3883, 3802, 3459, 2924, 1737, 1370, 1135, 805, 707 cm\(^{-1}\); HRMS (ESI, m/z): [M+ Na]\(^+\) Calcd. for C\(_{16}\)H\(_{22}\)BClNaO\(_2\), 315.1294, found, 315.1293.
2-(3-(3-Bromophenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5e)

![Structure](image)

20.8 mg, 62% yield; light yellow oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): RF = 0.35; 1H NMR (400 MHz, CDCl₃) δ 7.54 (t, J = 1.6 Hz, 1H), 7.39 - 7.36 (m, 1H), 7.33 - 7.30 (m, 1H), 7.17 (t, J = 8.0 Hz, 1H), 5.23 (s, 1H), 5.10 (d, J = 1.2 Hz, 1H), 2.56 (t, J = 8.0 Hz, 2H), 1.23 (s, 12H), 1.03 - 0.90 (m, 2H); 13C NMR (100 MHz, CDCl₃) δ 149.2, 144.0, 130.1, 129.7, 129.3, 124.8, 122.4, 112.2, 83.1, 29.2, 24.8; IR (KBr): 3889, 3612, 3298, 2924, 1641, 1552, 1143, 796, 708 cm⁻¹; HRMS (ESI, m/z): [M+Na]⁺ Calcd. for C₁₆H₂₁BBrNaO₂, 359.0788, found, 359.0786.

2-(3-(3,4-dichlorophenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5f)

![Structure](image)

25.8 mg, 79% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): RF = 0.36; 1H NMR (400 MHz, CDCl₃) δ 7.48 (d, J = 2.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.23 (dd, J = 8.4, 2.0 Hz, 1H), 5.24 (s, 1H), 5.12 (s, 1H), 2.54 (t, J = 8.0 Hz, 2H), 1.23 (s, 12H), 1.01 - 0.90 (m, 2H); 13C NMR (100 MHz, CDCl₃) δ 148.2, 141.8, 132.2, 130.9, 130.0, 128.1, 125.6, 112.6, 83.1, 29.1, 24.8; IR (KBr): 3883, 3612, 3296, 2925, 1471, 1372, 1144, 797, 703 cm⁻¹; HRMS (ESI, m/z): [M+Na]⁺ Calcd. for C₁₆H₁₂BCl₂NaO₂, 349.0904, found, 349.0903.

4,4,5,5-Tetramethyl-2-(3-(naphthalen-2-yl)but-3-en-1-yl)-1,3,2-dioxaborolane (5g)

![Structure](image)

25.3 mg, 82% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): RF = 0.28; 1H NMR (400 MHz, CDCl₃) δ 7.87 - 7.76 (m, 4H), 7.60 (d, J = 8.4, 1.6 Hz, 1H), 7.40 - 7.31 (m, 2H), 5.40 (s, 1H), 5.20 (d, J = 1.2 Hz, 1H), 2.77 - 2.70 (m, 2H), 1.25 (s, 12H), 1.11 - 1.02 (m, 2H); 13C NMR (100 MHz, CDCl₃) δ 150.2, 138.9, 133.4, 132.7, 128.1, 127.6, 127.5, 125.9, 125.6, 124.9, 124.7, 111.6, 83.0, 29.3, 24.8; IR (KBr): 3884, 3296, 3060, 2927, 1735, 1371, 1237, 1146, 965 cm⁻¹; HRMS (ESI, m/z): [M+Na]⁺ Calcd. for C₂₀H₁₅BNaO₂, 331.1840, found, 331.1849.

4,4,5,5-Tetramethyl-2-(3-(naphthalen-1-yl)but-3-en-1-yl)-1,3,2-dioxaborolane (5h)

![Structure](image)

24.0 mg, 78% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): RF = 0.28; 1H
NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 - 8.03 (m, 1H), 7.84 - 7.80 (m, 1H), 7.73 (d, $J$ = 8.0 Hz, 3H), 7.48 - 7.38 (m, 1H), 7.29 - 7.22 (m, 1H), 5.38 (s, 1H), 5.02 (d, $J$ = 1.2 Hz, 1H), 2.60 (t, $J$ = 8.0 Hz, 2H), 1.22 (s, 12H), 1.03 - 0.94 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 150.8, 141.8, 133.7, 131.5, 128.1, 127.0, 126.1, 125.6, 125.5, 125.2, 125.1, 113.7, 83.1, 32.7, 24.9; IR (KBr): 3919, 3617, 3454, 2920, 1642, 1368, 1138, 794, 707 cm$^{-1}$; HRMS (ESI, m/z): [M+Na]$^+$ Calcd. for C$_{20}$H$_{25}$BNaO$_2$, 331.1840, found, 331.1849.

**G. Elaboration of Homoallyl Boronates**

![Chemical structure](image)

In a 25 mL sealed test tube, a mixture of olefins 4j (0.25 mmol), bis[(pinacolato)boryl]methane 2a (0.1 mmol), Pd(OAc)$_2$ (10 mol %), AgBF$_4$ (20 mol %), KH$_2$PO$_4$ (2 equiv), BQ (4 equiv), DDQ (1 equiv), 1,2-bis(phenylsulfinyl)ethane (10 mol %) and 2 mL of anhydrous dioxane was vigorously stirred together at 50 $^\circ$C for 24 h. After completion of the reaction and quenched by saturated brines, the mixture was extracted with ethyl acetate (3 × 10 mL). The combined ethyl acetate layer was then dried over anhydrous sodium sulfate and concentrated in vacuum. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) afforded the pure product 7b.

19.7 mg, 78% yield; colorless oil; TLC (petroleum ether/ethyl acetate = 50/1, v/v): $R_f$ = 0.31; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.25 (t, $J$ = 4.0 Hz, 2H), 6.83 - 6.78 (m, 2H), 6.32 (d, $J$ = 16.0 Hz, 1H), 6.13 (dt, $J$ = 16.0, 6.4 Hz, 1H), 3.79 (s, 3H), 2.31 (dd, $J$ = 14.0, 6.4 Hz, 2H), 1.24 (s, 12H), 0.97 (t, $J$ = 8.0 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.6, 130.9, 130.7, 128.2, 127.0, 113.9, 83.1, 55.3, 27.3, 24.9; IR (KBr): 3885, 3607, 3295, 2924, 1736, 1456, 1145, 801, 694 cm$^{-1}$; HRMS (ESI, m/z): [M+Na]$^+$ Calcd. for C$_{17}$H$_{23}$BNaO$_3$, 311.1788; found, 311.1794.

![Chemical structure](image)
A solution of 3a (52 mg, 0.20 mmol) in THF (2.0 mL) and H₂O (2.0 mL) was added NaBO₃·4H₂O (0.18 g, 1.2 mmol, 6.0 equiv) at room temperature. The reaction mixture was stirred for 12 h and quenched by addition of saturated aq. Na₂S₂O₃ (5.0 mL). The mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with water and brine, dried (Na₂SO₄) and concentrated in vacuo to give a crude product. Purification by flash column chromatography (silica gel, eluting with petroleum ether/ethyl acetate) afforded the (E)-4-phenylbut-3-en-1-ol (8) as yellow oil (25.5 mg, 86%). ¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 8.0 Hz, 2H), 7.21 (t, J = 7.2 Hz, 1H), 6.49 (d, J = 16.0 Hz, 1H), 6.20 (dt, J = 16.0, 6.0 Hz, 1H), 3.75 (t, J = 8.0 Hz, 2H), 2.48 (q, J = 8.0 Hz, 2H), 1.73 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 137.2, 132.8, 128.5, 127.2, 126.3, 126.0, 62.0, 36.4; IR (KBr): 3779, 3267, 2829, 2400, 1807, 1188, 913, 555 cm⁻¹; HRMS (EI, m/z): [M]+ Calcd. for C₁₀H₁₂O, 171.0780, found, 171.0778.

A solution of 3a (52 mg, 0.20 mmol) in toluene (1.0 mL) and Cu(OAc)₂ (10 mol %), Ag₂CO₃ (2.0 equiv) was added. The reaction mixture was stirred for 20 h at 100 °C. After the completion of the reaction, the mixture was extracted with ethyl acetate (3 × 10 mL mL). The combined organic layers were washed with water and brine, dried (Na₂SO₄) and concentrated in vacuo to give a crude product. Purification by flash column chromatography (silica gel, eluting with petroleum ether/ethyl acetate) afforded the (E)-N-ethyl-N-(4-phenylbut-3-en-1-yl)aniline (9) as yellow oil (39.2 mg, 78%). ¹H NMR (400 MHz, CDCl₃) δ 7.37 - 7.27 (m, 4H), 7.22 (dd, J = 16.0, 7.2 Hz, 3H), 6.75 - 6.63 (m, 3H), 6.46 (d, J = 16.0 Hz, 1H), 6.23 (dt, J = 16.0, 6.0 Hz, 1H), 3.47 - 3.34 (m, 4H), 2.50 (dd, J = 14.4, 7.2 Hz, 2H), 1.17 (t, J = 8.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 147.7, 137.5, 131.6, 129.3, 128.5, 127.7, 127.1, 126.0, 115.6, 111.9, 50.3, 45.0, 31.3, 12.4; IR (KBr): 3666, 3359, 2866, 1806, 1382, 1184, 949, 529 cm⁻¹; HRMS (EI, m/z): [M]+ Calcd. for C₁₈H₂₂N, 252.1747, found, 252.1748.

H. References
I. NMR Spectra for New Compounds

![NMR Spectra](image-url)
$3i$
3I:3\textquotesingle I=1.2:1

3I:3\textquotesingle I=1.2:1
$\text{Bpin}$

*3p*
$5g$
3a