# Nickel-Catalyzed Regioselective Alkenylboration of

# **Alkenylarenes to Access Homoallyl Boronic Esters**

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## 1. General Considerations

All manipulations were conducted with Schlenk tube. <sup>1</sup>H NMR spectra were recorded on JNM-ECZ400S/L1 and JNM-ECZ600R/S1 spectrometers. Chemical shifts (in ppm) were referenced to tetramethylsilane ( $\delta = 0$  ppm) in CDCl<sub>3</sub> as an internal standard. Data were reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz), integration and assignment. <sup>13</sup>C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl<sub>3</sub> ( $\delta$  = 77.00 ppm). <sup>19</sup>F NMR spectra were obtained by the same NMR and CF<sub>3</sub>COOH was employed as external standard for the <sup>19</sup>F-NMR measurement. GC analysis was completed on an Agilent Technologies GC-7890B gas chromatograph, using ethyl acetate for sample preparation and nitrogen as a carrier gas. GC-MS analysis was completed on a Shimadzu GCMS-QP2010SE gas chromatograph mass spectrometer, using ethyl acetate for sample preparation and helium as a carrier gas. High resolution mass spectrometry (HRMS) data were obtained on a QTOF mass analyzer with electrospray ionization (ESI) through a Waters Acquity UPLC Class I/Xevo G2 Q-Tof. Substrates were purchased from Aldrich, TCI, Acros, Energy, Aladdin, or synthesized according to the procedures outlined below. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

### 2. Synthesis of Substrates

## 2.1 Synthesis of alkenylarenes

These substrates were prepared according to the corresponding literature reports. Analytical data (<sup>1</sup>H NMR, <sup>13</sup>C NMR) matches with the literature.



A suspension of methyltriphenylphosphonium bromide (2.9 g, 8.1 mmol) in dry THF (30 ml) under inert atmosphere was cooled at 0 °C with an ice bath. Then *n*-BuLi (3.2 ml, 2.5 M in n-hexane, 8.1 mmol) was added dropwise. After stirring for 30 min, corresponding aldehyde (5.4 mmol) (dissolved in THF (20 ml)) was added dropwise and the reaction mixture was warmed to room temperature for an additional hour. Then the reaction mixture was quenched with sat. NH<sub>4</sub>Cl aq. (20 mL) and extracted with EtOAc (20 mL × 3). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the alkenylarenes **1**.



2-phenyl-5-vinylthiophene (1r). The general procedure was followed using

5-phenylthiophene-2-carbaldehyde (1.02 g, 5.4 mmol), afforded product **1r** (663 mg, 66% yield). yellow solid. <sup>1</sup>**H NMR** (CDCl<sub>3</sub>, 600 MHz)  $\delta$ : 7.60-7.59 (m, 2H), 7.37 (t, J = 7.8 Hz, 2H), 7.29-7.26 (m, 1H), 7.18 (d, J = 3.6 Hz, 1H), 6.94 (d, J = 3.6 Hz, 1H), 6.79 (dd,  $J_1 = 17.4$ ,  $J_2 = 10.8$  Hz, 1H), 5.58 (d, J = 17.4 Hz, 1H), 5.16 (d, J = 10.8 Hz, 1H); <sup>13</sup>**C NMR** (CDCl<sub>3</sub>, 150 MHz)  $\delta$ : 143.0, 142.4, 134.2, 129.9, 128.9, 127.5, 127.0, 125.6, 123.2, 113.2 ppm; **HRMS** (ESI-TOF) *m/z* calcd for C<sub>12</sub>H<sub>11</sub>S (M + H)<sup>+</sup>: 187.0582, found 187.0585.



**1-methyl-4-vinyl-1***H***-indole (1v).** The general procedure was followed using 1-methyl-1H-indole-4-carbaldehyde (860 mg, 5.4 mmol), afforded product **1v** (593 mg, 70% yield) yellow oil. <sup>1</sup>**H NMR** (CDCl<sub>3</sub>, 600 MHz)  $\delta$ : 7.25-7.22 (m, 1H), 7.18-7.15 (m, 2H), 7.12-7.05 (m, 1H), 6.97 (d, J = 3.6 Hz, 1H), 6.64 (d, J = 3.0 Hz, 1H), 5.89 (d, J = 18.0 Hz, 1H), 5.35 (d, J = 11.4 Hz, 1H), 3.63 (s, 3H); <sup>13</sup>**C NMR** (CDCl<sub>3</sub>, 150 MHz)  $\delta$ : 137.0, 135.3, 129.9, 129.0, 126.5, 121.4, 116.8, 114.4, 108.7, 99.2, 32.8 ppm; **HRMS** (ESI-TOF) *m/z* calcd for C<sub>11</sub>H<sub>12</sub>N (M + H)<sup>+</sup>: 158.0970, found 158.0967.

## 2.2 Synthesis of Alkenyl Bromides

These substrates were prepared according to the corresponding literature reports. Analytical data (<sup>1</sup>H NMR, <sup>13</sup>C NMR) matches with the literature.



## 3. The effect of different reaction conditions

MeO 1a	<sup>≈</sup> + B <sub>2</sub> Pin <sub>2</sub> +	$Br = \frac{1}{1,4}$ 2a ( <i>E</i> / <i>Z</i> = 84:16)	liCl <sub>2</sub> •glyme (5 mol%) <b>L1</b> (7 mol%) Base (2.0 equiv) -Dioxane, 30 °C, 24 h MeO	BPin 3a
	Entry	Bases	Yield (%) <sup>b</sup>	
	1	LiOMe	79	
	2	NaOMe	31	
	3	KOMe	26	
	4	LiO <sup>t</sup> Bu	40	
	5	NaO <sup>t</sup> Bu	26	
	6	K <sub>3</sub> PO <sub>4</sub>	38	
	7	Na <sub>2</sub> CO <sub>3</sub>	15	
-	8	KF	0	

Table S1. The effect of different bases <sup>a</sup>

<sup>*a*</sup> Standard conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), B<sub>2</sub>Pin<sub>2</sub> (0.4 mmol), NiCl<sub>2</sub>•glyme (0.01 mmol), **L1** (0.014 mmol), Base (0.4 mmol), 1,4-Dioxane (2.0 mL), at 30 °C for 24 h. <sup>*b*</sup> Yields determined by GC using *n*-dodecane as the internal standard.



## Table S2. The effect of different Solvents<sup>*a*</sup>

<sup>a</sup> Standard conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), B<sub>2</sub>Pin<sub>2</sub> (0.4 mmol), NiCl<sub>2</sub>•glyme (0.01 mmol), **L1** (0.014 mmol), LiOMe (0.4 mmol), Solvent (2.0 mL), at 30 °C for 24 h. <sup>b</sup> Yields determined by GC using *n*-dodecane as the internal standard.



## Table S3. The effect of different [Ni]-salts<sup>*a*</sup>

<sup>a</sup> Standard conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), B<sub>2</sub>Pin<sub>2</sub> (0.4 mmol), Ni-salt (0.01 mmol), **L1** (0.014 mmol), LiOMe (0.4 mmol), DMA (2.0 mL), at 30 °C for 24 h. <sup>*b*</sup> Yields determined by GC using *n*-dodecane as the internal standard. <sup>*c*</sup> Isolated yield.

MeO 1a	+ B₂Pin₂ +	<b>2a</b> ( <i>E</i> /Z = 84:16)	Ni(ClO <sub>4</sub> ) <sub>2</sub> •6H <sub>2</sub> O (5 mol%) Ligand (7 mol%) LiOMe (2.0 equiv) DMA, 30 °C, 24 h	BPin 3a
	Entry	Ligands	Yield (%) <sup>b</sup>	_
	1	L1	93	
	2	L2	76	
	3	L3	89	
	4	L4	0	
	5	L5	0	
	6	L6	0	
	7	L7	0	
	8	L8	0	
	9	L9	0	
	10	none	0	

## Table S4. The effect of different ligands<sup>*a*</sup>

<sup>a</sup> Standard conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), B<sub>2</sub>Pin<sub>2</sub> (0.4 mmol), Ni(ClO<sub>4</sub>)<sub>2\*</sub> 6H<sub>2</sub>O (0.01 mmol), Ligand (0.014 mmol), LiOMe (0.4 mmol), DMA (2.0 mL), at 30 °C for 24 h. <sup>*b*</sup> Yields determined by GC using *n*-dodecane as the internal standard.



#### 4. General procedure for the reaction

General procedure :



In an oven dried 25-ml Schlenk tube, which contained a stirring bar, was charged with Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (3.7 mg, 0.01 mmol, 5 mol%), L1 (3.2 mg, 0.014 mmol, 7 mol%), B<sub>2</sub>Pin<sub>2</sub> (102 mg, 0.4 mmol, 2.0 equiv), and LiOMe (15 mg, 0.4 mmol, 2.0 equiv). The tube was evacuated and back-filled under a N<sub>2</sub> flow (this sequence was repeated three times), then anhydrous DMA (2.0 ml) was added under N<sub>2</sub>. After above, 1 (0.2 mmol, 1.0 equiv) and 2 (0.4 mmol, 2.0 equiv) was added subsequently under N<sub>2</sub>, the tube was stirred at 30 °C for 24 h. *n*-Dodecane (23  $\mu$ L) was added as an internal standard for GC analysis. The resulting mixture was diluted with EtOAc (2 mL) and quenched by H<sub>2</sub>O (2 mL), then it was extracted with EtOAc (10 ml  $\times$  3), the organic layer was combined and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated by rotary evaporation. The residue was purified by silica gel column chromatography to afford the product **3** or **4**.

#### 5. Analytical data for compounds



(*E*)-2-(2-(4-methoxyphenyl)-4-phenylbut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a): The general procedure A was followed using 1-methoxy-4-vinylbenzene (1a, 27 mg, 0.20 mmol) and (2-bromovinyl)benzene (2a, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3a as a yellow solid (64mg, 88% yield): Rf = 0.7 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.33-7.30 (m, 2H), 7.28-7.24 (m, 2H), 7.22-7.15 (m, 3H), 6.85-6.82 (m, 2H), 6.42-6.32 (m, 2H), 3.81-3.71 (m, 4H), 1.41-1.31 (m, 2H), 1.14 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 157.9, 137.9, 137.7, 136.0, 128.4, 128.0, 126.8, 126.1, 113.7, 83.1, 55.2, 43.5, 24.8, 24,7 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>23</sub>H<sub>30</sub>BO<sub>3</sub> (M + H)<sup>+</sup>: 364.2324, found 364.2333.



(*E*)-4-(4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-yl)phenyl acetate (**3b**): The general procedure A was followed using 4-vinylphenyl acetate (**1b**, 32 mg, 0.20 mmol) and (2-bromovinyl)benzene (**2a**, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product **3b** as a yellow solid (60 mg, 76% yield): Rf = 0.2 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.33-7.31 (m, 2H), 7.29-7.24 (m, 4H), 7.19-7.15 (m, 1H), 7.01-6.98 (m, 2H), 6.43-6.31 (m, 2H), 3.78 (q, *J* = 7.6 Hz, 1H), 2.27 (s, 3H), 1.42-1.32 (m, 2H), 1.14 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 169.5, 148.9, 143.3, 137.5, 135.3, 128.5, 128.42, 128.39, 127.0, 126.1, 121.3, 83.2, 43.8, 24.8, 24.7, 21.1 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>24</sub>H<sub>28</sub>BO<sub>4</sub> (M - H)<sup>-</sup>: 390.2117, found 390.2107.



(*E*)-2-(2-(4-(tert-butyl)phenyl)-4-phenylbut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan e (3c): The general procedure A was followed using 1-(tert-butyl)-4-vinylbenzene (1c, 32 mg, 0.20 mmol) and (2-bromovinyl)benzene (2a, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3c as a yellow solid (66 mg, 84% yield): Rf = 0.7 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.34-7.25 (m, 6H), 7.24-7.20 (m, 2H), 7.19-7.14 (m, 1H), 6.46-6.34 (m, 2H), 3.76 (q, *J* = 7.6 Hz, 1H), 1.43-1.35 (m, 2H), 1.30 (s, 9H), 1.13 (s, 6H), 1.12 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 148.8, 142.7, 137.7, 135.7, 128.4, 128.1, 127.0, 126.8, 126.2, 125.2, 83.1, 43.9, 34.3, 31.4, 24.8, 24.6 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>26</sub>H<sub>36</sub>BO<sub>2</sub> (M + H)<sup>+</sup>: 390.2845, found 390.2850.



(*E*)-4,4,5,5-tetramethyl-2-(4-phenyl-2-(p-tolyl)but-3-en-1-yl)-1,3,2-dioxaborolane (3d): The general procedure A was followed using1-methyl-4-vinylbenzene (1d, 24 mg, 0.20 mmol) and (2-bromovinyl)benzene (2a, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3d as a yellow solid (56 mg, 80% yield): Rf = 0.8 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) & 7.33-7.30 (m, 2H), 7.29-7.27 (m, 1H), 7.26-7.24 (m, 1H), 7.19-7.14 (m, 3H), 7.11-7.08 (m, 2H), 6.44-6.33 (m, 2H), 3.75 (q, J = 7.6 Hz, 1H), 2.31 (s, 3H), 1.43-1.31 (m, 2H), 1.15 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) & 142.8, 137.7, 135.8, 135.5, 129.0, 128.4, 128.1, 127.3, 126.8, 126.1, 83.1, 43.9, 24.8, 24.7, 21.0 ppm; HRMS (ESI-TOF) *m*/*z* calcd for C<sub>23</sub>H<sub>30</sub>BO<sub>2</sub> (M + H)<sup>+</sup>: 348.2375, found 348.2371.



(*E*)-4,4,5,5-tetramethyl-2-(4-phenyl-2-(o-tolyl)but-3-en-1-yl)-1,3,2-dioxaborolane (3e): The general procedure A was followed using 1-methyl-3-vinylbenzene (1e, 24 mg, 0.20 mmol) and (2-bromovinyl)benzene (2a, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3e as yellow solid (50 mg, 72% yield): Rf = 0.8 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)  $\delta$ : 7.34-7.32 (m, 2H), 7.29-7.27 (m, 1H), 7.26-7.24 (m, 1H), 7.18-7.15 (m, 2H), 7.09-7.07 (m, 2H), 6.99-6.98 (m, 1H), 6.44-6.35 (m, 2H), 3.75 (q, *J* = 7.8 Hz, 1H), 2.32 (s, 3H), 1.41-1.33 (m, 2H), 1.14 (s, 12H);

<sup>13</sup>**C NMR** (CDCl<sub>3</sub>, 150 MHz) δ: 145.7, 137.8, 137.7, 135.7, 128.4, 128.23, 128.19, 126.9, 126.8, 126.2, 124.4, 83.1, 44.3, 24.8, 24.7, 21.4 ppm; **HRMS** (ESI-TOF) *m/z* calcd for C<sub>23</sub>H<sub>30</sub>BO<sub>2</sub> (M + H)<sup>+</sup>: 348.2375, found 348.2377.



(*E*)-4,4,5,5-tetramethyl-2-(4-phenyl-2-(o-tolyl)but-3-en-1-yl)-1,3,2-dioxaborolane (3f): The general procedure A was followed using 1-methyl-2-vinylbenzene (1f, 24 mg, 0.20 mmol) and (2-bromovinyl)benzene (2a, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3f as yellow solid (48 mg, 69% yield): Rf = 0.8 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.31-7.27 (m, 3H), 7.26-7.22 (m, 2H), 7.19-7.12 (m, 2H), 7.11-7.05 (m, 2H), 6.40-6.32 (m, 2H), 4.03-3.98 (m, 1H), 2.40 (s, 3H), 1.39-1.36 (m, 2H), 1.11 (s, 6H), 1.09 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 143.5, 137.7, 135.8, 135.4, 130.2, 128.4, 128.1, 126.8, 126.5, 126.1, 125.9, 83.1, 39.8, 24.7, 24.6, 19.7 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>23</sub>H<sub>30</sub>BO<sub>2</sub> (M + H)<sup>+</sup>: 348.2375, found 348.2372.



#### (E)-2-(2-(4-fluorophenyl)-4-phenylbut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

(3g): The general procedure A was followed using 1-fluoro-4-vinylbenzene (1g, 24 mg, 0.20 mmol) and (2-bromovinyl)benzene (2a, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3g as a yellow solid (56 mg, 79% yield): Rf = 0.7 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.33-7.31 (m, 2H), 7.28-7.26 (m, 1H), 7.25-7.21 (m, 3H), 7.20-7.15 (m, 1H), 6.99-6.94 (m, 2H), 6.41-6.30 (m, 2H), 3.77 (q, *J* = 7.2 Hz, 1H), 1.41-1.31 (m, 2H), 1.13 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 161.3 (d, *J* = 242.6 Hz), 141.4 (d, *J* = 3.1 Hz), 137.4, 135.5, 128.9 (d, *J* = 7.7 Hz), 128.43, 128.38, 127.0, 126.1, 115.0 (d, *J* = 21.0 Hz), 83.2, 43.6, 24.8, 24.7 ppm; <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz)  $\delta$ : -117.14 - -117.21 (m, 1F). HRMS (ESI-TOF) *m/z* calcd for C<sub>22</sub>H<sub>27</sub>BFO<sub>2</sub> (M + H)<sup>+</sup>: 352.2124, found 352.2133.



(*E*)-2-(2-(4-chlorophenyl)-4-phenylbut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h): The general procedure A was followed using 1-chloro-4-vinylbenzene (1h, 28 mg, 0.20 mmol) and (2-bromovinyl)benzene (2a, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3h as a yellow solid (58 mg, 78% yield): Rf = 0.7 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.33-7.30 (m, 2H), 7.29-7.24 (m, 4H), 7.23-7.16 (m, 3H), 6.42-6.29 (m, 2H), 3.76 (q, *J* = 7.6 Hz, 1H), 1.41-1.30 (m, 2H), 1.14 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 144.2, 137.4, 135.0, 131.7, 128.9, 128.7, 128.5, 128.4, 127.1, 126.2, 83.3, 43.7, 24.8, 24.7 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>22</sub>H<sub>25</sub>BClO<sub>2</sub> (M - H)<sup>:</sup> 366.1672, found 366.1674.



(*E*)-4,4,5,5-tetramethyl-2-(4-phenyl-2-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)-1,3,2-dioxab orolane (3i): The general procedure A was followed using 1-(trifluoromethyl)-4-vinylbenzene (1i, 34 mg, 0.20 mmol) and (2-bromovinyl)benzene (2a, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3i as a yellow solid (44 mg, 55% yield): Rf = 0.6 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) & 7.55-7.53 (m, 2H), 7.40-7.38 (m, 2H), 7.33-7.25 (m, 4H), 7.21-7.16 (m, 1H), 6.45-6.30 (m, 2H), 3.84 (q, *J* = 7.6 Hz, 1H), 1.45-1.33 (m, 2H), 1.14 (s, 6H), 1.13 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) & 149.9, 137.2, 134.4, 129.1, 128.5, 127.8, 127.2, 126.2, 125.3 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 270.4 Hz), 83.3, 44.2, 24.8, 24.6 ppm; <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz) &: -62.17; HRMS (ESI-TOF) *m/z* calcd for C<sub>23</sub>H<sub>27</sub>BF<sub>3</sub>O<sub>2</sub> (M + H)<sup>+</sup>: 402.2093, found 402.2088.



methyl(E)-4-(4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-yl)benzoate

(3j): The general procedure A was followed using methyl 4-vinylbenzoate (1j, 32 mg, 0.20 mmol) and (2-bromovinyl)benzene (2a, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3j as a yellow solid (41 mg, 52% yield): Rf = 0.3 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.96 (d, J = 8.4 Hz, 2H), 7.37-7.31 (m, 4H), 7.29-7.25 (m, 2H), 7.21-7.17 (m, 1H), 6.44-6.31 (m, 2H), 3.90 (s, 3H), 3.84 (q, J = 7.6 Hz, 1H), 1.45-1.34 (m, 2H), 1.14 (s, 6H), 1.13 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 167.1, 151.2, 137.3, 134.6, 129.8, 129.0, 128.5, 128.0, 127.5, 127.1, 126.2, 83.3, 52.0, 44.4, 24.8, 24.7 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>24</sub>H<sub>30</sub>BO<sub>4</sub> (M + H)<sup>+</sup>: 392.2274, found 392.2277.



(*E*)-2-(2-([1,1'-biphenyl]-4-yl)-4-phenylbut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan e (3k): The general procedure A was followed using 4-vinyl-1,1'-biphenyl (1k, 36 mg, 0.20 mmol) and (2-bromovinyl)benzene (2a, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3k as a yellow solid (65 mg, 79% yield): Rf = 0.6 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.59-7.51 (m, 4H), 7.44-7.25 (m, 9H), 7.20-7.16 (m, 1H), 6.49-6.38 (m, 2H), 3.84 (q, *J* = 7.6 Hz, 1H), 1.47-1.38 (m, 2H), 1.15 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 144.9, 141.1, 139.0, 137.6, 135.4, 128.7, 128.5, 128.4, 127.9, 127.1, 126.99, 126.95, 126.2, 83.2, 44.1, 24.8, 24.7 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>28</sub>H<sub>32</sub>BO<sub>2</sub> (M + H)<sup>+</sup>: 410.2532, found 410.2527.



#### (E)-4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)-4-phenylbut-3-en-1-yl)-1,3,2-dioxaborolane

(31): The general procedure A was followed using 2-vinylnaphthalene (11, 31 mg, 0.20 mmol) and (2-bromovinyl)benzene (2a, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 31 as a yellow solid (62 mg, 81% yield): Rf = 0.6 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.79-7.72 (m, 4H), 7.45-7.38 (m, 3H), 7.35-7.31 (m, 2H), 7.29-7.28 (m, 1H), 7.26-7.24 (m, 1H), 7.19-7.15 (m, 1H), 6.46-6.38 (m, 2H), 3.99-3.93 (m, 1H), 1.53-1.44 (m, 2H), 1.12 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 143.2, 137.6, 135.4, 133.6, 132.2, 128.6, 128.4, 127.9, 127.7, 127.5, 127.0, 126.5, 126.2, 125.8, 125.4, 125.2, 83.2, 44.4, 24.8, 24.7 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>26</sub>H<sub>28</sub>BO<sub>2</sub> (M - H)<sup>-</sup>: 382.2219, found 382.2224.



(*E*)-4,4,5,5-tetramethyl-2-(2-(naphthalen-1-yl)-4-phenylbut-3-en-1-yl)-1,3,2-dioxaborolane (3m): The general procedure A was followed using 1-vinylnaphthalene (1m, 31 mg, 0.20 mmol) and (2-bromovinyl)benzene (2a, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3m as yellow solid (57 mg, 74% yield): Rf = 0.6 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)  $\delta$ : 8.26 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.52-7.43 (m, 4H), 7.32-7.31 (m, 2H), 7.26-7.23 (m, 2H), 7.18-7.15 (m, 1H), 6.53-6.46 (m, 2H), 4.63 (q, *J* = 7.2 Hz, 1H), 1.58-1.51 (m, 2H), 1.12 (s, 6H), 1.07(s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)  $\delta$ :  $\delta$  141.7, 137.5, 135.3, 133.9, 131.4, 128.7, 128.4, 126.9, 126.7, 126.1, 125.7, 125.5, 125.3, 123.93, 123.88, 83.2, 39.0, 24.8, 24.6. ppm; HRMS (ESI-TOF) *m*/*z* calcd for C<sub>26</sub>H<sub>30</sub>BO<sub>2</sub> (M + H)<sup>+</sup>: 384.2375, found 384.2370.



(*E*)-2-(2-(2,3-dihydrobenzofuran-5-yl)-4-phenylbut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxa borolane (3n): The general procedure A was followed using 5-vinyl-2,3-dihydrobenzofuran (1n, 29 mg, 0.20 mmol) and (2-bromovinyl)benzene (2a, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3n as a yellow solid (57 mg, 76% yield): Rf = 0.4 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.34-7.31 (m, 2H), 7.29-7.23 (m, 2H), 7.18-7.14 (m, 1H), 7.11-7.10 (m, 1H), 7.03-7.00 (m, 1H), 6.71-6.69 (d, *J* = 8.0 Hz, 1H), 6.42-6.32 (m, 2H), 4.52 (t, *J* = 8.8 Hz, 2H), 3.72 (q, *J* = 7.2 Hz, 1H), 3.15 (t, *J* = 8.8 Hz, 2H), 1.40-1.31 (m, 2H), 1.14 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 158.4, 137.9, 137.7, 136.1, 128.4, 127.8, 126.92, 126.85, 126.8, 126.1, 123.9, 108.8, 83.1, 71.1, 43.7, 29.8, 24.8, 24.7 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>24</sub>H<sub>28</sub>BO<sub>3</sub> (M - H)<sup>-</sup>: 374.2168, found 374.2158.



(*E*)-2-(2-(benzo[*d*][1,3]dioxol-5-yl)-4-phenylbut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxabor olane (30): The general procedure A was followed using 5-vinylbenzo[*d*][1,3]dioxole (10, 30 mg, 0.20 mmol) and (2-bromovinyl)benzene (2a, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3o as a white solid (57 mg, 76% yield): Rf = 0.5 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.33-7.31 (m, 2H), 7.28-7.24 (m, 2H), 7.19-7.15 (m, 1H), 6.78-6.71 (m, 3H), 6.42-6.29 (m, 2H), 5.90 (s, 2H), 3.71 (q, *J* = 7.6 Hz, 1H), 1.35-1.30 (m, 2H), 1.16 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 147.5, 145.7, 139.8, 137.6, 135.6, 128.4, 128.2, 126.9, 126.1, 120.2, 108.0, 100.7, 83.2, 44.0, 24.8, 24.7 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>23</sub>H<sub>28</sub>BO<sub>4</sub> (M + H)<sup>+</sup>: 378.2117, found 378.2114.



(*E*)-(4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-yl)-*ferrocene* (3p): The general procedure A was followed using vinylferrocene (1p, 42 mg, 0.20 mmol) and (2-bromovinyl)benzene (2a, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product **3p** as a red solid (59 mg, 67% yield): Rf = 0.7 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) & 7.38-7.36 (m, 2H), 7.32-7.27 (m, 2H), 7.21-7.17 (m, 1H), 6.45-6.32 (m, 2H), 4.14 (s, 5H), 4.11-4.09 (m, 1H), 4.08-4.06 (m, 3H), 3.49-3.43 (m, 1H), 1.38-1.30 (m, 2H), 1.20 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) & 137.8, 135.2, 128.5, 128.3, 126.8, 126.1, 94.9, 83.1, 68.4, 67.2, 67.0, 66.9, 66.6, 38.2, 25.1, 24.7 ppm; HRMS (ESI-TOF) *m*/*z* calcd for C<sub>26</sub>H<sub>32</sub>BO<sub>2</sub>Fe (M + H)<sup>+</sup>: 441.1896, found 441.1903.



(*E*)-4,4,5,5-tetramethyl-2-(4-phenyl-2-(5-phenylfuran-2-yl)but-3-en-1-yl)-1,3,2-dioxaborolane (3q): The general procedure A was followed using 2-phenyl-5-vinylfuran (1q, 34 mg, 0.20 mmol), and (2-bromovinyl)benzene (2a, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3q as a yellow solid (57 mg, 71% yield): Rf = 0.7 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)  $\delta$ : 7.64-7.63 (m, 2H), 7.37-7.33 (m, 4H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.22-7.19 (m, 2H), 6.56 (d, *J* = 3.6 Hz, 1H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.34 (dd, *J*<sub>1</sub> = 15.6, *J*<sub>2</sub> = 7.8 Hz, 1H), 6.14 (dd, *J*<sub>1</sub> = 3.3, *J*<sub>2</sub> = 0.9 Hz, 1H), 3.90 (q, *J* = 7.8 Hz, 1H), 1.50-1.46 (m, 1H), 1.37-1.33 (m, 1H), 1.20 (s, 6H), 1.18 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)  $\delta$ : 158.3, 152.4, 137.4, 132.4, 131.2, 129.7, 128.5, 128.4, 127.1, 126.8, 126.2, 123.4, 106.5, 105.6, 83.3, 38.4, 24.8, 24.7 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>26</sub>H<sub>30</sub>BO<sub>3</sub> (M + H)<sup>+</sup>: 400.2324, found 400.2329.



(*E*)-4,4,5,5-tetramethyl-2-(4-phenyl-2-(5-phenylthiophen-2-yl)but-3-en-1-yl)-1,3,2-dioxaborol ane (3r): The general procedure A was followed using 2-phenyl-5-vinylthiophene (1r, 37 mg, 0.20 mmol) and (2-bromovinyl)benzene (2a, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3r as a yellow solid (51 mg, 62% yield): Rf = 0.7 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.56-7.54 (m, 2H), 7.37-7.26 (m, 6H), 7.24-7.18 (m, 2H), 7.14 (d, *J* = 3.6 Hz, 1H), 6.84 (d, *J* = 3.6, 1H), 6.50 (d, *J* = 7.6 Hz, 1H), 6.35 (dd, *J*<sub>1</sub> = 16.0, *J*<sub>2</sub> = 8.0 Hz, 1H), 4.03 (q, *J* = 7.6 Hz, 1H), 1.53-1.37 (m, 2H), 1.18 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 149.9, 142.1, 137.3, 134.7, 134.5, 129.1, 128.8, 128.5, 127.2, 127.0, 126.3, 125.5, 124.2, 122.6, 83.3, 40.2, 24.9, 24.7 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>26</sub>H<sub>28</sub>BO<sub>2</sub>S (M - H)<sup>-</sup>: 414.1939, found 414.1937.



(*E*)-2-(2-(benzofuran-2-yl)-4-phenylbut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3s): The general procedure A was followed using 2-vinylbenzofuran (1s, 29 mg, 0.20 mmol), and (2-bromovinyl)benzene (2a, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3s as a yellow solid (56 mg, 74% yield): Rf = 0.8 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.49-7.46 (m, 1H), 7.42-7.35 (m, 3H), 7.31-7.26 (m, 2H), 7.21-7.14 (m, 3H), 6.54 (d, *J* = 16.0 Hz, 1H), 6.45 (s, 1H), 6.37 (dd, *J*<sub>1</sub> = 16.0, *J*<sub>2</sub> = 8.0 Hz, 1H), 3.98 (q, *J* = 8.4 Hz, 1H), 1.54-1.48 (m, 1H), 1.42-1.36 (m, 1H),1.20 (s, 6H), 1.19 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 161.9, 154.8, 137.2, 131.6, 130.3, 128.8, 128.5, 127.3, 126.3, 123.2, 122.4, 120.4, 110.9, 101.4, 83.4, 38.6, 24.9, 24.7 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>24</sub>H<sub>28</sub>BO<sub>3</sub> (M + H)<sup>+</sup>: 374.2168, found 374.2169.



(*E*)-2-(2-(benzo[*b*]thiophen-2-yl)-4-phenylbut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborol ane (3t): The general procedure A was followed using 2-vinylbenzo[*b*]thiophene (1t, 32 mg, 0.20 mmol) and (2-bromovinyl)benzene (2a, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 3t as a yellow solid (39 mg, 51% yield): Rf = 0.8 (EtOAc : petroleum ether = 1 : 20); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.75 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.37-7.34 (m, 2H), 7.31-7.26 (m, 3H), 7.24-7.18 (m, 2H), 7.09 (s, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.38 (dd, *J*<sub>1</sub> = 16.0, *J*<sub>2</sub> = 8.0 Hz, 1H), 4.10 (q, *J* = 7.6 Hz, 1H), 1.53-1.44 (m, 2H), 1.17 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 151.2, 140.0, 139.4, 137.2, 134.0, 129.6, 128.5, 127.2, 126.3, 124.0, 123.5, 122.9, 122.2, 119.6, 83.4, 40.6, 24.9, 24.7 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>24</sub>H<sub>26</sub>BO<sub>2</sub>S (M - H)<sup>-</sup>: 390.1783, found 390.1786.



(*E*)-6-(4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-yl)quinoline (3u): The general procedure B was followed using 6-vinylquinoline (1u, 31 mg, 0.20 mmol) and (2-bromovinyl)benzene (2a, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3u as a white solid (60 mg, 78% yield): Rf = 0.4 (EtOAc : petroleum ether = 1 : 5); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 8.86 (dd,  $J_I$  = 4.0,  $J_2$  = 1.6 Hz, 1H), 8.12-8.03 (m, 2H), 7.70-7.67 (m, 2H), 7.38-7.33 (m, 3H), 7.29-7.25 (m, 2H), 7.20-7.16 (m, 1H), 6.50-6.40 (m, 2H), 4.02-3.97 (m, 1H), 1.54-1.43 (m, 2H), 1.12 (s, 6H), 1.11 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 149.8, 147.3, 144.1, 137.3, 135.8, 134.9, 130.2, 129.3, 129.0, 128.4, 128.3, 127.1, 126.2, 125.2, 121.0, 83.2, 44.2, 24.74, 24.65 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>25</sub>H<sub>27</sub>BNO<sub>2</sub> (M + H)<sup>+</sup>: 383.2328, found 383.2315.



(*E*)-1-methyl-4-(4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-yl)-1H-in dole (3v): The general procedure A was followed using 1-methyl-4-vinyl-1H-indole (1v, 31 mg, 0.20 mmol) and (2-bromovinyl)benzene (2a, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3v as a yellow solid (60 mg, 78% yield): Rf = 0.4 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)  $\delta$ : 7.32-7.30 (m, 2H), 7.24-7.21 (m, 2H), 7.19-7.12 (m, 3H), 7.04 (dd,  $J_1$  = 5.4,  $J_2$  = 2.5 Hz, 1H), 7.01 (d, J = 3.6 Hz, 1H), 6.66 (d, J = 3.0 Hz, 1H), 6.54-6.48 (m, 2H), 4.23-4.20 (m, 1H), 3.75 (s, 3H), 1.58-1.48 (m, 2H), 1.13 (s, 6H), 1.12 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)  $\delta$ : 138.1, 137.9, 136.8, 135.4, 128.3, 128.2, 128.0, 127.1, 126.7, 126.1, 121.7, 116.8, 107.3, 99.9, 83.1, 42.0, 32.9, 24.8, 24.6 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>25</sub>H<sub>29</sub>BNO<sub>2</sub> (M - H)<sup>-</sup>: 385.2328, found 385.2327.



(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-((*E*)-4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bu t-3-en-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[*a*]phenanthren-17-one (3*w*): The general procedure A was followed using (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[*a*]phenanthren-17-one (1*w*, 56 mg, 0.20 mmol) and (2-bromovinyl)benzene (2*a*, 73 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 3*w* as a yellow solid (62 mg, 61% yield): Rf = 0.2 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ: 7.34-7.32 (m, 2H), 7.27-7.25 (m, 2H), 7.22-7.21 (m, 1H), 7.18-7.16 (m, 1H), 7.09-7.07 (m, 1H), 7.01 (s, 1H), 6.45 (d, *J* = 15.6 Hz, 1H), 6.38-6.34 (m, 1H), 3.73 (q, *J* = 7.8 Hz, 1H), 2.89-2.87 (m, 2H), 1.262-2.47 (m, 1H), 1.65-1.61 (m, 1H), 1.53-1.47 (m, 3H), 1.43-1.36 (m, 2H), 1.33-1.30 (m, 2H), 1.16 (s, 12H), 0.9 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ: 221.0, 143.5, 137.7, 137.5, 136.3, 135.4, 128.4, 128.3, 128.0, 127.9, 126.9, 126.2, 125.4, 124.9, 124.7, 83.2, 50.5, 48.0, 44.3, 43.9, 38.2, 35.9, 31.6, 29.5, 26.6, 25.7, 24.9, 24.7, 21.6, 13.8 ppm; HRMS (ESI-TOF) *m/z* calcd for  $C_{34}H_{44}BO_3$  (M + H)<sup>+</sup> : 510.3420, found 510.3415.



(*E*)-4,4,5,5-tetramethyl-2-(2-phenyl-4-(*p*-tolyl)but-3-en-1-yl)-1,3,2-dioxaborolane (4b): The general procedure A was followed using styrene (1x, 21 mg, 0.20 mmol) and 1-(2-bromovinyl)-4-methylbenzene (2b, 79 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 4b as a yellow solid (65 mg, 93% yield): Rf = 0.7 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.28-7.27 (m, 3H), 7.24-7.14 (m, 4H), 7.07-7.06 (m, 2H), 6.41-6.26 (m, 2H), 3.76 (q, *J* = 7.6 Hz, 1H), 2.30 (s, 3H), 1.43-1.33 (m, 2H), 1.13 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 145.9, 136.6, 134.8, 134.6, 129.1, 128.3, 128.1, 127.4, 126.0, 83.1, 44.4, 24.8, 24.7, 21.1 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>23</sub>H<sub>30</sub>BO<sub>2</sub> (M + H)<sup>+</sup>: 348.2375, found 348.2371.



(*E*)-4,4,5,5-tetramethyl-2-(2-phenyl-4-(*m*-tolyl)but-3-en-1-yl)-1,3,2-dioxaborolane (4c): The general procedure A was followed using styrene (1x, 21 mg, 0.20 mmol) and 1-(2-bromovinyl)-3-methylbenzene (2c, 79 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 4c as a yellow solid (63mg, 90% yield): Rf = 0.8 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)  $\delta$ : 7.28-7.25 (m, 4H), 7.18-7.11 (m, 4H), 7.00-6.98 (m, 1H), 6.40-6.34 (m, 2H), 3.79-3.75 (m, 1H), 2.30 (s, 3H), 1.42-1.33 (m, 2H), 1.14 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)  $\delta$ : 145.8, 137.9, 137.6, 135.5, 128.31, 128.29, 127.7, 127.5, 126.8, 126.1, 123.4, 83.1, 44.4, 24.8, 24.7, 21.4 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>23</sub>H<sub>30</sub>BO<sub>2</sub> (M + H)<sup>+</sup>: 348.2375, found 348.2373.



(*E*)-4,4,5,5-tetramethyl-2-(2-phenyl-4-(*o*-tolyl)but-3-en-1-yl)-1,3,2-dioxaborolane (4d): The general procedure A was followed using styrene (1x, 21 mg, 0.20 mmol) and 1-(2-bromovinyl)-2-methylbenzene1 (2d, 79 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 4d as a yellow solid (61 mg, 87% yield): Rf = 0.8 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)  $\delta$ : 7.40-7.38 (m, 1H), 7.30-7.26 (m, 4H), 7.18-7.15 (m, 1H), 7.11-7.08 (m, 3H), 6.63 (dd,  $J_I$  = 15.6,  $J_2$  = 1.2 Hz, 1H), 6.24 (dd,  $J_I$  = 15.6,  $J_2$  = 7.8 Hz, 1H), 3.82-3.78 (m, 1H), 2.31 (s, 3H), 1.43-1.35 (m, 2H), 1.13 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)  $\delta$ : 145.8, 137.0, 136.7, 135.1, 130.1, 128.3, 127. 5, 126.8, 126.1, 126.0, 125.9, 125.6, 83.1, 44.6, 24.8, 24.7, 19.8 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>23</sub>H<sub>30</sub>BO<sub>2</sub> (M + H)<sup>+</sup>: 348.2375, found 348.2369.



S23

(*E*)-2-(4-(4-(tert-butyl)phenyl)-2-phenylbut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan e (4e): The general procedure A was followed using styrene (1x, 21 mg, 0.20 mmol) and 1-(2-bromovinyl)-4-(tert-butyl)benzene (2e, 96 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 4e as a yellow solid (73 mg, 94% yield): Rf = 0.8 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.30-7.25 (m, 8H), 7.19-7.14 (m, 1H), 6.42-6.30 (m, 2H), 3.77 (q, *J* = 7.6 Hz, 1H 1.40-1.35 (m, 2H), 1.29 (s, 9H), 1.14 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 149.9, 145.9, 134.93, 134.85, 128.3, 128.0, 127.5, 126.0, 125.8, 125.3, 83.1, 44.3, 34.5, 31.3, 24.8, 24.7 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>26</sub>H<sub>36</sub>BO<sub>2</sub> (M + H)<sup>+</sup>: 390.2845, found 390.2846.



(*E*)-2-(4-(4-methoxyphenyl)-2-phenylbut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4f): The general procedure A was followed using styrene (1x, 21 mg, 0.20 mmol) and 1-(2-bromovinyl)-4-methoxybenzene (2f, 85 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 4f as a yellow solid (57 mg, 78% yield): Rf = 0.5 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.28-7.24 (m, 6H), 7.20-7.14 (m, 1H), 6.81-6.79 (m, 2H), 6.36 (d, *J* = 15.6 Hz, 1H), 6.21 (dd, *J*<sub>1</sub> = 15.6, *J*<sub>2</sub> = 7.2 Hz, 1H), 3.81-3.73 (m, 4H), 1. 42-1.33 (m, 2H), 1.13 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 158.6, 146.0, 133.4, 130.4, 128.3, 127.6, 127.4, 127.2, 126.0, 113.8, 83.1, 55.2, 44.3, 24.8, 24.6 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>23</sub>H<sub>30</sub>BO<sub>3</sub> (M + H)<sup>+</sup>: 364.2324, found 364.2327.



(*E*)-4,4,5,5-tetramethyl-2-(2-phenyl-4-(4-(trifluoromethoxy)phenyl)but-3-en-1-yl)-1,3,2-dioxa borolane (4g): The general procedure A was followed using styrene (1x, 21 mg, 0.20 mmol) and 1-(2-bromovinyl)-4-(trifluoromethoxy)benzene (2g, 107 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 4g as a yellow solid (69 mg, 83% yield): Rf = 0.5 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.33-7.27 (m, 6H), 7.20-7.16 (m, 1H), 7.13-7.09 (m, 2H), 6.42-6.32 (m, 2H), 3.80-3.75 (m, 1H), 1.41-1.36 (m, 2H), 1.13 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 148.0, 145.4,

136.8, 136.4, 128.4, 127.4, 127.3, 126.8, 126.2, 121.0, 120.4 (q, J = 255.4 Hz), 83.2, 44.3, 24.8, 24.7 ppm; <sup>19</sup>**F** NMR (CDCl<sub>3</sub>, 376 MHz)  $\delta$ : -57.77. **HRMS** (ESI-TOF) *m/z* calcd for C<sub>23</sub>H<sub>27</sub>BF<sub>3</sub>O<sub>3</sub> (M + H)<sup>+</sup>: 418.2042, found 418.2045.



## (E)-2-(4-(4-fluorophenyl)-2-phenylbut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

(**4h**): The general procedure A was followed using styrene (**1x**, 21 mg, 0.20 mmol) and 1-(2-bromovinyl)-4-fluorobenzene (**2h**, 80 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product **4h** as a yellow solid (64 mg, 91% yield): Rf = 0.8 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.29-7.25 (m, 6H), 7.19-7.15 (m, 1H), 6.97-6.92 (m, 2H), 6.39-6.25 (m, 2H), 3.76 (q, *J* = 7.6 Hz, 1H), 1.42-1.35 (m, 2H), 1.13 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 161.9 (d, *J* = 244.5 Hz), 145.6, 135.4 (d, *J* = 2.3 Hz), 133.7 (d, *J* = 3.2 Hz), 128.4, 127.5 (d, *J* = 7.9 Hz), 127.4, 127.1, 126.1, 115.2 (d, *J* = 21.3 Hz), 83.2, 44.3, 24.8, 24.6 ppm; <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz)  $\delta$ : -115.41- -115.49 (m, 1F). HRMS (ESI-TOF) *m/z* calcd for C<sub>22</sub>H<sub>27</sub>BFO<sub>2</sub> (M + H)<sup>+</sup>: 352.2124, found 352.2118.



### (E)-2-(4-(4-chlorophenyl)-2-phenylbut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

(4i): The general procedure A was followed using styrene (1x, 21 mg, 0.20 mmol) and 1-(2-bromovinyl)-4-chlorobenzene (2i, 87 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 4i as a yellow solid (63 mg, 85% yield): Rf = 0.8 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.31-7.26 (m, 4H), 7.24-7.16 (m, 5H), 6.39-6.30 (m, 2H), 3.79-3.74 (m, 1H), 1.40-1.33 (m, 2H), 1.13 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 145.5, 136.4, 136.1, 132.5, 128.5, 128.4, 127.4, 127.3, 127.1, 126.2, 83.2, 44.4, 24.8, 24.7 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>22</sub>H<sub>27</sub>BClO<sub>2</sub> (M + H)<sup>+</sup>: 368.1829, found 368.1828.



(*E*)-4,4,5,5-tetramethyl-2-(2-phenyl-4-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)-1,3,2-dioxab orolane (4j): The general procedure A was followed using styrene (1x, 21 mg, 0.20 mmol) and 1-(2-bromovinyl)-4-fluorobenzene (2j, 100 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 4j as a yellow solid (58 mg, 72% yield): Rf = 0.8 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.52-7.50 (m, 2H), 7.42-7.40 (m, 2H), 7.32-7.26 (m, 4H), 7.21-7.17 (m, 1H), 6.52-6.41 (m, 2H), 3.80 (q, *J* = 7.6 Hz, 1H), 1.44-1.35 (m, 2H), 1.14 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 145.1, 141.1, 138.4, 128.4, 127.4, 127.1, 126.3, 126.2, 125.4 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 270.3 Hz), 83.2, 44.4, 24.8, 24.6 ppm; <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz)  $\delta$ : -62.25; HRMS (ESI-TOF) *m/z* calcd for C<sub>23</sub>H<sub>27</sub>BF<sub>3</sub>O<sub>2</sub> (M + H)<sup>+</sup>: 402.2093, found 402.2086.



(*E*)-4-(3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl)benzonitrile

(4k): The general procedure A was followed using styrene (1x, 21 mg, 0.20 mmol) and 4-(2-bromovinyl)benzonitrile (2k, 83 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 4k as a yellow solid (54 mg, 75% yield): Rf = 0.2 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.56-7.53 (m, 2H), 7.40-7.37 (m, 2H), 7.32-7.26 (m, 4H), 7.22-7.17 (m, 1H), 6.55-6.38 (m, 2H), 3.80 (q, *J* = 7.6 Hz, 1H), 1.42-1.35 (m, 2H), 1.13 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 144.8, 142.1, 139.9, 132.3, 128.5, 127.4, 126.9, 126.6, 126.4, 119.1, 110.1, 83.2, 44.5, 24.7, 24.6 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>23</sub>H<sub>27</sub>BNO<sub>2</sub> (M + H)<sup>+</sup>: 359.2171, found 359.2178.



Methyl(*E*)-4-(3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl)benzoate (4l): The general procedure A was followed using styrene (1x, 21 mg, 0.20 mmol) and methyl 4-(2-bromovinyl)benzoate (2l, 96 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product 4l as a yellow solid (73 mg, 93% yield): Rf = 0.2 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ: 7.95-7.92 (m, 2H), 7.38-7.36 (m, 2H), 7.32-7.25 (m, 4H), 7.21-7.16 (m, 1H), 6.54-6.42 (m, 2H), 3.89 (s, 3H), 3.80 (q, *J* = 7.6 Hz, 1H), 1.44-1.34 (m, 2H), 1.13 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ: 166.9, 145.2, 142.2, 138.5, 129.8, 128.4, 127.5, 127.4, 126.3, 126.0, 83.2, 51.9, 44.5, 24.8, 24.6 ppm; HRMS (ESI-TOF) *m*/*z* calcd for C<sub>24</sub>H<sub>30</sub>BO<sub>4</sub> (M + H)<sup>+</sup>: 392.2274, found 392.2282.



## (*E*)-4,4,5,5-tetramethyl-2-(4-(naphthalen-2-yl)-2-phenylbut-3-en-1-yl)-1,3,2-dioxaborolane (4m): The general procedure A was followed using styrene (1x, 21 mg, 0.20 mmol) and 2-(2-bromovinyl)naphthalene (2m, 93 mg, 0.30 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 4m as a yellow solid (66 mg, 86% yield): Rf = 0.6 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) & 7.77-7.67 (m, 4H), 7.57-7.54 (m, 1H), 7.45-7.37 (m, 2H), 7.34-7.28 (m, 4H), 7.21-7.17 (m, 1H), 6.61-6.48 (m, 2H), 3.84 (q, J = 7.6 Hz, 1H), 1.48-1.37 (m, 2H), 1.14 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) & 145.7, 136.1, 135.1, 133.7, 132.7, 128.5, 128.4, 128.0, 127.8, 127.6, 127.5, 126.2, 126.1, 125.7, 125.5, 123.7, 83.2, 44.5, 24.8, 24.7 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>26</sub>H<sub>30</sub>BO<sub>2</sub> (M + H)<sup>+</sup>: 384.2375, found 384.2376.



(*E*)-2-(4-(furan-2-yl)-2-phenylbut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4n): The general procedure A was followed using styrene (1x, 21 mg, 0.20 mmol) and 2-(2-bromovinyl)furan (2n, 69 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 4n as a yellow solid (55 mg, 84% yield): Rf = 0.6 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.30-7.26 (m, 5H), 7.19-7.15 (m, 1H), 6.37-6.31 (m, 2H), 6.19 (dd,  $J_I$  = 15.6 Hz,  $J_2$  = 1.2 Hz, 1H), 6.12 (d, J = 3.6 Hz, 1H), 3.77-3.71 (m, 1H), 1.37-1.34 (m, 2H), 1.13 (s, 6H), 1.12 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 153.2, 145.4, 141.3, 134.7, 128.3, 127.5, 126.2, 117.1, 111.1, 106.5, 83.2, 44.1, 24.72, 24.65 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>20</sub>H<sub>24</sub>BO<sub>3</sub> (M - H)<sup>-</sup>: 322.1855, found 322.1852.



(*E*)-4,4,5,5-tetramethyl-2-(2-phenyl-4-(thiophen-2-yl)but-3-en-1-yl)-1,3,2-dioxaborolane (4o): The general procedure A was followed using styrene (1x, 21 mg, 0.20 mmol) and 2-(2-bromovinyl)thiophene (2o, 76 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 4o as a yellow solid (53 mg, 78% yield): Rf = 0.6 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.30-7.25 (m, 4H), 7.19-7.15 (m, 1H), 7.07-7.05 (m, 1H), 6.91-6.89 (m, 1H), 6.86-6.84 (m, 1H), 6.51 (dd,  $J_1$  = 15.6 Hz,  $J_2$  = 1.2 Hz, 1H), 6.23 (dd,  $J_1$  = 15.6 Hz,  $J_2$  = 6.8 Hz, 1H), 3.77-3.71 (m, 1H), 1.39-1.32 (m, 2H), 1.14 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 145.4, 142.8, 135.5, 128.3, 127.5, 127.1, 126.1, 124.6, 123.3, 121.7, 83.2, 44.1, 24.8, 24.7 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>20</sub>H<sub>24</sub>BO<sub>2</sub>S (M - H)<sup>-</sup>: 338.1626, found 338.1620.



(E)-2-methoxy-5-(3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl)pyri dine (4p): The general procedure A was followed using styrene (1x, 21 mg, 0.20 mmol) and

5-(2-bromovinyl)-2-methoxypyridine (**2p**, 85 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product **4p** as a yellow solid (55 mg, 76% yield): Rf = 0.3 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 8.04 (d, J = 2.4 Hz, 1H), 7.61 (dd,  $J_1 = 8.8$ Hz,  $J_2 = 2.4$  Hz, 1H), 7.31-7.26 (m, 4H), 7.20-7.16 (m, 1H), 6.66 (d, J = 8.8 Hz, 1H), 6.37-6.23 (m, 2H), 3.91 (s, 3H), 3.80-3.73 (m, 1H), 1.43-1.31 (m, 2H), 1.14 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 163.2, 145.6, 145.1, 135.4, 135.0, 128.4, 127.4, 126.7, 126.2, 124.4, 110.7, 83.2, 53.4, 44.4, 24.8, 24.7 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>22</sub>H<sub>29</sub>BNO<sub>3</sub> (M + H)<sup>+</sup>: 365.2277, found 365.2287.



**2-((3***E***,5***E***)-2,6-diphenylhexa-3,5-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4q): The general procedure A was followed using styrene (1x, 21 mg, 0.20 mmol) and ((1E)-4-bromobuta-1,3-dien-1-yl)benzene (2a, 84 mg, 0.40 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product 4q as a yellow solid (56 mg, 78% yield, >20:1 dr): Rf = 0.5 (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) \delta: 7.36-7.33 (m, 2H), 7.31-7.25 (m, 5H), 7.24-7.23 (m, 1H), 7.20-7.15 (m, 2H), 6.75 (dd, J\_1 = 15.6 Hz, J\_2 = 10.0 Hz, 1H), 6.44 (d, J = 15.6 Hz, 1H), 6.22 (dd, J\_1 = 15.2Hz, J\_2 = 10.4 Hz, 1H), 5.99 (dd, J\_1 = 15.2 Hz, J\_2 = 7.2 Hz, 1H), 3.71 (q, J = 7.6 Hz, 1H), 1.35-1.32 (m, 2H), 1.14 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) \delta: 145.7, 140.3, 137.6, 133.5, 132.6, 130.7, 129.2, 129.0, 128.5, 128.3, 127.4, 127.1, 126.13, 126.09, 83.2, 44.3, 24.8, 24.7 ppm; HRMS (ESI-TOF) m/z calcd for C<sub>24</sub>H<sub>30</sub>BO<sub>2</sub> (M + H)<sup>+</sup>: 360.2375, found 360.2383.** 

#### 6. Further transformations for the product

#### 6-1 Gram scale reaction



In an oven dried 250-ml Schlenk tube, which contained a stirring bar, was charged with Ni(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O (146 mg, 0.4 mmol), L1 (127 mg, 0.56 mmol), B<sub>2</sub>Pin<sub>2</sub> (4.06 g, 16.0 mmol), and LiOMe (608 mg, 16.0 mmol). The tube was then evacuated and back-filled under a N<sub>2</sub> flow (this sequence was repeated three times). Anhydrous DMA (80 ml) was added under N<sub>2</sub>, then 1-methoxy-4-vinylbenzene (1a, 1.07 g, 8.0 mmol) and (2-bromovinyl)benzene (2a, 2.93 g, 16.0 mmol) was added subsequently under N<sub>2</sub>, the tube was stirred at 30 °C for 24 h. The resulting mixture was diluted with EtOAc (80 mL) and quenched by H<sub>2</sub>O (80 mL). Then it was extracted with EtOAc (100 ml  $\times$  3). The organic layer was combined and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated by rotary evaporation. The residue was purified by chromatography on silica gel (EtOAc : petroleum ether = 1 : 50) afforded product 3a as a yellow solid (2.53 g, 87% yield). 6-2 Procedure for synthesis of 7<sup>[13]</sup>



In an oven dried 10-ml Schlenk tube, which contained a stirring bar, was charged with **3a** (73 mg, 0.2 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (3.7 mg, 0.004 mmol), NaO<sup>*t*</sup>Bu (77 mg, 0.8 mmol), and Ruphos (3.7 mg, 0.008 mmol) the tube was then evacuated and back-filled under a N<sub>2</sub> flow (this sequence was repeated three times). Anhydrous toluene (1.0 mL), H<sub>2</sub>O (60 ul) and bromobenzene (94 mg, 0.6 mmol) was added subsequently under N<sub>2</sub>, the resulting mixture was allowed to stir at 80 °C for 24 hours. The reaction mixture diluted with EtOAc (5.0 ml) and H<sub>2</sub>O (5.0 ml). Then it was extracted with EtOAc (5.0 ml × 3). The organic layer was combined and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated by rotary evaporation. The residue was purified by silica gel chromatography (EtOAc : petroleum ether = 1 : 40) to afford the product 7 as a colorless oil (43 mg, 68% yield): R<sub>f</sub> = 0.6 (EtOAc : petroleum ether = 1 : 20); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)  $\delta$ : 7.29-7.14 (m, 4H), 7.22-7.10 (m, 6H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.39 (dd,  $J_I = 15.6$  Hz,  $J_2 = 7.2$  Hz, 1H), 6.27 (d, *J* = 15.6 Hz, 1H), 3.76 (s, 3H), 3.68 (q, *J* = 7.8 Hz, 1H), 3.12-3.03 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)  $\delta$ : 158.0, 140.0, 137.5, 135.7, 133.6, 129.6, 129.2, 128.8, 128.4, 128.1, 127.0, 126.1, 125.9, 113.8, 55.2, 49.9, 42.7 ppm; HRMS (ESI-TOF) m/z calcd for C<sub>23</sub>H<sub>23</sub>O (M + H)<sup>+</sup>: 315.1749, found 315.1757.

#### 6-3 Procedure for synthesis of 8<sup>[14]</sup>



In an oven dried 10-ml Schlenk tube, which contained a stirring bar, was charged with the solution of **3a** (73 mg, 0.2 mmol, THF 2 ml), NaBO<sub>3</sub>·4H<sub>2</sub>O (154 mg, 1.0 mmol) and H<sub>2</sub>O (2.0 mL) were added. The resulting mixture was allowed to stir at 25 °C for three hours. The reaction mixture diluted with EtOAc (5.0 ml) and H<sub>2</sub>O (5.0 ml). Then it was extracted with EtOAc (5.0 ml × 3). The organic layer was combined and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated by rotary evaporation. The residue was purified by silica gel chromatography (EtOAc : petroleum ether = 1 : 5) to afford the product **3a-OH** as a white solid (47 mg, 92% yield):  $R_f = 0.2$  (EtOAc : petroleum ether = 1 : 5); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.38-7.35 (m, 2H), 7.31-7.27 (m, 2H), 7.23-7.19 (m, 3H), 6.91-6.88 (m, 2H), 6.52-6.32 (m, 2H), 3.88 (d, *J* = 6.8 Hz, 2H), 3.80 (s, 3H), 3.65 (q, *J* = 7.2 Hz, 1H), 1.61 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 158.6, 137.0, 132.7, 131.8, 130.0, 129.0, 128.5, 127.4, 126.2, 114.2, 66.4, 55.3, 50.9 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>17</sub>H<sub>19</sub>O<sub>2</sub> (M + H)<sup>+</sup>: 255.1385, found 255.1382.

In an oven dried 10-ml Schlenk tube, which contained a stirring bar, was charged with **3a-OH** (51 mg, 0.2 mmol), NaHCO<sub>3</sub> (50 mg, 0.6 mmol, 3.0 equiv.), I<sub>2</sub> (102 mg, 0.4 mmol, 2.0 equiv.), then CH<sub>3</sub>CN (4 mL) were added under N<sub>2</sub>. The resulting mixture was allowed to stir at 25 °C for 12 hours. A saturated solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (2 mL) was added, the reaction mixture diluted with EtOAc (5 ml) and H<sub>2</sub>O (5 ml). Then it was extracted with EtOAc (5 ml × 3). The organic layer was combined and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated by rotary evaporation. The residue was purified by silica gel chromatography (EtOAc : petroleum ether = 1 : 20) to afford the product **8** as a white solid (60 mg, 79% yield):  $R_f = 0.6$  (EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)  $\delta$ : 7.54-7.51 (m, 2H), 7.41-7.32 (m, 3H), 7.26-7.22 (m, 2H), 6.91-6.89 (m, 2H), 5.16 (d, *J* = 13.8 Hz, 1H), 4.34 (t, *J* = 13.2 Hz, 1H), 4.11 (t, *J* = 13.2 Hz, 1H), 3.92 (t, *J* = 14.4 Hz, 1H), 3.80-3.73 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)  $\delta$ : 159.0, 138.4, 130.2, 128.5, 128.5, 128.3, 126.6, 114.3, 89.6, 74.0, 56.5, 55.2, 36.9 ppm; HRMS (ESI-TOF) *m/z* calcd for C<sub>17</sub>H<sub>16</sub>IO<sub>2</sub> (M - H)<sup>-</sup>: 379.0195, found 379.0199.

6-4 Procedure for synthesis of 9<sup>[15]</sup>



In an oven dried 10-ml Schlenk tube, which contained a stirring bar, was charged with **3a** (73 mg, 0.2 mmol), the tube was then evacuated and back-filled under a  $N_2$  flow (this sequence was repeated three times). Then THF (2.0 mL) and bromochloromethane (78 mg, 129 mmol) was

added and the reaction was cooled to -78 °C, followed by the dropwise addition of n-BuLi (0.24 mL, 2.5 M in hexanes, 0.6 mmol) at -78 °C. The reaction stirred at -78 °C for 10 minutes, then warmed to 25 °C and stirred for 12 h. The reaction mixture was quenched by H<sub>2</sub>O (10 mL), then it was extracted with EtOAc (10 ml  $\times$  3). The organic layer was combined and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated by rotary evaporation. The residue was dissolved in THF (2.0 mL). NaBO<sub>3</sub>.4H<sub>2</sub>O (154 mg, 1.0 mmol,) and H<sub>2</sub>O (2.0 mL) were added, the resulting mixture was allowed to stir at 25 °C for three hours. The reaction mixture diluted with EtOAc (5.0 ml) and H<sub>2</sub>O (5.0 ml), then it was extracted with EtOAc (5.0 ml  $\times$  3). The organic layer was combined and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated by rotary evaporation. The residue was purified by silica gel chromatography (EtOAc: petroleum ether = 1:5) to afford the product 9 as a colorless oil (42 mg, 78% yield):  $R_f = 0.3$  (EtOAc: petroleum ether = 1:5); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)  $\delta$ : 7.34-7.33 (m, 2H), 7.29-7.24 (m, 2H), 7.20-7.17 (m, 3H), 6.87-6.86 (m, 2H), 6.41 (d, J = 16.2 Hz, 1H), 6.31 (dd, *J*<sub>1</sub> = 16.2 Hz, *J*<sub>2</sub> = 7.8 Hz, 1H), 3.79 (s, 3H), 3.69-3.58 (m, 3H), 2.10-1.99 (m, 2H), 1.41 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ: 158.1, 137.3, 135.7, 133.8, 129.3, 128.51, 128.45, 127.1, 126.1, 114.0, 60.9, 55.2, 44.5, 38.4 ppm; **HRMS** (ESI-TOF) m/z calcd for C<sub>18</sub>H<sub>21</sub>BO<sub>2</sub> (M + H)<sup>+</sup>: 269.1541, found 269.1548.

6-5 Procedure for synthesis of **10**<sup>[16]</sup>



In an oven dried 10-ml Schlenk tube, which contained a stirring bar, was charged with **3a** (73 mg, 0.2 mmol), the tube was then evacuated and back-filled under a N2 flow (this sequence was repeated three times). Then THF (2.0 mL) and vinylMgBr (0.80 mL, 1 M in THF, 0. 80 mmol) was added at 25 °C, The resulting mixture was allowed to stir at same temperature for 0.5 h. A solution of I<sub>2</sub> (203 mg, 0.8 mmol, 2 mL MeOH) was then slowly added to the reaction mixture at -78 °C and stirred for 0.5 h. Then a solution of NaOMe (130 mg, 2.4 mmol, 2.4 mL MeOH) was added slowly at -78 °C. The resulting mixture was then warmed to 25 °C and stirred for 1 h. The reaction mixture was quenched by saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (5 mL), then it was extracted with EtOAc (10 ml  $\times$  3). The organic layer was combined and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated by rotary evaporation. The residue was purified by silica gel chromatography ((EtOAc : petroleum ether = 1 : 20) to afford the product 10 as a yellow oil (47 mg, 88% yield):  $R_f$ = 0.8 ((EtOAc : petroleum ether = 1 : 10); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)  $\delta$ : 7.34-7.32 (m, 2H), 7.28-7.25 (m, 2H), 7.21-7.15 (m, 3H), 6.87-6.84 (m, 2H), 6.38-6.31 (m, 2H), 5.79-5.72 (m, 1H), 5.06-4.97 (m, 2H), 3.78 (s, 3H), 3.48 (q, J = 7.2 Hz, 1H), 2.59-2.51 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) & 158.0, 137.4, 136.6, 135.8, 133.8, 129.4, 128.6, 128.4, 127.0, 126.1, 116.2, 113.8, 55.2, 48.0, 40.2 ppm; **HRMS** (ESI-TOF) m/z calcd for C<sub>19</sub>H<sub>19</sub>O (M - H)<sup>-</sup>: 263.1436, found 263.1439.

## 7. Competition reaction of different Reactants.



In an oven dried 25-ml Schlenk tube, which contained a stirring bar, was charged with Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (3.7 mg, 0.01 mmol), L1 (3.2 mg, 0.014 mmol), B<sub>2</sub>Pin<sub>2</sub> (102 mg, 0.4 mmol), and LiOMe (15 mg, 0.4 mmol). The tube was then evacuated and back-filled under a N<sub>2</sub> flow (this sequence was repeated three times), anhydrous DMA (2.0 ml) was added under N<sub>2</sub>. then 1a (27 mg, 0.2 mmol), 5 (0.2 mmol) and 2a (73 mg, 0.4 mmol) was added subsequently under N<sub>2</sub>, the tube was stirred at 30 °C for 24 h. The resulting mixture was diluted with EtOAc (2 mL) and quenched by H<sub>2</sub>O (2 mL), then it was extracted with EtOAc (10 ml  $\times$  3), the organic layer was combined and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated by rotary evaporation give the crude product. *n*-Dodecane (23 µL) was added as an internal standard for GC-MS and GC analysis.

## 8. Some failed reaction



<sup>a</sup> Standard conditions: **5** (0.2 mmol), **2a** (0.4 mmol), Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.01 mmol), **L1** (0.014 mmol), LiOMe (0.4 mmol), DMA (2.0 mL), at 30  $^{\circ}$ C for 24 h.

## 9. discussion on mechanism

+ 
$$B_2Pin_2$$
 +  $Ph$  Br standard conditions  
E/Z = 84:16

As shown at eq. 9-1, radical clock experiment was carried, but this chemistry did not work with this kind of substrate.

$$Ph$$

$$BPin (eq. 9-2)$$

$$2a (E/Z = 84:16)$$

$$4a, 19\% yield$$

When this reaction was carried without alkene substrate, the product 4a could be isolated with 19% yield (eq. 9-2). This data indicated that styrene should be produced in the reaction system. Based on the above result and the literatures, the proposed mechanism for the formation of 4a was shown as Scheme S9-1. Notably, the compound III should be generated as key intermediate in this transformation.<sup>17</sup> The above information could verify the rationality of the proposed reaction mechanism in the text.



Scheme S9-1. The mechanism for the formation of 4a

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10 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)























x0 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -25 f1 (spm)

























401 397 395





















## 













x 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -25 f1 (ppm)




























