

## Supporting Information

### Stereoconvergent Synthesis of Chiral Allylboronates from *E/Z* Mixture of Allylic Aryl Ethers Using 6-NHC-Cu(I) Catalyst

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## **1. General Information**

### 1.1 General Procedure

All commercially available reagents were used without purification unless otherwise noted. Some substrates were synthesized according to the literature. Column chromatography was performed using silica gel from Merck (230-400 mesh). Visualization of the compounds was accomplished with UV light (254 nm), alkaline KMnO<sub>4</sub> solution followed by heating.

### 1.2 Instrumentation

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> operating at 400 MHz spectrometer operating at 400.172 and 100.623 MHz, respectively, and 600 MHz spectrometer operating at 600.133 and 150.914 MHz, respectively. Proton chemical shifts are reported relative to the residual proton signals of the deuterated solvent CDCl<sub>3</sub> (7.26 ppm) or CD<sub>2</sub>Cl<sub>2</sub> (5.32 ppm) or TMS. Carbon chemical shifts were internally referenced to the deuterated solvent signals in

CDCl<sub>3</sub> (77.00 ppm) or CD<sub>2</sub>Cl<sub>2</sub> (53.8 ppm). Data are represented as follows: chemical shift, multiplicity (bs = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet), coupling constant in Hertz (Hz), and integration. Products were identified by comparison to spectral data reported in the literature. Gas chromatographic (GC) analyses were performed using a GC equipped with an autosampler, a flame ionization detector (FID), and a column (Astec CHIRALDEX<sup>TM</sup> β-DM : 30 m × 0.25 mm × 0.12 μm and γ-TA : 30 m × 0.25 mm × 0.12 μm). Elemental analyses were performed by Atlantic Microlabs, Inc.

## 2. Experimental Section

### 2.1 Synthesis of 6-NHC copper complex, **1b**

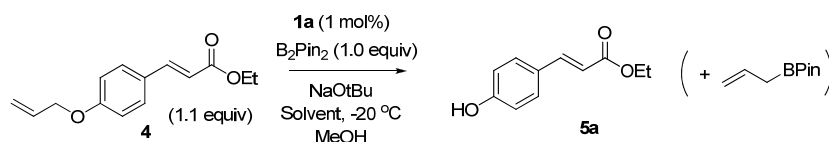
Intermediates for the 6-NHC copper complex, **1b** were synthesized according to the same procedure in the literature.<sup>1</sup>

#### **((2S,3S)-(6-(4-tert-butyl-2,6-dimethylphenyl)-2,3-diphenyl-2,3,5,6-tetrahydroimidazo[1,2-c]quinazolin-5-yl)copper(I) chloride, **1b****

Imidazoquinazolium salt (100 mg, 0.189 mmol) and CuCl (21.0 mg, 0.212 mmol) were charged into a schlenk flask and placed under high vacuum for 1 h. After releasing the pressure, anhydrous THF was added to the mixture at 0 °C. KO<sup>t</sup>Bu solution in THF (212 μl, 0.212 mmol, 1 M solution in THF) was added to the mixture dropwise. During the addition of KO<sup>t</sup>Bu, a blue color appeared and immediately disappeared. After complete addition of KO<sup>t</sup>Bu solution, the blue color maintained for ten seconds and then changed to light brown. After 10 min, THF was carefully removed under vacuum and CH<sub>2</sub>Cl<sub>2</sub> was added to the reaction mixture. The reaction mixture was stirred for 18 h. The reaction mixture was filtered through Celite and washed with CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was reduced under high vacuum. The crude product was used for asymmetric reactions without further purification.

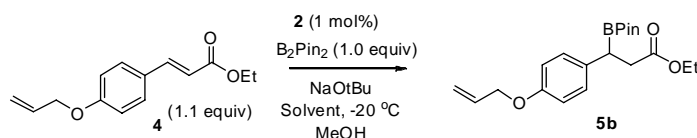
$^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  9.13 (s, 1H) 7.76 (s, 1H) 7.67 (s, 1H) 7.50-7.42 (m, 10H) 7.33 (s, 1H) 7.28 (s, 1H) 6.79 (s, 1H) 5.63 (s, 1H) 5.48 (s, 1H) 2.18 (s, 3H) 1.98 (s, 3H) 1.38 (s, 9H)  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 150 MHz) :  $\delta$  196.7, 154.1, 152.1, 140.3, 139.7, 137.9, 137.2, 136.8, 134.9, 134.7, 130.3, 130.1, 129.8, 129.5, 128.7, 128.1, 127.20, 127.15, 127.1, 118.0, 113.1, 77.4, 75.1, 35.0, 31.4, 18.25, 18.18. IR (neat) 2961, 1655, 1624, 1471, 1456, 1389, 1276, 1063, 1033  $[\alpha]_{\text{D}}^{25} = -87.1^\circ$  (c=0.40,  $\text{CH}_2\text{Cl}_2$ ) Anal. Calcd for  $\text{C}_{31}\text{H}_{28}\text{ClCuN}_3$ : C, 69.97; H, 5.87; Cl, 7.40. N, 6.07 Found: C, 69.19; H, 5.90; N, 7.04

## 2.2 Typical reaction condition for chemoselectivity comparisons

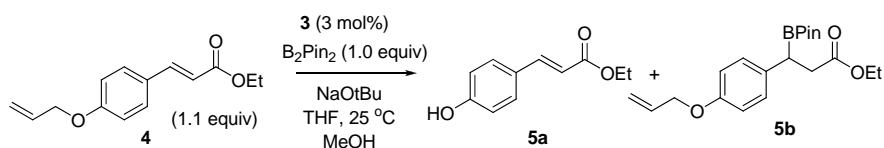


Substrate, **4** (51mg, 0.22 mmol) and bis(pinacolato) diboron (51 mg, 0.20 mmol) were dissolved in  $\text{Et}_2\text{O}$  (1 mL).  $\text{NaOtBu}$  (6 mg, 0.060 mmol) was added to the reaction mixture. And then the reaction mixture was cooled down to  $-20^\circ\text{C}$  and MeOH (18  $\mu\text{L}$ , 0.4 mmol) was added. After 5 min, 6-NHC copper catalyst, **1a** (1.1 mg, 0.0020 mmol) was added. After complete consumption of bis(pinacolato) diboron, the reaction mixture was filtered through silica gel and washed with  $\text{Et}_2\text{O}$ . The filtrate was concentrated under rotary evaporator.  $^1\text{H}$  NMR of crude product was taken for the determination of the ratio of deallylated product to borylated product (25/1). The resulting residue was purified by column chromatography (Hexane :  $\text{EtOAc}$  = 6 : 1 to 4 : 1) to afford the shown product, **5a** (27 mg, 70% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) 7.63 (d,  $J=15.3$  Hz, 1H) 7.43 (d,  $J=8.9$  Hz, 2H) 6.85 (d,  $J=8.6$  Hz, 2H) 6.30 (d,  $J=16.0$  Hz, 1H) 4.26 (q,  $J=7.1$  Hz, 2H) 1.34 (t,  $J=7.1$  Hz, 3H)  $^{13}\text{C}$  NMR (150

MHz, CDCl<sub>3</sub>)  $\delta$  167.8, 157.9, 144.6, 130.2, 127.5, 116.1, 115.9, 60.7, 14.6 HRMS(EI) calcd for C<sub>11</sub>H<sub>12</sub>O<sub>3</sub> 192.07865 found : 192.0786



Substrate, **4** (51mg, 0.22 mmol) and bis(pinacolato) diboron (51 mg, 0.20 mmol) were dissolved in Et<sub>2</sub>O (1 mL). NaOtBu (6 mg, 0.060 mmol) was added to the reaction mixture. And then the reaction mixture was cooled down to -20 °C and MeOH (18  $\mu$ L, 0.4 mmol) was added. After 5 min, 5-NHC copper catalyst, **2** (0.8 mg, 0.0020 mmol) was added. After complete consumption of bis(pinacolato) diboron, the reaction mixture was filtered through silica gel and washed with Et<sub>2</sub>O. The filtrate was concentrated under rotary evaporator. <sup>1</sup>H NMR of crude product was taken for the determination of the ratio of deallylated product to borylated product (1/24). The resulting residue was purified by column chromatography (Hexane : EtOAc = 50 : 1 to 20 : 1) to afford the illustrated product, **5b** (51 mg, 71% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.13-7.11 (m, 2H) 6.83-6.80 (m, 2H) 6.08-6.02 (m, 1H) 5.40 (ddd, J=17.2 Hz, 3.1 Hz, 1.6 Hz, 1H) 5.26 (ddd, J=10.5 Hz, 2.8 Hz, 1.4 Hz, 1H) 4.49 (dt, J=5.3 Hz, 1.5 Hz, 2H) 4.11-4.06 (m, 2H) 2.82 (dd, J=16.2 Hz, 9.8 Hz, 1H) 2.67 (dd, J=9.8 Hz, 6.2 Hz, 1H) 2.61 (dd, J=16.2 Hz, 6.2 Hz, 1H) 1.22-1.20 (m, 9H) 1.17 (s, 6H) <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  173.7, 157.0, 133.81, 133.77, 129.4, 117.7, 115.0, 83.7, 69.1, 60.5, 37.8, 24.8, 24.7, 14.5 HRMS(EI) calcd for C<sub>20</sub>H<sub>29</sub>BO<sub>5</sub> 360.21081 found : 360.21141



Xantphos, **3** (8.7 mg, 0.015 mmol), CuCl (1.5 mg, 0.015 mmol) and NaOtBu (4.3 mg, 0.045 mmol) were dissolved in THF (0.4 mL) and the reaction mixture was stirred for 30 min. Bis(pinacolato) diboron (127 mg, 0.50 mmol) were added to the reaction mixture. After 3 min, stirring, the substrate, **4** (128 mg, 0.55 mmol) in solution with THF (1.6 mL) was added to the reaction mixture, followed by the addition of MeOH (45  $\mu$ L, 1.0 mmol). After complete consumption of bis(pinacolato) diboron, the reaction mixture was filtered through silica gel and washed with Et<sub>2</sub>O. The filtrate was concentrated under rotary evaporator. <sup>1</sup>H NMR of crude product was taken for the determination of the ratio of deallylated product, **5a** to borylated product, **5b** (1/1.3). The resulting residue was purified by column chromatography (Hexane : EtOAc = 8 : 1 to 6 : 1) to afford the desired products, **5a** (17 mg, 16% yield).

**Table S-1.** Chemoselectivity comparison results

Entry	Catalyst	Temp.	Time	Ratio <sup>a</sup> ( <b>5a/5b</b> )	Yield <sup>b</sup> (%)
1	<b>1a</b> (1 mol%)	-20 °C	10 min	>25/1	88 ( <b>5a</b> ) (70)
2	<b>2</b> (1 mol%)	-20 °C	20 min	<1/24	88 ( <b>5b</b> ) (71)
3 <sup>c</sup>	<b>3</b> (3 mol%)	rt	6 h	1/1.5	65 ( <b>5a+5b</b> ) (16) <sup>d</sup>

<sup>a</sup>Ratios were determined by <sup>1</sup>H NMR. <sup>b</sup>Yields were determined by <sup>1</sup>H NMR and isolated yields were shown in parenthesis. <sup>c</sup>Reaction was carried out in THF. <sup>d</sup>Isolated yield of **5a**

Figure S-1. Crude  $^1\text{H}$  NMR data for each reaction

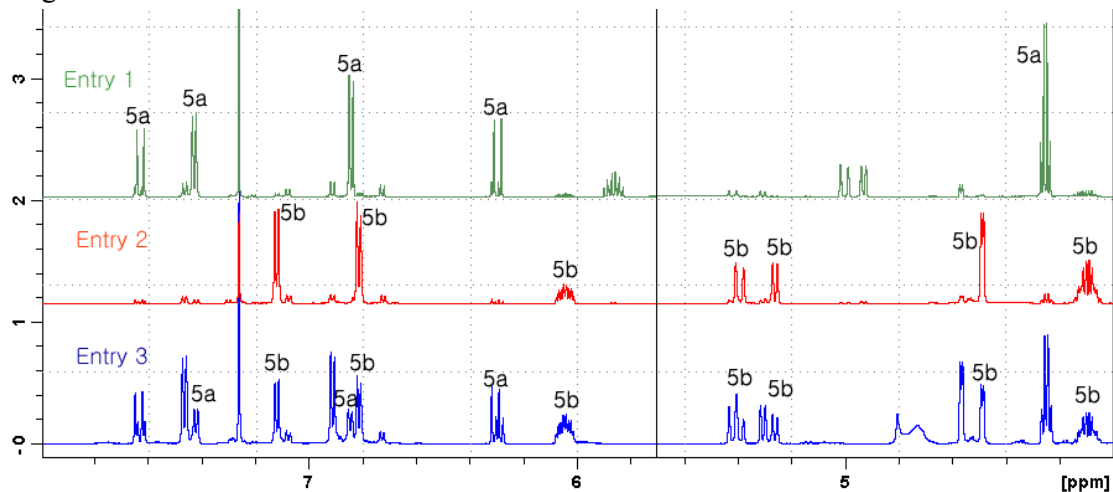
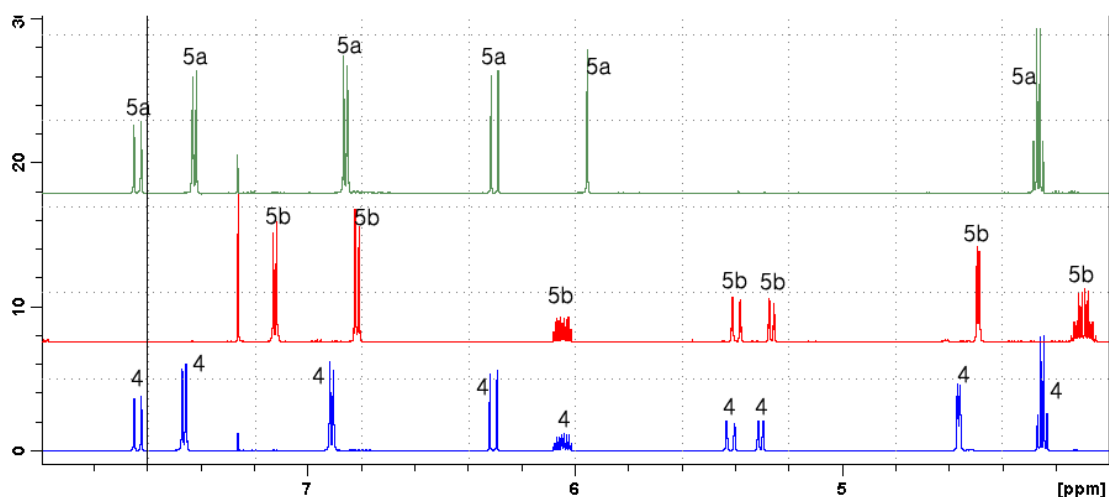


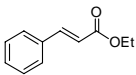
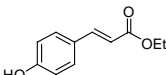
Figure S-2.  $^1\text{H}$  NMR data of **4**, **5a** and **5b**



### 2.3 Validation of reaction condition for Xantphos catalyzed reaction

We tried to reproduce the  $\beta$ -borylation reaction of ethyl cinnamate using Yun's reaction conditions.<sup>2</sup> And we had same results as Yun's group. However, when we tested ethyl 4-hydroxy cinnamate, we had a significant lower yield. We thought aromatic hydroxyl group

could be deleterious effect on the active catalytic species, which could explain why we had a low yield in the reaction using Xantphos, **3** in Table S-1.

Entry	Substrate	Temp.	Reaction time	Yield (%) <sup>a</sup>
1		rt	2 h	99 %
2		rt	5 h	68 %

<sup>a</sup>Yields were determined by <sup>1</sup>H NMR.

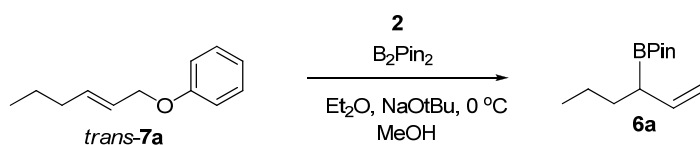
## 2.4 Catalyst comparison for allylic substitution reactions



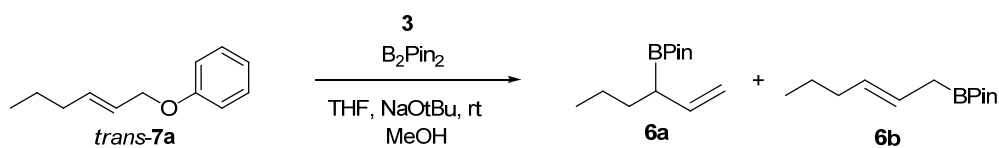
(*E*)-(hex-2-enyloxy)benzene, **7a** (35 mg, 0.20 mmol) and bis(pinacolato) diboron (57 mg, 0.22 mmol) were dissolved in Et<sub>2</sub>O (1 mL). NaOtBu (6 mg, 0.060 mmol) was added to the reaction mixture. And then the reaction mixture was cooled down to 0 °C and MeOH (18 μL, 0.4 mmol) was added, followed by the addition of cyclooctane solution (100 μL, 1.0 M in Et<sub>2</sub>O). After 5 min, 6-NHC copper catalyst, **1a** (1.1 mg, 0.0020 mmol) were added. The reaction was monitored by GC according to the time and GC yield was determined by the calibration of area ratio between product peak and internal standard (cyclooctane) peak. After



20 min, the reaction mixture was filtered through silica gel and washed with Et<sub>2</sub>O. The filtrate was concentrated under rotary evaporator. The resulting residue was purified by column chromatography (Hexane) to afford the desired products, **6a** (37 mg, 86% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 5.79 (ddd, J=17.1 Hz, 10.1 Hz, 8.8 Hz, 1H) 4.97 (ddd, J=17.1 Hz, 1.8 Hz, 1.2 Hz, 1H) 4.92 (ddd, J=10.1 Hz, 1.8 Hz, 0.7 Hz, 1H) 1.84 (q, J=7.8 Hz, 1H) 1.56-1.50 (m, 1H) 1.44-1.25 (m, 3H) 1.24 (s, 6H) 1.23 (s, 6H) 0.89 (t, J=7.3 Hz, 3H) <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 140.0, 113.6, 83.3, 32.7, 24.94, 24.85, 22.3, 14.3 HRMS(EI) calcd for C<sub>12</sub>H<sub>23</sub>BO<sub>2</sub> 210.17912 found : 210.18004

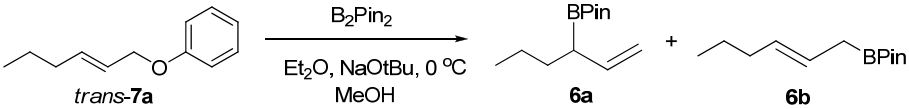


(*E*)-(hex-2-enyloxy)benzene (35mg, 0.20 mmol) and bis(pinacolato) diboron (57 mg, 0.22 mmol) were dissolved in Et<sub>2</sub>O (1 mL). NaOtBu (6 mg, 0.060 mmol) was added to the reaction mixture. And then the reaction mixture was cooled down to 0 °C and MeOH (18 μL, 0.4 mmol) was added, followed by the addition of cyclooctane solution (100 μL, 1.0 M in Et<sub>2</sub>O). After 5 min, 5-NHC copper catalyst (0.8 mg, 0.0020 mmol) were added. The reaction was monitored by GC according to the time and GC yield was determined by the calibration of area ratio between product peak and internal standard (cyclooctane) peak. The reaction was carried out until no conversion was detected.



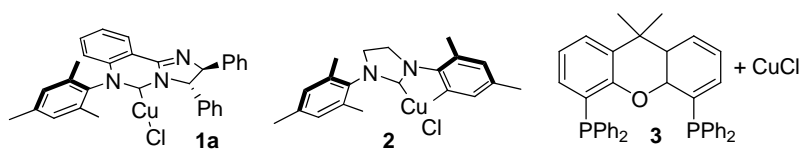
Xantphos (8.7 mg, 0.015 mmol), CuCl (1.5 mg, 0.015 mmol) and NaOtBu (4.3 mg, 0.045 mmol) were dissolved in THF (0.4 mL) and the reaction mixture was stirred for 30 min. Bis(pinacolato) diboron (127 mg, 0.50 mmol) were added to the reaction mixture. After 3 min, stirring, (*E*)-(hex-2-enyloxy)benzene (88 mg, 0.50 mmol) solution in THF (1.6 mL) was added to the reaction mixture, followed by the addition of cyclooctane solution (100  $\mu$ L, 1.0 M in Et<sub>2</sub>O) and MeOH (45  $\mu$ L, 1.0 mmol). The reaction was monitored by GC according to the time and GC yield was determined by the calibration of area ratio between product peak and internal standard (cyclooctane) peak. The reaction was carried out until no conversion was detected.

## 2.5 Experimental details for ratio determination of branched product (6a) and linear product (6b)

				
Entry	Catalyst (mol%)	Time	<b>6a/6b</b> <sup>a</sup>	Yield(%) <sup>b</sup>
1	<b>1a</b> (1 mol%)	20 min	>99/1	91 % (86 %) <sup>c</sup>
2	<b>2</b> (1 mol%)	3 h	>99/1	17 %
3 <sup>d</sup>	<b>3</b> (3 mol%)	22 h	14/1	11 %

<sup>a</sup>Ratio was determined by GC. <sup>b</sup>Yields were determined by GC using internal standard (cyclooctane). <sup>c</sup>Isolated

yield. <sup>d</sup>Reaction was carried out in THF at rt.



Linear product (**6b**) was synthesized and confirmed by comparison with known data.<sup>3</sup> We didn't observe any peak of **6b** in GC chromatogram for **1a** or **2** catalyzed allylic substitution reaction (see below GC chromatogram).

Figure S-3. Calibration curve between product, **6a** (1.0 equiv) and cyclooctane (0.5 equiv)

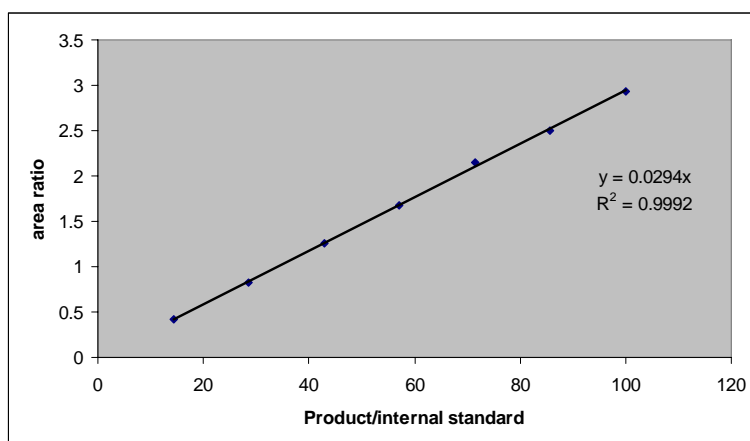
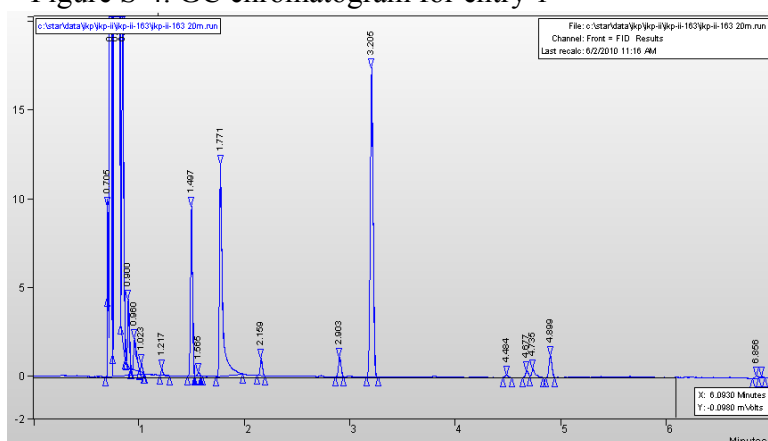


Figure S-4. GC chromatogram for entry 1



1.497 min : cyclooctane

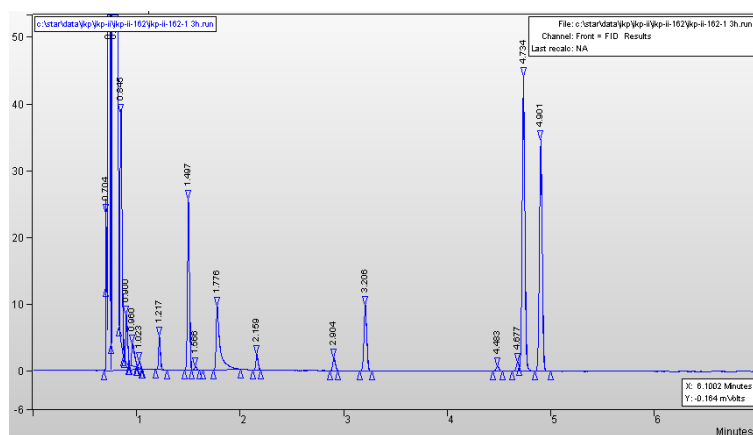
3.205 min : **6a**

4.735 min : *trans*-**7a**

4.899 min : B<sub>2</sub>Pin<sub>2</sub>

	1.497 min	3.205 min	3.787 min	4.735 min	4.899 min
Area	12.2	31.6	0	1.25	2.39

Figure S-5. GC chromatogram for entry 2



	1.497 min	3.206 min	3.787 min	4.734 min	4.901 min
Area	35.3	18.0	0	77.8	65.4

Figure S-6. GC chromatogram for entry 3

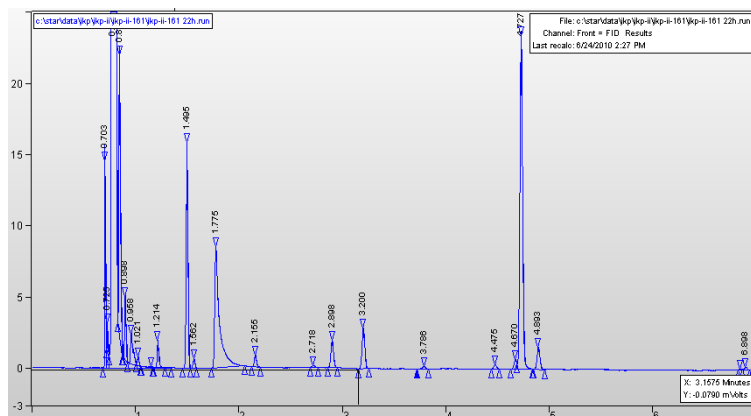
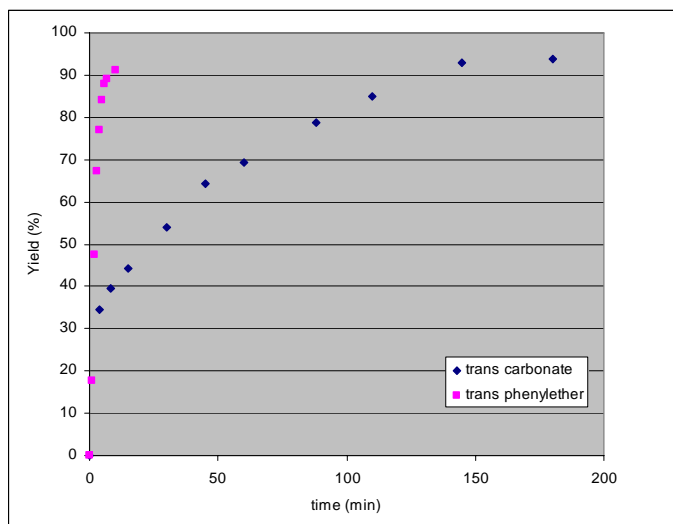




Figure S-8. Reaction profile by GC



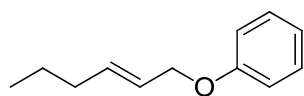
## 2.7 Synthesis of substrates for leaving group screen

Representative Procedure A<sup>4</sup>: A 7 mL screw-top vial was equipped with a stir bar and charged with aryl iodide (1 equiv), allylic alcohol (2 equiv), copper iodide (10 mol %), cesium carbonate (2 equiv), 1, 10-phenanthroline (20 mol %) and 1 mL toluene. The vial was sealed and heated to 110 °C with stirring for 48 hours, after which time it was cooled to room temperature and filtered through a pad of silica gel, using diethyl ether as an eluent. The solvent was removed under vacuum, and the crude product was purified by silica gel flash chromatography (9:1 Hexanes: EtOAc). Any remaining aryl iodide was removed by vacuum distillation to yield the pure desired compounds.

Representative Procedure B<sup>4</sup>: Sodium hydride (1.3 equiv) was carefully weighed out and placed in a 100 mL 3-necked round-bottom flask with fitted with a condenser and stir bar, then suspended in 10 mL dry DMF. A solution of the allylic alcohol (1 equiv) in 10 mL dry

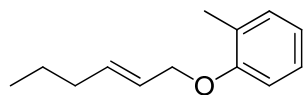
DMF was added dropwise over 30 minutes, then the solution was stirred for an additional hour. A solution of the aryl fluoride (2 equiv) in 2 mL DMF was added dropwise and the entire solution was stirred at room temperature for 1 hour, then stirred at 50 °C for 14 hours, after which time the solution became a bright yellow color. The reaction was quenched with 10 mL *saturated* ammonium chloride solution, and extracted with 4 x 20 mL diethyl ether. The combined organic layers were washed with 20 mL of 1 M HCl solution and brine, then dried over MgSO<sub>4</sub> and concentrated under vacuum. Flash chromatography of the crude product, and subsequent vacuum distillation yielded the pure desired compounds.

**(*E*)-(hex-2-en-1-yloxy)benzene, *trans*-7a**



Produced by procedure A. Isolated as a yellow oil in 78% yield. *R*<sub>f</sub> (9:1 Hexanes:EtOAc) = 0.67. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.30-7.26 (m, 2H) 6.96-6.91 (m, 3H) 5.88-5.81 (m, 1H) 5.75-5.67 (m, 1H) 4.48 (dt, *J*=5.9 Hz, 1.0 Hz, 2H) 2.10-2.05 (m, 2H) 1.44 (hd, *J*=7.4 Hz, 1.0 Hz, 2H) 0.92 (td, *J*=7.4Hz, 1.4Hz, 3H) <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 159.0, 135.7, 129.6, 125.2, 120.9, 115.0, 69.0, 34.6, 22.3, 13.9 HRMS(EI) calcd for C<sub>12</sub>H<sub>16</sub>O 176.12012 found : 176.11988

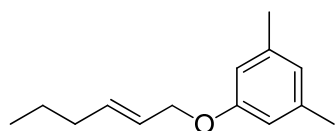
**(*E*)-1-(hex-2-en-1-yloxy)-2-methylbenzene, *trans*-7b**



Produced by procedure A. Isolated as a dark yellow oil in 62% yield. *R*<sub>f</sub> (9:1 Hexanes:EtOAc) = 0.68. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ = 0.92 (t, *J* = 7.4 Hz, 3H, **CH**<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHCH), 1.44 (sx, *J* = 7.4 Hz, 2H, CH<sub>3</sub>**CH**<sub>2</sub>CH<sub>2</sub>CHCH), 2.07 (dq, *J* = 1.0, 7.9, 14.7 Hz, 2H, CH<sub>3</sub>CH<sub>2</sub>**CH**<sub>2</sub>CHCH), 2.25 (s, 3H, CHCHCH<sub>2</sub>O**PhMe**), 4.49 (dd, *J* = 1.0, 5.7 Hz, 2H, CHCH**CH**<sub>2</sub>O**PhMe**), 5.69 – 5.86 (m, 2H, **CHCH**CH<sub>2</sub>O**PhMe**),

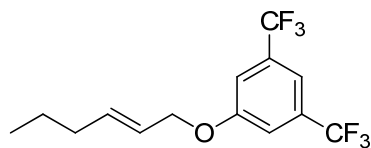
6.83 (d,  $J = 8.4$  Hz, 1H, CHCHCH<sub>2</sub>O<sup>Ph</sup>Me), 6.85 (dt,  $J = 0.9, 7.5$  Hz, 1H, CHCHCH<sub>2</sub>O<sup>Ph</sup>Me), 7.14 (m, 2H, CHCHCH<sub>2</sub>O<sup>Ph</sup>Me). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz):  $\delta = 157.0, 134.5, 130.6, 127.0, 126.6, 125.4, 120.3, 111.6, 68.9, 34.4, 22.2, 16.3, 13.6$ . IR (neat, cm<sup>-1</sup>): 3023, 2959, 2928, 2872, 1602, 1494, 1461, 1379, 1307, 1207, 1240, 1192, 1120, 1050, 1013. LRMS ( $m/z$ , CI<sup>+</sup>): Calcd. 190.28, found 191.2.

**(*E*)-1-(hex-2-en-1-yloxy)-3,5-dimethylbenzene, *trans*-7c**



Produced by procedure A. Isolated as a dark yellow oil in 95% yield.  $R_f$  (9:1 Hexanes:EtOAc) = 0.69. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)  $\delta = 0.91$  (t,  $J = 7.4$  Hz, 3H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHCH), 1.43 (sx,  $J = 7.4$  Hz, 2H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHCH), 2.07 (dq,  $J = 0.9, 7.7$  Hz, 2H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHCH), 2.28 (s, 6H, CHCHCH<sub>2</sub>O<sup>Ph</sup>Me<sub>2</sub>), 4.44 (dd,  $J = 0.96, 6.0$  Hz, 2H, CHCHCH<sub>2</sub>O<sup>Ph</sup>Me<sub>2</sub>), 5.69 – 5.84 (m, 2H, CHCHCH<sub>2</sub>O<sup>Ph</sup>Me<sub>2</sub>), 6.55 (s, 2H, CHCHCH<sub>2</sub>O<sup>Ph</sup>Me<sub>2</sub>), 6.59 (s, 1H, CHCHCH<sub>2</sub>O<sup>Ph</sup>Me<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)  $\delta = 159.0, 139.3, 135.34, 125.4, 122.6, 112.7, 68.8, 34.6, 22.3, 21.6, 13.8$ . IR (neat cm<sup>-1</sup>): 3015, 2958, 2925, 2869, 1612, 1594, 1458, 1376, 1323, 1293, 1090. LRMS ( $m/z$ , CI<sup>+</sup>): Calcd. 204.3, found 205.2.

**(*E*)-1-(hex-2-en-1-yloxy)-3,5-bis(trifluoromethyl)benzene, *trans*-7d**

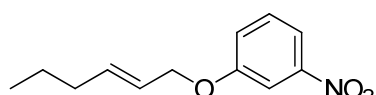


Produced by procedure A. Isolated as a light yellow oil in 88% yield.  $R_f$  (9:1 Hexanes:EtOAc) = 0.79. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)  $\delta = 0.91$  (t,  $J = 7.4$  Hz, 3H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHCH), 1.43 (sx,  $J = 7.4$  Hz, 2H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHCH), 2.08 (dq,  $J = 0.84, 7.4$  Hz, 2H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHCH), 4.57 (dd,  $J = 0.90, 6.1$  Hz, 2H, CHCHCH<sub>2</sub>O<sup>Ph</sup>), 5.67 – 5.90 (m, 2H, CHCHCH<sub>2</sub>O<sup>Ph</sup>).



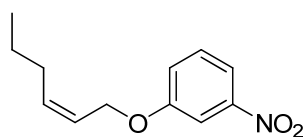
**CHCHCH<sub>2</sub>OPh**), 7.30 (s, 2H, **CHCHCH<sub>2</sub>OPh**), 7.44 (s, 1H, **CHCHCH<sub>2</sub>OPh**). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ = 159.4, 137.0, 132.9 (q, J = 33 Hz), 123.7, 123.4 (q, J = 273 Hz), 115.4, 114.3 (t, J = 3.8 Hz), 69.7, 34.5, 22.2, 13.7. IR (neat, cm<sup>-1</sup>): 2963, 2932, 2675, 1614, 1467, 1395, 1369, 1320, 1275, 1173, 1131, 1110, 1015. LRMS (*m/z*, EI<sup>+</sup>): Calcd. 312.09, found 312.0.

**(*E*)-1-(hex-2-en-1-yloxy)-3-nitrobenzene, *trans*-7e**



Produced by procedure **B**. Isolated as a dark yellow oil in 90% yield. *R<sub>f</sub>* (7:3 Hexanes:EtOAc) = 0.58. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ = 0.91 (t, J = 7.3 Hz, 3H, **CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHCH**), 1.44 (sx, J = 7.4 Hz, 2H, **CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHCH**), 2.08 (dq, J = 0.96, 7.8, 14.7 Hz, 2H, **CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHCH**), 4.56 (dd, J = 1.0, 6.1 Hz, 2H, **CHCHCH<sub>2</sub>OPhNO<sub>2</sub>**), 5.66 – 5.91 (m, 2H, **CHCHCH<sub>2</sub>OPhNO<sub>2</sub>**), 7.23 (dq, J = 0.72, 2.5, 8.3 Hz, 1H, **CHCHCH<sub>2</sub>OPhNO<sub>2</sub>**), 7.41 (t, J = 8.2 Hz, 1H, **CHCHCH<sub>2</sub>OPhNO<sub>2</sub>**), 7.74 (t, J = 2.3 Hz, 1H, **CHCHCH<sub>2</sub>OPhNO<sub>2</sub>**), 7.81 (dq, J = 0.72, 1.2, 7.3 Hz, 1H, **CHCHCH<sub>2</sub>OPhNO<sub>2</sub>**). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ = 159.4, 149.4, 136.8, 129.9, 123.9, 122.2, 115.8, 109.2, 66.6, 34.5, 22.2, 13.8. IR (neat, cm<sup>-1</sup>): 2960, 2922, 2884, 1619, 1579, 1510, 1482, 1461, 1349, 1320, 1284, 1243, 1092, 1011. LRMS (*m/z*, EI<sup>+</sup>): Calcd. 221.1, found 221.1

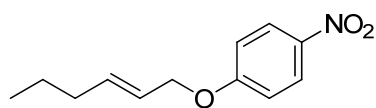
**(*Z*)-1-(hex-2-en-1-yloxy)-3-nitrobenzene, *cis*-7e**



Prepared by procedure **B**. Isolated as a bright yellow oil in 91% yield. *R<sub>f</sub>* (7:3 Hexanes:EtOAc) = 0.58. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600

MHz)  $\delta$  = 0.95 (t,  $J$  = 7.4 Hz, 3H, **CH**<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHCH), 1.46 (sx,  $J$  = 7.4 Hz, 2H, CH<sub>3</sub>**CH**<sub>2</sub>CH<sub>2</sub>CHCH), 2.15 (q,  $J$  = 7.5 Hz, 2H, CH<sub>3</sub>CH<sub>2</sub>**CH**<sub>2</sub>CHCH), 4.66 (d,  $J$  = 6.1, 2H, CHCH**CH**<sub>2</sub>OPhNO<sub>2</sub>), 5.65 – 5.76 (m, 2H, **CHCH**CH<sub>2</sub>OPhNO<sub>2</sub>), 7.23 (ddd,  $J$  = 0.72, 2.6, 8.3 Hz, 1H, CHCHCH<sub>2</sub>**OPh**NO<sub>2</sub>), 7.42 (t,  $J$  = 8.2, 1H, CHCHCH<sub>2</sub>**OPh**NO<sub>2</sub>), 7.73 (t,  $J$  = 2.3, 1H, CHCHCH<sub>2</sub>**OPh**NO<sub>2</sub>), 7.82 (ddd,  $J$  = 0.72, 2.0, 5.2 Hz, 1H, CHCHCH<sub>2</sub>**OPh**NO<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)  $\delta$  = 159.4, 149.4, 135.5, 130.0, 123.8, 122.2, 115.9, 109.1, 64.8, 30.0, 22.7, 13.9. IR (neat, cm<sup>-1</sup>): 2960, 1607, 1592, 1511, 1496, 1461, 1381, 1255, 1173, 1111, 971, 861, 844, 752, 690. LRMS ( $m/z$ , EI<sup>+</sup>): Calcd. 221.1, found 221.0.

**(*E*)-1-(hex-2-en-1-yloxy)-4-nitrobenzene, *trans*-7f**

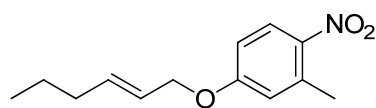


Prepared by procedure **B**. Isolated as a yellow oil in 89% yield.

$R_f$  (9:1 Hexanes:EtOAc) = 0.42. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)

$\delta$  = 0.91 (t,  $J$  = 7.3 Hz, 3H, CH<sub>2</sub>**CH**<sub>3</sub>), 1.44 (sx,  $J$  = 7.4 Hz, 2H, **CH**<sub>2</sub>CH<sub>3</sub>), 2.08 (dq,  $J$  = 0.96, 6.8, 13.6 Hz, 2H, CHCH**CH**<sub>2</sub>CH<sub>2</sub>O), 4.57 (dd,  $J$  = 0.96, 6.1 Hz, 2H, CHCHCH<sub>2</sub>**CH**<sub>2</sub>O), 5.65 – 5.70 (m, 1H, **CHCH**CH<sub>2</sub>CH<sub>2</sub>O), 5.85 – 5.90 (m, 1H, CH**CHCH**<sub>2</sub>CH<sub>2</sub>O), 6.95 (dd,  $J$  = 3.4, 5.5 Hz, 2H, **Ph**), 8.19 (dd,  $J$  = 3.4, 5.5 Hz, 2H, **Ph**). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)  $\delta$  = 163.8, 141.5, 136.8, 125.9, 125.9, 123.6, 114.7, 114.7, 69.6, 34.3, 22.0, 13.6. IR (neat, cm<sup>-1</sup>): 2960, 1607, 1592, 1511, 1496, 1461, 1381, 1255, 1173, 1111, 971, 861, 844, 752, 690. LRMS ( $m/z$ , EI<sup>+</sup>): Calcd. 221.1, found 221.0.

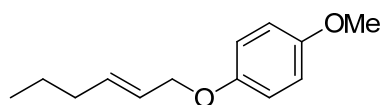
**(*E*)-4-(hex-2-en-1-yloxy)-2-methyl-1-nitrobenzene, *trans*-7g**



Prepared according to procedure **B**. Isolated as a dark yellow

oil in 41% yield.  $R_f$  (7:3 Hexanes:EtOAc) = 0.66.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  = 0.91 (t,  $J$  = 7.3 Hz, 3H,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}$ ), 1.43 (sx,  $J$  = 7.4 Hz, 2H,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}$ ), 2.08 (dq,  $J$  = 1.0, 7.4, 14.8 Hz, 2H,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}$ ), 2.62 (s, 3H,  $\text{CHCHCH}_2\text{OPhMe}$ ), 4.54 (dd,  $J$  = 1.0, 6.1 Hz, 2H,  $\text{CHCHCH}_2\text{OPhMe}$ ), 5.64 – 5.88 (m, 2H,  $\text{CHCHCH}_2\text{OPhMe}$ ), 6.77 – 6.81 (m, 2H,  $\text{CHCHCH}_2\text{OPhMe}$ ), 8.08 (d,  $J$  = 8.8 Hz, 1H,  $\text{CHCHCH}_2\text{OPhMe}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  = 162.4, 142.3, 137.1, 136.7, 127.6, 123.9, 118.4, 112.6, 69.5, 34.5, 22.2, 21.8, 13.8. IR (neat,  $\text{cm}^{-1}$ ): 2960, 2931, 2872, 1671, 1606, 1579, 1510, 1469, 1456, 1362, 1334, 1269, 1248, 1173, 1077, 1035. LRMS ( $m/z$ , EI $^+$ ): Calcd. 235.1, found 235.0.

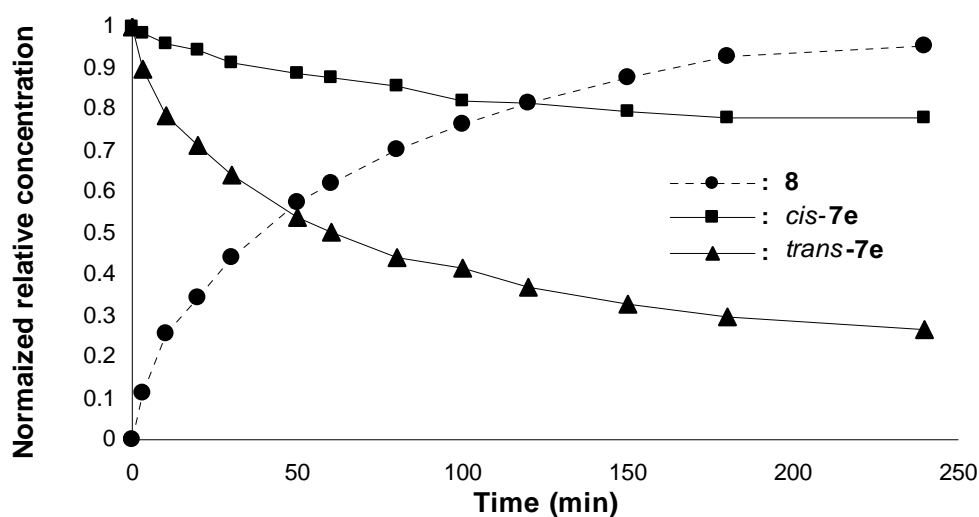
**(*E*)-1-(hex-2-en-1-yloxy)-4-methoxybenzene, *trans*-7h**



Prepared according to procedure **A**. Isolated as a light yellow liquid in 80% yield.  $R_f$  (9:1 Hexanes:EtOAc) = 0.46.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$  = 0.90 (t,  $J$  = 7.3 Hz, 3H,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}$ ), 1.43 (sx,  $J$  = 7.4 Hz, 2H,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}$ ), 2.06 (dq,  $J$  = 0.9, 7.7, 14.7 Hz, 2H,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}$ ), 3.76 (s, 3H,  $\text{CHCHCH}_2\text{OPhOMe}$ ), 4.42 (dd,  $J$  = 0.9, 6.1 Hz, 2H,  $\text{CHCHCH}_2\text{OPhOMe}$ ), 5.67 – 5.83 (m, 2H,  $\text{CHCHCH}_2\text{OPhOMe}$ ), 6.80 – 6.84 (m, 4H,  $\text{CHCHCH}_2\text{OPhOMe}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  = 154.0, 153.1, 135.4, 125.4, 115.9, 114.8, 69.7, 55.9, 34.6, 22.3, 13.8. LRMS ( $m/z$ , EI $^+$ ): Calcd. 206.1, found 206.0.

## 2.8 Reaction profile between *trans* and *cis* substrates

(*E*)-1-(hex-2-en-1-yloxy)-3-nitrobenzene, *trans*-**7e** (44 mg, 0.2mol) and (*Z*)-1-(hex-2-en-1-yloxy)-3-nitrobenzene, *cis*-**7e** (44 mg, 0.2 mol) and bis(pinacolato) diboron (51 mg, 0.2 mol) and cyclooctane (13  $\mu$ L), as an internal standard, were dissolved in diethyl ether (1.5 mL). NaOtBu (6 mg, 0.06 mol) was added to the reaction mixture. And then the reaction mixture was cooled to -55  $^{\circ}$ C and MeOH (18  $\mu$ L) was added. After 5 min the 6-NHC copper catalyst (1.2 mg 0.002 mol), **1b** was added. Reaction was then monitored by taking aliquots of the reaction mixture at set times and analyzing the sample by GC and then analyzing by  $^1\text{H}$  NMR removing the solvent. All measurements taken were normalized by the internal standard. Internal standard calibration curve can be viewed in Figure S-3.



### GC Analysis for reaction yield

Time (min)	Peak Area		P/IS	Yield (%)*
	Internal Standard (IS)	Product (P)		
0	37	0	0.00	<b>0</b>
3	37	12.8	0.35	<b>12</b>
10	35.8	27.4	0.77	<b>26</b>
20	32.1	33.3	1.04	<b>35</b>
30	29.8	39.6	1.33	<b>44</b>
50	30.7	53	1.73	<b>58</b>
60	29	54	1.86	<b>62</b>
80	27.2	57.2	2.10	<b>70</b>
100	23.2	53.1	2.29	<b>76</b>
120	25	61.3	2.45	<b>82</b>
150	23.2	61	2.63	<b>88</b>
180	37.8	105	2.78	<b>93</b>
240	23.9	68.4	2.86	<b>95</b>

\*Yield is based on a maximum value of P/IS =2.94 value based on calibration curve

### <sup>1</sup>H NMR Analysis for *E/Z* ratio

Time	Ratio of Isomer Based on Peak Area		<i>E</i> (%) <sup>*</sup>	<i>Z</i> (%) <sup>*</sup>	<i>E/Z</i> ratio	
	<i>Z</i>	<i>E</i>			<i>E</i> (%) <sup>**</sup>	<i>Z</i> (%) <sup>**</sup>
0	1	1	0.5	0.5	<b>1</b>	<b>1</b>
3	21.16	19.29	0.52	0.48	<b>0.99</b>	<b>0.90</b>
10	11.41	9.30	0.55	0.45	<b>0.96</b>	<b>0.78</b>
20	8.70	6.57	0.57	0.43	<b>0.94</b>	<b>0.71</b>
30	6.04	4.25	0.59	0.41	<b>0.91</b>	<b>0.64</b>
50	5.74	3.47	0.62	0.38	<b>0.89</b>	<b>0.54</b>
60	4.34	2.51	0.63	0.37	<b>0.87</b>	<b>0.50</b>
80	3.62	1.88	0.66	0.34	<b>0.86</b>	<b>0.44</b>
100	3.50	1.78	0.66	0.34	<b>0.82</b>	<b>0.42</b>
120	3.95	1.78	0.69	0.31	<b>0.81</b>	<b>0.37</b>
150	3.22	1.33	0.71	0.29	<b>0.80</b>	<b>0.33</b>
180	2.88	1.09	0.72	0.28	<b>0.78</b>	<b>0.30</b>
240	3.01	1.03	0.75	0.25	<b>0.78</b>	<b>0.27</b>

\* Ratio of specific isomer (*E* or *Z*) over total area (*E*+*Z*)

\*\*Based on Formation of Product

Figure S-9. GC chromatogram for reaction progress.

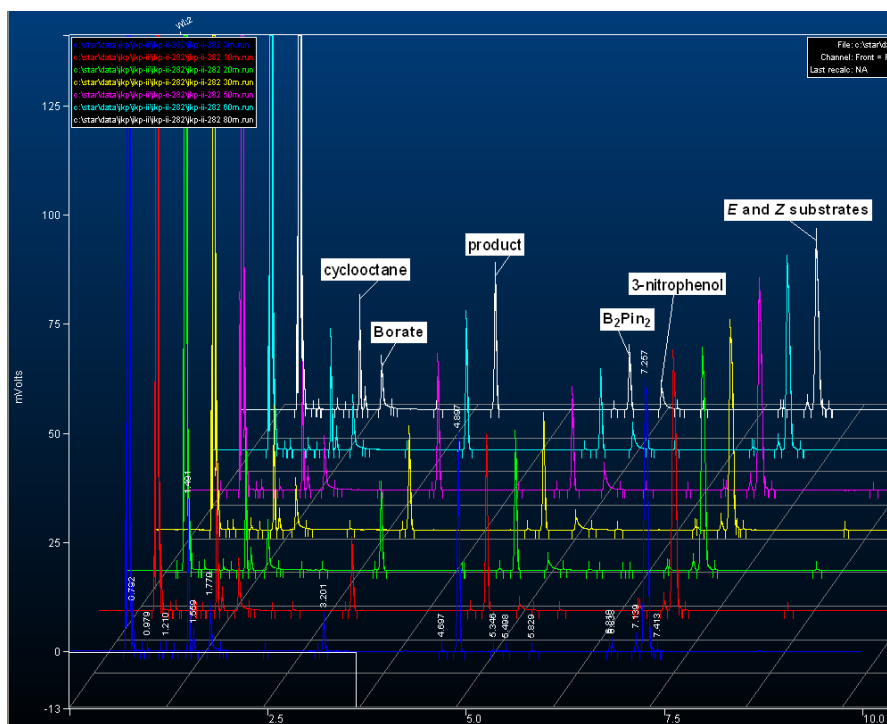


Figure S-10.  $^1\text{H}$  NMR data for *E/Z* ratio changing

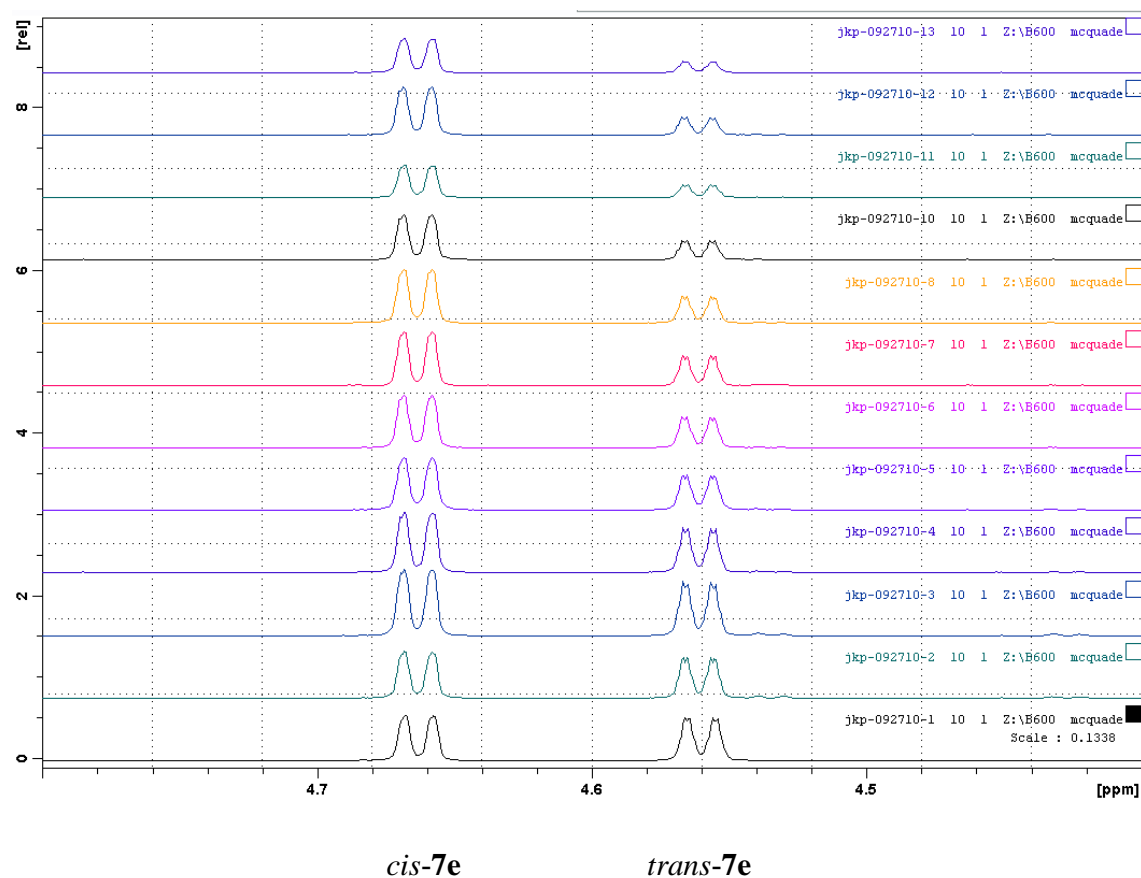


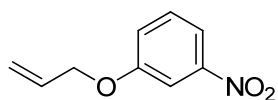
Figure S-11. GC chromatogram for enantioselectivity of **6a**





## 2.9 Synthesis of substrates for substrate scope in Table 4

### 1-(allyloxy)-3-nitrobenzene (**9**)<sup>5</sup>



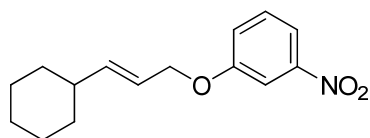
A 250 mL round-bottom flask was charged with 3-nitrophenol (5 g, 35.9 mmol, 1 equiv), allyl bromide (4.67 mL, 53.9 mmol, 1.5 equiv), anhydrous K<sub>2</sub>CO<sub>3</sub> (9.94 g, 71.9 mmol, 2 equiv) and 120 mL acetone (0.3 M) and stirred at room temperature for 14 hours. The reaction mixture was then filtered through Celite and concentrated by N<sub>2</sub> flow. The product was redissolved into hexanes, and filtered through Celite to remove KBr salt. Desired product was isolated as a bright yellow oil in 98 % yield. R<sub>f</sub> (7:3 Hexanes:EtOAc) = 0.66. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ = 4.62 (m, 2H, CH<sub>2</sub>CHCH<sub>2</sub>OPhNO<sub>2</sub>), 5.35 (dd, J = 1.2, 10.6 Hz, 1H, CH<sub>2</sub>CHCH<sub>2</sub>OPhNO<sub>2</sub>), 5.45 (dd, J = 1.4, 17.3 Hz, 1H, CH<sub>2</sub>CHCH<sub>2</sub>OPhNO<sub>2</sub>), 6.02 – 6.09 (m, 1H, CH<sub>2</sub>CHCH<sub>2</sub>OPhNO<sub>2</sub>), 7.25 (ddd, J = 0.6, 2.5, 8.3 Hz, 1H, CH<sub>2</sub>CHCH<sub>2</sub>OPhNO<sub>2</sub>), 7.42 (t, J = 8.2 Hz, 1H, CH<sub>2</sub>CHCH<sub>2</sub>OPhNO<sub>2</sub>), 7.74 (t, J = 2.3 Hz, 1H, CH<sub>2</sub>CHCH<sub>2</sub>OPhNO<sub>2</sub>), 7.83 (m, 1H, CH<sub>2</sub>CHCH<sub>2</sub>OPhNO<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ = 159.1, 149.2, 132.1, 130.0, 121.9, 118.5, 115.9, 109.1, 69.4. IR (neat, cm<sup>-1</sup>) = 3097, 2871, 1617, 1582, 1524, 1481, 1460, 1424, 1349, 1321, 1286, 1242, 1230, 1157, 1096, 1022. LRMS (*m/z*, EI<sup>+</sup>): Calcd. 179.1, found 179.1.

### Representative Metathesis Procedure<sup>6</sup>:

A 50 mL round-bottom flask was flame-dried and kept under N<sub>2</sub> atmosphere. The flask was charged with **9** (4 equiv), terminal olefin (1 equiv) and methylene chloride (0.2 M) and stirred at room temperature for 10 minutes. Grubbs' 1<sup>st</sup> generation catalyst was added (5 mol %) and the reaction was heated to reflux (45 °C) for 14 hours, then cooled to room temperature. The

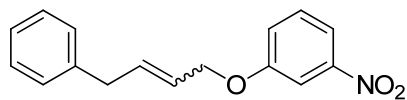
crude material was adsorbed onto silica and flash chromatography was used to isolate the product (10% Et<sub>2</sub>O in Hexanes). Remaining **9** was then removed by Kugelrohr distillation (100 °C at 150 mTorr), and the dimer of **9** was precipitated out of solution by dissolving in methanol, yielding the desired product.

### 1-((3-Cyclohexylallyl)oxy)-3-nitrobenzene, **10b**



Isolated as a brown oil in 37% yield. *R<sub>f</sub>* (19:1 Hexanes:Et<sub>2</sub>O) = 0.49. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz, *E*-isomer only) δ = 1.07 – 1.35 (m, 5H, **CyCHCH**), 1.71 – 1.76 (m, 5H, **CyCHCH**), 2.00 – 2.05 (m, 1H, **CyCHCH**), 4.55 (d, *J* = 6.1 Hz, 2H, CHCHCH<sub>2</sub>OAr), 5.60 – 5.85 (m, 2H, **CHCHCH**CH<sub>2</sub>OAr), 7.23 (ddd, *J* = 0.72, 2.5, 8.9 Hz, 1H, CHCHCH<sub>2</sub>OAr), 7.41 (t, *J* = 8.2 Hz, 1H, CHCHCH<sub>2</sub>OAr), 7.73 (t, *J* = 2.3 Hz, 1H, CHCHCH<sub>2</sub>OAr), 7.81 (ddd, *J* = 0.60, 1.8, 7.9 Hz, 1H, CHCHCH<sub>2</sub>OAr). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz): δ = 159.3, 149.2, 142.3, 129.8, 122.0, 121.2, 115.7, 109.1, 69.7, 40.4, 32.5, 26.1, 25.9. IR (neat, cm<sup>-1</sup>): 2924, 2851, 1620, 1579, 1523, 1481, 1448, 1348, 1285, 1244, 1075, 1012. LRMS (*m/z*, EI<sup>+</sup>): Calcd. 261.1, found 261.0.

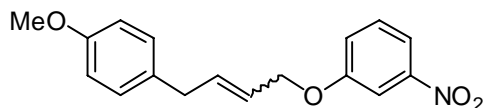
### 1-Nitro-3-((4-phenylbut-2-en-1-yl)oxy)benzene, **10c**



Isolated as a dark brown oil in 31% yield. *R<sub>f</sub>* (9:1 Hexanes:Et<sub>2</sub>O) = 0.33. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz, *E/Z* = 4.6/1) δ = 3.44 (d, *J* = 6.8 Hz, 2H, PhCH<sub>2</sub>CHCHCH<sub>2</sub>OAr), 4.59 (dd, *J* = 1.0, 5.8 Hz, 2H, PhCH<sub>2</sub>CHCHCH<sub>2</sub>OAr), 5.73 – 5.77 (m, 1H, PhCH<sub>2</sub>CHCHCH<sub>2</sub>OAr), 6.02 – 6.06 (m, 1H, PhCH<sub>2</sub>CHCHCH<sub>2</sub>OAr), 7.17 – 7.23 (m, 4H, PhCH<sub>2</sub>CHCHCH<sub>2</sub>OAr), 7.30 (t, *J* = 7.6 Hz, 2H,

**PhCH<sub>2</sub>CHCHCH<sub>2</sub>OAr**), 7.31 (t, J = 8.2 Hz, 1H, **PhCH<sub>2</sub>CHCHCH<sub>2</sub>OAr**), 7.73 (t, J = 2.3 Hz, 1H, **PhCH<sub>2</sub>CHCHCH<sub>2</sub>OAr**), 7.81 (ddd, J = 0.78, 2.1, 8.2 Hz, 1H, **PhCH<sub>2</sub>CHCHCH<sub>2</sub>OAr**). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz): δ = 159.3, 149.4, 139.5, 134.8, 130.0, 128.72, 128.67, 126.5, 125.3, 122.1, 115.9, 109.3, 69.2, 38.8. IR (neat, cm<sup>-1</sup>) 3028, 1617, 1581, 1528, 1494, 1481, 1453, 1347, 1321, 1286, 1244, 1093, 1012. LRMS (*m/z*, EI<sup>+</sup>): Calcd. 269.1, found 269.1.

**1-(4-(4-Methoxyphenoxy)but-2-en-1-yl)-3-nitrobenzene, 10d**



Isolated as a dark brown oil in 49 % yield. R<sub>f</sub> (9:1

Hexanes:Et<sub>2</sub>O) = 0.27. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz,

*E/Z* = 5.5/1): δ = 3.38 (d, J = 6.7 Hz, 2H,

CHCH**CH<sub>2</sub>**PhOMe), 3.79 (s, 3H, CHCHCH**CH<sub>2</sub>**PhOMe), 4.58 (dd, J = 1.0, 5.9 Hz, 2H,

ArO**CH<sub>2</sub>**CHCH), 6.04 – 5.70 (m, 2H, ArOCH**CHCH**), 6.84 (dt, J = 3.8, 6.8 Hz, 2H,

CHCHCH**CH<sub>2</sub>**PhOMe), 7.10 (dt, J = 2.9, 4.7 Hz, 2H, CHCHCH**CH<sub>2</sub>**PhOMe), 7.22 (ddd, J = 0.72,

2.4, 8.3 Hz, 1H, ArOCH**CHCH**), 7.41 (t, J = 8.3 Hz, 1H, ArOCH**CHCH**), 7.30 (t, J = 2.3 Hz,

1H, ArOCH**CHCH**), 7.81 (ddd, J = 0.72, 2.0, 8.0 Hz, 1H, ArOCH**CHCH**). <sup>13</sup>C NMR

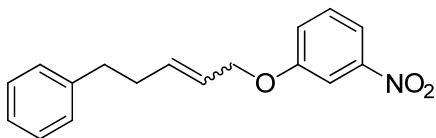
(CDCl<sub>3</sub>, 150 MHz): δ = 159.3, 158.3, 149.3, 135.3, 134.1, 129.7, 129.4, 125.0, 122.1, 115.9,

114.2, 109.3, 69.2, 55.4, 37.9. IR (neat, cm<sup>-1</sup>): 2918, 1611, 1581, 1523, 1511, 1482, 1463,

1349, 1321, 1299, 1286, 1244, 1177, 1094, 1034, 1012. LRMS (*m/z*, EI<sup>+</sup>): Calcd. 299.1,

found 299.1.

**1-Nitro-3-((5-phenylpent-2-en-1-yl)oxy)benzene, 10e**



Isolated as a light yellow oil in 79% yield.  $R_f$  (9:1

Hexanes:Et<sub>2</sub>O) = 0.33. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz, *E/Z*

= 3.3/1):  $\delta$  = 2.42 (q, *J* = 7.1 Hz, 2H, PhCH<sub>2</sub>**CH**<sub>2</sub>CHCH),

2.73 (t, *J* = 7.4 Hz, 2H, Ph**CH**<sub>2</sub>CH<sub>2</sub>CHCH), 4.54 (dd, *J* = 0.84, 6.0 Hz, 2H, CHCH**CH**<sub>2</sub>OAr),

5.69 – 5.94 (m, 2H, **CH**CHCH<sub>2</sub>OAr), 7.17 (t, *J* = 7.0 Hz, 3H, **Ph**CH<sub>2</sub>CH<sub>2</sub>CHCH), 7.21 (dd, *J*

= 2.2, 7.7 Hz, 1H, CHCHCH<sub>2</sub>OAr), 7.27 (t, *J* = 7.6 Hz, 2H, **Ph**CH<sub>2</sub>CH<sub>2</sub>CHCH), 7.41 (t, *J*

= 8.2 Hz, 1H, CHCHCH<sub>2</sub>OAr), 7.72 (t, *J* = 2.3 Hz, 1H, CHCHCH<sub>2</sub>OAr), 7.81 (ddd, *J* = 0.72,

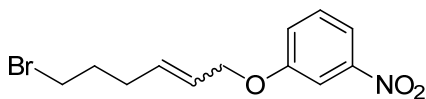
2.1, 8.2 Hz, 1H, CHCHCH<sub>2</sub>OAr). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz):  $\delta$  = 159.3, 149.4, 141.5,

135.6, 130.0, 128.7, 128.6, 128.5, 128.5, 126.1, 124.5, 122.1, 115.9, 109.2, 69.4, 35.5, 34.1.

IR (neat, cm<sup>-1</sup>): 3027, 2920, 1618, 1580, 1526, 1495, 1481, 1454, 1383, 1348, 1321, 1285,

1243, 1076, 1010. LRMS (*m/z*, EI<sup>+</sup>): Calcd. 283.1, found 283.1.

**1-((6-Bromohex-2-en-1-yl)oxy)-3-nitrobenzene, 10f**



Isolated as a bright orange oil in 47% yield.  $R_f$  (9:1

Hexanes:Et<sub>2</sub>O) = 0.27. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz, *E/Z* =

3.3/1):  $\delta$  = 1.98 (p, *J* = 6.8 Hz, 2H, BrCH<sub>2</sub>**CH**<sub>2</sub>CH<sub>2</sub>CHCH), 2.28 (q, *J* = 7.0 Hz, 2H,

BrCH<sub>2</sub>CH<sub>2</sub>**CH**<sub>2</sub>CHCH), 3.42 (t, *J* = 6.6 Hz, 2H, Br**CH**<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CHCH), 4.57 (d, *J* = 5.8 Hz,

2H, CHCH**CH**<sub>2</sub>OAr), 5.74 – 5.88 (m, 2H, **CH**CHCH<sub>2</sub>OAr), 7.23 (dd, *J* = 2.3, 8.2 Hz, 1H,

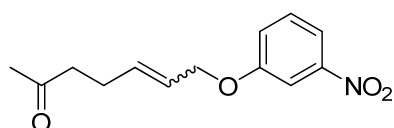
CHCHCH<sub>2</sub>OAr), 7.42 (t, *J* = 8.2 Hz, 1H, CHCHCH<sub>2</sub>OAr), 7.73 (d, 1.7 Hz, 1H,

CHCHCH<sub>2</sub>OAr), 7.82 (d, *J* = 8.1 Hz, 1H, CHCHCH<sub>2</sub>OAr). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz):  $\delta$  =

159.3, 149.4, 134.1, 130.0, 125.5, 122.1, 116.0, 109.2, 69.2, 33.0, 31.8, 30.7. IR (neat, cm<sup>-1</sup>):

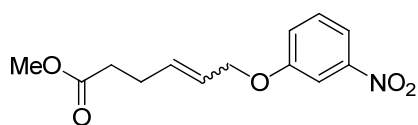
2941, 1619, 1579, 1528, 1482, 1459, 1349, 1321, 1285, 1242, 1093, 1011. HRMS(CI+) calcd for C<sub>12</sub>H<sub>15</sub>O<sub>3</sub>BrN 300.02353 found : 300.02355.

### 7-(3-Nitrophenoxy)hept-5-en-2-one, 10g



Isolated as a dark brown oil in 51% yield. *R<sub>f</sub>* (7:3 Hexanes:EtOAc) = 0.32. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz, *E/Z* = 3.2/1): δ = 2.16 (s, 3H, **CH**<sub>3</sub>COCH<sub>2</sub>CH<sub>2</sub>CHCH), 2.39 (q, *J* = 7.0 Hz, 2H, CH<sub>3</sub>COCH<sub>2</sub>**CH**<sub>2</sub>CHCH), 2.57 (t, *J* = 7.0 Hz, 2H, CH<sub>3</sub>COCH<sub>2</sub>**CH**<sub>2</sub>CHCH), 4.55 (d, *J* = 5.8, 2H, CHCH**CH**<sub>2</sub>OAr), 5.66 – 5.91 (m, 2H, **CH**CHCH<sub>2</sub>OAr), 7.22 (dd, *J* = 2.1, 8.3 Hz, 1H, CHCHCH<sub>2</sub>OAr), 7.42 (t, *J* = 8.2 Hz, 1H, CHCHCH<sub>2</sub>OAr), 7.72 (s, 1H, CHCHCH<sub>2</sub>OAr), 7.82 (d, *J* = 8.0 Hz, 1H, CHCHCH<sub>2</sub>OAr). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz): δ = 207.5, 159.1, 149.2, 134.4, 129.9, 124.8, 121.9, 115.8, 109.1, 69.1, 42.6, 29.9, 26.3. IR (neat, cm<sup>-1</sup>): 3097, 2918, 1715, 1619, 1579, 1524, 1482, 1410, 1349, 1322, 1286, 1243, 1163, 1012. LRMS (*m/z*, EI+): Calcd. 249.1, found 249.1.

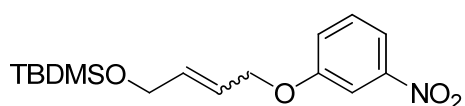
### Methyl 6-(3-nitrophenoxy)hex-4-enoate, 10h



Isolated as a brown oil in 57% yield. *R<sub>f</sub>* (7:3 Hexanes:EtOAc) = 0.48. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz, *E/Z* = 1.1/1) δ = 2.29 – 2.32 (m, 1.3H, *Z*-MeOOCCH<sub>2</sub>CH<sub>2</sub>CHCH), 2.35 – 2.39 (m, 2.5H, *E*-MeOOCCH<sub>2</sub>CH<sub>2</sub>CHCH), 2.44 (m, 4H, *E*-MeOOCCH<sub>2</sub>CH<sub>2</sub>CHCH), 2.46 – 2.51 (m, 3.4H, *Z*-MeOOCCH<sub>2</sub>CH<sub>2</sub>CHCH), 3.68 (s, 3H, *Z*-MeOOCCH<sub>2</sub>CH<sub>2</sub>CHCH), 3.69 (s, 3H, *E*-MeOOCCH<sub>2</sub>CH<sub>2</sub>CHCH), 4.56 (dd, *J* = 0.6, 5.8 Hz, 2H, *E*-CHCHCH<sub>2</sub>OAr), 4.70 (dd, *J* = 0.6, 5.8 Hz, 1.8H, *Z*-CHCHCH<sub>2</sub>OAr), 5.66 – 5.92 (m,

2H, *E/Z*- **CHCHCH<sub>2</sub>OAr**), 7.23 (m, 1H, *E/Z*- **CHCHCH<sub>2</sub>OAr**), 7.42 (m, 1H, *E/Z*- **CHCHCH<sub>2</sub>OAr**), 7.73 (m, 1H, *E/Z*- **CHCHCH<sub>2</sub>OAr**), 7.82 (m, 1H, *E/Z*- **CHCHCH<sub>2</sub>OAr**). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz): δ = 173.3, 159.3, 149.4, 134.1, 130.1, 130.0, 129.6, 129.2, 122.0, 116.0, 109.2, 69.6, 64.7, 51.7, 34.1, 33.6, 27.6, 23.5. IR (neat, cm<sup>-1</sup>): 3023, 2952, 2913, 1736, 1617, 1580, 1523, 1482, 1437, 1349, 1321, 1286, 1243, 1196, 1167, 1093, 1011. LRMS (*m/z*, EI<sup>+</sup>): Calcd. 265.3, found 265.1.

**tert-Butyldimethyl((4-(3-nitrophenoxy)but-2-en-1-yl)oxy)silane, *trans*-10i**



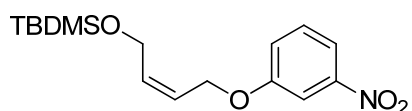
Isolated as a dark brown oil in 47% yield. *R<sub>f</sub>* (7:3

Hexanes:EtOAc) = 0.67. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz,

*E/Z* = 12/1) δ = 0.08 (s, 6H, **TBDMSOCH<sub>2</sub>CHCH**),

0.91 (s, 9H, **TBDMSOCH<sub>2</sub>CHCH**), 4.23 (m, 2H, **TBDMSOCH<sub>2</sub>CHCH**), 4.62 (m, 2H, **CHCHCH<sub>2</sub>OAr**), 5.91 – 6.00 (m, 2H, **CHCHCH<sub>2</sub>OAr**), 7.27 (ddd, *J* = 0.72, 2.4, 8.3 Hz, 1H, **CHCHCH<sub>2</sub>OAr**), 7.42 (t, *J* = 8.2 Hz, 1H, **CHCHCH<sub>2</sub>OAr**), 7.73 (t, 2.3 Hz, 1H, **CHCHCH<sub>2</sub>OAr**), 7.82 (ddd, *J* = 0.9, 2.1, 8.2 Hz, 1H, **CHCHCH<sub>2</sub>OAr**). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz): δ = 159.3, 149.3, 134.2, 130.0, 123.5, 122.0, 115.9, 109.3, 68.8, 62.9, 26.0, 18.5, -5.2. IR (neat, cm<sup>-1</sup>): 2950, 2930, 2884, 2857, 1616, 1581, 1530, 1472, 1463, 1349, 1321, 1286, 1248, 1101, 1024. LRMS (*m/z*, CI<sup>+</sup>): Calcd. 323.1, found 324.2.

**(*Z*)-tert-Butyldimethyl((4-(3-nitrophenoxy)but-2-en-1-yl)oxy)silane, *cis*-10i**



*cis*-2-Butene-1,4-diol (2.18 mL, 26.5 mmol, 4 equiv),

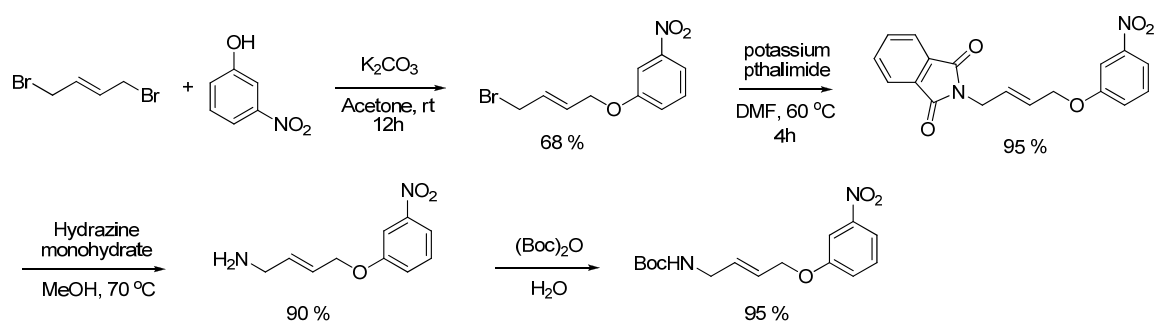
DMAP (81 mg, 0.66 mmol, 10 mole%) and triethylamine

(1.2 mL, 8.6 mmol, 1.3 equiv) were charged to a 100 mL round-bottom flask and dissolved in 20 mL DCM (0.3 M). A solution of *t*-Butylchlorodimethylsilane (1 g, 6.6 mmol, 1 equiv) in 2 mL DCM was added dropwise at room temperature over 3 hours, then stirred at room temperature for an additional hour before the reaction was quenched with a brine solution. The aqueous phase was extracted with 3 x 20 mL DCM, then the combined organic layers were washed with brine and dried over MgSO<sub>4</sub>. The crude product was purified by flash chromatography (3:1 hexanes:EtOAc), yielding 815 mg (61 % yield) of (Z)-4-((tert-Butyldimethylsilyl)oxy)but-2-en-1-ol.

The above product (815 mg, 4 mmol, 1 equiv), 1-iodo-3-nitrobenzene (1.5 g, 6 mmol, 1.5 equiv), copper iodide (76.8 mg, 0.4 mmol, 10 mol%), 1,10-phenanthroline (145 mg, 0.8 mmol, 20 mol%) and cesium carbonate (1.96 g, 6 mmol, 1.5 equiv) were charged to a 7 mL screw-top vial with 3 mL toluene. The vial was sealed tightly and stirred at 100 °C for 36 hours. After cooling to room temperature, the reaction mixture was filtered through a pad of silica gel with diethyl ether. The filtrate was concentrated and the resulting residue was purified by gradient flash chromatography, using two column-lengths of pentanes to flush and eluting with 7:3 hexanes:EtOAc. The reaction yielded 250 mg desired product as a dark yellow liquid (19 % yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ = 0.10 (s, 6H, **TBDMSOCH<sub>2</sub>CHCH**), 0.92 (s, 9H, **TBDMSOCH<sub>2</sub>CHCH**), 4.32 – 4.34 (m, 2H, **TBDMSOCH<sub>2</sub>CHCH**), 4.74 (dd, J = 1.3, 6.0 Hz, 2H, **CHCHCH<sub>2</sub>OAr**), 5.69 – 5.82 (m, 2H, **CHCHCH<sub>2</sub>OAr**), 7.23 (ddd, J = 0.78, 2.6, 8.3 Hz, 1H, **CHCHCH<sub>2</sub>OAr**), 7.42 (t, J = 8.2 Hz, 1H, **CHCHCH<sub>2</sub>OAr**), 7.73 (t, J = 2.3 Hz, 1H, **CHCHCH<sub>2</sub>OAr**), 7.82 (ddd, J = 0.96, 2.2, 8.2 Hz, 1H, **CHCHCH<sub>2</sub>OAr**). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz): δ = 159.3, 149.4, 133.8, 130.1, 124.8, 122.0, 116.0, 109.1, 65.1, 60.2, 26.0, 18.5, -

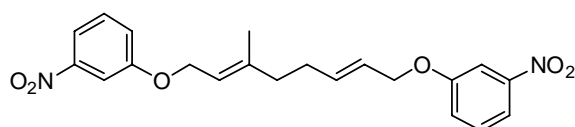
5.1. IR (neat,  $\text{cm}^{-1}$ ): 2954, 2930, 2857, 1620, 1581, 1530, 1471, 1408, 1350, 1319, 1286, 1251, 1091, 1023. LRMS ( $m/z$ ,  $\text{CI}^+$ ): Calcd. 323.1, found 324.1.

**tert-butyl 4-(3-nitrophenoxy)but-2-enylcarbamate, 10j**



Isolated as a light yellow solid.  $R_f$  (3:1 Hexanes:EtOAc) = 0.26.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  = 1.45 (s, 9H, **BocHNCH<sub>2</sub>CHCH**), 3.82 (br s, 2H, **BocHNCH<sub>2</sub>CHCH**), 4.60 (dd,  $J$  = 1.1, 5.4 Hz, 2H, **CHCHCH<sub>2</sub>OAr**), 5.82 – 5.93 (m, 2H, **CHCHCH<sub>2</sub>OAr**), 7.23 (ddd,  $J$  = 0.78, 2.6, 8.3 Hz, 1H, **CHCHCH<sub>2</sub>OAr**), 7.43 (t,  $J$  = 8.2 Hz, 1H, **CHCHCH<sub>2</sub>OAr**), 7.73 (t,  $J$  = 2.3 Hz, 1H, **CHCHCH<sub>2</sub>OAr**), 7.83 (ddd,  $J$  = 0.72, 2.2, 8.2 Hz, 1H, **CHCHCH<sub>2</sub>OAr**).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  = 159.2, 155.8, 149.4, 131.9, 130.1, 125.4, 121.9, 116.0, 109.2, 79.7, 68.6, 42.0, 28.5. IR (neat,  $\text{cm}^{-1}$ ): 3432, 3337, 2978, 1700, 1619, 1524, 1483, 1391, 1365, 1350, 1243, 1168, 1074, 1014. LRMS ( $m/z$ ,  $\text{EI}^+$ ): Calcd. 308.1, found 309.1.

**3,3'-(((2E,6E)-3-methylocta-2,6-diene-1,8-diyl)bis(oxy))bis(nitrobenzene), 10k**



Isolated as a orange solid.  $R_f$  (7:3 Hexanes:EtOAc) = 0.65.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.81 (d,  $J$ =8.7 Hz, 2H),



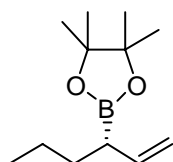
7.72 (t, J=2.4 Hz, 2H), 7.41 (t, J=9.2 Hz, 2H), 7.22 (td, J=2.5 Hz, J=8.2 Hz, 2H), 5.90-5.82 (m, 1H), 5.74-5.67 (m, 1H), 4.61 (d, J=6.8 Hz, 2H), 4.53 (d, J=6.2, 2H), 2.28 (q, J=7.2 Hz, 2H), 2.20 (t, J=7.0 Hz, 2H), 1.78 (s, 3H)  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 159.1, 149.2, 141.3, 135.3, 129.8, 124.4, 122.1, 122.0, 109.0, 108.9, 69.2, 65.4, 38.7, 30.3, 16.7 HRMS(EI) calcd for  $\text{C}_{21}\text{H}_{22}\text{O}_6\text{N}_2$  398.14779 found : 398.14843

## 2.10 Typical reaction condition for allylic substitution reactions

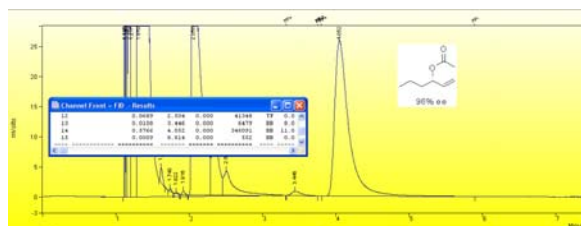
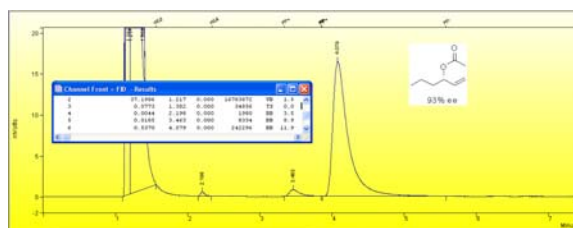
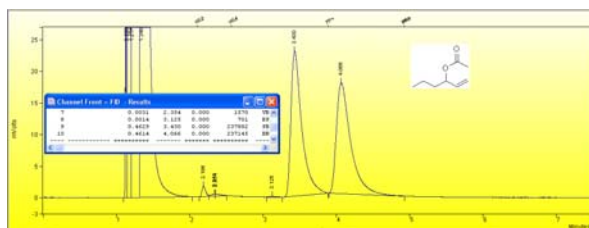
Allylic aryl ethers (0.20 mmol) and bis(pinacolato) diboron (56 mg, 0.22 mmol) were dissolved in  $\text{Et}_2\text{O}$  (1 mL).  $\text{NaOtBu}$  (6 mg, 0.060 mmol) was added to the reaction mixture. And then the reaction mixture was cooled to  $-55\text{ }^\circ\text{C}$  and MeOH (18  $\mu\text{L}$ , 0.40 mmol) was added. After 5 min, 6-NHC copper catalyst, **1b** (1.2 mg, 0.0020 mmol) was added. After complete consumption of allylic aryl ethers, the reaction mixture was filtered through silica gel and washed with  $\text{Et}_2\text{O}$ . The filtrate was concentrated under rotary evaporator. The resulting residue was purified by column chromatography (Hexane: $\text{Et}_2\text{O}$ ) to afford the desired products. Absolute configuration was determined by comparison with known data.

## 2.11 Reaction results and data for allylic substitutions

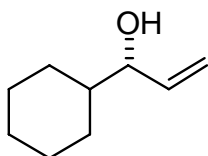
### (S)-2-(hex-1-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, **11a**



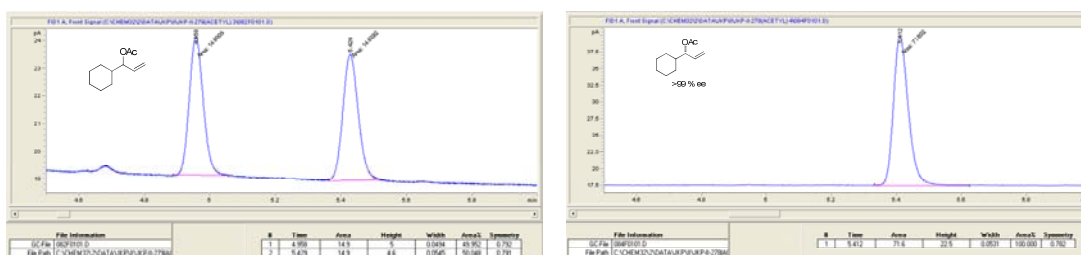
Boronate, **11a** was prepared according to the general procedure from *E* and *Z* isomer substrates and purified by column chromatography (Hexanes to Hexanes: Et<sub>2</sub>O 20:1). From the *E* isomer: **11a** was isolated as clear oil (90 % yield, 93 % ee). From the *Z* isomer: **11a** was isolated as a clear oil (80 % yield, 96 % ee). *R*<sub>f</sub> (20:1 Hexanes:EtOAc) = 0.47. Ee was determined by GC analysis after oxidation and acetylation of the alcohol. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 5.79 (ddd, *J*=17.1 Hz, 10.1 Hz, 8.8 Hz, 1H) 4.97 (ddd, *J*=17.1 Hz, 1.8 Hz, 1.2 Hz, 1H) 4.92 (ddd, *J*=10.1 Hz, 1.8 Hz, 0.7 Hz, 1H) 1.84 (q, *J*=7.8 Hz, 1H) 1.56-1.50 (m, 1H) 1.44-1.25 (m, 3H) 1.24 (s, 6H) 1.23 (s, 6H) 0.89 (t, *J*=7.3 Hz, 3H) <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 140.0, 113.6, 83.3, 32.7, 24.94, 24.85, 22.3, 14.3 [*α*]<sub>D</sub><sup>25</sup> = +11.1° (*c*=1.5, CH<sub>2</sub>Cl<sub>2</sub>, 96% ee) HRMS(EI) calcd for C<sub>12</sub>H<sub>23</sub>BO<sub>2</sub> 210.17912 found : 210.18004. Absolute configuration was determined by comparison with known data of acetylated product. Observed data [*α*]<sub>D</sub><sup>25</sup> = -4.4° (*c*=0.3, CHCl<sub>3</sub>), known data for *S* configuration [*α*]<sub>D</sub><sup>25</sup> = -30.7° (*c*=3.8, CHCl<sub>3</sub>)<sup>7</sup>



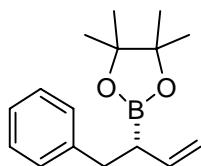
**(R)-1-cyclohexylprop-2-en-1-ol, 12b**



Boronate, **11b** was prepared according to the general procedure. The boronate ester was oxidized to the alcohol, **12b** and purified by column chromatography (Hexanes to Hexanes: Et<sub>2</sub>O 10:1). **12b** was isolated as clear oil (84 % yield, >99 % ee). *R<sub>f</sub>* (10:1 Hexanes:EtOAc) = 0.12. Ee was determined by GC analysis (β-DM column, 110 °C, 4 mL/min) after acetylation of the alcohol. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 5.86 (ddd, *J*=6.5 Hz, 10.4 Hz, 17.0 Hz, 1H) 5.21 (dt, *J*=1.4 Hz, *J*=17.2 Hz, 1H) 5.15 (dt, *J*=1.3 Hz, *J*=10.4 Hz, 1H) 3.85 (t, *J*=6.1 Hz, 1H) 1.85 (d, *J*=12.7 Hz, 1H) 1.80-1.72 (m, 2H), 1.71-1.64 (m, 2H) 1.48-1.44 (br, 1H), 1.44-1.37 (m, 1H), 1.28-.95 (m, 5H) <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 139.8, 115.5, 43.5, 28.8, 28.3, 26.5, 26.2, 26.1. [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +14.7° (*c*=0.70, CHCl<sub>3</sub>) HRMS(Cl<sup>+</sup>) calcd for C<sub>9</sub>H<sub>15</sub>O 139.11230 found : 139.11196. Absolute configuration was determined by comparison with known data for *S* configuration, [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -16.04° (*c*=2.35, CHCl<sub>3</sub>, >99% ee).<sup>8</sup>

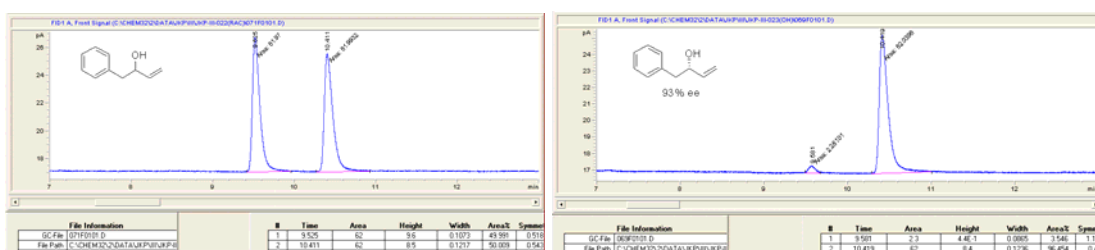


**(S)-4,4,5,5-tetramethyl-2-(1-phenylbut-3-en-2-yl)-1,3,2-dioxaborolane, 11c**

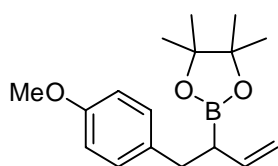


Boronate, **11c** was prepared according to the general procedure and purified by column chromatography (Hexanes to Hexanes:Et<sub>2</sub>O 20:1). **11c** was isolated as a clear oil (95 % yield, 93 % ee). *R<sub>f</sub>* (20:1

Hexanes:EtOAc = 0.28. Ee was determined by GC ( $\beta$ -DM column, 110 °C, 4 mL/min) after oxidation to the alcohol.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26-7.20 (m, 4H), 7.16-7.13 (m, 1H), 5.84 (ddd,  $J=8.3$  Hz,  $J=9.36$  Hz,  $J=17.5$  Hz, 1H) 5.00 (dt,  $J=1.4$  Hz,  $J=17.2$  Hz, 1H) 4.95 (dt,  $J=1.02$  Hz,  $J=10.3$  Hz, 1 H) 2.89 (dd,  $J=8.5$  Hz,  $J=13.7$  Hz, 1H) 2.78 (dd,  $J=7.6$  Hz,  $J=13.7$  Hz, 1H) 2.2 (q,  $J=8.1$  Hz, 1H) 1.17 (s, 6H) 1.15 (s, 6H)  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  141.6, 138.8, 128.9, 128.0, 125.7, 114.1, 83.3, 36.4, 24.6.  $[\alpha]_{\text{D}}^{25} = +3.88^\circ$  ( $c=1.34$ ,  $\text{CHCl}_3$ ) HRMS( $\text{CI}^+$ ) calcd for  $\text{C}_{16}\text{H}_{24}\text{BO}_2$  259.1869 found : 259.1867. Absolute configuration was determined by comparison with known data of alcohol product. Observed data  $[\alpha]_{\text{D}}^{25} = 10.4^\circ$  ( $c=0.7$ ,  $\text{CHCl}_3$ ), known data for *R* configuration  $[\alpha]_{\text{D}}^{25} = -12.5^\circ$  ( $c=1.0$ ,  $\text{CHCl}_3$ , 95% ee)<sup>9</sup>



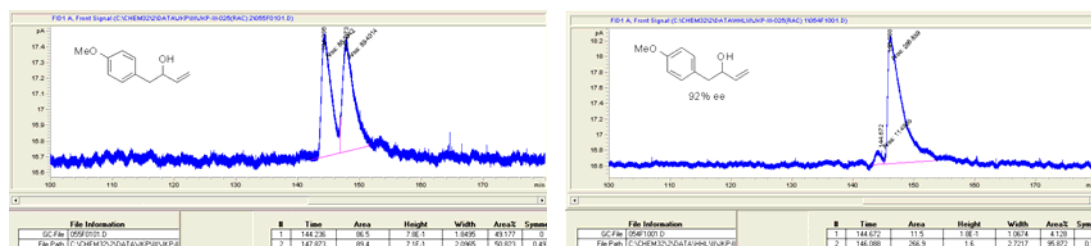
## 2-(1-(4-methoxyphenyl)but-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, **11d**



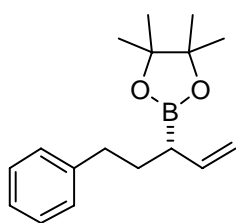
Boronate, **11d** was prepared according to the general procedure and purified by column chromatography (Hexanes to Hexanes:Et<sub>2</sub>O 10:1). **11d** was isolated as a clear oil (87 % yield, 92 % ee).  $R_f$  (20:1

Hexanes:EtOAc) = 0.09 Ee was determined by GC ( $\beta$ -DM column, 90 °C, 1.6 mL/min) after oxidation to the alcohol.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.13 (d,  $J=8.6$  Hz, 2H), 6.79 (d,  $J=8.6$  Hz, 2H), 5.82 (ddd,  $J=8.3$  Hz,  $J=9.4$  Hz,  $J=17.8$  Hz, 1H) 5.02 (dt,  $J=1.4$  Hz,  $J=17.2$  Hz, 1H) 4.94 (d,  $J=10.2$  Hz, 1H) 3.77 (s, 3H) 2.83 (dd,  $J=8.5$  Hz,  $J=13.3$  Hz, 1H) 2.72 (dd,  $J=7.6$  Hz,

J=13.9 Hz, 1H) 2.19 (q, J=8.2 Hz, 1H) 1.17 (s, 6H) 1.15 (s, 6H)  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  157.7, 138.8, 133.8, 129.8, 114.1, 113.5, 83.3, 55.2, 35.5, 24.7, 24.6.  $[\alpha]_{\text{D}}^{25} = -1.03^\circ$  (c=1.00,  $\text{CHCl}_3$ ) HRMS( $\text{CI}^+$ ) calcd for  $\text{C}_{17}\text{H}_{26}\text{BO}_3$  289.1975 found : 289.1971



### (S)-4,4,5,5-tetramethyl-2-(5-phenylpent-1-en-3-yl)-1,3,2-dioxaborolane, **11e**

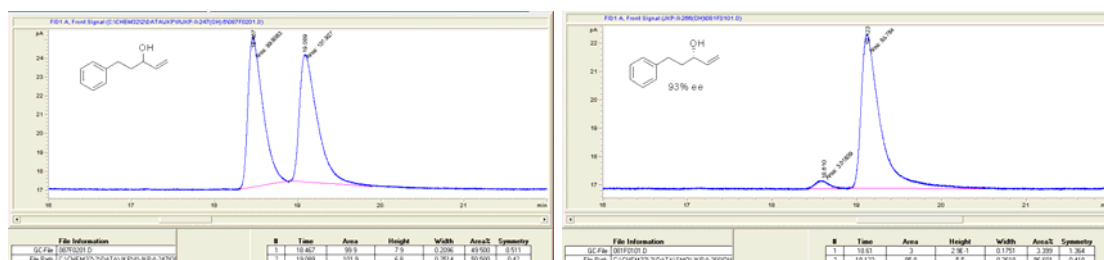


Boronate, **11e** was prepared according to general procedure and purified by column chromatography (Hexanes to Hexanes: $\text{Et}_2\text{O}$  20:1).

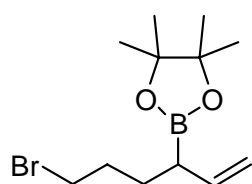
**11e** was isolated as a clear oil (88 % yield, 93 % ee).  $R_f$  (20:1

Hexanes: $\text{EtOAc}$ ) = 0.27. Ee was determined by GC ( $\beta$ -DM column,

110  $^\circ\text{C}$ , 4 mL/min) after oxidation to the alcohol.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28-7.15 (m, 5H) 5.82 (ddd, J=8.1 Hz, J=10.2 Hz, J=18.6 Hz, 1H) 5.04-4.98 (m, 2H) 2.68-2.54 (m, 2H) 1.92-1.89 (m, 2H) 1.79-1.70 (m, 1H) 1.24 (s, 12H)  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  142.7, 139.2, 128.5, 128.2, 125.6, 114.0, 83.2, 35.2, 24.7, 24.6  $[\alpha]_{\text{D}}^{25} = -4.90^\circ$  (c=1.00,  $\text{CH}_2\text{Cl}_2$ ) HRMS( $\text{CI}^+$ ) calcd for  $\text{C}_{17}\text{H}_{26}\text{BO}_2$  273.20259 found : 273.20373 Absolute configuration was determined by comparison with known data of boronate.  $[\alpha]_{\text{D}}^{25} = -5.12^\circ$  (c=1.04,  $\text{CH}_2\text{Cl}_2$ )<sup>10</sup>

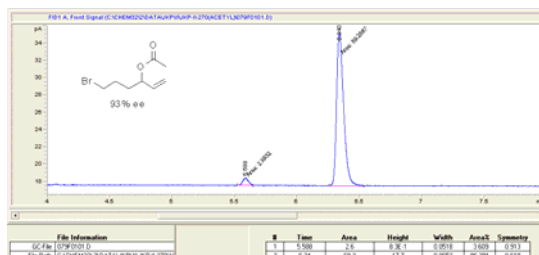
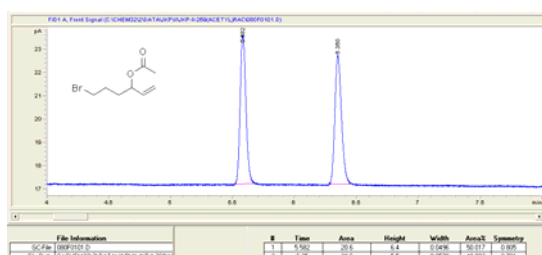


## 2-(6-bromohex-1-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, **11f**

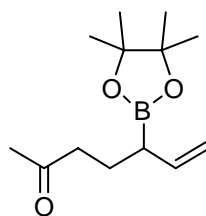


Boronate, **11f** was prepared according to the general procedure and purified by column chromatography (Hexanes to Hexanes:Et<sub>2</sub>O 20:1).

**11f** was isolated as a clear oil (92 % yield, 93 % ee). *R*<sub>f</sub> (10:1 Hexanes:Et<sub>2</sub>O) = 0.28. Ee was determined by GC (β-DM column, 110 °C, 4 mL/min) after oxidation and acetylation of the alcohol. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 5.76 (ddd, *J*=8.7 Hz, *J*=10.1, *J*=17.1 Hz, 1H) 5.02-4.96 (m, 2H) 3.40 (td, *J*=2.6 Hz, *J*=8.0 Hz, 2H) 1.96-1.88 (m, 1H) 1.88-1.80 (m, 2H) 1.73-1.65 (m, 1H) 1.60-1.53 (m, 1H) 1.25 (s, 12H) <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 138.8, 114.2, 83.3, 33.7, 32.2, 28.7, 24.7, 24.6. [*α*]<sub>D</sub><sup>25</sup> = +5.96° (*c*=1.33, CHCl<sub>3</sub>) HRMS(CI<sup>+</sup>) calcd for C<sub>12</sub>H<sub>23</sub>BO<sub>2</sub>Br 289.0974 found : 289.0968.



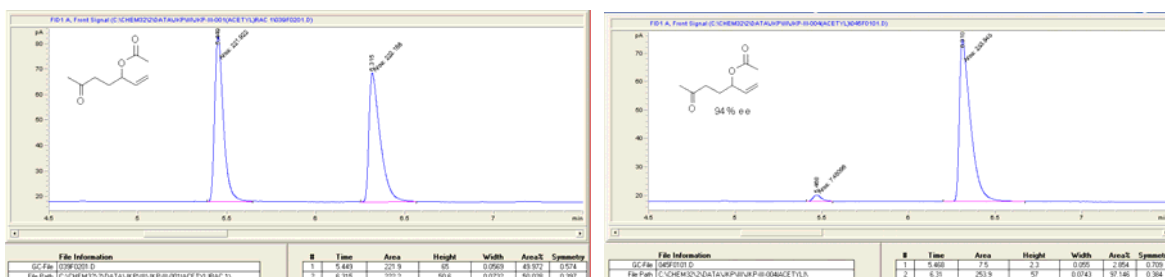
## 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-6-en-2-one, **11g**



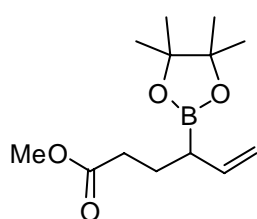
Boronate, **11g** was prepared according to the general procedure and purified by column chromatography (Hexanes to Hexanes:Et<sub>2</sub>O 5:1).

**11g** was isolated as a clear oil (50 % yield, 94 % ee). *R*<sub>f</sub> (5:1 Hexanes:Et<sub>2</sub>O) = 0.16. Ee was determined by GC analysis (β-DM column, 100 °C, 4 mL/min) after oxidation and acetylation of the alcohol. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 5.74 (ddd, *J*=8.6 Hz, *J*=10.2 Hz, 17.2 Hz, 1H) 5.01-4.97 (m, 2H) 2.50-2.38 (m, 2H) 2.13 (s,

3H) 1.87-1.68 (m, 3H) 1.24 (s, 12H)  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  209.1, 138.7, 114.4, 83.3, 42.9, 29.9, 24.7, 24.6, 24.0.  $[\alpha]_{\text{D}}^{25} = +3.76^\circ$  ( $c=0.90$ ,  $\text{CHCl}_3$ ) HRMS( $\text{CI}^+$ ) calcd for  $\text{C}_{13}\text{H}_{24}\text{BO}_3$  239.18186 found : 239.18199.



### methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate, **11h**

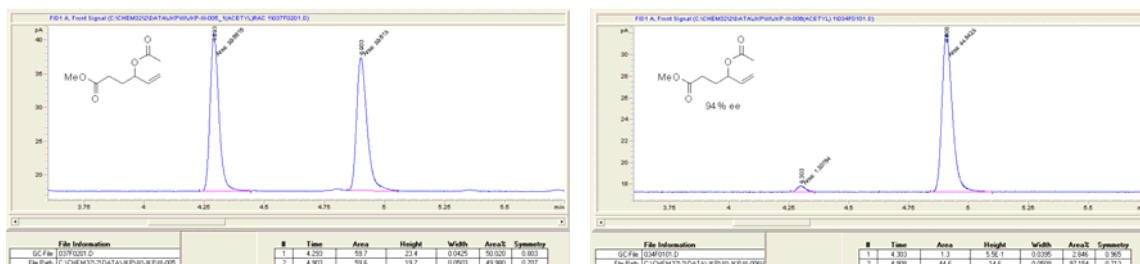


Boronate, **11h** was prepared according to the general procedure and purified by column chromatography (Hexanes to Hexanes: $\text{Et}_2\text{O}$  10:1).

**11h** was isolated as a clear oil (>95 % yield, 94 % ee).  $R_f$  (5:1

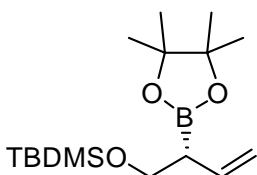
Hexanes: $\text{EtOAc}$ ) = 0.52. Ee was determined by GC analysis ( $\beta$ -DM

column, 110  $^\circ\text{C}$ , 4 mL/min) after oxidation and acetylation of the alcohol.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  5.78-5.72 (m, 1H) 5.02-4.98 (m, 2H) 3.66 (s, 3H) 2.39-2.34 (m, 1H) 2.33-2.28 (m, 1H) 1.93-1.87 (m, 1H) 1.83-1.73 (m, 2H) 1.24 (s, 12H)  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  174.1, 138.4, 114.6, 83.3, 51.4, 33.3, 25.2, 24.7, 24.6.  $[\alpha]_{\text{D}}^{25} = +5.1^\circ$  ( $c=0.08$ ,  $\text{CHCl}_3$ ) HRMS( $\text{CI}^+$ ) calcd for  $\text{C}_{13}\text{H}_{24}\text{BO}_4$  255.1768 found : 255.1772

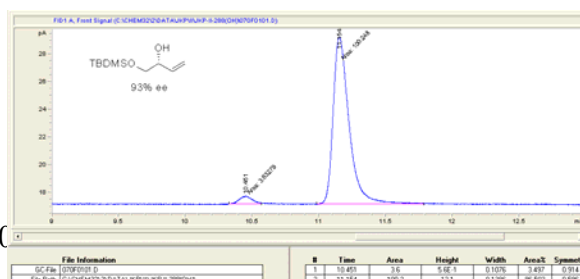
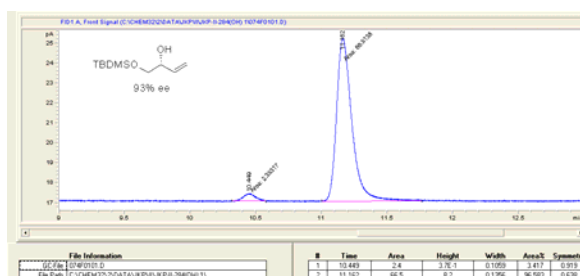
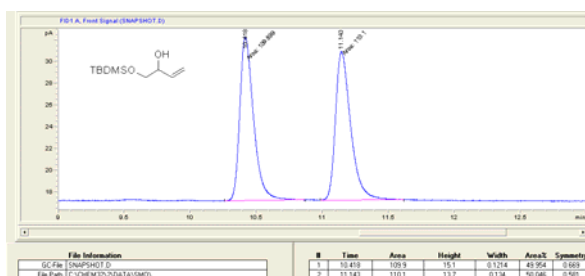


tert-butyldimethyl((2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-yl)oxy)silane,

**11i**

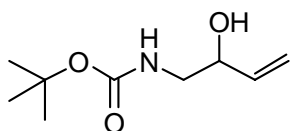


Boronate, **11i** was prepared according to the general procedure with both the *E* and *Z* alkene isomers, respectively and purified by column chromatography (Hexanes to Hexanes:Et<sub>2</sub>O 20:1). From the predominately *cis* isomer, **11i** was isolated as a clear oil (91 % yield, 93 % ee). From the predominately *trans* isomer, **11i** was isolated as a clear oil (83 % yield, 93 % ee). R<sub>f</sub> (20:1 Hexanes:EtOAc) = 0.26. Ee was determined by GC analysis (β-DM column, 80 °C, 4 mL/min) after oxidation. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 5.82 (ddd, J=8.6 Hz, J=10.2 Hz, 17.3 Hz, 1H) 5.04 (dt, J=1.6 Hz, J=16.9 Hz, 1H) 4.99 (dd, J=1.56 Hz, J=10.4 Hz, 1 H) 3.78-3.72 (m, 2H) 2.12 (q, J=7.4 Hz, 1H) 1.24 (s, 12H) 0.88 (s, 9H) 0.04 (s, 6H) <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 136.6, 115.0, 83.2, 64.3, 25.9, 24.7, 18.3, -5.4 [α]<sub>D</sub><sup>25</sup> = +0.87° (c=1.2, CHCl<sub>3</sub>) HRMS(CI<sup>+</sup>) calcd for C<sub>16</sub>H<sub>34</sub>BO<sub>3</sub>Si 313.23704 found : 313.23701. Absolute configuration was determined by comparison with known data of alcohol product. Observed data [α]<sub>D</sub><sup>25</sup> = +4.0° (c=0.7, CHCl<sub>3</sub>), known data for *S* configuration [α]<sub>D</sub><sup>25</sup> = +4.6° (c=1.0, CHCl<sub>3</sub>).<sup>11</sup>





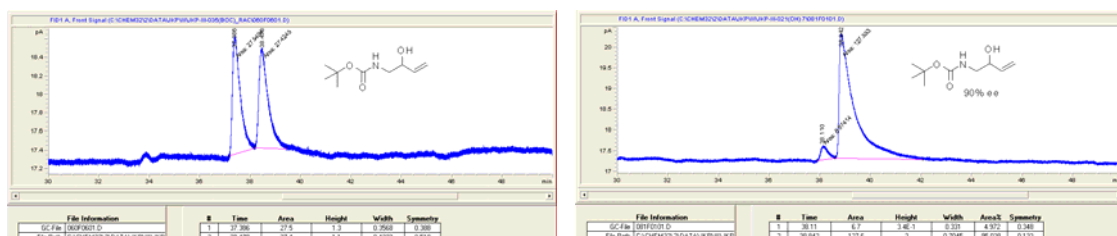
***tert*-butyl (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl)carbamate, **12j****



Boronate, **11j** was prepared according to the general procedure.

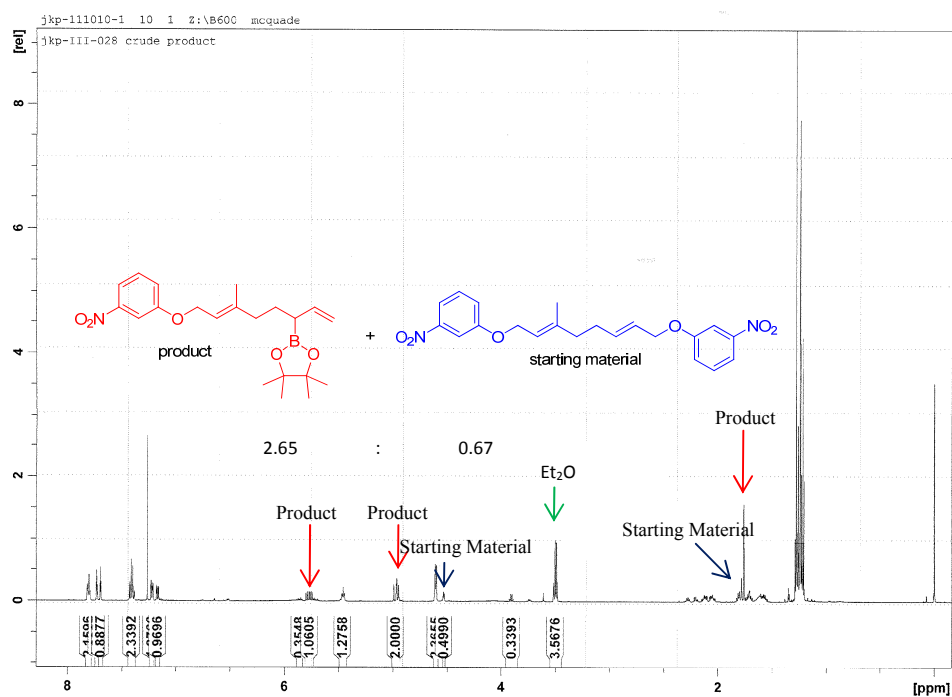
The boronate was oxidized to the alcohol, **12i** and purified by column chromatography (Hexanes:Et<sub>2</sub>O 1:1). **12i** was isolated as

clear oil (92 % yield, 90 % ee). *R<sub>f</sub>* (1:1 Hexanes:Et<sub>2</sub>O) = 0.32. Ee was determined by GC analysis (β-DM column, 115 °C, 4 mL/min) after oxidation. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 5.86 (ddd, *J*=5.5 Hz, *J*=10.5 Hz, *J*=17.1 Hz 1H) 5.34 (dt, *J*=1.4 Hz, *J*=17.2, 1H) 5.20 (d, *J*=10.6, 1H) 5.03-4.90 (br, 1H) 4.29-4.20 (br, 1H) 3.43-3.32 (br, 1H) 3.12-3.07 (m, 1H) 2.72-2.66 (br, 1H) 1.45 (s, 9H) <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 156.8, 138.0, 116.2, 79.7, 72.4, 46.3, 28.3 [*α*]<sub>D</sub><sup>25</sup> = -2.69° (c=1.40, CHCl<sub>3</sub>) HRMS(CI<sup>+</sup>) calcd for C<sub>9</sub>H<sub>18</sub>O<sub>3</sub>N 188.12867 found : 188.12815.



### Testing the reactivity of the tri-substituted alkene versus the di-substituted alkene

Allylic aryl ether, **10k** (19 mg, 0.048 mmol) and bis(pinacolato) diboron (12 mg, 0.053 mmol) was dissolved in Et<sub>2</sub>O (1 mL). NaOtBu (1.5 mg, 0.015 mmol) was added to the reaction mixture. And then the reaction mixture was cooled to -55° C and MeOH (5 µL, 0.1 mmol) was added. After 5 min, 6-NHC copper catalyst, **4** (0.3 mg, 0.000480 mmol) was added. The reaction was quenched after 18 hours. Solvent was evaporated *in vacuo* and <sup>1</sup>H NMR was taken of the crude mixture (80% yield based on unreacted starting material).



### 3. References:

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