

*Supporting Information for*

**Copper-Catalyzed Three-component Carboboration of Alkynes and Alkenes**

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Contents

<b>General Remarks</b>	<b>S2</b>
<b>Alkynes</b>	<b>S2</b>
<b>Carbon Electrophiles</b>	<b>S2</b>
<b>Experimental Procedures and Characterization Data of Products</b>	<b>S3</b>
<b>References</b>	<b>S14</b>
<b><math>^1\text{H}</math> and <math>^{13}\text{C}</math> Spectra of Products</b>	<b>S15</b>

### General Remarks.

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on a Varian 400-MR ( $^1\text{H}$ , 400 MHz;  $^{13}\text{C}$ , 100 MHz) spectrometer or a Varian System 500 ( $^1\text{H}$ , 500 MHz;  $^{13}\text{C}$ , 125 MHz) spectrometer using residual chloroform ( $^1\text{H}$ ,  $\delta$  = 7.26) or  $\text{CDCl}_3$  ( $^{13}\text{C}$ ,  $\delta$  = 77.0) as an internal standard.  $^1\text{H}$  NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, br = broad, m = multiplet), coupling constants (Hz), integration. High-resolution mass spectra were obtained with a Thermo Fisher Scientific LTQ Orbitrap XL. Preparative recycling gel permeation chromatography was performed with JAI LC-908 or JAI LC-9201 equipped with JAI GEL-1H and -2H columns (chloroform as an eluent). Column chromatography was carried out using Merck Kieselgel 60. Unless otherwise noted, commercially available reagents were used without purification. Toluene and THF were distilled from sodium/benzophenone ketyl. DMF and DMI were distilled from  $\text{CaH}_2$ . Acetonitrile was distilled from  $\text{P}_2\text{O}_5$ .

### Alkynes.

1,2-Bis(4-methoxyphenyl)ethyne (**1b**), 1-(4-methoxyphenyl)-2-phenylethyne (**1c**), 1-(4-bromophenyl)-2-phenylethyne (**1d**) and 1-phenyl-2-(2-thienyl)ethyne (**1e**) were prepared according to literature procedures.<sup>1,2</sup>

### Carbon Electrophiles.

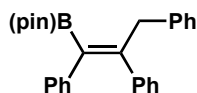
Cinnamyl diethyl phosphate (**3i**)<sup>3</sup> and methyl 4-methylbenzenesulfonate (**3k**)<sup>4</sup> were prepared according to literature.

### Cu-Catalyzed Carboboration of Alkynes: A General Procedure.

A schlenk tube equipped with a magnetic stirring bar was charged with  $\text{Cu}(\text{OAc})_2$  (6.0  $\mu\text{mol}$ ), tricyclohexylphosphine (25wt% solution in toluene, 0.021 mmol), an alkyne (0.30 mmol), bis(pinacolato)diboron (0.39 mmol), a carbon electrophile (0.90 mmol), potassium *tert*-butoxide (1 M solution in THF, 0.45 mmol) and DMF (0.55 mL). The mixture was stirred at 50  $^\circ\text{C}$  for the period as specified in Tables 2 and 3, diluted with ethyl acetate before filtration through a Celite plug. The organic solution was washed two times with brine and dried over  $\text{MgSO}_4$ . Evaporation of the solvent followed by silica gel-column chromatography (hexane/ethyl acetate as an eluent) or gel permeation chromatography (chloroform as an eluent) gave the product.

In  $^{13}\text{C}$  NMR spectra, boron-bound carbons were not detected because of quadrupolar relaxation.

**(Z)-4,4,5,5-Tetramethyl-2-(1,2,3-triphenylprop-1-en-1-yl)-1,3,2-dioxaborolane (4aa)**



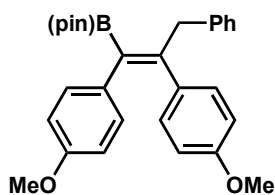
Isolated in 67% as a pale yellow solid: mp 124.7–126.2 °C

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.31 (s, 12 H), 4.06 (s, 2 H), 6.78–6.81 (m, 2 H), 6.96–7.00 (m, 6 H), 7.05 (t,  $J = 7.0$  Hz, 2 H), 7.12 (t,  $J = 7.0$  Hz, 1 H), 7.18–7.23 (m, 4 H)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.74, 44.43, 83.81, 125.36, 125.83, 126.18, 127.37, 127.46, 128.08, 129.07, 129.193, 129.64, 139.60, 141.43, 141.84, 151.59

HRMS Calcd for  $\text{C}_{27}\text{H}_{29}\text{O}_2\text{BNa}$ :  $[\text{M}+\text{Na}]^+$ , 419.21528. Found:  $m/z$ , 419.21613

**(Z)-2-(1,2-Bis(4-methoxyphenyl)-3-phenylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ba)**



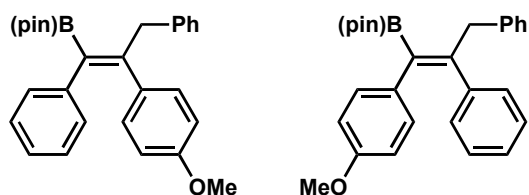
Isolated in 67% as a pale yellow solid: mp 123.7–125.8 °C

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.30 (s, 12 H), 3.67 (s, 3 H), 3.71 (s, 3 H), 4.02 (s, 2 H), 6.54 (d,  $J = 8.7$  Hz, 2 H), 6.62 (d,  $J = 8.7$  Hz, 2 H), 6.75 (d,  $J = 8.6$  Hz, 2 H), 6.89 (d,  $J = 8.6$  Hz, 2 H), 7.12 (t,  $J = 7.3$  Hz), 7.18–7.24 (m, 4 H)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.69, 44.39, 54.89, 54.93, 83.66, 112.83, 112.99, 125.68, 128.01, 128.97, 130.36, 130.71, 133.91, 134.23, 139.91, 149.90, 157.15, 157.67

HRMS Calcd for  $\text{C}_{29}\text{H}_{33}\text{O}_4\text{BNa}$ :  $[\text{M}+\text{Na}]^+$ , 479.23641. Found:  $m/z$ , 479.23651

**A mixture of (Z)-2-(2-(4-methoxyphenyl)-1,3-diphenylprop-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ca) and (Z)-2-(1-(4-methoxyphenyl)-2,3-diphenylprop-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4'ca)**



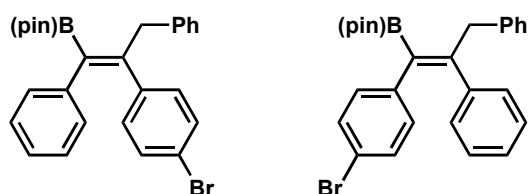
Isolated in 84% as a pale yellow oil

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.21 (s), 1.23 (s), 3.56 (s), 3.59 (s), 3.96 (s), 3.97 (s), 6.44 (d,  $J$  = 8.7 Hz), 6.51 (d,  $J$  = 8.7 Hz), 6.66 (d,  $J$  = 8.8 Hz), 6.72–6.74 (m), 6.81 (d,  $J$  = 8.5 Hz), 6.90–6.93 (m), 6.97–7.04 (m), 7.09–7.17 (m)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.68, 24.71, 44.35, 44.43, 54.85, 54.89, 83.67, 83.71, 112.77, 112.93, 125.19, 125.73, 126.02, 127.40, 127.49, 128.00, 128.02, 128.98, 129.01, 129.18, 129.66, 130.33, 130.66, 133.65, 134.10, 139.67, 139.84, 141.73, 142.01, 150.52, 150.95, 157.27, 157.79

HRMS Calcd for  $\text{C}_{28}\text{H}_{31}\text{O}_3\text{BNa}$ :  $[\text{M}+\text{Na}]^+$ , 449.22585. Found:  $m/z$ , 449.22574

**A mixture of**  
**(Z)-2-(2-(4-bromophenyl)-1,3-diphenylprop-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4da) and**  
**(Z)-2-(1-(4-bromophenyl)-2,3-diphenylprop-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4'ea)**



Isolated in 58% as a colorless solid: mp 92.3–94.8 °C

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.30 (s), 1.30 (s), 4.02 (s), 4.06 (s), 6.65 (d,  $J$  = 8.3 Hz), 6.76–6.77 (m), 6.83 (d,  $J$  = 8.6 Hz), 6.94–7.21 (m)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.71, 44.18, 44.32, 83.90, 119.34, 120.18, 125.56, 125.98, 126.98, 126.39, 127.54, 127.66, 128.07, 128.18, 129.00, 129.02, 129.04, 129.51, 130.56, 130.86, 131.39, 139.18, 139.31, 140.52, 140.71, 141.02, 141.49, 150.16, 152.98

HRMS Calcd for  $\text{C}_{27}\text{H}_{28}\text{O}_2\text{BrNa}$ :  $[\text{M}+\text{Na}]^+$ , 497.12579. Found:  $m/z$ , 497.12579

**A mixture of**  
**(Z)-2-(1,3-diphenyl-2-(thiophen-2-yl)prop-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ea) and**  
**(Z)-2-(2,3-diphenyl-1-(thiophen-2-yl)prop-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4'ea)**



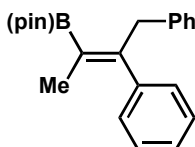
Isolated in 49% as a pale yellow solid: mp 92.3–94.8 °C

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.24 (s), 1.40 (s), 3.92 (s), 4.14 (s), 6.55 (d,  $J = 3.7$  Hz), 6.65 (t,  $J = 4.4$  Hz), 6.75–6.78 (m), 6.86 (dd,  $J = 7.3, 2.1$  Hz), 6.95–6.98 (m), 7.13–7.28 (m), 7.36 (d,  $J = 7.8$  Hz)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.60, 24.09, 43.97, 45.64, 83.77, 84.25, 125.08, 125.66, 125.71, 125.80, 125.97, 126.00, 126.14, 126.98, 127.08, 127.83, 128.07, 128.12, 128.19, 128.72, 129.02, 129.28, 129.30, 139.79, 139.86, 141.63, 141.87, 142.94, 143.15, 143.48, 149.85

HRMS Calcd for  $\text{C}_{25}\text{H}_{27}\text{O}_2\text{BNaS}$ :  $[\text{M}+\text{Na}]^+$ , 425.17170. Found:  $m/z$ , 425.17188

**(Z)-2-(3,4-Diphenylbut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4fa)**



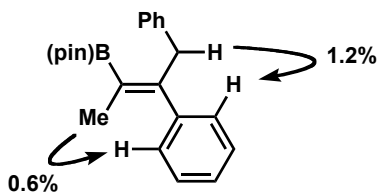
Isolated in 54% as a pale yellow oil

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.35 (s, 12 H), 1.61 (s, 3 H), 4.00 (s, 2 H), 6.85 (d,  $J = 7.0$  Hz, 2 H), 7.07–7.22 (m, 10 H)

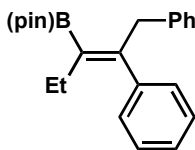
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  18.36, 24.58, 43.90, 83.28, 125.53, 126.13, 127.68, 127.82, 128.09, 129.07, 140.15, 142.77, 153.55

HRMS Calcd for  $\text{C}_{22}\text{H}_{27}\text{O}_2\text{BNa}$ :  $[\text{M}+\text{Na}]^+$ , 357.19963. Found:  $m/z$ , 357.19980

The stereochemistry was determined by NOE as shown below:



**(Z)-2-(1,2-Diphenylpent-2-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ga)**



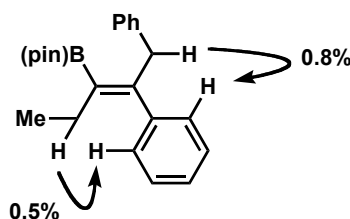
Isolated in 50% as a pale yellow oil

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.89 (t,  $J = 7.5$  Hz, 3 H), 1.35 (s, 12 H), 1.98 (q,  $J = 7.5$  Hz, 2 H), 3.92 (s, 2 H), 6.81 (dd,  $J = 7.9, 1.5$  Hz, 2 H), 7.05 (d,  $J = 7.4$  Hz, 2 H), 7.09–7.19 (m, 8 H)

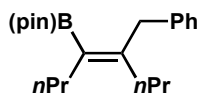
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.99, 24.86, 25.65, 44.35, 83.30, 125.56, 126.07, 127.56, 127.84, 128.06, 129.13, 139.97, 142.61, 151.74

HRMS Calcd for  $\text{C}_{23}\text{H}_{29}\text{O}_2\text{BNa}$ :  $[\text{M}+\text{Na}]^+$ , 371.21528. Found:  $m/z$ , 371.21543

The stereochemistry was determined by NOE as shown below:



**(*E*)-2-(5-Benzyl-oct-4-en-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ha)**



Isolated in 57% as a pale yellow oil

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.85 (t,  $J = 7.3$  Hz, 3 H), 0.92 (t,  $J = 7.5$  Hz, 3 H), 1.26 (s, 12 H), 1.30–1.42 (m, 4 H), 1.93 (t,  $J = 7.9$  Hz, 2 H), 2.16 (t,  $J = 7.7$  Hz, 2 H), 3.66 (s, 2 H), 7.16 (t,  $J = 6.8$  Hz, 1 H), 7.22–7.27 (m, 4 H)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.31, 14.52, 21.87, 23.74, 24.76, 33.00, 33.53, 41.68, 82.87, 125.55, 128.01, 128.90, 141.36, 151.56

HRMS Calcd for  $\text{C}_{21}\text{H}_{33}\text{O}_2\text{BNa}$ :  $[\text{M}+\text{Na}]^+$ , 351.24658. Found:  $m/z$ , 351.24658

**A mixture of (*E*)-2-(3-benzyl-oct-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ia) and (*E*)-4,4,5,5-tetramethyl-2-(2-methyl-1-phenyloct-2-en-3-yl)-1,3,2-dioxaborolane (4'ia)**



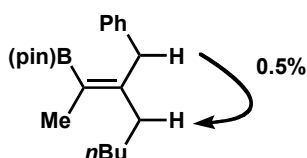
Isolated in 46% as a pale yellow oil

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.84 (t,  $J = 6.8$  Hz), 0.88 (t,  $J = 6.6$  Hz), 1.21–1.35 (m), 1.59 (s), 1.75 (s), 1.96 (t,  $J = 7.7$  Hz), 2.16 (t,  $J = 7.1$  Hz), 3.66 (s), 3.72 (s), 7.15–7.18 (m), 7.22–7.26 (m)

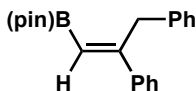
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.00, 14.07, 16.30, 18.10, 22.49, 22.62, 24.56, 24.78, 27.47, 29.73, 30.93, 31.08, 31.92, 32.16, 41.59, 44.30, 82.90, 83.15, 125.58, 125.62, 128.02, 128.07, 128.87, 128.96, 141.15, 141.31, 147.97, 154.19

HRMS Calcd for  $\text{C}_{21}\text{H}_{33}\text{O}_2\text{BNa}$ :  $[\text{M}+\text{Na}]^+$ , 351.24658. Found:  $m/z$ , 351.24661

The regiochemistry was determined by NOE as shown below:



**(*E*)-2-(2,3-Diphenylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ja)**



Isolated in 44% as a pale yellow solid: mp 56.1–58.5 °C

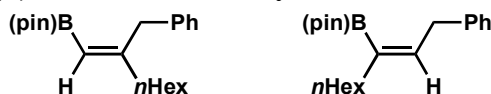
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.29 (s, 12 H), 4.27 (s, 2 H), 5.85 (s, 1 H), 7.18–7.25 (m, 6 H), 7.40 (dd,  $J$  = 8.0, 1.5 Hz, 2 H)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.80, 39.28, 83.09, 125.64, 126.65, 127.78, 128.10, 128.55, 128.85, 140.24, 142.92, 160.35

HRMS Calcd for  $\text{C}_{21}\text{H}_{25}\text{O}_2\text{BNa}$ :  $[\text{M}+\text{Na}]^+$ , 343.18398. Found:  $m/z$ , 343.18431

The regiochemistry was determined by the coupling constants.

**A mixture of (*E*)-4,4,5,5-tetramethyl-2-(1-phenylnon-2-en-3-yl)-1,3,2-dioxaborolane (4ka) and (*Z*)-2-(2-benzyloct-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4'ka)**



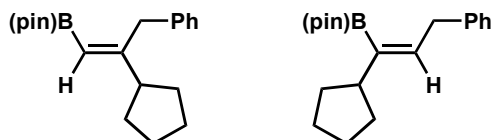
Isolated in 51% as a pale yellow oil

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.84 (t,  $J$  = 7.0 Hz), 0.86 (t,  $J$  = 7.0 Hz), 1.19–1.27 (m), 1.28 (s), 1.29 (s), 1.35–1.42 (m), 1.97 (t,  $J$  = 7.6 Hz), 2.11 (t,  $J$  = 7.4 Hz), 3.68 (d,  $J$  = 7.7 Hz), 3.77 (s), 5.25 (s), 6.11 (t,  $J$  = 7.6 Hz), 7.16–7.29 (m)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.07, 14.10, 22.54, 22.61, 24.82, 27.60, 28.97, 30.18, 31.70, 31.77, 36.83, 37.62, 38.22, 40.93, 82.76, 82.95, 125.67, 125.78, 128.13, 128.28, 128.60, 128.87, 140.53, 141.58, 143.75, 165.14

HRMS Calcd for  $\text{C}_{21}\text{H}_{33}\text{O}_2\text{BNa}$ :  $[\text{M}+\text{Na}]^+$ , 351.24658. Found:  $m/z$ , 351.24661

**A mixture of**  
**(*E*)-2-(2-cyclopentyl-3-phenylprop-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane**  
**(4la)**  
**and**  
**(*E*)-2-(1-cyclopentyl-3-phenylprop-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane**  
**(4'la)**



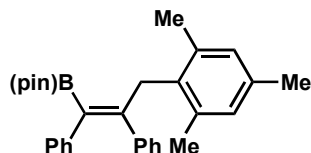
Isolated in 48% as a pale yellow oil

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.27 (s), 1.30 (s), 1.36–1.76 (m), 2.33 (m), 2.52 (m), 3.62 (d,  $J$  = 7.8 Hz), 3.83 (s), 5.33 (s), 6.06 (t,  $J$  = 7.5 Hz), 7.17 (t,  $J$  = 6.9 Hz), 7.21–7.29 (m)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.80, 24.84, 24.98, 25.08, 31.96, 32.40, 37.77, 41.18, 46.71, 47.08, 82.74, 83.02, 125.67, 125.68, 128.08, 128.27, 128.59, 128.83, 139.67, 140.70, 141.55, 168.32

HRMS Calcd for  $\text{C}_{20}\text{H}_{29}\text{O}_2\text{BNa}$ :  $[\text{M}+\text{Na}]^+$ , 335.2128. Found:  $m/z$ , 335.21561

**(*Z*)-2-(3-Mesityl-1,2-diphenylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ab)**



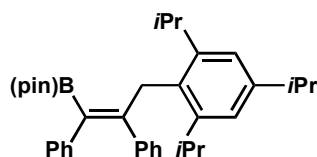
Isolated in 67% as a pale yellow solid: mp 134.4–135.3 °C

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.39 (s, 12 H), 2.18 (s, 6 H), 2.25 (s, 3H), 4.18 (s, 2 H), 6.56 (dt,  $J$  = 6.8 Hz, 1.2 Hz, 2 H), 6.75 (s, 2 H), 6.88–6.98 (m, 6 H), 7.04 (t,  $J$  = 7.2 Hz, 2 H)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  20.43, 20.79, 24.85, 38.25, 83.64, 124.99, 125.68, 126.70, 127.19, 128.67, 128.86, 129.92, 132.41, 135.33, 137.66, 141.19, 141.74, 152.28

HRMS Calcd for  $\text{C}_{30}\text{H}_{35}\text{O}_2\text{BNa}$ :  $[\text{M}+\text{Na}]^+$ , 461.26223. Found:  $m/z$ , 461.26196

**(*Z*)-2-(1,2-Diphenyl-3-(2,4,6-triisopropylphenyl)prop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ac)**



Isolated in 60% as a pale yellow solid: mp 124.7–126.8 °C

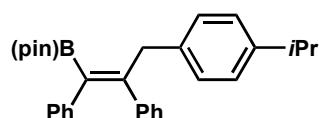


$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.05 (m, 12 H), 1.25 (d,  $J = 7.0$  Hz), 1.37 (s, 12 H), 2.86 (m,  $J = 7.0$  Hz, 1 H), 3.15 (m,  $J = 7.0$  Hz, 2 H), (s, 2 H), 6.43 (d,  $J = 6.9$  Hz, 2 H), 6.82–6.94 (m, 8 H), 7.00 (t,  $J = 7.3$  Hz, 2 H)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.13, 24.85, 29.09, 34.09, 35.80, 83.62, 120.67, 124.89, 125.61, 126.60, 127.19, 129.28, 129.37, 129.73, 140.98, 141.92, 146.86, 147.86, 153.88,

HRMS Calcd for  $\text{C}_{36}\text{H}_{47}\text{O}_2\text{BNa}$ :  $[\text{M}+\text{Na}]^+$ , 545.35613. Found:  $m/z$ , 545.35583

**(Z)-2-(3-(4-Isopropylphenyl)-1,2-diphenylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ad)**



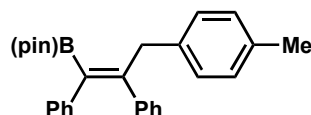
Isolated in 70% as a colorless solid: mp 107.9–109.3 °C

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.24 (d,  $J = 7.0$  Hz, 6 H), 1.34 (s, 12 H), 2.87 (m,  $J = 6.9$  Hz, 1 H), 4.08 (s, 2 H), 6.85–6.87 (m, 2 H), 7.00–7.04 (m, 6 H), 7.07–7.11 (m, 4 H), 7.19 (d,  $J = 8.2$  Hz, 2 H),

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.00, 24.72, 33.59, 43.95, 83.73, 125.26, 126.09, 127.29, 127.40, 128.90, 129.23, 129.64, 136.91, 141.55, 142.02, 146.20, 151.84

HRMS Calcd for  $\text{C}_{30}\text{H}_{35}\text{O}_2\text{BNa}$ :  $[\text{M}+\text{Na}]^+$ , 461.26223. Found:  $m/z$ , 461.26193

**(Z)-2-(1,2-Diphenyl-3-(p-tolyl)prop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ae)**



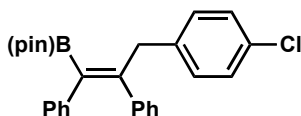
Isolated in 57% as a colorless solid: mp 111.3–113.7 °C

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.32 (s, 12 H), 2.28 (s, 3 H), 4.03 (s, 2 H), 6.81–6.82 (m, 2 H), 6.97–7.02 (m, 8 H), 7.06 (t,  $J = 7.56$ , 2 H), 7.12 (d,  $J = 7.5$  Hz, 2 H)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  21.01, 24.71, 83.76, 125.28, 126.10, 127.31, 127.42, 128.77, 128.90, 129.20, 129.63, 135.17, 136.42, 141.48, 141.88, 151.73

HRMS Calcd for  $\text{C}_{28}\text{H}_{31}\text{O}_2\text{BNa}$ :  $[\text{M}+\text{Na}]^+$ , 433.23093. Found:  $m/z$ , 433.23062

**(Z)-2-(3-(4-Chlorophenyl)-1,2-diphenylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4af)**



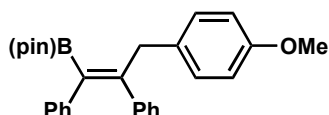
Isolated in 46% as a colorless solid: mp 136.0–137.7 °C

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.33 (s, 12 H), 4.04 (s, 2 H), 6.80–6.81 (m, 2 H), 6.96–7.02 (m, 6 H), 7.07 (t,  $J = 7.0$  Hz, 2 H), 7.17 (s, 4 H)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.73, 43.73, 83.87, 125.44, 126.31, 127.47, 127.48, 128.16, 129.13, 129.58, 130.36, 131.57, 138.07, 141.22, 141.49, 151.16

HRMS Calcd for  $\text{C}_{27}\text{H}_{28}\text{O}_2\text{BClNa}$ :  $[\text{M}+\text{Na}]^+$ , 453.17631. Found:  $m/z$ , 453.17618

**(Z)-2-(3-(4-Methoxyphenyl)-1,2-diphenylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ag)**



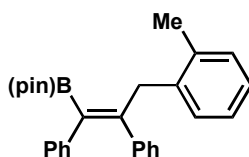
Isolated in 45% as a pale yellow solid: mp 128.0–130.0 °C

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.33 (s, 12 H), 3.75 (s, 3 H), 4.00 (s, 2 H), 6.76 (d,  $J = 8.7$  Hz, 2 H), 6.80–6.81 (m, 2H), 6.97–7.01 (m, 6 H), 7.06 (t,  $J = 7.5$  Hz, 2 H), 7.15 (d,  $J = 8.6$  Hz, 2 H)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.73, 43.58, 55.11, 83.78, 113.45, 125.30, 126.11, 127.33, 127.43, 129.20, 129.62, 129.96, 131.60, 141.43, 141.85, 151.88, 157.72

HRMS Calcd for  $\text{C}_{28}\text{H}_{31}\text{O}_3\text{BNa}$ :  $[\text{M}+\text{Na}]^+$ , 449.22585. Found:  $m/z$ , 449.22571

**(Z)-2-(1,2-Diphenyl-3-(*o*-tolyl)prop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ah)**



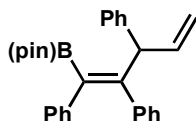
Isolated in 61% as a pale yellow solid: mp 83.3–84.6 °C

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.27 (s, 12 H), 2.25 (s, 3 H), 4.14 (s, 2 H), 6.87–6.89 (m, 2 H), 7.01–7.13 (m, 10 H), 7.15–7.18 (m, 1 H), 7.47 (d,  $J = 7.5$  Hz, 1 H),

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  19.78, 24.60, 40.97, 83.62, 125.31, 125.78, 125.82, 126.12, 127.30, 127.44, 128.93, 128.95, 129.60, 129.66, 136.43, 138.27, 141.59, 142.23, 151.35

HRMS Calcd for  $\text{C}_{28}\text{H}_{31}\text{O}_2\text{BNa}$ :  $[\text{M}+\text{Na}]^+$ , 433.23093. Found:  $m/z$ , 433.23044

**(Z)-4,4,5,5-Tetramethyl-2-(1,2,3-triphenylpenta-1,4-dien-1-yl)-1,3,2-dioxaborolane (4ai)**



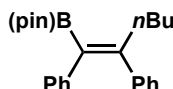
Isolated in 51% as a pale yellow oil

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.32 (s, 12 H), 5.12 (d,  $J = 8.6$  Hz, 1 H), 5.22 (d,  $J = 10.1$  Hz, 1 H), 5.35 (d,  $J = 16.9$  Hz, 1 H), 6.08 (ddd,  $J = 18.1, 9.0, 9.0$  Hz, 1 H), 6.55 (d,  $J = 7.2$  Hz, 2 H), 6.90–7.02 (m, 8 H), 7.21 (t,  $J = 7.1$  Hz, 1 H), 7.27–7.33 (m, 4 H)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.75, 24.78, 56.51, 83.84, 116.82, 125.27, 126.07, 126.17, 126.87, 127.32, 128.07, 128.30, 129.41, 130.19, 138.19, 139.56, 141.10, 142.11, 153.79

HRMS Calcd for  $\text{C}_{29}\text{H}_{31}\text{O}_2\text{BNa}$ :  $[\text{M}+\text{Na}]^+$ , 445.23093. Found:  $m/z$ , 445.23080

**(Z)-2-(1,2-Diphenylhex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4aj)**



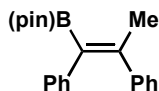
Isolated in 60% as a pale yellow oil

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.88 (t,  $J = 6.9$  Hz, 3 H), 1.33–1.36 (m, 16 H), 2.70 (t,  $J = 7.3$  Hz, 2 H), 6.94 (d,  $J = 7.8$  Hz, 2 H), 6.98–6.99 (m, 3 H), 7.03–7.13 (m, 5 H)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  13.98, 22.73, 24.73, 31.15, 38.68, 83.55, 125.09, 126.12, 127.39, 127.51, 129.05, 129.54, 141.46, 142.20, 153.39

HRMS Calcd for  $\text{C}_{24}\text{H}_{31}\text{O}_2\text{BNa}$ :  $[\text{M}+\text{Na}]^+$ , 385.23093. Found:  $m/z$ , 385.23157

**(Z)-2-(1,2-Diphenylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ak)**



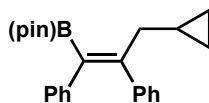
Isolated in 39% as a pale yellow solid: mp 110.3–112.3 °C

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.34 (s, 12 H), 2.38 (s, 3 H), 6.92–6.94 (m, 2 H), 6.99–7.02 (m, 3 H), 7.05–7.13 (m, 5 H)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.73, 24.99, 83.63, 125.18, 126.25, 127.45, 127.58, 128.55, 129.62, 141.7, 143.62, 149.02

HRMS Calcd for  $\text{C}_{21}\text{H}_{25}\text{O}_2\text{BNa}$ :  $[\text{M}+\text{Na}]^+$ , 343.18398. Found:  $m/z$ , 343.18433

**(Z)-2-(3-Cyclopropyl-1,2-diphenylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4al)**



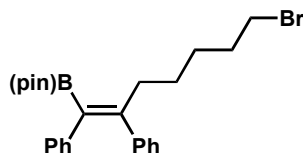
Isolated in 30% as a pale yellow solid: mp 90.9–92.6 °C

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.11–0.14 (m, 2 H), 0.31–0.35 (m, 2 H), 0.66–0.74 (m, 1 H), 1.31 (s, 12 H), 2.61 (d,  $J$  = 7.0 Hz, 2 H), 6.93–6.95 (m, 2 H), 6.94–7.13 (m, 8 H)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.38, 10.35, 24.73, 43.07, 83.61, 125.14, 126.08, 127.39, 127.47, 129.15, 129.61, 141.38, 142.48, 152.90

HRMS Calcd for  $\text{C}_{24}\text{H}_{29}\text{O}_2\text{BNa}$ :  $[\text{M}+\text{Na}]^+$ , 383.21528. Found:  $m/z$ , 383.21555

**(Z)-2-(7-Bromo-1,2-diphenylhept-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4am)**



Isolated in 36% as a pale yellow solid: mp 87.4–89.0 °C

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.33 (s, 12 H), 1.36–1.48 (m, 4 H), 1.83 (m,  $J$  = 7.1 Hz, 2 H), 2.71 (t,  $J$  = 7.5 Hz, 2 H), 3.37 (t,  $J$  = 6.9 Hz, 2 H), 6.91 (d,  $J$  = 7.8 Hz, 2 H), 6.95–6.99 (m, 3 H), 7.02–7.12 (m, 5 H)

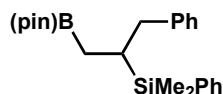
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.76, 27.88, 27.91, 32.56, 33.95, 38.50, 83.63, 125.17, 126.25, 127.42, 127.60, 127.96, 129.04, 129.56, 141.42, 142.00, 153.14

HRMS Calcd for  $\text{C}_{25}\text{H}_{32}\text{O}_2\text{BBrNa}$ :  $[\text{M}+\text{Na}]^+$ , 477.15709. Found:  $m/z$ , 477.15704

**Cu-Catalyzed Carboboration of Alkenes: A General Procedure.**

A schlenk tube equipped with a magnetic stirring bar was charged with  $\text{SiMe}_3\text{CuCl}$  (6.0  $\mu\text{mol}$ ), an alkene (0.30 mmol), bis(pinacolato)diboron (0.39 mmol), benzyl chloride (0.90 mmol), potassium *tert*-butoxide (1 M solution in THF, 0.45 mmol), and DMF (0.55 mL). The mixture was stirred at RT for the period as specified in Scheme 2, diluted with ethyl acetate before filtration through a Celite plug. The organic solution was washed two times with brine and dried over  $\text{MgSO}_4$ . Evaporation of the solvent followed by gel permeation chromatography (chloroform as an eluent) gave the product. In  $^{13}\text{C}$  NMR spectra, boron-bound carbons were not detected because of quadrupolar relaxation.

**Dimethyl(phenyl)(1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)silane (6aa)**



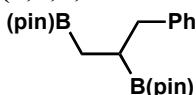
Isolated in 85% as a pale yellow oil

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.23 (s, 3 H), 0.23 (s, 3 H), 0.75 (dd,  $J = 16.3, 7.4$  Hz, 1 H), 0.89 (dd,  $J = 16.2, 6.4$  Hz, 1H), 1.14 (s, 6 H), 1.16 (s, 6 H), 1.52–1.57 (m, 1 H), 2.49 (dd,  $J = 13.8, 9.8$  Hz, 1 H), 2.76 (dd,  $J = 13.9, 5.7$  Hz, 1 H), 7.12–7.16 (m, 3 H), 7.21–7.24 (m, 2 H), 7.33–7.35 (m, 3 H), 7.52–7.54 (m, 2 H)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -4.27, -4.21, 22.10, 24.79, 24.96, 38.45, 82.79, 82.87, 125.53, 127.57, 127.98, 128.68, 129.10, 134.10, 138.60, 142.42

HRMS Calcd for  $\text{C}_{23}\text{H}_{33}\text{O}_2\text{BNaSi}$ :  $[\text{M}+\text{Na}]^+$ , 403.22351. Found:  $m/z$ , 403.22391

**2,2'-(3-Phenylpropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6ba)**



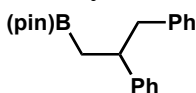
Isolated in 68% as a pale yellow oil

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.82 (d,  $J = 7.9$ , 2 H), 1.16 (s, 6 H), 1.19 (s, 6 H), 1.22 (s, 12 H), 1.46 (m,  $J = 7.9$  Hz), 2.60 (dd,  $J = 13.4, 8.5$  Hz, 1 H), 2.79 (dd,  $J = 13.7, 7.4$  Hz), 7.13 (t,  $J = 7.0$  Hz, 1 H), 7.18–7.24 (m, 4 H)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.74, 24.77, 24.82, 24.89, 39.48, 82.86, 82.93, 125.45, 127.91, 129.09, 142.31

HRMS Calcd for  $\text{C}_{21}\text{H}_{34}\text{O}_4\text{B}_2\text{Na}$ :  $[\text{M}+\text{Na}]^+$ , 395.25354. Found:  $m/z$ , 395.25458

**2-(2,3-Diphenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6ca)**



Isolated in 65% as a pale yellow oil

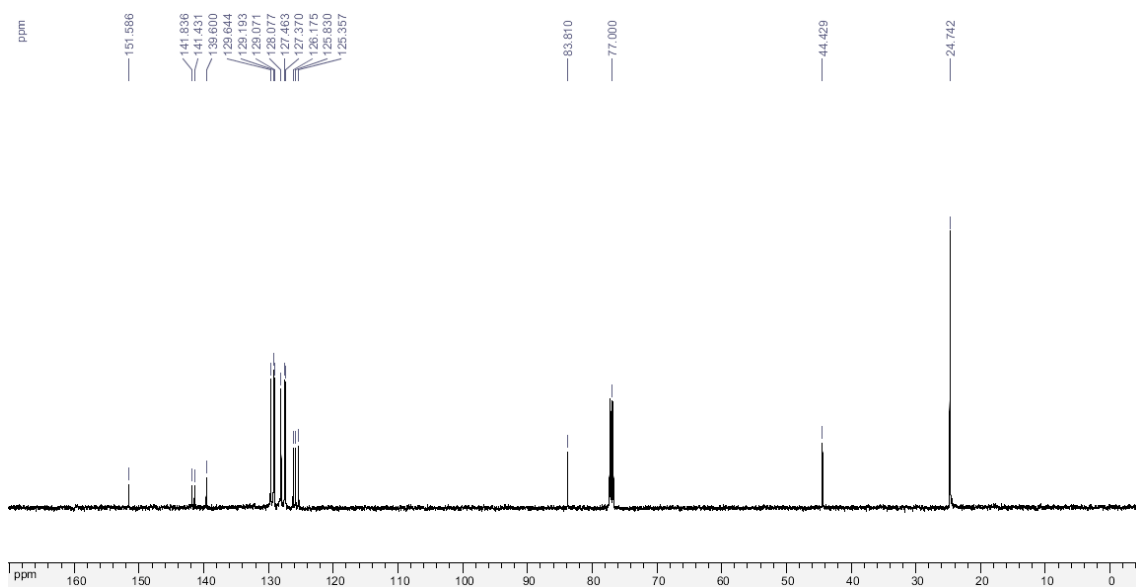
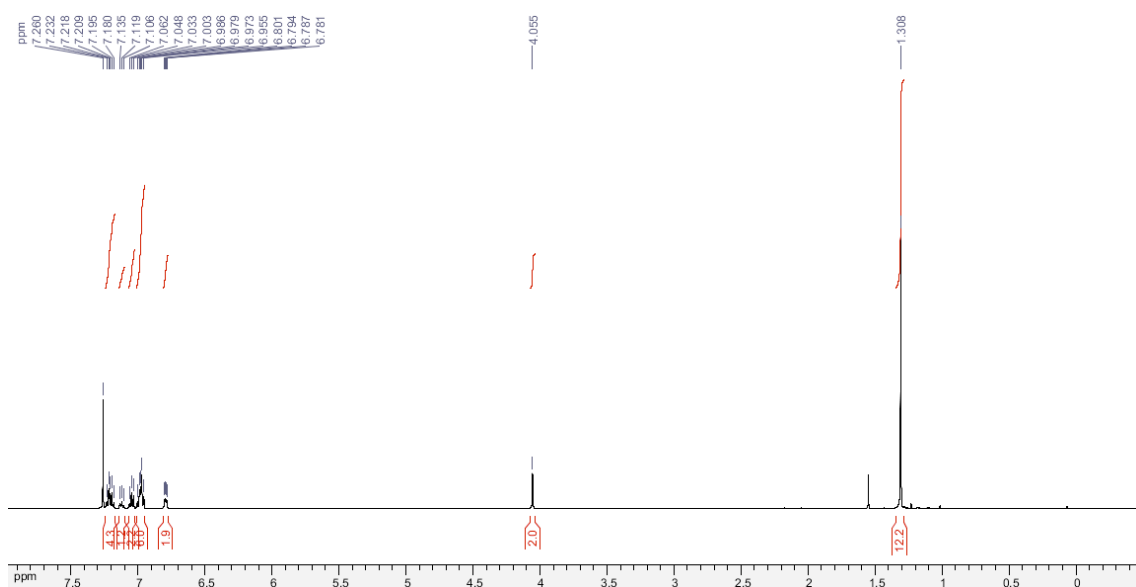
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.06 (s, 6 H), 1.08 (s, 6 H), 1.15–1.25 (m, 2 H), 2.84–2.93 (m, 2 H), 3.11–3.18 (m, 1 H), 7.05 (d,  $J = 7.0$  Hz, 2 H), 7.12–7.24 (m, 8 H)

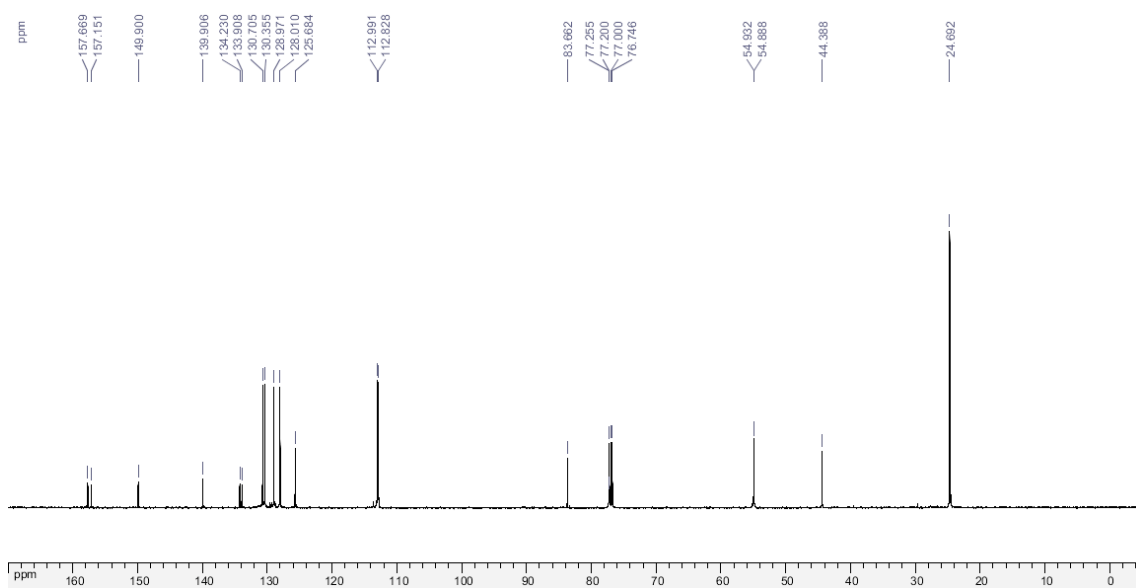
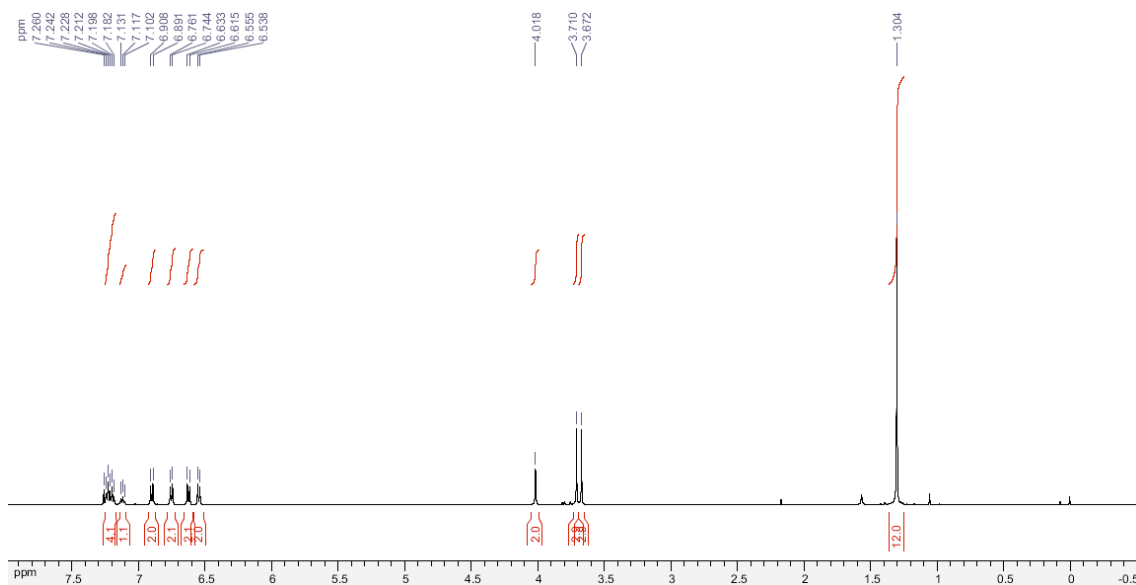
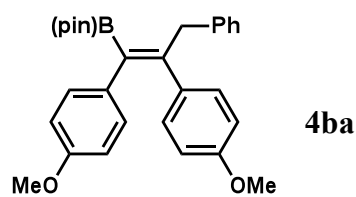
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.53, 24.65, 43.57, 46.17, 82.89, 125.68, 125.84, 127.50, 127.90, 127.94, 129.31, 140.69, 146.41

HRMS Calcd for  $\text{C}_{21}\text{H}_{27}\text{O}_2\text{BNa}$ :  $[\text{M}+\text{Na}]^+$ , 345.19963. Found:  $m/z$ , 345.19992

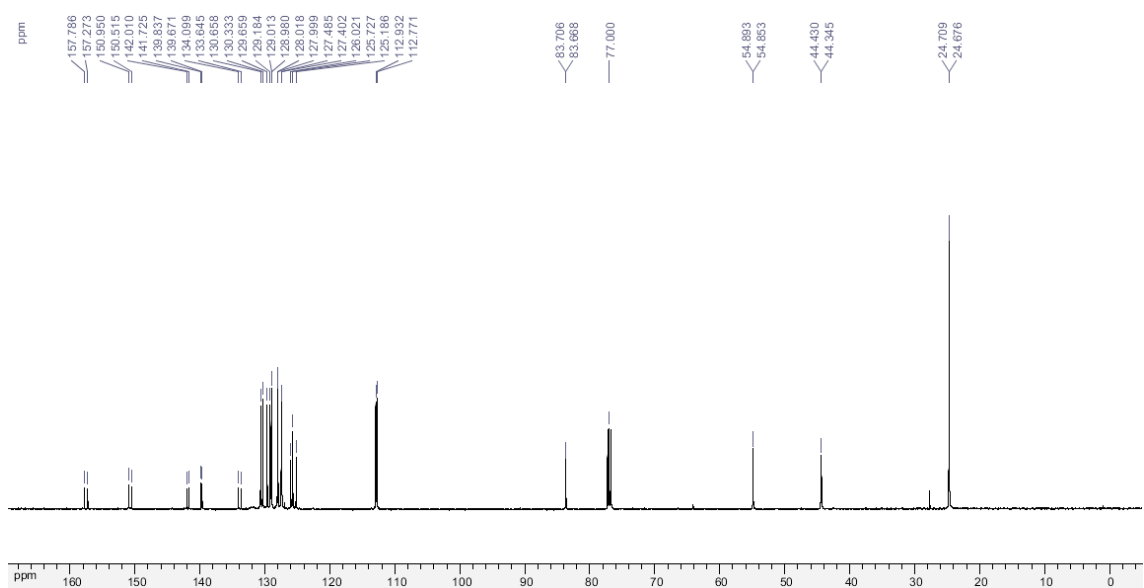
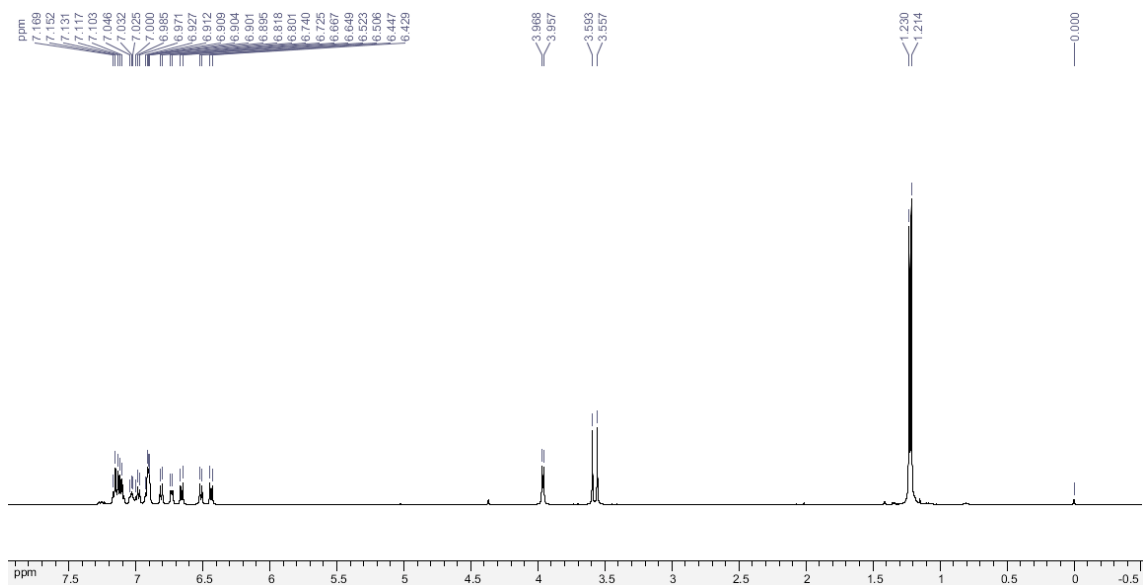
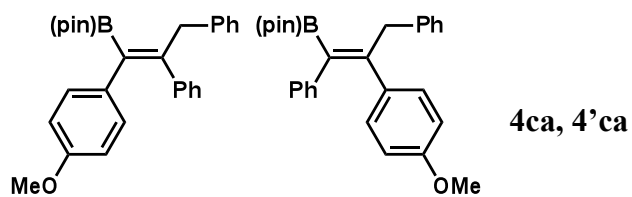
## References

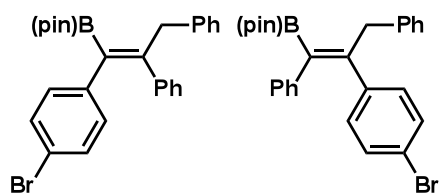
1. Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *50*, 4467.
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3. Murahashi, S.; Taniguchi, Y.; Imada, Y.; Tanigawa, Y. *J. Org. Chem.* **1989**, *54*, 3292.
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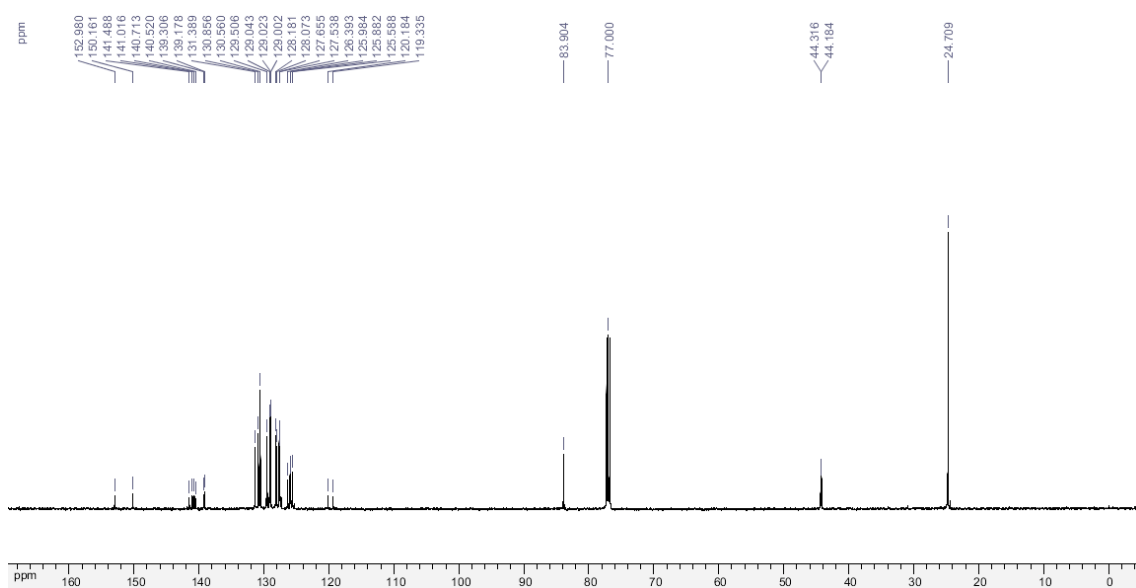
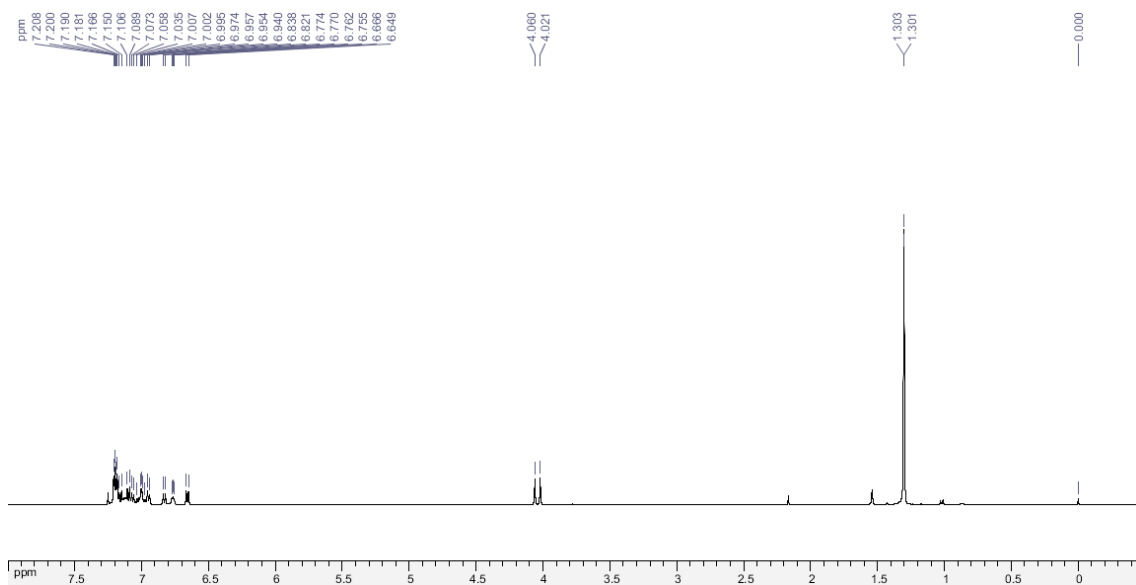


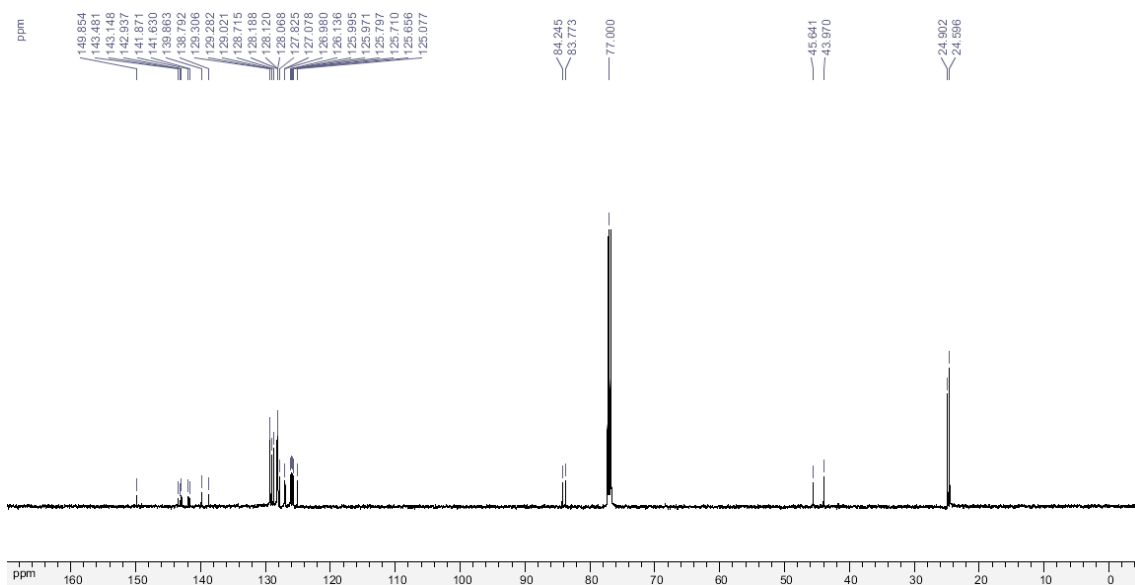
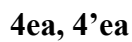


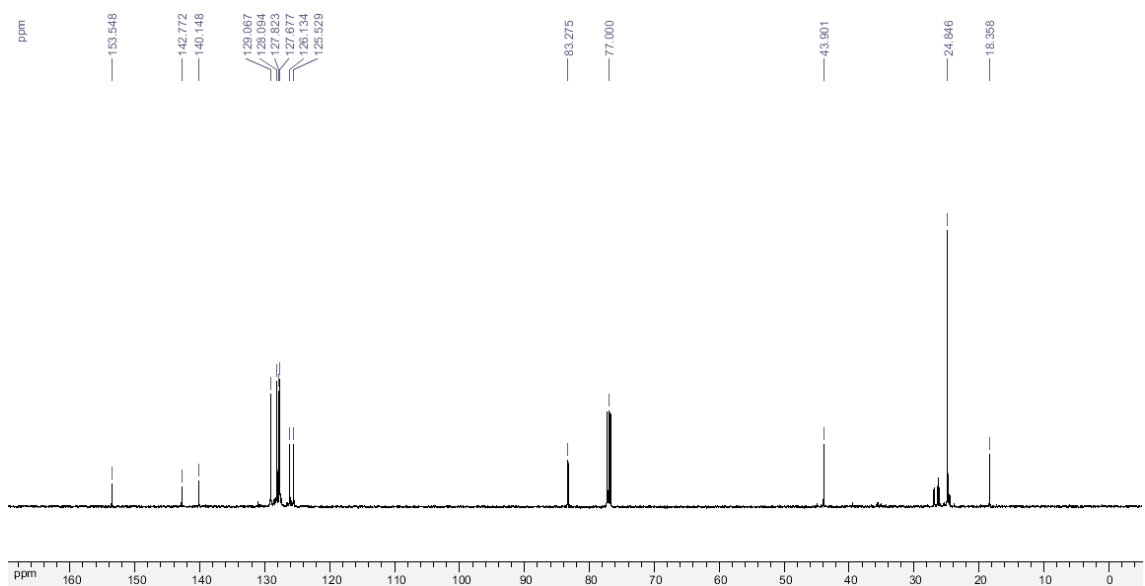
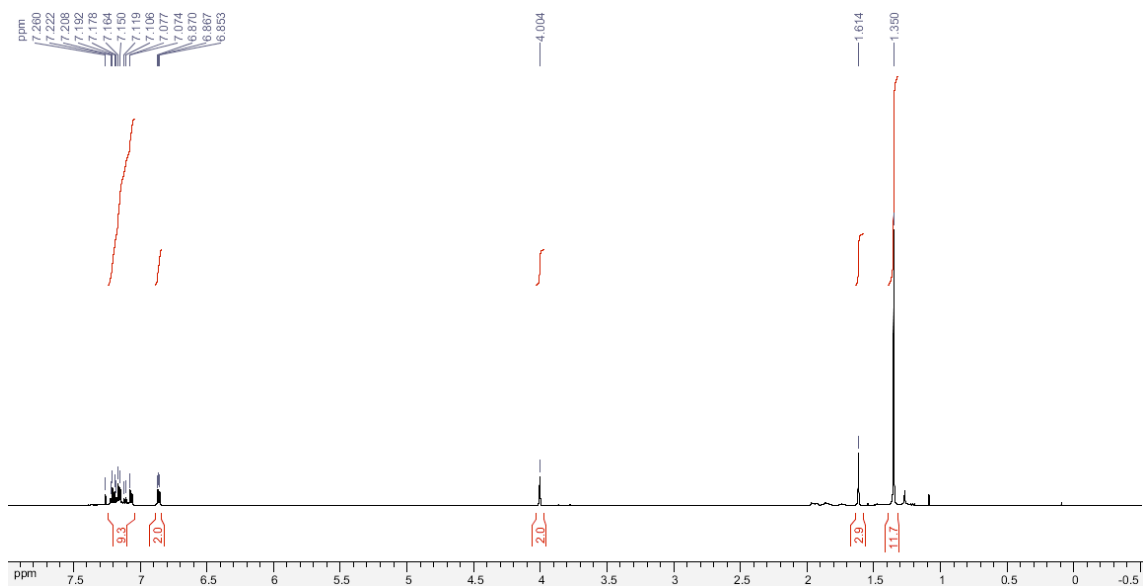
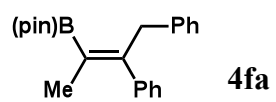


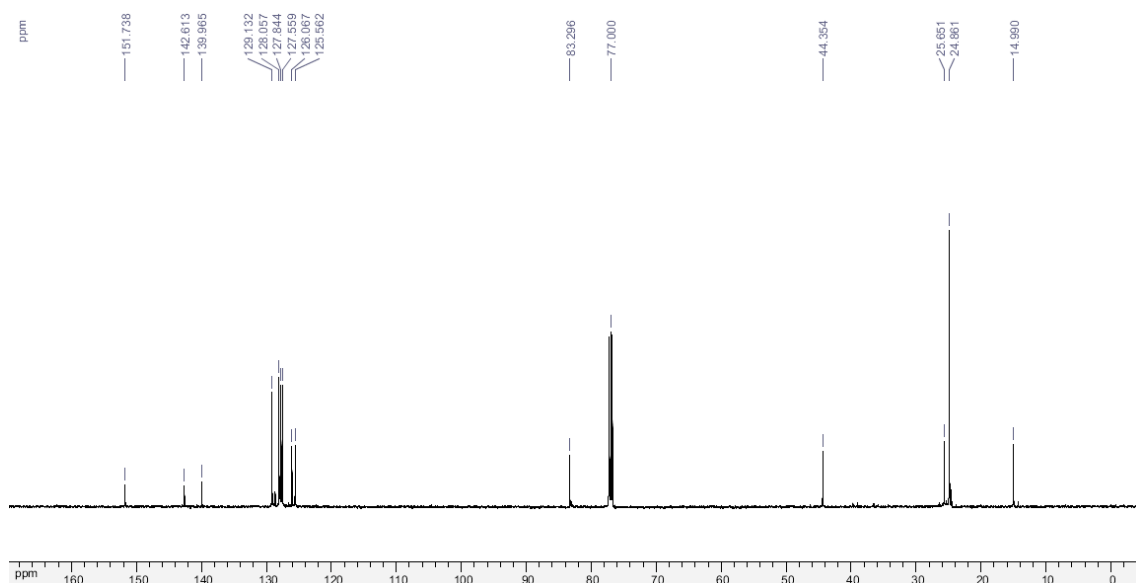
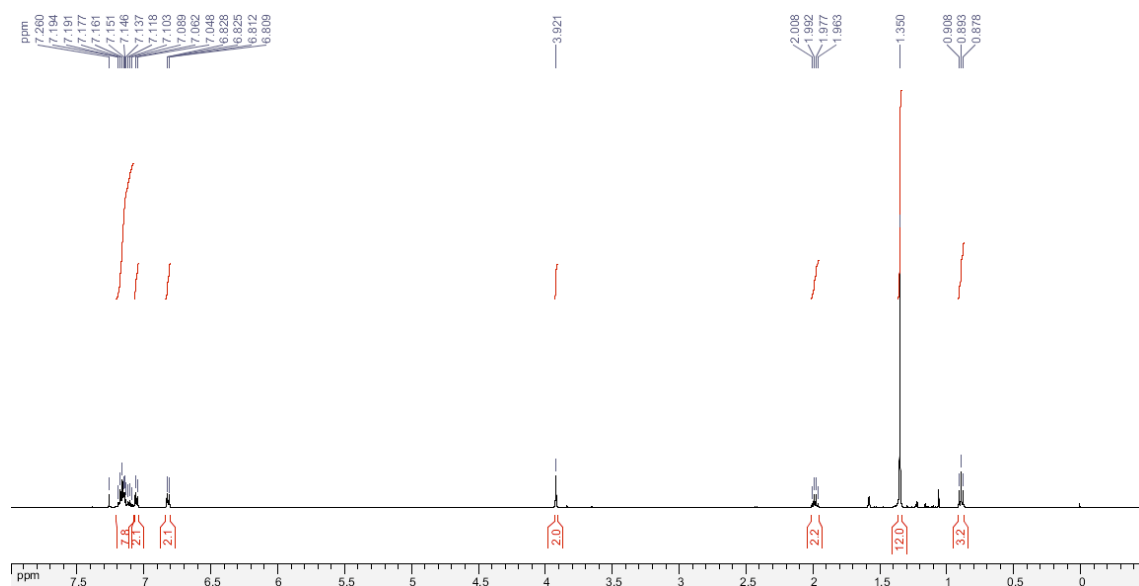
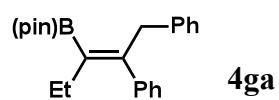


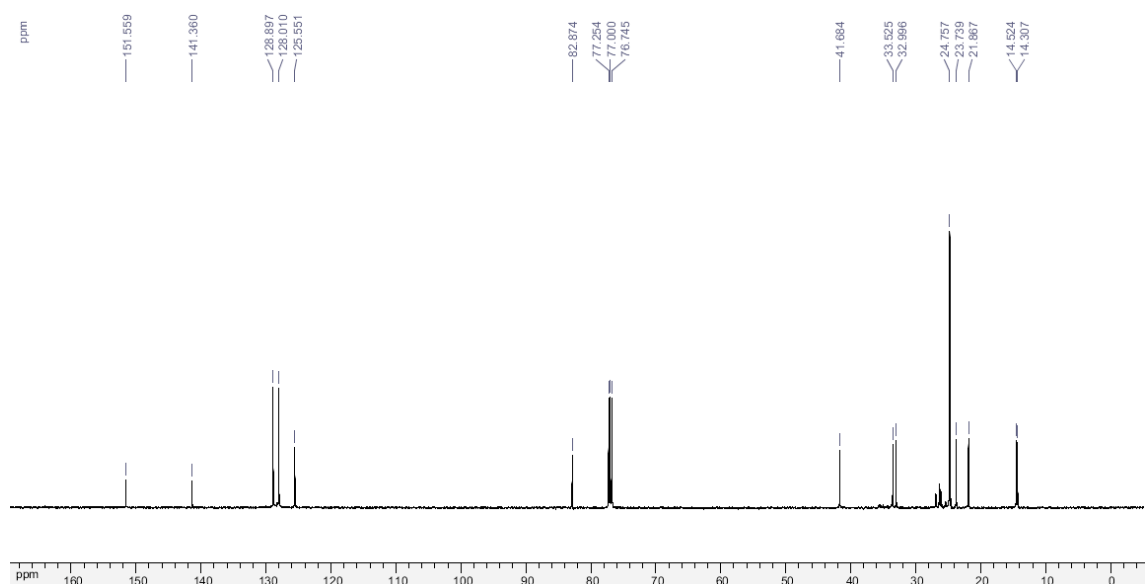
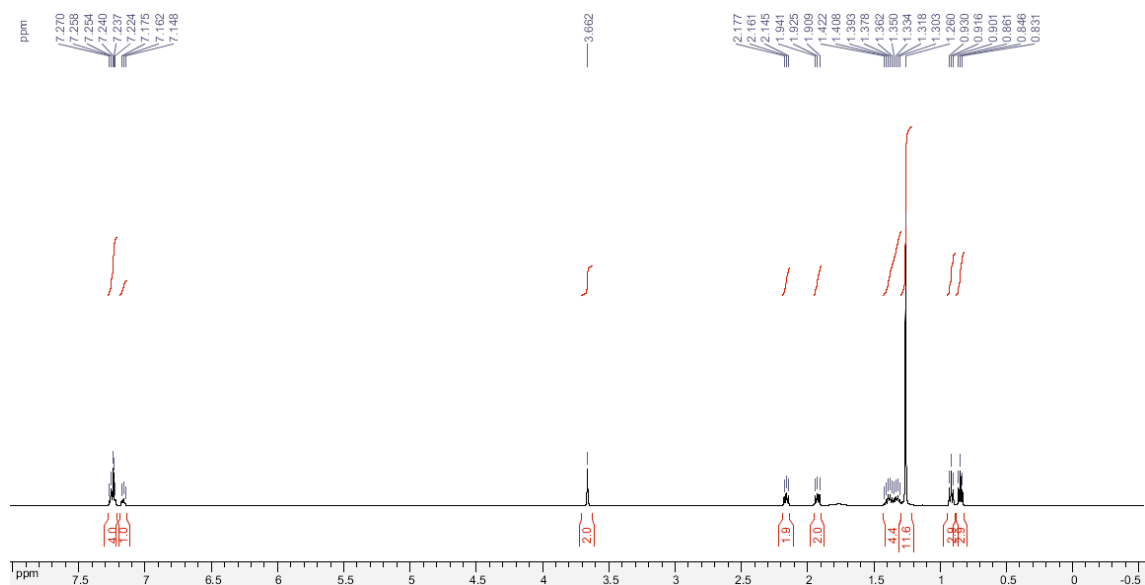
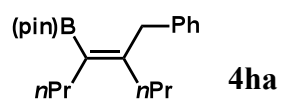
4da, 4'da

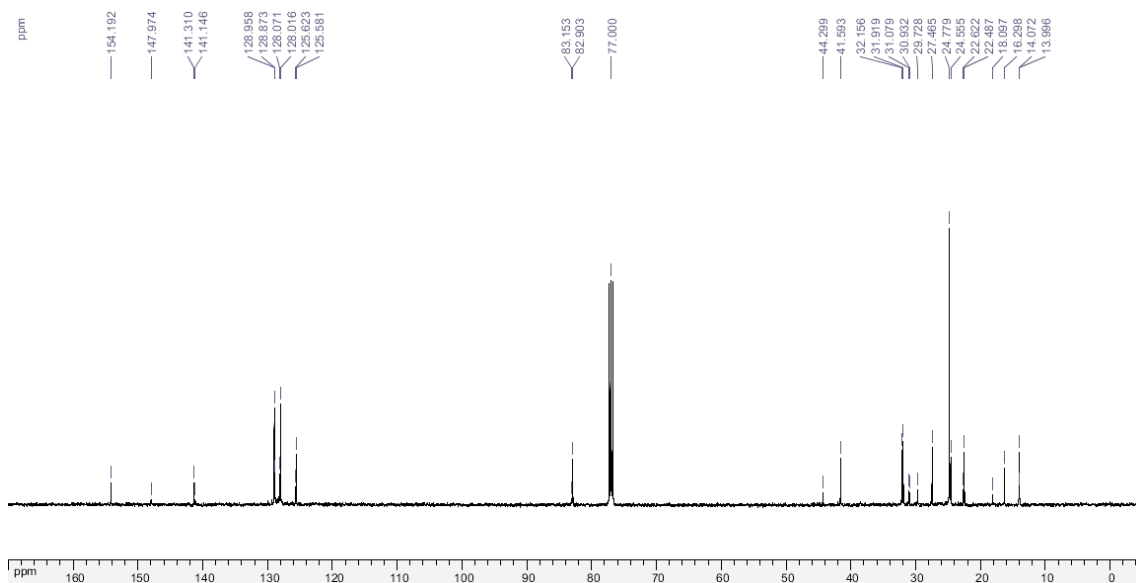
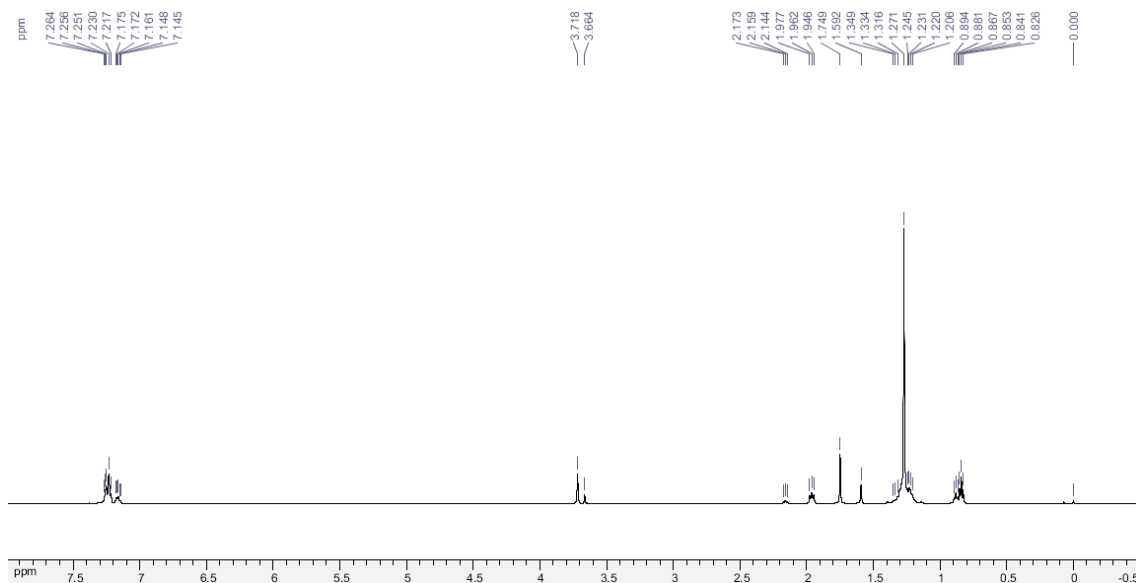
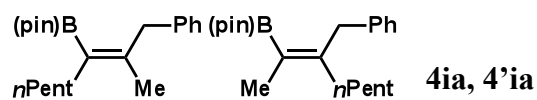


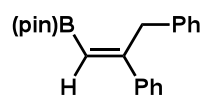












**4ja**

