

## Supporting Information

### Highly Regio- and Stereoselective Synthesis of Boron-substituted Enynes via Copper-catalyzed Borylation of Conjugate Diynes

DingXi Li, Yeong Eun Kim, and Jaesook Yun\*

Department of Chemistry and Institute of Basic Science,  
Sungkyunkwan University, Suwon 440-746, Korea  
Fax: (+82)-31-290-7075; e-mail: jaesook@skku.edu

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**General Methods:** CuCl, NaO*t*-Bu, bis(pinacolato)diboron and other commercial substrates were purchased from Aldrich and used as received. THF was distilled from sodium benzophenone ketyl under nitrogen. All symmetrical diynes (**1a–1g**) were prepared by homocoupling of terminal alkynes<sup>1</sup> and unsymmetrical diynes (**4a–4f**) were prepared by Sonogashira coupling of terminal alkyne with alkynyl bromides.<sup>2</sup> All reactions with oxygen- and moisture-sensitive materials were carried out with standard Schlenk technique. Flash chromatography was performed on silica gel from Merck (70–230 mesh). Thin layer chromatography (TLC) was performed on glass plates coated with silica gel 60 with F254 indicator and visualization was accomplished with UV light and/or *p*-anisaldehyde followed by heating. GC analysis was performed on a Younglin Acme 9000 series. Infrared spectra (IR) were obtained on Nicolet 205 FT-IR and are recorded in cm<sup>-1</sup>. All <sup>1</sup>H NMR spectra were obtained on Varian Mercury 300 systems and reported in parts per million (ppm) downfield from tetramethylsilane. <sup>13</sup>C NMR spectra are reported in ppm referenced to deuteriochloroform (77.16 ppm) or deuterioacetone (206.26 ppm). <sup>11</sup>B NMR (500 MHz) spectra are reported in ppm. High resolution mass spectra (HRMS) were obtained at Korea Basic Science Institute (Daegu, Korea) and reported in the form of *m/z* (intensity relative to base peak = 100).

## **General Procedure for the Copper-catalyzed Monoborylation of Conjugated Diynes**

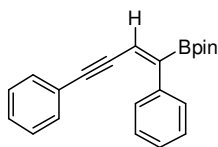
### **A. For pinacolboronate (Bpin) compounds (2a–2g in Table 2 and 5a–5f in Table 3)**

A mixture of CuCl (0.025 mmol, 2.5 mg), NaO*t*-Bu (0.05 mmol, 5.2 mg), and ligand (0.03 mmol) in anhydrous THF (0.5 mL) was stirred for 30 min in a Schlenk tube under an atmosphere of N<sub>2</sub>. Bis(pinacolato)diboron (0.55 mmol, 139.6 mg) dissolved in THF (0.5 mL) was added to the reaction mixture and stirred for 5 min at room temperature. Then the Schlenk tube was moved to the 11 °C cooling bath or at room temperature and stirred for another 5 min. Starting material (0.5 mmol) with THF (0.5 mL) was added, followed by MeOH (1 mmol, 40  $\mu$ L). The reaction tube was washed with further THF (0.5 mL), sealed, and stirred for 2–6 h. The reaction was monitored by GC. The reaction mixture was filtered through a pad of Celite with ether and concentrated. The crude sample was purified by flash column chromatography (less than 10 min) on silica gel at 0 °C to obtain the pinacolboronates.

### **B. For potassium trifluoroborate salts (BF<sub>3</sub><sup>-</sup>K<sup>+</sup>) (3a–3g in Table 2 and 6a–6f in Table 3)**

When the reaction was complete, the reaction mixture was filtered through a pad of Celite with ether and concentrated. The concentrate was dissolved with hexanes, filtered through a pad of Celite, and concentrated. KHF<sub>2</sub> (2.5 mmol, 195 mg), ether (2 mL), and H<sub>2</sub>O (1 mL) were added to the crude sample and stirred for 2–6 h at room temperature. The reaction was monitored by TLC. The reaction mixture was concentrated and washed by acetone. The solution was concentrated and precipitated by hexanes to obtain the corresponding potassium trifluoroborate salts.

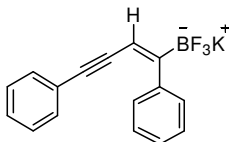
**(Z)-2-(1,4-Diphenylbut-1-en-3-yn-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a, Table 1)**



**2a**

Following the general procedure A using  $P(p\text{-tol})_3$  as the ligand, the title compound was isolated in 70% yield (115.5 mg).  $^1\text{H}$  NMR: (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80–7.61 (m, 2H), 7.42–7.14 (m, 8H), 6.74 (s, 1H), 1.26 (s, 12H);  $^{13}\text{C}$  NMR: (75 MHz,  $\text{CDCl}_3$ )  $\delta$  139.2, 131.7, 129.1, 128.5, 128.3, 127.6, 127.4, 123.3, 122.1, 96.9, 88.8, 84.0, 24.8;  $^{11}\text{B}$  NMR: (160 MHz,  $\text{CDCl}_3$ )  $\delta$  30.60; IR (neat)  $\tilde{\nu}$  2979, 1377, 1325, 1145, 1061, 989, 856, 762, 694  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{22}\text{H}_{23}\text{BO}_2$  330.1791, found 330.1792.

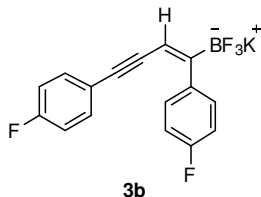
**Potassium (Z)-(1,4-diphenylbut-1-en-3-yn-1-yl)trifluoroborate (3a, Table 2)**



**3a**

Following the general procedure B, the title compound was isolated in 76% yield (118 mg).  $^1\text{H}$  NMR: (300 MHz, acetone- $d_6$ )  $\delta$  7.80–7.65 (m, 2H), 7.40–7.07 (m, 8H), 6.10 (s, 1H);  $^{13}\text{C}$  NMR: (100 MHz, acetone- $d_6$ )  $\delta$  145.5, 131.8, 129.7, 129.2, 128.0, 127.6, 126.1, 126.0, 108.5, 92.7, 90.1.

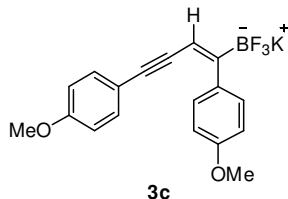
**Potassium (Z)-(1,4-bis(4-fluorophenyl)but-1-en-3-yn-1-yl)trifluoroborate (3b, Table 2)**



**3b**

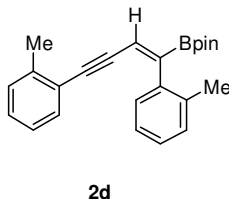
Following the general procedure B using  $\text{PPh}_3$  as the ligand, the title compound was isolated in 74% yield (128 mg).  $^1\text{H}$  NMR: (300 MHz, acetone- $d_6$ )  $\delta$  7.76–7.61 (m, 2H), 7.34–7.24 (m, 2H), 7.14–6.93 (m, 4H), 6.06 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz, acetone- $d_6$ )  $\delta$  162.9, 162.2, 160.9, 160.3, 140.08, 140.06, 133.0, 132.9, 130.42, 130.36, 121.01, 120.99, 115.6, 115.4, 113.6, 113.4, 108.41, 108.38, 90.8, 88.8; IR (neat) 3662, 2974, 2861, 1598, 1503, 1219, 1096, 1089, 981, 878, 837  $\text{cm}^{-1}$ ; HRMS (FAB) calcd for  $\text{C}_{16}\text{H}_9\text{BF}_5\text{K}_2$   $[\text{M}+\text{K}]^+$ . 384.9992, found 384.9991.

**Potassium (*Z*)-(1,4-bis(4-methoxyphenyl)but-1-en-3-yn-1-yl)trifluoroborate (3c, Table 2)**



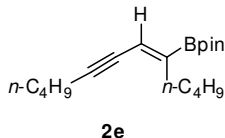
Following the general procedure B using  $P(OEt)_3$  as the ligand, the title compound was isolated in 70% yield (129.5 mg).  $^1H$  NMR: (300 MHz, acetone- $d_6$ )  $\delta$  7.75–7.72 (d,  $J$  = 9.0 Hz, 2H), 7.24–7.21 (d,  $J$  = 9.0 Hz, 2H), 6.87–6.84 (d,  $J$  = 9.0 Hz, 2H), 6.83–6.80 (d,  $J$  = 9.0 Hz, 2H), 6.03 (s, 1H), 3.78 (s, 3H), 3.77 (s, 3H);  $^{13}C$  NMR (100 MHz, acetone- $d_6$ )  $\delta$  159.7, 158.5, 137.1, 132.9, 130.7, 117.8, 114.6, 112.8, 107.7, 91.1, 90.1, 55.4, 55.1;  $^{11}B$  NMR: (160 MHz, acetone- $d_6$ )  $\delta$  7.996; IR (neat) 3344, 2948, 2833, 1024, 672  $cm^{-1}$ ; HRMS (FAB) calcd for  $C_{18}H_{15}BF_3K_2O_2$   $[M+K]^+$  409.0391, found 409.0390.

**(*Z*)-2-(1,4-Di-*o*-tolylbut-1-en-3-yn-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d, Table 2)**



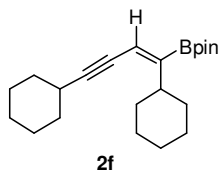
Following the general procedure A using  $P(p\text{-tol})_3$  as the ligand, the title compound was isolated in 72% yield (129 mg).  $^1H$  NMR: (300 MHz,  $CDCl_3$ )  $\delta$  7.28–6.98 (m, 8H), 6.80 (s, 1H), 2.25 (s, 3H), 1.97 (s, 3H), 1.26 (s, 12H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  140.7, 140.1, 135.1, 132.2, 129.8, 129.4, 128.7, 128.6, 127.0, 125.5, 125.4, 124.6, 123.0, 96.2, 92.0, 84.0, 24.8, 20.2, 20.1; IR (neat) 3707, 3344, 2973, 2832, 1455, 1374, 1327, 1144, 1026, 856, 757, 674  $cm^{-1}$ ; HRMS (EI) calcd for  $C_{24}H_{27}BO_2$  358.2104, found 358.2102.

**(*Z*)-2-(Dodec-5-en-7-yn-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e, Table 2)**



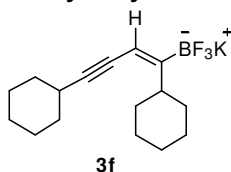
Following the general procedure A using  $P(p\text{-tol})_3$  as the ligand, the title compound was isolated in 83% yield (120.5 mg).  $^1H$  NMR: (300 MHz,  $CDCl_3$ )  $\delta$  6.20–6.18 (t,  $J$  = 2.1 Hz, 1H), 2.55–2.32 (m, 4H), 1.60–1.20 (m, 20H), 0.95–0.85 (m, 6H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  122.8, 98.6, 83.4, 78.6, 31.8, 31.4, 31.0, 25.1, 24.8, 22.7, 22.0, 19.5, 14.2, 13.7; HRMS (ESI) calcd for  $C_{18}H_{31}BNaO_2$   $[M+Na]^+$  313.2309, found 313.2313.

**(*Z*)-2-(1,4-Dicyclohexylbut-1-en-3-yn-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f, Table 2)**



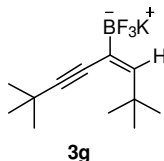
Following the general procedure A using  $\text{P}(\text{OEt})_3$  as the ligand, the title compound was isolated in 70% yield (120 mg).  $^1\text{H}$  NMR: (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.12 (d,  $J$  = 2.0 Hz, 1H), 2.80–2.66 (m, 1H), 2.64–2.52 (m, 1H), 1.87–1.05 (m, 32H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  121.2, 102.5, 83.2, 78.8, 42.7, 32.7, 31.4, 30.0, 26.9, 26.2, 26.1, 24.8, 24.7, 22.8, 14.3; IR (neat) 3080, 2925, 2855, 2778, 1576, 1369, 1144, 1095, 971  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{22}\text{H}_{35}\text{BO}_2$  342.2730, found 342.2728.

**Potassium (Z)-(1,4-dicyclohexylbut-1-en-3-yn-1-yl)trifluoroborate (3f, Table 2)**



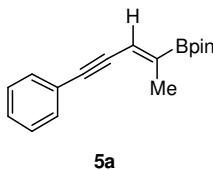
Following the general procedure B using  $\text{P}(\text{OEt})_3$  as the ligand, the title compound was isolated in 75% yield (121 mg).  $^1\text{H}$  NMR: (300 MHz, acetone- $d_6$ )  $\delta$  5.55 (s, 1H), 2.72 (m, 1H), 2.58 (m, 1H), 2.00–1.20 (m, 20H);  $^{13}\text{C}$  NMR (100 MHz, acetone- $d_6$ )  $\delta$  108.2, 108.2, 95.5, 81.3, 78.7, 44.0, 33.4, 31.9, 30.0, 30.0, 27.6, 26.8, 26.3, 24.7.

**Potassium (Z)-(2,2,7,7-tetramethyloct-3-en-5-yn-4-yl) trifluoroborate (3g, Table 2)**



Following the general procedure B using  $\text{P}(\text{OEt})_3$  as the ligand, the title compound was isolated in 68% yield (92 mg).  $^1\text{H}$  NMR: (500 MHz, acetone- $d_6$ )  $\delta$  5.89 (s, 1H), 1.22 (s, 9H), 1.15 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz, acetone- $d_6$ )  $\delta$  150.0, 150.0, 103.8, 83.1, 33.8, 31.3, 30.2, 28.5; HRMS (ESI) calcd for  $\text{C}_{12}\text{H}_{19}\text{BF}_3\text{K}_2$   $[\text{M}+\text{K}]^+$  309.0806, found 309.0803.

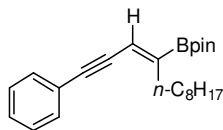
**(Z)-2-(5-Phenylpent-2-en-4-yn-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5a, Table 3)**



Following the general procedure A using  $\text{P}(\text{OEt})_3$  as the ligand, the title compound was isolated in 87% yield (116.5 mg).  $^1\text{H}$  NMR: (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49–7.43 (m, 2H), 7.34–7.28 (m, 3H), 6.44–6.43 (q,  $J$  = 1.6 Hz, 1H), 2.03–2.02 (d,  $J$  = 1.6 Hz, 3H), 1.28 (s, 12H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  131.7, 128.4, 123.7, 122.4, 97.9, 87.4, 83.8, 24.9, 17.6; HRMS (ESI) calcd for  $\text{C}_{17}\text{H}_{21}\text{BNaO}_2$   $[\text{M}+\text{Na}]^+$

291.1527, found 291.1530.

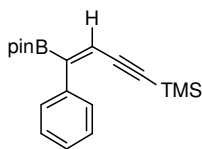
**(Z)-2-(1-phenyldodec-3-en-1-yn-4-yl)- 4,4,5,5-tetramethyl- 1,3,2-dioxaborolane (5b, Table 3)**



**5b**

Following the general procedure A using  $\text{P}(\text{OEt})_3$  as the ligand, the title compound was isolated in 71% yield (130 mg).  $^1\text{H}$  NMR: (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47–7.42 (m, 2H), 7.33–7.28 (m, 3H), 6.42 (s, 1H), 2.49–2.44 (t,  $J$  = 7.5 Hz, 2H), 1.52–1.42 (m, 2H), 1.39–1.21 (m, 22H), 0.88–0.83 (t,  $J$  = 7.5 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  131.7, 128.4, 128.3, 123.8, 121.9, 97.0, 87.6, 83.7, 32.1, 32.1, 29.7, 29.6, 29.5, 29.4, 24.8, 22.8, 14.3; HRMS (ESI) calcd for  $\text{C}_{24}\text{H}_{35}\text{BNaO}_2$   $[\text{M}+\text{Na}]^+$  389.2622, found 389.2627.

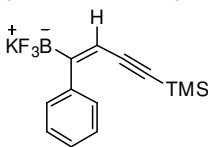
**(Z)-Trimethyl(4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yn-1-yl)silane (5c, Table 3)**



**5c**

Following the general procedure A using  $\text{P}(\text{OEt})_3$  as the ligand, the title compound was isolated in 75% yield (122.5 mg).  $^1\text{H}$  NMR: (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80–7.65 (m, 2H), 7.42–7.30 (m, 3H), 6.55 (s, 1H), 1.36 (s, 12H), 0.20 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.9, 129.2, 127.6, 127.6, 121.9, 104.0, 103.4, 84.2, 24.9, –0.2; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{27}\text{BNaO}_2\text{Si}$   $[\text{M}+\text{Na}]^+$  349.1766, found 349.1769.

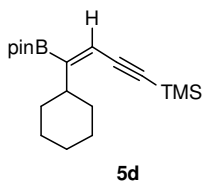
**Potassium (Z)-(1-phenyl-4-(trimethylsilyl)but-1-en-3-yn-1-yl) trifluoroborate (6c, Table 3)**



**6c**

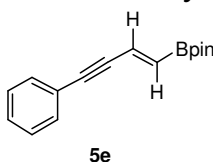
Following the general procedure B using  $\text{P}(\text{OEt})_3$  as the ligand, the title compound was isolated in 82% yield (125.5 mg).  $^1\text{H}$  NMR: (500 MHz, acetone- $d_6$ )  $\delta$  7.73–7.69 (m, 2H), 7.25–7.20 (m, 2H), 7.15–7.10 (m, 1H), 5.94 (s, 1H), 0.10 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz, acetone- $d_6$ )  $\delta$  144.8, 129.6, 127.6, 126.1, 108.7, 108.7, 108.6, 94.3, 0.1.

**(Z)-(4-Cyclohexyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yn-1-yl)trimethylsilane (5d, Table 3)**



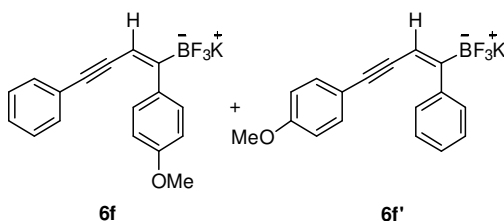
Following the general procedure A using  $\text{P}(\text{OEt})_3$  as the ligand, the title compound was isolated in 84% yield (139.5 mg).  $^1\text{H}$  NMR: (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.10 (s, 1H), 2.82–2.66 (m, 1H), 1.80–1.20 (m, 22H), 0.19 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  120.1, 103.1, 102.3, 83.4, 43.1, 31.3, 26.8, 26.2, 24.8, 0.1;  $^{11}\text{B}$  NMR: (160 MHz,  $\text{CDCl}_3$ )  $\delta$  30.314; IR (neat) 3591, 3083, 2906, 2772, 1364, 1247, 1141, 968, 851  $\text{cm}^{-1}$ ; HRMS(EI) calcd for  $\text{C}_{19}\text{H}_{33}\text{BO}_2\text{Si}$  332.2343, found 332.2342.

**(E)-2-(4-Phenylbut-1-en-3-yn-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5e, Table 3)**



Following the general procedure A using  $\text{P}(\text{OEt})_3$  as the ligand, The title compound was isolated in 85% yield (108 mg).  $^1\text{H}$  NMR: (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54–7.43 (m, 2H), 7.43–7.28 (m, 3H), 6.65 (d,  $J$  = 18.0 Hz, 1H), 6.11 (d,  $J$  = 18.0 Hz, 1H), 1.28 (s, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  131.9, 129.4, 128.7, 128.4, 123.1, 93.4, 89.5, 83.7, 24.9; HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{19}\text{BNaO}_2$   $[\text{M}+\text{Na}]^+$  277.1370, found 277.1373.

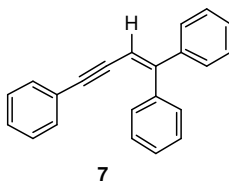
**Potassium (Z)- (1-(4-methoxyphenyl)-4-phenylbut-1-en-3-yn-1-yl) trifluoroborate (6f, Table 3) and Potassium (Z)- (4-(4-methoxyphenyl)-1-phenylbut-1-en-3-yn-1-yl) trifluoroborate (6f', Table 3)**



Following the general procedure A using  $\text{P}(\text{OEt})_3$  as the ligand. The crude H NMR showed two isomers and the ratio of **5f** and **5f'** was close to 1:1. The title compounds (**6f** and **6f'**) were isolated in 72% yield (122.5 mg) in 67:33 ratio.

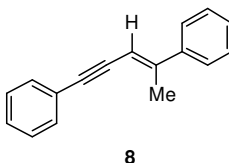
## Derivatization of Boron-Substituted Enynes (Scheme 2)

### 1,1,4-Triphenyl-1-buten-3-yne<sup>5</sup> (**7**)



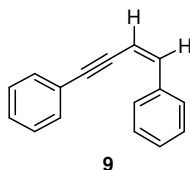
To a suspension of PdCl<sub>2</sub>(dppf) (9 mg, 0.025 mmol, 5 mol %) in THF (2.5 mL) in a Schlenk tube was added **2a** (82.5 mg, 0.25 mmol) followed by iodobenzene (51 mg, 0.25 mmol) at room temperature under N<sub>2</sub>. After aqueous 3 M KOH (0.75 mmol, 0.25 ml) was added, the reaction mixture turned deep brown immediately. The reaction mixture was stirred for overnight at room temperature. After the reaction was complete, the reaction mixture was quenched with sat. NH<sub>4</sub>Cl solution and then extracted with ethyl acetate (10 mL x 2). The combined organic layers were washed with brine and dried over MgSO<sub>4</sub>. Isolation by silica gel chromatography afforded the title compound (79% yield, 55.5 mg). <sup>1</sup>H NMR: (300 MHz, CDCl<sub>3</sub>) δ 7.57–7.52 (m, 2H), 7.45–7.36 (m, 3H), 7.31–7.62 (m, 5H), 7.31–7.27 (m, 5H), 6.24 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 152.8, 141.5, 139.3, 131.5, 130.3, 128.4, 128.4, 128.3, 128.2, 128.1, 127.9, 123.8, 107.2, 93.8, 89.3.

### (*E*)-1-Methyl-1,4-diphenyl-1-buten-3-yne<sup>6</sup> (**8**)



Following the preparation procedure of compound **7**, the title compound was isolated in 76% yield (41.5 mg). <sup>1</sup>H NMR: δ 7.53–7.46 (m, 4H), 7.40–7.29 (m, 6H), 6.12 (q, *J* = 1.1 Hz, 1H), 2.41 (d, *J* = 1.1 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 148.4, 141.0, 131.5, 128.6, 128.5, 128.2, 128.1, 125.6, 123.9, 106.7, 95.4, 88.4, 18.8.

### (*Z*)-1,4-Diphenyl-1-buten-3-yne<sup>7</sup> (**9**)

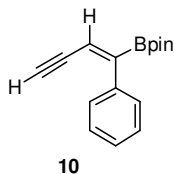


**3a** (77.5 mg, 0.25 mmol) was added to CH<sub>3</sub>COOH (2.5 mL) in a tube and stirred at 110 °C overnight. After the reaction was complete, the reaction was cooled to room temperature and extracted with ethyl acetate (10 mL x 2). The combined organic layers were washed with brine and dried over MgSO<sub>4</sub>. Purification by silica gel chromatography gave the title compound (86% yield, 44 mg). <sup>1</sup>H NMR: (300 MHz, CDCl<sub>3</sub>) δ 8.00–7.90 (m, 2H), 7.55–7.30 (m, 8H), 6.70 (d, *J* = 12.0 Hz,



1H), 5.92 (d,  $J$  = 12.0 Hz, 1H).

**(Z)-2-(1-Phenylbut-1-en-3-yn-1-yl)- 4,4,5,5-tetramethyl -1,3,2-dioxaborolane (10)**



**5c** (81.6 mg, 0.25 mmol) and  $K_2CO_3$  (69.1 mg, 0.5 mmol) were added to  $CH_3OH$  (2.5 mL) in a flask and stirred at room temperature overnight. After the reaction was complete, the reaction mixture was extracted with ethyl acetate (10 mL x 2). The combined organic layers were washed with brine and dried over  $MgSO_4$ . Purification by silica gel chromatography afforded the title compound (68% yield, 43.2 mg)  $^1H$  NMR:  $\delta$  7.61–7.55 (m, 2H), 7.38–7.24 (m, 3H), 6.47 (d,  $J$  = 2.5 Hz, 1H), 3.17 (d,  $J$  = 2.5 Hz, 1H), 1.30 (s, 12H).

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