Supplementary Information

NHC-copper-thiophene-2-carboxylate complex for the hydroboration of terminal alkynes

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General methods: CuTC, HBpin, and other commercial reagents were purchased from Aldrich and used as received. HBdan was prepared by following literature procedures. Toluene was purified using PureSolv solvent purification system, from Innovative Technology, Inc. Reactions with oxygen- and moisture-sensitive materials were carried out using the standard Schlenk technique. Flash chromatography was performed on silica gel from Merck (70–230 mesh). All 1H NMR spectra were obtained on Varian Mercury 300 systems or Bruker at 500 systems and reported in parts per million (ppm) downfield from tetramethylsilane. 13C NMR spectra were reported in ppm referenced to deuteriochloroform (77.16 ppm). 11B NMR spectra were obtained on Bruker at 400 systems at Kyonggi University (Suwon, Korea). Elemental analysis was obtained at Sogang Center for Research Facilities of Sogang University.

General procedure for the synthesis of SIPr–CuTC complex (1)

In an argon-filled glove box, 1,3-bis-(2,6-diisopropylphenyl)imidazolinium chloride (SIPr•HCl, 213.5 mg, 0.5 mmol) and potassium tert-butoxide (KOt-Bu, 61.7 mg, 0.55 mmol) were placed in a Schlenk flask, and 3 mL of THF was added. The reaction mixture was stirred at room temperature for 4 h. Then, the reaction mixture was filtered through a small plug of Celite, and washed with several portions of toluene, resulting in a clear pale yellow solution. The filtrate was concentrated, and redissolved in 6 mL of toluene. Copper(I) thiophene-2-carboxylate (CuTC, 95.3 mg, 0.5 mmol) was added to the solution, and the suspension was stirred at room temperature for 16 h. After 16 h, the remaining solid material was filtered off by washing with dichloromethane. The filtrate was dried in vacuo, dissolved in a minimal amount of dichloromethane, and precipitated with hexanes. The precipitate was filtered, and washed by additional hexanes to afford SIPr–CuTC as a white solid (206 mg, 71%). Crystals suitable for X-ray diffraction studies were obtained by slow diffusion of pentane to a concentrated CH2Cl2 solution of the complex at 4°C. 1H NMR (500 MHz, CDCl3) 6 7.41 (t, J = 8.0 Hz, 2H), 7.31 (d, J = 2.5 Hz, 1H), 7.26 (d, J = 8.0 Hz, 4H), 7.13 (d, J = 4.5 Hz, 1H), 6.81 (dd, J = 4.5, 2.5 Hz, 1H), 4.04 (s, 4H), 3.13–3.05 (m, 4H), 1.39 (d, J = 7.0 Hz, 12H), 1.35 (d, J = 7.0 Hz, 12H); 13C NMR (125 MHz, CDCl3) 6 203.2, 167.0, 146.7, 141.7, 134.5, 130.2, 129.9, 128.6, 126.8, 124.6, 53.8,
29.0, 25.4, 24.0. (Found: C, 66.36; H, 6.82; N, 4.74; S, 5.41%. Calc. for C_{32}H_{41}CuN_2O_2S: C, 66.12; H, 7.11; N, 4.82; S, 5.52%)

General procedure for the copper-catalyzed hydroboration of terminal alkynes with HBpin or HBdan

SiPr–CuTC (1 or 5 mol %, 0.005 or 0.025 mmol) in toluene (3 mL) was stirred for 5 min in a Schlenk tube under nitrogen atmosphere. HBpin or HBdan (1.2 equiv, 0.6 mmol) was added to the reaction mixture and the mixture was stirred for another 15 min at room temperature. Substrate 2 (1 equiv, 0.5 mol) dissolved in toluene (3 mL) was added. The reaction mixture was stirred at room temperature and monitored by TLC. Upon completion of the reaction, the reaction mixture was filtered through a pad of Celite and concentrated. The product was purified by silica gel chromatography.

Characterization of alkenylboron compounds 3 and 4 (Table 1, 2)

(\textit{E})-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (3a) (table 1): Following the general procedure, 3a was obtained in 98% yield (colorless oil). The characterization data for 3a was concordant with that previously reported in the literature.\(^3\) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.50–7.48 (m, 2H), 7.40 (d, \(J = 18.5\) Hz, 1H), 7.35–7.28 (m, 3H), 6.17 (d, \(J = 18.5\) Hz, 1H), 1.32 (s, 12H); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 149.5, 137.5, 128.9, 128.6, 127.1, 83.4, 24.8; \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \(\delta\) 29.4.

(\textit{E})-4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (3b) (table 2): Following the general procedure, 3b was obtained in 88% yield (colorless oil). The characterization data for 3b was concordant with that previously reported in the literature.\(^3\) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.60–7.56 (m, 4H), 7.40 (d, \(J = 18.5\) Hz, 1H), 7.35–7.28 (m, 3H), 6.26 (d, \(J = 18.5\) Hz, 1H), 1.32 (s, 12H); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 147.7, 140.8, 130.5 (q, \(J = 32\) Hz), 127.2, 125.6 (q, \(J = 3.5\) Hz), 124.1 (q, \(J = 270\)), 83.6, 24.8.
(E)-2-(4-bromostyril)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c) (table 2): Following the general procedure, 3c was obtained in 97% yield (white solid). The characterization data for 3c was concordant with that previously reported in the literature.\(^1\) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.47–7.45 (m, 2H), 7.35–7.33 (m, 2H), 7.32 (d, \(J = 18.5\) Hz, 1H), 6.15 (d, \(J = 18.5\) Hz, 1H), 1.31 (s, 12H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 148.1, 136.4, 131.8, 128.5, 122.9, 83.5, 122.9, 83.5, 24.8.

(E)-2-(4-methoxystyril)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d) (table 2): Following the general procedure, 3d was obtained in 83% yield (colorless oil). The characterization data for 3d was concordant with that previously reported in the literature.\(^3\) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.44–7.43 (m, 2H), 7.35 (d, \(J = 18.5\) Hz, 1H), 6.88–7.86 (m, 2H), 6.01 (d, \(J = 18.5\) Hz, 1H), 3.81 (s, 3H), 1.31 (s, 12H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 160.3, 149.1, 130.4, 128.5, 114.0, 83.2, 55.3, 24.8.

(E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl) phenyl acetate (3e) (table 2): Following the general procedure, 3e was obtained in 86% yield (white solid). The characterization data for 3e was concordant with that previously reported in the literature.\(^4\) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.50–7.48 (m, 2H), 7.37 (d, \(J = 18.5\) Hz, 1H), 7.07–7.05 (m, 2H), 6.11 (d, \(J = 18.5\) Hz, 1H), 2.30 (s, 3H), 1.31 (s, 12H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 169.3, 151.1, 148.3, 135.3, 128.1, 121.7, 83.4, 24.8, 21.2.

(E)-2-(4-methoxystyril)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f) (table 2): Following the general procedure, 3f was obtained in 79% yield (colorless solid). The characterization data for 3f was concordant with that previously reported in the literature.\(^5\) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.39–7.37 (m, 2H), 7.33 (d, \(J = 18.5\) Hz, 1H), 6.80–6.78 (m, 2H), 6.00 (d, \(J = 18.5\) Hz, 1H), 5.13 (brs, 1H), 1.31 (s, 12H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 156.4, 149.1, 130.6, 128.7, 115.5, 83.3, 24.8.
(E)-4,4,5,5-tetramethyl-2-(4-methylstyril)-1,3,2-dioxaborolane (3g)

Following the general procedure, 3g was obtained in 92% yield (white solid). The characterization data for 3g was concordant with that previously reported in the literature.\(^3\) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.39–7.35 (m, 3H), 7.15–7.13 (m, 2H), 6.11 (d, \(J = 18.5\) Hz, 1H), 2.34 (s, 3H), 1.31 (s, 12H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 149.5, 139.0, 134.8, 129.3, 127.0, 83.3, 24.8, 21.3.

(E)-2-(2-cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h)

Following the general procedure, 3h was obtained in 90% yield (colorless oil). The characterization data for 3h was concordant with that previously reported in the literature.\(^3\) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 6.58 (dd, \(J = 18.0, 6.0\) Hz, 1H), 5.37 (d, \(J = 18.0, 1.5\) Hz, 1H), 2.04–1.99 (m, 1H), 1.75–1.70 (m, 4H), 1.66–1.62 (m, 1H), 1.27 (s, 12H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 159.9, 83.0, 43.3, 31.9, 26.2, 26.0, 24.8.

(E)-2-(2-cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i)

Following the general procedure, 3i was obtained in 82% yield (colorless oil). The characterization data for 3i was concordant with that previously reported in the literature.\(^6\) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.36–7.27 (m, 5H), 6.69 (dt, \(J = 18.0, 4.5\) Hz, 1H), 5.76 (dt, \(J = 18.0, 1.5\) Hz, 1H), 4.54 (s, 2H), 4.11 (dd, \(J = 4.5, 1.5\) Hz, 2H), 1.27 (s, 12H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 149.2, 138.3, 128.4, 127.6, 127.5, 83.3, 72.3, 71.7, 24.8.

(E)-2-styryl-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (4a)

Following the general procedure, 4a was obtained in 82% yield (yellow solid). The characterization data for 4a was concordant with that previously reported in the literature.\(^2\) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.53–7.52 (m, 2H), 7.41–7.38 (m, 2H), 7.34–7.32 (m, 1H), 7.17–7.12 (m, 3H), 7.06–7.04 (m, 2H), 6.37 (d, \(J = 7.0\) Hz, 2H), 6.33 (d, \(J = 18.5\) Hz, 1H), 5.85 (brs, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 143.7, 141.2, 137.6, 136.4, 128.7, 127.6, 126.8, 119.9, 117.7, 105.8; \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \(\delta\) 27.8.
(E)-2-(4-(trifluoromethyl)styryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (4b) (table 2): Following the general procedure, 4b was obtained in 86% yield (yellow solid). The characterization data for 4b was concordant with that previously reported in the literature. \(^{2}\) \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.64–7.59 (m, 4H), 7.18–7.11 (m, 3H), 7.05–7.04 (m, 2H), 6.43 (d, \(J = 18.5\) Hz, 1H), 6.38 (d, \(J = 7.5\) Hz, 2H), 5.86 (brs, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 142.0, 140.9, 136.4, 130.3 (q, \(J = 31\) Hz), 128.2, 127.7, 126.9, 125.7 (q, \(J = 3.7\) Hz), 124.2 (q, \(J = 270\) Hz), 120.0, 117.9, 106.0.

(E)-2-(4-bromostyryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (4c) (table 2): Following the general procedure, 4c was obtained in 75% yield (yellow solid). The characterization data for 4c was concordant with that previously reported in the literature. \(^{2}\) \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.51–7.49 (m, 2H), 7.38–7.36 (m, 2H), 7.14–7.02 (m, 5H), 6.37 (d, \(J = 7.5\) Hz, 2H), 6.31 (d, \(J = 18.5\) Hz, 1H), 5.84 (brs, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 142.3, 141.0, 136.5, 136.4, 131.9, 128.3, 127.6, 122.6, 119.9, 117.8, 105.9.

(E)-2-(4-methoxystyryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (4d) (table 2): Following the general procedure, 4d was obtained in 80% yield (yellow solid). The characterization data for 4d was concordant with that previously reported in the literature. \(^{2}\) \(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.47–7.45 (m, 2H), 7.13–7.09 (m, 3H), 7.03–7.01 (m, 2H), 6.92–6.90 (m, 2H), 6.36 (d, \(J = 7.0\) Hz, 2H), 6.17 (d, \(J = 18.5\) Hz, 1H), 5.84 (brs, 2H), 3.84 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 160.2, 143.2, 141.2, 136.4, 130.5, 128.1, 127.6, 119.8, 117.5, 114.1, 105.7, 53.4.

(E)-2-(3-fluorostyryl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (4e) (table 2): Following the general procedure, 4e was obtained in 78% yield (yellow solid). The characterization data for 4e was concordant with that previously reported in the literature. \(^{2}\) \(^{1}\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.37–7.27 (m, 2H), 7.25–6.97 (m, 7H), 6.37 (d, \(J = 7.2\) Hz, 2H), 6.33 (d, \(J = 18.6\) Hz, 1H), 5.85 (brs, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 163.2 (d, \(J = 245\) Hz), 142.3 (d, \(J = 2.5\) Hz), 141.0, 139.9 (d, \(J = 7.5\) Hz), 136.4, 130.1 (d, \(J = 7.5\) Hz), 127.6, 122.8, 119.9, 117.8, 115.4 (d, \(J = 22.5\) Hz), 113.0 (d, \(J = 21.3\) Hz), 105.9.
(E)-2-(3-(benzyloxy)prop-1-en-1-yl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (4f) (table 2): Following the general procedure, 4f was obtained in 75% yield (yellow oil). The characterization data for 4f was concordant with that previously reported in the literature.\(^2\) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.42–7.34 (m, 5H), 7.15–7.04 (m, 4H), 6.42 (dt, \(J = 18.5, 5.0\) Hz, 1H), 6.33 (d, \(J = 7.5\) Hz, 2H), 5.88 (d, \(J = 18.6\) Hz, 1H), 5.76 (brs, 2H), 4.60 (d, \(J = 2.5\) Hz, 2H), 4.17 (d, \(J = 5.0\) Hz, 2H); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 142.7, 141.1, 138.2, 136.4, 128.5, 127.8, 127.7, 119.9, 117.6, 105.8, 72.6, 72.1.

**Mechanism studies**

\[ \text{PhCH=CH}_2 \quad 1 \text{ equiv SIPr–CuTC} \quad \text{benzene-\d_6, rt, 0.5 h} \quad \text{No rxn} \]

SIPr–CuTC (1 equiv, 0.2 mmol) in benzene-\(\text{d}_6\) (1 mL) was stirred for 5 min in a Schlenk tube under nitrogen atmosphere. Phenylacetylene (1 equiv, 0.2 mmol) was added to the reaction mixture and the mixture was stirred for 30 min at room temperature. Internal standard (0.25 equiv, 0.05 mmol) was added and reaction solution was analyzed by NMR spectroscopy.
The reaction was carried out with the modified literature procedure. SPr–CuTC (1 equiv, 0.1 mmol) in benzene-$d_6$ was stirred for 5 min in Schlenk tube under nitrogen atmosphere. HBpin (1 equiv, 0.1 mmol) was added to the reaction mixture and the mixture was stirred for 30 min at room temperature. The solution was degassed by one freeze-pump-thaw cycle, then exposed to an atmosphere of CO$_2$. The yellow solution turned colorless, and white solid precipitated. The reaction mixture was stirred at room temperature for 30 min. The resulting solution was concentrated and the white solid was analyzed by NMR spectroscopy. $^1$H NMR (500 MHz, THF-$d_8$) δ 7.88 (s, 1H), 7.36 (t, $J = 8.0$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 4H), 4.07 (s, 4H), 3.23–3.18 (m, 4H), 1.38 (d, $J = 7.0$ Hz, 12H), 1.33 (d, $J = 7.0$ Hz, 12H); $^{13}$C NMR (125 MHz, THF-$d_8$) δ 203.5, 162.4, 146.8, 135.3, 129.3, 124.2, 53.7, 28.7, 24.7, 23.9.
Deuterium labeling experiments

Phenylacetylene-\textit{d} (2a-\textit{d}) was prepared by following the literature procedure.\textsuperscript{8} SIPr–CuTC (5 mol %, 0.025 mmol) in toluene (3 mL) was stirred for 5 min in a Schlenk tube under nitrogen atmosphere. HBpin (1.2 equiv, 0.6 mmol) was added to the reaction mixture and the mixture was stirred for 15 min at room temperature, followed by 2a-\textit{d} (1 equiv, 0.5 mol) in toluene (3 mL). The reaction mixture was stirred at room temperature and monitored by TLC. Upon completion of the reaction, the reaction mixture was filtered through a pad of Celite and concentrated. The product was purified by silica gel chromatography. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.50–7.48 (m, 2H), 7.40 (brs, 1H), 7.36–7.28 (m, 3H), 1.32 (s, 12H).
**X-ray crystallography data**

Single-crystal X-ray diffraction measurements for SIPr–CuTC were carried out on a Bruker APEX-II CCD diffractometer equipped with a monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The data were collected at low temperature of 100 K by the φ–ω scan method and integrated by using Bruker-SAINT software. An absorption correction was applied with the SADABS program.⁹ The structures were solved and refined through the least-squares method with SHELXTL program.¹⁰ All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions using riding model. The crystallographic data and structural refinements for SIPr–CuTC were presented in Table S1. Structural information was deposited at the Cambridge Crystallographic Data Centre (CCDC reference numbers are 1908511 for SIPr–CuTC).

![Figure S1](image1.png)

**Figure S1.** Crystal structure of SIPr–CuTC with the both major- and minor-disorder components. Thermal ellipsoids for non-H atoms are shown at the 25% probability level. The PART command was used to model two-part disorder. (a) The major-disorder component is occupied with 53.8% fractional site. (b) The minor-disorder component is shown with 46.2% fractional site occupation.
**Figure S2.** Packing crystal structure showing the view along the a axis

**Table S1.** X-ray data collection and structure refinement

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<th>Description</th>
<th>Experimental value</th>
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Completeness (%) to theta = 29.70° 99.4
Data/restraints/parameters 17550/19/758
Goodness-of-fit on F^2 1.052
Final R indices (I >2sigma(I)) R1,a = 0.0403, wR2,b = 0.1129
R indices (all data) R1 = 0.0596, wR2 = 0.1251
Largest diff. peak and hole (e Å^-3) 0.486 and -0.292

References
