9-Borobicyclo[3.3.1]nonane-Catalyzed Hydroboration of Terminal Aromatic Alkynes with Pinacolborane

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ABSTRACT
Organoboron compounds are extensively used in organic synthesis. The alkenylboronic acid pinacol esters formed from the hydroboration reaction of alkynes with pinacolborane are stable, easy to handle, and useful in many synthetic transformations. However, pinacolborane lacks the reactivity necessary to undergo facile hydroboration reaction with terminal aromatic alkynes. 9-Borobicyclo[3.3.1]nonane (9-BBN) can be used to catalyze the hydroboration reaction of phenylacetylene with pinacolborane. The hydroboration reaction parameters and product purification conditions were evaluated to maximize the yield of (*E*)-2-phenylethenylboronic acid pinacol ester. It was found that the optimal reaction conditions for the 9-BBN-catalyzed hydroboration of phenylacetylene with pinacolborane were: phenylacetylene (1.0 equiv), pinacolborane (1.2 equiv), 9-BBN (20 mol%), and THF [0.2] at 65 °C. The compatibility of these reaction conditions with *p*-substituted terminal aromatic alkynes bearing electronically diverse groups was studied. Moderate to good yield (49–76%) of the hydroboration products were isolated after purification by liquid-liquid extraction and flash chromatography.

KEYWORDS
Organic Synthesis; Catalysis; Methods Development; Hydroboration; Reaction Optimization; Alkenylboronic Ester; Alkyne; Pinacolborane; 9-Borobicyclo[3.3.1]nonane

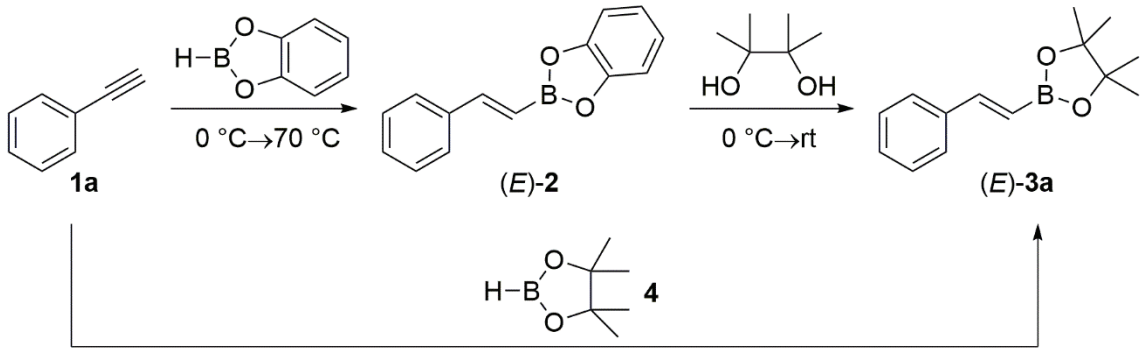
INTRODUCTION

Boron containing organic compounds are useful reagents in the synthesis of important carbon-containing medicines, materials, and fine chemicals. The utility of these reagents is evident from the variety of bonds, and therefore functional groups, which can be substituted for the C–B bond. For example, the hydroboration-oxidation reaction of an alkene ultimately transforms the C–B bond into a C–O bond.[1] The C–B bond can be substituted for a C–H bond by protonolysis,[2] or a C–X bond by halogenation.[3] In addition, the use of transition-metal catalysis has allowed for the substitution of a C–B bond for a C–C,[4, 5, 6, 7] C–H,[8, 9] C–N,[10, 11, 12, 13, 14] C–O,[15, 16, 17] C–P,[18, 19] or C–S bond,[20, 21] and include asymmetric variants.[22]

The hydroboration reaction of unsaturated organic substrates with hydroboron reagents is a straight-forward method to prepare alkyl- and alkenylboron compounds. An early example of the hydroboration reaction of alkenes was reported by Brown in 1956.[1, 23] In 1966, Woods and Strong reported that alkynes undergo sluggish hydroboration with 4,4,6-trimethyl-1,3,2-dioxaborinane in a sealed tube of superheated ether to provide the alkenylboron products in low yield.[24] Chemists have sought to catalyze the hydroboration reaction with transition metals,[25, 26, 27, 28, 29, 30, 31, 32] and alkaline earth metals,[33, 34] aluminum,[35, 35, 36, 37] base,[38, 39] *N*,*N*-dimethylacetamide,[40] and benzoic acid derivatives.[41, 42] Boron reagents are also known to catalyze the hydroboration reaction.[43, 44, 45, 46, 47, 48] In 1990, Periasamy *et al.* reported that a BH_3·*N*,*N*-diethylaniline complex could catalyze the hydroboration of terminal alkynes with catecholborane.[43] Hoshi *et al.* later reported that dicyclohexylborane could catalyze the hydroboration reaction of terminal alkynes with pinacolborane in good to excellent yield.[44]

Our interest in the hydroboration reaction originated with the need to synthesize (*E*)-2-phenylethenyl boronic acid pinacol ester (*E*)-**3a** (Scheme 1) for use as an organometallic donor in Suzuki-Miyaura cross-coupling reactions.[7] The reagent (*E*)-**3a** could be synthesized by hydroboration reaction with catecholborane followed by diol exchange with pinacol.[51] However, the use of catecholborane is not ideal. For example, catechol is sensitive to oxidation, and the catecholborane product can decompose upon exposure to air or moisture.[52] To avoid the use of catechol, a direct hydroboration reaction of **1a** with pinacolborane **4** was sought. The reagent **4** is commercially available and more stable than catecholborane. Although the increased stability of **4** also lessens its reactivity in the hydroboration reaction. For example, the hydroboration reaction of **1a** (1 equiv) with **4** (1.2 equiv) is sluggish in refluxing THF (65 °C), and only trace amounts of product (*E*)-**3a** was observed after 7 h *vide infra*. It was found that 9-borobicyclo[3.3.1]nonane (9-BBN) could be used to catalyze the hydroboration reaction of **1a** with **4**.[7] The initially evaluated

reaction conditions were determined to be satisfactory at the time and were not optimized. The reaction parameters and purification conditions have since been studied in detail and are described here.



Scheme 1.

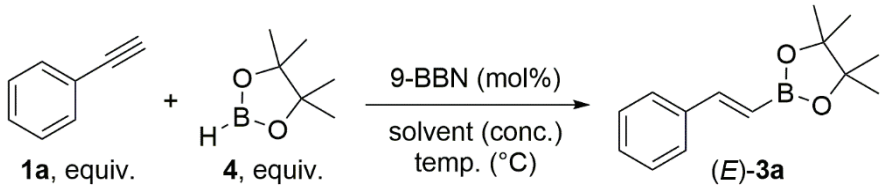
RESULTS AND DISCUSSION

This study began with the use of the previously published reaction conditions: **1a** (1.0 equiv), **4** (1.0 equiv), 9-BBN (10 mol%) in refluxing 0.2 M THF solution (Table 1).[7] On a 1 mmol scale, the hydroboration product (*E*)-**3a** was isolated from this reaction as a slightly yellow oil in 62% yield after purification by liquid-liquid extraction and flash chromatography (entry 1). The effect of reagent stoichiometry on the yield of (*E*)-**3a** was then evaluated. Increasing the amount of **4** to 1.2 equiv increased the yield to 73% (entry 2). Further increasing the amount of **4** to 1.4 equivalents decreased the yield of (*E*)-**3a** (entry 3). The use of excess **1a** (1.2 equiv) and **4** (1.0 equiv) as the limiting reactant provided a 69% yield of (*E*)-**3a** (entry 4). A range from 0-30 mol% of 9-BBN was tested, and 20 mol% was found to provide the highest yield of (*E*)-**3a** (entries 12-15).

The reaction parameters of concentration, temperature, and a NaOH additive were also evaluated. It was found that concentrations between 0.2 M and neat[49] caused little change in the amount of (*E*)-**3a** that was isolated (entries 5–7). However, a more dilute reaction (0.04 M) produced significantly less (*E*)-**3a** (entry 5). Toluene and 1,4-dioxane were evaluated as solvent and were found to provide a lower yield than when THF was used as the reaction solvent (entries 10 and 11). A decreased reaction temperature resulted in a decreased yield of (*E*)-**3a** (entry 8). An increased reaction temperature resulted in an increased yield of (*E*)-**3a** when 1,4-dioxane was used as solvent (entries 9 and 10). However, the yield of (*E*)-**3** was higher when the reaction was run in THF at 65 °C than when the reaction was run in 1,4-dioxane at 85 °C (compare entries 2 and 10). The addition of NaOH (5 mol%) resulted in a slightly decreased yield of (*E*)-**3a** (entry 16).[38]

Various stationary phases were evaluated for the purification of (*E*)-**3a** by flash chromatography. The use of a boric acid capped silica provided a negligible difference in yield and purity as determined by ^{1}H NMR (entry 17).[50] The crude product (*E*)-**3a** was entirely lost when the flash chromatography was conducted with a dry, neutral alumina stationary phase (entry 18).

Table 1. Evaluation of the reaction parameters of the 9-BBN-catalyzed hydroboration reaction of **1a** with **4**.

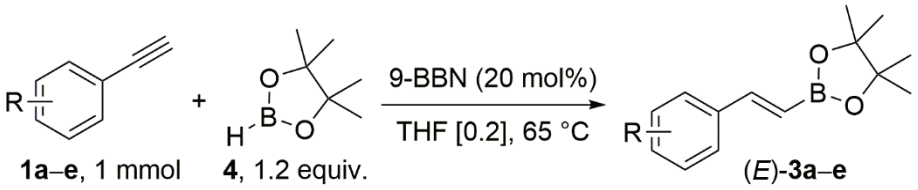


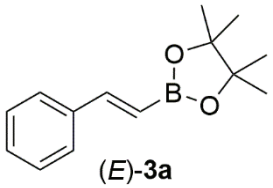
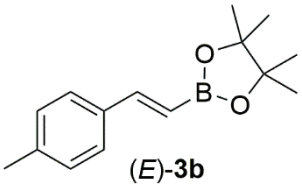
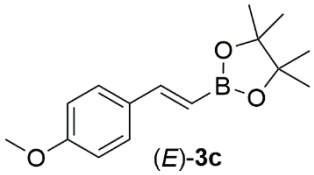
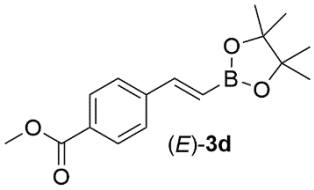
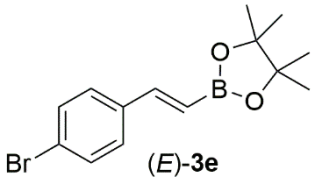
entry	HB(pin), mmol	9-BBN, mol%	solvent, conc.	temp., °C	yield,[a] %
1	1	10	THF, 0.2	65	62
2	1.2	10	THF, 0.2	65	73
3	1.4	10	THF, 0.2	65	67
4[b]	1	10	THF, 0.2	65	69
5	1.2	10	THF, 0.04	65	53
6	1.2	10	THF, 1.0	65	71
7	1.2	10	neat[c]	65	69
8	1.2	10	THF, 0.2	45	54
9	1.2	10	dioxane, 0.2	65	48
10	1.2	10	dioxane, 0.2	85	59
11	1.2	10	toluene, 0.2	65	54
12	1.2	–	THF, 0.2	65	0[d]
13	1.2	5	THF, 0.2	65	46
14	1.2	20	THF, 0.2	65	76
15	1.2	30	THF, 0.2	65	71
16[e]	1.2	10	THF, 0.2	65	66
17[f]	1.2	10	THF, 0.2	65	63
18[g]	1.2	10	THF, 0.2	65	0

[a]Yield of isolated, purified product.
[b]1.2 equiv of phenylacetylene was used.
[c]9-BBN was used as a 0.5 M solution in THF. The final reaction concentration was 2.5 M.
[d]No product was observed after 7 h.
[e]NaOH (5 mol%) was added as a co-catalyst.
[f]Borated silica was used as the chromatography stationary phase.
[g]Dry, neutral alumina was used as the chromatography stationary phase

The optimized reaction conditions of **1** (1.0 equiv), **4** (1.2 equiv), 9-BBN (20 mol%), and THF [0.2] at 65 °C were then used to evaluate the scope of compatible *p*-substituted terminal aromatic alkynes **1a–e**. The electronically neutral parent alkyne **1a** provided the highest yield (76%) and was found to react the fastest under the optimized reaction conditions (entry 1). Substrates with electron-donating methyl and methoxy groups provided a good yield of the desired products (*E*)-**3b** and (*E*)-**3c** (entries 2 and 3). A substrate bearing an electron-withdrawing methyl ester group provided the lowest yield of the substrates evaluated (entry 4). The good yield of the bifunctional, 4-bromo derivative (*E*)-**3e** is especially interesting because it could be used as an organic electrophile or organometallic donor in a Suzuki-Miyaura cross-coupling reaction. Complete control of the alkene geometry of (*E*)-**3a–e** was observed by ^{1}H NMR spectroscopy in all of the cases studied.

Table 2. Evaluation of the optimized reaction conditions with **1a** and electronically diverse *p*-substituted terminal aromatic alkynes **1b**–**1e**.



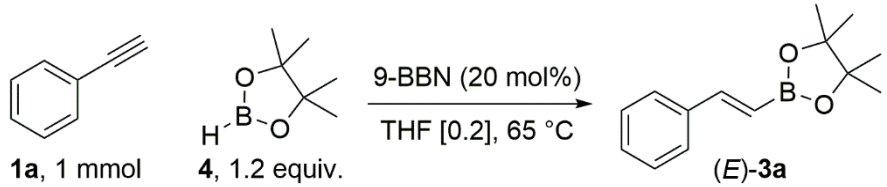
entry	product	yield %	reaction time (h)
1	 (*E*)-**3a**	76%	1.5
2	 (*E*)-**3b**	64%	2
3	 (*E*)-**3c**	63%	3
4	 (*E*)-**3d**	49%	7
5	 (*E*)-**3e**	72%	3

METHODS AND PROCEDURES

General Procedure: An oven-dried, round-bottom flask equipped with a magnetic stir-bar was fitted with an oven-dried Liebig condenser and sealed with high-vacuum grease. The reflux apparatus was capped with a septum and purged with a balloon of argon that was introduced and evacuated through a needle for 15 minutes. The following were added sequentially by syringe under a balloon of argon: the terminal aromatic alkyne, pinacolborane, 9-BBN ([0.5] in THF), and finally a small portion of solvent to wash all of the reagents into the round-bottomed flask. The reaction solution was refluxed in a preheated oil bath at 65 °C. Reaction aliquots were analyzed by thin-layer chromatography (TLC) to monitor the disappearance of the alkyne starting material. When the reaction was determined to be complete, it was cooled to room temperature, extracted with ethyl acetate, washed with water, brine, dried with sodium sulfate, filtered and concentrated by rotary evaporation (50 °C, 2 torr). The crude product was purified by flash chromatography on silica. The amount of silica used in the chromatography was approximately 65 times the mass of the concentrated crude product. The eluent began with 98.5:1.5, hexane/ethyl acetate and increased to 95:5,

hexane/ethyl acetate until the product was completely eluted. The product was concentrated *in vacuo* (2 torr) to afford the desired product.

*Procedure for the Synthesis of 4,4,5,5-Tetramethyl-2-[(1E)-2-phenylethenyl]-1,3,2-dioxaborolane ((E)-**3a**)*



Following the General Procedure, phenylacetylene (110 μL, 1.0 mmol, 1.0 equiv), pinacolborane (174 μL, 1.2 mmol, 1.2 equiv), 9-BBN (0.400 mL, [0.5], 0.2 mmol, 0.2 equiv), and THF (5 mL) were combined and heated to 65 °C for 1.5 h. Purification by aqueous workup and flash chromatography afforded 175 mg (76%) of (*E*)-**3a** as a slightly yellow oil.[38]

Data *for 4,4,5,5-Tetramethyl-2-[(1E)-2-phenylethenyl]-1,3,2-dioxaborolane ((E)-**3a**)*:

^{1}H NMR: (400 MHz, $CDCl_3$)
7.48–7.45 (m, 2 H), 7.40 (d, *J* = 18.5, 1 H), 7.33–7.23 (m, 3 H) 6.17 (d, *J* = 18.5, 1 H), 1.29 (s, 12 H).

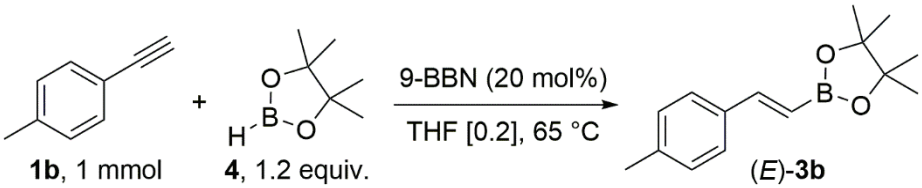
^{13}C NMR: (101 MHz, $CDCl_3$)
149.5, 137.5, 128.9, 128.6, 127.1, 83.4, 24.9.

IR: (neat)
3080 (w), 3054 (w), 3018 (w), 2978 (w), 2928 (w), 1623 (m), 1577 (w), 1495 (w), 1450 (m), 1391 (m), 1371 (m), 1346 (s), 1322 (s), 1271 (m), 1237 (m), 1210 (m), 1142 (s), 1109 (w), 997 (m), 969 (m), 899 (m), 851 (m), 748 (m), 692 (m), 660 (w), 641 (w).

MS: (EI, 70 eV)
230 ($[M]^+$, 49), 229 (12), 215 (24), 157 (11), 145 (38), 144 (69), 143 (10), 131 (56), 130 (100), 129 (92), 118 (16), 114 (14), 105 (31), 104 (15), 103 (16), 85 (10), 78 (12), 77 (21).

TLC: R_f 0.53 (hexane/ethyl acetate, 95:5) [silica gel, aqueous $KMnO_4$]

*Procedure for the Synthesis of 4,4,5,5-Tetramethyl-2-[(1E)-2-(4-methylphenyl)ethenyl]-1,3,2-dioxaborolane ((E)-**3b**)*



Following the General Procedure, 4-tolylacetylene (127 μL, 1.0 mmol, 1.0 equiv), pinacolborane (174 μL, 1.2 mmol, 1.2 equiv), 9-BBN (0.400 mL, [0.5], 0.2 mmol, 0.2 equiv), and THF (5 mL) were combined and heated to 65 °C for 2 h. Purification by aqueous workup and flash chromatography afforded 157 mg (64%) of (*E*)-**3b** as a slightly yellow oil.[37]

*Data for 4,4,5,5-Tetramethyl-2-[(1E)-2-(4-methylphenyl)ethenyl]-1,3,2-dioxaborolane ((E)-**3b**)*

^{1}H NMR: (400 MHz, $CDCl_3$)
7.40–7.38 (m, 2 H), 7.38 (d, *J* = 18.5, 1 H), 7.15–7.13 (m, 2 H), 6.11 (d, *J* = 18.5, 1 H), 2.34 (s, 3 H), 1.31 (s, 12 H).

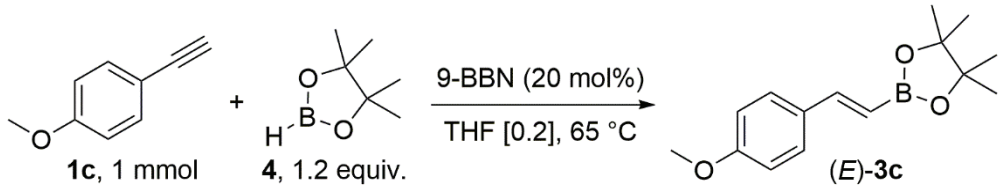
^{13}C NMR: (101 MHz, $CDCl_3$)
149.6, 139.1, 134.9, 129.4, 127.2, 83.4, 25.0, 21.5.

IR: (neat)
2976 (w), 2926 (w), 1625 (m), 1569 (w), 1511 (w), 1479 (w), 1451 (w), 1411 (w), 1379 (m), 1370 (m), 1345 (m), 1320 (s), 1285 (w), 1264 (w), 1220 (w), 1204 (w), 1178 (w), 1165 (w), 1138 (s), 1109 (m), 1019 (s), 999 (m), 969 (m), 950 (w), 901 (w), 853 (w), 843 (m), 829 (w), 796 (s), 759 (w), 712 (w), 676 (w), 659 (w), 642 (w), 580 (w), 517 (w), 492 (m), 453 (w).

MS: (EI, 70 eV)
245 ($[M+1]^+$, 12), 244 ($[M]^+$, 69), 243 ($[M-1]^+$, 17), 229 (21), 171 (12), 159 (40), 158 (54), 145 (38), 144 (92), 143 (100), 132 (19), 128 (47), 127 (13), 119 (17), 118 (12), 117 (43), 116 (29), 115 (36), 91 (18), 43 (15), 41 (17), 40 (11).

TLC: R_f 0.42 (hexane/ethyl acetate, 95:5) [silica gel, aqueous $KMnO_4$]

*Procedure for synthesis of 2-[(1E)-2-(4-Methoxyphenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((E)-**3c**)*



Following the General Procedure, 4-ethynylanisole (130 mg, 1.0 mmol, 1.0 equiv), pinacolborane (174 μL, 1.2 mmol, 1.2 equiv), 9-BBN (0.400 mL, [0.5], 0.2 mmol, 0.2 equiv), and THF (5 mL) were combined and heated to 65 °C for 3 h. Purification by aqueous workup and flash chromatography afforded 132 mg (51%) of (*E*)-**3c** as a slightly yellow oil.[46]

*Data for 2-[(1E)-2-(4-Methoxyphenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((E)-**3c**)*

^{1}H NMR: (400 MHz, $CDCl_3$)
7.45–7.42 (m, 2 H), 7.35 (d, *J* = 18.4, 1 H), 6.88–6.85 (m, 2 H), 6.01 (d, *J* = 18.4, 1 H), 3.81 (s, 3 H), 1.31 (s, 12 H).

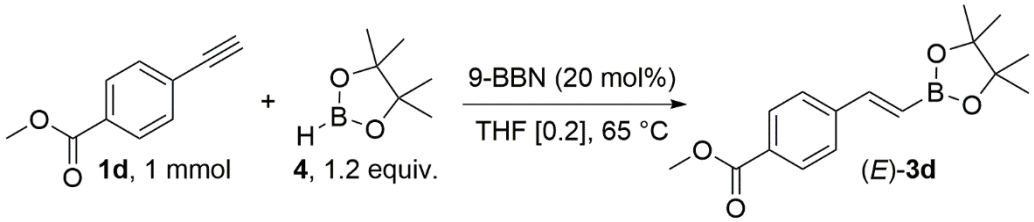
^{13}C NMR: (101 MHz, $CDCl_3$)
160.4, 149.2, 130.6, 128.6, 114.1, 83.4, 55.4, 25.0.

IR: (neat)
2976 (w), 2932 (w), 2836 (w),1697 (w), 1624 (w), 1624 (w), 1603 (m), 1575 (w), 1509 (m), 1457 (w), 1379 (w), 1370 (w), 1351 (m), 1319 (m), 1303 (m), 1291 (w), 1250 (m), 1210 (m), 1194 (w), 1170 (m),1140 (m), 1105 (w), 1032 (m), 995 (w), 969 (m), 900 (w), 852 (m), 814 (m), 758 (w), 734 (w), 720 (w), 699 (w), 675 (w), 644 (w), 607 (w), 607 (w), 597 (w), 578 (w), 541 (w), 519 (m), 450 (w).

MS: (EI, 70 eV)
261 ([M+1]$^+$, 17), 260 ([M]$^+$, 100), 259 ([M-1]$^+$, 24), 245 (17), 175 (30), 174 (19), 161 (45), 160 (78), 159 (47), 148 (15), 146 (10), 145 (23), 144 (99), 143 (28), 135 (15), 121 (16), 117 (24), 77 (12), 43 (13), 41 (15), 40 (14).

TLC: R_f 0.26 (hexane/ethyl acetate, 95:5) [silica gel]

*Procedure for the Synthesis of 4-[(1E)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethenyl]benzoic acid methyl ester ((E)-**3d**)*



Following the General Procedure, methyl 4-ethynylbenzoate (160 mg, 1.0 mmol, 1.0 equiv), pinacolborane (174 μL, 1.2 mmol, 1.2 equiv), 9-BBN (0.400 mL, [0.5], 0.2 mmol, 0.2 equiv), and THF (5 mL) were combined and heated to 65 °C for 7 h. Purification by aqueous workup and flash chromatography afforded 149 mg (52%) of (*E*)-**3d** as off-white crystals.[46]

*Data for 4-[(1E)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethenyl]benzoic acid methyl ester ((E)-**3d**)*

^{1}H NMR: (400 MHz, $CDCl_3$)
8.00–7.98 (m, 2 H), 7.53–7.51 (m, 2 H), 7.40 (d, *J* = 18.4, 1 H), 3.89 (s, 3 H), 1.30 (s, 12 H).

^{13}C NMR: (101 MHz, $CDCl_3$)
166.8, 148.2, 141.8, 130.2, 130.0, 127.0, 83.6, 52.2, 24.9.

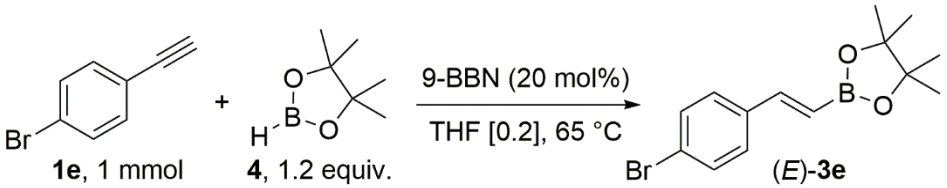
IR: (neat)
2975 (w), 2950 (w), 2931 (w), 2848 (w), 1712 (s), 1672 (w), 1627 (m), 1605 (m), 1566 (w), 1487 (w), 1441 (m), 1413 (w), 1380 (w), 1368 (m), 1349 (s), 1319 (s), 1275 (s), 1214 (m), 1195 (m), 1173 (m), 1149 (m), 1111 (s), 1015 (w), 1002 (m), 972 (m), 902 (w), 872 (m), 855 (m), 844 (m), 835 (m), 804 (w), 758 (s), 703 (m), 690 (m), 667 (w), 652 (w), 638 (m), 630 (m), 579 (w), 518 (w), 508 (m), 487 (w), 479 (w), 451 (w).

MS: (EI, 70 eV)
288 ([M]$^+$, 49), 287 ([M-1]$^+$, 15), 273 (32), 257 (19), 203 (29), 202 (57), 189 (20), 188 (30), 187 (53), 176 (18), 172 (13), 171 (15), 158 (11), 157 (100), 156 (32), 143 (45), 130 (11), 129 (39), 128 (17), 77 (29), 59 (15), 43 (20), 41 (21).

MP: 108-109 °C

TLC: R_f 0.18 (hexane/ethyl acetate, 95:5) [silica gel, aqueous $KMnO_4$]

*Procedure for the Synthesis of 2-[(1E)-2-(4-Bromophenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((E)-**3e**)*



Following the General Procedure, 1-bromo-4-ethynylbenzene (309 mg, 1.0 mmol, 1.0 equiv), pinacolborane (174 μL, 1.2 mmol, 1.2 equiv), 9-BBN (0.400 mL, [0.5], 0.2 mmol, 0.2 equiv), and THF (5 mL) were combined and heated to 65 °C for 3 h. Purification by aqueous workup and flash chromatography afforded 220 mg (71%) of (*E*)-**3e** as white crystals.[37]

*Data for 2-[(1E)-2-(4-Bromophenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((E)-**3e**)*

^{1}H NMR: (400 MHz, $CDCl_3$)
7.47–7.44 (m, 2 H), 7.36–7.32 (m, 2 H), 7.32 (d, *J* = 18.5, 1 H), 6.14 (d, *J* = 18.5, 1 H), 1.31(s, 12 H).

^{13}C NMR: (101 MHz, $CDCl_3$)
148.2, 136.6, 131.9, 128.7, 123.0, 83.6, 25.0.

IR: (neat)
3087 (w), 3059 (w), 3046 (w), 3007 (w), 2973 (w), 2929 (w), 2290 (w), 1906 (w), 1701 (w), 1624 (m), 1583 (w), 1564 (w), 1486 (m), 1467 (w), 1401 (m), 1378 (w), 1370 (w), 1343 (m), 1319 (s), 1301 (m), 1296 (m), 1268 (m), 1209 (m), 1165 (w), 1138 (m), 1110 (m), 1067 (m), 1006 (m), 991 (m), 968 (m), 952 (w), 899 (w), 852 (m), 820 (w), 799 (s), 706 (w), 693 (w), 667 (w), 653 (w), 638 (m), 628 (w), 598 (w), 579 (w), 515 (s), 485 (w), 453 (w).

MS: (EI, 70 eV)
310 ([M+2]$^+$, 50), 309 ([M+1]$^+$, 21), 308 ([M]$^+$, 51), 307 ([M-1]$^+$, 14), 295 (22), 293 (22), 225 (22), 224 (48), 223 (24), 222 (47), 211 (27), 210 (85), 209 (65), 208 (89), 207 (39), 198 (16), 196 (17), 194 (23), 192 (23), 144 (31), 143 (100), 139 (10), 131 (10), 130 (59), 129 (92), 128 (47), 103 (14), 102 (23), 101 (11), 85 (21), 77 (55), 76 (12), 75 (11), 59 (13), 57 (12), 43 (34), 42 (11), 41 (36), 40 (39).

MP: 78-79 °C

TLC: R_f 0.42 (hexanes/ethyl acetate, 95:5) [silica gel, aqueous $KMnO_4$]

CONCLUSION

(*E*)-2-phenylethenyl boronic acid pinacol ester derivatives can be readily prepared by 9-BBN-catalyzed hydroboration reaction of terminal aromatic alkynes with pinacolborane. The use of 20 mol% of 9-BBN was found to provide the best yield of the hydroboration product. A variety of electronically diverse substrates provided moderate to good yields of the (*E*)-2-phenylethenyl boronic acid pinacol ester derivatives (*E*)-**3a–e**. The bifunctional, 4-bromo derivative is especially interesting because it could be used as an organic electrophile or organometallic donor in a cross-coupling reaction. Complete control of the alkene geometry of the alkenylboronic ester product was observed in all of the cases studied. We intend to continue to explore the scope of this reaction and the synthetic utility of the boronic acid pinacol ester products.

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PRESS SUMMARY

Boron containing organic compounds are useful reagents in the synthesis of important carbon-containing medicines, materials, and fine chemicals. The alkenylboronic acid pinacol esters formed from hydroboration reaction of alkynes with pinacolborane are stable, easy to handle, and useful in many synthetic transformations. However, pinacolborane lacks the reactivity necessary to undergo facile hydroboration reaction with terminal aromatic alkynes. It was discovered that 9-borobicyclo[3.3.1]nonane (9-BBN) can be used to catalyze the hydroboration reaction of terminal aromatic alkynes with pinacolborane. The parameters of the experimental procedure were evaluated and an optimal set of reaction conditions were found. This work provides synthetic chemists with a method to prepare these important compounds.