Practical solvent-free microwave-assisted hydroboration of alkynes

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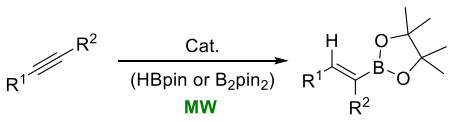
Abstract: A simple and rapid protocol for the *anti*-Markovnikov hydroboration of alkynes assisted by microwave irradiation has been developed. Pinacolborane smoothly reacts with terminal alkynes to obtain (*E*)-alkenyl boronates in good yields and short reactions times in the absence of solvent. Further transformations on the carbon-boron bond of the adducts can be sequentially achieved without the need of purifying the alkenyl boronates.

Introduction

Alkenyl boronates are versatile building blocks in organic synthesis.[1] The development of the Suzuki–Miyaura cross-coupling reactions set them as privileged substrates in the formation of new C-C bonds.[2] Moreover, the alkene group of these compounds has been used in cycloadditions,[3] hydro- and difunctionalizations[4] and radical reactions[5] among others. The main interest of these reactions is that the boronate groups are able to undergo further functionalizations, thus transforming the C-B bond in new C-C and C-heteroatom bonds.[6]

The preparation of alkenyl boronates can be achieved by different methodologies.[7] In particular, (*E*)-alkenyl boronates have been prepared by olefin metathesis,[8] dehydrogenative borylation of alkenes,[9] Heck type reactions[10] or coupling/dehydroboration of epoxides[11] among others. However, hydroboration of alkynes represents a prominent strategy to obtain (*E*)-alkenyl boronates. A plethora of transition metals has been used to catalyzed and control the regio- and stereoselectivity of this process.[7,12] More recently, transition metal-free protocols have been reported to obtain the *trans* isomers of alkenyl boronates, including the use of several boranes,[13] *N*-heterocyclic carbenes,[14] 4-(dimethylamino)benzoic acid,[15] different bases[16] (NaOH, LiO*t*Bu, NaO*t*Bu/PhI(OAc)$_2$) or main-group metals[17] as catalysts. Furthermore, non-catalyzed reactions were previously studied by Brown and Knochel.[18] However, long reactions times are often necessary for the reaction to be completed. Microwave irradiation commonly reduces reaction times in organic synthesis, and some examples of metal-catalyzed hydroborations with microwave heating have been reported using rhodium and zirconium complexes (Scheme 1).[19] Very recently, tris(3,4,5-trifluorophenyl)borane[20] and 4-(dimethylamino)benzoic acid[21] have been applied as transition metal-free catalysts in the hydroboration of alkynes.



· Catalyst:
- [ML$_n$], M = Rh, Zr (ref. 19)
- B(2,4,6-Ar^F)$_3$ (ref. 20)
- 4-(dimethylamino)benzoic acid (ref. 21)

Scheme 1. Microwave assisted synthesis of (*E*)-alkenyl boronates.

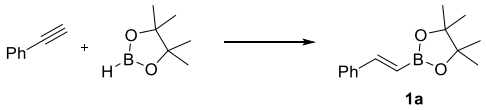
In this work, we have focused on the development of a simple, fast and general solvent-free microwave-assisted hydroboration of alkynes with commercially available pinacolborane.

Results and Discussion

Initially, we investigated the hydroboration of phenylacetylene with pinacolborane under microwave irradiation as a model reaction at a constant temperature. No solvent, or additive were added, and the reagents were mixed in open air. Initial experiments showed that phenylacetylene was not fully consumed below 200 ºC after 20-30 min, when low to moderate yields were obtained (Table 1, entries 1-2). Remarkably, despite the slow reaction rate, hydroboration was completely regio- and stereoselective, yielding (*E*)-styryl pinacolboronate (**1a**) as the only product. Increasing the temperature to 215 ºC gave rise to a complete consumption of the alkyne in 20 min, with a slight increase in the reaction yield (entry 3). Using an excess of two equivalents of pinacolborane gave a satisfactory 80% yield of the alkenyl boronate **1a** (entry 4). The outcome of the reaction was similar for a range of different reaction scales (1.75-4.5 mmol, see Supporting Information for more details) and further excess of pinacolborane had no significant impact on the reaction yield. For comparison, the same reaction under identical conditions but using conventional heating instead of microwave irradiation gave a 25% yield after 20 minutes (entry 6). Finally, the reaction time was optimized to 18 minutes, leading to a 79% yield of (*E*)-styryl pinacolboronate in 4.5 mmol scale (entry 7).[22]

No additives were added to the reaction mixture, so a catalyst-free hydroboration is suggested to take place under these reaction conditions. However, some type of catalysis cannot be completely ruled out for this process. Hence, palladium traces could be present in the used alkynes, and metal catalyzed reactions have been described to proceed at ultra-low catalyst concentrations under microwave irradiation.[23] Additionally, some decomposition of pinacolborane by oxygen or moisture is expected to occur under these reaction conditions, and borane derivatives has been previously described as catalysts on alkyne hydroboration.[13]

Table 1. Hydroboration optimization for phenylacetylene.[a]



1a

Entry	Temp. [°C]	time [min]	HBpin [equiv]	Yield [%]
1	175	30	1.5	35[b]
2	200	20	1.5	60[b]
3	215	20	1.5	67[c]
4	215	20	2	80[c]
5	215	20	2.5	81[c]
6	215[d]	20	2	25[c]
7	215	18	2	79[c]

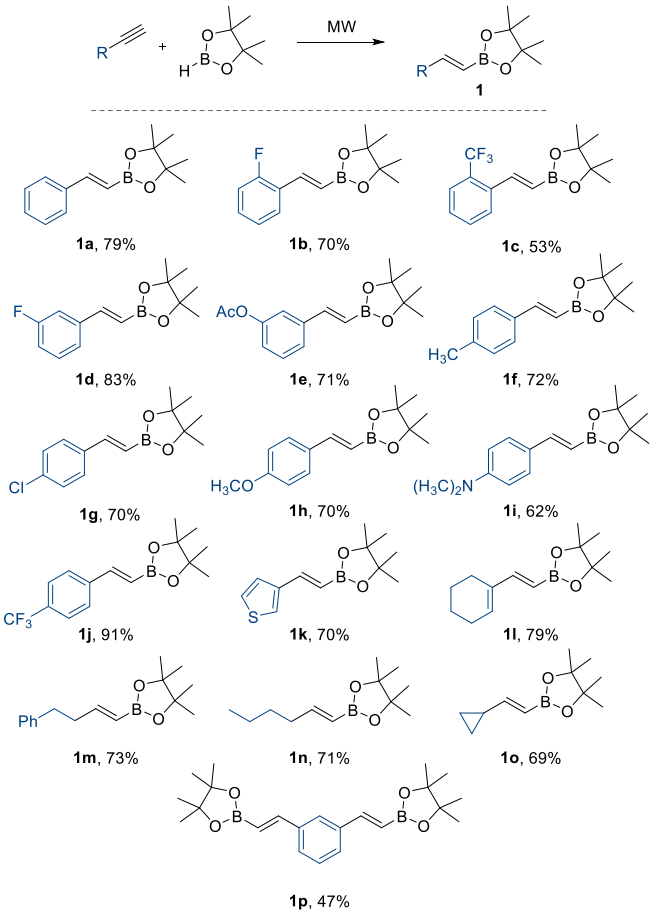
[a] Reaction conditions: phenylacetylene, pinacolborane, microwave irradiation. Entries 1-3: 3 mmol scale; entries 4-7: 4.5 mmol scale. [b] Yields determined by ^{1}H NMR analysis in the reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [c] Isolated yield. [d] Conventional heating.

We next investigated the scope of our microwave-assisted hydroboration protocol with different alkynes (Table 2). We initially tested phenylacetylene derivatives with *ortho*-, *meta*-, and *para*-substituents with different steric and electronic properties, including halogen, trifluoromethyl, ether, ester, amine and alkyl groups (**1a**-**1j**). In all the cases, moderate to excellent yields were obtained (53-91%) under the optimized hydroboration conditions and complete regio- and stereoselectivity was observed, to obtain exclusively the corresponding (*E*)-alkenyl boronates. Electron-withdrawing substituents in the aromatic ring generally increased the yield of the reaction, unlike electron-donating substituents, and lower results were obtained for *ortho*-substituted substrates (**1b**,**1c**). 3-Ethynyl thiophene was tested as an heteroaromatic alkyne showing similar results to other electron-rich substituents (**1k**, 70%). Next, we explored the reactivity of 1-ethynylcyclohex-1-ene. Notably, the chemoselective hydroboration of the alkyne group with no trace of

reaction on the alkene group was observed, with (*E*)-alkenyl boronate **1l** being the only product detected by NMR in the reaction mixture.

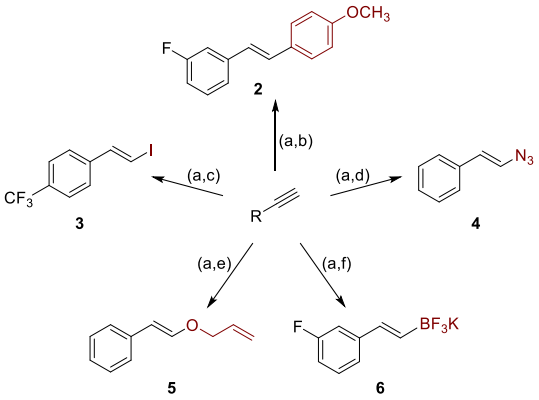
In addition to aryl rings and alkenyl substituents, aliphatic chains including 2-phenylethyl (**1m**), butyl (**1n**), and cyclopropyl (**1o**) also showed excellent reactivity under the same reaction conditions. In these alkyl derivatives, the regioselectivity was not complete (β:α ≥ 85:15), but good yields of the (*E*)-alkene β-products could be isolated (69-73%). Finally, with the bis-alkyne 1,3-diethynylbenzene, the corresponding diboronate product was obtained in moderate yield (**1p**, 47%). An internal alkyne, such as prop-1-yn-1-ylbenzene, did not react under these reaction conditions.

Table 2. Substrate scope of the hydroboration reaction of terminal alkynes.[a]



[a] Yield of isolated compounds **1a**-**1p**. Reaction conditions: alkyne (4.5 mmol), pinacolborane (9 mmol), microwave irradiation, 215 ºC, 18 min. 18 mmol of pinacolborane were used to get **1p**.

The synthesized alkenyl boronates are versatile intermediates for the transformation of the C-B bond into a variety of new C-C or C-heteroatom bonds.[6] The versatility of our optimized alkyne hydroboration protocol was demonstrated by performing several stereoselective transformations over unpurified (*E*)-alkenyl boronates, in a sequential manner (Scheme 2). Thus, a stilbene derivative could be obtained *via* sequential hydroboration/Suzuki-Miyaura cross-coupling in good yield (**2**, 63%, two steps). In a similar fashion, the boronate group could be exchanged by different heteroatoms (iodine, nitrogen or oxygen) after the hydroboration process, successfully getting the corresponding vinyl iodide (**3**, 65%, two steps), vinyl azide (**4**, 52%, two steps) and vinyl ether (**5**, 33%, two steps). All these products are valuable alkenes employed on different organic transformations. Finally, the trifluoroborate salt was obtained *via* sequential hydroboration/treatment with KHF_2 (62%, two steps), without the need of further purification by column chromatography.



Scheme 2. Sequential hydroboration-boronate transformation reactions. Reaction conditions: (a) alkyne (4.5 mmol, 1 equiv), pinacolborane (2 equiv), microwave irradiation, 215 ºC, 18 min. (b) $Pd(OAc)_2$ (0.05 equiv), tBu$_3$PHBF$_4$ (0.1 equiv), K_2CO_3 (1.2 equiv), 1-bromo-4-methoxybenzene (1.2 equiv), DMF, inert atmosphere, 90 ºC, 18 h, 63%. (c) NaOH (3 equiv), I_2 (2 equiv), THF, 25 ºC, 2 h, 65%. (d) NaN_3 (1.5 equiv), $CuSO_4$ (0.6 equiv), MeOH, 25 ºC, 16 h, 52%. (e) $Cu(OAc)_2$ (2 equiv), NEt_3 (4 equiv), allyl alcohol (8 mL), 25 ºC, 16 h, 33% (f) KHF_2 (5 equiv) MeOH/H_2O, 25 ºC, 24 h, 62%.

Conclusion

In conclusion, we have described a simple, efficient and rapid protocol for the solvent-free microwave-assisted *anti*-Markovnicov hydroboration of terminal alkynes, in a chemo-, regio-, and stereoselective process. The reaction proceeds in good to excellent yields without any additives or solvents. Several organic transformations can be performed sequentially to the hydroboration reaction in good overall yields, to get vinyl iodine, azide, ether, cross-coupled products or trifluoroborate salts without purification of the alkenyl boronates.

Experimental Section

General Experimental Procedures: All commercially available compounds were used as received unless stated otherwise. Pinacolborane was purified by distillation before use it and keeped under inert atmosphere. Microwave reactions were carried out using a Biotage Initiator 2.5 microwave synthesizer operating at 0−400 W irradiation power, at a normal absorption level and controlling the reaction temperature by an external IR sensor. Reaction times refer to hold times at the temperatures indicated, not to total irradiation times. Analytical thin layer chromatography was carried out using TLC-aluminium sheets with 0.2 mm of silica gel (Merck 60 F254) and UV light as visualizing agent or phosphomolybdic acid solution as developing agent. Chromatography purifications were carried out using silica gel (40-63 µm, 60 Å). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. NMR spectra were recorded at 298 K using either a Varian Mercury VX-300, Varian Unity 300, or Varian Unity 500 MHz spectrometer. Chemical shift values for ^{1}H and ^{13}C are reported as δ values (ppm) relative to the deuterated solvent ($CDCl_3$: 7.26 ppm, 77.16 ppm; CD_3CN: 1.94 ppm, 1.32 ppm) and coupling constants (*J*) in Hz. All melting points were determined in open capillary tubes using a Stuart Scientific SMP3 melting point apparatus. High-resolution analysis (HRMS) was performed using an Agilent 6210.

General procedure A. The corresponding alkyne (4.5 mmol) and pinacolborane (9 mmol) were mixed in a microwave vial and heated at 215 ºC for 18 minutes by microwave irradiation. The crude was purified by flash column chromatography (hexane/AcOEt) to obtain the (E)- alkenylboronate. **General procedure B**. The corresponding alkyne (3 mmol), pinacolborane (9 mmol) and decane (0.5 mL) were mixed in a microwave vial and heated at 215 ºC for 25 minutes by microwave irradiation. The crude was purified by flash column chromatography (hexane/AcOEt) to obtain the (*E*)-alkenylboronate.

Characterization data 1a-1p, 2-6.

(*E*)-4,4,5,5-Tetramethyl-2-styryl-1,3,2-dioxoborolane (1a). Prepared from phenylacetylene (0.49 mL, 4.5 mmol) and pinacolborane (1.31 mL, 9 mmol) following the general procedure A and purified by flash chromatography (hexane/EtOAc, 95/5). Yellow oil (818 mg, 79%). By using general procedure B, 587 mg (85%) were obtained. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H), 7.40 (d, *J* = 18.7 Hz, 1H), 7.36 – 7.28 (m, 3H), 6.17 (d, *J* = 18.4 Hz, 1H), 1.32 (s, 12H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 149.5, 137.4, 128.9, 128.5, 127.0, 116.4 (bs), 83.3, 24.8 ppm; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 30.2 ppm. NMR data were in accordance with those previously reported. [12b]

***(E)*-2-(2-Fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (1b).** Prepared from 1-ethynyl-2-fluorobenzene (0.51 mL, 4.5 mmol) and pinacolborane (1.31 mL, 9 mmol) following the general procedure A and purified by flash chromatography (hexane/EtOAc, 94/6). Yellow oil (783 mg, 70%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 18.7 Hz, 1H), 7.59 – 7.50 (m, 1H), 7.29 – 7.18 (m, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.05 – 6.97 (m, 1H), 6.25 (d, *J* = 18.6 Hz, 1H), 1.30 (s, 12H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.6 (d, *J* = 251.1 Hz), 141.2 (d, *J* = 3.9 Hz), 130.2 (d, *J* = 8.5 Hz), 127.4 (d, *J* = 3.2 Hz), 125.3 (d, *J* = 11.6 Hz), 124.1 (d, *J* = 3.5 Hz), 119.3 (bs), 115.8 (d, *J* = 22.0 Hz), 83.5, 24.9 ppm; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -107.7 ppm; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 30.0 ppm. NMR data were in accordance with those previously reported. [24a]

(*E*)-4,4,5,5-Tetramethyl-2-(2-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (1c). Prepared from 1-ethynyl-2-(trifluoromethyl)benzene (0.55 mL, 4 mmol) and pinacolborane (1.31 mL, 9 mmol) following the general procedure A and purified by flash chromatography (hexane/EtOAc, 95/5). Yellow oil (631 mg, 53%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.82 – 7.67 (m, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 6.16 (d, *J* = 18.1 Hz, 1H), 1.31 (s, 12H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.8, 137.0, 132.0, 128.3, 127.8 (q, *J* = 30.3 Hz), 127.5, 124.4 (q, *J* = 274.0 Hz) 125.7 (q, *J* = 5.6 Hz), 121.9 (bs), 83.6, 24.8 ppm; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -53.3 ppm; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 30.1 ppm. NMR data were in accordance with those previously reported. [24a]

***(E)*-2-(3-Fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (1d).** Prepared from 1-ethynyl-3-fluorobenzene (0.52 mL, 4.5 mmol) and pinacolborane (1.31 mL, 9 mmol) following the general procedure A and purified by flash chromatography (hexane/EtOAc, 95/5). Yellow oil (932 mg, 83%). By using general procedure B, 609 mg (82%) were obtained. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 18.4 Hz, 1H), 7.28 – 7.17 (m, 2H), 7.17 – 7.10 (m, 1H), 6.98 – 6.88 (m, 1H), 6.14 (d, *J* = 18.4 Hz, 1H), 1.27 (s, 12H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 163.1 (d, *J* = 245.9 Hz), 148.04 (d, J = 2.4 Hz), 139.90 (d, J = 7.4 Hz), 130.03 (d, J = 8.6 Hz), 123.00 (d, J = 2.4 Hz), 118.3 (bs), 115.7 (d, J = 21.3 Hz), 113.3 (d, J = 21.4 Hz), 83.4, 24.8 ppm; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -107.7 ppm; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 30.1 ppm. NMR data were in accordance with those previously reported. [24a]

(*E*)-3-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxoborolan-2-yl)vinyl)phenyl acetate (1e). Prepared from 3-ethynylphenyl acetate (721 mg, 4.5 mmol) and pinacolborane (1.31 mL, 9 mmol) following the general procedure A and purified by flash chromatography (hexane/EtOAc, 95/5). Yellow oil (923 mg, 71%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 18.3 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.21 – 7.16 (m, 1H), 7.05 – 6.98 (m, 1H), 6.15 (d, *J* = 18.4 Hz, 1H), 2.28 (s, 3H), 1.29 (s, 12H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.3, 150.9, 148.3, 139.2, 129.5, 124.6, 121.9, 119.8, 83.4, 24.8, 21.1 ppm (C-B signal not observed due to low intensity); **^{11}B NMR** (160 MHz, $CDCl_3$) δ 29.9 ppm; **HRMS-ESI** m/z calcd for $C_{16}H_{22}BO_4$ $[M+H]^+$ 289.1609, found 289.1605.

(*E*)-4,4,5,5-Tetramethyl-2-(4-methylstyryl)-1,3,2-dioxoborolane (1f). Prepared from 1-ethynyl-4-methylbenzene (0.57 mL, 4.5 mmol) and pinacolborane (1.31 mL, 9 mmol) following the general procedure A and purified by flash chromatography (hexane/EtOAc, 95/5). Yellow oil (792 mg, 72%). By using general procedure B, 556 mg (76%) were obtained. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.38 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.11 (d, *J* = 18.5 Hz, 1H), 2.34 (s, 3H), 1.31 (s, 12H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 149.6, 139.0, 134.9, 129.4, 127.1, 115.3 (bs), 83.3, 24.9, 21.4 ppm; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 30.3 ppm. NMR data were in accordance with those previously reported.[12b]

(*E*)-2-(4-Chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (1g). Prepared from 1-ethynyl-4-chlorobenzene (615 mg, 4.5 mmol) and pinacolborane (1.31 mL, 9 mmol) following the general procedure A and purified by flash chromatography (hexane/EtOAc, 95/5). Yellow oil (837 mg, 70%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 18.5 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.13 (d, *J* = 18.4 Hz,

1H), 1.31 (s, 12H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 147.9, 135.9, 134.6, 128.8, 128.2, 117.3 (bs), 83.5, 25.0 ppm; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 30.0 ppm. NMR data were in accordance with those previously reported. [24a]

(*E*)-2-(4-Methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (1h). Prepared from 1-ethynyl-4-methoxybenzene (0.58 mL, 4.5 mmol) and pinacolborane (1.31 mL, 9 mmol) following the general procedure A and purified by flash chromatography (hexane/EtOAc, 95/5). Yellow oil (822 mg, 70%). By using general procedure B, 549 mg (70%) were obtained. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.35 (d, *J* = 18.4 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.01 (d, *J* = 18.4 Hz, 1H), 3.79 (s, 3H), 1.30 (s, 12H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.2, 149.0, 130.4, 128.4, 114.3, 114.0 (bs), 83.2, 55.3, 25.0 ppm; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 30.2 ppm. NMR data were in accordance with those previously reported.[12b]

(*E*)-*N,N*-Dimethyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxoborolan-2-yl)vinyl)aniline (1i). Prepared from 1-ethynyl-*N,N*-dimethylaniline (0.65 mL, 4.5 mmol) and pinacolborane (1.31 mL, 9 mmol) following the general procedure A and purified by flash chromatography (hexane/EtOAc, 95/5). Off-white solid (759 mg, 62%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 18.4 Hz, 1H), 6.67 (d, *J* = 8.8 Hz, 2H), 5.92 (d, J=18.5 Hz, 1H), 2.98 (s, 6H), 1.31 (s, 12H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.0, 149.9, 128.4, 126.0, 112.0, 83.1, 40.3, 24.9 ppm (C-B signal not observed due to low intensity) ; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 30.4 ppm; **m.p.** 92-93ºC. NMR data were in accordance with those previously reported. [24b]

(*E*)-4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxoborolane (1j). Prepared from 1-ethynyl-4-(trifluoromethyl)benzene (0.74 mL, 4.5 mmol) and pinacolborane (1.31 mL, 9 mmol) following the general procedure A and purified by flash chromatography (hexane/EtOAc, 95/5). Yellow oil (1.22 g, 91%). By using general procedure B, 821 mg (92%) were obtained. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.57 (s, 4H), 7.41 (d, *J* = 18.4 Hz, 1H), 6.27 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 147.8, 140.9, 130.6 (q, *J* = 32.6 Hz), 127.3, 125.6 (q, *J* = 3.6 Hz), 124.2 (q, *J* = 271.9 Hz), 119.8 (bs), 83.7, 24.9 ppm; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -57.0 ppm; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 30.0 ppm. NMR data were in accordance with those previously reported. [12b]

(*E*)-4,4,5,5-Tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxoborolane (1k). Prepared from 3-ethynylthiophene (0.48 mL, 4.5 mmol) and pinacolborane (1.31 mL, 9 mmol) following the general procedure A and purified by flash chromatography (hexane/EtOAc, 95/5). Brown oil (737 mg, 70%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.38 (d, *J* = 18.4 Hz, 1H), 7.32 – 7.25 (m, 3H), 5.94 (d, *J* = 18.4 Hz, 1H), 1.30 (s, 12H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.3, 141.3, 126.2, 125.1, 125.0, 116.2 (bs), 83.4, 24.9 ppm; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 30.2 ppm. NMR data were in accordance with those previously reported. [12b]

(*E*)-2-(2-(Cyclohex-1-en-1-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (1l). Prepared from 1-ethynylcyclohex-1-ene (0.53 mL, 4.5 mmol) and pinacolborane (1.31 mL, 9 mmol) following the general procedure A and purified by flash chromatography (hexane/EtOAc, 95/5). Yellow oil (825 mg, 79%). By using general procedure B, 417 mg (60%) were obtained. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.02 (d, *J* = 18.3 Hz, 1H), 5.97-5.95 (m, 1H), 5.42 (d, *J* = 18.2 Hz, 1H), 2.14 (m, 4H), 1.69-1.55 (m, 4H), 1.27 (s, 12H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 153.3, 137.1, 134.2, 111.9 (bs), 83.0, 26.2, 24.8, 23.8, 22.4, 22.4 ppm; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 30.1 ppm. NMR data were in accordance with those previously reported.[12c]

(*E*)- 4,4,5,5-Tetramethyl-2-(4-phenylbut-1-en-1-yl)-1,3,2-dioxoborolane (1m). Prepared from but-3-yn-1-ylbenzene (0.63 mL, 4.5 mmol) and pinacolborane (1.31 mL, 9 mmol) following the general procedure A and purified by flash chromatography (hexane/EtOAc, 95/5). Colorless liquid (848 mg, 73%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.21 – 7.17 (m, 3H), 6.71 (dt, *J* = 18.0, 6.2 Hz, 1H), 5.50 (dt, *J* = 18.0, 1.6 Hz, 1H), 2.76-2.72 (m, 2H), 2.53 – 2.43 (m, 2H), 1.27 (s, 12H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.9, 141.3, 128.1, 125.6, 119.1 (bs), 82.7, 37.4, 34.5, 24.8 ppm; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 29.8 ppm. NMR data were in accordance with those previously reported. [24c]

(*E*)-2-(Hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (1n). Prepared from hex-1-yne (0.55 mL, 4.5 mmol) and pinacolborane (1.31 mL, 9 mmol) following the general procedure A and purified by flash chromatography (hexane/EtOAc, 95/5). Yellow oil (803 mg, 71%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.63 (dt, *J* = 18.0, 6.4 Hz, 1H), 5.42 (dt, *J* = 18.0, 1.5 Hz, 1H), 2.15 (td, *J* = 8.0, 1.5 Hz, 2H), 1.44 – 1.28 (m, 4H), 1.26 (s, 12H), 0.88 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 154.5, 118.8 (bs), 82.9, 35.6, 30.5, 24.9,

22.4, 14.0 ppm; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 29.7 ppm. NMR data were in accordance with those previously reported. [12b]

(*E*)-2-(2-Cyclopropylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (1o). Prepared from ethynylcyclopropane (0.41 mL, 4.5 mmol) and pinacolborane (1.31 mL, 9 mmol) following the general procedure A and purified by flash chromatography (hexane/EtOAc, 95/5). Colorless oil (599 mg, 69%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.88 (dd, *J* = 17.8, 9.1 Hz, 1H), 5.28 (d, *J* = 17.7 Hz, 1H), 1.39 – 1.24 (m, 1H), 1.06 (s, 12H), 0.69 – 0.54 (m, 2H), 0.38 – 0.27 (m, 2H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.2, 115.1 (bs), 82.7, 24.9, 17.0, 7.9 ppm; **^{11}B NMR** (160 MHz, $CDCl_3$) δ 29.6 ppm. NMR data were in accordance with those previously reported. [24a]

1,3-Bis((*E*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxoborolan-2-yl)vinyl)benzene (1p). Prepared from 1,3-diethynylbenzene (0.6 mL, 4.5 mmol) and pinacolborane (2.66 mL, 18 mmol) following the general procedure A and purified by flash chromatography (hexane/EtOAc, 95/5). Pale yellow solid (810 mg, 47%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.42 (d, *J* = 7.7 Hz, 2H), 7.37 (d, *J* = 18.4 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 6.16 (d, *J* = 18.4 Hz, 2H), 1.30 (s, 24H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.3, 137.9, 129.0, 127.5, 126.3, 83.5, 25.0 ppm (C-B signal not observed due to low intensity); **^{11}B NMR** (160 MHz, $CDCl_3$) δ 30.0 ppm; **m.p.** 140-141 ºC. NMR data were in accordance with those previously reported. [24d]

(*E*)-1-Fluoro-3-(4-methoxystyryl)benzene (2). After hydroboration of 1-ethynyl-3-fluorobenzene (0.52 mL, 4.5 mmol) following the general procedure A, the crude was dissolved in deoxygenated DMF (15 mL) under inert conditions, and $Pd(OAc)_2$ (50.5 mg, 0.23 mmol), *t*Bu_3PHBF_4 (156 mg, 0.45 mmol) and K_2CO_3 (746 mg, 5.4 mmol) were added, stirring at rt for 10 minutes. 1-Bromo-4-methoxybenzene (678 µL, 5.4 mmol) was then added and the flask was heated at 90 °C for 18 hours. The reaction was then cooled to rt and the organic phase was extracted with EtOAc and washed with water and brine. Then it was dried over Na_2SO_4 and concentrated under vacuum. The crude was purified by flash chromatography (hexane/EtOAc, 95/5). White solid (648 mg, 63%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.7 Hz, 2H), 7.33 – 7.17 (m, 3H), 7.07 (d, *J* = 16.3 Hz, 1H), 6.97 – 6.88 (m, 4H), 3.84 (s, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 163.4 (d, *J* = 244.9 Hz), 159.7, 140.2 (d, *J* = 7.8 Hz), 130.2 (d, *J* = 8.5 Hz), 129.8, 129.7, 128.1, 125.5 (d, *J* = 2.6 Hz), 122.3, 114.3, 114.1 (d, *J* = 21.5 Hz), 112.6 (d, *J* = 21.7 Hz), 55.5 ppm; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -108.0 ppm; **m.p.** 106-108 ºC. NMR data were in accordance with those previously reported. [24e]

(*E*)-1-(2-Iodovinyl)-4-(trifluoromethyl)benzene (3). After hydroboration of 1-ethynyl-4-(trifluoromethyl)benzene (0.74 mL, 4.5 mmol) following the general procedure A, the crude was dissolved in THF (45 mL), and an aqueous 3.0 M solution of NaOH (4.5 mL,13.5 mmol) was added, stirring at room temperature for 10 minutes. I_2 (2,28 g, 9 mmol) was added and the reaction continued stirring for 2 hours. The organic solution was diluted in Et_2O and washed with a saturated solution of $Na_2S_2O_3$ and brine. The organic phase was dried over Na_2SO_4 and concentrated under vacuum. The crude was purified by flash chromatography (hexane/EtOAc, 98/2). Pale yellow solid (875 mg, 65%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 15.0 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 15.0 Hz, 1H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ ppm. 143.8, 140.9, 130.2 (q, *J* = 32.4 Hz), 126.3, 125.9 (q, *J* = 3.5 Hz), 124.1 (d, J = 267.1 Hz), 80.1 ppm; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -57.0 ppm; **m.p.** 40-41 ºC. NMR data were in accordance with those previously reported.[24f]

(*E*)-(2-Azidovinyl)benzene (4). After hydroboration of phenylacetylene (0.49 mL, 4.5 mmol) following the general procedure A, the crude was dissolved in MeOH (18 mL), sodium azide (439 mg, 6.75 mmol) and $CuSO_4$ (431 mg, 2.7 mmol) were added and the reaction was stirred overnight. The crude was purified by flash chromatography (hexane/ EtOAc, 95/5). Yellow oil (338 mg, 52 %). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.44 – 7.21 (m, 5H), 6.64 (d, *J* = 13.8 Hz, 1H), 6.33 (d, *J* = 13.8 Hz, 1H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 135.0, 128.7, 127.3, 126.6, 125.8, 119.7 ppm. NMR data were in accordance with those previously reported.[6b]

(*E*)-(2-(Allyloxy)vinyl)benzene (5). After hydroboration of phenylacetylene (0.49 mL, 4.5 mmol) following the general procedure A, the crude was dissolved in prop-2-en-1-ol (8 mL) and triethylamine (2.51 mL, 18 mmol) and $CuSO_4$ (1.63 g, 9 mmol) were added and the reaction was stirred overnight. The reaction was diluted in Et_2O and washed with water and brine. The organic phase was dried over Na_2SO_4 and concentrated under vacuum. The crude was purified by flash chromatography (hexane). Pale yellow oil (238 mg, 33%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43 – 7.30 (m, 4H), 7.29 – 7.20 (m, 1H), 7.10 (d, *J* = 12.9 Hz, 1H), 6.18 – 6.05 (m, 1H), 6.02 (d, *J* = 12.9 Hz, 1H), 5.55 – 5.44 (m, 1H), 5.43 – 5.32 (m, 1H), 4.50 – 4.39 (m, 2H)

ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 147.4, 136.3, 133.2, 128.5, 125.7, 125.1, 117.7, 106.6, 70.8 ppm. NMR data were in accordance with those previously reported.[6c]

(*E*)-Trifluoro(3-fluorostyryl)borate, potassium salt (6). After hydroboration of 1-ethynyl-3-fluorobenzene (0.52 mL, 4.5 mmol) following the general procedure A, the crude was dissolved in MeOH (8 mL), KHF_2 (1.76 g, 22.5 mmol in 5 mL of water) was added dropwise and the reaction was stirred at room temperature for 24 hours. After the evaporation of the solvent under vacuum, the residual pinacol was removed by adding two portions of MeOH:H_2O (8:2) (5 mL) and further concentrating via rotary evaporator. The solid obtained was triturated with acetone and filtered through a plug of Celite. The acetone solution was evaporated to yield a solid that is washed with CH_2Cl_2 (2 x 5 mL). The solid was dissolved in CH_3CN (8 mL), filtrated and evaporated to yield 598 mg (62%) of an off-white solid. **^{1}H NMR** (500 MHz, CD_3CN) δ 7.29 (dd, *J* = 14.1, 7.9 Hz, 1H), 7.19 (dd, *J* = 23.4, 9.4 Hz, 2H), 6.89 (t, *J* = 8.5 Hz, 1H), 6.63 (d, *J* = 18.2 Hz, 1H), 6.35 (d, *J* = 18.2 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, CD_3CN) δ 164.1 (d, *J* = 242.0 Hz), 143.9 (d, *J* = 7.4 Hz), 137.1 (bs), 135.5 – 134.9 (m), 130.9 (d, *J* = 8.6 Hz), 123.0 (d, *J* = 2.4 Hz), 113.8 (d, *J* = 21.6 Hz), 112.8 (d, *J* = 21.3 Hz) ppm; **^{19}F NMR** (282 MHz, CD_3CN) δ -57.1 ppm; **^{11}B NMR** (160 MHz, CD_3CN) δ 2.5 ppm; **m.p.** 102-103 ºC; **HRMS-ESI** m/z calcd for $C_8H_6BF_4$ $[M-K]^-$ 189.0506, found 189.0582.

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Keywords: alkynes • hydroboration • microwaves • alkenyl boronates • solvent-free

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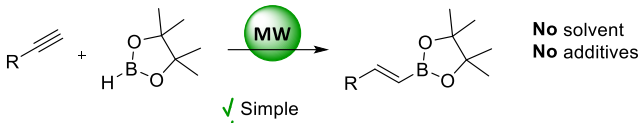
Alkyne hydroboration



√ Simple
√ Efficient (47-91%)
√ Rapid (18 min.)
√ Sequential transformations in the C-B bond

A general method for solvent-free hydroboration of alkynes has been developed by microwave irradiation, to get (*E*)-alkenyl boronates. Several functionalizations in the C-B bond can be performed sequentially without the purification of the intermediates.

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