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Suzuki−Miyaura Cross-Coupling Reactions of Potassium Alkenyltrifluoroborates

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We have previously reported that the palladium-catalyzed cross-coupling reaction of air-stable potassium alkenyltrifluoroborates with aryl halides and triflates proceeds readily with good yields. Recent progress in outlining the scope and limitations of such reactions is described herein. The palladium-catalyzed cross-coupling reaction of potassium alkenyltrifluoroborates with aryl and heteroaryl halides and triflates proceeds readily with moderate to excellent yields. The alkenyl cross-coupling reaction can generally be effected using 2 mol % of $PdCl_2(dppf)\cdot CH_2Cl_2$ as catalyst in *i*-PrOH−H_2O in the presence of *t*-$BuNH_2$ as the base. A variety of functional groups are tolerated in both partners, and the process is stereospecific with regard to the alkenyltrifluoroborate starting material.

Introduction

Transition-metal-mediated cross-coupling reactions have revolutionized organic synthesis. Many highly efficient and mild protocols for bond construction have emerged by the mastery of such reactions. Perhaps the most utilized carbon−carbon bond-forming cross-coupling reactions are those that use tin (Stille coupling)[1] and boron derivatives (Suzuki−Miyaura coupling)[2] because of their tolerance of a broad range of functional groups. The Suzuki−Miyaura cross-coupling is particularly valued because boron compounds present many advantages in relation to other organometallic compounds, including ease of accessibility and ultimate product isolation, minimal toxicity, and other environmental factors.

Diverse organoboron components have been utilized effectively for Suzuki−Miyaura coupling reactions. For example, alkenyldialkylboranes are generally efficient partners,[3] but these compounds possess a relatively high molecular weight, and thus a large amount of waste is produced that must be separated from the cross-coupled products and disposed. Boronic acids and boronic esters are also widely used in Suzuki−Miyaura cross-coupling reactions. There are several potential problems with these derivatives as well. Boronic acids are sometimes difficult to purify because they form cyclic trimers with loss of water to generate boroxines. Because the boronic acids are difficult to distinguish between a mixture of the boroxines and water, the determination of precise stoichiometry can be difficult. Boronic esters or diethanolamine adducts are often utilized as a means to purify these organoboron species, but some of these esters are hydrolytically stable and/or difficult to handle. Furthermore, the diols utilized to create these derivatives (e.g., catechol, pinacol, or the diethanolamine) add considerable expense to the overall process and, additionally, must be separated from the desired product. A lack of atom economy also exists for the boronic esters in coupling processes, wherein again the diols comprising these reagents must be separated from the final product and disposed.

There are also considerable problems specific to alkenyl boronic acids and esters in Suzuki−Miyaura coupling. For example, vinylboronic acid is readily polymerized and cannot be isolated.[4] Furthermore, vinylboronic esters are not selective in the cross-coupling reactions, yielding mixtures of Suzuki−Miyaura and Heck coupled products.[5] Finally, superstoichiometric amounts of toxic thallium bases must often be used for efficient coupling of alkenylboronic acids.[6]

Many of the recent development efforts on the cross-coupling reaction have focused on catalyst systems that

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(1) (a) Stille, J, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508−524. (b) Farina, V.; Krishnamurthy, V.; Scott, W. J. *Org. React.* **1997**, *50*, 1−652.

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(4) (a) Matteson, D. S. *J. Am. Chem. Soc.* **1960**, *82*, 4228−4233. Although one procedure has been developed to avoid this, it appears rather cumbersome to implement: (b) Kerins, F.; O'Shea, D. F. *J. Org. Chem.* **2002**, *67*, 4968−4971.

(5) (a) Hunt, A. R.; Stewart, S. K.; Whiting, A. *Tetrahedron Lett.* **1993**, *34*, 3599−3602. (b) Stewart, S. K.; Whiting, A. *J. Organomet. Chem.* **1994**, *482*, 293−300.

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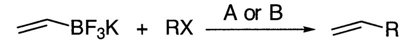
facilitate the cross-coupling and expand its scope.[3d,g,h] Fewer endeavors have concentrated on expanding the range of the organoboron coupling partner. With regard to the use of alternative organoboron derivatives, it has been revealed that potassium organotrifluoroborates offer solutions to the problems that occur through the use of other organoboron partners. These materials are readily prepared by the addition of inexpensive KHF_2 to a variety of organoboron intermediates.[7] The trifluoroborates are monomeric, crystalline solids that are readily isolated and indefinitely stable in the air.[7a,8] Despite their advantages, in comparison to other organoboron species organotrifluoroborates have seen minimal use in palladium-catalyzed cross-coupling reactions.[8−14]

Preliminary results of Suzuki−Miyaura cross-coupling reactions between alkenyl trifluoroborates and aryl halides and triflates have been previously reported by our research group.[15] In that study, the coupled products were obtained in good yields using $PdCl_2(dppf){\cdot}CH_2Cl_2$ as catalyst, in THF/water or *n*-PrOH, using Cs_2CO_3 or Et_3N as base (eq 1).



R= Alkenyl or Aryl

X= Halide or Triflate (1)

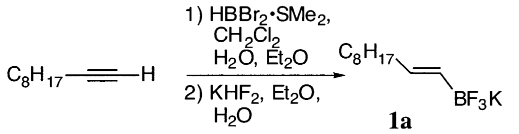
A= $PdCl_2$ (dppf)$\cdot CH_2Cl_2$ (2%), Et_3N, *n*-PrOH

B= $PdCl_2$(dppf)$\cdot CH_2Cl_2$ (9%), Cs_2CO_3, THF-H_2O

Herein we provide a full account of our exploration of these reactions, including the coupling of a variety of alkenyltrifluoroborates with functionalized aryl halides or triflates and with heteroaryl halides.

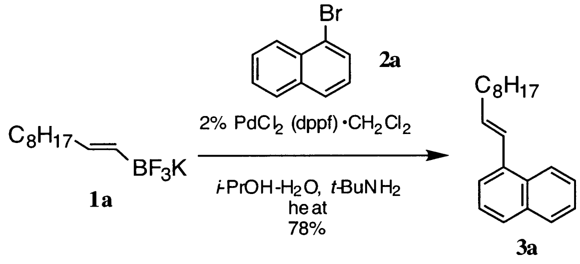
Results and Discussion

We initially focused our attention on the use of potassium *trans*-1-dec-1-enyl trifluoroborate (**1a**) in the cross-coupling reaction. This salt was prepared from 1-decyne (eq 2) using known procedures. Hydroboration with $HBBr_2{\cdot}SMe_2$[16] followed by treatment of the resulting dibromoborane with KHF_2 in the presence of water afforded **1a** in 71% yield for the two-step, one-pot process.



(2)

The cross-coupling of **1a** was optimized by using 1-bromonaphthalene (**2a**) as the electrophile, $PdCl_2(dppf){\cdot}CH_2Cl_2$ or $PdCl_2$ as catalyst, a variety of different bases (e.g., Et_3N, Hunig's base, *t*-$BuNH_2$, K_2CO_3, Cs_2CO_3), and different solvent systems (MeOH, EtOH, *n*-PrOH, *i*-PrOH, THF, DME, dioxane) under both anhydrous and aqueous conditions. Among the solvents examined, the mixture of *i*-PrOH−H_2O (2:1) provided the best results. In this mixture, not all of the aryl halides and triflates were completely soluble, but over time the reaction mixtures turned more homogeneous. In the presence of 2 mol % of $PdCl_2(dppf){\cdot}CH_2Cl_2$ and 3 equiv of *t*-$BuNH_2$ this solvent system proved to be the best (eq 3), furnishing *trans*-1-decen-1-yl-naphthalene **3a** in 78% yield. Because the reaction demonstrated sensitivity to oxygen, it was necessary to degas the solvent, base, and the reagents before the reaction was performed.



(3)

The use of Et_3N as base and the use of anhydrous *n*-PrOH also provided good results. Curiously, *n*-PrOH−H_2O mixtures did not provide the product in as satisfactory yields as the *i*-PrOH−H_2O mixture. Between these two options, we decided to use *i*-PrOH−H_2O, considering it is less expensive and the most environmentally sound among the other successful combinations tested.

The optimized conditions were subsequently applied to the coupling reaction of **1a** with different aryl halides and -triflates. As outlined in Table 1, the reaction proceeded with satisfactory yields in most cases. The reaction was tolerant of a variety of functional groups including ethers, ketones, nitriles and nitro groups despite the aqueous, basic conditions. Moreover, electrophiles bearing both electron-withdrawing and electron-donating groups react with the trifluoroborates, affording the desired products in good yields.

ortho-Substituted substrates (entries 4 and 8) react to provide the coupling products in satisfactory yields. Even in the case of the highly hindered 2-bromomesitylene (entry 10), a 38% yield of the desired product was obtained.

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(7) (a) Vedejs, E.; Chapman, R. W.; Fields, S. C.; Lin, S.; Schrimpf, M. R. *J. Org. Chem.* **1995**, *60*, 3020−3027. (b) Vedejs, E.; Fields, S. C.; Hayashi, R.; Hitchock, S. R. Powell, D. R.; Schrimpf, M. R. *J. Am. Chem. Soc.* **1999**, *121*, 2460−2470.

(8) Coupling of organotrifluoroborates with arenediazonium salts: (a) Darses, S.; Michaud, G.; Genêt, J.-P. *Eur. J. Org. Chem.* **1999**, 1875−1883. (b) Darses, S.; Michaud, G.; Genêt, J.-P. *Tetrahedron Lett.* **1998**, *39*, 5045−5084. (c) Darses, S.; Michaud, G.; Genêt, J.-P.; Brayer, J.-L.; Demounte J. P. *Tetrahedron Lett.* **1997**, *38*, 4393−4396.

(9) Coupling of organotrifluoroborates with diaryliodonium salts: Xia, M.; Chen, Z. C. *Synth. Commun.* **1999**, *29*, 2457−2465.

(10) Coupling of vinyltrifluoroborate with halopyrimidines: Puentener, K.; Scalone, M. Eur. Pat. Appl. EP 1,057,831 A2, 2000.

(11) Use of tetraalkylammonium trifluoroborates in cross-coupling reactions: Batey, R. A.; Quach, T. D. *Tetrahedron Lett.* **2001**, *42*, 9099−9103.

(12) Cross-coupling of alkyltrifluoroborates: Molander, G. A.; Ito, T. *Org. Lett.* **2001**, *3*, 393−396.

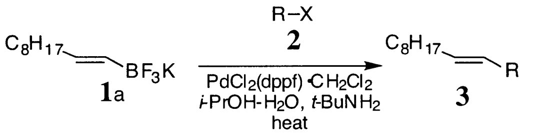
(13) Cross-coupling of aryltrifluoroborates: Molander, G. A.; Biolatto, B. *Org. Lett.* **2002**, *4*, 1867−1870.

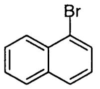
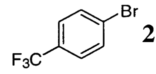
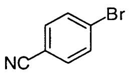
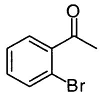
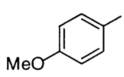
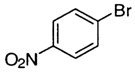
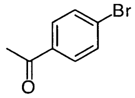
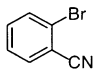
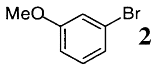
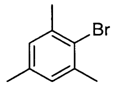
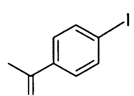
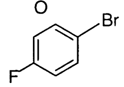
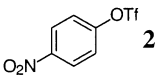
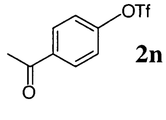
(14) Cross-coupling of alkynyltrifluoroborates: Molander, G. A.; Machrouhi, F.; Katona, B. *J. Org. Chem.*, **2002**, *67*, 8416−8423.

(15) Molander, G. A.; Rodriguez Rivero, M. *Org. Lett.* **2002**, *4*, 107−109.

(16) Brown, H. C.; Bhat, N. G.; Somayaji, V. *Organometallics* **1983**, *2*, 1311−1316.

TABLE 1. Cross-Coupling of Aryl Halides and Triflates with Potassium *trans*-1-Dec-1-enyl Trifluoroborate 1a



entry	RX		time (h)	coupling product	% isolated yield
1		**2a**	10	**3a**	78
2		**2b**	10	**3b**	65
3		**2c**	6	**3c**	87
4		**2d**	14	**3d**	63
5		**2e**	6	**3e**	60
6		**2f**	2	**3f**	71
7		**2g**	6	**3g**	69
8		**2h**	6	**3h**	75
9		**2i**	6	**3i**	61
10		**2j**	14	**3j**	38[a]
11		**2k**	2	**3g**	65
12		**2l**	14	**3l**	59[a]
13		**2m**	3	**3f**	76
14		**2n**	8	**3g**	60

[a] Using Et_3N as base.

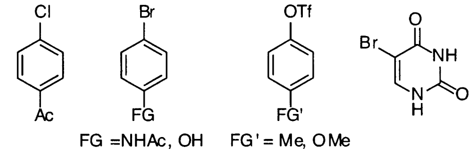


FIGURE 1. Unsuccessful coupling partners.

It was necessary to use 4-iodoanisole as a partner in order to achieve high yields of product for coupling of the 4-methoxybenzene moiety (entry 5). The use of the corresponding triflate or bromide resulted in a complex mixture of products, as the initial cross-coupled products appear to be oligomerized over the long reaction times. Rigorous kinetic studies have not been carried out, but the order of reactivity of the electrophiles appears to be I > Br ≥ OTf (cf. entries 7, 11, and 14).

Although the method for cross-coupling proved reasonably general, little or no coupling occurred with several coupling partners (Figure 1). These included aryl chlorides and some electron-rich aryl bromides and triflates, as well as 5-bromouracil.

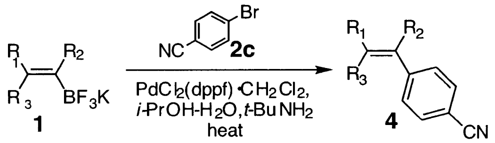
Having demonstrated that **1a** can be an efficient alkenylating agent of aryl halides and triflates, we investigated the scope of the coupling reaction using more substituted potassium alkenyltrifluoroborates (Table 2). Some of these organotrifluoroborates (**1a**, **1e**, and **1f**) were obtained by hydroboration of the alkyne with dibromoborane,[16] followed by reaction with KHF_2 as shown in eq 2. Organotrifluoroborate salts **1d** and **1g** were obtained from the corresponding commercially available boronic acids. Isopropenyl trifluoroborate (**1b**) was obtained by treatment of 2-bromopropene with *t*-BuLi, followed by addition of trimethylborate and in situ aqueous KHF_2.[15] Vinyl trifluoroborate **1c** was obtained from vinylmagnesium bromide by a similar procedure.[15]

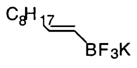
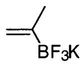
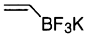
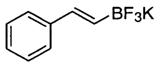
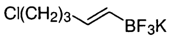
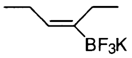
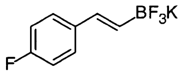
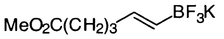
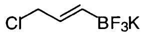
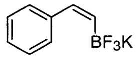
In most cases, the cross-coupling reaction of these trifluoroborates with 4-bromobenzonitrile (**2c**) proceeded with good yields. Potassium *tran*-styryl trifluoroborate (**1d**) and the *cis* isomer (**1j**) were easily converted stereospecifically to the corresponding stilbenes. The influence of α-substituted organoboron partners (entries 2 and 6) was investigated, and satisfactory yields were obtained. Alkenyltrifluoroborates with halide substitution within the organic moiety were also evaluated. For entries 5 and 7, the cross-coupling proceeded with good yields. However, the use of allylic chloride **1i** did not afford the desired product, perhaps as a result of competitive π-allylpalladium formation.

The presence of an ester group (entry 8) did not impede the cross-coupling reaction. However, the yield of product obtained was much lower in this case. The prolonged reaction time, combined with the basic reaction conditions, probably conspired to promote hydrolysis of the ester.

Continuing with our investigation, we explored the reaction of potassium alkenyl trifluoroborates with heteroaryl halides. A single example of this reaction was already reported by our research group, wherein potassium *trans*-styryl trifluoroborate **1d** reacted with 2-bromopyridine (**5f**), resulting in the cross-coupled product in good yield.[15] In the present study a variety of diverse heteroaryl halides were reacted with **1d** as outlined in Table 3. Utilizing the same conditions used in the aryl halide and aryl triflate cross-coupling [*i*-PrOH−H_2O, 2 mol % of $PdCl_2(dppf)\cdot CH_2Cl_2$, *t*-$BuNH_2$], good yields were obtained in most cases. In some cases, Et_3N provided better results than *t*-$BuNH_2$. For example, the use of

TABLE 2. Cross-Coupling of 4-Bromobenzonitrile 2c with Different Potassium Alkenyltrifluoroborates



entry	substrate	time (h)	coupling product	(%) isolated yield
1	 **1a**	6	**3c**	87
2	 **1b**	5	**4b**	70
3	 **1c**	6	**4c**	76[a]
4	 **1d**	6	**4d**	80
5	 **1e**	6	**4e**	52
6	 **1f**	7	**4f**	70
7	 **1g**	6	**4g**	73
8	 **1h**	14	**4h**	33
9	 **1i**	24	**4i**	0
10	 **1j**	6	**4j**	86

[a] Using Et_3N as base.

t-$BuNH_2$ resulted in the conversion of **5a** into **6a** in 47% yield. The same substrate afforded **6a** in 83% yield using Et_3N as base. On the other hand, 3-bromopyridine **5i** (entry 9) was converted to **6i** in 31% yield when Et_3N was employed as the base. The same reaction was realized in 57% yield upon changing the amine to *t*-$BuNH_2$.

The use of Et_3N proved to be advantageous for the couplings with heteroaryl chloride partners (entries 10–13). When *t*-$BuNH_2$ was used in these cases, complex mixtures of products were obtained, resulting in a decrease in yield and making it difficult to isolate the coupling products by chromatography.

Interesting selectivity was observed for entries 10–12. The reaction of 1 equiv of **1d** in the presence of 2 mol % $PdCl_2(dppf)\cdot CH_2Cl_2$ and 3 equiv of base yielded the monosubstituted product **6j** in 55% yield, along with the formation of some disubstituted product. By using 3.5 equiv of **1d**, 2 mol % $PdCl_2(dppf)\cdot CH_2Cl_2$, and 6 equiv of base, 72% yield of **6j′** was obtained. For the trichlorotriazine **5k** (entry 12) it was not possible to obtain the monosubstituted product, even when 1 equiv of potassium styryltrifluoroborate and 3 equiv of base were used. This implies equal reactivity of the chlorides on the aromatic ring even as each is successively replaced by an alkene. The trisubstituted product **6k** was readily obtained by using 3.5 equiv of styryl trifluoroborate and 6 equiv of base.

The use of triflate **5g** (entry 7) provided the desired product **6f** in lower yield over a longer reaction time as compared to the analogous bromide (entry 6). Presumably, the long reaction time and basic conditions led to competitive hydrolysis of the triflate.

A key question remains as to whether the trifluoroborates remain intact during the coupling or whether they react with the alcohol or water during the course of the reaction, forming boronic acids or esters that subsequently couple. Protic solvents clearly facilitate many of the trifluoroborate coupling reactions,[11,12] and as determined by NMR studies, one or more hydroxy or alkoxy groups can be found attached to the boron of the tetracoordinate species that undergoes the transmetalation step.[13,17] Despite these investigations, the exact nature of the reactive species generated has not been well elucidated. It will be necessary to perform in depth mechanistic studies to resolve this issue.

Conclusion

In summary, palladium-catalyzed cross-coupling reactions of potassium alkenyltrifluoroborates with aryl and heteroaryl halides and triflates have been achieved with good yields. A variety of functional groups were tolerated in the coupling reactions, and even the *o,o*-disubstituted aryl halide partners and α-substituted organoboron partners provided the desired cross-coupling products. The organoboron derivatives can be prepared by different routes, including transmetalation and noncatalyzed hydroboration. The organotrifluoroborates thus generated are monomeric solids that possess several advantages over the corresponding boronic acids and esters. The ease of isolation, purification, storage, and handling makes them highly attractive intermediates for laboratory scale and industrial processes and especially useful for combinatorial chemistry. Although some of the simpler, *trans*-disubstituted products generated by cross-coupling

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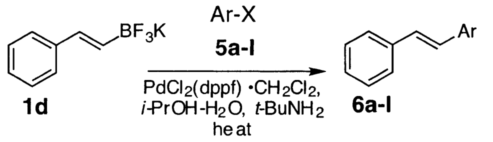
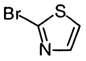
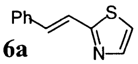
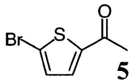
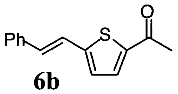
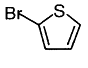
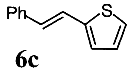
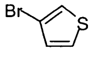
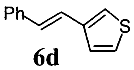
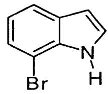
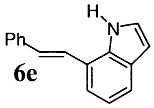
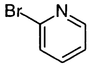
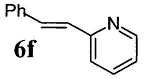
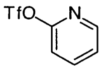
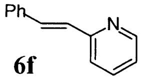
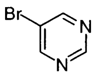
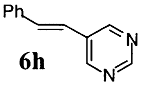
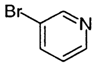
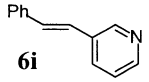
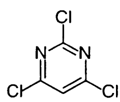
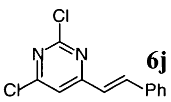
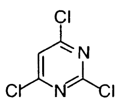
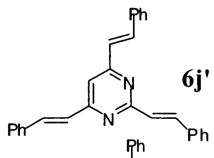
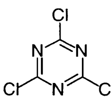
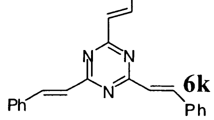
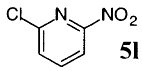
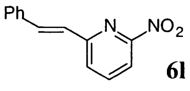
(17) Matos, K.; Soderquist, J. A. *J. Org. Chem.* **1998**, *63*, 461–470.

TABLE 3. Cross Coupling of Heteroaryl Halides with Potassium *trans*-Styryl Trifluoroborate



entry	substrate	time (h)	coupled product	isolated yield (%)
1	 **5a**	3	**6a** 	83[a]
2	 **5b**	3	 **6b**	91
3	 **5c**	3	 **6c**	69
4	 **5d**	5	 **6d**	80
5	 **5e**	9	 **6e**	70
6	 **5f**	4	 **6f**	70
7	 **5g**	18	 **6f**	41
8	 **5h**	6	 **6h**	73
9	 **5i**	4	 **6i**	57
10[b]	 **5j**	5	 **6j**	55[a]
11[c]	 **5j**	7	 **6j'**	72[a]
12	 **5k**	8	 **6k**	64[a]
13	 **5l**	18	 **6l**	51[a]

[a] Et_3N used as base. [b] Using 1 equiv of trifluoroborate. [c] Using 3.5 equiv of trifluoroborate.

might be prepared more efficiently by Heck-type reactions, the current method is obviously advantageous when *cis*-disubstituted or more highly substituted, stereodefined alkene products are required.

Experimental Section

General. All of the experiments were carried out under a nitrogen atmosphere. ^1H, ^{13}C, and ^{19}F NMR spectra were measured on spectrometers at 500.13, 125.77, and 470.53 MHz, respectively. ^{19}F NMR chemical shifts were referenced to external $CFCl_3$ (0.0 ppm). All ^{11}B chemical shifts were referenced to external $BF_3{\cdot}OEt_2$ (0.0 ppm) with a negative sign indicating an upfield shift.

The triflates, halides, and palladium catalyst were obtained from commercial sources. t-$BuNH_2$ was distilled from calcium hydride, and Et_3N was distilled from calcium hydroxide. The i-$PrOH/H_2O$ mixture was degassed using nitrogen.

General Preparation of Potassium Alkenyl Trifluoroborates. Preparation of Potassium *trans*-1-Dec-1-enyl Trifluoroborate (1a). Literature procedures for the hydroboration of 1-decyne with dibromoborane and subsequent hydrolysis to the corresponding boronic acid were employed to synthesize *trans*-1-dec-1-enyl dibromoborane.[16] To a solution of 1-decyne (5 mmol, 0.69 g) in CH_2Cl_2 (2.5 mL) at 0 °C was added $Br_2BH{\cdot}SMe_2$ (1 M in CH_2Cl_2, 5 mmol, 5 mL). The mixture was stirred at room temperature for 4 h. Subsequently, the light green solution was added by a double-ended needle to a mixture of diethyl ether/water (5 mL of diethyl ether and 2 mL of water) at 0 °C. The mixture was stirred at room temperature for 15 min. The aqueous layer was separated, and the organic phase was washed with cold water and then brine. The organic phase was subsequently dried with magnesium sulfate. The solvents were evaporated to provide *trans*-1-dec-1-enyl boronic acid as a white solid in 89% yield.

To a solution of the *trans*-1-dec-1-enyl boronic acid thus prepared (1.83 g, 10 mmol) in diethyl ether (20 mL) was added KHF_2 (2.18 g, 28 mmol), followed by water (9 mL) during 30 min. (This reaction can be carried out in normal glassware, although the glassware will become etched. Very simple Nalgene beakers or wide-mouthed bottles can also be employed). After stirring at room temperature for 3 h, the solution was concentrated, and the crude material was dissolved in acetone, filtered, and concentrated. The resulting white solid was purified by dissolving in hot acetone and precipitating with Et_2O, resulting in a white solid (2.04 g, 8.30 mmol, 83%): mp > 260 °C; ^1H NMR (500 MHz, DMSO-d_6) δ 5.44 (dt, $J = 17.5$, 6.2 Hz, 1H), 5.16−5.21 (m, 1H), 1.85 (t, $J = 6.0$ Hz, 2H), 1.19−1.27 (m, 12H), 0.85 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 133.49, 133.45, 35.37, 31.31, 29.25, 29.03, 28.81, 28.74, 22.09, 13.94; ^{19}F NMR (471 MHz, DMSO-d_6) δ −137.68 Hz; ^{11}B NMR (64.2 MHz, DMSO-d_6) δ 3.55. Anal. Calcd for $C_{10}H_{19}BF_3K$: C, 48.79; H, 7.78. Found: C, 48.63; H, 7.62. IR (neat): 1636, 922 cm^{-1}.

Representative Procedure for Cross-Coupling Reaction of Potassium Alkenyltrifluoroborates. Preparation of *trans*-1-Dec-1-enyl-naphthalene (3a). A solution of potassium *trans*-1-dec-1-enyl trifluoroborate (**1a**) (123.4 mg, 0.5 mmol), $PdCl_2(dppf){\cdot}CH_2Cl_2$ (8.1 mg, 0.01 mmol), 1-bromonaphthalene (**2a**) (103.5 mg, 0.5 mmol), and t-$BuNH_2$ (109.7 mg, 1.5 mmol) in i-$PrOH-H_2O$ (2:1, 5 mL) was heated at reflux under a nitrogen atmosphere. The reaction mixture was stirred at reflux for 10 h, then cooled to room temperature, and diluted with water (10 mL), followed by extraction of diethyl ether. The organic layers were combined and washed with 1 N HCl and brine, dried over $MgSO_4$, and then filtered. The solvent was removed under vacuum, and the crude product was purified by silica gel chromatography (eluting with hexane/ethyl acetate) to afford a colorless oil (103.7 mg, 78%): ^1H NMR (500 MHz, $CDCl_3$) δ 8.12 (dd, $J = 8.0$, 1.0 Hz, 1H), 7.83 (dd, $J = 8.5$, 1.7 Hz, 1H), 7.73 (d, $J = 8.1$ Hz, 1H), 7.55 (d, $J = 7.1$ Hz, 1H), 7.40−7.51 (m, 3H), 7.10 (d, $J = 15.5$ Hz, 1H), 6.23

(dd, $J = 15.5$, 6.9 Hz, 1H), 2.33 (m, 2H), 1.25−1.41 (m, 13 H), 0.89 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 135.79, 134.58, 133.60, 131.12, 128.42, 127.14, 126.83, 125.72, 125.64, 125.58, 123.96, 123.46, 33.45, 31.90, 29.50, 29.41, 29.31, 29.26, 22.68, 14.11; HRMS (CI) *m*/*z* calcd for $C_{20}H_{26}$ 266.2034, found 266.2043; IR (neat) 1502, 1377 cm^{-1}.

***trans*-4-Dec-1-enyl-nitrobenzene (3f).** This product was obtained by the general method from *trans*-1-dec-1-enyl trifluoroborate (**1a**) and 4-nitrophenyl bromide (**2f**) (71% yield), and also from 4-nitrophenyl trifluoromethylsulfonate (**2m**) by the following procedure: To a solution of potassium *trans*-1-dec-1-enyl trifluoroborate (**1a**) (123.4 mg, 0.5 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (8.1 mg, 0.01 mmol), and 4-nitrophenyl trifluoromethylsulfonate (135.6 mg, 0.5 mmol) in *i*-PrOH−H_2O (2:1, 5 mL) was added *t*-$BuNH_2$ (109.7 mg, 1.5 mmol). The reaction mixture was stirred under argon at reflux for 3 h, then cooled to room temperature and diluted with water, followed by extraction with diethyl ether. The organic layers were combined and washed with 1 N HCl and brine, dried over $MgSO_4$, and then filtered. The solvent was removed under vacuum, and the crude product was purified by silica gel chromatography (eluting with hexane/ethyl acetate) to afford a yellow oil (99 mg, 76% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, $J = 8.8$ Hz, 2H), 7.44 (d, $J = 8.8$ Hz, 2H), 6.43−6.44 (m, 2H), 2.25 (m, 2H), 1.49 (m, 2H), 1.27−1.34 (m, 10H), 0.88 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 146.36, 144.44, 128.03, 126.27 (2C), 123.92 (2C), 33.20, 31.83, 29.41, 29.22, 28.96, 22.63, 14.07; HRMS (CI) *m*/*z* calcd for $C_{16}H_{21}NO_2$ 261.1723, found 261.1720; IR (neat) 1596, 1514, 1341 cm^{-1}.

***trans*-1-(β-Phenylvinyl)thiazole (6a).**[18] This compound was obtained from potassium styryltrifluoroborate (**1d**) and 2-bromothiazole (**5a**) by the general procedure. After extraction, the ethereal solution was washed with 1 N $NaHCO_3$ and brine, filtered, and then dried over $MgSO_4$ to afford the title product in 47% when *t*-$BuNH_2$ was used as base, and 83% yield using Et_3N as base. The spectral data obtained were in accordance with those described in the literature. Mp 57−58 °C (lit.[18] 57−59 °C).

Acknowledgment. We thank Johnson & Johnson, Aldrich Chemical Co., Merck Research Laboratories, Array Biopharma, and Johnson Matthey for their generous suport. C.R.B. thanks the Fundação Coordenação de Aperfeiçoamento de Pessoal de Nivel Superior -CAPES (Brazil) for a doctoral fellowship.

Supporting Information Available: Full experimental details, copies of all NMR spectra (^{1}H, ^{13}C, ^{19}F, and ^{11}B). This material is available free of charge via the Internet at http://pubs.acs.org.

JO026236Y

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[18] Dondoni, A.; Fantin, G.; Fogagnolo, M.; Medici, A.; Pedrini, P. *Tetrahedron* **1988**, *44*, 2021−2031.