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Preparation of Trifluorostyrenes via Palladium-Catalyzed Coupling of Aryl Boronic Acids with Chloro- and Bromo-Trifluoroethylene

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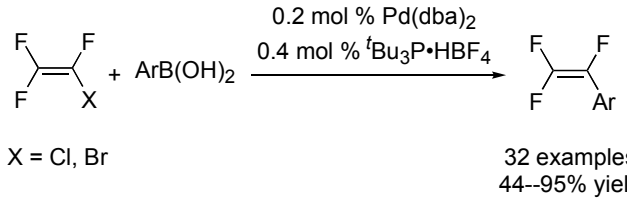


Abstract. A high efficient and cost-effective method for the preparation of α,β,β-trifluorostyrene (TFS) and its derivatives is described. The method required only 0.2 mol % of $Pd(dba)_2$ and 0.4 mol % of P^tBu_3 and occurred to full conversion within 2.0 h. With this method, a wide range of aryl boronic acids were efficiently incorporated to generate α,β,β-trifluorostyrene derivatives.

Introduction

α,β,β-Trifluorostyrene (TFS) and its derivatives are a type of interesting monomers for fluorinated polymers,[1-2] mainly due to its unique structure that combines a trifluorovinyl group and a benzene ring. The polymers contain a perfluorinated main chain often exhibit high thermal, chemical stability and more importantly, high solubility that allows the polymers more processible. The presence of the benzene ring ensures the possibility of introducing a variety of functional groups. For example, copolymers of trifluorostyrene and substituted trifluorostyrene developed by Stone and coworkers at Ballard have been used as membrane electrolytes in proton exchange membrane fuel cell (PEMFC), a leading candidate to replace the aging alkaline fuel cell.[3] Thus, development of efficient methods for the preparation of α,β,β-trifluorostyrene in good yields and high purity have become the subject of special interest.[4]

Most of the early methods for the syntheses of TFS derivatives typically required multisteps and suffered from low overall yields.[5,6] A more direct method was reported in 1980s[7] through the Pd-catalyzed cross-coupling of trifluorovinyl zinc or tin reagent with aryl halides. More recently, a stable trifluorovinyl borate was developed to replace the zinc or tin reagent, thus provide a more convenient route for the preparation of TFS derivatives.[8] These trifluorovinyl reagents were synthesized from easily available chlorotrifluoroethylene or 1,1,1,2-tetrafluorethane (HFC-134a) with butyl lithium through halogen exchanging or deprotonation. Direct coupling of tetrafluoroethylene with diphenylzinc reagent was also reported by Ogoshi recently.[9] While these methods are quite effective for the preparation of TFS and its derivatives, we envisioned that if a direct cross-coupling of chloro- or bromo-trifluoroethene with aryl boronic acids can be realized, a more efficient and straightforward strategy could be developed for the preparation of TFS and its derivatives (Scheme 1). In this context, in 2010, we reported in a patent for the first time that $Pd(PPh_3)_4$ were able to couple chlorotrifluoroehtylene with a variety of aryl boronic acids in good yields, albeit with 5.0 mol% catalyst loading.[10] In 2012, Yamamoto and Yamakawa reported that when 1-3 mol% of $Pd(dppf)Cl_2$ was used as the catalyst, various of functionalized aryl boronic acids were coupled with chlorotrifluoroethylene to give the corresponding trifluorostyrene derivatives in good to excellent yields.[11] Herein, we report that the same transformation can be realized when a combination of $Pd(dba)_2$ with P^tBu_3 was used. Most importantly, the reactions require only 0.2 mol% of the palladium catalyst and tolerates a variety of functional groups. In addition, under slightly modified conditions, the coupling of bromotrifluoroethylene with aryl boronic acids also occurred to good to excellent yields.[12]

Scheme 1. Strategies for the preparation of α,β,β-trifluorostyrene

Previous work

$CF_3COCl \rightleftharpoons PhCFClCF_3 \xrightarrow[EtOH]{Zn} PhCF=CF_2$ ref. 5 (1)

$CF_2=CF_2 \xrightarrow[Et_2O,\ -78\ ^oC]{PhLi} PhCF=CF_2 + PhCF=CFPh$ ref. 6 (2)

$\begin{matrix} CF_2=CFX \\ or \\ CF_3CH_2F \end{matrix} \longrightarrow CF_2=CFM \xrightarrow[[Pd]]{ArY} ArCF=CF_2$ ref. 7-8 (3)

X = H, Cl, Br, or I; M = ZnR, SnR'_3 or $B(OMe)_3K$

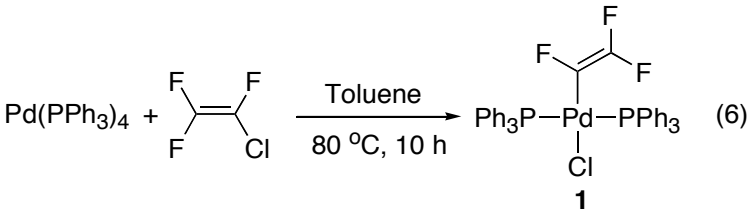
$CF_2=CF_2 + Ph_2Zn \xrightarrow[LiI]{[Pd]} PhCF=CF_2$ ref. 9 (4)

This work

$CF_2=CFX + ArB(OH)_2 \xrightarrow{[Pd]} ArCF=CF_2$ (5)

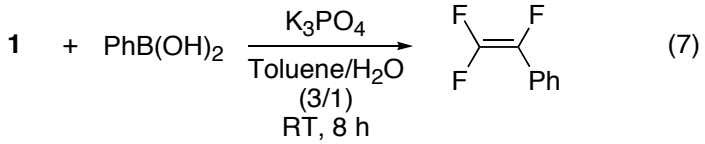
Results and Discussion

We began our investigation by isolation of the [$LPd(CF=CF_2)(Cl)$] species and testing its stoichiometric reaction with aryl boronic acid in the presence of base under various conditions. Heating of a mixture of [$Pd(PPh_3)_4$] with excess chlorotrifluoroethylene in toluene in a screw-caped Schlenk tube at 80 ^oC for 10 h generated the [*trans*-$(PPh_3)_2Pd(CF=CF_2)(Cl)$] **1** in 60% yield (Eq. 6), while no formation of oxidative-addition product **1** was observed when the reaction was conducted at room temperature.



(6)

1



(7)

Complex **1** was characterized by ^1H, ^{13}C, ^{19}F, ^{31}P NMR spectroscopies and element analysis. Structure of complex [(*trans*)-$Pd(PPh_3)_2(CF=CF_2)(Cl)$] **1** was further confirmed by single crystal X-ray diffraction (see the supporting information of details).[13] Interestingly, Stone reported that while

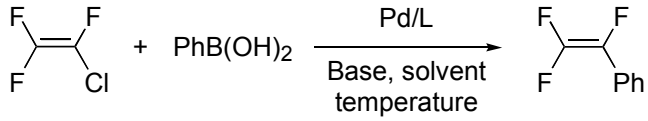
$[(PPh_3)_2PdCl_2]$ was formed when $[Pd(PPh_3)_4]$ was reacted with chlorotrifluoroethylene in acetone, reaction of $[Pd(PPh_2Me)_4]$ with chlorotrifluoroethylene did generate [(*trans*)-$Pd(PPh_2Me)_2(CF=CF_2)(Cl)$] in high yield in benzene.[14] Treatment of Complex **1** with one equivalent of phenyl boronic acid in toluene /water (3/1) using K_3PO_4 as the base at room temperature for 8 h afforded the corresponding α,β,β-trifluorostyrene in 74% yield (Eq 7). These results clearly indicated that oxidative-addition of chlorotrifluoroethylene to Pd(0) species was much slower than those of transmetalation and reductive-elimination steps. Thus, if a suitable ligand can be identified to facilitate the oxidative-addition of chlorotrifluoroethylene to Pd(0) species, the efficient Pd-catalyzed cross-coupling of chlorotrifluoroethylene and aryl boronic acids might be accomplished under mild conditions.

Guided by these stoichiometric investigations, we first examined various supporting ligands, especially those known to accelerate the oxidative-addition step for the model reaction between chlorotrifluoroethylene and phenyl boronic acid. After careful investigation, we discovered that reaction of chlorotrifluoroethylene and phenyl boronic acid in the presence of a combination of 0.2 mol% $Pd_2(dba)_3$ and 0.4 mol% P^tBu_3[15,16] occurred to 51% yield after 8 h at 80 ^oC using K_3PO_4 as the base and a mixture of toluene and water (3:1, v/v) as the solvent. Reaction using $Pd(OAc)_2$ or $Pd(PPh_3)_2Cl_2$ as the catalyst precursor occurred in much lower yields. When K_2CO_3, Na_2CO_3 or Na_3PO_4 was used as the base, yields dropped slightly to 35-38%, while the yield of the reaction decreased significantly to less than 5% when CsF was used as the base. Reactions in dioxane/H_2O (3/1) or benzene/H_2O (3/1) occurred to 34% yield. Interestingly, when a mixture of DMF/H_2O (3/1) was used as the solvent, the yield increased dramatically to over 95%. However, this optimized reaction conditions were not general. When other aryl boronic acid such as 4-biphenyl boronic acid was used, only 38 % of the desired product was observed.

We then chose the reaction 4-biphenyl boronic acid with chlorotrifluoroethylene to further optimize the reaction conditions, as summarized in Table 2. It was discovered that when a mixture of DMF/toluene/water was used as the solvent, the desired product was generated in 95% yield. The

reaction was much faster in these mixed solvent than those in DMF/H_2O. Typically, the reaction occurred to complete conversion after 2 h. Using of $^tBu_3P$ as the reaction was critical for the reaction. Bidentate ligands with a rigid backbone such as DPPF or BINAP were ineffective at all under these conditions (Table 2, entries 8 and 9). Reactions using triphenylphosphine as the ligand occurred to give the desired product in moderate 29% yield (Table 2, entry 10). Other monodentated electron-rich alkyl phosphines such as PCy_3 or $BuP(Ad)_2$ were less efficient (Table 2, entries 11 and 12). *N*-heterocyclic carbene (IPr), which have been used in a variety of cross-coupling reactions, was again ineffective (Table 2, entry 13). The dialkylbiaryl phosphine ligands developed by Buchwald and coworkers[17] were known to accelerate the oxidative addition of aryl halides to Pd(0). Surprisingly, (^{t}Bu)DavePhos, JohnPhos and SPhos were ineffective while reaction using (Cy)JohnPhos as the ligand occurred to 65% yield (Table 2, entries 14-17).

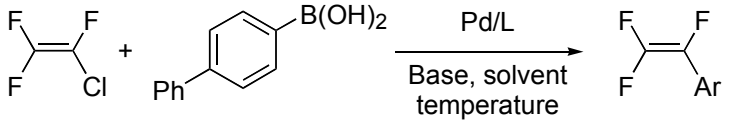
Table 1. Optimization for Pd-catalyzed coupling of chlorotrifluoro-ethylene with aryl boronic acid.[a]



entry	Pd source	ligand	solvent	base	temp. (^oC)	time (h)	yield (%)[b]
1	$Pd_2(dba)_3$	tBu_3P	tol/H_2O [c]	K_3PO_4	80	8	29
2	$Pd_2(dba)_3$	tBu_3P	tol/H_2O	K_3PO_4	80	8	51
3	$Pd_2(dba)_3$	tBu_3P	tol/H_2O [d]	K_3PO_4	80	8	2
4	$Pd(OAc)_2$	tBu_3P	tol/H_2O	K_3PO_4	80	8	16
5	$Pd(PPh_3)_2Cl_2$	tBu_3P	tol/H_2O	K_3PO_4	80	8	13
6	$Pd(dba)_2$	tBu_3P	tol/H_2O	K_2CO_3	80	8	35
7	$Pd(dba)_2$	tBu_3P	tol/H_2O	Na_2CO_3	80	8	36
8	$Pd(dba)_2$	tBu_3P	tol/H_2O	Na_3PO_4	80	8	38
9	$Pd(dba)_2$	tBu_3P	tol/H_2O	CsF	80	8	<5
10	$Pd(dba)_2$	tBu_3P	dioxane/H_2O	K_3PO_4	80	8	34
11	$Pd(dba)_2$	tBu_3P	PhH/H_2O	K_3PO_4	80	8	34
12	$Pd(dba)_2$	tBu_3P	DMF/H_2O	K_3PO_4	80	8	>95

[a]Reaction conditions: aryl boronic (1.0 mmol), excess chlorotrifluoroethylene, palladium precursor (0.2 mol %), ligand (0.4 mol %), base (3.0 mmol) in 5.4 mL of mixed solvent (solvent/H_2O is 3:1). [b]The yield was determined by ^{19}F NMR spectroscopy with fluorobezene as an internal standard. [c]The ratio of solvent/H_2O is 5:1; [d]The ratio of solvent/H_2O is 1:1.

Table 2. Optimization for Pd-catalyzed coupling of chlorotrifluoro-ethylene with aryl boronic acid.[a]



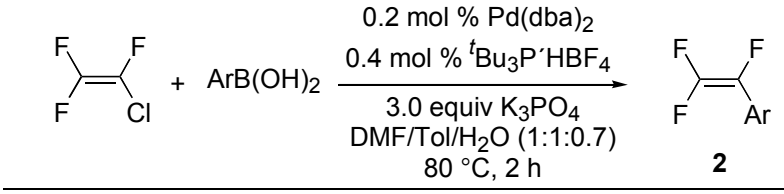
entry	Pd source	ligand	solvent	base	temp. (°C)	time (h)	yield (%)[b]
1	$Pd(dba)_2$	tBu_3P	DMF/tol/H_2O	K_3PO_4	80	8	>95
2	$Pd(dba)_2$	tBu_3P	DMF/tol/H_2O	K_3PO_4	80	6	>95
3	$Pd(dba)_2$	tBu_3P	DMF/tol/H_2O	K_3PO_4	80	4	90
4	**$Pd(dba)_2$**	**tBu_3P**	**DMF/tol/H_2O**	**K_3PO_4**	**80**	**2**	**>95**
5	$Pd(dba)_2$	tBu_3P	DMF/tol/H_2O	K_3PO_4	60	2	50
6	$Pd(dba)_2$	tBu_3P	DMF/tol/H_2O	K_3PO_4	40	2	7
7	$Pd(dba)_2$	tBu_3P	DMF/tol/H_2O	K_3PO_4	RT	2	4
8	$Pd(dba)_2$	dppf	DMF/tol/H_2O	K_3PO_4	80	2	<5
9	$Pd(dba)_2$	BINAP	DMF/tol/H_2O	K_3PO_4	80	2	<5
10	$Pd(dba)_2$	PPh_3	DMF/tol/H_2O	K_3PO_4	80	2	29
11	$Pd(dba)_2$	PCy_3	DMF/tol/H_2O	K_3PO_4	80	2	<5
12	$Pd(dba)_2$	$BuPAd_2$	DMF/tol/H_2O	K_3PO_4	80	2	70
13	$Pd(dba)_2$	IPr(NHC)	DMF/tol/H_2O	K_3PO_4	80	2	5
14	$Pd(dba)_2$	CyJohnPhos	DMF/tol/H_2O	K_3PO_4	80	2	65
15	$Pd(dba)_2$	JohnPhos	DMF/tol/H_2O	K_3PO_4	80	2	<5
16	$Pd(dba)_2$	*t*BuDavePhos	DMF/tol/H_2O	K_3PO_4	80	2	<5
17	$Pd(dba)_2$	SPhos	DMF/tol/H_2O	K_3PO_4	80	2	<5

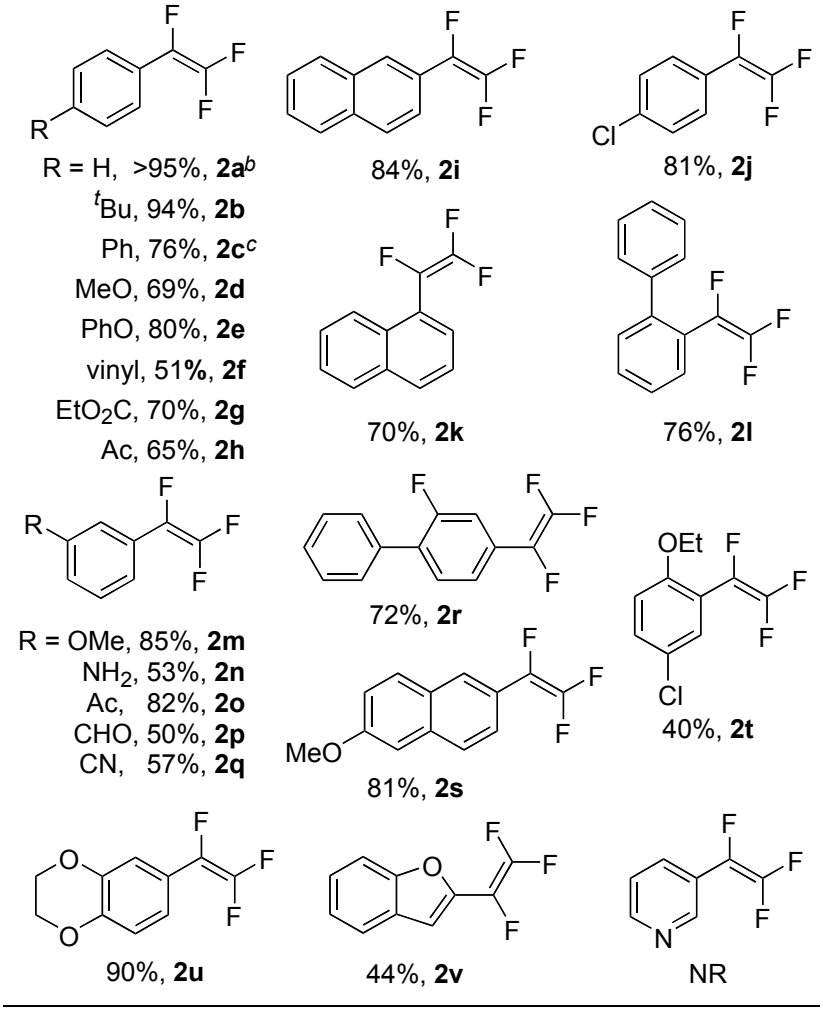
[a]Reaction conditions: aryl boronic (1.0 mmol), excess chlorotrifluoroethylene, palladium precursor (0.2 mol %), ligand (0.4 mol %), base (3.0 mmol) in 5.4 mL of mixed solvent. [b]The yield was determined by ^{19}F NMR spectroscopy with fluorobezene as an internal standard.

The superior reaction efficiencies of the palladium catalyst prompted us to further explore the scope of the reaction, as summarized in Table 3. A wide range of arylboronic acids were readily converted to the corresponding trifluorostyrene derivatives in moderate to excellent yields. Reactions of both electron-rich and electron-poor aryl boronic acids gave the corresponding products in good to excellent yields. It was found that the reaction conditions were compatible with various functional groups. Reactions of arylboronic acids with functional groups such as enolizable ketones, aldehyde, ester, amine, cyano group occurred in good to excellent yields (Table 3, entries **2n**-**q**). Notably, 4-chlorophenylboronic acid also coupled with chlorotrifluoroethylene to give the corresponding in 81% yield (Table 3, entry **2j**), which indicated that C-Cl bond in chlorotrifluoroethylene is more reactive than those in aryl chlorides. The presence of chloride in the products is very useful for further

synthetic manipulations. Reaction of heteroaryl boronic acid such as 3-pyridyl boronic acid, however, didn't generate the corresponding coupled product.

Table 3. Scope of Pd-catalyzed coupling of chlorotrifluoroethylene with low loading.[a]



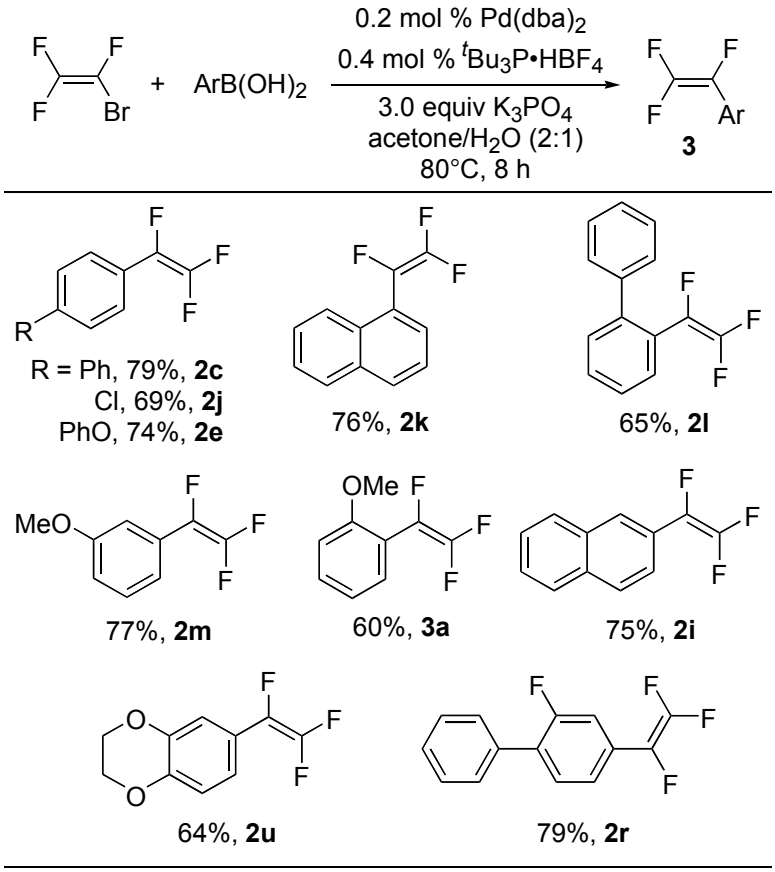


[a]Reaction conditions: aryl boronic (1.0 mmol), excess chlorotrifluoro –ethylene, $Pd(dba)_2$ (0.2 mol %), P^tBu_3•HBF_4 (0.4 mol %), K_3PO_4 (3.0 mmol) in 5.4 mL of toluene/DMF/H_2O (1/1/0.7). [b]The yield was determined by ^{19}F NMR spectroscopy with fluorobezene as an internal standard. [c]The yield was 88% when 4-bipheyl pinacol boronate was used.

Encouraged by the high efficiency and broad scope of the Pd-catalyzed coupling reaction of chlorotrifluoroethylene, we tried to extend this method for the coupling of bromotrifluoroethylene. While catalyst generated from $Pd(dba)_2$/P(o-tol)$_3$, $Pd(dba)_2$/P(tBu$_3$P)$_3$ or $Pd(dba)_2$/Xantphos gave the desired product in good yield for the reaction of bromotrifluoroethylene with 4-biphenyl boronic acid

in mixed DMF/H_2O (3/1), less than 40% conversion was observed for the reaction of bromotrifluoroethylene with 3-cyanophenyl boronic acid under these conditions even with prolong reaction time. After a quick screening of the conditions, it was found that switching the solvent system to 2/1 ratio of acetone/water results in significant improvement for the reactions of bromotrifluoroethylene. The results were summarized in Table 4. A variety of aryl boronic acids were subjected to the catalytic conditions to give the product in moderate to good yield. Generally, unlike other cross-coupling reaction, couplings of bromotrifluoroethylene were much slower and less effective than those of chlorotrifluoroethylene under the current reaction conditions.

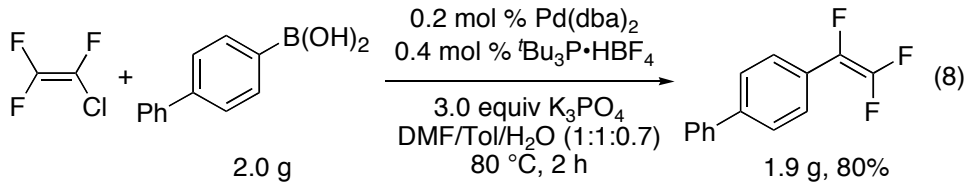
Table 4. Scope of Pd-catalyzed coupling of bromotrifluoroethylene with low loading.[a]



[a]Reaction conditions: aryl boronic (1.0 mmol), excess bromo-trifluoroethylene, $Pd(dba)_2$ (0.2 mol %), P^tBu_3•HBF_4 (0.4 mol %), K_3PO_4 (3.0 mmol) in 3 mL of acetone/H_2O (2/1).

To further demonstrate the synthetic application of our methodology for preparation of α,β,β-Trifluorostyrene (TFS) and its derivatives, we attempted to scale up the reaction of 4-biphenyl boronic

acid (2.0 g) with chlorotrifluoroethylene under the optimized conditions. The reaction occurred smoothly to give the corresponding product in 80% yield (Eq. 8).



Conclusion

In summary, a high efficient and cost-effective method for the preparation of α,β,β-trifluorostyrene (TFS) and its derivatives has been successfully developed.[15-16] The method required only 0.2 mol % of $Pd(dba)_2$ and 0.4 mol % of P^tBu_3 and occurred to full conversion within 2.0 h. With this method, a wide range of aryl boronic acids were efficiently incorporated to generate α,β,β-trifluorostyrene derivatives. The method could also be extended to the coupling of bromotrifluoroethylene with simple change of the solvent. In addition, the reaction can be easily scale up without loss in efficiency. Work is ongoing to scale up the reaction to kilogram and to elucidate the mechanism of the reaction.

Experimental Section

Preparation of *trans*-$Pd(CF=CF_2)(PPh_3)_2Cl$.

A 25 mL Schlenk tube was added tetrakis(triphenyl)phosphine (1.2 g, 1.0 mmol) and toluene (10.0 mL). The Schlenk tube was sealed and then subjected to three freeze-pump-thraw cycles before the addition of chlorotrifluoroethylene (1.2 g, 10 mmol). The autoclave was heated at 80 ^oC for 10 h and then was cooled to room temperature. The solvent was evaporated under reduced pressure and the residue was recrystallized from chloroform to give *trans*-$Pd(CF=CF_2)(PPh_3)_2Cl$ as a orange solid (448 mg, 60% yield).

^1H NMR (300 MHz, $CDCl_3$, 293 K, TMS) δ 7.73-7.68 (m, 12 H), 7.46-7.38 (m, 18 H); ^{13}C NMR (125 MHz，$CDCl_3$，293K, TMS) δ 135.0, 134.5, 130.5, 130.4, 128.2, 128.0; ^{19}F NMR (282.4 MHz, $CDCl_3$, 298 K, TMS) δ -95.87 (ddt, *J* = 102.2, 40.5.0, 7.1 Hz, 1 F), δ -128.21 (m, 1 F), -148.76 (ddt, *J* = 105.6, 40.5, 6.2 Hz, 1 F) ppm; $^{31}P\{^1H\}$ NMR δ18.2 ppm. MS (EI): *m/z* (%) 746 (100).

General Procedure A for preparation of trifluorostyrenes via palladium-catalyzed coupling of CF_2=CFCl.

A 25 mL Schlenk-type sealed tube (with a Teflon high-pressure valve and side arm) equipped with a magnetic stir bar was charged with the aryl boronic acid (1.0 mmol), potassium phosphate (3.0 mmol), $Pd(dba)_2$ (0.2 mmol %), tri-*tert*-butylphosphine tetrafluoroborate (0.4 mmol %). The reaction tube was capped, then evacuated briefly under high vacuum and charged with argon, repeated three times. Then freshly distilled toluene (2.0 mL) and DMF (2.0 mL), deionized water (1.4 mL) was added, and chlorotrifluoroethene was bubbled about 5 min (saturated). Then the valve was screwed. The reaction mixture was stirred at 80 °C for 2 h. Subsequently, the reaction vessel was cooled to room temperature, 10 mL of deionized water and 10 mL of pentane (AR) was added. The organic phase was separated and washed with deionized water three times. The aqueous phase was extracted with pentane (3×10 mL). The organic phase was combined, dried with anhydrous Na_2SO_4 and added silica gel, then evacuated under rotary evaporator, the resulting residue was purified by silica gel flash column chromatography using pentane or pentane and ethyl ether mixed solvent as eluent.

General Procedure B for preparation of trifluorostyrenes via palladium-catalyzed coupling of CF_2=CFBr.

A 25 mL Schlenk-type sealed tube (with a Teflon high-pressure valve and side arm) equipped with a magnetic stir bar was charged with the aryllboronic acid (1.0 mmol), potassium phosphate (3.0 mmol), $Pd(dba)_2$ (0.2 mmol %), tri-*tert*-butylphosphine tetrafluoroborate (0.4 mmol %). The reaction tube was capped, then evacuated briefly under high vacuum and charged with argon, repeated three times. Then freshly distilled acetone (2.0 mL) and deionized water (1.0 mL) was added, and bromotrifluoroethene was bubbled about 1.0 min. Then the valve was screwed. The reaction mixture was stirred at 80 °C for 8 h. Subsequently, the reaction vessel was cooled to room temperature, 10 mL of CH_2Cl_2 was added and filtered through a celite. The CH_2Cl_2 phase was separated and washed with deionized water three times. The aqueous phase was extracted with CH_2Cl_2 (3×5 mL). The CH_2Cl_2 phase was combined, dried with anhydrous Na_2SO_4 and added silica gel, then evacuated under rotary

evaporator, the resulting residue was purified by silica gel flash column chromatography using pentane or pentane and ethyl ether mixed solvent as eluent.

(1,2,2-Trifluorovinyl)benzene 2a.[7d] When the reaction vessel was cooled to room temperature, fluorobenznene (1.0 mol) was added as internal standard. Yield was determined to be >95% by ^{19}F NMR spectroscopy.

1-*tert*-Butyl-4-(1,2,2-trifluorovinyl)benzene 2b.[18] The general procedure A with 4-*tert*-butylphenylboronic acid (180 mg, 1.00 mmol), $Pd(dba)_2$ (1.2 mg) and $^tBu_3PHBF_4$ (1.2 mg) gave 202.0 mg (94%) of 1-*tert*-butyl-4-(1,2,2-trifluorovinyl)benzene as a colorless liquid. ^{1}H NMR (300.0 MHz, $CDCl_3$, 298 K, TMS) δ 7.42 (dd, J = 7.45, 7.40 Hz, 4 H), 1.33 (s, 9 H) ppm; ^{19}F NMR (282.4 MHz, $CDCl_3$, 298 K, TMS) δ -101.20 (dd, J = 73.5, 32.0 Hz, 1 F), δ -116.11 (dd, J = 109.2, 73.4 Hz, 1 F), -177.21 (dd, J = 109.5, 32.2 Hz, 1 F) ppm; ^{13}C NMR (100.5 MHz, $CDCl_3$, 298 K, TMS) 153.8 (ddd, J = 289.9, 282.0, 50.1 Hz), 152.6, 128.8 (ddd, J = 226.3, 45.6, 19.5 Hz), 125.6, 124.5 (d, J = 6.6 Hz), 124.3 (dd, J = 10.5, 6.1 Hz), 34.7, 31.1 ppm.

4-(1,2,2-Trifluorovinyl)biphenyl 2c.[18] The general procedure A with biphenyl-4-ylboronic acid (200 mg, 1.00 mmol), $Pd(dba)_2$ (1.2 mg) and $^tBu_3PHBF_4$ (1.2 mg) gave 177.8 mg (76%) of 4-(1,2,2-trifluorovinyl)biphenyl as a white solid. ^{1}H NMR (300.1 MHz, $CDCl_3$, 298 K, TMS) δ 7.60-7.30 (m, 9 H) ppm; ^{19}F NMR (282.4 MHz, $CDCl_3$, 298 K, TMS) δ -99.47 (dd, J = 70.6, 32.5 Hz, 1 F), -114.32 (dd, J = 109.0, 70.6 Hz, 1 F), -176.87 (dd, J = 109.0, 32.2 Hz, 1 F) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, 299 K, TMS) δ 154.1 (ddd, J = 290.8, 283.0, 49.8 Hz), 141.7, 140.2, 129.0, 128.8 (ddd, J = 225.4, 45.7, 19.7 Hz,), 126.3 (dd, J = 22.3, 6.8 Hz), 127.9, 127.4, 127.1, 124.9 ppm; IR: 3034, 1756, 1605, 1557, 1488, 1450, 1407, 1343, 1293, 1153, 1130, 1115, 1028, 1005, 984, 840, 764, 743, 721, 690 cm^{-1}. MS (EI) m/z(%) 234.2 (100); HRMS (ESI): Calculated for $C_{14}H_9F_3$: 234.0656, Found 234.0659; Mp: 57 – 59℃。

1-Methoxy-4-(1,2,2-trifluorovinyl)benzene (Table 2, 2d).[7d] The general procedure A with 4-methoxyphenylboronic acid (155 mg, 1.00 mmol), $Pd(dba)_2$ (1.2 mg) and $^tBu_3PHBF_4$ (1.2 mg) gave 129.7 mg (69%) of 1-methoxy-4-(1,2,2-trifluorovinyl)benzene as a colorless liquid. ^{1}H NMR (399.6

MHz, $CDCl_3$, 298 K, TMS) δ 7.41 (d, *J* = 8.7 Hz, 2 H), 6.96 (d, *J* = 8.7 Hz, 2 H), 3.84 (s, 3 H) ppm; ^{19}F NMR (376.0 MHz, $CDCl_3$, 298 K, TMS) δ -102.41 (dd, *J* = 77.7, 31.7 Hz, 1 F), -117.40 (dd, *J* = 110.0, 77.7 Hz, 1 F), -175.48 (dd, *J* = 110.3, 31.7 Hz, 1 F) ppm; ^{13}C NMR (100.5 MHz, $CDCl_3$, 298 K, TMS) δ 159.9, 153.4 (ddd, *J* = 288.9, 280.4, 50.6 Hz), 128.6 (ddd, *J* = 226.1, 46.2, 19.7 Hz), 126.1 (dd, *J* = 10.0, 6.0 Hz), 119.6 (dd, *J* = 23.0, 6.4 Hz) 114.1, 55.2 ppm.

1-Phenoxy-4-(1,2,2-trifluorovinyl)benzene 2e. The general procedure A with 4-phenoxyphenylboronic acid (214 mg, 1.00 mmol), $Pd(dba)_2$ (1.2 mg) and $^tBu_3PHBF_4$ (1.2 mg) gave 200.0 mg (80%) of 1-phenoxy-4-(1,2,2-trifluorovinyl)benzene as a colorless liquid. ^1H NMR (399.6 MHz, $CDCl_3$, 298 K, TMS) δ 7.47-7.38 (m, 4 H), 7.26-7.17 (m, 1 H), 7.09-7.06 (m, 4 H) ppm; ^{19}F NMR (376.0 MHz, $CDCl_3$, 298 K, TMS) δ -101.12 (dd, *J* = 74.8, 32.1 Hz, 1 F), -116.15 (dd, *J* = 110.1, 74.7 Hz, 1 F), -175.76 (dd, *J* = 109.9, 32.1 Hz, 1 F) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, 298 K, TMS) 158.0, 156.3, 153.6 (ddd, *J* = 289.9, 281.4, 50.1 Hz), 129.9, 128.5 (ddd, *J* = 226.3, 46.0, 20.0 Hz), 126.2 (dd, *J* = 10.2, 6.1 Hz), 124.1 (d, *J* = 25.0 Hz), 121.8 (dd, *J* = 22.7, 6.5 Hz), 119.5, 118.5 ppm. IR: ν_{max} 1762, 1612, 1591, 1509, 1490, 1289, 1244, 1202, 1172, 1148, 1109, 1071, 984, 908, 870, 838, 798, 757, 693 cm^{-1}; MS (EI) m/z(%) 250.1(100); HRMS (ESI): Calculated for $C_{14}H_9F_3O$: 250.0605; Found: 250.0604.

1-(1,2,2-Trifluorovinyl)-4-vinylbenzene 2f. The general procedure A with 4-vinylphenylboronic acid (148 mg, 1.00 mmol), $Pd(dba)_2$ (1.2 mg) and $^tBu_3PHBF_4$ (1.2 mg) gave 93.8 mg (51%) of 1-(1,2,2-trifluorovinyl)-4-vinylbenzene as a colorless liquid. ^1H NMR (400.1 MHz, $CDCl_3$, 300 K, TMS) δ 7.52-7.47 (m, 4 H), 6.77 (dd, *J* = 17.6, 10.9 Hz, 1 H), 5.85 (d, *J* = 17.6 Hz, 1 H), 5.37 (d, *J* = 10.9 Hz, 1 H) ppm; ^{19}F NMR (282.4 MHz, $CDCl_3$, 297 K, TMS) δ -99.61 (dd, *J* = 70.3, 32.3 Hz, 1 F), -114.25 (dd, *J* = 108.9, 70.4 Hz, 1 F), -176.95 (dd, *J* = 108.9, 32.3 Hz, 1 F) ppm; ^{13}C NMR (100.5 MHz, $CDCl_3$, 298 K, TMS) δ 153.9 (ddd, *J* = 291.0, 283.3, 50.1 Hz), 138.1, 136.00, 128.7 (ddd, *J* = 226.4, 45.3, 19.8 Hz), 126.5 (dd, *J* = 22.2, 6.8 Hz), 126.5, 124.5 (dd, *J* = 10.6, 6.6 Hz), 115.1 ppm. IR: ν_{max} 3092, 3046, 3012, 2928, 1758, 1631, 1558, 1515, 1406, 1288, 1261, 1211, 1151, 1118, 984, 909, 843,

735, 605 cm^{-1}; MS (EI): m/z (%) 166 (100); HRMS (ESI): Calculated for $C_{10}H_7F_3$: 184.0500; Found: 184.0504.

Ethyl 4-(1,2,2-trifluorovinyl)benzoate 2g. The general procedure A with 4-(ethoxycarbonyl)phenylboronic acid (194 mg, 1.00 mmol), $Pd(dba)_2$ (1.2 mg) and $^tBu_3PHBF_4$ (1.2 mg) gave 161.0 mg (70%) of ethyl 4-(1,2,2-trifluorovinyl)benzoate as a colorless liquid. ^1H NMR (400.1 MHz, $CDCl_3$, 299 K, TMS) δ 8.06 (d, *J* = 8.5 Hz, 2 H), 7.49 (d, *J* = 8.4 Hz, 2 H), 4.38 (q, *J* = 7.1, Hz, 2 H), 1.39 (t, *J* = 7.1 Hz, 3 H) ppm; ^{19}F NMR (282.4 MHz, $CDCl_3$, 297 K, TMS) δ -97.50 (dd, *J* = 70.3, 32.1 Hz, 1 F), -112.05 (dd, *J* = 108.7, 63.6 Hz, 1 F), -178.16 (dd, *J* = 108.7, 33.3 Hz, 1 F) ppm; ^{13}C NMR (100.5 MHz, $CDCl_3$, 298 K, TMS) δ 165.6, 154.1 (ddd, *J* = 293.0, 285.4, 49.3 Hz), 131.3 (dd, *J* = 21.9, 7.1 Hz), 130.5, 129.7, 128.2 (ddd, *J* = 228.4, 44.5, 20.1 Hz), 123.9 (dd, *J* = 11.0, 6.9 Hz), 61.1, 14.1 ppm; IR: ν_{max} 2985, 2940, 2908, 1755, 1720, 1621, 1569, 1465, 1447, 1412, 1390, 1368, 1336, 1314, 1277, 1186, 1154, 1108, 1023, 985, 857, 771, 733, 697, 495 cm^{-1}; MS (EI): m/z (%) 185.1 (100); HRMS (ESI): Calculated for $C_{11}H_9F_3O_2$: 230.0555; Found: 230.0559.

1-(4-(1,2,2-Trifluorovinyl)phenyl)ethanone 2h.[11] The general procedure A with 4-acetylphenylboronic acid (164 mg, 1.00 mmol), $Pd(dba)_2$ (1.2 mg) and $^tBu_3PHBF_4$ (1.2 mg) gave 130.0 mg (65%) of 1-(4-(1,2,2-trifluorovinyl)phenyl)ethanone as a colorless liquid. ^1H NMR (300.0 MHz, $CDCl_3$, 298 K, TMS) δ 7.95 (d, *J* = 8.4 Hz, 2 H), 7.50 (d, *J* = 8.4 Hz, 2 H), 2.56 (s, 3 H) ppm; ^{19}F NMR (282.4 MHz, $CDCl_3$, 298 K, TMS) δ -96.94 (dd, *J* = 62.3, 33.0 Hz, 1 F), -111.56 (dd, *J* = 108.4, 62.4 Hz, 1 F), -178.10 (dd, *J* = 108.5, 33.0 Hz, 1 F) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, 298 K, TMS) 196.9, 154.2 (ddd, *J* = 293.4, 285.8, 49.2 Hz), 136.8, 131.5 (dd, *J* = 21.9, 7.2 Hz), 129.0, 128.2 (ddd, *J* = 226.8, 45.4, 20.0 Hz), 124.82-123.61 (m), 26.42 ppm.

2-(1,2,2-Trifluorovinyl)naphthalene 2i.[11] The general procedure A with naphthalen-2-ylboronic acid (172 mg, 1.00 mmol), $Pd(dba)_2$ (1.2 mg) and $^tBu_3PHBF_4$ (1.2 mg) gave 174.7 mg (84%) of 2-(1,2,2-trifluorovinyl)naphthalene as a colorless liquid. ^1H NMR (399.6 MHz, $CDCl_3$, 298 K, TMS) δ 7.97 (s, 1 H), 7.90-7.84 (m, 3 H), 7.58-7.53 (m, 3 H) ppm; ^{19}F NMR (376.0 MHz, $CDCl_3$, 298 K, TMS) δ -99.15 (dd, *J* = 70.5, 32.2 Hz, 1 F), -114.34 (dd, *J* = 108.8, 70.5 Hz, 1 F), -176.22 (dd, *J* = 108.8, 32.2

Hz, 1 F) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, 299 K, TMS) δ 154.0 (ddd, *J* = 290.7, 283.3, 50.0 Hz), 133.0, 132.9, 128.7 (ddd, *J* = 245.2, 42.9, 17.8 Hz), 128.5, 128.3, 127.7, 127.00, 126.8, 124.6 (dd, *J* = 22.0, 6.9 Hz), 124.0 (m), 121.5 (m) ppm; MS (EI) m/z (%) 234.2 (100) ppm.

1-Chloro-4-(1,2,2-trifluorovinyl)benzene 2j.[7d] The general procedure A with 4-chlorophenylboronic acid (156 mg, 1.00 mmol), $Pd(dba)_2$ (1.2 mg) and $^tBu_3PHBF_4$ (1.2 mg) gave 155.5 mg (81%) of 1-chloro-4-(1,2,2-trifluorovinyl)benzene as a colorless liquid. ^{1}H NMR (399.6 MHz, $CDCl_3$, 298 K, TMS) δ 7.41 (s, 4 H) ppm; ^{19}F NMR (376.0 MHz, $CDCl_3$, 298 K, TMS) δ -98.96 (dd, *J* = 69.6, 33.1 Hz, 1 F), -113.78 (dd, *J* = 109.6, 69.6 Hz, 1 F), -176.97 (dd, *J* = 109.6, 33.0 Hz, 1 F) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, 298 K, TMS) 153.7 (ddd, *J* = 291.7, 283.4, 49.6 Hz), 134.7, 130.0, 128.2, 128.1 (ddd, *J* = 240.9, 44.9, 19.9 Hz), 125.8 (dd, *J* = 20.2, 6.9 Hz), 125.5 (m) ppm.

1-(1,2,2-Trifluorovinyl)naphthalene 2k.[7g] The general procedure A with naphthalen-1-ylboronic acid (172 mg, 1.00 mmol), $Pd(dba)_2$ (1.2 mg) and $^tBu_3PHBF_4$ (1.2 mg) gave 145.6 mg (70%) of 1-(1,2,2-trifluorovinyl)naphthalene as a colorless liquid. ^{1}H NMR (399.6 MHz, $CDCl_3$, 298 K, TMS) δ 8.03-7.91 (m, 3 H), 7.61-7.50 (m, 4 H) ppm; ^{19}F NMR (376.0 MHz, $CDCl_3$, 298 K, TMS) δ -101.49 (dd, *J* = 74.0, 29.1 Hz, 1 F), -117.14 (dd, *J* = 117.5, 74.2 Hz, 1 F), -159.91 (dd, *J* = 117.7, 29.1 Hz, 1 F) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, 299 K, TMS) δ 154.1 (ddd, *J* = 290.8, 283.0, 49.8 Hz), 133.7, 131.4, 128.9, 128.7, 127.7 (ddd, *J* = 232.2, 45.7, 19.7 Hz), 127.3, 126.9, 125.0, 124.8, 123.8 (dd, *J* = 20.7, 4.1 Hz) ppm; MS (EI) m/z(%) 234.2 (100).

2-(1,2,2-Trifluorovinyl)biphenyl 2l.[7c] The general procedure A with biphenyl-2-ylboronic acid (198 mg, 1.00 mmol), $Pd(dba)_2$ (1.2 mg) and $^tBu_3PHBF_4$ (1.2 mg) gave 177.8 mg (76%) of 2-(1,2,2-trifluorovinyl)biphenyl as a colorless liquid. ^{1}H NMR (300.1 MHz, $CDCl_3$, 298 K, TMS) δ 7.72-7.49 (m, 9 H) ppm; ^{19}F NMR (282.4 MHz, $CDCl_3$, 298 K, TMS) δ -102.73 (dd, *J* = 73.9, 29.7 Hz, 1 F), -118.24 (dd, *J* = 116.7, 74.6 Hz, 1 F), -159.64 (dd, *J* = 116.8, 29.6 Hz, 1 F) ppm; ^{13}C NMR (100.5 MHz, $CDCl_3$, 298 K, TMS) δ 152.9 (ddd, *J* = 289.9, 276.9, 50.3 Hz), 142.7, 140.2, 130.7, 130.7, 130.6, 130.5 (m), 128.4, 127.6 (ddd, *J* = 231.5, 52.0, 20.0 Hz), 127.6, 127.4, 125.1 (dd, *J* = 20.2, 4.5 Hz) ppm; IR: ν_{max} 3064, 3029, 1783, 1597, 1566, 1481, 1450, 1437, 1247, 1141, 1104, 1075, 1056,

1009, 982, 953, 909, 766, 757, 742, 700, 617, 603, 570, 545, 476 cm^{-1}; MS (EI) m/z (%) 234.1(100); HRMS (ESI): Calculated for $C_{14}H_9F_3$: 234.0656; Found: 234.0659.

1-Methoxy-3-(1,2,2-trifluorovinyl)benzene 2m.[7g] The general procedure A with 3-methoxyphenylboronic acid (152 mg, 1.00 mmol), $Pd(dba)_2$ (1.2 mg) and $^tBu_3PHBF_4$ (1.2 mg) gave 159.8 mg (85%) of 1-methoxy-3-(1,2,2-trifluorovinyl)benzene as a colorless liquid. ^1H NMR (300.1 MHz, $CDCl_3$, 297 K, TMS) δ 7.61 (t, *J* = 8.0 Hz, 1 H), 7.34 (d, *J* = 7.8 Hz, 1 H), 7.28 (s, 1 H), 7.18 (d, *J* = 8.2 Hz, 1 H), 4.10 (s, 3 H) ppm; ^{19}F NMR (282.4 MHz, $CDCl_3$, 297 K, TMS) δ -99.31 (dd, *J* = 70.2, 32.7 Hz, 1 F), -113.70 (dd, *J* = 109.1, 70.2 Hz, 1 F), -176.07 (dd, *J* = 109.1, 32.7 Hz, 1 F) ppm; ^{13}C NMR (100.5 MHz, $CDCl_3$, 298 K, TMS) δ 159.8, 154.0 (ddd, *J* = 290.5, 283.0, 49.7 Hz), 129.8, 128.6 (ddd, *J* = 225.4, 44.4, 19.3 Hz), 128.6 (dd, *J* = 22.1, 6.7 Hz), 116.9, 114.5, 110.0, 55.5 ppm.

3-(1,2,2-Trifluorovinyl)aniline 2n. The general procedure A with 3-aminophenylboronic acid (137 mg, 1.00 mmol), $Pd(dba)_2$ (1.2 mg) and $^tBu_3PHBF_4$ (1.2 mg) gave 91.7 mg (53%) of 3-(1,2,2-trifluorovinyl)aniline as a colorless liquid. ^1H NMR (400.1 MHz, $CDCl_3$, 299 K, TMS) δ 7.21 (t, *J* = 7.9 Hz, 1 H), 6.88 (d, *J* = 7.8 Hz, 1 H), 6.79 (s, 1 H), 6.67 (dd, *J* = 8.0, 2.1 Hz, 1 H). 3.73 (br, 2 H); ^{19}F NMR (282.4 MHz, $CDCl_3$, 297 K, TMS) δ -99.69 (dd, *J* = 71.4, 32.3 Hz, 1 F), -113.91 (dd, *J* = 108.9, 71.4 Hz, 1 F), -176.00 (dd, *J* = 108.9, 32.3 Hz, 1 F) ppm; ^{13}C NMR (100.5 MHz, $CDCl_3$, 298 K, TMS) δ 153.9 (ddd, *J* = 290.1, 282.8, 50.2 Hz), 146.7, 129.6 (d, *J* = 6.3 Hz), 128.8 (ddd, *J* = 226.0, 44.6, 19.5 Hz), 128.3 (dd, *J* = 21.9, 6.5 Hz), 115.5, 114.8 (m), 110.7 (dd, *J* = 10.6, 6.3 Hz) ppm; IR: ν_{max} 3465, 3381, 3222, 2928, 1757, 1622, 1589, 1496, 1455, 1345, 1308, 1292, 1244, 1173, 1144, 1080, 1027, 1012, 909, 866, 783, 734, 688, 620, 526, 453 cm^{-1}; MS (EI): m/z (%) 173 (100); HRMS (ESI): Calculated for $C_8H_6F_3N$: 173.0452; Found: 173.0450.

1-(3-(1,2,2-Trifluorovinyl)phenyl)ethanone 2o. The general procedure A with 3-acetylphenylboronic acid (164 mg, 1.00 mmol), $Pd(dba)_2$ (1.2 mg) and $^tBu_3PHBF_4$ (1.2 mg) gave 164.0 mg (82%) of 1-(3-(1,2,2-trifluorovinyl)phenyl)ethanone as a colorless liquid. ^1H NMR (400.1 MHz, $CDCl_3$, 299 K, TMS) δ 7.96 (s, 1 H), 7.86 (d, *J* = 7.6 Hz, 1 H), 7.56 (d, *J* = 7.8 Hz, 1 H), 7.46 (t, *J* = 7.8 Hz, 1 H), 2.55 (s, 3 H) ppm; ^{19}F NMR (282.4 MHz, $CDCl_3$, 297 K, TMS) δ -99.12 (dd, *J* =

68.7, 33.0 Hz, 1 F), -114.03 (dd, *J* = 109.8, 68.6 Hz, 1 F), -177.67 (dd, *J* = 109.6, 33.1 Hz, 1 F) ppm; ^{13}C NMR (100.5 MHz, $CDCl_3$, 298 K, TMS) δ 196.9, 153.9 (ddd, *J* = 291.7, 283.7, 49.4 Hz), 137.4, 129.0, 128.5-128.2 (m), 128.1 (ddd, *J* = 226.6, 45.0, 20.0 Hz), 127.7 (dd, *J* = 22.5, 6.8 Hz), 123.9 (dd, *J* = 10.8, 6.3 Hz), 26.2 ppm; IR: ν_{max} 3364, 3076, 3007, 2926, 1758, 1691, 1604, 1583, 1488, 1434, 1360, 1328, 1297, 1243, 1151, 1109, 1085, 1021, 1008, 957, 914, 795, 735, 687, 619, 590 cm^{-1}; MS (EI): m/z (%) 185 (100); HRMS (ESI): Calculated for $C_{10}H_7F_3O$: 200.0449; Found: 200.0448.

3-(1,2,2-Trifluorovinyl)benzaldehyde 2p. The general procedure A with 3-formylphenylboronic acid (150 mg, 1.00 mmol), $Pd(dba)_2$ (1.2 mg) and ^{t}Bu$_3$PHBF$_4$ (1.2 mg) gave 93.0 mg (50%) of 3-(1,2,2-trifluorovinyl)benzaldehyde as a colorless liquid. ^{1}H NMR (400.1 MHz, $CDCl_3$, 299 K, TMS) δ 10.04 (d, *J* = 0.7 Hz, 1 H), 7.97 (s, 1 H), 7.88 (d, *J* = 7.7 Hz, 1 H), 7.72 (d, *J* = 7.9 Hz, 1 H), 7.62 (t, *J* = 7.7 Hz, 1 H) ppm; ^{19}F NMR (282.4 MHz, $CDCl_3$, 297 K, TMS) δ -98.23 (dd, *J* = 66.9, 33.1 Hz, 1 F), -113.27 (dd, *J* = 109.5, 67.1 Hz, 1 F), -177.94 (dd, *J* = 109.5, 33.3 Hz, 1 F) ppm; ^{13}C NMR (100.5 MHz, $CDCl_3$, 298 K, TMS) δ 191.3, 153.0 (ddd, *J* = 292.5, 284.2, 49.1 Hz), 136.8, 129.6 (dd, *J* = 15.7, 7.5 Hz), 129.0, 128.4 (m), 127.9 (ddd, *J* = 226.7, 45.1, 20.2 Hz), 125.4 (dd, *J* = 10.8, 6.6 Hz) ppm; IR: ν_{max} 3389, 3072, 2836, 2739, 1757, 1704, 1604, 1584, 1484, 1442, 1384, 1333, 1296, 1287, 1190, 1172, 1145, 1088, 1027, 1013, 909, 853, 798, 733, 706, 686, 651, 619, 432 cm^{-1}; MS (EI): m/z (%) 186.1 (100); HRMS (ESI): Calculated for $C_9H_5F_3O$: 186.0292; Found: 186.0290.

3-(1,2,2-Trifluorovinyl)benzonitrile 2q.[18b] The general procedure A with 3-cyanophenylboronic acid (147 mg, 1.00 mmol), $Pd(dba)_2$ (1.2 mg) and ^{t}Bu$_3$PHBF$_4$ (1.2 mg) gave 104.3 mg (57%) of 3-(1,2,2-trifluorovinyl)benzonitrile as a colorless liquid. ^{1}H NMR (400.1 MHz, $CDCl_3$, 299 K, TMS) δ 7.77 (s, 1 H), 7.73 (d, *J* = 8.0 Hz, 1 H), 7.67 (d, *J* = 7.8 Hz, 1 H), 7.59 (t, *J* = 7.9 Hz, 1 H); ^{19}F NMR (282.4 MHz, $CDCl_3$, 297 K, TMS) δ -98.23 (dd, *J* = 64.7, 33.7 Hz, 1 F), -111.58 (dd, *J* = 109.8, 64.3 Hz, 1 F), -178.06 (dd, *J* = 109.8, 33.7 Hz, 1 F) ppm; ^{13}C NMR (100.5 MHz, $CDCl_3$, 298 K, TMS) δ 154.0 (ddd, *J* = 293.6, 284.9, 48.6 Hz), 132.1 (dd, *J* = 4.3, 2.4 Hz), 129.7, 128.8 (dd, *J* = 22.8, 7.0 Hz), 128.2 (ddd, *J* = 7.7, 5.9, 4.0 Hz), 127.9 – 127.5 (m), 127.3 (ddd, *J* = 227.0, 45.0, 20.6 Hz), 117.9, 113.4 ppm; IR: ν_{max} 2235, 1757, 1488, 1432, 1422, 1334, 1298, 1187, 1152, 1141, 1089, 1030, 1013, 912,

824, 800, 735, 684, 475 cm^{-1}; MS (EI): m/z (%) 183 (100); HRMS (ESI): Calculated for $C_9H_4F_3N$: 183.0296; Found: 183.0295.

2-Fluoro-4-(1,2,2-trifluorovinyl)biphenyl 2r. The general procedure A with 2-fluorobiphenyl-4-ylboronic acid (216 mg, 1.00 mmol), $Pd(dba)_2$ (1.2 mg) and $^tBu_3PHBF_4$ (1.2 mg) gave 181.4 mg (72%) of 2-fluoro-4-(1,2,2-trifluorovinyl)biphenyl as a white solid. ^1H NMR (400.1 MHz, $CDCl_3$, 299 K, TMS) δ 8.06 – 6.45 (m, 8 H) ppm; ^{19}F NMR (282.4 MHz, $CDCl_3$, 297 K, TMS) δ -98.24 (dd, *J* = 66.7, 32.7 Hz, 1 F), -112.84 (dd, *J* = 109.0, 66.9 Hz, 1 F), -117.02 (t, *J* = 9.3 Hz, 1 F), -172.24 - -181.09 (m, 1 F) ppm; ^{13}C NMR (100.5 MHz, $CDCl_3$, 298 K, TMS) δ 159.8 (d, *J* = 250.7 Hz), 154.1 (ddd, *J* = 292.1, 284.2, 49.2 Hz), 134.9 (d, *J* = 0.9 Hz), 131.1 (d, *J* = 3.0 Hz), 129.5 (d, *J* = 14.2 Hz), 129.0 (d, *J* = 3.1 Hz), 128.6, 128.2 (ddd, *J* = 14.1, 8.8, 1.6 Hz), 128.2 (d, *J* = 4.9 Hz), 127.9 (dddd, *J* = 206.0, 45.2, 20.0, 2.9 Hz), 120.2 (m), 112.9 (m) ppm; IR: ν_{max} 3078, 3031, 2926, 1756, 1618, 1580, 1557, 1522, 1486, 1448, 1410, 1347, 1305, 1245, 1197, 1156, 1134, 1125, 1075, 1038, 1026, 1018, 869, 829, 768, 721, 697, 641, 589, 552, 514, 490, 458 cm^{-1}; MS (EI): m/z (%) 252 (100); HRMS (ESI): Calculated for $C_{14}H_8F_4$: 252.0562; Found: 252.0566. mp: 44-45℃.

2-Methoxy-6-(1,2,2-trifluorovinyl)naphthalene 2s. The general procedure A with 6-methoxynaphthalen-2-ylboronic acid (202 mg, 1.00 mmol), $Pd(dba)_2$ (1.2 mg) and $^tBu_3PHBF_4$ (1.2 mg) gave 192.8 mg (81%) of 2-methoxy-6-(1,2,2-trifluorovinyl)naphthalene as a colorless liquid. ^1H NMR (399.6 MHz, $CDCl_3$, 298 K, TMS) δ 7.88 (s, 1 H), 7.77 (d, *J* = 8.7 Hz, 1 H), 7.76 (d, *J* = 8.9 Hz, 1 H), 7.52 (d, *J* = 8.7 Hz, 1 H), 7.20 (dd, *J* = 9.0, 2.2 Hz, 1 H),7.14 (d, *J* = 2.3 Hz, 1 H), 3.94 (s, 3 H) ppm; ^{19}F NMR (376.0 MHz, $CDCl_3$, 298K, TMS) δ -100.28 (dd, *J* = 73.3, 31.8 Hz, 1 F), -115.44 (dd, *J* = 109.1, 73.3 Hz, 1 F), -175.97 (dd, *J* = 108.9, 31.8 Hz, 1 F) ppm; ^{13}C NMR (100.5 MHz, $CDCl_3$, 298 K, TMS) 158.5, 153.9 (ddd, *J* = 290.4, 282.2, 50.3 Hz), 134.4, 129.8, 129.0 (ddd, *J* = 214.7, 45.3, 19.8 Hz), 128.3, 127.3 (d, *J* = 1.4 Hz), 123.9 (m), 122.3 (dd, *J* = 22.1, 6.6 Hz), 122.1 (m), 119.7, 105.6, 55.3 ppm. IR: ν_{max} 3060, 3007, 2962, 2937, 2839, 1754, 1631, 1603, 1507, 1488, 1462, 1440, 1413, 1393, 1288, 1260, 1207, 1164, 1135, 1031, 1021, 905, 894, 855, 815, 749, 698 cm^{-1}; MS (EI) m/z(%) 238.1(100); HRMS (ESI): Calculated for $C_{13}H_9F_3O$: 238.0605; Found: 238.0603.

4-Chloro-1-ethoxy-2-(1,2,2-trifluorovinyl)benzene 2t. The general procedure A with 5-chloro-2-ethoxyphenylboronic acid (200 mg, 1.00 mmol), $Pd(dba)_2$ (1.2 mg) and $^tBu_3PHBF_4$ (1.2 mg) gave 94.4 mg (40%) of 4-chloro-1-ethoxy-2-(1,2,2-trifluorovinyl)benzene as a colorless liquid. ^{1}H NMR (400.1 MHz, $CDCl_3$, 299 K, TMS) δ 7.38 (m, 1 H), 7.36 (d, *J* = 0.9 Hz, 1 H), 6.90 (d, *J* = 9.5 Hz, 1 H), 4.10 (q, *J* = 7.0 Hz, 2 H), 1.45 (t, *J* = 7.0 Hz, 3H); ^{19}F NMR (282.4 MHz, $CDCl_3$, 297 K, TMS) δ -101.40 (ddd, *J* = 69.0, 30.8 Hz, 1 F), -114.50 (dd, *J* = 113.7, 69.2 Hz, 1 F), -166.83 (dd, *J* = 114.2, 30.3 Hz, 1 F) ppm; ^{13}C NMR (100.5 MHz, $CDCl_3$, 298 K, TMS) δ 155.2, 153.4 (ddd, *J* = 289.1, 279.2, 50.4 Hz), 131.9, 130.1, 124.8, 1284.7 (ddd, *J* = 230.8, 52.2, 22.1 Hz), 117.5 (dd, *J* = 21.5, 4.6 Hz), 113.6, 64.6, 14.9 ppm; IR: ν_{max} 2968, 2933, 1778, 1599, 1496, 1474, 1396, 1326, 1293, 1277, 1245, 1149, 1125, 1042, 1007, 998, 924, 888, 824, 807, 793, 662 cm^{-1}; MS (EI): m/z (%) 207 (100); HRMS (ESI): Calculated for $C_{10}H_8F_3OCl$: 236.0216; Found: 236.0215.

6-(1,2,2-Trifluorovinyl)-2,3-dihydrobenzo[b][1,4]dioxine 2u. The general procedure A with 2,3-dihydrobenzo[b][1,4]dioxin-6-ylboronic acid (180 mg, 1.00 mmol), $Pd(dba)_2$ (1.2 mg) and $^tBu_3PHBF_4$ (1.2 mg) gave 194.4 mg (90%) of 6-(1,2,2-trifluorovinyl)-2,3-dihydrobenzo[b][1,4]dioxine as a colorless liquid. ^{1}H NMR (400.1 MHz, $CDCl_3$, 299 K, TMS) δ 7.03 (d, *J* = 1.9 Hz, 1 H), 6.99(dd, *J* = 8.4, 1.6 Hz, 1 H)6.94 (d, *J* = 8.5 Hz, 1H), 4.31 (s, 4 H) ppm; ^{19}F NMR (282.4 MHz, $CDCl_3$, 297 K, TMS) δ -101.65 (dd, *J* = 73.5, 32.0 Hz, 1 F), -116.34 (dd, *J* = 109.8, 75.5 Hz, 1 F), -175.39 (dd, *J* = 109.8, 31.9 Hz, 1 F) ppm; ^{13}C NMR (100.5 MHz, $CDCl_3$, 298 K, TMS) δ 153.9 (ddd, *J* = 289.0, 281.2, 50.3 Hz), 144.1, 143.7 (d, *J* = 1.9 Hz), 128.4 (ddd, *J* = 226.1, 45.7, 19.9 Hz), 120.5 (dd, *J* = 23.1, 6.5 Hz), 118.0 (m), 117.6, 113.8 (m), 64.4, 64.3 ppm; IR: ν_{max} 2985, 2938, 2881, 1762, 1618, 1585, 1514, 1461, 1433, 1426, 1339, 1327, 1296, 1264, 1250, 1253, 1193, 1123, 1070, 1025, 1019, 1007, 932, 893, 865, 814, 750, 699, 634, 585 cm^{-1}; MS (EI): m/z (%) 216.0 (100); HRMS (ESI): Calculated for $C_{10}H_7F_3O_2$: 216.0398; Found: 216.0400.

2-(1,2,2-Trifluorovinyl)benzofuran 2v. The general procedure A with benzofuran-2-ylboronic acid (162 mg, 1.00 mmol), $Pd(dba)_2$ (1.2 mg) and $^tBu_3PHBF_4$ (1.2 mg) gave 87.1 mg (44%) of 2-(1,2,2-trifluorovinyl)benzofuran as a colorless liquid. ^{1}H NMR (400.1 MHz, $CDCl_3$, 299 K, TMS) δ 7.50 (d,

J = 7.4 Hz, 1 H), 7.42 (d, *J* = 8.1 Hz, 1 H), 7.25 (t, *J* = 7.6 Hz, 1 H), 7.18 (t, *J* = 7.3 Hz, 1 H), 6.81 (s, 1 H) ppm; ^{19}F NMR (282.4 MHz, $CDCl_3$, 297 K, TMS) δ -97.72 (dd, *J* = 60.0, 30.0 Hz, 1 F), -111.22 (dd, *J* = 110.5, 60.0 Hz, 1 F), -184.23 (dd, *J* = 110.5, 30.0 Hz, 1 F) ppm; ^{13}C NMR (100.5 MHz, $CDCl_3$, 298 K, TMS) δ 155.2, 153.4 (ddd, *J* = 292.8, 288.4, 45.0 Hz), 143.2 (dd, *J* = 32.9, 8.3 Hz), 127.5, 125.5, 123.5, 123.4 (ddd, *J* = 223.6, 48.9, 24.0 Hz), 121.4, 111.5, 105.8 (dd, *J* = 7.5, 5.3 Hz) ppm; IR: ν_{max} 3068, 2928, 1764, 1653, 1616, 1575, 1558, 1541, 1507, 1476, 1452, 1378, 1351, 1302, 1256, 1180, 1152, 1143, 1108, 1032, 940, 910, 880, 855, 808, 749, 737, 658 cm^{-1}; MS (EI): m/z (%) 198.0 (100); HRMS (ESI): Calculated for $C_{10}H_5F_3O$: 198.0292; Found: 198.0293.

1-Methoxy-2-(1,2,2-trifluorovinyl)benzene 3a.[8a] The general procedure B with 2-methoxyphenylboronic acid (152 mg, 1.00 mmol), $Pd(dba)_2$ (1.2 mg) and ^{t}Bu$_3$PHBF$_4$ (1.2 mg) gave 112.8 mg (60%) of 1-methoxy-2-(1,2,2-trifluorovinyl) -benzene as a colorless liquid. ^{1}H NMR (399.6 MHz, $CDCl_3$, 298 K, TMS) δ 7.45 (t, *J* = 7.9 Hz, 1 H), 7.37 (d, *J* = 7.6 Hz, 1 H), 7.03 (t, *J* = 7.5 Hz, 1 H), 6.98 (d, *J* = 8.4 Hz, 1 H), 3.88 (s, 3 H); ^{19}F NMR (282.4 MHz, $CDCl_3$, 298 K, TMS) δ -101.93 (dd, *J* = 73.2, 29.3 Hz, 1 F), -116.00 (dd, *J* = 115.2, 73.4 Hz, 1 F), -164.45 (dd, *J* = 115.1, 29.4 Hz, 1 F); ^{13}C NMR (100.5 MHz, $CDCl_3$, 298 K, TMS) δ 157.6, 153.4 (ddd, *J* = 288.4, 277.2, 51.1 Hz), 132.0 (d, *J* = 1.6 Hz), 130.6 (d, *J* = 2.2 Hz), 125.6 (ddd, *J* = 231.0, 52.2, 21.1 Hz), 120.4, 115.7 (dd, *J* = 21.1, 4.5 Hz), 111.2, 55.6 ppm.

Procedure of the scaled-up reaction.

A 250 mL Schlenk-type sealed tube (with a Teflon high-pressure valve and side arm) equipped with a magnetic stir bar was charged with the biphenyl-4-ylboronic acid (2.0 g, 10.0 mmol), potassium phosphate (6.36 g, 30.0 mmol), $Pd(dba)_2$ (12 mg, 2.0 mmol %), tri-*tert*-butylphosphine tetrafluoroborate (12 mg, 4.0 mmol %). The reaction tube was capped, then evacuated briefly under high vacuum and charged with argon, repeated three times. Then freshly distilled toluene (20.0 mL) and DMF (20.0 mL), deionized water (14.0 mL) was added, and chlorotrifluoroethene was bubbled about 15 min (excess). Then the valve was screwed. The reaction mixture was stirred at 80 ^{o}C for 2 h. The reaction vessel was then cooled to room temperature, filtered through a short plug of Celite. 20

mL of Deionized water and 20 mL of pentane (AR) was added. The organic phase was separated and washed with deionized water three times. The aqueous phase was extracted with pentane (3×10 mL). The organic phase was combined, dried with anhydrous Na_2SO_4 and added silica gel, then evacuated under vacuum. The residue was purified by silica gel flash column chromatography using pentane as eluent to give 4-(1,2,2-trifluorovinyl)biphenyl a white solid (1.9 g, 80% yield).

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Supporting Information Available: Experimental details, spectra for compounds **2b-v**, **3a-g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) A provisional patent (application No PCT/CN2012/074374) on this work has been filed on April 19, 2012.

(13) CCDC 887510 contains the supplementary crystallographic data for the comlex [*trans*-$(PPh_3)_2Pd(CF{=}CF_2)(Cl)$] **1** reported in this communication. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or pm application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK [fax: +44-1223/336-033; email: deposit@ccdc.cam.ac.uk].

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