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Preparation of Trifluorostyrenes via Palladium-Catalyzed Coupling of Arylboronic Acids with Chloro- and Bromotrifluoroethylene

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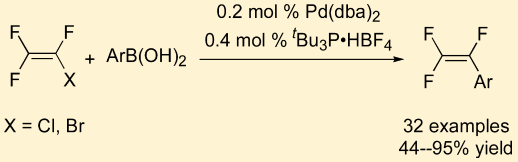
Supporting Information

ABSTRACT: A highly 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 arylboronic acids were efficiently incorporated to generate α,β,β-trifluorostyrene derivatives.



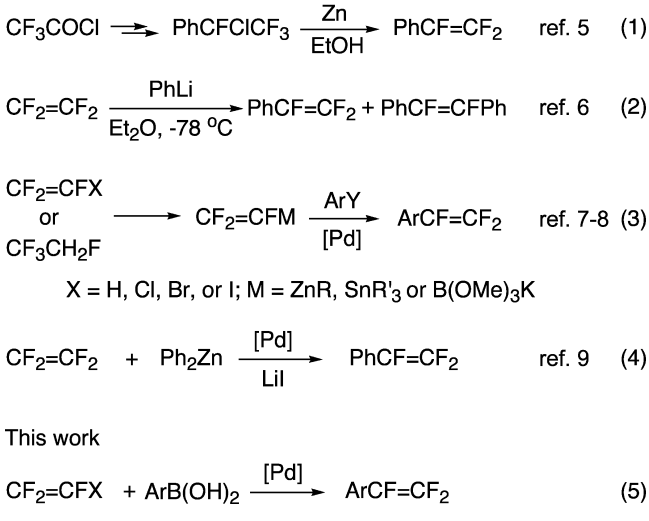
INTRODUCTION

α,β,β-Trifluorostyrene (TFS) and its derivatives are interesting monomers for fluorinated polymers,[1,2] mainly due to their unique structure that combines a trifluorovinyl group and a benzene ring. The polymers contain a perfluorinated main chain and often exhibit high thermal and chemical stability and, more importantly, high solubility that allows the polymers to be more processable. 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 co-workers at Ballard have been used as membrane electrolytes in the 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 has become the subject of special interest.[4]

Most of the early methods for the syntheses of TFS derivatives typically required multiple steps and suffered from low overall yields.[5,6] A more direct method was reported in the 1980s[7] through the Pd-catalyzed cross-coupling of trifluorovinylzinc or tin reagent with aryl halides. More recently, a stable trifluorovinyl borate was developed to replace the zinc or tin reagent, thus providing 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 butyllithium through halogen exchange 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 bromotrifluoroethene with arylboronic 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 $Pd(PPh_3)_4$ was able to couple chlorotrifluoroethylene with a variety of arylboronic 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 functionalized arylboronic 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 tolerate a variety of functional groups. In addition, under slightly modified conditions, the coupling of bromotrifluoroethylene with arylboronic acids also occurred in good to excellent yields.[12]

Scheme 1. Strategies for the Preparation of α,β,β-Trifluorostyrene

Previous work



This work

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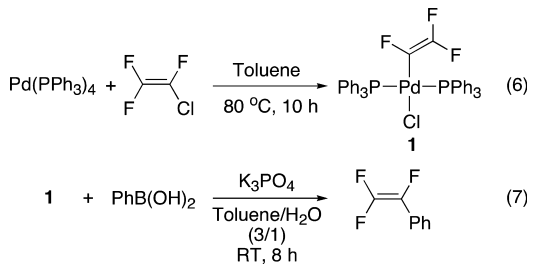
RESULTS AND DISCUSSION

We began our investigation by isolation of the [LPd(CF=CF$_2$)(Cl)] species and testing its stoichiometric reaction with arylboronic 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 °C for 10 h generated the [*trans*-(PPh$_3$)$_2$Pd(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.



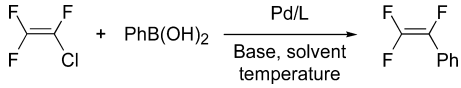
Complex **1** was characterized by ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectroscopies and element analysis. The structure of complex [(*trans*)-Pd(PPh$_3$)$_2$(CF=CF$_2$)(Cl)] (**1**) was further confirmed by single-crystal X-ray diffraction (see the Supporting Information for details).[13] Interestingly, Stone reported that while [(PPh$_3$)$_2$PdCl$_2$] was formed when [Pd(PPh$_3$)$_4$] was reacted with chlorotrifluoroethylene in acetone, reaction of [Pd(PPh$_2$Me)$_4$] with chlorotrifluoroethylene did generate [(*trans*)-Pd(PPh$_2$Me)$_2$(CF=CF$_2$)(Cl)] in high yield in benzene.[14] Treatment of complex **1** with 1 equiv of phenylboronic acid in toluene/water (3/1) using K$_3$PO$_4$ 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 arylboronic 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 phenylboronic acid (Table 1). After careful investigation, we discovered that reaction of chlorotrifluoroethylene and phenylboronic acid in the presence of a combination of 0.1 mol % of Pd$_2$(dba)$_3$ and 0.4 mol % of P^{t}Bu$_3$[15,16] occurred in 51% yield after 8 h at 80 °C using K$_3$PO$_4$ 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$_3$)$_2$Cl$_2$ as the catalyst precursor occurred in much lower yields. When K$_2$CO$_3$, Na$_2$CO$_3$, or Na$_3$PO$_4$ 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$_2$O (3/1) or benzene/H$_2$O (3/1) occurred in 34% yield. Interestingly, when a mixture of DMF/H$_2$O (3/1) was used as the solvent, the yield increased dramatically to over 95%. However, these optimized reaction conditions were not general. When another arylboronic acid such as 4-biphenylboronic acid was used, only 38% of the desired product was observed.

We then chose the reaction 4-biphenylboronic 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 solvents than those in DMF/H$_2$O. Typically, the reaction occurred to complete conversion after 2 h. Using of ^{t}Bu$_3$P as the ligand was critical for the reaction.

Bidentate ligands with a rigid backbone such as DPPF or BINAP were ineffective 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 alkylphosphines such as PCy$_3$ or BuP(Ad)$_2$ were less efficient (Table 2, entries 11 and 12). *N*-Heterocyclic carbene (IPr), which has been used in a variety of cross-coupling reactions,

Table 1. Optimization for Pd-Catalyzed Coupling of Chlorotrifluoroethylene with Arylboronic Acid[a]



entry	Pd source	ligand	solvent	base	temp (°C)	time (h)	yield[b] (%)
1	Pd$_2$(dba)$_3$	tBu$_3$P	tol/H$_2$O[c]	K$_3$PO$_4$	80	8	29
2	Pd$_2$(dba)$_3$	tBu$_3$P	tol/H$_2$O	K$_3$PO$_4$	80	8	51
3	Pd$_2$(dba)$_3$	tBu$_3$P	tol/H$_2$O[d]	K3PO$_4$	80	8	2
4	Pd(OAc)$_2$	tBu$_3$P	tol/H$_2$O	K$_3$PO$_4$	80	8	16
5	Pd(PPh$_3$)$_2$Cl$_2$	tBu$_3$P	tol/H$_2$O	K$_3$PO$_4$	80	8	13
6	Pd(dba)$_2$	tBu$_3$P	tol/H$_2$O	K$_2$CO$_3$	80	8	35
7	Pd(dba)$_2$	tBu$_3$P	tol/H$_2$O	Na$_2$CO$_3$	80	8	36
8	Pd(dba)$_2$	tBu$_3$P	tol/H$_2$O	Na$_3$PO$_4$	80	8	38
9	Pd(dba)$_2$	tBu$_3$P	tol/H$_2$O	CsF	80	8	<5
10	Pd(dba)$_2$	tBu$_3$P	dioxane/H$_2$O	K$_3$PO$_4$	80	8	34
11	Pd(dba)$_2$	tBu$_3$P	PhH/H$_2$O	K$_3$PO$_4$	80	8	34
12	Pd(dba)$_2$	tBu$_3$P	DMF/H$_2$O	K$_3$PO$_4$	80	8	>95

[a]Reaction conditions: arylboronic acid (1.0 mmol), excess chlorotrifluoroethylene, palladium precursor (0.2 mol %), ligand (0.4 mol %), and base (3.0 mmol) in 5.4 mL of mixed solvent (solvent/H$_2$O is 3:1). [b]The yield was determined by ^{19}F NMR spectroscopy with fluorobenzene as an internal standard. [c]The ratio of solvent/H$_2$O is 5:1. [d]The ratio of solvent/H$_2$O is 1:1.

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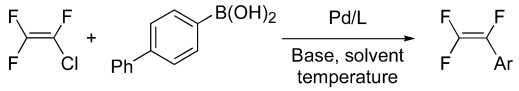
Table 2. Optimization for Pd-Catalyzed Coupling of Chlorotrifluoroethylene with Arylboronic Acid[a]



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	$Pd(dba)_2$	tBuDavePhos	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

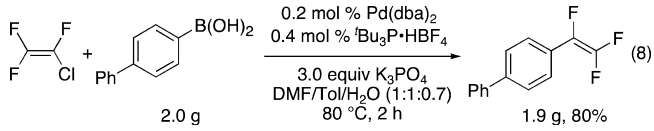
[a]Reaction conditions: arylboronic acid (1.0 mmol), excess chlorotrifluoroethylene, palladium precursor (0.2 mol %), ligand (0.4 mol %), and base (3.0 mmol) in 5.4 mL of mixed solvent. [b]The yield was determined by ^{19}F NMR spectroscopy with fluorobenzene as an internal standard.

was again ineffective (Table 2, entry 13). The dialkylbiarylphosphine ligands developed by Buchwald and co-workers[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 with 65% yield (Table 2, entries 14−17).

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 arylboronic 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, and 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 product in 81% yield (Table 3, entry **2j**), which indicated that the 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 a heteroarylboronic acid such as 3-pyridylboronic acid, however, did not generate the corresponding coupled product.

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 $Pd(dba)_2/P(o\text{-tol})_3$, $Pd(dba)_2/(t\text{-}Bu_3P)$, or $Pd(dba)_2$/Xantphos gave the desired product in good yield for the reaction of bromotrifluoroethylene with 4-biphenylboronic acid in mixed DMF/H_2O (3/1), less than 40% conversion was observed for the reaction of bromotrifluoroethylene with 3-cyanophenylboronic acid under these conditions even with prolonged reaction time. After a quick screening of the conditions, it was found that switching the solvent system to a 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 arylboronic acids were subjected to the catalytic conditions to give the product in moderate to good yield. Generally, unlike other cross-coupling reactions, couplings of bromotrifluoroethylene were much slower and less effective than those of chlorotrifluoroethylene under the current reaction conditions.

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-biphenylboronic 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 arylboronic 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 scaled up without loss in efficiency. Work is ongoing to scale up the reaction to kilograms and to elucidate the mechanism of the reaction.

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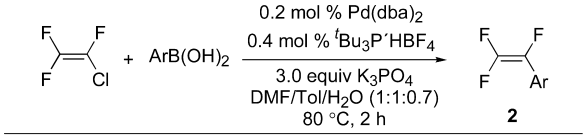
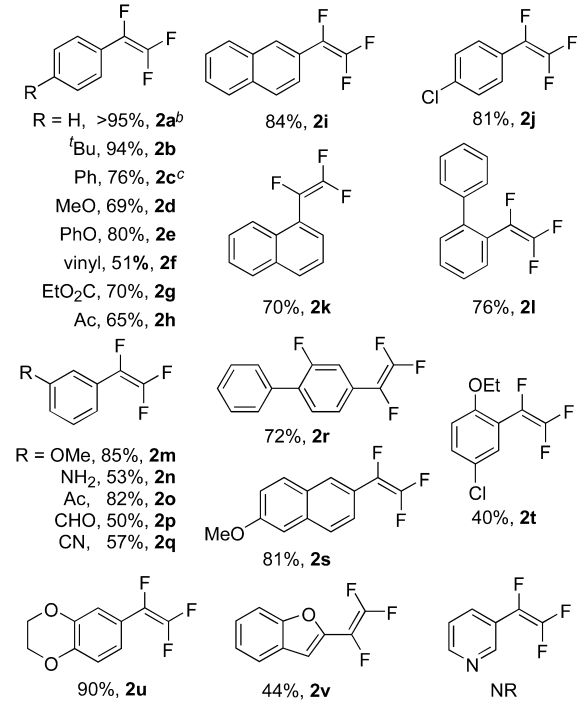
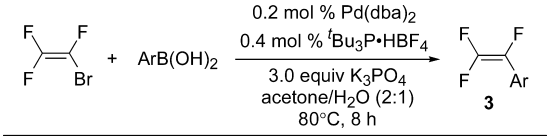
Table 3. Scope of Pd-Catalyzed Coupling of Chlorotrifluoroethylene with Low Loading[a]

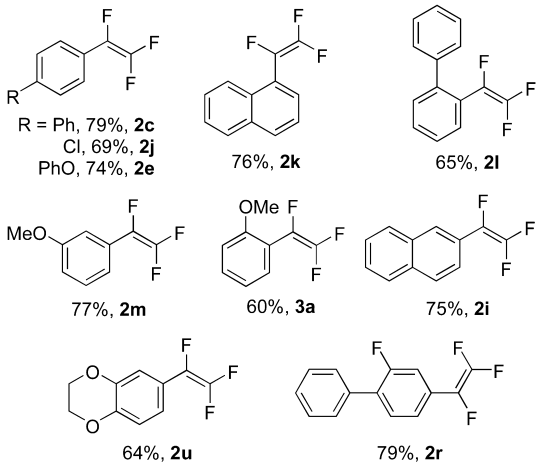




[a]Reaction conditions: arylboronic acid (1.0 mmol), excess chlorotrifluoroethylene, $Pd(dba)_2$ (0.2 mol %), $P^tBu_3{\cdot}HBF_4$ (0.4 mol %), K_3PO_4 (3.0 mmol) in 5.4 mL of toluene/DMF/H_2O (1/1/0.7). [b]The yield was determined by ^{19}F NMR spectroscopy with fluorobenzene as an internal standard. [c]The yield was 88% when 4-bipheylpinacol boronate was used.

Table 4. Scope of Pd-Catalyzed Coupling of Bromotrifluoroethylene with Low Loading[a]





[a]Reaction conditions: arylboronic acid (1.0 mmol), excess bromotrifluoroethylene, $Pd(dba)_2$ (0.2 mol %), $P^tBu_3{\cdot}HBF_4$ (0.4 mol %), K_3PO_4 (3.0 mmol) in 3 mL of acetone/H_2O (2/1).

EXPERIMENTAL SECTION

Preparation of *trans*-Pd(CF=CF$_2$)(PPh$_3$)$_2$Cl. To a 25 mL Schlenk tube were added tetrakis(triphenyl)phosphine palladium(0) (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 °C 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$_3$)$_2$Cl 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, 7.1 Hz, 1 F), δ −128.21 (m, 1 F), −148.76 (ddt, J = 105.6, 40.5, 6.2 Hz, 1 F); $^{31}P\{^1H\}$ NMR δ18.2; 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 arylboronic acid (1.0 mmol), potassium phosphate (3.0 mmol), $Pd(dba)_2$ (0.2 mmol %), and tri-*tert*-butylphosphine tetrafluoroborate (0.4 mmol %). The reaction tube was capped and then evacuated briefly under high vacuum and charged with argon, repeated three times. Freshly distilled toluene (2.0 mL) and DMF (2.0 mL) and deionized water (1.4 mL) were added, and chlorotrifluoroethene was bubbled for 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, and 10 mL of deionized water and 10 mL of pentane (AR) were 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 and dried with anhydrous Na_2SO_4, and silica gel was added. The mixture was evacuated under a rotary evaporator, and 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 %), and tri-*tert*-butylphosphine tetrafluoroborate (0.4 mmol %). The reaction tube was capped, 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) were added, and bromotrifluoroethene was bubbled for 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 the mixture was 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 and dried with anhydrous Na_2SO_4, and silica gel was added. The mixture was evacuated under a rotary evaporator, and 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, fluorobenzene (1.0 mol) was added as internal standard. The 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: ^1H NMR (300.0 MHz, $CDCl_3$, 298 K, TMS) δ 7.43 (d, J = 8.7 Hz, 2 H), 7.39 (d, J = 8.4 Hz, 2 H), 1.33 (s, 9 H); ^{19}F NMR (282.4

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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); ^{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.

*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); ^{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); ^{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; 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 (EI) calcd for $C_{14}H_9F_3$ 234.0656, found 234.0659; mp 57−59 °C.

*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); ^{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); ^{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.

*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: ^{1}H 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); ^{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); ^{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; 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 (EI) calcd 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: ^{1}H 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); ^{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); ^{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; 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 (EI) calcd 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: ^{1}H 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); ^{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); ^{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; 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 (EI) calcd 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: ^{1}H 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); ^{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); ^{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.

*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: ^{1}H 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); ^{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); ^{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); MS (EI) m/z 234.2 (100).

*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); ^{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); ^{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).

*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); ^{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); ^{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); 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); ^{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); ^{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); 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 (EI) calcd 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: ^{1}H 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); ^{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); ^{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.

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: ^{1}H 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); ^{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); 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 (EI) calcd 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: ^{1}H 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); ^{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); ^{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; 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) calcd 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 $^tBu_3PHBF_4$ (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); ^{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); ^{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); 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 (EI) calcd 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 $^tBu_3PHBF_4$ (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); ^{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; 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 (EI) calcd 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: ^{1}H NMR (400.1 MHz, $CDCl_3$, 299 K, TMS) δ 8.06−6.45 (m, 8 H); ^{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); ^{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); 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 (EI) calcd for $C_{14}H_8F_4$ 252.0562, found 252.0566; mp 44−45 °C.

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: ^{1}H 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); ^{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); ^{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; 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 (EI) calcd 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); ^{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; 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 (EI) calcd 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); ^{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); ^{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; 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 (EI) calcd 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 $^{t}Bu_3PHBF_4$ (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); ^{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); ^{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); 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 (EI) calcd 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 $^{t}Bu_3PHBF_4$ (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.

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 %), and tri-*tert*-butylphosphine tetrafluoroborate (12 mg, 4.0 mmol %). The reaction tube was capped, evacuated briefly under high vacuum, and charged with argon, repeated three times. Then freshly distilled toluene (20.0 mL) and DMF (20.0 mL) and deionized water (14.0 mL) were added, and chlorotrifluoroethene was bubbled through for about 15 min (excess). Then the valve was screwed. The reaction mixture was stirred at 80 °C for 2 h. The reaction vessel was then cooled to room temperature and filtered through a short plug of Celite. Twenty milliliters of deionized water and 20 mL of pentane (AR) were 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 and dried with anhydrous Na_2SO_4, and silica gel was added. The mixture was 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 as a white solid (1.9 g, 80% yield).

■ ASSOCIATED CONTENT

Supporting Information

Experimental details; spectra for compounds **2b**−**v** and **3a**−**g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(13) CCDC 887510 contains the supplementary crystallographic data for the complex [*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 by application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (fax: +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).

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