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Palladium-catalyzed Suzuki–Miyaura reaction of fluorinated vinyl chloride: a new approach for synthesis α and α,β-trifluoromethylstyrenes

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ABSTRACT

A mild and efficient palladium-catalyzed cross-coupling between fluorinated vinyl chloride and arylboronic acids is described. The use of ligand B successfully overcomes the strong electronic withdrawing of trifluoromethylated substrates and allows the efficient synthesis of a wide range of α and α,β-trifluoromethyl containing olefins. By using this method, the key intermediate for synthesis of Efavirenz can be obtained in a simple route. The efficient conversion of two freon molecules into useful α and α,β-trifluoromethyl containing olefins is a useful route in organic chemistry.

1. Introduction

Trifluoromethylation of compounds such as pharmaceuticals, agricultural chemicals, and functional materials in most cases, significantly improves their performances.[1] α-Trifluoromethylstyrene derivatives have attracted considerable attention because they are industrially important compounds in the fields of medicinal, agricultural and material sciences.[2,3] Conjugated aromatic systems with trifluoromethyl groups such as β-trifluoromethylstyrene derivatives have been found wide use in Organic Light Emitting Diodes (OLEDs) and other material chemistry.[4] With regard to the metal-catalyzed coupling for synthesis of α and β-trifluoromethylstyrene derivatives, several research groups have reported methods for preparing of this kind of substrates.[5,6] However, all of those methods use either toxic reagents or expensive substrates. On the other hand, less attention has been paid to the development of efficient and general methods for tri and tetra-substituted olefins.[7] Especially for trifluoromethylation and fluorinated containing substrates.[8,9] Therefore, it is of great interest to develop general and efficient strategies for synthesizing these compounds.

Suzuki–Miyaura reaction is a well-established and important cross-coupling reaction in organic synthesis. It is widely used to synthesize, poly-olefins, styrenes, and substituted biphenyls. Several reviews have been published describing advancements and the development of the Suzuki–Miyaura reaction.[10] But, there is still a difficulty for Suzuki–Miyaura reaction in fluorinated aryl halide or halogenated hydrocarbon.

It is considered that freon molecules are involved in ozon layer destruction, tremendous stocks of freons have been accumulated during last century, which need to be utilized. Nowadays, how to convert them into fine chemical products is a challenging and urgent problem. 2-chloro-3,3,3-trifluoroprop-1-ene (HCFO-1233xf), is a commercially available compound with a boiling point of 27.7 °C at 760 mmHg, usually used as a refrigerant in automotive industry. If it is considered as a raw material for various useful chemicals, then opportunities exist for its use. Very few examples related to its chemical conversion were reported.[11] However, as we know, the coupling of HCFO-1233xf with aryl boronic acids has not been reported in any literature. As part of our systematic studies on transition-metal-catalyzed reactions for

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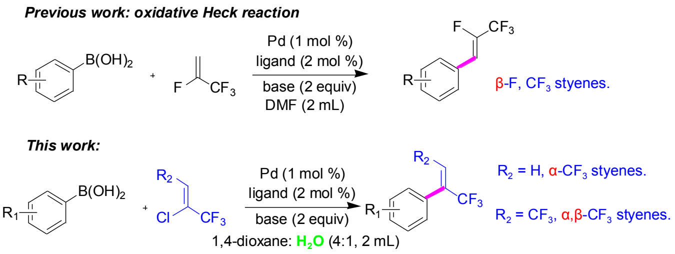
the efficient synthesis of fluorinated olefins (Scheme 1),[12] we report an efficient cross-coupling reaction for synthesis of trifluoromethylstyrenes by using trifluoromethylated vinyl chloride and arylboronic acids via palladium-catalyzed Suzuki–Miyaura reaction.

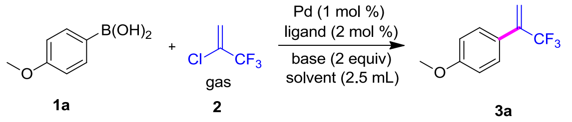


Scheme 1. Palladium-catalyzed for synthesis of α and α(β)-trifluoromethylstyrenes.

2. Results and discussion

We initially chose 4-methoxyphenylboronic acid **1a** as a substrate for the screening of this coupling transformation. A solution of 4-methoxyphenylboronic acid **1a** and 2-chloro-3,3,3-trifluoroprop-1-ene **2** in 1,4-dioxane and water (4:1) was stirred using $Pd(OAc)_2$ (1 mol %) as a catalyst, PCy_3 (2 mol %) as a ligand and Na_2CO_3 as a base. Only 1-methoxy-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene **3a** was formed in a low yield of 39% (Table 1, entry 1). Control experiments revealed that the metal and ligand were both indispensable for the reaction (Table 1, entries 2 and 3). Next, the influence of palladium source was examined. It could be seen that $Pd(PPh_3)_2Cl_2$ was the best pre-catalyst for the reaction (Table 1, entries 4–6). When the ligand was switched from PCy_3 to **B**, a better yield was obtained (Table 1, entries 7–11). Thirdly, the influence of base was examined, and it was observed that $NaHCO_3$ was the best base for the reaction (Table 1, entries 12–15). Moreover, when the reaction solvent was changed to water, the target product **3a** was achieved in an acceptable yield of 66% (Table 1, entry 16). Suggesting that this strategy provided a useful route for synthesis of trifluoromethylation substituted olefins. However, when 1,4-dioxane used as solvent alone, the product **3a** can be obtained in yield of 58% (Table 1, entry 17). Finally, when the amount of **2** was decreased to 2 equiv, a poor yield of **3a** (22%) was obtained (Table 1, entry 18). In summary, the best reaction conditions for this coupling process were obtained using $Pd(PPh_3)_2Cl_2$ (1 mol %), B (2 mol %), $NaHCO_3$ (2 equiv) 1,4-dioxane and water (4:1, 2.5 mL) as the mixture solvent, at 100 °C for 5 h.

Table 1
Optimization of palladium-catalyzed arylboronic acid coupling with 2-chloro-3,3,3-trifluoroprop-1-ene[a]



Entry	Catalyst	Ligand	Base	Solvent[b]	Yield (%)[c]
1	$Pd(OAc)_2$	PCy_3	Na_2CO_3	4:1	39
2	—	PCy_3	Na_2CO_3	4:1	0
3	$Pd(OAc)_2$	—	Na_2CO_3	4:1	0
4	$PdCl_2$	PCy_3	Na_2CO_3	4:1	30
5	$Pd(PPh_3)_2Cl_2$	PCy_3	Na_2CO_3	4:1	45
6	$Pd(PhCN)_2Cl_2$	PCy_3	Na_2CO_3	4:1	29
7	$Pd(PPh_3)_2Cl_2$	PPh_3	Na_2CO_3	4:1	2
8	$Pd(PPh_3)_2Cl_2$	DPPP	Na_2CO_3	4:1	4
9	$Pd(PPh_3)_2Cl_2$	BINAP	Na_2CO_3	4:1	12
10	$Pd(PPh_3)_2Cl_2$	A	Na_2CO_3	4:1	13
11	$Pd(PPh_3)_2Cl_2$	B	Na_2CO_3	4:1	65
12	$\mathbf{Pd(PPh_3)_2Cl_2}$	**B**	$\mathbf{NaHCO_3}$	4:1	**97**
13	$Pd(PPh_3)_2Cl_2$	B	Na_2HPO_4	4:1	63
14	$Pd(PPh_3)_2Cl_2$	B	NEt_3	4:1	71
15	$Pd(PPh_3)_2Cl_2$	B	K_2CO_3	4:1	55
16	$Pd(PPh_3)_2Cl_2$	B	$NaHCO_3$	H_2O	66
17	$Pd(PPh_3)_2Cl_2$	B	$NaHCO_3$	1,4-Dioxane	58
18[d]	$Pd(PPh_3)_2Cl_2$	B	$NaHCO_3$	4:1	22

Bold entry signifies the best reaction condition.

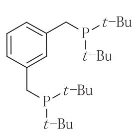
[a] Reaction conditions: **1a** (1 mmol), **2** (18 mmol), catalyst (1 mol %), ligand (2 mol %), base (2 mmol), solvent (2.5 mL), 100 °C, 5 h.

[b] 1,4-Dioxane: H_2O.

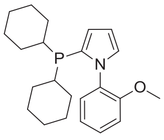
[c] NMR yields were calculated by ^{19}F NMR integration of products relative to the internal standard of ethyl *p*-fluoroacetophenone.

[d] **2** (5 mmol) was added.

Structures of ligands:



A:



B:

To explore the scope of the coupling reaction, various arylboronic acids were then examined for coupling with 2-chloro-3,3,3-trifluoroprop-1-ene **2** by using $Pd(PPh_3)_2Cl_2$/**B** as a catalyst and $NaHCO_3$ as a base. The results are summarized in Table 2. *Para*-substituted phenylboronic acids reacted smoothly with 2-chloro-3,3,3-trifluoroprop-1-ene **2** to afford excellent Yields (Table 2, **3a**–**3g**). In general, electron-rich substituted boronic acid demonstrated a higher reactivity than it is electron-withdrawing analogues. For instance, the yield of **3a** was significantly higher than that of **3e**. Substrates having *m*- or *o*-substituents also reacted with acceptable yields (Table 2, **3h**–**3n**). Disubstituted arylboronic acids were also tested, and good yields were obtained (Table 2, **3o**–**3q**). Furthermore, a carbazole-derived boronic acid could also be converted into the corresponding product in moderate yield (Table 2, **3r**).

Tri-substituted olefins are difficult to synthesize, in general, they were synthesized by two steps,[13] especially for trifluoromethyl substituents.[14] By using this method, we could obtain α,β-trifluoro substituted styrenes in one step directly when using (*Z*)-2-chloro-1,1,1,4,4,4-hexafluorobut-2-ene **3** as a coupling reagent.

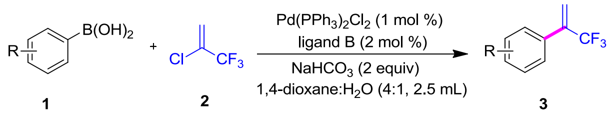
A range of functional groups were tolerated in this transformation (Table 3). Comparing electron-rich and electron-withdrawing substituted phenylboronic acids, it was found that electron-rich substituted arylboronic acids were well suited for this process (Table 3, **4a**–**4c**). Moreover, di-substituted arylboronic acids could react smoothly with **3** catalyzed by palladium, and gave acceptable yields (Table 3, **4d**–**4e**).

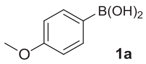
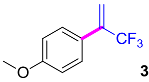
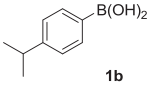
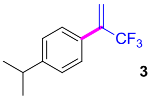
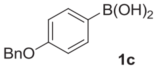
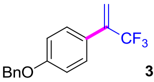
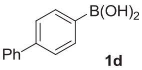
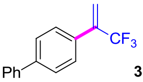
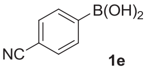
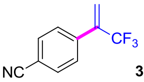
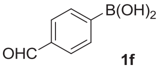
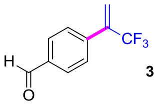
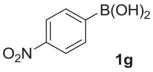
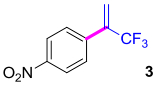
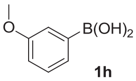
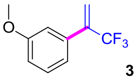
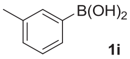
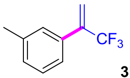
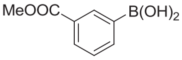
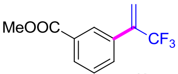
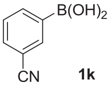
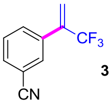
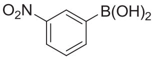
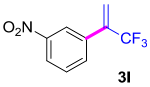
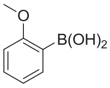
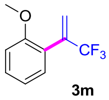
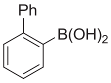
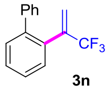
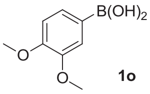
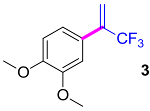
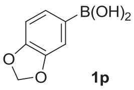
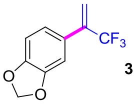
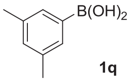
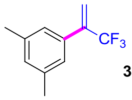
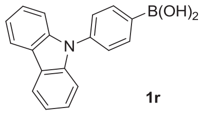
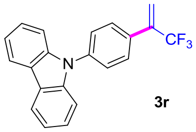
Efavirenz is a potent non-nucleoside HIV reverse transcriptase inhibitor approved by the FDA for the treatment of AIDS.[15] The trifluoroketone **6** is a key intermediate for the preparation of Efavirenz.[16] Several research groups have reported synthesis methods for the trifluoroketone **5a**.[17] However, all of those methods use either expensive materials or suffer from strict reaction conditions. By using this method, we could prepare the trifluorostyrene **5a** easily, and the styrene could convert into trifluoroketone **6** by using $NaIO_4$ and OsO_4, followed by hydrogenation (Scheme 2).[18]

A plausible mechanism of this Suzuki–Miyaura reaction is described in the perspective of the palladium catalyst (Scheme 3). The first step is the oxidative addition of palladium (**A**) to the halide (**2**) to form the organopalladium species (**B**). Reaction with base gives intermediate (**C**), which via transmetalation[19] with the boron-ate complex (produced by reaction of the boronic acid with base) forms the organopalladium species (**D**). Reductive elimination of the desired product restores the original palladium catalyst[20] which completes the catalytic cycle. The use of ligand B possibly promotes the step of oxidative addition.

Table 2

Conversion of arylboronic acids to α-(trifluoromethyl)styrenes via Pd-catalyzed Suzuki–Miyaura reaction[a]



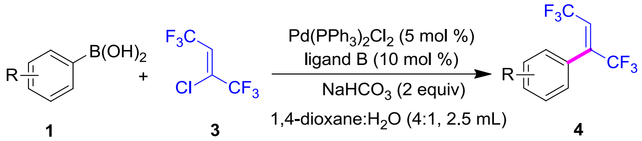
Entry	Boronic acid	Product	Yield (%)[b]
1	 **1a**	 **3a**	95
2	 **1b**	 **3b**	81
3	 **1c**	 **3c**	91
4	 **1d**	 **3d**	83
5	 **1e**	 **3e**	79
6	 **1f**	 **3f**	82
7	 **1g**	 **3g**	71
8	 **1h**	 **3h**	85
9	 **1i**	 **3i**	76
10	 **1j**	 **3j**	84
11	 **1k**	 **3k**	73
12	 **1l**	 **3l**	73
13	 **1m**	 **3m**	77
14	 **1n**	 **3n**	65
15	 **1o**	 **3o**	88
16	 **1p**	 **3p**	89
17	 **1q**	 **3q**	75
18	 **1r**	 **3r**	72

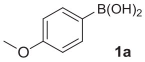
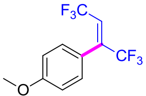
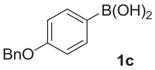
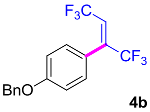
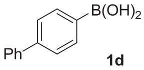
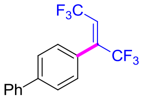
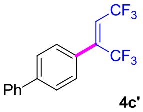
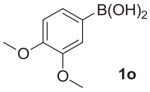
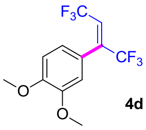
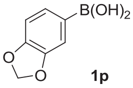
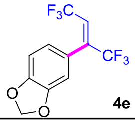
[a] Reaction conditions: **1** (1 mmol), **2** (18 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (1 mol %), **B** (2 mol %), NaHCO$_3$ (2 mmol), 1,4-dioxane: H$_2$O (4; 1, 2.5 mL), 100 °C, 5 h.

[b] Isolated yield.

Table 3

Conversion of arylboronic acids to (*E*)-α,β-(trifluoromethyl)styrenes via Pd-catalyzed Suzuki–Miyaura reaction[a]



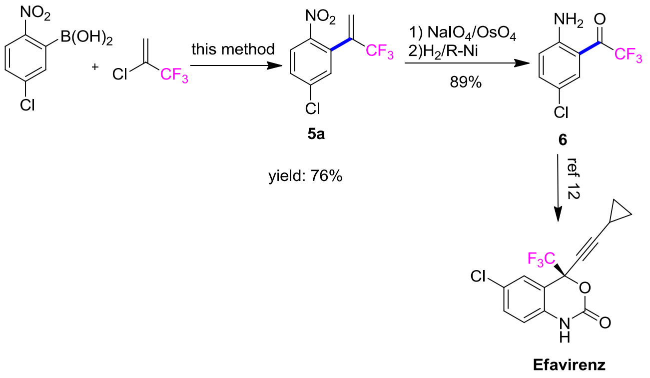
Entry	Boronic acid	Product	Yield (%)[b]
1	 **1a**	 **4a**	72
2	 **1c**	 **4b**	76
3	 **1d**	 **4c**	53
		 **4c'**	20 (total 73)
4	 **1o**	 **4d**	69
5	 **1p**	 **4e**	66

[a] Reaction conditions: **1** (1 mmol), **3** (18 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (5 mol %), B (10 mol %), NaHCO$_3$ (2 mmol), 1,4-dioxane: H$_2$O (4; 1, 2.5 mL), 100 °C, 12 h.

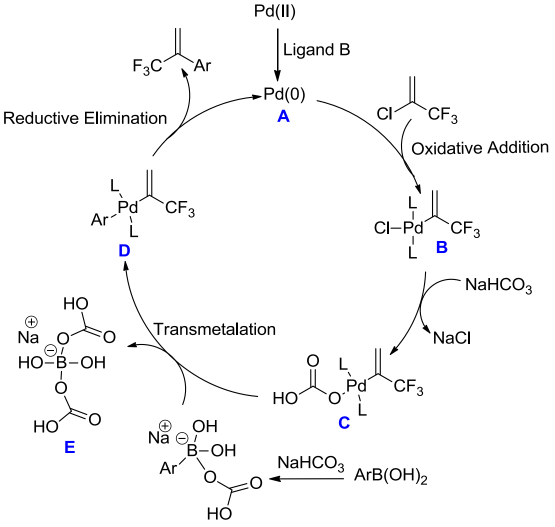
[b] Isolated yield.

3. Conclusion

In summary, we developed a new strategy for a facile synthesis of α,β-(trifluoromethyl)styrene derivatives via the palladium-



Scheme 2. A new strategy for synthesis of key intermediate for Efavirenzs.



Scheme 3. A Plausible mechanism for this Suzuki–Miyaura reaction.

catalyzed Suzuki–Miyaura reaction with commercially available 2-chloro-3,3,3-trifluoroprop-1-ene and (*Z*)-2-chloro-1,1,1,4,4,4-hexafluorobut-2-ene as fluorine sources. The wide scope, and the remarkable tolerance in particularly to a large number of important arylboronic acids, makes this strategy remarkably practical for the efficient synthesis of functional styrenes.

4. Experimental section

The coupling reaction was conducted under an atmosphere of argon. Flash column chromatography was performed over silica gel 300–400 mesh. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker (800 MHz, 500 MHz, respectively) instruments internally referenced to tetramethylsilane (TMS). High-resolution mass spectra were recorded on micr OTOF-Q III (Bruker Daltonics Inc.). The structures of known compounds were further corroborated by comparing their NMR data and MS data with those reported in the literature. Reagents were used as received without any further purification.

4.1. General procedure: (3a, 5a)

The reaction was carried out in an autoclave containing a 10 mL Teflon reaction tube. $Pd(PPh_3)_2Cl_2$ (1 mol %), **B** (2 mol %) and a magnetic stir bar were placed in the tube, followed by addition of arylboronic acid (1 mmol), $NaHCO_3$ (2 mmol), 1,4-dioxane (2 mL) and water (0.5 mL). the tube was capped with a stopper. The autoclave was cooled down to −100 °C by liquid nitrogen, and 2-chloro-3,3,3-trifluoroprop-1-ene (**2**, 18 mmol) was added to the reaction. Finally the autoclave was heated in an oil bath at 100 °C for 5 h. After the reaction, the autoclave was then cooled to room temperature and vented to discharge the excessive 2,3,3,3-tetrafluoropropylene carefully. Water (60 mL) was added, and the product was extracted with dichloromethane (3*15 mL). The organic layers were washed with brine (30 mL), dried over Na_2SO_4, and the organic solvent was evaporated by a rotary evaporator under atmospheric pressure. The crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate as eluents).

4.2. General procedure: (4a)

The reaction was carried out in an autoclave containing a 10 mL Teflon reaction tube. $Pd(PPh_3)_2Cl_2$ (5 mol %), **B** (10 mol %) and a magnetic stir bar were placed in the tube, followed by addition of arylboronic acid (1 mmol), $NaHCO_3$ (2 mmol), 1,4-dioxane (2 mL) and water (0.5 mL) to the tube. The tube was capped with a stopper. The autoclave was cooled down to −100 °C by liquid nitrogen, and (*Z*)-2-chloro-1,1,1,4,4,4-hexafluorobut-2-ene (**3**, 18 mmol) was added. Finally the autoclave was heated in an oil bath at 100 °C for 12 h. After the reaction, the autoclave was then cooled to room temperature and vented to discharge the excessive (*Z*)-2-chloro-1,1,1,4,4,4-hexafluorobut-2-ene carefully. Water (60 mL) was added, and the product was extracted with dichloromethane (3*15 mL). The organic layers were washed with brine (30 mL), dried over Na_2SO_4, and the organic solvent was evaporated by a rotary evaporator under atmospheric pressure. The crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate as eluents).

*4.2.1. 1-Methoxy-4-(1,1,1-trifluoroprop-2-en-2-yl)benzene (**3a**).* Colorless oil. R_f=0.7 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, 2H, J=8.5 Hz), 6.90 (d, 2H, J=9.0 Hz), 5.86 (d, 1H, J=1.5 Hz), 5.69 (q, 1H, J=1.5 Hz), 3.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 138.4 (q, J=29.6 Hz), 128.6, 126.0, 123.5 (q, J=272.4 Hz), 118.8 (q, J=5.9 Hz), 114.0, 55.3. ^{19}F NMR (470.0 MHz) δ −64.8 (s, 3F).

IR (KBr): 1687, 1607, 1406, 1358, 1259, 1195, 1178, 1085, 962 cm^{-1}.

HRMS (ESI): calcd for [M]$^+$ 202.0605; found: 202.0601.

*4.2.2. 1-Isopropyl-4-(1,1,1-trifluoroprop-2-en-2-yl)benzene (**3b**).* Colorless oil. R_f=0.7 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, 2H, J=8.0 Hz), 7.24 (d, 2H, J=8.5 Hz), 5.90 (d, 1H, J=1.5 Hz), 5.73 (q, 1H, J=1.5 Hz), 2.92 (m, 3H), 1.26 (s, 3H), 1.25 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 138.9 (q, J=29.6 Hz), 131.1, 127.3, 126.9, 123.5 (q, J=231.0 Hz), 119.6 (q, J=5.8 Hz), 33.9, 23.7. ^{19}F NMR (470.0 MHz) δ −64.7 (s, 3F).

IR (KBr): 1689, 1607, 1407, 1360, 1268, 1193, 1171, 1124, 1088, 957, 846 cm^{-1}.

HRMS (ESI): calcd for [M]$^+$ 214.0969; found: 214.0966.

*4.2.3. 1-(Benzyloxy)-4-(1,1,1-trifluoroprop-2-en-2-yl)benzene (**3c**).* White solid. R_f=0.7 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, 2H, J=7.0 Hz), 7.40–7.37 (m, 4H), 7.34 (d, 1H, J=6.0 Hz), 5.86 (d, 1H, J=1.0 Hz), 5.69 (q, 1H, J=2.0 Hz), 5.08 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 138.3 (q, J=29.6 Hz), 136.7, 128.5, 127.5, 126.3, 124.5, 122.4, 118.9 (q, J=5.9 Hz), 114.9, 70.1. ^{19}F NMR (470.0 MHz) δ −65.0 (s, 3F).

IR (KBr): 1612, 1521, 1456, 1362, 1294, 1256, 1171, 1153, 1109, 1015 cm^{-1}.

HRMS (ESI): calcd for [M]$^+$ 278.0918; found: 278.0910.

*4.2.4. 4-(1,1,1-Trifluoroprop-2-en-2-yl) biphenyl (**3d**).* White solid. R_f=0.7 (petroleum ether); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.61 (t, 4H, J=5.0 Hz), 7.54 (d, 2H, J=10.0 Hz), 7.45 (t, 2H, J=10.0 Hz), 7.37 (t, 1H, J=10.0 Hz), 5.98 (d, 1H, J=5.0 Hz), 5.83 (d, 1H, J=5.0 Hz). ^{13}C NMR (125 MHz, CDCl$_3$) δ 141.8, 140.3, 138.7 (q, J=35.9 Hz), 132.5, 138.8 (q, J=35.9 Hz), 131.3 (d, J=7.4 Hz), 122.3 (d, J=7.4 Hz), 119.1 (qd, J=272.6 Hz, J=41.6 Hz), 114.3, 111.0, 55.3. ^{19}F NMR (470.0 MHz) δ −64.6 (s, 3F).

IR (KBr): 1610, 1521, 1366, 1255, 1184, 1152, 1088, 966, 857 cm^{-1}.

HRMS (ESI): calcd for [M]$^+$ 248.0813; found: 248.0810.

*4.2.5. 4-(1,1,1-Trifluoroprop-2-en-2-yl)benzonitrile (**3e**).* Colorless oil. R_f=0.7 (petroleum ether); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.70 (d, 2H, J=5.0 Hz), 7.58 (d, 2H, J=5.0 Hz), 6.11 (d, 1H, J=1.5 Hz), 5.88 (q, 1H, J=1.5 Hz). ^{13}C NMR (125 MHz, CDCl$_3$) δ 137.9, 137.7 (q, J=30.6 Hz), 132.4, 128.1, 122.8 (q, J=272.3 Hz), 122.8 (q, J=5.6 Hz), 118.2, 112.9. ^{19}F NMR (470.0 MHz) δ −65.0 (s, 3F).

IR (KBr): 1610, 1513, 1404, 1352, 1263, 1196, 1177, 1127, 1077, 1021 cm^{-1}.

HRMS (ESI): calcd for [M]$^+$ 197.0452; found: 197.0450.

*4.2.6. 4-(1,1,1-Trifluoroprop-2-en-2-yl)benzaldehyde (**3f**).* Colorless oil. R_f=0.7 (petroleum ether); ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.04 (s, 1H), 7.91 (d, 2H, J=8.5 Hz), 7.63 (d, 2H, J=8.5 Hz), 6.09 (d, 1H, J=1.0 Hz), 5.90 (q, 1H, J=1.0 Hz). ^{13}C NMR (125 MHz, CDCl$_3$) δ 191.6, 139.3, 138.2 (q, J=30.5 Hz), 136.5, 129.9, 128.0, 123.0 (q, J=272.3 Hz), 122.4 (q, J=5.6 Hz). ^{19}F NMR (470.0 MHz) δ −64.6 (s, 3F).

IR (KBr): 1707, 1610, 1571, 1413, 1354, 1193, 1179, 1129, 1080, 1018 cm^{-1}.

HRMS (ESI): calcd for [M]$^+$ 200.0449; found: 200.0440.

*4.2.7. 1-Nitro-4-(1,1,1-trifluoroprop-2-en-2-yl)benzene (**3g**).* Colorless oil. R_f=0.7 (petroleum ether); ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.25 (d, 2H, J=9.5 Hz), 7.62 (d, 2H, J=9.0 Hz), 6.15 (d, 1H, J=1.0 Hz), 5.95 (q, 1H, J=1.5 Hz). ^{13}C NMR (125 MHz, CDCl$_3$) δ 148.1, 139.7, 137.4 (q, J=24.0 Hz), 124.8, 123.8, 122.8 (q, J=272.3 Hz), 123.3 (q, J=5.5 Hz). ^{19}F NMR (470.0 MHz) δ −64.8 (s, 3F).

IR (KBr): 1603, 1524, 1347, 1185, 1130, 1079, 956, 862, 841 cm^{-1}.

HRMS (ESI): calcd for [M]$^+$ 217.0351; found: 217.0350.

*4.2.8. 1-Methoxy-3-(1,1,1-trifluoroprop-2-en-2-yl)benzene (**3h**).* Colorless oil. R_f=0.7 (petroleum ether); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.28 (t, 1H, J=8.0 Hz), 7.03 (d, 2H, J=7.5 Hz), 6.98 (s, 1H), 6.92 (dd, 1H, J=8.5 Hz, 2.5 Hz), 5.94 (d, 1H, J=1.0 Hz), 5.75 (q, 1H, J=2.0 Hz), 3.81 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 159.4, 138.9 (q, J=30.0 Hz), 135.0, 129.6, 123.3 (q, J=272.4 Hz), 120.6 (q, J=5.8 Hz), 119.9, 114.3, 113.4, 55.2. ^{19}F NMR (470.0 MHz) δ −64.9 (s, 3F).

IR (KBr): 1583, 1492, 1356, 1291, 1250, 1174, 1127, 1047, 950, 788 cm^{-1}.

HRMS (ESI): calcd for [M]$^+$ 202.0605; found: 202.0601.

*4.2.9. 1-Methyl-3-(1,1,1-trifluoroprop-2-en-2-yl)benzene (**3i**).* Colorless oil. R_f=0.7 (petroleum ether); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.28–7.18 (m, 4H), 5.92 (d, 1H, J=1.5 Hz), 5.73 (q, 1H, J=1.5 Hz), 2.36 (m, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 139.2 (q, J=29.8 Hz), 138.3, 133.7, 129.7, 128.5, 128.1, 124.5, 122.3, 120.2 (q, J=5.8 Hz), 21.4. ^{19}F NMR (470.0 MHz) δ −64.8 (s, 3F).

IR (KBr): 1598, 1486, 1355, 1198, 1180, 1088, 956, 766 cm^{-1}.

HRMS (ESI): calcd for [M]$^+$ 186.0656; found: 186.0656.

*4.2.10. Methyl 3-(1,1,1-trifluoroprop-2-en-2-yl)benzoate (**3j**).* Colorless oil. R_f=0.7 (petroleum ether); ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.13 (s, 1H), 8.06 (d, 1H, J=3.0 Hz), 7.64 (d, 1H, J=8.0 Hz), 7.74 (t, 1H, J=8.0 Hz), 6.02 (d, 1H, J=1.0 Hz), 5.83 (q, 1H, J=1.5 Hz). ^{13}C NMR (125 MHz, CDCl$_3$) δ 166.4, 138.2 (q, J=30.2 Hz), 133.9, 131.6, 130.7, 130.0, 128.72, 128.70, 123.1 (q, J=272.2 Hz), 121.4 (q, J=5.8 Hz), 52.1. ^{19}F NMR (470.0 MHz) δ −64.8 (s, 3F).

IR (KBr): 1730, 1442, 1353, 1280, 1171, 1132, 1098, 953, 768 cm^{-1}.

HRMS (ESI): calcd for [M]$^+$ 230.0555; found: 230.0550.

*4.2.11. 3-(1,1,1-Trifluoroprop-2-en-2-yl)benzonitrile (**3k**).* Colorless oil. R_f=0.7 (petroleum ether); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.74 (s, 1H), 7.70–7.57 (m, 2H), 7.53 (t, 1H, J=7.5 Hz), 6.09 (d, 1H, J=1.5 Hz), 5.85 (q, 1H, J=1.5 Hz). ^{13}C NMR (125 MHz, CDCl$_3$) δ 137.3 (q, J=30.9 Hz), 134.8, 132.4, 131.7, 131.0, 123.9, 122.8 (q, J=272.3 Hz), 122.5 (q, J=6.0 Hz), 118.2, 113.1. ^{19}F NMR (470.0 MHz) δ −65.0 (s, 3F).

IR (KBr): 1612, 1575, 1464,1353, 1224, 1168, 1130, 956 cm^{-1}.

HRMS (ESI): calcd for [M]$^+$ 197.0452; found: 197.0450.

*4.2.12. 1-Nitro-4-(1,1,1-trifluoroprop-2-en-2-yl)benzene (**3l**).* Colorless oil. R_f=0.7 (petroleum ether); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.39 (d, 2H, J=8.0 Hz), 7.24 (d, 2H,J=8.5 Hz), 5.90 (d, 1H, J=1.5 Hz), 5.73 (q, 1H, J=1.5 Hz), 2.92 (m, 3H), 1.26 (s, 3H), 1.25 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 149.8, 138.9 (q, J=29.6 Hz), 131.1, 127.3, 126.9, 123.5 (q, J=231.0 Hz), 119.6 (q, J=5.8 Hz), 33.9, 23.7. ^{19}F NMR (470.0 MHz) δ −64.7 (s, 3F).

IR (KBr): 1645, 1536, 1415, 1353, 1194, 1174, 1127, 952, 906 cm^{-1}.

HRMS (ESI): calcd for [M]$^+$ 217.0351; found: 217.0350.

*4.2.13. 1-Methoxy-2-(1,1,1-trifluoroprop-2-en-2-yl)benzene (**3m**).* Colorless oil. R_f=0.7 (petroleum ether); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.36–7.32 (m, 1H), 7.21 (d, 1H, J=6.5 Hz), 6.94 (q, 1H, J=6.5 Hz), 6.07 (d, 1H, J=1.5 Hz), 5.83 (q, 1H, J=1.5 Hz), 3.79 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 157.1, 136.1 (q, J=31.4 Hz), 130.7, 130.2, 129.5, 123.3 (q, J=5.3 Hz), 123.1 (q, J=271.8 Hz), 120.3, 111.3, 55.9. ^{19}F NMR (470.0 MHz) δ −65.8 (s, 3F).

IR (KBr): 1600, 1580, 1495, 1465, 1439, 1350, 1253, 1171, 1127, 1077 cm^{-1}.

HRMS (ESI): calcd for [M]$^+$ 202.0605; found: 202.0601.

*4.2.14. 1-Benzene-2-(1,1,1-trifluoroprop-2-en-2-yl)benzene (**3n**).* Colorless oil. R_f=0.7 (petroleum ether); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.42 (t, 2H, J=7.5 Hz), 7.37–7.29 (m, 4H), 7.28–7.22 (m, 3H), 5.90 (s, 1H), 5.25 (s, 1H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 141.8, 140.3, 138.7 (q, J=35.9 Hz), 132.5, 128.8, 127.8, 127.7, 127.3, 127.1, 125.8, (q, J=272.5 Hz), 120.2 (q, J=5.8 Hz). ^{19}F NMR (470.0 MHz) δ −64.8 (s, 3F).

IR (KBr): 1482, 1364, 1174, 1127, 1077, 952, 747, 702, 630 cm^{-1}.

HRMS (ESI): calcd for [M]$^+$ 248.0813; found: 248.0811.

*4.2.15. 1,2-Dimethoxy-4-(1,1,1-trifluoroprop-2-en-2-yl)benzene (**3o**).* Colorless oil. R_f=0.7 (petroleum ether); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.03 (d, 1H, J=8.5 Hz), 6.96 (s, 1H), 6.86 (d, 1H, J=8.5 Hz), 5.88 (d, 1H, J=1.5 Hz), 5.71 (q, 1H, J=2.0 Hz). ^{13}C NMR (125 MHz, CDCl$_3$) δ 149.6, 148.8, 138.5 (q, J=29.6 Hz), 126.3, 123.4 (q, J=272.3 Hz), 120.3, 119.2 (q, J=5.8 Hz), 111.0, 110.5, 55.9, 55.8. ^{19}F NMR (470.0 MHz) δ −64.8 (s, 3F).

IR (KBr): 1606, 1583, 1524, 1468, 1365, 1347, 1259, 1159, 1124, 1026 cm^{-1}.

HRMS (ESI): calcd for [M]$^+$ 232.0711; found: 232.0710.

*4.2.16. 5-(1,1,1-Trifluoroprop-2-en-2-yl)benzo[d][1,3]dioxole (**3p**).* Colorless oil. R_f=0.7 (petroleum ether); ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.94 (d, 2H, J=8.0 Hz), 6.81 (d, 1H, J=8.0 Hz), 5.98 (s, 2H), 5.87 (d, 1H, J=1.0 Hz), 5.67 (q, 1H, J=1.5 Hz). ^{13}C NMR (125 MHz, CDCl$_3$) δ 148.3, 147.9, 138.5 (q, J=29.9 Hz), 127.5, 123.3 (q, J=272.2 Hz), 121.5, 119.6 (q, J=11.4 Hz), 108.3, 107.9, 101.3. ^{19}F NMR (470.0 MHz) δ −64.8 (s, 3F).

IR (KBr): 1509, 1449, 1366, 1233, 1120, 1044, 955, 865 cm^{-1}.

HRMS (ESI): calcd for [M]$^+$ 216.0398; found: 216.0391.

*4.2.17. 1,3-Dimethyl-5-(1,1,1-trifluoroprop-2-en-2-yl)benzene (**3q**).* Colorless oil. R_f=0.7 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (s, 2H), 7.01 (s, 1H), 5.90 (s, 1H), 5.70 (d, 1H, J=1.5 Hz), 2.32 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.3 (q, J=29.6 Hz), 138.0, 133.5, 130.6, 124.6, 123.5 (q, J=272.4 Hz), 120.0 (q, J=5.8 Hz), 21.3. ^{19}F NMR (470.0 MHz) δ −64.6 (s, 3F).

IR (KBr): 1603, 1362, 1274, 1168, 1127, 1106, 944, 859, 709 cm^{-1}.

HRMS (ESI): calcd for $[M]^+$ 200.0813; found: 200.0811.

*4.2.18. 9-(4-(1,1,1-Trifluoroprop-2-en-2-yl)phenyl)-9H-carbazole (**3r**).* White solid. R_f=0.6 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, 2H, J=8.0 Hz), 7.70 (d, 2H, J=8.5 Hz), 7.61 (d, 2H, J=9.0 Hz), 7.46–7.40 (m, 4H), 7.30 (t, 2H, J=7.5 Hz), 6.06 (d, 1H, J=1.5 Hz), 5.91 (q, 1H, J=2.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.6, 138.4, 138.2 (q, J=32.0 Hz), 132.5, 129.0, 127.0, 126.1, 123.6, 123.3 (q, J=272.4 Hz), 120.9 (q, J=5.6 Hz), 120.4, 120.2, 109.8. ^{19}F NMR (470.0 MHz) δ −64.8 (s, 3F).

IR (KBr): 1609, 1521, 1450, 1359, 1233, 1171, 1130, 1079, 945 cm^{-1}.

HRMS (ESI): calcd for $[M]^+$ 337.1078; found: 337.1074.

*4.2.19. (E)-1-(1,1,1,4,4,4-Hexafluorobut-2-en-2-yl)-4-methoxybenzene (**4a**).* Colorless oil. R_f=0.6 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, 2H, J=8.5 Hz), 6.93 (d, 2H, J=8.5 Hz), 6.45 (qd, 1H, J=7.5 Hz, J=1.5 Hz), 3.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 143.6 (qq, J=259.5 Hz, J=37.0 Hz), 130.1, 122.5 (qq, J=35.3 Hz, J=11.1 Hz), 122.0 (qd, J=276.3 Hz, J=44.3 Hz), 120.9, 114.1, 113.9, 55.2. ^{19}F NMR (470.0 MHz) δ −68.4 (s, CF_3), −58.0 (d, J=5.6 Hz, CF_3).

IR (KBr): 1618, 1518, 1277, 1177, 1147, 1032, 835 cm^{-1}.

HRMS (ESI): calcd for $[M]^+$ 270.0479; found: 270.0476.

*4.2.20. (E)-1-(Benzyloxy)-4-(1,1,1,4,4,4-hexafluorobut-2-en-2-yl) benzene (**4b**).* White solid. R_f=0.6 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44–7.39 (m, 4H), 7.34 (t, 1H, J=8.5 Hz), 7.23 (d, 2H, J=8.5 Hz), 7.01 (d, 2H, J=8.5 Hz), 6.44 (qd, 1H, J=7.5 Hz, J=1.5 Hz), 5.08 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 141.1 (qq, J=19.5 Hz, J=3.1 Hz), 136.4, 130.2, 128.7, 128.1, 127.6, 122.5 (qq, J=35.2 Hz, J=5.6 Hz), 122.1(qd, J=287.8 Hz, J=75.0 Hz), 121.2, 114.7, 70.1. ^{19}F NMR (470.0 MHz) δ −70.7 (s, CF_3), −60.5 (d, J=5.6 Hz, CF_3).

IR (KBr): 1606, 1521, 1450, 1359, 1233, 1171, 1130, 1085, 950 cm^{-1}.

HRMS (ESI): calcd for $[M]^+$ 346.0792; found: 346.0790.

*4.2.21. (E)-1-(Benzene)-4-(1,1,1,4,4,4-hexafluorobut-2-en-2-yl)benzene (**4c**).* White solid. R_f=0.6 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65–7.59 (m, 4H), 7.46 (t, 2H, J=8.0 Hz), 7.40–7.36 (m, 2H), 6.52 (qd, 1H, J=7.5 Hz, J=1.5 Hz). ^{13}C NMR (800 MHz NMR, 200 MHz, $CDCl_3$) δ 142.7, 141.1 (qq, J=31.4 Hz, J=5.2 Hz), 139.9, 129.2, 128.9, 128.8, 127.9, 127.7, 127.2, 127.1, 122.9(qq, J=35.4 Hz, J=5.6 Hz), 121.5(qd, J=270.4 Hz, J=80.2 Hz). ^{19}F NMR (470.0 MHz) δ −68.1 (s, CF_3), -57.9 (d, J=5.6 Hz, CF_3).

IR (KBr): 1695, 1612, 1568, 1409, 1362, 1274, 1197, 1171, 1124, 1085 cm^{-1}.

HRMS (ESI): calcd for $[M]^+$ 316.0687; found: 316.0681.

*4.2.22. (Z)-1-(1,1,1,4,4,4-Hexafluorobut-2-en-2-yl)-4-biphenyl (**4c′**).* White solid. R_f=0.6 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, 2H, J=8.5 Hz), 7.59 (d, 2H, J=7.5 Hz), 7.46 (t, 4H, J=7.5 Hz), 7.39 (t, 2H, J=7.0 Hz), 6.52 (q, 1H, J=8.5 Hz). ^{13}C NMR (800 MHz NMR, 200 MHz, $CDCl_3$) δ 143.1, 141.3 (qq, J=34.0 Hz, J=5.6 Hz), 131.9, 128.9, 129.2, 128.3, 128.1, 127.5, 127.1, 125.6 (qq, J=38.6 Hz, J=2.8 Hz), 121.5 (qd, J=270.2 Hz, J=103.2 Hz). ^{19}F NMR (470.0 MHz) δ −68.1 (s, CF_3), −57.9 (d, J=5.6 Hz, CF_3).

IR (KBr): 1699, 1622, 1565, 1449, 1322, 1278, 1107, 1161, 1024 cm^{-1}.

HRMS (ESI): calcd for $[M]^+$ 316.0687; found: 316.0681.

*4.2.23. (E)-4-(1,1,1,4,4,4-Hexafluorobut-2-en-2-yl)-1,2-dimethoxybenzene (**4d**).* Colorless oil. R_f=0.7 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.91–6.89 (m, 2H), 6.79 (s, 1H), 6.45 (qd, 1H, J=7.0 Hz, J=1.0 Hz),3.91 (s, 3H), 3.89 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2, 148.7, 141.0 (qq, J=31.3 Hz, J=5.0 Hz), 122.5 (qq, J=35.3 Hz, J=5.5 Hz), 121.8, 121.1, 119.1(qd, J=257.1 Hz, J=46.9 Hz), 110.7, 110.6, 55.9, 55.8. ^{19}F NMR (470.0 MHz) δ −68.1 (s, CF_3), −57.9 (d, J=6.1 Hz, CF_3).

IR (KBr): 1521, 1462, 1418, 1330, 1271, 1247, 1141, 1024, 856 cm^{-1}.

HRMS (ESI): calcd for $[M]^+$ 300.0585; found: 300.0584.

*4.2.24. (E)-5-(1,1,1,4,4,4-hexafluorobut-2-en-2-l)benzo[d][1,3]dioxole (**4e**).* Colorless oil. R_f=0.7 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84 (d, 1H, J=8.5 Hz), 6.77 (d, 2H, J=7.0 Hz), 6.45 (qd, 1H, J=7.5 Hz, J=1.5 Hz), 6.02 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.1, 147.7, 140.8 (qq, J=31.5 Hz, J=5.3 Hz), 122.9 (qq, J=29.0 Hz, J=5.6 Hz), 121.9 (qd, J=285.2 Hz, J=41.1 Hz), 109.1, 108.3, 101.6. ^{19}F NMR (470.0 MHz) δ −68.5 (s, CF_3), −58.0 (d, J=6.1 Hz, CF_3).

IR (KBr): 1507, 1446, 1365, 1243, 1171, 1129, 1043, 944, 816, 641 cm^{-1}.

HRMS (ESI): calcd for $[M]^+$ 284.0272; found: 284.0271.

*4.2.25. 4-Chloro-1-nitro-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**5a**).* Colorless oil. R_f=0.5 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, 1H, J=2.0 Hz), 7.37 (d, 1H, J=6.5 Hz), 7.33 (s, 1H), 6.00 (q, 1H, J=1.5 Hz), 5.79 (q, 1H, J=1.5 Hz). ^{19}F NMR (470.0 MHz) δ −65.1 (s, CF_3).

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Supplementary data

Supplementary data (Text files giving additional experimental and characterization data. Copies of the ^{1}H, ^{13}C and ^{19}F NMR spectra of the products produced in this study) associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2016.07.085.

References and notes

1. For reviews on trifluoromethylation, see (a) Schlosser, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 5432–5446; (b) Ma, J.-A.; Cahard, D. *J. Fluorine Chem.* **2007**, *128*, 975–996; (c) Ma, J.-A.; Cahard, D. *Chem. Rev.* **2008**, *108*, PR1–PR43; (d) Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V. *Chem. Soc. Rev.* **2008**, *37*, 320–330; (e) Tomashenko, O. A.; Grushin, V. V. *Chem. Rev.* **2011**, *111*, 4475–4521; (f) Studer, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 8950–8958.
2. (a) Tan, L.; Chen, C. Y.; Tillyer, R. D.; Grabowski, E. J. J.; Reider, P. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 711–713; (b) Walkowiak-Kulikowska, J.; Szwajca, A.; Boschet, F.; Gouverneur, V.; Ameduri, B. *Macromolecules* **2014**, *47*, 8634–8644; (c) Kobayashi, T.; Eda, T.; Tamura, O.; Ishibashi, H. *J. Org. Chem.* **2002**, *67*, 3156–3159.
3. (a) Kishimura, S.; Endo, M.; Sasago, M.; Shirai, M.; Kadooka, M. Kokai Tokkyo Koho JP2002 (b) Allen, R. D.; Brock, P. J.; Ito, H.; Wallraff, G. N. US Patent 0164 538 **2002**.
4. Shimizu, M.; Takeda, Y.; Higashi, M.; Hiyama, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 3653–3656.
5. For synthesis α-trifluoromethylstyrene derivatives see (a) Jiang, B.; Xu, Y. *J. Org. Chem.* **1991**, *56*, 7336–7340; (b) Kobayashi, O.; Uraguchi, D.; Yamakawa, T. *J. Fluorine Chem.* **2009**, *130*, 591–594; (c) Pan, R.; Liu, X.; Deng, M. *J. Fluorine Chem.* **1999**, *95*, 167–170; (d) Jiang, B.; Wang, Q.; Yang, C.; Xu, M. *Tetrahedron Lett.* **2001**, *42*, 4083–4085; (e) Walkowiak, J.; Campo, T. M.; Ameduri, B.; Gouverneur, V. *Synthesis* **2010**, *11*, 1883–1890; (f) Zhao, Q.; Besset, T.; Poisson, T.; Bouillon, J. –P.; Pannecoucke, X. *Eur. J. Org. Chem.* **2016**, 76–82.
6. For synthesis β-trifluoromethylstyrene derivatives see (a) Fuchikami, T.; Yatabe, M.; Ojima, I. *Synthesis* **1981**, 365–366; (b) Kitazume, T.; Ishikawa, N. *J. Am. Chem. Soc.* **1985**, *107*, 5186–5191; (c) Chen, Q.; Duan, J. *Chem. Commun.* **1993**, 1389–1391; (d) Duan, J.; Dolbier, W. R.; Chen, Q. *J. Org. Chem.* **1998**, *63*,

9486–9489; (e) Duan, J.; Su, D.; Chen, Q. *J. Fluorine Chem.* **1993**, *61*, 279–284; (f) Hanamoto, T.; Morita, N.; Shindo, K. *Eur. J. Org. Chem.* **2003**, 4279–4285; (g) Dubbaka, S. R.; Vogel, P. *Chem.—Eur. J.* **2005**, *11*, 2633–2641; (h) Landge, S. M.; Borkin, D. A.; Torok, B. *Lett. Org. Chem.* **2009**, *6*, 439–443; (i) Prakash, G. K. S.; Krishnan, H. S.; Jog, P. V.; Iyer, A. P.; Olah, G. A. *Org. Lett.* **2012**, *14*, 1146–1149; (j) Lishchynskyi, A.; Mazloomi, Z.; Grushin, V. *Synlett* **2015**, *26*, 45–50.

7. (a) Eugene, F.; Langlois, B.; Laurent, E. *J. Fluorine Chem.* **1994**, *66*, 301–309; (b) Nakamura, M.; Fujimoto, T.; Endo, K.; Nakamura, E. *Org. Lett.* **2004**, *6*, 4837–4840; (c) González-Bobes, F.; Fu, G. C. *J. Am. Chem. Soc.* **2006**, *128*, 5360–5361; (d) Shi, Y.; Peterson, S. M.; Haberaecker, W. W.; Blum, S. A. *J. Am. Chem. Soc.* **2008**, *130*, 2168–2169; (e) Falck, J. R.; Bejot, R.; Barma, D. K.; Bandyopadhyay, A.; Joseph, S.; Mioskowski, C. *J. Org. Chem.* **2006**, *71*, 8178–8182; (f) Brachet, E.; Hamze, A.; Peyrat, J.-F.; Brion, J.-D.; Alami, M. *Org. Lett.* **2010**, *12*, 4042–4045; (g) Pospíšil, J.; Pospíšil, T.; Markó, I. E. *Org. Lett.* **2005**, *7*, 2373–2376.
8. (a) Ghosh, A. K.; Zajc, B. *J. Org. Chem.* **2009**, *74*, 8531–8540; (b) Song, X.; Chang, J.; Zhu, D.; Li, J.; Xu, C.; Liu, Q.; Wang, M. *Org. Lett.* **2015**, *17*, 1712–1715; (c) Tellier, F.; Sauvêtre, R.; Normant, J.-F.; Chuit, C. *Tetrahedron Lett.* **1987**, *28*, 3335–3338; (d) Nakayama, Y.; Kitazume, T.; Ishikawa, N. *J. Fluorine Chem.* **1985**, *29*, 445–458; (e) Chevrie, D.; Lequeux, T.; Demouteb, J. P.; Pazenokb, S. *Tetrahedron Lett.* **2003**, *44*, 8127–8130; (f) Burton, D. J.; Wesolowski, C. A.; Liu, Q.; Davis, C. R. *J. Fluorine Chem.* **2010**, *131*, 989–995.
9. (a) Jeong, I. H.; Park, Y. S.; Kim, M. S.; Song, Y. S. *J. Fluorine Chem.* **2003**, *120*, 195–209; (b) Zhu, N.; Wang, F.; Chen, P.; Ye, J.; Liu, G. *Org. Lett.* **2015**, *17*, 3580–3583; (c) Tomita, R.; Koike, T.; Akita, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 12923–12927.
10. (a) Suzuki, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 6722–6737; (b) Seechurn, C. C. C. J.; Kitching, M. O.; Colacot, T. J.; Snieckus, V. *Angew. Chem., Int. Ed.* **2012**, *51*, 5062–5085; (c) *Boronic Acids, Preparation and Applications in Organic Synthesis and Medicine*; Hall, D. G., Ed.; Wiley-VCH: 2005; pp 12–14.
11. (a) Teinza, K.; Manuela, S. R.; Chenb, B. B.; Pigamoc, A.; Doucetc, N.; Kemnitza, E. *Appl. Catal., B* **2015**, *165*, 200–208; (b) Mao, W.; Wang, B.; Ma, Y.; Zhang, W.; Du, Y.; Qin, Y.; Kang, J.; Lu, J. *Catal. Commun.* **2014**, *49*, 73–77.
12. Li, Y.; Tu, D.-H.; Gu, Y.-J.; Wang, B.; Wang, Y.-Y.; Liu, Z.-T.; Liu, Z.-W.; Lu, J. *Eur. J. Org. Chem.* **2015**, 4340–4343.
13. (a) Hamze, A.; Giraud, A.; Messaoudi, S.; Provot, O.; Peyrat, J.-F.; Bignon, J.; Liu, J.-M.; Wdzieczak-Bakala, J.; Thoret, S.; Dubois, J.; Brion, J.-D.; Alami, M. *ChemMedChem* **2009**, *4*, 1912–1924; (b) Messaoudi, S.; Tréguier, B.; Hamze, A.; Provot, O.; Peyrat, J.-F.; Rodrigo De Losada, J. R.; Liu, J.-M.; Bignon, J.; Wdzieczak-Bakala, J.; Thoret, S.; Dubois, J.; Brion, J.-D.; Alami, M. *J. Med. Chem.* **2009**, *52*, 4538–4542; (c) Barluenga, J.; Tomás-Gamasa, M.; Moriel, P.; Aznar, F.; Valdes, C. *Chem.—Eur. J.* **2008**, *14*, 4792–4795; (d) Barluenga, J.; Tomas-Gamasa, M.; Moriel, P.; Amar, F.; Valdes, C. *Chem.—Eur. J.* **2008**, *14*, 4792–4795; (e) Barluenga, J.; Escribano, M.; Moriel, P.; Aznar, F.; Valdés, C. *Chem.—Eur. J.* **2009**, *15*, 13291–13294; (f) Treguier, B.; Hamze, A.; Provot, O.; Brion, J. D.; Alami, M. *Tetrahedron Lett.* **2009**, *50*, 6549–6552; (g) Zhao, X.; Jing, J.; Lu, K.; Zhang, Y.; Wang, J. *Chem. Commun.* **2010**, 1724–1726.
14. (a) Jeong, I. H.; Park, Y. S.; Chung, M. W.; Kim, B. T. *Synth. Commun.* **2001**, *31*, 2261–2270; (b) Shimizu, M.; Fujimoto, T.; Liu, X.; Minezaki, H.; Hata, T.; Hiyama, T. *Tetrahedron* **2003**, *59*, 9811–9813; (c) Wang, F.; Qi, X.; Liang, Z.; Chen, P.; Liu, G. *Angew. Chem., Int. Ed.* **2014**, *53*, 1881–1886; (d) Wang, F.; Wang, D.; Mu, X.; Chen, P.; Liu, G. *J. Am. Chem. Soc.* **2014**, *136*, 10202–10205; (e) Liang, Z.; Wang, F.; Chen, P.; Liu, G. *J. Fluorine Chem.* **2014**, *167*, 55–60; (f) Liang, Z.; Wang, F.; Chen, P.; Liu, G. *Org. Lett.* **2015**, *17*, 2438–2441.
15. Young, S. D.; Britcher, S. F.; Tan, L.; Payne, L. S.; Lumma, W. C.; Lyle, T. A.; Huff, J. R.; Anderson, P. S.; Olsen, D. B.; Carroll, S. S.; Pettibone, D. J.; O'Brien, J. A.; Ball, R. G.; Balani, S. K.; Lin, J. H.; Chen, I. W.; Schleif, W. A.; Sardana, V. V.; Long, W. J.; Byrnes, V. W.; Emini, E. A. *Antimicrob. Agents Chemother.* **1995**, *39*, 2602–2605.
16. Thompson, A.; Corley, E. C.; Huntington, M. F.; Crabowski, E. J. J.; Remenar, J. F.; Collum, D. B. *J. Am. Chem. Soc.* **1998**, *120*, 2028–2038.
17. (a) Huffman, M. A.; Yasuda, N.; DeCamp, A. E.; Grabowski, E. J. J. *J. Org. Chem.* **1995**, *60*, 1590–1594; (b) Thompson, A. S.; Corely, E. G.; Huntington, M. F.; Grabowski, E. J. J. *Tetrahedron Lett.* **1995**, *36*, 8937–8940.
18. Pierce, M. E.; Parsons, R. L.; Radesca, L. A., Jr.; Lo, Y. S.; Silverman, S.; Moore, J. R.; Islam, Q.; Choudhury, Q. A.; Fortunak, J. M. D.; Nguyen, D.; Luo, C.; Morgan, S. J.; Davis, W. P.; Confalone, P. N. *J. Org. Chem.* **1998**, *63*, 8536–8543.
19. Amatore, C.; Jutand, A.; Le Duc, G. *Chem.—Eur. J.* **2011**, *17*, 2492–2503.
20. Matos, K.; Soderquist, J. A. *J. Org. Chem.* **1998**, *63*, 461–470.